Pergamon

Tetrahedron 54 (1998) 13237–13252

TETRAHEDRON

Simple and High Yielding Syntheses of β-Keto esters Catalysed by Zeolites[§].

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Received 12 June 1998; revised 12 August 1998; accepted 19 August 1998

Abstract

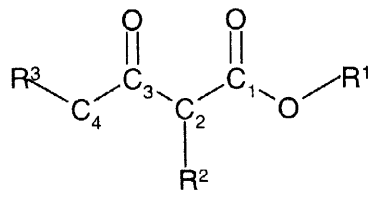
Simple and high yielding syntheses of several β-keto esters, catalysed by zeolite Hβ are reported. The methods developed include condensation of aldehydes with ethyl diazoacetate and transesterification of β-keto esters with primary, secondary, allylic and benzylic alcohols etc., all catalysed by Hβ. It was further observed that under microwave irradiation the yields of many aromatic β-keto esters were enhanced appreciably.

Key words: ethyl diazoacetate, β-keto esters, microwave irradiation, transesterification, zeolite

Introduction

β–Keto esters [1] are multicoupling reagents having electrophilic carbonyl and nucleophilic carbon which make them a valuable tool for the synthesis of complex molecules. They are one of the basic building blocks in the total synthesis of sex pheromones like serricornine [2] and other natural products like thiolactomycin [3], trichodiene [4], polyoximic acid [5], chokol [6], prostaglandin $PGF_{2\alpha}$ [7], *ar*–pseudotsugonoxide [8], syncarpic acid [9], diplodialide [10] and podophyllotoxin [11].

Many procedures for the synthesis of β-keto esters have been reported over a long time, but there exist many drawbacks and disadvantages necessitating improved methods for their synthesis. Of the many models of bond formation that exist for β-keto ester synthesis, two notable ones are C2-C3 bond formation and C1-O bond formation. The primary reactions involved in these are condensation of



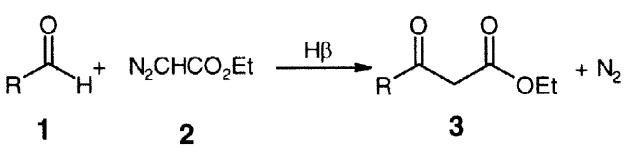
PII: S0040-4020(98)00804-7

aldehydes with ethyl diazoacetate and transesterification of β-keto esters with different alcohols. The subject matter in this paper revolves round these two important bond formations.

Some of the preliminary results of this study, i.e. synthesis of β-keto esters by condensation of aldehydes with ethyl diazoacetate catalysed by zeolites and by transesterification of β-keto esters with different alcohols also catalysed by zeolites, have been communicated recently [12,13]. In this paper, we present the full details of our work as well as the application of microwave irradiation to improve yields in some of the transesterification reactions.

(a) Condensation of aldehydes with ethyl diazoacetate

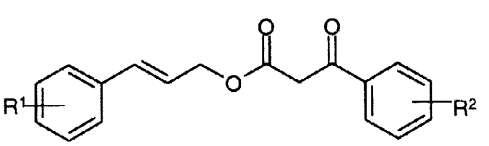
Several methods are available for the C2-C3 bond formation. The earlier works date back to 1980s when Fernandez et al. [14] and Pellicciari et al. [15] reported the condensation of aldehydes with ethyl diazoacetate. However, an improved method using a variety of Lewis-acids was later reported by Roskamp and Holmquist [16]. Similarly Mali et al. [17] reported a simple route to β-keto esters using activated alumina. The main drawback of all the earlier methods was the low yield of the corresponding β-keto esters when aromatic aldehydes were used as one of the substrates. A comparative study of Roskamp's and Mali's routes suggests that a judicious combination of Lewis-acid activity with surface activity in a catalyst would be an ideal route for β-keto ester synthesis. Such catalytic properties are found widely in microporous materials, especially zeolites [18]. Thus, the application of our idea of utilising zeolites for the condensation reaction worked well, resulting in an improved synthesis of β-keto esters. Of the various catalysts screened, Hβ was found to be the ideal catalyst for this condensation. Table 1 lists the β-keto esters **3a-q** obtained from corresponding aldehydes **1** according to the reaction represented in Scheme 1.



1 **2** **3**

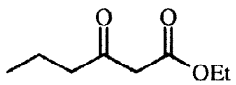
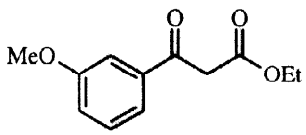
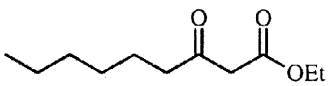
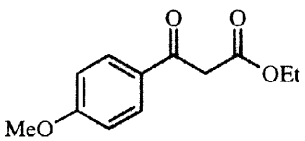
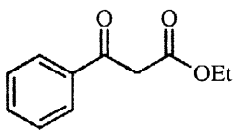
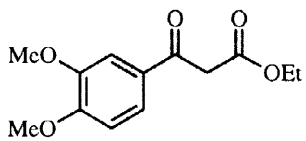
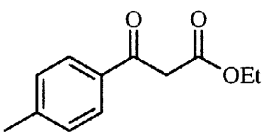
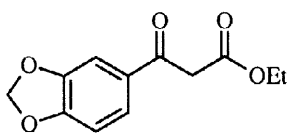
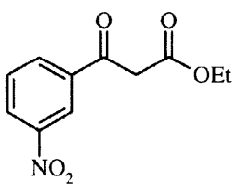
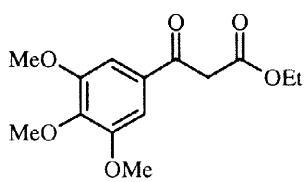
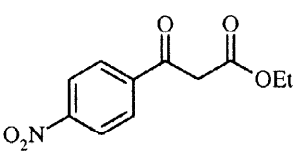
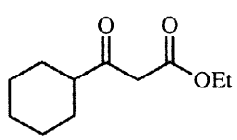
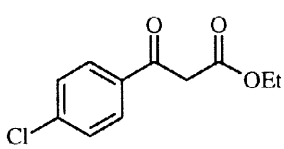
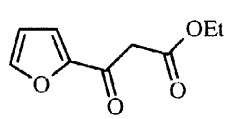
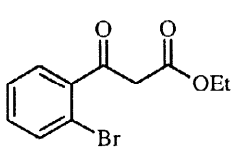
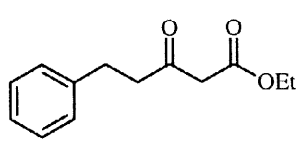
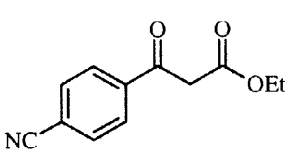
Scheme 1

A major limitation of the above route to β-keto esters is the accessibility of the required diazo esters. β-Keto esters such as **6g**, **6k**, **6l** were not obtainable [§] because of difficulties encountered in the preparation of the corresponding cinnamyl diazo esters.



