JOC The Journal of Organic Chemistry

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Catalyst-Free Synthesis of Skipped Dienes from Phosphorus Ylides, Allylic Carbonates, and Aldehydes via a One-Pot S_N2' Allylation–Wittig Strategy

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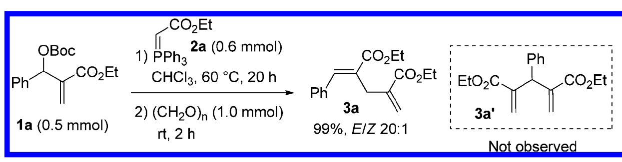
Supporting Information

ABSTRACT: A catalyst-free allylic alkylation of stabilized phosphorus ylides with allylic carbonates via a regioselective S_N2' 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_N2' 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[1−4] like polyunsaturated fatty acids.[1] They are also versatile synthetic building blocks in organic syntheses of many important molecules.[5−7] Because of their great utility, many powerful synthetic methods for the construction of 1,4-dienes have been developed,[8] including various transition-metal-catalyzed cross-couplings,[9−12] ene reactions,[13,14] olefinations,[15−20] Morita–Baylis–Hillman transformations,[21,22] 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 alkylation reactions.[23−28] An elegant work by Chen and co-workers[29] 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-amino-α-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.[30−37] Recently, You[17] and Tian[20] 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[19] 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,[38] we envisaged that a catalyst-free allylation reaction of stabilized phosphorus ylides with allylic carbonates via a distinct S_N2' 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 alkylation reactions of P-ylides, to our knowledge, the S_N2' reaction of P-ylides with allylic compounds has been scarcely explored.[39,40] Herein, we report the results from such an investigation.

The Morita–Baylis–Hillman (MBH) carbonates **1**[41,42] 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 **1** should favor a S_N2' reaction of P-ylides. In addition, *tert*-butyl oxide anion generated *in situ* by the S_N2' 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 (2.0 equiv) at room temperature for 2 h. To our delight, the anticipated S_N2' 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



(1)

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

Received: February 16, 2014
Published: March 25, 2014

   dx.doi.org/10.1021/jo500375q | J. Org. Chem. 2014, 79, 3696−3703

Scheme 1. Tandem Reaction Patterns of Phosphorus Ylides as Nucleophiles

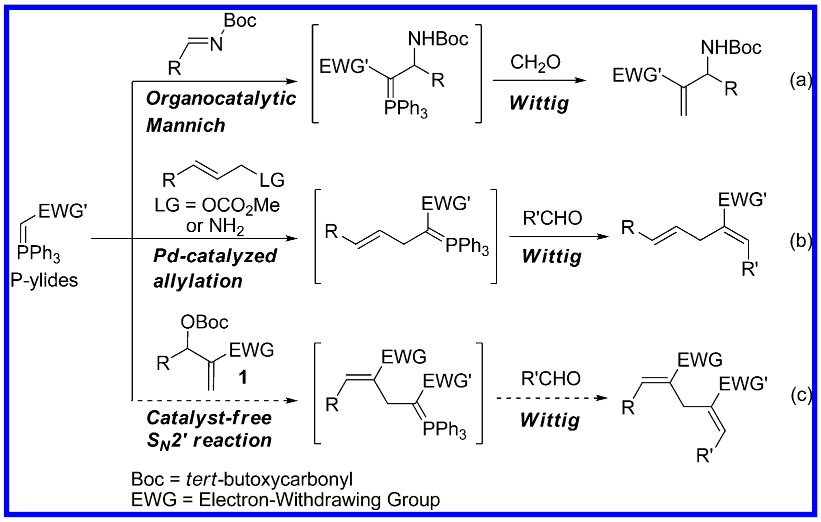
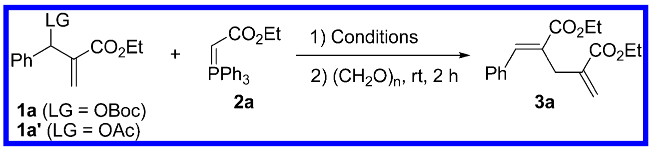


Table 1. Investigations on Reaction Conditions[a]



entry	solvent	time (h)	**3a**, yield[b] (%)	*E*/*Z*[c]
1	$CHCl_3$	20	99	20:1
2	CH_2Cl_2	6	97	12:1
3	EtOAc	34	96	20:1
4	CH_3CN	18	95	17:1
5	toluene	30	97	20:1
6	1,4-dioxane	23	96	20:1
7	DMSO	25	92	12:1
8	DMF	27	71	10:1
9	THF	24	35	15:1
10	EtOH	48	trace	
11[d]	$CHCl_3$	72	91	20:1
12[e]	$CHCl_3$	20	96	20:1
13[f]	$CHCl_3$	20	98	20:1
14[g]	$CHCl_3$	48	81	15:1

[a]MBH carbonate **1a** (0.5 mmol) and phosphorus ylide **2a** (0.6 mmol) were stirred in the specified solvent (2.0 mL) at 60 °C (40 °C for entry 2) under N_2 atmosphere. After the consumption of **1a**, paraformaldehyde (1.0 mmol) was added and stirred for another 2 h at room temperature. [b]Overall yields based on **1a**. [c]Determined by ^1H NMR assay. [d]The reaction was conducted at room temperature. [e]5.0 mL of solvent was used. [f]1.0 mL of solvent was adopted. [g]Ethyl 2-(acetoxy(phenyl)methyl)acrylate **1a′** was used instead of **1a**, and K_2CO_3 (0.6 mmol) was added.

