Rapid Library Synthesis of Amphiphiles based on a Dioxinone Scaffold and Identification of Nonlamellar Liquid Crystals

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General

NMR spectra were collected using a JEOL model ECP-400 in the indicated solvent. Chemical shifts are reported in units of parts per million (ppm) relative to the signal (0.00 ppm) for internal tetramethylsilane for solutions in CDCl₃ (7.26 ppm for ¹H, 77.0 ppm for ¹³C). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; dd, doublet of doublets; dddd, doublet of doublets of doublets of doublets; ddt, doublet of doublets of triplets; dt, doublet of triplets; t, triplet; tt, triplet of triplets; q, quartet; quin, quintet; m, multiplet; br, broad; and, J, coupling constants in Hertz (Hz). IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Only the strongest and/or structurally important peaks are reported as the IR data given in cm⁻¹. The HRMS (ESI-TOF) were measured with a Waters LCT Premier™ XE. A polarizing optical microscope Olympus BX51 was used for visual observation. SAXS analysis was performed using a

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NANO-Viewer (Rigaku) with Cu Kα radiation (λ = 0.1542 nm). All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica-gel plates (60F-254) with UV light, visualized by 10% ethanolic p-anisaldehyde solution, ceric sulfate aqueous solution. Dry THF and toluene were obtained using a Glasscontour solvent purification system. Dry (i-Pr)₂NH was distilled from KOH. Dry MeOH was distilled from magnesium containing a catalytic amount of iodine.

**General procedure for preparation of alkylated dioxinones**

To a stirred solution of alcohol (1.00 eq.) in dry THF was added a solution of PBr₃ (0.400 eq.) in dry THF dropwise at 0 °C under argon atmosphere. After being stirred at the same temperature for 30 min, the reaction mixture was poured into H₂O at 0 °C. The aqueous layer was extracted with two portions of ether. The combined extract was washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was used in the next reaction without further purification.

To a stirred solution of (i-Pr)₂NH (2.40 eq.) in dry THF was added n-BuLi (1.60 M solution in hexane, 2.20 eq.) dropwise at -78 °C under argon atmosphere. After being stirred at 0 °C for 30 min, 2,2,6-trimethyl-1,3-dioxin-4-one (7) (2.00 eq.) in dry THF was added dropwise at -78 °C under argon atmosphere. After being stirred at 0 °C for 30 min, crude alkylbromide in dry THF was added dropwise at -78 °C under argon atmosphere. After being stirred at 0 °C for time, the reaction mixture was poured into saturated aqueous NH₄Cl at 0 °C. The aqueous layer was extracted with three portions of ether. The combined extract was washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel with 95 : 5 hexane : ethyl acetate to give a product as a colorless oil.

**Alkylated dioxinones 8a and 8c**

![Diagram of 8a and 8c](image)

**alcohol** geraniol (1) (1.00 g, 6.48 mmol, 1.00 eq.) in dry THF (15.9 mL)

PBr₃ (0.245 mL, 2.59 mmol, 0.400 eq.) in dry THF (10.0 mL)

(i-Pr)₂NH (2.19 mL, 15.6 mmol, 2.40 eq.) in dry THF (20.0 mL)

n-BuLi (5.42 mL, 14.3 mmol, 2.20 eq.)

2,2,6-trimethyl-1,3-dioxin-4-one (7) (1.71 mL, 13.0 mmol, 2.00 eq.) in dry THF (4.00 mL)
**CuBr-MeS** (1.33 g, 6.48 mmol, 1.00 eq.) in dry THF (4.00 mL)

**alkylbromide 4** in dry THF (4.00 mL)

**time** 1 h

**product 8** (1.16 g, 4.17 mmol, 64% in 2 steps, 8a : 8c = 86 : 14)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8a: 5.23 (s, 1H), 5.06-5.09 (m, 2H), 2.25-2.26 (m, 4H), 2.06 (dt, 2H, \(J = 7.2,\ 7.2\) Hz), 1.98 (t, 2H, \(J = 7.2\) Hz), 1.68 (s, 9H), 1.62 (s, 3H), 1.60 (s, 3H), 8c: 5.74 (dd, 1H, \(J = 10.7,\ 17.6\) Hz), 5.19 (s, 1H), 5.04-5.06 (m, 2H), 4.95 (d, 1H, \(J = 18.1\) Hz), 2.23 (m, 2H), 1.88-1.94 (m, 2H), 1.66 (s, 6H), 1.62 (s, 3H), 1.59 (s, 3H), 1.35-1.40 (m, 2H), 1.09 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 8a: 171.5, 161.3, 137.1, 131.5, 124.0, 121.6, 106.2, 93.3, 39.5, 33.7, 26.5, 25.6, 25.0, 24.2, 17.6, 16.1; FT-IR (KBr) 2968, 2919, 1736, 1635, 1440, 1390, 1309, 1271, 1252, 1205, 1108, 1014, 963, 902, 807, 741, 617, 511 (cm\(^{-1}\)); HRMS (ESI-TOF) calcd. for C\(_{17}\)H\(_{27}\)O\(_3\) [M+H]\(^+\) 279.1960 found 279.1964.

**Alkylated dioxinones 9a-9c**

![Alkylated dioxinones 9a-9c](image)

**alcohol** tetrahydrornerololid (2) (500 mg, 2.21 mmol, 1.00 eq.) in dry THF (6.00 mL)

**PBr\(_3\)** (0.084 mL, 0.884 mmol, 0.400 eq.) in dry THF (2.80 mL)

**(i-Pr)\(_2\)NH** (0.743 mL, 5.30 mmol, 2.40 eq.) in dry THF (7.00 mL)

**n-BuLi** (1.83 mL, 4.86 mmol, 2.20 eq.)

**2,2,6-trimethyl-1,3-dioxin-4-one** (7) (0.582 mL, 4.42 mmol, 2.00 eq.) in dry THF (1.00 mL)

**CuBr-MeS** (454 mg, 2.21 mmol, 1.00 eq.) in dry THF (1.50 mL)

**alkylbromide 5** in dry THF (1.50 mL)

**time** 2.5 h

**product 9** (422 mg, 1.20 mmol, 54% in 2 steps, 9a : 9b : 9c = 66 : 23 : 11)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9a: 5.23 (s, 1H), 5.06 (br, 1H), 2.23-2.25 (m, 4H), 1.94 (t, 2H, \(J = 7.8\) Hz), 1.67 (s, 6H), 1.60 (s, 3H), 1.52 (m, 1H), 1.00-1.38 (m, 11H), 0.84-0.88 (m, 9H), 9b: 5.23 (s, 1H), 5.06 (br, 1H), 2.23-2.25 (m, 4H), 1.98 (t, 2H, \(J = 7.8\) Hz), 1.67 (s, 9H), 1.52 (m, 1H), 1.00-1.38 (m, 11H), 0.84-0.88 (m, 9H), 9c: 5.73 (dd, 1H, \(J = 11.2,\ 17.6\) Hz), 5.18 (s, 1H), 5.03 (d, 1H, \(J = 11.2\) Hz), 4.93 (d, 1H, \(J = 17.6\) Hz), 2.22 (m, 2H), 1.67 (s, 6H), 1.00-1.38 (m, 17H), 0.84-0.88 (m, 9H);
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 9a: 171.5, 161.2, 137.5, 121.4, 106.2, 93.3, 39.8, 39.3, 37.2, 36.6, 33.7, 32.6, 27.9, 25.2, 25.0, 24.7, 24.2, 22.6, 19.6, 16.0; FT-IR (KBr) 3452, 2928, 1736, 1635, 1389, 1271, 1204, 1013, 901, 806 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{22}$H$_{30}$O$_3$ [M+H]$^+$ 351.2899 found 351.2892.

Alkylated dioxinones 10a-10c

**alcohol** isophytol (3) (500 mg, 1.69 mmol, 1.00 eq.) in dry THF (4.00 mL)

**PBr$_3$** (0.064 mL, 0.676 mmol, 0.400 eq.) in dry THF (2.76 mL)

(i-Pr)$_2$NH (0.569 mL, 4.06 mmol, 2.40 eq.) in dry THF (5.45 mL)

**n-BuLi** (1.41 mL, 3.72 mmol, 2.20 eq.)

2,2,6-trimethyl-1,3-dioxin-4-one (7) (0.444 mL, 3.38 mmol, 2.00 eq.) in dry THF (1.00 mL)

**CuBr-Me$_3$S** (347 mg, 1.69 mmol, 1.00 eq.) in dry THF (1.00 mL)

**alkylbromide** 6 in dry THF (1.00 mL)

**time** 1 h

**product** 10 (406 mg, 0.965 mmol, 57% in 2 steps, 10a : 10b : 10c = 72 : 14 : 14)

$^1$H NMR (400 MHz, CDCl$_3$) δ 10a: 5.23 (s, 1H), 5.06 (br, 1H), 2.22-2.25 (m, 4H), 1.94 (t, 2H, J = 7.6 Hz), 1.68 (s, 6H), 1.60 (s, 3H), 1.52 (m, 1H), 1.07-1.36 (m, 18H), 0.83-0.87 (m, 12H), 10b: 5.23 (s, 1H), 5.06 (br, 1H), 2.22-2.25 (m, 4H), 1.98 (t, 2H, J = 6.4 Hz), 1.68 (s, 9H), 1.52 (m, 1H), 1.07-1.36 (m, 18H), 0.83-0.87 (m, 12H), 10c: 5.73 (dd, 1H, J = 11.2, 17.6 Hz), 5.18 (s, 1H), 5.03 (d, 1H, J = 11.2 Hz), 4.92 (d, 1H, J = 18.1 Hz), 2.22 (m, 2H), 1.68 (s, 6H), 1.07-1.36 (m, 24H), 0.83-0.87 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 10a: 208.1, 171.6, 161.4, 137.6, 121.4, 106.3, 93.4, 39.9, 39.4, 37.4, 37.3, 36.7, 33.8, 32.8, 32.7, 28.0, 25.3, 25.0, 24.8, 24.5, 24.2, 22.7, 22.6, 19.7, 16.0; FT-IR (KBr) 3452, 2928, 1737, 1635, 1462, 1376, 1271, 1204, 1013, 901, 806 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{22}$H$_{30}$O$_3$ [M+H]$^+$ 421.3682 found 421.3693.

