

Enantioselective Electrophilic Trifluoromethylthiolation of β -Ketoesters: A Case of Reactivity and Selectivity Bias for Organocatalysis**

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The incorporation of an SCF_3 group into small molecules is of great interest to the pharmaceutical and agrochemical industries,^[1] because the high lipophilicity and high electron-withdrawing character of the SCF_3 group may have beneficial effects on the pharmacokinetics of drug molecules.^[2] Thus, the development of efficient methods for the introduction of a SCF_3 group into organic compounds has recently become a subject of intense study^[3] and tremendous progress has been achieved in the transition-metal-catalyzed trifluoromethylthiolation of aryl, alkenyl, or alkynyl substrates under mild conditions.^[4] In particular, there has been a growing interest in the stereoselective introduction of SCF_3 groups to generate chiral centers.^[5] While there is a growing number of methods for the catalytic enantioselective trifluoromethylation,^[6] to the best of our knowledge, the analogous catalytic asymmetric direct trifluoromethylthiolation has never been reported.

We recently reported the preparation of an electrophilic trifluoromethylthiolated hypervalent iodine reagent (**1**), which is stable in the most common solvents even at 80 °C.^[7] This reagent is remarkably reactive and allows the trifluoromethylthiolation of a variety of nucleophiles, such as aryl or vinyl boronic acids, alkynes, aldehydes, and amides, under mild conditions. More specifically, reactions of β -ketoesters with compound **1** gave the corresponding trifluoromethylthiolated products in excellent yields when *N,N*-dimethylaminopyridine (DMAP) was used as the base. We wondered if it is possible to influence the stereoselectivity of the reaction by employing a chiral organic Lewis base. Herein, we report the asymmetric trifluoromethylthiolation reaction of β -ketoesters with good to excellent enantioselectivity in the presence of a quinine or quinine-based phase-transfer catalyst.

We initially chose the reaction of indanone-derived β -ketoester **2a–c** with reagent **1** to optimize the reaction conditions. We used quinine as the base because of the ability of cinchona alkaloids to function as effective organic chiral Lewis bases and nucleophilic catalysts.^[8,9] The reaction of β -ketoester **2a** with reagent **1** in THF was complete after 12 h at room temperature in the presence of 20 mol% of quinine, affording the trifluoromethylthiolated product in 90% yield with 42% *ee* (Table 1, entry 1). The reaction proceeded much more slowly for more hindered β -ketoesters **2b** or **2c** (Table 1, entries 2 and 3). However, to our delight, the enantioselectivity of the trifluoromethylthiolation increased significantly to 90% *ee* when β -ketoester **2c** was employed (Table 1, entry 3). The reactions of β -ketoester **2c** with reagent **1** in other ethers, such as diethyl ether, dioxane, DME, or diglyme, occurred with similar enantioselectivity, but the reaction in diethyl ether was faster than those in other solvents (Table 1, entries 4–7). Reactions in more polar solvents, such as CH_3CN and acetone, or a less polar solvent, such as CH_2Cl_2 , generated the corresponding products with slightly lower enantioselectivity (Table 1, entries 8–10). Interestingly, when CHCl_3 or toluene were used as the solvent, the enantioselectivity of the reaction was increased to 92% *ee* (Table 1, entries 11 and 12). As reactions in toluene were faster than those in CHCl_3 , we further optimized the reaction conditions using toluene as the solvent. We found that reaction in toluene was complete after 36 h at 40 °C, giving the desired product in 90% yield with 92% *ee* (Table 1, entry 13). Other cinchona alkaloids, such as cinchonidine (**3b**), hydroquinine (**3c**), quinidine (**3d**), cinchonine (**3e**), and hydroquinidine (**3f**), were then tested under the optimized conditions, but the reactions in the presence of these bases generally occurred with lower enantioselectivity (Table 1, entries 14–18). The hydroxy group of quinine is important for the high reactivity of the catalyst. The use of ester derivative **3g** or thiourea derivative **3h** as the catalyst led to the complete shutdown of the reaction (Table 1, entries 19 and 20).

