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Alkynylation and Cyanation of Alkenes Using Diverse Properties of a Nitro Group

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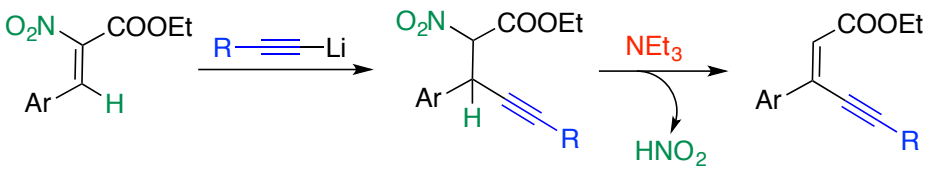
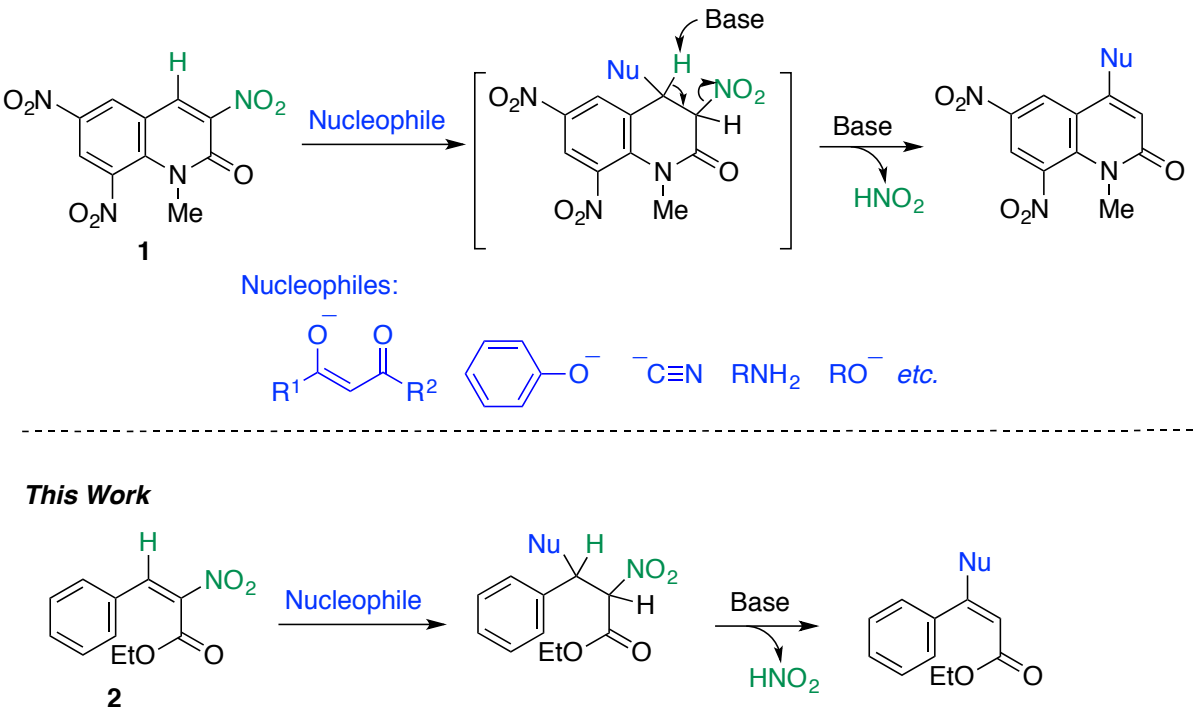


Abstract: In the work being reported here, β-nitrostyrenes bearing an ethoxycarbonyl group at the β-position serve as scaffolds for the synthesis of α,β-difunctionalized alkenes. Nitrocinnamates undergo Michael addition reactions with versatile sp^3- and sp^2-nucleophiles such as alcohols, Grignard reagents, alkylcopper, and dialkylzinc to afford β-substituted nitroethane derivatives. However, various attempts to obtain a double bond *via* nitrous acid elimination failed because steric repulsion between the newly introduced sp^3/sp^2-substituent and the nitro group hampered the required anti-coplanar conformation. This problem was successfully overcome using a smaller sp-nucleophile such as lithium acetylide, potassium cyanide, or trimethylsilyl cyanide. While treatment of the adduct with a strong base did not lead to the elimination of nitrous acid, the weaker triethylamine efficiently afforded functionalized enynes and acrylonitriles in high yields.

Introduction

Nitro compounds are an important family of organic compounds, widely used as functional materials or their synthetic intermediates.[1] The versatile reactivity of the members of this family originates from the diverse properties of the nitro group, which 1) is a strong electron-withdrawing group that reduces the electron density of the adjacent atom or double bond through both inductive and resonance effects, 2) stabilizes anionic intermediates, 3) is easily eliminated as nitrous acid with concomitant double bond formation.[2] These properties can be exploited to functionalize the heterocyclic framework. Indeed, the synthesis of unnatural 1-methyl-2-quinolone derivatives *via* an addition–elimination protocol has been demonstrated. When 1-methyl-3,6,8-trinitro-2-quinolone (**1**) was allowed to react with nucleophiles such as 1,3-dicarbonyl compounds,[3] phenols,[3] cyanides,[4] amines,[5] and alcohols,[6] regioselective nucleophilic substitution proceeded at the 4-position, accompanied by elimination of the 3-nitro group in what is called *cine*-substitution. In this process, the 3- and 4-positions of quinolone **1** act as an activated nitroalkene.[4] Inspired by these results, it was assumed that α-nitrocinnamate **2**, which is structurally related to **1**, should exhibit a reactivity similar to that of **1**, leading to functionalized alkenes *via* said addition−elimination mechanism (Scheme 1). Facile syntheses of functionalized enynes and acrylonitriles using α-functionalized nitroalkenes have been demonstrated.

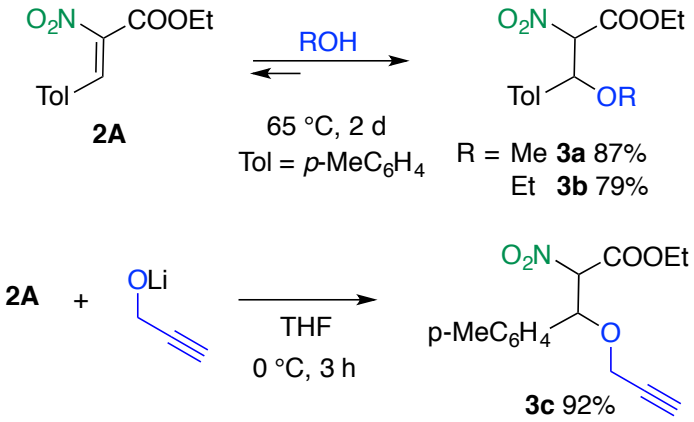


Scheme 1. *cine*-Substitution of trinitroquinolone **1** and synthetic strategy for functionalized alkenes *via* an addition–elimination mechanism.

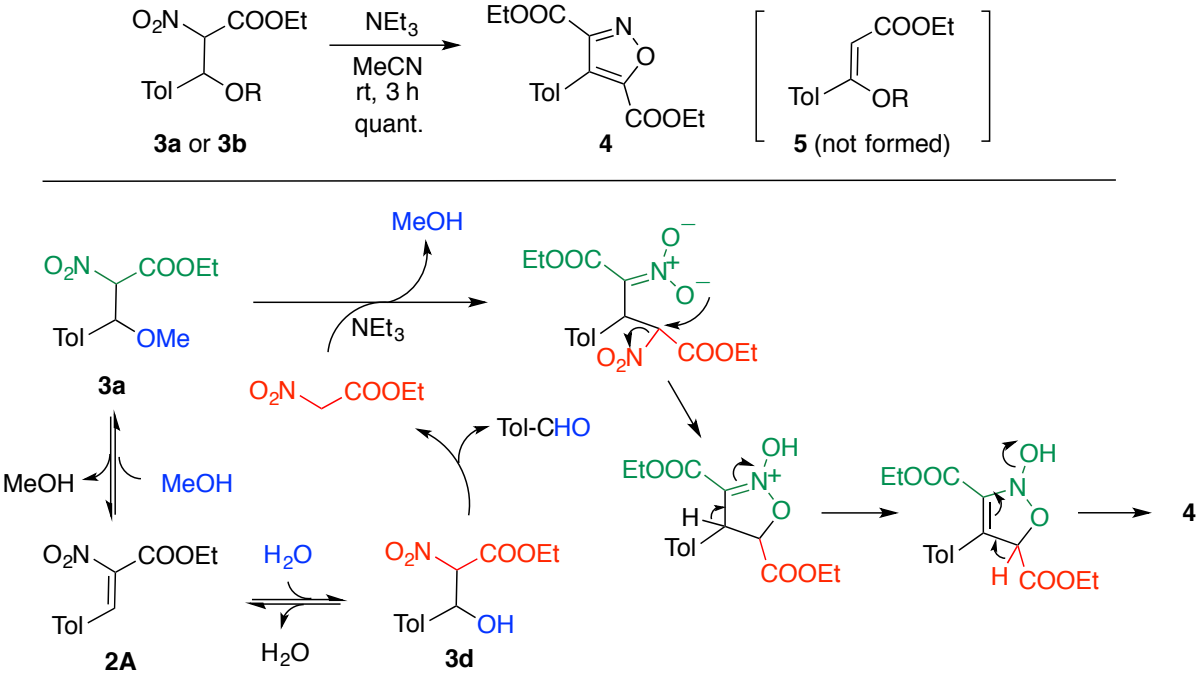
Results and Discussion

When a methanol solution of α-nitrocinnamate **2A**[7] (*E*/*Z* mixture, ca. 3/2 ratio) was heated at solvent reflux for 2 days, adduct **3a** was obtained in 87% yield as a mixture of diastereomers in 73:27 ratio (Scheme 2). Ethanol was also a suitable solvent for this addition reaction. Compound **3b** was obtained in 79% yield upon heating **2A** in this alcohol. It was also possible to use a stoichiometric amount of the lithium alkoxide in THF to afford **3c** in high yield even at 0 °C (Scheme 2). Then, adducts **3a** and **3b** were treated with triethylamine to promote nitrous acid elimination and lead to the formation of a double bond. However, bis(ethoxycarbonyl)isoxazole **4** was quantitatively obtained in the absence of any detectable β-alkoxycinnamates **5a** and **5b** in both cases (Scheme 3). Adduct **3a** is presumably converted into **3d** *via* **2A** in the presence of water contained in the solvent. Furthermore, **3d** is then

hydrolyzed to afford ethyl nitroacetate, which reacts with **3a** leading to **4** *via* cyclization followed by aromatization (Scheme 3).[8]



