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# Catalytic asymmetric transformations of racemic $\alpha$ -borylmethyl-(*E*)-crotylboronate via kinetic resolution or enantioconvergent reaction pathways†

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We report herein catalytic asymmetric transformations of racemic  $\alpha$ -borylmethyl-(*E*)-crotylboronate. The Brønsted acid-catalyzed kinetic resolution–allylboration reaction sequence of the racemic reagent gave (*Z*)- $\delta$ -hydroxymethyl-*anti*-homoallylic alcohols with high *Z*-selectivities and enantioselectivities upon oxidative workup. In parallel, enantioconvergent pathways were utilized to synthesize chiral nonracemic 1,5-diols and  $\alpha,\beta$ -unsaturated aldehydes with excellent optical purity.

## Introduction

Enantioenriched molecules are indispensable components in organic chemistry and modern drug discovery.<sup>1</sup> In the past twenty years, asymmetric catalysis has been the most adopted approach to synthesize such compounds.<sup>2</sup> Other strategies, however, also play important roles in different research settings. For instance, by taking advantage of the different reaction rates of each enantiomer of a racemate with a chiral, nonracemic reagent or catalyst, kinetic resolution enables access to a variety of highly enantiomerically enriched molecules.<sup>3</sup> On the other hand, enantioconvergent processes operate in a way such that both enantiomers of the racemate are converted into the same enantiomer of the product.<sup>4</sup>

(*Z*)-2-Methyl-3-pentene-1,5-diols and their reduced forms (highlighted in red and blue in Fig. 1) are common structural motifs in numerous bioactive natural products.<sup>5</sup> Methods that allow for the access to such structural entities mainly rely on a multistep reaction sequence.<sup>6</sup> For example, in the synthesis of a fragment of discodermolide reported by the Cossy group, enantioenriched homoallylic alcohol **I** was converted into lactone **II** in two steps. DIBAL reduction of **II** gave a lactol intermediate, which was reduced by NaBH<sub>4</sub> to give (*Z*)-2-methyl-3-pentene-1,5-diol **III** (Scheme 1a).<sup>6a</sup> In the total synthesis of dictyostatin, Curran and co-workers transformed chiral nonracemic propargylic mesylate **IV** into (*Z*)-vinyl iodide **V** in four steps. Li-halogen exchange of **V** and addition of the resulting vinyl lithium to an aldehyde gave **VI** as

a mixture of two diastereomers (Scheme 1b).<sup>6b</sup> While these methods can deliver the desired alcohol products with a meaningful quantity, streamlined synthesis of these molecules *via* catalytic asymmetric transformations would also be valuable. As part of our ongoing research program in acyclic stereochemical control *via* novel organoboron compounds,<sup>7</sup> we describe herein asymmetric synthesis of (*Z*)-2-methyl-3-pentene-1,5-diols **4** *via* chiral phosphoric acid-catalyzed kinetic resolution–allylation using racemic  $\alpha$ -borylmethyl-(*E*)-crotylboronate ( $\pm$ )-**3** (Scheme 1). Moreover, enantioconvergent syntheses of diols **6** and aldehydes **9** were accomplished from the same racemic boron reagent ( $\pm$ )-**3**, where both enantiomers of the racemate were converted into **6** or **9** with high enantioselectivities.

