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A highly regio- and stereo-selective [3+2] annulation of allylic compounds and 2-substituted 1,1-dicyanoalkenes through a catalytic carbon–phosphorus ylide reaction

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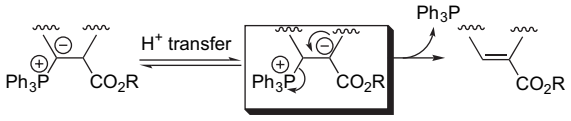
Abstract—A highly regio- and stereo-selective phosphine-catalyzed [3+2] annulation reaction between allylic compounds and 2-substituted 1,1-dicyanoalkenes through a catalytic phosphorus ylide reaction was developed. This reaction has the total reversed regioselectivity compared to that of the reactions of activated alkenes without the 2-substituents or reactions using the allenoates as the C3 component.

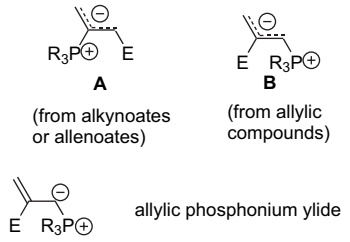
1. Introduction

To make a stoichiometric reaction catalytic has been long-standing goal in modern organic synthesis. Recently, reports on phosphines as nucleophilic catalysts in the reaction of alkynoates or allenoates have grown significantly.[1,2] The major reason for the success of the phosphine-catalyzed isomerization, α-, γ-addition and [3+2] cycloaddition of alkynoates or allenoates, is ascribed to the presence of an electron-withdrawing group, which facilitates the nucleophilic addition and the important proton-transfer step making the elimination of phosphine possible to complete the catalytic cycles (Scheme 1).

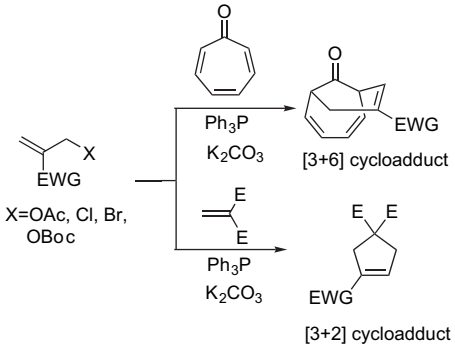


Scheme 1. The importance of electron-withdrawing group for the regeneration of phosphine catalyst.

With this in mind, it was thought that phosphine-catalyzed reactions might be realized via a modified allylic phosphonium ylide B. Thus, simple allylic compounds can be used as the starting materials instead of the complex alkynoates or allenoates (Scheme 2). Recently, the phosphine-catalyzed [3+2] and [3+6] annulation reactions through a phosphorus ylide were reported (Scheme 3).[3] These novel approaches involve cycloaddition of electron-deficient olefins with electron-deficient allylic compounds as the three-carbon unit.



Scheme 2. The possibility of using allylic compounds as the starting material.



Scheme 3. The phosphine-catalyzed [3+2] and [3+6] annulation reactions through a phosphonium ylide.

Keywords: Carbon–phosphorus ylide; Phosphine; Allylic compounds; 2-Substituted 1,1-dicyanoalkenes.
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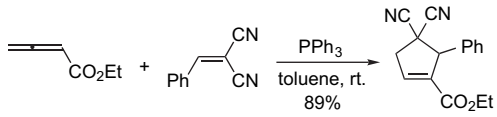
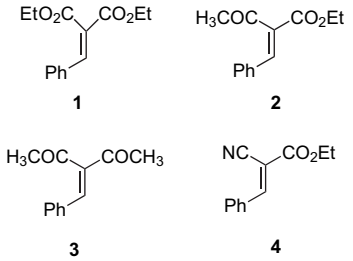
While the [3+2] annulation reactions using tertiary phosphine as catalysts are well developed, as far as we know, only terminal alkenes can be used in the phosphine-catalyzed [3+2] reaction except for the intramolecular annulation reactions[1] and those using enones[2a] or dually activated olefins such as diethyl fumarate or diethyl maleate as the substrate.[1] Also, a pair of regioisomers was produced in almost every case.[1] Recently, the [3+2] annulation reaction of allenoates and 2-substituted 1,1-dicyanoalkenes was reported showing high reactivity of the olefin and high regioselectivity of the reaction (Scheme 4).[4] Herein, we wish to report our recent results on the highly regio- and stereoselective [3+2] annulation of modified allylic compounds with 2-substituted 1,1-dicyanoalkenes through a catalytic carbon–phosphorus ylide reaction and the different regioselectivity than that of the [3+2] annulation reaction from allenoates and 2-substituted 1,1-dicyanoalkenes.[4]



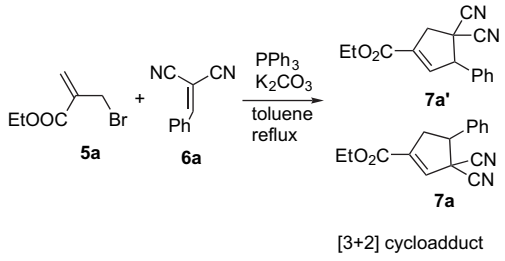
Scheme 4. Phosphine-catalyzed [3+2] annulation reaction of allenoates and 2-substituted 1,1-dicyanoalkenes.

