# Organic Azides. 5.* A Simple Synthesis of Alkyl 3-Azido-2-alkenoates

Hanno Priebe

Nycomed International, P.O. Box 4220 Torshov, N-0401 Oslo 4, Norway

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The title compounds are derived from alkyl 2-alkynoates and aqueous sodium azide solution under ultrasonic irradiation. At low reaction temperatures the *Z*-configuration is favoured. Ultrasonic irradiation is decisive for good conversion and in most cases no additional stirring is necessary. Stirring without ultrasonic irradiation gives low conversion. The reaction conditions show high selectivity between nucleophilic addition and nucleophilic substitution.

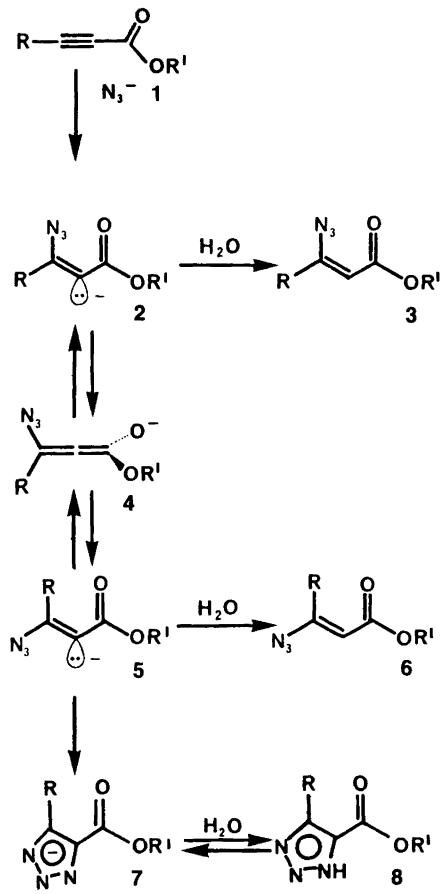
Water (as polar protic solvent) and alkyl 2-alkynoates form an immiscible two-phase system. Azide ions from the water phase can then react (Scheme 1) with the alkynoate only at the interface. An increase in interface area will presumably increase the rate of reaction, and the two phases were therefore emulsified by rapid stirring combined with ultrasonic irradiation. Since Erlenmeyer flasks, with their large bottom diameter, expose more area to the ultrasound they are preferred as reaction vessels.

Various alkyl 2-alkynoates (**1**) with different substituents (Table 1) were tested under these reaction conditions. The molar ratio of the educts, reaction conditions, product distribution and isolated yields are summarized in Table 2 and show clear tendencies: An excess of sodium azide

*Table 1.* Substitution pattern of alkyl 2-alkynoates (**1**).

| | R | R′ |
|---|---|---|
| **a** | H | $CH_3$ |
| **b** | H | Et |
| **c** | H | $CH_2$–$CH_2Br$ |
| **d** | $CH_3$ | $CH_3$ |
| **e** | $CH_2Cl$ | $CH_3$ |
| **f** | Et | $CH_3$ |
| **g** | $COOCH_3$ | $CH_3$ |

*Part 4, see Ref. 1.




*Scheme 1.* Formation of alkyl 3-azido-2-alkenoates.

*Table 2.* Reaction conditions and product distribution.

