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PBu_3-Mediated Vinylogous Wittig Reaction of α-Methyl Allenoates with Aldehydes and Mechanistic Investigations

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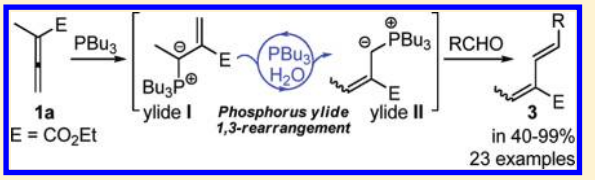
Supporting Information

ABSTRACT: A highly stereoselective PBu_3-mediated vinylogous Wittig olefination between α-methyl allenoates and a variety of aldehydes is presented as the first example of a practical and synthetically useful vinylogous Wittig reaction. Mechanistic experiments including deuterium-labeling, intermediate entrapment, and NMR monitoring have been deliberately conducted. On the basis of mechanistic investigations, a reliable mechanism for the vinylogous Wittig reaction is proposed, which features a water/phosphine-coassisted allylic phosphorus ylide 1,3-rearrangement pathway, rather than previous retro-Diels–Alder ones. It is noteworthy that mechanistic findings in this work also provide supportive evidence for typical mechanisms of important phosphine-mediated reactions of allenoates.

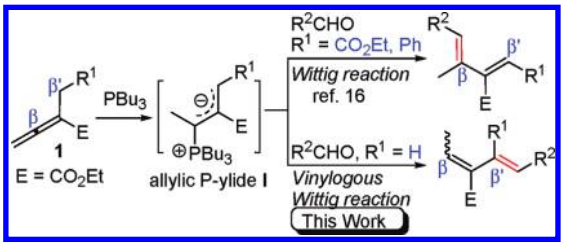


INTRODUCTION

The principle of vinylogy, first formulated by Fuson[1] in 1935, explains anomalous reactivity of some unsaturated compounds with extended electrophilic or nucleophilic character of a functional group through π systems of double or triple bonds or aromatic moieties. Over the past decades, the vinylogy rule has been widely applied to a number of important reactions such as aldol,[2] Mannich,[3] Michael addition,[4] and others[5−8] as an immensely useful, strategic maneuver in the art of contemporary organic synthesis. In this context, vinylogous Wittig type reactions were far less explored,[9−12] although the Wittig olefination[13] occupies a central position in the construction of C=C double bonds. By principle, allylic phosphorus ylides may undergo a vinylogous Wittig type reaction to generate regiodifferentiated isomeric dienes. In 2007, Ghosh et al.[9] first disclosed a vinylogous Horner–Wadsworth–Emmons reaction between α-cyano vinylphosphonates and aldehydes, leading to a stereoselective synthesis of densely substituted 1,3-butadienes. For the vinylogous Wittig reaction, its history can be traced back to 1974 when Corey[10] recorded the first example in the olefination reaction of (*E*)-3-methoxycarbonyl-2-methylallyltriphenylphosphonium bromide with hexanal, giving a regio- and stereoisomeric mixture of dienes. It is until recently that our group[11] and Kwon[12] independently reported two triarylphosphine-mediated vinylogous Wittig reactions of α-methyl allenoates, albeit both with very limited aldehydes. To our knowledge, no other vinylogous Wittig type reactions have been reported. Despite its significant synthetic potential as a useful complement to the normal Wittig reaction, the vinylogous Wittig reaction is still in its infancy with regard to the generality, stereochemistry, and mechanism.

During our investigation on the olefination reactions of in situ-generated allylic phosphorus ylides with aldehydes,[14−16] two regioselective olefinations between tertiary phosphines, α-substituted allenoates, and aldehydes were observed (Scheme 1). When R^1 in allenoates **1** was a conjugative group such as ethoxycarbonyl or phenyl, a normal Wittig olefination of aldehydes with in situ-generated allylic phosphorus ylide **I** from allenoates and PBu_3 readily gave 1,2,3,4-tetrasubstituted 1,3-dienes.[16] In contrast, when α-methyl allenoate (**1a**, R^1 = H) was employed under the same conditions, a vinylogous Wittig olefination occurred from **1a**, PBu_3, and aldehydes, producing 1,2,4-trisubstituted 1,3-dienes (Scheme 1). Further studies disclosed that this PBu_3-mediated vinylogous Wittig reaction readily proceeded with a broad array of aldehydes, constituting an efficient and stereoselective synthesis of trisubstituted 1,3-dienes. This reaction represents the first example of practical and synthetically useful vinylogous Wittig reaction. Herein we report our research findings on this reaction, particularly its mechanism.

Scheme 1. Distinct Olefinations of α-Substituted Allenoates and Aldehydes under the Mediation of PBu_3



RESULTS AND DISCUSSION

Condition Optimization. Optimization of reaction conditions was carried out using the reaction of α-methyl allenoate (**1a**) and benzaldehyde (**2a**) as a probe (Table 1). A series of

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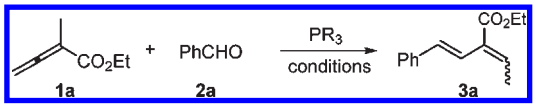
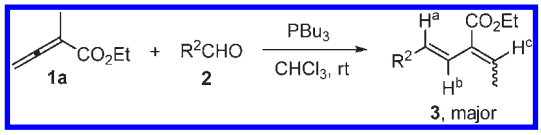
Table 1. Survey of Conditions for the Vinylogous Wittig Reaction[a]



entry	PR_3	solvent	time (h)	yield (%)[b]	E/Z[c]
1	PBu_3	$CHCl_3$	12	83	4:1
2	$PPhMe_2$	$CHCl_3$	12	65	1:1
3	$PMePh_2$	$CHCl_3$	12	30	3:1
4	PTA	$CHCl_3$	24	37	3:1
5	PPh_3	$CHCl_3$	24	8	1.5:1
6	$P(NMe_2)_3$	$CHCl_3$	24	—	—
7	$P(OMe)_3$	$CHCl_3$	24	—	—
8	PBu_3	CH_2Cl_2	12	76	4:1
9	PBu_3	toluene	12	25	3:1
10	PBu_3	THF	12	23	3:1
11	PBu_3	CH_3CN	12	37	3:1
12	PBu_3	DMF	12	trace	—
13	PBu_3	1,4-dioxane	12	26	2:1
14	PBu_3	ethanol	12	—	—
15[d]	PBu_3	$CHCl_3$	12	78	3:1
16[e]	PBu_3	$CHCl_3$	12	78	2:1
17[f]	PBu_3	$CHCl_3$	12	79	6:1
18[f,g]	PBu_3	$CHCl_3$	12	58	6:1
19[f,h]	PBu_3	$CHCl_3$	12	69	6:1
20[f,i]	PBu_3	$CHCl_3$	12	77	5:1
21[f,j]	PBu_3	$CHCl_3$	12	67	5:1
22[f,k]	PBu_3	$CHCl_3$	12	80	5:1

[a] Typical procedure: allenoate **1a** (0.3 mmol) was added under N_2 atmosphere to a solution of aldehyde **2a** (0.2 mmol) and phosphorus reagent (0.3 mmol) in the indicated solvent (5 mL). [b] Combined yield of E/Z isomers based on **2a**. [c] Based on ^1H NMR analysis of the crude product. [d] 2 mL of chloroform was used. [e] Run at 60 °C. [f] Allenoate **1a** (0.3 mmol) in chloroform (3 mL) was added dropwise over 30 min to the solution of aldehyde **2a** (0.2 mmol) and PBu_3 (0.3 mmol) in chloroform (2 mL). [g] $BF_3 \cdot Et_2O$ (0.03 mmol, 10 mol %) was added. [h] LiCl (0.3 mmol, 100 mol %) was added. [i] Water (0.3 mmol, 100 mol %) was added. [j] AcOH (0.06 mmol, 20 mol %) was added. [k] PhOH (0.06 mmol, 20 mol %) was added.

Table 2. Generality of PBu_3-Mediated Vinylogous Wittig Olefination of α-Methyl Allenoates[a]



entry	R^2 in **2**	time (h)	yield (%)[b]	E/Z[c]
1	C_6H_5 (**2a**)	12	**3a**, 79	6:1
2	4-ClC_6H_4 (**2b**)	12	**3b**, 96	5:1
3	3-ClC_6H_4 (**2c**)	12	**3c**, 99	5:1
4	4-BrC_6H_4 (**2d**)	12	**3d**, 71	5:1
5	2-FC_6H_4 (**2e**)	12	**3e**, 77	5:1
6	4-FC_6H_4 (**2f**)	24	**3f**, 96	4:1
7	4-IC_6H_4 (**2g**)	24	**3g**, 92	5:1
8	3-Br-4-$MeOC_6H_3$ (**2h**)	12	**3h**, 82	6:1
9	2-$MeOC_6H_4$ (**2i**)	36	**3i**, 75	5:1
10	4-$MeOC_6H_4$ (**2j**)	36	**3j**, 77	4:1
11	4-MeC_6H_4 (**2k**)	36	**3k**, 72	5:1
12	3-MeO-2-$NO_2C_6H_3$ (**2l**)	12	**3l**, 65	3:1
13	4-$CO_2MeC_6H_4$ (**2m**)	12	**3m**, 69	3:1
14	2-$CF_3C_6H_4$ (**2n**)	24	**3n**, 44	4:1
15	4-$CF_3C_6H_4$ (**2o**)	12	**3o**, 60	4:1
16[d,e]	3-$NO_2C_6H_4$ (**2p**)	12	**3p**, 40	4:1
17	1-naphthyl (**2q**)	36	**3q**, 98	4:1
18	2-furyl (**2r**)	24	**3r**, 87	5:1
19	2-thiofuryl (**2s**)	12	**3s**, 83	4:1
20[e]	3-pyridyl (**2t**)	12	**3t**, 60	4:1
21	*E*-C_6H_5–CH=CH- (**2u**)	24	**3u**, 85	3:1
22[e]	1,4-C_6H_4- (**2v**)	12	**3v**, 56	5:1
23[f]	4-ClC_6H_4 (**2b**)	12	**3w**, 98	6:1

[a] Typical conditions: to a stirred solution of aldehyde **2** (0.2 mmol) and PBu_3 (0.3 mmol) in $CHCl_3$ (2.0 mL) was dropwise added a solution of allenoate **1a** (0.3–0.5 mmol) in $CHCl_3$ (3.0 mL) over 30 min, and the resulting mixture was stirred for the specified time. [b] Isolated yield based on aldehyde **2** as a mixture of E/Z isomers. [c] Ratio for trisubstituted alkene determined by ^1H NMR assay of the crude product **3**. [d] AcOH (0.2 mmol) and NaOAc (0.2 mmol) were added as additives. [e] E/Z ratios of the disubstituted alkene subunit were observed for **3p** (5:1), **3t** (10:1), and **3v** (12:1). [f] Benzyl α-methyl allenoate **1b** was employed instead of **1a**.

nucleophilic phosphorus reagents were examined. PBu_3 was the best, providing diene **3a** in 83% yield with exclusive *E*-selectivity for the newly formed disubstituted double bond and a 4:1 E/Z selectivity for the trisubstituted alkene subunit (Table 1, entry 1). $PPhMe_2$, $PMePh_2$, PPh_3, and 1,3,5-triaza-7-phosphaadamantane (PTA)[17] were also effective but gave diene **3a** in lower yields and stereoselectivity (entries 2–5). Hexamethyl phosphorus triamide (HMPT) and trimethyl phosphite, however, could not mediate the reaction (entries 6, 7). With the choice of PBu_3, screening of common solvents revealed that halogenated solvents such as $CHCl_3$ and CH_2Cl_2 gave higher yields (entries 1, 8). Such polar solvents as THF, CH_3CN, DMF, 1,4-dioxane, and ethanol were detrimental to the reaction (entries 10–14). A higher concentration of substrates or an elevated reaction temperature resulted in the decrease of E/Z selectivity (entries 15, 16). In contrast, slow addition of allenoate **1a** to the reaction mixture to maintain a low concentration of **1a** improved E/Z selectivity of **3a** (6:1) (entry 17). Addition of Lewis acid BF_3 or LiCl did not improve either E/Z selectivity or yield of product **3a** (entries 18, 19). Additional protic additives such as water, acetic acid, and phenol also failed to improve the reaction efficiency (entries 20–22). Thus, the optimized conditions were established: PBu_3 used as the phosphine mediator, chloroform as the solvent, at room temperature, and slow addition of the allenoate **1a**.

