Electronic Supplementary Material (ESI) for ChemComm.

Supplementary data

One-pot synthesis of *β*-*N*-glycosyl imidazole analogues *via* a palladium-catalysed decarboxylative allylation

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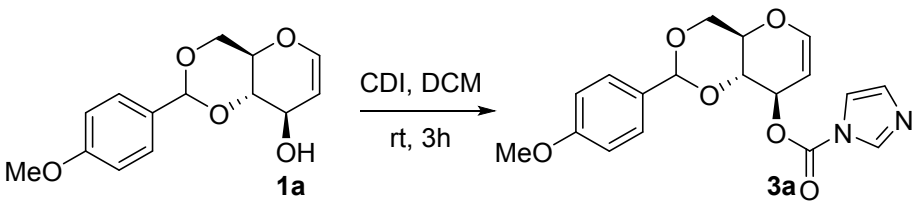
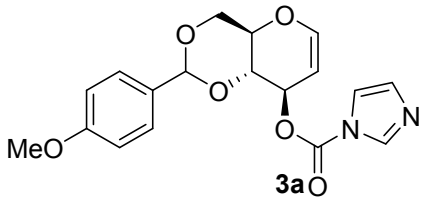
General experimental details

All reactions were performed under a nitrogen atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using Merck TLC silica gel 60 F254 plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel 60 (0.010-0.063 mm) and a gradient solvent system (EtOAc/hexane as eluent). Melting points were obtained in open capillary tubes in Omega MPA 100 melting point apparatus. Optical rotations were measured in $CHCl_3$ and CH_2Cl_2 on a Schmidt + Haensdch polarimeter with a 1 cm cell (c given in g/100 ml). ^{1}H and ^{13}C NMR spectra were measured on 400 MHz Bruker AVIII 400 spectrometer. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet or unsolved). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. Infrared spectra were recorded on a FTIR Restige-21 (Shimadzu) spectrometer. Solid samples were examined as a thin film between NaCl salt plates. Low resolution mass spectra were determined on a Finnigan LCQ mass spectrometer and reported in units of mass to charge (*m/z*). High resolution mass spectra (HRMS) were recorded on Waters Q-Tof premier™ mass spectrometer. X-ray crystallographic data was collected by using a Bruker X8Apex diffractometer with Mo K/α radiation (graphite monochromator).

Procedure for the preparing compound 3a

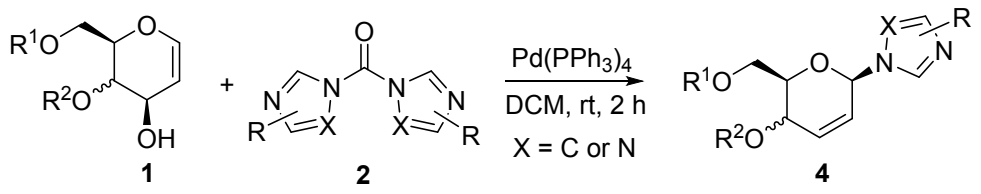


To a solution of CDI (1.5 equiv) in DCM (0.1 M) was added a solution of 4,6-*para*-methoxybenzylidene glucal **1a** (1.0 equiv) in DCM dropwisely at 0 °C. Then the mixture was allowed to warm to room temperature and stirred for 3 h. After that, the mixture was washed wish with H_2O, brine, and then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with n-hexane/EA=1:1) to provide the desired carbamate compound **3a**.



Compound **3a** was obtained in 94% yield as a white solid. M.p. 127-129 °C; $[\alpha]_D^{23}$ –150 (*c* 1.0, $CHCl_3$); IR (neat) *v*: 3016, 1759, 1641, 1614, 1518, 1392, 1236, 1094 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.37-7.45 (m, 3H), 7.06 (s, 1H), 6.86-6.92 (m, 2H), 6.49 (dd, J_1 = 6.1 Hz, J_2 = 1.2 Hz, 1H), 5.76 (dt, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 5.59 (s, 1H), 4.92 (dd, J_1 = 6.1 Hz, J_2 = 2.1 Hz, 1H), 4.41 (dd, J_1 = 10.6 Hz, J_2 = 5.1 Hz, 1H), 4.18 (dd, J_1 = 10.4 Hz, J_2 = 7.7 Hz, 1H), 4.06 (td, J_1 = 10.2 Hz, J_2 = 5.1 Hz, 1H), 3.89 (t, J = 10.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 148.3, 146.7, 137.1, 130.6, 128.9, 127.5, 117.1, 113.7, 101.7, 99.1, 76.4, 73.0, 68.8, 68.0, 55.3; HRMS (ESI) calcd. for $C_{17}H_{21}O_7$ $[M+H]^+$: 359.1243, found: 359.1238.

General procedure for the preparing *N*-glycosyl imidazole analogues from the glycals 1

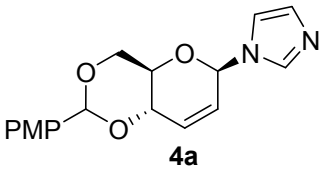


To a solution of CDI analogues (0.3 mmol) and $Pd(PPh_3)_4$ (0.01 mmol) in DCM (2 mL) was added a solution of glucal compound **1** (0.2 mmol) in DCM (2 mL) slowly at 0 °C under nitrogen atmosphere. Then the mixture was allowed to warm to room temperature and stirred for 2 h. After that, the solvent DCM was removed under reduced pressure. The residue was purified by column chromatography on silica gel to provide the desired *N*-glycosyl imidazole analogues compound **4** in 83-96% yields.

Characterization of the *N*-glycosyl imidazole analogues

The synthesis of compound 4a

1-((4a*R*,6*R*,8a*S*)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-1*H*-imidazole (4a)

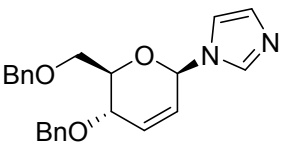


4a

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a**[1] (52.8 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4a** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:2) in 93% yield as a white solid. M.p. 160-162 °C; $[\alpha]_D^{22}$ +85.8 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2941, 2881, 1614, 1517, 1249, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.79-3.86 (m, 4H), 3.87-3.94 (m, 1H), 4.29 (dd, J_1 = 10.0, J_2 = 4.2 Hz, 1H), 4.38-4.44 (m, 1H), 5.60 (s, 1H), 5.88 (ddd, J_1 = 10.2, J_2 = 2.4, J_3 = 1.9 Hz, 1H), 6.14-6.18 (m, 1H), 6.38 (d, J = 10.2 Hz, 1H), 6.88-6.94 (m, 2H), 7.04 (s, 1H), 7.10 (s, 1H), 7.41-7.46 (m, 2H), 7.67 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.3, 68.7, 71.6, 74.1, 81.1, 102.2, 113.7, 117.3, 125.6, 127.5, 129.4, 130.0, 132.8, 136.5, 160.3 ppm; HRMS (ESI) calcd. for $C_{17}H_{19}O_4N_2$ [M+H]: 315.1345; found: 315.1345.

The synthesis of compound 4b

1-((2*R*,5*S*,6*R*)-5-(benzyloxy)-6-(benzyloxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)-1*H*-imidazole (4b)



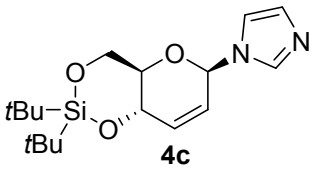
4b

Following the general procedure, the reaction of 4,6-dibenzyl glucal **1b**[2] (65.2 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4b** was obtained by column chromatography on silica gel (eluted with MeOH/DCM=1:60) in 89% yield as a white solid. M.p. 82-84 °C; $[\alpha]_D^{22}$ +121.5 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2941, 2866, 1616, 1495, 1452, 1265, 1072 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.66 (dd, J_1 = 11.0, J_2 = 5.3 Hz, 1H), 3.73 (dd, J_1 = 11.0, J_2 = 2.1 Hz, 1H), 3.86-3.91 (m, 1H), 4.13-

4.18 (m, 1H), 4.48-4.58 (m, 3H), 4.64 (d, J = 11.4 Hz, 1H), 5.82 (dt, J_1 = 10.2, J_2 = 1.5 Hz, 1H), 5.96-5.99 (m, 1H), 6.24 (dt, J_1 = 10.2, J_2 = 1.8 Hz, 1H), 7.01 (s, 1H), 7.06 (s, 1H), 7.24-7.36 (m, 10H), 7.63 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 68.9, 69.4, 71.7, 73.4, 77.7, 80.4, 117.4, 126.1, 127.6, 127.8, 127.9, 128.0, 128.3, 128.4, 129.5, 131.9, 136.4, 137.4, 137.9 ppm; HRMS (ESI) calcd. for $C_{23}H_{25}O_3N_2$ [M+H]: 377.1865; found: 377.1862.

The synthesis of compound 4c

1-((4a*R*,6*R*,8a*S*)-2,2-di-*tert*-butyl-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3,2]dioxasilin-6-yl)-1*H*-imidazole (4c)

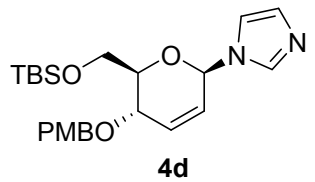


4c

Following the general procedure, the reaction of 4,6- di-*tert*-butylsilyl glucal **1c** (57.3 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4c** was obtained by column chromatography on silica gel (eluted with MeOH/DCM=1:60) in 85% yield as a white solid. M.p. 139-141 °C; $[\alpha]_D^{22}$ +45.5 (*c* 1.0, $CHCl_3$); IR (neat) ν: 2931, 2858, 1613, 1472, 1129, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.01 (s, 9H), 1.07 (s, 9H), 3.80 (ddd, J_1 = 10.4, J_2 = 8.6, J_3 = 5.0 Hz, 1H), 3.91 (t, J = 10.2 Hz, 1H), 4.17 (dd, J_1 = 10.0, J_2 = 4.9 Hz, 1H), 4.57-4.63 (m, 1H), 5.72-5.77 (m, 1H), 6.06-6.09 (m, 1H), 6.27 (dt, J_1 = 10.2, J_2 = 2.6 Hz, 1H), 7.00 (s, 1H), 7.07 (s, 1H), 7.63 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.0, 22.7, 26.9, 27.4, 66.4, 69.3, 75.1, 80.8, 117.3, 124.1, 129.8, 135.9, 136.4 ppm; HRMS (ESI) calcd. for $C_{17}H_{29}O_3N_2Si$ [M+H]: 337.1947; found: 337.1945.

The synthesis of compound 4d

1-((2*R*,5*S*,6*R*)-6-((*tert*-butyldimethylsilyloxy)methyl)-5-(4-methoxybenzyloxy)-5,6-dihydro-2*H*-pyran-2-yl)-1*H*-imidazole (4d)



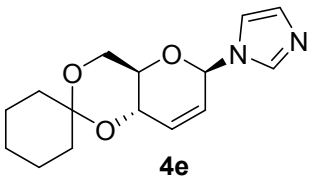
4d

Following the general procedure, the reaction of 4-methoxybenzyl-6-*tert*-butyldimethylsilyl glucal **1d**[4] (76.1

mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4d** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:2) in 90% yield as colorless oil. $[\alpha]_D^{22}$ +110.2 (*c* 1.0, $CHCl_3$); IR (neat) ν: 2926, 2853, 1607, 1514, 1458, 1254, 1105 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ -0.06 (s, 3H), -0.01 (s, 3H), 0.84 (s, 9H), 3.70 (ddd, J_1 = 8.5, J_2 = 4.0, J_3 = 2.6 Hz, 1H), 3.77-3.86 (m, 5H), 4.18 (ddd, J_1 = 8.5, J_2 = 4.3, J_3 = 2.0 Hz, 1H), 4.55 (d, J = 11.2 Hz, 1H), 4.62 (d, J = 11.2 Hz, 1H), 5.81 (dt, J_1 = 10.3, J_2 = 1.7 Hz, 1H), 5.94-5.97 (m, 1H), 6.22 (dt, J_1 = 10.3, J_2 = 1.9 Hz, 1H), 6.87-6.91 (m, 2H), 6.98 (s, 1H), 7.04 (s, 1H), 7.26-7.30 (m, 2H), 7.61 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ -5.31, -5.26, 18.3, 25.8, 55.2, 62.3, 68.6, 71.6, 78.9, 80.4, 113.9, 117.4, 125.8, 129.4, 129.6, 129.8, 132.5, 136.3, 159.4 ppm; HRMS (ESI) calcd. for $C_{23}H_{35}O_4N_2Si$ [M+H]: 431.2366; found: 431.2380.

The synthesis of compound 4e

1-((4a'*R*,6'*R*,8a'*S*)-4',4a',6',8a'-tetrahydrospiro[cyclohexane-1,2'-pyrano[3,2-d][1,3]dioxine]-6'-yl)-1*H*-imidazole (4e)

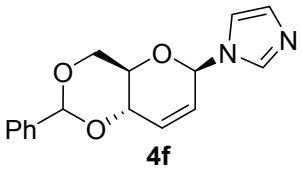


4e

Following the general procedure, the reaction of 4,6-cyclohexylidene glucal **1e**[5] (45.2 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4e** was obtained by column chromatography on silica gel (eluted with MeOH/DCM=1:60) in 91% yield as yellow oil. $[\alpha]_D^{22}$ +67.0 (*c* 1.0, $CHCl_3$); IR (neat) ν: 2934, 2860, 2939, 1637, 1495, 1267, 1105 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.39-1.69 (m, 8H), 1.88-2.05 (m, 2H), 3.68-3.76 (m, 1H), 3.81 (t, J = 10.2 Hz, 1H), 3.88 (dd, J_1 = 10.5, J_2 = 5.2 Hz, 1H), 4.45-4.51 (m, 1H), 5.76 (dt, J_1 = 10.3, J_2 = 2.2 Hz, 1H), 6.10-6.14 (m, 1H), 6.26 (d, J = 10.2 Hz, 1H), 7.02 (s, 1H), 7.07 (s, 1H), 7.64 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.5, 22.7, 25.5, 27.6, 38.0, 61.7, 65.9, 72.9, 81.2, 100.3, 117.4, 125.3, 129.8, 133.7, 136.5 ppm; HRMS (ESI) calcd. for $C_{15}H_{21}O_3N_2$ [M+H]: 277.1552; found: 277.1552.

The synthesis of compound 4f

1-((4a*R*,6*R*,8a*S*)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-1*H*-imidazole (4f)

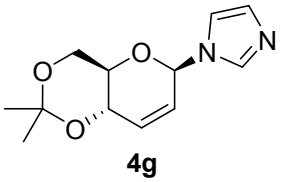


4f

Following the general procedure, the reaction of 4,6-benzylidene glucal **1f**[6] (46.8 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4f** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:2) in 93% yield as a white solid. M.p. 142-144 °C; $[\alpha]_D^{22}$ +85.1 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2976, 2878, 1614, 1495, 1402, 1223, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): *δ* 3.81-3.95 (m, 2H), 4.31 (dd, J_1 = 9.8, J_2 = 4.1 Hz, 1H), 4.40-4.45 (m, 1H), 5.64 (s, 1H), 5.82 (dt, J_1 = 10.3, J_2 = 1.9 Hz, 1H), 6.14-6.18 (m, 1H), 6.39 (d, J = 10.3 Hz, 1H), 7.04 (s, 1H), 7.10 (s, 1H), 7.36-7.42 (m, 3H), 7.47-7.54 (m, 2H), 7.67 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 68.7, 71.6, 74.1, 81.1, 102.1, 117.3, 125.6, 126.1, 128.4, 129.3, 130.0, 132.7, 136.5, 136.9 ppm; HRMS (ESI) calcd. for $C_{16}H_{17}O_3N_2$ [M+H]: 285.1239; found: 285.1238.

The synthesis of compound 4g

1-((4a'*R*,6'*R*,8a'*S*)-4',4a',6',8a'-tetrahydrospiro[cyclohexane-1,2'-pyrano[3,2-d][1,3]dioxine]-6'-yl)-1*H*-imidazole (4g)



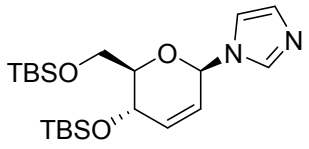
4g

Following the general procedure, the reaction of 4,6-dimethylidene glucal **1g**[7] (37.2 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4g** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:3) in 95% yield as yellow oil. $[\alpha]_D^{22}$ +70.5 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2993, 2885, 1614, 1494, 1375, 1267, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): *δ* 1.45 (s, 3H), 1.45 (s, 3H), 3.68-3.76 (m, 1H), 3.81 (t, J = 10.4 Hz, 1H), 3.90 (dd, J_1 = 10.5, J_2 = 5.0 Hz,

1H), 4.43-4.49 (m,1 H), 5.75-5.80 (m, 1H), 6.10-6.14 (m, 1H), 6.24 (d, J = 10.2 Hz, 1H), 7.00 (s, 1H), 7.06 (s, 1H), 7.62 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.9, 29.0, 62.3, 66.7, 72.6, 81.1, 100.1, 117.3, 125.2, 129.8, 133.5, 136.4 ppm; HRMS (ESI) calcd. for $C_{12}H_{17}O_3N_2$ [M+H]: 237.1239; found: 237.1239.

The synthesis of compound 4h

1-((2*R*,5*S*,6*R*)-5-(*tert*-butyldimethylsilyloxy)-6-((*tert*-butyldimethylsilyloxy)methyl)-5,6-dihydro-2*H*-pyran-2-yl)-1*H*-imidazole (4h)

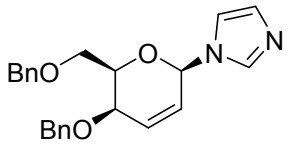


4h

Following the general procedure, the reaction of 4,6- di-*tert*-butyldimethylsilyl glucal **1h**[8] (74.9 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4h** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:1) in 88% yield as a white solid. IR (neat) ν: 2954, 2929, 2857, 1613, 1494, 1471, 1256, 1096 cm^{-1}; ^{1}H NMR of the major product (β-isomer) ($CDCl_3$, 400 MHz): δ -0.08 (s, 3H), -0.04 (s, 3H), 0.11 (s, 3H), 0.13 (s, 3H), 0.83 (s, 9H), 0.90 (s, 9H), 3.53-3.58 (m, 1H), 3.79-3.82 (m, 2H), 4.38-4.43 (m, 1H), 5.75 (dt, J_1 = 10.2, J_2 = 1.5 Hz, 1H), 5.94-5.97 (m, 1H), 6.05 (dt, J_1 = 10.2, J_2 = 1.7 Hz, 1H), 6.98 (s, 1H), 7.03 (s, 1H), 7.61 (s, 1H) ppm; ^{13}C NMR of the major product (β-isomer) ($CDCl_3$, 100 MHz): δ -5.31, -5.26, 18.3, 25.8, 55.2, 62.3, 68.6, 71.6, 78.9, 80.4, 113.9, 117.4, 125.8, 129.4, 129.6, 129.8, 132.5, 136.3, 159.4 ppm; HRMS (ESI) calcd. for $C_{21}H_{41}O_3N_2Si_2$ [M+H]: 425.2656; found: 425.2657.

The synthesis of compound 4i

1-((2*R*,5*R*,6*R*)-5-(benzyloxy)-6-(benzyloxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)-1*H*-imidazole (4i)



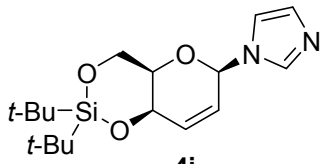
4i

Following the general procedure, the reaction of 4,6-dibenzyl galactal **1i** (65.2 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred

for 2 h at rt. Then the desired product **4i**[9] was obtained by column chromatography on silica gel (eluted with MeOH/DCM=1:60) in 89% yield as colorless oil. $[\alpha]_D^{23}$ –81.2 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 3030, 2918, 2868, 1614, 1495, 1454, 1269, 1069 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.71 (dd, J_1 = 10.0, J_2 = 6.6 Hz, 1H), 3.75 (dd, J_1 = 10.0, J_2 = 5.6 Hz, 1H), 3.86-3.92 (m, 1H), 4.03 (td, J_1 = 6.4, J_2 = 2.3 Hz, 1H), 4.50 (d, J = 11.9 Hz, 1H), 4.58 (d, J = 11.9 Hz, 1H), 4.61 (d, J = 11.9 Hz, 1H), 4.68 (d, J = 11.9 Hz, 1H), 5.91-5.98 (m, 2H), 6.30 (ddd, J_1 = 10.0, J_2 = 5.2, J_3 = 1.4 Hz, 1H), 7.04-7.10 (m, 2H), 7.26-7.37 (m, 10H), 7.66 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 67.1, 69.3, 71.0, 73.6, 76.1, 80.5, 117.5, 127.6, 127.7(2C), 127.8, 128.3, 128.4, 129.3, 129.4, 129.6, 136.5, 137.8, 138.1 ppm; HRMS (ESI) calcd. for $C_{23}H_{25}O_3N_2$ [M+H]: 377.1865; found: 377.1866.

The synthesis of compound 4j

1-((4a*R*,6*R*,8a*R*)-2,2-di-*tert*-butyl-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3,2]dioxasilin-6-yl)-1*H*-imidazole (4j)

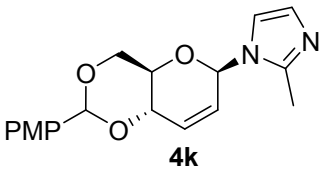


4j

Following the general procedure, the reaction of 4,6- di-*tert*-butylsilyl galactal **1j**[10] (57.3 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4j** was obtained by column chromatography on silica gel (eluted with MeOH/DCM=1:60) in 83% yield as a white solid. M.p. 118-120 °C; $[\alpha]_D^{23}$ –39.5 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2933, 2859, 1614, 1497, 1474, 1263, 1146, 1070 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.97 (s, 9H), 1.06 (s, 9H), 3.67-3.72 (m, 1H), 4.17 (dd, J_1 = 12.8, J_2 = 1.6 Hz, 1H), 4.36 (dd, J_1 = 12.8, J_2 = 2.3 Hz, 1H), 4.50-4.55 (m, 1H), 5.92-5.97 (m, 2H), 6.30-6.37 (m, 1H), 7.06 (s, 2H), 7.66 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3, 23.1, 27.1, 27.4, 64.8, 66.2, 73.2, 81.0, 117.9, 127.0, 129.5, 132.2, 136.8 ppm; HRMS (ESI) calcd. for $C_{17}H_{29}O_3N_2Si$ [M+H]: 337.1947; found: 337.1947.

