Supporting Information

Stereocontrolled Total Synthesis of (-)-Callipeltoside A

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Methyl-(2*E*,5*S*,6*E*,8*E*)-5-hydroxy-9-iodo-3-methyl-2,6,8-nontrienoate **10**

To a suspension of calcium hydride (4.27 g, 104.0 mmol, 20 eq.) and (*R*)-BINOL (1 g, 3.5 mmol, 0.5 eq.) in THF (8 ml) was added titanium tetraisopropoxide (1 M in THF, 3.5 ml, 0.5 eq.) resulting in a deep orange slurry. After stirring for 1 h at r.t. the reaction was cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of aldehyde **9** (1.45 g, 6.99 mmol 1 eq.) in THF (8 ml) was added. A solution of silyl ketene acetal **8** (3.19 ml, 13.97 mmol 2 eq.) in THF (4 ml) was added slowly after another 30 min at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 70 h at $-78\text{ }^{\circ}\text{C}$ in the dark before being quenched by carefully pouring the mixture into a cooled ($0\text{ }^{\circ}\text{C}$) NaHCO_3 solution (300 ml). Et_2O (200 ml) was added and the phases were separated. The aqueous phase was extracted with Et_2O (4 x 100 ml). The combined organic extracts were dried (MgSO_4), and concentrated *in vacuo*. The crude product was purified by flash column chromatography (3 % Et_3N in PE/ EtOAc 9:1) to give the alcohol **10** (2.16 g, 96%) as a colourless oil with an enantiomeric excess of 94 %, as determined by chiral HPLC.

R_f 0.14 (PE/ EtOAc 4:1); $[\alpha]_D^{20} = +22.6$ ($c = 1.65$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 3434 (s, C-OH), 1716 (s, C=O);

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.02 (1H, ddd, $J = 14.4, 10.8, 0.7$ Hz, $\text{C}_{16}\text{-H}$), 6.38 (1H, d, $J = 14.4$ Hz, $\text{C}_{17}\text{-H}$), 6.21 (1H, ddd, $J = 15.3, 10.8, 1.5$ Hz, $\text{C}_{15}\text{-H}$), 5.75 – 5.70 (1H, m, $\text{C}_{14}\text{-H}$), 5.74 (1H, d, $J = 1.3$ Hz, $\text{C}_{10}\text{-H}$), 4.28 – 4.42 (1H, m, $\text{C}_{13}\text{-H}$), 3.69 (3H, s, $\text{C}_9\text{-OCH}_3$), 2.37 (1H, d, $J =$

1.2 Hz, C₁₂-H_XH_Y), 2.35 (1H, d, $J = 1.0$ Hz, C₁₂-H_XH_Y), 2.20 (3H, d, $J = 1.2$ Hz, C₁₁-CH₃), 1.67 (1H, bs, OH);

HRMS calculated for C₁₁H₁₅IO [M+Na]⁺ 344.9964, found 344.9974;

HPLC: 10 % isopropanol in hexane, (*R*)-enantiomer: retention time = 11.22 min, (*S*)-enantiomer: retention time = 23.81 min. The ratio of the enantiomers was determined with 98.1:1.9 (96 % ee).

Methyl-(2*E*,5*S*,6*E*,8*E*)-5-(*tert*-butyldimethylsilyloxy)-9-iodo-3-methyl-2,6,8-nontrienoate

R_f 0.57 (PE/EtOAc 4:1); $[\alpha]_D^{20} = +8.3$ ($c = 0.95$, CHCl₃);

IR $\nu_{\max}$ (cm⁻¹, thin film) = 1722 (s, C=O);

¹H NMR (400 MHz, CDCl₃) δ = 7.00 (1H, dd, $J = 14.3, 10.6$ Hz, C₁₆-H), 6.32 (1H, d, $J = 14.3$ Hz, C₁₇-H), 6.10 (1H, ddd, $J = 16.0, 10.8, 1.0$ Hz, C₁₅-H), 5.67 (1H, dd, $J = 15.0, 6.3$ Hz, C₁₄-H), 5.67 (1H, d, $J = 1.2$ Hz, C₁₀-H), 4.26 – 4.31 (1H, m, C₁₃-H), 3.68 (3H, s, C₉-OCH₃), 2.34 (1H, ddd, $J = 13.0, 7.3, 0.8$ Hz, C₁₂-H_XH_Y), 2.26 (1H, ddd, $J = 13.0, 5.5, 0.7$ Hz, C₁₂-H_XH_Y), 2.17 (3H, d, $J = 1.5$ Hz, C₁₁-CH₃), 0.87 (9H, s, SiC(CH₃)₃), 0.01 (3H, s, Si-CH₃), 0.00 (3H, s, Si-CH₃);

¹³C NMR (100 MHz, CDCl₃) δ = 166.9, 155.7, 144.4, 136.8, 129.4, 118.3, 79.3, 71.1, 50.8, 49.6, 25.8, 19.6, -4.5, -5.0.

HRMS calculated for C₁₇H₂₉IO₃Si [M+Na]⁺ 459.0828, found 459.0825.

Methyl-(2*E*,5*S*,6*E*,8*E*)-5-(*tert*-butyldimethylsilyloxy)-9-iodo-3-methyl-2,6,8-nontrien-1-ol

R_f 0.27 (PE/EtOAc 4:1); $[\alpha]_D^{20} = +3.5$ ($c = 1.02$, CHCl₃);

IR $\nu_{\max}$ (cm^{-1} , thin film) = 3355 (s, C-OH);

^1H NMR (400 MHz, CDCl_3) δ = 7.00 (1H, dd, J = 14.6, 10.8 Hz, C₁₆-H), 6.28 (1H, d, J = 14.6 Hz, C₁₇-H), 6.08 (1H, ddd, J = 15.3, 10.8, 1.3 Hz, C₁₅-H), 5.69 (1H, dd, J = 15.3, 6.0 Hz, C₁₄-H), 5.42 (1H, tq, J = 6.8, 1.2 Hz, C₁₀-H), 4.26 – 4.20 (1H, m, C₁₃-H), 4.14 (2H, d, J = 7.0 Hz, C₉-H), 2.24 (1H, dd, J = 13.2, 7.0 Hz, C₁₂-H_XH_Y), 2.15 (1H, dd, J = 13.3, 6.0 Hz, C₁₂-H_XH_Y), 1.68 (3H, d, J = 1.3 Hz, C₁₁-CH₃), 0.88 (9H, s, SiC(CH₃)₃), 0.02 (3H, s, Si-CH₃), 0.01 (3H, s, Si-CH₃);

HRMS calculated for C₁₆H₂₉IO₂Si [M+Na]⁺ 431.0879, found 431.0864.

Methyl-(2*E*,5*S*,6*E*,8*E*)-5-(*tert*-butyldimethylsilyloxy)-9-iodo-3-methyl-2,6,8-nontrienal **5**

R_f 0.58. (PE/EtOAc 2:1); **$[\alpha]_D^{20}$** = + 2.4 (c = 1.00, CHCl_3);

IR $\nu_{\max}$ (cm^{-1} , thin film) = 1667 (s, C=O);

^1H NMR (400 MHz, CDCl_3) δ = 9.98 (1H, d, J = 8.0 Hz, C₉-H), 7.00 (1H, dd, J = 14.6, 10.8 Hz, C₁₆-H), 6.34 (1H, d, J = 14.6 Hz, C₁₇-H), 6.11 (1H, dd, J = 15.1, 10.8 Hz, C₁₅-H), 5.87 (1H, dd, J = 8.0, 1.2 Hz, C₁₀-H), 5.67 (1H, dd, J = 15.3, 6.2 Hz, C₁₄-H), 4.30 – 4.35 (1H, m, C₁₃-H), 2.41 (1H, dd, J = 13.1, 7.3 Hz, C₁₂-H_XH_Y), 2.34 (1H, dd, J = 13.1, 5.2 Hz, C₁₂-H_XH_Y), 2.19 (3H, d, J = 1.3 Hz, C₁₁-CH₃), 0.87 (9H, s, SiC(CH₃)₃), 0.02 (3H, s, Si-CH₃), 0.01 (3H, s, Si-CH₃);

HRMS calculated for C₁₆H₂₇IO₂Si [M+Na]⁺ 429.0723, found 429.0711.

