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

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We report herein catalytic asymmetric transformations of racemic α-borylmethyl-(*E*)-crotylboronate. The Brønsted acid-catalyzed kinetic resolution–allylboration reaction sequence of the racemic reagent gave (*Z*)-δ-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 α,β-unsaturated aldehydes with excellent optical purity.

Introduction

Enantioenriched molecules are indispensable components in organic chemistry and modern drug discovery.[1] In the past twenty years, asymmetric catalysis has been the most adopted approach to synthesize such compounds.[2] 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.[3] 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.[4]

(*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.[5] Methods that allows for the access to such structural entities mainly rely on a multistep reaction sequence.[6] 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 $NaBH_4$ to give (*Z*)-2-methyl-3-pentene-1,5-diol **III** (Scheme 1a).[6a] 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).[6b] 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,[7] 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 α-borylmethyl-(*E*)-crotylboronate (±)-**3** (Scheme 1). Moreover, enantioconvergent syntheses of diols **6** and aldehydes **9** were accomplished from the same racemic boron reagent (±)-**3**, where both enantiomers of the racemate were converted into **6** or **9** with high enantioselectivities.

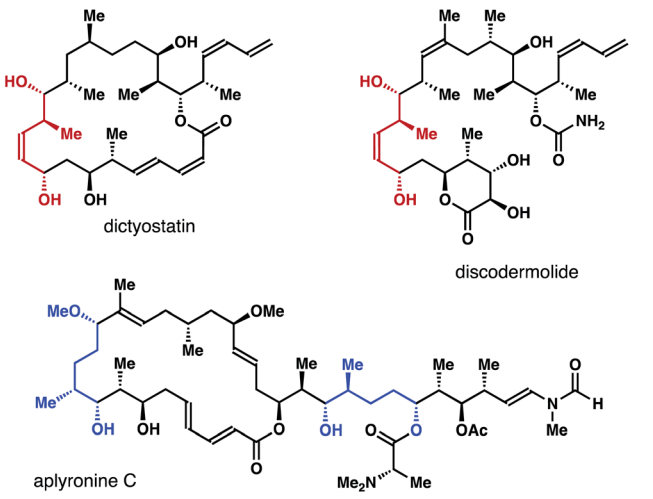

Fig. 1 Selected natural products that contain (*Z*)-2-methyl-3-pentene-1,5-diols or their reduced forms.

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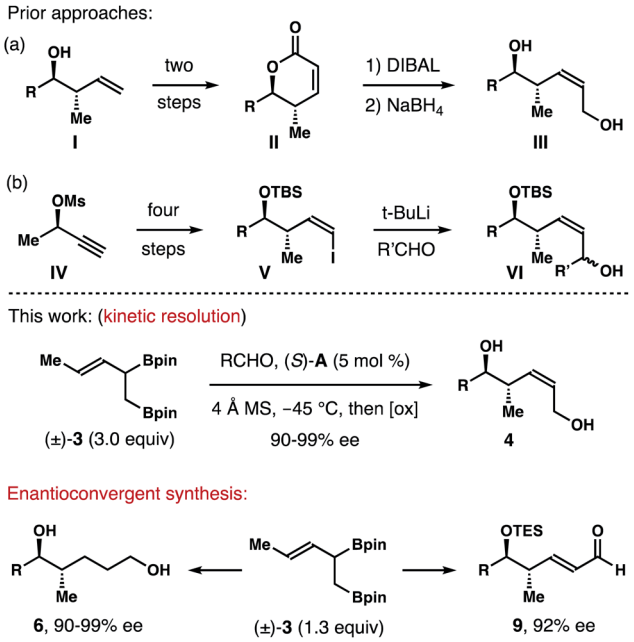
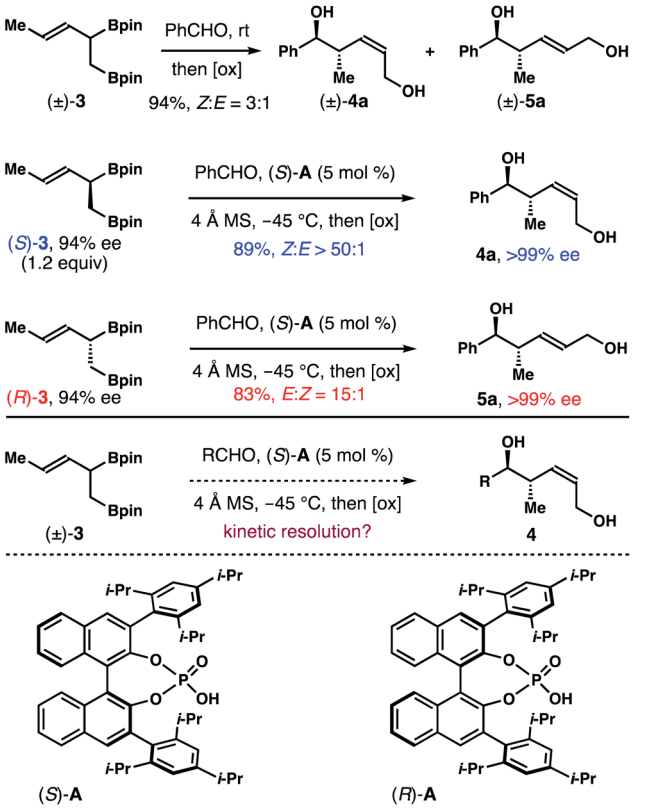


