Supporting Information

Radical Reactions with 2-Bromobenzylidene Group, a Protecting/Radical-Translocating Group for the 1,6-Radical Hydrogen Transfer Reaction

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Contents: Experimental procedures and spectroscopic data of all new compounds, NOE and/or NOESY data of key compounds (Figure S1), ^{1}H, ^{13}C, and ^{1}H-2D NMR spectra of the radical reaction substrates **4** and **9**, and the products **5b**, **10**, and **11** (13 pages).

Experimental Section

Chemical shifts are reported in ppm downfield from tetramethylsilane , and coupling constants are given in Hz. All of the ^{1}H NMR assignments described were in agreement with COSY spectra. Thin-layer chromatography was done on Merck coated plate $60F_{254}$. Silica gel chromatography was done on Merck silica gel 5715. Reactions were carried out under an argon atmosphere.

2,3-*O*-*Endo*-(2-bromobenzylidene)-D-ribose (2). A mixture of D-ribose (6.00 g, 40.0 mmol), 2-Br-PhCH(OEt)$_2$ (18.5 mL, 91.7 mmol), and TsOH (unhydrous, 2.07 g, 12 mmol) in DMF (130 mL) was stirred at room temperature for 14 h, and then Et_3N (5 mL) was added. The solvent was evaporated, and the residue was purified by silica gel column chromatography (AcOEt/hexane, 1:3-1:1) to give **2** (5.35 g, 42%, □:□ = 1:19) as a white solid: ^{1}H NMR (270 MHz, $CDCl_3$); for □-anomer □ 7.73-7.23 (m, 4 □, aromatic), 6.11 (s, 1 H, benzyl), 5.59 (s, 1 H, H-1), 4.98 (d, 1 H, H-3, $J_{3,2}$= 6.6 Hz), 4.73 (d, 1 H, H-2, $J_{2,3}$= 5.9 Hz), 4.60 (s,1 H, H-4), 3.82 (m, 2 H, H-5a,5b), 3.03 (br s, 1 H, 5-OH-5); HRMS (FAB) calcd for $C_{12}H_{18}{}^{79}BrNaO_5$ 338.9844, found 338.9843 (MNa^+).

2,3-*O*-*Endo*-(2-bromobenzylidene)-5-*O*-(*tert*-butyldiphenylsily)-D-ribose (3). A mixture of **2** (12 g, 38 mmol), Et_3N (6.4 mL, 46 mmol), DMAP (4.7 g, 38 mmol), and TBDPSCl (15 mL, 57 mmol) in CH_2Cl_2 (380 mL) was stirred at room temperature for 4 h, and the MeOH was added. The solvent was evaporated, and the residue was partitioned between AcOEt and H_2O. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane, 1:20-1:5) to give **2** (16 g, 76%, □:□ = 1:5) as an oil: ^{1}H NMR (270 MHz, $CDCl_3$) for □-anomer □ 7.73-7.21 (m, 14 H, aromatic), 6.13 (s, 1 H, benzyl), 5.52 (d, 1 H, H-1, $J_{1,OH}$= 10.6 Hz), 4.88 (d, 1 H, $J_{3,2}$= 5.9 Hz), 4.77 (d, 1 H, H-2, $J_{2,3}$= 5.9 Hz), 4.71 (d, 1 H, OH, $J_{OH,1}$= 11.2 Hz), 4.46 (m, 1 H, H-4), 3.83 (dd, 1 H, H-5a, $J_{5a,4}$ = 2.6, $J_{5a,5b}$= 11.2 Hz), 3.70 (dd, 1 H, H-5b, $J_{5b,4}$ = 2.6 Hz, $J_{5b,5a}$= 11.2 Hz), 1.08 (s, 9 H, *t*-Bu); HRMS (FAB) calcd for $C_{28}H_{31}{}^{79}BrNaO_5Si$ 577.1022, found 577.1018 (MNa^+)

2,3-*O*-*Endo*-(2-bromobenzylidene)-5-*O*-(*tert*-butyldiphenylsilyl)-1-*O*-(3-fluorobenzoyl)-□-D-ribose (4). To a solution of **3** (496 mg, 0.89 mmol), PPh_3 (703 mg, 2.7mmol), and 3-F-PhCO_2H (250 mg, 1.8 mmol) was added a solution of DIAD (352 □L, 1.8 mmol) in CH_2Cl_2 (5 mL) slowly at 0 °C, and the resulting mixture was stirred at room temperature for 1 h. After addition of MeOH, the solvent was evaporated, and the residue was purified by short silica gel column chromatography (AcOEt/hexane, 1:30) to give crude **4**, of which □/□ ratio was 97:3 from the ^{1}H NMR spectrum. After further purification by silica gel flash column chromatography (Et_2O/hexane, 1:33), the □-anomer **4** (452 mg, 75%) was obtained as an oil in a pure form, along with a □/□-mixture (□:□ = 4:1, 100 mg, 17%): ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.75-7.00 (m, 18 H, aromatic), 6.61 (d, 1 H, H-1, $J_{1,2}$= 4.6 Hz), 6.33 (s, 1 H, benzyl), 5.15 (dd, 1 H, H-2, $J_{2,3}$= 6.6, $J_{2,1}$= 4.6 Hz), 5.03 (dd, 1 H, H-3, $J_{3,2}$= 6.6, $J_{3,4}$= 2.0 Hz), 4.64 (m, 1 H, H-4, $J_{3,4}$= 2.0 Hz), 3.91 (dd, 1 H, H-5a, $J_{5a,4}$=2.6 Hz, $J_{5a,5b}$= 11.2 Hz), 3.83 (dd, 1 H, H-5b, $J_{5b,4}$= 2.6 Hz, $J_{5b,5a}$= 11.2 Hz), 1.10 (s, 9 H,

t-Bu); ^{13}C NMR (100 MHz, $CDCl_3$); 19.4, 27.0, 64.5, 80.6, 82.7, 83.0, 97.9, 106.3, 116.5, 116.7, 119.9, 120.1, 122.8, 125.6, 125.6, 127.1, 127.8, 128.4, 129.6, 129.7, 129.8, 129.9, 130.8, 132.3, 132.5, 132.7, 134.5, 135.4, 135.5, 160.9, 163.8; HRMS (FAB) calcd for $C_{35}H_{34}{}^{79}BrFNaO_6Si$ 699.1190, found 699.1187 (MNa^+).

2,3-*O*-*Endo*-(2-bromobenzylidene)-1-*O*-(3-fluorobenzoyl)-β-D-ribose (8). A mixture of **4** (456 mg, 0.67 mmol) and NH_4F (1.4 g, 37 mmol) in EtOH/MeOH (1:1, 14 mL) was stirred at room temperature for 2 days. After addition of AcOEt, the resulting mixture was filtered though Celite, and the filtrate was evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane, 1:3) to give **8** (262 mg, 89%) as an oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.75-6.99 (m, 8 H, aromatic), 6.56 (d, 1 H, H-1, $J_{1,2}$= 4.6 Hz), 6.35 (s, 1 H, benzyl), 5.07 (dd, 1 H, H-2, $J_{2,3}$= 7.3, $J_{2,1}$= 4.6 Hz), 4.97 (dd, 1 H, H-3, $J_{3,2}$= 7.3, $J_{3,4}$= 3.3 Hz), 4.64 (m, 1 H, H-4), 3.96 (dd, 1 H, H-5a, $J_{5a,4}$=2.6 Hz, $J_{5a,5b}$= 12.5 Hz), 3.84 (dd, 1 H, H-5b, $J_{5b,4}$= 2.6 Hz, $J_{5b,5a}$= 12.5 Hz), 2.05 (br s, 1 H, OH).

