Organocatalysis

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The Organocatalytic Asymmetric Prins Cyclization**

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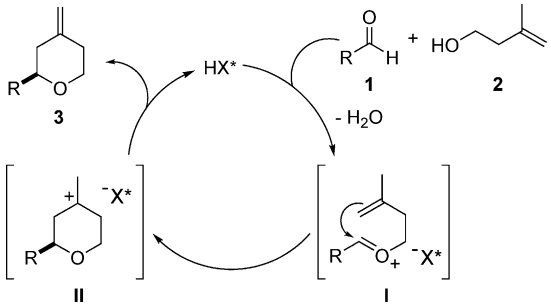
Abstract: *We describe here the design and development of an organocatalytic Prins cyclization. In the presence of a confined chiral imidodiphosphoric acid catalyst, salicylaldehydes react with 3-methyl-3-buten-1-ol to afford highly functionalized 4-methylenetetrahydropyrans in excellent regio- and enantioselectivity. The extreme steric demand of the acid catalyst is key for the success of this transformation.*

The acid-catalyzed condensation between homoallylic alcohols and aldehydes, known as the Prins cyclization, is a direct and efficient method to construct functionalized tetrahydropyran (THP) rings.[1] Due to the prevalence of THPs in natural products and pharmaceuticals, the Prins cyclization has become an important strategy in novel and elegant total syntheses of THP-containing targets.[2] Since the first report by Hanschke in 1955 on forming the THP rings by combining 3-buten-1-ol with aldehydes or ketones in the presence of an acid,[3] great strides have been made towards understanding the mechanism,[4] scope,[5] and selectivity[6] of the Prins cyclization. New catalytic systems[7] and cascade reactions[8] have also been developed to improve efficiency and broaden reactivity. Despite this tremendous progress, surprisingly only one example of an enantioselective Prins cyclization using a dual phosphoric acid and CuCl catalytic system has been recently reported affording up to 80:20 enantiomeric ratio.[9] A purely organocatalytic variant, until today, has remained entirely unknown. Here we report a highly enantioselective Prins cyclization that is catalyzed by our recently introduced confined chiral imidodiphosphate catalysts.

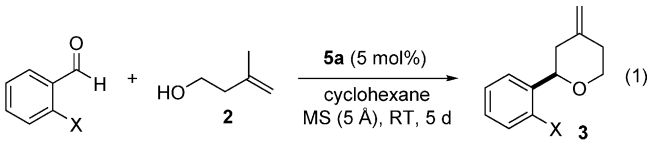
A key intermediate in the Prins cyclization pathway is the oxocarbenium ion **I** formed in the condensation between the olefinic alcohol and the aldehyde (Scheme 1).[1b] This highly reactive intermediate is subsequently attacked by the pendant alkene creating a stereogenic center in cation **II**. We envisioned that this key enantiodiscriminating C–C bond-forming step can be governed by our newly developed C_2-symmetric imidodiphosphoric acid catalysts **5**, which have demonstrated excellent enantiocontrol over the nucleophilic attack to oxocarbenium ions in asymmetric acetalization

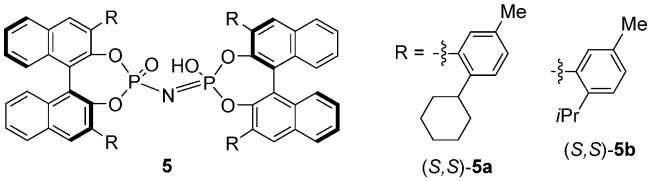


Scheme 1. Chiral Brønsted acid catalyzed asymmetric Prins cyclization.

reactions.[10] The role of the chiral counteranion (X^{*-}) is twofold: 1) enantio-induction by asymmetric counteranion-directed catalysis (ACDC)[11] and 2) deprotonation to generate the alkene product.