Substrate Scope. Under the optimized conditions, the scope of the PBu_3-mediated vinylogous Wittig reaction of **1a** was investigated. Benzaldehydes bearing either electron-donating or -withdrawing substituents at ortho, meta, or para positions all worked well, giving vinylogous Wittig products **3** in fair to excellent yields (Table 2, entries 1–16). 1-Naphthyl aldehyde and heteroaromatic aldehydes such as 2-furyl, 2-thiofuryl, and 3-pyridyl aldehydes were also effective, furnishing the corresponding products in good yields (entries 17–20). The substrate scope was further extended to α,β-unsaturated aldehydes and dialdehydes, affording the corresponding triene and tetraene products

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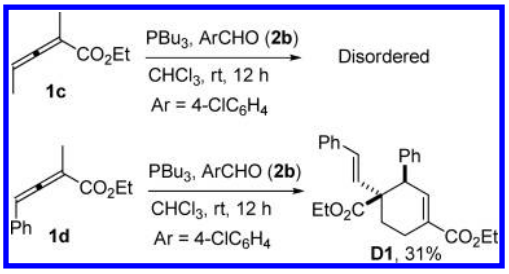
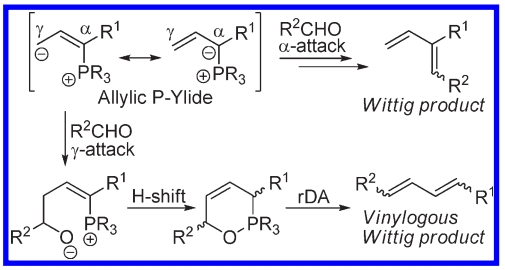
Scheme 2. Investigations on α,γ-Dimethyl Allenoate 1c and α-Methyl γ-Phenyl Allenoate 1d



Scheme 3. A Proposed Retro-Diels–Alder (rDA) Pathway for Vinylogous Wittig Reaction



in good yields (entries 21, 22). But alkyl aldehydes such as propyl, butyl, and neopentyl aldehydes all failed in giving the vinylogous olefination products. Variation of the ester group of **1a** did not interfere with the vinylogous Wittig reaction, as shown in the case of benzyl α-methyl allenoate **1b** (entry 23). Of note is that substituent introduction to the γ-carbon of allenoate **1a**, however, deflected the reaction. For example, α,γ-dimethyl allenoate **1c** produced a complex mixture, while α-methyl γ-phenyl allenoate **1d** gave a dimerization product **D1** under the standard conditions (Scheme 2). Of all cases, the vinylogous Wittig olefination exhibited exclusive *E*-selectivity for the newly formed disubstituted alkene except for products **3p**, **3t**, and **3v** (*E*/*Z* ratios of 5:1 to 12:1, Table 2, entries 16, 20, and 22). In contrast, the trisubstituted alkene subunit, which was regenerated from the allenic double bonds, showed only a modest *E*/*Z* selectivity in all of products **3** (Table 2). The structure and geometry assignments for dienes **3** were determined by 1D and 2D NMR spectroscopy and further confirmed by X-ray crystallographic analysis. ^{1}H NMR data provided diagnostic evidence on the *E*-configuration assignment of the disubstituted double bonds of **3** by the coupling constant magnitude (ca. 16 Hz) between the olefinic protons H^a and H^b. The *E*/*Z* configuration for the trisubstituted double bonds of **3** was assigned according to the chemical shift of the vinylic proton H^c, which is about 0.7 ppm downfield for the *E* isomer compared with that for the *Z* isomer, and was further confirmed by NOESY analysis of product (*E*,*E*)-**3p**. In addition, X-ray crystallographic analysis for (*E*,*E*)-**3l** (CCDC 829382) provided unambiguous evidence for the structure and stereochemistry assignments of products **3** (see Supporting Information).

Mechanism Investigation. A retro-Diels–Alder (rDA) pathway, first proposed by Corey,[10] was often adopted to interpret the formation of vinylogous olefination products as well as stereo outcomes (Scheme 3).[9,12] In such a mechanism, an allylic phosphorus ylide initially adds to an aldehyde at the γ-carbanion, followed by a H-shift to form a six-membered 1,2-oxaphosphonine which subsequently undergoes a retro-Diels–Alder (rDA) reaction to fulfill a vinylogous Wittig transformation. This mechanism benefits from the ability of allylic phosphorus ylide to undertake γ-addition on aldehydes.[18−20] Yet, theoretical or experimental evidence for it remains elusive. To account for formation of dienes **3** in this work, we found that the retro-Diels–Alder pathway is, however, quite contradictory to the observed distinct stereoselectivities of the di- and trisubstituted double bonds of product **3**. To pursue an accurate mechanism, we then focused on mechanistic investigations.

First, deuterium-labeling experiments were conducted to probe the mechanism (Scheme 4). Under standard conditions,

Scheme 4. Deuterium-Labeling Experiments

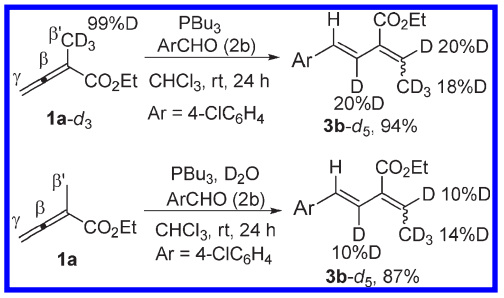
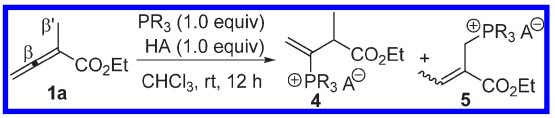


Table 3. Entrapment and Isolation of Intermediates from the Reaction of 1a and Phosphines[a]



entry	PR_3	HA	**4**, yield (%)[b]	**5**, yield (%)[b], *E*/*Z*[c]
1	PBu_3	CF_3CO_2H	**4a**, 99	–
2	$PPhMe_2$	CF_3CO_2H	**4b**, 99	–
3	PPh_3	CF_3CO_2H	**4c**, 94	–
4	PBu_3	AcOH	–	**5a**, 89, 6:1
5	PBu_3	$PhCO_2H$	–	**5b**, 82, 5:1
6	PBu_3	PhOH	–	**5c**, 74, 10:1
7	$PPhMe_2$	AcOH	–	**5d**, 94, 8:1
8	PPh_3	AcOH	–	trace
9	PBu_3	H_2O	–	–
10	PBu_3	EtOH	–	trace

[a] For details, see Experiment Section. [b] Isolated yield. [c] Determined by ^{31}P NMR assay.

α-methyl-deuterated allenoate **1a**-d_3 (purity >99%) was reacted with PBu_3 and *p*-chlorobenzaldehyde **2b**, affording a 94% yield of **3b**-d_5 with ca. 20% deuterium incorporations at the β, β′, and γ-carbons. Normal allenoate **1a** also afforded **3b**-d_5 in 87% yield with similar deuterium distribution when 1.5 equiv of D_2O was introduced into the reaction. These results pointed to the involvement of water in a set of proton transfers of this olefination reaction.[21−23] They also suggested that the H/D exchanges might occur prior to the olefination, for there was no detectable deuterium incorporation at the olefinic carbon originated from the aldehyde in **3b**-d_5.

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Intrigued by the results from deuterium-labeling experiments, we intended to investigate the transformations between allenoate **1a** and phosphines (PBu_3, $PPhMe_2$, and PPh_3) in the presence of a series of protic additives. To our delight, two kinds of phosphonium salts **4** and **5** were successfully isolated with the aid of appropriately acidic additives (Table 3). With trifluoroacetic acid (TFA), the reactions of **1a** with all three selected phosphines produced corresponding vinylphosphonium salts **4** in almost quantitative yields (entries 1−3). Replacing TFA with a weakly acidic additive such as acetic acid, benzoic acid, and phenol led to the isolation of an allylic phosphonium salt **5** in good yield with 5:1 to 10:1 *Z*/*E* ratio from the reaction of **1a** and PBu_3 (entries 4−6). In the presence of acetic acid, $PPhMe_2$ also afforded the corresponding allylic phosphonium salt **5d** in 94% yield and 8:1 *Z*/*E* ratio (entry 7), but weakly nucleophilic PPh_3 failed (entry 8).[24−26] In contrast, using neutral protic additives such as water and ethanol, neither corresponding phosphonium salts **4** nor **5** could be trapped and isolated from the reaction of **1a** and PBu_3 (entries 9, 10). Isolated phosphonium salts **4** and **5** were fully identified by spectrometric methods including HRMS, 1D-NMR (^{31}P, ^{1}H, ^{13}C) and 2D-COSY, HMQC, and NOESY (see Supporting Information).

Formation of vinylphosphonium salts **4** most likely results from the nucleophilic addition of tertiary phosphine to allenoate **1a** followed by protonation with TFA; however, the occurrence of allylic phosphonium salts **5** in which the phosphorus moiety is attached to the β'-carbon of allenoate **1a** represents an unprecedented process.

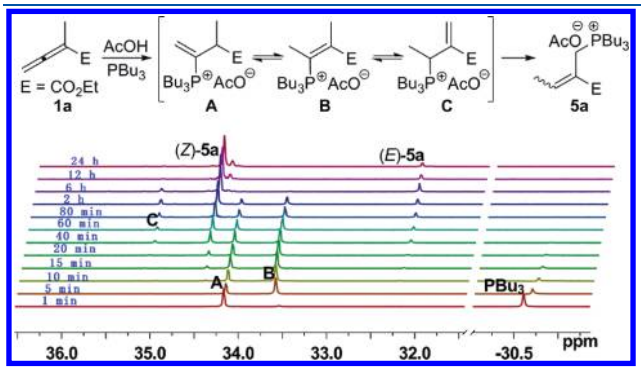

Figure 1. ^{31}P NMR monitoring of the reaction between **1a**, PBu_3, and acetic acid.

