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_2Cl_2 and DMF were dried using a Puresolv^{TM} solvent purification system. Et_3N 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 ºC-15 ºC) 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_6D_6 and $(CD_3)_2CO$ at ambient temperature on a Bruker AMX-400 spectrometer operating at 400.16 MHz with residual protic solvent as the internal reference ($CDCl_3$, δ = 7.26 ppm; C_6D_6, δ = 7.16 ppm, CD_2Cl_2, δ = 5.29 ppm, and CD_3OD, δ = 4.48 and 3.31 ppm); chemical shifts (δ) are given in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz). The proton spectra are reported as follows: δ (multiplicity, coupling constant *J*, number of protons). ^{13}C-NMR spectra were recorded in $CDCl_3$, C_6D_6, $CD_2Cl_2$and and CD_3OD at ambient temperature in the same spectrometer operating at 101.62 MHz with the central peak of $CDCl_3$ (δ_C = 77.2 ppm), C_6D_6 (δ_C = 128.0 ppm), CD_2Cl_2 (δ_C = 53.4 ppm) and CD_3OD (δ_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.

(2*E*,4*E*,6*E*)-3-Methyl-7-tributylstannylocta-2,4,6-trienol 6. To a cooled (-78 ºC) solution of (2*E*,4*E*,6*E*)-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 ºC 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 Et_2O (3x) and dried (Na_2SO_4). The solvent was evaporated and the residue was purified by column chromatography (silica gel, from 97:1:2 hexane/EtOAc/Et_3N to 70:30 hexane/EtOAc) to afford 0.77 g (95%) of a product identified as (2*E*,4*E*,6*E*)-3-methyl-7-tributylstannylocta-2,4,6-trienol **6**.

(2*E*,4*E*,6*E*)-3-Methyl-7-tributylstannylocta-2,4,6-trienal 7. To a cooled (0 ºC) solution of (2*E*,4*E*,6*E*)-3-methyl-7-tributylstannylocta-2,4,6-trienol **6** (0.42 g, 0.99 mmol) in CH_2Cl_2 (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 (2*E*,4*E*,6*E*)-3-methyl-7-tributylstannylocta-2,4,6-trienal **7**, which was used without further purification. **^{1}H-NMR** (400.13 MHz, C_6D_6): δ 9.98 (d, *J* = 7.8 Hz, 1H, CHO), 6.92 (dd, *J* = 15.3, 10.6 Hz, 1H, H_5), 6.45 (d, *J* = 10.6 Hz, 1H, H_6), 6.02 (d, *J* = 15.3 Hz, 1H, H_4), 5.93 (d, *J* = 7.8 Hz, 1H, H_2), 2.02 (s, 3H, C_7-CH_3), 1.74 (s, 3H, CH_3), 1.65-1.50 (m, 6H, 3 x CH_2), 1.42-1.33 (m, 6H, 3 x CH_2), 1.09-0.99 (m, 6H, 3 x CH_2), 0.95-0.92 (m, 9H, 3 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, C_6D_6): 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 $C_{21}H_{39}O^{119}Sn$ ($[M+H]^+$), 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): λ_{max} 340 nm.

(2*E*,4*E*,6*E*)-7-Iodo-3-methylocta-2,4,6-trienal 8. To a solution of (2*E*,4*E*,6*E*)-3-methyl-7-tributylstannylocta-2,4,6-trienal **7** (0.38 g, 0.89 mmol) in CH_3CN (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 Na_2SO_3 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 (Na_2SO_4) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, from 92:5:3 hexane/EtOAc/Et_3N to 90:10 hexane/EtOAc) to afford 0.22 g (96%) of a product identified as (2*E*,4*E*,6*E*)-7-iodo-3-methylocta-2,4,6-trienal **8**. **^{1}H-NMR** (400.13 MHz, C_6D_6): δ 9.92 (d, *J* = 7.7 Hz, 1H, CHO), 6.60 (ddd, *J* = 11.1, 1.3, 0.8 Hz, 1H, H_6), 6.15 (dd, *J* = 15.2, 11.1 Hz, 1H, H_5), 5.85 (d, *J* = 7.7 Hz, 1H, H_2), 5.60 (d, *J* = 15.2 Hz, 1H, H_4), 2.06 (s, 3H, CH_3), 1.54 (s, 3H, CH_3) ppm. **^{13}C-NMR** (100.62 MHz, C_6D_6): 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 $C_9H_{12}IO$ ($[M+H]^+$), 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): λ_{max} 335 nm. **M.p.**: 70-73 ºC (hexane/Et_2O).

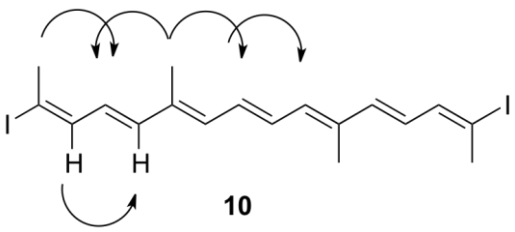
(3*E*,5*E*,7*E*)-8-Iodo-4-methylnona-1,3,5,7-tetraene 9. To a suspension of methyltriphenylphosphonium bromide (0.26 g, 0.69 mmol) in THF (16.4 mL) was added *n*BuLi (0.41 mL, 1.5 M in hexane, 0.61 mmol) and DMPU (0.07 mL, 0.57 mmol) and the resulting mixture was stirred for 30 min at room temperature. The mixture was cooled down to -78 ºC and a solution of (2*E*,4*E*,6*E*)-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 (Na_2SO_4) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 90:8:2 hexane/EtOAc/Et_3N) to afford 0.08 g (82%) of a yellow oil identified as (3*E*,5*E*,7*E*)-8-iodo-4-methylnona-1,3,5,7-tetraene **9**. **^{1}H-NMR** (400.13 MHz, C_6D_6): δ 6.84 (d, *J* = 10.9 Hz, 1H, H_7), 6.63-6.53 (m, 1H, H_2), 6.15-6.04 (m, 2H, H_3 + H_6), 5.98 (d, *J* = 15.2 Hz, 1H, H_5), 5.20 (d, *J* = 16.7 Hz, 1H, H_{1E}), 5.08 (d, *J* = 10.1 Hz, 1H, H_{1Z}), 2.18 (s, 3H, CH_3), 1.61 (s, 3H, CH_3) ppm. **^{13}C-NMR** (100.62 MHz, C_6D_6): 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

(43), 83 (78), 82 (44), 81 (88), 79 (55), 77 (58), 71 (80), 70 (45), 69 (61), 67 (63). **HRMS** (EI): Calcd. for $C_{10}H_{13}I$, 260.0062 found, 260.0066. **IR** (NaCl): ν 2913 (m, C-H), 2848 (w, C-H), 1659 (w), 1424 (w), 959 (s) cm^{-1}. **UV** (MeOH): λ_{max} 290 nm.

(2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-2,15-Diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 10. To a degassed solution of (3*E*,5*E*,7*E*)-8-iodo-4-methylnona-1,3,5,7-tetraene **9** (0.060 g, 0.23 mmol) in CH_2Cl_2 (4.4 mL) containing a few drops of a solution of BHT in toluene (0.2 g/100 mL) was added Grubbs 2nd generation catalyst (0.020 g, 0.023 mmol). After stirring at 25 ºC 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 (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-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 (2*Z*,14*Z*)-**10** isomers.

Data for (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene *all-trans*-**10**: **^{1}H-NMR** (400.13 MHz, C_6D_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_6D_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_{max} 423, 399, 375, 355, 336 nm. **M.p.**: > 85 ºC (acetone/MeOH, dec.).

NOE enhancements:

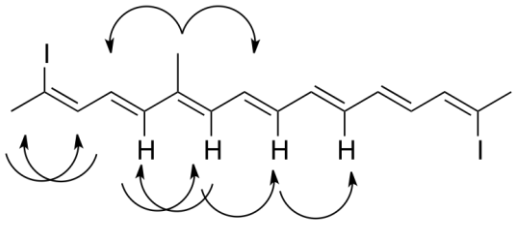


10

Data for (2*Z*,4*E*,6*E*,8*E*,10*E*,12*E*,14*Z*)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene (2*Z*,14*Z*)-**10**: **^{1}H-NMR** (400.13 MHz, C_6D_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

CH_3) 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 $C_{18}H_{22}I_2$, 491.9811; found, 491.9812.

NOE enhancements:



(2*Z*,14*Z*)-**10**

(*E*)-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 Bu_3SnH (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 ºC for 4 h and the solvent was evaporated. The residue was purified by column chromatography (C_{18} silica gel, 60:40 CH_3CN/CH_2Cl_2) to afford 1.90 g (79%) of a colourless oil identified as (*E*)-tributyl(2-(2,6,6-trimethylcyclohex-1-enyl)vinyl)stannane **12**. **^{1}H-NMR** (400.13 MHz, C_6D_6): δ 6.63 (dd, *J* = 19.7, 0.9 Hz, 1H, H_2), 6.13 (d, *J* = 19.7 Hz, 1.9 Hz, 1H, H_1), 1.95 (t, *J* = 6.1 Hz, 2H, CH_2), 1.82 (s, 3H, CH_3), 1.72-1.56 (m, 8H, 4 x CH_2), 1.49-1.45 (m, 2H, CH_2), 1.43-1.36 (m, 6H, 3 x CH_2), 1.16 (s, 6H, 2 x CH_3), 1.04-1.00 (m, 6H, 3 x CH_2), 0.97-0.93 (m, 9H, 3 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, C_6D_6): 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), 1458 (m), 1373 (w) cm^{-1}.

***β,β*-Carotene 1.**

General procedure for the Suzuki cross-coupling. To a solution of (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-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 $Pd(PPh_3)_4$ (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 TlOH (0.30 mL, 0.139 mmol) were added. After stirring for 4 h at 25 ºC, the mixture was diluted with Et_2O (with a few drops of the solution of BHT in toluene), washed with brine (3x) and dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by column chromatography (C_{18} silica gel, from CH_3CN to 50:50 CH_3CN/CH_2Cl_2) to afford 7.1 mg (73%) of a red solid identified as *β,β*-carotene **1**. **^{1}H-NMR** (400.13 MHz, C_6D_6): δ 6.79 (dd, *J* = 14.8, 11.4 Hz, 2H, $2H_{11}$), 6.70-6.67 (m, 2H, $2H_{15}$), 6.49 (d, *J* = 14.8 Hz, 2H, $2H_{12}$), 6.42-6.31 (m, 8H, $2H_7$ + $2H_8$ + $2H_{10}$ + $2H_{14}$), 1.99 (t, *J* = 5.6 Hz, 4H, 2 x CH_2), 1.94 (s, 6H, 2 x CH_3), 1.88 (s, 6H, 2 x CH_3), 1.82 (s, 6H, 2 x CH_3), 1.64-1.56 (m, 4H, 2 x CH_2), 1.52-1.49 (m, 4H, 2 x CH_2), 1.16 (s, 12H, 4 x CH_3) ppm. **MS** (EI): *m/z* (%) 536 (M^+, 51), 209 (31), 171 (40), 169 (35), 159 (60), 157 (62), 145 (71), 143 (54), 133 (57), 131 (43), 121 (53), 119 (99), 107 (56), 105 (100), 95 (57), 93 (53), 91 (62). **HRMS** (EI): Calcd. for $C_{40}H_{56}$, 536.4382; found, 536.4387. **UV** (MeOH): λ_{max} 449, 280, 241 nm.[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 (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-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 $[Ph_2PO_2][NBu_4]$ (20 mg, 0.05 mmol). Then CuTC (3.4 mg, 0.018 mmol) and $Pd(PPh_3)_4$ (4.20 mg, 0.004 mmol) were added and the reaction mixture was stirred for 1 h. Et_2O (containing a few drops of a solution of BHT in toluene) was added and the organic layer was washed with H_2O (3x). The combined aqueous layers were extracted with Et_2O (3x) and dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by column chromatography (C_{18} silica gel, from CH_3CN to 50:50 CH_3CN/CH_2Cl_2) to afford 8.40 mg (86%) of a red solid identified as *β,β*-carotene **1**.[1]

(1*E*,3*E*)- and (1*E*,3*Z*)-2-[-4,8-Dimethylnona-1,3,7-trienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16. To a solution of $CrCl_2$ (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

[1] Zeng, F.; Negishi, E.-i. *Org. Lett.* **2001,** *3*, 719.

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 Et_2O (2x). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. The residue was dissolved in Et_2O 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 (1*E*,3*E*)- and (1*E*,3*Z*)-2-[4,8-dimethylnona-1,3,7-trienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes **16**. The isomers were separated by HPLC (Prep Nova-Pak® HR Silica 60Å, 6 μm, 19x300 mm, 98:2 hexane/EtOAc, 3 mL/min, t_R (*Z*) = 37.8 min and t_R (*E*) = 43.4 min).

Data for (1*E*,3*E*)-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_6D_6): δ 7.77 (dd, *J* = 17.4, 11.0 Hz, 1H, H_2), 6.07 (d, *J* = 11.0 Hz, 1H, H_3), 5.90 (d, *J* = 17.4 Hz, 1H, H_1), 5.1-5.0 (m, 1H, H_7), 2.2-2.1 (m, 2H, CH_2), 2.0-1.9 (m, 2H, CH_2), 1.61 (s, 3H, CH_3), 1.58 (d, *J* = 0.8 Hz, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.11 (s, 12H, 4 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, C_6D_6): 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 $C_{17}H_{30}BO_2$ ($[M+H]^+$), 277.23364; found, 277.23303**. IR** (NaCl): ν 2978 (m, C-H), 2925 (m, C-H), 2860 (w, C-H), 1638 (w), 1601 (m), 1363 (s), 1340 (s), 1320 (s), 1146 (s) cm^{-1}. **UV** (MeOH): λ_{max} 262 nm.

Data for (1*E*,3*Z*)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_6D_6): δ 7.77 (dd, *J* = 17.4, 11.1 Hz, 1H, H_2), 6.02 (d, *J* = 11.1 Hz, 1H, H_3), 5.87 (d, *J* = 17.4 Hz, 1H, H_1), 5.1-5.0 (m, 1H, H_7), 2.17 (t, *J* = 7.7 Hz, 2H, CH_2), 2.1-2.0 (m, 2H, CH_2), 1.61 (d, *J* = 0.9 Hz, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.10 (s, 12H, 4 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, C_6D_6): 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 $C_{17}H_{30}BO_2$ ($[M+H]^+$), 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): λ_{max} 262 nm.

Lycopene 2. Following the general procedure for the Suzuki cross-coupling, the reaction of (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-2,15-diiodo-6,11-dimethylhexadeca-

2,4,6,8,10,12,14-heptaene **10** (9.5 mg, 0.019 mmol), (1*E*,3*E*)-2-[4,8-dimethylnona-1,3,7-trienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **16** (14.0 mg, 0.05 mmol), $Pd(PPh_3)_4$ (4.5 mg, 0.004 mmol), a freshly prepared 10% aqueous solution of TlOH (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/acetone), 5.4 mg (52%) of a red solid identified as lycopene **2**. **^{1}H-NMR** (400.13 MHz, C_6D_6): δ 6.77 (dd, *J* = 14.8, 11.3 Hz, 2H, $2H_7$ or $2H_{11}$), 6.71-6.64 (m, 4H, $2H_7$ or $2H_{11}$ + $2H_{15}$), 6.49 (d, *J* = 14.8 Hz, 2H, $2H_8$ or $2H_{12}$), 6.44 (d, *J* = 15.2 Hz, 2H, $2H_8$ or $2H_{12}$), 6.37-6.34 (m, 4H, $2H_6$ or $2H_{10}$ + $2H_{14}$), 6.16 (d, *J* = 11.1 Hz, 2H, $2H_6$ or $2H_{10}$), 5.24 (t, *J* = 6.3 Hz, 2H, $2H_2$), 2.4-2.0 (m, 8H, 4 x CH_2), 1.93 (s, 6H, 2 x CH_3), 1.88 (s, 6H, 2 x CH_3), 1.75 (s, 6H, 2 x CH_3), 1.68 (s, 6H, 2 x CH_3), 1.57 (s, 6H, 2 x CH_3) 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 $C_{40}H_{56}$, 536.4382; found, 536.4374. **UV** (MeOH): λ_{max} 360, 327, 282, 241 nm.[2]

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 CH_2Cl_2 (4.6 mL) were added pyridine (0.09 mL, 1.1 mmol) and Tf_2O (0.25 mL, 1.5 mmol) and the reaction mixture was stirred for 2 h at 25 ºC. A saturated aqueous solution of NH_4Cl was added and the mixture was extracted with CH_2Cl_2 (3x). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 80:20 hexane/Et_2O) to afford 0.32 g (96%) of a colourless oil identified as 4-bromo-2,3-dimethylphenyl trifluoromethanesulfonate **18**. **^{1}H-NMR** (400.13 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.8 Hz, 1H, ArH), 6.99 (d, *J* = 8.8 Hz, 1H, ArH), 2.43 (s, 3H, CH_3), 2.34 (s, 3H, CH_3) ppm. **^{13}C-NMR** (100.62 MHz, $CDCl_3$): δ 147.5 (s), 139.5 (s), 131.6 (s), 131.0 (d), 124.9 (s), 120.0 (d), 118.7 (q, $J_{C\text{-}F}$ = 320.4 Hz), 20.4 (q), 14.5 (q) ppm. **MS** (EI): *m/z* (%) 334 ($[M]^+$ ^{81}[Br], 26), 332 ($[M]^+$ ^{79}[Br], 25), 201 (98), 199 (100), 173 (16), 171 (16), 92 (31), 91 (35). **HRMS** (EI): Calcd. for $C_9H_8O_3F_3S^{81}Br$, 333.9309; found, 333.9318 and $C_9H_8O_3F_3S^{79}Br$, 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}.

[2] Ji, M.; Choi, H.; Park, M.; Kee, M.; Jeong, Y. C.; Koo, S. *Angew. Chem. Int. Ed.* **2001,** *40*, 3627.