The synthesis of compound 4k

1-((4a*R*,6*R*,8a*S*)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-2-methyl-1*H*-imidazole (4k)

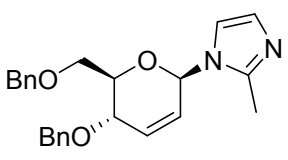


4k

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), 1,1'-Carbonylbis(2-methylimidazole) (57.1 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4k** was obtained by column chromatography on silica gel (eluted with MeOH/DCM=1:40) in 96% yield as a white solid. M.p. 136-138 °C; $[\alpha]_D^{23}$ +66.9 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2970, 2933, 2879, 1614, 1517, 1417, 1249, 1092 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): *δ* 2,46 (s, 3H), 3.78-3.86 (m, 4H), 3.90 (ddd, J_1 = 10.3, J_2 = 8.4, J_3 = 4.4 Hz, 1H), 4.28 (dd, J_1 = 10.0, J_2 = 4.2 Hz, 1H), 4.36-4.42 (m, 1H), 5.59 (s, 1H), 5.77 (ddd, J_1 = 10.3, J_2 = 2.4, J_3 = 2.0 Hz, 1H), 6.08-6.12 (m, 1H), 6.35 (d, J = 10.3 Hz, 1H), 6.88-6.93 (m, 4H), 7.41-7.46 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 13.1, 55.2, 68.6, 71.5, 74.1, 80.1, 102.0, 113.6, 116.7, 125.8, 127.4, 127.5, 129.4, 132.2, 145.1, 160.2 ppm; HRMS (ESI) calcd. for $C_{18}H_{21}O_4N_2$ [M+H]: 329.1501; found: 329.1501.

The synthesis of compound 4l

1-((2*R*,5*S*,6*R*)-5-(benzyloxy)-6-(benzyloxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)-2-methyl-1*H*-imidazole (4l)



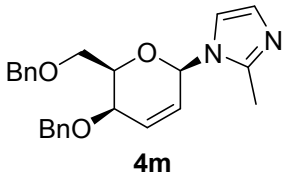
4l

Following the general procedure, the reaction of 4,6-dibenzyl glucal **1b** (65.2 mg, 0.2 mmol), 1,1'-Carbonylbis (2-methylimidazole) (57.1 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4l** was obtained by column chromatography on silica gel (eluted with MeOH/DCM=1:40) in 92% yield as yellow oil. $[\alpha]_D^{23}$ +83.9 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 3030, 2920, 2866, 1614, 1531, 1454, 1417, 1273, 1092 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): *δ* 2.44 (m, 3H), 3.68 (dd, J_1 = 11.0, J_2 = 5.1 Hz, 1H), 3.74 (dd, J_1

= 11.0, J_2 = 2.0 Hz, 1H), 3.86-3.92 (m, 1H), 4.14-4.20 (m, 1H), 4.47-4.58 (m, 3H), 4.64 (d, J = 11.4 Hz, 1H), 5.78-5.83 (m, 1H), 5.91-5.95 (m, 1H), 6.21-6.27 (m, 1H), 6.87 (s, 1H), 6.88 (s, 1H), 7.24-7.37 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.2, 69.0, 69.5, 71.7, 73.4, 77.7, 79.6, 117.0, 126.2, 127.2, 127.6, 127.7, 127.9(2C), 128.3, 128.4, 131.6, 137.5, 137.9, 145.1 ppm; HRMS (ESI) calcd. for $C_{24}H_{27}O_3N_2$ [M+H]: 391.2022; found: 391.2021.

The synthesis of compound 4m

1-((2*R*,5*R*,6*R*)-5-(benzyloxy)-6-(benzyloxymethyl)-5,6-dihydro-2*H*-pyran-2-yl)-2-methyl-1*H*-imidazole (4m)

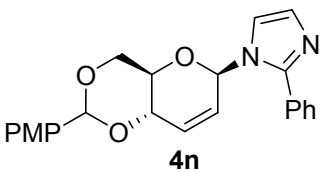


4m

Following the general procedure, the reaction of 4,6-dibenzyl galactal **1i** (65.2 mg, 0.2 mmol), 1,1'-Carbonylbis (2-methylimidazole) (57.1 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4m** was obtained by column chromatography on silica gel (eluted with MeOH/DCM=1:40) in 94% yield as yellow oil. $[\alpha]_D^{23}$ −82.6 (*c* 1.0, $CHCl_3$); IR (neat) *v*: 2920, 2868, 1614, 1537, 1497, 1545, 1417, 1273, 1097 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.46 (m, 3H), 3.74 (dd, J_1 = 10.0, J_2 = 6.5 Hz, 1H), 3.82 (dd, J_1 = 10.0, J_2 = 5.7 Hz, 1H), 3.89-3.94 (m, 1H), 4.06 (td, J_1 = 6.2, J_2 = 2.3 Hz, 1H), 4.53 (d, J = 11.8 Hz, 1H), 4.61 (d, J = 11.8 Hz, 1H), 4.63 (d, J = 11.9 Hz, 1H), 4.70 (d, J = 11.9 Hz, 1H), 5.88-5.92 (m, 1H), 5.98 (dd, J_1 = 10.2, J_2 = 1.2 Hz, 1H), 6.33 (ddd, J_1 = 10.1, J_1 = 5.3, J_2 = 1.8 Hz, 1H), 6.93 (d, J = 1.2 Hz, 1H), 6.98 (d, J = 1.2 Hz, 1H), 7.29-7.40 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.3, 67.1, 69.3, 71.1, 73.6, 76.2, 79.8, 117.3, 127.3, 127.6, 127.7(2C), 128.4, 129.1, 129.6, 137.9, 138.2, 145.1 ppm; HRMS (ESI) calcd. for $C_{24}H_{27}O_3N_2$ [M+H]: 391.2022; found: 391.2022.

The synthesis of compound 4n

1-((4a*R*,6*R*,8a*S*)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-2-phenyl-1*H*-imidazole (4n)



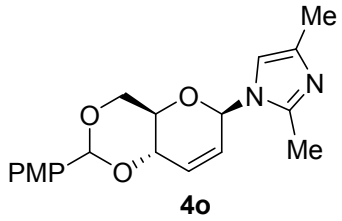
4n

Following the general procedure, the reaction of 4,6-*para*-

methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), 1,1'-Carbonylbis(2-phenylimidazole) (94.3 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4n** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:1) in 86% yield as a white solid. M.p. 186-188 °C; $[\alpha]_D^{23}$ –38.5 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2933, 2868, 1614, 1517, 1467, 1250, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.80 (s, 3H), 3.84-3.94 (m, 2H), 4.29-4.39 (m, 1H), 4.40-4.48 (m, 1H), 5.61 (s, 1H), 5.73 (dt, J_1 = 10.3, J_2 = 2.1 Hz, 1H), 6.16-6.21 (m, 1H), 6.32 (d, J = 10.2 Hz, 1H), 6.88-6.93 (m, 2H), 7.13 (d, J = 1.2 Hz, 1H), 7.16 (d, J = 1.2 Hz, 1H), 7.40-7.51 (m, 5H), 7.68-7.74 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.3, 68.7, 71.6, 74.2, 80.4, 102.1, 113.7, 117.7, 126.3, 127.5, 128.6, 129.0, 129.1, 129.2, 129.4, 129.9, 132.0, 148.3, 160.2 ppm; HRMS (ESI) calcd. for $C_{23}H_{23}O_4N_2$ [M+H]: 391.1658; found: 391.1658.

The synthesis of compound 4o

1-((4a*R*,6*R*,8a*S*)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-2,4-dimethyl-1*H*-imidazole (4o)



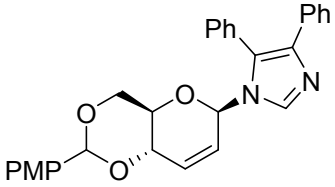
4o

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), 1,1'-Carbonylbis(2,4-dimethylimidazole) (65.5 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4o** was obtained by column chromatography on silica gel (eluted with DCM/MeOH=50:1) in 92% yield as a yellow oil. $[\alpha]_D^{21}$ +78.9 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2969, 2935, 2870, 1616, 1521, 1469, 1249, 1097 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 2.16 (s, 3H), 2.42 (s, 3H), 3.77-3.91 (m, 5H), 4.27 (dd, J_1 = 9.6 Hz, J_2 = 3.8 Hz, 1H), 4.34-4.40 (m, 1H), 5.58 (s, 1H), 5.74 (dt, J_1 = 10.2, J_2 = 2.0 Hz, 1H), 6.00-6.05 (m, 1H), 6.32 (d, J = 10.2 Hz, 1H), 6.62 (s, 1H), 6.87-6.93 (m, 2H), 7.40-7.46 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.9, 13.4, 55.2, 68.7, 71.4, 74.2, 80.1, 102.1, 112.8, 113.7, 126.1, 127.4, 129.5, 132.0, 136.5, 144.4, 160.2 ppm; HRMS (ESI) calcd. for

$C_{19}H_{23}O_4N_2$ [M+H]: 343.1658; found: 343.1655.

The synthesis of compound 4p

1-((4a*R*,6*R*,8a*S*)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-4,5-diphenyl-1*H*-imidazole (4p)

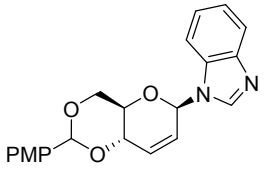


4p

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), 1,1'-Carbonylbis(4,5-diphenylimidazole) (140.0 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4p** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:1) in 75% yield as a yellow solid. M.p. 189-191 °C; $[\alpha]_D^{21}$ +5.8 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2983, 2940, 2874, 1620, 1523, 1467, 1253, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 3.73-3.86 (m, 5H), 4.26 (dd, J_1 = 9.6 Hz, J_2 = 3.8 Hz, 1H), 4.28-4.33 (m, 1H), 5.56 (s, 1H), 5.76 (dt, J_1 = 10.2, J_2 = 2.2 Hz, 1H), 5.84-5.88 (m, 1H), 6.27 (d, J = 10.2 Hz, 1H), 6.86-6.91 (m, 2H), 7.12-7.23 (m, 3H), 7.38-7.49 (m, 9H), 7.76 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.3, 68.7, 71.6, 74.1, 79.5, 102.1, 113.7, 125.8, 126.6, 126.8, 127.5, 128.1(2C), 128.9(2C), 129.5, 129.8, 131.2, 132.4, 134.1, 135.3, 138.6, 160.2 ppm; HRMS (ESI) calcd. for $C_{29}H_{27}O_4N_2$ [M+H]: 467.1971; found: 467.1975.

The synthesis of compound 4q

1-((4aR,6R,8aS)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-1H-benzo[d]imidazole (4q)



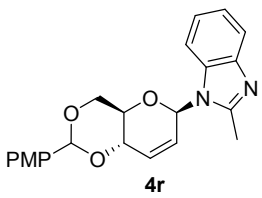
4q

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), 1,1'-Carbonylbisbenzimidazole (78.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4q** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:1) in 85% yield as a white solid.a light yellow oil. $[\alpha]_D^{23}$

= +63.2 (c = 1.0 in $CHCl_3$); IR (neat) ν: 2968, 2937, 2871, 1615, 1520, 1466, 1254, 1095 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.77-3.87 (m, 4H), 4.00 (ddd, J_1 = 10.2 Hz, J_2 = 8.6 Hz, J_3 = 4.7 Hz, 1H), 4.30 (dd, J_1 = 10.4 Hz, J_2 = 4.6 Hz, 1H), 7.92-8.40 (m, 1H), 4.47-4.54 (m, 1H), 5.63 (s, 1H), 5.86-5.95 (m, 1H), 6.41-6.50 (m, 2H), 6.88-6.95 (m, 2H), 7.27-7.36 (m, 2H), 7.40-7.48 (m, 2H), 7.48-7.58 (m, 1H), 7.76-7.89 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 68.7, 71.7, 74.3, 80.5, 102.2, 110.7, 113.7, 120.7, 122.9, 123.5, 125.6, 127.5, 129.5, 133.2, 160.3 ppm; HRMS (ESI) calcd. for $C_{21}H_{21}N_2O_4$ $[M+H]^+$: 365.1501, found: 365.1497.

The synthesis of compound 4r

1-((4aR,6R,8aS)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-2-methyl-1H-benzo[d]imidazole (4r)



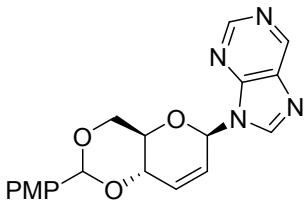
4r

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), 1,1'-Carbonylbis(2-methylbenzimidazole) (87.1 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4r** was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:1) in 78% yield as light yellow oil. $[\alpha]_D^{23}$ = +132.3 (c = 1.0 in $CHCl_3$); IR (neat) ν: 2935, 2870, 1614, 1518, 1467, 1253, 1099 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.68 (s, 3H), 3.81 (s, 3H), 3.86 (t, J = 10.3 Hz, 1H), 4.02 (ddd, J_1 = 10.2 Hz, J_2 = 8.5 Hz, J_3 = 4.6 Hz, 1H), 4.31 (dd, J_1 = 10.3 Hz, J_2 = 4.6 Hz, 1H), 4.51-4.59 (m, 1H), 5.66 (s, 1H), 5.81-5.88 (m, 1H), 6.37-6.46 (m, 2H), 6.88-6.96 (m, 2H), 7.18-7.28 (m, 2H), 7.39-7.49 (m, 3H), 7.64-7.73 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 55.3, 68.7, 71.9, 74.5, 80.4, 102.3, 110.7, 113.8, 119.4, 122.5(2C), 126.5, 127.5, 129.5, 132.1, 133.8, 142.8, 151.5, 160.3 ppm; HRMS (ESI) calcd. for $C_{22}H_{23}N_2O_4$ $[M+H]^+$: 379.1658, found: 379.1669.

The synthesis of compound 4s

9-((4aR,6R,8aS)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-

d][1,3]dioxin-6-yl)-9H-purine (4s)

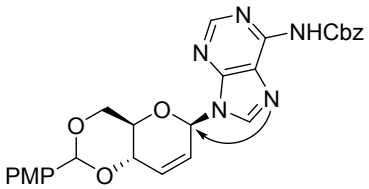


4s

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), 1,1'-Carbonylbis(2-methylbenzimidazole) (79.8 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4s** was obtained by column chromatography on silica gel (eluted with DCM/MeOH =50:1) in 83% yield as a colorless oil. $[\alpha]_D^{21}$ +34.0 (*c* 1.0, $CHCl_3$); IR (neat) *ν*: 2944, 2875, 1618, 1521, 1475, 1250, 1104 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.78-3.86 (m, 4H), 4.02 (ddd, J_1 = 10.2, J_2 = 8.5, J_3 = 4.7 Hz, 1H), 4.33 (dd, J_1 = 10.4, J_2 = 4.6 Hz, 1H), 4.47-4.53 (m, 1H), 5.63 (s, 1H), 5.90 (dt, J_1 = 10.2, J_2 = 2.2 Hz, 1H), 6.51 (d, J = 10.2 Hz, 1H), 6.81-6.84 (m, 1H), 6.88-6.94 (m, 2H), 7.42-7.47 (m, 2H), 8.22 (s, 1H), 9.04 (s, 1H), 9.18 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 68.5, 71.8, 74.0, 77.9, 102.2, 113.7, 124.5, 127.4, 129.3, 133.9, 134.1, 143.1, 148.9, 150.9, 153.0, 160.2 ppm; HRMS (ESI) calcd. for $C_{19}H_{19}N_4O_4$ $[M+H]^+$: 367.1406, found: 367.1401.

The synthesis of compound 4t

benzyl(9-((4aR,6R,8aS)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-9*H*-purin-6-yl)carbamate (4t)

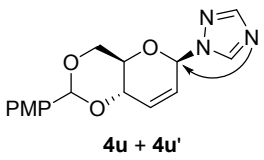


4t + 4t'

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), CDI analogue **2t** (169.4 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **4t** was obtained by column chromatography on silica gel (eluted with DCM/MeOH =50:1) in 42% yield as yellow oil. ^1H NMR of the major product (400 MHz, $CDCl_3$): δ 3.76-3.87 (m, 4H), 3.99 (ddd, J_1 = 10.2, J_2 = 8.6, J_3 = 4.7 Hz, 1H), 4.32 (dd, J_1 = 10.3, J_2 = 4.6 Hz, 1H), 4.42-4.48 (m, 1H), 5.30 (s, 2H), 5.61 (s, 1H), 5.80 (dt, J_1 = 10.3, J_2 = 2.3 Hz, 1H), 6.47 (d, J = 10.2 Hz, 1H), 6.71-6.75 (m, 1H), 6.88-6.94 (m, 2H), 7.33-7.46 (m, 7H),

8.05 (s, 1H), 8.80 (s, 1H), 8.97 (s, 1H) ppm; ^{13}C NMR of the major product (100 MHz, $CDCl_3$): δ 55.3, 67.8, 68.6, 71.8, 74.0, 78.2, 102.2, 113.7, 121.9, 124.5, 127.5, 128.5(2C), 128.6, 129.3, 133.9, 135.4, 140.8, 149.6, 151.0, 151.1, 153.3, 160.3 ppm; HRMS (ESI) calcd. for $C_{27}H_{26}N_5O_6[M+H]^+$: 516.1883, found: 516.1891.

The synthesis of compound 4u and 4u'

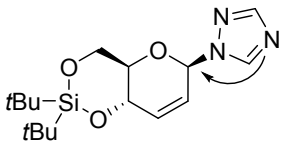


4u + 4u'

Following the general procedure, the reaction of 4,6-*para*-methoxybenzylidene glucal **1a** (52.8 mg, 0.2 mmol), 1,1'-carbonyl-di-(1,2,4-triazole) (49.3 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired products **4u** and **4u'** (an inseparable mixture with a ratio of 10:1) were obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:2) in 93% yield as a white solid. IR (neat) ν: 2933, 2887, 1614, 1516, 1375, 1252, 1103 cm^{-1}; ^{1}H NMR of the major product ($CDCl_3$, 400 MHz): δ 3.75-3.90 (m, 4H), 3.91-4.00 (m, 1H), 4.32 (dd, J_1 = 10.1, J_2 = 4.3 Hz, 1H), 4.42-4.49 (m, 1H), 5.61 (s, 1H), 5.87-5.94 (m, 1H), 6.38-6.48 (m, 2H), 6.87-6.97 (m, 2H), 7.39-7.50 (m, 2H), 8.01 (s, 1H), 8.27 (s, 1H) ppm; ^{13}C NMR of the major product ($CDCl_3$, 100 MHz): δ 55.3, 68.6, 71.7, 74.0, 83.0, 102.2, 113.7, 124.2, 127.5, 129.4, 133.3, 142.7, 152.4, 160.3 ppm; HRMS (ESI) calcd. for $C_{16}H_{18}O_4N_3$ [M+H]: 316.1297; found: 316.1297.

The synthesis of compound 4v and 4v'

Following the general procedure, the reaction of 4,6-di-*tert*-butylsilyl glucal **1c** (57.3 mg, 0.2 mmol), 1,1'-carbonyl-di-(1,2,4-triazole) (49.3 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired products **4v** and **4v'** (an inseparable mixture with a ratio of 5:1) were obtained by column chromatography on silica gel (eluted with *n*-hexane/EA=1:1) in 90% yield as a white solid. IR (neat) ν: 2964, 2932, 2884, 2859, 1635, 1504, 1473, 1277, 1130, 1094 cm^{-1}; ^{1}H NMR of the major product ($CDCl_3$, 400 MHz): δ 1.01 (s, 9H), 1.07 (s, 9H), 3.81-3.89 (m, 1H), 3.94 (t, J = 10.3 Hz, 1H), 4.21 (dd, J_1 = 9.8, J_2 = 4.8 Hz, 1H),

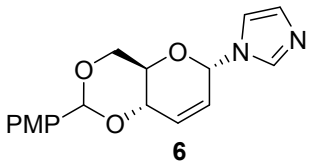


4v + 4v'

4.63-4.68 (m, 1H), 5.81-5.87 (m, 1H), 6.31-6.36 (m, 2H), 7.98 (s, 1H), 8.24 (s, 1H) ppm; ^{13}C NMR of the major product ($CDCl_3$, 100 MHz): δ 20.0, 22.6, 26.9, 27.3, 66.3, 69.1, 75.2, 82.8, 122.7, 136.5, 142.6, 152.2 ppm; HRMS (ESI) calcd. for $C_{16}H_{28}O_3N_3Si$ [M+H]: 338.1900; found: 338.1897.

The synthesis of compound 6

1-((4a*R*,6*S*,8a*S*)-2-(4-methoxyphenyl)-4,4a,6,8a-tetrahydropyrano[3,2-d][1,3]dioxin-6-yl)-1*H*-imidazole (6)



6

Following the general procedure, the reaction of compound **5** (52.8 mg, 0.2 mmol), CDI (48.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) in DCM (4 mL) was stirred for 2 h at rt. Then the desired product **6** (α:β=17:1) was obtained by column chromatography on silica gel (eluted with *n*-hexane/EA =1:2) in 80% yield as a white solid. IR (neat) ν: 2967, 2934, 2882, 1614, 1518, 1302, 1250, 1096 cm^{-1}; ^{1}H NMR of compound **6** (α-isomer) ($CDCl_3$, 400 MHz): δ 3.61-3.68 (m, 1H), 3.76 (t, J = 10.2 Hz, 1H), 3.80 (s, 3H), 4.7 (dd, J_1 = 10.2, J_2 = 4.6 Hz, 1H), 4.23-4.29 (m, 1H), 5.57 (s, 1H), 5.94 (dt, J_1 = 10.2, J_2 = 2.6 Hz, 1H), 5.98-6.02 (m, 1H), 6.46 (d, J = 10.2 Hz, 1H), 6.87-6.93 (m, 2H), 7.14 (s, 2H), 7.39-7.44 (m, 2H), 7.73 (s, 1H) ppm; ^{13}C NMR of compound **6** (α-isomer) ($CDCl_3$, 100 MHz): δ 55.3, 64.9, 69.0, 74.3, 78.1, 102.2, 113.7, 118.5, 123.4, 127.5, 129.4, 129.6, 133.5, 136.9, 160.3 ppm; HRMS (ESI) calcd. for $C_{17}H_{19}O_4N_2$ [M+H]: 315.1345; found: 315.1346.