2. Results and discussion

In our initial study, we tried various 2-substituted alkenes with two electron-withdrawing groups at the 1-position (**1**–**4**, Scheme 5) in order to enhance the reactivity of the alkenes. Unfortunately, none of the substrates gave satisfactory results. When the electron-withdrawing groups in **1**–**4** were changed from ester or ketone to nitrile at the same reaction conditions (10 mol % of Ph_3P as the nucleophilic catalyst, 1.5 equiv of K_2CO_3 as the base, refluxing in toluene for 3 h), we obtained the cycloadduct **7** from **5a** and **6a**[5] with 83% isolated yield (Scheme 6).



Scheme 5. Various 2-substituted alkenes.

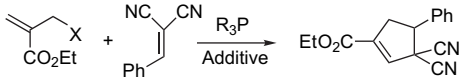


Scheme 6. Phosphine-catalyzed annulation reaction of allylic compounds with 2-substituted 1,1-dicyanoalkenes.

The ^1H NMR of the cycloadduct did not meet the anticipated structure **7a′** (Scheme 6), but exhibited the structure **7a** with reversed regioselectivity. Then compound **6a** was used to react with allylic compounds with different leaving groups (**5a**–**5d**) and $EtPh_2P$ was also used as the catalyst. In all cases, the reaction occurred yielding **7a** as the only product with high yield and high regioselectivity (Table 1). To choose a milder and homogeneous reaction conditions, compound **5c** was selected as the substrate, because it generated the yilide intermediate by the in situ formed base without the necessity of external additives. Using Boc-substituted allylic compound **5c** as the substrate and $EtPh_2P$ as the catalyst, the reaction could occur at room temperature within 1 h with high yields. This was selected as the optimized condition.

Then, using allylic carbonate as the C3 component and $EtPh_2P$ as the catalyst, different 2-substituted 1,1-dicyanoalkenes were tried for this [3+2] annulation reaction as shown in Table 2. Both aromatic (Table 2, entries 1–6) and aliphatic

Table 1. Phosphine-catalyzed [3+2] annulation reaction of allylic compounds with benzylidenemalononitrile (**6a**)[a]



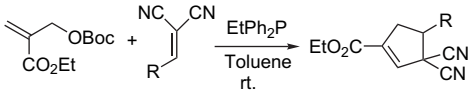
5a, X=Br
5b, X=OAc
5c, X=OBoc
5d, X=OCO_2Me

6a **7a**

Allylic substrate	R_3P	Temp (°C)	Time (h)	Yield[b] (%)
5a	Ph_3P	Reflux	3	83
5b	Ph_3P	Reflux	3	81
5c	Ph_3P	Reflux	3	84[c]
5c	Ph_3P	rt	5	53[c]
5c	$EtPh_2P$	rt	1	95[c]
5d	$EtPh_2P$	rt	1	90[c]

[a] Typical reaction conditions: under Ar, allylic substrates (0.60 mmol), **6a** (0.50 mmol), and K_2CO_3 (0.75 mmol) in toluene (2.5 mL), phosphine (0.05 mmol), stirred.
[b] Isolated yield.
[c] Without the addition of K_2CO_3.

Table 2. $EtPh_2P$-catalyzed [3+2] cycloaddition of allylic carbonate and 2-substituted 1,1-dicyanoalkenes[a]



5c **6** **7**

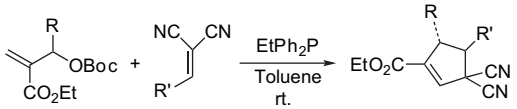
Entry	R	Product	Yield[b] (%)
1	α-Naphthyl (**6b**)	**7b**	92
2	4-MeO–C_6H_4– (**6c**)	**7c**	96
3	4-Cl–C_6H_4– (**6d**)	**7d**	97
4	4-NO_2–C_6H_4– (**6e**)	**7e**	87
5	2,4-Dichlorophenyl (**6f**)	**7f**	95
6	2-Furyl (**6g**)	**7g**	94
7	^{n}Pr (**6h**)	**7h**	89
8	^{i}Pr (**6i**)	—	NR

[a] Reaction conditions: under Ar, C3 component (0.60 mmol), C2 component (0.50 mmol), and $EtPh_2P$ (0.05 mmol) in toluene (2.5 mL), stirred at room temperature for 1 h.
[b] Isolated yield.

