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Enantioselective Prins cyclization: BINOL-derived phosphoric acid and CuCl synergistic catalysis†

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The first catalytic enantioselective Prins cyclization is disclosed. The reaction is catalyzed by the combination of a chiral BINOL-derived bis-phosphoric acid and CuCl. The process consists of a tandem Prins/Friedel–Crafts cyclization that affords the hexahydro-1*H*-benzo[*f*]isochromenes products with three new contiguous stereogenic centers in high yields, and good enantio- and excellent diastereoselectivities.

The Prins cyclization reaction[1] between a homoallylic alcohol and an aldehyde in the presence of an acidic promoter or catalyst is a powerful C–C bond forming transformation and one of the most elegant approach to access highly substituted tetrahydropyrans with excellent diastereoselectivities.[2] Despite the recent advances and the increasing interest in the stereochemical outcome and the mechanism of the Prins cyclization,[3] to date, to our knowledge, no asymmetric version has been reported.[4] The main drawback associated with the development of the enantioselective Prins cyclization is the racemization due to the Oxonia Cope rearrangement, the allyl transfer or the solvolysis.[5] Recently Feng and coworkers succeeded in the synthesis of optically pure 4-OH-tetrahydropyrans by a catalytic asymmetric ene reaction followed by a $FeCl_3$ Prins cyclization.[3d] However so far direct access to tetrahydropyrans by catalytic enantioselective Prins cyclization has not been achieved and it is therefore highly required.

Since the seminal independent reports of Akiyama[6] and Terada,[7] the ability of BINOL-derived chiral phosphoric acids to direct the enantioselective addition to imines is well established.[8] Nevertheless the enantioselective addition to oxocarbenium ions is much less developed.[9] We recently reported the unprecedented synergistic effect in Prins cyclization between non-reactive Brønsted and Lewis acids that lack the ability to catalyze the reaction if used alone, such as *p*-TSA and $MgBr_2$.[10] Inspired by the successful examples on the enantioselective addition to oxocarbenium ions and in continuation of our interest in the Prins cyclization reaction,[11] we reasoned that the combination of the chiral Brønsted acid with an achiral Lewis acid[12] could promote the reaction and we envisioned that chiral phosphoric acids could activate the oxonium ion intermediate and ensure the enantioselectivity.

Herein we report our preliminary results for the first catalytic enantioselective Prins cyclization.

We chose as model substrates homoallylic alcohols such as 6-phenylhex-3-en-1-ol **1** containing a tethered nucleophile.[13] The advantage in using those kind of substrates consists in a simplified reaction system to study. Indeed, most of the Prins cyclization reactions are promoted by stoichiometric amounts of Lewis acid that play a double role, as a promoter and nucleophile source to trap the carbocation species which is formed after the cyclization. The embedded phenyl moiety prevents the use of a stoichiometric external nucleophile which can interfere with the catalytic system, and moreover allows a tandem Prins/Friedel–Crafts process to take place.[13e]

We began our studies by investigating the reaction between (*Z*)-6-phenylhex-3-en-1-ol (*Z*)-**1** and *p*-methoxy-benzaldehyde **2a** in DCE (1,2-dichloroethane) at 40 °C, leading to the hexahydro-1*H*-benzo[*f*]isochromenes product **5a** with three new contiguous stereogenic centers.

A screening of known chiral phosphoric acids **3–4** (Table 1, entries 1–4) gave only disappointing results summarized in a lack of reactivity. We hypothesized that the Brønsted acid alone is not prone to activate the electrophilic carbonyl group. We reasoned that a catalytic system integrating a phosphoric acid and a metal catalyst should synergistically enable our reaction. To confirm our hypothesis we first examined the combination of phosphoric acids **3** with different achiral Lewis acids. As shown in Table 1, $MgBr_2$ is completely inactive (entry 5), in contrast first raw transition metal salts such as $Cu(OTf)_2$ and $FeCl_3$ (entries 6–9) could catalyze the reaction with up to 45% yield, unfortunately without any enantioselection. The association between the bis-phosphoric acid[14] **4** and $FeCl_3$ (entry 10) also failed to selectively promote the reaction.