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 Et_3N (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 (Na_2SO_4) 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): **^{1}H-NMR** (400.13 MHz, $CDCl_3$): δ 7.45 (s, 2H, 2ArH), 3.88 (s, 3H, CO_2CH_3), 2.52 (s, 3H, CH_3), 2.43 (s, 3H, CH_3) ppm. **^{13}C-NMR** (100.62 MHz, $CDCl_3$): 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 $C_{10}H_{11}O_3{}^{81}Br$, 243.9922 found, 243.9924 and calcd. for $C_{10}H_{11}O_3{}^{79}Br$, 241.9942; found, 241.9950. **IR** (NaCl): ν 2996 (w, C-H), 2950 (w, C-H), 1724 (s, C=O), 1574 (m), 1434 (m), 1287 (m), 1252 (s) cm^{-1}. **M.p.**: 34-35 ºC (hexane/EtOAc).

Data for dimethyl 2,3-dimethylterephthalate **20** (minor product): **^{1}H-NMR** (400.13 MHz, $CDCl_3$): δ 7.57 (s, 2H, 2ArH), 3.90 (s, 6H, 2 x CO_2CH_3), 2.46 (s, 6H, 2 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, $CDCl_3$): 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 $C_{12}H_{15}O_4$ ($[M+H]^+$), 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), $Pd(dppf)Cl_2$ (0.04 g, 0.05 mmol), CuI (0.01 g, 0.06 mmol), $(i\text{Pr})_2NH$ (1.4 mL, 9.99 mmol) in DMF (1.4 mL) at 25 ºC was added trimethylsilylacetylene **21** (0.23 mL, 1.65 mmol) and the reaction mixture was stirred at 80 ºC for 2.5 h. Then EtOAc was added and the organic layer was washed with water (5x) and dried (Na_2SO_4) 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-trimethylsilylethyn-1-yl)-benzoate **22**. **^{1}H-NMR** (400.13 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.1 Hz, 1H, ArH), 7.32 (d, *J* = 8.1 Hz, 1H, ArH), 3.87 (s, 3H, CO_2CH_3), 2.45 (s, 6H, 2 x CH_3), 0.27 (s, 9H, 3 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, $CDCl_3$): 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 $C_{15}H_{20}O_2Si$, 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), 1291 (m), 1435 (m), 1250 (s) cm^{-1}.

Methyl 4-Ethynyl-2,3-dimethylbenzoate 23. A solution of methyl 2,3-dimethyl-4-(2-trimethylsilylethyn-1-yl)-benzoate **22** (0.49 g, 1.88 mmol) in THF (12.4 mL) was treated with $(n\text{Bu})_4NF$ (2.068 mL, 1 M in THF, 2.068 mmol) and the reaction mixture was stirred for 2 h. The mixture was treated with Et_2O and water and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine (1x), dried (Na_2SO_4) and the solvent was evapored. The residue was purified by column chromatography (silica gel, 95:5 hexane/Et_2O) to afford 0.28 g (80%) of a white solid identified as methyl 4-ethynyl-2,3-dimethylbenzoate **23**. **^{1}H-NMR** (400.13 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 1H, ArH), 7.34 (d, *J* = 8.0 Hz, 1H, ArH), 3.87 (s, 3H, CO_2CH_3), 3.36 (s, 1H, C≡CH), 2.44 (s, 6H, 2 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, $CDCl_3$): 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 $C_{12}H_{12}O_2$, 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 ºC (MeOH/H_2O).

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-ethynyl-2,3-dimethylbenzoate **23** (0.02 g, 0.10 mmol), Bu_3SnH (0.035 mL, 0.13 mmol) and 2-2'-azo-bis-isobutyronitrile (AIBN) (0.7 mg, 0.004 mmol) in toluene (0.4 mL) afforded, after purification by column chromatography (C_{18} silica gel, from 100% CH_3CN to 90:10 CH_3CN/CH_2Cl_2), 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 CH_3CN/THF, 3 mL/min, t_R (*Z*) = 80 min and t_R (*E*) = 85 min).

Data for methyl (*E*)-2,3-dimethyl-4-(2-(tributylstannyl)vinyl)benzoate **24** (major product): **^{1}H-NMR** (400.13 MHz, C_6D_6): 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, H_2), 6.82 (d, *J* = 19.3 Hz, 1H, H_1), 3.53 (s, 3H, CO_2CH_3), 2.50 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 1.75-1.54 (m, 6H, 3 x CH_2), 1.45-1.36 (m, 6H, 3 x CH_2), 1.13-0.98 (m, 6H, 3 x CH_2), 0.95 (t, *J* = 7.3 Hz, 9H, 3 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, C_6D_6): 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 $C_{24}H_{41}O_2{}^{119}Sn$ ($[M+H]^+$), 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): **^{1}H-NMR** (400.13 MHz, C_6D_6): δ 7.83 (d, *J* = 8.0 Hz, 1H, ArH), 7.67 (d, *J* = 13.6 Hz, 1H, H_2), 7.21 (d, *J* = 8.0 Hz, 1H, ArH), 6.40 (d, *J* = 13.6 Hz, 1H, H_1), 3.49 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.47-1.39 (m, 6H, 3 x CH_2), 1.32-1.23 (m, 6H, 3 x CH_2), 0.90-0.72 (m, 15H, 3 x CH_3 + 3 x CH_2) ppm. **^{13}C-NMR** (100.62 MHz, C_6D_6): 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 $C_{24}H_{41}O_2{}^{119}Sn$ ($[M+H]^+$), 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), 1256 (m) cm^{-1}.

Dimethyl (1*E*,3*E*,5*E*,7*E*,9*E*,11*E*,13*E*,15*E*,17*E*) 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-tributylstannylvin-1-yl)-benzoate **24** (20.0 mg, 0.042 mmol) and (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene **10** (9.0 mg, 0.018 mmol), $[NBu_4][Ph_2PO_2]$ (0.021 g, 0.045 mmol), CuTC (3.4 mg, 0.018 mmol), $Pd(PPh_3)_4$ (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 (C_{18} silica gel, from CH_3CN to 50:50 CH_3CN/CH_2Cl_2), 8.8 mg (79%) of a solid identified as dimethyl (1*E*,3*E*,5*E*,7*E*,9*E*,11*E*,13*E*,15*E*,17*E*)-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**. **^{1}H-NMR** (400.13 MHz, CD_2Cl_2): 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, $H_1 + H_{18}$), 6.83 (d, *J* = 15.8 Hz, 2H, $H_2 + H_{17}$), 6.76-6.66 (m, 4H, $H_5 + H_9 + H_{11} + H_{14}$), 6.47 (d, *J* = 14.9 Hz, 2H, $H_6 + H_{13}$), 6.39 (d, *J* = 11.6 Hz, 2H, $H_4 + H_{15}$), 6.33 (dd, *J* = 8.2, 1.6 Hz, 2H, $H_7 + H_8$), 3.85 (s, 6H, 2 x CO_2CH_3), 2.47 (s, 6H, 2 x CH_3), 2.33 (s, 6H, 2 x CH_3), 2.08 (s, 6H, 2 x CH_3), 2.01 (s, 6H, 2 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, CD_2Cl_2): δ 169.5 (s, 2x, CO_2Me), 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), 52.3 (q, 2x), 17.6 (q, 2x), 16.1 (q, 2x), 13.2 (q, 2x), 13.1 (q, 2x) ppm. **HRMS** (ESI^+): Calcd. for $C_{42}H_{49}O_4$ ($[M+H]^+$), 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 $KOSiMe_3$ (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 (C_{18} silica gel, 90:10 $MeOH/H_2O$) and then crystallized with $MeOH/CH_2Cl_2$ to afford 4.3 mg (98%) of a red solid identified as synechoxanthin **3**. **^{1}H-NMR** (400.13 MHz, CD_3OD): δ 7.33 (d, *J* = 8.0 Hz, 2H, $2H_5$), 7.17 (d, *J* = 8.0 Hz, 2H, $2H_4$), 6.90 (d, *J* = 15.8 Hz, 2H, $2H_7$), 6.78-6.71 (m, 6H, $2H_8 + 2H_{11} + 2H_{14}$), 6.46 (d, *J* = 14.8 Hz, 2H, $2H_{12}$), 6.37-6.32 (m, 4H, $2H_{10} + 2H_{15}$), 2.37 (s, 6H, 2 x CH_3), 2.30 (s, 6H, 2 x CH_3), 2.06 (s, 6H, 2 x CH_3), 2.00 (s, 6H, 2 x CH_3). **^{13}C-**

NMR (100.62 MHz, CD_3OD): δ 179.8 (s, 2 x CO_2H), 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}): λ_{max} 500 (sh), 470 (36.400), 445 (sh) nm.

4,4´-Diapo-ψ,ψ-carotene-4,4´-dial 4. Following the general procedure for the Stille reaction using Fürstner conditions, the reaction of (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene **9** (9.0 mg, 0.018 mmol), (2*E*,4*E*)-2-methyl-5-(tributylstannyl)penta-2,4-dienal **31** (15.0 mg, 0.038 mmol), $[NBu_4][Ph_2PO_2]$ (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 ºC for 30 min afforded, after purification by column chromatography (C_{18} silica gel, from 90:10 MeOH/CH_2Cl_2 to CH_2Cl_2) and subsequent washing with hexane, 6.0 mg (78%) of a dark red solid identified as 4,4´-diapo-ψ,ψ-carotene-4,4´-dial **4**. **^{1}H-NMR** (400.13 MHz, CD_2Cl_2): δ 9.43 (s, 2H, CHO), 6.96 (dd, *J* = 10.6, 1.0 Hz, 2H, H_6 + $H_{6'}$), 6.78 (d, *J* = 14.9 Hz, 2H, H_8 + $H_{8'}$), 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_2Cl_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}): λ_{max} 545 (sh), 515 (87.100), 480 (sh) nm.

Scattered data for this compound can be found in the following publications: UV [(a) H. Kleinig, R. Schmitt, W. Meister, G. Englert and H. Thommen, *Z. Naturforsch.* **1979**, *34c*, 181-185. (b) H. Kleinig and R. Schmitt, *Z. Naturforsch.* **1982**, *37c*, 758-760], ^{1}H-NMR (Lockwood, S. F. et al., PCT Int. Appl., 2007147163 to Cardax Pharmaceuticals). Moreover, Hoffmann-La Roche is listed in article *Org. Biomol. Chem*. **2007**, *5*, 2803, as source of this compound.

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 (2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene **9** (65.0 mg, 0.132 mmol), (2*E*,4*E*)-2-methyl-5-(tributylstannyl)penta-2,4-dienal **31** (106.7 mg, 0.277 mmol), $[NBu_4][Ph_2PO_2]$ (139.8 mg, 0.304 mmol), CuTC (25.2 mg, 0.132 mmol), $Pd(PPh_3)_4$ (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 ºC for 30 min afforded, after purification by column chromatography (C_{18} silica gel, from 90:10 MeOH/CH_2Cl_2 to CH_2Cl_2) 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), $Pd(dppf)Cl_2$ (0.03 g, 0.04 mmol), CuI (9 mg, 0.045 mmol), $(i\text{Pr})_2NH$ (1.1 mL, 7.85 mmol) in DMF (1.1 mL) at 25 ºC 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**.

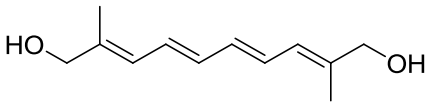
Data for 2-(4-bromo-2,3-dimethylphen-1-yl)-ethynyl-trimethylsilane **32** (minor product): **^{1}H-NMR** (400.13 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.3 Hz, 1H, ArH), 7.14 (d, *J* = 8.3 Hz, 1H, ArH), 2.46 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 0.27 (s, 9H, 3 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, $CDCl_3$): 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 ($[M]^+$ ^{81}[Br], 25), 280 ($[M]^+$ ^{79}[Br], 26), 268 (19), 267 (100), 266 (18), 128 (11). **HRMS** (EI): Calcd. for $C_{13}H_{17}Si^{81}Br$, 282.0262; found, 282.0276 and $C_{13}H_{17}Si^{79}Br$, 280.0283; found, 280.0296. **IR** (NaCl): ν 2957 (m, C-H), 2922 (w, C-H), 2896 (w, C-H), 2850 (w, C-H), 2147 (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): **^{1}H-NMR** (400.13 MHz, $CDCl_3$): δ 7.24 (s, 2H, 2ArH), 2.40 (s, 6H, 2 x

CH_3), 0.27 (s, 18H, 6 x CH_3) ppm. **^{13}C-NMR** (100.62 MHz, $CDCl_3$): 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 $C_{18}H_{26}Si_2$, 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-(Bromoethynyl)-2,3-dimethylbenzoate 34. Following the general procedure for the carbonylation catalyzed by palladium, the reaction of 2-(4-bromo-2,3-dimethylphen-1-yl)-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), Et_3N (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, afeter purification by column chromatography (silica gel, from 100% hexane to 93:7 hexane/Et_2O) to afford 21.0 mg (44%) of a solid identified as methyl 4-(bromoethynyl)-2,3-dimethylbenzoate **34**. **^{1}H-NMR** (400.13 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.3 Hz, 1H, ArH), 7.24 (d, *J* = 8.3 Hz, 1H, ArH), 3.84 (s, 3H, CO_2CH_3), 2.50 (s, 3H, CH_3), 2.39 (s, 3H, CH_3) ppm. **^{13}C-NMR** (100.62 MHz, $CDCl_3$): 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), 84.3 (s), 53.0 (q), 20.1 (q), 19.3 (q) ppm. **MS** (EI): *m/z* (%) 268 ($[M]^+$ ^{81}[Br], 50), 266 ($[M]^+$ ^{79}[Br], 54), 237 (61), 235 (64), 210 (84), 208 (98), 129 (35), 128 (100), 127 (37). **HRMS** (ESI^+): Calcd. for $C_{12}H_{12}O_2{}^{79}Br$ ($[M+H]^+$), 267.0015; found, 267.0026. **IR** (NaCl): ν 3084 (w, C-H), 3004 (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}.

(2*E*,4*E*,6*E*,8*E*)-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**).

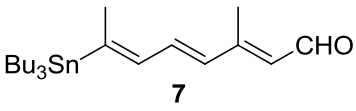


^{1}H-NMR (400.13 MHz, C_6D_6): δ 6.54-6.44 (m, 2H), 6.37-6.30 (m, 2H), 6.15 (dd, *J* = 11.1, 1.3 Hz, 2H, H_5 + H_6), 3.76 (d, *J* = 4.1 Hz, 4H, 2 x CH_2), 1.59 (s, 6H, 2 x CH_3)

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.

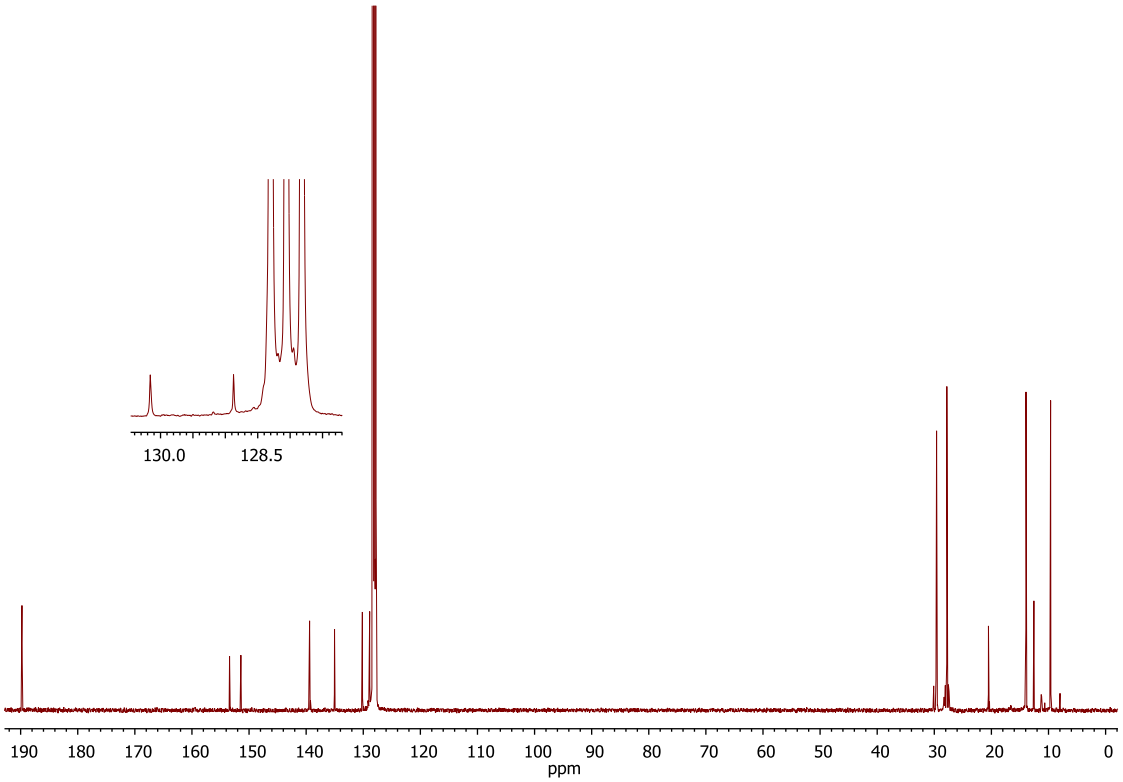
(2*E*,4*E*,6*E*)-3-Methyl-7-tributylstannylocta-2,4,6-trienal 7.

