Migration of oxygen from tantalum to the imino carbon would give an η^2-acylimidoyl complex **6**,[15] which would produce 2-tantalofuran **7** via oxygen-assisted elimination of NAr. The affinity of tantalum for heteroatoms (and hence the formation of the η^2-acylimidoyl complex **6**) is the driving force for this migration process. The presence of the 2-tantalofuran **7** was ascertained by the fact that quenching of the reaction mixture of **7b** with alkaline D_2O afforded 2-deuterated furan *d*-**8b** ($R^1 = R^2 = n\text{-}C_5H_{11}$, $R^3 = n\text{-}C_3H_7$, 47% yield, 91% deuterated).

(15) For η^2-acylimidoyl complexes of tantalum, see: (a) Takahashi, Y.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sugiyama, K. *Chem. Lett.* **1978**, 525. For η^2-acyl complexes of tantalum, see: (b) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421. (c) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

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Supplementary Material Available: A typical experimental procedure for the synthesis of 2-octyl-3,4-dipentylfuran (**8a**) and spectral data for all new compounds (5 pages). Ordering information is given on any current masthead page.

Articles

New Functionalized Horner–Wadsworth–Emmons Reagents: Useful Building Blocks in the Synthesis of Polyunsaturated Aldehydes. A Short Synthesis of (±)-(*E*,*E*)-Coriolic Acid

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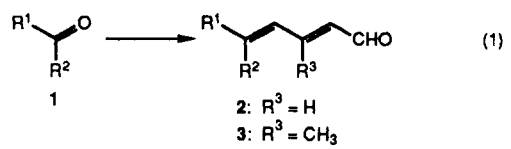
The new Horner–Wadsworth–Emmons reagents **4** and **5** transform carbonyl compounds into 2,4-pentadienals and 3-methyl-2,4-pentadienals, respectively. Reagent **4** gives good yields of the desired products with a variety of aldehydes and ketones; reagent **5** generally gives good yields with aldehydes, but gives lower yields with ketones. The reactions proceed under mild conditions and give the products as predominantly 2*E*,4*E* isomers, with moderate to good stereoselectivity. In general, pure samples of the 2*E*,4*E*-dienals can be obtained after chromatography. Reagents **4** have been used in the key step in a short synthesis of (±)-13-hydroxy-9(*E*),11(*E*)-octadecadienoic acid ((*E*,*E*)-coriolic acid, **45**).

Introduction

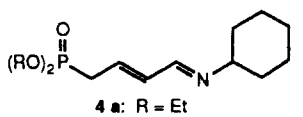
The direct transformation of a carbonyl compound **1** into an elongated conjugated dienal (**2** or **3**, eq 1) is a very attractive reaction from a synthetic point of view.

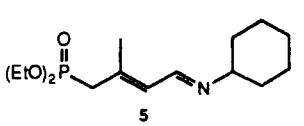


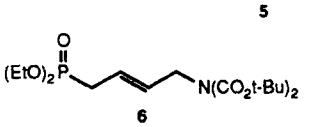
(1)

From the dienals, substructures of many interesting target compounds can be obtained in a few steps: (1) a polyene derivative can be obtained by a further condensation reaction (e.g. Horner–Wadsworth–Emmons[2] (HWE) or Wittig[3]); (2) selective nucleophilic addition to the carbonyl group will give a polyunsaturated secondary allylic alcohol; (3) the dienal itself, or compounds derived from it, can participate in cycloaddition reactions[4] to give carbo- or heterocyclic rings. Synthetic applications include many classes of natural products with useful biological activity.

We recently introduced the functionalized HWE reagent **4a**, which converts carbonyl compounds directly into dienals **2** (eq 1; $R^3 = H$).[5] We now introduce the reagent **5**, which transforms carbonyl compounds directly into methyl-substituted dienals **3** (eq 1; $R^3 = CH_3$). In other work, we had previously developed the related reagent **6**.[6]



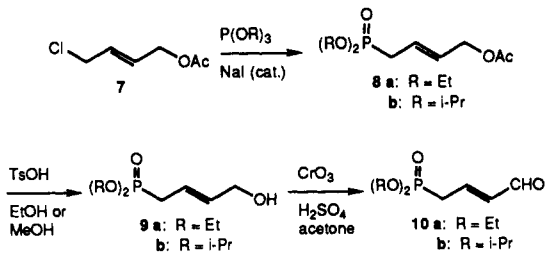




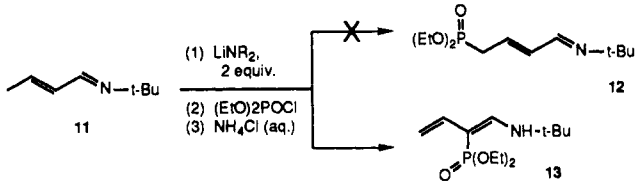
(1) (a) Royal Institute of Technology. (b) University of Notre Dame.
(2) For reviews, see: (a) Wadsworth, W. S. *Org. React.* (*N.Y.*) **1977**, *25*, 73–253. (b) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87–99.
(3) For reviews, see: (a) Pommer, H. *Angew. Chem.* **1977**, *89*, 437–443. (b) Maryanoff, B.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.
(4) For some relevant examples, see: (a) Takeda, K.; Yano, S.-G.; Yoshii, E. *Tetrahedron Lett.* **1988**, *29*, 6951–6954. (b) Roush, W. R.; Brown, B. B.; Drozda, S. E. *Ibid.* **1988**, *29*, 3541–3544. (c) Tapolczay, D. J.; Thomas, E. J.; Whitehead, J. W. F. *J. Chem. Soc., Chem. Commun.* **1985**, 143–145. (d) Roush, W. R.; Peseckis, S. M.; Walts, A. E. *J. Org. Chem.* **1984**, *49*, 3429–3432.
(5) Rein, T.; Åkermark, B.; Helquist, P. *Acta Chem. Scand., Ser. B* **1988**, *42*, 569–572.

0022-3263/90/1955-5312$02.50/0 © 1990 American Chemical Society

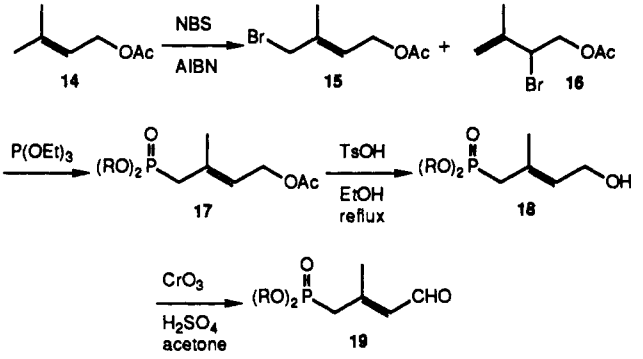
Scheme I



Scheme II



Scheme III



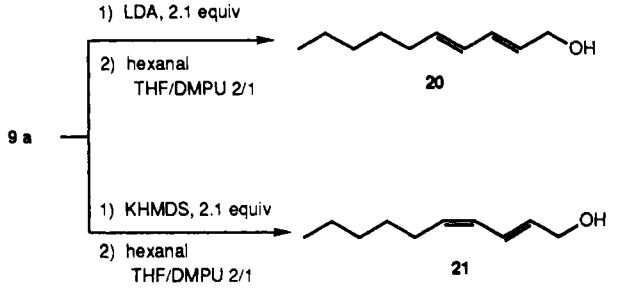
In this paper, we describe in detail our study of the preparation and the condensation reactions of **4** and **5** with carbonyl compounds.

Results and Discussion

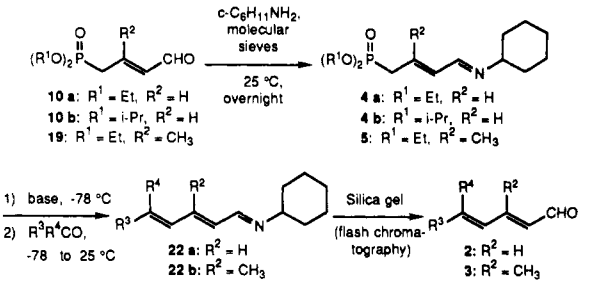
The phosphoryl imines **4** and **5** were prepared in situ from the aldehydes **10** and **19** (vide infra).

Preparation of Aldehyde 10 (Scheme I). The chloro acetate **7** (*E*:*Z* = ca. 90:10) was obtained in good yield (65–75%) from 1,3-butanediene using a palladium(II)-catalyzed 1,4-acetoxychlorination reaction.[7] An Arbuzov reaction[8] was then employed to arrive at the phosphoryl acetates **8** (**8a**, 81%; **8b**, 54%; *E*:*Z* = ca. 90:10 in both cases). For the transformation of **8** into the corresponding alcohols **9**, we first tried standard alkaline hydrolysis conditions. These attempts were frustrated, however, by the simultaneous formation of the phosphoryl diene $H_2C{=}CHCH{=}CHP(O)(OEt)_2$ in comparable amounts.[9,10] When **8** was instead heated at reflux in ethanol or methanol with a catalytic amount of *p*-toluenesulfonic acid present, the desired phosphoryl alcohols **9** were smoothly obtained in almost quantitative yield (95–97%; *E*:*Z* = ca. 90:10 in both cases). Of the several methods attempted for the oxidation of the alcohols **9** to the aldehydes **10**

Scheme IV



Scheme V



(PDC,[11,12] CrO_3/pyridine,[13] Swern,[14] DDQ,[11,15] MnO_2,[16] $BaMnO_4$,[17] $K_2Cr_2O_7$/Adogen 464,[18] DDQ/H_5IO_6[19]), the most useful proved to be the Jones oxidation.[20] Chromatographic purification must be carried out by using water-deactivated silica gel (ca. 10% w/w), since the aldehydes **10** partly decompose on untreated silica gel. Once obtained in pure form, the phosphoryl aldehydes are reasonably stable if stored under argon at −20 °C. Nevertheless, use of the freshly prepared aldehydes is recommended for further transformations. When samples of pure (*Z*)-**9a** were oxidized according to this procedure, essentially pure (*E*)-**10** was obtained, apparently due to facile double bond isomerization.[21]

We also attempted the preparation of related reagents by the direct phosphorylation of the unsaturated imine **11**.[22] However, instead of the desired product **12**, the regioisomeric compound **13** was obtained (Scheme II) despite the use of several different bases.[23,24]

(6) Connell, R. D.; Helquist, P.; Åkermark, B. *J. Org. Chem.* **1989**, *54*, 3359–3370.
(7) (a) Bäckvall, J.-E.; Nyström, J.-E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676–3686. (b) Nyström, J.-E.; Rein, T.; Bäckvall, J.-E. *Org. Synth.* **1988**, *67*, 105–113.
(8) Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415–430.
(9) Ståhlberg, A.; Rein, T., unpublished results.
(10) Åkermark, B.; Nyström, J.-E.; Rein, T.; Bäckvall, J.-E.; Helquist, P.; Aslanian, R. *Tetrahedron Lett.* **1984**, *25*, 5719–5722.
(11) Abbreviations used in the text: AIBN, azoisobutyronitrile; DDQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; 4-DMAP, 4-(dimethylamino)pyridine; DME, dimethoxyethane; KHMDS, potassium hexamethyl disilazide (potassium bis(trimethylsilyl)amide); LDA, lithium diisopropylamide; LTMP, lithium 2,2,6,6-tetramethylpiperidide; MPLC, medium-pressure liquid chromatography; NaHMDS, sodium hexamethyl disilazide (sodium bis(trimethylsilyl)amide); NBS, *N*-bromosuccinimide; PDC, pyridinium dichromate.
(12) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399–402.
(13) Ratcliffe, R.; Rodehurst, R. *J. Org. Chem.* **1970**, *35*, 4000–4001.
(14) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480–2482.
(15) Burn, D.; Petrow, V.; Weston, G. O. *Tetrahedron Lett.* **1960** (No. 9), 14–15.
(16) Fatiadi, A. J. *Synthesis* **1976**, 65–104.
(17) Al-Hassan, M. *Gazz. Chim. Ital.* **1985**, *115*, 441.
(18) Hutchins, R. O.; Natale, N. R.; Cook, W. J.; Ohr, J. *Tetrahedron Lett.* **1977**, 4167–4170.
(19) Cacchi, S.; La Torre, F.; Paolucci, G. *Synthesis* **1978**, 848–849.
(20) Harding, K. E.; May, L. M.; Dick, K. F. *J. Org. Chem.* **1975**, *40*, 1664–1665.
(21) This kind of isomerization is well known: Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer-Verlag: Berlin, 1984.
(22) Kieczykowski, G. R.; Schlessinger, R. H.; Sulsky, R. B. *Tetrahedron Lett.* **1976**, 597–600.
(23) Haag, I.; Rein, T., unpublished results.
(24) For γ-silylation of a lithiated imine, see: (a) Takabe, K.; Fujiwara, H.; Katagiri, T.; Tanaka, J. *Tetrahedron Lett.* **1975**, 1237–1238. (b) Meyers, A. I.; Tomioka, K.; Fleming, M. P. *J. Org. Chem.* **1978**, *43*, 3788–3799.

Preparation of Aldehyde 19 (Scheme III). Acetate **14** is easily available in quantity, by acetylation of the corresponding commercially available alcohol. Wohl–Ziegler bromination[25] afforded a crude mixture of the allylic bromides **15** and **16** ((*E*)-**15**:(*Z*)-**15**:**16** = ca. 4:2:1) in ca. 50% yield after distillation. The mixture of regioisomeric bromides was treated directly with triethyl phosphite under Arbuzov conditions to provide the phosphoryl acetate **17** (54%; *E*:*Z* = 67:33). Acid-catalyzed transesterification then gave the phosphoryl alcohol **18** (*E*:*Z* = 70:30) in 71% yield. Finally, Jones oxidation delivered the phosphoryl aldehyde **19** in 86% yield (*E*:*Z* = 55:45). For aldehyde **19**, double bond isomerization is again facile. When a sample of isomerically pure (*E*)-**18** was oxidized under the Jones conditions, the aldehyde **19** was still obtained as a ca. 55:45 mixture of *E* and *Z* isomers. We also attempted to use two other chromium(VI) reagents (PDC and 2,2′-bipyridinium chlorochromate[26]) in this transformation, but in neither case was the stereoselectivity significantly improved.

Condensation Reactions with the Phosphoryl Alcohol 9a. With the phosphoryl alcohol **9a** available, we first performed a short duty of its utility in HWE condensations. The direct transformation of carbonyl compounds into 2,4-pentadienols (see **20**) would have synthetic utility in its own right. These attempts had limited success, however, and low product yields were obtained (≤25%),[27] perhaps due to side reactions promoted by the alkoxide group.[28] Interestingly, when the dilithio derivative of **9a** was condensed with hexanal, the stereoselectivity of double bond formation depended strongly on the counterion (Scheme IV).[29] When lithium was used as the counterion, the 2*E*,4*E* isomer **20** was formed in excess (2*E*,4*E*:2*E*,4*Z* = 77:23; combined yield ca. 20%), whereas the 2*E*,4*Z* isomer **21** was favored with potassium as the counterion (2*E*,4*E*:2*E*,4*Z* = 25:75; combined yield ca. 25%).[30]

Condensation Reactions with Phosphoryl Imines 4 and 5. The condensations were performed as one-pot procedures, from the starting phosphoryl aldehydes (**10** and **19**) to the pentadienals **2** and **3** (Scheme V).

