Asymmetric Allylation

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Highly Stereoselective Synthesis of *Z*-Homoallylic Alcohols by Kinetic Resolution of Racemic Secondary Allyl Boronates**

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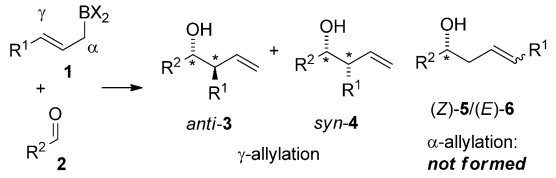
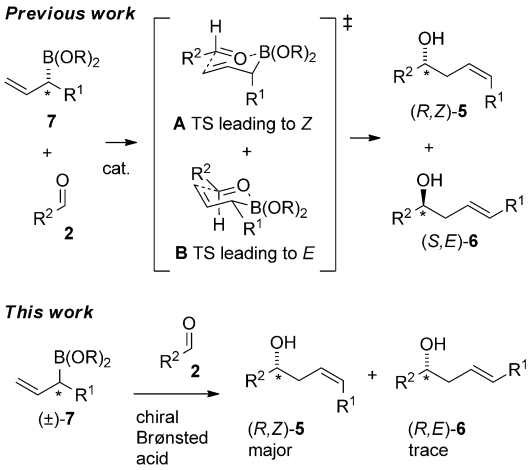
Asymmetric allylation of aldehydes with stoichiometric amounts of chiral allylboron reagents **1** has evolved into an efficient and well-established practical method for the synthesis of enantiomerically enriched homoallylic alcohols (Scheme 1).[1] Chiral auxiliary based reagents were superseded by asymmetric catalytic methods that relied on the efficient transfer of chirality from the catalyst.[2] The reaction proceeds through a closed transition state and results in the products of γ-allylation with excellent diastereocontrol: *E* alkenes give *anti* diastereoisomer **3** and *Z* alkenes give rise to *syn* isomer **4**, whereas the products of α-allylation **5**/**6** are not normally observed.[3] Secondary allylboron reagents have to be employed for the synthesis of linear isomers **5**/**6**.[4]



Scheme 1. Allylation with primary allylboron reagents.



Scheme 2. Allylation with chiral secondary allyl boronates.

Homochiral secondary allyl boronates **7** (Scheme 2) are known to competently relay their chirality into the products without the need for an external chiral controller.[5–7] However, the two competing cyclic transition states, where the group R^1 occupies either the axial (**A**) or equatorial (**B**) position, give rise to a mixture of *Z*/*E* isomers (**5** and **6**), which belong to the opposite enantiomeric series and thus lower the effective enantioselectivity of the process. Geometrical selectivity strongly depends on the nature of the group R^1 and is usually high for α-heteroatom-substituted derivatives,[7] whereas simple alkyl substituents give rise to synthetically inadequate *E*/*Z* ratios. Attempts to control the geometrical selectivity typically involve varying the nature of the catalysts and tuning the steric and electronic properties of the chiral boronate fragment, which frequently requires a laborious synthetic input.[5,6] However, these efforts brought only a partial solution to the problem—providing facile access to (*E*)-homoallylic alcohols **6**[5a,6a–d]—whereas a general catalytic approach to *Z* isomers **5**, where R^1 is a simple alkyl group, remains underdeveloped.

Herein we introduce a novel, conceptually different method that involves an efficient kinetic resolution of chiral racemic allyl boronates **7** in a face- and *Z*-selective allylation of aldehydes **2** catalyzed by chiral Brønsted acids (Scheme 2).