6g $R^1 = R^2 = H$
6k $R^1 = H$, R^2 = 3,4,5-trimethoxy
6l R^1 = 3,4-methylenedioxy, R^2 = 3,4,5-trimethoxy

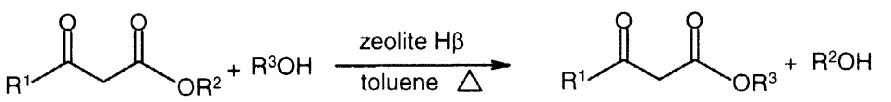
Table I. Condensation of ethyl diazoacetate with various aldehydes

	β-keto ester	Yield %		β-keto ester	Yield %
3a		>90	**3j**		62
3b		>90	**3k**		61
3c		72	**3l**		60
3d		76	**3m**		68
3e		85	**3n**		56
3f		71	**3o**		71
3g		74	**3p**		52
3h		81	**3q**		74
3i		84			

(b) Transesterification of β-keto esters with various alcohols catalysed by zeolites

An industrially important reaction, i.e. transesterification [19], was considered as an alternative method. Due to the fact that, β-keto acids can very readily undergo decarboxylation, a direct esterification method could not be successfully applied to β-keto ester synthesis. A simple and widely used method is based on reacting alcohols with "diketene". Alternatively a diketene free method to prepare β-keto esters is transesterification of acetoacetates in the presence of pTSA [20] or 4-DMAP [21] or distannoxanes [22] or solid super acids [23]. However, none of the methods mentioned above could be successfully applied to prepare **6g, 6k** and **6l**. Moreover, transesterification with allylic alcohols is rather difficult, since the product readily undergoes a decarboxylative rearrangement, i.e. Carroll rearrangement [24]. It has been reported by Keane [25], that the liquid phase hydrogenation of methyl acetoacetate in the presence of Ni-exchanged Y-zeolite proceeds with transesterification. However, by treating the catalyst with NH_3 or pyridine the transesterification reaction was suppressed.

Thus the area of transesterification with zeolite remained unexplored. In this regard application of zeolite Hβ for transesterification of β-keto ester was found to be advantageous and the reactions proceeded satisfactorily. Several alcohols could be used for transesterification by this simple and efficient method (**Scheme 2**) and the β-keto esters prepared by this procedure are listed in Table 2.



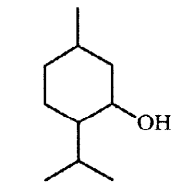
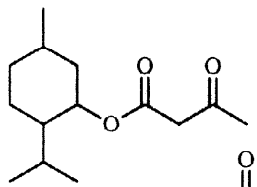
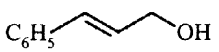
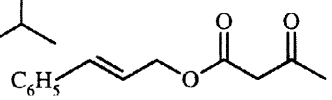
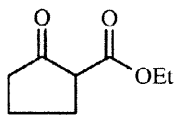
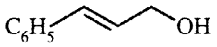
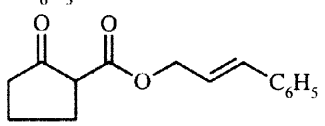
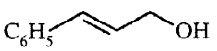
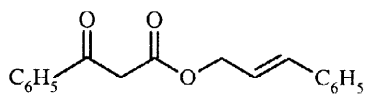
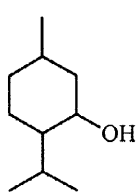
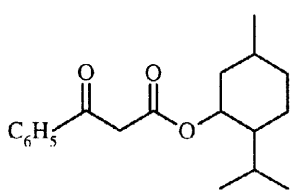
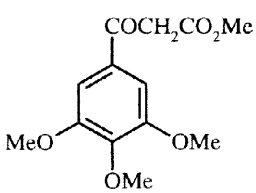
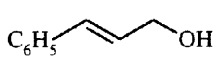
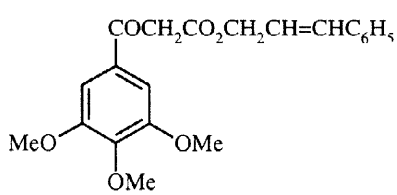
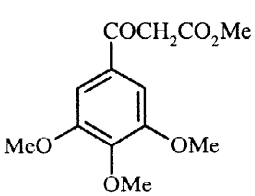
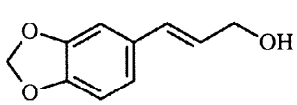
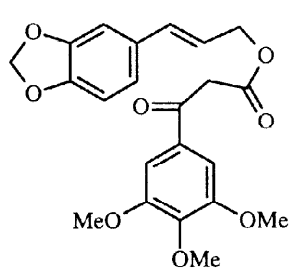
4 5 6

Scheme 2

Microwave assisted transesterification of β-keto esters

In order to improve the yields of transesterification of alkyl benzoylacetates **6g, 6h** it was felt worthwhile to explore the use of microwave irradiation. Microwave assisted organic reactions have attracted much attention in the past few years [26] and the MORE (Microwave-induced Organic Reaction Enhancement) chemistry has been developed by Bose et al. [27]. Microwave irradiation can be used as an efficient source for thermal energy which may lead to faster and cleaner reactions without thermal decomposition of product and minimisation of unwanted side reactions. Dry reaction conditions [28] often used in microwave induced reactions have several advantages. Using reagents supported on inorganic solid materials in the absence of solvent or the dry media conditions together with microwave irradiation leads to good results under very simple and safe conditions. Since solvents are not used at all, the waste disposal is minimal. The term "dry reaction conditions" used in microwave should not be confused with the "dry reaction conditions" of organic reactions. In the latter, it is the rigorous purification of solvents to exclude moisture whereas in the former it is the complete absence of solvent itself. The transesterification reactions, which gave only ~55-60 % of β-keto esters with solid catalysts were attempted first, with a view to improve the yields. It was gratifying to note that the reaction furnished more than 70-80 % of the corresponding products in 10-15 min as compared to a time of 8 h for thermal reactions (**Table 3**). Further, it was observed that, as in thermal reactions,