We initially investigated the reaction between benzaldehyde (**1a**) and 3-methyl-3-buten-1-ol (**2**) [Eq. (1)]. We tested





different chiral Brønsted acids, including phosphoric acids,[12] disulfonimides,[13] and imidodiphosphates,[10] which all showed either poor yield and/or low enantioselectivity (see the Supporting Information). The highest e.r. (95:5) was obtained with catalyst **5a** but the yield was not synthetically useful (11%) and significant side-product formation was observed. Remarkably, salicylaldehyde (**1b**) gave a significantly improved reaction profile with 62% yield and an excellent e.r. of 97:3. After extensive optimization of the reaction conditions we found that using cyclohexane as the solvent with 5 Å molecular sieves at room temperature gave the optimal combination of yield and enantioselectivity. Catalyst **5a** exhibited superior control in both enantioselectivity and regioselectivity. The exocyclic alkene product **3** was isolated as the sole product.[14]

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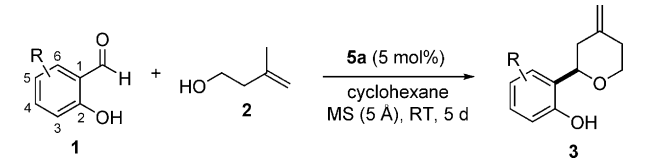
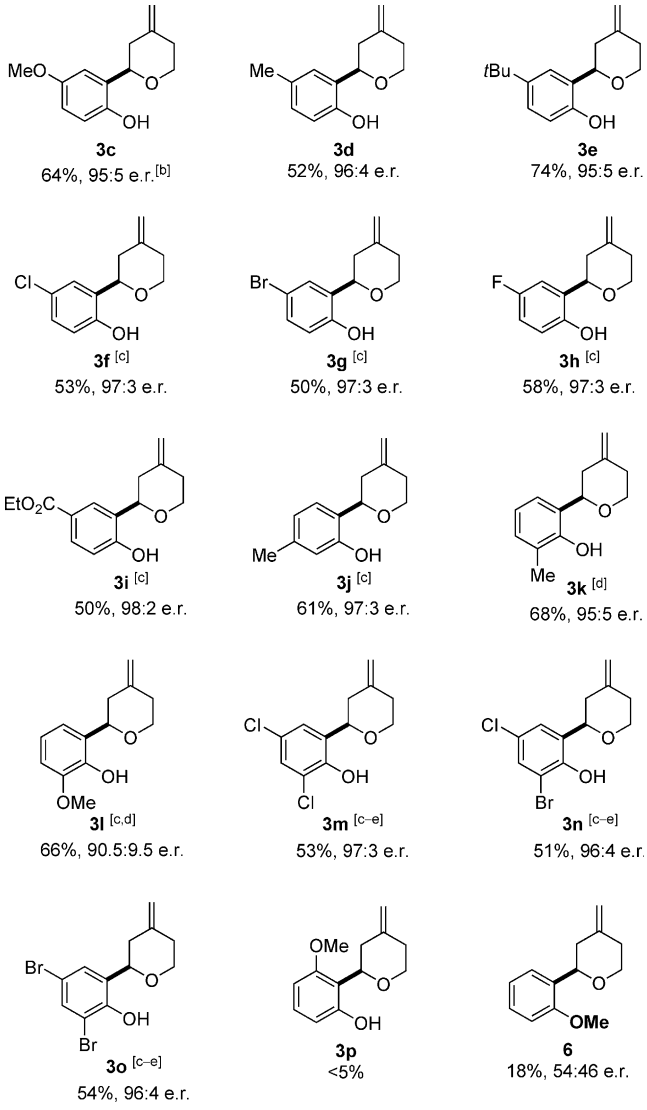
Table 1: Asymmetric Prins cyclization of salicylaldehyde derivatives.[a]



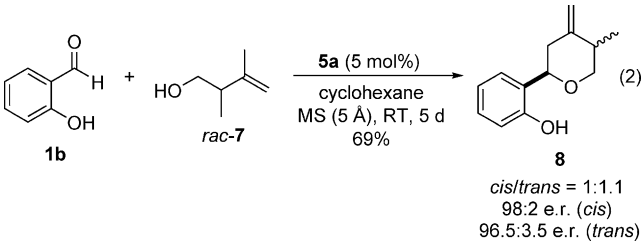


[a] Unless specified otherwise, reactions were performed using catalyst **5a** (5 mol%), 1.0 equivalent each of **1** and **2** and 5 Å molecular sieves (0.3 g mmol^{-1}) in cyclohexane (0.125 M), at room temperature for 5 days. [b] The enantiomeric ratios were determined by GC and HPLC on a chiral stationary phase, regioselectivities all >20:1. [c] Solvent = cyclohexane/toluene (9:1 v/v). [d] At 45 °C. [e] Catalyst = **5b**.