Methyl-3-(3,4-dimethoxy-benzyloxy)-2-(*R*)- propionate

R_f 0.49 (PE/EtOAc 1:1); **$[\alpha]_D^{20}$** = - 8.5 (c = 1.14, CHCl_3);

IR $\nu_{\max}$ (cm^{-1} , thin film) = 1737 (s, C=O);

^1H NMR (400 MHz, CDCl_3) δ = 6.85 – 6.79 (3H, m, ArH), 4.43 (2H, s, OCH_2Ar), 3.86 (3H, s, ArOCH_3), 3.84 (3H, s, ArOCH_3), 3.66 (3H, s, $\text{C}_7\text{-OCH}_3$), 3.62 (1H, dd, J = 9.3, 7.3 Hz $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 3.44 (1H, dd, J = 9.2, 5.8 Hz $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 2.80 – 2.71 (1H, m, $\text{C}_6\text{-H}$), 1.15 (3H, d, J = 7.0 Hz, $\text{C}_6\text{-CH}_3$);

^{13}C NMR (100 MHz, CDCl_3) δ = 175.2, 148.9, 148.5, 130.6, 120.0, 110.9, 110.8, 72.9, 71.6, 55.8, 55.7, 51.6, 40.1, 13.9;

HRMS calculated for $\text{C}_{14}\text{H}_{20}\text{O}_5$ $[\text{M}+\text{NH}_4]^+$ 286.1654, found 286.1649.

(R)-3-(3,4-Dimethoxy-benzyloxy)-N-methoxy-N-2-dimethylpropionate

R_f 0.21 (PE/EtOAc 1:1); $[\alpha]_D^{20}$ = - 7.9 (c = 1.04, CHCl_3);

IR $\nu_{\max}$ (cm^{-1} , thin film) = 1650 (s, C=O);

^1H NMR (400 MHz, CDCl_3) δ = 6.87–6.80 (3H, m, ArH), 4.45 (2H, AB system, J_{AB} = 12.0 Hz, OCH_2Ar), 3.87 (3H, s, ArOCH_3), 3.86 (3H, s, ArOCH_3), 3.71–3.67 (1H, m, $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 3.69 (3H, s, $\text{C}_7\text{-NOCH}_3$), 3.40 (1H, dd, J = 8.8, 5.8 Hz, $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 3.30 – 3.23 (1H, m, $\text{C}_6\text{-H}$), 3.20 (3H, s, $\text{C}_7\text{-NCH}_3$), 1.11 (3H, d, J = 7.0 Hz, $\text{C}_6\text{-CH}_3$);

^{13}C NMR (125 MHz, CDCl_3) δ = 175.9, 148.9, 148.4, 130.9, 120.0, 110.9, 110.8, 73.0, 72.3, 65.1, 61.4, 55.8, 55.7, 35.8, 14.1;

HRMS calculated for $\text{C}_{15}\text{H}_{23}\text{O}_5$ $[\text{M}+\text{H}]^+$ 298.1654, found 298.1651.

3-(3,4-Dimethoxy-benzyloxy)-2-(R)-methylpentan-3-one 6

R_f 0.48 (PE/EtOAc 1:1); $[\alpha]_D^{20} = -19.3$ ($c = 1.31$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 1714 (s, C=O);

$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 6.84 - 6.80$ (3H, m, ArH), 4.40 (2H, s, OCH_2Ar), 3.87 (3H, s, ArOCH_3), 3.85 (3H, s, ArOCH_3), 3.59 (1H, dd, $J = 8.9, 8.1$ Hz $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 3.42 (1H, dd, $J = 9.0, 5.4$ Hz $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 2.91 – 2.82 (1H, m, $\text{C}_6\text{-H}$), 2.49 (2H, q, $J = 7.3$ Hz, $\text{C}_8\text{-H}_2$), 1.05 (3H, d, $J = 6.9$ Hz, $\text{C}_6\text{-CH}_3$), 1.02 (3H, t, $J = 7.4$ Hz, $\text{C}_8\text{-CH}_3$);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) $\delta = 213.6, 149.0, 148.5, 130.7, 120.0, 110.9, 110.8, 73.0, 72.1, 55.8, 55.7, 46.1, 35.2, 13.6, 7.5$;

HRMS calculated for $\text{C}_{15}\text{H}_{22}\text{O}_4$ $[\text{M}+\text{NH}_4]^+$ 284.1862, found 284.1861.

(6E,10E,12E)(2R,4R,5R,13R)-9-(tert-Butyl-dimethyl-silanyloxy)-1-(3,4-dimethoxy-benzyloxy)-5-hydroxy-13-iodo-2,4,7-trimethyl-trideca-6,10,12-trien-3-one 11

R_f 0.31 (PE/EtOAc 1:1); $[\alpha]_D^{20} = -13.3$ ($c = 1.14$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 3520 (br, C-OH), 1714 (s, C=O);

$^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 6.99$ (1H, dd, $J = 14.3, 10.7$ Hz, $\text{C}_{16}\text{-H}$), 6.83 – 6.82 (3H, m, Ar-H), 6.27 (1H, d, $J = 14.5$ Hz, $\text{C}_{17}\text{-H}$), 6.07 (1H, dd, $J = 15.0, 10.7$ Hz, $\text{C}_{15}\text{-H}$), 5.69 (1H, dd, $J = 15.4, 6.0$ Hz, $\text{C}_{14}\text{-H}$), 5.12 (1H, dd, $J = 9.0, 1.1$ Hz, $\text{C}_{10}\text{-H}$), 4.50 (1H, td, $J = 9.0, 4.1$ Hz, $\text{C}_9\text{-H}$), 4.44 and 4.41 (2H, AB system, $J_{\text{AB}} = 11.8$ Hz, OCH_2Ar), 4.30 – 4.26 (1H, m, $\text{C}_{13}\text{-H}$), 3.88 (3H, s, ArOCH_3), 3.87 (3H, s, ArOCH_3), 3.67 (1H, t, $J = 8.8$ Hz, $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 3.42 (1H, dd, $J = 9.0, 4.9$ Hz, $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 3.09 – 3.05 (1H, m, $\text{C}_6\text{-H}$), 2.71 (1H, dq, $J = 8.6, 7.2$ Hz, $\text{C}_8\text{-H}$), 2.53 (1H, d, $J = 4.1$ Hz $\text{C}_9\text{-OH}$), 2.28 (1H, ddd, $J = 13.4, 6.2, 0.9$ Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 2.18 (1H, ddd, $J = 13.4, 5.9, 0.9$ Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 1.72 (3H, d, $J = 1.3$ Hz, $\text{C}_{11}\text{-CH}_3$), 1.06 (3H, d, $J = 7.1$ Hz, $\text{C}_6\text{-CH}_3$), 1.00 (3H, d, $J = 7.2$ Hz, $\text{C}_8\text{-CH}_3$), 0.88 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.03 (3H, s, SiCH_3), 0.01 (3H, s, SiCH_3);

^{13}C NMR (100 MHz, CDCl_3) δ = 217.28, 149.0, 148.6, 144.6, 137.4, 136.6, 130.4, 129.0, 128.5, 120.1, 110.92, 110.85, 78.6, 73.2, 71.9, 71.7, 70.3, 55.9, 55.8, 52.4, 48.1, 45.8, 25.8, 18.2, 18.0, 13.5, 13.4, -4.5, -4.8;

HRMS calculated for $\text{C}_{31}\text{H}_{49}\text{IO}_6\text{Si}$ $[\text{M}+\text{NH}_4]^+$ 690.2687, found 690.2684.

Propionic acid (1*R*,5*R*)-5-(*tert*-butyl-dimethyl-silanyloxy)-1-[(1*S*,2*R*,3*S*)-4-(3,4-dimethoxy-benzyloxy)-1,3-dimethyl-2-hydroxy-butyl]-(2*E*,6*E*,8*E*)-9-iodo-3-methyl-nona-2.6.8-trienyl ester

R_f 0.35 (PE/EtOAc 2:1); $[\alpha]_D^{20}$ = -20.1 (c = 1.20, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 3502 (s, C-OH), 1731 (s, C=O);

^1H NMR (400 MHz, CDCl_3) δ = 6.95 (1H, dd, J = 14.1, 10.5 Hz, $\text{C}_{16}\text{-H}$), 6.86 – 6.81 (3H, m, Ar-H), 6.25 (1H, d, J = 14.6 Hz, $\text{C}_{17}\text{-H}$), 6.03 (1H, ddd, J = 15.1, 10.6, 1.0 Hz, $\text{C}_{15}\text{-H}$), 5.63 (1H, dd, J = 15.0, 6.0 Hz, $\text{C}_{14}\text{-H}$), 5.47 (1H, app. t, J = 9.6 Hz, $\text{C}_9\text{-H}$), 5.06 (1H, dd, J = 9.6, 1.3 Hz, $\text{C}_{10}\text{-H}$), 4.47 and 4.43 (2H, AB system, J_{AB} = 11.8 Hz, OCH_2Ar), 4.28 – 4.23 (1H, m, $\text{C}_{13}\text{-H}$), 3.88 (3H, s, ArOCH_3), 3.87 (3H, s, ArOCH_3), 3.52 (1H, d, J = 6.0, $\text{C}_7\text{-H}$), 3.49 (1H, dt, J = 9.3, 2.2 Hz, $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 3.29 (1H, d, 2.8 Hz, $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 2.36 – 2.23 (3H, m, CH_2CH_3 and $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 2.16 (1H, dd, J = 13.3, 7.3 Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 1.94 – 1.87 (1H, m, $\text{C}_6\text{-H}$), 1.79 – 1.71 (1H, m, $\text{C}_8\text{-H}$), 1.76 (3H, d, J = 1.5 Hz, $\text{C}_{11}\text{-CH}_3$), 1.12 (3H, t, J = 7.5 Hz, CH_2CH_3), 0.88 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.82 (3H, d, J = 7.0 Hz, $\text{C}_6\text{-CH}_3$), 0.80 (3H, d, J = 7.0 Hz, $\text{C}_8\text{-CH}_3$), 0.03 (3H, s, SiCH_3), 0.01 (3H, s, SiCH_3);

