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Enantioselective [1,2]-Stevens rearrangement of thiosulfonates to construct dithio-substituted quaternary carbon centers†

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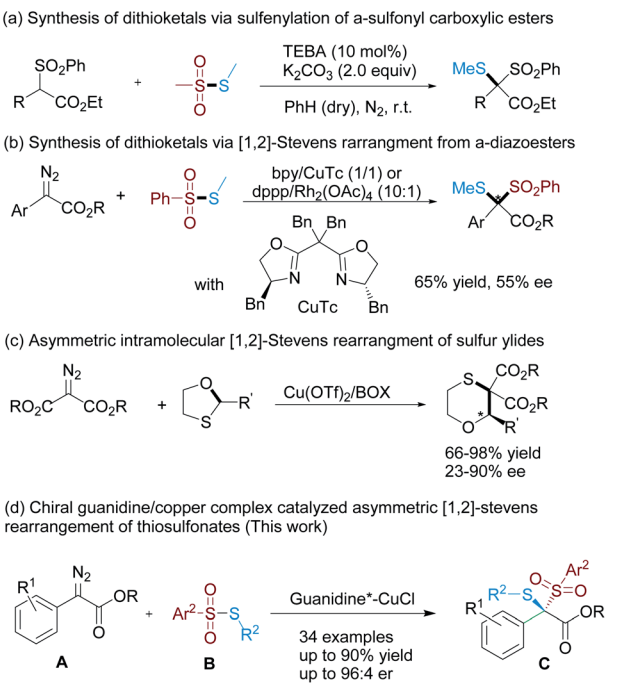
An enantioselective [1,2] Stevens rearrangement was realized by using chiral guanidine and copper(I) complexes. Bis-sulfuration of α-diazocarbonyl compounds was developed through using thiosulfonates as the sulfenylating agent. It was undoubtedly an atom-economic process providing an efficient route to access novel chiral dithioketal derivatives, affording the corresponding products in good yields (up to 90% yield) and enantioselectivities (up to 96 : 4 er). A novel catalytic cycle was proposed to rationalize the reaction process and enantiocontrol.

Introduction

Organosulfur compounds, including thioethers and the oxidized derivatives such as sulfoxides or sulfones, have attracted significant attention owing to their wide occurrence in natural products and biologically active molecules.[1] Furthermore, they could also serve as useful reagents and ligands in organic synthesis.[2] Thiosulfonate is considered the line of defense against cyanide intoxication,[3] and could be used for both sulfenylation and sulfonylation.[4] For example, sulfenylation of α-sulfonyl carboxylic esters with *S*-methyl methanethiosulfonate resulted in dithioketals containing two sulfur substitutions with different oxidation states at the same carbon center[4a] (Scheme 1a). The carbene insertion reaction of α-diazoesters to the S–S bond of thiosulfonates could simultaneously introduce two different sulfur-groups into the stereogenic carbon center in the presence of the bpy/CuTc[4b] or dppp/$Rh_2(OAc)_4$ (ref. 4c) catalyst (Scheme 1b). The reaction occurred *via* a [1,2]-Stevens rearrangement of sulfonium ylide,[5,6] but enantiocontrol remains difficult. Xu's group explored the possibility of an asymmetric version by screening a variety of bisoxazoline ligands, and the highest ee of 55% was obtained.[4b] Tang and co-workers demonstrated an efficient catalytic asymmetric [1,2]-Stevens rearrangement of sulfonium ylide using side-armed bisoxazoline/$Cu(OTf)_2$ as the catalyst (Scheme 1c),[6a] but the stereogenic center lied in an O-based carbon center rather than the carbon of metal carbenoid species.[7]

Sigmatropic rearrangements of ylides represent a powerful set of reactions for the construction of heterocycles and interesting small molecules with functional groups. Different from asymmetric [2,3]-sigmatropic rearrangements and other transformations of onium ylides which have been well studied,[8,9] the enantioselective [1,2]-Stevens rearrangement of onium ylides is limited and challenging.[10] The intricacy mainly lies in the unclear mechanism where diradical pairs, concerted or ion pair propositions have an unpredictable influence on the



Scheme 1 Synthesis of dithioketals from thiosulfonates and asymmetric catalytic [1,2]-Stevens rearrangements of sulfonium ylides.

