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Two tandem sequential reactions catalyzed by [Au], *N*-heterocyclic carbenes (NHC) and organic bases

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ABSTRACT

Herein we describe two coupling reactions of aldehydes and activated alkynes to give chalcones or alkenyl esters depending on the base used. Chalcones were obtained by activation of alkynes by Au^I and of aldehydes by NHC in presence of triethylamine. Alkenyl esters were obtained via generation of gold nanoparticles, aerial oxidation of aldehydes to carboxylates and their subsequent nucleophilic addition to the alkyne functionality.

1. Introduction

Chalcones represent a synthetically versatile class of organic molecules possessing interesting biological properties. Biological activities comprise antioxidants,[1] anti-inflammatory,[2] anti-cancer,[3] cytotoxic,[4] hypoglycaemic[5] and antimitotic activities.[6] Moreover, chalcones can be found as intermediates in the synthesis of flavonoids.[7,8] The α,β-unsaturated moiety of chalcones allowed several transformations, including epoxidations,[9,10] Michael additions,[11,12] cyclocondensation[13] and synthesis of pyrazoline through a modified reaction of the 'Huisgen Zwitterion'.[14] Although chalcones could be prepared via the classic Claisen–Schmidt condensation, over the last 20 years a number of synthetic methodologies have been developed, including Suzuki[15] and Julia–Kocienski olefination.[16] Our interest in NHC chemistry prompted us to investigate a modification of the classic Stetter reaction,[17] in order to develop a new synthesis of chalcone derivatives **1** (Fig. 1). It was reasoned that, while the NHCs chemistry would activate an aldehyde **2** resulting in the generation of a nucleophile,[17] a concomitant gold-catalyzed activation of an electrophilic component, for example, an alkyne **3**, could be exploited to build an α,β-unsaturated moiety in a tandem NHC/Au catalyzed process.

In the last decade there has been a fast growing interest in gold catalysis. Gold is present in three different oxidative states: Au^0, Au^I and Au^{III}, where the catalytic active species is finally Au^I or Au^{III}.[18–22] Alkynes are the most common substrates used in the gold catalysis as Au^I can activate the π-system by coordination, allowing a nucleophilic attack. Based on these concepts, a huge variety of gold-catalyzed reactions have been developed and various examples are reported in literature.[23–28]

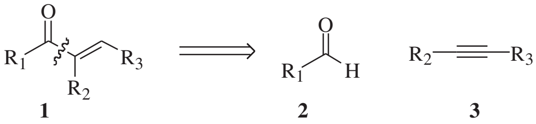

Fig. 1. Disconnection proposed for the preparation of chalcones **1**.

A tandem reaction involving aldehydes and alkynes was therefore planned according to the following principles (Scheme 1): a. NHC **4** reacts with aldehyde **2** to give a Breslow intermediate **5**, which acts as a nucleophile (Nu);[29–35] b. Au^I coordinates alkyne **3** generating a more electrophilic species, which could be then attacked by nucleophile **5**.[18–22]

2. Results and discussion

To test our hypothesis, we carried out a simple experiment heating diphenylacetylene **8** and benzaldehyde **2a** under the catalysis of 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (IMes) **6** and Au^{III} using triethylamine as the base (Table 1, entries 1–3). In these experiments, IMes **6**, aldehyde **2a** and triethylamine were allowed to react in order to engage the NHC in a Breslow intermediate and avoiding formation of an NHC gold complex.[22]

Under these conditions, no formation of chalcone **1a** was observed and starting materials **8** and **2a** were recovered after 24 h. We then performed an in depth screening including variation of temperature, reactants, solvent, base and reaction time. Results collected with activated alkynes, such as arylpropynoic acid esters

