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Kinetic Resolution of α-Silyl-Substituted Allylboronate Esters via Chemo- and Stereoselective Allylboration of Aldehydes

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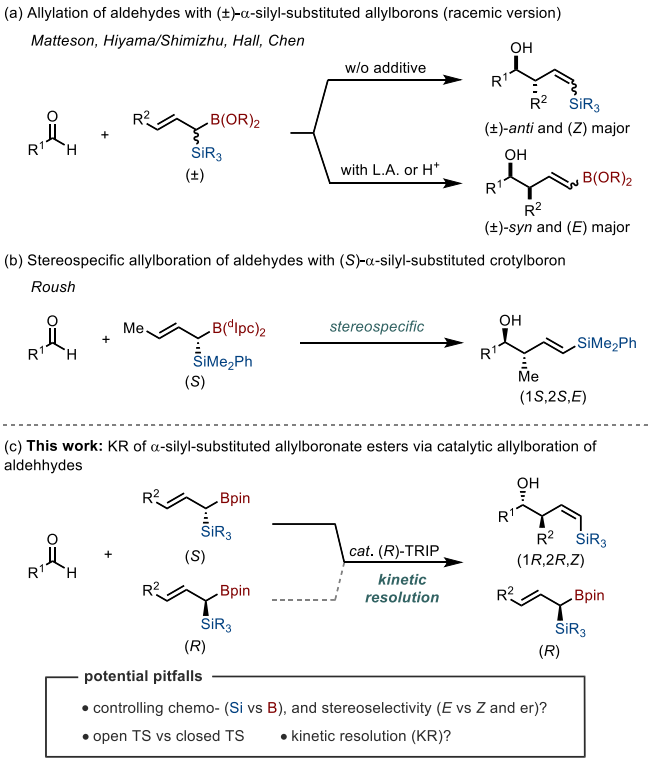
Abstract. We describe the kinetic resolution of α-silyl-allylboronate esters via chiral phosphoric acid-catalyzed chemo-, diastereo- and enantioselective allylboration of aldehydes. This process provides two synthetically versatile enantioenriched compounds, (*Z*)-δ-silyl-substituted *anti*-homoallylic alcohols and α-silyl-substituted allylboronate esters, with a selectivity factor up to 328. We propose that the reaction proceeds through a closed chair-like transition state with the silane moiety occupying a pseudo-axial position, thus readily resolving α-silyl-allylboronate esters. The synthetic utility of the obtained enantioenriched compounds is highlighted by their further transformations to give a diverse set of enantioenriched molecules.

Keywords: Allylboration; Boron; Silicon; Chemoselectivity; Enantioselectivity

Kinetic resolution (KR) of racemic materials is one of the most widely used techniques for the preparation of enantioenriched compounds. However, the kinetic resolution generally suffers from a practical limitation because the reaction occurs with a theoretical maximum yield of 50%.[1] In this vein, the development of a kinetic resolution process that affords both synthetically useful starting materials and products with high selectivity would be valuable in organic synthesis.[2]

Chemo- and stereoselective allylation of aldehydes with allylic *gem*-dimetalloids is an attractive approach to prepare homoallylic alcohols bearing a metalloid at the terminal alkene;[3],[4] the alkene component of homoallylic-alcohol products can undergo further functionalizations, serving as versatile building blocks in the synthesis of complex molecules. Elegant studies on the chemo- and enantioselective allylation of aldehydes with allylic *gem*-dimetalloids, such as chiral α-stannyl-substituted allylsilanes[5]/boranes,[6] chiral α-silyl-substituted allylsilanes,[7] or racemic α-boryl-substituted allylboronate esters,[8] have been disclosed. Despite these advances, chemo-and stereoselective allylation of aldehydes with α-silyl-substituted allylboron reagents has rarely been reported.[9]



Scheme 1. Chemo- and stereoselective allylation of aldehydes with α-silyl-substituted allylboron reagents. Pin = pinacol.

Since the pioneering work by Matteson and coworkers on the racemic version of allylboration of aldehydes with α-silyl-substituted allylboronate

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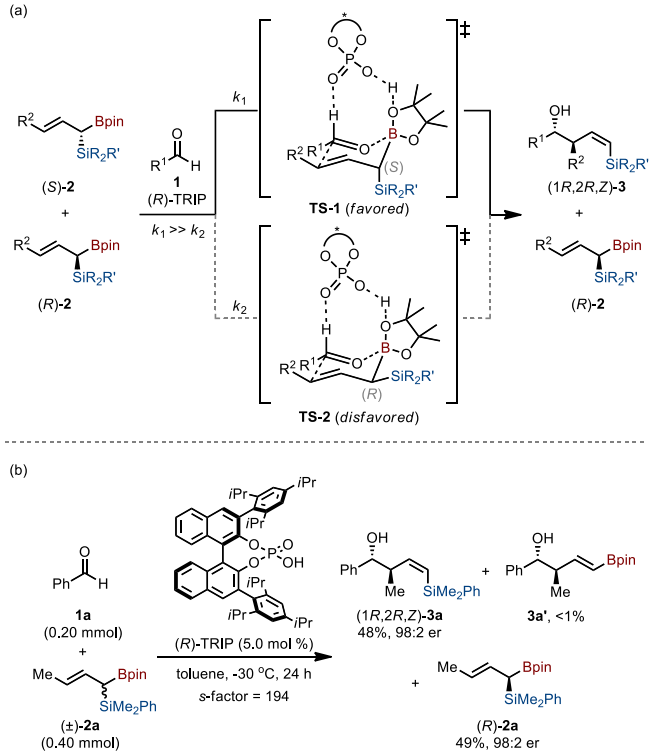
esters,[9a] Hiyama/Shimizhu,[9b] Hall,[9c] and Chen[9d] have extended the scope to include various α-silyl-



Scheme 2. (a) Proposed transition states for kinetic resolution of (±)-**2**. (b) Results for (*R*)-TRIP-catalyzed kinetic resolution of (±)-**2a** via allylboration of benzaldehyde. The yields of **3a** and **2a** were determined based on the (±)-**2a** initially used.

substituted allylboronate esters for chemo-and stereoselective allylborations, producing racemic products with moderate to excellent *E*/*Z* ratios (Scheme 1a). They also revealed that the addition of a Lewis acid or a Brønsted acid could promote Sakurai-type allylation of α-silyl-substituted allylboronate esters, giving a mixture of (*E*) or (*Z*)-δ-boryl-substituted homoallylic alcohols. In 2013, Roush et al. described the first chemo-, diastereo- and enantioselective crotylation of aldehydes with chiral α-silyl-substituted crotylboranes, prepared by hydroboration of an allenylsilane with diisopinocampheylborane [(^{d}Ipc)$_2$BH], thereby providing access to enantioenriched (*E*)-δ-silyl-substituted *anti*-homoallylic alcohols (Scheme 1b).[10] While highly useful, the reaction showed limited scope with respect to α-silyl- substituted allylboron reagents and required the use of a stoichiometric amount of costly chiral boron reagents to achieve high levels of enantioselectivity; to the best of our knowledge, the catalytic chemo- and enantioselective variants of those reactions with racemic α-silyl-allylboron reagents have remained unexplored.

Herein, we describe the kinetic resolution of α-silyl-substituted allylboronate esters through the catalytic, chemo- and enantioselective allylboration of aldehydes (Scheme 1c). The developed protocol occurs with a selectivity factor up to 328, generating highly enantioenriched, α-silyl-substituted allylboronate esters **2** and (*Z*)-δ-silyl-substituted *anti*-homoallylic alcohols **3**. Both compounds can serve as versatile intermediates to synthesize a diverse set of enantioenriched compounds.

Based on the recent achievements on the enantioselective allylboration of aldehydes with allyboronate esters catalyzed by (*R*)-3,3'-bis(2,4,6-triisopropylphenyl)-binol phosphoric acid (TRIP),[11] we sought that (*R*)-TRIP could catalyze the kinetic resolution of α-silyl-substituted allylboronate esters (±)-**2** by the reaction with aldehyde **1** if the reaction would proceed through a chair-like transition state (**TS-1** or **TS-2**) by the double coordination of (*R*)-TRIP to the C-H bond of an aldehyde and the pseudoaxial oxygen atom of Bpin (Scheme 2a).[12] However, the studies by Hall and coworkers indicated that aldehydes reacted preferentially with the allylsilane motif, rather than the allylboron, in the presence of a Brønsted acid.[9c] Thus, it was unclear whether the α-silyl-substituted allylboronate esters would undergo the allylboration via the proposed chair-like transition states with (*R*)-TRIP as a catalyst.

To test the feasibility of our proposal, we performed reactions between benzaldehyde **1a** and (*E*)-α-dimethylphenylsilyl-substituted crotylboronate ester (±)-**2a** in the presence of (*R*)-TRIP as a catalyst (Scheme 2b). The reaction of **1a** (0.20 mmol) with (±)-**2a** (0.40 mmol) in toluene at -30 °C yielded (1*R*,2*R*,*Z*)-δ-dimethylphenylsilyl-substituted *anti*-homoallylic alcohol **3a** with 98:2 er. Notably, the slow reacting enantiomer, (*R*)-**2a**, was recovered with 98:2(selectivity factor of 194).[13] Moreover, we were not able to detect (*E*)-δ-boryl-substituted homoallylic alcohol **3a'** resulting from the reaction of the allylsilane motif, during the reaction process. These results suggest that the allylboronate ester is more reactive toward the reaction with aldehyde **1a** than the allylsilane in the presence of (*R*)-TRIP. In addition, the chair-like transition state **TS-1**, which occupied the silane moiety at a pseudo-axial position, is more favourable thane **TS-2**, which placed the silane group at a pseudo-equatorial position, to minimize the steric repulsion between the Bpin and silane groups (k_1>> k_2).

Under the (*R*)-TRIP-catalyzed conditions, an array of α-silyl-substituted allylboronate esters (±)-**2** can be resolved by the enantioselective allylboration of aldehyde **1a** (Table 1a). Reactions of **1a** with (±)-**2** containing various silane substituents, such as benzyldimethyl-, diethylphenyl-, methyldiphenyl-, *tert*-butyldimethyl-, and trimethylsilane, afforded highly enantioenriched homoallylic alcohols **3b**-**3f** as well as unreacted allylboronate esters **2b**-**2f**. This process can effectively resolve (*E*)-α-dimethylphenylsilyl-γ-alkyl- substituted allylboronate esters. For instance,the reactions of substrates

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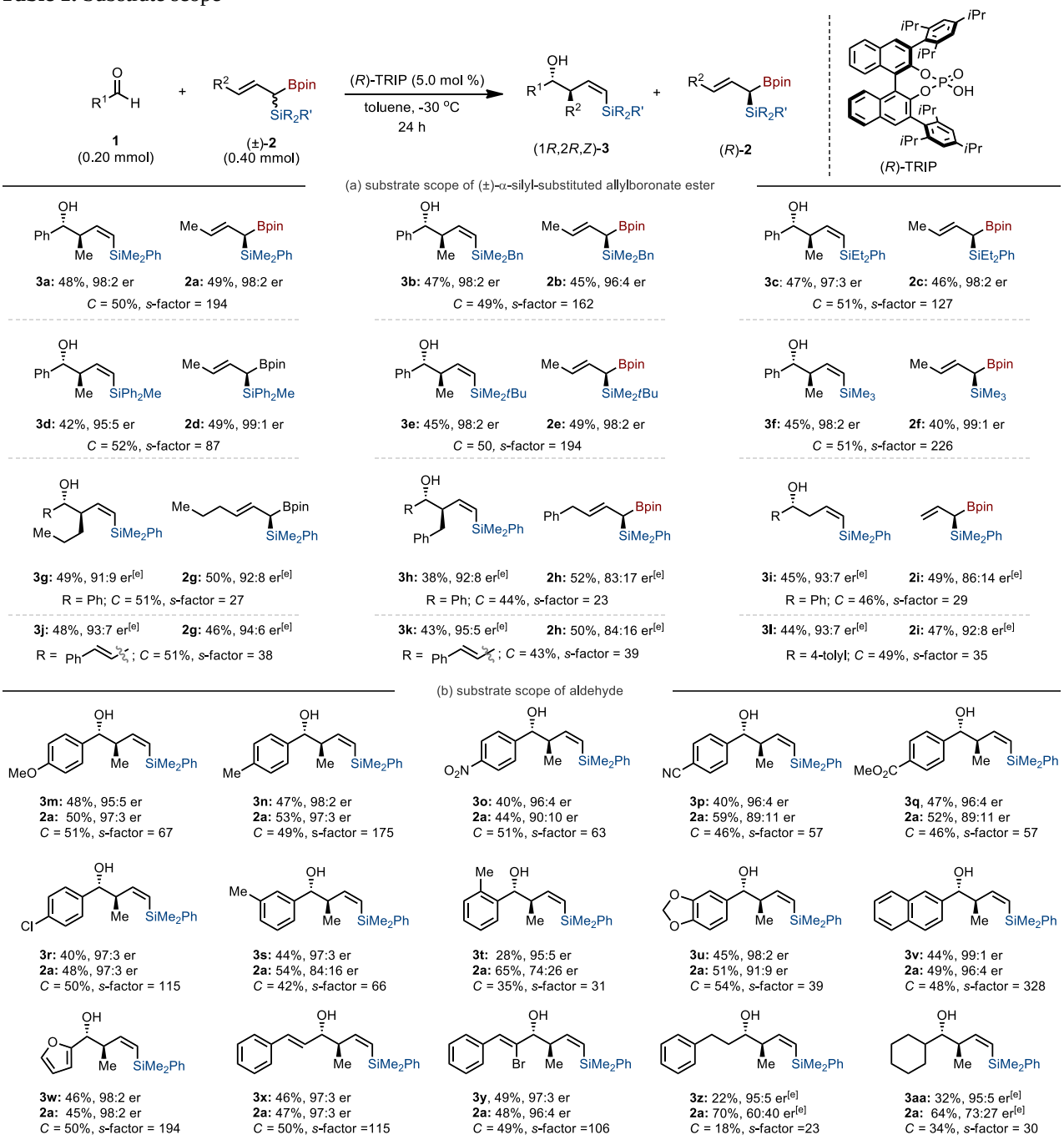
containing γ-propyl and γ-benzyl as R^1 substituents led to the formation of **3g** and **3h** along with **2g** and **2h**, although the reaction to generate **3h** required an increased catalyst loading (10 mol %) and a prolonged reaction time (72 h) to reach high

Table 1. Substrate scope[a]-[c]



[a] Reaction conditions: **1** (0.20 mmol), (±)-**2** (0.40 mmol), (*R*)-TRIP (5.0 mol %), and toluene (1.0 mL) at -30 °C for 24 h. [b] The yields of **3** and **2** were determined based on the (±)-**2** initially used. [c] The enantiomeric ratios (er) were determined by HPLC analysis. [d] Calculated conversion, $C = ee_2/(ee_2 + ee_3)$; selectivity (*s*) factor = $\ln[(1 - C)(1 - ee_2)]/\ln[(1 - C)(1 + ee_2)]$. [e] The reaction was performed for 72 h in the presence of 10 mol % of (*R*)-TRIP

conversion of **1a**. We assumed that the low reactivity and enantiomeric ratios might be attributed the the steric nature of alkyl substitutents. Nonsubstituted α-dimethylphenylsilyl-substituted allylboronate ester (R^1 = H) also smoothly underwent allylboration, furnishing **3i** and **2i** in the presence of 10 mol % (*R*)-TRIP after 72 h. In this case, we speculated that the relatively slow reaction of (±)-**2i** with benzaldehyde might be reponsible for the low er. While the recovered **2g**, **2h**, and **2i** showed relatively low er, reactions of (±)-**2g** and (±)-**2h** with cinnamaldehyde delivered **3j/2g** and **3k/2h** with a slightly improved selectivity.

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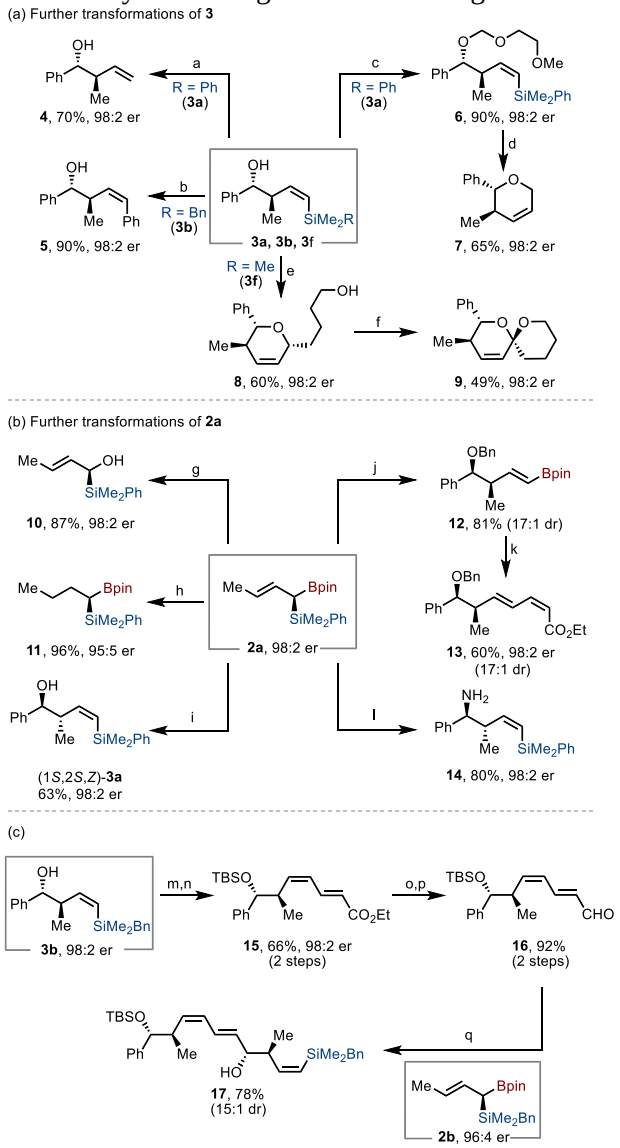
Furthermore, allylboration of (±)-**2i** with 4-tolylaldehyde afforded **3l** and **2i** with good er.[14]

A range of aldehydes **1** were selectively reacted with one enantiomer of (±)-**2a** to generate (*Z*)-δ-silyl-substituted *anti*-homoallylic alcohols in the presence of (*R*)-TRIP (Table 1b). The reactions of benzaldehydes bearing electron-donating and



Scheme 3. Transformations of enantioenriched (*Z*)-δ-silyl-substituted *anti*-homoallylic alcohol **3** and α-silyl-substituted allylboronate ester **2a**: [a] TBAF, DMSO, -78 °C, 3 h. [b] *cat.* $Pd(dba)_2$, iodobenzene, $TBAF{\cdot}3H_2O$, THF, rt, 1 h. [c] MEMCl, DIPEA, CH_2Cl_2. rt, 12 h. [d] $TiCl_4$, CH_2Cl_2, -78 °C, 0.5 h. [e] Methoxy tetrahydropyran, $EtAlCl_2$, CH_2Cl_2, -78 °C to rt, 12 h, and then HCl, MeOH, 3 h. [f] DDQ, CH_2Cl_2, -78 °C to rt, 12 h. [g] H_2O_2, NaOH, THF/H_2O, rt, 3 h. [h] $TsNHNH_2$, NaOAc, THF/H_2O, 50 °C, 12 h. [i] benzaldehyde, *n*-hexane, rt, 24 h. [j] TMSOTf, TMSOBn, CH_2Cl_2, -78 °C, 18 h. [k] *cat.* $PdCl_2(dppf){\cdot}CH_2Cl_2$, K_3PO_4, ethyl-(*Z*)-3-iodoacrylate, THF/H_2O, 70 °C, 12 h. [l] N-H phenylmethanimine, toluene, 80 °C, 24 h. [m] *cat.* $Pd(dba)_2$, ethyl-(*E*)-3-iodoacrylate, $TBAF{\cdot}3H_2O$, THF, rt, 24 h. [n] TBSCl, imidazole, DMF, rt, 12 h. [o] DIBAL-H, toluene, -78 °C, 2 h. [p] *cat.* TPAP, NMO, CH_2Cl_2, rt, 1 h. [q] **2b**, *n*-hexane, rt, 48 h.

electron-withdrawing substituents at the C4 position of the arene ring afforded **3m**-**3r** with high selectivties. In these cases, the resolution of (±)-**2a** to (*R*)-**2a** is sensitive to the electronic environment of aldehyde **1**. While the reactions of (±)-**2a** with benzaldehydes possessing electron-donating substituents at the C4 position displayed a high er of **2a**, those with benzaldehydes bearing electron-withdrawing substituents gave a relatively low er of **2a** except for that with 4-chlorobenzaldehyde. The allylborations of aldehydes with substituents at the *meta*- or *ortho*-positions delivered products **3s** and **3t** with good er, although they provided a quite low er of unreacted **2a**. Aldehydes, such as 1,3-benzodioxole-5-carboxaldehyde, 2-naphthyl aldehyde, and 2-furaldehyde reacted with (±)-**2a** to furnish **3u**-**3w** and **2a** with high er values. α,β-Unsaturated aldehydes, such as cinnamyl aldehyde, and (*Z*)-2-bromo-3-phenylacrylaldehyde were proven to be effective electrophiles in the allylborations, forming enantioenriched **3x** and **3y** along with **2a** with high selectivity factors. In addition, aliphatic aldehydes were also applicable to the developed process, leading to the formation of **3z** and **3aa**, albeit with moderate selectivity factors.

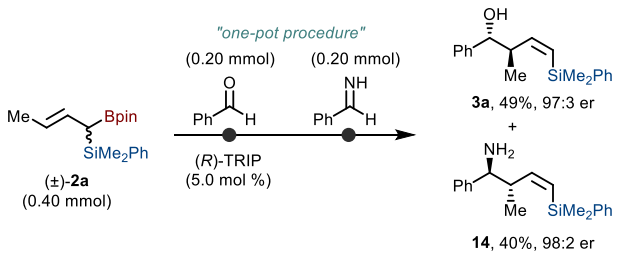
The obtained (*Z*)-δ-dimethylphenylsilyl-substituted *anti*-homoallylic alcohols **3** can be readily transformed into other structural motifs (Scheme 3a). The desilylation of **3a** by treatment with tetrabutylammonium fluoride (TBAF) afforded homoallylic alcohol **4**. Homoallylic alcohol **3b** also reacted smoothly with iodobenzene under the palladium-catalyzed Hiyama cross-coupling conditionsto yield δ-arylated product **5** with complete (*Z*)-selectivity. Protection of the hydroxyl group of **3a** with methoxyethoxymethyl (MEM) chloride delivered MEM ether **6**; subsequent $TiCl_4$-mediated cyclization gave cyclic ether **7**.[15] The reaction of **3f** with 2-methoxytetrahydropyran in the presence of ethylaluminium dichloride afforded product **8** as a single diastereomer, which could then undergo the oxidative cyclization to deliver dioxaspiro compound **9**,[16] a core structure in biologically active compounds.[17]

The unreacted, enantioenriched α-silyl-substituted allylboronate ester **2** from the (*R*)-TRIP-catalyzed kinetic resolution also could serve as a synthetically versatile intermediate in several transformations (Scheme 3b). Oxidation of the Bpin group of **2a** with aqueous H_2O_2 and NaOH gave α-silyloxy allylic silane **10**. The reduction of alkene of **2a** with $TsNHNH_2$ and NaOAc delivered the enantioenriched 1,1-silylboronate ester **11** with a

slightly decreased er. Compound **2a** reacted with benzaldehyde in *n*-hexane at room temperature to form the (1*S*,2*S*,*Z*)-**3a** with complete stereospecificity. The reaction of **2a** with benzaldehyde in the presence of stoichiometric amounts of trimethylsilyl triflate and benzyloxyltrimethylsilane led to the formation of δ-boryl-substituted *syn*-homoallylic alcohol **12** with 17:1 dr.[8b] Following palladium-catalyzed Suzuki-Miyaura cross-coupling of **12** with ethyl-(*Z*)-3-iodoacrylate yielded enantioenriched 1,3-diene **13**. Moreover, **2a** underwent the stereospecific allylboration with *in situ* generated N-H phenylmethanimine, producing (1*S*,2*S*,*Z*)-δ-silyl-substituted *anti*-homoallylic amine **14**.[18]

