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Syntheses of α,β-Unsaturated Carbonyl Compounds from the Reactions of Monosubstituted Ozonides with Stable Phosphonium Ylides

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Abstract—Ozonides derived from terminal alkenes reacted with 1.3 mol equiv. of stable phosphonium ylides to give (*E*)-α,β-unsaturated carbonyl compounds in good to excellent yields. No reducing agent is needed in the reaction. However, alkoxyalkyl-substituted ozonides afforded a mixture of (*Z*)- and (*E*)-α,β-unsaturated carbonyl compounds under similar condition. The *E*/*Z* isomeric ratio is affected by the position of the heteroatom in the substituent of the ozonides. The possible mechanism of this reaction will be discussed.

Introduction

The ozonolysis of alkenes is an important technique in organic synthesis.[1] The intermediate was either ozonide or α-alkoxy hydrogen peroxide dependent on the solvent used in the reaction. Without isolation, they were usually reduced directly to the corresponding carbonyls or alcohols.[2] They might also be oxidized to the corresponding carboxylic acids.[3] In our earlier communication, we have reported that the reaction of monosubstituted ozonide with 1.3 mol equiv. of stable phosphonium ylide afforded the (*E*)-α,β-unsaturated carbonyl compounds in excellent yields.[4] It is worthy to mention that no reducing agent was needed in the reaction. In other words, this Wittig-type reaction can be used ozonide instead of aldehyde as starting material. Interestingly, we needed only 1.3 mol equiv. of the stable phosphonium ylide to achieve the high yield reaction. Apparently, the α,β-unsaturated carbonyl products were formed by the Wittig reaction. However, we still need to work out several puzzles in order to understand its reaction mechanism. For example, we need to know: (1) why we need only 1.3 mol equiv. of the stable phosphonium ylide; (2) what the role of the stable phosphonium ylide is in the reaction; (3) how the aldehyde is formed from the corresponding ozonides without reducing agent. In this report, we will summarize the scope of this reaction and figure out its possible reaction mechanism.

Results and Discussion

The ozonide formation and its reaction with phosphonium ylides

The terminal alkenes (i.e. the δ,ϵ-unsaturated ketones **1a**–**1e**) were prepared from the corresponding conjugated enone and allyltrimethylsilane in the presence of titanium (IV) chloride according to the reported procedure.[5] When 3-allylcyclohexan-1-one (**1a**) was carried out the ozonolysis in CH_2Cl_2 at −78°C followed by the addition of excess amount of methyl sulfide, the reaction was incomplete even after 12 h stirring at rt. Presumably, the reduction of this ozonide by methyl sulfide is sluggish. We did not wait until the reaction completed and did not try to separate the ozonide **2a** and aldehyde **3a** although they were separable. The mixtures were reacted with 2 mol equiv. of $Ph_3P{=}CHCO_2Me$ (**4a**) at rt. We found that both the ozonide **2a** and aldehyde **3a** were consumed completely and the corresponding (*E*)-α,β-unsaturated ester **5aa** was isolated in high yield. The yield is higher than that we estimated from the aldehyde present in the reaction mixture. This result indicated that both the aldehyde and ozonide have reactivity with stable phosphonium ylide. In order to prove this hypothesis, we prepared and isolated the ozonide **2a** and found that it could react with $Ph_3P{=}CHCO_2Me$ (**4a**) (2 mol equiv.) at rt for 12 h to give compound **5aa** in high yield. At this stage, we understand that the ozonide has reactivity with stable phosphonium ylide to give the Wittig

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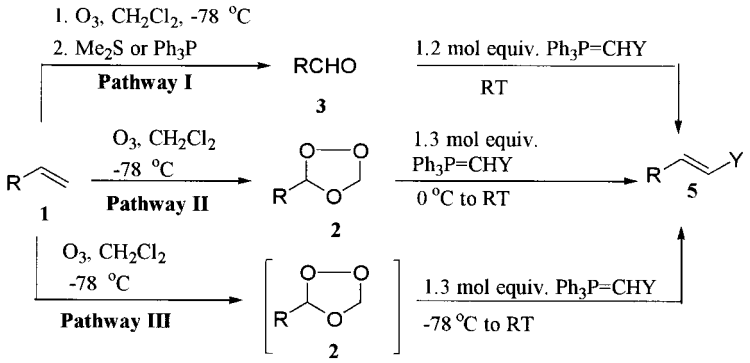


Scheme 1. *Phosphonium ylide:* Y=CO_2Me (**4a**), Y=COPh (**4b**), Y=COMe (**4c**), Y=CO_2CH_2Ph (**4d**), Y=CO_2Bu-*t* (**4e**), Y=CHO (**4f**), Y=Ph (**4g**).

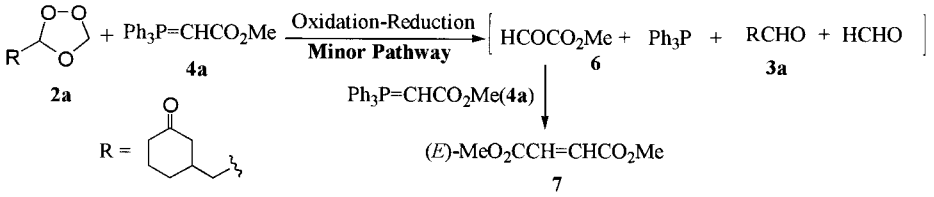
reaction product. In order to investigate its optimal conditions, we found that 1.3 mol equiv. of the stable phosphonium ylide were sufficient to complete the reaction and the product was isolated in 85% yield (Scheme 1; Entry 1, Table 1). Intrigued by these two interesting observations, we started our work in the area of the ozonide chemistry.[6]

In general, the mono-substituted ozonides were prepared from terminal alkenes in CH_2Cl_2 at −78°C in excellent yields and purified by silica gel column chromatography. They were stable in the freezer for more than 2 weeks and decomposed slowly at room temperature.[6a] When the ozonide **2a** was treated with phosphonium ylide **4a** (1.3 mol equiv.) in CH_2Cl_2 at rt for 12 h, we obtained the Wittig reaction product in high yield. However, we isolated dimethyl fumarate (**7**) as byproduct in 2–3% yield. The phosphonium ylide **4a** was known to be oxidized by oxaziridine to give compound **7**.[7] Therefore, the formation of the minor product **7** was rationalized as follows. The phosphonium ylide **4a** was oxidized by ozonide **2a** to give methyl glyoxylate (**6**), which subsequently underwent Wittig reaction with the remaining phosphonium ylide **4a** to give dimethyl fumarate (**7**) (Eq. (1)). Interestingly, this side reaction could be avoided if the reaction was controlled at 0°C and then warmed slowly to room temperature. By using this protocol, the ozonides reacted with 1.3 mol equiv. of $Ph_3P{=}CHCO_2Me$ (**4a**) to give (*E*)-α,β-unsaturated esters in excellent yields (Pathway II of Scheme 1; Entries 1, 3, 5, 7 and 9, Table 1). The (*E*)-α,β-unsaturated ketones could also be formed in modest to good yields from the corresponding ozonides (Entries 2, 4, 6, 8 and 10). Interestingly, for compounds **2a**–**2e**, the phosphonium ylides could chemoselectively react with the ozonide moieties in the presence of keto groups (Entries 1–10).

Since the ozonide formation from terminal olefins was excellent, it was feasible to carry out the ozonolysis followed by reaction with phosphonium ylide in the same flask. The ozonide was generated at −78°C and phosphonium ylide was subsequently added to the solution, which was then warmed up slowly to ambient temperature (Pathway III, Scheme 1). The α,β-unsaturated carbonyl compounds (i.e. **5da**, **5db**, **5ea** and **5eb**) were formed in excellent yields by this one-flask process (Entries 7–10, Table 1). In general, the yields from Pathway III are better than those from Pathway II starting from alkenes **1** (Entries 7–10). The α,β-unsaturated carbonyl compounds tethered with a keto group (Entries 1–10, Table 1) were useful starting materials in the construction of the bridgehead hydroxyl compounds stereoselectively induced by samarium (II) iodide.[8]

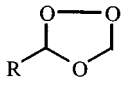
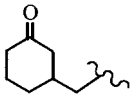
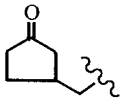
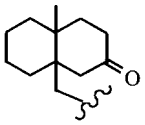
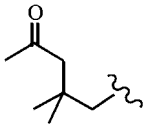
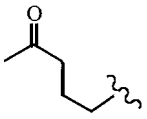
In order to understand the scope of this newly developed reaction. The ozonide **2f**, derived from 4-phenyl-1-butene (**1f**), was treated with several different kinds of phosphonium ylides (1.3 mol equiv.) at −78°C and then warmed slowly to rt. We found that the reactions were efficient to prepare (*E*)-α,β-unsaturated esters (Y=CO_2Me, CO_2CH_2Ph, CO_2Bu-*t*) (Entries 11, 14, 15, Table 1) and (*E*)-α,β-unsaturated ketones (Y=COPh and COMe) (Entries 12 and 13) in good yields. The progresses of these reactions were monitored carefully by thin layer chromatography. We found that the disappearance of the ozonide **2f** was concomitant with the formation of aldehyde **3f**, which was then slowly consumed to give the Wittig reaction product. In other words, the aldehyde **3g** is generated before proceeding the Wittig reaction.