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† Electronic supplementary information (ESI) available: ^{1}H,$^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR, HPLC spectra (PDF). X-ray crystallographic data for **D1**. CCDC **D1** 2113309. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d2sc00419d

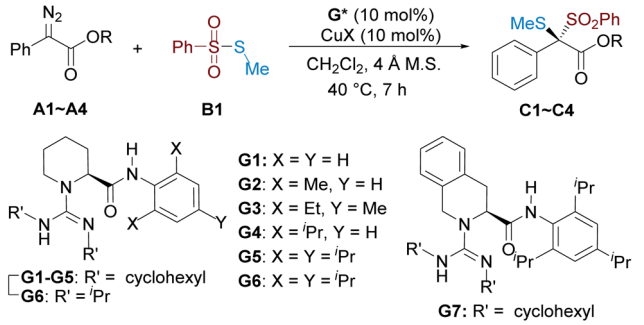
stereoselectivity, regardless of chiral metal-bound or free ylide intermediates.

Recently, our group has realized several asymmetric catalytic rearrangements[9b,d,e] and carbene–insertion reactions[12d,e,13a] based on α-diazo carbonyl compounds. Guanidines as a kind of multi-nitrogen-containing compound have versatile functionality as organocatalysts and ligands for asymmetric catalytic reactions.[11] Previously, we utilized chiral amino acids to construct bifunctional acyclic guanidine-amide compounds for organocatalysis[12a–c] and metal complex catalysis.[13] Their combination with copper(I) salt[13] showed an obvious accelerating effect in carbenoid insertion of terminal alkynes[13a] or HCN,[13e] enabling enantioselective construction of both axial and center chirality. In view of these studies and the characteristics of readily modified subunits of guanidine-amides, we explored their application in [1,2]-Stevens rearrangement between thiosulfonates and α-diazoesters (Scheme 1d). Herein we describe the results of enantioselective synthesis of dithio-substituted carbon centers *via* [1,2]-Stevens rearrangement to simultaneously introduce two C–S bonds with a chiral guanidine/CuCl catalyst.

Results and discussion

Initially, we carried out the reaction with *S*-methyl benzenesulfonothioate **B1** as the dithio-source, and (*R*)-2-pipecolic acid derived guanidine-amide **G5** and CuCl as the catalyst, and the selected results are listed in Table 1. The reaction with α-diazoesters **A1–A4** tethered to different ester groups could be performed with moderate to good yield and enantioselectivity in CH_2Cl_2 at 40 °C (Table 1, entries 1–4). Especially, 4-fluorobenzyl 2-diazo-2-phenylacetate **A4** could get better results with 75% yield and 91.5 : 8.5 er (entry 4). In comparison with the weak transformation in the presence of CuCl salt itself, the addition of guanidine also dramatically increased the reactivity. The use of other metal salts, such as CuBr, CuI, or CuTc, resulted in sluggish reactivity even with the assistance of guanidine **G5** (entries 5–7). The dithio-substituted racemic product **C4** was generated with low yield in the presence of metal salts such as $Rh_2(OAc)_4$, $Pd_2(dba)_3$, or AgOTf (entry 8; see the ESI† for details). Moreover, it was found that the steric hindrance of the substitution on the amide unit of guanidines had a dramatic influence on the enantioselectivity. Only the racemic product **C4** was isolated if aniline-based **G1** was used as the ligand (entry 9). The enantioselectivity gradually enhanced as the steric hindrance of substitutions at the 2,4,6-positions of anilines increased (**G1–G5**, entries 9–12 *vs.* entry 4). Using isopropyl groups instead of cyclohexyl groups at the *N*-substituents of the amidine part of guanidine afforded similar er values but slightly lower yields (**G6** *vs.* **G5**; entry 13 *vs.* entry 4). The amino acid backbone was also critical, for tetrahydroisoquinoline-3-carboxylic acid-based guanidine **G7** decreased the enantioselectivity a lot (entry 14). A screening of other chiral guanidines with variation at different subunits identified that the combination of CuCl and guanidine **G5** was the optimal catalyst for the reaction (see the ESI† for details). Increasing the catalyst loading to 15 mol% led to a slightly higher yield and enantioselectivity (entry 15, 78% yield with 92 : 8 er).

