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Bifunctionalized Allenes, Part IX: An Efficient Method for Regioselective Synthesis of 4-Heteroatom-Functionalized Allenecarboxylates

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ABSTRACT: *An efficient method for regioselective synthesis of 4-heteroatom-functionalized allenecarboxylates by an atom economical [2,3]-sigmatropic rearrangement of the mediated 2-heteroatom-functionalized alk-3-ynecarboxylates is described. Alkyl 4-(dimethoxyphosphoryl), (diphenylphosphinoyl), (benzenesulfinyl), or (methanesulfonyl)-alka-2,3-dienoates can be readily prepared via reactions of alkyl 2-hydroxy-alk-3-ynoates with dimethylchlorophosphite, chlorodiphenylphosphine, benzensulfanyl chloride, or methanesulfinyl chloride, respectively, in the presence of a base.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem. 24:322–331, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21096

INTRODUCTION

In the past three decades, the synthesis and use of allene derivatives have been expanded in preparative organic chemistry. The presence of two π electron clouds separated by a single sp hybridized carbon atom is the identifying structural characteristic of allenes, and it is this unique structural and electronic arrangement that is responsible for the extraordinary reactivity profile displayed by allenic compounds [1].

Functionalized allenes have attracted a growing attention because of their versatility as key building blocks for organic synthesis. The synthetic potential of functionalized allenes has been extensively explored in recent years and this has led to the development of novel methods for the construction of a variety of functionalized heterocyclic and carbocyclic systems [2].

A plethora of methods exists for the construction of alka-2,3-dienoates, including the Wittig [3], Wittig–Horner [4], or the Horner–Wadsworth–Emons [5] olefination of ketenes, iron-catalyzed olefination of ketenes with diazoacetate [6], and by other methods [7]. There are methods [8] for the synthesis of phosphorus-containing allenes (phosphonates [9], phosphinates [10], and phosphine oxides [11]) including reactions of α-alkynols with chloride-containing derivatives of phosphorus acids followed by [2,3]-sigmatropic rearrangement. The reaction of propargyl alcohols with halogen-containing sulfur reagents, such as sulfanyl halides [12] and sulfinyl chlorides [13], is a convenient method for the preparation of propargyl compounds (sulfenates or sulfinates), which usually undergo [2,3]-sigmatropic rearrangement to allenic products (sulfoxides or sulfones) [12–14]. An alternative route, which enables the preparation of 2-thio- [15a], 2-sulfinyl- [15a,15b],

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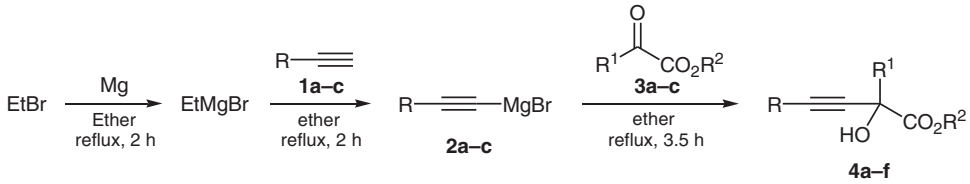


SCHEME 1

and 2-sulfonyl-substituted [15a] allenecarboxylates, starts from methyl 4-hydroxy-2-alkynoate.

As a part of our research program on the chemistry of the bifunctionalized allenes, we required a convenient method to introduce a heteroatom-functionalized group, such as phosphonate, phosphine oxide, sulfoxide, or sulfone group, in the four-position to the ester group of the allenecarboxylates. The above-mentioned groups attract increasing attention as useful functionalities in organic synthesis. Of particular interest are the applications of these groups as temporary transformers of chemical reactivity of the allenic system in the synthesis of eventually heterocyclic compounds.

In a continuation to our previous reports on the synthesis [16a,16b,16g,16h] and electrophilic cyclization reactions [16,16a–f] of bifunctionalized allenes, we have found an efficient method for regioselective synthesis of 4-heteroatom-functionalized allenecarboxylates by an atom economical [2,3]-sigmatropic rearrangement of the mediated 2-heteroatom-functionalized alk-3-ynecarboxylates.

RESULTS AND DISCUSSION

Since its discovery five decades ago [9a,10a,10b], the reversible interconversion of propargylic phosphites, phosphonites, and phosphinites to allenyl phosphonates, phosphinates, and phosphine oxides has become one of the most studied and synthetically useful [2,3]-sigmatropic rearrangement. Numerous synthetic applications of the rearrangement have been reported, including its use in the synthesis of allenic steroids as substrate-induced inactivation of aromatase [17a], in the efficient synthesis of (2*R*)-2-amino-5-phosphonopentanoic acid as a powerful and selective *N*-methyl-D-aspartate antagonist [17b], in the preparation of the phosphonate analogues of phosphatidyl derivatives [17c,17d], and, in the synthesis of new acyclic analogues of nucleotides containing a purine or pyrimidine moiety and an allenic skeleton [17e,17f].

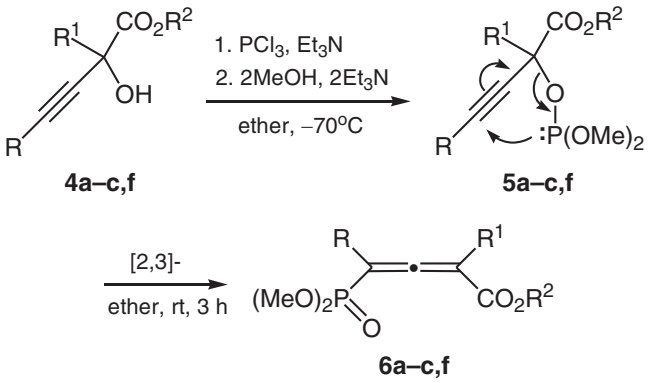
Our strategy for the synthesis of the 4-heteroatom-functionalized allenecarboxylates, using our experience on the preparation of the vinylallenyl sulfoxides [18], sulfones [19], and phosphine oxides [20], relies on the well-precedented 2,3-sigmatropic shift of propargylic phosphites to allenephosphonates [9], propargylic phosphinites to allenyl phosphine oxides [11], propargylic sulfenates to allenyl sulfoxides [12, 14], and propargylic sulfinates to allenyl sulfones [13, 14]. Precedence exists for such an approach to the synthesis of allenic compounds. However, to the best of our knowledge, the use of propargylic alcohols bearing an electron-withdrawing group such as **4**, to give the corresponding allenic esters **6**, **8**, **10**, and **12**, has not been reported. To assess this approach toward the target 4-heteroatom-functionalized allenecarboxylates **6**, **8**, **10**, and **12**, a range of propargylic alcohols **4a–f** was prepared by the reaction of the metallated acetylenes **2a–c** with commercially available alkyl 2-oxoalkanoates (pyruvic acid esters) **3a–c** (Scheme 1 and Table 1) [21–23].