Chiral Brønsted acid catalysts provided excellent enantiofacial selectivity in the reaction of achiral primary allyl boronates with aldehydes, as revealed by Hall and coworkers[2b–d] as well as Jain and Antilla.[2g] Therefore, it was reasonable to assume that the combination of chiral Brønsted acid catalysts with racemic secondary allyl boronate **7** should also favor the formation of **5** and **6** in the same enantiomeric series. In this case, the main challenge for the efficient kinetic resolution to operate would be to enforce a preference for the transition state with either an equatorial (leading to (*E*)-**6**) or axial (leading to (*Z*)-**5**) position of the R^1 group. Since *E* isomers can be readily obtained by a number of existing methods,[3,5c,6a–d] we focused our attention on *Z* isomers, for which there are currently only a few examples, in which chiral auxiliaries or the chiral pool are employed.[6e,f,8]

Reports by Hoffmann and Weidmann[9] as well as Pietruszka and Schone[6e] demonstrated that the *E*/*Z* ratio of the homoallylic alcohols in the noncatalyzed allylation of aldehydes with secondary alkylallyl boronates depends on the steric size of the boronate fragment. Larger groups, such as pinacolate or benzpinacolate, favor the formation of the

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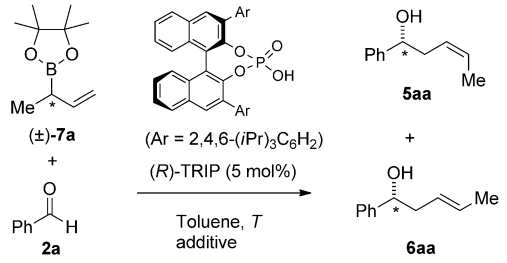
Z isomer, whereas smaller groups, such as dimethoxy, tend to lead to formation of the *E* alkene preferentially. Therefore, for preliminary investigations we opted for racemic pinacol boronate **7a** (Table 1).

Table 1: Optimization of the reaction conditions.[a]



Entry	Add. (mol%)	*T* [°C]	*t* [h]	**5**/**6**[b]	*ee* [%] (**5**/**6**)[c]
1	–	RT	18	67:33	60:91
2	–	−30	72	66:34	91:97
3	HCl[d]	−30	18	75:25	91:97
4	TFA (2.5)	−30	18	72:28	80:79
5	AcOH (2.5)	−30	18	75:25	85:88
6	TFA (1)	−30	18	65:35	85:87
7	AcOH (1)	−30	18	75:25	89:91
8	AcOH (1)	−78	72	80:20	96:98

[a] The reactions were carried out with 0.2 mmol of **2** and 0.5 mmol (2.5 equiv) of **7a** in toluene (2 mL) at the temperature specified. Full conversion of **2a** was observed in all cases. [b] Determined from ^{1}H NMR spectroscopy of a crude reaction mixture. [c] Determined by HPLC on a chiral stationary phase (see Supporting Information for details). The products were of *R* configuration. [d] Trace quantities of HCl in TRIP.

Reaction of benzaldehyde (**2a**) with 2.5 equivalents of (±)-**7a** at RT in the presence of (*R*)-TRIP (5 mol%) produced a 2:1 mixture of **5aa** and **6aa** (entry 1). Importantly, both isomers were of the same enantiomeric series, thus indicating that the stereoselectivity in the allylation of **2a** catalyzed by (*R*)-TRIP relies on the enantiofacial discrimination of the carbonyl group aided by kinetic preference for the axially oriented α-methyl substituent of boronate **7a** in the chairlike transition state. Note that kinetic resolution[10] alone, without face selectivity, would yield a mixture of **5aa** and **6aa** as opposite enantiomers. Lowering the reaction temperature to −30°C improved the enantioselectivity without changing the *Z*/*E* ratio, but the reaction became slow (entry 2). A brief screening of solvents confirmed toluene as the optimal choice, with CH_2Cl_2 and THF, in particular, producing inferior results in terms of enantioselectivity, thus mirroring the observations of Jain and Antilla.[2g]

