Supporting Information

Stereocontrolled Total Synthesis of (-)-Callipeltoside A

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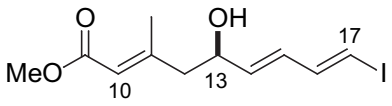
Methyl-(2*E*,5*S*,6*E*,8*E*)-5-hydroxy-9-iodo-3-methyl-2,6,8-nontrienoate **10**



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 °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 °C. The reaction mixture was stirred for 70 h at –78 °C in the dark before being quenched by carefully pouring the mixture into a cooled (0 °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);

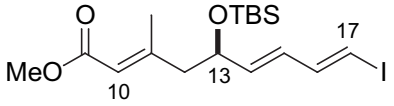
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 (1H, ddd, *J* = 14.4, 10.8, 0.7 Hz, C_{16}-H), 6.38 (1H, d, *J* = 14.4 Hz, C_{17}-H), 6.21 (1H, ddd, *J* = 15.3, 10.8, 1.5 Hz, C_{15}-H), 5.75 – 5.70 (1H, m, C_{14}-H), 5.74 (1H, d, *J* = 1.3 Hz, C_{10}-H), 4.28 – 4.42 (1H, m, C_{13}-H), 3.69 (3H, s, C_9-OCH_3), 2.37 (1H, d, *J* =

1.2 Hz, C_{12}-$\underline{H}_x H_y$), 2.35 (1H,d, J = 1.0 Hz, C_{12}-$H_x\underline{H}_y$), 2.20 (3H, d, J = 1.2 Hz, C_{11}-$C\underline{H}_3$), 1.67 (1H, bs, O$\underline{H}$);

HRMS calculated for $C_{11}H_{15}IO$ $[M+Na]^+$ 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



$\boldsymbol{R_f}$ 0.57 (PE/EtOAc 4:1); $[\alpha]_D^{20}$ = + 8.3 (c = 0.95, $CHCl_3$);

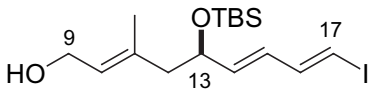
IR ν_{max} (cm^{-1}, thin film) = 1722 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (1H, dd, J = 14.3, 10.6 Hz, C_{16}-$\underline{H}$), 6.32 (1H, d, J = 14.3 Hz, C_{17}-$\underline{H}$), 6.10 (1H, ddd, J = 16.0, 10.8, 1.0 Hz, C_{15}-$\underline{H}$), 5.67 (1H, dd, J = 15.0, 6.3 Hz, C_{14}-$\underline{H}$), 5.67 (1H, d, J = 1.2 Hz, C_{10}-$\underline{H}$), 4.26 – 4.31 (1H, m, C_{13}-$\underline{H}$), 3.68 (3H, s, C_9-O$C\underline{H}_3$), 2.34 (1H, ddd, J = 13.0, 7.3, 0.8 Hz, C_{12}-$\underline{H}_x H_y$), 2.26 (1H, ddd, J = 13.0, 5.5, 0.7 Hz, C_{12}-$H_x\underline{H}_y$), 2.17 (3H, d, J = 1.5 Hz, C_{11}-$C\underline{H}_3$), 0.87 (9H, s, SiC($C\underline{H}_3$)$_3$), 0.01 (3H, s, Si-$C\underline{H}_3$), 0.00 (3H, s, Si-$C\underline{H}_3$);

^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{17}H_{29}IO_3Si$ $[M+Na]^+$ 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



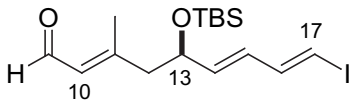
$\boldsymbol{R_f}$ 0.27 (PE/EtOAc 4:1); $[\alpha]_D^{20}$ = + 3.5 (c = 1.02, $CHCl_3$);

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

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (1H, dd, *J* = 14.6, 10.8 Hz, C_{16}-H), 6.28 (1H, d, *J* = 14.6 Hz, C_{17}-H), 6.08 (1H, ddd, *J* = 15.3, 10.8, 1.3 Hz, C_{15}-H), 5.69 (1H, dd, *J* = 15.3, 6.0 Hz, C_{14}-H), 5.42 (1H, tq, *J* = 6.8, 1.2 Hz, C_{10}-H), 4.26 – 4.20 (1H, m, C_{13}-H), 4.14 (2H, d, *J* = 7.0 Hz, C_9-H), 2.24 (1H, dd, *J* = 13.2, 7.0 Hz, C_{12}-H_xH_y), 2.15 (1H, dd, *J* = 13.3, 6.0 Hz, C_{12}-H_xH_y), 1.68 (3H, d, *J* = 1.3 Hz, C_{11}-CH_3), 0.88 (9H, s, $SiC(CH_3)_3$), 0.02 (3H, s, Si-CH_3), 0.01 (3H, s, Si-CH_3);

HRMS calculated for $C_{16}H_{29}IO_2Si$ $[M+Na]^+$ 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**



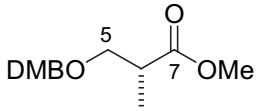
R_f 0.58. (PE/EtOAc 2:1); $[\alpha]_D^{20}$ = + 2.4 (*c* = 1.00, $CHCl_3$);

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

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.98 (1H, d, *J* = 8.0 Hz, C_9-H), 7.00 (1H, dd, *J* = 14.6, 10.8 Hz, C_{16}-H), 6.34 (1H, d, *J* = 14.6 Hz, C_{17}-H), 6.11 (1H, dd, *J* = 15.1, 10.8 Hz, C_{15}-H), 5.87 (1H, dd, *J* = 8.0, 1.2 Hz, C_{10}-H), 5.67 (1H, dd, *J* = 15.3, 6.2 Hz, C_{14}-H), 4.30 – 4.35 (1H, m, C_{13}-H), 2.41 (1H, dd, *J* = 13.1, 7.3 Hz, C_{12}-H_xH_y), 2.34 (1H, dd, *J* = 13.1, 5.2 Hz, C_{12}-H_xH_y), 2.19 (3H, d, *J* = 1.3 Hz, C_{11}-CH_3), 0.87 (9H, s, $SiC(CH_3)_3$), 0.02 (3H, s, Si-CH_3), 0.01 (3H, s, Si-CH_3):

HRMS calculated for $C_{16}H_{27}IO_2Si$ $[M+Na]^+$ 429.0723, found 429.0711.

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



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

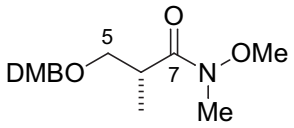
IR ν_{max} (cm^{-1}, thin film) = 1737 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.85 – 6.79 (3H, m, Ar<u>H</u>), 4.43 (2H, s, OC<u>H</u>$_2$Ar), 3.86 (3H, s, ArOC<u>H</u>$_3$), 3.84 (3H, s, ArOC<u>H</u>$_3$), 3.66 (3H, s, C_7-OC<u>H</u>$_3$), 3.62 (1H, dd, *J* = 9.3, 7.3 Hz C_5-<u>H</u>$_X$H$_Y$), 3.44 (1H, dd, *J* = 9.2, 5.8 Hz C_5- H$_X$<u>H</u>$_Y$), 2.80 – 2.71 (1H, m, C_6-<u>H</u>), 1.15 (3H, d, *J* = 7.0 Hz, C_6-C<u>H</u>$_3$);

^{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 $C_{14}H_{20}O_5$ $[M+NH_4]^+$ 286.1654, found 286.1649.