TABLE 1 Preparation of the Propargylic Alcohols **4a–f** from the Metallated Acetylenes **2a–c** and the Alkyl 2-oxoalkanoates **3a–c**

Entry	*Product*	*R*	*R1*	*R2*	*Yield[a] (%)*
1	**4a**	Pr	Me	Et	76
2	**4b**	Pr	Ph	Me	77
3	**4c**	Bu	Me	Et	73
4	**4d**	Bu	Ph	Me	72
5	**4e**	Ph	Me	Et	73
6	**4f**	Ph	Ph	Et	75

[a]Isolated yields by chromatographical purification.

With the required propargyl alcohols **4a–f** in hand, we were then able to investigate the proposed reactions with the corresponding chloro-containing phosphorus and sulfur reagents, such as dimethylchlorophosphite, chlorodiphenylphosphine, benzenesulfanyl chloride, and methanesulfinyl chloride in the presence of a base and subsequent [2,3]-sigmatropic rearrangement of the mediated 2-heteroatom-functionalized alk-3-ynecarboxylates **5**, **7**, **9**, and **11**. In the first instance, the alkyl 4-(dimethoxyphosphoryl)-alka-2,3-dienoates **6a–c,f** can be readily prepared via an atom economical 2,3-sigmatropic rearrangement of the mediated alkoxycarbonyl-functionalized propargyl phosphite **5a–c,f**, intermediate formed by the



SCHEME 2

TABLE 2 Synthesis of the Alkyl 4-(dimethoxyphosphoryl)-alka-2,3-dienoates **6a–c,f** by [2,3]-Sigmatropic Rearrangement of the Mediated 2-(Dimethoxyphosphinooxy)-alk-3-ynoates **5a–c,f** Prepared via Reactions of the Alkyl 2-hydroxy-alk-3-ynoates **4a–c,f** with Dimethylchlorophosphite in the Presence of a Base

Entry	*Product*	*R*	R^1	R^2	*Yield*[a] *(%)*
1	**6a**	Pr	Me	Et	62
2	**6b**	Pr	Ph	Me	69
3	**6c**	Bu	Me	Et	63
4	**6f**	Ph	Ph	Et	65

[a]Isolated yields by chromatographical purification.

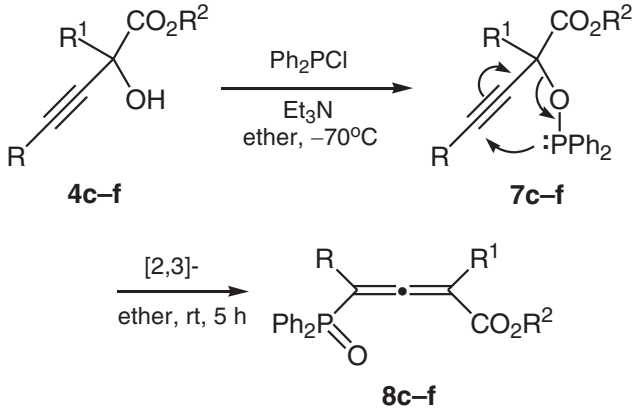
reaction of the alkyl 2-hydroxy-alk-3-ynoates **4a–c,f** with dimethylchlorophosphite, prepared in situ from phosphorus trichloride, 2 equiv of methanol, and 2 equiv of triethylamine, in the presence of triethylamine, according to Scheme 2 and Table 2.

Pleasingly, the reaction of the alkyl 2-hydroxy-alk-3-ynoates **4c–f** with chlorodiphenylphosphine in the presence of triethylamine at –70°C gave the expected alkyl 4-(diphenylphosphinoyl)-allenoates **8c–f** in moderate yields (Table 3) as a result of [2,3]-sigmatropic rearrangement of the 2-(diphenylphosphinooxy)-propargyl esters **7c–f** for 5 h at room temperature, according to the reaction sequence outlined in Scheme 3.

TABLE 3 Synthesis of the Alkyl 4-(diphenylphosphinoyl)-alka-2,3-dienoates **8c–f** by [2,3]-Sigmatropic Rearrangement of the Mediated 2-(Diphenylphosphinooxy)-alk-3-ynoates **7c–f** Prepared via Reactions of the Alkyl 2-hydroxy-alk-3-ynoates **4c–f** with Chlorodiphenylphosphine in the Presence of a Base

Entry	*Product*	*R*	R^1	R^2	*Yield*[a] *(%)*
1	**8c**	Bu	Me	Et	60
2	**8d**	Bu	Ph	Me	58
3	**8e**	Ph	Me	Et	57
4	**8f**	Ph	Ph	Et	62

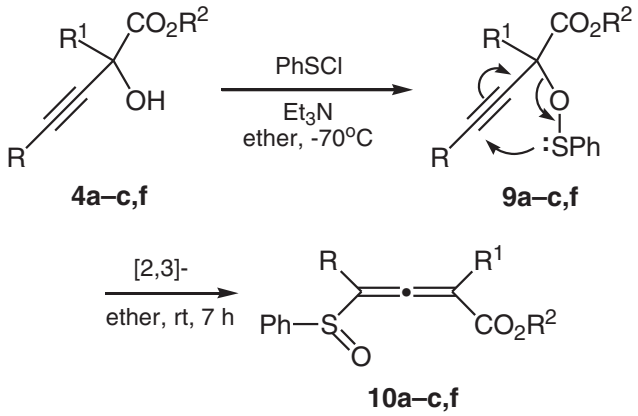
[a]Isolated yields by chromatographical purification.



SCHEME 3

The strategy for the synthesis of sulfur-containing allenes (sulfoxides and sulfones) relies on the well-precedented [2,3]-sigmatropic rearrangement of propargylic sulfenates and sulfinates to allenyl sulfoxides and sulfones [12–14]. Pleasingly, the reaction of the propargylic alcohols **4a–c,f** with benzenesulfanyl chloride in the presence of triethylamine led to the formation of the expected 4-(benzenesulfinyl)-allenoates **8a–c,f**, which were isolated in 59–67% yield after purification by column chromatography as a result of [2,3]-sigmatropic rearrangement of the mediated formed 2-(benzenethiooxy)-alk-3-ynecarboxylates **9a–c,f** for 7 h at room temperature, as outlined in Scheme 4 and Table 4.

