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# Fe(OTf)<sub>2</sub>-Catalyzed *Thia*-Michael Addition Reaction: A Green Synthetic Approach to β-Thioethers

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**Abstract:** A convenient Fe(OTf)<sub>2</sub>-catalyzed Michael addition reaction of thiols to  $\alpha$ , $\beta$ -unsaturated carbonyl compounds was developed. The use of a simple procedure (EtOH, room temperature, air atmosphere) allowed to set up effective green catalytic conditions for the C–S bond formation. The scope of the reaction was demonstrated using various substituted thiols and original Michael acceptors. The corresponding  $\beta$ -thioethers were obtained in good to excellent yields (up to 99%). Also, the derivatization into the one-pot *thia*-Michael addition/oxidation reaction of 3-(3-(phenylthio)butanoyI)oxazolidin-2-one using H<sub>2</sub>O<sub>2</sub> has proven to be efficient.

#### Introduction

Synthetic strategies towards C-S bond formation is gaining widespread interest, owing to the biological activity of sulfur containing molecules.<sup>[1]</sup> Among them, the nucleophilic addition reaction of thiols to α,β-unsaturated carbonyl compounds remains an important and widely documented transformation.<sup>[2]</sup> The incorporation of a sulfur group has been demonstrated using heterogeneous catalysis,<sup>[3]</sup> odorless and cheap sulfur salts,<sup>[4]</sup> and miscellaneous catalysts, *i.e.*, I<sub>2</sub>, simple amines, or trichlorotriazine.<sup>[5]</sup> Previous work in homogeneous catalysis has been disclosed using various Lewis acids, derived from  $V^{IV,\,{\sc [6]}}$  $In^{III,[7]} Yb^{III,[8]} Re^{v,[9]} La^{III,[10]} Ni^{II,[11]}, Cu^{II,[12]} Zn^{II,[13]} Bi^{III,[14]} and Fe^{III}$ salts,[15] as effective catalysts for the thia-Michael addition reaction. However, most of these methods are suitable for  $\alpha$ , $\beta$ unsaturated ketones, esters and aldehydes, while  $\alpha$ , $\beta$ unsaturated oxazolidin-2-ones are reported in very few examples (Scheme 1a). With the progress made in metal-catalyzed thia-Michael addition reaction, there is still room for the development of greener synthetic approaches. The adoption of green chemistry within drug manufacturing has direct benefits on economical, technological, and environmental issues.<sup>[16]</sup> The interest behind using  ${\rm Fe}^{\rm I\!I}/{\rm Fe}^{\rm I\!I}$  salts to replace noble transition metals in homogeneous catalysis has recently emerged to provide efficient alternatives with high availability, low toxicity, low cost, and environmental-friendliness.<sup>[17]</sup> In order to avoid the use of chlorinated solvents, a few conjugate 1,4-addition reactions of thiols have been developed in recyclable ionic liquids,[18] and in water.<sup>[19]</sup> Besides low impacts on health and environment, a solvent should fulfil low energy issues related to its manufacture

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and disposal.<sup>[20]</sup> Ionic liquids have severe drawbacks, e.g., very energy consuming syntheses.<sup>[21]</sup> Water, even though highly attractive in organic synthesis,<sup>[22]</sup> is associated with solubility problems. Consequently, it is clearly essential to broaden the scope of green organic solvents applicable for this transformation.

Scheme 1. Lewis acid-catalyzed *thia*-Michael addition reaction–Background a) Lewis acid catalysis: Michael acceptor types



Previously, iron catalysts have been studied in our laboratory for various synthetic transformations, *i.e.*, the asymmetric *thia*-Michael addition and other reactions.<sup>[23]</sup> Hence, a green and simple Michael addition reaction of thiols to  $\alpha$ , $\beta$ -unsaturated systems using Fe(OTf)<sub>2</sub> as an environmentally benign catalyst is disclosed herein (Scheme 1b). Importantly, the scope of the reaction was broadened to  $\alpha$ , $\beta$ -unsaturated ketones and amides, including the choice of original substrates. In addition, the one-pot two-step oxidation of the  $\beta$ -thioethers is demonstrated.

