Rhodium(I)-Catalyzed Cycloisomerization of 1,3-Dienes with Alkenes in a Tether

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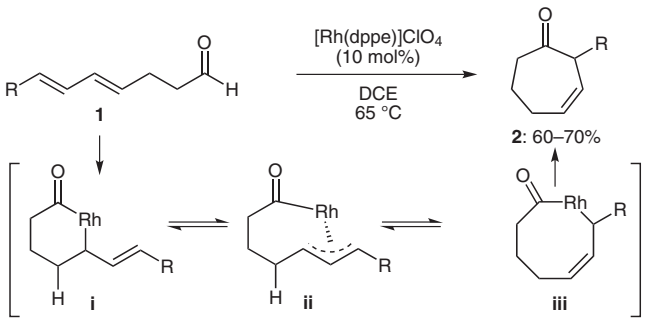
Abstract: A rhodium(I)-catalyzed cycloisomerization of 1,3-dienes with alkenes in a tether proceeded smoothly, giving cyclopentene or cyclohexene derivatives in good yields. The existence of a hetero atom between the 1,3-diene moiety and the olefin in the tether affected the reaction course. In the case of the substrate having no hetero atom between the 1,3-diene moiety and olefin in the tether, cycloisomerization reaction proceeded, giving the corresponding cyclic product. On the other hand, in the case of the substrate having a hetero atom between the 1,3-diene moiety and olefin in the tether, the reaction course was completely changed to give a [4+2] cycloaddition product.

Key words: cyclizations, dienes, alkenes, rhodium, transition metals

The development of efficient, clean, and fast methods to synthesize polycyclic complex molecules from simple starting materials is one of the most important challenges in modern synthetic organic chemistry. In this context, transition-metal-catalyzed reactions offer many attractive possibilities for constructing various cyclic structures not easily made by conventional methods.[1] We have recently reported a rhodium(I)-catalyzed intramolecular hydroacylation of 4,6-dienals by which various cycloheptenones were obtained in good yields (Scheme 1).[2]

During our ongoing investigation of this hydroacylation, it was found that the reaction of 4,6-dienal **3a**, having an olefin in the tether, gave cyclopentene **4a** in 77% yield via cycloisomerization of the 1,3-diene moiety and the tethered olefin (Scheme 2).



Scheme 1

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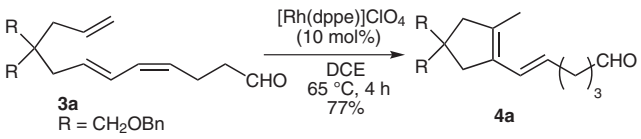
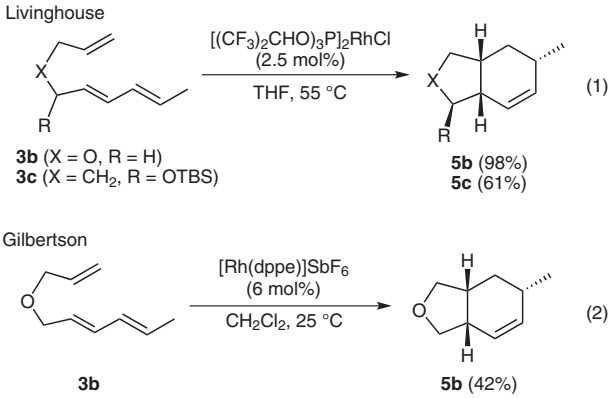


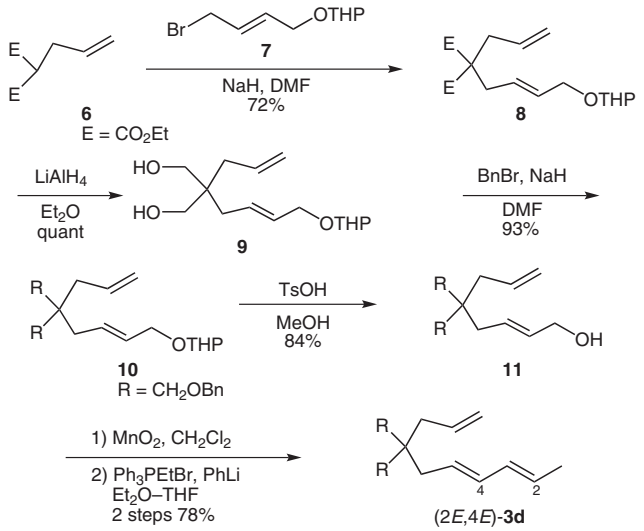
Scheme 2

Various transition-metal-catalyzed cycloisomerizations accompanying a C–C bond formation between multiple bonds have been reported in the literature.[3] However, for cycloisomerization between 1,3-diene and alkene, only an iron-catalyzed cycloisomerization has been reported by Takacs, in which 1,5-diene products were formed.[4] Thus, there has been no report on cycloisomerization of 1,3-dienes with alkenes giving 1,3-diene products. For rhodium(I)-catalyzed reactions of the substrate having a 1,3-diene moiety and a tethered alkene, [4+2] cycloadditions have been reported.[5] Livinghouse reported [4+2] cycloadditions in **3b** and **3c** catalyzed by $[(CF_3)_2CHO)P]_2RhCl$, giving **5b** and **5c**, respectively, in good yields at 55 °C (Scheme 3, Equation 1).[5a–e] Gilbertson reported that the [4+2] cycloaddition in **3b** proceeded even at room temperature with a cationic rhodium(I) catalyst, $[Rh(dppe)]SbF_6$,[5f,g] a catalyst similar to that used in our reaction shown in Scheme 2 (Scheme 3, Equation 2).

Thus, we were interested in the novel cycloisomerization reaction and report herein the results of further investigations of this reaction.[6] Initially, the reaction of (2*E*,4*E*)-**3d**, having no aldehyde moiety, was carried out in order to investigate the effect of an aldehyde group in the substrate



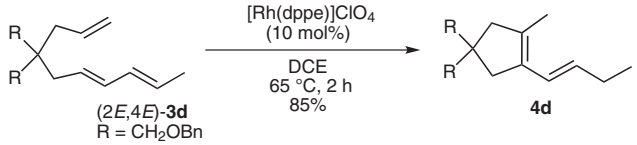
Scheme 3



Scheme 4

3 on this reaction. The substrates (2*E*,4*E*)-**3d** was synthesized in a stereoselective manner, as shown in Scheme 4.

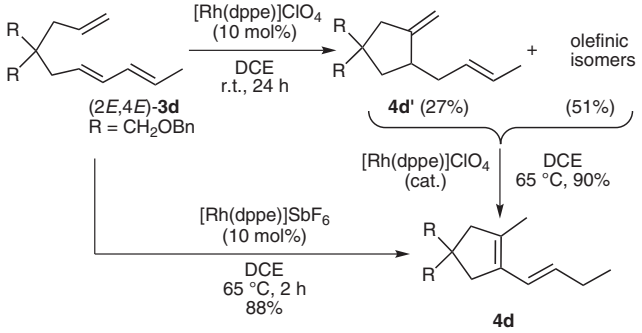
Treatment of (2*E*,4*E*)-**3d** with 10 mol% of [Rh(dppe)]ClO_4 in dichloroethane at 65 °C for two hours gave cycloisomerization product **4d** in 85% yield as the sole product (Scheme 5).



Scheme 5

This result indicates that an aldehyde group in the substrate is not necessary for this cycloisomerization. As mentioned above, [4+2] cycloadditions of 1,3-dienes with alkenes under similar conditions (catalytic [Rh(dppe)]SbF_6, CH_2Cl_2, 25 °C) have already been reported by Gilbertson.[5f,g] Thus, in order to confirm the effect of the reaction temperature, the reaction of (2*E*,4*E*)-**3d** was carried out at room temperature using [Rh(dppe)]ClO_4 as a catalyst in dichloroethane (Scheme 6). As a result, **4d′** was obtained in 27% yield along with an inseparable mixture of the products (51% yield). When the mixture of inseparable products was treated again with a catalytic amount of [Rh(dppe)]ClO_4 in dichloroethane at 65 °C, **4d** was obtained as a single isomer in 90% yield, indicating that the mixture did not contain [4+2] cycloaddition products and should be transient isomers of **4d**. Additionally, it was found that only cycloisomerization proceeded at 65 °C even with the use of [Rh(dppe)]SbF_6 as a catalyst, giving the cyclized product **4d** in 88% yield (Scheme 6).

These results indicate that this cycloisomerization proceeds even at room temperature and also by using

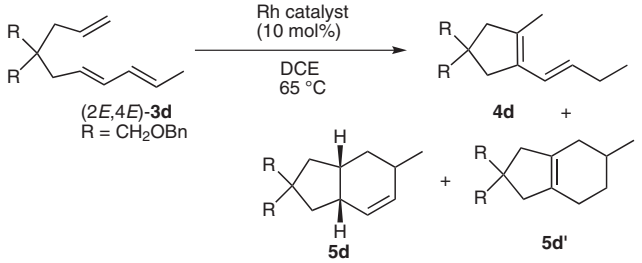


Scheme 6

[Rh(dppe)]SbF_6 as a catalyst and that a [4+2] cycloaddition does not occur under our conditions.

