SUPPORTING INFORMATION

Stereospecific [3+2] Cycloaddition of 1,2-Cyclopropanated Sugars and Ketones Catalyzed by SnCl₄: an Efficient Synthesis of Multi-Substituted Perhydrofuro[2,3-b]furans and Perhydrofuro[2,3-b]pyrans

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1. General

All reactions sensitive to air or moisture were carried out under nitrogen or argon atmosphere with anhydrous solvents. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Thin-layer chromatography was performed using silica gel GF254 precoated plates (0.20–0.25 mm thickness) with a fluorescent indicator. Visualization on TLC was achieved by UV light (254 nm) and a typical TLC indication solution (10% sulfuric acid / ethanol solution). Column chromatography was performed on silica gel 90, 200-300 mesh. Optical rotations were measured with a Perkin Elmer M341 Digital Polarimeter. $^1$H and $^{13}$C NMR (600 and 150 MHz, respectively) spectra were recorded on a Bruker Avance 600 spectrometer. $^1$H NMR chemical shifts are reported in ppm ($\delta$) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl$_3$, $\delta$ 7.26 ppm; CD$_3$COCD$_3$, $\delta$ 2.05 ppm). Data are reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $q$ = quartet, $m$ = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl$_3$, $\delta$ 77.0 ppm; CD$_3$COCD$_3$, $\delta$ 39.5). HRESIMS spectra were recorded on BioTOFQ.

Preparation of Starting Materials:

1-C-Acetyl-3,4,6-tri-O-benzyl-1,2-cyclopropane-1,2-deoxy-$\alpha$-D-galactopyranose (1a), 1-C-Acetyl-3,4,6-tri-O-benzyl-1,2-cyclopropane-1,2-deoxy-$\alpha$-D-glucopyranose (1b) and 1-C-Acetyl-3,4-Di-O-benzyl-1,2-cyclopropane-1,2-deoxy-$\alpha$-D-lyxofuranose (1c) were obtained as our previously reported methods.

General procedure for SnCl$_2$-catalyzed transformation for cyclopropanated sugars to per-substituted perhydrofuro[2,3-b]pyran and furan derivatives.

Method A: Under an argon atmosphere, SnCl$_4$ (2.3 $\mu$L, 0.02 mmol) in 0.5 mL CH$_2$Cl$_2$ was added to a mixture of 4 Å M.S. (50 mg), cyclopropanated sugars 1 (0.1 mmol) and ketones 2 (0.4 mmol)
in 0.5 mL CH₂Cl₂. The solution was stirred at 0 °C to 4 °C until the reaction was completed as detected by TLC. Then the reaction was quenched with a vigorously stirred solution of saturated aqueous NaHCO₃ (10 mL), and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:10 to 1:6) to afford products 3 as a single diastereoisomer.

**Method B:** Under an argon atmosphere, SnCl₄ (2.3 μL, 0.02 mmol) in 0.5 mL CH₂Cl₂ was added to a mixture of 4 Å M.S. (50 mg), cyclopropanated sugars 1 (0.1 mmol) and ketones 2 (1.0 mmol) in 0.5 mL CH₂Cl₂. The solution was stirred at 0 °C to 4 °C until the reaction was completed as detected by TLC. Then the reaction was quenched with a vigorously stirred solution of saturated aqueous NaHCO₃ (10 mL), and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:6) to afford products 3 as a single diastereoisomer.

**Experimental Procedures and Spectral Data**

(2S,3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-phenylhexahydrofuro[2,3-b]pyran (3aa)

![Chemical Structure](attachment:structure.png)

Compound 3aa was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and ketone 2a (47.2 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3aa (47.4 mg, 0.080 mmol, 80%) as colorless syrup. [α]D₃₀ +65.9 (c 0.14, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.42 (d, J = 7.9 Hz, 2H), 7.37 – 7.25 (m, 17H), 5.85 (d, J = 4.3 Hz, 1H), 4.80 (d, J = 11.7 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.51 (d, J = 11.9 Hz, 1H), 4.46 (d, J = 11.7 Hz, 1H), 4.38 (d, J = 11.8 Hz, 1H), 4.06 (t, J = 6.6 Hz, 1H), 3.92 (d, J = 11.8 Hz, 1H), 3.91 (s, 1H), 3.67 (d, J = 6.6 Hz, 2H), 3.48 (d, J = 1.7 Hz, 1H), 3.09 (dd, J = 10.0, 2.1 Hz, 1H), 2.78 (ddd, J = 10.1, 4.2, 2.0 Hz, 1H), 2.27 (s, 3H),...
1.42 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 208.1, 148.5, 138.5, 137.9, 137.9, 128.7, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 126.9, 124.1, 101.2, 82.0, 78.2, 74.0, 73.6, 72.1, 71.4, 70.2, 68.6, 62.8, 43.9, 32.1, 29.7, 27.5; ESI-HRMS: m/z calcd for C$_{38}$H$_{40}$NaO$_6$[M+Na]$^+$: 615.2717; found: 615.2714.

(2S,3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzzyloxy)methyl]-2-methyl-2-(4-tolyl)hexahydrofuro[2,3-b]pyran (3ab)

Compound 3ab was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and ketone 2b (56.2 $\mu$L, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3ab (53.4 mg, 0.088 mmol, 88%) as colorless syrup. [\(\alpha\)]$_D^{20}$ +68.2 (c 0.24, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.36 – 7.26 (m, 15H), 7.12 (d, $J$ = 7.9 Hz, 2H), 7.09 (s, 2H), 5.84 (d, $J$ = 4.3 Hz, 1H), 4.80 (d, $J$ = 11.7 Hz, 1H), 4.55 (d, $J$ = 11.7 Hz, 1H), 4.52 (d, $J$ = 11.7 Hz, 1H), 4.47 (d, $J$ = 11.7 Hz, 1H), 4.39 (d, $J$ = 11.8 Hz, 1H), 4.06 (t, $J$ = 6.7 Hz, 1H), 3.97 (d, $J$ = 11.8 Hz, 1H), 3.82 (s, 1H), 3.67 (d, $J$ = 6.5 Hz, 2H), 3.47 (s, 1H), 3.11 (dd, $J$ = 9.8, 1.3 Hz, 1H), 2.79 – 2.77 (m, 1H), 2.36 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 208.2, 145.5, 138.5, 137.9, 137.8, 136.4, 129.3, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 124.0, 101.1, 82.1, 78.1, 73.9, 73.6, 72.1, 71.3, 70.2, 68.6, 62.9, 43.9, 32.1, 29.7, 27.5, 21.0; ESI-HRMS: m/z calcd for C$_{39}$H$_{42}$NaO$_6$[M+Na]$^+$: 629.2874; found: 629.2862.