It was noticed that when TRIP (synthesized in-house) contained traces of HCl after the isolation,[11] the reactivity markedly increased (entry 3). This prompted us to investigate the influence of various acid additives on the stereoselectivity of the process. At 2.5 mol% loading, both trifluoroacetic acid (TFA) and acetic acid (AcOH) resulted in good acceleration, however at the expense of enantioselectivity (entries 4 and 5). When the additive loading was reduced to 1 mol%, the enantioselectivity improved with no detriment to the geometrical selectivity or the reaction rate (entries 6 and 7). AcOH resulted in the best overall performance. The role of the acid additive is not clear at the moment, but it is assumed to suppress formation of catalytically inactive aggregates of TRIP in the nonpolar medium. At −78°C, the enantioselectivity reached a respectable level of 96 and 98% *ee* for **5aa** and **6aa**, respectively, with the *Z*/*E* ratio also improving to 4:1 (entry 8); however, the latter still remained insufficient from a synthetic viewpoint, and indicates that kinetic resolution was not operating competently.

Next we focused on the structure of the boronate fragment. To avoid random experimental screening of various boronate scaffolds we turned instead to in silico analysis (Figure 1).

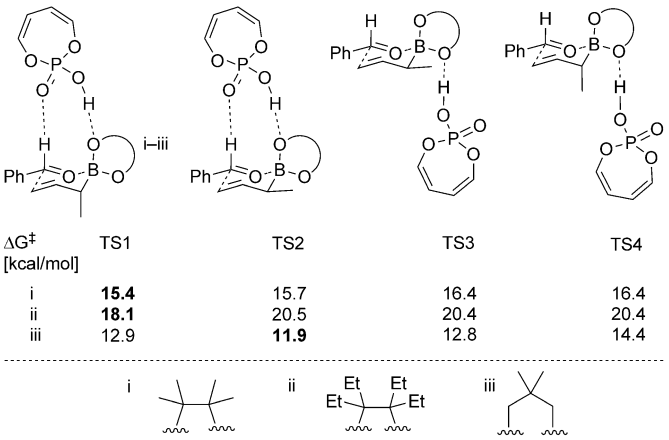


Figure 1. Computational analysis of transition-state structures with different boronate fragments.

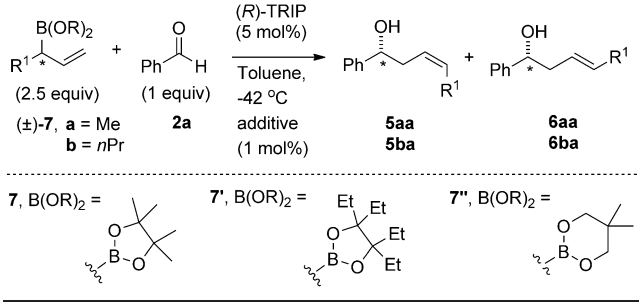
DFT level calculations[12] were carried out to elucidate the influence of the steric size of the cyclic boronate moiety on the *E*/*Z* ratio of the resulting homoallylic alcohols. A pinacol group (i) was compared to tetraethylethylene glycol (ii) and 2,2-dimethylpropan-1,3-diol (iii). Protonation of the allyl boronate fragment by a Brønsted acid can occur at either of the two boronate oxygen atoms. A recent mechanistic investigation by Goodman and co-workers[13] into the asymmetric addition of primary allyl boronates to aldehydes catalyzed by a chiral phosphoric acid revealed the preference for a double coordination mode involving the pseudoaxial oxygen atom (TS1, TS2) over interaction with the pseudoequatorial oxygen atom (TS3, TS4). To make sure that this mechanism also extends to the secondary allyl boronates, all four transition states TS1–TS4, which correspond to the formation of the *E* and *Z* isomers through both modes of activation, were analyzed.

First, the computations revealed that the two-point activation mode described by Goodman and co-workers is favored for all three boronates. Secondly, a clear trend emerged that indicated that the larger the steric size of the boronate (ii > i > iii), the more pronounced the preference for the formation of the *Z* isomer. Importantly, the calculation predicted that the tetraethylethylene glycol derivative (Epin,

ii) should afford a highly enhanced Z/E ratio of almost 100:1, whereas 2,2-dimethylpropan-1,3-diol (iii), in contrast, should favor the E isomer.