Reference

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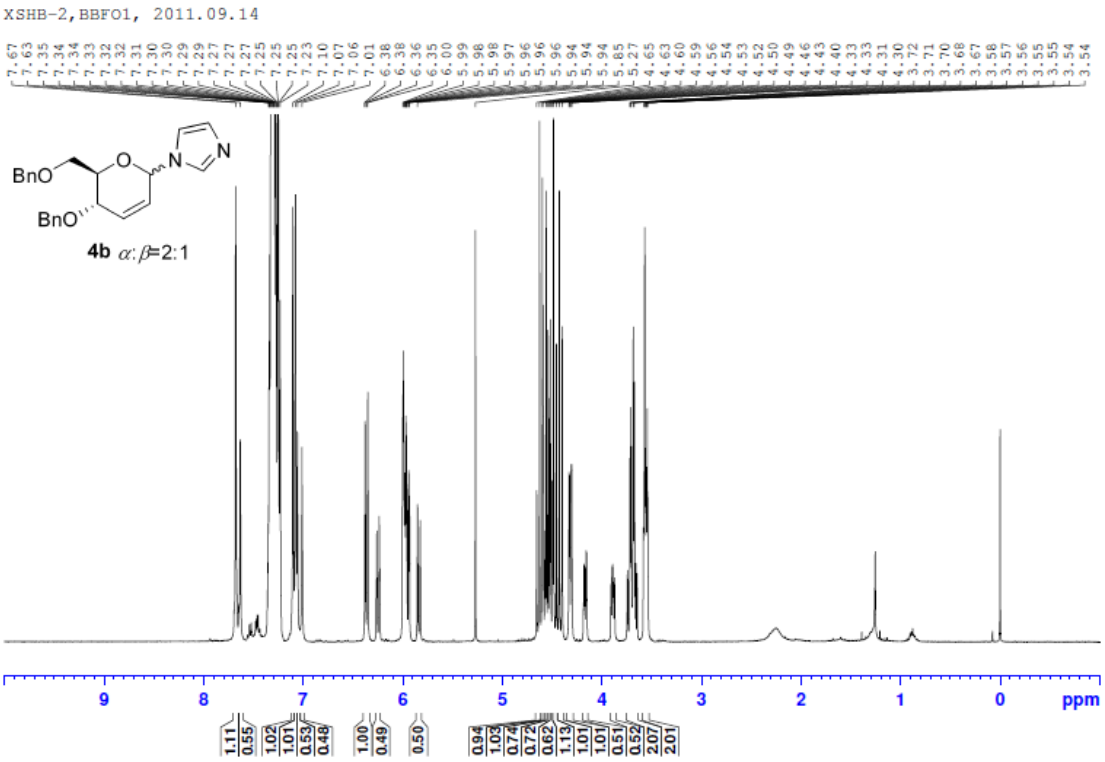
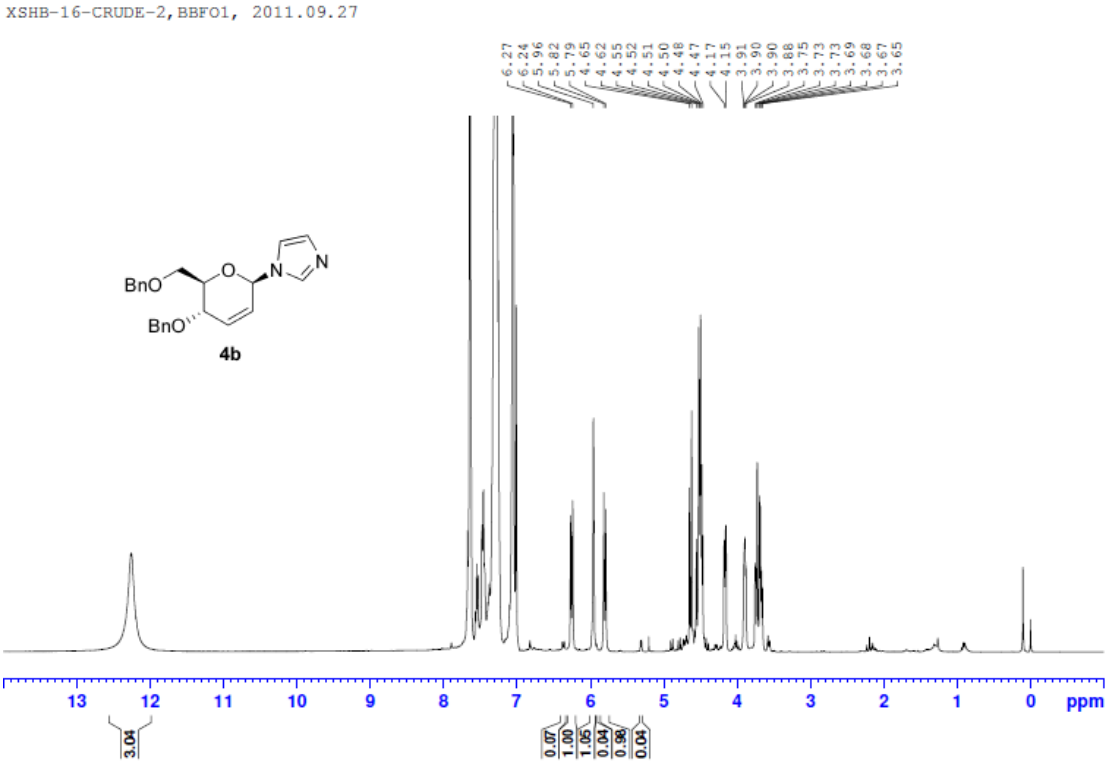
^{1}H NMR Spectral for 4b-4d with or without palladium catalyst

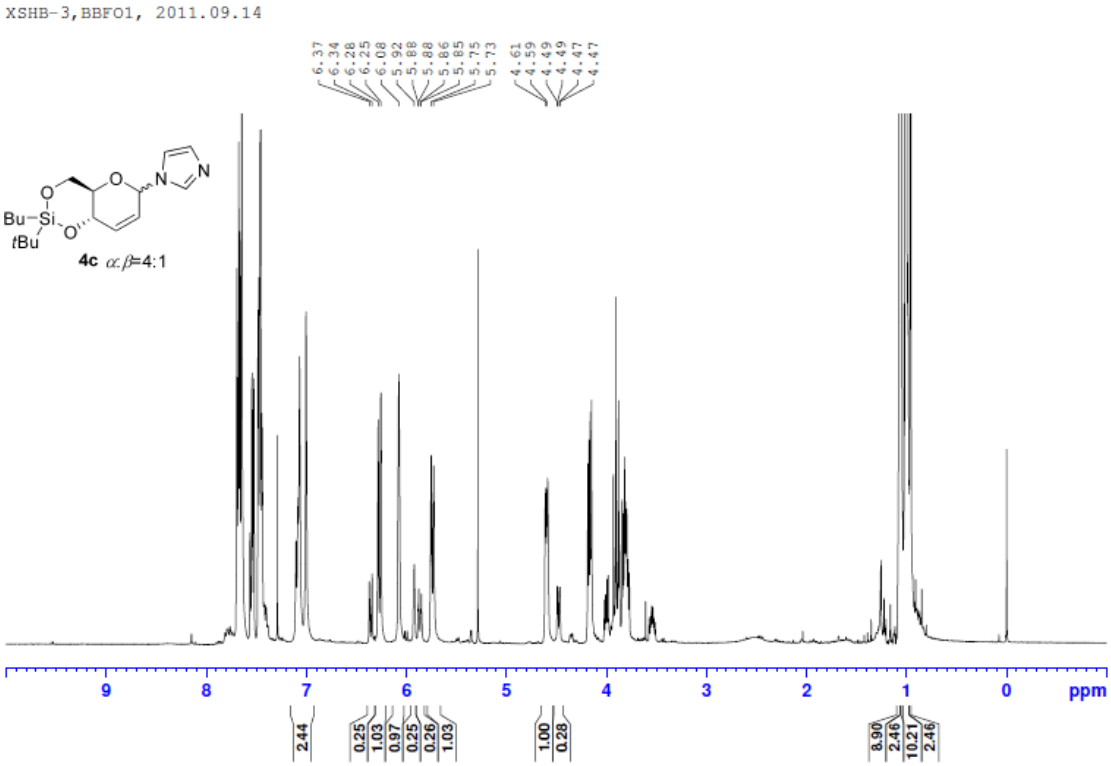
^{1}H NMR spectral of 4b without $Pd(PPh_3)_4$



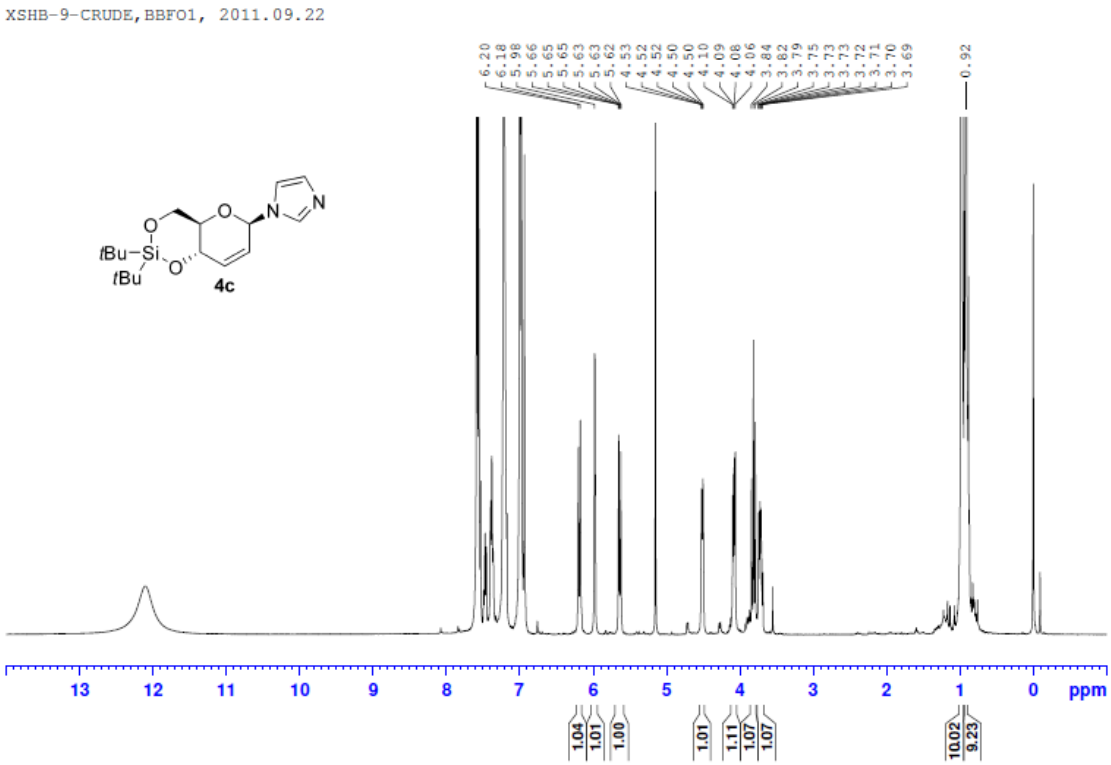
^{1}H NMR spectral of Crude 4b with $Pd(PPh_3)_4$



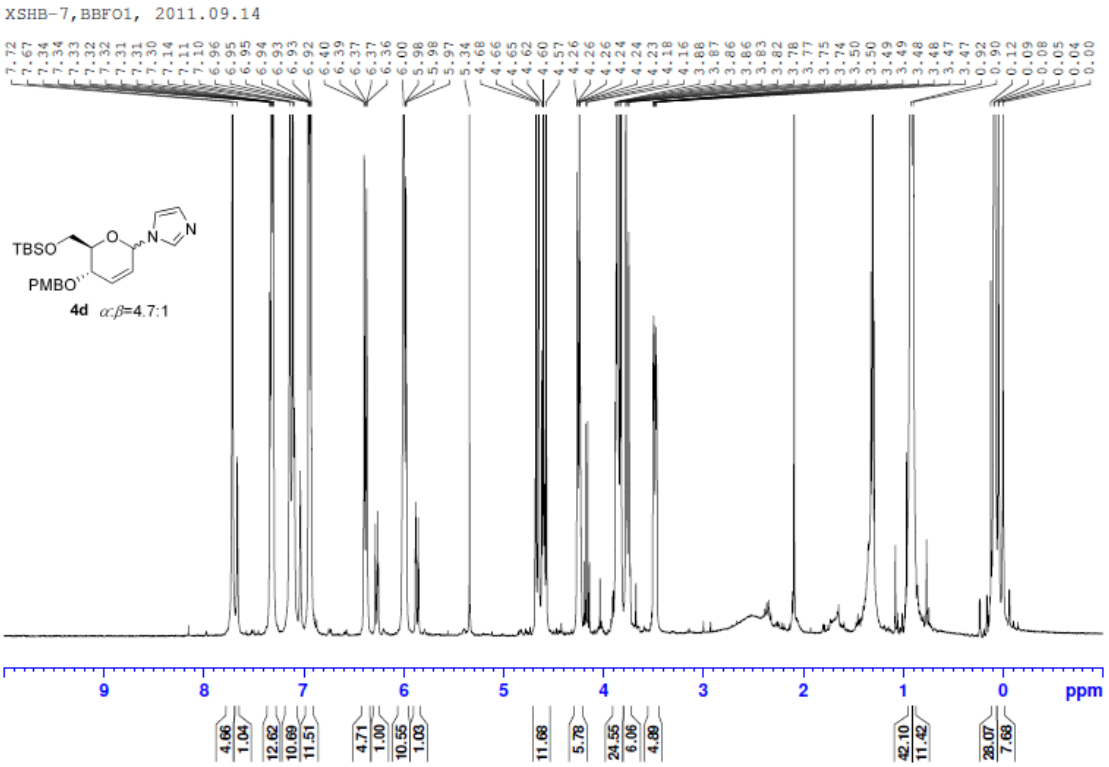
^{1}H NMR spectral of 4c without $Pd(PPh_3)_4$



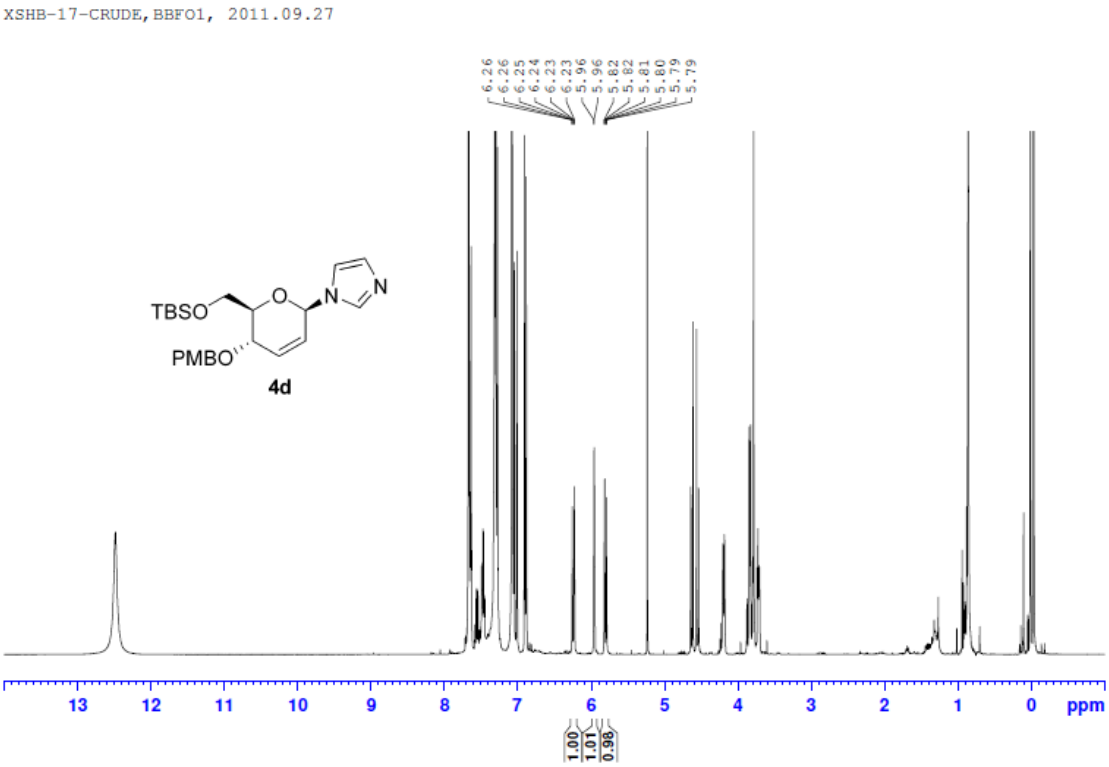
^{1}H NMR spectral of Crude 4c with $Pd(PPh_3)_4$



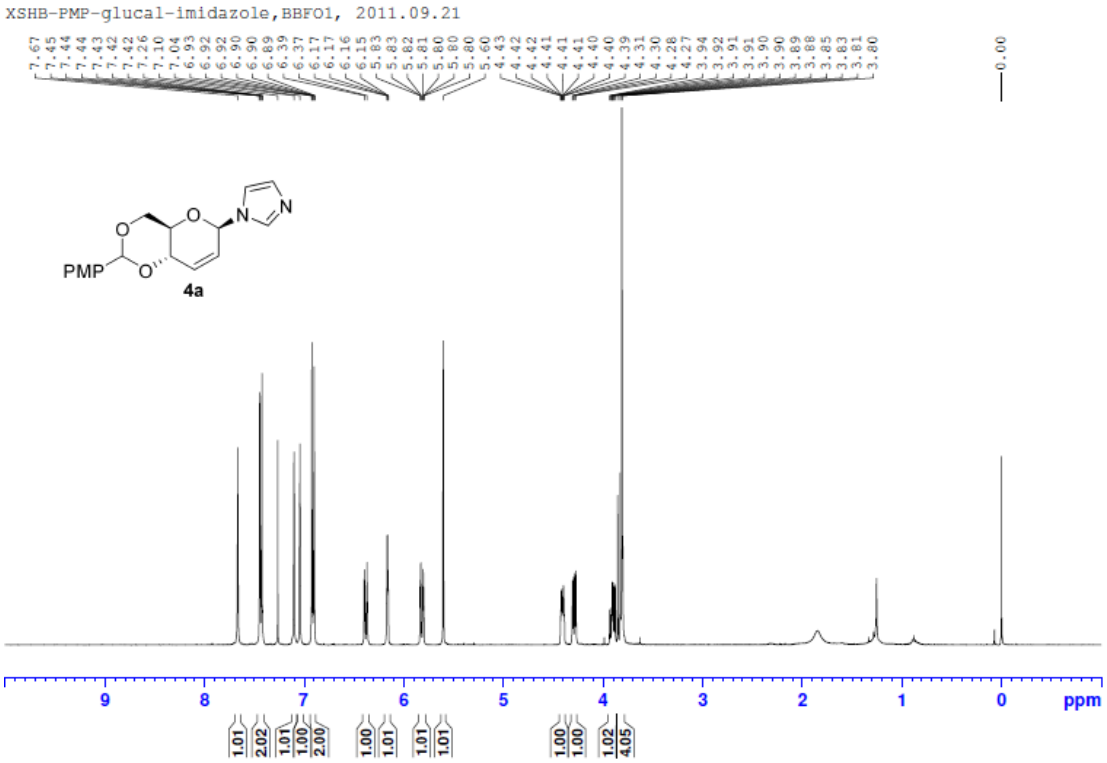
^{1}H NMR spectral of 4d without $Pd(PPh_3)_4$

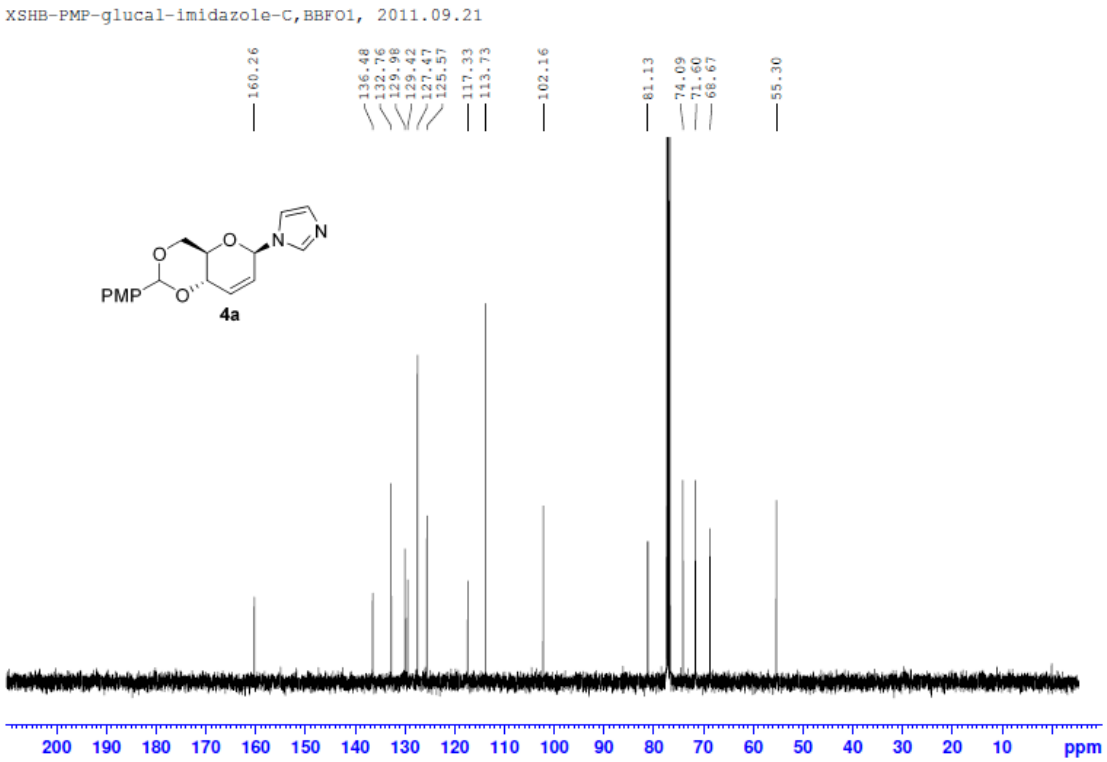


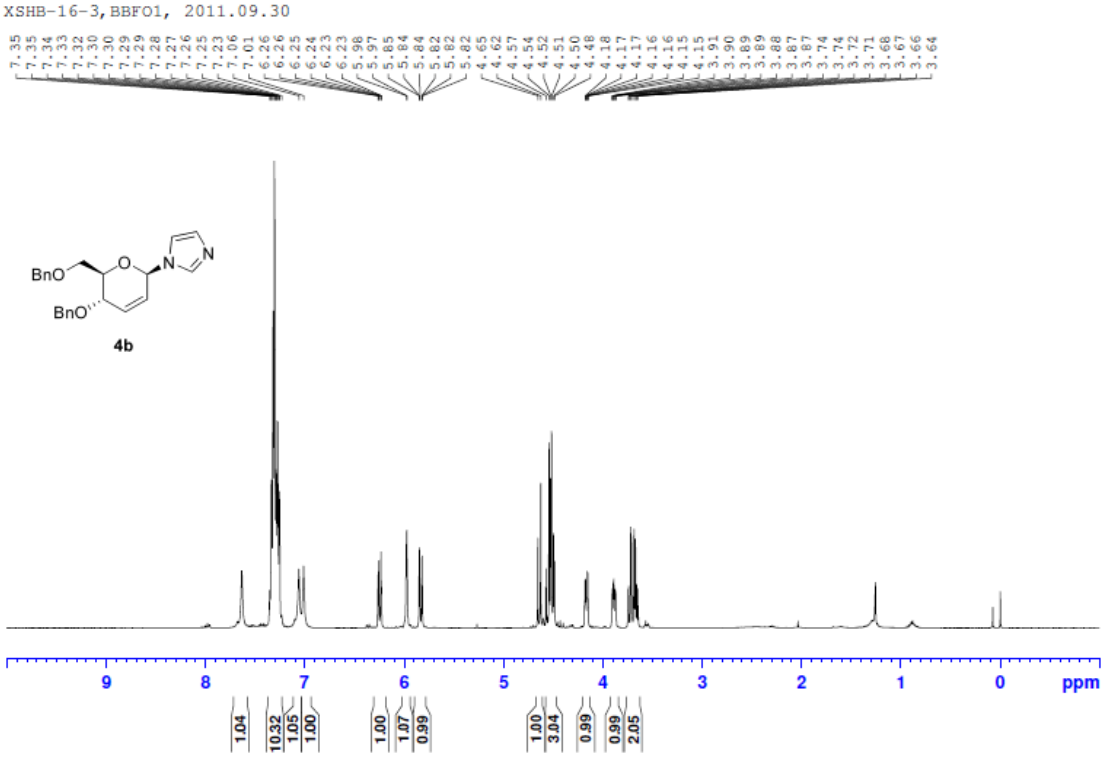
^{1}H NMR spectral of Crude 4d with $Pd(PPh_3)_4$