(2S,3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzzyloxy)methyl]-2-methyl-2-(4-chlorophenyl)hexahydrofuro[2,3-b]pyran (3ac)

Compound 3ac was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and ketone 2c (53.5 $\mu$L, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3ac (52.0 mg, 0.083 mmol,
(2S,3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-
2-methyl-2-(4-bromophenyl)hexahydrofuro[2,3-b]pyran (3ad)

Compound 3ad was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated
sugars 1a and ketone 2d (81.2 mg, 0.4 mmol), after purified by column chromatography on silica
gel (ethyl acetate/petroleum ether = 1:9), afforded the desired product 3ad (53.6 mg, 0.080 mmol,
80%) as colorless syrup. [α]D^20 = +80.2 (c 0.19, CHCl₃); ^1H NMR (600 MHz, CDCl₃) δ 7.40 – 7.25
(m, 15H), 7.20 (d, J = 8.6 Hz, 2H), 7.09 – 7.05 (m, 2H), 5.80 (d, J = 4.4 Hz, 1H), 4.81 (d, J = 11.7
Hz, 1H), 4.57 (d, J = 11.7 Hz, 1H), 4.52 (d, J = 11.8 Hz, 1H), 4.48 (d, J = 11.7 Hz, 1H), 4.44 (d, J
= 12.1 Hz, 1H), 4.00 (dd, J = 12.7, 7.7 Hz, 2H), 3.86 (s, 1H), 3.67 (dd, J = 11.7, 5.6 Hz, 2H), 3.29
d, J = 1.9 Hz, 1H), 3.01 (dd, J = 12.7, 7.7 Hz, 2H), 2.76 (dd, J = 9.9, 4.3, 2.2 Hz, 1H), 2.28 (s,
3H), 1.38 (s, 3H); ^13C NMR (150 MHz, CDCl₃) δ 207.7, 147.4, 138.4, 137.8, 137.5, 131.7, 128.5,
128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 125.5, 101.0, 81.6, 77.5, 74.0, 73.7, 72.2, 70.7, 69.9, 68.5, 62.9,
43.9, 31.9, 29.7, 27.2; ESI-HRMS: m/z calcd for C_{38}H_{39}BrNaO_{8}[M+Na]^+: 693.1822; found:
693.1848.

(2S,3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-
2-methyl-2-(4-trifluoromethylphenyl)hexahydrofuro[2,3-b]pyran (3ae)

83%) as colorless syrup. [α]D^20 = +62.4 (c 0.19, CHCl₃); ^1H NMR (600 MHz, CDCl₃) δ 7.38 – 7.22
(m, 17H), 7.07 (d, J = 7.4 Hz, 2H), 5.80 (d, J = 4.4 Hz, 1H), 4.81 (d, J = 11.7 Hz, 1H), 4.56 (d, J
= 11.7 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.48 (d, J = 11.8 Hz, 1H), 4.44 (d, J = 12.1 Hz, 1H), 4.01
(dd, J = 16.0, 9.2 Hz, 2H), 3.86 (s, 1H), 3.67 (d, J = 4.4 Hz, 1H), 3.30 (d, J = 1.7 Hz, 1H), 3.02 (dd,
J = 10.0, 1.7 Hz, 1H), 2.76 (ddd, J = 6.4, 4.0, 2.0 Hz, 1H), 2.25 (s, 3H), 1.36 (s, 3H); ^13C NMR
(150 MHz, CDCl₃) δ 207.7, 146.8, 138.4, 137.8, 137.5, 132.6, 128.8, 128.5, 128.3, 128.1,
128.0, 128.0, 127.9, 127.8, 127.7, 125.5, 101.0, 81.6, 77.5, 74.0, 73.7, 72.2, 70.7, 69.9, 68.5, 62.9,
43.9, 31.9, 29.7, 27.2; ESI-HRMS: m/z calcd for C_{38}H_{39}ClNaO_{6}[M+Na]^+: 649.2333; found:
649.2325.
Compound 3ae was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and ketone 2e (76.8 mg, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:9), afforded the desired product 3ae (42.9 mg, 0.065 mmol, 65%) as colorless syrup. [α]D 20 +61.4 (c 0.24, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.52 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.31 (dd, J = 10.1, 5.9 Hz, 8H), 7.24 – 7.19 (m, 3H), 7.04 (d, J = 6.5 Hz, 2H), 5.82 (d, J = 4.4 Hz, 1H), 4.82 (d, J = 11.7 Hz, 1H), 4.57 (d, J = 11.7 Hz, 1H), 4.53 (d, J = 11.7 Hz, 1H), 4.48 (d, J = 11.7 Hz, 1H), 4.43 (d, J = 12.2 Hz, 1H), 4.02 (t, J = 6.6 Hz, 1H), 3.97 (s, 1H), 3.68 (d, J = 12.2 Hz, 1H), 3.29 (d, J = 11.7 Hz, 1H), 2.95 (dd, J = 10.0, 2.1 Hz, 1H), 2.80 – 2.74 (m, 1H), 2.28 (s, 3H), 1.38 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 207.6, 152.1, 138.3, 137.8, 137.4, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 125.7, 124.4, 101.1, 81.6, 77.3, 74.1, 73.7, 72.2, 70.5, 69.8, 68.5, 62.7, 44.0, 32.0, 29.7, 27.3; ESI-HRMS: m/z calcd for C39H39F3NaO6[M+Na]+: 683.2591; found: 683.2604.

(2S,3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-ethyl-2-phenylhexahydrofuro[2,3-b]pyran (3af)

Compound 3af was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and ketone 2f (54.3 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:9), afforded the desired product 3af (47.4 mg, 0.080 mmol, 80%) as colorless syrup. [α]D 20 +51.5 (c 0.20, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.39 – 7.27 (m, 13H), 7.25 – 7.22 (m, 4H), 7.04 (s, 2H), 5.82 (d, J = 4.3 Hz, 1H), 4.80 (d, J = 11.7 Hz, 1H), 4.53 (d, J = 11.7 Hz, 1H), 4.50 (s, 1H), 4.46 (d, J = 11.7 Hz, 1H), 4.33 (d, J = 11.7 Hz, 1H), 4.09 (t, J = 6.6 Hz, 1H), 3.86 (d, J = 11.7 Hz, 1H), 3.79 (s, 1H), 3.69 – 3.65 (m, 2H), 3.49 (s, 1H), 3.08 (d, J = 10.4 Hz, 1H), 2.72 (dd, J = 10.3, 4.3 Hz, 1H), 2.30 (s, 3H), 0.88 (t, J = 5.8 Hz, 2H), 0.60 (t, J =
7.2 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 208.5, 146.1, 138.5, 137.9, 137.7, 128.4, 128.3, 128.1, 128.1, 127.9, 127.8, 127.7, 127.6, 126.7, 124.8, 101.5, 84.8, 78.3, 74.0, 73.7, 72.1, 71.5, 70.2, 68.7, 63.6, 43.6, 32.4, 31.4, 29.7, 8.4; ESI-HRMS: m/z calcd for C$_{30}$H$_{43}$NaO$_6$[M+Na]$^+$: 629.2874; found: 629.2854.

