Catalyst-Free Synthesis of Skipped Dienes from Phosphorus Ylides, Allylic Carbonates, and Aldehydes via a One-Pot S$_{N}$2′ Allylation—Wittig Strategy

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Supporting Information

ABSTRACT: A catalyst-free allylic alkylation of stabilized phosphorus ylides with allylic carbonates via a regioselective S$_{N}$2′ process is presented. Subsequent one-pot Wittig reaction with both aliphatic and aromatic aldehydes as well as ketenes provides structurally diverse skipped dienes (1,4-dienes) in generally high yields and moderate to excellent stereoselectivity with flexible substituent patterns. This one-pot S$_{N}$2′ allylation—Wittig strategy constitutes a convenient and efficient synthetic method for highly functionalized skipped dienes from readily available starting materials.

Skipped dienes (1,4-dienes) are embedded as ubiquitous components in a vast array of biologically important natural products like polyunsaturated fatty acids. They are also versatile synthetic building blocks in organic syntheses of many important molecules. Because of their great utility, many powerful synthetic methods for the construction of 1,4-dienes have been developed, including various transition-metal-catalyzed cross-couplings, olefinations, Morita–Baylis–Hillman transformations, and so on. Despite the effectiveness of the existing processes, developing stereoselective and practical assembly of structurally diverse 1,4-dienes from readily available starting materials remains an important objective.

Stabilized phosphorus ylides (P-ylides) represent an important class of intermediates in synthetic organic chemistry. In addition to their vital role in the Wittig reaction for building alkenes, P-ylides have been widely utilized as nucleophiles in Michael type and allylation reactions. An elegant work by Chen and co-workers has unveiled that P-ylides can be used as nucleophiles in an organocatalytic Mannich reaction, which, followed by a Wittig reaction with formaldehyde, affords β-aminooxy-methylene carbonyl compounds (Scheme 1, eq a). By employing activated alkenes such as nitroolefins and vinyl ketones as the Michael acceptors, the corresponding tandem Michael–Wittig reactions including intramolecular variants have been established.

Recently, You and Tian have developed novel Pd-catalyzed allylation reactions of P-ylides with allylic carbonates or amines, which afforded functionalized 1,4-dienes by a follow-up Wittig reaction (Scheme 1, eq b). More recently, Zhu and co-workers have demonstrated similar organocatalytic allylation-Wittig reaction in the presence of chiral amine catalyst. Intrigued by these elegant studies, and a pioneering Wittig olefination between phosphines, allylic carbonates, and aldehydes for the construction of conjugated 1,3-dienes, we envisaged that a catalyst-free allylation reaction of stabilized phosphorus ylides with allylic carbonates via a distinct S$_{N}$2′ approach could be realized, and subsequent one-pot Wittig reaction would give easy access to 1,4-dienes (Scheme 1, eq c). In contrast to the well-established Michael and allylation reactions of P-ylides, to our knowledge, the S$_{N}$2′ reaction of P-ylides with allylic compounds has been scarcely explored.

Herein, we report the results from such an investigation. The Morita–Baylis–Hillman (MBH) carbonates were selected as the allylation agents in our investigations. We expected that the electrophilic C=C bond and the good leaving group tert-butoxycarbonyloxy of MBH carbonates should favor a S$_{N}$2′ reaction of P-ylides. In addition, tert-butyl oxide anion generated in situ by the S$_{N}$2′ reaction may act as a strong base to promote subsequent Wittig reaction under salt-free conditions (see discussion on mechanism below). In the initial investigation, the reaction of MBH carbonate 1a with P-ylide 2a was performed in chloroform at 60 °C for 20 h, which was followed by the Wittig reaction with paraformaldehyde at room temperature for 2 h. To our delight, the anticipated S$_{N}$2′ allylation–Wittig product, diethyl 2-benzylidene-4-methylenepentanedioate (3a), was obtained in 99% yield with excellent $E/Z$ selectivity ($E/Z = 20:1$) (eq 1, and

Table 1, entry 1). Notably, the regiodifferentiated diene product, diethyl 2,4-dimethylene-3-phenylpentanedioate

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The reaction parameters were further investigated using the above reaction as a probe (Table 1). The reaction was compatible with a variety of solvents such as dichloromethane, ethyl acetate, acetonitrile, toluene, 1,4-dioxane, and DMSO (entries 2–7). However, THF and DMF as the solvents afforded poor results, and ethanol completely shut down the reaction (entries 8–10). Therefore, chloroform still served as the best solvent in terms of the yield, stereoselectivity, and time. It was found that temperature had significant impact on the SN2′-allylation reaction, as the reaction at room temperature required much longer time for a complete transformation (entry 11). In addition, the reaction was found to be hardly affected by the changes in concentration of the reactants (entries 12 and 13). Finally, it was verified that MBH acetate, ethyl 2-[(acetoxy)(phenyl)methyl]acrylate 1a′, was also effective for the SN2′ allylation reaction but additional base should be employed to promote subsequent Wittig reaction (entry 14).