<u>(*R*)-3-(3,4-Dimethoxy-benzyloxy)-*N*-methoxy-*N*-2-dimethylpropionoate</u>



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

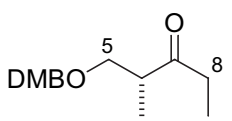
IR ν_{max} (cm^{-1}, thin film) = 1650 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87–6.80 (3H, m, Ar<u>H</u>), 4.45 (2H, AB system, J_{AB} = 12.0 Hz, OC<u>H</u>$_2$Ar), 3.87 (3H, s, ArOC<u>H</u>$_3$), 3.86 (3H, s, ArOC<u>H</u>$_3$), 3.71-3.67 (1H, m, C_5- <u>H</u>$_X$H$_Y$), 3.69 (3H, s, C_7-NOC<u>H</u>$_3$), 3.40 (1H, dd, *J* = 8.8, 5.8 Hz, C_5- H$_X$<u>H</u>$_Y$), 3.30 – 3.23 (1H, m, C_6-<u>H</u>), 3.20 (3H, s, C_7-NC<u>H</u>$_3$), 1.11 (3H, d, *J* = 7.0 Hz, C_6-C<u>H</u>$_3$);

^{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 $C_{15}H_{23}O_5$ $[M+H]^+$ 298.1654, found 298.1651.

<u>3-(3,4-Dimethoxy-benzyloxy)-2-(*R*)-methylpentan-3-one **6**</u>



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

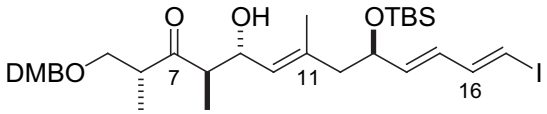
IR ν_{max} (cm^{-1}, thin film) = 1714 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.84 – 6.80 (3H, m, Ar<u>H</u>), 4.40 (2H, s, OC<u>H</u>$_2$Ar), 3.87 (3H, s, ArOC<u>H</u>$_3$), 3.85 (3H, s, ArOC<u>H</u>$_3$), 3.59 (1H, dd, *J* = 8.9, 8.1 Hz C_5- <u>H</u>$_X$H$_Y$), 3.42 (1H, dd, *J* = 9.0, 5.4 Hz C_5- H$_X$<u>H</u>$_Y$), 2.91 – 2.82 (1H, m, C_6-<u>H</u>), 2.49 (2H, q, *J* = 7.3 Hz, C_8-<u>H</u>$_2$), 1.05 (3H, d, *J* = 6.9 Hz, C_6-C<u>H</u>$_3$), 1.02 (3H, t, *J* = 7.4 Hz, C_8-C<u>H</u>$_3$);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 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 $C_{15}H_{22}O_4$ $[M+NH_4]^+$ 284.1862, found 284.1861.

<u>(6*E*,10*E*,12*E*)(2*R*,4*R*,5*R*,13*R*)-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</u> **<u>11</u>**



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

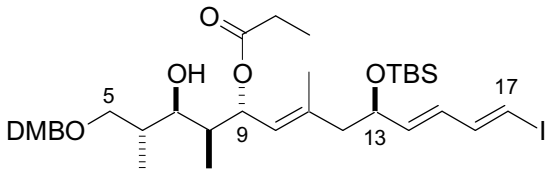
IR ν_{max} (cm^{-1}, thin film) = 3520 (br, C-OH), 1714 (s, C=O);

^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.99 (1H, dd, *J* = 14.3, 10.7 Hz, C_{16}-<u>H</u>), 6.83 – 6.82 (3H, m, Ar-<u>H</u>), 6.27 (1H, d, *J* = 14.5 Hz, C_{17}-<u>H</u>), 6.07 (1H, dd, *J* = 15.0, 10.7 Hz, C_{15}-<u>H</u>), 5.69 (1H, dd, *J* = 15.4, 6.0 Hz ,C_{14}-<u>H</u>), 5.12 (1H, dd, *J* = 9.0, 1.1 Hz, C_{10}-<u>H</u>), 4.50 (1H, td, *J* = 9.0, 4.1 Hz, C_9-<u>H</u>), 4.44 and 4.41 (2H, AB system, J_{AB} = 11.8 Hz, OC<u>H</u>$_2$Ar), 4.30 – 4.26 (1H, m, C_{13}-<u>H</u>), 3.88 (3H, s, ArOC<u>H</u>$_3$), 3.87 (3H, s, ArOC<u>H</u>$_3$), 3.67 (1H, t, *J* = 8.8 Hz, C_5-<u>H</u>$_X$H$_Y$), 3.42 (1H, dd, *J* = 9.0, 4.9 Hz, C_5-H$_X$<u>H</u>$_Y$), 3.09 – 3.05 (1H, m, C_6-<u>H</u>), 2.71 (1H, dq, *J* = 8.6, 7.2 Hz, C_8-<u>H</u>), 2.53 (1H, d, *J* = 4.1 Hz C_9-O<u>H</u>), 2.28 (1H, ddd, *J* = 13.4, 6.2, 0.9 Hz, C_{12}-<u>H</u>$_X$H$_Y$), 2.18 (1H, ddd, *J* = 13.4, 5.9, 0.9 Hz, C_{12}-H$_X$<u>H</u>$_Y$), 1.72 (3H, d, *J* = 1.3 Hz, C_{11}-C<u>H</u>$_3$), 1.06 (3H, d, *J* = 7.1 Hz, C_6-C<u>H</u>$_3$), 1.00 (3H, d, *J* = 7.2 Hz, C_8-C<u>H</u>$_3$), 0.88 (9H, s, SiC(C<u>H</u>$_3$)$_3$), 0.03 (3H, s, SiC<u>H</u>$_3$), 0.01 (3H, s, SiC<u>H</u>$_3$);

^{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 $C_{31}H_{49}IO_6Si$ $[M+NH_4]^+$ 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, $CHCl_3$);

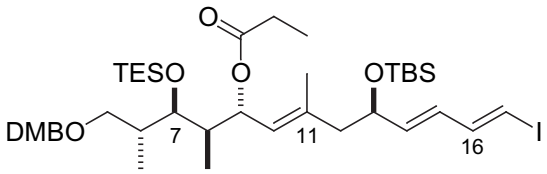
IR ν_{max} (cm^{-1}, thin film) = 3502 (s, C-OH), 1731 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.95 (1H, dd, *J* = 14.1, 10.5 Hz, C_{16}-H), 6.86 – 6.81 (3H, m, Ar-H), 6.25 (1H, d, *J* = 14.6 Hz, C_{17}-H), 6.03 (1H, ddd, *J* = 15.1, 10.6, 1.0 Hz, C_{15}-H), 5.63 (1H, dd, *J* = 15.0, 6.0 Hz, C_{14}-H), 5.47 (1H, app. t, *J* = 9.6 Hz, C_9-H), 5.06 (1H, dd, *J* = 9.6, 1.3 Hz, C_{10}-H), 4.47 and 4.43 (2H, AB system, J_{AB} = 11.8 Hz, OCH_2Ar), 4.28 – 4.23 (1H, m, C_{13}-H), 3.88 (3H, s, $ArOCH_3$), 3.87 (3H, s, $ArOCH_3$), 3.52 (1H, d, *J* = 6.0, C_7-H), 3.49 (1H, dt, *J* = 9.3, 2.2 Hz, C_5-H_XH_Y), 3.29 (1H, d, 2.8 Hz, C_5-H_XH_Y), 2.36 – 2.23 (3H, m, CH_2CH_3 and C_{12}-H_XH_Y), 2.16 (1H, dd, *J* = 13.3, 7.3 Hz, C_{12}-H_XH_Y), 1.94 – 1.87 (1H, m, C_6-H), 1.79 – 1.71 (1H, m, C_8-H), 1.76 (3H, d, *J* = 1.5 Hz, C_{11}-CH_3), 1.12 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 0.88 (9H, s, $SiC(CH_3)_3$), 0.82 (3H, d, *J* = 7.0 Hz, C_6-CH_3), 0.80 (3H, d, *J* = 7.0 Hz, C_8-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 $C_{34}H_{55}IO_7Si$ $[M+NH_4]^+$ 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-dimethoxy-benzyloxy)-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, $CHCl_3$);