Table 2. Transesterification of various β-keto esters with alcohols

Substrate **4**	Alcohol **5**	Product **6**		Yield %
$CH_3COCH_2CO_2C_2H_5$	$C_6H_5(CH_2)_2OH$	$CH_3COCH_2CO_2(CH_2)_2C_6H_5$	**6a**	96
$CH_3COCH_2CO_2C_2H_5$	$C_{12}H_{25}OH$	$CH_3COCH_2CO_2C_{12}H_{25}$	**6b**	86
$CH_3COCH_2CO_2C_2H_5$	$C_6H_5CH_2OH$	$CH_3COCH_2CO_2CH_2C_6H_5$	**6c**	81
$CH_3COCH_2CO_2C_2H_5$			**6d**	95
$CH_3COCH_2CO_2C_2H_5$			**6e**	95
			**6f**	84
$C_6H_5COCH_2CO_2CH_3$			**6g**	66
$C_6H_5COCH_2CO_2CH_3$	$C_6H_5(CH_2)_3OH$	$C_6H_5COCH_2CO_2(CH_2)_3C_6H_5$	**6h**	64
$C_6H_5COCH_2CO_2CH_3$	$C_{12}H_{25}OH$	$C_6H_5COCH_2CO_2C_{12}H_{25}$	**6i**	71
$C_6H_5COCH_2CO_2CH_3$			**6j**	69
			**6k**	62
			**6l**	59

primary alcohols underwent transesterification faster than secondary alcohols. With a few primary alcohols (bromoethanol, chloroethanol) the reaction proceeded even in the absence of the catalyst.

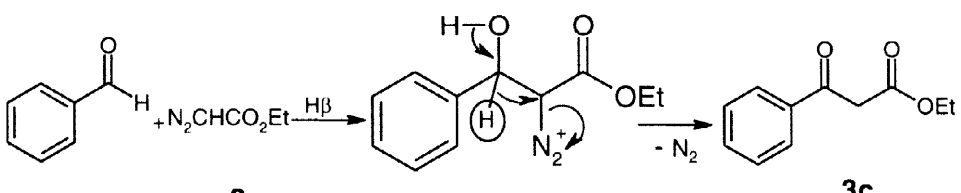
Table 3. Transesterification of β-keto esters under microwave irradiation

Entry	β–Keto ester	Alcohol	Thermal		Microwave	
			Time	Yield	Time	Yield
1	Methyl acetoacetate	3-Phenylpropanol	-	-	10 min	95
2	Ethyl benzoylacetate	Cinnamyl alcohol	8 h	66	13 min	78
3	Ethyl benzoylacetate	3-Phenylpropanol	8 h	64	15 min	80
4	Ethyl benzoylacetate	2-Ethoxyethanol	-	-	10 min	72
5	Ethyl benzoylacetate	2-Chloroethanol	-	-	11 min	70
6	Ethyl benzoylacetate	2-Bromoethanol	-	-	11 min	73
7	Ethyl benzoylacetate	2-Phenylethanol	-	-	10 min	80
8	Ethyl 3,4,5-trimethoxy-benzoylacetate	3-Phenylpropanol	-	-	15 min	69

Results and discussion

Due to simple manipulative operations with zeolite, the reactions of aromatic aldehydes with ethyl diazoacetate catalysed by zeolite was studied initially. All the previously described methods gave low yields of β–keto esters with aromatic aldehydes; it was thus felt worthwhile to study this reaction with heterogeneous catalysts, especially zeolites. Thus, the condensation of ethyl diazoacetate with benzaldehyde in the presence of H-ZSM-5 gave a product in 55% yield.

Encouraged by this modest yield with H-ZSM-5, other acidic zeolite like HY, Hβ etc. were tried with a view to increase the yield of the β–keto ester formed. Whereas an yield of 70% was obtained with HY, Hβ was found to be the ideal catalyst yielding more than 75% of the β–keto ester. Study of the reaction in the presence of various solvents suggested that 1,2-dichloroethane is ideal for the transformation.



Scheme 3

Progress in the knowledge of the mechanism of action of most solid catalyst still remains limited [29], due to the fact that the nature of the catalyst-reactant interactions are still uncertain. However, according to a plausible mechanism shown in **Scheme 3**, the formation of β–keto ester

proceeds via α-diazo-β-hydroxy ester intermediate **7** generated by the electrophilic attack of the species formed by the complexation of aldehyde with the acid sites of the catalyst on ethyl diazoacetate. The loss of nitrogen followed by 1,2- hydride shift is expected to lead to the observed β-keto ester.

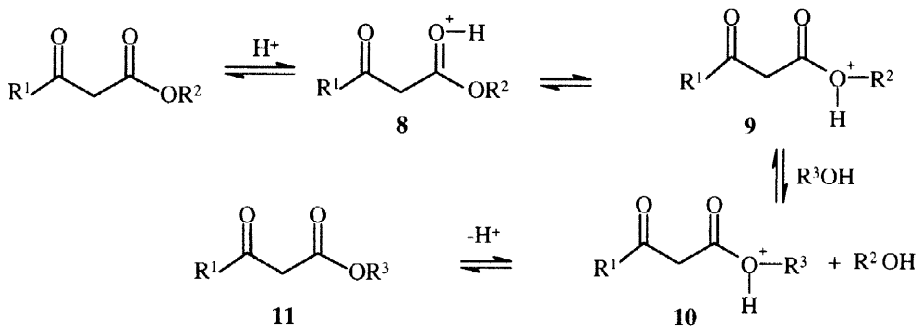
It was observed that neither α,β unsaturated aldehydes like cinnamaldehyde, hexadienal nor the ketones like acetophenone, cyclododecanone underwent condensation. A probable explanation may be that in the case of unsaturated aldehyde, due to the delocalisation, the carbonyl carbon is less electropositive. Hence it cannot form a complex with the acid sites of the catalyst and that makes the compound unreactive for condensation. In the case of ketones, because of the lower reactivity of ketones in comparison with aldehydes, the addition step leading to intermediate **7** is disfavoured. Hence they also did not undergo condensation. Similarly, attempted condensation of either diazomalonate or diazoacetylacetone did not yield any condensed product. Acidity of the catalyst is not sufficient enough to bring about the condensation as the electron withdrawing groups present in the diazo compounds stabilise the latter to a greater extent. The observed experimental results are in good agreement with the proposed mechanism.