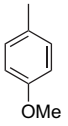
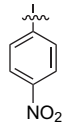
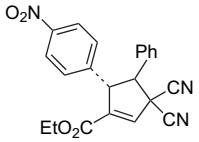
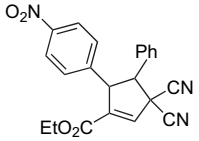
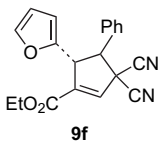
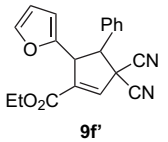
(Table 2, entry 7) substituents at the 2-position of 1,1-dicyanoalkenes have no influence to this reaction. The products were afforded in comparable yields with high regioselectivity. When the 2-substituent was a bulky group such as ^{i}Pr (Table 2, entry 8), the reaction was completely suppressed.

Next, both different C2 and C3 components with substituents were examined to study the application scope of this reaction. As revealed in Table 3, in most cases, trans-isomers were obtained selectively in [3+2] annulation reaction. The stereochemistry was determined by the 2D-NOESY spectra of compounds **9a**, **9e**, and **9f** (Table 3, entries 1, 5, and 6). When R was *p*-nitrophenyl (or furyl) and R′ was phenyl, two isomers **9e** and **9e′** (or **9f** and **9f′**) were obtained (Table 3, entries 5 and 6).

Table 3. $EtPh_2P$-catalyzed [3+2] cycloaddition for different substrates[a]



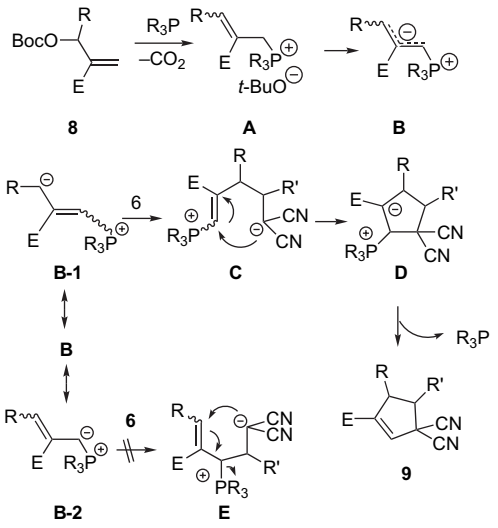
8 **6** **9**

Entry	R	R′	Product	Yield[b] (%)
1	^{n}Pr (**8a**)	Ph (**6a**)	**9a**	90
2	^{i}Pr (**8b**)	Ph (**6a**)	**9b**	87
3	^{n}Pr (**8a**)	 **6c**	**9c**	93
4	^{i}Bu (**8c**)	Ph (**6a**)	**9d**	91
5	 **8d**	Ph (**6a**)	 **9e**	78
			 **9e′**	19
6	 **8e**	Ph (**6a**)	 **9f**	78
			 **9f′**	19

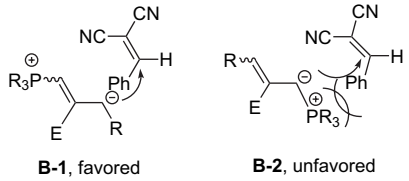
[a] Reaction conditions: under argon, C3 component (0.60 mmol), C2 component (0.50 mmol), and $EtPh_2P$ (0.05 mmol) in toluene (2.5 mL), stirred at room temperature for 1 h.

[b] Isolated yield.

The mechanism and special regioselectivity of this reaction might be explained as shown in Scheme 7. As elucidated in our previous paper, the phosphonium salt **A** was formed via a S_N2' mechanism from R_3P and the allylic substrate **8** first, followed by deprotonation by the in situ generated *tert*-butoxide anion affording an ylide **B**. Subsequent nucleophilic addition, of the γ-position of the ylide **B-1**, to 2-substituted 1,1-dicyanoalkenes (**6**) yielded intermediates **C**, followed by cyclization via intramolecular conjugate addition affording **D**. Finally, elimination of the phosphine completed the catalytic cycle to yield product **9**. The trans stereochemistry of the two substituents in **9** is reasonable because of their neighboring position in a cyclopentene ring. Another pathway for addition of the α-position of the ylide **B-2** to **6** was unfavorable due to the steric hindrance of the bulky phosphine group and the substituents at the 2-position of **6** as shown in Scheme 8. It is also reasonable that for electron-deficient alkenes without 2-substituents, products with regioselectivity like **7a′** were formed (Scheme 6).[3a,6]



Scheme 7. Proposed mechanism for the [3+2] cycloadditions of allylic carbonates and 2-substituted 1,1-dicyanoalkenes.



Scheme 8. Regioselectively favored reaction path.

In summary, we have developed a highly regio-selective phosphine-catalyzed [3+2] annulation reaction between allylic compounds and 2-substituted 1,1-dicyanoalkenes through a catalytic phosphorus ylide reaction. This reaction has the total reversed regioselectivity compared to that of the activated alkenes without the 2-substituents or that using the allenoates as the C3 components. Significantly, this reaction gave cyclopentenes in excellent yields with high stereoselectivity when the substituted C3 components were used. Further efforts on the asymmetric version of the reaction are in progress.

