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STEREOSELECTIVE SYNTHESIS
OF
2-ALKYLIDENE-4-KETONITRILES and -4-KETOESTERS

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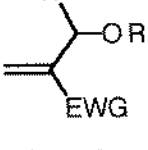
ABSTRACT: Conjugated addition of nitroalkanes to the Baylis-Hillman acetates **1b** and **2b** in the presence of NaOH (0.45N) in THF gave 2-alkylidene-4-nitronitriles **3**-(*Z,E*) and -4-nitroesters **4**-(*Z,E*) which were further converted via the Nef reaction into the corresponging 2-alkylidene-4-ketonitriles **5**-(*Z,E*) and -4-ketoesters **6**-(*Z,E*) in high stereoselectivity and good yields.

RESUME: L'addition conjuguée de nitroalcanes primaires aux acétates de type Baylis-Hillman **1b** et **2b** en présence de soude (0.45N) dans le THF conduit d'une manière stéréosélective aux 2-alkylidène-4-nitronitriles **3**-(*Z,E*) et -4-nitroesters **4**-(*Z,E*), lesquels sont aisément convertis via la réaction de Nef en 2-alkylidène-4-cétonitriles **5**-(*Z,E*) et -4-cétoesters **6**-(*Z,E*) avec de bons rendements.

The Baylis-Hillman reaction (1-3) provides functionalized allyl alcohols which can be transformed into numerous polyfunctionalized derivatives. In order to extend the potential synthetic utility of this class of compounds, we undertook the exploration of the electrophilic reactivity of allylic acetates **1b** (4) and **2b** (5) derived from 2-(hydroxyalkyl)alk-2-enenitriles **1a** (6) and 2-(hydroxyalkyl)alk-2-enoates **2a** (7).

Conjugate addition of nitroalkanes (8,9) to α,β-unsaturated ketones or esters (10-12), provides a convenient method to prepare the corresponding nitro compounds which are valuable intermediates for further transformation into various functionalities (13).



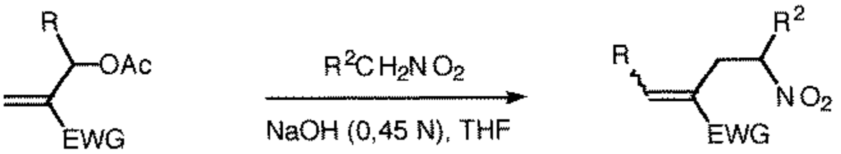
1b or **2b**

EWG : CN **1a** : R^1= H ; **1b** : R^1= Ac

EWG :COOEt **2a** : R^1= H ; **2b** : R^1= Ac

Scheme 1

We have shown that the reaction-coupling of nitroalkanes and allyl acetates **1b** or **2b** is regioselective and proceeds via a S_N2' substitution to produce a mixture of *(E,Z)*-2-alkylidene-4-nitronitriles **3** or *(E,Z)*-2-alkylidene-4-nitroesters **4** in good yields. This result can be explained by the existence of electron deficiency of the allyl acetates **1b** and **2b** supported by the nitrile or the carboxylate groups on the same carbon atom. Initial investigation of allyl acetates **1b** and **2b** indicated that the conjugate addition of nitroalkanes under basic condition (NaOH, 0.45N, THF) is particularly facile and provides better results (Table 1).



1b or **2b**

EWG = CN, COOEt

(Z,E)-**3** or -**4**

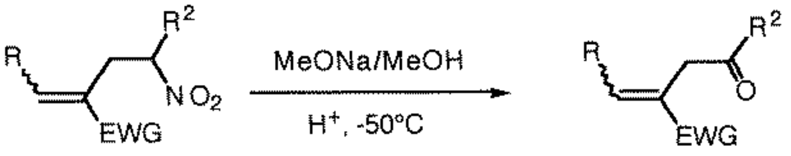
Scheme 2

Table 1: *(Z/E)-2-Alkylidene-4-nitronitriles **3** and -4-nitroesters **4** from allyl acetates **1b** and **2b**.*

R	R^2	Time (h)	<u>4-Nitronitriles</u> **3**- *(Z/E , %*)*	Yield (%)	R	R^2	Time (h)	<u>4-Nitroesters</u> **4**-*(Z/E, %*)*	Yield (%)
CH_3	CH_3	6	**3a** (26/74)	87	H	CH_3	48	**4l** -	85
C_2H_5	CH_3	20	**3b** (11/89)	81	CH_3	CH_3	62	**4m** (15/85)	75
n-C_3H_7	CH_3	20	**3c** (43/57)	83	C_2H_5	CH_3	62	**4n** (20/80)	84
C_6H_5	CH_3	42	**3d** (21/79)	83	n-C_3H_7	CH_3	62	**4o** (17/83)	68
n-C_5H_{11}	CH_3	62	**3e** (12/88)	88	n-C_5H_{11}	CH_3	86	**4p** (17/83)	67
C_2H_5	C_2H_5	62	**3f** (10/90)	76	H	C_2H_5	62	**4q** -	84
n-C_3H_7	C_2H_5	62	**3g** (11/89)	70	n-C_3H_7	C_2H_5	62	**4r** (15/85)	77
C_6H_5	C_2H_5	86	**3h** (30/70)	74					

(*) Stereochemical assignements and isomeric purities were based on difference in chemical shifts and integration ratio of isomeric vinylic protons in ^1H NMR analysis.

In continuation of our effort in the synthesis of *(E,Z)*-2-alkylidene-1,4-and-1,5-difunctionalized compounds (5a,14,15) to complete these series, it is therefore of interest to convert the adducts **3** and **4** into the corresponding 4-ketonitriles **5** and 4-ketosters **6**. Indeed, there are several methods for the conversion a nitro group into a carbonyl, but specially in this case, we found that the Nef (16) reaction is the most appropriate method for further transformation of nitro derivatives **3** and **4** via their nitronate anions after addition of a methanolic solution of concentrated sulphuric acid at -50°C, into the corresponding ketonitriles **5** and ketoesters **6** (Table 2).



(Z,E) -**3** or -**4**

EWG = CN, COOEt

(Z,E) -**5** or -**6**

Scheme 3

In conclusion, we reported a facile, quick and inexpensive method for effective conversion of various allyl acetates of Baylis-Hillman adducts to the corresponding 2-alkylidene-4-ketonitriles and -4-ketoesters, via the Nef reaction. Chemioselective reduction of the latter compounds into the corresponding homoallylic alcohols followed by lactonization (17), is currently under investigation.