#### **Results and Discussion**

The Michael addition reaction of thiophenol **2a** to (*E*)-3crotonoyloxazolidin-2-one **1a**, catalyzed by  $Fe(CIO_4)_3 \cdot 6H_2O$ , was firstly selected as the model reaction for the screening of green solvents (Table 1). Only traces of the desired product were obtained when EtOAc and H<sub>2</sub>O were used as solvents (entries 1 and 2). CO<sub>2</sub>-derived solvents, such as propylene carbonate (PC) and dimethyl carbonate (DMC), are highly biodegradable, low in toxicity, and synthesized through green industrial processes.<sup>[24]</sup> Unfortunately, they afforded **3a** with low to moderate conversions

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Table 1. Fe<sup>III</sup>-catalyzed thia-Michael addition reaction: green solvent optimization<sup>[a]</sup>

	`O <sup>+</sup> PhSH ∫ 1.1 equiv. <b>2a</b>	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O (5 mol-%)	SPh 0 0 ↓ ↓ ↓
		solvent, air 25 °C, 3 h	3a
Entry	Solvent	Conversion	<sup>[b]</sup> (%)
1	EtOAc	4	
2	H <sub>2</sub> O	8	
3	PC	5	
4	DMC	41	
5	Et <sub>2</sub> O	10	
6	CPME	14	
7	THF	32	
8	2-Me-THF	61	
9	EtOH	72	

[a] Conditions: Fe(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (5 mol-%), **1a** (0.250 mmol), **2a** (0.275 mmol), solvent (0.25 mL). [b] Calculated by <sup>1</sup>H NMR.

(entries 3 and 4). Coordinating ether solvents, such as Et<sub>2</sub>O and CPME, led to low conversions (entries 5 and 6). 2-Me-THF, known as a biomass-originated solvent,<sup>[25]</sup> afforded **3a** with an increased conversion, as compared with THF (entry 8 *vs.* 7). EtOH afforded an optimum 72% conversion (entry 9), and, thereby, this cheap and environmentally benign solvent was chosen for further studies.

The optimization process was further extended to various Fe<sup>III</sup> (Table 2, entries 1 and 2) and Fe<sup>II</sup> salts (entries 3-6). Other Fe<sup>III</sup> salts were studied, i.e., FeCl3 and Fe(OTf)3, but led to lower conversions than their CIO4<sup>-</sup> counterion analogue (entries 1 and 2 vs. Table 1, entry 9). FeCl<sub>2</sub> afforded 3a with a high conversion (entry 3). Then, cationic Fe<sup>II</sup> salts, such as Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, allowed conversions up to 92% (entries 4 and 5). The formation of β-thioether 3a was complete in only 3 hours when Fe(OTf)<sub>2</sub> was used and a 94% yield was afforded (entry 6). Furthermore, various green Lewis acids were tested to compare their catalytic activity (entries 7-10). Ca(OTf)<sub>2</sub> showed a promising reactivity with a high conversion in the desired product (entry 7). Catalysts derived from other main metal salts allowed low to moderate conversions of 3a (entries 8 and 9). Bill-catalyzed 1,4-conjugate addition reaction have been scarcely described;<sup>[14,</sup> <sup>26]</sup> in this case, only 39% conversion was obtained (entry 10). Virtually no conversion was observed when the Michael addition reaction of thiophenol 2a was run in the absence of a catalyst (entry 11). This green catalytic system using Fe(OTf)<sub>2</sub>/EtOH was efficient, and, consequently, was chosen as the optimized conditions.

The scope of the reaction was next investigated using various  $\alpha$ , $\beta$ -unsaturated Michael acceptors (Scheme 2). In terms of reactivity, the electronic properties of the R<sup>1</sup> substituent were compared to the model substrate (1a). Besides solubility issues related to substrates 1b and 1c, the addition of thiol 2a remained more

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Table 2. Metal-catalyzed thia-Michael addition reaction: Lewis acid optimization  $^{\left[ a\right] }$ 

	0 0 + PhSH 1.1 equiv. 1a 2a	MX <sub>n</sub> (5 mol-%) EtOH, air 25 °C, 3 h 3a
Entry	MX <sub>n</sub>	Conversion <sup>[b]</sup> (%)
1	FeCl <sub>3</sub>	10
2	Fe(OTf) <sub>3</sub>	26
3	FeCl <sub>2</sub>	88
4	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	90
5	Fe(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	92
6	Fe(OTf) <sub>2</sub>	100 (94) <sup>[c]</sup>
7	Ca(OTf) <sub>2</sub>	94
8	Ga(OTf) <sub>3</sub>	58
9	Al(OTf) <sub>3</sub>	17
10	Bi(OTf) <sub>3</sub> ·4H <sub>2</sub> O	39
11	None	5

