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Supporting Information of

Double Cyclizative Polymerization of Trienes Catalyzed by Pd Complexes. Combined Ring-forming and Chain-walking Reactions of the Growing End

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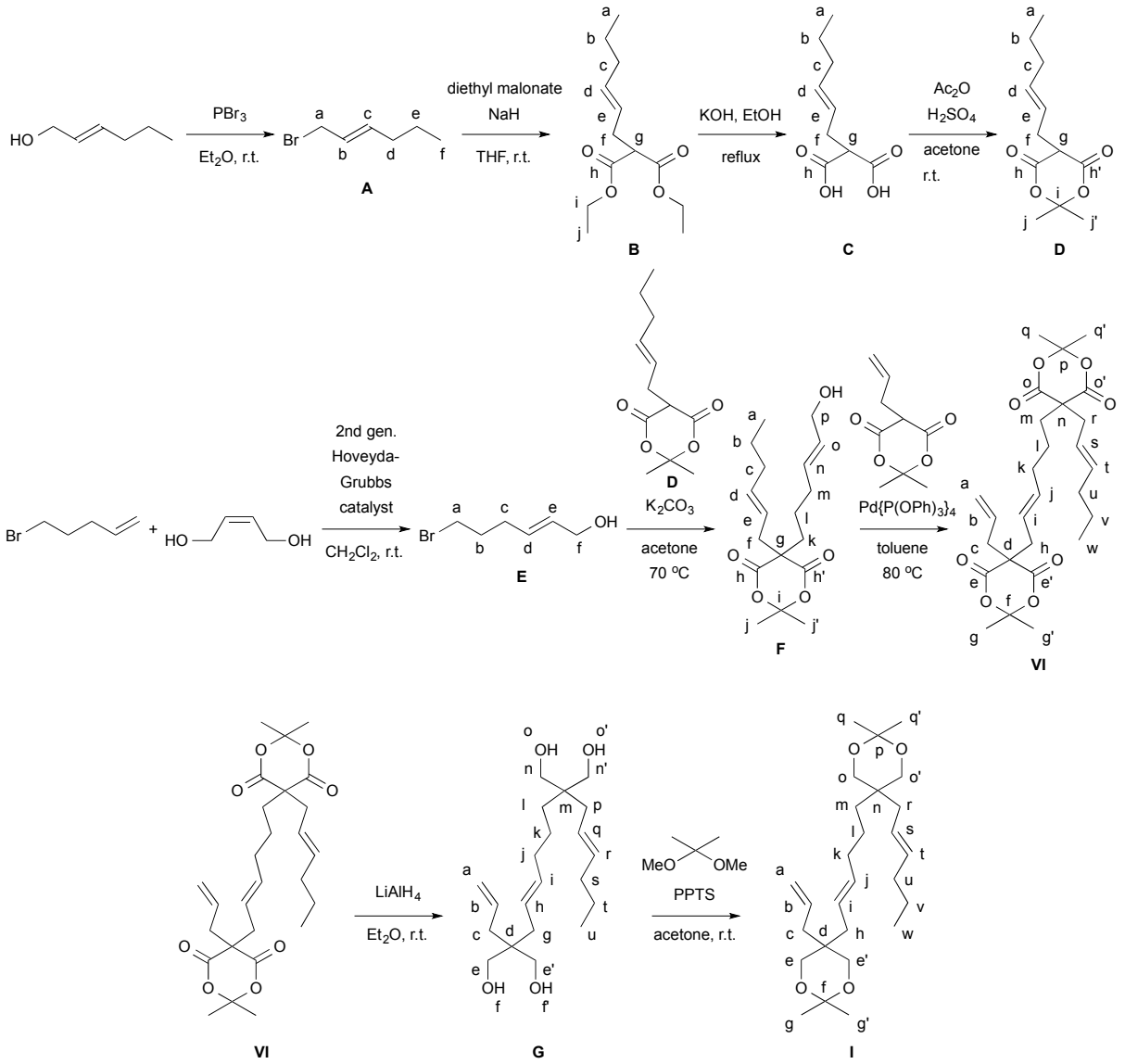
Preparation Procedure and spectroscopic data of monomers

Syntheses of 4,11-bis(4,4-dimethyl-3,5-dioxapentamethylene)-1,6,13-heptadecatriene (I) and 4,11-bis(4,4-dimethyl-2,6-dioxo-3,5-dioxapentamethylene)-1,6,13-heptadecatriene (VI)



Synthesis of (*E*)-1-bromohex-2-ene (A)[1)]

To a 200 mL Schlenk flask containing (*E*)-1-hexenol (2.55 g, 25.5 mmol) and ether (60 mL) was added phosphorous tribromide (25 g, 105 mmol) at 0 °C and stirred for 3 h at room temperature. The reaction mixture was filtered and the filtrate was dried over Na_2SO_4. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/ether = 10:1, Rf = 0.24) to afford (*E*)-1-bromohex-2-ene (**A**) as a colorless

liquid in 80 % yield (3.34 g, 20.5 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.73 (m, 2H, H_b and H_c), 3.94 (d, J = 9.0 Hz, 2H, H_a), 2.02 (q, J = 6.0 Hz, 2H, H_d), 1.42 (m, 2H, H_e), 0.90 (t, J = 6.0 Hz, 3H, H_f).

Synthesis of (2*E*)-2-hexenylmalonate (B)[2)]

To a 500 mL Schlenk flask containing sodium hydride (100 mg, 4.2 mmol) and THF (10 mL) was added diethyl malonate (640 mg, 4.0 mmol) at 0 °C and stirred for 1 h at room temperature. After attiring for 1h, (*E*)-1-bromohex-2-ene (**A**) (580 mg, 4.80 mmol) was added and the reaction mixture was stirred for 12 h at room temperature. The reaction was quenched with water and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na_2SO_4. Volatile fractions were evaporated to afford diethyl (2*E*)-2-hexenylmalonate (**B**) as yellow liquid in 64 % yield (616 mg, 2.54 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.49 (m, J = 6.0 Hz, 1H, H_e), 5.38 (m, 1H, H_d), 4.17 (q, J = 6.0 Hz, 4H, H_i), 3.36 (t, J = 6.0 Hz, 1H, H_g), 2.57 (t, J = 6.0 Hz, 2H, H_f), 1.93 (q, J = 6.0 Hz, 2H, H_c), 1.38 (m, 2H, H_b), 1.26 (t, J = 9.0 Hz, 6H, H_j), 0.86 (t, J = 9.0 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, r.t.): δ 168.9 (C_h), 133.6 (C_e), 125.3 (C_d), 61.1 (C_i), 52.2 (C_g), 34.4 (C_c), 31.7 (C_f), 22.3 (C_b), 14.0 (C_j), 13.4 (C_a).

Synthesis of 5-(2*E*)-2-hexenylmalonic acid (C)

To a 50 mL Schlenk flask containing ethanol (9.8 mL), KOH (3.26 g, 58.1 mmol) and H_2O (9.8 mL) was added diethyl (2*E*)-2-hexenylmalonate (**B**) (4.71 g, 19.4 mmol). After refluxed for 6 h, the organic phase was separated. Aqueous phase was neutralized with 1M HCl and the organic phase was extracted with ether. Combined organic phase was washed with water and brine and dried over $MgSO_4$. Volatile fractions were evaporated to afford 5-(2*E*)-2-hexenylmalonic acid (**C**) as a white solid in 85 % yield (3.08 g, 16.5 mmol).

^{1}H NMR(300MHz, $CDCl_3$, r.t.): δ 5.55 (m, 1H, H_e), 5.41 (m, 1H, H_d), 3.48 (t, J = 7.4 Hz,

1H, H_g), 2.64 (t, J = 6.9 Hz, 2H, H_f), 1.95 (q, J = 7.0 Hz, 2H, H_c), 1.34 (m, 2H, H_b), 0.86 (t, J = 7.3 Hz, 3H, H_a).

