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Enantioselective Reactions of 2-Sulfonylalkyl Phenols with Allenic Esters: Dynamic Kinetic Resolution and [4+2] Cycloaddition Involving *ortho*-Quinone Methide Intermediates

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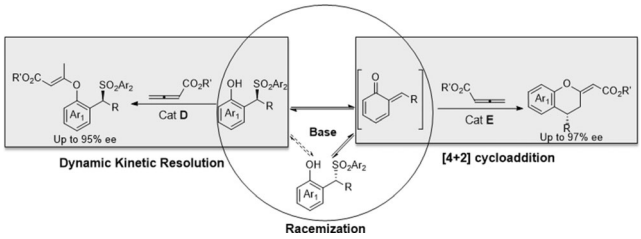
Abstract: *We report herein a dynamic kinetic resolution (DKR) involving ortho-quinone methide (o-QM) intermediates. In the presence of Et_3N and the cinchonine-derived nucleophilic catalyst* ***D****, the DKR of 2-sulfonylalkyl phenols with allenic esters afforded chiral benzylic sulfones in 57–79 % yield with good to excellent enantioselectivity (85–95 % ee). Furthermore, with 2-(tosylmethyl)sesamols or 2-(tosylmethyl)-naphthols, from which stable o-QM substrates can be generated, a formal [4+2] cycloaddition delivered 4-aryl- or alkyl-substituted chromans with excellent enantioselectivity (88–97 % ee).*

Sulfones have found numerous applications in agricultural science and medicinal chemistry, and have been widely used in organic synthesis as versatile synthons.[1] Over the past decades, a number of methods have been reported for the synthesis of achiral and/or racemic sulfones.[2] However, the development of asymmetric catalytic methodologies for direct access to enantiomerically enriched sulfones is much less advanced.[3] In particular, the efficient catalytic preparation of both aryl- and alkyl-substituted benzylic sulfones remains challenging.

In 2015, we developed the first organic-base-catalyzed asymmetric reaction with *o*-QMs generated in situ.[4] Notably, 2-(tosylmethyl)phenol, a precursor to *o*-QMs in the presence of a base, bears a benzylic sulfone group, which provides an excellent platform for the design of a new DKR of racemic 2-(tosylmethyl)phenol (**1**). It was envisioned that the DKR of racemic **1** would be possible by reaction with a suitable electrophilic partner in the presence of a chiral catalyst and a base, whereby the chiral catalyst might preferentially promote the reaction of one enantiomer of **1**, while the base could effectively mediate racemization via an *o*-QM intermediate, thus leading to the full conversion of **1** into a chiral benzylic sulfone. Although several asymmetric reactions involving *o*-QM intermediates, such as dialkoxylation, carboalkoxylation,[5] 1,4-addition,[6] transfer hydrogenation,[7] and cycloaddition reactions,[8] have been developed, to the best of our knowledge, there has been no report of a DKR involving *o*-QMs.

Herein, we report the results of our investigation. Through the racemization of 2-sulfonylalkyl phenols **1** via *o*-QM intermediates and subsequent asymmetric addition catalyzed by a nucleophilic amine, the developed DKR afforded benzylic sulfones with good to excellent enantioselectivity (85–95 % *ee*; Scheme 1, left). Furthermore, a highly enantioselective [4+2] cycloaddition process was developed by the use of 2-(tosylmethyl)sesamol or 2-(tosylmethyl)naphthol, which could generate stable *o*-QMs as the substrates to deliver 4-substituted chromans with excellent enantioselectivity (88–97 % *ee*; Scheme 1, right).



Scheme 1. Different reaction pathways of 2-sulfonylalkyl phenols with allenic esters via *o*-QM intermediates: DKR versus [4+2] cycloaddition.

To test the viability of the DKR, we began our studies by examining the racemization of enantiomerically enriched 2-(tosylmethyl)phenol **1a** (80 % *ee*) in the presence of bases (see the Supporting Information). Et_3N was found to be most effective for the racemization, affording nearly racemic **1a** (4 % *ee*) in 2 h at room temperature.