Under the optimized conditions, the substrate scope of the SN2′ allylation−Wittig reaction was studied (Table 2). First, with P-ylide 2a as a reactant, a range of structurally different MBH carbonates 1 were studied. Aromatic MBH carbonates featuring either an electron-donating or an electron-withdrawing group on the ortho-, meta-, or para-position of the benzene ring all worked well under the standard conditions, delivering the 1,4-dienes 3a–e in excellent yields (91–99%) and good selectivity (E/Z 5:1 to 20:1) (entries 1–5). Heteroaromatic MBH carbonate 1f was also effective to produce the 1,4-diene 3f in 80% yield and 12:1 E/Z ratio (entry 6). Notably, aliphatic MBH carbonates are also feasible in the SN2′ allylation−Wittig reaction giving the corresponding 1,4-dienes in good yields and moderate E/Z selectivity (entries 7–10). For a nonsubstituted MBH carbonate 1i (R1 = H, entry 9), a symmetrical skipped diene 3i was generated in 71% yield, which is an important precursor for bioactive compounds.35 E-Styryl MBH carbonate 1j could also participate in the reaction giving triene 3j in 92% yield and good stereoselectivity (entry 10). In addition, MBH carbonates 1 bearing different electron-withdrawing groups (EWG), e.g., methoxycarbonyl (1k), cyano (1l), and acetyl (1m), were compatible with the SN2′ allylation−Wittig reaction (entries 11–13). In these cases, however, the cyano MBH carbonate 1l afforded a low E/Z ratio (2:1), while the acetyl counterpart 1m provided a modest yield (43%). Subsequently, variation of the electron-withdrawing groups (EWG′) of P-ylides 2 was investigated. It was found that both benzyloxycarbonyl P-ylide (2b) and benzoyl P-ylide (2c) worked well with all selected MBH carbonates 1 (R = aryl, alkyl, or H), producing the corresponding 1,4-dienes 3n–s in good yields and high stereoselectivity (entries 14–19). However, under the standard conditions, cyano P-ylide 2d
failed to produce the desired products but afforded complex mixtures, probably due to severe ylide hydrolysis encountered in the reaction (entries 20 and 21).

Further extension of the scope of the $\text{SN}_2'$ alllylation–Wittig reaction to aromatic or aliphatic aldehydes failed under the standard conditions. Noteworthy is that these aldehydes were rarely explored in previous P-ylide initiated tandem reactions. 37 probably due to their lower reactivity compared to formaldehyde. We conceived that the switch of triphenylphosphorus ylide to a more reactive trialkylphosphorus ylide may compensate for the low reactivity of the aldehydes. Gratifyingly, with \textit{in situ} generated trialkylphosphorus ylide 2\textit{e} as a reactant, the desired $\text{SN}_2'$ alllylation–Wittig reaction with aromatic or aliphatic aldehydes was successfully realized (Table 3). Under similar conditions, representative MBH carbonates 1 and P-ylides gave generally high yields and good stereoselectivity. The Baylis–Hillman carbonates 11 gives generally high yields and good stereoselectivity. The Morita–Baylis–Hillman reaction has a broad substrate scope, and those generated from substituted MBH carbonates 1i with benzaldehyde or (E)-cinnamaldehyde produced the same products (3a and 3j) as those generated from substituted MBH carbonates 1a or 1j with paraformaldehyde, albeit with lower yields and stereoselectivity (entries 7 and 8 of Table 3 vs entries 1 and 10 of Table 2). Under similar conditions, however, ketones such as acetones and acetonophene failed in giving any diene products. The structure of all the dienes 3 listed in Tables 2 and 3 was well identified by $^1$H and $^{13}$C{1H} NMR, IR, and HRMS, and the stereochemistry was confirmed by NOESY analysis for representative products 3a, 3v, and 3x (see the Supporting Information).

To further demonstrate the scope of the $\text{SN}_2'$ alllylation–Wittig reaction with \textit{in situ} generated ketenes as the carbonyl compound was briefly studied. Under the standard conditions, the reaction between MBH carbonate 1a, P-ylide 2a, and acetyl chloride or propionyl chloride in the presence of triethylamine generated ketenes as the carbonyl substituent with flexibility substituents at the 1,5-positions (entries 1–6). An exceptionally low stereoselectivity was observed in the construction of 1,5-dialkyl substituted diene 3y (entry 6). Interestingly, the $\text{SN}_2'$ alllylation–Wittig reaction of non-substituted MBH carbonate 1i with benzaldehyde or (E)-cinnamaldehyde produced the same products (3a and 3j) as those generated from substituted MBH carbonates 1a or 1j with paraformaldehyde, albeit with lower yields and stereoselectivity (entries 7 and 8 of Table 3 vs entries 1 and 10 of Table 2). Under similar conditions, however, ketones such as acetones and acetonophene failed in giving any diene products. The structure of all the dienes 3 listed in Tables 2 and 3 was well identified by $^1$H and $^{13}$C{1H} NMR, IR, and HRMS, and the stereochemistry was confirmed by NOESY analysis for representative products 3a, 3v, and 3x (see the Supporting Information).