To gain more mechanistic information, the reaction of **1a** and PBu_3 was run in $CDCl_3$ with acetic acid or benzoic acid used as the additive, and monitored by ^{31}P and ^{1}H NMR spectroscopy (Figures 1 and 2). Gratifyingly, the NMR monitoring experiments clearly unveiled the transformation process of **1a** to the allylic phosphonium salt **5a**. As shown in a ^{31}P NMR monitoring experiment (Figure 1), vinylphosphonium salts **A** and **B** were detected shortly after **1a** and PBu_3 were mixed in an NMR tube, and they lasted in the reaction mixture for up to 2 h. The signal of free PBu_3 diminished after 40 min, and at that time, an allylic phosphonium salt **C** gradually appeared in the NMR spectra. The signals from allylic phosphonium salt **5a** as a pair of *Z*/*E* isomers became observable after 15 min, and their intensities gradually increased as the reaction proceeded. In the period from 60 min to 2 h, intermediates **A**, **B**, and **C** and product **5a** accounted for all phosphorus-containing species in the reaction. After 12 h, the reaction was complete and exclusively gave allylic phosphonium salt **5a**.[27] The transformation process of **1a** to the allylic phosphonium salt **5a** was also monitored by ^{1}H NMR spectroscopy (Figure 2). The assigned structures of intermediates **A**, **B**, and **C** were highly consistent with both ^{1}H and ^{31}P NMR data. Intermediate **A** could be identified by analogy with the well-identified analogue **4a**. The assigned structure of intermediate **B** was strongly supported by the signals of a singlet (δ 2.12 ppm, CH_3) and a doublet (δ 2.16 ppm, J_{P-H} = 13.2 Hz, CH_3) in ^{1}H NMR monitoring spectra at the time scale of 5 min to 2 h. In the time scale of 40 min to 6 h, two doublets from olefinic protons (δ 6.47 ppm, J = 2.9 Hz and 6.42 ppm, J = 3.9 Hz, vinylic CH_2) and one multiplet at δ 4.43 ppm (CH) in ^{1}H NMR spectra provided diagnostic evidence for intermediate **C**. With benzoic acid employed as the additive, the same NMR monitoring experiments presented a similar transformation process of **1a** to **5b** which, however, proceeded in a slower pace (for detail, see Supporting Information).

In light of the results from NMR monitoring experiments and Table 3, we believed that the acetate or benzoate anion also acts as a base in a set of proton transfers during the transformations between the intermediates such as **A**, **B**, and **C**. An appropriate basicity of the conjugate base of an acidic additive should be an essential prerequisite for the conversion of **1a** into allylic phosphonium salt **5**. As a validation for this speculation, the conversion of vinylphosphonium trifluoroacetate **4a** or **4b** into the corresponding **5** could be readily revivified by addition of a base

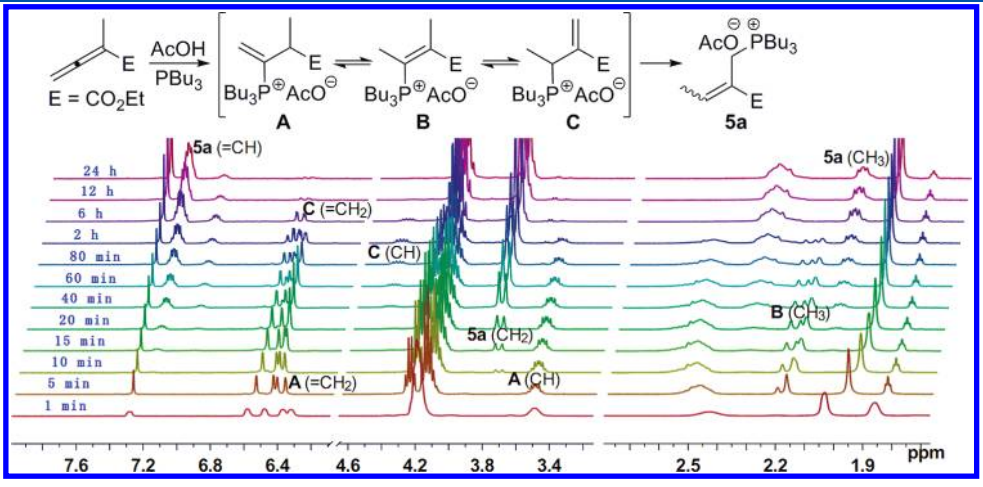

Figure 2. ^{1}H NMR monitoring of the reaction between **1a**, PBu_3, and acetic acid.

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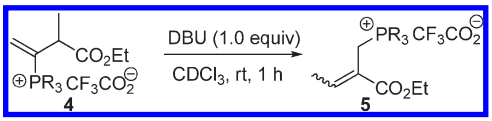
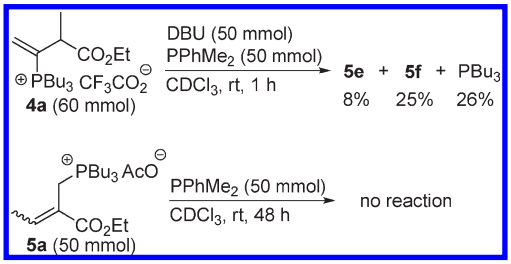
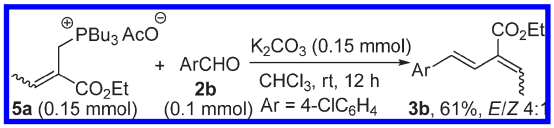
Scheme 5. DBU-Aided Formation of 5 from 4



Scheme 6. Control Experiments



Scheme 7. Formation of the Olefination Product 3b from 5a

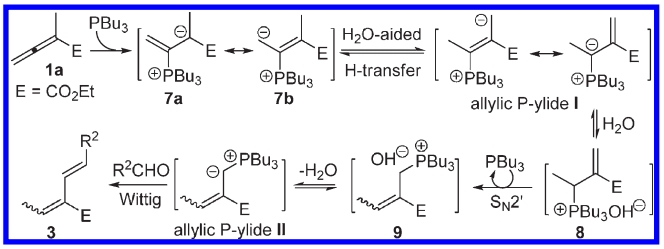


DBU (Scheme 5; for details, also see Supporting Information). On the other hand, in the formation of allylic phosphonium salt **5a**, as shown in Figure 1, the transformation of intermediate **C** into **5a** represents an allylic phosphonium 1,3-rearrangement[28−30] which presumably proceeds via a phosphine-involved S_N2' pathway, rather than via an intramolecular phosphonium 1,3-migration. A ^{31}P NMR monitoring experiment clearly revealed that the signal of intermediate **C** did not show up until the concentration of free PBu_3 substantially decreased (Figure 1). Control experiments also provided solid evidence for the phosphine-involved S_N2' pathway (Scheme 6): addition of $PPhMe_2$ resulted in the formation of **5f** from vinylphosphonium salt **4a** under the mediation of DBU by interception of a trifluoroacetate analogue of intermediate **C**, and no detectable phosphine exchange was observed between **5a** (an analogue of **5e**) and $PPhMe_2$ (for detail, see Supporting Information).

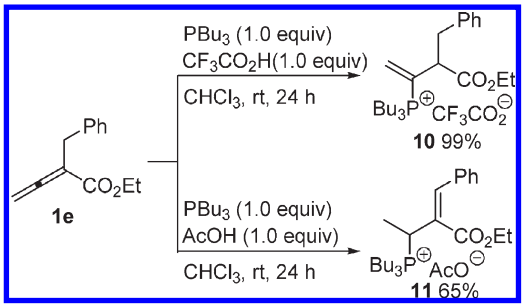
The normal Wittig olefination of allylic phosphonium salt **5a** with *p*-chlorobenzaldehyde **2b** may build a bridge between the formation of allylic phosphonium salt **5** and the occurrence of vinylogous Wittig olefination of allenoate **1a**. Under the aid of K_2CO_3, the olefination product **3b** was readily obtained in 61% yield (Scheme 7). Notably, the stereoselectivity of **3b** in this stepwise synthesis (exclusive *E*-configuration for newly formed alkene and 4:1 *E*/*Z* ratio for the regenerated ones) was in good consistency with that observed in the vinylogous Wittig reaction of **1a** and **2b** (Table 2, entry 2). Additionally, with a mixture of AcOH−NaOAc (1:1) used as an additive, the vinylogous Wittig olefination of allenoate **1a** and electron-deficient 3-nitrobenzaldehyde **2p** proceeded well, giving diene **3p** in 40% yield (Table 2, entry 16). The above results strongly point to a hypothesis that an allylic phosphonium salt such as **5a** is a key intermediate for stereoselective formation of the vinylogous Wittig product **3**.

On the basis of the above mechanistic findings, a plausible mechanism for the vinylogous Wittig reaction of this study is

Scheme 8. Plausible Mechanism for PBu_3-Mediated Vinylogous Wittig Olefination between 1a and Aldehydes



Scheme 9. Reactions of α-Benzyl Allenoate 1e and PBu_3 in the Presence of an Acid



depicted in Scheme 8, which features an allylic phosphorus ylide 1,3-rearrangement pathway. Initially, the nucleophilic attack of PBu_3 at allenoate **1a** forms a resonance-stabilized zwitterionic intermediate **7**. Through a water-aided hydrogen shift,[16,21−23] **7** reversibly converts into an allylic phosphorus ylide **I**,[31] which is subsequently protonated with adventitious protic additives, e.g., water, yielding allylic phosphonium salt **8**. An allylic phosphonium 1,3-rearrangement of **8** via a PBu_3-involved S_N2' process then generates phosphonium salt **9**, which undergoes deprotonation by hydroxyl anion to produce a rearranged allylic phosphorus ylide **II**. Finally, a normal Wittig olefination of the ylide **II** with aldehyde accomplishes the formation of diene **3**. By this mechanism, the high stereoselectivity of the PBu_3-mediated vinylogous Wittig olefination could be well rationalized in terms of the Wittig reaction of a stabilized allylic phosphorus ylide **II** under neutral and salt-free conditions.[15,32] Although an intramolecular allylic phosphonium 1,3-migration process was also proposed by Corey[10] as one of three possible mechanistic pathways for vinylogous Wittig reaction, it was not determined how it worked. On the basis of experimental investigations, our mechanism is explicitly defined as an allylic phosphorus ylide 1,3-rearrangement pathway which encompasses an allylic phosphonium 1,3-rearrangement via a phosphine-involved S_N2' process, while its validity for other allylic phosphorus ylides, including Corey's, needs further efforts to verify.

To rationalize the distinct reactivity between α-methyl allenoate **1a** and α-benzyl allenoate **1e** (normal Wittig reaction),[16] reactions of α-benzyl allenoate **1e** and PBu_3 in the presence of an acidic additive were conducted (Scheme 9). When allenoate **1e**, PBu_3 and equivalent TFA were mixed, a vinylphosphonium salt **10** which is analogous to **4** was obtained in almost quantitative yield. Interestingly, using acetic acid as the additive, an unrearranged allylic phosphonium salt **11** was solely isolated in 65%

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yield under otherwise the same conditions. Presumably, the steric hindrance imposed by the phenyl group retards subsequent allylic phosphonium 1,3-rearrangement of **11** which leads to a vinylogous Wittig transformation. Furthermore, identification of **11** also corroborates the existence of the intermediates **C** and **8**.