Synthesis of 5-(2*E*)-2-hexenyl-2,2-dimethyl-1,3-dioxane-4,6-dione (D)

To a 25 mL Schlenk flask containing 5-(2*E*)-2-hexenylmalonic acid (**C**) (3.08 g, 16.5 mmol) and acetic anhydride (4.0 mL, 42.4 mmol) was added several drops of conc. H_2SO_4 and distilled acetone (2.7 mL, 35.7 mmol) at 0 °C. After warmed to room temperature and stirred for 52 h, the reaction quenched with water and the organic phase was extracted with $CHCl_3$, washed successively with water and brine, and dried over Na_2SO_4. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/ether = 1:1, Rf = 0.37) to afford 5-(2*E*)-2-hexenyl-2,2-dimethyl-1,3-dioxane-4,6-dione (**D**) as a yellow solid in 67 % yield (2.50 g, 11.1 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.62 (m, 1H, H_e), 5.46 (m, 1H, H_d), 3.54 (t, J = 5.4 Hz, 1H, H_g), 2.83 (t, J = 7.2 Hz, 2H, H_f), 1.94 (q, J = 6.0 Hz, 2H, H_c), 1.79, 1.76 (s, 6H, H_j and $H_{j'}$), 1.34 (m, 2H, H_b), 0.87 (t, J = 7.5 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 165.2 (C_h and $C_{h'}$), 135.4 (C_e), 123.6 (C_d), 104.7 (C_i), 46.2 (C_g), 34.2 (C_c), 29.1, 28.0 (C_j and $C_{j'}$), 26.6 (C_f), 21.9 (C_b), 13.2 (C_a).

Synthesis of 6-bromo-hex-2-enol (E)[3)]

To a 25 mL Schlenk flask containing CH_2Cl_2 solution (1.0 mL) of 2nd generation Hoveyda-Grubbs catalyst (10.4 mg, 0.017 mmol) was added 5-bromo-1-pentene (0.25 g, 1.65 mmol) and *cis*-2-butene-1,4-diol (0.29 g, 3.30 mmol) at room temperature. After stirred for 4 h, the reaction mixture was evaporated and the residue was purified by column chromatography (silica gel, hexane/ether = 1:1, Rf = 0.26) to afford 6-bromo-hex-2-enol (**E**) as a yellow solid in 74% yield (218 mg, 1.22 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.69 (m, 2H, H_d and H_e), 4.12 (d, J = 4.4 Hz, 2H, H_f),

3.41 (t, J = 6.6 Hz, 2H, H_a), 2.21 (q, J = 5.4 Hz, 2H, H_c), 1.95 (m, 2H, H_b).

Synthesis of 5-{(2*E*)-2-hexenyl}-5-{(4*E*)-6-hydroxy-hex-4-enyl}-2,2-dimethoxy- 1,3-dioxane-4,6-dione (F)

To a two-necked flask containing K_2CO_3 (4.56 g, 33.0 mmol) and distilled acetone (47 mL) was added 5-(2*E*)-2-hexenyl-2,2-dimethyl-1,3-dioxane-4,6-dione (**D**) (2.49 g, 11.0 mmol) and 6-bromo-hex-2-enol (**E**) (2.36 g, 13.2 mmol) and stirred for 22 h at 70 ˚C. The reaction quenched with water and the organic phase was extracted with $CHCl_3$, washed successively with water and brine, and dried over Na_2SO_4. Volatile fractions were evaporated and the residue was purified by column chromatography (silica gel, hexane/ether = 1:1, Rf = 0.16) to afford 5-{(2*E*)-2-hexenyl}-5-{(4*E*)-6-hydroxy-hex-4-enyl}-2,2-dimethoxy-1,3-dioxane- 4,6-dione (**F**) as brown powder in 49 % yield (1.74 g, 5.37 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.62 (m, 3H, H_e, H_n and H_o), 5.32 (m, 1H, H_d), 4.08 (s, J = 5.5 Hz, 2H, H_p), 2.69 (d, J = 8.0 Hz, 2H, H_f), 2.02 (m, 6H, H_c, H_k and H_m), 1.72, 1.69 (s, 6H, H_j and $H_{j'}$), 1.34 (m, 4H, H_b and H_l), 0.86 (t, J = 7.4 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, r.t.): δ 169.2 (C_h and $C_{h'}$), 137.5 (C_e), 131.2 (C_n or C_o), 130.1 (C_n or C_o), 122.6 (C_d), 105.6 (C_i), 63.5 (C_p), 55.5 (C_g), 41.9 (C_f), 39.0 (C_k or C_m), 34.5 (C_c), 31.8 (C_k or C_m), 30.1, 29.7(C_j and $C_{j'}$), 25.0 (C_l), 22.0 (C_b), 13.7 (C_a).

Synthesis of 4,11-bis(4,4-dimethyl-2,6-dioxo-3,5-dioxatetramethylene)-1,6,13-heptadeca-triene (VI)

To a 100 mL Schlenk flask containing MS4A and distilled toluene (29 mL) was added 5-allyl-2,2-dimethyl-1,3-dioxan-4,6-dione (1.76 g, 9.60 mmol) and 5-(2E)-2-hexenyl- 5-(4*E*)-6-hydroxy-hex-4-enyl-2,2-dimethoxy-1,3-dioxane-4,6-dione (**F**) (1.42 g, 4.40 mmol) and stirred for 24 h at 80 °C. After filtration, the filtrate was evaporated and the residue was purified by column chromatography (silica gel, hexane/ether = 2:1, Rf = 0.30) to afford 4,11-

bis(4,4-dimethyl-2,6-dioxo-3,5-dioxatetramethylene)-1,6,13-heptadecatriene (**VI**) as yellow solid in 88 % yield (1.84 g, 0.39 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.57 – 5.19 (m, 7H, H_a, H_b, H_i, H_j, H_s and H_t), 2.67 (m, 6H, H_c, H_h and H_r), 1.93 (m, 6H, H_k, H_m and H_u), 1.67 (m, 12H, H_g, $H_{g'}$, H_q and $H_{q'}$), 1.33 (m, 4H, H_l and H_v), 0.86 (t, J =7.3 Hz, Hz, 3H, H_w). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, r.t.): δ 169.0 (C_e and $C_{e'}$ or C_o and $C_{o'}$), 168.5 (C_e and $C_{e'}$ or C_o and $C_{o'}$), 137.5 (C_s), 135.8 (C_i or C_j), 130.9 (C_b), 123.4 (C_i or C_j), 122.5 (C_t), 121.3 (C_a), 105.7 (C_f and C_p), 55.7 (C_d or C_n), 55.4 (C_d or C_n), 42.4 (C_c or C_h), 42.0 (C_c or C_h), 41.7 (C_r), 39.0 (C_k or C_m), 34.5 (C_u), 32.1 (C_k or C_m), 30.0, 29.9, 29.8, 29.6 (C_g, $C_{g'}$, C_q and $C_{q'}$), 24.9 (C_l), 22.0 (C_b), 13.6 (C_w).

Synthesis of 4,4,11,11-tetrakis(hydroxymethyl)-1,6,13-heptadecatriene (G)

To a 200 mL three-necked round-bottomed flask containing lithium aluminum hydride (650 mg, 12.6 mmol) and ether (35 mL) was added 4,11-bis(4,4-dimethyl-2,6-dioxo- 3,5-dioxatetramethylene)-1,6,13-heptadecatriene (**VI**) (1.00 g, 2.10 mmol) at 0 °C and stirred at 0 °C for 30 min and at r.t. for 36 h. The reaction mixture was cooled to 0 °C and NH_4Cl aq. (0.7 mL) and NaOH aq. (1.00 M, 1.5 mL) was added dropwise, which was refluxed for 24 h. The reaction mixture was filtered, and the filtrate was dried over $MgSO_4$. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 1:5, Rf = 0.20) to afford 4,4,11,11-tetrakis(hydroxymethyl)- 1,6,13-heptadecatriene (**G**) as a colorless liquid in 44 % yield (324 mg, 0.91 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.79 (m, 1H, H_b), 5.44 (m, 4H, H_h, H_i, H_q and H_r), 5.08 (m, 2H, H_a), 3.57 (s, 8H, H_e, $H_{e'}$, H_n and $H_{n'}$), 2.27 (s, 4H, H_f, $H_{f'}$, H_o and $H_{o'}$), 2.02 (m, 10H, H_c, H_g, H_j, H_p and H_s), 1.33 (m, 6H, H_k, H_l and H_t), 0.89 (t, J = 7.3 Hz, 3H, H_u)