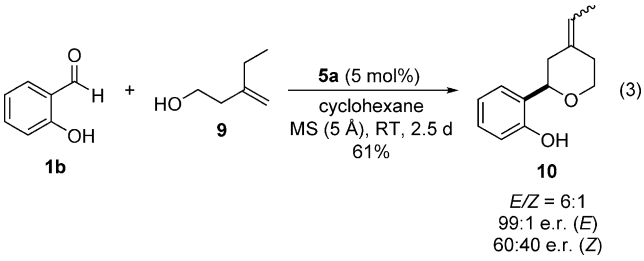
Next, we studied the scope of the asymmetric Prins cyclization (Table 1). A variety of commercially available salicylaldehyde derivatives bearing different substituents were subjected to the reaction conditions using 5 mol% of catalyst **5a**. Functional groups including electron-rich (**3c**), electron-poor (**3i**), sterically demanding (**3e**), and halogens (**3f–h**) were tolerated at the 5-position of the aromatic ring. Some substrates were not completely soluble in cyclohexane and required a mixed solvent system, cyclohexane/toluene (9:1 v/v). Substituents at the 4- and 3-positions were also tolerated (**3j–l**). However, the latter required heating to 45 °C to reach comparable yields.

Dihalogenated products **3m–o** could also be obtained in high enantioselectivities. A substrate substituted at the 6-position did not provide the corresponding product (**3p**). A control experiment using 2-methoxybenzaldehyde gave product **6** in only low yield and poor enantioselectivity. The absolute configuration of product **3b** was unambiguously determined by single-crystal X-ray analysis of a derivative (see the Supporting Information).

We also explored homoallylic alcohols with additional substituents. For example, racemic alcohol **7** gave the corresponding product as an inseparable mixture of *cis*/*trans* isomers [Eq. (2)]. Both isomers were formed with excellent

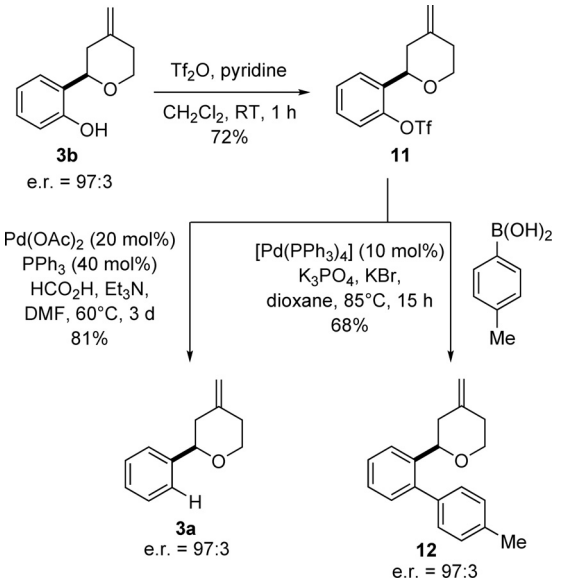


enantioselectivity in a stereodivergent, parallel kinetic resolution. When the reaction was stopped after 56% conversion, no significant enantiomer differentiation was observed (*cis*/*trans* = 1:1.3, e.r.$_{cis}$ = 97.5:2.5, e.r.$_{trans}$ = 97.5:2.5). We also studied alcohol **9**, which could potentially lead to different exo- and endocyclic alkene regioisomers [Eq. (3)]. Consistent with



the results in Table 1, the exocyclic alkene product **10** was obtained exclusively. The *E* isomer was favored and obtained in excellent enantioselectivity; the minor *Z* isomer gave poor enantioselectivity. We have also tested several other unsaturated alcohols as substrates but found them to be less reactive.[15]

