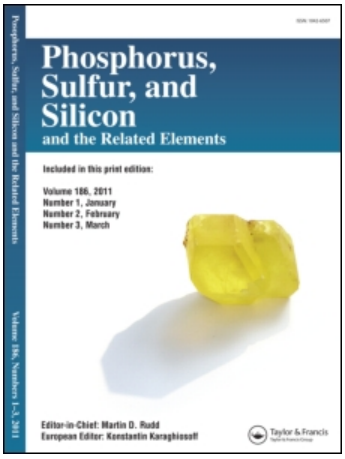

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Developments of Asymmetric Synthesis Mediated by Chiral Sulfur Reagents

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Our work on the thio-Claisen rearrangement mediated by an adjacent sulfinyl group is reviewed. The substrates could easily be prepared on a large scale from diacetone-D-glucose. The rearrangement was effected with a diastereoselectivity of 95:5, in favor of the (S,S) or the (R,R) isomer. An approach to natural bis(lactones) was investigated, using a halolactonization reaction and a second [3,3] sigmatropic shift, again mediated by the sulfinyl group. The second part deals with the catalytic enantioselective benzylidenation of aldehydes, mediated by chiral sulfur ylides. We have introduced simple C_2 symmetric thiolanes for that purpose. The procedure is very practical and enantiomeric excesses up to 96% have been reported for the model of stilbene oxide. A series of ferrocenyl sulfides with planar chirality has also been investigated, leading to unexpected diastereoselectivities and enantiomeric excesses up to 94%.

Keywords Chiral sulfur ylides; epoxides; ferrocenes; sulfoxides; thio-Claisen rearrangement

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Our developments have been made possible by a group of dedicated and enthusiastic chemists at Caen. The thio-Claisen studies were started by Carole Alayrac and Stéphanie Nowaczyk; applications were achieved by Virginie Blot and Vincent Reboul. The sulfur ylide adventure started with Karine Julienne, and has continued mainly with Jacques Zanardi, Stéphanie Minière, Jean-François Brière, and Marion Davoust. Thanks also to Bianca Bonini, Mariafrancesca Fochi, Juan Carlos Carretero, and Ramon Gómez Arrayás for their kind and efficient collaboration. We gratefully acknowledge the "PunchOrga" Network (Pôle Universitaire Normand de Chimie Organique), the "Ministère de la Recherche et des Nouvelles Technologies," CNRS (Centre National de la Recherche Scientifique), the "Région Basse-Normandie," and the European Union (FEDER funding) for financial support.

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INTRODUCTION

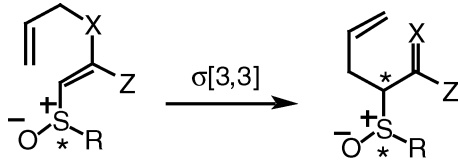
The need to produce enantioenriched compounds in a direct fashion led us to propose asymmetric versions of two classical chemical reactions for which the sulfur reagents bring significant advantages or specific reactivity.

We review here our recent progress on the thio-Claisen rearrangement stereocontrolled by a chiral sulfinyl group. The source of chirality, *D*-glucose, is used in a stoichiometric and very easy fashion.

The second reaction is the conversion of aldehydes into epoxides, using sulfur ylides. We have developed an asymmetric version, with a catalytic amount of chiral sulfide. Two types of structures were efficient: C_2 symmetric thiolanes and planar chiral ferrocenyl sulfides.

STEREOCONTROLLED CLAISEN REARRANGEMENT MEDIATED BY A SULFINYL GROUP

The Claisen rearrangement[1–6] is a powerful reaction for the construction of complex molecules, including natural products and biologically active molecules. We have wished to develop a new version of this reaction, in which the absolute and relative stereochemistries would be directed by a sulfinyl group, located in an adjacent position to the pericyclic [3,3] sigmatropic nucleus (Scheme 1). Indeed, sulfoxides have been largely used for the stereocontrol of a variety of reactions,[7–12] but not for the Claisen rearrangement.

