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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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\(_2\)SO\(_4\). 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.): $\delta$ 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 (2E)-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 1 h, (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$_2$SO$_4$. Volatile fractions were evaporated to afford diethyl (2E)-2-hexenylmalonate (B) as yellow liquid in 64% yield (616 mg, 2.54 mmol).

$^1$H NMR (300MHz, CDCl$_3$, r.t.): $\delta$ 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.): $\delta$ 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$_j$), 22.3 (C$_b$), 14.0 (C$_i$), 13.4 (C$_a$).

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

To a 50 mL Schlenk flask containing ethanol (9.8 mL), KOH (3.26 g, 58.1 mmol) and H$_2$O (9.8 mL) was added diethyl (2E)-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-(2E)-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.): $\delta$ 5.55 (m, 1H, H$_c$), 5.41 (m, 1H, H$_d$), 3.48 (t, $J = 7.4$ Hz, S-3
1H, H₂), 2.64 (t, J = 6.9 Hz, 2H, H₁), 1.95 (q, J = 7.0 Hz, 2H, H₃), 1.34 (m, 2H, H₆), 0.86 (t, J = 7.3 Hz, 3H, H₆).

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

To a 25 mL Schlenk flask containing 5-((2E)-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. H₂SO₄ 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 CHCl₃, washed successively with water and brine, and dried over Na₂SO₄. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/ether = 1:1, Rf = 0.37) to afford 5-((2E)-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).

¹H NMR (300MHz, CDCl₃, r.t.): δ 5.62 (m, 1H, H₆), 5.46 (m, 1H, H₅), 3.54 (t, J = 5.4 Hz, 1H, H₇), 2.83 (t, J = 7.2 Hz, 2H, H₄), 1.94 (q, J = 6.0 Hz, 2H, H₈), 1.79, 1.76 (s, 6H, H₁ and H₂), 1.34 (m, 2H, H₆), 0.87 (t, J = 7.5 Hz, 3H, H₆). ¹³C{¹H} NMR (125 MHz, CDCl₃, r.t.): δ 165.2 (C₆ and C₇), 135.4 (C₅), 123.6 (C₄), 104.7 (C₃), 46.2 (C₂), 34.2 (C₁), 29.1, 28.0 (C₆ and C₇), 26.6 (C₅), 21.9 (C₇), 13.2 (C₆).

**Synthesis of 6-bromo-hex-2-enol (E)**

To a 25 mL Schlenk flask containing CH₂Cl₂ 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).

¹H NMR (300MHz, CDCl₃, r.t.): δ 5.69 (m, 2H, H₆ and H₇), 4.12 (d, J = 4.4 Hz, 2H, H₇),
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-{(2E)-2-hexenyl}-5-{(4E)-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-(2E)-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$_2$SO$_4$. Volatile fractions were evaporated and the residue was purified by column chromatography (silica gel, hexane/ether = 1:1, Rf = 0.16) to afford 5-{(2E)-2-hexenyl}-5-{(4E)-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.): $\delta$ 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, $H_i$), 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.): $\delta$ 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$_p$), 41.9 (C$_i$), 39.0 (C$_k$ or C$_m$), 34.5 (C$_e$), 31.8 (C$_k$ or C$_m$), 30.1, 29.7(C$_j$ and C$_{j'}$), 25.0 (C$_i$), 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-(4E)-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$_l$), 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$_q$), 39.0 (C$_k$ or C$_m$), 34.5 (C$_a$), 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$_4$Cl 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$_b$, H$_i$, H$_q$ and H$_p$), 5.08 (m, 2H, H$_k$), 3.57 (s, 8H, H$_c$, H$_c'$, H$_n$ and H$_n'$), 2.27 (s, 4H, H$_f$, H$_f'$, H$_o$ and H$_o'$), 2.02 (m, 10H, H$_e$, H$_g$, H$_j$, H$_p$ and H$_u$), 1.33 (m, 6H, H$_k$, H$_l$ and H$_o$), 0.89 (t, $J$ = 7.3 Hz, 3H, H$_w$)

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$_2$SO$_4$. 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.): $\delta$ 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.): $\delta$ 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)

To a 500 mL Schlenk flask containing imidazole (8840 mg, 129.9 mmol) and CH₂Cl₂ (246 mL) was added 6-bromo-hex-2-enol (E) (9871 mg, 55.0 mmol) and tert-butyll(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 CH₂Cl₂, washed successively with water and brine, and dried over MgSO₄. 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).

