Organocatalytic γ-oxidation of α,β-unsaturated aldehydes

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Abstract
Direct, organocatalytic γ-oxidation of α,β-unsaturated aldehydes via dienamine catalysis has been developed. The reaction of 2-hexenal with dibenzoyl peroxide (BPO) catalyzed by the MacMillan catalyst gave desired γ-benzoyloxy aldehyde in a moderate yield, notably the formation of α-substituted product was greatly suppressed. γ-Benzoyloxy-α,β-unsaturated aldehyde turned out to be a useful building block in the synthesis of highly functionalized molecules.

Keywords: Oxidations, catalysis, aldehydes, dienamines, BPO

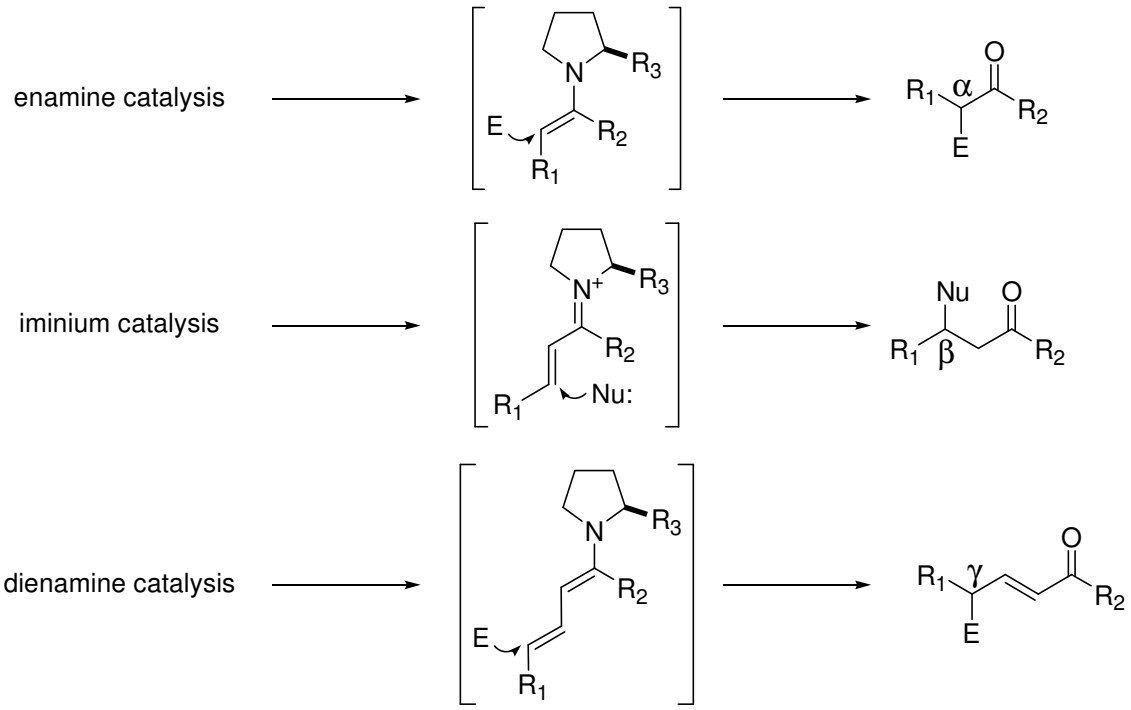
Introduction

Asymmetric organocatalysis has recently emerged as a powerful tool in organic synthesis.[1,2] Beginning from the discovery of the L-proline-catalyzed aldol reaction,[3-5] over the years, it evolved into a general strategy for the activation of carbonyl compounds. Ten years ago, this mode of activation was limited to the formation of enamines and iminium ions as intermediates (Scheme 1). Recently, dienamine and trienamine catalysis has become available for remote functionalizations of α,β-unsaturated compounds.[6-8]

In 2006 Jørgensen disclosed a dienamine concept by showing the direct γ-functionalization of α,β-unsaturated aldehydes.[9] Pentenal reacts with diethyl azodicarboxylate (DEAD) in the presence of 2-[bis(3,5)-bistrifluoromethylphenyl)-trimethylsilanyloxymethyl]pyrrolidyne (silyl protected diarylprolinol) and benzoic acid furnishing the γ-amino substituted product in 56% yield. It was proposed that the reaction proceeds *via* a [2+4]-cycloaddition pathway.

