A Straightforward and Highly Diastereoselective Synthesis of 2,2-Di-Substituted Perhydrofuro[2,3-*b*]pyran (and furan) Derivatives Promoted by $BiCl_3$

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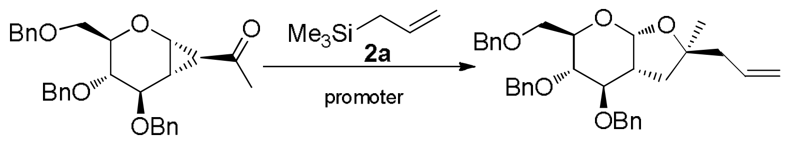
1. General Information:

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 (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). ESI-HRMS spectra were recorded on BioTOFQ.

2. Screening the reaction conditions

Table S1. The cyclization reaction of 1,2-cyclopropaneacetylatedsugar **1a** and olefin **2a** under different conditions [a]



1a **3a**

Entry	Lewis Acid (LA)	Equiv. of LA	Solvent	Yield(%) [b]
1	TMSOTf	1.2	CH_3CN	complex
2	BF_3•Et_2O	1.2	CH_3CN	36
3	I_2	1.2	CH_3CN	53
4	$BiCl_3$	1.2	CH_3CN	78 [c]
5	$AlCl_3$	1.2	CH_3CN	78 [d]
6	$ZnCl_2$	1.2	CH_3CN	70 [e]
7	AgOTf	1.2	CH_3CN	n.r.

8	$PdCl_2$	1.2	CH_3CN	n.r.
9	$FeCl_3$	1.2	CH_3CN	58
10	$BiCl_3$	4.0	CH_3CN	89
11	$BiCl_3$	4.0	CH_2Cl_2	42
12	$BiCl_3$	4.0	$CHCl_3$	56
13	$BiCl_3$	4.0	Acetone	n.d.
14	$BiCl_3$	4.0	DMSO	trace
15	$BiCl_3$	4.0	DMF	trace
16	$BiCl_3$	4.0	Et_2O	n.d.
17	$BiCl_3$	4.0	Toluene	92
18	$BiCl_3$	4.0	1,4-Dioxane	n.d.
19	$BiCl_3$	4.0	THF	n.d.
20	$BiCl_3$	2.0	Toluene	87
21	**$BiCl_3$ (2.5 eq)**	**2.5**	**Toluene**	**91**
22	$BiCl_3$ (3.0 eq)	3.0	Toluene	91

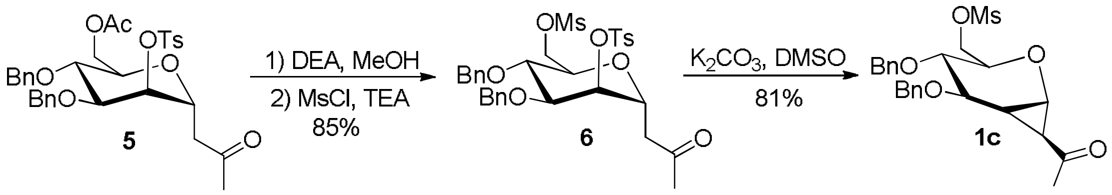
[a] All reaction were carried out using 0.1mmol 1,2-cyclopropaneacetylated sugar, 0.4 mmol allyltrimethylsilane and 0.12mmol promoter in 1mL solvent at -40°C-rt unless otherwise noted. [b] Isolated yield. [c] The reaction did not complete in this condition (83% conversion rate). [d] The reaction did not complete in this condition (80% conversion rate). [e] The reaction did not complete in this condition (78% conversion rate). n.r. = no reaction. n.d. = not detected.

Various Lewis acids including TMSOTf, $BF_3{\cdot}Et_2O$, I_2, $BiCl_3$, and $AlCl_3$ were surveyed. As shown in Table 1, when TMSOTf was used (Table 1, entry 1), we did not detect major product. When $BF_3{\cdot}Et_2O$ was employed as Lewis acid (Table 1, entry 2), perhydrofuro[2,3-*b*]pyran was obtained exclusively in 36% yield. I_2 and $FeCl_3$ also offered the dicyclic product despite with lower yield (Table 1, entries 3, 9). Other Lewis acids such as AgOTf and $PdCl_2$ did not promote the reaction (Table 1, entries 7, 8). Encouragingly, when $ZnCl_2$ was used，the yield was increased to 70% (Table 1, entry 6). The best results were obtained using $BiCl_3$ and $AlCl_3$ as promoters. Under the conditions, the perhydrofuro [2,3-*b*]pyran derivative was obtained in 78% yield, despite the reaction did not go to completion (Table 1, entries 4, 5). Since the bismuth (Ш) compounds are relatively stable in air, and easy to handle, and have been given much attention by organic chemist in recent years, we selected $BiCl_3$ as a promoter. To investigate the influence of different amounts of promoter on the yield of the final product, the quantity of $BiCl_3$ was increased to 4.0 equiv., satisfactorily, the reaction achived the complete conversion and furnished the product in 89% yield (Table 1, entry 10).

Further optimization of the reaction conditions found that the reaction could also go to completion with 2.5 equiv. of $BiCl_3$ in toluene, and the fused cycle product was obtain in 91% yield (table 1. entry 21).

3. Preparation of Starting Materials:

1-*C*-Acetyl-3,4,6-tri-*O*-benzyl-1,2-cyclopropane-1,2-deoxy-α-D-glucopyranose (**1a**), 1-*C*-Acetyl-6-*O*-acetyl-3,4-di-*O*-benzyl-1,2-cyclopropane-1,2-deoxy-α-D-glucopyranose (**1b**) and 1-*C*-Acetyl-3,4,6-tri-*O*-benzyl-1,2-cyclopropane-1,2-deoxy-α-D-galctopyranose (**1d**) were obtained as our previously reported merhods.



1-*C*-(3′,4′-Di-*O*-benzyl-6′-*O*-methylsulfonyl-2′-*O*-tosyl-*α*-D-mannopyranosyl)-acetone (6) To a solution of **5** (2.0 g, 3.35 mmol) in MeOH 100 mL was added diethylamine (DEA, 2.0 mL), the mixture was stirred at room temperature overnight. After the reaction was complete, the mixture was concentrated. The crude oil was dissolved in dichloromethane (22 mL) and cooled to 0 ºC, 0.79 mL MsCl and 0.9 mL triethylamine were added, and the solution was warmed to room temperature slowly in 8 h. Then 20 mL H_2O MeOH was added and extracted with dichloromethane 3 × 10 mL, the extract was washed with brine (2 × 20 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford **6** (1.8 g, 2.85 mmol, 85%) as a colourless syrup; $[\alpha]_D^{20}$ +8.8 (*c* 0.82, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.27 (m, 8H), 7.20 (d, *J* = 5.7 Hz, 4H), 4.74 (dd, *J* = 7.0, 2.8 Hz, 1H), 4.55 (dd, *J* = 11.6, 3.8 Hz, 2H), 4.53 – 4.48 (m, 2H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.27 (dd, *J* = 11.3, 3.6 Hz, 1H), 3.91 – 3.87 (m, 1H), 3.79 (dd, *J* = 5.7, 2.8 Hz, 1H), 3.55 – 3.50 (m, 1H), 2.98 (s, 3H), 2.55 (qd, *J* = 16.3, 6.6 Hz, 2H), 2.43 (d, *J* = 12.4 Hz, 3H), 2.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.8, 145.3, 137.1, 137.0, 133.4, 130.0 128.6(2), 128.2, 128.1(3), 127.9, 76.9, 74.9, 74.1, 73.3, 73.2, 73.1, 67.4, 67.1. 43.9, 37.6, 30.7, 21.7; ESI-HRMS: m/z calcd for

$C_{31}H_{36}NaO_{10}S_2$[M+Na]$^+$: 655.1642; found: 655.1657.

1-*C*-Acetyl-6-*O*-methylsulfonyl-3,4-di-*O*-benzyl-1,2-cyclopropane-1,2-deoxy-*α*-D-glucopyranose (1c) To a solution of **6** (1.2 g, 1.9 mmol) in DMSO (22 mL) was added K_2CO_3 (1.2 g, 8.7 mmol). The suspension was stirred at 50 °C for 5 h. The mixture was cooled to room temperature, diluted with dichloromethane (100 mL), washed with water, brine, and dried over Na_2SO_4. The filtrate was concentrated in vacuo, and purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 10:1) to afford compound **1c** (0.7 g, 1.52 mmol, 80%) as a colourless syrup; $[\alpha]_D^{20}$ +32.5 (*c* 0.50, $CHCl_3$); ^{1}H NMR (600 MHz, Acetone-d$_6$): δ 7.53 – 7.10 (m, 10H), 4.77 (t, *J* = 12.2 Hz, 2H), 4.67 (d, *J* = 9.0 Hz, 1H), 4.65 (d, *J* = 9.4 Hz, 1H), 4.55 (dd, *J* = 11.3, 6.9 Hz, 1H), 4.29 (dd, *J* = 11.3, 2.8 Hz, 1H), 3.92 (ddd, *J* = 8.7, 6.0, 2.1 Hz, 2H), 3.80 (dd, *J* = 7.1, 1.9 Hz, 1H), 3.62 (t, *J* = 5.6 Hz, 1H), 3.09 (s, 3H), 2.58 (dd, *J* = 5.7, 1.8 Hz, 1H), 2.20 (s, 3H), 1.89 (t, *J* = 5.8 Hz, 1H); ^{13}C NMR (150 Hz, Acetone-d$_6$): δ 203.6, 138.5, 138.3, 128.3, 128.3, 127.8, 127.6, 127.6, 74.8, 74.8, 72.7, 71.0, 68.8, 58.9, 36.6, 31.9, 29.9, 25.8. ESI-HRMS: m/z calcd for $C_{24}H_{28}NaO_7S$ [M+Na]$^+$: 483.1448; found: 483.1446.

Synthesis of 1,2-Cyclopropaneacetylated lyxose (1e)

3,5-Di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose (7).[1] A mixture of D-xylose (10.0 g, 66.6 mmol), dry $CuSO_4$ (20.4 g, 127.5 mmol), and concentrated H_2SO_4 (0.82 mL) in acetone (82 mL) was stirred at 25 °C for15 h. The mixture was suction filtration, and the solid was washed with acetone (3 × 30 mL). The filtrate was neutralized with concentrated NH_4OH, and the resulting white solid was removed by suction filtration. Removal of the solvent in vacuo from the filtrate gave syrup that was treated with aqueous 0.1 N HCl (61.2 mL) for 0.5 h at 25 °C, during which time the reaction mixture turned to a clear solution. The reaction was quenched with solid $NaHCO_3$ to a pH of 7.5. The solution was washed with ether once, and the aqueous fraction was evaporated in vacuo to yield a pale yellow syrup, which was dissolved in $CHCl_3$ (40.8 mL) prior to drying (Na_2SO_4). Filtration and removal of the solvent in vacuo, afforded pale yellow syrup. NaH (60% in dispersion in mineral oil, 6.4 g, 160 mmol) was added in batches over 30 min to an ice-cold solution of this syrup in DMF (60 mL). The mixture was stirred at 0 °C for 1 h, subsequently, benzyl bromide (19.0 mL, 160 mmol) was added dropwise to the reaction mixture over 1h. The resulting mixture was then warmed gradually to ambient and stirred for 5 h, then extracted with ethyl acetate (3 × 150 mL), the extract was washed with H_2O (3 × 300 mL), brine (3 × 300 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford **7** as colorless syrup (20.4 g, 55.1 mmol, 83%).$[\alpha]_D^{20}$ -41.4 (*c* 1.27, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 10H), 5.96 (d, *J* = 3.8 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.65 – 4.59 (m, 2H), 4.54 (dd, *J* = 11.9, 6.0 Hz, 2H), 4.44 (td, *J* = 6.1, 3.3 Hz, 1H), 4.00 (d, *J* = 3.2 Hz, 1H), 3.79 (qd, *J* = 9.9, 6.1 Hz, 2H), 1.51 (s, 3H), 1.34 (s, 3H).

3-*C*-(3, 5-Di-*O*-benzyl-α-D-xylofuranosyl)-propene (8).[2] Under nitrogen atmosphere, a solution of the 1,2-*O*-isopropylidene-xylofuranose derivatives **7** (17.4 g, 47 mmol) in 140 mL of dry CH_2Cl_2 at 0 °C was treated with allyltrimethylsilane (13.6 mL, 70.5 mmol) and BF_3•OEt_2 (9.0 mL, 70.5 mmol). The reaction mixture was warmed to room temperature and allowed to react overnight. The reaction mixture was treated with a saturated aqueous solution of $NaHCO_3$ (80 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The organic phase was dried with Na_2SO_4, concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to afford **8** as colorless syrup (14.8 g, 41.7 mmol, 89%). $[\alpha]_D^{20}$ -21.3 (*c* 0.39, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 10H), 5.91 – 5.82 (m, 1H), 5.11 (dd, *J* = 21.5, 13.7 Hz, 2H), 4.62 (dd, *J* = 11.9, 8.6 Hz, 2H), 4.53 (d, *J* = 12.0 Hz, 2H), 4.25 (dd, *J* = 11.1, 5.2 Hz, 1H), 4.03 (dd, *J* = 4.3, 2.5 Hz, 1H), 3.91 (dd, *J* = 4.9, 2.4 Hz, 1H), 3.76 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.14 (s, 1H), 2.90 (dt, *J* = 12.9, 6.6 Hz, 2H), 2.54 – 2.47 (m, 1H), 2.40 (dt, *J* = 14.3, 7.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 138.1, 134.3, 128.4, 128.3, 127.8, 127.8, 127.6, 127.5, 117.5, 85.4, 84.0, 79.3, 79.3, 73.5, 71.9, 68.9, 42.3, 38.0; ESI-HRMS: m/z calcd for $C_{22}H_{26}NaO_4$ $[M + Na]^+$: 377.1723; found: 377.1729.

3-*C*-(3,5-Di-*O*-benzyl-2-*O*-tosyl-α-D-xylofuranosyl)-propene (9). TsCl (20.4 g, 75.6 mmol) was added to an ice-cold solution of the mixture of propene deriavtes **8** (14.8 g, 41.7 mmol) in pyridine (100 mL).The mixture was stirred at room temperature overnight, and washed with 10% HCl aqueous, H_2O, brine respectively. The organic phase was dried with Na_2SO_4, concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to afford **8** as colorless syrup (18.1 g, 35.6 mmol, 85%). $[\alpha]_D^{20}$ -54.2 (*c* 0.48, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.22 (m, 12H), 5.57 (ddt, *J* = 17.2, 9.9, 7.0 Hz, 1H), 4.95 – 4.89 (m, 2H), 4.65 (d, *J* = 2.6 Hz, 1H), 4.57 (t, *J* = 11.9 Hz, 2H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.16 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.09 (d, *J* = 3.7 Hz, 1H), 3.91 (td, *J* = 6.6, 2.9 Hz, 1H), 3.69 (d, *J* = 5.5 Hz, 2H), 2.45 (s, 3H), 2.30 (dq, *J* = 14.7, 7.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 138.1, 137.5, 133.5, 133.4, 130.0, 129.6, 128.4, 128.4, 128.0, 127.8, 127.8, 127.6, 127.0, 117.7, 84.8, 82.8, 82.6, 80.1, 73.4, 71.7, 68.0, 42.00, 37.5, 21.7; ESI-HRMS: m/z calcd for $C_{29}H_{32}NaO_6S$ $[M + Na]^+$: 531.1812; found: 531.1812.