2,3-*O*-*Endo*-(2-bromobenzylidene)-5-*O*-(diphenylvinylsilyl)-1-*O*-(3-fluorobenzoyl)-β-D-ribose (9). A mixture of **8** (1.3 g, 3.0 mmol), DMAP (74 mg, 0.61 mmol, 0.2 eq.), Et_3N (845 μL, 6.1 mmol), and diphenylvinylsilyl chloride (1.34 mL, 6.1 mmol) in toluene (30 mL) was stirred at room temperature for 1.5 h, and then MeOH was added. The resulting mixture was partitioned between AcOEt and H_2O, and the organic layer was washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane, 1:30) to give **9** (1.9 g, 98%) as an oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.72-6.97 (m, 18 H, aromatic), 6.52 (dd, 1 H, CH_2=C<u>H</u>-, *J*= 15.1 Hz, *J*= 19.8 Hz), 6.49 (d, 1 H, H-1, $J_{1,2}$= 4.0 Hz), 6.34 (dd, 1 H, C<u>H</u>$_2$=CH-, *J*= 15.1 Hz, *J*= 4.0 Hz), 6.29 (s, 1 H, benzyl), 5.95 (dd, 1 H, C<u>H</u>$_2$=CH-, *J*= 19.8 Hz, *J*= 4.0 Hz), 5.00 (m, 2 H, H-2,3), 4.65 (m, 1 H, H-4), 4.03 (dd, 1 H, H-5a, $J_{5a,4}$=2.6 Hz, $J_{5a,5b}$= 11.2 Hz), 3.95 (dd, 1 H, H-5b, $J_{5b,4}$= 2.6 Hz, $J_{5b,5a}$= 11.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$); 64.5, 80.9, 82.8, 83.3, 98.0, 106.7, 116.8, 117.1, 120.2, 120.4, 123.6, 125.9, 127.3, 128.1, 128.3, 128.5, 128.7, 129.9, 130.0, 131.1, 132.0, 132.1, 133.5, 133.5, 134.7, 134.8, 135.1, 135.1, 138.1, 161.2, 163.6, 164.1; HRMS (FAB) calcd for $C_{33}H_{28}BrFO_6SiNa$ 669.0720, found 669.0714 (MNa+).

Deuterium–Labeling Reaction with the Substrate 4. A mixture of **4** (61 mg, 0.090 mmol) Bu_3SnD (73 μL, 0.21 mmol), and AIBN (9 mg, 0.054 mmol) was refluxed under argon for 1 h. The solvent was evaporated, and the residue was purified by column chromatography with silica gel containing 20% of KF (AcOEt/hexane, 1:1) to give a mixture of the reaction products as an oil. The mixture was further purified by silica gel column chromatography (AcOEt/hexane, 1:30 then 1:20) to give **5b** (19 mg) as an oil and a mixture of **5a**, **6** and **7** (24 mg) as an oil. The ratio of **5a** and **6** to **7** was determined by ESI-MS, and the ratio of **5a** and **6** was determined by ^{2}H NMR. Based on these ratios, yields of **5a**, **6** and **7** were calculated, respectively.

2,3-*O*-*Endo*-(benzylidene)-5-*O*-(*tert*-butyldiphenylsilyl)-1-*O*-(3-fluorobenzoyl)-β-D-[4-^{2}H]ribos

e (5a). ^{1}H NMR (400 MHz, $CDCl_3$); 7.70-7.14 (m, 19 H, aromatic), 6.58 (d, 1 H, H-1, $J_{1,2}$= 4.5 Hz), 6.07 (s, 1 H, benzyl), 5.11 (dd, 1 H, H-2, $J_{2,3}$= 6.7 Hz, $J_{2,1}$= 4.5 Hz), 5.00 (d, 1 H, H-3, $J_{3,2}$= 6.7 Hz), 3.90 (d, 1 H, H-5a, $J_{5a,5b}$= 11.1 Hz), 3.83 (d, 1 H, H-5b, $J_{5b,5a}$= 11.1 Hz), 1.10 (s, 9 H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$);); 19.4, 27.0, 64.3, 80.7, 82.4, 98.0, 107.7, 116.4, 116.7, 119.7, 125.5, 126.3, 127.8, 129.2, 129.5, 129.6, 129.8, 129.9, 132.4, 132.7, 135.4, 135.5, 135.8; ^{2}H NMR (400 MHz, THF); 4.54 (br s, 1 ^{2}H, ^{2}H -4); HRMS (FAB) calcd for $C_{35}H_{34}DFO_6SiNa$ 622.2147, found 621.2154 (MNa+).

2,3-*O*-*Endo*-(benzylidene)-5-*O*-(*tert*-butyldiphenylsilyl)-1-*O*-(3-fluorobenzoyl)--L-[4-^{2}H]lyxos e (5b). ^{1}H NMR (400 MHz, $CDCl_3$); 7.70-7.13 (m, 19 H, aromatic), 6.26 (d, 1 H, H-1, $J_{1,2}$= 4.0 Hz), 6.03 (s, 1 H, benzyl), 5.02 (dd, 1 H, H-2, $J_{2,3}$= 6.4 Hz, $J_{2,1}$= 4.0 Hz), 4.99 (d, 1 H, H-3, $J_{3,2}$= 6.4), 4.18 (d, 1 H, H-5a, $J_{5a,5b}$= 10.3 Hz), 4.03 (d, 1 H, H-5b, $J_{5b,5a}$= 11.2 Hz), 1.04 (s, 9 H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$; 19.4, 26.9, 62.3, 80.1, 80.5, 96.7, 107.5, 116.4, 116.6, 119.8. 120.0, 125.4, 126.4, 127.5, 127.5, 127.9, 129.1, 129.5, 129.5, 131.5, 133.1, 133.2, 135.4, 135.5, 135.9; ^{2}H NMR (400 MHz, THF); 4.30 (br s, 1 ^{2}H, ^{2}H -4); HRMS (FAB) calcd for $C_{35}H_{34}DFO_6SiNa$ 622.2147, found 622.2143 (MNa+).

2,3-*O*-*Endo*-([2-^{2}H]benzylidene)-5-*O*-(*tert*-butyldiphenylsilyl)-1-*O*-(3-fluorobenzoyl)--D-ribos e (6). ^{1}H NMR (400 MHz, $CDCl_3$); 7.70-7.14 (m, 18 H, aromatic), 6.58 (d, 1 H, H-1, $J_{1,2}$= 4.5 Hz), 6.07 (s, 1 H, benzyl), 5.11 (dd, 1 H, H-2, $J_{2,3}$= 6.7 Hz, $J_{2,1}$= 4.5 Hz), 5.00 (dd, 1 H, H-3, $J_{3,2}$= 6.7 Hz, $J_{3,4}$= 1.1 Hz), 4.64 (m, 1 H, H-4), 3.90 (d, 1 H, H-5a, $J_{5a,4}$= 2.4 Hz, $J_{5a,5b}$= 11.1 Hz), 3.83 (d, 1 H, H-5b, $J_{5b,4}$= 2.1 Hz, $J_{5b,5a}$= 11.1 Hz), 1.10 (s, 9 H, *t*-Bu); ^{2}H NMR (400 MHz, THF); 7.45 (br s, 1 ^{2}H, aromatic).

2,3-*O*-*Endo*-(benzylidene)-5-*O*-(*tert*-butyldiphenylsilyl)-1-*O*-(3-fluorobenzoyl)--D-ribose (7). ^{1}H NMR (400 MHz, $CDCl_3$) 7.70-7.14 (m, 19 H, aromatic), 6.58 (d, 1 H, H-1, $J_{1,2}$= 4.5 Hz), 6.07 (s, 1 H, benzyl), 5.11 (dd, 1 H, H-2, $J_{2,3}$= 6.7 Hz, $J_{2,1}$= 4.5 Hz), 5.00 (dd, 1 H, H-3, $J_{3,2}$= 6.7 Hz, $J_{3,4}$= 1.1 Hz), 4.64 (m, 1 H, H-4), 3.90 (d, 1 H, H-5a, $J_{5a,4}$= 2.4 Hz, $J_{5a,5b}$= 11.1 Hz), 3.83 (d, 1 H, H-5b, $J_{5b,4}$= 2.1 Hz, $J_{5b,5a}$= 11.1 Hz), 1.10 (s, 9 H, *t*-Bu).

2,3-*O*-*Endo*-(benzylidene)-5-*O*-(*tert*-butyldiphenylsilyl)-1-*O*-(3-fluorobenzoyl)--L-lyxose (5b'). Compound **5b'** was obtained from **4** with Bu_3SnH instead of Bu_3SnD as described for the synthesis of **5b**: ^{1}H NMR (400 MHz, $CDCl_3$); 7.70-7.13 (m, 19 H, aromatic), 6.26 (d, 1 H, H-1, $J_{1,2}$= 4.0 Hz), 6.03 (s, 1 H, benzyl), 5.02 (dd, 1 H, H-2, $J_{2,3}$= 6.4 Hz, $J_{2,1}$= 4.0 Hz), 4.99 (dd, 1 H, H-3, $J_{3,2}$= 6.4, $J_{3,4}$= 4.3 Hz,), 4.35 (ddd, 1 H, H-4, $J_{4,3}$= 4.3 Hz, $J_{4,5a}$= $J_{4,5b}$= 6.6 Hz), 4.18 (dd, 1 H, H-5a, $J_{5a,4}$= 6.6 Hz, $J_{5a,5b}$= 10.3 Hz), 4.03 (dd, 1 H, H-5b, $J_{5b,4}$= 6.6 Hz, $J_{5b,5a}$= 11.2 Hz), 1.04 (s, 9 H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$); 19.1, 26.7, 62.2, 79.5, 80.4, 96.6, 107.4, 116.31, 125.3, 126.3, 127.4, 127.4, 127.8, 129.0, 129.4, 133.0, 135.4; HRMS (FAB) calcd for $C_{35}H_{35}FO_6SiNa$ 621.2085, found 621.2097 (MNa+).