Mechanistic findings in this work also provide supportive evidence for typical mechanisms of extensively studied phosphine-mediated reactions of allenoates.[33−35] Though generation of a putative zwitterionic intermediate such as **7** through nucleophilic attack of a tertiary phosphine on an allenoate has been commonly proposed, this type of intermediate has never been directly observed.[36] The successful entrapment and identification of vinylphosphonium salts **4** and **10** and direct NMR observation of intermediates such as **A** and **B** (Figure 1) provide solid evidence for the true existence of the zwitterionic intermediate **7**, for these phosphorus-containing species are most likely generated from the in situ protonation of the zwitterionic intermediate **7** by the corresponding acidic protic additive. In addition, formation of the similar allylic phosphorus ylide **I** is commonly proposed in the mechanisms of the phosphine-mediated reactions of α-alkyl allenoates.[16,25,26,37,38] Identification of allylic phosphonium salt **11** and the intermediates such as **C** (Figure 1, 2), which are most likely generated from protonation of the corresponding allylic phosphorus ylide **I**, certainly validates those plausible mechanisms. It is also noteworthy that NMR monitoring experiments in this work highly corroborate the computational studies by Yu on a water-catalyzed [1,4]-proton shift process.[38]

■ CONCLUSION

We have developed a highly stereoselective PBu_3-mediated vinylogous Wittig reaction between α-methyl allenoates and a variety of aldehydes as a facile synthetic protocol for trisubstituted 1,3-dienes. This reaction represents the first example of practical and synthetically useful vinylogous Wittig reaction. On the basis of a series of mechanistic investigations, a reliable mechanism for the vinylogous Wittig reaction is proposed, which features a water/phosphine-coassisted allylic phosphorus ylide 1,3-rearrangement pathway, rather than previous retro-Diels−Alder ones. Mechanistic insights from this work will benefit the development of vinylogous Wittig reactions. Mechanistic investigations of this work also provide useful experimental evidence for typical mechanisms of actively studied phosphine-mediated reactions of allenoates including [3 + 2] and [4 + 2] annulations,[39,40] γ-umpolung[41−43] and β′-umpolung additions,[25,26] and others.[16] Isolation and identification of phosphonium salts **4**, **5**, **10**, and **11**, and direct spectrometric observation of the transformation process between intermediates **A**, **B**, and **C** give illuminating information for the better understanding those reactions. Our future efforts will be directed toward further investigation on vinylogous Wittig reactions and developing new phosphine-mediated synthetic reactions of allenoates.

■ EXPERIMENTAL SECTION

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere. Column chromatography was performed on silica gel (200−300 mesh). α-Substituted allenoates **1a**,**c**−**e** and α-methyl-deuterated allenoate **1a**-d_3 are known compounds, which were prepared by previous procedures.[40,44] Allenoate **1b** was prepared by a similar method from the literature.[44] ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal reference. ^{31}P NMR experiments were conducted in $CDCl_3$ with 85% H_3PO_4 as the external standard.

Synthesis of Benzyl 2-Methylbuta-2,3-dienoate 1b[45]. To a stirred solution of (benzyloxycarbonylmethylidene)triphenylphosphorane (12.30 g, 30 mmol) in chloroform (50 mL) was added 1.1 equiv of iodomethane (4.69 g, 33 mmol) at room temperature. The reaction mixture was refluxed for 24 h, and all volatile components were evaporated under reduced pressure. The resulting phosphonium salt was dissolved in anhydrous dichloromethane (100 mL), and 2.2 equiv of triethylamine (6.67 g, 66 mmol) was added. After the resulting mixture was stirred for 2 h, a solution of 1.1 equiv of acetyl chloride (2.59 g, 33 mmol) in dichloromethane (30 mL) was dropwise added over 30 min at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for additional 4 h. After most of the solvent was carefully distilled, the residue was thoroughly extracted with petroleum ether (bp 30−60 °C, 5 × 60 mL). The combined extract was concentrated, and the residue was subjected to column chromatography on silica gel (eluant: 5% EtOAc in petroleum ether) to give allenoate **1b** as slightly yellow oil (2.65 g, yield 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 5H), 5.20 (s, 2H), 5.09 (m, 2H), 1.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.3, 167.4, 136.2, 128.5, 128.0, 127.8, 95.3, 78.0, 66.5, 14.7; HRMS-ESI calcd for $C_{12}H_{12}O_2$ $[M + Na]^+$ 211.0730, found 211.0737.

General Procedure for the Vinylogous Wittig Olefination. A solution of allenoate **1a** or **1b** (0.3 mmol) in chloroform (3.0 mL) was slowly dropwise added over 30 min to a stirred solution of PBu_3 (71 μL, 0.3 mmol) and aldehyde **2** (0.2 mmol) in chloroform (2.0 mL) at room temperature. After 12 h, aldehyde **2** was completely consumed in most cases, as monitored by TLC. For less reactive aldehydes, additional allenoate **1** and PBu_3 (0.1−0.2 mmol) were added by means of microsyringe, and the reaction mixture was stirred for a further 12−24 h. A sample was then taken from the reaction mixture for ^{1}H NMR assay to determine the *E*/*Z* ratio of the product **3**. The solvent was removed under reduced pressure, and the residue was purified through column chromatography on silica gel (gradient eluant: 1−5% diethyl ether in petroleum ether) to afford the diene **3** as a pair of *E*/*Z* isomers with respect to its trisubstituted double bonds.

*Ethyl 2-Styrylbut-2-enoate (**3a**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), benzaldehyde (21 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3a** as an inseparable stereoisomeric mixture in 79% yield; (2*E*,4*E*)-**3a**:(2*Z*,4*E*)-**3a** = 6:1; colorless oil; NMR data for (2*E*,4*E*)-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.33 (m, 2H), 7.24 (m, 1H), 7.04 (d, *J* = 16.4 Hz, 1H), 6.90 (d, *J* = 16.4 Hz, 1H), 6.86 (q, *J* = 7.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.00 (d, *J* = 7.4 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 138.0, 137.6, 133.5, 131.2, 128.6, 127.7, 126.5, 120.8, 60.6, 14.7, 14.3; selected NMR data for (2*Z*,4*E*)-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 6.74 (d, *J* = 16.3 Hz, 1H), 6.60 (d, *J* = 16.3 Hz, 1H), 6.12 (q, *J* = 7.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.96 (d, *J* = 7.3 Hz, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 137.2, 134.3, 133.8, 129.2, 127.5, 126.7, 126.4, 60.7, 15.6, 14.3; HRMS-ESI calcd for $C_{14}H_{16}O_2$ $[M + Na]^+$ 239.1042, found 239.1047.

*Ethyl 2-(4-Chlorostyryl)but-2-enoate (**3b**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 4-chlorobenzaldehyde (28 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3b** as a colorless oil in 96% yield; (2*E*,4*E*)-**3b**:(2*Z*,4*E*)-**3b** = 5:1; NMR data for (2*E*,4*E*)-**3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 16.4 Hz, 1H), 6.88 (q, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 16.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.00 (d, *J* = 7.4 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 138.5, 136.0, 133.3, 132.1, 130.9, 128.7, 127.7, 121.3, 60.7, 14.7, 14.2; selected NMR data for (2*Z*,4*E*)-**3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (d, *J* = 16.3 Hz, 1H), 6.55

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(d, J = 16.3 Hz, 1H), 6.14 (q, J = 7.3 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.96 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 140.0, 136.0, 134.5, 133.3, 130.9, 127.6, 123.7, 60.8, 15.8, 14.3; HRMS-ESI calcd for $C_{14}H_{15}ClO_2$ $[M + Na]^+$ 273.0653, found 273.0656.

*Ethyl 2-(3-Chlorostyryl)but-2-enoate (**3c**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 3-chlorobenzaldehyde (28 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3c** as a colorless oil in 99% yield; (2*E*,4*E*)-**3c**:(2*Z*,4*E*)-**3c** = 5:1; NMR data for (2*E*,4*E*)-**3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.31 (d, J = 7.4 Hz, 1H), 7.22 (m, 2H), 7.01 (d, J = 16.4 Hz, 1H), 6.91 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H), 2.01 (d, J = 7.4 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 139.5, 139.0, 134.5, 132.0, 130.8, 129.8, 127.6, 126.2, 124.8, 122.1, 60.7, 14.7, 14.2; selected NMR data for (2*Z*,4*E*)-**3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.73 (d, J = 16.3 Hz, 1H), 6.54 (d, J = 16.3 Hz, 1H), 6.16 (q, J = 7.3 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.97 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 139.1, 135.1, 133.9, 131.5, 128.1, 127.7, 127.4, 126.2, 124.6, 60.8, 15.8, 14.3; HRMS-ESI calcd for $C_{14}H_{15}ClO_2$ $[M + Na]^+$ 273.0653, found 273.0656.

*Ethyl 2-(4-Bromostyryl)but-2-enoate (**3d**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 4-bromobenzaldehyde (37 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3d** as a colorless oil in 71% yield; (2*E*,4*E*)-**3d**:(2*Z*,4*E*)-**3d** = 5:1; NMR data for (2*E*,4*E*)-**3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 16.4 Hz, 1H), 6.89 (d, J = 16.4 Hz, 1H), 6.89 (q, J = 7.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.00 (d, J = 7.4 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 138.7, 136.5, 132.2, 131.7, 130.9, 128.0, 127.9, 121.4, 60.7, 14.8, 14.3; selected NMR data for (2*Z*,4*E*)-**3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 16.3 Hz, 1H), 6.54 (d, J = 16.3 Hz, 1H), 6.15 (q, J = 7.3 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.96 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7, 134.1, 132.5, 131.0, 127.5, 121.6, 60.8, 15.8, 14.4; HRMS-ESI calcd for $C_{14}H_{15}BrO_2$ $[M + Na]^+$ 317.0148, found 317.0142.

*Ethyl 2-(2-Fluorostyryl)but-2-enoate (**3e**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 2-fluorobenzaldehyde (25 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3e** as a colorless oil in 77% yield; (2*E*,4*E*)-**3e**:(2*Z*,4*E*)-**3e** = 5:1; NMR data for (2*E*,4*E*)-**3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, J = 7.6 Hz, 1H), 7.24 (m, 1H), 7.17 (d, J = 16.6 Hz, 1H), 7.12 (m, 1H), 7.04 (m, 1H), 6.98 (d, J = 16.6 Hz, 1H), 6.91 (q, J = 7.4 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.01 (d, J = 7.4 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 160.4 (d, J_{CF} = 249.8 Hz), 138.9, 134.9, 131.2, 128.9 (d, J_{CF} = 8.3 Hz), 127.1 (d, J_{CF} = 3.5 Hz), 125.9 (d, J_{CF} = 3.8 Hz), 124.1 (d, J_{CF} = 3.3 Hz), 123.0 (d, J_{CF} = 10.3 Hz), 115.7 (d, J_{CF} = 22.1 Hz), 60.7, 14.8, 14.2; selected NMR data for (2*Z*,4*E*)-**3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 16.5 Hz, 1H), 6.75 (d, J = 16.5 Hz, 1H), 6.18 (q, J = 7.3 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.97 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 160.2 (d, J_{CF} = 249.8 Hz), 134.3, 128.7 (d, J_{CF} = 8.5 Hz), 126.9 (d, J_{CF} = 3.3 Hz), 125.3 (d, J_{CF} = 11.9 Hz), 121.5 (d, J_{CF} = 3.5 Hz), 115.7 (d, J_{CF} = 22.1 Hz), 60.8, 15.8, 14.3; HRMS-ESI calcd for $C_{14}H_{15}FO_2$ $[M + Na]^+$ 257.0948, found 257.0947.