Under the same conditions, $Ph_3P{=}CHCHO$ (**4f**) (1.3 mol equiv.) reacted with ozonide **2f** to give 3-phenylpropanal (**3f**) instead of (*E*)-unsaturated aldehyde **5ff**. In order to obtain the (*E*)-α,β-unsaturated aldehyde **5ff**, the reaction temperature should be raised to reflux in tetrahydrofuran for 12 h (Entry 16). This result indicated that 3-phenylpropanal was formed as the primary product before



(1)

Table 1. Yields of the ozonide formations and their reaction with stable phosphonium ylides

Entry	$RCH{=}CH_2$ R=	 Yield (%)	*trans*-RCH=CHY Formation	
			Pathway II, yield (%) from ozonide	Pathway III, yield (%) from alkene
1	 **1a**	**2a** 95	Y=CO_2Me **5aa** 85	–
2			Y=COPh **5ab** 55	–
3	 **1b**	**2b** 90	Y=CO_2Me **5ba** 93	–
4			Y=COPh **5bb** 72	–
5	 **1c**	**2c** 92	Y=CO_2Me **5ca** 93	–
6			Y=COPh **5cb** 62	–
7	 **1d**	**2d** 93	Y=CO_2Me **5da** 92	Y=CO_2Me **5da** 90
8			Y=COPh **5db** 65	Y=COPh **5db** 64
9	 **1e**	**2e** 93	Y=CO_2Me **5ea** 91	Y=CO_2Me **5ea** 91
10			Y=COPh **5eb** 67	Y=COPh **5eb** 67
11	$PhCH_2CH_2$– **1f**	**2f** 94	–	Y=CO_2Me **5fa** 82
12	$PhCH_2CH_2$– **1f**		–	Y=COPh **5fb** 78
13	$PhCH_2CH_2$– **1f**		–	Y=COMe **5fc** 82
14	$PhCH_2CH_2$– **1f**		–	Y=CO_2Bn **5fd** 74
15	$PhCH_2CH_2$– **1f**		–	Y=CO_2Bu-t **5fe** 82
16	$PhCH_2CH_2$– **1f**		–	Y=CHO **5ff** 84[a]
17	$PhCH_2CH_2$– **1f**		–	Y=Ph **5fg** 78[b]

[a] The reaction was carried out in refluxing THF for 12 h.
[b] The reaction was carried out in the presence of 2.2 mol equiv. of the ylide at −78°C and the *E*/*Z* ratio of compound **5fg** was 5/2.

forming the Wittig product. When we used 1.3 mol equiv. of $Ph_3P{=}CHPh$ (**4g**) to react with ozonide **2f**, only 3-phenylpropanal (**3f**) was formed even though the reaction temperature was heated to reflux in THF. In order to give the Wittig reaction product **5fg** (*E*/*Z*=5:2, 84% yield) in good yield, 2.2 mol equiv. of the ylide **4g** were needed (Entry 17, Table 1). Apparently, in comparison with the stable ylide (**4a**–**4f**), one extra mol equiv. of the semistable ylide **4g** is necessary to give the Wittig reaction product in high yield. We will explain their difference in reactivity in the later part of the paper.

Interestingly, we found that the ozonide derived from 3-benzyloxy-1-propene (**1g**) reacted with 1.3 mol equiv. of $Ph_3P{=}CHCO_2Me$ to give a mixture of the α,β-unsaturated esters **5ga** in 60% yield. The *E*/*Z* ratio is 1:1.1 (Entry 1, Pathway III, Table 2). Since the α-alkoxyaldehyde **3g** is generated before proceeding the Wittig reaction and the α-alkoxyaldehyde is known to react with stable phosphonium ylides to give a mixture of *E*- and *Z*-olefins.[9] Under similar conditions, both 4-benzyloxy-1-butene (**1h**) and 5-benzyloxy-1-pentene (**1i**) gave the Wittig product in good yields and their *E*/*Z* ratio were 7.5:1 and 11:1, respectively (Entries 3 and 5, Table 2). Results of entries 1, 3 and 5 indicate that the *E*/*Z* ratio of the α,β-unsaturated esters is affected significantly by the chain length of the methylene unit between the benzyloxy group and the aldehyde. The longer of the linking methylene chain, the more *E*-isomers

Table 2. The *E/Z* ratio yields of the Wittig reaction from Pathway I and III

Entry	Alkene	RCHO Yield (%)	$PhCH_2O(CH_2)_nCH{=}CHCOY$ Formation		
				Pathway I, yield (%) (*E/Z*) from aldehyde	Pathway III, yield (%) (*E/Z*) from alkene
1	$PhCH_2OCH_2CH{=}CH_2$ **1g**	**3g** 81	Y=OMe **5ga**	59 (4.1:1)	60 (1:1.1)
2	$PhCH_2OCH_2CH{=}CH_2$ **1g**		Y=Me **5gc**	66 (10:1)	48 (8:1)
3	$PhCH_2O(CH_2)_2CH{=}CH_2$ **1h**	**3h** 86	Y=OMe **5ha**	51 (10:1)	78 (7.5:1)
4	$PhCH_2O(CH_2)_2CH{=}CH_2$ **1h**		Y=Me **5hc**	70 (22:1)	51 (27:1)
5	$PhCH_2O(CH_2)_3CH{=}CH_2$ **1i**	**3i** 86	Y=OMe **5ia**	84 (17:1)	74 (11:1)
6	$PhCH_2O(CH_2)_3CH{=}CH_2$ **1i**		Y=Me **5ic**	64 (1:0)	49 (1:0)
7	$Ph_3COCH_2CH{=}CH_2$ **1j**	**3j** 72	Y=OMe **5ja**	62 (1.8:1)	60 (1.6:1)
8	$Ph_3COCH_2CH{=}CH_2$ **1j**		Y=Me **5jc**	63 (10:1)	68 (9:1)

were formed (Entries 1, 3 and 5). When a bulky triphenylmethoxy group replaced the benzyloxy, the *E/Z* ratio of the α,β-unsaturated ester formations was changed from 1:1.1 to 1.6:1 (Entries 1 and 7). The *E/Z* ratio was determined by the integration of the olefinic proton of the α,β-unsaturated esters in their ^1H NMR spectra. The *E*- and *Z*- isomers were easily separated by silica gel column chromatography and the *Z*-isomer was found to be the less polar one. As for the α,β-unsaturated ketones formation, we also found that the longer of the linking methylene chain, the more *E*-isomers were formed (Entries 2, 4 and 8). Interestingly, 5-benzyloxy-1-pentene (**1i**) was converted to (*E*)-enone (**5ic**) exclusively (Entry 6). In general, the *E/Z* ratio of the α,β-unsaturated ketones is usually higher than those for the α,β-unsaturated esters (Pathway III, Table 2). However, it is not clear why the position of the heteroatom on the aldehyde will affect the stereochemical outcome of the products.

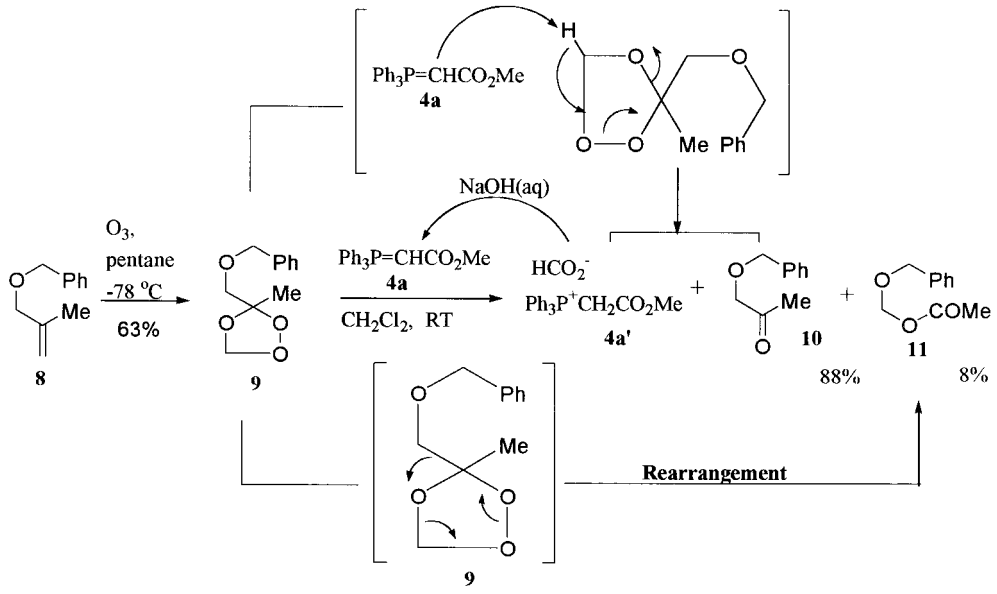
In order to compare the result of the traditional Wittig reaction (Pathway I) with our 'one-flask' protocol (Pathway III), the ozonolysis of the terminal olefins (**1g–1j**) followed by reduction with Ph_3P to give the aldehydes (**3g–3j**) in good yields (Table 2). The aldehydes were then reacted with 1.2 mol equiv. of stable phosphonium ylides in CH_2Cl_2 at room temperature to give the corresponding Wittig reaction products in 12 h (Pathway I, Table 2). The results in Table 2 indicate that our 'one-flask' process (Pathway III) give a better yield in comparison with the traditional Wittig reaction (Pathway I). In general, more *Z* isomer was formed from Pathway III in comparison with those from Pathway I (Table 2). The possible reason for their difference will be discussed later.