Table 2: *(Z/E)-2-Alkylidene-4-ketonitriles* **5** *and -4-ketoesters* **6** *prepared.*

R	R^2	Time (h)	4-Ketonitriles **5** (*Z/E*, %*)	Yield (%)	R	R^2	Time (h)	4-Ketoesters **6** (*Z/E*, %*)	Yield (%)
CH_3	CH_3	1	**5a** (09/91)	70	H	CH_3	3	**6l** -	65
C_2H_5	CH_3	1	**5b** (13/87)	88	CH_3	CH_3	3	**6m** (15/85)	84
n-C_3H_7	CH_3	1	**5c** (43/57)	64	C_2H_5	CH_3	3	**6n** (19/81)	71
C_6H_5	CH_3	3	**5d** (24/76)	85	n-C_3H_7	CH_3	3	**6o** (16/82)	64
n-C_5H_{11}	CH_3	2	**5e** (13/87)	81	n-C_5H_{11}	CH_3	3	**6p** (20/80)	61
C_2H_5	C_2H_5	3	**5f** (13/87)	66	H	C_2H_5	3	**6q** -	72
n-C_3H_7	C_2H_5	3	**5g** (12/88)	82	n-C_3H_7	C_2H_5	3	**6r** (15/84)	82
C_6H_5	C_2H_5	3	**5h** (49/50)	60					

(*) Stereochemical assignements and isomeric purities were based on difference in chemical shifts and integration ratio of isomeric vinylic protons in ^{1}*H NMR analysis.*

Experimental Section

Reaction progress and purity of products were monitored on an Intersmat 20M gas chromatograph using a 3mx3mm column packed with 10% SE 30. Thin-layer chromatography was performed on precoated silica gel plates (Merck F_{254}) and silica gel GEDURAN SI 60 (70-230mesh, Merck) was used for preparative chromatography. ^1H and ^{13}C NMR spectra were recorded on a Jeol C-HL 60 MHz and Bruker 300MHz instruments in $CDCl_3$ solution with TMS as the internal standard. Mass spectra were obtained on a VARIAN MAT 112 with double focalisation at 70eV.

Synthesis of *(E,Z)*-2-alkylidene-4-nitronitriles 3 and *(E,Z)*-2-alkylidene-4-nitroesters 4

General procedure: To a mixture of acetate **1b** or **2b** (10 mmol) and nitroalkane (40 mmol) dissolved in THF (25 mL) was added a solution of NaOH (0.45N, 1.5 eqv.). After the addition was complete, the mixture was stirred at room temperature for the time indicated in table 1, then diluted with H_2O and extracted with ether (3x30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed to give an oil which was purified by column chromatography on silica gel (AcOEt/hexane, 2:8).

(E,Z)-2-Ethylidene-4-nitropentanenitrile 3a:

IR ($CHCl_3$, νcm^{-1}): 1640(C=C) ; 2219(CN) ; 1559(C-NO_2). ^1H NMR($CDCl_3$,δ ppm): 6.63(q, 1H, 7.8*Hz*, *Z*) ; 6.38(q, 1H, 7.6*Hz*, *E*) ; 4.79(m, 1H) ; 3.0(m,2H) ; 2.01(d, 3H, 7,6*Hz*, *E*) ; 1.87(d, 3H, 7.8*Hz*, *Z*) ; 1.64(d, 3H, 7.1*Hz*, *Z*) ; 1.61(d, 3H, 7.0*Hz*, *E*). ^{13}C NMR($CDCl_3$,TMS): 147.4(*C*H=C,*E*) ; 147.3(*C*H=C,*Z*) ; 118.4(*C*N, *Z*) 116.1(*C*N, *E*) ; 109.5(CH=*C*, *E*) ; 108.0(CH=*C*, *Z*) ; 81.2(*C*HNO_2, *E*) ; 80.7(*C*HNO_2, *Z*) ; 38.7(*C*H_2, *E*) ; 33.0(*C*H_2, *Z*) ; 18.6(*C*H_3CHNO_2, *E*) ; 18.4(*C*H_3CHNO_2, *Z*) ; 17.1(*C*H3CH=C, *E*) ; 14.4(*C*H3CH=C, *Z*). Mass m/z (i%): 108(56) ; 107(92) ; 81(57) ; 80(79) ; 79(41) ; 53(100) ; 41(44).

(E,Z)-2-Propylidene-4-nitropentanenitrile 3b:

IR ($CHCl_3$, νcm^{-1}): 1637(C=C) ; 2220(CN) ; 1556(C- NO_2). ^{1}H NMR($CDCl_3$,δ ppm): 6.50(t, 1H, 7.7*Hz*, *Z*) ; 6.32(t, 1H, 7.6*Hz*, *E*) ; 4.83(m, 1H, *E*) ; 4.40(m, 1H, *Z*) ; 2.8(m,2H) ; 2.36(m, 2H, *E*) ; 2.27(m, 2H, *Z*) ; 1.60(d, 3H, 7.3*Hz*) ; 1.06(t, 3H, 6.9*Hz*). ^{13}C NMR($CDCl_3$,TMS): 157.5(*C*H=C, *E*) ; 153.7(*C*H=C, *Z*) ; 119.4(*C*N, *Z*) 116.1(*C*N, *E*) ; 107.7(CH=*C*, *E*) ; 107.0(CH=*C*, *Z*) ; 81.2(*C*HNO_2, *E*) ; 80.5(*C*HNO_2, *Z*) ; 40.2(*C*H2CHNO$_2$, *Z*) ; 38.6(*C*H_2CHNO_2, *E*) ; 24.8(*C*H_2CH=C, *E*) ; 21.7(*C*H_2CH=C, *Z*) ; 18.5(*C*H_3CHNO_2, *E*) ; 18.5(*C*H_3CHNO_2, *Z*) ; 12.5(*C*H_3CH_2, *Z*) ; 12.4(*C*H_3CH_2, *E*). Mass m/z (i%): 121(57) ; 106(87) ; 94(38) ; 80(70) ; 79(63) ; 67(87) ; 53(98) ; 41(100).

(E,Z)-2-Butylidene-4-nitropentanenitrile 3c:

IR ($CHCl_3$, νcm^{-1}): 1637(C=C) ; 2220(CN) ; 1561(C–NO_2). ^{1}H NMR($CDCl_3$,δ ppm): 6.61(m, 1H, *Z*) ; 6.34(m, 1H, *E*) ; 4.92(m, 1H, *Z*) ; 4.60(m, 1H, *E*) ; 3.1(m,2H, *Z*) ; 2.8(m, 2H, *E*) ; 2.38(m, 2H, *E*) ; 2.17(m, 2H, *Z*) ; 1.50(m, 3H) ; 0.95(m, 5H). ^{13}C NMR(CDCl3,TMS): 153.1(*C*H=C,*E*) ; 152.7(*C*H=C, *Z*) ; 119.0(*C*N, *Z*) ; 116.4(*C*N, *E*) ; 108.7(CH=*C*, *Z*) ; 107.7(CH=*C*, *E*) ; 77.0(*C*HNO_2, *E*) ; 76.6(*C*HNO_2, *Z*) ;37.1(*C*H_2CHNO_2, *Z*) ; 36.9(*C*H_2CHNO_2, *E*) ; 33.5(*C*H_2CH=C, *E*) ; 33.1(*C*H_2CH=C, *Z*) ; 30.5(*C*H_3CHNO_2, *E*) ; 30.5(*C*H_3CHNO_2, *Z*) ; 21.3(*C*H_2CH_3, *E*) ; 21.2(*C*H_2CH_3, *Z*) ; 13.1(*C*H_3CH_2, *E*) ; 13.0(*C*H_3CH_2, *Z*). Mass m/z (i%): 127(33) ; 93(52) ; 80(100) ; 66(50).

