Supplementary Material for Organic & Biomolecular Chemistry

Catalytic Diastereo- and Positionselective Oxidative Mono-Cyclization of 1,5,9-Trienes and Polyenes

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Supporting Information

Analytical Data for compounds 7a, 7c-d, 8, 19, 21, 22, 29, 32 and the corresponding ketols

6-(tert-Butyl-diphenyl-silanyloxy)-1-[5-(1-hydroxy-1-methyl-ethyl)-2-methyl-tetrahydro-furan-2-yl]-4-methyl-hex-4-en-1-ol (7a)

IR (KBr): ν_{max} 3433, 2963, 2931, 2857, 1761, 1719, 1472, 1463, 1428, 1379, 1113, 1064, 823, 741, 703, 614, 506; NMR: δ_H 1.03 (9 H, s, SiC(CH_3)$_3$), 1.11 (3 H, s, C(2)-CH_3), 1.15 (3 H, s, C(5)-C(OH)(CH_3)$_2$), 1.23 (3 H, s, C(5)-C(OH)(CH_3)$_2$), 1.44 (3 H, s, CH$_2$C(CH_3)=CH), 1.49 (2 H, m, C(2)-CHOHCH_2), 1.63 (1 H, m, C(3)-H^a), 1.88 (3 H, m, C(4)-H_2 and C(3)-H^b), 2.02 (1 H, C(2)-CH(OH)CH$_2$CH^a), 2.25 (1 H, C(2)-CH(OH)CH$_2$CH^b), 3.36 (1 H, m, C(2)-CHOH), 3.84 (1 H, m, C(5)-H), 4.21 (2 H, d, J 6.3, CH_2OTBDPS), 5.40 (1 H, tq, J 6.3 and 1.1, CH$_2$C(CH$_3$)=CHCH$_2$), 7.36 (6 H, m, Ar), 7.67 (4 H, m, Ar); δ_C 16.4 (CH$_2$C(*C*H$_3$)=CHCH$_2$), 19.1 (Si*C*(CH$_3$)$_3$) 21.0 (C(5)-COH(*C*H$_3$)$_2$), 24.8 (C(2)-*C*H$_3$), 26.6 (*C*(4)), 28.8 (SiC(*C*H$_3$)$_3$), 27.3 (C(5)-COH(*C*H$_3$)$_2$), 30.1 (C(2)-CH(OH)*C*H$_2$), 35.1 (*C*(3)), 36.3 (C(2)-CH(OH)CH$_2$*C*H$_2$), 61.1 (*C*H$_2$OTBDPS), 71.6 (C(5)-*C*OH(CH$_3$)$_2$), 77.1 (C(2)-*C*OHCH$_2$), 85.2 (*C*(5)), 85.8 (*C*(2)), 124.2 (CH$_2$C(CH$_3$)=*C*HCH$_2$), 127.5 (4 x Ar), 129.5 (2 x Ar), 134.0 (2 x Ar), 135.6 (4 x Ar), 137.1 (CH$_2$*C*(CH$_3$)=CHCH$_2$); MS (EI) *m/z* 510 ([M]$^+$, 1 %), 483 ([M – OH]$^+$, 1), 467 (2), 451 ([M – (CH$_3$)$_2$C(OH)]$^+$, 3), 435 (4), 347 (5), 199 ([Ph$_2$SiOH]$^+$, 89), 143 ([(CH$_3$)$_2$(OH)C-THF-CH$_3$]$^+$, 59), 135 (29), 71 ([THF – H]$^+$, 57), 43 ([C$_3$H$_7$]$^+$, 100); HRMS (EI) *m/z* 451.2669 ([M]$^+$, C$_{28}$H$_{39}$O$_3$Si requires 451.2674).

6-(*tert*-Butyl-diphenyl-silanyloxy)-1-[5-(1-hydroxy-1-methyl-ethyl)-2-methyl-tetrahydro-furan-2-yl]-4-methyl-hex-4-en-1-one (10a)