The imines **4** and **5** were not isolated but were instead prepared in situ from cyclohexylamine and the aldehydes[31] (**10** and **19**, respectively). As judged by ^{1}H NMR, these transformations proceeded virtually quantitatively. The desired reagents were actually formed as mixtures of the imine tautomers **4** and the dienamine tautomers $(R'O)_2P(O)CH{=}CHCH{=}CHNH\text{-cyclo-}C_6H_{11}$. The reagent **5**, on the other hand, was formed only as the imine tautomer (*E*:*Z* = 55:45). The solutions were dried with molecular sieves (3 or 4 Å) and then used directly in condensation reactions. The intermediate imines **22** were not purified but were instead hydrolyzed during flash chromatography[33] to produce the desired dienals (**2** or **3**).[34] The results of the condensations are presented in Tables I and II.

In general, **4** gave useful yields of the desired products, both with aldehydes (Table I, entries 1–19) and ketones (entries 20–23), when appropriate conditions were used; in reactions with conjugated aldehydes the yields were sensitive to the choice of counterion and solvent. Reagent **5** gave good yields with all aldehydes tried, including saturated aliphatic (Table II, entries 1–6), aromatic (entries 7–11), and conjugated unsaturated (entries 12–19). It gave, however, only a modest yield of the desired dienal when condensed with cyclohexanone (entry 20). An attempted condensation of reagent **5** with acetophenone gave a low yield of the desired product and substantial amounts of uncharacterized byproducts.

The condensations of **4** and **5** with conjugated unsaturated aldehydes were studied in somewhat more detail because a number of synthetic applications would rely on such a reaction. In these condensations, conjugate addition of the phosphonate anion to the aldehyde could be expected to compete with the desired HWE condensation.[35] The results obtained in the condensations with cinnamaldehyde (Table I, entries 13–15, and Table II, entries 13–18) show that the yield depended on a proper choice of both base and solvent. In the reactions with **4**, NaHMDS/THF turned out to be the best combination while LDA/THF and KHMDS/THF gave significantly lower yields. Furthermore, the yields obtained with DME as solvent were lower than when THF was used for all three bases (these runs are not included in Table I). Reagent **5** performed best when KHMDS/THF was used, although NaHMDS/DME gave nearly as good results. Other combinations of base and solvent resulted in distinctly lower yields.

Besides flash chromatography, other methods for hydrolyzing the imines **22** were tried (two-phase system, organic solvent/dilute oxalic acid or acetate buffer;[24b,31] SiO_2/weak acid[36]), but they consistently gave ca. 20% lower isolated yields of dienals **2** and **3**. Also, the chromatographic hydrolysis is convenient since purification is effected simultaneously. Still, even when using the chromatographic hydrolysis, we observed that the yields of the unsaturated imines before hydrolysis were generally 15–25% higher (in the range of 75–95%) than the yields of dienals obtained after hydrolysis.

Reaction Stereochemistry. The stereoselectivity[37] in favor of the 2*E*,4*E* isomer is generally good (84–95%) for the reactions of reagent **4** with aldehydes (Table I, entries

(25) *Houben-Weyl Methoden der Organischen Chemie*; G. Thieme Verlag: Stuttgart, 1960; Vol. V/4, pp 29–34 and 221–233.

(26) Guziec, F. S., Jr.; Luzzio, F. A. *Synthesis* **1980**, 691–694.

(27) For studies of the dianion of 4-(diphenylphosphoryl)-1-hydroxy-2-butene, see: Vedejs, E.; Campbell, J. B., Jr.; Gadwood, R. C.; Rodgers, J. D.; Spear, K. L.; Watanabe, Y. *J. Org. Chem.* **1982**, *47*, 1534–1546. For studies of 3-methyl-4-(diphenylphosphoryl)-2-buten-1-ol and 1-(diphenylphosphoryl)-2-penten-4-ol, see: Brown, P. S.; McElroy, A. B.; Warren, S. *Tetrahedron Lett.* **1985**, *26*, 249–252.

(28) When the alcohol substituent in **9a** was protected as a THP or t-BuMe$_2$Si ether, attempted condensation reactions afforded only the phosphoryl diene and/or decomposition products presumably derived from it. For use of a reagent containing a benzyloxy group, see ref 4a. See also ref 6.

(29) Rein, T. Ph.D. Dissertation, Royal Institute of Technology, 1989.

(30) (a) Takacs, J. M.; Helle, M. A.; Seely, F. L. *Tetrahedron Lett.* **1986**, *27*, 1257–1260. (b) Redjal, A.; Seyden-Penne, J. *Tetrahedron Lett.* **1974**, 1733–1736.

(31) Nagata, W.; Hayase, Y. *J. Chem. Soc. C* **1969**, 460–466. Less useful was the corresponding *tert*-butyl imine or an oxime ether.

(32) Compare with predominant formation of the enamine tautomer $(EtO)_2P(O)CH{=}CHNH(c\text{-}C_6H_{11})$ (ref 31).

(33) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

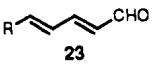
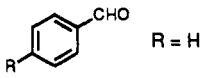
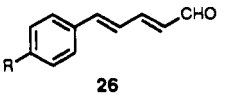
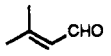
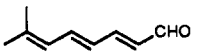
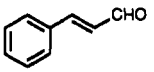
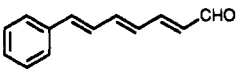
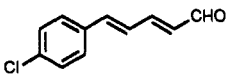
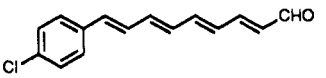
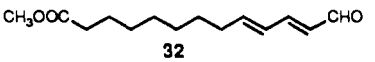
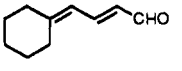
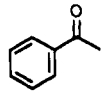
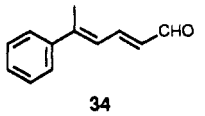
(34) Hydrolysis of certain α,β-unsaturated aldimines occurs during chromatography whereas others survive. See ref 35 and Yamasaki, Y.; Maekawa, T.; Ishihara, T.; Ando, T. *Chem. Lett.* **1985**, 1387–1390.

(35) (a) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 5411–5423. (b) Moorhoff, C. M.; Schneider, D. F. *Tetrahedron Lett.* **1987**, *28*, 559–562. (c) Masamune, S.; Brooks, D. W.; Morio, K.; Sobczak, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 8277–8279. (d) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1973**, *106*, 3779–3787. (e) Bergmann, E.; Solomonovici, A. *Tetrahedron* **1971**, *27*, 2675–2678. (f) Schlessinger, R. H.; Graves, D. D. *Tetrahedron Lett.* **1987**, *28*, 4385–4388. (g) Hanessian, S.; Hodges, P. J.; Sahoo, S. P.; Roy, P. J. *Ibid.* **1986**, *26*, 2949–2952.

(36) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63–65.

(37) Stereochemical assignments are based on ^{1}H NMR data. For some of the polyenals (**26**, **41**) the stereochemical assignments have been made in analogy with similar compounds, because of difficulties in determining all relevant coupling constants. Isomer ratios were determined from the integrals for the C*H*O protons.

Table I. Condensation Reactions of Carbonyl Compounds with Phosphonate Reagents 4[a]

entry	carbonyl compound	base	reaction time,[b] h	product	yield, %	isomer ratio[c]
1	RCHO, R = *n*-C_5H_{11}	LDA	2	 **23**	78	84:14:2 (87:13:2)
2		t-BuOK	22		54	44:56:– (not det)
3	R = *n*-C_7H_{15}	LDA	3	**24**	71[d]	85:12:3 (81:16:3)
4		NaHMDS	4		72[d]	73:25:2 (72:28:–)
5		KHMDS	4		72[d]	64:34:2 (61:39:–)
6	R = c-C_6H_{11}	LDA	19	**25**	70	90:7:3 (91:9:–)
7		NaHMDS	20		78	88:9:3 (not det)[e]
8	 R = H			 **26**	65	94:4:2 (90:6:4)
9	R = Cl	LDA	17	**27**	75	94:4:2 (91:9:–)
10	R = OCH_3	LDA	15	**28**	73	93:6:1 (not det)
11		LDA	15	 **29**	45	88:9:3 (85:15:–)
12		NaHMDS	17		61	92:6:2 (not det)
13		LDA	6	 **30**	25	90:7:3 (not fdet)
14		NaHMDS	16		53	92:6:2 (88:12:–)
15		KHMDS	23		29	95:2:3 (not det)
16		NaHMDS	24	 **31**	60	87:10:3 (88:9:3)
17		LDA	2	 **32**	65	83:14:3 (not det)
18		LDA	20		33	90:7:3 (not det)[e]
19		KHMDS	4		60	85:13:2 (85:15:–)[e]
20		LDA	21	 **33**	73	98:2 (≥98:2)
21		NaHMDS	25		79	96:4 (not det)[e]
22		LDA	111[f]	 **34**	77	80:18:2 (80:20:–)[g,h]
23		LDA	38		91	75:22:3 (not det)

[a] General reaction conditions: 1.25–2.0 equiv of phosphonate (**4a** unless otherwise indicated), 1.2–1.9 equiv of base, ca.0.2 M in THF, –78 °C (ca. 1 h) to 25 °C. [b] Reaction time at 0–25 °C. [c] All-*E*:2*E*,4*Z*:2*Z*,4*E*; *E*:*Z* in entries 20 and 21. Values within parentheses refer to ratios of the corresponding cyclohexyl imines before hydrolysis. [d] Yield calculated from ^{1}H NMR (see experimental part). [e] **4b** was used in this entry. [f] This reaction time may well be unnecessarily long. [g] The assignments of the isomers were confirmed by NOE experiments. [h] In this entry, 3.0 equiv of phosphate and 2.9 equiv of base were used.

1–19), and only slightly lower (75–80%) with the unsymmetrical ketone acetophenone (Table I, entries 22 and 23). In these reactions, the second most abundant isomer is generally the one with *Z* stereochemistry about the double bond formed in the reaction. The selectivity for 2*E* stereochemistry is uniformly very good (≥96%). When comparing the isomer distribution of the product dienals with that of the intermediate dienyl imines, a good correlation is observed, which indicates that, in general, very little isomerization takes place during the hydrolysis of the products from **4** (the isomer distribution before hydrolysis was determined by ^{1}H NMR analysis of the crude imine).

With reagent **5**, the stereoselectivity is quite good in certain reactions (Table II, entries 7–10, 17–20) but somewhat lower in the others (entries 3–6, 12). For several of the products obtained from **5**, one can sometimes observe a slight amount of isomerization during the hydrolysis, since the proportions of the 2*E*,4*E* isomer increase somewhat in these reactions (entries 4, 8, 14, 15, 17, 18). The second most predominant isomer of the dienals **3** formed from **5** was the 2*Z*,4*E* isomer. The new double bond was generally formed with virtually complete *E* selectivity. In contrast, ca. 5–15% of the product with 4*Z* stereochemistry was generally formed from **4**. This difference can be explained as being caused by the increased steric bulk of the side chain R^1 in phosphonate **5**, due to the additional methyl substituent (Scheme VI; Met = metal counterion).

Scheme VI

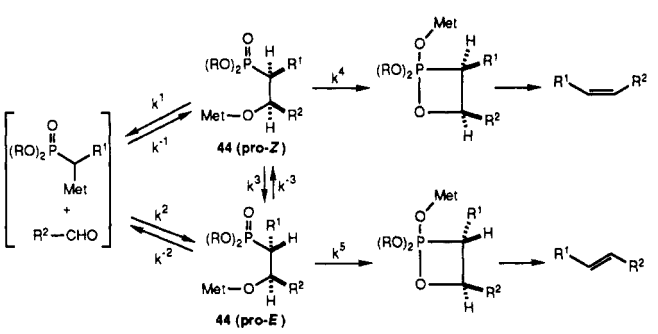
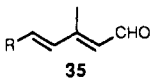
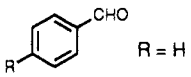
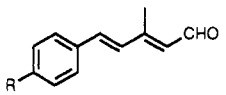
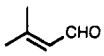
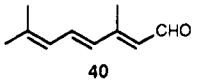
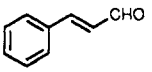
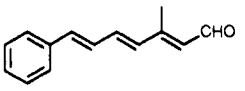
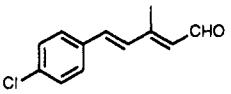
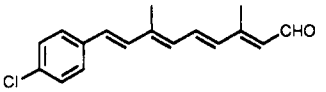
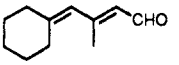


Table II. Condensation Reactions of Carbonyl Compounds with Phosphonate Reagent 5[a]

entry	carbonyl compound	base	solvent	reaction time,[b] h	product	yield, %	isomer ratio[c]
1	RCHO, R = n-C_7H_{15}	LDA	THF	3	 **35**	63	75:–:25 (75:–:25)
2		LDA	DME	3		58	73:–:27 (73:–:27)
3		NaHMDS	THF	3		66	60:4:36 (62:–:38)
4		NaHMDS	DME	3		62	68:–:32 (58:–:42)
5	R = c-C_6H_{11}	LDA	THF	6	**36**	84	63:–:37 (63:–:37)
6		LDA	THF	20		54	62:–:38 (61:–:39)[d]
7	 R = H	LDA	THF	18	 **37**	72	85:–:15 (87:–:13)
8	R = Cl	LDA	THF	18	**38**	71	89:–:11 (84:–:16)
9		LDA	DME	18		61	87:–:13 (85:–:15)
10	R = OCH_3	LDA	THF	18	**39**	67	88:–:12 (89:–:11)[e]
11		KHMDS	THF	20		58	80:–:20 (not det)
12		KHMDS	THF	20	 **40**	63	68:–:32 (68:–:32)
13		LDA	THF	19	 **41**	52	79:–:21 (80:–:20)
14		LDA	DME	21		43	83:–:17 (77:–:23)
15		NaHMDS	THF	18		50	77:–:23 (73:–:27)
16		NaHMDS	DME	19		74	71:–:29 (71:–:29)
17		KHMDS	THF	21		78	84:–:16 (80:–:20)
18		KHMDS	DME	14		56	86:–:14 (80:–:20)
19		KHMDS	THF	21	 **42**	75	84:–:16 (88:–:12)
20		LDA	THF	20	 **43**	39	≥98:2 (≥98:2)

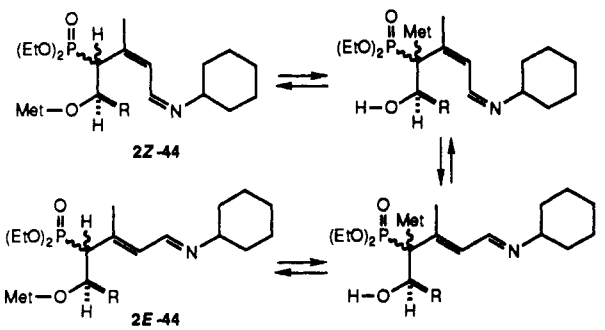
[a] General reaction conditions: 1.3–1.4 equiv of phosphonate **5**, 1.3–1.4 equiv of base, ca. 0.2 M in THF, –78 °C (ca. 1 h) to 25 °C, unless otherwise noted. [b] Reaction time at 0–25 °C. [c] All-*E*:2*E*,4*Z*:2*Z*,4*E*; *E*:*Z* in entry 20. Values within parentheses refer to ratios of the corresponding cyclohexyl imines before hydrolysis. [d] The solution of the phosphonate anion was warmed to 0 °C for 30 min before addition of the aldehyde. [e] The assignments of the isomers were confirmed by NOE experiments.