To test the theoretical conclusions, boronates **7**, **7′**, and **7″** were synthesized by using a single-step protocol recently developed by Singaram and co-workers.[14] With the set of racemic allyl boronates in hand, their kinetic resolution was investigated in the model reaction with benzaldehyde (**2a**; Table 2). In excellent agreement with the computational data,

Table 2: Optimization of boronate **7**.[a]



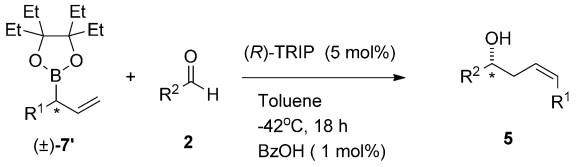
	7, R^1	Add.	t [h]	**5**/**6** calcd[b]	**5**/**6** exp[c]	*ee* [%] (**5**/**6**)[d]
1	**7a**, Me	AcOH	72[e]	2:1	80:20	96:98
2	**7′a**, Me	AcOH	48	100:1	96:4	98 (**5**)
3	**7′a**, Me	BzOH	18		97:3	97 (**5**)
4	**7″a**, Me	BzOH	72[f]	1:8	40:60	41:40
5	**7b**, *n*Pr	BzOH	18	–	67:33	60:72
6	**7′b**, *n*Pr	BzOH	18	–	98:2	94 (**5**)

[a] The reactions were carried out on a 0.2 mmol scale in toluene (2 mL). Full conversion of **2a** was observed in all cases. [b] Predicted by quantum chemical calculations. [c] Determined from ^{1}H NMR spectroscopic analysis of a crude reaction mixture. [d] Determined by HPLC on a chiral stationary phase (see Supporting Information for details). [e] The reaction was carried out at −78 °C. [f] 4.0 equiv of **7″a** were used. Bz = benzoyl.

tetraethyl analogue **7′a** exhibited far superior Z selectivity than the parent pinacol boronate **7a** (see entries 1 and 2). Importantly, the homoallylic alcohol **5aa** was obtained in 98% *ee*. At this point it was also found that the reaction rate can be further enhanced by employing benzoic acid as an additive (entry 3). With the least sterically biased boronate **7″a**, the Z/E ratio of the products swung in favor of the E isomer, as predicted computationally, and was accompanied by a significant drop in enantioselectivity (entry 4). The superior selectivity shown by the tetraethylethylene glycol group further extends to the propyl homologues **7b** and **7′b**, the latter producing virtually geometrically pure **5ba** with high enantioselectivity (see entries 5 and 6).

After establishing the optimal conditions and fine-tuning the structure of the boronate unit, we next examined the reaction scope. Boronates **7′a** and **7′b** were employed in the allylation of a range of recipient aldehydes (Table 3). The reaction proved to be very efficient in every instance, with the enantioselectivity varying in the range 85–99% *ee*, essentially irrespective of the nature of aldehyde **2** and the boronate **7**, with the more sterically demanding boronate **7′b** (entries 12–14) mirroring the trend shown by **7′a** (entries 1–11). Signifi-

Table 3: Scope of the kinetic resolution of racemic secondary allyl boronates **7′**.[a]