**General procedure for preparation of β-ketoesters**
To a stirred solution of dioxinone (1.00 eq.), a solution of alcohol in dry toluene at room temperature under an argon atmosphere. After being stirred at 130 °C for time, the reaction mixture was cooled and concentrated in vacuo. The residue was purified by procedure to give a product.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-3-oxobutanoate (14)

![Chemical structure of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-3-oxobutanoate](image)

dioxinone 2,2,6-trimethyl-1,3-dioxin-4-one (7) (1.00 g, 7.03 mmol, 1.00 eq.)
alcohol (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (11) (1.30 mL, 10.5 mmol, 1.50 eq.)
toluene (30.0 mL)
time 3.5 h
procedure column chromatography on silica gel with 80 : 20 hexane : ethyl acetate
product 14 (1.76 g, quant.) colorless oil

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.33 (dd, 1H, \(J = 6.3, 6.3, 5.8, 5.8\) Hz), 4.23 (dd, 1H, \(J = 11.6, 5.8\) Hz), 4.16 (dd, 1H, \(J = 11.6, 5.8\) Hz), 4.09 (dd, 1H, \(J = 8.7, 6.3\) Hz), 3.75 (dd, 1H, \(J = 8.7, 6.3\) Hz), 3.51 (s, 2H), 2.28 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.1, 166.8, 109.9, 73.3, 66.2, 65.4, 49.8, 30.1, 26.6, 25.3; FT-IR (KBr) 2989, 1748, 1655, 1413, 1372, 1318, 1217, 1154, 1055, 841, 542, 516 (cm\(^{-1}\)); HRMS (ESI-TOF) calcd. for C\(_{10}\)H\(_{16}\)O\(_3\)Na [M+Na]\(^+\) 239.0895 found 239.0894.

2,6,7-Trioxybicyclo[2.2.2]octan-4-ylmethyl-3-oxobutanoate (15)

![Chemical structure of 2,6,7-Trioxybicyclo[2.2.2]octan-4-ylmethyl-3-oxobutanoate](image)

dioxinone 2,2,6-trimethyl-1,3-dioxin-4-one (7) (0.156 mL, 1.18 mmol, 1.00 eq.)
alcohol 2,6,7-trioxybicyclo[2.2.2]octan-4-ylmethanol (12) (208 mg, 1.30 mmol, 1.10 eq.)
toluene (6.00 mL)
time 4 h
procedure column chromatography on silica gel with 76 : 24 : 0.2 hexane : ethyl acetate : triethylamine
product 15 (224 mg, 0.973 mmol, 82%) white solid

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.55 (s, 1H), 4.01 (s, 6H), 3.95 (s, 2H), 3.50 (s, 2H), 2.27 (s, 3H); \(^1\)C
NMR (100 MHz, CDCl₃) δ 199.6, 166.4, 101.9, 68.1, 62.7, 49.5, 34.5, 30.2; FT-IR (KBr) 2953, 2892, 1749, 1718, 1476, 1413, 1363, 1318, 1269, 1154, 1044, 997, 914, 859, 541 (cm⁻¹); mp 69 °C; HRMS (ESI-TOF) calcd. for C₁₀H₁₅O₆ [M+H]^⁺ 231.0869 found 231.0870.

(E)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (16)

![Structure of (E)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (16)]

dioxinone alkylated dioxinone 8 (207 mg, 0.744 mmol, 1.00 eq.)
alcohol (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (11) (0.137 mL, 1.12 mmol, 1.50 eq.)
toluene (3.72 mL)
time 2 h
procedure column chromatography on silica gel with 90 : 10 hexane : ethyl acetate
product 16 (236 mg, 0.670 mmol, 90%) colorless oil

¹H NMR (400 MHz, CDCl₃) δ 5.07-5.09 (m, 2H), 4.30-4.36 (m, 1H), 4.14-4.25 (m, 2H), 4.06-4.10 (m, 1H), 3.73-3.78 (m, 1H), 3.49 (s, 2H), 2.57 (t, 2H, J = 7.3 Hz), 2.29 (dt, 2H, J = 7.3, 7.3 Hz), 1.95-2.06 (m, 4H), 1.68 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 202.1, 166.9, 136.7, 131.3, 124.0, 121.9, 109.8, 73.3, 66.1, 65.3, 48.9, 43.0, 39.5, 26.6, 26.5, 25.6, 25.2, 22.0, 17.6, 15.9; FT-IR (KBr) 2986, 2931, 1750, 1719, 1453, 1372, 1218, 1159, 1085, 841, 516 (cm⁻¹); HRMS (ESI-TOF) calcd. for C₂₆H₃₇O₅ [M+H]^⁺ 353.2328 found 353.2315.

(E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (17)

![Structure of (E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (17)]

dioxinone alkylated dioxinone 8 (259 mg, 0.931 mmol, 1.00 eq.)
alcohol 2,6,7-trioxabicyclo[2.2.2]octan-4-ylmethanol (12) (164 mg, 1.02 mmol, 1.10 eq.)
toluene (5.00 mL)
time 4 h
procedure column chromatography on silica gel with 85 : 15 hexane : ethyl acetate
product 17 (282 mg, 0.768 mmol, 83%) colorless oil

¹H NMR (400 MHz, CDCl₃) δ 5.56 (s, 1H), 5.07 (m, 2H), 4.01 (s, 6H), 3.94 (s, 2H), 3.47 (s, 2H), 3.14 (s, 3H), 2.18 (s, 3H), 1.96 (s, 3H), 1.49 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.29 (s, 3H), 1.12 (s, 3H), 1.00 (s, 3H), 0.90 (s, 3H), 0.75 (s, 3H), 0.57 (s, 3H), 0.38 (s, 3H), 0.28 (s, 3H), 0.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.6, 166.4, 101.9, 68.1, 62.7, 49.5, 34.5, 30.2; FT-IR (KBr) 2953, 2892, 1749, 1718, 1476, 1413, 1363, 1318, 1269, 1154, 1044, 997, 914, 859, 541 (cm⁻¹); mp 69 °C; HRMS (ESI-TOF) calcd. for C₂₆H₃₇O₅ [M+H]^⁺ 353.2328 found 353.2315.
2.54 (t, 2H, J = 7.3 Hz), 2.29 (dt, 2H, J = 7.3, 6.8 Hz), 2.06 (dt, 2H, J = 7.3, 7.3 Hz), 1.98 (t, 2H, J =
7.3 Hz), 1.68 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H); ^13^C NMR (100 MHz, CDCl$_3$) δ 201.8, 166.6, 137.1, 131.5,
124.1, 121.7, 102.0, 68.1, 62.6, 48.8, 43.3, 39.6, 34.6, 26.6, 25.7, 22.2, 17.7, 16.0; FT-IR (KBr) 2891, 1754, 1718, 1374, 1271,
1157, 1038, 999, 928, 859 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{20}$H$_{31}$O$_6$ [M+H]$^+$ 367.2121 found 367.2127.

(E)-1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-7,11-dimethyl-3-oxododeca-6,10-die
noate (18)

![Diagram](image)

dioxinone alkylated dioxinone 8 (400 mg, 1.44 mmol, 1.00 eq.)
alcohol 1,3-bis(2,2-dimethyl-1,3-dioxan-5-yloxy)propan-2-ol (13) (506 mg, 1.58 mmol, 1.10 eq.)
toluene (7.00 mL)
time 2 h
procedure column chromatography on silica gel with 68 : 32 hexane : ethyl acetate
product 18 (726 mg, 1.34 mmol, 93%) colorless oil

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.05-5.12 (m, 3H), 3.93-3.97 (m, 4H), 3.66-3.74 (m, 8H), 3.44-3.47
(m, 4H), 2.56 (t, 2H, J = 7.3 Hz), 2.28 (dt, 2H, J = 7.3, 7.3 Hz), 2.05 (dt, 2H, J = 7.3, 7.3 Hz), 1.97 (t,
2H, J = 7.3 Hz), 1.68 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H), 1.42 (s, 6H), 1.39 (s, 6H); ^13^C NMR (100
MHz, CDCl$_3$) δ 202.1, 166.5, 136.6, 131.3, 124.0, 121.9, 98.0, 72.4, 66.8, 62.3, 62.2, 49.1, 42.9,
39.5, 26.5, 25.5, 23.9, 23.0, 22.0, 17.5, 15.9; FT-IR (KBr) 2919, 1747, 1718, 1454, 1375, 1251, 1199,
1155, 1087, 830, 520 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{29}$H$_{49}$O$_9$ [M+H]$^+$ 541.3377 found
541.3378.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 19

![Diagram](image)

dioxinone alkylated dioxinone 9 (250 mg, 0.713 mmol, 1.00 eq.)
alcohol (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (11) (0.180 mL, 1.43 mmol, 2.00 eq.)
**toluene** (3.50 mL)

**time** 2 h

**procedure** column chromatography on silica gel with 93:7 hexane : ethyl acetate

**product** **19** (206 mg, 0.485 mmol, 70%, mixture of E/Z-isomers) colorless oil

$E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.04-5.06 (m, 1H), 4.33 (dddd, 1H, $J = 5.8$, 5.8, 5.3, 5.3 Hz), 4.22 (dd, 1H, $J = 11.6$, 5.3 Hz), 4.15 (dd, 1H, $J = 11.6$, 5.3 Hz), 4.08 (dd, 1H, $J = 8.7$, 5.8 Hz), 3.74 (dd, 1H, $J = 8.7$, 5.8 Hz), 3.48 (s, 2H), 2.56 (t, 2H, $J = 7.3$ Hz), 2.28 (dt, 2H, $J = 7.3$, 7.3 Hz), 1.92 (t, 2H, $J = 6.8$ Hz), 1.60 (s, 3H), 1.52 (m, 1H), 1.42 (s, 3H), 1.36 (s, 3H), 1.02-1.42 (m, 11H), 0.86 (d, 6H, $J = 6.8$ Hz), 0.84 (d, 3H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.2, 167.0, 137.3, 121.7, 109.9, 73.4, 66.3, 65.4, 49.0, 43.1, 39.9, 39.3, 37.3, 36.7, 32.7, 28.0, 26.7, 25.3, 24.8, 22.7, 22.6, 22.1, 19.7, 15.9; FT-IR (KBr) 2930, 1750, 1720, 1461, 1371, 1218, 1159, 1058, 841, 516 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{22}$H$_{45}$O$_5$ [M+H]$^+$ 425.3267 found 425.3274.