(2S,3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(furan-2-yl)hexahydrofuro[2,3-b]pyran (3ag)

Compound 3ag was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and ketone 2g (44.5 mg, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3ag (46.0 mg, 0.079 mmol, 79%) as colorless syrup. $[\alpha]_D^{20} +88.0$ (c 0.14, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.35 – 7.24 (m, 16H), 6.28 (dd, $J = 3.1$, 1.8 Hz, 1H), 6.19 (d, $J = 3.2$ Hz, 1H), 5.65 (d, $J = 4.5$ Hz, 1H), 4.85 (d, $J = 11.7$ Hz, 1H), 4.60 (d, $J = 11.7$ Hz, 2H), 4.49 (d, $J = 11.8$ Hz, 1H), 4.46 (d, $J = 11.8$ Hz, 1H), 4.26 (d, $J = 12.0$ Hz, 1H), 4.06 (t, $J = 6.8$ Hz, 1H), 3.96 (s, 1H), 3.68 (t, $J = 8.6$ Hz, 1H), 3.63 (dd, $J = 9.0$, 5.5 Hz, 1H), 3.55 (s, 1H), 3.48 (dd, $J = 9.7$, 1.9 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.12 (s, 3H), 1.42 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 207.0, 157.7, 142.1, 138.5, 138.0, 137.9, 128.5, 128.4, 128.3, 128.0, 127.8, 127.6, 110.3, 105.3, 100.9, 78.5, 77.7, 73.9, 73.6, 72.1, 71.1, 70.1, 68.4, 60.4, 43.1, 31.9, 29.7, 23.0; ESI-HRMS: m/z calcd for C$_{36}$H$_{38}$NaO$_7$[M+Na]$^+$: 605.2510; found: 605.2516.

Spiroyclic compound 3ah

Compound 3ah was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and ketone 2h (64.5 mg, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:10), afforded the desired product 3ah (45.0 mg, 0.071 mmol, 71%) as light red syrup. $[\alpha]_D^{20} +163.0$ (c 0.32, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.60
(d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.35 – 7.29 (m, 15H), 6.83 (t, J = 7.4 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 5.99 (d, J = 4.5 Hz, 1H), 4.89 (d, J = 11.6 Hz, 1H), 4.78 (d, J = 11.7 Hz, 1H), 4.62 (d, J = 11.6 Hz, 1H), 4.59 (d, J = 11.7 Hz, 1H), 4.53 – 4.49 (m, 1H), 4.46 (d, J = 11.9 Hz, 1H), 4.28 (d, J = 8.4 Hz, 1H), 4.18 (t, J = 6.5 Hz, 1H), 4.04 (s, 1H), 3.68 – 3.60 (m, 2H), 3.46 (d, J = 2.5 Hz, 1H), 3.16 – 3.11 (m, 1H), 2.76 (s, 3H), 1.92 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 204.3, 198.6, 162.5, 138.8, 138.6, 138.3, 138.0, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 125.3, 119.4, 118.8, 110.2, 103.7, 94.9, 77.7, 74.0, 73.4, 72.4, 71.7, 70.5, 68.4, 58.7, 42.3, 31.2, 29.7, 29.6; ESI- HRMS: m/z calcd for C39H39NNaO7[M+Na]+: 656.2619; found: 656.2625.

**Spirocyclic compound 3ai**

![Spirocyclic compound 3ai](image)

Compound 3ai was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and ketone 2i (41.9 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3ai (50.2 mg, 0.088 mmol, 88%) as colorless syrup. [α]D 20 +56 (c 0.40, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.40 – 7.25 (m, 15H), 5.44 (d, J = 4.4 Hz, 1H), 4.86 (d, J = 11.7 Hz, 1H), 4.67 (d, J = 12.1 Hz, 1H), 4.62 (d, J = 11.7 Hz, 1H), 4.50 (d, J = 11.8 Hz, 1H), 4.47 (d, J = 11.8 Hz, 1H), 4.34 (d, J = 12.1 Hz, 1H), 4.05 (t, J = 5.9 Hz, 1H), 4.01 (s, 1H), 3.73 – 3.63 (m, 2H), 3.35 (dd, J = 9.4, 1.9 Hz, 1H), 2.74 (dt, J = 9.5, 4.0 Hz, 1H), 2.66 (d, J = 3.7 Hz, 1H), 2.12 (s, 3H), 1.60 (dd, J = 16.9, 7.8 Hz, 4H), 1.48 (d, J = 13.0 Hz, 1H), 1.40 (s, 2H), 1.34 (td, J = 12.9, 3.8 Hz, 1H), 1.15 – 1.05 (m, 1H), 0.97 (t, J = 11.3 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ = 207.5, 138.5, 138.0, 137.8, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.9, 99.7, 80.5, 78.6, 73.8, 73.6, 72.2, 70.5, 70.0, 68.3, 63.3, 43.8, 40.6, 33.0, 32.2, 25.1, 23.0, 22.2; ESI- HRMS: m/z calcd for C36H42NaO6[M+Na]+: 593.2874; found: 593.2873.

(3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2,2-di-methylhexahydrofurao[2,3-b]pyran (3aj)

![Compound 3aj](image)
Compound 3aj was prepared according to Method B using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and acetone 2j (74.2 μL, 1.0 mmol), after purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:6), afforded the desired product 3aj (49.3 mg, 0.093 mmol, 93%) as colorless syrup. [α]²⁰D +48.5 (c 0.46, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.39 – 7.27 (m, 15H), 5.43 (d, J = 4.4 Hz, 1H), 4.85 (d, J = 11.7 Hz, 1H), 4.68 (d, J = 12.1 Hz, 1H), 4.63 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 11.8 Hz, 1H), 4.48 (d, J = 11.8 Hz, 1H), 4.35 (d, J = 12.1 Hz, 1H), 4.04 (t, J = 6.7 Hz, 1H), 4.01 (s, 1H), 3.70 (t, J = 8.4 Hz, 1H), 3.65 (dd, J = 9.3, 5.9 Hz, 1H), 3.37 (dd, J = 9.2, 1.9 Hz, 1H), 2.84 (dt, J = 9.0, 4.4 Hz, 1H), 2.76 (d, J = 4.3 Hz, 1H), 2.10 (s, 3H), 1.25 (s, 3H), 1.07 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 207.0, 138.5, 138.0, 137.8, 128.6, 128.4, 128.1, 128.0, 127.7, 127.6, 99.6, 79.0, 78.5, 73.8, 73.5, 72.5, 70.5, 70.1, 68.2, 63.0, 44.1, 31.6, 31.3, 24.8; ESI-HRMS: m/z calcd for C₃₃H₃₈NaO₆ [M+Na]⁺: 553.2561; found: 553.2551.