General Procedure for the Intramoleculer C–C Bond Formation with the Substrate 9. Method A. A mixture of **9** (67 mg, 0.1 mmol), Bu_3SnH (81 L, 0.30 mmol), and AIBN (10 mg, 0.060 mmol, entries 1-4) or Et_3B (1.0 M hexane solution, 100 L, 0.10 mmol, entry 5) was refluxed under argon

(entries 1-4) or stirred at room temperature under atmosphere (entry 5) until **9** disappeared on TLC. In the case of entry 5, air (3 mL) was bubbled into the reaction mixture at the beginning of stirring. The solvent was evaporated, and the residue was partitioned between hexane and MeCN, and the MeCN layer was evaporated. A mixture of the residue, KHF_2 (0.80 mmol) and *m*-CPBA (0.80 mmol) in DMF (1 mL) was sirred at 50 °C for 2.5 h, and then aqueous saturated $Na_2S_2O_3$ was added. The resulting mixture was partition between AcOEt and H_2O, and the organic layer was washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel column chromatography (AcOEt/hexane, 1:3 then 1:1) to give to **10**, **11** and **12** as an oil, respectively. **Method B.** To a refluxing solution of **9** (67 mg, 0.1 mmol) in benzene or chlorobenzene (10 mL) added a solution of Bu_3SnH (81 μL, 0.30 mmol) and AIBN (10 mg, 0.060 mmol) in the same solvent (6 mL) slowly over 6 h. The resulting mixture was treated as described in the above Method A.

2,3-*O*-*Endo*-(benzylidene)-1-*O*-(3-fluorobenzoyl)-4-hydroxymethyl-5-methyl-β-D-ribose (10). ^{1}H NMR (270 MHz, $CDCl_3$) for a diastereomer at the 5-position δ 7.58-7.17 (m, 9 H, aromatic), 6.55 (d, 1 H, H-1, $J_{1,2}$= 4.7 Hz), 6.10 (s, 1 H, benzyl), 5.10-5.00 (m, 2 H, H-2,3), 4.12 (m, 1 H, H-2, -Si-CH-CH_3), 4.11 (d, 1 H, H-5a, $J_{5a,5b}$= 12.3 Hz), 4.02 (d, 1 H, H-5b, $J_{5b,5a}$= 12.3 Hz), 2.6-2.2 (br s, OH), 1.39 (d, 3 H, -CH_3, *J*= 6.4 Hz); for the other diastereomer at the 5-position δ 7.58-7.17 (m, 9 H, aromatic), 6.51 (d, 1 H, H-1, $J_{1,2}$= 3.5 Hz), 6.10 (s, 1 H, benzyl), 5.10-5.00 (m, 2 H, H-2,3), 4.28 (d, 1 H, H-5a, $J_{5a,5b}$= 11.7 Hz), 4.22 (m, 1 H, H-2, -Si-CH-CH_3), 3.83 (d, 1 H, H-5b, $J_{5b,5a}$= 11.7 Hz), 2.6-2.2 (br s, OH), 1.32 (d, 3 H, -CH_3, *J*= 6.4 Hz); HRMS (FAB) calcd for $C_{21}H_{21}FO_7Na$ 427.1169, found 427.1176 (MNa^+). **2,3-*O*-*Endo*-(benzylidene)-5-deoxy-1-*O*-(3-fluorobenzoyl)-4-hydroxymethyl-β-L-*lyxo*-hexofuranose (11).** ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.57-7.13 (m, 9 H, aromatic), 6.47 (d, 1 H, H-1, $J_{1,2}$= 4.6 Hz), 6.08 (s, 1 H, benzyl), 5.14 (dd, 1 H, H-2, $J_{2,3}$= 7.3, $J_{2,1}$= 4.6 Hz), 4.88 (d, 1 H, H-3, $J_{3,2}$= 7.3 Hz), 4.15 (d, 1 H, H-5a, $J_{5a,5b}$= 11.9 Hz), 3.94 (d, 1 H, H-5b, $J_{5b,5a}$= 11.9 Hz), 3.90 (t, 2 H, -CH_2-CH_2-OH, *J*= 5.3 Hz), 2.66 (br s, 1 H, -OH), 2.17-1.98 (m, 2 H, -CH_2-CH_2-OH), 1.25 (m, 1 H, -OH); ^{13}C NMR(70 MHz,$CDCl_3$); 38.5, 58.2, 64.4, 80.8, 85.6, 86.7, 96.7, 108.3, 116.4, 116.7, 120.0, 120.3, 125.5, 125.5, 126.3, 128.1, 129.5, 129.8, 129.9, 135.4; HRMS (FAB) calcd for $C_{21}H_{21}FO_7Na$ 427.1169, found 427.1165 (MNa^+).

2,3-*O*-*Endo*-(benzylidene)-1-*O*-(3-fluorobenzoyl)-β-D-ribose (12). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.16 (m, 9 H, aromatic), 6.54 (d, 1 H, H-1, $J_{1,2}$= 4.4 Hz), 6.11 (s, 1 H, benzyl), 5.04 (dd, 1 H, H-2, $J_{2,3}$= 7.3, $J_{2,1}$= 4.4 Hz), 4.94 (dd, 1 H, H-3, $J_{3,2}$= 7.3, $J_{3,4}$= 2.9 Hz), 4.64 (m, 1 H, H-4), 3.97 (dd, 1 H, H-5a, $J_{5a,4}$=2.9 Hz, $J_{5a,5b}$= 12.3 Hz), 3.84 (dd, 1 H, H-5b, $J_{5b,4}$= 3.2 Hz, $J_{5b,5a}$= 12.3 Hz), 1.25 (s, 1 H, OH); HRMS (FAB) calcd for $C_{19}H_{17}FO_6Na$ 383.0907, found 383.0898 (MNa+).

(5R or S)-5-*O*-Acetyl-4-acetoxymethyl-2,3-*O*-*endo*-(benzylidene) -1-*O*-(3-fluorobenzoyl)-5-methyl-β-D-ribose (10a,b). A mixture of **10** (6.2 mg, 0.015 mmol), DMAP (0.4 mg, 0.03 mmol) and Ac_2O (3.2 mL, 0.034 mmol) in pyridine (0.15 mL) was stirred at room temperature

for 30 min, and then MeOH was added. The resulting mixture was partitioned between AcOEt and H_2O, and the organic layer was washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel preparative TLC (AcOEt/hexane, 3:7) to give **10a** (higher Rf, 2.1 mg, 28%) and **10b** (lower Rf, 1.3 mg, 17%) as an oil, respectively. **10a**: ^{1}H NMR (270 MHz, $CDCl_3$) 7.53-7.12 (m, 9 H, aromatic), 6.50 (d, 1 H, H-1, $J_{1,2}$= 4.6 Hz), 6.05 (s, 1 H, benzyl), 5.32-5.25 (m, 1 H, -Si-CH-CH_3), 5.04 (dd, 1 H, H-2, $J_{2,3}$= 6.6, $J_{2,1}$= 4.6 Hz), 4.80 (d, 1 H, H-3, $J_{3,2}$= 6.6 Hz), 4.66 (d, 1 H, H-5a, $J_{5a,5b}$= 11.2 Hz), 4.34 (d, 1 H, H-5b, $J_{5b,5a}$= 11.9 Hz), 2.15 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 1.32 (d, 3 H, -CH_3, J= 5.9 Hz); HRMS (FAB) calcd for $C_{25}H_{25}FO_9Na$ 511.1380, found 511.1393 (MNa^+). **10b**: ^{1}H NMR (270 MHz, $CDCl_3$) 7.55-7.07 (m, 9 H, aromatic), 6.48 (d, 1 H, H-1, $J_{1,2}$= 4.6 Hz), 6.08 (s, 1 H, benzyl), 5.34-5.26 (m, 1 H, -Si-CH-CH_3), 5.08 (dd, 1 H, H-2, $J_{2,3}$= 6.6, $J_{2,1}$= 4.6 Hz), 4.97 (d, 1 H, H-3, $J_{3,2}$= 6.6 Hz), 4.80 (d, 1 H, H-5a, $J_{5a,5b}$= 12.5 Hz), 4.41 (d, 1 H, H-5b, $J_{5b,5a}$= 13.1 Hz), 2.12 (s, 6 H, Ac×2), 1.40 (d, 3 H, -CH_3, J= 6.6 Hz); HRMS (FAB) calcd for $C_{25}H_{25}FO_9Na$ 511.1380, found 511.1382 (MNa^+).

