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An Expedient Stereoselective Synthesis of (E)- $\alpha$ , $\beta$ -Unsaturated Esters and Thioesters Using FeCl<sub>3</sub>.6H<sub>2</sub>O

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An Expedient Stereoselective Synthesis of $(E)$ - $\alpha,\beta$ -Unsatur	rated Esters and Thioesters Using
FeCl <sub>3</sub> .6H <sub>2</sub> O	
Amar R. Mohite, Trimbak B. Mete, Ramakrishna G. Bhat*	$\begin{array}{c} \begin{array}{c} 1. \ FeCl_{3}6H_{2}O(0.001-0.005 \ equiv) \\ R^{1} \cdot OH \ or \ R^{1} \cdot SH \ (1 \ equiv) \\ CH_{3}NO_{2}, \ MW, \ 15 \ min \\ \hline 2. \ Piperidine \ (cat.), \ MW, \ 15 \ min \\ \hline \begin{array}{c} 0 \\ P \\ \end{array} \end{array} \begin{array}{c} Or \\ R \\ \hline \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \end{array} \end{array} $ \end{array}
	High yield , >99% E-selectivity, gram scale synthesis (Sunscreen Agent)



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# An Expedient Stereoselective Synthesis of (E)- $\alpha$ , $\beta$ -Unsaturated Esters and Thioesters Using FeCl<sub>3</sub>.6H<sub>2</sub>O

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### ABSTRACT

Facile and convenient synthesis of  $\alpha$ , $\beta$ -unsaturated esters and thioesters from alkylidene derivatives of Meldrum's Acid is described. This method uses catalytic amount of FeCl<sub>3</sub>.6H<sub>2</sub>O (0.001 – 0.005 equiv) with alcohols/thiols (1 equiv) in dry CH<sub>3</sub>NO<sub>2</sub> followed by catalytic amount of piperidine. A variety of  $\alpha$ , $\beta$ -unsaturated esters and thioesters have been synthesized with high *E*-stereoselectivity in good to excellent yields. The application of this methodology is demonstrated by gram scale synthesis of octinoxate, a sunscreen agent, and other *p*-methoxycinnamate esters.

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#### Introduction

 $\alpha,\beta$ -Unsaturated esters have been utilized as versatile building blocks in organic synthesis and they find significant use in industry.<sup>1</sup> Owing to the importance of these products, many stereoselective methods have been developed,<sup>2</sup> including syntheses based on Wittig and Wittig-Horner-Emmons (HWE) reactions.<sup>3</sup> Some of these methods, though reliable, are mostly non-catalytic, use a strong base, and formation of undesirable organophosphorus by-products is unavoidable. Moreover, Wittig and HWE reactions afford Z-isomers as minor products, necessitating mixture separation. Efficient catalytic conversion of alkynyl aldehydes into  $\alpha,\beta$ -unsaturated esters in variable yields has been reported.<sup>4</sup>  $\alpha,\beta$ -Unsaturated esters have also been prepared via decarboxylative Doebner-Knoevenagel condensation but with variable E/Z selectivity<sup>5</sup> in a protocol that requires various malonic half-esters to generate different  $\alpha,\beta$ unsaturated esters.  $\alpha,\beta$ -Unsaturated esters have also been elegantly synthesized by cross-metathesis of acrylic esters with terminal olefins,<sup>6</sup> though different alkyl acrylates would be required in order to give a variety of cinnamate esters. Finally, palladium catalyzed carbon-carbon bond forming process is an alternative powerful approach that has been used for the synthesis of  $\alpha,\beta$ -unsaturated esters.<sup>2c,7</sup>

*p*-Methoxycinnamates are commonly used as sunscreen chemical filters in industry and octyl methoxycinnamate (Octinoxate, OMC) is a common ingredient in most sunscreen lotions.<sup>8</sup> This chemical, of commercial significance, has been the target of synthesis by various routes. One notable synthesis has

employed Pd-catalyzed coupling of 2-ethylhexyl acrylate with *p*-haloanisole or 4-methoxybenzenediazonium tetrafluoroborate.<sup>9</sup> Recently, OMC has been synthesized by cross-metathesis of 2-ethylhexyl acrylate (6 equiv) and a phenylpropanoid derived from an essential oil.<sup>10</sup> In spite of these available methods, there is a challenge to develop a cost-effective catalytic route for the synthesis of  $\alpha$ , $\beta$ -unsaturated esters.