The plausible mechanism for the Wittig reaction from ozonides and phosphonium ylides

(a) Phosphonium ylide played as a base in its reaction with ozonide. Our earlier study showed that the ozonide ring protons were easily removed by weak base such as triethylamine regioselectively to give the carbonyl compounds.[10] We have also described that the monosubstituted ozonides reacted with phosphonium ylide to give the aldehydes as intermediates before proceeding the Wittig reaction (Entry 16, Table 1). In order to have direct evidence to support that the basicity of the stable phosphonium ylide is strong enough to abstract the ozonide ring proton, we carried out the reaction of the 1,1-disubstituted ozonide with stable phosphonium ylide. Methallyl benzyl ether (**8**) was converted to 1,1-disubstituted ozonide **9** by ozonolysis in pentane at −78°C in 63% yield. The ozonide **9** was isolated and treated with 1.3 mol equiv. of phosphonium ylide **4a** in CH_2Cl_2 at room temperature for 14 h to give α-benzyloxyacetone (**10**) in 88% yield and benzyloxymethyl acetate (**11**) in 8% yield (Scheme 2). There is no Wittig-type product formation here since ketone **10** is not reactive with stable ylide.[11] The minor product, benzyloxymethyl acetate (**11**), might come from the Baeyer–Villiger type rearrangement of the ozonide **9** as shown in Scheme 2.[12] The reaction mixture in Scheme 2 was chromatographed on a silica gel column. Compounds **10** and **11** were separated from the reaction mixture easily. The polar component was then eluted out by a mixed solvents of 10% MeOH in CH_2Cl_2 from silica gel column chromatography. The polar component could be converted by aqueous sodium hydroxide to give the phosphonium ylide **4a** in high yield. In other words, the structure of the polar component in the reaction mixture should be the phosphonium formate **4a′**. Therefore, it is evident that the phosphonium ylide can abstract the ozonide ring proton followed by ring fragmentation to give the carbonyl compound **10** and phosphonium formate **4a′** (Scheme 2).

(b) The reactivity of the phosphonium formate with aldehyde. Now we understand that the ozonide ring proton is easily removed by the stable phosphonium ylide **4a** to give the aldehyde and phosphonium formate **4a′**. However, it needs only 1.3 mol equiv. of the ylide to react with ozonide to give the Wittig reaction product in high yield. In other words, most of ylide have been converted to the phosphonium formate **4a′** in the first step. The phosphonium formate **4a′** should have reactivity with aldehyde **3f**. Otherwise, we cannot explain why the Wittig reaction yield is high (Pathways II and III, Scheme 1). However, it is known that the phosphonium salt such as phosphonium bromide **4b′** does not react with aldehyde. Therefore, we have to prepare the phosphonium formate **4a′** and demonstrate its reactivity with aldehyde.

The phosphonium formate **4a′** was prepared in excellent yield by the addition of 1 mol equiv. of formic acid to the phosphonium ylides **4a**.[13] Interestingly, the phosphonium formate **4a′** can react with 3-phenylpropanal (**3f**) in



Scheme 2.

CH_2Cl_2 at room temperature in 0.5 h to give the Wittig reaction product in excellent yield. Therefore, it is reasonable to propose the mechanism of the reaction between ozonide and ylide as follows. The ozonide ring proton was removed regioselectively by the stable phosphonium ylides **4a**. The ring fragmentation then occurred to give aldehyde **3f** as well as phosphonium formate **4a′** as intermediates. The phosphonium formate **4a′** subsequently reacted with aldehyde **3f** to give α,β-unsaturated carbonyl compound **5aa** in good yield (Fig. 1).[13]

We are interesting in understanding why the phosphonium bromide **4a″** and phosphonium formate **4a′** are so different in their reactivity with aldehyde. In order to answer this question, both the proton-coupled and proton-decoupled ^{13}C NMR spectra of the phosphonium bromide **4a″** and phosphonium formate **4a′** were taken and their partial spectra was shown in Fig. 2.

The phosphonium bromide **4a″** has no reactivity with aldehyde and its α-carbon appears at δ 31.7 ppm as a doublet (J_{P-C}=56.5 Hz) in proton-decoupled ^{13}C NMR spectrum (bottom one, Fig. 2); a triplet of doublet (J_{H-C}=133.6 Hz, J_{P-C}=56.5 Hz) in proton-coupled ^{13}C NMR spectrum (top one, Fig. 2). It means that the α-carbon is coupled with the adjacent phosphorus and hydrogen nuclei. The phosphonium formate **4a′** has excellent reactivity with aldehyde and its α-carbon appears as a doublet (J_{P-C}=56.5 Hz) at δ 30.2 ppm in both proton-coupled and proton-decoupled ^{13}C NMR spectra (Fig. 2). It means that the α-carbon is coupled with the adjacent phosphorus but not with hydrogen nuclei. The absence of the C–H coupling in compound **4a′** may be ascribed to the rapid intramolecular proton exchange between the activated methylene group and formate anion. On the other hand, the presence of the C–H coupling (J_{H-C}=133.6 Hz) in compound **4a″** indicates that C–H bond of the methylene group does not exchange with bromide intramolecularly. Since the formate is a stronger base than bromide, the rate of the intramolecular proton exchange may be dependent on the basicity of the counteranion.[13] Therefore, the proton-coupled ^{13}C NMR splitting pattern of the α-carbon provides a valuable information to predict the reactivity of the phosphonium salts. In other words, with the α-carbon splitting pattern appeared as a doublet for the phosphonium salts, excellent reactivity in the Wittig reaction is expected. On

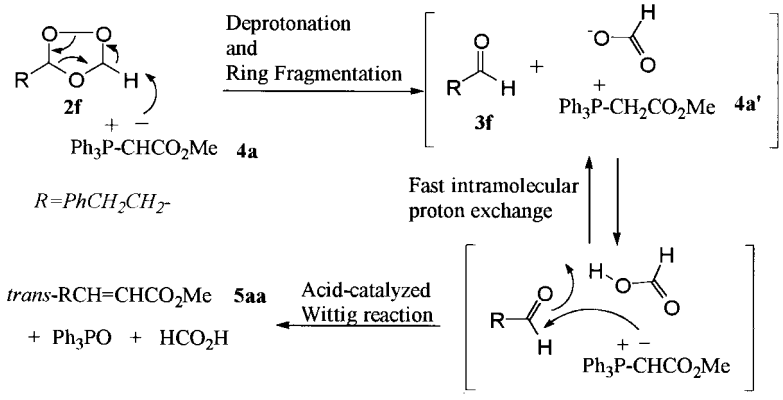


Figure 1. The possible mechanism for the formation of compound **5aa** from the reaction of ozonide **2f** and stable phosphonium ylide **4a**.

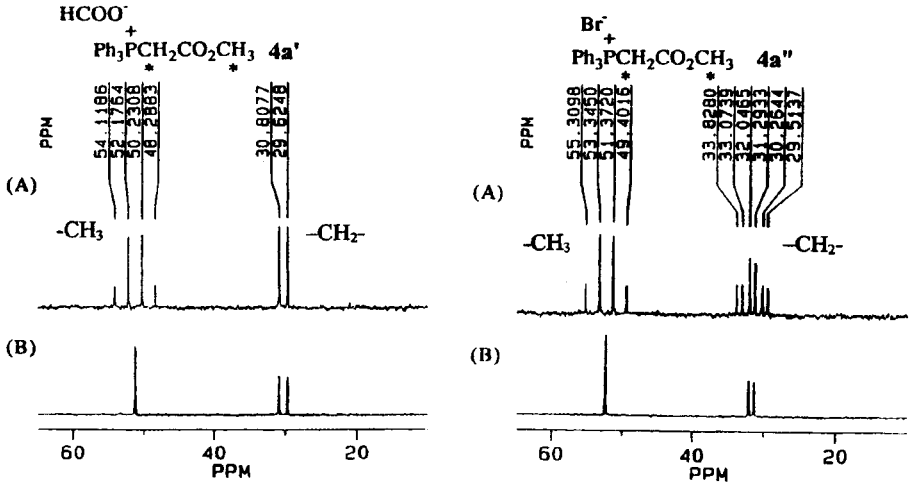


Figure 2. The characteristic ^{13}C NMR signals for the phosphonium formate **4a′** and bromide **4a″**. (A: Proton-coupled; B: Proton-decoupled).

