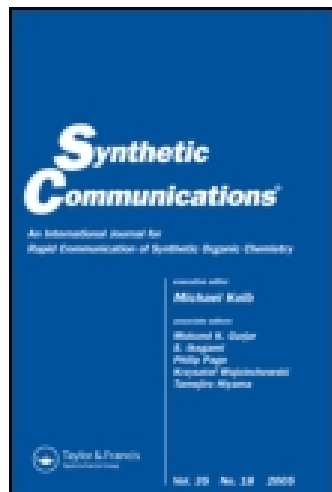




Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

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Olfa Mhasni^{a, b}, Imen Erray^a & Farhat Rezgui^a

^a Faculty of Sciences de Tunis, Laboratoire de Chimie Organique Structurale, Université of Tunis El Manar, Tunis, Tunisia

^b Institute for Research and Physicochemical Analysis (INRAP), Pôle Technologique, Sidi Thabet, Tunisia

Accepted author version posted online: 18 Jul 2014. Published online: 26 Sep 2014.

To cite this article: Olfa Mhasni, Imen Erray & Farhat Rezgui (2014) General and Efficient Transesterification of β -Keto Esters with Various Alcohols Using Et_3N as a Brønsted Base Additive, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 44:22, 3320-3327, DOI: [10.1080/00397911.2014.932812](https://doi.org/10.1080/00397911.2014.932812)

To link to this article: <http://dx.doi.org/10.1080/00397911.2014.932812>

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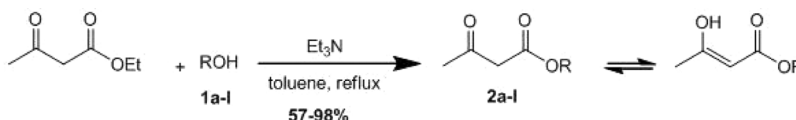
GENERAL AND EFFICIENT TRANSESTERIFICATION OF β -KETO ESTERS WITH VARIOUS ALCOHOLS USING Et_3N AS A BRØNSTED BASE ADDITIVE

Olfa Mhasni,^{1,2} Imen Erray,¹ and Farhat Rezgui¹

¹Faculty of Sciences de Tunis, Laboratoire de Chimie Organique Structurale, Université of Tunis El Manar, Tunis, Tunisia

²Institute for Research and Physicochemical Analysis (INRAP), Pôle Technologique, Sidi Thabet, Tunisia

GRAPHICAL ABSTRACT



Abstract Transesterification of β -keto esters with a wide variety of allyl, benzyl, propargyl, and alkyl alcohols using, for the first time, commercially available and inexpensive Et_3N as a Brønsted base additive, is efficiently performed in toluene at reflux. The corresponding esters are exclusively obtained in 57–98% yields with no trace amounts of γ,δ -ketones, usually expected from the decarboxylative Carroll rearrangement.

Keywords Alcohols; Brønsted base; β -keto esters; transesterification

INTRODUCTION

Transesterification, a transformation of an ester to ester through interchange of the alkoxy moiety, has attracted much attention from synthetic organic chemists.^[1–9] Because common ethyl and methyl esters as well as β -keto esters are commercially available, they are usually used as starting materials for the convenient synthesis of other useful esters.^[10,11]

The preparation of β -keto esters through the conventional esterification reaction between the corresponding β -keto acids and alcohols is not, in general, an efficient method because of the equilibrium process and the low solubility of acids, especially those having long aliphatic tails, in organic solvents,^[12] as well as their undesired facile decarboxylation by simply heating them.^[13]

Because β -keto esters have been found to be useful intermediates in numerous synthetic methods^[14,15] and common moieties in natural products as well as

Received April 30, 2014.

Address correspondence to Farhat Rezgui, University of Tunis El Manar, Faculty of Science, Campus, 2092 Tunis, Tunisia. E-mail: rez_far@yahoo.fr

pharmaceutical compounds,^[16] their synthesis has attracted great interest. In this regard, in the 1980s, two common methods were mainly employed for the transesterification of β-keto esters, i.e., the reaction of diketene with primary or secondary alcohols^[17] and dimethylaminopyridine (DMAP)-catalyzed ester exchange reactions in the presence of molecular sieves in refluxing toluene.^[18] As diketene was found to be corrosive and DMAP is both toxic and expensive, the two previous methods became less attractive and therefore a large variety of catalysts have been proposed for the transesterification protocols such as zinc(II) oxide,^[19] niobium(V) oxide,^[20] borate zirconia,^[21] diode,^[22] and Zn/I₂.^[23] Moreover, recent reports dealing with this topic have demonstrated that noncorrosive and environmentally benign catalysts including boric acid,^[24] montmorillonite K-10,^[25] and natural clays^[26,27] can be used as efficient and reusable catalysts.