α,β-Unsaturated aldehydes react with secondary amines generating dienamines as reactive species. As such, their electrophilic character is transformed into the nucleophilic one enabling the reaction with electrophiles at α- and γ-positions. A chiral catalyst not only forms dienamine

but also differentiates between the two faces of the double bond providing an enantioselective process.



Scheme 1. Enamine, iminium and dienamine catalysis.

The γ-nucleophilic character of dienamine was exploited in the vinylogous aldol,[10-12] and Michael[13,14] reactions. For example, the reaction of allyl ketones with isatins catalyzed by L-valine-derived bifunctional tertiary amine/thiourea catalyst gave *E*-configured vinylogous aldol adducts in high yield and *ee* up to 99%.[11] In the Michael reaction, 9-amino cinchona alkaloids were used as catalysts. This mode of activation was also applied in the elegant synthesis of tocopherol[10] and chromenes.[12] The organocatalytic formal [4+2] cycloaddition reaction of α,β-unsaturated aldehydes was applied in the synthesis of (+)-palitantin.[14]

Dienamines are electron-rich dienes and can react in Diels-Alder reactions, for example in cyclization of unsaturated dicarbonyl compounds.[15] Vicario and co-workers developed an efficient method for the synthesis of isochromenes via a cascade [4+2] cycloaddition/elimination process starting from α,β-unsaturated aldehydes.[16]

Alkylation of dienamines was shown to proceed via S_N1 mechanism.[17-19] Stabilized carbocations act as electrophiles in the diphenylprolinol silyl ether-catalyzed reaction with unsubstituted enals furnishing γ-alkylated products.[17] Linear unbranched and β-substituted α,β-unsaturated aldehydes favor γ-substitution while γ-disubstituted react at the α-position. Nevertheless, in the presence of cinchona-derived catalyst branched enals afford the desired γ-product.[18,19]

Despite an increased number of reports on dienamine catalysis, to the best of our knowledge, only nitrogen and carbon electrophiles were studied in intermolecular substitution reactions. To further develop the potential of dienamine catalysis, an oxygen based electrophile was studied in the synthesis of γ-oxygenated aldehydes.

Results and Discussion

There are numerous organocatalytic procedures for α-oxygenation of aldehydes and ketones.[20,21] For this purpose various electrophilic oxidizing agents were employed including benzoyl peroxide (BPO),[22-25] molecular oxygen,[26,27] hydroperoxides,[28] *o*-quinones,[29,30] oxaziridine,[31] iodosobenzene,[32,33] and iodoarenes/MCPBA.[32,33] In 2009, three groups independently reported direct organocatalytic asymmetric α-oxygenation of aldehydes with BPO.[22-24] Maruoka's group used tritylpyrrolidine as a catalyst with hydroquinone as an additive.[22] As the reaction proceeded in the presence of a radical scavenger the ionic pathway for this reaction was proposed. Similar results were obtained when diphenylprolinol silyl ether was employed with no radical scavenger added.[23] Hayashi *et al*. found that in their reaction both basic and acidic additives cause a decrease in yield. While, in Tomkinson's established conditions for this reaction the MacMillan catalyst worked best when used with *p*-nitrobenzoic acid.[24]

Inspired by these reports we envisaged that electrophilic BPO could, in a similar manner, react with dienamines. Since various organocatalysts have been used to generate dienamine from α,β-unsaturated aldehydes we tested a broad range of amino acids **1**-**6** and their derivatives **7**-**9** as organocatalysts in the reaction of (*E*)-2-hexenal (**10**) with dibenzoyl peroxide (Figure 1).