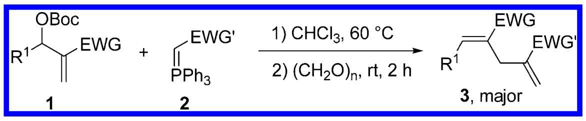
3a′,[19,21,22] could not be detected in the reaction mixture, which suggested a highly regioselective S_N2' allylation process occurred in the reaction.

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, which all furnished excellent yields (92–99%), albeit with somewhat decreased *E*/*Z* ratios observed in dichloromethane, acetonitrile, 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 S_N2'-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 S_N2' allylation reaction but additional base should be employed to promote subsequent Wittig reaction (entry 14).

Under the optimized conditions, the substrate scope of the S_N2' 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 S_N2' 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** (R^1 = H, entry 9), a symmetrical skipped diene **3i** was generated in 71% yield, which is an important precursor for bioactive compounds.[43] *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 S_N2' 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 benzoxycarbonyl 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**

dx.doi.org/10.1021/jo500375q | J. Org. Chem. 2014, 79, 3696–3703

Table 2. Substrate Scope of MBH Carbonates 1 and P-Ylides 2[a]



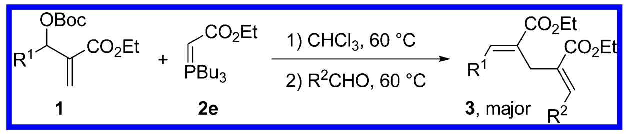
entry	R^1, EWG in **1**	EWG′ in **2**	time (h)	**3**, yield[b] (%)	*E*/*Z*[c]
1	C_6H_5, CO_2Et (**1a**)	CO_2Et (**2a**)	20	**3a**, 99	20:1
2	4-$CH_3C_6H_4$, CO_2Et (**1b**)	CO_2Et (**2a**)	23	**3b**, 91	20:1
3	3-$NO_2C_6H_4$, CO_2Et (**1c**)	CO_2Et (**2a**)	19	**3c**, 92	5:1
4	4-ClC_6H_4, CO_2Et (**1d**)	CO_2Et (**2a**)	25	**3d**, 98	12:1
5	2-ClC_6H_4, CO_2Et (**1e**)	CO_2Et (**2a**)	24	**3e**, 96	9:1
6	2-furyl, CO_2Et (**1f**)	CO_2Et (**2a**)	30	**3f**, 80	12:1
7	CH_3, CO_2Et (**1g**)	CO_2Et (**2a**)	14	**3g**, 51	8:1
8	C_2H_5, CO_2Et (**1h**)	CO_2Et (**2a**)	36	**3h**, 84	5:1
9	H, CO_2Et (**1i**)	CO_2Et (**2a**)	7	**3i**,[d] 71	
10	(*E*)-PhCH=CH, CO_2Et (**1j**)	CO_2Et (**2a**)	38	**3j**, 92	7:1[e]
11	C_6H_5, CO_2Me (**1k**)	CO_2Et (**2a**)	21	**3k**, 97	20:1
12	C_6H_5, CN (**1l**)	CO_2Et (**2a**)	20	**3l**, 95	2:1
13	C_2H_5, COMe (**1m**)	CO_2Et (**2a**)	24	**3m**, 43	>20:1
14	C_6H_5, CO_2Et (**1a**)	CO_2Bn (**2b**)	36	**3n**, 98	20:1
15	4-$CH_3C_6H_4$, CO_2Et (**1b**)	CO_2Bn (**2b**)	54	**3o**, 92	20:1
16	CH_3, CO_2Et (**1g**)	CO_2Bn (**2b**)	18	**3p**, 87	8:1
17	H, CO_2Et (**1i**)	CO_2Bn (**2b**)	13	**3q**, 98	
18	C_6H_5, CO_2Et (**1a**)	COPh (**2c**)	60	**3r**, 83	>20:1
19	CH_3, CO_2Et (**1g**)	COPh (**2c**)	72	**3s**, 46	8:1
20[f]	C_6H_5, CO_2Et (**1a**)	CN (**2d**)	72		
21[f]	CH_3, CO_2Et (**1g**)	CN (**2d**)	72		

[a]For details, see the Experimental Section. [b]Overall yields based on **1**. [c]Determined by ^1H NMR assay. [d]Diene **3i** is a known compound; see ref 22. [e]Refers to the major (*E*,*E*)-**3j** versus the sum of others. [f]The reaction gave a complex mixture.

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 S_N2' allylation−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,[17,20,29−37] 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 *in situ* generated tributylphosphorus ylide **2e** as a reactant, the desired S_N2' allylation−Wittig reaction with aromatic or aliphatic aldehydes was successfully realized (Table 3). Under similar conditions, representative MBH carbonates **1**

Table 3. Substrate Scope of Aldehydes[a]

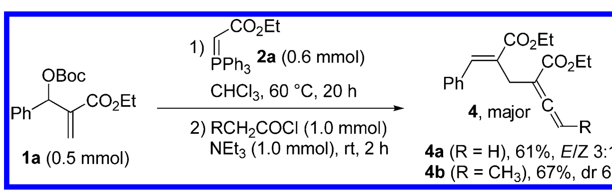


entry	R^1	R^2	time[b] (h)	**3**, yield[c] (%)	dr[d]
1	C_6H_5 (**1a**)	C_6H_5	31 (11)	**3t**, 55	6:1
2	C_6H_5 (**1a**)	3-$NO_2C_6H_4$	30 (9)	**3u**, 58	10:1
3	C_6H_5 (**1a**)	4-$CH_3C_6H_4$	28 (10)	**3v**, 61	>20:1
4	C_6H_5 (**1a**)	4-ClC_6H_4	30 (10)	**3w**, 49	20:1
5	C_6H_5 (**1a**)	C_2H_5	27 (9)	**3x**, 50	11:1
6	C_2H_5 (**1h**)	C_2H_5	26 (10)	**3y**, 48	1.3:1
7	H (**1i**)	C_6H_5	21 (9)	**3a**, 49	4:1[e]
8	H (**1i**)	(*E*)-PhCH=CH	22 (11)	**3j**, 71	1.4:1