1H NMR (300MHz, CDCl₃, 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 \{(2E)-2-hexenyl\}-%{\{4E\}-6-tert-butyldimethylsilyloxyhex-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 (2E)-2-hexenylmalonate (B) (410 mg, 1.69 mmol) at 0 °C and stirred for 1 h at room temperature. After attiring for 1 h, (2E)-6-bromohex-2-enyl 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 \{(2E)-2-hexenyl\}-%{\{4E\}-6-tert-butyldimethylsilyloxyhex-4-enyl\} malonate (J) as a colorless liquid in 86 % yield (660 mg, 1.45 mmol).

\(^1H\) NMR (500 MHz, CDCl_3, r.t.): \(\delta\) 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_q), 2.54 (m, 2H, H_m), 1.93 (q, J = 12.8 Hz, 2H, H_c), 1.80 (m, 4H, H_k and H_i), 1.32 (m, 2H, H_h), 1.20 (m, 6H, H_j), 0.87 (s, 9H, H_g), 0.83 (t, J = 12.5 Hz, 3H, H_a), 0.04 (s, 6H, H_q).

\(^13C\)\(^1H\) NMR (125 MHz, CDCl_3, r.t.): \(\delta\) 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_j), 25.9 (C_t), 23.4 (C_l), 22.5 (C_b), 14.0 (C_r), 13.5 (C_a), 0.06 (C_p)

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

To a 500 mL Schlenk containing diethyl \{(2E)-2-hexenyl\}-%{\{4E\}-6-tert-butyldimethylsilyloxyhex-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 \( \text{CH}_2\text{Cl}_2 \), washed successively with water and brine, and dried over \( \text{Na}_2\text{SO}_4 \). After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/EtOAc = 1:5, \( \text{Rf} = 0.40 \)) to afford \((4E, 11E)-7,7\)-bis(hydroxymethyl)-trideca-4,11-dien-13-ol \((\text{K})\) as a colorless liquid in 41% yield (2.04 g, 7.94 mmol).

\(^1\)H NMR (500 MHz, CDCl\(_3\), r.t.): \( \delta \) 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, \( H_i \)), 1.87 (m, 2H, \( H_l \)), 1.32 (m, 4H, \( H_b \) and \( H_k \)), 1.22 (m, 2H, \( H_f \)), 0.85 (t, \( J = 5.0 \) Hz, 3H, \( H_a \)).

\(^{13}\)C\{\(^1\)H\} NMR (125 MHz, CDCl\(_3\)): \( \delta \) 133.7 (C\(_e\)), 132.7 (C\(_m\)), 129.2 (C\(_a\)), 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-{(2E)-2-hexenyl}-5-{(4E)-6-hydroxy-hex-4-enyl}-2,2-dimethyl-1,3-dioxane \((\text{L})\)**

To a 100 mL Schlenk flask containing pyridinium \( p \)-toluenesulfonate (296 mg, 0.89 mmol) and distilled acetone (5.2 mL) was added \((4E, 11E)-7,7\)-bis(hydroxymethyl)-trideca-4,11-dien-13-ol \((\text{J})\) (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 \( \text{Na}_2\text{SO}_4 \). Volatile fractions were evaporated and the residue was purified by column chromatography (silica gel, hexane/Et\(_2\)O = 1:2, \( \text{Rf} = 0.45 \)) to 5-{(2E)-2-hexenyl}-5-{(4E)-6-hydroxy-hex-4-enyl}-2,2-dimethyl-1,3-dioxane \((\text{L})\) as a colorless liquid in 93% yield (2.20 g, 7.42 mmol).