Increased steric interactions between R^1 and R^2 in the intermediate oxyanion **44** will retard the rate-determining[2] elimination of dialkylphosphate, and the retardation will be largest for elimination from the pro-*Z* diastereomer of **44**. As a consequence, equilibration between the diastereomers of **44** will be more fully developed in the reactions with **5**. Accordingly, formation of 4*E*-dienals will be favored more greatly from **5** than from **4**.[38]

The 2*E* selectivity obtained in the some of the condensations of **5** with aromatic aldehydes (Table II, entries 7, 8, 10) is noteworthy, considering the fact that **5** is an almost 1:1 mixture of *E* and *Z* isomers. It is known that the anions of reagents related to **8** can isomerize with relative ease,[39] and there is also the possibility that a proton transfer/isomerization sequence can take place in the intermediate oxyanion **44** (Scheme VII). Both of these factors could, in principle, contribute to the increased 2*E* selectivity.

To gain some more information on these matters, we performed a condensation of **5** with cyclohexanecarboxaldehyde in which the anion of **5** was warmed to 0 °C for 30 min before addition of the aldehyde, to allow a full equilibrium to be established between the isomers of the

Scheme VII

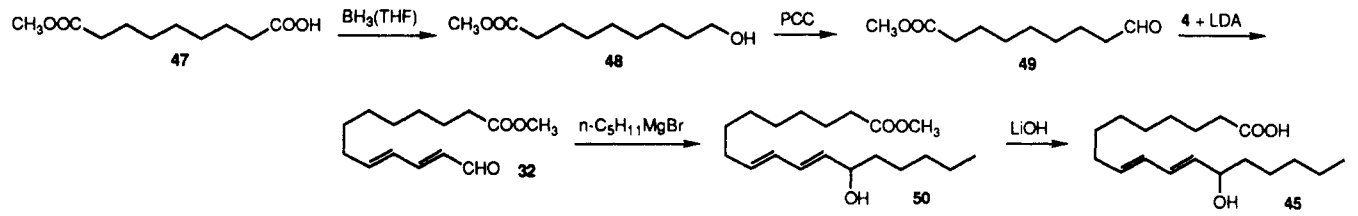


phosphonate anion (Table II, entry 6). The fact that the stereochemical outcome was virtually identical with that obtained under the "standard" conditions (entry 5) suggests that the observed ratio of 2*E* and 2*Z* isomers for dienal **36** is close to the thermodynamic ratio between the phosphonate anion isomers.[40] Even if the slight amount

(38) Bottin-Strzalko, T. *Tetrahedron* **1973**, *29*, 4199–4204.
(39) (a) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1974**, *39*, 821–825. (b) Pattenden, G.; Weedon, B. C. L. *J. Chem. Soc. C* **1968**, 1997–2006.

(40) Corey and Erickson (ref 39a) performed a condensation between lithiated methyl (2*E*)-4-(diethoxyphosphoryl)-3-methyl-2-butenoate and hexanal, at –50 °C for 6 h and recovered some unreacted phosphonate with an isomer distribution of *E*:*Z* = 63:37 (i.e. the same ratio as that between the 2*E* and 2*Z* isomers in our condensations of **5** with cyclohexanecarboxaldehyde).

Scheme VIII



of isomerization during hydrolysis is taken into account (vide supra), the reactions of **5** with aromatic aldehydes give a small but distinct increase in 2*E* selectivity (2*E*:2*Z* ≥ 84:16) as compared to the reactions with cyclohexanecarboxaldehyde (2*E*:2*Z* = ca. 63:37). This increase can be explained by assuming that the thermodynamic ratio of the 2*E* and 2*Z* isomers of the intermediate oxyanion **44** in general is larger than the thermodynamic ratio between the 2*E* and 2*Z* isomers of the phosphonate anion formed from **5**. If the initial addition of the phosphonate anion to aromatic aldehydes is slower and more reversible than in the case of aliphatic aldehydes, then more efficient 2*E*–2*Z* equilibration of the oxyanion **44** may occur.

Since it is known that the nature of the counterion[30,41] and the nature of the alkyl group in the phosphonate [R in $(RO)_2PO$][42] affect the stereoselectivity of formation of the new double bond in HWE condensations, we decided to study these parameters in more detail in the reactions with reagent **4**. In a comparison of data from condensations with hexanal (Table I, entries 1, 2), octanal (entries 3–5), and methyl 9-oxononanoate (entries 17–19), it is clear that the *E* selectivity decreases in the order Li > Na > K, which may reflect the relative chelation abilities of these metals and/or the ionic character of the metal–oxygen bonds in the intermediates **44**. The lower *E* selectivity obtained with sodium or potassium as the counterion can be explained by assuming that under these conditions the intermediate oxyanions **44** are not in full equilibrium, due to a relatively fast final elimination step arising from greater reactivity of the oxyanions and a lowered degree of chelation (Scheme VI). Apparently, the exact nature of the base employed is also of consequence, since t-BuOK gives substantially larger amounts of the *Z* isomer than does KHMDS[11] (compare entries 2 and 5). Furthermore, changing from R = Et to R = i-Pr in the phosphonate gives slightly increased *E* selectivity (compare entries 5 and 19).[42a,c,e,g,h] When these effects were combined in order to achieve maximum *E* selectivity (entry 18), the yield became unacceptably low, however.

In contrast, the effect of the counterion on the stereoselectivity is quite small in the condensations of **4** with cinnamaldehyde (entries 13–15). One possible explanation is that the degree of reversibility of the initial addition step (formation of the β-oxyanion **44**) is larger in the reactions with cinnamaldehyde than in the reactions with saturated aldehydes, regardless of the counterion;[30b,38] thus, the diastereomeric intermediates **44** may equilibrate more efficiently, and elimination from the pro-*E* diastereomer will predominate. The effect of the metal ion on the stereochemistry of the newly formed double bond is much smaller in the case of reagent **5** compared to **4**.

The phosphoryl aldehyde **10** (R = CH_3)[29] was also prepared to determine whether the corresponding imines would show a synthetically useful level of *Z* stereoselectivity in HWE condensations.[42c] To our disappointment, this reagent gave low chemical yields in condensations with aldehydes and lacked stereoselectivity (2*E*,4*E*:2*E*,4*Z* = ca. 1:1).

It is worth emphasizing that pure 2*E*,4*E* isomers of **2** and **3** are obtained after the chromatographic hydrolysis in some cases (e.g. **28** and **38**). In almost all cases, 2*E*,4*E* isomers of high purity can be obtained by chromatographing the mixture of isomers a second time (e.g. **26** and **35**).

Synthesis of (±)-(*E*,*E*)-Coriolic Acid. We have used the reagents **4** in the key step of a short synthesis of (±)-(*E*,*E*)-coriolic acid (**45**), a double bond isomer of naturally occurring coriolic acid (13-hydroxy-9(*Z*),11(*E*)-octadecadienoic acid, **46**).[43] Compound **46**, which has been isolated from rice (*Oryza sative* L.) as a partially racemic mixture[43e] in which the *S* enantiomer predominates, acts as a self-defense substance against rice blast disease. Furthermore, (*S*)-**46** is present in heart mitochondria as well as in the sera of patients with familial Mediterranean fever, and it also possesses calcium-specific ionophoric activity. In addition, **46** has recently been shown to exhibit physiological properties which indicate that it plays a significant role in controlling thrombosis.[43b,c] The enantiomer (*R*)-**46** has been isolated as the major fatty acid in the seed oil of *Coriaria nepalensis* Wall.[44] Very recently, it has been demonstrated that both enantiomers of **46**, as well as some analogues of (*S*)-**46**, including (*S*)-(*E*,*E*)-coriolic acid [(*S*)-**45**], possess activities against rice blast fungus that are comparable to, or even higher than, the activity of (*S*)-**46** itself.[43c] It was shown that (*S*)-**45** is more active than (*S*)-**46**, and (*R*)-**46** was found to be only slightly less active. Based upon these observations, we considered (±)-**45** to be an attractive target for synthesis, since this compound could be expected to have interesting and po-

(41) Etemad-Moghadam, G.; Seyden-Penne, J. *Tetrahedron* **1984**, *40*, 5153–5166.

(42) (a) Marshall, J. A.; DeHoff, B. S.; Cleary, D. G. *J. Org. Chem.* **1986**, *51*, 1735–1741. (b) Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405–4408. (c) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873–3888. (d) Breuer, E.; Bannet, D. M. *Tetrahedron* **1978**, *34*, 997–1002. (e) Boschelli, D.; Takemasa, T.; Nishitani, Y.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 5239–5242. (f) Still, W. C.; Shaw, K. R. *Tetrahedron Lett.* **1981**, *22*, 3725–3728. (g) Dugger, R. W.; Heathcock, C. H. *Synth. Commun.* **1980**, *10*, 509–515. (h) Meyers, A. I.; Tomioka, K.; Roland, D. M.; Comins, D. *Tetrahedron Lett.* **1978**, *16*, 1375–1378. See also ref 4d.

(43) Enantioselective syntheses: (a) de Montarby, L.; Mosset, P.; Greé, R. *Tetrahedron Lett.* **1988**, *29*, 3937–3940. (b) Chan, C.; Cox, P. B.; Roberts, S. M. *J. Chem. Soc., Chem. Commun.* **1988**, 971–972. (c) Kobayashi, Y.; Okamoto, S.; Shimazaki, T.; Ochiai, Y.; Sato, F. *Tetrahedron Lett.* **1987**, *28*, 3959–3962. (d) Moustakis, C. A.; Weerasinghe, D. K.; Mosset, P.; Falck, J. R.; Mioskowski, C. *Tetrahedron Lett.* **1986**, *27*, 303–304. (e) Suemune, H.; Hayashi, N.; Funakoshi, K.; Akita, H.; Oishi, T.; Sakai, K. *Chem. Pharm. Bull.* **1985**, *33*, 2168–2170. Racemic syntheses: (f) Rama Rao, A. V.; Rajarathnam Reddy, E.; Sharma, G. V. M.; Yadagiri, P.; Yadav, J. S. *Tetrahedron* **1986**, *42*, 4523–4532. (g) Rama Rao, A. V.; Pulla, Reddy, S.; Rajarathnam Reddy, E. *J. Org. Chem.* **1986**, *51*, 4158–4159. (h) Rama Rao, A. V.; Rajarathnam Reddy, E.; Sharma, G. V. M.; Yadagiri, P.; Yadav, J. S. *Tetrahedron Lett.* **1985**, *26*, 465–468. (i) Gunn, B. P. *Heterocycles* **1985**, *23*, 3061–3067.

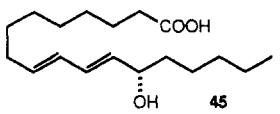
(44) Tallent, W. H.; Harris, J.; Wolff, I. A.; Lundin, R. E. *Tetrahedron Lett.* **1966**, 4329–4334.

(45) Yoon, N. M.; Pak, C. S.; Brown, H. C.; Krishnamurthy, S.; Stocky, T. P. *J. Org. Chem.* **1973**, *38*, 2786–2792.

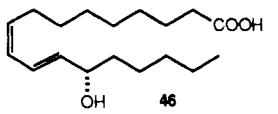
(46) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647–2650.

(47) The overall yield for preparation of (±)-**45** with 90% *E*,*E* selectivity is 20%.

tentially useful properties also in racemic form.



45



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Our route to (±)-**45** is illustrated in Scheme VIII. The key step was condensation of **49** with the lithio derivative of phosphonate **4a**, leading to **32** in 65% yield (Table I, entry 17; isomeric distribution 9*E*,11*E*:9*Z*,11*E*:9*E*,11*Z* = 83:14:3, improved to 92:7:1 after chromatographic purification). Grignard addition followed by ester hydrolysis then gave (±)-(*E*,*E*)-coriolic acid.

Conclusions

We have introduced the new functionalized Horner–Wadsworth–Emmons reagents **4** and **5** which transform carbonyl compounds directly into conjugated dienals **2** and **3** under mild conditions and in good yields. Other, previously reported reagents may also be employed,[48-52] but the present reagents have the general advantages of HWE reagents over these alternative classes of reagents (enhanced nucleophilicity, and hence potentially greater generality than phosphonium ylides and arsonium ylides; ease of workup;[2] lower toxicity than organoarsenic compounds; reduced basicity, and hence wider compatibility with base-sensitive functionality when compared to related vinyllithium reagents). The synthetic utility of our reagents is illustrated by the short synthesis of (±)-9(*E*),11(*E*)-coriolic acid (**54**). Also, **42** (Table II, entry 19) can be regarded as a retinoid analogue.

Experimental Section

General. All reactions requiring anhydrous conditions were performed in oven-dried glassware. Flash chromatography was performed as described by Still et al.[33] (Merck silica gel, 230–400 mesh, column diameter 20–40 mm) and medium-pressure liquid chromatography (MPLC) as described by Baeckström et al.[53] Azelaic acid monomethyl ester was bulb-to-bulb distilled before use. *N*-Bromosuccinimide was recrystallized from acetic acid. *n*-Butyllithium (1.6 or 2.5 M in hexanes) was titrated with diphenylacetic acid.[54] Carbonyl compounds used in the condensation reactions were freshly distilled or recrystallized. Cyclohexylamine and triethylamine were distilled from CaH_2 and stored over 4-Å molecular sieves. Diisopropylamine was distilled from CaH_2. DME and THF were distilled from sodium/benzophenone ketyl. LDA was prepared in situ from diisopropylamine (1.0–1.05 equiv) and *n*-butyllithium (1.0 equiv), at 0 °C. *n*-Pentylmagnesium bromide in ether was titrated with benzyl alcohol in toluene.[55] Potassium *tert*-butoxide was sublimed. KHMDS (0.5 M in toluene) and NaHMDS (1.0 M in THF) were purchased from Aldrich. Pyridinium chlorochromate (PCC)[46] was prepared according to a published procedure. Sodium iodide was dried by heating in a Kugelrohr apparatus (ca. 150 °C, 0.05 Torr) for 1–2 h. Triethyl phosphite was stored over 4-Å molecular sieves; triisopropyl phosphite (Aldrich, 90%) was distilled and then stored over 4-Å molecular sieves. TLC analyses were performed on Merck aluminum-backed F_{254} silica gel plates, using UV light and phosphomolybdic acid. GLC analyses were performed with a BP-1 (methylsilicone, 25 m) capillary column. For HPLC analysis, a differential refractometer and a Waters μ-Porasil column were used. ^{13}C NMR assignments were supported by DEPT experiments. ^1H NMR assignments were assisted by NOE difference, ^1H–^1H COSY and ^1H–^{13}C heteronuclear correlation experiments. Mass spectra were recorded on a GC–MS unit equipped with an OV-1 capillary column. For reactions in which mixtures of isomeric products were obtained, detailed data are generally given in this paper for only the major isomers; data for minor isomers may be found in the supplementary material.