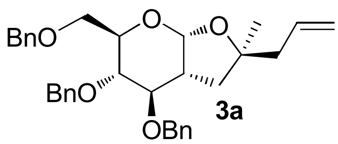
1-*C*-(3,5-Di-*O*-benzyl-2-*O*-tosyl-α-D-xylofuranosyl)-acetone (10). Jones reagent (2 M, 6.8 mL) was added to an ice-cold solution of the mixture of propene deriavtes **9** (2.5 g, 4.9 mmol) and $Hg(OAc)_2$ in acetone/H_2O (V:V = 4:1, 20 mL). The mixture was stirred at room temperature for 4 h, quenched withe MeOH. Then, the mixture was exacted with ethyl acetate, washed with H_2O, saturated aqueous $NaHCO_3$, brine respectively. The organic phase was dried with Na_2SO_4, concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford **10** as colorless syrup (1.89 g, 3.61 mmol, 74%). $[\alpha]_D^{20}$ -42.7 (*c* 0.31, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.25 (m, 10H), 7.21 (d, *J* = 7.0 Hz, 2H), 4.79 (d, *J* = 1.5 Hz, 1H), 4.59 – 4.45 (m, 3H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.34 – 4.27 (m, 1H), 4.18 (dd, *J* = 9.9, 5.5 Hz, 1H), 4.11 (t, *J* = 4.4 Hz, 1H), 3.72 – 3.59 (m, 2H), 2.77 (dd, *J* = 16.1, 7.7 Hz, 1H), 2.64 (dd, *J* = 16.1, 5.5 Hz, 1H), 2.44 (d, *J* = 4.0 Hz, 3H), 2.09 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.7, 145.3, 138.0, 137.3, 133.4, 130.0, 128.5, 128.4, 128.0, 127.9, 127.9, 127.7, 127.7, 127.7, 85.1, 82.3, 80.0, 79.0, 73.4, 72.0, 67.9, 46.9, 30.6, 21.7; ESI-HRMS: m/z calcd for $C_{29}H_{32}NaO_7S$ $[M + Na]^+$: 547.1761; found: 547.1764.

1′-*C*-Acetyl-3,5-Di-*O*-benzyl-1,2-cyclopropane-1,2-deoxy-α-D-lyxofuranose (1e). To a solution of acetone derivates **10** (2.18 g, 4.16 mmol) in DMSO (61 mL) was added K_2CO_3 (4.32 g, 31.3 mmol). The mixture was stirred at 60 °C for 18 h. After cooled to room temperature, the reaction mixture was exacted with ethyl acetate (50 mL), and washed with brine. The organic phase was dried with Na_2SO_4, concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford **1e** as colorless syrup (1.05 g, 2.99 mmol, 72%). $[\alpha]_D^{20}$ -36.3 (*c* 1.12, acetone); ^1H NMR (600 MHz, acetone-d_6) δ 7.38 – 7.24 (m, 10H), 4.60 (dd, *J* = 12.1, 6.6 Hz, 2H), 4.52 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 2.6 Hz, 1H), 4.48 – 4.45 (m, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.04 (d, *J* = 5.9 Hz, 1H), 3.69 (dd, *J* = 10.6, 4.0 Hz, 1H), 3.48 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.57 (td, *J* = 5.5, 3.9 Hz, 1H), 2.52 (d, *J* = 3.3 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, acetone-d_6) δ 202.2, 138.9, 138.4, 128.3, 128.1, 127.6, 127.5, 127.4, 127.2, 88.1, 78.5, 72.7, 70.5, 69.0, 67.9, 36.3, 32.8, 29.8; ESI-HRMS: m/z calcd for $C_{22}H_{25}O_4$ $[M + H]^+$: 353.1747; found: 353.1746.

4. General procedure for $BiCl_3$-promoted transformation for cyclopropanated sugars to perhydrofuro[2,3-*b*]pyran derivatives.

Under an argon atmosphere, $BiCl_3$ (0.25 mmol) in 0.5 mL toluene was cooled to -40 ºC, to this mixture was added slowly cyclopropanated sugars **1** (0.1 mmol) and olefins **2** (0.4 mmol) in 0.5 mL toluene. The solution was then warmed slowly to room temperature, and stirred until the reaction was completed detected be 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 single diastereoisomer.

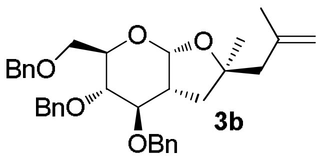
(*2S*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-2-allyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methylhexahydro-furo [2,3-*b*]pyran (3a)



3a

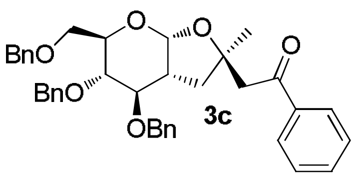
Colorless syrup, 47 mg, yield: 91%, $[\alpha]_D^{20}$ +46.2 (*c* 0.41, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.29 (m, 15H), 5.88 – 5.77 (m, 1H), 5.50 (d, *J* = 5.1 Hz, 1H), 5.12 (t, *J* = 12.2 Hz, 2H), 4.83 (d, *J* = 11.8 Hz, 1H), 4.75 (d, *J* = 11.1 Hz, 1H), 4.69 (d, *J* = 4.2 Hz, 1H), 4.67 (d, *J* = 4.6 Hz, 1H), 4.58 (t, *J* = 11.8 Hz, 2H), 3.95 (dt, *J* = 8.9, 3.0 Hz, 1H), 3.82 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.79 (dd, *J* = 8.9, 6.9 Hz, 1H), 3.74 (dd, *J* = 10.6, 2.5 Hz, 1H), 3.70 (t, *J* = 6.9 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.30 – 2.21 (m, 2H), 2.01 (dd, *J* = 13.3, 8.4 Hz, 1H), 1.77 (dd, *J* = 13.3, 5.4 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.4, 138.2(2), 128.4(2), 128.0, 127.9(2), 127.8(2), 127.6, 118.2, 100.6, 80.9, 80.2, 77.4, 73.7, 73.5, 73.3, 71.9, 69.2, 47.0, 43.9, 38.0, 27.7; ESI-HRMS: m/z calcd for $C_{33}H_{38}NaO_5$ $[M+Na]^+$: 537.2617; found: 537.2611.

(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-2-(2-methylallyl)hexa hydro-furo[2,3-*b*]pyran (3b)



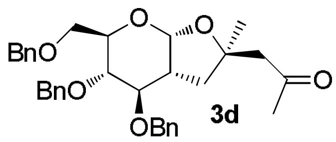
Colorless syrup, 40 mg, yield: 75%, $[\alpha]_D^{20}$ +52.1 (*c* 0.17, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.19 (m, 19H), 5.44 (d, *J* = 5.1 Hz, 1H), 4.86 (s, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.70 (d, *J* = 11.4 Hz, 2H), 4.65 (d, *J* = 3.4 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 12.6 Hz, 1H), 3.89 (dt, *J* = 8.9, 2.9 Hz, 1H), 3.79 – 3.73 (m, 2H), 3.70 (dd, *J* = 10.6, 2.5 Hz, 1H), 3.66 (t, *J* = 6.8 Hz, 1H), 2.42 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.20 (d, *J* = 13.5 Hz, 1H), 2.13 (d, *J* = 13.4 Hz, 1H), 2.05 – 2.00 (m, 1H), 1.80 (s, 3H), 1.76 (dd, *J* = 13.2, 5.6 Hz, 1H), 1.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.7, 138.5, 138.2, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 114.7, 100.5, 81.5, 80.1, 76.8, 73.7, 73.5, 73.3, 71.9, 69.2, 49.9, 43.8, 38.9, 27.8, 24.3; ESI-HRMS: m/z calcd for $C_{34}H_{40}NaO_5$ $[M+Na]^+$: 551.2773; found: 551.2768.

(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-2-[(benzoyl)methyl]-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-hexahydro-furo[2,3-*b*]pyran (3c)



Colorless syrup, 39 mg, yield: 66%, $[\alpha]_D^{20}$ +26.7 (*c* 0.20, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 3H), 7.37 – 7.24 (m, 24H), 7.21 (d, *J* = 6.7 Hz, 3H), 5.41 (d, *J* = 5.1 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 2H), 4.52 (dd, *J* = 11.6, 3.1 Hz, 2H), 3.90 (d, *J* = 8.8 Hz, 1H), 3.77 – 3.66 (m, 5H), 3.20 (d, *J* = 2.4 Hz, 2H), 2.43 (d, *J* = 5.9 Hz, 1H), 2.35 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.02 (dd, *J* = 13.8, 5.8 Hz, 1H), 1.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.6, 138.3, 138.2, 138.1, 137.5, 133.2, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6, 100.5, 80.7, 79.8, 77.1, 73.6, 73.5, 73.2, 69.2, 49.8, 43.6, 38.4, 29.7, 28.6; ESI-HRMS: m/z calcd for $C_{38}H_{40}NaO_6$ $[M+Na]^+$: 615.2717; found: 615.2717.

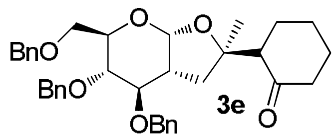
(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-2-[(acetyl)methyl]-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methylhexahydro-furo[2,3-*b*]pyran (3d)



3d

Colorless syrup, 46 mg, yield: 86%, $[\alpha]_D^{20}$ +39.2 (*c* 0.26, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.08 (m, 15H), 5.46 (d, *J* = 5.1 Hz, 1H), 4.76 (d, *J* = 11.7 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.67 – 4.61 (m, 2H), 4.54 (d, *J* = 3.7 Hz, 1H), 4.52 (d, *J* = 4.8 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.76 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.75 – 3.71 (m, 1H), 3.69 (dd, *J* = 10.6, 2.5 Hz, 1H), 3.65 (t, *J* = 6.8 Hz, 1H), 2.66 (d, *J* = 14.9 Hz, 1H), 2.56 (d, *J* = 14.9 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.17 (s, 3H), 2.14 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.89 (dd, *J* = 13.6, 5.5 Hz, 1H), 1.33(s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.4, 138.3, 138.1, 138.1, 128.5, 128.4, 128.3, 128.1, 127.9, 127.9, 127.8, 127.8, 127.6, 100.6, 79.9, 79.8, 77.1, 73.7, 73.5, 73.3, 72.0, 69.1, 54.8, 43.6, 38.8, 31.9, 28.0; ESI-HRMS: m/z calcd for $C_{33}H_{38}NaO_6$ $[M+Na]^+$: 553.2550; found:553.2561.

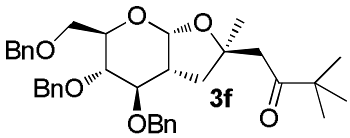
(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-(1-cyclohexanon-2-yl)-2-methylhexahydro-furo[2,3-*b*]pyran (3e)



3e

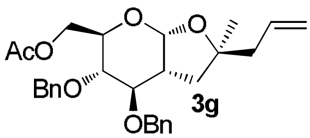
Colorless syrup, 43.9 mg, yield: 88%, $[\alpha]_D^{20}$ +88.0 (*c* 0.09, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.21 (m, 15H), 5.40 (d, *J* = 5.0 Hz, 1H), 4.81 (d, *J* = 11.5 Hz, 1H), 4.75 (d, *J* = 11.0 Hz, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 10.9 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 3.90 – 3.87 (m, 1H), 3.79 (dd, *J* = 10.5, 3.6 Hz, 1H), 3.73 – 3.68 (m, 3H), 2.57 (dd, *J* = 12.7, 5.0 Hz, 1H), 2.31(1H, s), 2.29 – 2.25 (m, 3H), 2.15 – 2.06 (m, 3H), 2.01 (dd, *J* = 14.2, 3.6 Hz, 1H), 1.65 – 1.62 (m, 3H), 1.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 211.6, 138.4, 138.2, 138.1, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 101.6, 82.1, 81.4, 77.6, 74.2, 73.9, 73.6, 72.1, 69.0, 62.2, 44.6, 43.5, 36.1, 29.3, 28.9, 28.3, 25.3; ESI-HRMS: m/z calcd for $C_{32}H_{36}NaO_7$ $[M+Na]^+$: 522.2256; found: 522.2251.

(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-[(2,2-dimethyl-propionyl)methyl]-2-methylhexahydro-furo[2,3-*b*]pyran (3f)



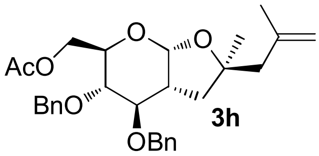
Colorless syrup, 40.1 mg, yield: 70%, $[\alpha]_D^{20}$ +50.7 (*c* 0.31, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.26 (m, 14H), 7.22 (d, *J* = 6.7 Hz, 1H), 5.46 (d, *J* = 5.0 Hz, 1H), 4.80 – 4.77 (m, 1H), 4.72 (d, *J* = 11.1 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.54 (dd, *J* = 14.5, 11.8 Hz, 2H), 3.90 (dd, *J* = 5.8, 3.1 Hz, 1H), 3.80 – 3.76 (m, 1H), 3.76 – 3.72 (m, 1H), 3.72 – 3.67 (m, 2H), 2.84 (d, *J* = 17.4 Hz, 1H), 2.68 (d, *J* = 17.4 Hz, 1H), 2.39 (d, *J* = 12.6 Hz, 1H), 2.25 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.01 (dd, *J* = 14.5, 5.6 Hz, 1H), 1.36 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 214.1, 138.3, 138.1, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.5, 100.5, 80.3, 80.2, 77.3, 73.8, 73.5, 73.5, 72.0, 69.1, 47.8, 44.6, 43.9, 38.8, 29.7, 27.9, 26.2; ESI-HRMS: m/z calcd for $C_{36}H_{44}NaO_6$ $[M+Na]^+$: 595.3030; found: 595.3049.

(*2S*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-6-[(acetyloxy)methyl]-2-allyl-4,5-bis(benzyloxy)-2-methyl-hexahydro-furo[2,3-*b*]pyran (3g)



Colorless syrup, 40 mg, yield: 85%, $[\alpha]_D^{20}$ +51.0 (*c* 0.31, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (dt, *J* = 24.2, 11.7 Hz, 10H), 5.78 (td, *J* = 17.3, 7.3 Hz, 1H), 5.42 (d, *J* = 5.1 Hz, 1H), 5.08 (t, *J* = 12.9 Hz, 2H), 4.76 (d, *J* = 11.8 Hz, 1H), 4.71 (d, *J* = 11.2 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.1 Hz, 1H), 4.30 (t, *J* = 4.2 Hz, 2H), 4.01 – 3.95 (m, 1H), 3.69 (t, *J* = 6.2 Hz, 1H), 3.55 (dd, *J* = 8.7, 6.1 Hz, 1H), 2.51 – 2.44 (m, 1H), 2.21 (dd, *J* = 16.8, 10.3 Hz, 2H), 2.07 – 2.04 (s, 3H), 1.97 (dd, *J* = 13.2, 8.6 Hz, 1H), 1.77 (dd, *J* = 13.2, 6.2 Hz, 1H), 1.27 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.9, 138.2, 137.7, 134.1, 128.5, 128.5, 128.0, 128.0, 127.9, 118.3, 100.2, 81.4, 79.4, 73.5, 73.1, 70.2, 63.7, 46.8, 43.6, 37.7, 27.6, 20.9; ESI-HRMS: m/z calcd for $C_{28}H_{34}NaO_6$ $[M+Na]^+$: 489.2248; found: 489.2253.