3. Experimental

3.1. General

NMR spectra were recorded on a Varian Mercury V×300 spectrometer. Infrared spectra were obtained on a Bio-Rad FTS-185 instrument. Mass spectra were provided on Agilent 5973 or Agilent 1100. Elemental analyses were carried out on Elementar Vario EL instruments. All solvents were dried and distilled before use according to the standard procedure. All melting points are uncorrected.

3.2. $EtPh_2P$-catalyzed annulation reaction of allylic compounds and 2-substituted 1,1-dicyanoalkenes

The allylic compounds **5a**–**5d**[3a,7,8] and 2-substituted 1,1′-dicyanoalkenes (**6**)[9] were prepared according to the literature methods.

3.2.1. General procedure for the $EtPh_2P$-catalyzed annulation reaction of allylic compounds and 2-substituted 1,1-dicyanoalkenes. Under argon, $EtPh_2P$ (11 μL, 0.05 mmol) was added by a syringe to a solution of **5** (0.6 mmol) and **6** (0.5 mmol) in toluene (2.5 mL). The reaction mixture was stirred at room temperature for 1 h. After the reaction was completed as monitored by TLC, the reaction mixture was concentrated and purified by column chromatography to obtain the product **7**.

3.2.1.1. 1-Ethoxycarbonyl-3,3-dicyano-4-phenylcyclopentene (7a). Oil; yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.45 (m, 5H), 6.64 (t, J=2.1 Hz, 1H), 4.33 (q, J=7.2 Hz, 2H), 4.19 (t, J=9.0 Hz, 1H), 3.33–3.15 (m, 2H), 1.38 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.3, 144.3, 133.7, 131.2, 129.4, 129.1, 128.0, 114.0, 111.3, 61.8, 55.7, 46.3, 35.1, 14.0. IR (oil): ν 2986, 2251, 1724, 1255 cm^{-1}. MS (*m*/*z*) 266 (M^+), 238 (100), 221, 193, 166. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.21; H, 5.39; N, 10.40.

3.2.1.2. 1-Ethoxycarbonyl-3,3-dicyano-4-(α-naphthyl)cyclopentene (7b). White solid; yield: 92%; mp 90 °C–91 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J=8.7 Hz, 1H), 7.96–7.92 (m, 2H), 7.69–7.63 (m, 2H), 7.60–7.53 (m, 2H), 6.64 (t, J=2.1 Hz, 1H), 5.22 (t, J=8.1 Hz, 1H), 4.35 (q, J=7.2 Hz, 2H), 3.50–3.31 (m, 2H), 1.38 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4, 144.5, 134.0, 131.6, 131.2, 130.5, 130.0, 129.3, 127.2, 126.3, 125.7, 125.1, 122.2, 114.2, 111.6, 61.9, 48.8, 46.2, 37.3, 14.1. IR (neat): ν 2989, 2250, 1726, 1270 cm^{-1}. MS (*m*/*z*) 316 (M^+), 288 (100), 243, 214. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.83; H, 4.97; N, 8.86.

3.2.1.3. 1-Ethoxycarbonyl-3,3-dicyano-4-(*p*-methoxyphenyl)cyclopentene (7c). Oil; yield: 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.36 (m, 2H), 6.99–6.94 (m, 2H), 6.61 (dd, J_1=J_2=2.1 Hz, 1H), 4.31 (q, J=7.2 Hz, 2H), 4.15 (dd, J_1=J_2=9.0 Hz, 1H), 3.84 (s, 3H), 3.27–3.10 (m, 2H), 1.36 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.3, 160.2, 144.4, 131.2, 129.2, 125.6, 114.4, 114.1, 111.5, 61.7, 55.4, 55.2, 46.5, 35.3, 14.0. IR (oil): ν 3091, 2984, 2841, 2251, 2046, 1722, 1636, 1613, 1517, 1184, 1108 cm^{-1}. MS (EI): *m*/*z*: 296 (M^+), 268 (100), 251, 223, 208, 196, 180, 153, 121, 77. HRMS: Calcd for $C_{17}H_{16}N_2O_3$: 296.1161. Found: 296.1165.

3.2.1.4. 1-Ethoxycarbonyl-3,3-dicyano-4-(*p*-chlorophenyl)cyclopentene (7d). White solid; yield: 97%; mp 56 °C–57 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.39 (m, 4H), 6.63 (t, J=1.8 Hz, 1H), 4.32 (q, J=7.2 Hz, 2H), 4.17 (t, J=8.7 Hz, 1H), 3.20 (dd, J=9.0 Hz, 1.5 Hz, 2H), 1.37 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 144.3, 135.6, 132.2, 131.1, 129.5, 129.4, 113.8, 111.2, 62.0, 55.2, 46.2, 35.3, 14.1. IR (neat): ν 2989, 2250, 1724, 1497 cm^{-1}. MS (*m*/*z*) 300 (M^+), 272 (100), 255, 192. Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31. Found: C, 63.82; H, 4.43; N, 9.28.

