

Organocatalytic Asymmetric Direct C_{sp}³–H Functionalization of Ethers: A Highly Efficient Approach to Chiral Spiroethers**

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The asymmetric synthesis of chiral spiroethers, which are present in numerous bioactive natural products (Figure 1)

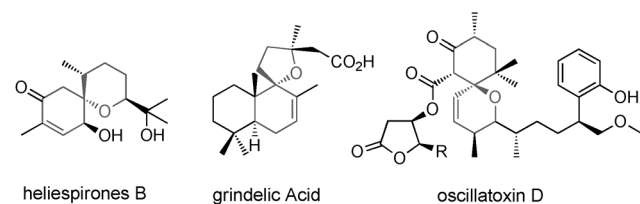
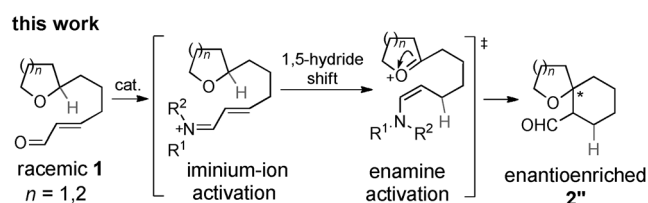
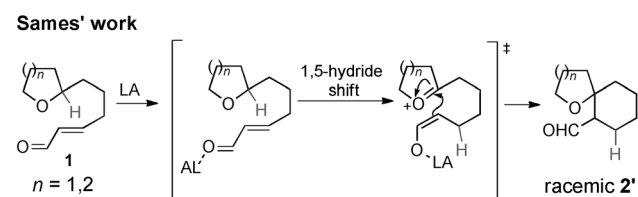


Figure 1. Natural products containing a spiroether moiety.

and pharmaceuticals,^[1] is an important endeavor in organic synthesis. Tremendous efforts have been made during the past few years toward developing methods for the synthesis of spiroethers,^[2] although of the methods developed, many involve multiple steps and only a few are enantioselective.^[2d–i] Therefore, the development of methods that are highly efficient, catalytic, and enantioselective is still required.

The direct and selective functionalization of inactive C_{sp}³–H bonds is not only a significant and actively studied subject in fundamental organic chemistry,^[3] it is also becoming a practical method for organic synthesis because of its atom- and step economy.^[4] Among the reported transformations, intramolecular redox processes for the direct functionalization of C_{sp}³–H bonds that are α to heteroatoms are important for the synthesis of structurally diverse amine and ether derivatives.^[5] Furthermore, since the pioneering work of Kim and co-workers,^[6] there have many good results reported in the area of intramolecular redox processes for the direct enantioselective C_{sp}³–H functionalization at positions α to nitrogen atoms.^[7] However, examples of the corresponding

enantioselective reaction of ethers are scarce. In 2005, Sames and co-workers reported that Sc(OTf)₃ or BF₃·Et₂O could initiate a direct functionalization of C_{sp}³–H bonds of cyclic ethers **1** to give racemic spiroethers **2'** (Scheme 1). This



Scheme 1. Asymmetric functionalization of C_{sp}³–H bonds for preparing enantiopure spiroethers. LA = Lewis acid.

transformation proceeds through a tandem 1,5-hydride transfer/cyclization redox process.^[5b] These results suggested that an asymmetric catalytic variant should be possible, a process that would involve the conversion of a racemic mixture of a cyclic ether into enantiomerically enriched spiroether.

Organocatalysis has emerged as an important method in organic chemistry and it has been used to effect many enantioselective transformations.^[8] To accomplish the above enantioselective C–H bond functionalization, we envisioned that the formation of an iminium ion through the reaction between a cyclic ether containing an α,β-unsaturated aldehyde group (**1**) and a chiral organocatalyst (R¹NHR²) would initiate a 1,5-hydride shift and that the resulting enamine and oxocarbenium moieties would react to give chiral spiroether **2''** (Scheme 1). Herein, we present our success toward this goal.