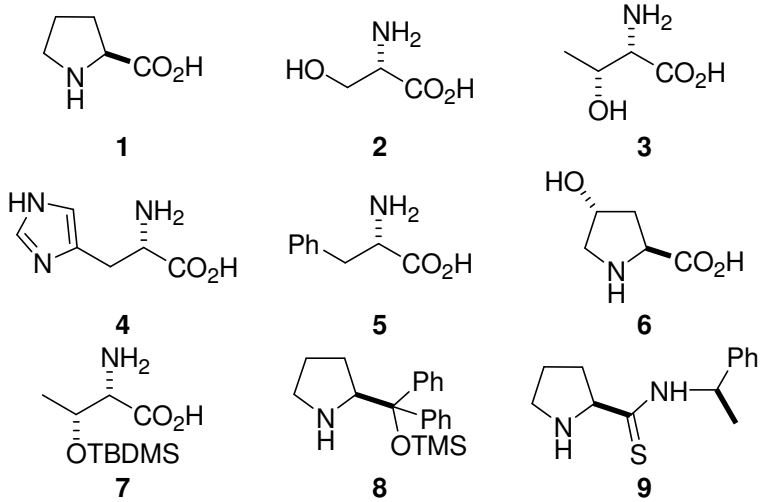
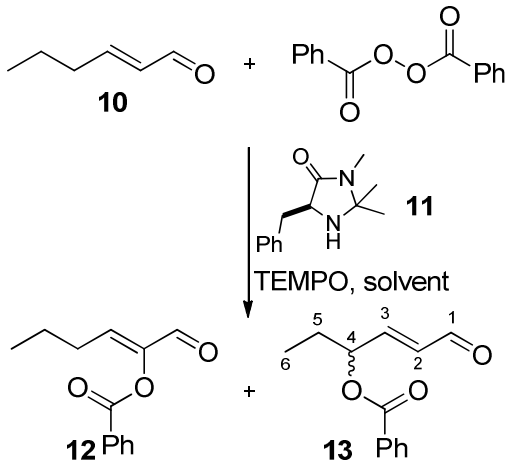


Figure 1. Amino acids **1**-**6** and their derivatives **7**-**9** as organocatalysts in the reaction of (*E*)-2-hexenal (**10**) with dibenzoyl peroxide.

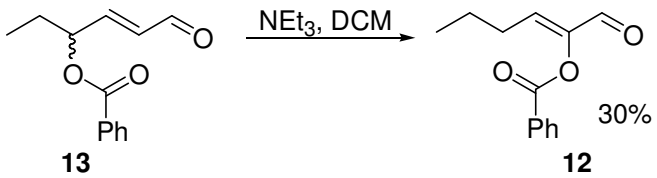
Quickly it was established that most of the catalysts studied led to either low conversion or gave a complex mixture of products. Only in imidazolidinone **11** (MacMillan catalyst) catalyzed reaction performed in toluene two products **12** and **13** were easily distinguished.



Scheme 2. Synthesis of γ-benzoyloxy-aldehyde **13**.

Desired product **13** was isolated in 11% yield. The position of the benzyloxy group was unambiguously established based on one- and two-dimensional NMR spectroscopy (^{1}H, ^{13}C, COSY, HMBC, HSQC). The resonance from the aldehyde group was clearly seen at δ = 9.60 ppm. This dublet signal correlates to one proton signal at δ = 6.30 ppm in COSY, which in turn possesses a characteristic cross-peak for C4 in HMBC. Carbon 4 produces cross-peak (HMBC) with protons at 2, 3, 5 and 6 positions and has a HSQC correlation for a proton present at δ = 5.73 ppm. The C4 proton then correlates to protons present at C3 and C5 in COSY, thus proving the structure of product **13**.

The formation of product **13** was accompanied by a more polar by-product which upon treatment with NEt_3 transformed into α- substituted benzoyloxy-2-hexenal **12**. Unfortunately, at the same time desired γ-benzoyloxy-aldehyde **13** slowly converted into product **12**. We assumed that in the presence of NEt_3 compound **13** rearranged into α-benzoyloxy substituted *Z*-hexenal **12** (30%) (Scheme 3).



Scheme 3. Rearrangement of γ-benzoyloxy substituted *Z*-hexenal **13** into α-benzoyloxy substituted *Z*-hexenal **12**

Furthermore, to avoid possible radical reactions involving BPO we have tested TEMPO as a radical scavenger. In our case, contrary to Maruoka's observation for the diphenylprolinol silyl ether-catalyzed reaction, a decrease in yield was observed (5%). However, when it was used in combination with benzoic acid the yield remained the same. Thus both additives were applied for further studies, followed by an investigation into various solvents. Most of the solvents studied, this included hexane, CH_2Cl_2, $CHCl_3$, DMF, MeOH and H_2O, furnished only traces of product **13**. A twofold increase in the yield was obtained in toluene (25%). In this case α-benzoyloxy-substituted 2-hexenal **12** was formed in 7%. Similar results were obtained in *t*BuOMe but the reaction mixture was more complex.

In the absence of an acidic co-catalyst the reaction in toluene gave product **13** in 18% yield. It has been already established that in organocatalyzed reactions the type of acid co-catalyst used may influence the yield and stereoselectivity of the reaction. With the goal of finding a correlation between pK_a of the acid and outcome of the benzoyloxylation reaction we studied both organic and inorganic acids (Table 1).