The starting materials in the synthesis of the alkyl 4-(methanesulfonyl)-alka-2,3-dienoates **12c–f** are the appropriate α-alkoxycarbonyl-α-alkynols **4c–f**, which react with methanesulfinyl chloride in the presence of triethylamine. Reflux of the intermediate formed alkoxycarbonyl-propargyl sulfinates **11c–f** (which may or may not be isolated) in dry toluene for 8 h provokes a [2,3]-sigmatropic

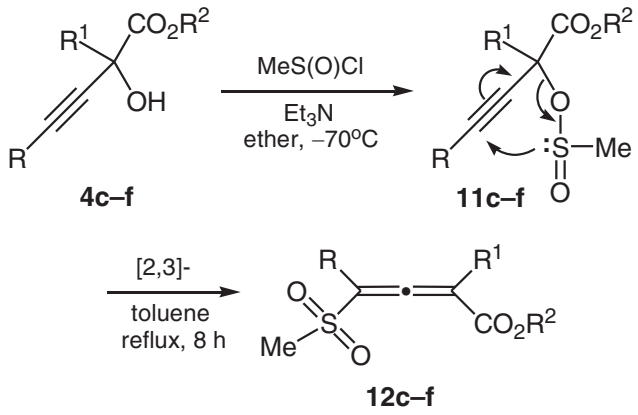


SCHEME 4

TABLE 4 Synthesis of the Alkyl 4-(benzenesulfinyl)-alka-2,3-dienoates **10a–c,f** by [2,3]-Sigmatropic Rearrangement of the Mediated 2-(Benzenethiooxy)-alk-3-ynoates **9a–c,f** Prepared via Reactions of the Alkyl 2-hydroxy-alk-3-ynoates **4a–c,f** with Benzenesulfanyl Chloride in the Presence of a Base

Entry	*Product*	*R*	R^1	R^2	*Yield*[a] *(%)*
1	**10a**	Pr	Me	Et	64
2	**10b**	Pr	Ph	Me	64
3	**10c**	Bu	Me	Et	67
4	**10f**	Ph	Ph	Et	59

[a]Isolated yields by chromatographical purification.



SCHEME 5

rearrangement to the expected 3-alkoxycarbonyl-allenyl sulfones **12c–f**, which were purified by column chromatography on silica gel with 46–52% yield (see Scheme 5 and Table 5).

After a conventional workup, all allenic products **6**, **8**, **10**, and **12** were isolated by column chromatography and identified by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectra as well as by elemental analysis. Some characteristic chemical shifts and coupling constants in the ^{13}C and ^{31}P NMR spectra of the prepared 1,3-bifunctionalized allenes **6**, **8**, **10**, and **12** are summarized in Table 6.

TABLE 5 Synthesis of the Alkyl 4-(Methanesulfonyl)-alka-2,3-dienoates **12c–f** by [2,3]-Sigmatropic Rearrangement of the Mediated 2-(Methanesulfinyloxy)-alk-3-ynoates **11c–f** Prepared via Reactions of the Alkyl 2-Hydroxy-alk-3-ynoates **4c–f** with Methanesulfinyl Chloride in the Presence of a Base

Entry	*Product*	*R*	R^1	R^2	*Yield*[a,b] *(%)*
1	**12c**	Bu	Me	Et	48
2	**12d**	Bu	Ph	Me	47
3	**12e**	Ph	Me	Et	46
4	**12f**	Ph	Ph	Et	52 (54)[c]

[a]Isolated yields by chromatographical purification.
[b]Overall yields without isolation of the alkynes **11c–f**.
[c]Overall yield with isolation of the alkyne **11f**.

CONCLUSIONS

In conclusion, a convenient and efficient method for regioselective synthesis of a new family of 1,3-diacceptor-substituted allenes, namely 4-heteroatom-functionalized allenecarboxylates, derived by [2,3]-sigmatropic rearrangement of the intermediate formed 2-heteroatom-functionalized alk-3-ynecarboxylates in the reactions of alkyl 2-hydroxy-alk-3-ynoates with dimethylchlorophosphite, chlorodiphenylphosphine, benzensulfanyl chloride, or methanesulfinyl chloride in the presence of a base has been explored.

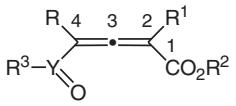
Further investigations on this potentially important synthetic methodology are currently in progress. At the same time, the synthetic application of the prepared 4-heteroatom-functionalized allenecarboxylates for the synthesis of different heterocyclic compounds is now under investigation in our laboratory as a part of our general synthetic strategy for investigation of the scope and limitations of the electrophilic cyclization reactions of bifunctionalized allenes. Results of these investigations will be reported in due course.

EXPERIMENTAL

General

All new synthesized compounds were purified by column chromatography and characterized on the basis of NMR, IR, and microanalytical data. NMR spectra were recorded on DRX Brucker Avance-250 (Bruker BioSpin, Karlsruhe, Germany) (^{1}H at 250.1 MHz, ^{13}C at 62.9 MHz, ^{31}P at 101.2 MHz) and Brucker Avance II+600 (Bruker BioSpin) (^{1}H at 600.1 MHz, ^{13}C at 150.9 MHz, ^{31}P at 242.9 MHz) spectrometers for solutions in CDCl3. Chemical shifts are in parts per million downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). *J* values are given in hertz. IR spectra were recorded with an FT-IR Afinity-1 Shimadzu spectrophotometer (Shimadzu, Japan). Elemental analyses were carried out by the Microanalytical Service Laboratory of Faculty of Chemistry and Pharmacy, University of Sofia using Vario EL*3* CHNS(O) (Elementar Analysensysteme, Hanau, Germany). Column chromatography was performed on Kieselgel F_{254}60 (70–230 mesh ASTM, 0.063–0.200 nm; Merck). The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. Reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for purity on TLC plates Kieselgel F_{254}60 (Merck).