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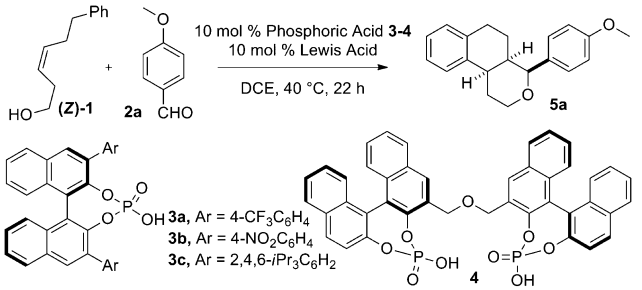
Table 1 Catalysts identification and reaction optimization of the enantioselective Prins cyclization[a]



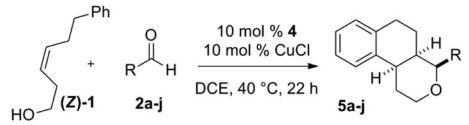
Entry	Catalyst	Lewis acid	Yield 5a[b,c] (%)	e.r.[d,e] 5a
1	**3a**	—	n.r.	—
2	**3b**	—	n.r.	—
3	**3c**	—	n.r.	—
4	**4**	—	n.r.	—
5	**3a**	$MgBr_2$	n.r.	—
6	**3a**	$Cu(OTf)_2$	20	53 : 47
7	**3b**	$FeCl_3$	45	50 : 50
8	**3b**	$Cu(OTf)_2$	28	50 : 50
9	**3c**	$Cu(OTf)_2$	34	50 : 50
10	**4**	$FeCl_3$	52	50 : 50
11	**4**	$Cu(OTf)_2$	24	80 : 20
12	**4**	$CuCl_2$	65	79 : 21
13	**4**	CuCl	70	80 : 20
14	**4**[f]	CuCl	29	67 : 33

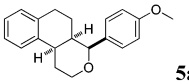
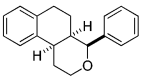
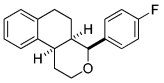
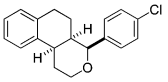
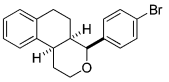
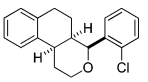
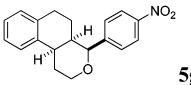
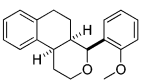
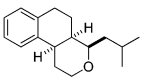
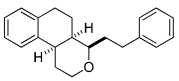
[a] General conditions: (*Z*)-**1** (0.1 mmol), **2a** (0.12 mmol), **3–4** (10 mol%), Lewis acid (10 mol%) in DCE (c = 0.1 M) at 40 °C for 22 h. [b] Yields refer to isolated products. [c] n.r. = no reaction. [d] Enantiomeric ratio was determined by chiral HPLC analysis. [e] d.r. > 95 : 5. [f] The (*E*)-**1** isomer was used.

To our delight the combination of **4** and $Cu(OTf)_2$ (entry 11) afforded the desired product **5a** with an exciting 80 : 20 enantiomeric ratio (e.r.) and as a single diastereomer (d.r. >95 : 5), the *cis*-fused hexahydro-1*H*-benzo[*f*]isochromene dictated by the *Z* geometry of the double bond, even if in moderated yields (24%). Different trifluoromethanesulfonates such as $Zn(OTf)_2$, $Ni(OTf)_2$, $Bi(OTf)_3$, AgOTf or LiOTf failed to give better results, in contrast the variation of the copper source ($CuCl_2$ and CuCl entries 12 and 13 respectively) improved the yield up to 70% (see ESI†). Finally the effect of the alkene geometry was evaluated and it was observed that changing the double bond to *E* resulted in a dramatic loss in reactivity and selectivity (entry 14), thus the *trans*-fused hexahydro-1*H*-benzo[*f*]isochromene was obtained with only 29% yield and 67 : 33 e.r. An exploration of different reaction conditions was set out to optimize the selectivity. A solvent screening revealed chlorinated solvents to be superior (see ESI†), in particular DCE gave slightly better yields and enantiomeric ratios than CH_2Cl_2. Decreasing the temperature was detrimental for the reactivity. The increase of the phosphoric acid loading to 20 mol% did not benefit the enantioselectivity.