(E,Z)-2-Benzylidene-4-nitropentanenitrile 3d:

IR ($CHCl_3$, νcm^{-1}): 1622(C=C) ; 2214(CN) ; 1561(C–NO_2). ^{1}H NMR($CDCl_3$,δ ppm) : 7.65(m, 2H, *Z*) ; 7.60(m, 2H, *E*) ; 7.29(m, 3H, *E*) ; 7.17(m, 3H, *Z*) ; 7.11(s, 1H, *Z*) ; 6.90(s, 1H, *E*) ; 4.78(m, 1H) ; 3.0(m,2H, *Z*) ; 2.80(m,2H, *E*) ; 1.51(d, 3H, 7.2*Hz*, *Z*) ; 1.48(d, 3H, 6.7*Hz*, *E*). ^{13}C NMR($CDCl_3$,TMS): 147.7(*C*H=C, *E*) ; 147.1(*C*H=C, *Z*) ; 132.6(*C*arom) ; 130.8 ; 129.6 ; 128.9 ; 128.6(5*C*Harom) ; 118.6(*C*N, *Z*) 117.5(*C*N, *E*) ; 105.5(CH=*C*, *Z*) ; 104.4(CH=*C*, *E*) ; 81.2(*C*HNO_2, *E*) ; 80.5(*C*HNO_2, *Z*) ;40.5(*C*H_2CHNO_2, *E*) ; 33.8(*C*H_2CHNO_2, *Z*) ; 18.6(*C*H_3CHNO_2, *Z*) ; 18.5(*C*H_3CHNO_2, *E*). Mass m/z (i%):140(20) ; 130(22) ; 115(18) ; 43(100).

(E,Z)-2-Hexylidene-4-nitropentanenitrile 3e:

IR ($CHCl_3$, νcm^{-1}): 1640(C=C) ; 2220(CN) ; 1556(C–NO_2). ^{1}H NMR($CDCl_3$,δ ppm): 6.50(t, 1H, 7.8*Hz*, *Z*) ; 6.29(t, 1H, 7.7*Hz*, *E*) ; 4.80(m, 1H) ; 3.05(m, 2H, *Z*) ; 2.95(m, 2H, *E*) ; 2.64(m, 2H, *E*) ; 2.36(m, 2H, *Z*) ; 1.64(d, 3H, 7.6*Hz*, *Z*) ; 1.61(d, 3H, 7.5*Hz*, *E*) ; 1.43(m, 2H) ; 1.29(m, 4H) ; 0.89(t, 3H, 6.6*Hz*). ^{13}C NMR($CDCl_3$,TMS): 155.5(*C*H=C,*Z*) ; 152.7(*C*H=C, *E*) ; 119.9(*C*N, *Z*) 116.3(*C*N, *E*) ; 108.3(CH=*C*, *E*) ; 106.7(CH=*C*, *Z*) ; 81.3(*C*HNO_2, *E*) ; 80.8(*C*HNO_2, *Z*) ; 41.0(*C*H_2CHNO_2, *Z*) ; 38.9(*C*H_2CHNO_2, *E*) ; 33.5(*C*H_2CH=C, *E*) ; 31.4(*C*H_2CH=C, *Z*) ; 31.0(*C*$H_2(CH_2)_2CH_3$) ; 28.4(*C*$H_2CH_2CH_3$) ; 22.0(*C*H_2CH_3)

; 18.6(CH_3CHNO_2, *Z*) ; 18.4(CH_3CHNO_2, *E*) ; 13.7(CH_3CH_2). Mass m/z (i%): 148(11) ; 120(40) ; 108(30) ; 107(39) ; 106(37) ; 95(20) ; 55(59) ; 41(100).

(E,Z)-2-Propylidene-4-nitrohexanenitrile 3f:

IR ($CHCl_3$, νcm^{-1}): 1640(C=C) ; 2220(CN) ; 1559(C-NO_2). ^1H NMR($CDCl_3$,δ ppm): 6.55(t, 1H, 7.8*Hz*, *Z*) ; 6.26(t, 1H, 7.7*Hz*, *E*) ; 4.65(m, 1H) ; 2.8(m,2H) ; 2.36(m, 2H, *E*) ; 2.17(m, 2H, *Z*) ; 2.10(m, 2H, *E*) ; 2.0(m, 2H, *Z*) ; 1.03(t, 3H, 7.3*Hz*) ; 1.01(t, 3H, 6.9*Hz*). ^{13}C NMR($CDCl_3$,TMS): 154.2(CH=C) ; 119.0(CN, *Z*) 116.4(CN, *E*) ; 108.4(CH=C, *Z*) ; 108.3(CH=C, *E*) ; 88.4($CHNO_2$, *E*) ; 87.9($CHNO_2$, *Z*) ; 38.0(CH_2CHNO_2, *Z*) ; 32.6(CH_2CHNO_2, *E*) ; 27.8($CH_3CH_2CHNO_2$) ; 25.5(CH_2CH=C, *E*) ; 22.4(CH_2CH=C, *Z*) ; 13.2(CH_3CH_2) ; 10.4($CH_3CH_2CHNO_2$). Mass m/z (i%): 136(28) ; 135(36) ; 120(34) ; 106(28) ; 93(70) ; 67(100) ; 41(63).

(E,Z)-2-Butylidene-4-nitrohexanenitrile 3g:

IR ($CHCl_3$, νcm^{-1}): 1638(C=C) ; 2220(CN) ; 1556(C-NO_2). ^1H NMR($CDCl_3$,δ ppm): 6.50(t, 1H, 7.8*Hz*, *Z*) ; 6.26(t, 1H, 7.7*Hz*, *E*) ; 4.65(m, 1H) ; 3.0(m, 2H, *Z*) ; 2.80(m, 2H, *E*) ; 2.37(m, 2H, *E*) ; 2.32(m, 2H, *Z*) ; 2.01(m, 2H, *E*) ; 1.99(m, 2H, *Z*) ; 1.45(m, 2H) ; 1.03(t, 3H, 7.3*Hz*) ; 0.94(t, 3H, 6.9*Hz*). ^{13}C NMR($CDCl_3$,TMS): 152.4(CH=C, *Z*) ; 152.3(CH=C, *E*) ; 119.1(CN, *Z*) 116.4(CN, *E*) ; 108.8(CH=C, *Z*) ; 108.7(CH=C, *E*) ; 87.9($CHNO_2$, *E*) ; 87.0($CHNO_2$, *Z*) ; 37.7(CH_2CHNO_2, *Z*) ; 33.4(CH_2CHNO_2, *E*) ; 32.2(CH_2CH=C, *Z*) ; 30.4(CH_2CH=C, *E*) ; 26.5($CH_2CH_2CH_3$) ; 21.5(CH_2CH_3) ; 13.4(CH_3CH_2) ; 10.0($CH_3CH_2CH_2$). Mass m/z (i%): 150(35) ; 149(27) ; 120(41) ; 108(75) ; 105(60) ; 81(100) ; 29(51).

(E,Z)-2-Benzylidene-4-nitrohexanenitrile 3h:

IR ($CHCl_3$, νcm^{-1}): 1623(C=C) ; 2214(CN) ; 1556(C-NO_2). ^1H NMR($CDCl_3$,δ ppm) : 7.70(m, 2H, *Z*) ; 7.69(m, 2H, *E*) ; 7.43(m, 3H, *E*) ; 7.42(m, 3H, *Z*) ; 7.41(s, 1H, *Z*) ; 7.0(s, 1H, *E*) ; 4.79(m, 1H) ; 3.2(m,2H, *Z*) ; 2.90(m,2H, *E*) ; 2.01(m, 2H, *E*) ; 1.95(m, 2H, *Z*) ; 1.01(t, 3H, 7.3*Hz*) ; 0.98(t, 3H, 7.4*Hz*). ^{13}C NMR($CDCl_3$,TMS): 148.0(CH=C, *Z*) ; 147.1(CH=C, *E*) ; 132.6(Carom) ; 130.7 ; 129.8 ; 128.8 ; 128.7(5CHarom) ; 119.0(CN, *Z*) 117.6(CN, *E*) ; 104.6(CH=C, *Z*) ; 104.5(CH=C, *E*) ; 87.9($CHNO_2$, *E*) ; 87.2($CHNO_2$, *Z*) ; 30.4(CH_2CHNO_2, *E*) ; 32.4(CH_2CHNO_2, *Z*) ; 26.7(CH_2CH_3, *E*) ; 26.6(CH_2CH_3, *Z*) ; 9.99(CH_3CH_2, *E*) ; 9.87(CH_3CH_2, *Z*). Mass m/z (i%): 183(49) ; 154(100) ; 142(65) ; 115(90).