The above results clearly demonstrated that the $\text{SN}_2'$ alllylation–Wittig reaction has a broad substrate scope, and gives generally high yields and good stereoselectivity. The MBH allylic carbonates 1 can be conveniently prepared from the Morita–Baylis–Hillman adducts 31,42 by a simple one-step operation. 44 Phosphorus ylides 2 can also be easily prepared (or generated \textit{in situ}) from the corresponding bromides and

![Table 2. Substrate Scope of MBH Carbonates 1 and P-Ylides](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>R$^1$, EWG in 1</th>
<th>EWG$^{\prime}$ in 2</th>
<th>time (h)</th>
<th>3, yield$^{ab}$ (%)</th>
<th>E/$^{\prime}c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_2$H$_5$, CO$_2$Et (1a)</td>
<td>CO$_2$Et (2a)</td>
<td>20</td>
<td>3a, 99</td>
<td>20:1</td>
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<tr>
<td>2</td>
<td>4-CH$_3$C$_6$H$_5$, CO$_2$Et (1b)</td>
<td>CO$_2$Et (2a)</td>
<td>23</td>
<td>3b, 91</td>
<td>20:1</td>
</tr>
<tr>
<td>3</td>
<td>3-NO$_2$C$_6$H$_4$, CO$_2$Et (1c)</td>
<td>CO$_2$Et (2a)</td>
<td>19</td>
<td>3c, 92</td>
<td>5:1</td>
</tr>
<tr>
<td>4</td>
<td>4-ClC$_6$H$_4$, CO$_2$Et (1d)</td>
<td>CO$_2$Et (2a)</td>
<td>25</td>
<td>3d, 98</td>
<td>12:1</td>
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<td>5</td>
<td>2-ClC$_6$H$_4$, CO$_2$Et (1e)</td>
<td>CO$_2$Et (2a)</td>
<td>24</td>
<td>3e, 96</td>
<td>9:1</td>
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<tr>
<td>6</td>
<td>2-furyl, CO$_2$Et (1f)</td>
<td>CO$_2$Et (2a)</td>
<td>30</td>
<td>3f, 80</td>
<td>12:1</td>
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<tr>
<td>7</td>
<td>CH$_3$, CO$_2$Et (1g)</td>
<td>CO$_2$Et (2a)</td>
<td>14</td>
<td>3g, 51</td>
<td>8:1</td>
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<tr>
<td>8</td>
<td>C$_2$H$_5$, CO$_2$Et (1h)</td>
<td>CO$_2$Et (2a)</td>
<td>36</td>
<td>3h, 84</td>
<td>5:1</td>
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<tr>
<td>9</td>
<td>H, CO$_2$Et (1i)</td>
<td>CO$_2$Et (2a)</td>
<td>7</td>
<td>3i, 71</td>
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<tr>
<td>10</td>
<td>(E)-PhCH=CH, CO$_2$Et (1j)</td>
<td>CO$_2$Et (2a)</td>
<td>38</td>
<td>3j, 92</td>
<td>7:1$^b$</td>
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<tr>
<td>11</td>
<td>C$_6$H$_5$, CO$_2$Me (1k)</td>
<td>CO$_2$Et (2a)</td>
<td>21</td>
<td>3k, 97</td>
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<td>12</td>
<td>C$_6$H$_5$, CN (1l)</td>
<td>CO$_2$Et (2a)</td>
<td>20</td>
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<td>13</td>
<td>C$_6$H$_5$, COMe (1m)</td>
<td>CO$_2$Et (2a)</td>
<td>24</td>
<td>3m, 43</td>
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<td>14</td>
<td>C$_2$H$_5$, CO$_2$Et (1a)</td>
<td>CO$_2$BN (2b)</td>
<td>36</td>
<td>3n, 98</td>
<td>20:1</td>
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<tr>
<td>15</td>
<td>4-CH$_3$C$_6$H$_4$, CO$_2$Et (1b)</td>
<td>CO$_2$BN (2b)</td>
<td>54</td>
<td>3o, 92</td>
<td>20:1</td>
</tr>
<tr>
<td>16</td>
<td>CH$_3$, CO$_2$Et (1g)</td>
<td>CO$_2$BN (2b)</td>
<td>18</td>
<td>3p, 87</td>
<td>8:1</td>
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<tr>
<td>17</td>
<td>H, CO$_2$Et (1i)</td>
<td>CO$_2$BN (2b)</td>
<td>13</td>
<td>3q, 98</td>
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</tr>
<tr>
<td>18</td>
<td>C$_2$H$_5$, CO$_2$Et (1a)</td>
<td>COPh (2c)</td>
<td>60</td>
<td>3r, 83</td>
<td>&gt;20:1</td>
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<tr>
<td>19</td>
<td>CH$_3$, CO$_2$Et (1g)</td>
<td>COPh (2c)</td>
<td>72</td>
<td>3s, 46</td>
<td>8:1</td>
</tr>
</tbody>
</table>

