GENERAL METHODS

Solvents were dried according to published methods and distilled before use. All other reagents were commercial compounds of the highest purity available. All reactions were carried out under an argon atmosphere, and those not involving aqueous reagents were carried out in oven-dried glassware. All solvents and anhydrous solutions were transferred through syringes and cannules previously dried in the oven for at least 12h and kept in a dessicator with KOH. THF, CH$_2$Cl$_2$ and DMF were dried using a Puresolv™ solvent purification system. Et$_3$N and Py were dried by distillation over CaH$_2$. For reactions at low temperature, ice-water or CO$_2$-acetone systems were used. For different temperatures, a HaaKe EK90 Immersion Cooler (-90 °C-15 °C) was used. Analytical TLC was performed on aluminium plates with Merck Kieselgel 60F$_{254}$ and visualized by UV irradiation (254 nm) or by staining with a solution of phosphomolibdic acid or anisaldehyde. Flash column chromatography was carried out using Merck Kieselgel 60 (230-400 mesh) under pressure. UV/Vis spectra were recorded on a Cary 100 Bio spectrophotometer in MeOH as solvent. IR spectra were obtained on a JASCO FTIR 4200 spectrophotometer, from a thin film deposited onto a NaCl glass. Melting points were measured in a Stuart Scientific apparatus. Electron Impact (EI) mass spectra were taken on a GC-TOF instrument (Waters Micromass). Electrospray ionization HRMS (ESI$^+$) were taken on a Apex III FT ICR mass spectrometer (Bruker Daltonics). $^1$H-NMR spectra were recorded in CDCl$_3$, C$_6$D$_6$ and (CD$_3$)$_2$CO at ambient temperature on a Bruker AMX-400 spectrometer operating at 400.16 MHz with residual protic solvent as the internal reference (CDCl$_3$, $\delta$ = 7.26 ppm; C$_6$D$_6$, $\delta$ = 7.16 ppm, CD$_2$Cl$_2$, $\delta$ = 5.29 ppm, and CD$_3$OD, $\delta$ = 4.48 and 3.31 ppm); chemical shifts ($\delta$) are given in parts per million (ppm) and coupling constants ($J$) are given in Hertz (Hz). The proton spectra are reported as follows: $\delta$ (multiplicity, coupling constant $J$, number of protons). $^{13}$C-NMR spectra were recorded in CDCl$_3$, C$_6$D$_6$, CD$_2$Cl$_2$ and and CD$_3$OD at ambient temperature in the same spectrometer operating at 101.62 MHz with the central peak of CDCl$_3$ ($\delta$$_C$ = 77.2 ppm), C$_6$D$_6$ ($\delta$$_C$ = 128.0 ppm), CD$_2$Cl$_2$ ($\delta$$_C$ = 53.4 ppm) and CD$_3$OD ($\delta$$_C$ = 50.7 ppm) as the internal reference. DEPT-135 pulse sequence was used to aid in the assignment of signals in the $^{13}$C-NMR spectra. For stannanes, the coupling constant are not given due to difficulties on extracting these data from the $^1$H- and $^{13}$C-NMR spectra, even for the most abundant isotopomers.
(2E,4E,6E)-3-Methyl-7-tributylstannylocta-2,4,6-trienol 6. To a cooled (-78 °C) solution of (2E,4E,6E)-ethyl 3-methyl-7-tributylstannylocta-2,4,6-trienoate 5 (0.89 g, 1.89 mmol) in THF (19.3 mL) was added a solution of DIBAL-H (1M in THF, 7.6 mL, 7.58 mmol). The reaction was stirred at -78 °C for 1 h and then a saturated aqueous solution of sodium potassium tartrate was carefully added. After stirring for 1-2 h, the layers were separated and brine was added. The resulting mixture was extracted with Et2O (3x) and dried (Na2SO4). The solvent was evaporated and the residue was purified by column chromatography (silica gel, from 97:1:2 hexane/EtOAc/Et3N to 70:30 hexane/EtOAc) to afford 0.77 g (95%) of a product identified as (2E,4E,6E)-3-methyl-7-tributylstannylocta-2,4,6-trienol 6.

(2E,4E,6E)-3-Methyl-7-tributylstannylocta-2,4,6-trienal 7. To a cooled (0 °C) solution of (2E,4E,6E)-3-methyl-7-tributylstannylocta-2,4,6-trienol 6 (0.42 g, 0.99 mmol) in CH2Cl2 (19.3 mL) was added manganese dioxide (1.6 g, 17.81 mmol) and sodium carbonate (1.89 g, 17.81 mmol). The reaction was stirred at 25 ºC for 2 h and then the mixture was filtered through a pad of Celite®. The solvent was evaporated to afford 0.38 g (90%) of a yellow solid identified as (2E,4E,6E)-3-methyl-7-tributylstannylocta-2,4,6-trienal 7, which was used without further purification. ^1H-NMR (400.13 MHz, C6D6): δ 9.98 (d, J = 7.8 Hz, 1H, CHO), 6.92 (dd, J = 15.3, 10.6 Hz, 1H, H3), 6.45 (d, J = 10.6 Hz, 1H, H6), 6.02 (d, J = 15.3 Hz, 1H, H4), 5.93 (d, J = 7.8 Hz, 1H, H2), 2.02 (s, 3H, C7-CH3), 1.74 (s, 3H, CH3), 1.65-1.50 (m, 6H, 3 x CH2), 1.42-1.33 (m, 6H, 3 x CH2), 1.09-0.99 (m, 6H, 3 x CH2), 0.95-0.92 (m, 9H, 3 x CH3) ppm. ^13C-NMR (100.62 MHz, C6D6): δ 189.8 (d), 153.4 (s), 151.4 (s), 139.4 (d), 135.0 (d), 130.2 (d), 128.9 (d), 29.6 (t, 3x), 27.8 (t, 3x), 20.5 (q), 13.9 (q, 3x), 12.6 (q), 9.6 (t, 3x) ppm. HRMS (ESI^+): Calcd. for C21H30O119Sn ([M+H]^+), 427.2017; found, 427.2016. IR (NaCl): ν 2955 (s, C-H), 2924 (s, C-H), 2851 (m, C-H), 1662 (s, C=O), 1593 (s) cm⁻¹. UV (MeOH): λmax 340 nm.

(2E,4E,6E)-7-Iodo-3-methylocta-2,4,6-trienal 8. To a solution of (2E,4E,6E)-3-methyl-7-tributylstannylocta-2,4,6-trienal 7 (0.38 g, 0.89 mmol) in CH3CN (2 mL) was added N-iodosuccinimide (0.40 g, 1.78 mmol) in one portion. After 20 min, the mixture was treated with a saturated aqueous solution of Na2SO3 and vigorously stirred until a
clear colourless solution was obtained. The mixture was diluted with a 1:1 v/v mixture of hexane/EtOAc, the layers were separated and the organic layer was washed with a 1 M aqueous solution of NaOH (1x) and brine (1x). The mixture was dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, from 92:5:3 hexane/EtOAc/Et₃N to 90:10 hexane/EtOAc) to afford 0.22 g (96%) of a product identified as (2E,4E,6E)-7-iodo-3-methylocta-2,4,6-trienal 8. ¹H-NMR (400.13 MHz, C₆D₆): δ 9.92 (d, J = 7.7 Hz, 1H, CHO), 6.60 (ddd, J = 11.1, 1.3, 0.8 Hz, 1H, H₆), 6.15 (dd, J = 15.2, 11.1 Hz, 1H, H₅), 5.85 (d, J = 7.7 Hz, 1H, H₂), 5.60 (d, J = 15.2 Hz, 1H, H₄), 2.06 (s, 3H, CH₃), 1.54 (s, 3H, CH₃) ppm. ¹³C-NMR (100.62 MHz, C₆D₆): δ 189.9 (d), 152.1 (s), 140.6 (d), 135.8 (d), 130.8 (d), 128.8 (d), 102.6 (s), 28.2 (q), 12.3 (q) ppm. HRMS (ESI⁺): Calcd. for C₉H₁₂IO ([M+H]⁺), 262.9927; found, 262.9926.