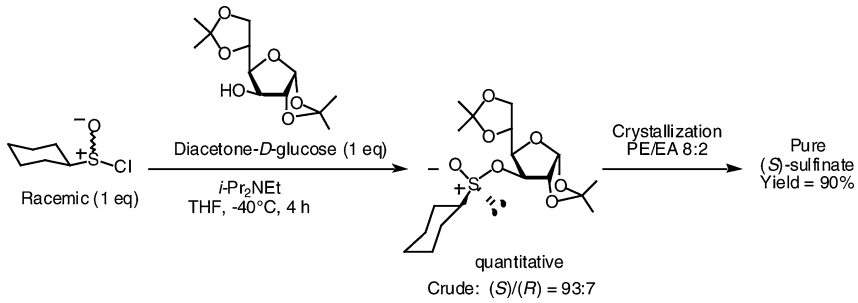


SCHEME 1

Despite the potential of this strategy, some drawbacks were associated. The transposition normally needs heating to be accomplished, under conditions in which the product might not survive, as a result of facile sulfenic acid elimination. This was indeed observed by Posner and his group,[13] ending up with a conjugated diunsaturated ester. From our own experience and literature results,[14,15] we planned to introduce a second sulfur atom in the substrate. Replacing the oxygen atom of a Claisen pericyclic nucleus by a sulfur atom leads to an acceleration

of the rearrangement.[16–18] A 5–7 kcal/mol decrease of the activation enthalpy is observed, mainly as a result of the easy cleavage of a C—S bond, relative to a C—O one. The thio-Claisen transposition[15] is usually carried out at ambient temperature, or at temperatures that do not exceed 100°C.

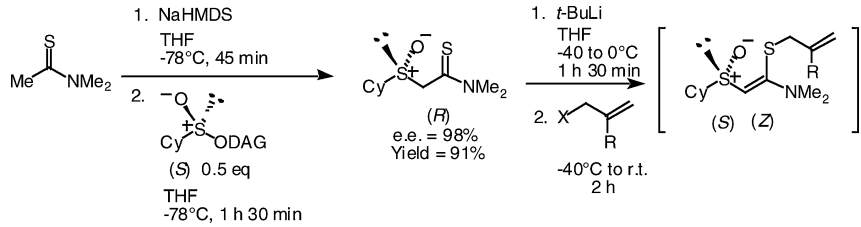
A second way to modulate the elimination of sulfenic acid was to play on the nature of the R group linked to sulfur. Our initial tests led us to choose a cyclohexyl group. This choice prevented us from using a popular source of enantiopure sulfoxides: methyl *para*-toluenesulfinate.[7,19] The choice of Ellman *tert*-butyl *tert*-butanethiosulfinate,[20] obtained easily by catalytic asymmetric oxidation of *tert*-butyl disulfide,[21,22] was not appropriate either. Our need was fulfilled by a nice method developed by Fernandez, Khiar, and Alcudia, which we feel it is still overlooked.[7,23] As a source of chiral alkanesulfinates, they used one of the cheapest enantiopure sources: *D*-glucose. We applied it to the case of racemic cyclohexanesulfinyl chloride.[24] Esterification by diacetone-*D*-glucose (Scheme 2) in the presence of diisopropylethylamine provided, after a simple crystallization, a 90% yield of diastereomerically pure (*S*)-sulfinate. The same reaction with pyridine furnished the pure (*R*)-sulfinate oil, after fishing out a small amount of the crystalline (*S*)-isomer.



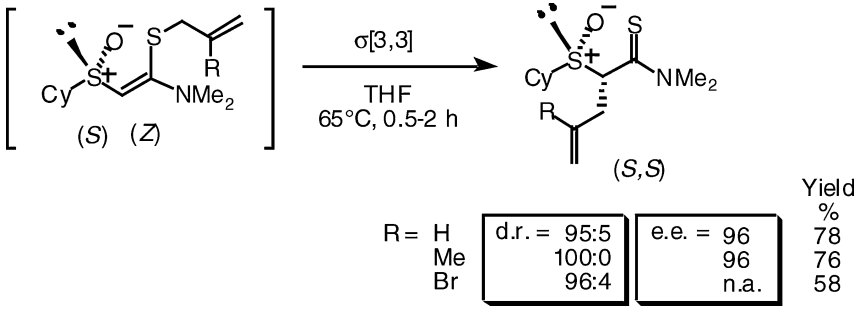
SCHEME 2

The substrates for the Claisen rearrangement have been prepared by Carole Alayrac and Stéphanie Nowaczyk[25] through the following steps (Scheme 3): Andersen type reaction of a thioamide enethiolate with ⟨⟨DAG⟩⟩ cyclohexanesulfinate, subsequent deprotonation of the sulfinylthioamide and *S*-allylation.