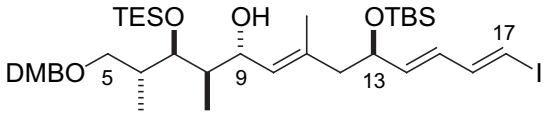
IR ν_{max} (cm^{-1}, thin film) = 1732 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.95 (1H, dd, *J* = 14.4, 10.8 Hz, C_{16}-H), 6.90 – 6.82 (3H, m, Ar-H), 6.24 (1H, d, *J* = 14.5 Hz, C_{17}-H), 6.01 (1H, ddd, *J* = 15.0, 11.0, 1.3 Hz, C_{15}-H), 5.62 (1H, dd, *J* = 15.3, 6.0 Hz ,C_{14}-H), 5.12 (1H, app. t, *J* = 9.8, C_9-H), 4.93 (1H, dd, *J* = 9.5, 1.2 Hz, C_{10}-H), 4.47 and 4.43 (2H, AB system, J_{AB} = 11.8 Hz, OCH_2Ar), 4.28 – 4.22 (1H, m, C_{13}-H), 3.89 (3H, s, Ar OCH_3), 3.88 (3H, s, $ArOCH_3$), 3.74 (1H, dd, *J* = 7.5, 1.8, C_7-H), 3.52 (1H, dd, *J* = 8.8, 4.3 Hz, C_5-H_XH_y), 3.24 (1H, dd, *J* = 9.0, 7.5 Hz, C_5-H_XH_y), 2.29 (1H, dd, *J* = 13.3, 5.5 Hz, C_{12}-H_XH_y), 2.28 (2H, qd, *J* = 7.8, 3.2 Hz, CH_2CH_3), 2.16 (1H, dd, *J* = 13.0, 8.0 Hz, C_{12}-H_XH_y), 1.93 – 1.87 (1H, m, C_6-H), 1.82 – 1.75 (1H, m, C_8-H), 1.77 (3H, d, *J* = 1.2 Hz, C_{11}-CH_3), 1.08 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 0.93 (9H, t, *J* = 7.8 Hz, $SiCH_2CH_3$), 1.0 – 0.91 (3H, m, C_6-CH_3), 0.88 (9H, s, $SiC(CH_3)_3$), 0.76 (3H, d, *J* = 7.0 Hz, C_8-CH_3), 0.56 (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 = 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 $C_{40}H_{69}IO_7Si_2$ $[M+Na]^+$ 867.3524, found: 867.3550.

(6*E*,10*E*,12*E*)(2*R*,3*S*,4R,5*R*,9*R*)-9-(*tert*-Butyl-dimethyl-silanyloxy)-1-(3,4-dimethoxy-benzyloxy)-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, $CHCl_3$);

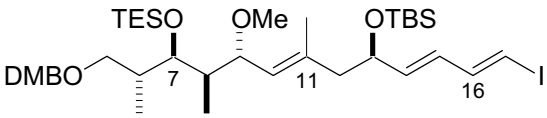
IR ν_{max} (cm^{-1}, thin film) = 3527 (s, C-OH);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99 (1H, ddd, *J* = 14.6, 10.8, 0.5 Hz, C_{16}-H), 6.92 – 6.82 (3H, m, Ar-H), 6.27 (1H, d, *J* = 14.3 Hz, C_{17}-H), 6.07 (1H, ddd, *J* = 15.1, 10.6, 1.0 Hz, C_{15}-H), 5.68 (1H, dd, *J* = 15.3, 6.0 Hz, C_{14}-H), 5.13 (1H, dd, *J* = 9.0, 1.0 Hz, C_{10}-H), 4.47 and 4.42 (2H, AB system, J_{AB} = 11.8 Hz, OCH_2Ar), 4.28 (1H, app. qd, *J* = 6.0, 1.3 Hz, C_{13}-H), 4.18 (1H, app. td, *J* = 9.3, 3.0 Hz ,C_9-H), 3.96 (1H, dd, *J* = 7.5, 2.0, C_7-H), 3.89 (3H, s, $ArOCH_3$), 3.88 (3H, s, $ArOCH_3$), 3.61 (1H, dd, *J* = 9.0, 4.2 Hz, C_5-H_XH_y), 3.29 (1H, dd, *J* = 8.8, 7.8 Hz, C_5-H_XH_y), 2.29 (1H, dd, *J* = 13.3, 6.0 Hz, C_{12}-H_XH_y), 2.17 (1H,dd, *J* = 13.3, 6.7 Hz, C_{12}-H_XH_y), 2.00 – 1.99 (1H, m, C_6-H), 1.98 – 1.95 (1H, m, C_8-H), 1.69 (3H, d, *J* = 1.2 Hz, C_{11}-CH_3), 1.64 – 1.59 (1H, m, C_9-OH), 0.98 – 0.95 (3H, m, C_6-CH_3), 0.96 (9H, t, *J* = 7.8 Hz, $SiCH_2CH_3$), 0.89 (9H, s, $SiC(CH_3)_3$), 0.76 (3H, d, *J* = 6.8 Hz, C_8-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 $C_{37}H_{65}IO_6Si_2$ $[M+NH_4]^+$ 806.3708, found: 806.3712.

(6*E*,10*E*,12*E*)(2*R*,3*S*,4R,5*R*,9*R*)-9-(*tert*-Butyl-dimethyl-silanyloxy)-1-(3,4-dimethoxy-benzyloxy)-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, $CHCl_3$);