Transesterification being an equilibrium process can be effected in the presence of acid catalysts, with efficient removal of the lower alcohol by azeotropic distillation. Use of solid heterogeneous catalysts like zeolites was invoked in the present work for this purpose, as our experience with such catalysts in β-keto ester synthesis has been very rewarding (**Scheme 1**). Additionally, zeolites which are essentially microporous aluminosilicates can be used as substitutes for molecular sieves in the effective removal of water, lower alcohols etc. Hence the utility of these catalysts in the present study has been explored in detail.

The yields of the products **6g- 6l (Table 2)** obtained from benzoylacetates are moderate only; this may be attributed to the bulkiness of the substrate. Higher acid strength of Hβ (*vis-a-vis* Y type zeolite) coupled with large pore openings and void space (*vis-a-vis* ZSM-5, ZSM-12) may be responsible for its better activity.

In order to understand and attribute the reasons for low yields associated with the transesterification of benzoylacetate, the basic principles underlying the acidity [30] of zeolite should be considered. The Bronsted acidity of solid acid is the ability to donate or at least partially transfer a proton which comes in contact with the surface anions.

In a catalytic reaction diffusion of reactant through the zeolite micropores to reach an active site, adsorption of the reactants on the active sites, chemical reaction to give the adsorbed product, desorption of the product and finally diffusion of the product through the zeolite channels takes place. It is therefore the bulkiness of the product, which makes it unable to come out through the pores, resulting in moderate yield of the reactions of benzoylacetates. Due to the presence of Lewis and Bronsted acidity, it is still not clear whether transesterification is a surface catalysed reaction or a pore selective reaction. A probable mechanism for the transesterification is represented in Scheme 4.



Scheme 4

The β-keto ester complexes with the acid sites of the catalyst which is followed by the nucleophilic attack of the alkoxide and elimination of H^+ to yield **11**. In support of the postulated mechanism, attempts were made to transesterify various esters with alcohols. Esters like aromatic (methyl benzoate), α,β unsaturated (ethyl cinnamate), α-halo (ethyl bromoacetate), saturated (methyl butanoate), α-keto (methyl pyruvate) and γ-keto (methyl levulinate) were selected. However, none of these esters could be transesterified. The difference in reactivity of β-keto esters from that of the other esters in transesterification may probably be due to the formation of an acyl ketene intermediate in the former as proposed by Campbell and Lawrie [31]. None of the other esters has the possibility of forming a 6-membered intermediate which can stabilise the charge polarisation. It is therefore the typical enol form of the β-keto ester which enables it to undergo facile and efficient transesterification with various alcohols.

Conclusion

A facile and efficient preparation of β-keto esters by the condensation of ethyl diazoacetate with aldehydes using zeolite as the catalyst has been achieved. Even with the less reactive aromatic aldehydes, this method has been shown to improve the yields of the corresponding β-keto esters considerably. The methodology avoids use of strong bases that are normally employed in conventional methods. The catalysts are easy to separate by simple filtration and are recycled at least three times without much loss in their activity. The catalysts are associated with minimum environmental hazards. In the case of transesterification of primary and secondary alcohols with alkyl acetoacetates, excellent yields have been obtained (>90 %). For the first time, aromatic β–keto esters **6g, 6k** and **6l** have been prepared *via* transesterification, although the yields are only moderate (50-60 %), which may be attributed to their steric bulk. Transesterification has been found to be very selective for β-keto esters: other esters like α-keto, γ-keto, α–halo and saturated and unsaturated esters were not transesterified. Several catalysts with Lewis-acid acidity like HY, Hβ, H-ZSM-5, H-ZSM-12, Re-Y were screened and Hβ was found to be the best catalyst for the present work. It has been demonstrated that under microwave irradiation conditions, transesterification of β-keto esters with different alcohols proceeds with higher yields, in a very short reaction time and avoids the use of aromatic solvents that are generally employed in thermal reactions. This ideal situation of "dry reaction conditions" enables minimum waste and offers an environmentally friendly procedure.

Experimental

General remarks

All solvents were distilled prior to use. Petroleum ether refers to the fraction collected in the boiling range 60-80°C. The IR spectra were recorded on Perkin-Elmer spectrophotometer model 683B or 1605 FT-IR. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker WH-90 and Bruker AC-200 instruments using tetramethylsilane as the internal standard using $CDCl_3$ as solvent. The mass spectra were recorded on Finnigan MAT-1020-B-70eV mass spectrometer. Microwave irradiations were carried out in a Batliboi Eddy domestic microwave oven model No. ER 5054D operating at 2450 MHz. Reactions were performed at 70 % of its full power. Ethyl diazoacetate was prepared according to literature procedure [32]. Commercially available zeolite Hβ was used for the reactions. Activation of the catalyst was carried out prior to use. The **^{1}H NMR** values within the bold square bracket represents the chemical shifts due to the keto and enolic forms of the methylene protons.

General procedure for condensation of ethyl diazoacetate with aldehydes

A solution of the aldehyde (5.0 mmol) and ethyl diazoacetate (7.5 mmol) in dichloroethane (10 ml) containing zeolite Hβ (50 mg, 10 % w/w) was refluxed for 8 h under N_2 atm. The catalyst was recovered by filtration and distillation of solvent under reduced pressure furnished the crude material. It was purified by silicagel column chromatography.

Ethyl 3-oxohexanoate 3a [33]

Yield: 742 mg (94 %). **IR** (neat) cm^{-1}: 1730, 1700, 1470. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 4.2 (q, J=7 Hz, 2H), 3.3 (s, 2H), 2.4-2.1 (m, 4H), 1.2-1.0 (m, 6H).

Ethyl 3-oxononanoate 3b [34]

Yield: 930 mg (93 %). **IR** (neat) cm^{-1}:1735, 1695, 1450. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 4.15 (q, J=7 Hz, 2H), 3.27 (s, 2H), 2.45 (t, J=7 Hz, 2H), 1.4-1.1 (br, 11H), 0.9-0.8 (m, 3H).

Ethyl 3-phenyl-3-oxopropanoate 3c [35]

Yield: 691 mg (72 %). **IR** (neat) cm^{-1}: 3340, 1735, 1690, 1590. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 8.1-8.0 (m, 2H), 7.8-7.4 (m, 3H), 4.23-4.15 (m, 2H), [4.0,5.7,12.3] (s, 2H), 1.3-1.15 (m, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 192.25 (s), 167.17 (s), 135.79 (s), 133.29 (d), 128.67 (d), 128.40 (d), 125.68 (d), 87.05 (enolic), 60.85 (t), 45.48 (t), 13.66 (q).