the other hand, with the α-carbon splitting patterns appeared as the triplet of doublet for those phosphonium salts, poor reactivity in Wittig reaction is expected.[13]

The α-methylene group of the phosphonium formate **4a′** is quite acidic so that the intramolecular proton exchange rate between the α-methylene group and formate is too fast to be differentiated by NMR. This exchange process gives a transient intermediate (i.e. ylide and formic acid) which can subsequently undergo Wittig reaction with aldehyde (Fig. 1). The formic acid formed in the transient intermediate serves as a catalyst to accelerate the Wittig reaction (Fig. 1). Therefore, the reaction rate of the phosphonium acetate with aldehyde should be faster than the reaction involving the phosphonium ylide only.[14]

We have described that 2.2 mol equiv. of the semistable ylide **4g** were needed to react with ozonide **2f** to give 78% yield of the Wittig reaction product (Entry 17, Table 1). The reaction of the ozonide **2f** with semistable phosphonium ylide **4g** should give aldehyde **3f** and triphenylbenzylphosphonium formate ($Ph_3P^+CH_2Ph\ HCO_2^-$, **4g′**) according to proposed mechanism in Fig. 1. The methylene group of the phosphonium formate **4g′** should not be acidic enough to exchange with its counteranion (i.e. formate) effectively because the phenyl group is not an effective electron-withdrawing group. The regeneration of the phosphonium ylide **4g** as the transient intermediate via proton exchange process is not possible. Therefore, one more equiv. of the phosphonium ylide **4g** was required to consume the aldehyde **3f**.

We have also described that more *Z* isomers were formed from Pathway III in comparison with those from traditional Wittig reaction (i.e. Pathway I) (Table 2). There are several factors to control the isomeric ratio. For example, the *E*/*Z* ratio of compound **5ha** formation from Pathway I was reported from 98:2 to 9.1:1 by simply changing the reaction temperature and solvent.[15] According to the proposed mechanism in Fig. 1, 1 mol equiv. of the formic acid was formed in Pathway III. The presence of the formic acid in the reaction mixture is possibly responsible for the difference of the *E*/*Z* ratio between these two pathways.

Conclusions

The newly developed method is efficient for the preparation of α,β-unsaturated esters and ketones from the reaction of mono-substituted ozonides and stable phosphonium ylides. The yields were excellent for the ester formation and were modest to good for the ketone formation. Only (*E*)-isomers were formed if the substituents containing no heteroatom. However, alkoxyalkyl-substituted ozonides afforded a mixture of (*Z*)- and (*E*)-α,β-unsaturated carbonyls and the *E*/*Z* isomeric ratio is affected by the position of the heteroatom in the substituent of the ozonides. For the stable phosphonium ylides, it only needed 1.3 mol equiv. to complete the reaction. For the semistable phosphonium ylides **4g**, however, it needed 2.2 mol equiv. to complete the reaction at low temperature. In general, the yields of the one-flask reactions (Pathway III) were higher than those from the corresponding two-step process (Pathway II). Our one-flask protocol (Pathway III) is more efficient than the traditional Wittig reaction (Pathway I).

Experimental

All reactions were carried out under nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points were determined by using a Yanaco micro melting point apparatus and were uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 and Bruker Avance APX-400 spectrometer, and chemical shifts were given in ppm downfield from tetramethylsilane (TMS). IR spectra were taken with a Perkin–Elmer 883 spectrophotometer and only noteworthy absorptions were listed. Mass spectra were measured on a VG 70-250S spectrometer by electronic impact at 70 eV (unless otherwise indicated). High Resolution Mass Spectroscopy (HRMS) was measured on a JEOL JMS-HX 110 (National Hsing-Hua University) or VG-11-250J (Academia Sinica) Mass Spectrometer. The elemental analyses were measured on Heraeus NCH-RAPID and Perkin–Elmer 2400 CHN analyzer.

General procedure for the ozonolysis of terminal alkenes

In a 25 mL of two-neck flask, equipped with a magnetic stirrer, a drying tube and a gas dispersing tube (with porous fritted tip), were placed 15 mL of CH_2Cl_2 and 3-allylalkanone **1d** (423.4 mg, 3.0 mmol). A stream of ozone was bubbled through the solution at −78°C. Ozone treatment was terminated when the mixtures assumed a blue color. A stream of nitrogen was used to remove excess ozone. The mixtures were then allowed to warm up to room temperature. It was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (1/20) to give ozonide **2d** (527.7 mg, 93% yield) as a colorless oil.

General procedure for the reaction of ozonide with phosphonium ylide

To a solution of ozonide **2d** (378.3 mg, 2 mmol) in 10 mL of CH_2Cl_2 was added $Ph_3P{=}CHCO_2Me$ (**4a**) (869.3 mg, 2.6 mmol) at 0°C and the reaction was warmed slowly to ambient temperature. After 12 h, the reaction mixture was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (1/8) to give (*E*)-methyl ester **5da** (364.8 mg, 92% yield) as a colorless oil.

General procedure for the sequential ozonolysis and Wittig-type reactions

In an 100 mL of two-neck flask, equipped with a magnetic stirrer, a drying tube and a gas dispersing tube (with porous fritted tip), were placed 30 mL of CH_2Cl_2 and 3-allylalkanone **1d** (807 mg, 5.76 mmol). A stream of ozone was bubbled through the solution at −78°C. Ozone treatment was terminated when the mixtures assumed a blue color. A stream of nitrogen removed excess ozone. A solution of $Ph_3P{=}CHCO_2Me$ (**4a**) (2502.9 mg, 7.49 mmol) in 15 mL of CH_2Cl_2 was added to the solution. The reaction was warmed slowly to room temperature and stirred for 12 h. The reaction mixture was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (1/8) to give (*E*)-methyl ester **5da** (1027.8 mg, 90% yield) as a colorless oil.

Methoxycarbonylmethyltriphenylphosphonium formate (4a′). To a stirring solution of the $Ph_3P{=}CHCO_2Me$ (**4a**) (403.3 mg, 1.21 mmol) in 4 mL of anhydrous CH_2Cl_2 was added a solution of formic acid (55.5 mg, 1.21 mmol) in 1 mL of anhydrous CH_2Cl_2 at rt under nitrogen. The reaction mixture was stirred for 5 min and concentrated in vacuo to give 440 mg of phosphonium formate **4a′** as a white solid in 96% yield. mp 136–138°C; ^{1}H NMR ($CDCl_3$) δ 3.51 (s, 3H, OCH_3), 5.18 (s, 2H, $-CH_2-$), 7.50–7.73 (m, 15H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 30.1 (d, $^1J_{P-C}$=110.6 Hz), 50.4, 125.4 (d, $^1J_{P-C}$=91.0 Hz), 128.5, 128.9 (d, $^3J_{P-C}$=12.4 Hz), 132.5, 132.9 (d, $^2J_{P-C}$=9.9 Hz), 166.5, 170.1 (d, J_{P-C}=8.5 Hz); IR (KBr) 1742, 1613, 1438 cm^{-1}; MS *m/z* (relative intensity): 334 (M^+-HCO_2H, 25), 277 (57), 152 (100); Anal. Cacld for $C_{22}H_{21}O_4P$: C, 69.47; H, 5.56. Found: C, 69.49; H, 5.70.

General procedure for the reaction of the triphenylphosphonium formate 4a′ with aldehyde 3f

To a stirring solution of the triphenylphosphonium formate **4a′** (879.8 mg, 2.31 mmol) in 5 mL of anhydrous CH_2Cl_2 was added aldehyde **3f** (278.9 mg, 2.08 mmol) at room temperature under nitrogen. The reaction mixture was stirred for 30 min and was concentrated. The residue was purified by silica gel column chromatography to give (*E*)-α,β-unsaturated ester **5fa** in 92% yield.

4-(3-Oxocyclohexyl)-2(*E*)-butenoic acid methyl ester (5aa). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.25–2.42 (m, 11H), 3.74 (s, 3H, OMe), 5.85 (dt, *J*=15.5, 1.8 Hz, C=C*H*CO), 6.90 (dt, *J*=15.5, 7.7 Hz, 1H, C*H*=CHCO); ^{13}C NMR ($CDCl_3$) δ 24.79, 30.72, 38.06, 38.77, 41.08, 47.54, 51.34 (OCH_3), 122.91 (*C*=C–CO), 145.86 (*C*=C–CO), 166.50 (C=O), 210.55 (C=O); IR (CH_2Cl_2): 1714 (C=O), 1654, 1437, 1317, 1270, 1203, 986 cm^{-1}; MS (*m/z*): 196 (M^+, 3), 165 (10), 120 (16), 97 (100), 91 (33), 69 (56), 55 (32), 41 (51); HRMS Calcd for $C_{11}H_{16}O_3$ *m/z* 196.1099, found: 196.1088.