(2R,3S,3aR,4R,5R,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-ethyl-2-methylhexahydrofuro[2,3-b]pyran (3ak)

Compound 3ak was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and 2-butanone 2k (36.2 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:6), afforded the desired product 3ak (44.1 mg, 0.081 mmol, 81%) as colorless syrup. [α]²⁰D +40.9 (c 0.25, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.39 – 7.27 (m, 15H), 5.43 (d, J = 4.5 Hz, 1H), 4.86 (d, J = 11.7 Hz, 1H), 4.67 (d, J = 12.2 Hz, 1H), 4.63 (d, J = 11.7 Hz, 1H), 4.48 (q, J = 11.9 Hz, 3H), 4.33 (d, J = 12.2 Hz, 1H), 4.01 (t, J = 4.8 Hz, 2H), 3.68 (t, J = 8.5 Hz, 1H), 3.63 (dd, J = 9.1, 5.6 Hz, 1H), 3.34 (dd, J = 9.5, 1.7 Hz, 1H), 2.82 (dt, J = 9.4, 4.2 Hz, 1H), 2.76 (d, J = 3.6 Hz, 1H), 2.10 (s, 3H), 1.50 (dt, J = 14.8, 7.3 Hz, 1H), 1.43 (td, J = 14.7, 7.3 Hz, 1H), 1.02 (s, 3H), 0.87 (dt, J = 14.4, 6.9 Hz, 2H), 0.79 (t, J = 7.4 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 207.5, 138.5, 138.0, 137.9, 128.6, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 100.0, 81.3, 78.2, 73.8, 73.6, 72.2, 70.3, 69.9, 68.3, 61.0, 43.7, 36.4, 31.5, 29.7, 21.9, 8.7; ESI-HRMS: m/z calcd for C₃₄H₄₆NaO₆ [M+Na]⁺: 567.2717; found: 567.2708.
Compound 3al was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and 2l (50.5 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:6), afforded the desired product 3al (50.4 mg, 0.088 mmol, 88%) as colorless syrup. [α]D20 +54.2 (c 0.24, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.40 – 7.28 (m, 15H), 5.41 (d, J = 4.2 Hz, 1H), 4.86 (d, J = 11.7 Hz, 1H), 4.67 (d, J = 12.2 Hz, 1H), 4.63 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 11.8 Hz, 1H), 4.47 (d, J = 11.7 Hz, 1H), 4.33 (d, J = 12.2 Hz, 1H), 3.99 (dd, J = 13.8, 7.3 Hz, 2H), 3.70 (t, J = 8.6 Hz, 1H), 3.63 (dd, J = 9.1, 5.5 Hz, 1H), 3.34 (d, J = 9.6 Hz, 1H), 2.78 (dd, J = 9.0, 4.3 Hz, 1H), 2.72 (d, J = 3.2 Hz, 1H), 2.09 (s, 3H), 1.74 – 1.65 (m, 1H), 1.41 (dd, J = 14.3, 4.5 Hz, 1H), 1.20 (dd, J = 14.4, 7.4 Hz, 1H), 1.05 (s, 3H), 0.89 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H); 13C NMR (150 MHz, CDCl3) δ 207.4, 138.5, 138.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.6, 99.8, 81.1, 78.3, 73.9, 73.6, 72.2, 70.3, 69.8, 68.4, 63.3, 52.8, 43.0, 31.6, 24.9, 24.5, 24.1, 22.1; ESI-HRMS: m/z calcd for C36H44NaO6 [M+Na]+: 595.3030; found: 595.3022.

Compound 3am was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1a and 2m (38.0 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3am (52.3 mg, 0.094 mmol, 94%) as colorless syrup. [α]D20 +63.6 (c 0.42, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.38 – 7.28 (m, 15H), 5.39 (d, J = 4.5 Hz, 1H), 4.85 (d, J = 11.7 Hz, 1H), 4.68 (d, J = 12.2 Hz, 1H), 4.62 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 11.8 Hz, 1H), 4.47 (d, J = 11.8 Hz, 1H), 4.37 (d, J = 12.1 Hz, 1H), 4.02 – 3.96 (m, 2H), 3.68 (t, J = 8.3 Hz, 1H), 3.66 – 3.61 (m, 1H), 3.40 (d, J = 9.0 Hz, 1H), 3.00 (d,
(2S,3S,3aR,4R,5S,6R,7aS)-3-acetyl-4,5-bis(benzylxoy)-6-[(benzyxoy)methyl]-2-methyl-2-phenylhexahydrofuro[2,3-b]pyran

Compound 3ba was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1b and ketone 2a (47.2 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3ba (50.9 mg, 0.086 mmol, 86%) as colorless syrup. [α]D +27.3 (c 0.25, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, J = 7.5 Hz, 2H), 7.38 − 7.22 (m, 16H), 7.13 − 7.09 (m, 2H), 5.72 (d, J = 5.4 Hz, 1H), 4.63 (d, J = 12.1 Hz, 1H), 4.59 (t, J = 11.6 Hz, 2H), 4.46 (d, J = 12.1 Hz, 1H), 4.43 (s, 2H), 4.15 − 4.11 (m, 1H), 3.76 (ddd, J = 14.1, 10.6, 4.2 Hz, 2H), 3.64 (ddd, J = 17.4, 13.3, 6.2 Hz, 2H), 3.42 (t, J = 4.9 Hz, 1H), 3.05 (dt, J = 7.6, 5.4 Hz, 1H), 1.92 (s, 3H), 1.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 206.8, 146.1, 138.3, 138.2, 137.8, 128.6, 128.5, 128.4, 128.4, 127.9, 127.8, 127.7, 127.6, 127.4, 125.0, 98.8, 83.5, 76.9, 76.4, 73.5, 72.8, 72.6, 72.4, 69.2, 62.6, 45.1, 31.9, 29.7, 24.4. ESI-HRMS: m/z calcd for C₃₈H₄₀NaO₆[M+Na⁺]: 615.2717; found: 615.2731.