| | Educts/mmol | | | | AS[a] | Conditions | | | Products/mol % | | | | | | Yield[b]/% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **1** | $NaN_3$ | $KH_2PO_4$ | $Na_2B_4O_7$ | | $H_2O$/ml | °C | min | **3** | **6** | **13** | **14** | **9** | **10** | |
| **a** | 10 | 20 | 15 | 15 | – | 60 | 50 | 45 | 89 | 11 | 0 | 0 | 0 | 0 | 71 |
| **a** | 10 | 20 | 15 | 15 | – | 60 | 70 | 20 | 75 | 13 | 0 | 0 | 12 | 0 | 73 |
| **a** | 30 | 150 | 45 | 45 | – | 210 | 25 | 140 | 100 | 0 | 0 | 0 | 0 | 0 | 86 |
| **b** | 20 | 200 | 22 | 22 | – | 35 | 50 | 30 | 49 | 11 | 37 | 0 | 2 | 1 | 78 |
| **b** | 50 | 500 | 55 | 55 | – | 88 | 60 | 30 | 23 | 6 | 59 | 8 | 3 | 0 | 48[c] |
| **b** | 10 | 100 | 11 | 11 | – | 17 | 70 | 30 | 40 | 4 | 20 | 31 | 5 | 0 | – |
| **b** | 20 | 200 | 30 | 30 | + | 200 | 5 | 180 | 91 | 9 | 0 | 0 | 0 | 0 | 97 |
| **c** | 10 | 100 | 15 | 15 | – | 80 | 5 | 100 | 82 | 17 | 1 | 0 | 0 | 0 | 70 |
| **c** | 10 | 100 | 20 | 20 | – | 20 | 50 | 30 | 60 | 25 | 8 | 4 | 3 | 0 | 63 |
| **c** | 10 | 100 | 11 | 11 | + | 200 | 5 | 240 | 88 | 12 | 0 | 0 | 0 | 0 | 95 |
| **d** | 10 | 20 | 15 | 15 | – | 60 | 35 | 60 | 100 | 0 | 0 | 0 | 0 | 0 | – |
| **e** | 7 | 15 | 0 | 0 | – | 10 | 76 | 120 | 100 | 0 | – | – | – | – | 15 |
| **e** | 7 | 15 | 9 | 0 | – | 10 | 76 | 120 | 100 | 0 | – | – | – | – | 41 |
| **e** | 10 | 20 | 15 | 15 | – | 60 | 50 | 30 | 100 | 0 | – | – | – | – | 79 |
| **f** | 10 | 20 | 15 | 15 | – | 60 | 40 | 60 | 83 | 17 | – | – | – | – | 5 |
| **f** | 10 | 200 | 15 | 15 | + | 60 | 50 | 120 | 86 | 14 | – | – | – | – | 66[d] |
| **f** | 10 | 200 | 15 | 15 | + | 60 | 22 | 240 | 81 | 19 | 0 | 0 | 0 | 0 | 77 |
| **f** | 20 | 400 | 30 | 30 | + | 120 | 50 | 120 | 100 | 0 | 0 | 0 | 0 | 0 | 35 |
| **g** | 10 | 20 | 15 | 15 | – | 60 | 23 | 140 | 37 | 63 | 0 | 0 | 0 | 0 | 100 |
| **g** | 10 | 400 | 15 | 0 | – | 100 | −10 | 200 | 84 | 16 | 0 | 0 | 0 | 0 | 92 |
| **g** | 10 | 20 | 15 | 15 | + | 60 | 23 | 215 | 50 | 50 | 0 | 0 | 0 | 0 | 68[e] |
| **g** | 10 | 20 | 15 | 15 | – | 60 | 50 | 60 | 11 | 89 | 0 | 0 | 0 | 0 | – |

[a]AS = additional stirring. [b]Isolated yield of **3**+**6**. [c]Isolated yield of **13**. [d]Plus 1 mol % $NBu_4Br$. [e]Without ultrasound.

increases the rate of nucleophilic attack of azide ion on **1**. Protonation of the vinyl anions **2** and **5** in the course of the reaction leads to an increase in pH, and the products **3** and **6** may saponify; under these circumstances the isolated yield is low.

However, in the presence of an equimolar sodium tetraborate/potassium dihydrogen phosphate buffer (pH 7.8) saponification is suppressed and the isolated yield is much higher. The use of potassium dihydrogen phosphate as sole buffer component (pH 5–6) gives comparable yields, but the products are much more coloured.

