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A new route to 2-alkenyl-1,3-dicarbonyl compounds, intermediates in the synthesis of dihydrofurans

Roberto Antonioletti,* Paolo Bovicelli and Savina Malancona

Dipartimento di Chimica, Centro CNR di Studio per la Chimica delle Sostanze Organiche Naturali, Università 'La Sapienza', P. le A. Moro, Box 34, Roma 62, 5-00185 Rome, Italy

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Abstract—A two step synthetic strategy for obtaining 2-alkenyl-1,3-dicarbonyl compounds from the corresponding 1,3-dicarbonyl compounds is reported. The method is based on a Knoevenagel condensation and a Michael addition using a high order organocuprate procedure, and proves to be of general value. Obtained compounds are useful starting materials for the synthesis of furan derivatives.

In recent years we have been studying the iodoenolcyclisation of 2-alkenyl-1,3-dicarbonyl compounds. Reaction products are dihydrofuran derivatives, units common in a wide variety of naturally occurring substances and a simple method for their synthesis is of particular interest.[1]

To render our methodology viable, we needed a general route to 2-alkenyl-1,3-dicarbonyl compounds, but methods reported in the literature presented several limitations.

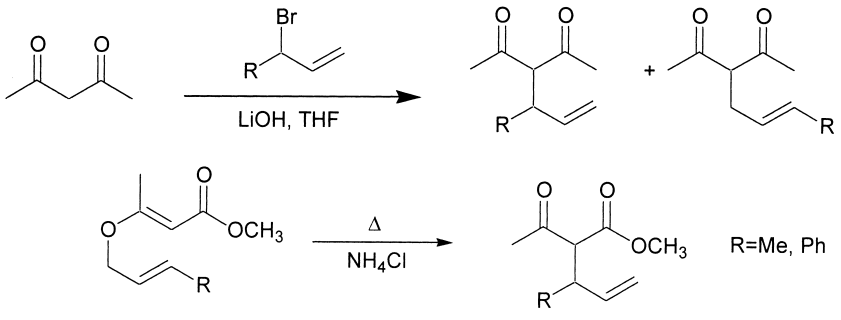
For example, the allylation of dicarbonyl compounds by using lithium hydroxide and allyl bromide is not applicable to secondary allyl bromides,[2] since in this case a mixture of regioisomers which are difficult to separate is always obtained. Another way is the Claisen rearrangement of allyl–vinyl ethers, but this only works in a few selected cases (Scheme 1).[3]

In this work we report the strategy employed to obtain diversely substituted 2-alkenyl-1,3-dicarbonyl compounds in good to excellent yield. The method is of general value since we were able to prepare a large number of compounds.

The synthesis was performed in two steps, the first being an aldol condensation to give α,β-unsaturated-1,3-diketones of type **3**, and the second Michael addition using high-order organocuprates (Scheme 2).

In the first step, method A[4] (see Section 1) was used for aromatic aldehydes, while for volatile and unstable aldehydes, more controlled reaction conditions were necessary, and method B[5] was preferred. The highly hindered pivalic aldehyde did not react under any condition, except method C,[6] a variant of the classic Knoevenagel reaction which permitted us to obtain the condensation product, although in low yield.

For the second step we initially performed Grignard



Scheme 1.

Keywords: 2-alkenyl-1,3-dicarbonyl compounds; Knoevenagel condensation; Michael addition.
* Corresponding author; e-mail: roberto.antonioletti@uniromal.it

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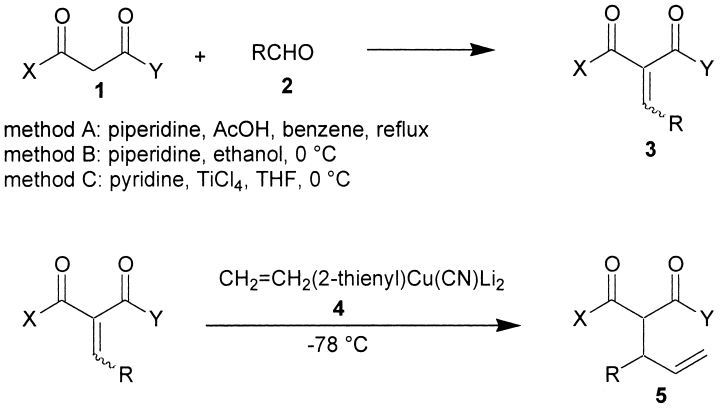
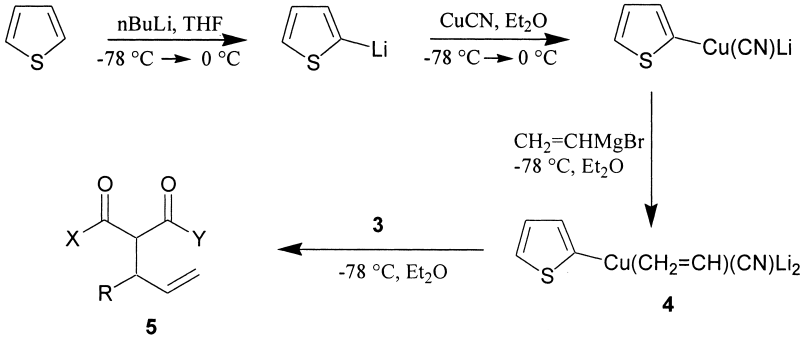


Scheme 2.



Scheme 3.

reactions catalysed by Cu(I), but results were not encouraging due to the high reactivity of the substrates giving a mixture of products derived from 1,4 and 1,2 additions. Instead, good results were obtained by using the high-order cuprate vinyl(1-thienyl)Cu(CN)Li_2 **4**.[7]

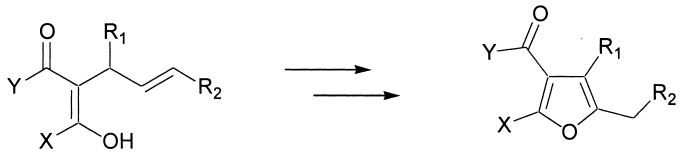
The choice of this reagent is due to its high stability and capability to perform conjugated additions with respect to other cuprates.[8] The commercially available compound did not give satisfactory results, so we prepared the organocuprate in situ and performed the condensation in a one-pot procedure, as reported in Scheme 3.

The reported methodology appears to be applicable to prepare a wide range of 2-alkenyl-1,3-dicarbonyl compounds, as reported in Table 1.

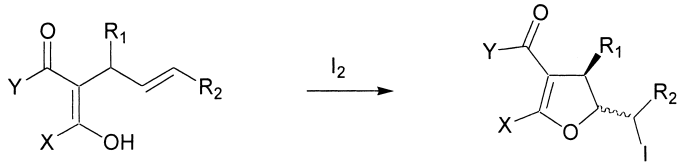
Table 1.

3, **5**	X	Y	R	Synthesis of **3**			Synthesis of **5**	
				Method	Time (h)	Yield (%)	Time	Yield (%)
a	Me	Me	Ph	A	18	60	5 h	45
b	Ph	Ph	Ph	A	2	93	3 h	50
c	Et	Et	Ph	A	5	95	14 h	50
d	Me	OMe	Ph	A	3	98	3 h	64
e	Ph	OEt	Ph	A	3	90	5 h	87
f	*i*-Prop	OEt	Ph	A	3	93	3 h	97
g	*n*-Prop	OEt	Ph	A	3	94	1 h	75
h	Me	Me	Me	B	48	64	30 min	87
i	Et	Et	Me	B	6	70	5 min	77
j	Me	OMe	Me	B	1	80	30 min	63
k	Ph	OEt	Me	B	5	98	30 min	61
l	*i*-Prop	OEt	Me	B	4	90	5 min	41
m	*n*-Prop	OEt	Me	B	6	95	5 min	53
n	Me	OMe	*n*-Prop	B	5	60	5 min	62
o	Me	OMe	*i*-Prop	B	12	68	5 min	62
p	Me	OMe	2-Furyl	A	8	74	5 min	53
q	Me	OMe	*t*-Butyl	C	12	14	5 min	60

All yields refer to isolated compounds.