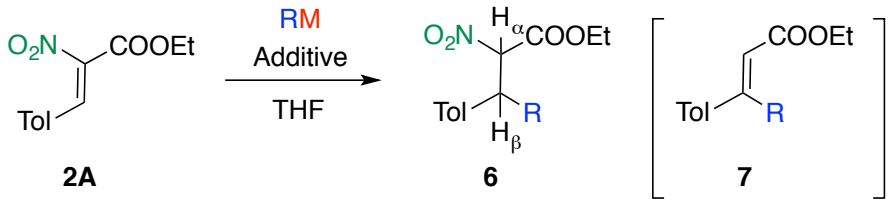
Scheme 2. Addition of an alcohol to nitrocinnamate **2A**.



Scheme 3. Formation of bis(ethoxycarbonyl)isoxazole **4**.

Although adducts **3** were efficiently obtained, the subsequent elimination of a nitrous acid from **3** was not observed rather the predominant reaction sequence to form isoxazole **4** occurred. Hence, carbon nucleophiles were used for the reaction with cinnamate **2A** as C–C bonds are not cleaved as easily as C–O bonds. Upon addition of a dialkylcopperlithium, or dialkylzinc to cinnamate **2A**, the corresponding adducts **6** were efficiently obtained in high yield, however, in cases of adducts **6a** and **6c**, the yields were moderate because of further reaction with another molecule of Grignard reagent (Table 1). This reaction facilitates the introduction of an alkyl or aryl group at the β-position of α-nitrocinnamate **2A**. However, subsequent elimination of nitrous acid from the obtained adducts **6** did not occur even after treatment with an acid such as *p*-toluenesulfonic acid or trifluoroborane etherate, or upon treatment with a base such as triethylamine, pyridine, diazabicycloundecene (DBU), sodium ethoxide, lithium diisopropylamide, or sodium hydride. The low reactivity toward the desired elimination is believed to arise from steric repulsion between the substituents, preventing the β-hydrogen (H_β) and nitro group from taking the necessary *anti*-coplanar conformation (Figure 1, upper left). In order to overcome this problem, less bulky acetylides and cyanides were employed as nucleophiles to avoid steric repulsion between the nitro group and the introduced substituent (Figure 1, upper right). There is another possibility that a *syn*-elimination proceeds in parallel to a sulfoxide elimination, in which the nitro group assists the deprotonation at the adjacent position. Even if the elimination proceeds in such mode, eclipsed conformation of an adduct derived from sp^2-nucleophile is less stable than that derived from sp-nucleophile (Figure 1, lower). Moreover, it was envisioned that the electronegative sp-carbon would increase the acidity of the adjacent H_β to accelerate the elimination of nitrous acid, thus affording functionalized enynes and acrylonitriles (Figure 1, right).

Table 1. Reactions of **2A** with several organometallic reagents.



Entry	Reagent (equiv.)	Additive (equiv.)	Temp. Time	Product R		Yield/%
1	EtMgBr (1.5)	None	0 °C, 1 d	Et	**6a**	49
2	*i*-PrMgBr (1.5)	LiCl (1.5)	rt, 3 h	*i*-Pr	**6b**	90
3	PhMgBr (1.7)	None	rt, 1 h	Ph	**6c**	20
4	Et_2Zn (1.5)	None	rt, 1 h	Et	**6a**	89[a]
5	BuLi (4)	CuI (4), BF_3•OEt_2 (3)	-78 °C~rt, 1 d	Bu	**6d**	62
6	BuLi (6)	CuI (6) BF_3•OEt_2 (6)	-78 °C~rt, 1 d	Bu	**6d**	quant

[a] Ethyl β-ethylcinnamate **7a**[9] was also obtained in 3% yield.

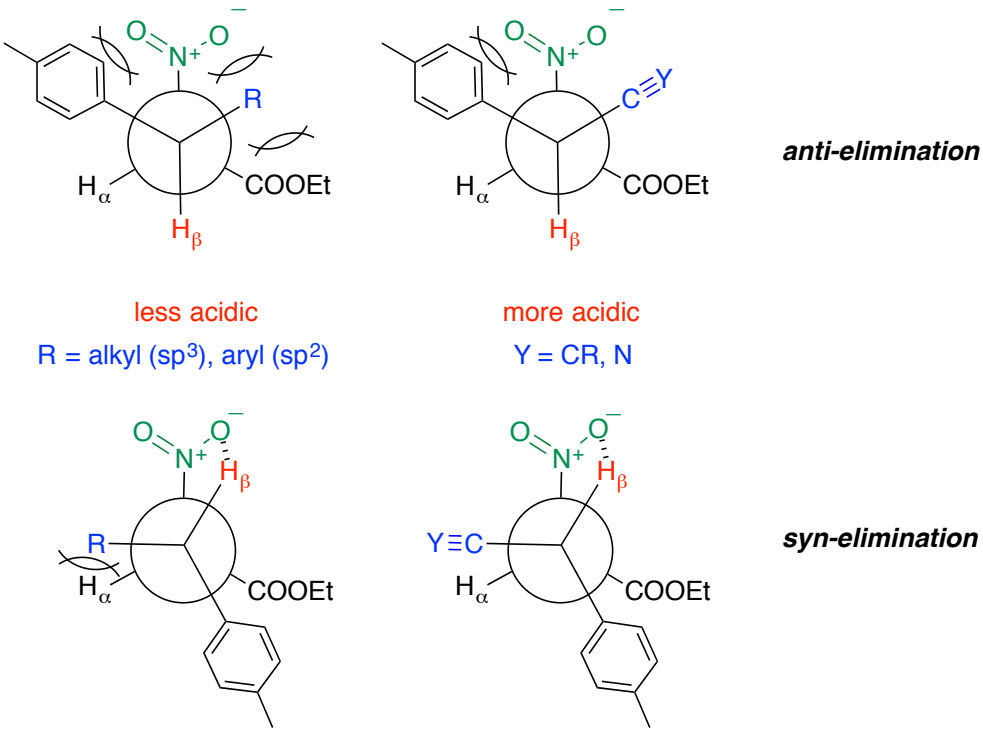
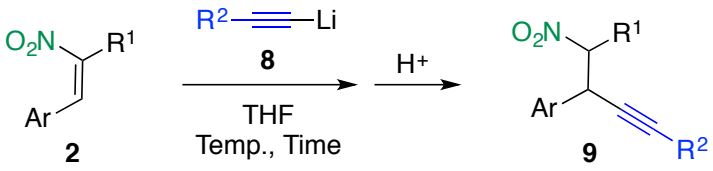


Figure 1. Required conformation of **6** for the elimination of nitrous acid leading to **7**.

Table 2. Reactions of nitroalkene **2** with several lithium acetylides **8**.

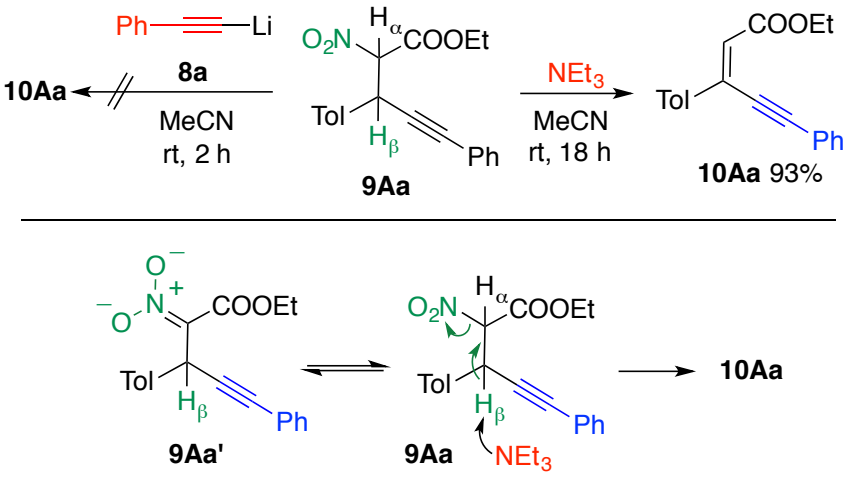


Entry	Nitroalkene **2**			Acetylide **8**		Temp.	Time	Product	
	Ar	R^1		R^2		/°C	/h		Yield/%
1	*p*-MeC_6H_4 (Tol)	COOEt	**2A**	Ph	**8a**	0	1	**9Aa**	90
2	*p*-MeC_6H_4	COOEt	**2A**	*p*-$CF_3C_6H_4$	**8b**	0	3	**9Ab**	31
3	*p*-MeC_6H_4	COOEt	**2A**	Bu	**8c**	0	3	**9Ac**	92
4	*p*-MeC_6H_4	COOEt	**2A**	*tert*-Bu	**8d**	0	3	**9Ad**	92
5	*p*-MeC_6H_4	COOEt	**2A**	$SiMe_3$	**8e**	0	3	**9Ae**	79
6	*p*-$MeOC_6H_4$	COOEt	**2B**	Ph	**8a**	0	2	**9Ba**	83
7	Ph	COOEt	**2C**	Ph	**8a**	-40	2	**9Ca**	94
8	*p*-ClC_6H_4	COOEt	**2D**	Ph	**8a**	-40	1	**9Da**	92
9	2-Furyl	COOEt	**2E**	Ph	**8a**	-40	1	**9Ea**	18
10	*p*-MeC_6H_4	Me	**2F**	Ph	**8a**	0	1	**9Fa**	—[a]