The formed *S*-allyl aminothioketeneacetals were rearranged by reflux in THF.[25] The expected *C*-allyl sulfinylthioamides were formed in good yields (Scheme 4). The diastereoselectivity was rewarding: ratios were equal or superior to 95:5, in favor of the (*S*,*S*)-isomer.

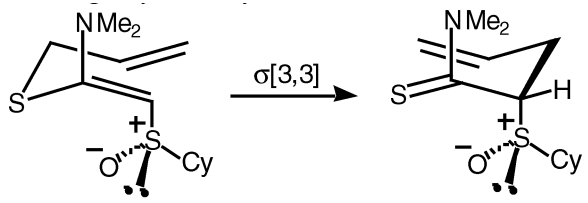


SCHEME 3



SCHEME 4

To explain this control, a model was proposed[26] as an extension of the Felkin Anh one (Scheme 5). The *S*-allyl moiety (electrophilic) approaches the keteneaminothioacetal bond (nucleophilic) with substituents oriented on the chiral sulfur atom so that placing the most electron-donating group in an antiperiplanar position will maximize orbital overlap. The oxygen atom (linked to sulfur) occupies the inside allylic position, and the large cyclohexyl the outside one.

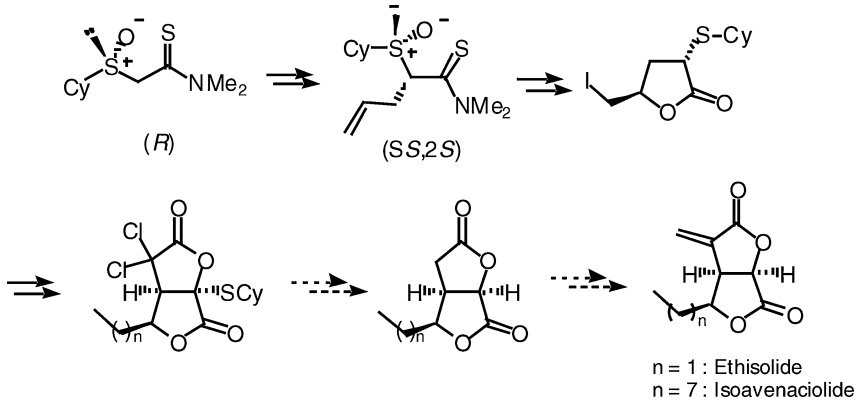


SCHEME 5

The easy access to this attractive, small, functionalized synthon (thioamide, sulfinyl and alkenyl groups, plus two asymmetric centers) led us to use it for further transformations and applications to the

synthesis of natural products. Our project was to develop a scheme tending to avoid protection/deprotection steps.

Virginie Blot and Vincent Reboul have started an enantioselective synthesis of natural bis(lactones), ethisolide, and isoavenaciolide (Scheme 6). The first key step is the halolactonization of γ-unsaturated lactams,[27] obtained by conversion of the thiocarbonyl group into a carbonyl. We observed that the sulfinyl group was detrimental to the stereocontrol of the lactonization, probably in connection to participation of the sulfinyl oxygen atom.[28,29] Reaction of a sulfanyl amide led to the efficient formation of the *trans* lactone.[27] The synthesis is now being pursued with the alkylation of the iodides and formation of unsaturated sulfinyl lactones. A key step will involve a second [3,3] sigmatropic shift, which was developed by Marino and his group.[30] It consists of the addition of dichloroketene to an unsaturated sulfoxide and transposition and attack of the arising carboxylate anion to a thionium cation, achieving the formation of the second lactone ring. Our results will be reported in due course.