Scheme 4.



Scheme 5.

In a previous paper we reported a synthesis in which compounds such as **5** were used to prepare tetrasubstituted furans (Scheme 4).[1b]

The method was limited to products with R_1=R_2=Me or R_1=Me, Ph; R_2=H, since at that time only compounds **3** with such substituents could be prepared by known methods.

With the method reported in this paper that limitation is now overcome since compounds **5** with various R_1 and R_2 groups can be prepared in a convenient way. Moreover, several compounds **5** being easily available, it is now also possible to better study the stereochemistry of the iodocyclisation reaction (Scheme 5), which is our major interest in this field.

1. Experimental

1.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 300 and Varian Gemini 200 spectrometers in $CDCl_3$ as the solvent, if not specified. All chemical shifts are reported in parts per million against internal tetramethylsilane. Coupling constants *J* were measured in Hz. All reactions were monitored by GC. GC analyses were performed on a HP 5880A chromatograph equipped with a OV 101 capillary column and a flame ionisation detector. GC–MS analyses were performed on a HP 5890 chromatograph and HP 5971 as mass detector. IR spectra were recorded in 1% $CHCl_3$ solution, on a Shimadzu IR 470 apparatus. Silica gel Merck (200–400 mesh) was used for flash chromatography. All starting compounds are commercially available from the Aldrich company.

1.2. Synthesis of α,β-unsaturated-1,3-dicarbonyl compounds: general procedures

Method A. In a round flask equipped with a Dean–Stark apparatus, 1,3-dicarbonyl compound (10 mmol) was dissolved in benzene (50 ml). The aldehyde (10 mmol), glacial acetic acid and piperidine (catalytic amounts) were added. The mixture was refluxed until the substrate disappeared. After the required time (Table 1) the mixture was cooled, diluted with diethyl ether (50 ml) and water (25 ml). The organic layer was separated, washed with water (25 ml), HCl 1 M solution (2×25 ml) and sodium hydrogen carbonate solution until neutrality. The organic layer was dried (Na_2SO_4) and the solvent evaporated in vacuo. The crude product was purified by flash chromatography (hexane/diethyl ether).

Method B. To a mixture of 1,3-dicarbonyl compound (10 mmol) in ethanol (10 ml) at −5°C, was added piperidine (catalytic amount) and the aldehyde (10 mmol). The reaction was monitored by GC until the substrate disappeared. The mixture was diluted with diethyl ether (50 ml) and water (25 ml). The organic layer was separated and washed with water (2×25 ml) dried (Na_2SO_4) and the solvent evaporated in vacuo. The crude product was purified by flash chromatography (hexane/diethyl ether).

Method C. To a cold solution (0°C) of $TiCl_4$ (10 mmol) in CCl_4 (2.5 ml), under an argon atmosphere, of anhydrous THF (20 ml) was added under stirring. After a yellow precipitate was formed, pivalic aldehyde (5 mmol, 0.54 ml) and methyl acetoacetate (5 mmol, 0.54 ml) were added, then a solution of pyridine (20 mmol) in anhydrous THF (3 ml) was added dropwise in 2 h. After 24 h the mixture was quenched with water (10 ml) and diethyl ether (10 ml). The water solution was separated and extracted with diethyl ether (2×10 ml). The organic layer was washed with brine (2×10 ml), dried (Na_2SO_4) and the solvent evaporated in vacuo. The crude product was purified by flash chromatography (hexane/diethyl ether).

All compounds were prepared as oils. *E* and *Z* geometric isomers were separated, when possible, by flash chromatography (hexane/ethyl acetate) for the complete characterisation, otherwise they were characterised as a mixture.[9] In each case they were used as mixture of isomers for the further reactions.

1.2.1. 3-Benzylidene-pentane-2,4-dione (3a). ν_{max}: 1740, 1720, 1680, 1380, 1260, 1240, 700 cm^{-1}; ^{1}H NMR δ (ppm): 2.26 (3H, s, *Me*-CO), 2.40 (3H, s, *Me*-CO), 7.36–7.38 (5H, m, Ph), 7.47 (1H, s, C*H*=C); ^{13}C NMR δ (ppm): 26.1, 31.3, 129.0, 129.7, 130.6, 132.9, 139.8, 142.8, 196.7, 205.7; *m/z* 188 (85, M^+), 173 (20), 145 (38), 131 (100), 109 (30), 77

(11). Calcd for $C_{12}H_{12}O_2$ C 76.57, H 6.43; found C 76.4, H 6.2.

1.2.2. 2-Benzylidene-1,3-diphenyl-propane-1,3-dione (3b). ν_{max}: 1650, 1600, 1460, 1220, 1240, 1260, 950, 680 cm^{-1}; ^1H NMR δ (ppm): 7.15–7.67 (12H, m,, Ph), 7.80–8.50 (4H, m, Ph and C*H*═C); ^{13}C NMR δ (ppm): 128.6, 128.7, 128.8, 129.5, 129.6, 130.2, 130.5, 132.7, 133.1, 134.0, 136.4, 137.5, 139.6, 144.0, 195.2, 197.2; *m/z* 312 (8, M^+), 207 (23), 131 (12), 105 (100), 77 (50). Calcd for $C_{22}H_{16}O_2$ C 84.59, H 5.16; found C 84.4, H 5.1.

1.2.3. 4-Benzylidene-heptane-3,5-dione (3c). ν_{max}: 1710, 1610, 1180, 910 cm^{-1}; ^1H NMR δ (ppm): 1.05 (3H, t, *J*=7.2 Hz, *Me*), 1.13 (3H, t, *J*=7.2 Hz, *Me*), 2.47 (2H, q, *J*=7.2 Hz, CH_2CO), 2.7 (2H, q, *J*=7.2 Hz, CH_2CO), 7.24–7.39 (5H, m, Ph), 7.52 (1H, s, C*H*═C); ^{13}C NMR δ (ppm): 7.2, 7.7, 31.6, 37.1, 128.9, 129.5, 130.6, 133.3, 138.6, 142.4, 199.2, 208.6; *m/z* 216 (19, M^+), 187 (35), 159 (8), 131 (100), 103 (11), 77 (8), 57 (58). Calcd for $C_{14}H_{16}O_2$ C 77.75, H 7.46; found C 77.9, H 7.7.

1.2.4. 3-Phenyl-2-propionyl-acrylic acid methyl ester (3d). Two isomers. ν_{max}: 1720, 1620, 1260, 1180, 900 cm^{-1}; ^1H NMR δ (ppm): 2.35 (1.5H, s, *Me*CO), 2.43 (1.5H, s, *Me*CO), 3.80 (3H, s, *Me*O), 7.3–7.4 (5H, m, Ph), 7.58 (0.5H, s, C*H*═C), 7.68 (0.5H, s, C*H*═C); ^{13}C NMR δ (ppm): 26.7, 31.4, 47.6, 52.8, 127.0, 127.1, 127.9, 128.7, 128.8, 129.5, 133.3, 134.2, 134.8, 134.9, 141.4, 142.2, 165.5, 168.9, 195.4, 204.1; *m/z* (in mixture) 204 (84, M^+), 203 (100), 173 (15), 121 (69), 102 (23). Calcd for $C_{12}H_{12}O_3$ C 70.57, H 5.92; found C 70.3, H 5.9.