[a] Conditions: MX<sup>*n*</sup> (5 mol-%), **1a** (0.250 mmol), **2a** (0.275 mmol), EtOH (0.25 mL). [b] Calculated by <sup>1</sup>H NMR. [c] Isolated yield of **3a**.

challenging when the electron-properties of R<sup>1</sup> were changed (**3b** and **3c** *vs.* **3a**). However, the electron-donating group at the  $\alpha$ -position (R<sup>2</sup> = Me) also led to poor solubility and reactivity of the substrate (**3d**). Although  $\beta$ -thioethers **3e** and **3f** were obtained in high yields, an extended reaction time was required for **3f** (60 h *vs.* 15 h). The absence of a dicarbonyl chelating system with Fe<sup>II</sup> decreased the reactivity of  $\alpha$ , $\beta$ -unsaturated amide **1g**, and due to incomplete conversion, a modest 51% yield of  $\beta$ -thioether **3g** was afforded.  $\alpha$ , $\beta$ -Unsaturated ketone derivatives, such as pyridyl, pyridyl *N*-oxide, and phenyl as R<sup>3</sup> substituents, allowed a comparison of the differences in the chelation with Fe<sup>II</sup>. Shorter reaction times and higher yields in the corresponding  $\beta$ -thioethers were obtained (**3h**–**3k** *vs.* **3b**). It is noteworthy to mention that no reaction occurred when ester **1I** was used in the optimized conditions (0% of **3I**, recovered starting material).

Since the activation of the dicarbonyl core of (*E*)-3crotonoyloxazolidin-2-one **1a** by  $Fe(OTf)_2$  would provide a more reactive Michael acceptor, the nucleophilic character of the thiol was examined; hence, aromatic, heterocyclic, and aliphatic thiols were used (Scheme 3). Various thiophenols, such as *para*- and *ortho*-substituted ones, afforded the desired products in high yields, independently of the electronic nature of the substituent (**4b**-**4f**). Benzylthiols **2g**-**k**, comprising electron-donating and electron-withdrawing substituents, afforded the corresponding  $\beta$ thioethers from moderate to high yields (**4g**-**4k**). The difference in reaction times provided a clear evidence that a thiol linked to the aromatic ring led to better nucleophilic ability and reactivity of the S-atom. The developed catalytic method tolerated heterocyclic thiols, and high yields were obtained for both the 2mercaptopyridyl and furfuryl thiols (**4I** and **4m**). Extended reaction

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Scheme 2. Fe(OTf)\_2-catalyzed conjugate addition reaction of thiophenol to  $\alpha,\beta$ -unsaturated carbonyl compounds^{[a]}



[a] Conditions:  $Fe(OTf)_2$  (5 mol-%), **1a–I** (0.250 mmol), **2a** (0.275 mmol), EtOH (0.25 mL). [b] 2 equiv. of thiol **2a** were used. [c] 2 equiv. of thiol **2a** and 0.5 mL of EtOH were used.

times were needed to complete the 1,4-addition reaction of aliphatic thiols, but moderate to good yields were afforded (**4n** and **4o**). A stoichiometric amount of thiol was no longer suitable when less reactive thiols **2g–o** were used, and up to 5 equivalents of thiol were required in order to form  $\beta$ -thioethers **4g–o** in reasonable reaction times. Nevertheless, the excess of thiol was easily separated in the purification process.

Comparison with literature precedent, together with a control experiment, was performed to gain insights into the reaction mechanism (Scheme 4). As explained from previous studies on the thia-Michael addition reaction.<sup>[23b]</sup> DFT calculations supported the idea of a hepta-coordinated Fe<sup>II</sup> chelated by the two carbonyls of the  $\alpha,\beta$ -unsaturated oxazolidin-2-one. In this work, the hypothesized model of a transition state, in which 1a chelated  $Fe(OTf)_2$  to form a stable 6-membered cycle complex (A), was postulated in agreement with these precedents (Scheme 4a). In this model, the thiol would attack the β-carbon of the Michael acceptor, electronically-impoverished by the Lewis acid activation, to give an Fe<sup>ll</sup>-enolate intermediate. Finally, a protonation step would occur and generate the expected β-thioether. As highlighted with 1g, 1k, and 1l, the mono activation of the substrates by Fe<sup>II</sup> was considered. As expected, higher electrophilicity of the ketone 1k vs. amide 1g increased the reactivity of the substrate toward the nucleophilic addition, but, surprisingly, no reaction occurred with the ester analogue 11 in the conditions. Moreover, the hypothesis that a catalytic quantity of