Earlier the bis-electrophilic nature of alkylidene Meldrum's acid has been explored for the synthesis of coumarins and chromones from phenols.<sup>11</sup>

In this report, we present a convenient and practical procedure for the stereoselective synthesis of  $\alpha,\beta$ -unsaturated esters, and thioesters from derivatives of cyclic 1,3-di-esters. We anticipated that reaction of alkylidene Meldrum's Acid (MA) with alcohols in the presence of catalytic FeCl<sub>3</sub>.6H<sub>2</sub>O would yield  $\alpha,\beta$ unsaturated esters.<sup>12</sup> To our knowledge, the reactivity of alkylidene MA with alcohols/thiols is explored for the first time here.

Different alkylidene MA derivatives were prepared by condensing aldehydes with MA (2,2-dimethyl-1,3-dioxane-4,6-dione) in water.<sup>13</sup>

We first examined the model reaction of pmethoxybenzylidene derivative of MA (1a) with MeOH (1 equiv) 2a in presence of 0.005 equiv (0.5 mol%) FeCl<sub>3</sub>.6H<sub>2</sub>O using nitromethane<sup>14</sup> as solvent under microwave irradiation (2.5 GHz, 15 min). However, instead of the expected methyl pmethoxycinnamate 3a, the product was the alkylidene malonic acid half-ester. Even prolonged microwave irradiation (2 h) of

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the reaction mixture did not facilitate the decarboxylation of this half-ester. However, the alkylidene malonate half-ester underwent facile decarboxylation on treatment with a catalytic amount of piperidine (6.5 mol%) in CH<sub>3</sub>NO<sub>2</sub> under microwave irradiation (15 min) to afford methyl *p*-methoxycinnamate **3a** in excellent yield (93%).

We next carried out a one-pot, two-step synthesis of methyl *p*-methoxycinnamate **3a** starting from **1a** and MeOH **2a** (1 equiv). The reaction was carried out under microwave irradiation (15 min) in the presence of FeCl<sub>3</sub>.6H<sub>2</sub>O (0.005 equiv) in CH<sub>3</sub>NO<sub>2</sub>, followed by the addition of piperidine (6.5 mol%) and subsequent microwave irradiation (15 min). This reaction afforded **3a** in 94% yield (entry 1, Table 1). The catalytic conversion was neat and led to volatile by-products.

 Table 1 Selective esterification of p-methoxy-benzylidene Meldrum's Acid

 with various alcohols



<sup>a</sup>1 equiv Alcohol (R<sup>1</sup>-OH), <sup>b</sup>anhydrous CH<sub>3</sub>NO<sub>2</sub> as solvent, <sup>c</sup>Microwave irradiation (2.5 GHz,100 W), <sup>d</sup>99% *E*-selectivity observed for (**3a**, **3b**, **3e**, **3g**, **3h**, **3i**, **3k**, **3l**); ~98% *E*-selectivity for **3d**, **3j**; however **3c**, **3f** gave an E/Z = 94:6 ratio (<sup>1</sup>H NMR analysis) <sup>e</sup>isolated yield after purification by column chromatography

However, reaction did not work in the absence of catalyst. In order to expand the scope of this methodology, a range of primary alcohols (1 equiv), including alkenyl and alkynyl alcohols, were treated with *p*-methoxy-benzylidene derivative of MA (**1a**) under optimized reaction conditions (Table 1). The corresponding  $\alpha,\beta$ -unsaturated esters (**3b-3f**) were obtained in moderate to excellent yields (79 to 96%).

Secondary alcohols (entries 7 & 8, Table 1) also reacted smoothly with **1a** to furnish the corresponding unsaturated esters (**3g**, **3h**). We next explored the procedure using a chiral alcohol:(+)-menthol to give the corresponding chiral ester **3i** in 71% yield (entry 9, Table 1). The compatibility of the methodology with a bromine-substituted alcohol was also investigated and the corresponding unsaturated ester **3k** was obtained in 57% yield (entry 11, Table 1). Notably, we observed that (*E*)-stereoisomers were formed as major products (~98-99%) using this protocol, however, compounds **3c** and **3f** were obtained in an E/Z = 94.6 ratio. *E*-stereochemistry was assigned on the basis on <sup>1</sup>H-NMR coupling constants.