1.2.5. (*Z*)-2-Benzoyl-3-phenyl-acrylic acid ethyl ester (3e). ν_{max}: 1720, 1680, 1620, 1460, 1260, 1240, 1220, 1180, 910 cm^{-1}; ^1H NMR δ (ppm): 1.15 (3H, t, *J*=7.12 Hz, *Me*), 4.20 (2H, q, *J*=7.12 Hz, CH_2CO), 7.20–7.95 (8H, m, Ph), 7.90–7.95 (3H, m, C*H*═C, Ph); ^{13}C NMR δ (ppm): 13.7, 61.4, 128.8, 128.9, 129.2, 130.2, 130.4, 131.4, 132.9, 133.9, 136.2, 142.7, 165.2, 195.9; *m/z* 280 (73, M^+), 206 (19), 176 (15), 105 (100), 77 (58). Calcd for $C_{18}H_{16}O_3$ C 77.12, H 5.75; found C 77.1, H 5.6.

1.2.6. 2-Isobutyryl-3-phenyl-acrylic acid ethyl ester (3f). Two isomers. *E*/*Z* ratio 2.2:1.[9] ν_{max}: 1720, 1620, 1260, 1115, 1100, 680 cm^{-1}; ^1H NMR δ (ppm) isomer *E*: 1.04 (6H, d, *J*=6.9 Hz, *Me*-CH), 1.29 (3H, t, *J*=7.1 Hz, *Me*-CH_2O), 2.65 (1H, ept, *J*=6.9 Hz, C*H*Me_2), 4.28 (2H, q, *J*=7.1 Hz, CH_2O), 7.30–7.48 (5H, m, Ph), 7.76 (1H, s, C*H*═C); isomer *Z*: 1.15 (6H, d, *J*=6.8 Hz, *Me*-CH), 1.26 (3H, t, *J*=7.1 Hz, *Me*-CH_2O), 3.18 (1H, ept, *J*=6.8 Hz, C*H*Me_2), 4.25 (2H, q, *J*=7.1 Hz, CH_2O), 7.30–7.48 (5H, m, Ph), 7.58 (1H, s, C*H*═C); ^{13}C NMR ν (ppm) isomer *E*: 13.9, 17.7, 41.6, 61.4, 128.9, 129.6, 129.8, 130.6, 133.5, 141.4, 165.4, 200.7; isomer *Z*: 13.6, 18.8, 36.0, 61.6, 128.9, 129.8, 129.9, 130.4, 133.7, 140.9, 165.6, 200.4; *m/z* (in mixture) 246 (13, M^+), 203 (100), 175 (15), 135 (31), 107 (15), 77 (8). Calcd for $C_{15}H_{18}O_3$ C 73.15, H 7.37; found C 73.1, H 7.5.

1.2.7. 2-Butyryl-3-phenyl-acrylic acid ethyl ester (3g). Two isomers. *E*/*Z* ratio 2.4:1.[9] ν_{max}: 2980, 1705, 1600, 1480, 1380, 1220 cm^{-1}; ^1H NMR δ (ppm) isomer *E*: 0.87 (3H, t, *J*=7.1 Hz, CH_2CH_2*Me*), 1.29 (3H, t, *J*=6.6 Hz, *Me*CH_2O), 1.52–1.58 (2H, m, CH_2*C*H_2Me), 2.50 (2H, t, *J*=8 Hz, CH_2CO), 4.28 (2H, q, *J*=6.6 Hz, MeCH_2O), 7.30–7.48 (5H, m, Ph), 7.78 (1H, s, C*H*═C); isomer *Z*: 0.95 (3H, t, *J*=7.2 Hz, CH_2CH_2*Me*), 1.25 (3H, t, *J*=6.8 Hz, *Me*CH_2O), 1.52–1.58 (2H, m, CH_2CH_2Me), 2.68 (2H, t, *J*=8 Hz, CH_2CO), 4.29 (2H, q, *J*=6.8 Hz, MeCH_2O), 7.30–7.48 (5H, m, Ph), 7.58 (1H, s, C*H*═C); ^{13}C NMR δ (ppm) isomer *E*: 13.7, 14.3, 17.0, 45.7, 61.8, 128.8, 129.3, 130.1, 131.1, 134.9, 141.0, 165.3, 206.4; isomer *Z*: 13.9, 14.0, 17.6, 40.9, 62.0, 128.8, 129.4, 130.2, 131.1, 134.7, 140.9, 168.6, 197.5; *m/z* (*E*) 246 (26, M^+), 203 (100), 175 (11), 135 (33), 107 (30), 77 (13); *m/z* (*Z*) 246 (37, M^+), 203 (100), 175 (16), 135 (40), 107 (38), 77 (7). Calcd for $C_{15}H_{18}O_3$ C 73.15, H 7.37; found C 73.0, H 7.5.

1.2.8. 3-Ethylidene-pentane-2,4-dione (3h). ν_{max}: 1702, 1666, 1633, 1433, 1395, 1277, 761 cm^{-1}; ^1H NMR δ (ppm): 1.88 (3H, d, *J*=7.2 Hz, *Me*CH═C), 2.28 (3H, s, *Me*CO), 2.29 (3H, s, *Me*CO), 6.78 (1H, q, *J*=7.2 Hz, C*H*═C); ^{13}C NMR δ (ppm): 15.1, 25.6, 31.2, 142.1, 146.1, 197.2, 203.8; *m/z* 126 (9, M), 111 (43), 69 (100). Calcd for $C_7H_{10}O_2$ C 66.65, H 7.99; found C 66.6, H 8.0.

1.2.9. 4-Ethylidene-heptane-3,5-dione (3i). ν_{max}: 2985, 1700, 1668, 1663, 1465, 1392, 1214, 1100, 909 cm^{-1}; ^1H NMR δ (ppm): 1.06 (3H, t, *J*=7.3 Hz, *Me*CH_2), 1.07 (3H, t, *J*=7.3 Hz, *Me*CH_2), 1.83 (3H, d, *J*=7.2 Hz, *Me*CH), 2.55 (2H, q, *J*=7.3 Hz, CH_2CO), 2.62 (2H, q, *J*=7.3 Hz, CH_2CO), 6.75 (1H, q, *J*=7.2 Hz, CH_2═C); ^{13}C NMR δ (ppm): 7.1, 7.6, 15.1, 30.8, 37.0, 139.8, 145.7, 199.9, 207.3; *m/z* 154 (16, M), 125 (52), 69 (100), 57 (90). Calcd for $C_9H_{14}O_2$ C 70.10, H 9.15; found C 69.8, H 8.9.

1.2.10. 2-Acetyl-but-2-enoic acid methyl ester (3j). Two isomers. ν_{max}: 1723, 1589, 1400, 1322, 1222 cm^{-1}; ^1H NMR δ (ppm): 1.86 (1.5H, d, *J*=7.8 Hz) and 1.91 (1.5H, d, *J*=7 Hz, *Me*CH), 2.22 (1.5H, s) and 2.28 (1.5H, s, *Me*CO), 3.76 (1.5H, s) and 3.80 (1.5H, s, *Me*O), 6.93 (0.5H, q, *J*=7.8 Hz), 6.87 (0.5H, q, *J*=7 Hz, C*H*═C); ^{13}C NMR δ (ppm): 15.0, 15.5, 26.4, 26.5, 51.6, 52.0, 137.8, 138.0, 144.3, 144.4, 165.1, 166.9, 195.3, 200.1; *m/z* (1st isomer) 142 (24, M^+), 127 (28), 110 (100), 95 (44), 82 (44), 69 (56), 59 (41); *m/z* (2nd isomer) 142 (28, M^+), 127 (87), 110 (100), 95 (60), 82 (30), 69 (95), 59 (61). Calcd for $C_7H_{10}O_3$ C 59.14, H 7.09; found C 58.9, H 7.2.