*Ethyl 2-(4-Fluorostyryl)but-2-enoate (**3f**).* Following the general procedure, the reaction of allenoate **1a** (51 mg, 0.4 mmol), 4-fluorobenzaldehyde (25 mg, 0.2 mmol), and PBu_3 (95 μL, 0.4 mmol) was performed for 24 h to afford **3f** as a colorless oil in 96% yield; (2*E*,4*E*)-**3f**:(2*Z*,4*E*)-**3f** = 4:1; NMR data for (2*E*,4*E*)-**3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, J = 6.2 Hz, 2H), 7.02 (m, 3H), 6.87 (q, J = 7.3 Hz, 1H), 6.82 (d, J = 16.5 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.00 (d, J = 7.3 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 162.4 (d, J_{CF} = 247.2 Hz), 138.1, 133.7 (d, J_{CF} = 3.2 Hz), 132.1, 131.0, 128.0 (d, J_{CF} = 7.9 Hz), 120.5 (d, J_{CF} = 1.9 Hz), 115.5 (d, J_{CF} = 21.7 Hz), 60.6, 14.7, 14.2; selected NMR data for (2*Z*,4*E*)-**3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 6.1 Hz, 2H), 6.66 (d, J = 16.4 Hz, 1H), 6.56 (d, J = 16.4 Hz, 1H), 6.12 (q, J = 7.3 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.96 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 162.4 (d, J_{CF} = 247.3 Hz), 139.9, 131.8, 127.9 (d, J_{CF} = 8.5 Hz), 126.5 (d, J_{CF} = 1.9 Hz), 115.1 (d, J_{CF} = 21.5 Hz), 60.7, 15.7, 14.3; HRMS-ESI calcd for $C_{14}H_{15}FO_2$ $[M + Na]^+$ 257.0948, found 257.0952.

*Ethyl 2-(4-Iodostyryl)but-2-enoate (**3g**).* Following the general procedure, the reaction of allenoate **1a** (51 mg, 0.4 mmol), 4-iodobenzaldehyde (46 mg, 0.2 mmol), and PBu_3 (95 μL, 0.4 mmol) was performed for 24 h to afford **3g** as a colorless oil in 92% yield; (2*E*,4*E*)-**3g**:(2*Z*,4*E*)-**3g** = 5:1; NMR data for (2*E*,4*E*)-**3g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 16.4 Hz, 1H), 6.89 (d, J = 16.4 Hz, 1H), 6.88 (q, J = 7.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.99 (d, J = 7.4 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 138.7, 137.6, 137.0, 132.2, 131.0, 128.1, 121.4, 93.0, 60.7, 14.8, 14.2; selected NMR data for (2*Z*,4*E*)-**3g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.2 Hz, 2H), 6.72 (d, J = 16.2 Hz, 1H), 6.52 (d, J = 16.2 Hz, 1H), 6.14 (q, J = 7.4 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.95 (d, J = 7.4 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 137.3, 134.7, 134.0, 128.1, 128.0, 127.4, 92.7, 60.8, 15.8, 14.3; HRMS-ESI calcd for $C_{14}H_{15}IO_2$ $[M + Na]^+$ 365.0009, found 365.0008.

*Ethyl 2-(3-Bromo-4-methoxystyryl)but-2-enoate (**3h**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 3-bromo-4-methoxybenzaldehyde (43 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3h** as a colorless oil in 82% yield; (2*E*,4*E*)-**3h**:(2*Z*,4*E*)-**3h** = 6:1; NMR data for (2*E*,4*E*)-**3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 2.1 Hz, 1H), 7.33 (dd, J = 8.5, 2.1 Hz, 1H), 6.94 (d, J = 16.4 Hz, 1H), 6.84 (m, 2H), 6.77 (d, J = 16.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 2.00 (d, J = 7.4 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 155.5, 137.9, 131.8, 131.5, 131.0, 130.9, 127.0, 120.0, 112.0, 111.8, 60.7, 56.3, 14.7, 14.3; selected NMR data for (2*Z*,4*E*)-**3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 2.1 Hz, 1H), 7.27 (m, 1H), 6.61 (d, J = 16.2 Hz, 1H), 6.48 (d, J = 16.2 Hz, 1H), 6.10 (q, J = 7.4 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 1.95 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 133.7, 131.5, 127.3, 126.8, 126.1, 60.7, 56.3, 15.7, 14.3; HRMS-ESI calcd for $C_{15}H_{17}BrO_3$ $[M + Na]^+$ 347.0253, found 347.0247.

*Ethyl 2-(2-Methoxystyryl)but-2-enoate (**3i**).* Following the general procedure, the reaction of allenoate **1a** (64 mg, 0.5 mmol), 2-methoxybenzaldehyde (27 mg, 0.2 mmol), and PBu_3 (119 μL, 0.5 mmol) was performed for 36 h to afford **3i** as a colorless oil in 75% yield; (2*E*,4*E*)-**3i**:(2*Z*,4*E*)-**3i** = 5:1; NMR data for (2*E*,4*E*)-**3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.6, 1.4 Hz, 1H), 7.33 (d, J = 16.6 Hz, 1H), 7.22 (m, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 16.6 Hz, 1H), 6.85 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 2.00 (d, J = 7.4 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 157.0, 137.6, 131.8, 128.8, 128.5, 126.5, 124.1, 121.4, 120.6, 110.8, 60.6, 55.5, 14.8, 14.3; selected NMR data for (2*Z*,4*E*)-**3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.6, 1.4 Hz, 1H), 6.77 (d, J = 16.4 Hz, 1H), 6.13 (q, J = 7.3 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.96 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 134.8, 133.3, 128.6, 127.1, 126.7, 126.4, 55.4, 15.7, 14.3; HRMS-ESI calcd for $C_{15}H_{18}O_3$ $[M + Na]^+$ 269.1148, found 269.1152.

*Ethyl 2-(4-Methoxystyryl)but-2-enoate (**3j**).* Following the general procedure, the reaction of allenoate **1a** (64 mg, 0.5 mmol), 4-methoxybenzaldehyde (27 mg, 0.2 mmol), and PBu_3 (119 μL, 0.5 mmol) was performed for 36 h to afford **3j** as a colorless oil in 77% yield; (2*E*,4*E*)-**3j**:(2*Z*,4*E*)-**3j** = 4:1; NMR data for (2*E*,4*E*)-**3j**: ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.40 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 16.4 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H), 6.80 (q, J = 7.4 Hz, 1H), 6.78 (d, J = 16.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.99 (d, J = 7.4 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 159.4, 137.0, 132.8, 131.3, 130.3, 127.7, 118.7, 114.0, 60.6, 55.2, 14.7, 14.2; selected NMR data for (2*Z*,4*E*)-**3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.7 Hz, 2H), 6.62 (d, J = 16.4 Hz, 1H), 6.53 (d, J = 16.4 Hz, 1H), 6.06 (q, J = 7.3 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.94 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 159.2, 132.5, 128.6, 127.6, 124.7, 60.7, 55.2, 15.6, 14.3; HRMS-ESI calcd for $C_{15}H_{18}O_3$ $[M + Na]^+$ 269.1148, found 269.1144.

*Ethyl 2-(4-Methylstyryl)but-2-enoate (**3k**).* Following the general procedure, the reaction of allenoate **1a** (64 mg, 0.5 mmol), 4-methylbenzaldehyde (24 mg, 0.2 mmol), and PBu_3 (119 μL, 0.5 mmol) was performed for 36 h to afford **3k** as a colorless oil in 72% yield; (2*E*,4*E*)-**3k**:(2*Z*,4*E*)-**3k** = 5:1; NMR data for (2*E*,4*E*)-**3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 16.4 Hz, 1H), 6.86 (d, J = 16.4 Hz, 1H), 6.83 (q, J = 7.5 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 2.00 (d, J = 7.5 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 137.7, 137.5, 134.7, 133.3, 131.3, 129.3, 126.4, 119.8, 60.6, 21.2, 14.7, 14.3; selected NMR data for (2*Z*,4*E*)-**3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.1 Hz, 2H), 6.69 (d, J = 16.3 Hz, 1H), 6.56 (d, J = 16.3 Hz, 1H), 6.09 (q, J = 7.3 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.94 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 137.4, 134.5, 133.1, 129.1, 126.3, 125.7, 60.7, 15.7, 14.3; HRMS-ESI calcd for $C_{15}H_{18}O_2$ $[M + Na]^+$ 253.1199, found 253.1205.

*Ethyl 2-(3-Methoxy-2-nitrostyryl)but-2-enoate (**3l**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 3-methoxy-2-nitrobenzaldehyde (36 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3l** as a semisolid in 65% yield; (2*E*,4*E*)-**3l**:(2*Z*,4*E*)-**3l** = 3:1; pure (2*E*,4*E*)-**3l** was obtained by recrystallization from a mixture of ethyl acetate−hexanes (1:20, V/V) as colorless crystals, mp 52−54 °C; NMR data for (2*E*,4*E*)-**3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 8.2 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.00 (q, J = 7.4 Hz, 1H), 6.96 (d, J = 16.3 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.86 (d, J = 16.3 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.99 (d, J = 7.4 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 150.8, 140.9, 138.2, 131.1, 130.7, 130.4, 126.2, 125.5, 117.7, 111.2, 60.9, 56.4, 15.0, 14.2; selected NMR data for (2*Z*,4*E*)-**3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.1 Hz, 1H), 6.81 (d, J = 16.0 Hz, 1H), 6.50 (d, J = 16.0 Hz, 1H), 6.27 (q, J = 7.4 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 3.89 (s, 3H), 2.01 (d, J = 7.4 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 133.9, 132.1, 128.8, 126.4, 121.0, 111.0, 16.0, 14.2; HRMS-ESI calcd for $C_{15}H_{17}NO_5$ $[M + Na]^+$ 314.0999, found 314.0993.

*Ethyl 2-(4-Methoxycarbonylstyryl)but-2-enoate (**3m**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), methyl 4-formylbenzoate (33 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3m** as a colorless oil in 69% yield; (2*E*,4*E*)-**3m**:(2*Z*,4*E*)-**3m** = 3:1; NMR data for (2*E*,4*E*)-**3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 16.4 Hz, 1H), 7.02 (d, J = 16.4 Hz, 1H), 6.93 (q, J = 7.4 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 2.03 (d, J = 7.4 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9(2C), 142.0, 139.5, 135.7, 132.3, 130.0, 126.4, 126.2, 123.1, 60.8, 52.1, 14.8, 14.3; selected NMR data for (2*Z*,4*E*)-**3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 16.3 Hz, 1H), 6.64 (d, J = 16.3 Hz, 1H), 6.21 (q, J = 7.3 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 1.98 (d, J = 7.3 Hz, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 141.7, 134.1, 130.8, 129.2, 129.1, 128.8, 60.8, 15.9, 14.3; HRMS-ESI calcd for $C_{16}H_{18}O_4$ $[M + Na]^+$ 297.1097, found 297.1090.

