

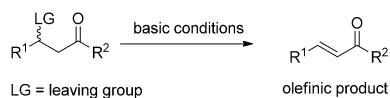
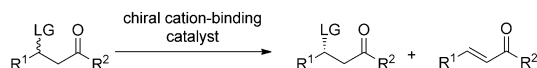
Kinetic Resolution of  $\beta$ -Sulfonyl Ketones through Enantioselective  $\beta$ -Elimination using a Cation-Binding Polyether CatalystLiang Li<sup>†</sup>, Yidong Liu<sup>†</sup>, Yang Peng, Lei Yu, Xiaoyan Wu, and Hailong Yan\*

**Abstract:** Reported herein is the first enantioselective  $\beta$ -elimination reaction catalyzed by a chiral cation-binding polyether. By using this catalytic protocol, a wide range of  $\beta$ -sulfonyl ketones could be effectively resolved with high stereoselectivity (*S* up to >300). Key to the success of this process is the favorable secondary interactions of the catalyst with the Lewis basic groups on the sulfone substrate. The enone product of this process can be easily converted into the racemic starting material, and allows an effective recycling and overall synthesis of chiral  $\beta$ -sulfonyl ketones in high yield and excellent enantioselectivity.

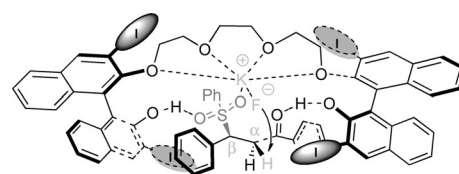
Vicinal elimination<sup>[1]</sup> of a hydrogen and a leaving group, such as halogen, carboxylate, sulfone, etc., is one of the most fundamental organic transformations for the construction of C=C bonds and has been widely employed in the synthesis of natural products as well as medicines.<sup>[2]</sup> In particular,  $\beta$ -elimination of ketones provides efficient access to enones which are valuable functionalities and intermediates in organic synthesis (Scheme 1a). Although various catalytic

tiomer of a racemic substrate to produce the enone product, an efficient kinetic resolution<sup>[5]</sup> of such functionalized molecules can be realized. Herein, we report the first example of such a reaction to access a wide range of  $\beta$ -sulfonyl ketones in high enantiopurity, and it is promoted by a chiral ion-pairing catalyst.<sup>[6]</sup>

In our studies, we chose chiral sulfones as the target, because they are known to possess a wide spectra of biological activities,<sup>[7]</sup> such as cancer agents,<sup>[7d]</sup> secretase inhibitors for the treatment of Alzheimer's disease,<sup>[7f]</sup> and antibacterial agents.<sup>[7g]</sup> Previous syntheses of these functionalities mainly focused on metal-catalyzed hydrogenation,<sup>[8]</sup> substitution,<sup>[9]</sup> cycloaddition,<sup>[10]</sup> and C–H insertion.<sup>[11]</sup> Lewis acid mediated Diels–Alder reactions have also been developed to produce the desired targets in high enantioselectivity.<sup>[12]</sup> More specifically, organocatalytic methods have also been successfully applied to the preparation of chiral sulfones, most notably from the groups of Alexakis, Deng, Tian, Chen, and Chi.<sup>[13]</sup> Our group has been interested in the use of chiral polyethers as cation-binding catalysts in asymmetric catalysis,<sup>[14]</sup> and we were curious whether these catalysts could be applicable to asymmetric  $\beta$ -elimination reactions. As proposed in Scheme 2, while the polyether catalyst can capture KF by

a) Traditional  $\beta$ -elimination of ketonesb) This work: Asymmetric  $\beta$ -elimination of ketonesScheme 1. Base-promoted  $\beta$ -elimination of ketones.

systems have been developed to achieve excellent efficiency of this process,<sup>[3]</sup> to the best of our knowledge, an enantioselective variant of the  $\beta$ -elimination reaction of a  $\beta$ -functional ketone has never been reported in the literature.<sup>[4]</sup> As shown in Scheme 1b, one can imagine that, if a chiral environment can induce selective elimination of one enan-



Scheme 2. Proposed reaction transition state.