Scheme 1 Approaches to (*Z*)-2-methyl-3-pentene-1,5-diols.



Scheme 2 Initial studies with single enantiomer reagents.

Results and discussion

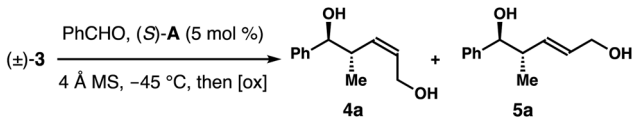
To evaluate the feasibility of proposed kinetic resolution approach to synthesize (*Z*)-2-methyl-3-pentene-1,5-diols **4**, we obtained racemic boronate (±)-**3** according to the reported protocols.[8] In the absence of any catalyst, the reaction of (±)-**3** with benzaldehyde gave a 3 : 1 mixture of two products upon oxidative workup, favouring the *Z*-isomer, (±)-**4a**. The results indicate the pseudo axial preference (3 : 1) of the α-CH_2Bpin group of reagent (±)-**3** in the reaction transition state. On the basis of recent studies on *Z*-selective allylboration catalyzed by chiral phosphoric acids,[9,10] 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 (±)-**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 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 α-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 (±)-**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 (±)-**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 (±)-**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 (±)-**3**. When 2 equiv. of (±)-**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 (±)-**3** (entry 3). Finally, 10 : 1 *Z*-selectivity was achieved when 3.0 equiv. of (±)-**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 (±)-**3** to balance the amount of (±)-**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 (±)-**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 α,β-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 (±)-**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%.

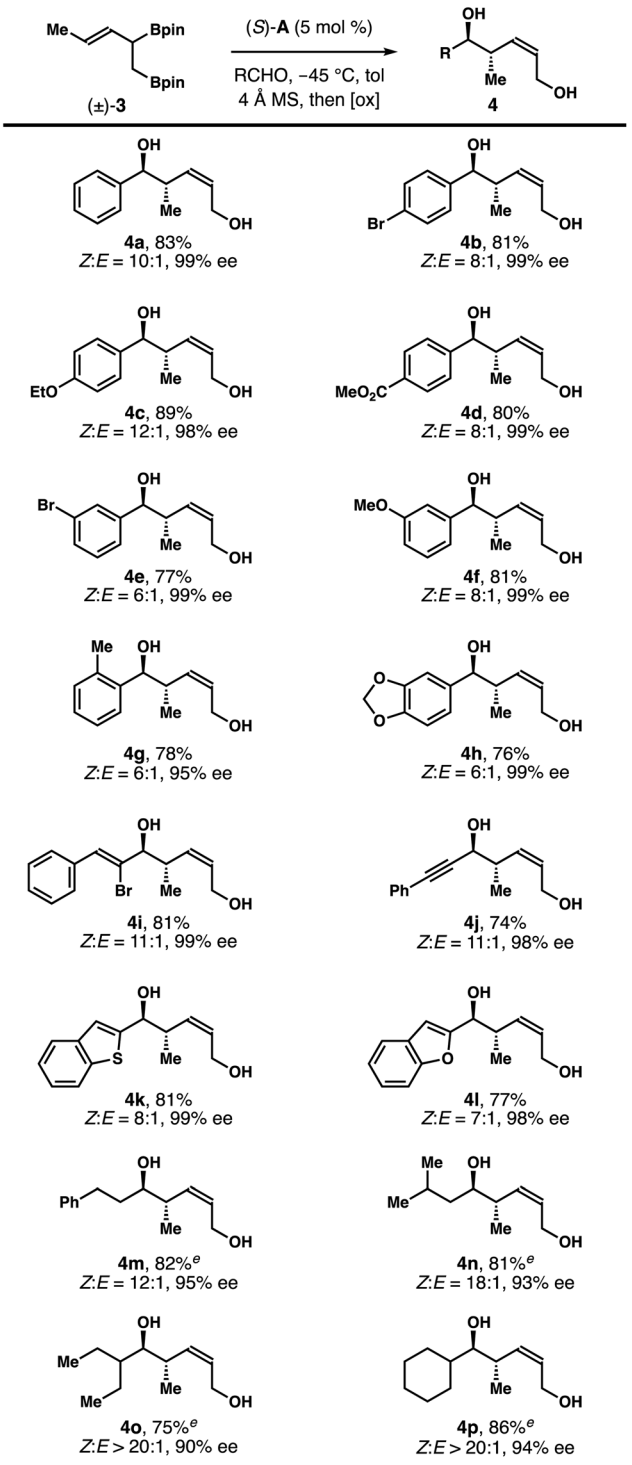
Table 1 Evaluation of reaction conditions for kinetic resolution allylboration with α-borylmethyl-(*E*)-crotylboronate (±)-**3**[a,b,c,d]



Entry	Equiv. (**3**)	**4a** : **5a**	ee (**4a**/**5a**)	ee (recovered **3**)	Yield (**4a** + **5a**)
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[e]

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

Table 2 Substrate scope[a,b,c,d]



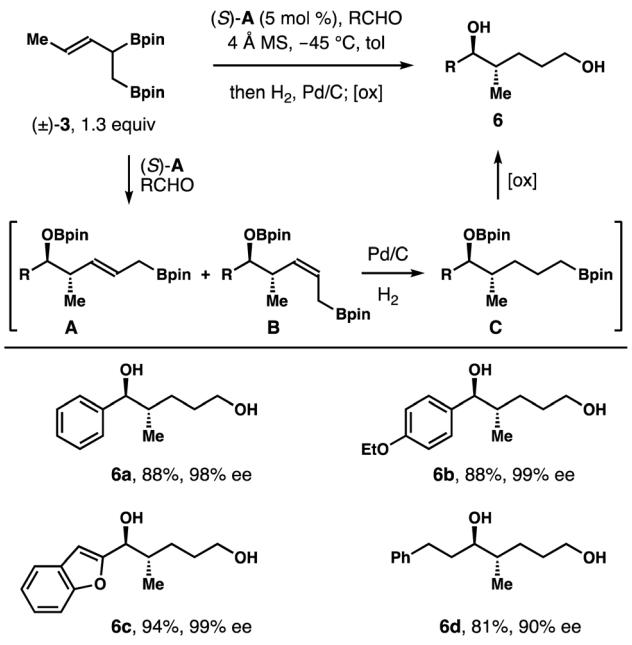
[a] Reaction conditions: allylboronate (±)-**3** (0.3 mmol, 3.0 equiv.), aldehyde (0.1 mmol, 1.0 equiv.), (*S*)-**A** (5 mol%), 4 Å molecular sieves, toluene, −45 °C; then NaOH, H_2O_2, 0 °C. [b] *Z*/*E*-selectivities were determined by ^{1}H NMR analysis of the crude reaction products. [c] Yields of isolated products **4** are listed. [d] Enantiopurities of **4** were determined by HPLC analysis. [e] 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 (±)-**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 α-CH_2Bpin 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 (±)-**3** can be utilized to form enantioenriched 1,5-diol products **6**, and large excess of reagent (±)-**3** will not be required as it is in the kinetic resolution pathway.

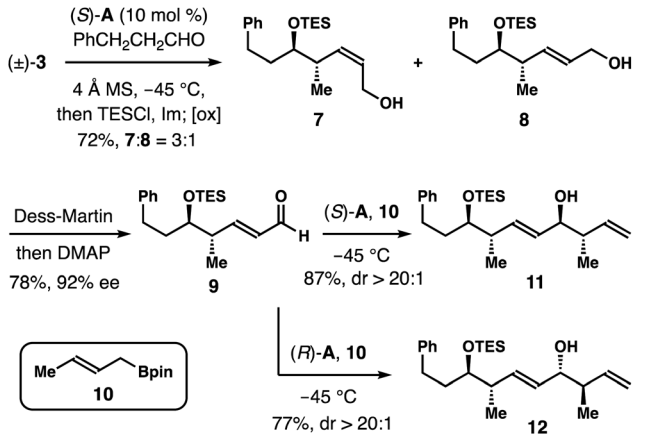
To validate our hypothesis, reactions of several aldehydes with reagent (±)-**3** (1.3 equiv.) were conducted in the presence of the catalyst (*S*)-**A**. After completion of the allylation, the resulting mixture, presumably intermediates **A** and **B** (Scheme 3), was subjected to the standard hydrogenation 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_2O_2) 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 highly valuable because only a slight excess of racemic reagent (±)-**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 (±)-**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.[11,12] 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.

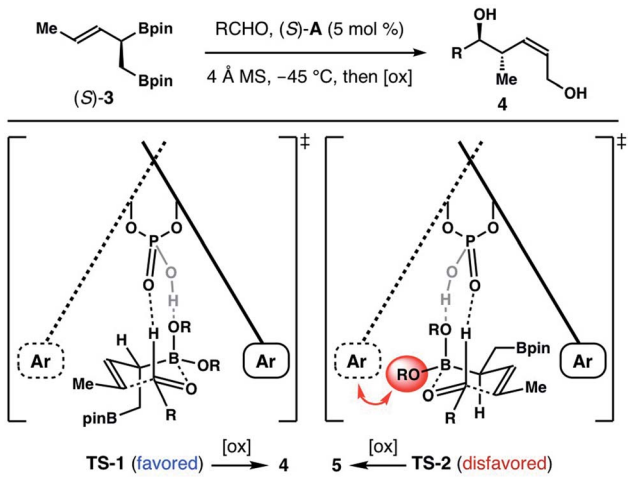
We and other groups have documented that chiral biaryl phosphoric acid-catalyzed reactions of α-substituted achiral allylboronates with aldehydes form homoallylic alcohols with excellent *Z*-selectivity. And the origins of observed *Z*-selectivity were further explored by extensive computational studies.[10] These reports provide foundation for us to rationalize the *Z*-selectivity in chiral phosphoric acid (*S*)-**A**-catalyzed reactions with boronate (±)-**3** (Scheme 5). In Scheme 2, we showed that the reaction of an aldehyde with the (*S*)-enantiomer of (±)-**3** is stereochemically matched when acid catalyst (*S*)-**A** is used. Therefore, the reaction of (*R*)-enantiomer of (±)-**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 3 Enantioconvergent synthesis of diols **6**.



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



Scheme 5 Rationale for the observed *Z*-selectivity.

(*S*)-**A**.[9] 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_2Bpin 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_2Bpin 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 α-borylmethyl-(*E*)-crotylboronate (±)-**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 (±)-**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 (±)-**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 (±)-**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.†

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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