Ethyl 2-methylene-4-nitropentanoate 4l:

IR ($CHCl_3$, νcm^{-1}): 1632(C=C) ; 1715(CO) ; 1560(C-NO_2). ^1H NMR($CDCl_3$,δ ppm): 6.27(s, 1H) ; 5.66(s, 1H) ; 4.87(m, 1H) ; 4.22(q, 2H, 7.0*Hz*) ; 2.86(m, 2H) ; 1.56(d, 3H, 7.3*Hz*) ; 1.31(t, 3H, 7.0*Hz*). ^{13}C NMR($CDCl_3$,TMS): 165.6(COO) ; 134.8(CH=C) ; 128.6(CH=C) ; 82.1($CHNO_2$) ; 60.8(CH_2OCO) ; 37.6(CH_3CH_2) ; 19.8(CH_2CHNO_2) ; 13.7(CH_3CHNO_2). Mass m/z (i%): 106(52) ; 181(42) ; 41(100) ; 29(56).

Ethyl 2-ethylidene-4-nitropentanoate 4m:

IR ($CHCl_3$, νcm^{-1}): 1649(C=C) ; 1713(CO) ; 1556(C-NO_2). ^1H NMR($CDCl_3$,δ ppm): 7.05(q, 1H, 7.2*Hz*, *E*) ; 7.20(q, 1H, 7.3*Hz*, *Z*) ; 4.81(m, 1H) ; 4.28(q, 2H, 7.0*Hz*) ; 2.9(m, 2H) ; 1.03(d, 3H, 7.3*Hz*, *Z*)

; 1.84(d, 3H, 7.2*Hz*, *E*) ; 1.53(d, 3H, 6.69*Hz*, *E*) ; 1.35(d, 3H, 6.7*Hz*, *Z*) ; 1.30(t, 3H, 7.0*Hz*). ^{13}C NMR($\mathrm{CDCl_3}$,TMS): 166.6(COO, *E*) ; 142.0(COO, *Z*) ; 142.0(CH=C, *Z*) ; 141.8(CH=C, *E*) ; 127.3(CH=C, *E*) ; 124.2(CH=C, *Z*) ; 82.6($\mathrm{CHNO_2}$, *Z*) ; 82.02($\mathrm{CHNO_2}$, *E*) ; 60.6($\mathrm{CH_2OCO}$, *E*) ; 60.3($\mathrm{CH_2OCO}$, *Z*) ; 40.3($\mathrm{CH_3CH_2}$) ; 32.4($\mathrm{CH_2CHNO_2}$, *E*) ; 30.0($\mathrm{CH_2CHNO_2}$, *Z*) ; 18.8($\mathrm{CH_3CHNO_2}$) ; 14.2($\mathrm{CH_3}$CH=C, *Z*) ; 13.9($\mathrm{CH_3}$CH=C, *E*). Mass m/z (i%): 154(45) ; 126(37) ; 81(100) ; 79(35) ; 53(29) ; 29(41).

Ethyl (Z,E)-2-propylidene-4-nitropentanoate 4n:
IR ($\mathrm{CHCl_3}$, vcm^{-1}): 1644(C=C) ; 1708(CO) ; 1551(C-$\mathrm{NO_2}$). ^{1}H NMR($\mathrm{CDCl_3}$,δ ppm): 6.94(t, 1H, 7.2*Hz*, *E*) ; 6.15(t, 1H, 7.3*Hz*, *Z*) ; 4.82(m, 1H) ; 4.22(q, 2H, 7.0*Hz*) ; 2.9(m, 2H) ; 2.33(m, 2H, *Z*) ; 2.08(m, 2H, *E*) ; 1.53(d, 3H, 7.3*Hz*, *Z*) ; 1.44(d, 3H, 7.2*Hz*, *E*) ; 1.31(t, 3H, 7.0*Hz*) ; 0.72(t, 3H, 6.9*Hz*). ^{13}C NMR($\mathrm{CDCl_3}$,TMS): 169.8(COO, *Z*) ; 166.4(COO, *E*) ; 149.8(CH=C, *Z*) ; 148.5(CH=C, *E*) ; 125.6(CH=C, *E*) ; 125.2(CH=C, *Z*) ; 82.7($\mathrm{CHNO_2}$, *Z*) ; 82.2($\mathrm{CHNO_2}$, *E*) ; 60.7($\mathrm{CH_2OCO}$, *E*) ; 60.4($\mathrm{CH_2OCO}$, *Z*) ; 40.3($\mathrm{CH_3CH_2OCO}$) ; 32.5($\mathrm{CH_2CHNO_2}$, *E*) ; 29.5($\mathrm{CH_2CHNO_2}$, *Z*) ; 27.03($\mathrm{CH_2}$CH=C, *Z*) ; 23.1($\mathrm{CH_2}$CH=C, *E*) ; 20.8($\mathrm{CH_3CHNO_2}$) ; 13.9($\mathrm{CH_3CH_2}$CH=C). Mass m/z (i%): 170(25) ; 123(33) ; 111(23) ; 95(100) ; 81(25) ; 55(40) ; 29(47).

Ethyl (Z,E)-2-butylidene-4-nitropentanoate 4o:
IR ($\mathrm{CHCl_3}$, vcm^{-1}): 1645(C=C) ; 1699(CO) ; 1552(C-$\mathrm{NO_2}$). ^{1}H NMR($\mathrm{CDCl_3}$,δ ppm): 6.94(t, 1H, 7.4*Hz*, *E*) ; 6.03(t, 1H, 7.5*Hz*, *Z*) ; 4.79(m, 1H) ; 4.17(q, 2H, 7.0*Hz*) ; 2.9(m, 2H) ; 2.47(m, 2H, *Z*) ; 2.06(m, 2H, *E*) ; 1.51(d, 3H, 7.2*Hz*) ; 1.39(m, 2H) ; 1.35(t, 3H, 7.0*Hz*) ; 0.92(t, 3H, 6.9*Hz*).^{13}C NMR($\mathrm{CDCl_3}$,TMS): 166.6(COO, *E*) ; 166.4(COO, *Z*) ; 148.5(CH=C, *Z*) ; 147.2(CH=C, *E*) ; 126.4(CH=C, *E*) ; 126.0(CH=C, *Z*) ; 82.9($\mathrm{CHNO_2}$, *Z*) ; 82.3($\mathrm{CHNO_2}$, *E*) ; 60.8($\mathrm{CH_2OCO}$, *E*) ; 60.5($\mathrm{CH_2OCO}$, *Z*) ; 40.6($\mathrm{CH_3CH_2OCO}$) ; 32.7($\mathrm{CH_2CHNO_2}$, *E*) ; 31.7($\mathrm{CH_2CHNO_2}$, *Z*) ; 22.4($\mathrm{CH_2}$CH=C, *Z*) ; 22.0($\mathrm{CH_2}$CH=C, *E*) ; 19.1($\mathrm{CH_2CH_3}$) ; 14.2($\mathrm{CH_3CHNO_2}$) ; 13.9($\mathrm{CH_3CH_2}$). Mass m/z (i%) : 184(35) ; 112(33) ; 107(35) ; 95(29) ; 84(100).