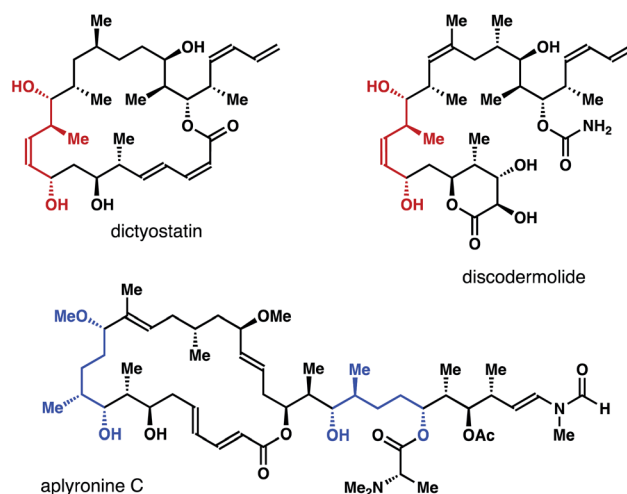
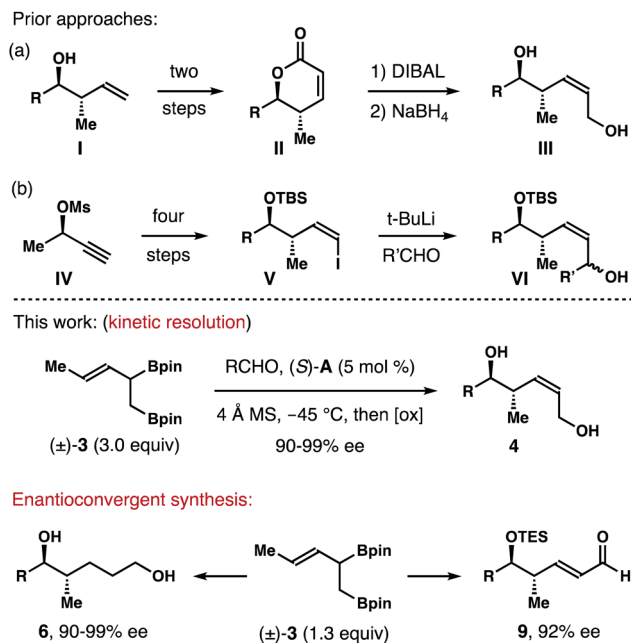


Fig. 1 Selected natural products that contain (*Z*)-2-methyl-3-pentene-1,5-diols or their reduced forms.

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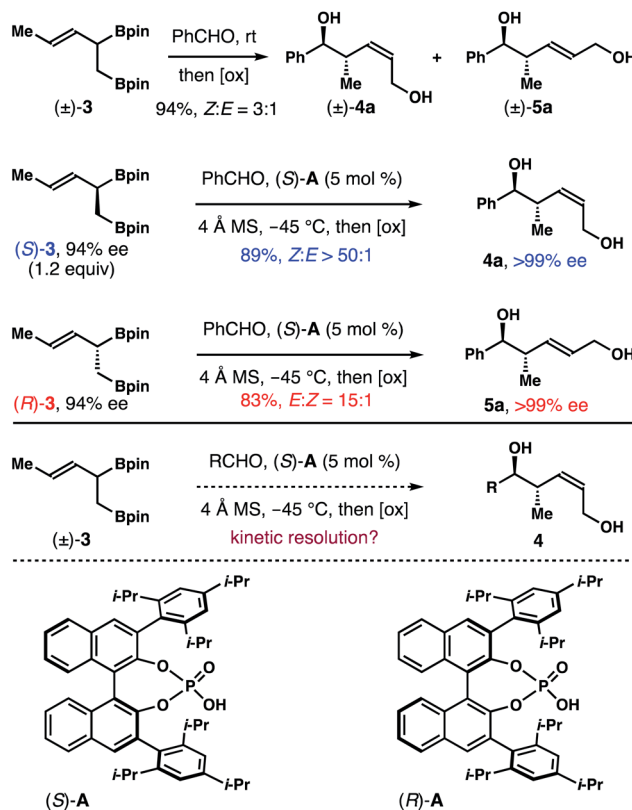


Scheme 1 Approaches to (Z)-2-methyl-3-pentene-1,5-diols.

## Results and discussion

To evaluate the feasibility of proposed kinetic resolution approach to synthesize (Z)-2-methyl-3-pentene-1,5-diols **4**, we obtained racemic boronate ( $\pm$ )-**3** according to the reported protocols.<sup>8</sup> In the absence of any catalyst, the reaction of ( $\pm$ )-**3** with benzaldehyde gave a 3 : 1 mixture of two products upon oxidative workup, favouring the Z-isomer, ( $\pm$ )-**4a**. The results indicate the pseudo axial preference (3 : 1) of the  $\alpha$ -CH<sub>2</sub>Bpin group of reagent ( $\pm$ )-**3** in the reaction transition state. On the basis of recent studies on Z-selective allylboration catalyzed by chiral phosphoric acids,<sup>9,10</sup> we suspect that the Z-selectivity could be enhanced by using a proper phosphoric acid catalyst. However, a more pertinent question is whether the catalyst could differentiate the two enantiomers of racemate ( $\pm$ )-**3** in reactions with aldehydes such that Z-isomer **4** could be obtained with high enantioselectivities.