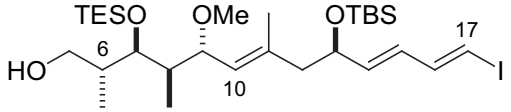
IR ν_{max} (cm^{-1}, thin film) = 1594 and 1516 (aromatic C=C)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.97 (1H, ddd, *J* = 14.3, 10.5, 0.5 Hz, C_{16}-H), 6.91 – 6.81 (3H, m, Ar-H), 6.25 (1H, d, *J* = 14.3 Hz, C_{17}-H), 6.05 (1H, dd, *J* = 15.3, 10.8 Hz, C_{15}-H), 5.68 (1H, dd, *J* = 15.3, 6.3 Hz, C_{14}-H), 4.92 (1H, dd, *J* = 9.6, 1.0 Hz, C_{10}-H), 4.49 and 4.41 (2H, AB system, J_{AB} = 11.8 Hz, OCH_2Ar), 4.30 – 4.25 (1H, m, Hz, C_{13}-H), 3.98 (1H, dd, *J* = 8.3, 1.8, C_7-H), 3.87 (3H, s, $ArOCH_3$), 3.86 (3H, s, $ArOCH_3$), 3.67 (1H, app. t, *J* = 9.5 Hz, C_9-H), 3.55 (1H, dd, *J* = 8.8, 3.8 Hz, C_5-H_XH_Y), 3.22 (1H, app. t, *J* = 8.5 Hz, C_5-H_XH_Y), 3.14 (3H, s, C_9-OCH_3), 2.37 (1H, dd, *J* = 13.2, 5.1 Hz, C_{12}-H_XH_Y), 2.23 (1H, dd, *J* = 13.4, 7.7 Hz, C_{12}-H_XH_Y), 1.92 - 1.82 (1H, m, C_6-H), 1.68 (3H, d, *J* = 1.2 Hz, C_{11}-CH_3), 1.61 – 1.53 (1H, m, C_8-H), 0.96 (9H, t, *J* = 8.0 Hz, $SiCH_2CH_3$), 0.92 (3H, d, *J* = 6.8 Hz, C_6-CH_3), 0.89 (9H, s, $SiC(CH_3)_3$), 0.70 (3H, d, *J* = 7.0 Hz, C_8-CH_3), 0.63 (6H, q, *J* = 8.0 Hz, $SiCH_2CH_3$), 0.05 (3H, s, $SiCH_3$), 0.03 (3H, s, $SiCH_3$);

^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{38}H_{67}IO_6Si_2$ $[M+NH_4]^+$ 820.3865, found: 820.3864.

(6*E*,10*E*,12*E*)(2*R*,3*S*,4R,5*R*,9*R*)-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); $[\alpha]_D^{20}$ = - 6.8 (*c* = 1.23, $CHCl_3$);

IR ν_{max} (cm^{-1}, thin film) = 3444 (s, C-OH);

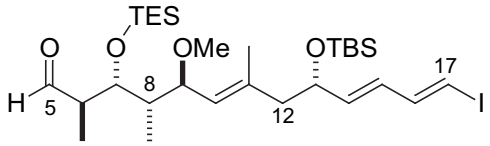
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.98 (1H, dd, *J* = 14.3, 10.5 Hz, C_{16}-H), 6.27 (1H, d, *J* = 14.6 Hz, C_{17}-H), 6.06 (1H, dd, *J* = 15.3, 10.8 Hz, C_{15}-H), 5.68 (1H, dd, *J* = 15.3, 6.3 Hz, C_{14}-H), 4.92 (1H, d, *J* = 9.8 Hz, C_{10}-H), 4.32 – 4.27 (1H, m, C_{13}-H), 4.13 (1H, dd, *J* = 6.5, 1.5 Hz, C_5-H_XH_Y), 3.66 (1H, app. t, *J* = 9.6 Hz ,C_9-H), 3.61 – 3.50 (2H, m, C_5-H_XH_Y and C_7-H), 3.18 (3H, d, *J* = 4.0 Hz C_9-OCH_3), 2.67 – 2.64 (1H, m, C_5-OH), 2.38 (1H, ddd, *J* = 13.3, 5.5, 1.0 Hz, C_{12}-H_XH_Y), 2.24 (1H, dd, *J* = 13.3, 7.6 Hz, C_{12}-H_XH_Y), 1.88 - 1.81 (1H, m, C_6-H), 1.69 (3H, d, *J* = 1.2 Hz, C_{11}-CH_3), 1.57 – 1.56 (1H, m, C_8-H), 1.00 (9H, t, *J* = 8.0 Hz, $SiCH_2CH_3$), 0.90 (9H, s, $SiC(CH_3)_3$),

0.85 (3H, d , J = 7.0 Hz, C_6-C$\underline{H}_3$), 0.75 (3H, d, J = 7.0 Hz, C_8-C$\underline{H}_3$), 0.63 (6H, q, J = 7.8 Hz, SiC$\underline{H}_2$CH$_3$), 0.06 (3H, s, SiC$\underline{H}_3$), 0.04 (3H, s, SiC$\underline{H}_3$);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 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 $C_{29}H_{57}IO_4Si_2$ $[M+Na]^+$ 675.27378, found: 675.27530.

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



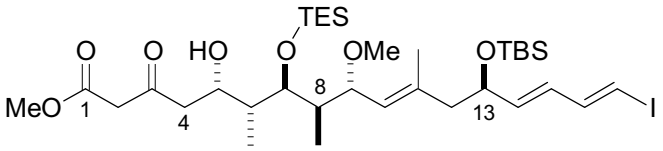
$\boldsymbol{R_f}$ 0.76 (PE/EtOAc 2:1); $[\alpha]_D^{20}$ = + 2.2 (c = 0.99, $CHCl_3$);

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

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.73 (1H, d, J = 3.0 Hz, C_5-$\underline{H}$), 6.97 (1H, ddd, J = 14.3, 10.8, 0.8 Hz, C_{16}-$\underline{H}$), 6.28 (1H, d, J = 14.6 Hz, C_{17}-$\underline{H}$), 6.05 (1H, dd, J = 15.3, 10.8 Hz, C_{15}-$\underline{H}$), 5.67 (1H, dd, J = 15.3, 6.3 Hz, C_{14}-$\underline{H}$), 4.91 (1H, dd, J = 9.5, 1.3 Hz, C_{10}-$\underline{H}$), 4.41 (1H, dd, J = 7.8, 1.8 Hz, C_7-$\underline{H}$), 4.29 (1H, app. q, J = 6.0 Hz, C_{13}-$\underline{H}$), 3.69 (1H, app. t, J = 9.8 Hz, C_9-$\underline{H}$), 3.15 (3H, s, C_9-OC$\underline{H}_3$), 2.51 (1H, app. qnd, J = 7.0, 3.0, Hz, C_6-$\underline{H}$), 2.37 (1H, ddd, J = 13.3, 5.5, 1.0 Hz, C_{12}-$\underline{H}_X$H$_Y$), 2.24 (1H,dd, J = 13.3, 7.5 Hz, C_{12}-H$_X$$\underline{H}_Y$), 1.69 (3H, d, J = 1.5 Hz, C_{11}-C$\underline{H}_3$), 1.58 – 1.50 (1H, m, C_8-$\underline{H}$), 0.99 (3H, d, J = 7.0 Hz, C_6-C$\underline{H}_3$), 0.96 (9H, t, J = 7.8 Hz, SiCH$_2$C$\underline{H}_3$), 0.88 (9H, s, SiC(C$\underline{H}_3$)$_3$), 0.74 (3H, d, J = 7.0 Hz, C_8-C$\underline{H}_3$), 0.62 (6H, q, J = 7.8 Hz, SiC$\underline{H}_2$CH$_3$), 0.05 (3H, s, SiC$\underline{H}_3$), 0.03 (3H, s, SiC$\underline{H}_3$);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 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.