4-(3-Oxocyclopentyl)-2(*E*)-butenoic acid methyl ester (5ba). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.45–2.44 (m, 9H), 3.74 (s, 3H, OCH_3), 5.87 (dt, *J*=15.6, 1.9 Hz, 1H, C=C*H*CO), 6.93 (dt, *J*=15.6, 7.7 Hz, 1H, C*H*=CHCO); ^{13}C NMR ($CDCl_3$) δ 28.89, 35.84, 37.60, 37.98, 44.34, 51.33, 122.49 (C=*C*CO), 148.20 (*C*=C–CO), 168.53, 218.04 (C=O); IR (CH_2Cl_2): 2956, 1737 (C=O), 1653, 1553, 1525, 1400 cm^{-1}; MS (*m/z*): 183 ($M+1^+$, 18), 182 (M^+, 18), 151 (32), 150 (31), 122 (11), 100 (35), 96 (64), 83 (100), 55 (28); HRMS Calcd for $C_{10}H_{14}O_3$ *m/z* 182.0943, found: 182.0941.

8a-(3-Methoxycarbonyl-2(*E*)-propenyl)-4a-methyloctahydronaphthalen-2-one (5ca). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.38–2.60 (m, 17 H), 3.73 (s, 3H, OCH_3), 5.87 (dt, *J*=15.5, 1.7 Hz, 1H, C=C*H*CO), 6.94 (dt, *J*=15.5, 7.6 Hz, 1H, C*H*=CHCO); ^{13}C NMR ($CDCl_3$) δ 21.53, 24.20, 26.78, 27.59, 34.02, 37.69, 41.83, 47.49, 51.33 (OCH_3), 124.15 (C=*C*HCO), 144.01 (*C*=CHCO), 166.39 (C=O), 211.92 (C=O); IR (CH_2Cl_2): 1706, 1652, 1442, 1274 cm^{-1}; MS (*m/z*): 250 (M^+, 2), 219 (12), 191 (3), 151 (100), 133 (52), 109 (33), 100 (68), 91 (27), 81 (41), 67 (40); HRMS Calcd for $C_{15}H_{22}O_3$ *m/z* 250.1569, found: 250.1567.

5,5-Dimethyl-7-oxo-2(*E*)-octenoic acid methyl ester (5da). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 6H, $C(CH_3)_2$), 2.11 (s, 3H, CH_3CO), 2.26 (dd, *J*=8.0, 1.3 Hz, 2H, CH_2–C=C), 2.34 (s, 2H, CH_2CO), 3.73 (s, 3H, OCH_3), 5.84 (dt, *J*=16.7, 1.4 Hz, 1H, C=C*H*CO), 6.95 (dt, *J*=16.7, 8.0 Hz, 1H, C*H*=C–CO); ^{13}C NMR ($CDCl_3$) δ 27.23, 32.15, 33.83, 44.01, 51.29, 53.05, 123.42 (C=*C*–C=O), 145.84 (*C*=C–C=O), 166.65 (C=O), 207.94 (C=O); IR (CH_2Cl_2): 2955, 1720, 1652, 1588, 1433 cm^{-1}; MS (*m/z*): 198 (M^+, 4), 183 (7), 166 (8), 141 (28), 125 (16), 109 (31), 100 (64), 81 (32), 43 (100); HRMS Calcd for $C_{11}H_{18}O_3$ *m/z* 198.1256, found: 198.1254.

7-Oxo-2(*E*)-octenoic acid methyl ester (5ea). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.75 (quin, *J*=7.2 Hz, 2H), 2.11 (s, 3H), 2.18 (q, *J*=7.2 Hz, 2H), 2.42 (t, *J*=7.2 Hz, 2H), 3.69

(s, 3H), 5.80 (dt, J=15.6, 1.5 Hz, 1H), 6.89 (dt, J=15.6, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.76, 29.85, 31.21, 42.43, 51.32 (OCH_3), 121.52, 148.23, 166.81 (C=O), 207.93 (C=O); IR (CH_2Cl_2): 2952, 1716, 1656, 1433, 1258 cm^{-1}; MS (*m/z*): 170 (M^+, 3), 138 (98), 113 (100), 110 (21), 100 (56), 95 (50), 93 (16), 81 (71), 68 (20), 58 (45); HRMS Calcd for $C_9H_{14}O_3$ *m/z* 170.0943, found: 170.0925.

3-(4-Oxo-4-phenyl-2(*E*)-butenyl)cyclohexanone (5ab). White solid, mp 55–56°C; ^{1}H NMR ($CDCl_3$) δ 1.35–2.55 (m, 11H), 6.86–7.08 (m, 2H, CH=CH), 7.44–7.61 (m, 3H, aromatic-H), 7.91–7.95 (m, 2H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 24.80, 30.80, 38.20, 39.37, 41.12, 47.66, 127.72, 128.39, 128.44, 132.67, 138.22, 145.95 (*C*=C–CO), 190.21 (C=O), 210.61 (C=O); IR (CH_2Cl_2): 3055, 2940, 1705, 1667, 1621, 1252, 730 cm^{-1}; MS (*m/z*): 242 (M^+, 10), 224 (6), 180 (7), 157 (10), 146 (80), 145 (32), 137 (12), 131 (11), 123 (14), 120 (23), 115 (14), 110 (65), 105 (100), 97 (24), 91 (13), 77 (75), 69 (68), 67 (11), 55 (54), 41 (90); HRMS Calcd for $C_{16}H_{18}O_2$ *m/z* 242.1307, found: 242.1310.

3-(4-Oxo-4-phenyl-2(*E*)-butenyl)cyclopentanone (5bb). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.63–2.47 (m, 9H), 6.89–7.08 (m, 2H, CH=CH), 7.43–7.61 (m, 3H, aromatic-H), 7.90–7.95 (m, 2H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 28.99, 35.98, 38.00, 28.20, 44.43, 127.16 (C=*C*–CO), 128.32, 128.41, 132.66 (C=*C*–CO), 137.54, 146.23 (*C*=C–CO), 190.18 (C=O), 218.06 (C=O); IR (CH_2Cl_2): 3061, 1737, 1673, 1616, 1445, 1403 cm^{-1}; MS (*m/z*): 228 (M^+), 185, 146, 122, 105 (100), 97, 83, 77, 69, 55; HRMS Calcd for $C_{15}H_{16}O_2$ *m/z* 228.1151, found: 228.1150.

8a-(4-Phenyl-4-oxo-2(*E*)-butenyl)-4a-methyloctahydronaphthalen-2-one (5cb). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.43–2.42 (m, 17H), 6.89–7.27 (m, 2H, CH=CH), 7.43–7.61 (m, 3H, aromatic-H), 7.93–8.22 (m, 2H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 21.51, 24.32, 26.79, 27.59, 34.26, 37.61, 37.78, 42.24, 42.46, 47.25, 128.41, 128.89, 132.66, 137.58, 143.97, 189.80 (C=O), 212.17 (C=O); IR (CH_2Cl_2): 3056, 1714, 1668, 1618, 1447, 1283, 1233 cm^{-1}; MS (*m/z*): 296 (M^+, 28), 278 (10), 191 (10), 177 (9), 151 (38), 122 (42), 105 (100), 84 (80), 69 (15); HRMS Calcd for $C_{20}H_{24}O_2$ *m/z* 296.1777, found: 296.1775.

5,5-Dimethyl-1-phenyl-2(*E*)-octen-1,7-dione (5db). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 6H, $C(CH_3)_2$), 2.12 (s, 3H, CH_3CO), 2.39 (s, 2H, CH_2CO), 2.49 (d, J=7.6 Hz, 2H, CH_2–C=C), 6.92 (d, J=15.4 Hz, 2H, C=C*H*COPh), 7.04 (sextet, J=7.6 Hz, 1H, –C*H*=CHCOPh), 7.40–7.60 (m, 3H, aromatic-H), 7.90–7.98 (m, 2H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 27.47, 32.18, 34.12, 44.53, 53.16, 128.42, 132.63, 145.96 (*C*=CHCO), 190.21, 208.02 (C=O); IR (CH_2Cl_2): 3059, 1712, 1667 cm^{-1}; MS (*m/z*): 244 (M^+, 12), 187 (100), 171 (72), 146 (90), 145 (43), 131 (15), 105 (68), 91 (10), 77 (23); HRMS Calcd for $C_{16}H_{20}O_2$ *m/z* 244.1464, found: 244.1465.