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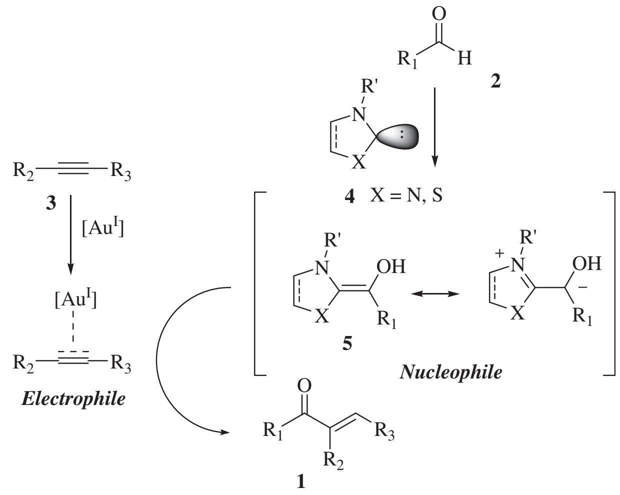
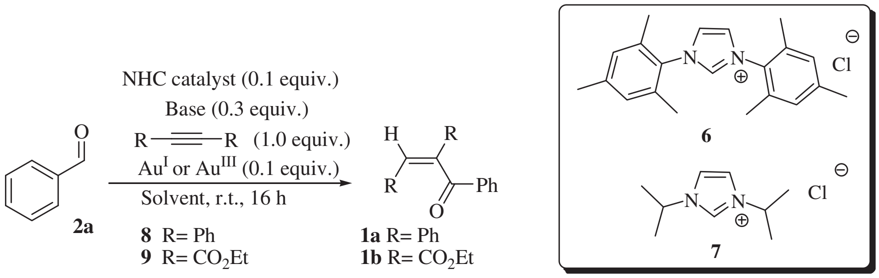


Scheme 1. Tandem sequential reaction to prepare chalcones **1**.

Table 1
Identification of suitable conditions for the NHC/Au^x-catalyzed preparation of chalcones **1**



Entry	NHC	Au	Alkyne	Base	Solvent	Product	Yield[a] (%)
1	**6**	Au^{III}	**8**	Et_3N	DCM	**1a**	—
2	**6**	Au^{III}	**8**	Et_3N	Toluene	**1a**	—
3	**6**	Au^{III}	**8**	Et_3N	Et_3N	**1a**	—
4	**7**	Au^{I}	**9**	Et_3N	THF	**1b**	38
5	**7**	Au^{III}	**9**	Et_3N	THF	**1b**	5
6	**7**	—	**9**	Et_3N	THF	**1b**	—
7	**7**	Au^{I}	**9**	Et_3N	DCM	**1b**	70

[a] Isolated yields after column chromatography on silica gel.

arylpropynoic acid esters, arylpropynenitriles or diarylpropynones gave disappointing results, however, when the more reactive but-2-ynedioic acid diethyl ester **9** was used as the electrophilic component, Au^{III} was switched to Au^{I} and THF was used as solvent, chalcone **1b** was isolated in 38% yield (Table 1, entry 4). The reaction was further optimised by replacing IMes **6** with 1,3-diisopropyl imidazolinium chloride **7** and changing THF with DCM (Table 1, entry 7).

Notably, the reaction did not proceed without Au^{I} (Table 1, entry 6) or without NHC or base. Importantly, studies by Nair[36] and Shi[37] have established that triethylamine did not catalyse the addition of electrophilic alkynes to aldehydes under similar conditions, validating the catalytic cycle proposed for the formation of compound **1c**. Other aromatic aldehydes were also submitted to reaction with alkyne **9**. Aldehydes **2b**–**e** containing an electron withdrawing group reacted well under the optimised conditions giving chalcones **1c**–**f** in good yields (Table 2). Conversely, aldehydes holding electron donating groups reacted sluggishly furnishing the pinacol as the main product.