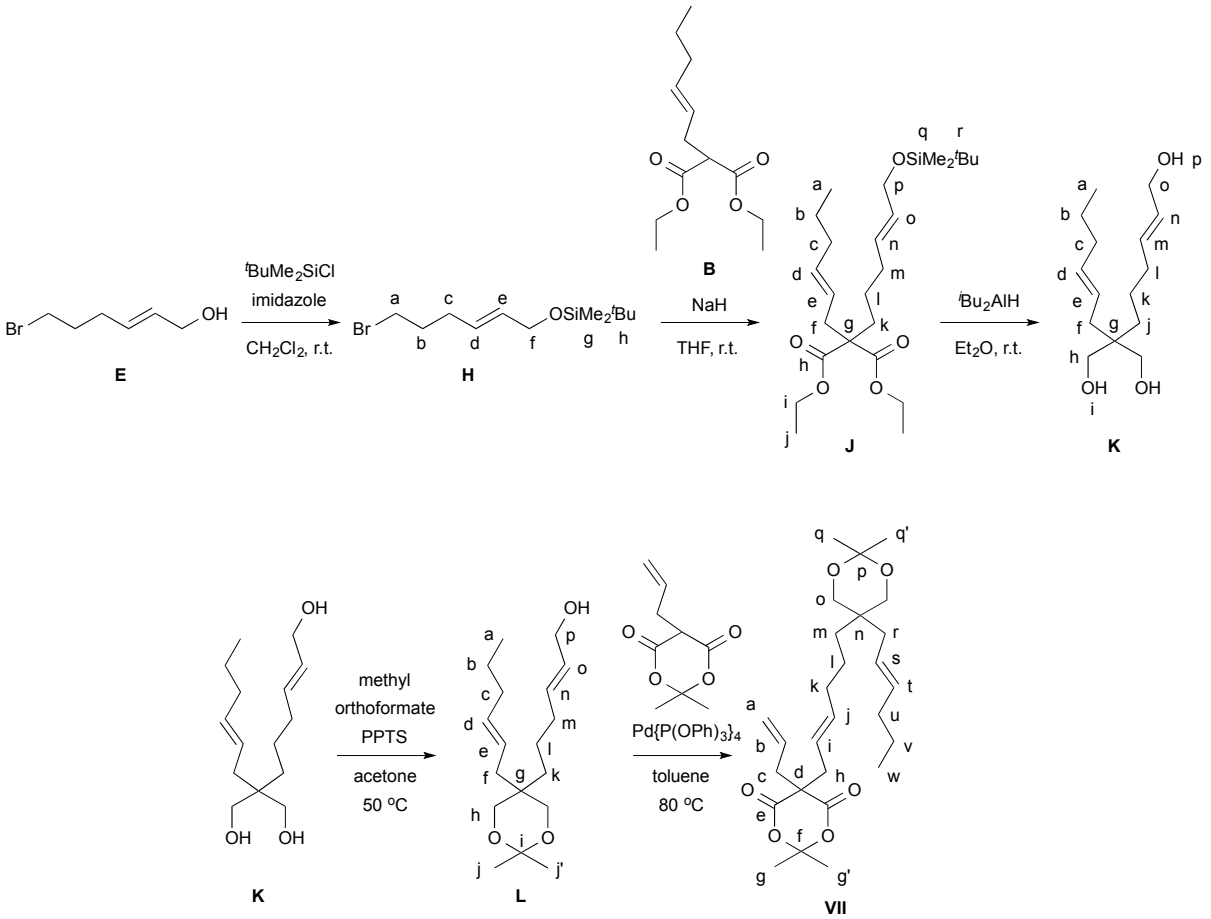
Synthesis of 4,11-bis(4,4-dimethyl-3,5-dioxapentamethylene)-1,6,13-heptadecatriene (I)

To a 300 mL Schlenk flask containing pyridinium *p*-toluenesulfonate (49.3 mg, 0.18 mmol)

and distilled acetone (41 mL) was added 4,4,11,11-tetrakis(hydroxymethyl)- 1,6,13-heptadecatriene (**G**) (3.11 g, 8.77 mmol) and 2,2-dimethoxypropane (2.63 mL, 22.1 mmol) and the mixture was stirred at room temperature for 38 h. The reaction was quenched with $NaHCO_3$ aq. and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na_2SO_4. Volatile fractions were evaporated to afford 4,11-bis(4,4-dimethyl-3,5-dioxapentamethylene)-1,6,13-heptadecatriene (**I**) as a colorless liquid in 87 % yield (3.33 g, 7.66 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.79 (m, 1H, H_b), 5.45 (m, 2H, H_i and H_j), 5.31 (m, 2H, H_s and H_t), 5.08 (m, J = 5.0 Hz, 2H, H_a), 3.52 (s, 8H, H_e, $H_{e'}$, H_o and $H_{o'}$), 2.11 – 1.96 (m, 12H, H_c, H_h, H_k, H_m, H_r and H_u), 1.39 (s, 12H, H_g, $H_{g'}$, H_q and $H_{q'}$), 1.34 (m, 4H, H_l and H_v), 0.87 (t, J = 5.0 Hz, 3H, H_w). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 134.1 (C_i and C_j), 133.3 (C_b), 124.6 (C_s and C_t), 118.2 (C_a), 97.9 (C_f and C_p), 67.7, 67.2(C_e, $C_{e'}$, C_o and $C_{o'}$), 36.7 (C_c), 35.6 (C_d), 35.3 (C_h, C_k, C_r or C_u), 35.2 (C_h, C_k, C_r or C_u), 35.0 (C_n), 34.7, 33.4 (C_h, C_k, C_r or C_u), 31.9 (C_m), 24.3, 23.8, 23.7, 23.3 (C_g, $C_{g'}$, C_q and $C_{q'}$), 22.6, 22.5 (C_l and C_v), 13.6 (C_w). Anal. Calcd (found) for $C_{22}H_{28}O_8$: C, 74.61(74.29); H, 10.67(11.03).

Synthesis of 4-(4,4-dimethyl-2,6-dioxo-3,5-dioxatetramethylene)-11-(4,4-dimethyl- 3,5-dioxapentamethylene)-1,6,13-heptadecatriene (VII)



Synthesis of (*E*)-6-bromohex-2-eny *tert*-butyldimethylsilyl ether (H)

To a 500 mL Schlenk flask containing imidazole (8840 mg, 129.9 mmol) and CH_2Cl_2 (246 mL) was added 6-bromo-hex-2-enol (**E**) (9871 mg, 55.0 mmol) and *tert*-buthyl(chloro)dimethylsilane (9938 mg, 66.0 mmol) at 0 °C. After the reaction mixture was stirred for 7 h at room temperature, the reaction was quenched with water (115 mL) and 1N HCl aq. (46 mL). The organic phase was extracted with CH_2Cl_2, washed successively with water and brine, and dried over $MgSO_4$. Volatile fractions were evaporated and the residue was purified by column chromatography (silica gel, hexane/ether = 20:1, Rf = 0.64) to afford (*E*)-6-bromohex-2-eny *tert*-butyldimethylsilyl ether (**H**) as a colorless liquid in 87 % yield (13.95 g, 47.6 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.60 (s, 2H, H_d and H_e), 4.12 (s, 2H, H_f), 3.41 (t, J = 6.7

Hz, 2H, H_a), 2.20 (m, 2H, H_c), 1.94 (m, 2H, H_b), 0.90 (s, 9H, H_h), 0.07 (s, 6H, H_g)

Synthesis of diethyl {(2*E*)-2-hexenyl}-{(4*E*)-6-*tert*-buthyldimethylsilyloxyhex-4-enyl} malonate (J)