1-Phenyl-2(*E*)-octen-1,7-dione (5eb). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.86 (quint, J=7.2 Hz, 2H, CH_2–C*H*$_2$–CH_2), 2.20 (s, 3H, C*H*$_3$C=O), 2.40 (q, J=7.2 Hz, 2H, CH_2–C=O), 2.55 (t, J=7.3 Hz, 2H, CH_2–C=O), 6.93 (d, J=14.5 Hz, 1H, C=C*H*COPh), 7.02–7.61 (m, 5H, olefinic and aromatic-H), 7.94–7.99 (m, 2H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 21.87, 29.80, 31.74, 42.47, 126.31 (C=*C*HCO), 128.35, 132.53, 137.66, 148.35 (*C*=C–C=O), 190.51, 207.96 (C=O); IR (CH_2Cl_2): 1707, 1668, 1620, 1447, 1356, 1291, 1179, 1017 cm^{-1}; MS (*m/z*): 216 (M^+, 30), 198 (21), 173 (10), 159 (72), 146 (38), 120 (22), 105 (100), 91 (31), 77 (70); HRMS Calcd for $C_{14}H_{16}O_2$ *m/z* 216.1151, found: 216.1148.

5-Phenyl-2(*E*)-pentenoic acid methyl ester (5fa). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.50–2.58 (m, 2H), 2.78 (t, J=7.4 Hz, 2H), 3.72 (s, 3H), 5.85 (dt, J=15.6, 1.6 Hz, 1H), 7.17–7.33 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 33.84, 34.31, 51.39 (OCH_3), 121.44 (CH=*C*HCO), 126.15, 128.30, 128.45, 140.71, 148.31 (*C*H=CHCO), 166.97 (C=O); IR (CH_2Cl_2): 2949, 1717, 1653, 1431, 1316, 1256 cm^{-1}; MS (*m/z*): 190 (M^+, 8), 159 (7), 158 (8), 130 (15), 91 (100), 65 (9); HRMS Calcd for $C_{12}H_{14}O_2$ *m/z* 190.0994, found: 190.0997.

1,5-Diphenyl-2(*E*)-penten-1-one (5fb). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.58–2.68 (m, 2H), 2.70–3.00 (m, 2H), 6.85 (d, J=14.2 Hz, 1H), 7.00–7.12 (m, 1H), 7.12–7.44 (m, 5H), 7.45 (m, 3H), 7.86–7.90 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 34.43, 126.13, 126.52, 128.45, 132.57 (C=*C*HCO), 140.75, 148.34 (CH_2*C*H=CH), 190.79 (C=O); IR (CH_2Cl_2): 3052, 2985, 1702, 1647, 1603, 1419, 1275, 1213 cm^{-1}; MS (*m/z*) (60 eV): 236 (M^+, 10), 116 (20), 105 (33), 91 (100), 77 (18); HRMS Calcd for $C_{17}H_{16}O$ *m/z* 236.1201, found: 236.1206.

6-Phenyl-3(*E*)-hexen-2-one (5fc). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H, Me), 2.48–2.61 (m, 2H), 2.79 (t, J=6.9 Hz, 2H), 6.09 (dt, J=16.0, 1.4 Hz, 1H), 6.82 (dt, J=16.0, 6.6 Hz, 1H), 7.15–7.30 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 26.67 (*C*H$_3$CO), 33.88, 34.21, 126.03, 128.13, 128.31, 131.51 (CH=*C*HCO), 140.46, 140.84 (CH_2*C*H=C), 198.26 (C=O); IR (CH_2Cl_2): 3029, 1664, 1623, 1356, 1313, 1246, 1184 cm^{-1}; MS (*m/z*) (60 eV): 174 (M^+, 5), 159 (5), 131 (7), 116 (18), 91 (100); HRMS Calcd for $C_{12}H_{14}O$ *m/z* 174.1045, found: 174.1047.

5-Phenyl-2(*E*)-pentenoic acid benzyl ester (5fd). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.43–2.54 (m, 2H), 2.74 (t, J=8.2 Hz, 2H, CH_2Ph), 5.15 (s, 2H, OCH_2Ph), 5.88 (dt, J=15.7, 1.5 Hz, 1H), 7.04 (dt, J=15.7, 6.7 Hz, 1H), 7.12–7.36 (m, 10H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 33.80, 34.16, 65.90 (O*C*H$_2$Ph), 121.41 (CH=*C*HCO), 126.06, 128.03, 128.19, 128.38, 136.02, 140.61, 148.62 (CH_2*C*H=CH), 166.17 (C=O); IR (CH_2Cl_2): 3033, 2943, 1715, 1650, 1308, 1250, 1168 cm^{-1}; MS (*m/z*) (33 eV): 266 (M^+, 2), 181 (10), 175 (22), 159 (12), 91 (100), 65 (10); HRMS Calcd for $C_{18}H_{18}O_2$ *m/z* 266.1307, found: 266.1305.

5-Phenyl-2(*E*)-pentenoic acid *tert*-butyl ester (5fe). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 9H, $OCMe_3$), 2.42–2.54 (m, 2H), 2.76 (m, 2H, C*H*$_2$Ph), 5.78 (dt, J=15.7, 1.6 Hz, 1H, C=C*H*CO), 6.90 (dt, J=15.7, 6.7 Hz, 1H, C*H*=CHCO), 7.10–7.33 (m, 5H, aromatic-H); ^{13}C

NMR ($CDCl_3$) δ 28.14, 33.78, 34.43, 80.08 (O*C*Me_3), 123.50 (*C*H=CHCO), 126.10, 128.30, 128.44, 140.97, 146.74 (C=*C*HCO), 165.96 (C=O); IR (CH_2Cl_2): 3029, 3004, 2977, 1701, 1648, 1365, 1297, 1114 cm^{-1}; MS (*m/z*) (40 eV): 176 ($M^+-C_4H_8$, 18), 159 (18), 130 (12), 91 (100), 65 (8); HRMS Calcd for $C_{11}H_{12}O_2$ *m/z* 176.0837, found: 176.0833.

5-Phenyl-2(*E*)-pentenal (5ff). Colorless oil; ^1H NMR ($CDCl_3$) δ 2.67 (q, *J*=6.3 Hz, 2H), 2.84 (t, *J*=8.5 Hz, 2H), 6.13 (dd, *J*=15.5, 7.9 Hz, 1H), 6.86 (dt, *J*=15.6, 6.3 Hz, 1H), 9.49 (d, *J*=7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 34.17, 126.34, 128.28, 128.55, 133.37, 140.22, 157.21, 193.89; IR (CH_2Cl_2): 3063, 3030, 2931, 1686, 1490, 1121 cm^{-1}; Mass (*m/z*) (50 eV): 160 (M^+, 8), 142 (5), 116 (20), 91 (100), 77 (6), 65 (16); HRMS Calcd for $C_{17}H_{16}O$ *m/z* 160.0888, found: 160.0895.

1,4-Diphenyl-1-butene (5fg-*E* and 5fg-*Z*). Benzylidenetriphenylphosphorane (Ph_3P=CHPh) was prepared from the reaction of benzyltriphenylphosphonium bromide (4289.9 mg, 9.9 mmol) and *n*-BuLi (6.2 mL, 1.6 M in hexane) in 20 mL of THF at −78°C for 0.5 h. To a solution of ozonide **2f**, prepared from 4-phenyl-1-butene (**1f**) (633.6 mg, 4.8 mmol), in 10 mL of THF was added the THF solution of Ph_3P=CHPh at −78°C and the reaction was warmed slowly to ambient temperature. After 3 h, the reaction mixture was concentrated and chromatographed on a silica gel by elution with hexane to give a mixture of *E*-and *Z*-olefin **5fg** (731.2 mg, 78% yield) as a colorless oil. The *E*/*Z* ratio is approximately 5/2 and the *Z*-isomer is less polar than *E*-isomer on TLC. Preparative TLC separated them with hexane as a developing solvent.

1,4-Diphenyl-1(*E*)-butene (5fg-*E*). White solid, mp 31.5–32.5°C; ^1H NMR ($CDCl_3$) δ 2.47–2.56 (m, 2H), 2.79 (t, *J*=7.2 Hz, 2H) 6.24 (dt, *J*=16.0, 6.6 Hz, 1H, –C*H*=CHPh), 6.41 (d, *J*=16.0 Hz, 1H, –CH=C*H*Ph), 7.16–7.33 (m, 10H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 34.83, 35.86, 125.86, 125.97, 126.90, 128.34, 128.45, 129.94, 130.37,137.72, 141.73; IR (CH_2CL_2): 3082, 3060, 3025, 2929, 2855, 1598, 1488, 1446 cm^{-1}; MS (*m/z*): 208 (M^+, 25), 117 (100), 91 (28), 77 (8) 65 (7); HRMS Calcd for $C_{16}H_{16}$ *m/z* 208.1253, found: 208.1252.

1,4-Diphenyl-1(*Z*)-butene (5fg-*Z*). Colorless oil; ^1H NMR ($CDCl_3$) δ 2.61–2.68 (m, 2H), 2.74–2.81 (m, 2H), 5.69 (dt *J*=11.6, 6.7 Hz, 1H, –C*H*=CHPh), 6.43 (d, *J*=11.6 Hz, 1H, –CH=C*H*Ph), 7.15–7.49 (m, 10H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 30.40, 36.07, 125.91, 126.56, 128.14, 128.34, 128.46, 128.71, 129.43, 131.80, 137.57, 141.67; IR (CH_2Cl_2): 3080, 3060, 3024, 2924, 2855, 1599, 1490, 1445, 1073, 1026, 962 cm^{-1}; MS (*m/z*): 208 (M^+, 20), 180 (10), 117 (100), 91 (28), 77 (6), 65 (8); HRMS Calcd for $C_{16}H_{16}$ *m/z* 208.1253, found: 208.1252.