Spectral data for 4a-4p and 6 with palladium catalyst



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4b
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7
6
5
4
3
2
1
0
ppm
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1.05
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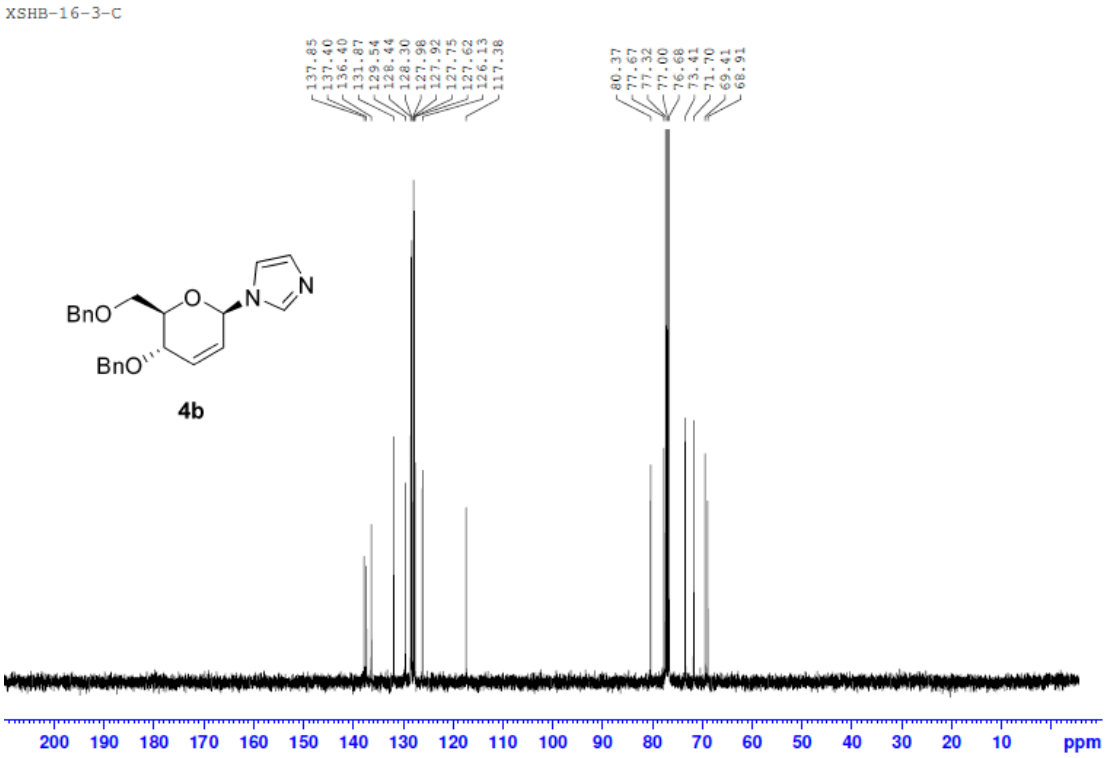
1.00
1.07
0.99
1.00
3.04
0.99
0.99
2.05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150
140
130
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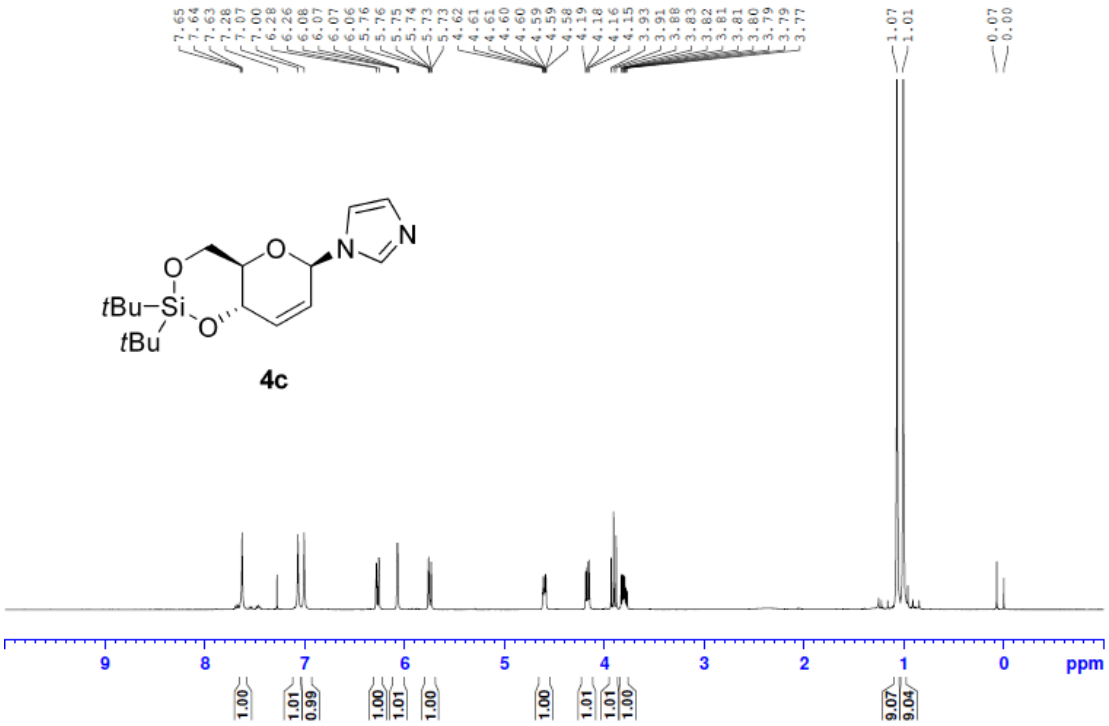
80
70
60
50
40
30
20
10
ppm

XSHB-12-Si-CDI,BBFO1, 2011.09.23



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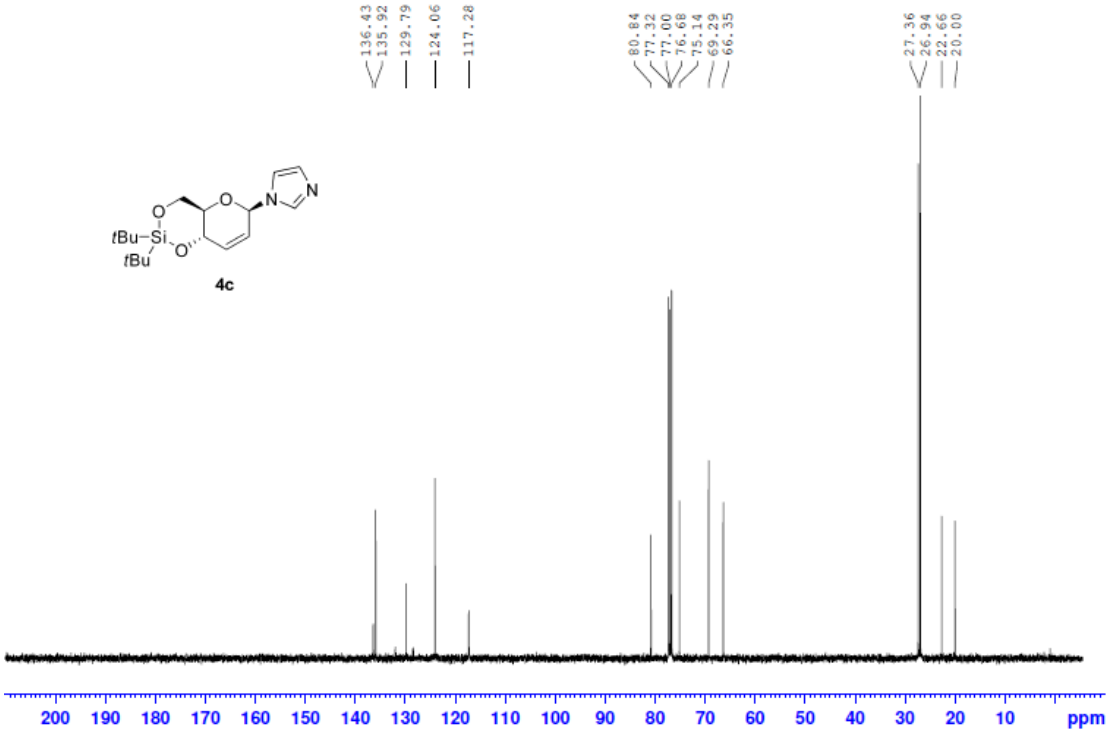
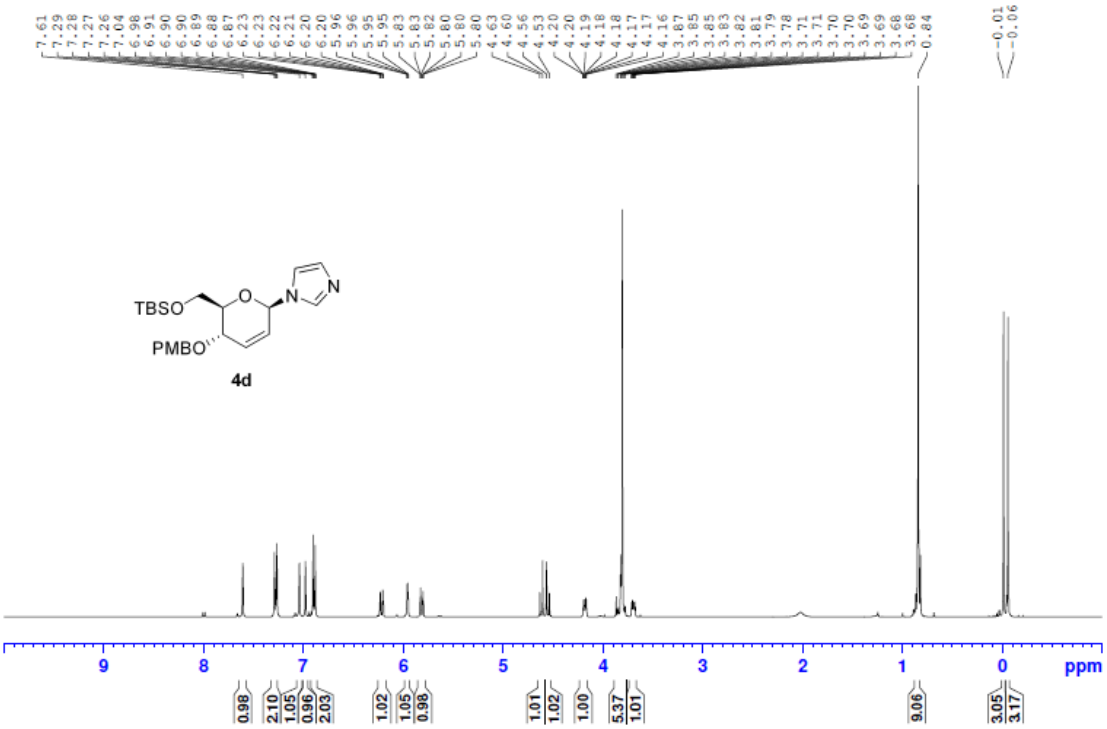
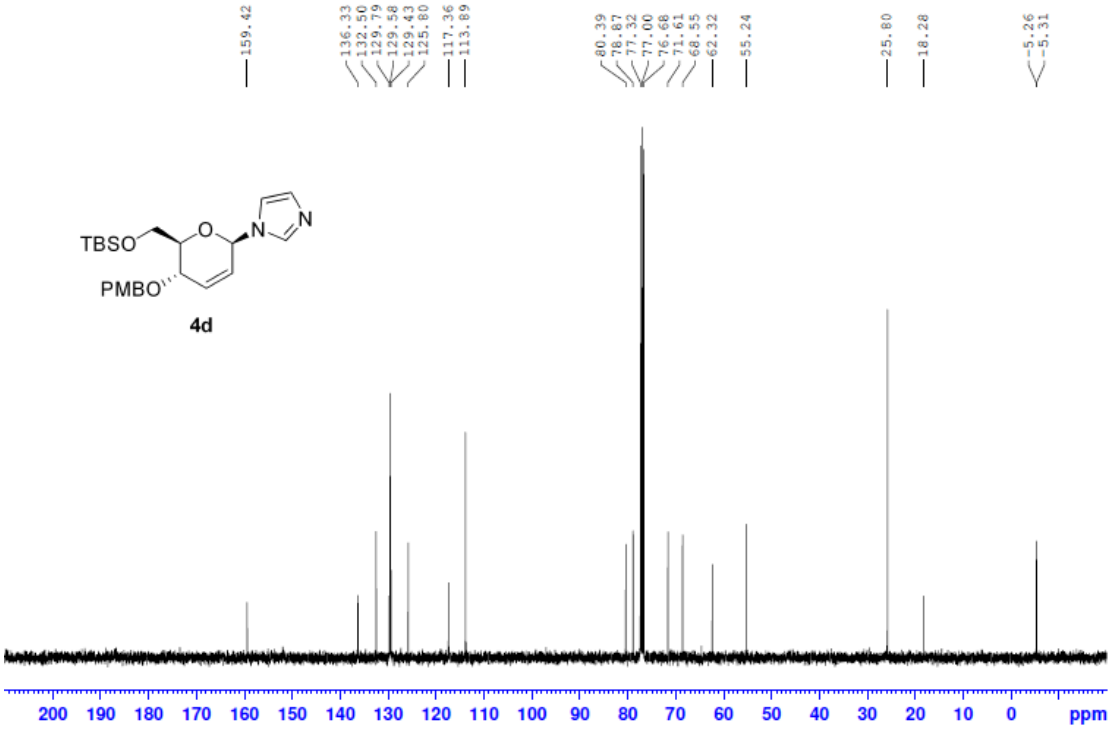


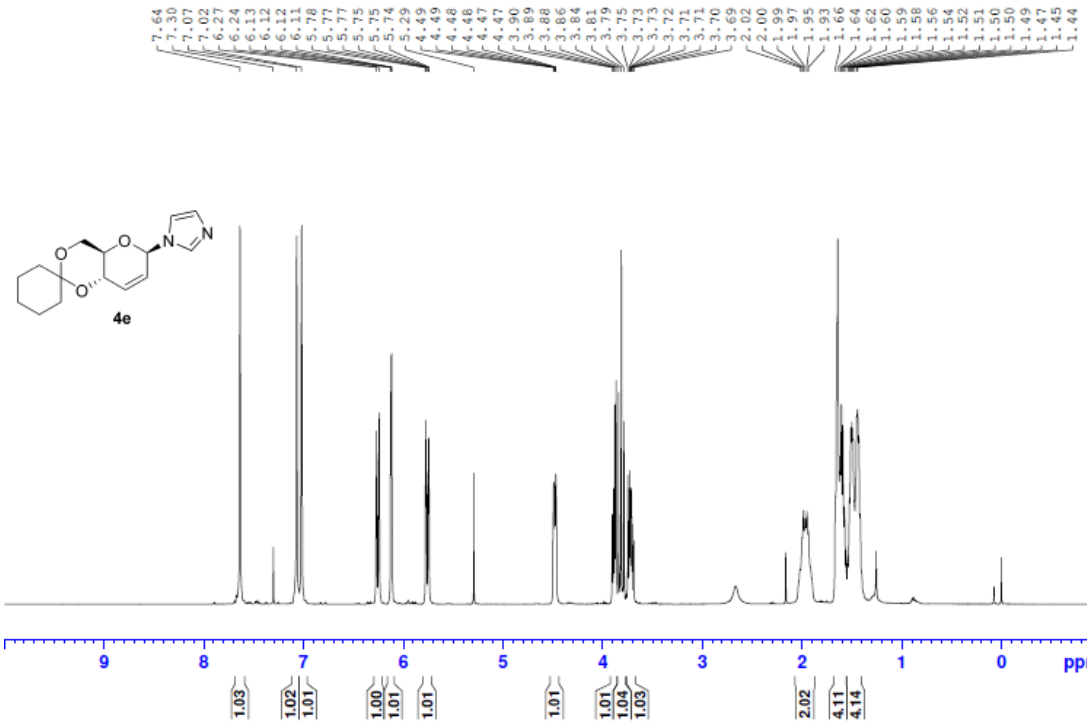
XSHB-17-1, 400 BBFO1, 1H, CDCl3



XSHB-17-1-C, 400 BBFO1, 1H, CDCl3



XSHB-18,BBFO1, 2011.09.28



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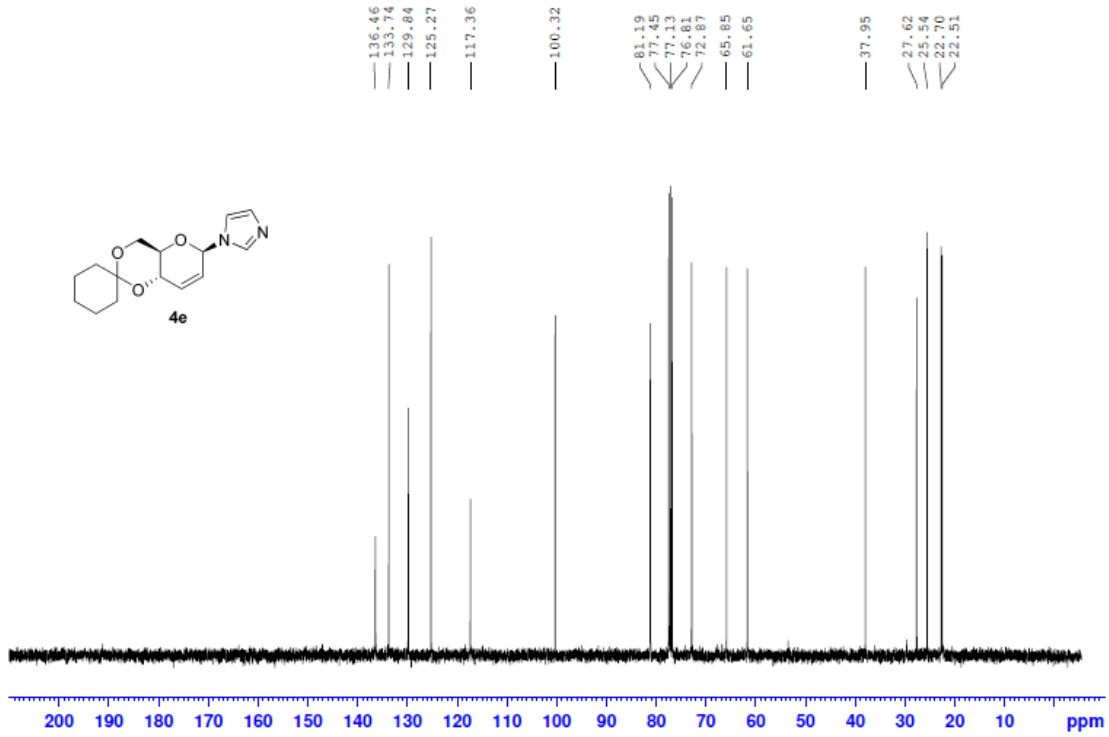
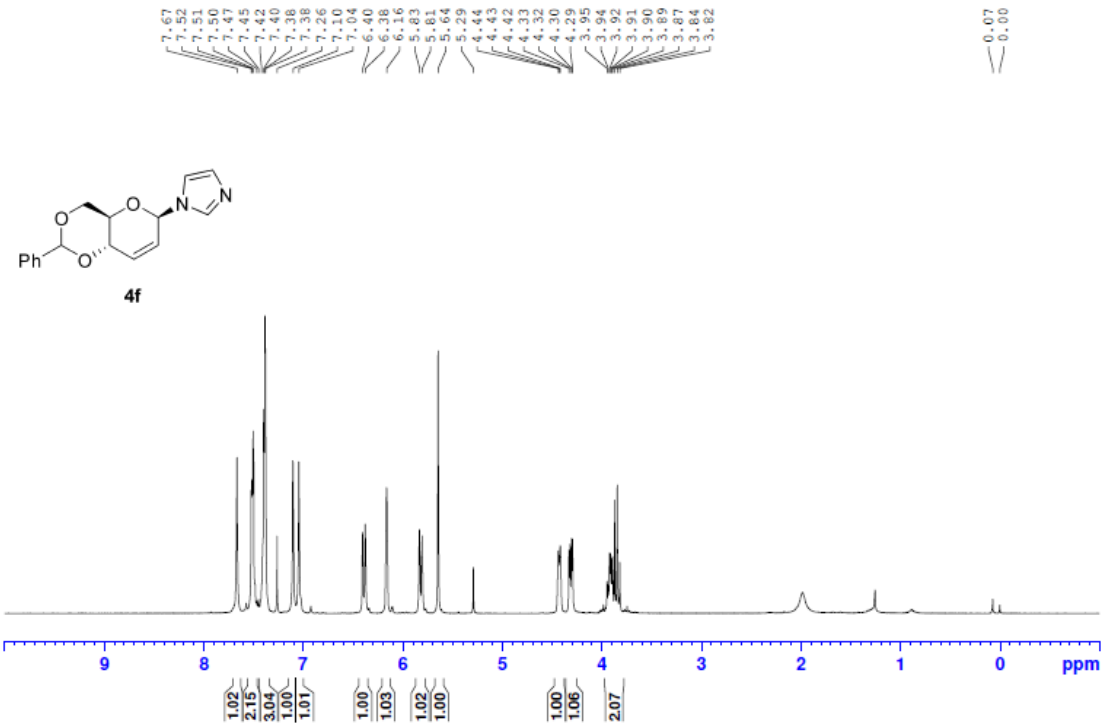
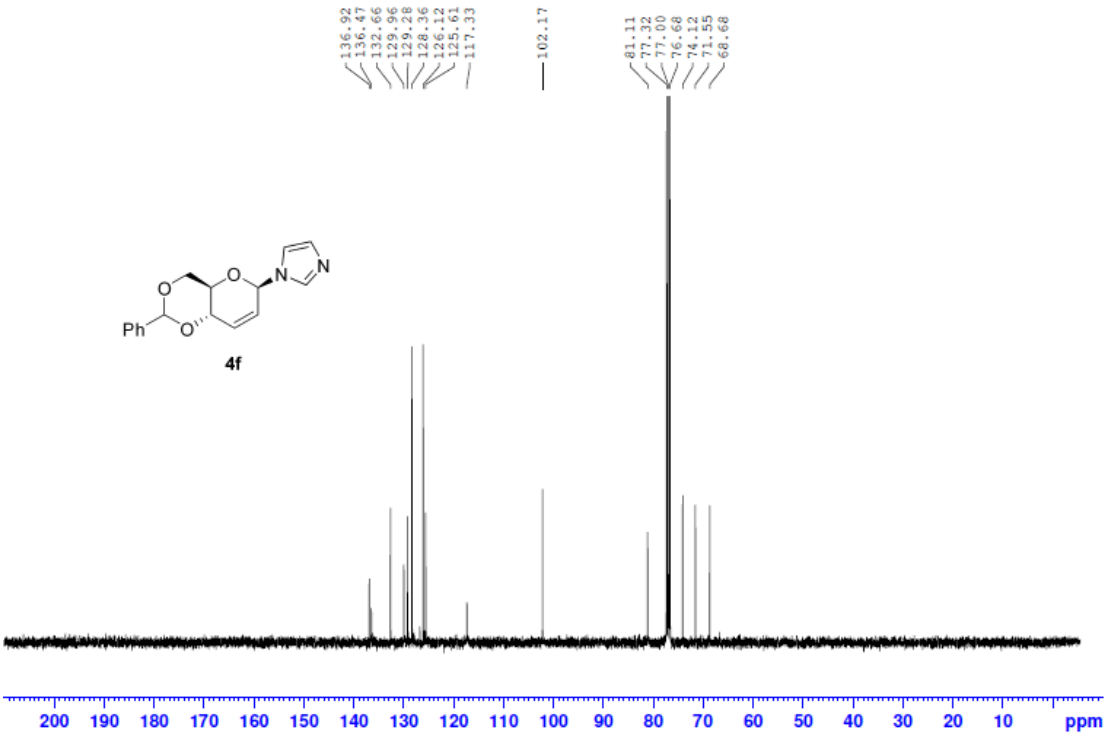