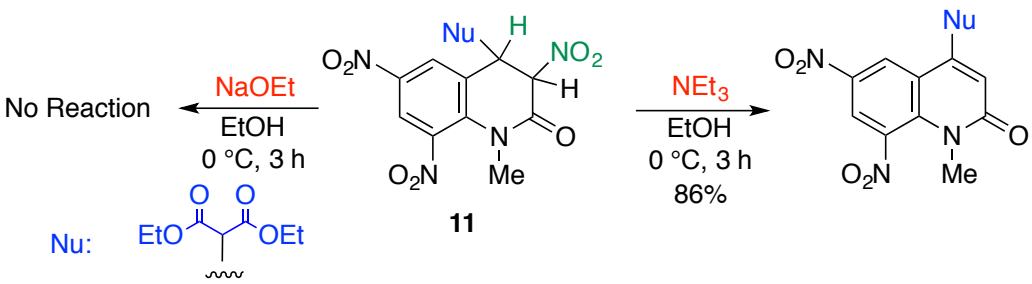
[a] A complex mixture was obtained.

Based on these considerations, the addition of acetylide **8** to cinnamate **2** was studied. When nitrocinnamate **2A** was allowed to react with lithium phenylacetylide **8a** in THF at 0 °C for 3 h, adduct **9Aa** was efficiently obtained (Table 2, Entry 1). Even the acetylide **8b** possessing an electron-withdrawing group underwent the addition reaction to afford **9Ab** although the yield became lower, which was presumably due to low nucleophilicity of **8b** and instability of **9Ab** (Entry 2). Aliphatic acetylides **8c** and **8d** revealed similar reactivity leading to **9Ac** and **9Ad** in high yields, respectively (Entries 3 and 4, respectively). Functionalized acetylide **8d** also underwent this reaction furnishing **9Ae** (Entry 5). This reaction was considerably influenced by the electronic properties of the aryl group of cinnamate **2** (Entries 1 and 6–8),

while electron-rich cinnamates **2A** and **2B** underwent the addition reaction at 0 °C, the reaction mixture was complex in the cases of more reactive electron-poor cinnamates **2C** and **2D** under the same conditions. In such cases, conducting the reaction at -40 °C was effective in obtaining **9Ca** and **9Da** in high yield. Furthermore, nitroalkene **2E** was also successfully transformed into furan-substituted adduct **9Ea** (Entry 9). In contrast, a complex mixture was obtained when using alkyl substituted nitroalkene **2F**, presumably because the anionic intermediate was not sufficiently stabilized by the nitro group (Entry 10). When the aryl group of **2A** was displaced to an alkyl group, the subsequent reaction with acetylides **8** could not be conducted because of the instability of the nitroalkene.



Scheme 4. Different behavior of **9Aa** depending on the base.

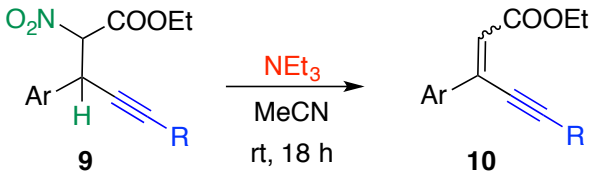


Scheme 5. Different behavior of adduct **11** depending on the base.

Next, elimination of nitrous acid from **9Aa** was studied to obtain enyne **10Aa**. When **9Aa** (a mixture of diasteromers with 1:1 ratio) was treated with equimolar lithium acetylide **8a** at room temperature, no reaction occurred. In contrast, functionalized enyne **10Aa** was efficiently formed with high *Z*:*E* ratio upon treatment of **9Aa** with triethylamine (Scheme 4). Similar reactivity was observed in the reaction of trinitroquinolone **1** with diethyl malonate; while no reaction occured upon treatment of the adduct **11** with sodium ethoxide, elimination of nitrous acid efficiently proceeded upon treatment with triethylamine (Scheme 5).[10] Adduct **9Aa** has two protons, H_α and H_β, of which H_α is more acidic. Thus, nitronate **9Aa'** is exclusively formed upon reaction with a strong base (acetylide) without elimination of nitrous acid. Conversely, when a weak base (triethylamine) is used, **9Aa** exists in equilibrium with **9Aa'** in the reaction mixture, facilitating the elimination of nitrous acid to afford **10Aa**.

To confirm this hypothesis, several other stronger bases were tested, such as sodium hydride, potassium *tert*-butoxide, sodium ethoxide and guanidine. However, only complex reaction mixture was obtained in each case, while excess amounts of lithium acetylide caused no change, which might be due to the stabilization effect of nitronate **9Aa'** by lithium ion. Hence, it has not been clarified why weaker triethylamine was effective for the elimination of nitrous acid. In addition, the influence of the acidity of H_β for this elimination was also studied. When **9Aa** was treated with triethylamine at 0 °C, only 13% of **10Aa** was formed even after 2 d. To the contrary, **9Ab** possessing an electron-withdrawing trifuloromethyl group exhibited higher reactivity to undergo the elimination reaction under the same conditions to furnish **10Ab** in 50% yield, which supported the acidity of H_β was important for the elimination of nitrous acid. Thus, the sp-nucleophile is considered to be advantageous for this reaction from viewpoints of the less bulkiness and the electronegativity compared with sp^2/sp^3-nucleophiles as shown in Figure 1.

Table 3. Synthesis of functionalized enynes **10**.



Entry	Substrate **9**			Product **10**	
	Ar	R		Yield/%	*Z*:*E*
1	*p*-MeC_6H_4	Ph	**Aa**	93	97:3
2	*p*-MeC_6H_4	*p*-$CF_3C_6H_4$	**Ab**	98	99:1
3	*p*-MeC_6H_4	Bu	**Ac**	99	98:2
4	*p*-MeC_6H_4	*tert*-Bu	**Ad**	quant.	98:2
5	*p*-MeC_6H_4	$SiMe_3$	**Ae**	98	97:3
6	*p*-$MeOC_6H_4$	Ph	**Ba**	86	98:2
7	Ph	Ph	**Ca**	98	99:1
8	*p*-ClC_6H_4	Ph	**Da**	97	98:2
9	2-Furyl	Ph	**Ea**	99	92:8

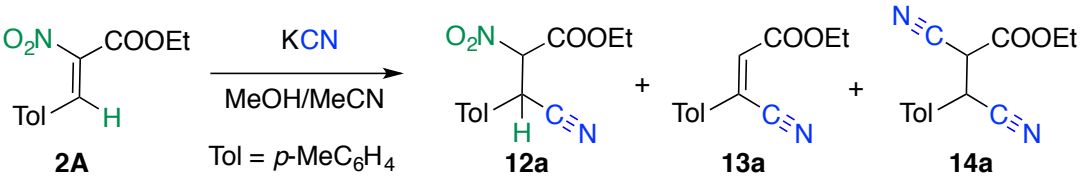
This protocol using triethylamine was applied to other adducts **9** (Table 3). Elimination of nitrous acid efficiently proceeded to afford the corresponding enynes **10** as a mixture of *Z*- and *E*-isomers in almost quantitative yield.

The enyne framework is often found in natural products and biologically active compounds, in addition to being present in useful precursors for functional materials.[11] Although numerous enynes have been synthesized,[12] a practical battery of preparative methods for functionalized enynes is not available. Coupling reactions are the most common approach to desired enynes; however, it is necessary to use expensive noble transition metals.[13] Functionalized enynes can also be synthesized by sequential reaction of propargylic dithioacetal with butyl lithium and α–bromo esters, followed by treatment with alumina.[14]

The [2+2] cycloaddition of an alkynyl ketone with a ynolate and subsequent electro-cyclic reaction leads to enyne compounds bearing a carbonyl group.[15] In addition, functionalized enynes are also formed by oxidation of β-functionalized semicarbazones with selenium dioxide.[16] Although these methods are useful approaches to functionalized enynes, they present several limitations, such as low availability of starting materials, low reaction efficiency, and narrow substrate scope. In contrast, the reaction described have represented a supplementary preparative method for functionalized enynes that does not require a transition metal and/or special reagent.

The abovementioned successful results prompted us to investigate the synthesis of functionalized acrylonitriles by Michael addition of cyanide to cinnamate **1** and subsequent elimination of nitrous acid. A similar synthetic method for the preparation of dicyanoalkanes *via* double conjugate addition of cyanide to nitroalkenes has been demonstrated, in which a small amount of an acrylonitrile derivative was also obtained, however, this method has not been applied to the synthesis of functionalized acrylonitriles.[17]

Table 4. Synthesis of functionalized nitriles.