	7′, R^1	**2**, R^2	**5**	Yield [%]	**5**, *ee* [%][b,c]
1	**7′a**, Me	**2a**, Ph	**5aa**	96	97
2	**7′a**, Me	**2b**, PhCH=CH	**5ab**	84	97
3	**7′a**, Me	**2c**, $PhCH_2CH_2$	**5ac**	81	91[d]
4	**7′a**, Me	**2d**, 4-$MeOC_6H_4$	**5ad**	70	98
5	**7′a**, Me	**2e**, 4-FC_6H_4	**5ae**	80	85
6	**7′a**, Me	**2f**, 4-ClC_6H_4	**5af**	81	99
7	**7′a**, Me	**2g**, 2-naphthyl	**5ag**	78	98
8	**7′a**, Me	**2h**, 2-MeC_6H_4	**5ah**	75[e]	91
9	**7′a**, Me	**2i**, 2-thienyl	**5ai**	78	99
10	**7′a**, Me	**2j**, 4-$CF_3C_6H_4$	**5aj**	80	96
11	**7′a**, Me	**2k**, *c*-C_6H_{11}	**5ak**	72	88
12	**7′b**, *n*Pr	**2a**, Ph	**5ba**	90	94
13	**7′b**, *n*Pr	**2b**, PhCH=CH	**5bb**	97[f]	93
14	**7′b**, *n*Pr	**2c**, $PhCH_2CH_2$	**5bc**	80[f]	87[d,g]

[a] The reactions were carried out on a 0.2 mmol scale in toluene (2 mL). [b] Determined by HPLC on a chiral stationary phase (see Supporting Information for details). The absolute configuration has not been rigorously established, but is assumed to be *R* in analogy to **5aa**. [c] In all cases, unless stated otherwise, the Z/E ratio was $>25:1$ (determined from ^{1}H NMR spectroscopic analysis of a crude reaction mixture). [d] The product was *S*-configured as a result of the change in the preference of the substituents in the Cahn–Ingold–Prelog system. [e] Reaction time 42 h. [f] Reaction time 60 h. [g] Z/E ratio 13:1.

cantly, all but one of the resulting homoallylic alcohols were obtained with an impressive Z selectivity of $>25:1$.

In conclusion, we have developed a highly efficient protocol for the kinetic resolution of chiral racemic secondary allyl boronates in the allylation of aldehydes catalyzed by the chiral phosphoric acid (*R*)-TRIP. The success of this resolution method depends on the contribution of the two major factors: 1) the enantiofacial selectivity in the C–C bond formation and 2) kinetic preference towards the axially oriented α-alkyl substituent of the boronate in the transition state. Quantum chemical calculations identified the tetraethylethylene glycol boronate scaffold (B(Epin)) as optimal to favor the Z-selective reaction pathway. A wide range of Z-homoallylic alcohols were obtained with high geometrical and enantiomeric purity. Further investigation to expand the reaction scope and to elucidate the mechanism of the enantio- and stereodifferentiation are in progress.

Experimental Section

General procedure for the kinetic resolution of racemic allyl boronates in the allylation of aldehydes: A reaction tube was fitted with a stirring bar, and then the vessel evacuated, backfilled with N_2, and then charged successively with a solution of (*R*)-TRIP (12.6 mg, 0.0168 mmol, 5 mol%) in dry toluene (0.5 mL) and a 0.5 M stock solution of benzoic acid in toluene (6.7 μL, 0.0034 mmol, 1 mol%). The solution was cooled to −42 °C. Aldehyde (0.34 mmol, 1 equiv) dissolved in dry toluene (0.5 mL) was added, followed by the dropwise addition of a solution of allyl boronate (0.84 mmol,

2.5 equiv) in dry toluene (0.5 mL). After the reaction was complete, as evidenced by TLC, a saturated solution of $NaHCO_3$ (5 mL) was added, the mixture stirred for 1 h, and then the organic phase extracted with ethyl acetate (3 × 15 mL). The organic layers were combined and dried over Na_2SO_4 before removing the solvent under vacuum. Flash chromatography on silica gel with a gradient eluent system (100% hexane to 95:5, hexane/ethyl acetate) afforded the target homoallylic alcohol. Note: the aldehyde should be fully consumed before stopping the reaction, otherwise a background reaction occurring during work-up may result in reduced enantio- and stereoselectivity.