The optimized reaction conditions summarized in entry 13 in Table 1 were used to study the scope of the quinine-catalyzed asymmetric trifluoromethylthiolation of a variety of β -ketoesters (Table 2). In general, indanone-derived β -ketoesters generated the corresponding products in high yields with excellent enantioselectivities (86–94% *ee*), regardless of the nature and position of the substituents on the β -ketoester derivatives (Table 2, **4a–k**). Reactions of substrates with electron-withdrawing groups occurred with similar enantioselectivity to those of substrates with electron-donating groups (Table 2, **4c–e** vs. **4g–k**). The size of the ester group has a huge influence on the enantioselectivity of the

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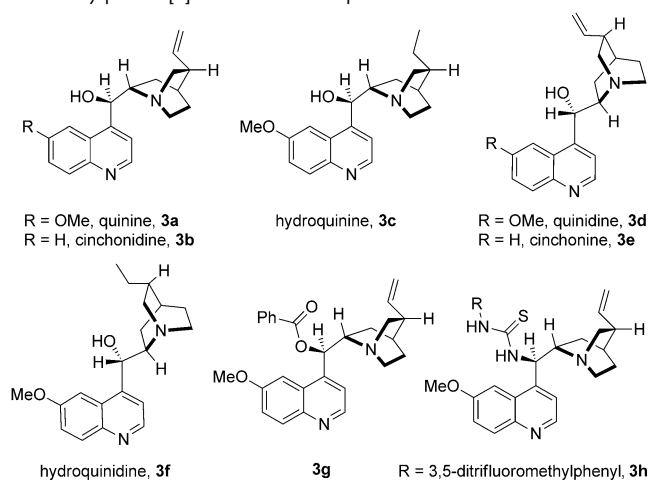
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Table 1: Optimization of the catalytic asymmetric trifluoromethylthiolation of β -ketoesters.^[a]

Entry	2	Cat.	Solvent	T [°C]	t [h]	Yield [%] ^[b]	ee [%] ^[c]
1	2a	3a	THF	RT	12	90	42 (R)
2	2b	3a	THF	RT	12	57	49 (R)
3	2c	3a	THF	RT	24	44	90 (R)
4	2c	3a	Et ₂ O	RT	24	72	90 (R)
5	2c	3a	dioxane	RT	24	41	91 (R)
6	2c	3a	DME	RT	24	59	91 (R)
7	2c	3a	diglyme	RT	24	52	91 (R)
8	2c	3a	CH ₃ CN	RT	24	47	85 (R)
9	2c	3a	acetone	RT	24	36	81 (R)
10	2c	3a	CH ₂ Cl ₂	RT	24	56	74 (R)
11	2c	3a	CHCl ₃	RT	24	51	92 (R)
12	2c	3a	toluene	RT	24	66	92 (R)
13	2c	3a	toluene	40	36	91 (90 ^[d])	92 (R)
14	2c	3b	toluene	40	36	76	72 (R)
15	2c	3c	toluene	40	36	98	86 (R)
16	2c	3d	toluene	40	36	83	88 (S)
17	2c	3e	toluene	40	36	55	55 (S)
18	2c	3f	toluene	40	36	88	82 (S)
19	2c	3g	toluene	40	36	< 5	-
20	2c	3h	toluene	40	36	< 5	-

[a] Reaction conditions: β -ketoester (0.1 mmol), reagent **1** (0.12 mmol), catalyst (20 mol %). **2a**: R = Me; **2b**: R = Et; **2c**: R = Ad. [b] Yields were determined by ¹⁹F NMR spectroscopy in the presence of an internal standard. [c] The ee values were determined by HPLC analysis on a chiral stationary phase. [d] Yield of isolated product.



reaction. For example, the 2-methyl-2-adamantyl ester of indanone was converted to the trifluoromethylthiolated product in lower enantioselectivity than the adamantyl ester of indanone (87 % ee vs. 92 % ee; Table 2, **4a** and **4b**). Finally, the cyclopentanone-derived β -ketoester was successfully converted to the corresponding product in 95 % yield with 94 % ee (**4i**). Under the optimized conditions, reactions of acyclic β -ketoesters occurred with less than 2 % conversion (see the Supporting Information for details).

