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SUPPORTING INFORMATION

Stereospecific [3+2] Cycloaddition of 1,2-Cyclopropanated Sugars and Ketones Catalyzed by $SnCl_4$: an Efficient Synthesis of Multi-Substituted Perhydrofuro[2,3-*b*]furans and Perhydrofuro[2,3-*b*]pyrans

Xiaofeng Ma,[a] Jichao Zhang,[a] Qin Tang,[a] Jun Ke,[a] Wei Zou,[b] and Huawu Shao*[a]

[a] *Natural Products Research Center, Chengdu Institute of Biology,*

Chinese Academy of Sciences, Chengdu, 610041, China

[b] *Institute for Biological Sciences, National Research Council of Canada,*

100 Sussex Drive, Ottawa, Ontario K1A 0R6.

*Correspondence author: E-mail: shaohw@cib.ac.cn
Fax: (+86) 28-82890288

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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. 1H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm; CD_3COCD_3, δ 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 ($CDCl_3$, δ 77.0 ppm; CD_3COCD_3, δ 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-α-D-galactopyranose (**1a**), 1-*C*-Acetyl-3,4,6-tri-*O*-benzyl-1,2-cyclopropane-1,2-deoxy-α-D-glucopyranose (**1b**) and 1-*C*-Acetyl-3,4-Di-*O*-benzyl-1,2-cyclopropane-1,2-deoxy-α-D-lyxofuranose (**1c**) were obtained as our previously reported methods.

General procedure for $SnCl_4$-catalyzed transformation for cyclopropanated sugars to per-substituted perhydrofuro[2,3-*b*]pyran and furan derivatives.

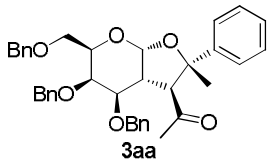
Method A: Under an argon atmosphere, $SnCl_4$ (2.3 μL, 0.02 mmol) in 0.5 mL CH_2Cl_2 was added to a mixture of 4 Á M.S. (50 mg), cyclopropanated sugars **1** (0.1 mmol) and ketones **2** (0.4 mmol)

in 0.5 mL CH_2Cl_2. The solution was stirred at 0 ºC to 4 ºC until the reaction was completed as detected by TLC. Then the reaction was quenched with a vigorously stirred solution of saturated aqueous $NaHCO_3$ (10 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over Na_2SO_4 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, $SnCl_4$ (2.3 μL, 0.02 mmol) in 0.5 mL CH_2Cl_2 was added to a mixture of 4 Á M.S. (50 mg), cyclopropanated sugars **1** (0.1 mmol) and ketones **2** (1.0 mmol) in 0.5 mL CH_2Cl_2. The solution was stirred at 0 ºC to 4 ºC until the reaction was completed as detected by TLC. Then the reaction was quenched with a vigorously stirred solution of saturated aqueous $NaHCO_3$ (10 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over Na_2SO_4 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)

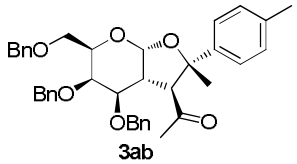


3aa

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. $[\alpha]_D^{20}$ +65.9 (*c* 0.14, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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), 3.81 (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, $CDCl_3$) δ 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.

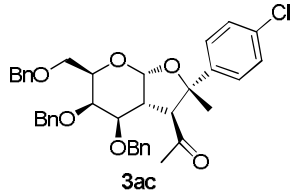
(*2S*,3*S*,*3aR*,*4R*,*5R*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(4-tolyl)hexahydrofuro[2,3-*b*]pyran (3ab)



3ab

Compound **3ab** was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars **1a** 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 **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, $CDCl_3$) δ7.36 – 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, $CDCl_3$) δ 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*,3*S*,*3aR*,*4R*,*5R*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(4-chlorophenyl)hexahydrofuro[2,3-*b*]pyran (3ac)

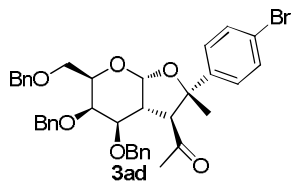


3ac

Compound **3ac** was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars **1a** and ketone **2c** (53.5 μL, 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,

83%) as colorless syrup. $[\alpha]_D^{20}$ +62.4 (*c* 0.19, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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* = 6.2 Hz, 2H), 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.7, 146.8, 138.4, 137.8, 137.5, 132.6, 128.8, 128.5, 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.