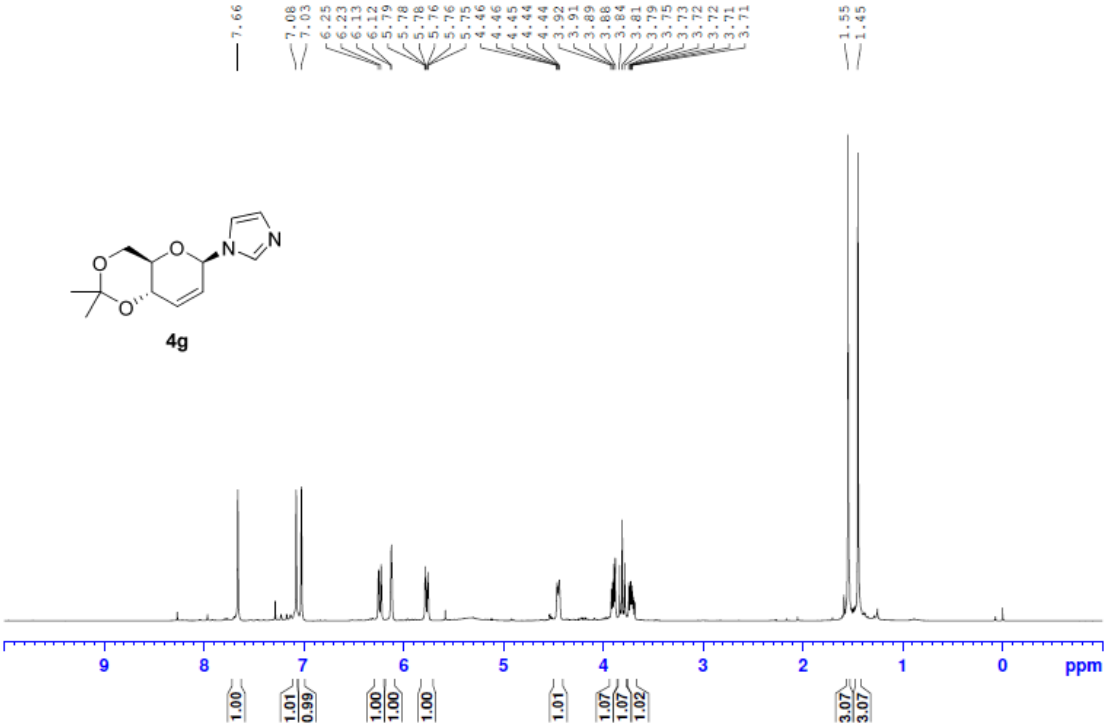
XSHB-34-3, 400 BBFO1, CDCl3



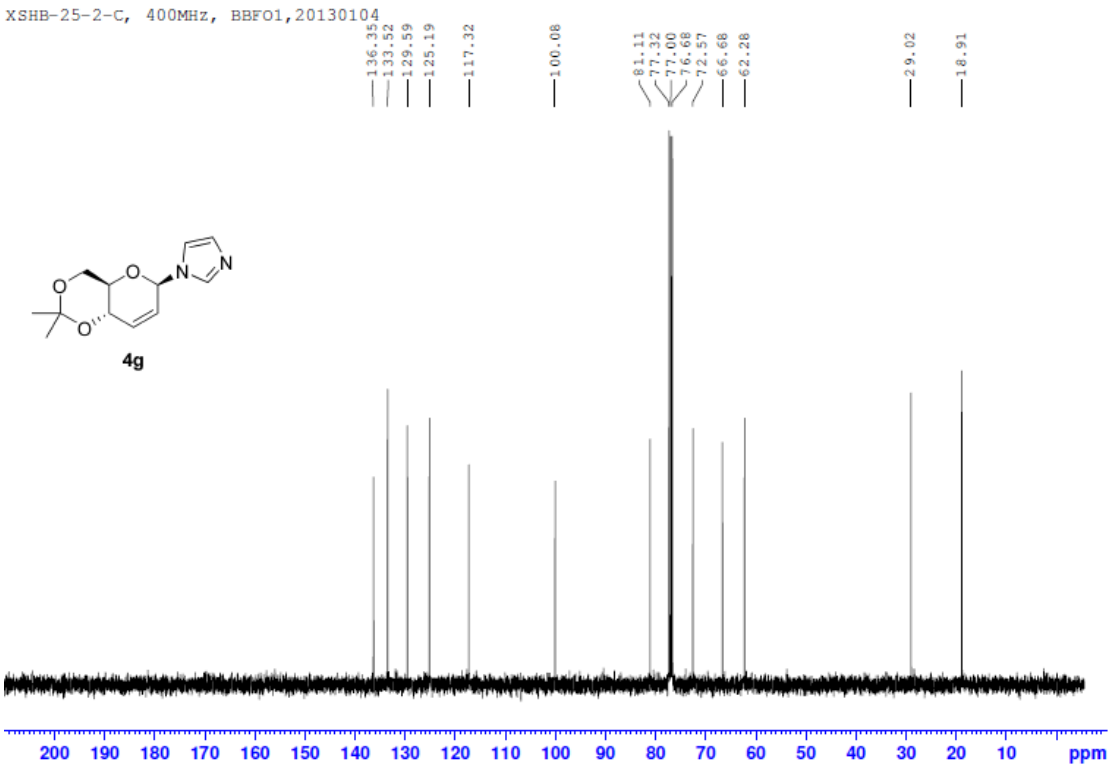
XSHB-34-C, 400 BBFO1, CDCl3



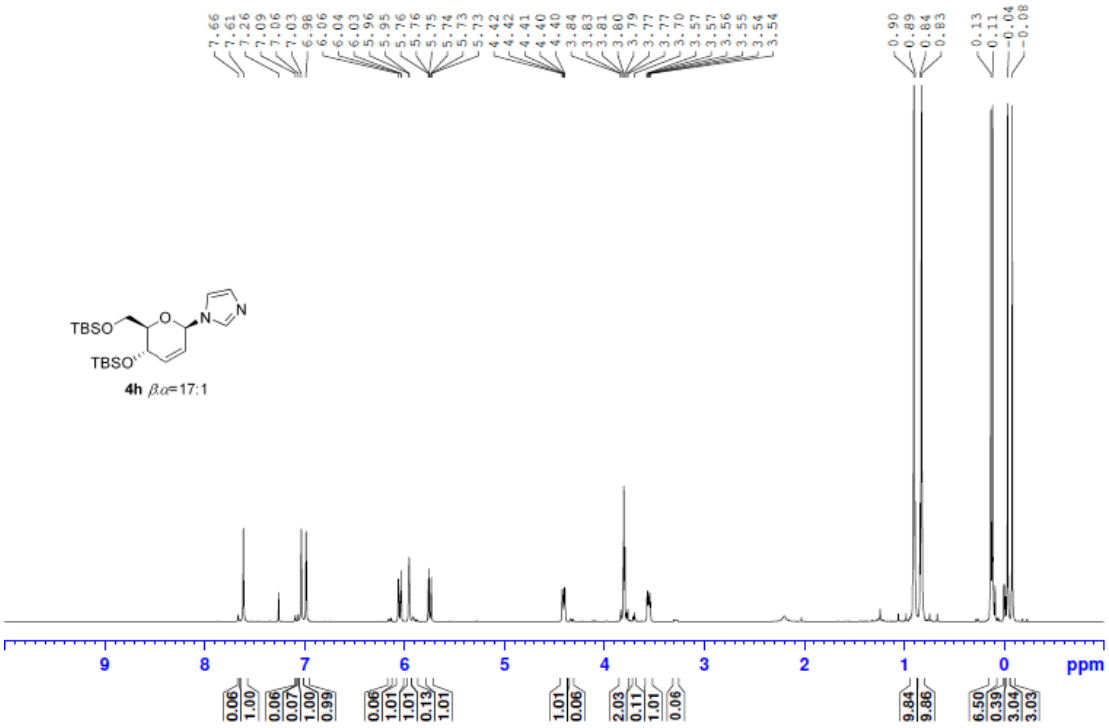
XSHB-25-2,400MHz,BBFO1,20130104



XSHB-25-2-C, 400MHz, BBFO1,20130104

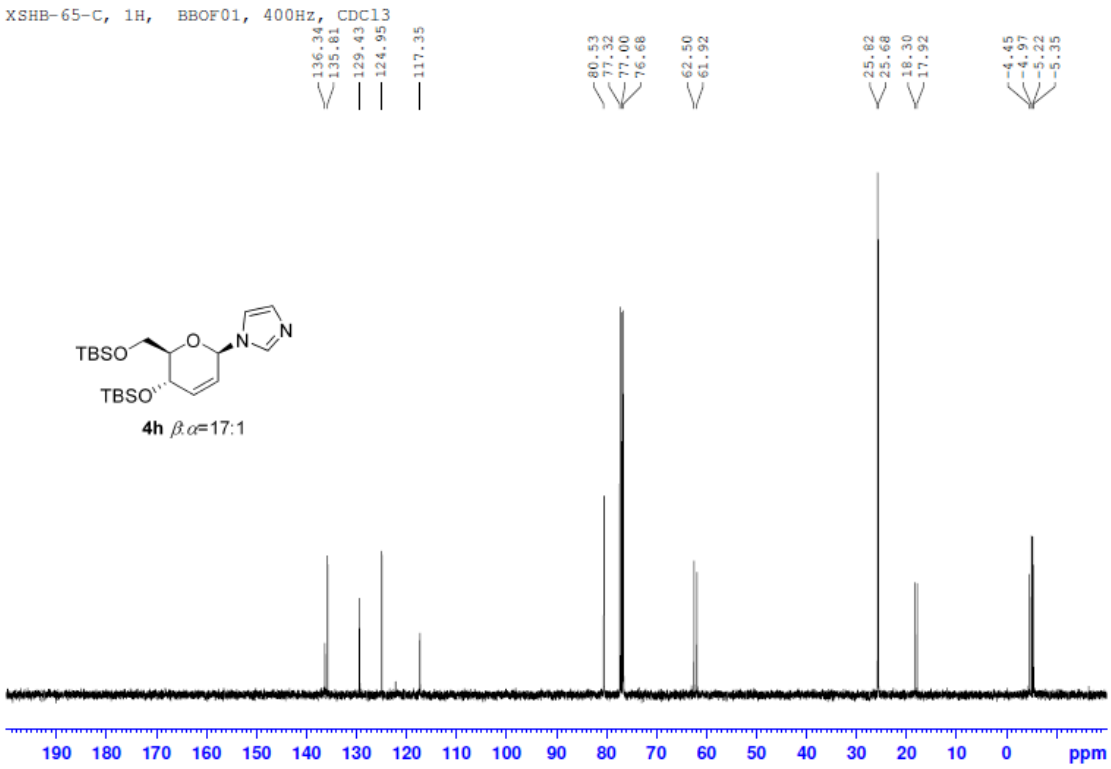


XSHB-65, 1H, BBOF01, 400Hz, CDCl3

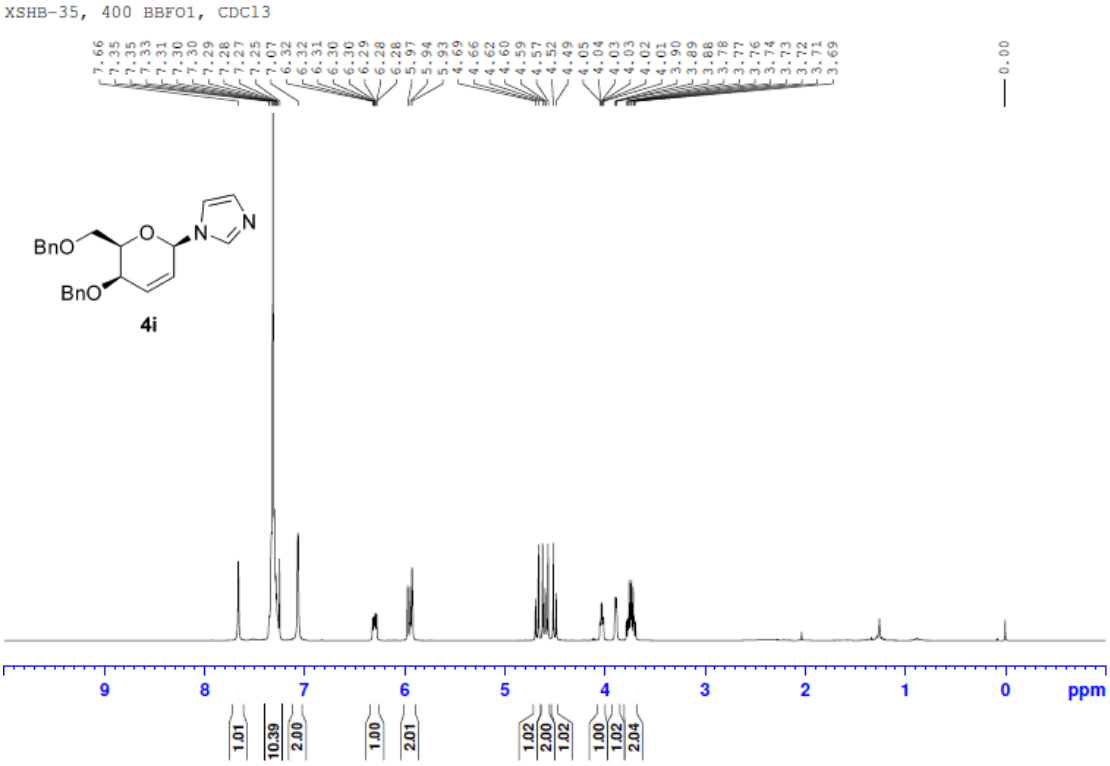


4h $\beta\alpha$=17:1

XSHB-65-C, 1H, BBOF01, 400Hz, CDCl3



4h $\beta\alpha$=17:1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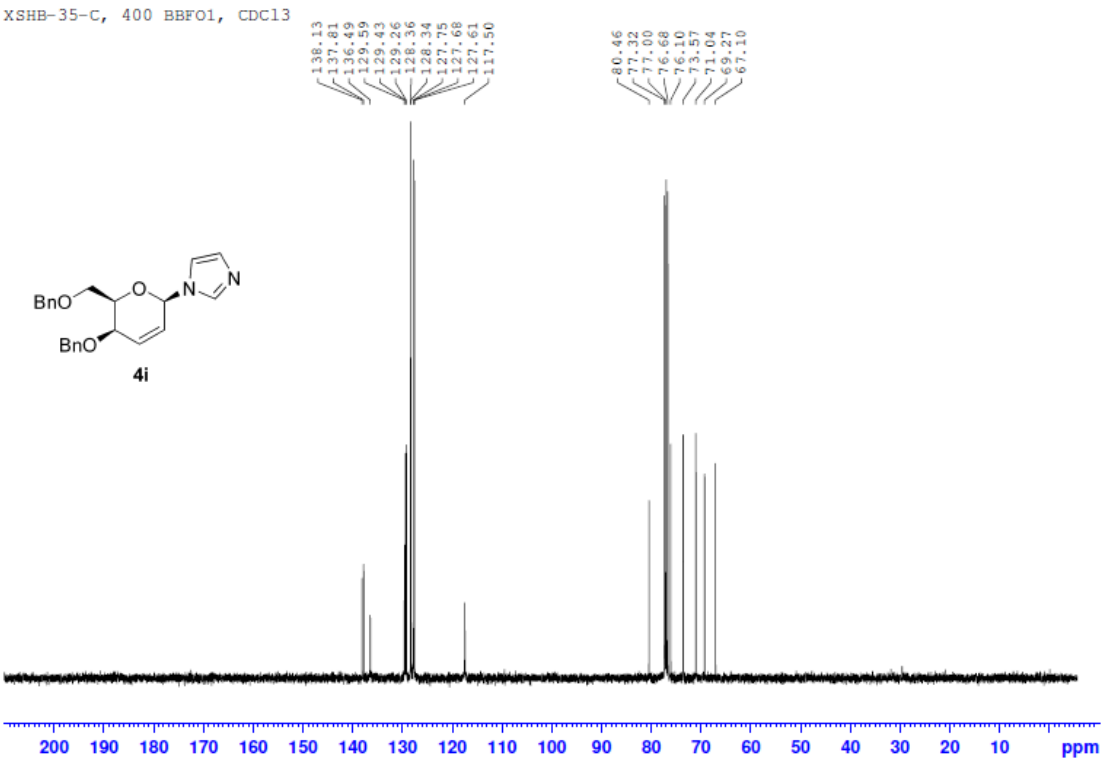
N
N
O
4i
ppm


XSHB-35-C, 400 BBFO1, CDCl3
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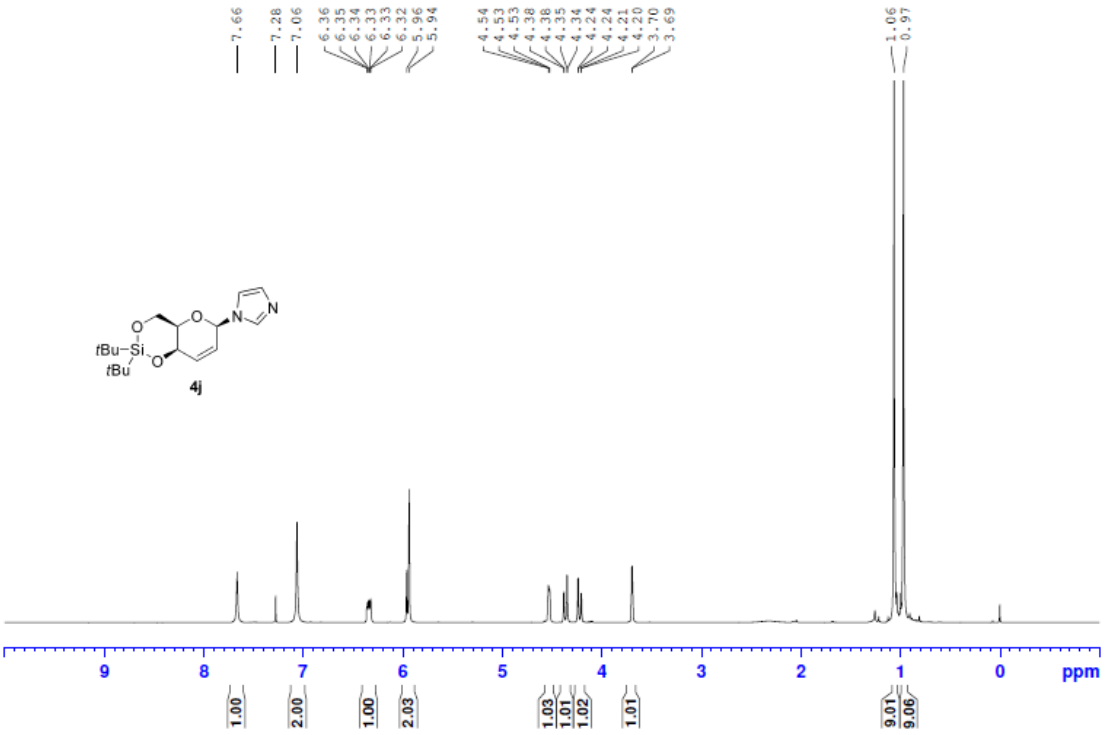
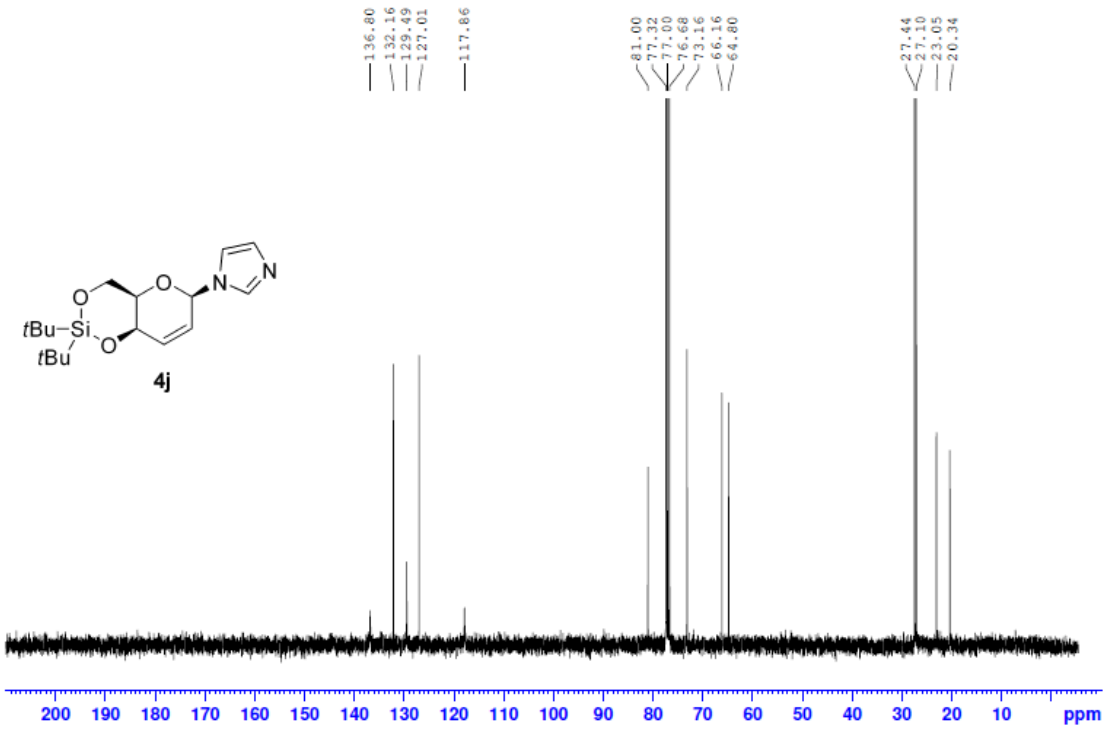
BnO
N
N
O
4i
ppm