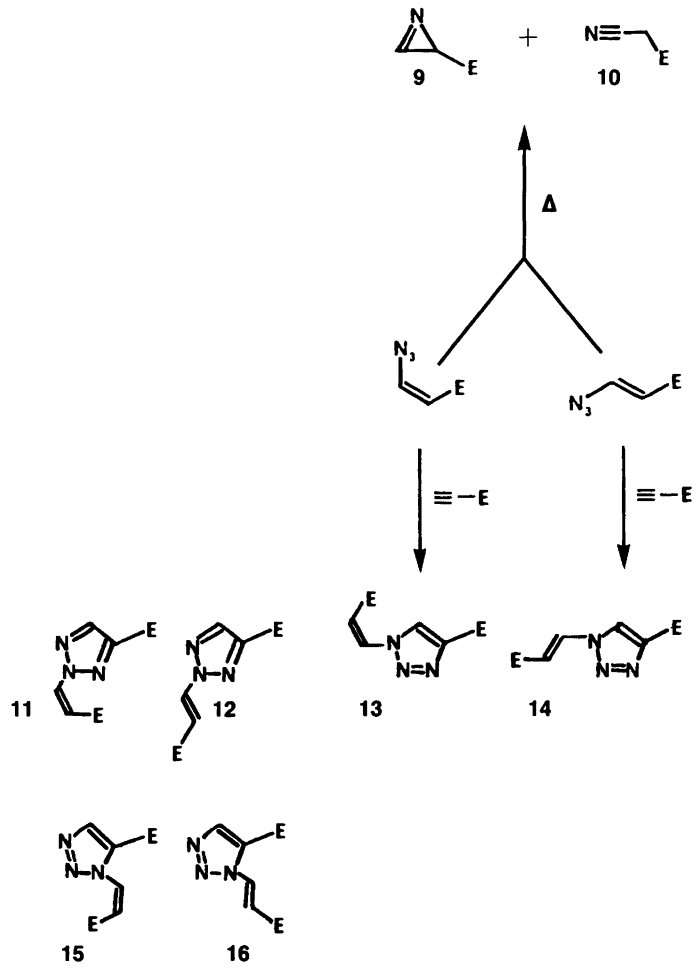
The reaction conditions show a high degree of selectivity between nucleophilic addition and nucleophilic substitution: Neither chloride in an allylic position, as in **3e**, is substituted by azide, nor bromide in a primary aliphatic position, as in **3c**.

The nature of the groups R,R′ and the reaction conditions influence the *syn/anti* ratio of the products formed by addition to the triple bond. Small substituents such as H, $CH_3$, Et or $CH_2Cl$ in the R position lead to alkyl 3-azido-2-alkenoates, predominantly or exclusively with the *Z*-configuration. The yield of **6** increases in the order of R′ = $CH_3$ < Et < $CH_2$–$CH_2Br$. In the case of **1f**, additional stirring of the reaction mixture suppresses the formation of **6f** and only **3f** is isolated.

Reaction temperature has the greatest influence on the *E*/*Z* ratio. The common tendency is most significant in the case of **1g**: the *Z*-isomer **3g** is the major product at low temperatures whereas higher temperatures favour the formation of the *E*-isomer **6g**. The lower limit to the reaction temperature is set by the freezing point of the water/sodium azide solution: The eutectic point for this system occurs at −15.1 °C for 21.6% (*w*/*w*) $NaN_3$.[2]

The formation of triazole by-products is observed only in the case of **1b** and **1c** (see Scheme 2).