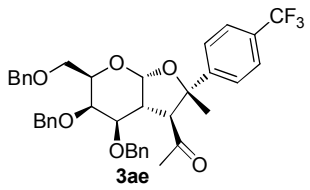
(*2S*,3*S*,*3aR*,*4R*,*5R*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(4-bromophenyl)hexahydrofuro[2,3-*b*]pyran (3ad)



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. $[\alpha]_D^{20}$ +80.2 (*c* 0.19, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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* = 10.0, 2.1 Hz, 1H), 2.76 (ddd, *J* = 9.9, 4.3, 2.2 Hz, 1H), 2.28 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.7, 147.4, 138.4, 137.8, 137.5, 131.7, 128.5, 128.5, 128.3, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 125.8, 120.8, 101.1, 81.6, 77.4, 74.0, 73.7, 72.2, 70.7, 69. 9, 68.5, 62.8, 43.9, 32.0, 29.7, 27.2; ESI-HRMS: m/z calcd for $C_{38}H_{39}BrNaO_6[M+Na]^+$: 693.1822; found: 693.1848.

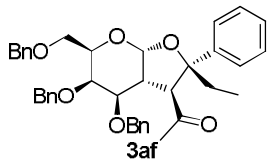
(*2S*,3*S*,*3aR*,*4R*,*5R*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(4-trifluoromethylphenyl)hexahydrofuro[2,3-*b*]pyran (3ae)



3ae

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. $[\alpha]_D^{20}$ +61.4 (*c* 0.24, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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 (d, *J* = 12.2 Hz, 1H), 3.87 (s, 1H), 3.68 (d, *J* = 6.4 Hz, 2H), 3.29 (d, *J* = 1.8 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.6, 152.1, 138.3, 137.8, 137.4, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 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 $C_{39}H_{39}F_3NaO_6[M+Na]^+$: 683.2591; found: 683.2604.

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

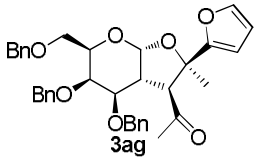


3af

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. $[\alpha]_D^{20}$ +51.5 (*c* 0.20, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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, $CDCl_3$) δ 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 $C_{39}H_{42}NaO_6[M+Na]^+$: 629.2874; found: 629.2854.

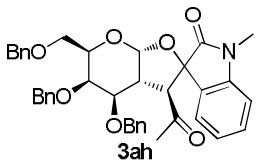
(*2S*,3*S*,*3aR*,*4R*,*5R*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(furan-2-yl)hexahydrofuro[2,3-*b*]pyran (3ag)



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, $CDCl_3$) δ 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, $CDCl_3$) δ 207.0, 157.7, 142.1, 138.5, 138.0, 137.9, 128.5, 128.4, 128.3, 128.0, 127.8, 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.

Spirocyclic compound 3ah

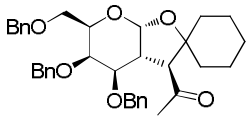


3ah

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, $CDCl_3$) δ 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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, 127.83, 127.8, 127.7, 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 $C_{39}H_{39}NNaO_7$[M+Na]$^+$: 656.2619; found: 656.2625.

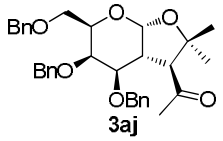
Spirocyclic compound 3ai



3ai

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. $[\alpha]_D^{20}$ +56 (*c* 0.40, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 207.5, 138.5, 138.0, 137.8, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.8, 127.6, 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 $C_{36}H_{42}NaO_6$[M+Na]$^+$: 593.2874; found: 593.2873.