Ethyl 3-(4-methylphenyl)-3-oxopropanoate 3d [35]

Yield: 783 mg (76 %). **IR** (neat) cm^{-1}: 3320, 1735, 1700, 1595. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.9-7.2 (m, 4H), 4.20-4.1 (m, 2H), [4.0,5.6,12.6] (s, 2H), 2.40 (s, 3H), 1.26-1.15 (m, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 191.64 (s), 167.16 (s), 144.09 (s), 133.62 (s), 128.06 (d), 126.29 (d), 86.32 (enolic), 60.74 (t), 60.54 (t), 45.42 (t), 21.05 (q), 13.68 (q), 13.50 (q).

Ethyl 3-(3-nitrophenyl)-3-oxopropanoate 3e [36]

Yield: 1.007 gm (85 %). **M.Pt**: 78-80°C (Lit. [36] 78-79°C). **IR** (nujol) cm^{-1}: 3310, 1740, 1700, 1595, 1540. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 8.1-7.9 (m, 2H), 7.6-7.3 (m, 2H), 4.1 (q, J= 7Hz, 2H), [3.9,5.7,12.6] (s, 2H), 1.1 (t, J= 7Hz, 2H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 190.55 (s), 165.78 (s), 147.70 (s), 135.09 (s), 132.80 (d), 128.89 (d), 123.85 (d), 121.74 (d), 88.99 (enolic), 61.25 (t), 45.64 (t), 13.58 (q).

Ethyl 3-(4-nitrophenyl)-3-oxopropanoate 3f [36]

Yield: 841 mg (71 %). **M.Pt.**: 70-72°C (Lit. [36]. 70-73°C). **IR** (nujol) cm^{-1}: 3315, 1735, 1710, 1590, 1530. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 8.4-7.9 (m, 4H), 4.25-4.1 (m, 2H), [4.0,5.7,12.6] (s, 2H), 1.28-1.1 (m, 3H).

Ethyl 3-(4-chlorophenyl)-3-oxopropanoate 3g [37]

Yield: 839 mg (74 %). **IR** (neat) cm^{-1}: 1750, 1715, 1590, 810. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.9-7.3 (m, 4H), 4.2-4.1 (m, 2H), [4.0,5.6,12.5] (s, 2H), 1.35-1.2 (m, 3H).

Ethyl 3-(2-bromophenyl)-3-oxopropanoate 3h

Yield: 1.098 gm (81 %). **IR** (neat) cm^{-1}: 3310, 1730, 1710, 1030, 900. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.4-7.0 (m, 3H), 4.05 (q, J= 7.4Hz, 2H), [3.9,5.2,12.1] (s, 2H), 1.0 (t, J=7.4Hz, 3H).

Ethyl 3-(4-cyanophenyl)-3-oxopropanoate 3i [38]

Yield: 911 mg (84 %). **M.Pt.**: 63°C (Lit. [38] 63-64°C). **IR** (nujol) cm^{-1}: 2240, 1740, 1700, 1260. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.2 (s, 4H), 4.1 (q, J= 8Hz, 2H), [3.9,5.4,12.1] (s, 2H), 1.0 (t, J=8Hz, 3H).

Ethyl 3-(3-methoxyphenyl)-3-oxopropanoate 3j

Yield: 679 mg (62 %). **IR** (neat) cm^{-1}: 3320, 1730, 1695, 1590. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.4-6.8 (m, 4H), 4.1 (q, J= 7Hz, 2H), 3.75 (s, 3H), [3.9,5.5,12.3] (s, 2H), 1.2 (t, J= 7Hz, 3H).

Ethyl 3-(4-methoxyphenyl)-3-oxopropanoate 3k [35]

Yield: 677 mg (61 %). **IR** (neat) cm^{-1}: 3300, 1725, 1695, 1590, 1420. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.4-6.9 (m, 4H), 4.1-4.0 (m, 2H), [3.9,5.6,12.6] (s, 2H), 3.8 (s, 3H), 1.2-1.0 (m, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 190.92 (s), 167.65 (s), 163.90 (s), 131.8 (s), 130.9 (d), 130.75 (d), 114.21 (d), 113.81 (d), 61.11 (t), 55.34 (q), 45.55 (t), 13.91 (q).

Ethyl 3-(3,4-dimethoxyphenyl)-3-oxopropanoate 3l

Yield: 756 mg (60 %). **IR** (neat) cm^{-1}: 3310, 1730, 1695, 1595. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.3-7.2 (m, 2H), 6.9 (d, J= 8Hz, 1H), 4.1 (q, J= 8Hz, 2H), 3.9 (s, 8H), 1.0 (t, J= 8Hz, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 191.03 (s), 167.71 (s), 153.87 (s), 149.19 (s), 129.30 (s), 126.70 (d), 123.51 (d), 110.50 (d), 61.32 (t), 56.10 (q), 55.92 (q), 45.64 (t), 14.06 (q).

Ethyl 3-(3,4-methylenedioxyphenyl)-3-oxopropanoate 3m [17]

Yield: 802 mg (68 %). **M.Pt.**: 41°C (Lit. [17] 41°C). **IR** (nujol) cm^{-1}: 1740, 1680, 1635. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.60-7.55 (m, 1H), 7.45 (d, J= 7Hz, 1H), 6.95 (d, J= 7Hz, 1H), 6.05 (s, 2H), 4.25 (q, J= 7.4Hz, 2H), [3.95,5.6,12.6] (s, 2H), 1.24 (t, J= 7.4Hz, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 190.61 (s), 167.66 (s), 152.40 (s), 148.43 (s), 130.97 (s), 125.19 (d), 108.05 (d), 108.00 (d), 102.12 (t), 61.40 (t), 45.82 (t), 14.09 (q).

Ethyl 3-(3,4,5-trimethoxyphenyl)-3-oxopropanoate 3n

Yield: 790 mg (56 %). **IR** (neat) cm^{-1}: 3315, 1735, 1700, 1590. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.0 (s, 2H), 4.1 (q, J= 8Hz, 2H), 3.8 (s, 9H), [3.75,5.5,12.4] (s, 2H), 1.3 (t, J= 8Hz, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 191.31 (s), 167.58 (s), 153.21 (s), 143.39 (s), 131.26 (s), 106.90 (d), 106.31 (d), 61.48 (t), 60.90 (q), 56.33 (q), 46.04 (t), 14.11 (q). **Mass** (70 eV) m/z: 282 (M^+), 283 (M+1), 267, 253, 236, 221, 209, 195 (base peak), 181, 167, 152, 137, 122, 107, 95, 77.