Allenic ester **2a** was selected as the reaction partner of **1a** for its high electrophilicity.[9] Since Et_3N may provide racemic products as a result of a possible background reaction, control experiments were first performed to examine the effect of different organic bases in promoting this model reaction of **1a** with **2a** (Table 1, entries 1 and 2). Gratifyingly, Et_3N was found to be ineffective for the transformation even at 100 mol % loading (Table 1, entry 1). On the other hand, the stronger nucleophilic base DABCO could induce the reaction to give the corresponding product **3a** with high reactivity (Table 1, entry 2). Encouraged by these results, we proceeded to examine the catalytic potential of some cinchona-derived nucleophilic catalysts **A**–**D**. The reaction of **1a** and **2a** with catalyst **A**[10] proceeded smoothly to give product **3a** with 43 % *ee* and 53 % conversion in 12 h (Table 1, entry 3). This result suggested that catalyst **A** alone could be

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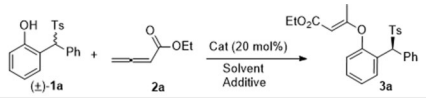
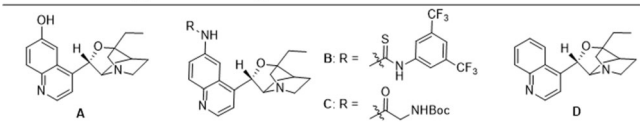
Table 1: Optimization of the reaction conditions for DKR.[a]



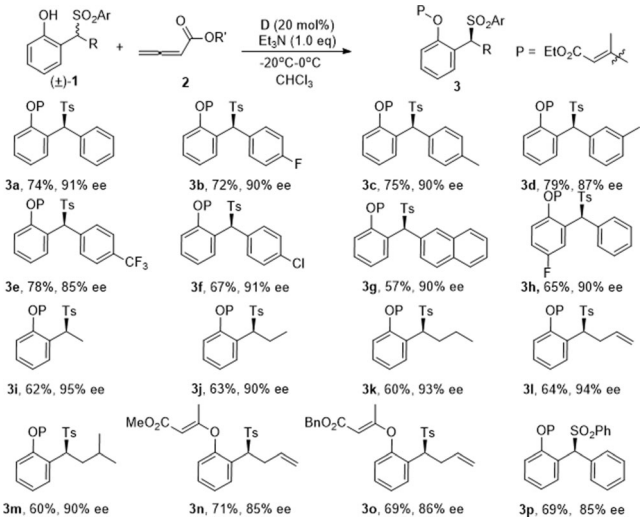


Entry	Catalyst	Solvent	Additive	Conv. [%][b]	*ee* [%][c]
1[d]	Et_3N	CH_2Cl_2	none	0	
2	DABCO	CH_2Cl_2	none	>90	
3	**A**	CH_2Cl_2	none	53	43
4	**A**	CH_2Cl_2	Et_3N[d]	>90	43
5	**A**	$CHCl_3$	Et_3N[d]	>90	54
6	**B**	$CHCl_3$	Et_3N[d]	>90	21
7	**C**	$CHCl_3$	Et_3N[d]	trace	n.d.
8	**D**	$CHCl_3$	Et_3N[d]	>90	75
9[e]	**D**	$CHCl_3$	Et_3N[d]	>90	91

[a] Unless otherwise specified, reactions were conducted with **1a** (0.1 mmol), **2a** (2.0 equiv, 0.2 mmol), and the catalyst (0.02 mmol, 20 mol%) in the solvent (1.0 mL) at room temperature for 12 h. [b] Conversion was determined by ^{1}H NMR spectroscopy of the crude mixture. [c] The *ee* value was determined by HPLC analysis on a chiral stationary phase. [d] Et_3N (1.0 equiv). [e] Reaction temperature: −20 °C for 5 days and then 0 °C for another day. Boc = *tert*-butoxycarbonyl, Ts = *p*-toluenesulfonyl, n.d. = not determined.

used to mediate the kinetic resolution of **1a** with **2a**. To improve the efficiency of the reaction, we performed the DKR with 1.0 equivalent of Et_3N as an additive. Under otherwise identical conditions, the reaction proceeded to completion in 6 h with similar enantioselectivity (Table 1, entry 4). After solvent screening (see the Supporting Information), chloroform was identified as the solvent of choice for subsequent optimization of the reaction (Table 1, entry 5). The quinidine-derived catalysts **B**[11] and **C**[12] did not afford satisfactory enantioselectivity (Table 1, entries 6 and 7). To our delight, the use of cinchonine-derived catalyst **D**[13] significantly improved the enantioselectivity (75% *ee*) without loss of reactivity (Table 1, entry 8). By lowering the reaction temperature to −20 °C, the enantioselectivity of the catalysis was improved to 91% *ee* albeit with the need for a prolonged reaction time for full conversion of **1a** (Table 1, entry 9).