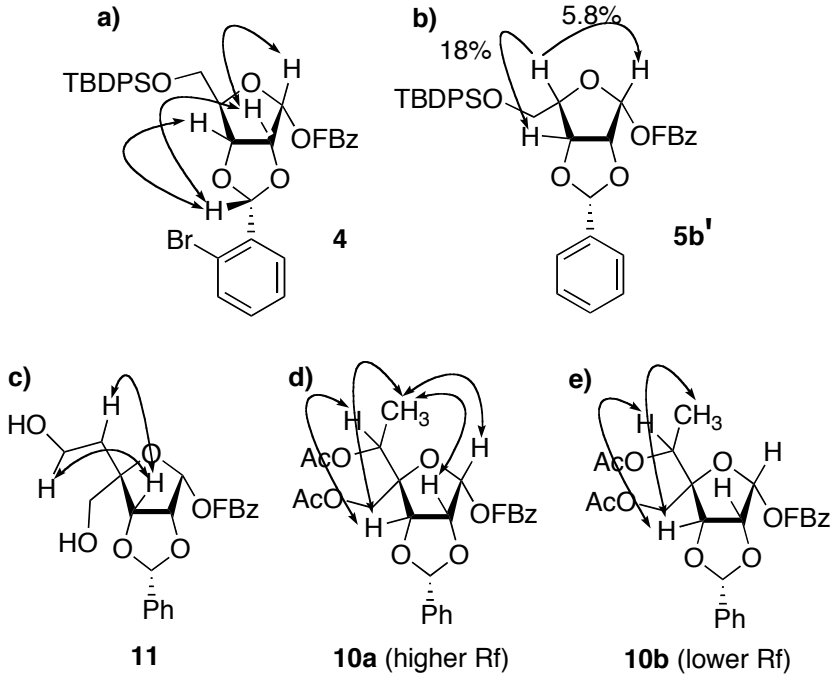
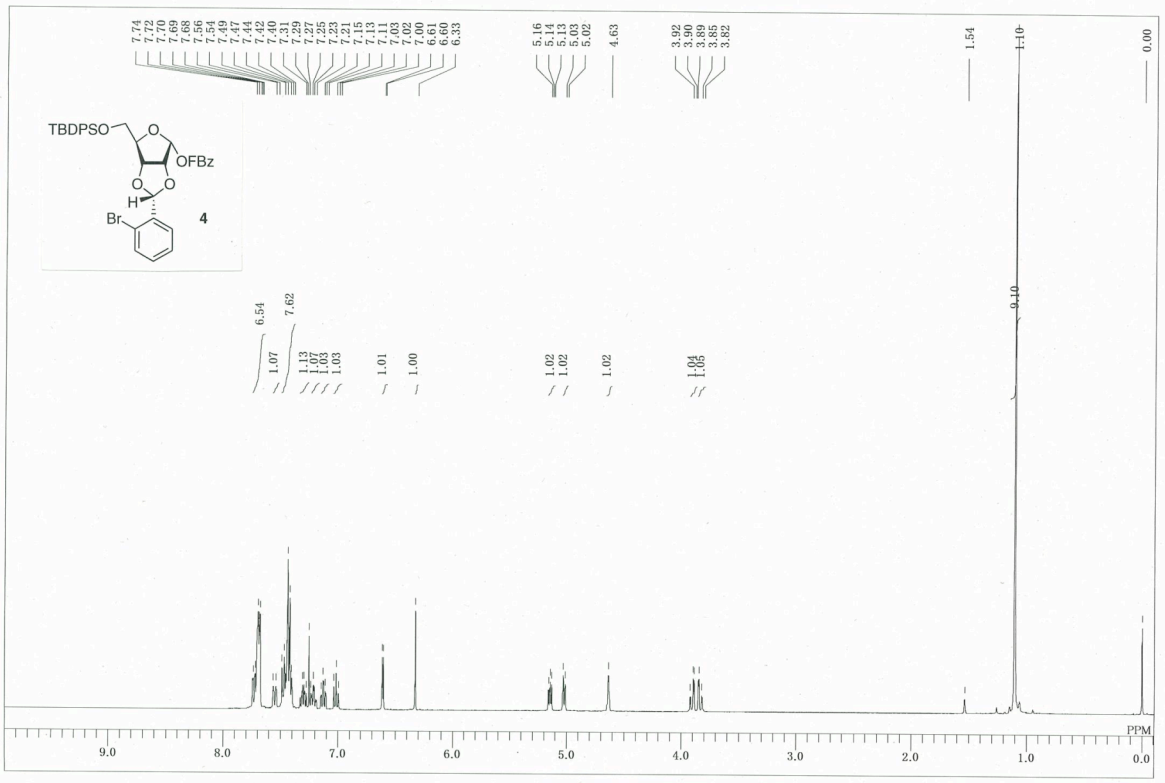


Figure S1. NOE and NOESY data of key compounds. The stereochemistry at the 4-position of the deuterium-labeled products **5a** and **5b** was determined based on the NOE experiments of the corresponding unlabeled compound **5b'** (b). After conversion of **10** into the corresponding acetates **10a** and **10b**, their stereochemistries were determined by NOESY data (d and e).

NAT1-71-2(400)



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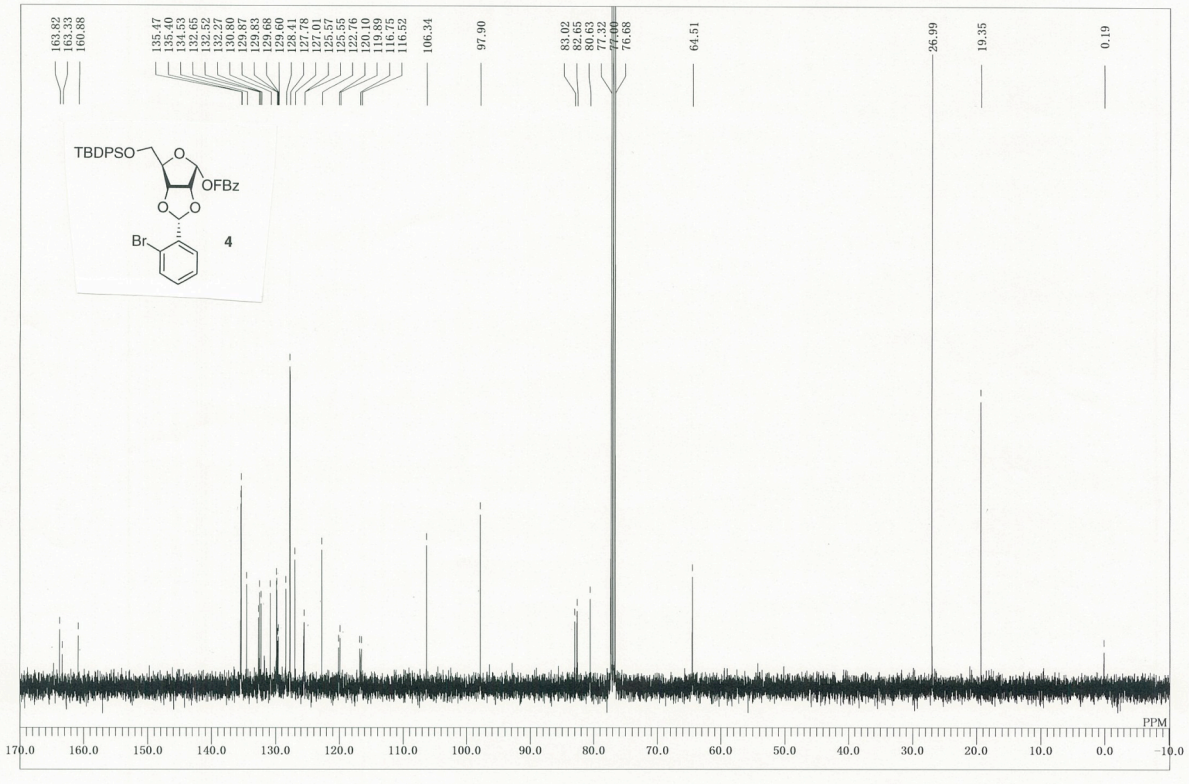