The use of elevated temperatures, less water, and a saturated salt solution with solid precipitates increase the yield of triazoles, whereas ad-




*Scheme 2.* Formation of thermal decomposition by-products and 1,2,3-triazoles.

ditional stirring, low temperatures and higher dilution of the salts have the opposite effect. Of the six possible triazoles **11–16**, only **13** and **14** are formed. On heating crude **13b** and **14b** above 100 °C an isomer sublimes from the mixture to which the structure **12b** is assigned. On heating pure **13b** to 170 °C for 3 h no isomerisation to **12b** occurs. Therefore, an intramolecular addition-elimination mechanism with the ring N-2 as nucleophile could be excluded. On heating pure **13b** with traces of sodium hydroxide or sodium azide to 100 °C for 1 h the isomers **11b**, **12b** and **14b** are formed, whereas traces of phosphorous acid left **13b** unchanged.

The isomerization of **13b** occurs by a base-catalysed addition-elimination mechanism. When traces of base are excluded, **13b** can be sublimed unchanged at 65 °C/13 Pa (0.1 mmHg). Side reactions to give the corresponding azirine **9** and nitrile **10** occur only at elevated temperatures[3] in the case of **1a–c**.

The ratio of the isomeric alkyl 3-azido-2-alkenoates **3** and **6** represents the ratio of their anionic precursors **2** and **5** for the following reasons:

1. **3** and **6** do not interconvert under the conditions of their information.

2. The reaction conditions favour rapid protonation of the anions **2** and **5**.

Since **3** is the main product at low temperatures it is presumed that nucleophilic attack of azide ion on alkyl 2-alkynoates (**1**) leads initially to the vinyl anion **2**. If **2** is not protonated at once, isomerisation to **5** may proceed through the allenic form **4**.[4-7] The **2/5** inversion barrier is lowered at elevated temperatures. The protonation of **5** must be rapid enough to suppress cyclization to the triazolyl anion **7** since the triazole **8** was not found in any of the experiments.

Both **7** and **8** are potential nucleophiles that can attack the starting material **1** at both N-1 and N-2.[8-9] This interpretation was excluded since triazole by-products with side chains only at N-1 were formed under the described conditions. The triazole **13b** could be synthesized independently, as sole product and in excellent yield, by a 1,3-dipolar cycloaddition reaction of **3b** with **1b** in boiling ether. This indicates that the triazole by-products **13** and **14** are formed by cycloaddition reaction of **3** and **6** with neat **1**.

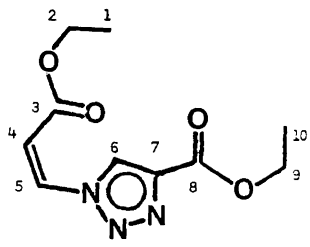
## Experimental

*Warning.* All azido compounds are known to be potentially explosive and appropriate caution should be exercised. All the alkyl (*Z*)-3-azido-2-alkenoates described here were exposed to an open flame. They did not explode but they burned rapidly.

*Starting materials.* 2-Bromoethyl 2-propynoate (**1c**)[10-11] and methyl 4-chloro-2-butynoate (**1e**)[12] were prepared according to the literature. Methyl 2-pentynoate (**1f**) was prepared by a general one-pot procedure for synthesis of 1-alken-5-yne derivatives.[13] All other starting materials were commercially available.

*$^{13}C$ NMR spectral data.* The carbon atoms in 3-azide-2-alkenoates are numbered from the carbonyl group, first along the main carbon chain and then along the alkoxy carbon chain. The carbon atoms in the triazoles **12**, **13** and **14** are numbered as shown in Scheme 3.

*Synthesis of alkyl 3-azido-2-alkenoates. General procedure.* The molar ratios of the educts, the water volumes, reaction temperatures, reaction times and isolated yields are listed in Table 2. The alkyl 2-alkynoate (**1**) is added to an aqueous solution of sodium tetraborate, potassium dihydrogen phosphate and sodium azide in an Erlenmeyer flask (10–13 cm diameter) equipped with a stirrer. The flask is immersed 1–2 cm below the water surface in an ultrasonic cleaner (Bandelin, Sonorex RK 510H, 450W/35 kHz). The water bath is equipped with a thermostat and an immersion cooler connected to a cryostat (Lauda, TK 30). At temperatures below 0 °C a 20 % aqueous solution of diethylene glycol is used as ultrasonic medium. In this way stable reaction temperatures from −10 °C to +80 °C are available. The crude product is extracted with ether (5×50 ml). The ether solution is dried over calcium chloride and concentrated at 25 °C under reduced pressure (water pump).