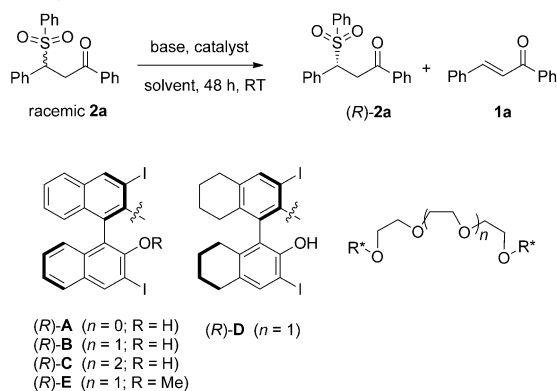
a phase-transfer pathway, its Brønsted-acidic moieties may be involved in secondary interactions, such as hydrogen bonding, with the Lewis basic groups on the sulfonyl ketone substrate, and preferentially with one of the enantiomers over the other. The activated fluoride anion would then act as a base to deprotonate the  $\alpha$ -proton. The elimination of  $\beta$ -sulfone would follow to afford the  $\alpha,\beta$ -unsaturated ketone and lead to a kinetic resolution of the racemic starting sulfonyl ketones.

We initiated our studies by examining the elimination of racemic **2a** in the presence of potassium fluoride and a BINOL-based cation-binding catalyst (Table 1). Different catalysts were examined at 10 mol% loading in 1,4-dioxane at 25 °C. Based on our knowledge of the catalytic performance of chiral bis(hydroxy) polyethers, we systematically modified the length of the polyether chain, which is known to be responsible for the formation of a suitable chiral coordination cage for a potassium cation. Indeed, the length of the

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**Table 1:** Optimization of the reaction conditions.<sup>[a]</sup>

Entry	Catalyst	Solvent	Conv. [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>	<i>S</i> <sup>[d]</sup>
1	( <i>R</i> )- <b>A</b>	1,4-dioxane	49	75	18
2	( <i>R</i> )- <b>B</b>	1,4-dioxane	51	90	42
3	( <i>R</i> )- <b>C</b>	1,4-dioxane	48	52	6
4	( <i>R</i> )- <b>D</b>	1,4-dioxane	11	n.d.	n.d.
5	( <i>R</i> )- <b>E</b>	1,4-dioxane	26	< 5	n.d.
6	–	1,4-dioxane	26	0	n.d.
7	( <i>R</i> )- <b>B</b>	CH <sub>2</sub> Cl <sub>2</sub>	45	43	5
8	( <i>R</i> )- <b>B</b>	toluene	52	54	5
9	( <i>R</i> )- <b>B</b>	furan	57	62	5
10	( <i>R</i> )- <b>B</b>	THF	45	56	9
11 <sup>[e]</sup>	( <i>R</i> )- <b>B</b>	1,4-dioxane	50	97	> 200

[a] Reaction conditions: **2a** (0.1 mmol), KF (0.12 mmol), catalyst (0.01 mmol) in solvent (0.75 mL) at room temperature for 48 h, unless otherwise specified. [b] Determined by <sup>1</sup>H NMR analysis. [c] The ee value was determined by HPLC analysis (see the Supporting Information). The absolute configuration of the unreacted (*R*)-**2a** was assigned by comparison of the measured optical rotation with the reported value. [d] Selectivity values were calculated by the methods of Fiaud:  $S = \ln[(1 - \text{Conv.})(1 - ee_1)] / \ln[(1 - \text{Conv.})(1 + ee_1)]$ . [e] 1.5 equiv KF, 1.0 mL solvent was used. n.d. = not determined, THF = tetrahydrofuran.