^{13}C NMR (100 MHz, CDCl_3) δ = 174.1, 148.9, 148.5, 144.7, 137.7, 137.4, 130.5, 128.9, 126.1, 120.2, 110.9, 110.8, 78.5, 75.2, 73.2, 73.1, 72.2, 71.5, 55.9, 55.8, 48.4, 39.3, 36.0, 27.8, 25.8, 18.2, 18.0, 13.5, 9.2, 8.2, -4.5, -4.9;

HRMS calculated for $\text{C}_{34}\text{H}_{55}\text{IO}_7\text{Si}$ $[\text{M}+\text{NH}_4]^+$ 753.2661, found 753.2660.

Propionic acid (1*R*,5*R*)-5-(*tert*-butyl-dimethyl-silanyloxy)-1-[(1*R*,2*R*,3*R*)-4-(3,4-dimethoxybenzyloxy)-1,3-dimethyl-2-triethylsilanyloxy-butyl]-(2*E*,6*E*,8*E*)-9-iodo-3-methyl-nona-2,6,8-trienyl ester

R_f 0.66 (PE/EtOAc 2:1); $[\alpha]_D^{20} = +2.3$ ($c = 0.97$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 1732 (s, C=O);

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 6.95 (1H, dd, $J = 14.4, 10.8$ Hz, C₁₆-H), 6.90 – 6.82 (3H, m, Ar-H), 6.24 (1H, d, $J = 14.5$ Hz, C₁₇-H), 6.01 (1H, ddd, $J = 15.0, 11.0, 1.3$ Hz, C₁₅-H), 5.62 (1H, dd, $J = 15.3, 6.0$ Hz, C₁₄-H), 5.12 (1H, app. t, $J = 9.8$, C₉-H), 4.93 (1H, dd, $J = 9.5, 1.2$ Hz, C₁₀-H), 4.47 and 4.43 (2H, AB system, $J_{\text{AB}} = 11.8$ Hz, OCH₂Ar), 4.28 – 4.22 (1H, m, C₁₃-H), 3.89 (3H, s, Ar OCH₃), 3.88 (3H, s, ArOCH₃), 3.74 (1H, dd, $J = 7.5, 1.8$, C₇-H), 3.52 (1H, dd, $J = 8.8, 4.3$ Hz, C₅-H_XH_Y), 3.24 (1H, dd, $J = 9.0, 7.5$ Hz, C₅-H_XH_Y), 2.29 (1H, dd, $J = 13.3, 5.5$ Hz, C₁₂-H_XH_Y), 2.28 (2H, qd, $J = 7.8, 3.2$ Hz, CH₂CH₃), 2.16 (1H, dd, $J = 13.0, 8.0$ Hz, C₁₂-H_XH_Y), 1.93 – 1.87 (1H, m, C₆-H), 1.82 – 1.75 (1H, m, C₈-H), 1.77 (3H, d, $J = 1.2$ Hz, C₁₁-CH₃), 1.08 (3H, t, $J = 7.5$ Hz, CH₂CH₃), 0.93 (9H, t, $J = 7.8$ Hz, SiCH₂CH₃), 1.0 – 0.91 (3H, m, C₆-CH₃), 0.88 (9H, s, SiC(CH₃)₃), 0.76 (3H, d, $J = 7.0$ Hz, C₈-CH₃), 0.56 (6H, q, $J = 7.8$ Hz, SiCH₂CH₃), 0.04 (3H, s, SiCH₃), 0.02 (3H, s, SiCH₃);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 173.5, 149.0, 148.8, 144.8, 137.5, 137.3, 131.4, 128.9, 126.2, 120.1, 110.93, 110.88, 78.3, 77.2, 73.1, 72.9, 72.2, 71.4, 55.9, 55.8, 48.7, 39.2, 38.8, 27.8, 25.8, 18.2, 17.8, 14.4, 9.3, 9.1, 7.1, 5.4, -4.5, -4.8;

HRMS calculated for $\text{C}_{40}\text{H}_{69}\text{IO}_7\text{Si}_2$ $[\text{M}+\text{Na}]^+$ 867.3524, found: 867.3550.

(6*E*,10*E*,12*E*)(2*R*,3*S*,4*R*,5*R*,9*R*)-9-(*tert*-Butyl-dimethyl-silanyloxy)-1-(3,4-dimethoxybenzyloxy)-13-iodo-2,4,7-trimethyl-3-triethylsilanyloxy-trideca-6,10,12-trien-5-ol

R_f 0.53 (PE/EtOAc 2:1); $[\alpha]_D^{20} = +2.0$ ($c = 1.28$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 3527 (s, C-OH);

^1H NMR (400 MHz, CDCl_3) δ = 6.99 (1H, ddd, $J = 14.6, 10.8, 0.5$ Hz, $\text{C}_{16}\text{-H}$), 6.92 – 6.82 (3H, m, Ar-H), 6.27 (1H, d, $J = 14.3$ Hz, $\text{C}_{17}\text{-H}$), 6.07 (1H, ddd, $J = 15.1, 10.6, 1.0$ Hz, $\text{C}_{15}\text{-H}$), 5.68 (1H, dd, $J = 15.3, 6.0$ Hz, $\text{C}_{14}\text{-H}$), 5.13 (1H, dd, $J = 9.0, 1.0$ Hz, $\text{C}_{10}\text{-H}$), 4.47 and 4.42 (2H, AB system, $J_{\text{AB}} = 11.8$ Hz, OCH_2Ar), 4.28 (1H, app. qd, $J = 6.0, 1.3$ Hz, $\text{C}_{13}\text{-H}$), 4.18 (1H, app. td, $J = 9.3, 3.0$ Hz, $\text{C}_9\text{-H}$), 3.96 (1H, dd, $J = 7.5, 2.0$, $\text{C}_7\text{-H}$), 3.89 (3H, s, ArOCH_3), 3.88 (3H, s, ArOCH_3), 3.61 (1H, dd, $J = 9.0, 4.2$ Hz, $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 3.29 (1H, dd, $J = 8.8, 7.8$ Hz, $\text{C}_5\text{-H}_\text{X}\text{H}_\text{Y}$), 2.29 (1H, dd, $J = 13.3, 6.0$ Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 2.17 (1H, dd, $J = 13.3, 6.7$ Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 2.00 – 1.99 (1H, m, $\text{C}_6\text{-H}$), 1.98 – 1.95 (1H, m, $\text{C}_8\text{-H}$), 1.69 (3H, d, $J = 1.2$ Hz, $\text{C}_{11}\text{-CH}_3$), 1.64 – 1.59 (1H, m, $\text{C}_9\text{-OH}$), 0.98 – 0.95 (3H, m, $\text{C}_6\text{-CH}_3$), 0.96 (9H, t, $J = 7.8$ Hz, SiCH_2CH_3), 0.89 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.76 (3H, d, $J = 6.8$ Hz, $\text{C}_8\text{-CH}_3$), 0.63 (6H, q, $J = 7.8$ Hz, SiCH_2CH_3), 0.04 (3H, s, SiCH_3), 0.02 (3H, s, SiCH_3);

^{13}C NMR (100 MHz, CDCl_3) δ = 149.0, 148.5, 144.7, 137.5, 135.4, 131.3, 131.0, 129.0, 120.1, 111.0, 110.9, 78.5, 74.2, 73.1, 72.9, 71.8, 69.5, 55.9, 55.8, 48.2, 42.3, 37.6, 25.8, 18.2, 17.9, 15.1, 10.7, 7.1, 5.3, -4.5, -4.8;

HRMS calculated for $\text{C}_{37}\text{H}_{65}\text{IO}_6\text{Si}_2$ $[\text{M}+\text{NH}_4]^+$ 806.3708, found: 806.3712.