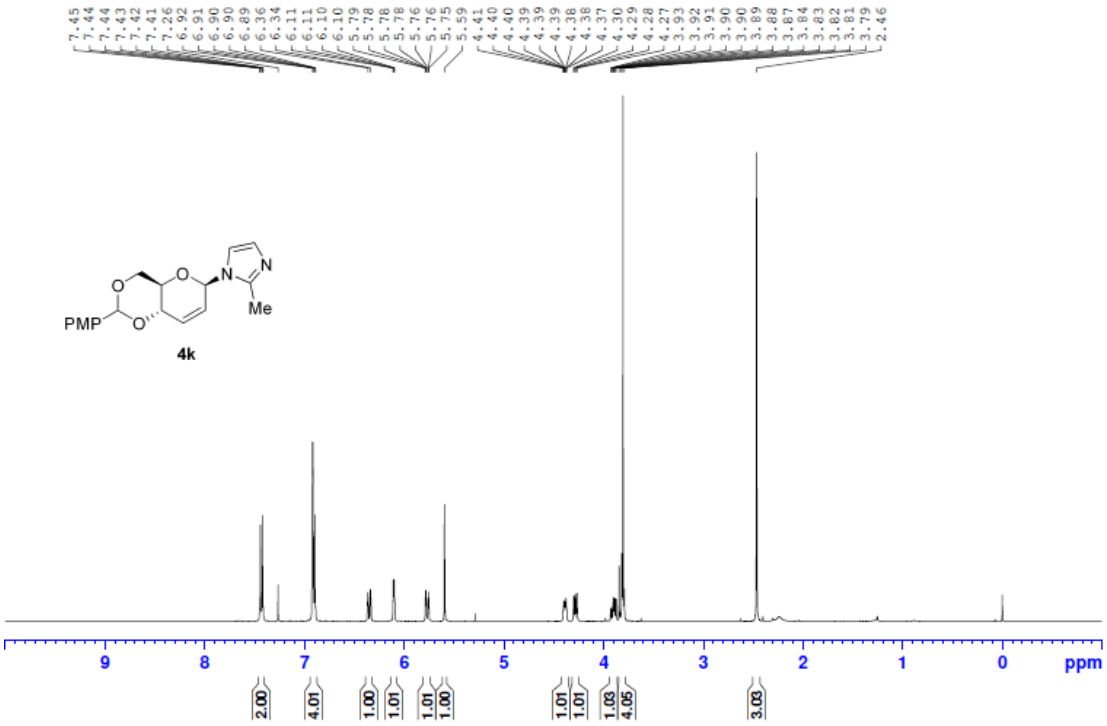
XSHB-64, 1H, BBOF01, 400Hz, CDCl3



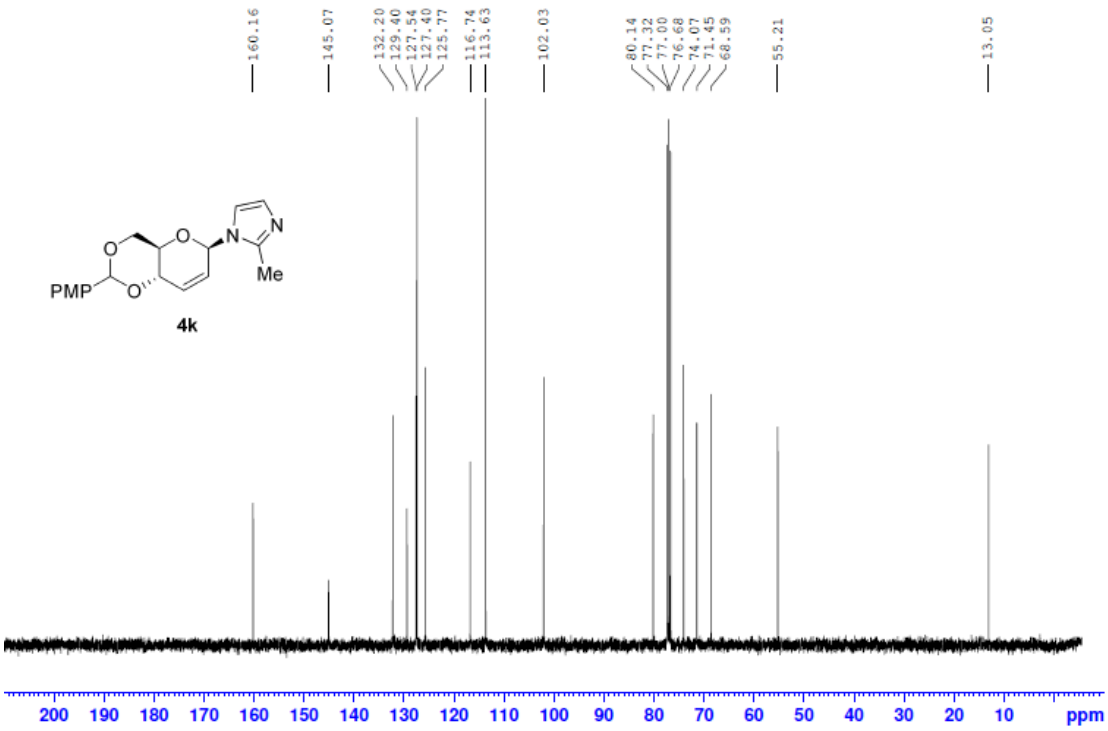
XSHB-64-C, 1H, BBOF01, 400Hz, CDCl3

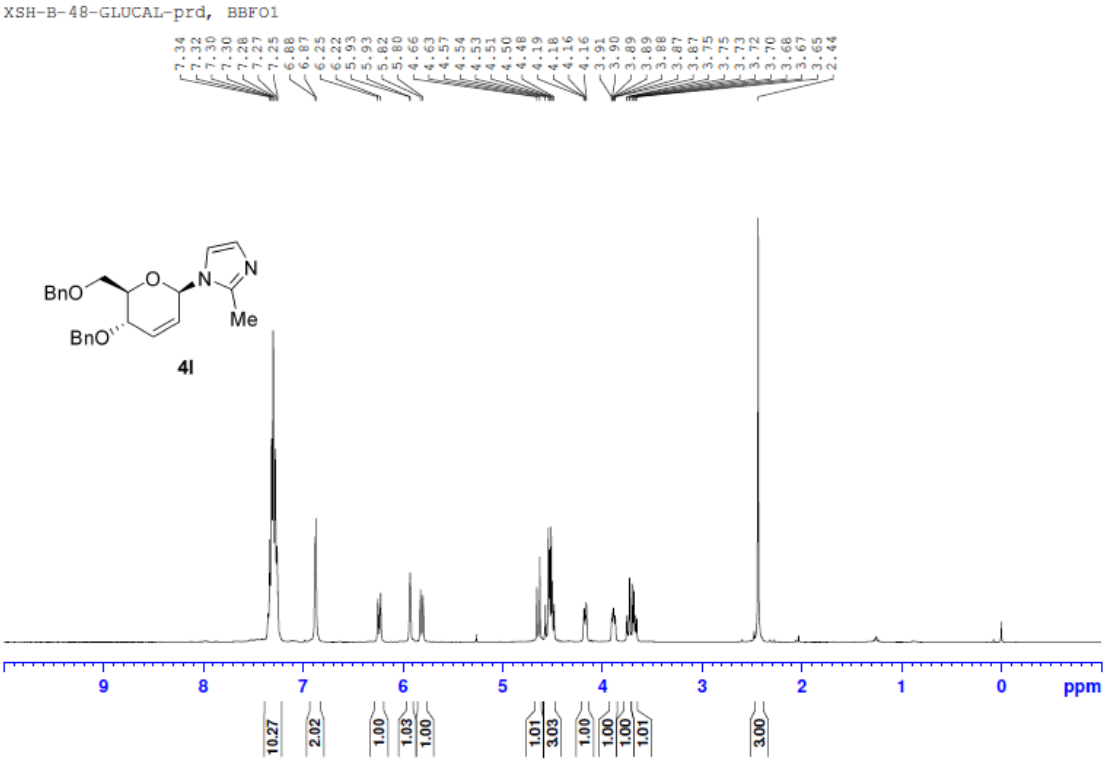


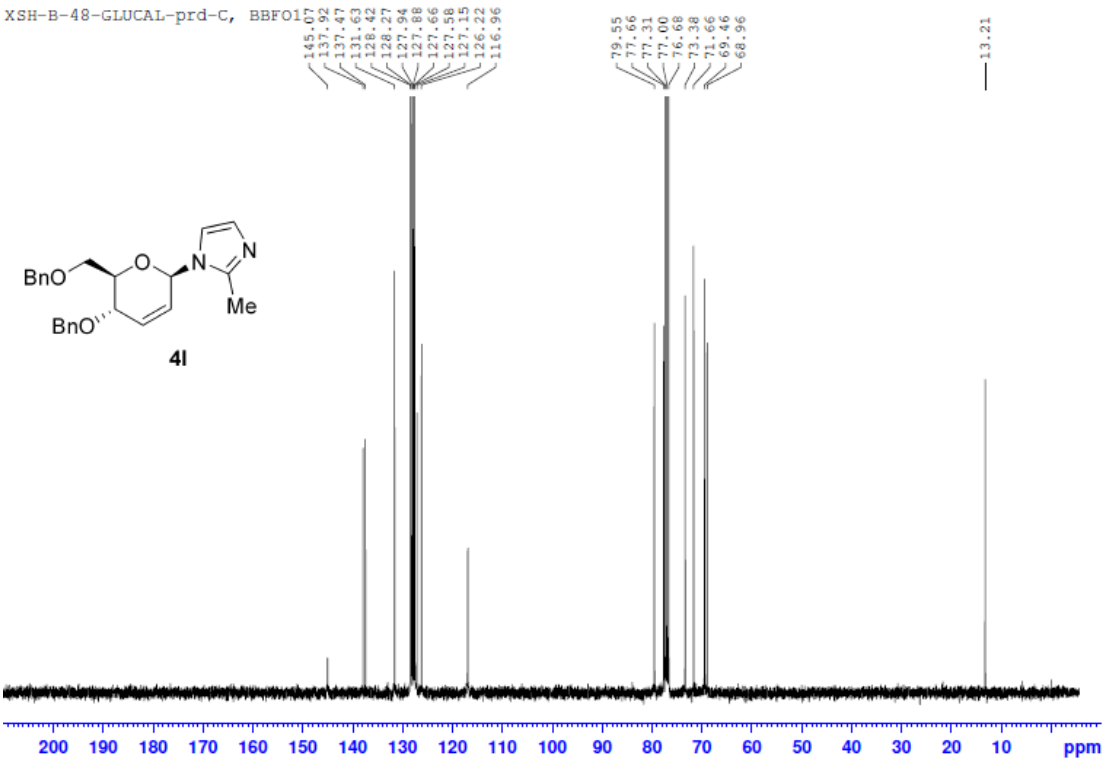
XSHB-19-2, 400 BBFO1, 1H, CDCl3

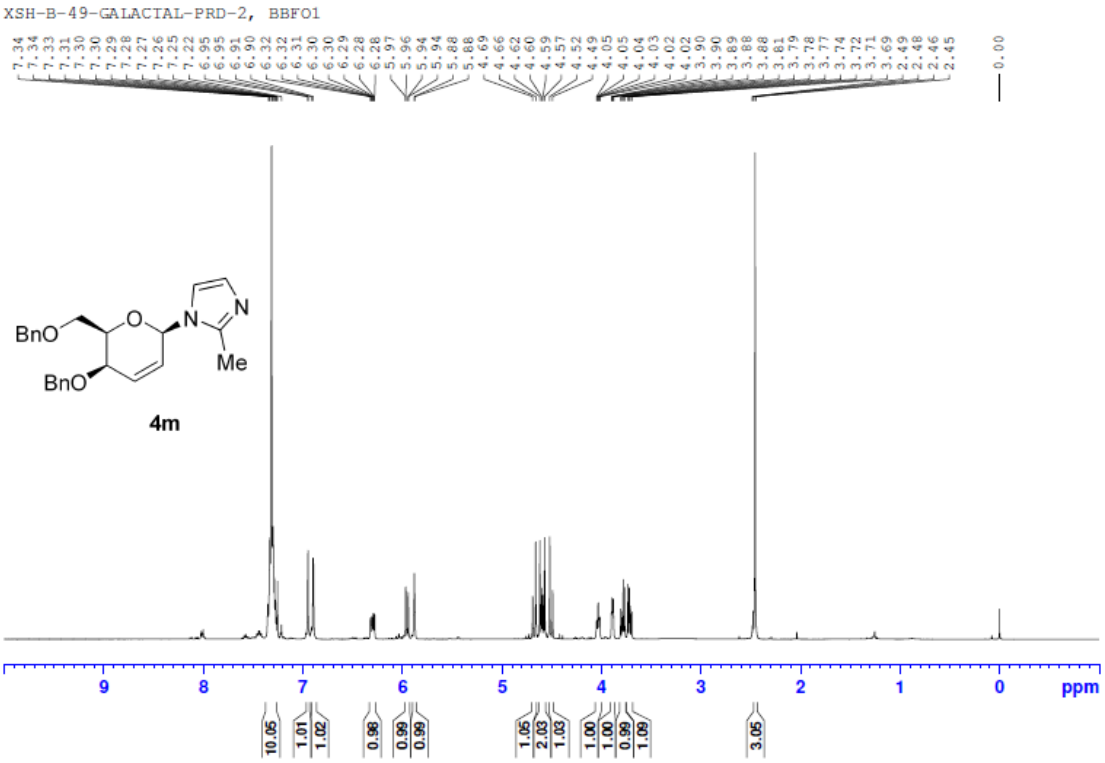


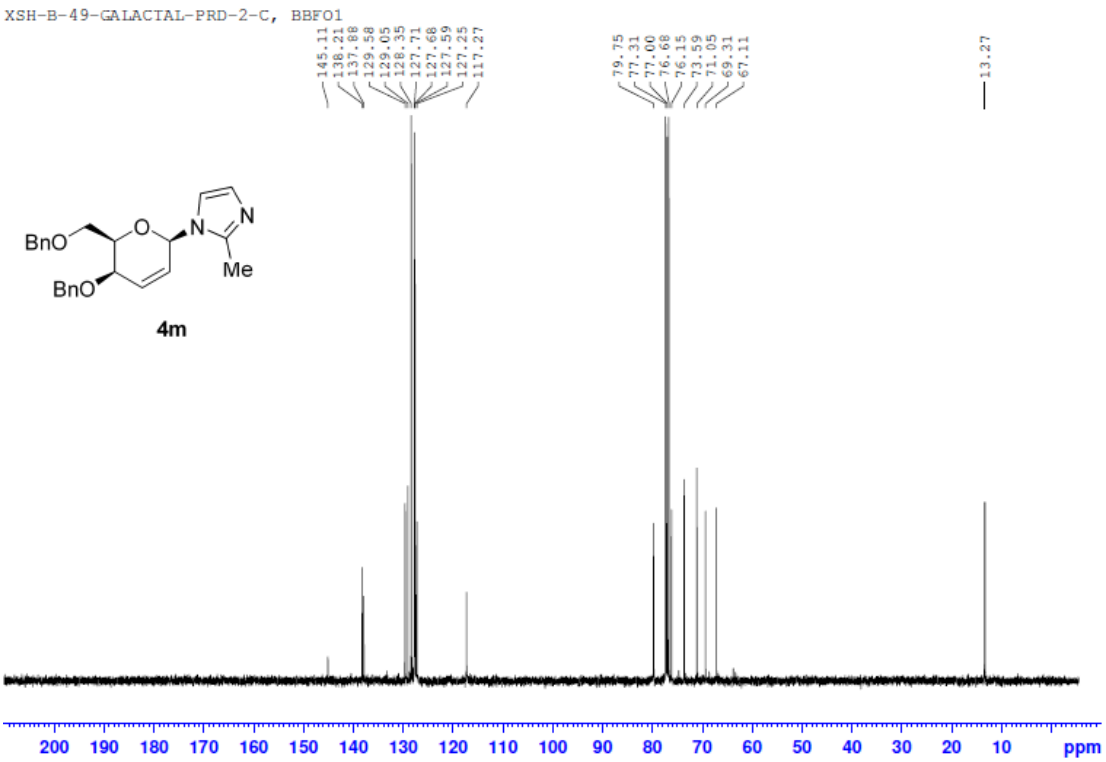
XSHB-19-C, 400 BBFO1, CDCl3

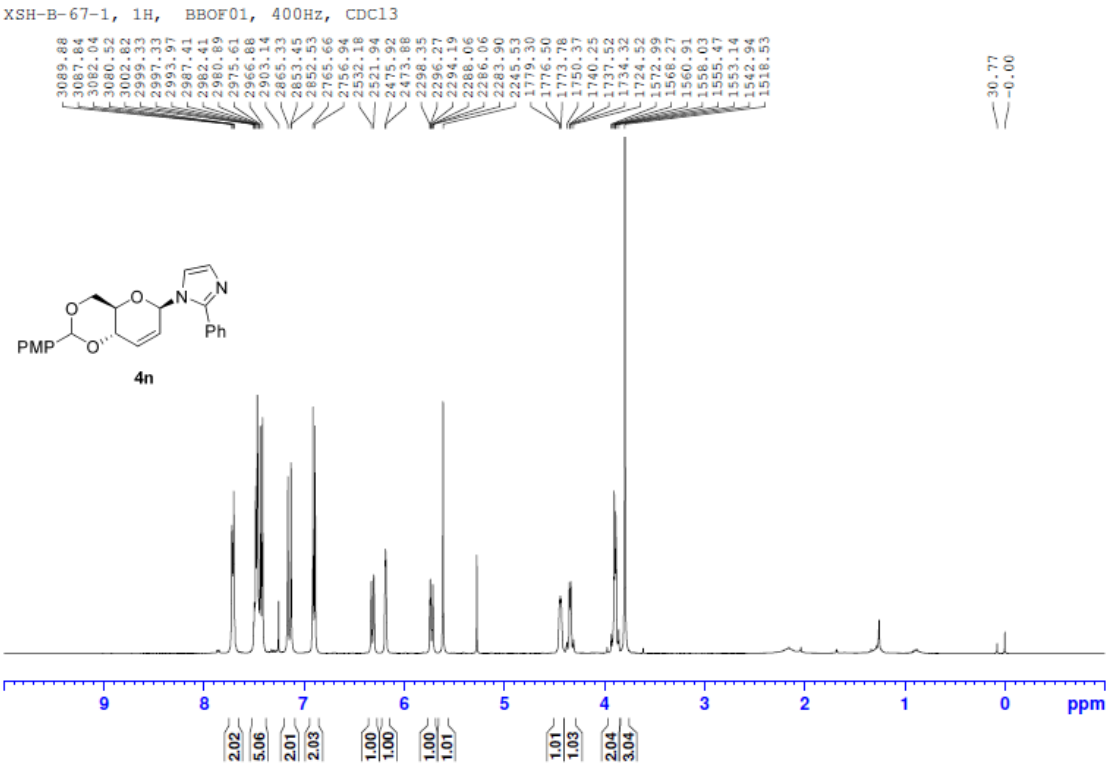


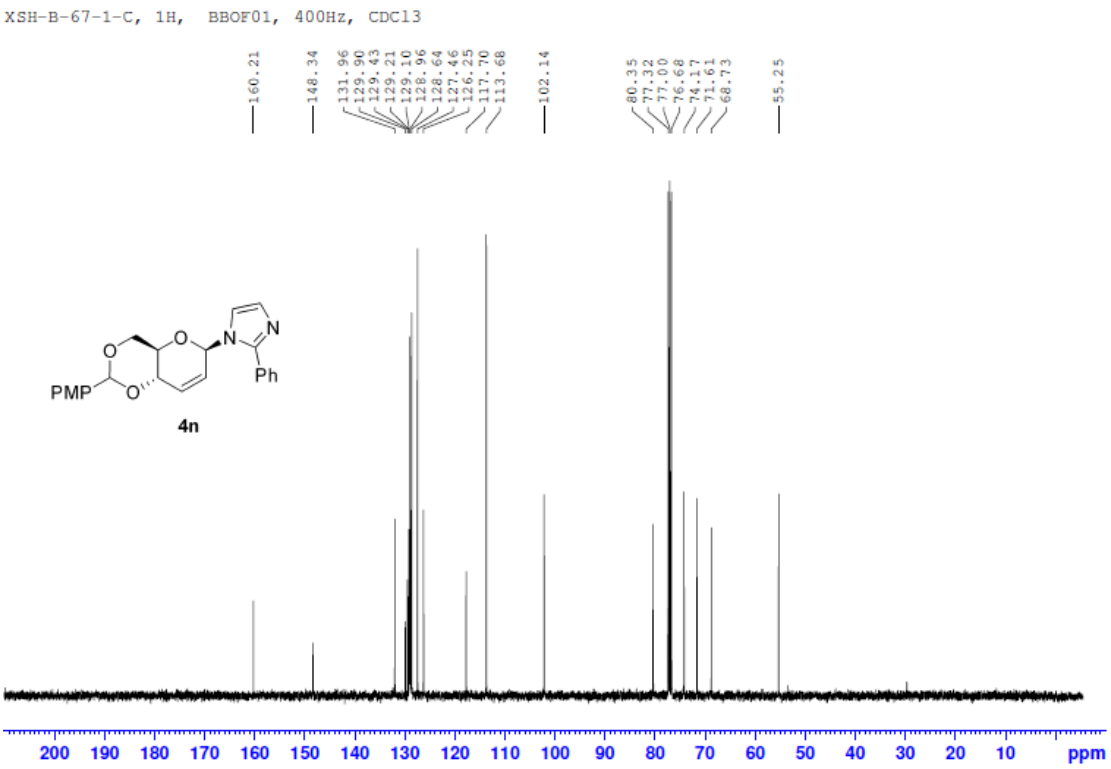

XSH-B-48-GLUCAL-prd, BBFO1
7.34
7.32
7.30
7.30
7.28
7.27
7.25
6.88
6.87
6.25
6.22
5.93
5.93
5.82
5.80
4.66
4.63
4.57
4.54
4.53
4.51
4.50
4.48
4.19
4.18
4.16
4.16
3.91
3.90
3.89
3.89
3.88
3.87
3.87
3.75
3.75
3.73
3.72
3.70
3.68
3.67
3.65
2.44
BnO
BnO
O
N
N
Me
4l
9
8
7
6
5
4
3
2
1
0
ppm
10.27
2.02
1.00
1.03
1.00
1.01
3.03
1.00
1.00
1.00
1.01
3.00