**Scheme 1.** Application of the methodology to industrially significant sunscreen filters on a gram scale<sup>a</sup>



<sup>a</sup>Gram scale synthesis of **3m** and **3n** was carried out in presence of 0.001 equiv of FeCl<sub>3.6</sub>H<sub>2</sub>O and 0.005 equiv of FeCl<sub>3.6</sub>H<sub>2</sub>O was used for small scale synthesis, <sup>b</sup>1 equiv R<sup>1</sup>-OH, <sup>c</sup>anhydrous CH<sub>3</sub>NO<sub>2</sub> as solvent, <sup>d</sup>Microwave irradiation (2.5 GHz, 100 W); <sup>e</sup> > 99% *E*-selectivity observed for **3m**, **3n** (<sup>1</sup>H NMR analysis), <sup>f</sup>isolated yileds after purification by column chromatography are given in paranthesis

In order to explore the wider scope of this method, we synthesized two of the well-known sunscreen filters (**3m**, **3n**) following the optimized reaction conditions (Scheme 1). Treatment of compound **1a** with 2-ethyl 1-hexanol **2m** and 2-ethoxyethanol **2n** under optimal reaction conditions furnished the expected unsaturated esters **3m** and **3n** respectively in very good yields (81% and 78%) (Scheme 1).

To make this approach of wider applicability,  $\alpha,\beta$ -unsaturated esters **3m** and **3n** were synthesized (Scheme 1, 84, 80%) on 5 g scale from the corresponding alcohols **2m** and **2n**.<sup>15,16</sup> It is noteworthy that on this larger scale, catalyst loading was successfully reduced to 0.001 equiv (0.1 mol%). Notably, this direct and straightforward approach avoids the late stage transesterification.

Different alkylidene MA derivatives modified in the aryl moiety were prepared to establish the generality and efficiency of this protocol. Compounds **1b-1f**<sup>12</sup> when treated with alcohols (**2d** and **2b**) in the presence of 0.005 equiv FeCl<sub>3</sub>.6H<sub>2</sub>O afforded the corresponding  $\alpha$ , $\beta$ -unsaturated esters (**3o-3s**) in good yield (Table

2). Aromatic as well as heteroaromatic substrates reacted efficiently. Moreover, different functional groups and substituents did not affect the rate or yield of reactions. However, attempted reactions of aliphatic alkylidene Meldrum's acid derivatives were unsuccessful.

 Table 2
 Selective esterification of derivatives Cyclic 1, 3-Diesters with alcohols



<sup>a</sup>1 equiv Alcohol, <sup>b</sup>anhydrous CH<sub>3</sub>NO<sub>2</sub> as solvent, <sup>c</sup>Microwave irradiation (2.5 GHz, 100 W), <sup>d</sup>>99% *E*-selectivity observed in **30**, **3s** (<sup>1</sup>H NMR analysis), <sup>e</sup>isolated yield after purification by column chromatography

Likewise, thioesters are <u>also</u> very important and useful organosulfur compounds and they also play a significant role as precursors of many important bioactive molecules and natural products.<sup>17</sup>

The enhanced reactivity of thioseters in comparison to oxoesters has been explored successfully for a range of synthetic organic transformations. Interestingly,  $\alpha,\beta$ -unsaturated thioesters have marked reactivity as Michael acceptors and they are proved to be excellent substrates in the synthesis of several natural products.<sup>18</sup> Although, it is a very useful intermediate, traditional syntheses of thioesters are encountered with the occasional difficulties such as 1,4-addition of thiolate and subsequent separation from the main product.<sup>19</sup> Olefin cross-metathesis has been elegantly explored to construct  $\alpha,\beta$ -unsaturated thioesters using thioacrylate.<sup>20</sup>

Encouraged by the success of synthesis of  $\alpha,\beta$ -unsaturated esters, we planned to extend the protocol for the straightforward synthesis of  $\alpha,\beta$ -unsaturated thioesters using the optimized reaction conditions for esters.

In order to compare the reactivity and to extend the application, thiols (4a, 4b) (1 equiv) were treated with few

benzylidene derivative of MA (**1a**, **1b**, **1e**) under optimized reaction conditions (Table 3). The corresponding  $\alpha,\beta$ -unsaturated thioesters (**5a-5e**) were obtained in good to excellent yields (76 to 90%) in just 15 minutes.

