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Nitrone Cycloadditions to Isolevoglucosenone: a Ready Access to a New Class of Directly Linked (1→3)-Imino-C-disaccharides

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SUPPORTING INFORMATION

Experimental section

General Remarks: All operations were carried out under inert gas and with anhydrous solvents where required. Rf values refer to TLC on 0.25-mm silica gel plates (Merck F254) with the same eluent used for separation of the compound by flash column chromatography. Melting points (m.p.) were measured with an RCH Kofler apparatus and are uncorrected. Optical rotation measurements were carried out with a Jasco DIP-370 polarimeter or a Perkin-Elmer 241 polarimeter. NMR spectra were recorded with Varian Gemini (1H, 200 MHz) or Avance Bruker (1H, 400 MHz, 500 MHz, 600 MHz) instruments, the NMR spectroscopic data are reported in δ (ppm) from TMS at 25 °C. IR spectra were recorded with a Perkin-Elmer 881 spectrophotometer. Mass spectra (EI, 70 eV) were recorded with a QMD 1000 Carlo Erba instrument by direct inlet. Elemental analyses were carried out with a Perkin-Elmer 2400 instrument.

Synthesis of compound 13.

A solution of nitrone 11 (68.7 mg, 0.3 mmol) and isolevoglucosenone (7, 37.8 mg, 0.3 mmol) in toluene (0.6 mL) was stirred at room temperature for 1.5 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (elucent petroleum ether/AcOEt, 4:1) gave 13 as a white solid (Rf = 0.33, 95 mg, 0.268 mmol, 89%). - m.p. 93-95 °C; [α]D 20 = -25.3 (c = 0.97, CHCl3). 1H NMR (CDCl3, 400 MHz) δ = 5.58 (s, 1 H, H-1), 4.61 (t, J = 3.4 Hz, 1 H, H-5), 4.36 (d, J = 7.6 Hz, 1 H, H-2), 4.02 (br s, 1 H, H-2’), 3.91-3.86 (m, 3 H, Ha-6, Hb-6, H-3’), 3.65 (dd, J = 12.2, 6.4 Hz, 1 H, Ha-4’), 3.63 (br d, J = 6.4 Hz, 1 H, H-1’), 3.42 (dd, J = 7.6, 7.3 Hz, 1 H, H-3), 2.67 (dd, J = 12.2, 4.9 Hz, 1 H, Hb-4’), 1.17 (s, 9 H, tBu), 1.14 (s, 9 H, tBu). 13C NMR (CDCl3, 50 MHz) δ = 203.5 (s, C=O), 100.5 (d, C-1), 80.5 (d, C-2’), 78.5 (d, C-5), 77.7 (d, C-3’), 76.5 (d, C-2), 75.2 (d, C-1’), 74.6 (s, 1 C, (CH3)3C-O), 74.0 (s, 1 C, (CH3)3C-O), 66.2 (t, C-6), 61.9 (t, C-4’), 54.1 (d, C-3), 28.2 (q, 6 C, (CH3)3C-O). MS, m/z (%): 355 (M+, 12), 298 (M+-tBu, 19), 241 (13), 168 (29), 85 (53), 83 (99.6), 81 (39), 56 (100). IR (KBr): 2969, 2934, 2900, 1733, 1471, 1371 cm⁻¹. C18H29NO6 (355.43): calcd. C 60.83, H 8.22, N 3.94; found C 61.05, H 8.30, N 3.78.
Synthesis of compound 14.

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\begin{array}{c}
\text{O} \\
\text{O} \\
\text{N} \\
\text{O} \\
H \text{BuO} \\
5 \quad 6 \\
3 \quad 2 \\
1 \\
\text{O} \\
\text{O} \\
\text{N} \\
\text{O} \\
\end{array}
\]

A solution of nitrone 12 (25.1 mg, 0.16 mmol) and isolevoglucosenone (7, 20.2 mg, 0.16 mmol) in toluene (0.32 mL) was stirred at room temperature for 2.5 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (elucent petroleum ether/AcOEt, 2:1) gave 14 as a white solid (Rf = 0.28, 40.2 mg, 0.142 mmol, 89%). m.p. 103-105 °C; [α]D 25 = +18.4 (c = 0.67, CHCl 3). 1H NMR (CDCl3, 200 MHz) δ = 5.62 (s, 1 H, H-1), 4.66 (dd, J = 3.7, 3.3 Hz, 1 H, H-5), 4.27 (d, J = 4.0, 3.3 Hz, 1 H, H-2), 4.07 (dt, J = 7.3, 3.3 Hz, 1 H, H-2'), 3.71 (dd, J = 7.7 Hz, 1 H, H-3), 3.16 (dd, J = 7.7, 4.0 Hz, 1 H, H-3'), 2.39-2.21 (m, 1 H, H-3'), 1.80-1.65 (m, 1 H, Hb-3'), 1.19 (s, 9 H, tBu). 13C NMR (CDCl3, 50 MHz) δ = 203.2 (s, C=O), 101.6 (s, 1 C, (CH3)3C-O), 78.3 (t, C-2'), 75.8 (d, C-2'), 74.0 (s, 1 C, (CH3)2C-O), 66.5 (t, C-6), 55.2 (d, C-3), 33.2 (t, C-3'), 28.4 (q, 3 C, (CH3)2C-O). MS, m/z (%): 284 (M ++1, 4), 227 (M + tBu, 35), 184 (10), 152 (22), 84 (88), 57 (100). IR (KBr): 2983, 1726 cm -1. C14H21NO5 (283.32): calcd. C 59.35, H 7.47, N 4.94; found C 59.64, H 7.41, N 5.10.

Synthesis of compound 16.

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\begin{array}{c}
\text{O} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{O} \\
5 \quad 6 \\
3 \quad 2 \\
1 \\
\end{array}
\]

A solution of nitrone 15 (53.4 mg, 0.34 mmol) and isolevoglucosenone (7, 21.4 mg, 0.17 mmol) in toluene (0.34 mL) was stirred at room temperature for 2.5 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography with an eluent of increasing polarity afforded 16 (Rf = 0.23, eluent pentane/AcOEt, 3:2, 31.1 mg, 0.11 mmol, 32%) and the recovered (-)-15 (Rf = 0.29, eluent AcOEt/MeOH, 10:1, 27 mg, 0.172 mmol, 50%). 16: white solid. Crystals for X-ray crystal structure determination were obtained by slow evaporation from AcOEt. m.p. 165-167 °C; [α]D 26 = +50.8 (c = 0.44, CHCl3). 1H NMR (CDCl3, 600 MHz) δ = 5.55 (s, 1 H, H-1), 4.87 (dd, J = 5.9, 5.5 Hz, 1 H, H-3'), 4.78 (d, J = 6.6 Hz, 1 H, H-2'), 4.67 (dd, J = 4.4, 2.2 Hz, 1 H, H-5), 4.33 (d, J = 8.4 Hz, 1 H, H-2), 3.91-3.87 (m, 3 H, Ha-6, Hb-6, H-1'), 3.02 (dd, J = 8.4, 8.1 Hz, 1 H, Hb-4'), 2.87 (dd, J = 12.5, 5.1 Hz, 1 H, Hb-4'), 1.50 (s, 3 H, Me), 1.30 (s, 3 H, Me). 13C NMR (CDCl3, 50 MHz) δ = 202.9 (s, C=O), 112.2 (s, 1 C, (CH3)2C) 101.2 (d, C-1), 81.1 (d, C-2'), 78.5 (d, C-5), 78.3 (d, C-3'), 77.1 (d, C-2), 75.4 (d, C-6), 59.5 (t, C-4'), 53.1 (d, C-3), 26.3 (q, 1 C, (CH3)2C), 24.8 (q, 1 C, (CH3)2C). MS, m/z (%): 283 (M', 5), 268 (M'-Me, 2), 183 (3), 149 (5), 86 (69), 84 (100), 51 (44). IR (KBr): 2980, 2946, 2920, 1725 cm -1. C13H17NO6 (283.32): calcd. C 59.35, H 7.47, N 4.94; found C 59.64, H 7.41, N 5.10.
Synthesis of compound 17.

A 1.5 M solution of DIBAL-H in toluene (0.5 mL, 0.75 mmol), was added dropwise under nitrogen atmosphere to a solution of 14 (141.5 mg, 0.5 mmol) in dry CH₂Cl₂ (1 mL), cooled to –78°C. After stirring at –78 °C for 4 h, cooled MeOH (–78°C, 200 µL) was added and the cooling bath was removed. Once at 0°C, 1 M aq HCl (1 mL) was added. The mixture was extracted with CH₂Cl₂ (20 mL, 4 times). The organic phase was washed with a saturated aqueous solution of NaHCO₃ (5 mL), dried over Na₂SO₄, filtered and concentrated. Purification of the crude reaction mixture by flash column chromatography (eluent AcOEt/pentane, 4:1) gave 17 as a waxy solid (Rᶠ = 0.31, 106 mg, 0.372 mmol, 74%). [α]D₂⁶ = -21.9 (c = 0.51, CHCl₃). ¹H NMR (CDCl₃, 600 MHz) δ = 5.43 (s, 1 H, H-1), 4.46-4.44 (m, 1 H, H-5), 4.09 (dd, J = 7.5, 0.7 Hz, 1 H, H_exo-6), 4.05 (dd, J = 8.1, 4.2 Hz, 1 H, H-4), 3.86 (dd, J = 5.9, 1.8 Hz, 1 H, H-2), 3.79 (dt, J = 7.0, 4.0 Hz, 1 H, H-2'), 3.73 (dd, J = 7.5, 5.9 Hz, 1 H, H_exo-6), 3.47-3.45 (m, 1 H, H-1'), 3.34-3.30 (m, 2 H, H-4'), 2.51 (dd, J = 8.1, 5.9 Hz, 1 H, H-3), 2.14-2.08 (m, 1 H, H_a-3'), 1.73-1.67 (m, 1 H, H_b-3'), 1.20 (s, 9 H, tBu). ¹³C NMR (CDCl₃, 50 MHz) δ = 98.3 (d, C-1), 78.0 (d, 1 C), 76.3 (d, 1 C), 75.1 (d, 1 C), 74.0 (s, 1 C, (CH₃)₃C-O), 68.3 (d, C-1'), 62.8 (t, C-6'), 56.7 (t, C-4'), 50.5 (d, C-3), 34.7, (t, C-3'), 28.6 (q, 3 C, (CH₃)₃C-O). MS, m/z (%): 228 (M⁺-tBu, 38), 200 (5), 136 (25), 84 (69), 57 (100). IR (CDCl₃): 3612, 3379 (broad), 2977, 1365 cm⁻¹.

Synthesis of compound 18.

A mixture of 17 (51.3 mg, 0.18 mmol) in pyridine (0.3 mL) and acetic anhydride (0.2 mL) was stirred at room temperature for 5.5 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (eluent AcOEt/pentane, 1:1) gave 18 as a white solid (Rᶠ = 0.42, 44.1 mg, 0.135 mmol, 75%). - m.p. 177-178 °C; [α]D₂⁶ = 177 364 °C; ¹H NMR (CDCl₃, 200 MHz) δ = 5.45 (br s, 1 H, H-1), 5.12 (dd, J = 8.1, 4.4 Hz, 1 H, H-4), 4.60 (t, J = 4.8 Hz, 1 H, H-5), 4.00 (d, J = 7.7 Hz, 1 H, H-exo-6), 3.90 (br d, J = 5.9 Hz, 1 H, H-2'), 3.79-3.70 (m, 2 H, H_exo-6, H-2'), 3.40 (d, J = 3.7 Hz, 1 H, H-1'), 3.34-3.26 (m, 2 H, H-4'), 2.65 (dd, J = 8.1, 6.2 Hz, 1 H, H-3), 2.18-2.00 (m, 1 H, Ha-3'), 2.05 (s, 3 H, Me), 1.76-1.60 (m, 1 H, Hb-3'), 1.16 (s, 9 H, tBu). ¹³C NMR (CDCl₃, 50 MHz) δ = 169.6 (s, C=O), 98.6 (d, C-1), 78.2 (d, 1 C), 76.5 (d, 1 C), 76.1 (d, 1 C), 73.5 (s, 1 C, (CH₃)₃C-O), 71.9 (d, 1 C), 70.4 (d, 1 C), 63.2 (t, C-6'), 56.6 (t, C-4'), 47.7 (d, C-3), 34.7 (t, C-3'), 28.9 (q, 3 C, (CH₃)₂C-O), 20.8 (q, 1 C, CH₃C=O). MS, m/z (%): 327 (M⁺, 13), 270 (M⁺-tBu, 95), 210 (39), 136 (42), 58 (65), 55 (100). IR (KBr): 2973, 2935, 1728, 1367, 1243, 1231 cm⁻¹. C₁₆H₂₅NO₆ (327.37): calcd. C 58.70, H 7.70, N 4.28; found C 58.91, H 8.04, N 4.33.
Synthesis of compound 19.

\[ \text{NaBH}_4 (40 \text{ mg, 1.06 mmol), was slowly added to a solution of 14 (86.9 mg, 0.307 mmol) in ethanol (4 mL), cooled to 0°C. After 10 minutes the cooling bath was removed and the mixture was stirred at room temperature for 2.5 h. After concentration under reduced pressure, CH}_2\text{Cl}_2 (10 mL) and water (10 mL) were added and the two phases were separated. The aqueous phase was extracted with CH}_2\text{Cl}_2 (5 mL, 3 times). The combined organic phases were dried over Na}_2\text{SO}_4, filtered, and concentrated, to give a 4:1 mixture of alcohols 19 and 17 (determined by 200 MHz } ^1\text{H NMR integration). Purification of the crude reaction mixture by flash column chromatography with an eluent of increasing polarity afforded 19 (} \text{R}_f = 0.14, \text{AcOEt/petroleum ether, 2:1, 61.8 mg, 0.217 mmol, 71%}) and 17 (} \text{R}_f = 0.25, \text{eluent AcOEt/petroleum ether, 3:1, 17.1 mg, 0.06 mmol, 19%).\]

19: viscous oil. [\alpha]_{D}^{26} = -86.4 (c = 0.73, CHCl}_3). \text{H NMR (CDCl}_3, 600 MHz) \delta = 5.50 (br s, 1 H, H-1), 4.56 (dm, } J = 5.9 \text{ Hz, 1 H, H-5), 3.84-3.80 (m, 2 H), 3.75 (dd, } J = 7.9, 1.3 \text{ Hz, 1 H), 3.73 (dd, } J = 5.1, 1.8 \text{ Hz, 1 H), 3.64-3.62 (m, 2 H), 3.39-3.29 (m, 2 H, H-4’), 2.83 (t, } J = 5.9 \text{ Hz, 1 H, H-3), 2.16-2.10 (m, 1 H, Ha-3’), 1.73-1.67 (m, 1 H, Hb-3’), 1.18 (s, 9 H, tBu). \text{C NMR (CDCl}_3, 50 MHz) \delta = 98.0 (d, C-1), 77.4 (d, 1 C), 76.0 (d, 1 C), 74.8 (d, 1 C), 73.6 (s, 1 C, (CH}_3)_3C-O), 73.4 (d, 1 C), 66.3 (d, C-1’), 64.1 (t, C-6), 56.3 (t, C-4’), 44.1 (d, C-3), 34.2 (t, C-3’), 28.5 (q, 3 C, (CH}_3)_3C-O). MS, m/z (%): 285 (M+, 6), 228 (M+-tBu, 100), 200 (9), 86 (61), 84 (99), 57 (61). IR (CDCl}_3): 3547, 3381 (broad), 2977, 2899, 1364 cm^{-1}. C_{16}H_{25}NO_6 (327.37): calcd. C 58.70, H 7.70, N 4.28; found C 58.75, H 7.85, N 4.56.

Synthesis of compound 20.

\[ A \text{ mixture of 19 (19.1 mg, 0.067 mmol) in pyridine (0.3 mL) and acetic anhydride (0.15 mL) was stirred at room temperature for 16 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (eluent AcOEt) gave 20 as a white solid (} \text{R}_f = 0.17, 19.6 mg, 0.06 mmol, 90%).\]

A mixture of 19 (19.1 mg, 0.067 mmol) in pyridine (0.3 mL) and acetic anhydride (0.15 mL) was stirred at room temperature for 16 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (eluent AcOEt) gave 20 as a white solid (\text{R}_f = 0.17, 19.6 mg, 0.06 mmol, 90%). Crystals for X-ray crystal structure determination were obtained by slow evaporation from AcOEt. - m.p. 172-174 °C; [\alpha]_{D}^{26} = -124.7 (c = 0.28, CHCl}_3). \text{H NMR (CDCl}_3, 600 MHz) \delta = 5.54 (s, 1 H, H-1), 4.87 (dd, } J = 7.0, 1.8 \text{ Hz, 1 H, H-4), 4.61-4.59 (m, 1 H, H-5), 3.84-3.80 (m, 1 H, H-6), 3.81-3.76 (m, 2 H, H-2, H-2’), 3.41 dt (J = 12.4, 7.0 Hz, 1 H, Ha-4’), 3.39 (d, } J = 4.4 \text{ Hz, 1 H, H-1’), 3.15 (dt, } J = 12.4, 7.1 \text{ Hz, 1 H, Hb-4’), 2.82 (dd, } J = 6.7, 6.1 \text{ Hz, 1 H, H-3), 2.20 (s, 3 H, Me), 2.04 (dq, } J = 12.7, 6.5 \text{ Hz, 1 H, Ha-3’), 1.70-1.65 (m, 1 H, Hb-3’), 1.19 (s, 9 H, tBu). \text{C NMR (CDCl}_3, 50 MHz) \delta = 171.2 (s, C=O), 98.8 (d, C-1), 77.3 (d, 1 C), 74.6 (d, 1 C), 73.7 (s, 1 C, (CH}_3)_3C-O), 73.3 (d, 1 C), 72.9 (d, 1 C), 67.6 (d, 1 C), 64.9 (t, C-6), 56.1 (t, C-4’), 44.1 (d, C-3), 33.5 (t, C-3’), 28.6 (q, 3 C, (CH}_3)_3C-O), 21.3 (q, 1 C, CH}_3C=O). MS, m/z (%): 327 (M+, 13), 312 (M+-Me, 0.3), 270 (M+-tBu, 100), 226 (8), 163 (18), 84 (52), 58 (49), 57 (26), 55 (98). IR (CDCl}_3): 2977, 1735, 1374, 1238 cm^{-1}. C_{16}H_{25}NO_6 (327.37): calcd. C 58.70, H 7.70, N 4.28; found C 58.75, H 7.85, N 4.56.
Synthesis of compound 24.

A mixture of alcohol 17 (42.8 mg, 0.15 mmol) and p-toluenesulfonic acid (51.6 mg, 0.3 mmol) in MeOH (1 mL) was heated at reflux for 3.5 h. Evaporation of the solvent afforded crude 21, that was again dissolved in MeOH (10 mL) and stirred under H₂ atmosphere over Pd(OH)₂/C (50 mg) at room temperature for 12 h. The catalyst was filtered off and the solvent evaporated under reduced pressure. Crude 22 was then dissolved in trifluoroacetic anhydride (2 mL) and trifluoroacetic acid (4 mL) and the mixture was stirred at room temperature overnight. The mixture was concentrated and the residue was dissolved in MeOH (6 mL). 6 Drops of 35% aqueous NH₃ were added, and after 10 minutes the solvent was evaporated under reduced pressure, affording crude 23, that was dissolved in pyridine (1.2 mL) and acetic anhydride (0.4 mL). After stirring at room temperature overnight, the mixture was concentrated under reduced pressure and filtered over silica gel (eluent AcOEt), affording 24 as a white foam ($R_f = 0.86$, 20 mg, 0.044 mmol, 29% yield from 17).

1H NMR (CDCl₃, 200 MHz) δ = 5.59-5.56 (m, 1 H, H-2'), 5.41 (d, J = 2.2 Hz, 1 H, H-1), 5.15 (dd, J = 11.4, 4.4 Hz, 1 H, H-4), 4.59 (t, J = 4.4 Hz, 1 H, H-2), 4.59 (t, J = 4.4 Hz, 1 H, H-3), 4.35 (d, J = 8.0 Hz, 1 H, H-1'), 4.02 (d, J = 8.0 Hz, 1 H, H-endo-6), 3.78 (ddd, J = 11.4, 4.8, 4.3 Hz, 1 H, H-3), 2.19-2.02 (m, 2 H, H-3'), 2.08 (s, 3 H, Me), 2.08 (s, 3 H, Me), 2.04 (s, 3 H, Me). 13C NMR (CDCl₃, 50 MHz, detected signals) δ = 170.2 (s, C=O), 169.9 (s, C=O), 169.6 (s, C=O), 98.6 (d, C-1), 74.3 (d, 1 C), 71.7 (d, 1 C), 71.1 (d, 1 C), 68.6 (d, 1 C), 64.8 (d, 1 C), 64.1 (t, C-6), 44.2 (t, C-4'), 34.9 (d, C-3), 30.6 (t, C-3'), 20.9 (q, 1 C, CH₃C=O), 20.8 (q, 1 C, CH₃C=O), 20.7 (q, 1 C, CH₃C=O).

Synthesis of compounds 25α, 25β.

The triacetate 24 (20 mg, 0.0442 mmol) was dissolved in acetic anhydride (1.5 mL) and trifluoroacetic acid (1 mL) was added. After stirring at room temperature overnight, the mixture was diluted with ethyl acetate (20 mL) and washed with a 5% aqueous solution of NaHCO₃. The aqueous phase was again extracted with ethyl acetate (10 mL) and the combined organic phases dried over Na₂SO₄, filtered and concentrated to afford a 1.4:1 mixture (determined by 200 MHz 1H NMR integration) of 25β and 25α. Purification of the crude reaction mixture by flash column chromatography (eluent petroleum ether/AcOEt, 3:2) gave 25β ($R_f = 0.32$, 16.4 mg, 0.0295 mmol, 67%, impure of 25α, ratio 25β/25α = 5.5/1) and 25α ($R_f = 0.32$, 6.4 mg, 0.0115 mmol, 26%), both as viscous oils that are inclined to retain solvents.

25β:[α]D²² = -31.3 (c = 0.43, CHCl₃), 1H NMR (CDCl₃, 400 MHz) δ = 6.08 (d, J = 4.2 Hz, 1 H, H-1), 5.47 (d, J = 4.4 Hz, 1 H, H-2'), 5.41 (dd, J = 8.2, 4.4 Hz, 1 H, H-4), 5.00 (t, J = 3.9 Hz, 1 H, H-2'), 4.52 (d, J = 8.2 Hz, 1 H, H-1'), 4.47 (td, J = 6.5, 4.5 Hz, 1 H, H-5), 4.24 (dd, J = 11.5, 6.7 Hz, 1 H, Ha-6), 4.18 (dd, J = 11.5, 6.4 Hz, 1 H, Hb-6), 3.95-3.88 (m, 1 H, Ha-4'), 3.66-3.61 (m, 1 H, Hb-4'), 2.66 (td, J = 8.2, 3.6 Hz, 1 H, H-3), 2.38-2.27 (m, 2 H, H-3'), 2.13 (s, 3 H, Me), 2.11 (s, 3 H, Me, 2.11 (s, 3 H, Me).
Me), 2.08 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.03 (s, 3 H, Me). $^{13}$C NMR (CDCl$_3$, 50 MHz, detected signals) δ = 170.4 (s, C=O), 170.2 (s, C=O), 170.1 (s, C=O), 169.9 (s, C=O), 168.2 (s, C=O), 89.8 (d, C-1), 74.7 (d, 1 C), 69.9 (d, 1 C), 69.0 (d, 1 C), 68.2 (d, 1 C), 63.9 (d, 1 C), 62.4 (t, C-6), 44.3 (t, C-4'), 36.6 (d, C-3), 29.5 (t, C-3'), 21.1 (q, 1 C, CH$_3$C=O), 20.9 (q, 1 C, CH$_3$C=O), 20.8 (q, 2 C, CH$_3$C=O), 20.7 (q, 1 C, CH$_3$C=O). MS, m/z (%): 512 (M$^+$-CH$_3$CO, 3), 496 (M$^+$-CH$_3$COO, 25), 435 (10), 380 (10), 333 (26), 224 (100), 166 (58), 164 (96). IR (CDCl$_3$): 2963, 2928, 2855, 1747, 1697, 1447, 1372, 1231 cm$^{-1}$. C$_{22}$H$_{28}$F$_3$NO$_{12}$ (555.16): calcd. C 47.57, H 5.08, N 2.52; found C 47.94, H 5.18, N 2.60.

$^{25}$α: [α]$_D^{22}$ = +9.8 (c = 0.15, CHCl$_3$). $^1$H NMR (CDCl$_3$, 400 MHz) δ = 6.20 (d, J = 4.1 Hz, 1 H, H-1), 5.38-5.36 (m, 2 H, H-2', H-4), 5.33 (dd, J = 3.9, 3.8 Hz, 1 H, H-2), 4.75 (d, J = 7.4 Hz, 1 H, H-1'), 4.51 (td, J = 6.3, 3.1 Hz, 1 H, H-5), 4.18-4.10 (m, 2 H, H-6), 3.90-3.83 (m, 1 H, Ha-4'), 3.69-3.63 (m, 1 H, Hb-4'), 2.51-2.41 (m, 2 H, H-3, Ha-3'), 2.21-2.10 (m, 1 H, Hb-3'), 2.12 (s, 3 H, Me), 2.10 (s, 3 H, Me), 2.08 (s, 3 H, Me), 2.08 (s, 3 H, Me), 2.03 (s, 3 H, Me). $^{13}$C NMR (CDCl$_3$, 50 MHz, detected signals) δ = 170.5 (s, 2 C, C=O), 170.4 (s, C=O), 169.9 (s, C=O), 169.1 (s, C=O), 89.3 (d, C-1), 74.1 (d, 1 C), 69.4 (d, 1 C), 68.6 (d, 1 C), 66.6 (d, 1 C), 64.0 (d, 1 C), 61.5 (t, C-6), 43.9 (t, C-4'), 38.9 (d, C-3), 29.7 (t, C-3'), 20.9 (q, 1 C, CH$_3$C=O), 20.9 (q, 1 C, CH$_3$C=O), 20.8 (q, 2 C, CH$_3$C=O), 20.7 (q, 1 C, CH$_3$C=O). MS, m/z (%): 512 (M$^+$-CH$_3$CO, 0.1), 496 (M$^+$-CH$_3$COO, 2), 435 (2), 333 (10), 224 (70), 165 (100). IR (CDCl$_3$): 2961, 2928, 2849, 1748, 1697, 1447, 1373, 1231 cm$^{-1}$. C$_{22}$H$_{28}$F$_3$NO$_{12}$ (555.16): calcd. C 47.57, H 5.08, N 2.52; found C 47.69, H 4.99, N 2.63.
$^1$H NMR (CDCl$_3$, 400 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz) of compound 13.
$^1$H NMR (CDCl$_3$, 200 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz) of compound 14.
$^1$H NMR (CDCl$_3$, 600 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz) of compound 16.
${}^1$H NMR (CDCl$_3$, 600 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz) of compound 17.
$^1$H NMR (CDCl$_3$, 200 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz) of compound 18.
$^1$H NMR (CDCl$_3$, 600 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz) of compound 19.
$^1$H NMR (CDCl$_3$, 600 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz) of compound 20.
$^1$H NMR (CDCl$_3$, 200 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz, detected signals) of compound 24.
$^1$H NMR (CDCl$_3$, 400 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz, detected signals) of compound 25β.
$^1$H NMR (CDCl$_3$, 400 MHz) and $^{13}$C NMR (CDCl$_3$, 50 MHz, detected signals) of compound 25α.