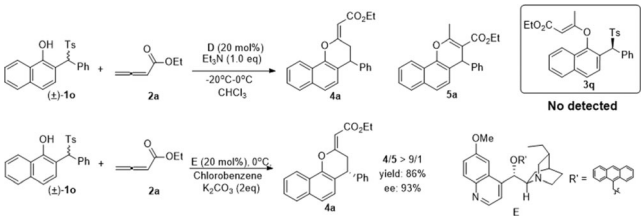
The scope of the DKR procedure was studied with **D** as the catalyst under the optimized reaction conditions (Scheme 2). A broad range of 2-(tosylmethyl)phenols with various aryl substituents reacted smoothly with **2a** to afford the desired products **3a**–**h** with good to high enantioselectivity (85–91% *ee*). However, no reaction was observed for substrates bearing an *ortho*-substituted phenyl ring (with an *ortho* substituent either on the R group or on the quinone methide fragment), probably owing to the severe steric congestion. Notably, alkyl-substituted 2-(tosylmethyl)phenols were also suitable substrates, giving the corresponding products **3i**–**m** with even higher enantioselectivity (up to 95% *ee*). The effects of the ester group (COOR′) on the allenic ester were investigated. It was found that methyl ester **2b** and benzyl ester **2c** were amenable to the reaction,



Scheme 2. Scope of the DKR. Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), **D** (0.04 mmol), Et_3N (0.2 mmol), $CHCl_3$ (2.0 mL), −20 °C, 5 days and then 0 °C, 1 day. Yields are for the isolated product after column chromatography. The *ee* values were determined by HPLC analysis on a chiral stationary phase. Bn = benzyl.

affording the corresponding products **3n**,**o** with 85 and 86% *ee*. When the tolyl group of 2-(tosylmethyl)phenol **1a** was replaced with a phenyl group, the DKR reaction proceeded smoothly and gave the corresponding product **3p** in 69% yield with 85% *ee*. The absolute configuration of the DKR product **3a** was unambiguously assigned as *S* by single-crystal X-ray diffraction analysis (see the Supporting Information), and that of others was assigned by analogy.

During our studies on the scope of the DKR, the reaction of **1o** with **2a** under the standard conditions gave an isomeric mixture of the 4-substituted chromans **4a** and **5a**, instead of the expected DKR product **3q** (Scheme 3). Similar results

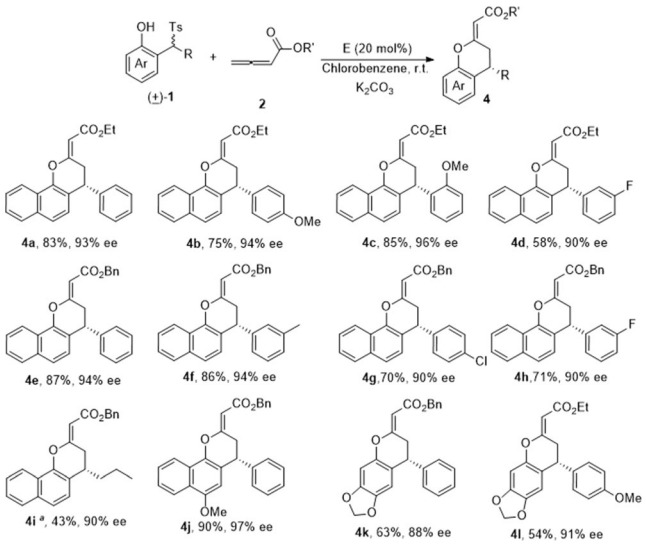


Scheme 3. Reactions between 2-(tosylmethyl)naphthol **1o** and allenic ester **2a**.

were obtained in reactions of 2-(tosylmethyl)sesamol and allenic esters. These results suggested that substrates **1**, which can generate more stable *o*-QMs, reacted with allenic esters preferentially through a [4+2] cycloaddition pathway to give the corresponding 4-substituted chromans. In view of the observed bioactivity of natural products and pharmaceuticals containing a chiral chroman structure,[14] we hoped to establish this new methodology with high efficiency. Gratifyingly, the screening of various chiral nucleophilic amine catalysts[15] (see the Supporting Information) led to the identification of cinchona alkaloid catalyst **E**,[16] the use of

which in the presence of K_2CO_3 gave **4a** with 93% *ee* in 86% yield (Scheme 3).