Synthesis of Reagents 4 (General Procedure): Diethyl (1-Acetoxy-2-buten-1-yl)phosphonate (8a). A mixture of 1-acetoxy-4-chloro-2-butene (**7**)[7] (7.37 g, 49.6 mmol; *E*:*Z* = ca. 90:10), $(EtO)_3P$ (8.80 g, 52.9 mmol), and NaI (0.744 g, 4.96 mmol) was heated to 125 °C for 5 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 (50 mL), the solution was washed with 10% aqueous $Na_2S_2O_3$ (20 mL), and the aqueous phase was extracted with another portion of CH_2Cl_2 (50 mL). Drying ($MgSO_4$) and evaporation yielded the crude product as a yellowish oil. Purification by bulb-to-bulb distillation (180 °C, 0.15 Torr) gave 10.07 g (81%) of **8a** as a colorless oil (*E*:*Z* = ca. 90:10; purity ≥95% by NMR and GLC). (*E*)-**8a**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.75–5.64 (m, 2 H, C*H*=C*H*), 4.50–4.47 (m, 2 H, CH_2OAc), 4.09–4.00 (m, 4 H, CH_3CH_2O), 2.55 (br dd, *J* = 22.4 (J_{PH}), 5.8 Hz, 2 H, PCH_2), 1.99 (s, 3 H, $OCOCH_3$), 1.26 (t, *J* = 7.1 Hz, 6 H, CH_3CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.48 ($OCOCH_3$), 129.05 (d, J_{PC} = 14.6 Hz) and 124.17 (d, J_{PC} = 11.6 Hz, *C*H=*C*H), 64.21 (CH_2OAc), 61.84 (d, J_{PC} = 6.7 Hz, 2 C, CH_3CH_2O), 30.21 (d, J_{PC} = 140.3 Hz, PCH_2), 20.73 ($OCOCH_3$), 16.26 (d, J_{PC} = 6.7 Hz, 2 C, CH_3CH_2O); IR (CCl_4) 2983, 2907, 1746, 1444, 1382, 1030, 967 cm^{-1}; EIMS *m*/*z* (rel intensity) 250 (16), 208 (100); HRMS *m*/*z* calcd for $C_{10}H_{19}O_5P$ 250.0970, found 250.0973; TLC R_f = 0.34 (CH_2Cl_2–MeOH, 95:5).

Bis(1-methylethyl) (4-Acetoxy-2-buten-1-yl)phosphonate (8b). Prepared as described above using **7** (4.61 g, 31.0 mmol; *E*:*Z* = ca. 90:10), $(i\text{-}PrO)_3P$ (6.79 g, 32.6 mmol), and NaI (0.899 g, 6.0 mmol) at 140 °C for 5 h. Bulb-to-bulb distillation (175 °C, 0.1 torr) provided 4.64 g (54%) of **8b** as a colorless oil (*E*:*Z* = ca. 90:10; purity ≥95% by NMR). (*E*)-**8b**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.72–5.60 (m, 2 H, C*H*=C*H*), 4.61 (d of septets, *J* = 7.9 (J_{PH}), 6.2 Hz, 2 H, $(CH_3)_2CHO$), 4.47–4.45 (m, 2 H, CH_2OAc) 2.49 (br dd, *J* = 22.0 (J_{PH}), 6.1 Hz, 2 H, PCH_2), 1.97 (s, 3 H, $OCOCH_3$), 1.24 (d, *J* = 6.2 Hz, 6 H) and 1.22 (d, *J* = 6.2 Hz, 6 H) [$(CH_3)_2CH$]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.45 ($OCOCH_3$), 128.72 (d, J_{PC} = 14.1 Hz) and 124.76 (d, J_{PC} = 10.8 Hz, *C*H=*C*H), 70.25 (d, J_{PC} = 6.3 Hz, $(CH_3)_2CHO$), 64.25 (CH_2OAc), 31.35 (d, J_{PC} = 140.5 Hz, PCH_2), 23.86 (d, J_{PC} = 5 Hz) and 23.81 (d, J_{PC} = 5 Hz, $(CH_3)_2CH$), 20.69 ($OCOCH_3$); IR (CCl_4) 2981, 2937, 1746, 1452, 1009, 987, 888 cm^{-1}; EIMS *m*/*z* (rel intensity) 278 (4), 152 (100); TLC R_f = 0.42 (CH_2Cl_2–MeOH, 95:5).

Preparation of 4-(Dialkoxyphosphoryl)-2-buten-1-ols (General Procedure): Diethyl (4-Hydroxy-2-buten-1-yl)phosphonate (9a). A solution of **8a** (8.46 g, 33.8 mmol, *E*:*Z* = ca. 90:10) and *p*-TsOH (0.636 g, 3.3 mmol) in 150 mL of EtOH (99.5%) was refluxed for 20 h. After the mixture was cooled, 0.5 g of K_2CO_3 was added, and the ethanol was evaporated. Standard extractive workup afforded the crude product as a yellowish oil. Bulb-to-bulb distillation (150 °C, 0.1 Torr) gave 6.65 g (95%) of **9a** (*E*:*Z* = ca. 90:10) as a colorless oil. A sample of pure *E* isomer and a sample of the *Z* isomer of 80% isomeric purity were obtained by flash chromatography (2–5% MeOH in CH_2Cl_2). (*E*)-**9a**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.79 (dtdt, *J* = 15.3, 5.2, 4.9 (J_{PH}), 1.1

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Hz, 1 H, =C*H*CH$_2$OH), 5.64 (dtdt, J = 15.4, 7.2, 6.4 (J_{PH}), 1.4 Hz, 1 H, PCH$_2$C*H*=), 4.12–4.02 (m, 6 H, CH$_3$C*H*$_2$O and C*H*$_2$OH), 2.74 (br t, J = 5 Hz, 1 H, CH$_2$O*H*), 2.57 (br ddd, J = 21.7 (J_{PH}), 7.3, 1.1 Hz, 2 H, PC*H*$_2$), 1.29 (t, J = 7.1 Hz, 6 H, C*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.91 (d, J_{PC} = 14.0 Hz) and 119.93 (d, J_{PC} = 10.8 Hz, *C*H=CH), 62.58 (d, J_{PC} = 2.3 Hz, *C*H$_2$OH), 61.88 (d, J_{PC} = 6.3 Hz, 2 C, CH$_3$*C*H$_2$O), 29.94 (d, J_{PC} = 139.9 Hz, P*C*H$_2$), 16.27 (d, J_{PC} = 5.9 Hz, 2 C, *C*H$_3$); IR (CCl$_4$) 3396, 2983, 2908, 1444, 1030, 970 cm^{-1}. Anal. (mixture of *E*:*Z* = ca. 90:10). Calcd for C$_8$H$_{17}$O$_4$P: C, 46.15; H, 8.23. Found: C, 46.1; H, 8.15.

Bis(1-methylethyl) (4-Hydroxy-2-buten-1-yl)phosphonate (9b). Prepared as described above using **8b** (4.97 g, 17.9 mmol; *E*:*Z* = ca. 90:10), *p*-TsOH (0.170 g, 0.89 mmol), and methanol (100 mL) at reflux for 15 h. Methanol was used as solvent since the transesterification was inconveniently slow in 2-propanol. We could not detect any transesterification of the diisopropoxyphosphoryl group during this reaction. Extractive workup and bulb-to-bulb distillation (175 °C, 0.05 Torr) afforded 4.09 g of **9b** as a colorless oil (97%; *E*:*Z* = ca. 90:10). Flash chromatography (2–5% MeOH in CH$_2$Cl$_2$) gave a sample of the pure *E* isomer and a sample of the *Z* isomer in 65% isomeric purity. (*E*)-9b: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.72 (dtdt, J = 15.4, 5.2, 4.9 (J_{PH}), 1.1 Hz, 1 H, =C*H*CH$_2$OH), 5.57 (dtdt, J = 15.4, 7.3, 6.3 (J_{PH}), 1.3 Hz, 1 H, PCH$_2$C*H*=), 4.60 (d of septets, J = 7.9 (J_{PH}), 6.2 Hz, 2 H, (CH$_3$)$_2$C*H*O), 4.02 (app br q, J = ca. 5 Hz, 2 H, C*H*$_2$OH), 3.35 (br t, J = 5.3 Hz, 1 H, CH$_2$O*H*), 2.47 (br, ddd, J = 21.8 (J_{PH}), 7.3, 1.0 Hz, 2 H, PC*H*$_2$), 1.24 (d, J = 6.2 Hz, 6 H) and 1.22 (d, J = 6.2 Hz, 6 H, (C*H*$_3$)$_2$CH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.66 (d, J_{PC} = 14.2 Hz) and 120.42 (d, J_{PC} = 11.2 Hz, *C*H=*C*H, 70.30 (d, J_{PC} = 7.4 Hz, 2 C, (CH$_3$)$_2$*C*HO), 62.59 (d, J_{PC} = 2.1 Hz, *C*H$_2$OH), 31.16 (d, J_{PC} = 141.0 Hz, P*C*H$_2$), 23.87 (d, J_{PC} = 4 Hz) and 23.83 (d, J_{PC} = 4 Hz, (CH$_3$)$_2$*C*H); IR (CCl$_4$) 3387, 2981, 2936, 1467, 1455, 989, 888 cm^{-1}; EIMS m/z (rel intensity) 236 (6), 152 (100); HRMS m/z calcd for C$_{10}$H$_{21}$O$_4$P 236.1177, found 236.1181; TLC R_f = 0.17 (CH$_2$Cl$_2$–MeOH, 95:5).

Preparation of 4-(Dialkoxyphosphoryl)-2-butenals (General Procedure): (*E*)-4-(Diethoxyphosphoryl)-2-butenal (10a). A solution of CrO$_3$ (1.00 g, 10.0 mmol) in 2 N H$_2$SO$_4$ (20 mL) was added dropwise over 30 min to a solution of **9a** (2.08 g, 10.0 mmol; *E*:*Z* = ca. 90:10) in acetone (60 mL) at 0 °C under argon. When the addition was complete, the mixture was stirred for another 15 min, and the chromic acid was quenched by addition of 1.5 mL of i-PrOH. After 5 min, 1.4 g of solid NaHCO$_3$ was added, and the reaction mixture was filtered through a glass filter. The filtrate was concentrated on a rotary evaporator (25 °C). Standard extractive workup provided 1.92 g of crude product as a greenish oil. Purification by MPLC (ca. 60 g of deactivated[56] silica gel, 0–8% MeOH in CH$_2$Cl$_2$) afforded 1.40 g (68%) of **10a** (E:Z ≥ 98:2; purity ≥95% by NMR) as a nearly colorless oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.55 (d, J = 7.8 Hz, 1 H, C*H*O), 6.79 (d app q, J = 15.5, 7.7 Hz, 1 H, CH$_2$C*H*=), 6.23 (dddt J = 15.6, 7.8, 4.6 (J_{PH}), 1.3 Hz, 1 H, =C*H*CHO), 4.18–4.11 (m, 4 H, C*H*$_2$O), 2.88 (ddd, J = 23.2 (J_{PH}), 7.8, 1.3 Hz, 2 H, PC*H*$_2$), 1.34 (t, J = 7.1 Hz, 6 H, C*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.87 (d, J_{PC} = 2.7 Hz, *C*HO), 146.25 (d, J_{PC} = 11.7 Hz, CH$_2$*C*H=), 136.30 (d, J_{PC} = 12.4 Hz, =*C*HCHO), 62.41 (d, J_{PC} = 6.7 Hz, 2 C, *C*H$_2$O), 31.15 (d, J_{PC} = 137.5 Hz, P*C*H$_2$), 16.26 (d, J_{PC} = 6.0 Hz, 2 C, *C*H$_3$); IR (CCl$_4$) 2984, 2908, 2815, 2734, 1700, 1641, 973, 909, 866 cm^{-1}; EIMS m/z (rel intensity) 206 (2), 177 (100); HRMS m/z calcd for C$_7$H$_{14}$O$_3$P (M$^+$ – 29) 177.0681, found 177.0682; TLC R_f (*E* isomer) = 0.38 (CH$_2$Cl$_2$–MeOH, 95:5). The compound is stable for at least a few weeks when stored at –20 °C under argon, but use of freshly prepared reagent is recommended.

(*E*)-4-[Bis(1-methylethoxy)phosphoryl]-2-butenal (10b). Prepared as described above using **9b** (2.36 g, 10.0 mmol; *E*:*Z* = ca. 90:10), CrO$_3$ (1.00 g, 10.0 mmol), 2 N H$_2$SO$_4$ (20 mL), and acetone (60 mL) at 0 °C for 45 min. Obtained was 2.37 g of a bluish-green oil as crude product. Purification by MPLC (ca. 60 g of deactivated[56] silica gel, 0–8% MeOH in CH$_2$Cl$_2$) gave 1.53 g (65%) of **10b** (*E*:*Z* ≥ 98:2; purity ≥95% by NMR) as a colorless oil: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.55 (d, J = 7.8 Hz, 1 H, C*H*O), 6.79 (d app q, J = 15.5, 7.6 Hz, 1 H, CH$_2$C*H*=), 6.21 (dddt, J = 15.6, 7.8, 4.5 (J_{PH}), 1.3 Hz, 1 H, =C*H*CHO), 4.73 (d of septets, J = 7.9 (J_{PH}), 6.2 Hz, 2 H, (CH$_3$)$_2$C*H*O), 2.84 (ddd, J = 23.2 (J_{PH}), 7.8, 1.3 Hz, 2 H, PC*H*$_2$), 1.34 (d, J = 6.0 Hz, 6 H) and 1.32 (d, J = 5.9 Hz, 6 H, (C*H*$_3$)$_2$CH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.94 (*C*HO), 146.99 (d, J_{PC} = 10.8 Hz, CH$_2$*C*H=), 136.16 (d, J_{PC} = 12.5 Hz, =CHCHO), 71.06 (d, J_{PC} = 7.3 Hz, 2 C, (CH$_3$)$_2$*C*HO), 32.51 (d, J_{PC} = 138.8 Hz, P*C*H$_2$), 23.90 (d, J_{PC} = 4.5 Hz, two overlapping signals, (*C*H$_3$)$_2$CH); IR (CDCl$_3$) 2984, 2936, 2826, 2743, 1693, 1641, 996 cm^{-1}; EIMS m/z (rel intensity) 234 (<1), 150 (100); CIMS (isobutane) m/z (rel intensity) 235 (100, M$^+$ + 1); HRMS m/z calcd for C$_9$H$_{18}$O$_3$P (M$^+$ – 29) 205.0994, found 205.0985; TLC R_f (*E* isomer) = 0.38 (CH$_2$Cl$_2$–MeOH, 95:5). The stability of this compound is similar to **10a**.