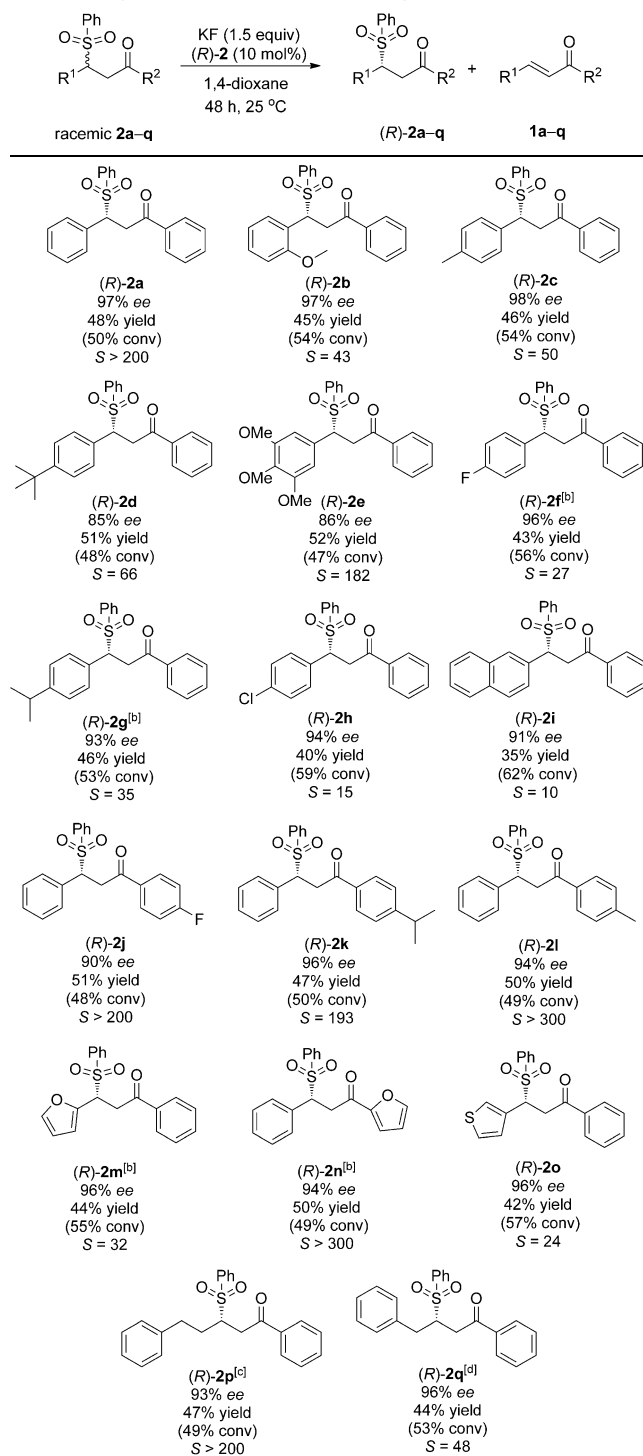
polyether chain proved to play a crucial role in the catalytic performance in our reaction (entries 1–3). The catalyst bearing three ether units [(*R*)-**B**;  $S = 42$ ] proved to be a much more effective catalyst than the catalysts bearing longer [four ether units; (*R*)-**C**;  $S = 6$ ] or shorter [two ether units; (*R*)-**A**;  $S = 18$ ] ether units. The 3,3'-diiodo-substituted catalyst (*R*)-**B** showed the highest activity and enantioselectivity, and can be explained by the polarizability of the iodine atoms and strong coordination of the iodine atoms to the potassium cation. The large radius of the iodine atom might also influence the chiral environment of the transition state, thus resulting in the observed enhancement of enantioselectivity. More catalysts, such as (*R*)-**D**, derived from a chiral backbone, were also examined and demonstrated a reduced catalytic performance in terms of both conversion and enantioselectivity (entry 4). When the reaction was carried out using a catalyst in which the 2,2'-hydroxy groups were methylated, low conversion and negligible enantioselectivity were observed (entry 5). Meanwhile, the background reaction was also examined, and the same level of conversion and enantioselectivity compared to the result shown in entry 5 were observed under the same reaction conditions. This result indicated that the di-O-methyl protected (*R*)-**E** was com-

pletely inactive and the free terminal hydroxy group at the 2,2'-position of the BINOL backbone played an essential role in maintaining the superior catalytic performance of the multifunctional catalyst. In further experiments, the enantioselectivity was found to be highly dependent on the choice of solvent, with 1,4-dioxane remaining the optimal one (entries 7–10). Further optimization of the reaction conditions on potassium fluoride loading and concentration identified the optimal reaction conditions for both conversion and enantioselectivity (entry 11).<sup>[15]</sup>