To a 50 mL Schlenk flask containing sodium hydride (53 mg, 2.20 mmol) and THF (5.5 mL) was added diethyl (2*E*)-2-hexenylmalonate (**B**) (410 mg, 1.69 mmol) at 0 °C and stirred for 1 h at room temperature. After attiring for 1 h, (2*E*)-6-bromohex-2-eny *tert*-butyldimethylsilyl ether (**H**) (741 mg, 2.53 mmol) was added and stirred for 12 h at room temperature. The reaction quenched with water and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na_2SO_4. Volatile fractions were evaporated and the residue was purified by column chromatography (silica gel, hexane/ ether = 20:1, Rf = 0.64) to afford diethyl {(2*E*)-2-hexenyl}-{(4*E*)-6-*tert*-buthyldimethyl-silyloxyhex-4-enyl}malonate (**J**) as a colorless liquid in 86 % yield (660 mg, 1.45 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.50 (m, 3H, H_d, H_n and H_o), 5.20 (m, 1H, H_e), 4.13 (m, 4H, H_i), 4.08 (d, J = 6.8 Hz, 2H, H_p), 2.54 (d, J = 9.0 Hz, 2H, H_f), 2.54 (m, 2H, H_m), 1.93 (q, J = 12.8 Hz, 2H, H_c), 1.80 (m, 4H, H_k and H_l), 1.32 (m, 2H, H_b), 1.20 (m, 6H, H_j), 0.87 (s, 9H, H_r), 0.83 (t, J = 12.5 Hz, 3H, H_a), 0.04 (s, 6H, H_q). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 171.3 (C_h), 134.8 (C_d), 130.4 (C_n), 130.0 (C_o), 123.6 (C_e), 63.9 (C_p), 61.2 (C_i), 57.5 (C_g), 36.0 (C_m), 34.6(Cc), 32.2 (C_f), 25.9 (C_r), 23.4 (C_l), 22.5 (C_b), 14.0 (C_r), 13.5 (C_a), 0.06 (C_p)

Synthesis of (4*E*, 11*E*)-7,7-bis(hydroxymethyl)-trideca-4,11-dien-13-ol (K)

To a 500 mL Schlenk containing diethyl {(2*E*)-2-hexenyl}-{(4*E*)-6-*tert*-buthyldimethyl-silyloxyhex-4-enyl}malonate (**J**) (8.84 g, 19.44 mmol) and ether (215 mL) was added diisobutylaluminum hydride in hexane (1M, 97 mL, 97 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with MeOH (100 mL) and the mixture was added to potassium sodium (+)-tartrate aq. (300 mL) and

stirred for 3 h. The organic phase was extracted with CH_2Cl_2, washed successively with water and brine, and dried over Na_2SO_4. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/EtOAc = 1:5, Rf = 0.40) to afford (4*E*, 11*E*)-7,7-bis(hydroxymethyl)-trideca-4,11-dien-13-ol (**K**) as a colorless liquid in 41 % yield (2.04 g, 7.94 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.59 (m, 2H, H_m and H_n), 5.40 (m, 1H, H_e), 5.31 (m, 1H, H_d), 4.00 (m, 2H, H_o), 3.45 (m, 4H, H_h), 1.98 (m, 2H, H_c), 1.93 (m, 2H, H_l), 1.87 (m, 2H, H_f), 1.32 (m, 4H, H_b and H_k), 1.22 (m, 2H, H_i), 0.85 (t, J = 5.0 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 133.7 (C_e), 132.7 (C_m), 129.2 (C_n), 124.9 (C_d), 67.6 (C_h), 63.2 (C_o), 41.5 (C_g), 34.7 (C_l), 34.7 (C_f), 32.7 (C_c), 29.7 (C_j), 22.6 (C_k), 22.2 (C_b), 13.6 (C_a).

Synthesis of 5-{(2*E*)-2-hexenyl}-5-{(4*E*)-6-hydroxy-hex-4-enyl}-2,2-dimethyl-1,3-dioxane (L)

To a 100 mL Schlenk flask containing pyridinium *p*-toluenesulfonate (296 mg, 0.89 mmol) and distilled acetone (5.2 mL) was added (4*E*, 11*E*)-7,7-bis(hydroxymethyl)-trideca-4,11-dien-13-ol (**J**) (2036 mg, 7.94 mmol) and methyl orthoformate (3.86 mL, 35.7 mmol) and was stirred at 50 °C for 21 h. The reaction quenched with $NaHCO_3$ aq. and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na_2SO_4. Volatile fractions were evaporated and the residue was purified by column chromatography (silica gel, hexane/Et_2O = 1:2, Rf = 0.45) to 5-{(2E)-2-hexenyl}- 5-{(4E)-6-hydroxy-hex-4-enyl}-2,2-dimethyl-1,3-dioxane (**L**) as a colorless liquid in 93 % yield (2.20 g, 7.42 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.64 (m, 2H, H_n and H_o), 5.46 (m, 1H, H_e), 5.32 (m, 1H, H_d), 4.07 (d, J = 4.2 Hz, 2H, H_p), 3.54 (m, 4H, H_h), 2.05 – 1.98 (m, 2H, H_c, H_f and H_m), 1.39 (s, 6H, H_j and $H_{j'}$), 1.35 (m, 2H, H_b), 1.31 (m, 6H, H_k and H_l), 0.87 (t, J = 7.3 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 134.1 (C_e), 132.8 (C_n), 129.3 (C_o), 124.4 (C_d), 97.9

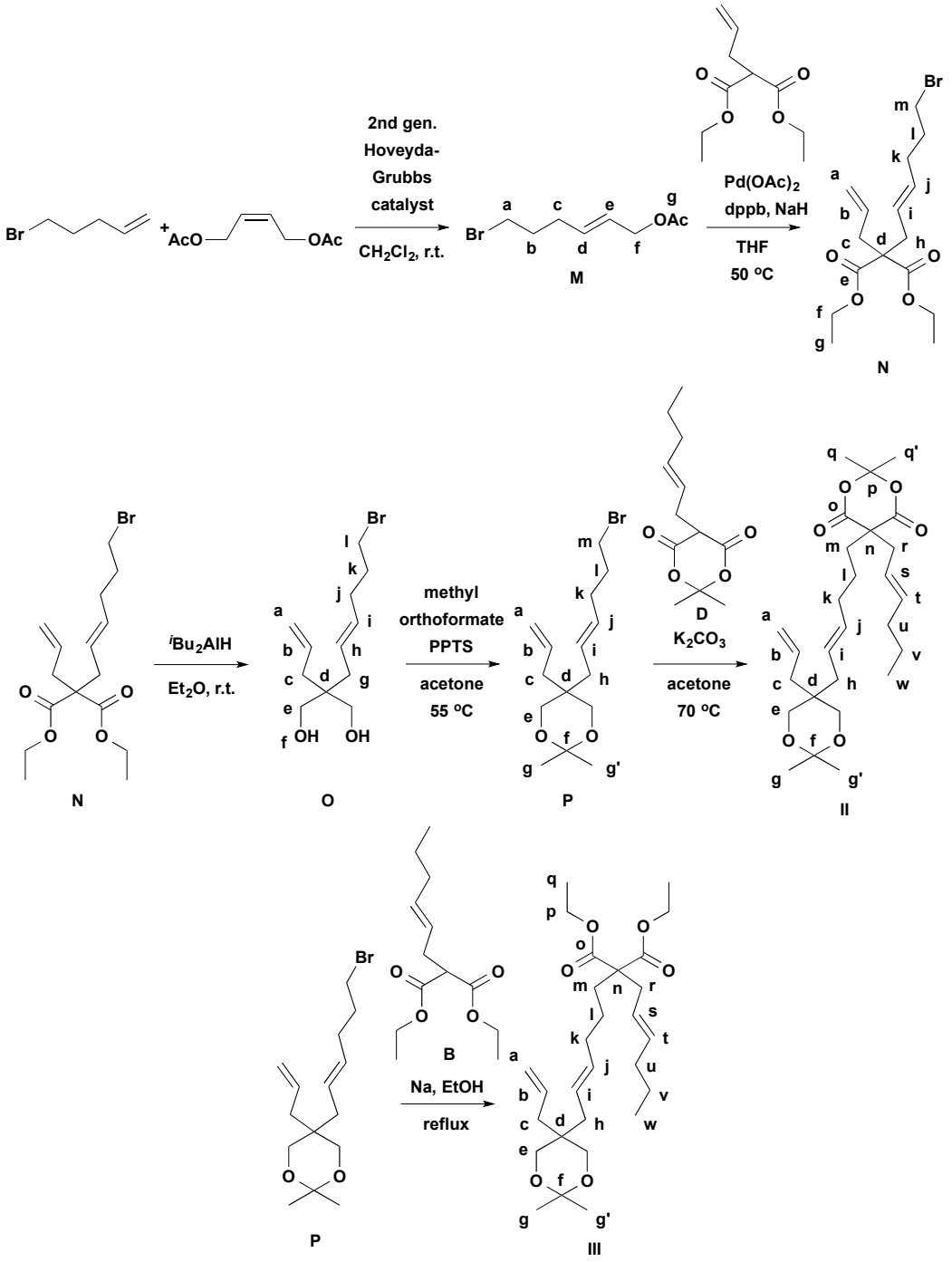
(C_i), 67.7 (C_h), 63.7 (C_p), 35.3 (C_c or C_f or C_m), 35.0 (C_g), 34.7 (C_c or C_f or C_m), 32.8 (C_c or C_f or C_m), 31.7 (C_k), 24.0, 23.6 (C_j and $C_{j'}$), 22.6 (C_b), 22.2 (C_l), 13.6 (C_a).