\(^1\)H NMR (500 MHz, CDCl\(_3\), r.t.): \( \delta \) 5.64 (m, 2H, \( H_m \) and \( H_n \)), 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 \( H_g \)), 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.): \( \delta \) 134.1 (C\(_e\)), 132.8 (C\(_n\)), 129.3 (C\(_o\)), 124.4 (C\(_d\)), 97.9
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-dioxapentamethylene)-1,6,13-heptadecatriene (VII) as a colorless liquid in 89 % yield (140 mg, 0.30 mmol).

\[^1\text{H}\] NMR (500 MHz, CDCl\_3, r.t.): \(\delta\) 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\_i), 1.96 (m, 6H, H\_k, H\_m and H\_a), 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\_i and H\_h), 0.87 (t, \(J = 7.1\) Hz, 3H, H\_w). \[^{13}\text{C}\]{[^1\text{H}]} NMR (125 MHz, CDCl\_3, r.t.): \(\delta\) 168.6 (C\_e), 137.3 (C\_i or C\_j or C\_s or C\_l), 134.1 (C\_i or C\_j or C\_s or C\_l), 131.0 (C\_b), 124.4 (C\_i or C\_j or C\_s or C\_l), 122.6 (C\_i or C\_j or C\_s or C\_l), 121.2 (C\_a), 105.7 (C\_d), 97.9 (C\_p), 67.7 (C\_o), 42.6, 42.1 (C\_c and C\_b), 35.2, 34.9, 34.7, 33.2, 31.8 (C\_d, C\_k, C\_n, C\_m, C\_r and C\_a), 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-dioxapentamethylene)-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 CH₂Cl₂ (32 mL) was added 5-bromo-1-pentene (3.8 mL, 31.7 mmol) and cis-1,4-
diacetoxy-2-butyne (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.): $\delta$ 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{(2E)-6-bromohex-2-enyl}malonate (N)**

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$_2$Cl$_2$ = 1:1, Rf = 0.38) to afford diethyl allyl{(2E)-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.): $\delta$ 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-{(2E)-6-bromohex-2-enyl}-1,3-propanediol (O)**

To a 500 mL Schlenk containing diethyl allyl{(2E)-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 CH₂Cl₂, washed successively with water and brine, and dried over Na₂SO₄. Volatile fractions were evaporated to afford 2-allyl-2-\{(2E)-6-bromohex-2-enyl\}-1,3-propanediol (O) as a colorless liquid in 62% yield (2.45 g, 8.85 mmol).

¹H NMR (300MHz, CDCl₃, r.t.): δ 5.82 (m, 1H, H₀), 5.47 (m, 2H, Hₗ and Hᵣ), 5.08 (m, 2H, Hₕ), 3.58 (s, 4H, Hₑ), 3.40 (t, J = 6.0 Hz, 2H, Hᵢ), 2.18 (m, 2H, Hₗ), 2.04 (m, 4H, Hₙ and Hₖ), 1.88 (m, 2H, Hₜ).

**Synthesis of 5-allyl-5-\{(2E)-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-\{(2E)-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-\{(2E)-6-bromohex-2-enyl\}-2,2-dimethyl-1,3-dioxane (P) as a colorless liquid in 97% yield (4.80 g, 15.2 mmol).

¹H NMR (300MHz, CDCl₃, r.t.): δ 5.77 (m, 1H, H₀), 5.45 (m, 2H, Hᵢ and Hᵣ), 5.08 (m, J = 9.0 Hz, 2H, Hₕ), 3.56 (s, 4H, Hₑ), 3.40 (t, J = 6.0 Hz, 2H, Hₗ), 2.17 (m, 2H, Hₗ), 2.10 (m, 4H, Hₙ and Hₖ), 1.92 (m, 2H, Hₗ), 1.41 (s, 6H, Hₕ).

¹³C{¹H} NMR (125 MHz, CDCl₃, r.t.): δ 133.1 (Cₜ), 132.0, 126.1 (Cᵢ and Cᵣ), 118.2 (Cₙ), 97.9 (Cₗ), 67.1 (Cₑ), 36.6 (Cₗ or Cₙ), 35.5 (Cₗ), 35.2 (Cₗ or Cₗ), 33.1 (Cₗ), 32.1 (Cₗ), 30.9 (Cₗ), 23.9, 23.6 (Cₗ and Cₗ).
To a 25 mL two-necked flask containing K$_2$CO$_3$ (134 mg, 0.97 mmol) and distilled acetone (2.0 mL) was added 5-{(2E)-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$_2$O = 2:1, Rf = 0.46) to afford 4-(4,4-dimethyl-3,5-dioxapentamethylene)-11-(4,4-dimethyl-2,6-dioxo-3,5-dioxapentamethylene)-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$_i$), 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$_c$ or H$_h$), 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$_a$), 1.92 (q, J = 3.0 Hz, 2H, H$_q$), 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$_d$), 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$_j$), 67.0 (C$_e$), 55.3 (C$_n$), 41.7 (C$_i$), 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$_w$), 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 (2E)-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$_2$O and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na$_2$SO$_4$. After volatile fractions were evaporated, the residue was purified by
column chromatography (silica gel, hexane/Et₂O = 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).