Thus, the scope of the [4+2] cycloaddition was investigated (Scheme 4). 2-(Tosylmethyl)naphthols with both electron-donating and electron-withdrawing substituents at different positions on the phenyl ring (R) reacted with allenic

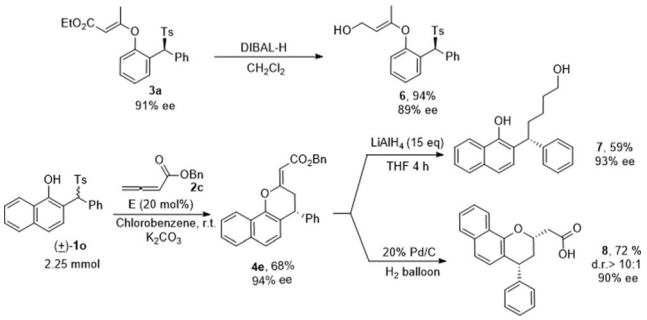


Scheme 4. Scope of the [4+2] cycloaddition. Reaction conditions: **1** (0.2 mmol), **2** (0.5 mmol, 2.5 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), **E** (0.04 mmol, 20 mol%), chlorobenzene (4.0 mL), 24 h. Yields are for the isolated product after column chromatography. The *ee* values were determined by HPLC analysis on a chiral stationary phase. [a] The reaction was carried out with a 40 mol% catalyst loading for 5 days.

esters (**2a** or **2c**) to afford the corresponding products **4a**–**h** with excellent enantioselectivity (90–96% *ee*). A substrate bearing an alkyl group (R) was also tolerated with a higher catalyst loading and longer reaction time (product **4i**, 90% *ee*). Different substituents on the quinone methide fragment were tolerated as well, and chroman products **4j**–**l** were obtained with 88–97% *ee*. The absolute configuration of **4a** was established as *R* on the basis of X-ray crystallographic analysis (see the Supporting Information).

To evaluate the practical utility of the DKR and [4+2] cycloaddition, we conducted several further synthetic transformations (Scheme 5). The enantiomerically enriched benzylic sulfone **3a**, which bears an α,β-unsaturated ester group, could be further reduced to the corresponding allylic alcohol **6** in good yield. Meanwhile, a gram-scale [4+2] cycloaddition of **1o** and **2c** under the standard conditions provided the desired product **4e** in 68% yield with 94% *ee*. Reduction of the olefin and removal of the benzyl group through hydrogenation with Pd/C proceeded readily in a one-pot process to form **8** in good yield with high diastereoselectivity. Notably, the treatment of **4e** with a large amount of $LiAlH_4$ provided chiral alcohol **7** with 93% *ee*.

To verify the proposed [4+2] cycloaddition pathway via stable *o*-QM intermediates, the reaction of an isolated *o*-QM as a diene with allenic ester **2c** in the presence of catalyst **E** to form **4l** was investigated (see the Supporting Information).



Scheme 5. Synthetic transformations of products **3** and **4**. DIBAL-H = diisobutylaluminum hydride.

The observation that the product was formed with the same enantioselectivity (91% *ee*) as in the reaction of the corresponding 2-(tosylmethyl)sesamol confirms the [4+2] cycloaddition pathway via *o*-QM intermediates.

On the basis of the above control experiment and the absolute configuration of the products, we propose the following reaction mechanism to explain the different pathways from the key *o*-QM intermediates (Figure 1): 2-(Tosylmethyl)phenols **1** may undergo rapid racemization in the presence of Et_3N via *o*-QM intermediates ($K_2 \gg K_1$). At the same time, catalyst **D** reacts with the allenic ester **2** to generate a chiral zwitterionic intermediate **9**, which could deprotonate the phenol group in 2-(tosylmethyl)phenol **1** to