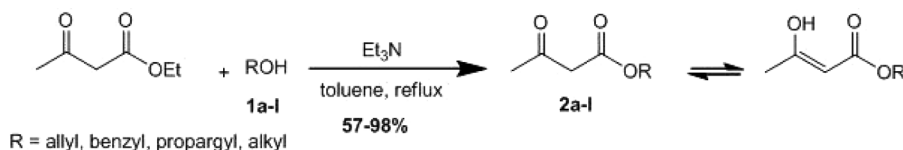
Although triethylamine is one of the most common amines, it is well known that it only catalyzes the esterification of highly reactive substrates such as diketenes and oxazolinones.^[28] Moreover, with the exception of the DMAP-catalyzed ester exchange reactions,^[8] it is notable that none of these methods reported that tertiary bases, such as Et₃N, could efficiently catalyze transesterification of β-keto esters.

In the course of our study on the BH chemistry, we have reported that the DMAP-promoted direct *C*-allylation of β-ketoesters with BH alcohols,^[29] whereas Et₃N promoted their transesterification.^[30] In continuation of our investigation on the use of amines in these transesterification protocols, we report herein our results on this topic involving a variety of allyl, benzyl, propargyl, and alkyl alcohols, using commercially available and inexpensive Et₃N for the first time as a Brønsted base additive.

RESULTS AND DISCUSSION

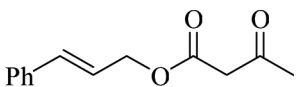
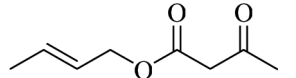
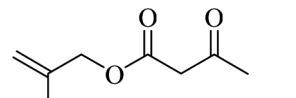
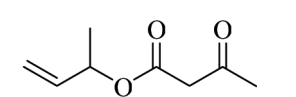
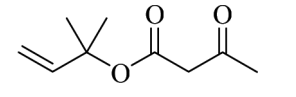
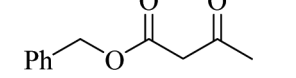
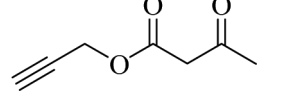
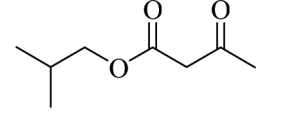
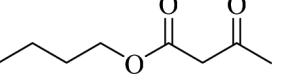
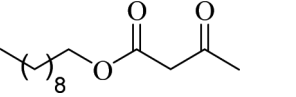
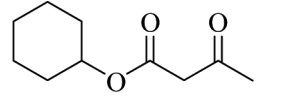
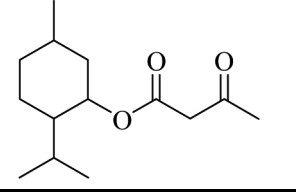
Encouraged by our successful results dealing with the transesterification of β-ketoesters with functionalized allyl alcohols, we were curious to determine whether our previous protocol still worked with various alcohols that are devoid of electron-withdrawing groups, in contrast to those of Baylis–Hillman.^[30] For this purpose, we have investigated and optimized the reaction between cinnamyl alcohol **1a** (5 mmol) and ethyl acetoacetate (10 mmol) in toluene at reflux with azeotropic removal of EtOH, using Et₃N (10 mmol) as one of the most common amines. The transesterification reaction was completed within 5 h, affording the sole ester **2a** in 95% yield, with no trace amounts of the Carroll decarboxylative rearrangement ketone (Scheme 1, Table 1, entry 1).^[31,32]

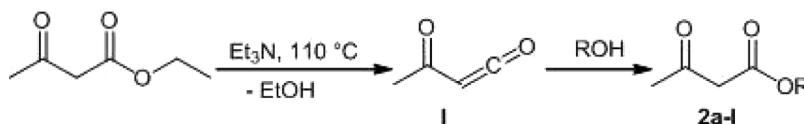
Next, to explore the scope of this transesterification methodology, we have selected a variety of alcohols. As shown in Table 1, the present protocol worked well with various classes of allyl, benzyl, and propargyl alcohols (Table 1, entries 1–7), as



Scheme 1. Et₃N-mediated transesterification of ethyl acetoacetate with various alcohols.