^{1}H-NMR (400.13 MHz, C_6D_6):



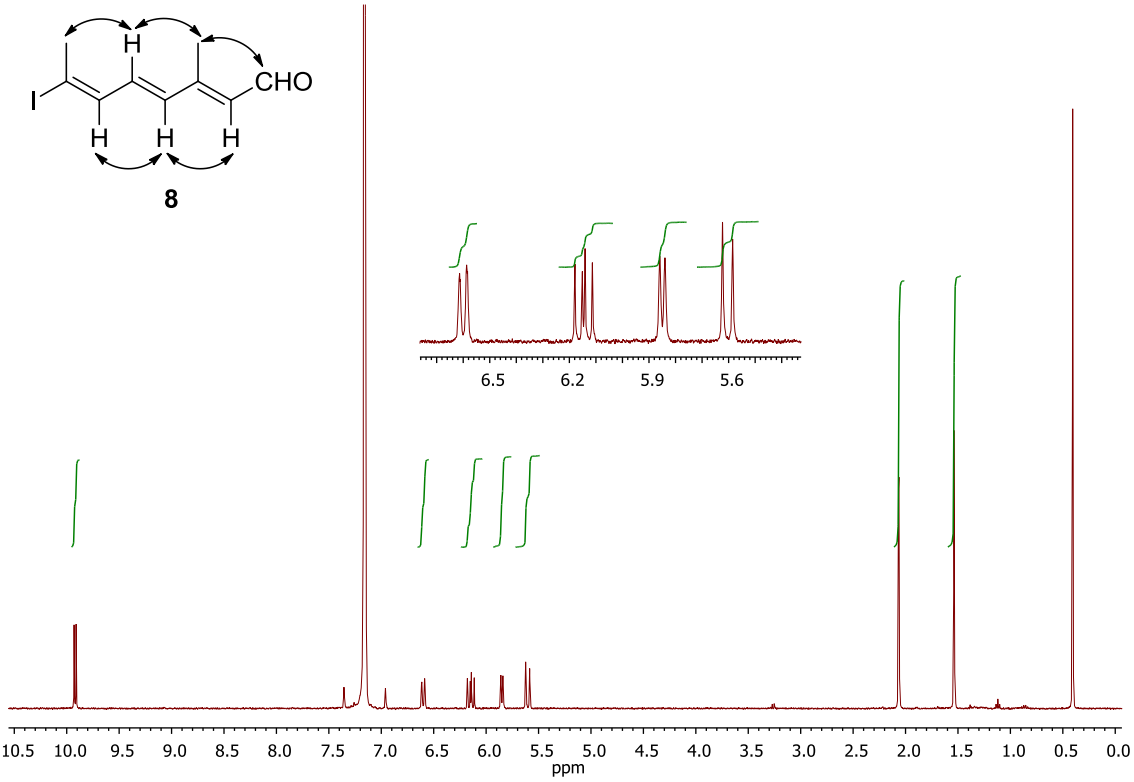
7

^{13}C-NMR (100.62 MHz, C_6D_6):

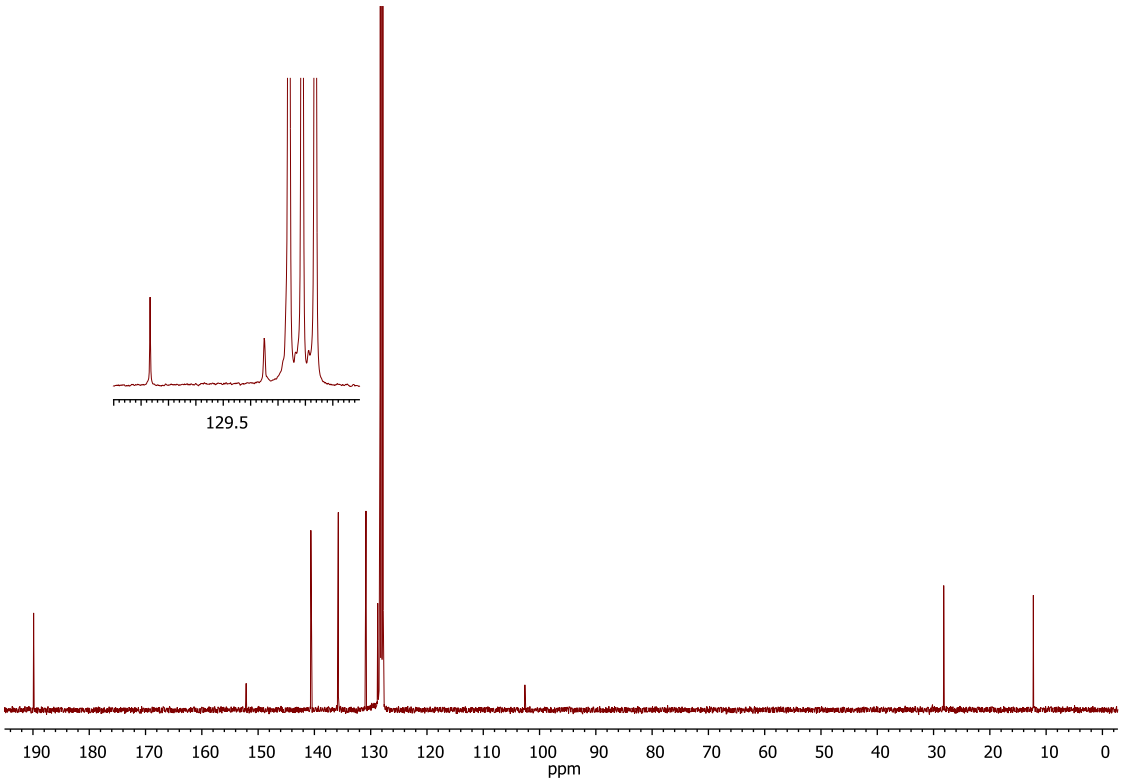


(2*E*,4*E*,6*E*)-7-Iodo-3-methylocta-2,4,6-trienal 8.

^{1}H-NMR (400.13 MHz, C_6D_6):

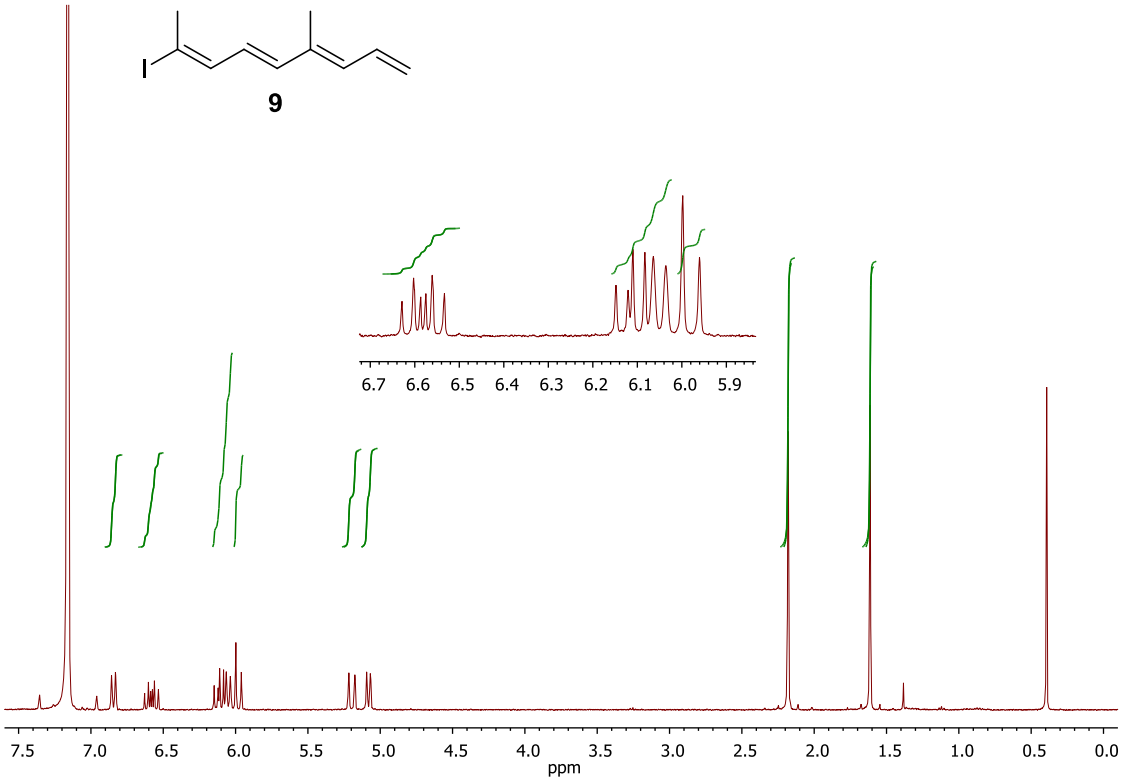


^{13}C-NMR (100.62 MHz, C_6D_6):

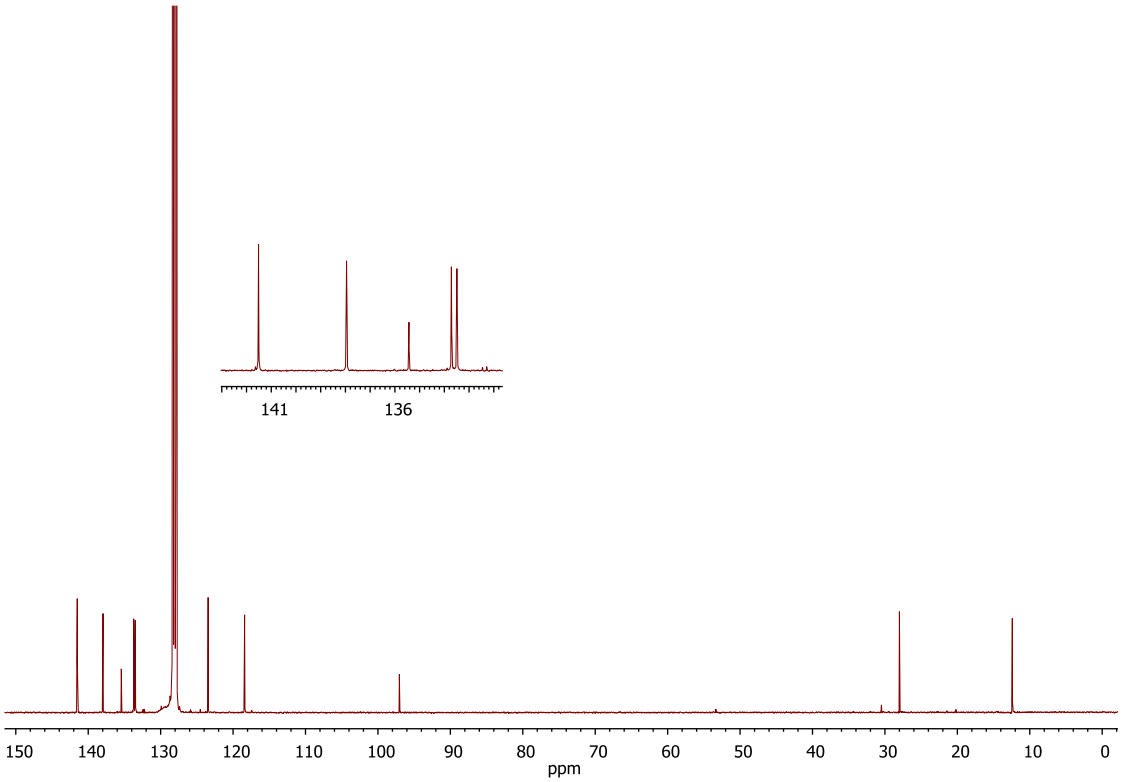


(3*E*,5*E*,7*E*)-8-Iodo-4-methylnona-1,3,5,7-tetraene 9.

^{1}H-NMR (400.13 MHz, C_6D_6):

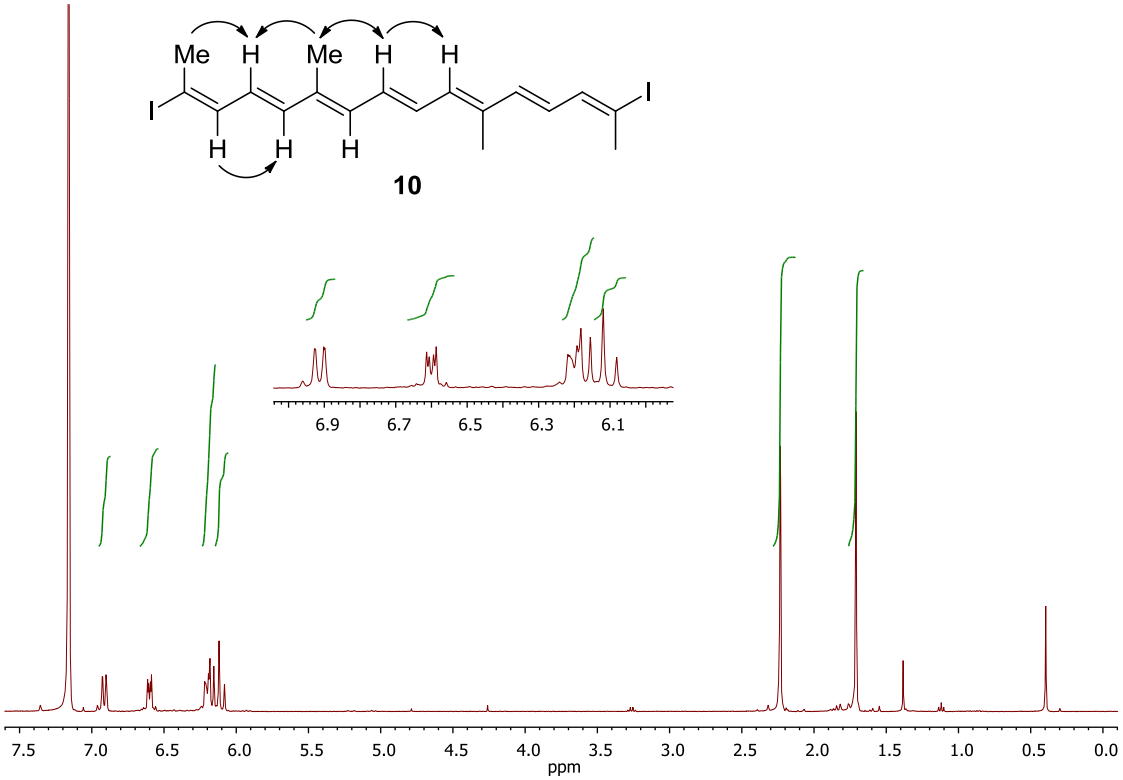


^{13}C-NMR (100.62 MHz, C_6D_6):

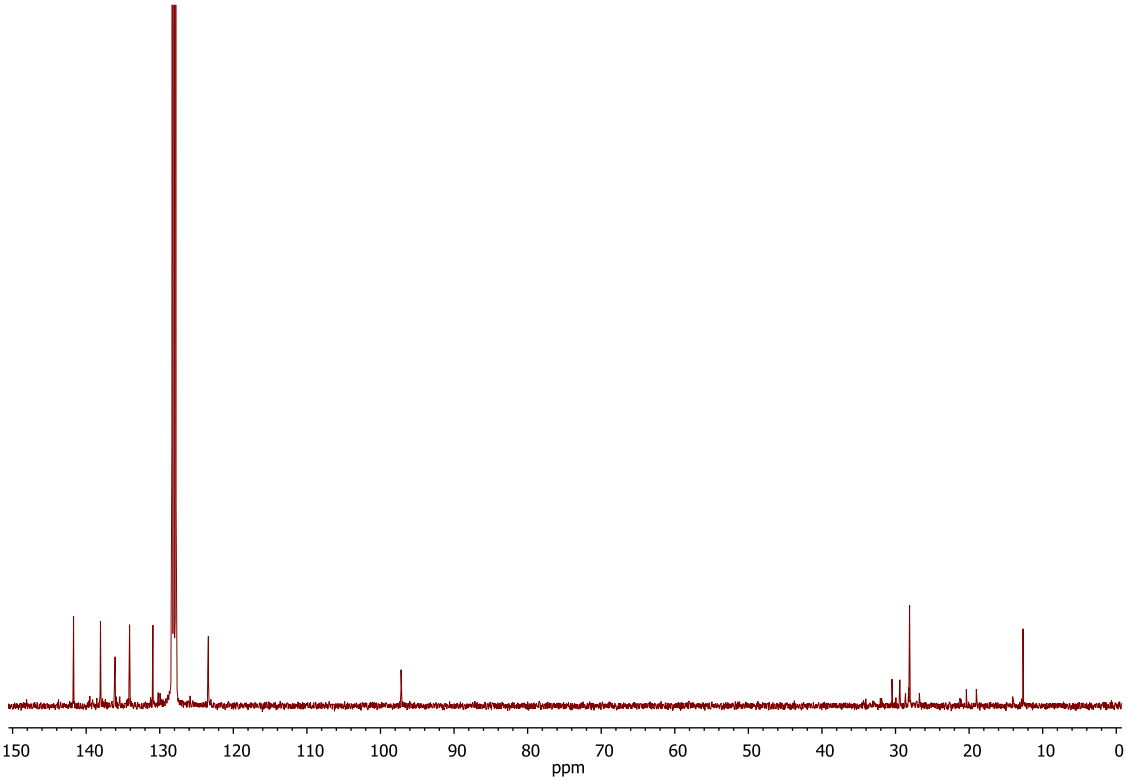


(2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*)-2,15-Diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 10.

^{1}H-NMR (400.13 MHz, C_6D_6):

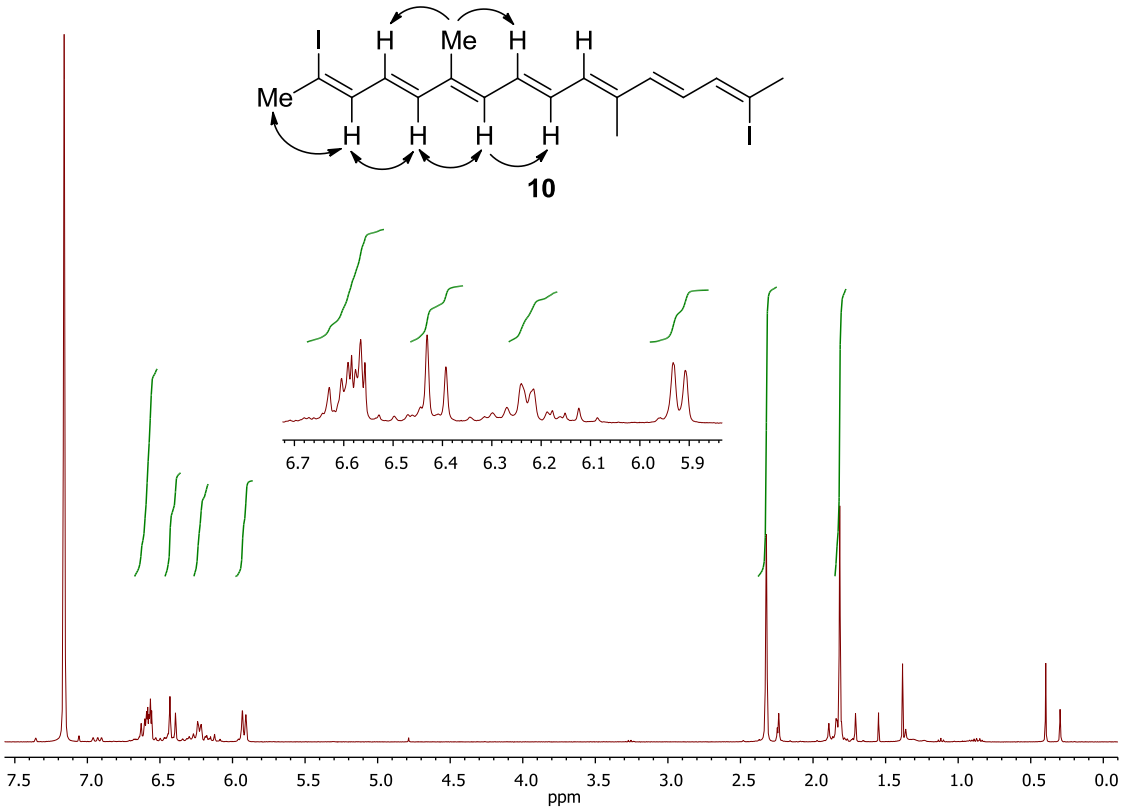


^{13}C-NMR (100.62 MHz, C_6D_6):



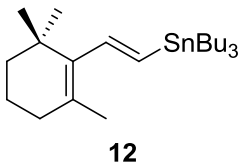
(2*Z*,4*E*,6*E*,8*E*,10*E*,12*E*,14*Z*)-2,15-diiodo-6,11-dimethylhexadeca-2,4,6,8,10,12,14-heptaene 10.