[a]For details, see the Experimental Section. [b]Total time for two steps; the value in parentheses corresponds to the time for the second step. [c]Overall yields based on **1**. [d]Refers to the major (*E*,*E*)-**3** versus the sum of others and determined by ^1H NMR assay. [e]*E*/*Z* ratio.

bearing aryl, alkyl, or hydrogen substituents readily incorporated with both aromatic and aliphatic aldehydes in the presence of ylide **2e**, producing the corresponding polysubstituted 1,4-dienes **3** in acceptable yields and good stereoselectivity with flexible substituents at the 1,5-positions (entries 1−6). An exceptionally low stereoselectivity was observed in the construction of 1,5-dialkyl skipped diene **3y** (entry 6). Interestingly, the S_N2' allylation−Wittig reaction of nonsubstituted 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 acetophenone failed in giving any diene products. The structure of all the dienes **3** listed in Tables 2 and 3 was well identified by ^1H 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).

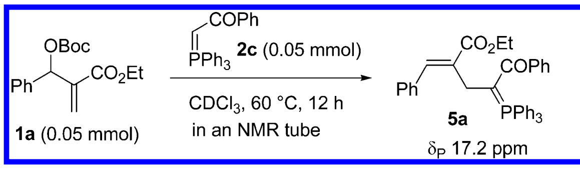
To further demonstrate the scope, the S_N2' allylation−Wittig reaction with *in situ* generated ketenes as the carbonyl compound was briefly studied. Under the standard conditions, the reaction between MBH carbonate **1a**, P-ylide **2a**, and acetyl chloride or propionyl chloride in the presence of triethylamine readily proceeded, producing synthetically important[44,45] allenoates **4** in good yields and moderate stereoselectivity (eq 2).



(2)

The above results clearly demonstrated that the S_N2' allylation−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[41,42] by a simple one-step operation.[46] Phosphorus ylides **2** can also be easily prepared (or generated *in situ*) from the corresponding bromides and phosphines with a base. Therefore, this one-pot catalyst-free S_N2' 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.[17,19−22] Finally, the S_N2' allylation−Wittig reaction also exhibits excellent regioselectivity; none of regioisomeric diene products of type **3a′** could be detected in all cases.

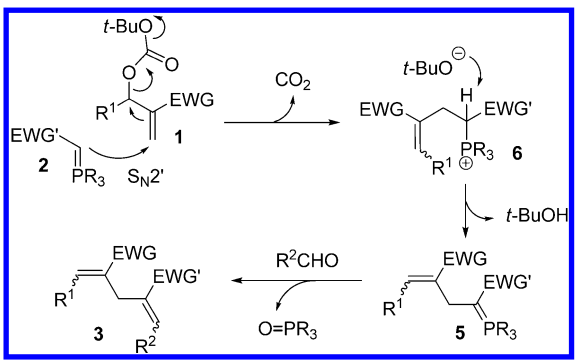
To gain insight into the mechanism for the S_N2' allylation−Wittig reaction, a $^{31}P\{^1H\}$ NMR tracking experiment was conducted. When MBH carbonate **1a** (0.05 mmol) and P-ylide **2c** (0.05 mmol) were mixed in $CDCl_3$ (0.6 mL) at 60 °C for 12 h in an NMR tube, a new signal at δ 17.2 ppm was observed 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**[47] (eq 3). Based on the experimental results



(3)

and relative literatures,[19,38,39,46,48] a plausible mechanism for the formation of 1,4-dienes **3** is depicted in Scheme 2. Initially,

Scheme 2. Possible Mechanism for the Formation of 1,4-Dienes 3



P-ylide **2** as a nucleophile undertakes a regioselective S_N2' 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_N2' 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_N2' 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

Unless otherwise noted, all reactions were carried out in nitrogen atmosphere under anhydrous conditions. Solvents were purified according to standard procedures. MBH carbonates **1** was prepared from Morita−Baylis−Hillman alcohols with Boc_2O/DMAP according to a reported procedure.[46] P-Ylides **2** were generated from phosphines and corresponding bromides with K_2CO_3 according to the literature.[49] Liquid aldehydes were redistilled prior to use. Other reagents from commercial sources were used without further purification. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and NOESY NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. IR spectra were recorded on a FT-IR spectroscopy (KBr). HRMS data were obtained in ESI mode (positive ion) with the mass analyzer of TOF used. Column chromatography was performed on silica gel (200−300 mesh) using a mixture of petroleum ether (bp 60−90 °C)/ethyl acetate as the eluant.

General Procedures for the Synthesis of 1,4-Dienes 3. *Procedure A (for Table 2).* Under N_2 atmosphere, to a solution of MBH carbonates **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_2CO_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-methylenepentanedioate (**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 **1i**, P-ylide **2e**, 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); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 166.6, 141.4, 138.3, 134.9, 129.1, 128.9, 128.8, 128.5, 124.3, 60.9, 60.8, 29.6, 14.09, 14.05, selected NMR data for (*Z*)-**3a**, ^1H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 1H), 5.60 (s, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.36 (s, 2H), 1.08 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.7, 166.4, 135.9, 128.1, 127.9, 127.7, 126.6, 60.7, 60.5, 37.0, 13.6; IR (KBr) ν_{max} = 2982, 1713, 1633, 1452, 1262, 764, 700 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_4Na^+$ requires 311.1259, found 311.1265.