3.2.1.5. 1-Ethoxycarbonyl-3,3-dicyano-4-(*p*-nitrophenyl)cyclopentene (7e). Oil; yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, J=9.0 Hz, 2H), 7.67 (d, J=9.0 Hz, 2H), 6.66 (t, J=2.1 Hz, 1H), 4.33 (q, J=7.2 Hz, 2H), 4.29 (t, J=8.7 Hz, 1H), 3.28 (dd, J=8.7 Hz, 2.1 Hz, 2H), 1.37 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9, 148.5, 144.2, 140.7, 130.9, 129.2, 124.4, 113.4, 110.9, 62.1, 54.9, 45.9, 35.2, 14.1. IR (oil): ν 3088, 2987, 2941, 2459, 2255, 1724, 1638, 1608, 1525, 1352 cm^{-1}. MS (EI): *m*/*z*: 311 (M^+), 283, 266 (100), 236, 219, 208, 192, 164, 104, 84. HRMS: Calcd for $C_{16}H_{13}N_3O_4$: 311.0906. Found: 311.0905.

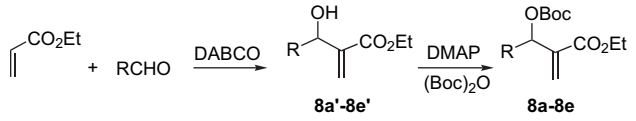
3.2.1.6. 1-Ethoxycarbonyl-3,3-dicyano-4-(2,4-dichlorophenyl)cyclopentene (7f). Oil; yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J=1.5 Hz, 1H), 7.40–7.33 (m, 2H), 6.58 (t, J=1.8 Hz, 1H), 4.87 (t, J=7.2 Hz, 1H), 4.32 (q, J=7.2 Hz, 2H), 3.35–3.09 (m, 2H), 1.36 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0, 144.0, 135.8, 135.7, 131.3, 130.9, 130.0, 129.5, 127.8, 113.2, 111.3, 61.9, 49.1, 45.4, 36.7, 14.0. IR (oil): ν 2987, 2252, 1724, 1526, 1351 cm^{-1}. MS (*m*/*z*) 334 (M^+), 306, 271 (100), 227, 89. HRMS: Calcd for $C_{16}H_{12}N_2O_2Cl_2$: 334.0276. Found: 334.0281.

3.2.1.7. 1-Ethoxycarbonyl-3,3-dicyano-4-(α-furyl)cyclopentene (7g). Oil; yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J=1.8 Hz, 1H), 6.59 (t, J=1.8 Hz, 1H), 6.47 (d, J=2.7 Hz, 1H), 6.44–6.42 (m, 1H), 4.34–4.25 (m, 3H), 3.20 (dd, J=9.0 Hz, 1.8 Hz, 2H), 1.35 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0, 147.9, 143.8, 143.7, 130.8, 113.6, 110.8, 110.6, 109.5, 61.7, 49.0, 44.62, 34.0, 13.9. IR (oil): ν 2987, 2252, 1725, 1263 cm^{-1}. MS (*m*/*z*) 256 (M^+), 228 (100), 211, 199. HRMSEI: Calcd for $C_{14}H_{13}N_2O_3$ (M^++1): 257.0921. Found: 257.0908.

3.2.1.8. 1-Ethoxycarbonyl-3,3-dicyano-4-*n*-propylcyclopentene (7h). Oil; yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.55 (t, J=2.1 Hz, 1H), 4.27 (q, J=7.2 Hz, 2H), 3.02–2.91 (m, 2H), 2.51–2.48 (m, 1H), 1.91–1.75 (m, 2H), 1.58–1.49 (m, 2H), 1.33 (t, J=7.2 Hz, 3H), 1.04 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4, 144.3, 131.6, 114.4, 111.4, 61.7, 50.5, 43.6, 36.2, 33.3, 21.0, 14.1, 13.8. IR (oil): ν 3098, 2965, 2935, 2877, 2251, 1726, 1639, 1467, 1374, 1262 cm^{-1}. MS (EI): *m*/*z*: 233 (M^++1), 206, 175, 131, 103, 56 (100). HRMS: Calcd for $C_{13}H_{16}N_2O_2$: 232.1212. Found: 232.1216.

3.3. $EtPh_2P$-catalyzed annulation reaction of substituted allylic compounds (8) and 2-substituted 1,1-dicyanoalkenes

3.3.1. Preparation of substituted allylic compounds (8). First, the substituted allylic alcohols (**8a′**–**8e′**) were prepared from the Baylis–Hillman reaction of ethyl acrylate and substituted aldehydes.[8,10] Then, the allylic alcohols were reacted with Boc_2O using the following procedure to obtain **8a**–**8e**.



3.3.1.1. Typical procedure for the preparation of (8a). To an ice-water cooled solution of **8a′** (10 mmol) in dry CH_2Cl_2 (20 mL) were added Boc_2O (11 mmol) and DMAP (0.5 mmol) in dry CH_2Cl_2 (20 mL) over half an hour. The reaction mixture was stirred at room temperature overnight. The solution was washed with aqueous hydrochloric acid (15%, 20 mL), saturated sodium bicarbonate (20 mL), and brine (20 mL) sequentially, dried over anhydrous sodium sulfate, concentrated, and purified by column chromatography to get the product **8a**.