^{1}H-NMR (400.13 MHz, C_6D_6):



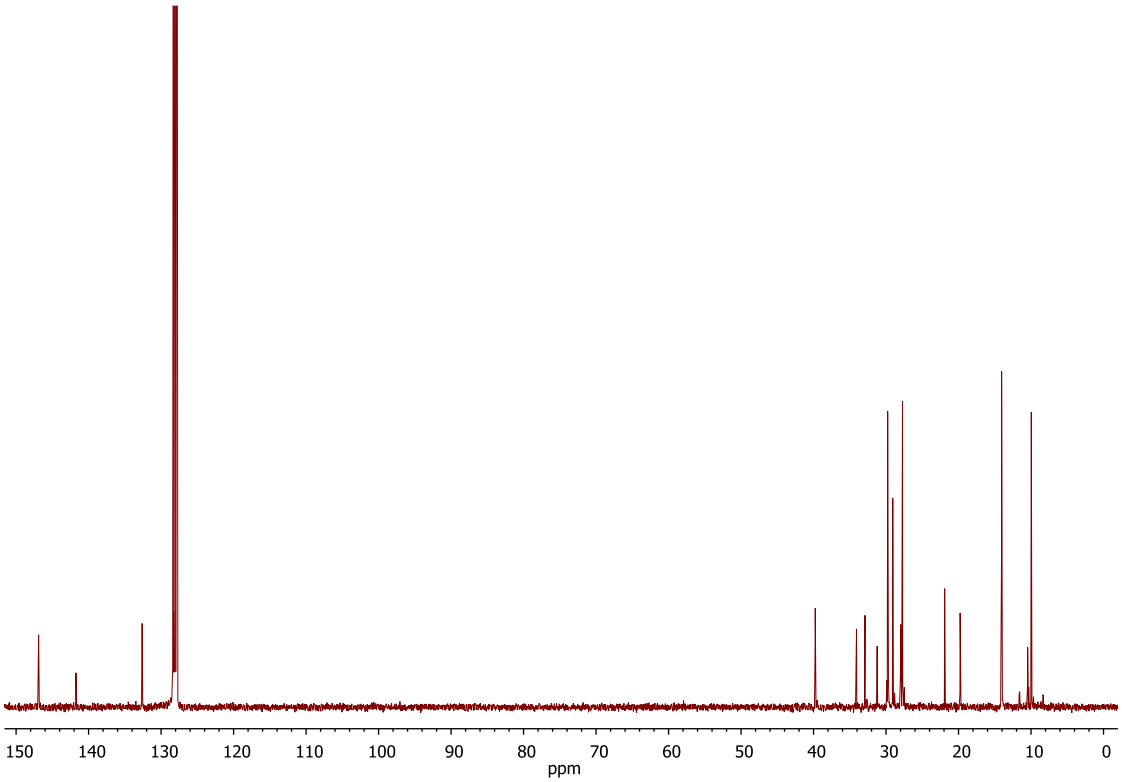
(*E*)-tributyl(2-(2,6,6-trimethylcyclohex-1-enyl)vinyl)stannane 12.

^{1}H-NMR (400.13 MHz, C_6D_6):



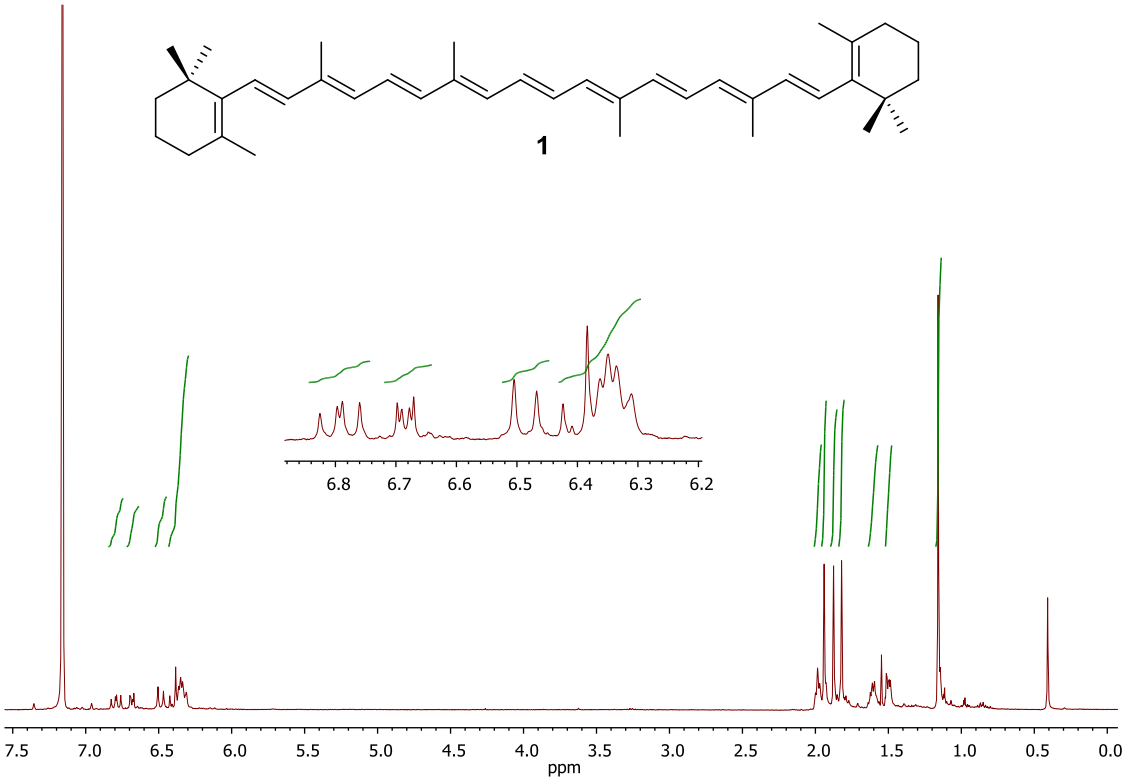
12

^{13}C-NMR (100.62 MHz, C_6D_6):



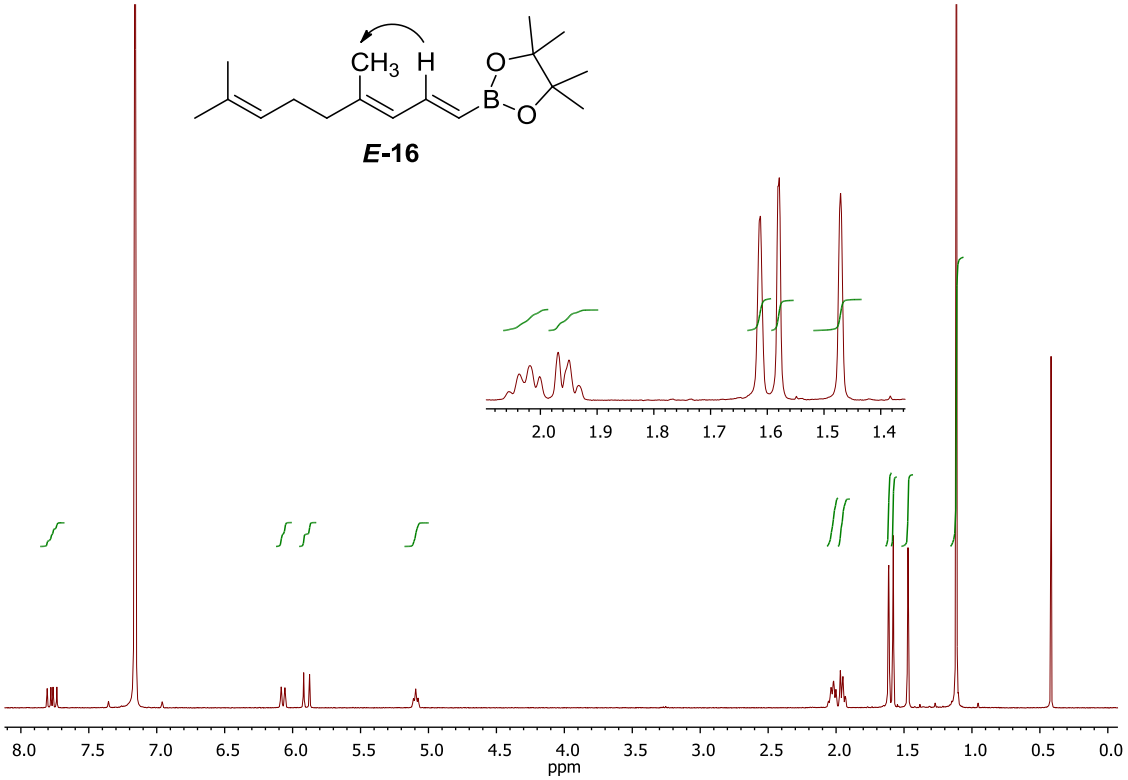
***β,β*-Carotene 1.**

^{1}H-NMR (400.13 MHz, C_6D_6):

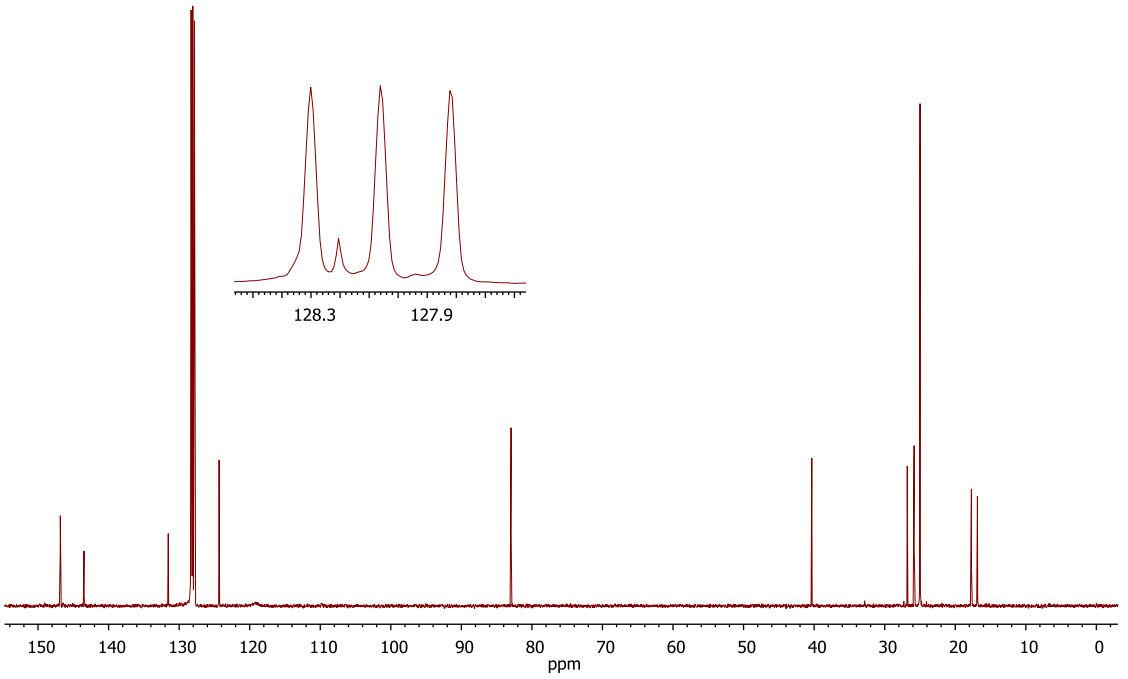


(1*E*,3*E*)-2-[-4,8-Dimethylnona-1,3,7-trienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16.

^{1}H-NMR (400.13 MHz, C_6D_6):

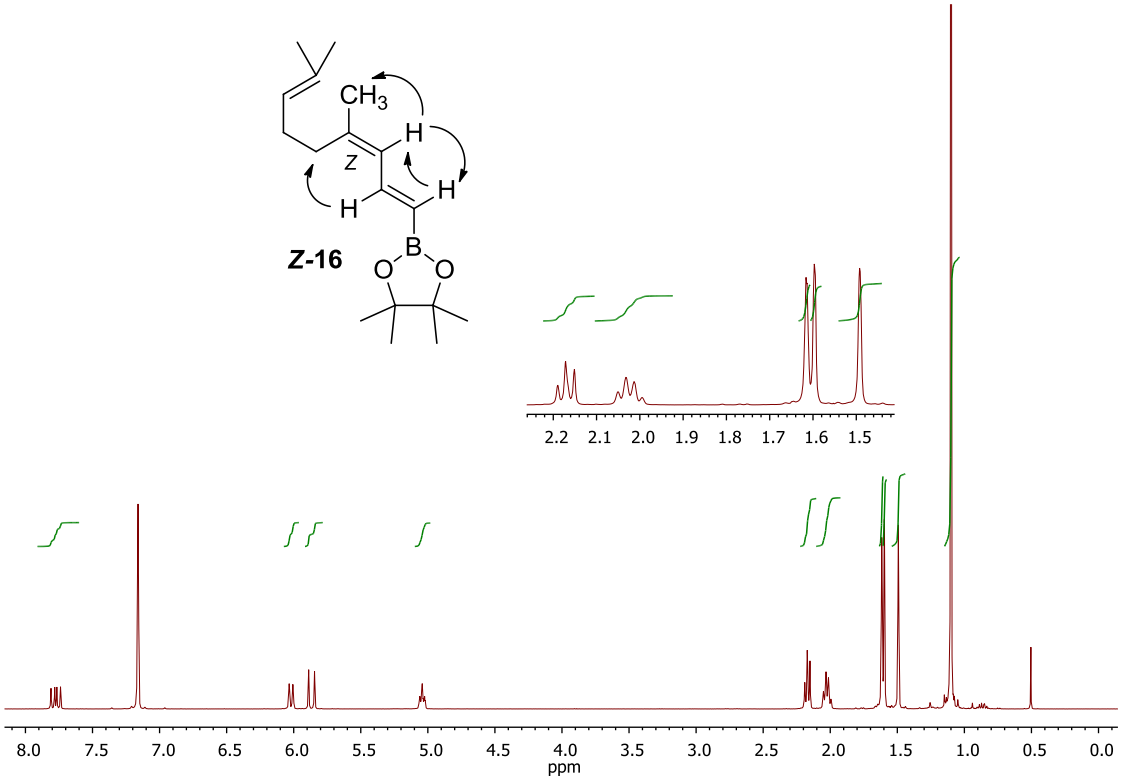


^{13}C-NMR (100.62 MHz, C_6D_6):

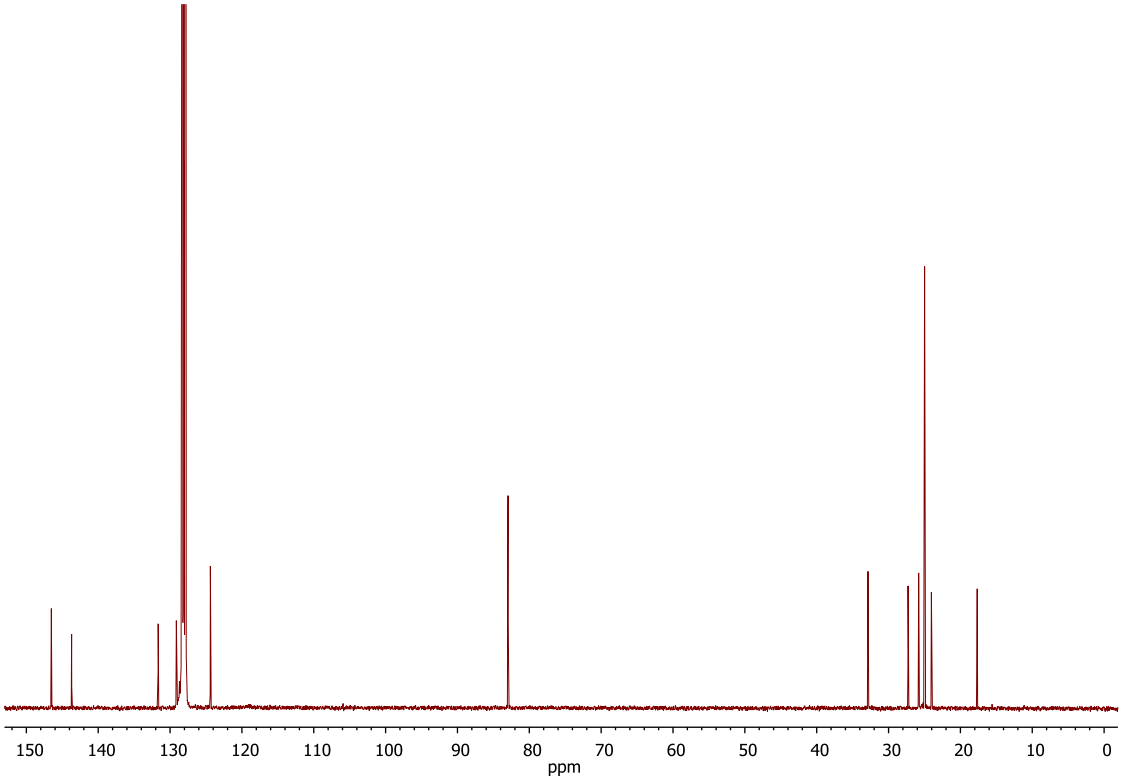


(1*E*,3*Z*)-2-[-4,8-Dimethylnona-1,3,7-trienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16.