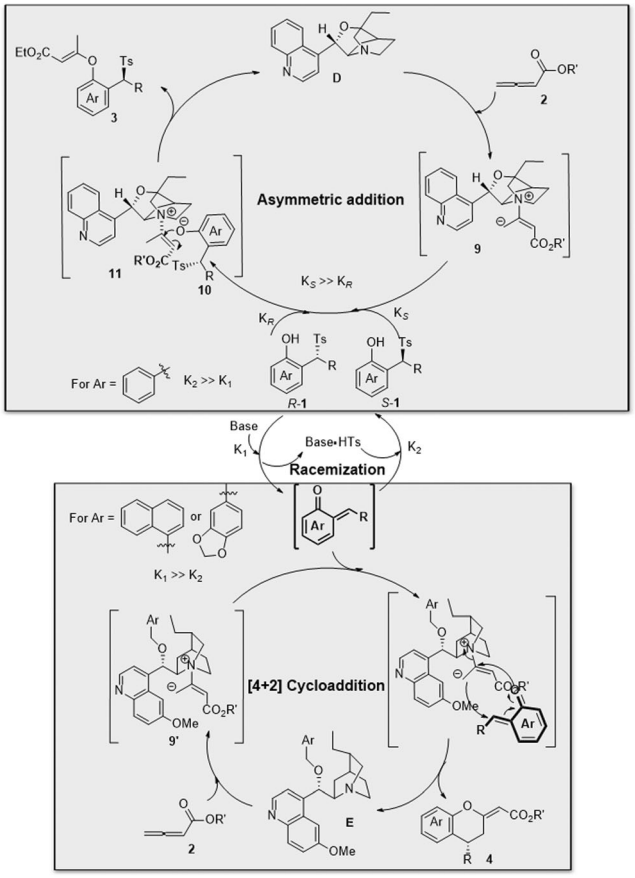


Figure 1. Catalytic cycles of the DKR and [4+2] cycloaddition.

give intermediates **10** and **11**. Subsequently, the nucleophilic addition of **10** to **11** would produce **3** and regenerate the catalyst. In this step, the reaction of (*S*)-**10** with **11** would be much faster than that of (*R*)-**10** ($K_S \gg K_R$, according to calculations and control experiments between allenic esters **2** with ester groups of different sizes and 2-(tosylmethyl)phenol **1a**; see the Supporting Information) owing to steric hindrance between the ester group and the Ts group, thus resulting in an enantiomerically enriched product **3** through DKR. For 2-(tosylmethyl)sesamol and 2-(tosylmethyl)naphthol substrates, stable *o*-QMs would be generated in the presence of a base ($K_1 \gg K_2$). The subsequent [4+2] reaction between the *o*-QM generated in situ and the zwitterionic intermediate **9′**, which is formed by the attack of catalyst **E** on allenic ester **2**, provides chromans **4**.

In conclusion, we have developed a highly efficient protocol for the DKR of racemic 2-sulfonylalkyl phenols on the basis of asymmetric nucleophilic addition to allenic esters and racemization via an *o*-QM intermediate, to afford a variety of optically active benzylic sulfones with high enantioselectivity (up to 95% *ee*). With 2-(tosylmethyl)sesamols and 2-(tosylmethyl)naphthols as the substrates, enantioselective [4+2] cycloaddition reactions with allenic esters led to a wide range of 4-substituted chromans with high enantioselectivity (88–97% *ee*).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: benzylic sulfones · chromans · cycloaddition · dynamic kinetic resolution · *ortho*-quinone methides

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Communications

Organocatalysis

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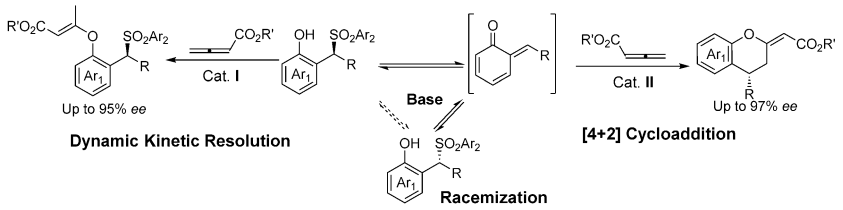
Enantioselective Reactions of 2-Sulfonylalkyl Phenols with Allenic Esters: Dynamic Kinetic Resolution and [4+2] Cycloaddition Involving *ortho*-Quinone Methide Intermediates



Resolutely following the chosen path: 2-Sulfonylalkyl phenols were transformed into chiral benzylic sulfones with Et_3N and a cinchonine-derived catalyst I by dynamic kinetic resolution (DKR) via an *ortho*-quinone methide (*o*-QM; see scheme). In contrast, 2-(tosylmethyl)-sesamols and -naphthols, which form stable *o*-QMs, underwent formal [4+2] cycloaddition under similar conditions with another cinchona alkaloid catalyst II to give 4-substituted chromans.