Ethyl 3-(3-cyclohexyl)-3-oxopropanoate 3o [16]

Yield: 703 mg (71 %). **IR** (neat) cm^{-1}: 1730, 1700, 1450, 1000. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 4.2 (q, J= 7Hz, 2H), 3.45 (s, 2H), 2.7-2.6 (m, 1H), 1.9-1.7 (m, 4H), 1.6-1.1 (m, 6H), 1.0 (t, J= 7Hz, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 205.66 (s), 167.39 (s), 61.10 (t), 50.77 (d), 47.28 (t), 28.17 (t), 25.14 (t), 25.30 (t), 14.06 (q). **Mass** (70 eV) m/z: 198 (M^+), 180, 151, 143, 130, 125, 111, 105, 95, 87, 81, 67, 55 (base peak).

Ethyl 3-(2-furanyl)-3-oxopropanoate 3p

Yield: 473 mg (52 %). **IR** (neat) cm^{-1}: 3315, 1742, 1695. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.6-7.5 (m, 1H), 6.6-6.5 (m, 2H), 4.15 (q, J= 6Hz, 2H), [3.8,5.4,12.4] (s, 2H), 1.3 (t, J= 6Hz, 3H).

Ethyl 5-phenyl-3-oxopentanoate 3q [16]

Yield: 814 mg (74 %). **IR** (neat) cm^{-1}: 3300, 1735, 1695. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.3-7.1 (m, 5H), 4.2 (q, J= 7Hz, 2H), [3.6,5.5,12.4], (s, 2H), 3.2-3.0 (m, 2H), 2.8-2.6 (m, 2H), 1.2 (t, J= 7Hz, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 202.60 (s), 168.05 (s), 141.74 (s), 128.58 (d), 127.98 (d), 123.93 (d), 82.60 (enolic), 62.13 (t), 47.35 (t), 37.58 (t), 29.01 (t), 13.98 (q).

Transesterification of β–keto ester with various alcohols

General procedure:

In a typical experiment 5 mmol of the β–keto ester and 5 mmol of the alcohol were dissolved in dry toluene (25 ml) to which 10 % (w/w of β–keto ester) of the catalyst was added. The resultant mixture was heated to 110°C (bath temp.) with azeotropic removal of ethanol/methanol. After 8 h the reaction mixture was cooled, the catalyst was filtered off and washed with more solvent (10 ml). The combined organic solvent was removed under reduced pressure. Purification by column chromatography yielded the product.

2-Phenylethyl 3-oxobutanoate 6a

Yield: 989 mg (96 %). **IR** (neat) cm^{-1}: 3310,1729,1690. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.3-7.2 (m, 5H), 4.3 (t, J= 7Hz, 2H), [3.2, 4.9, 12.5] (s, 2H), 2.9 (t, J= 7Hz), 2.2 (s, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 200.38(s), 166.91 (s), 137.40 (s), 128.73 (d), 128.39 (d), 126.49 (d), 89.2 (enolic), 65.48 (t), 49.71 (t), 34.72 (t), 29.75 (q). **Mass** (70 eV) m/z: 220 (M^+), 136, 117 (base peak), 104, 91, 85, 77, 65, 57.

Dodecyl 3-oxobutanoate 6b

Yield: 1.161 gm (86 %). **IR** (neat) cm^{-1}: 3300,1740,1700. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 4.0 (t, J= 6.8Hz, 2H), [3.4, 4.9, 12.2] (s, 2H), 2.2 (s, 3H), 1.3-1.1 (m, 20H), 0.85-0.75 (m, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 199.80 (s), 166.83 (s), 89.39 (enolic), 64.99 (t), 49.64 (t), 31.74 (t), 29.49 (t), 29.18 (t), 29.06 (t), 28.35 (t), 25.65 (t), 22.47 (t), 20.68 (q), 13.80 (q).

Benzyl 3-oxobutanoate 6c

Yield: 778 mg (81 %). **IR** (neat) cm^{-1}: 3320,1738,1695. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.3-7.1 (m, 5H), 5.1 (s, 2H), 3.45 (s, 2H), 2.2 (s, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 200.19 (s), 166.81 (s), 135.37 (s), 128.43 (d), 128.22 (d), 128.14 (d), 66.76 (t), 49.70 (t), 29.73 (q).

5-Methyl-2-(1-methylethyl)cyclohexyl 3-oxobutanoate 6d

Yield: 1.140 gm (95 %). **IR** (neat) cm^{-1}: 3320,1738,1695. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 4.75 (dt, J= 12 and 6 Hz, 1H), [3.45, 4.9, 12.2] (s, 2H), 2.25 (s, 3H), 2.1-1.9 (m, 3H), 1.75-1.65 (m, 2H), 1.5-1.4 (m, 2H), 1.2-0.9 (m, 10H), 0.85 (d, J= 6Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): 199.70 (s), 166.22 (s), 89.49 (enolic), 74.60 (d), 49.86 (t), 46.56 (d), 40.38 (t), 33.87 (t), 31.02 (d), 29.36 (q), 25.74 (d), 23.01 (t), 21.59 (q), 20.30 (q), 15.78 (q).

(E)-3-Phenyl-2-propenyl 3-oxobutanoate 6e

Yield: 1.036 gm (95 %). **IR** (neat) cm^{-1}: 3320,1738,1695. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.4-7.2 (m, 5H), 6.65 (d, J= 15Hz, 1H), 6.3-6.2 (m, 1H), 4.8 (dd, J= 6.4 and 1 Hz, 2H), 3.45 (s, 2H), 2.2 (s, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 200.30 (s), 166.89 (s), 136.12 (s), 134.77, (d), 128.66 (d), 128.23 (d), 126.71 (d), 122.59 (d), 65.84 (t), 49.99 (t), 30.12 (q). **Mass** (70 eV) m/z: 218 (M^+), 200, 168, 160, 133, 117 (base peak), 105, 91, 85, 77, 69, 65, 55.