*Scheme 3.* $^{13}C$ NMR carbon atom numbering.

*Methyl (Z)-3-azido-2-propenoate* (**3a**). The product can be sublimed at 25 °C/13 Pa (0.1 mmHg). M.p. 65 °C. Anal. $C_4H_5N_3O_2$: C, H, N. IR(KBr): 3070 (m), 2990 (m), 2960 (m), 2140 (vs), 1725 (vs), 1625 (vs), 1235 (s), 1175 (s), 800 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.77 (1H, d, *J* 8.5 Hz), 5.27 (1H, d), 3.72 (3H, s). $^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ 164.22 (C-1), 139.87 (C-3), 106.89 (C-2), 51.07 (C-4). UV[$CH_3CN$; $\lambda_{max}$ (log ε)] = 210 (3.84), 261 (4.19) nm. MS[IP 70eV; *m/e* (% rel. int.)]: 127 (9, M), 99 (16), 96 (14), 59 (100), 40 (90).

*Ethyl (Z)-3-azido-2-propenoate* (**3b**). The isomers **3b** and **6b** can be separated by column chromatography on silica gel with methylene chloride as eluent. IR(film): 3030 (m), 2990 (m), 2120 (vs), 1715 (vs), 1625 (vs), 1225 (vs), 1185 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 6.72 (1H, d, *J* 8.5 Hz), 5.26 (1H, d), 4.18 (2H, q, *J* 7.1 Hz), 1.28 (3H, t). $^{13}C$ NMR (75.4 MHz, $CDCl_3$):

δ 163.95 (C-1), 139.74 (C-3), 107.49 (C-2), 60.14 (C-4), 14.13 (C-5). UV[$CH_3CN$; $\lambda_{max}$ (log ε)] = 261 (4.15), 210 (3.83) nm. MS[IP 70eV; *m/e* (% rel. int.)]: 141 (2, M), 113 (6), 96 (10), 85 (74), 68 (100).

*2-Bromoethyl (Z)-3-azido-2-propenoate* (**3c**). **3c** and **6c** are separated by chromatography on a silica gel column with methylene chloride; $R_f$ (**6c**): 0.42; $R_f$ (**3c**): 0.35. **3c** remains as slightly yellowish liquid which is sensitive to light and heat. IR(film): 3090 (w), 2980 (m), 2130 (vs), 1720 (vs), 1620 (vs), 1225 (vs), 1160 (vs), 810 (s) $cm^{-1}$. $^1H$ NMR (75.4 MHz, $CDCl_3$): δ 6.79 (1H, d, *J* 8.5 Hz), 5.30 (1H, d), 4.43 (2H, t, *J* 6.2 Hz), 3.53 (2H, t). $^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ 162.88 (C-1), 140.85 (C-3), 105.94 (C-2), 63.15 (C-4), 28.44 (C-5). UV[$CH_3CN$; $\lambda_{max}$ (log ε)] = 210 (3.83), 264 (4.20) nm. MS[IP 70eV; *m/e* (% rel. int.)]: 219 (1, M), 193 (2), 107 (60), 68 (100), 40 (80).

*2-Bromoethyl (E)-3-azido-2-propenoate* (**6c**). $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.34 (1H, d, *J* 13.4 Hz), 5.68 (1H, d), 4.45 (2H, t, *J* 6.01 Hz), 3.53 (2H, t), $^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ 165.11 (C-1), 145.10 (C-3), 108.52 (C-2), 63.78 (C-4), 28.66 (C-5).

