Bridging the Final Gap in Stereocontrolled Wittig Reactions: Methoxymethoxy-Armed Allylic Phosphorus Ylides Affording Conjugated Dienes with High *cis* Selectivity

Qian Wang, Mirella El Khoury, and Manfred Schlosser*[a]

Abstract: After treatment with an appropriate base (butyllithium or sodium amide), 2-alkenyltris(2-methoxymethoxyphenyl)phosphonium salts carrying an allyl, crotyl, or prenyl (3-methyl-2-butenyl) side chain condense with saturated or unsaturated aldehydes to give conjugated dienes with *Z*/*E* ratios ranging from 90:10 to >99:1 and averaging 96:4. Owing to steric congestion, yields are only moderate (on average 41%; extremes 10–79%). The nonvolatile tris(2-methoxymethoxyphenyl)phosphine oxide by-product can be readily isolated and reduced to recover the phosphane starting material, or it may be hydrolyzed to the water-soluble tris(2-hydroxyphenyl)phosphine oxide.

Keywords: alkenes · asymmetric synthesis · 1,3-dienes · phosphorus ylides · Wittig reactions

Introduction

This report concludes our long efforts to introduce stereoselectivity into the Wittig procedure. At the beginning of our systematic investigations, some 35 years ago, we were lucky enough to discover ways to control the outcome of the reaction between a phosphorus ylide having an alkyl side chain (a so-called *reactive ylide*) and an aldehyde, thus making either one of the two possible stereoisomers optionally accessible. The *cis* selectivity achieved in media free of lithium salts initially averaged *Z*/*E* ratios of only 95:5,[1–3] but was later improved to reach the 99:1 level in many cases.[4] The *trans*-selective olefination,[2, 3, 5] relying on betaine ylides as readily epimerizing intermediates, met the mark of $Z/E < 1{:}99$ from the outset.

Prior to our work, α-methoxycarbonyl- and α-ethoxycarbonyl-substituted phosphorus ylides had been studied and were found to react with aldehydes with moderate *trans* selectivity (e.g., $Z/E \approx 15{:}85$).[6, 7] As was found later, the *E* isomer is formed almost exclusively ($Z/E \leq 1{:}99$) when α-alkyl-branched, α-acyl-substituted, and α-formylated triphenylphosphonio ylides (e.g., 1-methoxycarbonylethylidenetriphenylphosphorane,[8] acetonylidenetriphenylphosphorane,[9] and formylmethylenetriphenylphosphorane[10, 11]) or tri*alkyl*-phosphonio ylides (e.g. methoxycarbonylmethylenetricyclohexylphosphorane[12]) are employed. Ylides carrying strongly electron-withdrawing heterofunctional substituents (in particular, acyl and alkoxycarbonyl groups) at the α-position of the side chain are called "stabilized" since they resist hydrolytic and oxidative decomposition under ordinary conditions. All of them favor more or less the formation of *E* olefins. The corresponding PO ylides ("Horner reagents"), however, can be structurally tuned to afford predominantly either *Z* or *E* isomers. For example, when consecutively treated with a base and an aldehyde, diethyl (or dimethyl) methoxycarbonylmethyl phosphonate[13, 14] and 1-(methoxycarbonyl)ethyl phosphonate[8, 15, 16] produce *Z*/*E* ratios averaging 5:95, but the corresponding di(2,2,2-trifluoroethyl)phosphonates give mainly the *Z* isomers (*Z*/*E* 87:13–98:2).[8, 17–23] Even diethyl and dimethyl α-ester phosphonates become *cis*-selective when they are allowed to react with α-alkoxyalkanals[21, 24–29] or α-(*N*-sulfonylamino)alkanals[18] in polar protic solvents such as methanol.[30] Diphenyl or diaryl ethoxycarbonylmethyl phosphonates or 1-(ethoxycarbonyl)ethyl phosphonate reveal an intrinsic tendency to afford mainly the *Z*-configured enesters (*Z*/*E* 78:22–99:1) when condensed with saturated, α,β-unsaturated, and aromatic aldehydes.[31, 32] Conversely, diisopropyl phosphonates carrying an α-ester side chain provide particularly elevated *E* selectivities.[33–36]

Unlike their reactive or stabilized congeners, *moderated ylides* are not a uniform class of compounds (see Table 1 below). They comprise a variety of structures such as α-halo-, α-alkoxy- or α-aryloxy-, α-alkylthio- or α-arylthio-, α-1-alkenyl- or α-1-alkynyl-, and α-aryl- or α-heteroaryl-substituted phosphorus ylides. It is quite difficult to achieve stereocontrol with such reagents, and progress has indeed

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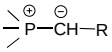
Table 1. Survey of the *Z*- and *E*-selective options offered by Wittig and Horner–Wittig reactions.



Type of ylide	α-substituent R	*cis*-Selective olefination	*trans*-Selective olefination
reactive	alkyl	salt-free protocol[1–3]	betaine–ylide epimerization[2,3,5]
moderated	Cl, Br, I, OCH_3	methoxymethoxy-armed ylides[47]	no need! (see text)
moderated	2-alkenyl	*methoxymethoxy-armed ylides: present work*	alkyl P^+ ylides;[38, 39] PO ylides[40, 41]
moderated	(hetero)aryl	methoxymethoxy-armed ylides[46]	no need! (see text)
stabilized	OC_2H_5	in methanol;[23–30] PO ylides[16–22, 31, 32]	alkyl P^+ ylides;[2, 6–8] PO ylides[13–16, 33–36]

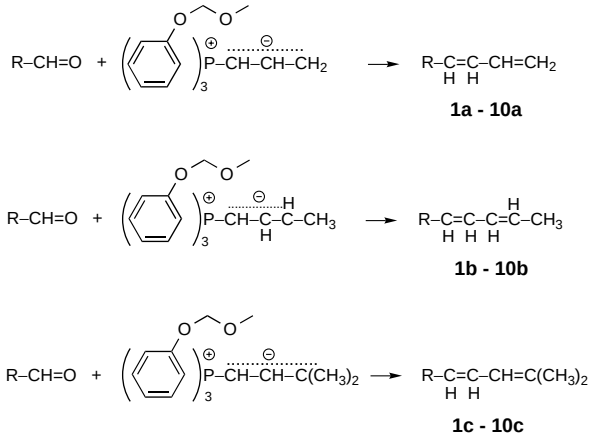
been slow in this area. As far as the *trans* selectivity is concerned, it was not urgent to act. Stereomixtures of stilbene-type alkenes can be easily and quantitatively converted into the pure *E* isomers by any radical-chain-triggering photochemical process. The treatment of β-substituted vinyl halides with the required amount of an alkoxide allows the selective destruction of the *Z* isomer (by antiperiplanar elimination) and isolation of the unconsumed *E* component.[37] Using allyl-, 2-methylallyl-, crotyl- and prenyl- (3-methyl-2-butenyl-), geranyl- and cinnamylphosphonium salts prepared from alkyldiphenylphosphanes[38] or tributylphosphane,[39] it was possible to make dienes having *Z*/*E* ratios in the range of 12:88–2:98 with respect to the newly formed double bond. Thus, the finding of a more convenient, more general and more selective access to (*E*)-dienes by Wittig–Horner reaction with α-deprotonated allylic diphenylphosphine oxides[40] and phosphonates[41] was certainly welcome but not indispensable. The situation was far more critical on the other side. The only case of notable *cis* selectivity experienced with a moderated ylide concerned the olefination of aldehydes with triphenylphosphonio-2-(sodiooxycarbonyl)-2-propenide[42] with reported *Z*/*E* ratios of $>95{:}5$.