(*E*)-4-Benzyloxycrotonic acid methyl ester (5ga-*E*). Colorless oil; ^1H NMR ($CDCl_3$) δ 3.75 (s, 3H, OCH_3), 4.18 (dd, *J*=4.2, 2.1 Hz, 2H), 4.57 (s, 2H, Ph–CH_2), 6.15 (dt, *J*=15.7, 2.1 Hz, 1H), 7.00 (dt, *J*=15.7, 4.2 Hz, 1H), 7.29–7.37 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 51.50, 68.47, 72.66, 120.82, 127.54, 127.74, 128.38, 137.60, 144.48, 166.66 (C=O); IR (CH_2Cl_2):3032, 1721 (C=O), 1437, 1286, 1117, 1105, 1044, 724 cm^{-1}; MS (*m/z*): 206 (M^+, 5), 175 (18), 161 (20), 146 (21), 135 (40), 117 (20), 100 (30), 91 (100), 84 (20), 71 (18); HRMS Calcd for $C_{12}H_{14}O_3$ *m/z* 206.0943, found: 206.0944.

(*Z*)-4-Benzyloxycrotonic acid methyl ester (5ga-*Z*). Colorless oil; ^1H NMR ($CDCl_3$) δ 3.70 (s, 3H, OCH_3), 4.55 (s, 2H) 4.65 (dd, *J*=4.9, 2.3 Hz, 2H), 5.83 (dt, *J*=11.7, 2.3 Hz, 1H), 6.45 (dt, *J*=11.7, 4.9 Hz, 1H), 7.25–7.36 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 51.25, 68.40, 72.84, 119.04, 127.72, 128.38, 137.86, 148.50, 166.36 (C=O); IR (CH_2Cl_2): 3031, 1719, 1641, 1436, 1202, 1092, 724 cm^{-1}; MS (*m/z*): 206 (M^+, 5), 164 (35), 149 (45), 135 (100), 115 (32), 100 (70), 91 (77), 83 (32), 77 (30), 71 (20), 65 (30); HRMS Calcd for $C_{12}H_{14}O_3$ *m/z* 206.0943, found: 206.0958.

5-Benzyloxy-2(*E*)-pentenoic acid methyl ester (5ha-*E*). Colorless oil; ^1H NMR ($CDCl_3$) δ 2.48 (qd, *J*=6.5, 1.4 Hz, 2H), 3.58 (t, *J*=6.5 Hz, 2H), 3.72 (s, 3H), 4.52 (s, 2H), 5.90 (dt, *J*=15.7, 1.5 Hz, 1H), 6.99 (dt, *J*=15.7, 6.9 Hz, 1H), 7.29–7.39 (m, 5H, aromatic-H); IR (CH_2Cl_2): 3033, 1716 (C=O), 1652, 1436, 1320, 1274, 1179, 1106, 1034, 978, 741, 703 cm^{-1}; MS (*m/z*): 220 (M^+, 2), 190 (3), 176 (3), 160 (17), 145 (4), 130 (8), 122 (18), 144 (21) 105 (20), 100 (79), 91 (100), 77 (6), 69 (28); HRMS Calcd for $C_{13}H_{16}O_3$ *m/z* 220.1099, found: 220.1109.

5-Benzyloxy-2(*Z*)-pentenoic acid methyl ester (5ha-*Z*). Colorless oil; ^1H NMR ($CDCl_3$) δ 2.99 (qd, *J*=6.3, 1.8 Hz, 2H), 3.60 (t, *J*=6.3 Hz, 2H), 3.71 (s, 3H), 4.53 (s, 2H), 5.86 (dt, *J*=11.5, 1.8 Hz, 1H), 6.35 (dt, *J*=11.5, 3.6 Hz, 1H), 7.30–7.36 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 29.55, 50.97, 68.98, 72.77, 120.56, 127.56, 128.31, 138.29, 147.05, 183.92 (C=O); IR (CH_2Cl_2): 2947, 1717 (C=O), 1652, 1439, 1322, 1273, 1179, 1104, 1034, 978, 740, 703 cm^{-1}; MS (*m/z*) (15 eV): 221 (M^++1, 3), 188 (35), 176 (18), 160 (76), 146 (23), 130 (36), 114 (98), 100 (56), 91 (100); HRMS Calcd for $C_{13}H_{16}O_3$ *m/z* 220.1099, found: 220.1084.

6-Benzyloxy-2(*E*)-hexenoic acid methyl ester (5ia-*E*). Colorless oil; ^1H NMR ($CDCl_3$) δ 1.73 (quint, *J*=7.0 Hz, 2H), 2.30 (qd, *J*=7.0, 1.4 Hz, 2H), 3.48 (t, *J*=7.0 Hz, 2H), 3.71 (s, 3H), 4.49 (s, 2H, CH_2Ph), 5.83 (dt, *J*=15.7, 1.4 Hz, 1H), 6.97 (dt, *J*=15.7, 7.0 Hz, 1H), 7.25–7.47 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 28.08, 28.89, 51.35, 69.17, 72.91, 121.18, 127.56, 128.34, 148.89, 167.05 (C=O); IR (CH_2Cl_2): 3027, 2940, 1704 (C=O), 1647, 1430, 1262, 1201, 1086, 1038, 974, 733 cm^{-1}; MS (*m/z*): 234 (M^+, 2), 220 (2), 202 (2), 188 (5), 174 (5), 160 (38), 145 (10), 130 (18), 121 (10), 114 (60), 100 (10), 91 (100); HRMS Calcd for $C_{14}H_{18}O_3$ *m/z* 234.1256, found: 234.1243.

6-Benzyloxy-2(*Z*)-hexenoic acid methyl ester (5ia-*Z*). Colorless oil; ^1H NMR ($CDCl_3$) δ 1.78 (quint, *J*=6.6 Hz, 2H), 2.75 (qd, *J*=6.6, 1.7 Hz, 2H), 3.51 (t, *J*=6.6 Hz, 2H), 3.70 (s, 3H), 4.50 (s, 2H), 5.79 (dt, *J*=11.5, 1.7 Hz, 1H, C=C*H*–CO), 6.26 (dt, *J*=11.5, 6.6 Hz, 1H, C*H*=CH–CO), 7.28–7.35 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 25.91, 29.11, 50.98, 69.78, 72.93, 119.56, 127.50, 127.61, 128.32, 138.49, 150.02, 166.76 (C=O); IR (CH_2Cl_2): 2937, 1705 (C=O), 1645, 1432, 1261, 1205,

1086, 1038, 974 cm^{-1}; MS (*m/z*): 234 (M^+, 2), 160 (40), 144 (48), 91 (100); HRMS Calcd for $C_{13}H_{16}O_3$ *m/z* 234.1256, found: 234.1239.

4-Trityloxy-2(*E*)-butenoic acid methyl ester (5ja-*E*). Colorless oil; ^1H NMR ($CDCl_3$) δ 3.77 (s, 3H, OCH_3), 3.80 (dd, *J*=3.8, 2.1 Hz, 2H), 6.37 (dt, *J*=15.6, 2.1 Hz, 1H, C═C*H*–CO), 6.97 (dt, *J*=15.6, 3.8 Hz, 1H, C*H*═CH–CO), 6.90–7.50 (m, 15H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 51.58, 63.06, 87.08 (–*C*Ph_3), 119.95, 126.95, 127.21, 127.95, 128.51, 128.71, 128.83, 143.68, 145.16, 167.04 (C═O); IR (CH_2Cl_2): 3178, 3055, 1706 (C═O), 1465, 1282, 1161, 1079, 927 cm^{-1}; MS (*m/z*) (27 eV): 359 ($M+1^+$, 4), 281 (18), 144 (50), 243 (100), 165 (26), 105 (78), 99 (23); HRMS Calcd for $C_{24}H_{22}O_3$ *m/z* 359.1647, found: 359.1622.

4-Trityloxy-2(*Z*)-butenoic acid methyl ester (5ja-*Z*). Colorless oil; ^1H NMR ($CDCl_3$) δ 3.60 (s, 3H, OCH_3), 4.33 (dd, *J*=4.7, 2.5 Hz, 2H), 5.70 (dt, *J*=11.7, 2.5 Hz, 1H, C═C*H*–CO), 6.47 (dt, *J*=11.7, 4.7 Hz, 1H, C*H*═CH–CO), 7.20–7.51 (m, 15H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 51.12, 63.03, 87.03, 118.14, 127.04, 127.84, 128.09, 128.67, 143.90, 149.06, 166.27 (C═O); IR (CH_2Cl_2): 3054, 1706 (C═O), 1587, 1466, 1284, 1161, 1079, 927 cm^{-1}; MS (*m/z*) (70 eV): 358 (M^+, 1), 259 (M^+-CH_2CH═$CHCO_2Me$, 6) 243 (10), 228 (3), 165 (6), 105 (8), 78 (100); HRMS Calcd for $C_{24}H_{22}O_3$ *m/z* 358.1569, found: 358.1558.