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 20

![](image)

**dioxinone** alkylated dioxinone 9 (166 mg, 0.474 mmol, 1.00 eq.)

**alcohol** 2,6,7-trioxabicyclo[2.2.2]octan-4-ylmethanol (12) (76.0 mg, 0.521 mmol, 1.10 eq.)

**toluene** (2.37 mL)

**time** 2.5 h

**procedure** column chromatography on silica gel with 80:20 hexane : ethyl acetate

**product** 20 (167 mg, 0.381 mmol, 80%, mixture of E/Z-isomers) colorless oil

$E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.55 (s, 1H), 5.05 (t, 1H, $J = 5.9$ Hz), 4.01 (s, 6H), 3.94 (s, 2H), 3.47 (s, 2H), 2.54 (t, 2H, $J = 7.6$ Hz), 2.29 (dt, 2H, $J = 7.3$, 5.9 Hz), 1.93 (t, 2H, $J = 7.3$ Hz), 1.60 (s, 3H), 1.52 (m, 1H), 1.00-1.38 (m, 11H), 0.86 (d, 6H, $J = 6.4$ Hz), 0.84 (d, 3H, $J = 9.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.8, 166.6, 137.5, 121.4, 101.9, 68.1, 62.6, 48.7, 43.3, 39.9, 39.3, 37.2, 36.6, 34.5, 32.6, 27.9, 25.3, 24.7, 22.7, 22.6, 22.1, 19.6, 15.9; FT-IR (KBr) 3440, 2930, 1754, 1718, 1468, 1368, 1312, 1157, 1039, 999, 929, 859 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{23}$H$_{45}$O$_6$ [M+H]$^+$ 439.3060 found 439.3061.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate 21

S-12
**dioxinone** alkylated dioxinone 10 (150 mg, 0.357 mmol, 1.00 eq.)

**alcohol** (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (11) (90.0 μL, 0.710 mmol, 2.00 eq.)

**toluene** (2.00 mL)

**time** 2 h

**procedure** column chromatography on silica gel with 94 : 6 hexane : ethyl acetate

**product 21** (170 mg, 0.344 mmol, 91%, mixture of E/Z-isomers) colorless oil

E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 5.05 (t, 1H, $J = 6.8$ Hz), 4.32 (dddd, 1H, $J = 6.3, 6.3, 5.7, 5.7$ Hz), 4.22 (dd, 1H, $J = 11.6, 5.7$ Hz), 4.16 (dd, 1H, $J = 11.6, 5.7$ Hz), 4.08 (dd, 1H, $J = 8.7, 6.3$ Hz), 3.74 (dd, 1H, $J = 8.7, 6.3$ Hz), 3.48 (s, 2H), 2.56 (t, 2H, $J = 7.3$ Hz), 2.28 (dt, 2H, $J = 7.3, 6.8$ Hz), 1.92 (t, 2H, $J = 7.3$ Hz), 1.60 (s, 3H), 1.52 (m, 1H), 1.42 (s, 3H), 1.36 (s, 3H), 1.01-1.37 (m, 18H), 0.86 (d, 6H, $J = 6.8$ Hz), 0.84 (d, 6H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.2, 167.0, 137.3, 121.6, 109.9, 73.4, 66.3, 65.4, 49.0, 43.1, 39.9, 39.4, 37.4, 37.3, 36.8, 32.8, 32.7, 32.0, 28.0, 26.7, 25.3, 24.8, 24.5, 23.3, 22.7, 22.6, 22.1, 19.7, 15.9; FT-IR (KBr) 2929, 1751, 1720, 1462, 1380, 1218, 1159, 1058, 842 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{30}$H$_{55}$O$_3$ [M+H]$^+$ 495.4050 found 495.4072.

2,6,7-Trioxabicyclo[2.2.2]octan-4-ymethyl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate 22

**dioxinone** alkylated dioxinone 10 (195 mg, 0.464 mmol, 1.00 eq.)

**alcohol** 2,6,7-trioxabicyclo[2.2.2]octan-4-ylmethanol (12) (97.0 mL, 6.48 mmol, 1.30 eq.)

**toluene** (2.3 mL)

**time** 2 h

**procedure** column chromatography on silica gel with 88 : 12 hexane : ethyl acetate

**product 22** (201 mg, 0.394 mmol, 85%, mixture of E/Z-isomers) colorless oil

E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 5.55 (s, 1H), 5.03 (t, 1H, $J = 6.8$ Hz), 4.00 (s, 6H), 3.94 (s, 2H), 3.47 (s, 2H), 2.54 (t, 2H, $J = 7.3$ Hz), 2.29 (dt, 2H, $J = 7.3, 6.8$ Hz), 1.93 (t, 2H, $J = 6.9$ Hz), 1.60 (s, 3H), 1.52 (m, 1H), 1.02-1.38 (m, 18H), 0.86 (d, 6H, $J = 6.3$ Hz), 0.84 (d, 6H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.8, 166.6, 137.6, 121.4, 102.0, 68.1, 62.6, 48.8, 43.4, 39.9, 39.4,
37.4, 37.3, 36.7, 34.6, 32.8, 32.7, 32.0, 28.0, 25.3, 24.8, 24.5, 22.7, 22.6, 22.1, 19.7, 15.9; FT-IR (KBr) 2928, 1753, 1719, 1464, 1376, 1271, 1157, 1039, 999, 929, 859 (cm\(^{-1}\)); HRMS (ESI-TOF) calcd. for C\(_{30}\)H\(_{53}\)O\(_6\) [M+H]\(^+\) 509.3842 found 509.3851.

1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-7,11,15,19-tetramethyl-3-oxicos-6-enoate 23

![Structure 23](image)

dioxinone alkylated dioxinone 10 (205 mg, 0.487 mmol, 1.00 eq.)
alcohol 1,3-bis(2,2-dimethyl-1,3-dioxan-5-yl)oxy)propan-2-ol (13) (172 mg, 0.536 mmol, 1.10 eq.)
toluene (2.44 mL)
time 2.5 h
procedure column chromatography on silica gel with 70 : 30 hexane : ethyl acetate
product (317 mg, 0.464 mmol, 95%, mixture of E/Z-isomers) colorless oil

\(E\)-isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.10 (quin, 1H, \(J = 5.1\) Hz), 5.05 (t, 1H, \(J = 6.8\) Hz), 3.92-3.97 (m, 4H), 3.63-3.74 (m, 8H), 3.42-3.47 (m, 4H), 2.55 (t, 2H, \(J = 7.3\) Hz), 2.28 (dt, 2H, \(J = 7.3, 6.8\) Hz), 1.92 (t, 2H, \(J = 7.3\) Hz), 1.59 (s, 3H), 1.42 (s, 6H), 1.39 (s, 6H), 1.52 (m, 1H), 1.05-1.36 (m, 18H), 0.86 (d, 6H, \(J = 6.8\) Hz), 0.84 (d, 6H, \(J = 6.8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 202.2, 166.6, 137.3, 121.7, 98.2, 72.6, 71.1, 67.0, 62.5, 62.4, 49.3, 43.1, 40.1, 39.4, 37.4, 37.3, 32.8, 32.7, 28.0, 25.4, 24.8, 24.5, 24.1, 23.0, 22.7, 22.6, 22.1, 19.7, 19.7, 15.9; FT-IR (KBr) 2928, 1747, 1718, 1371, 1250, 1199, 1087, 831, 732 (cm\(^{-1}\)); HRMS (ESI-TOF) calcd. for C\(_{30}\)H\(_{70}\)O\(_3\)Na [M+Na]\(^+\) 705.4918 found 705.4918.

General procedure for preparation of branched lipids

To a stirred solution of \(\beta\)-ketoester (1.00 eq.) and geranyl methyl carbonate (24) in dry THF was added Pd\(_3\)(dba)\(_2\) (0.0250 eq.) and dppe (0.100 eq.) at room temperature under an argon atmosphere. After being stirred at 60 °C for time, the reaction mixture was cooled, filtered through Celite and concentrated in vacuo. The residue was purified by procedure to give a product as a colorless oil.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2-acetyl-5,9-dimethyldeca-4,8-dienoate 25
\( \beta \)-ketoester (2,2-dimethyl-1,3-dioxolan-4-yl)methyl-3-oxobutanoate (14) (498 mg, 2.31 mmol, 1.00 eq.)

geranyl methyl carbonate (24) (490 mg, 2.31 mmol, 1.00 eq.)

THF (7.00 mL)

Pd(dba)\(_3\) (53.0 mg, 0.0580 mmol, 0.0250 eq.)
dppe (92.0 mg, 0.231 mmol, 0.100 eq.)

time 9 h

procedure column chromatography on silica gel with 96 : 4 hexane : ethyl acetate

product 25 (527 mg, 1.50 mmol, 65%, mixture of E/Z-isomers)

\( E \)-isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 5.02 (m, 2H), 4.28 (ddt, 1H, \( J = 5.8, 5.8, 5.3 \) Hz), 4.16 (d, 2H, \( J = 5.3 \) Hz), 4.04 (dd, 1H, \( J = 8.7, 5.8 \) Hz), 3.71 (dd, 1H, \( J = 8.7, 5.8 \) Hz), 3.48 (dd, 1H, \( J = 7.3, 7.3 \) Hz), 2.54 (dd, 2H, \( J = 7.3, 6.8 \) Hz), 2.21 (s, 3H), 2.01-2.04 (m, 2H), 1.96 (t, 2H, \( J = 7.3 \) Hz), 1.65 (s, 3H), 1.61 (s, 3H), 1.57 (s, 3H), 1.40 (s, 3H), 1.33 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 202.7, 169.3, 138.6, 131.5, 123.9, 119.5, 109.8, 73.3, 66.2, 65.2, 59.5, 39.6, 29.2, 26.9, 26.6, 26.5, 25.6, 25.3, 17.6, 16.0; FT-IR (KBr) 2987, 2932, 1747, 1719, 1453, 1372, 1213, 1155, 1057, 841, 515 (cm\(^{-1}\)); HRMS (ESI-TOF) calcd. for C\(_{20}\)H\(_{30}\)O\(_5\) [M+H]\(^+\) 353.2328 found 353.2329.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethyldeca-4,8-dienoate 26

\( \beta \)-ketoester (2,2-dimethyl-1,3-dioxolan-4-yl)methyl-3-oxobutanoate (14) (216 mg, 1.00 mmol, 1.00 eq.)

geranyl methyl carbonate (24) (531 mg, 2.50 mmol, 2.50 eq.)

THF (3.00 mL)

Pd(dba)\(_3\) (22.9 mg, 0.0250 mmol, 0.0250 eq.)
dppe (39.8 mg, 0.100 mmol, 0.100 eq.)

time 15 h

procedure column chromatography on silica gel with 90 : 10 hexane : ethyl acetate
**Product 26** (421 mg, 0.861 mmol, 86%, mixture of E/Z-isomers)

_E-isomer:_ $^1$H NMR (400 MHz, CDCl$_3$) δ 5.01 (t, 2H, $J = 6.8$ Hz), 4.87 (t, 2H, $J = 6.8$ Hz), 4.25 (ddddd, 1H, $J = 5.8$, 5.8, 5.3, 5.3 Hz), 4.17 (dd, 1H, $J = 11.1$, 5.3 Hz), 4.06 (dd, 1H, $J = 11.1$, 5.3 Hz), 4.01 (dd, 1H, $J = 8.7$, 5.8 Hz), 3.68 (dd, 1H, $J = 8.7$, 5.8 Hz), 2.55 (d, 4H, $J = 6.8$ Hz), 2.09 (s, 3H), 2.01 (dt, 4H, $J = 6.8$ Hz), 1.95 (t, 4H, $J = 6.8$ Hz), 1.64 (s, 6H), 1.56 (s, 12H), 1.38 (s, 3H), 1.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.6, 171.9, 138.9, 131.4, 123.9, 117.7, 109.7, 73.1, 66.3, 65.1, 63.5, 39.8, 30.0, 26.8, 26.6, 26.4, 25.6, 25.2, 17.6, 16.1; FT-IR (KBr) 2985, 2919, 1716, 1451, 1380, 1215, 1179, 1159, 1061, 976, 841, 516 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{30}$H$_{40}$O$_5$ [M+H]$^+$ 489.3580 found 489.3579.