*Ethyl 2-(2-(Trifluoromethyl)styryl)but-2-enoate (**3n**).* Following the general procedure, the reaction of allenoate **1a** (51 mg, 0.4 mmol), 2-(trifluoromethyl)benzaldehyde (35 mg, 0.2 mmol), and PBu_3 (95 μL, 0.4 mmol) was performed for 24 h to afford **3n** as a colorless oil in 44% yield; (2*E*,4*E*)-**3n**:(2*Z*,4*E*)-**3n** = 4:1; NMR data for (2*E*,4*E*)-**3n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.36 (m, 2H), 6.99 (q, J = 7.4 Hz, 1H), 6.89 (d, J = 16.2 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.03 (d, J = 7.4 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 139.8, 136.6, 131.8, 131.0, 127.6 (q, J_{CF} = 29.8 Hz), 129.4, 127.3, 126.9, 125.8 (q, J_{CF} = 5.8 Hz), 124.8, 124.3 (q, J_{CF} = 273.9 Hz), 60.9, 14.9, 14.2; selected NMR data for (2*Z*,4*E*)-**3n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 15.8 Hz, 1H), 6.22 (q, J = 7.3 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.00 (d, J = 7.3 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 136.4, 131.7, 130.5, 127.1, 126.8, 15.8, 14.1; HRMS-ESI calcd for $C_{15}H_{15}F_3O_2$ $[M + Na]^+$ 307.0920, found 307.0920.

*Ethyl 2-(4-(Trifluoromethyl)styryl)but-2-enoate (**3o**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (35 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3o** as a colorless oil in 60% yield; (2*E*,4*E*)-**3o**:(2*Z*,4*E*)-**3o** = 4:1; NMR data for (2*E*,4*E*)-**3o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 16.4 Hz, 1H), 6.99 (d, J = 16.4 Hz, 1H), 6.94 (q, J = 7.4 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.03 (d, J = 7.4 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.1, 139.5, 132.0, 130.8, 129.5 (q, J_{CF} = 32.3 Hz), 126.6, 125.5 (q, J_{CF} = 3.7 Hz), 124.2 (q, J_{CF} = 271.7 Hz), 123.2, 60.8, 14.8, 14.3; selected NMR data for (2*Z*,4*E*)-**3o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 16.3 Hz, 1H), 6.64 (d, J = 16.3 Hz, 1H), 6.21 (q, J = 7.3 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.99 (d, J = 7.3 Hz, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 135.9, 133.9, 129.2, 127.7, 60.8, 15.8, 14.3; HRMS-ESI calcd for $C_{15}H_{15}F_3O_2$ $[M + Na]^+$ 307.0920, found 307.0918.

*Ethyl 2-(3-Nitrostyryl)but-2-enoate (**3p**):*[12]. Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 3-nitrobenzaldehyde (30 mg, 0.2 mmol), PBu_3 (71 μL, 0.3 mmol), AcOH (12 mg, 0.2 mmol), and AcONa (16 mg, 0.2 mmol) was performed for 12 h to afford **3p** as a semisolid in 40% yield; (2*E*,4*E*)-**3p**:(2*Z*,4*E*)-**3p**:(2*E*,4*Z*)-**3p** = 4:1:1; pure (2*E*,4*E*)-**3p** was obtained by recrystallization from a mixture of ethyl acetate−hexanes (1:20, V/V) as a yellow solid, mp 57−58 °C; NMR data for (2*E*,4*E*)-**3p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.09 (dd, J = 8.0, 1.5 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.16 (d, J = 16.4 Hz, 1H), 7.03 (d, J = 16.4 Hz, 1H), 6.98 (q, J = 7.4 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.05 (d, J = 7.4 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 148.6, 140.1, 139.4, 132.4, 130.9, 130.4, 129.5, 123.5, 122.2, 120.9, 60.8, 14.9, 14.3; HRMS-ESI calcd for $C_{14}H_{15}NO_4$ $[M + Na]^+$ 284.0893, found 284.0888.

*Ethyl 2-(2-(1-Naphthyl)vinyl)but-2-enoate (**3q**).* Following the general procedure, the reaction of allenoate **1a** (64 mg, 0.5 mmol), 1-naphthaldehyde (31 mg, 0.2 mmol), and PBu_3 (119 μL, 0.5 mmol) was performed for 36 h to afford **3q** as a colorless oil in 98% yield; (2*E*,4*E*)-**3q**:(2*Z*,4*E*)-**3q** = 4:1; NMR data for (2*E*,4*E*)-**3q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 16.0 Hz, 1H), 7.87 (m, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 7.0 Hz, 1H), 7.52 (m, 3H), 6.99 (q, J = 7.4 Hz, 1H), 6.98 (d, J = 16.0 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.10 (d, J = 7.4 Hz, 3H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 138.5, 135.4, 134.6, 133.6, 131.3, 130.8, 128.5, 128.1, 126.1, 125.8, 125.6, 123.9, 123.6, 123.4, 60.7, 14.8, 14.3; selected NMR data for (2*Z*,4*E*)-**3q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 7.1 Hz, 1H), 6.82 (d, J = 15.9 Hz, 1H), 6.25 (q, J = 7.3 Hz, 1H), 4.44 (q, J = 7.1 Hz, 2H), 2.05 (d, J = 7.3 Hz, 3H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 138.1, 135.0, 134.8, 134.5, 133.5, 129.6, 127.9, 126.3, 123.7, 123.3, 121.0, 60.7, 15.7, 14.4; HRMS-ESI calcd for $C_{18}H_{18}O_2$ $[M + Na]^+$ 289.1199, found 289.1193.

*Ethyl 2-(2-(2-Furyl)vinyl)but-2-enoate (**3r**).* Following the general procedure, the reaction of allenoate **1a** (51 mg, 0.4 mmol), 2-furylaldehyde (19 mg, 0.2 mmol), and PBu_3 (95 μL, 0.4 mmol) was performed for 24 h to afford **3r** as a yellow oil in 87% yield; (2*E*,4*E*)-**3r**:(2*Z*,4*E*)-**3r** = 5:1; NMR data for (2*E*,4*E*)-**3r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 6.99 (d, J = 16.3 Hz, 1H), 6.86 (d, J = 16.3 Hz, 1H), 6.82 (q, J = 7.4 Hz, 1H), 6.39 (m, 1H), 6.31 (d, J = 3.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.99 (d, J = 7.4 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 153.3, 142.2, 138.0, 130.7, 120.9, 118.8, 111.6, 109.2, 60.6, 14.5, 14.3; selected NMR data for (2*Z*,4*E*)-**3r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.67 (d, J = 16.1 Hz, 1H), 6.25 (d, J = 3.1 Hz, 1H), 6.11 (q, J = 7.4 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 1.95 (d, J = 7.4 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 142.1, 134.2, 134.0, 125.3, 117.2, 111.5, 108.6, 60.7, 15.7, 14.3; HRMS-ESI calcd for $C_{12}H_{14}O_3$ [M + Na]$^+$ 229.0835, found 229.0843.

*Ethyl 2-(2-(2-Thiofuryl)vinyl)but-2-enoate (**3s**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 2-thiofurylaldehyde (22 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3s** as a colorless oil in 83% yield; (2*E*,4*E*)-**3s**:(2*Z*,4*E*)-**3s** = 4:1; NMR data for (2*E*,4*E*)-**3s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 16.1 Hz, 1H), 7.18 (d, J = 4.9 Hz, 1H), 7.02 (s, 1H), 6.98 (m, 1H), 6.83 (q, J = 7.4 Hz, 1H), 6.74 (d, J = 16.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.99 (d, J = 7.4 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 143.1, 138.0, 134.0, 130.6, 127.6, 126.4, 124.5, 120.1, 60.6, 14.6, 14.2; selected NMR data for (2*Z*,4*E*)-**3s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 4.2 Hz, 1H), 6.56 (d, J = 16.1 Hz, 1H), 6.09 (q, J = 7.3 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.95 (d, J = 7.3 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 142.6, 133.8, 127.4, 126.3, 126.0, 124.3, 122.3, 60.7, 14.6, 14.3; HRMS-ESI calcd for $C_{12}H_{14}O_2S$ [M + Na]$^+$ 245.0607, found 245.0611.

*Ethyl 2-(2-(3-Pyridyl)vinyl)but-2-enoate (**3t**).* Following the general procedure, the reaction of allenoate **1a** (38 mg, 0.3 mmol), 3-pyridylaldehyde (21 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3t** as a brown oil in 60% yield; (2*E*,4*E*)-**3t**:(2*Z*,4*E*)-**3t**:(2*E*,4*Z*)-**3t** = 8:2:1; NMR data for (2*E*,4*E*)-**3t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.48 (d, J = 4.6 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.27 (dd, J = 7.9, 4.9 Hz, 1H), 7.08 (d, J = 16.5 Hz, 1H), 6.97 (d, J = 16.5 Hz, 1H), 6.94 (q, J = 7.4 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.02 (d, J = 7.4 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 148.6, 148.5, 139.3, 133.2, 132.7, 130.6, 129.7, 123.4, 122.7, 60.7, 14.7, 14.2; selected ^{1}H NMR data for (2*Z*,4*E*)-**3t**: δ 6.80 (d, J = 16.3 Hz, 1H), 6.60 (d, J = 16.3 Hz, 1H), 6.21 (q, J = 7.4 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.99 (d, J = 7.4 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H); selected ^{1}H NMR data for (2*E*,4*Z*)-**3t**: δ 6.62 (d, J = 12.6 Hz, 1H), 6.34 (d, J = 12.6 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 1.60 (d, J = 7.2 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); HRMS-ESI calcd for $C_{13}H_{15}NO_2$ [M + Na]$^+$ 240.0995, found 240.0992.

*Ethyl 2-Ethylidene-6-phenylhexa-3,5-dienoate (**3u**).* Following the general procedure, the reaction of allenoate **1a** (51 mg, 0.4 mmol), cinnamaldehyde (26 mg, 0.2 mmol), and PBu_3 (95 μL, 0.4 mmol) was performed for 24 h to afford **3u** as a yellow oil in 85% yield; (2*E*,4*E*,6*E*)-**3u**:(2*Z*,4*E*,6*E*)-**3u** = 3:1; NMR data for (2*E*,4*E*,6*E*)-**3u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.23 (m, 1H), 6.90 (m, 2H), 6.79 (q, J = 7.4 Hz, 1H), 6.63 (d, J = 14.5 Hz, 1H), 6.49 (d, J = 14.6 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.96 (d, J = 7.4 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 137.7, 137.3, 134.0, 133.4, 131.2, 129.8, 128.6, 127.6, 126.4, 124.7, 60.6, 14.6, 14.3; selected NMR data for (2*Z*,4*E*,6*E*)-**3u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (d, J = 16.5 Hz, 1H), 6.31 (d, J = 15.7 Hz, 1H), 6.04 (q, J = 7.3 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.92 (d, J = 7.3 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 133.6, 132.9, 130.6, 129.9, 129.0, 127.5, 126.3, 60.7, 15.7, 14.3; HRMS-ESI calcd for $C_{16}H_{18}O_2$ [M + Na]$^+$ 265.1199, found 265.1204.