^{1}H-NMR (400.13 MHz, C_6D_6):

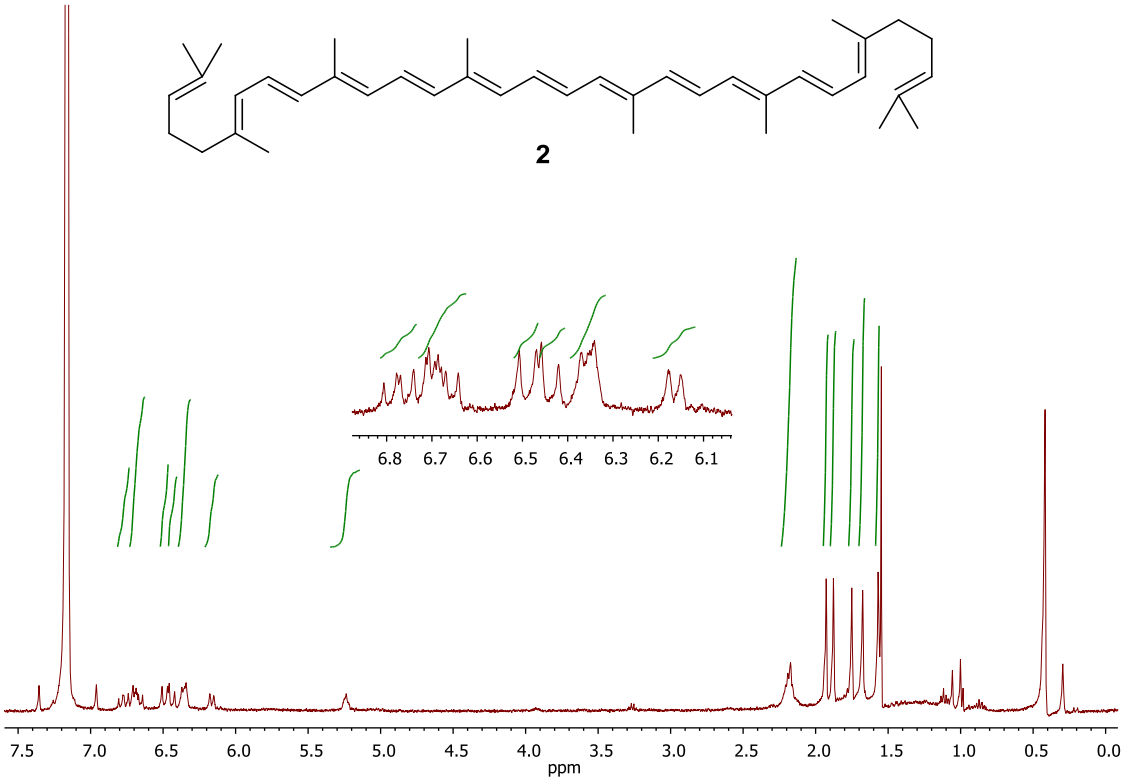


^{13}C-NMR (100.62 MHz, C_6D_6):



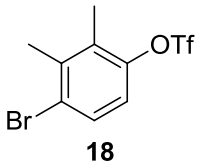
Lycopene 2.

^{1}H-NMR (400.13 MHz, C_6D_6):

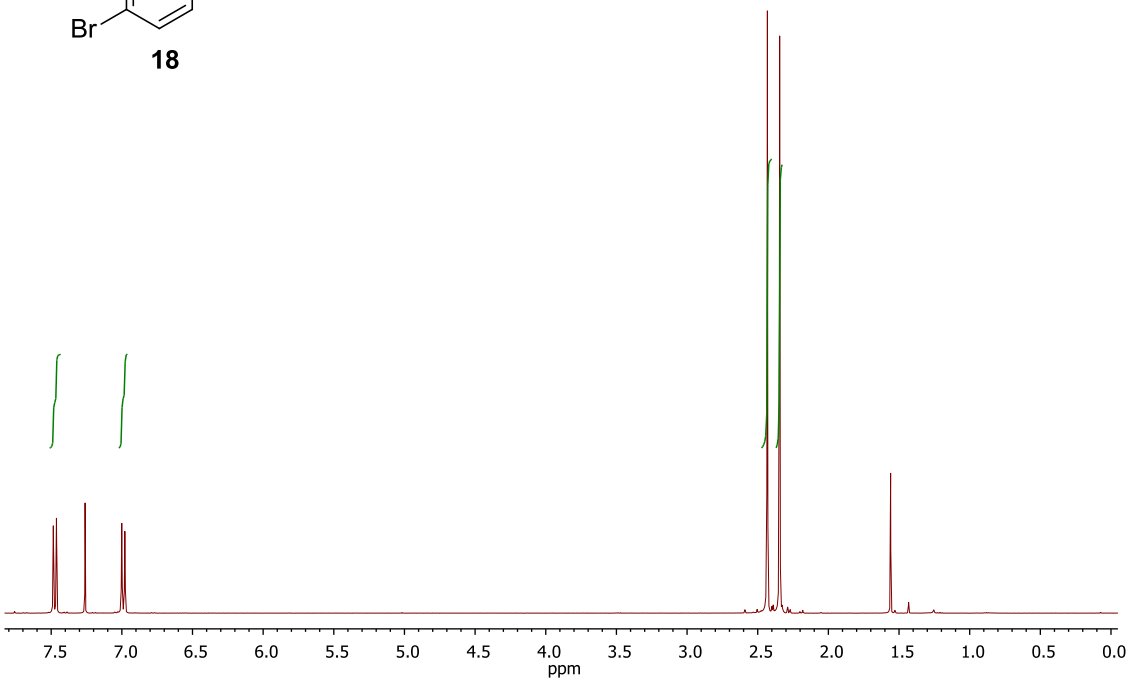


4-Bromo-2,3-dimethylphenyl trifluoromethanesulfonate 18.

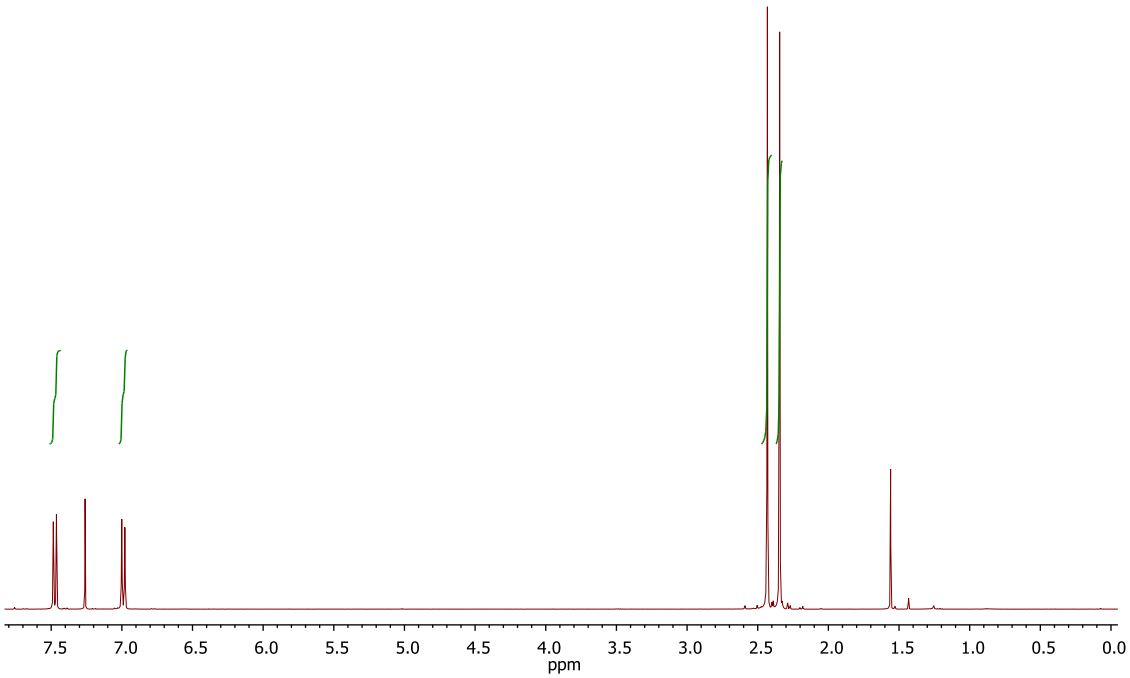
^{1}H-NMR (400.13 MHz, $CDCl_3$):



18

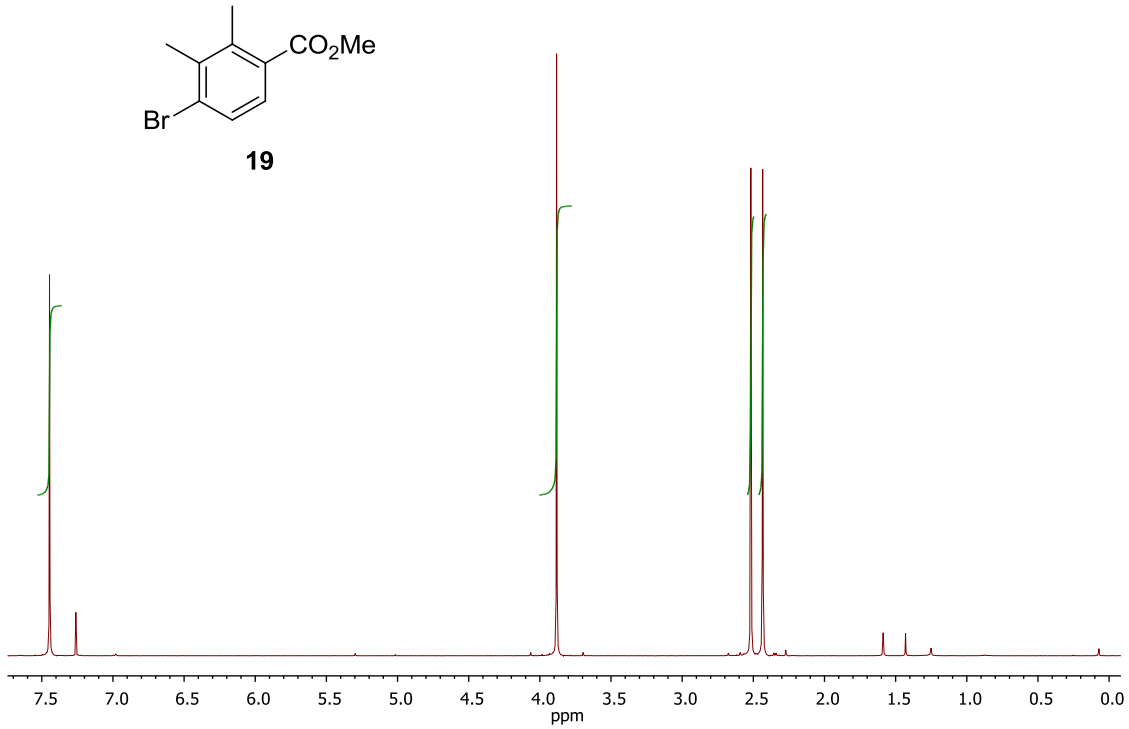


^{13}C-NMR (100.62 MHz, $CDCl_3$):

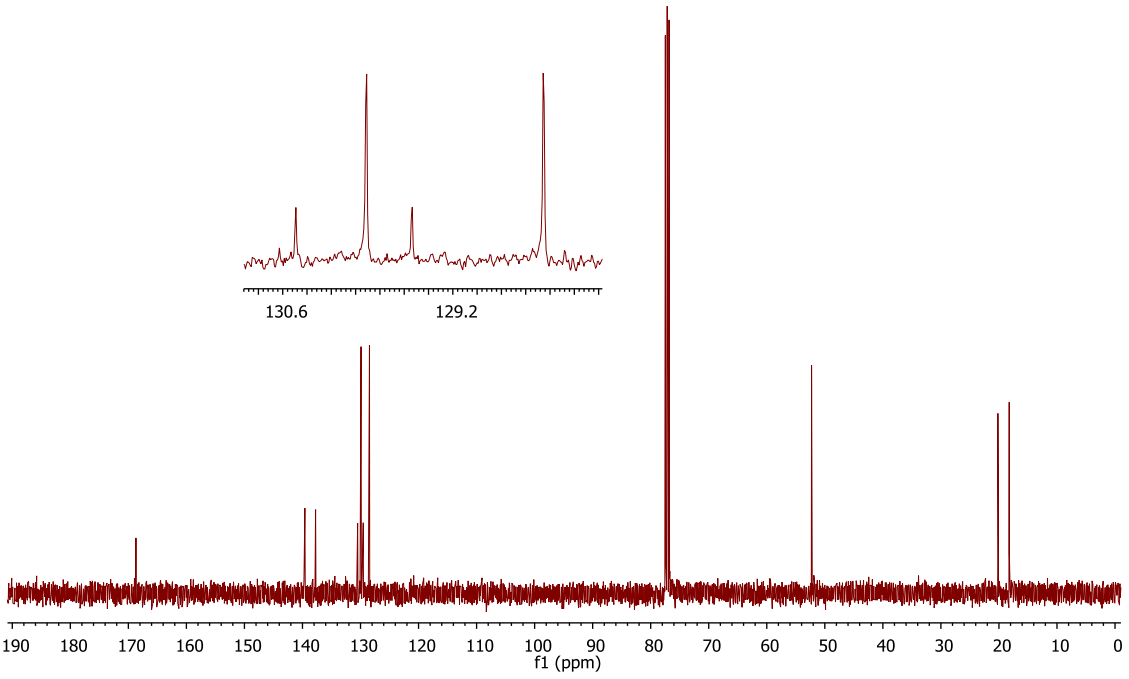


Methyl 4-Bromo-2,3-dimethylbenzoate 19.

^{1}H-NMR (400.13 MHz, $CDCl_3$):

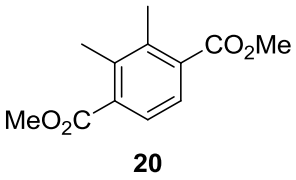


^{13}C-NMR (100.62 MHz, $CDCl_3$):



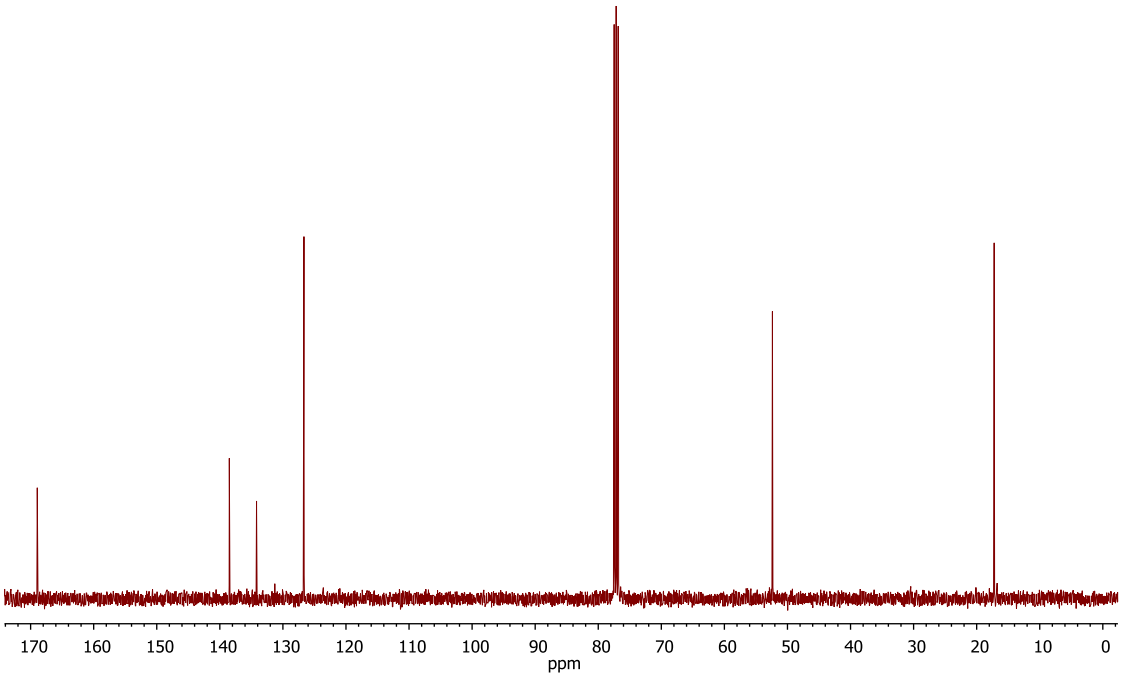
Dimethyl 2,3-Dimethylterephthalate 20.