(E)-3-Phenyl-2-propenyl 2-oxocyclopentanecarboxylate 6f

Yield: 1.025 gm (84 %). **IR** (neat) cm^{-1}: 3320,1738,1695. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 7.4-7.3 (m, 5H), 6.70 (d, J= 15Hz, 1H), 6.3-6.2 (m, 1H), 4.8 (dd, J= 6.4 and 1 Hz, 2H), 4.2-4.1 (m, 1H), 3.2 (t, J= 9Hz, 2H), 2.5-2.0 (m, 4H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 211.95 (s), 169.05 (s), 136.04 (s), 133.99 (d), 128.44 (d), 127.91 (d), 126.49 (d), 122.70 (d), 65.53 (t), 54.58 (d), 37.80 (t), 27.22 (t), 20.74 (t). Analysis for $C_{15}H_{16}O_3$ (244.29). Calculated C 73.75, H 6.60. Observed C 73.46, H 6.38.

(E)-3-Phenyl-2-propenyl 3-oxo-3-3-phenylpropanoate 6g

Yield: 924 mg (66 %). **IR** (neat) cm^{-1}: 3320,1738,1690,1579. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 8.0 (dd, J= 7 and 1.4 Hz, 2H), 7.7-7.4 (m, 8H), 6.85 (d, J= 14Hz, 1H), 6.4-6.3 (m, 1H), 4.9 (dd, J= 4 and 1.2 Hz, 2H), [4.1,5.75,12.55] (s, 2H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 192.35 (s), 167.26 (s), 136.16 (s), 136.02 (s), 134.22 (d), 128.73 (d), 128.47 (d), 128.25 (d), 126.64 (d), 122.70 (d), 87.2 (enolic), 65.73 (t), 45.75 (t). **Mass** (70 eV) m/z: 280(M^+), 252, 206, 192, 146, 133, 117, 105, 91, 77 (base peak), 69, 65, 55.

3-Phenylpropyl 3-oxo-3-phenylpropanoate 6h

Yield: 902 mg (64 %). **IR** (neat) cm^{-1}: 3325,1740,1687, 1625, 1579. **^{1}H NMR** δ (90 MHz, $CDCl_3$): 8.0 (dd, J= 7 and 1.6 Hz, 2H), 7.5-7.4 (m, 3H), 7.3-7.15 (m, 5H), 4.25 (t, J= 6Hz, 2H), [4.0,5.7,12.6] (s, 2H), 2.65 (t, J= 6Hz, 2H), 2.1-2.0 (m, 2H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 192.22 (s), 167.21 (s), 140.85 (s), 135.82 (s), 133.40 (d), 128.51 (d), 128.18 (d), 125.75 (d), 87.08 (enolic), 64.26 (t), 45.57 (t), 31.64 (t), 29.73 (t). Analysis for $C_{18}H_{18}O_3$ (282.34). Calculated C 76.57, H 6.43. Observed C 76.34, H 6.24.

Dodecyl 3-oxo-3-phenylpropanoate 6i

Yield: 1.180 gm (71 %). **IR** (neat) cm^{-1}: 3320,1740,1695,1590. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 8.0 (dd, J=7 and 1.4 Hz, 2H), 7.4-7.2 (m, 3H), 4.05 (t, J= 7Hz, 2H), 3.8 (s, 2H), 1.3-1.0 (m, 20 H), 0.9-0.7 (m, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): 191.91 (s), 167.15 (s), 133.27 (s), 128.46 (d), 128.30 (d), 125.84 (d), 87.03 (enolic), 65.12 (t), 45.68 (t), 31.82, 29.57 (q), 29.27 (t), 29.10 (t), 28.41 (t), 25.67 (t), 22.57 (t), 13.92 (q). Analysis for $C_{21}H_{32}O_3$ (332.49). Calculated C 75.86, H 9.70. Observed C 76.03, H 9.91.

5-Methyl-2-(1-methylethyl)cyclohexyl 3-oxo-3-phenylpropanoate 6j

Yield: 1.043 gm (69 %). **IR** (neat) cm^{-1}: 3320,1730,1698, 1595. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 8.0 (dd, J=7 and 1.6 Hz, 2H), 7.6-7.4 (m, 3H), 4.75 (dt, J=12 and 6 Hz, 1H), [4.0,5.65,12.6] (s, 2H), 2.1-1.9 (m, 3H), 1.75-1.65 (m, 2H), 1.5-1.4 (m, 2H), 1.2-0.9 (m, 10H), 0.85 (d, J=6 Hz, 3 H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 192.02 (s), 166.70 (s), 136.00 (s), 133.28 (s), 128.46 (d), 128.25 (d), 125.80 (d), 87.35 (enolic), 75.04 (d), 46.66 (d), 46.18 (t), 40.44 (t), 33.99 (t), 31.15 (d), 25.74 (d), 23.01 (t), 21.78 (q), 20.50 (q), 15.88 (q). **Mass** (70 eV) m/z: 302 (M^+), 280, 272, 259, 208, 165, 147, 138, 122, 105 (base peak), 95, 91, 81, 77.

(E)-3-Phenyl-2-propenyl 3-(3,4,5-trimethoxyphenyl)-3-oxopropanoate 6k

Yield: 1.148 gm (62 %). **IR** (neat) cm^{-1}: 3320,1738,1695. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.5-7.4 (m, 5H), 7.35 (s, 1H), 7.25 (s, 1H), 6.70 (d, J=15 Hz, 1H), 6.35-6.25 (m, 1H), 4.8 (dd, J=6 and 1.2 Hz, 2H), 4.05,3.95 (s, 9H), [3.85,5.6,12.4] (s, 2H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 191.04 (s), 167.28 (s), 153.10 (s), 143.21 (s), 136.01 (s), 134.47 (d), 131.08 (s), 128.55 (d), 128.10 (d), 126.54 (d), 122.51 (d), 106.15 (d), 86.72 (enolic), 65.84 (t), 60.81 (q), 56.2 (q), 45.92 (t). Analysis for $C_{21}H_{22}O_6$ (370.41). Calculated C 68.10, H 5.99. Observed C 67.84, H 5.65.

(E)-3-(3,4-Methylenedioxyphenyl)-2-propenyl 3-(3,4,5-trimethoxyphenyl)-3-oxopropanoate 6l
Yield: 1.223 gm (59 %). **IR** (neat) cm^{-1}: 3320,1738,1695. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.2 (s, 2H), 6.95 (s, 1H), 6.75-6.7 (m, 2H), 6.6 (d, J=14 Hz, 1H), 6.2-6.1 (m, 1H), 5.95 (s, 2H), 4.8 (dd, J=6 and 1.2 Hz, 2H), 4.05,3.95 (two s, 11H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 191.03 (s), 167.27 (s), 153.02 (s), 147.95 (s), 147.58 (s), 143.10 (s), 134.25 (d), 131.01 (s), 130.35 (s), 121.41 (d), 120.57 (d), 108.11 (d), 106.07 (d), 105.62 (d), 101.08 (t), 87.4 (enolic), 65.87 (t), 60.70 (q), 56.10 (q), 45.82 (t). Analysis for $C_{22}H_{22}O_8$ (414.42). Calculated C 63.76, H 5.35. Observed C 63.52, H 5.42.