Scheme 3. Fe(OTf)\_2-catalyzed conjugate addition reaction of thiols to (E)-3-crotonoyloxazolidin-2-one^{[a]}



[a] Conditions:  $Fe(OTf)_2$  (5 mol-%), **1a** (0.250 mmol), **2a–o** (0.275 mmol), EtOH (0.25 mL). [b] 5 equiv. of thiol were used. [c] 2 equiv. of thiol were used.

triflic acid, possibly released by the hydrolysis of Fe(OTf)<sub>2</sub>, could act as a Brønsted acid was disclaimed when 2,6-di-*tert*-butyl pyridine was used in the optimized conditions (Scheme 4b).<sup>[27]</sup> The formation of **3a** with an excellent yield, thus, suggests an exclusive Lewis acid activation.

Scheme 4. Insights into the reaction mechanism

a) Postulated model of a transition state



In order to illustrate the utility of the developed greener conditions and their preparative value, the conjugate addition reaction of thiophenol **2a** to (*E*)-3-crotonoyloxazolidin-2-one **1a** was performed on a multigram scale (Scheme 5). Treatment of **1a** on a 4 gram scale (25 mmol) allowed the preparation of  $\beta$ -thioether **3a** with an excellent yield of 93%. The viability of a gram-scale

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Scheme 5. Thia-Michael addition: gram-scale reaction



synthesis using an air-stable  $\mbox{Fe}^{\mbox{\tiny II}}$  catalyst and undried EtOH was therefore demonstrated.

Further derivatization of the  $\beta$ -thioether obtained by the thia-Michael addition reaction was undertaken. In the recent years, iron salts have been conjointly used with PhI(OAc)2, [28] O2, [29] or urea-hydrogen peroxide (UHP),<sup>[30]</sup> for the highly selective sulfide oxidation reaction. Iron-catalyzed asymmetric versions have disclosed high enantioselectivities of aromatic sulfoxides obtained by catalytic methods using  $H_2O_2$  as a green oxidant.<sup>[23c, 31]</sup> Also, m-CPBA<sup>[32]</sup> and Na<sub>2</sub>WO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub><sup>[33]</sup> have been reported as efficient systems for the oxidation, in a separate step, of enantioenriched β-thioethers to the respective sulfones without racemization. In this study, the oxidation step of  $\beta$ -thioether **3a** using the green Fe<sup>II</sup>/H<sub>2</sub>O<sub>2</sub> catalytic system was considered (Table 3). While increasing the amount of H<sub>2</sub>O<sub>2</sub> (30%) from 1.1 to 4 equivalents, the formation of sulfoxide 5a was thus accelerated and a complete selectivity in the first oxidation product was observed (entries 1-3). A large excess in the oxidizing agent only showed the appearance of sulfone 6a, in addition to sulfoxide 5a, before complete consumption of sulfide 3a (entry 4). Uncomplete conversions were observed with reaction times inferior to 5 hours (entries 5 and 6). However, sulfoxide 5a was slowly oxidized in a prolonged reaction time (entry 7). A low 16% conversion was obtained when  $H_2O_2$  was used in the absence of the Fe<sup>II</sup> salt (entry 8). The highly selective Fe(OTf)<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> catalytic system afforded an optimal 88% yield of sulfoxide 5a (entry 3).

Table 3. Fe(OTf)\_2-catalyzed oxidation of  $\beta\text{-thioether}\ \textbf{3a}^{[a]}$ 



[a] Conditions: Fe(OTf)<sub>2</sub> (5 mol-%), **3a** (0.250 mmol), H<sub>2</sub>O<sub>2</sub> (30 wt.-% in H<sub>2</sub>O; 0.275–2.50 mmol), EtOH (0.25 mL). [b] Ratio **3a:5a:6a** calculated by <sup>1</sup>H NMR.  $\beta$ -Sulfoxide **5a** was obtained as a 53:47 mixture of diastereoisomers. [c] Isolated yield of **5a** (%). [d] No Fe(OTf)<sub>2</sub> was used.

Scheme 6. One-pot reaction in green synthetic conditions



Overall, a one-pot *thia*-Michael addition/oxidation reaction using completely green conditions was developed (Scheme 6). Indeed, sulfoxide **5a** was obtained as the major product (<sup>1</sup>H NMR: 5% of **1a**, 7% of **3a**, 82% of **5a**, and 6% of **6a**) and an overall 71% yield was obtained. Hence, the first example of a *thia*-Michael addition/oxidation reaction of an  $\alpha$ , $\beta$ -unsaturated oxazolidin-2-one compound in a one-pot fashion was demonstrated.