Ethyl (Z,E)-2-hexylidene-4-nitropentanoate 4p:
IR ($\mathrm{CHCl_3}$, vcm^{-1}): 1645(C=C) ; 1698(CO) ; 1552(C-$\mathrm{NO_2}$). ^{1}H NMR($\mathrm{CDCl_3}$,δ ppm): 6.95(t, 1H, 7.6*Hz*, *E*) ; 6.04(t, 1H, 7.7*Hz*, *Z*) ; 4.84(m, 1H) ; 4.22(q, 2H, 7.0*Hz*) ; 3.85(m, 2H) ; 2.46(m, 2H, *Z*) ; 2.19(m, 2H, *E*) ; 1.55(d, 3H, 7.3*Hz*, *E*) ; 1.52(d, 3H, 7.4*Hz*, *Z*) ; 1.45(m, 9H) ; 1.34(t, 3H, 7.0*Hz*). ^{13}C NMR($\mathrm{CDCl_3}$,TMS): 166.8(COO, *E*) ; 167.7(COO, *Z*) ; 148.7(CH=C,*Z*) ; 147.5(CH=C, *E*) ; 126.2(CH=C, *E*) ; 125.7(CH=C, *Z*) ; 82.9($\mathrm{CHNO_2}$, *Z*) ; 82.3($\mathrm{CHNO_2}$, *E*) ; 60.8($\mathrm{CH_2OCO}$, *E*) ; 60.5($\mathrm{CH_2OCO}$, *Z*) ; 40.6($\mathrm{CH_3CH_2OCO}$) ; 31.5($\mathrm{CH_2CHNO_2}$, *E*) ; 31.4($\mathrm{CH_2CHNO_2}$, *Z*) ; 29.7($\mathrm{CH_2}$CH=C, *Z*) ; 28.8($\mathrm{CH_2}$CH=C, *E*) ; 28.4($\mathrm{CH_2(CH_2)_2CH_3}$) ; 22.4($\mathrm{CH_2CH_2CH_3}$) ; 19.0($\mathrm{CH_2CH_3}$) ; 14.2($\mathrm{CH_3CHNO_2}$) ; 13.9($\mathrm{CH_3CH_2}$). Mass m/z (i%): 212(21) ; 167(30) ; 137(24) ; 111(100) ; 95(69) ; 93(42) ; 81(72) ; 29(78).

Ethyl 2-methylene-4-nitrohexanoate 4q:
IR ($\mathrm{CHCl_3}$, vcm^{-1}): 1632(C=C) ; 1715(CO) ; 1560(C-$\mathrm{NO_2}$). ^{1}H NMR($\mathrm{CDCl_3}$,δ ppm): 6.25(s, 1H) ; 5.64(s, 1H) ; 4.66(m, 1H) ; 4.33(q, 2H, 7.0*Hz*) ; 2.8(d, 2H, 7.3*Hz*) ; 1.86(m, 2H) ; 1.43(t, 3H, 7.0*Hz*) ; 1.31(m, 3H). ^{13}C NMR($\mathrm{CDCl_3}$,TMS): 166.1(COO) ; 135.0(CH=C) ; 129.0(CH=C) ; 89.3($\mathrm{CHNO_2}$) ;

61.3(CH_2OCO) ; 36.5(CH_3CH_2OCO) ; 27.3(CH_2CHNO_2) ; 21.1($CH_3CH_2CHNO_2$) ; 10.3(CH_3CH_2). Mass m/z (i%): 127(28) ; 109(64) ; 81(100) ; 79(32) ; 55(21) ; 53(20) ; 41(32) ; 29(42).

Ethyl (Z,E)-2-butylidene-4-nitrohexanoate 4r:

IR ($CHCl_3$, νcm^{-1}): 1645(C=C) ; 1697(CO) ; 1551(C-NO_2). ^1H NMR($CDCl_3$,δ ppm): 6.96(t, 1H, 7.6*Hz*, *E*) ; 6.03(t, 1H, 7.7*Hz*, *Z*) ; 4.65(m, 1H) ; 4.22(q, 2H, 7.0*Hz*) ; 2.9(m, 2H, *E*) ; 2.79(m, 2H, *Z*) ; 2.6(m, 2H, *Z*) ; 2.17(m, 2H, *E*) ; 2.12(m, 2H) ; 1.47(m, 2H) ; 1.32(t, 3H, 7.0*Hz*) ; 1.02(m, 6H).^{13}C NMR($CDCl_3$,TMS): 167.2(COO, *E*) ; 167.0(COO, *Z*) ; 148.8(CH=C, *Z*) ; 147.5(CH=C, *E*) ; 126.7(CH=C, *E*) ; 126.2(CH=C, *Z*) ; 90.1($CHNO_2$, *Z*) ; 89.5($CHNO_2$, *E*) ; 61.2(CH_2OCO, *E*) ; 60.9(CH_2OCO, *Z*) ; 39.5(CH_3CH_2OCO) ; 31.8(CH_2CHNO_2, *E*) ; 31.0(CH_2CHNO_2, *Z*) ; 27.5($CH_3CH_2CHNO_2$) ; 27.3(CH_2CH=C, *E*) ; 22.4(CH_2CH=C, *Z*) ; 14.6(CH_2CH_3) ; 14.2($CH_3CH_2CHNO_2$) ; 10.6(CH_3CH_2). Mass m/z (i%) : 198(26) ; 151(21) ; 123(27) ; 109(39) ; 83(57) ; 81(100) ; 55(64) ; 29(55).

Synthesis of *(E,Z)*-2- alkylidene-4-Ketonitriles 5 and *(E,Z)*-2-alkylidene-4-Ketoesters 6

General procedure: To a solution of absolute methanol (40mL), Na (18.8mmol) was added. The nitro derivative **3** or **4** (15mmol) was added to obtain the corresponding nitronate. MeOH (40mL) and concentrated H_2SO_4 (8mL) was added at -50°C to the mixture. After 10mn, water (80mL) was added and the solution was concentrated in order to reduce the excess of MeOH. The mixture was extracted with CH_2Cl_2 (100mL) washed with 1% NaOH (40mL), brine (40 mL) and dried on $MgSO_4$. The solvent was evaporated under reduced pressure to give a crude product which was purified by chromatography (AcOEt/hexane, 2:8).

