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DABCO-mediated substitution of vinylic iodides: synthesis of β-cyano Baylis–Hillman acetates

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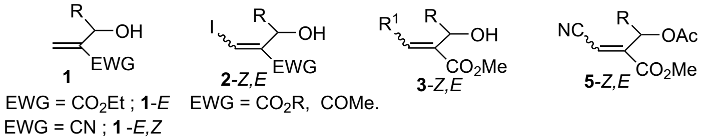
ABSTRACT

Nucleophilic substitution of vinyl β-iodo Baylis–Hillman acetates using 1,4-diazabicyclo[2.2.2] octane (DABCO) and then KCN, provides a stereoselective method for the synthesis of the corresponding β-cyano Baylis–Hillman acetates in high yields.

1. Introduction

The Baylis–Hillman reaction is one of the few reactions, which allow the direct α-functionalisation of acrylic compounds.[1] The resulting new C–C bond between an aldehyde and the electron deficient olefin generates building blocks of type **1** (R^1=H) for some synthetic uses.[2] The α-substitution of 2-alkenoic esters providing β-branched Baylis–Hillman adducts **3** is difficult to obtain and has serious limitations.[3] Several solutions have been proposed in order to overcome this problem.[4] Most of the solutions involve the generation of an α-carbanion from some alk-2-enoates or substituted acetylenic esters then coupling with aldehydes or ketones.[5] As part of our research program on the synthesis and the reactivity of α-functional substrates **1**, we have reported the first examples of successful tandem bromination–formylation–hydrolysis of readily available Baylis–Hillman products **1** (R^1=H) leading to the preparation of (*E*)-2-(hydroxymethyl) alk-2-enoates **1** (R=H) and (*E*,*Z*)-2-(hydroxymethyl) alk-2-enenitriles **1** (R=H) in good yields[6] (Scheme 1).



Scheme 1.

2. Results and discussion

The synthesis of multifunctionalized trisubstituted alkenes in a stereoselective fashion is still an important objective in synthetic organic chemistry.[7] Thus, some methods for the synthesis of β-iodo Baylis–Hillman products **2-*Z*,*E*** have been reported[8] and used in an original way by one of our group[9] to prepare β-branched Baylis–Hillman products **3-*Z*,*E*** (Scheme 2).

This result prompts us to report here a convenient method to accomplish a one-pot synthesis of β-cyano Baylis–Hillman acetates **5** in high yields involving an indirect substitution of β-iodo Baylis–Hillman acetates **4-*Z*,*E*** using potassium cyanide in aqueous THF. In order to explain the synthetic strategy for the formation of compounds **5**, we specify firstly that the lower reactivity of cyanide ion

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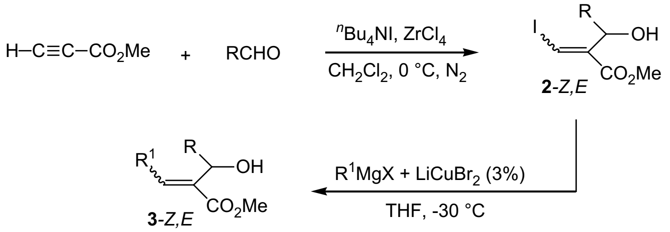
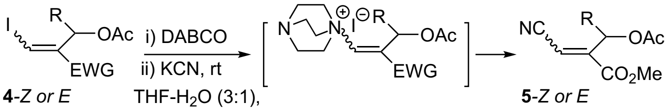


Scheme 2.

as nucleophilic reagent[10] is unfavourable for the displacement of vinylic iodide of **4** and secondly, that repeated efforts to overcome this substitution starting from the hydroxylated derivative **2** failed. In this regard, we propose a convenient method to convert the most substituted Baylis–Hillman acetates to the α-cyanomethylated esters through DABCO-assisted successive S_N2'–S_N2' reaction of allyl acetates with KCN.[11] To the DABCO salt resulting from the reaction of each separated β-iodo Baylis–Hillman acetate **4-*Z*** or **4-*E*** (1 equiv) and DABCO (1.4 equiv) in THF–H_2O (10 mL, 3:1) was added KCN (1.5 equiv) under stirring at room temperature. In this way, unexpectedly, only the β-cyano Baylis–Hillman acetate **5-*Z*** or **5-*E*** was formed as the result of direct nucleophilic vinylic substitution reaction[12] in excellent yields (Scheme 3).