Synthesis of 4-(4,4-dimethyl-2,6-dioxo-3,5-dioxatetramethylene)-11-(4,4-dimethyl- 3,5-dioxapentamethylene)-1,6,13-heptadecatriene (VII)

To a 25 mL Schlenk flask containing MS4A (10 mg), $Pd\{P(OPh)_3\}_4$ (2.3 mg, 0.016 mmol) and distilled toluene (2.5 mL) was added allyl Merdrum's acid (74.5 mg, 0.41 mmol) and 5-{(2E)-2-hexenyl}- 5-{(4E)-6-hydroxy-hex-4-enyl}-2,2-dimethyl-1,3-dioxane (**L**) (100 mg, 0.34 mmol) at 80 °C and stirred for 18 h. The reaction mixture was filtered, and the organic phase was dried over $MgSO_4$. Volatile fractions were removed and the residue was purified by column chromatography (silica gel, hexane/Et_2O = 3:1, Rf = 0.33) to afford 4-(4,4-dimethyl-2,6-dioxo-3,5-dioxatetramethylene)-11-(4,4-dimethyl-3,5-dioxapentamethyl-ene)-1,6,13-heptadecatriene (**VII**) as a colorless liquid in 89 % yield (140 mg, 0.30 mmol).

^1H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.63 (m, 2H, H_b), 5.52 (m, 1H, H_t), 5.38 (m, 1H, H_j), 5.25 (m, 2H, H_i and H_s), 5.12 (m, 2H, H_a), 3.54, 3.50 (d, J = 6.9 Hz, 4H, H_o and $H_{o'}$), 2.72 (d, J = 7.6 Hz, 2H, H_c), 2.62 (d, J = 7.3 Hz, 2H, H_h), 2.05 (d, J = 7.3 Hz, 2H, H_r), 1.96 (m, 6H, H_k, H_m and H_u), 1.67, 1.65 (s, 6H, H_g and $H_{g'}$), 1.38 (s, 6H, H_q and $H_{q'}$), 1.35 (m, 4H, H_l and H_v), 0.87 (t, J = 7.1 Hz, 3H, H_w). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, r.t.): δ 168.6 (C_e), 137.3 (C_i or C_j or C_s or C_t), 134.1 (C_i or C_j or C_s or C_t), 131.0 (C_b), 124.4 (C_i or C_j or C_s or C_t), 122.6 (C_i or C_j or C_s or C_t), 121.2 (C_a), 105.7 (C_f), 97.9 (C_p), 67.7 (C_o), 42.6, 42.1 (C_c and C_h), 35.2, 34.9, 34.7, 33.2, 31.8 (C_d, C_k, C_n, C_m, C_r and C_u), 30.0, 29.8 (C_g and $C_{g'}$), 24.2, 23.4 (C_q and $C_{q'}$), 22.6 (C_v), 22.1 (C_l), 13.6 (C_w).

Synthesis of 4-(4,4-dimethyl-3,5-dioxapentamethylene)-11-(4,4-dimethyl-2,6-dioxo- 3,5-dioxapentamethylene)-1,6,13-heptadecatriene (II) and 4-(4,4-dimethyl-3,5-dioxa-pentamethylene)-11,11-bis(ethoxycarbonyl)-1,6,13-heptadecatriene (III)



Synthesis of (*E*)-6-bromohex-2-enyl acetate (M)

To a 500 mL Schlenk containing 2nd generation Hoveyda-Grubbs catalyst (200 mg, 0.317 mmol) and CH_2Cl_2 (32 mL) was added 5-bromo-1-pentene (3.8 mL, 31.7 mmol) and *cis*-1,4-

diacetoxy-2-butene (5.4 mL, 63.4 mmol) at room temperature. After stirred for 4 h, volatiles were evaporated and the residue was purified by column chromatography (silica gel, hexane/ether = 6:1, Rf = 0.44) to afford (*E*)-6-bromohex-2-enyl acetate (**M**) as a yellow liquid in 81% yield (5.676 g, 25.7 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.69 (m, 2H, H_d and H_e), 4.50 (d, J = 5.8 Hz, 2H, H_f), 3.40 (t, J = 6.6 Hz, 2H, H_a), 2.22 (q, J = 7.14 Hz, 2H, H_c), 2.06 (s, 3H, H_g), 1.95 (pent, J = 6.57 Hz, 2H, H_b).

Synthesis of diethyl allyl{(2*E*)-6-bromohex-2-enyl}malonate (N) [4)]

To a 100 mL Schlenk flask containing sodium hydride (240 mg, 10 mmol) and THF (15 mL) was added diethyl malonate (3.0 g, 15 mmol) at 0 °C and stirred for 1 h at room temperature. To a 100 mL Schlenk flask containing $Pd(OAc)_2$ (112.5 mg, 0.50 mmol), dppb (853 mg, 2.0 mmol), and THF (25 mL) was added (E)-6-bromohex-2-enyl acetate (**L**) (2210 mg, 10 mmol) at r.t. and stirred for 0.5 h. The THF solution of sodium hydride and diethyl malonate was transferred to the reaction mixture and stirred at 50 °C for 3 h. Volatiles were evaporated and the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 1:1, Rf = 0.38) to afford diethyl allyl{(2*E*)-6-bromohex-2-enyl}malonate (**N**) as a colorless liquid in 100 % yield (3.63 g, 10 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.60 (m, 1H, H_b), 5.44 (m, 1H, H_i), 5.35 (m, 1H, H_j), 5.07 (m, 2H, H_a), 4.16 (q, J = 10.0 Hz, 4H, H_f), 3.38 (t, J = 10.0 Hz, 2H, H_m), 2.60 (m, 4H, H_c and H_h), 2.13 (q, J = 10.0 Hz, 2H, H_k), 1.88 (m, J = 10.0 Hz, 2H, H_k), 1.24 (m, J = 10.0 Hz, 6H, H_g).

Synthesis of 2-allyl-2-{(2*E*)-6-bromohex-2-enyl}-1,3-propanediol (O)

To a 500 mL Schlenk containing diethyl allyl{(2*E*)-6-bromohex-2-enyl}malonate (**N**) (5.15 g, 14.2 mmol) and ether (153 mL) was added diisobutylaluminum hydride in hexane (1M, 85

mL, 85 mmol) at 0 °C. After warmed to room temperature and the reaction mixture was stirred for 27 h at room temperature. The reaction was quenched with MeOH (100 mL), and the reaction mixture was added to potassium sodium (+)-tartrate aq. (200 mL) and stirred for 12 h. The organic phase was extracted with CH_2Cl_2, washed successively with water and brine, and dried over Na_2SO_4. Volatile fractions were evaporated to afford 2-allyl-2-{(2*E*)-6-bromohex-2-enyl}-1,3-propanediol (**O**) as a colorless liquid in 62% yield (2.45 g, 8.85 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.82 (m, 1H, H_b), 5.47 (m, 2H, H_h and H_i), 5.08 (m, 2H, H_a), 3.58 (s, 4H, H_e), 3.40 (t, J = 6.0 Hz, 2H, H_l), 2.18 (m, 2H, H_j), 2.04 (m, 4H, H_c and H_g), 1.88 (m, 2H, H_k).