(6E,10E,12E)(2R,3S,4R,5R,9R)-9-(tert-Butyl-dimethyl-silanyloxy)-1-(3,4-dimethoxybenzyloxy)-13-iodo-5-methoxy-2,4,7-trimethyl-3-triethylsilanyloxy-trideca-6,10,12-triene **12**

R_f 0.55 (PE/EtOAc 2:1); $[\alpha]_D^{20} = -2.8$ ($c = 1.43$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 1594 and 1516 (aromatic C=C)

¹H NMR (400 MHz, CDCl₃) δ = 6.97 (1H, ddd, J = 14.3, 10.5, 0.5 Hz, C₁₆-H), 6.91 – 6.81 (3H, m, Ar-H), 6.25 (1H, d, J = 14.3 Hz, C₁₇-H), 6.05 (1H, dd, J = 15.3, 10.8 Hz, C₁₅-H), 5.68 (1H, dd, J = 15.3, 6.3 Hz, C₁₄-H), 4.92 (1H, dd, J = 9.6, 1.0 Hz, C₁₀-H), 4.49 and 4.41 (2H, AB system, J_{AB} = 11.8 Hz, OCH₂Ar), 4.30 – 4.25 (1H, m, Hz, C₁₃-H), 3.98 (1H, dd, J = 8.3, 1.8, C₇-H), 3.87 (3H, s, ArOCH₃), 3.86 (3H, s, ArOCH₃), 3.67 (1H, app. t, J = 9.5 Hz, C₉-H), 3.55 (1H, dd, J = 8.8, 3.8 Hz, C₅-H_XH_Y), 3.22 (1H, app. t, J = 8.5 Hz, C₅-H_XH_Y), 3.14 (3H, s, C₉-OCH₃), 2.37 (1H, dd, J = 13.2, 5.1 Hz, C₁₂-H_XH_Y), 2.23 (1H, dd, J = 13.4, 7.7 Hz, C₁₂-H_XH_Y), 1.92 - 1.82 (1H, m, C₆-H), 1.68 (3H, d, J = 1.2 Hz, C₁₁-CH₃), 1.61 – 1.53 (1H, m, C₈-H), 0.96 (9H, t, J = 8.0 Hz, SiCH₂CH₃), 0.92 (3H, d, J = 6.8 Hz, C₆-CH₃), 0.89 (9H, s, SiC(CH₃)₃), 0.70 (3H, d, J = 7.0 Hz, C₈-CH₃), 0.63 (6H, q, J = 8.0 Hz, SiCH₂CH₃), 0.05 (3H, s, SiCH₃), 0.03 (3H, s, SiCH₃);

¹³C NMR (100 MHz, CDCl₃) δ = 149.0, 148.4, 144.7, 137.4, 136.7, 131.5, 129.2, 128.8, 120.1, 111.0, 110.9, 78.5, 77.6, 73.4, 72.9, 72.3, 71.8, 55.9, 55.8, 55.0, 48.7, 40.5, 38.5, 25.8, 18.2, 17.9, 14.5, 9.2, 7.1, 5.6, -4.4, -4.8;

HRMS calculated for C₃₈H₆₇IO₆Si₂ [M+NH₄]⁺ 820.3865, found: 820.3864.

(6E,10E,12E)(2R,3S,4R,5R,9R)-9-(tert-Butyl-dimethyl-silanyloxy)-13-iodo-5-methoxy-2,4,7-trimethyl-3-triethylsilanyloxy-trideca-6,10,12-trienol **13**

R_f 0.62 (PE/EtOAc 2:1); [α]_D²⁰ = - 6.8 (c = 1.23, CHCl₃);

IR $\nu_{\max}$ (cm⁻¹, thin film) = 3444 (s, C-OH);

¹H NMR (400 MHz, CDCl₃) δ = 6.98 (1H, dd, J = 14.3, 10.5 Hz, C₁₆-H), 6.27 (1H, d, J = 14.6 Hz, C₁₇-H), 6.06 (1H, dd, J = 15.3, 10.8 Hz, C₁₅-H), 5.68 (1H, dd, J = 15.3, 6.3 Hz, C₁₄-H), 4.92 (1H, d, J = 9.8 Hz, C₁₀-H), 4.32 – 4.27 (1H, m, C₁₃-H), 4.13 (1H, dd, J = 6.5, 1.5 Hz, C₅-H_XH_Y), 3.66 (1H, app. t, J = 9.6 Hz, C₉-H), 3.61 – 3.50 (2H, m, C₅-H_XH_Y and C₇-H), 3.18 (3H, d, J = 4.0 Hz, C₉-OCH₃), 2.67 – 2.64 (1H, m, C₅-OH), 2.38 (1H, ddd, J = 13.3, 5.5, 1.0 Hz, C₁₂-H_XH_Y), 2.24 (1H, dd, J = 13.3, 7.6 Hz, C₁₂-H_XH_Y), 1.88 - 1.81 (1H, m, C₆-H), 1.69 (3H, d, J = 1.2 Hz, C₁₁-CH₃), 1.57 – 1.56 (1H, m, C₈-H), 1.00 (9H, t, J = 8.0 Hz, SiCH₂CH₃), 0.90 (9H, s, SiC(CH₃)₃),

0.85 (3H, d, $J = 7.0$ Hz, C₆-CH₃), 0.75 (3H, d, $J = 7.0$ Hz, C₈-CH₃), 0.63 (6H, q, $J = 7.8$ Hz, SiCH₂CH₃), 0.06 (3H, s, SiCH₃), 0.04 (3H, s, SiCH₃);

¹³C NMR (100 MHz, CDCl₃) $\delta = 144.62, 137.3, 137.1, 129.2, 128.2, 78.72, 78.68, 73.7, 71.8, 66.3, 55.2, 48.7, 40.6, 40.2, 25.8, 18.2, 17.9, 13.3, 10.4, 7.0, 5.3, -4.4, -4.8$;

HRMS calculated for C₂₉H₅₇IO₄Si₂ [M+Na]⁺ 675.27378, found: 675.27530.

(6E,10E,12E)(2R,3S,4R,5R,9R)-9-(tert-Butyl-dimethyl-silanyloxy)-13-iodo-5-methoxy-2,4,7-trimethyl-3-triethylsilanyloxy-trideca-6,10,12-trienal **14**

R_f 0.76 (PE/EtOAc 2:1); $[\alpha]_D^{20} = +2.2$ ($c = 0.99$, CHCl₃);

IR $\nu_{\max}$ (cm⁻¹, thin film) = 1731 (s, C=O);

¹H NMR (400 MHz, CDCl₃) $\delta = 9.73$ (1H, d, $J = 3.0$ Hz, C₅-H), 6.97 (1H, ddd, $J = 14.3, 10.8, 0.8$ Hz, C₁₆-H), 6.28 (1H, d, $J = 14.6$ Hz, C₁₇-H), 6.05 (1H, dd, $J = 15.3, 10.8$ Hz, C₁₅-H), 5.67 (1H, dd, $J = 15.3, 6.3$ Hz, C₁₄-H), 4.91 (1H, dd, $J = 9.5, 1.3$ Hz, C₁₀-H), 4.41 (1H, dd, $J = 7.8, 1.8$ Hz, C₇-H), 4.29 (1H, app. q, $J = 6.0$ Hz, C₁₃-H), 3.69 (1H, app. t, $J = 9.8$ Hz, C₉-H), 3.15 (3H, s, C₉-OCH₃), 2.51 (1H, app. qnd, $J = 7.0, 3.0$ Hz, C₆-H), 2.37 (1H, ddd, $J = 13.3, 5.5, 1.0$ Hz, C₁₂-H_XH_Y), 2.24 (1H, dd, $J = 13.3, 7.5$ Hz, C₁₂-H_XH_Y), 1.69 (3H, d, $J = 1.5$ Hz, C₁₁-CH₃), 1.58 – 1.50 (1H, m, C₈-H), 0.99 (3H, d, $J = 7.0$ Hz, C₆-CH₃), 0.96 (9H, t, $J = 7.8$ Hz, SiCH₂CH₃), 0.88 (9H, s, SiC(CH₃)₃), 0.74 (3H, d, $J = 7.0$ Hz, C₈-CH₃), 0.62 (6H, q, $J = 7.8$ Hz, SiCH₂CH₃), 0.05 (3H, s, SiCH₃), 0.03 (3H, s, SiCH₃);

¹³C NMR (100 MHz, CDCl₃) $\delta = 205.1, 144.6, 137.3, 137.2, 129.3, 128.3, 78.6, 77.2, 72.0, 71.8, 55.0, 51.3, 48.7, 41.2, 25.8, 18.2, 17.9, 11.3, 9.4, 7.0, 5.4, -4.4, -4.8$.