Our investigation started with the use of tetrahydrofuran **1a**, which contains both an α,β-unsaturated aldehyde and a diethylmalonate moiety, as the model substrate for identifying a suitable catalytic system. We envisioned that the presence of strong acid would be required to ensure that the iminium ion would be of sufficient electrophilicity for facilitating the transfer of the α-hydrogen atom from the THF moiety of **1a**. Thus the combination of a catalytic amount of (+)-camphorsulphonic acid (CSA) and a proline-derived

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secondary amine **3** was tested first. When **1a** was treated with this combination of catalysts in 1,2-dichloroethane (DCE) at 30 °C for 5 days, the expected spiroether **2a''** was not obtained (Table 1, entry 1); the use of stronger acids, such as TfOH and HClO₄, in combination with either amine **3** or **4**, also led to no reaction (Table 1, entries 2–4). Given the outstanding perfor-

(80 %), *ee* value (77 %), and d.r. value (3.5:1; Table 1, entry 8) than that of AgBF₄ (Table 1, entry 7). In the presence of only **7**, that is, in the absence of AgSbF₆ or AgBF₄, the reaction did not proceed at all (Table 1, entry 9). Variation of the solvent and reaction temperature (Table 1, entries 10–12) showed that the solvent, CHCl₃, and a reaction temperature of 20 °C were optimal (91 % *ee* and 5:1 d.r.; Table 1, entry 12).

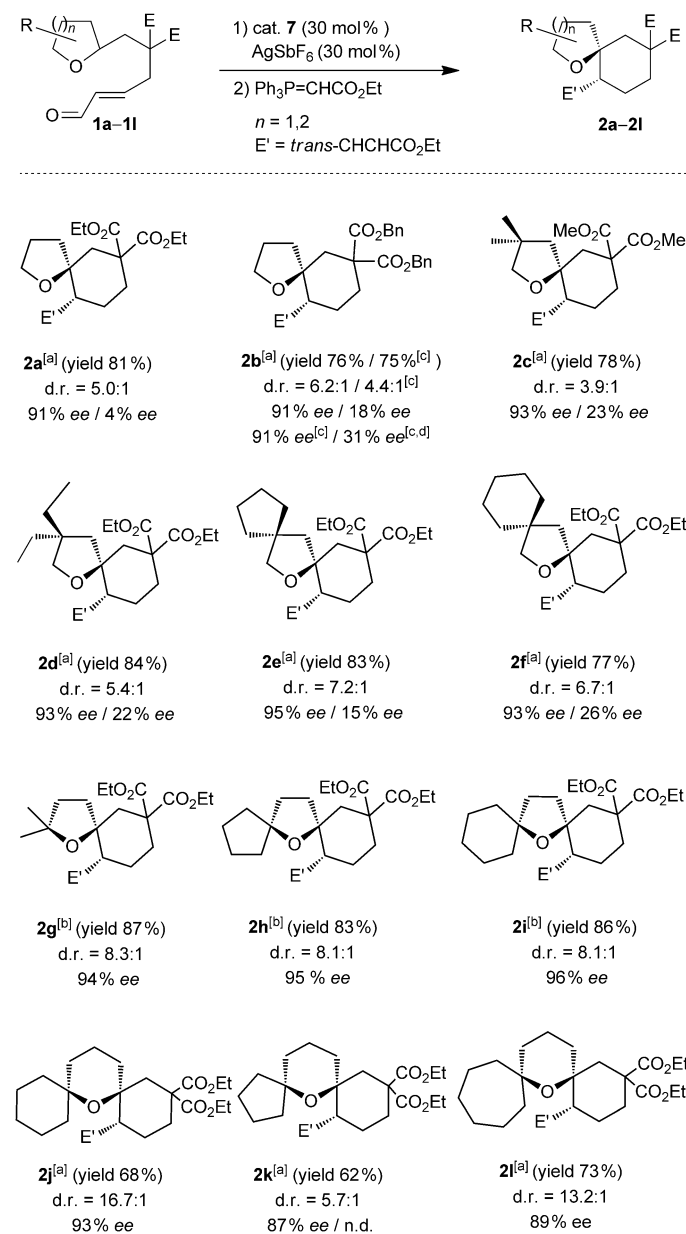
Table 1: Optimization of the redox reaction of **1a**.^[a]

3 R ¹ = 3,5-bis(CF ₃)C ₆ H ₃ , R ² = TMS 4 R ¹ = Ph, R ² = H						
Entry	Cat.	Additive	Solvent	<i>t</i> [days]	Yield [%] ^[b]	<i>ee</i> [%] ^[d]
1	3	(+)-CSA	C ₂ H ₄ Cl ₂	5	n.r.	—
2	3	TfOH	C ₂ H ₄ Cl ₂	5	n.r.	—
3	3	HClO ₄	C ₂ H ₄ Cl ₂	5	n.r.	—
4	4	HClO ₄	C ₂ H ₄ Cl ₂	5	n.r.	—
5	5	HClO ₄	C ₂ H ₄ Cl ₂	5	trace	—
6	6	HClO ₄	C ₂ H ₄ Cl ₂	5	72 (3.1:1) ^[c]	44/8
7	7	AgBF ₄	C ₂ H ₄ Cl ₂	3	58 (1.2:1) ^[c]	67/20
8	7	AgSbF ₆	C ₂ H ₄ Cl ₂	3	80 (3.5:1) ^[c]	77/11
9	7	—	C ₂ H ₄ Cl ₂	5	n.r.	—
10	7	AgSbF ₆	CH ₂ Cl ₂	3	85 (3.0:1) ^[c]	71/7
11	7	AgSbF ₆	CHCl ₃	3	81 (5.0:1) ^[c]	89/4
12 ^[e]	7	AgSbF ₆	CHCl ₃	4	81 (5.0:1) ^[c]	91/4