IR (KBr): ν_{max} 3442, 2975, 2933, 1717, 1451, 1381, 1274, 1114, 1071, 1026, 952, 714; NMR: δ_H 1.03 (9 H, s, SiC(CH_3)$_3$), 1.09 (3 H, s, C(2)-CH_3), 1.29 (3 H, s, Me), 1.40 (3 H, s, Me), 1.42 (3 H, s, Me), 1.77 (3 H, m, C(4)-H_2 and C(3)-H^a), 2.21 (3 H, m, C(3)-H^b, C(2)-C(=O)CH_2), 2.61 (2 H, C(2)-C(=O)CH$_2$CH_2), 3.15 (2 H, br s, OH), 3.90 (1 H, m, C(5)-H), 4.20 (2 H, dd, J 6.2 and 0.6, CH_2OTBDPS), 5.35 (1 H, tq, J 7.0 and 1.2, CH$_2$C(CH$_3$)=CHCH$_2$), 7.36 (6 H, m, Ar), 7.66 (4 H, m, Ar); δ_C 16.5 (CH$_2$C(*C*H$_3$)=CHCH$_2$), 19.1 (Si*C*(CH$_3$)$_3$), 23.9 (C(5)-COH(*C*H$_3$)$_2$), 24.8 (C(2)-*C*H$_3$), 25.8 (*C*(4)), 26.8 (SiC(*C*H$_3$)$_3$), 27.7 (C(5)-C(OH)(*C*H$_3$)$_2$), 32.9 (C(2)-C(=O)*C*H$_2$), 35.4 (C(2)-CH(OH)CH$_2$*C*H$_2$), 36.1 (*C*(3)), 60.9 (*C*H$_2$OTBDPS), 70.6 (C(5)-*C*(OH)(CH$_3$)$_2$), 86.8 (*C*(5)), 88.2 (*C*(2)), 124.4 (CH$_2$C(CH$_3$)=*C*HCH$_2$), 127.5 (4 x Ar), 129.4 (2 x Ar), 133.9 (2 x Ar), 135.5 (4 x Ar), 135.7 (CH$_2$*C*(CH$_3$)=CHCH$_2$), 212.8 (C(2)-*C*(=O)CH$_2$); MS (EI) *m/z* 508 ([M]$^+$, 1 %), 465 ([M – C$_3$H$_7$]$^+$, 3), 451 ([M – ^{t}Bu]$^+$, 2), 433 (M – ^{t}Bu – H$_2$O]$^+$, 3), 241 (43), 235 ([M – Ph$_2$SiO – H$_2$O]$^+$, 30), 199 ([(CH$_3$)$_2$(OH)C-THF(CH$_3$)-C(=O)CH$_2$CH$_2$]$^+$, 59), 163 (45), 143 ([(CH$_3$)$_2$(OH)C-THF(CH$_3$)]$^+$, 100); HRMS (EI) *m/z* 451.2312 ([M – C$_4$H$_9$]$^+$, C$_{27}$H$_{35}$O$_4$Si requires 451.2305).

4-Nitro-benzoic acid 6-hydroxy-6-[5-(1-hydroxy-1-methyl-ethyl) - 2 - methyl-tetrahydro-furan - 2 - yl]- 3 -methyl-hex-2 -enyl ester (7c)

IR (KBr): ν_{max} 3427, 2972, 1723, 1608, 1529, 1459, 1348, 1274, 721; NMR: δ_H 1.07 (3 H, s, C(2)-CH_3), 1.12 (3 H, s, C(5)-C(OH)(CH_3)$_2$), 1.19 (3 H, s, C(5)-C(OH)(CH_3)$_2$), 1.51 (2 H, m, C(2)-CH(OH)CH_2), 1.60 (1 H, m, C(3)-H^a), 1,74 (3 H, s, CH$_2$C(CH_3)=CH), 1.85 (3 H, m, C(4)-H_2 and C(3)-H^b), 2.09 (1 H, m, C(2)-CH(OH)CH$_2$CH^a), 2.35 (1 H, m, C(2)-CH(OH)CH$_2$CH^b), 3.34 (1 H, m, C(2)-CHOH), 3.81 (1 H, m, C(5)-H), 4.85 (2 H, d, J 7.0, CH_2OBzNO$_2$), 5.46 (1 H, m, CH$_2$C(CH$_3$)=CHCH$_2$), 8.17 (2 H, m, Ar), 8.21 (2 H, m, Ar); δ_C 16.7 (CH$_2$C(*C*H$_3$)=CHCH$_2$), 21.1 (C(5)-COH(*C*H$_3$)$_2$), 25.0 (C(2)-*C*H$_3$), 26.7 (*C*(4)), 27.4 (C(5)-C(OH)(*C*H$_3$)$_2$), 30.1 (C(2)-CH(OH)*C*H$_2$), 35.3 (*C*(3)), 36.5 (C(2)-CH(OH)CH$_2$*C*H$_2$), 62.8 (*C*H$_2$OBzNO$_2$), 71.6 (C(5)-*C*(OH)(CH$_3$)$_2$), 77.4 (C(2)-*C*(OH)CH$_2$), 85.2 (*C*(5)), 85.8 (*C*(2)), 117.9 (CH$_2$C(CH$_3$)=*C*HCH$_2$), 123.5 (2 x Ar), 130.8 (2 x Ar), 135.9 (Ar), 143.4 (CH$_2$*C*(CH$_3$)=CHCH$_2$), 150.5 (Ar), 164.8 (O*C*(=O)Ar); MS (pos. FAB) *m/z* 444 ([M + Na]$^+$, 10 %), 322 ([M + H]$^+$, 3), 404 ([M – OH]$^+$, 2), 255 ([M – O$_2$C-Ph-NO$_2$]$^+$, 11), 275 (1), 251 (2), 239 (2), 233 ([M – (CH$_3$)$_2$(OH)C-THF-CH$_3$]+, 1), 143 ([(CH$_3$)$_2$(OH)-THF-CH$_3$]$^+$, 33).