The absolute configuration (*R*) of the stereogenic center in compound **4** was determined by X-ray crystallographic

Table 2: Scope for quinine-catalyzed asymmetric trifluoromethylthiolation of β -ketoesters.^[a,b]

2	1	4	
			4a , 90%, 92% ee
			4b , 92%, 87% ee ^[c]
			4c , 97%, 86% ee
			4d , 95%, 94% ee
			4e , 91%, 94% ee
			4f , 87%, 92% ee
			4g , 83%, 93% ee
			4h , 81%, 92% ee
			4i , 82%, 89% ee
			4j , 84%, 92% ee
			4k , 90%, 93% ee
			4l , 95%, 94% ee ^[d]

[a] Reaction conditions: β -ketoester (0.2 mmol), reagent **1** (0.24 mmol), quinine (20 mol %) in toluene (1.0 mL) at 40 °C for 36 h. [b] Yields of isolated products and ee values were determined by HPLC analysis on a chiral stationary phase. [c] R = 2-methyl-2-adamantyl. [d] The ee value was determined by HPLC analysis of the 2,4-dinitrophenylhydrazine derivative on a chiral stationary phase.

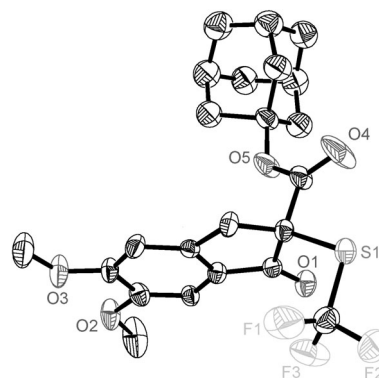


Figure 1. ORTEP view of trifluoromethylthiolated compound **4e**. Thermal ellipsoids are set at 50% probability.

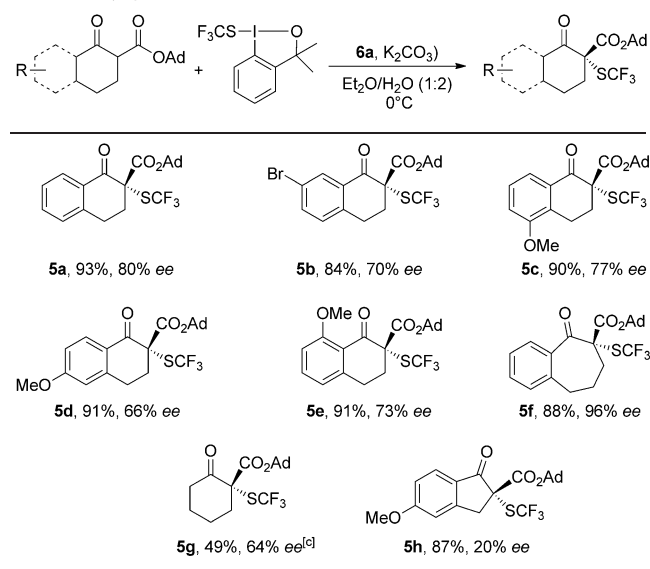
analysis of a single crystal of **4e** (Figure 1).^[10] The configurations of the other products were assigned on the assumption of a uniform mechanistic pathway.