Table 3 One pot direct synthesis of  $\alpha,\beta$ -unsaturated thioesters



<sup>a</sup>1 equiv thiol, <sup>b</sup>anhydrous CH<sub>3</sub>NO<sub>2</sub> as solvent, <sup>c</sup>Microwave irradiation (2.5 GHz, 100 W), <sup>d</sup>>99% *E*-selectivity observed in **5a**, **5b**, **5c**; ~98% *E*-selectivity for **5e**; ~97% *E*-selectivity for **5d** (<sup>1</sup>H NMR analysis), <sup>e</sup>isolated yield after purification by column chromatography

#### Conclusions

In conclusion, we have described an efficient procedure<sup>21</sup> to generate  $\alpha,\beta$ -unsaturated esters and thioesters from alkylidene Meldrum's Acids using an inexpensive catalyst. Microwave assisted one-pot, two-step synthesis of  $\alpha,\beta$ -unsaturated esters and thioesters are relatively rapid, high yielding and reliably selective. Reactions are neat and by-products formed are volatile. The novel protocol described for the selective esterification and decarboxylation uses very low catalyst loading (0.001 – 0.005 equiv, 0.1-0.5 mol%). This methodology provides an easy access to a range of  $\alpha,\beta$ -unsaturated esters and thioesters, including compounds of high industrial value on a gram scale.

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#### **Supplementary Material**

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI:

#### **References and notes**

- Selected examples of synthesis of  $\alpha,\beta$ -unsaturated esters and their 1 applications: (a) Franklin AS. J Chem Soc. Perkin Trans. 1 1998, 2451; (b) Shen Y. Acc Chem Res 1998, 31, 584; (c) Hayashi T, Yamasaki K. Chem Rev. 2003, 103, 2829; (d) López F, Harutyunyan SR, Meetsma A, Minnaard AJ, Feringa BL. Angew Chem Int Ed. 2005, 44, 2752; (e) Ryu DH, Corey EJ. J Am Chem Soc 2003, 125, 6388; (f) Chen D, Guo L, Liu J, Kirtane S, Cannon JF, Li G. Org Lett. 2005, 7, 921.
- 2 Few selected references: (a) Katritzky AR. Comprehensive Organic *Functional Group Transformations*; Katritzky, ÅR. Ed. Pergamon: Oxford, 1995; Vol. 5, pp 154-161. (b) Concellón JM, Pérez-Andrés JA, Rodríguez-Solla H. Angew Chem Int Ed. 2000, 39, 2773; (c) Beletskaya IP, Cheprakov AV. Chem Rev. 2000, 100, 3009; (d) Chatterjee, AK, Toste FD, Choi T-L, Grubbs RH. Adv Synth Catal. 2002, 344, 634; (e) Blakemore PR. J Chem Soc. Perkin Trans. 1 2002, 2563; (f) van Staden LF, Gravestock D, Ager DJ. Chem Soc Rev. 2002, 195.
- (a) Maryanoff, BE, Reitz AB. Chem Rev. 1989, 89, 863; (b) Spinella A, 3 Fortunati T, Soriente A. Synlett 1997, 93; (c) Still, WC, Gennari C. Tetrahedron Lett. 1983, 24, 4405; (d) Ando, K. Tetrahedron Lett. 1995, 36, 4105; (e) Ando K. J Org Chem. 1999, 64, 6815.
- Zeitler K. Org Lett. 2006, 8, 637.
- 5 (a) List B, Doehring A, Hechavarria Fonseca MT, Wobser K, van Thienen H, Torres RR, Galilea PL. Adv Synth Catal. 2005, 347, 1558; (b) List B, Doehring A, Hechavarria Fonseca MT, Job A, Torres RR, Tetrahedron 2006, 62, 476.
- (a) Choi T-L, Lee CW, Chatterjee AK, Grubbs RH. J Am Chem Soc. 6 2001, 123, 10417;(b) Thortsensson F, Kvarnstrom I, Mussil D, Nilsson I, Samuelsso B. J Med Chem. 2003, 46, 1165.
- (a) Moreno-Mañas M, Pérez M, Pleixants R. Tetrahedron Lett. 1996, 7 37, 7449; (b) Beller M, Riermeier TH. Tetrahedron Lett. 1996, 37, 635.
- 8 Ringk, WF. Kirk Othmer Encyclopedia of Chemical Technology 3rd ed.; John Wiley and Sons: New York, 1981; Vol. 6; pp 143-149.
- Selected examples: (a) Littke, AF, Fu, GC J Am Chem Soc. 2001, 123, 9 6989; (b) Poetsch E, Meyer V, Heywang U, Christ R, Seubert J. German Patent 4405830, 1995; Chem Abstr. 1995, 123, 227816; (b) Kaufmann D, Hesse C, Himmler T. European Patent 564919, 1993; Chem Abstr. 1994, 120, 134050; (c) Gygax P. World Patent 9405621, 1994; (d) Selvakumar K, Zapf A, Spannenberg A, Beller M. Chem. A European J. 2002, 8, 3901.
- Lummiss JAM, Oliveira KC, Pranckevicius AMT, Santos AG, dos 10 Santos EN, Fogg DE. J Am Chem Soc. 2012, 134, 18889.