As suggested by the "propeller model" mechanism[43] of the Wittig reaction, a systematic investigation had confirmed that *ortho* substituents at the "stationary" rings attached to the phosphorus atom can considerably enhance the *cis* selectivity of reactive ylides.[44, 45] Following this lead, we developed tris(2-methoxymethoxyphenyl)phosphonio(arylmethanides) as tailor-made Wittig reagents for the synthesis of *Z* stilbenes.[46] The *Z*/*E* ratios achieved with these "methoxymethoxy-armed" benzylic ylides ranged from 93:7 to 96:4 in typical cases.[47]

Abstract in German: *Behandelt man 2-Alkenyltris(2-methoxymethoxyphenyl)phosphonium-Salze (2-Alkenyl = Allyl, Crotyl oder Prenyl) nacheinander mit einer starken Base (Butyllithium oder Natriumamid) und einem gesättigten oder ungesättigten Aldehyd, so entstehen konjugierte Diene mit Z/E-Verhältnissen von 90:10 bis >99:1 (im Durchschnitt 96:4). Die sperrigen Aryl-Gruppen behindern die Addukt-Bildung zwischen Aldehyd und Ylid, weshalb sich nur mäßige Ausbeuten erzielen lassen (meist um 45 %; Extremwerte 10–79 %). Das als Nebenprodukt anfallende Tris(2-methoxymethoxyphenyl)phosphinoxid läßt sich leicht abtrennen und sodann zum Phosphin reduzieren oder zum wasserlöslichen Tris(2-hydroxyphenyl)phosphinoxid hydrolysieren.*

Results and Discussion

We have now turned to methoxymethoxy-armed *allylic* ylides to access conjugated *Z* dienes. Tris(2-methoxymethoxyphenyl)phosphonio-2-propenide [allylidenetris(2-methoxymethoxyphenyl)phosphorane] was found to react with saturated and α,β-unsaturated aliphatic and aromatic aldehydes to afford the corresponding products (**1a**, **2a**, **4a**, **8a**–**10a**; see Scheme 1 and Table 2) in poor yields (10–46 %, on the



Scheme 1. Reaction of methoxymethoxy-armed ylides with aldehydes to furnish the products **1**–**10**.

average 27 %) but with excellent *cis* selectivities (*Z*/*E* ratios around 98:2). Tris(2-methoxymethoxyphenyl)phosphonio-2(*E*)-butenide [crotylidenetris(2-methoxymethoxyphenyl)-phosphorane] and tris(2-methoxymethoxyphenyl)phosphonio-3-methyl-2-butenide [prenylidenetris(2-methoxymethoxyphenyl)phosphorane] gave the olefins **1b**–**4b**, **9b**–**10b**, and **1c**–**10c** in better yields (on average 49 % and 45 %, respectively) though with somewhat lower stereoselectivity (*Z*/*E* ratios of about 95:5; see Table 2).

Good stereoselectivity can only be achieved at very low temperatures. The reaction between benzaldehyde and the prenylphosphonium-derived ylide, a typical case, may exemplify this. The product **9c** is formed at +25, −25, −50, −75, and −100 °C in *Z*/*E* ratios of 59:41, 79:21, 84:16, 89:11, and 99:1, respectively.

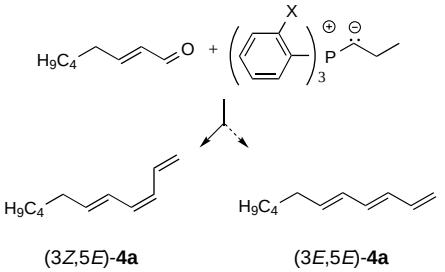
The standard Wittig reagents provide better yields throughout, but inferior stereoselectivities. The preparation of (3*Z*,5*E*)-1,3,5-undecatriene[49, 50] (**4a**, aldehyde $R'' = H_9C_4$), a stereoisomer of galbanum constituents[49] and of a brown

Table 2. Reaction between three methoxymethoxy-armed phosphorus ylides [R′ = 2-methoxymethoxyphenyl] of the allyl type and a variety of aldehydes at −100 °C: *Z*/*E* ratios at the newly formed double bond and, in parentheses, product yields.

R−CH=O	$R'_3\overset{+}{P}-\overset{-}{C}H-CH=CH_2$	$R'_3\overset{+}{P}-\overset{-}{C}H-CH=CH-CH_3$[a]	$R'_3\overset{+}{P}-\overset{-}{C}H-CH=C(CH_3)_2$
$H_{13}C_6-CH=O$	**1a** 98:2 (12%)	**1b** 93:7 (34%)	**1c** 93:7 (32%)
$(H_5C_2)_2CH-CH=O$	**2a** 99:1 (22%)	**2b** 94:6 (47%)	**2c** 93:7 (12%)
$(H_3C)_3C-CH=O$	**3a**[b] – (0%)	**3b**[c] 100:0 (81%)	**3c**[c] 96: 4 (47%)
$R''CH_2-CH=CH-CH=O$	**4a**[d] 98:2 (10%)	**4b**[e] 90:10 (25%)	**4c**[e, f] 96:4 (25%)
$H_{11}C_5-CH=CH-CH=CH-CH=O$	**5a**[g] –	**5b**[g] –	**5c** 92:8 (36%)
$H_9C_4-CH=C(C_3H_7)-CH=O$	**6a**[g] –	**6b**[g] –	**6c** 91:9 (22%)
$(H_3C)_2C=CH-CH=O$	**7a**[g] –	**7b**[g] –	**7c** 90:10 (47%)
$H_3CO-C_6H_4-CH=O$ (*p*)	**8a** 97:3 (34%)	**8b**[g] –	**8c** 97:3 (75%)
$C_6H_5-CH=O$	**9a** 97:3 (46%)	**9b** 98:2 (54%)	**9c** 99:1 (79%)
$NC-C_6H_4-CH=O$ (*p*)	**10a** 98:2 (35%)	**10b** 95:5 (50%)	**10c** 99:1 (71%)