*3.3.1.1.1. 1-n-Propyl-2-ethoxycarbonylallyl tert-butylcarbonate (**8a**).* Oil; yield: 42%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30 (s, 1H), 5.82 (t, J=1.2 Hz, 1H), 5.47–5.43 (m, 1H), 4.24 (dq, J=1.8 Hz, 7.2 Hz, 2H), 1.74–1.61 (m, 2H), 1.48 (s, 9H), 1.47–1.35 (m, 2H), 1.31 (t, J=7.2 Hz, 3H), 0.93 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.1, 152.6, 140.5, 124.3, 82.0, 74.1, 60.7, 36.6, 27.6, 18.5, 14.0, 13.6. IR (oil): ν 2982, 1811, 1747, 1634 cm^{-1}. MS (*m/z*) 216 ($M^+-C_4H_8$), 171, 154, 57 (100). Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.55; H, 8.98.

*3.3.1.1.2. 1-i-Propyl-2-ethoxycarbonylallyl tert-butylcarbonate (**8b**).* Oil; yield: 52%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.34 (d, J=1.2 Hz, 1H), 5.79 (t, J=1.2 Hz, 1H), 5.30 (dd, J=0.9 Hz, 5.4 Hz, 1H), 5.29–4.18 (m, 2H), 2.06–2.00 (m, 1H), 1.47 (s, 9H), 1.31 (t, J=7.2 Hz, 3H), 0.95 (d, J=6.3 Hz, 3H), 0.92 (d, J=6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 153.0, 139.7, 125.4, 82.0, 78.6, 60.8, 31.7, 27.7, 18.7, 17.0, 14.1. IR (oil): ν 2978, 1748, 1720, 1633 cm^{-1}. MS (*m/z*) 217 (M^++1-C_4H_8), 155, 109, 57 (100). HRMS: Calcd for $C_{14}H_{24}O_5$ ($M^+-C_4H_8$): 216.0998. Found: 216.1000.

*3.3.1.1.3. 1-n-Butyl-2-ethoxycarbonylallyl tert-butylcarbonate (**8c**).* Oil; yield: 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (s, 1H), 5.82 (s, 1H), 5.50 (dd, J=3.6 Hz, 9.6 Hz, 1H), 4.28–4.19 (m, 2H), 1.74–1.61 (m, 3H), 1.48 (s, 9H), 1.31 (t, J=7.2 Hz, 3H), 0.97 (d, J=6.9 Hz, 3H), 0.93 (d, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0, 152.6, 141.1, 124.0, 82.0, 72.9, 60.7, 43.9, 27.6, 24.7, 23.0, 21.4, 14.0. IR (oil): ν 2962, 1812, 1747, 1719, 1631 cm^{-1}. MS (*m/z*) 287 (M^++1), 231, 169 (100), 153. HRMS: Calcd for $C_{15}H_{26}O_5Na^+$ (M^++Na): 309.1673. Found: 309.1674.

*3.3.1.1.4. 1-α-Furyl-2-ethoxycarbonylallyl tert-butylcarbonate (**8d**).* White solid; yield: 88%; mp 50 °C–51 °C;. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (t, J=1.2 Hz, 1H), 6.56 (s, 1H), 6.49 (s, 1H), 6.34–6.32 (m, 2H), 6.04 (s, 1H), 4.23–4.15 (m, 2H), 1.48 (s, 9H), 1.24 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.6, 150.1, 143.2, 137.1, 126.4, 110.4, 109.9, 82.9, 68.8, 61.0, 27.7, 14.0. IR (neat): ν 3157, 2989, 1748, 1711, 1637 cm^{-1}. MS (*m/z*) 240 ($M^+-C_4H_8$), 194, 179, 122, 57 (100). Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.81; H, 6.79.

*3.3.1.1.5. Preparation of 1-(p-nitrophenyl)-2-ethoxycarbonylallyl tert-butylcarbonate (**8e**).* Compound **8e′** (20 mmol) and Boc_2O (21 mmol) were dissolved in dry benzene (50 mL) and DMAP (0.1 mmol) was added. The reaction mixture was refluxed for 1 h under N_2. It was cooled, concentrated, and purified by column chromatography to get the product **8e**. Oil; yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22–8.20 (m, 2H), 7.62–7.59 (m, 2H), 6.53 (s, 1H), 6.47 (s, 1H), 6.01 (d, J=0.9 Hz, 1H), 4.17 (qd, J=1.2 Hz, 7.2 Hz, 2H), 1.47 (s, 9H), 1.25 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2, 151.9, 147.6, 144.9, 138.6, 128.3, 126.4, 123.5, 83.1, 74.5, 61.1, 27.5, 13.9. IR (oil): ν 3116, 2984, 2939, 1750, 1728, 1635, 1609 cm^{-1}. MS (EI): *m/z*: 295 ($M^+-C_4H_8$), 249, 205, 150, 115, 57 (100). HRMS: Calcd for $C_{13}H_{13}NO_7$ ($M^+-C_4H_8$): 295.0692. Found: 295.0692.