*Diethyl 2-(4-Methylbenzylidene)-4-methylenepentanedioate (**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), 7.24 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.27 (d, *J* = 0.9 Hz, 1H), 5.48 (d, *J* = 0.9 Hz, 1H), 4.29−4.20 (m, 4H), 3.56 (s, 2H), 2.36 (s, 3H), 1.36−1.28 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.9, 166.9, 141.6, 139.1, 138.3, 132.2, 129.3, 129.2, 128.2, 124.4, 60.92, 60.89,

dx.doi.org/10.1021/jo500375q | J. Org. Chem. 2014, 79, 3696−3703

29.7, 21.3, 14.24, 14.19; selected NMR data for (*Z*)-**3b**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H), 5.68 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.43 (s, 2H), 2.33 (s, 3H); IR (KBr) ν_{max} = 2980, 1712, 1631, 1445, 1255, 812, 755 cm^{-1}; HRMS calcd for $C_{18}H_{22}O_4Na^+$ requires 325.1416, found 325.1421.

*Diethyl 2-Methylene-4-(3-nitrobenzylidene)pentanedioate (**3c**).* Following general procedure A, the diene **3c** was obtained as a yellow oil in 153 mg, 92% yield, *E*/*Z* ratio =5:1: NMR data for (*E*)-**3c**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.17 (m, 2H), 7.89 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.59−7.56 (m, 1H), 6.31 (d, *J* = 0.7 Hz, 1H), 5.51 (d, *J* = 0.7 Hz, 1H), 4.33−4.19 (m, 4H), 3.54 (s, 2H), 1.36−1.29 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8, 166.2, 148.2, 138.3, 137.8, 136.5, 134.5, 132.2, 129.5, 124.7, 123.6, 123.2, 61.2, 60.9, 29.5, 14.00, 13.99; selected NMR data for (*Z*)-**3c**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−8.11 (m, 2H), 6.80 (s, 1H), 5.71 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.49 (s, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 166.1, 147.8, 137.6, 137.1, 134.3, 134.2, 133.5, 128.8, 127.1, 123.0, 122.3, 60.8, 36.9, 13.6; IR (KBr) ν_{max} = 2983, 1714, 1630, 1531, 1351, 1254, 763, 730 cm^{-1}; HRMS calcd for $C_{17}H_{19}NO_6Na^+$ requires 356.1110, found 356.1118.

*Diethyl 2-(4-Chlorobenzylidene)-4-methylenepentanedioate (**3d**).* Following general procedure A, the diene **3d** was obtained as a colorless oil in 158 mg, 98% yield, *E*/*Z* ratio =12:1: NMR data for (*E*)-**3d**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.28 (d, *J* = 0.8 Hz, 1H), 5.48 (d, *J* = 0.8 Hz, 1H), 4.29−4.21 (m, 4H), 3.54 (s, 2H), 1.35−1.29 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 166.5, 140.0, 138.1, 134.7, 133.4, 130.2, 129.8, 128.7, 124.4, 61.0, 60.9, 29.6, 14.10, 14.07; selected NMR data for (*Z*)-**3d**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 1H), 6.70 (s, 1H), 5.68 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.44 (s, 2H), 1.12 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.3, 166.3, 137.5, 134.7, 134.3, 133.6, 132.1, 129.5, 128.1, 126.8, 60.8, 60.7, 37.0, 13.7; IR (KBr) ν_{max} = 2978, 1715, 1625, 1580, 1491, 1262, 807, 762 cm^{-1}; HRMS calcd for $C_{17}H_{19}ClO_4Na^+$ requires 345.0870, found 345.0876.

*Diethyl 2-(2-Chlorobenzylidene)-4-methylenepentanedioate (**3e**).* Following general procedure A, the diene **3e** was obtained as a colorless oil in 155 mg, 96% yield, *E*/*Z* ratio = 9:1: NMR data for (*E*)-**3e**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.45−7.38 (m, 1H), 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), 1.32 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.0, 166.4, 138.4, 138.3, 134.0, 133.6, 131.3, 129.7, 129.5, 129.2, 126.6, 124.4, 61.0, 60.8, 29.4, 14.1, 14.0; selected NMR data for (*Z*)-**3e**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.33 (m, 1H), 6.90 (s, 1H), 6.31 (s, 1H), 5.73 (s, 1H), 4.25−4.23 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.49 (s, 2H), 0.98 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.5, 166.4, 137.7, 135.3, 134.6, 133.2, 132.7, 129.7, 128.9, 128.8, 126.7, 126.0, 60.4, 36.2, 13.5; IR (KBr) ν_{max} = 2981, 1716, 1635, 1590, 1468, 1256, 755, 738 cm^{-1}; HRMS calcd for $C_{17}H_{19}ClO_4Na^+$ requires 345.0870, found 345.0876.

*Diethyl 2-(Furan-2-ylmethylene)-4-methylenepentanedioate (**3f**).* Following general procedure A, the diene **3f** was obtained as a brown oil in 111 mg, 80% yield, *E*/*Z* ratio = 12:1: NMR data for (*E*)-**3f**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.6 Hz, 1H), 6.16 (d, *J* = 1.0 Hz, 1H), 5.39 (d, *J* = 1.0 Hz, 1H), 4.32−4.19 (m, 4H), 3.75 (s, 2H), 1.35−1.27 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.7, 167.0, 151.0, 144.5, 137.7, 127.7, 125.5, 123.8, 115.5, 112.0, 60.9, 60.7, 29.7, 14.6, 14.1; selected NMR data for (*Z*)-**3f**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 1.6 Hz, 1H), 6.55 (s, 1H), 6.42 (dd, *J* = 3.4, 1.6 Hz, 1H), 6.27 (s, 1H), 5.66 (s, 1H), 3.42 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.9, 126.7, 124.5, 113.1, 111.8, 60.8, 60.6, 37.0, 14.1; IR (KBr) ν_{max} = 1710, 1632, 1269, 944 cm^{-1}; HRMS calcd for $C_{15}H_{18}O_5Na^+$ requires 301.1052, found 301.1059.