$^a$Refers to the major (E,E)-3 versus the sum of others. $^b$The reaction gave a complex mixture.

![Table 3. Substrate Scope of Aldehydes$^a$](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>R$^1$</th>
<th>R$^2$</th>
<th>time$^b$ (h)</th>
<th>3, yield$^c$ (%)</th>
<th>dr$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_2$H$_5$ (1a)</td>
<td>C$_2$H$_5$</td>
<td>31 (11)</td>
<td>3t, 55</td>
<td>6:1</td>
</tr>
<tr>
<td>2</td>
<td>C$_2$H$_5$ (1a)</td>
<td>3-NO$_2$C$_6$H$_4$</td>
<td>30 (9)</td>
<td>3u, 58</td>
<td>10:1</td>
</tr>
<tr>
<td>3</td>
<td>C$_2$H$_5$ (1a)</td>
<td>4-CH$_3$C$_6$H$_4$</td>
<td>28 (10)</td>
<td>3v, 61</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>4</td>
<td>C$_2$H$_5$ (1a)</td>
<td>4-ClC$_6$H$_4$</td>
<td>30 (10)</td>
<td>3w, 49</td>
<td>20:1</td>
</tr>
<tr>
<td>5</td>
<td>C$_2$H$_5$ (1a)</td>
<td>C$_2$H$_5$</td>
<td>27 (9)</td>
<td>3x, 50</td>
<td>11:1</td>
</tr>
<tr>
<td>6</td>
<td>C$_2$H$_5$ (1b)</td>
<td>C$_2$H$_5$</td>
<td>26 (10)</td>
<td>3y, 48</td>
<td>13:1</td>
</tr>
<tr>
<td>7</td>
<td>H (1i)</td>
<td>C$_2$H$_5$</td>
<td>21 (9)</td>
<td>3z, 49</td>
<td>4:1$^e$</td>
</tr>
<tr>
<td>8</td>
<td>H (1i)</td>
<td>(E)-PhCH=CH</td>
<td>22 (11)</td>
<td>3a, 71</td>
<td>1:4:1</td>
</tr>
</tbody>
</table>

$^a$For details, see the Experimental Section. $^b$Overall time for two steps. $^c$The value in parentheses corresponds to the time for the second step. $^d$Overall yields based on 1. $^e$Refers to the major (E,E)-3 versus the sum of others. $^f$The reaction gave a complex mixture.

The above results clearly demonstrated that the $\text{SN}_2'$ alllylation–Wittig reaction has a broad substrate scope, and gives generally high yields and good stereoselectivity. The MBH allylic carbonates 1 can be conveniently prepared from the Morita–Baylis–Hillman adducts by a simple one-step operation. Phosphorus ylides 2 can also be easily prepared (or generated \textit{in situ}) from the corresponding bromides and

![Diagram](image)
phosphines with a base. Therefore, this one-pot catalyst-free S$_2^\prime$ allylation–Wittig reaction constitutes a simple, efficient, and general method for the stereoselective synthesis of functionalized 1,4-dienes. In addition, the substitution patterns of the obtained 1,4-dienes are quite flexible and different from those in previous reports. Finally, the S$_2^\prime$ allylation–Wittig reaction also exhibits excellent regioselectivity; none of regioisomeric diene products of type 3a could be detected in all cases.

To gain insight into the mechanism for the S$_2^\prime$ allylation–Wittig reaction, a $^{31}$P{1H} NMR tracking experiment was conducted. When MBH carbonate 1a (0.05 mmol) and P-ylide 2c (0.05 mmol) were mixed in CDCl$_3$ (0.6 mL) at 60 °C for 12 h in an NMR tube, a new signal at δ 17.2 ppm was observed in the $^{31}$P{1H} NMR measurement. Upon addition of paraformaldehyde (0.05 mmol) into the tube at room temperature for 2 h, the signal basically decayed while another signal at 29.2 ppm corresponding to O=PPh$_3$ appeared instead (for $^{31}$P{1H} NMR tracking spectra, see the Supporting Information). This result indicated that the signal at δ 17.2 ppm most likely corresponded to the in situ generated phosphorus ylide intermediate 5a

and relative literatures, a plausible mechanism for the formation of 1,4-dienes 3 is depicted in Scheme 2. Initially, P-ylide 2 as a nucleophile undertakes a regioselective S$_2^\prime$ attack on the MBH carbonates 1. With the release of one molecule of CO$_2$, the phosphonium tert-butoxide salt 6 is produced. Deprotonation by the tert-butoxide anion then generates the phosphorus ylides 5, which undergoes the salt-free, E-selective Wittig reaction with aldehydes to deliver the functionalized 1,4-dienes 3.