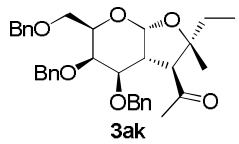
(3*S*,*3aR*,*4R*,*5R*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2,2-di-methylhexahydrofuro[2,3-*b*]pyran (3aj)



3aj

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. $[\alpha]_D^{20}$ +48.5 (*c* 0.46, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ7.39 – 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.0, 138.5, 138.0, 137.8, 128.6, 128.4, 128.4, 128.3, 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 $C_{33}H_{38}NaO_6[M+Na]^+$: 553.2561; found: 553.2551.

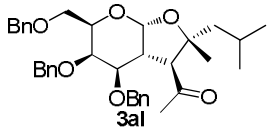
(*2R*,3*S*,*3aR*,*4R*,*5R*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-ethyl-2-methylhexahydrofuro[2,3-*b*]pyran (3ak)



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. $[\alpha]_D^{20}$ +40.9 (*c* 0.25, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.27 (m,15H), 5.45 (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); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.5, 138.5, 138.0, 137.9, 128.6, 128.4, 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 $C_{34}H_{40}NaO_6[M+Na]^+$: 567.2717; found: 567.2708.

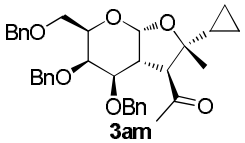
(*2R*,3*S*,*3aR*,*4R*,*5R*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-*i*-butyl-2-methylhexahydrofuro[2,3-*b*]pyran (3al)



3al

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. $[\alpha]_D^{20}$ +54.2 (*c* 0.24, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.4, 138.5, 138.0, 137.8, 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 $C_{36}H_{44}NaO_6[M+Na]^+$: 595.3030; found: 595.3022.

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

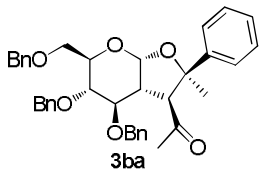


3am

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. $[\alpha]_D^{20}$ +63.6 (*c* 0.42, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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,

J = 4.6 Hz, 1H), 2.88 (dt, *J* = 9.0, 4.6 Hz, 1H), 2.15 (s, 3H), 1.01 (s, 3H), 0.93 – 0.87 (m, 1H), 0.47 – 0.36 (m, 3H), 0.29 – 0.24 (d, *J* = 5.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.0, 138.5, 138.0, 128.5, 128.4, 128.3, 128.3, 128.0, 128.0, 127.9, 127.8, 127.6, 99.1, 79.9, 78.5, 73.7, 73.6, 72.7, 70.6, 70.2, 68.2, 63.8, 43.5, 31.6, 29.7, 23.2, 22.0, 2.5, 1.1; ESI-HRMS: m/z calcd for $C_{35}H_{40}NaO_6[M+Na]^+$: 579.2717; found: 579.2722.

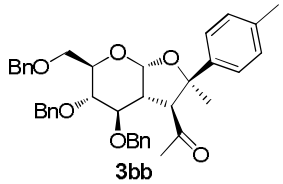
(*2S*,3*S*,*3aR*,*4R*,*5S*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-phenylhexahydrofuro[2,3-*b*]pyran



3ba

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. $[\alpha]_D^{20}$ +27.3 (*c* 0.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{38}H_{40}NaO_6[M+Na]^+$: 615.2717; found: 615.2731.

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

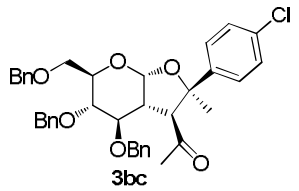


3bb

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, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 206.8, 143.1, 138.3, 138.3, 137.8, 137.0, 129.2, 128.4, 128.4, 128.4, 127.9, 127.9, 127.8, 127.7, 127.6, 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.

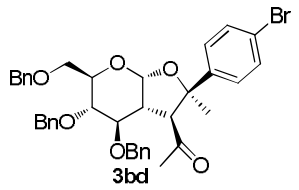
(*2S*,3*S*,*3aR*,*4R*,*5S*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(4-chlorophenyl)hexahydrofuro[2,3-*b*]pyran (3bc)



3bc

Compound **3bc** was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars **1b** and ketone **2c** (53.5 μL, 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, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 206.4, 144.8, 138.2, 137.7, 133.3, 128.7, 128.5, 128.4, 128.4, 127.9, 127.9, 127.8, 127.6, 126.6, 98.6, 83.2, 76.4, 76.1, 73.5, 72.7, 72.6, 72.4, 69.1, 62.4, 45.1, 31.8, 29.7, 24.3; ESI-HRMS: m/z calcd for $C_{38}H_{39}ClNaO_6[M+Na]^+$: 649.2327; found: 649.2325.