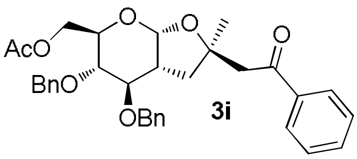
(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-6-[(acetyloxy)methyl]-4,5-bis(benzyloxy)-2-methyl-2-(2-methylallyl)-hexahydro-furo[2,3-*b*]pyran (3h)



3h

Colorless syrup, 40 mg, yield: 83%, $[\alpha]_D^{20}$ +35.5 (*c* 0.15, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.45 – 7.17 (m, 10H), 5.41 (d, *J* = 5.2 Hz, 1H), 4.87 (s, 1H), 4.76 (d, *J* = 11.8 Hz, 1H), 4.71 (d, *J* = 11.1 Hz, 1H), 4.69 (s, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.2 Hz, 1H), 4.31 (dd, *J* = 11.7, 4.8 Hz, 1H), 4.29 – 4.25 (m, 1H), 3.97 (d, *J* = 3.8 Hz, 1H), 3.69 (t, *J* = 6.1 Hz, 1H), 3.55 (dd, *J* = 8.7, 6.1 Hz, 1H), 2.47 (dd, *J* = 13.4, 6.9 Hz, 1H), 2.19 (d, *J* = 13.5 Hz, 1H), 2.13 (d, *J* = 13.5 Hz, 1H), 2.10 – 1.97 (m, 5H), 1.80 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.9, 142.69, 138.2, 137.7, 133.1, 128.5, 128.5, 128.0, 127.9, 114.8, 100.1, 81.9, 79.4, 73.5, 73.1, 70.1, 63.7, 49.7, 43.5, 38.6, 29.7, 27.8, 24.3, 20.9; ESI-HRMS: m/z calcd for $C_{29}H_{36}NaO_6$ $[M+Na]^+$: 503.2404; found: 503.2390.

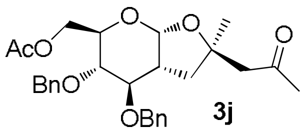
(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-6-[(acetyloxy)methyl]-2-[(benzoyl)methyl]-4,5-bis(benzyloxy)-2-methyl-hexahydro-furo[2,3-*b*]pyran (3i)



3i

Colorless syrup, 39 mg, yield: 71%, $[\alpha]_D^{20}$ +34.7 (*c* 0.26, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.96 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (dd, *J* = 14.4, 6.8 Hz, 1H), 7.39 – 7.23 (m, 11H), 5.37 (d, *J* = 5.2 Hz, 1H), 4.71 (dd, *J* = 11.3, 8.7 Hz, 2H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.50 (d, *J* = 11.2 Hz, 1H), 4.28 (qd, *J* = 12.0, 3.8 Hz, 2H), 4.01 – 3.94 (m, 1H), 3.72 (t, *J* = 6.0 Hz, 1H), 3.54 (dd, *J* = 8.7, 5.9 Hz, 1H), 3.20 (s, 2H), 2.61 (s, 1H), 2.49 (dt, *J* = 12.2, 6.3 Hz, 1H), 2.37 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.04 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.6, 170.9, 138.0, 137.6, 137.5, 133.3, 133.1, 130.1, 128.6, 128.5, 128.3, 128.0, 128.0, 127.9, 127.7, 100.2, 81.2, 79.0, 73.5, 73.0, 70.3, 63.7, 49.5, 43.3, 38.1, 29.7, 28.6, 20.9; ESI-HRMS: m/z calcd for $C_{35}H_{36}NaO_7$$[M+Na]^+$: 567.2348; found: 567.2353.

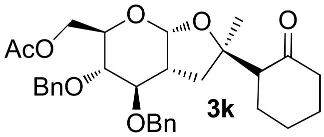
(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-2-[(acetyl)methyl]-6-[(acetyloxy)methyl]-4,5-bis(benzyloxy)-2-methyl-hexahydro-furo[2,3-*b*]pyran (3j)



3j

Colorless syrup, 31 mg, yield: 64%, $[\alpha]_D^{20}$ +22.5 (*c* 0.04, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 – 7.01 (m, 10H), 5.47 (d, *J* = 5.8 Hz, 1H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.58 (d, *J* = 12.2 Hz, 1H), 4.36 (s, 2H), 4.30 (dd, *J* = 12.0, 6.4 Hz, 1H), 4.20 (d, *J* = 11.9 Hz, 1H), 3.97 (s, 1H), 3.53 (s, 1H), 3.47 (d, *J* = 6.8 Hz, 1H), 3.31 (d, *J* = 10.4 Hz, 1H), 3.26 – 3.21 (m, 1H), 2.08 – 2.00 (m, 8H), 1.03 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 205.3, 171.0, 138.0, 137.4, 128.5(2), 128.1, 127.9, 97.6, 81.1, 75.8, 74.8, 71.9, 71.5, 69.9, 63.7, 60.9, 42.8, 31.0, 29.7, 24.3, 20.9; ESI-HRMS: m/z calcd for $C_{28}H_{34}NaO_7[M+Na]^+$: 505.2197; found: 505.2195.

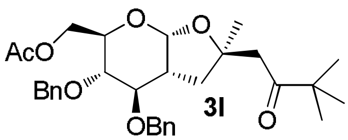
(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-4,5-bis(benzyloxy)-6-[(acetyloxy)methyl]-2-(1-cyclohexanon-2-yl)-2-methylhexahydro-furo[2,3-*b*]pyran (3k)



3k

Colorless syrup, 44.4 mg, yield: 85%, $[\alpha]_D^{20}$ +30.9 (*c* 0.14, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 10H), 5.37 (d, *J* = 5.2 Hz, 1H), 4.78 (dd, *J* = 12.5, 8.2 Hz, 2H), 4.70 (d, *J* = 11.5 Hz, 1H), 4.56 (d, *J* = 11.2 Hz, 1H), 4.31 (dd, *J* = 9.8, 3.7 Hz, 2H), 3.98 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.74 (t, *J* = 7.3 Hz, 1H), 3.55 – 3.51 (m, 1H), 2.58 (dd, *J* = 12.8, 4.9 Hz, 1H), 2.29 (ddd, *J* = 22.2, 16.5, 10.7 Hz, 3H), 2.15 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.10 – 2.00 (m, 6H), 1.94 – 1.92 (m, 1H), 1.66 – 1.60 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 211.5, 170.9, 138.1, 137.7, 128.5, 128.5, 128.1, 128.0, 127.9, 101.1, 82.5, 80.8, 74.1, 73.7, 70.5, 63.5, 62.0, 44.5, 43.5, 36.0, 29.7, 29.4, 28.9, 28.3, 25.3, 20.9; ESI-HRMS: m/z calcd for $C_{31}H_{38}NaO_7[M+Na]^+$: 545.2510; found: 545.2510.

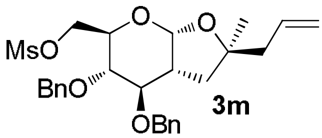
(*2R*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-6-[(acetyloxy)methyl]-4,5-bis(benzyloxy)-2-[(2,2-dimethyl-propionyl)methyl]-2-methylhexahydro-furo[2,3-*b*]pyran (3l)



3l

Colorless syrup, 37.7 mg, yield: 72%, $[\alpha]_D^{20}$ +41.2 (*c* 0.20, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.24 (m, 10H), 5.41 (d, *J* = 5.1 Hz, 1H), 4.74 (dd, *J* = 13.5, 11.4 Hz, 2H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.1 Hz, 1H), 4.32 – 4.26 (m, 2H), 4.00 – 3.93 (m, 1H), 3.71 (t, *J* = 6.6 Hz, 1H), 3.54 (dd, *J* = 8.9, 6.5 Hz, 1H), 2.83 (d, *J* = 17.3 Hz, 1H), 2.67 (d, *J* = 17.3 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.27 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.05 (s, 3H), 2.00 (dd, *J* = 13.5, 7.7 Hz, 1H), 1.37 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 214.1, 170.9,138.1, 137.7, 128.5, 128.5, 128.0, 128.0, 127.9, 100.2, 80.6, 79.7, 73.7, 73.4, 70.3, 63.6, 47.5, 44.7, 43.6, 38.6, 27.9, 26.2, 20.9; ESI-HRMS: m/z calcd for $C_{31}H_{40}NaO_7$ $[M+Na]^+$: 547.2666; found: 547.2645.

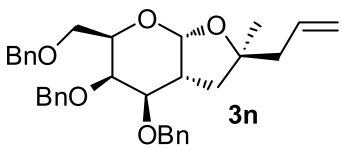
(*2S*,*3aR*,*4R*,*5S*,*6R*,*7aR*)-2-allyl-4,5-bis(benzyloxy)-6-[(methanesulfonyloxy)methyl] 2-methylhexahydro-furo[2,3-*b*]pyran (3m)



3m

Colorless syrup, 45 mg, yield: 90%, $[\alpha]_D^{20}$ +29.9 (*c* 0.26, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.49 – 7.15 (m, 16H), 5.76 (td, *J* = 17.3, 7.3 Hz, 1H), 5.41 (d, *J* = 5.4 Hz, 1H), 5.08 (t, *J* = 13.4 Hz, 2H), 4.74 (d, *J* = 11.9 Hz, 1H), 4.72 (d, *J* = 11.2 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.58 (d, *J* = 11.1 Hz, 1H), 4.45 (dd, *J* = 11.4, 4.5 Hz, 1H), 4.39 (dd, *J* = 11.3, 2.3 Hz, 1H), 4.00 – 3.95 (m, 1H), 3.68 (t, *J* = 5.9 Hz, 1H), 3.59 (dd, *J* = 9.0, 5.6 Hz, 1H), 3.04 (s, 4H), 2.50 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.19 (d, *J* = 13.6 Hz, 2H), 1.96 (dd, *J* = 13.3, 8.5 Hz, 1H), 1.75 (dd, *J* = 13.3, 6.7 Hz, 1H), 1.26 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.0, 138.0, 137.5, 133.9, 128.6(2), 128.1(2), 128.0, 118.4, 100.3, 81.7, 78.8, 76.5, 73.6, 73.0, 70.1, 69.2, 46.7, 43.3, 37.8, 37.5, 29.7, 27.5; ESI-HRMS: m/z calcd for $C_{27}H_{34}NaO_7S$$[M+Na]^+$: 525.1917 found: 525.1903.

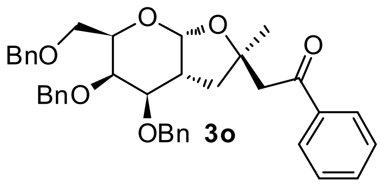
(2*S*,3*aR*,4*R*,5*R*,6*R*,7*aR*)-2-allyl-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methylhexahydro-furo [2,3-*b*]pyran (3n)



3n

Colorless syrup, 43.7 mg; Yield: 85%, $[\alpha]_D^{20}$ +23.5 (*c* 0.17, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 15H), 5.81 – 5.73 (m, 1H), 5.38 (d, *J* = 4.3 Hz, 1H), 5.05 (t, *J* = 12.6 Hz, 2H), 4.87 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.8 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.47 (t, *J* = 9.6 Hz, 2H), 4.39 (d, *J* = 11.8 Hz, 1H), 4.02 (s, 2H), 3.68 (t, *J* = 8.6 Hz, 1H), 3.60 (dd, *J* = 8.9, 5.2 Hz, 1H), 3.46 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 1H), 2.23 – 2.16 (m, 2H), 2.00 (dd, *J* = 13.3, 8.0 Hz, 1H), 1.65 (d, *J* = 13.5 Hz, 1H), 1.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 138.0, 137.8, 134.2, 128.5, 128.4, 128.3, 128.0, 128.0, 127.8, 127.6, 125.8, 118.4, 118.2, 100.8, 79.6, 78.9, 74.1, 73.5, 73.3, 71.7, 70.7, 70.1, 68.5, 47.5, 40.4, 37.9, 29.7, 28.1; ESI-HRMS: m/z calcd for $C_{33}H_{38}NaO_5$ $[M + Na]^+$: 537.2611; found: 537.2608.

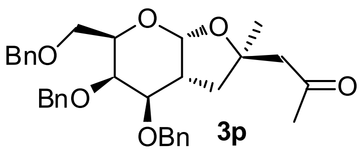
(*2R*,*3aR*,*4R*,*5R*,*6R*,*7aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-(2-oxo-2-phenylethyl)hexahydro-furo[2,3-*b*]pyran (3o)



3o

Colorless syrup, 47.4 mg; Yield: 80%, $[\alpha]_D^{20}$ +16.1 (*c* 0.23, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.27 (m, 15H), 5.38 (d, *J* = 4.2 Hz, 1H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 9.5 Hz, 2H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.02 (s, 2H), 3.66 (d, *J* = 7.6 Hz, 1H), 3.59 (dd, *J* = 17.9, 8.9 Hz, 1H), 3.49 (d, *J* = 9.5 Hz, 1H), 3.26 – 3.18 (m, 2H), 2.50 (d, *J* = 20.4 Hz, 1H), 2.31 (dd, *J* = 13.7, 7.9 Hz, 1H), 1.98 (d, *J* = 13.6 Hz, 1H), 1.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 138.0, 137.8, 134.2, 128.5, 128.4, 128.3, 128.0, 128.0, 127.8, 127.6, 125.8, 118.4, 118.2, 100.8, 79.6, 78.9, 74.1, 73.5, 73.3, 71.7, 70.7, 70.1, 68.5, 47.5, 40.4, 37.9, 29.7, 28.1; ESI-HRMS: m/z calcd for $C_{38}H_{40}NaO_6$ $[M+H]^+$: 615.2717; found: 615.2722.

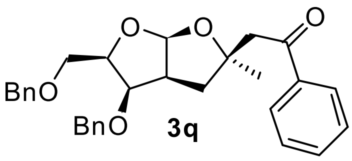
(2*R*,3*aR*,4*R*,5*R*,6*R*,7*aR*)-4,5-bis(benzyloxy)-6-[(benzyloxy)methyl]-2-methyl-(2-oxopropyl)hexahydro-furo[2,3-*b*]pyran (3p)



3p

Colorless syrup, 39.2 mg, Yield: 74%, $[\alpha]_D^{20}$ +37.1(*c* 0.14, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 15H), 5.03 (d, *J* = 3.5 Hz, 1H), 4.86 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.43 – 4.38 (m, 2H), 3.98 – 3.94 (m, 2H), 3.67 – 3.63 (m, 2H), 3.56 (dd, *J* = 9.2, 5.8 Hz, 1H), 2.96 (dd, *J* = 11.5, 3.2 Hz, 1H), 2.76 (dd, *J* = 17.0, 5.4 Hz, 1H), 2.44 (dd, *J* = 17.0, 8.6 Hz, 1H), 2.02 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.8, 138.8, 138.1, 137.9, 128.6, 128.4, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.7 127.5, 126.5, 98.4, 78.4, 77.5, 74.4, 73.5, 71.8, 71.4, 69.8, 69.4, 41.9, 36.8, 30.4, 30.0, 29.7.