1.2.11. 2-Benzoyl-but-2-enoic acid ethyl ester (3k). Two isomers. Ratio 3.2:1. ν_{max}: 1716, 1674, 1601, 1455, 1370, 1270 cm^{-1}; ^1H NMR δ (ppm) major isomer: 1.08 (3H, t, *J*=7.1 Hz, *Me*CH_2O), 1.85 (3H, d, *J*=7.2 Hz, *Me*CH═C), 4.12 (2H, q, *J*=7.1 Hz, MeCH_2O), 7.21 (1H, q, *J*=7.2 Hz, C*H*═C), 7.3–7.6 (3H, m, Ph), 7.7–8.1 (2H, m, Ph); minor isomer: 1.1 (3H, t, *J*=7.1 Hz, *Me*CH_2O), 2.12 (3H, d, *J*=7.3 Hz, *Me*CH═C), 4.12 (2H, q, *J*=7.1 Hz, MeCH_2O), 6.76 (1H, q, *J*=7.3 Hz, C*H*═C), 7.3–7.6 (3H, m, Ph), 7.7–8.1 (2H, m, Ph); ^{13}C NMR δ (ppm): 10.1, 13.5, 13.6, 15.1, 60.7, 60.9, 128.5, 128.6, 128.8, 128.9, 129.0, 132.8, 133.8, 134.8, 136.8, 143.5, 146.9, 164.6, 165.1, 194.7, 198.2; *m/z* (in mixture) 218 (3, M^+), 172 (7), 144 (20), 105 (100), 77 (34), 51 (6). Calcd for $C_{13}H_{14}O_3$ C 71.54, H 6.47; found C 71.6, H 6.4.

1.2.12. 2-Isobutyryl-but-2-enoic acid ethyl ester (3l). Two isomers. ν_{max}: 2985, 1710, 1708, 1699, 1261, 1195, 754 cm^{-1}; ^1H NMR δ (ppm): 1.07 (3H, d, J=6.9 Hz) and 1.1 (3H, d, J=7.0 Hz, Me_2CH), 1.26 (1.5H, t, J=7.1 Hz) and 1.30 (1.5H, t, J=7.1 Hz, $MeCH_2O$), 1.81 (1.5H, d, J=7.3 Hz) and 1.96 (1.5H, d, J=7.2 Hz, $MeCH$=C), 2.92 (0.5H, ept, J=6.9 Hz) and 3.05 (0.5H, ept, J=7.0 Hz, $CHMe_2$), 4.18 (1H, q, J=7.1 Hz) and 4.25 (1H, q, J=7.1 Hz, $MeCH_2O$), 6.88 (0.5H, q, J=7.2 Hz) and 7.01 (0.5H, q, J=7.3 Hz, CH=C); ^{13}C NMR δ (ppm): 13.8, 15.1, 15.4, 17.5, 17.6, 18.4, 36.3, 40.4, 41.0, 46.9, 60.9, 61.0, 136.3, 137.2, 143.0, 143.4, 164.6, 167.2, 202.2, 208.0. m/z (in mixture) 184 (8, M^+), 141 (100), 138 (12), 113 (69), 95 (24), 71 (10), 69 (18). Calcd for $C_{10}H_{16}O_3$ C 65.19, H 8.75; found C 65.0, H 8.4.

1.2.13. 2-Butyryl-but-2-enoic acid ethyl ester (3m). Two isomers. ν_{max}: 2980, 1714, 1392, 1265, 1243, 1106, 749 cm^{-1}; ^1H NMR δ (ppm): 0.92 (1.5H, t, J=7.2 Hz) and 0.96 (1.5H, t, J=7.2 Hz, $MeCH_2O$), 1.23 (1.5H, t, J=7.1 Hz) and 1.31 (1.5H, t, J=7.1 Hz, $MeCH_2CH_2$), 1.5–1.7 (2H, m, $MeCH_2CH_2$), 1.83 (1.5H, d, J=7.4 Hz) and 1.93 (1.5H, d, J=7.2 Hz, $MeCH$=C), 2.5–2.7 (2H, m, $MeCH_2CH_2$), 4.20 (1H, q, J=7.2 Hz) and 4.28 (1H, q, J=7.0 Hz, $MeCH_2O$), 6.90 (0.5H, q, J=7.2 Hz) and 6.96 (0.5H, q, J=7.4 Hz, CH=C); ^{13}C NMR δ (ppm): 13.2, 13.3, 13.7, 13.9, 16.7, 17.1, 40.7, 44.6, 45.1, 49.0, 60.8, 60.9, 136.8, 138.0, 142.7, 143.2, 164.8, 166.7, 197.7, 204.1; m/z (1st isomer) 184 (6, M^+), 169 (19), 141 (100), 139 (18), 138 (14), 113 (69), 95 (19), 82 (8), 71 (14), 69 (15); (2nd isomer) 184 (1, M^+), 169 (24), 141 (100), 139 (21), 138 (6), 113 (84), 95 (27), 82 (7), 71 (22), 69 (28). Calcd for $C_{10}H_{16}O_3$ C 65.19, H 8.75; found C 64.9, H 8.5.

1.2.14. 2-Acetyl-hex-2-enoic acid methyl ester (3n). Two isomers. ν_{max}: 2965, 1718, 1663, 1261, 1241, 730 cm^{-1}; ^1H NMR δ (ppm): 0.8 (1.5H, t, J=7.1 Hz) and 1.0 (1.5H, t, J=7.1 Hz, $MeCH_2CH_2$), 1.4–1.6 (2H, m, $MeCH_2CH_2$), 2.1–2.3 (2H, m, CH_2CH=C), 2.29 (1.5H, s) and 2.34 (1.5H, s, $MeCO$), 3.76 (1.5H, s) and 3.80 (1.5H, s, MeO), 6.83 (0.5H, t, J=7.7 Hz) and 6.91 (0.5H, t, J=7.9 Hz, CH=C); ^{13}C NMR δ (ppm): 12.7, 13.4, 21.3, 21.5, 25.2, 26.4, 30.8, 30.9, 51.6, 51.8, 137.1, 139.0, 148.8, 149.0, 165.0, 167.0, 195.3, 201.7; m/z (1st isomer) 170 (4, M^+), 139 (31), 138 (100), 123 (61), 113 (77), 110 (21), 97 (24), 96 (91), 95 (70), 81 (38), 69 (13), 68 (19), 67 (25), 59 (23), 57 (17), 55 (25), 53 (15); (2nd isomer) 170 (2, M^+), 139 (32), 138 (73), 123 (52), 113 (100), 110 (16), 100 (12), 97 (34), 96 (72), 95 (49), 81 (30), 69 (17), 68 (25), 67 (27), 59 (28), 57 (16), 55 (43), 53 (22). Calcd for $C_9H_{14}O_3$ C 63.51, H 8.29; found C 63.4, H 8.3.

