An Efficient Modular Synthesis of Conjugated ω-(*p*-Hexyloxyphenyl)-polyenals

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Abstract: Convenient precursors (α,β-unsaturated aldehydes **1**–**5)** for *all-E* conjugated ω-(*p*-hexyloxyphenyl)polyenals having two (**15**), four (**16**), five, (**19**), six (**17**) and eight (**18**) conjugated double bonds were synthesized in a modular synthesis using reactive silyl enol ethers [1-(trimethylsilyloxy)-1,3-butadiene or 1-(trimethylsilyloxy)-1,3,5-hexatriene)] as building blocks, and 5,5-diethoxypenta-2-enal (**1**) as a template. Polyene **8** containing three conjugated double bonds in its structure was obtained from ω-(*p*-hexyloxyphenyl)propenal (**6**) and butadienyl ethyl ether as starting materials.

Key words: acetals, aldehydes, aldol reactions, alkenes, eliminations

Conjugated polyene chains, consisting of alternating double and single carbon–carbon bonds, are widespread molecular architectures encountered in many systems (like carotenoids,[1] retinal proteins,[2] antibiotics,[3] metabolites,[4] natural pigments,[5] antioxidating agents[6]) exhibiting distinct biological activities. Terminally substituted conjugated *all-E* polyenes have often been used as model compounds for a variety of applications including electron transfer,[7] light harvesting,[7b,8] nonlinear optics,[9] and conductivity.[7a]

The central point of the synthesis of such π-conjugated structures consists mainly in the double bond-forming procedures to access given polyenic backbones, which can, therefore, be grafted on the electron-releasing and/or electron-withdrawing end groups. The polyene segment can be accessed either in a single step (by combining two carotenoide-type polyenes,[10] or via a sequential vinylic homologation.[11] In the latter case, a variety of polyene aldehyde and dialdehyde precursors, bearing various donor and/or acceptor units, have been extensively applied.[12]

The most representative method of the double-bond formation in the conjugated system is the Wittig reaction or one of its variants (Wittig–Horner, WH; Horner–Wadsworth–Emmons, HWE).[10,13] A site of unsaturation in the conjugated structure can also be generated by means of ring opening metathesis oligomerization,[14] retro-Diels–Alder reaction,[15] transition-metal-catalyzed reaction,[16] homocoupling reaction of unsaturated silanes[17] or allylboration reaction.[18] Knoevenagel condensation affords a possibility for incorporation of a double bond and donor or acceptor entity at one time and is commonly used to prepare conjugated polyenes with various functional groups.[19]

Although the synthetic achievements in the area of conjugated double-bond compounds are of great importance, they might be unsatisfactory for the structures containing more than five conjugated double bonds. Most of the known procedures[3b,11] for $n \geq 5$ reveal many by-products, low yields and poor or limited chemo- and stereoselectivity. In our paper we report a convenient synthetic approach for ω-(*p*-hexyloxyphenyl)polyenals containing between 2–6 and 8 double bonds in the molecular structure. Thus, in a modular synthesis, which involves reactive silyl enol ethers [i.e., 1-(trimethylsilyloxy)-1,3-butadiene and 1-(trimethylsilyloxy)-1,3,5-hexatriene[20]] as building blocks, a series of oligomeric precursors [i.e., 5,9,9-triethoxynona-2,6-dienal (**2**), 5,9,13,13-tetraethoxy-2,6,10-trienal (**3**), 5,9,13,17,17-pentaethoxyheptadeca-2,6,10,14-tetraenal (**4**), and 7,11,11-triethoxyundeca-2,4,8-trienal (**5**)] are obtained in a reaction which is related to aldol-type homologations. For the synthesis of 7-(4-hexyloxyphenyl)-5-ethoxyhepta-2,6-dienal (**7**) butadienyl ethyl ether had to be applied as building block. As shown in Schemes 1 and 2, we envisaged the use of 5,5-diethoxypenta-2-enal (**1**)[21] or ω-(*p*-hexyloxyphenyl)propenal (**6**) (both comprising conjugation in their structure) as a template to generate the chain extended derivatives.

Each particular step of the designed iterative process, independently of the applied template, involves two steps. The first one (reaction 1 in Schemes 1 and 2) denotes the acetalization of respective α,β-unsaturated aldehyde with triethyl orthoformate in the presence of pyridinium *p*-toluenesulfonate (PPTS). The second one (reaction 2 in Schemes 1 and 2) represents the reaction of the nucleophilic building block to the above mentioned acetal in the presence of catalytic amounts of $ZnCl_2$, giving rise to δ-ethoxy-α,β-unsaturated aldehydes. The presented synthetic approach allowed to access precursors **2**–**5** and **7** with yields of 82%, 86%, 78%, 60% and 80%, respectively. All these compounds were found to be well soluble in organic solvents and showed chemical stability. Additionally, the derivatives **2**–**5** are well suited to a nucleophilic reaction with a Grignard reagent (Scheme 3). Thus, by reacting the

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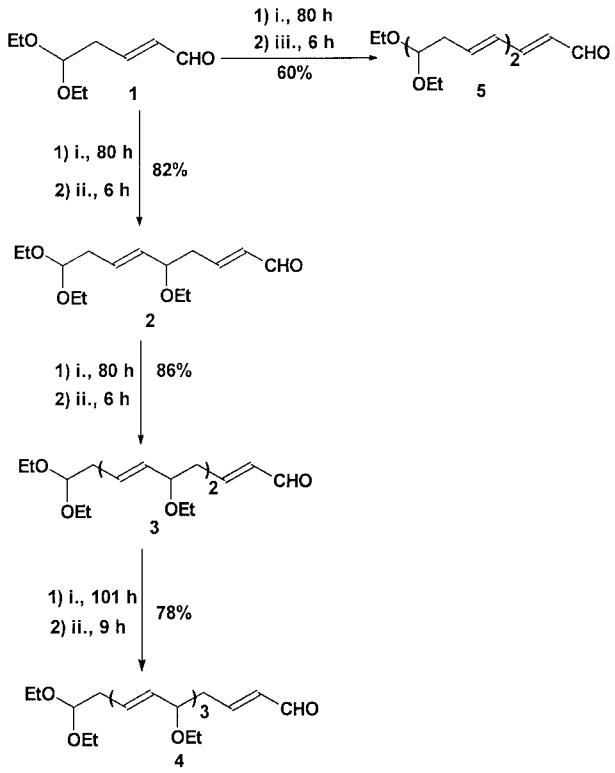
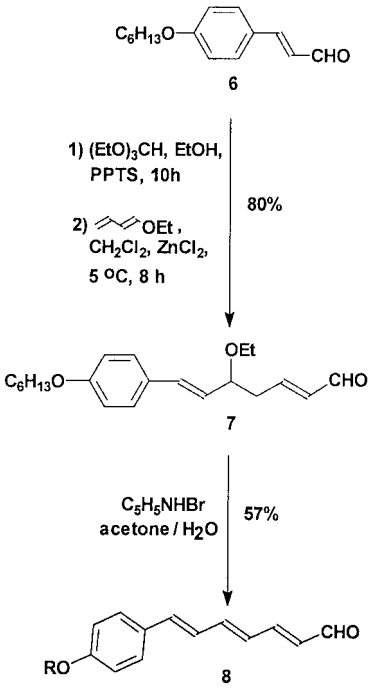


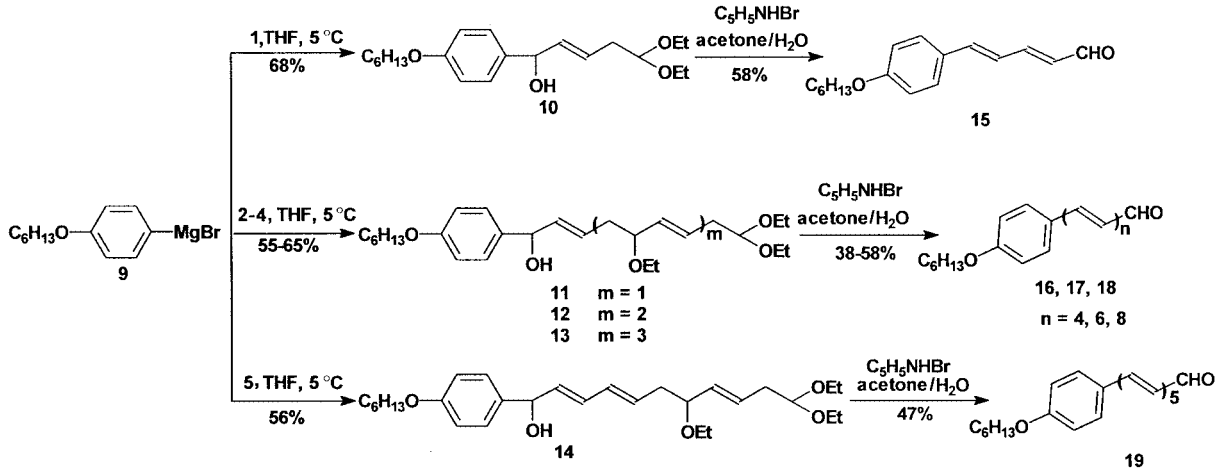
Scheme 1 i. $(EtO)_3OH$, EtOH, PPTS, r.t., ii. CH_2=CHCH=CHOSiMe_3, $ZnCl_2$, Et_2O, 5 °C, iii. CH_2=CH(CH=CH)$_2$OSiMe_3, $ZnCl_2$, Et_2O, 5 °C.



Scheme 2

alkoxyphenylmagnesium bromide **9** with compounds **1**–**5** under the standard Grignard reaction conditions[22] the adducts **10**–**14** could be obtained in 68%, 65%, 59%, 55% and 56% yield, respectively. In order to complete the synthesis of conjugated ω-(*p*-hexyloxyphenyl)polyenals, water or/and ethanol must be eliminated, double bonds shifted and the acetal moiety hydrolyzed in a cascade of four simultaneous reactions. The intermediates are carbocations, which are stable because of their allylic character.[23] The mentioned process carried out in the presence of pyridinium hydrobromide[24] (Schemes 2 and 3) give thermodynamically stable pure *all-E* isomers comprising two, three, four, five, six and eight double bonds. The overall yields for the given series of amphiphilic conjugated polyenes **8** and **15**–**19** ranged between 40–49%.

All synthesized precursors **1**–**5** (structures **1** and **2** have previously been reported[21]) and conjugated polyenals **8** and **15**–**19** were purified by column chromatography or/and radial chromatography in darkness under N_2 and identified unambiguously by NMR and IR spectroscopy. The structure and stereochemistry of precursors **1**–**5**, **7** and conjugated polyenals **8** and **15**–**19** were studied by ^{1}H NMR spectroscopy using one- (^{1}H, ^{13}C) and two-dimensional spectra (^{1}H-^{1}H and ^{1}H-^{13}C correlated spectroscopy - COSY). At 300 MHz these two methods allowed identi-



Scheme 3

fication of almost all protons of the studied polyenic chains and determination of the coupling constants $J_{CH=CH}$ (14.0–14.5 Hz and 14.7–15.5 Hz for precursors **1**–**5** and polyenals, respectively) and J_{CH-CH} (6.1–7.7 Hz and 10.2–11.2 Hz for precursors **1**–**5** and polyenals **8** and **15**–**19**, respectively), which are characteristic for *all-E* structures.[25] The stereochemical homogeneity of all obtained aldehyde structures was evidenced by the presence of a single doublet (at about 9.5 ppm for structures **1**–**5** and 9.6 ppm for **8** and **15**–**19**) corresponding to the CHO.

Summing up, we have described a new efficient synthetic route to obtain a number of polyene aldehydes containing long polyenic backbones − convenient reagents for the synthesis of push-pull structures.[26] The obtained π-conjugated skeletons do not deform into bond alternant geometry.[27] The presented synthetic approach reveals the following features: rapid construction of carbon skeleton, readily available building blocks, chemical stability of intermediate products, chemical versatility of precursors, conjugation state systems, which sometimes can be unstable, generated under mild conditions in the last synthetic step and *all-E* configuration of the π system.

Starting materials were of the highest commercial quality and were used without further purification. 5,5-Diethoxypenta-2-enal (**1**), 5,9,9-triethoxynona-2,6-dienal (**2**) and 1-(trimethylsilyloxy)-1,3,5-hexatriene were synthesized as published in the literature.[20, 21] All reactions were carried out under a protective atmosphere of N_2 gas using oven-dried glassware. THF was freshly distilled from $LiAlH_4$ prior to use. Electrospray ionization (ESI) spectra were obtained with a Finnigan TSQ-700 mass spectrometer (San Jose, CA). Mps were determined on a Kofler block and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AMX-300 spectrometer (Karlsruhe, Germany). ^{1}H chemical shifts (at 300.13 MHz) are referenced in $CDCl_3$ to residual protons of $CDCl_3$ (7.24 ppm). Coupling constants (*J*) are given in Hz. ^{13}C chemical shifts we determined at 75.5 MHz with the $CDCl_3$ signal as reference (77.5 ppm). IR spectra were obtained on a Perkin Elmer System 2000 FT-IR spectrometer. Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer (Norwalk, CT). Chromatographic purification was accomplished by column chromatography using Silica Gel 60 (Merck, particle size 70–230 mesh) or/and radial chromatography[28] at 60 rpm on Silica Gel 60 GF_{254} (Merck, layer thickness 2 mm, flow rate 6 mL/min) with Chromatotron apparatus (Harrison Research).

5,9,13,13-Tetraethoxydodeca-2,6,9-trienal (3)

A mixture of **2** (13.0 g, 48 mmol), $CH(OEt)_3$ (10 mL, 60 mmol) and PPTS (100 mg, 0.40 mmol) in anhyd Et_2O (10 mL) was stirred at r.t. for 80 h. Then the mixture was poured into 5% aq NH_4OH solution (50 mL) and the aqueous layer was extracted with Et_2O (4 × 100 mL). The combined organic layers were washed with brine, dried with K_2CO_3 and the solvent was evaporated under reduced pressure. Then the residual oil was dissolved in a solution of $ZnCl_2$ (1.0 g, 7.34 mmol) in anhyd Et_2O (5 mL), 1-trimethylsilyloxy-1,3-butadiene (10.0 g, 70 mmol) in anhyd Et_2O (10 mL) was added dropwise. After 6 h of stirring at 5 °C the reaction mixture was poured into cold water (200 mL) and Et_2O (200 mL) was added. The organic phase was washed with brine, dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography (hexane–EtOAc, 3:1 v/v). Yield: 15.20 g (86%). Spectroscopic data are reported in Table 1.

Table 1 Compounds **3**–**5**

Compd.	Yield	^{1}H NMR[a] δ, ppm (J [Hz])	IR (film, cm^{-1})	MS (MH^+)[b]
3	86%	1.2 (4 × t, 12 H), 1.82–1.98 (m, 4 H), 2.24 (dd, 2 H, *J* = 5.8, 6.6), 3.5 (m, 8 H), 4.16–4.21 (m, 2 H), 4.66 (t, 1 H, *J* = 5.8), 5.60 (2 × dd, 2 H), 5.79 (2 × dd, 2 H), 6,05 (dd, 1H, *J* = 7.8, 14.9), 6.8 (dd, 1 H, *J* = 14.0, 6.1), 9.51 (d, 1 H, *J* = 7.8).	3363, 3020, 2935, 2811, 2745, 1695, 1659, 1478, 1443, 1368, 1345, 1225, 1218, 1212, 1136, 1125 , 1058, 972, 965, 920, 851, 554.	369.1
4	78%	1.23 (5 × t, 15 H, *J* = 7.0), 1.78–1.98 (m, 6 H), 2.25 (dd, 2 H, *J* = 5.9, 6.7), 3.52 (m, 10 H), 4.18–4.23 (m, 3 H), 4.68 (t, 1 H, *J* = 5.9), 5.58 (3 × dd, 3 H), 5.80 (3 × dd, 3 H), 6.07 (dd, 1 H, *J* = 7.7, 14.4), 6.81 (dd, 1 H, *J* = 14.5, 7.7), 9.48 (d, 1 H, *J* = 7.9).	3369, 3025, 2930, 2795, 1700, 1668, 1473, 1445, 1370, 1340, 1250, 1210, 1140, 1122, 1218, 1055, 970, 960, 921, 852, 549.	467.1
5	60%	1.19 (t, 9 H, *J* = 6.8), 2.28 (dd, 2 H, *J* = 6.8, 5.7), 2.6 (dd, 2 H, *J* = 6.6, 5.8), 3.51 (m, 6 H), 4.15 (m, 1 H), 4.68 (t, 1 H, *J* = 5.65), 5.65 (dd, 1 H, *J* = 14.1, 6.2), 5.8 (dd, 1 H, *J* = 14.1, 7.0), 6.05 (dd, 1 H, J = 7.8, 14.8), 6.16 (dd, 1 H, *J* = 7.2, 15.1), 6.8 (m, 1 H), 6.82 (dt, 1 H, *J* = 7.0, 15.2), 9.48 (d, 1 H, *J* = 8.2).	3360, 3025, 2930, 2795, 1700, 1668, 1670, 1473, 1445, 1370, 1340, 1250, 1210, 1140, 1122, 1218, 1055, 970, 960, 921, 852, 549.	296.2

[a] $CDCl_3$.
[b] ESI−MS.

Anal. Calcd for $C_{21}H_{36}O_5$ (368.51): C, 68.45; H, 9.85. Found: C, 68.70; H, 9.75.

5,9,13,17,17-Pentaethoxyheptadeca-2,6,10,14-tetraenal (4)

A mixture of **3** (8.0 g, 22 mmol), $CH(OEt)_3$ (10 mL, 60 mmol) and PPTS (100 mg, 0.40 mmol) in anhyd Et_2O (10 mL) was stirred at r.t. for 85 h. Then the mixture was poured into 5% aq NH_4OH solution (50 mL) and the aqueous layer was extracted with Et_2O (4 × 100 mL). The combined organic layers were washed with brine, dried with K_2CO_3 and the solvent was evaporated under reduced pressure. Then the residual oil was dissolved in a solution of $ZnCl_2$ (1.0 g, 7.34 mmol) in anhyd Et_2O (5 mL). To this mixture 1-trimethylsilyloxy-1,3-butadiene (3.3 g, 23 mmol) in anhyd Et_2O was added dropwise. After 9 h of stirring at 5 °C the reaction mixture was poured into cold water (200 mL) and Et_2O (200 mL) was added. The organic phase was washed with brine, dried with $MgSO_4$ and evaporated. The residue was purified by flash and then radial chromatography (hexane–EtOAc, 3:1 v/v). Yield: 8.0 g (78%). Spectroscopic data are reported in Table 1.

Anal. Calcd for $C_{27}H_{46}O_6$ (466.66): C, 69.49; H, 9.94. Found: C, 69.66; H, 9.78.

1-(Trimethylsilyloxy)-1,3,5-hexatriene
The labile 1-(trimethylsilyloxy)-1,3,5-hexatriene was obtained according to the method described by Iqubal and Khan[20a] starting from 2,4-hexadienal (12.50 g, 130 mmol) and Me_3SiCl (13.60 g, 125 mmol). The product was distilled under reduced pressure (12 mmHg, 78–80 °C, Lit. 90–100 °C/10 mmHg[20a]) and immediately used after distillation. Yield: 13.40 g (63.5%, lit. 60%[20]).

Anal. Calcd for $C_9H_{16}OSi$ (168.31): C, 64.23; H, 9.58. Found: C, 64.01; H, 9.66.

7,11,11-Triethoxyundeca-2,4,8-trienal (5)
A mixture of **1** (8.0 g, 22 mmol), $CH(OEt)_3$ (10 mL, 60 mmol) and PPTS (100 mg, 0.40 mmol) in anhyd Et_2O (10 mL) was stirred at r.t. for 80 h. Then the mixture was poured into 5% aq NH_4OH solution (50 mL) and the aqueous layer was extracted with Et_2O (4 × 80 ml). The combined organic layers were washed with brine, dried with K_2CO_3 and the solvent was evaporated under reduced pressure. 1-Trimethylsilyloxy-1,3,5-hexatriene (11.0 g, 36 mmol) in anhyd Et_2O (20 mL) was then added dropwise to a well-stirred, ice-cooled solution of bis-acetal and $ZnCl_2$ (1.0 g, 7.34 mmol) in anhyd Et_2O (20 mL). After 36 h of stirring at 5 °C the reaction mixture was poured into ice-water (100 mL). The organic phase was shaken with sat. aq $NaHCO_3$ solution and water, dried with $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by column chromatography (hexane–EtOAc, 3:1 v/v). Yield: 5.30 g (60%). Spectroscopic data are reported in Table 1.

Anal. Calcd for $C_{17}H_{28}O_4$ (296.41): C, 68.89; H, 9.52. Found: C, 68.61; H, 9.66.

3-(4-Hexyloxyphenyl)propenal (6)
The synthesis was performed according to the procedure described by Reddy et al.,[29] starting from 4-hexyloxybenzaldehyde. Spectroscopic data for **6** are reported in Table 2. Mp. 32–34 °C.

Anal. Calcd for $C_{15}H_{20}O_2$ (232.32): C, 77.55; H, 8.68. Found: C, 77.37; H, 8.77.

7-(4-Hexyloxyphenyl)-5-ethoxyhepta-2,6-dienal (7)
A mixture of **6** (7.0 g, 30 mmol), $CH(OEt)_3$ (10 ml, 60 mmol) and PPTS (100 mg, 0.40 mmol) in anhyd Et_2O (25 mL) was stirred at r.t. for 10 h. Then the mixture was poured into 5% aq NH_4OH solution (50 mL) and the aqueous layer was extracted with Et_2O (4 × 80 mL). The combined organic layers were washed with brine, dried with K_2CO_3 and the solvent was evaporated under reduced pressure. A solution of $ZnCl_2$ (2.0 g, 14.68 mmol) in EtOAc (5 mL) was then added to a well-stirred ice-cooled solution of acetal (27 mmol) and butadienyl ether (4.0 g, 41 mmol) in CH_2Cl_2 (30 mL). After 3 h of stirring at 5 °C and 5 h at r.t. the reaction mixture was poured into cold water and CH_2Cl_2 was added. The phases were separated, the organic phase washed with water, dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (silicagel, hexane–isopropylether, 7:3 v/v) to give 7.90 g (80%) of **7**.

Anal. Calcd for $C_{21}H_{30}O_3$ (330.47): C, 76.33; H, 9.15. Found: C, 76.15; H, 9.28.

^{1}H NMR: δ = 0.91 (t, 3 H, *J* = 7.1), 1.2 (m, 3 H), 1.32–1.80 (m, 6 H), 1.82 (m, 2 H, *J* = 6.7), 2.5 (m, 2 H), 3.9 (t, 2 H, *J* = 6.8), 3.5 (m, 3 H), 4.17 (m, 1 H), 5.65 (dd, 1 H, *J* = 6.6, 14.8), 6.10 (dd, 1 H, *J* = 8.0, 15.0), 6.25 (d, 1 H, *J* = 14.9), 6.7–6.9 (m, 3 H), 7.33 (d, 2 H), 9.51 (d, 1 H, *J* = 8.1).

7-(4-Hexyloxyphenyl)hepta-2,4,6-trienal (8)
To a solution of **7** (6.60 g, 20 mmol) in acetone (30 mL) was added pyridine hydrobromide (0.60 g), H_2O (2 mL) and HBr (62%, two drops). The reaction mixture was stirred at r.t. for 24 h and at 50 °C for 10 h. Then the reaction mixture was cooled to –15 °C and filtered to remove the solid, which was washed with cold acetone and dried under reduced pressure. The products were crystallized from CH_3CN to obtain red-brown fine crystals, mp. 91–93 °C. Spectroscopic data for **8** are reported in Table 2.

Anal. Calcd for $C_{19}H_{24}O_2$ (284.40): C, 80.24; H, 8.51. Found: C, 80.09; H, 8.66.

Compounds 10–14; General Procedure
To a stirred solution of freshly obtained Grignard reagent **9** (10 mmol) in anhyd THF (20 mL) solution was added the appropriate acetal **1**–**5** (10 mmol) in anhyd THF (50 mL) at 5 °C. Then the mixture was stirred at 5 °C for 2–6 h and at r.t. for 1 h. The crude product was isolated by liquid chromatography (hexane–AcOEt, 3:1).

5-(4-Hexyloxyphenyl)-1,1-diethoxy-5-hydroxypenta-3-ene (10)
Yield 2.40 g (68%).

Anal. Calcd for $C_{21}H_{34}O_4$ (350.5): C, 71.96; H, 9.78. Found: C, 71.66; H, 9.89.

^{1}H NMR: δ = 0.9 (t, 3 H, *J* = 6.9), 1.20 (t, 6 H, *J* = 7.2), 1.30–1.83 (m, 8 H), 2.46 (dd, 2 H, *J* = 5.8), 3.50–3.65 (m, 4 H), 3.97 (t, 2 H, *J* = 6.54), 4.39–4.5 (ddt, 2 H), 5.59 (dd, 1 H, *J* = 9.4, 14.9), 5.70 (d, 1 H, *J* = 9.0), 6.02 (dd, 1 H, *J* = 6.9, 14.0), 6.86 (d, 2 H, *J* = 8.7), 7.36 (d, 2 H, *J* = 8.8).

IR (film): 3430, 2932, 2870, 1724, 1676, 1618, 1591, 1512, 1467, 1422, 1266, 1239, 1154, 1139, 1122, 1083, 1014, 969, 801, 754, 613 cm^{-1}.

9-(4-Hexyloxyphenyl)-1,1,5-triethoxy-9-hydroxynona-3,7-diene (11)
Yield: 2.90 g (65%).

Anal. Calcd for $C_{27}H_{44}O_5$ (448.64): C, 72.28; H, 9.89. Found: C, 72.11; H, 9.99.

^{1}H NMR: δ = 0.90 (t, 3 H, *J* = 7.0), 1.18 (t, 9 H, *J* = 7.1), 1.31–1.83 (m, 8 H), 2.08 (dd, 2 H, *J* = 6.0), 2.50 (dd, 2 H, *J* = 5.9, 6.0), 3.40 (m, 6 H), 3.97 (t, 2 H, *J* = 7.1), 4.0 (m, 1 H), 4.38–4.48 (ddt, 2 H), 5.60 (dd, 1 H, *J* = 8.8, 14.6), 5.72 (d, 1 H, *J* = 8.8), 5.85 (m, 1 H), 6.0 (dd, 1 H, *J* = 7.1, 14.0), 6.68 (m, 1 H), 6.88 (d, 2 H, *J* = 8.8), 7.34 (d, 2 H, *J* = 8.9).

IR (film): 3433, 2930, 2869, 1728, 1680, 1610, 1599, 1515, 1466, 1420, 1270, 1235, 1150, 1135, 1119, 1091, 1015, 971, 800, 754 cm^{-1}.

13-(4-Hexyloxyphenyl)-1,1,5,9-tetraethoxy-13-hydroxy-trideca-3,7,9-triene (12)
Yield: 3.20 g (59%).

Anal. Calcd for $C_{33}H_{54}O_6$ (546.79): C, 72.49; H, 9.95. Found: C, 72.31; H, 10.1.

^{1}H NMR: δ = 0.91 (t, 3 H, *J* = 7.0), 1.18, (4 × t, 12 H, *J* = 6.8), 1.29–1.85 (m, 8 H), 2.1 (dd, 2 H, *J* = 6.0), 2.50 (dd, 2 H, *J* = 6.0), 2.55 (dd, 2 H, *J* = 6.0), 3.35 (m, 8 H), 4.00 (m, 2 H), 4.05 (t, 2 H, *J* = 7.1), 4.39–4.49 (dd+t, 2 H), 5.62, (dd, 1 H, *J* = 6.9, 15.0), 5.71 (d, 1 H, *J* = 8.9), 5.90 (m, 3 H), 6.10 (dd, 1 H, *J* = 7.1, 14.2), 6.68 (m, 1 H), 6.85 (d, 2 H, *J* = 8.6), 7.41 (d, 2 H, *J* = 8.8).

IR (film): 3624, 3035, 3023, 2845, 1670, 1632, 1550, 1514, 1462, 1382, 1230, 1235, 1157, 1050, 970, 790 cm^{-1}.

17-(4-Hexyloxyphenyl)-1,1,5,9,13-pentaethoxy-17-hydroxy-heptadeca-3,7,11,15-tetraene (13)
Yield: 3.41 g (55%).

Anal. Calcd for $C_{39}H_{64}O_7$ (644.93): C, 72.63; H, 10.00. Found: C, 72.41; H, 10.15.

^{1}H NMR: δ = 0.91 (t, 3 H, *J* = 6.9), 1.2 (5 × t, 15 H, *J* = 6.8), 1.27–1.84 (m, 8 H), 2.1 (dd, 2 H, *J* = 6.2), 2.49 (m, 6 H), 3.35 (m, 10 H), 4.0 (t, 2 H, *J* = 7.1), 4.1 (m, 3 H), 4.39–4.45 (tdd, 2 H), 5.62 (dd, 1 H, *J* = 15, 7.0), 5.70 (d, 1 H, *J* = 8.9), 5.85 (m, 2 H), 5.91 (m, 3 H), 6.1 (dd, 1 H, *J* = 7.0, 14.2), 6.68 (m, 1 H), 6.81 (d, 2 H, *J* = 8.8), 7.40 (d, 2 H, *J* = 8.9).

IR (film): 3625, 3033, 3025, 2850, 1668, 1630, 1625, 1548, 1515, 1460, 1380, 1350, 1232, 1234, 1152, 1051, 967, 788 cm^{-1}.

11-(4-Hexyloxyphenyl)-1,1,5-triethoxy-11-hydroxyundecka-3,7,9-triene (14)

Yield: 2.63 g, 56%.

Anal. Calcd for $C_{29}H_{46}O_5$ (474.68): C, 73.38; H, 9.77. Found: C, 73.18; H, 9.93.

^{1}H NMR: δ = 0.89 (t, 3 H, *J* = 6.9), 1.2 (3 × t, 9 H, *J* = 7.1), 1.25 – 1.82 (m, 8 H), 2.2 (dd, 2 H, *J* = 6.2, 7.0), 2.50 (m, 2 H), 3.35 (m, 6 H), 3.97–4.15 (m, 4 H), 4.93 (t, 1 H, *J* = 6.9), 5.67 (m, 1 H), 5.72 (d, 1 H, 8.9), 5.70 (dd, 1 H, *J* = 7.1, 15, 0), 6.08–6.16 (2 × dd, 2 H), 6.79 (d, 2 H, *J* = 8.8), 6.80–6.83 (m, 2 H), 7.38 (d, 2 H, *J* = 8.8).

IR (film): 3625, 3033, 3025, 2850, 1668, 1630, 1625, 1548, 1515, 1460, 1380, 1350, 1232, 1234, 1152, 1051, 967, 788 cm^{-1}.

Table 2 Amphiphilic Conjugated Polyenes $C_6H_{13}OC_6H_4(CH{=}CH)_nCHO$

Compd.	Yield	^{1}H NMR[a] δ, ppm (*J*, Hz)	^{13}C NMR[a] δ, ppm	IR (cm^{-1})	MS[b] (MH^+)
6	40%	0.90 (t, 3 H, *J* = 6.9), 1.30–1.80 (m, 6 H), 1.81 (m, 2 H, *J* = 6.5), 3.99 (t, 2 H, *J* = 6.6), 6.35 (dd, 1 H, *J* = 15.4, 7.8), 6.95 (d, 2 H, *J* = 8.7), 7.40 (d, 1 H, *J* = 15.4), 7.50 (d, 2 H, *J* = 8.7), 9.60 (d, 1 H, *J* = 7.71).	14.7, 23.09, 26.5, 29.9, 33.8, 66.1, 111.0 (2C), 123.0, 127.1 (2C), 149.1, 151.4, 152.5, 193.3.	2932, 2859, 1677, 1621, 1602, 1571, 1512, 1250, 1175, 1127, 971	233.1
8	57%	0.90 (t, 3 H, *J* = 6.9), 1.29–1.80 (m, 6 H), 1.80 (m, 2 H, *J* = 6.6), 3.97 (t, 2 H, *J* = 6.5), 6.21 (dd, 1 H, *J* = 15.2, 7.9), 6.55 (dd, 1 H, *J* = 14.4, 11.3), 6.78 (d, 1 H, *J* = 14.8), 6.82 (dd, 1 H, *J* = 14.5, 11.2), 6.85 (d, 2 H, *J* = 8.7), 6.89 (dd, 1 H, *J* = 14.7, 11.2), 7.19 (dd, 1 H, *J* = 15.1, 11.2), 7.36 (d, 2 H, *J* = 8.6), 9.56 (d, 1 H, *J* = 8.0)	14.4, 23.3, 26.0, 29.8, 33.1, 66.1, 112.0 (2C), 120.9, 126.5, 128.5 (2C), 131.0, 138.8, 142.6, 146.8, 152.6, 155.4, 193.3	3023, 2940, 2857, 1665, 1622, 1586, 1510, 1472, 1423, 1408, 1395, 1314, 1302, 1291, 1237, 1256, 1177, 1146, 1109, 1058, 1027, 1019, 997, 858, 826, 796, 730, 644, 626, 593, 528	285.1
15	58%	0.90 (t, 3 H, *J* = 6.9), 1.30–1.79 (m, 6 H), 1.80 (m, 2 H, *J* = 6.6), 3.97 (t, 2 H, *J* = 6.54), 6.21 (dd, 1 H, *J* = 15.1, 8.0), 6.84 (d, 1 H, *J* = 15.7), 6.91 (dd, 1 H, *J* = 10.2, 15.7), 6.97 (d, 2 H, *J* = 8.7), 7.24 (dd, 1 H, *J* = 15.1, 10.2), 7.43 (d, 2 H, *J* = 8.8), 9.58 (d, 1 H, *J* = 8.0)	14.8, 23.1, 27.0, 29.4, 33.6, 66.1, 118 (2C), 121.3, 124.0, 128.5 (2C), 130.9, 142.6, 150.0, 152.0, 193.3	2940, 2851, 1665, 1590, 1510, 1471, 1396, 1309, 1249, 1180, 1028, 970, 844, 796, 640	259.2
16	58%	0.90 (t, 3 H, *J* = 7.0), 1.30–1.81 (m, 6 H), 1.83 (m, 2 H, *J* = 6.5), 3.96 (t, 2 H, *J* = 6.9), 6.16 (dd, 1 H, *J* = 7.9, 15.2), 6.39 (dd, 1 H, *J* = 15.1, 11.2), 6.45 (dd, 1 H, *J* = 11.0, 15.2), 6.62–6.64 (2 × dd, 2 H), 6.72–7.75 (2 × dd, 2 H), 6.90 (dd, 2 H, *J* = 8.7), 7.13 (dd, 1 H, *J* = 11.0, 15.0), 7.40 (dd, 2 H, *J* = 8.8), 9.63 (d, 1 H, J_{HH} = 8.0)	15.0, 22.8, 26.1, 29.2, 33.5, 59.9, 119.9 (2C), 120.9, 126.3 (2C), 129.0, 130.3, 130.6, 132.5, 136.5, 139.6, 142.2, 150.1, 152.5, 193.2	3022, 2950, 2858, 1730, 1640, 1620, 1601, 1575, 1511, 1248, 1180, 1025, 975, 835, 795, 645, 615, 532	311.2
17	47%	0.91 (t, 3 H, *J* = 6.9), 1.33–1.80 (m, 6 H), 1.82 (m, 2 H, *J* = 6.6), 3.94 (t, 2 H, *J* = 6.5), 6.24 (dd, 1 H, *J* = 15.3, 7.3), 6.32–6.45 (4 × dd, 4 H), 6.54–6.58 (3 × dd, 3 H), 6.55 (d, 1 H, *J* = 15.0), 6.72 – 6.75 (2 × dd, 2 H), 6.84 (d, 2 H, *J* = 8.7), 7.13 (dd, 1 H, *J* = 10.1, 15.1), 7.35 (d, 2 H, *J* = 8.7), 9.56 (d, 1 H, *J* = 8.3)	14.1, 22.7, 25.7, 29.2, 31.6, 68.1, 114.8 (2C), 126.8, 127.8 (2C), 129.7, 130.7, 131.3, 131.8, 133.9, 136.1, 137.0, 139.1, 142.8, 143.6, 149.9, 151.8, 159.2, 193.5.	3027, 2961, 2937, 2853, 1677, 1586, 1508, 1471, 1392, 1302, 1289, 1254, 1237, 1175, 1146, 1118, 1109, 1026, 1011, 989, 923, 855, 828, 795, 643, 625, 533	363.1
18	38%	0.91 (t, 3 H, *J* = 6.9), 1.33–1.80 (m, 6 H), 1.82 (m, 2 H, *J* = 6.6), 3.94 (t, 2 H, *J* = 6.9), 6.24 (dd, 1 H, *J* = 15.5, 7.9), 6.32–6.45 (6 × dd, 6 H), 6.54–6.58 (5 × dd, 5 H), 6.55 (d, 1 H, *J* = 15.0), 6.72–6.75 (2 × dd, 2 H), 6.84 (d, 2 H, *J* = 8.8), 7.23 (dd, 1 H, *J* = 10.5, 15.5), 7.34 (d, 2 H, *J* = 8.8), 9.56 (d, 1 H, *J* = 8.3)	14.0, 22.6, 25.7, 29.3, 31.7, 66.2, 111.2 (2C), 120.3, 126.9, 127.9 (2C), 129.6, 130.2, 130.8, 131.2, 131.7, 134.7, 136.2, 137.8, 138.5, 139.2, 142.8, 143.2, 146.8, 149.0, 149.5, 151.8, 193.4		415.2
19	47%	0.90 (t, 3 H, *J* = 6.9), 1.34–1.82 (m, 6 H), 1.83 (m, 2 H, *J* = 6.5), 3.97 (t, 2 H, *J* = 6.6), 6.15 (dd, 1 H, *J* = 15.0, 8.0), 6.36–6.45 (3 × dd, 3 H), 6.53–6.56 (2 × dd, 2 H), 6.58 (d, 1 H, *J* = 14.9), 6.72–6.75 (2 × dd, 2 H), 6.84 (d, 2 H, *J* = 8.8), 7.32 (dd, 1 H, *J* = 15.2, 11.0), 7.48 (d, 2 H, *J* = 8.8), 9.56 (d, 1 H, *J* = 8.3).	14.3, 22.6, 25.7, 29.2, 31.9, 66.1, 111.9 (2C), 120.8, 126.1 (2C), 129.4, 130.1, 130.5, 131.0, 131.6, 134.4, 137.1, 139.2, 142.9, 151.9, 193.5	3022, 2950, 2858, 1731, 1640, 1636, 1630, 1625, 1601, 1575, 1511, 1248, 1180, 1025, 975, 832, 793, 645, 610, 531	337.2

[a] $CDCl_3$. [b] ESI−M.

(4-Hexyloxyphenyl)polyenals $C_6H_{13}OC_6H_4(CH=CH)_nCHO$ 15–19 (n = 2, 4, 5, 6, 8); General Procedure

The appropriate acetal (**10–14**) was added to a solution of a pyridine hydrobromide (0.10 g, 600 mmol) in acetone containing water (0.2 mL). The mixture was stirred at 40 °C for 20–46 h, then poured into cold water (25 mL) and extracted with anhyd Et_2O (2 × 25 mL). The organic phase was washed with cold water, dried with $MgSO_4$ and evaporated. The residue was purified first by column and than by radial chromatography (hexane–EtOAc, 3:1→ 4:1) to give polyenals **15–19**. Yields and spectroscopic data for polyenals **15–19** are reported in Table 2.

(2*E*,4*E*)-5-(4-Hexyloxyphenyl)penta-2,4-dienal (15)

Pale, fine, yellow crystals, mp 76–78 °C.

Anal. Calcd for $C_{17}H_{22}O_2$ (258.36): C, 79.03; H, 5.58. Found: C, 78.99; H, 5.64.

(2*E*,4*E*,6*E*,8*E*)-9-(4-Hexyloxyphenyl)nona-2,4,6,8-tetraenal (16)

Brown, fine crystals, mp 100–101 °C.

Anal. Calcd for $C_{21}H_{26}O_2$ (310.44): C, 81.25; H, 8.44. Found: C, 81.12; H, 8.52.

(2*E*,4*E*,6*E*,8*E*,10*E*,12*E*)-13-(4-Hexyloxyphenyl)trideca-2,4,6,8,10,12-hexaenal (17)

Brown, fine crystals, mp 121–123 °C.

Anal. Calcd for $C_{25}H_{30}O_2$ (362.51): C, 72.43; H, 8.34. Found: C, 72.2; H, 8.21.

(2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*)-17-(4-Hexyloxyphenyl)-heptadeca-2,4,6,8,10,12,14,16-octaenal (18)

Dark, brown solid, mp 135–137 °C.

Anal. Calcd for $C_{29}H_{34}O_2$ (414.59): C, 84.02; H, 8.27. Found: C, 83.9; H, 8.3.

(2*E*,4*E*,6*E*,8*E*,10*E*)-11-(4-Hexyloxyphenyl)undeca-2,4,6,8,10-pentaenal (19)

Brown, fine crystals, mp 113–115 °C.

Anal. Calcd for $C_{23}H_{28}O_2$ (336.47): C, 82.1; H, 8.39. Found: C, 82.0; H, 8.50.

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