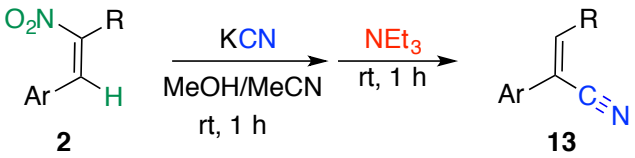
Entry	KCN/ equiv.	Temp. /°C	Time /h	Additive (equiv.)	Yield/%[a]		
					12a	**13a**	**14a**
1	1	60	4	—	0	11	56
2	1	rt	1	—	60	21	12
3	2	rt	1	—	55	11	44
4	1	rt	24	—	0	75	22
5	1	rt	2	NEt_3 (2)	0	90	8

[a] Based on KCN

When cinnamate **1a** was treated with potassium cyanide at 60 °C, the desired acrylonitrile **13a** was obtained albeit in low yield (Table 4, Entry 1). In this reaction, α,β-dicyano-β-tolylpropionate **14a** was the main product, which was resulted from the excess addition of cyanide to **13a**. The same reaction at lower temperature suppressed the double addition, and adduct **12a** was predominantly formed (Entry 2). When two equivalents of cyanide were employed, the yield of double adduct **14a** increased, indicating that the cyanide serves only as a nucleophile and not as a base (Entry 3). Although the yield of **13a** could be increased by extending the reaction period to 24 h, the addition of triethylamine was more effective providing a yield of 90% of product in 2 h (Entries 4 and 5).

This protocol can also be conducted in one pot. After a solution of nitroalkene **2A** was stirred with potassium cyanide at room temperature for 1 h, triethylamine was added to the reaction mixture and stirred for further 1 h, which afforded acrylonitrile **13a** in similar yield but with simpler experimental operation (Table 4, Entry 5 and Table 5, Entry 1).

Table 5. One-pot synthesis of functionalized acrylonitriles **13**.

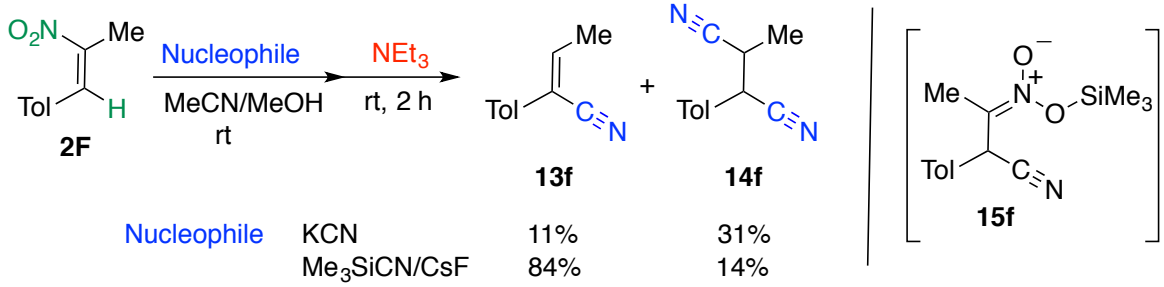


Entry	Substrate			Product	
	Ar	R			Yield/%
1	*p*-MeC_6H_4	COOEt	**2A**	**13a**	86
2	*p*-$MeOC_6H_4$	COOEt	**2B**	**13b**	90
3	Ph	COOEt	**2C**	**13c**	92
4	*p*-ClC_6H_4	COOEt	**2D**	**13d**	85
5[a]	2-Furyl	COOEt	**2E**	**13e**	66
6	*p*-MeC_6H_4	COPh	**2G**	**13g**	80

[a] The reaction was conducted at -30 °C for 3 h.

Cinnamates **2B–D** exhibited similar reactivity to afford the corresponding acrylonitriles **13b–d** in high yield (Table 5, Entries 2-4). It was possible to replace the phenyl group by a furyl group leading to **13e**, although a lower reaction temperature was needed (Entry 5). Furthermore, nitroalkene **2G** bearing a benzoyl group could be used as the substrate to afford benzoylacrylonitrile **13g** in 80% yield (Entry 6).

Next, a cyanation procedure was applied to nitroalkene **2F**, which is not activated by an electron-withdrawing group. In the reaction of **2F** under the same conditions, only a small amount of acrylonitrile **13f**[18] was detected, and the main product was double adduct **14f**,[17] which was formed by Michael addition of cyanide to **13f** (Scheme 5). This problem was overcome using a combination of trimethylsilyl cyanide and cesium fluoride instead of potassium cyanide, successfully affording **13f** in 84% yield. In this case, the silyl nitronate intermediate **15f** is believed to prevent any side reactions.



Scheme 6. Reaction of nitroalkene **2F** with two kinds of cyanides.

Conclusion

β-Nitrostyrenes **2** bearing an ethoxycarbonyl group at the α-position have been demonstrated to serve as excellent precursors for α,β-difunctionalized alkenes. Nitrocinnamate **2** easily reacts with versatile sp^3- and sp^2-nucleophiles such as alcohols, Grignard reagents,

alkylcopper, and dialkylzinc to afford Michael adducts. Although this reaction is useful for alkoxylation, alkylation, and arylation transformations, the subsequent elimination of nitrous acid does not proceed due to the favored elimination of an alcohol, steric repulsion, and lower electronegativity of the newly introduced carbon nucleophile. This problem was addressed using smaller sp-carbon nucleophiles such as lithium acetylide, potassium cyanide, and trimethylsilyl cyanide. Treatment of the adducts with triethylamine efficiently afforded functionalized enynes **10** and acrylonitriles **13** in high yields. This protocol can be carried out by a simple procedure under mild conditions and is transition-metal free. These features are advantageous in practical synthesis methods; the present protocol is thus a useful tool for researchers working on the synthesis of functional materials.

Experimental Section

One-pot synthesis of isoxazoledicarboxylate 4

A solution of α-nitrocinnamate **2A** (76 mg, 0.32 mmol) in methanol (2 mL) was heated at 65 °C for 2 d. Concentration of the reaction mixture afforded a mixture of **3a** and unreacted **2A**, which is difficult to separate, thus the yield and diastereomeric ratio of **3a** was determined by ^{1}H NMR by comparing the integral values with that of the internal standard, 1,1,2,2-tetrachloroethane. When ethanol was used as a solvent, similar result was obtained. Further reaction was conducted using the mixture without separation. To a solution of the mixture in acetonitrile (3.5 mL), triethylamine (97 μL, 0.7 mmol) was added, and the resultant mixture was stirred at room temperature for 3 h. After removal of the solvent, 1 M hydrochloric acid (0.7 mL, 0.7 mmol) was added, and the mixture was extracted with dichloromethane (30 mL × 3). The combined organic layer was dried over magnesium sulfate, concentrated, and chromatographed on silica gel to afford isoxazole **4** (eluted with hexane/ethyl acetate = 90/10, 85 mg, 0.28 mmol, quant.) as a colorless oil.

Ethyl 3-methoxy-3-(4-methyphenyl)-2-nitropropanoate (3a) (dr = 1 : 2.7)

Pale yellow oil (NMR yield 87%, 23 mg (0.086 mmol, 27%) was isolated in a pure form). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.36 (s, 3H), 3.22 (s, 3H), 3.95–4.04 (m, 2H), 4.97 (d, *J* = 9.6 Hz, 1H), 5.28 (d, *J* = 9.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 21.2 (CH_3), 56.9 (CH_3), 62.8 (CH_2), 81.3 (CH), 92.2 (CH), 127.9 (CH), 129.5 (CH), 131.2 (C), 139.5 (C), 161.8 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.2, 7.2 Hz, 3H), 2.44 (s, 3H), 3.25 (s, 3H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.94 (d, *J* = 8.0 Hz, 1H), 5.23 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.24-7.27 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 21.2 (CH_3), 57.2 (CH_3), 63.1 (CH_2), 81.0 (CH), 91.3 (CH), 127.7 (CH), 129.5 (CH), 132.0 (C), 136.9 (C), 163.2 (C). IR (NaCl) 1320, 1515, 1740 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{13}H_{17}NO_5Na$ 290.0999; Found 290.0993.

Ethyl 3-ethoxy-3-(4-methyphenyl)-2-nitropropanoate (3b) (dr = 1 : 3)

Pale yellow oil (NMR yield 79%, 18 mg (0.064 mmol, 20%) was isolated in a pure form). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (dd, *J* = 7.2, 7.2 Hz, 3H),1.11 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.36 (s, 3H), 3.35–3.44 (m, 2H), 3.94–4.03 (m, 2H), 5.08 (d, *J* = 9.6 Hz, 1H), 5.28 (d, *J* = 9.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 14.8 (CH_3), 21.2 (CH_3), 62.8 (CH_2), 64.8 (CH_2), 79.5 (CH) 92.3 (CH), 127.8 (CH), 129.4 (CH), 132.0 (C), 139.3 (C), 161.9 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (t, *J* = 7.2, Hz, 3H), 1.36 (dd, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 3.35–3.44 (m, 2H), 4.33 (q, *J* =7.2 Hz, 2H), 5.06 (d, *J* = 8.4 Hz, 1H), 5.22 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 14.9 (CH_3), 21.6 (CH_3), 63.0 (CH_2), 65.1 (CH_2), 79.2 (CH), 91.5 (CH), 127.6 (CH), 129.5 (CH), 132.8 (C), 139.3 (C), 162.7 (C). IR (KBr) 1310, 1565, 1749 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{14}H_{19}NO_5Na$ 304.1155; Found 304.1149.