(2S,3S,3aR,4R,5S,6R,7aS)-3-acetyl-4,5-bis(benzylxoy)-6-[(benzyxoy)methyl]-2-methyl-2-(4-toly)-hexahydrofuro[2,3-b]pyran (3bb)

Compound 3bb was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1b and ketone 2b (56.2 μL, 0.4 mmol), after purified by column chromatography on silica
gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3bb (51.5 mg, 0.085 mmol, 85%) as colorless syrup. \([\alpha]_D^{20} +63.9 \ (c \ 0.30, \ \text{CHCl}_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.28 (m, 10H), 7.25 (dd, \(J = 7.1, 2.6\) Hz, 5H), 7.15 (d, \(J = 8.0\) Hz, 2H), 7.14 – 7.09 (m, 2H), 5.71 (d, \(J = 5.4\) Hz, 1H), 4.63 (d, \(J = 12.1\) Hz, 1H), 4.59 (t, \(J = 12.1\) Hz, 2H), 4.48 (d, \(J = 12.1\) Hz, 1H), 4.43 (s, 2H), 4.15 – 4.10 (m, 1H), 3.77 (dd, \(J = 10.6, 4.8\) Hz, 1H), 3.73 (dd, \(J = 10.6, 3.5\) Hz, 1H), 3.66 – 3.60 (m, 2H), 3.43 (t, \(J = 4.7\) Hz, 1H), 3.07 (dt, \(J = 8.2, 5.3\) Hz, 1H), 2.36 (s, 3H), 1.92 (s, 3H), 1.40 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 206.8, 143.1, 138.3, 138.3, 137.8, 137.0, 129.2, 128.4, 128.4, 127.9, 127.9, 127.7, 127.6, 126.4, 124.9, 98.7, 83.5, 76.4, 73.4, 72.7, 72.5, 72.3, 69.3, 62.6, 45.0, 31.8, 29.7, 24.3, 21.0; ESI-HRMS: m/z calcd for C\(_{39}\)H\(_{42}\)NaO\(_6\)[M+Na\(^+\): 629.2874; found: 629.2891.

\((2S,3S,3aR,4R,5S,6R,7aS)-3\)-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(4-chlorophenyl)hexahydrofuro[2,3-b]pyran (3bc)

Compound 3bc was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1b and ketone 2c (53.5 \(\mu\)L, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3bc (51.4 mg, 0.082 mmol, 82%) as colorless syrup. \([\alpha]_D^{20} +40.0 \ (c \ 0.13, \ \text{CHCl}_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.43 (d, \(J = 8.5\) Hz, 2H), 7.35 – 7.28 (m, 11H), 7.24 (dd, \(J = 12.4, 4.6\) Hz, 4H), 7.11 (dd, \(J = 6.2, 2.8\) Hz, 2H), 5.67 (d, \(J = 5.2\) Hz, 1H), 4.59 (q, \(J = 12.1\) Hz, 3H), 4.49 (d, \(J = 12.2\) Hz, 1H), 4.43 (s, 2H), 4.12 – 4.08 (m, 1H), 3.77 (dd, \(J = 10.5, 5.1\) Hz, 1H), 3.72 (dd, \(J = 10.5, 3.7\) Hz, 1H), 3.62 (dd, \(J = 6.6, 4.8\) Hz, 1H), 3.56 (d, \(J = 8.3\) Hz, 1H), 3.39 (t, \(J = 4.8\) Hz, 1H), 3.02 (dt, \(J = 9.5, 5.2\) Hz, 1H), 1.91 (s, 3H), 1.38 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 206.4, 144.8, 138.2, 137.7, 133.3, 128.7, 128.5, 128.4, 127.9, 127.9, 127.8, 127.6, 126.6, 98.6, 83.2, 76.4, 73.4, 72.7, 72.6, 72.4, 69.1, 62.4, 45.1, 31.8, 29.7, 24.3; ESI-HRMS: m/z calcd for C\(_{39}\)H\(_{39}\)ClNaO\(_6\)[M+Na\(^+\]: 649.2327; found: 649.2325.

\((2S,3S,3aR,4R,5S,6R,7aS)-3\)-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(4-bromophenyl)hexahydrofuro[2,3-b]pyran (3bd)
Compound 3bd was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1b and ketone 2d (81.2 mg, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3bd (55.0 mg, 0.082 mmol, 82%) as colorless syrup. [α]D20 +35.0 (c 0.29, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.45 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.35 – 7.26 (m, 11H), 7.22 (d, J = 7.0 Hz, 2H), 7.12 (s, 2H), 5.67 (d, J = 5.2 Hz, 1H), 4.63 – 4.57 (m, 3H), 4.48 (d, J = 12.2 Hz, 1H), 4.44 (s, 2H), 4.12 – 4.07 (m, 1H), 3.77 (dd, J = 10.3, 5.1 Hz, 1H), 3.74 – 3.69 (m, 1H), 3.64 – 3.60 (m, 1H), 3.55 (d, J = 8.1 Hz, 1H), 3.39 (t, J = 8.4 Hz, 1H), 3.01 (dt, J = 8.4, 5.3 Hz, 1H), 1.92 (s, 3H), 1.37 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 206.4, 145.3, 138.2, 137.7, 131.7, 128.5, 128.4, 128.4, 127.9, 127.8, 127.6, 126.9, 121.4, 98.6, 83.3, 76.4, 76.1, 73.5, 72.7, 72.7, 72.4, 69.0, 62.3, 45.2, 31.9, 29.7, 24.3; ESI-HRMS: m/z calcd for C38H39BrNaO6 [M+Na]+: 693.1822; found: 693.1830.

(3S,3aR,4R,5S,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2,2-di-methylhexahydrofuro[2,3-b]pyran (3bj)

Compound 3bj was prepared according to Method B using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1b and acetone 2j (74.2 μL, 1.0 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:6), afforded the desired product 3bj (48.8 mg, 0.092 mmol, 92%) as colorless syrup. [α]D20 +47.8 (c 0.32, CHCl3); 1H NMR (600 MHz, CDCl3) δ 7.36 – 7.27 (m, 13H), 7.15 – 7.12 (m, 2H), 5.48 (d, J = 5.9 Hz, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.59 (dd, J = 12.3 Hz, 2H), 4.53 (d, J = 12.1 Hz, 1H), 4.35 (s, 2H), 3.95 – 3.90 (m, 1H), 3.68 (dd, J = 4.2, 2.4 Hz, 2H), 3.65 (d, J = 7.2 Hz, 1H), 3.52 (t, J = 3.2 Hz, 1H), 3.29 (d, J = 10.1 Hz, 1H), 3.22 – 3.17 (m, 1H), 2.06 (s, 3H), 1.55 (s, 3H), 1.03 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 205.6, 138.3, 138.2, 137.8, 128.4, 128.3, 128.1, 127.9, 127.8, 97.9, 80.8, 76.0, 75. 5, 73.4, 72.1,
(2R,3S,3aR,4R,5S,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-ethyl-2-methylhexahydrofuro[2,3-b]pyran (3bk)