With the optimal catalytic conditions in hand, we turned to the investigation of substrate scope. As shown in Table 2, the high selectivity achieved by (*R*)-**B** could be extended to a wide range of aryl and heteroaryl sulfones. Substrates with aryl groups were well-tolerated, including those bearing either electron-donating or electron-withdrawing groups [(*R*)-**2a–l**;  $S$  value from 10 to 327]. Additionally, heteroaryl substrates proved to be excellent substrates for the reaction, thus affording the unreacted sulfones with high enantioselectivity as well as selectivity factors [(*R*)-**2m–o**;  $S$  value from 24 to 327]. The position of the substituents, however, affected the selectivity of the reaction. As a general trend, substrates with substituents on  $R^2$  showed higher selectivity [(*R*)-**2j**,  $S > 200$ ; (*R*)-**2k**,  $S = 193$ ; (*R*)-**2l**,  $S > 300$ ; (*R*)-**2n**,  $S > 300$ ]. In most cases, the unreacted secondary sulfones were recovered in high to excellent enantiopurity. Moreover, extensive efforts were also spent on the reaction of sulfones with an aliphatic chain. Only the primary-alkyl-substituted substrates can be resolved with good selectivity [(*R*)-**2p**,  $S > 200$ ; (*R*)-**2q**,  $S = 48$ ].

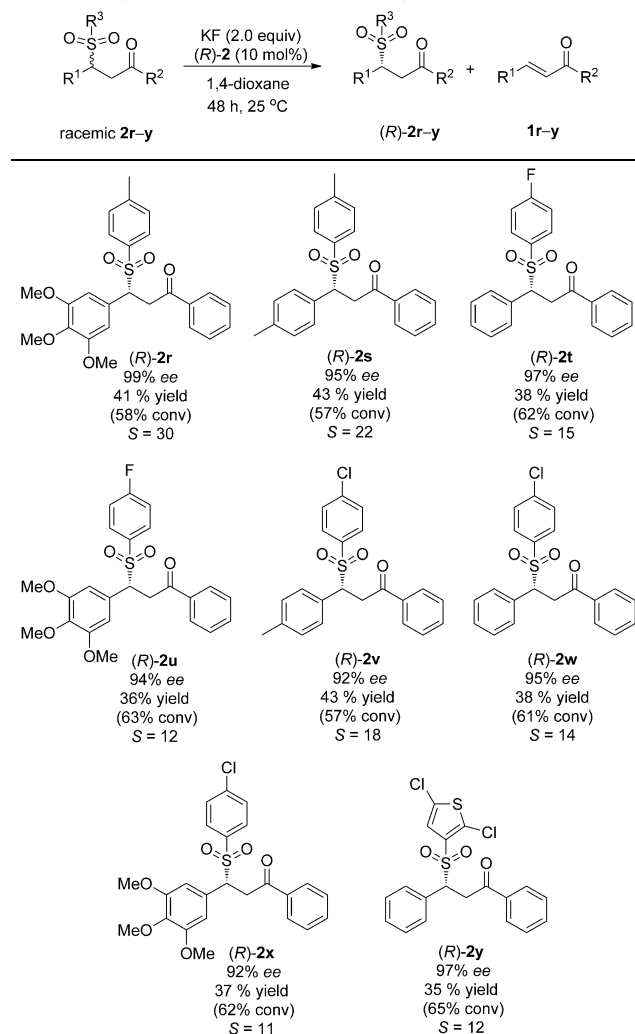
In addition to a wide range of substitutions on  $R^1$  and  $R^2$ , different functional groups ( $R^3$ ) on the sulfone were also tolerated under our catalytic system (Table 3). Substrates bearing both electron-donating and electron-withdrawing groups underwent  $\beta$ -elimination smoothly to give the unreacted sulfones in high enantioselectivity [(*R*)-**2r–x**;  $S$  value from 11 to 30]. In addition, a heteroaryl sulfone substrate was also well-tolerated [(*R*)-**2y**,  $S = 12$ ].