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dime thyldeca-4,8-dienoate 27

![](image)

**$\beta$-ketoester** 2,6,7-trioxabicyclo[2.2.2]octan-4-ylmethyl-3-oxobutanoate (15) (197 mg, 0.854 mmol, 1.00 eq.)

**Geranyl methylcarbonate** (24) (453 mg, 2.14 mmol, 2.50 eq.)

**THF** (2.50 mL)

**Pd$_2$(dba)$_3$** (20.0 mg, 0.0214 mmol, 0.0250 eq.)

**dppe** (34.0 mg, 0.0854 mmol, 0.100 eq.)

**Time** 13 h

**Procedure** column chromatography on silica gel with 90 : 10 hexane : ethyl acetate

**Product 27** (387 mg, 0.770 mmol, 90%, mixture of E/Z-isomers)

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.54 (s, 1H), 5.03 (t, 2H, $J = 6.8$ Hz), 4.87 (t, 2H, $J = 6.8$ Hz), 3.96 (s, 6H), 3.88 (s, 2H), 2.57 (d, 4H, $J = 6.8$ Hz), 2.10 (s, 3H), 1.97-2.07 (m, 8H), 1.67 (s, 6H), 1.59 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.3, 171.7, 139.4, 131.6, 123.9, 117.4, 101.9, 68.1, 63.7, 62.7, 39.9, 34.6, 30.3, 26.9, 26.4, 25.6, 17.7, 16.2; FT-IR (KBr) 2919, 1716, 1447, 1376, 1279, 1215, 156, 1035, 998, 925, 859 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{30}$H$_{47}$O$_6$ [M+H]$^+$ 503.3373 found 503.3373.
(6E)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 28

\[
\text{\textbeta-ketoester} \quad (2,2\text{-dimethyl-1,3-dioxolan-4-yl})\text{methyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (16)}
\]

(121 mg, 0.343 mmol, 1.00 eq.)

**geranyl methyl carbonate (24)** (73.0 mg, 0.343 mmol, 1.00 eq.)

**THF** (1.03 mL)

**Pd\textsubscript{3}(dba)\textsubscript{3}** (7.9 mg, 0.00858 mmol, 0.0250 eq.)

**dppe** (13.7 mg, 0.0343 mmol, 0.100 eq.)

**time** 9 h

**procedure** column chromatography on silica gel with 93 : 7 hexane : ethyl acetate

**product 28** (105 mg, 0.215 mmol, 63%, mixture of E/Z-isomers)

\(E\)-isomer: \(^1\text{H}NMR\ (400 \text{ MHz, CDCl}_3) \downarrow 5.00-5.07 \text{ (m, 4H), 4.27 (ddt, 1H, } J = 5.8, 5.8, 5.3 \text{ Hz), 4.14 (d, } 2H, J = 5.3 \text{ Hz), 4.03 (dd, 1H, } J = 8.7, 5.8 \text{ Hz), 3.70 (dd, 1H, } J = 8.7, 5.8 \text{ Hz), 3.49 (t, 1H, } J = 7.3 \text{ Hz), 2.45-2.62 (m, 4H), 2.24 (dt, 2H, } J = 7.3, 7.3 \text{ Hz), 2.02 (m, 4H), 1.94 (t, 4H, } J = 7.3 \text{ Hz), 1.65 (s, 6H), 1.60 (s, 3H), 1.59 (s, 3H), 1.57 (s, 6H), 1.40 (s, 3H), 1.33 (s, 3H); } \text{^13C NMR (100 MHz, CDCl}_3) \downarrow 204.6, 169.3, 138.4, 136.5, 131.5, 131.3, 124.1, 123.9, 122.2, 119.6, 109.7, 73.3, 66.2, 65.2, 65.1, 58.8, 58.7, 42.4, 39.6, 26.9, 26.6, 26.5, 26.4, 25.6, 25.3, 25.2, 22.0, 17.6, 16.0, 15.9; FT-IR (KBr) 2968, 2925, 1749, 1718, 1452, 1380, 1215, 1158, 1058, 841 \text{ (cm}^{-1}); \text{ HRMS (ESI-TOF) calcd. for C}_{30}\text{H}_{49}\text{O}_5 [M+H]^{+} 489.3580 \text{ found 489.3577.}
\]

(6E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 29

\[
\text{\textbeta-ketoester} \quad 2,6,7\text{-trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (17)}
\]

(216 mg, 0.589 mmol, 1.00 eq.)

**geranyl methyl carbonate (24)** (125 mg, 0.589 mmol, 1.00 eq.)

**THF** (1.80 mL)

**Pd\textsubscript{3}(dba)\textsubscript{3}** (13.0 mg, 0.0147 mmol, 0.0250 eq.)
**dppe** (23.0 mg, 0.0589 mmol, 0.100 eq.)

**time** 13 h

**procedure** column chromatography on silica gel with 94 : 6 hexane : ethyl acetate

**product 29** (170 mg, 0.338 mmol, 57%, mixture of E/Z-isomers)

\[ E \text{-isomer: } ^1H \text{ NMR (400 MHz, CDCl}_3\text{) } \delta 5.55 (s, 1H), 5.01-5.09 (m, 4H), 3.97 (s, 6H), 3.91 (s, 2H), 3.49 (t, 1H, } J = 7.6 \text{ Hz), 2.51-2.56 (m, 4H), 2.27 (dt, 2H, } J = 7.3, 7.3 \text{ Hz), 1.98-2.05 (m, 8H), 1.68 (s, 6H), 1.62 (s, 3H), 1.61 (s, 3H), 1.60 (s, 6H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) } \delta 204.4, 169.0, 139.0, 136.9, 131.6, 131.4, 124.1, 123.8, 121.9, 119.3, 101.9, 68.1, 62.5, 58.6, 42.7, 39.6, 34.6, 27.1, 26.6, 26.5, 25.6, 22.1, 17.7, 16.1, 16.0; \text{ FT-IR (KBr) } 2967, 2919, 1750, 1717, 1448, 1376, 1262, 1210, 1156, 1109, 1036, 999, 924, 859, 750, 619 (cm}^1); \text{ HRMS (ESI-TOF) calcd. for } C_{30}H_{47}O_6 [M+H]^+ \text{ 503.3373 found 503.3368.}

(\text{6E})-1,3-Bis[2,2-dimethyl-1,3-dioxan-5-yl]oxy]propan-2-yl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxodeca-6,10-dienoate 30

\[ \text{β-ketoester}
1,3-bis[2,2-dimethyl-1,3-dioxan-5-yl]oxy]propan-2-yl-7,11-dimethyl-3-oxodeca-6,10-dienoate (18) (100 mg, 0.185 mmol, 1.00 eq.)

**geranyl methyl carbonate** (24) (39.0 mg, 0.426 mmol, 1.00 eq.)

**THF** (1.00 mL)

**Pd\text{(dba)}_3** (6.0 mg, 0.0050 mmol, 0.025 eq.)

**dppe** (8.0 mg, 0.020 mmol, 0.10 eq.)

**time** 11 h

**procedure** column chromatography on silica gel with 80 : 20 hexane : ethyl acetate

**product 30** (81.2 mg, 0.146 mmol, 77%, mixture of E/Z-isomers)

\[ E \text{-isomer: } ^1H \text{ NMR (400 MHz, CDCl}_3\text{) } \delta 5.01-5.09 (m, 5H), 3.93 (dd, 4H, } J = 11.9, 4.2 \text{ Hz), 3.62-3.72 (m, 8H), 3.40-3.50 (m, 3H), 2.47-2.61 (m, 4H), 2.25 (dt, 2H, } J = 7.3, 7.3 \text{ Hz), 1.94-2.04 (m, 8H), 1.67 (s, 6H), 1.62 (s, 3H), 1.61 (s, 3H), 1.59 (s, 6H), 1.41 (s, 6H) 1.39 (s, 6H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) } \delta 204.4, 169.0, 138.4, 136.5, 131.5, 124.1, 123.9, 122.2, 119.7, 98.2, 72.3, 71.0, 67.0, 66.9, 62.4, 62.3, 58.8, 42.4, 39.7, 39.6, 26.9, 26.6, 26.5, 25.6, 24.2, 22.9, 22.8, 22.0, 17.6, 16.1, \text{ S-18} \]
16.0; FT-IR (KBr) 2920, 1745, 1716, 1453, 1373, 1251, 1199, 1155, 1088, 831 (cm⁻¹); HRMS (ESI-TOF) calcd. for C₉H₆₅O₉ [M+H]+ 677.4629 found 677.4648.

\[(6E)-(2,2\text{-dimethyl-1,3-dioxolan-4-yl}methyl-2,2\text{-bis}(3,7\text{-dimethylocta-2,6-dien-1-yl})-7,11\text{-dimethyl-3-oxododeca-6,10-dienoate 31}\]

\[\beta\text{-ketoester} \ (2,2\text{-dimethyl-1,3-dioxolan-4-yl}methyl-7,11\text{-dimethyl-3-oxododeca-6,10-dienoate (16)}}\]

(181 mg, 0.851 mmol, 2.50 eq.)