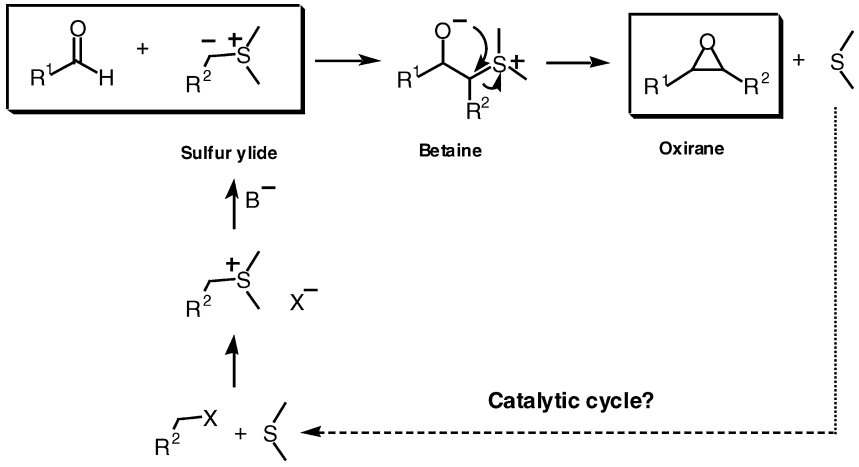


SCHEME 6

Our studies have shown that the thio-Claisen substrates could easily be prepared on a large scale from diacetone-*D*-glucose. The transposition proceeded under mild conditions. We observed neither sulfenic acid elimination nor epimerization. The rearrangement was effected with a diastereoselectivity of 95:5 in favor of the (*S*,*S*) or the (*R*,*R*) isomer. We have also achieved a synthesis of the (S^*,R^*) isomer[31] and a stereocontrolled approach of molecules bearing 3 stereogenic centers.[25] The small and functionalized synthon was further transformed by halolactonization. The formed lactones were elaborated into precursors of a natural bis(lactone), ethisolide or isoavenaciolide.

ASYMMETRIC SYNTHESIS OF EPOXIDES MEDIATED BY CHIRAL CATALYTIC SULFIDES AND YLIDE CHEMISTRY

Until about 10 years ago, there was no efficient synthesis of enantioenriched epoxides using the Johnson–Corey reaction of chiral sulfur ylides with carbonyl compounds (Scheme 7).[32–34] Significant contributions have been made by Solladié-Cavallo[35–38] with the stoichiometric use of Eliel oxathiane, derived from pulegone, and by Aggarwal[39–44] with an efficient catalytic process[34,45,46] involving a sulfide obtained from camphorosulfonic acid.

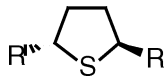


SCHEME 7

In need of an enantiopure oxirane used in the synthesis of a fungicide, we have explored the sulfur ylide chemistry and searched for a simple new sulfide and a procedure that could be scaled up industrially. Later on, some other groups have entered this field and proposed a variety of sulfide structures. We will review here some of our studies, which have acquired a broader outlook from the initial one.

Our initial design of a sulfide incorporated the principle of C_2 symmetric. Among the challenges for stereocontrol of the epoxidation[44] is the formation of a single diastereomeric sulfonium salt. This led us to a thiolane (Scheme 8), flanked by two methyl groups, adjacent to the sulfur atom and in a *trans* arrangement. Karine Julienne achieved[47] a straightforward synthesis in two simple steps from commercial (2*S*,5*S*)-hexanediol, which can be prepared by baker's yeast reduction of 2,5-hexanedione. This diol, its enantiomer, and analogues (methyl replaced by ethyl, isopropyl . . .) are now available from Chirotech (UK) and Jülich

(DE) companies and are commonly used in asymmetric synthesis, with the Duphos ligands.