1.2.15. 2-Acetyl-4-methyl-pent-2-enoic acid methyl ester (3o). Two isomers. *E*/*Z* ratio 1:2. ν_{max}: 2970, 1723, 1638, 1263, 1250, 767 cm^{-1}; ^1H NMR δ (ppm) isomer *E*: 1.0 (6H, d, J=8.0 Hz, Me_2CH), 2.33 (3H, s, $MeCO$), 2.61 (1H, m, $CHMe_2$), 3.75 (3H, s, MeO), 6.68 (1H, d, J=10.7 Hz, CH=C); isomer *Z*: 1.05 (6H, d, J=6.7 Hz, Me_2CH), 2.28 (3H, s, $MeCO$), 2.65 (1H, m, $CHMe_2$), 3.80 (3H, s, MeO), 6.58 (1H, d, J=10.6 Hz, CH=C); ^{13}C NMR δ (ppm) isomer *E*: 21.7 (2C), 28.5, 31.0, 51.9, 133.3, 154.7, 165.2, 201.3; isomer *Z*: 21.6 (2C), 26.4, 29.4, 51.9, 134.8, 154.4, 167.2, 195.6; m/z (isomer *E*) 170 (0.5, M^+), 139 (26), 138 (100), 123 (56), 120 (32), 96 (60), 95 (48), 81 (30), 67 (34), 55 (20), 53 (33); (isomer *Z*) 170 (0.4, M^+), 139 (34), 138 (100), 123 (62), 120 (27), 96 (50), 95 (42), 81 (33), 67 (34), 55 (36), 53 (23). Calcd for $C_9H_{14}O_3$ C 63.51, H 8.29; found C 63.3, H 8.4.

1.2.16. 2-Acetyl-3-furan-2-yl-acrylic acid methyl ester (3p). Two isomers in 3:7 ratio. ν_{max}: 1717, 1628, 1250, 1241, 1186, 1171, 910 cm^{-1}; ^1H NMR δ (ppm): 2.32 (2.1H, s) and 2.48 (0.9H, s, Me), 3.78 (0.9H, s) and 3.90 (2.1H, s, MeO), 6.42 (0.3H, dd, J=1.8, 3.3 Hz) and 6.51 (0.7H, dd, J=1.8, 3.3 Hz, C^4-H furyl), 6.65 (0.3H, d, J=3.3 Hz) and 6.86 (0.7H, d, J=3.3 Hz, C^3-H furyl), 7.27 (0.7H, s) and 7.35 (0.3H, s, CH=C), 7.50 (0.3H, d, J=1.8 Hz) and 7.56 (0.7H, d, J=1.8 Hz, C^5-H furyl); ^{13}C NMR δ (ppm): 26.3, 31.2, 52.4 (2C), 112.7, 113.0, 118.0, 119.1, 126.2, 126.9, 129.3, 129.8, 146.5, 146.8, 149.0, 150.2, 164.0, 168.3, 194.3, 201.0; m/z (major isomer) 194 (49, M^+), 179 (24), 163 (20), 162 (15), 152 (11), 134 (12), 121 (61), 120 (100), 111 (71), 92 (13), 77 (15), 65 (14), 64 (11), 63 (21), 59 (13); (minor isomer) 194 (70, M^+), 179 (32), 163 (20), 162 (16), 152 (12), 134 (12), 121 (55), 120 (100), 111 (68), 92 (12), 77 (14), 65 (11), 64 (9), 63 (16), 59 (8). Calcd for $C_{10}H_{10}O_4$ C 61.85, H 5.19; found C 61.8, H 5.0.

1.2.17. (*Z*)-2-Acetyl-4,4-dimethyl-pent-2-enoic acid methyl ester (3q). ν_{max}: 2009, 1720, 1646, 1363, 1212, 830 cm^{-1}; ^1H NMR δ (ppm): 1.11 (9H, s, Me_3C), 2.25 (3H, s, $MeCO$), 3.72 (3H, s, MeO), 6.66 (1H, s, CH=C); ^{13}C NMR δ (ppm): 25.6, 28.6 (3C), 33.9, 51.9, 134.1, 154.5, 168.4, 195.8; m/z 169 (100), 153 (34), 152 (62), 137 (65), 135 (15), 134 (18), 124 (17), 111 (18), 110 (31), 109 (65), 95 (36), 81 (55), 69 (33), 67 (25). Calcd for $C_{10}H_{16}O_3$ C 65.19, H 8.75; found C 65.3, H 8.6.

1.3. Synthesis of β-alkyl-γ,δ-unsaturated-1,3-dicarbonyl compounds: general procedure

In a rigorously dried Claisen flask, a solution of thiophene (1.1 mmol) in anhydrous THF (0.5 ml) was injected. The solution was cooled to −78°C and *n*-butyllithium (1.1 mmol) was added via cannula. After 5 min the mixture was warmed to 0°C and stirred for an additional 30 min. The mixture was added, via cannula, to a cold (−78°C) solution of CuCN (1.1 mmol) in freshly dried diethyl ether (1 ml). The mixture was warmed to 0°C to favour the formation of (2-thienyl)Cu(CN)Li, then cooled to −78°C. Vinylmagnesium bromide (1.1 mmol) was added and the mixture was warmed again to 0°C. Finally, a solution of the α,β-unsaturated 1,3-dicarbonyl compound (1 mmol) in anhydrous THF (1 ml) was added at −78°C via cannula. The reaction was monitored by GC. When the substrate was completely consumed, the reaction was quenched with an aqueous 10% concentrated NH_4OH–90% saturated NH_4Cl solution (20 ml). The mixture was diluted with diethyl ether (25 ml) and the organic layer separated. The aqueous layer was extracted with diethyl ether (3×20 ml). Combined extracts were washed with brine (10 ml), dried (Na_2SO_4) and the solvent evaporated in vacuo. The crude product was purified by flash chromatography (hexane/diethyl ether). All compounds were prepared as oils.

1.3.1. 3-(1-Phenyl-allyl)-pentane-2,4-dione (5a). ν_{max}: 2987, 1707, 1590, 1370, 1189, 900 cm^{-1}; ^1H NMR ν (ppm): 1.86 (3H, s, *Me*CO), 2.22 (3H, s, *Me*CO), 4.13 (1H, dd, *J*=7.7, 11.7 Hz, C*H*CH=CH_2), 4.25 (1H, d, *J*=11.7 Hz, COC*H*CO), 5.0–5.1 (2H, m, CH=CH_2), 5.84 (1H, ddd, *J*=10.9, 11.7, 17.0 Hz, C*H*=CH_2), 7.1–7.3 (5H, m, Ph); ^{13}C NMR δ (ppm): 22.7, 22.8, 31.3, 74.5, 116.3, 126.7, 128.9, 129.5, 140.1, 142.3, 208.3, 210.6; *m/z* 216 (19, M^+), 188 (61), 187 (35), 173 (16), 131 (100), 103 (33), 77 (15). Calcd for $C_{14}H_{16}O_2$ C 77.75, H 7.46; found C 77.5, H 7.3.

1.3.2. 1,3-Diphenyl-2-(1-phenyl-allyl)-propane-1,3-dione (5b). ν_{max}: 1698, 1665, 1290, 1272, 729, 490 cm^{-1}; ^1H NMR δ (ppm): 4.63 (1H, dd, *J*=7.9, 10.2 Hz, C*H*CH=CH_2), 4.98 (1H, dd, *J*=1.5, 18 Hz) and 5.01 (1H, dd, *J*=1.5, 10.2 Hz, CH=CH_2), 5.87 (1H, d, *J*=10.2 Hz, COC*H*CO), 6.00 (1H, ddd, *J*=7.9, 10.2, 18 Hz, C*H*=CH_2), 7–8 (15H, m, Ph); ^{13}C NMR δ (ppm): 50.7, 62.0, 116.9, 126.9, 128.5, 128.6, 128.7 (2C), 128.9, 129.0, 133.4, 133.7, 136.9, 137.2, 138.3, 140.7, 194.5, 194.6; *m/z* 235 (48), 152 (11), 105 (100), 91 (11), 77 (46). Calcd for $C_{24}H_{20}O_2$ C 84.68, H 5.92; found C 84.5, H 5.7.