Table 1. Various acids studied in the oxidation reaction[a]

Entry	Acid	pK_a	Yield for **13** [%][b]
1	none		18
2	HCl	-8	traces
3	TFA	0.26	6
4	Br_2HCCO_2H	2.86	6
5	L-tartaric	2.99	19[c], 26[d]
6	salicylic acid	3	traces
7	$PhCO_2H$	4.20	27

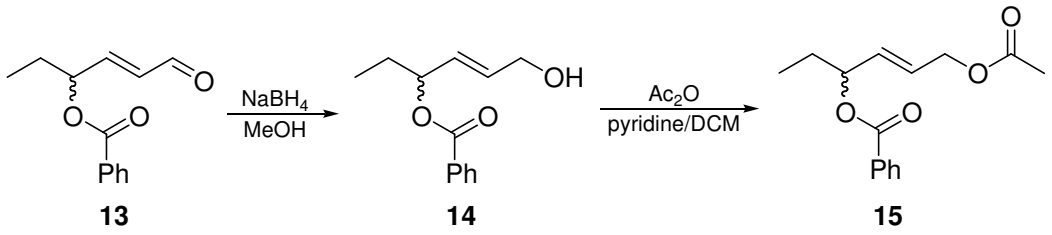
[a]conditions: aldehyde **10** (1 mmol), acid (0.2 eq.), TEMPO (0.2 eq.), MacMillan catalyst (0.2 eq.), BPO (1.2 eq.), toluene (1 ml).
[b]isolated yields, the reaction conversion was full.
[c]no by-product of similar polarity formed.
[d]reaction in a diluted solution (0.5 M).

The data presented in Table 1 show that the weaker the acid the higher the yield of the reaction. The use of tartaric acid as a co-catalyst not only eliminated substitution at the α-position but also suppressed the formation of unwanted by-products (entry 5). The yield further increased when the reaction was conducted at lower concentration - 0.5 M. The use of THF instead of toluene simplified the purification of the reaction mixture; only desired product **13** was formed.

Disappointingly all reactions studied gave racemic product **13** or with very low enantiomeric excess. Unfortunately, the reaction in the presence of simple secondary amine – pyrrolidyne

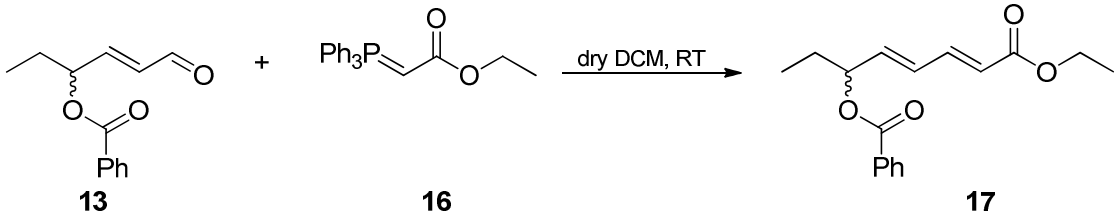
failed to furnish desired product **13**. Further studies aiming at improving the direct γ-benzoyloxylation process are in progress.

Subsequently, we have established that 4-benzoyloxy-2-hexen-1-al **13** is a useful starting material in the synthesis of more functionalized compounds. For example, it can be easily reduced to allylic alcohol **14** which after protection with an acetyl group gave diol **15** with two different protecting groups (Scheme 4).



Scheme 4. Synthsis of diol **15**.

The Wittig reaction produced ethyl ester of 5-benzoyloxy-1,3-octadienoic acid (**17**) in 67% yield (Scheme 5).



Scheme 5. The Wittig reaction of γ-benzoyloxy substituted *Z*-hexenal **13** with ylide **16**.

While we were working on γ-oxygenation of carbonyl compounds, List and co-workers reported that treatment of α-branched α,β-unsaturated aldehydes with BPO in the presence of quinine-derived amine and trichloroacetic acid as a co-catalyst led predominantly to benzoyloxylation at the α-position.[25] The α/γ ratio was high for acyclic substrates but in some cases it diminished by a silica gel mediated allylic rearrangement of α-benzoyloxy products to their γ-counterparts.[34]

Conclusions

In conclusion, we have described direct γ-benzoyloxylation of α,β-unsaturated aldehydes and proved their usefulness in the synthesis of highly functionalized molecules. List's and our observations on the benzoyloxylation reaction of α,β-unsaturated aldehydes suggest that the

regioselectivity of this reaction is governed by the type of amine catalyst and by the substitution pattern on the starting material. Though, the reaction of 2-hexenal (**10**) with BPO gave desired product **13** in moderate yield it is the first example of the successful direct γ-benzoyloxylation of α,β-unsaturated aldehydes.