\[\text{geranyl methylcarbonate (24) (181 mg, 0.851 mmol, 2.50 eq.)}\]

\[\text{THF (1.00 mL)}\]

\[\text{Pd(gdba)}_2 \ (8.0 \text{ mg, 0.0085 mmol, 0.025 eq.)}\]

\[\text{dppe (14.0 mg, 0.0340 mmol, 0.100 eq.)}\]

\[\text{time 4 h}\]

\[\text{procedure column chromatography on silica gel with 96 : 4 hexane : ethyl acetate}\]

\[\text{product 31 (208 mg, 0.332 mmol, 97%, mixture of E/Z-isomers)}\]

\[\text{E-isomer: } ^1\text{H NMR (400 MHz, CDCl₃) } \delta \text{ 5.02-5.07 (m, 4H), 4.88 (t, 2H, } J = 6.8 \text{ Hz), 4.27 (dddd, 1H, } J = 5.8, 5.8, 5.3, 5.3 \text{ Hz), 4.18 (dd, 1H, } J = 11.6, 5.3 \text{ Hz), 4.06 (dd, 1H, } J = 11.6, 5.3 \text{ Hz), 4.03 (dd, 1H, } J = 8.7, 5.8 \text{ Hz), 3.70 (dd, 1H, } J = 8.7, 5.8 \text{ Hz), 2.58 (d, 4H, } J = 6.8 \text{ Hz), 2.43 (t, 2H, } J = 7.3 \text{ Hz), 2.23 (dt, 2H, } J = 7.3, 7.3 \text{ Hz), 1.94-2.03 (m, 12H), 1.67 (s, 9H), 1.59 (s, 9H), 1.58 (s, 9H), 1.40 (s, 3H), 1.33 (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl₃) } \delta \text{ 206.5, 172.1, 138.9, 136.3, 131.5, 131.4, 124.2, 124.0, 122.6, 117.8, 109.8, 73.2, 66.4, 65.2, 63.4, 39.9, 39.7, 39.3, 30.1, 26.7, 26.5, 25.6, 25.3, 22.3, 17.7, 16.2, 15.9; FT-IR (KBr) 2966, 2922, 1746, 1714, 1448, 1380, 1215, 1178, 1089, 1057, 839, 771 (cm⁻¹); HRMS (ESI-TOF) calcd. for C₄₀H₆₅O₅ [M+H]+ 625.4832 found 625.4848.}\]

\[(6E)-2,6,7\text{-Trioxabicyclo[2.2.2]octan-4-ylmethyl-2,2\text{-bis}(3,7\text{-dimethylocta-2,6-dien-1-yl})-7,11\text{-dimethyl-3-oxododeca-6,10-dienoate 32}\]

S-19
**β-ketoster** 2,6,7-trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (17) (110 mg, 0.300 mmol, 1.00 eq.)

**geranymethylcarbonate (24)** (159 mg, 0.750 mmol, 2.50 eq.)

**THF** (1.00 mL)

Pd_{2}(dba)$_3$ (7.0 mg, 0.0075 mmol, 0.025 eq.)

dppe (12.0 mg, 0.0300 mmol, 0.100 eq.)

**time** 11 h

**procedure** column chromatography on silica gel with 96 : 4 hexane : ethyl acetate

**product 32** (182 mg, 0.284 mmol, 96%, mixture of $E/Z$-isomers)

$E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.54 (s, 1H), 5.02-5.09 (m, 4H), 4.85 (t, 2H, $J$ = 6.8 Hz), 3.95 (s, 6H), 3.86 (s, 2H), 2.58 (d, 4H, $J$ = 6.8 Hz), 2.39 (t, 2H, $J$ = 7.3 Hz), 2.24 (dt, 2H, $J$ = 7.3, 7.3 Hz), 1.94-2.04 (m, 12H), 1.67 (s, 9H), 1.59 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.3, 171.8, 139.3, 136.6, 131.6, 131.4, 124.1, 123.9, 122.3, 117.4, 101.9, 68.1, 63.5, 62.7, 39.9, 39.7, 39.4, 34.6, 30.3, 26.6, 26.4, 25.6, 22.2, 17.7, 16.3, 16.0; FT-IR (KBr) 2920, 1715, 1446, 1376, 1156, 1036, 998, 925 (cm$^{-1}$); HRMS (ESI-TOF) calcld. for C$_{40}$H$_{63}$O$_6$ [M+H]$^+$ 639.4625 found 639.4626.

(6$E$)-1,3-Bis[2,2-dimethyl-1,3-dioxan-5-yl]oxypropan-2-yl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 33

**β-ketoster**

1,3-bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-7,11-dimethyl-3-oxododeca-6,10-dienoate (18) (250 mg, 0.462 mmol, 1.00 eq.)

**geranymethylcarbonate (24)** (245 mg, 1.16 mmol, 2.50 eq.)

**THF** (1.40 mL)

Pd$_2$(dba)$_3$ (11.0 mg, 0.0116 mmol, 0.0250 eq.)

dppe (18.0 mg, 0.0462 mmol, 0.100 eq.)

**time** 16 h

**procedure** column chromatography on silica gel with 94 : 6 hexane : ethyl acetate

**product 33** (346 mg, 0.3426 mmol, 96%, mixture of $E/Z$-isomers)
E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 5.04-5.10 (m, 5H), 4.86 (t, 2H, J = 6.8 Hz), 3.92 (dd, 4H, J = 12.0, 4.4 Hz), 3.67 (dd, 4H, J = 12.0, 6.2 Hz), 3.60 (d, 4H, J = 5.9 Hz), 3.42 (dt, 2H, J = 6.2, 4.4 Hz), 2.56 (d, 4H, J = 6.8 Hz), 2.45 (t, 2H, J = 7.3 Hz), 2.23 (dt, 2H, J = 7.3, 7.3 Hz), 1.92-2.02 (m, 12H), 1.67 (s, 9H), 1.57-1.60 (m, 18H), 1.41 (s, 6H), 1.38 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 206.5, 171.8, 138.8, 136.3, 131.5, 131.3, 124.2, 124.0, 122.6, 117.9, 98.2, 72.3, 71.0, 66.9, 63.2, 62.4, 40.0, 39.7, 39.1, 30.0, 26.7, 26.5, 25.6, 24.5, 23.7, 22.6, 22.3, 17.7, 16.3, 16.0; FT-IR (KBr) 2968, 2917, 1713, 1449, 1376, 1251, 1199, 1155, 1102, 938, 832, 733, 521 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{40}$H$_{61}$O$_5$ [M+H]$^+$ 813.5881 found 813.5901.

General procedure for deprotection

To a stirred solution of **protected lipid** (1.00 eq.) in **THF/H$_2$O** (4 : 1) was added **TFA** at room temperature under argon atmosphere. After being stirred under **condition**, the reaction mixture was cooled and concentrated in vacuo. The residue was purified by **procedure** to give **product** as a colorless oil.

**(E)-2,3-Dihydroxypropyl-7,11-dimethyl-3-oxodeca-6,10-dienoate (34)**

![E-2,3-Dihydroxypropyl-7,11-dimethyl-3-oxodeca-6,10-dienoate](image)

**protected lipid** (2,2-dimethyl-1,3-dioxolan-4-yl)methyl-7,11-dimethyl-3-oxodeca-6,10-dienoate (16) (295 mg, 0.837 mmol, 1.00 eq.)

**THF/H$_2$O** (4.30 mL)

**TFA** (70.0 μL, 0.920 mmol, 1.10 eq.)

**condition** 60 °C, 20 h

**procedure** column chromatography on silica gel with 98 : 2 chloroform : methanol

**product 34** (238 mg, 0.762 mmol, 91%)

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.04 (m, 2H), 4.21 (d, 2H, J = 5.8 Hz), 3.93 (ddt, 1H, J = 5.8, 5.8, 3.9 Hz), 3.67 (dd, 1H, J = 11.6, 3.9 Hz), 3.58 (dd, 1H, J = 11.6, 5.8 Hz), 3.50 (s, 2H), 3.28 (br-s, 2H), 2.54 (t, 2H, J = 7.3 Hz), 2.25 (dt, 2H, J = 7.3, 5.8 Hz), 2.03 (dt, 2H, J = 6.8, 7.3 Hz), 1.94 (t, 2H, J = 6.8 Hz), 1.65 (s, 3H), 1.58 (s, 3H), 1.57 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 203.5, 167.2, 136.9, 131.4, 124.0, 121.7, 69.8, 65.9, 63.1, 49.0, 43.2, 39.5, 26.5, 25.6, 22.0, 17.6, 15.9; FT-IR (KBr) 3407, 2926, 1742, 1714, 1412, 1377, 1319, 1179, 1121, 1048, 583 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{17}$H$_{29}$O$_5$ [M+H]$^+$ 313.2015 found 313.2025.
2,3-Dihydroxypropyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 35

protected lipid \((2,2\text{-dimethyl-1,3-dioxolan-4-yl)methyl-7,11,15\text{-trimethyl-3-oxohexadec-6-enoate}}\) 19 (190 mg, 0.447 mmol, 1.00 eq.)

THF/H$_2$O (2.50 mL)

TFA (37.0 μL, 0.492 mmol, 1.10 eq.)

condition 60 °C, 20 h

procedure column chromatography on silica gel with 98 : 2 chloroform : methanol

product 35 (128 mg, 0.334 mmol, 78%, mixture of \(E/Z\)-isomers)

\(E\)-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.05 (t, 1H, $J$ = 5.8 Hz), 4.26 (d, 2H, $J$ = 5.4 Hz), 3.96-3.98 (m, 1H), 3.71-3.73 (m, 1H), 3.63 (dd, 1H, $J$ = 11.1, 5.3 Hz), 3.52 (s, 2H), 3.20 (br-s, 2H), 2.57 (t, 2H, $J$ = 7.3 Hz), 2.29 (dt, 2H, $J$ = 7.3, 5.8 Hz), 1.93 (t, 2H, $J$ = 6.8 Hz), 1.60 (s, 3H), 1.52 (m, 1H), 1.01-1.36 (m, 11H), 0.87 (d, 6H, $J$ = 6.8 Hz), 0.84 (d, 3H, $J$ = 6.8 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.4, 167.2, 137.5, 121.4, 69.8, 66.0, 63.1, 49.1, 43.3, 39.9, 39.3, 37.2, 36.7, 32.6, 27.9, 25.3, 24.8, 22.7, 22.6, 22.1, 19.7, 15.9; FT-IR (KBr) 3420, 2955, 2929, 1743, 1715, 1462, 1411, 1317, 1052, 735 (cm$^{-1}$); HRMS (ESI-TOF) calc'd. for C$_{32}$H$_{44}$O$_5$ [M+H]$^+$ 385.2954 found 385.2939.

3-Hydroxy-2,2-bis(hydroxymethyl)propyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 36

protected lipid 2,6,7-trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 20 (71 mg, 0.162 mmol, 1.00 eq.)