Synthesis of 5-allyl-5-{(2*E*)-6-bromohex-2-enyl}-2,2-dimethyl-1,3-dioxane (P)

To a 100 mL Schlenk flask containing pyridinium *p*-toluenesulfonate (478 mg, 1.56 mmol) and distilled acetone (9.6 mL) was added 2-allyl-2-{(2*E*)-6-bromohex-2-enyl}- 1,3-propanediol (**O**) (4.36 g, 15.7 mmol) and methyl orthoformate (6.9 mL, 62.5 mmol) and stirred for 7 h at 55 °C. Volatiles were evaporated and the residue was purified by column chromatography (silica gel, hexane/EtOAc = 10:1, Rf = 0.51) to afford 5-allyl-5-{(2*E*)-6-bromohex-2-enyl}-2,2-dimethyl-1,3-dioxane (**P**) as a colorless liquid in 97% yield (4.80 g, 15.2 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 5.77 (m, 1H, H_b), 5.45 (m, 2H, H_i and H_j), 5.08 (m, J = 9.0 Hz, 2H, H_a), 3.56 (s, 4H, H_e), 3.40 (t, J = 6.0 Hz, 2H, H_m), 2.17 (m, 2H, H_k), 2.10 (m, 4H, H_c and H_h), 1.92 (m, 2H, H_l), 1.41 (s, 6H, H_g). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 133.1 (C_b), 132.0, 126.1 (C_i and C_j), 118.2 (C_a), 97.9 (C_f), 67.1 (C_e), 36.6 (C_c or C_h), 35.5 (C_d), 35.2 (C_c or C_h), 33.1 (C_m), 32.1 (C_l), 30.9 (C_k), 23.9, 23.6 (C_g and $C_{g'}$)

Synthesis of 4-(4,4-dimethyl-3,5-dioxapentamethylene)-11-(4,4-dimethyl-2,6-dioxo- 3,5-dioxapentamethylene)-1,6,13-heptadecatriene (II)

To a 25 mL two-necked flask containing K_2CO_3 (134 mg, 0.97 mmol) and distilled acetone (2.0 mL) was added 5-{(2*E*)-2-hexenyl}-2,2-dimethyl-1,3-dioxane-4,6-dione (**D**) (115 mg, 0.56 mmol) and 5-allyl-5-{(2E)-6-bromo-hex-2-enyl}-2,2-dimethyl-1,3-dioxane (**P**) (420 mg, 1.33 mmol) and the mixture was stirred at 70 °C for 38 h. The reaction mixture was filtered, and the organic phase was dried over $MgSO_4$. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/Et_2O = 2:1, Rf = 0.46) to afford 4-(4,4-dimethyl-3,5-dioxapentamethylene)-11-(4,4-dimethyl-2,6-dioxo-3,5-dioxapenta-methylene)-1,6,13-heptadecatriene (**II**) as a colorless liquid in 47% yield (84 mg, 0.18 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ, 5.69 (m, 1H, H_b), 5.45 (m, 2H, H_j and H_t), 5.37 (m, 1H, H_i), 5.09 (m, 2H, H_a), 4.14 (q, J = 5.0 Hz, 4H, H_p and $H_{p'}$), 3.53 (s, 4H, H_e), 2.56(d, J = 6.0 Hz, 2H, H_r), 2.10 (d, J = 6.0 Hz, 2H, H_c or H_h), 2.04 (d, J = 6.0 Hz, 2H, H_c or H_h), 2.00 (m, 2H, H_k), 1.92 (q, J = 3.0 Hz, 2H, H_u), 1.83 (m, 2H, H_m), 1.38 (s, 6H, H_g and $H_{g'}$), 1.32 (m, 2H, H_v), 1.22 (m, 8H, H_l, H_q and $H_{q'}$), 0.85 (t, J = 10.0 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 168.9 (C_o), 137.1 (C_s), 133.0 (C_b), 132.4, 125.4 (C_i and C_j), 122.5 (C_t), 118.0 (C_a), 105.3 (C_p), 97.7 (C_f), 67.0 (C_e), 55.3 (C_n), 41.7 (C_r), 38.9 (C_k or C_m), 36.5 (C_c or C_h), 35.4 (C_d), 35.1 (C_c or C_h), 34.3 (C_u), 32.0 (C_k or C_m), 29.9, 29.4 (C_q and $C_{q'}$), 25.1 (C_l), 23.6 (C_g and $C_{g'}$), 21.9 (C_v), 13.5 (C_w).

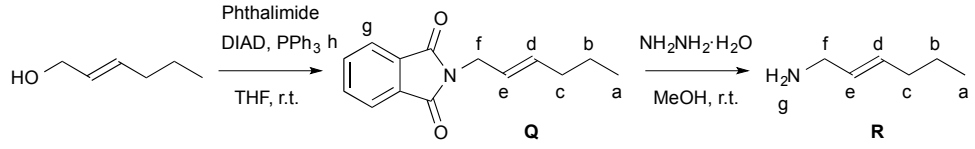
Synthesis of 4-(4,4-dimethyl-3,5-dioxapentamethylene)-11,11-bis(ethoxycarbonyl)-1,6,13-heptadecatriene (III)

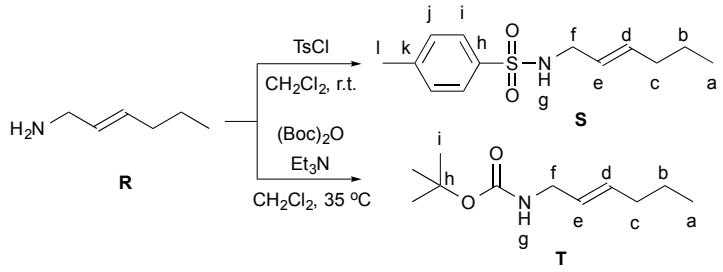
To a 50 mL Schlenk flask containing Na (417 mg, 18.0 mmol) and EtOH (9.0 mL) was added diethyl (2*E*)-2-hexenylmalonate (**B**) (3150 mg, 13 mmol). After stirring for 1 h, 5-allyl-5-{(2E)-6-bromohex-2-enyl}-2,2-dimethyl-1,3-dioxane (**O**) (3161 mg, 10 mmol) was added and the reaction mixture was refluxed for 22 h. The reaction was quenched with H_2O and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na_2SO_4. After volatile fractions were evaporated, the residue was purified by

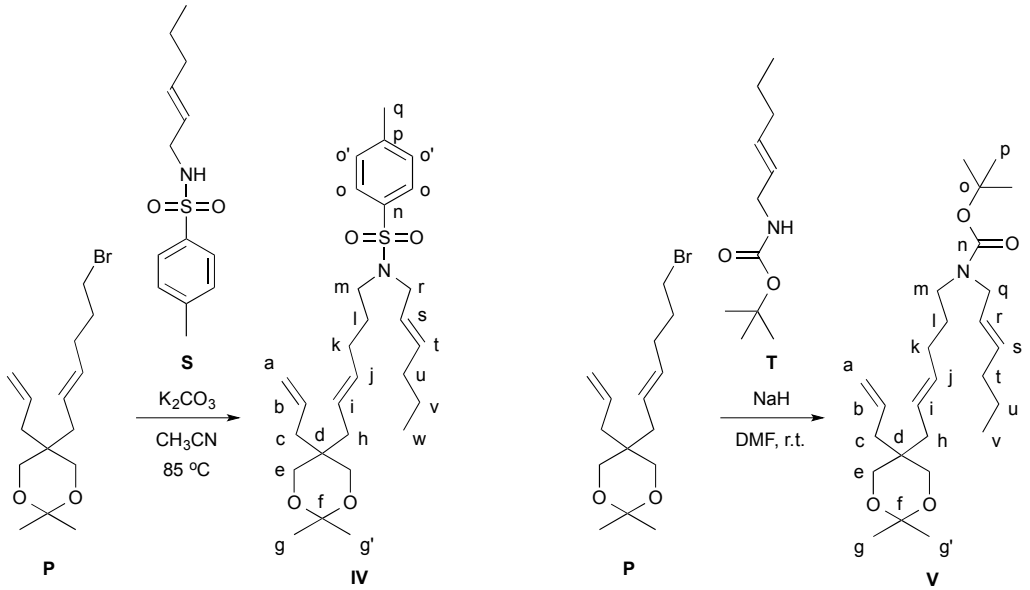
column chromatography (silica gel, hexane/Et_2O = 5:1, Rf = 0.31) to afford 4-(4,4-dimethyl-3,5-dioxapentamethylene)-11,11-bis(ethoxycarbonyl)-1,6,13-heptadecatriene (**III**) as a colorless liquid in 59 % yield (2.816 g, 5.88 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.75 (m, 1H, H_b), 5.45 (m, 2H, H_j and H_t), 5.37 (m, 1H, H_i), 5.09 (m, 2H, H_a), 4.14 (q, J = 7.5 Hz, 4H, H_p), 3.54, 3.53 (s, 4H, H_e), 2.55 (d, J = 7.5 Hz, 2H, H_r), 2.10 (d, J = 7.0 Hz, 2H, H_c or H_h), 2.04 (d, J = 7.0 Hz, 2H, H_c or H_h), 2.00 (m, 2H, H_k), 1.92 (q, J = 7.5 Hz, 2H, H_u), 1.83 (m, 2H, H_m), 1.38 (s, 6H, H_g and $H_{g'}$), 1.32 (m, 2H, H_v), 1.22 (m, 8H, H_l, H_q and $H_{q'}$), 0.85 (t, J = 7.5 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.) : δ 171.4 (C_o), 134.9 (C_j), 133.6 (C_t), 133.2 (C_b), 124.9 (C_i), 123.7 (C_s), 118.2 (C_a), 97.9 (C_f), 67.2 (C_e), 60.9 (C_p and $C_{p'}$), 57.5 (C_n), 36.6 (C_c), 35.7 (C_r), 35.6 (C_d), 35.3 (C_h), 34.6 (C_u), 32.8 (C_k), 31.6 (C_m), 23.8, 23.7 (C_l, C_g and $C_{g'}$), 22.5 (C_v), 14.1 (C_q), 13.5 (C_w).