Ethyl 3-(4-methyphenyl)-2-nitro-3-(prop-2-yn-1-yloxy)propanoate (3c) (dr = 1 : 2.4)

Colorless oil (85 mg, 0.29 mmol, 92%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.36 (s, 3H), 2.44 (dd, *J* = 2.4, 2.4 Hz, 1H), 3.89 (dd, *J* = 2.4, 15.6 Hz, 1H), 3.93–4.06 (m, 2H), 4.12 (dd, *J* = 2.4, 15.6 Hz, 1H), 5.35 (d, *J* = 9.8 Hz, 1H), 5.38 (d, *J* = 9.8 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 21.1 (CH_3), 55.8 (CH_2), 62.9 (CH_2), 75.5 (CH), 78.2 (C), 78.2 (CH), 91.8 (CH), 128.3 (CH), 129.6 (CH), 130.2 (C), 139.8 (C), 161.6 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 2.45 (dd, *J* = 2.4, 2.4 Hz, 1H), 3.91 (dd, *J* = 2.4, 15.6 Hz, 1H), 4.13 (dd, *J* = 2.4, 15.6 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H),5.30 (d, *J* = 9.1 Hz, 1H), 5.35 (d, *J* = 9.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 21.1 (CH_3), 56.0 (CH_2), 63.2 (CH_2), 75.5 (CH), 77.7(CH), 78.0 (C), 91.1 (CH), 128.0 (CH), 129.6 (CH), 131.1 (C), 139.8 (C), 162.3 (C). IR (NaCl) 1310, 1567, 1749, 2120 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{15}H_{17}NO_5Na$ 314.0999; Found 314.1007.

Reaction of organometallic reagent with cinnamate 2A

To a solution of α-nitrocinnamate **2A** (50 mg, 0.21 mmol) in THF (2.5 mL), 0.97 M THF solution of ethylmagnesium bromide (330 μL, 0.31 mmol) was added at 0 °C for over 10 minutes, and the resultant mixture was stirred for 1 day. After quenching the reaction with 1 M hydrochloric acid (0.5 mL, 0.5 mmol), the mixture was extracted with diethyl ether (20 m L × 3). The organic layer was dried over magnesium sulfate and concentrated. The diastereomeric ratio was determined by ^{1}H NMR of the residue. The reaction mixture was treated with column chromatography on silica gel to afford adduct **6a** (eluted with hexane/diethyl ether = 9/1, 27.1 mg, 0.1 mmol, 49%) as a colorless oil. When other organometallic reagents were used, the experiments were conducted in a similar way.

Ethyl 3-(4-methyphenyl)-2-nitropentanoate (6a) (dr = 1 : 1.1)

Colorless oil (50 mg, 0.19 mmol, 89%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (t, *J* = 7.2, 7.2 Hz, 3H), 0.99 (dd, *J* = 7.2 Hz, 3H), 1.58–1.80 (m, 2H), 2.31 (s, 3H), 3.47–3.54 (m, 1H), 3.92–4.03 (m, 2H), 5.25 (d, *J* = 10.8 Hz, 1H), 7.07 (d, *J* = 9.2 Hz, 2H), 7.12 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4 (CH_3), 13.5 (CH_3), 21.1 (CH_3), 25.3 (CH_2), 48.2 (CH), 62.6 (CH_2), 93.0 (CH), 128.5 (CH), 129.5 (CH), 113.6 (C), 137.6 (C), 163.3 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.58–1.80 (m, 2H), 2.32 (s, 3H), 3.47 (td, *J* = 10.8, 3.6 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 5.29 (d, *J* = 10.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.5 (CH_3), 13.9 (CH_3), 21.1 (CH_3), 24.9 (CH_2), 48.0 (CH), 63.0 (CH_2), 93.0 (CH), 128.0 (CH), 129.5 (CH), 134.5 (C), 137.5 (C), 163.8 (C). IR (KBr) 1308, 1559, 1749 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{14}H_{19}NO_4Na$ 288.1206; Found 288.1212.

Ethyl 3-(4-methyphenyl)-2-pentenoate (7a)

Colorless oil (1.3 mg, 0.006 mmol, 3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 2.37 (s, 3H), 2.55 (q, *J* = 7.2 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (CH_3), 14.3 (CH_3), 20.8 (CH_2), 21.3 (CH_3), 60.6 (CH_2), 129.2 (CH), 129.3 (CH), 133.0 (C), 134.3 (C), 138.3 (CH), 138.4 (C), 168.5 (C); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{19}O_2$ 219.1380; Found 219.1384.

Ethyl 4-methyl-3-(4-methyphenyl)-2-nitropentanoate (6b) (dr = 1 : 1.7)

Colorless oil (53 mg, 0.19 mmol, 90%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (d, *J* = 7.2 Hz, 6H), 0.98 (dd, *J* = 7.2, 7.2 Hz, 3H), 1.95–2.08 (m, 1H), 2.31 (s, 3H), 3.60 (dd, *J* = 10.8, 10.8 Hz, 1H), 3.90–4.12 (m, 2H), 5.57 (d, *J* = 10.8 Hz, 1H), 7.02 (*J* = 8.0 Hz, 2H), 7.10 (*J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4 (CH_3), 17.7 (CH_3), 21.0 (CH_3), 21.0 (CH_3), 29.2 (CH), 51.9 (CH), 62.6 (CH_2), 90.8 (CH), 128.9 (CH), 129.5 (CH), 131.7 (C),

137.3 (C), 164.1 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (d, *J* = 7.2 Hz, 6H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.95–2.08 (m, 1H), 2.30 (s, 3H), 3.59 (dd, *J* = 10.8, 10.8 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 5.61 (d, *J* = 10.8 Hz, 1H), 7.05 (*J* = 8.0 Hz, 2H), 7.07 (*J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 17.8 (CH_3), 21.0 (CH_3), 21.6 (CH_3), 29.3 (CH), 51.9 (CH), 63.0 (CH_2), 91.1 (CH), 128.9 (CH), 129.1 (CH), 132.0 (C), 137.3 (C), 163.3 (C). IR (NaCl) 1307, 1564, 1748 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{15}H_{21}NO_4Na$ 302.1363; Found 302.1356.

Ethyl 3-(4-methyphenyl)-2-nitro-3-phenylpropanoate (6c) (dr = 1 : 1.2)

Colorless oil (13 mg, 0.04 mmol, 20%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.27 (s, 3H), 3.97–4.10 (m, 2H), 4.98 (d, *J* = 12.0 Hz, 1H), 5.92 (d, *J* = 12.0 Hz, 1H), 7.08–7.32 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 21.0 (CH_3), 52.0 (CH), 62.9 (CH_2), 91.3 (CH), 127.2 (CH), 127.7 (CH), 128.2 (CH), 129.1 (CH), 129.8 (CH), 135.4 (C), 137.5 (C), 137.9 (C), 163.3 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.27 (s, 3H), 3.97–4.10 (m, 2H), 4.98 (d, *J* = 12.0 Hz, 1H), 5.92 (d, *J* = 12.0 Hz, 1H), 7.08–7.32 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 21.0 (CH_3), 52.0 (CH), 63.0 (CH_2), 91.3 (CH), 127.3 (CH), 127.7 (CH), 128.1 (CH), 129.0 (CH), 129.6 (CH), 134.6 (C), 137.6 (C), 138.7 (C), 163.2 (C). IR (NaCl) 1315, 1563, 1749 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{19}NO_4Na$ 336.1206; Found 336.1206.

Ethyl 3-(4-methyphenyl)-2-nitroheptanoate (6d) (dr = 1 : 1)

Colorless oil (62 mg, 0.21 mmol, quant.). Isomer A: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (dd, *J* = 7.2, 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 3.58 (td, *J* = 10.8 Hz, 3.6 Hz, 1H), 3.91–4.03 (m, 2H), 5.23 (d, *J* = 10.8, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 13.7 (CH_3), 21.0 (CH_3), 22.2 (CH_2), 28.8 (CH_2), 31.7 (CH_2), 46.5 (CH), 62.5 (CH_2), 93.1 (CH), 128.0 (CH), 129.4 (CH), 133.9 (C), 137.5 (C), 163.8 (C). Isomer B: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2

Hz, 3H), 2.31 (s, 3H), 3.58 (td, *J* = 10.8, 3.6 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 5.27 (d, *J* = 10.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 13.9 (CH_3), 21.0 (CH_3), 22.2 (CH_2), 28.9 (CH_2), 31.3 (CH_2), 46.3 (CH), 63.0 (CH_2), 93.2 (CH), 128.4 (CH), 129.4 (CH), 134.8 (C), 137.4 (C), 163.3 (C). IR (NaCl) 1372, 1558, 1748 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{16}H_{23}NO_4Na$ 316.1519; Found 316.1507.

Ethynylation of cinnamate 2A

To a solution of ethynylbenzene (76 μL, 0.7 mmol) in THF (1 mL), 2.6 M hexane solution of butyllithium (226 μL, 0.6 mmol) was added at 0 °C with over 5 min. The resultant mixture was added to a solution of α-nitrocinnamate **2A** (115 mg, 0.5 mmol) in THF at 0 °C with over 15 min. period, and the resultant mixture was stirred for further 1 h. After quenching the reaction with 1 M hydrogen chloride (0.6 mL, 0.6 mmol), the mixture was extracted with diethyl ether (30 mL × 3). The organic layer was dried over magnesium sulfate concentrated. The diastereomeric ratio was determined by ^{1}H NMR of the residue. The reaction mixture was treated with column chromatography on silica gel to afford ethynylated product **9Aa** (eluted with hexane/ethyl acetate = 90/10, 144.1 mg, 0.43 mmol, 90%) as a colorless oil. When other acetylides were used, the experiments were conducted in a similar way.