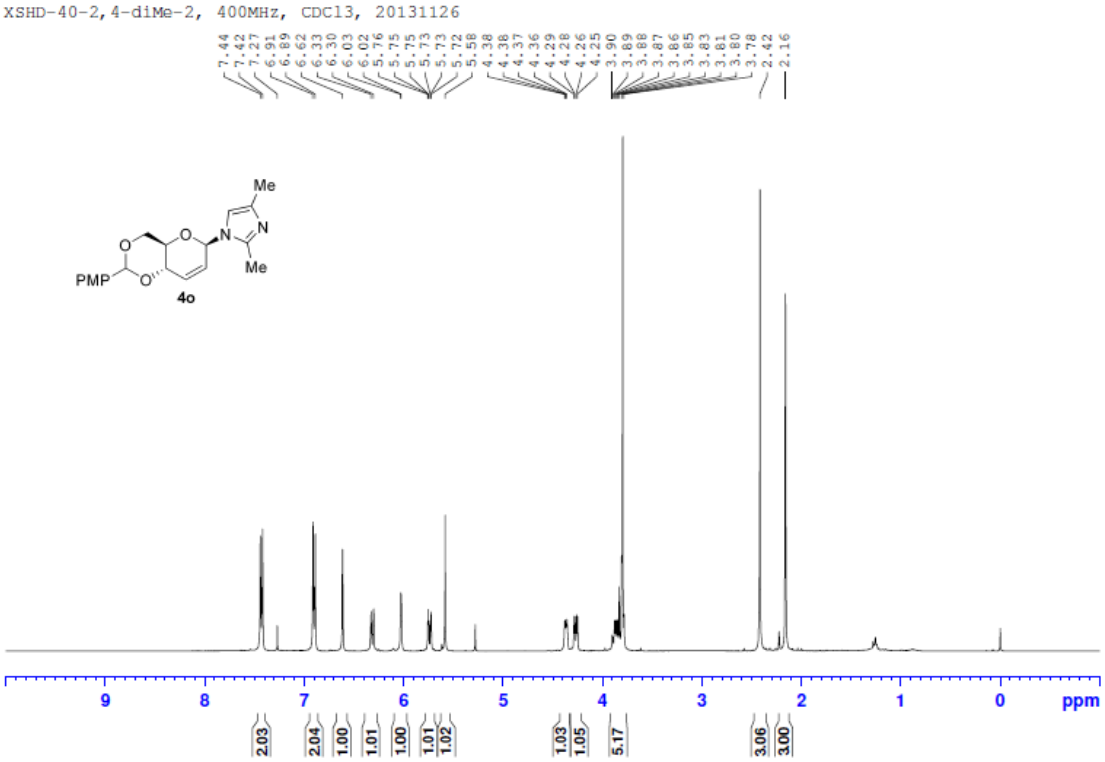

XSH-B-48-GLUCAL-prd-C, BBFO1
145.07
137.92
137.47
131.63
128.42
128.27
127.94
127.88
127.66
127.58
127.15
126.22
116.96
79.55
77.66
77.31
77.00
76.68
73.38
71.66
69.46
68.96
13.21
BnO
BnO
O
N
N
Me
4l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


XSH-B-49-GALACTAL-PRD-2, BBFO1
BnO
BnO
N
O
N
Me
4m
9
8
7
6
5
4
3
2
1
0
ppm
10.05
1.01
1.02
0.98
0.99
0.99
1.05
2.03
1.03
1.00
1.00
0.99
1.09
3.05


XSH-B-49-GALACTAL-PRD-2-C, BBFO1
BnO
BnO
N
O
N
Me
4m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


XSH-B-67-1, 1H, BBOF01, 400Hz, CDCl3
PMP
Ph
4n
ppm


XSH-B-67-1-C, 1H, BBOF01, 400Hz, CDCl3
PMP
Ph
4n
ppm


XSHD-40-2,4-diMe-2, 400MHz, CDCl3, 20131126
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7.42
7.27
6.91
6.89
6.62
6.33
6.30
6.03
6.02
5.76
5.75
5.75
5.73
5.73
5.72
5.58
4.38
4.38
4.37
4.36
4.29
4.28
4.26
4.25
3.90
3.89
3.88
3.87
3.86
3.85
3.83
3.81
3.80
3.78
2.42
2.16
Me
N
N
Me
O
O
O
PMP
4o
9
8
7
6
5
4
3
2
1
0
ppm
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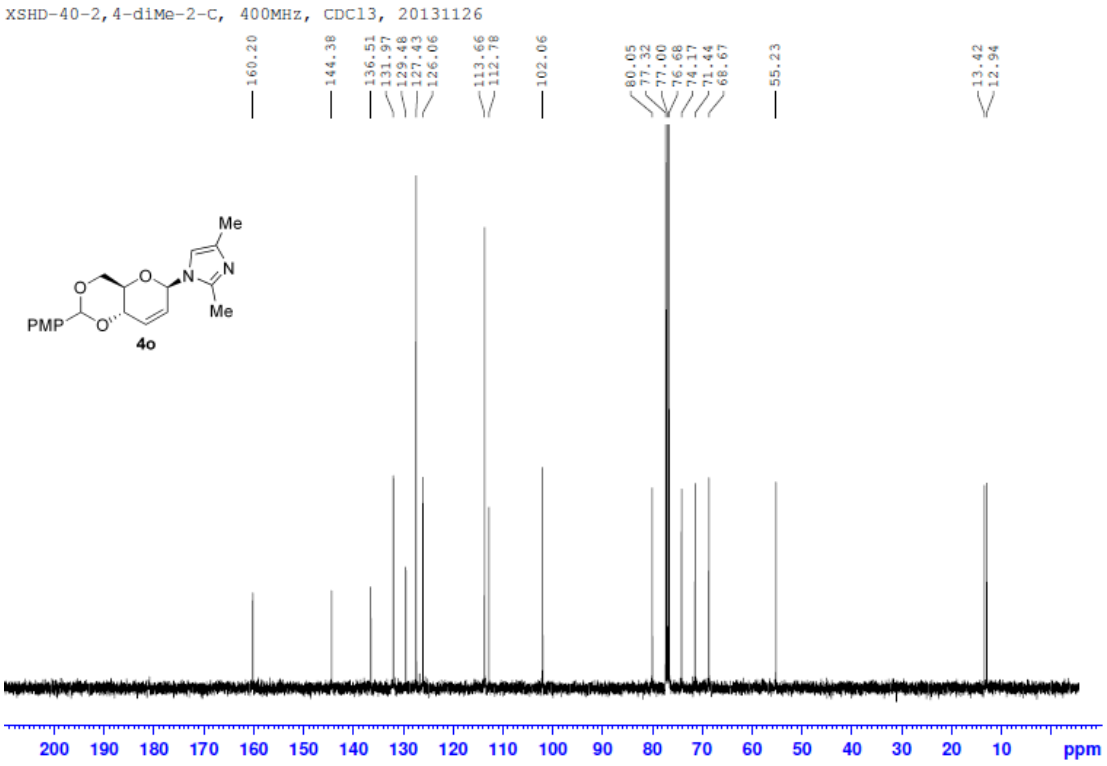
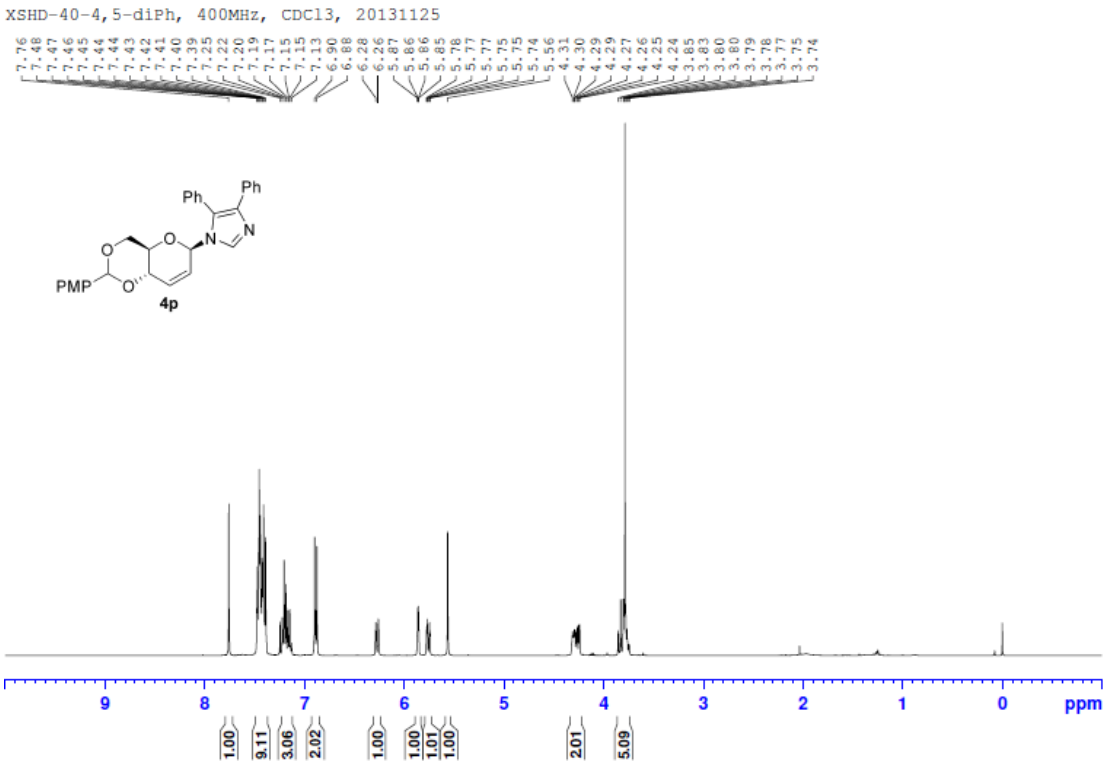
2.04
1.00
1.01
1.00
1.01
1.02
1.03
1.05
5.17
3.06
3.00


XSHD-40-2,4-diMe-2-C, 400MHz, CDCl3, 20131126
160.20
144.38
136.51
131.97
129.48
127.43
126.06
113.66
112.78
102.06
80.05
77.32
77.00
76.68
74.17
71.44
68.67
55.23
13.42
12.94
Me
N
N
Me
O
O
O
PMP
4o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


XSHD-40-4,5-diPh, 400MHz, CDCl3, 20131125
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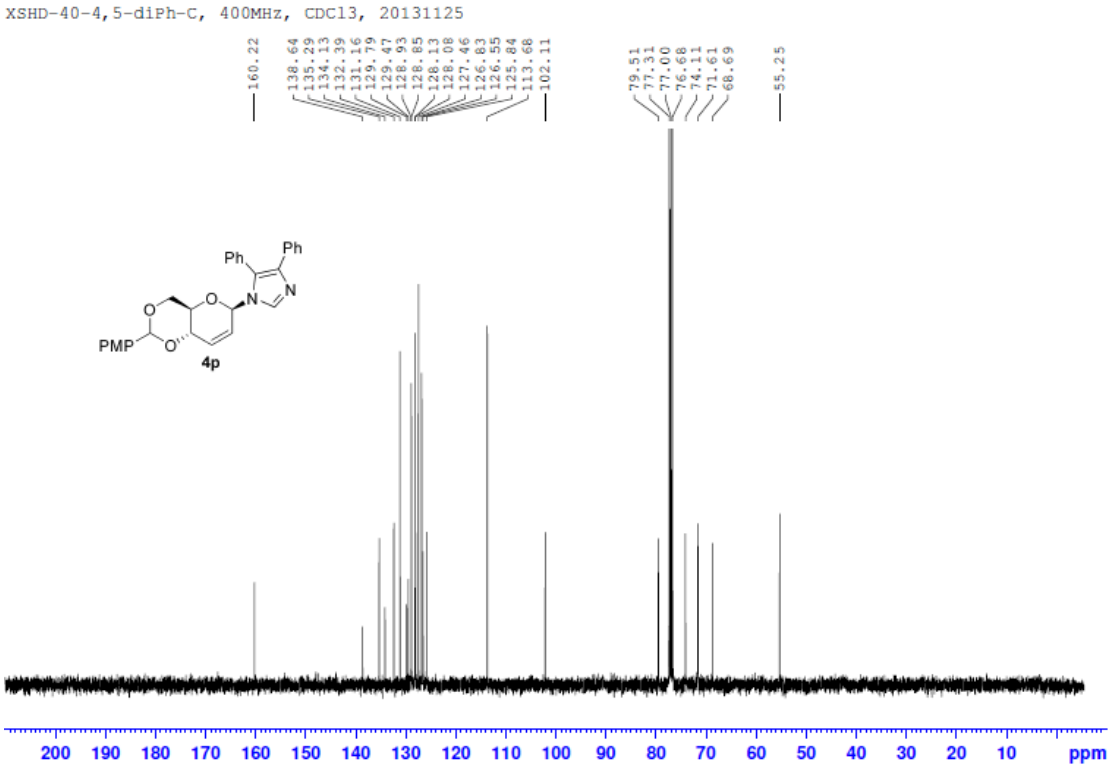
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.41
7.40
7.39
7.25
7.22
7.20
7.19
7.17
7.15
7.15
7.13
6.90
6.88
6.28
6.26
6.87
5.86
5.86
5.85
5.78
5.77
5.77
5.75
5.75
5.74
5.56
4.31
4.30
4.29
4.29
4.27
4.26
4.25
4.24
4.24
3.85
3.83
3.80
3.80
3.79
3.78
3.77
3.75
3.74
Ph
Ph
N
O
O
PMP
O
4p
9
8
7
6
5
4
3
2
1
0
ppm
1.00
9.11
3.06
2.02
1.00
1.00
1.01
1.00
2.01
5.09


XSHD-40-4,5-diPh-C, 400MHz, CDCl3, 20131125
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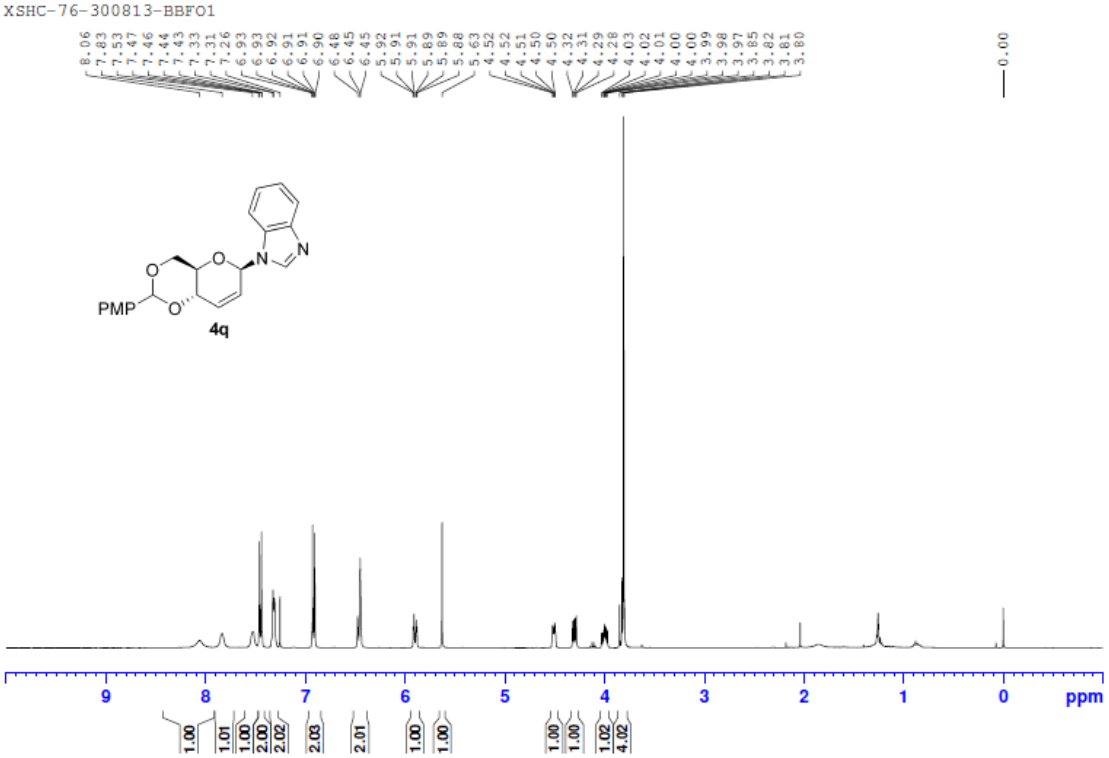
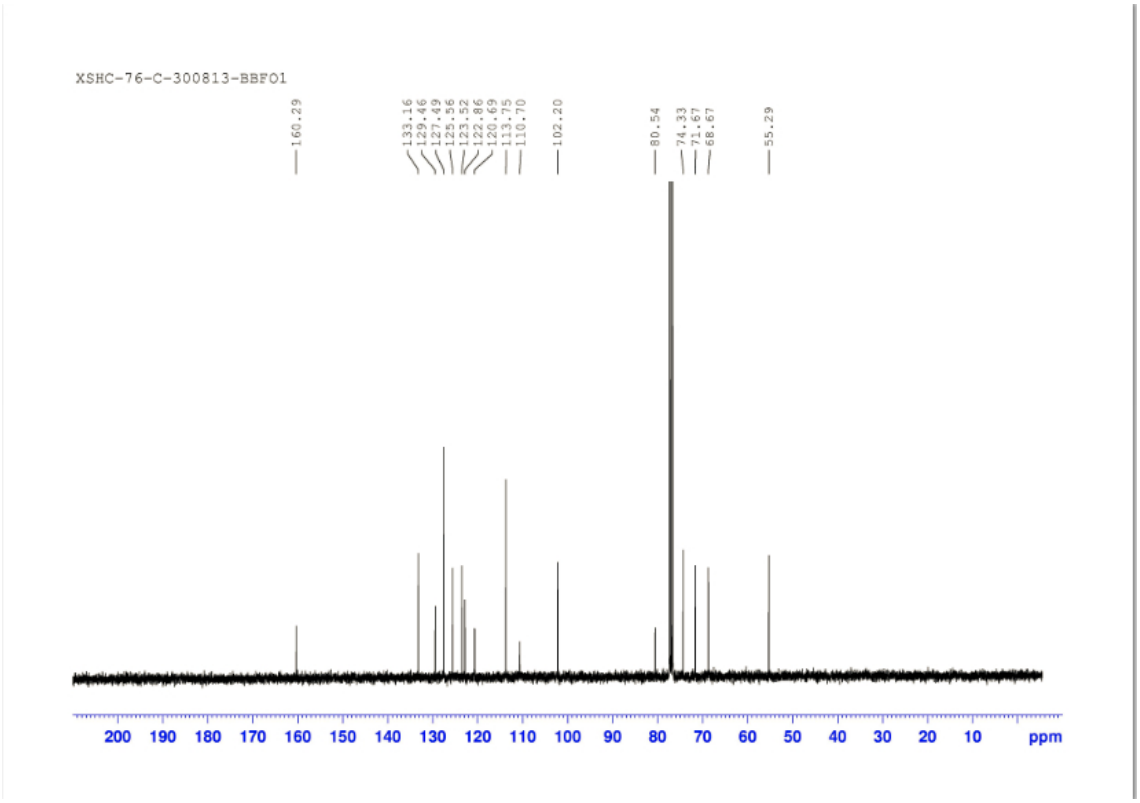
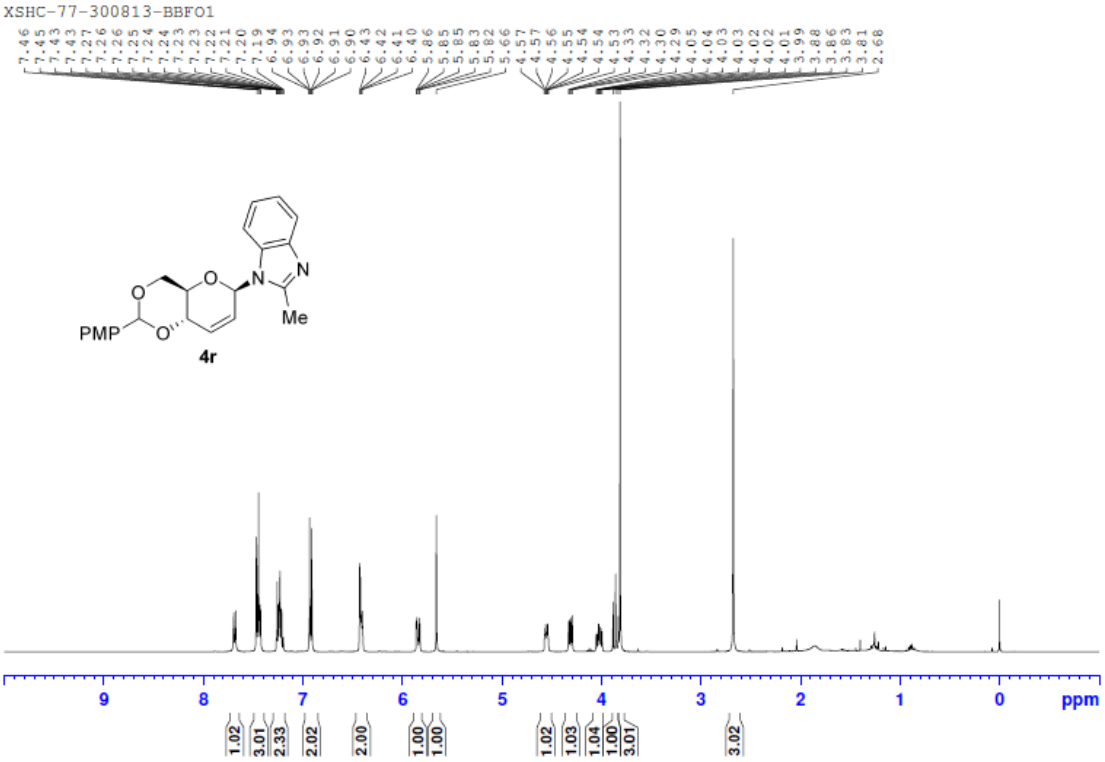
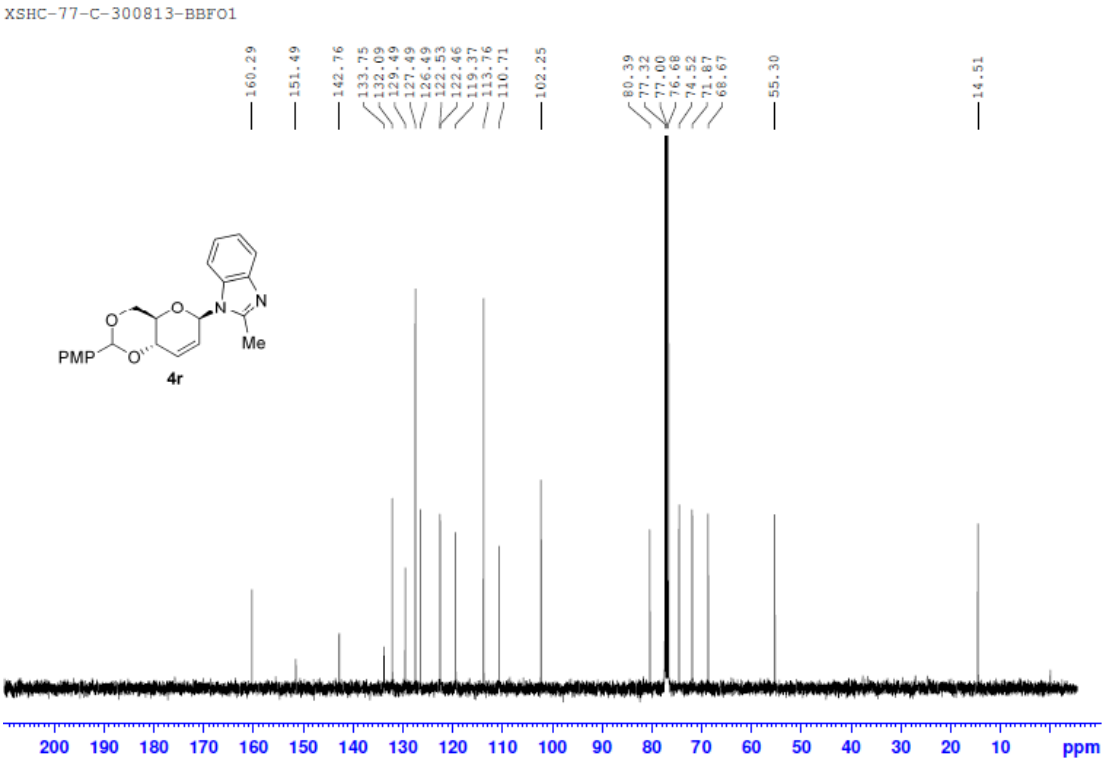
135.29
134.13
132.39
131.16
129.79
129.47
128.93
128.85
128.13
128.08
127.46
126.83
126.55
125.84
113.68
102.11
79.51
77.31
77.00
76.68
74.11
71.61
68.69
55.25
Ph
Ph
N
O
O
PMP
O
4p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