To gather more experimental data to answer this question, we prepared enantioenriched boron reagents (*S*)-**3** and (*R*)-**3** (94% ee, see ESI† for detailed procedure). And allylation studies with the single enantiomer reagents in the presence of chiral phosphoric acid catalyst (*S*)-**A** were conducted. As shown in Scheme 2, the reaction between (*S*)-**3** (1.2 equiv.) and benzaldehyde with 5 mol% (*S*)-**A** as the catalyst gave product **4a** in 89% yield with >50 : 1 Z-selectivity and >99% ee. Intriguingly, the reaction with the enantiomeric reagent (*R*)-**3** in the presence of the same catalyst (*S*)-**A** generated *E*-isomer **5a** in 83% yield with 15 : 1 *E*-selectivity and >99% ee. The data described here bear several important implications. First, it is apparent that the two enantiomers of **3**, (*S*)-**3** and (*R*)-**3**, reacted with benzaldehyde in the presence of the same acid catalyst (*S*)-**A** formed products **4a** and **5a** that are not enantiomers, which is reminiscent of pathways for enantiodivergent reactions. Second, both **4a** and **5a** have the



Scheme 2 Initial studies with single enantiomer reagents.

same relative and absolute configurations at the stereocenters with a hydroxyl group and a methyl group, only differing in the olefin geometry. Lastly, perhaps the most significant aspect, the enantiomeric excesses of **4a** and **5a** are amplified (>99% ee vs. 94% ee of (*S*)-**3** and (*R*)-**3**). It is well-established that the reactions of aldehydes with chiral nonracemic  $\alpha$ -substituted crotylboronates proceed *via* chirality transfer; and the optical purity of the starting allylboron reagents will be retained in the reaction products. In another word, we would expect 94% ee for products **4a** and **5a**, given the enantiomeric excess of starting allylboron reagents (*S*)-**3** and (*R*)-**3** is 94% ee. The amplification of enantiopurity and high Z-selectivity in the reaction with (*S*)-**3** indicate that the minor component (*R*)-**3** in the starting boron reagent (3% based on 94% ee of (*S*)-**3**) likely did not participate in the reaction with benzaldehyde. Otherwise, formation of the *E*-isomer **5a** would be observed. With (*S*)-**A** as the catalyst, only (*S*)-**3** (97% based on 94% ee of (*S*)-**3**) reacted with benzaldehyde to deliver **4a** with outstanding Z-selectivity and enantioselectivity. On the other hand, in the reaction of (*R*)-**3** with the same acid (*S*)-**A** as the catalyst, the selectivity (15 : 1) is inferior to the one from the reaction with (*S*)-**3** (>50 : 1). Therefore, we infer that the reaction of (*S*)-**3** with aldehydes in the presence of catalyst (*S*)-**A** is stereochemically matched. The reaction with the (*R*)-**3**/(*S*)-**A** pairing is likely mismatched. These results form the basis of a potential kinetic resolution of racemic reagent ( $\pm$ )-**3** using single enantiomer acid catalyst (*S*)-**A** and would eliminate the need to synthesize enantioenriched boron reagents (*e.g.* (*S*)-**3**) for use in allylboration reactions.



To identify the optimal conditions for the kinetic resolution process, the reactions of benzaldehyde with various amounts of reagent ( $\pm$ )-3 in the presence of 5 mol% catalyst (*S*)-A were conducted. As shown in Table 1, the reaction with 1.3 equiv. of reagent ( $\pm$ )-3 formed a 3 : 1 mixture of **4a** and **5a** in a combined 89% yield. The enantiomeric excess of **4a** is 96% ee, and 99% ee for **5a**. Excellent enantiopurity was also observed for the recovered reagent **3**. With the aim to improve the *Z*-selectivity, we increased the amount of starting reagent ( $\pm$ )-3. When 2 equiv. of ( $\pm$ )-3 was used, the *Z*-selectivity was enhanced to 5 : 1 (entry 2). Further improvement of the *Z*-selectivity (7 : 1) was observed with 2.5 equiv. of reagent ( $\pm$ )-3 (entry 3). Finally, 10 : 1 *Z*-selectivity was achieved when 3.0 equiv. of ( $\pm$ )-3 was used in the reaction (entry 4). In all cases, enantiopurities of both **4a** and **5a** remained excellent; the optical purity of recovered reagent **3** decreased as anticipated (96% to 28% ee).