(10E,14E,16E)(5S,6R,7R,8R,9R,13R)-13-(tert-Butyl-dimethyl-silanyloxy)-5-hydroxy-17-iodo-9-methoxy-6,8,11-trimethyl-3-oxo-7-triethylsilanyloxy-heptadeca-10,14,16-trienoic acid methyl ester **15**

R_f 0.64 (PE/EtOAc 2:1); $[\alpha]_D^{20} = -9.1$ ($c = 1.03$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 3482 (m, C-OH), 1748 (s, C=O), 1714 (s, C=O);

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 6.98 (1H, ddd, $J = 14.3, 10.5, 0.8$ Hz, $\text{C}_{16}\text{-H}$), 6.26 (1H, d, $J = 14.3$ Hz, $\text{C}_{17}\text{-H}$), 6.05 (1H, dd, $J = 15.3, 10.5$ Hz, $\text{C}_{15}\text{-H}$), 5.67 (1H, dd, $J = 15.3, 6.3$ Hz, $\text{C}_{14}\text{-H}$), 4.92 (1H, dd, $J = 9.6, 1.2$ Hz, $\text{C}_{10}\text{-H}$), 4.43 (1H, app. dq, $J = 8.8, 2.8$ Hz, $\text{C}_5\text{-H}$), 4.31 – 4.26 (1H, m, $\text{C}_{13}\text{-H}$), 4.10 (1H, dd, $J = 5.5, 2.3$ Hz, $\text{C}_7\text{-H}$), 3.74 (3H, s, CO_2CH_3), 3.68 (1H, app. t, $J = 9.6$ Hz, $\text{C}_9\text{-H}$), 3.51 (2H, s, $\text{C}_2\text{-H}_2$), 3.16 (3H, s, $\text{C}_9\text{-OCH}_3$), 3.03 (1H, d, $J = 2.8$ Hz, OH), 2.79 (1H, dd, $J = 16.6, 9.3$ Hz, $\text{C}_4\text{-H}_\text{X}\text{H}_\text{Y}$), 2.54 (1H, dd, $J = 16.6, 3.2$ Hz, $\text{C}_4\text{-H}_\text{X}\text{H}_\text{Y}$), 2.37 (1H, ddd, $J = 13.3, 5.5, 1.0$ Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 2.23 (1H, ddd, $J = 13.3, 7.5, 0.8$ Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 1.72 – 1.67 (1H, m, $\text{C}_8\text{-H}$), 1.69 (3H, d, $J = 1.3$ Hz, $\text{C}_{11}\text{-CH}_3$), 1.51 – 1.47 (1H, m, $\text{C}_6\text{-H}$), 0.99 (9H, t, $J = 8.0$ Hz, SiCH_2CH_3), 0.93 – 0.88 (3H, m, $\text{C}_6\text{-CH}_3$), 0.89 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.75 (3H, d, $J = 7.0$ Hz, $\text{C}_8\text{-CH}_3$), 0.67 (6H, q, $J = 7.5$ Hz, SiCH_2CH_3), 0.05 (3H, s, SiCH_3), 0.03 (3H, s, SiCH_3);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 202.9, 167.5, 144.6, 137.3, 137.0, 129.2, 128.1, 78.6, 78.5, 74.7, 71.9, 67.2, 55.2, 52.3, 49.7, 48.7, 48.4, 42.3, 41.0, 25.8, 18.1, 17.9, 10.43, 10.35, 7.1, 5.5, -4.4, -4.8;

HRMS calculated for $\text{C}_{34}\text{H}_{63}\text{IO}_7\text{Si}_2$ [$\text{M}+\text{NH}_4$]: 784.3501, found: 784.3486.

2-{6-[6-(tert-Butyl-dimethyl-silanyloxy)-10-iodo-2-methoxy-1,4-dimethyl-deca-3,7,9-trienyl]-4-hydroxy-2-methoxy-5-methyl-tetrahydro-pyran-2-yl}-acetic acid methyl ester **16**

R_f 0.26 (PE/EtOAc 1:1); $[\alpha]_D^{20}$ - 31.0 (c = 0.99, CHCl_3);

IR ν_{max} (cm^{-1} , ATR) = 3433 (br, C-OH), 1741 (s, C=O);

^1H NMR (500 MHz, C_6D_6) δ = 6.86 (1H, dd, J = 14.3, 10.7 Hz, $\text{C}_{16}\text{-H}$), 5.95 (1H, d, J = 14.5 Hz, $\text{C}_{17}\text{-H}$), 5.88 (1H, dd, J = 15.1, 10.9 Hz, $\text{C}_{15}\text{-H}$), 5.47 (1H, dd, J = 15.4, 6.4 Hz, $\text{C}_{14}\text{-H}$), 5.03 (1H, dd, J = 9.6, 1.1 Hz, $\text{C}_{10}\text{-H}$), 4.19 (1H, app. q, J = 6.4 Hz, $\text{C}_{13}\text{-H}$), 4.06 (1H, dd, J = 10.9, 1.7 Hz, $\text{C}_7\text{-H}$), 4.03 (1H, app. t, J = 9.8 Hz, $\text{C}_9\text{-H}$), 3.76 – 3.69 (1H, m, $\text{C}_5\text{-H}$), 3.37 (3H, s, CO_2CH_3), 3.31 (3H, s, $\text{C}_3\text{-OCH}_3$), 3.12 (3H, s, $\text{C}_9\text{-OCH}_3$), 2.67 and 2.60 (2H, AB system, J_{AB} = 13.4 Hz, $\text{C}_2\text{-H}_2$), 2.43 (1H, dd, J = 12.6, 4.7 Hz, $\text{C}_4\text{-H}_\text{X}\text{H}_\text{Y}$), 2.33 (1H, ddd, J = 13.0, 5.6, 0.7 Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 2.22 (1H, dd, J = 13.2, 7.1 Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 1.88 – 1.812 (1H, m, $\text{C}_8\text{-H}$), 1.76 (1H, dd, J = 12.8, 11.1 Hz, $\text{C}_4\text{-H}_\text{X}\text{H}_\text{Y}$), 1.67 (3H, d, J = 1.3 Hz, $\text{C}_{11}\text{-CH}_3$), 1.44 – 1.29 (1H, m, $\text{C}_6\text{-H}$), 0.99 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.90 (3H, d, J = 6.6 Hz, $\text{C}_6\text{-CH}_3$), 0.84 (3H, d, J = 7.1 Hz, $\text{C}_8\text{-CH}_3$), 0.07 (3H, s, SiCH_3), 0.04 (3H, s, SiCH_3);

^{13}C NMR (100 MHz, C_6D_6) δ = 168.3, 144.8, 137.7, 136.9, 130.0, 129.7, 99.3, 79.3, 77.5, 72.5, 72.2, 70.0, 55.2, 51.2, 49.0, 47.9, 43.7, 42.3, 40.2, 39.0, 26.1, 18.4, 18.1, 12.2, 9.1, -4.1, -4.6;

HRMS calculated for $\text{C}_{29}\text{H}_{51}\text{IO}_7\text{Si}$ [$\text{M}+\text{NH}_4$]: 684.2793, found: 684.2794.

2-{6-[6-(*tert*-Butyl-dimethyl-silanyloxy)-10-iodo-2-methoxy-1,4-dimethyl-deca-3,7,9-trienyl]-4-(*tert*-butyl-dimethyl-silanyloxy)-2-methoxy-5-methyl-tetrahydro-pyran-2-yl}-acetic acid methyl ester

R_f 0.84 (PE/EtOAc 2:1); $[\alpha]_D^{20}$ - 19.8 (c = 1.07, CHCl_3);

IR ν_{max} (cm^{-1} , ATR) = 1744 (s, C=O);

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 6.99 (1H, dd, J = 14.3, 10.8 Hz, $\text{C}_{16}\text{-H}$), 6.27 (1H, d, J = 14.6 Hz, $\text{C}_{17}\text{-H}$), 6.05 (1H, dd, J = 15.6, 10.8 Hz, $\text{C}_{15}\text{-H}$), 5.68 (1H, dd, J = 15.3, 6.3 Hz, $\text{C}_{14}\text{-H}$), 4.93 (1H, dd, J = 9.3, 1.3 Hz, $\text{C}_{10}\text{-H}$), 4.31 – 4.27 (1H, m, $\text{C}_{13}\text{-H}$), 3.86 (1H, app. t, J = 9.8 Hz, $\text{C}_9\text{-H}$), 3.72 (1H, dd, J = 10.6, 1.8 Hz, $\text{C}_7\text{-H}$), 3.70 – 3.64 (1H, m, $\text{C}_5\text{-H}$), 3.66 (3H, s, CO_2CH_3), 3.23 (3H, s, $\text{C}_3\text{-OCH}_3$), 3.11 (3H, s, $\text{C}_9\text{-OCH}_3$), 2.66 and 2.62 (2H, AB system, J_{AB} = 13.6 Hz $\text{C}_2\text{-H}_2$), 2.38 (1H, dd, J = 13.3, 5.0 Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 2.23 (1H, dd, J = 13.6, 7.5 Hz, $\text{C}_{12}\text{-H}_\text{X}\text{H}_\text{Y}$), 2.12 (1H, dd, J = 12.8, 4.5 Hz, $\text{C}_4\text{-H}_\text{X}\text{H}_\text{Y}$), 1.73 – 1.64 (2H, m, $\text{C}_4\text{-H}_\text{X}\text{H}_\text{Y}$ and $\text{C}_8\text{-H}$), 1.70 (3H, d, J = 1.3 Hz, $\text{C}_{11}\text{-CH}_3$), 1.44 – 1.35 (1H, m, $\text{C}_6\text{-H}$), 0.889 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.887 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.84 (3H, d, J = 6.5 Hz, $\text{C}_6\text{-CH}_3$), 0.69 (3H, d, J = 7.0 Hz, $\text{C}_8\text{-CH}_3$), 0.062 (3H, s, SiCH_3), 0.060 (3H, s, SiCH_3), 0.054 (3H, s, SiCH_3), 0.03 (3H, s, SiCH_3);