SCHEME 8

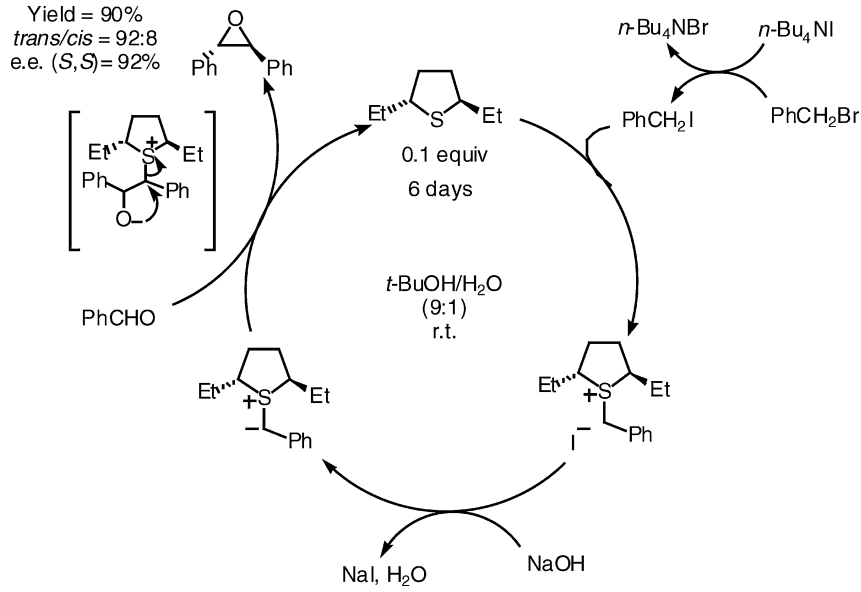
Our first experiments with dimethylthiolane were extremely disappointing: sluggish formation of the sulfonium salt, unfavorable equilibrium, and instability of the yield, and so forth. We decided to develop a one-pot synthesis, in which all the reagents were added from the start. Karine Julienne discovered[47,48] that efficient chemical conversion and stereoselectivity were achieved in polar solvents, acetonitrile and *tert*-butanol, incorporating some water. With a stoichiometric amount of sulfide, yields of *trans* oxiranes were in the range of 80–90% and enantiomeric excesses from 75 to 94%. The formation of the (*S*,*S*) enantiomer was easily explained from the initial design of the auxiliary.

A variety of examples were screened.[48] Efficient epoxidation was achieved with aromatic, branched aliphatic, heteroaromatic, α-unsaturated aldehydes. Benzylic bromides worked nicely, and we reported[49] the first examples of allyl halides used for the synthesis of enantioenriched vinyl oxiranes.

Initial attempts to make the reaction catalytic in terms of the amount of the sulfide showed that the reaction was feasible (0.1–0.2 equiv) but the kinetic rates were frustratingly slow and the reaction conditions unpractical.

Analysis of the rates for the various steps led to attempts to accelerate the initial formation of the sulfonium salt. Jacques Zanardi uncovered[50] that addition of sodium or tetra-*n*-butylammonium iodide led to the acceleration of the epoxidation. As an erosion of the enantiomeric excess was observed is some cases, we introduced the diethyl thiolane as a mediator for this reaction (Scheme 9). Indeed, using this chiral sulfide (0.1 equiv in 6 days at room temperature [rt]) led to stilbene oxide in 90% yield, 92:8 *trans*/*cis* ratio, and an enantiomeric excess of 92%.

To extend the epoxidation to various substrates, solve the diastereomeric issue, and boost the kinetic rates, we have explored other sulfide structures. Some information available from ylides derived from thietanes or thianes confirmed that geometrical features are critical: flexibility of the ring and torsion angles between the ylide moiety and the substituents on the stereogenic centers.



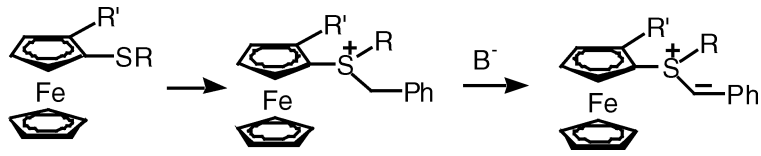
SCHEME 9

Jean-François Brière and Marion Davoust have prepared a new chiral C_2 symmetric thiolane from mannitol. It bears an adjacent acetal ring to lock the otherwise flexible five-membered sulfide ring. The methyl and alkoxy group are located in a *cis* arrangement, resulting in a quasi-axial position for the methyl groups.

Preliminary experiments with mannitol sulfide (0.2 equiv) revealed that the expected reaction took place in one day, with an 88% yield, and an enantiomeric excess up to 96%. Study of the scope of this new auxiliary is underway.