During this study, it was noted that replacement of NEt_3 with DBU lead to formation of unexpected alkenyl ester **10c** (Table 3). This reaction was set up as a homogeneous mixture, however an identified dark solid was found in suspension after few minutes. The formation of the dark solid was established an essential requisite for the occurrence of compound **10c**. An explanation of this result may involve the formation of Au^0 nanoparticles, which arose from reduction of Au^I by amines.[38,39] The gold nanoparticles isolated as a powder. In turn, the gold nanoparticles catalyzed the aerobic oxidation of aldehydes to carboxylates. Finally, carboxylates added to alkyne **9** to give compound **10c** as observed by Liang.[40] We have briefly investigated the oxidation of aromatic aldehydes to carboxylic acids under the conditions described in Table 3. This study revealed that aromatic aldehydes, for example, benzaldehyde **2a**, could be efficiently converted in less than 16 h to benzoic acid, which were isolated in good to excellent yields.

The structure of alkenyl ester **10c** was confirmed by comparison of its analytical data with the correlated dimethyl ester **11**, for which X-ray diffraction was obtained (Fig. 2).[41] The validity of this new protocol was shown by reacting aldehydes **2a**–**e** under similar conditions to afford alkenyl esters **10a**–**e** (Table 3) in good isolated yields.

3. Conclusion

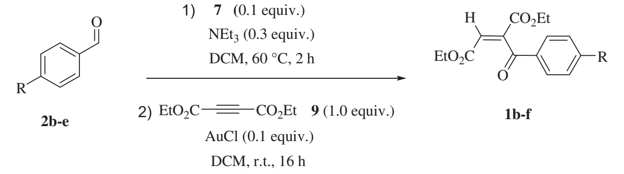
In conclusion, we have shown a conceptually new coupling of aldehydes and electrophilic alkenes. The process relied on generation of a nucleophile by addition of NHC to aldehydes and on enhancement of alkyne electrophilicity furnished by Au^I. A modified procedure of this reaction, e.g., replacement of triethylamine with DBU, allowed the formation of alkenyl esters in good isolated yields.

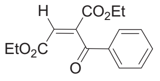
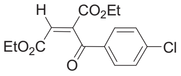
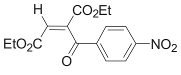
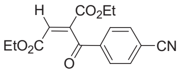
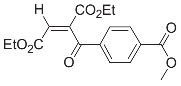
4. Experimental section

4.1. General experimental

Melting points were determined using a Stuart scientific melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded as KBr discs using a Bruker Tensor27 FT-IR instrument. Absorption maximum (ν_{max}) was reported in wave numbers (cm^{-1}) and only selected peaks are reported. NMR experiments were performed on a Bruker Avance 400 instrument and samples were obtained in $CDCl_3$ (referenced to 7.26 ppm for ^1H and 77.0 for ^{13}C) and in DMSO-d_6 (referenced to 2.52 and

Table 2
Isolated yields for chalcones **1b**–**f**



Entry	R	Product	Yield[a] (%)
1	H **2a**	 **1b**	70
2	Cl **2b**	 **1c**	68
3	NO_2 **2c**	 **1d**	70
4	CN **2d**	 **1e**	80
5	$COOCH_3$ **2e**	 **1f**	49

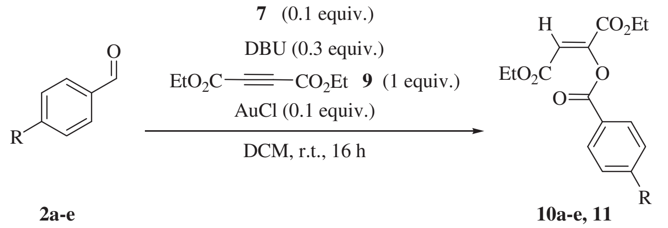
[a] Isolated yields after column chromatography on silica gel.