The mechanism of  $\beta$ -elimination of sulfones to form the olefins have been the subject of a large number of investigations.<sup>[16]</sup> In our catalytic system, all the experimental results (see the Supporting Information for more details) strongly support a stepwise carbanion elimination mechanism. The proposed catalytic cycle is illustrated in Scheme 3. The catalyst is believed to chelate the potassium ion from KF to form a chiral ion pair, which then engages the sulfone substrate to afford the complex **I**. Although it was difficult to isolate **I** in an analytically pure form, it could be observed by HR-MS. Deprotonation of the  $\alpha$ -proton by fluoride then leads to the formation of the complex **II**. Finally, the elimination of the PhSO<sub>2</sub> group from the  $\beta$ -carbon atom yields the olefinic product, the potassium salt, and regenerates the catalyst. In this catalytic cycle, the formation of **I** serves as the enantiodetermining step, and the chiral environment of the *R*-configured catalyst only permits the *S*-configured sulfonyl ketone to enter the catalytic cycle. It is proposed that both the sulfone and the ketone oxygen atom on *S*-configured sulfonyl ketone, both of which are hydrogen-bond acceptors and electron-deficient, are essential for

**Table 2:** Scope of kinetic resolution with respect to the sulfones.<sup>[a]</sup>

[a] Unless otherwise indicated, the reactions were carried out with **2** (0.1 mmol), 1.5 equiv of potassium fluoride, and catalyst (10 mol%) in 1,4-dioxane at 25 °C for 48 hours. [b] The reaction time was 60 hours. [c] The reaction time was 20 hours. [d] The reaction time was 28 hours, 20% mmol catalyst, 2.0 equiv of KF.

forming **1** from the chiral ion pair through hydrogen-bonding interactions and Lewis acidic potassium. Moreover, the  $\pi$ , $\pi$ -stacking between the aryl ring of the substrate and the

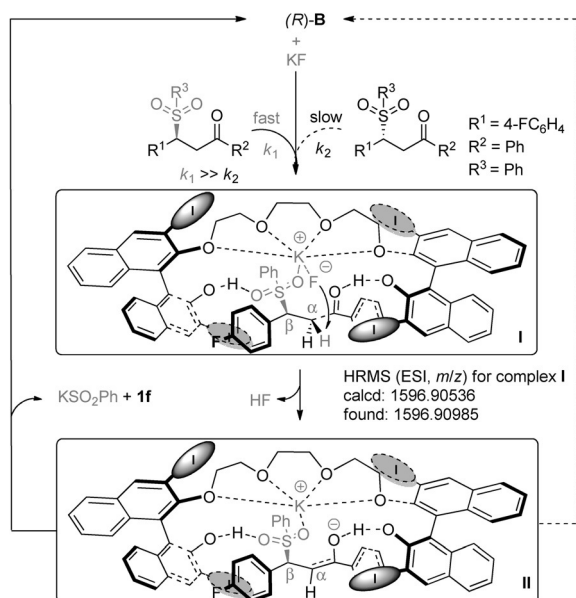
**Table 3:** Scope of kinetic resolution with respect to the sulfones.<sup>[a]</sup>

[a] Unless otherwise indicated, the reactions were carried out with **2** (0.1 mmol), 2.0 equiv of potassium fluoride, and catalyst (10 mol%) in 1,4-dioxane at 25 °C for 48 hours.