Table 1 Optimization of reaction conditions[a]

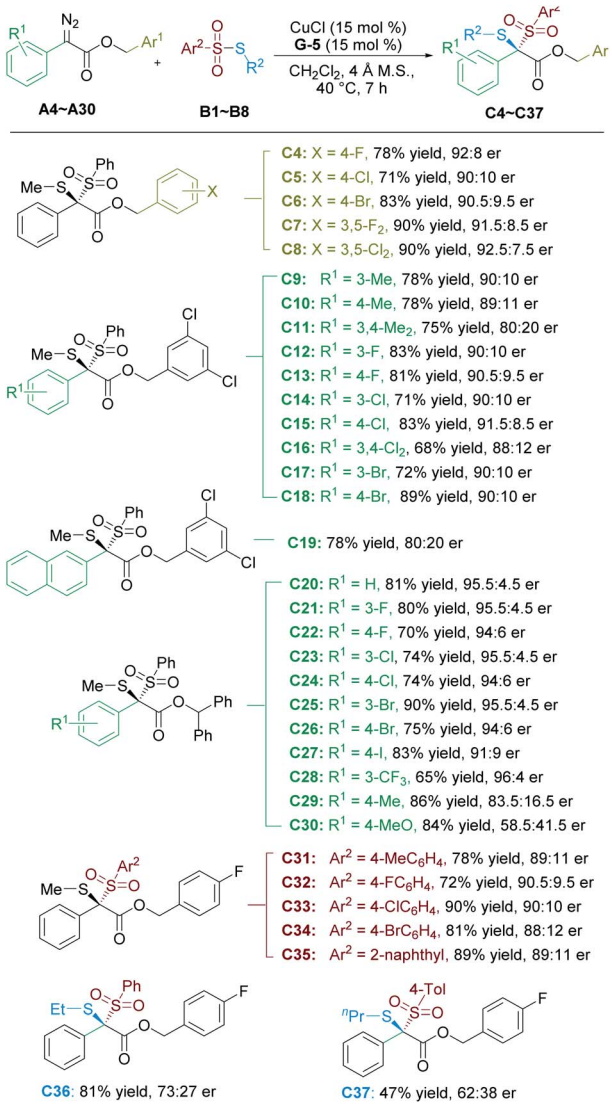


Entry	R; CuX; G*	C/Yield (%)	er
1	Me; CuCl; **G5**	**C1**; 66	77.5 : 22.5
2	Et; CuCl; **G5**	**C2**; 80	80 : 20
3	Bn; CuCl; **G5**	**C3**; 71	90 : 10
4	4-$FC_6H_4CH_2$; CuCl; **G5**	**C4**; 75	91.5 : 8.5
5	4-$FC_6H_4CH_2$; CuBr; **G5**	**C4**; trace	—
6	4-$FC_6H_4CH_2$; CuI; **G5**	**C4**; N.R.	—
7	4-$FC_6H_4CH_2$; CuTc; **G5**	**C4**; trace	—
8	4-$FC_6H_4CH_2$; $Rh_2(OAc)_4$; **G5**	**C4**; 32	50 : 50
9	4-$FC_6H_4CH_2$; CuCl; **G1**	**C4**; 32	50 : 50
10	4-$FC_6H_4CH_2$; CuCl; **G2**	**C4**; 76	76.5 : 23.5
11	4-$FC_6H_4CH_2$; CuCl; **G3**	**C4**; 81	87 : 13
12	4-$FC_6H_4CH_2$; CuCl; **G4**	**C4**; 52	86 : 14
13	4-$FC_6H_4CH_2$; CuCl; **G6**	**C4**; 63	90 : 10
14	4-$FC_6H_4CH_2$; CuCl; **G7**	**C4**; 78	75 : 25
15[b]	4-$FC_6H_4CH_2$; CuCl; **G5**	**C4**; 78	92 : 8

[a] Unless otherwise noted, all reactions were carried out with **A** (0.20 mmol), **B1** (0.10 mmol), CuX/guanidine (1 : 1, 10 mol%), and 4 Å MS (60 mg) in CH_2Cl_2 (1.0 mL) at 40 °C for 7 h. Isolated yields. The er was determined by HPLC analysis on a chiral stationary phase. [b] CuCl/**G5** (1 : 1, 15 mol%). N.R. = no reaction.