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[1] a) S. R. Chemler, W. R. Roush in *Modern Carbonyl Chemistry* (Ed.: J. Otera), Wiley-VCH, Weinheim, **2000**, pp. 403 – 490; b) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763 – 2793; c) T. Herold, R. W. Hoffmann, *Angew. Chem.* **1978**, *90*, 822 – 823; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 768 – 769; d) H. C. Brown, P. K. Jadhav, *J. Am. Chem. Soc.* **1983**, *105*, 2092 – 2093; e) H. C. Brown, K. S. Bhat, *J. Am. Chem. Soc.* **1986**, *108*, 293 – 294; f) S. Masamune, B. Kim, J. Garcia, *J. Org. Chem.* **1987**, *52*, 4831 – 4832; g) S. Masamune, R. P. Short, *J. Am. Chem. Soc.* **1989**, *111*, 1892 – 1894; h) E. J. Corey, C. Yu, S. S. Kim, *J. Am. Chem. Soc.* **1989**, *111*, 5495 – 5496; i) W. R. Roush, A. E. Walts, L. K. Hoong, *J. Am. Chem. Soc.* **1985**, *107*, 8186 – 8190; j) W. R. Roush, A. D. Palkowitz, K. Ando, *J. Am. Chem. Soc.* **1990**, *112*, 6348 – 6359; k) W. R. Roush, K. Ando, D. D. Powers, A. D. Palkowitz, R. L. Halterman, *J. Am. Chem. Soc.* **1990**, *112*, 6339 – 6348; l) E. Canales, K. G. Prasad, J. A. Soderquist, *J. Am. Chem. Soc.* **2005**, *127*, 11572 – 11573; for the first allylation of aldehydes using allylboron regarents, see m) B. M. Mikhailov, Y. N. Bubnov, *Russ. Chem. Bull.* **1964**, *13*, 1774 – 1776.

[2] a) R. Wada, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2004**, *126*, 8910 – 8911; b) V. Rauniyar, D. G. Hall, *Angew. Chem.* **2006**, *118*, 2486 – 2488; *Angew. Chem. Int. Ed.* **2006**, *45*, 2426 – 2428; c) V. Rauniyar, H. Zhai, D. G. Hall, *J. Am. Chem. Soc.* **2008**, *130*, 8481 – 8490; d) V. Rauniyar, D. G. Hall, *J. Org. Chem.* **2009**, *74*, 4236 – 4241; e) S. Lou, P. N. Moquist, S. E. Schaus, *J. Am. Chem. Soc.* **2006**, *128*, 12660 – 12661; f) D. S. Barnett, P. N. Moquist, S. E. Schaus, *Angew. Chem.* **2009**, *121*, 8835 – 8838; *Angew. Chem. Int. Ed.* **2009**, *48*, 8679 – 8682; g) P. Jain, J. C. Antilla, *J. Am. Chem. Soc.* **2010**, *132*, 11884 – 11886; for the related asymmetric propargylation, see h) D. S. Barnett, S. E. Schaus, *Org. Lett.* **2011**, *13*, 4020 – 4023; i) P. Jain, H. Wang, K. N. Houk, J. C. Antilla, *Angew. Chem.* **2012**, *124*, 1420 – 1423; *Angew. Chem. Int. Ed.* **2012**, *51*, 1391 – 1394; j) M. Chen, W. R. Roush, *J. Am. Chem. Soc.* **2012**, *134*, 10947 – 10952; k) L. R. Reddy, *Org. Lett.* **2012**, *14*, 1142 – 1145; for the related asymmetric allenylation, see l) L. R. Reddy, *Chem. Commun.* **2012**, *48*, 9189 – 9191.

[3] For asymmetric α-crotylation methods, see a) J. Nokami, M. Ohga, H. Nakamoto, T. Matsubara, I. Hussain, K. Kataoka, *J. Am. Chem. Soc.* **2001**, *123*, 9168 – 9169; b) J. Nokami, K. Nomiyama, S. Matsuda, N. Imai, K. Kataoka, *Angew. Chem.* **2003**, *115*, 1311 – 1314; *Angew. Chem. Int. Ed.* **2003**, *42*, 1273 – 1276; c) T.-P. Loh, C.-L. K. Lee, K.-T. Tan, *Org. Lett.* **2002**, *4*, 2985 – 2987; d) A. V. Malkov, M. A. Kabeshov, M. Barłóg, P. Kočovský, *Chem. Eur. J.* **2009**, *15*, 1570 – 1573; e) A. V. Malkov, O. Kysilka, M. Edgar, A. Kadlčíková, M. Kotora, P. Kočovský, *Chem. Eur. J.* **2011**, *17*, 7162 – 7166.