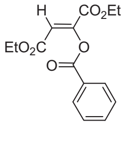
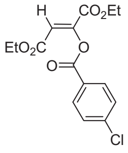
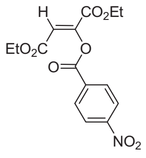
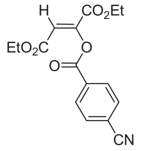
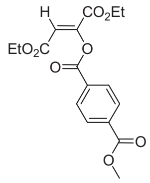
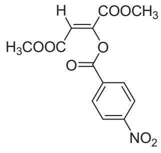
3.35 ppm for ^{1}H and 40.0 for ^{13}C). Coupling constants (*J*) are in hertz. Multiplicities are reported as follows: s, singlet, d, doublet, dd, doublets of doublets, t, triplet, q, quartet, m, multiplet, c, complex, and br, broad. High resolution mass spectra were obtained on a Waters Micro mass LCT and low resolution mass spectra were recorded on Waters Micro mass Quattro LC–MS spectrometers at 70 eV. Tetrahydrofuran was freshly distilled over sodium benzophenone prior to use according to standard procedure. All other reagents and solvents were used as purchased from Aldrich. Reactions were checked for completion by TLC (EM Science, silica gel 60 F_{254}). Flash chromatography was performed using silica gel 60 (0.040–0.063 mm, 230–400 mesh).

4.2. General procedure for the preparation of chalcones 1b–f

1,3-Diisopropyl imidazolium chloride **7** (19 mg, 0.1 mmol, 0.1 equiv), triethylamine (42 μL, 0.3 mmol, 0.3 equiv) and aldehyde **2** (1 mmol, 1 equiv) were dissolved in DCM (4 mL) and the reaction mixture was stirred for 2 h at 60 °C. Diethyl acetylene dicarboxylate **9** (170 μL, 1 mmol, 1 equiv) and AuCl (24 mg, 0.1 mmol, 0.1 equiv) were then added and the reaction stirred at room temperature for further 16 h. Then the solvent was evaporated and the residue purified by flash chromatography on silica gel eluting with petroleum ether and 4% EtOAc to give the title compounds **1b**–**f** as yellow liquids.

Table 3
Isolated yields for alkenyl esters **10a**–**e, 11**



Entry	R	Product	Yield[a] (%)
1	H **2a**	 **10a**	40
2	Cl **2b**	 **10b**	45
3	NO_2 **2c**	 **10c**	62
4	CN **2d**	 **10d**	67
5	$COOCH_3$ **2e**	 **10e**	43
6	NO_2 **2c**	 **11**	58[b]

[a] Isolated yields after column chromatography on silica gel.
[b] Performed by using but-2-ynedioic acid dimethyl ester.

4.2.1. *2-Benzoyl-but-2-enedioic acid diethyl ester* ***1b***.

Yellow liquid (193 mg, 70%). R_f=0.60 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 3125, 2978, 1729, 1687, 1520; δ_H (400 MHz, $CDCl_3$) 7.82–7.37 (m, 5H, Ar), 6.99 (s, 1H, *CH*), 4.17 (q, *J*=7.2, 2H, $-OCH_2CH_3$), 3.97 (q, *J*=7.2, 2H, $-OCH_2CH_3$), 1.12 (t, *J*=7.2, 3H, $-OCH_2CH_3$), 0.99 (t, *J*=7.2, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, $CDCl_3$) 192.3, 163.8, 163.2, 142.2, 135.2, 133.8, 130.6, 128.8, 128.2, 62.5, 61.7, 13.9, 13.6; *m/z*: 276 (45%, M^-); HRMS: *m/z* found [M^-] 276.0914, $C_{15}H_{16}O_5$ requires 276.0998.

4.2.2. *2-(4-Chloro-benzoyl)-but-2-enedioic acid diethyl ester* ***1c***.

Yellow liquid (212 mg, 68%). R_f=0.65 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 3130, 2989, 1728, 1680, 1520; δ_H