*Diethyl 2-Ethylidene-4-methylenepentanedioate (**3g**).* Following general procedure A, the diene **3g** was obtained as a colorless oil in 58 mg, 51% yield, *E*/*Z* ratio = 8:1: NMR data for (*E*)-**3g**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (q, *J* = 7.1 Hz, 1H), 6.18 (dd, *J* = 2.7, 1.3 Hz, 1H), 5.42 (dd, *J* = 3.1, 1.7 Hz, 1H), 4.25−4.14 (m, 4H), 3.35 (s, 2H), 1.80 (d, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 166.9, 139.9, 137.6, 130.0, 124.5, 60.7, 60.4, 28.0, 14.4, 14.15, 14.13; selected NMR data for (*Z*)-**3g**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 1.2 Hz, 1H), 6.10 (q, *J* = 7.2 Hz, 1H), 5.55−5.53 (m, 1H), 3.27 (s, 2H), 2.02 (dt, *J* = 7.2, 0.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 166.8, 139.4, 138.8, 129.8, 125.7, 60.6, 60.1, 36.0, 15.7; IR (KBr) ν_{max} = 2970, 1718, 1270, 879 cm^{-1}; HRMS calcd for $C_{12}H_{18}O_4Na^+$ requires 249.1103, found 249.1113.

*Diethyl 2-Methylene-4-propylidenepentanedioate (**3h**).* Following general procedure A, the diene **3h** was obtained as a colorless oil in 101 mg, 84% yield, *E*/*Z* ratio = 5:1: NMR data for (*E*)-**3h**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (t, *J* = 7.5 Hz, 1H), 6.09 (d, *J* = 1.2 Hz, 1H), 5.34 (d, *J* = 1.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.26 (s, 2H), 2.16−2.05 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 166.8, 146.5, 138.0, 128.4, 124.3, 60.6, 60.4, 28.1, 22.0, 14.08, 14.07, 13.0; selected NMR data for (*Z*)-**3h**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 1H), 5.89 (t, *J* = 7.4 Hz, 1H), 5.46 (d, *J* = 1.3 Hz, 1H), 3.19 (s, 2H), 2.45−2.37 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.2, 166.7, 146.3, 138.8, 128.3, 125.6, 60.6, 60.0, 35.9, 22.9, 13.7; IR (KBr) ν_{max} = 2979, 1717, 1267, 847 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_4Na^+$ requires 263.1259, found 263.1270.

*Diethyl 2,4-Dimethylenepentanedioate (**3i**).*[22] Following general procedure A, the diene **3i** was obtained as a colorless oil in 75 mg, 71% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 2H), 5.59 (d, *J* = 0.9 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 4H), 3.34 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 138.0, 126.5, 60.7, 33.7, 14.1.

*Diethyl 2-Methylene-4-(3-phenylallylidene)pentanedioate (**3j**).* Following general procedure A, the triene **3j** was obtained from MBH carbonate **1j**, P-ylide **2a**, and paraformaldehyde as a colorless oil in 144 mg, 92% yield, dr =7:1, with (*E*,*E*)-**3j** as the major isomer (Table 2, entry 10). Following general procedure B, **3j** was obtained from MBH carbonate **1i**, P-ylide **2e**, and (*E*)-cinnamaldehyde in 111 mg, 71% yield, dr =1.4:1 (Table 3, entry 8): NMR data for (*E*,*E*)-**3j**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 11.2 Hz, 1H), 7.40−7.37 (m, 2H), 7.29−7.19 (m, 3H), 6.95 (dd, *J* = 15.5, 11.2 Hz, 1H), 6.82 (d, *J* = 15.5 Hz, 1H), 6.13 (d, *J* = 1.1 Hz, 1H), 5.41 (d, *J* = 1.1 Hz, 1H), 4.18−4.11 (m, 4H), 3.46 (s, 2H), 1.24−1.19 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.5, 166.8, 140.5, 140.3, 138.0, 136.2, 128.8, 128.7, 128.1, 127.1, 125.2, 123.6, 60.8, 60.6, 28.6, 14.2, 14.1; selected NMR data for a minor isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 15.6, 11.3 Hz, 1H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.56 (d, *J* = 11.3 Hz, 1H), 6.16 (s, 1H), 5.51 (d, *J* = 1.3 Hz, 1H), 3.31 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8, 166.7, 142.0, 139.2, 138.7, 136.6, 128.6, 128.5, 127.5, 127.1, 126.0, 125.6, 60.7, 60.3, 36.0; IR (KBr) ν_{max} = 2981, 1711, 1614, 1448, 1141, 750, 691 cm^{-1}; HRMS calcd for $C_{19}H_{22}O_4Na^+$ requires 337.1416, found 337.1418.