Compound 3bk was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1b and 2k (36.2 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:6), afforded the desired product 3bk (45.2 mg, 0.083 mmol, 83%) as colorless syrup. [α]_D^{20} +9.0 (c 0.37, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.38 – 7.26 (m, 13H), 7.16 (d, J = 7.7 Hz, 2H), 5.47 (d, J = 5.7 Hz, 1H), 4.64 (t, J = 10.1 Hz, 2H), 4.59 (d, J = 12.1 Hz, 1H), 4.54 (d, J = 12.1 Hz, 1H), 4.40 (s, 2H), 3.97 (dt, J = 8.4, 4.4 Hz, 1H), 3.72 – 3.66 (m, 2H), 3.63 (dd, J = 6.9, 3.2 Hz, 1H), 3.52 (t, J = 3.9 Hz, 1H), 3.29 (d, J = 9.3 Hz, 1H), 3.14 – 3.09 (m, 1H), 2.02 (s, 3H), 1.78 (q, J = 7.4 Hz, 2H), 1.26 (s, 3H), 0.99 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 206.1, 138.3, 138.3, 137.9, 128.5, 128.3, 128.1, 128.1, 127.8, 127.8, 127.5, 97.8, 83.0, 76.1, 76.0, 73.4, 72.3, 71.8, 71.6, 69.4, 59.1, 43.5, 35.0, 31.9, 31.1, 29.7, 22.0, 8.5; ESI-HRMS: m/z calcd for C₃₄H₄₀NaO₆[M+Na]^+: 567.2717; found: 567.2733.

(2R,3S,3aR,4R,5S,6R,7aS)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-cyclopropyl-2-methyl-hexahydrofuro[2,3-b]pyran (3bm)

Compound 3bm was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars 1b and 2m (38.0 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3bm (52.8 mg, 0.095 mmol, 95%) as colorless syrup. [α]_D^{20} +13.0 (c 0.26, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.36 – 7.25 (m, 13H), 7.15 (d, J = 6.4 Hz, 2H), 5.43 (d, J = 5.9 Hz, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.59 (d, J = 8.7 Hz, 1H), 4.57 (d, J = 8.6 Hz, 1H), 4.54 (d, J = 12.1 Hz, 1H), 4.36 (s, 2H), 3.96 (dt, J = 8.7, 4.5 Hz, 1H), 3.67 (d, J = 4.4 Hz, 2H), 3.61 (dd, J = 7.2, 1.6 Hz, 1H), 3.53 (t, J = 3.1 Hz, 1H), 3.49 (d,
\( J = 10.5 \text{ Hz, 1H}), 3.23 – 3.17 \text{ (m, 1H)}, 2.12 \text{ (s, 3H)}, 1.20 – 1.13 \text{ (m, 1H)}, 0.95 \text{ (s, 3H)}, 0.88 \text{ (t, } J = 6.9 \text{ Hz, 1H)}, 0.74 – 0.67 \text{ (m, 1H)}, 0.54 – 0.44 \text{ (m, 2H);} ^{13} \text{C NMR (150 MHz, CDCl}_3) \delta 206.0, 138.3, 138.3, 137.9, 128.4, 128.4, 128.3, 128.0, 127.8, 127.8, 127.5, 97.4, 81.9, 75.9, 75.5, 73.4, 72.0, 71.6, 71.5, 69.6, 61.6, 42.9, 31.3, 29.7, 21.6, 21.4, 2.8, 1.2; \text{ ESI-HRMS: m/z calcd for C}_{35}\text{H}_{40}\text{NaO}_6\text{[M+Na]}^+: 579.2717; \text{ found: 579.2721.}

\((2S,3S,3aS,4R,5R,6aR)-3\text{-acetyl-4-(benzylloxy)-5-[(benzylloxy)methyl]-2-methyl-2-phenyl-hexahydrofuro[2,3-b]furan (3ca)}\)

Compound 3ca was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated sugars 1c and ketone 2a (47.2 \mu L, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3ca (41.1 mg, 0.087 mmol, 87\%) as colorless syrup. \([\alpha]_D^{20} -29.2 \text{ (c 0.27, CHCl}_3)\); \(^1\text{H NMR (600 MHz, CDCl}_3) \delta 7.57 \text{ (d, } J = 7.3 \text{ Hz, 2H)}, 7.39 – 7.22 \text{ (m, 11H)}, 7.14 \text{ (d, } J = 6.6 \text{ Hz, 2H)}, 5.67 \text{ (d, } J = 5.0 \text{ Hz, 1H)}, 4.63 \text{ (d, } J = 12.1 \text{ Hz, 1H)}, 4.57 \text{ (d, } J = 12.1 \text{ Hz, 1H)}, 4.40 \text{ (d, } J = 11.4 \text{ Hz, 1H)}, 4.36 – 4.31 \text{ (m, 3H)}, 3.86 \text{ (dd, } J = 10.3, 4.1 \text{ Hz, 1H)}, 3.82 \text{ (dd, } J = 13.8, 8.7 \text{ Hz, 1H)}, 3.75 \text{ (dd, } J = 10.2, 5.6 \text{ Hz, 2H)}, 1.77 \text{ (s, 3H)}, 1.44 \text{ (s, 3H);} ^{13} \text{C NMR (150 MHz, CDCl}_3) \delta 206.1, 145.1, 138.3, 137.6, 128.6, 128.4, 127.8, 127.7, 127.6, 127.5, 127.0, 125.7, 106.1, 88.8, 79.8, 78.0, 73.67, 73.43, 69.8, 62.1, 50.5, 31.6, 29.7, 22.9; \text{ ESI-HRMS: m/z calcd for C}_{30}\text{H}_{32}\text{NaO}_5\text{[M+Na]}^+: 495.2142; \text{ found: 495.2144.}

\((2S,3S,3aS,4R,5R,6aR)-3\text{-acetyl-4-(benzylloxy)-5-[(benzylloxy)methyl]-2-methyl-2-(4-tolyl)-hexahydrofuro[2,3-b]furan (3cb)}\)