A second new type of chiral sulfides has been investigated in the ferrocenyl series. Whereas planar chiral ferrocenes have led to significant progresses in asymmetric synthesis,[51–55] their sulfur derivatives have been explored only recently and remain underexploited.[51,53–63]

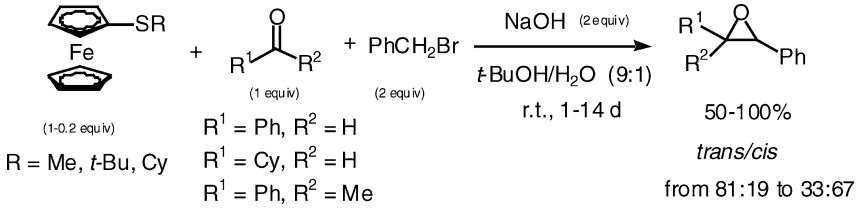
We assumed that formation of ferrocenyl sulfonium salts (unknown) would be facilitated (Scheme 10), in analogy to ferrocenyl



SCHEME 10

carbocations.[64,65] Deprotonation should furnish new ylides with original electronic structures. Such species have not yet been reported.

Stéphanie Minière has first tested[66] the epoxidation reaction of achiral sulfides under our standard conditions (Scheme 11). The formation of the oxiranes proceeded well. A surprising diastereoselectivity was observed, with *trans*/*cis* ratio around 2:1 for the typical example of stilbene oxide. Monitor experiments revealed that the formation of the *anti* betaine is irreversible and that of the *syn* betaine is only partially reversible. This stands in contrast with dialkyl sulfides, for which the reversibility of the *syn* betaine formation has been evidenced and interpreted[44,67] by Aggarwal *et al*.

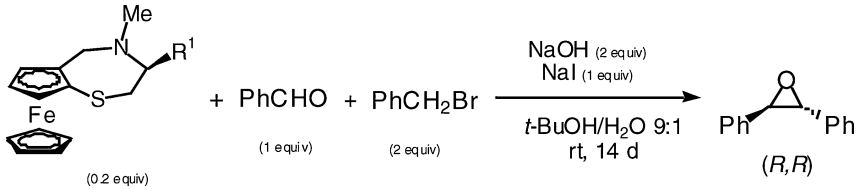


SCHEME 11

A number of planar chiral sulfides have been prepared. Our first breakthrough was achieved in collaboration with Juan Carlos Carretero and Ramon Gómez Arrayás (University of Madrid). A promising enantiomeric excess of 67% in favor of (*S,S*)-stilbene oxide represented the first example[68] of planar chirality in asymmetric epoxidation reaction.

We then searched a more rigid structure by incorporating the sulfur atom in a ring adjacent to one of the cyclopentadienyl rings of ferrocene. An opportunity to test this structure was provided to us by Bianca Bonini and Mariafrancesca Fochi (University of Bologna), who had very recently reported[60] the synthesis of planar and central chiral ferrocenyl sulfides. The sulfides were prepared from ferrocenyl thiol and 1,2-aminoalcohol derivatives (nucleophilic substitution of the activated alcohol, and electrophilic attack of an intermediate iminium salt to the *ortho* position of the cyclopentadienyl ring). Two diastereomers were formed and separated. Six sulfides were tested for epoxidation (Scheme 12), again with our standard conditions.[68] In contrast to the phenyl and *iso*-propyl derivatives, the *tert*-butyl compounds (R^1) led to an efficient formation of stilbene oxide, with an enantiomeric excess (ee) of 83 or 77%. Surprisingly, the absolute configuration is the same for the epoxide, starting from any of the *tert*-butyl diastereomers, differing by planar chirality. We propose that the *tert*-butyl locks the seven-membered ring by adopting an equatorial position and favors a

pseudo-chair ring (confirmed by X-ray). Further examples of epoxidation have been achieved with the sulfide (R^1 = *tert*-Bu) of Scheme 11, with ee's up to 94 %.



SCHEME 12

In conclusion, we have introduced a very simple C_2 symmetric thiolane for catalytic enantioselective benzylidenation of aldehydes. Optimization is on the way with a conformationally locked new sulfide, accessible from mannitol. We have explored planar (and central) chiral ferrocenyl sulfides. Despite long reaction times at ambient temperature, we have demonstrated that planar chirality leads to enantiomeric excesses, up to 94%, and evidenced an unexpected case of stereoconvergence. The *trans*/*cis* diastereoselectivity remains a challenge for the future as well as the scope of the reaction, which deserves further extension, and the acceleration of the epoxidation.

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