(10*E*,14*E*,16*E*)(5*S*,6*R*,7*R*,8*R*,9*R*,13*R*)-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, $CHCl_3$);

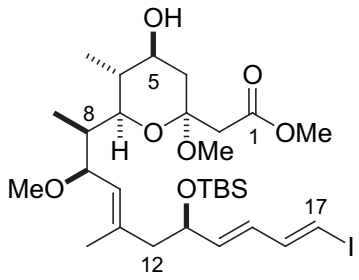
IR ν_{max} (cm^{-1}, thin film) = 3482 (m, C-OH), 1748 (s, C=O), 1714 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.98 (1H, ddd, *J* = 14.3, 10.5, 0.8 Hz, C_{16}-H), 6.26 (1H, d, *J* = 14.3 Hz, C_{17}-H), 6.05 (1H, dd, *J* = 15.3, 10.5 Hz, C_{15}-H), 5.67 (1H, dd, *J* = 15.3, 6.3 Hz ,C_{14}-H), 4.92 (1H, dd, *J* = 9.6, 1.2 Hz, C_{10}-H), 4.43 (1H, app. dq, *J* = 8.8, 2.8 Hz, C_5-H), 4.31 – 4.26 (1H, m, C_{13}-H), 4.10 (1H, dd, *J* = 5.5, 2.3 Hz, C_7-H), 3.74 (3H, s, CO_2CH_3), 3.68 (1H, app. t, *J* = 9.6 Hz, C_9-H), 3.51 (2H, s, C_2-H_2), 3.16 (3H, s, C_9-OCH_3), 3.03 (1H, d, *J* = 2.8 Hz, OH), 2.79 (1H, dd, *J* = 16.6, 9.3 Hz, C_4-H_XH_y), 2.54 (1H, dd, *J* = 16.6, 3.2 Hz, C_4-H_XH_y), 2.37 (1H, ddd, *J* = 13.3, 5.5, 1.0 Hz, C_{12}-H_XH_y), 2.23 (1H, ddd, *J* = 13.3, 7.5, 0.8 Hz, C_{12}-H_XH_y), 1.72 – 1.67 (1H, m, C_8-H), 1.69 (3H, d, *J* = 1.3 Hz, C_{11}-CH_3), 1.51 – 1.47 (1H, m, C_6-H), 0.99 (9H, t, *J* = 8.0 Hz, $SiCH_2CH_3$), 0.93 – 0.88 (3H, m, C_6-CH_3) 0.89 (9H, s, SiC(CH_3)$_3$), 0.75 (3H, d, *J* = 7.0 Hz, C_8-CH_3), 0.67 (6H, q, *J* = 7.5 Hz, Si$CH_2$$CH_3$), 0.05 (3H, s, SiCH_3), 0.03 (3H, s, SiCH_3);

^{13}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 $C_{34}H_{63}IO_7Si_2$ [M+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, $CHCl_3$);

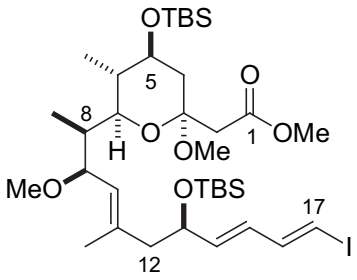
IR ν_{max} (cm^{-1}, ATR) = 3433 (br, C-OH), 1741 (s, C=O);

^{1}H NMR (500 MHz, C_6D_6) δ = 6.86 (1H, dd, J = 14.3, 10.7 Hz, C_{16}-H), 5.95 (1H, d, J = 14.5 Hz, C_{17}-H), 5.88 (1H, dd, J = 15.1, 10.9 Hz, C_{15}-H), 5.47 (1H, dd, J = 15.4, 6.4 Hz ,C_{14}-H), 5.03 (1H, dd, J = 9.6, 1.1 Hz, C_{10}-H), 4.19 (1H, app. q, J = 6.4 Hz, C_{13}-H), 4.06 (1H, dd, J = 10.9, 1.7 Hz, C_7-H), 4.03 (1H, app. t, J = 9.8 Hz, C_9-H), 3.76 – 3.69 (1H, m, C_5-H), 3.37 (3H, s, CO_2CH_3), 3.31 (3H, s, C_3-OCH_3), 3.12 (3H, s, C_9-OCH_3), 2.67 and 2.60 (2H, AB system, J_{AB} = 13.4 Hz, C_2-H_2), 2.43 (1H, dd, J = 12.6, 4.7 Hz, C_4-H_XH_Y), 2.33 (1H, ddd, J = 13.0, 5.6, 0.7 Hz, C_{12}-H_XH_Y), 2.22 (1H, dd, J = 13.2, 7.1 Hz, C_{12}-H_XH_Y), 1.88 – 1.812 (1H, m, C_8-H), 1.76 (1H, dd, J = 12.8, 11.1 Hz, C_4-H_XH_Y), 1.67 (3H, d, J = 1.3 Hz, C_{11}-CH_3), 1.44 – 1.29 (1H, m, C_6-H), 0.99 (9H, s, $SiC(CH_3)_3$), 0.90 (3H, d, J = 6.6 Hz, C_6-CH_3), 0.84 (3H, d, J = 7.1 Hz, C_8-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 $C_{29}H_{51}IO_7Si$ [M+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, $CHCl_3$);

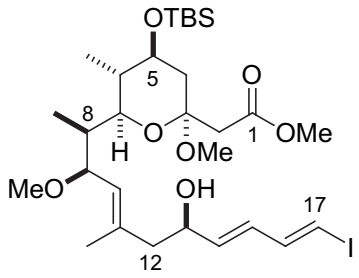
IR ν_{max} (cm^{-1}, ATR) = 1744 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99 (1H, dd, *J* = 14.3, 10.8 Hz, C_{16}-H), 6.27 (1H, d, *J* = 14.6 Hz, C_{17}-H), 6.05 (1H, dd, *J* = 15.6, 10.8 Hz, C_{15}-H), 5.68 (1H, dd, *J* = 15.3, 6.3 Hz, C_{14}-H), 4.93 (1H, dd, *J* = 9.3, 1.3 Hz, C_{10}-H), 4.31 – 4.27 (1H, m, C_{13}-H), 3.86 (1H, app. t, *J* = 9.8 Hz, C_9-H), 3.72 (1H, dd, *J* = 10.6, 1.8 Hz, C_7-H), 3.70 – 3.64 (1H, m, C_5-H), 3.66 (3H, s, CO_2CH_3), 3.23 (3H, s, C_3-OCH_3), 3.11 (3H, s, C_9-OCH_3), 2.66 and 2.62 (2H, AB system, J_{AB} = 13.6 Hz C_2-H_2), 2.38 (1H, dd, *J* = 13.3, 5.0 Hz, C_{12}-H_XH_Y), 2.23 (1H, dd, *J* = 13.6, 7.5 Hz, C_{12}-H_XH_Y), 2.12 (1H, dd, *J* = 12.8, 4.5 Hz, C_4-H_XH_Y), 1.73 – 1.64 (2H, m, C_4-H_XH_Y and C_8-H), 1.70 (3H, d, *J* = 1.3 Hz, C_{11}-CH_3), 1.44 – 1.35 (1H, m, C_6-H), 0.889 (9H, s, $SiC(CH_3)_3$), 0.887 (9H, s, $SiC(CH_3)_3$), 0.84 (3H, d, *J* = 6.5 Hz, C_6-CH_3), 0.69 (3H, d, *J* = 7.0 Hz, C_8-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}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 $C_{35}H_{65}IO_7Si_2$[M+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, $CHCl_3$);

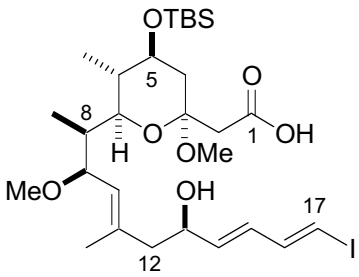
IR ν_{max} (cm^{-1}, thin film) = 3440 (s, C-OH), 1738 (s, C=O);