Compound 3cb was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated sugars 1c and ketone 2b (56.2 \mu L, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3cb (38.9 mg, 0.080 mmol,
80%) as colorless syrup. [α] D 20° -133.9 (c 0.12, CHCl 3); 1 H NMR (600 MHz, CDCl 3) δ 7.45 (d, J = 8.2 Hz, 2H), 7.36 – 7.27 (m, 8H), 7.14 (d, J = 7.8 Hz, 4H), 5.65 (d, J = 5.0 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 12.1 Hz, 1H), 4.40 (d, J = 11.4 Hz, 1H), 4.32 (dd, J = 8.9, 6.0 Hz, 1H), 3.86 (dd, J = 10.3, 4.0 Hz, 1H), 3.84 – 3.79 (m, 1H), 3.76 (dd, J = 10.4, 6.0 Hz, 1H), 3.73 (d, J = 10.0 Hz, 1H), 2.35 (s, 3H), 1.77 (s, 3H), 1.42 (s, 3H); 13 C NMR (150 MHz, CDCl 3) δ 206.2, 142.2, 138.3, 137.6, 137.3, 129.0, 128.4, 128.3, 127.8, 127.6, 127.5, 125.6, 106.0, 88.7, 79.7, 78.0, 73.6, 73.4, 69.9, 62.2, 50.3, 31.6, 29.7, 21.0; ESI-HRMS: m/z calcd for C 31 H 34 NaO 5 [M+Na] + : 509.2298; found: 509.2304.

(2S,3S,3aS,4R,5R,6aR)-3-acetyl-4-(benzyloxy)-5-[(benzyloxy)methyl]-2-methyl-2-(4-bromophenyl)hexahydrofuro[2,3-b]furan (3cd)

Compound 3cd was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated sugars 1c and ketone 2d (81.2 mg, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3cd (42.9 mg, 0.078 mmol, 78%) as colorless syrup. [α] D 20° -70.2 (c 0.17, CHCl 3); 1 H NMR (600 MHz, CDCl 3) δ 7.43 (s, 2H), 7.33 – 7.26 (m, 10H), 7.13 (d, J = 6.8 Hz, 2H), 5.64 (d, J = 4.9 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 4.55 (d, J = 11.9 Hz, 1H), 4.40 (d, J = 11.4 Hz, 1H), 4.35 – 4.27 (m, 4H), 3.82 (dd, J = 10.3, 4.3 Hz, 1H), 3.81 – 3.76 (m, 1H), 3.72 (d, J = 9.9 Hz, 1H), 3.69 (dd, J = 10.3, 6.0 Hz, 1H), 1.77 (s, 3H), 1.40 (s, 3H); 13 C NMR (150 MHz, CDCl 3) δ 205.8, 144.5, 138.1, 137.5, 131.4, 128.4, 127.9, 127.8, 127.6, 127.5, 126.1, 106.1, 88.5, 79.7, 77.9, 73.8, 73.5, 69.6, 61.8, 50.6, 31.7, 23.0; ESI-HRMS: m/z calcd for C 36 H 31 BrNaO 5 [M+Na] + : 573.1247; found: 573.1258.

(2S,3S,3aS,4R,5R,6aR)-3-acetyl-4-(benzyloxy)-5-[(benzyloxy)methyl]-2-ethyl-2-phenyl-hexahydrofuro[2,3-b]furan (3cf)

Compound 3cf was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated
sugars 1c and ketone 2f (54.3 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3cf (36.5 mg, 0.075 mmol, 75%) as colorless syrup. \([\alpha]_D^{20} -23.0 (c 0.37, CHCl_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, \(J = 7.7\) Hz, 2H), 7.37 – 7.24 (m, 11H), 7.12 (d, \(J = 6.6\) Hz, 2H), 5.69 (d, \(J = 5.2\) Hz, 1H), 4.64 (d, \(J = 12.1\) Hz, 1H), 4.55 (d, \(J = 12.0\) Hz, 1H), 4.40 (d, \(J = 11.5\) Hz, 1H), 4.38 – 4.34 (m, 1H), 4.32 (dd, \(J = 13.3, 4.7\) Hz, 2H), 3.83 (dd, \(J = 10.4, 4.2\) Hz, 1H), 3.81 – 3.76 (m, 1H), 3.74 (dd, \(J = 10.4, 6.7\) Hz, 1H), 3.64 (d, \(J = 9.8\) Hz, 1H), 1.87 (s, 3H), 1.83 (dt, \(J = 14.6, 7.3\) Hz, 1H), 1.68 (dq, \(J = 14.5, 7.2\) Hz, 1H), 0.76 (t, \(J = 7.3\) Hz, 3H); \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 206.5, 143.3, 138.3, 137.5, 128.4, 127.8, 127.7, 127.6, 127.5, 127.3, 125.8, 106.1, 91.3, 80.0, 78.1, 73.5, 73.4, 70.1, 62.4, 50.9, 32.3, 27.6, 7.7; ESI-HRMS: m/z calcd for C\(_{31}\)H\(_{34}\)NaO\(_5\)\([M+Na]^+\): 509.2298; found: 509.2305.

\((2S,3S,3aS,4R,5R,6aR)-3\text{-acetyl-4-(benzyloxy)-5-[(benzyloxy)methyl]-2-(furan-2-yl)}\)

\(2\text{-methyl-hexahydrofuro[2,3-b]furan (3cg)}\)

Compound 3cg was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated sugars 1c and ketone 2g (44.5 mg, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3cg (28.7 mg, 0.062 mmol, 62%) as colorless syrup. \([\alpha]_D^{20} -40.0 (c 0.09, CHCl_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.28 (m, 9H), 7.20 (d, \(J = 7.2\) Hz, 2H), 6.36 (d, \(J = 3.2\) Hz, 1H), 6.34 (d, \(J = 1.7\) Hz, 1H), 5.64 (d, \(J = 5.6\) Hz, 1H), 4.69 (d, \(J = 12.2\) Hz, 1H), 4.58 (d, \(J = 12.2\) Hz, 1H), 4.44 (d, \(J = 8.4\) Hz, 1H), 4.40 – 4.36 (m, 3H), 4.14 (d, \(J = 9.3\) Hz, 1H), 3.97 (d, \(J = 5.3\) Hz, 2H), 3.86 (td, \(J = 8.6, 5.8\) Hz, 1H), 1.80 (s, 3H), 1.36 (s, 3H); \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 204.8, 155.0, 142.6, 138.3, 137.7, 128.4, 128.3, 127.8, 127.7, 127.5, 127.4, 110.4, 107.9, 106.4, 82.6, 80.6, 78.1, 73.5, 73.2, 70.1, 58.3, 47.3, 30.3, 21.3; ESI-MS: m/z calcd for C\(_{28}\)H\(_{36}\)NaO\(_5\)[M+Na]^+: 485.1935; found: 485.1951.