- (a) Nair V. Synth Commun. 1987, 17, 723; (b) Fillion E, Dumas AM, 11 Kuropatwa BA, Malhotra NR, Sitler TC. J Org Chem. 2006, 71, 409. Mohite AR, Bhat RG. Org Lett. 2013, 15, 4564. (Earlier, we
- 12 demonstrated that FeCl<sub>3</sub>.6H<sub>2</sub>O efficiently catalyzes the synthesis of  $\alpha_{,\beta}$ unsaturated carboxylic acids by the controlled mono-electrophilic reactivity of alkylidene Meldrum's Acids with water)
- 13 Bigi F, Carloni S, Ferrari L, Maggi R, Mazzacani A, Sartori G. Tetrahedron Lett. 2001, 42, 5203.
- Several solvents such as EtOAc, MeOH, ACN, THF were found to be 14 ineffective as reaction did not work in these solvents.
- Synthesis of 3m and 3n can also be successfully achieved under conventional refluxing conditions at 110 °C for 3.5-4 h. 15
- 16 Provisional Patent filed in India, App No:2437/MUM/2013
- (a) Shimizu T, Seki M. *Tetrahedron Lett.* **2002**, *43*, 1039; (b) Dieter RK. *Tetrahedron*. **1999**, *55*, 4177; (c) Tokuyama H, Yokoshima S, Yamashita T, Fukuyama T. *Tetrahedron Lett.* **1998**, *39*, 3189;(d) 17 Kobayashi S, Uchiro H, Fujishita Y, Shiina I, Mukaiyama T. J Am Chem Soc. 1991, 113, 4247;(e) Mukaiyama T, Araki M, Takey H. J Am Chem Soc. 1973, 95, 4763.
- (a) Des Mazery R, Pullez M, López F, Harutyunyan SR, Minnaard AJ, Feringa BL. J Am Chem Soc 2005, 127, 9966;(b) Howell GP, Fletcher, 18 SP, Geurts K, ter Horst B, Feringa BL, J Am Chem Soc. 2006, 128, 14977; c) van Summeren RP, Moody DB, Feringa BL, Minnaard, AJ. J Am Chem Soc. 2006, 128, 4546; (d) ter Horst B, Feringa BL, Minnaard A J. Org Lett. 2007, 9, 3013.
- Classical methods such as coupling of acids with thiols using 19 DCC/DMAP and transesterification with trimethylsilyl thioethers in presence of AlCl<sub>3</sub> occasionaly lead to some amount of side product due to 1.4-addition of thiolate to the product (See:Thesis entitled <sup>16</sup> Enantioselective copper catalyzed allylic alkylation using Grignard reagents' submitted by van Zijl, AW, University of Groningen) van Zijl AW, Minnaard AJ, Feringa BL. *J Org Chem.* **2008**, *73*, 5651.
- 20
- General Procedure for the Synthesis of  $\alpha$ ,  $\beta$ -Unsaturated esters: In a 21 pressure tube (capped) containing a mixture of 1a (200 mg, 0.76 mmol), catalyst FeCl<sub>3</sub>.6H<sub>2</sub>O (1 mg, 0.0037 mmol) and MeOH (2a) (31 µL, 0.76 mmol) in dry nitromethane (2 mL), was microwave irradiated for 15 min. In the same reaction flask piperidine (5  $\mu$ L, 0.05 mmol) was added and microwaved again for 15 min. The reaction mixture was cooled to room temperature, concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography ( $R_f = 0.6$ , Eluent:Pet. Ether:EtOAc (80:20)) to furnish compound 3a as a white solid

### Highlights

- Catalytic access to  $\alpha, \beta$ -unsaturated esters and thioesters •
- Low catalytic amount (0.1-0.5 mol%) •
- Scrip Gram scale (5 g) synthesis of sunscreen agent-Octinoxate •
- High *E*-stereoselectivity (>99%)
- Protocol does not rely on transesterification •