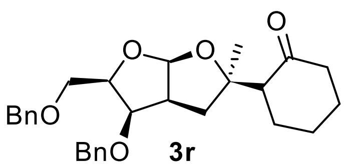
(2*R*,3*aS*,4*R*,5*R*,6*aS*)-4-(benzyloxy)-5-[(benzyloxy)methyl]-2-methyl-2-(2-oxo-2-phenylethyl)hexahydro-furo[2,3-*b*]furan (3q)



3q

Colorless syrup; 35.0 mg; Yield: 78%, $[\alpha]_D^{20}$ -2.9 (*c* 0.64, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.45 (dd, *J* = 13.2, 7.3 Hz, 2H), 7.37 – 7.22 (m, 11H), 5.46 (d, *J* = 5.4 Hz, 1H), 4.63 – 4.59 (m, 1H), 4.54 (d, *J* = 11.7 Hz, 2H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.16 (d, *J* = 4.9 Hz, 2H), 3.85 (d, *J* = 10.1 Hz, 1H), 3.75 (dd, *J* = 10.3, 5.8 Hz, 1H), 3.23 (d, *J* = 15.1 Hz, 1H), 3.14 (d, *J* = 15.1 Hz, 1H), 3.04 (s, 1H), 2.30 – 2.20 (m, 2H), 1.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.8, 138.3, 137.9, 137.7, 133.1, 128.6, 128.5, 128.4, 128.3, 128.3, 127.8, 127.7, 127.6, 127.5, 127.5, 108.6, 86.9, 80.2, 78.5, 73.4, 72.9, 69.5, 49.5, 47.4, 34.6, 29.7, 28.7; ESI-HRMS: m/z calcd for $C_{30}H_{32}O_5$ $[M + H]^+$: 495.2142; found: 495.2140.

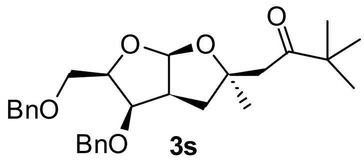
(2*R*,3*aS*,4*R*,5*R*,6*aS*)-4-(benzyloxy)-5-[(benzyloxy)methyl]-2-methyl-(2-oxocyclohexyl)hexahydrofuro[2,3-*b*]furan (3r)



3r

Colorless syrup, 32.9 mg; Yield: 73%, $[\alpha]_D^{20}$ -15.7 (*c* 0.60, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 10H), 5.53 (d, *J* = 5.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (dd, *J* = 12.8, 6.7 Hz, 2H), 4.43 (t, *J* = 11.3 Hz, 1H), 4.13 (dt, *J* = 17.6, 6.3 Hz, 2H), 3.85 (dt, *J* = 9.3, 4.7 Hz, 1H), 3.75 (dd, *J* = 10.2, 6.3 Hz, 1H), 2.90 (dd, *J* = 11.4, 5.3 Hz, 1H), 2.58 (dd, *J* = 12.5, 4.8 Hz, 1H), 2.38 – 2.21 (m, 3H), 2.06 (s, 1H), 1.99 (t, *J* = 11.8 Hz, 2H), 1.93 (t, *J* = 11.9 Hz, 2H), 1.64 (s, 2H), 1.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.8, 138.3, 137.9, 128.4, 128.3, 127.8, 127.7, 127.5, 108.8, 88.7, 80.3, 79.7, 78.6, 78.5, 73.4, 73.0, 72.9, 69.5, 69.4, 60.9, 48.5, 43.7, 32.3, 29.3, 28.7, 28.5, 25.2; ESI- HRMS: m/z calcd for $C_{28}H_{34}NaO_5$ $[M + Na]^+$: 473.2298; found: 473.2308.

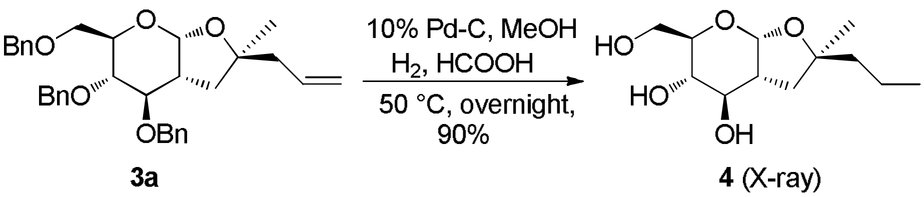
(2*R*,3*aS*,4*R*,5*R*,6*aS*)-4-(benzyloxy)-5-[(benzyloxy)methyl]-(3,3-dimethyl-2-oxo-*tert*--butyl)-2-methylhexahydro-furo[2,3-*b*]furan (3s)



3s

Colorless syrup; 29.4 mg; 0.065 mmol; Yield: 65%, $[\alpha]_D^{20}$ -4.1 (*c* 0.45, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 14.4, 7.0 Hz, 10H), 5.55 (d, *J* = 5.2 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 10.7 Hz, 2H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.16 (d, *J* = 4.8 Hz, 2H), 3.85 (d, *J* = 8.5 Hz, 1H), 3.75 (s, 1H), 3.08 (s, 1H), 2.82 (d, *J* = 17.1 Hz, 1H), 2.69 (d, *J* = 17.2 Hz, 1H), 2.18 (dd, *J* = 17.7, 8.7 Hz, 2H), 1.41 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 214.1, 138.3, 137.9, 128.4, 128.3, 127.8, 127.7, 127.5, 108.6, 86.7, 80.1, 78.5, 73.4, 72.9, 69.4, 47.6, 47.4, 34.9, 29.7, 26.2; ESI-HRMS: m/z calcd for $C_{28}H_{36}NaO_5$ $[M + Na]^+$: 475.2455; found: 475.2471.

5. The Catalystic Hydrogenation of the product 3a

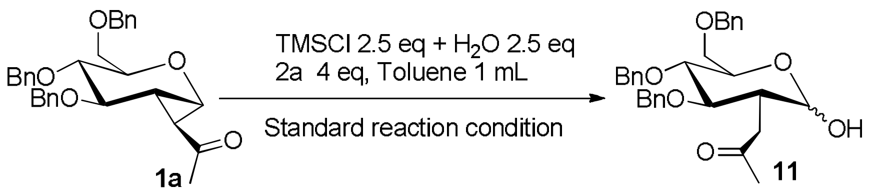


To a solution of **3a** (0.26 g, 0.51 mmol) in MeOH 10 mL was added 10% Pd-C 0.026 g and HCOOH 0.5 mL. The mixture was stirred at 50 °C under atmosphere of H_2 overnight. The mixture was cooled to room temperature, filter over diatomaceous earth, and concentrated in vacuo, purified by silica gel flash column chromatography (ethyl acetate/ MeOH = 20:1) to afford compound **4** (0.11 g, 0.46 mmol, 90%) as a colourless solid; $[\alpha]_D^{20}$ +30.9 (*c* 0.14, $CHCl_3$); ^{1}H NMR (600 MHz, MeOH-d_4): δ 5.36 (d, *J* = 4.5

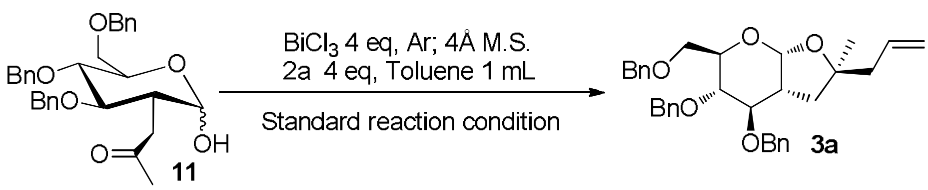
Hz, 1H), 3.78 (dd, J = 11.9, 2.6 Hz, 1H), 3.74 (dd, J = 11.9, 4.9 Hz, 1H), 3.64 (ddd, J = 9.4, 4.8, 2.6 Hz, 1H), 3.56 (t, J = 8.8 Hz, 1H), 3.35 (t, J = 9.1Hz, 1H), 2.10 – 2.05 (m, 1H), 2.02 (dd, J = 13.1, 7.6 Hz, 1H), 1.97 (dd, J = 13.2, 2.2 Hz, 1H), 1.49 (ddd, J = 16.3, 11.0, 4.8 Hz, 2H), 1.39 (ddd, J = 16.4, 12.2, 6.2 Hz, 2H), 1.35 (s, 3H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, MeOH-d$_4$): δ 100.8, 80.5, 74.5, 74.0, 69.9, 61.3, 45.3, 45.2, 38.5, 26.5, 17.3, 13.5; ESI-HRMS: m/z calcd for $C_{12}H_{22}NaO_5[M+Na]^+$: 269.1359 found: 269.1362.

6. The parallel experiments to verify our hypothesis mechanism:

In order to further test our hypothesis, some parallel experiments were designed as follows. Firstly, promoter $BiCl_3$ was replaced with trimethylsilyl chloride (TMSCl).[3] Under the same condition, the 2-*C*-branched hemiacetal as the exclusive product was isolated (eq 1), and the addition of $BiCl_3$ to the hemiacetal gave the cyclization product with good yield (eq 2). Then, some other protic acid and catalytic amounts of $BiCl_3$ were used. Interestingly, in the presence of protic acids including HCl, H_2SO_4, TsOH, HBr, HOAc, only the 2-*C*-branched hemiacetal **11**was obtained. While catalytic amounts of $BiCl_3$ furnished the bicyclo-product **3a** with lower yield because of lower conversion. The later experiments seem to support the first reaction pathway (path-1). So it is also possible that the reaction was proceed via one-step process.

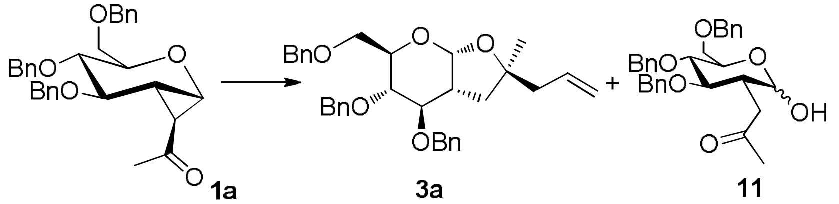


(1)



(2)

Table 2. The reaction of 1,2-cyclopropaneacetylated sugar **1a** using different Lewis acid promoted [a]



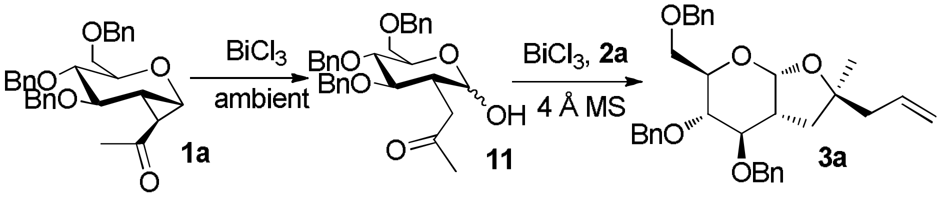
(3)

Entry	Promoter	Product	Yield (%) [b]

1	HCl	**11**	Quant.
2	H_2SO_4	**11**	Quant.
3	33%HBr-HOAc	**11**	Quant.
4	TsOH	**11**	50
5	TFA	**11**	Quant.
6 [c]	$BiCl_3$	**3a**	30
7 [d]	$BiCl_3$	**3a**	54

[a] All reaction were carried out using 0.1 mmol 1,2-cyclopropaneacetylated sugar, 0.4 mmol nucleophile and 2.5 equiv. promoter in 1 mL toluene unless otherwisenoted. [b] Isolated yield. [c] 0.1 equiv. $BiCl_3$ was used. [d] 0.5 equiv. $BiCl_3$ was used.

Then, we examined the reaction by the stepwise procedure. It was found that hydrolysis of the 1,2-cyclopropaneacetylated sugar consumed 1.2 equiv. of $BiCl_3$, while the cyclization from hemiacetal needed 2.0 equiv. of $BiCl_3$ in order to maintain good yield (eq.4).



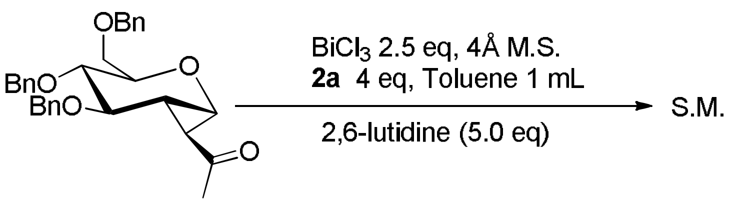
(4)

The mechanism of perhydrofuran formation has been investigated: [4-11]

1) Firstly, it is well know that the $BiCl_3$ can react with the water to form the BiOCl and HCl as showed in eq5.[12]

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl \qquad (5)$$

2) When we added 2,6-lutidine in our reaction system, only the starting material 1,2-cyclopropanated sugar was recovered (2,6-lutidine has been extensively used as a proton scavenger in the synthesis of sugar orthoesters and some other reactions in which a acid proton was produced[13]).

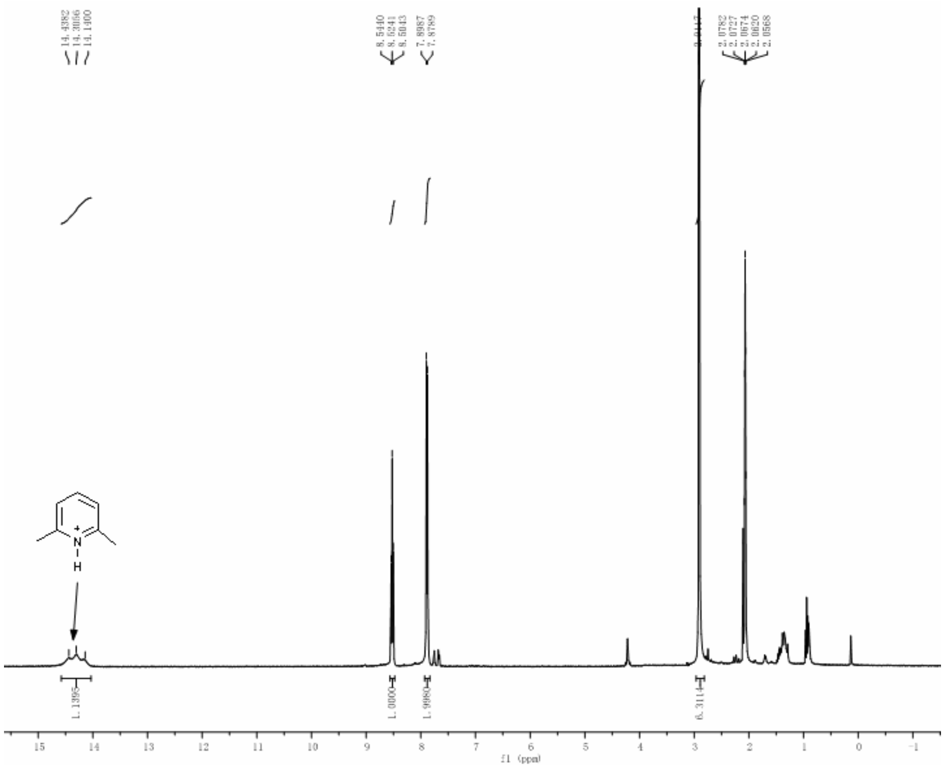


(6)

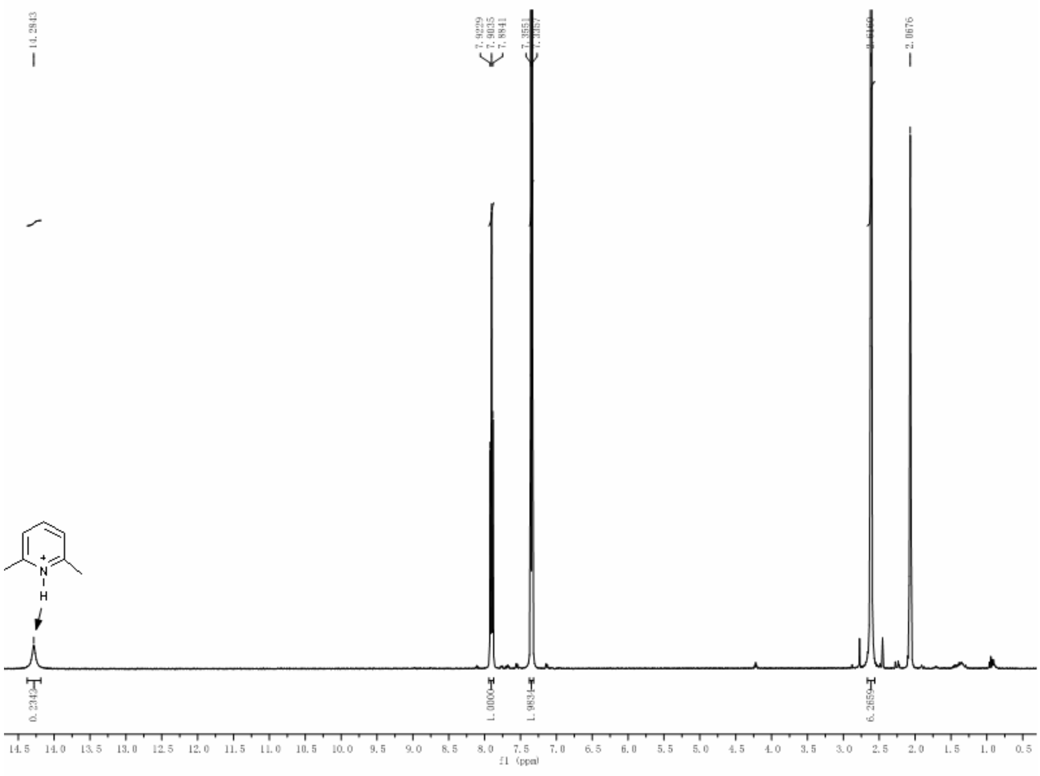
3) We isolated also the hydrolyzed product of the cyclopropanated sugar, while the hydrolyzed product was exposed to the $BiCl_3$, the fused bicyclic product was obtained (see: the supporting information).

4) The commercial $BiCl_3$ obviously containing acid proton as detected by ^{1}H-NMR (see NMR spectra), though we described anhydrous conditions in the experimental procedure, the commercial $BiCl_3$ still worked very well in the reaction. Besides, we tried to dry the $BiCl_3$ by using $SOCl_2$ overnight and used it in the glove-box, but it still contained acid proton as detected. From the ^{1}H-NMR, we obviously observed the presence of the acid proton in 14.3 ppm (see NMR spectra). Thus, it is possible that this acid proton also take part in the reaction.

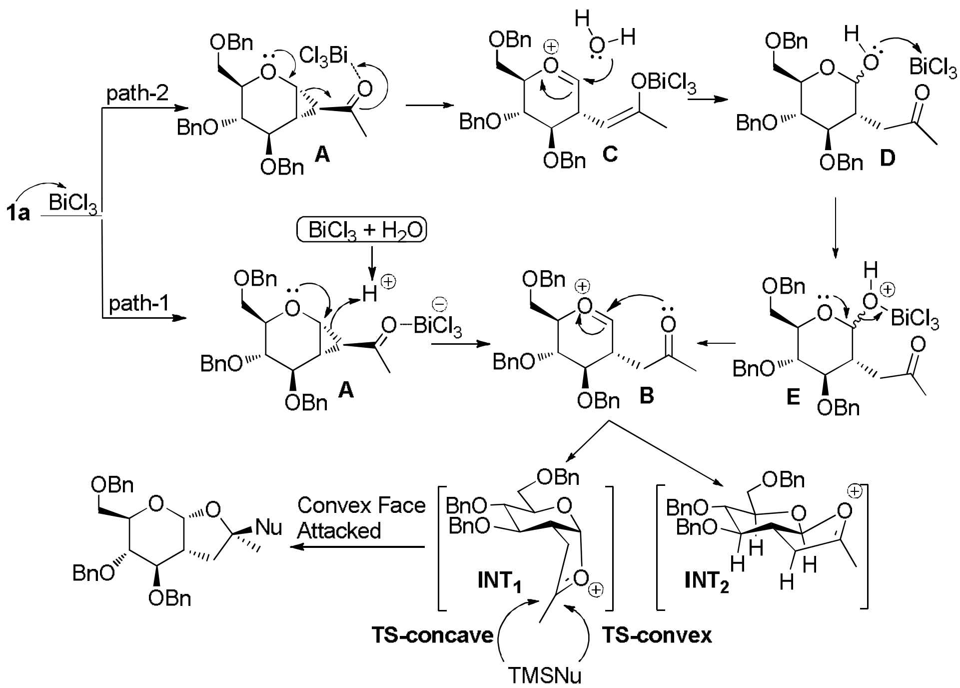
Commercial $BiCl_3$ reacted with 0.5 eq 2,6-lutidine in acetone-d_6



$BiCl_3$ dried by using $SOCl_2$ reacted with 0.5 eq 2,6-lutidine in acetone-d_6



On the basis of the above results, we considered that the H_2O was taken part in the reaction, and a plausible mechanism is proposed for the formation of perhydrofuro[2,3-*b*]pyran (and furan) derivatives under the $BiCl_3$ promoted conditions (Scheme S1).



Scheme S1. Plausible mechanism of $BiCl_3$ promoted cyclization via oxocarbenium ion intermediates

7. Reference:

1) Z. X. Wang, L. I. Wiebe, J. Balzarini, E. De Clercq, E. E. Knaus, *J. Org. Chem.*, 2000, ***65***, 9214.

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3) Evans and co-workers has demonstrated that in the presence of H_2O, $BiBr_3$ and trimethylsilyl bromide could generate HBr, which then catalyzed cyclization δ-trialkylsilyloxy aldehydes and ketones built substituted tetrahydropyrans. See: P. A. Evans, J. Cui, S. J. Gharpure, R. J. Hinkle, *J. Am. Chem. Soc.*, 2003, ***125***, 11456.

4) L. Hernández-García, L. Quintero, H. Höpfl, M. Sosa, F. Sartillo-Piscil, *Tetrahedron*, 2009, ***65***, 139.

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9) H. C. Li, Y. Y. Qiao, *Int. J. Quantum. Chem*, 2013, DOI:10.1002/qua.24422.

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13) 2,6-lutidine has been extensively used as a proton scavenger in the synthesis of sugar orthoesters and some other reactions in which a acid proton was produced selected examples: (a) F.-Z. Kong, *Carbohydr. Res.*, 2007, **342**, 345; (b) H.-C. Xu, K. D. Moeller, *J. Am. Chem. Soc.*, 2008, **130**, 13542; (c) A. Sutterer, K. D. Moeller, *J. Am. Chem. Soc.*, 2000, **122**, 5636.

8. DFT calculation

To rationalize the selectivity in this reaction, density functional theory (DFT)[1] studies have been performed with the GAUSSIAN09 program[2] at the B3LYP[3]/6-31+G** level . The structures were optimized with SMD[4] method in toluene. For all calculated structures, harmonic vibration frequency calculations were carried out and thermal corrections were made. All structures were shown to be transition states (with one imaginary frequency) or stationary points (with no imaginary frequency).

1). INT1 and INT2

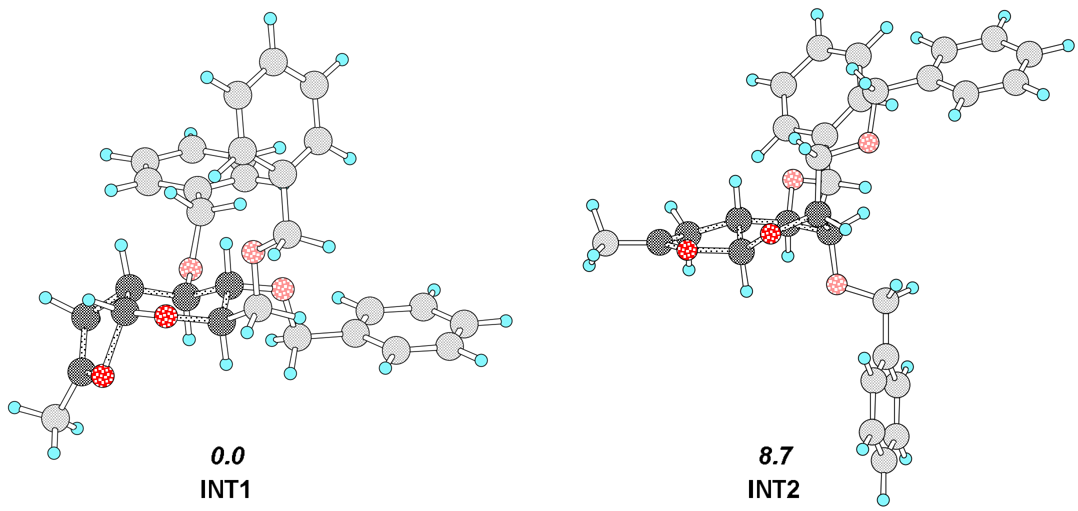

Figure S1. The optimized structures of INT1 and INT2. The relative free energies in solvent G_{sol} are in kcal/mol. Calculated at B3LYP[3]/6-31+G** level.

2). The transition states

As shown in Figure S2, four convex and four concave transition states were located.

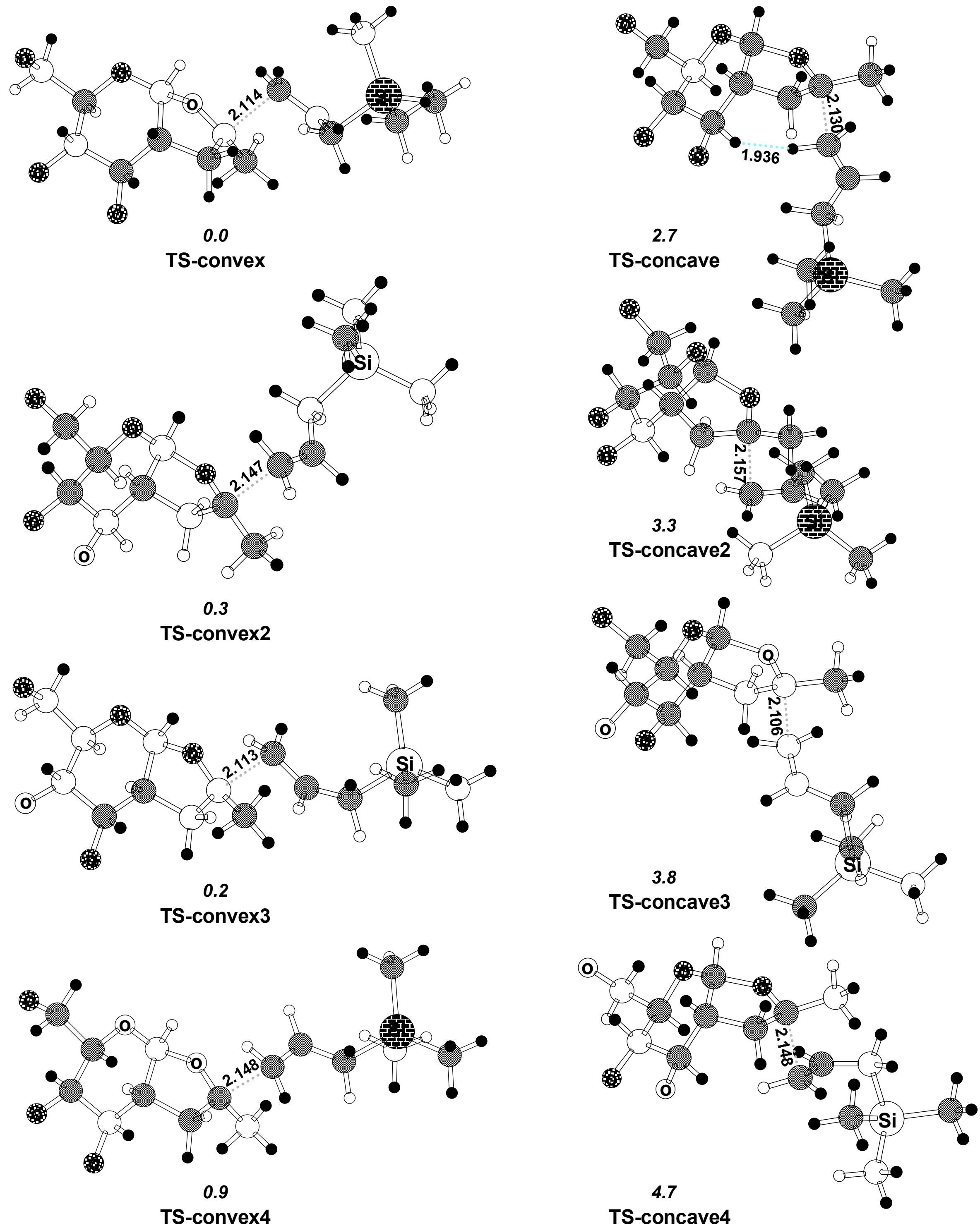

Figure S2. The optimized transition states. The Bn groups were omitted for clarity. The selected bond lengths are in angstroms, and the relative free energies in solvent G_{sol} are in kcal/mol. Calculated at B3LYP/6-31+G** level.

In **TS-concave**, hydrogen atom H_a on the trimethylsilyl nucleophile is very close to H_b on the six-membered ring (1.936 Å), which is shorter than the Van de Waals distance between two hydrogen atoms (2.18 Å), indicating there is steric repulsion, thus, the nucleophile will approach the **INT1** from convex face to offer one diastereomeric perhydrofuro[2,3-*b*]pyran and (furan) derivatives.

3). References:

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(2) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J.Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K.Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, M. J. Frisch, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R.Gomperts, R. E. Stratmann, O.Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A.Voth, P. Salvador, J. J. Dannengerg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L.Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03,* Revision D.01; Gaussian, Inc., Wallingford CT, 2004.

(3) (*a*) A. D. Becke, *J. Chem.Phys.*, 1993, ***98***, 5648. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev.*, 1988, ***B37***, 785.

(4) A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem B.*, 2009, ***113***, 6378.

4). Calculated Total Energies and Geometrical Coordinates

INT1

E(RB3LYP) = -1539.06562810 Hartree
Sum of electronic and thermal Free Energies= -1538.562375 Hartree

C,0,0.1514838759,-0.4291943589,-0.7165544955
C,0,1.0356334269,-1.081657493,-1.8036370379
C,0,0.2658921208,-3.2641088781,-1.0526090555
C,0,-0.8695469796,-2.691592182,-0.2283177782
C,0,-1.1639074595,-1.2117713814,-0.5779528739
H,0,0.5646518899,-1.0241458979,-2.790948772
H,0,0.7115154329,-0.4707008394,0.2220287171
H,0,0.658887633,-4.23154988,-0.7366959378
H,0,-0.5725200006,-2.7726833312,0.8220927599
H,0,-1.6826601858,-1.1849067822,-1.5446025527
O,0,1.2342830629,-2.5171645607,-1.5251727343
C,0,2.4315354338,-0.489034812,-1.8881631049

H,0,3.0252607956,-1.0755727302,-2.6060656057
H,0,2.3483194509,0.5377486142,-2.2726904008
O,0,-0.0212731586,0.9571739455,-0.965887869
O,0,-2.108067702,-0.6564998437,0.3216085368
O,0,-0.699536926,-3.8654148282,-2.377032663
C,0,-2.0761474039,-3.5950939864,-0.5307970589
H,0,-2.096064433,-4.5021996415,0.0913611608
H,0,-3.0393523268,-3.0966165751,-0.3891567934
C,0,-1.867780258,-4.0317094725,-1.9501118511
C,0,-2.9146235122,-4.6211143619,-2.8105094133
H,0,-3.704860993,-3.8741522176,-2.9627019283
H,0,-2.5138595557,-4.9452191907,-3.7710682921
H,0,-3.3858955015,-5.4605437335,-2.2852410501
O,0,3.0145206715,-0.5078629163,-0.6021158936
C,0,4.3401218857,0.0485237107,-0.5671427242
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C,0,4.9803875752,1.2953776685,2.9759980147
H,0,4.084851095,2.1091847242,1.1915324436
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H,0,5.6341830308,-1.8878472183,0.8562917972
C,0,5.6162304208,0.1919829785,3.5530761252
H,0,4.8031223483,2.1915957559,3.5638049248
H,0,6.3510136112,-1.811482471,3.2301050885
H,0,5.9349642467,0.2284157753,4.5909500373
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H,0,-0.6230844297,0.9198776172,-2.9753090122
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H,0,-0.943738745,0.5803080985,1.5352926863
C,0,-0.9277208537,2.8583931971,-2.1062389746
C,0,0.0183576323,3.5233941532,-2.8989802399
C,0,-1.8681816738,3.6147027454,-1.3932533229
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H,0,-5.3996559321,-1.2517419928,4.2347822246
H,0,-4.456267059,2.9010699626,3.6123365959
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E(RB3LYP) = -1539.05289615 Hartree
Sum of electronic and thermal Free Energies = -1538.548535 Hartree
C,0,0.8385150324,-0.4834982937,-1.5116482633
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C,0,-3.5849731669,1.4954306811,2.0166760458
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C,0,-3.7030518704,4.2464590221,2.4840390871
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H,0,3.6591470365,5.4108989181,-2.1802601423

TS-convex

E(RB3LYP) = -2065.67266783 Hartree

Sum of electronic and thermal Free Energies= -2064.999332 Hartree

C,0,-1.407894294,0.1216024545,-0.6056767756
C,0,-1.1415915435,1.2117634788,-1.6684022417
C,0,1.1895486454,1.302571419,-1.0000969143
C,0,1.083390304,0.0549946234,-0.1214766769
C,0,-0.1712533278,-0.7793713435,-0.4689258425
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O,0,0.0583103583,1.9669753105,-1.3464236855
C,0,-2.2660957356,2.2292037282,-1.7729907761
H,0,-1.9698726035,3.0134473117,-2.4868489062
H,0,-3.1574753755,1.7234789966,-2.1706631826
O,0,-2.6110611152,-0.588075143,-0.8851385094
O,0,-0.3177437644,-1.8773482656,0.4249113214
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C,0,3.0561243406,-1.1794503308,-2.9793670248
H,0,2.1441436469,-1.7370311447,-3.2317459569
H,0,3.3923635951,-0.6593808432,-3.8787435422
H,0,3.8144932403,-1.8938678078,-2.6561001168
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H,0,-3.3893030021,4.5470863539,-1.1747561303
H,0,-4.5211722429,3.2014173712,-0.896986923
C,0,-3.8680910635,4.1977310509,0.8971407309
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C,0,-3.2656224464,5.3766920253,1.3564234438
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H,0,-3.0117053858,6.7421070872,3.0054850281
H,0,-4.4726406406,5.4390515101,4.5410935693
C,0,-2.5860394978,-1.588515241,-1.9263539892
H,0,-1.9288205812,-2.4139870713,-1.629869954

H,0,-2.2077789943,-1.159583319,-2.8638780511
C,0,-0.8876390956,-1.6032727881,1.7253419168
H,0,-0.3868410558,-0.7422787864,2.1867979913
H,0,-1.9508921866,-1.3662046182,1.6137615991
C,0,-3.9903884202,-2.100207501,-2.1259957369
C,0,-4.8653836743,-1.4699059858,-3.0220459108
C,0,-4.4439362679,-3.2160975901,-1.409274933
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H,0,-6.8375994468,-1.4421050643,-3.8910795644
H,0,-6.085547401,-4.5555471474,-1.0159041201
H,0,-7.62832273,-3.4154658235,-2.5998223636
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C,0,0.6702618298,-4.1858969047,4.0607131333
H,0,1.3015706104,-2.3206879688,3.1873193878
C,0,-1.5745798862,-4.9012561938,3.5137486219
H,0,-2.687354173,-3.5919884177,2.2121914081
C,0,-0.3666660882,-5.1168022311,4.1823507379
H,0,1.6074078444,-4.3436417748,4.5874067484
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H,0,-0.2351039983,-6.0005988937,4.7999706531
C,0,5.4895901766,0.0206269188,-1.4325854682
C,0,4.4758129851,0.9232783958,-1.6957324889
H,0,5.9403314519,-0.4856702371,-2.286909089
H,0,4.1328925947,1.569306333,-0.8909249469
H,0,4.3840476138,1.3233175719,-2.7006201167
C,0,6.015207408,-0.3261603601,-0.1301773032
H,0,5.3641136347,-0.0316748337,0.7003938235
H,0,6.2972927667,-1.3827367422,-0.0523781678
Si,0,7.7164410157,0.6290842826,0.2249379008
C,0,8.2323939411,0.0367636518,1.9345362095
H,0,7.4774028275,0.2729352093,2.6931129243
H,0,8.4098758415,-1.0445555317,1.956303195
H,0,9.1649662263,0.5296739893,2.2359998017
C,0,7.3611342461,2.4763132671,0.2060121187
H,0,6.5833401669,2.7495787564,0.9290108041
H,0,8.2661953363,3.0335620117,0.4784866592
H,0,7.0466129145,2.8306407461,-0.7821164226
C,0,8.9661208243,0.1386442118,-1.092230408

H,0,9.1222684758,-0.9460836508,-1.1235686584
H,0,8.669157223,0.4690612001,-2.0942927301
H,0,9.937811867,0.5994769455,-0.8750746929

TS-convex2

E(RB3LYP) = -2065.67343296 Hartree
Sum of electronic and thermal Free Energies= -2064.998846 Hartree

C,0,1.1247807655,0.0856620585,0.3876640962
C,0,0.1126754553,0.9643622829,1.1578433872
C,0,-1.706267625,0.0334396091,-0.1396783169
C,0,-0.839170822,-1.0837922612,-0.7212789198
C,0,0.4795647987,-1.2716111013,0.0675094109
H,0,-0.1550697522,0.4974395953,2.1144464318
H,0,1.3712026803,0.6155699006,-0.5366773686
H,0,-2.4650050814,0.3933061468,-0.84066777
H,0,-0.6106814846,-0.8455938415,-1.7628368054
H,0,0.2392516379,-1.7645105375,1.0178911833
O,0,-1.1073037667,1.1324287233,0.3842887951
C,0,0.6281691693,2.3634548898,1.4505010616
H,0,-0.1814789797,2.9483608415,1.9147267636
H,0,1.452089525,2.2875914883,2.1743160268
O,0,2.3640278535,-0.0103388906,1.0831357315
O,0,1.3284291664,-2.2086999006,-0.5859419124
O,0,-2.4794741864,-0.7054320783,0.9385883877
C,0,-1.7556401709,-2.3209064158,-0.6051108156
H,0,-2.2903625497,-2.5287672626,-1.5322871402
H,0,-1.1977824893,-3.227800361,-0.3490655041
C,0,-2.6914609535,-1.9526369494,0.553357895
C,0,-2.9631501057,-2.9276380872,1.6613276402
H,0,-1.9994354734,-3.1579771327,2.1359377535
H,0,-3.6244651628,-2.5059561102,2.419835574
H,0,-3.3764319142,-3.8628539685,1.2791248466
O,0,1.0673815108,2.9733556235,0.2523041172
C,0,1.6253202413,4.2766800997,0.4704179761
H,0,0.8582558854,4.9359719946,0.9037088049
H,0,2.452081887,4.1994510956,1.1926395071
C,0,2.1180609829,4.8320843344,-0.8404716231
C,0,3.3820441912,4.4734523075,-1.3318093324
C,0,1.3194761439,5.702896081,-1.5936778535
C,0,3.8368016953,4.9730477318,-2.554121472
H,0,4.0111889325,3.8022403878,-0.7522402935
C,0,1.772263145,6.2071887176,-2.8162039253

H,0,0.3402848314,5.9910748435,-1.2186266444
C,0,3.0321774481,5.8419611262,-3.2986159765
H,0,4.8195775032,4.6914970149,-2.9218933309
H,0,1.1457215635,6.8865378496,-3.3873958395
H,0,3.3882704142,6.2369016898,-4.2459798588
C,0,2.4353701001,-0.8793869899,2.234283165
H,0,2.3543715049,-1.9244390156,1.9125115608
H,0,1.6153372717,-0.6633949256,2.9316104158
C,0,2.0697911512,-1.7422050112,-1.7365760434
H,0,1.4058121758,-1.2103532635,-2.4302856688
H,0,2.8518433763,-1.0495922634,-1.4073776878
C,0,3.7591852211,-0.6495796395,2.9193624918
C,0,3.8808775849,0.3011803087,3.942412046
C,0,4.8936396708,-1.3767850453,2.5334071881
C,0,5.1107439082,0.5243379086,4.566232135
H,0,3.0067633242,0.8664664811,4.2570293631
C,0,6.1258255835,-1.1563117245,3.1536927579
H,0,4.8096644904,-2.1227846088,1.7472159548
C,0,6.236829636,-0.2039440717,4.1711168813
H,0,5.1892767581,1.2609014672,5.3608886799
H,0,6.9962999433,-1.7291698423,2.84671665
H,0,7.1932282686,-0.0348568624,4.6575764261
C,0,2.6766396016,-2.9374788261,-2.4254544798
C,0,1.9850925954,-3.6015683338,-3.4484432712
C,0,3.9413099463,-3.4083001336,-2.0470390948
C,0,2.5421374281,-4.7173176497,-4.0780045101
H,0,1.0081913107,-3.2379095193,-3.7598128822
C,0,4.5015612866,-4.5249591087,-2.672342138
H,0,4.4909706826,-2.8927761875,-1.2637391339
C,0,3.8022080696,-5.1819395256,-3.6889425824
H,0,1.9995426892,-5.217969393,-4.8750429843
H,0,5.4844692229,-4.8767221705,-2.3718857436
H,0,4.2401117582,-6.0459000106,-4.1806875297
C,0,-5.4240510869,-1.5371541422,0.4818387517
C,0,-4.5493370104,-1.9018940055,-0.5205787664
H,0,-5.8713480291,-2.3370874689,1.0731406535
H,0,-4.5349294578,-2.9338081442,-0.8592534687
H,0,-4.2387817651,-1.1537439987,-1.245940333
C,0,-5.775123079,-0.184190298,0.8559646027
H,0,-5.8726201838,-0.0690989765,1.9424320179
H,0,-5.0937470154,0.570405726,0.4494150877
Si,0,-7.5675366522,0.3189805763,0.198141008
C,0,-7.873247543,2.0300894048,0.9187986399
H,0,-7.8737255263,2.0138759222,2.0149017088

H,0,-7.1189681053,2.7549334949,0.5913532067
H,0,-8.851977909,2.4062723101,0.5955630377
C,0,-8.8123170328,-0.9365345996,0.843871443
H,0,-8.7612853397,-1.0398362617,1.9344816011
H,0,-9.8321859366,-0.6162823653,0.5970953062
H,0,-8.6711426072,-1.9291930649,0.4008799391
C,0,-7.5196246932,0.3516666663,-1.6824848082
H,0,-6.7494518828,1.0342492383,-2.0608772813
H,0,-7.3365055982,-0.6403938839,-2.1112496211
H,0,-8.4825573532,0.7014556997,-2.0749425986

TS-convex3

E(RB3LYP) = -2065.67259686 Hartree
Sum of electronic and thermal Free Energies= -2064.998975 Hartree

C,0,-1.407822475,0.1439546481,-0.4991152354
C,0,-0.9336469107,1.3022001535,-1.4049268946
C,0,1.2307162682,1.2808714537,-0.3022338013
C,0,0.958717963,-0.0532375681,0.399458385
C,0,-0.2331274598,-0.8094447855,-0.2348925057
H,0,-0.6119354501,0.9252967635,-2.3844903866
H,0,-1.7507167551,0.5925234965,0.4374877515
H,0,1.8197059344,1.9728248721,0.3064747669
H,0,0.7490948433,0.138721736,1.4547229435
H,0,0.1003482274,-1.2148376089,-1.1978195885
O,0,0.1884214001,1.9971164669,-0.7952957054
C,0,-2.0039279726,2.3560994148,-1.637944161
H,0,-1.5661211902,3.1834194264,-2.2180978364
H,0,-2.8113298722,1.9081786027,-2.2348084213
O,0,-2.5663380394,-0.4923638877,-1.0288348177
O,0,-0.5590423813,-1.9721302334,0.5188824413
O,0,2.1569757972,0.8604216942,-1.4236888811
C,0,2.286407702,-0.8205893318,0.2091453425
H,0,2.9306617092,-0.7561341564,1.0862111421
H,0,2.1208304699,-1.8849858768,0.0129310948
C,0,2.908524853,-0.1560708326,-1.0234653359
C,0,3.5006881898,-0.9585275337,-2.1408907301
H,0,2.6737882094,-1.4825510827,-2.63872326
H,0,3.9878612964,-0.3224682421,-2.8830164213
H,0,4.2028835177,-1.7064582276,-1.7716203166
O,0,-2.4928058964,2.8175103053,-0.3929667504
C,0,-3.5364677444,3.791077749,-0.5313066268
H,0,-3.1568880007,4.655794031,-1.0962775816

H,0,-4.3704306193,3.3531909261,-1.0995959746
C,0,-3.9958861652,4.2167185757,0.8390344717
C,0,-5.0290017647,3.5277504455,1.4898597526
C,0,-3.3829990534,5.2949696678,1.4925938049
C,0,-5.4409709575,3.9072221814,2.770001884
H,0,-5.5133033222,2.6923351429,0.9899691298
C,0,-3.7916582268,5.6772570588,2.7727548035
H,0,-2.584062324,5.8387388077,0.994077668
C,0,-4.8223274531,4.9832854487,3.4139362114
H,0,-6.2463938465,3.3686795774,3.2615306419
H,0,-3.3118096134,6.5182065571,3.2657594706
H,0,-5.1454237128,5.2832815132,4.406884566
C,0,-2.4006066424,-1.4033883838,-2.1371155097
H,0,-1.8326807649,-2.2819837765,-1.8096307127
H,0,-1.8556989024,-0.9196739427,-2.9580559702
C,0,-1.3123795456,-1.7801596264,1.7371701463
H,0,-0.8408877995,-1.005906228,2.3568673219
H,0,-2.3284913483,-1.4540922112,1.4916661097
C,0,-3.7697031631,-1.8224727348,-2.6102827396
C,0,-4.4115496488,-1.1404929552,-3.6532578995
C,0,-4.4266341925,-2.9014472946,-2.002051949
C,0,-5.6870188639,-1.5233490363,-4.0766686241
H,0,-3.9096519293,-0.3084101323,-4.1417843573
C,0,-5.702310438,-3.2862186816,-2.4206369607
H,0,-3.9327897597,-3.4444235896,-1.2003693895
C,0,-6.3356927642,-2.5964823345,-3.4588582857
H,0,-6.171646668,-0.9886298677,-4.8887025998
H,0,-6.1986545646,-4.1255463556,-1.941695708
H,0,-7.3262410785,-2.8973752359,-3.7879731845
C,0,-1.3473388214,-3.0882693043,2.4850230989
C,0,-0.2510226376,-3.4969509722,3.2587873011
C,0,-2.4753288756,-3.9165074215,2.4204192091
C,0,-0.2767851066,-4.7116541941,3.9461528125
H,0,0.625281822,-2.8564613464,3.3272790574
C,0,-2.5063848737,-5.1330496835,3.1086092133
H,0,-3.3361891233,-3.6045049942,1.8345587393
C,0,-1.4065826905,-5.5333661547,3.8716050496
H,0,0.5772002703,-5.0136504208,4.5461276832
H,0,-3.3892768792,-5.7634054085,3.0530337484
H,0,-1.4307248548,-6.4762455738,4.410360098
C,0,5.5331557748,-0.013785852,0.0453913523
C,0,4.5659979104,0.9212117182,-0.2762031378
H,0,5.4414875687,-0.5221758911,1.0068553113
H,0,3.9970951531,1.3632250389,0.5372566672

H,0,4.7113894315,1.5459609299,-1.1539222191
C,0,6.6677703653,-0.3860043797,-0.7709205553
H,0,6.9357510733,-1.4440965895,-0.6724321966
H,0,6.563540636,-0.1014275954,-1.8231910074
Si,0,8.2987903134,0.5621779711,-0.1634188917
C,0,9.678264858,-0.1552372439,-1.2220453443
H,0,9.812184865,-1.2287615183,-1.0461615907
H,0,9.4912788283,-0.0066163876,-2.2917933029
H,0,10.628906439,0.3380574936,-0.9837657753
C,0,8.5588777789,0.194884183,1.6637249084
H,0,8.5580027264,-0.8822894774,1.868382325
H,0,9.5304064577,0.5850956999,1.99102643
H,0,7.7936485752,0.662101044,2.2943139545
C,0,8.0512348713,2.3988550105,-0.4835793539
H,0,7.8341942085,2.6041843597,-1.5385732949
H,0,7.2378634901,2.8192965737,0.1185081692
H,0,8.9635858988,2.951121756,-0.2264939733

TS-convex4

E(RB3LYP) = -2065.67245180 Hartree
Sum of electronic and thermal Free Energies= -2064.997925 Hartree

C,0,1.0974598038,0.0992890129,0.4104334282
C,0,0.0501538011,0.9249311044,1.1902932042
C,0,-1.7262191565,-0.0810895365,-0.1193776535
C,0,-0.8048497167,-1.1430601811,-0.7216760759
C,0,0.5135025854,-1.2805291491,0.0760014232
H,0,-0.1886088633,0.4468603456,2.1487849596
H,0,1.3182961419,0.6513313239,-0.50695849
H,0,-2.5043361015,0.2531621241,-0.8119160297
H,0,-0.5829694413,-0.8767905265,-1.7580637572
H,0,0.2823348162,-1.7858592026,1.0216053921
O,0,-1.1821125307,1.0370515999,0.4245251242
C,0,0.5038944194,2.3469348587,1.47831102
H,0,-0.3309745125,2.8993805783,1.93713395
H,0,1.3282791201,2.3082834505,2.2045390306
O,0,2.3423140548,0.0490687966,1.1004329992
O,0,1.4092280865,-2.1764747941,-0.5712719722
O,0,-2.4596787048,-0.8780601019,0.9436612546
C,0,-1.659975484,-2.4255037829,-0.6322870307
H,0,-2.1914486443,-2.6284947535,-1.5626534966
H,0,-1.0578410411,-3.3118415351,-0.4097635061
C,0,-2.6042610406,-2.1296177663,0.5400838197

C,0,-2.818481918,-3.1352092545,1.6286666153
H,0,-1.8428708193,-3.305347743,2.1049632653
H,0,-3.5116782667,-2.7756770556,2.390518099
H,0,-3.1617924362,-4.0916439484,1.2299735904
O,0,0.9232226362,2.9659305056,0.2772930928
C,0,1.4761043158,4.2720028897,0.4867668743
H,0,0.7026761221,4.9412504084,0.8916923433
H,0,2.2871141629,4.2037868245,1.2276496415
C,0,2.0021610618,4.8038054029,-0.8217199561
C,0,3.2245790695,4.3402543659,-1.3311616623
C,0,1.2825421578,5.7591288099,-1.5509986175
C,0,3.7146602581,4.8190336336,-2.5475702155
H,0,3.7934476637,3.6036238119,-0.7692262887
C,0,1.7724356061,6.2445246923,-2.7674640521
H,0,0.3363647944,6.128170283,-1.1628086368
C,0,2.9891107678,5.7742374558,-3.2681215917
H,0,4.6644988983,4.4553333291,-2.9295618735
H,0,1.2073791019,6.9901810316,-3.3198059
H,0,3.374325332,6.1533879936,-4.2105656297
C,0,2.4624128167,-0.8401860913,2.231547546
H,0,2.3763769617,-1.8803064371,1.8974320553
H,0,1.6684057078,-0.6407489414,2.96343693
C,0,2.1476223128,-1.6700998872,-1.7066829804
H,0,1.4705351562,-1.1606716541,-2.4050784269
H,0,2.894448475,-0.9465820371,-1.3628895164
C,0,3.8111469797,-0.6175543284,2.8687614588
C,0,3.9928972234,0.3877989949,3.8291143129
C,0,4.9068775211,-1.412737654,2.5058965651
C,0,5.2444915485,0.5995266258,4.411383113
H,0,3.1494256775,1.0060644377,4.1266713837
C,0,6.160733125,-1.2054757973,3.0871766518
H,0,4.7754546724,-2.2009291483,1.7688165372
C,0,6.331819083,-0.1977839918,4.0404711091
H,0,5.3705193869,1.3800798368,5.1563663442
H,0,7.0006947439,-1.8318521302,2.8003308875
H,0,7.3045770473,-0.0378516887,4.4967706214
C,0,2.8173384428,-2.8327147905,-2.3940780641
C,0,2.1046708037,-3.6334775585,-3.2986764218
C,0,4.1613552339,-3.1340146973,-2.13718097
C,0,2.7196027449,-4.7163774288,-3.9298857695
H,0,1.0637893708,-3.4033344556,-3.5142651628
C,0,4.7816694993,-4.2163085384,-2.7682110093
H,0,4.7260444615,-2.5139831904,-1.4455880225
C,0,4.0613511808,-5.0100353645,-3.6645990852

H,0,2.1582067167,-5.3251597159,-4.6331428729
H,0,5.8258603493,-4.4356026256,-2.5641130907
H,0,4.5431954246,-5.8482026906,-4.1599311934
C,0,-5.4138897431,-1.8975427001,0.4432714978
C,0,-4.470170637,-2.1820643544,-0.5226649836
H,0,-5.5492750707,-0.849011565,0.7121490425
H,0,-4.3983783659,-3.194759944,-0.912666227
H,0,-4.169831088,-1.3846146282,-1.1959598549
C,0,-6.2401810506,-2.8549083501,1.1474870167
H,0,-5.8736758287,-3.8845205994,1.0766391505
H,0,-6.4153148096,-2.5721600327,2.1922796516
Si,0,-8.0633371928,-2.9156089411,0.3799670212
C,0,-8.9925011869,-4.1354392642,1.4698589032
H,0,-8.5321927238,-5.1301359157,1.4549769765
H,0,-9.0390078257,-3.7985621592,2.5118260918
H,0,-10.0243260523,-4.2456762693,1.113765776
C,0,-7.9285535411,-3.5316606665,-1.3935814984
H,0,-7.3991446907,-4.4901573013,-1.4515875762
H,0,-8.9295610005,-3.6882312081,-1.8143554215
H,0,-7.4100737766,-2.8174280259,-2.0432825172
C,0,-8.8095771383,-1.1902191512,0.4670801733
H,0,-8.7871881662,-0.7840022029,1.4853863252
H,0,-8.2947254124,-0.4826917259,-0.1931509209
H,0,-9.8604445565,-1.2189258789,0.1531370311

TS-concave

E(RB3LYP) = -2065.66873022 Hartree
Sum of electronic and thermal Free Energies= -2064.995704 Hartree

C,0,1.0760639029,-0.4074656738,-0.28092038
C,0,1.4460083858,-1.4617820765,-1.3499913328
C,0,0.5782861521,-3.2147905418,0.1006415777
C,0,-0.1230842326,-2.2116177139,1.0208376498
C,0,-0.2455059804,-0.8054798671,0.3920749353
H,0,0.6903070086,-1.4944333901,-2.1460151682
H,0,1.8872483397,-0.3977807085,0.4521100419
H,0,1.0097882706,-4.0549646071,0.6504991957
H,0,0.4620500214,-2.1392865263,1.9413796857
H,0,-1.016104713,-0.8384485486,-0.3823650233
O,0,1.5343520395,-2.784622819,-0.7581414716
C,0,2.7980145036,-1.1977397361,-1.9948955777
H,0,3.0386902978,-2.0316642371,-2.672548398
H,0,2.725094731,-0.2790139914,-2.5944001664

O,0,1.077014784,0.9103218774,-0.8222307078
O,0,-0.7643306647,0.1417759229,1.3200128401
O,0,-0.5807192716,-3.8822929575,-0.6416682752
C,0,-1.4741180347,-2.8998287859,1.2827970101
H,0,-1.4043150071,-3.5889676257,2.1358434957
H,0,-2.2839816207,-2.2032818307,1.5026364551
C,0,-1.7090207211,-3.7620735256,0.0489671772
C,0,-2.535366729,-5.0149567505,0.1376188139
H,0,-3.4899407264,-4.8271439272,0.6321829918
H,0,-2.7045951768,-5.4656407289,-0.8421202981
H,0,-1.9662391168,-5.7341470816,0.7416029211
O,0,3.779615229,-1.0649592567,-0.9856575968
C,0,5.0756120841,-0.7303355592,-1.500793438
H,0,5.4079614512,-1.5152463694,-2.1963334277
H,0,5.0109595308,0.2152091883,-2.0599013157
C,0,6.0409964437,-0.6013523444,-0.3508717472
C,0,6.1681825262,0.6138548698,0.3371913806
C,0,6.8138621168,-1.6968657885,0.0578171102
C,0,7.0469892453,0.7306457691,1.4167617596
H,0,5.5774048464,1.4710306566,0.0234073745
C,0,7.6949673836,-1.5836908671,1.1365580639
H,0,6.7256369481,-2.6418040988,-0.4727648868
C,0,7.8128437645,-0.3686919449,1.8178279806
H,0,7.1406332691,1.6787574866,1.9388834845
H,0,8.2921383769,-2.4389953291,1.4400521528
H,0,8.5020663845,-0.2770060933,2.6525388299
C,0,-0.0133588935,1.293795883,-1.684047596
H,0,-0.9501182466,1.3118179266,-1.1143694029
H,0,-0.1193514184,0.5781669492,-2.5103892006
C,0,0.1393343791,0.6659375907,2.3208137945
H,0,0.6096467003,-0.1549411902,2.8776427917
H,0,0.9255418809,1.2517602615,1.8336104398
C,0,0.2742381142,2.6680939974,-2.2346166762
C,0,1.1084461285,2.8307495018,-3.3502311993
C,0,-0.2871992812,3.8047441052,-1.6377523538
C,0,1.3836170121,4.1036318666,-3.8533835186
H,0,1.5432604483,1.9570074909,-3.829451943
C,0,-0.017192345,5.0806618406,-2.1404735165
H,0,-0.9411841835,3.6900968767,-0.7770331655
C,0,0.8205192427,5.2320323725,-3.2485334276
H,0,2.0306694013,4.2156322272,-4.71867377
H,0,-0.4613786955,5.9531173064,-1.6698077951
H,0,1.0306875914,6.2224387784,-3.6419125524
C,0,-0.6568205946,1.5371527189,3.258535165

C,0,-1.3528682809,0.9768066489,4.339429927
C,0,-0.7194350984,2.9228431228,3.0578790739
C,0,-2.1016040215,1.7833364212,5.1993119936
H,0,-1.3004718275,-0.0955777265,4.5135708193
C,0,-1.4667695376,3.7337409029,3.9165401728
H,0,-0.1711872664,3.3682858751,2.2316638528
C,0,-2.1608405096,3.164723121,4.9879654687
H,0,-2.6292653092,1.3378170039,6.0380473678
H,0,-1.5005242713,4.8072545624,3.7537330086
H,0,-2.7366328117,3.7942652295,5.6603665239
C,0,-4.0670915999,-2.3910987265,-0.6556174872
C,0,-2.8951753068,-2.6641991228,-1.3377689547
H,0,-4.8260845898,-3.1745918621,-0.634032783
H,0,-2.8845093219,-3.4705884842,-2.0644722616
H,0,-2.2029908636,-1.8511184058,-1.5293187005
C,0,-4.3823303366,-1.1708257802,0.0553368042
H,0,-4.9372144037,-1.3568430873,0.9833031349
H,0,-3.5133141127,-0.5338753398,0.2464776531
Si,0,-5.6404379671,-0.0280825342,-0.9611172787
C,0,-5.8177969875,1.5130019793,0.102319344
H,0,-6.2052961547,1.2779493578,1.1002306978
H,0,-4.8612929311,2.0330955741,0.2267215879
H,0,-6.5175373579,2.2163672793,-0.3657495404
C,0,-7.2691964792,-0.9550813781,-1.1302528642
H,0,-7.6740123729,-1.2449521227,-0.1533465815
H,0,-8.0176151125,-0.3153837042,-1.614096736
H,0,-7.1750290589,-1.8608019463,-1.7402712596
C,0,-4.8764194019,0.3596607526,-2.635959287
H,0,-3.8993757607,0.8468144097,-2.536759205
H,0,-4.7483413195,-0.5391458384,-3.2497863742
H,0,-5.5243225449,1.0459921581,-3.1951435129

TS-concave2

E(RB3LYP) = -2065.66743003 Hartree
Sum of electronic and thermal Free Energies= -2064.994059 Hartree

C,0,-0.7421348775,-0.2402836506,-0.2005637741
C,0,-0.0372295347,-1.6108935961,-0.0856730119
C,0,0.6254190267,-1.4436533889,-2.4257930323
C,0,0.340426895,0.0629720802,-2.4646576573
C,0,0.1228600961,0.6874344072,-1.0671618023
H,0,0.9492188927,-1.5026696863,0.3854054427

H,0,-1.7096697468,-0.4178909074,-0.6786597801
H,0,0.327629347,-1.9489293764,-3.3480033235
H,0,-0.5742600782,0.2024071878,-3.0465880791
H,0,1.0933874959,0.7914334868,-0.5727950091
O,0,0.1476771762,-2.1939274723,-1.4025524193
C,0,-0.8316844567,-2.6311288798,0.7149410208
H,0,-0.3047245645,-3.5977019213,0.6789267226
H,0,-0.8709254824,-2.3019372754,1.76378606
O,0,-1.0725079536,0.2956181308,1.0753704047
O,0,-0.3346112694,2.0306539823,-1.1631360378
O,0,2.1517348643,-1.5258881629,-2.5088106204
C,0,1.557052425,0.6240192148,-3.2225649441
H,0,1.368955852,0.6614019444,-4.3040932662
H,0,1.8340720839,1.6337583975,-2.9170840476
C,0,2.6583234018,-0.4130878976,-3.0148396597
C,0,3.7198625979,-0.5971344143,-4.0653202743
H,0,4.2643430714,0.3284418332,-4.2605453329
H,0,4.4132849217,-1.3976566178,-3.8062868606
H,0,3.2024683937,-0.887149314,-4.9903576583
O,0,-2.130741852,-2.7429051911,0.1703787015
C,0,-2.9660450865,-3.6605709783,0.8898639802
H,0,-2.5059424261,-4.660093816,0.877480707
H,0,-3.0473879983,-3.3351487301,1.9376505217
C,0,-4.3248025965,-3.697510992,0.2403185419
C,0,-5.330535106,-2.8086527833,0.6450642553
C,0,-4.5964684401,-4.6057185699,-0.7923253969
C,0,-6.5837186026,-2.8240653263,0.0275948047
H,0,-5.1301063399,-2.1044853887,1.4488262786
C,0,-5.8485234691,-4.6243119467,-1.412232853
H,0,-3.824237741,-5.3022105746,-1.110297071
C,0,-6.8445851352,-3.7323061403,-1.0029524959
H,0,-7.3560388314,-2.1330320985,0.3535770279
H,0,-6.0487687951,-5.3355781766,-2.2087168839
H,0,-7.820254766,-3.7488623002,-1.480405695
C,0,-0.0170022927,0.8811408248,1.8653244732
H,0,0.3894095037,1.7593886019,1.3512377546
H,0,0.7945807082,0.1562860789,2.0193771603
C,0,-1.7173345652,2.2478259687,-1.5257016026
H,0,-1.9375809239,1.7602331524,-2.4846861707
H,0,-2.3738097611,1.8204703272,-0.7608848276
C,0,-0.5925430551,1.291428648,3.1973815524
C,0,-0.725171912,0.3619669239,4.239040578
C,0,-1.0076863264,2.6125944514,3.4118451077
C,0,-1.2648833542,0.7431408937,5.4692590398

H,0,-0.4027100171,-0.6655754476,4.0888104707
C,0,-1.5469236896,2.9986422285,4.642009407
H,0,-0.9036229293,3.34243586,2.6130023825
C,0,-1.677496574,2.0638922063,5.6726084436
H,0,-1.3589664797,0.013958088,6.2690257983
H,0,-1.8612547813,4.0269823855,4.7960579431
H,0,-2.093647129,2.3632296744,6.6302745738
C,0,-1.9445440162,3.7342771974,-1.6347332885
C,0,-1.5110276961,4.4421277238,-2.765616079
C,0,-2.5883050976,4.432044812,-0.6045176671
C,0,-1.7101081238,5.8205490862,-2.8620418331
H,0,-1.0190561974,3.9096139312,-3.5762507957
C,0,-2.7927503396,5.811861198,-0.6988924267
H,0,-2.9378010304,3.8916638998,0.2715203738
C,0,-2.3521501353,6.5086326161,-1.8268027778
H,0,-1.3741889039,6.3568808848,-3.7451166433
H,0,-3.2987164776,6.3395373166,0.1045929593
H,0,-2.5139914202,7.5800016993,-1.9033656212
C,0,4.7985240538,-0.4126459951,-1.2298145762
C,0,3.8104595149,0.5238634034,-1.4507499215
H,0,5.6780767676,-0.3766094987,-1.8736681471
H,0,3.0168988573,0.6242333607,-0.7179684075
H,0,4.0458808828,1.4133603592,-2.0273682329
C,0,4.7748006708,-1.4652325071,-0.2359447047
H,0,3.7794198414,-1.6394363636,0.1856067762
H,0,5.2009528172,-2.4014943416,-0.616792669
Si,0,5.9441010995,-1.0343115841,1.2967547289
C,0,5.934817846,-2.5896342539,2.3553014242
H,0,4.9197849743,-2.8755973114,2.6544734654
H,0,6.3843001153,-3.4396856993,1.8293575475
H,0,6.513443356,-2.4259275328,3.2727421633
C,0,5.2022714022,0.4356723565,2.2070944662
H,0,4.1903101065,0.2231799384,2.5718491903
H,0,5.8156723585,0.6833328691,3.0821972022
H,0,5.1559563073,1.3327044858,1.5789450179
C,0,7.6667537801,-0.653898228,0.6412292128
H,0,8.0457264082,-1.4577407699,-0.0013509254
H,0,7.7000884816,0.2812000337,0.0703048799
H,0,8.3718965099,-0.5484488517,1.4750760617

TS-concave3

E(RB3LYP) = -2065.66891704 Hartree
Sum of electronic and thermal Free Energies= -2064.993343 Hartree

C,0,-1.0338739902,-0.4515587562,0.0034958139
C,0,-0.9236885187,-1.8942793727,0.5463212907
C,0,0.002053432,-2.6266163109,-1.5804196349
C,0,0.3502721644,-1.1880137359,-1.9950378384
C,0,0.1948656352,-0.1439714717,-0.8640755714
H,0,-0.0173118165,-2.0202537137,1.1555780237
H,0,-1.9454480221,-0.4134333695,-0.5987465081
H,0,-0.3584817123,-3.2256413273,-2.4204885118
H,0,-0.325154487,-0.9113982244,-2.8082247271
H,0,1.0779529474,-0.1903371539,-0.2201739667
O,0,-0.868529069,-2.8339710448,-0.5582777217
C,0,-2.1210957808,-2.3065828594,1.3887555088
H,0,-2.0228119121,-3.3729480684,1.6452608537
H,0,-2.1120742223,-1.7276251569,2.3235517047
O,0,-1.2593250003,0.4972150688,1.0405492053
O,0,0.253095426,1.1817087255,-1.3814910693
O,0,1.3522164626,-3.2662914018,-1.2896572023
C,0,1.7922815479,-1.3271068501,-2.5128099034
H,0,1.7971784225,-1.5910475234,-3.5791933691
H,0,2.3904305809,-0.4226466577,-2.4043901307
C,0,2.3505364022,-2.5390941544,-1.7763594832
C,0,3.4838837148,-3.327308566,-2.3662754144
H,0,4.3308342836,-2.6871816137,-2.6171439002
H,0,3.8069191371,-4.1358420805,-1.7077805198
H,0,3.1089798232,-3.7811433758,-3.2934755772
O,0,-3.3085305185,-2.067617395,0.6597901764
C,0,-4.4945780781,-2.3963500856,1.3957742026
H,0,-4.4853896918,-3.4685258893,1.6437501925
H,0,-4.5072628434,-1.8286204574,2.3381546122
C,0,-5.6997344353,-2.0560082735,0.5581888089
C,0,-6.2703689934,-0.777181434,0.6229710702
C,0,-6.2518909801,-3.002709,-0.3157066766
C,0,-7.3725912337,-0.4491489741,-0.1703832079
H,0,-5.8488762598,-0.0378488441,1.2997150724
C,0,-7.3536923753,-2.678327805,-1.1113959044
H,0,-5.817318009,-3.9978919358,-0.3710494701
C,0,-7.9160502604,-1.4001652062,-1.0396664108
H,0,-7.8094317318,0.5435147538,-0.1066986304
H,0,-7.7756056978,-3.4219898259,-1.7816793421
H,0,-8.7768277802,-1.1484993405,-1.6528551605
C,0,-0.1505089643,0.8679883365,1.8838267341
H,0,0.6333223247,1.3416189084,1.2814505696
H,0,0.2717984145,-0.0185182747,2.3769111422

C,0,-0.9365315681,1.7153910822,-2.0024625176
H,0,-1.2902920552,1.0378440506,-2.7918720125
H,0,-1.7301369029,1.8175311944,-1.2556124424
C,0,-0.6496004764,1.8448889312,2.9190211827
C,0,-1.1106053791,1.4009836531,4.1660182351
C,0,-0.6678768952,3.218655364,2.6390224787
C,0,-1.5859175392,2.3105037905,5.1142840025
H,0,-1.0952084345,0.339048108,4.399428025
C,0,-1.1429325814,4.1309242803,3.5840783699
H,0,-0.3065661505,3.5735860941,1.6769700557
C,0,-1.6039522327,3.6776930568,4.8238649508
H,0,-1.9382705896,1.9536323696,6.0779363649
H,0,-1.1498445128,5.1929064526,3.3554725391
H,0,-1.9710043947,4.3861310609,5.5609144018
C,0,-0.5990876589,3.0628073951,-2.5900790931
C,0,0.2469110439,3.1652194464,-3.7050375056
C,0,-1.1349192845,4.2330091345,-2.0377356305
C,0,0.5557001901,4.4118609396,-4.2510794441
H,0,0.6626140239,2.2639457191,-4.1490640529
C,0,-0.8335859874,5.4835937314,-2.5867797668
H,0,-1.7965173273,4.1655908116,-1.1777921432
C,0,0.014386288,5.5753632264,-3.6926001204
H,0,1.2098141521,4.477746217,-5.1160738069
H,0,-1.2615722339,6.3819702746,-2.1512171489
H,0,0.2487137692,6.5453513568,-4.1216878936
C,0,4.1898949095,-0.967355869,-0.2997292059
C,0,3.2453386307,-1.9241780094,0.0286576946
H,0,3.8410397483,0.0596055204,-0.4205572381
H,0,3.5766816363,-2.9177463851,0.3186293591
H,0,2.3181751493,-1.5944499322,0.4826690026
C,0,5.6038134998,-1.1919503022,-0.501063287
H,0,5.8663011116,-2.2460016574,-0.6381104199
H,0,6.0255505223,-0.5716467477,-1.3007764708
Si,0,6.6338059818,-0.6190922081,1.0945623484
C,0,8.426607044,-0.9618830378,0.6401888349
H,0,8.5973856803,-2.0217353805,0.4183452238
H,0,8.7473208631,-0.3773395293,-0.2296722518
H,0,9.0826179151,-0.6928477666,1.4775822609
C,0,6.0719254802,-1.6589974935,2.5580301456
H,0,6.1621530828,-2.7331703994,2.3577209814
H,0,6.6961980288,-1.4395028091,3.433088325
H,0,5.0334839976,-1.4518303219,2.8402165372
C,0,6.3221444209,1.2140574871,1.3785641877
H,0,6.567869578,1.8133066223,0.4939308742

H,0,5.2816794143,1.4243737826,1.6518115252
H,0,6.9511068629,1.5774910713,2.2007078462

TS-concave4

E(RB3LYP) = -2065.66764818 Hartree
Sum of electronic and thermal Free Energies= -2064.991893 Hartree

C,0,-0.9475765826,-0.3397234922,-0.1192264745
C,0,-0.4113610845,-1.7740456059,0.0835126817
C,0,0.5111453034,-1.7444345392,-2.168704487
C,0,0.3932540872,-0.2174976344,-2.2694128659
C,0,0.0761852808,0.4740713646,-0.9225375425
H,0,0.5313978238,-1.7651590731,0.6483277585
H,0,-1.8864832606,-0.4292570028,-0.6724957346
H,0,0.2714778874,-2.2440853169,-3.1108221172
H,0,-0.421788529,-0.0023007251,-2.9651512766
H,0,0.9913392514,0.523703584,-0.3261394248
O,0,-0.1700279424,-2.4070705948,-1.19957566
C,0,-1.3904781969,-2.6749267021,0.8208479038
H,0,-0.9866896853,-3.6991569018,0.8394245541
H,0,-1.4769401033,-2.3216989668,1.858582912
O,0,-1.3212683027,0.2640105323,1.1155136418
O,0,-0.2552931301,1.8449171472,-1.113890756
O,0,2.012311415,-1.9858470385,-2.0493184757
C,0,1.7463239227,0.1854769155,-2.884444565
H,0,1.6950010769,0.1864556562,-3.9818137127
H,0,2.0907386178,1.1766755682,-2.5842811575
C,0,2.6995188479,-0.9452784027,-2.5021989644
C,0,3.8662455493,-1.2687069004,-3.3896700232
H,0,4.480948689,-0.3881771772,-3.5850006955
H,0,4.4802505842,-2.0758571921,-2.9890452107
H,0,3.4484098868,-1.6097869653,-4.3469619966
O,0,-2.6451061033,-2.6368559933,0.1704164727
C,0,-3.65804627,-3.3827849541,0.858840734
H,0,-3.379287691,-4.44667367,0.8858795994
H,0,-3.7292026564,-3.0228329537,1.8965276247
C,0,-4.9723623477,-3.1994608053,0.1449644748
C,0,-5.7300878347,-2.0368566209,0.3498310533
C,0,-5.4500542924,-4.1734249442,-0.7415121609
C,0,-6.9395403648,-1.8494791891,-0.3222389101
H,0,-5.3694755956,-1.27846404,1.0405137637
C,0,-6.6623523361,-3.9908462195,-1.4138018401

H,0,-4.8720672587,-5.0798673923,-0.9050466115
C,0,-7.4085173587,-2.8278112123,-1.2055509339
H,0,-7.5187687182,-0.9462375051,-0.1519002015
H,0,-7.0243768759,-4.7556550167,-2.0952112035
H,0,-8.3523804802,-2.6855955011,-1.7243718343
C,0,-0.2767057397,0.7458468937,1.9863508132
H,0,0.2912919125,1.5374777868,1.4848073195
H,0,0.4102415187,-0.0701167016,2.2498020281
C,0,-1.5876915737,2.1549612535,-1.5791802346
H,0,-1.8009840301,1.6113652728,-2.5094855359
H,0,-2.3223801999,1.8534858072,-0.8257082194
C,0,-0.9166146052,1.2987542549,3.2350603908
C,0,-1.1794629618,0.4711759059,4.3356035366
C,0,-1.2631554341,2.655030854,3.3089092276
C,0,-1.7811054211,0.9863419184,5.4862916391
H,0,-0.9076388771,-0.5809676629,4.2949730827
C,0,-1.8648387655,3.1742922979,4.4578394757
H,0,-1.0546607597,3.3067066355,2.4642512159
C,0,-2.1264492135,2.3397336472,5.5483961576
H,0,-1.9772770802,0.3348400054,6.3331498264
H,0,-2.1255977729,4.2278417828,4.5034325327
H,0,-2.5916782141,2.7427321218,6.4434032793
C,0,-1.6711069006,3.6408874844,-1.8209430538
C,0,-1.0865319044,4.213980152,-2.9601638731
C,0,-2.3370594919,4.4723312468,-0.9112234377
C,0,-1.1590970163,5.5903383058,-3.181545627
H,0,-0.5761011613,3.5784524519,-3.6799143269
C,0,-2.4156083628,5.8509304656,-1.1313819037
H,0,-2.803258631,4.0371506295,-0.0309271894
C,0,-1.8246030489,6.4125181874,-2.2657363739
H,0,-0.7054516633,6.0215071009,-4.0696404599
H,0,-2.9396211658,6.483024108,-0.4200635236
H,0,-1.8866911237,7.4828516168,-2.4402411671
C,0,4.4596507458,-1.1503540995,-0.3299928453
C,0,3.7508637754,-0.0805421125,-0.8412678208
H,0,3.9147695014,-1.8460221596,0.3096518667
H,0,2.8535920713,0.2265307147,-0.3185325221
H,0,4.2801088731,0.7035479214,-1.3773392781
C,0,5.8545020464,-1.4525927498,-0.560175815
H,0,6.0471350627,-2.5293543439,-0.637226789
H,0,6.2905013048,-0.9114074769,-1.4061306869
Si,0,6.9423923113,-0.9134509407,1.0053401372
C,0,8.6825809155,-1.4992955988,0.5989396351
H,0,8.7250805242,-2.5860991586,0.4640809448

H,0,9.0687490549,-1.0287095783,-0.3123477704
H,0,9.3659655465,-1.2418080645,1.4177185194
C,0,6.2602048887,-1.7749715268,2.5327643522
H,0,6.2019366259,-2.861610359,2.397971099
H,0,6.9183332152,-1.5904512182,3.3908123907
H,0,5.2632997883,-1.4119236799,2.8077642953
C,0,6.8453063176,0.958531142,1.1570896844
H,0,7.2106522227,1.460276994,0.2532862025
H,0,5.8235238529,1.3055988524,1.3484193743
H,0,7.4674238025,1.3014158004,1.993083538