*Methyl (Z)-3-azido-2-butenoate* (**3d**). The product can be sublimed at 40 °C/13 Pa (0.1 mmHg) as yellowish plates; m.p. 51 °C. Anal. $C_5H_7N_3O_2$: C, H, N. IR($CCl_4$): 3000 (m), 2960 (m), 2120 (vs), 1720 (vs), 1630 (vs), 1260 (vs), 1190 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 5.21 (1H, q, *J* 0.9 Hz), 3.79 (3H, s), 2.15 (3H, d). $^{13}C$ NMR ($CDCl_3$): δ 164.34 (C-1), 148.38 (C-3), 105.09 (C-2), 50.85 (C-5), 20.25 (C-4). UV[$CH_3CN$; $\lambda_{max}$ (log ε)] = 264 (3.97), 211 (3.75) nm. MS[IP 70eV; *m/e* (% rel. int.)]: 141 (15, M), 113 (35), 110 (36), 82 (100), 67 (22), 58 (42), 54 (66), 43 (60).

*Methyl (Z)-3-azido-4-chloro-2-butenoate* (**3e**). The product can be sublimed at 40 °C/13 Pa (0.1 mmHg) as slightly yellowish plates; m.p. 76 °C (decompn.). Anal. $C_5H_6ClN_3O_2$: C, H, N. IR (KBr): 3060 (m), 3030 (m), 2940 (w), 2130 (vs), 1700 (vs), 1630 (vs), 1275 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 5.57 (1H, s), 4.12 (2H, s), 3.74 (3H, s). $^{13}C$ NMR (75.4 MHz, $CDCl_3$): 164.10 (C-1), 147.29 (C-3), 107.71 (C-2), 51.52 (C-5), 44.09 (C-4, J(C-4, H-2), 5.9 Hz). UV[$CH_3CN$; $\lambda_{max}$ (log ε)] = 210 (3.80), 265 (4.12) nm. MS[IP 70eV; *m/e* (% rel. int.)]: 175 (9, M), 144 (52), 137 (11), 116 (100), 112 (75), 88 (78), 77 (68), 67 (60), 57 (78), 49 (60), 42 (46).

*Methyl (Z)-3-azido-2-pentenoate* (**3f**). The product was purified by chromatography on a short silica gel column and eluted with methylene chloride; slightly yellowish liquid. $R_f$ (**3f**): 0.38; $R_f$ (**6f**): 0.54. IR(film): 2940 (m), 2110 (vs), 1715 (vs), 1630 (vs), 1260 (vs), 1190 (vs), 830 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 5.32 (1H, t, *J* 0.9 Hz), 3.70 (3H, s), 2.40 (2H, q, *J* 7.4 Hz), 1.22 (3H, t). $^{13}C$ NMR (75.4 MHz, $CDCl_3$): δ 164.58 (C-1), 153.96 (C-3), 103.59 (C-2), 50.84 (C-6), 27.73 (C-4, *J* (C-4, H-2) 5.0 Hz). UV[$CH_3CN$; $\lambda_{max}$ (log ε)] = 265 (4.13), 212 (3.92) nm. MS[IP 70eV; *m/e* (% rel. int.)]: 155 (1, M), 127 (25), 113 (9), 99 (59), 96 (41), 82 (72), 68 (100).

*Dimethyl 2-azidofumarate* (**3g**) *and dimethyl 2-azidomaleate* (**3g**). **3g** and **6g** are obtained as a pale yellow liquid. The separation of the compounds and their spectral data are described in the literature.[14]

*Ethyl (E)- and (Z)-3-(4-ethoxycarbonyl)-1H-1,2,3-triazol-1-yl)propenoate* (**14b**) *and* (**13b**). The general procedure for **3b** (88 ml $H_2O$, 60 °C, 30 min) is used without additional stirring. **3b** and **6b** are removed by Kugelrohr distillation at 40 °C/13 Pa (0.1 mmHg). The residue is freed from basic impurities by flash chromatography on silica gel with methylene chloride as eluent. The *Z*-isomer **13b** can be sublimed at 65 °C/13 Pa (0.1 mmHg), whereas the *E*-isomer **4b** remains in the residue.