TABLE 6 Some Characteristic ^{13}C and ^{31}P NMR Spectral Data of the Prepared 1,3-Bifunctionalized Allenes **6**, **8**, **10**, and **12**



6, Y=P-OMe, R^3=OMe
8, Y=P-Ph, R^3=Ph
10, Y=S, R^3=Ph
12, Y=S=O, R^3=Me

Allene	δ_{C-1}	δ_{C-2}	δ_{C-3}	δ_{C-4}	$^3J_{P-C}$	$^2J_{P-C}$	$^1J_{P-C}$	$\delta^{31}P$
6a	166.7	97.6	213.3	95.9	15.2	4.9	181.9	19.3
6b	165.8	104.6	214.6	98.7	15.6	4.9	184.8	17.4
6c	166.7	97.6	213.2	96.0	15.2	5.0	181.7	19.1
6f	164.7	105.9	218.1	105.8	15.7	4.7	185.2	15.6
8c	166.8	98.1	212.4	102.4	13.0	6.5	94.5	31.8
8d	165.8	105.2	213.3	104.4	12.9	6.4	92.9	29.9
8e	165.9	99.0	215.8	104.3	12.3	6.4	95.4	30.6
8f	164.6	106.1	217.4	107.2	12.8	7.1	97.9	29.6
10a	166.0	102.5	206.8	115.8	-	-	-	-
10b	161.9	106.3	209.5	111.1	-	-	-	-
10c	166.4	108.9	213.7	115.4	-	-	-	-
10f	167.8	109.1	216.0	108.4	-	-	-	-
12c	165.2	111.4	216.1	115.5	-	-	-	-
12d	164.7	110.8	210.4	117.4	-	-	-	-
12e	165.3	111.5	212.3	116.5	-	-	-	-
12f	163.5	110.7	213.9	117.4	-	-	-	-

Starting Materials

Benzenesulfanyl chloride was prepared from diphenyl disulfide and sulfuryl chloride in dichloromethane and distilled in vacuo (bp 80–81°C/20 mm Hg) before used [24]. Methanesulfinyl chloride was prepared from dimethyl disulfide and sulfuryl chloride in acetic acid and distilled in vacuo (bp 36°C/20 mm Hg) before used [25]. Alkyl 2-oxoalkanoates, pentyne, hexyne, phenylacetylene, phosphorus trichloride, triethylamine, pyridine, chlorodiphenylphosphine, diphenyl disulfide, and dimethyl disulfide were commercially available and were purified by usual methods.

*General Procedure for Synthesis of Alkyl 2-hydroxy-alk-3-ynoate (**4**)*

Ethylmagnesium bromide [prepared from magnesium (1.22 g, 50 mmol) and ethyl bromide (5.50 g, 50 mmol) in dry diethyl ether (50 mL)] is added dropwise under stirring to monosubstituted alkynes **1** [pentyne, hexyne, or phenylacetylene (50 mmol)] and then the mixture is refluxed for 2 h. The solution of the prepared monosubstituted alkynyl magnesium bromides **3** is added dropwise under stirring to the alkyl 2-oxoalkanoates **3** (100 mmol). The mixture is refluxed for 3.5 h and after cooling is hydrolyzed with a saturated aqueous solution of ammonium chloride. The organic layer is separated, washed with water, and dried over magnesium sulfate. Solvent and the excess of 2-oxoalkanoate are removed by distillation. Purification of the residue is achieved by column chromatography (silica gel, Kieselgel Merck 60 F_{254}) with ethyl acetate/hexane. The pure products had the following properties.

*Ethyl 2-hydroxy-2-methyl-hept-3-ynoate (**4a**).* The compound was described in a U.S. Patent [21] without giving experimental, NMR, and IR spectral details. Orange oil, yield: 76%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.82; IR (neat, cm^{-1}): 1732 (C=O), 2254 (C≡C), 3496 (OH). ^1H NMR ($CDCl_3$, 250.1 MHz, δ): 1.00 (t, J 7.1 Hz, 3H, $\underline{Me}(CH_2)_2$), 1.32 (t, J 7.2 Hz, 3H, $\underline{Me}CH_2O$), 1.49 (m, 2H, $MeC\underline{H_2}CH_2$), 1.53 (s, 3H, Me), 2.21 (m, 2H, $MeCH_2C\underline{H_2}$), 4.03 (s, 1H, OH), 4.27 (m, 2H, $MeC\underline{H_2}O$). ^{13}C NMR ($CDCl_3$, 62.9 MHz, δ): 13.3 (CH_3), 13.9 (CH_3), 22.6 (CH_2), 22.9 (CH_2), 25.6 (CH_3), 61.4 (CH_2), 72.9 (C), 78.4 (C), 81.3 (C), 165.7 (C). $C_{10}H_{16}O_3$ (184.23). Calcd: C 65.19, H 8.75; found: C 65.13, H 8.68.

*Methyl 2-hydroxy-2-phenyl-hept-3-ynoate (**4b**).* The compound was described in a U.S. Patent [22] without giving experimental, NMR, and IR spectral details. Light yellow oil, yield: 77%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.79; IR (neat, cm^{-1}): 1450, 1493 (Ph), 1732 (C=O), 2251 (C≡C), 3493 (OH). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 1.03 (t, J 7.3 Hz, 3H, $\underline{Me}(CH_2)_2$), 1.61 (m, 2H, $MeC\underline{H_2}CH_2$), 2.30 (m, 2H, $MeCH_2C\underline{H_2}$), 3.77 (s, 3H, MeO), 4.16 (s, 1H, OH), 7.32–7.70 (m, 5H, Ph) ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.6 (CH_3), 20.9 (CH_2), 21.9 (CH_2), 54.2 (CH_3), 72.9 (C), 78.4 (C), 87.7 (C), 126.1–139.9 (Ph), 173.2 (C). $C_{14}H_{16}O_3$ (232.28). Calcd: C 72.39, H 6.94; found: C 72.31, H 7.01.

*Ethyl 2-hydroxy-2-methyl-oct-3-ynoate (**4c**).* The compound was described in a U.S. Patent [21] without giving experimental, NMR, and IR spectral details. Yellow oil, yield: 73%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.79; IR (neat, cm^{-1}): 1736 (C=O), 2253 (C≡C), 3497 (OH). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 0.90 (t, J 7.2 Hz, 3H, $\underline{Me}(CH_2)_3$), 1.33 (t, J 7.1 Hz, 3H, $\underline{Me}CH_2O$), 1.40 (m, 2H, $MeC\underline{H_2}(CH_2)_2$), 1.49 (m, 2H, $MeCH_2C\underline{H_2}CH_2$), 1.65 (s, 3H, Me), 2.25 (m, 2H, $MeCH_2CH_2C\underline{H_2}$), 3.48 (s, 1H, OH), 4.29 (q, J 7.1 Hz, 3H, $MeC\underline{H_2}O$). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.6 (CH_3), 14.1 (CH_3), 18.3 (CH_2), 21.9 (CH_2), 27.4 (CH_3), 30.4 (CH_2), 62.7 (CH_2), 67.9 (C), 79.8 (C), 85.0 (C), 173.5 (C). $C_{11}H_{18}O_3$ (198.26). Calcd: C 66.64, H 9.15; found: C 66.56, H 9.09.