THF/H$_2$O (0.810 mL)

TFA (16.0 μL, 0.209 mmol, 1.29 eq.)

condition 50 °C, 7 h

procedure column chromatography on silica gel with 95 : 5 chloroform : methanol

product 36 (60.0 mg, 0.140 mmol, 86%, mixture of \(E/Z\)-isomers)

\(E\)-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.05 (t, 1H, $J$ = 6.6 Hz), 4.22 (s, 2H), 3.64 (s, 6H), 3.53 (s,
2,3-Dihydroxypropyl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate 37

\[
\begin{align*}
\text{protected lipid} \quad & (2,2\text{-dimethyl-1,3-dioxolan-4-yl)methyl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate} \\
& 21 \ (150 \text{ mg, 0.303 mmol, 1.00 eq.}) \\
\text{THF/H}_2\text{O} \ (1.50 \text{ mL}) \\
\text{TFA} \ (25.0 \mu\text{L, 0.333 mmol, 1.10 eq.}) \\
\text{condition} \quad & 60 \degree\text{C, 20} \text{ h} \\
\text{procedure} \quad & \text{column chromatography on silica gel with 98 : 2 chloroform : methanol} \\
\text{product} \quad & 37 \ (90.4 \text{ mg, 0.199 mmol, 71%, mixture of } E/Z-\text{isomers})
\end{align*}
\]

\(E\)-isomer: \(^1\text{H} \text{NMR (400 MHz, CDCl}_3\) \(\delta 5.05 \ (t, 1\text{H, } J = 5.8 \text{ Hz}), 4.26 \ (d, 2\text{H, } J = 5.4 \text{ Hz}), 3.97 \ (br-s, 1\text{H}), 3.71 \ (br-d, 1\text{H, } J = 10.2 \text{ Hz}), 3.63 \ (br-s, 1\text{H}), 3.52 \ (s, 2\text{H}), 3.20 \ (br-s, 2\text{H}), 2.56 \ (t, 2\text{H, } J = 7.3 \text{ Hz}), 2.29 \ (dt, 2\text{H, } J = 7.3, 5.8 \text{ Hz}), 1.93 \ (t, 2\text{H, } J = 7.3 \text{ Hz}), 1.60 \ (s, 3\text{H}), 1.52 \ (m, 1\text{H}), 1.05-1.36 \ (m, 18\text{H}), 0.87 \ (d, 6\text{H, } J = 6.8 \text{ Hz}), 0.84 \ (d, 6\text{H, } J = 6.8 \text{ Hz}); \) \(^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\) \(\delta 203.4, 167.2, 137.5, 121.4, 69.8, 66.0, 63.1, 49.1, 43.3, 39.9, 39.3, 37.4, 37.3, 32.7, 27.9, 25.3, 24.8, 24.4, 22.7, 22.6, 22.1, 19.7, 19.6, 15.9; \) \text{FT-IR (KBr) 3421, 2955, 2928, 2870, 1743, 1716, 1463, 1378, 1318, 1053 (cm}^{-1}); \) \text{HRMS (ESI-TOF) calcd. for C}_{24}\text{H}_{45}\text{O}_6 \ [M+H]^+ 455.3737 \text{ found 455.3721.}
\]

3-Hydroxy-2,2-bis(hydroxymethyl)propyl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate 38

\[
\begin{align*}
\text{protected lipid} \quad & 2,6,7\text{-trioxbicyclo[2.2.2]octan-4-ylmethyl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate} \ 22 \ (171 \text{ mg, 0.335 mmol, 1.00 eq.}) \\
\text{THF/H}_2\text{O} \ (1.70 \text{ mL}) \\
\text{TFA} \ (50.0 \mu\text{L, 0.670 mmol, 2.00 eq.})
\end{align*}
\]
condition 60 °C, 10 h

procedure column chromatography on silica gel with 98 : 2 chloroform : methanol

product 38 (90.9 mg, 0.188 mmol, 56%, mixture of E/Z-isomers)

E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.05 (t, 1H, $J = 7.3$ Hz), 4.27 (s, 2H), 3.66 (s, 6H), 3.53 (s, 2H), 2.84 (br-s, 3H), 2.56 (t, 2H, $J = 7.3$ Hz), 2.29 (dt, 2H, $J = 7.3$, 7.3 Hz), 1.93 (t, 2H, $J = 6.9$ Hz), 1.60 (s, 3H), 1.52 (m, 1H), 1.02-1.36 (m, 18H), 0.87 (d, 6H, $J = 6.8$ Hz), 0.85 (d, 6H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.3, 167.8, 137.6, 121.4, 63.9, 63.3, 49.2, 45.3, 43.5, 39.9, 39.4, 37.4, 37.3, 32.8, 32.7, 27.9, 25.4, 24.8, 24.5, 22.7, 22.6, 22.1, 19.7, 19.7, 15.9; FT-IR (KBr) 3416, 2954, 2928, 1740, 1713, 1464, 1411, 1378, 1319, 1178, 1037, 585 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{29}$H$_{55}$O$_5$ [M+H]$^+$ 499.3999 found 499.3999.

1,3-Bis[(1,3-dihydroxypropan-2-yl)oxy]propan-2-yl-7,11,15,19-tetramethyl-3-oxicos-6-enoate

![Diagram](image)

protected lipid

1,3-bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-7,11,15,19-tetramethyl-3-oxicos-6-enoate

23 (83.0 mg, 0.122 mmol, 1.00 eq.)

THF/H$_2$O (0.61 mL)

TFA (12.0 µL, 0.157 mmol, 1.29 eq.)

condition 50 °C, 2 h

procedure column chromatography on silica gel with 93 : 7 chloroform : methanol

product 39 (70.0 mg, 0.116 mmol, 95%, mixture of E/Z-isomers)

E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.18 (quin, 1H, $J = 5.0$ Hz), 5.04 (t, 1H, $J = 7.2$ Hz), 3.79-3.88 (m, 4H), 3.62-3.76 (m, 8H), 3.48-3.52 (m, 4H), 3.38 (br-s, 4H), 2.55 (t, 2H, $J = 7.2$ Hz), 2.27 (dt, 2H, $J = 7.2$, 7.2 Hz), 1.92 (t, 2H, $J = 6.3$ Hz), 1.59 (s, 3H), 1.52 (m, 1H), 0.99-1.37 (m, 18H), 0.87 (d, 6H, $J = 6.8$ Hz), 0.84 (d, 6H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.3, 166.8, 137.5, 121.4, 81.2, 72.6, 67.9, 62.1, 62.0, 49.2, 43.4, 39.9, 39.3, 37.4, 37.3, 37.2, 36.8, 32.7, 27.9, 25.4, 24.8, 24.4, 22.7, 22.6, 22.0, 19.7, 19.6, 15.9; FT-IR (KBr) 3393, 2928, 1743, 1714, 1463, 1378, 1126, 1051, 736 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{33}$H$_{65}$O$_5$ [M+H]$^+$ 603.4472 found 603.4489.
2,3-Dihydroxypropyl-2-acetyl-5,9-dimethyldeca-4,8-dienoate 40

![Chemical Structure](image)

**protected lipid** (2,2-dimethyl-1,3-dioxolan-4-yl)methyl-2-acetyl-5,9-dimethyldeca-4,8-dienoate 25

(124 mg, 0.352 mmol, 1.00 eq.)

THF/H₂O (1.75 mL)

TFA (35.0 μL, 0.457 mmol, 1.30 eq.)

**condition** 50 °C, 24 h

**procedure** column chromatography on silica gel with 95 : 5 chloroform : methanol

**product 40** (115 mg, quant., mixture of E/Z-isomers)

*E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 5.00 (m, 2H), 4.10-4.22 (m, 2H), 3.86-3.92 (m, 1H), 3.47 3.66 (m, 3H), 2.53 (dd, 2H, J = 7.3, 6.6 Hz), 2.20 (s, 3H), 2.01 (dt, 2H, J = 7.1, 6.6 Hz), 1.94 (t, 2H, J = 7.1 Hz), 1.63 (s, 3H), 1.59 (s, 3H), 1.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 204.2, 169.6, 138.7, 131.5, 123.8, 119.3, 69.8, 65.8, 63.1, 59.5, 39.5, 29.3, 26.9, 26.3, 25.5, 17.6, 16.0; FT-IR (KBr) 3418, 2923, 1742, 1714, 1448, 1359, 1270, 1204, 1154, 1053, 985, 841, 563 (cm⁻¹); HRMS (ESI-TOF) calcd. for C₁₇H₂₉O₅ [M+H]^+ 313.2015 found 313.2017.

2,3-Dihydroxypropyl-2-acetyl-2-(3,7-dimethyleneocta-2,6-dien-1-y1)-5,9-dimethyldeca-4,8-dienoate 41

![Chemical Structure](image)

**protected lipid** (2,2-dimethyl-1,3-dioxolan-4-yl)methyl-2-acetyl-2-(3,7-dimethyleneocta-2,6-dien-1-y1)-5,9-dimethyldeca-4,8-dienoate 26 (83 mg, 0.170 mmol, 1.00 eq.)

THF/H₂O (0.850 mL)

TFA (17.0 μL, 0.222 mmol, 1.30 eq.)

**condition** 50 °C, 24 h

**procedure** column chromatography on silica gel with 95 : 5 chloroform : methanol

**product 41** (76.0 mg, quant., mixture of E/Z-isomers)
E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.02 (t, 2H, $J = 6.4$ Hz), 4.90 (t, 2H, $J = 6.8$ Hz), 4.14-4.23 (m, 2H), 3.92 (tt, 1H, $J = 5.0, 5.0$ Hz), 3.55-3.70 (m, 4H), 2.57 (d, 4H, $J = 6.8$ Hz), 2.12 (s, 3H), 1.97-2.03 (m, 8H), 1.66 (s, 6H), 1.58 (s, 6H), 1.57 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.1, 172.3, 139.3, 131.5, 123.9, 117.5, 69.9, 65.8, 63.8, 63.2, 39.8, 30.3, 26.9, 26.4, 25.6, 17.6, 16.2; FT-IR (KBr) 3419, 2919, 1713, 1445, 1377, 1281, 1217, 1180, 1109, 1062, 986, 830, 564 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{27}$H$_{45}$O$_5$ [M+H]$^+$ 449.3267 found 449.3278.