Interestingly, when more-enolizable tetralone- or 1-benzosuberone-derived β -ketoesters (with six- or seven-membered rings, respectively) were subjected to the optimized reaction conditions, less than 5 % of the β -ketoesters were converted to the corresponding trifluoromethylthiolated compounds after 36 h at 40 °C. We next turned our attention to the reactions of these substrates mediated by cinchona alkaloid based chiral phase-transfer catalysts (PTC) to study the reactivity and selectivity. After a quick screening of the

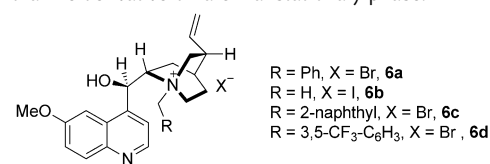
conditions, we discovered that the reaction of the tetralone-derived β -ketoester with reagent **1** using the quinine-derived PTC **6a** resulted in full conversion after 36 h at 0 °C to give the corresponding trifluoromethylthiolated compound in 91 % yield with 73 % *ee*. Several other commonly used PTCs (**6b–d**) were also tested under these conditions, but generated the products with lower enantioselectivity (see Table S1 in the Supporting Information).

With these optimized reaction conditions in hand, we explored the generality of the protocol for the trifluoromethylthiolation of tetralone- and 1-benzosuberone-derived β -ketoesters (Table 3). Tetralone-derived adamantyl β -keto-

Table 3: Scope of asymmetric trifluoromethylthiolation of β -ketoesters mediated by quinine-derived PTCs.^[a,b]



[a] Reaction conditions: β -ketoester (0.2 mmol), reagent **1** (0.24 mmol), **6a** (20 mol %), and K_2CO_3 (0.4 mmol) in Et_2O (1.0 mL) and water (2.0 mL) at 0 °C for 36 h. [b] Yields of isolated products and *ee* values were determined by HPLC analysis on a chiral stationary phase. [c] The *ee* value was determined by HPLC analysis of the 2,4-dinitrophenylhydrazine derivative on a chiral stationary phase.

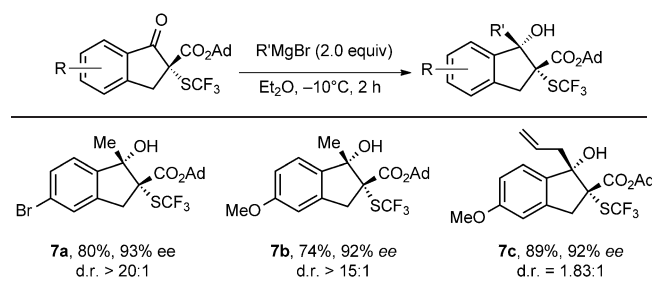


esters generated the corresponding trifluoromethylthiolated products with moderate to good enantioselectivities (Table 3, **5a–e**), while the 1-benzosuberone-derived adamantyl β -ketoester generated the product with excellent enantioselectivity (Table 3, **5f**). The absolute configuration (*R*) of the stereogenic center in compound **5f** was determined by X-ray crystallographic analysis of a single crystal of **5f** (see the Supporting Information for details).^[10] The cyclohexanone-derived adamantyl ester formed the corresponding product with moderate enantioselectivity (Table 3, **5g**). Interestingly, the reaction of the indanone-derived β -ketoester mediated by PTC **6a** occurred with low enantioselectivity (Table 3, **5h**), in

contrast to the high enantioselectivity obtained when quinine was used as catalyst. Under the optimized conditions, the reactions of acyclic β -ketoesters were slow and less than 10 % of the starting materials were converted.

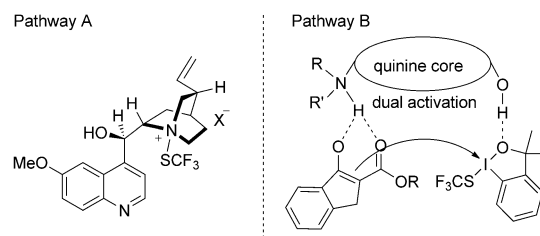
In order to demonstrate the synthetic utility of this catalytic approach, we further transformed the trifluoromethylthiolated products. Adducts **4d** and **4h** were treated with methyl or allyl Grignard reagents in Et_2O at –10 °C, giving the α -SCF₃-substituted β -hydroxyesters **7a–c** in high yields and good to excellent diastereoselectivities (Table 4). The

Table 4: Transformations of trifluoromethylthiolated products.



relative configuration of adduct **7b** was determined by NOE experiments (see the Supporting Information). The configuration might arise from the formation of a Mg^{2+} chelate with the carbonyl groups of the keto and ester functionalities, which is attacked by the nucleophile from the less hindered face.