Table 1. Et₃N-mediated transesterification of ethyl acetoacetate with various alcohols

Entry	Alcohol	Time (h)	Ester 2	Yield (%)	Keto/enol (%)
1	1a	5	2a : 	95	93/7
2	1b	10	2b : 	91	91/9
3	1c	5	2c : 	87	91/9
4	1d	6	2d : 	82	91/9
5	1e	24	2e : 	57	92/8
6	1f	3	2f : 	72	91/9
7	1g	7	2g : 	78	93/7
8	1h	25	2h : 	74	92/8
9	1i	27	2i : 	80	92/8
10	1j	22	2j : 	97	91/9
11	1k	8	2k : 	84	92/8
12	1l	21	2l : 	98	90/10



Scheme 2. Proposed mechanism for Et₃N-mediated transesterification of ethyl acetoacetate with alcohols ROH.

well as alkyl alcohols (Table 1, entries 8 – 10) and cyclic ones (Table 1, entries 11 and 12), in 57–98% yields.

All β-keto esters **2** exist as a mixture of two tautomeric forms in CDCl₃ solution, whose relative ratios were determined by means of ¹H NMR spectroscopy (Table 1). For example, the singlet at δ_H 3.46 of **1a** was assigned to the methylene proton (–CO–CH₂–CO–) of the corresponding keto tautomer whereas the two singlets at δ_H 5.02 and δ_H 12.06 were respectively assigned to the vinyl proton (–C(–OH)=CH–) and the hydroxyl one (OH) of the corresponding enol tautomer.

Mechanistically, we assumed that ethyl acetoacetate, for instance, can undergo, in the presence of Et₃N, as a nitrogen Brønsted base, a β-elimination of EtOH to give an α-keto ketene intermediate **I**, highly reactive, on which further addition of alcohols ROH generates esters **2a-l**. This reaction mechanism, involving α-keto ketene, was previously proposed by other authors^[33–37] and supported by Witzeman studies (Scheme 2).^[38,39]

CONCLUSION

We have successfully developed a simple and efficient Et₃N-mediated transesterification of β-keto esters with various allyl, benzyl, propargyl, and aliphatic alcohols. The desired esters were obtained in moderate to excellent yields with no trace amounts of the Carroll decarboxylative rearrangement ketones.

EXPERIMENTAL

All chemicals were purchased from specialized suppliers with analytical purity and without further purification. ¹H NMR and ¹³C NMR spectra were recorded either on a Bruker AC-300 spectrometer (300 MHz for ¹H and 75 MHz for ¹³C) in CDCl₃, using tetramethylsilane (TMS) as an internal standard (chemical shifts in δ values, *J* in hertz). High-resolution mass spectra (HRMS) were recorded as EI-HRMS on an Autospec Ultima/micromass mass spectrometer. Analytical thin-layer chromatography (TLC) was performed using Fluka Kieselgel 60 F254 precoated silica-gel plates. Visualization was achieved by ultraviolet (UV) light (254 nm). Column chromatography was performed using Fluka silica gel 60 (70–230 mesh ASTM) and a gradient solvent system (petroleum ether/ether as eluent).

General Procedure for the Transesterification of β-Keto Esters Using Various Alcohols

A mixture of alcohol **1a** (0.67 g, 5 mmol), ethyl acetoacetate (1.30 g, 10 mmol), and Et₃N (1.01 g, 10 mmol) in toluene (50 mL) was heated to 110 °C in a two-necked,

round-bottomed flask provided with a distillation condenser to remove ethanol. After completion (TLC), the reaction mixture was cooled, washed with brine, and dried. The toluene was removed and the residue was purified by column chromatography on silica gel (40% ether/petroleum ether) to give the pure allylic ester **2a**.