*5-Ethyl 1-Methyl 2-benzylidene-4-methylenepentanedioate (**3k**).* Following general procedure A, the diene **3k** was obtained as a colorless oil in 133 mg, 97% yield, *E*/*Z* ratio =20:1: NMR data for (*E*)-**3k**, ^{1}H NMR (400 MHz, $CDCl_3$) 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 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.1, 166.6, 141.7, 138.2, 134.8, 128.9, 128.8, 128.7, 128.5, 124.3, 60.8, 52.0, 29.6, 14.0; selected NMR data for (*Z*)-**3k**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 1H), 5.59 (s, 1H), 3.52 (s, 2H); IR (KBr) ν_{max} = 2952, 1718, 1632, 1435, 1267, 768, 698 cm^{-1}; HRMS calcd for $C_{16}H_{18}O_4Na^+$ requires 297.1103, found 297.1112.

*Ethyl 4-Cyano-2-methylene-5-phenylpent-4-enoate (**3l**).* Following general procedure A, the diene **3l** was obtained as a colorless oil in 114 mg, 95% yield, *E*/*Z* ratio = 2:1: NMR data for (*E*)-**3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.70 (m, 2H), 7.43−7.39 (m, 3H), 7.06 (s, 1H), 6.40 (s, 1H), 5.82 (d, *J* = 0.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.39 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 145.3, 136.0, 133.4, 130.1, 128.7, 128.6, 128.5, 118.2, 108.1, 60.9, 38.0, 14.0; selected NMR data for (*Z*)-**3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (s, 1H), 5.78 (d, *J* = 1.1 Hz, 1H), 3.49 (s, 2H);

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 146.0, 135.7, 133.4, 129.5, 127.9, 127.1, 119.7, 111.9, 61.0, 32.0, 13.9; IR (KBr) ν_{max} = 2982, 2211, 1716, 1633, 1496, 1145, 750, 693 cm^{-1}; HRMS calcd for $C_{15}H_{15}NO_2Na^+$ requires 264.1000, found 264.1010.

Ethyl 4-Acetyl-2-methylenehept-4-enoate (3m). Following general procedure A, the diene **3m** was obtained as a colorless oil in 45 mg, 43% yield, *E*/*Z* ratio >20:1: NMR data for (*E*)-**3m**, ^1H NMR (400 MHz, $CDCl_3$) δ 6.79 (t, *J* = 7.3 Hz, 1H), 6.13 (d, *J* = 1.2 Hz, 1H), 5.30 (d, *J* = 1.2 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.31 (s, 2H), 2.33 (s, 3H), 2.29−2.18 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8, 167.0, 147.7, 138.2, 138.0, 124.2, 60.8, 27.1, 25.6, 22.5, 14.2, 13.1; IR (KBr) ν_{max} = 2964, 1717, 1672, 1269, 1138, 805 cm^{-1}; HRMS calcd for $C_{12}H_{18}O_3Na^+$ requires 233.1154, found 233.1162.

1-Benzyl 5-Ethyl 4-benzylidene-2-methylenepentanedioate (3n). Following general procedure A, the diene **3n** was obtained as a colorless oil in 172 mg, 98% yield, *E*/*Z* ratio = 20:1: NMR data for (*E*)-**3n**, ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.28−7.17 (m, 10H), 6.23 (s, 1H), 5.43 (s, 1H), 5.12 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.50 (s, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 166.4, 141.5, 138.0, 135.8, 134.9, 129.0, 128.9, 128.8, 128.5, 128.4, 128.1, 127.9, 125.0, 66.5, 60.9, 29.6, 14.1; selected NMR data for (*Z*)-**3n**, ^1H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 1H), 5.78 (s, 1H), 5.09 (s, 2H), 3.36 (s, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); IR (KBr) ν_{max} = 2980, 1714, 1633, 1496, 1264, 747, 693 cm^{-1}; HRMS calcd for $C_{22}H_{22}O_4Na^+$ requires 373.1416, found 373.1431.

1-Benzyl 5-Ethyl 4-(4-methylbenzylidene)-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, $CDCl_3$) 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), 4.23 (q, *J* = 7.1 Hz, 2H), 3.59 (s, 2H), 2.35 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.9, 166.6, 141.7, 139.2, 138.1, 135.9, 132.1, 129.3, 129.2, 128.5, 128.2, 128.1, 128.0, 125.1, 66.6, 60.9, 29.7, 21.3, 14.2; selected NMR data for (*Z*)-**3o**, ^1H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1H), 5.72 (d, *J* = 1.2 Hz, 1H), 5.21 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.45 (s, 2H), 2.33 (s, 3H); IR (KBr) ν_{max} = 2979, 1701, 1632, 1455, 1271, 742, 697 cm^{-1}; HRMS calcd for $C_{23}H_{24}O_4Na^+$ requires 387.1572, found 387.1578.

1-Benzyl 5-Ethyl 4-ethylidene-2-methylenepentanedioate (3p). Following general procedure A, the diene **3p** was obtained as a colorless oil in 125 mg, 87% yield, *E*/*Z* ratio = 8:1: NMR data for (*E*)-**3p**, ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.22 (m, 5H), 6.96 (q, *J* = 7.1 Hz, 1H), 6.14 (s, 1H), 5.36 (s, 1H), 5.11 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.28 (s, 2H), 1.67 (d, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.1, 166.6, 139.9, 137.3, 135.9, 129.9, 128.4, 128.04, 127.97, 125.0, 66.4, 60.4, 28.0, 14.3, 14.1; selected NMR data for (*Z*)-**3p**, ^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 5.98 (q, *J* = 7.1 Hz, 1H), 5.49 (s, 1H), 5.09 (s, 2H), 3.20 (s, 2H), 1.90 (d, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 139.4, 138.5, 129.6, 127.9, 126.3, 66.3, 60.0, 35.9, 15.6; IR (KBr) ν_{max} = 2985, 1716, 1637, 1451, 1269, 761, 699 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_4Na^+$ requires 311.1259, found 311.1270.