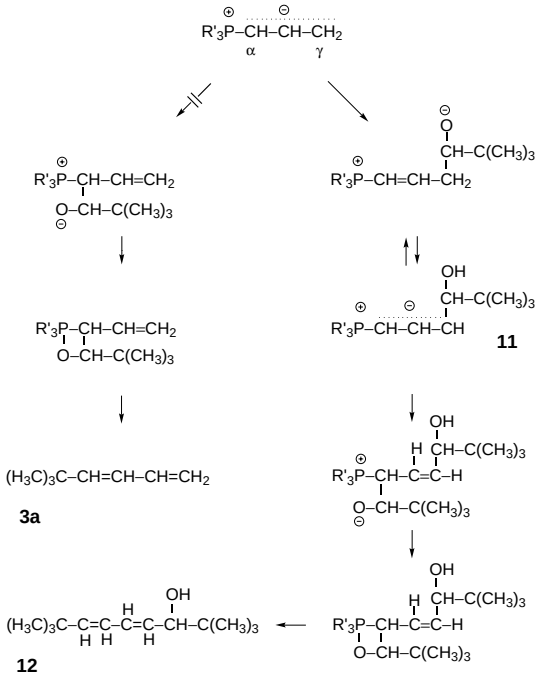
[a] $E \rightarrow Z$ Isomerization of the existing double bond in the crotyl chain occurred in the course of the reaction to the extent of 0–8%. Under standard reaction conditions, (*E*)-triphenylphosphonio-2-butenide (crotylidenetriphenylphosphorane)[48] gives rise to considerably more stereorandomization. [b] No 5,5-dimethyl-1,3-hexadiene (**3a**) was identified, but a derivative (**12**; see text) was isolated in 82% yield. [c] Reaction performed at −75 °C rather than −100 °C. [d] (*E*)-2-Octenal ($R'' = C_4H_9$) was used as the carbonyl component to afford (3*Z*,5*E*)-1,3,5-undecatriene (see also text). [e] (*E*)-2-Hexenal ($R'' = C_2H_5$) was used as the carbonyl component to afford (2*E*,4*Z*,6*E*)-2,4,6-decatriene or (2*E*,4*Z*,6*E*)-2-methyl-2,4,6-decatriene. [f] When (*E*)-2-nonenal ($R'' = C_5H_{11}$) was used as the carbonyl component, the (2*Z*,4*E*,6*E*) and (2*E*,4*E*,6*E*) isomers of 2-methyl-2,4,6-tredecatriene (28%) were obtained in a ratio of 94:6. [g] The preparation was not attempted.

algae gametoattractant,[50] is a typical illustration (Scheme 2). The triphenylphosphonio-2-propenide and (*E*)-2-octenal gave a 70:30 (3*Z*,5*E*) and (3*E*,5*E*) mixture in 37% yield, whereas the methoxymethoxy-armed ylide provided a 98:2 isomeric ratio, although in only a 10% yield. The steric congestion in



Scheme 2. Stereoselective preparation of 1,3,5-undecatriene (**4a**).

the vicinity of the ylide α-carbon atom is at the origin of the unsatisfactory degree of olefination. The methoxymethoxy-armed ylide and the aldehyde, whatever its individual structure, combine at −100 °C or even at −75 °C extremely slowly, as witnessed by the time (about 1 h) required for the complete decoloration of the reaction mixture. In the meanwhile, base-catalyzed self-transformations (mainly aldol condensation or Cannizzaro and Tishchenko redox processes) may consume a significant amount of the carbonyl component. Moreover, when the aldehyde does become attached to the ylide, this may occur at the unhindered γ-position rather than at the α-position.[51] Actually, this appears to be the favored reaction mode at least of the parent ylide. When tris(2-methoxymethoxyphenyl)phosphonio-2-propenide was treated at −100 °C with pivalaldehyde and the mixture was gradually warmed to 25 °C where it was kept for 2 h, no trace of the direct olefination product **3a** was detected, but 86% of compound **12** was isolated (Scheme 3). As shown by the incorporation of two *tert*-butyl groups, the formation of the dienol **12** must have been preceded by an initial γ-addition of pivalaldehyde. Then tautomerization of the resulting ene-phosphonio-alkoxide to a new allylic phosphorus ylide **11**



Scheme 3. Addition at the γ- rather than the α-position of the allyl group, illustrated by the favored formation of compound **12**.

occurred by intra- or intermolecular deprotonation. The new intermediate **11** eventually reacted with a second molecule of pivalaldehyde to afford the final product **12**.

The *ortho* substitution of the "stationary" phenyl parts of the ylide has once more proven an efficacious means to boost *cis* selectivity. On the basis of previous work,[44] other substituents such as fluoro or methyl can be expected to act in the same way. The methoxymethoxy group offers the advantage of facile preparation of the triarylphosphane starting material. Moreover, the tris(2-methoxymethoxyphenyl)phosphine oxide by-product can be readily extracted from the reaction mixture after acid hydrolysis to the trisphenol. Alternatively, it may be isolated and converted back to the phosphane by reduction with aluminum hydride.[52]

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Experimental Section

For standard operations and abbreviations see recent publications from this laboratory.[53] Proton nuclear magnetic resonance spectra were recorded at 400 MHz, the samples having been dissolved in deuterochloroform. The stationary phases employed for gas chromatography were silicon rubbers (SE-30, DB-1, DB-1701, and DB-210), polyethylene glycols (C-20M, DB-WAX, and DB-FFAP), and Apiezon-L hydrocarbon grease (AP-L).

1. Starting materials

2-Propenyltris(2-methoxymethoxyphenyl)phosphonium bromide: Allyl bromide (3-bromopropene; 9.3 mL, 12 g, 0.11 mol) and tris(2-methoxymethoxyphenyl)phosphane[45, 46] (44 g, 0.10 mol) were dissolved in toluene (0.80 L). After 1 h at 50 °C, the fine white powder formed was collected by filtration, washed with diethyl ether and dried; 52 g (92 %); m.p. 137–139 °C (decomp); ^{1}H NMR: $\delta = 7.72$ (tt, $J = 8.5$, 1.5 Hz, 3H), 7.46 (ddd, $J =$ 15.0, 7.9, 1.5 Hz, 3H), 7.38 (ddd, $J = 8.5$, 5.6, 0.7 Hz, 3H), 7.25 (tdd, $J = 7.9$, 2.6, 0.9 Hz, 3H), 5.62 (m, 2H), 5.3 (m, 1H), 5.22 (s, 6H), 4.36 (dd, $J = 16.5$, 6.2 Hz, 2H), 3.14 (s, 9H); $[C_{27}H_{32}O_6P]Br$ (563.42): calcd C 57.56, H 5.72; found C 57.74, H 5.74.

(*E*)-2-Butenyltris(2-methoxymethoxyphenyl)phosphonium bromide: Obtained in the same way from (*E*)-2-butenyl bromide (1-bromo-2-butene; 2.6 mL, 3.4 g, 25 mmol)[54] and tris(2-methoxymethoxyphenyl)phosphane[45, 46] (11 g, 25 mmol); 13.1 g (91 %); m.p. 181–183 °C (decomp); ^{1}H NMR: $\delta = 7.73$ (tt, $J = 7.7$, 1.6 Hz, 3H), 7.51 (ddd, $J = 14.8$, 7.7, 1.6 Hz, 3H), 7.37 (dd, $J = 8.1$, 5.9 Hz, 3H), 7.26 (td, $J = 7.7$, 2.7 Hz, 3H), 6.1 (m, 1H), 5.01 (s, 6H), 5.1 (m, 1H), 4.30 (dd, $J = 15.9$, 7.0 Hz, 2H), 3.14 (s, 9H), 1.54 (tm, $J = 5.6$ Hz, 3H); $[C_{28}H_{34}O_6P]Br$ (577.45): calcd C 58.24, H 5.93; found C 58.23, H 5.80.