Ethyl 3-(4-methyphenyl)-2-nitro-5-phenyl-4-pentynoate (9Aa) (dr = 1 : 1.1)

Colorless oil (152 mg, 0.45 mmol, 90%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.34 (s, 3H), 4.04–4.16 (m, 2H), 4.87 (d, *J* = 9.6 Hz, 1H), 5.39 (d, *J* = 9.6 Hz, 1H), 7.15–7.42 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.1 (CH_3), 39.7 (CH), 63.3 (CH_2), 84.3 (C), 85.8 (C), 91.9 (CH), 122.3 (C), 128.3 (CH), 128.5 (CH), 128.6 (CH), 130.0 (CH), 131.2 (C), 131.9 (CH), 138.5 (C), 162.3 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.87 (d, *J* = 9.6 Hz, 1H), 5.38 (d, *J* = 9.6 Hz, 1H), 7.15-7.42 (m, 9H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 13.9 (CH_3), 21.1 (CH_3), 39.6 (CH), 63.1 (CH_2), 84.9 (C), 86.4 (C), 92.0 (CH), 122.3 (C), 128.2 (CH), 128.3 (CH), 128.7 (CH), 130.0 (CH), 131.7 (CH), 132.1 (C), 138.5 (C), 162.5 (C) ppm. IR (ATR) 1563, 1749, 2354 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{19}NO_4Na$ 360.1206; Found 360.1199.

Ethyl 3-(4-methyphenyl)-2-nitro-5-(4-trifluoromethyl)phenyl-4-pentynoate (9Ab) (dr = 2 : 1)

Pale yellow oil (57 mg, 0.14 mmol, 31%). Major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, J = 7.2 Hz, 3H), 2.35 (s, 3H), 4.05–4.18 (m, 2H), 4.89 (d, J = 9.6 Hz, 1H), 5.40 (d, J = 9.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.1 (CH_3), 39.7 (CH), 63.3 (CH_2), 84.3 (C), 87.5 (C), 91.7 (CH), 123.8 (q, J_{CF} = 271 Hz, C), 125.2 (q, J_{CF} = 3.6 Hz, CH), 126.1 (C), 128.4 (CH), 129.8 (CH), 130.4 (q, J_{CF} = 33 Hz, C), 130.7 (C), 132.1 (CH), 138.8 (C), 162.1 (C). Minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 4.30–4.38 (m, 2H), 4.89 (d, J = 9.6 Hz, 1H), 5.40 (d, J = 9.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 21.1 (CH_3), 39.5 (CH), 63.4 (CH_2), 84.9 (C), 86.9 (C), 91.5 (CH), 125.3 (q, J_{CF} = 3.6 Hz, CH), 126.2 (C), 128.1 (CH), 129.9 (CH), 130.4 (q, J_{CF} = 39 Hz, C), 131.5 (C), 132.0 (CH), 138.8 (C), 162.3 (C). one peak derived from CF_3 was not identified. IR (ATR) 1323, 1566, 1751, 2206 cm^{-1}; HRMS (EI, $[M]^+$) Calcd. for $C_{21}H_{18}F_3NO_4$ 405.1188; Found 405.1190.

Ethyl 3-(4-methylphenyl)-2-nitro-4-nonynoate (9Ac) (dr = 1 : 1)

Colorless oil (146 mg, 0.46 mmol, 92%). Isomer A: ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (dd, J = 7.2, 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H), 1.34–1.50 (m, 4H), 2.18 (td, J = 7.2, 2.0 Hz, 2H), 2.31 (s, 3H), 4.00–4.11 (m, 2H), 4.61 (dt, J = 10.0 Hz, 2.0 Hz, 1H), 5.27 (d, J = 10.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5

(CH_3), 13.6 (CH_3), 18.3 (CH_2), 21.0 (CH_3), 21.8 (CH_2), 30.1 (CH_2), 39.4 (CH), 62.9 (CH_2), 75.7 (C), 86.4 (C), 92.2 (CH), 128.4 (CH), 130.1 (CH), 131.8 (C), 138.2 (C), 162.4 (C). Isomer B: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 1.34–1.50 (m, 4H), 2.18 (td, *J* = 7.2, 2.0 Hz, 2H), 2.32 (s, 3H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.61 (dt, *J* = 10.0 Hz, 2.0 Hz, 1H), 5.26 (d, *J* = 10.0 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 13.9 (CH_3), 18.4 (CH_2), 21.0 (CH_3), 21.8 (CH_2), 30.1 (CH_2), 39.1 (CH), 63.1 (CH_2), 75.1 (C), 87.1 (C), 92.4 (CH), 128.0 (CH), 130.0 (CH), 132.7 (C), 138.2 (C), 162.6 (C). IR (ATR) 1307, 1559, 1749, 2337 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{23}NO_4Na$ 340.1519; Found 340.1506.

Ethyl 6,6-dimethyl-3-(4-methylphenyl)-2-nitro-4-heptynoate (9Ad) (dr = 1 : 1.1)

Colorless oil (146 mg, 0.46 mmol, 92%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (dd, *J* = 7.2, 7.2 Hz, 3H), 1.19 (s, 9H), 2.32 (s, 3H), 4.02–4.11 (m, 2H), 4.60 (d, *J* = 9.6 Hz, 1H), 5.24 (d, *J* = 9.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.1 (CH_3), 27.5 (C), 30.8 (CH_3), 39.2 (CH), 62.9 (CH_2), 74.3 (C), 92.6 (CH), 94.9 (C), 128.4 (CH), 129.5 (CH), 132.8 (C), 138.2 (C), 162.4 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.34 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.31 (s, 3H), 4.27–4.36 (m, 2H), 4.60 (d, *J* = 9.6 Hz, 1H), 5.22 (d, *J* = 9.6 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 21.1 (CH_3), 27.5 (C), 30.8 (CH_3), 39.0 (CH), 63.1 (CH_2), 73.6 (C), 92.5 (CH), 95.4 (C), 128.0 (CH), 129.5 (CH), 131.8 (C), 138.2 (C), 162.6 (C). IR (NaCl) 1307, 1361, 1566, 1752, 2245 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{23}NO_4Na$ 340.1519; Found 340.1507.

Ethyl 3-(4-methylphenyl)-5-trimethylsilyl-2-nitro-4-pentynoate (9Ae) (dr = 1 : 1.1)

Colorless oil (132 mg, 0.40 mmol, 79%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H), 1.08 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.33 (s, 3H), 3.91–4.13 (m, 2H), 4.65 (d, *J* = 10.0 Hz, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ -0.2 (CH_3), 13.7 (CH_3), 21.2 (CH_3), 40.1 (CH), 63.1 (CH_2), 91.1 (C), 92.1 (CH), 101.3 (C), 128.6 (CH), 129.7 (CH), 131.0 (C), 138.5 (C), 162.3 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H), 1.35 (dd, *J* = 7.2, 7.2 Hz, 3H), 2.32 (s, 3H), 4.27–4.39 (m, 2H), 4.66 (d, *J* = 10.0 Hz, 1H), 5.27 (d, *J* = 10.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2 (CH_3), 14.0 (CH_3), 21.2 (CH_3), 39.9 (CH), 63.3 (CH_2), 91.7 (C), 92.1 (CH), 100.5 (C), 128.2 (CH), 129.8 (CH), 132.0 (C), 138.5 (C), 162.5 (C). IR (ATR) 1564, 1751, 2180 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd. for $C_{17}H_{23}NO_4SiNa$ 356.1289; Found 356.1290.

Ethyl 3-(4-methoxyphenyl)-2-nitro-5-phenyl-4-pentynoate (9Ba) (dr = 1 : 1.1)

Colorless oil (147 mg, 0.42 mmol, 83%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (dd, *J* = 7.2, 7.2 Hz, 3H), 3.80 (s, 3H), 4.05–4.17 (m, 2H), 4.86 (d, *J* = 9.6 Hz, 1H), 5.37 (d, *J* = 9.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 7.32-7.45 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 39.4 (CH), 55.3 (CH_3), 63.1 (CH_2), 84.9 (C), 85.7 (C), 92.0 (CH), 114.4 (CH), 122.3 (C), 126.0 (C), 128.3 (CH), 128.6 (CH), 129.8 (CH), 131.8 (CH), 159.8 (C), 162.3 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 3.78 (s, 3H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.86 (d, *J* = 9.6 Hz, 1H), 5.36 (d, *J* = 9.6 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 7.32–7.45 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 39.2 (CH), 55.3 (CH_3) 63.3 (CH_2), 84.3 (C), 86.4 (C), 91.9 (CH), 114.5 (CH), 126.9 (C), 128.3 (CH), 128.7 (CH), 129.5 (CH), 131.7 (CH), 131.8 (C), 159.8 (C), 162.3 (C). IR (ATR) 1560, 1749, 2355 cm^{-1}; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd. for $C_{20}H_{19}NO_5Na$ 376.1155; Found 376.1141.