1-Benzyl 5-Ethyl 2,4-dimethylenepentanedioate (3q). Following general procedure A, the diene **3q** was obtained as a colorless oil in 134 mg, 98% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.29 (m, 5H), 6.31 (s, 1H), 6.24 (s, 1H), 5.62 (s, 1H), 5.57 (s, 1H), 5.19 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.36 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.4, 166.3, 137.9, 137.7, 135.8, 128.4, 128.1, 127.9, 127.1, 126.6, 66.4, 60.7, 33.7, 14.0; IR (KBr) ν_{max} = 2989, 1718, 1635, 1500, 1271, 734, 687 cm^{-1}; HRMS calcd for $C_{16}H_{18}O_4Na^+$ requires 297.1103, found 297.1119.

Ethyl 4-Benzoyl-2-benzylidenepent-4-enoate (3r). Following general procedure A, the diene **3r** was obtained as a yellow oil in 133 mg, 83% yield, *E*/*Z* ratio >20:1: NMR data for (*E*)-**3r**, ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.50−7.44 (m, 1H), 7.40−7.25 (m, 7H), 5.71 (d, *J* = 1.6 Hz, 1H), 5.62 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.8, 167.9, 145.6, 141.7, 137.5, 135.0, 132.3, 129.6, 129.3, 129.1, 128.9, 128.6, 128.2, 125.4, 61.0, 30.0, 14.3; IR (KBr) ν_{max} = 2979, 1709, 1658, 1447, 1264, 748, 694 cm^{-1}; HRMS calcd for $C_{21}H_{20}O_3Na^+$ requires 343.1310, found 343.1320.

Ethyl 4-Benzoyl-2-ethylidenepent-4-enoate (3s). Following general procedure A, the diene **3s** was obtained as a yellow oil in 59 mg, 46% yield, *E*/*Z* ratio = 8:1: NMR data for (*E*)-**3s**, ^1H NMR (400 MHz, $CDCl_3$) δ 7.70−7.63 (m, 2H), 7.49−7.43 (m, 1H), 7.38−7.32 (m, 2H), 7.01 (q, *J* = 7.1 Hz, 1H), 5.66 (s, 1H), 5.53 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.41 (s, 2H), 1.78 (d, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.9, 167.3, 145.2, 140.1, 137.6, 132.2, 130.0, 129.5, 128.1, 125.5, 60.5, 28.5, 14.5, 14.2; selected NMR data for (*Z*)-**3s**, ^1H NMR (400 MHz, $CDCl_3$) δ 6.11 (q, *J* = 7.2 Hz, 1H), 5.76 (s, 1H), 5.56 (s, 1H), 3.34 (s, 2H), 1.95 (d, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.6, 146.2, 129.5, 126.5, 60.1, 36.6, 15.8; IR (KBr) ν_{max} = 2979, 1709, 1655, 1444, 1276, 745, 691 cm^{-1}; HRMS calcd for $C_{16}H_{18}O_3Na^+$ requires 281.1154, found 281.1161.

Diethyl 2,4-Dibenzylidenepentanedioate (3t). Following general procedure B, the diene **3t** was obtained as a slightly yellow oil in 100 mg, 55% yield, dr = 6:1, with (*E,E*)-**3t** as the major isomer: NMR data for (*E,E*)-**3t**, ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 2H), 7.28−7.26 (m, 10H), 4.21 (q, *J* = 7.1 Hz, 4H), 3.92 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.1, 139.0, 135.4, 131.1, 129.3, 128.21, 128.16, 60.8, 26.2, 14.2; selected NMR data for a minor isomer, ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); IR (KBr) ν_{max} = 2980, 1709, 1632, 1446, 1248, 767, 697 cm^{-1}; HRMS calcd for $C_{23}H_{24}O_4Na^+$ requires 387.1572, found 387.1571.

Diethyl 2-Benzylidene-4-(3-nitrobenzylidene)pentanedioate (3u). Following general procedure B, the diene **3u** was obtained as a yellow oil in 109 mg, 58% yield, dr = 10:1, with (*E,E*)-**3u** as the major isomer: NMR data for (*E,E*)-**3u**, ^1H NMR (400 MHz, $CDCl_3$) δ 8.11−8.04 (m, 2H), 7.59−7.57 (m, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.44−7.38 (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), 1.30 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 167.4, 148.0, 139.7, 137.2, 136.2, 135.1, 134.6, 134.2, 130.4, 129.2, 129.0, 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, ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 1H); IR (KBr) ν_{max} = 2962, 1710, 1632, 1575, 1493, 1260, 736, 699 cm^{-1}; HRMS calcd for $C_{23}H_{23}NO_6Na^+$ requires 432.1423, found 432.1429.

Diethyl 2-Benzylidene-4-(4-methylbenzylidene)pentanedioate (3v). Following general procedure B, the diene **3v** was obtained as a yellow oil in 115 mg, 61% yield, dr > 20:1, with (*E,E*)-**3v** as the major isomer: NMR data for (*E,E*)-**3v**, ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.50 (s, 1H), 7.21−7.18 (m, 5H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 4.16−4.09 (m, 4H), 3.85 (s, 2H), 2.26 (s, 3H), 1.20−1.17 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.2, 168.1, 139.1, 138.9, 138.3, 135.4, 132.5, 131.3, 130.3, 129.41, 129.36, 129.0, 128.20, 128.18, 60.8, 60.7, 26.3, 21.3, 14.16, 14.15; IR (KBr) ν_{max} = 2959, 1713, 1632, 1443, 1258, 766, 697 cm^{-1}; HRMS calcd for $C_{24}H_{26}O_4Na^+$ requires 401.1729, found 401.1735.