3.3.2. General procedure for the $EtPh_2P$-catalyzed annulation of substituted allylic compounds (8) and 2-substituted 1,1-dicyanoalkenes (6). The procedure was similar to that of the unsubstituted allylic compounds.

3.3.2.1. (*trans*)-1-Ethoxycarbonyl-3,3-dicyano-4-phenyl-5-*n*-propylcyclopentene (9a). Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.39 (m, 5H), 6.56 (d, J=1.8 Hz, 1H), 4.37–4.29 (m, 2H), 3.83 (d, J=7.5 Hz, 1H), 3.63–3.60 (m, 1H), 1.84–1.67 (m, 2H), 1.38 (t, J=7.2 Hz, 3H), 1.28–1.18 (m, 2H), 0.85 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6, 147.5, 134.8, 130.2, 129.4, 129.3, 128.3, 114.4, 111.7, 61.7, 60.3, 48.7, 45.6, 33.5, 19.6, 14.1, 14.0. IR (oil): ν 2963, 2935, 2875, 2250, 1725 cm^{-1}. MS (*m/z*) 279 ($M^+-C_2H_5$), 234, 193, 91 (100). HRMSEI: Calcd for $C_{19}H_{20}N_2O_2$: 308.1525. Found: 308.1511. The stereochemistry was further determined by NOESY spectra (see Supplementary data).

3.3.2.2. (*trans*)-1-Ethoxycarbonyl-3,3-dicyano-4-phenyl-5-*i*-propylcyclopentene (9b). White solid; mp 87 °C–89 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.37 (m, 5H), 6.51 (d, J=1.8 Hz, 1H), 4.32 (q, J=7.2 Hz, 2H), 3.90 (d, J=6.9 Hz, 1H), 3.68–3.63 (m, 1H), 2.57–2.46 (m, 1H), 1.37 (t, J=7.2 Hz, 3H), 0.90 (d, J=6.9 Hz, 3H), 0.74 (d, J=6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.7, 147.2, 136.5, 130.0, 129.13, 129.09, 128.2, 114.3, 111.8, 61.6, 55.5, 55.3, 46.1, 28.3, 20.6, 17.2, 14.0. IR (neat): ν 3101, 2962, 2257, 1725, 1632, 1602 cm^{-1}. MS (EI): *m/z*: 308 (M^+), 253, 193, 105, 43 (100). HRMS: Calcd for $C_{19}H_{20}N_2O_2$: 308.1525. Found: 308.1531.

3.3.2.3. (*trans*)-1-Ethoxycarbonyl-3,3-dicyano-4-(*p*-methoxyphenyl)-5-*n*-propylcyclopentene (9c). Oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, J=2.1 Hz, 6.6 Hz,

2H), 6.95 (dd, J=2.1 Hz, 6.6 Hz, 2H), 6.53 (d, J=2.1 Hz, 1H), 4.35–4.27 (m, 2H), 3.83 (s, 3H), 3.78 (d, J=7.5 Hz, 1H), 3.55–3.53 (m, 1H), 1.81–1.63 (m, 2H), 1.36 (t, J=7.2 Hz, 3H), 1.28–1.16 (m, 2H), 0.84 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6, 160.1, 147.4, 130.2, 129.5, 126.5, 114.4, 114.4, 111.8, 61.6, 59.8, 55.2, 48.6, 45.6, 33.3, 19.5, 14.0. IR (oil): ν 2963, 2936, 2249, 1724, 1516, 1257 cm^{-1}. MS (m/z) 339 (M^++1), 338, 309, 295, 121, 43 (100). HRMSEI: Calcd for $C_{20}H_{23}N_2O_3$ (M^++1): 339.1703. Found: 339.1709.

3.3.2.4. (*trans*)-1-Ethoxycarbonyl-3,3-dicyano-4-phenyl-5-*i*-butylcyclopentene (9d). Oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.35 (m, 5H), 6.52 (d, J=1.8 Hz, 1H), 4.32 (qd, J=2.1 Hz, 7.2 Hz, 2H), 3.81 (d, J=6.0 Hz, 1H), 3.60–3.53 (m, 1H), 1.83–1.76 (m, 1H), 1.56–1.44 (m, 2H), 1.38 (t, J=7.2 Hz, 3H), 0.86 (d, J=6.6 Hz, 3H), 0.74 (d, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.5, 148.5, 135.8, 129.7, 129.4, 129.2, 128.1, 114.5, 111.8, 61.7, 61.1, 48.3, 45.8, 42.5, 25.8, 23.4, 21.4, 14.1. IR (oil): ν 3091, 2961, 2250, 1725, 1638, 1371 cm^{-1}. MS (EI): m/z: 322 (M^+), 293, 234, 193, 166, 84 (100). HRMS: Calcd for $C_{20}H_{22}N_2O_2$: 322.1681. Found: 322.1684.