*Methyl 2-hydroxy-2-phenyl-oct-3-ynoate (**4d**).* The compound was described in a U.S. Patent [22] without giving experimental, NMR, and IR spectral details. Light yellow oil, yield: 72%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.81; IR (neat, cm^{-1}): 1450, 1493 (Ph), 1732 (C=O), 2255 (C≡C), 3493 (OH). ^1H NMR ($CDCl_3$, 250.1 MHz, δ): 0.93 (t, J 7.3 Hz, 3H, $\underline{Me}(CH_2)_3$), 1.37–1.64 (m, 4H, $Me(C\underline{H_2})_2CH_2$), 2.32 (m, 2H, $Me(CH_2)_2C\underline{H_2}$), 3.76 (s, 3H, MeO), 4.12 (s, 1H, OH), 7.31–7.69 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 62.9 MHz, δ): 13.7 (CH_3), 18.6 (CH_2), 22.1 (CH_2), 30.5 (CH_2), 54.1 (CH_3), 72.9 (C), 78.3 (C), 87.8 (C), 126.3–139.7 (Ph), 172.8 (C). $C_{15}H_{18}O_3$ (246.30). Calcd: C 73.15, H 7.37; found: C 73.19, H 7.31.

*Ethyl 2-hydroxy-2-methyl-4-phenyl-but-3-ynoate (**4e**).* The compound was described in a U.S. Patent [21] without giving experimental, NMR, and IR spectral details. Yellow oil, yield: 73%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.78; IR (neat, cm^{-1}): 1445, 1489 (Ph), 1732 (C=O), 2253 (C≡C), 3480 (OH). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 1.36 (t, J 7.1 Hz, 3H, $\underline{Me}CH_2O$), 1.78 (s, 3H, Me), 3.63 (s, 1H, OH), 4.34 (q, J 7.1 Hz, 3H, $MeC\underline{H_2}O$), 7.28–7.45 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 14.5 (CH_3), 27.3 (CH_3), 63.1 (CH_2), 68.4 (C), 83.9 (C), 88.4 (C), 122–131.7 (Ph), 173.3 (C). $C_{13}H_{14}O_3$ (218.25). Calcd: C 71.54, H 6.47; found: C 71.61, H 6.38.

*Ethyl 2-hydroxy-2,4-diphenyl-but-3-ynoate (**4f**).* Orange crystals, yield: 75%. Eluent for TLC: ethyl acetate:hexane = 1:4, R_f 0.80; mp 80–81°C. The product **4f** is a known compound whose spectroscopic properties were fully in accord with the reported one [23]. $C_{18}H_{16}O_3$ (280.32). Calcd: C 77.12, H 5.75; found: C 77.20, H 5.69.

*General Procedure for Synthesis of the Alkyl 4-(dimethoxyphosphoryl)-alka-2,3-dienoates (**6a–c,f**)*

To a solution of phosphorus trichloride (2.75 g, 20 mmol) and triethylamine (2.23 g, 22 mmol) in dry diethyl ether (60 mL) at –70°C, a solution of alkyl 2-hydroxy-alk-3-ynoates **4** (20 mmol) in the same solvent (20 mL) was added dropwise with stirring. After 30 min stirring at the same temperature, a solution of pyridine (3.16 g, 44 mmol) and methanol (1,28 g, 40 mmol) in dry diethyl ether (50 mL) was added. The reaction mixture was stirred for 1 h at the same temperature and for 3 h at room temperature. Then the mixture was washed with water, 2 N HCl, extracted with ether, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on a column (silica gel, Kieselgel Merck 60 F_{254}) with a mixture of ethyl acetate and hexane as an eluent to give the pure products as yellow oils, which had the following properties.

*Ethyl 4-(dimethoxyphosphoryl)-2-methyl-hepta-2,3-dienoate (**6a**).* Yellow oil, yield: 62%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.63; IR (neat, cm^{-1}): 1267 (P=O), 1454, 1491 (Ph), 1713 (C=O), 1949 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 0.97 (t, J 7.4 Hz, 3H, $\underline{Me}(CH_2)_2$), 1.26 (t, J 7.2 Hz, 3H, $\underline{Me}CH_2O$), 1.52–1.58 (m, 2H, $MeC\underline{H_2}CH_2$), 1.94 (d, J 6.6 Hz, 3H, Me), 2.23–2.28 (m, 2H, $MeCH_2C\underline{H_2}$), 3.77 (d, J 11.3 Hz, 3H, MeO), 4.19–4.23 (m, 2H, $MeC\underline{H_2}O$). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.5 (CH_3), 14.2 (CH_3), 14.4 (J 6.1 Hz, CH_3), 21.2 (J 6.6 Hz, CH_2), 30.7 (J 4.8 Hz, CH_2), 53.2 (J 6.1 Hz, CH_3), 61.3 (CH_2), 95.9 (J 181.9 Hz, C), 97.6 (J 15.2 Hz, C), 166.7 (J 7.7 Hz, C), 213.3 (J 4.9 Hz, C). ^{31}P NMR ($CDCl_3$, 242.9 MHz, δ): 19.3. $C_{12}H_{21}O_5P$ (276.27). Calcd: C 52.17, H 7.66; found: C 52.25, H 7.59.

*Methyl 4-(dimethoxyphosphoryl)-2-phenyl-hepta-2,3-dienoate (**6b**).* Yellow oil, yield: 69%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.61; IR (neat, cm^{-1}): 1263 (P=O), 1449, 1495 (Ph), 1726 (C=O), 1938 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 0.96 (t, J 7.3 Hz, 3H, $\underline{Me}(CH_2)_2$), 1.62 (m, 2H, $MeC\underline{H_2}CH_2$), 2.37 (m, 2H, $MeCH_2C\underline{H_2}$), 3.73, 3.80 (dd, J 11.3 Hz, 6H, 2MeO), 3.83 (s, 3H, MeO), 7.27–7.55 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.6 (CH_3), 21.4 (J 6.8 Hz, CH_2), 31.1 (J 4.3 Hz, CH_2), 52.6 (CH_3), 53.2, 53.4 (J 6.2 Hz, CH_3), 98.7 (J 184.8 Hz, C), 104.6 (J 15.6 Hz, C), 128.3–131.1 (Ph), 165.8 (J 7.6 Hz, C), 214.6 (J 4.9 Hz, C). ^{31}P NMR ($CDCl_3$, 242.9 MHz, δ): 17.4. $C_{16}H_{21}O_5P$ (324.31). Calcd: C 59.26, H 6.53; found: C 59.18, H 6.60.