[4] For the asymmetric synthesis of branched products from racemic secondary allyl boronates, see a) S. Kobayashi, T. Endo, U. Schneider, M. Ueno, *Chem. Commun.* **2010**, *46*, 1260 – 1262; b) S. Kobayashi, T. Endo, M. Ueno, *Angew. Chem.* **2011**, *123*, 12470 – 12473; *Angew. Chem. Int. Ed.* **2011**, *50*, 12262 – 12265.

[5] For the synthesis of α-chiral nonracemic allyl boronates, see a) J. Pietruszka, N. Schone, *Angew. Chem.* **2003**, *115*, 5796 – 5799; *Angew. Chem. Int. Ed.* **2003**, *42*, 5638 – 5641; b) E. Fernandez, J. Pietruszka, *Synlett* **2009**, 1474 – 1476; c) L. Carosi, D. G. Hall, *Angew. Chem.* **2007**, *119*, 6017 – 6019; *Angew. Chem. Int. Ed.* **2007**, *46*, 5913 – 5915; d) G. Y. Fang, V. K. Aggarwal, *Angew. Chem.* **2007**, *119*, 363 – 366; *Angew. Chem. Int. Ed.* **2007**, *46*, 359 – 362; e) M. Althaus, A. Mahmood, J. R. Suárez, S. P. Thomas, V. K. Aggarwal, *J. Am. Chem. Soc.* **2010**, *132*, 4025 – 4028; f) A. Guzman-Martinez, A. H. Hoveyda, *J. Am. Chem. Soc.* **2010**, *132*, 10634 – 10637; g) H. Ito, C. Kawakami, M. Sawamura, *J. Am. Chem. Soc.* **2005**, *127*, 16034 – 16035; h) H. Ito, S. Ito, Y. Sasaki, K. Matsuura, M. Sawamura, *J. Am. Chem. Soc.* **2007**, *129*, 14856 – 14857; i) H. Ito, S. Kunii, M. Sawamura, *Nat. Chem.* **2010**, *2*, 972 – 976; j) H. Ito, T. Miya, M. Sawamura, *Tetrahedron* **2011**, *68*, 3423 – 3437; k) H. E. Burks, L. T. Kliman, J. P. Morken, *J. Am. Chem. Soc.* **2009**, *131*, 9134 – 9135; l) J. K. Park, H. H. Lackey, B. A. Ondrusek, D. T. McQuade, *J. Am. Chem. Soc.* **2011**, *133*, 2410 – 2413.

[6] a) M. Chen, W. R. Roush, *Org. Lett.* **2010**, *12*, 2706 – 2709; b) S. M. Winbush, W. R. Roush, *Org. Lett.* **2010**, *12*, 4344 – 4347; c) F. Peng, D. G. Hall, *J. Am. Chem. Soc.* **2007**, *129*, 3070 – 3071; d) D. G. Hall, *Pure Appl. Chem.* **2008**, *80*, 913 – 927; e) J. Pietruszka, N. Schone, *Eur. J. Org. Chem.* **2004**, 5011 – 5019; f) J. Pietruszka, N. Schone, W. Frey, L. Grundl, *Chem. Eur. J.* **2008**, *14*, 5178 – 5197.