Condensations of Phosphonate Reagents 4 with Carbonyl Compounds (General Procedure): (A) Preparation of the Phosphoryl Imines 4. To a solution of the phosphoryl aldehyde (**10a** or **10b**) in THF (0.5–1 M) was added dropwise cyclohexylamine (1.0–1.05 equiv) over ca. 1 min at 25 °C under argon. After 30–60 min, freshly activated 4-Å molecular sieves (ca. 0.100 g/0.100 g of **10**) were added, and the mixture was stirred slowly overnight. This procedure gave the phosphoryl imines as mixtures of aldimine and dienamine tautomers in almost quantitative yield (^{1}H NMR). They were not isolated, but instead the solutions were used directly in the condensation reactions. Spectral data for **4a** and the dienamine tautomer: ^{1}H NMR (200 MHz, CDCl$_3$; assigned from a 2:3 mixture of **4a** and tautomer) δ 7.90 (d, J = 8 Hz, 1 H, C*H*=N), 7.07 (ddd, J = 21 (J_{PH})), 17, 11 Hz, 1 H, dienamine PCH=C*H*), 6.61 (dd, J = 13, 9 Hz, 1 H, =C*H*NH), 6.32 (ddd, J = 15, 8, 4 (J_{PH}) Hz, 1 H, =C*H*CH=N), 6.11 (app dq, J = 15, 7 Hz, 1 H, PCH$_2$C*H*=), 5.26 (dd, J = 13, 11 Hz, 1 H, C*H*=CHNH), 5.01 (dd, J = 21 (J_{PH}), 17 Hz, 1 H, PC*H*=), 4.21–4.02 (m, 4 H, CH$_3$C*H*$_2$O), ca. 4.15 (hidden by other peaks, one J = 9 Hz, 1 H, dienamine N*H*), 4.11–3.94 (m, 4 H, dienamine CH$_3$C*H*$_2$O), 3.18–2.90 (m, 2 H, =NC*H* and dienamine NHC*H*), 2.74 (dd, J = 23 (J_{PH}), 7 Hz, 2 H, aldimine PC*H*$_2$), 2.02–1.04 (m, 10 H, C*H*$_2$)$_5$ in both tautomers), 1.32 (t, J = 7 Hz, 6 H, aldimine C*H*$_3$), 1.32 (t, J = 7 Hz, 6 H, dienamine C*H*$_3$). Corresponding data were obtained for a 1:2 mixture of **4b** and the dienamine tautomer (supplementary material).

(B) Condensation Reactions with Reagents 4. In general, the reactions were performed on a 0.7–1.2-mmol scale. The bright orange solution of **4** (1.25–3.0 equiv) in THF was added to a solution of the appropriate base (LDA, NaHMDS, KHMDS, or t-BuOK; 1.2–2.9 equiv) in THF at –78 °C under argon. The color of the solution changed instantaneously to deep red. The solution was stirred at –78 °C for 30–60 min, and then the carbonyl compound (1.0 equiv) in THF (0.5–1 mL) was added. After being stirred at –78 °C for another h, the solution was brought to 0 °C and stirred at 0–25 °C for the indicated period of time. Water (5 mL) was added, and the mixture was stirred for a few minutes. The aqueous phase was extracted with ether or CH$_2$Cl$_2$, and the combined organic phases were dried (MgSO$_4$). Evaporation of the solvent provided the crude cyclohexyl imines as orange or red oils. Hydrolysis was effected during flash chromatography, which gave the desired polyenals. The proportions of product isomers were determined from ^{1}H NMR spectra (integrals for the C*H*O protons). In general, the product isomers separated fairly well but not completely during the chromatographic hydrolysis. After a second chromatographic separation, a mixture of the 2*E*,4*Z* and 2*Z*,4*E* isomers was generally obtained in the earlier fractions, and a sample of the 2*E*,4*E* isomer in essentially pure form (97 → 99% isomeric purity) in the later fractions. The dienals are reasonably stable when stored under argon at –20 °C, but they decompose at room temperature, especially in the presence of even trace amounts of molecular oxygen. Satisfactory elemental analyses were thus difficult to obtain, but the initially obtained products were pure according to ^{1}H NMR and TLC, with the different isomers of each product mixture exhibiting different R_f values as expected. The decomposition products invariably appear at distinctly lower R_f values on TLC.

2,4-Decadienal (23). Prepared from **10a** (0.229 g, 1.11 mmol), cyclohexylamine (0.116 g, 1.17 mmol), LDA [1.05 mmol, from 1.54 M *n*-BuLi (0.68 mL) and (i-Pr)$_2$NH (0.111 g, 1.10 mmol)], and *n*-hexanal (0.070 g, 0.70 mmol) in THF (6 mL) at 0–25 °C for 2

(56) Silica was deactivated by dissolving water (10–15% by weight of silica) in THF, adding the silica with intermediate shaking during a few minutes, and evaporating the solvent.

(57) Garcia Martinez, A.; Cruces Villalobos, A.; Oliver Ruiz, M. *Synthesis* **1988**, 58–60.

h, yield 0.083 g of **23** (78%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 84:14:2) as a light-yellow oil. (2*E*,4*E*)-**23**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 8.0 Hz, 1 H, C*H*O), 7.08 (app br ddd, J = 15.5, 9.0, 1.1 Hz, 1 H, C*H*=CHCHO), 6.32 (dd, J = 15.4, 9.0 Hz, 1 H, CH_2CH=C*H*), 6.28 (m, 1 H, CH_2CH=), 6.07 (dd, J = 15.3, 8.0 Hz, 1 H, =C*H*CHO), 2.22 (app br td, J = 7.4, 5.9 Hz, 2 H, CH_2CH=), 1.46 (app br quintet, J = 7.3 Hz, 2 H, CH_2CH_2CH=), 1.38–1.26 (m, 4 H, $CH_3(CH_2)_2$), 0.90 (br t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.85 (*C*HO), 152.81 and 147.37 (*C*H=CH*C*H=CHCHO), 129.99 and 128.59 (=*C*HCH=*C*HCH-O), 33.12, 31.12, 28.18, and 22.40 ($(CH_2)_4$), 13.92 (CH_3); IR (CCl_4) 2958, 2929, 2858, 2734, 1685, 1641, 1601, 1012, 988, 875 cm^{-1}; HRMS m/z calcd for $C_{10}H_{16}O$ 152.1201, found 152.1199; TLC R_f = 0.23 (pentane–ether, 90:10).

2,4-Dodecadienal (24). Prepared from **10a** (0.309 g, 1.5 mmol), cyclohexylamine (0.149 g, 1.5 mmol), LDA (1.0 mmol), and *n*-octanal (0.103 g, 0.80 mmol) at 0–25 °C for 3 h; yield 0.102 g of **33** (71%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 85:12:3). Bulb-to-bulb distillation gave a sample of **24** as a light-yellow oil from which the pure isomers were obtained by flash chromatography. (2*E*,4*E*)-**24**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 8.0 Hz, 1 H, C*H*O), 7.08 (app br ddd, J = 15.3, 9.0, 1.1 Hz, 1 H, C*H*=CHCHO), 6.32 (dd, J = 15.5, 9.2 Hz, 1 H, CH_2CH=C*H*), 6.28 (m, 1 H, CH_2CH=), 6.08 (dd, J = 15.3, 8.0 Hz, 1 H, =C*H*CHO), 2.22 (app br td, J = 7.3, 5.9 Hz, 2 H, CH_2CH=), 1.46 (app br quintet, J = 7.3 Hz, 2 H, CH_2CH_2CH=), 1.36–1.24 (m, 8 H, $CH_3(CH_2)_4$), 0.89 (br t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$ δ 193.91 (*C*HO), 152.86 (*C*H=CHCHO), 147.41 (CH_2CH=*C*H), 129.99 (=*C*HCHO), 128.61 (CH_2CH=*C*H), 33.18 (CH_2CH=), 31.72, 29.12, 29.04, 28.53, and 22.59 ($CH_3(CH_2)_5$), 14.03 (CH_3); IR (CCl_4) 2958, 2929, 2857, 2735, 1689, 1643, 1602, 1009, 987, 909 cm^{-1}; HRMS m/z calcd for $C_{12}H_{20}O$ 180.1514, found 180.1514; TLC R_f = 0.46 (pentane–ether, 80:20).

5-Cyclohexyl-2,4-pentadienal (25). Prepared from **10a** (0.327 g, 1.59 mmol), cyclohexylamine (0.158 g, 1.59 mmol), LDA (1.51 mmol), and cyclohexanecarboxaldehyde (0.119 g, 1.06 mmol) at 0–25 °C for 19 h; yield 0.122 g of **25** (70%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 90:7:3) as a light-yellow oil. (2*E*,4*E*)-**25**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (d, J = 8.0 Hz, 1 H, C*H*O), 7.08 (dd, J = 15.2, 9.9 Hz, 1 H, C*H*=CHCHO), 6.27 (dd, J = 15.3, 9.9 Hz, 1 H, $(CH_2)_2CHCH$=C*H*), 6.23 (dd, J = 15.3, 6.1 Hz, 1 H, $(CH_2)_2CHCH$=), 6.09 (dd, J = 15.3, 8.0 Hz, 1 H, =C*H*CHO), 2.19–2.10 (m, 1 H, $(CH_2)_2CHCH$=), 1.80–1.66 (m, 5 H), and 1.37–1.10 (m, 5 H, $(CH_2)_5$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.87 (*C*HO), 153.29 and 152.59 (*C*H=CH*C*H=CHCHO), 130.17 and 126.17 (=CHCH=CHCHO), 41.28 ($(CH_2)_2CHCH$=), 32.09 (2 C), 25.92 and 25.72 (2 C, $(CH_2)_5$); IR (CCl_4) 2930, 2854, 2810, 2734, 1688, 1641, 1600, 1009, 987, 967, 890 cm^{-1}; TLC R_f = 0.44 (pentane–ether, 80:20).

5-Phenyl-2,4-pentadienal (26). Prepared from **10a** (0.327 g, 1.59 mmol), cyclohexylamine (0.158 g, 1.59 mmol), LDA (1.51 mmol), and benzaldehyde (0.113 g, 1.06 mmol) at 0–25 °C for 18 h; yield 0.110 g of **26** (65%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 94:4:2) as a viscous orange oil. Imine form of **26**: ^{1}H NMR (200 MHz, $CDCl_3$; partial assignment from spectrum of crude product) δ 7.97 (d, J = 9 Hz, 1 H, C*H*=N), 6.91 (dd, J = 15, 10 Hz, 1 H, ArCH=C*H*), 6.74 (dd, J = 15, 10 Hz, 1 H, C*H*=CHCH=N), 6.72 (d, J = 15 Hz, 1 H, ArC*H*=), 6.44 (dd, J = 15, 9 Hz, 1 H, =C*H*CH=N). (2*E*,4*E*)-**26**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, J = 8.0 Hz, 1 H, C*H*O), 7.52–7.49 (m, 2 H) and 7.41–7.33 (m, 3 H, aromatic), 7.27 (app ddd, large J = 15.2 Hz, 1 H, C*H*=CHCHO), 7.06–6.96 (m, 2 H, PhC*H*=C*H*), 6.27 (dd, J = 15.2, 7.9 Hz, 1 H, =C*H*CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.51 (*C*HO), 151.96 (*C*H=CH-CHO), 142.39 (Ph*C*H=), 135.57 (ipso aromatic), 131.62, 129.66, 128.92 (2 C), 127.51 (2 C), and 126.18 (=CHCH=*C*HCHO and aromatic); IR (CCl_4) 3033, 2809, 2739, 1687, 1622, 1596, 1073, 1007, 986, 876 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.5; H, 6.32.

5-(4′-Chlorophenyl)-2,4-pentadienal (27). Prepared from **10a** (0.577 g, 2.8 mmol), cyclohexylamine (0.278 g, 2.8 mmol), LDA (2.6 mmol), and 4-chlorobenzaldehyde (0.281 g, 2.0 mol) at 0–25 °C for 17 h; yield 0.293 g of **27** as an orange-yellow oil (75%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 94:4:2). Imine form of **27**: ^{1}H NMR (400 MHz, $CDCl_3$; partial assignment from spectrum of crude product) δ 7.97 (d, J = 9.0 Hz, 1 H, C*H*=N), 6.86 (dd, J = 15.6, 10.5 Hz, 1 H, ArCH=C*H*), 6.71 (dd, J = 15.1, 10.7 Hz, 1 H, C*H*=CHCHO), 6.67 (br d, J = 15.5 Hz, 1 H, ArC*H*=), 6.45 (dd, J = 15.1, 9.0 Hz, 1 H, =C*H*CHO). (2*E*,4*E*)-**27**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, J = 7.8 Hz, 1 H, C*H*O), 7.45–7.42 (m, 2 H) and 7.37–7.34 (m, 2 H, aromatic), 7.25 (app ddd, J = 15.2, 6.3, 3.9 Hz, 1 H, C*H*=CHCHO), 7.02–6.93 (m, 2 H, ArC*H*=C*H*), 6.28 (dd, J = 15.2, 7.9 Hz, 1 H, =C*H*CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.40 (*C*HO), 151.39 (*C*H=CHCHO), 140.76 (ArCH=), 135.44 and 134.07 (ipso aromatic), 131.99, 129.17 (2 C), 128.61 (2 C) and 126.69 (=*C*HCH=*C*HCHO and aromatic); IR (CCl_4) 3040, 2811, 2738, 1688, 1625, 1590, 1013, 1006, 985, 909 cm^{-1}; EIMS m/z (rel intensity) 192 (M^+, 65), 129 (100); HRMS m/z calcd for $C_{11}H_9ClO$ 192.0342, found 192.0342; TLC R_f = 0.18 (pentane–ether, 80:20).

5-(4′-Methoxyphenyl)-2,4-pentadienal (28). Prepared from **10a** (0.258 g, 1.25 mmol), cyclohexylamine (0.129 g, 1.30 mmol), LDA (1.20 mmol), and *p*-methoxybenzaldehyde (0.136 g, 1.0 mmol) at 25 °C for 15 h; yield 0.138 g of **28** (73%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 93:6:1). (2*E*,4*E*)-**28**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, J = 7.9 Hz, 1 H, C*H*O), 7.47–7.43 (m, 2 H, aromatic), 7.24 (dd, J = 15.2, 10.6 Hz, 1 H, C*H*=CHCHO), 6.97 (d, J = 15.5 Hz, 1 H, ArC*H*=), 6.92–6.89 (m, 2 H, aromatic), 6.87 (dd, J = 15.5, 10.6 Hz, 1 H, ArCH=C*H*), 6.22 (dd, J = 15.2, 7.9 Hz, 1 H, =C*H*CHO), 3.84 (s, CH_3O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.52 (*C*HO), 160.91 (CH_3OC), 152.62 (*C*H=CHCHO), 142.23 (ArCH=), 130.55, 129.09 (2 C), 128.38, 124.05 and 114.38 (2 C, =*C*HCH=CHCHO and aromatic), 55.34 (CH_3O); IR (CCl_4) 3040, 3010, 2960, 2940, 2911, 2839, 2807, 2741, 2710, 1687, 1626, 1597, 1007, 985 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O$: C, 76.57; H, 6.43. Found: C, 76.7; H, 6.49.

7-Methyl-2,4,6-octatrienal (29). Prepared from **10a** (0.258 g, 1.25 mmol), cyclohexylamine (0.129 g, 1.30 mmol), LDA (1.20 mmol), and 3-methyl-2-butenal (0.084 g, 1.0 mmol) at 25 °C for 15 h; yield 0.062 g of **29** (45%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 88:9:3) as a yellow oil (purity ≥95% by ^{1}H NMR). (2*E*,4*E*)-**29**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, J = 8.0 Hz, 1 H, C*H*O), 7.17 (ddd, J = 15.1, 11.1, 0.5 Hz, 1 H, C*H*=CHCHO), 6.91 (dd, J = 14.7, 11.4 Hz, 1 H, C*H*=CHCH=CHCHO), 6.33 (dd, J = 14.7, 11.2 Hz, 1 H, =C*H*CH=CHCHO), 6.12 (dd, J = 15.2, 8.0 Hz, 1 H, =C*H*CHO), 6.01 (br d of septets, J = 11.4, 1.4 Hz, 1 H, $(CH_3)_2C$=C*H*), 1.89 (br s, 3 H) and 1.87 (br s, 3 H, $(CH_3)_2C$=); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.53 (*C*HO), 152.95 (*C*H=CH-CHO), 144.18 ($(CH_3)_2C$=), 139.43 (*C*H=CHCH=CHCHO), 130.07, 127.41 and 125.20 (=*C*HCH=CHCH=*C*HCHO), 26.54 and 18.84 ($(CH_3)_2C$=); IR (CCl_4) 3033, 2976, 2913, 2806, 2720, 1684, 1617, 1604, 1008, 988, 884 cm^{-1}; HRMS m/z calcd for $C_9H_{12}O$ 136.0888, found 136.0886; TLC R_f = 0.28 (pentane–ether, 80:20).