(E,Z)-2-Ethylidene-4-oxopentanenitrile 5a:

IR ($CHCl_3$, νcm^{-1}): 1645(C=C) ; 2221(CN) ; 1725(CO). ^1H NMR($CDCl_3$,δ ppm): 6.52(q, 1H, 7.2*Hz*, *Z*) ; 6.20(q, 1H, 7.0*Hz*, *E*) ; 3.28(s, 2H, *Z*) ; 3.24(s, 2H, *E*) ; 2.11(s, 3H, *Z*) ; 2.07(s, 3H, *E*) ; 1.91(d, 3H, 7.0*Hz*, *E*) ; 1.68(d, 3H, 7.2*Hz*, *Z*). ^{13}C NMR($CDCl_3$,TMS): 203.0(CO, *E*) ; 202.0(CO, *Z*) ; 146.9(CH=C,*E*) ; 146.6(CH=C,*Z*) ; 119.0(CN, *Z*) 116.6(CN, *E*) ; 108.1(CH=C, *E*) ; 107.9(CH=C, *Z*) ; 47.1(CH_2CO, *E*) ; 42.2(CH_2CO, *Z*) ; 29.2(CH_3CO, *Z*) ; 29.0(CH_3CO, *E*) ; 16.9(CH_3CH=C, *E*) ; 14.3(CH_3CH=C, *Z*). Mass m/z (i%): 123(M^+, 3) ; 53(8) ; 43(100).

(E,Z)-2-Propylidene-4-oxopentanenitrile 5b:

IR ($CHCl_3$, νcm^{-1}): 1640(C=C) ; 2221(CN) ; 1728(CO). ^1H NMR($CDCl_3$,δ ppm): 6.50(t, 1H, 7.8*Hz*, *Z*) ; 6.21(t, 1H, 7.6*Hz*, *E*) ; 3.32(s, 2H, *Z*) ; 3.28(s, 2H, *E*) ; 2.50(m, 2H, *Z*) ; 2.34(m, 2H, *E*) ; 2.16(s, 3H) ; 1.01(t, 3H, 7.0*Hz*). ^{13}C NMR($CDCl_3$,TMS): 203.9(CO, *E*) ; 202.1(CO, *Z*) ; 153.7(CH=C,*E*) ; 153.4(CH=C,*Z*) ; 119.2(CN, *Z*) 116.5(CN, *E*) ; 106.5(CH=C, *E*) ; 106.0(CH=C, *Z*) ; 47.2(CH_2CO, *E*) ; 42.5(CH_2CO, *Z*) ; 29.2(CH_3CO, *Z*) ; 29.0(CH_3CO, *E*) ; 24.7(CH_2CH=C, *E*) ; 21.9(CH_2CH=C, *Z*) ; 12.5(CH_3CH_2, *E*) ; 12.43(CH_3CH_2, *Z*). Mass m/z (i%): 137(M^+, 5) ; 94(13) ; 67(8) ; 43(100).

(E,Z)-2-Butylidene-4-oxopentanenitrile 5c:

IR ($CHCl_3$, νcm^{-1}): 1638(C=C) ; 2220(CN) ; 1725(CO). ^1H NMR($CDCl_3$,δ ppm): 6.36(t, 1H, 7.8*Hz*, *Z*) ; 6.29(t, 1H, 7.6*Hz*, *E*) ; 3.38(s, 2H, *Z*) ; 3.36(s, 2H, *E*) ; 2.47(m, 2H, *Z*) ; 2.37(m, 2H, *E*) ; 1.48(m, 3H) ; 0.96(m, 5H). ^{13}C NMR($CDCl_3$,TMS): 202.1(*C*O, *E*) ; 202.0(*C*O, *Z*) ; 151.9(*C*H=C,*E*) ; 150.6(*C*H=C,*Z*) ; 117.2(*C*N, *Z*) 116.5(*C*N, *E*) ; 102.7(CH=*C*, *Z*) ; 102.5(CH=*C*, *E*) ; 53.7(CH_2CO, *Z*) ; 53.3(CH_2CO, *E*) ; 33.4(CH_3CO, *Z*) ; 31.7(CH_3CO, *E*) ; 31.5(CH_2CH=C, *E*) ; 30.3(CH_2CH=C, *Z*) ; 21.5(CH_2CH_3, *Z*) ; 21.3(CH_2CH_3, *E*) ; 13.3(CH_3CH_2, *E*) ; 12.2(CH_3CH_2, *Z*). Mass m/z (i%): 127(23) ; 106(37) ; 80(100) ; 66(46) ; 55(48).

(E,Z)-2-Benzylidene-4-oxopentanenitrile 5d:

IR ($CHCl_3$, νcm^{-1}): 1622(C=C) ; 2216(CN) ; 1722(CO). ^1H NMR($CDCl_3$,δ ppm): 7.60(m, 2H) ; 7.26(m, 3H) ; 7.23(s, 1H, *Z*) ; 6.84(s, 1H, *E*) ; 3.43(s, 2H, *Z*) ; 3.38(s, 2H, *E*) ; 2.10(s, 3H) ^{13}C NMR($CDCl_3$,TMS): 203.1(*C*O, *E*) ; 202.8(*C*O, *Z*) ; 147.3(*C*H=C, *Z*) ; 147.0(*C*H=C, *E*) ; 132.8(*C*arom) ; 130.1; ; 129.4 ; 126.6 ; 128.3(5*C*Harom) ; 119.6(*C*N, *Z*) ; 118.1(*C*N, *E*) ; 107.5(CH=*C*, *E*) ; 103.3(CH=*C*, *Z*) ; 48.8(CH_2CO, *E*) ; 43.7(CH_2CO, *Z*) ; 29.5(CH_3CO, *Z*) ; 29.2($CH_{3s}CO$, *E*). Mass m/z (i%): 185(M^+, 5) ; 115(18) ; 43(100) ; 28(18).

(E,Z)-2-Hexylidene-4-oxopentanenitrile 5e:

IR ($CHCl_3$, νcm^{-1}): 1637(C=C) ; 2221(CN) ; 1722(CO). ^1H NMR($CDCl_3$,δ ppm): 6.57(t, 1H, 7.8*Hz*, *Z*) ; 6.18(t, 1H, 7.7*Hz*, *E*) ; 3.30(s, 2H, *Z*) ; 3.26(s, 2H, *E*) ; 2.34(m, 2H, *E*) ; 2.17(s, 3H, *Z*) ; 2.15(s, 3H, *E*) ; 2.14(m, 2H, *Z*) ; 1.39(m, 2H) ; 1.27(m, 4H) ; 0.84(m, 3H). ^{13}C NMR($CDCl_3$,TMS): 202.9(*C*O, *E*) ; 202.5(*C*O, *Z*) ; 152.3(*C*H=C,*E*) ; 151.9(*C*H=C,*Z*) ; 119.0(*C*N, *Z*) ; 116.8(*C*N, *E*) ; 107.1(CH=*C*, *E*) ; 106.9(CH=*C*, *Z*) ; 47.4(CH_3CO, *E*) ; 42.7(CH_2CO, *Z*) ; 31.4(CH_2CO, *Z*) ; 30.9(CH_3CO, *E*) ; 29.1(CH_2CH=C, *E*) ; 28.6(CH_2CH=C, *Z*) ; 27.5($CH_2(CH_2)_2CH_3$) ; 22.0($CH_2CH_2CH_3$) ; 21.9(CH_2CH_3) ; 13.6(CH_3CH_2). Mass m/z (i%): 179(M^+, 2) ; 95(3) ; 80(5) ; 53(3) ; 43(100).