Diethyl 2-Benzylidene-4-(4-chlorobenzylidene)pentanedioate (3w). Following general procedure B, the diene **3w** was obtained as a colorless oil in 98 mg, 49% yield, dr = 20:1, with (*E,E*)-**3w** as the major isomer: NMR data for (*E,E*)-**3w**, ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.44 (s, 1H), 7.24−7.15 (m, 5H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 4.17−4.09 (m, 4H), 3.80 (s, 2H), 1.21−1.17 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.81, 167.78, 139.2, 137.6, 135.3, 134.0, 133.8, 131.8, 130.8, 130.4, 129.2, 128.4, 128.3, 128.2, 60.9, 60.8, 26.0, 14.1(2C); selected NMR data for a minor isomer, ^1H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, *J* = 7.1 Hz, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.41 (s, 2H); IR (KBr) ν_{max} = 2959, 1714, 1633, 1592, 1446, 1259, 773, 693 cm^{-1}; HRMS calcd for $C_{23}H_{23}ClO_4Na^+$ requires 421.1183, found 421.1183.

Diethyl 2-Benzylidene-4-propylidenepentanedioate (3x). Following general procedure B, the diene **3x** was obtained as a yellow oil in 79 mg, 50% yield, dr = 11:1, with (*E,E*)-**3x** as the major isomer: NMR data for (*E,E*)-**3x**, ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.42−

7.34 (m, 5H), 6.66 (t, J = 7.4 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.62 (s, 2H), 2.09−1.95 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.0, 167.8, 145.0, 138.9, 135.7, 131.7, 129.6, 129.1, 128.3, 128.2, 60.7, 60.4, 25.1, 21.8, 14.13, 14.10, 12.9; selected NMR data for a minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 6.95 (t, J = 7.5 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.34 (s, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.07 (t, J = 7.5 Hz, 3H); IR (KBr) ν_{max} = 2978, 1713, 1637, 1446, 1244, 766, 698 cm^{-1}; HRMS calcd for $C_{19}H_{24}O_4Na^+$ requires 339.1572, found 339.1570.

Diethyl 2,4-Dipropylidenepentanedioate (3y). Following general procedure B, the diene **3y** was obtained as a colorless oil in 64 mg, 48% yield, (E,E)-**3y**:(E,Z)-**3y** = 1.3:1: NMR data for (E,E)-**3y**, ^1H NMR (400 MHz, $CDCl_3$) δ 6.71 (t, J = 7.4 Hz, 2H), 4.15 (q, J = 7.1 Hz, 4H), 3.34 (s, 2H), 2.33−2.25 (m, 4H), 1.26 (t, J = 7.1 Hz, 6H), 1.05 (t, J = 7.5 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.8, 144.9, 129.5, 60.4, 24.3, 22.0, 14.2, 13.1; NMR data for (E,Z)-**3y**, ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (t, J = 7.5 Hz, 1H), 5.76 (t, J = 7.4 Hz, 1H), 4.22−4.17 (m, 4H), 3.28 (s, 2H), 2.45−2.36 (m, 2H), 2.23−2.15 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.4 Hz, 3H), 0.98 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.9, 167.6, 146.1, 143.1, 128.9, 128.5, 60.4, 60.2, 30.1, 22.9, 22.0, 14.2(2C), 13.8, 13.1; IR (KBr) ν_{max} = 2969, 1715, 1242 cm^{-1}; HRMS calcd for $C_{15}H_{24}O_4Na^+$ requires 291.1572, found 291.1573.

Synthesis of Homoallylic Allenoates 4 (eq 2). Under N_2 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, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 213.2, 167.7, 166.6, 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, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 214.2, 168.5, 166.5, 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) ν_{max} = 2980, 1967, 1708, 1636, 1447, 1259, 759, 699 cm^{-1}; HRMS calcd for $C_{18}H_{20}O_4Na^+$ requires 323.1259, found 323.1259.

Diethyl 2-Benzylidene-4-(prop-1-enylidene)pentanedioate (4b). Colorless oil, 105 mg, 67% yield, dr = 6:1: NMR data for the major isomer, ^1H NMR (400 MHz, $CDCl_3$) 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 = 7.1 Hz, 3H), 1.22 (t, J = 4.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 210.0, 167.7, 167.0, 140.4, 135.3, 129.6, 129.1, 128.6, 128.5, 99.2, 91.8, 61.0, 60.8, 27.1, 14.30, 14.25, 12.9; selected NMR data for a minor isomer, ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H), 4.02 (q, J = 7.1 Hz, 2H), 3.35−3.22 (m, 2H), 1.66 (d, J = 7.3 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 211.0, 168.5, 166.9, 136.2, 136.1, 131.5, 128.3, 127.9, 127.7, 97.8, 90.7, 61.0, 60.5, 34.6, 13.7, 13.2; IR (KBr) ν_{max} = 2979, 1960, 1702, 1637, 1447, 1259, 734, 700 cm^{-1}; HRMS calcd for $C_{19}H_{22}O_4Na^+$ requires 337.1416, found 337.1410.

$^{31}P\{^1H\}$ NMR Tracking Experiment (eq 3). In a N_2-filled NMR tube, 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, which was subjected to a $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR test.

■ ASSOCIATED CONTENT

Supporting Information

^1H and $^{13}C\{^1H\}$ NMR spectra for **3** and **4**, NOESY spectra for **3a**, **3v**, and **3x**, and $^{31}P\{^1H\}$ NMR tracking spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 21305107) and the Fundamental Research Funds for the Central Universities (No. 08143076). We gratefully thank Prof. Zhengjie He (Nankai University) for constructive discussions and long-term support.

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