**Spirocyclic compound 3ci**

![Spirocyclic compound 3ci](image)
Compound 3ei was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated sugars 1c and ketone 2i (41.9 µL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3ei (39.6 mg, 0.088 mmol, 88%) as colorless syrup. $\left[\alpha\right]_{D}^{20}$ -10.0 (c 0.32, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.36 – 7.27 (m, 8H), 7.19 (d, $J$ = 7.4 Hz, 2H), 5.51 (d, $J$ = 5.2 Hz, 1H), 4.61 (s, 1H), 4.60 (s, 1H), 4.42 (d, $J$ = 11.7 Hz, 1H), 4.33 (d, $J$ = 11.6 Hz, 1H), 4.27 (d, $J$ = 5.2 Hz, 2H), 3.80 (dd, $J$ = 9.9, 2.5 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.69 (td, $J$ = 8.5, 4.5 Hz, 1H), 3.37 (d, $J$ = 9.1 Hz, 1H), 2.06 (s, 3H), 1.87 (d, $J$ = 13.1 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.58 (s, 4H), 1.48 (d, $J$ = 13.4 Hz, 1H), 1.07 (d, $J$ = 13.0 Hz, 1H), 0.88 (d, $J$ = 6.5 Hz, 1H), 0.79 (d, $J$ = 13.4 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 205.9, 138.3, 138.8, 128.3, 127.8, 127.8, 127.5, 127.8, 105.8, 86.5, 79.9, 78.2, 73.4, 73.3, 69.5, 60.6, 48.7, 38.8, 33.4, 31.5, 29.7, 25.4, 23.2, 21.5; ESI-HRMS: m/z calcd for C$_{28}$H$_{34}$NaO$_5$[M+Na]$^+$: 473.2298; found: 473.2304.

(3S,3aS,4R,5R,6aR)-3-acetyl-4-(benzylxoy)-5-[(benzylxoy)methyl]-2,2-di-methyl-hexahydrofuro[2,3-b]furan (3cj)

Compound 3cj was prepared according to Method B using (35.2 mg, 0.1 mmol) cyclopropanated sugars 1c and acetone 2j (74.2 µL, 1.0 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product 3cj (34.0 mg, 0.083 mmol, 83%) as colorless syrup. $\left[\alpha\right]_{D}^{20}$ -6.1 (c 0.16, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.36 – 7.26 (m, 8H), 7.20 (d, $J$ = 7.0 Hz, 2H), 5.50 (d, $J$ = 5.4 Hz, 1H), 4.62 (d, $J$ = 12.0 Hz, 1H), 4.58 (d, $J$ = 12.1 Hz, 1H), 4.43 (d, $J$ = 11.6 Hz, 1H), 4.35 (d, $J$ = 11.6 Hz, 1H), 4.31 – 4.25 (m, 2H), 3.82 (dd, $J$ = 10.3, 3.7 Hz, 1H), 3.75 – 3.69 (m, 2H), 3.49 (d, $J$ = 9.1 Hz, 1H), 2.05 (s, 3H), 1.52 (s, 3H), 1.01 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 205.7, 138.3, 137.7, 128.4, 128.3, 127.9, 127.8, 127.4, 106.1, 85.0, 80.0, 78.1, 73.5, 73.3, 69.5, 60.1, 49.1, 30.9, 29.8, 29.7, 24.7; ESI-HRMS: m/z calcd for C$_{25}$H$_{30}$NaO$_5$[M+Na]$^+$: 433.1985; found: 433.1994.

Selected IR data for the products:
The stereochemistry of the products

The configuration of the products was unambiguously assigned by extensively studied the NMR and NOE of the products. The coupling constants between H\textsubscript{7a} and H\textsubscript{3a} (\(J_{H7a,H3a} = 4.3 - 4.5\) Hz for the products from compound 1\textit{a}, \(J_{H7a,H3a} = 5.2 - 5.9\) Hz for the products from compound 1\textit{b} and \(J_{H6a,H3a} = 4.9 - 5.6\) Hz for the products from compound 1\textit{c}) showed convincingly that the fused ring system have a \textit{cis}-bicyclic configuration, the stereochemistry of C2 and C3 position were determined using the NOE difference spectra (Scheme S1).

For the stereochemistry of the 3\textit{c} series compounds, the coupling constants between H\textsubscript{6a} and H\textsubscript{3a} (\(J_{H6a,H3a} = 4.9 - 5.6\) Hz) manifested convincingly that the fused ring system have a \textit{cis}-bicyclic configuration. The stereochemistry of C3 position was determined by coupling constants between H\textsubscript{3a} and H\textsubscript{3} (\(J_{H3,H3a} = 9.1 - 10.0\) Hz), which demonstrated the \textit{cis}- correlation between them (Proton proton coupling constants in a \textit{bis}-THF system: \(J_{H3,H3a} > 7.0\) Hz for a \textit{cis}-stereochemistry, \(J_{H3,H3a} = 0\) Hz for a \textit{trans}-stereochemistry,\textsuperscript{1} The NOE between H\textsubscript{3} and H\textsubscript{4} further confirmed the \textit{cis}-stereochemistry between H\textsubscript{3} and H\textsubscript{4} and H\textsubscript{3a}. The stereochemistry of C2 was determined by NOE between H\textsubscript{ar1}, H\textsubscript{ar1’} and H\textsubscript{3}, the correlation signal between H\textsubscript{3} and H\textsubscript{ar1}, H\textsubscript{ar1’} manifested the \textit{cis}-relation of among them.\textsuperscript{2}

**Scheme S1 Key NOEs of Perhydrofuro[2,3-b]pyran Derivatives.**

[Diagram of 3ah, 3ab, and 3bj]

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a. 3ah: IR (KBr) \(\nu\) 3423.1, 2918.7, 2869.9, 1715.5, 1615.2, 1585.4, 1483.7, 1454.0, 1358.2, 1320.0, 1186.7, 1125.9, 1098.6, 1062.5, 1027.3, 969.1, 920.8, 751.8, 698.1.

b. 3cb: IR (neat) \(\nu\) 2920.0, 2867.9, 1710.4, 1514.1, 1596.4, 1453.6, 1378.8, 1352.8, 1244.6, 1120.5, 1104.1, 1053.2, 1028.1, 819.2, 737.7, 698.3.

c. 3cd: IR (neat) \(\nu\) 2916.5, 2867.9, 1711.6, 1590.7, 1495.0, 1453.7, 1397.7, 1356.4, 1243.2, 1103.3, 1083.1, 1047.2, 1007.8, 912.2, 829.4, 738.0, 698.6.
References:
