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O-Trimethylsilylenol ethers as versatile building blocks in a modular preparation of polyenic backbone

Beata W. Domagalska,[a] Ludwik Syper[b] and Kazimiera A. Wilk[a,*]

[a]*Institute of Organic and Polymer Technology, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*
[b]*Institute of Organic Chemistry, Biochemistry and Biotechnology, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

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Abstract—Versatility and synthetic potential of 1-(trimethylsilyloxy)-1,3-butadiene, 1-(trimethylsilyloxy)penta-1,3-diene, and their methyl substituted derivatives have been demonstrated in a modular synthetic methodology of stereodefined π-conjugated unsymmetrical, symmetrical two-dimensional, and octupolar polyenal structure.

1. Introduction

The conjugated polyenic backbone is an important structural unit in macrolide antibiotics and various classes of natural products (e g., retinoic acids, chrysophysarin A).[1] It has also been shown that conjugated polyenes can be used as model compounds for a variety of applications including electron transfer,[2] light harvesting,[3] nonlinear optics,[4,5] and conductivity[2] and are potentially useful compounds for electronic and non-linear optical materials.[6] Thus, it is not surprising that considerable efforts have been made to search for stereoselective methods of synthesis of such conjugated systems.

In the literature, the most common strategy of double-bond formation in the conjugated system is the Wittig reaction or one of its variants (Wittig–Horner, WH; Horner–Wadsworth–Emmons, HWE).[7] A site of unsaturation in the conjugated structure can also be generated by means of, for example, ring opening metathesis oligomerization,[8] retro-Diels–Alder reaction,[9] transition-metal-catalyzed reaction,[10] homocoupling reaction of unsaturated silanes[11] or allylboration reaction[12] and hydrozirconation-cross-coupling.[13] Knoevenagel condensation affords a possibility for incorporation of double bond, and donor or acceptor entity at one time and is commonly used to prepare conjugated polyenes with various functional groups.[14,15]

In our previous studies dealing with the synthesis of stereodefined (pure *all*-E) π-conjugated polyenes[16] we have devised new methodology for the synthesis of a polyenic backbone starting from 5,5-diethoxypenta-2-enal as a template and using 1-(trimethylsilyloxy)-1,3-butadiene as a building block. This modular method was successfully applied to the synthesis of linear, unsymmetrical amphiphilic conjugated *all*-E polyenals (ω,ω′-(*p*-alkoxyphenyl)-polyenals)[16] containing up to eight double bonds.

The main purpose of the present contribution is to illustrate the versatility and the efficient synthetic potential of *O*-trimethylsilylenol ethers (1-(trimethylsilyloxy)-1,3-butadiene **8**, 1-(trimethylsilyloxy)penta-1,3-diene **4** and their methyl substituted derivatives **5–7**) for the stereoselective preparation of unsymmetrical as well as symmetrical and octupolar conjugated polyenals with and without the methyl groups in the polyenic backbone. We generalize the modular method by use of 1-(trimethylsilyloxy)penta-1,3-diene **4**, 3-methyl-1-(trimethylsilyloxy)-1,3-butadiene **5**, 2-methyl-1-(trimethylsilyloxy)-1,3-butadiene **6**, 2-methyl-1-(trimethylsilyloxy)penta-1,3-diene **7** as building blocks and new templates (4-hexyloxy-3-methoxybenzaldehyde **1**(**0**), 3-(4-hexyloxy-3-methoxyphenyl)propenal **1**(**1**), 2-methoxy-5-methyl-isophtalaldehyde **2**, and 2,4,6-trimethoxy-1,3,5-benzenetricarbaldehyde **3**). These building blocks lead to new conjugated polyenes with an angular methyl group — very important class of carotenoid-type polyenes. We are also interested in the synthesis of symmetrical two-dimensional conjugated polyenals and octupolar structures. The use of template with two reactive carbonyl moieties (**2**) leads to new symmetrical, conjugated polyenals — precursors of acceptor or donor substituted polyenes which represent an approach to a molecular wire.[17] The new octupolar structures that are of particular interest in the field of nonlinear optics due to their potentially large two

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Keywords: *O*-Trimethylsilyl enol ethers; Unsymmetrical conjugated polyenes; Symmetrical conjugated polyenes; Octupolar conjugated polyenes.

* Corresponding author. Tel.: +48-71-3202828; fax.: +48-71-3203678; e-mail address: kazimiera.wilk@pwr.wroc.pl

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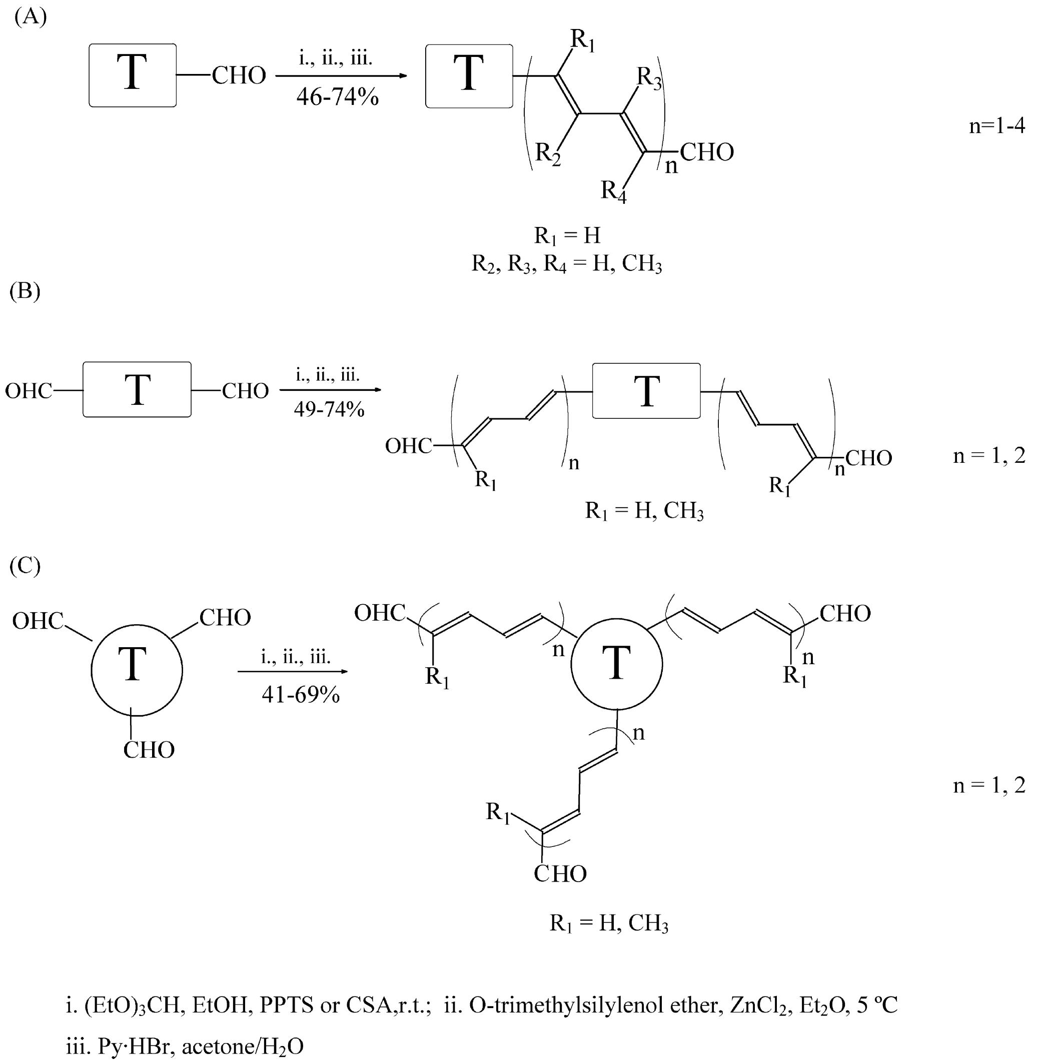


Scheme 1. The general synthetic approach for (A) unsymmetrical carotenoid-type polyenals, (B) symmetrical conjugated polyenals and (C) octupolar conjugated polyenals. Templates T and silyl enol ethers are presented in Table 1.

or three-dimensional quadratic nonlinearities can be obtained from the template with three reactive carbonyl moieties.

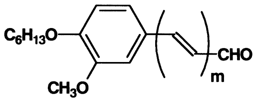
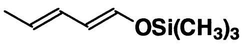
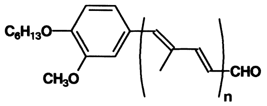
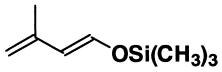
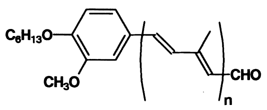
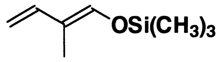
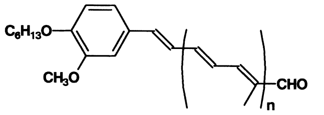
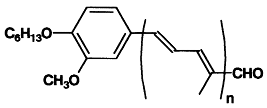
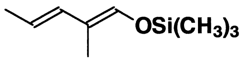
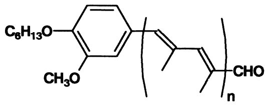
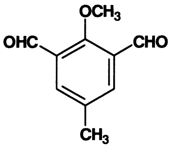
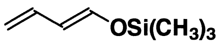
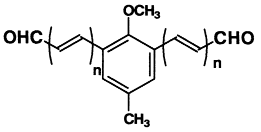
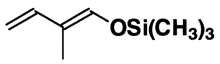
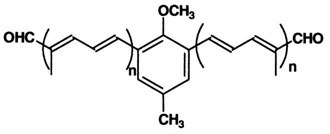
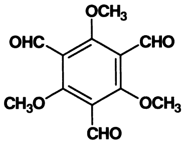
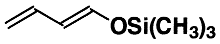
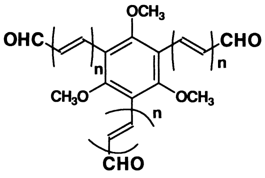
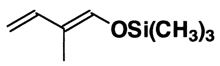
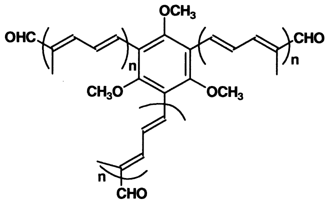
2. Results and discussion

Scheme 1 presents the synthetic approach for unsymmetrical carotenoid-type structures (A), as well as symmetrical (B) and octupolar (C) conjugated polyenals. Thus, in this modular synthesis, which involves reactive silyl enol ethers **4**–**8** as building blocks, and aldehyde comprising conjugation in its structure (**1**(**0**), **1**(**1**), **2**, **3**) as templates, a series of conjugated polyenals presented in Table 1 are obtained.

Each particular step of the designed iterative process, independent of the applied template, involves three steps. The first one — the slowest reaction step in the whole modular approach (reaction (i) in Scheme 1) — denotes the acetalization of the respective template (aldehyde comprising conjugation in its structure) with triethyl orthoformate in the presence of pyridinium *p*-toluenesulfonate (PPTS) or camphorsulfonic acid (CSA). In the case of PPTS, as the catalyst at 25 °C, the first step has been completed within 154 h for template **3** (see Table 2). Increasing temperature up to 50 °C makes the reaction time shorter (130 h), but unfortunately, the yield was diminished (Table 2). It is worth noting that CSA catalyzes the studied reaction effectively at 25 °C; tenfold reaction time decrease, high yield (see Table 2).

The second step (reaction (ii) in Scheme 1) 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 use of silyl enol ethers **4**–**8**, indicated in the first paragraph, made it possible to achieve in one step the carbon chain elongation of up to four atoms. Then, the **4**–**7** silyl enol ethers led, additionally to the methyl group introduction in the polyenic backbone and, furthermore, to the carotenoid-like structures **8**–**11**, **14**, **16** and polyenals **12**. The building block **8** is commercially available and the rest of used silyl enol ethers are easy to obtain from appropriate aldehydes according to method described in the literature.[18] In order to complete the synthesis of conjugated polyenals,

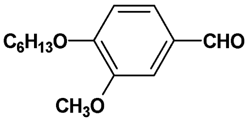
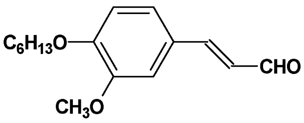
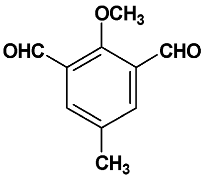
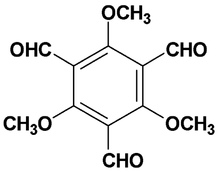
Table 1. Templates **1**–**3** and building blocks **4**–**6** leading to polyenals **8**–**16** by modular synthesis

Template	Building block	Product
 m = 0, or 1 **1(m)**	 **4**	 for m=0, **8(n)**; n = 1-4
	 **5**	 for m=0, **9(n)**; n = 1-4
	 **6**	 for m=1, **10(n)**; n = 1-4  for m=0, **11(n)**; n = 1-4
	 **7**	 for m=0, **12(n)**
 **2**	 **8**	 13(**n**); n = 1, 2
	 **6**	 14(**n**); n = 1, 2
 **3**	 **8**	 15(**n**), n = 1, 2
	 **6**	 16(**n**); n = 1, 2

water or/and ethanol are to 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.[11] The mentioned process carried out in the presence of pyridinium hydrobromide[12] (reaction (iii) Scheme 1) gave thermodynamically stable pure *all*-E isomers comprising two, three, four, five, six, seven and eight double bonds in one conjugated chain. The overall yields for the given series of conjugated polyenes **8–11**, **12**, **13**, **14**, **15** and **16** ranged between 53–75%, 43–62%, 51–74%, 49–72%, 41–69% and 40–67%, respectively.

All synthesized polyenals **8–16** were purified by medium pressure column chromatography (MPLC) or/and radial chromatography in darkness under N_2 and identified

Table 2. Experimental conditions of template **1**–**3** acetalization

Template	Catalyst	T (°C)	t^a (h)	Yield[b]
 **1**(**0**)	PPTS[c]	25	9	90
	CSA[d]	25	0.5	93
 **1**(**1**)	PPTS[c]	25	18	94
	CSA[d]	25	1.5	96
 **2**	PPTS[c]	25	35	89
	PPTS[c]	50	8.5	85
	CSA[d]	25	2.5	93
 **3**	PPTS[c]	25	154	87
	PPTS[c]	50	130	85
	CSA[d]	25	10	90

[a] The progress of reaction was followed by TLC on silica gel with ethyl acetate/hexane (v/v, 3:1) as eluent.
[b] Isolated.
[c] Pyridinium p-toluenesulfonate.
[d] Camphorsulfonic acid.

unambiguously by NMR. The structure and stereochemistry of conjugated polyenals **8**–**16** were studied by 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 identification of almost all protons of the studied polyenic chains and determination of the coupling constants $J_{\mathrm{CH{=}CH}}$ (14.1–15.4 Hz) and $J_{\mathrm{CH-CH}}$ (10.1–11.2 Hz) which are characteristic for *all*-E structures.[13] The stereochemical homogeneity of all obtained aldehyde structures was evidenced by the presence of a single doublet (at about 9.6 ppm) corresponding to the CHO. As in other *all*-E polyenes described in the literature the UV–vis spectra of compounds **8**–**16** are characterized by an intense, structureless and broad absorption band in the visible and ultraviolet region.[15,19] The π–π* transition is responsible for the first absorption band.[15,19] Symmetry of the first absorption band and lack of the additional bands in the longer wavelength region of the spectra evidence the existence of *all*-E isomer in the $CHCl_3$ solution. The IR spectrum in KBr of all studied compounds is very complex but detailed analysis confirms the structure and *all*-E configuration for the new polyenals **8**–**15**. The IR spectrum of all polyenals has absorption band between 1665 and 1685 cm^{-1} indicating the presence of long conjudated system (C=C–C=C and C=C–C=O). We do not observe any bands between 1400 and 1420 cm^{-1} and 660 and 730 cm^{-1} what confirms the absence of *Z* isomer. All spectroscopic analysis indicate *all*-E configuration for the studied compounds.

3. Conclusion

Summing up, we have described the use of *O*-trimethylsilyl enol ethers as versatile building blocks in modular synthesis of unsymmetrical, symmetrical and octupolar conjugated polyenals containing long polyenic backbones. In spite of difficulties with purity of conjugated polyenes MPLC and radial chromatography proved effective purification methods (purity was confirmed by elemental analysis, ESI-MS, NMR and UV–vis spectroscopy). Thus, obtained and purified derivatives, identified by NMR, UV–vis and IR spectroscopy, represent in ground state only one *all*-E isomer.

The unsymmetrical polyenals are convenient reagents for the synthesis of push–pull structures.[15,20] Push–pull polyenes as well as symmetrical and octupolar polyenals and their derivatives play important role as: molecular wires, novel NLO materials or electroluminescent material for light-emitting diodes.[21–23]

4. Experimental

4.1. General methods and materials

Starting materials were of the highest commercial quality and were used without further purification. All reactions were carried out under a protective atmosphere of N_2 gas using oven-dried glassware. Mps were determined on a Kofler block and are uncorrected. Elemental analyses were carried out with a Perkin–Elmer 2400 CHN analyzer (Norwalk, CT). Chromatographic purification was accomplished by medium pressure column chromatography (MPLC, Büchi Labortechnik AG, silica gel, flow rate 20 mL min^{-1}, eluent—hexane/ethyl acetate, 3:1) or/and radial chromatography (Chromatotron, Harrison Research Inc., N_2, 60 rpm, 2 mm layer of Silica Gel 60 GF254, flow rate 6 mL min^{-1}, eluent — hexane/ethyl acetate, 4:1). Electrospray ionization (ESI) spectra were obtained with a Finnigan TSQ-700 mass spectrometer. 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). The UV–Vis absorption spectra of freshly prepared solutions of all obtained polyenes were measured in CH_3Cl at room temperature using UV–Vis Unicam (Thermo Spectronic) spectrophotometer. IR spectra were obtained on FT-IR Nexus (Thermo Nicolet) spectrophotometer.

4.2. General procedure for the preparation of unsymmetrical conjugated polyenals 8(n)-12(n)

A mixture of appropriate aldehyde (template **1**(**m**), or polyenal **8**(**n**)–**12**(**n**) (22 mmol), $CH(OEt)_3$ (10 mL, 60 mmol) and catalyst (PPTS or CSA, 100 mg) in anhyd Et_2O (10 mL) was stirred at rt for 16–120 h (reaction progress was controlled by TLC analysis). Then the mixture was poured into 5% aq ammonium hydroxide 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. The appropriate silyl enol ether (**4**, **5**, **6**, or **7**) (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 stirring at 5 °C, the reaction mixture was poured into the ice–water (100 mL). The organic phase was shaken with sat. aq $NaHCO_3$ and water, dried with $MgSO_4$ and the solvent was removed in vacuo. The obtained brown oil was added to a solution of a pyridine hydrobromide (0.10 g, 0.31 mmol) in acetone containing 0.2 mL of water. 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 by medium pressure column chromatography or radial chromatography (hexane/EtOAc, 3:1 v/v).

4.2.1. (2*E*,4*E*)-5-(4-Hexyloxy-3-methoxyphenyl)-4-methyl-penta-2,4-dienal (8(1)). Brown solid, mp 30–35 °C, yield 75%. Anal. Calcd for $C_{19}H_{26}O_3$ (302.4): C, 75.46; H, 8.67. Found: C, 75.26; H, 8.85. ESI-MS: MH^+=303.2. ν_{max} (KBr) 2940, 2851, 1668, 1591, 1507, 1470, 1395, 1310, 1249, 1180, 1028, 968, 850, 795, 640 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.40 (1H, d, *J*=8.1 Hz, C*H*O), 7.20 (1H, d, *J*=15.0 Hz, C*H*═CHCHO), 6.82 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.80 (1H, s, ArC*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.65 (1H, d, *J*=3.0 Hz), 6.20 (1H, dd, *J*=8.0, 15.1 Hz, C*H*CHO), 3.97 (2H, t, *J*=6.5 Hz, CH_2O), 3.89 (3H, s, O*Me*), 1.90 (3H, s, CH═C*Me*), 1.30–1.80 (8H, m, Me(CH_2)$_4$), 0.90 (3H, t, *J*=6.9 Hz, *Me*(CH$_2$)$_4$). $\lambda_{max}(CHCl_3)$=354 nm, $\varepsilon=2.8\times10^5$.

4.2.2. (2*E*,4*E*,6*E*,8*E*)-9-(4-Hexyloxy-3-methoxyphenyl)-4,8-dimethyl-nona-2,4,6,8-tetraenal (8(2)). Brown solid, mp 49–54 °C, yield 67%. Anal. Calcd for $C_{24}H_{32}O_3$ (368.5): C, 78.22; H, 8.75. Found: C, 78.0; H 8.9. ESI-MS: MH^+=369.22. ν_{max} (KBr) 3020, 2949, 2860, 1730, 1640, 1620, 1600, 1537, 1510, 1250, 1180, 1024, 975, 835, 795, 645, 645 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.42 (1H, d, *J*=8.1 Hz, C*H*O), 6.98 (1H, d, *J*=15.0 Hz, C*H*═CHCHO), 6.82 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.80 (1H, s, ArC*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.70 (1H, dd, *J*=14.9, 7.9 Hz, MeCCH═C*H*), 6.66 (1H, d, *J*=14.9 Hz, MeCC*H*═CH), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.44 (1H, d, *J*=7.9 Hz, C*H*═C(Me)), 6.22 (1H, dd, *J*=14.9, 8.1 Hz, C*H*CHO), 3.97 (2H, t, *J*=6.54 Hz, CH_2O), 3.89 (3H, s, O*Me*), 1.90 (6H, s, 2×C*Me*), 1.30–1.80 (8H, m, Me(CH_2)$_4$), 0.90 (3H, t, *J*=6.9 Hz, *Me*(CH$_2$)$_4$). $\lambda_{max}(CHCl_3)$=394 nm, $\varepsilon=4.2\times10^5$.

4.2.3. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*)-13-(4-Hexyloxy-3-methoxyphenyl)-4,8,12-trimethyl-trideca-2,4,6,8,10, 12-heksaenal (8(3)). Brown solid, mp 62–68 °C, yield 60%. Anal. Calcd for $C_{29}H_{38}O_3$ (434.61): C, 80.14; H, 8.81. Found: C, 79.9; H, 8.9. ESI-MS: MH^+=435.3. ν_{max} (KBr) 3025, 2960, 2937, 2853, 1677, 1586, 1508, 1470, 1390, 1302, 1290, 1254, 1240, 1175, 1150, 1120, 1010, 990, 920, 855, 795, 650, 625 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.40 (1H, d, *J*=8.1 Hz, C*H*O), 6.82 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.80 (1H, s, ArC*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.73–6.78 (2H, m, ((Me)CCH═C*H*CH═)$_2$), 6.71 (1H, dd, *J*=14.9, 7.9 Hz, MeCCH═C*H*), 6.70 (1H, d, *J*=15.0 Hz, C*H*═CHCHO), 6.66 (1H, d, *J*=14.9 Hz, MeCC*H*═CH), 6.65 (1H, d, *J*=3.0 Hz), 6.44 (2H, 2×d, *J*=7.9 Hz, (C*H*═C(Me)CH═CH)$_2$), 6.22 (1H, dd, *J*=14.9, 8.1 Hz, C*H*CHO), 3.97 (2H, t, *J*=6.54 Hz, CH_2O), 3.89 (3H, s, O*Me*), 1.90 (9H, s, 3×CH═C*Me*), 1.30–1.80 (8H, m, Me(CH_2)$_4$), 0.90 (3H, t, *J*=6.9 Hz, *Me*(CH$_2$)$_4$). $\lambda_{max}(CHCl_3)$=422 nm, $\varepsilon=4.9\times10^5$.

4.2.4. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*)-17-(4-Hexyloxy-3-methoxyphenyl)-4,8,12,16-tetramethyl-heptadeca-2,4,6,8,10,12,14,16-octaenal (8(4)). Brown solid, mp 79–84 °C, yield 54%. Anal. Calcd for $C_{34}H_{44}O_3$ (500.72): C, 81.56; H, 8.86. Found: C, 81.3; H, 9.0. ESI-MS: MH^+=501.4. ν_{max} (KBr) 3020, 2935, 2855, 1665, 1590, 1510, 1465, 1395, 1300, 1267, 1465, 1260, 1140, 1120, 1030, 970, 850, 645 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.40 (1H, d, *J*=8.0 Hz, C*H*O), 6.98 (1H, d, *J*=15.0 Hz, C*H*═CHCHO), 6.82 (1H, dd, *J*=9.0, 3.0 Hz, Ar*H*), 6.80 (1H, s, ArC*H*), 6.73–6.78 (4H, m, (C*H*CH═C(Me)CH)$_3$+Ar*H*), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.60 (3H, 3×d, *J*=14.9 Hz, (C*H*═CHCH═CMe)$_3$), 6.42 (3H, 3×d, *J*=7.9 Hz, (C*H*═C(Me)CH═CH)$_3$), 6.22 (1H, dd, *J*=8.1, 14.9 Hz, C*H*CHO), 3.97 (2H, t, *J*=6.54 Hz, CH_2O), 3.89 (3H, s, O*Me*), 1.90 (12H, s, 4×CH═C*Me*), 1.30–1.80 (8H, m, Me(CH_2)$_4$), 0.90 (3H, t, *J*=6.9 Hz, *Me*(CH$_2$)$_4$). $\lambda_{max}(CHCl_3)$=445 nm, $\varepsilon=5.7\times10^5$.

4.2.5. (2*E*,4*E*)-5-(4-Hexyloxy-3-methoxyphenyl)-3-methyl-penta-2,4-dienal (9(1)). Brown solid, mp 32–36 °C, yield 74%. Anal. Calcd for $C_{19}H_{26}O_3$ (302.41): C, 75.46; H, 8.67. Found: C, 75.2; H, 8.9. ESI-MS: MH^+=303.2. ν_{max} (KBr) 2950, 2862, 1663, 1590, 1508, 1470, 1395, 1305, 1250, 1150, 1025, 965, 850, 642 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.42 (1H, d, *J*=8.0 Hz, C*H*O), 6.82 (1H, dd, *J*=8.7, 3.0 Hz), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.70 (1H, d, *J*=15.1 Hz, ArC*H*), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.63 (1H, d, *J*=15.4 Hz, ArCH═C*H*), 6.32 (1H, d, *J*=8.0 Hz, C*H*CHO), 3.97 (2H, t, *J*=6.54 Hz, CH_2O), 3.89 (3H, s, O*Me*), 1.88 (3H, s, CH═C*Me*), 1.30–1.80 (8H, m, Me(CH_2)$_4$), 0.90 (3H, t, *J*=6.9 Hz, *Me*(CH$_2$)$_4$). $\lambda_{max}(CHCl_3)$=345 nm, $\varepsilon=2.5\times10^5$.

4.2.6. (2*E*,4*E*,6*E*,8*E*)-9-(4-Hexyloxy-3-methoxyphenyl)-3,7-dimethyl-nona-2,4,6,8-tetraenal (9(2)). Brown solid, mp 49–54 °C, yield 68%. Anal. Calcd for $C_{24}H_{32}O_3$ (368.52): C, 78.22; H, 8.75. Found: C, 78.0; H, 8.9. ESI-MS: MH^+=369.2. ν_{max} (KBr) 2930, 2890, 1670, 1638, 1620, 1510, 1470, 1380, 1253, 1135, 999, 836, 792, 645 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.45 (1H, d, *J*=8.0 Hz, C*H*O), 6.82 (1H, dd, *J*=8.9, 3.0 Hz), 6.77 (1H, d, *J*=8.6 Hz), 6.75 (1H, dd, *J*=9.0, 14.8 Hz, C*H*═CHC(Me)), 6.71 (1H, d, *J*=15.3 Hz, ArC*H*), 6.65 (1H, d, *J*=3.0 Hz), 6.64 (1H, d, *J*=8.9 Hz, MeC═C*H*CH), 6.63 (1H, d, *J*=15.0 Hz, ArCH═C*H*), 6.41 (1H, d, *J*=15.0 Hz, C*H*C(Me)═CHCHO), 6.32 (1H, d, *J*=7.9 Hz, C*H*CHO), 3.97 (2H, t, *J*=6.54 Hz, CH_2O), 3.89 (3H, s, O*Me*), 1.90 (6H, s, 2×CH═C*Me*), 1.30–1.79 (8H, m, Me(CH_2)$_4$), 0.90 (3H, t, *J*=6.9 Hz, *Me*(CH$_2$)$_4$). $\lambda_{max}(CHCl_3)$=384 nm, $\varepsilon=4.0\times10^5$.