¹H NMR (500 MHz, CDCl₃, r.t.): δ 5.75 (m, 1H, H₄), 5.45 (m, 2H, H_j and H_k), 5.37 (m, 1H, H_l), 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_q and H_q'), 0.85 (t, J = 7.5 Hz, 3H, H_a). ¹³C{¹H} NMR (125 MHz, CDCl₃, r.t.): δ 171.4 (C_o), 134.9 (C_j), 133.6 (C_i), 124.9 (C_s), 118.2 (C_a), 97.9 (C_d), 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_i, C_g and C_g'), 22.5 (C_s), 14.1 (C_q), 13.5 (C_w).
Synthesis of $N$-($p$-toluenesulfonfyl)-{(2$E$)-hex-2-enyl}-[7-(4,4-dimethyl-3,5-dioxa pentamethylene)-deca-4,9-dienyl]amine (IV) and $N$-(tert-butoxycarbonyl)-{(2$E$)-hex-2-enyl}-[7-(4,4-dimethyl-3,5-dioxa pentamethylene)-deca-4,9-dienyl]amine (V)

To a 50 mL Schlenk flask containing phthalimide (190 mg, 1.29 mmol), Ph$_3$P (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$_2$O = 5:1, Rf = 0.33) to afford $N$-(hex-2-enyl)phthalimide (Q) as a yellow liquid in 91 % yield (209 mg, 0.91 mmol).

$^{1}$H NMR (300MHz, CDCl$_3$, r.t.): $\delta$ 7.85 (m, 2H, H$_h$), 7.71 (m, 2H, H$_g$), 5.71 (m, 1H, H$_e$),...
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$_2$NNH$_2$·H$_2$O (1.81 mL, 35.7 mmol) and the mixture was stirred for 12 h. 35% HCl (65 mL) and H$_2$O (127 mL) was added and the mixture was stirred for 12 h. The reaction mixture was filtered, diluted with an equal amount of H$_2$O, and acidified by HCl. The reaction mixture extracted with Et$_2$O, successively washed with H$_2$O 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.): $\delta$, 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.): $\delta$ 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)-(2E)-hex-2-enylamine (S)

To a 50 mL Schlenk containing p-toluenesulfonyl chloride (419 mg, 2.2 mmol), CH$_2$Cl$_2$ (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$_2$O 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)-(2E)-hex-2-enylamine (S) as yellow liquid in 67 % yield (341 mg, 1.35 mmol).

$^1$H NMR (300MHz, CDCl$_3$, r.t.): $\delta$ 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$_c$), 5.40 (m, 1H, H$_d$), 4.27 (br, 1H, H$_g$), 3.52 (t, $J = 5.1$ Hz, 2H, H$_l$), 2.43 (s, 3H,
\( ^{13}C\{^{1}H\} \) NMR (125 MHz, CDCl\( _3 \), r.t.): \( \delta \) 143.1 (C\( _k \)), 137.0 (C\( _h \)), 134.4 (C\( _e \)), 129.5 (C\( _j \)), 127.1 (C\( _c \)), 124.4 (C\( _d \)), 45.2 (C\( _f \)), 34.0 (C\( _c \)), 21.9 (C\( _b \)), 21.4 (C\( _i \)), 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\( _2 \)Cl\( _2 \) (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).