[7] a) R. W. Hoffmann, B. Landmann, *Tetrahedron Lett.* **1983**, *24*, 3209 – 3212; b) R. W. Hoffmann, B. Landmann, *Angew. Chem.* **1984**, *96*, 427 – 428; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 437 – 438; c) R. W. Hoffmann, B. Landmann, *Angew. Chem.* **1986**, *98*, 186 – 187; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 189 – 190; d) R. W. Hoffmann, *Pure Appl. Chem.* **1988**, *60*, 123 – 130; e) R. W. Hoffmann, J. J. Wolff, *Chem. Ber.* **1991**, *124*, 563 – 569.

[8] a) J. Nokami, K. Nomiyama, S. Matsuda, S. M. Shafi, K. Kataoka, *Org. Lett.* **2004**, *6*, 1261 – 1264; b) C.-L. K. Lee, C.-H. A. Lee, K.-T. Tan, T.-P. Loh, *Org. Lett.* **2004**, *6*, 1281 – 1283.

[9] R. W. Hoffmann, U. Weidmann, *J. Organomet. Chem.* **1980**, *195*, 137 – 146.

[10] For overviews, see a) H. B. Kagan, J. C. Fiaud, *Top. Stereochem.* **1988**, *18*, 249 – 330; b) J. M. Keith, J. F. Larrow, E. N. Jacobsen, *Adv. Synth. Catal.* **2001**, *343*, 5 – 26; c) D. E. J. E. Robinson, S. D. Bull, *Tetrahedron: Asymmetry* **2005**, *14*, 1407 – 1446; for our previous report on combining enantiofacial discrimination with dynamic kinetic resolution, see d) A. V. Malkov, S. Stončius, K. Vranková, M. Arndt, P. Kočovský, *Chem. Eur. J.* **2008**, *14*, 8082 – 8085.

[11] M. Klussmann, L. Ratjen, S. Hoffmann, V. Wakchaure, R. Goddard, B. List, *Synlett* **2010**, 2189 – 2192.

[12] To save computational time and resources, buta-1,3-diene-1,4-diol-phosphoric acid was used as a simplified model for TRIP. For details, see the Supporting Information.

[13] a) M. A. Grayson, S. P. Pellegrinet, J. M. Goodman, *J. Am. Chem. Soc.* **2012**, *134*, 2716 – 2722; for the mechanism of Lewis acid catalysis, see b) K. Sakata, H. Fujimoto, *J. Am. Chem. Soc.* **2008**, *130*, 12519 – 12526; for the most recent contribution, see Ref. [2i] and c) H. Wang, P. Jain, J. C. Antilla, K. N. Houk, *J. Org. Chem.* **2013**, DOI: 10.1021/jo302787m.

[14] J. W. Clary, T. J. Rettenmaier, R. Snelling, W. Bryks, J. Banwell, W. T. Wipke, B. Singaram, *J. Org. Chem.* **2011**, *76*, 9602 – 9610; for details, see the Supporting Information.

Communications

Asymmetric Allylation

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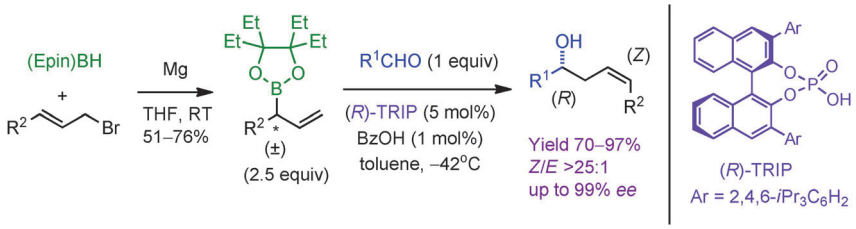
Highly Stereoselective Synthesis of *Z*-Homoallylic Alcohols by Kinetic Resolution of Racemic Secondary Allyl Boronates



α to *Z*: Racemic α-chiral allyl boronates, which are readily synthesized from the respective primary allyl halides, undergo a highly efficient kinetic resolution in a face- and *Z*-selective allylation of aldehydes catalyzed by the chiral Brønsted acid (*R*)-TRIP (see scheme; Epin = tetraethylethylene glycol).