In conclusion, a catalyst-free regioselective S$_2^\prime$ allylation of stabilized phosphorus ylides with Morita–Baylis–Hillman carbonates has been developed. The synthetic utility was demonstrated by a follow-up salt-free Wittig reaction with both aliphatic and aromatic aldehydes which provides an efficient synthesis of 1,2,4,5-tetrasubstituted skipped dienes (1,4-dienes) in good overall yields, moderate to excellent stereoselectivity, and high variability of substituents. This one-pot S$_2^\prime$ allylation–Wittig process has been extended to the synthesis of homoallylic allenoates in good yields. Due to its simplicity, high efficiency, broad substrate scope, and readily available starting materials, this method for preparation of 1,4-dienes is expected to find wide applications in organic synthesis.

### EXPERIMENTAL SECTION

**General Procedures for the Synthesis of 1,4-Dienes 3.**

**Procedure A (for Table 2).** Under N$_2$ atmosphere, to a solution of MBH carbonate 1 (0.5 mmol) in chloroform (2.0 mL) in a Schlenk tube (25 mL) was added phosphorus ylide 2 (0.6 mmol) at room temperature. The reaction mixture was stirred at 60 °C until the MBH carbonates 1 disappeared, as monitored by TLC. Paraformaldehyde (30 mg, 1.0 mmol) was then added and stirred for 2 h at room temperature. All volatile components were removed on a rotary evaporator under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with gradient petroleum ether/ethyl acetate, v/v 20:1 to 5:1) to afford the 1,4-dienes 3a–s.

**Procedure B (for Table 3).** Under N$_2$ atmosphere and at room temperature, a mixture of tributylphosphine (150 μL, 0.6 mmol), ethyl bromoacetate (66 μL, 0.6 mmol), and anhydrous K$_2$CO$_3$ (83 mg, 0.6 mmol) in chloroform (2.0 mL) was stirred for 10 min in a Schlenk tube (25 mL) for the in situ generation of tributylphosphorus ylide 2e. After MBH carbonate 1 (0.5 mmol) was introduced, the mixture was stirred at 60 °C until 1 was consumed. Aldehydes (0.5 mmol) were then added, and the mixture was further stirred at 60 °C until no transformation could be observed. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (eluted with gradient petroleum ether/ethyl acetate, v/v 30:1 to 5:1) to afford the 1,4-dienes 3t–y.

**Diethyl 2-Benzylidene-4-methylenepentadioate (3a).** Following general procedure A, the diene 3a was obtained from MBH carbonate 1a, P-ylide 2a, and paraformaldehyde as a colorless oil in 143 mg, 99% yield, E/Z ratio = 20:1 (Table 2, entry 1); following the general procedure B, the diene 3a was obtained from MBH carbonate 1a, P-ylide 2a, and benzaldehyde in 71 mg, 49% yield, E/Z ratio = 4:1 (Table 3, entry 7); NMR data for (E)-3a, 1H NMR (400 MHz, CDCl$_3$) δ 7.82 (s, 1H), 7.43–7.05 (m, 5H), 6.19 (s, 1H), 5.41 (s, 1H), 4.23–4.11 (m, 4H), 3.48 (s, 2H), 1.25–1.19 (m, 6H); 13C{1H} NMR (100 MHz, CDCl$_3$) δ 167.5, 166.6, 141.4, 138.3, 134.9, 129.1, 128.9, 128.2, 124.4, 60.92, 60.89, 168.7, 166.4, 135.9, 128.1, 127.9, 127.7, 126.6, 60.5, 60.3, 37.0, 13.6; IR (KBr) ν$_{max}$ = 2982, 1713, 1633, 1452, 1426, 764, 700 cm$^{-1}$; HRMS data for C$_{17}$H$_{20}$O$_4$Na$^+$ requires 311.1259, found 311.1265.