(E,Z)-2-Propylidene-4-oxohexanenitrile 5f:

IR ($CHCl_3$, νcm^{-1}): 1640(C=C) ; 2221(CN) ; 1721(CO). ^1H NMR($CDCl_3$,δ ppm): 6.55(t, 1H, 7.7*Hz*, *Z*) ; 6.23(t, 1H, 7.6*Hz*, *E*) ; 3.33(s, 2H, *Z*) ; 3.29(s, 2H, *E*) ; 2.34(m, 4H) ; 1.03(m, 6H). ^{13}C NMR($CDCl_3$,TMS): 205.9(*C*O, *E*) ; 205.0(*C*O, *Z*) ; 153.6(*C*H=C,*E*) ; 153.4(*C*H=C, *Z*) ; 119.0(*C*N, *Z*) 117.1(*C*N, *E*) ; 107.0(CH=*C*) ; 46.6(CH_2CO, *E*) ; 41.9(CH_2CO, *Z*) ; 35.7(CH_3CH_2CO) ; 26.6(CH_2CH=C, *E*) ; 22.4(CH_2CH=C, *Z*) ; 13.0(CH_3CH_2) ; 7.6(CH_3CH_2CO). Mass m/z (i%): 151(M^+, 1) ; 94(9) ; 67(6) ; 57(100) ; 29(46).

(E,Z)-2-Bytylidene-4-oxohexanenitrile 5g:

IR ($CHCl_3$, νcm^{-1}): 1642(C=C) ; 2221(CN) ; 1721(CO). ^1H NMR($CDCl_3$,δ ppm): 6.53(t, 1H, 7.7*Hz*, *Z*) ; 6.20(t, 1H, 7.6*Hz*, *E*) ; 3.59(s, 2H, *Z*) ; 3.26(s, 2H, *E*) ; 2.49(m, 2H) , 2.25(m, 2H, *E*) ; 2.06(m, 2H, *Z*) ; 1.47(m, 2H) ; 1.04(t, 3H, 6.9*Hz*) ; 0.92(t, 3H, 7.3*Hz*). ^{13}C NMR($CDCl_3$,TMS): 205.8(*C*O, *E*) ; 205.0(*C*O, *Z*) ; 152.1(*C*H=C,*E*) ; 151.9(*C*H=C,*Z*) ; 119.0(*C*N, *Z*) ; 117.2(*C*N, *E*) ; 107.6(CH=*C*) ; 46.5(CH_2CO, *E*) ; 41.9(CH_2CO, *Z*) ; 35.6(CH_3CH_2CO, *E*) ; 33.6(CH_3CH_2CO, *Z*) ; 30.8(CH_2CH=C) ;

21.5(CH_2CH_3) ; 13.5(CH_3CH_2) ; 7.5(CH_3CH_2CO). Mass m/z (i%): 165(M^+, 2) ; 80(3) ; 58(4) ; 57(100) ; 29(32).

(E,Z)-2-Benzylidene-4-oxohexanenitrile 5h:

IR ($CHCl_3$, νcm^{-1}): 1620(C=C) ; 2215(CN) ; 1725(CO). ^1H NMR($CDCl_3$,δ ppm): 7.73(m, 2H) ; 7.40(m, 3H) ; 7.26(s, 1H, *Z*) ; 6.97(s, 1H, *E*) ; 3.39(s, 2H, *E*) ; 3.50(s, 2H, *Z*) ; 2.58(q, 2H, 6.9*Hz*) ; 1.11(t, 3H, 6.9*Hz*) ^{13}C NMR($CDCl_3$,TMS): 207.8(CO, *Z*) ; 206.3(CO, *E*) ; 147.8(CH=C, *Z*) ; 144.0(CH=C, *E*) ; 133.5(Carom) ; 133.4; 120.9 ; 129.3 ; 129.2(5CHarom) ; 118.9(CN, *Z*) ; 118.1(CN, *E*) ; 111.1(CH=C, *E*) ; 111.0(CH=C, *Z*) ; 64.7(CH_2CO, *E*) ; 48.7(CH_2CO, *Z*) ; 36.3(CH_3CH_2CO) ; 8.0(CH_3CH_2CO). Mass m/z (i%): 199(M^+,7) ; 115(13) ; 57(100) ; 29(32).

Ethyl 2-methylene-4-oxopentanoate 6l:

IR ($CHCl_3$, νcm^{-1}): 1634(C=C) ; 1714(COO) ; 1720(CO). ^1H NMR($CDCl_3$,δ ppm): 6.30(s, 1H) ; 5.65(s, 1H) ; 4.20(q, 2H, 7.0*Hz*) ; 3.43(s, 2H) ; 2.21(s, 3H) ; 1.29(t, 3H, 7.0*Hz*). ^{13}C NMR($CDCl_3$,TMS): 204.9(CO) ; 166.0(COO) ; 134.3(CH=C) ; 128.1(CH=C) ; 60.7(CH_2OCO) ; 46.2(CH_3CH_2) ; 29.5(CH_2CO) ; 13.0(CH_3CO). Mass m/z (i%): 156(M^+,3) ; 106(52) ; 81(42) ; 41(100) ; 29(56).

Ethyl (Z,E)-2-ethylidene-4-oxopentanoate 6m:

IR ($CHCl_3$, νcm^{-1}): 1651(C=C) ; 1700(COO) ; 1722(CO). ^1H NMR($CDCl_3$,δ ppm): 7.01(q, 1H, 7.0*Hz*, *E*) ; 6.15(q, 1H, 7.1*Hz*, *Z*) ; 4.12(q, 2H, 7.0*Hz*) ; 3.36(s, 2H, *E*) ; 3.21(s, 2H, *Z*) ; 2.12(s, 3H) ; 1.78(d, 3H, 7.1*Hz*, *Z*) ; 1.72(d, 3H, 7.0*Hz*, *E*) ; 1.20(t, 3H, 7.0*Hz*). ^{13}C NMR($CDCl_3$,TMS): 205.2(CO, *Z*) ; 205.1(CO, *E*) ; 166.7(COO, *E*) ; 166.6(COO, *Z*) ; 142.0(CH=C, *Z*) ; 140.3(CH=C, *E*) ; 126.9(CH=C, *E*) ; 126.0(CH=C, *Z*) ; 60.5(CH_2OCO, *E*) ; 60.4(CH_2OCO, *Z*) ; 41.0(CH_3CH_2O) ; 32.3(CH_2CO, *Z*) ; 29.5(CH_2CO, *E*) ; 15.8(CH_3CO, *Z*) ; 15.7(CH_3CO, *E*) ; 14.0(CH_3CH=C, *Z*) ; 13.9(CH_3CH=C, *E*). Mass m/z (i%): 170(M^+, 2) ; 128(57) ; 125(21) ; 100(42) ; 82(28) ; 54(21) ; 43(100) ; 29(16).

Ethyl (Z,E)-2-propylidene-4-oxopentanoate 6n:

IR ($CHCl_3$, νcm^{-1}): 1649(C=C) ; 1714(COO) ; 1717(CO). ^1H NMR($CDCl_3$,δ ppm): 6.94(t, 1H, 7.0*Hz*, *E*) ; 6.15(t, 1H, 7.3*Hz*, *Z*) ; 4.19(q, 2H, 7.0*Hz*) ; 3.5(s, 2H) ; 2.60(m, 2H, *Z*) ; 2.18(m, 2H, *E*) ; 2.19(s, 3H) ; 1.08(t, 3H, 7.0*Hz*) ; 1.07(t, 3H, 6.9*Hz*). ^{13}C NMR($CDCl_3$,TMS): 205.3(CO, *E*) ; 205.1(CO, *Z*) ; 167.5(COO, *Z*) ; 167.0(COO, *E*) ; 149.2(CH=C, *Z*) ; 147.5(CH=C, *E*) ; 125.4(CH=C, *E*) ; 124.9(CH=C, *Z*) ; 60.6(CH_2OCO, *E*) ; 60.3(CH_2OCO, *Z*) ; 41.3(CH_3CH_2OCO) ; 29.5(CH_2CO, *E*) ; 29.0(CH_2CO, *Z*) ; 22.9(CH_2CH=C, *Z*) ; 22.2(CH_2CH=C, *E*) ; 14.0(CH_3CO) ; 13.6(CH_3CH_2CH=C). Mass m/z (i%): 142(33) ; 138(37) ; 113(25) ; 95(27) ; 67(34) ; 43(100).