*Ethyl 4-(dimethoxyphosphoryl)-2-methyl-octa-2,3-dienoate (**6c**).* Yellow oil, yield: 63%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.63; IR (neat, cm^{-1}): 1267 (P=O), 1713 (C=O), 1952 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 0.91 (t, J 7.3 Hz, 3H, $\underline{Me}(CH_2)_3$), 1.26 (t, J 7.1 Hz, 3H, $\underline{Me}CH_2O$), 1.39 (m, 2H, $MeC\underline{H}_2(CH_2)_2$), 1.49 (m, 2H, $MeCH_2C\underline{H}_2CH_2$), 1.94 (s, 3H, Me), 2.28 (m, 2H, $MeCH_2CH_2C\underline{H}_2$), 3.74 (d, J 11.2 Hz, 6H, 2MeO), 4.21 (q, J 7.1 Hz, 3H, $MeC\underline{H}_2O$). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.8 (CH_3), 14.2 (CH_3), 14.4 (J 6.1 Hz, CH_2), 21.9 (CH_3), 28.4 (J 5.0 Hz, CH_2), 30.0 (J 6.5 Hz, CH_2), 53.1 (J 9.2 Hz, CH_3), 61.4 (CH_2), 96.0 (J 181.7 Hz, C), 97.6 (J 15.2 Hz, C), 166.7 (J 7.7 Hz, C), 213.2 (J 5.0 Hz, C). ^{31}P NMR ($CDCl_3$, 242.9 MHz, δ): 19.1. $C_{13}H_{23}O_5P$ (290.29). Calcd: C 53.79, H 7.99; found: C 53.88, H 8.05.

*Ethyl 4-(dimethoxyphosphoryl)-2,4-diphenyl-buta-2,3-dienoate (**6f**).* Yellow oil, yield: 65%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.62; IR (neat, cm^{-1}): 1265 (P = O), 1447, 1493 (Ph), 1721 (C=O), 1929 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 1.36 (t, J 7.1 Hz, 3H, $\underline{Me}CH_2O$), 3.84 (d, J 10.9 Hz, 6H, 2MeO), 4.36 (q, J 7.1 Hz, 2H, $MeC\underline{H}_2O$), 7.35–7.68 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 14.3 (CH_3), 53.6 (J 14.6 Hz, CH_3), 61.8 (CH_2), 101.6 (J 185.2 Hz, C), 105.9 (J 15.7 Hz, C), 127.8–129.2 (2Ph), 164.7 (C), 218.1 (J 4.7 Hz, C). ^{31}P NMR ($CDCl_3$, 242.9 MHz, δ): 15.6. $C_{20}H_{21}O_5P$ (372.35). Calcd: C 64.51, H 5.68; found: C 64.43, H 5.72.

*General Procedure for Synthesis of the Alkyl 4-(Diphenylphosphinoyl)-alka-2,3-dienoates (**8c–f**)*

To a solution of alkyl 2-hydroxy-alk-3-ynoates **4** (20 mmol) and triethylamine (2.23 g, 22 mmol) in dry diethyl ether (60 mL) at –70°C, a solution of freshly distilled chlorodiphenylphosphine (4.41 g, 20 mmol) in the same solvent (20 mL) was dropwise added with stirring. The reaction mixture was stirred for 1 h at the same temperature and for 5 h at room temperature. Then the mixture was washed with water, 2 N HCl, extracted with diethyl ether, and the extract was washed with saturated NaCl, and dried over anhydrous sodium sulfate. The solvent was removed using a rotatory evaporator, and the residue was purified by column chromatography on a silica gel (Kieselgel Merck 60 F_{254}) with ethyl acetate/hexane to give the pure products as oils, which had the following properties.

*Ethyl 4-(diphenylphosphinoyl)-2-methyl-octa-2,3-dienoate (**8c**).* Yellow oil, yield: 60%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.61; IR (neat, cm^{-1}): 1121 (P=O), 1439, 1488 (Ph), 1713 (C=O), 1946 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 0.85 (t, J 7.2 Hz, 3H, $\underline{Me}(CH_2)_3$), 1.36 (t, J 7.1 Hz, 3H, $\underline{Me}CH_2O$), 1.53 (d, J 8.8 Hz, 3H, Me), 2.31 (m, 2H, $\underline{Me}(C\underline{H}_2)_2CH_2$), 2.46 (m, 2H, $Me(CH_2)C\underline{H}_2$), 4.23 (q, J 7.1 Hz, 3H, $MeC\underline{H}_2O$), 7.41–7.98 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.7 (CH_3), 13.9 (CH_3), 14.5 (CH_3), 22.8 (CH_2), 27.4 (J 5.2 Hz, CH_2), 30.4 (J 7.6 Hz, CH_2), 61.3 (CH_2), 98.1 (J 13.0 Hz, C), 102.4 (J 94.5 Hz, C), 128.5–132.7 (2Ph), 166.8 (J 4.3 Hz, C), 212.4 (J 6.5 Hz, C). ^{31}P NMR ($CDCl_3$, 242.9 MHz, δ): 31.8. $C_{23}H_{27}O_3P$ (382.43). Calcd: C 72.23, H 7.12; found: C 72.30, H 7.21.

*Methyl 4-(diphenylphosphinoyl)-2-phenyl-octa-2,3-dienoate (**8d**).* Orange oil, yield: 58%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.64; IR (neat, cm^{-1}): 1121 (P=O), 1439, 1485 (Ph), 1726 (C=O), 1931 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 0.85 (t, J 7.4 Hz, 3H, $\underline{Me}(CH_2)_3$), 1.33–1.39 (m, 4H, $Me(C\underline{H}_2)_2CH_2$, 1.56–1.62 (m, 2H, $Me(CH_2)_2C\underline{H}_2$), 3.38 (s, 3H, MeO), 7.27–7.94 (m, 15H, 3Ph,). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.8 (CH_3), 15.0 (CH_3), 22.3 (CH_2), 27.8 (J 4.9 Hz, CH_2), 30.3 (J 5.9 Hz, CH_2), 52.4 (CH_3), 104.4 (J 92.9 Hz, C), 105.2 (J 12.9 Hz, C), 126.4–133.2 (3Ph), 165.8 (J 6.7 Hz, C), 213.3 (J 6.4 Hz, C). ^{31}P NMR ($CDCl_3$, 242.9 MHz, δ): 29.9. $C_{27}H_{27}O_3P$ (430.48). Calcd: C 75.33, H 6.32; found: C 75.41, H 6.25.

*Ethyl 4-(diphenylphosphinoyl)-2-methyl-4-phenyl-buta-2,3-dienoate (**8e**).* Orange oil, yield: 57%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.60; IR (neat, cm^{-1}): 1179 (P=O), 1439, 1487 (Ph), 1714 (C=O), 1940 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 1.34 (t, J 7.1 Hz, 3H, $\underline{Me}CH_2O$), 1.56 (d, J 5.6 Hz, 3H, Me), 4.16–4.27 (m, 2H, $MeC\underline{H}_2O$), 7.22–7.97 (m, 15H, 3Ph). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.7 (J 4.8 Hz, CH_3), 14.5 (CH_3), 61.4 (CH_2), 99.0 (J 12.3 Hz, C), 104.3 (J 95.4 Hz, C), 128.1–132.4 (3Ph), 165.9 (J 6.4 Hz, C), 215.8 (J 5.9 Hz, C). ^{31}P NMR ($CDCl_3$, 242.9 MHz, δ): 30.6. $C_{25}H_{23}O_3P$ (402.42). Calcd: C 74.62, H 5.76; found: C 74.69, H 5.68.