IR (NaCl): ν 2933 (w, C=H), 2847 (w, C=H), 2781 (w, C=H), 2728 (w, C=H), 1645 (s, C=O), 1586 (s) cm⁻¹. UV (MeOH): λmax 335 nm. M.p.: 70-73 ºC (hexane/Et₂O).

(3E,5E,7E)-8-Iodo-4-methylnona-1,3,5,7-tetraene 9. To a suspension of methyltriphenylphosphonium bromide (0.26 g, 0.69 mmol) in THF (16.4 mL) was added nBuLi (0.41 mL, 1.5 M in hexane, 0.61 mmol) and DMPU (0.07 mL, 0.57 mmol) and the resulting mixture was stirred for 30 min at room temperature. The mixture was cooled down to -78 ºC and a solution of (2E,4E,6E)-7-iodo-3-methylocta-2,4,6-trienal 8 (0.1 g, 0.38 mmol) in THF (4.8 mL) containing a few drops of a solution of BHT in toluene (0.2 g/100 mL) was added. After stirring for 1.5 h at -78 ºC and for 4.5 h at room temperature, hexane (with a few drops of a solution of BHT in toluene) was added. The combined organic layers were washed with brine (3x) and water (3x), dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 90:8:2 hexane/EtOAc/Et₃N) to afford 0.08 g (82%) of a yellow oil identified as (3E,5E,7E)-8-iodo-4-methylnona-1,3,5,7-tetraene 9. ¹H-NMR (400.13 MHz, C₆D₆): δ 6.84 (d, J = 10.9 Hz, 1H, H₇), 6.63-6.53 (m, 1H, H₂), 6.15-6.04 (m, 2H, H₃ + H₆), 5.98 (d, J = 15.2 Hz, 1H, H₅), 5.20 (d, J = 16.7 Hz, 1H, H₁E), 5.08 (d, J = 10.1 Hz, 1H, H₁Z), 2.18 (s, 3H, CH₃), 1.61 (s, 3H, CH₃) ppm. ¹³C-NMR (100.62 MHz, C₆D₆): δ 141.5 (d), 138.0 (d), 135.4 (s), 133.7 (d), 133.5 (d), 123.4 (d), 118.4 (t), 97.0 (s), 28.0 (q), 12.4 (q) ppm. MS (EI): m/z (%) 260 ([M]⁺, 45), 178 (81), 161 (52), 137 (78), 133 (100), 117 (53), 115 (50), 105 (98), 97 (65), 95 (97), 93 (50), 91 (84), 85
(2E,4E,6E,8E,10E,12E,14E)-2,15-Diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 10. To a degassed solution of (3E,5E,7E)-8-iodo-4-methylnona-1,3,5,7-tetraene 9 (0.060 g, 0.23 mmol) in CH$_2$Cl$_2$ (4.4 mL) containing a few drops of a solution of BHT in toluene (0.2 g/100 mL) was added Grubbs 2$^{\text{nd}}$ generation catalyst (0.020 g, 0.023 mmol). After stirring at 25 °C for 6.5 h the solvent was evaporated and the residue was purified by precipitation in a mixture of acetone/MeOH to afford 0.024 g (43%) of a red solid identified as (2E,4E,6E,8E,10E,12E,14E)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene all-trans-10 and 5.8 mg (10%) of a 1:1 mixture of all-trans-10 and (2Z,14Z)-10 isomers.

Data for (2E,4E,6E,8E,10E,12E,14E)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene all-trans-10: $^1$H-NMR (400.13 MHz, C$_6$D$_6$): δ 6.91 (dd, J = 10.5, 1.3 Hz, 2H, H$_3$ + H$_{14}$), 6.64-6.56 (m, 2H, H$_8$ + H$_9$), 6.22-6.16 (m, 4H, H$_4$ + H$_7$ + H$_{10}$ + H$_{13}$), 6.10 (d, J = 15.0 Hz, 2H, H$_5$ + H$_{12}$), 2.24 (s, 6H, 2 x CH$_3$), 1.71 (s, 6H, 2 x CH$_3$) ppm. $^{13}$C-NMR (100.62 MHz, C$_6$D$_6$): δ 141.7 (d, 2x), 138.1 (d, 2x), 136.1 (s, 2x), 134.1 (d, 2x), 130.9 (d, 2x), 123.4 (d, 2x), 97.2 (s, 2x), 28.1 (q, 2x), 12.7 (q, 2x) ppm. MS (EI): m/z (%) 493 ([M+1]$^+$, 21), 492 ([M]$^+$, 100), 184 (28), 169 (32), 143 (24), 128 (24), 128 (66), 127 (42), 119 (89), 115 (32), 91 (35). HRMS (EI): Calcd. for C$_{18}$H$_{22}$I$_2$, 491.9811; found, 491.9813. IR (NaCl): ν 3029 (w, C=H), 2919 (m, C=H), 2853 (w, C=H), 1578 (w), 1430 (w), 964 (s) cm$^{-1}$. UV (MeOH): λ$_{\text{max}}$ 423, 399, 375, 355, 336 nm. M.p.: > 85 °C (acetone/MeOH, dec.).

NOE enhancements:

Data for (2Z,4E,6E,8E,10E,12E,14Z)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene (2Z,14Z)-10: $^1$H-NMR (400.13 MHz, C$_6$D$_6$): δ 6.63-6.56 (m, 4H, H$_4$ + H$_8$ + H$_9$ + H$_{13}$), 6.41 (d, J = 15.3 Hz, 2H, H$_5$ + H$_{12}$), 6.23 (d, J = 10.0 Hz, 2H, H$_7$ + H$_{10}$), 5.92 (d, J = 9.8 Hz, 2H, H$_3$ + H$_{14}$), 2.32 (s, 6H, 2 x CH$_3$), 1.82 (s, 6H, 2 x...
CH₃) ppm. **MS (EI):** m/z (%) 493 ([M+1]⁺, 171), 492 ([M]⁺, 100), 184 (20), 169 (24), 143 (17), 131 (19), 129 (22), 128 (47), 127 (36), 119 (69), 117 (19), 115 (27), 91 (43).
**HRMS (EI):** Calcd. for C₁₈H₂₂I₂, 491.9811; found, 491.9812.