With the optimized reaction conditions in hand, the substrate scope was then explored (Table 2). The established optimal reaction conditions exhibited similar tolerance to phenyl substituted α-diazo compounds with substituted benzyl esters (**C5–C8**), or more sterically hindered benzhydryl ester (**C20**). However, the electronic nature of substitution at the *ortho*-, *meta*-, or *para*-positions of the aromatic rings of α-diazoesters had a dramatic influence on the enantioselectivity. Products with electron-deficient aryl groups (**C12–C18**, and **C20–C28**) were universally generated in moderate to good yields (65–90%) with higher enantioselectivities (90 : 10–96 : 4 er), nevertheless, the products containing electron-donating substituents (**C9–C11**, **C29** and **C30**) were accessible with high yields (75–86%) but with decreased enantioselectivities (only 58.5 : 41.5 er for 4-MeO substituted **C30**). The electronic effect of substitutions on the enantioselectivity was uniform no matter what the ester group, implying that the stability of the sulfonium ylide intermediate was significant to the enantiocontrol. Additionally, 2-naphthyl substituted dithioketal **C19** was obtained with a decreased er value due to the steric

Table 2 Substrate scope for thiosulfonates and α-diazoestersa[a]

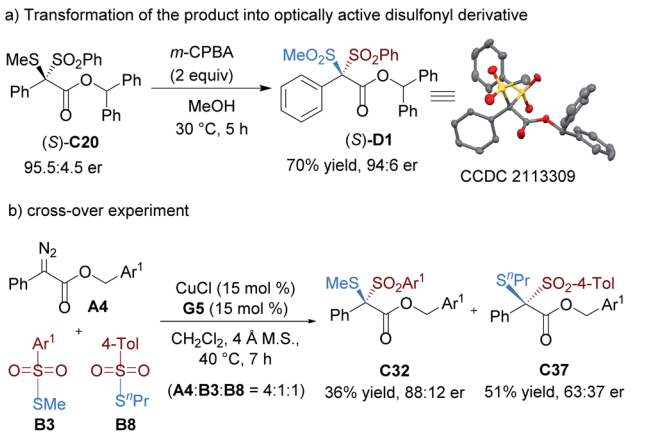


[a] Unless otherwise noted, all reactions were performed with **A** (0.20 mmol), **B** (0.10 mmol), **G5**/CuCl (1 : 1, 15 mol%) in CH_2Cl_2 (0.1 mL) at 40 °C. Isolated yield. The er was determined by HPLC analysis on a chiral stationary phase.

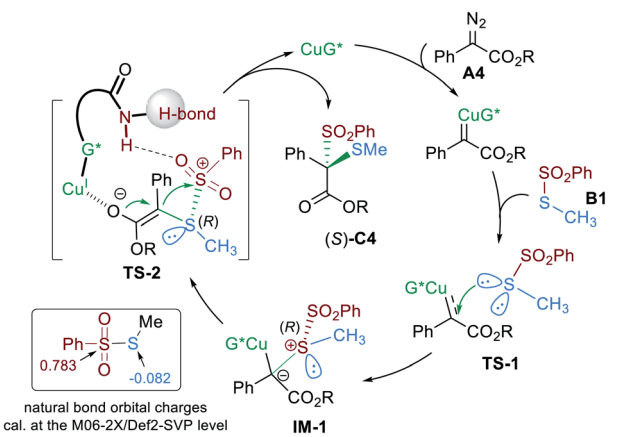
hindrance. Unfortunately, the reaction of ethyl 2-diazopropanoate delivered the desired product with 42% yield as a racemate, and other alkyl α-diazoesters resulted in poor reactivity under the current conditions (see the ESI† for details).