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.02 (1H, dd, *J* = 14.3, 10.7 Hz, C_{16}-H), 6.34 (1H, d, *J* = 14.5 Hz, C_{17}-H), 6.19 (1H, dd, *J* = 15.1, 10.7 Hz, C_{15}-H), 5.74 (1H, dd, *J* = 15.4, 6.0 Hz, C_{14}-H), 5.04 (1H, dd, *J* = 9.6, 1.3 Hz, C_{10}-H), 4.32 – 4.27 (1H, m, C_{13}-H), 3.91 (1H, t, *J* = 9.6 Hz, C_9-H), 3.73 (1H, d, *J* = 10.9 Hz, C_7-H), 3.70 – 3.64 (1H, m, C_5-H), 3.67 (3H, s, CO_2CH_3), 3.24 (3H, s, C_3-OCH_3), 3.14 (3H, s, C_9-OCH_3), 2.67 and 2.62 (2H, AB system, J_{AB} = 13.5 Hz C_2-H_2), 2.31 – 2.29 (2H, m, C_{12}-H_2), 2.12 (1H, dd, *J* = 13.0, 4.7 Hz, C_4-H_XH_Y), 1.76 – 1.66 (2H, m, C_4-H_XH_Y and C_8-H), 1.74 (3H, s, C_{11}-CH_3), 1.44 – 1.39 (1H, m, C_6-H), 0.89 (9H, s, $SiC(CH_3)_3$), 0.84 (3H, d, *J* = 6.4 Hz, C_6-CH_3), 0.70 (3H, d, *J* = 7.0 Hz, C_8-CH_3), 0.06 (6H, s, $Si(CH_3)_2$);

^{13}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 $C_{29}H_{51}IO_7Si$ [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, $CHCl_3$);

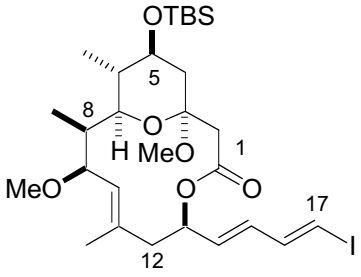
IR ν_{max} (cm^{-1}, thin film) = 3422 (s, C-OH), 1711 (s, C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 (1H, dd, *J* = 14.3, 10.5 Hz, C_{16}-H), 6.35 (1H, d, *J* = 14.6 Hz, C_{17}-H), 6.19 (1H, dd, *J* = 15.3, 10.8 Hz, C_{15}-H), 5.74 (1H, dd, *J* = 15.3, 6.3 Hz, C_{14}-H), 5.06 (1H, dd, *J* = 9.5, 1.0 Hz, C_{10}-H), 4.30 (1H, app. q, *J* = 6.3 Hz, C_{13}-H), 3.90 (1H, dd, *J* = 10.8, 1.8 Hz, C_7-H), 3.87 (1H, app. t, *J* = 9.5 Hz ,C_9-H), 3.75 – 3.65 (1H, m, C_5-H), 3.27 (3H, s, C_3-OCH_3), 3.16 (3H, s, C_9-OCH_3), 2.83 and 2.62 (2H, AB system, J_{AB} = 15.0 Hz C_2-H_2), 2.32 – 2.27 (2H, m, C_{12}-H_2), 2.10 (1H, dd, *J* = 13.1, 4.8 Hz, C_4-H_XHy), 1.83 – 1.76 (1H, m, C_8-H), 1.73 (3H, d, *J* = 1.3 Hz, C_{11}-CH_3), 1.59 (1H, dd, *J* = 13.1, 10.8 Hz, C_4-$H_X$$H_y$), 1.52 – 1.45 (1H, m, C_6-H), 0.88 (9H, s, SiC(CH_3)$_3$), 0.87 (3H, d, *J* = 6.8 Hz, C_6-CH_3), 0.78 (3H, d, *J* = 7.0 Hz, C_8-CH_3), 0.064 (3H, s SiCH_3), 0.058(3H, s SiCH_3);

^{13}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 $C_{28}H_{49}IO_7Si$ [M+Na]: 675.2190, found: 675.2204.

13-(*tert*-butyldimethylsilyoxy)-5-(4-iodobuta-1,3-dienyl)-1,9-dimethoxy-7,10,12-trimethyl-4,15-dioxa-bicyclo[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);

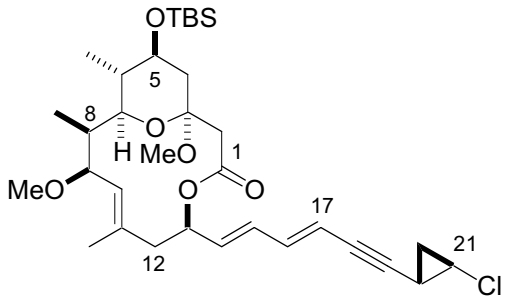
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99 (1H, dd, *J* = 14.4, 10.7 Hz, C_{16}-H), 6.38 (1H, d, *J* = 14.3 Hz, C_{17}-H), 6.18 (1H, dd, *J* = 15.3, 10.8 Hz, C_{15}-H), 5.70 (1H, dd, *J* = 15.3, 6.5 Hz, C_{14}-H), 5.49 – 5.43 (1H, m, C_{13}-H), 5.30 (1H, d, *J* = 9.3 Hz, C_{10}-H), 3.89 (1H, dd, *J* = 10.0, 2.5 Hz, C_9-H),

3.54 (1H, d, J = 10.3 Hz ,C_7-H), 3.47 (1H, td, J = 10.8, 4.3 Hz, C_5-H), 3.27 (3H, s, C_3-OCH_3), 3.22 (3H, s, C_9-OCH_3), 2.59 and 2.44 (2H, AB system, J_{AB} = 12.6 Hz C_2-H_2), 2.42 – 2.36 (1H, m, C_{12}-H_xH_y), 2.27 (1H, dd, J = 13.2, 2.9, Hz C_{12}-H_xH_y), 2.23 – 2.18 (1H, m, C_8-H), 2.12 (1H, dd, J = 13.2, 4.4 Hz, C_4-H_XH_Y), 1.65 (3H, s, C_{11}-CH_3), 1.48 – 1.38 (1H, m, C_6-H), 1.29 – 1.23(1H, m, C_4-H_XH_Y), 1.00 (3H, d, J = 7.0 Hz, C_8-CH_3), 0.90 (3H, obs., C_6-CH_3), 0.89 (9H, s, SiC(CH_3)$_3$), 0.07 (3H, s SiCH_3), 0.06 (3H, s SiCH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ =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 $C_{28}H_{47}IO_6Si$ [M+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-dioxa-bicyclo[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, C=O);