^{1}H-NMR (400.13 MHz, $CDCl_3$):



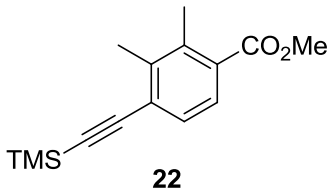
20

^{13}C-NMR (100.62 MHz, $CDCl_3$):



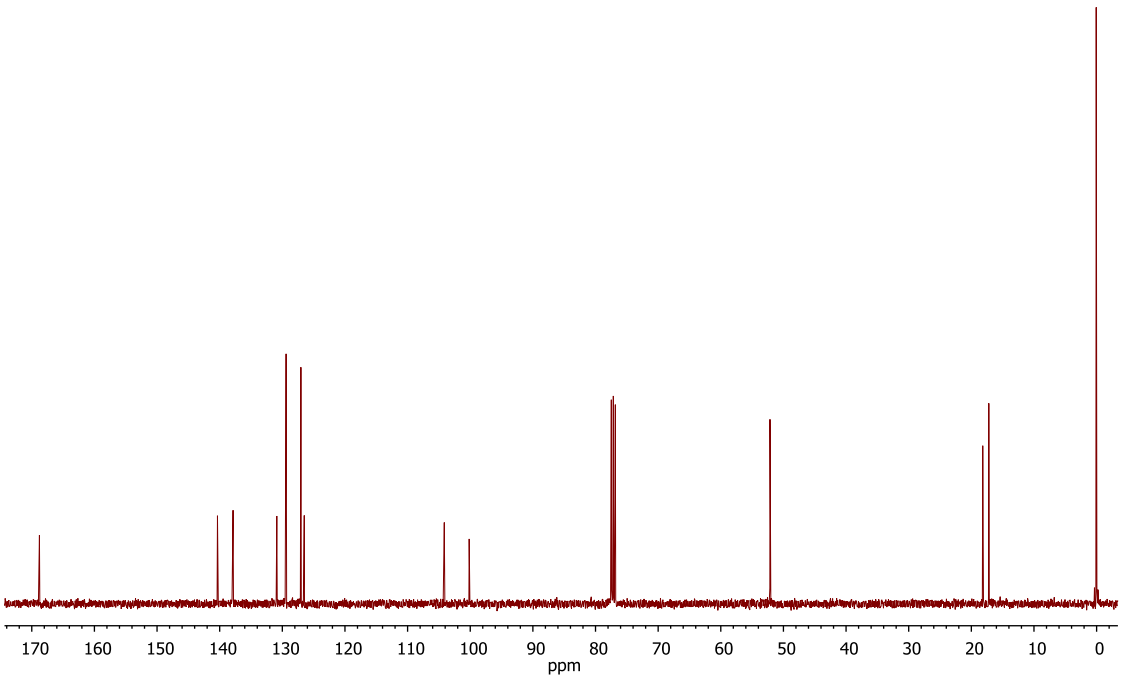
Methyl 2,3-Dimethyl-4-(2-trimethylsilyl-ethyn-1-yl)-benzoate 22.

^{1}H-NMR (400.13 MHz, $CDCl_3$):



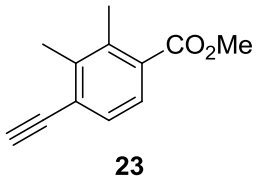
22

^{13}C-NMR (100.62 MHz, $CDCl_3$):



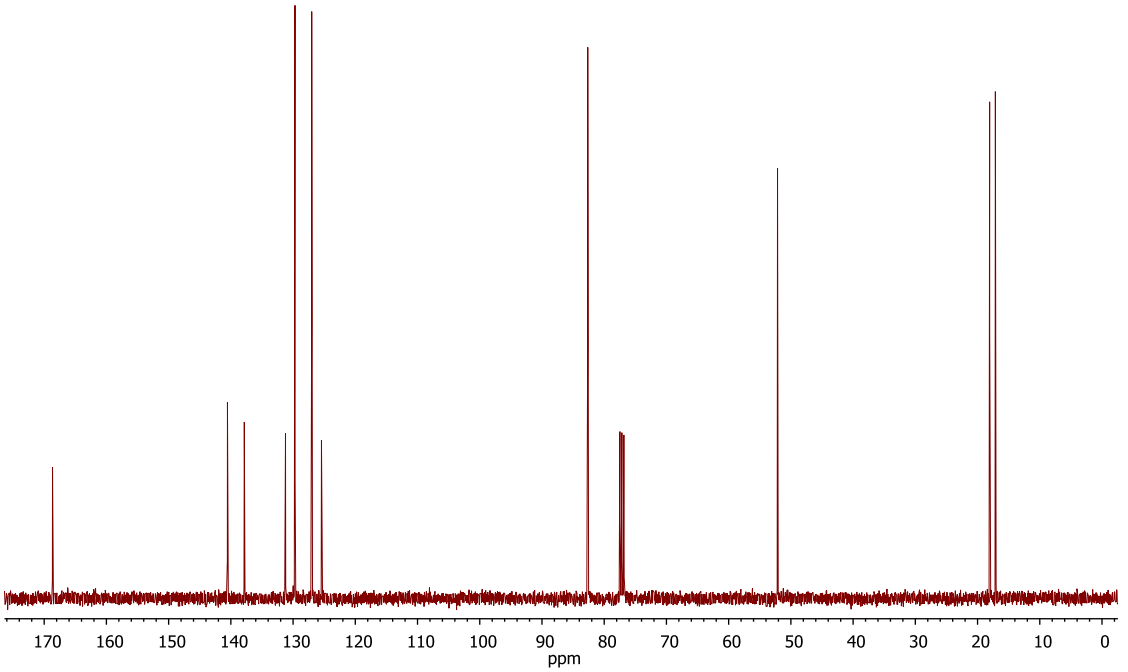
Methyl 4-Ethynyl-2,3-dimethylbenzoate 23.

^{1}H-NMR (400.13 MHz, $CDCl_3$):



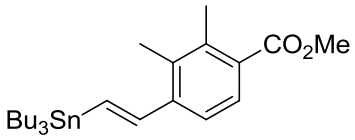
23

^{13}C-NMR (100.62 MHz, $CDCl_3$):

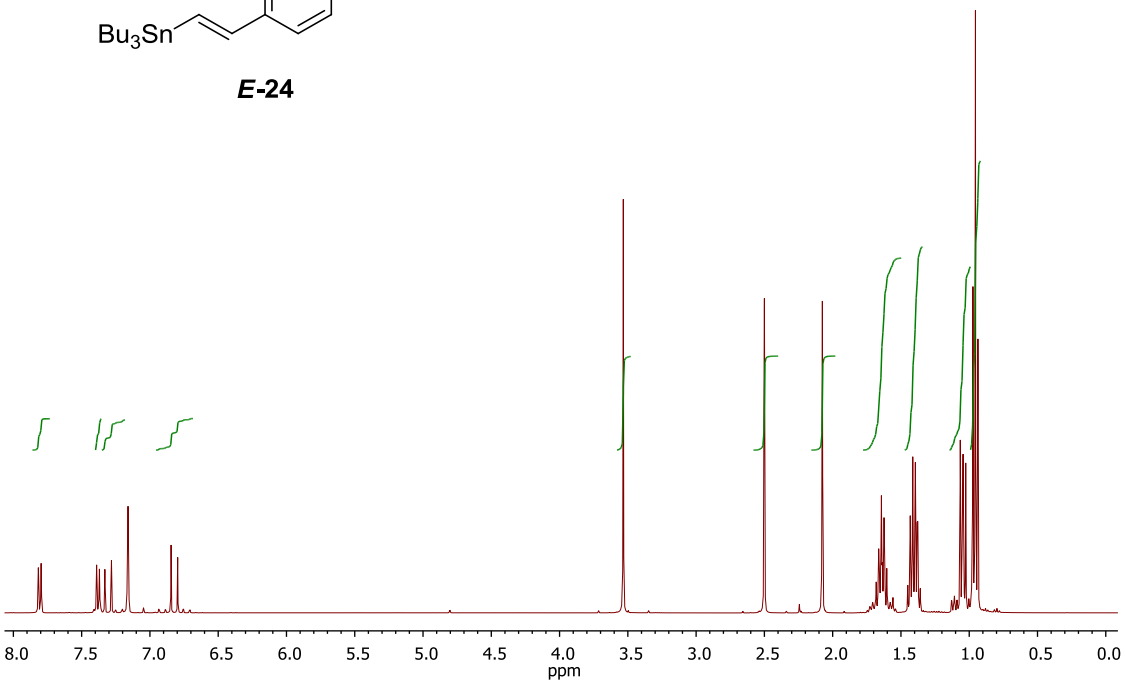


(*E*)-Methyl 2,3-Dimethyl-4-(2-tributylstannylvin-1-yl)benzoate 24.

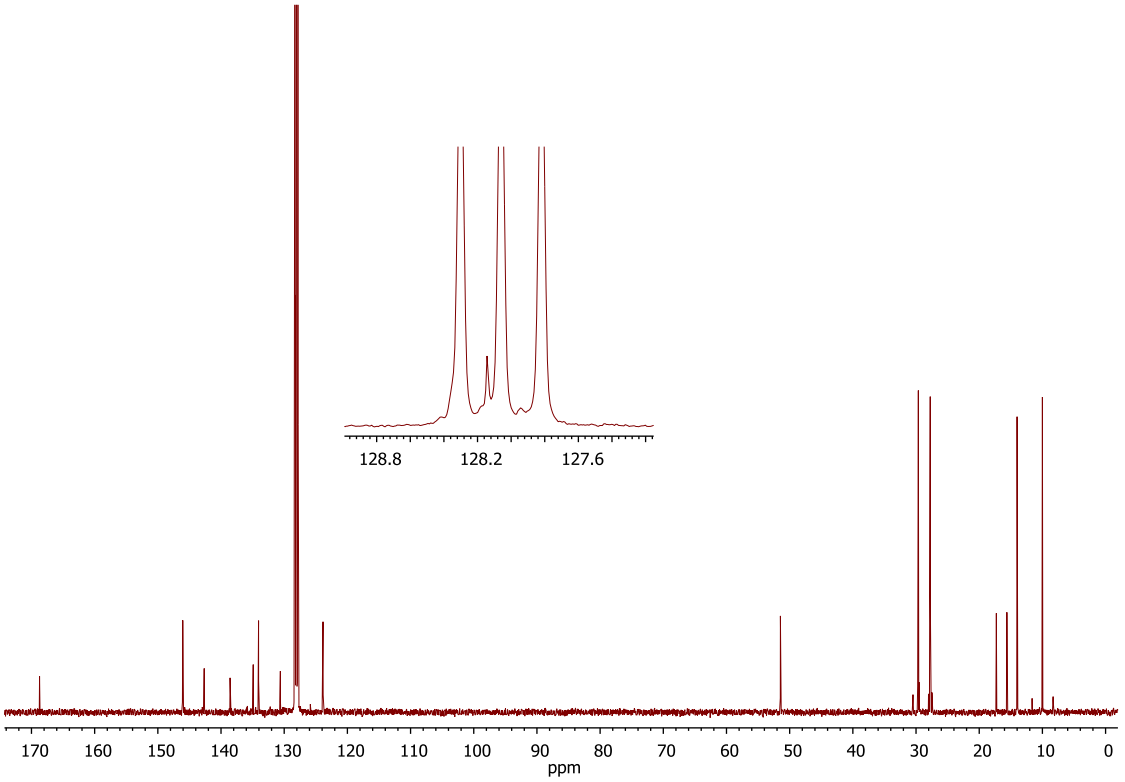
^{1}H-NMR (400.13 MHz, C_6D_6):



***E*-24**

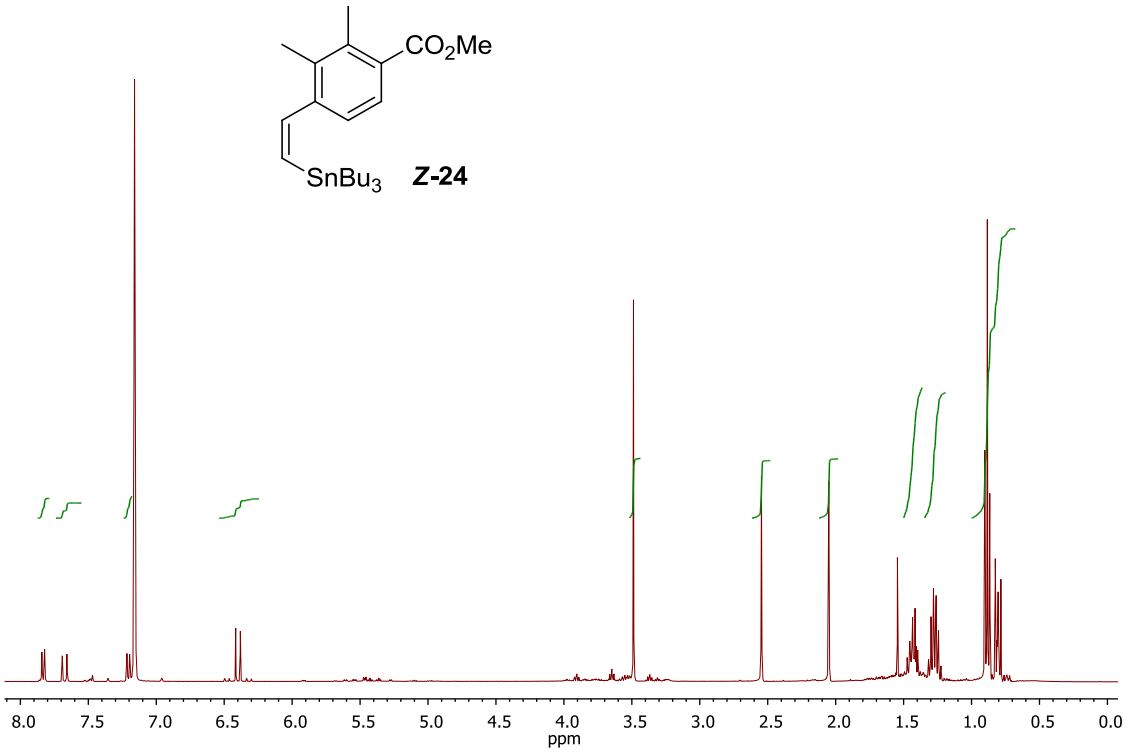


^{13}C-NMR (100.62 MHz, C_6D_6):

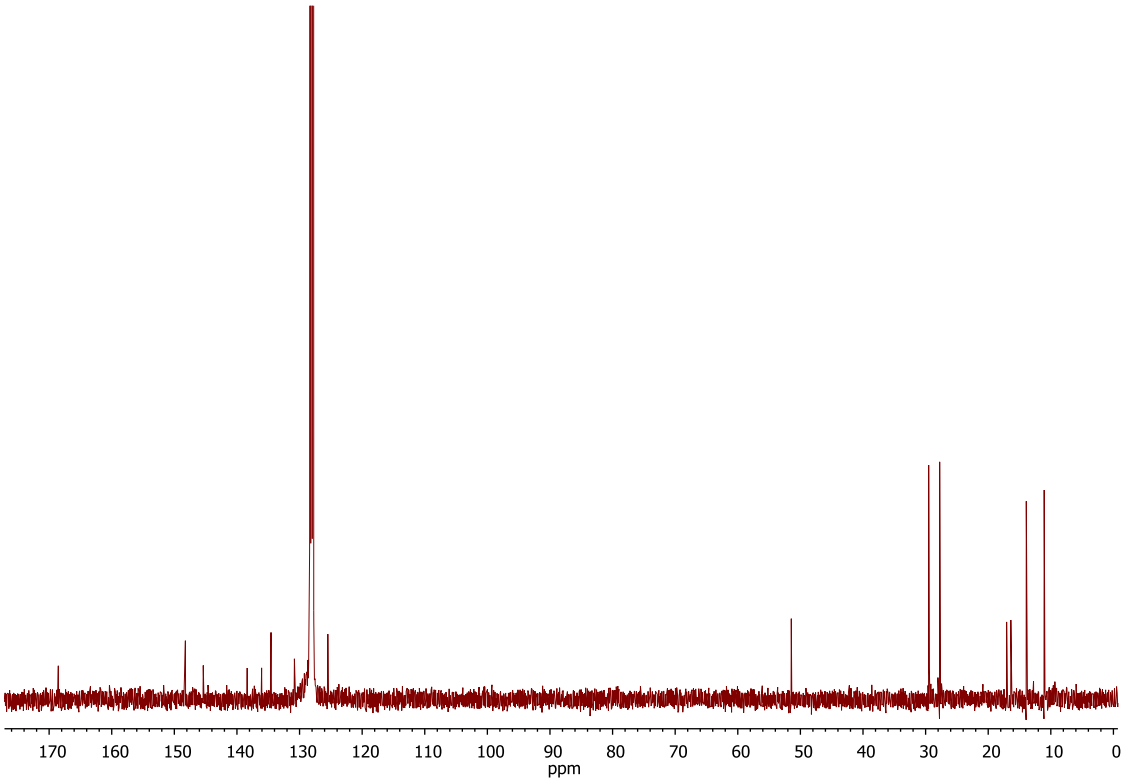


(*Z*)-Methyl 2,3-Dimethyl-4-(2-tributylstannylvin-1-yl)benzoate 24.