(*E*)-6-(tetrahydro-5-(2-hydroxypropan- 2 - yl) - 2 - methyl- furan-2-yl)-3-methyl - 6 - oxohex - 2 - enyl-4-nitrobenzoate (ketol corresponding to compound 7c)

IR (KBr): ν_{max} 3434, 2975, 1724, 1608, 1529, 1449, 1348, 1274, 1102, 1015, 874, 785, 721; NMR: δ_H 1.04 (3 H, s, C(5)-C(OH)(CH_3)$_2$), 1.24 (3 H, s, C(5)-C(OH)(CH_3)$_2$), 1.36 (3 H, s, C(2)-CH_3), 1.69 (1 H, m, C(4)-H^a), 1.76 (3 H, s, CH$_2$C(CH_3)=CH), 1.78 (2 H, m, C(4)-H^b and C(3)-H^a), 2.20 (1 H, m, C(3)-H^b), 2.30 (2 H, t, J 7.5, C(2)-CH(=O)CH_2), 2.68 (2 H, dt, J 7.5 and 1.6, C(2)-CH(OH)CH$_2$CH_2), 3.02 (1 H, br s, OH), 3.86 (1 H, m, C(5)-H), 4.81 (2 H, d, J 7.0, CH_2OBzNO$_2$), 5.42 (1 H, m, CH$_2$C(CH$_3$)=CHCH$_2$), 8.16 (2 H, m, Ar), 8.21 (2 H, m, Ar); δ_C 16.7 (CH$_2$C(*C*H$_3$)=CHCH$_2$), 23.8 (C(2)-*C*H$_3$), 24.8 (C(5)-C(OH)(*C*H$_3$)$_2$), 25.8 (*C*(4)), 27.7 (C(5)-C(OH)(*C*H$_3$)$_2$), 32.9 (C(2)-C(=O)*C*H$_2$), 35.1 (C(2)-CH(OH)CH$_2$*C*H$_2$), 36.0 (*C*(3)), 62.4 (*C*H$_2$OBzNO$_2$), 70.4 (C(5)-*C*OH(CH$_3$)$_2$), 86.7 (*C*(5)), 88.2 (*C*(2)), 118.2 (CH$_2$C(CH$_3$)=*C*HCH$_2$), 123.4 (2 x Ar), 130.6 (2 x Ar), 135.7 (Ar), 141.9 (CH$_2$*C*(CH$_3$)=CHCH$_2$), 150.4 (Ar-NO$_2$), 164.6 (O*C*(=O)Ar), 212.5 (C(2)-*C*(=O)CH$_2$); MS (EI) *m/z* 404 ([M – CH$_3$]$^+$, 1 %), 373 ([M – NO$_2$]$^+$, 1), 237 ([M – CH$_3$ – O$_2$N-PhCO$_2$H]$^+$, 2), 211 ([(CH$_3$)$_2$(OH)C-THF(CH$_3$)-C(=O)CH$_2$CH$_2$C]$^+$, 2), 194 ([M – C$_3$H$_7$O – O$_2$N-PhCO$_2$]$^+$, 3), 143 ([(CH$_3$)$_2$(OH)C-THF-CH$_3$]$^+$, 100), 125 ([143 – H$_2$O]$^+$, 18), 43 ([C$_3$H$_7$]$^+$, 46).