Experimental Section

General. High resolution ESI mass spectra were recorded on a Mariner and SYNAPT spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 25 ^{o}C on Bruker 500 and Varian 500 MHz instruments with TMS as an internal standard. Elemental analyses were obtained from the Institute of Organic Chemistry PAS. Flash chromatography was performed using Merck Silica Gel (230-400 mesh). Thin layer chromatography (TLC) was performed using Merck Silica Gel GF254, 0.20 mm thickness.
All solvents and chemicals used in the syntheses were of reagent grade and were used without further purification.

(Z)-1-oxohex-2-en-2-yl benzoate (12, $C_{13}H_{14}O_3$). Aldehyde **13** (100 mg, 0.46 mmol) was dissolved in DCM (0.5 cm^3) and NEt_3 (30 μl) was added. The reaction was stirred at room temperature for 18 h. It was diluted with DCM, washed with water, dried over Na_2SO_4, concentrated *in vacuo* and purified using flash chromatography (1:10 AcOEt : Hex) giving compound **12** (30 mg, 30%) as a colorless, viscous oil. R_f 0.50 (1:10 AcOEt:Hex); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 9.39 (1H, s), 8.15-8.12 (2H, m), 7.65-7.46 (3H, m), 6.51 (1H, t, *J* 7.6 Hz), 2.34 (2H, q, *J* 7.5 Hz), 1.57 (2H, m, overlapping with water), 0.98 (3H, t, *J* 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_c 185.1, 185.0, 163.7, 148.2, 142.3, 133.8, 130.3, 128.6, 28.4, 21.4, 13.8; HRMS ESI (4 eV) *m/z* calcd for $C_{13}H_{14}O_3Na$ $[M+Na]^+$ 241.08352, found 241.08434.
(E)-6-oxohex-4-en-3-yl benzoate (13, $C_{13}H_{14}O_3$).[35] Aldehyde **10** (116 μl, 1 mmol), TEMPO (31 mg, 0.2 mmol), (L)-tartaric acid (30 mg, 0.2 mmol) and first generation MacMillan catalyst **11** (43 mg, 0.2 mmol) were dissolved in THF (2 cm^3). BPO (290 mg, 2.4 mmol) was then added and the reaction was stirred at room temperature for 18 h. It was diluted with DCM, washed with water, dried over Na_2SO_4 and filtred through aluminium oxide. The mixture was concentrated *in vacuo* and purified using flash chromatography, 1:1:8 DCM : AcOEt:Hex giving product **13** (52 mg, 24%) as a colorless, viscous oil. R_f 0.28 (1:1:8 AcOEt:DCM:Hex); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 9.59 (1H, d, *J* 7.7 Hz, C**H**O), 8.07 (2H, m, $\mathbf{H}_{Ar}$), 7.59 (1H, m, $\mathbf{H}_{Ar}$), 7.47 (2H, m, $\mathbf{H}_{Ar}$), 6.84 (1H, dd, *J* 4.7, 15.8 Hz, H3), 6.30 (1H, m, H2), 5.73 (1H, m, H4), 1.91 (2H, m, H5), 1.05 (3H, t, *J* 7.4 Hz, H6); ^{13}C NMR (125 MHz, $CDCl_3$): δ_c 192.9 (**C**HO), 165.5 (**C**OO), 153.6 (C3), 133.4($\mathbf{C}_{Ar}$), 131.8 (C2), 129.6 ($\mathbf{C}_{Ar}$), 128.5 ($\mathbf{C}_{Ar}$), 73.7 (C4), 26.9 (C5), 9.3 (C6); HRMS ESI (4 eV) *m/z* calcd for $C_{13}H_{14}O_3Na$ $[M+Na]^+$ 241.08352, found 241.08376. Anal. Calcd for $C_{13}H_{14}O_3$: C 71.54; H 6.47%. Found: C 71.58; H 6.56%.