Cinnamyl 3-Oxobutanoate (**2a**)^[27]

Yellow oil (1.03 g, 95% yield); keto (93%)–enol (7%); δ_{H} (keto, CDCl_3) 7.38–7.23 (m, 5H), 6.64 (d, J 15.0 Hz, 1H), 6.25 (dt, J 15.0 and 6.0 Hz, 1H), 4.77 (d, J 6.0 Hz, 2H), 3.46 (s, 2H), 2.23 (s, 3H); δ_{H} (enol, CDCl_3) 12.06 (s, 1H), 7.38–7.23 (m, 5H), 6.64 (d, J 15.0 Hz, 1H), 6.25 (dt, J 15.0 and 6.0 Hz, 1H), 5.02 (s, 1H), 4.77 (d, J 6.0 Hz, 2H), 1.93 (s, 3H); δ_{C} (keto, CDCl_3) 200.4, 166.8, 136.0, 134.7, 128.6, 128.1, 127.0, 122.5, 65.8, 49.9, 30.0; δ_{C} (enol, CDCl_3) 175.8, 172.2, 136.1, 134.0, 128.6, 128.1, 126.9, 123.1, 89.5, 64.2, 21.1. HRMS (EI): $[\text{M} + \text{Na}]^+$, found 241.0835. $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Na}$ requires 241.0841.

But-2-enyl 3-Oxobutanoate (**2b**)^[18]

Yellow oil (0.71 g, 91% yield); keto (91%)–enol (9%); δ_{H} (keto, CDCl_3) 5.85–5.77 (m, 1H), 5.63–5.55 (m, 1H), 4.57–4.54 (m, 2H), 3.46 (s, 2H), 2.26 (s, 3H), 1.72 (m, 3H); δ_{H} (enol, CDCl_3) 12.04 (s, 1H), 5.85–5.77 (m, 1H), 5.63–5.55 (m, 1H), 4.99 (s, 1H), 4.71–4.69 (m, 2H), 1.94 (s, 3H), 1.72 (m, 3H); δ_{C} (keto, CDCl_3) 200.5, 167.0, 131.9, 124.7, 65.9, 50.0, 30.0, 17.5; δ_{C} (enol, CDCl_3) 175.6, 172.4, 131.3, 125.2, 89.6, 64.6, 21.1, 17.7. HRMS (EI): M^+ , found 156.0786. $\text{C}_8\text{H}_{12}\text{O}_3$ requires 156.0786.

2-Methylprop-2-enyl 3-Oxobutanoate (**2c**)

Yellow oil (0.68 g, 87% yield); keto (91%)–enol (9%); δ_{H} (keto, CDCl_3) 4.99 (s, 1H), 4.95 (s, 1H), 4.56 (s, 2H), 3.50 (s, 2H), 2.27 (s, 3H), 1.76 (s, 3H); δ_{H} (enol, CDCl_3) 12.02 (s, 1H), 5.04 (s, 1H), 4.99 (s, 1H), 4.95 (s, 1H), 4.56 (s, 2H), 1.96 (s, 3H), 1.76 (s, 3H); δ_{C} (keto, CDCl_3) 200.4, 166.8, 139.4, 113.5, 68.5, 49.9, 30.1, 19.4; δ_{C} (enol, CDCl_3) 175.9, 172.2, 140.0, 112.8, 89.5, 67.0, 21.1, 19.4. HRMS (EI): M^+ , found 156.0786. $\text{C}_8\text{H}_{12}\text{O}_3$ requires 156.0786.

1-Methylprop-2-enyl 3-Oxobutanoate (**2d**)^[18]

Yellow oil (0.64 g, 82% yield); keto (91%)–enol (9%); δ_{H} (keto, CDCl_3) 5.90–5.79 (m, 1H), 5.44–5.35 (m, 1H), 5.30–5.14 (m, 2H), 3.46 (s, 2H), 2.26 (s, 3H), 1.34 (d, J 6.0 Hz, 3H); δ_{H} (enol, CDCl_3) 12.08 (s, 1H), 5.90–5.79 (m, 1H), 5.44–5.35 (m, 1H), 5.30–5.14 (m, 2H), 4.99 (s, 1H), 1.95 (s, 3H), 1.34 (d, J 6.0 Hz, 3H); δ_{C} (keto, CDCl_3) 200.5, 166.3, 137.1, 116.3, 72.1, 50.3, 30.0, 19.8; δ_{C} (enol, CDCl_3) 175.6, 171.9, 137.7, 115.6, 89.9, 70.5, 21.1, 20.0. HRMS (EI): M^+ , found 156.0786. $\text{C}_8\text{H}_{12}\text{O}_3$ requires 156.0786.