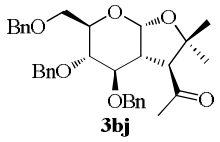
(*2S*,3*S*,*3aR*,*4R*,*5S*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(4-bromophenyl)hexahydrofuro[2,3-*b*]pyran (3bd)



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. $[\alpha]_D^{20}$ +35.0 (*c* 0.29, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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* = 4.7 Hz, 1H), 3.01 (dt, *J* = 8.4, 5.3 Hz, 1H), 1.92 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.4, 145.3, 138.2, 137.7, 131.7, 128.5, 128.4, 128.4, 127.9, 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 $C_{38}H_{39}BrNaO_6[M+Na]^+$: 693.1822; found: 693.1830.

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

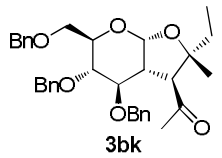


3bj

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. $[\alpha]_D^{20}$ +47.8 (*c* 0.32, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.6, 138.3, 138.2, 137.8, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 127.5, 97.9, 80.8, 76.0, 75. 5, 73.4, 72.1,

71.5, 71.3, 69.5, 61.2, 43.1, 31.1, 29.8, 29.7, 24.4; ESI-HRMS: m/z calcd for $C_{33}H_{38}NaO_6[M+Na]^+$: 553.2561; found: 553.2550.

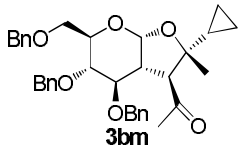
(*2R*,*3S*,*3aR*,*4R*,*5S*,*6R*,*7aS*)-3-acetyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-ethyl-2-methylhexahydrofuro[2,3-*b*]pyran (3bk)



3bk

Compound **3bk** was prepared according to Method A using (47.3 mg, 0.1 mmol) cyclopropanated sugars **1b** 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 **3bk** (45.2 mg, 0.083 mmol, 83%) as colorless syrup. $[\alpha]_D^{20}$ +9.0 (*c* 0.37, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 138.3, 138.3, 137.9, 128.5, 128.4, 128.3, 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 $C_{34}H_{40}NaO_6[M+Na]^+$: 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)

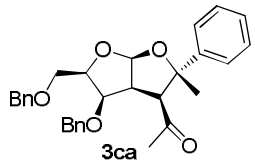


3bm

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. $[\alpha]_D^{20}$ +13.0 (*c* 0.26, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 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,

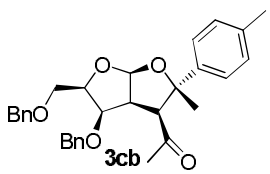
J = 10.5 Hz, 1H), 3.23 – 3.17 (m, 1H), 2.12 (s, 3H), 1.20 – 1.13 (m, 1H), 0.95 (s, 3H), 0.88 (t, *J* = 6.9 Hz, 1H), 0.74 – 0.67 (m, 1H), 0.54 – 0.44 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.0, 138.3, 138.3, 137.9, 128.4, 128.4, 128.3, 128.0, 127.8, 127.8, 127.5, 97.4, 81.9, 75.9, 75.5, 73.4, 72.0, 71.6, 71.5, 69.6, 61.6, 42.9, 31.3, 29.7, 21.6, 21.4, 2.8, 1.2; ESI-HRMS: m/z calcd for $C_{35}H_{40}NaO_6[M+Na]^+$: 579.2717; found: 579.2721.