3.3.2.5. (*trans*)-1-Ethoxycarbonyl-3,3-dicyano-4-phenyl-5-(*p*-nitrophenyl)cyclopentene (9e). Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18–8.13 (m, 2H), 7.45 (s, 5H), 7.31–7.27 (m, 2H), 6.89 (d, J=2.1 Hz, 1H), 4.82 (dd, J=9.6 Hz, 2.1 Hz, 1H), 4.22–4.10 (m, 2H), 3.96 (d, J=9.6 Hz, 1H), 1.17 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5, 147.4, 145.8, 145.4, 132.7, 131.2, 130.0, 129.4, 128.5, 128.2, 124.1, 113.3, 111.1, 64.2, 61.9, 53.4, 45.6, 13.8. IR (oil): ν 3083, 2985, 2251, 1726, 1682 cm^{-1}. MS (EI): m/z: 387 (M^+), 359, 288 (100), 268, 191. HRMS: Calcd for $C_{22}H_{17}N_3O_4$: 387.1219. Found: 387.1218. The stereochemistry was further determined by NOESY spectra (see Supplementary data).

3.3.2.6. (*cis*)-1-Ethoxycarbonyl-3,3-dicyano-4-phenyl-5-(*p*-nitrophenyl)cyclopentene (9e′). Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38–8.35 (m, 2H), 7.78–7.74 (m, 2H), 7.64–7.61 (m, 2H), 7.50–7.47 (m, 3H), 6.59 (d, J=2.4 Hz, 1H), 4.65 (d, J=9.6 Hz, 1H), 4.38 (dd, J=2.4 Hz, 9.6 Hz, 1H), 4.21 (q, J=7.2 Hz, 2H), 1.26 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 148.6, 139.9, 138.4, 130.6, 130.3, 129.8, 129.3, 126.4, 124.4, 113.8, 112.3, 62.5, 57.5, 52.9, 47.5, 14.1. IR (oil): ν 3114, 3085, 2985, 2249, 1737, 1684 cm^{-1}. MS (EI): m/z: 387 (M^+), 386, 314, 288 (100), 268, 191. HRMS: Calcd for $C_{22}H_{17}N_3O_4$: 387.1219. Found: 387.1220. The stereochemistry was further determined by NOESY spectra (see Supplementary data).

3.3.2.7. (*trans*)-1-Ethoxycarbonyl-3,3-dicyano-4-phenyl-5-(α-furyl)cyclopentene (9f). Oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 5H), 7.33 (d, J=1.2 Hz, 1H), 6.76 (d, J=2.1 Hz, 1H), 6.28 (dd, J=2.4 Hz, 3.6 Hz, 1H), 6.17 (d, J=2.7 Hz, 1H), 4.81 (dd, J=9.0 Hz, 2.4 Hz, 1H), 4.29–4.12 (m, 3H), 1.26 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.7, 149.8, 144.5, 142.4, 132.7, 131.4, 129.5, 129.2, 128.2, 113.5, 111.3, 110.6, 108.1, 61.6, 60.5, 47.3, 45.0, 13.8. IR (oil): ν 2986, 2251, 1727, 1242 cm^{-1}. MS (m/z) 333 (M^++1), 332, 89, 43 (100). HRMSEI: Calcd for $C_{20}H_{16}N_2O_3Na^+$ (M^++Na): 355.1053. Found: 355.1060. The stereochemistry was further determined by NOESY spectra (see Supplementary data).

3.3.2.8. (*cis*)-1-Ethoxycarbonyl-3,3-dicyano-4-phenyl-5-(α-furyl)cyclopentene (9f′). Oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.61 (m, 2H), 7.54 (d, J=1.8 Hz, 1H), 7.48–7.43 (m, 3H), 6.58 (d, J=3.0 Hz, 1H), 6.51 (d, J=2.4 Hz, 1H), 6.46 (dd, J=2.1 Hz, 3.3 Hz, 1H), 4.70 (d, J=9.0 Hz, 1H), 4.36 (dd, J=2.4 Hz, 9.6 Hz, 1H), 4.25 (q, J=6.9 Hz, 2H), 1.30 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.7, 149.8, 144.5, 142.4, 132.7, 131.4, 129.5, 129.2, 128.2, 113.5, 111.3, 110.6, 108.1, 61.6, 60.5, 47.3, 45.0, 13.8. IR (oil): ν 2986, 2251, 1727, 1242 cm^{-1}. MS (m/z) 333 (M^++1), 332, 89, 43 (100). HRMSEI: Calcd for $C_{20}H_{16}N_2O_3Na^+$ (M^++Na): 355.1053. Found: 355.1057. The stereochemistry was further determined by NOESY spectra (see Supplementary data).

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Supplementary data

Experimental procedure, characterization data, copies of ^{1}H and ^{13}C NMR spectra for new compounds, and NOESY spectra of compounds **9a**, **9e**, **9e′**, **9f**, and **9f′** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.02.115.

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