1.3.3. 4-(1-Phenyl-allyl)-heptane-3,5-dione (5c). ν_{max}: 3010, 1710, 1480, 1370, 1120, 910 cm^{-1}; ^1H NMR δ (ppm): 0.69 (3H, t, *J*=7.3 Hz, *Me*), 0.99 (3H, t, *J*=7.2 Hz, *Me*), 2.05 (1H, dq, *J*=7.2, 18 Hz) and 2.23 (1H, dq, *J*=7.2, 18 Hz, C$H_2$$CH_3$), 2.56 (2H, q, *J*=7 Hz, C$H_2$$CH_3$), 4.19 (1H, d, *J*=8.7 Hz, COC*H*CO), 4.21 (1H, dd, *J*=6.0, 8.7 Hz, C*H*CH=CH_2), 5.00 (1H, dd, *J*=1.4, 11.2 Hz) and 5.02 (1H, dd, *J*=1.4, 17 Hz, CH=CH_2), 5.7–5.9 (1H, m, C*H*=CH_2), 7.1–7.3 (5H, m, Ph); ^{13}C NMR δ (ppm): 6.9, 7.1, 35.4, 36.1, 49.7, 72.8, 116.4, 127.1, 128, 128.9, 138.3, 140.2, 205.5 (2C); *m/z* 244 (2, M^+), 187 (88), 159 (15), 117 (71), 91 (21), 77 (11), 57 (100). Calcd for $C_{16}H_{20}O_2$ C 78.65, H 8.25; found C 78.6, H 8.2.

1.3.4. 2-Acetyl-3-phenyl-pent-4-enoic acid methyl ester (5d). Two isomers. ν_{max}: 1724, 1710, 1522, 1130, 980 cm^{-1}; ^1H NMR δ (ppm) 1.95 (1.5H, s) and 2.27 (1.5H, s, *Me*CO), 3.45 (1.5H, s) and 3.71 (1.5H, s, *Me*O), 3.9–4.2 (2H, m, COC*H*CO and C*H*CH=CH_2), 5.0–5.2 (2H, m, CH=CH_2), 5.8–6.1 (1H, m, C*H*=CH_2), 7.1–7.3 (5H, m, Ph); ^{13}C NMR δ (ppm): 29.6, 29.9, 49.2, 49.3, 51.2, 51.4, 64.6, 65.0, 116.3, 116.8, 127.1, 127.2, 127.9, 128.0, 128.7, 128.9, 137.9, 138.2, 139.8, 140.0, 168.5, 168.9, 201.8, 202.0; *m/z* (in mixture) 232 (3, M^+), 217 (46), 189 (54), 157 (46), 129 (49), 117 (100), 116 (54), 91 (38), 77 (13). Calcd for $C_{14}H_{16}O_3$ C 72.39, H 6.94; found C 72.1, H 6.7.

1.3.5. 2-Benzoyl-3-phenyl-pent-4-enoic acid ethyl ester (5e). Two isomers. ν_{max}: 1719, 1680, 1220, 1210, 800 cm^{-1}; ^1H NMR δ (ppm): 0.87 (1.5H, t, *J*=7.0 Hz) and 1.19 (1.5H, t, *J*=6.9 Hz, OCH_2CH_3), 3.83 (1H, q, *J*=7.0 Hz) and 4.12 (1H, q, *J*=6.9 Hz, OCH_2CH_3), 4.3–4.5 (1H, m, C*H*CH=CH_2), 4.8–5.2 (3H, m, COC*H*CO and CH=CH_2), 5.8–6.2 (1H, m, C*H*=CH_2), 7.2–8.1 (10H, m; Ph); ^{13}C NMR δ (ppm): 13.4, 13.8, 49.1, 49.4, 59.0, 59.3, 61.2, 61.5, 116.4, 116.5, 126.8, 127.1, 128.0, 128.3, 128.5 (8C), 128.6 (4C), 128.8 (4C), 133.5, 133.7, 136.8, 136.9, 140.2, 140.7, 167.7, 167.9, 193.0, 193.2; *m/z* 235 (35), 203 (15), 157 (13), 105 (100), 91 (8), 77 (33). Calcd for $C_{20}H_{20}O_3$ C 77.90, H 6.54; found C 77.7, H 6.4.

1.3.6. 2-Isobutyryl-3-phenyl-pent-4-enoic acid ethyl ester (5f). Two isomers. ν_{max}: 3005, 1720, 1706, 1310, 1270, 1350 cm^{-1}; ^1H NMR δ (ppm): 0.60 (1.5H, d, *J*=8 Hz) and 0.90 (1.5H, d, *J*=8 Hz, *Me*CH), 0.93 (1.5H, t, *J*=6.7 Hz) and 1.22 (1.5H, t, *J*=6.7 Hz, *Me*CH_2), 1.08 (1.5H, d, *J*=8 Hz) and 1.10 (1.5H, d, *J*=8 Hz, *Me*CH), 2.30 (0.5H, ept, *J*=8 Hz) and 2.75 (0.5H, ept, *J*=8 Hz, Me_2CH), 3.75 (1H, q, *J*=8 Hz) and 4.15 (1H, q, *J*=8 Hz, CH_2O), 4.15–4.25 (2H, m, COC*H*CO and C*H*CH=CH_2), 4.9–5.2 (2H, m, CH=CH_2), 5.8–6.1 (1H, m, C*H*=CH_2), 7.1–7.3 (5H, m, Ph); ^{13}C NMR δ (ppm): 13.5, 13.9, 16.9, 17.3, 17.5, 17.6, 41.9, 42.0, 49.4 (2C), 61.1, 61.3, 62.3, 62.5, 116.2, 116.8, 127.0, 127.1, 128.2 (2C), 128.4 (2C), 128.6 (2C), 128.7 (2C), 138.2, 138.3, 140.3, 140.4, 167.6, 167.9, 207.3, 207.4; *m/z* 274 (3, M^+), 256 (7), 203 (29), 175 (12), 157 (24), 117 (100), 115 (29), 91 (35). Calcd for $C_{17}H_{22}O_3$ C 74.42, H 8.08; found C 74.4, H 8.2.