6 - Fluoro - 1 - [5 - (1 - hydroxy - 1 - methyl-ethyl) - 2 -methyl-tetrahydro-furan-2-yl]-4-methyl-hex-4-en-1-ol (8)

IR (KBr): ν_{max} 3392, 2976, 2935, 2873, 1451, 1411, 1377, 1184, 1079, 925; NMR: δ_H 1.08 (3 H, s, Me), 1.12 (3 H, d, *J* 7.7, Me), 1.20 (3 H, d, *J* 2.1, Me), 1.38 (3 H, dd, *J* 21.6 and 5.8, C(C*H*$_3$)=CHCH$_2$F), 1.41 (2 H, m, C(3)-*H*$_2$), 1.65 (2 H, m, C(4)-*H*$_2$), 1.86 (3 H, m, C(2)-CH(OH)C*H*$_2$C*H*^{a}), 2.00 (1 H, m, C(2)-CH(OH)CH$_2$C*H*^{b}), 3.34 (1 H, m, C(2)-C*H*(OH)CH$_2$), 3.82 (1 H, m, C(5)-*H*), 5.07 (ddt, *J* 11.0 and 7.8 and 1.0, CH$_2$C(CH$_3$)C=CHC*H*$_2$F), 5.22 (1 H, m, CH$_2$C(CH$_3$)C= CHC*H*$_2$F), 5.84 (1 H, m, CH$_2$C(CH$_3$)C=C*H*CH$_2$F); δ_C 21.0 (*C*(4)), 24.9 (Me), 25.1 (C(2)-CH(OH)*C*H$_2$), 26.0 (Me), 26.4 (Me), 27.4 (Me), 35.2 (*C*(3)), 37.2 (C(2)-CH(OH)CH$_2$CH$_2$), 71.7 (C(5)-*C*(OH)(CH$_3$)$_2$), 77.6 (C(2)-*C*H(OH)CH$_2$), 85.3 (*C*(2) and *C*(5)), 85.9 (*C*H$_2$F), 113.3 (C(CH$_3$)=*C*HCH$_2$F), 140.8 (*C*(CH$_3$)=CHCH$_2$F); MS (pos. FAB) *m/z* 297 ([M + Na]$^+$, 100 %), 255 ([M – F]$^+$, 21), 237 ([M – F – H$_2$O]$^+$, 52), 143 ([(CH$_3$)$_2$(OH)C-THF-CH$_3$]$^+$, 60), 71 ([THF + H]$^+$, 83), 43 ([C$_3$H$_7$]$^+$, 60).

Benzoic acid 1-{hydroxy-[5-(1-hydroxy-propyl)-tetrahydro-furan-2-yl]-methyl}-but-3-enyl ester (21)

NMR data for the first diastereoisomer of compound **21**:
NMR: δ_H 0.93 (3 H, t, *J* 7.6, C(5)-CH(OH)CH$_2$C*H*$_3$), 1.37 (2 H, m, C(5)-CH(OH)C*H*$_2$CH$_3$), 1.73 (1 H, m, C(4)-*H*^{a}), 1.98 (3 H, m, C(3)-*H*$_2$), 2.56 (1 H, m, CH$_2$=CHC*H*^{a}), 2.70 (1 H, m, CH$_2$=CHC*H*^{b}), 3.65 (1 H, dd, *J* 7.0 and 2.5, C(2)-C*H*(OH)), 3.81 (1 H, ddd, *J* 8.1 and 5.4 and 2.9, C(5)-C*H*(OH)CH$_2$CH$_3$), 3.92 (1 H, dt, *J* 7.0 and 2.8, C(5)-*H*), 4.10 (1 H, dt, *J* 6.9 and 2.5, C(2)-*H*), 5.02 (1 H, m, *H*$_2$C=CHCH$_2$), 5.09 (1 H, ddd, *J* 17.1 and 3.0 and 1.4, *H*$_2$C=CHCH$_2$), 5.19 (1 H, ddd, *J* 7.4 and 7.4 and 3.7, C(2)-CH(OH)C*H*(OBz)CH$_2$), 5.83 (1 H, m, H$_2$C=C*H*CH$_2$), 7.41 (2 H, m, Ar), 7.53 (1 H, m, Ar), 8.02 (2 H, m, Ar); δ_C 10.3 (C(5)-CH(OH)CH$_2$*C*H$_3$), 24.1 (C(5)-CH(OH)*C*H$_2$CH$_3$), 26.3 (*C*(4)), 28.9 (*C*(3)), 35.0 (H$_2$C=CH*C*H$_2$), 74.1 (C(2)-*C*H(OH)), 74.5 (C(2)-CH(OH)*C*H(OBz)CH$_2$), 74.8 (C(5)-*C*H(OH)CH$_2$CH$_3$), 77.9 (*C*(2)), 82.5 (*C*(5)), 118.0 (H$_2$*C*=CH-CH$_2$), 128.3 (2 x Ar), 129.8 (2 x Ar), 133.0 (Ar), 133.7 (Ar), 166.0 (CHO*C*(=O)Ph); IR and MS data are the same as for compound **20**.