1,1-Dimethylprop-2-enyl 3-Oxobutanoate (**2e**)

Yellow oil (0.49 g, 57% yield); keto (92%)–enol (8%); δ_{H} (keto, CDCl_3) 6.09–6.05 (m, 1H), 5.13–5.09 (m, 2H), 3.38 (s, 2H), 2.24 (s, 3H), 1.54 (s, 6H);

δ_{H} (enol, CDCl₃) 12.1 (s, 1H), 6.09–6.05 (m, 1H), 5.13–5.09 (m, 2H), 4.93 (s, 1H), 1.91 (s, 3H), 1.54 (s, 6H); δ_{C} (keto, CDCl₃) 200.8, 166.3, 141.9, 113.1, 82.1, 51.1, 30.0, 26.3; δ_{C} (enol, CDCl₃) 175.1, 172.1, 142.8, 112.4, 90.7, 80.9, 26.7, 21.1. HRMS (EI): M^+ , found 170.0945. C₉H₁₄O₃ requires 170.0943.

Benzyl 3-Oxobutanoate (2f)^[21–23,25]

Viscous yellow liquid (0.69 g, 72% yield); keto (91%)–enol (9%); δ_{H} (keto, CDCl₃) 7.35–7.30 (m, 5H), 5.15 (s, 2H), 3.47 (s, 2H), 2.21 (s, 3H); δ_{H} (enol, CDCl₃) 12.05 (s, 1H), 7.35–7.30 (m, 5H), 5.15 (s, 2H), 5.04 (s, 1H), 1.93 (s, 3H); δ_{C} (keto, CDCl₃) 200.4, 166.9, 135.3, 128.5, 128.4, 128.1, 67.0, 49.9, 30.0; δ_{C} (enol, CDCl₃) 175.9, 172.3, 135.9, 128.5, 128.4, 128.1, 89.6, 65.6, 21.1. HRMS (EI): M^+ , found 192.0784. C₁₁H₁₂O₃ requires 192.0786.

Propargyl 3-Oxobutanoate (2g)^[13,14]

Yellow oil (0.55 g, 78% yield); keto (93%)–enol (7%); δ_{H} (keto, CDCl₃) 4.74 (s, 2H), 3.52 (s, 2H), 2.59 (s, 1H), 2.28 (s, 3H); δ_{H} (enol, CDCl₃) 11.8 (s, 1H), 5.05 (s, 1H), 4.74 (s, 2H), 2.59 (s, 1H), 1.95 (s, 3H); δ_{C} (keto, CDCl₃) 200.2, 166.4, 77.2, 75.5, 52.7, 49.6, 30.1; δ_{C} (enol, CDCl₃) 176.6, 171.5, 89.1, 76.7, 75.0, 50.1, 21.2. HRMS (EI): M^+ , found 140.0471. C₇H₈O₃ requires 140.0473.

2-Methylpropyl 3-Oxobutanoate (2h)^[23,24]

Yellow oil (0.59 g, 74% yield); keto (92%)–enol (8%); δ_{H} (keto, CDCl₃) 3.92 (d, *J* 6.0 Hz, 2H), 3.48 (s, 2H), 2.27 (s, 3H), 1.98–1.93 (m, 1H), 0.94 (d, *J* 6.0 Hz, 6H); δ_{H} (enol, CDCl₃) 12.08 (s, 1H), 5.01 (s, 1H), 3.92 (d, *J* 6.0 Hz, 2H), 1.98–1.93 (m, 4H), 0.94 (d, *J* 6.0 Hz, 6H); δ_{C} (keto, CDCl₃) 200.5, 167.2, 71.3, 50.0, 30.0, 27.5, 19.2; δ_{C} (enol, CDCl₃) 175.5, 172.7, 89.7, 69.9, 27.7, 21.1, 19.2. HRMS (EI): M^+ , found 158.0931. C₈H₁₄O₃ requires 158.0943.

Butyl 3-Oxobutanoate (2i)^[23–25,27]

Spectroscopic data of compound **2i** are in agreement with those reported in the literature.^[40,41] Yellow oil (0.63 g, 80% yield); keto (92%)–enol (8%); δ_{H} (keto, CDCl₃) 4.14 (t, *J* 6.0 Hz, 2H), 3.46 (s, 2H), 2.27 (s, 3H), 1.68–1.59 (m, 2H), 1.45–1.35 (m, 2H), 0.94 (t, *J* 6.0 Hz, 3H); δ_{H} (enol, CDCl₃) 12.11 (s, 1H), 4.99 (s, 1H), 4.14 (t, *J* 6.0 Hz, 2H), 1.95 (s, 3H), 1.68–1.59 (m, 2H), 1.45–1.35 (m, 2H), 0.94 (t, *J* 6.0 Hz, 3H); δ_{C} (keto, CDCl₃) 200.6, 167.3, 65.1, 49.8, 30.6, 30.0, 19.1, 13.9; δ_{C} (enol, CDCl₃) 175.5, 172.8, 89.7, 62.4, 30.8, 21.1, 19.1, 13.9.