(*2S*,*3S*,*3aS*,*4R*,*5R*,*6aR*)-3-acetyl-4-(benzyloxy)-5-[(benzyloxy)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 μL, 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 (*c* 0.27, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.22 (m, 11H), 7.14 (d, *J* = 6.6 Hz, 2H), 5.67 (d, *J* = 5.0 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 11.4 Hz, 1H), 4.36 – 4.31 (m, 3H), 3.86 (dd, *J* = 10.3, 4.1 Hz, 1H), 3.82 (dd, *J* = 13.8, 8.7 Hz, 1H), 3.75 (dd, *J* = 10.2, 5.6 Hz, 2H), 1.77 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 145.1, 138.3, 137.6, 128.6, 128.4, 127.8, 127.7, 127.6, 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; ESI-HRMS: m/z calcd for $C_{30}H_{32}NaO_5[M+Na]^+$: 495.2142; found: 495.2144.

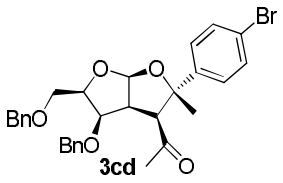
(*2S*,*3S*,*3aS*,*4R*,*5R*,*6aR*)-3-acetyl-4-(benzyloxy)-5-[(benzyloxy)methyl]-2-methyl-2-(4-tolyl)-hexahydrofuro[2,3-*b*]furan (3cb)



Compound **3cb** was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated sugars **1c** and ketone **2b** (56.2 μL, 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. $[\alpha]_D^{20}$ -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, 3H), 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, 127.8, 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, 22.9, 21.0; ESI-HRMS: m/z calcd for $C_{31}H_{34}NaO_5[M+Na]^+$: 509.2298; found: 509.2304.

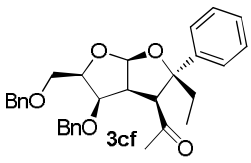
(*2S*,*3S*,*3aS*,*4R*,*5R*,*6aR*)-3-acetyl-4-(benzyloxy)-5-[(benzyloxy)methyl]-2-methyl-2-(4-bromophenyl)hexahydrofuro[2,3-*b*]furan (3cd)



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. $[\alpha]_D^{20}$ -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, 127.7, 127.6, 127.6, 121.6, 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 $C_{30}H_{31}BrNaO_5[M+Na]^+$: 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)

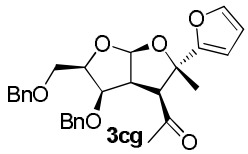


3cf

Compound **3cf** was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated

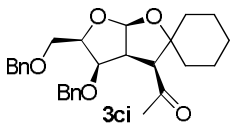
sugars **1c** and ketone **2f** (54.3 μL, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product **3cf** (36.5 mg, 0.075 mmol, 75%) as colorless syrup. $[\alpha]_D^{20}$ -23.0 (*c* 0.37, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 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-acetyl-4-(benzyloxy)-5-[(benzyloxy)methyl]-2-(furan-2-yl) 2-methyl-hexahydrofuro[2,3-*b*]furan (3cg)



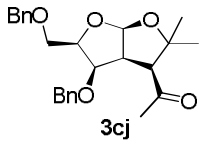
Compound **3cg** was prepared according to Method A using (35.2 mg, 0.1 mmol) cyclopropanated sugars **1c** and ketone **2g** (44.5 mg, 0.4 mmol), after purified by column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:9), afforded the desired product **3cg** (28.7 mg, 0.062 mmol, 62%) as colorless syrup. $[\alpha]_D^{20}$ -40.0 (*c* 0.09, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ7.35 – 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.8, 155.0, 142.6, 138.6, 137.7, 128.4, 128.3, 127.8, 127.7, 127.5, 127.4, 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-HRMS: m/z calcd for $C_{28}H_{30}NaO_6[M+Na]^+$: 485.1935; found: 485.1951.

Spirocyclic compound 3ci



Compound **3ci** 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 **3ci** (39.6 mg, 0.088 mmol, 88%) as colorless syrup. $[\alpha]_D^{20}$ -10.0 (*c* 0.32, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 205.9, 138.3, 137.8, 128.4, 128.3, 127.8, 127.8, 127.5, 127.4, 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-(benzyloxy)-5-[(benzyloxy)methyl]-2,2-di-methyl-hexahydrofuro[2,3-*b*]furan (3cj)



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. $[\alpha]_D^{20}$ -6.1 (*c* 0.16, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 205.7, 138.3, 137.7, 128.4, 128.3, 127.9, 127.8, 127.6, 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:

a. **3ah**: IR (KBr) ν 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) ν 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.