1.3.7. 2-Butyryl-3-phenyl-pent-4-enoic acid ethyl ester (5g). Two isomers. ν_{max}: 1720, 1700, 1130, 680 cm^{-1}; ^1H NMR δ (ppm): 0.61 (1.5H, t, *J*=7.3 Hz) and 0.87 (1.5H, t, *J*=7.3 Hz, *Me*CH_2CH_2), 0.92 (1.5H, t, *J*=7.2 Hz) and 1.19 (1.5H, t, *J*=7.2 Hz, *Me*CH_2O), 1.2 (1H, m) and 1.58 (1H, m, MeCH_2CH_2), 2–2.5 (2H, m, CH_2CO), 3.82 (1H, q, *J*=7.5 Hz) and 4.20 (1H, q, *J*=7.5 Hz, CH_2O), 3.9–4.2 (2H, m, COC*H*CO, C*H*CH=CH_2), 4.9–5.1 (2H, m, CH=CH_2), 5.8–6.1 (1H, m, C*H*=CH_2), 7.1–7.4 (5H, m, Ph); ^{13}C NMR δ (ppm): 13.3, 13.6, 13.7, 13.9, 16.6, 16.9, 45.2, 45.5, 49.5, 49.6, 61.5, 61.8, 64.5, 64.7, 116.6, 117.0, 127.4, 127.5, 128.5 (2C), 128.6 (2C), 129.0 (2C), 129.2 (2C), 138.6, 138.8, 140.6, 140.8, 168.1, 168.5, 204.2, 204.3; *m/z* (in mixture) 274 (2, M^+), 256 (19), 203 (44), 175 (25), 157 (42), 117 (100), 115 (35), 91 (36), 71 (50). Calcd for $C_{17}H_{22}O_3$ C 74.42, H 8.08; found C 74.6, H 8.2.

1.3.8. 3-(1-Methyl-allyl)-pentane-2,4-dione (5h). ^1H NMR δ (ppm): 1.01 (3H, d, *J*=6.7 Hz, *Me*CH), 2.14 (3H, s, *Me*CO), 2.22 (3H, s, *Me*CO), 3.0–3.2 (1H, m, C*H*CH=CH_2), 3.62 (1H, d, *J*=10.5 Hz, COC*H*CO), 5.04 (1H, dd, *J*=1.5, 10.2 Hz) and 5.07 (1H, dd, *J*=1.5, 17 Hz, CH=CH_2), 5.66 (ddd, 1H, *J*=8, 10.2, 17.0 Hz, C*H*=CH_2); ^{13}C NMR δ (ppm): 18.0, 29.3, 29.6, 38.2, 75.3, 115.7, 139.8, 203.8, 203.9. IR (cm^{-1}): 1716, 1695, 1368, 1167, 1145, 757; *m/z* 154 (2, M^+), 110 (12), 111 (25), 97 (15), 43 (100). Calcd for $C_9H_{14}O_2$ C 70.0, H 9.15; found C 70.2, H 9.3.

1.3.9. 4-(1-Methyl-allyl)-heptane-3,5-dione (5i). ν_{max}: 1705, 1645, 1236, 1027, 1001, 701 cm^{-1}; ^1H NMR δ (ppm): 0.92 (3H, d, *J*=7.0 Hz, *Me*CH), 0.94 (3H, t, *J*=7.2 Hz, *Me*CH_2), 1.00 (3H, t, *J*=7.2 Hz, *Me*CH_2), 2.3–2.6 (4H, m, MeCH_2), 2.9–3.1 (1H, m, C*H*CH=CH_2), 3.60 (1H, d, *J*=10.6 Hz, COC*H*CO), 4.95 (1H, dd, *J*=2, 13.2 Hz) and 5.02 (1H, dd, *J*=2, 17.1 Hz, CH=CH_2), 5.59 (1H, ddd, *J*=7.9, 13.2, 17.1 Hz, C*H*=CH_2); ^{13}C NMR δ (ppm): 7.5, 8.2, 15.4, 37.2, 37.6, 38.3, 74.3, 116.8, 140.1, 203.5, 203.9; *m/z* 182 (1, M^+), 126 (14), 125 (21), 111 (18), 97 (22), 57 (100). Calcd for $C_{11}H_{18}O_2$ C 72.49, H 9.95; found C 72.4, H 9.8.

1.3.10. 2-Acetyl-3-methyl-pent-4-enoic acid methyl ester (5j). Two isomers. ν_{max}: 2965, 1737, 1710, 1367, 1290, 1224, 1144, 910 cm^{-1}; ^1H NMR δ (ppm): 0.99 (1.5H, d, J=7.0 Hz) and 1.03 (1.5H, d, J=6.9 Hz, *Me*CH), 2.16 (1.5H, s) and 2.20 (1.5H, s, *Me*CO), 2.9–3.0 (1H, m, C*H*CH=CH_2), 3.35 (1H, d, J=9.6 Hz, COC*H*CO), 3.66 (1.5H, s) and 3.69 (1.5H, s, *Me*O), 4.9–5.1 (2H, m, CH=CH_2), 5.5–5.8 (1H, m, C*H*=CH_2); ^{13}C NMR δ (ppm): 17.7, 17.9, 29.2, 29.3, 37.6, 37.8, 51.9, 52.1, 65.5, 65.6, 115.4, 115.6, 139.7, 139.8, 169.2, 169.3, 202.6, 202.7; *m/z* (in mixture) 170 (1, M^+), 142 (29), 141 (11), 127 (23), 97 (10), 96 (11), 95 (15), 71 (100), 55 (13). Calcd for $C_9H_{14}O_3$ C 63.51, H 8.29; found C 63.5, H 8.1.

1.3.11. 2-Benzoyl-3-methyl-pent-4-enoic acid ethyl ester (5k). Two isomers. ν_{max}: 1720, 1685, 1293, 1289, 1177, 910 cm^{-1}; ^1H NMR δ (ppm): 1.02 (1.5H, d, J=6.9 Hz) and 1.09 (1.5H, d, J=7 Hz, *Me*CH), 1.12 (1.5H, t, J=7.5 Hz) and 1.16 (1.5H, t, J=7.7 Hz, *Me*CH_2), 3.1–3.3 (1H, m, C*H*CH=CH_2), 4.0–4.3 (3H, m, COC*H*CO and MeCH_2O), 4.8–5.1 (2H, m, CH=CH_2), 5.6–5.9 (1H, m, C*H*=CH_2), 7.4–7.6 (3H, m) and 7.9–8.1 (2H, m, Ph); ^{13}C NMR δ (ppm): 13.7, 13.8, 17.4, 18.2, 37.5, 38.0, 59.5, 60.0, 61.1, 61.2, 115.3, 115.4, 128.5 (2C), 128.6 (2C), 128.7 (2C), 128.8 (2C), 133.5, 133.6, 136.7, 136.9, 140.1, 140.3, 168.6, 168.8, 194.0, 194.2; *m/z* (in mixture) 246 (2, M^+), 192 (7), 173 (8), 141 (5), 113 (5), 105 (100), 77 (45). Calcd for $C_{15}H_{18}O_3$ C 73.15, H 7.37; found C 73.3, H 7.2.

1.3.12. 2-Isobutyryl-3-methyl-pent-4-enoic acid ethyl ester (5l). Two isomers. ν_{max}: 3175, 1775, 1747, 1348, 1245, 1199, 1042 cm^{-1}; ^1H NMR δ (ppm): 0.8–1.3 (12H, m, Me_2CH, *Me*CH_2O and *Me*CH), 2.5–2.8 (1H, m, Me_2C*H*), 2.8–3.0 (1H, m, C*H*CH=CH_2), 3.49 (0.5H, d, J=6.9 Hz) and 3.51 (0.5H, d, J=7.0 Hz, COC*H*CO), 4.0–4.2 (2H, m, CH_2O), 4.9–5.1 (2H, m, CH=CH_2), 5.5–5.8 (1H, m, C*H*=CH_2); ^{13}C NMR δ (ppm): 13.8, 14.1, 17.5 (2C), 17.6 (2C), 17.7, 17.9, 37.6, 37.8, 41.3, 41.5, 60.9, 61.1, 62.8, 62.9, 115.2, 115.5, 140.1, 140.2, 168.4, 168.6, 208.1, 208.3; *m/z* (in mixture) 212 (1, M^+), 142 (13), 141 (10), 123 (24), 115 (25), 97 (10), 96 (10), 95 (15), 87 (19), 71 (100), 55 (28). Calcd for $C_{12}H_{20}O_3$ C 67.89, H 9.50; found C 67.7, H 9.2.