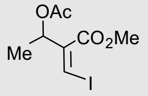
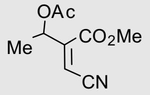
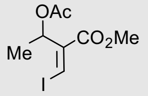
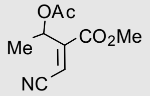
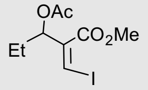
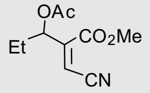
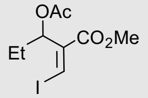
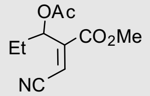
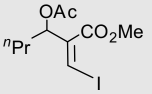
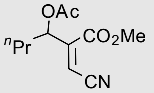
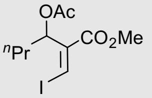
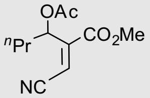
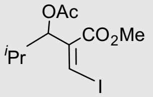
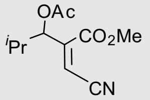
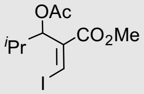
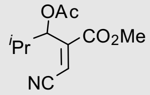
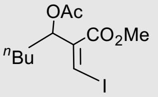
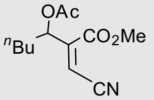
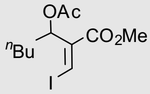
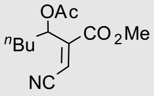
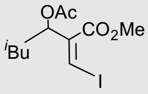
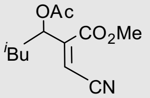
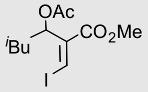
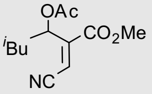


Scheme 3.

Due to the electron-withdrawing nature associated with the iodo group, the elimination of the allylic acetoxy group cannot occur. Thus, the attack of DABCO on the β carbon yielded a carbanion followed by the loss of iodide ion leading to the functionalised ammonium intermediate, which can react with cyanide ion to give the β-cyano Baylis–Hillman acetate **5** with complete stereoselectivity (100% *Z* or *E*) (Table 1). To the best of our knowledge, no studies concerning the displacement of vinylic halides by DABCO have been were reported previously. However, taking into account the different results of nucleophilic vinylic substitution of strongly activated systems such as **4** and the good leaving group as the iodide ion, it seems that the most plausible reaction mechanism predicts a direct substitution or an addition-elimination process (Ad_N-*E*) with a retained geometric configuration.[12,13]

In conclusion, we have demonstrated that the nucleophilic substitution of vinylic iodide ion by a poor nucleophilic ion such as cyanide can be achieved indirectly by using DABCO and then KCN. When applied to the pure β-iodo Baylis–Hillman acetate **4-*Z*** or **4-*E***, the reaction gives rise to the corresponding β-cyano derivative **5-*Z*** or **5-*E*** with total stereoselectivity and high yields. The stereoisomer assignments are based on spectroscopic evidence (position of the vinylic proton in the trisubstituted ethylenic moiety).[14,15]

Table 1
Synthesis of β-cyano Baylis–Hillman acetates **5a–f**

Entry	Vinyl iodide **4a–f**	Time (h)	β-Cyano BH acetates **5a–f**	Yield (%)
1	**4a-*Z*** 	2	**5a-*Z*** 	85
2	**4a-*E*** 	2	**5a-*E*** 	81
3	**4b-*Z*** 	2.25	**5b-*Z*** 	84
4	**4b-*E*** 	2.25	**5b-*E*** 	80
5	**4c-*Z*** 	2.3	**5c-*Z*** 	90
6	**4c-*E*** 	2.3	**5c-*E*** 	85
7	**4d-*Z*** 	2.5	**5d-*Z*** 	94
8	**4d-*E*** 	2.5	**5d-*E*** 	95
9	**4e-*Z*** 	2.5	**5e-*Z*** 	82
10	**4e-*E*** 	25	**5e-*E*** 	81
11	**4f-*Z*** 	2.5	**5f-*Z*** 	60
12	**4f-*E*** 	2.5	**5f-*E*** 	72

3. Experimental

3.1. General

^1H and ^{13}C NMR spectra were recorded on Bruker AMX 300 in $CDCl_3$ as solvent and TMS as the internal standard. (^1H: 300 MHz, ^{13}C: 75 MHz). IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer. The wave number (ν) is expressed in cm^{-1}. The chemical shifts (δ) and coupling constants (J) are, respectively, expressed in parts per million and hertz. Microananlyses were performed by the Service Central d'Analyses of CNRS in Vernaison (France). Merck silica gel 60 (70–230 mesh) and (0.063–0.200 mm) were used for flash chromatography. Reactions involving anhydrous conditions were conducted in dry glassware under a nitrogen atmosphere.

3.2. Synthesis of β-cyano Baylis–Hillman acetates 5-*Z*,*E*: typical procedure

To a mixture of methyl 2-(1-acetoxyalkyl)-3-iodo prop-2-enoates **4** (2.25 mmol) in 10 mL of mixture of THF–H_2O (3:1) was added 1,4-diazabicyclo[2.2.2] octane (DABCO) (3.15 mmol). The reaction mixture was stirred for 10–25 min at room temperature, then KCN (3.38 mmol) was added. After stirring for about 2 h, the reaction was complete as monitored by TLC. After addition of saturated solution of NH_4Cl (10 mL), the mixture was extracted with ether (3×20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was separated by chromatography on silica gel (Hexane–AcOEt, 98:2), to afford β-cyano Baylis–Hillman acetates **5**-***Z***,***E***.

3.2.1. Methyl 3-acetoxy-2-(cyanomethylene) butanoate ***5a-Z***

Compound **5a**-***Z*** was prepared from **4a**-***Z*** (670 mg) as described above in 85% yield as a yellow liquid. (377 mg); IR ν_{max} (cm^{-1}): ν=2230 (CN), 1747 (C=O), 1738 (C=O), 1638 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (d, 3H, CH_3CH, J=6.8 Hz), 2.12 (s, 3H, CH_3CO), 3.91 (s, 3H, CH_3OCO), 5.75 (q, 1H, CH_3CH, J=6.8 Hz), 5.98 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.2 (CH_3CH), 20.9 (CH_3CO), 53.0 (CH_3OCO), 68.1 (CH_3CH), 104.7 (CH=), 114.6 (CN), 152.5 (C=CHCN), 162.7 (CH_3OCO), 169.1 (CH_3CO). Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.73; H, 5.51; N, 7.12.

3.2.2. Methyl 3-acetoxy-2-(cyanomethylene) butanoate ***5a-E***

Compound **5a**-***E*** was prepared from **4a**-***E*** (670 mg) as described above in 81% yield as a yellow liquid. (359 mg); IR ν_{max} (cm^{-1}): ν=2230 (CN), 1746 (C=O), 1737 (C=O), 1637 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (d, 3H, CH_3CH, J=6.8 Hz), 2.10 (s, 3H, CH_3CO), 3.80 (s, 3H, CH_3OCO), 5.65 (q, 1H, CH_3CH, J=6.8 Hz), 6.37 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.5 (CH_3CH), 20.4 (CH_3CO), 53.2 (CH_3OCO), 67.9 (CH_3CH), 106.5 (CH=), 114.1 (CN), 152.5 (C=CHCN), 163.5 (CH_3OCO), 170.0 (CH_3CO). Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.72; H, 5.70; N, 7.11.

3.2.3. Methyl 3-acetoxy-2-(cyanomethylene) pentanoate ***5b-Z***

Compound **5b**-***Z*** was prepared from **4b**-***Z*** (702 mg) as described above in 84% yield as a yellow liquid. (399 mg); IR ν_{max} (cm^{-1}): ν=2230 (CN), 1747 (C=O), 1736 (C=O), 1633 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, 3H, CH_3CH_2CH, J=7.5 Hz), 1.92 (qd, 2H, CH_3CH_2CH, J=7.5 Hz, J=7.5 Hz), 2.12 (s, 3H, CH_3CO), 3.91 (s, 3H, CH_3OCO), 5.67 (t, 1H, CH_3CH_2CH, J=7.5 Hz), 5.95 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.6 (CH_3CH_2), 21.0 (CH_3CO), 24.5 (CH_3CH_2), 53.0 (CH_3OCO), 72.6 ($CHCH_2CH_3$), 115.1 (CH=), 119.3 (CN), 151.8 (CH=C), 162.9 (CH_3OCO), 179.6 (CH_3CO). Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.81; H, 6.22; N, 6.57.

3.2.4. Methyl 3-acetoxy-2-(cyanomethylene) pentanoate ***5b-E***

Compound **5b**-***E*** was prepared from **4b**-***E*** (702 mg) as described above in 80% yield as a yellow liquid. (380 mg); IR ν_{max} (cm^{-1}): ν=2230 (CN), 1746 (C=O), 1735 (C=O), 1632 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (t, 3H, CH_3CH_2CH, J=7.5 Hz), 1.90 (qd, 2H, CH_3CH_2CH, J=7.5 Hz, J=7.5 Hz), 2.20 (s, 3H, CH_3CO), 3.85 (s, 3H, CH_3OCO), 5.60 (t, 1H, CH_3CH_2CH, J=7.5 Hz), 6.47 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.7 (CH_3CH_2), 20.3 (CH_3CO), 25.6 (CH_3CH_2), 53.2 (CH_3OCO), 72.5 ($CHCH_2CH_3$), 107.0 (CH=), 114.3 (CN), 151.6 (CH=C), 163.6 (CH_3OCO), 170.3 (CH_3CO). Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.83; H, 6.19; N, 6.68.

3.2.5. Methyl 3-acetoxy-2-(cyanomethylene) hexanoate ***5c-Z***

Compound **5c**-***Z*** was prepared from **4c**-***Z*** (733 mg) as described above in 90% yield as a yellow liquid. (456 mg); IR ν_{max} (cm^{-1}): ν=2229 (CN), 1748 (C=O), 1734 (C=O), 1632 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, 3H, $CH_3(CH_2)_2CH$, J=7.5 Hz), 1.27(tq, 2H, $CH_3CH_2CH_2$, J=7.5 Hz, J=7.5 Hz), 1.62(dt, 2H, $CH_3CH_2CH_2CH$, J=7.5 Hz, J=7.5 Hz), 2.04 (s, 3H, CH_3CO), 3.84 (s, 3H, CH_3OCO), 5.61 (t, 1H, $CH_3(CH_2)_2CH$, J=7.5 Hz), 5.81 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.4 ($CH_3(CH_2)_2$), 19.5 (CH_3CH_2), 20.0 (CH_3CO), 35.0 ($CH_3CH_2CH_2$), 52.0 (CH_3OCO), 70.4 ($CH(CH_2)_2CH_3$), 103.8 (CH=), 113.4 (CN), 151.0 (CH=C), 161.6 (CH_3OCO), 169.3 (CH_3CO). Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.49; H, 6.66; N, 6.19.

3.2.6. Methyl 3-acetoxy-2-(cyanomethylene) hexanoate ***5c-E***

Compound **5c**-***E*** was prepared from **4c**-***E*** (733 mg) as described above in 85% yield as a yellow liquid. (431 mg); IR ν_{max} (cm^{-1}): ν=2229 (CN), 1743 (C=O), 1733 (C=O), 1630 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, 3H, $CH_3(CH_2)_2CH$, J=7.5 Hz), 1.35 (tq, 2H, $CH_3CH_2CH_2$, J=7.5 Hz, J=7.5 Hz), 1.75 (dt, 2H, $CH_3CH_2CH_2CH$, J=7.5 Hz, J=7.5 Hz), 2.10 (s, 3H, CH_3CO), 3.78 (s, 3H, CH_3OCO), 5.59 (t, 1H, $CH_3(CH_2)_2CH$, J=7.5 Hz), 6.34 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.6 ($CH_3(CH_2)_2$), 19.1 (CH_3CH_2), 19.5 (CH_3CO), 34.4 ($CH_3CH_2CH_2$), 51.5 (CH_3OCO), 70.1 ($CH(CH_2)_2CH_3$), 105.7 (CH=), 113.1 (CN), 150.8 (CH=C), 162.4 (CH_3OCO), 169.1 (CH_3CO). Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.44; H, 6.58; N, 6.31.

3.2.7. Methyl 3-acetoxy-2-(cyanomethylene)-4-methylpentanoate ***5d-Z***

Compound **5d**-***Z*** was prepared from **4d**-***Z*** (733 mg) as described above in 94% yield as a yellow liquid. (476 mg); IR ν_{max} (cm^{-1}): ν=2227 (CN), 1746 (C=O), 1733 (C=O), 1635 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (d, 3H, CH_3CH, J=7.0 Hz), 0.96 (d, 3H, CH_3CH, J=7.0 Hz), 2.03–2.08 (m, 1H, $(CH_3)_2CHCH$), 2.12 (s, 3H, CH_3CO), 3.91 (s, 3H, CH_3OCO), 5.57 (d,1H, $(CH_3)_2CHCH$, J=6.5 Hz), 5.81 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.7 ($(CH_3)_2CH$), 20.9 (CH_3CO), 31.6 ($(CH_3)_2CH$), 53.04 (CH_3OCO), 75.6 ($(CH_3)_2CHCH$), 105.3 (CH=), 114.5 (CN), 151.5 (CH=C), 163.7 (CH_3OCO), 169.5 (CH_3CO). Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.32; H, 6.45; N, 6.32.

3.2.8. Methyl 3-acetoxy-2-(cyanomethylene)-4-methylpentanoate ***5d-E***

Compound **5d**-***E*** was prepared from **4d**-***E*** (733 mg) as described above in 95% yield as a yellow liquid. (481 mg); IR ν_{max} (cm^{-1}): ν=2227 (CN), 1741 (C=O), 1730 (C=O), 1634 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (d, 3H, CH_3CH, J=7,0 Hz), 1.05 (d, 3H, CH_3CH, J=7.0 Hz), 2.18–2.22 (m, 1H, $(CH_3)_2CHCH$), 2.18 (s, 3H, CH_3CO), 3.85 (s, 3H, CH_3OCO), 5.50 (d,1H, $(CH_3)_2CHCH$, J=6.5 Hz), 6.46 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.6 ($(CH_3)_2CH$), 20.3 (CH_3CO), 31.4 ($(CH_3)_2CH$), 52.6 (CH_3OCO), 75.4 ($(CH_3)_2CHCH$), 107.6 (CH=), 114.6 (CN), 151.0 (CH=C), 162.9 (CH_3OCO), 170.4 (CH_3CO). Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.51; H, 6.54; N, 6.29.

3.2.9. Methyl 3-acetoxy-2-(cyanomethylene) heptanoate ***5e-Z***

Compound **5e**-***Z*** was prepared from **4e**-***Z*** (765 mg) as described above in 82% yield as a yellow liquid. (441 mg); IR ν_{max} (cm^{-1}): ν=2226 (CN), 1748 (C=O), 1734 (C=O), 1633 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, 3H, $CH_3(CH_2)_3CH$, J=7.5 Hz), 1.27–1.30 (m, 4H, $CH_3(CH_2)_2CH_2$), 1.77 (dt, 2H, $CH_3(CH_2)_2CH_2CH$, J=7.5 Hz, J=7.5 Hz), 2.12 (s, 3H, CH_3CO), 3.91 (s, 3H, CH_3OCO), 5.67 (t, 1H, $CH_3(CH_2)_2CH_2CH$, J=7.5 Hz), 5.89 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.6 ($CH_3(CH_2)_3$), 19.5 (CH_3CO), 21.0 (CH_3CH_2), 26.0 ($CH_3CH_2CH_2$) 32.7 ($CH_3(CH_2)_2CH_2$), 52.3 (CH_3OCO), 70.3 ($CH_3(CH_2)_3CH$), 103.5 (CH=), 113.5 (CN), 150.5 (CH=C),161.7 (CH_3OCO), 169.2 (CH_3CO). Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.31; H, 7.27; N, 5.79.

3.2.10. Methyl 3-acetoxy-2-(cyanomethylene) heptanoate ***5e-E***

Compound **5e**-***E*** was prepared from **4e**-***E*** (765 mg) as described above in 81% yield as a yellow liquid. (436 mg); IR ν_{max} (cm^{-1}): ν=2226 (CN), 1743 (C=O), 1730 (C=O), 1630 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, 3H, $CH_3(CH_2)_3CH$, J=7.5 Hz), 1.28–1.31(m, 4H, $CH_3(CH_2)_2CH_2$), 1.77 (dt, 2H, $CH_3(CH_2)_2CH_2CH$, J=7.5 Hz, J=7.5 Hz), 2.10 (s, 3H, CH_3CO), 3.78 (s, 3H, CH_3OCO), 5.58 (t, 1H, $CH_3(CH_2)_2CH_2CH$, J=7.5 Hz), 6.34 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.9 ($CH_3(CH_2)_3$), 19.6 (CH_3CO), 21.3 (CH_3CH_2), 26.5 ($CH_3CH_2CH_2$) 32.3 ($CH_3(CH_2)_2CH_2$), 52.2 (CH_3OCO), 70.7 ($CH_3(CH_2)_3CH$), 105.9 (CH=), 113.0 (CN), 151.0 (CH=C), 162.7

(CH_3OCO), 169.3 (CH_3CO). Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.16; H, 7.22; N, 5.91.

3.2.11. Methyl 3-acetoxy-2-(cyanomethylene)-5-methylhexanoate ***5f-Z***

Compound **5f**-***Z*** was prepared from **4f**-***Z*** (765 mg) as described above in 60% yield as a yellow liquid. (323 mg); IR ν_{max} (cm^{-1}): ν=2225 (CN), 1742 (C=O), 1732 (C=O), 1636 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (d, 3H, CH_3CH, J=6.0 Hz), 0.96 (d, 3H, CH_3CH, J=6.0 Hz), 1.26 (dd, 2H, $(CH_3)_2CHCH_2CH$, J=7.5 Hz, J=7.5 Hz), 1.83–1.87 (m, 1H, $(CH_3)_2CHCH_2$), 2.10 (s, 3H, CH_3CO), 3.91 (s, 3H, CH_3OCO), 5.72 (t, 1H, $(CH_3)_2CHCH_2CH$, J=7.5 Hz), 5.87 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0 (CH_3CO), 22.2 ($(CH_3)_2CH$), 23.2 ($(CH_3)_2CH$), 43.4 ($(CH_3)_2CHCH_2$), 52.8 (CH_3OCO), 70.5 ($(CH_3)_2CHCH_2CH$), 104.6 (CH=), 114.8 (CN), 152.8 (CH=C), 162.9 (CH_3OCO), 169.6 (CH_3CO). Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.31; H, 7.12; N, 5.77.

3.2.12. Methyl 3-acetoxy-2-(cyanomethylene)-5-methylhexanoate ***5f-E***

Compound **5f**-***E*** was prepared from **4f**-***E*** (765 mg) as described above in 72% yield as a yellow liquid. (387 mg); IR ν_{max} (cm^{-1}): ν=2225 (CN), 1741 (C=O), 1730 (C=O), 1635 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (d, 3H, CH_3CH, J=6.0 Hz), 0.97 (d, 3H, CH_3CH, J=6.0 Hz), 1.26 (dd, 2H, $(CH_3)_2CHCH_2CH$, J=7.5 Hz, J=7.5 Hz), 1.83–1.87 (m, 1H, $(CH_3)_2CHCH_2$), 2.04 (s, 3H, CH_3CO), 3.85 (s, 3H, CH_3OCO), 5.71 (t, 1H, $(CH_3)_2CHCH_2CH$, J=7.5 Hz), 6.39 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0 (CH_3CO), 20.3 ($(CH_3)_2CH$), 21.9 ($(CH_3)_2CH$), 41.2 ($(CH_3)_2CHCH_2$), 51.8 (CH_3OCO), 68.7 ($(CH_3)_2CHCH_2CH$), 105.2 (CH=), 113.1 (CN), 151.5 (CH=C), 162.2 (CH_3OCO), 170.0 (CH_3CO). Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.18; H, 7.21; N, 5.92.

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