$^{13}\text{C NMR}$ (100 MHz, C_6D_6) δ = 169.9, 144.7, 137.4, 136.9, 129.2, 129.0, 98.8, 78.5, 77.2, 71.9, 71.7, 70.7, 55.2, 51.5, 48.7, 47.7, 43.4, 42.0, 39.9, 38.6, 29.7, 25.89, 25.84, 17.9, 18.0, 12.4, 8.7, -4.1, -4.4, -4.7, -4.8;

HRMS calculated for $\text{C}_{35}\text{H}_{65}\text{IO}_7\text{Si}_2[\text{M}+\text{Na}]$: 803.3211, found: 803.3260.

2-{6-[6-(*tert*-Butyl-dimethyl-silanyloxy)-10-iodo-2-methoxy-1,4-dimethyl-deca-3,7,9-trienyl]-4-hydroxy-2-methoxy-5-methyl-tetrahydro-pyran-2-yl}-acetic acid methyl ester

R_f 0.36 (PE/EtOAc 7:3); $[\alpha]_D^{20} = -7.1$ ($c = 0.18$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 3440 (s, C-OH), 1738 (s, C=O);

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 7.02 (1H, dd, $J = 14.3, 10.7$ Hz, C₁₆-H), 6.34 (1H, d, $J = 14.5$ Hz, C₁₇-H), 6.19 (1H, dd, $J = 15.1, 10.7$ Hz, C₁₅-H), 5.74 (1H, dd, $J = 15.4, 6.0$ Hz, C₁₄-H), 5.04 (1H, dd, $J = 9.6, 1.3$ Hz, C₁₀-H), 4.32 – 4.27 (1H, m, C₁₃-H), 3.91 (1H, t, $J = 9.6$ Hz, C₉-H), 3.73 (1H, d, $J = 10.9$ Hz, C₇-H), 3.70 – 3.64 (1H, m, C₅-H), 3.67 (3H, s, CO₂CH₃), 3.24 (3H, s, C₃-OCH₃), 3.14 (3H, s, C₉-OCH₃), 2.67 and 2.62 (2H, AB system, $J_{\text{AB}} = 13.5$ Hz C₂-H₂), 2.31 – 2.29 (2H, m, C₁₂-H₂), 2.12 (1H, dd, $J = 13.0, 4.7$ Hz, C₄-H_XH_Y), 1.76 – 1.66 (2H, m, C₄-H_XH_Y and C₈-H), 1.74 (3H, s, C₁₁-CH₃), 1.44 – 1.39 (1H, m, C₆-H), 0.89 (9H, s, SiC(CH₃)₃), 0.84 (3H, d, $J = 6.4$ Hz, C₆-CH₃), 0.70 (3H, d, $J = 7.0$ Hz, C₈-CH₃), 0.06 (6H, s, Si(CH₃)₂);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 169.9, 144.4, 136.6, 136.4, 129.9, 129.7, 98.9, 79.4, 77.2, 71.7, 70.6, 69.6, 55.3, 51.6, 47.9, 47.7, 43.3, 42.0, 39.9, 38.5, 25.9, 18.0, 17.2, 12.4, 8.8, -4.1, -4.7;

HRMS calculated for C₂₉H₅₁IO₇Si [M+Na]: 689.2347, found: 689.2344.

2-{6-[6-(*tert*-Butyl-dimethyl-silanyloxy)-10-iodo-2-methoxy-1,4-dimethyl-deca-3,7,9-trienyl]-4-hydroxy-2-methoxy-5-methyl-tetrahydro-pyran-2-yl}-acetic acid

R_f 0.77 (PE/EtOAc 1:1); $[\alpha]_D^{20} = -10.3$ ($c = 1.30$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 3422 (s, C-OH), 1711 (s, C=O);

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.02 (1H, dd, $J = 14.3, 10.5$ Hz, C₁₆-H), 6.35 (1H, d, $J = 14.6$ Hz, C₁₇-H), 6.19 (1H, dd, $J = 15.3, 10.8$ Hz, C₁₅-H), 5.74 (1H, dd, $J = 15.3, 6.3$ Hz, C₁₄-H), 5.06 (1H, dd, $J = 9.5, 1.0$ Hz, C₁₀-H), 4.30 (1H, app. q, $J = 6.3$ Hz, C₁₃-H), 3.90 (1H, dd, $J = 10.8, 1.8$ Hz, C₇-H), 3.87 (1H, app. t, $J = 9.5$ Hz, C₉-H), 3.75 – 3.65 (1H, m, C₅-H), 3.27 (3H, s, C₃-OCH₃), 3.16 (3H, s, C₉-OCH₃), 2.83 and 2.62 (2H, AB system, $J_{\text{AB}} = 15.0$ Hz C₂-H₂), 2.32 – 2.27 (2H, m, C₁₂-H₂), 2.10 (1H, dd, $J = 13.1, 4.8$ Hz, C₄-H_XH_Y), 1.83 – 1.76 (1H, m, C₈-H), 1.73 (3H, d, $J = 1.3$ Hz, C₁₁-CH₃), 1.59 (1H, dd, $J = 13.1, 10.8$ Hz, C₄-H_XH_Y), 1.52 – 1.45 (1H, m, C₆-H), 0.88 (9H, s, SiC(CH₃)₃), 0.87 (3H, d, $J = 6.8$ Hz, C₆-CH₃), 0.78 (3H, d, $J = 7.0$ Hz, C₈-CH₃), 0.064 (3H, s SiCH₃), 0.058 (3H, s SiCH₃);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 144.4, 137.1, 136.2, 130.0, 129.1, 98.9, 79.6, 77.5, 72.8, 70.1, 69.6, 55.4, 48.3, 47.8, 43.0, 40.0, 38.4, 30.3, 25.8, 18.0, 17.2, 12.4, 9.2, -4.1, -4.8 (carboxylic carbon could not be detected);

HRMS calculated for C₂₈H₄₉IO₇Si [M+Na]: 675.2190, found: 675.2204.

13-(tert-butyldimethylsilyloxy)-5-(4-iodobuta-1,3-dienyl)-1,9-dimethoxy-7,10,12-trimethyl-4,15-dioxabicyclo[9.3.1]pentadec-7-en-3-one 2

R_f 0.20 (DCM); $[\alpha]_D^{20} = +38.0$ ($c = 0.66$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 1729 (s, C=O);

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 6.99 (1H, dd, $J = 14.4, 10.7$ Hz, C₁₆-H), 6.38 (1H, d, $J = 14.3$ Hz, C₁₇-H), 6.18 (1H, dd, $J = 15.3, 10.8$ Hz, C₁₅-H), 5.70 (1H, dd, $J = 15.3, 6.5$ Hz, C₁₄-H), 5.49 – 5.43 (1H, m, C₁₃-H), 5.30 (1H, d, $J = 9.3$ Hz, C₁₀-H), 3.89 (1H, dd, $J = 10.0, 2.5$ Hz, C₉-H),

3.54 (1H, d, $J = 10.3$ Hz, $C_7\text{-H}$), 3.47 (1H, td, $J = 10.8, 4.3$ Hz, $C_5\text{-H}$), 3.27 (3H, s, $C_3\text{-OCH}_3$), 3.22 (3H, s, $C_9\text{-OCH}_3$), 2.59 and 2.44 (2H, AB system, $J_{AB} = 12.6$ Hz $C_2\text{-H}_2$), 2.42 – 2.36 (1H, m, $C_{12}\text{-H}_x\text{H}_y$), 2.27 (1H, dd, $J = 13.2, 2.9$ Hz $C_{12}\text{-H}_x\text{H}_y$), 2.23 – 2.18 (1H, m, $C_8\text{-H}$), 2.12 (1H, dd, $J = 13.2, 4.4$ Hz, $C_4\text{-H}_x\text{H}_y$), 1.65 (3H, s, $C_{11}\text{-CH}_3$), 1.48 – 1.38 (1H, m, $C_6\text{-H}$), 1.29 – 1.23 (1H, m, $C_4\text{-H}_x\text{H}_y$), 1.00 (3H, d, $J = 7.0$ Hz, $C_8\text{-CH}_3$), 0.90 (3H, obs., $C_6\text{-CH}_3$), 0.89 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.07 (3H, s, SiCH_3), 0.06 (3H, s, SiCH_3);

^{13}C NMR (100 MHz, CDCl_3) $\delta = 168.6, 144.2, 132.8, 132.4, 131.6, 127.1, 100.1, 80.5, 80.4, 77.2, 76.5, 70.7, 70.1, 55.1, 51.4, 45.7, 43.8, 40.9, 40.3, 38.2, 25.8, 18.0, 15.5, 12.9, -4.1, -4.7$;

HRMS calculated for $\text{C}_{28}\text{H}_{47}\text{IO}_6\text{Si}$ [$\text{M}+\text{Na}$]: 657.2084, found: 657.2074.