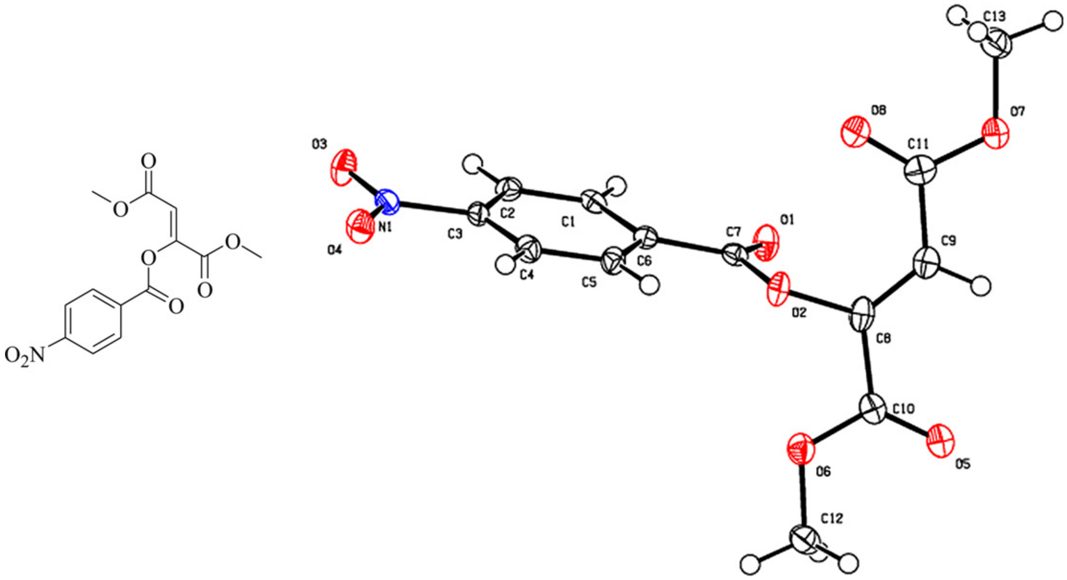


Fig. 2. Planar and crystal structure of compound **11**.

(400 MHz, $CDCl_3$) 7.76–7.35 (m, 4H, Ar), 6.98 (s, 1H, *CH*), 4.16 (q, J=7.2, 2H, $-OCH_2CH_3$), 4.00 (q, J=7.2, 2H, $-OCH_2CH_3$), 1.12 (t, J=7.2, 3H, $-OCH_2CH_3$), 1.02 (t, J=7.2, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, $CDCl_3$) 191.1, 163.7, 162.9, 144.8, 140.1, 134.2, 130.8, 130.0, 129.1, 62.5, 61.8, 13.9, 13.7; *m*/*z*: 310 (20%, M^-); HRMS: *m*/*z* found $[M^-]$ 310.0621, $C_{15}H_{15}ClO_5$ calculated 310.0608.

4.2.3. 2-(4-Nitro-benzoyl)-but-2-enedioic acid diethyl ester ***1d***. Yellow liquid (224 mg, 70%); R_f=0.6 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 3113, 2929, 1742, 1694, 1531; δ_H (400 MHz, $CDCl_3$) 8.27–7.97 (m, 4H, Ar), 7.05 (s, 1H, *CH*), 4.19 (q, J=7.2, 2H, $-OCH_2CH_3$), 4.03 (q, J=7.2, 2H, $-OCH_2CH_3$), 1.15 (t, J=7.2, 3H, $-OCH_2CH_3$), 1.07 (t, J=7.2, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, $CDCl_3$) 191.0, 163.8, 162.6, 150.6, 144.5, 140.1, 131.6, 129.6, 124.1, 62.8, 62.1, 14.0, 13.8; *m*/*z*: 320 (26%, M^-); HRMS: *m*/*z* found $[M^-]$ 320.0810, $C_{15}H_{15}NO_7$, calculated 321.0849.

4.2.4. 2-(4-Cyano-benzoyl)-but-2-enedioic acid diethyl ester ***1e***. Yellow liquid (240 mg, 80%); R_f=0.55 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 3130, 2969, 1710, 1690, 1528; δ_H (400 MHz, $CDCl_3$) 7.92–7.89 (m, 4H, Ar), 7.03 (s, 1H, *CH*), 4.18 (q, J=7.2, 2H, $-OCH_2CH_3$), 4.02 (q, J=7.2, 2H, $-OCH_2CH_3$), 1.14 (t, J=7.2, 3H, $-OCH_2CH_3$), 1.06 (t, J=7.2, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, $CDCl_3$) 191.1, 163.7, 162.6, 144.4, 138.6, 132.6, 131.5, 128.9, 117.8, 116.8, 62.7, 62.0, 13.9, 13.7; *m*/*z*: 301(36%, M^-); HRMS: *m*/*z* found $[M^+]$ 301.0941, $C_{16}H_{15}NO_5$ calculated 301.0950.