#### Conclusions

In summary, an Fe<sup>II</sup>-catalyzed Michael addition reaction of various thiols to  $\alpha,\beta$ -unsaturated carbonyl compounds was developed. Green synthetic conditions using Fe(OTf)<sub>2</sub> and EtOH afforded  $\beta$ -thioethers in high yields (up to 99%). Aromatic, heterocyclic and aliphatic thiols, and less reactive  $\alpha,\beta$ -unsaturated amides were substrates of choice. In addition, a highly efficient one-pot sulfide oxidation using H<sub>2</sub>O<sub>2</sub> as a green oxidant was also presented in this study. The simplicity of the described method lies in the use of room temperature and air atmosphere, highlighting practical and easy conditions for the catalyzed reaction. Further development will be reported in due course.

#### **Experimental Section**

General Procedure A: Fe<sup>II</sup>-Catalyzed Thia-Michael Addition Reaction to α,β-Unsaturated Carbonyl Compounds: In a glass test tube, Fe(OTf)2 (4.4 mg, 0.0125 mmol, 0.050 equiv.) was added to EtOH (0.10 mL). Michael acceptor 1a-I (0.250 mmol, 1.0 equiv.) was introduced before EtOH (0.15 mL) was added. After magnetic stirring at 25 °C under air atmosphere for 5 min, thiol 2a-o (0.275 mmol, 1.1 equiv.) was added dropwise. The mixture was stirred at 25 °C, and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with  $H_2O$  (10 mL), and the residue was extracted with Et<sub>2</sub>O (3 x 10 mL). The combined organic layers were washed with saturated aqueous NaHCO3 (10 mL), brine (10 mL), and dried over anhydrous MgSO<sub>4</sub>. After filtration and evaporation of the solvent in vacuo, the crude product was purified using a normal phase chromatography (Biotage<sup>®</sup>SNAP Ultra 25 g/Biotage<sup>®</sup>HP-Sphere<sup>™</sup> 25 µm) with a gradient elution of hexane/EtOAc = 90:10-40:60 (3a-f, and 4b-o), hexane/EtOAc = 80:20-10:90 (3g), hexane/EtOAc = 95:5-70:30 (3h-i), hexane/EtOAc = 80:20-20:80 (3j), and hexane/EtOAc = 99:1-95:5 (3k) to give the corresponding  $\beta$ -thioethers.

General Procedure B: Fe<sup>II</sup>-Catalyzed Oxidation Reaction of  $\beta$ -Thioether 3a to  $\beta$ -Sulfoxide 5a: In a glass test tube, Fe(OTf)<sub>2</sub> (4.4 mg, 0.0125 mmol, 0.050 equiv.) was added to EtOH (0.10 mL).  $\beta$ -Thioether 3a (66.6 mg, 0.250 mmol, 1.0 equiv.) was introduced before EtOH (0.15 mL) was added. After magnetic stirring at 25 °C under air atmosphere for 5 min, H<sub>2</sub>O<sub>2</sub> (30 wt.-% in H<sub>2</sub>O; 102 µL, 1.00 mmol, 4.0 equiv.) was added and the mixture was stirred for 5 hours. H<sub>2</sub>O (10 mL) was added to quench the reaction mixture and the residue was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with saturated aqueous NaHCO<sub>3</sub> (10 mL), brine (10 mL), and dried over anhydrous MgSO<sub>4</sub>. After

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filtration and evaporation of the solvent *in vacuo*, the crude product was purified using a normal phase chromatography (Biotage<sup>®</sup>SNAP Ultra 25 g/Biotage<sup>®</sup>HP-Sphere<sup>TM</sup> 25 µm) with a gradient elution of hexane/EtOAc = 40:60–5:95 to give sulfoxide diastereoisomers **5a** and **5a'** as a white solid.

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### **Entry for the Table of Contents**

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A convenient Fe(OTf)<sub>2</sub>-catalyzed Michael addition reaction of thiols to  $\alpha$ , $\beta$ unsaturated carbonyl compounds was developed. The use of a simple procedure (EtOH, room temperature, air atmosphere) allowed to set up effective green catalytic conditions for the C–S bond formation. Iron Catalysis

Samuel Lauzon, Mao Li, Hoda Keipour, Thierry Ollevier\*

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