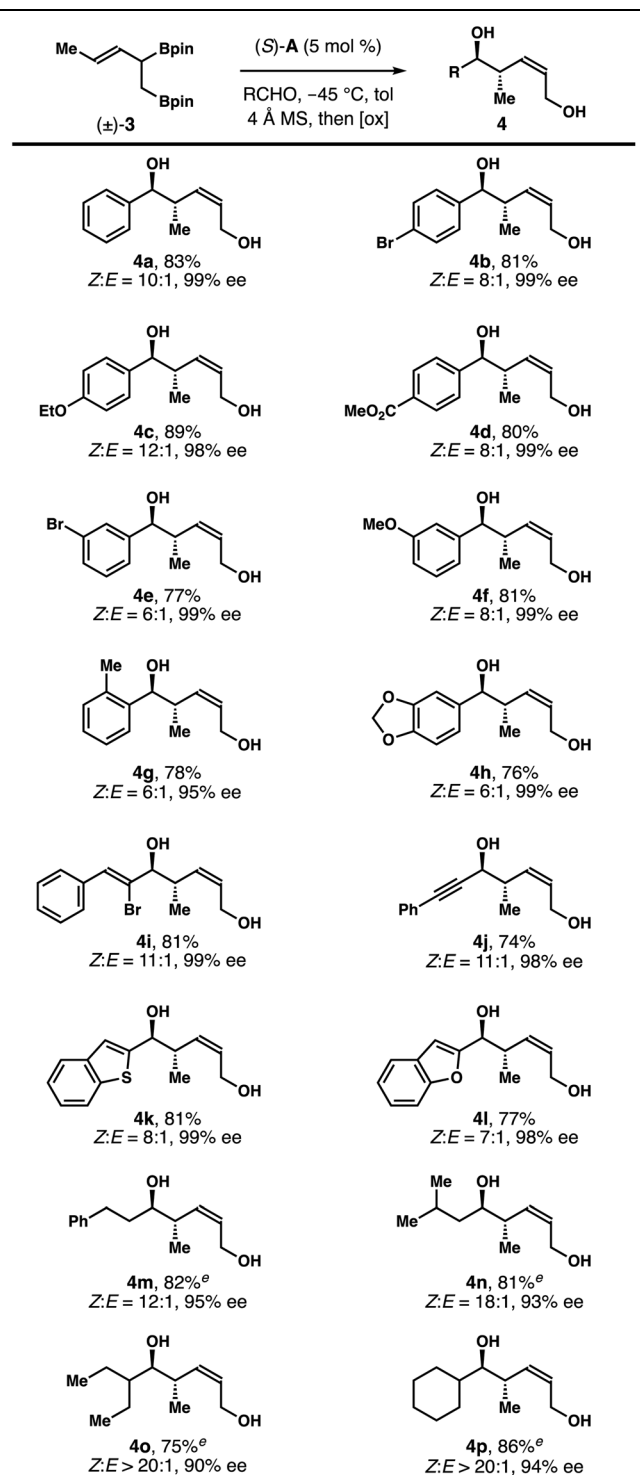
Although further enhancement of the *Z*-selectivity might be achievable, we decided to explore the reaction scope with 3.0 equiv. of ( $\pm$ )-3 to balance the amount of ( $\pm$ )-3 used in the reaction and the *Z*-selectivity of products **4**. As summarized in Table 2, under the developed conditions, the reactions worked reasonably well for a broad range of aldehyde substrates. For instance, reactions of ( $\pm$ )-3 with aromatic aldehydes with a substituent at the *para*-position gave products **4b–4d** with (8–12) : 1 *Z*-selectivity and 98–99% ee. Reactions of aromatic aldehydes with other substitution patterns proceeded to generate diols **4e–4h** with (6–8) : 1 *Z*-selectivity and 95–99% ee. Reactions with  $\alpha,\beta$ -unsaturated aldehydes occurred smoothly to form products **4i** and **4j** with 11 : 1 *Z*-selectivity and 98–99% ee. Heteroaromatic aldehydes are tolerated under the reaction conditions, affording diols **4k** and **4l** with (8 and 7) : 1 *Z*-selectivity and 98–99% ee. Importantly, aliphatic aldehydes also participated in the reactions with ( $\pm$ )-3 to deliver products **4m–4p** with (12–20) : 1 *Z*-selectivity and 90–95% ee. It should be noted that the reactions with aliphatic aldehydes were slow with 5 mol% of the acid catalyst. Optimal reactions rates and selectivities were achieved by increasing the catalyst loading to 10 mol%.