3-Hydroxy-2,2-bis(hydroxymethyl)propyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethylhyldeca-4,8-dienoate 42

\[
\begin{align*}
\text{protected} & \quad \text{lipid} \\
2,6,7\text{-trioxabicyclo[2.2.2]octan-4-ylmethyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethyl} & \\
\text{deca-4,8-dienoate 27 (361 mg, 0.718 mmol, 1.00 eq.)} \\
\text{THF/H$_2$O (3.60 mL)} & \\
\text{TFA (107 µL, 1.44 mmol, 2.00 eq.)} & \\
\text{condition} & \quad 60 \, ^{\circ}\text{C, 10 h} \\
\text{procedure} & \quad \text{column chromatography on silica gel with 98 : 2 chloroform : methanol} \\
\text{product 42 (249 mg, 0.520 mmol, 72%, mixture of E/Z-isomers)} & \\
E-isomer: & \quad \text{$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.04 (t, 2H, $J = 6.6$ Hz), 4.90 (t, 2H, $J = 6.8$ Hz), 4.19 (s, 2H), 3.63 (d, 6H, $J = 5.4$ Hz), 2.68 (br-s, 3H), 2.59 (d, 4H, $J = 6.8$ Hz), 2.13 (s, 3H), 1.98-2.05 (m, 8H), 1.67 (s, 6H), 1.60 (s, 6H), 1.59 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.7, 172.8, 139.4, 131.6, 123.9, 117.5, 64.0, 63.6, 63.5, 45.2, 39.9, 30.4, 26.9, 26.4, 25.6, 17.7, 16.2; FT-IR (KBr) 3418, 2925, 1709, 1444, 1377, 1281, 1218, 1182, 1045 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{29}$H$_{49}$O$_6$ [M+H]$^+$ 493.3529 found 493.3528.}
\end{align*}
\]

(6E)-2,3-Dihydroxypropyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxodeca-6,10-dienoate 43

\[
\begin{align*}
\text{protected} & \quad \text{lipid} \\
(2,2\text{-dimethyl-1,3-dioxolan-4-yl)methyl} & \\
(E)-2\{(E)-3,7\text{-dimethylocta-2,6-dien-1-yl}\}-7,11\text{-dimethyl-3-oxodeca-6,10-dienoate 28 (74.0 mg,}
\end{align*}
\]

S-26
0.151 mmol, 1.00 eq.)

**THF/H$_2$O** (0.750 mL)

**TFA** (15.0 µL, 0.196 mmol, 1.30 eq.)

**condition** 50 °C, 24 h

**procedure** column chromatography on silica gel with 95 : 5 chloroform : methanol

**product 43** (60.0 mg, 0.134 mmol, 88%, mixture of E/Z-isomers)

$E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 5.01-5.07 (m, 4H), 4.81 (br-s, 2H), 4.15-4.27 (m, 2H), 3.95 (ddt, 1H, $J = 5.8$, 5.8, 3.9 Hz), 3.71 (dd, 1H, $J = 11.6$, 3.9 Hz), 3.61 (dd, 1H, $J = 11.6$, 5.8 Hz), 3.53 (t, 1H, $J = 7.5$ Hz), 2.49-2.60 (m, 4H), 2.24 (dt, 2H, $J = 7.3$, 7.3 Hz), 1.94-2.02 (m, 8H), 1.66 (s, 6H), 1.61 (s, 3H), 1.59 (s, 3H), 1.58 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 206.4, 169.8, 138.9, 136.8, 131.6, 131.4, 124.1, 123.8, 121.9, 119.3, 69.9, 65.7, 63.0, 58.9, 42.6, 39.6, 27.1, 26.6, 26.4, 25.6, 22.0, 17.6, 16.0, 15.9; FT-IR (KBr) 3415, 2967, 2920, 1744, 1714, 1448, 1377, 1195, 1161, 1109, 1055, 984, 836 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{27}$H$_{48}$O$_2$ [M+H]$^+$ 449.3267 found 449.3278.

(6$E$)-3-Hydroxy-2,2-bis(hydroxymethyl)propyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyloctadeca-6,10-dienoate 44

![Structural diagram of 44](image)

**protected** | **lipid**
---|---
2,6,7-trioxabicyclo[2.2.2]octan-4-ylmethyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyloctadeca-6,10-dienoate 29 (53.0 mg, 0.105 mmol, 1.00 eq.)

**THF/H$_2$O** (0.530 mL)

**TFA** (11.0 µL, 0.144 mmol, 1.37 eq.)

**condition** 50 °C, 10 h

**procedure** column chromatography on silica gel with 95 : 5 chloroform : methanol

**product 44** (48.0 mg, 0.0974 mmol, 92%, mixture of E/Z-isomers)

$E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 5.03-5.09 (m, 4H), 4.25 (d, 1H, $J = 11.4$ Hz), 4.20 (d, 1H, $J = 11.4$ Hz), 3.61 (s, 6H), 3.54 (t, 1H, $J = 7.6$ Hz), 2.91 (br-s, 3H), 2.51-2.59 (m, 4H), 2.26 (dt, 2H, $J = 7.3$, 7.3 Hz), 1.96-2.04 (m, 8H), 1.68 (s, 6H), 1.63 (s, 3H), 1.61 (s, 3H), 1.59 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 205.9, 170.3, 138.9, 136.9, 131.6, 131.5, 124.1, 123.8, 121.9, 119.3, 63.8, 63.2, 58.9, 45.4, 42.8, 39.6, 27.2, 26.6, 26.5, 25.6, 22.0, 17.6, 16.1, 16.0; FT-IR (KBr) 3408, 2925, 1739, 1713, 1448, 1377, 1267, 1198, 1161, 1043, 835, 588 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{28}$H$_{49}$O$_6$...
$[\text{M+H}]^+ 493.3529$ found 493.3539.

$(6E)$-1,3-Bis[(1,3-dihydroxypropan-2-yl)oxy]propan-2-yl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 45

\[
\text{protected lipid}
\]

1,3-bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 30 (170 mg, 0.251 mmol, 1.00 eq.)

THF/H$_2$O (1.50 mL)

TFA (25.0 µL, 0.335 mmol, 1.10 eq.)

**condition** 60 °C, 14 h

**procedure** column chromatography on silica gel with 96 : 4 chloroform : methanol

**product** 45 (138 mg, 0.238 mmol, 96%, mixture of $E$/Z-isomers)

$E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.97-5.16 (m, 5H), 3.61-3.81 (m, 12H), 3.44-3.52 (m, 3H), 3.21 (br-s, 4H), 2.48-2.58 (m, 4H), 2.25 (dt, 2H, $J = 7.3$, 7.3 Hz), 1.94-2.04 (m, 8H), 1.67 (s, 6H), 1.62 (s, 3H), 1.61 (s, 3H), 1.59 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.1, 169.1, 138.7, 136.7, 131.6, 131.4, 124.1, 123.9, 122.0, 119.4, 81.1, 76.7, 72.4, 67.9, 67.8, 62.2, 62.0, 58.6, 42.9, 39.6, 27.0, 26.6, 26.5, 25.6, 22.0, 17.6, 16.1, 16.0; FT-IR (KBr) 3394, 2926, 1743, 1713, 1452, 1377, 1202, 1125, 1049, 839 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{33}$H$_{57}$O$_9$ $[\text{M+H}]^+$ 597.4003 found 597.4000.

$(6E)$-2,3-Dihydroxypropyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 46

\[
\text{protected lipid}
\]

(2,2-dimethyl-1,3-dioxolan-4-yl)methyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethyldeca-4,8-dienoate 31 (125 mg, 0.200 mmol, 1.00 eq.)

THF/H$_2$O (1.00 mL)
**TFA** (20.0 µL, 0.261 mmol, 1.30 eq.)

**condition** 50 °C, 48 h

**procedure** column chromatography on silica gel with 95 : 5 chloroform : methanol

**product 46** (82.0 mg, 0.140 mmol, 70%, mixture of E/Z-isomers)

$E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.01-5.05 (m, 4H), 4.89 (t, 2H, $J = 5.8$ Hz), 4.16-4.18 (m, 2H), 3.89 (ddt, 1H, $J = 5.6$, 5.1, 4.7 Hz), 3.65 (dd, 1H, $J = 11.4$, 4.7 Hz), 3.55 (dd, 1H, $J = 11.4$, 5.6 Hz), 2.64 (br-s, 2H), 2.58 (d, 4H, $J = 5.8$ Hz), 2.43 (t, 2H, $J = 7.3$ Hz), 2.22 (q, 2H, $J = 7.3$ Hz), 1.93-2.02 (m, 12H), 1.66 (s, 9H), 1.58 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.5, 172.5, 139.1, 136.4, 131.5, 131.4, 124.1, 123.9, 122.4, 117.7, 69.9, 65.9, 63.6, 63.2, 39.9, 39.6, 39.2, 30.3, 26.6, 26.4, 25.6, 22.2, 17.6, 16.2, 15.9; FT-IR (KBr) 3424, 2968, 2919, 1712, 1447, 1377, 1216, 1178, 1109, 1057, 833 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{35}$H$_{60}$O$_5$ [M+H]$^+$ 585.4519 found 585.4521.

\[
(6E)-3$\text{-Hydroxy-2,2$\text{-bis$(hydroxymethyl)propyl-2,2$-bis$(3,7$-dimethylocta-2,6-dien-1-yl)-7,11$-dimethyl-3$-oxododeca-6,10$-dienoate}$ 47

\[
\begin{center}
\includegraphics[width=0.5\textwidth]{image}
\end{center}

protected lipid

\[
2,6,7$\text{-trioxabicyclo[2.2.2]$\text{octan-4$-ylmethyl-2,2$-bis$(3,7$-dimethylocta-2,6-dien-1-yl)-7,11$-dimethyl-3$-oxododeca-6,10$-dienoate}$ 32 (170 mg, 0.266 mmol, 1.00 eq.)

**THF/H$_2$O** (1.25 mL)

**TFA** (40.0 µL, 0.532 mmol, 2.00 eq.)

**condition** 60 °C, 8 h

**procedure** column chromatography on silica gel with 98 : 2 chloroform : methanol

**product 47** (163 mg, 0.264 mmol, 98%, mixture of E/Z-isomers)

$E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.02-5.09 (m, 4H), 4.89 (t, 2H, $J = 7.1$ Hz), 4.20 (s, 2H), 3.62 (s, 6H), 2.59 (t, 4H, $J = 7.1$ Hz), 2.44 (t, 2H, $J = 7.5$ Hz), 2.23 (dt, 2H, $J = 7.5$, 7.5 Hz), 1.94-2.03 (m, 12H), 1.67 (s, 9H), 1.59 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.5, 173.1, 139.3, 136.6, 131.6, 131.4, 124.1, 123.9, 122.4, 117.6, 64.0, 63.8, 63.6, 45.3, 39.9, 39.7, 39.3, 30.4, 26.6, 26.5, 25.6, 22.1, 17.7, 16.3, 16.0; FT-IR (KBr) 3419, 2967, 2918, 1709, 1446, 1377, 1278, 1217, 1180, 1045, 833, 588 (cm$^{-1}$); HRMS (ESI-TOF) calcd. for C$_{39}$H$_{65}$O$_6$ [M+H]$^+$ 629.4781 found 629.4787.
(6E)-1,3-Bis[(1,3-dihydroxypropan-2-yl)oxy]propan-2-yl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 48

protected lipid

1,3-bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 33 (300 mg, 0.369 mmol, 1.00 eq.)