The utility of our (*R*)-TRIP-catalyzed kinetic resolution can also be highlighted by the synthesis of **17** through the use of both **2a** and **3b** obtained from the allylboration process as substrates (Scheme 3c). Hiyama cross-coupling of **3b** with ethyl-(*E*)-3-iodoacrylate followed by TBS-protection of OH group delivered **15**. Subsequent reduction of ester to alcohol with diisobutylaluminium hydride (DIBAL-H) and oxidation of alcohol in the presence of catalytic amounts of tetra-*n*-propylammonium perruthenate (TPAP) and *N*-methylmorpholine *N*-oxide (NMO) furnished the corresponding aldehyde **16**. Finally, the stereospecific allylboration of **16** with **2b** afforded the product **17** bearing four stereogenic centers with a high diastereoselectivity (15:1 dr).

Furthermore, we developed enantioselective allylborations of two different electrophiles, benzaldehyde and N-H phenylmethanimine, with (±)-**2a** in a one-pot sequence (Scheme 4). After performing (*R*)-TRIP-catalyzed allylboration of **1a** with (±)-**2a** at -30 °C, N-H phenylmethanimine was added to the same reaction vessel, and the reaction mixture was heated at 80 °C to provide homoallylic alcohol **3a** and homoallylic amine **14** without deteriorating the er.



Scheme 4. One-pot allylboration of benzaldehyde and N-H phenylmethanimine with (±)-**2a**

In summary, we have developed the (*R*)-TRIP-catalyzed kinetic resolution of α-silyl-allylboronate esters via chemo-, diastereo-, and enantioselective allylboration of aldehydes. This reaction provides two highly enantioenriched compounds, namely, (*Z*)-δ-silyl-substituted *anti*-homoallylic alcohols and α-silyl-substituted allylboronate esters, which serve as useful intermediates for the synthesis of a diverse set of chiral building blocks. We anticipate that this strategy would be applicable to the synthesis of a wide range of chiral target molecules. Further efforts to develop chemo- and enantioselective transformations of α-silyl-allylboronate ester with other electrophiles are underway in our laboratory.

Experimental Section

Representative procedure for the synthesis of (1*R*,2*R*,*Z*)-3a and (*R*)-2a. Inside the nitrogen filled glove-box, (*R*)-TRIP (7.5 mg, 0.010 mmol), benzaldehyde (21 mg, 0.20 mmol) and toluene (0.50 mL) were added to an oven-dried 4.0 mL dram vial equipped with a magnetic stir bar. The vial was sealed with an assembled screw cap with hole with PTFE/silicone septum, removed from the glove box and cooled to -30 °C. To this mixture, α-silyl-substituted allyl boronate ester (±)-**2a** (0.13 g, 0.40 mmol) in toluene (0.50 mL) was added in one portion and stirred for 24 h at the same temperature. The reaction was quenched with a saturated aqueous $NaHSO_3$ solution (1.0 mL) and MeOH (0.50 mL) and stirred for 30 min at room temperature. The reaction mixture was poured into the separate funnel and the aqueous layer was extracted with EtOAc (5.0 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give enantioenriched (Z)-α-silyl-substituted *anti*-homoallylic alcohol **3a** and α-silyl-substituted allylboronate ester **2a**. Enantiomeric purity was determined by HPLC analysis. Analogous mixtures of enantiomers were prepared by the reaction of benzaldehyde and (±)-**2a** in *n*-hexane for 24 h at room temperature.

Acknowledgements

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[13] The absolute and relative configurations of **3a** and **2a** were determined after converting **3a** and **2a** to known compounds. The configurations of other products were assigned by analogy. See the Supporting Information for details.

[14] See the Supporting Information for details.

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