The following alternative set of conditions gave the indicated results: **10a** with NaHMDS in THF, at 0–25 °C for 17 h, 61% yield (purity ≥95% by ^{1}H NMR), 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 92:6:2. A 0.060-g portion of the product (with isomer ratio 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 94:4:2) was chromatographed once more, yielding 0.048 g of (2*E*,4*E*)-**29** (isomeric purity ≥98%).

7-Phenyl-2,4,6-heptatrienal (30). Prepared from **10a** (0.330 g, 1.60 mmol), cyclohexylamine (0.159 g, 1.60 mmol), NaHMDS (1.60 mL, 1.0 M in THF, 1.60 mmol), and cinnamaldehyde (0.151 g, 1.14 mmol) at 0–25 °C for 16 h; yield 0.112 g of **30** (53%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 92:6:2). A second chromatography gave 0.092 g of (2*E*,4*E*,6*E*)-**30** (isomeric purity ≥99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, J = 8.0 Hz, 1 H, C*H*O), 7.47–7.44 (m, 2 H) and 7.38–7.27 (m, 3 H, aromatic), 7.19 (dd, J = 15.2, 11.2 Hz, 1 H, C*H*=CHCHO), 6.91 (dd, J = 15.2, 10.3 Hz, 1 H, PhCH=C*H*), 6.84 (dd, J = 14.2, 10.2 Hz, 1 H, PhCH=CHC*H*=), 6.81 (d, J = 15.3 Hz, 1 H, PhC*H*=), 6.57 (dd, J = 14.0, 11.2 Hz, 1 H, =C*H*CH=CHCHO), 6.20 (dd, J = 15.2, 7.9 Hz, 1 H, =C*H*CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.42 (*C*HO), 151.65 (*C*H=CH-CHO), 142.67 (PhCH=*C*HCH=), 138.30 (Ph*C*H=), 136.30 (ipso aromatic), 131.17 (=*C*HCHO), 130.11 (=CHCH=CHCHO), 128.81 (two overlapping signals; 3 C, aromatic), 127.67 (Ph*C*H=), 126.98 (2 C, aromatic); IR (CCl_4) 3030, 2808, 2744, 2715, 1684, 1626, 1610, 1009, 991, 930, 890, 851 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.6; H, 6.59.

9-(4′-Chlorophenyl)-2,4,6,8-nonatetraenal (31). Prepared from **10a** (0.144 g, 0.7 mmol), cyclohexylamine (0.070 g, 0.7 mmol), NaHMDS (0.70 mL, 1.0 M in THF, 0.7 mmol), and **27** (0.096 g, 0.5 mmol; ≥98% 2*E*,4*E*) at 0–25 °C for 24 h; yield 0.075 g of **31** (60%; all-*E*:4*Z*:2*Z* = 87:10:3). A second chromatography gave 0.065 g of (2*E*,4*E*,6*E*,8*E*)-**31** (isomeric purity ≥99%): ^{1}H NMR (400

MHz, $CDCl_3$) δ 9.57 (d, *J* = 8.0 Hz, 1 H, C*H*O), 7.36–7.28 (m, 4 H, aromatic), 7.15 (dd, *J* = 15.2, 11.2 Hz, 1 H, C*H*=CHCHO), 6.84 (dd, *J* = 15.4, 10.7 Hz, 1 H, ArCH=C*H*), 6.74 (dd, *J* = 14.6, 11.3 Hz, 1 H, C*H*=CHCH=CHCHO), 6.64 (d, J = 15.7 Hz, 1 H, ArC*H*=), 6.62 (dd, *J* = 14.8, 10.7 Hz, 1 H, ArCH=CHC*H*=), 6.49 (dd, *J* = 14.7, 11.2 Hz, 1 H, =C*H*CH=CHCHO), 6.45 (dd, *J* = 15.2, 11.1 Hz, 1 H, ArCH=CHCH=C*H*), 6.17 (dd, *J* = 15.2, 7.9 Hz, 1 H, =C*H*CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.36 (*C*HO), 151.49 (*C*H=CHCHO), 142.30 (*C*H=CHCH=CHCHO), 138.39, 135.23, 134.43, 133.88, 132.31, 131.17, 130.28, 128.93, (2 C), 128.87 and 127.82 (2 C, Ar*C*H=*C*H*C*H=*C*H*C*H=*C*HCHO and aromatic); IR ($CDCl_3$) 3029, 1671, 1626, 1595, 1578, 1013, 998 cm^{-1}; HRMS *m*/*z* calcd for $C_{15}H_{13}ClO$ 244.0655, found 244.0652; TLC R_f = 0.15 (pentane–ether, 80:20).

Methyl 13-Oxo-9(*E*),11(*E*)-tridecadienoate (32). Prepared from **10a** (577 mg, 2.8 mmol), cyclohexylamine (278 mg, 2.8 mmol), LDA (2.4 mmol), and **49** (373 mg, 2.0 mmol) in THF (1.0 mL) at 0 °C for 2 h; yield 0.309 g (65%) of **32** as a light yellow oil (9*E*,11*E*:9*Z*,11*E*:9*E*,11*Z* = 83:14:3 by ^1H NMR). Further chromatography afforded 9(*E*),11(*E*)-**32** (96% isomeric purity): ^1H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, *J* = 8.0 Hz, 1 H, C*H*O), 7.08 (app br dd, *J* = 15.3, 9.8 Hz, 1 H, C*H*=CHCHO), 6.32 (br dd, *J* = 15.0, 9.0 Hz, 1 H, CH_2CH=C*H*), 6.27 (br dt, *J* = 15.0, 6.3 Hz, 1 H, CH_2C*H*=CH), 6.08 (dd, *J* = 15.4, 8.0 Hz, 1 H, CH=C*H*CHO), 3.67 (s, 3 H, OCH_3), 2.31 (t, *J* = 7.5 Hz, 2 H, CH_2COOCH_3), 2.22 (app br q, *J* = 6.9 Hz, 2 H, CH_2CH=CH), 1.62 (app br quintet, *J* = 7.1 Hz, 2 H), 1.46 (app br quintet, *J* = 7.0 Hz, 2 H) and 1.35–1.29 (m, 6 H, $CH_2(CH_2)_5CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.82 (*C*HO), 174.14 (*C*OOCH$_3$), 152.71 and 147.13 (*C*H=CH*C*H=CHCHO), 130.02 and 128.65 (CH=*C*HCH=*C*HCHO), 51.37 (OCH_3), 33.96, 33.07, 28.93 (2 C), 28.88, 28.39, and 24.79 (CH_2)$_7$); IR (CCl_4) 2932, 2858, 2810, 2740, 1742, 1689, 1643, 1009, 987 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56, H, 9.30. Found: C, 70.34; H, 9.23.

The following alternative conditions gave the indicated results: **10b** with LDA in THF, 6 h at 0 to 25 °C, 33% yield, 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 90:7:3.

5-Cyclohexylidene-2,4-pentadienal (33). Prepared from **10a** (0.309 g, 1.50 mmol), cyclohexylamine (0.149 g, 1.50 mmol), LDA (1.43 mmol), and cyclohexanone (0.098 g, 1.0 mmol) at 0–25 °C for 21 h; yield 0.110 g of **33** (73%; 2*E*,2*Z* = 98:2) as an almost colorless oil. (*E*)-**33**: ^1H NMR (400 MHz, $CDCl_3$) δ 9.57 (d, *J* = 8.1 Hz, 1 H, C*H*O), 7.46 (dd, *J* = 15.0, 11.6 Hz, 1 H, C*H*=CHCHO), 6.10 (br d, *J* = 11.6 Hz, 1 H, $(CH_2)_2C$=C*H*), 6.09 (dd, *J* = 15.1, 7.9 Hz, 1 H, =C*H*CHO), 2.45–2.43 (m, 2 H), and 2.28–2.26 (m, 2 H) ((CH_2)$_2$C=), 1.70–1.60 (m, 6 H, $CH_2(CH_2)_3CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.05 (*C*HO), 157.44 ((CH_2)$_2$*C*=), 147.95 (*C*H=CHCHO), 129.89 and 121.04 (=CHCH=*C*HCHO), 37.98, 29.97, 28.49, 27.94 and 26.38 ((CH_2)$_5$); IR (CCl_4) 2935, 2860, 2715, 1686, 1634, 1004, 970, 884, 855 cm^{-1}; TLC R_f = 0.31 (pentane–ether, 80:20).

5-Phenyl-2,4-hexadienal (34). Prepared from **10a** (0.619 g, 3.00 mmol), cyclohexylamine (0.298 g, 3.0 mmol), LDA (2.90 mmol), and acetophenone (0.120 g, 1.0 mmol) at 0–25 °C for 111 h; yield 0.133 g of **34** (77%; 2*E*,4*E*:2*E*,4*Z*:2*Z*,4*E* = 80:18:2) as an orange oil. (2*E*,4*E*)-**34**: ^1H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 8.0 Hz, 1 H, C*H*O), 7.57 (dd, *J* = 15.0, 11.5 Hz, 1 H, C*H*=CHCHO), 7.53–7.50 (m, 2 H) and 7.41–7.32 (m, 3 H) (aromatic), 6.71 (app d of quintets, *J* = 12.5, 1.4 Hz, 1 H, PhC(CH_3)=C*H*), 6.26 (dd, *J* = 15.0, 7.9 Hz, 1 H, =C*H*CHO), 2.35 (d, *J* = 1.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.66 (*C*HO), 147.88 (*C*H=CHCHO), 147.83 (Ph*C*(CH_3)=), 141.45 (ipso), 131.77 (=*C*HCHO), 128.82, 128.52 (2 C) and 126.03 (2 C, aromatic), 124.80 (PhC(CH_3)=*C*H), 16.66 (CH_3); IR (CCl_4) 3060, 3036, 2926, 2808, 2742, 2716, 1686, 1617, 1028, 1002, 969, 894 cm^{-1}; EIMS *m*/*z* (rel intensity) 172 (17), 157 (100); HRMS *m*/*z* calcd for $C_{12}H_{12}O$ 172.0888, found 172.0886; TLC R_f = 0.25 (pentane–ether, 80:20).

Synthesis of Reagent 5. 1-Acetoxy-3-methyl-2-butene (14). To a solution of 1-hydroxy-3-methyl-2-butene (10.23 g, 118 mmol), Et_3N (33.1 mL, 237 mmol), and 4-DMAP[11] (0.726 g, 5.9 mmol) in CH_2Cl_2 (150 mL) at 0 °C was added 237 anhydride (22.5 mL, 237 mmol) dropwise. After 5 min the solution was warmed to 25 °C and stirred for 3 h. The reaction was quenched with MeOH (15 mL). The solution was washed with 1 N HCl and water, and the combined aqueous layers were extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The crude product was distilled (760 Torr, bp 150–152 °C), providing 12.79 g (84%) of **14** as a colorless oil: ^1H NMR (200 MHz, $CDCl_3$) δ 5.38–5.32 (tm, *J* = 7 Hz, 1 H, =C*H*), 4.57 (d, *J* = 7 Hz, 2 H, CH_2OAc), 2.05 (s, 3 H, OCOCH_3), 1.77 (s, 3 H) and 1.71 (s, 3 H) ((CH_3)$_2$C=CH); IR (CCl_4) 2976, 2937, 1748, 1677, 1048, 1027, 955 cm^{-1} (lit.[49] bp, IR, ^1H NMR).

1-Acetoxy-4-(diethoxyphosphoryl)-3-methyl-2-butene (17). A mixture of **14** (20.0 g, 156 mmol), NBS (22.2 g, 125 mmol), and AIBN[11] (0.35 g, 2.2 mmol) in CCl_4 (300 mL) was heated at reflux for 2.5 h. After cooling, the mixture was filtered, and the filtrate was concentrated. The residue was diluted with ether, washed with 10% aqueous $NaHCO_3$, 10% aqueous Na_2CO_3, and brine, and dried ($MgSO_4$). Evaporation of the solvent and distillation (3 Torr, 62–65 °C) yielded 13.2 g (51%) of a crude mixture of allylic bromides as a yellow oil ((*E*)-**15**:(*Z*)-**15**:**16** = ca. 4:2:1 by NMR). A mixture of these bromides (23.24 g, 112.2 mmol) and $(EtO)_3P$ (18.65 mL, 112.2 mmol) was heated to 110 °C for 7.5 h. Distillation (114 °C, 1 Torr) gave 15.98 g (54%) of **17** as a colorless oil (>95% pure by NMR, *E*:*Z* = 67:33). (*E*)-**17**: ^1H NMR (200 MHz, $CDCl_3$) δ 5.51 (app qm, *J* = 7.0 Hz, 1 H, =C*H*), 4.61 (dd, *J* = 7.0, 4.3 (J_{PH}) Hz, 2 H, CH_2OAc), 4.18–4.03 (m, 4 H, CH_3CH_2O), 2.59 (d, J_{PH} = 22.3 Hz, 2 H, PCH_2), 2.05 (s, 3 H, OCOCH_3), 1.87 (d, J_{PH} = 3.4 Hz, 3 H, C(CH_3)=), 1.32 (t, *J* = 7.1 Hz, 6 H, CH_3CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.94 (OCOCH$_3$), 132.78 (d, J_{PC} = 11.6 Hz, *C*(CH_3)=), 123.54 (d, J_{PC} = 12.5 Hz, =*C*H), 61.94 (d, J_{PC} = 6.5 Hz, 2 C, CH_3CH_2O), 60.95 (CH_2OAc), 36.92 (d, J_{PC} = 137.3 Hz, PCH_2), 20.91 (OCOCH_3), 17.74 (C(CH_3)=), 16.39 (d, J_{PC} = 6.0 Hz, 2 C, CH_3CH_2); IR (CCl_4) 2983, 2932, 2908, 1743, 1030, 963 cm^{-1}; HRMS *m*/*z* calcd for $C_{11}H_{21}O_5P$ 264.1127, found 264.1128; TLC R_f = 0.40 (CH_2Cl_2–MeOH, 95:5).