NMR data for the second diastereoisomer of compound **21**:
δ_H 0.91 (3 H, t, *J* 7.4, C(5)-CH(OH)CH$_2$C*H*$_3$), 1.33 (2 H, m, C(5)-CH(OH)C*H*$_2$CH$_3$), 1.72 (1 H, m, C(4)-*H*$_2$), 1.94 (3 H, m, C(3)-*H*$_2$), 2.56 (2 H, m, CH$_2$=CHC*H*$_2$), 3.59 (1 H, dd, *J* 5.0 and 3.7 C(2)-C*H*(OH)), 3.68 (1 H, m, C(5)-C*H*(OH)CH$_2$CH$_3$), 3.87 (1 H, dt, *J* 6.9 and 3.0, C(5)-*H*), 4.08 (1 H, m, C(2)-*H*), 5.04 (1 H, m, *H*$_2$C=CHCH$_2$), 5.12 (1 H, ddd, *J* 17.2 and 3.0 and 1.4, *H*$_2$C=CHCH$_2$), 5.32 (1 H, ddd, *J* 7.7 and 5.1 and 5.1, C(2)-CH(OH)C*H*(OBz)CH$_2$), 5.81 (1 H, m, H$_2$C=C*H*CH$_2$), 7.40 (2 H, m, Ar), 7.52 (1 H, m, Ar), 8.02 (2 H, m, Ar); δ_C 10.3 (C(5)-CH(OH)CH$_2$*C*H$_3$), 24.0 (C(5)-CH(OH)*C*H$_2$CH$_3$), 26.0 (*C*(4)), 28.8 (*C*(3)), 35.4 (H$_2$C=CH*C*H$_2$), 73.8 (C(2)-*C*H(OH)), 74.7 (C(2)-CH(OH)*C*H(OBz)CH$_2$), 77.3 (C(5)-*C*H(OH)CH$_2$CH$_3$), 78.9 (*C*(2)), 82.8 (*C*(5)), 118.2 (H$_2$*C*=CH-CH$_2$), 128.3 (2 x Ar), 129.7 (2 x Ar), 133.0 (Ar), 133.4 (Ar), 166.5 (CHO*C*(=O)Ph); IR and MS data are the same as for compound **20**.

Benzoesäure - 2,3,6 - trihydroxy-6-[5-(1-hydroxy-1-methyl-ethyl) - 2 - methyl - tetrahydrofuran - 2 - yl] - 3 - methyl-hexylester (23b)