Table 1 Evaluation of reaction conditions for kinetic resolution allylboration with  $\alpha$ -borylmethyl-(*E*)-crotylboronate ( $\pm$ )-3<sup>a,b,c,d</sup>

Entry	Equiv. ( <b>3</b> )	<b>4a</b> : <b>5a</b>	ee ( <b>4a/5a</b> )	ee (recovered <b>3</b> )	Yield ( <b>4a</b> + <b>5a</b> )
1	1.3	3 : 1	96/99	96	89
2	2.0	5 : 1	98/99	58	94
3	2.5	7 : 1	98/99	39	90
4	3.0	10 : 1	99/99	28	83 <sup>e</sup>

<sup>a</sup> Reaction conditions: allylboronate ( $\pm$ )-3, (*S*)-A (5 mol%), PhCHO (0.1 mmol, 1.0 equiv.), toluene (0.3 mL),  $-45\text{ }^{\circ}\text{C}$ , 12 h. <sup>b</sup> The ratios of **4a** and **5a** were determined by  $^1\text{H}$  NMR analysis of the crude reaction products. <sup>c</sup> Yields of isolated products are listed. <sup>d</sup> Enantiomeric excesses were determined by HPLC analysis. <sup>e</sup> Yield of **4a** is listed.

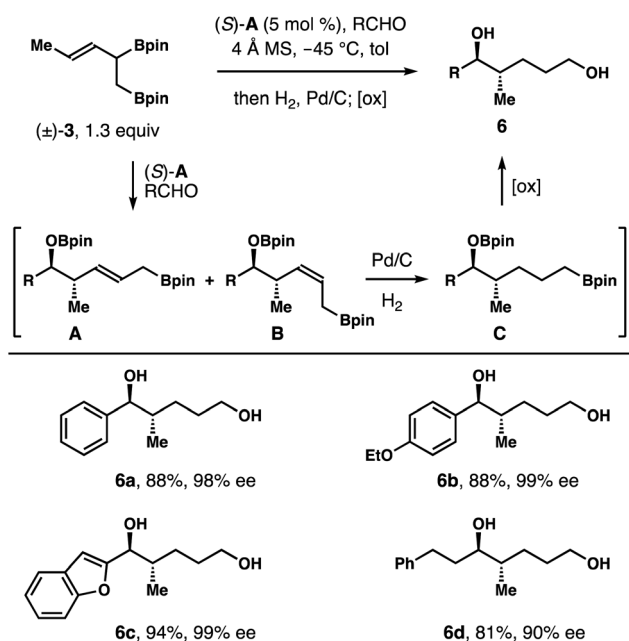
Table 2 Substrate scope<sup>a,b,c,d</sup>



<sup>a</sup> Reaction conditions: allylboronate ( $\pm$ )-3 (0.3 mmol, 3.0 equiv.), aldehyde (0.1 mmol, 1.0 equiv.), (*S*)-A (5 mol%), 4 Å molecular sieves, toluene,  $-45\text{ }^{\circ}\text{C}$ ; then NaOH,  $\text{H}_2\text{O}_2$ ,  $0\text{ }^{\circ}\text{C}$ . <sup>b</sup> *Z*/*E*-selectivities were determined by  $^1\text{H}$  NMR analysis of the crude reaction products. <sup>c</sup> Yields of isolated products **4** are listed. <sup>d</sup> Enantiopurities of **4** were determined by HPLC analysis. <sup>e</sup> The reactions were conducted with 10 mol% of (*S*)-A.