*Diethyl 2,2′-(2,2′-(1,4-Phenylene)bis(ethene-2,1-diyl))dibut-2-enoate (**3v**):*[46]. Following the general procedure, the reaction of allenoate **1a** (76 mg, 0.6 mmol), terephthalaldehyde (27 mg, 0.2 mmol), and PBu_3 (190 μL, 0.8 mmol) was performed for 12 h to afford **3v** as a colorless oil in 56% yield; (2*E*,4*E*)-**3v**:(2*Z*,4*E*)-**3v**:(2*E*,4*Z*)-**3v** = 10: 2: 1; NMR data for (2*E*,4*E*)-**3v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 4H), 7.04 (d, J = 16.4 Hz, 2H), 6.92 (d, J = 16.4 Hz, 2H), 6.86 (q, J = 7.3 Hz, 2H), 4.27 (q, J = 7.1 Hz, 4H), 2.02 (d, J = 7.3 Hz, 6H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 138.0, 137.1, 133.0, 131.2, 126.8, 120.7, 60.6, 14.7, 14.3; selected ^{1}H NMR data for (2*Z*,4*E*)-**3v**: δ 6.75 (d, J = 16.2 Hz, 2H), 6.58 (d, J = 16.2 Hz, 2H), 6.13 (q, J = 7.3 Hz, 2H), 4.36 (q, J = 7.1 Hz, 4H), 1.96 (d, J = 7.3 Hz, 6H), 1.39 (t, J = 7.1 Hz, 6H); selected ^{1}H NMR data for (2*E*,4*Z*)-**3v**: δ 6.63 (d, J = 12.0 Hz, 2H), 6.21 (d, J = 12.0 Hz, 2H), 4.09 (q, J = 7.1 Hz, 4H), 1.63 (d, J = 7.2 Hz, 6H), 1.16 (t, J = 7.1 Hz, 6H); HRMS-ESI calcd for $C_{22}H_{26}O_4$ [M + Na]$^+$ 377.1723, found 377.1721.

*Benzyl 2-(4-Chlorostyryl)but-2-enoate (**3w**).* Following the general procedure, the reaction of benzyl α-methyl allenoate **1b** (56 mg, 0.3 mmol), 4-chlorobenzaldehyde (28 mg, 0.2 mmol), and PBu_3 (71 μL, 0.3 mmol) was performed for 12 h to afford **3w** as a colorless oil in 98% yield; (2*E*,4*E*)-**3w**:(2*Z*,4*E*)-**3w** = 6:1; NMR data for (2*E*,4*E*)-**3w**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.33 (m, 7H), 7.28 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 16.4 Hz, 1H), 6.93 (q, J = 7.4 Hz, 1H), 6.88 (d, J = 16.4 Hz, 1H), 5.24 (s, 2H), 1.99 (d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 139.2, 136.01, 135.95, 133.3, 132.2, 130.5, 128.7, 128.5, 128.2, 128.1, 127.7, 121.1, 66.4, 14.8; selected NMR data for (2*Z*,4*E*)-**3w**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, J = 16.3 Hz, 1H), 6.46 (d, J = 16.3 Hz, 1H), 6.14 (q, J = 7.3 Hz, 1H), 5.32 (s, 2H), 1.93 (d, J = 7.3 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 135.7, 135.5, 135.0, 133.7, 133.1, 130.6, 128.6, 128.4, 128.0, 127.5, 127.1, 66.5, 15.8; HRMS (ESI) calcd for $C_{19}H_{17}ClO_2$ [M + Na]$^+$ 335.0809, found 335.0810.

*Diethyl cis-3-Phenyl-4-styrylcyclohex-1-ene-1,4-dicarboxylate (**D1**).* yield 31%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.10 (m, 10H), 7.07 (d, J = 4.8 Hz, 1H), 6.21 (d, J = 16.4 Hz, 1H), 5.73 (d, J = 16.4 Hz, 1H), 4.41 (d, J = 4.8 Hz, 1H), 4.22 (m, 4H), 2.64 (dd, J = 18.7, 5.6 Hz, 1H), 2.48 (m, 1H), 2.31 (dd, J = 13.5, 6.3 Hz, 1H), 1.89 (ddd, J = 13.5, 10.9, 6.3 Hz, 1H), 1.28 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 167.0, 139.3, 138.2, 136.9, 131.8, 130.7, 130.1, 129.4, 128.4, 127.9, 127.4, 127.2, 126.2, 61.3, 60.5, 51.2, 47.7, 24.5, 22.1, 14.2, 14.1; HRMS (ESI) calcd for $C_{26}H_{28}O_4$ [M + Na]$^+$ 427.1880, found 427.1878.

General Procedure for Formation of Phosphonium Salts 4, 5, 10, and 11. To a stirred solution of allenoate **1a** or **1e** (0.2 mmol) and an acidic additive (0.2 mmol) in anhydrous chloroform (2.0 mL) was added phosphine (0.2 mmol) at room temperature. The resulting reaction mixture was stirred for 12 or 24 h. After evaporation of all volatile components under reduced pressure, the corresponding phosphonium salt was obtained. By the above procedure, phosphonium salts **4a**, **4b**, and **10** were obtained in quantitative yield and high purity. For pure phosphonium salts **4c**, **5a**−**d**, and **11**, purification through column chromatography on silica gel (gradient eluant: 10−50% EtOH in dichloromethane) was needed.

*Tributyl(4-ethoxy-3-methyl-4-oxobut-1-en-2-yl)phosphonium Trifluoroacetate (**4a**).* yield 99%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, J_{HP} = 41.3 Hz, 1H), 6.41 (d, J_{HP} = 19.6 Hz, 1H), 4.18 (m, 2H), 3.52 (dq, J_{HP} = 14.0 Hz, J = 7.0 Hz, 1H), 2.43 (m, 6H), 1.49 (m, 15H), 1.27 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 6.8 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (d, J_{CP} = 4.3 Hz), 160.3 (q, J_{CF} = 35.2 Hz), 137.3 (d, J_{CP} = 6.0 Hz), 130.1 (d, J_{CP} = 67.4 Hz), 116.6 (q, J_{CF} = 293.0 Hz), 62.0, 40.6 (d, J_{CP} = 9.3 Hz), 23.6 (d, J_{CP} = 16.0 Hz), 23.4 (d, J_{CP} = 4.4 Hz), 18.4 (d, J_{CP} = 47.9 Hz), 17.7 (d, J_{CP} = 4.3 Hz), 13.9, 13.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.8; HRMS-ESI calcd for $C_{19}H_{38}O_2P^+$ 329.2604, found 329.2610.

*Dimethylphenyl(4-ethoxy-3-methyl-4-oxobut-1-en-2-yl)phosphonium Trifluoroacetate (**4b**).* yield 99%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 3H), 7.67 (m, 2H), 6.54 (d, J_{HP} = 45.3 Hz, 1H), 6.36 (d, J_{HP} = 22.6 Hz, 1H), 4.03 (m, 2H), 3.42 (dq, J_{HP} = 13.7 Hz, J = 6.7 Hz,

1H), 2.41 (d, J_{HP} = 13.7 Hz, 6H), 1.42 (d, J = 6.9 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 (d, J_{CP} = 3.6 Hz), 160.6 (q, J_{CF} = 33.6 Hz), 136.8 (d, J_{CP} = 8.6 Hz), 134.6 (d, J_{CP} = 2.8 Hz), 133.1 (d, J_{CP} = 75.7 Hz), 131.7 (d, J_{CP} = 10.3 Hz), 130.0 (d, J_{CP} = 12.6 Hz), 119.6 (d, J_{CP} = 86.5 Hz), 117.0 (q, J_{CF} = 295.3 Hz), 61.8, 41.1 (d, J_{CP} = 10.8 Hz), 16.8 (d, J_{CP} = 5.3 Hz), 13.7, 8.9 (d, J_{CP} = 56.2 Hz), 8.5 (d, J_{CP} = 56.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.5; HRMS-ESI calcd for $C_{15}H_{22}O_2P^+$ 265.1352, found 265.1353.

*Triphenyl(4-ethoxy-3-methyl-4-oxobut-1-en-2-yl)phosphonium Trifluoroacetate (**4c**).* yield 94%; white solid; mp 131−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, J = 6.9 Hz, 3H), 7.73 (m, 12H), 7.02 (d, J_{HP} = 47.2 Hz, 1H), 6.37 (d, J_{HP} = 22.1 Hz, 1H), 3.86 (m, 1H), 3.69 (m, 1H), 3.58 (m, 1H), 1.56 (d, J = 7.1 Hz, 3H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (d, J_{CP} = 2.7 Hz), 160.1 (q, J_{CF} = 33.2 Hz), 141.8 (d, J_{CP} = 7.7 Hz), 135.5 (d, J_{CP} = 2.7 Hz), 134.3 (d, J_{CP} = 10.3 Hz), 130.1 (d, J_{CP} = 75.3 Hz), 130.4 (d, J_{CP} = 12.9 Hz), 117.3 (q, J_{CF} = 298.2 Hz), 116.4 (d, J_{CP} = 88.1 Hz), 61.6, 41.8 (d, J_{CP} = 11.0 Hz), 16.9 (d, J_{CP} = 6.0 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.9; HRMS-ESI calcd for $C_{25}H_{26}O_2P^+$ 389.1665, found 389.1669.

*Tributyl(2-(ethoxycarbonyl)but-2-enyl)phosphonium Acetate (**5a**).* yield 89%; (*Z*)-**5a**:(*E*)-**5a** = 6:1; colorless oil; NMR data for (*Z*)-**5a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.87 (d, J_{HP} = 16.1 Hz, 2H), 2.42 (m, 6H), 2.13 (m, 3H), 1.99 (s, 3H), 1.50 (m, 12H), 1.32 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 6.5 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 166.7, 145.7 (d, J_{CP} = 8.7 Hz), 122.2 (d, J_{CP} = 9.9 Hz), 61.5, 23.9 (d, J_{CP} = 15.5 Hz), 23.8, 23.6 (d, J_{CP} = 4.8 Hz), 19.1 (d, J_{CP} = 46.2 Hz), 19.0 (d, J_{CP} = 48.0 Hz), 16.0 (d, J_{CP} = 2.0 Hz), 14.1, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.4; selected NMR data for (*E*)-**5a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (m, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.86 (d, J_{HP} = 16.0 Hz, 2H), 2.10 (m, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.3, 24.2 (d, J_{CP} = 14.2 Hz), 18.8 (d, J_{CP} = 46.5 Hz), 14.2, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1; HRMS-ESI calcd for $C_{19}H_{38}O_2P^+$ 329.2604, found 329.2603.