Decanlyl 3-Oxobutanoate (2j)^[25]

Yellow oil (1.17 g, 97% yield); keto (91%)–enol (9%); δ_{H} (keto, CDCl₃) 4.05 (t, *J* = 6.0 Hz, 2H), 3.37 (s, 2H), 2.19 (s, 3H), 1.59–1.52 (m, 2H), 1.23–1.19 (m, 14H), 0.80 (t, *J* = 6.0 Hz, 3H); δ_{H} (enol, CDCl₃) 12.03 (s, 1H), 4.90 (s, 1H), 4.05 (t, *J* 6.0 Hz, 2H), 1.87 (s, 3H), 1.59–1.52 (m, 2H), 1.23–1.19 (m, 14H), 0.80 (t, *J* 6.0 Hz,

3H); δ_C (keto, $CDCl_3$) 200.2, 167.0, 65.3, 49.9, 31.5, 29.8, 29.4, 29.3, 29.1, 29.0, 28.4, 25.7, 22.5, 13.9; δ_C (enol, $CDCl_3$) 175.2, 172.5, 89.6, 63.9, 31.7, 29.4, 29.3, 29.1, 29.0, 28.4, 25.7, 22.5, 20.9, 13.9. HRMS (EI): M^+ , found 242.1883. $C_{14}H_{26}O_3$ requires 242.1882.

Cyclohexyl 3-Oxobutanoate (2k)^[21,23–25,27]

Yellow oil (0.77 g, 84% yield); keto (92%)–enol (8%); δ_H (keto, $CDCl_3$) 4.85–4.77 (m, 1H), 3.43 (s, 2H), 2.26 (s, 3H), 1.88–1.83 (m, 2H), 1.75–1.69 (m, 2H), 1.53–1.25 (m, 6H); δ_H (enol, $CDCl_3$) 12.1 (s, 1H), 4.96 (s, 1H), 4.85–4.77 (m, 1H), 1.94 (s, 3H), 1.88–1.83 (m, 2H), 1.75–1.69 (m, 2H), 1.53–1.25 (m, 6H); δ_C (keto, $CDCl_3$) 200.7, 166.6, 73.7, 50.4, 31.4, 30.0, 25.4, 23.6; δ_C (enol, $CDCl_3$) 175.2, 172.2, 90.2, 72.2, 31.7, 25.4, 23.6, 21.1. HRMS (EI): M^+ , found 184.1022. $C_{10}H_{16}O_3$ requires 184.1021.

Menthyl 3-Oxobutanoate (2l)^[21,23,24,27]

Yellow oil (1.18 g, 98% yield); keto (90%)–enol (10%); δ_H (keto, $CDCl_3$) 4.70–4.61 (m, 1H), 3.36 (s, 2H), 2.17 (s, 3H), 1.97–1.93 (m, 1H), 1.84–1.79 (m, 1H), 1.65–1.58 (m, 2H), 1.43–1.27 (m, 2H), 1.02–0.90 (m, 2H), 0.86–0.78 (m, 7H), 0.69 (d, J 9.0 Hz, 3H); δ_H (enol, $CDCl_3$) 12.1 (s, 1H), 4.88 (s, 1H), 4.70–4.61 (m, 1H), 1.97–1.93 (m, 1H), 1.91 (s, 3H), 1.84–1.79 (m, 1H), 1.65–1.58 (m, 2H), 1.43–1.27 (m, 2H), 1.02–0.90 (m, 2H), 0.86–0.78 (m, 7H), 0.69 (d, J 9.0 Hz, 3H); δ_C (keto, $CDCl_3$) 200.1, 166.4, 75.1, 50.2, 46.7, 40.5, 34.0, 31.2, 29.7, 26.0, 23.2, 21.8, 20.5, 16.0; δ_C (enol, $CDCl_3$) 175.1, 172.1, 89.8, 73.4, 46.9, 40.9, 34.1, 31.2, 26.2, 23.4, 21.8, 20.9, 20.5, 16.3. HRMS (EI): M^+ , found 240.1724. $C_{14}H_{24}O_3$ requires 240.1725.

FUNDING

We are grateful to the DGRST, Ministry of Higher Education, Tunisia, for financial support of this work.

SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher's website.

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