As shown in Table 1, both products **4a** and **5a** generated from racemic boron reagent ( $\pm$ )-**3** have identical relative and absolute configuration at the stereocenters bearing a hydroxyl group and a methyl group. The only difference is the geometry of the alkene unit. The results imply that the chiral phosphoric acid catalyst (*S*)-**A** controls the face selective addition to the aldehyde substrates, regardless of the absolute configuration of reagent **3**, (*R*) or (*S*). The *Z* or *E* olefin geometry of **4a** or **5a** reflects the pseudo axial or equatorial orientation of the  $\alpha$ -CH<sub>2</sub>Bpin group in the reaction transition states. As shown in Fig. 1, the reduced form (e.g. **6**, Scheme 3) of 2-methyl-3-pentene-1,5-diol is also a prevalent structural motif in a myriad of biologically relevant molecules. We envisioned that reduction of the alkene units of diols **4a** and **5a** should converge both compounds into the exact same product **6a**. Therefore, the overall reaction could proceed through an enantioconvergent pathway such that both enantiomers of racemic boron reagent ( $\pm$ )-**3** can be utilized to form enantioenriched 1,5-diol products **6**, and large excess of reagent ( $\pm$ )-**3** will not be required as it is in the kinetic resolution pathway.

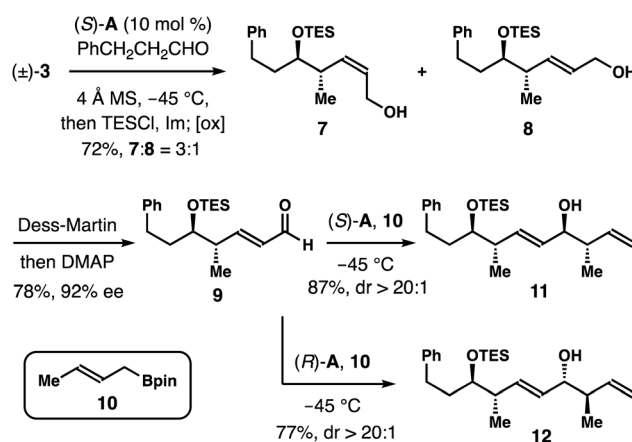
To validate our hypothesis, reactions of several aldehydes with reagent ( $\pm$ )-**3** (1.3 equiv.) were conducted in the presence of the catalyst (*S*)-**A**. After completion of the allylation, the resulting mixture, presumably intermediates **A** and **B** (Scheme 3), was subjected to the standard hydrogenation conditions in the same reaction vessel. Upon full reduction of the alkene unit, the resulting intermediate (e.g., **C**) was treated with oxidative workup conditions (NaOH, H<sub>2</sub>O<sub>2</sub>) to give diol product **6**. As summarized in Scheme 3, several representative aldehydes, including aromatic, heteroaromatic and aliphatic aldehydes, reacted under these conditions to give diols **6a–6d** in 81–94% yields with 90–99% ee. In the case of **6d**, 10 mol% of catalyst (*S*)-**A** was employed for an optimal reaction rate. This process is

Scheme 3 Enantioconvergent synthesis of diols **6**.

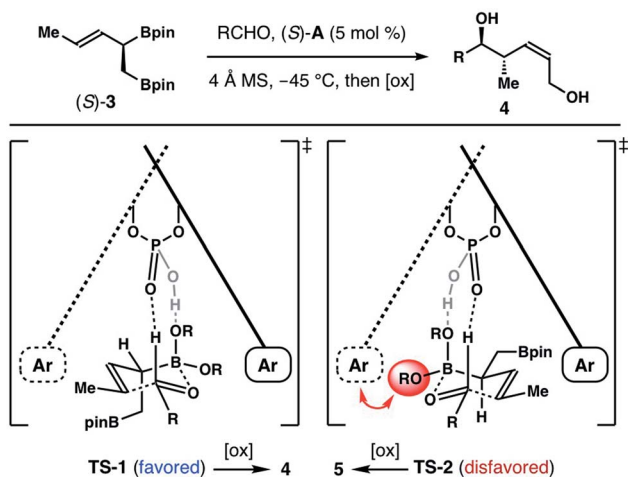
highly valuable because only a slight excess of racemic reagent ( $\pm$ )-**3** is required to generate highly enantioenriched diol products **6** and only a catalytic amount of chiral phosphoric acid catalyst (*S*)-**A** is needed as the source of asymmetric induction for the reactions.