^{1}H-NMR (400.13 MHz, C_6D_6):

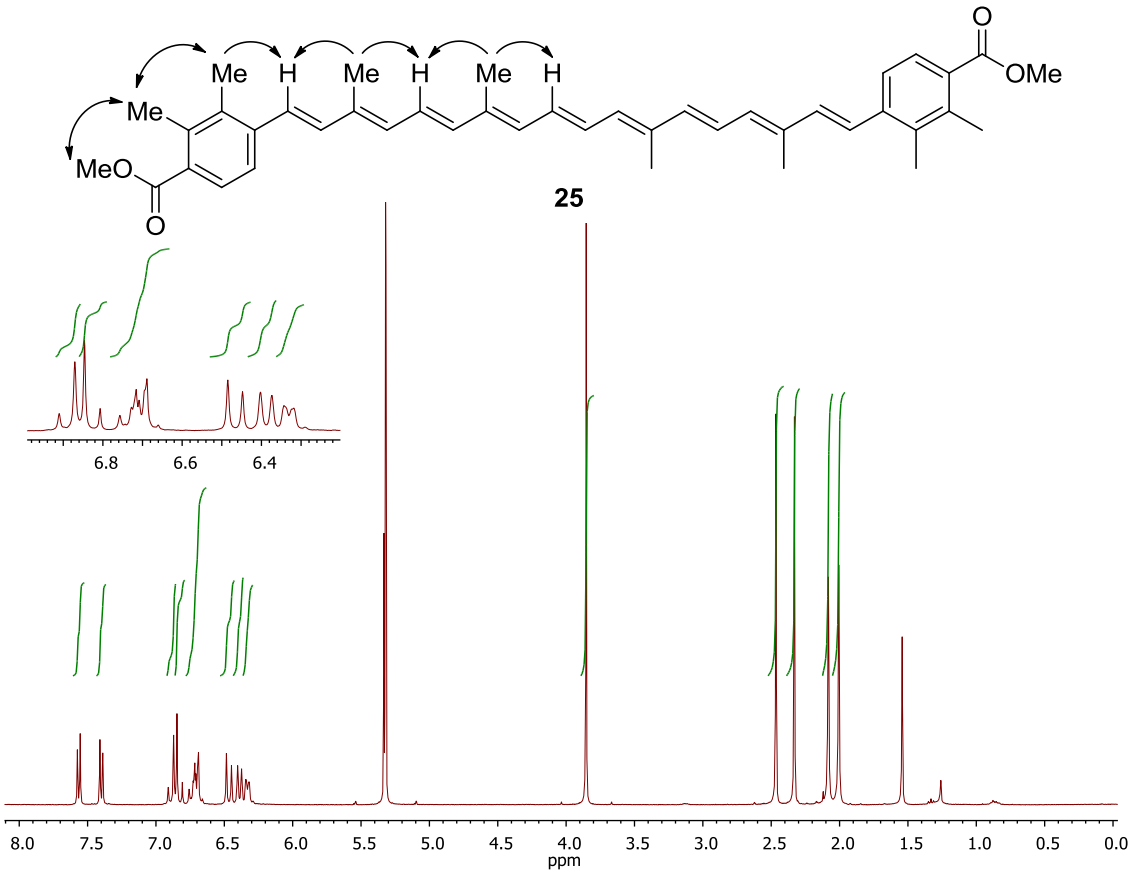


^{13}C-NMR (100.62 MHz, C_6D_6):

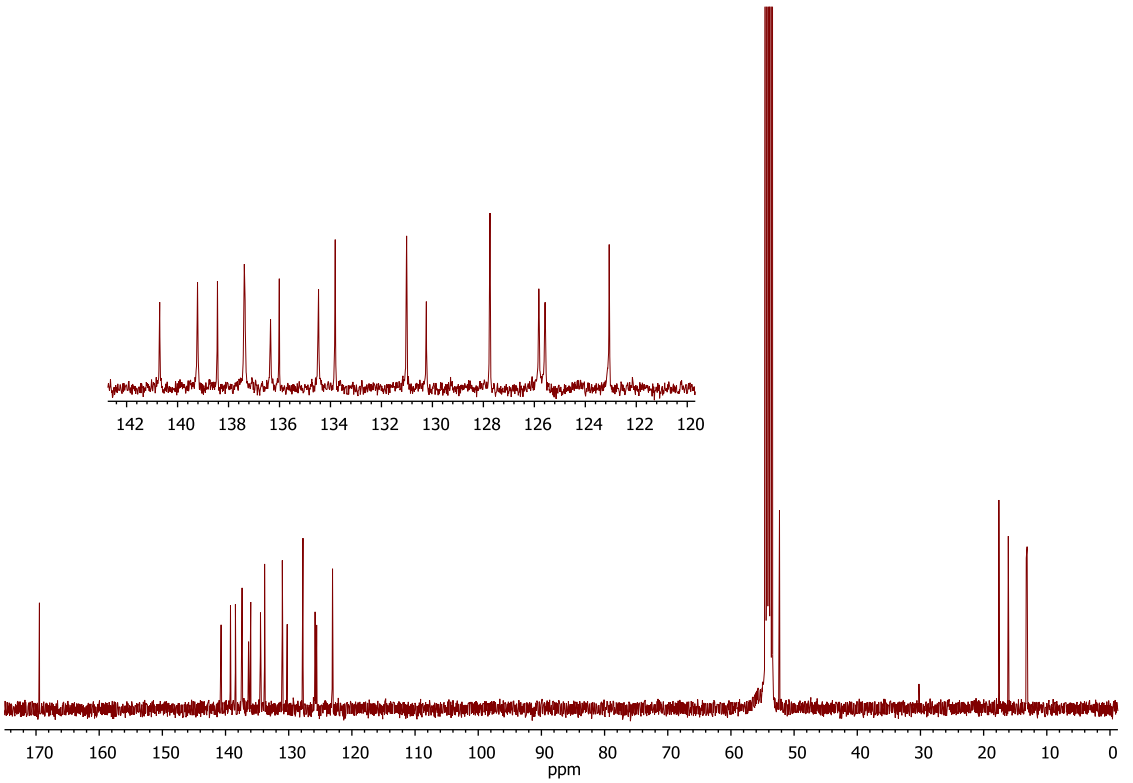


Synechoxanthin dimethyl ester 25.

^{1}H-NMR (400.13 MHz, CD_2Cl_2):

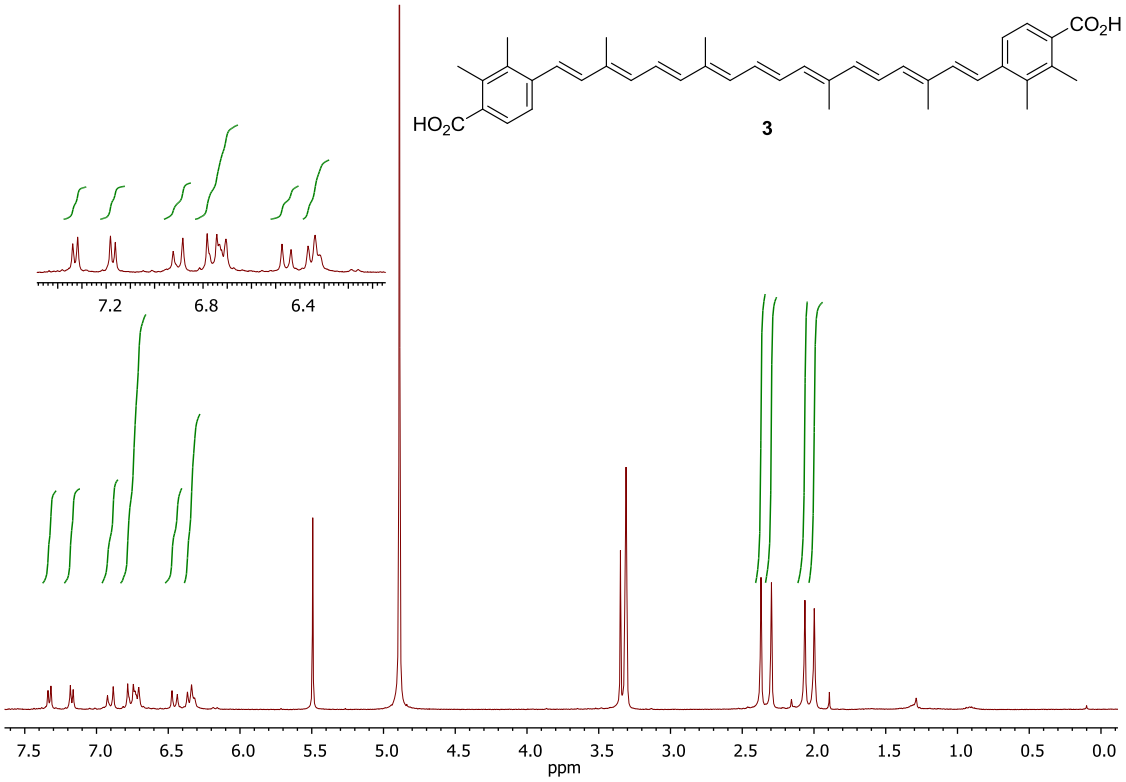


^{13}C-NMR (100.62 MHz, CD_2Cl_2):

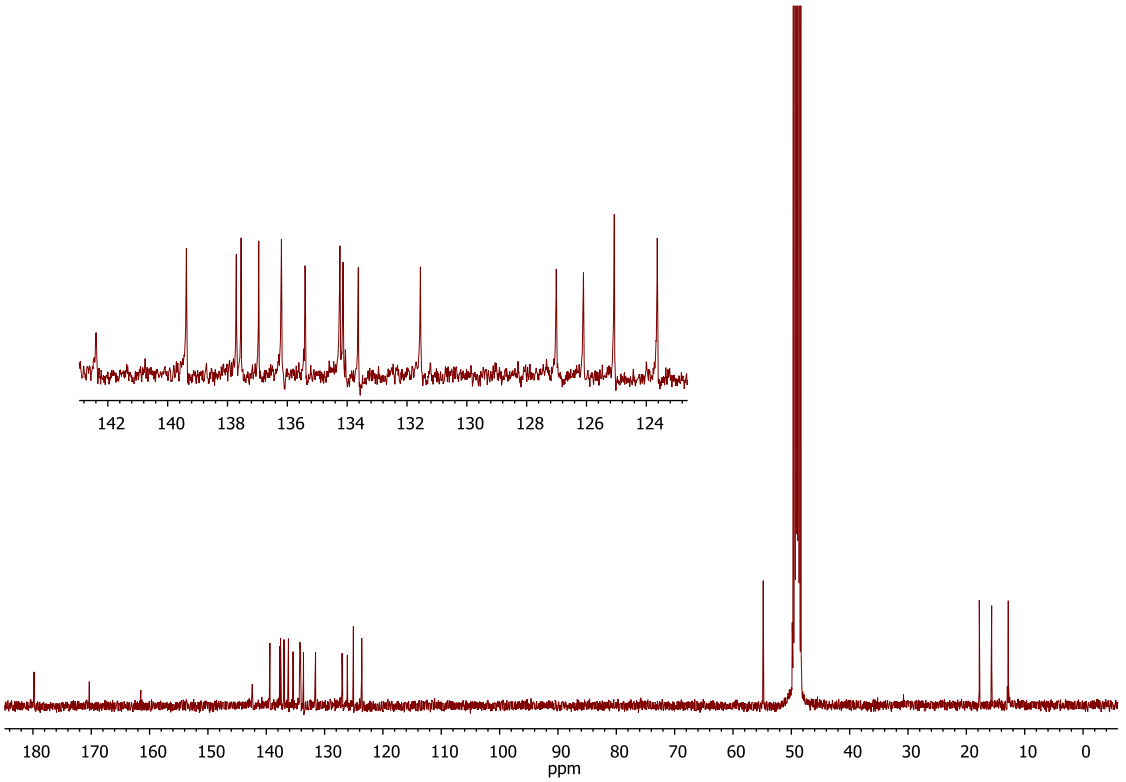


Synechoxanthin 3.

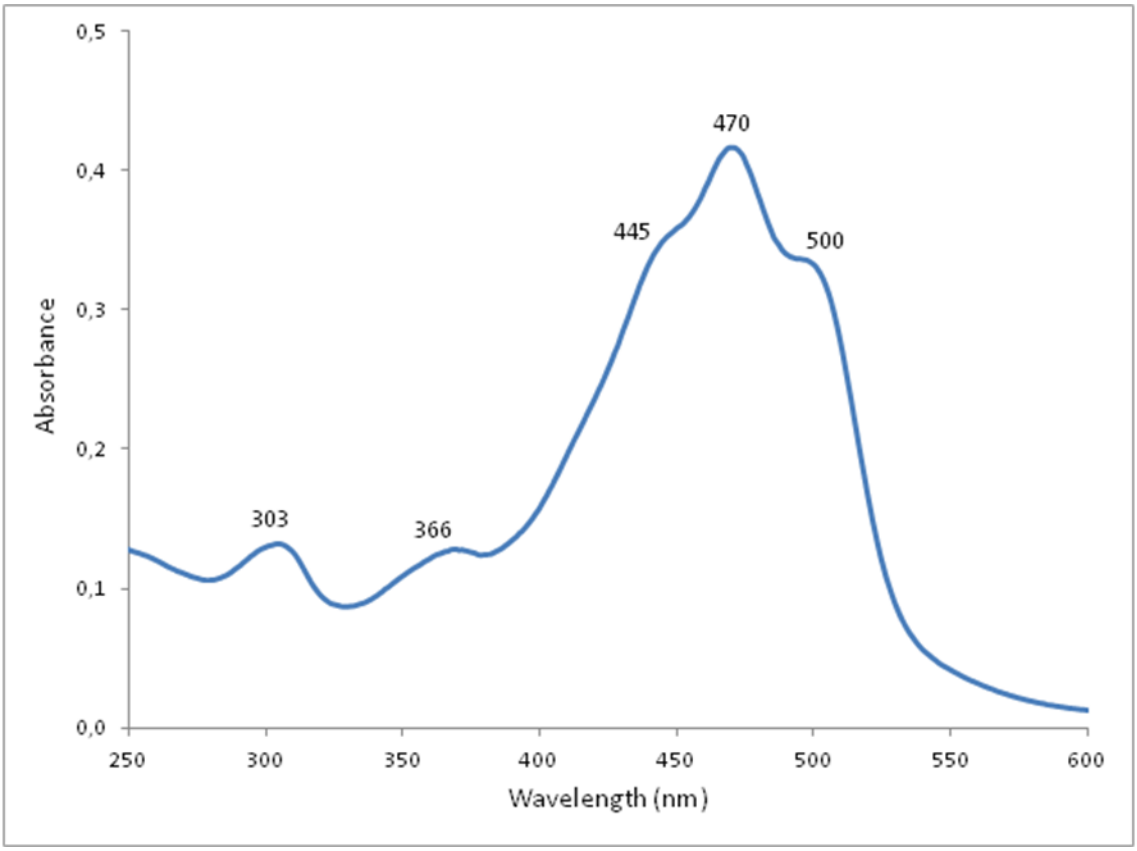
^{1}H-NMR (400.13 MHz, MeOD):



^{13}C-NMR (100.62 MHz, MeOD):

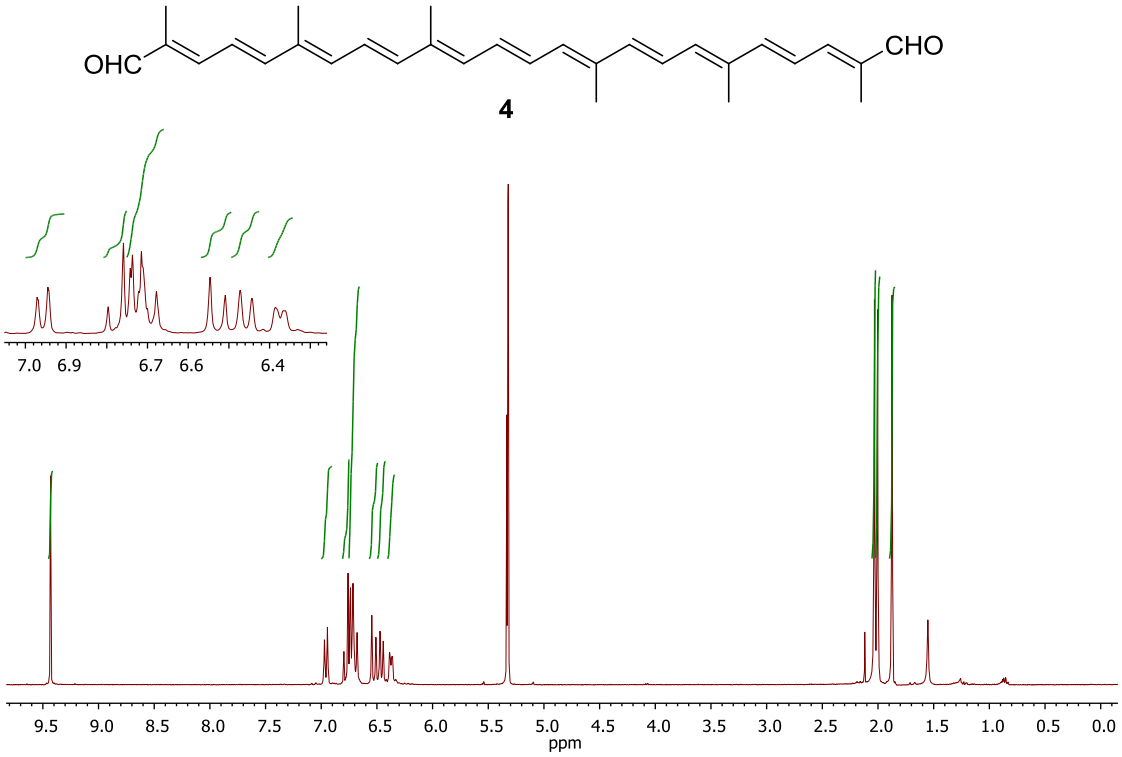


UV-Vis (MeOH)

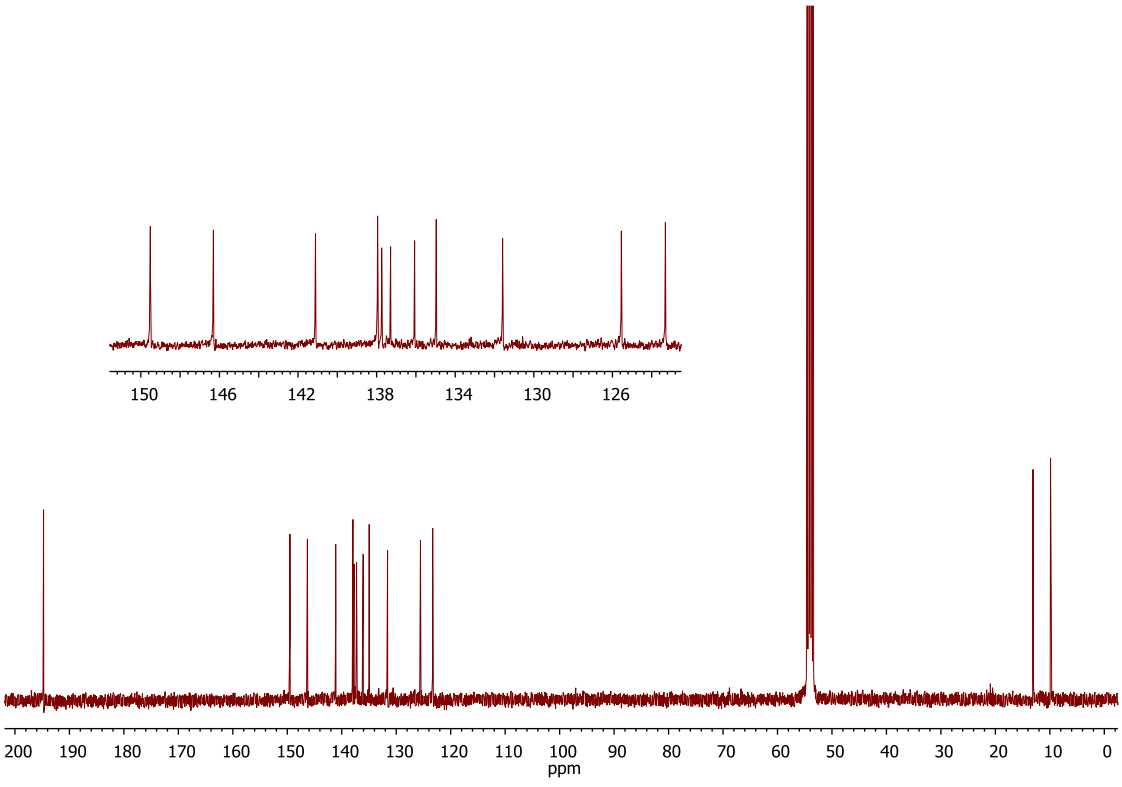

0,5
0,4
0,3
0,2
0,1
0,0
Absorbance
303
366
445
470
500
250
300
350
400
450
500
550
600
Wavelength (nm)

4,4´-diapo-ψ,ψ-carotenodial 4.