**NOE enhancements:**

\[
(2Z,14Z)-10
\]

**NOE enhancements:**

\[\text{(E)}\text{-tributyl(2-(2,6,6-trimethylcyclohex-1-enyl)vinyl)stannane 12.} \]

To a solution of 2-ethynyl-1,3,3-trimethylcyclohex-1-ene (0.85 g, 5.3 mmol) in toluene (125 mL) were sequentially added Bu₃SnH (7.5 mL, 0.21 mmol) and 2,2'-azo-bis-isobutyronitrile (AIBN) (0.87 mg, 0.53 mmol). The reaction was stirred at 130 °C for 4 h and the solvent was evaporated. The residue was purified by column chromatography (C₁₈ silica gel, 60:40 CH₃CN/CH₂Cl₂) to afford 1.90 g (79%) of a colourless oil identified as (E)-tributyl(2-(2,6,6-trimethylcyclohex-1-enyl)vinyl)stannane 12. **¹H-NMR** (400.13 MHz, C₆D₆): δ 6.63 (dd, J = 19.7, 0.9 Hz, 1H, H₂), 6.13 (d, J = 19.7 Hz, 1.9 Hz, 1H, H₁), 1.95 (t, J = 6.1 Hz, 2H, CH₂), 1.82 (s, 3H, CH₃), 1.72-1.56 (m, 8H, 4 x CH₂), 1.49-1.45 (m, 2H, CH₂), 1.43-1.36 (m, 6H, 3 x CH₂), 1.16 (s, 6H, 2 x CH₃), 1.04-1.00 (m, 6H, 3 x CH₂), 0.97-0.93 (m, 9H, 3 x CH₃) ppm. **¹³C-NMR** (100.62 MHz, C₆D₆): δ 146.9 (d), 141.8 (s), 132.6 (d), 127.8 (s), 39.8 (t), 34.1 (s), 32.9 (t), 29.8 (t, 3x), 29.1 (q), 27.7 (t, 3x), 21.9 (q), 19.8 (t), 14.06 (q, 3x), 10.0 (t, 3x) ppm. **MS (EI):** m/z (%) 493 ([M+1]⁺, 21), 492 ([M]⁺, 100), 184 (28), 169 (32), 143 (24), 128 (24), 128 (66), 127 (42), 119 (89), 115 (32), 91 (35). **IR (NaCl):** ν 2956 (s, C-H), 2925 (s, C-H), 2870 (m, C-H), 2853 (m, C-H), 1548 (m), 1373 (w) cm⁻¹.

**β,β-Carotene 1.**

**General procedure for the Suzuki cross-coupling.** To a solution of (2E,4E,6E,8E,10E,12E,14E)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene, all-trans-10 (9.0 mg, 0.018 mmol) in THF (0.3 mL) containing a few drops of a solution of BHT in toluene (0.2 g/100 mL) was added Pd(PPh₃)₄ (4.3 mg, 0.004 mmol). The resulting mixture was stirred for 5 min at room temperature and then a solution of (E)-4,4,5,5-tetramethyl-2-(2-(2,6,6-trimethylcyclohex-1-enyl)-vinyl)-1,3,2-
dioxaborolane 11 (13 mg, 0.047 mmol) in THF (0.3 mL) containing a few drops of a solution of BHT in toluene (0.2 g /100 mL) and a freshly prepared 10% aqueous solution of TiOH (0.30 mL, 0.139 mmol) were added. After stirring for 4 h at 25 °C, the mixture was diluted with Et₂O (with a few drops of the solution of BHT in toluene), washed with brine (3x) and dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by column chromatography (C₁₈ silica gel, from CH₃CN to 50:50 CH₃CN/CH₂Cl₂) to afford 7.1 mg (73%) of a red solid identified as β,β-carotene 1.

General procedure for the Stille reaction using Fürstner conditions. A degassed solution of (E)-tributyl[2-(2,6,6-trimethylcyclohex-1-enyl)-vin-1-yl]stannane 12 (20 mg, 0.04 mmol) and (2E,4E,6E,8E,10E,12E,14E)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene, all-trans-10 (9 mg, 0.018 mmol) in DMF (0.5 mL) was added to flamed-dried [Ph₂PO₂][NBu₄] (20 mg, 0.05 mmol). Then CuTC (3.4 mg, 0.018 mmol) and Pd(PPh₃)₄ (4.20 mg, 0.004 mmol) were added and the reaction mixture was stirred for 1 h. Et₂O (containing a few drops of a solution of BHT in toluene) was added and the organic layer was washed with H₂O (3x). The combined aqueous layers were extracted with Et₂O (3x) and dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by column chromatography (C₁₈ silica gel, from CH₃CN to 50:50 CH₃CN/CH₂Cl₂) to afford 8.40 mg (86%) of a red solid identified as β,β-carotene 1.

(1E,3E)- and (1E,3Z)-2-[4,8-Dimethylnona-1,3,7-trienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16. To a solution of CrCl₂ (1.33 g, 10.83 mmol) in THF (13.5 mL) was added dichloromethyl-4,4,5,5-tetramethyl-1,3-dioxaborolane 15 (0.57 g, 2.71 mmol) in THF (3.4 mL). Then a solution of LiCl (0.72 g, 5.42 mmol) in THF (6.8 mL) and a solution of geranial 14 (0.206 g, 1.354 mmol) in THF (3.4 mL) were added sequentially.

and the resulting mixture was stirred for 2 h at room temperature. The reaction mixture was poured into a large excess of water and then extracted with Et₂O (2x). The combined organic layers were dried (MgSO₄) and the solvent was evaporated. The residue was dissolved in Et₂O and filtered through a pad of Celite® and the solvent was evaporated. The resulting residue was purified by column chromatography (silica gel, 98:2 hexane/EtOAc) to afford 0.30 g (79%) of a product identified as a 2:1 mixture of (1E,3E)- and (1E,3Z)-2-[4,8-dimethylnona-1,3,7-triethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes 16. The isomers were separated by HPLC (Prep Nova-Pak® HR Silica 60 Å, 6 μm, 19x300 mm, 98:2 hexane/EtOAc, 3 mL/min, tᵣ (Z) = 37.8 min and tᵣ (E) = 43.4 min).

Data for (1E,3E)-2-[4,8-dimethylnona-1,3,7-triethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16: ¹H-NMR (400.13 MHz, C₆D₆): δ 7.77 (dd, J = 17.4, 11.0 Hz, 1H, H₂), 6.07 (d, J = 11.0 Hz, 1H, H₃), 5.90 (d, J = 17.4 Hz, 1H, H₁), 5.1-5.0 (m, 1H, H₇), 2.2-2.1 (m, 2H, CH₂), 2.0-1.9 (m, 2H, CH₂), 1.61 (s, 3H, CH₃), 1.58 (d, J = 0.8 Hz, 3H, CH₃), 1.47 (s, 3H, CH₃), 1.11 (s, 12H, 4 x CH₂) ppm. ¹³C-NMR (100.62 MHz, C₆D₆): δ 146.9 (d), 143.5 (s), 131.5 (s), 128.2 (d), 124.4 (d), 119.0 (d), 83.0 (s, 2x), 40.3 (t), 26.8 (t), 25.8 (q), 25.0 (q, 4x), 17.7 (q), 16.9 (q) ppm. HRMS (ESI⁺): Calcd. for C₁₇H₃₀BO₂ ([M+H]+), 277.23364; found, 277.23303. IR (NaCl): ν 2978 (m, C-H), 2927 (m, C-H), 2860 (w, C-H), 1638 (w), 1601 (m), 1363 (s), 1340 (s), 1320 (s), 1146 (s) cm⁻¹. UV (MeOH): λₘₐₓ 262 nm.

Data for (1E,3Z)-2-[4,8-dimethylnona-1,3,7-triethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16: ¹H-NMR (400.13 MHz, C₆D₆): δ 7.77 (dd, J = 17.4, 11.1 Hz, 1H, H₂), 6.02 (d, J = 11.1 Hz, 1H, H₃), 5.87 (d, J = 17.4 Hz, 1H, H₁), 5.1-5.0 (m, 1H, H₇), 2.17 (t, J = 7.7 Hz, 2H, CH₂), 2.1-2.0 (m, 2H, CH₂), 1.61 (d, J = 0.9 Hz, 3H, CH₃), 1.60 (s, 3H, CH₃), 1.49 (s, 3H, CH₃), 1.10 (s, 12H, 4 x CH₂) ppm. ¹³C-NMR (100.62 MHz, C₆D₆): δ 146.5 (d), 143.7 (s), 131.6 (s), 129.1 (d), 124.4 (d), 118.8 (d), 83.0 (s, 2x), 32.9 (t), 27.3 (t), 25.8 (q), 25.0 (q, 4x), 24.0 (q), 17.7 (q) ppm. HRMS (ESI⁺): Calcd. for C₁₇H₃₀BO₂ ([M+H]+), 277.23364; found, 277.23295. IR (NaCl): ν 2977 (m, C-H), 2927 (m, C-H), 2864 (w, C-H), 1637 (w), 1600 (m), 1369 (s), 1335 (s), 1144 (s) cm⁻¹. UV (MeOH): λₘₐₓ 262 nm.

**Lycopene 2.** Following the general procedure for the Suzuki cross-coupling, the reaction of (2E,4E,6E,8E,10E,12E,14E)-2,15-diiodo-6,11-dimethylhexadeca-
2,4,6,8,10,12,14-heptaene 10 (9.5 mg, 0.019 mmol), (1E,3E)-2-[4,8-dimethylnona-1,3,7-trietyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16 (14.0 mg, 0.05 mmol), Pd(PPh₃)₄ (4.5 mg, 0.004 mmol), a freshly prepared 10% aqueous solution of TIOH (0.32 mL, 0.32 g, 0.15 mmol) in THF (0.6 mL) and a few drops of a solution of BHT in toluene (0.2 g/100 mL) afforded, after purification by column chromatography (silica gel, from 100% hexane to 98:2 hexane/aceton), 5.4 mg (52%) of a red solid identified as lycopene 2. ¹H-NMR (400.13 MHz, C₆D₆): δ 6.77 (dd, J = 14.8, 11.3 Hz, 2H, 2H₇ or 2H₁₁), 6.71-6.64 (m, 4H, 2H₇ or 2H₁₁ + 2H₁₅), 6.49 (d, J = 14.8 Hz, 2H, 2H₈ or 2H₁₂), 6.44 (d, J = 15.2 Hz, 2H, 2H₈ or 2H₁₂), 5.24 (t, J = 6.3 Hz, 2H, 2H₂), 2.4-2.0 (m, 8H, 4 x CH₂), 1.93 (s, 6H, 2 x CH₃), 1.88 (s, 6H, 2 x CH₃), 1.75 (s, 6H, 2 x CH₃), 1.68 (s, 6H, 2 x CH₃), 1.57 (s, 6H, 2 x CH₃) ppm. MS (EI): m/z (%) 536 ([M]+, 10), 171 (27), 169 (25), 157 (42), 145 (51), 119 (45), 105 (64), 93 (40), 91 (63), 81 (39), 69 (100). HRMS (EI): Calcd. for C₄₀H₅₆, 536.4382; found, 536.4374. UV (MeOH): λ max 360, 327, 282, 241 nm.

4-Bromo-2,3-dimethylphenyl Trifluoromethanesulfonate 18. To a cooled (0 ºC) solution of 4-bromo-2,3-dimethylphenol 17 (0.20 g, 1.0 mmol) in CH₂Cl₂ (4.6 mL) were added pyridine (0.09 mL, 1.1 mmol) and Tf₂O (0.25 mL, 1.5 mmol) and the reaction mixture was stirred for 2 h at 25 ºC. A saturated aqueous solution of NH₄Cl was added and the mixture was extracted with CH₂Cl₂ (3x). The combined organic layers were dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 80:20 hexane/Et₂O) to afford 0.32 g (96%) of a colourless oil identified as 4-bromo-2,3-dimethylphenyl trifluoromethanesulfonate 18. ¹H-NMR (400.13 MHz, CDCl₃): δ 7.47 (d, J = 8.8 Hz, 1H, ArH), 6.99 (d, J = 8.8 Hz, 1H, ArH), 2.43 (s, 3H, CH₃), 2.34 (s, 3H, CH₃) ppm. ¹³C-NMR (100.62 MHz, CDCl₃): δ 147.5 (s), 139.5 (s), 131.6 (s), 131.0 (d), 124.9 (s), 120.0 (d), 118.7 (q, J_C-F = 320.4 Hz), 20.4 (q), 14.5 (q) ppm. MS (EI): m/z (%) 334 ([M]+, 81 [Br], 26), 332 ([M]+, 79 [Br], 25), 301 (98), 199 (100), 173 (16), 171 (16), 92 (31), 91 (35). HRMS (EI): Calcd. for C₇₉H₆₅O₇S₈Br, 333.9309; found, 333.9318 and C₇₀H₆₃O₇S₇Br, 331.9330; found, 331.9336. IR (NaCl): ν 3087 (w, C-H), 3010 (w, C-H), 2932 (w, C-H), 2873 (w, C-H), 1461 (m), 1423 (s), 1389 (m), 1252 (s), 1221 (s) cm⁻¹.

Methyl 4-Bromo-2,3-dimethylbenzoate 18 and Dimethyl 2,3-Dimethylterephthalate 20.

General procedure for the carbonylation reaction and methanol trapping catalyzed by palladium. To a stirred solution of 4-bromo-2,3-dimethylphenyl trifluoromethanesulfonate 18 (0.36 g, 1.08 mmol) in DMSO (6.6 mL) and MeOH (6.6 mL) were added Et₃N (0.38 mL, 2.70 mmol), Pd(OAc)₂ (7.0 mg, 0.032 mmol) and 1,3-bis(diphenylphosphino)propane (0.013 g, 0.032 mmol). The reaction was saturated with carbon monoxide and heated at 70 ºC for 80 min. Then the mixture was cooled down to 25 ºC, poured into water and extracted with EtOAc (3x). The combined organic layers were dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, from 95:5 hexane/EtOAc to 93:7 hexane/EtOAc) to afford 0.22 g (85%) of a white solid identified as methyl 4-bromo-2,3-dimethylbenzoate 19 and 0.012 g (4%) of another solid identified as dimethyl 2,3-dimethylterephthalate 20.

Data for 4-bromo-2,3-dimethylbenzoate 19 (major product): ¹H-NMR (400.13 MHz, CDCl₃): δ 7.45 (s, 2H, 2ArH), 3.88 (s, 3H, CO₂CH₃), 2.52 (s, 3H, CH₃), 2.43 (s, 3H, CH₃) ppm. ¹³C-NMR (100.62 MHz, CDCl₃): δ 168.7 (s), 139.6 (s), 137.7 (s), 130.5 (s), 129.9 (d), 129.5 (s), 128.4 (d), 52.3 (q), 20.2 (q), 18.2 (q) ppm. MS (EI): m/z (%) 244 ([M]⁺ 81[Br], 44), 242 ([M]⁺ 79[Br], 46), 213 (94), 212 (86), 211 (100), 209 (81), 185 (36), 183 (38), 104 (30), 103 (44), 77 (22). HRMS (EI): Calcd. for C₁₀H₁₁O₃Br, 243.9924; found, 243.9922.

IR (NaCl): ν 2966 (w, C-H), 2957 (w, C-H), 2924 (w, C-H), 1724 (s, C=O), 1574 (m), 1438 (m), 1287 (m), 1253 (s) cm⁻¹. M.p.: 34-35 ºC (hexane/EtOAc).

Data for dimethyl 2,3-dimethylterephthalate 20 (minor product): ¹H-NMR (400.13 MHz, CDCl₃): δ 7.57 (s, 2H, 2ArH), 3.90 (s, 6H, 2 x CO₂CH₃), 2.46 (s, 6H, 2 x CH₃) ppm. ¹³C-NMR (100.62 MHz, CDCl₃): δ 169.0 (s, 2x), 138.5 (s, 2x), 134.2 (s, 2x), 126.7 (d, 2x), 52.4 (q, 2x), 17.2 (q, 2x) ppm. HRMS (ESI⁺): Calcd. for C₁₂H₁₅O₄ ([M+H]⁺), 223.0965; found, 223.0971. IR (NaCl): ν 3012 (w, C-H), 2957 (w, C-H), 2924 (w, C-H), 2849 (w, C-H), 1730 (s, C=O), 1438 (m), 1294 (m), 1262 (m) cm⁻¹.

Methyl 2,3-Dimethyl-4-(2-trimethylsilyl-ethyn-1-yl)-benzoate 22. General procedure for the Sonogashira coupling. To a solution of 4-bromo-2,3-dimethylbenzoate 19 (0.2 g,
0.82 mmol), Pd(dppf)Cl₂ (0.04 g, 0.05 mmol), CuI (0.01 g, 0.06 mmol), (iPr)₂NH (1.4 mL, 9.99 mmol) in DMF (1.4 mL) at 25 °C was added trimethylsilylacetylene 21 (0.23 mL, 1.65 mmol) and the reaction mixture was stirred at 80 °C for 2.5 h. Then EtOAc was added and the organic layer was washed with water (5x) and dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 97:3 hexane/EtOAc) to afford 0.21 g (97%) of a yellow oil identified as methyl 2,3-dimethyl-4-(2-trimethylsilyl-1-yl)-benzoate 22. ¹H-NMR (400.13 MHz, CDCl₃): δ 7.54 (d, J = 8.1 Hz, 1H, ArH), 7.32 (d, J = 8.1 Hz, 1H, ArH), 3.87 (s, 3H, CO₂CH₃), 2.45 (s, 6H, 2 x CH₃), 0.27 (s, 9H, 3 x CH₃) ppm. ¹³C-NMR (100.62 MHz, CDCl₃): δ 168.8 (s), 140.3 (s), 137.9 (s), 130.9 (s), 129.4 (d), 127.0 (d), 126.5 (s), 104.1 (s), 100.2 (s), 52.1 (q), 18.2 (q), 17.2 (q), 0.1 (q, 3x) ppm. MS (EI): m/z (%) 260 ([M]+, 39), 246 (26), 245 (100), 229 (9). HRMS (EI): Calcd. for C₁₅H₂₀O₂Si, 260.1233; found, 260.1240.

IR (NaCl): ν 2954 (m, C-H), 2900 (w, C-H), 2148 (m, C≡C), 1725 (s, C=O), 1590 (w), 1435 (m), 1291 (m), 1250 (s) cm⁻¹.

Methyl 4-Ethynyl-2,3-dimethylbenzoate 23. A solution of methyl 2,3-dimethyl-4-(2-trimethylsilyl-1-yl)-benzoate 22 (0.49 g, 1.88 mmol) in THF (12.4 mL) was treated with (nBu)₄NF (2.068 mL, 1 M in THF, 2.068 mmol) and the reaction mixture was stirred for 2 h. The mixture was treated with Et₂O and water and the aqueous layer was extracted with Et₂O (3x). The combined organic layers were washed with brine (1x), dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 95:5 hexane/Et₂O) to afford 0.28 g (80%) of a white solid identified as methyl 4-ethynyl-2,3-dimethylbenzoate 23. ¹H-NMR (400.13 MHz, CDCl₃): δ 7.54 (d, J = 8.0 Hz, 1H, ArH), 7.34 (d, J = 8.0 Hz, 1H, ArH), 3.87 (s, 3H, CO₂CH₃), 3.36 (s, 1H, C≡CH), 2.44 (s, 6H, 2 x CH₃) ppm. ¹³C-NMR (100.62 MHz, CDCl₃): δ 168.7 (s), 140.6 (s), 137.8 (s), 131.2 (s), 129.7 (d), 127.0 (s), 125.4 (d), 82.7 (s), 82.6 (d), 52.1 (q), 18.1 (q), 17.1 (q) ppm. MS (EI): m/z (%) 188 ([M]+, 57), 161 (18), 157 (100), 156 (71), 149 (74), 128 (44), 127 (16). HRMS (EI): Calcd. for C₁₂H₁₂O₂, 188.0837; found, 188.0838. IR (NaCl): ν 3291 (m, br, ≡C-H), 2995 (w, C-H), 2951 (w, C-H), 1721 (s, C=O), 1592 (w), 1434 (m), 1292 (m), 1261 (s) cm⁻¹. M.p.: 37-38 °C (MeOH/H₂O).
Methyl (E)- and (Z)-2,3-Dimethyl-4-(2-tributylstannylvin-1-yl)benzoate 24.

Following the general procedure for the radical hydrostannylation, the reaction of methyl 4-ethyl-2,3-dimethylbenzoate 23 (0.02 g, 0.10 mmol), Bu3SnH (0.035 mL, 0.13 mmol) and 2-2'-azobisisobutyronitrile (AIBN) (0.7 mg, 0.004 mmol) in toluene (0.4 mL) afforded, after purification by column chromatography (C18 silica gel, from 100% CH3CN to 90:10 CH3CN/CH2Cl2), 0.02 g (50%) of a colourless oil identified as a mixture of methyl (E)- and (Z)-2,3-dimethyl-4-(2-(tributylstannyl)vinyl)benzoate 24. The isomers, in a 8.5:1 ratio, were separated by HPLC (Prep Nova-Pak® HR Silica, 6 μm, 19x300 mm, 95:5 CH3CN/THF, 3 mL/min, tR (Z) = 80 min and tR (E) = 85 min).

Data for methyl (E)-2,3-dimethyl-4-(2-(tributylstannyl)vinyl)benzoate 24 (major product): 1H-NMR (400.13 MHz, C6D6): δ 7.81 (d, J = 8.2 Hz, 1H, ArH), 7.38 (d, J = 8.2 Hz, 1H, ArH), 7.31 (d, J = 19.3 Hz, 1H, H2), 6.82 (d, J = 19.3 Hz, 1H, H1), 3.53 (s, 3H, CO2CH3), 2.50 (s, 3H, CH3), 2.08 (s, 3H, CH3), 1.75-1.54 (m, 6H, 3 x CH2), 1.45-1.36 (m, 6H, 3 x CH2), 1.13-0.98 (m, 6H, 3 x CH2), 0.95 (t, J = 7.3 Hz, 9H, 3 x CH3) ppm. 13C-NMR (100.62 MHz, C6D6): δ 168.7 (s), 146.0 (d), 142.7 (s), 138.6 (s), 134.9 (s), 134.1 (d), 130.6 (s), 128.1 (d), 123.9 (d), 51.5 (q), 29.6 (t, 3x), 27.8 (t, 3x), 17.3 (q), 15.6 (q), 14.0 (q, 3x), 10.00 (t, 3x) ppm. HRMS (ESI+): Calcd. for C24H41O2119Sn ([M+H]+), 481.2127; found, 481.2118. IR (NaCl): ν 2955 (m, C-H), 2924 (m, C-H), 2870 (w, C-H), 2850 (w, C-H), 1724 (s, C=O), 1589 (w), 1433 (w), 1289 (m), 1261 (m) cm⁻¹.

Data for methyl (Z)-2,3-dimethyl-4-(2-(tributylstannyl)vinyl)benzoate 24 (minor product): 1H-NMR (400.13 MHz, C6D6): δ 7.83 (d, J = 8.0 Hz, 1H, ArH), 7.67 (d, J = 13.6 Hz, 1H, H2), 7.21 (d, J = 8.0 Hz, 1H, ArH), 6.40 (d, J = 13.6 Hz, 1H, H1), 3.49 (s, 3H, CH3), 2.55 (s, 3H, CH3), 2.05 (s, 3H, CH3), 1.47-1.39 (m, 6H, 3 x CH2), 1.32-1.23 (m, 6H, 3 x CH2), 0.90-0.72 (m, 15H, 3 x CH3 + 3 x CH2) ppm. 13C-NMR (100.62 MHz, C6D6): δ 168.5 (s), 148.2 (d), 145.4 (s), 138.4 (s), 136.1 (s), 134.6 (d), 130.8 (s), 128.0 (d), 125.5 (d), 51.4 (q), 29.5 (t, 3x), 27.8 (t, 3x), 17.0 (q), 16.4 (q), 13.9 (q, 3x), 11.1 (t, 3x) ppm. HRMS (ESI+): Calcd. for C24H41O2119Sn ([M+H]+), 481.2127; found, 481.2121. IR (NaCl): ν 2955 (m, C-H), 2924 (m, C-H), 2871 (w, C-H), 2852 (w, C-H), 1725 (s, C=O), 1578 (w), 1459 (w), 1435 (w), 1288 (m), 1265 (m) cm⁻¹.

Dimethyl (1E,3E,5E,7E,9E,11E,13E,15E,17E) 4,4'-(3,7,12,16-tetramethyloctadeca-1,3,5,7,9,11,13,15,17)-nonaene-1,18-diyl)-bis-(2,3-dimethylbenzoate) 25.
(Synechoxanthin Dimethyl Ester). Following the general procedure for the Stille reaction using Fürstner conditions, the reaction of methyl (E)-2,3-dimethyl-4-(2-tributylstannyllvin-1-yl)-benzoate 24 (20.0 mg, 0.042 mmol) and (2E,4E,6E,8E,10E,12E,14E)-2,15-diido-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 10 (9.0 mg, 0.018 mmol), [NBu₄][Ph₃PO₂] (0.021 g, 0.045 mmol), CuTC (3.4 mg, 0.018 mmol), Pd(PPh₃)₄ (4.2 mg, 0.004 mmol) in DMF (0.5 mL) containing a few drops of solution of BHT in toluene (0.2 g/100 mL) at 25 ºC for 3 h afforded, after purification by column chromatography (C₁₈ silica gel, from CH₃CN to 50:50 CH₃CN/CH₂Cl₂), 8.8 mg (79%) of a solid identified as dimethyl (1E,3E,5E,7E,9E,11E,13E,15E,17E)-4,4’-(3,7,12,16-tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene-1,18-diyl)-bis-(2,3-dimethylbenzoate) 25. ¹H-NMR (400.13 MHz, CD₂Cl₂): δ 7.56 (d, J = 8.3 Hz, 1H, ArH), 7.40 (d, J = 8.3 Hz, 2H, ArH), 6.89 (d, J = 15.8 Hz, 2H, H₁ + H₁₈), 6.83 (d, J = 15.8 Hz, 2H, H₂ + H₁₇), 6.76-6.66 (m, 4H, H₅ + H₉ + H₁₁ + H₁₄), 6.47 (d, J = 14.9 Hz, 2H, H₆ + H₁₃), 6.39 (d, J = 11.6 Hz, 2H, H₄ + H₁₅), 6.33 (dd, J = 8.2, 1.6 Hz, 2H, H₇ + H₈), 3.85 (s, 6H, 2 x CO₂CH₃), 2.47 (s, 6H, 2 x CH₃), 2.33 (s, 6H, 2 x CH₃), 2.08 (s, 6H, 2 x CH₃), 2.01 (s, 6H, 2 x CH₃) ppm. ¹³C-NMR (100.62 MHz, CD₂Cl₂): δ 169.5 (s, 2x, CO₂Me), 140.7 (s, 2x), 139.2 (d, 2x), 138.4 (s, 2x), 137.4 (d, 2x), 137.4 (s, 2x), 136.4 (s, 2x), 136.0 (s, 2x), 134.5 (d, 2x), 133.8 (d, 2x), 131.0 (d, 2x), 130.2 (s, 2x), 127.7 (d, 2x), 125.8 (d, 2x), 125.6 (d, 2x), 123.1 (d, 2x), 132.3 (q, 2x), 17.6 (q, 2x), 16.1 (q, 2x), 13.2 (q, 2x), 13.1 (q, 2x) ppm. HRMS (ESI⁺): Calcd. for C₄₂H₉₀O₄ ([M+H]⁺), 617.3625; found, 617.3632. IR (neat): ν 2922 (s, C-H), 2851 (m, C-H), 1716 (s, C=O), 1586 (w), 1458 (w), 1434 (w) cm⁻¹.

Synechoxanthin 3. To a Schlenk flask charged with KOSiMe₃ (40.0 mg, 0.298 mmol) was added a solution of synechoxanthin dimethyl ester 25 (4.6 mg, 0.0075 mmol) in THF (1 mL). The reaction was stirred at 65 ºC for 1 h and 30 min at 75 ºC. The reaction mixture was cooled down to 25 ºC and the solvent was evaporated. The residue was purified by column chromatography (C₁₈ silica gel, 90:10 MeOH/H₂O) and then crystallized with MeOH/CH₂Cl₂ to afford 4.3 mg (98%) of a red solid identified as synechoxanthin 3. ¹H-NMR (400.13 MHz, CD₃OD): δ 7.33 (d, J = 8.0 Hz, 2H, 2H₃), 7.17 (d, J = 8.0 Hz, 2H, 2H₄), 6.90 (d, J = 15.8 Hz, 2H, 2H₅), 6.78-6.71 (m, 6H, 2H₈ + 2H₁₁ + 2H₁₄), 6.46 (d, J = 14.8 Hz, 2H, 2H₁₂), 6.37-6.32 (m, 4H, 2H₁₀ + 2H₁₃), 2.37 (s, 6H, 2 x CH₃), 2.30 (s, 6H, 2 x CH₃), 2.06 (s, 6H, 2 x CH₃), 2.00 (s, 6H, 2 x CH₃). ¹³C-
NMR (100.62 MHz, CD$_3$OD): δ 179.8 (s, 2 x CO$_2$H), 142.4 (s, 2x), 139.4 (d, 2x), 137.7 (s, 2x), 137.6 (s, 2x), 137.0 (s, 2x), 136.2 (d, 2x), 135.4 (s, 2x), 134.2 (d, 2x), 134.1 (d, 2x), 133.6 (s, 2x), 131.6 (d, 2x), 127.0 (d, 2x), 126.1 (d, 2x), 125.1 (d, 2x), 123.6 (d, 2x), 17.8 (q, 2x), 15.7 (q, 2x), 13.0 (q, 2x), 12.8 (q, 2x) ppm. HRMS (ESI): Calcd. for C$_{40}$H$_{43}$O$_4$ ([M-H]), 587.3167; found, 587.3184. UV (MeOH) (ε M$^{-1}$ cm$^{-1}$): $\lambda_{max}$ 500 (sh), 470 (36.4000), 445 (sh) nm.

4,4′-Diapo-$\psi$-$\psi$-carotene-4,4′-dial 4. Following the general procedure for the Stille reaction using Fürstner conditions, the reaction of (2E,4E,6E,8E,10E,12E,14E)-2,15-diodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 9 (9.0 mg, 0.018 mmol), (2E,4E)-2-methyl-5-(tributylstannyl)penta-2,4,6-dienal 31 (15.0 mg, 0.038 mmol), [NBu$_4$][Ph$_2$PO$_2$] (19.0 mg, 0.042 mmol), CuTC (3.4 mg, 0.018 mmol), Pd(PPh$_3$)$_4$ (4.2 mg, 0.004 mmol) in DMF (0.8 mL), containing a few drops of a solution of BHT in toluene (0.2 g/100 mL), at 25 °C for 30 min afforded, after purification by column chromatography (C$_{18}$ silica gel, from 90:10 MeOH/CH$_2$Cl$_2$ to CH$_2$Cl$_2$) and subsequent washing with hexane, 6.0 mg (78%) of a dark red solid identified as 4,4′-diapo-$\psi$-$\psi$-carotene-4,4′-dial 4. $^1$H-NMR (400.13 MHz, CD$_2$Cl$_2$): δ 9.43 (s, 2H, CHO), 6.96 (dd, J = 10.6, 1.0 Hz, 2H, H$_6$ + H$_8$), 6.78 (d, J = 14.9 Hz, 2H, H$_5$ + H$_8$), 6.74-6.68 (m, 6H, H$_7$ + H$_{11}$ + H$_{14}$ + H$_7$ + H$_{11}′$ + H$_{14}′$), 6.53 (d, J = 14.8 Hz, 2H, H$_{12}$ + H$_{12}′$), 6.46 (d, J = 11.6 Hz, 2H, H$_{10}$ + H$_{10}′$), 6.39-6.36 (m, 2H, H$_{15}$ + H$_{15}′$), 2.03 (s, 3H, 2 x CH$_3$), 2.00 (s, 3H, 2 x CH$_3$), 1.87 (s, 3H, 2 x CH$_3$) ppm. $^{13}$C-NMR (100.62 MHz, CD$_2$Cl$_2$): δ 194.7 (d, CHO), 149.5 (d), 146.3 (d), 141.1 (d), 138.0 (d), 137.7 (s), 137.3 (s), 136.1 (s), 135.0 (d), 131.6 (d), 125.6 (d), 123.3 (d), 13.1 (q), 13.08 (q), 9.9 (q) ppm. HRMS (ESI$^+$): Calcd. for C$_{30}$H$_{37}$O$_2$ ([M+H])$^+$, 429.2788; found, 429.2791. IR (neat): ν 3034 (w, C-H), 2980 (w, C-H), 2918 (w, C-H), 2824 (w, C-H), 2723 (w, C-H), 1667 (s, C=O), 1607 (m), 1538 (s), 1177 (s) cm$^{-1}$. UV (MeOH) (ε M$^{-1}$ cm$^{-1}$): $\lambda_{max}$ 545 (sh), 515 (87.100), 480 (sh) nm.

4,4′-Diapo-ψ,ψ-carotene-4,4′-dial 4 (scaled-up). Following the general procedure for the Stille reaction using Fürstner conditions, the reaction of (2E,4E,6E,8E,10E,12E,14E)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 9 (65.0 mg, 0.132 mmol), (2E,4E)-2-methyl-5-(tributylstannyl)penta-2,4-dienal 31 (106.7 mg, 0.277 mmol), [NBu₄][Ph₂PO₂] (139.8 mg, 0.304 mmol), CuTC (25.2 mg, 0.132 mmol), Pd(PPh₃)₄ (30.0 mg, 0.026 mmol) in DMF (5.9 mL), containing a few drops of a solution of BHT in toluene (0.2 g/100 mL), at 25 °C for 30 min afforded, after purification by column chromatography (C₁₈ silica gel, from 90:10 MeOH/CH₂Cl₂ to CH₂Cl₂) and subsequent washing with hexane, 42.7 mg (76%) of a dark red solid identified as 4,4′-diapo-ψ,ψ-carotene-4,4′-dial 4.

2-(4-Bromo-2,3-dimethylphen-1-yl)-ethynyl-trimethylsilane 32 and (2,3-Dimethyl-1,4-phenylene)-bis(ethyne-2,1-diyl)-bis(trimethylsilane) 33. Following the general procedure for Sonogashira coupling, the reaction of 4-bromo-2,3-dimethylphenyl trifluoromethanesulfonate 17 (210 mg, 0.64 mmol), trimethylsilylacetylene 21 (0.14 mL, 0.96 mmol), Pd(dppf)Cl₂ (0.03 g, 0.04 mmol), CuI (9 mg, 0.045 mmol), (iPr)₂NH (1.1 mL, 7.85 mmol) in DMF (1.1 mL) at 25 °C for 15 h afforded, after purification by column chromatography (silica gel, hexane), 56.0 mg (31%) of a white solid identified as 2-(4-bromo-2,3-dimethylphen-1-yl)-ethynyl-trimethylsilane 32 and 0.082 g (47%) of another white solid identified as (2,3-dimethyl-1,4-phenylene)-bis(ethyne-2,1-diyl)-bis(trimethylsilane) 33.

Data for 2-(4-bromo-2,3-dimethylphen-1-yl)-ethynyl-trimethylsilane 32 (minor product): \textsuperscript{1}H-NMR (400.13 MHz, CDCl₃): δ 7.33 (d, J = 8.3 Hz, 1H, ArH), 7.14 (d, J = 8.3 Hz, 1H, ArH), 2.46 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 0.27 (s, 9H, 3 x CH₃) ppm. \textsuperscript{13}C-NMR (100.62 MHz, CDCl₃): δ 140.8 (s), 136.5 (s), 130.8 (d), 129.8 (d), 126.1 (s), 122.6 (s), 104.1 (s), 98.6 (s), 20.1 (q), 19.2 (q), 0.1 (q, 3x) ppm. MS (EI): m/z (%) 282 ([M]⁺ \textsuperscript{81}Br), 25, 280 ([M]⁺ \textsuperscript{79}Br), 26, 268 (19), 267 (100), 266 (18), 128 (11). HRMS (EI): Calcd. for C₁₃H₁₇Si\textsuperscript{81}Br, 282.0262; found, 282.0262 and C₁₃H₁₇Si\textsuperscript{79}Br, 280.0283; found, 280.0296. IR (NaCl): ν 2957 (m, C-H), 2922 (w, C-H), 2986 (w, C-H), 2850 (w, C-H), 1474 (m, C=C), 1451 (w), 1406 (w), 1247 (m) cm⁻¹.

Data for (2,3-dimethyl-1,4-phenylene)-bis(ethyne-2,1-diyl)-bis(trimethylsilane) 33 (major product): \textsuperscript{1}H-NMR (400.13 MHz, CDCl₃): δ 7.24 (s, 2H, 2ArH), 2.40 (s, 6H, 2 x
CH₃), 0.27 (s, 18H, 6 x CH₃) ppm. ¹³C-NMR (100.62 MHz, CDCl₃): δ 139.2 (s, 2x), 129.5 (d, 2x), 123.4 (s, 2x), 104.6 (s, 2x), 99.3 (s, 2x), 18.1 (q, 2x), 0.2 (q, 6x) ppm. MS (EI): m/z (%) 299 ([M+1]⁺, 12), 298 ([M⁺], 40), 285 (12), 284 (32), 283 (100). HRMS (EI): Calcd. for C₁₈H₂₆Si₂, 298.1573; found, 298.1578.

IR (NaCl): ν 2958 (m, C-H), 2925 (w, C-H), 2898 (w, C-H), 2852 (w, C-H), 2152 (m, C≡C), 1471 (w), 1411 (m), 1249 (s) cm⁻¹.

Methyl 4-(Bromoethyl)-2,3-dimethylbenzoate 34. Following the general procedure for the carbonylation catalyzed by palladium, the reaction of 2-(4-bromo-2,3-dimethylphen-1-y1)-ethynyl-trimethylsilane 32 (50.0 mg, 0.18 mmol), Pd(OAc)₂ (1.2 mg, 0.005 mmol), 1,3-bis(diphenylphosphino)-propane (2.2 mg, 0.005 mmol), Et₃N (0.06 mL, 0.45 mmol) in DMSO (1.1 mL) and MeOH (1.1 mL) stirring with carbon monoxide for 16 h at 70 ºC to afford, after purification by column chromatography (silica gel, from 100% hexane to 93:7 hexane/Et₂O) to afford 21.0 mg (44%) of a solid identified as methyl 4-(bromoethyl)-2,3-dimethylbenzoate 34. ¹H-NMR (400.13 MHz, CDCl₃): δ 7.41 (d, J = 8.3 Hz, 1H, ArH), 7.24 (d, J = 8.3 Hz, 1H, ArH), 3.84 (s, 3H, CO₂CH₃), 2.50 (s, 3H, CH₃), 2.39 (s, 3H, CH₃) ppm. ¹³C-NMR (100.62 MHz, CDCl₃): δ 154.6 (s), 142.4 (s), 137.3 (s), 131.9 (d), 130.4 (d), 128.8 (s), 119.1 (s), 85.6 (s), 28.4 (q), 53.0 (q), 20.1 (q), 19.3 (q) ppm. MS (EI): m/z (%) 268 ([M⁺]⁺[Br], 50), 266 ([M⁺]⁺[Br], 54), 237 (61), 235 (64), 210 (84), 208 (98), 129 (35), 128 (100), 127 (37). HRMS (ESI⁺): Calcd. for C₁₂H₁₂O₂²⁻Br ([M⁺]⁺), 267.0015; found, 267.0026. IR (NaCl): ν 3084 (w, C-H), 3004 (w, C-H), 2952 (w, C-H), 2952 (w, C-H), 2924 (w, C-H), 2230 (w, C=C), 2209 (w, C=C), 1698 (s, C=O), 1572 (w), 1435 (w), 1300 (m), 1210 (m) cm⁻¹.

(2E,4E,6E,8E)-2,9-Dimethyldeca-2,4,6,8-tetraene-1,10-diol. (This compound was isolated in variable amounts from the Stille reactions of stannyldienal 30 and diiodoheptaene 10).
ppm. **MS** (EI): \( m/z \) (%) 194 ([M]+, 18), 176 (34), 174 (34), 160 (18), 159 (28), 147 (26), 145 (38), 143 (28), 129 (34), 128 (54), 119 (21), 117 (35), 116 (22), 115 (43), 92 (19), 91 (100), 80 (18), 79 (38), 77 (19) ppm. **HRMS** (EI): Calcd. for C\(_{12}\)H\(_{18}\)O\(_2\), 194.1307; found, 194.1308.
(2E,4E,6E)-3-Methyl-7-tributylstannylocta-2,4,6-trienal 7.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):
(2E,4E,6E)-7-Iodo-3-methylhexa-2,4,6-trienal 8.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):
(3E,5E,7E)-8-Iodo-4-methylnona-1,3,5,7-tetraene 9.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):
(2E,4E,6E,8E,10E,12E,14E)-2,15-Diido-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 10.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

![H-NMR spectrum](image)

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):

![C-NMR spectrum](image)
(2Z,4E,6E,8E,10E,12E,14Z)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 10.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):
(E)-tributyl(2-(2,6,6-trimethylcyclohex-1-enyl)vinyl)stannane 12.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):
**β,β-Carotene 1.**

**^1^H-NMR** (400.13 MHz, C$_6$D$_6$):

![NMR Spectrum](image)

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(1E,3E)-2-[-4,8-Dimethylnona-1,3,7-trienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):
(1E,3Z)-2-[4,8-Dimethylnona-1,3,7-triyl]-4,4,5,5-tetramethyl-1,3,2-
dioxaborolane 16.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):
Lycopene 2.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):
4-Bromo-2,3-dimethylphenyl trifluoromethanesulfonate 18.

$^1$H-NMR (400.13 MHz, CDCl$_3$):

$^{13}$C-NMR (100.62 MHz, CDCl$_3$):
Methyl 4-Bromo-2,3-dimethylbenzoate 19.

$^1$H-NMR (400.13 MHz, CDCl$_3$):

$^{13}$C-NMR (100.62 MHz, CDCl$_3$):
Dimethyl 2,3-Dimethylyterephthalate 20.

$^1$H-NMR (400.13 MHz, CDCl$_3$):

$^{13}$C-NMR (100.62 MHz, CDCl$_3$):
Methyl 2,3-Dimethyl-4-(2-trimethylsilyl-ethyn-1-yl)-benzoate 22.

$^1$H-NMR (400.13 MHz, CDCl$_3$):

$^{13}$C-NMR (100.62 MHz, CDCl$_3$):
Methyl 4-Ethynyl-2,3-dimethylbenzoate 23.

$^1$H-NMR (400.13 MHz, CDCl$_3$):

$^{13}$C-NMR (100.62 MHz, CDCl$_3$):
(E)-Methyl 2,3-Dimethyl-4-(2-tributylstannylvinyl-1-yl)benzoate 24.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):
(Z)-Methyl 2,3-Dimethyl-4-(2-tributylstannylvinyl-1-yl)benzoate 24.

$^1$H-NMR (400.13 MHz, C$_6$D$_6$):

$^{13}$C-NMR (100.62 MHz, C$_6$D$_6$):
Synechoxanthin dimethyl ester 25.

$^1$H-NMR (400.13 MHz, CD$_2$Cl$_2$):

$^{13}$C-NMR (100.62 MHz, CD$_2$Cl$_2$):
Synechoxanthin 3.

$^1$H-NMR (400.13 MHz, MeOD):

13C-NMR (100.62 MHz, MeOD):
UV-Vis (MeOH)
4,4'-diapo-$\psi$,-$\psi$-carotenodial 4.

$^1$H-NMR (400.13 MHz, CD$_2$Cl$_2$):

$^{13}$C-NMR (100.62 MHz, CD$_2$Cl$_2$):
UV-Vis (MeOH)
2-(4-Bromo-2,3-dimethylphen-1-yl)-ethynyl-trimethylsilane 32

$^1$H-NMR (400.13 MHz, CDCl$_3$):

![NMR spectrum of 32](image)

$^{13}$C-NMR (100.62 MHz, CDCl$_3$):
(2,3-Dimethyl-1,4-phenylene)-bis(ethyne-2,1-diyl)-bis(trimethylsilane) 33.

$^1$H-NMR (400.13 MHz, CDCl$_3$):

$^{13}$C-NMR (100.62 MHz, CDCl$_3$):
Methyl 4-(Bromoethyl)-2,3-dimethylbenzoate 34.

$^1$H-NMR (400.13 MHz, CDCl$_3$):

$^{13}$C-NMR (100.62 MHz, CDCl$_3$):
(2E,4E,6E,8E)-2,9-dimethyldeca-2,4,6,8-tetraene-1,10-diol.

\(^1\)H-NMR (400.13 MHz, C\(_6\)D\(_6\)): 

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