4-(Diethoxyphosphoryl)-3-methyl-2-buten-1-ol (18). Compound **17** (15.98 g, 60.5 mmol) and *p*-TsOH (1.15 g, 6.0 mmol) were dissolved in EtOH (300 mL, 99.5%), and the solution was heated at reflux for 7 h. The EtOH was evaporated, and the residue was dissolved in CH_2Cl_2 (120 mL) and washed with a solution of K_2CO_3 (1 g) in H_2O/brine (1:1, 50 mL). The aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated, leaving 14.21 g of a yellow oil. Bulb-to-bulb distillation (100 °C, 0.2 Torr) gave 12.42 g of crude product. Then MPLC (110 g of silica gel, 0–15% EtOAc in hexanes), performed in two batches, yielded 9.48 g (71%) of **18** as a yellow oil (pure by NMR, *E*:*Z* = 70:30). (*E*)-**18**: ^1H NMR (200 MHz, $CDCl_3$) δ 5.57 (app br q, *J* = 6.5 Hz, 1 H, =C*H*), 4.16 (app br t, *J* = 5.6 Hz, 2 H, CH_2OH), 4.14–4.06 (m, 4 H, CH_3CH_2O), 2.64 (br s, 1 H, CH_2OH), 2.57 (d, J_{PH} = 22.1 Hz, 2 H, PCH_2), 1.82 (dd, *J* = 3.4 (J_{PH}), 0.6 Hz, 3 H, C(CH_3)=), 1.32 (t, *J* = 7.1 Hz, 6 H, CH_3CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.2 (d, J_{PC} = 7 Hz, *C*(CH_3)=), 29.09 (d, J_{PC} = 12.9 Hz, =*C*H), 61.84 (d, J_{PC} = 7.0 Hz, 2 C, CH_3CH_2O), 58.91 (d, J_{PC} = 1.9 Hz, CH_2OH), 36.69 (d, J_{PC} = 137.1 Hz, PCH_2), 17.50 (C(*C*H$_3$)=), 16.34 (d, J_{PC} = 6.0 Hz, 2 C, CH_3CH_2); IR (CCl_4) 3396, 2983, 2908, 1059, 1030, 964 cm^{-1}. Anal. Calcd for $C_9H_{19}O_4P$: C, 48.64; H, 8.62. Found: C, 48.42; H, 8.50.

4-(Diethoxyphosphoryl)-3-methyl-2-butenal (19). To a solution of **18** (7.0 g, 31.5 mmol) in acetone (400 mL) at 0 °C under N_2 was added CrO_3 (3.15 g, 31.5 mmol) in 2 N H_2SO_4 (63 mL) over 20 min. The solution was stirred for 25 min. 2-Propanol (5.5 mL) was added to quench the excess CrO_3. After 15 min, solid $NaHCO_3$ (4.2 g) was added. The mixture was filtered through Celite, and the solvent was evaporated from the filtrate. The residue was diluted with brine and water, the mixture was extracted with CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated, leaving 9.32 g of a light-yellow oil. MPLC (ca. 110 g of deactivated[56] silica gel, 1–5% MeOH in CH_2Cl_2) yielded 5.94 g (86%) of pure **19** as a nearly colorless oil (*E*:*Z* = 55:45 by NMR). (*E*)-**19**: ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (d, *J* = 7.8 Hz, 1 H, C*H*O), 5.98–5.94 (m, 1 H, =C*H*), 4.17–4.09 (m, 4 H, CH_3CH_2O), 2.75 (dd, *J* = 23.9 (J_{PH}), 0.9 Hz, 2 H, PCH_2), 2.33 (dd, *J* = 3.5 (J_{PH}), 1.4 Hz, 3 H, C(CH_3)=), 1.33 (t, *J* = 7.1 Hz, 6 H, CH_3CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.97 (d, J_{PC} = 3.1 Hz, *C*HO), 153.38 (d, J_{PC} = 10.9 Hz, *C*(CH_3)=), 130.41 (d, J_{PC} = 7.7 Hz, =*C*H), 62.02 (d, J_{PC} = 7.2 Hz, 2 C, CH_3CH_2O), 38.11 (d, J_{PC} = 133.9 Hz, PCH_2), 18.43 (C(*C*H$_3$)=), 16.00 (2 C, CH_3CH_2); IR (CCl_4) 2984, 2931, 2908, 1682, 1635, 1029, 967 cm^{-1}; EIMS *m*/*z* (rel intensity) 220 (49), 82 (100); HRMS *m*/*z* calcd for $C_9H_{17}O_4P$ 220.0865, found 220.0862; TLC

R_f = 0.39 (CH_2Cl_2–MeOH, 95:5).

Condensations of Phosphonate Reagent 5 with Carbonyl Compounds. General Procedure: (A) Preparation of the Phosphoryl Imine 5. Reagent **5** was prepared from the phosphoryl aldehyde **19** according to the procedure for preparation of **4**. Compound **5** was obtained in solution as a mixture of isomers (*E*:*Z* = 55:45 by NMR). The solutions were almost colorless. (2*E*)-**5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.3 Hz, 1 H, C*H*=N), 6.10–6.05 (m, 1 H, =C*H*), 4.15–4.07 (m, 4 H, CH_3CH_2O), 3.04–2.98 (m, 1 H, =NC*H*), 2.67 (dd, *J* = 23.2 (J_{PH}), 0.8 Hz, 2 H, PCH_2), 2.08 (dd, *J* = 4.0 (J_{PH}), 1.4 Hz, 3 H, C(CH_3)=), 1.83–1.43 (m, 10 H, $(CH_2)_5$), 1.314 (t, *J* = 7.1 Hz, 6 H, CH_3CH_2). (2*Z*)-**8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.3 Hz, 1 H, C*H*=N), 6.18–6.12 (m, 1 H, =C*H*), 4.15–4.07 (m, 4 H, CH_3CH_2O), 3.04–2.98 (m, 1 H, =NC*H*), 2.87 (d, J_{PH} = 23.6 Hz, 2 H, PCH_2), 2.02 (dd, *J* = 4.0 (J_{PH}), 1.4 Hz, 3 H, C(CH_3)=), 1.83–1.43 (m, 10 H, $(CH_2)_5$), 1.31 (t, *J* = 7.1 Hz, 6 H, CH_3CH_2).

(B) Condensation Reactions with Reagent 5. The condensations were performed according to the procedure for condensations with reagents **4**.[5]

3-Methyl-2,4-dodecadienal (35). Prepared from **19** (0.308 g, 1.4 mmol), cyclohexylamine (0.140 g, 1.4 mmol), LDA (1.4 mmol), and *n*-octanal (0.128 g, 1.0 mmol) at 0–25 °C for 3 h; yield 0.122 g of **35** as a light-yellow oil (63%; 2*E*,4*E*:2*Z*,4*E* = 75:25). A second chromatography of 0.400 g of **35** gave 0.187 g of pure (2*E*,4*E*)-**35**: ^{1}H (400 MHz, $CDCl_3$) δ 10.10 (d, *J* = 8.2 Hz, 1 H, C*H*O), 6.30 (dt, *J* = 15.6, 6.8 Hz, 1 H, CH_2CH=), 6.20 (d, *J* = 15.8 Hz, 1 H, CH_2CH=C*H*), 5.89 (d, *J* = 8.2 Hz, 1 H, =C*H*CHO), 2.25 (d, *J* = 4.2 Hz, 3 H, C(CH_3)=), 2.21 (app br q, *J* = 7.2 Hz, 2 H, CH_2CH=CH), 1.49–1.41 (m, 2 H, CH_2CH_2CH=), 1.34–1.25 (m, 8 H, $CH_3(CH_2)_4$), 0.89 (br t, *J* = 7.0 Hz, 3 H, CH_3CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.40 (*C*HO), 154.89 (*C*(CH_3)=), 139.76 (CH_2CH=), 133.34 and 128.30 (=*C*HC(CH_3)=*C*HCHO), 33.20, 31.70, 29.12, 29.03, 28.82 and 22.60 ($(CH_2)_6$), 14.00 (CH_3CH_2), 13.02 (C(*C*H_3)=); IR (CCl_4) 2958, 2929, 2857, 2336, 1672, 1634, 968 cm^{-1}; EIMS *m*/*z* (rel intensity) 194 (16), 95 (100); HRMS *m*/*z* calcd for $C_{13}H_{22}O$ 194.1671, found 194.1666; TLC R_f = 0.29 (pentane–ether, 90:10).

5-Cyclohexyl-3-methyl-2,4-pentadienal (36). Prepared from **19** (0.616 g, 2.8 mmol), cyclohexylamine (0.280 g, 2.8 mmol), LDA (2.6 mmol), and cyclohexanecarboxaldehyde (0.224 g, 2.0 mmol) at 0–25 °C for 6 h; yield 0.300 g of **36** as a light-yellow oil (84%; 2*E*,4*E*:2*Z*,4*E* = 63:37). (2*E*,4*E*)-**36**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (d, *J* = 8.2 Hz, 1 H, C*H*O), 6.23 (dd, *J* = 15.8, 6.4 Hz, 1 H, $(CH_2)_5CHCH$=), 6.16 (d, *J* = 15.9 Hz, 1 H, $(CH_2)_5CHCH$=C*H*), 5.90 (d, *J* = 8.1 Hz, 1 H, =C*H*CHO), 2.28–2.18 (m, 1 H, $(CH_2)_5CHCH$=), 2.24 (d, *J* = 1.2 Hz, 3 H, C(CH_3)=), 1.81–1.64 (m, 5 H) and 1.37–1.09 (m, 5 H) ($(CH_2)_5$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.42 (*C*HO), 155.25 (*C*(CH_3)=), 144.97 [$(CH_2)_5CH$-CH=CH], 131.02 and 128.50 (=*C*HC(CH_3)=*C*HCHO), 41.39 ($(CH_2)_5CHCH$=CH), 32.43 (2 C), 25.94 and 25.79 (2 C, $(CH_2)_5$), 13.05 (C(*C*H_3)=); IR (CCl_4) 2929, 2854, 1672, 1630, 968 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.58; H, 10.01.

3-Methyl-5-phenyl-2,4-pentadienal (37). Prepared from **19** (0.924 g, 4.2 mmol), cyclohexylamine (0.417 g, 4.2 mmol), LDA (3.9 mmol), and benzaldehyde (0.318 g, 3.0 mmol) at 0–25 °C for 18 h; yield 0.375 g of **37** as a yellow oil (72%; 2*E*,4*E*:2*Z*,4*E* = 85:15). (2*E*,4*E*)-**37**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (d, *J* = 8.0 Hz, 1 H, C*H*O), 7.52–7.30 (m, 5 H, aromatic), 7.07 (d, *J* = 16.1 Hz, 1 H) and 6.89 (d, *J* = 16.1 Hz, 1 H, PhC*H*=C*H*), 6.08 (d, *J* = 8.1 Hz, 1 H, =C*H*CHO), 2.38 (d, *J* = 1.2 Hz, 3 H, C(CH_3)=); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.14 (CHO), 154.13 (*C*(CH_3)=), 135.83 (ipso aromatic), 135.63 131.28, 130.02, 129.17, 128.85 (2 C) and 127.31 (2 C) (PhCH=CH, =CHCHO, and aromatic), 13.03 (C(CH_3)=); IR (CCl_4) 3038, 2840, 2771, 1672, 1617, 1595, 1576, 880 cm^{-1}; EIMS *m*/*z* (rel intensity) 172 (96), 129 (100); HRMS *m*/*z* calcd for $C_{12}H_{12}O$ 172.0888, found 172.0888; TLC R_f = 0.11 (pentane–ether, 90:10).

5-(4′-Chlorophenyl)-3-methyl-2,4-pentadienal (38). Prepared from **19** (0.275 g, 1.25 mmol), cyclohexylamine (0.125 g, 1.25 mmol), LDA (1.36 mmol), and 4-chlorobenzaldehyde (0.141 g, 1.0 mmol) at 0–25 °C for 18 h; yield 0.150 g of **38** as an orange-yellow solid (71%; 2*E*,4*E*:2*Z*,4*E* = 89:11). (2*E*,4*E*)-**38**: ^{1}H (400 MHz, $CDCl_3$) δ 10.15 (d, *J* = 8.0 Hz, 1 H, C*H*O), 7.46–7.28 (m, 4 H, aromatic), 6.99 (d, *J* = 16.1 Hz, 1 H) and 6.84 (dd, *J* = 16.1, 0.6 Hz, 1 H, Ar-C*H*=C*H*), 6.07 (d, *J* = 8.0 Hz, 1 H, =C*H*CHO), 2.37 (d, *J* = 1.1 Hz, 3 H, C(CH_3)=); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.14 (*C*HO), 153.72 (*C*(CH_3)=), 134.96 and 134.38 (ipso aromatic), 134.22, 131.88, 130.37, 129.13 (2 C) and 128.47 (2 C) (ArCH=*C*H, =*C*HCHO, and aromatic), 13.06 (C(*C*H_3)=); IR (CCl_4) 2842, 1671, 1619, 1589, 1570, 1013, 964 cm^{-1}. Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.73; H, 5.36. Found: C, 69.67; H, 5.40.

5-(4′-Methoxyphenyl)-3-methyl-2,4-pentadienal (39). Prepared from **19** (0.308 g, 1.4 mmol), cyclohexylamine (0.140 g, 1.4 mmol), LDA (1.3 mmol), and 4-methoxybenzaldehyde (0.136 g, 1.0 mmol) at 0–25 °C for 18 h; yield 0.137 g of **39** as a yellow solid (67%; 2*E*,4*E*:2*Z*,4*E* = 88:12). (2*E*,4*E*)-**39**: ^{1}H (400 MHz, $CDCl_3$) δ 10.14 (d, *J* = 8.1 Hz, 1 H, C*H*O), 7.48–7.43 (m, 2 H, aromatic), 6.98 (d, *J* = 16.1 Hz, 1 H, one of ArC*H*=C*H*), 6.92–6.88 (m, 2 H, aromatic), 6.78 (dd, *J* = 15.9, 0.5 Hz, 1 H, one of ArC*H*=C*H*), 6.05 (d, *J* = 8.2 Hz, 1 H, =C*H*CHO), 3.84 (s, 3 H, CH_3O), 2.37 (d, *J* = 1.1 Hz, 3 H, C(CH_3)=); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.12 (*C*HO), 160.55 (CH_3OC), 154.68 (*C*(CH_3)=), 135.36, 129.26, 129.09, 128.82 (2 C), 128.63 and 114.34 (2 C) (ArCH=*C*H, =*C*HCHO, and aromatic), 55.33 (CH_3O), 13.02 (C(*C*H_3)=); IR (CCl_4) 2838, 1668, 1606, 1592, 1573, 1038, 963 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.2; H, 7.08.

3,7-Dimethyl-2,4,6-octatrienal (40). Prepared from **19** (0.617 g, 2.8 mmol), cyclohexylamine (0.279 g, 2.8 mmol), KHMDS (2.8 mmol, 0.5 M solution in toluene), and 3-methyl-2-butenal (0.224 g, 2.0 mmol) at 0–25 °C for 20 h; yield 0.247 g of **40** as a yellow oil (63%; 2*E*,4*E*:2*Z*,4*E* = 68:32). (2*E*,4*E*)-**40**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (d, *J* = 8.2 Hz, 1 H, C*H*O), 6.97 (dd, *J* = 15.2, 11.1 Hz, 1 H, $(CH_3)_2C$=CHC*H*=), 6.24 (d, *J* = 15.2 Hz, 1 H, =C*H*C(CH_3)=), 6.00 (d, *J* = 11.2 Hz, 1 H, $(CH_3)_2C$=C*H*), 5.94 (d, *J* = 7.6 Hz, 1 H, =C*H*CHO), 2.30 (d, *J* = 0.9 Hz, 3 H, C(CH_3)=), 1.88 (s, 6 H, $(CH_3)_2C$=); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.05 (*C*HO), 155.14 (*C*(CH_3)=CHCHO), 142.43 [$(CH_3)_2C$=], 132.60, 132.48, 128.61 and 125.35 (*C*H=), 26.45 and 18.81 ($(CH_3)_2C$=CH), 13.02 (C(*C*H_3)=CHCHO); IR (CCl_4) 2960, 2928, 2857, 1718, 1693, 1674, 1639, 1600, 974 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.80; H, 9.27.