Synthesis of *N*-(*p*-toluenesulfonyl)-{(2*E*)-hex-2-enyl}-{7-(4,4-dimethyl-3,5-dioxapenta-methylene)-deca-4,9-dienyl}amine (IV) and *N*-(*tert*-butoxycarbonyl)-{(2*E*)-hex-2-enyl}-{7-(4,4-dimethyl-3,5-dioxapentamethylene)-deca-4,9-dienyl}amine (V)







Synthesis of *N*-(hex-2-enyl)phthalimide (Q)

To a 50 mL Schlenk flask containing phthalimide (190 mg, 1.29 mmol), Ph_3P (338 mg, 1.29 mmol) and THF (9.0 mL) was added diisopropyl azodicarboxylate (DIAD) (0.26 mL, 1.30 mmol) and *trans*-2-hexen-1-ol (0.12 mL, 1.0 mmol) and stirred for 4 h at r.t. The reaction mixture was evaporated and the residue was purified by column chromatography (silica gel, hexane/Et_2O = 5:1, Rf = 0.33) to afford *N*-(hex-2-enyl)phthalimide (**P**) as a yellow liquid in 91 % yield (209 mg, 0.91 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ, 7.85 (m, 2H, H_h), 7.71 (m, 2H, H_g), 5.71 (m, 1H, H_e),

5.53 (m, 1H, H_d), 4.22 (d, J = 6.2 Hz, 2H, H_f), 1.97 (q, J = 7.5 Hz, 2H, H_c), 1.36 (m, 2H, H_b), 0.87 (t, J = 7.3 Hz, 3H, H_a)

Synthesis of (*E*)-hex-2-enylamine (R)

To a 25 mL Schlenk containing *N*-(hex-2-enyl)phthalimide (**Q**) (6786 mg, 29.6 mmol) and MeOH (126 mL) was added $H_2NNH_2 \cdot H_2O$ (1.81 mL, 35.7 mmol) and the mixture was stirred for 12 h. 35% HCl (65 mL) and H_2O (127 mL) was added and the mixture was stirred for 12 h. The reaction mixture was filtered, diluted with an equal amount of H_2O, and acidified by HCl. The reaction mixture extracted with Et_2O, successively washed with H_2O and brine. The organic phase was dried over $MgSO_4$. Volatile fractions were evaporated to afford (*E*)-hex-2-enylamine (**R**) as a yellow liquid in 62 % yield (2.04 g, 20.6 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ, 5.40 (s, 2H, H_d and H_e), 3.09 (s, 2H, H_f), 2.09 (br, 2H, H_g), 1.87 (s, 2H, H_c), 1.27 (m, 2H, H_b), 0.77 (t, J = 12.3 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 130.7 (C_d or C_e), 130.5 (C_d or C_e), 43.6 (C_f), 34.1 (C_c), 22.0 (C_b), 13.3 (C_a).

Synthesis of *N*-(*p*-toluenesulfonyl)-(2*E*)-hex-2-enylamine (S)

To a 50 mL Schlenk containing *p*-toluenesulfonyl chloride (419 mg, 2.2 mmol), CH_2Cl_2 (9 mL) and pyridiene (0.18 mL, 2.2 mmol) was added (*E*)-hex-2-enylamine (**Q**) (99 mg, 2.0 mmol) at 0 °C. After stirred at r.t. for 1h, the reaction mixture was extracted with EtOAc, successively washed with H_2O and brine, and dried over $MgSO_4$. After volatile fractions were evaporated and the residue was purified by column chromatography (silica gel, hexane/EtOAc = 5:1, Rf = 0.45) to afford *N*-(*p*-toluenesulfonyl)-(2*E*)-hex-2-enylamine (**S**) as yellow liquid in 67 % yield (341 mg, 1.35 mmol).

^{1}H NMR (300MHz, $CDCl_3$, r.t.): δ 7.73 (d, J = 8.5 Hz, 1H, H_i), 7.29 (d, J = 8.6 Hz, 1H, H_j), 5.52 (m, 1H, H_e), 5.40 (m, 1H, H_d), 4.27 (br, 1H, H_g), 3.52 (t, J = 5.1 Hz, 2H, H_f), 2.43 (s, 3H,

H_l), 1.91 (q, J = 7.0 Hz, 2H, H_c), 1.30 (m, 2H, H_b), 0.84 (t, J = 7.0 Hz, 3H, H_a). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, r.t.): δ 143.1 (C_k), 137.0 (C_h), 134.4 (C_e), 129.5 (C_j), 127.1 (C_i), 124.4 (C_d), 45.2 (C_f), 34.0 (C_c), 21.9 (C_b), 21.4 (C_l), 13.5 (C_a).

Synthesis of *N*-(*tert*-butoxycarbonyl)-(2*E*)-hex-2-enylamine (T)

To a 200 mL Schlenk flask containing (E)-hex-2-enamine (**R**) (3000 mg, 30.3 mmol), CH_2Cl_2 (76 mL) and pyridine (8.1 mL, 61 mmol) was added di-*tert*-butyl dicarbonate (7970 mg, 36.5 mmol) at 0 °C. The reaction mixture was stirred at 35 °C for 7 h, evaporated and the residue was purified by column chromatography (silica gel, hexane/ EtOAc = 20:1, Rf = 0.38) to afford *N*-(*tert*-butoxycarbonyl)-(2*E*)-hex-2-enylamine (**T**) as a orange liquid in 85 % yield (5.15 g, 25.8 mmol).

^1H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.55 (m, 1H, H_e), 5.43 (m, 1H, H_d), 4.55 (br, 1H, H_j), 3.66 (s, 2H, H_f), 1.96 (q, J = 12.2 Hz, 2H, H_c), 1.42 (s, 9H, H_i), 1.34 (m, 2H, H_b), 0.87 (t, J = 12.4 Hz, 3H, H_a). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, r.t.): δ 155.7 (C_g), 132.9 (C_e), 126.4 (C_d), 79.1 (C_h), 42.6 (C_f), 34.2 (C_c), 28.4 (C_i), 22.2 (C_b), 13.6 (C_a).