4.2.5. 2-(4-Methoxycarbonyl-benzoyl)-but-2-enedioic acid diethyl ester ***1f***. Yellow liquid (164 mg, 49%); R_f=0.52 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 3122, 2919, 1722, 1695, 1598; δ_H (400 MHz, $CDCl_3$) 8.08–7.87 (m, 4H, Ar), 7.02 (s, 1H, *CH*), 4.18 (q, J=7.2, 2H, $-OCH_2CH_3$), 4.00 (q, J=7.2, 2H, $-OCH_2CH_3$), 3.89 (s, 3H, OCH_3), 1.13 (t, J=7.2, 3H, $-OCH_2CH_3$), 1.02 (t, J=7.2, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, $CDCl_3$) 191.8, 166.1, 163.7, 162.9, 144.8, 138.8, 134.4, 131.1, 130.0, 128.5, 62.6, 61.9, 52.5, 13.9, 13.7; *m*/*z*: 334 (24%, M^-). HRMS: *m*/*z* found $[M^+]$ 334.1040, $C_{17}H_{18}O_7$ calculated 334.1053.

4.3. General procedure for the preparation of alkenoic acid esters 10a–e

To a solution of 1,3-diisopropyl imidazolium chloride **7** (19 mg, 0.1 mmol, 0.1 equiv.) in DCM (4 mL), were sequentially added DBU (45 μL, 0.3 mmol, 0.3 equiv.) and aldehyde **2** (0.1 mL, 1 mmol) and the reaction mixture stirred for 2 h at room temperature. Diethyl acetylene dicarboxylate **9** (170 μL, 1 mmol, 1 equiv.) and AuCl (24 mg, 0.1 mmol, 0.1 equiv.) were then added and the reaction was allowed to stir at room temperature for 16 h. The reaction mixture was concentrated in vacuo and the residue obtained purified by flash chromatography on silica gel eluting with petroleum ether and 4% EtOAc to give compound **10**.

4.3.1. 2-Benzoyloxy-but-2-enedioic acid diethyl ester ***10a***. Yellow liquid (110 mg, 40%), R_f=0.55 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 1736; δ_H (400 MHz, DMSO-d_6) 8.08–7.61 (m, 5H, Ar), 6.79 (s, 1H, *CH*), 4.27 (q, J=6.8, 2H, $-OCH_2CH_3$), 4.11 (q, J=7.2, 2H, $-OCH_2CH_3$), 1.24 (t, J=7.0, 3H, $-OCH_2CH_3$), 1.09 (t, J=7.2, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, $CDCl_3$) 163.7, 162.8, 161.1, 146.7, 134.0, 130.3, 128.6, 128.1, 117.4, 62.6, 61.1, 14.0, 13.9; *m*/*z*: 292 (80%, M^+). HRMS: *m*/*z* found $[M^+]$ 292.0914, $C_{15}H_{16}O_6$ requires 292.0947.

4.3.2. 1,2-Di(ethoxycarbonyl)vinyl 4-chlorobenzoate ***10b***. Yellow liquid (148 mg, 45%); R_f=0.55 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 1741; δ_H (400 MHz, DMSO-d_6) 8.00–7.70 (m, 4H, Ar), 6.81 (s, 1H, *CH*), 4.27 (q, J=7.0, 2H, $-OCH_2CH_3$), 4.11 (q, J=7.0, 2H, $-OCH_2CH_3$), 1.24 (t, J=7.0, 3H, $-OCH_2CH_3$), 1.10 (t, J=7.0, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, DMSO-d_6) 163.5, 160.6, 145.7, 139.8, 131.5, 130.3, 128.9, 128.6, 117.8, 61.8, 60.1, 14.0, 13.5; *m*/*z*: 292 (65%, M^+). HRMS: *m*/*z* found $[M^+]$ 326.0517, $C_{15}H_{15}ClO_6$ requires 326.0557.