5-Benzyloxy-3(*E*)-penten-2-one (5gc-*E*). Colorless oil; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3H, CH_3), 4.21 (dd, *J*=4.4, 2.0 Hz, 2H), 4.58 (s, 2H), 6.36 (dt, *J*=16.1, 1.9 Hz, 1H), 6.81 (dt, *J*=16.1, 4.4 Hz, 1H), 7.27–7.38 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 27.16, 68.71, 72.84, 127.60, 127.79, 128.41, 130.25, 137.53, 142.91, 198.04 (C═O); IR (CH_2Cl_2): 3031, 1675 (C═O), 1632, 1436, 1359, 1261, 1120, 1021, 975 cm^{-1}; MS (*m/z*): 189 (M^+-1, 20), 161 (50), 149 (82), 119 (40), 111 (42), 97 (58), 85 (73), 71 (100); HRMS Calcd for $C_{12}H_{13}O_2$ *m/z* 189.0916, found: 189.0935.

5-Benzyloxy-3(*Z*)-penten-2-one (5gc-*Z*). Colorless oil; ^1H NMR ($CDCl_3$) δ 2.22 (s, 3H, CH_3), 4.54 (s, 2H), 4.59 (dd, *J*=4.2, 2.0 Hz, 2H), 6.22–6.35 (m, 2H), 7.26–7.36 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 31.05, 69.47, 72.92, 125.95, 127.79, 127.93, 128.44, 147.03, 194.11 (C═O); IR (CH_2Cl_2): 2933, 1725 (C═O), 1684, 1612, 1544, 1490, 1394, 1252, 1184, 1100, 1021 cm^{-1}; MS (*m/z*): 190 (M^+, 2), 146 (10), 131 (12), 99 (21), 91 (100), 84 (51), 77 (52), 69 (18), 43 (21); HRMS Calcd for $C_{12}H_{14}O_2$ *m/z* 190.0994, found: 190.0990.

6-Benzyloxy-3(*E*)-hexen-2-one (5hc-*E*). Colorless oil; ^1H NMR ($CDCl_3$) δ 2.21 (s, 3H, CH_3), 2.50 (qd, *J*=6.7, 1.5 Hz, 2H), 3.57 (t, *J*=6.4 Hz, 2H), 4.49 (s, 2H), 6.10 (dt, *J*=16.0, 1.5 Hz, 1H), 6.80 (dt, *J*=16.0, 6.8 Hz, 1H), 7.24–7.35 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 26.49, 32.56, 67.93, 72.70, 127.39, 128.13, 132.35, 137.79, 144.60, 198.15 (C═O); MS (*m/z*): 204 (M^+, 1), 189 (1), 174 (2), 160 (1), 146 (1), 131 (2), 117 (1), 107 (1), 98 (35), 91 (100), 83 (9), 77 (2), 65 (8); HRMS Calcd for $C_{13}H_{16}O_2$ *m/z* 204.1151, found: 204.1098.

7-Benzyloxy-3(*E*)-hepten-2-one (5ic-*E*). Colorless oil; ^1H NMR ($CDCl_3$) δ 1.75–1.89 (m, 2H), 2.21 (s, 3H, CH_3), 2.37 (qd, *J*=7.1, 1.4 Hz, 2H), 3.49 (t, *J*=6.2 Hz, 2H), 4.49 (s, 2H), 6.06 (dt, *J*=16.0, 1.5 Hz, 1H), 6.81 (dt, *J*=16.0, 6.8 Hz, 1H), 7.26–7.35 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 26.75, 28.15, 29.16, 69.15, 72.88, 127.54, 128.30, 131.41, 138.26, 147.68, 198.51 (C═O); MS (*m/z*): 218 (M^+, 1), 200 (1), 175 (6), 160 (15), 142 (10), 127 (10), 105 (12), 91 (100), 84 (30), 69 (0); HRMS Calcd for $C_{14}H_{18}O_2$ *m/z* 218.1307, found: 218.1336.

5-Trityloxy-3(*E*)-penten-2-one (5jc-*E*). Viscous pale yellow oil; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3H, CH_3), 3.84 (dd, *J*=3.6, 1.8 Hz, 2H), 6.51 (dt, *J*=16.1, 1.8 Hz, 1H), 6.74 (dt, *J*=16.1, 3.1 Hz, 1H), 7.18–7.48 (m, 15H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 27.07, 63.09, 87.11, 127.19, 127.93, 128.46, 129.48, 143.60, 143.78, 198.41 (C═O); IR (CH_2Cl_2): 3027, 1680, 1650, 1630, 1481, 1436, 1355, 1251, 1210, 1150, 1065, 1018, 967 cm^{-1}; MS (*m/z*): 342 (M^+, 1), 324 (10), 265 (18), 243 (100), 228 (10), 183 (12), 165 (66), 160 (17), 149 (8), 105 (76), 91 (8), 83 (30), 77 (13); HRMS Calcd for $C_{24}H_{22}O_2$ *m/z* 342.1620, found: 342.1600.

General procedure for the ozonolysis of 1,1-disubstituted alkenes

In a 25 mL of two-neck flask, equipped with a magnetic stirrer, a drying tube and a gas dispersing tube (with porous fritted tip), were placed 15 mL of pentane and benzyl methallyl ether (**8**) (306 mg, 1.9 mmol). A stream of ozone was bubbled through the solution at −78°C. Ozone treatment was terminated when the mixtures assumed a blue color. A stream of nitrogen removed excess ozone. The mixtures were then allowed to warm up to room temperature. It was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (1/20) to give ozonide **9** (250 mg, 63% yield) as a colorless oil.

3-Benzyloxymethyl-3-methyl-1,2,4-trioxolane (9). Colorless oil; ^1H NMR ($CDCl_3$) δ 1.54 (s, 3H, CH_3), 3.44 (d, *J*=10.8 Hz, 1H), 3.54 (t, *J*=10.8 Hz, 1H), 4.57 (d, *J*=12.0 Hz, 1H), 4.64 (d, *J*=12.0 Hz, 1H), 5.03 (s, 1H), 5.18 (s, 1H), 7.28–7.36 (m, 5H, aromatic-H); ^{13}C NMR ($CDCl_3$) δ 19.05, 71.65, 73.51, 93.95, 108.21, 127.62, 127.92, 128.37, 137.80; IR (CH_2Cl_2): 3032, 1449, 1367, 1231, 1107, 1059, 1009, 945 cm^{-1}; MS (*m/z*): 210 (M^+, 1), 120 (20), 107 (5), 91 (100), 65 (6), 43 (10); HRMS Calcd for $C_{11}H_{14}O_4$ *m/z* 210.0892, found: 210.0890.

Reaction of 1,1-disubstituted ozonide with stable phosphonium ylide

To a solution of ozonide **9** (250 mg, 1.19 mmol) in 15 mL of CH_2Cl_2 was added Ph_3P═$CHCO_2Me$ (**4a**) (401.2 mg, 1.2 mmol) at 0°C and the reaction was warmed slowly to ambient temperature. After 12 h, the reaction mixture was concentrated and chromatographed on a silica gel column. 3-Benzyloxypropanone (**10**) (172 mg, 88% yield), benzyloxymethyl acetate (**11**) (17.1 mg, 8% yield) and the phosphonium salt (380 mg) were isolated. This phosphonium salt was treated with 1N NaOH and then extracted with

benzene to give the phosphonium ylide **4a** (329 mg, 0.98 mmol).

3-Benzyloxypropanone (10). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3H, CH_3), 4.59 (s, 2H, $PhCH_2$), 4.87 (s, 2H, $COCH_2$), 7.26–7.39 (m, 2H, aromatic-H); IR (CH_2Cl_2): 3032, 1726 (C═O), 1417, 1353, 1211, 1115, 1026, 976 cm^{-1}; MS (*m*/*z*): 164 (M^+, 2), 107 (50), 91 (100), 77 (8), 65 (15), 43 (40); HRMS Calcd for $C_{10}H_{12}O_2$ *m*/*z* 164.0837, found: 164.0830.

Benzyloxymethyl acetate (11). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3H, CH_3), 4.69 (s, 2H, $PhCH_2$), 5.34 (s, 2H, OCH_2O), 7.31–7.36 (m, 5H, aromatic-H); IR (CH_2Cl_2): 3032, 1736 (C═O), 1451, 1363, 1227, 1162, 1116, 1010, 945 cm^{-1}; MS (*m*/*z*): 180 (M^+, 2), 120 (58), 119 (27), 91 (100), 77 (8), 65 (10), 43 (31); HRMS Calcd for $C_{10}H_{12}O_3$ *m*/*z* 180.0786, found: 180.0781.

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