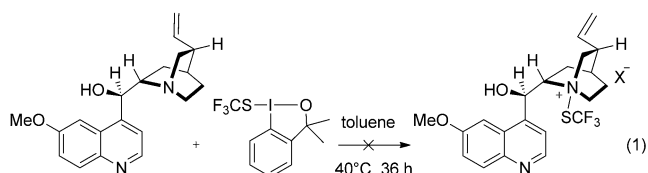
Mechanistically, the quinine-catalyzed trifluoromethylthiolation of β -ketoesters might proceed through two different pathways (Scheme 1). In pathway A, quinine first reacts



Scheme 1. Two possible pathways for quinine-catalyzed asymmetric trifluoromethylthiolation.

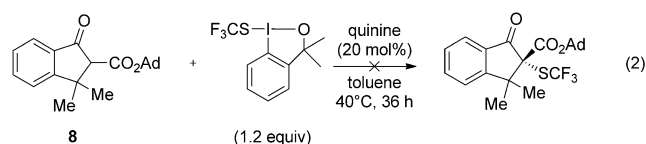
with reagent **1** to form an electrophilic SCF₃-substituted quarternary ammonium ion, which is then attacked by the enolized β -ketoester. Alternatively, quinine acts as a base to deprotonate the β -ketoester, thus forming a hydrogen-bonded intermediate that attacks reagent **1** to form the product (pathway B).

To probe whether the electrophilic SCF₃-substituted quarternary ammonium ion was formed in the reaction, we conducted a stoichiometric reaction of quinine with reagent **1** in toluene at 40 °C and monitored the reaction by ¹⁹F NMR spectroscopy [Eq. (1)]. No newly formed species was observed even after 36 h. This result clearly rules out the



possibility that the quinine-catalyzed asymmetric trifluoromethylthiolation proceeds through pathway A.

As the hydroxy group of quinine is very important for the reactivity of catalyst (see Table 1, entry 19), we propose that the reaction proceeds through dual activation that involves the simultaneous activation of the ketoester and reagent **1** through the formation of hydrogen bonds with quinine (Scheme 1). The activated species is sterically congested and thus sensitive to the reaction components. The indanone-derived β -ketoester forms a planar enolate, which fits well into the model, giving the corresponding product in excellent yield and enantioselectivity, while the tetralone- or 1-benzosuberone-derived β -ketoesters form nonplanar enolates that could not generate the dual-activated intermediate. Consequently, the reactions of these substrates resulted in low conversion. In agreement with this assumption, the reaction of sterically hindered dimethyl-substituted β -ketoester **8** with reagent **1** occurred with less than 5% conversion during 36 h at 40°C in toluene in the presence of 20 mol% of quinine [Eq. (2)]. However, the detailed mechanisms of the quinine-



catalyzed trifluoromethylthiolation and the asymmetric trifluoromethylthiolation mediated by a phase-transfer catalyst remain elusive at this stage.

In summary, we have developed the highly enantioselective trifluoromethylthiolation of β -ketoesters catalyzed by a chiral Lewis base or a phase-transfer catalyst. The reaction employs commercially available and fully recyclable catalysts and involves a simple experimental procedure. In addition, the reaction constitutes a practical and broadly applicable approach toward chiral building blocks with quaternary stereocenters that bear an SCF_3 group, and might lead to some drug candidates with high bioactivity. Further development of relevant catalytic systems and the elucidation of the mechanism of this reaction are in progress in our laboratory and will be reported in due course.^[11]

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- [10] CCDC 952517 (**4e**) and 952518 (**5f**) contain 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.
- [11] This Communication is published back-to-back with the following study: T. Bootwicha, X. Liu, R. Pluta, I. Atodiresei, M. Rueping, *Angew. Chem.* **2013**, *125*, 13093–13097; *Angew. Chem. Int. Ed.* **2013**, *52*, 12856–12859.