*Ethyl 4-(diphenylphosphinoyl)-2,4-diphenyl-buta-2,3-dienoate (**8f**).* Orange oil, yield: 52%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.61; IR (neat, cm^{-1}): 1152 (P=O), 1439, 1493 (Ph), 1717 (C=O), 1921 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 1.43 (t, J 6.9 Hz, 3H, $\underline{Me}CH_2O$), 4.35 (q, J 6.9 Hz, 2H, $MeC\underline{H}_2O$), 7.20–7.95 (m, 20H, 4Ph).

^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 14.5 (CH_3), 61.6 (CH_2), 106.1 (*J* 12.8 Hz, C), 107.2 (*J* 97.9 Hz, C), 127.8–132.4 (4Ph), 164.6 (C), 217.4 (*J* 7.1 Hz, C). ^{31}P NMR ($CDCl_3$, 242.9 MHz, δ): 29.6. $C_{30}H_{25}O_3P$ (464.49). Calcd: C 77.57, H 5.42; found: C 77.49, H 5.48.

*General Procedure for Synthesis of the Alkyl 4-(Benzenesulfinyl)-alka-2,3-dienoates (**10a–c,f**)*

To a solution of alkyl 2-hydroxy-alk-3-ynoates **4** (20 mmol) and triethylamine (2.23 g, 22 mmol) in dry diethyl ether (60 mL) at –70°C, a solution of freshly distilled benzenesulfanyl chloride (2.89 g, 20 mmol) in the same solvent (20 mL) was added dropwise with stirring. The reaction mixture was stirred for 1 h at the same temperature and for 7 h at room temperature. Then the mixture was washed with water, 2 N HCl, extracted with ether, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on a column (silica gel, Kieselgel Merck 60 F_{254}) with a mixture of ethyl acetate and hexane as an eluent to give the pure products as yellow oils, which had the following properties.

*Ethyl 4-(benzenesulfinyl)-2-methyl-hepta-2,3-dienoate (**10a**).* Yellow oil, yield: 64%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.59; IR (neat, cm^{-1}): 1051 (S=O), 1445, 1476 (Ph), 1715 (C=O), 1951 (C=C=C). ^{1}H NMR ($CDCl_3$, 250.1 MHz, δ): 1.00 (t, *J* 7.5 Hz, 3H, $\underline{Me}(CH_2)_2$), 1.33 (t, *J* 7.2 Hz, 3H, $\underline{Me}CH_2O$), 1.52 (m, 2H, $MeC\underline{H_2}CH_2$), 2.02 (s, 3H, $\underline{Me}$), 2.23 (m, 2H, $MeCH_2C\underline{H_2}$), 4.24 (m, 2H, $MeC\underline{H_2}O$), 7.46–7.80 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 62.9 MHz, δ): 13.3 (CH_3), 13.5 (CH_3), 14.4 (CH_3), 20.7 (CH_2), 26.9 (CH_2), 61.6 (CH_2), 102.9 (C), 115.8 (C), 124.6–131.4 (Ph), 166.0 (C), 206.8 (C). $C_{16}H_{20}O_3S$ (292.39). Calcd: C 65.72, H 6.89; found: C 65.82, H 6.95.

*Methyl 4-(benzenesulfinyl)-2-phenyl-hepta-2,3-dienoate (**10b**).* Yellow oil, yield: 64%. Eluent for TLC: ethyl acetate:hexane = 1:4, R_f 0.62; IR (neat, cm^{-1}): 1053 (S=O), 1434, 1495 (Ph), 1728 (C=O), 1943 (C=C=C). ^{1}H NMR ($CDCl_3$, 600.1 MHz, δ): 0.83 (t, *J* 7.3 Hz, 3H, $\underline{Me}(CH_2)_2$), 1.48 (m, 2H, $MeC\underline{H_2}CH_2$), 2.33 (m, 2H, $MeCH_2C\underline{H_2}$), 3.72 (s, 3H, MeO), 7.22–8.23 (m, 10H, 2Ph,). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 12.1 (CH_3), 19.4 (CH_2), 31.4 (CH_2), 52.7 (CH_3), 106.3 (C), 111.1 (C), 122.6–146.5 (2Ph), 161.9 (C), 209.5 (C). $C_{20}H_{20}O_3S$ (340.44). Calcd: C 70.56, H 5.92; found: C 70.65, H 6.01.

*Ethyl 4-(benzenesulfinyl)-2-methyl-octa-2,3-dienoate (**10c**).* Light yellow oil, yield: 67%. Eluent for TLC: ethyl acetate:hexane = 1:4, R_f 0.62; IR (neat, cm^{-1}): 1057 (S=O), 1440, 1475 (Ph), 1715 (C=O), 1951 (C=C=C). ^{1}H NMR ($CDCl_3$, 600.1 MHz, δ): 0.79 (t, *J* 6.9 Hz, 3H, $\underline{Me}(CH_2)_3$), 1.34 (t, *J* 7.2 Hz, 3H, $\underline{Me}CH_2O$), 1.67 (m, 4H, $Me(C\underline{H_2})_2CH_2$), 2.09 (s, 3H, Me), 2.35 (m, 2H, $Me(CH_2)_2C\underline{H_2}$), 4.28 (q, *J* 7.2 Hz, 3H, $MeC\underline{H_2}O$), 7.51–7.69 (m, 5H, Ph,). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 14.3 (CH_3), 15.0 (CH_3), 15.8 (CH_3), 22.5 (CH_2), 25.2 (CH_2), 29.9 (CH_2), 68.4 (CH_2), 108.9 (C), 115.4 (C), 132.6–148.4 (Ph), 166.4 (C), 213.7 (C). $C_{17}H_{22}O_3S$ (306.42). Calcd: C 66.63, H 7.24; found: C 66.73, H 7.30.