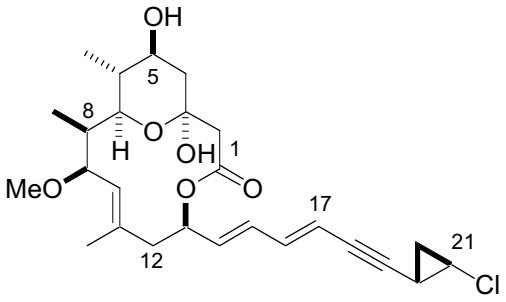
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.46 (1H, dd, J = 15.3, 10.8 Hz, C_{16}-H), 6.25 (1H, dd, J = 15.3, 10.8 Hz, C_{15}-H), 5.73 (1H, dd, J = 15.2, 6.7 Hz, C_{14}-H), 5.54 (1H, dd, J = 15.4, 1.9 Hz, C_{17}-H), 5.54 – 5.48 (1H, m, C_{13}-H), 5.30 (1H, d, J = 9.3 Hz, C_{10}-H), 3.89 (1H, dd, J = 9.9, 2.6 Hz, C_9-H), 3.54 (1H, dd, J = 10.5, 1.5 Hz, C_7-H), 3.47 (1H, td, J = 10.8, 4.3 Hz, C_5-H), 3.28 (3H, s, C_3-OCH_3), 3.22 (3H, s, C_9-OCH_3), 3.19 – 3.15 (1H, m, C_{21}-H) 2.59 and 2.44 (2H, AB system, J_{AB} = 12.6 Hz C_2-H_2), 2.42 – 2.36 (1H, m, C_{12}-H_xH_y), 2.27 (1H, dd, J = 13.2, 2.9 Hz, C_{12}-H_xH_y), 2.23 – 2.18 (1H, m, C_8-H), 2.12 (1H, dd, J = 13.2, 4.4 Hz, C_4-H_XH_Y), 1.82 – 1.77 (1H, m, C_{20}-H) 1.65 (3H, s, C_{11}-CH_3), 1.47 – 1.40 (1H, m, C_6-H), 1.30 – 1.25 (3H, m, C_4-H_XH_Y and C_{22}-H_2), 1.00

(3H, d, J = 7.0 Hz, C_8-C<u>H</u>$_3$), 0.90 (3H, obs., C_6-C<u>H</u>$_3$), 0.89 (9H, s, SiC(C<u>H</u>$_3$)$_3$), 0.07 (3H, s SiC<u>H</u>$_3$), 0.06 (3H, s SiC<u>H</u>$_3$);

^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{33}H_{51}ClO_6Si$ [M+Na]: 629.3041, found: 629.3057.

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



$\boldsymbol{R_f}$ 0.27 (PE/EtOAc 1:1); $[\alpha]_D^{20}$ = -33.4 (c = 0.53, $CHCl_3$);

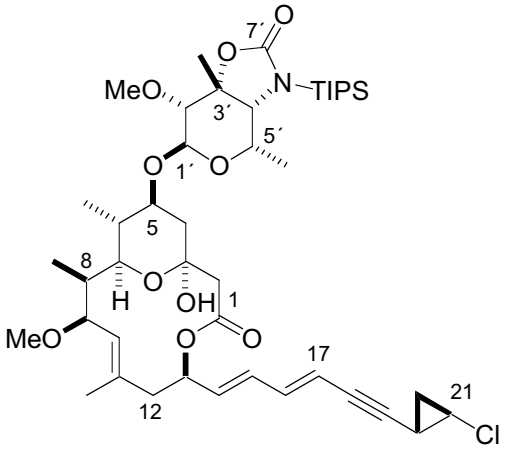
IR ν_{max} (cm^{-1}, thin film) = 3442 (C-OH), 1704 (C=O);

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.48 (1H, dd, J = 15.4, 10.9 Hz, C_{16}-<u>H</u>), 6.27 (1H, dd, J = 14.8, 10.8 Hz, C_{15}-<u>H</u>), 5.85 – 5.81 (1H, m, C_{13}-<u>H</u>), 5.76 (1H, dd, J = 14.9, 6.4 Hz, C_{14}-<u>H</u>), 5.57 (1H, dd, J = 15.6, 1.8 Hz, C_{17}-<u>H</u>), 5.31 (1H, dd, J = 9.7, 1.1 Hz, C_{10}-<u>H</u>), 5.02 (1H, d, J = 2.5 Hz, C_3-O<u>H</u>) 3.80 (1H, dd, J = 9.5, 2.5 Hz, C_9-<u>H</u>), 3.79 – 3.76 (1H, m, C_5-<u>H</u>), 3.61 (1H, dd, J = 10.3, 2.5 Hz, C_7-<u>H</u>), 3.23 (3H, s, C_9-OC<u>H</u>$_3$), 3.18 (1H, td, J = 5.7, 3.2, Hz, C_{21}-<u>H</u>), 2.55 and 2.44 (2H, AB system, J_{AB} = 12.8 Hz, C_2-<u>H</u>$_2$), 2.30 – 2.29 (2H, m, C_{12}-<u>H</u>$_2$), 2.24 – 2.19 (1H, m, C_8-<u>H</u>), 2.10 (1H, dd, J = 11.8, 4.5 Hz, C_4-<u>H</u>$_X$H$_Y$), 1.82 – 1.78 (1H, m, C_{20}-H), 1.73 (3H, d, J = 1.3 Hz, C_{11}-C<u>H</u>$_3$), 1.52 – 1.49 (1H, m, C_5-O<u>H</u>) 1.42 – 1.36 (1H, m, C_6-<u>H</u>), 1.31 – 1.28 (3H, m, C_4-H$_X$<u>H</u>$_Y$ and C_{22}-<u>H</u>$_2$), 0.98 (6H, d, J = 6.9 Hz, C_8-C<u>H</u>$_3$ and C_6-C<u>H</u>$_3$);

^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{26}H_{35}ClO_6Si$ [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-dioxa-8-oxo-7-triisopropylsilanyl-bicyclo[4.3.0]non-3-yl]1-hydroxy-9-methoxy-7,10,12-trimethyl-4,15-dioxa-bicyclo[9.3.1]pentadec-7-en-3-one



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

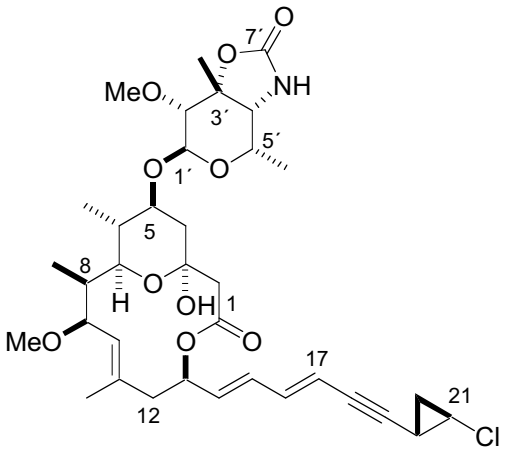
IR ν_{max} (cm^{-1}, thin film) = 1735 (s, C=O), 1714 (s, C=O)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.48 (1H, dd, *J* = 15.4, 10.9 Hz, C_{16}-H), 6.26 (1H, dd, *J* = 14.7, 10.7 Hz, C_{15}-H), 5.85 – 5.79 (1H, m, C_{13}-H), 5.76 (1H, dd, *J* = 14.5, 6.4 Hz, C_{14}-H), 5.57 (1H, d, *J* = 15.5 Hz, C_{17}-H), 5.30 (1H, d, *J* = 9.2 Hz, C_{10}-H), 4.91 (1H, d, *J* = 1.9 Hz, C_3-OH), 4.86 (1H, d, *J* = 6.1 Hz, $C_{1'}$-H), 3.94 – 3.88 (1H, m, $C_{5'}$-H), 3.80 (1H, dd, *J* = 9.4, 2.4 Hz, C_9-H), 3.78 – 3.73 (1H, m, C_5-H) 3.65 (1H, dd, *J* = 10.5, 2.4 Hz, C_7-H), 3.59 (3H, s, $C_{2'}$-OCH_3), 3.41 (1H, d, *J* = 2.3 Hz, $C_{4'}$-H), 3.28 – 3.22 (1H, m, $C_{2'}$-H), 3.24 (3H, s, C_9-OCH_3), 3.20 – 3.16 (1H, m, C_{21}-H) 2.51 and 2.43 (2H, AB system, J_{AB} = 12.9 Hz, C_2-H_2), 2.30 – 2.28 (2H, m, C_{12}-H_2), 2.26 – 2.21 (2H, C_8-H and C_4-H_xH_y), 1.83 – 1.78 (1H, m, C_{20}-H), 1.73 (3H, d, *J* = 1.0 Hz, C_{11}-CH_3), 1.53 (3H, s, C_3′-CH_3), 1.54 – 1.45 (1H, m, C_6-H), 1.39, (3H, spt., *J* = 7.3 Hz Si(CH(CH_3)$_2$)$_3$), 1.30 – 1.23 (6H, m, C_4-HxH_y, C_{22}-H_2 and C_5′-Me), 1.21 – 1.16 (18H, m, Si(CH(CH_3)$_2$)$_3$), 0.98 (6H, m, , C_6-CH_3 and C_8-CH_3);