3-Methyl-2-butenyltris(2-methoxymethoxyphenyl)phosphonium bromide: Obtained analogously from 3-methyl-2-butenyl bromide (prenyl bromide, 1-bromo-3-methyl-2-butene; 13 mL, 16 g, 0.11 mol) and tris(2-methoxymethoxyphenyl)phosphane;[45, 46] 52 g (87 %); m.p. 158–160 °C (decomp); ^{1}H NMR: $\delta = 7.75$ (tt, $J = 7.8$, 1.6 Hz, 3H), 7.4 (m, 6H), 7.30 (tdd, $J = 7.5$, 3.6, 1.4 Hz, 3H), 5.16 (s, 6H), 4.8 (m, 1H), 4.06 (dd, $J = 16.6$, 6.9 Hz, 2H), 3.15 (s, 9H), 1.75 (d, $J = 1.7$ Hz, 3H), 1.64 (dd, $J = 4.4$, 1.5 Hz, 3H); $[C_{29}H_{36}O_6P]Br$ (591.47): calcd C 58.89, H 6.13; found C 59.01, H 5.91.

2. *cis*-Selective Wittig reactions

(*Z*)-1,3-Decadiene (1a): At 25 °C, a suspension of sodium amide (1.0 g, 25 mmol), potassium *tert*-butoxide (0.3 g, 2.5 mmol), and 2-propenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.0 g, 25 mmol) in tetrahydrofuran (0.12 L) was stirred vigorously for 1 h. At −100 °C, heptanal (3.5 mL, 2.9 g, 25 mmol) was added. After 6 h of stirring at −100 °C, an aliquot of the reaction mixture was analyzed by gas chromatography (30 m, DB-1701, 60 °C; 30 m, DB-FFAP, 60 °C; decane as internal standard). Products **1a** was found to be present in 12 % yield and as a *Z*/*E* mixture in the ratio of 98:2. The reaction mixture was poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation the product was collected as a colorless liquid; b.p. 75–76 °C/10 Torr; n_D^{20} 1.4385 (ref. [55]: n_D^{20} 1.4551); ^{1}H NMR: $\delta = 6.31$ (dt, $J = 17.0$, 10.2 Hz, 1H), 6.00 (t, $J = 10.7$ Hz, 1H), 5.45 (dt, $J = 10.7$, 7.1 Hz, 1H), 5.07 (dm, $J = 17.0$ Hz, 1H), 4.95 (dm, $J = 10.2$ Hz, 1H), 2.07 (q, $J = 7.1$ Hz, 2H), 1.3 (m, 8H), 0.85 (t, $J =$ 7.0 Hz, 3H).

(*Z*)-5-Ethyl-1,3-heptadiene (2a): At −75 °C, a solution of butyllithium (25 mmol) in hexanes (17 mL) was added to a suspension of 2-propenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.0 g, 25 mmol) in tetrahydrofuran (0.12 L). After 30 min of vigorous stirring at 0 °C, a clear, deep red solution was obtained. At −100 °C, it was treated with 2-ethylbutyraldehyde (3.1 mL, 2.5 g, 25 mmol). After 6 h of stirring at −100 °C, gas chromatographic analysis (30 m, DB-1701, 40 °C; 30 m, DB-FFAP, 35 °C; nonane as internal standard) revealed the presence of 22 % of **2a**; *Z*/*E* = 99:1. The product was extracted as described above. Distillation afforded a colorless liquid; b.p. 30–31 °C/10 Torr; n_D^{20} 1.4510; ^{1}H NMR: $\delta =$ 6.62 (dtd, $J = 16.7$, 10.5, 1.1 Hz, 1H), 6.06 (tm, $J = 10.5$ Hz, 1H), 5.16 (ddt, $J = 16.7$, 2.1, 0.7 Hz, 1H), 5.12 (t, $J = 10.5$ Hz, 1H), 5.04 (d, $J = 10.5$ Hz, 1H), 2.3 (m, 1H), 1.4 (m, 2H), 1.2 (m, 2H), 0.84 (t, $J = 7.3$ Hz, 6H); C_9H_{16} (124.23): calcd C 87.02, H 12.98; found C 87.12, H 12.88.

(3*Z*,5*E*)-1,3,5-Undecatriene (4a): The reaction was carried out exactly as described in the preceding paragraph using (*E*)-2-octenal (3.2 g, 25 mmol) as the aldehyde component. According to gas chromatography (30 m, DB-1, 80 °C; 30 m, DB-WAX, 80 °C; dodecane as internal standard), product **4a** was formed in 10 % yield and the newly formed double bond with a *Z*/*E* ratio of 98:2. The reaction mixture was poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation a light yellow liquid was isolated; b.p. 68–70 °C/3 Torr (ref. [56]: b.p. 63 °C/ 2.2 Torr); n_D^{20} 1.5134 (ref. [56]: n_D^{20} 1.5122); ^{1}H NMR: $\delta = 6.80$ (dt, $J = 16.8$, 10.3 Hz, 1H), 6.49 (ddm, $J = 14.9$, 11.0 Hz, 1H), 5.97 (t, $J = 10.9$ Hz, 1H), 5.87 (t, $J = 11.0$ Hz, 1H), 5.72 (dt, $J = 14.9$, 7.2 Hz, 1H), 5.19 (d, $J = 16.8$ Hz, 1H), 5.09 (d, $J = 10.2$ Hz, 1H), 2.12 (q, $J = 7.2$ Hz, 2H), 1.4 (m, 2H), 1.3 (m, 4H), 0.88 (t, $J = 7.1$ Hz, 3H).

(*Z*)-1-(4-Methoxyphenyl)-1,3-butadiene (8a): At 25 °C, a suspension of sodium amide (1.0 g, 25 mmol), potassium *tert*-butoxide (0.3 g, 2.5 mmol), and 2-propenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.0 g, 25 mmol) in tetrahydrofuran (0.12 L) was stirred vigorously for 1 h. At −100 °C, anisaldehyde (3.0 mL, 3.4 g, 25 mmol) was added. After 6 h of stirring at −100 °C, 34 % of **8a** with a *Z*/*E* composition of 97:3 was detected by gas chromatography (3 m, 5 % C-20M, 150 °C; 3 m, 5 % SE-30, 150 °C; tetradecane as internal standard). The reaction mixture was absorbed on silica gel (25 mL) and evaporated to dryness. The powder was poured on top of a column filled with more silica gel (100 mL) and eluted with hexanes. The product was crystallized as colorless needles; m.p. 32–35 °C (ref. [57]: m.p. 46 °C); b.p. 68–70 °C/2 Torr (ref. [57]: b.p. 124 °C/ 6 Torr); n_D^{20} 1.5963; ^{1}H NMR: $\delta = 7.26$ (symm. m, 2H), 6.9 (m, 3H), 6.39 (d, $J = 11.5$ Hz, 1H), 6.18 (t, $J = 11.5$ Hz, 1H), 5.34 (d, $J = 17.0$ Hz, 1H), 5.19 (d, $J = 10.5$ Hz, 1H), 3.81 (s, 3H).