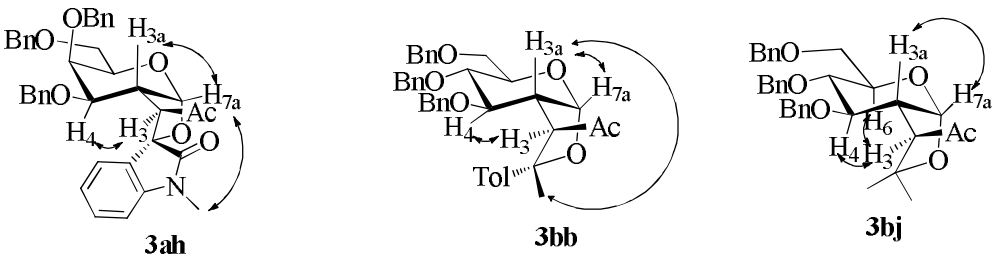
c. **3cd**: IR (neat) ν 2916.5, 2867.9, 1711.6, 1590.7, 1495.0, 1453.7, 1397.7, 1356.4, 1243.2, 1103.3, 1083.1, 1047.2, 1007.8, 912.2, 829.4, 738.0, 698.6.

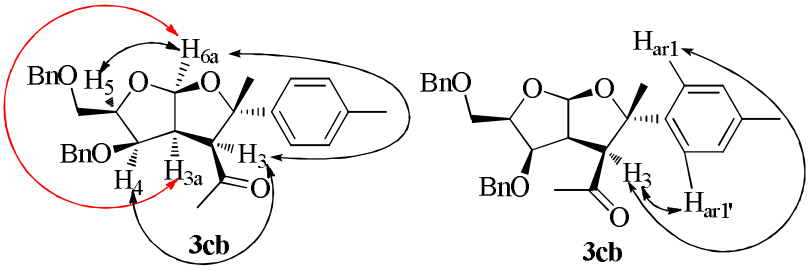
The stereochemistry of the products

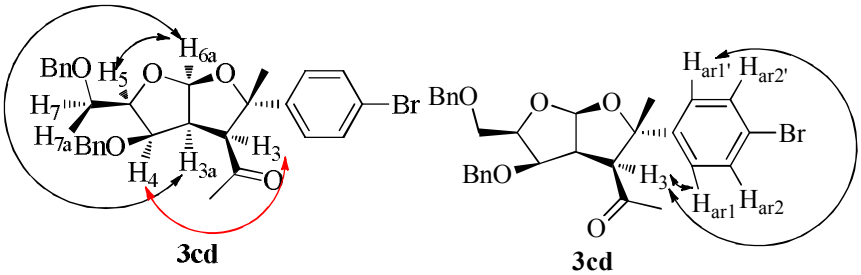
The configuration of the products was unambiguously assigned by extensively studied the NMR and NOE of the products. The coupling constants between H_{7a} and H_{3a} ($J_{H7a, H3a}$ = 4.3 – 4.5 Hz for the products from compound **1a**, $J_{H7a, H3a}$ = 5.2 – 5.9 Hz for the products from compound **1b**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

For the stereochemistry of the **3c** series compounds, the coupling constants between H_{6a} and H_{3a} ($J_{H6a, H3a}$ = 4.9 – 5.6 Hz) manifested convincingly that the fused ring system have a *cis*-bicyclic configuration. The stereochemistry of C3 position was determined by coupling constants between H_{3a} and H_3 ($J_{H3, H3a}$ = 9.1 – 10.0 Hz), which demonstrated the *cis*- correlation between them (Proton proton coupling constants in a *bis*-THF system: $J_{H3, H3a} >$ 7.0 Hz for a *cis*-stereochemistry, $J_{H3, H3a}$ = 0 Hz for a *trans*-stereochemistry,[1] The NOE between H_3 and H_4 further confirmed the *cis*-stereochemistry between H_3 and H_4 and H_{3a}. The stereochemistry of C2 was determined by NOE between H_{ar1}, H_{ar1}' and H_3, the correlation signal between H_3 and H_{ar1}, H_{ar1}' manifested the *cis*-relation of among them.[2]

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







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