Further investigations of the reaction of (2*E*,4*E*)-**3d** using various rhodium(I) complexes were carried out, and the results are summarized in Table 1. The reaction of (2*E*,4*E*)-**3d** with [Rh(dppp)]ClO_4 instead of [Rh(dppe)]ClO_4 decreased the yield of **4d** to 34% and also afforded the [4+2] cycloaddition product **5d′** in 41% yield (entry 2). The use of [Rh(dppb)]ClO_4 did not promote the cycloisomerization as much as it promoted the [4+2] cycloaddition, and **5d′** was obtained in 70% yield (entry 3). On the other hand, a neutral catalyst, [Rh(dppe)]Cl, which was generated in situ from $[Rh(coe)_2Cl]_2$ (5 mol%) and dppe (10 mol%), did not promote the reaction, and the starting material (2*E*,4*E*)-**3d** was recovered in 78% yield (entry 4). By the use of other neutral catalysts such as [Rh(dppb)]Cl and $RhCl(PPh_3)_3$, the [4+2] cycloaddition product **5d** was obtained as the main product in 42 and 81% yield, respectively (entries 5 and 6). These results

Table 1 Effect of Catalyst on Cycloisomerization of (2*E*,4*E*)-**3d**



Entry	Catalyst	Time (h)	**4d**	**5d**	**5d′**
1	[Rh(dppe)]ClO_4	2	85%	–	–
2	[Rh(dppp)]ClO_4	6	34%	–	41%
3	[Rh(dppb)]ClO_4	12	trace	–	70%
4[a]	[Rh(dppe)]Cl[b]	24	–	–	–
5[a]	[Rh(dppb)]Cl[c]	36	–	42%	–
6	$RhCl(PPh_3)_3$	30	–	81%	–

[a] (2*E*,4*E*)-**3d** was recovered in 78% (entry 4) and 56% yield (entry 5).
[b] $[Rh(coe)_2Cl]_2$ + dppe.
[c] $[Rh(coe)_2Cl]_2$ + dppb.

suggested that the reaction course of this cycloisomerization is strongly affected by the nature of ligands and that [Rh(dppe)]ClO_4 is the best catalyst for this cycloisomerization.

Next, solvent effects were investigated in the reaction of (2*E*,4*E*)-**3d** using 10 mol% of [Rh(dppe)]ClO_4 (Table 2). In the reaction of (2*E*,4*E*)-**3d** in toluene, a trace amount of cycloisomerization product **4d′** was obtained, and the [4+2] cycloaddition product **5d** was obtained in 22% yield as the major product. The use of THF or DMF as a solvent was not effective in the reaction of (2*E*,4*E*)-**3d**. These results indicate that dichloroethane is most effective for the cycloisomerization of (2*E*,4*E*)-**3d**.

Table 2 Effects of Solvents on Cycloisomerization of (2*E*,4*E*)-**3d**

(2*E*,4*E*)-**3d** → [Rh(dppe)]ClO_4 (10 mol%), 65 °C, 24 h → **4d** + **4d'** + **5d**

Entry	Solvent	4d	4d′	5d
1[a]	DCE	85%	–	–
2[b]	toluene	–	8%	22%
3[b]	THF	trace	3%	trace
4[b]	DMF	–	–	–

[a] The reaction was carried out at 65 °C for 2 h.
[b] (2*E*,4*E*)-**3d** was recovered in 56% (entry 2), 50% (entry 3), and 92% yield (entry 4).

Next, the scope and limitations of this cycloisomerization were investigated. Substrates (2*Z*,4*E*)-**3d**, **3e**, **3f**, and **3g** were synthesized as shown in Scheme 7.

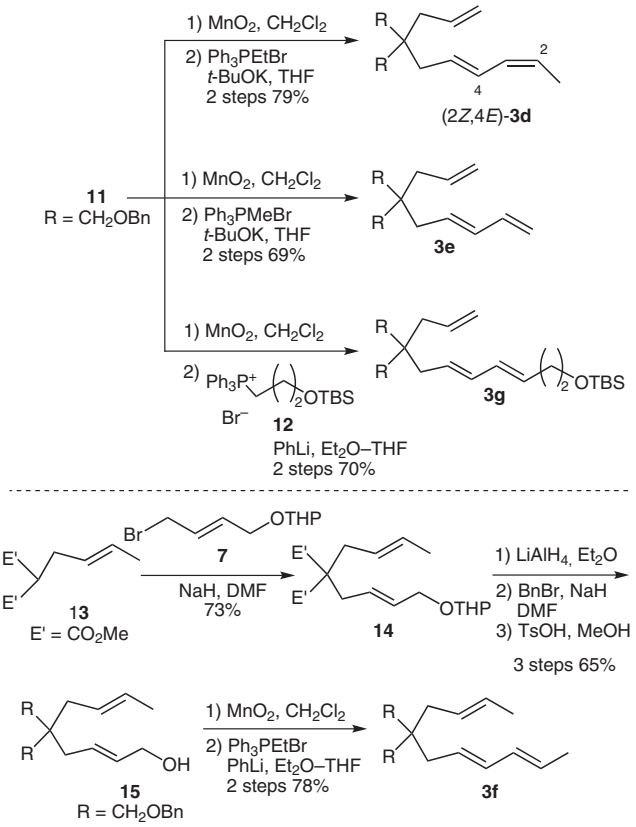
The reaction of (2*Z*,4*E*)-**3d**, having an olefinic isomer of (2*E*,4*E*)-**3d** with respect to C2 carbon, gave **4d** in 80% yield (Table 3, entry 1), indicating that the difference in geometry at the 1,3-diene moiety does not affect the reaction course.

In the reaction of the terminal diene **3e**, the corresponding cycloisomerization product **4e** was obtained in 59% yield (entry 2). The reaction of **3f**, having an internal diene and disubstituted olefin in a tether, also proceeded smoothly to give **4f** in 77% yield (entry 3). The existence of a silyloxy group in the side chain is tolerated in this cycloisomerization, and cyclopentene **4g** was obtained in 85% yield (entry 4).

Next, the construction of a 6-membered ring was examined. Substrates **19a** and **19b** were synthesized as shown in Scheme 8.

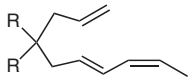
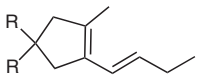
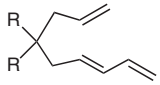
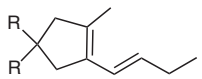
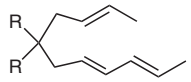
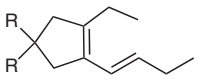
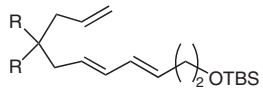
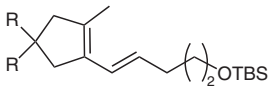
Treatment of **19a** with 10 mol% of [Rh(dppe)]ClO_4 in dichloroethane at 65 °C for 18 hours gave the 5-membered ring product **4f** in 83% yield (Scheme 9), and no desired 6-membered ring product was obtained.

This result suggested that olefin isomerization of **19a** occurred before cycloisomerization under the conditions, and cycloisomerization of **3f** successively occurred, giving **4f** via rhodacycle. On the other hand, the reaction of **19b** under the same conditions gave 6-membered ring compound **26b** in 60% yield along with 5-membered-ring compound **4h** in 13% yield. It was thought that the 5-membered ring compound **4h** was produced from **3h**,

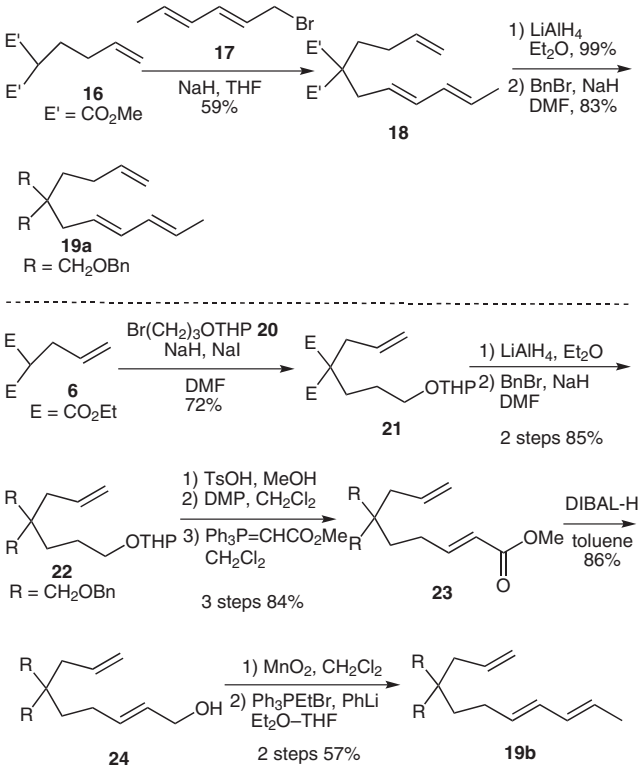


Scheme 7

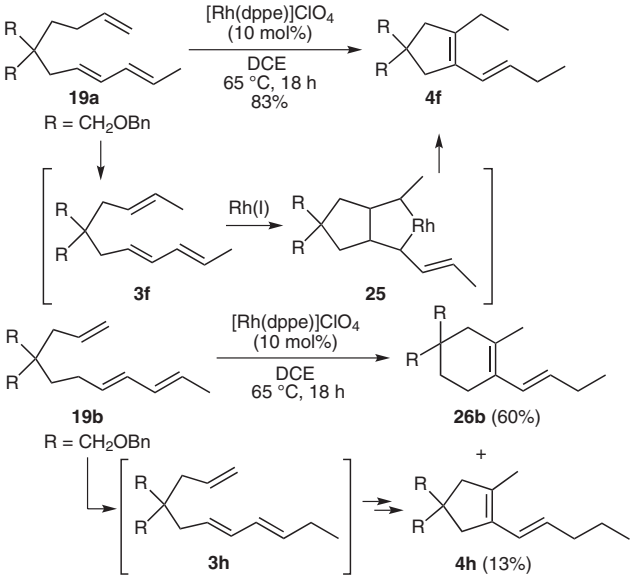
Table 3 Reactions of Various Trienes with [Rh(dppe)]ClO_4[a,b]

Entry	Substrate	Time (h)	Product
1	 (2*Z*,4*E*)-**3d**	14	 **4d** (80%)
2	 **3e**	12	 **4e** (59%)
3	 **3f**	18	 **4f** (77%)
4	 **3g**	4	 **4g** (85%)

[a] All reactions were carried out in DCE at 65 °C using 10 mol% [Rh(dppe)]ClO_4.
[b] R = CH_2OBn.