(*Z*)-1-Phenyl-1,3-butadiene (9a): In the same way as described in the preceding paragraph, a reaction with benzaldehyde (2.5 mL, 2.7 g, 25 mmol) was performed to give 46 % of **9a** in a *Z*/*E* ratio of 97:3 (by gas chromatography: 3 m, 5 % C-20M, 120 °C; 3 m, 5 % SE-30, 140 °C; dodecane as internal standard). Extraction and distillation afforded colorless liquid; b.p. 92–94 °C/15 Torr (ref. [58]: b.p. 71 °C/11 Torr); n_D^{20} 1.6088 (ref. [58]: n_D^{25} 1.5822); ^{1}H NMR: $\delta = 7.3$ (m, 5H), 6.88 (dtd, $J = 16.9$, 10.2, 1.1 Hz, 1H), 6.44 (d, $J = 11.6$ Hz, 1H), 6.25 (d, $J = 11.6$ Hz, 1H), 5.36 (d, $J = 16.9$ Hz, 1H), 5.21 (d, $J = 10.2$ Hz, 1H).

(*Z*)-1-(4-Cyanophenyl)-1,3-butadiene (10a): Analogously, 4-cyanobenzaldehyde (3.3 g, 25 mmol) gave 46 % of **10a** in a *Z*/*E* ratio of 97:3 (by gas chromatography: 3 m, 5 % C-20M, 150 °C; 3 m, 5 % SE-30, 150 °C; tetradecane as internal standard). After purification by column chromatography (eluent: hexanes), the product was obtained as colorless platelets; m.p. 67–69 °C (ref. [59] m.p. 51.5–52.0 °C); ^{1}H NMR: $\delta = 7.6$ (m, 2H), 7.4 (m, 2H), 6.79 (dt, $J = 16.9$, 10.2 Hz, 1H), 6.44 (d, $J = 11.2$ Hz, 1H), 6.37 (dd, $J = 11.2$, 10.2 Hz, 1H), 5.48 (d, $J = 16.9$ Hz, 1H), 5.34 (d, $J = 10.2$ Hz, 1H).

(2*E*,4*Z*)-2,4-Undecadiene (1b): At −75 °C, a solution of butyllithium (25 mmol) in hexanes (17 mL) was added to a suspension of (*E*)-2-butenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.4 g, 25 mmol) in tetrahydrofuran (0.12 L). After 30 min of vigorous stirring at 0 °C, a clear, deep red solution was obtained. At −100 °C, heptanal (3.5 mL, 2.9 g, 25 mmol) was added. After 6 h of stirring at −100 °C, an aliquot of the reaction mixture was analyzed by gas chromatography (30 m, DB-1701, 80 °C; 30 m, DB-FFAP, 65 °C; undecane as internal standard), which indicated the formation of product **1b** in 34 % yield and in a 93:7 *Z*/*E* ratio (at the new double bond). The reaction mixture was poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation a colorless liquid was collected; b.p. 81–82 °C/10 Torr; n_D^{20} 1.4626; ^{1}H NMR:[60] $\delta = 6.33$ (ddm, $J = 15.0$, 10.8 Hz, 1H), 5.95 (t, $J =$ 10.8 Hz, 1H), 5.67 (symm. m, 1H), 5.30 (dt, $J = 10.8$, 7.5 Hz, 1H), 2.18 (q, $J = 7.5$ Hz, 2H), 1.79 (d, $J = 7.1$ Hz, 3H), 1.3 (m, 8H), 0.88 (t, $J = 6.9$ Hz, 3H).

(2*E*,4*Z*)-6-Ethyl-2,4-octadiene (2b): Analogously, 2-ethylbutyraldehyde (3.1 mL, 2.5 g, 25 mmol) was converted into 47 % of **2b** having a (4*Z*/4*E*) ratio of 94:6 (by gas chromatography: 30 m, DB-1701, 30 °C; 30 m, DB-WAX, 25 °C; decane as internal standard). Extraction and distillation afforded a colorless liquid; b.p. 95–96 °C/80 Torr; n_D^{20} 1.4587; ^{1}H NMR: $\delta =$ 6.30 (ddm, $J = 14.9$, 11.1 Hz, 1H), 6.02 (dd, $J = 11.1$, 10.6 Hz, 1H), 5.65 (dq, $J = 14.9$, 6.8 Hz, 1H), 4.97 (dd, $J = 10.6$, 9.6 Hz, 1H), 2.28 (dquint, $J = 9.6$, 4.7 Hz, 1H), 1.73 (dd, $J = 6.8$, 1.1 Hz, 3H), 1.4 (m, 2H), 1.2 (m, 2H), 0.84 (t,

$J = 7.5$ Hz, 6H); $C_{10}H_{18}$ (138.25): calcd C 86.88, H 13.12; found C 87.18, H 12.74.

(2*E*,4*Z*)-6,6-Dimethyl-2,4-heptadiene (3b): In the same way, pivalaldehyde (2.8 mL, 2.2 g, 25 mmol) gave 81% of **3b** having a (4*Z*/4*E*) ratio of $\gg$ 99:1 (by gas chromatography: 30 m, DB-1701, 30 °C; 30 m, DB-WAX, 25 °C; nonane as internal standard). Upon extraction and distillation, a colorless liquid[61] was isolated; b.p. 78–81 °C/95 Torr; n_D^{20} 1.4578; ^{1}H NMR: $\delta = 6.55$ (dd, $J = 14.7$, 11.9 Hz, 1H), 5.81 (t, $J = 11.9$ Hz, 1H), 5.62 (dq, $J = 14.7$, 6.6 Hz, 1H), 5.26 (d, $J = 11.9$ Hz, 1H), 1.79 (dd, $J = 6.6$, 1.5 Hz, 3H), 1.17 (s, 9H).

(2*E*,4*Z*,6*E*)-2,4,6-Decatriene (4b): With (*E*)-2-hexenal (2.9 mL, 2.5 g, 25 mmol) as the aldehyde component, 25% of **4b** having a (4*Z*/4*E*) ratio of 90:10 was obtained (according to gas chromatography: 30 m, DB-1701, 50 °C; 50 m, Megasolve, 70 °C; decane as internal standard). Extraction and distillation afforded a light yellow liquid; b.p. 92–96 °C/30 Torr (ref. [62] b.p. 56 °C/4 Torr); n_D^{20} 1.5196; ^{1}H NMR: $\delta = 6.5$ (m, 2H), 5.8 (m, 2H), 5.7 (m, 2H), 2.1 (m, 2H), 1.80 (dd, $J = 7.0$, 1.5 Hz, 2H), 1.43 (symm. m, 1H), 0.92 (t, $J = 7.4$ Hz, 3H).