**Diethyl 2-(Methylbenzylidene)-4-methylenepentadioate (3b).** Following general procedure A, the diene 3b was obtained as a colorless oil in 137 mg, 91% yield, E/Z ratio = 20:1; NMR data for (E)-3b, 1H NMR (400 MHz, CDCl$_3$) δ 7.88 (s, 1H), 7.43–7.05 (m, 5H), 6.19 (s, 1H), 5.41 (s, 1H), 4.23–4.11 (m, 4H), 3.48 (s, 2H), 1.25–1.19 (m, 6H); 13C{1H} NMR (100 MHz, CDCl$_3$) δ 168.7, 166.4, 141.4, 135.9, 128.1, 127.9, 127.7, 126.6, 60.5, 60.3, 37.0, 13.6; IR (KBr) ν$_{max}$ = 2982, 1713, 1633, 1452, 1426, 764, 700 cm$^{-1}$; HRMS calc for C$_{18}$H$_{22}$O$_4$Na$^+$ requires 313.1279, found 313.1259.

**Diethyl 2-(Methylbenzylidene)-4-methylenepentadioate (3b).** Following general procedure A, the diene 3b was obtained as a colorless oil in 137 mg, 91% yield, E/Z ratio = 20:1; NMR data for (E)-3b, 1H NMR (400 MHz, CDCl$_3$) δ 7.88 (s, 1H), 7.43–7.05 (m, 5H), 6.19 (s, 1H), 5.41 (s, 1H), 4.23–4.11 (m, 4H), 3.48 (s, 2H), 1.25–1.19 (m, 6H); 13C{1H} NMR (100 MHz, CDCl$_3$) δ 168.7, 166.4, 141.4, 135.9, 128.1, 127.9, 127.7, 126.6, 60.5, 60.3, 37.0, 13.6; IR (KBr) ν$_{max}$ = 2982, 1713, 1633, 1452, 1426, 764, 700 cm$^{-1}$; HRMS calc for C$_{18}$H$_{22}$O$_4$Na$^+$ requires 313.1279, found 313.1259.
Diethyl 2-Methylene-4-(3-nitrobenzylidene)pentanedioate (3e).
Following general procedure A, the diene 3e was obtained as a yellow oil in 135 mg, 98% yield, E/Z ratio = 9:1: NMR data for (E)-3e; 1H NMR (400 MHz, CDCl3) δ 7.97 (s, 1H), 7.45–7.38 (m, 18), 7.30–7.16 (m, 3H), 6.26 (s, 1H), 5.49 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.45 (s, 2H), 3.12 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl3) δ 167.0, 166.4, 138.4, 133.0, 131.3, 129.7, 129.5, 129.2, 126.6, 124.4, 61.0, 29.8, 14.1, 14.0; selected NMR data for (Z)-3e; 1H NMR (400 MHz, CDCl3) δ 7.38–7.33 (m, 1H), 6.90 (s, 1H), 6.31 (s, 1H), 5.73 (s, 1H), 4.23–4.22 (m, 2H), 4.01 (q, J = 7.1 Hz, 2H), 3.49 (s, 2H), 0.98 (t, J = 7.1 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl3) δ 167.5, 166.4, 137.7, 134.3, 134.2, 132.7, 129.7, 128.9, 128.8, 126.7, 60.4, 36.2, 13.5; IR (KBr) vmax = 2981, 1716, 1635, 1590, 1468, 1256, 755, 738 cm⁻¹; HRMS calc for C18H14Cl2NO7 requires 345.0870, found 345.0876.

Diethyl 2-(Furan-2-ylmethylene)-4-(methylpentan-4-ynedioate (3g).
Following general procedure A, the diene 3g was obtained as a colorless oil in 133 mg, 97% yield, E/Z ratio = 20:1: NMR data for (E)-3g; 1H NMR (400 MHz, CDCl3) δ 7.83 (s, 1H), 7.34–7.16 (m, 5H), 6.19 (d, J = 0.7 Hz, 1H), 5.40 (d, J = 0.7 Hz, 1H), 4.15 (t, J = 7.1 Hz, 2H), 3.70 (s, 3H), 3.48 (s, 2H), 1.22 (s, J = 7.1 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl3) δ 168.1, 166.6, 147.1, 138.2, 138.9, 137.8, 136.8, 128.7, 128.5, 124.3, 60.8, 52.0, 29.6, 14.0; selected NMR data for (Z)-3g; 1H NMR (400 MHz, CDCl3) δ 6.66 (s, 1H), 5.59 (s, 1H), 3.52 (s, 2H); IR (KBr) vmax = 2952, 1718, 1632, 1435, 1267, 768, 698 cm⁻¹; HRMS calc for C18H16O4N requires 337.1416, found 337.1418.