Ethyl -2-nitro-3,5-diphenyl-4-pentynoate (9Ca) (dr = 1 : 1.1)

Colorless oil (152 mg, 0.47 mmol, 94%). Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (dd, *J* = 7.2, 7.2 Hz, 3H), 4.02–4.14 (m, 2H), 4.91 (d, *J* = 9.6 Hz, 1H), 5.42 (d, *J* = 9.6 Hz, 1H), 7.27–7.48 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 40.1 (CH), 63.2 (CH_2), 84.7 (C), 85.9 (C), 91.9 (CH), 122.2 (C), 134.2 (C), 162.3 (C). Minor isomer: ^{1}H NMR (400

MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 4.34 (d, *J* = 9.6 Hz, 1H), 4.91 (d, *J* = 9.6 Hz, 1H), 5.41 (d, *J* = 9.6 Hz, 1H), 7.27–7.48 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 39.9 (CH), 63.4 (CH_2), 84.0 (C), 86.6 (C), 91.7 (CH), 122.2 (C), 135.1 (C), 162.5 (C). In addition, other signals were observed as follows, however, they could not be assigned to which isomers although 30 signals were totally observed. 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 128.7 (CH), 128.7 (CH), 129.0 (CH), 129.0 (CH), 129.1 (CH), 131.7 (CH), 131.9 (CH), 131.9 (CH). IR (NaCl) 1562, 1749, 2357 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{17}NO_4Na$ 346.1050; Found 346.1044.

Ethyl 3-(4-chlorophenyl)-2-nitro-5-phenyl-4-pentynoate (9Da) (dr = 1 : 1.1)

Colorless oil (164 mg, 0.46 mmol, 92%). Major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (dd, *J* = 7.2, 7.2 Hz, 3H), 4.06–4.19 (m, 2H), 4.89 (d, *J* = 9.6 Hz, 1H), 5.39 (d, *J* = 9.6 Hz, 1H), 7.27–7.43 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 39.4 (CH), 63.4 (CH_2), 84.1 (C), 86.3 (C), 91.6 (CH), 122.0 (C), 128.3 (CH), 128.8 (CH), 129.2 (CH), 130.1 (CH), 131.8 (CH), 132.8 (C), 134.7 (C), 162.1 (C). Minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.89 (d, *J* = 9.6 Hz, 1H), 5.38 (d, *J* = 9.6 Hz, 1H), 7.30–7.41 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 39.2 (CH), 63.5 (CH_2), 83.5 (C), 86.9 (C), 91.5 (CH), 122.0 (C), 128.4 (CH), 128.9 (CH), 129.2 (C), 129.3 (CH), 129.8 (CH), 131.7 (CH), 133.6 (C), 162.2 (C). IR (NaCl) 1562, 1751, 2364 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{16}NO_4ClNa$ 380.0660; Found 380.0641.

Ethyl 3-(2-furyl)-2-nitro-5-phenyl-4-pentynoate (9Ea) (dr = 1 : 1.1)

Pale yellow oil (28 mg, 0.09 mmol, 18%). Major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (dd, *J* = 7.2, 7.2 Hz, 3H), 4.19–4.30 (m, 2H), 5.05 (d, *J* = 8.8 Hz, 1H), 5.58 (d, *J* = 8.8 Hz, 1H), 6.35–6.39 (m, 1H), 6.44 (d, *J* = 3.2 Hz, 1H), 7.28–7.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (CH_3), 34.1 (CH), 63.4 (CH_2), 81.7 (C), 85.5 (C), 89.2 (CH), 109.5 (CH), 110.8 (CH), 122.0 (C), 128.3 (CH), 128.8 (CH), 131.9 (CH), 143.2 (CH), 146.9 (C), 162.1

(C). Minor isomer: 1.30 (t, J = 7.2 Hz, 3H), 4.33 (q, J = 7.2 Hz, 2H), 5.08 (d, J = 8.8 Hz, 1H), 5.55 (d, J = 8.8 Hz, 1H), 6.35–6.39 (m, 1H), 6.42 (d, J = 3.2 Hz, 1H), 7.28–7.44 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 33.9 (CH), 63.4 (CH_2), 81.1 (C), 86.1 (C), 88.7 (CH), 109.3 (CH), 110.8 (CH), 121.9 (C), 128.3 (CH), 128.9 (CH), 131.8 (CH), 143.2 (CH), 147.4 (C), 162.1 (C). IR (KBr) 1567, 1753, 2354 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{17}H_{15}NO_5Na$ 336.0842; Found 336.0859.

Conversion of ethynylated product 9 to enynes 10

To a solution of adduct **9Aa** (144 mg, 0.43 mmol) in acetonitrile (0.5 mL), triethylamine (126 μL, 0.9 mmol) was added, and the resultant mixture was stirred at room temperature for 18 h. After removal of the solvent under reduced pressure, 1 M hydrochloric acid (1 mL, 1 mmol) was added, and the mixture was extracted with dichloromethane (50 mL × 3). The organic layer was dried over magnesium sulfate, and concentrated. The residue was subjected to the column chromatography on silica gel to afford enyne **10Aa** (eluted with hexane/ethyl acetate = 9/1, 116 mg, 0.40 mmol, 93%) as a colorless solid. When other adducts were used, the experiments were conducted in a similar way.

Ethyl (*Z*)-3-(4-methyphenyl)-5-phenyl-2-penten-4-ynoate (10Aa)

Colorless oil (116 mg, 0.40 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, J = 7.2 Hz, 3H), 2.39 (s, 3H), 4.30 (q, J = 7.2 Hz, 2H), 6.57 (s, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.36-7.38 (m, 3H), 7.63 (dd, J = 2.4 Hz, 6.0 Hz, 2H), 7.69 d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 21.3 (CH_3), 60.3 (CH_2), 87.0 (C), 101.9 (C), 121.9 (CH), 122.9 (C), 127.2 (CH), 128.4 (CH), 129.2 (CH), 129.4 (CH), 132.1 (CH), 134.4 (C), 136.2 (C), 140.2 (C), 165.5 (C); IR (ATR) 1587, 1715, 2203 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{19}O_2$ 291.1380; Found 291.1369.

Ethyl (*Z*)-3-(4-methyphenyl)-5-(4-trifluoromethyl)phenyl-2-penten-4-ynoate (10Ab)

Pale yellow oil (150 mg, 0.42 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, J = 7.2 Hz, 3H), 2.40 (s, 3H), 4.30 (q, J = 7.2 Hz, 2H), 6.61 (s, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.67 (dd, J = 2.4 Hz, 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 21.3 (CH_3), 60.4 (CH_2), 88.9 (C), 99.7 (C), 122.9 (CH), 123.9 (q, J_{CF} = 271 Hz, CH), 125.3 (q, J_{CF} = 3.6 Hz, CH), 125.4 (C), 127.1 (CH), 129.5 (CH), 130.7 (q, J_{CF} = 32 Hz, C), 132.2 (CH), 133.9 (C), 135.6 (C), 140.5 (C), 165.3 (C); IR (ATR) 1323, 1593, 1716, 2206 cm^{-1}; HRMS (EI, $[M]^+$) Calcd. for $C_{21}H_{17}F_3O_2$ 358.1181; Found 358.1181.

Ethyl (*Z*)-3-(4-methylphenyl)-2-nonen-4-ynoate (10Ac)

Colorless oil (131 mg, 0.43 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H),1.50 (tq, J = 7.2 Hz, 7.6 Hz, 2H),1.66 (tt, J = 7.2 Hz, 7.6 Hz, 2H), 2.36 (s, 3H) 2.56 (t, J = 7.2 Hz, 2H), 4.25 (q, J = 7.2 Hz, 2H), 6.47 (s, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 14.3 (CH_3), 19.8 (CH_2), 21.2 (CH_3), 22.1 (CH_2), 30.6 (CH_2), 60.1 (CH_2), 78.2 (C), 104.7 (C), 121.1 (CH), 127.1 (CH), 129.2 (CH), 135.0 (C), 137.1 (C), 139.9 (C), 165.7 (C); IR (NaCl) 1595, 1720, 2207 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{18}H_{23}O_2$ 271.1698; found 271.1682.

Ethyl (*Z*)-6,6-dimethyl-3-(4-methylphenyl)-2-hepten-4-ynoate (10Ad)

Colorless oil (117 mg, 0.43 mmol, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, J = 7.2 Hz, 3H), 1.37 (s, 9H), 2.37 (s, 3H), 4.26 (q, J = 7.2 Hz, 2H), 6.45 (s, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 21.2 (CH_3), 28.7 (C), 30.7 (CH_3), 60.9 (CH_2), 112.2 (C), 121.1 (CH), 121.1(C), 127.1 (CH), 129.2 (CH), 135.1 (C), 136.7 (C), 139.9 (C), 165.7 (C); IR (NaCl) 1595, 1721, 2215 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{23}O_2$ 271.1693; Found 271.1687.

Ethyl (*Z*)-3-(4-methylphenyl)-5-trimethylsilyl-2-penten-4-ynoate (10Ae)

Colorless oil (121 mg, 0.42 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 9H), 1.14 (t, J = 7.2 Hz, 3H), 2.17 (s, 3H), 4.07 (q, J = 7.2 Hz, 2H), 6.30 (s, 1H), 6.99 (d, J = 8.4 Hz, 2H),

7.40 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.00 (CH_3), 14.6 (CH_3), 21.5 (CH_3), 60.6 (CH_2), 101.7 (C), 108.9 (C), 123.2 (CH), 127.4 (CH), 129.5 (CH), 134.5 (C), 135.9 (C), 140.4 (C), 165.6 (C); IR (NaCl) 1698, 1724, 2149 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{23}O_2Si$ 287.1462; Found 287.1467.