(1*Z*,3*E*)-1-Phenyl-1,3-pentadiene (9b): At 25 °C, a suspension of sodium amide (1.0 g, 25 mmol), potassium *tert*-butoxide (0.3 g, 2.5 mmol) and (*E*)-2-butenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.4 g, 25 mmol) in tetrahydrofuran (0.12 L) was stirred vigorously for 1 h. At −100 °C, benzaldehyde (2.5 mL, 2.7 g, 25 mmol) was added. After 6 h of stirring at −100 °C, 54% of **9b** having a *Z*/*E* ratio of 98:2 had been formed (as determined by gas chromatography: 3 m, 6% C-20M, 130 °C; 50 m, Megasolve, 110 °C; tridecane as internal standard). The reaction mixture was poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried and concentrated. After extraction and distillation a colorless liquid was collected; b.p. 104–106 °C/10 Torr (ref. [2]: b.p. 106 °C/11 Torr); n_D^{20} 1.5876 (ref. [2]: n_D^{20} 1.6103); ^{1}H NMR: $\delta = 7.3$ (m, 5H), 6.61 (dd, $J = 15.0$, 11.2 Hz, 1H), 6.29 (d, $J = 11.2$ Hz, 1H), 6.20 (t, $J = 11.2$ Hz, 1H), 5.88 (dt, $J = 15.0$, 6.9 Hz, 1H), 1.80 (dd, $J = 6.9$, 1.8 Hz, 3H).

(1*Z*,3*E*)-1-(4-Cyanophenyl)-1,3-pentadiene (10b): At −75 °C, a solution of butyllithium (25 mmol) in hexanes (17 mL) was added to a suspension of 2-butenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.4 g, 25 mmol) in tetrahydrofuran (0.12 L) while this was vigorously stirred. After 30 min at 0 °C, a clear, deep red solution was obtained. At −100 °C, 4-cyanobenzaldehyde (3.3 g, 25 mmol) was added. After 6 h of stirring at −100 °C, the reaction mixture contained 50% of **10b** having a *Z*/*E* composition of 95:5 (gas chromatographic analysis: 30 m, DB-1701, 150 °C; 30 m, DB-FFAP, 150 °C; tridecane as internal standard). After extraction (see above) and upon distillation, a light yellow liquid was isolated; b.p. 108–111 °C/0.5 Torr; m.p. 25–28 °C; ^{1}H NMR: $\delta = 7.60$ (d, $J = 8.2$ Hz, 1.9H), 7.55 (d, $J = 8.5$ Hz, 0.1H), 7.42 (d, $J = 8.5$ Hz, 0.1H), 7.39 (d, $J = 8.2$ Hz, 1.9H), 6.83 (dd, $J = 15.8$, 10.4 Hz, 0.05H), 6.53 (ddq, $J = 15.0$, 10.9, 1.6 Hz, 0.95H), 6.40 (d, $J = 15.6$ Hz, 0.05H), 6.31 (t, $J = 11.1$ Hz, 0.95H), 6.24 (d, $J = 11.2$ Hz, 0.95H), 6.22 (dd, $J = 15.6$, 10.4 Hz, 0.05H), 6.0 (m, 1H), 1.86 (d, $J = 6.8$ Hz, 0.15H), 1.82 (dd, $J = 6.8$, 1.3 Hz, 2.85H); $C_{12}H_{11}N$ (169.23): calcd C 85.17, H 6.55; found C 84.54, H 6.39.

(4*Z*)-2-Methyl-2,4-undecadiene (1c): At 25 °C, a suspension of sodium amide (1.0 g, 25 mmol), potassium *tert*-butoxide (0.3 g, 2.5 mmol) and 3-methyl-2-butenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.8 g, 25 mmol) in tetrahydrofuran (0.12 L) was stirred vigorously for 1 h. At −100 °C, heptanal (3.5 mL, 2.9 g, 25 mmol) was added. After 6 h of stirring at −100 °C, 32% of **1c** with a *Z*/*E* ratio of 93:7 had formed (determined by gas chromatography: 30 m, DB-1701, 110 °C; 30 m, DB-FFAP, 80 °C; undecane as internal standard). Extraction and distillation afforded a colorless liquid; b.p. 125–127 °C/25 Torr; m.p. −69 to −67 °C; n_D^{20} 1.4722; ^{1}H NMR: $\delta = 6.21$ (ddt, $J = 15.1$, 10.6, 1.4 Hz, 0.1H), 6.16 (t, $J = 10.6$ Hz, 0.9H), 6.07 (d, $J = 10.6$ Hz, 0.9H), 5.79 (d, $J = 10.6$ Hz, 0.1H), 5.56 (dt, $J = 15.1$, 7.2 Hz, 0.1H), 5.33 (dt, $J = 10.6$, 7.7 Hz, 0.9H), 2.16 (q, $J = 7.7$ Hz, 1.8H), 2.08 (q, $J = 7.2$ Hz, 0.2H), 1.81 (s, 2.7H), 1.75 (s, 0.5H), 1.74 (s, 2.7H), 1.3 (m, 8H), 0.9 (m, 3H); $C_{12}H_{22}$ (166.31): calcd C 86.67, H 13.33; found C 86.56, H 13.23.

(4*Z*)-6-Ethyl-2-methyl-2,4-octadiene (2c): As described in the preceding paragraph, a reaction was carried out with 2-ethylbutyraldehyde (3.1 mL, 2.5 g, 25 mmol). According to gas chromatography (30 m, DB-1701, 120 °C; 30 m, DB-FFAP, 80 °C; undecane as internal standard), 12% of **2c** was obtained in a (4*Z*/4*E*) ratio of 93:7. Extraction and distillation provided a colorless liquid; b.p. 67–69 °C/10 Torr; n_D^{20} 1.4714; ^{1}H NMR: $\delta = 6.24$ (t, $J = 10.8$ Hz, 0.9H), 6.17 (dd, $J = 15.2$, 10.6 Hz, 0.1H), 6.06 (d, $J = 10.8$ Hz, 0.9H), 5.81 (d, $J = 10.6$ Hz, 0.1H), 5.29 (dd, $J = 15.2$, 8.9 Hz, 0.1H), 5.02 (t, $J = 10.8$ Hz, 0.9H), 2.3 (m, 1H), 1.80 (s, 2.7H), 1.76 (s, 2.7H), 1.75 (s, 0.5H), 1.5 (m, 2H), 1.2 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 6H); $C_{11}H_{20}$ (152.28): calcd C 86.76, H 13.24; found C 86.82, H 13.08.

(4*Z*)-2,6,6-Trimethyl-2,4-heptadiene (3c): A solution of butyllithium (25 mmol) in hexanes (17 mL) was added to a suspension of 3-methyl-2-butenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.8 g, 25 mmol) in tetrahydrofuran (0.10 L) at −75 °C. After 30 min of vigorous stirring at 0 °C, a clear, deep red solution was obtained. At −75 °C, pivalaldehyde (2.8 mL, 2.2 g, 25 mmol) was added. After 6 h of stirring at −75 °C, 47% of **3c** having a (4*Z*/4*E*) ratio 96:4 was detected by gas chromatography (30 m, DB-1701, 40 °C; 30 m, DB-FFAP, 40 °C; decane as internal standard). After extraction and distillation a colorless liquid was collected; b.p. 75–77 °C/40 Torr; n_D^{20} 1.4684; ^{1}H NMR:[39] $\delta = 6.29$ (d, $J = 12.1$ Hz, 1H), 5.99 (t, $J = 12.1$ Hz, 1H), 5.29 (d, $J = 12.1$ Hz, 1H), 1.80 (s, 3H), 1.72 (s, 3H), 1.16 (s, 9H).