Ethyl 4-Cyano-2-methylene-5-phenylpent-4-enoate (3I).
Following general procedure A, the diene 3i was obtained as a colorless oil in 114 mg, 95% yield, E/Z ratio = 2:1: NMR data for (E)-3i; 1H NMR (400 MHz, CDCl3) δ 7.58 (s, 1H), 7.47–7.39 (m, 5H), 6.82 (d, J = 7.2 Hz, 2H), 6.00 (d, J = 7.2 Hz, 2H), 4.15 (t, J = 7.1 Hz, 2H), 3.71 (s, 3H), 3.18 (s, 2H); 13C{1H} NMR (100 MHz, CDCl3) δ 165.7, 154.0, 133.6, 130.1, 128.7, 128.6, 128.5, 124.3, 60.8, 53.2, 30.6, 14.0; HRMS calc for C18H14O4N requires 310.0559, found 310.0559.

The Journal of Organic Chemistry
Following general procedure A, the diene 3 was obtained as a colorless oil in 172 mg, 98% yield, E/Z ratio = 20:1; NMR data for (E)-3o.

13C{1H} NMR (100 MHz, CDCl3) δ 176.0, 166.6, 144.1, 139.7, 138.1, 138.1, 135.9, 132.0, 129.3, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 125.1, 66.6, 60.9, 29.7, 21.3, 14.3; selected NMR data for (Z)-3o.

HRMS calcd for C17H20O4Na+ requires 323.1154, found 323.1162.

1-Benzyl-5-Ethyl-4-(methylbenzylidene)-2-methylenepentanedioate (3o).

Following general procedure A, the diene 3o was obtained as a colorless oil in 172 mg, 98% yield, E/Z ratio = 20:1; NMR data for (E)-3o.

1H NMR (400 MHz, CDCl3) δ 7.81 (s, 1H), 7.28−7.17 (m, 10H), 6.23 (s, 1H), 5.34 (s, 1H), 5.12 (s, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.50 (s, 2H), 2.17 (t, J = 7.1 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl3) δ 167.6, 166.4, 144.1, 138.0, 135.8, 134.9, 129.0, 128.8, 128.5, 127.9, 125.0, 66.0, 29.7, 21.3, 14.3; selected NMR data for (Z)-3o.

HRMS calcd for C17H20O4Na+ requires 323.1154, found 323.1162.

1-Benzyl-5-Ethyl-4-(4-methylbenzylidene)-2-methylenepentanedioate (3o).

Following general procedure A, the diene 3o was obtained as a colorless oil in 167 mg, 92% yield, E/Z ratio = 20:1; NMR data for (E)-3o.

1H NMR (400 MHz, CDCl3) δ 7.88 (s, 1H), 7.41−7.33 (m, 5H), 7.23 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 6.32 (d, J = 0.8 Hz, 1H), 5.52 (d, J = 0.8 Hz, 1H), 5.24 (s, 2H), 4.43 (q, J = 7.1 Hz, 2H), 3.59 (s, 2H), 2.35 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl3) δ 167.9, 166.6, 141.7, 139.1, 138.1, 138.1, 135.9, 132.1, 129.3, 128.5, 128.5, 128.1, 128.0, 125.1, 66.6, 60.9, 29.7, 21.3, 14.3; selected NMR data for (Z)-3o.

HRMS calcd for C17H20O4Na+ requires 323.1154, found 323.1162.

1-Benzyl-5-Ethyl-4-(4-benzylidene)-2-methylenepentanedioate (3o).

Following general procedure A, the diene 3o was obtained as a yellow oil in 167 mg, 92% yield, E/Z ratio = 20:1; NMR data for (E)-3o.

1H NMR (400 MHz, CDCl3) δ 7.88 (s, 1H), 7.41−7.33 (m, 5H), 7.23 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 6.32 (d, J = 0.8 Hz, 1H), 5.52 (d, J = 0.8 Hz, 1H), 5.24 (s, 2H), 4.43 (q, J = 7.1 Hz, 2H), 3.59 (s, 2H), 2.35 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl3) δ 167.9, 166.6, 141.7, 139.1, 138.1, 138.1, 135.9, 132.1, 129.3, 128.5, 128.5, 128.1, 128.0, 125.1, 66.6, 60.9, 29.7, 21.3, 14.3; selected NMR data for (Z)-3o.

HRMS calcd for C17H20O4Na+ requires 323.1154, found 323.1162.

Diethyl 2,4-Dibenzyldienemalonate (3t).

Following general procedure B, the diene 3t was obtained as a yellow oil in 115 mg, 61% yield, E/Z ratio = 20:1; NMR data for (E)-3t. 3t H NMR (400 MHz, CDCl3) δ 7.88−7.77 (m, 2H), 7.59−7.57 (m, 2H), 7,52 (d, J = 7.7 Hz, 1H), 7.47−7.38 (m, 1H), 7.31−7.26 (m, 3H), 7.23−7.19 (m, 2H), 4.25 (q, J = 7.2 Hz, 2H), 4.21 (q, J = 7.2 Hz, 2H), 3.87 (s, 2H), 3.10 (t, J = 7.2 Hz, 3H), 2.46 (s, J = 7.2 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl3) δ 167.6, 167.4, 148.0, 139.7, 137.2, 133.2, 132.2, 131.0, 134.0, 132.7, 132.4, 131.5, 14.3, 134.2, 130.4, 129.9, 128.5, 128.3, 123.7, 122.7, 61.2, 61.0, 25.9, 14.16, 14.15; selected NMR data for a minor isomer.