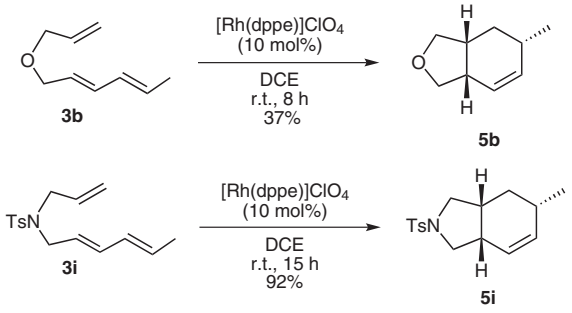
Scheme 8



Scheme 9

which would be formed through a double isomerization of two olefins of the 1,3-diene moiety in **19b** followed by cycloisomerization.

Encouraged by these results, the synthesis of heterocyclic compounds using this cycloisomerization was examined (Scheme 10). Interestingly, we found that only a [4+2] cycloaddition reaction proceeded in the case of **3b** and **3i**, each having a hetero atom between a 1,3-diene moiety and alkene in the tether, to give **5b** and **5i** in 37 and 92% yield, respectively.[7] These results are consistent with the above-mentioned reports of Gilbertson (Scheme 3, Equation 2)[5f,g] and indicate that a hetero atom in a tether strongly affects the reaction course; that is, a [4+2] cycloaddition product is obtained in the case of substrates having a hetero atom between a 1,3-diene moiety and alkene in the tether, while a cycloisomerization product is obtained in the case of substrates having no hetero atom between a 1,3-diene moiety and alkene in the tether.



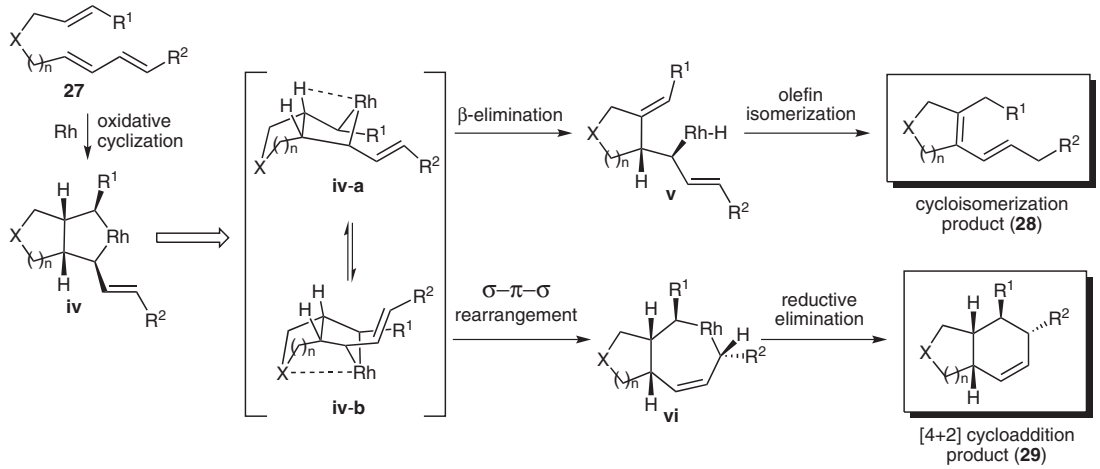
Scheme 10

A plausible reaction course of the cycloisomerization and [4+2] cycloaddition is shown in Scheme 11.

A rhodacyclopentane **iv** was initially formed via oxidative cycloaddition of triene **27** to a rhodium(I) complex, and the rhodacyclopentane **iv** would be in equilibrium with **iv-a** and **iv-b**. In the case of the substrate having no hetero atom in the tether (X = CR_2), cycloisomerization product **28** would be formed through *syn*-β-hydride elimination from **iv-a** followed by an olefin isomerization reaction. On the other hand, in the case of the substrate having a hetero atom in the tether (X = O, NTs), the hetero atom can transannularly coordinate to the rhodium center, which might stabilize the intermediate **iv-b** and inhibit *syn*-β-hydride elimination from **iv-a**. Thus, the rhodacycloheptene intermediate **vi** would be formed from **iv-b** via σ-π-σ rearrangement, and [4+2] cycloaddition product **29** would be preferentially formed via reductive elimination from **vi**.

In summary, we have succeeded in developing cycloisomerization of 1,3-dienes with alkenes in a tether and in the construction of 5- or 6-membered ring compounds. It was found that the existence of a hetero atom between a 1,3-diene moiety and alkene in the tether affected the reaction course.

All manipulations were performed under argon unless otherwise mentioned. Solvents were distilled under argon from sodium-benzophenone (THF, Et_2O, and toluene), CaH_2 (DMF, CH_2Cl_2, and DCE), or sodium (MeOH). Allylmalonic acid diethyl ester (**6**) was purchased from TCI. All other solvents and reagents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh), and flash chromatography was performed on silica gel 60 (Merck, 230–400 mesh) with the indicated solvent as eluent. IR spectra were obtained on a Perkin-Elmer FTIR 1605 spectrometer, and ^1H NMR and ^{13}C NMR spectroscopy were carried out on a Jeol EX270 or a



Scheme 11

Jeol AL400 NMR spectrometer. Mass spectra were obtained on a Jeol JMS-700TZ or a Jeol JMS-FAB mate mass spectrometer for LRMS (EI) and HRMS (EI), and a Jeol JMS-HX-110 mass spectrometer for LRMS (FAB) and HRMS (FAB).

Starting Materials 3a, 3d–g, 19a, and 19b

Diethyl 2-Allyl-2-[(*E*)-4-(tetrahydro-2*H*-pyran-2-yloxy)but-2-enyl]malonate (8)

To a suspension of NaH (60% oil suspension, 988 mg, 24.7 mmol) in DMF (30 mL) was added **6** (4.2 mL, 20.6 mmol) at 0 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture was added a solution of **7**[8] (4.84 g, 20.6 mmol) in DMF (11 mL) at 0 °C, and the mixture was stirred at r.t. for 1.5 h. To the mixture was added sat. aq NH_4Cl (50 mL), and the aqueous layer was extracted with EtOAc (3 × 70 mL). The combined organic layers were washed with brine (80 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 5:1); yield: 5.28 g (72%); colorless oil.

IR (neat): 2980, 2940, 1732, 1442, 1366, 1280, 1208, 1136, 1098, 1026 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 6 H), 1.50–1.60 (m, 4 H), 1.67–1.73 (m, 1 H), 1.78–1.85 (m, 1 H), 2.62 (d, *J* = 6.5 Hz, 2 H), 2.64 (d, *J* = 6.5 Hz, 2 H), 3.47–3.51 (m, 1 H), 3.82–3.87 (m, 1 H), 3.92 (dd, *J* = 12.3, 7.1 Hz, 1 H), 4.13–4.20 (m, 5 H), 4.60 (dd, *J* = 3.4, 3.4 Hz, 1 H), 5.08 (d, *J* = 10.2 Hz, 1 H), 5.10 (d, *J* = 16.4 Hz, 1 H), 5.55 (dt, *J* = 15.2, 7.1 Hz, 1 H), 5.59 (m, 2 H).

^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 14.1, 19.5, 25.4, 30.6, 35.3, 36.8, 57.3, 61.2, 62.2, 67.2, 97.7, 119.1, 127.2, 131.1, 132.3, 170.7.

LRMS (EI): *m*/*z* = 354 [M^+], 325, 309, 265, 253, 225, 179, 151, 105.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{30}O_6$: 354.2042; found: 354.2028.

2-Allyl-2-[(*E*)-4-(tetrahydro-2*H*-pyran-2-yloxy)but-2-enyl]propane-1,3-diol (9)

To a suspension of $LiAlH_4$ (1.6 g, 42 mmol) in Et_2O (40 mL) was added a solution of **8** (5.1 g, 14 mmol) in Et_2O (8 mL) at 0 °C, and the suspension was stirred at r.t. for 2 h. To the mixture was added H_2O (5.1 mL), 15% aq NaOH (5.1 mL), and H_2O (15.3 mL) at 0 °C, and the mixture was stirred at r.t. for 1 h. The solution was filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–EtOAc, 1:1); yield: 3.88 g (quant.); colorless oil.

IR (neat): 3420, 2942, 1442, 1118, 1024 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.52–1.62 (m, 4 H), 1.69–1.75 (m, 1 H), 1.80–1.84 (m, 1 H), 2.08 (d, *J* = 6.5 Hz, 2 H), 2.10 (d, *J* = 6.5 Hz, 2 H), 2.02 (br s, 2 H), 3.46–3.53 (m, 1 H), 3.58 (s, 4 H), 3.84–3.90 (m, 1 H), 3.98 (dd, *J* = 12.3, 5.8 Hz, 1 H), 4.19 (dd, *J* = 12.3, 5.8 Hz, 1 H), 4.62 (dd, *J* = 3.2, 3.2 Hz, 1 H), 5.09 (d, *J* = 10.0 Hz, 1 H), 5.10 (d, *J* = 16.5 Hz, 1 H), 5.67 (dt, *J* = 15.2, 5.8 Hz, 1 H), 5.71–5.89 (m, 2 H).

^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 19.5, 25.4, 30.6, 34.5, 36.1, 42.1, 62.3, 67.7, 68.0, 97.9, 118.0, 129.1, 129.8, 133.9.

LRMS (FAB): *m*/*z* = 271 [M^+ +H], 187, 169, 120, 107.

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{15}H_{27}O_4$: 271.1909; found: 271.1936.

2-(*E*)-5,5-Bis(benzyloxymethyl)octa-2,7-dienyloxytetrahydro-2*H*-pyran (10)

To a suspension of NaH (60% oil suspension, 1.70 g, 42.5 mmol) in DMF (14 mL) was added a solution of **9** (3.90 g, 14.4 mmol) in DMF (5 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. To the mixture was added BnBr (3.8 mL, 31 mmol) at 0 °C, and the mixture was stirred at r.t. for 11 h. To this mixture was added sat. aq NH_4Cl (30 mL), and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (60 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 30:1); yield: 6.0 g (93%); colorless oil.

IR (neat): 2940, 2856, 1200, 1116, 1078, 1024, 734, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.48–1.61 (m, 4 H), 1.67–1.73 (m, 1 H), 1.78–1.86 (m, 1 H), 2.11 (d, *J* = 7.5 Hz, 4 H), 3.30 (s, 4 H), 3.47–3.50 (m, 1 H), 3.84–3.94 (m, 2 H), 4.15 (dd, *J* = 12.5, 5.8 Hz, 1 H), 4.47 (s, 4 H), 4.6 (dd, *J* = 3.6, 3.6 Hz, 1 H), 5.03 (d, *J* = 11.1 Hz, 1 H), 5.04 (d, *J* = 15.0 Hz, 1 H), 5.67 (dt, *J* = 15.4, 5.8 Hz, 1 H), 5.67 (dt, *J* = 15.4, 7.5 Hz, 1 H), 5.73–5.58 (m, 1 H), 7.26–7.34 (m, 10 H).

^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 19.5, 25.5, 30.7, 35.0, 36.6, 42.2, 62.2, 67.7, 72.5, 73.2, 97.6, 117.6, 127.3, 127.3, 128.2, 129.4, 129.6, 134.3, 138.9.

LRMS (EI): *m*/*z* = 450 [M^+], 365, 359, 349, 275, 257, 167, 151, 91.

HRMS (EI): *m*/*z* calcd for $C_{29}H_{38}O_4$: 450.2770; found: 450.2766.

(*E*)-5,5-Bis(benzyloxymethyl)octa-2,7-dien-1-ol (11)

To a solution of **10** (6.00 g, 13.3 mmol) in MeOH (133 mL) was added *p*-TsOH·H_2O (259 mg, 1.36 mmol) at 0 °C, and the mixture was stirred at r.t. for 1.5 h. To the mixture was added sat. aq $NaHCO_3$ (50 mL). After removal of MeOH, the aqueous layer was extracted with EtOAc (3 × 70 mL). The combined organic layers

were washed with brine (80 mL), dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (silica gel, hexane–EtOAc, 5:1); yield: 4.1 g (84%); colorless oil.

IR (neat): 3382, 2978, 2858, 1454, 1364, 1098, 734, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.10–2.12 (m, 4 H), 3.29 (s, 4 H), 3.29 (br s, 1 H), 4.04 (d, *J* = 3.2 Hz, 2 H), 4.47 (s, 4 H), 5.02 (d, *J* = 10.7 Hz, 1 H), 5.03 (d, *J* = 15.5 Hz, 1 H), 5.63 (d, *J* = 15.3 Hz, 1 H), 5.64 (d, *J* = 15.3 Hz, 1 H), 5.63–5.83 (m, 1 H), 7.24–7.35 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.9, 36.6, 42.2, 63.7, 72.3, 73.1, 117.7, 127.3, 127.3, 128.2, 128.3, 132.0, 134.2, 138.7.

LRMS (EI): *m*/*z* = 275 [M^+ – Bn], 257, 227, 167, 137, 107, 91.

HRMS (EI): *m*/*z* [M^+ – Bn] calcd for $C_{17}H_{23}O_3$: 275.1647; found: 275.1640.

(4*Z*,6*E*)-Ethyl 9,9-Bis(benzyloxymethyl)dodeca-4,6,11-trienoate

To a solution of **11** (1.83 g, 5.00 mmol) in CH_2Cl_2 (20 mL) was added MnO_2 (4.4 g, 50 mmol) and the whole suspension was stirred at r.t. for 24 h. The solution was filtered on Celite, and removal of the solvent gave the crude intermediate aldehyde. To a suspension of $[Ph_3P(CH_2)_3CO_2Et]^+Br^-$ (3.4 g, 7.4 mmol) in THF (18 mL) was added *t*-BuOK (716 mg, 6.38 mmol) at –78 °C and the mixture was stirred for 1 h. To the mixture was added a solution of the crude aldehyde in THF (16 mL) at –78 °C, and the mixture was stirred at the same temperature for 1 h and then at r.t. for 1 h. To the mixture was added sat. aq NH_4Cl (20 mL), and the aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with brine (60 mL), dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (silica gel, hexane–EtOAc, 10:1); yield: 1.96 g (85% from **11**); colorless oil.

IR (neat): 2904, 2856, 1734, 1454, 1098, 736, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 3 H), 2.12 (d, *J* = 7.4 Hz, 2 H), 2.17 (d, *J* = 7.4 Hz, 2 H), 2.36 (dt, *J* = 7.4, 7.4 Hz, 2 H), 2.46 (dd, *J* = 7.4, 7.4 Hz, 2 H), 3.30 (s, 4 H), 4.12 (q, *J* = 7.1 Hz, 2 H), 4.47 (s, 4 H), 5.03 (d, *J* = 11.6 Hz, 1 H), 5.04 (d, *J* = 15.4 Hz, 1 H), 5.27 (dt, *J* = 10.3, 7.4 Hz, 1 H), 5.65 (dt, *J* = 15.0, 7.4 Hz, 1 H), 5.73–5.84 (m, 1 H), 5.96 (dd, *J* = 10.3, 10.3 Hz, 1 H), 6.33 (dd, *J* = 15.0, 10.3 Hz, 1 H), 7.24–7.34 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0, 23.9, 35.0, 36.3, 37.4, 43.2, 61.0, 73.2, 73.8, 118.3, 127.9, 127.9, 128.0, 128.7, 128.8, 130.4, 131.4, 139.4, 134.9, 173.5.

LRMS (EI): *m*/*z* = 371 [M^+ – Bn], 342, 314, 180, 145, 129, 117, 105, 91.

HRMS (EI): *m*/*z* [M^+ – Bn] calcd for $C_{23}H_{31}O_4$: 371.2222; found: 371.2218.

(4*Z*,6*E*)-9,9-Bis(benzyloxymethyl)dodeca-4,6,11-trienal (3a)

To a solution of the above ester (290 mg, 0.63 mmol) in toluene (2.6 mL) was added 1.0 M DIBAL-H in hexane (0.82 mL, 0.82 mmol) at –78 °C, and the solution was stirred at the same temperature for 20 min. To the solution was added MeOH (0.1 mL) and sat. aq potassium sodium tartrate (10 mL). After stirring the mixture at r.t. for 1 h, the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (10 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 10:1); yield: 254 mg (96%); colorless oil.

IR (neat): 3064, 3026, 2898, 2856, 1724, 1454, 1098, 736, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.12 (d, *J* = 7.2 Hz, 2 H), 2.17 (d, *J* = 7.2 Hz, 2 H), 2.43–2.54 (m, 4 H), 3.31 (s, 4 H), 4.48 (s, 4 H), 5.03 (d, *J* = 12.4 Hz, 1 H), 5.04 (d, *J* = 14.7 Hz, 1 H), 5.26 (dt, *J* = 10.1, 7.2 Hz, 1 H), 5.67 (dt, *J* = 14.8, 7.2 Hz, 1 H), 5.73–5.84 (m, 1 H), 5.97 (dd, *J* = 10.1, 10.1 Hz, 1 H), 6.32 (dd, *J* = 14.8, 10.1 Hz, 1 H), 7.26–7.35 (m, 10 H), 9.74 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 35.8, 36.8, 42.7, 43.8, 72.5, 73.2, 117.5, 126.8, 127.1, 127.1, 127.7, 128.0, 129.8, 131.0, 134.1, 138.6, 201.4.

LRMS (EI): *m*/*z* = 327 [M^+ – Bn], 309, 235, 201, 91.

Anal. Calcd for $C_{28}H_{34}O_3$: C, 80.35; H, 8.19. Found: C, 80.27; H, 8.32.

(2*E*,4*E*)-7,7-Bis(benzyloxymethyl)deca-2,4,9-triene [(2*E*,4*E*)-3d]

To a solution of **11** (1.1 g, 3.0 mmol) in CH_2Cl_2 (12 mL) was added MnO_2 (3.2 g, 37 mmol) and the whole suspension was stirred at r.t. for 19 h. The solution was filtered on Celite, and removal of the solvent gave the crude intermediate aldehyde. To a suspension of $[Ph_3PEt]^+Br^-$ (1.22 g, 3.29 mmol) in THF (9.6 mL) and Et_2O (4.8 mL) was added 1.5 M PhLi in Et_2O (2.2 mL, 3.3 mmol) at r.t., and the mixture was stirred for 30 min. To the mixture was added a solution of the crude aldehyde in Et_2O (4.8 mL) at –78 °C. After stirring the mixture at –78 °C for 5 min, a 1.5 M solution of PhLi in Et_2O (2.2 mL, 3.3 mmol) was added at the same temperature, and the mixture was warmed to –30 °C. To the mixture was added *t*-BuOK (503 mg, 4.49 mmol) and *t*-BuOH (0.45 mL, 4.49 mmol) at the same temperature and stirred at r.t. for 1 h, and then sat. aq NH_4Cl (30 mL) was added. The aqueous layer was extracted with EtOAc (3 × 50 mL) and the combined organic layers were washed with brine (60 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 50:1); yield: 875 mg (78% from **11**); colorless oil.

IR (neat): 2915, 2854, 1453, 1363, 1100, 734, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.72 (d, *J* = 6.1 Hz, 3 H), 2.10 (d, *J* = 7.6 Hz, 4 H), 3.29 (s, 4 H), 4.47 (s, 4 H), 5.02 (d, *J* = 11.1 Hz, 1 H), 5.03 (d, *J* = 16.4 Hz, 1 H), 5.46–5.60 (m, 2 H), 5.73–5.83 (m, 1 H), 5.98 (dd, *J* = 11.1, 8.1 Hz, 1 H), 6.01 (dd, *J* = 11.8, 8.1 Hz, 1 H), 7.24–7.36 (m, 10 H).

^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 18.2, 35.3, 36.7, 42.6, 72.4, 73.1, 117.4, 126.8, 127.0, 127.1, 128.0, 128.0, 131.5, 133.1, 134.1, 138.6.

LRMS (EI): *m*/*z* = 376 [M^+], 285, 262, 249, 193, 177, 147, 91.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{32}O_2$: 376.2402; found: 376.2390.

Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57. Found: C, 82.93; H, 8.62.

(2*Z*,4*E*)-7,7-Bis(benzyloxymethyl)deca-2,4,9-triene [(2*Z*,4*E*)-3d]

To a suspension of $[Ph_3PEt]^+Br^-$ (241 mg, 0.65 mmol) in THF (1 mL) was added *t*-BuOK (73 mg, 0.65 mmol) at –78 °C and the mixture was stirred for 1 h. To the mixture was added a solution of the crude aldehyde, which was prepared from **11** (184 mg, 0.50 mmol) using a similar procedure for the synthesis of (2*E*,4*E*)-**3d**, in THF (2.3 mL) at –78 °C, and the mixture was stirred at the same temperature for 1 h and then at r.t. for 1 h. To the mixture was added sat. aq NH_4Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried (Na_2SO_4), and concentrated The residue was purified by column chromatography (silica gel, hexane–EtOAc, 50:1); yield: 149 mg (79% from **11**); colorless oil.

IR (neat): 2916, 2856, 1453, 1364, 1099, 734, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.71 (d, *J* = 7.1 Hz, 3 H), 2.10 (d, *J* = 7.5 Hz, 2 H), 2.15 (d, *J* = 7.5 Hz, 2 H), 3.31 (s, 4 H), 4.47 (s, 4 H), 5.03 (d, *J* = 10.8 Hz, 1 H), 5.04 (d, *J* = 17.0 Hz, 1 H), 5.38 (dq, *J* = 11.0, 7.1 Hz, 1 H), 5.61 (dt, *J* = 14.9, 7.5 Hz, 1 H), 5.74–5.85

(m, 1 H), 5.95 (dd, *J* = 11.0, 11.0 Hz, 1 H), 6.35 (dd, *J* = 14.9, 11.0 Hz, 1 H), 7.25–7.34 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.3, 35.6, 36.7, 42.6, 72.6, 73.2, 117.6, 124.2, 127.3, 127.3, 128.2, 128.4, 129.5, 129.5, 134.5, 138.9.

LRMS (EI): *m*/*z* = 376 [M$^+$], 285, 267, 249, 193, 147, 133, 107, 91.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{32}O_2$: 376.2402; found: 376.2415.

Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57. Found: C, 82.99; H, 8.47.

(1*E*,3*E*)-6,6-Bis(benzyloxymethyl)nona-1,3,8-triene (3e)

To $[Ph_3PMe]^+Br^-$ (786 mg, 2.20 mmol) in THF (5.3 mL) was added *n*-BuLi (1.62 M in hexane, 1.36 mL, 2.20 mmol) at –78 °C and the mixture was stirred for 1 h. To the mixture was added a solution of the crude aldehyde, which was prepared from **11** (732 mg, 2.00 mmol) using a similar procedure for the synthesis of (2*E*,4*E*)-**3d**, in THF (2.3 mL) at –78 °C, and the mixture was stirred at the same temperature for 1 h and then at r.t. for 1 h. To the mixture was added sat. aq NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (40 mL), dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (silica gel, hexane–EtOAc, 50:1); yield: 496 mg (69% from **11**); colorless oil.

IR (neat): 2922, 2857, 1453, 1363, 1099, 734, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (d, *J* = 7.3 Hz, 2 H), 2.14 (d, *J* = 7.3 Hz, 2 H), 3.30 (s, 4 H), 4.47 (s, 4 H), 4.98–5.10 (m, 4 H), 5.66 (dt, *J* = 15.1, 7.3 Hz, 1 H), 5.74–5.84 (m, 1 H), 6.06 (dd, *J* = 15.1, 10.3 Hz, 1 H), 6.30 (ddd, *J* = 16.6, 10.3, 10.3 Hz, 1 H), 7.22–7.32 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.4, 36.8, 42.7, 72.5, 73.2, 114.8, 117.5, 127.1, 127.2, 128.0, 130.5, 133.7, 134.1, 137.0, 138.6.

LRMS (EI): *m*/*z* = 362 [M$^+$], 271, 245, 179, 163, 133, 91.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{30}O_2$: 362.2245; found: 362.2249.

Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.81; H, 8.41.

[(3*E*,5*E*)-8,8-Bis(benzyloxymethyl)undeca-3,5,10-trienyloxy](*tert*-butyl)dimethylsilane (3g)

To a suspension of phosphonium salt **12**[9] (1.43 g, 2.77 mmol) in THF (3.8 mL) and Et_2O (1.9 mL) was added 1.12 M PhLi in Et_2O (2.50 mL, 2.77 mmol) at r.t., and the mixture was stirred for 30 min. To the mixture was added a solution of the crude aldehyde, which was prepared from **11** (846 mg, 2.31 mmol) using a similar procedure for the synthesis of (2*E*,4*E*)-**3d**, in Et_2O (1.9 mL) at –78 °C. After stirring the mixture at –78 °C for 5 min, a 1.12 M solution of PhLi in Et_2O (2.50 mL, 2.77 mmol) was added at the same temperature, and the mixture was warmed to –30 °C. To the mixture was added *t*-BuOK (389 mg, 3.47 mmol) and *t*-BuOH (0.33 mL, 3.47 mmol) at the same temperature and stirred at r.t. for 1 h, and then sat. aq NH_4Cl (10 mL) was added. The aqueous layer was extracted with EtOAc (3 × 20 mL) and the combined organic layers were washed with brine (30 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 50:1); yield: 842 mg (70% from **11**); colorless oil.

IR (neat): 2927, 2856, 1099, 991 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 6 H), 0.90 (s, 9 H), 2.10 (d, *J* = 7.3 Hz, 2 H), 2.11 (d, *J* = 7.3 Hz, 2 H), 2.29 (dt, *J* = 7.3, 7.3 Hz, 2 H), 3.30 (s, 4 H), 3.64 (t, *J* = 7.3 Hz, 2 H), 4.47 (s, 4 H), 5.03 (d, *J* = 11.1 Hz, 1 H), 5.04 (d, *J* = 16.1 Hz, 1 H), 5.54 (dt, *J* = 14.4, 7.3 Hz, 2 H), 5.73–5.84 (m, 1 H), 6.00 (dd, *J* = 14.4, 7.9 Hz, 1 H), 6.03 (dd, *J* = 14.4, 7.9 Hz, 1 H), 7.24–7.35 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.9, 18.6, 26.1, 35.4, 36.4, 36.7, 42.7, 63.1, 72.5, 73.2, 117.4, 127.1, 127.2, 127.8, 128.0, 128.3, 132.0, 133.1, 134.2, 138.7.

LRMS (EI): *m*/*z* = 520 [M$^+$], 429, 412, 399, 355, 321, 249, 233, 189, 159, 91.

Anal. Calcd for $C_{33}H_{48}O_3Si$: C, 76.10; H, 9.29. Found: C, 76.20; H, 9.25.

Dimethyl 2-[(*E*)-But-2-enyl]-2-[(*E*)-4-(tetrahydro-2*H*-pyran-2-yloxy)but-2-enyl]malonate (14)

To a suspension of NaH (60% oil suspension, 3.56 g, 45.5 mmol) in DMF (46 mL) was added a solution of **13**[10] (7.0 g, 38 mmol) in DMF (10 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. To the mixture was added a solution of **7**[8] (10.7 g, 45.5 mmol) in DMF (10 mL) at 0 °C, and stirred at r.t. for 1.5 h. To the mixture was added sat. aq NH_4Cl (60 mL), and the aqueous layer was extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with brine (100 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 9:1); yield: 9.4 g (73%); colorless oil.

IR (neat): 2950, 2869, 1737, 1438, 1275, 1202, 1134, 1077, 1025, 970 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52–1.85 (m, 6 H), 1.64 (d, *J* = 6.4 Hz, 3 H), 2.55 (d, *J* = 7.4 Hz, 2 H), 2.62 (d, *J* = 6.4 Hz, 2 H), 3.47–3.52 (m, 1 H), 3.70 (s, 6 H), 3.82–3.94 (m, 2 H), 4.15 (dd, *J* = 12.6, 5.5 Hz, 1 H), 4.59–4.61 (m, 1 H), 5.24 (dt, *J* = 15.2, 7.4 Hz, 1 H), 5.47–5.57 (m, 2 H), 5.65 (dt, *J* = 15.2, 6.4 Hz, 1 H).

^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 18.0, 19.5, 25.4, 30.6, 35.4, 35.7, 52.2, 57.9, 62.1, 67.1, 97.6, 124.4, 127.3, 129.9, 130.9, 171.2.

LRMS (EI): *m*/*z* = 340 [M$^+$], 309, 279, 239, 207, 179, 119, 85.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{28}O_6$: 340.1886; found: 340.1888.

(2*E*,7*E*)-5,5-Bis(benzyloxymethyl)nona-2,7-dien-1-ol (15)

To a suspension of $LiAlH_4$ (2.27 g, 60.0 mmol) in Et_2O (57 mL) was added a solution of **14** (5.1 g, 15 mmol) in Et_2O (10 mL) at 0 °C, and the suspension was stirred at r.t. for 5 h. To the mixture was added H_2O (2.3 mL), 15% aq NaOH (2.3 mL), and H_2O (6.9 mL) at 0 °C, and stirred at r.t. for 1 h. The solution was filtered and the filtrate was concentrated in vacuo to give a crude diol. To a suspension of NaH (60% oil suspension, 1.68 g, 42.0 mmol) in DMF (43 mL) was added a solution of the crude diol in DMF (25 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. To the mixture was added BnBr (3.7 mL, 31 mmol) at 0 °C, and stirred at r.t. for 14 h. To this mixture was added sat. aq NH_4Cl (50 mL), and the aqueous layer was extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with brine (100 mL), and dried (Na_2SO_4). The solution was concentrated in vacuo to give the crude intermediate benzyl ether. To a solution of the benzyl ether in MeOH (130 mL) was added *p*-TsOH·H_2O (269 mg, 1.41 mmol) at 0 °C, and the mixture was stirred at r.t. for 10 h. To the mixture was added sat. aq $NaHCO_3$ (80 mL). After the removal of MeOH, the aqueous layer was extracted with EtOAc (3 × 120 mL). The combined organic layers were washed with brine (120 mL), dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (silica gel, hexane–EtOAc, 5:1); yield: 3.71 g (65% from **14**); colorless oil.

IR (neat): 3384, 2917, 2856, 1453, 1099, 1028, 972, 735, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 6.0 Hz, 1 H), 1.63 (d, *J* = 5.9 Hz, 3 H), 2.01 (d, *J* = 7.2 Hz, 2 H), 2.08 (d, *J* = 5.0 Hz, 2 H), 3.27 (s, 4 H), 4.03–4.04 (m, 2 H), 4.47 (s, 4 H), 5.36 (dt, *J* = 15.0, 7.2 Hz, 1 H), 5.44 (dq, *J* = 15.0, 5.9 Hz, 1 H), 5.62–5.64 (m, 2 H), 7.17–7.32 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 34.8, 35.0, 42.3, 63.7, 72.4, 73.1, 126.3, 127.3, 127.4, 128.1, 128.2, 128.6, 131.9, 138.9.

LRMS (EI): *m*/*z* = 289 [M^+ – Bn], 271, 163, 151, 107, 91.

HRMS (EI): *m*/*z* [M^+ – Bn] calcd for $C_{18}H_{25}O_3$: 289.1804; found: 289.1818.

(2*E*,4*E*,9*E*)-7,7-Bis(benzyloxymethyl)undeca-2,4,9-triene (3f)

The crude product prepared from **15** (689 mg, 1.88 mmol) by a procedure similar to that used for the synthesis of (2*E*,4*E*)-**3d**, was purified by column chromatography (silica gel, hexane–EtOAc, 5:1); yield: 575 mg (78% from **15**); colorless oil.

IR (neat): 2913, 2853, 1453, 1099 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63 (d, *J* = 6.3 Hz, 3 H), 1.73 (d, *J* = 6.1 Hz, 3 H), 2.01 (d, *J* = 7.6 Hz, 2 H), 2.07 (d, *J* = 6.4 Hz, 2 H), 3.27 (s, 4 H), 4.47 (s, 4 H), 5.36 (dt, *J* = 15.8, 7.6 Hz, 1 H), 5.40–5.44 (m, 1 H), 5.46–5.60 (m, 2 H), 5.98 (dd, *J* = 10.4, 5.6 Hz, 1 H), 6.01 (dd, *J* = 10.4, 5.6 Hz, 1 H), 7.23–7.34 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 18.1, 35.1, 35.1, 42.7, 72.5, 73.1, 126.5, 126.8, 127.2, 127.3, 127.3, 127.9, 128.1, 131.8, 133.2, 138.9.

LRMS (EI): *m*/*z* = 390 [M^+], 299, 282, 191, 173, 161, 133, 91.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{34}O_2$: 390.2559; found: 390.2573.

Anal. Calcd for $C_{27}H_{34}O_2$: C, 83.03; H, 8.77. Found: C, 83.19; H, 8.77.

Dimethyl 2-(But-3-enyl)-2-[(2*E*,4*E*)-hexa-2,4-dienyl]malonate (18)

To a suspension of NaH (60% oil suspension, 296 mg, 7.40 mmol) in THF (12 mL) was added a solution of **16**[11] (1.25 g, 6.71 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. To the mixture was added a solution of **17**[12] (1.2 g, 7.4 mmol) in THF (5 mL) at 0 °C, and stirred at r.t. for 1 h. To the mixture was added sat. aq NH_4Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 5:1); yield: 1.05 g (59%); colorless oil.

IR (neat): 2954, 2924, 1723, 1271, 1240, 1205, 1156, 991cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (d, *J* = 6.9 Hz, 3 H), 1.75–1.97 (m, 4 H), 2.65 (d, *J* = 7.5 Hz, 2 H), 3.71 (s, 6 H), 4.96 (d, *J* = 10.0 Hz, 1 H), 5.02 (d, *J* = 15.8 Hz, 1 H), 5.33 (dt, *J* = 13.1, 7.5 Hz, 1 H), 5.61 (dq, *J* = 13.1, 6.9 Hz, 1 H), 5.71–5.81 (m, 1 H), 5.95 (dd, *J* = 13.1, 10.6 Hz, 1 H), 6.35 (dd, *J* = 13.1, 10.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8, 28.4, 31.8, 36.1, 52.3, 57.7, 115.0, 124.2, 128.7, 131.1, 134.4, 137.5, 171.6.

LRMS (EI): *m*/*z* = 266 [M^+], 234, 212, 206, 147, 133, 105, 81.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{22}O_4$: 266.1518; found: 266.1518.

2-(But-3-enyl)-2-[(2*E*,4*E*)-hexa-2,4-dienyl]propane-1,3-diol

To a suspension of $LiAlH_4$ (342 mg, 9.01 mmol) in Et_2O (8 mL) was added a solution of **18** (799 mg, 3.00 mmol) in Et_2O (2 mL) at 0 °C, and the suspension was stirred at r.t. for 5 h. To the mixture was added H_2O (0.34 mL), 15% aq NaOH (0.34 mL), and H_2O (1.02 mL) at 0 °C, and the mixture was stirred at r.t. for 1 h. The mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–EtOAc, 1:1); yield: 624 mg (99%); colorless oil.

IR (neat): 3374, 2925, 2857, 1052, 1024, 990, 910 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36–1.42 (m, 2 H), 1.73 (d, *J* = 6.7 Hz, 3 H), 2.02–2.11 (m, 6 H), 3.58 (s, 2 H), 3.60 (s, 2 H), 4.95 (ddd, *J* = 10.7, 1.2, 1.2 Hz, 1 H), 5.03 (ddd, *J* = 17.0, 1.3, 1.3 Hz, 1 H), 5.52 (dt, *J* = 14.0, 7.3 Hz, 1 H), 5.61 (dq, *J* = 14.1, 6.7 Hz, 1 H), 5.66–5.86 (m, 1 H), 5.99–6.10 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2, 27.4, 30.3, 34.2, 42.0, 67.8, 114.1, 125.8, 127.4, 131.1, 133.2, 138.6.

LRMS (EI): *m*/*z* = 210 [M^+], 192, 174, 161, 145, 119, 105.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{22}O_2$: 210.1620; found: 210.1604.

(7*E*,9*E*)-5,5-Bis(benzyloxymethyl)undeca-1,7,9-triene (19a)

To a suspension of NaH (60% oil suspension, 240 mg, 6.00 mmol) in DMF (2 mL) was added a solution of the above-prepared 2-but-3-enyl-2-[(2*E*,4*E*)-hexa-2,4-dienyl]propane-1,3-diol (421 mg, 2.00 mmol) in DMF (2 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. To the mixture was added BnBr (0.5 mL, 4.2 mmol) at 0 °C, and stirred at r.t. for 14 h. To this mixture was added sat. aq NH_4Cl (5 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 30:1); yield: 648 mg (83%); colorless oil.

IR (neat): 2925, 2855, 1451, 1362, 1098, 990, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37–1.43 (m, 2 H), 1.73 (d, *J* = 6.1 Hz, 3 H), 1.96 (m, 2 H), 2.12 (d, *J* = 7.7 Hz, 2 H), 3.24 (s, 4 H), 4.47 (s, 4 H), 4.90 (dd, *J* = 10.2, 1.1 Hz, 1 H), 4.97 (dd, *J* = 17.2, 1.8 Hz, 1 H), 5.43–5.60 (m, 2 H), 5.73–5.84 (m, 1 H), 5.97 (dd, *J* = 11.0, 8.3 Hz, 1 H), 6.01 (dd, *J* = 11.0, 8.3 Hz, 1 H), 7.25–7.37 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3, 27.7, 31.5, 35.3, 42.2, 72.6 73.1, 113.8, 126.8, 126.9, 127.1, 127.2, 128.0, 131.5, 133.0, 138.7, 139.2.

LRMS (EI): *m*/*z* = 390 [M^+], 299, 282, 191, 173, 131, 91.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{34}O_4$: 390.2559, found: 390.2556.

Anal. Calcd for $C_{27}H_{34}O_2$: C, 83.03; H, 8.77. Found: C, 83.11; H, 8.59.

Diethyl 2-Allyl-2-[3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]malonate (21)

To a suspension of NaH (60% oil suspension, 840 mg, 21.0 mmol) in DMF (25 mL) was added a solution of **6** (3.60 mL, 17.5 mmol) in DMF (10 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. To the mixture was added a solution of **20**[13] (4.3 g, 19.3 mmol) in DMF (5 mL) and NaI (2.89 g, 19.3 mmol) at 0 °C, and stirred at 50 °C for 24 h. To the mixture was added sat. aq NH_4Cl (40 mL), and the aqueous layer was extracted with EtOAc (3 × 60 mL). The combined organic layers were washed with brine (80 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 5:1); yield: 4.3 g (72%); colorless oil.

IR (neat): 2942, 2871, 1732, 1444, 1201, 1034 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.1 Hz, 6 H), 1.47–1.82 (m, 8 H), 1.91–1.98 (m, 2 H), 2.66 (d, *J* = 7.6 Hz, 2 H), 3.37 (dd, *J* = 9.8, 7.6 Hz, 1 H), 3.47–3.51 (m, 1 H), 3.72 (dd, *J* = 9.8, 7.6 Hz, 1 H), 3.81–3.89 (m, 1 H), 4.18 (q, *J* = 7.1 Hz, 4 H), 4.57 (dd, *J* = 2.4, 2.4 Hz, 1 H), 5.08 (d, *J* = 9.9 Hz, 1 H), 5.10 (d, *J* = 17.6 Hz, 1 H), 5.66 (ddd, *J* = 17.6, 9.9, 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.3, 24.1, 25.3, 28.6, 30.5, 36.6, 56.9, 61.0, 62.0, 67.0, 98.4, 118.7, 132.2, 171.0.

LRMS (FAB): *m*/*z* = 343 [M^+ + H], 259, 241, 213, 154, 136, 121.

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{18}H_{30}O_6$: 343.2134; found: 343.2121.

2-[4,4-Bis(benzyloxymethyl)hept-6-enyloxy]tetrahydro-2*H*-pyran (22)

To a suspension of $LiAlH_4$ (569 mg, 15.0 mmol) in Et_2O (10 mL) was added a solution of **21** (1.7 g, 5.0 mmol) in Et_2O (7 mL) at 0 °C, and the suspension was stirred at r.t. for 5 h. To the mixture was added H_2O (0.57 mL), 15% aq NaOH (0.57 mL), and H_2O (1.7 mL) at 0 °C, and the mixture was stirred at r.t. for 1 h. The solution was filtered and the filtrate was concentrated in vacuo to give a crude diol. To a suspension of NaH (60% oil suspension, 540 mg, 13.5 mmol) in DMF (4.5 mL) was added a solution of the diol in DMF (4.5 mL) at 0 °C, and the mixture was stirred at the same temperature for 30 min. To the mixture was added BnBr (1.3 mL, 10.4 mmol) at 0 °C, and stirred at r.t. for 17 h. To this mixture was added sat. aq NH_4Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 50:1); yield: 1.87 g (85% from **21**); colorless oil.

IR (neat): 2941, 2860, 1453, 1364, 1117, 1030, 735, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.33–1.37 (m, 2 H), 1.53–1.57 (m, 6 H), 1.66–1.72 (m, 1 H), 1.81–1.86 (m, 1 H), 2.12 (d, *J* = 7.6 Hz, 2 H), 3.32–3.37 (m, 5 H), 3.45–3.50 (m, 1 H), 3.67 (dd, *J* = 9.4 Hz, 1 H), 3.82–3.88 (m, 1 H), 4.47 (s, 4 H), 4.56 (dd, *J* = 3.6, 3.6 Hz, 1 H), 5.01 (d, *J* = 10.0 Hz, 1 H), 5.04 (d, *J* = 17.8 Hz, 1 H), 5.77 (ddd, *J* = 17.8, 10.0, 7.6 Hz, 1 H), 7.26–7.33 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.6, 23.3, 25.4, 28.0, 30.7, 36.3, 41.3, 62.2, 68.1, 72.5, 73.0, 98.6, 117.4, 127.2, 127.2, 128.1, 134.3, 138.8.

LRMS (FAB): *m*/*z* = 439 [M^+ + H], 355, 245, 181, 154.

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{28}H_{39}O_4$: 439.2874; found: 439.2848.

(*E*)-Methyl 6,6-Bis(benzyloxymethyl)nona-2,8-dienoate (23)

To a solution of **22** (1.87 g, 4.27 mmol) in MeOH (43 mL) was added *p*-TsOH·H_2O (41 mg, 0.22 mmol) at 0 °C, and the mixture was stirred at r.t. for 36 h. To the mixture was added sat. aq $NaHCO_3$ (40 mL). After removal of MeOH, and the aqueous layer was extracted with EtOAc (3 × 60 mL). The combined organic layers were washed with brine (80 mL), dried (Na_2SO_4), and concentrated to give a crude alcohol. To a suspension of the Dess–Martin periodinane (DMP, 2.1 g, 5.0 mmol) in CH_2Cl_2 (30 mL) was added a solution of the crude alcohol in CH_2Cl_2 (10 mL) at 0 °C, and the mixture was stirred at r.t. for 1 h. To the mixture was added sat. aq $NaHCO_3$ (20 mL) and 10% aq $Na_2S_2O_3$ (20 mL), and the aqueous layer was extracted with EtOAc (3 × 60 mL). The combined organic layers were washed with brine (80 mL), dried (Na_2SO_4), and concentrated to give the crude intermediate aldehyde. To a solution of the crude aldehyde in CH_2Cl_2 (14 mL) was added $Ph_3P{=}CHCO_2Me$ (1.62 g, 4.85 mmol) at r.t., and the mixture was stirred at the same temperature for 12 h. After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 50:1); yield: 1.47 g (84% from **22**); colorless oil.

IR (neat): 2920, 2858, 1724, 1655, 1098 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.44–1.48 (m, 2 H), 2.11–2.17 (m, 2 H), 2.12 (d, *J* = 7.4 Hz, 2 H), 3.30 (s, 4 H), 3.71 (s, 3 H), 4.46 (s, 4 H), 5.03 (d, *J* = 12.0 Hz, 1 H), 5.04 (d, *J* = 14.0 Hz, 1 H), 5.68–5.80 (m, 2 H), 6.94 (dt, *J* = 15.5, 7.0 Hz, 1 H), 7.26–7.35 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.3, 30.6, 36.7, 41.6, 51.4, 72.4, 73.2, 117.6, 120.3, 127.2, 127.2, 128.1, 133.7, 138.4, 149.8, 166.8.

LRMS (FAB): *m*/*z* = 409 [M^+ + H], 181, 154, 136, 107.

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{26}H_{33}O_4$: 409.2407; found: 409.2379.

(*E*)-6,6-Bis(benzyloxymethyl)nona-2,8-dien-1-ol (24)

To a solution of **23** (1.45 g, 3.56 mmol) in toluene (12 mL) was added 0.95 M DIBAL-H in hexane (8.20 mL, 7.83 mmol) at –78 °C, and the solution was stirred at the same temperature for 1.5 h. To the solution was added MeOH (0.5 mL) and sat. aq potassium sodium tartrate (20 mL). After stirring the mixture at r.t. for 1 h, the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine (40 mL), and dried (Na_2SO_4). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane–EtOAc, 3:1); yield: 1.16 g (86%); colorless oil.

IR (neat): 3382, 2920, 2857, 1098, 735, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.20 (dt, *J* = 5.7 Hz, 1 H), 1.38–1.42 (m, 2 H), 2.00 (dt, *J* = 10.4, 4.5 Hz, 2 H), 2.12 (d, *J* = 7.7 Hz, 2 H), 3.30 (s, 4 H), 4.06 (dd, *J* = 5.7 Hz, 2 H), 4.47 (s, 4 H), 5.02 (d, *J* = 10.8 Hz, 1 H), 5.03 (d, *J* = 16.9 Hz, 1 H), 5.52–5.70 (m, 2 H), 5.72–5.81 (m, 1 H), 7.26–7.34 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.1, 31.6, 36.7, 41.7, 63.4, 72.6, 73.2, 117.3, 127.1, 127.1, 128.0, 128.4, 133.5, 138.4, 138.6.

LRMS (FAB): *m*/*z* = 381 [M^+ + H], 181, 154, 136, 107.

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{25}H_{33}O_3$: 381.2451; found: 381.2430.

(7*E*,9*E*)-4,4-Bis(benzyloxymethyl)undeca-1,7,9-triene (19b)

The crude product prepared from **24** (381 mg, 1.00 mmol) by a procedure similar to that used for the synthesis of (2*E*,4*E*)-**3d**, was purified by column chromatography (silica gel, hexane–EtOAc, 5:1); yield: 221 mg (57% from **25**); colorless oil.

IR (neat): 2914, 2856, 1451, 1099, 989, 909, 734, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.37–1.41 (m, 2 H), 1.72 (d, *J* = 6.4 Hz, 3 H), 1.97–2.03 (m, 2 H), 2.11 (d, *J* = 7.3 Hz, 2 H), 3.30 (s, 4 H), 4.47 (s, 4 H), 5.02 (d, *J* = 10.3 Hz, 1 H), 5.03 (d, *J* = 16.7 Hz, 1 H), 5.47–5.59 (m, 2 H), 5.76 (ddd, *J* = 16.7, 10.3, 7.3 Hz, 1 H), 5.96 (dd, *J* = 14.0, 10.3 Hz, 1 H), 5.99 (dd, *J* = 14.0, 10.3 Hz, 1 H), 7.24–7.34 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3, 26.5, 31.9, 36.7, 41.8, 72.7, 73.2, 117.4, 126.6, 127.2, 127.2, 128.1, 129.8, 131.5, 132.2, 134.2, 138.7.

LRMS (FAB): *m*/*z* = 391 [M^+ + H], 181, 154, 136, 107, 91.

Anal. Calcd for $C_{27}H_{34}O_2$: C, 83.03; H, 8.77. Found: C, 82.91; H, 8.66.

Cycloisomerization of Trienes; (*E*)-4,4-Bis(benzyloxymethyl)-1-(but-1-enyl)-2-methylcyclopentene (4d); Typical Procedure

A solution of [Rh(dppe)(nbd)]ClO_4 (11.1 mg, 0.016 mmol) in degassed DCE (0.62 mL) was stirred under H_2 atmosphere at r.t. for 1 h. Then the reaction vessel was flushed with argon, and a solution of triene (2*E*,4*E*)-**3d** (60.2 mg, 0.16 mmol) in degassed DCE (0.98 mL) was added to the mixture. The reaction mixture was stirred at 65 °C for 2 h. After removal of the solvent, the residue was purified by column chromatography (silica gel) to afford **4d** (51.1 mg, 85%) as a colorless oil. All cyclization reactions were carried out by this procedure.

IR (neat): 2925, 2850, 1453, 1361, 1102, 733, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 7.1 Hz, 3 H), 1.69 (s, 3 H), 2.13 (dq, *J* = 7.1, 7.1 Hz, 2 H), 2.28 (s, 2 H), 2.35 (s, 2 H), 3.43 (s, 4 H), 4.52 (s, 4 H), 5.52 (dt, *J* = 15.6, 7.1 Hz, 1 H), 6.26 (d, *J* = 15.6 Hz, 1 H), 7.25–7.34 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.2, 26.3, 40.0, 44.8, 45.7, 73.2, 74.2, 123.3, 127.1, 127.2, 128.0, 131.3, 131.6, 133.0 138.7.

LRMS: *m*/*z* = 376 [M^+], 268, 177, 162, 147, 91.

Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57. Found: C, 82.99; H, 8.69.

(*E*)-6-[4,4-Bis(benzyloxymethyl)-2-methylcyclopent-1-enyl]hex-5-enal (4a)

IR (neat): 3028, 2850, 1724, 1454, 1100, 736, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3 H), 1.73 (tt, *J* = 7.3, 7.3 Hz, 2 H), 2.15 (dt, *J* = 7.3, 7.3 Hz, 2 H), 2.29 (s, 2 H), 2.33 (s, 2 H), 2.42 (td, *J* = 7.3, 1.4 Hz, 2 H), 3.43 (s, 4 H), 4.52 (s, 4 H), 5.40 (dt, *J* = 15.5, 7.3 Hz, 1 H), 6.27 (d, *J* = 15.5 Hz, 1 H), 7.25–7.34 (m, 10 H), 9.76 (t, *J* = 1.4 Hz, 1 H).

^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 14.0, 22.0, 32.4, 39.8, 43.2, 44.7, 45.6, 73.2, 74.1, 125.6, 127.3, 127.3, 128.2, 128.3, 131.3, 134.1, 138.8, 202.5.

LRMS (EI): *m*/*z* = 400 [$M^+ - H_2O$], 310, 279, 105, 91.

Anal. Calcd for $C_{28}H_{34}O_3$: C, 80.35; H, 8.19. Found: C, 80.24; H, 8.23.

(*E*)-1,1-Bis(benzyloxymethyl)-3-(but-2-enyl)-4-methylenecyclopentane (4d′)

IR (neat): 2923, 2856, 1116, 1100 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.16–1.25 (m, 1 H), 1.64 (d, *J* = 5.1 Hz, 3 H), 1.87–1.95 (m, 2 H), 2.26–2.39 (m, 3 H), 2.42–2.51 (m, 1 H), 3.31–3.43 (m, 4 H), 4.52 (s, 4 H), 4.77 (s, 1 H), 4.84 (s, 1 H), 5.38 (dt, *J* = 15.3, 5.2 Hz, 1 H), 5.44 (dq, *J* = 15.3, 5.1 Hz, 1 H), 7.24–7.34 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 37.6, 37.8, 40.2, 41.8, 45.8, 72.8, 73.2, 74.7, 105.2, 125.9, 127.3, 127.4, 128.2, 129.7, 138.9, 154.9.

LRMS (EI): *m*/*z* = 376 [M^+ – Bn], 268, 207, 177, 147, 105, 91.

Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57. Found: C, 82.95; H, 8.63.

(*E*)-4,4-Bis(benzyloxymethyl)-1-methyl-2-(propen-1-yl)cyclopentene (4e)

IR (neat): 2911, 2850, 1452, 1361, 1100 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3 H), 1.78 (d, *J* = 6.8 Hz, 3 H), 2.27 (s, 2 H), 2.34 (s, 2 H), 3.43 (s, 4 H), 4.52 (s, 4 H), 5.48 (dq, *J* = 15.3, 6.8 Hz, 1 H), 6.28 (d, *J* = 15.3 Hz, 1 H), 7.23–7.33 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 18.8, 40.0, 44.8, 45.7, 73.2, 74.2, 124.4, 125.7, 127.1, 127.2, 128.1, 131.4, 132.8, 138.7.

LRMS (EI): *m*/*z* = 362 [M^+], 271, 254, 165, 148, 133, 91.

Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.64; H, 8.52.

(*E*)-4,4-Bis(benzyloxymethyl)-1-(but-1-enyl)-2-ethylcyclopentene (4f)

IR (neat): 2922, 2850, 1453, 1362, 1101 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.4 Hz, 3 H), 1.01 (t, *J* = 7.5 Hz, 3 H), 2.08–2.18 (m, 4 H), 2.31 (s, 2 H), 2.36 (s, 2 H), 3.44 (s, 4 H), 4.52 (s, 2 H), 4.53 (s, 2 H), 5.52 (dt, *J* = 15.6, 6.8 Hz, 1 H), 6.27 (d, *J* = 15.6 Hz, 1 H), 7.26–7.37 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 14.2, 21.5, 26.4, 40.1, 42.7, 44.6, 73.2, 74.1, 123.1, 127.1, 127.2, 128.0, 130.5, 131.6, 138.7, 138.9.

LRMS (EI): *m*/*z* = 390 [M^+], 298, 282, 191, 161, 131, 91.

Anal. Calcd for $C_{27}H_{34}O_2$: C, 83.03; H, 8.77. Found: C, 82.97; H, 9.06.

(*E*)-[5-4,4-Bis(benzyloxymethyl)-2-methylcyclopent-1-enyl-pent-4-enyloxy]-*tert*-butyldimethylsilane (4g)

IR (neat): 2927, 2854, 1100 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.01 (s, 6 H), 0.86 (s, 9 H), 1.57 (tt, *J* = 7.1, 7.1 Hz, 2 H), 1.65 (s, 3 H), 2.11 (dt, *J* = 7.1, 7.1 Hz, 2 H), 2.24 (s, 2 H), 2.30 (s, 2 H), 3.39 (s, 4 H), 3.57 (t, *J* = 7.1 Hz, 2 H), 4.46 (s, 4 H), 5.43 (dt, *J* = 15.6, 7.1 Hz, 1 H), 6.24 (d, *J* = 15.6 Hz, 1 H), 7.19–7.30 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –5.0, 14.1, 18.6, 26.2, 29.6, 32.9, 40.0, 44.7, 45.7, 62.6, 73.2, 74.1, 124.6, 127.1, 127.2, 128.0, 129.3, 131.3, 133.2, 138.7.

LRMS (EI): *m*/*z* = 520 [M^+], 505, 429, 412, 355, 321, 249, 181, 91.

HRMS (EI): *m*/*z* calcd for $C_{33}H_{48}O_3Si$: 520.3373; found: 520.3374.

(*E*)-4,4-Bis(benzyloxymethyl)-1-methyl-2-pent-1-enylcyclopentene (4h)

IR (neat): 2923, 2852, 1452, 1100, 734, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.5 Hz, 3 H), 1.40 (tq, *J* = 7.5, 7.5 Hz, 2 H), 1.69 (s, 3 H), 2.09 (dt, *J* = 7.5, 7.5 Hz, 2 H), 2.28 (s, 2 H), 2.35 (s, 2 H), 3.43 (s, 4 H), 4.52 (s, 4 H), 5.47 (dt, *J* = 15.4, 7.5 Hz, 1 H), 6.26 (d, *J* = 15.4 Hz, 1 H), 7.24–7.31 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 14.1, 23.1, 34.5, 40.0, 44.7, 45.7, 73.2, 74.2, 124.4, 127.1, 127.2, 128.0, 129.9, 131.4, 133.0, 138.7.

LRMS (EI): *m*/*z* = 390 [M^+], 299, 282, 191, 176, 161, 149, 131, 91.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{34}O_2$: 390.2559, found: 390.2558.

2,2-Bis(benzyloxymethyl)-5-methyl-*cis*-2,3,3a,4,5,7a-hexahydro-1*H*-indene (5d)

IR (neat): 2924, 2854, 2453, 1362, 1098, 733, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.92–0.95 (m, 1 H), 0.93 (d, *J* = 7.0 Hz, 3 H), 1.20–1.32 (m, 2 H), 1.50–1.55 (m, 1 H), 1.79–1.90 (m, 2 H), 2.09–2.10 (m, 2 H), 2.41–2.43 (m, 1 H), 3.35–3.46 (m, 4 H), 4.51 (s, 4 H), 5.46 (d, *J* = 10.1 Hz, 1 H), 5.67 (ddd, *J* = 10.1, 3.3, 3.3 Hz, 1 H), 7.24–7.30 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 31.1, 37.1, 37.3, 38.7, 38.9, 39.2, 47.6, 73.1, 74.1, 76.1, 127.0, 127.1, 128.0, 128.8, 133.1, 138.7.

LRMS (EI): *m*/*z* = 376 [M^+], 285, 267, 267, 177, 159, 147, 131, 91.

Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57. Found: C, 82.89; H, 8.53.

2,2-Bis(benzyloxymethyl)-5-methyl-2,3,4,5,6,7-hexahydro-1*H*-indene (5d′)

IR (neat): 2920, 2846, 1453, 1361, 1099, 734, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 6.5 Hz, 3 H), 1.16–1.25 (m, 1 H), 1.43–1.54 (m, 1 H), 1.63–1.68 (m, 2 H), 1.90–1.94 (m, 3 H), 2.06–2.17 (m, 4 H), 3.42 (s, 2 H), 3.43 (s, 2 H), 4.52 (s, 4 H), 7.23–7.34 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8, 25.6, 29.2, 31.4, 34.3, 42.6, 42.8, 45.9, 73.2, 74.4, 127.2, 127.4, 128.2, 131.9, 132.0, 139.1.

LRMS (EI): *m*/*z* = 376 [M^+], 268, 177, 162, 147, 91.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{32}O_2$: 376.2402; found: 376.2399.

(*E*)-4,4-Bis(benzyloxymethyl)-1-(but-1-enyl)-2-methylcyclohexene (26b)

IR (neat): 2921, 2852, 1453, 1099, 734, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, *J* = 7.3 Hz, 3 H), 1.60 (dd, *J* = 6.5, 6.5 Hz, 2 H), 1.73 (s, 3 H), 1.99 (s, 2 H), 2.11–2.17 (m, 4 H), 3.34 (d, *J* = 8.8 Hz, 2 H), 3.40 (d, *J* = 8.8 Hz, 2 H), 4.48 (s, 4

H), 5.59 (dt, *J* = 15.7, 7.2 Hz, 1 H), 6.45 (d, *J* = 15.7 Hz, 1 H), 7.23–7.33 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 19.2, 22.1, 26.4, 26.4, 37.9, 38.1, 73.3, 73.5, 126.5, 127.1, 127.3, 127.3, 128.2, 128.6, 129.2, 139.1.

LRMS (EI): *m*/*z* = 390 [M$^+$], 282, 191, 176, 161, 149, 133, 91.

HRMS (EI): *m*/*z* calcd for $C_{27}H_{34}O_2$: 390.2559; found: 390.2564.

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