(4*Z*,6*E*)-2-Methyl-2,4,6-decatriene (4c): At 25 °C, a suspension of sodium amide (1.0 g, 25 mmol), potassium *tert*-butoxide (0.3 g, 2.5 mmol) and 3-methyl-2-butenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.8 g, 25 mmol) in tetrahydrofuran (0.12 L) was stirred vigorously for 1 h. At −100 °C, (*E*)-2-hexenal (2.9 mL, 2.5 g, 25 mmol) was added. After 6 h of stirring at −100 °C, the reaction mixture was found by gas chromatographic analysis (55 m, AP-L, 135 °C) to contain 25% of **4c** in a (4*Z*/4*E*) ratio of 96:4. After chromatographic purification (see above; preparation of **8a**), a light yellow liquid[63] was isolated; b.p. 67–69 °C/10 Torr; n_D^{20} 1.4714; ^{1}H NMR: $\delta = 6.30$ (dm, $J = 12.0$ Hz, 1H), 6.1 (m, 1H), 6.05 (d, $J = 11.5$ Hz, 1H), 5.8 (m, 1H), 5.69 (hept, $J = 7.3$ Hz, 1H), 2.11 (quint, $J = 8.5$ Hz, 2H), 1.85 (s, 3H), 1.78 (s, 3H), 1.4 (m, 2H), 0.99 (td, $J = 7.4$, 3.0 Hz, 3H).

When (*E*)-2-nonenal (4.1 mL, 3.5 g, 25 mmol) was used as the carbonyl component, the (4*Z*,6*E*) and (4*E*,6*E*) isomers of **2-methyl-2,4,6-tridecatriene**[64] (28%) were analogously obtained in a 94:6 ratio and a total yield of 28% (by gas chromatography: 45 m, OV-17, 165 °C; 30 m, DB-1, 140 °C); ^{1}H NMR: $\delta = 6.3$ (m, 1H), 6.1 (m, 2H), 5.80 (d, $J = 10.6$ Hz, 1H), 5.69 (oct, $J = 6.6$ Hz, 1H), 2.11 (quint, $J = 6.6$ Hz, 2H), 1.83 (s, 3H), 1.76 (s, 3H), 1.3 (m, 8H), 0.9 (3H, m).

(4*Z*,6*E*,8*E*)-2-Methyl-2,4,6,8-tetradecatetraene (5c): In the same way, (2*E*,4*E*)-2,4-decadienal (4.4 mL, 3.8 g, 25 mmol) afforded 36% of **5c** having a (4*Z*/4*E*) ratio of 92:8 as determined by gas chromatography (45 m, OV-17, 160 °C; 30 m, DB-1, 160 °C). Upon column chromatography (see above), a light yellow liquid was obtained; m.p. −42 to −38 °C; b.p. 80–85 °C/0.6 Torr; n_D^{20} 1.5877; ^{1}H NMR: $\delta = 6.2$ (m, 5H), 5.8 (m, 1H), 5.7 (hex, $J = 7.1$ Hz, 1H), 2.11 (q, $J = 7.6$ Hz, 2H), 1.83 (s, 3H), 1.77 (s, 3H), 1.3 (m, 6H), 0.9 (m, 3H); $C_{15}H_{24}$ (204.35): calcd C 88.16, H 11.84; found C 88.14, H 11.87.

(4*Z*,6*E*)-2-Methyl-6-propyl-2,4,6-undecatriene (6c): Analogously, (*E*)-2-propyl-2-heptenal (4.5 mL, 3.9 g, 25 mmol) gave 22% of **6c** having a (4*Z*/4*E*) ratio of 91:9 as determined by gas chromatography (2 m, 7% AP-L, 220 °C; 3 m, 10% C-20M, 170 °C). The products were purified by column chromatography (see above; preparation of **8a**) to give a colorless liquid; m.p. −68 to −64 °C; b.p. 86–88 °C/0.6 Torr; n_D^{20} 1.5420; ^{1}H NMR: $\delta = 6.33$ (dd, $J = 15.5$, 11.0 Hz, 0.1H), 6.25 (d, $J = 10.4$ Hz, 1.8H), 6.15 (d, $J = 11.4$ Hz, 0.9H), 6.00 (d, $J = 15.5$ Hz, 0.1H), 5.85 (d, $J = 10.9$ Hz, 0.1H), 5.67 (d, $J = 11.1$ Hz, 0.9H), 5.42 (t, $J = 7.5$ Hz, 0.1H), 2.2 (m, 2H), 1.8 (m, 6H), 1.4 (m, 6H), 0.9 (m, 6H); $C_{15}H_{26}$ (206.37): calcd C 87.30, H 12.70; found C 87.05, H 12.69.

(4*Z*)-2,7-Dimethyl-2,4,6-octatriene (7c): Analogously, 3-methylcrotonaldehyde (2.4 mL, 2.1 g, 25 mmol) was converted into 47% of **7c** with a (4*Z*/4*E*) ratio of 90:10 as found by gas chromatographic analysis (30 m, DB-WAX, 50 °C; 30 m, DB-FFAP, 60 °C). Extraction and distillation afforded product as light yellow platelets; m.p. 36–37 °C; b.p. 60–65 °C/10 Torr (ref. [63]: b.p. 70–75 °C/16 Torr); n_D^{20} 1.4768 (ref. [63]: n_D^{20} 1.475); ^{1}H NMR: $\delta = 6.29$ (symm. m, 2H), 5.88 (symm. m, 2H), 1.80 (6H, s), 1.76 (6H, s).

(*Z*)-4-Methyl-1-(4-methoxyphenyl)-1,3-pentadiene (8c): An analogous reaction was performed with anisaldehyde (3.0 mL, 3.4 g, 25 mmol). According to gas chromatography (2 m, 10% SE-30, 205 °C; 3 m, 10% C-20M, 245 °C), 75% of **8c** with a *Z*/*E* ratio of 97:3 was formed. Column chromatographic purification (see above; preparation of **8a**) afforded a

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colorless liquid; m.p. −26 to −22 °C; b.p. 80–83 °C/0.3 Torr; n_D^{20} 1.6003; ^{1}H NMR: δ = 7.31 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 6.5 Hz, 2H), 6.3 (m, 3H), 3.83 (s, 3H), 1.84 (s, 6H); $C_{13}H_{16}O$ (188.27): calcd C 82.94, H 8.57; found C 82.93, H 8.63.

(*Z*)-4-Methyl-1-phenyl-1,3-pentadiene (9c): Analogously, benzaldehyde (2.5 mL, 2.7 g, 25 mmol) gave 79% of **9c** having a *Z*/*E* ratio of 99:1 as determined by gas chromatography (3 m, 5% AP-L, 150 °C; 3 m, 5% C-20M, 130 °C). After extraction and distillation, a colorless liquid was collected; b.p. 45–48 °C/2 Torr (ref. [65]: b.p. 125–130 °C/11 Torr); n_D^{20} 1.5963 (ref. [65]: n_D^{20} 1.5985); ^{1}H NMR: δ = 7.3 (m, 4H), 7.2 (m, 1H), 6.42 (t, J = 10.9 Hz, 1H), 6.4 (m, 1H), 6.30 (d, J = 10.9 Hz, 1H), 1.85 (s, 3H), 1.83 (s, 3H).