3-Methyl-7-phenyl-2,4,6-heptatrienal (41). Prepared from **19** (0.308 g, 1.4 mmol), cyclohexylamine (0.140 g, 1.4 mmol), LDA (1.4 mmol), and cinnamaldehyde (0.132 g, 1.0 mmol) at 0–25 °C for 19 h; yield 0.103 g of **41** as an orange-yellow solid (52%; 2*E*,4*E*:2*Z*,4*E* = 79:21). (2*E*,4*E*,6*E*)-**41**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (d, *J* = 8.0 Hz, 1 H, C*H*O), 7.46–7.42 (m, 2 H), 7.38–7.32 (m, 2 H) and 7.30–7.26 (m, 1 H, aromatic), 6.95–6.87 (m, 2 H), 6.83–6.77 (m, 1 H) and 6.46–6.41 (m, 1 H, PhC*H*=C*H*C*H*=C*H*), 6.00 (d, *J* = 8.0 Hz, 1 H, =C*H*CHO), 2.32 (d, *J* = 1.0 Hz, 3 H, C(CH_3)=); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.09 (*C*HO), 154.18 (*C*(CH_3)=), 137.22, 136.51, 136.30, 135.33, 129.57, 128.77 (2 C), 128.54, 128.15 and 126.83 (2 C) (PhCH=*C*HCH=*C*HC(CH_3)=CHCHO and aromatic), 12.97 (CH_3); IR (CCl_4) 3031, 2839, 2760, 2720, 1667, 1602, 1590, 1560, 988 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.73; H, 7.18.

The following alternative set of conditions gave the indicated results: KHMDS in THF, 21 h at 0–25 °C, 78% yield, 2*E*,4*E*:2*Z*,4*E* = 84:16.

9-(4′-Chlorophenyl)-3,7-dimethyl-2,4,6,8-nonatetraenal (42). Prepared from **19** (0.134 g, 0.61 mmol), cyclohexylamine (0.060 g, 0.61 mmol), KHMDS (0.61 mmol, 0.5 M solution in toluene), and **38** (0.090 g, 0.435 mmol) at 0–25 °C for 21 h; yield 0.089 g of **42** (75%; 2*E*,4*E*:2*Z*,4*E* = 84:16) as an orange solid (≥95% pure by ^{1}H NMR). (2*E*,4*E*,6*E*,8*E*)-**42**: ^{1}H (400 MHz, $CDCl_3$) δ 10.09 (d, *J* = 8.1 Hz, 1 H, C*H*O), 7.36–7.24 (m, 4 H, aromatic), 7.10 (dd, *J* = 15.1, 11.5 Hz, 1 H, C(CH_3)=CHC*H*=CH), 6.82 (d, *J* = 15.9 Hz, 1 H) and 6.62 (d, *J* = 16.0 Hz, 1 H, ArC*H*=C*H*), 6.39 (d, *J* = 15.1 Hz, 1 H, C(CH_3)=CHCH=C*H*), 6.32 (d, *J* = 11.5 Hz, 1 H, C(CH_3)=C*H*CH=), 5.96 (d, *J* = 8.1 Hz, 1 H, =C*H*CHO), 2.30 (d, *J* = 1.1 Hz, 3 H, C(C*H*$_3$)=CHCHO), 2.05 (d, *J* = 0.9 Hz, 3 H, C(C*H*$_3$)=CHCH=); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.05 (*C*HO), 154.30 (*C*(CH_3)=CHCHO), 140.17 (*C*(CH_3)=CHCH=), 135.80, 135.65, 133.38, 133.35, 131.96, 131.86, 129.52, 128.87 (2 C), 128.73 and 127.71 (2 C, =*C*H and aromatic), 13.07 (two overlapping signals, C(CH_3)=); IR (CCl_4) 3046, 2925, 2857, 1666, 1619, 1578, 1013, 965 cm^{-1}; HRMS *m*/*z* calcd for $C_{17}H_{17}OCl$ 272.0968, found 272.0967; TLC R_f = 0.15 (pentane–ether, 80:20).

5-Cyclohexylidene-3-methyl-2-pentadienal (43). Prepared from **19** (0.661 g, 3.0 mmol), cyclohexylamine (0.298 g, 3.0 mmol),

LDA (2.8 mmol), and cyclohexanone (0.143 g, 1.46 mmol) at 0–25 °C for 20 h; yield 0.094 g of **43** as a light-yellow oil (39%; ≥98% *E*). (*E*)-**43**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (d, *J* = 8.2 Hz, 1 H, C*H*O), 5.87 (br d, *J* = 8.2 Hz, 1 H, C(CH$_3$)=C*H*CHO), 5.72 (s, 1 H, $(CH_2)_5CH$=C*H*), 2.38–2.34 (m, 2 H) and 2.21–2.17 (m, 2 H) ($CH_2(CH_2)_3CH_2$), 2.23 (d, *J* = 1.3 Hz, 3 H, C(CH_3)=CHCHO), 1.66–1.52 (m, 6 H, $CH_2(CH_2)_3CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.39 (*C*HO), 157.09 (*C*(CH$_3$)=CHCHO), 149.46 [$(CH_2)_5CH$=CH, 128.45 (=CHCHO), 124.71 $(CH_2)_5CH$=*C*H), 38.39, 30.56, 28.61, 27.98 and 26.37 (CH_2), 18.32 (C(CH_3)=CHCHO); IR (CCl_4) 2935, 2857, 2751, 1673, 1639, 1614, 886 cm^{-1}; EIMS *m*/*z* (rel intensity) 164 (76), 121 (100); HRMS *m*/*z* calcd for $C_{11}H_{16}O$ 164.1201, found 164.1195; TLC R_f = 0.19 (pentane–ether, 90:10).

Methyl 9-Hydroxynonanoate (48). Azelaic acid monomethyl ester (4.46 g, 22.0 mmol) in THF (10 mL) was cooled to −20 °C under argon. BH_3·THF (22 mL, 1.0 M solution in THF, 22.0 mmol) was added over 30 min. The solution reached 25 °C over 13 h. The solution was stirred with water (15 mL) at 0 °C for a few minutes. K_2CO_3 (5.3 g) was added, the organic phase was separated, and the aqueous phase was extracted with ether. The combined organic extracts were washed with brine and dried ($MgSO_4$). MPLC (90 g of silica gel, 10–40% EtOAc in hexanes) gave 2.355 g (57%) of **48** as a colorless oil (purity ≥98% by NMR and capillary GLC), plus another 0.989 g of **48** (purity ca. 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (s, 3 H, OC*H*$_3$), 3.60 (t, *J* = 6.6 Hz, 2 H, C*H*$_2$OH), 2.28 (t, *J* = 7.5 Hz, 2 H, C*H*$_2$COOCH$_3$), 1.68 (br , 1 H, O*H*), 1.63–1.50 (m, 4 H) and 1.34–1.27 (m, 8 H, $CH_2(CH_2)_6CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.27 (*C*OOCH$_3$), 62.87 (*C*H$_2$OH), 51.37 (OCH$_3$), 34.01, 32.67, 29.12 (2 C), 28.97, 25.60, and 24.83 ($CH_2(CH_2)_7COOCH_3$); IR (CCl_4) 3638, 2933, 2858, 1742, 1052 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.80; H, 10.71. Found: C, 63.63; H, 10.57.

Methyl 9-Oxononanoate (49). To pyridinium chlorochromate (1.617 g, 7.5 mmol) and 4-Å molecular sieves (2.5 g)[58] in dry CH_2Cl_2 (10 mL) under argon was added **48** (0.949 g, 5.0 mmol) in dry CH_2Cl_2 (2.5 mL). The mixture was stirred at 25 °C for 2.5 h. Dry ether (15 mL) was added, and the mixture was stirred vigorously for a few minutes. The solution was decanted, and the black residue was leached with dry ether. The combined organic solutions were filtered through a short column of Florisil; the column was eluted with additional ether. Evaporation of the solvent gave 0.763 g (81%) of **49** as a colorless oil (purity ≥98% by NMR and capillary GLC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (t, *J* = 1.8 Hz, 1 H, C*H*O), 3.65 (s, 3 H, OC*H*$_3$), 2.41 (dt, *J* = 7.3, 1.8 Hz, 2 H, C*H*$_2$CHO), 2.29 (t, *J* = 7.4 Hz, 2 H, C*H*$_2$COOCH$_3$), 1.69–1.52 (m, 4 H) and 1.37–1.26 (m, 6 H, $CH_2(CH_2)_5CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.69 (*C*HO), 174.17 (*C*OOCH$_3$), 51.41 (OCH$_3$), 43.82, 33.99, 28.93, 28.91, 28.86, 24.80, and 21.96 (OHC(*C*H$_2$)$_7$COOCH$_3$); IR (CCl_4) 2935, 2859, 2817, 2716, 1741, 1462, 1437, 1363, 1250, 1198, 1173, 1104, 1017 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.37; H, 9.58.

Methyl 13-Hydroxy-9(*E*),11(*E*)-octadecadienoate (Methyl (*E*,*E*)-Coriolate, 50). To anhydrous THF (5 mL) containing a few crystals of 2,2′-biquinoline at 25 °C under argon was added *n*-C_5H_{11}MgBr (50 μL, 1.96 M in ether) until a violet color persisted. The solution was cooled to −20 °C, and **32** (243 mg, 1.02 mmol; 9*E*,11*E*:9*Z*,11*E*:9*E*,11*Z* = 92:7:1) in 2.5 mL of THF (this solution was dried over molecular sieves overnight) was added, followed by dropwise addition of *n*-C_5H_{11}MgBr (0.520 mL, 1.96 M in ether, 1.02 mmol) over 10 min. The yellow solution was stirred at −20 °C for 2.5 h. H_2O (5 mL) and saturated aqueous NH_4Cl (5 mL) were added, the mixture was extracted with ether, and the combined extracts were washed with brine, dried ($MgSO_4$), and concentrated to a yellow oil. Flash chromatography (hexanes–ether, 70:30) afforded 0.210 g (66%) of **50** (9*E*,11*E*:9*Z*,11*E* = 94:6 by NMR and HPLC). Further chromatography of a 0.200-g sample gave 0.140 g of the *E*,*E* isomer in 97% isomeric purity. (9*E*,11*E*)-**50**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dd, *J* = 15.2, 10.4 Hz, 1 H, C*H*=CHCH(OH)), 6.01 (ddt, *J* = 15.1, 10.4, 1.3 Hz, 1 H, CH_2CH=C*H*), 5.68 (dt, *J* = 15.1, 7.0 Hz, 1 H, CH_2CH=C*H*), 5.57 (dd, *J* = 15.1, 7.0 Hz, 1 H, CH=C*H*CH(OH)), 4.11 (app br q, *J* = 6.7 Hz, 1 H, C*H*(OH)), 3.67 (s, 3 H, OC*H*$_3$), 2.30 (t, *J* = 7.5 Hz, 2 H, C*H*$_2$COOCH$_3$), 2.07 (app qd, *J* = 7.0, 1.3 Hz, 2 H, C*H*$_2$CH=CH), 1.65–1.25 (complex m, 19 H, $CH_2(CH_2)_5CH_2$, $(CH_2)_4CH_3$, and O*H*), 0.88 (t, *J* = 6.9 Hz, 3 H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.30 (*C*OOCH$_3$), 135.88, 133.69, 130.90 and 129.49 (*C*H=*C*H*C*H=*C*H), 72.89 (*C*H(OH)), 51.45 (OCH$_3$), 37.28, 34.07, 32.56, 31.76, 29.10, 29.05 (2 C), 28.93, 25.12, 24.89, and 22.59 ((*C*H$_2$)$_7$ and $(CH_2)_4CH_3$), 14.03 (CH_2CH_3); IR (CCl_4) 3618, 2931, 2858, 1742, 990, 909 cm^{-1}. Anal. Calcd for $C_{19}H_{34}O_3$: C, 73.50; H, 11.04. Found: C, 73.2; H, 11.0.

13-Hydroxy-9(*E*),11(*E*)-octadecadienoic Acid ((*E*,*E*)-Coriolic Acid, 45). To **50** (52 mg, 0.17 mmol; 9*E*,11*E*:9*Z*,11*E* = 90:10) in THF (5 mL) was added LiOH (20 mg, 0.84 mmol) in H_2O (2.5 mL). The solution was stirred at 25 °C for 5 h. Formic acid (154 mg, 3.35 mmol) and H_2O (5 mL) were added, the mixture was extracted with ether, and the combined organic phases were washed with brine. Drying ($MgSO_4$) and evaporation gave 49 mg (99%) of a 90:10 mixture (by NMR) of (9*E*,11*E*)- and (9*Z*,11*E*)-**45** as a white solid. Flash chromatography gave product of 94% isomeric purity. (9*E*,11*E*)-**45**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dd, *J* = 15.2, 10.4 Hz, 1 H, C*H*=CHCH(OH)), 6.02 (ddt, *J* = 15.0, 10.5, 1.3 Hz, 1 H, CH_2CH=C*H*), 5.69 (dt, *J* = 15.0, 7.0 Hz, 1 H, CH_2CH=C*H*), 5.57 (dd, *J* = 15.2, 7.1 Hz, 1 H, CH=C*H*CH(OH)), 4.11 (app qd, *J* = 6.9, 0.8 Hz, 1 H, C*H*(OH)), 2.34 (t, *J* = 7.5 Hz, 2 H, C*H*$_2$COOH), 2.07 (app qd, *J* = 7.0, 1.3 Hz, 2 H, C*H*$_2$CH=CH), 1.65–1.25 (complex m, 19 H, $CH_2(CH_2)_5CH_2$, $(CH_2)_4CH_3$ and O*H*), 0.88 (t, *J* = 6.9 Hz, 3 H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.51 (COOH), 135.37, 133.57, 130.97 and 129.52 (*C*H=*C*H*C*H=*C*H), 72.95 (*C*H(OH)), 37.23, 33.95, 32.55, 31.76, 29.06, 29.00, 28.94, 28.88, 25.10, 24.62, and 22.59 ((*C*H$_2$)$_7$ and $(CH_2)_4CH_3$), 14.03 (CH_2CH_3); IR (CCl_4) 3618, 2931, 2858, 1712, 990 cm^{-1}. Anal. Calcd for $C_{18}H_{32}O_3$: C, 72.93; H, 10.88. Found: C, 72.5; H, 10.9 (9*Z*,11*E*)-**54**: ^{1}H NMR (400 MHz, $CDCl_3$; clearly visible peaks in spectrum of an isomeric mixture) δ 6.49 (dd app t, *J* = 15, 11, 1 Hz, 1 H, C*H*=CHCH(OH)), 5.44 (br dt, *J* = 11, 7.5 Hz, 1 H, CH_2CH=CH), 4.18 (app br q, *J* = 7 Hz, 1 H, C*H*OH), 2.19 (app br q, *J* = 7 Hz, 2 H, C*H*$_2$CH=CH).

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Supplementary Material Available: Spectroscopic data for minor isomers of the dienes and polyenes obtained in this work (50 pages). Ordering information is given on any current masthead page.

(58) For the use of molecular sieves in combination with chromium(VI) oxidants, see: Herscovici, J.; Egron, M.-J.; Antonakis, K. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1967–1973.