13-(*tert*-butyldimethylsilyoxy)-5-[6-(2-chlorocyclopropyl)-hexa-1,3-dien-5-ynyl]-1,9-dimethoxy-7,10,12-trimethyl-4,15-dioxabicyclo[9.3.1]pentadec-7-en-3-one **18**

R_f 051 (PE/EtOAc 4:1); $[\alpha]_D^{20} = -30.0$ ($c = 1.46$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 1729 (s, $\text{C}=\text{O}$);

^1H NMR (400 MHz, CDCl_3) $\delta = 6.46$ (1H, dd, $J = 15.3, 10.8$ Hz, $C_{16}\text{-H}$), 6.25 (1H, dd, $J = 15.3, 10.8$ Hz, $C_{15}\text{-H}$), 5.73 (1H, dd, $J = 15.2, 6.7$ Hz, $C_{14}\text{-H}$), 5.54 (1H, dd, $J = 15.4, 1.9$ Hz, $C_{17}\text{-H}$), 5.54 – 5.48 (1H, m, $C_{13}\text{-H}$), 5.30 (1H, d, $J = 9.3$ Hz, $C_{10}\text{-H}$), 3.89 (1H, dd, $J = 9.9, 2.6$ Hz, $C_9\text{-H}$), 3.54 (1H, dd, $J = 10.5, 1.5$ Hz, $C_7\text{-H}$), 3.47 (1H, td, $J = 10.8, 4.3$ Hz, $C_5\text{-H}$), 3.28 (3H, s, $C_3\text{-OCH}_3$), 3.22 (3H, s, $C_9\text{-OCH}_3$), 3.19 – 3.15 (1H, m, $C_{21}\text{-H}$), 2.59 and 2.44 (2H, AB system, $J_{AB} = 12.6$ Hz $C_2\text{-H}_2$), 2.42 – 2.36 (1H, m, $C_{12}\text{-H}_x\text{H}_y$), 2.27 (1H, dd, $J = 13.2, 2.9$ Hz, $C_{12}\text{-H}_x\text{H}_y$), 2.23 – 2.18 (1H, m, $C_8\text{-H}$), 2.12 (1H, dd, $J = 13.2, 4.4$ Hz, $C_4\text{-H}_x\text{H}_y$), 1.82 – 1.77 (1H, m, $C_{20}\text{-H}$), 1.65 (3H, s, $C_{11}\text{-CH}_3$), 1.47 – 1.40 (1H, m, $C_6\text{-H}$), 1.30 – 1.25 (3H, m, $C_4\text{-H}_x\text{H}_y$ and $C_{22}\text{-H}_2$), 1.00

(3H, d, $J = 7.0$ Hz, C₈-CH₃), 0.90 (3H, obs., C₆-CH₃), 0.89 (9H, s, SiC(CH₃)₃), 0.07 (3H, s, SiCH₃), 0.06 (3H, s SiCH₃);

¹³C NMR (100 MHz, CDCl₃) δ = 168.6, 140.4, 133.7, 132.9, 131.1, 127.0, 112.1, 100.1, 91.9, 80.4, 77.6, 77.2, 76.5, 70.9, 70.1, 55.0, 51.4, 45.8, 43.8, 40.9, 40.3, 34.3, 29.7, 25.8, 19.3 18.0, 15.5, 12.9, 12.1, -4.1, -4.7;

HRMS calculated for C₃₃H₅₁ClO₆Si [M+Na]: 629.3041, found: 629.3057.

5-[6-(2-chlorocyclopropyl)-hexa-1,3-dien-5-ynyl]-1,13-hydroxy-9-methoxy-7,10,12-trimethyl-4,15-dioxabicyclo[9.3.1]pentadec-7-en-3-one **19**

R_f 0.27 (PE/EtOAc 1:1); $[\alpha]_D^{20} = -33.4$ ($c = 0.53$, CHCl₃);

IR $\nu_{\max}$ (cm⁻¹, thin film) = 3442 (C-OH), 1704 (C=O);

¹H NMR (400 MHz, CDCl₃) δ = 6.48 (1H, dd, $J = 15.4, 10.9$ Hz, C₁₆-H), 6.27 (1H, dd, $J = 14.8, 10.8$ Hz, C₁₅-H), 5.85 – 5.81 (1H, m, C₁₃-H), 5.76 (1H, dd, $J = 14.9, 6.4$ Hz, C₁₄-H), 5.57 (1H, dd, $J = 15.6, 1.8$ Hz, C₁₇-H), 5.31 (1H, dd, $J = 9.7, 1.1$ Hz, C₁₀-H), 5.02 (1H, d, $J = 2.5$ Hz, C₃-OH) 3.80 (1H, dd, $J = 9.5, 2.5$ Hz, C₉-H), 3.79 – 3.76 (1H, m, C₅-H), 3.61 (1H, dd, $J = 10.3, 2.5$ Hz, C₇-H), 3.23 (3H, s, C₉-OCH₃), 3.18 (1H, td, $J = 5.7, 3.2$, Hz, C₂₁-H), 2.55 and 2.44 (2H, AB system, $J_{AB} = 12.8$ Hz, C₂-H₂), 2.30 – 2.29 (2H, m, C₁₂-H₂), 2.24 – 2.19 (1H, m, C₈-H), 2.10 (1H, dd, $J = 11.8, 4.5$ Hz, C₄-H_XH_Y), 1.82 – 1.78 (1H, m, C₂₀-H), 1.73 (3H, d, $J = 1.3$ Hz, C₁₁-CH₃), 1.52 – 1.49 (1H, m, C₅-OH) 1.42 – 1.36 (1H, m, C₆-H), 1.31 – 1.28 (3H, m, C₄-H_XH_Y and C₂₂-H₂), 0.98 (6H, d, $J = 6.9$ Hz, C₈-CH₃ and C₆-CH₃);

¹³C NMR (100 MHz, CDCl₃) δ = 171.8, 140.1, 132.7, 132.3, 130.9, 127.9, 112.5, 95.4, 92.3, 79.8, 77.5, 75.0, 71.5, 69.5, 55.2, 46.9, 44.8, 43.8, 40.1, 36.8, 34.3, 19.3, 16.1, 12.1, 12.0, 6.5;

HRMS calculated for C₂₆H₃₅ClO₆Si [M+Na]: 501.2020, found: 501.2052.

5-[(1*E*, 3*E*)-6-((1*S*, 2*R*)-2-chlorocyclopropyl)-hexa-1,3-dien-5-ynyl](1*S*, 11*S*, 13*S*, 5*R*, 9*R*, 10*R*, 12*R*)-13-[(3*S*, 5*S*, 1*R*, 2*R*, 6*R*)-7-aza-2-methoxy-1,5-dimethyl-4,9-dioxo-8-oxo-7-triisopropylsilanyl-bicyclo[4.3.0]non-3-yl]1-hydroxy-9-methoxy-7,10,12-trimethyl-4,15-dioxabicyclo[9.3.1]pentadec-7-en-3-one

R_f 0.38 (PE/EtOAc 3:2); $[\alpha]_D^{20} = -49.6$ ($c = 0.27$, CHCl_3);

IR ν_{max} (cm^{-1} , thin film) = 1735 (s, C=O), 1714 (s, C=O)