(*Z*)-1-(4-Cyanophenyl)-4-methyl-1,3-pentadiene (10c): In the same way, 4-cyanobenzaldehyde (3.3 g, 25 mmol) afforded 71% of **10c** with a *Z*/*E* ratio of 99:1 (by gas chromatographic analysis: 2 m, 10% SE-30, 200 °C; 3 m, 10% C-20M, 245 °C). After chromatographic purification (see above, preparation of **8a**), the product was crystallized as colorless needles; m.p. 55–57 °C (decomp); ^{1}H NMR: δ = 7.61 (dm, J = 8.5 Hz, 2H), 7.41 (dm, J = 8.1 Hz, 2H), 6.56 (t, J = 11.5 Hz, 1H), 6.28 (d, J = 11.5 Hz, 2H), 1.89 (s, 6H); $C_{13}H_{13}N$ (183.25): calcd C 85.21, H 7.15; found C 85.18, H 6.97.

(4*E*,6*Z*)-2,2,8,8-Tetramethyl-4,6-nonadien-3-ol (12): A solution of butyllithium (25 mmol) in hexanes (17 mL) was added to a suspension of 2-propenyltris(2-methoxymethoxyphenyl)phosphonium bromide (14.0 g, 25 mmol) in tetrahydrofuran (0.10 L) at −75 °C while this was stirred vigorously. After 30 min at 0 °C, a clear, deep red solution was obtained. At −75 °C, pivalaldehyde (2.8 mL, 2.2 g, 25 mmol) was added. After 6 h of stirring at −75 °C, the reaction mixture was poured into water (50 mL) and extracted with ether (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation, no trace of 5,5-dimethyl-1,3-hexadiene was obtained (its boiling point was supposed to be 106–107 °C/760 Torr[66]). Instead, the title product was collected as a colorless liquid which, according to ^{1}H and ^{13}C NMR spectroscopy as well as gas column chromatography on three columns of different polarity (30 m, DB-1, 100 °C; 30 m, DB-WAX, 100 °C; 3 m, 5% AP-L, 80 °C), contained exclusively (4*E*,6*Z*) isomer (>99%); b.p. 83–84 °C/0.5 Torr; m.p. 25–27 °C; n_D^{20} 1.4806; 4.0 g (82%); ^{1}H NMR: δ = 6.69 (dd, J = 15.0, 11.6 Hz, 1H), 5.82 (dd, J = 12.0, 11.6 Hz, 1H), 5.62 (dd, J = 15.0, 7.5 Hz, 1H), 5.38 (d, J = 12.0 Hz, 1H), 3.79 (d, J = 7.5 Hz, 1H), 1.7 (br, 1H), 1.16 (s, 9H), 0.91 (s, 9H); ^{13}C NMR: δ = 142.0, 133.6, 128.4, 126.3, 80.7, 35.1, 33.8, 31.4 (3C), 25.7 (3C); $C_{13}H_{24}O$ (196.33): calcd C 79.53, H 12.32; found C 79.17, H 12.15.

3. Recovery of the phosphorus component

Tris(2-methoxymethoxyphenyl)phosphine oxide: The residue obtained after the distillation of (*Z*)-4-methyl-1-phenyl-1,3-pentadiene (**9c**; see Section 2) was dissolved in ethyl acetate (250 mL) and filtered through a short column of neutral alumina (40 mL). Evaporation of the solvent and recrystallization from diethyl ether/pentanes (1:1) afforded colorless granular crystals; m.p. 128–129 °C; 9.3 g (81%); ^{1}H NMR: δ = 7.62 (ddd, J = 14.7, 7.6, 1.6 Hz, 3H), 7.43 (t, J = 8.0 Hz, 3H), 7.13 (dd, J = 8.3, 5.3 Hz, 3H), 7.01 (tdd, J = 7.3, 2.2, 0.7 Hz, 3H), 4.96 (s, 6H), 3.02 (s, 9H); ^{13}C NMR: δ = 159.0 (s, 3C), 134.7 (d, J = 9.6 Hz, 3C), 133.2 (s, 3C), 121.5 (d, J = 110 Hz, 3C), 121.2 (d, J = 12.9 Hz, 3C), 114.1 (d, J = 6.4 Hz, 3C), 93.8 (s, 3C), 55.7 (s, 3C); ^{31}P NMR: δ = 25.9; $C_{24}H_{27}O_7P$ (458.44): calcd C 62.88, H 5.94; found C 62.90, H 5.87.

Tris(2-hydroxyphenyl)phosphine oxide: Hydrochloric acid (6M, 25 mL) was added to a solution of tris(2-methoxymethoxyphenyl)phosphine oxide (11.5 g, 25 mmol) in tetrahydrofuran (100 mL). After 10 min of reflux, the mixture was cooled to 25 °C and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (4 × 20 mL); the combined organic layers were dried with anhydrous sodium sulfate. Removal of the solvents and sublimation gave the product as colorless granular crystals; m.p. 206–208 °C (ref. [67]: m.p. 214.5–216 °C); 6.6 g (81%); ^{1}H NMR: δ = 9.4 (br, 3H), 7.46 (dd, J = 8.2, 7.1 Hz, 3H), 7.0 (m, 6H), 6.90 (tdd, J = 7.2, 3.0, 1.0 Hz, 3H); ^{13}C NMR: δ = 162.2 (s, 3C), 135.5 (s, 3C), 131.8 (d, J = 11.2 Hz, 3C), 119.9 (d, J = 12.9 Hz, 3C), 118.9 (d, J = 6.4 Hz, 3C), 111.6 (d, J = 107 Hz, 3C); ^{31}P NMR: δ = 52.3; $C_{18}H_{15}O_4P$ (326.29): calcd C 66.26, H 4.63; found C 65.92, H 4.54.

Tris(2-methoxymethoxyphenyl)phosphane: A freshly prepared solution of aluminum hydride[68] (25 mmol) in tetrahydrofuran (50 mL) was added to a solution of tris(2-methoxymethoxyphenyl)phosphine oxide (11.5 g, 25 mmol) in tetrahydrofuran (50 mL). The mixture was refluxed for 30 min, before cold, anhydrous methanol (1 mL) was added. The mixture was filtered through Celite, which was then washed with hot tetrahydrofuran (3 × 20 mL). The filtrate was concentrated. After recrystallization from diethyl ether, the product was obtained as colorless platelets; m.p. 129–130 °C (ref. [45]: m.p. 128–129 °C); 10.5 g (95%); ^{1}H NMR: δ = 7.30 (td, J = 7.5, 1.8 Hz, 3H), 7.11 (ddd, J = 7.5, 4.5, 1.0 Hz, 3H), 6.90 (t, J = 7.5 Hz, 3H), 6.79 (ddd, J = 7.5, 4.5, 1.8 Hz, 3H), 5.11 (s, 6H), 3.23 (s, 9H).

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