Ethyl (Z,E)-2-butylidene-4-oxopentanoate 6o:

IR ($CHCl_3$, νcm^{-1}): 1650(C=C) ; 1713(COO) ; 1721(CO). ^1H NMR($CDCl_3$,δ ppm): 7.0(t, 1H, 7.5*Hz*, *E*) ; 6.02(t, 1H, 7.6*Hz*, *Z*) ; 4.20(q, 2H, 7.0*Hz*) ; 3.47(s, 2H, *E*) ; 3.34(s, 2H, *Z*) ; 2.57(m, 2H, *Z*) ; 2.20(s, 3H) ; 2.17(m, 2H, *E*) ; 1.65(m, 2H, *Z*) ; 1.47(m, 2H, *E*) ; 1.37(t, 3H, 7.0*Hz*) ; 1.29(t, 3H, 6.9*Hz*).^{13}C NMR($CDCl_3$,TMS): 206.3(CO, *E*) ; 206.1(CO, *Z*) ; 166.9(COO, *E*) ; 163.2(COO, *Z*) ; 145.9(CH=C, *Z*) ;

145.5($CH=C$, *E*) ; 126.5($CH=C$, *E*) ; 126.0($CH=C$, *Z*) ; 60.6(CH_2OCO, *E*) ; 60.5(CH_2OCO, *Z*) ; 51.7(CH_3CH_2OCO) ; 49.1(CH_2CO, *Z*) ; 41.4(CH_2CO, *E*) ; 31.7($CH_2CH=C$, *Z*) ; 30.8($CH_2CH=C$, *E*) ; 29.4(CH_3CO, *E*) ; 29.2(CH_3CO, *Z*) ; 22.3(CH_2CH_3, *Z*) ; 21.6(CH_2CH_3, *E*) ; 14.0(CH_3CH_2, *Z*) ; 13.7(CH_3CH_2, *E*). Mass m/z (i%) : 152(40) ; 109(18) ; 87(22) ; 81(29) ; 43(100).

Ethyl (Z,E)-2-hexylidene-4-oxopentanoate 6p:

IR ($CHCl_3$, νcm^{-1}): 1650(C=C) ; 1700(COO) ; 1721(CO). ^1H NMR($CDCl_3$,δ ppm): 6.92(t, 1H, 7.5*Hz*, *E*) ; 6.0(t, 1H, 7.7*Hz*, *Z*) ; 4.22(q, 2H, 7.0*Hz*) ; 3.55(s, 2H, *E*) ; 3.23(s, 2H, *Z*) ; 2.47(m, 2H, *Z*) ; 2.10(s, 3H) ; 2.07(m, 2H, *E*) ; 1.25(m, 9H) ; 1.12(t, 3H, 7.0*Hz*). ^{13}C NMR($CDCl_3$,TMS): 206.3(CO, *E*) ; 206.2(CO, *Z*) ; 167.5(COO, *E*) ; 166.7(COO, *Z*) ; 146.3($CH=C$, *E*) ; 145.9($CH=C$, *Z*) ; 126.0($CH=C$, *E*) ; 125.7($CH=C$, *Z*) ; 60.7(CH_2OCO, *E*) ; 60.3(CH_2OCO, *Z*) ; 51.9(CH_3CH_2OCO) ; 49.2(CH_2CO, *Z*) ; 41.6(CH_2CO, *E*) ; 31.5($CH_2CH=C$, *E*) ; 29.6($CH_2CH=C$, *Z*) ; 29.4(CH_3CO) ; 29.0($CH_2(CH_2)_2CH_3$) ; 22.4($CH_2CH_2CH_3$) ; 14.0(CH_2CH_3) ; 13.9(CH_3CH_2). Mass m/z (i%): 226(M^+, 1) ; 180(45) ; 137(18) ; 127(20) ; 114(22) ; 101(19) ; 43(100).

Ethyl 2-methylene-4-oxohexanoate 6q:

IR ($CHCl_3$, νcm^{-1}): 1649(C=C) ; 1695(COO) ; 1722(CO). ^1H NMR($CDCl_3$,δ ppm): 6.25(s, 1H) ; 5.56(s, 1H) ; 4.06(q, 2H, 7.0*Hz*) ; 2.80(s, 2H) ; 2.10(q, 2H, 7.3*Hz*) ; 1.45(t, 3H, 7.0*Hz*) ; 1.05(t, 3H, 7.3*Hz*). ^{13}C NMR($CDCl_3$,TMS): 207.9(CO) ; 166.3(COO) ; 134.7($CH=C$) ; 128.6($CH=C$) ; 60.9(CH_2OCO) ; 45.4(CH_3CH_2O) ; 35.8(CH_2CO) ; 14.3(CH_3CH_2CO) ; 7.7(CH_3CH_2CO). Mass m/z (i%): 170(M^+, 3) ; 141(10) ; 125(20) ; 113(15) ; 86(15) ; 68(10) ; 57(100).

Ethyl (Z,E)-2-butylidene-4-oxohexanoate 6r:

IR ($CHCl_3$, νcm^{-1}): 1650(C=C) ; 1713(COO) ; 1721(CO). ^1H NMR($CDCl_3$,δ ppm): 7.0(t, 1H, 7.6*Hz*, *E*) ; 6.0(t, 1H, 7.6*Hz*, *Z*) ; 4.26(q, 2H, 7.0*Hz*) ; 3.40(s, 2H, *E*) ; 3.31(s, 2H, *Z*) ; 2.17(m, 2H) ; 2.10(m, 2H) ; 1.50(m, 2H) ; 1.31(t, 3H, 7.0*Hz*) ; 1.23(t, 3H, 6.9*Hz*) ; 1.17(t, 3H, 6.9*Hz*).^{13}C NMR($CDCl_3$,TMS): 206.7(CO, *E*) ; 206.6(CO, *Z*) ; 167.0(COO, *E*) ; 166.9(COO, *Z*) ; 147.4($CH=C$, *Z*) ; 145.7($CH=C$, *E*) ; 126.5($CH=C$, *E*) ; 126.0($CH=C$, *Z*) ; 60.6(CH_2OCO, *E*) ; 60.2(CH_2OCO, *Z*) ; 51.7(CH_3CH_2OCO, *Z*) ; 48.0(CH_3CH_2OCO, *E*) ; 40.2(CH_2CO, *Z*) ; 35.5(CH_2CO, *E*) ; 31.5($CH_2CH=C$, *Z*) ; 30.9($CH_2CH=C$, *E*) ; 22.4(CH_3CH_2CO, *Z*) ; 21.7(CH_3CH_2CO, *E*) ; 14.0(CH_2CH_3) ; 13.7(CH_3CH_2CO) ; 13.5($CH_3CH_2CH_2$). Mass m/z (i%): 166(24) ; 81(12) ; 57(100) ; 29(45).

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