IR (KBr): ν_{max} 3422, 2970, 2929, 2874, 1717, 1602, 1585, 1452, 1383, 1316, 1275, 1178, 1121, 1071, 1027, 951, 919, 892, 805, 784, 714; NMR: δ_H 1.10/1.11 (3 H, 2 x s, Me), 1.16/1.17 (3 H, 2 x s, Me), 1.21/1.22 (3 H, 2 x s, C(2)-C*H*$_3$), 1.24/1.25 (3 H, 2 x s, C(C*H*$_3$)(OH)CH(OH)), 1.63-1.89 (8 H, m, C(3)-*H*$_2$ and C(4)-*H*$_2$ and C(2)-CH(OH)C*H*$_2$C*H*$_2$), 3.40 (1 H, t, *J* 6.7, C(2)-C*H*(OH)CH$_2$), 3.84 (2 H, m, C(5)-*H* and C*H*(OH)CH$_2$OBz), 4.27/4.30 (1 H, 2 x dd, *J* 11.7 and 1.9, PhC(=O)OC*H*^{a}), 4.54/4.58 (1 H, 2 x dd, *J* 11.7 and 2.8), 7.43 (2 H, m, Ar), 7.56 (1 H, m, Ar), 8.06 (2 H, m, Ar); δ_C 21.4/21.5 (*C*(4)), 22.0 (C(2)-*C*H$_3$), 25.0 (C(2)-CH(OH)*C*H$_2$), 25.6/25.8 (C(*C*H$_3$)(OH)CH$_2$(OH)), 26.7 (Me), 27.5 (Me), 35.3/35.4 (*C*(3)), 36.0 (C(2)-CH(OH)CH$_2$*C*H$_2$), 66.1/66.4 (*C*H$_2$OBz), 71.7 (C(5)-*C*(CH$_3$)$_2$(OH), 73.1/73.4 (*C*(CH$_3$)(OH)CH(OH), 74.1/74.4 (C(2)-*C*H(OH)CH$_2$), 75.7 (*C*(2)), 78.0/78.2 (*C*H(OH)CH$_2$OBz), 85.4/85.7 (*C*(5)), 128.4 (2 x Ar), 129.7 (3 x Ar), 133.2 (Ar), 167.0 (Ph*C*(=O)OCH$_2$); MS (EI) *m/z* 410 ([M]$^+$, 1 %), 403 (2), 374 ([M – 2 H$_2$O]$^+$, 1), 353 (1), 333 ([M – (CH$_3$)$_2$C(OH) – H$_2$O]$^+$, 1), 249 ([M – (CH$_3$)$_2$(OH)C-THF-CH$_3$ – H$_2$O]$^+$, 18), 227 ([M – PhCO – (CH$_3$)$_2$CHOH – H$_2$O]$^+$, 23), 209 ([227 – H$_2$O]$^+$, 11), 143 ([(CH$_3$)$_2$(OH)C-THF-CH$_3$]$^+$, 54), 125 ([143 – H$_2$O]$^+$, 26), 105 ([PhCO]$^+$, 100), 71 ([THF – H]$^+$, 53), 59 ([(CH$_3$)$_2$C(OH)]$^+$, 26), 43 ([C$_3$H$_7$]$^+$, 55); HRMS (EI) *m/z* 374.2085 ([M – 2 H$_2$O]$^+$, C$_{22}$H$_{30}$O$_5$ requires 374.2093).

6 - (*tert*-Butyl - diphenyl - silanyloxy) - 1 - [5 - (1 -hydroxy-1-methyl-ethyl)-2-methyl-tetrahydrofuran-2-yl]-4-methyl-hexan-1,4,5-triol (23a)

IR (KBr): ν_{max} 3499, 3072, 3049, 2967, 2933, 2889, 2858, 1769, 1718, 1472, 1463, 1428, 1382, 1363, 1236, 1145, 1113, 1064, 1029, 947, 918, 824, 740, 704, 614, 505; NMR: δ_H 1.08 (9 H, s, SiC(C*H*$_3$)$_3$), 1.11 (3 H, s, C(2)-C*H*$_3$), 1.16 (6 H, 2 x s, 2 x Me), 1.32 (3 H, s, C(C*H*$_3$)(OH)CH(OH)), 1.85 (8 H, m, C(3)-*H*$_2$ and C(4)-*H*$_2$ and C(2)-CH(OH)C*H*$_2$C*H*$_2$), 1.90 (4 H, br s, 4 x OH), 3.75 (3 H, m, C(5)-*H* and C(2)-CH(OH) and C*H*(OH)CH$_2$OTBDPS), 4.88 (2 H, dd, *J* 11.0 and 1.7, C*H*$_2$OTBDPS), 7.39 (6 H, m, Ar), 7.67 (4 H, m, Ar); δ_C 19.2 (Si*C*(CH$_3$)$_3$) 21.9 (*C*(4)), 24.1 (Me), 24.7 (Me), 26.1 (C(2)-*C*H$_3$), 26.6 (Si(C(*C*H$_3$)$_3$), 29.9 (C(2)-CH(OH)*C*H$_2$), 34.4 (C(2)-CH(OH)*C*H$_2$), 35.3 (*C*(3)), 39.8 (C(2)-CH(OH)CH$_2$*C*H$_2$), 62.3 (*C*H$_2$OTBDPS), 70.4 (C(5)-*C*(OH)(CH$_3$)$_2$), 77.0 (C(2)-*C*(OH)CH$_2$), 78.8 (*C*(CH$_3$)(OH)-CH(OH)), 83.4 (*C*(2)), 84.3 (*C*H(OH)CH$_2$OTBDPS), 85.8 (*C*(5)), 127.7 (4 x Ar), 129.8 (2 x Ar), 135.6

(4 x Ar); MS (EI) *m/z* 467 ([M – Ph]$^+$, 1 %), 449 ([M – Ph – H_2O]$^+$, 1), 407 (1), 425 (1), 347 (4), 281 ([C=CH-OTBDPS]$^+$, 6), 227 ([M – H_2O – C(OH)CH_2OTBDPS]$^+$, 38), 209 ([227 – H_2O]$^+$, 39), 199 ([Ph_2SiOH]$^+$, 100), 183 [Ph_2SiH]$^+$, 26), 143 ([$(CH_3)_2$(OH)C-THF-CH_3]$^+$, 18), 135 (36), 125 ([143 – H_2O]$^+$, 21), 71 ([THF – H]$^+$, 90).

1 - [5 - (1 - Hydroxy-1-methyl-ethyl)-2 -methyl-tetrahydro-furan-2-yl]-4,8-dimethyl-trideca-4,8-diene-1,10-dione (29)

IR (KBr): ν_{max} 3448, 2975, 1714, 1647, 1448, 1379, 1223, 1146, 1042, 865; NMR: δ_H 1.05 (3 H, s, Me), 1.22 (3 H, t, *J* 7.2, C(=O)OCH_2CH_3), 1.25 (3 H, s, Me), 1.36 (3 H, s, Me), 1.55/1.61 (3 H, 2 x s, Me), 1.74 (3 H, m, C(3)-H^a and C(4)-H_2), 2.09 (3H, s, Me), 2.10 (4 H, m, C(CH_3)=CHCH_2CH_2C(CH_3)=CH), 2.20 (3 H, m, C(3)-H^b and C(2)-C(=O)CH_2CH_2), 2.56 (2 H, m, C(2)-C(=O)CH_2), 3.18/3.24 (1 H, 2 x br s, OH), 3.86 (1 H, m, C(5)-*H*), 4.08 (2 H, q, *J* 7.2, C(=O)OC$H_2$$CH_3$), 5.04 (1 H, m, C(2)-C(=O)$(CH_2)_2$C(CH_3)=C*H*), 5.59 (1 H, 2 x s, C(CH_3)=C*H*CO_2Et); δ_C 14.2 (C(=O)OCH_2*C*H_3), 16.1 (Me), 18.7 (Me), 23.1/23.8 (Me), 24.7 (Me), 25.6/25.7 (C(CH_3)=CH*C*H_2CH_2C(CH_3)=CH), 25.8 (*C*(4)), 27.8 (Me), 33.2 (C(2)-C(=O)*C*H_2), 35.5/35.8 (C(2)-C(=O)CH_2*C*H_2), 36.0/36.1 (*C*(3)), 40.6/40.9 (C(CH_3)=CH-CH_2*C*H_2C(CH_3)=CH), 59.5 (C(=O)O*C*$H_2$$CH_3$), 70.7 (C(5)-*C*(OH)$(CH_3)_2$, 86.9 (*C*(5)), 88.3 (*C*(2)), 115.8 (C(CH_3)=*C*HCO_2Et), 123.5/124.7 (C(2)-C(=O)$(CH_2)_2$C(CH_3)=*C*H), 134.6/134.8 (C(2)-C(=O)$(CH_2)_2$*C*(CH_3)=CH), 159.6 (*C*(CH_3)=CHCO_2Et), 166.9 (*C*(=O)OEt), 213.2 (C(2)-*C*(=O)CH_2); MS (EI) *m/z* 380 ([M]$^+$, 1 %), 335 ([M – OEt]$^+$, 1), 322 ([M – $(CH_3)_2$(OH)C + H]$^+$, 1), 309 (2), 285 (3), 225 ([$(CH_3)_2$(OH)-THF(CH_3)-C(=O)$(CH_2)_2$]$^+$, 14), 143 ([$(CH_3)_2$(OH)C-THF-CH_3]$^+$, 100), 125 ([143 – H_2O]$^+$, 28); HRMS (EI) *m/z* 380.2573 ([M]$^+$, $C_{22}H_{36}O_5$ requires 380.2563).

Acetic acid 6-[5-(6-acetoxy-1-hydroxy-hex-4-enyl)-tetrahy- dro-furan-2-yl]-6-hydroxy-hex-2-enyl ester (32)

IR (KBr): ν_{max} 3442, 2941, 1740, 1446, 1383, 1365, 1236, 1073, 1026, 969; NMR: δ_H 1.51 (4 H, m, C(2)-CH(OH)CH_2), 1.71 (2 H, m, C(3)-H^a), 1.88 (2 H, m, C(3)-H^b), 2.00 (6 H, s, CH_3C(=O)O), 2.11 (2 H, m, C(2)-CH(OH)CH_2CH_2), 2.23 (2 H, m, C(2)-CH(OH)CH_2CH_2), 3.37 (2 H, ddd, *J* 8.9 and 5.2 and 3.9, C(2)-C*H*(OH)CH_2), 3.76 (2 H, m, C(2)-*H*), 4.45 (4 H, dd, *J* 6.5 and 0.8, CH_3C(=O)OCH_2), 5.54 (2 H, dtt, *J* 15.4 and 6.5 and 1.4, CH_3C(=O)CH_2C*H*=CH), 5.72 (2 H, m, CH_3C(=O)CH_2CH=C*H*); δ_C 20.9 *C*H_3C(=O)O), 27.9 (*C*(3)), 28.3 (C(2)-CH(OH)CH_2*C*H_2), 33.1 (C(2)-CH(OH)*C*H_2), 65.1 (CH_3C(=O)O*C*H_2), 73.4 (C(2)-*C*H(OH)CH_2), 85.5 (*C*(2)), 124.2 (CH_3C(=O)CH_2*C*H=CH), 135.7 (CH_3C(=O)OCH_2-*C*H=CH), 170.8 (CH_3*C*(=O)OCH_2); MS (EI) *m/z* 384 ([M]$^+$, 1 %), 366 ([M – H_2O]$^+$, 1), 324 ([M – CH_3COOH]$^+$, 1), 197 (4), 167 (12), 43 ([CH_3CO]$^+$, 100); HRMS (EI) *m/z* 384.2151 ([M]$^+$, $C_{20}H_{32}O_7$ requires 384.2148).

Acetic acid 6-[5-(6-acetoxy-hex-4-enoyl)-tetrahydro-furan-2-yl]-6-hydroxy-hex-2-enyl ester (ketol corresponding to compound 32)

IR (KBr): ν_{max} 3448, 2948, 1771, 1737, 1383, 1368, 1242, 1193, 1052, 1030, 977; NMR: δ_H 1.49 (1 H, m, C(5)-CH(OH)CH^a), 1.61 (1 H, m, C(5)-CH(OH)CH^b), 1.73 (1 H, m, C(4)-H^a), 1.89 (2 H, m, C(4)-H^b and C(3)-H^a), 2.00 (6 H, s, CH_3C(=O)OCH_2), 2.11 (1 H, m, C(3)-H^b), 2.20 (1 H, m, C(5)-CH(OH)CH_2CH^a), 2.28 (3 H, m, C(5)-CH(OH)CH_2CH^b and C(2)-C(=O)CH_2CH_2), 2.50 (2 H, m, C(2)-C(=O)CH_2), 3.37 (1 H, m, C(5)-C*H*(OH)CH_2), 3.66 (1 H, br s, OH), 3.91 (1 H, m, C(5)-*H*), 4.12 (1 H, m, C(2)-*H*), 4.43 (m, 4 H, CH_3C(=O)OCH_2), 5.54 (2 H, m, CH_3C(=O)OCH_2CH=C*H*), 5.70 (2 H, m, CH_3C(=O)OCH_2CH=C*H*); δ_C 20.9 (2 x *C*H_3C(=O)O), 25.7 (C(2)-C(=O)CH_2*C*H_2), 26.7 (*C*(4)), 28.4 (C(5)-CH(OH)CH_2*C*H_2), 29.2 (*C*(3)), 33.8 (C(5)-CH(OH)*C*H_2), 37.7 (C(2)-C(=O)*C*H_2), 64.7 (C(=O)O*C*$H_2$$CH_3$), 65.1 (C(=O)O*C*$H_2$$CH_3$), 72.0 (C(5)-*C*H(OH)$CH_2$), 82.6 (*C*(5)), 83.9 (*C*(2)), 124.1 (CH(OH)$(CH_2)_2$CH=*C*H), 125.1 (C(=O)$(CH_2)_2$CH=*C*H), 133.8 (C(=O)$(CH_2)_2$*C*H=CH), 135.8 (CH(OH)-$(CH_2)_2$C*H*=CH), 170.7 (CH_3*C*(=O)OCH_2), 170.8 (CH_3*C*(=O)OCH_2), 211.0 (C(2)-*C*(=O)CH_2); MS (EI) *m/z* 382 ([M]$^+$, 1 %), 294 (5), 241 (27), 183 ([CH_2CH(OH)-THF-C(=O)$(CH_2)_2$CH]$^+$, 19), 167 ([$(CH_2)_2$CH-THF-C(=O)CH_2]$^+$, 46), 85 (54), 43 ([CH_3CO]$^+$, 100).