HRMS calcd for C17H20O4Na+ requires 311.1272, found 311.1275.
Synthesis of Homoaallylic Allenoates 4 (eq 2). Under N₂ atmosphere, the mixture of MBH carbonate 1a (0.5 mmol) and P-ylide 2a (0.6 mmol) in chloroform (2.0 mL) was stirred at 60 °C in a Schlenk tube (25 mL) for 20 h. After cooling, acyl chlorides (1.0 mmol) and triethylamine (139 μL, 1.0 mmol) were added sequentially by the means of a microsyringe. The mixture was stirred at room temperature for 2 h. All volatile components were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluted with petroleum ether/ethyl acetate, v/v 10:1) to give the allenoates 4.

Diethyl 2-Benzylidene-4-vinylidenepentanedioate (4a). Colorless oil, 91 mg, 61% yield, E/ Z = 3:1; NMR data for (E)-4a. 1H NMR (400 MHz, CDCl₃) δ 7.82 (s, 1H), 7.39 – 7.30 (m, 5H), 5.13 (t, J = 4.1 Hz, 2H), 4.29 – 4.22 (m, 4H), 3.49 (t, J = 4.1 Hz, 2H), 1.34 – 1.28 (m, 6H); 13C{1H} NMR (100 MHz, CDCl₃) δ 213.2, 167.7, 166.0, 140.8, 136.4, 135.2, 129.1, 128.7, 128.5, 99.7, 80.7, 61.2, 60.9, 26.6, 14.3, 14.2; selected NMR data for (Z)-4a. 1H NMR (400 MHz, CDCl₃) δ 6.81 (s, 1H), 5.17 (t, J = 2.6 Hz, 2H), 4.10 (q, J = 7.1 Hz, 2H), 3.38 (br s, 2H), 1.10 (t, J = 7.1 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl₃) δ 214.2, 168.5, 166.3, 136.0, 131.0, 129.2, 128.3, 128.0, 127.8, 98.2, 79.7, 61.2, 60.6, 34.1, 13.8; IR (KBr) νmax = 2980, 1967, 1708, 1636, 1447, 1259, 759, 699 cm⁻¹; HRMS calcd for C₁₉H₂₄O₄Na⁺ requires 323.1259, found 323.1259.

Diethyl 2-Benzylidene-4-(prop-1-enylidene)pentanedioate (4b). Colorless oil, 105 mg, 67% yield, δr = 6:1; NMR data for the major isomer, 1H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H), 7.32 – 7.22 (m, 5H), 5.48 – 5.40 (m, 1H), 4.21 – 4.12 (m, 4H), 3.47 – 3.35 (m, 2H), 1.57 (d, J = 7.3 Hz, 3H), 1.25 (t, J = 7.3 Hz, 3H), 1.22 (t, J = 4.7 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl₃) δ 210.0, 167.7, 167.0, 140.4, 135.3, 129.6, 129.1, 128.6, 128.5, 99.2, 91.8, 60.1, 60.8, 27.1, 14.30, 14.25, 12.9; selected NMR data for a minor isomer, 1H NMR (400 MHz, CDCl₃) δ 6.72 (s, 1H), 4.02 (q, J = 7.1 Hz, 2H), 3.25 – 3.22 (m, 2H), 1.66 (d, J = 7.3 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H); 13C{1H} NMR (100 MHz, CDCl₃) δ 211.0, 168.5, 166.9, 136.2, 136.1, 131.5, 128.3, 127.9, 127.7, 97.8, 90.7, 60.5, 60.3, 34.6, 13.7, 13.2; IR (KBr) νmax = 2979, 1960, 1702, 1637, 1473, 1239, 734, 700 cm⁻¹; HRMS calcd for C₁₉H₂₄O₄Na⁺ requires 337.1416, found 337.1410.

31P{1H} NMR Tracking Experiment (eq 3). In a N₂-filled NMR tube, MBH carbonate 1a (0.05 mmol) and P-ylide 2c (0.05 mmol) were mixed in CDCl₃ (0.6 mL) at 60 °C for 12 h, which was subjected to a 31P{1H} NMR test. Subsequently, paraformaldehyde (0.05 mmol) was added, and the NMR tube was intermittently shaken for 2 h at room temperature, which was followed by another 31P{1H} NMR test.
(47) Attempts to isolate the phosphorus ylide intermediate 5a failed because of its propensity to hydrolyze during the purification by column chromatography on silica gel.