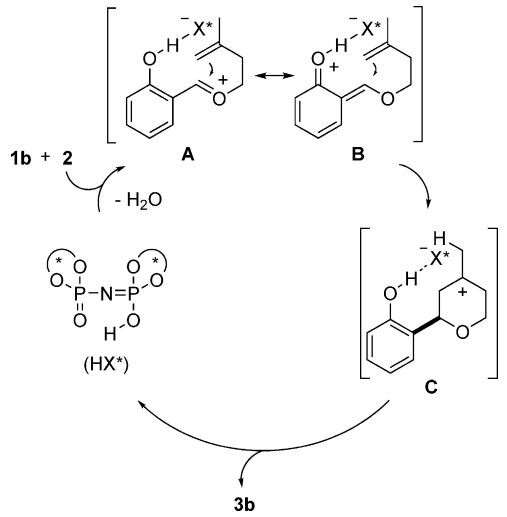
The hydroxy group in products **3** can serve as a useful synthetic handle for further derivatization (Scheme 2). For example, triflation of product **3b** took place smoothly to generate product **11**. Suzuki coupling between aryl triflate **11** and an arylboronic acid gave biaryl derivative **12**. Alternatively, a reductive detriflation protocol allowed the removal of the hydroxy group and afforded the previously challenging



Scheme 2. Derivatization of product **3b**.

phenyl-substituted THP product **3a** in high enantiopurity [cf. Eq. (1)]. Note that the enantiomeric ratios remained unchanged in the products of these transformations.

The results using a methyl ether instead of the salicylaldehyde giving product **6** clearly demonstrated that the hydroxy group *ortho* to the aldehyde is crucial for reactivity and enantioselectivity. The increased reactivity can be rationalized by invoking an internal activation through intramolecular hydrogen bonding between the hydroxy and carbonyl groups.[16] It is also known that the bifunctional catalyst can form intermolecular hydrogen bonds with both the hydroxy and carbonyl/imino groups in transition states, thus activating the aldehyde.[17] A plausible mechanism is suggested in Scheme 3. The initial condensation between aldehyde **1b** and alcohol **2** leads to the formation of the oxocarbenium ion in **A** which also contains the chiral imidodiphosphate counteranion. Ion pair **A** can also be described as a protonated *ortho*-quinone methide, resonance structure **B**.[18] The key enantiodifferentiating C–C bond formation furnishes THP **C** bearing a new chiral center and a tertiary carbocation. In the final deprotonation step, the sterically encumbering imidodiphosphate anion kinetically prefers removing a proton at the primary position to selectively afford the exocyclic alkene product **3b**.



Scheme 3. Proposed mechanism for the asymmetric Prins cyclization of salicylaldehyde **1b** and alcohol **2** catalyzed by a chiral imidodiphosphoric acid.

In summary, we have developed an organocatalytic asymmetric Prins cyclization. The reaction possibly proceeds by means of an unusual mode of enantiocontrol involving challenging *o*-quinone methide intermediates.[19] We have introduced the new sterically confined imidodiphosphoric acid **5a**, a powerful Brønsted acid catalyst controlling reactivity and enantio- and regioselectivity. Our method can be applied to the enantioselective synthesis of diverse functionalized tetrahydropyrans with an exocyclic methylene moiety. Further exploration of the asymmetric Prins cyclization, particularly towards expanding the substrate scope, is in progress in our laboratories.

Keywords: asymmetric catalysis · Brønsted acids · organocatalysis · Prins cyclization · tetrahydropyrans

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Angew. Chem. **2015**, *127*, 7814–7818

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[14] The 4-methylenetetrahydropyran core **3** is a common motif in macrocyclic natural products such as dactylolide and zampanolide. However, the control of exo- versus endocyclic alkene product is often difficult in acid-catalyzed cyclizations. For examples, see: a) B. V. S. Reddy, S. R. Anjum, G. M. Reddy, J. S. Yadav, *Tetrahedron Lett.* **2012**, *53*, 1790 – 1793; b) S. Bondalapati, U. C. Reddy, P. Saha, A. K. Saikia, *Org. Biomol. Chem.* **2011**, *9*, 3428 – 3438; c) T.-P. Loh, J.-Y. Yang, L.-C. Feng, Y. Zhou, *Tetrahedron Lett.* **2002**, *43*, 7193 – 7196.

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