Ethyl (*Z*)-3-(4-metoxhyphenyl)-5-phenyl-2-penten-4-ynoate (10Ba)

Colorless oil (114 mg, 0.37 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, J = 7.2 Hz, 3H), 4.29 (q, J = 7.2 Hz, 2H), 6.52 (s, 1H), 6.93 (d, J = 8.8 Hz, 2H), 7.36–7.38 (m, 3H), 7.63 (dd, J = 2.4 Hz, 8.8 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 55.4 (CH_3), 60.3 (CH_2), 87.0 (C), 101.8 (C), 114.0 (CH), 120.6 (CH), 122.8 (C), 128.4 (CH), 128.7 (CH), 129.2 (CH), 129.5 (C), 132.1 (CH), 135.8 (C), 161.2 (C), 165.6 (C); IR (KBr) 1601, 1731, 2201 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{19}O_3$ 307.1329; Found 307.1318.

Ethyl (*Z*)-3,5-diphenyl-2-penten-4-ynoate (10Ca)

Pale yellow oil (117 mg, 0.42 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.35 (t, J = 7.2 Hz, 3H), 4.31 (q, J = 7.2 Hz, 2H), 6.59 (s, 1H), 7.3–7.4 (m, 3H), 7.4–7.5 (m, 3H), 7.6–7.7 (m, 2H), 7.75–7.85 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.4 (CH_3), 60.4 (CH_3), 86.9 (C), 102.1 (C), 122.7 (C), 122.8 (CH), 127.2 (CH), 128.4 (CH), 128.7 (CH), 129.2 (CH), 129.9 (CH), 132.1 (CH), 136.3 (C), 137.2 (C), 165.4 (C); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{17}O_2$ 277.1223, Found 277.1215.

Ethyl (*Z*)-3-(4-chlorophenyl)-5-phenyl-2-penten-4-ynoate (10Da)

Colorless oil (130 mg, 0.42 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, J = 7.2 Hz, 3H), 4.30 (q, J = 7.2 Hz, 2H), 6.56 (s, 1H), 7.36–7.41 (m, 5H), 7.61–7.63 (m, 3H), 7.72 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 60.5 (CH_2), 86.5 (C), 102.4 (C), 122.5 (CH), 130.0 (CH), 128.5 (CH), 128.9 (CH), 128.9 (C), 129.4 (CH), 132.1 (CH), 135.0

(C), 135.6 (C), 136.0 (C), 165.2 (C); IR (NaCl) 1588, 1717, 2203 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{16}O_2Cl$ 311.0833; Found 311.0821.

Ethyl (*Z*)-3-(2-furyl)-5-phenyl-2-penten-4-ynoate (10Ea)

Pale yellow oil (113 mg, 0.43 mmol, 99%). ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.2 Hz, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 6.56 (s, 1H), 6.50 (dd, *J* = 1.6 Hz, 3.2 Hz, 1H), 6.63 (s, 1H), 6.92 (d, *J* = 3.2 Hz, 1H), 7.37–7.38 (m, 3H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.60–7.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 60.3 (CH_2), 84.4 (C), 99.0 (C), 112.3 (CH), 113.7 (CH), 118.2 (CH), 122.5 (C), 124.8 (C), 128.4 (CH), 129.3 (CH), 132.1 (CH), 144.4 (CH), 151.8 (C), 165.5 (C); IR (KBr) 1732, 2205 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{15}O_3$ 266.0943; Found 266.0946.

Cyanation of cinnamate 2A using potassium cyanide

Grinded potassium cyanide (7.1 mg, 0.1 mmol) was dissolved into a methanol (50 μL), and then diluted with acetonitrile (1 mL). The solution was added to a solution of nitrocinnamate **2A** (24 mg, 0.1 mmol) in acetonitrile (2.4 mL) at room temperature for over 3 min., and the resultant mixture was stirred for further 1 hour. Triethylamine (28 μL, 0.2 mmol) was added, and the mixture was stirred at room temperature for further 1 h. After removal of the solvent, 1 M hydrochloric acid (2 mL, 2 mmol) was added, and the mixture was extracted with dichloromethane (20 mL × 3). The organic layer was dried over magnesium sulfate, and concentrated. The residue was treated with silica gel column chromatography to afford cyanoalkene **13a** (18.5 mg, 0.09 mmol, 86%) as a pale yellow solid. When other nitroalkenes **2** were used, the experiments were conducted in a similar way.

Ethyl 3-cyano-3-(4-methylphenyl)-2-propenoate (13a)

Pale yellow solid (18.5 mg, 0.09 mmol, 86%), 56.6–57.5 ℃. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.38 (t, *J* = 7.2 Hz, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 6.83 (s, 1H), 7.27 (d, *J* = 6.8 Hz,

2H), 7.61 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 21.4 (CH_3), 61.2 (CH_2), 115.1 (C), 126.0 (C), 127.0 (CH), 128.2 (CH), 129.2 (C), 130.0 (CH), 142.3 (C), 163.4 (C); IR (ATR, cm^{-1}) 2363, 1717, 1566; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd.for $C_{13}H_{14}NO_2$ 216.1019, Found 216.1015.

Ethyl 3-cyano-3-(4-methoxyphenyl)-2-propenoate (13b)

Pale yellow solid (21 mg, 0.09 mmol, 90%), 105.8–106.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, J = 7.2 Hz, 3H), 3.87 (s, 3H), 4.45 (q, J = 7.2 Hz, 2H), 6.76 (s, 1H), 6.96 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 55.6 (CH_3), 61.6 (CH_2), 114.7 (CH), 115.2 (C), 124.3 (C), 125.6 (C), 126.5 (CH), 128.7 (CH), 162.4 (C), 163.6 (C); IR (ATR) 1593, 1707, 2357 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{13}H_{14}NO_3$ 232.0968; Found 232.0959.

Ethyl 3-cyano-3-phenyl-2-propenoate (13c)

Pale yellow oil (19 mg, 0.09 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.38 (t, J = 7.2 Hz, 3H), 4.36 (q, J = 7.2 Hz, 2H), 6.88 (s, 1H), 7.4–7.6 (m, 3H), 7.7–7.8 (dd, J = 7.0, 2.0 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.1 (CH_3), 61.8 (CH_2), 115.1 (C), 126.1 (C), 127.0 (CH), 129.3 (CH), 129.5 (CH), 131.5 (CH), 131.9 (CH), 163.2 (C); HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd. for $C_{12}H_{11}NO_2$ 202.0863, Found 202.0859.

Ethyl 3-(4-chlorophenyl)-3-cyano-2-propenoate (13d)

Pale yellow oil (20 mg, 0.085mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.38 (t, J = 7.2 Hz, 3H), 4.36 (q, J = 7.2 Hz, 2H), 6.85 (s, 1H), 7.44 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.1 (CH_3), 61.9 (CH_2), 114.7 (C), 124.9 (C), 128.3 (CH), 129.6 (CH), 129.8 (CH), 130.4 (C), 138.0 (C), 163.0 (C); HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd. for $C_{12}H_{11}ClNO_2$: 236.0473, Found: 236.0470.

Ethyl 3-cyano-3-(2-furyl)-2-propenoate (13e)

Brown oil (13 mg, 0.07 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, *J* = 7.2 Hz, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 6.57 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.79 (s, 1H), 6.98 (d, *J* = 3.2 Hz, 1H), 7.54 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 61.6 (CH_2), 113.1 (CH), 113.5 (C), 114.9 (C), 116.1 (CH), 124.3 (CH), 146.2 (CH), 147.9 (C), 163.4 (C); IR (ATR) 1586, 2326 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{10}H_9NO_3Na$ 214.0475; Found 214.0472.

2-(4-Methylphenyl)-4-oxo-4-phenyl-2-butenenitrile (13g)

Pale yellow oil (20 mg, 0.08 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.43 (s, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.5–7.6 (m, 2H), 7.6–7.7 (m, 1H), 7.7–7.8 (m, 2H), 7.88 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.1 (CH_3), 116.1 (C), 124.8 (C), 127.2 (CH), 128.6 (CH), 129.0 (CH), 129.8 (C), 130.1 (CH), 131.7 (CH), 133.9 (CH), 136.9 (C), 142.4 (C), 187.0 (C); HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{14}NO$ 248.1070, found 248.1065.

Ethyl 3-cyano-3-(4-methylphenyl)-2-nitro-2-propanoate (12a) (dr = 1 : 1.4)

Yellow oil (16 mg, 0.06 mmol, 60%). The diastereomeric ratio was determined by ^{1}H NMR of the reaction mixture. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (dd, *J* = 7.2, 7.2, Hz, 3H), 2.35 (s, 3H), 4.18–4.24 (m, 2H), 4.77 (d, *J* = 8.0 Hz, 1H), 5.43 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 6.4 Hz, 2H), 7.26 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.1 (CH_3), 40.0 (CH), 64.2 (CH_2), 88.5 (CH), 116.2 (C), 125.4 (C), 128.1 (CH), 130.3 (CH), 140.1 (C), 161.2 (C). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 4.78 (d, *J* = 8.0 Hz, 1H) 5.42 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 6.4 Hz, 2H), 7.26 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (CH_3), 21.1 (CH_3), 37.8 (CH), 64.3 (CH_2), 88.6 (CH), 115.9 (C), 126.0 (C), 128.1 (CH), 130.4 (CH), 140.2 (C), 161.2 (C); IR (KBr) 1756, 2252 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{13}H_{14}N_2O_4Na$ 285.0846; Found 285.0848.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. ^{1}H and ^{13}C NMR spectra for adducts **3**, **9**, **12** and functionalized alkenes **10**, **13** (PDF).

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