4.3.3. 1,2-Di(ethoxycarbonyl)vinyl 4-nitrobenzoate ***10c***. Yellow liquid (209 mg, 62%); R_f=0.52 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 1739; δ_H (400 MHz, DMSO-d_6) 8.45–8.31 (m, 4H, Ar), 6.86 (s, 1H, *CH*), 4.29 (q, J=7.2, 2H, $-OCH_2CH_3$), 4.12 (q, J=7.2, 2H, $-OCH_2CH_3$), 1.25 (t, J=7.0, 3H, $-OCH_2CH_3$), 1.11 (t, J=7.0, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, $CDCl_3$) 162.6, 162.0, 160.8, 151.1, 146.4, 133.7, 131.6, 123.8, 118.0, 62.9, 61.4, 14.1, 14.0; *m*/*z*: 337 (90%, M^+). HRMS: *m*/*z* found $[M^+]$ 337.0762, $C_{15}H_{15}NO_8$ requires 337.0798.

4.3.4. 1,2-Di(ethoxycarbonyl)vinyl 4-cyanobenzoate ***10d***. Yellow liquid (212 mg, 67%); R_f=0.5 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 1729; δ_H (400 MHz, DMSO-d_6) 8.23–8.10 (m, 4H, Ar), 6.84 (s, 1H, *CH*), 4.28 (q, J=7.2, 2H, $-OCH_2CH_3$), 4.12 (q, J=7.2, 2H, $-OCH_2CH_3$), 1.24 (t, J=7.0, 3H, $-OCH_2CH_3$), 1.10 (t, J=7.0, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, DMSO-d_6) 162.1, 162.0, 160.3, 145.4, 133.2, 131.2, 130.49, 117.9, 117.8, 116.7, 62.6, 61.1, 13.7, 13.7; *m*/*z*: 337

(90%, M^+). HRMS: m/z found [M^+] 317.0863, $C_{16}H_{15}NO_6$ requires 317.0899.

4.3.5. 1,2-Di(ethoxycarbonyl)vinyl methyl terephthalate ***10e***. Yellow liquid (158 mg, 43%); R_f=0.5 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 1732; δ_H (400 MHz, DMSO-d_6) 8.19–8.18 (m, 4H, Ar), 6.84 (s, 1H, *CH*), 4.28 (q, *J*=7.2, 2H, $-CH_2CH_3$), 4.11 (q, *J*=7.2, 2H, $-OCH_2CH_3$), 3.92 (s, 3H, OCH_3) 1.24 (t, *J*=7.0, 3H, $-OCH_2CH_3$), 1.09 (t, *J*=7.0, 3H, $-OCH_2CH_3$); δ_C (100.6 MHz, DMSO-d_6) 165.3, 162.6, 162.2, 160.4, 145.5, 134.6, 131.2, 130.3, 129.9, 129.8, 117.8, 62.6, 61.1, 52.7, 52.6, 13.7, 13.7; m/z: 350 (50%, M^+). HRMS: m/z found [M^+] 350.1010, $C_{17}H_{18}O_8$ requires 350.1003.

4.3.6. 1,2-Di(methoxycarbonyl)vinyl 4-nitrobenzoate ***11***. Colourless solid, mp 105–110 °C (180 mg, 58%); R_f=0.45 (petroleum ether/EtOAc 8:2 v/v); ν_{max} (KBr)/cm^{-1} 1729, 1525; δ_H (400 MHz, DMSO-d_6) 8.45–8.43 (m, 4H, Ar), 6.90 (s, 1H, *CH*), 3.83 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3); δ_C (100.6 MHz, DMSO-d_6) 162.6, 161.7, 160.8, 151.0, 145.4, 132.5, 131.4, 124.3, 117.7, 53.6, 52.3. m/z: 309 (55%, M^+). HRMS: m/z found [M^+] 309.0463, $C_{13}H_{11}NO_8$ requires 309.0485.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.05.135.

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