The easiest way to synthesize **13b** is to heat equimolar amounts of **3b** and **1b** in ether under reflux for 4d. **13b** is formed in excellent yield as the sole product.

**13b**: m.p. 89 °C. Anal. $C_{10}H_{13}N_3O_4$: C, H, N. IR(KBr): 3170 (w), 3110 (vw), 3060 (w), 2990 (w), 1740 (vs), 1718 (s), $\lambda_{max}$ 1660 (m), 1205 (vs), 1040 (s) $cm^{-1}$. UV[$CH_3CN$; $\lambda_{max}$ (log ε)] = 213 (4.13), 258 (4.12) nm. $^1H$ NMR (300 MHz, $CDCl_3$): δ 9.68 (1H, s), 7.68 (1H, d, *J* 10.9 Hz), 5.88 (1H, d), 4.46 (2H, q, *J* 7.1 Hz), 4.28 (2H, q, *J* 7.1 Hz), 1.43 (3H, t), 1.35 (3H, t). $^{13}C$ NMR

(75.4 MHz, $CDCl_3$): δ 163.57 (C-3), 160.11 (C-8), 139.99 (C-7), 132.82 (C-5), 129.83 (C-6), 109.68 (C-4), 61.37, 61.34 (C-9, C-2), 14.18, 13.91 (C-10, C-1); *J* (C-6, H-5) 4.8 Hz. MS[IP 70eV; *m/e* (% rel. int.)]: 239 (5, M), 194 (22), 166 (10), 138 (70), 111 (56), 70 (90), 28 (100).

**14b**: $^1$H NMR (300 MHz, $CDCl_3$): δ 8.62 (1H, s), 8.28 (1H, d, *J* 14.3 Hz), 6.74 (1H, d), 4.45 (2H, q, *J* 7.1 Hz), 4.31 (2H, q, *J* 7.1 Hz), 1.42 (3H, t), 1.35 (3H, t). $^{13}$C NMR (74.5 MHz, $CDCl_3$): δ 164.60 (C-3), 159.92 (C-8), 140.83 (C-7), 135.35 (C-5), 126.41 (C-6), 112.77 (C-4), 61.56, 61.29 (C-2, C-9), 14.09, 14.01 (C-1, C-10); *J* (C-6, H-5) 2.7 Hz.

*Ethyl (*E*)-2-(4-ethoxycarbonyl-*2H*-1,2,3-triazol-2-yl)propenoate* (**12b**). Crude **13b** and **14b** containing basic impurities such as sodium hydroxide or sodium azide are heated to 100 °C in a sublimation apparatus (13 Pa, 0.1 mmHg). After 1d, **12b** has sublimed to the cold finger and can be recrystallized from methanol yielding colourless needles; m.p. 80 °C. Anal. $C_{10}H_{13}N_3O_4$: C, H, N. IR(KBr): 3130, 3090 (m), 2990 (w), 1735 (vs), 1705 (vs), 1650 (w) $cm^{-1}$. UV[$CH_3CN$; $\lambda_{max}$ (log ε)] = 278 (4.34), 201 (3.89) nm. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.22 (1H, s), 8.20 (1H, d, *J* 14.1 Hz), 6.82 (1H, d), 4.46 (2H, q, *J* 7.1 Hz), 4.29 (2H, q, *J* 7.1 Hz), 1.43 (3H, t), 1.34 (3H, t). $^{13}$C NMR (75.4 MHz, $CDCl_3$): δ 165.06 (C-3), 159.85 (C-8), 142.67 (C-7), 139.06 (C-6), 138.79 (C-5), 112.56 (C-4), 61.97, 61.16 (C-2, C-9), 14.22, 14.20 (C-1, C-10).

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