^1H NMR (400 MHz, CDCl_3) δ = 6.48 (1H, dd, $J = 15.4, 10.9$ Hz, C₁₆-H), 6.26 (1H, dd, $J = 14.7, 10.7$ Hz, C₁₅-H), 5.85 – 5.79 (1H, m, C₁₃-H), 5.76 (1H, dd, $J = 14.5, 6.4$ Hz, C₁₄-H), 5.57 (1H, d, $J = 15.5$ Hz, C₁₇-H), 5.30 (1H, d, $J = 9.2$ Hz, C₁₀-H), 4.91 (1H, d, $J = 1.9$ Hz, C₃-OH), 4.86 (1H, d, $J = 6.1$ Hz, C₁-H), 3.94 – 3.88 (1H, m, C₅-H), 3.80 (1H, dd, $J = 9.4, 2.4$ Hz, C₉-H), 3.78 – 3.73 (1H, m, C₅-H), 3.65 (1H, dd, $J = 10.5, 2.4$ Hz, C₇-H), 3.59 (3H, s, C₂-OCH₃), 3.41 (1H, d, $J = 2.3$ Hz, C₄-H), 3.28 – 3.22 (1H, m, C₂-H), 3.24 (3H, s, C₉-OCH₃), 3.20 – 3.16 (1H, m, C₂₁-H), 2.51 and 2.43 (2H, AB system, $J_{\text{AB}} = 12.9$ Hz, C₂-H₂), 2.30 – 2.28 (2H, m, C₁₂-H₂), 2.26 – 2.21 (2H, C₈-H and C₄-H_XH_Y), 1.83 – 1.78 (1H, m, C₂₀-H), 1.73 (3H, d, $J = 1.0$ Hz, C₁₁-CH₃), 1.53 (3H, s, C₃'-CH₃), 1.54 – 1.45 (1H, m, C₆-H), 1.39, (3H, spt., $J = 7.3$ Hz Si(CH(CH₃)₂)₃), 1.30 – 1.23 (6H, m, C₄-H_XH_Y, C₂₂-H₂ and C₅'-Me), 1.21 – 1.16 (18H, m, Si(CH(CH₃)₂)₃), 0.98 (6H, m, C₆-CH₃ and C₈-CH₃);

^{13}C NMR (100 MHz, CDCl_3) δ = 171.7, 161.1, 140.2, 132.8, 132.3, 130.9, 127.9, 112.5, 101.9, 95.2, 92.2, 82.3, 82.2, 79.8, 77.5, 77.2, 75.0, 71.4, 65.4, 65.1, 61.3, 55.3, 46.9, 44.8, 43.1, 38.6, 36.8, 34.3, 22.4, 19.3, 19.0, 17.0, 16.1, 13.1, 12.2, 12.1, 6.5;

HRMS calculated for $C_{44}H_{68}NO_{10}Si_1Cl_1[M+Na]$: 856.4211 found: 856.4199.

(-)-Callipeltoside A (1)

R_f 0.35 (EtOAc); $[\alpha]_D^{20} = -17.0$ ($c = 0.34$, $CHCl_3$);

^1H NMR (500 MHz, $CDCl_3$) $\delta = 6.50$ (1H, dd, $J = 15.3, 10.6$ Hz, $C_{16}-H$), 6.33 (1H, dd, $J = 14.2, 10.8$ Hz, $C_{15}-H$), $5.86 - 5.78$ (1H, m, $C_{13}-H$ and $C_{14}-H$), 5.65 (1H, dd, $J = 15.4, 1.6$ Hz, $C_{17}-H$), 5.27 (1H, d, $J = 9.6$ Hz, $C_{10}-H$), 4.72 (1H, d, $J = 6.2$ Hz, $C_1'-H$), 3.96 (1H, dq, $J = 6.3, 1.7$ Hz $C_5'-H$), 3.88 (1H, dd, $J = 9.6, 2.2$ Hz, C_9-H), 3.73 (1H, td, $J = 10.7, 4.7$ Hz, C_5-H), 3.65 (1H, dd, $J = 10.4, 2.2$ Hz, C_7-H), 3.65 (3H, s, $C_2'-OCH_3$), 3.45 (1H, d, $J = 1.8$ Hz, $C_4'-H$), 3.43 (1H, d, $J = 6.2$ Hz C_2-H), 3.22 (3H, s, C_9-OCH_3), $3.26 - 3.23$ (1H, m, $C_{21}-H$), 2.55 and 2.47 (2H, AB system, $J_{AB} = 12.7$ Hz, C_2-H_2), $2.35 - 2.27$ (2H, m, $C_{12}-H_2$), $2.25 - 2.20$ (1H, C_8-H and C_4-H_{XHy}), $1.83 - 1.79$ (1H, m, $C_{20}-H$), 1.75 (3H, s, $C_{11}-CH_3$), $1.53 - 1.48$ (1H, m, C_6-H), 1.51 (3H, s, $C_3'-CH_3$), 1.40 (1H, t, $J = 11.7$ Hz, C_4-H_{XHy}), $1.29 - 1.25$ (2H, m, $C_{22}-H_2$), 1.09 (3H, d, $J = 6.5$ Hz, $C_5'-Me$), 1.00 (3H, d, $J = 6.5$ Hz, C_6-CH_3), 0.96 (3H, d, $J = 6.4$ Hz, C_8-CH_3);

^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 172.9, 161.1, 141.6, 134.4, 134.3, 132.1, 128.4, 113.5, 103.6, 96.6, 92.8, 83.9, 83.1, 81.4, 78.8, 78.4, 76.5, 72.7, 65.3, 62.7, 62.0, 55.4, 47.8, 46.1, 44.5, 39.9, 38.2, 35.1, 23.0, 19.8, 16.3, 15.9, 12.8, 12.7, 6.8$;

HRMS calculated for $C_{35}H_{48}NO_{10}Cl_1[M+Na]$: 700.2871 found: 700.2864

¹ H NMR signals in methanol-d ₄ (500 MHz)		
	natural callipeltoside A	synthetic callipeltoside A
atom	δ in ppm	δ in ppm
1		
2	2.56, d (12.7); 2.50, d (12.7)	2.55, d (12.8); 2.47, d (12.9)
3		
4	2.25, overlapped; 1.43, t (11.7)	2.21, m, overlapped; 1.40, t (11.7)
5	3.76, ddd (11.7, 5.9, 4.9)	3.73, td, (10.4, 4.7)
6	1.58, m	1.51, m, overlapped
7	3.68, dd (10.5, 2.4)	3.65, dd (10.4, 2.2)
8	2.27, m	2.24, m, overlapped
9	3.91, dd (9.5, 2.2)	3.88, dd (9.6, 2.2)
10	5.30, br dd (9.5)	5.27, br d (9.6)
11		
12	2.37, dd; 2.31, dd, overlapped	2.35, m; 2.29, m
13	5.86, overlapped	5.81, overlapped
14	5.87, overlapped	5.83, overlapped
15	6.37, dd (14.2, 10.5)	6.33, dd (14.2, 10.8)
16	6.53, dd (15.3, 10.5)	6.50, dd (15.3, 10.6)
17	5.68, dd (15.3, 1.7)	5.65, dd (15.4, 1.6)
18		
19		
20	1.85, m, overlapped	1.82, m
21	3.28, m	3.25, m
22	1.31, m	1.27, m
23(C11-Me)	1.78, s	1.75, s
24(C8-Me)	0.99, d (6.9)	0.96, d (7.0)
25(C6-Me)	1.03, d (6.4)	1.00, d (6.4)
OMe (C9)	3.25, s	3.22, s
OH		
1'	4.74, d (6.1)	4.72, d, (6.2)
2'	3.42, d (6.1)	3.43, d (6.2)
3'		
4'	3.48, d (1.7)	3.45, d (1.8)
5'	3.99, dq (6.5, 1.7)	3.96, dq (6.3, 1.7)
6'(C5'-Me)	1.12, d (6.5)	1.09, d (6.5)
7'		
8'(C3'-Me)	1.54, s	1.51, m, overlapped
OMe(C2')	3.63, s	3.65, s
NH		

¹³ C NMR signals in methanol-d ₄ (125 MHz)		
	natural callipeltoside A	synthetic callipeltoside A
atom	δ in ppm	δ in ppm
1	172.4	172.9
2	46.0	46.1
3	97.0	96.6
4	44.5	44.5
5	78.7	78.8
6	39.8	39.9
7	76.4	76.5
8	38.2	38.2
9	81.4	81.4
10	128.3	128.4
11	134.1	134.3
12	47.8	47.8
13	72.7	72.7
14	134.2	134.4
15	132.0	132.1
16	141.5	141.6
17	113.4	113.5
18	78.3	78.4
19	92.4	92.8
20*	12.8	12,8
21*	34.7	35.1
22	19,3	19,8
23(C11-Me)	16,3	16,4
24(C8-Me)	6,8	6,8
25(C6-Me)	12.8	12,8
OMe (C9)	55.4	55.4
OH		
1'	103.6	103.6
2'	83.2	83.0
3'	83.8	83.9
4'	62.7	62.7
5'	65.3	65.3
6'(C5'-Me)	15,9	15,9
7'	161.2	161.1
8'(C3'-Me)	23.0	23.0
OMe(C2')	62.0	62.0
NH		

*For the reassignment of C20 and C21, see the explanatory note in our earlier communication (footnote [25], Paterson, I.; Davies, R. D. M.; Marquez, R. *Angew. Chem. Int. Ed.* **2001**, *40*, 603.)

^1H -NMR of Callipetioside A in methanol- d_4