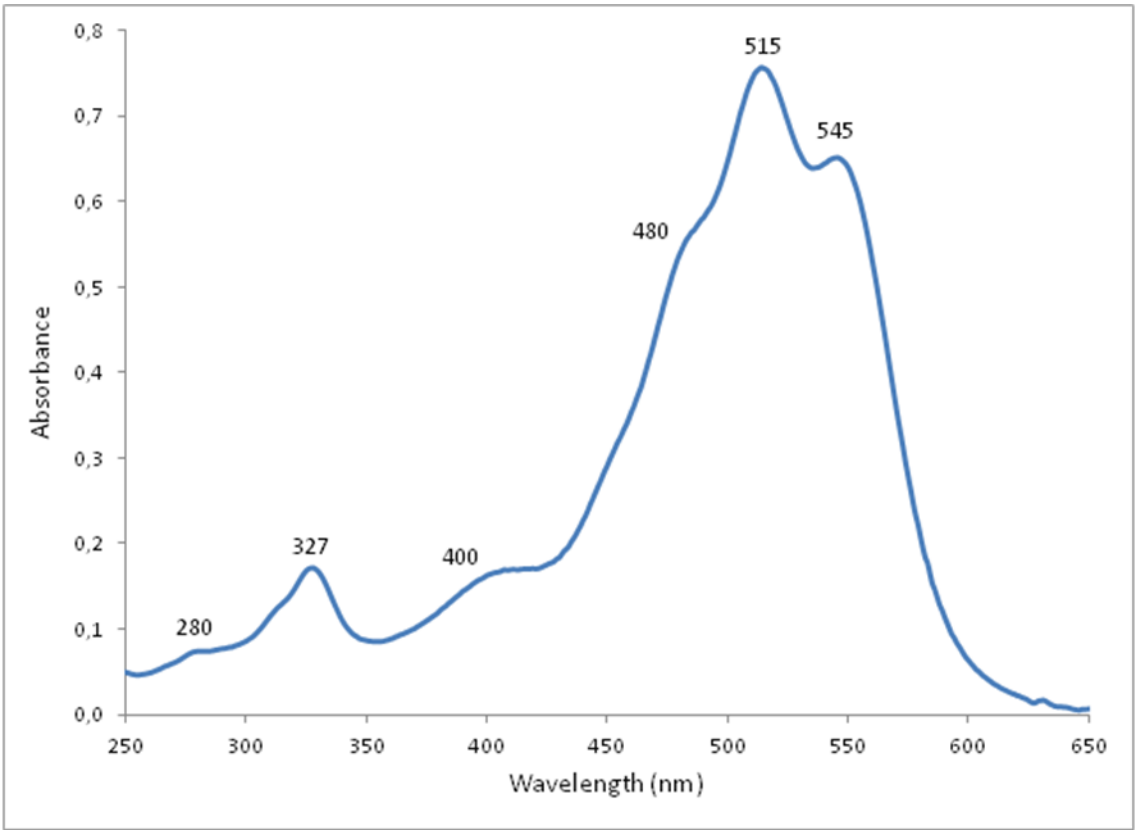
^{1}H-NMR (400.13 MHz, CD_2Cl_2):



^{13}C-NMR (100.62 MHz, CD_2Cl_2):

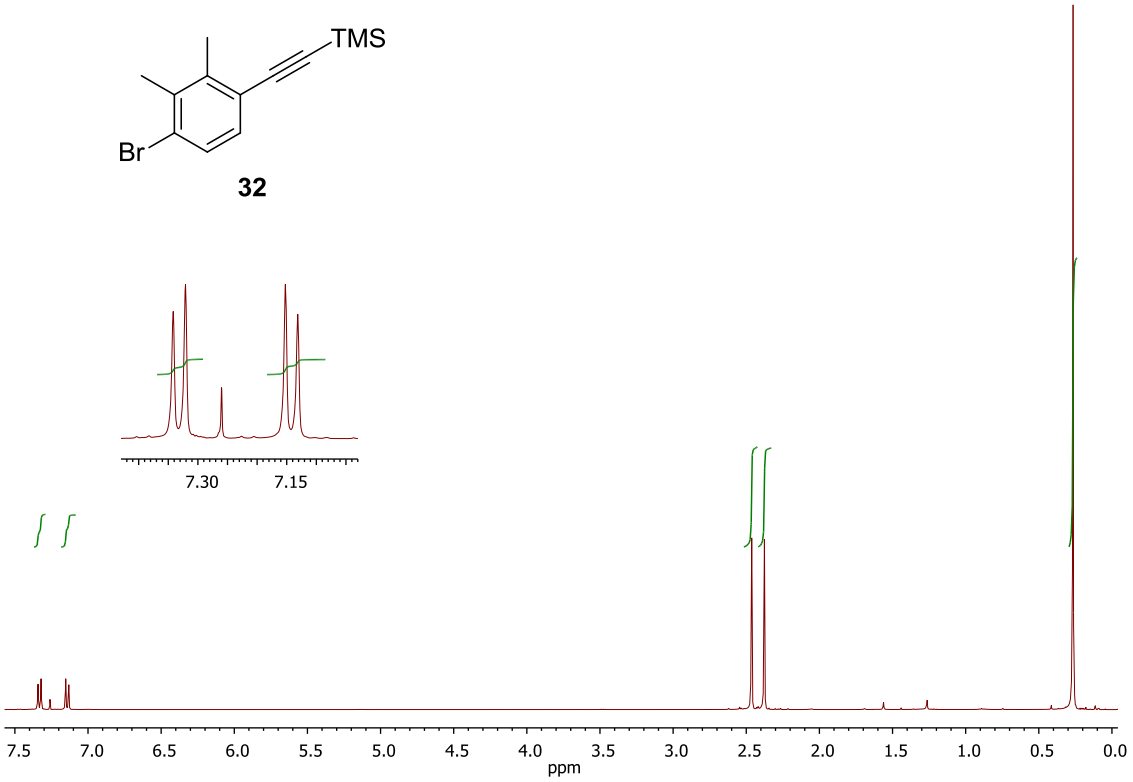


UV-Vis (MeOH)

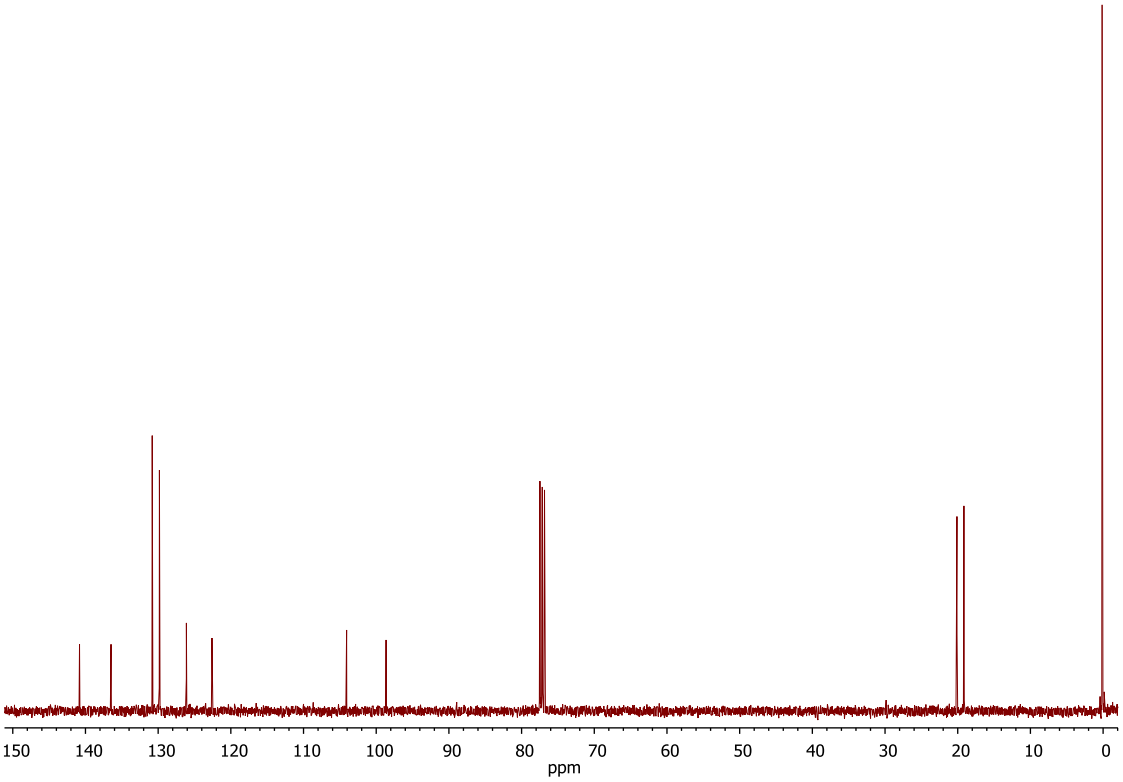


2-(4-Bromo-2,3-dimethylphen-1-yl)-ethynyl-trimethylsilane 32

^{1}H-NMR (400.13 MHz, $CDCl_3$):

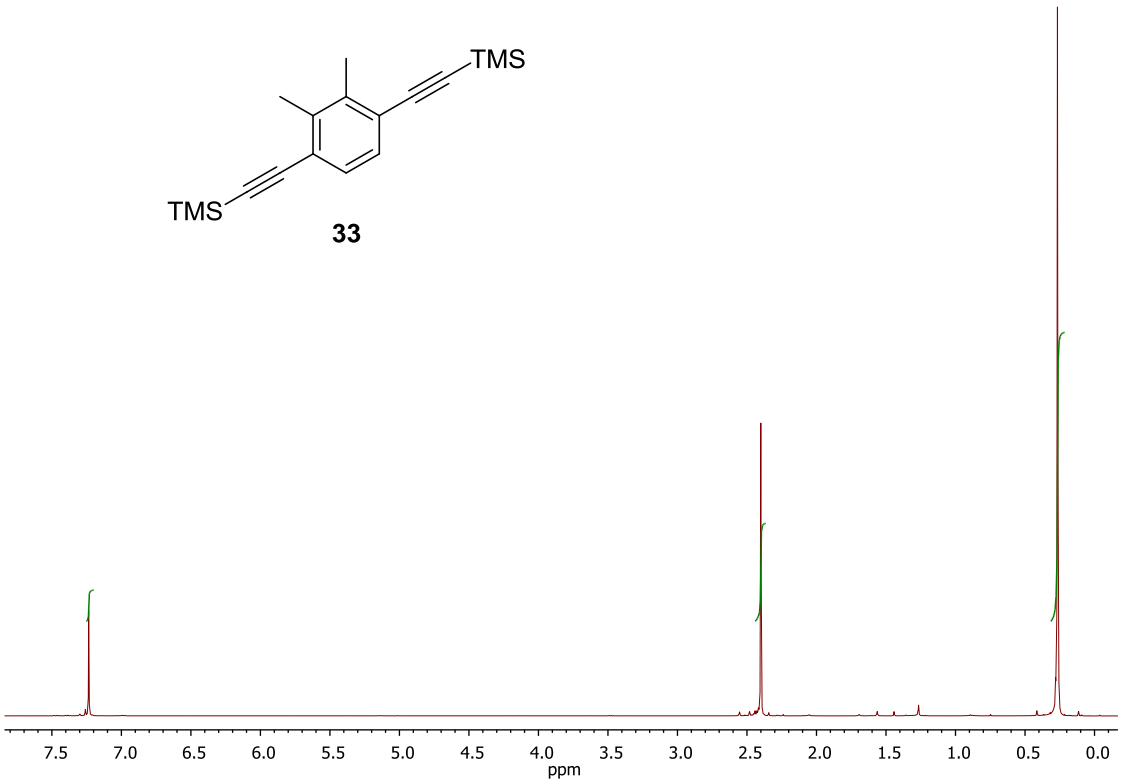


^{13}C-NMR (100.62 MHz, $CDCl_3$):

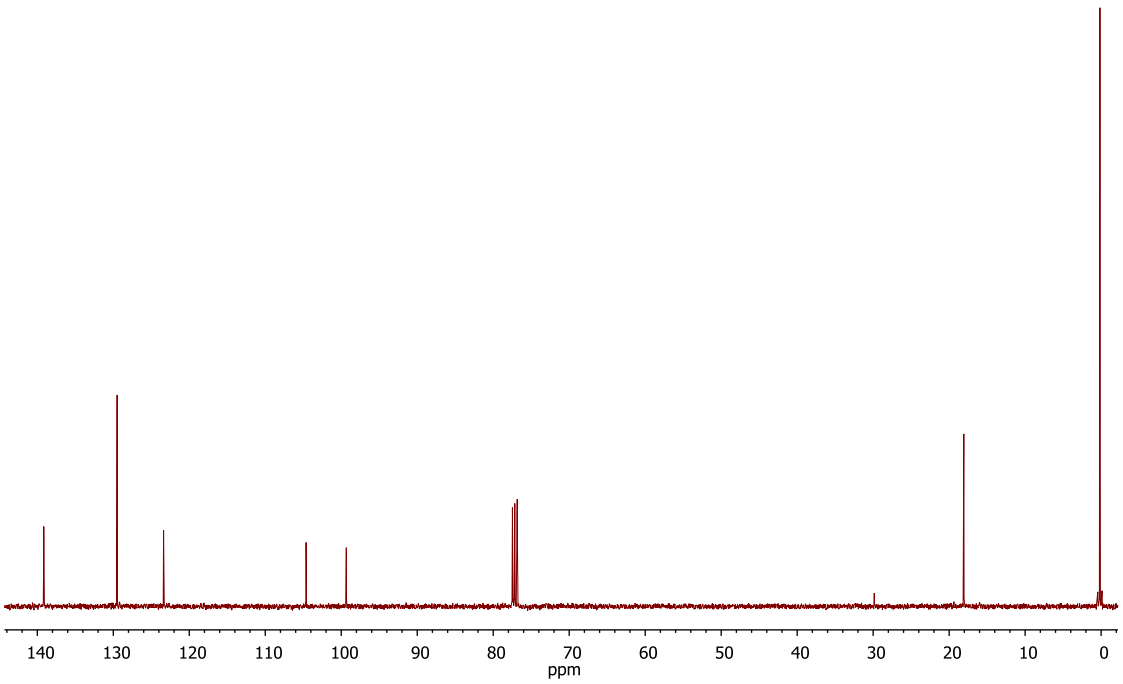


(2,3-Dimethyl-1,4-phenylene)-bis(ethyne-2,1-diyl)-bis(trimethylsilane) 33.

^{1}H-NMR (400.13 MHz, $CDCl_3$):

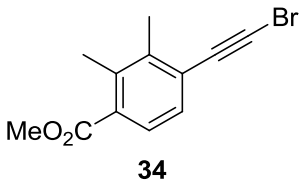


^{13}C-NMR (100.62 MHz, $CDCl_3$):



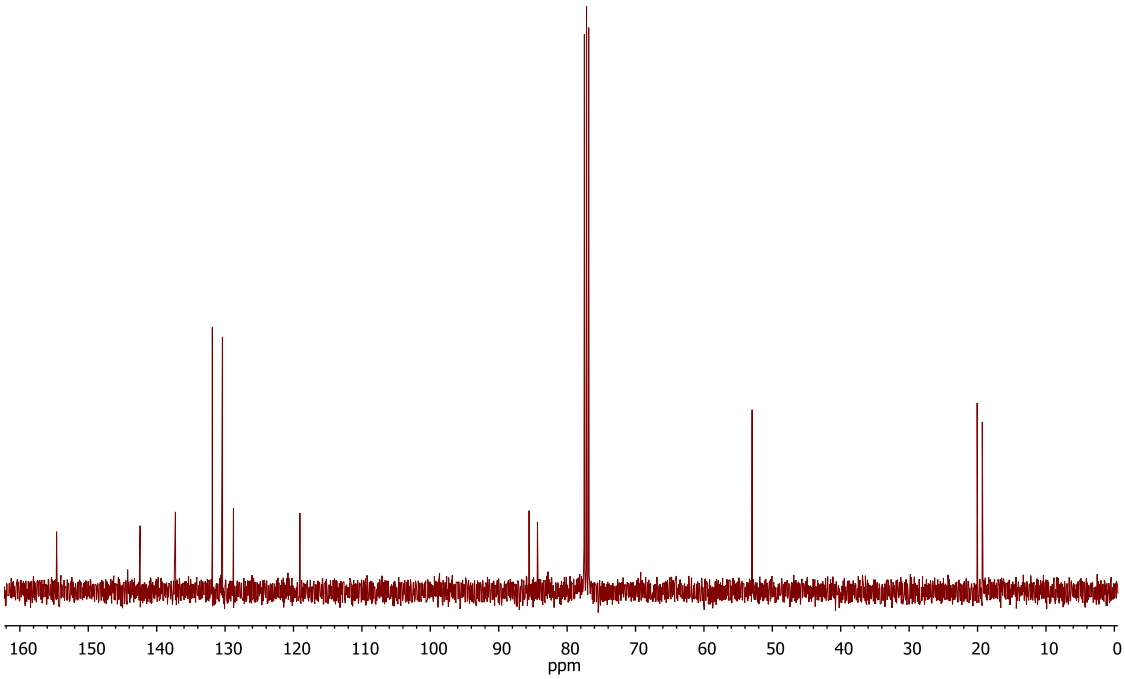
Methyl 4-(Bromoethynyl)-2,3-dimethylbenzoate 34.

^{1}H-NMR (400.13 MHz, $CDCl_3$):



34

^{13}C-NMR (100.62 MHz, $CDCl_3$):



(2*E*,4*E*,6*E*,8*E*)-2,9-dimethyldeca-2,4,6,8-tetraene-1,10-diol.

^{1}H-NMR (400.13 MHz, C_6D_6):