Subsequently, we turned our attention to the scope of thiosulfonates. Not surprisingly, benzenesulfonyl groups with substitutions, such as 4-Me, 4-F, 4-Cl, and 4-Br, were tolerated well in the reaction to yield the corresponding products smoothly (**C31–C34**, 72–90% yields, and 88 : 12–90.5 : 9.5 er). The product **C35** deriving from 2-naphthyl thiosulfonate could also be generated in 89% yield with 89 : 11 er. However, *S*-ethyl and *S*-propyl-substituted thiosulfonates delivered the related products **C36** and **C37** with unsatisfied results, highlighting the steric bias of sulfur substitution on enantioselectivity.

The oxidation of the dithioketal derivative **C20** led to the construction of the derivative **D1** (Scheme 2) with a disulfonyl substituted quaternary center, whose absolute configuration was determined to be *S* based on X-ray single crystal analysis.[14] Accordingly, the absolute configuration of the product **C20** was assigned as the same. Next, we carried out a cross-over experiment by subjecting α-diazoester **A4** and two kinds of thiosulfonate to the same catalytic system. It was found that two direct rearrangement products were detected, and there was no scrambling of the substituents in dithioketals. Primary theoretical calculations about the natural bond orbital charges of thiosulfonate **B1** showed that the sulfonyl center has a strong positive charge while the other thio-atom has a negative charge (Scheme 3), indicating that the homolytic cleavage of the S–S bond to generate a diradical intermediate is difficult. We proposed that the reaction is likely to proceed in a concerted ionic pathway. The above results are in consist with the electronic effect of aryl substituents of diazoesters on the reactivity. The electron-donating aryl group is advantageous for the final rearrangement to increase the yield but disadvantageous for the initial ylide formation step, which might determine the enantioselectivity.



Scheme 2 Transformation of the products and the control experiment.



Scheme 3 Possible asymmetric catalytic process.

In connection with the coordination ability of the guanidine functional group, we propose that it might act as a bifunctional ligand to form a chiral copper complex catalyst. As shown in Scheme 3, upon the addition of α-diazoester **A**, chiral copper carbenoid species are generated that undergo nucleophilic attack by thiosulfonate **B**. Different from the oxonium ylides, there is a S-based central chirality in the sulfonium ylide intermediate, generating from the discrimination of the two lone pair electrons of thiosulfonate which is extremely challenging, similar to asymmetric Sommelet–Houser rearrangement and 2,3-Stevens rearrangements.[9b,d] Moreover, if the reaction follows a stepwise 1,2-sigmatropic rearrangement or free ylide intermediate, the stereo-chemistry at sulfur disappears or racemizes, leading to a new, difficult to reconstruct stereogenic center at carbon.

We rationalize that the steric hindrance between the sulfonate group of thiosulfonate **B** and ester group of α-diazoester **A** would lead to selective attack of sulfur *via* **TS-1** to set up the chiral sulfonium ylide **IM-1**. Meanwhile, the hydrogen-bond between the amide of **G5** and sulfonate unit might also direct the approach of thiosulfonate. Next, in view of the instability of the SO_2Ph cation intermediate and the cross-over experiment, a stepwise process is ruled out. Thus, a concerted rearrangement occurs with the shift of sulfonate from the *Si*-face of the enolate *via* **TS-2** during which the chiral copper-bond enolate might prevent racemization of the sulfur center and assist the approach of the sulfonyl from the rear to construct the second C–S bond. Finally, the desired (*S*)-dithioketal derivative **C** is generated to recycle the chiral copper catalyst.

Conclusions

In summary, we have reported an efficient asymmetric catalytic [1,2]-Stevens rearrangement by using a type of chiral guanidine-copper(I) complex. The catalytic system enabled the direct introduction of two C–S bonds in an enantioselective manner, yielding various chiral dithioketal derivatives in good yield and enantioselectivity, shedding a shaft of light on the asymmetric 1,2-sigmatropic rearrangement. More research about the [1,2]-Stevens rearrangement and the application of the chiral guanidine/copper(I) catalytic system are undergoing.

Data availability

Further details of experimental procedure, ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR, HPLC spectra, X-ray crystallographic data for **D1** are available in the ESI.†

Author contributions

L. F. H. performed the experiments. J. Z. L. repeated data. X. M. F. and X. H. L. supervised the project. X. M. F., X. H. L., Y. Y. Z. and L. F. H. co-wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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14 CCDC 2113309 (**D1**) contains the supplementary crystallographic data for this paper.†