1.3.13. 2-Butyryl-3-methyl-pent-4-enoic acid ethyl ester (5m). Two isomers. ν_{max}: 2975, 1736, 1708, 1234, 1180 cm^{-1}; ^1H NMR δ (ppm): 0.84 (1.5H, t, J=7.1 Hz) and 0.87 (1.5H, t, J=7.0 Hz, *Me*CH_2CH_2), 0.97 (1.5H, d, J=6.8 Hz) and 1.03 (1.5H, d, J=6.7 Hz, *Me*CH), 1.20 (1.5H, t, J=7.0 Hz) and 1.23 (1.5H, t, J=6.8 Hz, *Me*CH_2O), 1.5–1.7 (2H, m, MeCH_2CH_2), 2.3–2.6 (2H, m, CH_2CO), 2.9–3.1 (1H, m, C*H*CH=CH_2), 3.34 (1H, d, J=9.8 Hz, COC*H*CO), 4.10 (1H, q, J=7.2 Hz) and 4.18 (1H, q, J=7.0 Hz, MeCH_2O), 4.9–5.1 (2H, m, CH=CH_2), 5.5–5.8 (1H, m, C*H*=CH_2); ^{13}C NMR δ (ppm): 13.1 (2C), 13.7 (2C), 16.2, 16.4, 17.6, 17.7, 37.4, 37.5, 44.3 (2C), 60.8, 61.0, 64.8 (2C), 115.1, 115.4, 139.9, 140.0, 168.5, 168.6, 204.4 (2C); *m/z* 212 (1, M^+), 142 (23), 141 (10), 127 (22), 113 (10), 97 (11), 96 (12), 95 (16), 71 (100), 69 (21), 55 (19). Calcd for $C_{12}H_{20}O_3$ C 67.89, H 9.50; found C 67.7, H 9.2.

1.3.14. 2-Acetyl-3-propyl-pent-4-enoic acid methyl ester (5n). Two isomers. ν_{max}: 3140, 1780, 1740, 1478, 1412, 1156 cm^{-1}; ^1H NMR δ (ppm): 0.75–0.95 (3H, m, *Me*CH_2CH_2), 1.2–1.4 (4H, m, MeCH_2CH_2), 2.15 (1.5H, s) and 2.20 (1.5H, s, *Me*CO), 2.7–2.9 (1H, m, C*H*CH=CH_2), 3.41 (0.5H, d, J=10 Hz) and 3.43 (0.5H, d, J=9.8 Hz, COC*H*CO), 3.64 (1.5H, s) and 3.70 (1.5H, s, *Me*CO), 5.0–5.1 (2H, m, CH=CH_2), 5.4–5.7 (1H, m, C*H*=CH_2); ^{13}C NMR δ (ppm): 13.5 (2C), 19.7, 19.9, 29.3 (2C), 34.3, 34.4, 43.7, 43.8, 52.0, 52.2, 65.0, 65.1, 117.4, 117.7, 138.1, 138.2, 169.2, 169.4, 202.8 (2C); *m/z* 198 (2, M^+), 156 (12), 113 (25), 43 (100). Calcd for $C_{11}H_{18}O_3$ C 66.64, H 9.15; found C 66.5, H 9.0.

1.3.15. 2-Acetyl-3-isopropyl-pent-4-enoic acid methyl ester (5o). Two isomers. ν_{max}: 3097, 1762, 1731, 1408, 1345, 1109 cm^{-1}; ^1H NMR δ (ppm): 0.79 (3H, d, J=6.6 Hz, *Me*CH), 0.86 (3H, d, J=6.6 Hz, *Me*CH), 1.5–1.8 (1H, m, Me_2C*H*), 2.14 (1.5H, s) and 2.20 (1.5H, s, *Me*CO), 2.5–2.8 (1H, m, C*H*CH=CH_2), 3.64 (1.5H, s) and 3.70 (1.5H, s, *Me*O), 3.6–3.7 (1H, m, COC*H*CO), 5.0–5.2 (2H, m, CH=CH_2), 4.9–5.3 (1H, m, C*H*=CH_2); ^{13}C NMR δ (ppm): 16.3 (2C), 17.1 (2C), 21.0, 21.1, 28.5, 28.8, 49.7, 50.0, 51.9, 52.2, 62.8, 63.0, 118.6, 119.1, 134.2, 134.7, 169.3, 169.5, 202.8, 202.9; *m/z* 198 (1, M^+), 156 (10), 113 (37), 43 (100). Calcd for $C_{11}H_{18}O_3$ C 66.64, H 9.15; found C 66.8, H 9.3.

1.3.16. 2-Acetyl-3-furan-2-yl-pent-4-enoic acid methyl ester (5p). Two isomers. ν_{max}: 1741, 1726, 1523, 1480, 1230 cm^{-1}; ^1H NMR δ (ppm): 2.09 (1.5H, s) and 2.22 (1.5H, s, *Me*CO), 3.60 (1.5H, s) and 3.69 (1.5H, s, *Me*O), 4.01 (0.5H, d, J=9.5 Hz) and 4.03 (0.5H, d, J=9 Hz, COC*H*CO), 4.1–4.3 (1H, m, C*H*CH=CH_2), 5.05–5.10 (2H, m, CH=CH_2), 5.7–6.0 (1H, m, C*H*=CH_2), 6.06 (1H, bs, 3-H furan), 6.25 (1H, dd, J=1.9, 3.3 Hz, 2-H furan), 7.28 (bs, 1H, 5-H furan); ^{13}C NMR δ (ppm): 29.3, 29.9, 42.6, 42.7, 52.3 (2C), 62.6, 62.7, 106.4, 106.9, 110.3, 110.5, 117.8, 118.3, 134.8, 135.1, 141.9 (2C), 152.9, 153.4, 168.2, 168.3, 201.3, 201.5; *m/z* 222 (1, M^+), 204 (25), 179 (100), 163 (54), 148 (30), 147 (77), 121 (21), 120 (19), 119 (15), 107 (83), 91 (28), 79 (34), 77 (36). Calcd for $C_{12}H_{14}O_4$ C 64.85, H 6.35; found C 64.6, H 6.3.

1.3.17. 2-Acetyl-3-*tert*-butyl-pent-4-enoic acid methyl ester (5q). Two isomers. ν_{max}: 3008, 1745, 1718, 1143, 1247 cm^{-1}; ^1H NMR δ (ppm): 0.84 (9H, s, Me_3C), 2.08 (1.5H, s) and 2.20 (1.5H, s, *Me*CO), 2.6–2.8 (1H, m, C*H*CH=CH_2), 3.50 (1H, d, J=8.7 Hz, COC*H*CO), 3.64 (1.5H, s) and 3.70 (1.5H, s, *Me*O), 5.0–5.1 (2H, m, CH=CH_2), 5.5–6.0 (1H, m, C*H*=CH_2); ^{13}C NMR δ (ppm): 27.3 (3C), 27.7 (3C), 28.7, 29.1, 33.2, 33.5, 52.0, 52.4, 53.1, 53.5, 60.8, 62.0, 118.5, 119.1, 135.6, 135.7, 170.0, 170.1, 202.7, 203.5; *m/z* 212 (1, M^+), 156 (15), 113 (100), 97 (13), 81 (32), 57 (63). Calcd for $C_{12}H_{20}O_3$ C 67.89, H 9.50; found C 67.9, H 9.5.

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