THF/H₂O (2.00 mL)

TFA (30.0 µL, 0.406 mmol, 1.10 eq.)

condition 60 °C; 2 h

procedure column chromatography on silica gel with 96:4 chloroform : methanol

product 48 (252 mg, 0.344 mmol, 98%, mixture of E/Z-isomers)

E-isomer: H NMR (400 MHz, CDCl₃) δ 5.15 (quin, 1H, J = 4.8 Hz), 5.02-5.09 (m, 4H), 4.88 (t, 2H, J = 6.6 Hz), 3.79 (d, 4H, J = 4.8 Hz), 3.66-3.73 (br, 8H), 3.48 (br, 2H), 2.76-2.88 (br, 4H), 2.58 (br-s, 4H), 2.46 (t, 2H, J = 7.3 Hz), 2.23 (dt, 2H, J = 7.3, 7.3 Hz), 1.93-2.05 (m, 12H), 1.67 (s, 9H), 1.59-1.60 (m, 18H); C NMR (100 MHz, CDCl₃) δ 207.7, 171.8, 139.2, 136.5, 131.6, 131.4, 124.1, 123.9, 122.4, 117.7, 81.1, 72.2, 67.9, 63.5, 62.4, 62.2, 39.9, 39.7, 39.3, 30.2, 26.7, 26.5, 25.6, 22.2, 17.7, 16.3, 16.0; FT-IR (KBr) 3405, 2926, 1710, 1445, 1377, 1277, 1217, 1124, 1050, 833 (cm⁻¹);

HRMS (ESI-TOF) calcd. for C₄₉H₇₂O₉ [M+H]+ 733.5255 found 733.5240.

Preparation of samples

The compounds 34-38, 42, 44, and 48 were treated with excess water and stirred well with a spatula. As a result, highly viscous and clear liquids were obtained for compounds 35 and 37, viscous and white liquids were obtained for compounds 42, 44, and 48, and less viscous and white liquid were obtained for compounds 34, 36, and 38 as described in the manuscript. These liquids were used for optical microscopy and SAXS analyses as described below.

Polarizing optical microscopy analysis
Figure S-1 Polarizing optical microscopy images of 8 compounds: 34-38, 42, 44, and 48.

SAXS analysis

SAXS measurements were performed by a NANO-Viewer (Rigaku) operating at 45 kV and 60 mA with Cu Kα radiation (\( \lambda = 0.1542 \text{ nm} \)), equipped with a confocal mirror. Imaging plates BAS-IP SR 127 (Fujifilm) were used as a detector (2300 × 2300 pixels, 50 μm/pixel, the dynamic range of ca. 2.6 × 10^5), which were read by an R-AXIS DS3C (Rigaku). Silver behenate (\( d_{001} = 5.8380 \text{ nm} \)) was used as a standard sample. Viscous liquids composed of amphiphiles and water (LC phases) were filled in a brass cell with a thickness of 2 mm and sealed by kapton® films. X-ray radiation to the sample cell was conducted for 1–2 h at room temperature, depending on scattering intensity of each sample. A sample-to-detector distance was set to 300–500 mm, depending on \( d \)-spacings of each LC phase.

Two-dimensional scattering patterns were converted to one-dimensional data [intensity vs scattering vector \( q = 4\pi \sin(\theta)/\lambda, \) where \( \theta \) is the Bragg angle and \( \lambda \) is the wavelength of X-ray) by the circular average method. In many cases, background contribution was estimated by the Sonneveld and Visser method. In other cases, lines or broad Gaussian functions were approximately used to represent background. After background subtraction, peak separation by pseudo-Voigt functions was performed using the damped least-squares method. A series of X-ray structure analyses were done using the handmade GUI software developed by Marubayashi.

References

Alkylated dioxinones 8a and 8c

$^1$H NMR
Alkylated dioxinones 9a-9c

$^1$H NMR

Alkylated dioxinones 9a-9c
$^{13}$C NMR

Alkylated dioxinones 10a-10c

$^1$H NMR

Alkylated dioxinones 10a-10c
$^{13}$C NMR

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-3-oxobutanoate (14)

$^1$H NMR

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-3-oxobutanoate (14)
$^{13}$C NMR

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-3-oxobutanoate (15)

$^1$H NMR

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-3-oxobutanoate (15)
(E)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (16)

$^1$H NMR
(E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (17)

$^{13}$C NMR

(E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (17)

$^1$H NMR

S-38
(E)-1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-7,11-dimethyl-3-oxododeca-6,10-dienoate (18) $^1$H NMR

(E)-1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-7,11-dimethyl-3-oxododeca-6,10-dienoate
noate (18) $^{13}$C NMR

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 19

$^1$H NMR

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 19

S-40
$^{13}$C NMR

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 20

$^1$H NMR

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 20
$^{13}$C NMR

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11,15,19-tetramethyl-3-oxicos-6-enoate 21

$^1$H NMR

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-7,11,15,19-tetramethyl-3-oxicos-6-enoate 21
$^{13}$C NMR

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11,19-tetramethyl-3-oxoicos-6-enoate 22

$^1$H NMR

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-7,11,19-tetramethyl-3-oxoicos-6-enoate 22
1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-7,11,15,19-tetramethyl-3-oxoicos-6-enolate

$^{13}$C NMR

1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-7,11,15,19-tetramethyl-3-oxoicos-6-enolate

$^1$H NMR
(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2-acetyl-5,9-dimethyldeca-4,8-dienoate 25

$^1$H NMR

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2-acetyl-5,9-dimethyldeca-4,8-dienoate 25
$^{13}$C NMR

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethyldeca-4,8-dienoate $^{1}$H NMR

$^{1}$H NMR
Iodeca-4,8-dienoate 26 $^{13}$C NMR

2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dime thyldeca-4,8-dienoate 27 $^1$H NMR
thyldeca-4,8-dienoate $^{13}$C NMR

(6E)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate $^1$H NMR

(6E)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate $^1$H NMR
(6E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 28 \(^{13}\)C NMR

(6E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 29 \(^1\)H NMR
(6E)-1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 30 $^1$H NMR

(6E)-1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate $^{13}$C NMR
7,11-dimethyl-3-oxododeca-6,10-dienoate $^{13}$C NMR

(6$E$)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate $^1$H NMR

(6$E$)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimeth
(6E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 31 $^{13}$C NMR

(6E)-2,6,7-Trioxabicyclo[2.2.2]octan-4-ylmethyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 32 $^1$H NMR
methyl-3-oxododeca-6,10-dienoate $^{13}$C NMR

(6$E$)-1,3-Bis[(2,2-dimethyl-1,3-dioxan-5-yl)oxy]propan-2-yl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate $^1$H NMR
(E)-2,3-Dihydroxypropyl-7,11-dimethyl-3-oxododeca-6,10-dienoate (34)

$^1$H NMR
$^{13}$C NMR

2,3-Dihydroxypropyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 35

$^1$H NMR

2,3-Dihydroxypropyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 35
$^{13}$C NMR

3-Hydroxy-2,2-bis(hydroxymethyl)propyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 36

$^1$H NMR

3-Hydroxy-2,2-bis(hydroxymethyl)propyl-7,11,15-trimethyl-3-oxohexadec-6-enoate 36
$^{13}$C NMR

2,3-Dihydroxypropyl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate 37

$^1$H NMR

2,3-Dihydroxypropyl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate 37
$^{13}$C NMR

3-Hydroxy-2,2-bis(hydroxymethyl)propyl-7,11,15,19-tetramethyl-3-oxicos-6-enoate 38

$^1$H NMR

3-Hydroxy-2,2-bis(hydroxymethyl)propyl-7,11,15,19-tetramethyl-3-oxicos-6-enoate 38
$^{13}$C NMR

1,3-Bis[(1,3-dihydroxypropan-2-yl)oxy]propan-2-yl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate

$^1$H NMR

1,3-Bis[(1,3-dihydroxypropan-2-yl)oxy]propan-2-yl-7,11,15,19-tetramethyl-3-oxoicos-6-enoate
2,3-Dihydroxypropyl-2-acetyl-5,9-dimethyldeca-4,8-dienoate 40

$^{13}$C NMR

2,3-Dihydroxypropyl-2-acetyl-5,9-dimethyldeca-4,8-dienoate 40

$^1$H NMR
2,3-Dihydroxypropyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethyldeca-4,8-dienoate

$^{13}$C NMR

2,3-Dihydroxypropyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethyldeca-4,8-dienoate

$^1$H NMR
3-Hydroxy-2,2-bis(hydroxymethyl)propyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethylocta-4,8-dienoate 41 $^{13}$C NMR

3-Hydroxy-2,2-bis(hydroxymethyl)propyl-2-acetyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-5,9-dimethylocta-4,8-dienoate 42 $^1$H NMR
hyldeca-4,8-dienoate $^{13}$C NMR

(6E)-2,3-Dihydroxypropyl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate $^{1}H$ NMR
dienoate $^{13}$C NMR

(6$E$)-3-Hydroxy-2,2-bis(hydroxymethyl)propyl-2-(3,7-dimethyleneocta-2,6-dien-1-yl)-7,11-dimethyldodeca-6,10-dienoate $^1$H NMR

(6$E$)-3-Hydroxy-2,2-bis(hydroxymethyl)propyl-2-(3,7-dimethyleneocta-2,6-dien-1-yl)-7,11-dimethyldodeca-6,10-dienoate $^1$H NMR
1-3-oxododeca-6,10-dienoate 44 $^{13}$C NMR

(6$E$)-1,3-Bis[(1,3-dihydroxypropan-2-yl)oxy]propan-2-yl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,1 1-dimethyl-3-oxododeca-6,10-dienoate 45 $^1$H NMR

(6$E$)-1,3-Bis[(1,3-dihydroxypropan-2-yl)oxy]propan-2-yl-2-(3,7-dimethylocta-2,6-dien-1-yl)-7,1
1-dimethyl-3-oxodeca-6,10-dienoate $^{13}$C NMR

(6E)-2,3-Dihydroxypropyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxodeca-6,10-dienoate $^1$H NMR

(6E)-2,3-Dihydroxypropyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxodeca-6
(6E)-3-Hydroxy-2,2-bis(hydroxymethyl)propyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate 46 \( ^{13}C \) NMR

(6E)-3-Hydroxy-2,2-bis(hydroxymethyl)propyl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-di
dimethyl-3-oxododeca-6,10-dienoate 47 \( ^{1}H \) NMR
methyl-3-oxododeca-6,10-dienoate $^{13}$C NMR

$^{(6E)}$-1,3-Bis[1,3-dihydroxypropan-2-yl]oxy]propan-2-yl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)-7,11-dimethyl-3-oxododeca-6,10-dienoate $^1$H NMR

$^{(6E)}$-1,3-Bis[1,3-dihydroxypropan-2-yl]oxy]propan-2-yl-2,2-bis(3,7-dimethylocta-2,6-dien-1-yl)