Encouraged by the promising level of enantiocontrol, our catalytic system was tested on different substituted aromatic aldehydes (Table 2, entries 1–8). Gratifyingly benzaldehyde **2b** (entry 2) smoothly participated in the reaction leading to the desired product **5b** with 73% yield, 80 : 20 e.r. and as a single diastereomer. The substitution of the aromatic ring in the *ortho* or *para* position with halogens (entries 3–6) is tolerated as in all

Table 2 Scope of the enantioselective Prins cyclization[a]



Entry	Product 5	Yield[b] (%)	e.r.[c,d]
1	 **5a**	70	80 : 20
2	 **5b**	73	80 : 20
3	 **5c**	78	77 : 23
4	 **5d**	76	76 : 24
5	 **5e**	62	80 : 20
6	 **5f**	62	72 : 28
7	 **5g**	63	67 : 33
8	 **5h**	76	60 : 40
9	 **5i**	63	65 : 35
10	 **5j**	72	60 : 40

[a] General conditions: (*Z*)-**1** (0.1 mmol), **2** (0.12 mmol), **4** (10 mol%), CuCl (10 mol%) in DCE (c = 0.1 M) at 40 °C for 22 h. [b] Yields refer to isolated products. [c] Enantiomeric ratio was determined by chiral HPLC analysis. [d] d.r. > 95 : 5.

the cases enantioenriched hexahydro-1*H*-benzo[*f*]isochromenes were obtained with the same range of yields and e.r. values. The *p*-NO_2 benzaldehyde also participated with a slight erosion of enantioselectivity (entry 7). The catalytic system proved to be efficient for aromatic aldehydes substituted with an electron donating group in the *para* position (entry 1) but it is less selective for the *o*-MeO substitution probably because of the steric hindrance (entry 8). Aliphatic aldehydes undergo Prins cyclization with high yields, excellent diastereoselectivities but moderate enantiocontrol (entries 9 and 10).

The absolute configuration of **5e** was unambiguously determined to be 4*S*,4*aR*,10*bR* by single crystal X-ray analysis[15] (Fig. 1). The three new contiguous stereogenic centers formed are a result of an attack of the alkene on the *Si* face of the

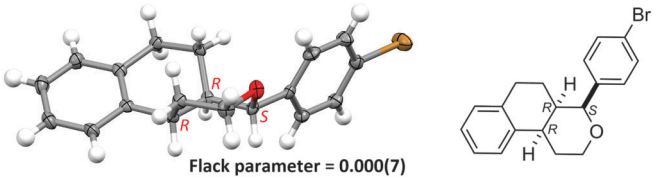


Fig. 1 ORTEP representation of the hexahydro-1*H*-benzo[*f*]isochromene product **5e**. The thermal ellipsoids are shown at 50% probability.

oxocarbenium ion, followed by a completely diastereoselective Friedel–Crafts reaction.

In conclusion, we have disclosed the first enantioselective Prins cyclization catalyzed by a synergistic combination of chiral BINOL-derived bis-phosphoric acid and CuCl under mild conditions. The present method demonstrates the feasibility of the asymmetric condensation between a homoallylic alcohol and an aldehyde and provides an efficient route to enantiomerically enriched tetrahydropyrans containing three contiguous stereogenic centers. Further research on the substrate scope and investigations to gain insight into the reaction mechanism are underway and will be reported in due course.

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