\( ^{1}H \) NMR (500 MHz, CDCl\( _3 \), r.t.): \( \delta \) 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\( _a \)). \( ^{13}C\{^{1}H\} \) NMR (125 MHz, CDCl\( _3 \), r.t.): \( \delta \) 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-dioxapentamethylene)-deca-4,9-dienyl}amine (IV)**

To a 25 mL Schlenk containing K\( _2 \)CO\( _3 \) (199 mg, 1.44 mmol), CH\( _3 \)CN (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\( _2 \)O = 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,
Synthesis of N-(tert-butoxycarbonyl)-{(2E)-hex-2-enyl}-{7-(4,4-dimethyl-3,5-dioxapentamethylene)-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)-(2E)-hex-2-enylamine (T) (381 mg, 1.91 mmol) at 0 °C and stirred at r.t. for 1 h. 5-Allyl-5-{(2E)-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\textsubscript{2}SO\textsubscript{4}. After volatile fractions were evaporated, the residue was purified by column chromatography (silica gel, hexane/EtOA\textsubscript{c} = 20:1, Rf = 0.18) to afford N-(tert-butoxycarbonyl)-{(2E)-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).

\begin{align*}
\text{Synthesis of } N-(&amp;\text{tert-butoxycarbonyl})-\{(2E)&amp;\text{-hex-2-enyl}\}-\{7-(&amp;\text{4,4-dimethyl-3,5-dioxapentamethylene})-\text{deca-4,9-dienyl}\}&amp;\text{amine (V)}
\end{align*}
J = 7.5 Hz, 2H, H_c), 2.06 (d, J = 7.3 Hz, 2H, H_a), 1.98 (q, J = 7.0 Hz, 4H, H_k and H_l), 1.55 (m, 2H, H_j), 1.44 (s, 9H, H_p), 1.39 (s, 6H, H_g and H_g'), 1.37 (d, J = 7.4 Hz, 2H, H_t), 0.89 (t, J = 7.4 Hz, 3H, H_v).

$^{13}$C{^1H} NMR (125 MHz, CDCl$_3$, 50 °C): $\delta$ 155.4 (C_n), 133.5 (C_i or C_j or C_r or C_q), 133.3 (C_h), 132.9 (C_i or C_j or C_r or C_q), 126.1 (C_i or C_j or C_r or C_q), 124.8 (C_i or C_j or C_r or C_q), 118.0 (C_a), 97.9 (C_i), 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_i), 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$_2$O): 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 (2E)-2-hexenylmalonate (B) (3150 mg, 13 mmol). After stirring for 1 h, diethyl allyl-(2E)-6-bromohex-2-enylmalonate (M) (3613 mg, 10 mmol) was added and stirred for 17 h. The reaction quenched with H₂O and the organic phase was extracted with ether, washed successively with water and brine, and dried over Na₂SO₄. 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).

¹H NMR (500 MHz, CDCl₃, r.t.): δ 5.58 (m, 1H, H₇), 5.41 (m, 2H, H₉ and H₁₀), 5.18 (m, 2H, H₆ and H₇), 5.01 (m, 2H, H₆), 4.11 (m, 8H, H₈, H₁₁, H₁₂ and H₁₃), 2.55 (d, J = 7.4 Hz, 2H, H₂), 2.51 (d, J = 7.3 Hz, 4H, H₃ and H₄), 1.90 (m, 4H, H₁₀ and H₁₁), 1.78 (m, 2H, H₁₁), 1.30 (m, 2H, H₁₁), 1.18 (m, 14H, H₁₂, H₁₃, H₁₄, H₁₅, H₁₆, H₁₇, H₁₈, H₁₉, H₂₀, H₂₁, H₂₂, H₂₃). ¹³C {¹H} NMR (125 MHz, CDCl₃, r.t.): δ 171.2, 170.7 (C₆ and C₇), 134.8, 134.4 (C₁ and C₁₁), 132.4 (C₁₂), 124.0, 123.6 (C₁₃ and C₁₄), 118.8 (C₁₅), 61.0, 60.8 (C₁₆ and C₁₇), 57.4, 57.3 (C₁₈ and C₁₉), 36.5 (C₂₀), 35.6, 35.4 (C₂₁ and C₂₂), 34.5, 32.7 (C₂₂ and C₂₃), 31.5 (C₂₃) 23.6 (C₂₄), 22.4 (C₂₅), 14.0 (C₂₆, C₂₇, C₂₈, C₂₉ and C₃₀), 13.4 (C₃₁).