4.2.7. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*)-13-(4-Hexyloxy-3-methoxyphenyl)-3,7,11-trimethyl-trideca-2,4,6,8,10, 12-heksaenal (9(3)). Brown solid, mp 62–66 °C, yield 59%. Anal. Calcd for $C_{29}H_{38}O_3$ (434.62): C, 80.14; H, 8.81. Found: C, 79.9; H, 9.0. ESI-MS: MH^+=435.3. ν_{max} (KBr) 3020, 2950, 2931, 2860, 1675, 1585, 1510, 1465, 1390, 1305, 1292, 1253, 1170, 1135, 1015, 998, 920, 855, 645 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.45 (1H, d, *J*=8.0 Hz, C*H*O), 6.82 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.76 (1H, d, *J*=8.7 Hz, Ar*H*), 6.72 (2H, dd, *J*=14.8, 9.0 Hz, C*H*=CHC(Me)), 6.70 (1H, d, *J*=15.3 Hz, ArC*H*), 6.65 (3H, m, (C(Me)=C*H*CH=CH)$_2$+Ar*H*), 6.64 (1H, d, *J*=15.0 Hz, ArCH=C*H*), 6.41 (2H, m, (C(Me)=C*H*CH=C*H*)$_2$), 6.30 (1H, d, *J*=7.9 Hz, C*H*CHO), 3.97 (2H, t, *J*=6.54 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (9H, s, 3×CH=C*Me*), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}($CHCl_3$)=415 nm, ε=5.1×10^5.

4.2.8. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*)-17-(4-Hexyloxy-3-methoxyphenyl)-3,7,11,14-tetramethyl-heptadeca-2,4,6,8,10,12,14,16-octaenal (9(4)). Brown solid, mp 80–85 °C, yield 55%. Anal. Calcd for $C_{34}H_{44}O_3$ (500.72): C, 81.56; H, 8.86. Found: C, 81.3; H, 9.0. ESI-MS: MH^+=501.3. ν_{max} (KBr) 3025, 2940, 2852, 1665, 1589, 1511, 1463, 1380, 1310, 1290, 1230, 1175, 1130, 1015, 998, 850, 795, 650 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.42 (1H, d, *J*=8.0 Hz, C*H*O), 6.82 (1H, dd, *J*=8.9, 2.9 Hz, Ar*H*), 6.76 (4H, m, (C*H*=CHC(Me)=CH)$_3$+Ar*H*), 6.70 (1H, d, *J*=15.3 Hz, ArCH), 6.66 (3H, m, (C*H*CH=CHCMe)$_3$), 6.65 (1H, d, *J*=2.98 Hz, Ar*H*), 6.63 (1H, d, *J*=15.0 Hz, ArCH=C*H*), 6.41 (3H, m, (C(Me)=C*H*CH=C*H*)$_3$), 6.32 (1H, d, *J*=8.0 Hz, C*H*CHO), 3.97 (2H, t, *J*=6.54 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (12H, s, 4×CH=C*Me*), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}($CHCl_3$)=438 nm, ε=5.9×10^5.

4.2.9. (2*E*,4*E*,6*E*)-7-(4-Hexyloxy-3-methoxyphenyl)-2-methyl-hepta-2,4,6-trienal (10(1)). Brown solid, mp 40–45 °C, yield 70%. Anal. Calcd for $C_{21}H_{28}O_3$ (328.45): C, 76.79; H, 8.59. Found: C, 75.12; H, 8.69. ESI-MS: MH^+=329.2. ν_{max} (KBr) 3000, 2930, 2860, 1720, 1660, 1604, 1512, 1465, 1270, 1031, 1020, 995, 845, 800, 645 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.43 (1H, s, C*H*O), 6.92 (1H, d, *J*=11.0 Hz, C*H*C(CH$_3$)CHO), 6.82 (dd, 1H, *J*=8.9, 3.0 Hz, Ar*H*), 6.80 (1H, dd, *J*=10.1, 15.0 Hz, ArCH=C*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.70 (1H, d, *J*=14.7 Hz, ArC*H*=CH), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.60 (2H, dd, *J*=15.0, 9.2 Hz, CH=C*H*) 3.97 (2H, t, *J*=6.54 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (3H, s, CH=C*Me*), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}($CHCl_3$)=369 nm, ε=2.4×10^5.

4.2.10. (2*E*,4*E*,6*E*,8*E*,10*E*)-11-(4-Hexyloxy-3-methoxyphenyl)-2,6-dimethyl-undeca-2,4,6,8,10-pentaenal (10(2)). Brown solid, mp 58–63 °C, yield 63%. Anal. Calcd for $C_{26}H_{34}O_3$ (394.55): C, 79.15; H, 8.69. Found: C, 78.9; H, 8.8. ESI-MS: MH^+=395.2. ν_{max} (KBr) 2999, 2930, 2859, 1720, 1659, 1600, 1510, 1465, 1270, 1250, 1175, 1140, 1029, 969, 845, 645 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.40 (s, 1H, C*H*O), 6.90 (1H, d, *J*=11.0 Hz, C*H*C(CH$_3$)-CHO), 6.82 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.79 (1H, dd, *J*=14.9, 9.8 Hz, ArC*H*=CH), 6.76 (1H, dd, *J*=14.8, 10.1 Hz, ArCH=C*H*), 6.76 (d, 1H, *J*=8.6 Hz, Ar*H*), 6.71 (1H, d, *J*=14.7 Hz, ArC*H*), 6.66 (1H, d, *J*=15.0 Hz, C(Me)C*H*), 6.65 (1H, d, *J*=3.0 Hz), 6.59 (2H, m, CH=CHC*H*=C*H*), 6.30 (1H, d, *J*=9.2 Hz, C*H*=CMe), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (6H, s, (CH=CHCH=C*Me*)$_2$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}($CHCl_3$)=415 nm, ε=2.8×10^5.

4.2.11. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-15-(4-Hexyloxy-3-methoxyphenyl)-2,6,10-trimethyl-pentadeca-2,4,6,8,10,12,14-heptaenal (10(3)). Brown solid, mp 70–74 °C, yield 59%. Anal. Calcd for $C_{31}H_{40}O_3$ (460.65): C, 80.83; H, 8.75. Found: C, 81.1; H, 9.0. ESI-MS: MH^+=461.3. ν_{max} (KBr) 3005, 2935, 2850, 1670, 1600, 1511, 1466, 1268, 1178, 1138, 1030, 835, 795, 650 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.41 (1H, s, C*H*O), 6.90 (1H, d, *J*=10.2 Hz, C*H*C(CH$_3$)-CHO), 6.82 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.79 (1H, dd, *J*=14.9, 9.8 Hz, ArC*H*=CH), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.76 (2H, m, (CH=C*H*CH=CMe)$_2$), 6.71 (1H, d, *J*=14.7 Hz, ArC*H*=CH), 6.65 (1H, d, *J*=2.9 Hz), 6.63 (2H, m, (C*H*=CHCH=CMe)$_2$), 6.59 (1H, dd, *J*=15.9, 9.0 Hz, CH=CHC*H*=CH), 6.58 (dd, 1H, *J*=14.9, 9.7 Hz, CH=CHCH=C*H*), 6.41 (2H, m, (C*H*=C(Me)CH=CH)$_2$), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (6H, s, (CH=CHCH=C*Me*)$_2$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}($CHCl_3$)=452 nm, ε=3.4×10^5.

4.2.12. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*,18*E*)-19-(4-Hexyloxy-3-methoxyphenyl)-2,6,10,14-tetramethylheptadeca-2,4,6,8,10,12,14,16,18-nonaenal (10(4)). Brown solid, mp 87–91 °C, yield 53%. Anal. Calcd for $C_{36}H_{46}O_3$ (526.75): C, 82.09; H, 8.80. Found: C, 81.7; H, 9.0. ESI-MS: MH^+=527.3. ν_{max} (KBr) 3029, 2952, 2856, 1662, 1587, 1510, 1471, 1365, 1137, 991, 863, 790, 742, 640 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.43 (1H, s, C*H*O), 6.91 (1H, d, *J*=10.2 Hz, C*H*C(CH$_3$)CHO), 6.82 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.79 (1H, dd, *J*=14.9, 9.8 Hz, ArC*H*=CH), 6.73–6.77 (4H, m, (CH=C*H*CH=CMe)$_3$+Ar*H*), 6.71 (1H, d, *J*=14.7 Hz, ArC*H*=CH), 6.62–6.66 (4H, m, (C*H*=CHCH=CMe)$_3$+Ar*H*), 6.59 (2H, m, CH=CHC*H*=C*H*), 6.40 (3H, m, (C*H*=C(Me)CH=CH)$_3$), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (12H, s, (CH=CHCH=C*Me*)$_2$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}($CHCl_3$)=467 nm, ε=4.0×10^5.

4.2.13. (2*E*,4*E*)-5-(4-Hexyloxy-3-methoxyphenyl)-2-methyl-penta-2,4-dienal (11(1)). Brown solid, mp 35–39 °C, yield 71%. Anal. Calcd for $C_{19}H_{26}O_3$ (302.41): H, 8.67; C, 75.46. Found: H, 8.7; C, 75.4. ESI-MS: MH^+=303.2. ν_{max} (KBr) 3030, 2950, 2860, 1670, 1590, 1511, 1475, 1265, 1135, 990, 860, 789, 745, 650 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.40 (1H, s, C*H*O), 6.90 (1H, d, *J*=10.8 Hz, C*H*=C(CH$_3$)CHO), 6.81 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.79 (1H, dd, *J*=14.7, 10.7 Hz, ArCH=C*H*), 6.76 (1H, d, *J*=8.6 Hz, ArH), 6.70 (1H, d, *J*=14.5 Hz, ArC*H*), 6.65 (1H, d, *J*=3.0 Hz), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.91 (3H, s, C*Me*), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}($CHCl_3$)=354 nm, ε=1.1×10^5.

4.2.14. (2*E*,4*E*,6*E*,8*E*)-9-(4-Hexyloxy-3-methoxyphenyl)-2,6-dimethylnona-2,4,6,8-tetraenal (11(2)). Brown solid, mp 50–54 °C, yield 65%. Anal. Calcd for $C_{24}H_{32}O_3$ (368.51): H, 8.75; C, 78.22. Found: H, 8.80; C, 78.18. ESI-MS: MH$^+$=369.3. ν_{max} (KBr) 3025, 2955, 2855, 1670, 1588, 1510, 1471, 1265, 1137, 991, 864, 791, 640 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.41 (1H, s, C*H*O), 6.90 (1H, d, *J*=10.3 Hz, C*H*=C(CH$_3$)CHO), 6.81 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.79 (1H, dd, *J*=10.1, 14.5 Hz, ArCH=C*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.79 (1H, dd, *J*=14.0, 10.1 Hz, ArCH=C*H*), 6.71 (1H, d, *J*=14.8 Hz, ArC*H*), 6.65 (1H, d, *J*=2.98 Hz, Ar*H*), 6.61 (1H, d, *J*=10.2 Hz, ArCH=CHC*H*), 6.30 (d, 1H, *J*=14.3 Hz, C(Me)C*H*), 3.97 (2H, t, *J*=6.6 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (6H, s, (CH=CHCH=C(*Me*))$_2$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}(CHCl$_3$) 410 nm, ε=1.7×10^5.

4.2.15. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*)-13-(4-Hexyloxy-3-methoxyphenyl)-2,6,10-trimethyl-trideca-2,4,6,8,10,12-heksaenal (11(3)). Brown solid, mp 69–73 °C, yield 58%. Anal. Calcd for $C_{29}H_{38}O_3$ (434.62): H, 8.81; C, 80.14. Found: H, 8.9; C, 80.1. ESI-MS: MH$^+$=435.3. ν_{max} (KBr) 3022, 2960, 2920, 2870, 1668, 1588, 1509, 1470, 1264, 1137, 990, 862, 879, 740, 640 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.41 ((1H, s, C*H*O), 6.89 (1H, d, *J*=10.2 Hz, C*H*=CMe-CHO), 6.81, (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.79 (1H, dd, *J*=10.1, 14.0 Hz, ArCH=C*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.70–6.73 (3H, m, (CH=C*H*CHCMe)$_2$+ArC*H*), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.63 (2H, m, (C*H*=CHCHCMe)$_2$), 6.61 (1H, d, *J*=10.2 Hz, ArCH=CHC*H*), 6.30 (d, 1H, *J*=9.8 Hz, (C*H*=CHC*H*CMe)$_2$), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (9H, s, (CH=CHCH=C(*Me*))$_3$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}(CHCl$_3$)=442 nm, ε=2.1×10^5.

4.2.16. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*)-17-(4-Hexyloxy-3-methoxyphenyl)-2,6,10,14-tetramethylheptadeca-2,4,6,8,10,12,14,16-octaenal (11(4)). Brown solid, mp 87–93 °C, yield 54%. Anal. Calcd for $C_{34}H_{44}O_3$ (500.72): H, 8.86; C, 81.56. Found: H, 8.9; C, 81.5. ESI-MS: MH$^+$=501,3. ν_{max} (KBr) 3025, 2955, 2950, 2860, 1672, 1587, 1510, 1472, 1265, 1140, 1125, 1030, 990, 860, 792, 742 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.41 (1H, s, C*H*O), 6.90 (1H, d, *J*=10.2 Hz, C*H*=CMeCHO), 6.81, (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.79 (1H, dd, *J*=10.1, 14.0 Hz, ArCH=C*H*), 6.74–6.77 (4H, m, Ar*H*+(CH=C*H*CHCMe)$_3$CHO), 6.71 (1H, d, *J*=14.8 Hz, ArC*H*), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.63 (3H, m, (C*H*=CHCHCMe)$_3$), 6.41 (3H, m, (C*H*=CMeCH=CH)$_3$), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (12H, s, (CH=CHCH=C(*Me*))$_4$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz). λ_{max}(CHCl$_3$)=458 nm, ε=2.5×10^5.

4.2.17. (2*E*,4*E*)-5-(4-Hexyloxy-3-methoxyphenyl)-2,4-dimethyl-penta-2,4-dienal (12(1)). Brown solid, yield 62%. Anal. Calcd for $C_{20}H_{28}O_3$ (316.44): H, 8.92; C, 75.91. Found: H, 9.0; C, 75.7. ESI-MS: MH$^+$=317.3. ν_{max} (KBr) 2980, 2930, 2850, 1668, 1637, 1510, 1466, 1377, 1253, 1135, 999 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.40 (1H, s, C*H*O), 7.23 (1H, s, C*H*=CMeCHO), 6.81, (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.39 (1H, s, ArC*H*), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.90 (6H, s, CH=C*Me*)$_2$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz).

4.2.18. (2*E*,4*E*,6*E*,8*E*)-9-(4-Hexyloxy-3-methoxyphenyl)-2,4,6,8-tetramethylnona-2,4,6,8-tetraenal (12(2)). Brown solid, yield 55%. Anal. Calcd for $C_{26}H_{36}O_3$ (396.57): H, 9.15; C, 78.75. Found: H, 9.35; C, 78.62. ESI-MS: MH$^+$=397.3. ν_{max} (KBr) 3010, 2985, 2933, 2860, 1668, 1625, 1510, 1460, 1340, 1255, 1140, 998 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.41 (1H, s, C*H*O), 7.20 (1H, s, C*H*=CMeCHO), 6.81 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.40 (1H, s, ArC*H*), 6.31 (2H, s, (C*H*CMe)$_2$), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.91 (12H, s, CH=C*Me*)$_4$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz).

4.2.19. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*)-13-(4-Hexyloxy-3-methoxyphenyl)-2,4,6,8,10,12-hexamethyltrideca-2,4,6,8,10,12-heksaenal (12(3)). Brown solid, yield 46%. Anal. Calcd for $C_{32}H_{44}O_3$ (476.70): H, 9.30; C, 80.63. Found: H, 9.55; C, 80.98. ESI-MS: MH$^+$=477.3. ν_{max} (KBr) 3025, 2965, 2935, 2857, 1670, 1596, 1511, 1468, 1360, 1254, 1240, 1175, 1150, 1010, 990, 855 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.41 (1H, s, C*H*O), 7.20 (1H, s, C*H*=CMeCHO), 6.81 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.40 (1H, s, ArC*H*), 6.30 (4H, s, (C*H*CMe)$_4$), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.91 (18H, s, (CH=C*Me*)$_6$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz).

4.2.20. (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*)-17-(4-Hexyloxy-3-methoxyphenyl)-2,4,6,8,10,12,14,16-octamethylheptadeca-2,4,6,8,10,12,14,16-octaenal (12(4)). Brown solid, yield 63%. Anal. Calcd for $C_{38}H_{52}O_3$ (556.83): H, 9.41; C, 81.97. Found: H, 9.7; C, 81.8. ESI-MS: MH$^+$=557.4. ν_{max} (KBr) 3023, 2985, 2964, 2937, 2855, 1672, 1599, 1510, 1465, 1366, 1250, 1180, 1145, 1009, 995, 858 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.41 (1H, s, C*H*O), 7.19 (1H, s, C*H*=CMeCHO), 6.81 (1H, dd, *J*=8.9, 3.0 Hz, Ar*H*), 6.76 (1H, d, *J*=8.6 Hz, Ar*H*), 6.65 (1H, d, *J*=3.0 Hz, Ar*H*), 6.40 (1H, s, ArC*H*), 6.30 (6H, s, (C*H*CMe)$_6$), 3.97 (2H, t, *J*=6.5 Hz, C*H*$_2$O), 3.89 (3H, s, O*Me*), 1.91 (24H, s, (CH=C*Me*)$_6$), 1.30–1.79 (8H, m, Me(C*H*$_2$)$_4$), 0.90 (3H, t, *J*=6.9 Hz).

4.3. General procedure for the preparation of symmetrical conjugated polyenals 13(n)–14(n)

Symmetrical conjugated polyenes **13**(**n**)–**14**(**n**) were obtained according to the procedure in Section 4.2 using 120 mmol of CH(OEt)$_3$ (20 mL) in the first step and 22 mmol of template **2** and 72 mmol of appropriate ether **6** or **8** in the second step of synthesis.

4.3.1. 5-[2-Methoxy-5-methyl-3-(5-oxo-penta-1,3-dienyl)-phenyl]-penta-2,4-dienal (13(2)). Brown solid, mp 42–45 °C, yield 74%. Anal. Calcd for $C_{18}H_{18}O_3$ (382.1): H, 6.43; C, 76.56. Found: H, 6.7; C, 76.2. ESI-MS: MH$^+$=383.3. ν_{max} (KBr) 3010, 2973, 2930, 1689, 1475, 1470, 1396, 1234, 1095, 1002, 877 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 9.50 (2H, d, *J*=8.0 Hz, 2×C*H*O), 7.8 (2H, s, *H*Ar*H*), 7.25 (2H, dd, *J*=14.8, 10.6 Hz, 2×C*H*=CHCHO), 6.93 (2H, d, *J*=15.2 Hz, *H*CArC*H*), 6.79 (2H, dd, *J*=10.4, 15.1 Hz, 2×CH=C*H*), 6.2 (2H, dd, *J*=8.1, 14.8 Hz, 2×C*H*CHO), 4.01 (3H, s, OCH$_3$), 2.40 (3H, s, Ar*Me*). λ_{max}(CHCl$_3$)=316 nm, ε=1.3×10^5.

4.3.2. 9-[2-Methoxy-5-methyl-3-(9-oxo-nona-1,3,5,7-teraenyl)-phenyl]-nona-2,4,6,8-tetraenal (13(4)). Brown solid, yield 51%. Anal. Calcd for $C_{26}H_{26}O_3$ (386.19): H, 6.79; C, 80.79. Found: H, 7.0; C, 80.5. ESI-MS: MH$^+$= 387.5. ν_{max} (KBr) 3025, 2970, 2932, 1690, 1472, 1470, 1400, 1235, 1170, 1002, 875 cm^{-1}. δ_H (300 MHz, CDCl$_3$) 9.51 (2H, d, *J*=8.1 Hz, 2×C*H*O), 7.8 (2H, s, *H*Ar*H*), 7.18 (2H, dd, *J*=15.1, 11.3 Hz, 2×C*H*=CHCHO), 6.93 (2H, d, *J*=15.0 Hz, *H*CArC*H*), 6.79 (2H, dd, *J*=15.2, 10.8 Hz, 2×CH=C*H*), 6.45–6.70 (8H, m, 2×(C*H*=C*H*)$_2$), 6.1 (2H, dd, *J*=8.1, 15.0 Hz, 2×C*H*CHO), 3.90 (3H, s, OCH$_3$), 2.40 (3H, s, Ar*Me*). λ_{max}(CHCl$_3$)=362 nm, ε=2.2×10^5.

4.3.3. 5-[2-Methoxy-5-methyl-3-(4-methyl-5-oxo-penta-1,3-dienyl)-phenyl]-2-methyl-penta-2,4-dienal (14(1)). Brown solid, yield 72%. Anal. Calcd for $C_{20}H_{22}O_3$ (310.39): H, 7.14; C, 77.39. Found: H, 7.3; C, 77.4. ESI-MS: MH$^+$=311.1. ν_{max} (KBr) 3030, 2970, 2861, 2756, 1690, 1477, 1396, 1235, 1170, 1090, 870 cm^{-1}. δ_H (300 MHz, CDCl$_3$) 9.41 (2H, s, 2×C*H*O), 7.8 (2H, s, *H*Ar*H*), 6.91 (2H, d, *J*=10.5 Hz, C*H*=CMeCHO), 6.75 (2H, dd, *J*=10.5, 14.5 Hz, *H*C=HCArCH=C*H*), 6.71 (2H, d, *J*=13.5 Hz, *H*CArC*H*), 3.90 (3H, s, OCH$_3$), 2.40 (3H, s, Ar*Me*), 1.90 (6H, s, 2×C*Me*CHO). λ_{max}(CHCl$_3$)=337 nm, ε=1.5×10^5.

4.3.4. 9-[3-(4,8-Dimethyl-9-oxo-nona-1,3,5,7-tetraenyl)-2-methoxy-5-methyl-phenyl]-2,6-dimethyl-nona-2,4,6,8-tetraenal (14(2)). Brown solid, yield 49%. Anal. Calcd for $C_{30}H_{34}O_3$ (442.60): H, 7.74; C, 81.41. Found: H, 7.88; C, 81.12. ESI-MS: MH$^+$=443.2. ν_{max} (KBr) 2975, 2932, 2856, 1690, 1625, 1475, 1470, 1396, 1233, 1100, 875 cm^{-1}. δ_H (300 MHz, CDCl$_3$) 9.41 (2H, s, 2×C*H*O), 7.60 (2H, s, *H*Ar*H*), 6.90 (2H, d, *J*=10.0 Hz, C*H*=CMeCHO), 6.79 (2H, dd, *J*=10.5, 14.5 Hz, *H*C=HCArCH=C*H*), 6.76 (2H, dd, *J*=14.1, 10.1 Hz, 2×C*H*CH=C(Me)CHO), 6.71 (2H, d, *J*=14.8 Hz, *H*CArC*H*), 6.61 (2H, d, *J*=10.2 Hz, *H*CHC=HCArCH=CHC*H*), 6.30 (2H, d, *J*=14.3 Hz, 2×CMeC*H*), 3.90 (3H, s, OCH$_3$), 2.40 (3H, s, Ar*Me*), 1.90 (12H, s, 4×C*Me*). λ_{max}(CHCl$_3$)=382 nm, ε=2.5×10^5.

4.4. General procedure for the preparation of symmetrical conjugated polyenals 15(n), 16(n)

Octupolar conjugated polyenes were obtained according to procedure described in Section 4.2 using 180 mmol of CH(OEt)$_3$ (30 mL) to acetalization reaction and 22 mmol of template **3** and 108 mmol of appropriate ether **6** or **8** in the second step of reaction.

4.4.1. 5-[2,4,6-Trimethoxy-3,5-bis-(5-oxo-penta-1,3-dienyl)-phenyl]-penta-2,4-dienal (15(2)). Brown solid, mp 98–102 °C, yield 69%. Anal. Calcd for $C_{24}H_{24}O_6$ (408.15): H, 5.93; C, 70.56. Found: H, 6.0; C, 70.5. ESI-MS: MH$^+$= 409.1. ν_{max} (KBr) 3029, 2954, 2856, 1705, 1637, 1510, 1467, 1132, 975, 870 cm^{-1}. δ_H (300 MHz, CDCl$_3$) 9.50 (3H, d, *J*=8.0 Hz, 3×C*H*O), 7.19 (3H, dd, *J*=14.8, 10.6 Hz, 3×C*H*=CHCHO), 6.93 (3H, d, *J*=15.2 Hz, Ar(C*H*)$_3$), 6.79 (3H, dd, *J*=10.4, 15.1 Hz, 3×CH=C*H*), 6.2 (3H, dd, *J*=8.1, 14.8 Hz, 3×C*H*CHO), 4.03 (9H, s, 3×OCH$_3$). λ_{max}(CHCl$_3$) 331 nm, ε=3.4×10^5.

4.4.2. 9-[2,4,6-Trimethoxy-3,5-bis-(9-oxo-nona-1,3,5,7-tetraenyl)-phenyl]-nona-2,4,6,8-tetraenal (15(4)). Brown solid, mp 135–139 °C, yield 41%. Anal. Calcd for $C_{36}H_{36}O_6$ (564.2): H, 6.43; C, 76.56. Found: H, 6.5; C, 76.4. ESI-MS: MH$^+$=565.7. ν_{max} (KBr) 2980, 2935, 2850, 1860, 1688, 1626, 1590, 1475, 1399, 1235, 1100, 1025, 880, 640 cm^{-1}. δ_H (300 MHz, CDCl$_3$) 9.51 (3H, d, *J*=8.1 Hz, 3×C*H*O), 7.18 (3H, dd, *J*=15.1, 11.3 Hz, 3×C*H*=CHCHO), 6.92 (3H, d, *J*=15.0 Hz, Ar(C*H*)$_3$), 6.80 (3H, dd, *J*=10.8, 15.2 Hz, 3×CH=C*H*), 6.45–6.70 (m, 12H), 6.1 (3H, dd, *J*=8.1, 15.0 Hz, 3×C*H*CHO), 3.90 (9H, s, 3×OCH$_3$).

4.4.3. 2-Methyl-5-[2,4,6-trimethoxy-3,5-bis-(4-methyl-5-oxo-penta-1,3-dienyl)-phenyl]-penta-2,4-dienal (16(1)). Brown solid, yield 67%. Anal. Calcd for $C_{27}H_{30}O_6$ (450.2): H, 6.72; C, 71.97. Found: H, 6.9; C, 71.8. ESI-MS: MH$^+$=451.5. ν_{max} (KBr) 2935, 2890, 1850, 1670, 1630, 1510, 1472, 1380, 1240, 1135, 889, 645 cm^{-1}. δ_H (300 MHz, CDCl$_3$) 9.50 (3H, s, 3×C*H*O), 6.90 (3H, d, *J*=10.8 Hz, 3×C*H*=CMe), 6.79 (3H, dd, *J*=10.7, 14.7 Hz, CH=C*H*), 6.70 (3H, d, *J*=14.5 Hz, Ar(C*H*)$_3$), 4.01 (9H, s, 3×OCH$_3$), 1.91 (9H, s, 3×C*Me*). λ_{max}(CHCl$_3$)=324 nm, ε=1.9×10^5.

4.4.4. 9-[3,5-Bis-(4,8-dimethyl-9-oxo-nona-1,3,5,7-tetraenyl)-2,4,6-trimethoxy-phenyl]-2,6-dimethyl-nona-2,4,6,8-tetraenal 16(2). Brown solid, yield 40%. Anal. Calcd for $C_{42}H_{48}O_6$ (648.3): H, 7.46; C, 77.74. Found: H, 7.6; C, 77.6. ESI-MS: MH$^+$=649.8. ν_{max} (KBr) 3020, 2940, 2839, 1680, 1580, 1476, 1390, 1310, 1230, 1170, 1015, 798, 650 cm^{-1}. δ_H (300 MHz, CDCl$_3$) 9.44 (3H, s, 3×C*H*O), 6.90 (3H, d, *J*=10.2 Hz, 3×C*H*=CMe), 6.79 (3H, dd, *J*=10.1, 14.5 Hz, 3×CH=C*H*), 6.76 (3H, dd, *J*=14.1, 10.2 Hz, 3×C*H*CH=C(Me)CHO), 6.71 (3H, d, *J*=14.8 Hz, Ar(C*H*)$_3$), 6.61 (3H, d, *J*=10.2 Hz, 3×C*H*=CHMe), 6.30 (3H, d, *J*=14.3 Hz, MeC=C*H*), 4.01 (9H, s, 3×OCH$_3$), 1.90 (18H, s, 6×C*Me*).

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