Synthesis of *N*-(*p*-toluenesulfonyl)-{(2*E*)-hex-2-enyl}-{7-(4,4-dimethyl-3,5-dioxapenta-methylene)-deca-4,9-dienyl}amine (IV)

To a 25 mL Schlenk containing K_2CO_3 (199 mg, 1.44 mmol), CH_3CN (5.2 mL) and *N*-(*p*-toluenesulfonyl)-(2*E*)-hex-2-enylamine (**S**) (122 mg, 0.48 mmol) was added 5-allyl-5-{(2E)-6-bromo-hex-2-enyl}-2,2-dimethyl-1,3-dioxane (**O**) (50 mg, 0.158 mmol) and the mixture was stirred at 80 °C for 15 h. The reaction mixture was added to water, and the organic phase was extracted with $CHCl_3$, washed with brine and dried over $MgSO_4$. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/Et_2O = 3:1, Rf = 0.33) to afford *N*-(*p*-toluenesulfonyl)-{(2*E*)-hex-2-enyl}- {7-(4,4-dimethyl-3,5-dioxapentamethylene)-deca-4,9-dienyl}amine (**IV**) as a colorless liquid in 37 % yield (57 mg,

0.12 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 7.60 (d, J = 7.7 Hz, 1H, H_o), 7.21 (d, J = 7.6 Hz, 1H, H_p), 5.69 (m, 1H, H_b), 5.47 (m, 1H, H_u), 5.33 (m, 2H, H_i and H_j), 5.15 (m, 1H, H_t), 5.01 (m, 2H, H_a), 3.65 (d, J = 6.4 Hz, 2H, H_s), 3.48 (s, 2H, H_e), 3.01 (t, J = 6.4 Hz, 2H, H_m), 2.34 (s, 3H, H_r), 2.03 (d, J = 7.3 Hz, 2H, H_c or H_h), 1.98 (d, J = 7.0 Hz, 2H, H_c or H_h), 1.92 (q, J = 7.1 Hz, 2H, H_k or H_u), 1.86 (q, J = 7.2 Hz, 2H, H_k or H_u), 1.50 (pent, J = 7.6 Hz, 2H, H_l), 1.33, 1.32 (s, 6H, H_g and $H_{g'}$), 1.25 (hex, J = 7.3 Hz, 2H, H_v), 0.77 (t, J = 7.3 Hz, 3H, H_w). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 142.8 (C_q), 137.1 (C_n), 135.3 (C_u), 133.1 (C_b), 133.0 (C_i or C_j), 129.4 (C_p), 127.0 (C_o), 125.0 (C_i or C_j), 124.5 (C_t), 118.2 (C_a), 97.8 (C_f), 67.1 (C_e), 49.8 (C_s), 46.5 (C_m), 36.5 (C_c), 35.5 (C_d), 35.1 (C_h), 34.0 (C_u), 29.7 (C_k), 28.0 (C_l), 23.8, 23.6 (C_g and $C_{g'}$), 22.0 (C_v), 21.3(Cq), 13.5 (C_w)

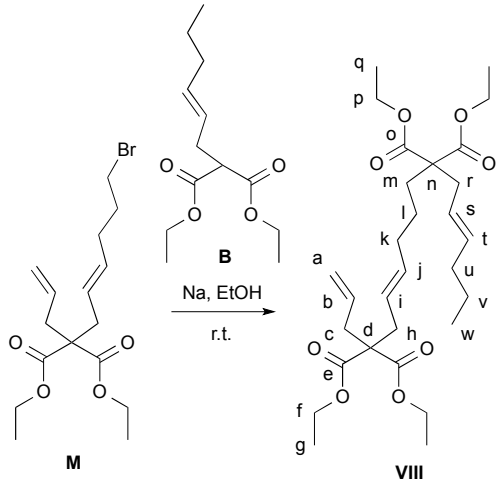
Synthesis of *N*-(*tert*-butoxycarbonyl)-{(2*E*)-hex-2-enyl}-{7-(4,4-dimethyl-3,5-dioxapenta-methylene)-deca-4,9-dienyl}amine (V)

To a 25 mL Schlenk flask containing sodium hydride (57 mg, 2.38 mmol) and DMF (6.3 mL) was added *N*-(*tert*-butoxycarbonyl)-(2*E*)-hex-2-enylamine (**T**) (381 mg, 1.91 mmol) at 0 °C and stirred at r.t. for 1 h. 5-Allyl-5-{(2*E*)-6-bromo-hex-2-enyl}- 2,2-dimethyl-1,3-dioxane (**O**) (400 mg, 1.27 mmol) was added and the mixture was stirred at r.t. for 24 h. The reaction was quenched with water and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na_2SO_4. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/$EtOA_c$ = 20:1, Rf = 0.18) to afford *N*-(*tert*-butoxycarbonyl)-{(2*E*)-hex-2-enyl}- {7-(4,4-dimethyl-3,5-dioxapentamethylene)-deca-4,9-dienyl}amine (**V**) as a colorless liquid in 23 % yield (128 mg, 0.29 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 5.76 (m, 1H, H_b), 5.49 (m, 2H, H_j and H_s), 5.39 (m, 2H, H_i and H_r), 5.10 (m, 2H, H_a), 3.72(br, 2H, H_q), 3.55 (s, 4H, H_e), 3.13 (br, 2H, H_m), 2.11 (d,

J = 7. 5 Hz, 2H, H_c), 2.06 (d, J = 7.3 Hz, 2H, H_h), 1.98 (q, J = 7.0 Hz, 4H, H_k and H_t), 1.55 (m, 2H, H_l), 1.44 (s, 9H, H_p), 1.39 (s, 6H, H_g and $H_{g'}$), 1.37 (d, J = 7.4 Hz, 2H, H_u), 0.89 (t, J = 7.4 Hz, 3H, H_v). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 50 °C) : δ 155.4 (C_n), 133.5 (C_i or C_j or C_r or C_s), 133.3 (C_b), 132.9 (C_i or C_j or C_r or C_s), 126.1 (C_i or C_j or C_r or C_s), 124.8 (C_i or C_j or C_r or C_s), 118.0 (C_a), 97.9 (C_f), 79.0 (C_o), 67.2 (C_e), 48.9 (C_q), 46.0 (C_m), 36.8 (C_c), 35.7 (C_d), 35.5 (C_h), 34.2 (C_t), 30.0 (C_k), 29.6 (C_l), 28.4 (C_p), 23.8 (C_g and $C_{g'}$), 22.3 (C_u), 13.5 (C_v). Anal. Calcd (found) for $C_{22}H_{28}O_8$(1.5 H_2O): C, 67.50(67.89); H, 10.46(10.40); N, 3.03(3.07).

Synthesis of 4,4,11,11-tetrakis(ethoxycarbonyl)-1,6,13-heptadecatriene (VIII)



To a 50 mL Schlenk flask containing Na (278 mg, 12 mmol) and EtOH (9.0 mL) was added diethyl (2*E*)-2-hexenylmalonate (**B**) (3150 mg, 13 mmol). After stirring for 1 h, diethyl allyl-{(2E)-6-bromohex-2-enyl}malonate (**M**) (3613 mg, 10 mmol) was added and stirred for 17 h. The reaction quenched with H_2O and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na_2SO_4. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/EtOAc = 10:1, Rf = 0.35) to afford 4,4,11,11-tetrakis(ethoxycarbonyl)- 1,6,13-heptadecatriene (**VIII**) as a yellow liquid in 52 % yield (2.74 g, 5.24 mmol).

^{1}H NMR (500 MHz, $CDCl_3$, r.t.): δ 5.58 (m, 1H, H_b), 5.41 (m, 2H, H_j and H_t), 5.18 (m, 2H, H_i and H_s), 5.01 (m, 2H, H_a), 4.11 (m, 8H, H_f, $H_{f'}$, H_p and $H_{p'}$), 2.55 (d, J = 7.4 Hz, 2H, H_c), 2.51 (d, J = 7.3 Hz, 4H, H_h and H_r), 1.90 (m, 4H, H_u and H_k), 1.78 (m, 2H, H_m), 1.30 (m, 2H, H_v), 1.18 (m, 14H, H_g, $H_{g'}$, H_l, H_q and $H_{q'}$), 0.81 (t, 3H, J = 7.4 Hz, H_w). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, r.t.): δ 171.2, 170.7 (C_e and C_o), 134.8, 134.4 (C_i and C_s), 132.4 (C_b), 124.0, 123.6 (C_j and C_t), 118.8 (C_a), 61.0, 60.8 (C_f and C_p), 57.4, 57.3 (C_d and C_n), 36.5 (C_c), 35.6, 35.4 (C_h and C_r), 34.5, 32.7(C_k and C_n), 31.5 (C_m) 23.6 (C_l), 22.4 (C_v), 14.0 (C_g, $C_{g'}$, C_q and $C_{q'}$), 13.4 (C_w).

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