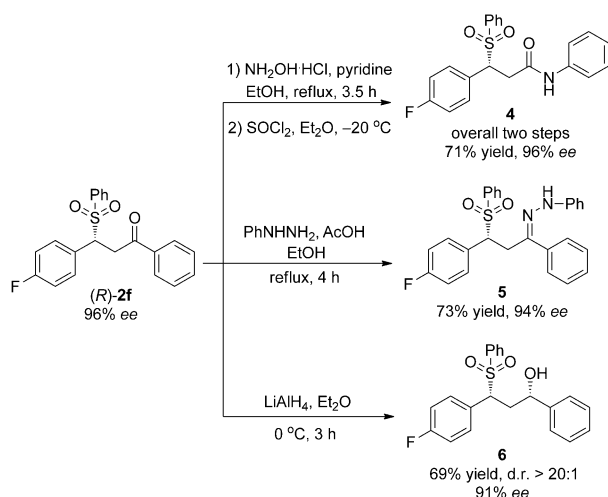
naphthalene moiety on the catalyst may be involved, as well to further lock the conformation of **1** during the elimination.

To demonstrate the potential utility of this method, several transformations of the sulfone (R)-**2f** were explored (Scheme 4). Under the Beckmann rearrangement reaction conditions, (R)-**2f** could be transformed into the amide product **4** in 71% yield with 96% ee. Moreover, the ketone group on (R)-**2f** could be readily converted into the hydrazone **5** or alcohol **6** in good yield under mild reaction conditions. The highly diastereoselective formation of **6** by LiAlH<sub>4</sub> reduction could be attributed by the stereocontrol of the chiral sulfone moiety on the substrate (R)-**2f**. These examples exhibit a diversified application of our products in the preparation of various precursors of biologically active compounds.<sup>[17]</sup>

A unique character of our  $\beta$ -elimination strategy is that the achiral enone product can be easily converted back into the racemic substrate by the addition of sulfinic acid. In this way, the inherent limitation of 50% yield of the kinetic

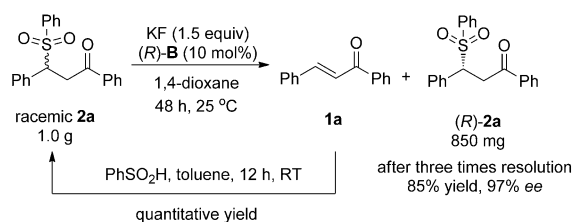


Scheme 3. Proposed reaction mechanism.



Scheme 4. Representative product transformations.

resolution process can be overcome by recycling the enone product. As an example, the substrate (*R*)-**2a** was tested for a multicycle experiment on a gram scale. As shown in Scheme 5, after the first enantioselective elimination reaction, the generated enone product **1a** could be easily separated and quantitatively converted into the racemic sulfone **2a**. The regenerated **2a** then underwent another

Scheme 5. Recycling experiment with **2a**.

catalytic enantioselective elimination. After three cycles of resolution, (*R*)-**2a** was obtained in 85% yield with 97% *ee*.

In conclusion, we have developed the first asymmetric  $\beta$ -elimination of sulfones catalyzed by a chiral cation-binding polyether and using potassium fluoride as the base. This catalytic procedure provides a practical preparation of various chiral secondary sulfones which are useful building blocks in organic synthesis. Current efforts in our laboratory are focused on the detailed mechanistic studies to further elucidate the origin of the asymmetric induction as well as extending the synthetic utility of the system to other functional molecules.

## Experimental Section

The secondary sulfone (**2a–y**; 0.1 mmol), potassium fluoride (8.7 mg, 0.15 mmol), and the catalyst (11.9 mg, 0.01 mmol) were added to a 10 mL flame-dried Schlenk tube containing a stirring bar. 1,4-Dioxane (1 mL) was injected into the tube at room temperature. After stirring for 48 hours, the mixture was purified by silica gel chromatography (petroleum ether/actone 7:1) to afford the products (*R*)-**2a–y** as white solids.

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**Keywords:** asymmetric catalysis · ion pairs · kinetic resolution · organocatalysis · sulfones

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