*Tributyl(2-(ethoxycarbonyl)but-2-enyl)phosphonium Benzoate (**5b**).* yield 82%; (*Z*)-**5b**:(*E*)-**5b** = 5:1; pale yellow oil; NMR data for (*Z*)-**5b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 3.6 Hz, 2H), 7.31 (m, 3H), 7.23 (m, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.94 (d, J_{HP} = 16.0 Hz, 2H), 2.41 (m, 6H), 2.14 (t, J = 6.2 Hz, 3H), 1.46 (m, 12H), 1.31 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 6.4 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 166.7, 145.8 (d, J_{CP} = 9.0 Hz), 140.0, 129.3, 128.7, 127.1, 122.2 (d, J_{CP} = 9.9 Hz), 61.5, 23.9 (d, J_{CP} = 15.4 Hz), 23.7 (d, J_{CP} = 4.8 Hz), 19.1 (d, J_{CP} = 46.0 Hz), 18.9 (d, J_{CP} = 46.4 Hz), 16.1 (d, J_{CP} = 1.5 Hz), 14.1, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.5; selected NMR data for (*E*)-**5b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (m, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.90 (d, J_{HP} = 16.0 Hz, 2H), 2.34 (m, 6H), 2.06 (t, J = 6.2 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0 (d, J_{CP} = 9.3 Hz), 120.6 (d, J_{CP} = 9.8 Hz), 61.2, 23.9 (d, J_{CP} = 15.2 Hz), 19.1 (d, J_{CP} = 48.1 Hz), 16.6 (d, J_{CP} = 1.9 Hz), 14.2, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2; HRMS-ESI calcd for $C_{19}H_{38}O_2P^+$ 329.2604, found 329.2609.

*Tributyl(2-(ethoxycarbonyl)but-2-enyl)phosphonium Phenolate (**5c**).* yield 74%; (*Z*)-**5c**:(*E*)-**5c** = 10:1; pale yellow oil; NMR data for (*Z*)-**5c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 1H), 7.11 (t, J = 7.8 Hz, 2H), 6.95 (d, J = 7.8 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.70 (d, J_{HP} = 15.5 Hz, 2H), 2.32 (m, 6H), 2.10 (dd, J = 7.3 Hz, J_{HP} = 4.4 Hz, 3H), 1.45 (m, 12H), 1.31 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 6.0 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 157.9, 145.7 (d, J_{CP} = 8.9 Hz), 128.8, 121.9 (d, J_{CP} = 9.9 Hz), 118.3, 115.7, 61.5, 23.8 (d, J_{CP} = 15.4 Hz), 23.5 (d, J_{CP} = 5.0 Hz), 19.4 (d, J_{CP} = 48.1 Hz), 19.2 (d, J_{CP} = 46.1 Hz), 16.5 (d, J_{CP} = 1.8 Hz), 14.0, 13.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.4; selected NMR data for (*E*)-**5c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (q, J = 7.1 Hz, 2H), 3.66 (d, J_{HP} = 15.5 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.3, 23.8 (d, J_{CP} = 15.3 Hz), 19.0 (d, J_{CP} = 46.3 Hz), 14.1, 13.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; HRMS-ESI calcd for $C_{19}H_{38}O_2P^+$ 329.2604, found 329.2608.

*Dimethylphenyl(2-(ethoxycarbonyl)but-2-enyl)phosphonium Acetate (**5d**).* yield 94%; (*Z*)-**5d**:(*E*)-**5d** = 8:1; colorless oil; NMR data for (*Z*)-**5d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.55 (m, 5H), 7.16 (m, 1H), 4.10 (d, J_{HP} = 16.4 Hz, 2H), 3.93 (q, J = 7.1 Hz, 2H), 2.50 (d, J_{HP} = 14.1 Hz, 6H), 2.01 (s, 3H), 1.90 (dd, J = 7.2, 5.0 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 166.0, 145.8 (d, J_{CP} = 10.0 Hz), 134.3 (d, J_{CP} = 3.0 Hz), 131.4 (d, J_{CP} = 9.6 Hz), 129.7 (d, J_{CP} = 12.3 Hz), 121.6 (d, J_{CP} = 10.8 Hz), 120.6 (d, J_{CP} = 82.3 Hz), 61.4, 24.0 (d, J_{CP} = 50.8 Hz), 23.8, 15.9 (d, J_{CP} = 2.3 Hz), 14.0, 8.1 (d, J_{CP} = 54.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.4; selected NMR data for (*E*)-**5d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (m, 1H), 2.44 (d, J_{HP} = 14.1 Hz, 6H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.0; HRMS-ESI calcd for $C_{15}H_{22}O_2P^+$ 265.1352, found 265.1358.

*Tributyl(3-benzyl-4-ethoxy-4-oxobut-1-en-2-yl)phosphonium Trifluoroacetate (**10**).* yield 99%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 3H), 7.18 (d, J = 6.9 Hz, 2H), 6.79 (d, J_{HP} = 40.9 Hz, 1H), 6.61 (d, J_{HP} = 19.6 Hz, 1H), 4.16 (m, 2H), 3.58 (m, 1H), 3.37 (dd, J = 13.7, 6.6 Hz, 1H), 3.00 (dd, J = 13.7, 9.0 Hz, 1H), 2.33 (m, 6H), 1.42 (dt, J_{HP} = 14.7 Hz, J = 7.1 Hz, 6H), 1.30 (m, 6H), 1.23 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7 (d, J_{CP} = 3.8 Hz), 160.8 (q, J_{CF} = 33.7 Hz), 138.8 (d, J_{CP} = 5.6 Hz), 136.8, 129.3, 128.9, 127.9 (d, J_{CP} = 67.1 Hz), 127.5, 116.9 (q, J_{CF} = 294.4 Hz), 62.2, 48.0 (d, J_{CP} = 9.1 Hz), 38.7 (d, J_{CP} = 4.0 Hz), 23.8 (d, J_{CP} = 16.3 Hz), 23.4 (d, J_{CP} = 4.5 Hz), 18.4 (d, J_{CP} = 47.5 Hz), 13.9, 13.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.8; HRMS-ESI calcd for $C_{25}H_{42}O_2P^+$ 405.2917, found 405.2910.

*Tributyl(3-(ethoxycarbonyl)-4-phenylbut-3-en-2-yl)phosphonium Acetate (**11**).* yield 65%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J_{HP} = 4.4 Hz, 1H), 7.31 (m, 3H), 7.23 (m, 2H), 4.85 (dq, J_{HP} = 14.5 Hz, J = 7.2 Hz, 1H), 4.09 (m, 2H), 2.47 (m, 6H), 1.99 (s, 3H), 1.55 (m, 15H), 1.02 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 169.2, 140.8 (d, J_{CP} = 10.5 Hz), 135.0 (d, J_{CP} =1.8 Hz), 128.6, 128.2(2C), 128.1, 61.5, 33.69 (d, J_{CP} = 43.6 Hz), 24.9, 24.16 (d, J_{CP} = 5.2 Hz), 24.06 (d, J_{CP} = 4.8 Hz), 18.46 (d, J_{CP} = 44.8 Hz), 13.4(2C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.4; HRMS-ESI calcd for $C_{25}H_{42}O_2P^+$ 405.2917, found 405.2913.

Typical Procedure for ^{31}P and ^{1}H NMR Monitoring Experiments. To a solution of allenoate **1a** (13 mg, 0.1 mmol) and acetic acid (6 mg, 0.1 mmol) in $CDCl_3$ (0.5 mL) in a N_2-filled NMR tube was added PBu_3 (24 μL, 0.1 mmol) via a microsyringe at room temperature. The sample was shaken up and immediately applied to ^{31}P NMR and ^{1}H NMR monitoring. To reduce time delay, the first NMR spectrum was acquired before a shimming operation was properly done. The sample was then continuously scanned at certain intervals as shown in the stacked NMR spectra (Figures 1 and 2). Selected NMR data for intermediates **A**, **B**, and **C** are listed below.

A: ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.2; ^{1}H NMR data (400 MHz, $CDCl_3$) δ 6.51 (d, J_{HP} = 41.0 Hz, 1H, =CH_2), 6.32 (d, J_{HP} = 18.9 Hz, 1H, =CH_2), 4.11 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 3.49 (dq, J_{HP} = 14.0, J = 7.0 Hz, 1H, CHCH$_3$), 1.90 (s, 3H, O=C−CH_3), 1.26 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1 (d, J_{CP} = 6.0 Hz, =CH_2).

B: ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 2.16 (d, J_{HP} = 13.2 Hz, 3H, P−C−CH_3), 2.12 (s, 3H, =C−CH_3), 1.90 (s, 3H, O=C−CH_3), 1.23 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3).

C: ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (d, J_{HP} = 2.9 Hz, 1H, =CH_2), 6.42 (d, J_{HP} = 3.9 Hz, 1H, =CH_2), 4.43 (m, 1H, P−CH), 1.90 (s, 3H, O=C−CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1 (=CH_2).

DBU-Aided Formation of 5 from 4 (Scheme 5). To a solution of phosphonium salt **4** (0.05 mmol) in $CDCl_3$ (0.5 mL) in a N_2-filled NMR tube was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (8 mg, 0.05 mmol) at room temperature. The sample was shaken and subjected to ^{31}P NMR monitoring, which unveiled a clear transformation process of **4** into the corresponding phosphonium salt **5**. The yields and *Z*/*E* ratios of **5** were measured at 1 h by ^{31}P NMR integration.

Control Experiments (Scheme 6). To a solution of phosphonium salt **4a** (27 mg, 0.06 mmol) and $PPhMe_2$ (7 mg, 0.05 mmol) in $CDCl_3$ (0.5 mL) in a N_2-filled NMR tube was added base DBU (8 mg, 0.05 mmol) at room temperature. The resulting sample was shaken and subjected to ^{31}P NMR monitoring. At 1 h, ^{31}P NMR measurement unveiled that a phosphonium salt **5f**, generated from phosphine exchange, was formed in 25% yield along with the normal product **5e** (8% yield) and PBu_3 (26% yield). In another experiment, a sample of phosphonium salt **5a** (19 mg, 0.05 mmol) and $PPhMe_2$ (7 mg, 0.05 mmol) in $CDCl_3$ (0.5 mL) in a N_2-filled NMR tube was subjected to ^{31}P NMR monitoring at room temperature. ^{31}P NMR measurement indicated no direct phosphine exchange between **5a**, and free $PPhMe_2$ was detected over 48 h.

Formation of Olefination Product 3b from 5a (Scheme 7). A mixture of **5a** (58 mg, 0.15 mmol), K_2CO_3 (21 mg, 0.15 mmol), and 4-chlorobenzaldehyde (14 mg, 0.1 mmol) in chloroform (2.0 mL) was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was isolated by column chromatography on silica gel (eluant: 5% diethyl ether in petroleum ether) to afford **3b** as an isomeric mixture in 61% yield with a 4:1 ratio of (2*E*,4*E*)-**3b** versus (2*Z*,4*E*)-**3b**.

■ ASSOCIATED CONTENT

Supporting Information. Copies of 1D-NMR (^1H, ^{13}C, ^{31}P) and 2D-NMR spectra of new compounds and NMR monitoring spectra; X-ray crystallographic data (CIF file) for (*E*,*E*)-**3l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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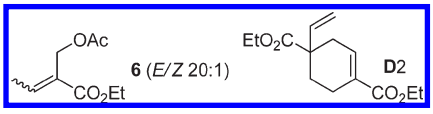

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