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An effective new access to ethyl 2-[(alkylamino)(cyano)methyl] acrylates: first synthesis of ethyl 3-cyano-2-(hydroxymethyl) acrylate

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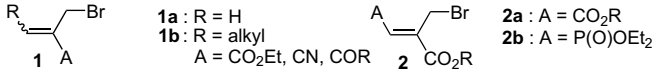
ABSTRACT

A regioselective coupling of ethyl 2-(bromomethyl)-3-cyanoacrylate and primary amines is described to give ethyl 2-[(alkylamino)(cyano)methyl] acrylates in good yields. Whereas the conversion of allyl bromide in the presence of TEAF leads to the first synthesis of ethyl 3-cyano-2-(hydroxymethyl) acrylate.

1. Introduction

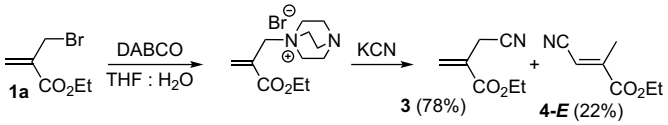
Acrylic compounds are good Michael acceptors due to their great reactivity as electrophiles towards various nucleophiles. Indeed, bromomethylation at the α position of these acrylic substrates reveals a range of useful products for organic synthesis, particularly in the preparation of natural[1–4] and biologically active compounds.[5–8] Bromomethylated esters of type **1** and their homologous difunctionalized products of type **2** are useful synthons in several synthetic applications. The allylic bromide **1a**[9,10] constitutes a basic intermediate to react as an electrophilic compound in a range of reactions[11–13] (Scheme 1).



Scheme 1.

2. Results and discussion

As part of our ongoing work on the synthesis of α-alkylidene-1,3-(cyano or ester) phosphonates,[14] α-alkylidene-1,4-(ketoesters or ketonitriles),[15–17] nitroesters,[18] succinonitrile[19] and α-alkylidene-1,5-(diesters,[20] ketoesters,[21] cyanoesters[22]), we have developed convenient methodology for the synthesis of a new family of 2-methylene-1,3-cyanoesters **3**. The reaction proceeds via substitution of a bromine atom by a tertiary amine such us 1,4-diazabicyclo[2.2.2]octane[23,24] providing a quaternary ammonium salt, which can be readily replaced through a direct substitution by cyanide anion[25,26] leading to the methylenic compounds **3**[27] in good yield (78%) in the presence of the unknown isomerization product **4** (22%). Repeated efforts to avoid the simultaneous formation of methylene derivatives **3** and β-cyanoester **4** failed. However, the mixture of regioisomers **3** and **4** can be easily separated by column chromatography (Scheme 2).



Scheme 2.

In previous work, we described a simple and convenient synthesis of β-functionalized α-(bromomethyl) acrylic acid ester **1a** and demonstrated that it can be utilized to prepare some α-(*gem*-difunctional methyl) acrylic acid esters.[28,29] It seemed plausible to elaborate a new electrophilic difunctional allylic bromide such as **5**, readily obtained using the known tandem

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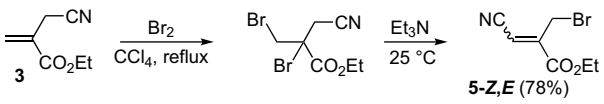
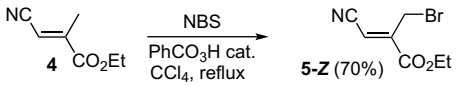
bromination–dehydrobromination of ethyl 2-(cyanomethyl) acrylate **3** in the presence of triethylamine according to the method published previously[30] (Scheme 3).



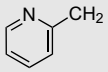
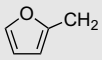
Scheme 3.

It is important to indicate that the regioisomer **4** could also be effectively converted into allyl bromide **5** through a simple transformation of the conjugated cyanoester **4** in the presence of *N*-bromosuccinimide (NBS)[31] using catalytic benzoyl peroxide under reflux of carbon tetrachloride in good yield (Scheme 4).