As shown in Scheme 4, an enantioconvergent synthesis of aldehyde **9** was also developed. The racemic boron reagent ( $\pm$ )-**3** (1.3 equiv.) was treated with hydrocinnamic aldehyde under the standard asymmetric allylation conditions first. After completion of the reaction, the secondary alcohol group was protected *in situ* as a TES ether. Final oxidative workup gave a 3 : 1 mixture of allylic alcohols **7** and **8** in a combined 72% yield. Dess–Martin oxidation of the mixture of **7** and **8** followed by treatment of the resulting crude aldehydes with DMAP gave aldehyde **9** in 78% yield with 92% ee. The aldehyde group in **9** can now serve as a handle for further chain elongation reactions. For example, chiral phosphoric acid (*S*)-**A**-catalyzed asymmetric crotylation of aldehyde **9** with crotylboron reagent **10** gave alcohol **11** in 87% yield with >20 : 1 dr.<sup>11,12</sup> When acid (*R*)-**A** was employed as the catalyst, the reaction of **9** with reagent **10** formed alcohol **12** in 77% yield again with >20 : 1 dr.

We and other groups have documented that chiral biaryl phosphoric acid-catalyzed reactions of  $\alpha$ -substituted achiral allylboronates with aldehydes form homoallylic alcohols with excellent *Z*-selectivity. And the origins of observed *Z*-selectivity were further explored by extensive computational studies.<sup>10</sup> These reports provide foundation for us to rationalize the *Z*-selectivity in chiral phosphoric acid (*S*)-**A**-catalyzed reactions with boronate ( $\pm$ )-**3** (Scheme 5). In Scheme 2, we showed that the reaction of an aldehyde with the (*S*)-enantiomer of ( $\pm$ )-**3** is stereochemically matched when acid catalyst (*S*)-**A** is used. Therefore, the reaction of (*R*)-enantiomer of ( $\pm$ )-**3**, (*R*)-**3**, with (*S*)-**A** as the catalyst is disfavoured under the kinetic resolution pathway. In the reaction of (*S*)-**3** and an aldehyde substrate with (*S*)-**A** as the catalyst, two competing transition states, **TS-1** and **TS-2**, will lead to the *Z*-product **4** and *E*-product **5** respectively. As depicted in Scheme 5, **TS-2** involves the addition to the *re*-face of the aldehyde substrate. This mode of addition is opposite to the sense of asymmetric induction of the acid catalyst,

Scheme 4 Enantioconvergent synthesis of aldehyde **9**.





Scheme 5 Rationale for the observed Z-selectivity.

(S)-A.<sup>9</sup> Consequently, unfavourable steric interactions between the pinacol group on boron and the aromatic moiety of the acid catalyst will be developed (shown with a red arrow in TS-2). In addition, the pseudo equatorially positioned CH<sub>2</sub>Bpin group in TS-2 will have *gauche* interactions with the pinacol group on boron, which further destabilizes TS-2. By contrast, the *si*-face addition to the aldehyde substrate in TS-1 is consistent with the sense of asymmetric induction of catalyst (S)-A, which eliminates the steric interactions between the pinacol group on boron and the catalyst. Moreover, the CH<sub>2</sub>Bpin group is oriented in a pseudo axial position. And the unfavourable *gauche* steric interactions are absent in TS-1. Therefore, the reaction proceeded *via* the favoured transition state TS-1 to give Z-isomer 4 as the major product.

## Conclusions

In summary, we developed asymmetric transformations of racemic  $\alpha$ -borylmethyl-(E)-crotylboronate ( $\pm$ )-3 *via* either a kinetic resolution or enantioconvergent reaction pathways. In the presence of a catalytic amount of chiral phosphoric acid (S)-A, kinetic resolution-allylation of reagent ( $\pm$ )-3 produces (Z)-2-methyl-3-pentene-1,5-diols 4 with high Z-selectivities and excellent enantioselectivities. In the enantioconvergent reaction manifold, both enantiomers of racemic reagent ( $\pm$ )-3 were converted into highly enantioenriched 1,5-diols 6 or aldehyde 9. Importantly, these compounds can serve as synthetically useful intermediates for stereochemically complex natural product synthesis. It is worth noting that the enantioconvergent processes do not demand a large excess of racemic reagent ( $\pm$ )-3; and only a catalytic amount of chiral phosphoric acid (S)-A is required as the source of asymmetric induction to obtain products with excellent optical purities. Synthetic applications of this method will be reported in due course.

## Data availability

All the data have been included in the ESI.<sup>†</sup>

## Author contributions

Shang Gao and Jiaming Liu contributed equally to the manuscript by conducting experiments in Tables 1, 2, and Schemes 3 and 4.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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