*Ethyl 4-(benzenesulfinyl)-2,4-diphenyl-buta-2,3-dienoate (**10f**).* Yellow oil, yield: 69%. Eluent for TLC: ethyl acetate:hexane = 1:4, R_f 0.60; IR (neat, cm^{-1}): 1026 (S=O), 1443, 1491 (Ph), 1719 (C=O), 1947 (C=C=C). ^{1}H NMR ($CDCl_3$, 600.1 MHz, δ): 1.38 (t, *J* 6.8 Hz, 3H, $\underline{Me}CH_2O$), 4.36 (q, *J* 6.8 Hz, 2H, $MeC\underline{H_2}O$), 7.23–7.84 (m, 15H, 3Ph). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 14.2 (CH_3), 61.9 (CH_2), 108.4 (C), 109.1 (C), 126.4–136.8 (3Ph), 167.8 (C), 216.0 (C). $C_{24}H_{20}O_3S$ (388.48). Calcd: C 74.20, H 5.19; found: C 74.16, H 5.27.

*General Procedure for Synthesis of the Alkyl 4-(methanesulfonyl)-alka-2,3-dienoates (**12c–f**)*

To a solution of alkyl 2-hydroxy-alk-3-ynoates **4** (20 mmol) and triethylamine (2.23 g, 22 mmol) in dry diethyl ether (60 mL) at –70°C, a solution of freshly distilled methanesulfinyl chloride (1.97 g, 20 mmol) in the same solvent (20 mL) was added dropwise with stirring. The reaction mixture was stirred for 1 h at the same temperature and for 2 h at room temperature. Then the mixture was washed with water, 2 N HCl, extracted with ether, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was dissolved in dried toluene (30 mL) and refluxed for 8 h. After evaporation of the solvent, the residue was chromatographed on a column (silica gel, Kieselgel Merck 60 F_{254}) with a mixture of ethyl acetate and hexane as an eluent to give the pure products as oils, which had the following properties.

*Ethyl 4-(methanesulfonyl)-2-methyl-octa-2,3-dienoate (**12c**).* Light orange oil, yield: 48%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.61; IR (neat, cm^{-1}): 1144, 1314 (SO_2), 1719 (C=O), 1960 (C=C=C). ^{1}H NMR ($CDCl_3$, 600.1 MHz, δ): 0.95 (t, *J* 7.3 Hz, 3H, $\underline{Me}(CH_2)_3$), 1.30 (t, *J* 7.1 Hz, 3H, $\underline{Me}CH_2O$), 1.46 (m, 2H, $MeC\underline{H_2}CH_2CH_2$), 1.58 (m,

2H, $MeCH_2C\underline{H_2}CH_2$), 2.07 (s, 3H, Me), 2.52 (m, 2H, $Me(CH_2)_2C\underline{H_2}$), 3.46 (s, 3H, $MeSO_2$), 4.26 (q, *J* 7.1 Hz, 3H, $MeC\underline{H_2}O$). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 13.9 (CH_3), 14.4 (CH_3), 14.9 (CH_3), 28.6 (CH_2), 33.8 (CH_2), 36.5 (CH_2), 49.2 (CH_3), 68.8 (CH_2), 111.4 (C), 115.5 (C), 165.2 (C), 216.1 (C). $C_{12}H_{20}O_4S$ (260.35). Calcd: C 55.36, H 7.74; found: C 55.28, H 7.79.

*Methyl 4-(methanesulfonyl)-2-phenyl-octa-2,3-dienoate (***12d***).* Light yellow oil, yield: 47%. Eluent for TLC: ethyl acetate:hexane = 1:3, R_f 0.65; IR (neat, cm^{-1}): 1142, 1315 (SO_2), 1450, 1488 (Ph), 1726 (C=O), 1947 (C=C=C). ^1H NMR ($CDCl_3$, 250.1 MHz, δ): 0.91 (t, *J* 7.2 Hz, 3H, $\underline{Me}(CH_2)_3$), 1.40 (m, 2H, $MeC\underline{H_2}CH_2CH_2$), 1.58 (m, 2H, $MeCH_2C\underline{H_2}CH_2$), 2.58 (m, 2H, $Me(CH_2)_2C\underline{H_2}$), 3.08 (s, 3H, $\underline{Me}SO_2$), 3.88 (s, 3H, MeO), 7.35–7.58 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 62.9 MHz, δ): 13.7 (CH_3), 22.1 (CH_2), 27.3 (CH_2), 29.5 (CH_2), 42.4 (CH_3), 53.0 (CH_3), 110.8 (C), 117.4 (C), 128.4–130.2 (Ph), 164.7 (C), 210.4 (C). $C_{16}H_{20}O_4S$ (308.39). Calcd: C 62.31, H 6.54; found: C 62.23, H 6.47.

*Ethyl 4-(methanesulfonyl)-2-methyl-4-phenyl-buta-2,3-dienoate (***12e***).* Light orange oil, yield: 46%. Eluent for TLC: ethyl acetate:hexane = 1:1, R_f 0.59; IR (neat, cm^{-1}): 1140, 1311 (SO_2), 1447, 1489 (Ph), 1722 (C=O), 1951 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 1.33 (t, *J* 7.1 Hz, 3H, $\underline{Me}CH_2O$), 2.10 (s, 3H, Me), 3.00 (s, 3H, $MeSO_2$), 4.30 (q, *J* 7.1 Hz, 3H, $MeC\underline{H_2}O$), 7.27–7.64 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 14.3 (CH_3), 14.7 (CH_3), 42.7 (CH_3), 62.3 (CH_2), 111.5 (C), 116.5 (C), 128.1–129.8 (Ph), 165.3 (C), 212.3 (C). $C_{14}H_{16}O_4S$ (280.34). Calcd: C 59.98, H 5.75; found: C 60.06, H 5.69.

*Ethyl 4-(methanesulfonyl)-2,4-diphenyl-buta-2,3-dienoate (***12f***).* Orange oil, yield: 52% (54%, in the case of isolation by column chromatography of **11f**). Eluent for TLC: ethyl acetate:hexane = 1:3, R_f 0.60; IR (neat, cm^{-1}): 1140, 1315 (SO_2), 1447, 1493 (Ph), 1724 (C=O), 1942 (C=C=C). ^1H NMR ($CDCl_3$, 600.1 MHz, δ): 1.38 (t, *J* 7.1 Hz, 3H, $\underline{Me}CH_2O$), 3.07 (s, 3H, Me), 4.38 (q, *J* 7.2 Hz, 3H, $MeC\underline{H_2}O$), 7.26–7.84 (m, 5H, 2Ph,). ^{13}C NMR ($CDCl_3$, 150.9 MHz, δ): 14.5 (CH_3), 42.8 (CH_3), 62.5 (CH_2), 110.7 (C), 117.4 (C), 126.8–132.6 (2Ph), 163.5 (C), 213.9 (C). $C_{19}H_{18}O_4S$ (342.41). Calcd: C 66.65, H 5.30; found: C 66.57, H 5.35.

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