[a] All reactions were performed using 0.1 mmol of **1a**, 0.03 mmol of catalyst in 2 mL of solvent at 30 °C. [b] Combined yield of diastereomers. [c] The d.r. values were determined by ¹H NMR spectroscopy prior to the addition of Ph₃P=CHCO₂Et. [d] Determined by HPLC analysis. [e] The reaction was carried out at 20 °C. n.r. = no reaction, TfOH = trifluoromethanesulfonic acid, TMS = trimethylsilyl.

mance of imidazolidinones **5** and **6** as LUMO-lowering catalysts through iminium-ion formation,^[9] we tested amines **5** and **6** in combination with HClO₄ (Table 1, entries 5 and 6). To our delight, when **1a** was treated with **6** and HClO₄ in DCE at 30 °C for 5 days, the desired spiroether **2a** was obtained in a yield of 72 % (Table 1, entry 6), albeit with a low *ee* value (44 %). Notably, in order to measure the *ee* value, the initial aldehyde product **2''** was subjected in situ to a Wittig reaction to give the corresponding unsaturated ethylester **2a**.^[10]

The presence of a counterion that is more weakly coordinating than ClO₄[−] would lead to an iminium ion with enhanced electrophilicity (Scheme 1), thus accelerating the hydride shift. The weakly coordinating anions, BF₄[−] and SbF₆[−], have been effective for many catalytic reactions.^[11] Therefore, substrate **1a** was treated with **7** (the hydrochloride salt of **6**) together with either AgBF₄ or AgSbF₆ (Table 1, entries 7 and 8). Both reactions were complete within 3 days, and the use of AgSbF₆ led to the product **2a** with higher yield



Scheme 2. Scope of the redox reaction. All reactions were performed using 0.1 mmol of substrate in CHCl₃ (0.05 M) unless noted otherwise. Yield of diastereomers after column chromatography are given in parentheses. The *ee* values of products were determined by HPLC. The d.r. values were determined by ¹H NMR spectroscopy prior to the addition of Ph₃P=CHCO₂Et. The absolute configurations of major products were determined based on X-ray crystallographic analysis.^[13] [a] Reactions were performed at 20 °C. [b] Reactions were performed at 0 °C. [c] Reaction was performed on a 1 mmol scale. Bn = benzyl, n.d. = not determined.

With optimized reaction conditions (Table 1, entry 12) established, the scope and generality of this reaction were investigated using various substituted tetrahydrofuran- or tetrahydropyran-based substrates containing an α,β -unsaturated aldehyde group (Scheme 2). Again, in order to measure *ee* values, the initial aldehyde products were converted in situ into their corresponding unsaturated ethylesters (**2a–2i**; $E' = \text{trans-CHCHCO}_2\text{Et}$). Firstly, the use of substrate **1b**, which contains a dibenzylmalonate moiety, gave the product **2b** with an *ee* value that was similar to **2a**, thus indicating that the nature of the malonate group does not have a significant impact on enantioselectivity. Further substitution of the THF moiety led to enhanced enantioselectivity (**2c–2i**, Scheme 2). In particular, the use of a spirocyclic substrate led to the corresponding product with an *ee* value of 96% (**2i**; Scheme 2). In addition, substrates having a *gem*-dialkyl group at the C5 atom of the THF ring reacted faster. As a result, for these types of substrates, the reaction temperature could be lowered from 20 °C to 0 °C and good yields and high levels of enantioselectivity were obtained (**2g–2i**; Scheme 2). This increase in rate could be due to the electron-donating character of the C5 substituents.^[12] To further expand the substrate scope, tetrahydropyran-based substrates were examined; good yields and high levels of enantioselectivity were obtained (Scheme 2, **2j–2l**). To evaluate the synthetic utility of this transformation, a reaction was conducted on a larger scale: when 1 mmol of substrate **1b** (438 mg) was subjected to the reaction conditions (room temperature), product **2b** was obtained with similar yield (75%) and similar levels of selectivity (91% *ee*, 4.4:1 d.r.) in comparison to those obtained in a reaction of smaller scale (Scheme 2).