(E)-6-hydroxyhex-4-en-3-yl benzoate (14, $C_{13}H_{16}O_3$). Aldehyde **13** (80 mg, 0.37 mmol), was dissolved in MeOH (1.3 cm^3) and cooled to 0 °C. $NaBH_4$ (24 mg, 0.63 mmol) was added and the reaction was stirred at room temperature for 30 min. It was then diluted with DCM, washed with 1N HCl and water and dried over Na_2SO_4. The mixture was concentrated *in vacuo* and purified using flash chromatography, 1:1:8 DCM : AcOEt:Hex giving alcohol **14** (54 mg, 66%) as a colorless, viscous oil. R_f 0.21 (3:7 AcOEt:Hex); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.05 (2H, m), 7.55 (1H, m), 7.44 (2H, m), 5.94 (1H, m), 5.78 (1H, m), 5.48 (1H, q, *J* 6.6 Hz), 4.17 (2H, m), 1.78 (3H, m), 0.99 (3H, t, *J* 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 166.0, 132.9, 131.9, 130.5, 129.6, 129.2, 128.3, 75.7, 62.8, 27.6, 9.5; HRMS ESI (4 eV) *m/z* calcd for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ 243.0997, found 243.0998. Anal. Calcd for $C_{13}H_{16}O_3$: C 70.89; H 7.32%. Found: C 70.78; H 7.29%.

(E)-6-acetoxyhex-4-en-3-yl benzoate (15, $C_{15}H_{18}O_4$). Alcohol **14** (179 mg, 0.8 mmol) was dissolved in dry DCM (2 cm^3). Pyridine (8 cm^3) and subsequently Ac_2O (0.6 cm^3) were then added and reaction was stirred at room temperature for 20 h. After this time it was diluted with DCM, washed three times with water and dried over Na_2SO_4. The mixture was concentrated *in vacuo* and purified using flash chromatography, 1:1:8 DCM:AcOEt:Hex giving protected diol **15** (143 mg, 68%) as a colorless, viscous oil. R_f 0.35 (1:9 AcOEt:Hex); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.07 (2H, m), 7.56 (1H, m), 7.45 (2H, m), 5.85 (2H, m), 5.47 (1H, q, *J* 6.3 Hz), 4.58 (2H, d, *J* 5.3 Hz), 2.07 (3H, s), 1.80 (2H, m), 0.98 (3H, t, *J* 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 170.6, 165.8, 132.9, 132.2, 130.4, 129.6, 128.3, 126.5, 75.2, 64.0, 27.4, 20.9, 9.4; HRMS ESI (4 eV) *m/z* calcd for $C_{15}H_{18}O_4Na$ $[M+Na]^+$ 285.10973, found 285.10832.

(4E,6E)-8-ethoxy-8-oxoocta-4,6-dien-3-yl benzoate (17, $C_{17}H_{20}O_4$). Aldehyde **13** (30 mg, 0.14 mmol), was dissolved in dry DCM (1.5 cm^3). Ylide **16** (63 mg, 0.18 mmol) was added and reaction was stirred at room temperature for 24 h. The mixture was concentrated *in vacuo* and purified using flash chromatography, 1:1:8 DCM:AcOEt:Hex giving ester **17** (27 mg, 67%) as a colorless, viscous oil. R_f 0.41 (1:1:8 AcOEt:DCM:Hex); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.07 (2H, m), 7.57 (1H, m), 7.46 (1H, t, *J* 7.6 Hz), 7.26 (2H, m), 6.42 (1H, dd, *J* 10.9, 15.5 Hz), 6.12 (1H, dd, *J* 6.7, 15.5 Hz), 5.90 (1H, d, *J* 15.1 Hz), 5.54 (1H, q, *J* 6.3 Hz), 4.20 (2H, d, *J* 7.1 Hz), 1.84 (2H, m), 1.28 (3H, t, *J* 7.1 Hz), 1.00 (3H, t, *J* 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 166.7, 165.7, 143.3, 139.6, 133.0, 130.2, 129.6, 129.5, 128.4, 122.4, 75.2, 60.3, 27.4, 14.2, 9.4; HRMS ESI (4 eV) *m/z* calcd for $C_{17}H_{20}O_4Na$ $[M+Na]^+$ 311.1259, found 311.1259. Anal. Calcd for $C_{17}H_{20}O_4$: C 70.81; H 6.99%. Found: C 70.76; H 6.91%.

Acknowledgements

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