^{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]: 856.4211found: 856.4199.

(–)-Callipeltoside A (**1**)



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

^{1}H NMR (500 MHz, $CDCl_3$) δ = 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_X$$H_Y$), 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-Hx**H**y) 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);

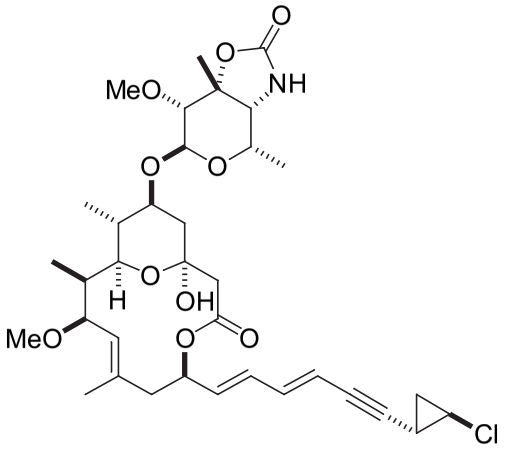
^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.9, 161.1, 141.6, 134.4, 134.3, 132.1, 128.4, 113.5, 103.6, 96.6, 92.8, 83.9, 83.1, 81.4, 78.8, 78.4, 76.5, 72.7, 65.3, 62.7, 62.0, 55.4, 47.8, 46.1, 44.5, 39.9, 38.2, 35.1, 23.0, 19.8, 16.3, 15.9, 12.8, 12.7, 6.8;

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

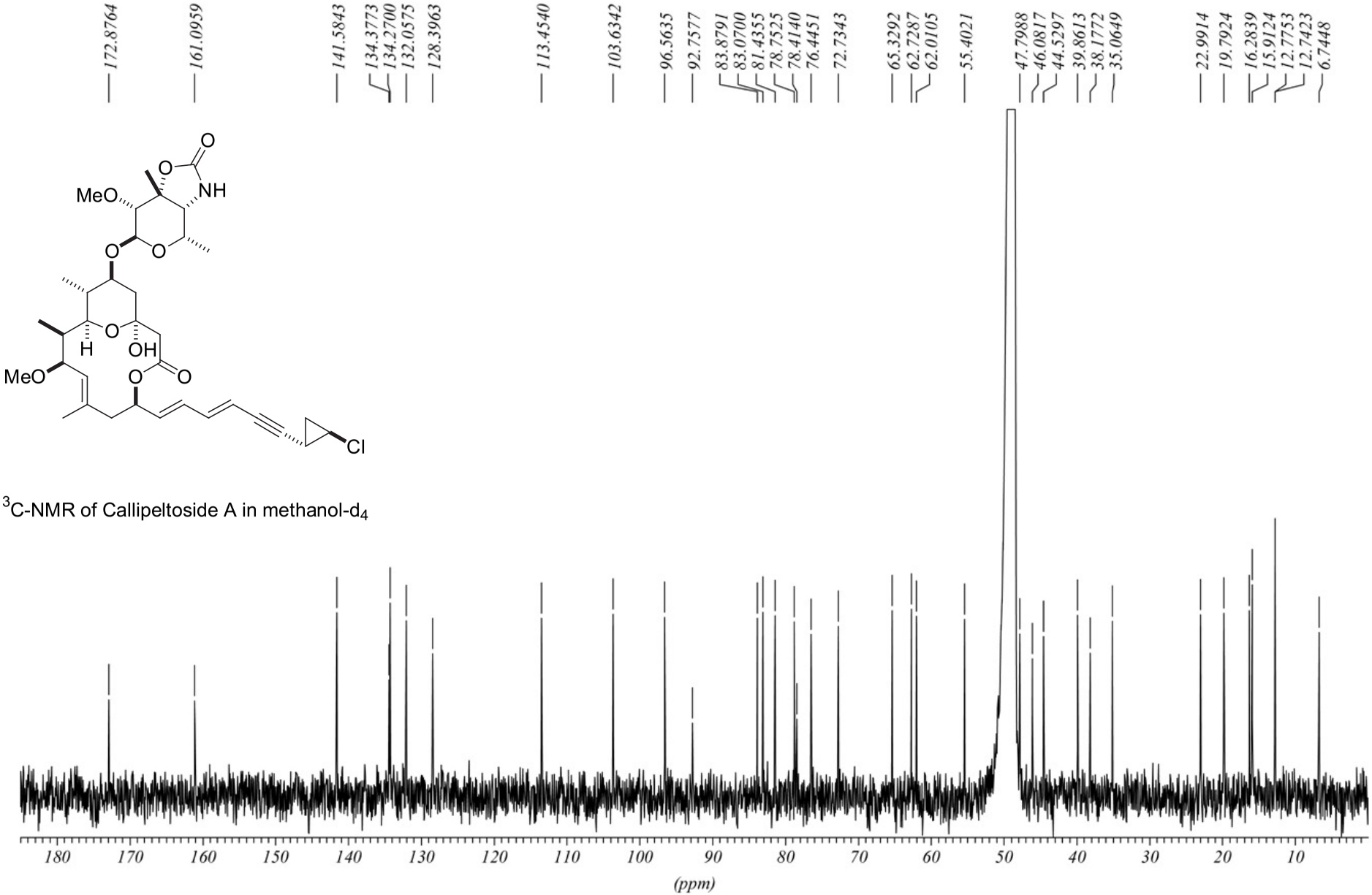
^{1}H NMR signals in methanol-d_4 (500 MHz)		
	natural callipeltoside A	synthetic callipeltoside A
atom	δ in ppm	δ in ppm
1		
2	2.56, d (12.7); 2.50, d (12.7)	2.55, d (12.8); 2.47, d (12.9)
3		
4	2.25, overlapped; 1.43, t (11.7)	2.21, m, overlapped; 1.40, t (11.7)
5	3.76, ddd (11.7, 5.9, 4.9)	3.73, td, (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.)



^{1}H-NMR of Callipeltoside A in methanol-d_4



^{13}C-NMR of Callipeltoside A in methanol-d_4