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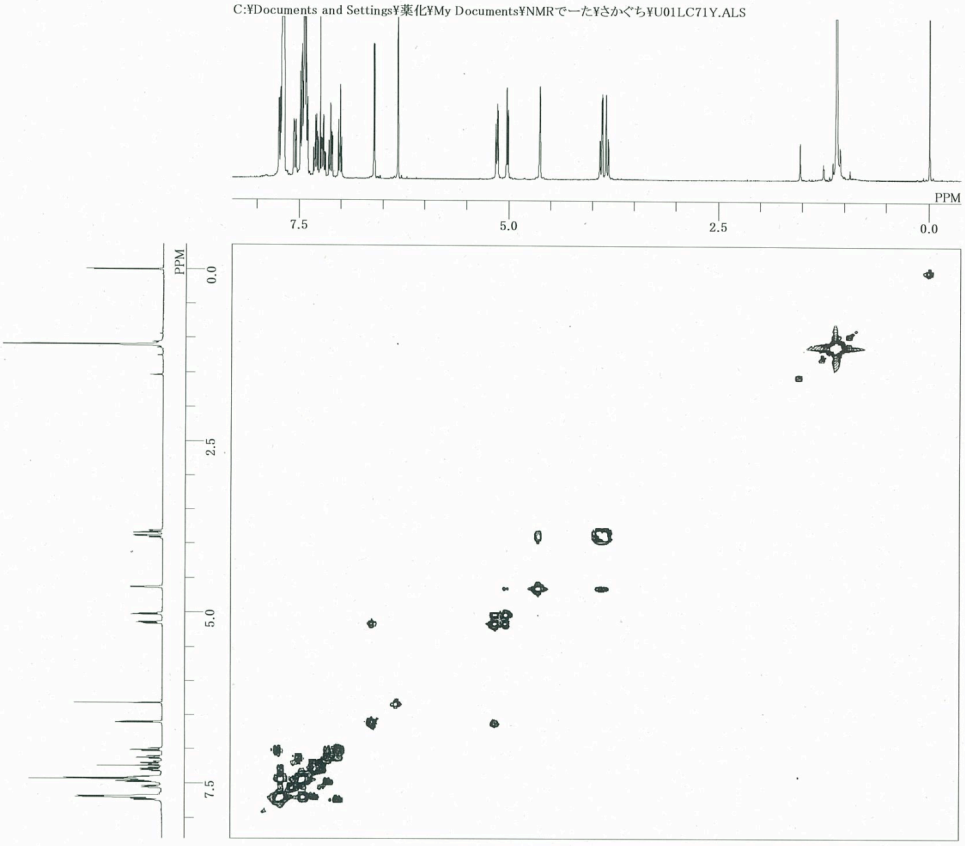
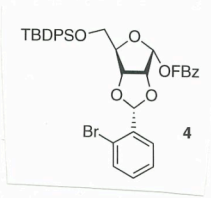
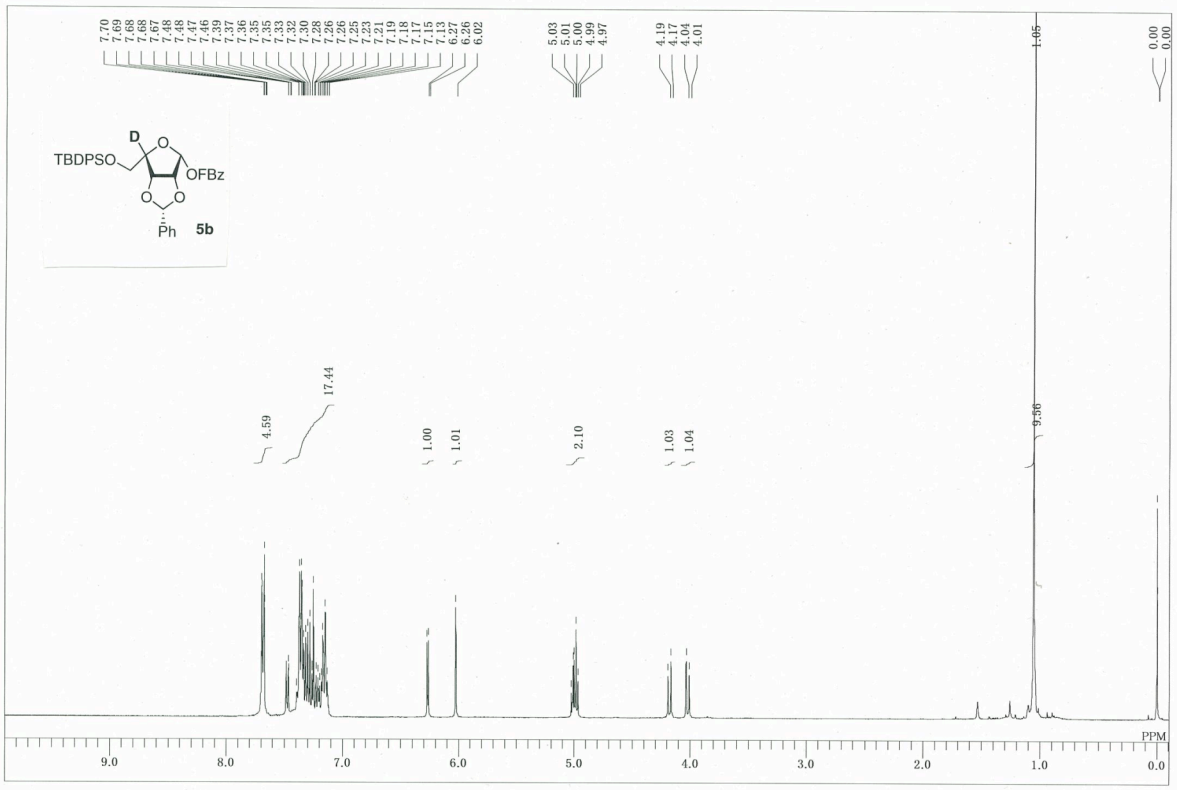




NAT2-64-2(inversion-D,400)



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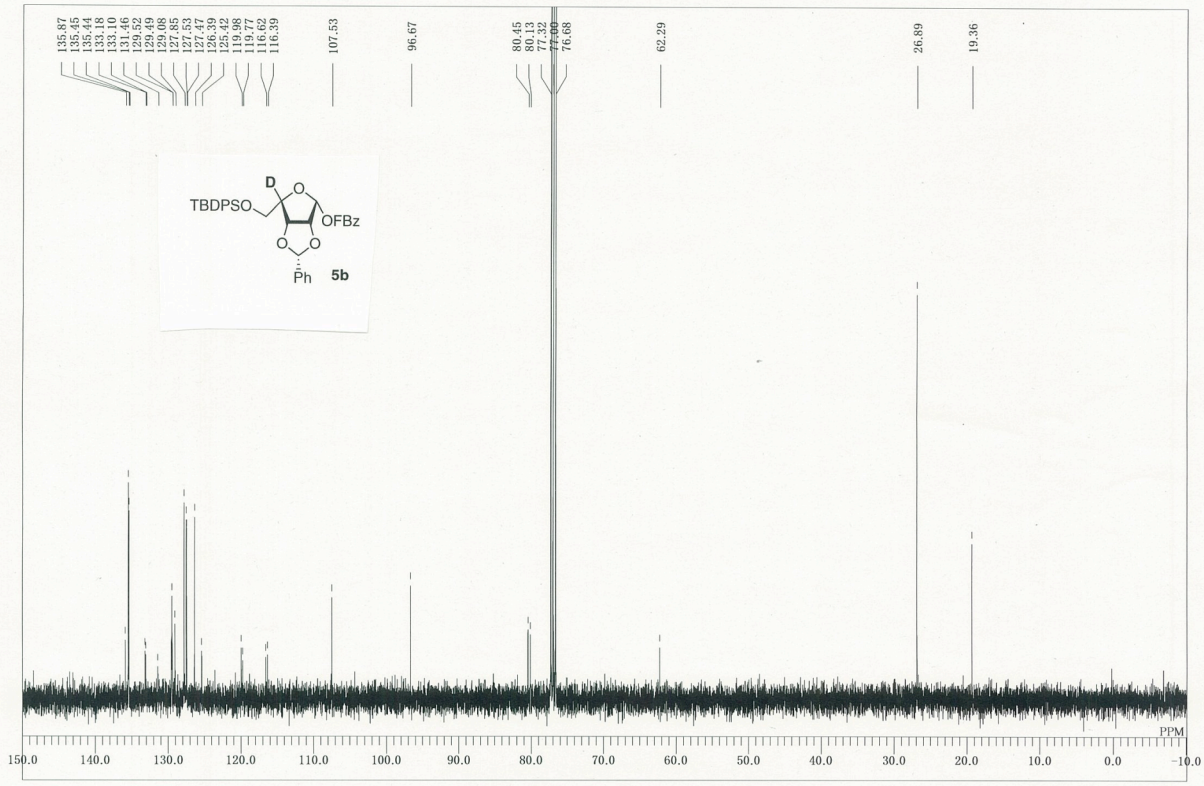

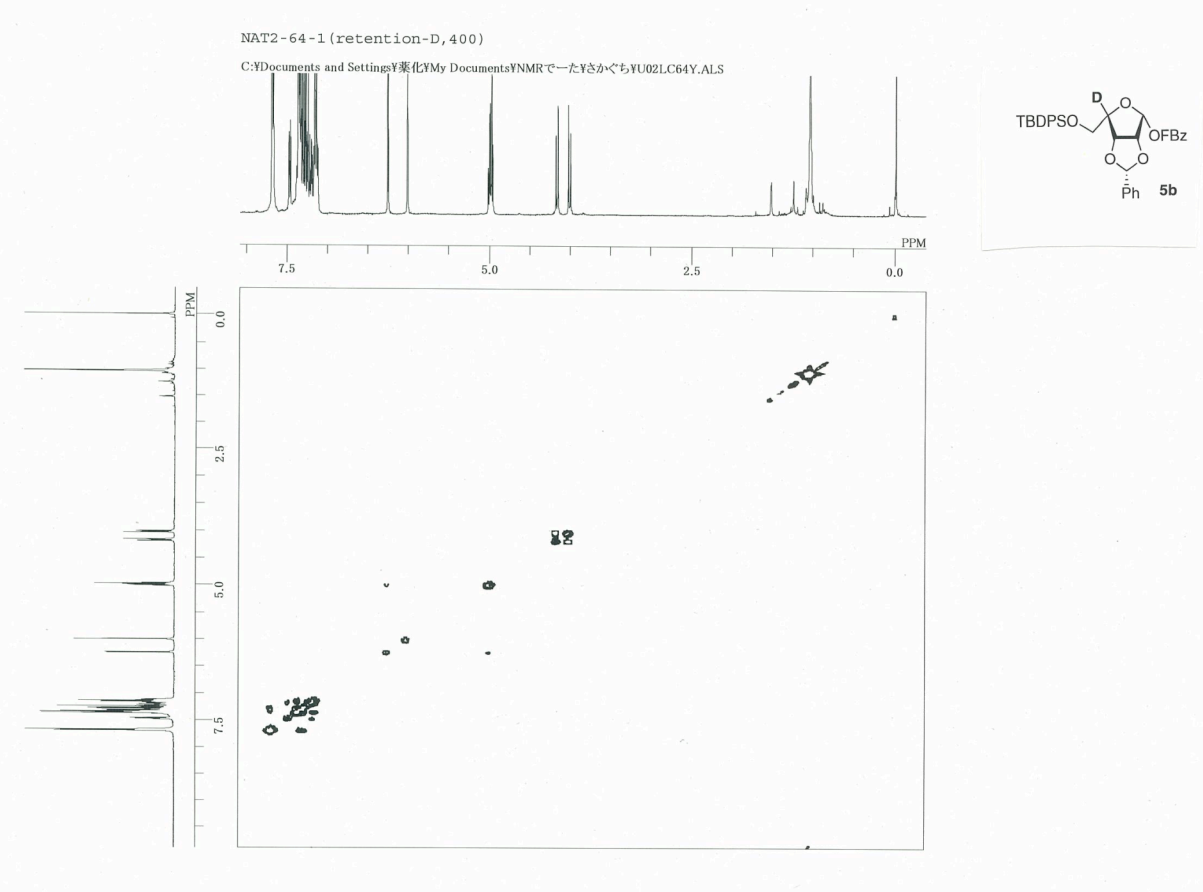

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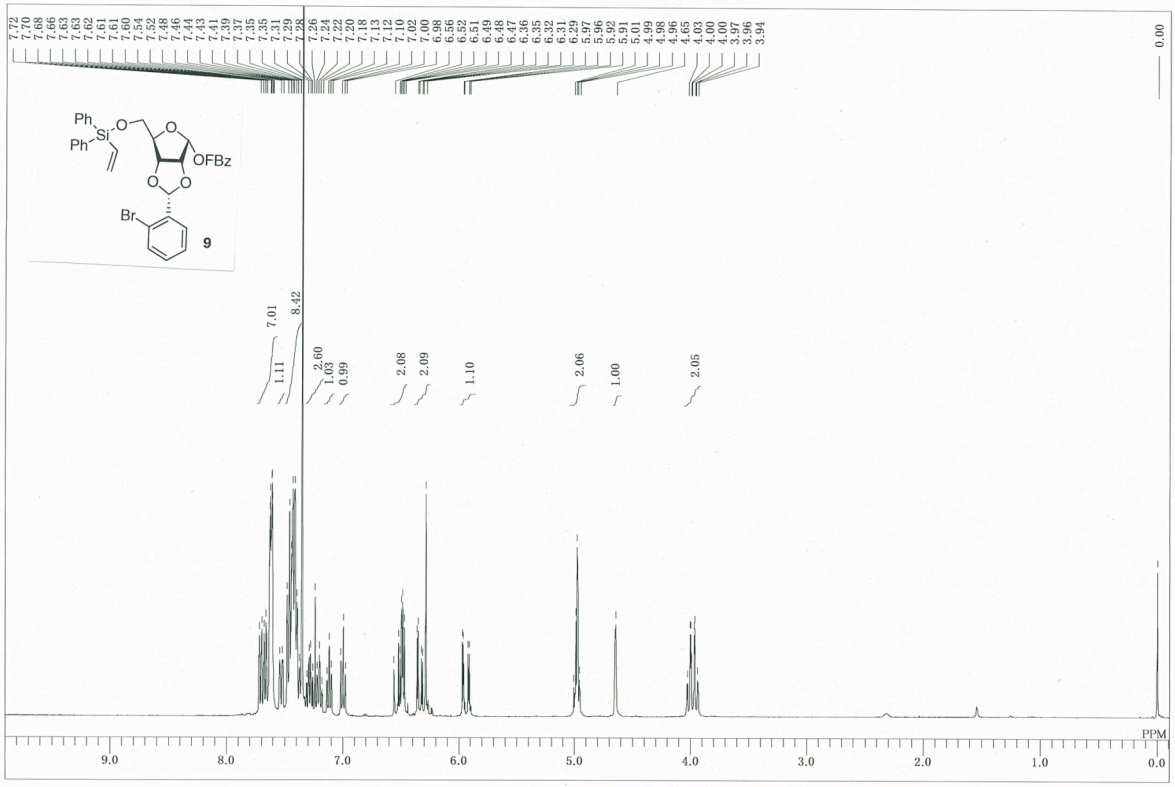

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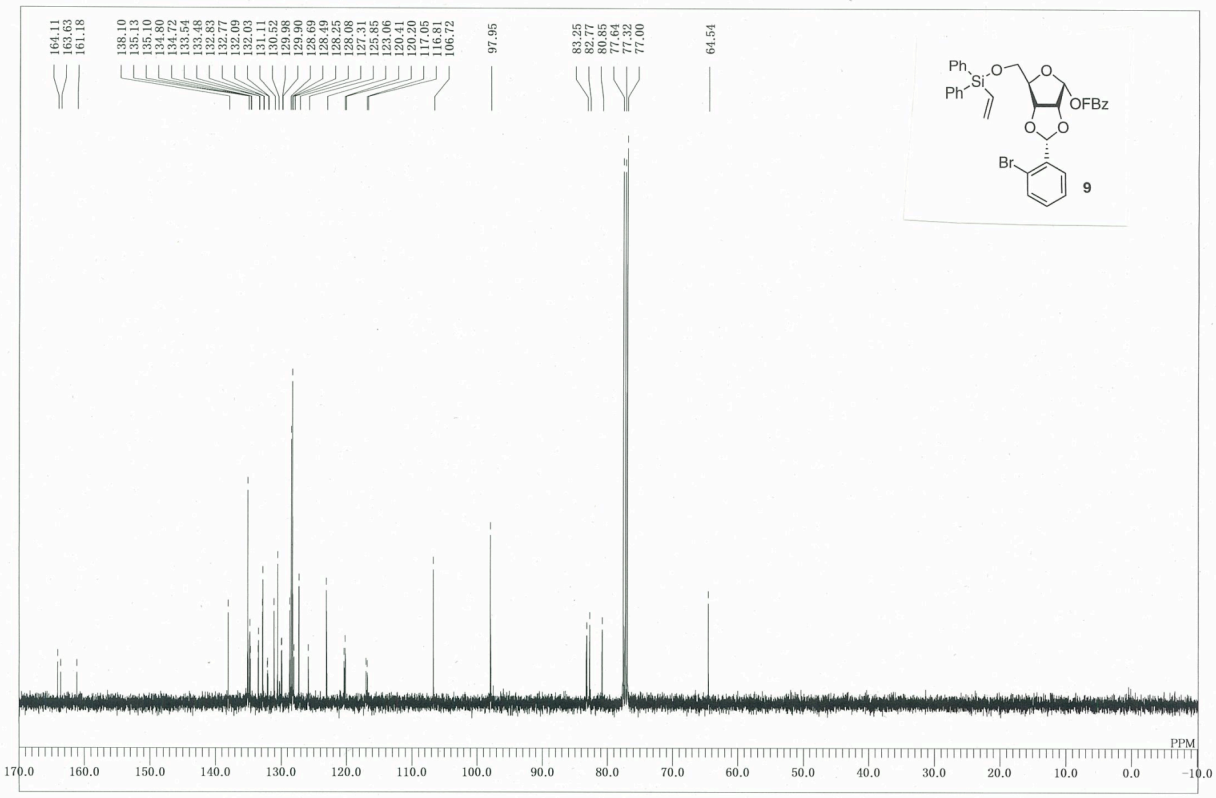

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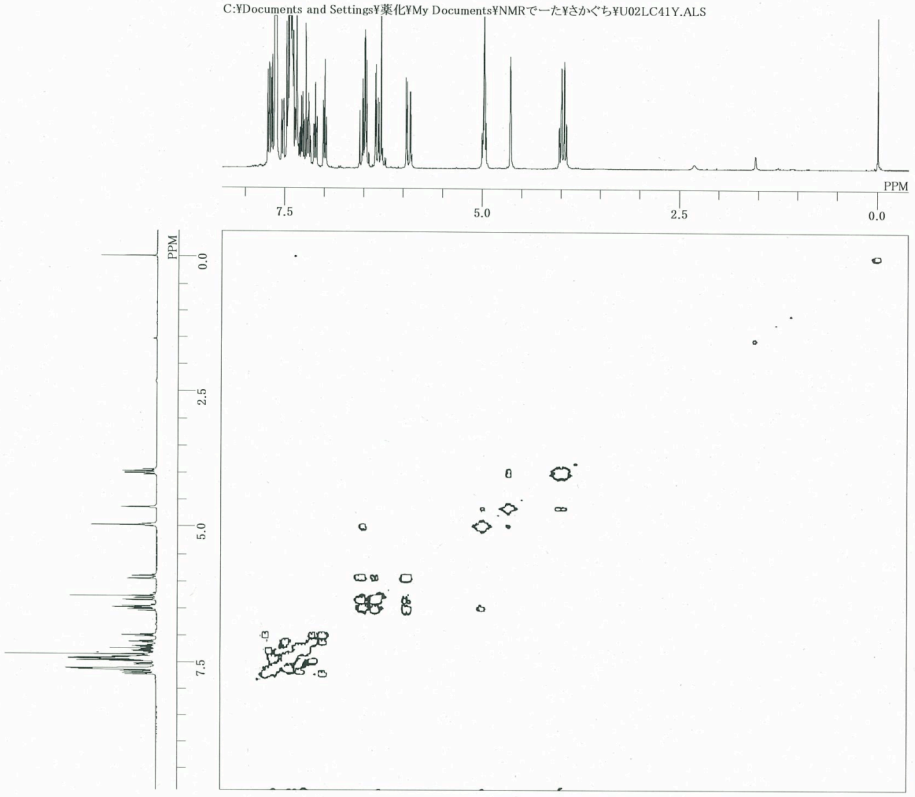
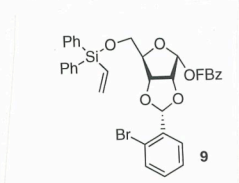
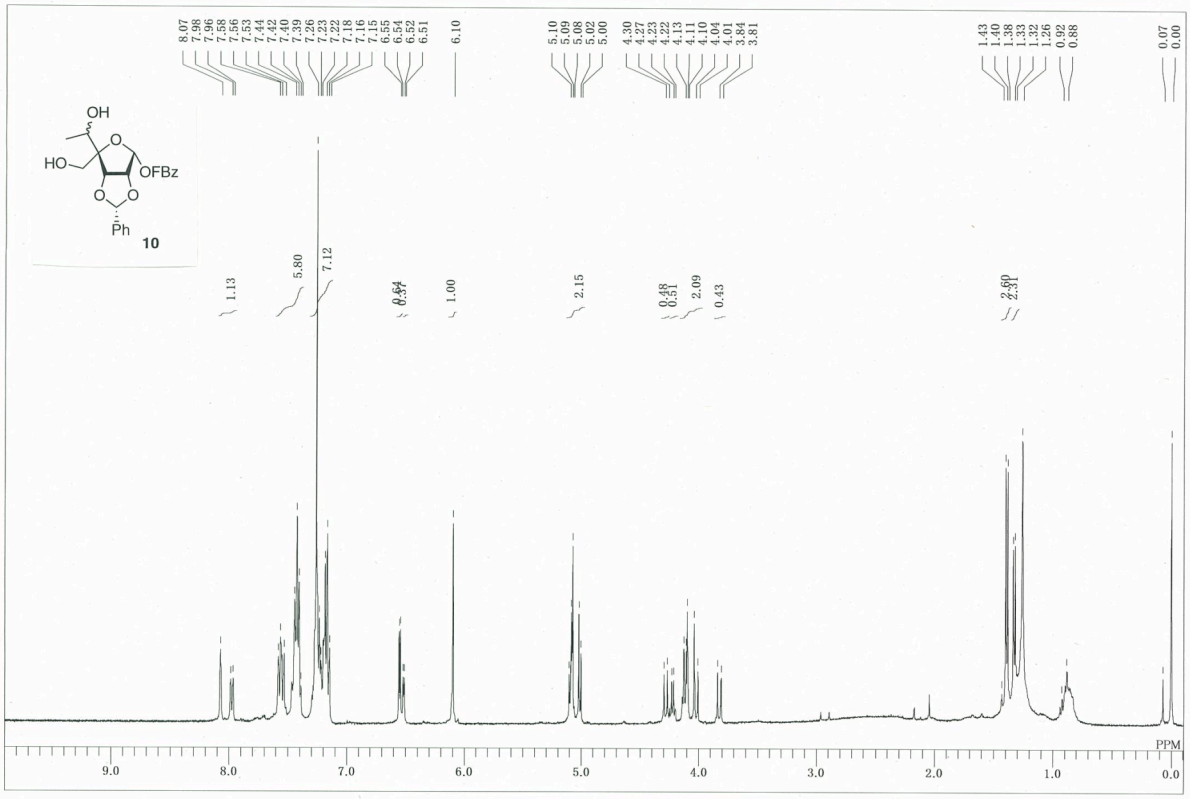




NAT2-54-1(400,cdcl3)



NAT2-71-2(400,CDCl3)

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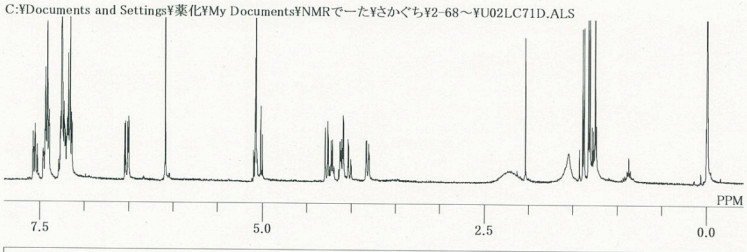

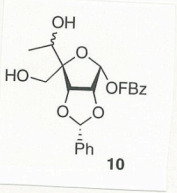

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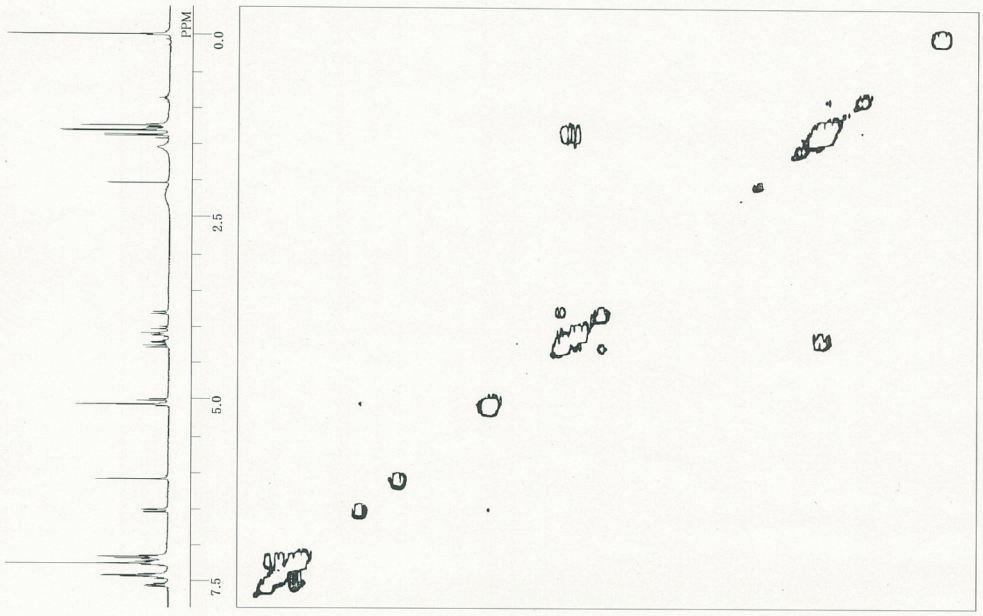

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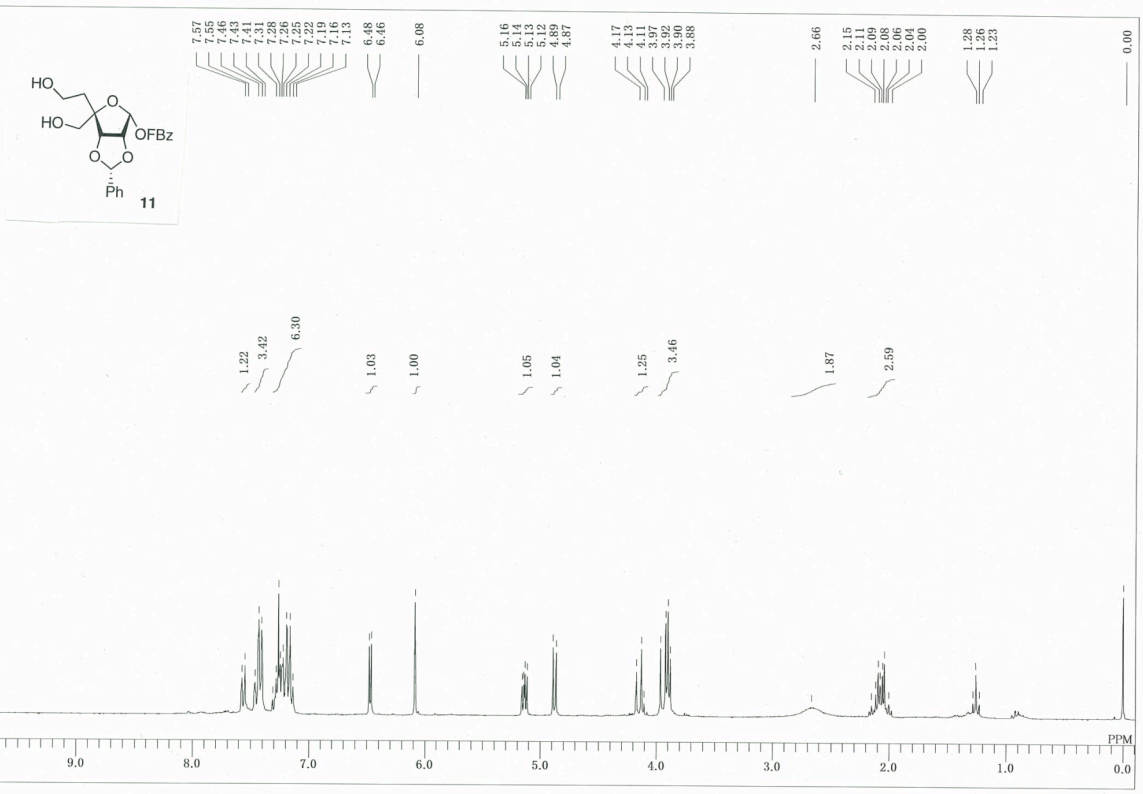

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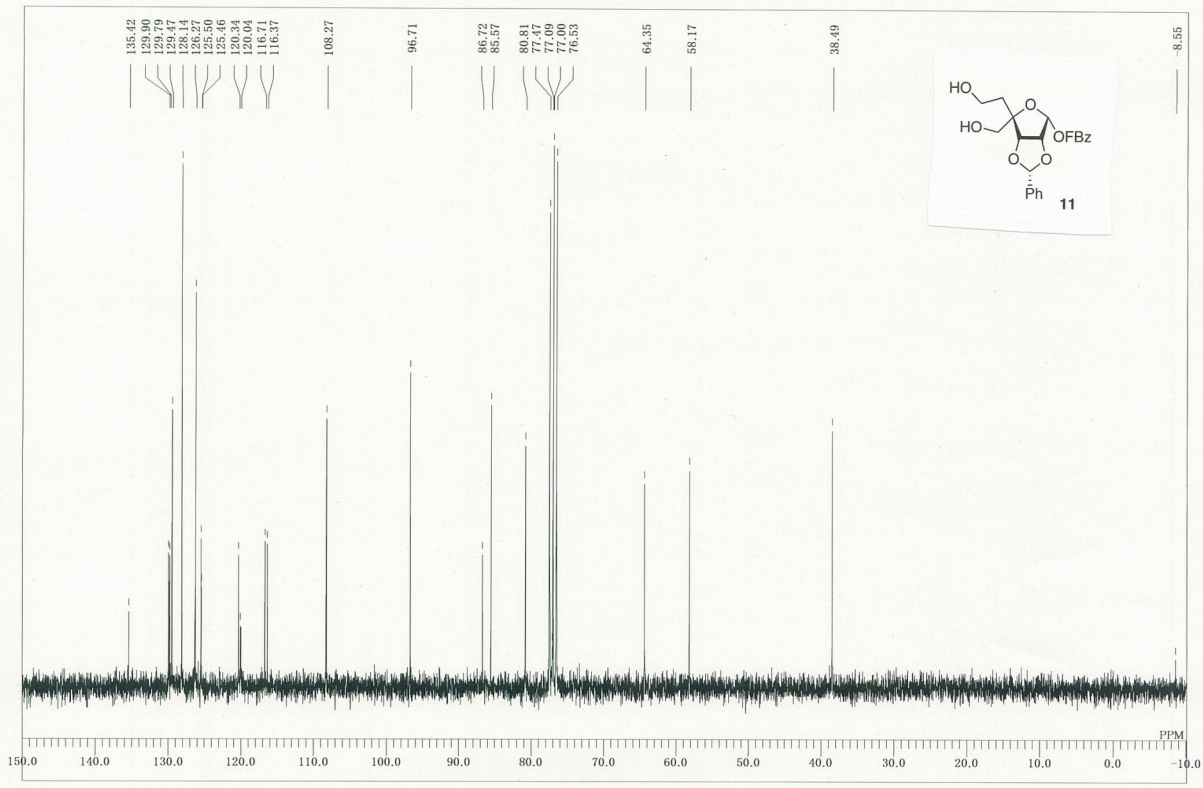

NAT2-25-4(400,cosy)

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