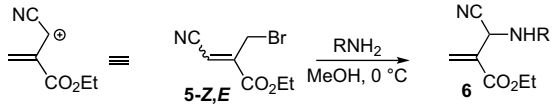


Scheme 4.

Table 1
Synthesis of ethyl 2-[(alkylamino)(cyano)methyl] acrylates **6a–h**

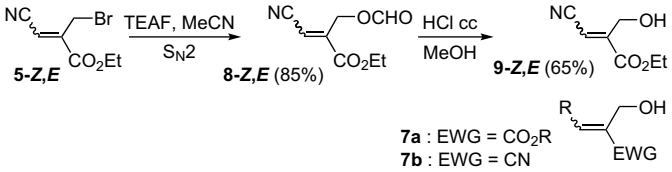
6a–h	R	Time (h)	Yield (%)
6a	$PhCH_2$	3	62
6b	$Ph(CH_3)CH$	3	60
6c	p-$FC_6H_4CH_2$	1	58
6d	p-$MeOC_6H_4CH_2$	1	56
6e	p-$ClC_6H_4CH_2$	1	76
6f	$^cC_6H_{11}$	1	70
6g		1	70
6h		1	55

Allylamines are interesting synthetic targets because of their key function as intermediates in several synthetic fields, as well as their physiological properties,[32] biological activities[33,34] and their presence in several natural products.[35,36] Two main pathways can be considered for the reaction of allyl bromide **5** with primary amines in methanol. The reactivity of these amines is governed essentially by their steric factor. The regioselective and abnormal (S_N2') substitution of bromide can be explained by the increased electrophilicity of the β-carbon **5** leading to a new family of ethyl 2-[(alkylamino)(cyano)methyl] acrylates **6**[30,37,38] that contain a terminal methylene group (Table 1, Scheme 5).



Scheme 5.

The easy conversion of the 2-functional allyl bromide into the corresponding allylic alcohols **7a**,**b**[39,40] considered as important raw materials for the foods industry led us to investigate the first synthesis of α,β-difunctional allylic alcohol **9** via the use of a tandem reaction: formylation–hydrolysis[41] starting from cyanoester **5-*Z*,*E***. Indeed, due to the reduced size of the formate anion compared with amines, the reaction of **5-*Z*,*E*** with an excess (2.5 equiv) of triethylammonium formate (TEAF) in acetonitrile at 0 °C afforded the corresponding allyl formate **8**[42–44] via a direct allylic substitution (S_N2) and subsequent hydrolysis in the presence of one drop of hydrochloric acid in methanol led to ethyl 3-cyano-2-(hydroxymethyl) acrylate **9** (1:1 mixture of *E*/*Z* isomers) as yellow liquid (Scheme 6).



Scheme 6.

3. Conclusion

Starting from Baylis–Hillman-derived bromide **1a**, we developed a simple method for the synthesis of allyl bromide **5**, a useful compound for the access to difunctionalized allylamines **6** and allylic alcohol **9**.

4. Experimental

4.1. General

All reactions were monitored by TLC on silica gel plates (Fluka Kieselgel 60 F_{254}). For column chromatography, Fluka Kieselgel 70–230 mesh was used. ^1H and ^{13}C NMR spectra (fully decoupled) were recorded on Bruker AMX 300 in $CDCl_3$ as solvent and TMS as the internal standard. IR spectra were recorded with a Perkin–Elmer paragon 1000 FT-IR spectrophotometer. Mass spectrometry was performed on an Autospec 200, Micromass (Waters) instrument.

4.2. Synthesis of ethyl 2-(cyanomethyl) acrylate 3 and ethyl 3-cyano-2-methylacrylate 4

4.2.1. Typical procedure

Into a 250 mL flask was introduced 5 g (25.90 mmol) of ethyl 2-(bromomethyl) acrylate **1a** in aqueous THF (104 mL, THF/H_2O=3:1). DABCO 3.20 g (28.49 mmol) was added and the mixture was stirred at room temperature for 2 h until the allyl bromide salt was formed. To the obtained salt was added under stirring at 0 °C for 2 h, 31.08 mmol (2 g) of potassium cyanide (KCN). The mixture was then hydrolyzed by addition of a saturated solution of NH_4Cl. After extraction with diethyl ether (3×75 mL), the organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure and the crude mixture was separated by chromatography on silica gel (AcOEt/Hexane, 1:10) to give the ethyl 2-(cyanomethyl) acrylate **3** (2.81 g, 78%) and ethyl 3-cyano-2-methylacrylate **4** (0.79 g, 22%).

*4.2.2. Ethyl 2-(cyanomethyl) acrylate **3***

Yield: (2.81 g, 78%) as a colourless oil; ν_{max} (liquid film) 2305, 1717, 1641 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, J Hz): 6.46 (s, 1H, H_2C=), 6.09 (1s, 1H, H_2C=), 4.25 (q, 2H, J=7.1, CH_2CH_3), 3.4 (s, 2H,CH_2CN), 1.33 (t, 3H, J=7.1, CH_2CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 164.6, 130.6, 128.3, 116.8, 61.7, 61.7, 14.1. HRMS calcd for $C_7H_9NO_2$: 139.0633; found: 139.0688.

*4.2.3. Ethyl 3-cyano-2-methylacrylate **4***

Yield: (0.79 g, 22%) as a colourless oil; ν_{max} (liquid film) 2226, 1714, 1626 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, J Hz): 6.32 (s, 1H, HC=), 4.30 (q, 2H, J=7.0, CH_2CH_3), 1.28 (s, 3H, CH_3), 1.36 (t, 3H, J=7.0, CH_2CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 164.7, 150.2, 115.5, 107.5, 62.2, 16.9, 13.9. HRMS calcd for $C_7H_9NO_2$: 139.0633; found: 139.0626.

4.3. Synthesis of ethyl 2-(bromomethyl)-3-cyanoacrylate 5: general procedure

*4.3.1. Allyl bromide **5** from **3***

To a mixture of 5 g (35.93 mmol) of ethyl 2-(cyanomethyl) acrylate **3** diluted in 35 mL of anhydrous carbon tetrachloride was added dropwise under magnetic stirring 1.90 mL (37.37 mol) of bromine in 25 mL of CCl_4 at such a rate that the bromine colour gradually disappeared. The end of the reaction was indicated by the persistence of the brownish colour. After the completion of the reaction indicated by TLC analysis, 7.51 mL (53.89 mmol) of anhydrous triethylamine was added at 0 °C. After stirring overnight, filtration under reduced pressure of the formed ammonium salt, then evaporation of the solvent, gave the oily residue that was purified by chromatography on silica gel (AcOEt/Hexane, 1:10) leading to a mixture of (*Z*/*E*: 41/59) allyl bromides **5** (6.11 g, 78%).

*4.3.2. Allyl bromide **5** from **4***

A mixture of 7.69 g (50.26 mmol) of ethyl 3-cyano-2-methyl-acrylate **4-*E*** diluted in 153 mL of anhydrous carbon tetrachloride, 10.74 g (60.30 mmol) of NBS and 0.10 g of benzoyl peroxide was added to a 250 mL flask fitted with a condenser protected by calcium drying tube. The mixture was stirred at reflux for 80 h and then filtered under reduced pressure. After evaporation of the solvent, the crude oil was purified by chromatography on silica gel (AcOEt/Hexane, 1:10) providing the pure allyl bromide **5-*Z*** (7.67 g, 70%).

*4.3.3. Ethyl 2-(bromomethyl)-3-cyanoacrylate **5-Z***

Yield: 6.11 g, 78%, as a viscous yellow oil; ν_{max} (liquid film) 2305, 1730, 1624, 693 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 6.07 (s, 1H, *H*C=), 4.37 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 4.22 (s, 2H, C*H*$_2$Br), 1.38 (t, 3H, *J*=7.0, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 161.8, 147.9, 114.4, 108.4, 62.9, 28.2, 13.8. HRMS calcd for $C_7H_8BrNO_2$: 216.9738; found: 216.9754.

*4.3.4. Ethyl 2-(bromomethyl)-3-cyanoacrylate **5-E***

Yield: 7.67 g, 70%, as a viscous yellow oil; ν_{max} (liquid film) 2305, 1724, 1623, 693 cm^{-1}. ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 6.40 (s, 1H, *H*C=), 4.33 (s, 2H, C*H*$_2$Br), 4.31 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 1.33 (t, 3H, *J*=7.0, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 162.4, 148.8, 114.1, 109.6, 62.8, 23.8, 14.0. HRMS calcd for $C_7H_8BrNO_2$: 216.9738; found: 216.9754.

4.4. Synthesis of ethyl 2-[(alkylamino)(cyano)methyl] acrylates 6a–h

4.4.1. General procedure

To a solution of ethyl 2-(bromomethyl)-3-cyanoacrylate **5** (1 g, 4.59 mmol) in 15 mL of absolute methanol was added dropwise primary amine (4.59 mmol). The mixture was stirred at room temperature at 0 °C for 1–3 h. The mixture was concentrated and the organic residue obtained was purified by chromatography on silica gel (AcOEt/Hexane, 1:10).

*4.4.2. Ethyl 2-((benzylamino)(cyano)methyl) acrylate **6a***

Yield: 0.69 g, 62%, as a yellow oil; ν_{max} (liquid film) 3393 (br), 2305, 1730, 1605 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 7.30 (m, 5H, C$_6$*H*$_5$), 6.44 (s, 1H, *H*$_2$C=), 6.07 (s, 1H, *H*$_2$C=), 4.54 (s, 1H, C*H*CN), 4.27 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 3.95 (q, 2H, J_{AB}=14.2, C*H*$_2$–Ph), 2.01 (br s, 1H, –N*H*–), 1.31 (t, 3H, *J*=6.5, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 164.5, 138.0, 135.5, 129.0, 128.8, 128.7, 128.0, 117.9, 61.8, 51.5, 51.4, 14.1. HRMS calcd for $C_{14}H_{16}N_2O_2$: 244.1212; found: 244.1224.

*4.4.3. Ethyl 2-(cyano(1-phenylethylamino)methyl) acrylate **6b***

Yield: 0.71 g, 60%, as a yellow oil; ν_{max} (liquid film) 3420 (br), 2305, 1715, 1636 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 7.31 (m, 5H, C$_6$*H*$_5$), 6.39 (s, 1H, *H*$_2$C=), 6.00 (s, 1H, *H*$_2$C=), 4.51 (s, 1H, C*H*CN), 4.26 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 1.98 (br s, 1H, –N*H*–), 1.40 (d, 3H, *J*=7.0, C*H*$_3$) 4.26 (t, 3H, *J*=7.0, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 164.3, 142.6, 135.7, 128.7, 128.6, 128.4, 118.1, 61.6, 56.9, 38.1, 24.6, 14.1. HRMS calcd for $C_{15}H_{18}N_2O_2$: 258.1368; found: 258.1381.

*4.4.4. Ethyl 2-(cyano(4-fluorobenzylamino)methyl) acrylate **6c***

Yield: 0.70 g, 58%, as a yellow oil; ν_{max} (liquid film) 3386 (br), 2305, 1730, 1604 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 7.32, 7.02 (2 m, 4H, C$_6$*H*$_4$), 6.44 (s, 1H, *H*$_2$C=), 6.08 (1s, 1H, *H*$_2$C=), 4.53 (s, 1H, C*H*CN), 4.27 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 3.92 (q, 2H, J_{AB}=14.2, C*H*$_2$Ph), 2.16 (br s, 1H, –N*H*–), 1.32 (t, 3H, *J*=7.0, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 164.3, 160.7, 135.2, 133.5, 130.1, 128.6, 117.6, 115.2, 61.7, 50.5, 31.0, 13.9. HRMS calcd for $C_{14}H_{15}FN_2O_2$: 262.1118; found: 262.1098.

*4.4.5. Ethyl 2-(cyano(4-methoxybenzylamino)methyl) acrylate **6d***

Yield: 0.70 g, 56%, as a yellow oil; ν_{max} (liquid film) 3367 (br), 2253, 1724, 1612 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 7.28, 6.88 (4H, C$_6$*H*$_4$), 6.44 (s, 1H, *H*$_2$C=), 6.06 (1s, 1H, *H*$_2$C=), 4.52 (s, 1H, C*H*CN), 4.27 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 3.87 (q, 2H, J_{AB}=14.2, C*H*$_2$Ph), 3.80 (s, 3H, OC*H*$_3$), 1.60 (br s, 1H, –N*H*–), 1.29 (t, 3H, *J*=7.0, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 164.4, 159.2, 135.3, 130.6, 129.7, 128.6, 117.8, 114.0, 61.7, 55.3, 50.8, 50.3, 14.1. HRMS calcd for $C_{15}H_{18}N_2O_3$: 274.1317; found: 274.1303.

*4.4.6. Ethyl 2-((4-chlorobenzylamino)(cyano)methyl) acrylate **6e***

Yield: 0.97 g, 76%, as a yellow oil; ν_{max} (liquid film) 3337 (br), 2305, 1727, 1669 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 7.30 (s, 4H, C$_6$*H*$_4$), 6.44 (s, 1H, *H*$_2$C=), 6.08 (s, 1H, *H*$_2$C=), 4.52 (s, 1H, C*H*CN), 4.27 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 3.92 (q, 2H, J_{AB}=14.2, C*H*$_2$Ph), 2.01 (br s, 1H, –N*H*–), 1.32 (t, 3H, *J*=7.0, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 164.3, 136.3, 135.1, 133.4, 128.7, 128.7, 117.8, 61.7, 50.5, 50.4, 15.3. HRMS calcd for $C_{14}H_{15}ClN_2O_2$: 278.0822; found: 278.0836.

*4.4.7. Ethyl 2-(cyano(cyclohexylamino)methyl) acrylate **6f***

Yield: 0.76 g, 70%, as a yellow oil; ν_{max} (liquid film) 3421 (br), 2305, 1715, 1669 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 6.41 (s, 1H, *H*$_2$C=), 6.08 (s, 1H, *H*$_2$C=), 4.65 (s, 1H, C*H*CN), 4.28 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 2.74 (qt, 1H, *J*=7.0, C$_6$*H*$_{11}$), 1.94 (br s, 1H, –N*H*–), 1.77 (m, 6H, C$_6$*H*$_{11}$), 1.30 (m, 4H, C$_6$*H*$_{11}$), 1.32 (m, 3H, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 164.4, 136.0, 127.9, 118.6, 61.8, 54.8, 48.3, 33.8, 25.8, 24.6, 14.0. HRMS calcd for $C_{13}H_{20}N_2O_2$: 236.1525; found: 236.1603.

*4.4.8. Ethyl 2-(cyano(pyridin-2-ylmethylamino)methyl) acrylate **6g***

Yield: 0.79 g, 70%, as a brown oil; ν_{max} (liquid film) 3421 (br), 2305, 1726, 1607 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 8.55 (m, 1H, C$_6$*H*$_4$N), 7.67 (m, 1H, C$_6$*H*$_4$N), 7.28 (m, 1H, C$_6$*H*$_4$N), 7.21 (m, 1H, C$_6$*H*$_4$N), 6.48 (s, 1H, *H*$_2$C=), 6.15 (s, 1H, *H*$_2$C=), 4.74 (s, 1H, C*H*CN), 4.29 (q, 2H, *J*=7.0, C*H*$_2$CH$_3$), 4.06 (q, 2H, J_{AB}=14.2, C*H*$_2$C$_6$H$_4$N), 2.07 (br s, 1H, –N*H*–), 1.32 (t, 3H, *J*=7.0, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 167.7, 164.3, 157.6, 149.5, 135.1, 122.9, 128.8, 122.4, 117.7, 61.7, 52.2, 50.6, 14.1. HRMS calcd for $C_{13}H_{15}N_3O_2$: 245.1164; found: 245.1160.

*4.4.9. Ethyl 2-(cyano(furan-2-ylmethylamino)methyl) acrylate **6h***

Yield: 0.59 g, 55%, as a brown oil; ν_{max} (liquid film) 3417 (br), 2305, 1725, 1640 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 7.39 (s, 1H, C$_5$*H*$_6$O), 6.45 (s, 1H, *H*$_2$C=), 6.33 (s, 1H, C$_5$*H*$_6$O), 6.29 (s, 1H, C$_5$*H*$_6$O), 6.09 (s, 1H, *H*$_2$C=), 4.57 (s, 1H, C*H*CN), 4.27 (q, 2H, *J*=8.0, C*H*$_2$CH$_3$), 3.95 (q, 2H, J_{AB}=14.2, C*H*$_2$C$_5$H$_6$O), 2.06 (br s, 1H, –N*H*–), 1.31 (t, 3H, *J*=7.8, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ ppm): 164.3, 151.4, 142.7, 134.9, 128.9, 117.6, 110.3, 108.4, 61.7, 50.7, 43.9, 14.1. HRMS calcd for $C_{12}H_{14}N_2O_3$: 234.1004; found: 234.1016.

4.5. Synthesis of ethyl 3-cyano-2-(hydroxymethyl) acrylate 9: general procedure

To a mixture of ethyl 2-(bromomethyl)-3-cyanoacrylate **5** (8.21 mmol) in 10 mL of acetonitrile at 0 °C placed in 25 mL flask fitted with a condenser protected by calcium drying tube were added 20.53 mmol of triethylammonium formate (TEAF). After hydrolysis, the organic layer was extracted by ether and then dried over $MgSO_4$. After evaporation of the solvent, the formate **8-*Z*,*E*** (44:56) (1.28 g, 85%) was purified by chromatography on silica gel (AcOEt/Hexane, 1:10). Two drops of concentrated hydrochloric acid were added to **8** diluted in 10 mL of absolute methanol with stirring for 1 h at 25 °C. The allylic alcohol **9-*Z*,*E*** (44:56) (0.83 g, 65%) formed was extracted with diethyl ether (3×25 mL), after workup the crude alcohol was purified on silica gel (AcOEt/Hexane, 1:10).

4.5.1. Ethyl 3-cyano-2-(formyloxymethyl) acrylate ***8-Z,E***

Yield: 1.28 g, 85%, as a yellow oil; ν_{max} (liquid film) 2830, 2306, 1734, 1696, 1636 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 8.22 (s, 1H, C*H*O), 6.66 (s, 1H-*E*, *H*C═), 6.11 (s, 1H-*Z*, *H*C═), 5.18 (s, 2H-*E*, CH_2), 5.07 (s, 2H-*Z*, CH_2), 4.32 (q, 2H, *J*=7.0, CH_2CH$_3$), 4.32 (t, 3H, *J*=7.0, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 162.8, 159.8, 146.1, 113.9, 111.2, 62.8, 59.4, 14.0. HRMS calcd for $C_8H_9NO_4$: 183.0532; found: 183.0522.

4.5.2. Ethyl 3-cyano-2-(hydroxymethyl) acrylate ***9-Z,E***

Yield: 0.83 g, 65%, as a yellow oil; ν_{max} (liquid film) 3378 (br), 2305, 1725, 1623 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 6.84 (s, 1H-*Z*, *H*C═), 6.14 (s, 1H-*E*, *H*C═), 4.85 (s, 2H-*Z*, CH_2), 4.48 (s, 2H-*E*, CH_2), 4.35 (q, 2H, *J*=7.0, CH_2CH$_3$), 2.70 (br s, 1H, O*H*), 1.38 (t, 3H, *J*=7.0, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 162.7, 151.7, 115.26, 104.2, 62.4, 61.3, 13.9. HRMS calcd for $C_7H_9NO_3$: 155.0582; found: 155.0590.

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