Microwave assisted transesterification

General procedure

2.5 mmol of β–keto ester and 2.5 mmol of the corresponding alcohol were mixed in a 5 ml round bottomed flask. To this neat mixture 10 % (w/w of β–keto ester) of the catalyst was added. The reactants were thoroughly mixed and kept for irradiation for 10-15 min. After the reaction was over (as monitored by TLC) the reaction mixture was cooled, diluted with dichloromethane and the catalyst was filtered off. Removal of the solvent under reduced pressure yielded practically pure transesterified product.

2-Chloroethyl 3-oxo-3-phenylpropanoate
Yield: 397 mg (70 %). **IR** (neat) cm^{-1}: 3320, 1724, 1690, 810. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 8.1-8.0 (m, 2H), 7.6-7.5 (m, 1H), 7.45-7.35 (m, 2H), 4.4 (t, J=7 Hz, 2H), [4.05,5.75,12.35] (s, 2H), 3.75 (t, J=7 Hz, 2H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 192.00 (s), 167.06 (s), 135.70 (s), 133.68 (d), 128.65 (d), 128.31 (d), 125.97 (d), 86.68 (enolic), 64.60 (t), 45.40 (t), 41.29 (t). **Mass** (70 eV) m/z: 228 (M+2), 226 (M^+), 220, 203, 190, 164, 146, 113, 105 (base peak), 91, 77, 69, 63.

2-Bromoethyl 3-oxo-3-phenylpropanoate
Yield: 495 (73 %). **IR** (neat) cm^{-1}: 3310, 1730, 1685, 690. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 8.1-8.0 (m, 2H), 7.7-7.45 (m, 3H), 4.5 (t, J=7 Hz, 2H), [4.0,5.7,12.4] (s, 2H), 3.55 (t, J=7 Hz, 2H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 192.26 (s), 167.16 (s), 136.13 (s), 133.90 (d), 128.97 (d), 128.79 (d), 126.31 (d), 87.05 (enolic), 64.70 (t), 45.70 (t), 28.79 (t). Analysis for $C_{11}H_{11}BrO_3$ (271.11). Calculated C 48.73, H 4.09, Br 29.47. Observed C 48.51, H 4.1, Br 29.01.

2-Ethoxyethyl 3-oxo-3-phenylpropanoate
Yield: 425 mg (72 %). **IR** (neat) cm^{-1}: 3310, 1735, 1690, 1595, 1420. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 8.0-7.9 (m, 2H), 7.7-7.35 (m, 3H), 4.35-4.25 (m, 2H), [3.9,5.7,12.6] (s, 2H), 3.7-3.6 (m, 2H), 3.35 (q, J=7 Hz, 2H), 1.25 (t, J=7 Hz, 3H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 191.61 (s), 166.81 (s), 135.63 (s), 133.07 (d), 128.21 (d), 128.09 (d), 125.57 (d), 86.75 (enolic), 67.55 (t), 65.83 (t), 63.87 (t), 45.15 (t), 14.16 (q).

2-Phenylethyl 3-oxo-3-phenylpropanoate

Yield: 536 mg (80 %). **M.Pt.**: 67°C. **IR** (nujol) cm^{-1}: 3315, 1740, 1690, 1595, 1410. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 8.1-8.0 (m, 2H), 7.6-7.4 (m, 4H), 7.35-7.2 (m, 4H), 4.4 (t, J=7 Hz, 2H), [3.9,5.7,12.6] (s, 2H), 3.0 (t, J=7 Hz, 2H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 192.31 (s), 167.36 (s), 137.52 (s), 133.65 (s), 128.82 (d), 128.75 (d), 128.47 (d), 126.56 (d), 87.28 (enolic), 65.76 (t), 45.76 (t), 34.86 (t). **Mass** (70 eV) m/z: 268(M^+), 250, 233, 219, 209, 179, 164, 146, 122, 105 (base peak), 91, 77.

3-Phenylpropyl 3-oxo-3-(3,4,5-trimethoxyphenyl)propanoate

Yield: 642 (69 %). **IR** (neat) cm^{-1}: 3320,1740,1690. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.25-7.15 (m, 7H), 4.25 (t, J=7 Hz, 2H), [3.8,5.7,12.6] (s, 2H), 3.95,3.85 (two s, 9H), 2.65 (t, J=7 Hz, 2H), 2.1-1.9 (m, 2H). **^{13}C NMR** (50 MHz, $CDCl_3$): 191.04 (s), 167.37 (s), 152.97 (s), 143.03 (s), 140.79 (s), 131.00 (s), 128.17 (d), 125.79 (d), 105.98 (d), 64.37 (t), 60.58 (q), 56.00 (q), 45.74 (t), 31.66 (t), 29.90 (t). Analysis for $C_{21}H_{24}O_6$ (372.42). Calculated C 67.73, H 6.50. Observed C 67.51, H 6.42.

3-Phenylpropyl 3-oxobutanoate

Yield: 523 mg (95 %). **IR** (neat) cm^{-1}: 1740, 1695, 1590. **^{1}H NMR** δ (200 MHz, $CDCl_3$): 7.3-7.2 (m, 5H), 4.2 (t, J=7 Hz, 2H), 3.5 (s, 2H), 2.7 (t, J=7 Hz, 2H), 2.25 (s, 3H), 2.1-1.9 (m, 2H). **^{13}C NMR** δ (50 MHz, $CDCl_3$): 200.26 (s), 166.88 (s), 140.86 (s), 128.21 (d), 125.81 (d), 89.6 (enolic), 64.26 (t), 49.64 (t), 31.77 (t), 29.86 (t), 29.75 (q). **Mass** (70 eV) m/z: 220(M^+), 136, 117 (base peak), 105, 91, 85, 77, 65, 57.

One of the authors (B.S.B) thanks CSIR, INDIA for a senior research fellowship. We thank Dr. T. Ravindranthan, Dr. H.R. Sonawane for helpful discussions and also Dr. S.G. Sudrik for assistance. We also thank Dr. Rajiv Kumar and Dr. A. P. Singh for providing the catalysts.

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