The absolute configuration of **2a** (2*S*, 6*R*) was determined by X-ray crystallographic analysis of its derivative **5a** (Figure 2).^[13] Based on the above results, a plausible mechanism is proposed (Scheme 3). First, substrate **1** reacts with **7** under acid catalysis to form the iminium-ion intermediate **8**.

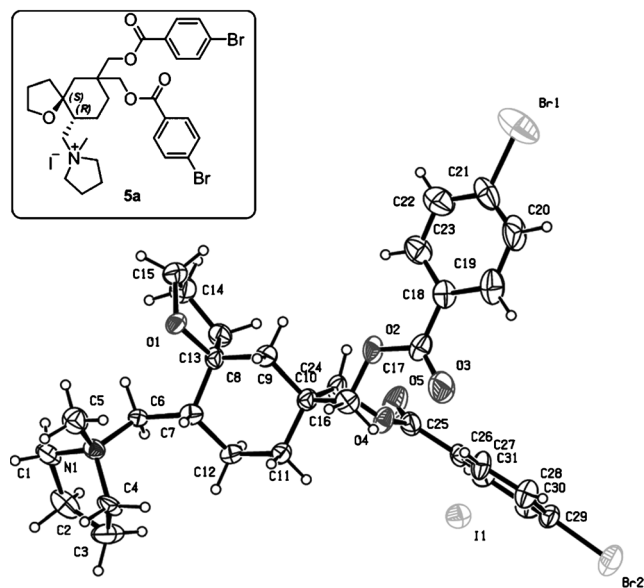
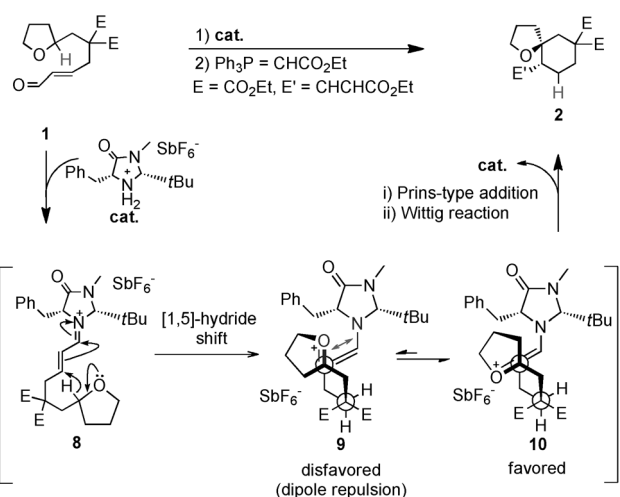


Figure 2. X-Ray crystallographic analysis of enantiopure **5a**. Thermal ellipsoids are shown at 30% probability.



Scheme 3. Proposed mechanism of the redox reaction.

Owing to the steric interaction of the bulky *tert*-butyl group,^[14] the *E* enamine is formed preferentially upon 1,5-hydride transfer of intermediate **8**, and exists in two possible conformers **9** and **10**. Because of the repulsion of dipoles of the cyclic-oxocarbenium-ion and enamine moieties in conformer **9**, we believe that **10** is the more favored conformer. Conformer **10** then undergoes intramolecular C–C bond formation to afford, after Wittig reaction, (2*S*, 6*R*)-**2a** as the major product.

In conclusion, a novel organocatalytic enantioselective $C_{sp^3}\text{--H}$ functionalization of the α position of ethers was developed. A series of chiral spiroethers with various substituents and ring sizes were prepared from racemic ethers with good to high levels of enantioselectivity. This transformation is efficient, economic, tolerant of the presence of bulky substituents, and proceeds under mild reaction conditions. Further studies on this type of catalytic enantioselective transformation and synthetic applications are underway.

Experimental Section

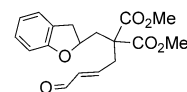
To a flame dried round-bottom flask were added CHCl_3 (1 mL), catalyst **7** (10.5 mg, slightly more than 0.03 mmol, 0.3 equiv),^[15] AgSbF_6 (10.3 mg, 0.03 mmol, 0.3 equiv) under argon. The mixture was stirred for 2 h at room temperature and then a solution of substrate **1** (0.1 mmol) in CHCl_3 (1 mL) was added at 20 °C. The reaction was monitored by TLC analysis. After completion, $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ (62.6 mg, 6.0 equiv) was added in one portion under argon and the mixture was warmed to 30 °C. After completion, the reaction mixture was purified directly by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1) to afford **2**.

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- [13] CCDC 883142 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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