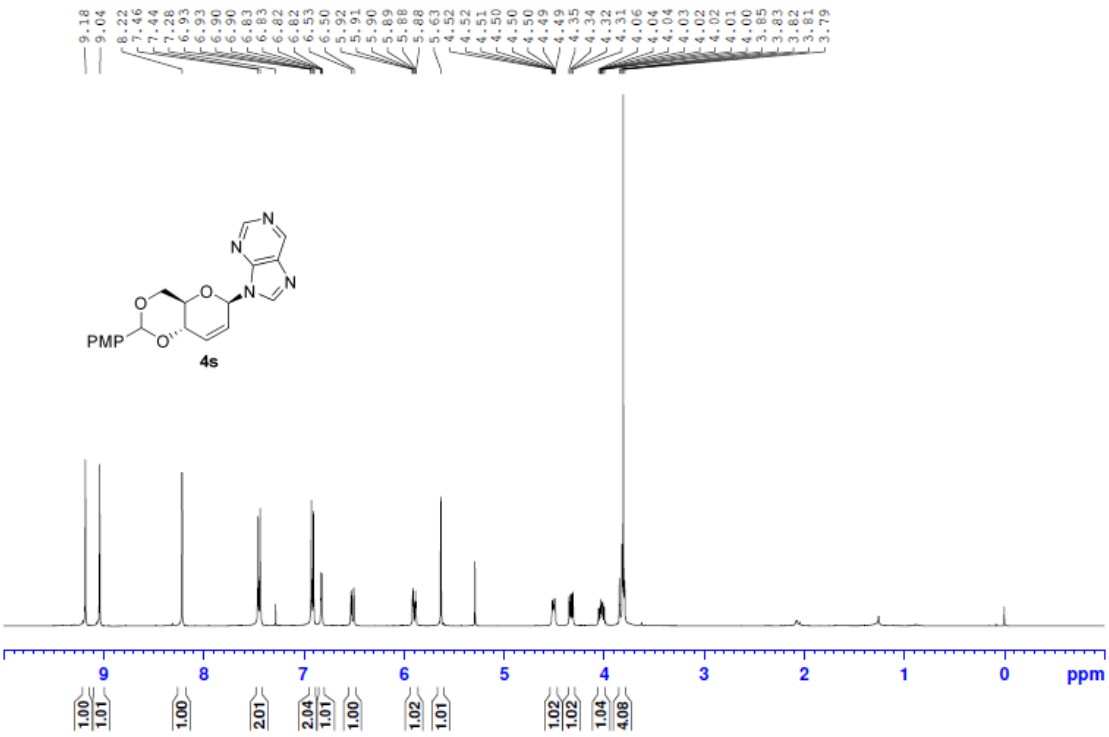

XSHC-76-300813-BBFO1
PMP
4q
ppm


XSHC-76-C-300813-BBFO1
ppm

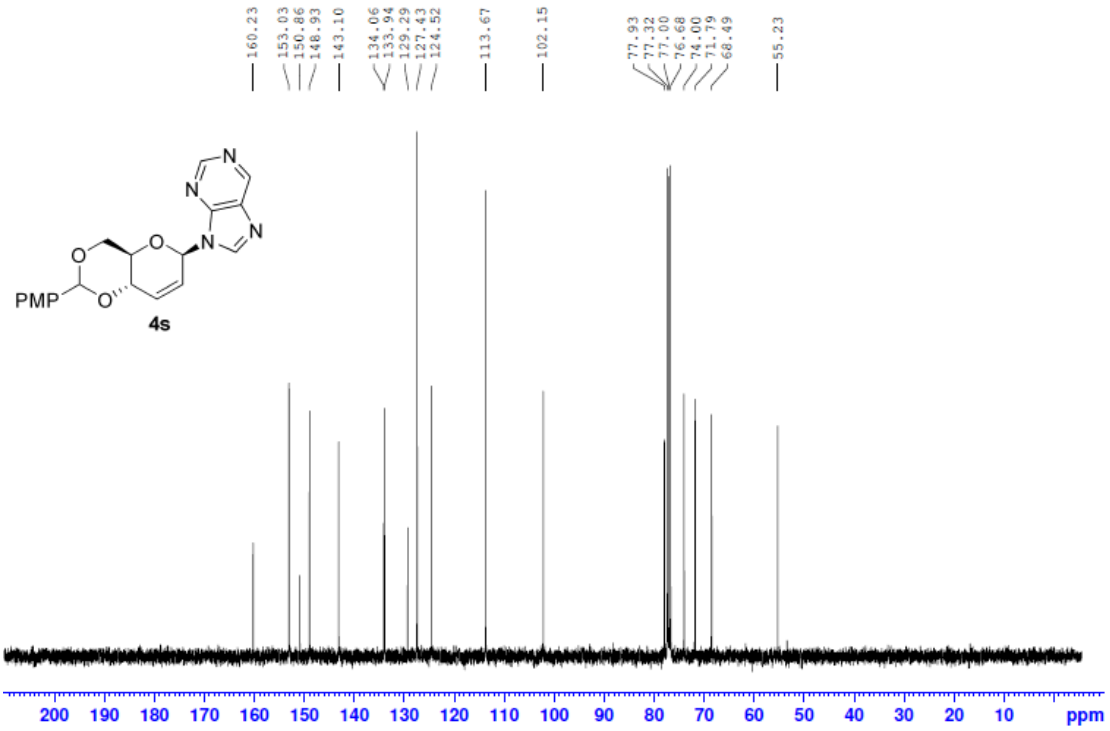

XSHC-77-300813-BBFO1
PMP
Me
4r
ppm

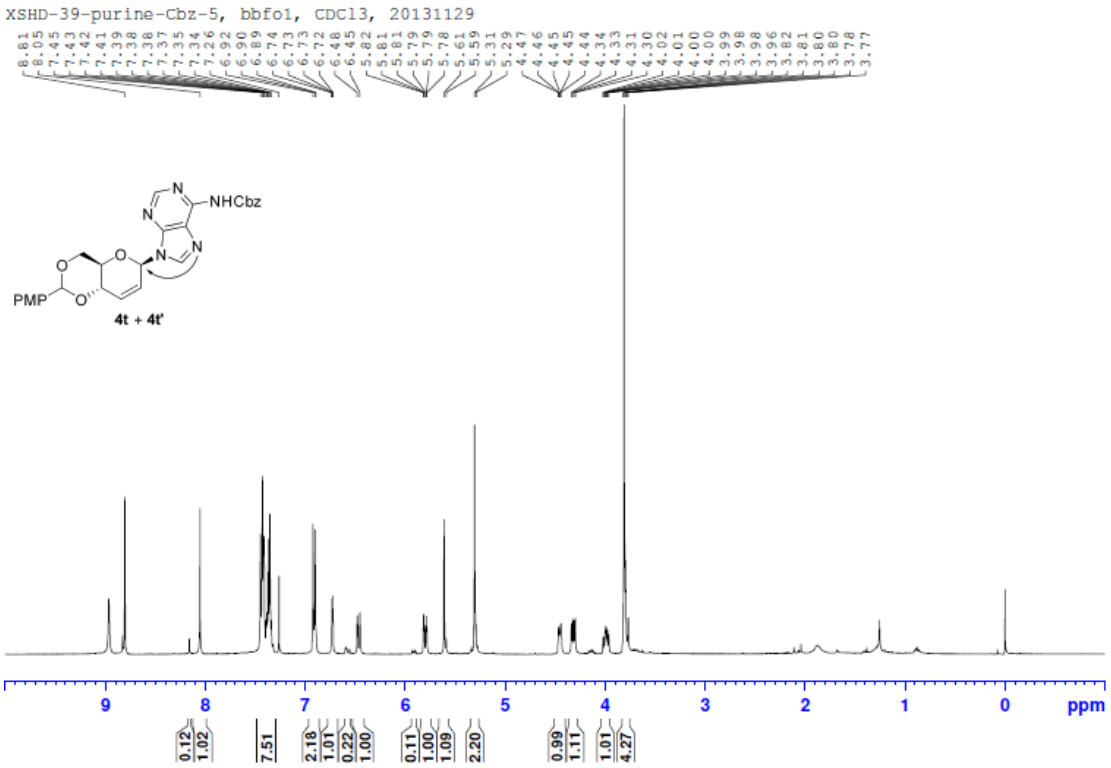

XSHC-77-C-300813-BBFO1
PMP
Me
4r
ppm

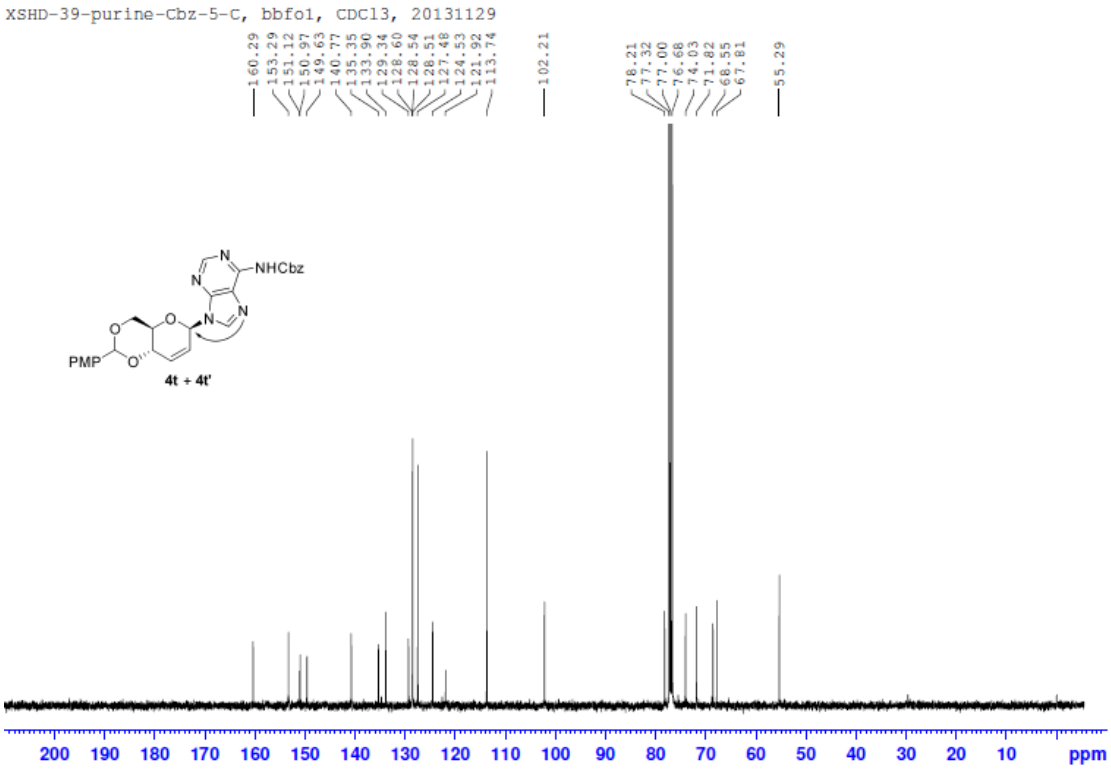
XSHD-39-purine-2, 400MHz, CDCl3, 20131126

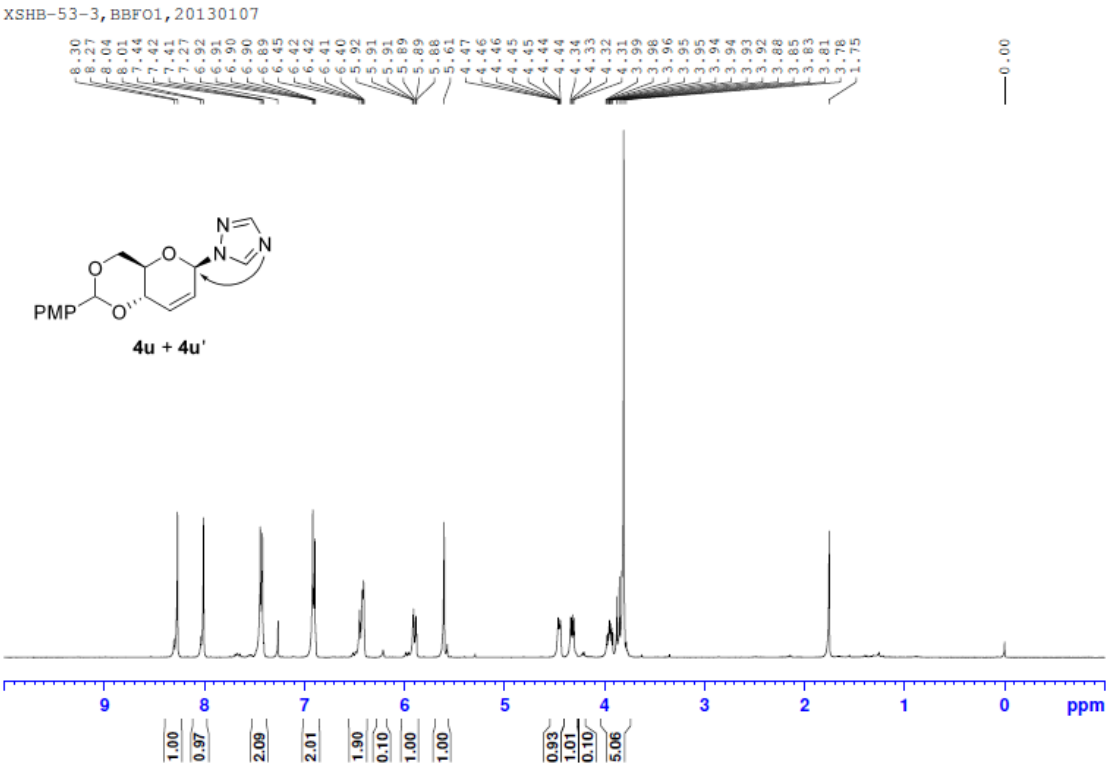


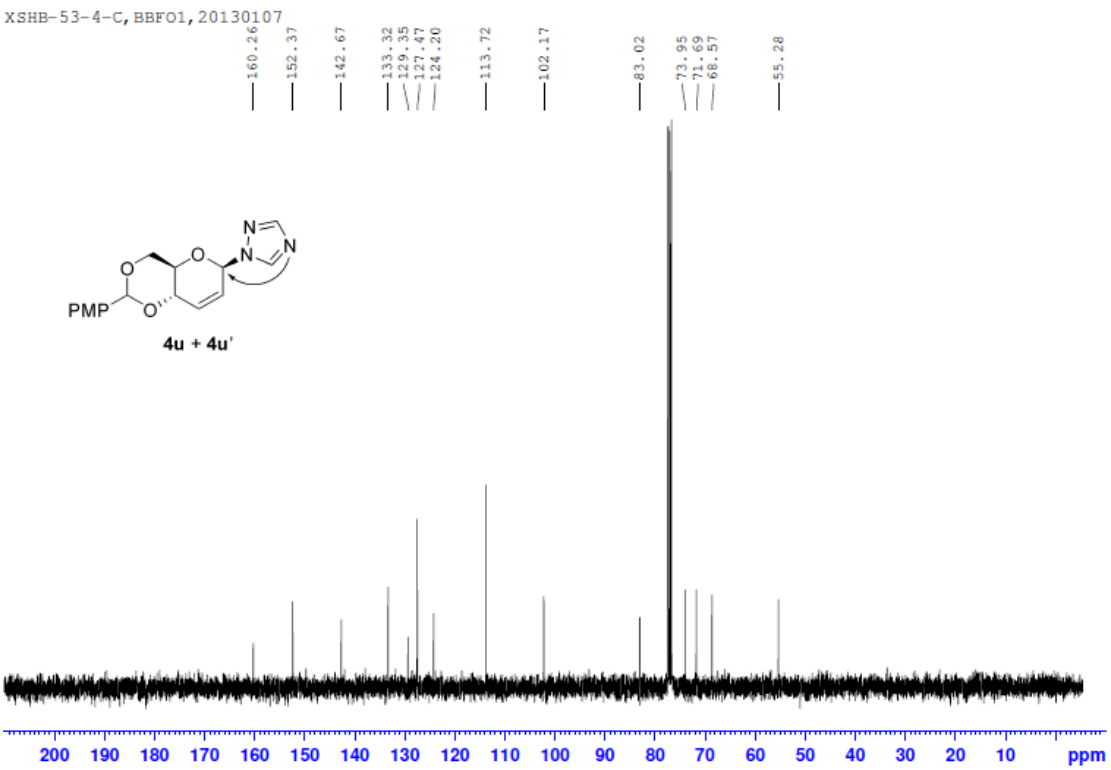
XSHD-39-purine-2-C, 400MHz, CDCl3, 20131126

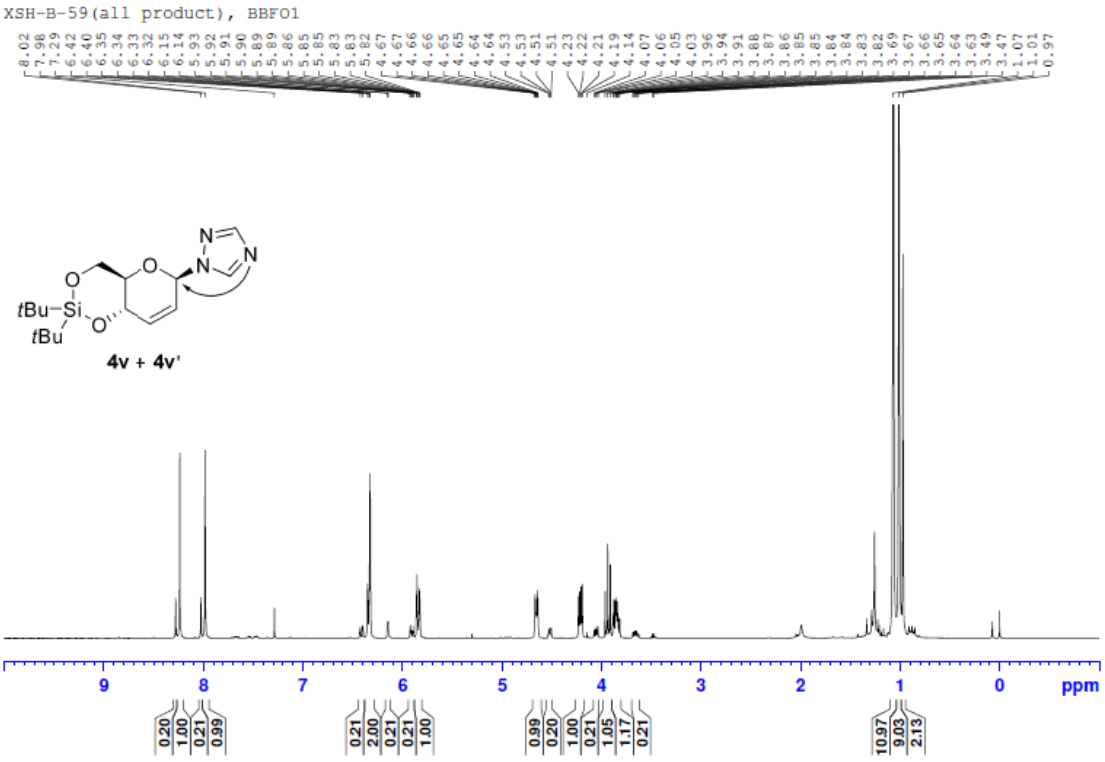


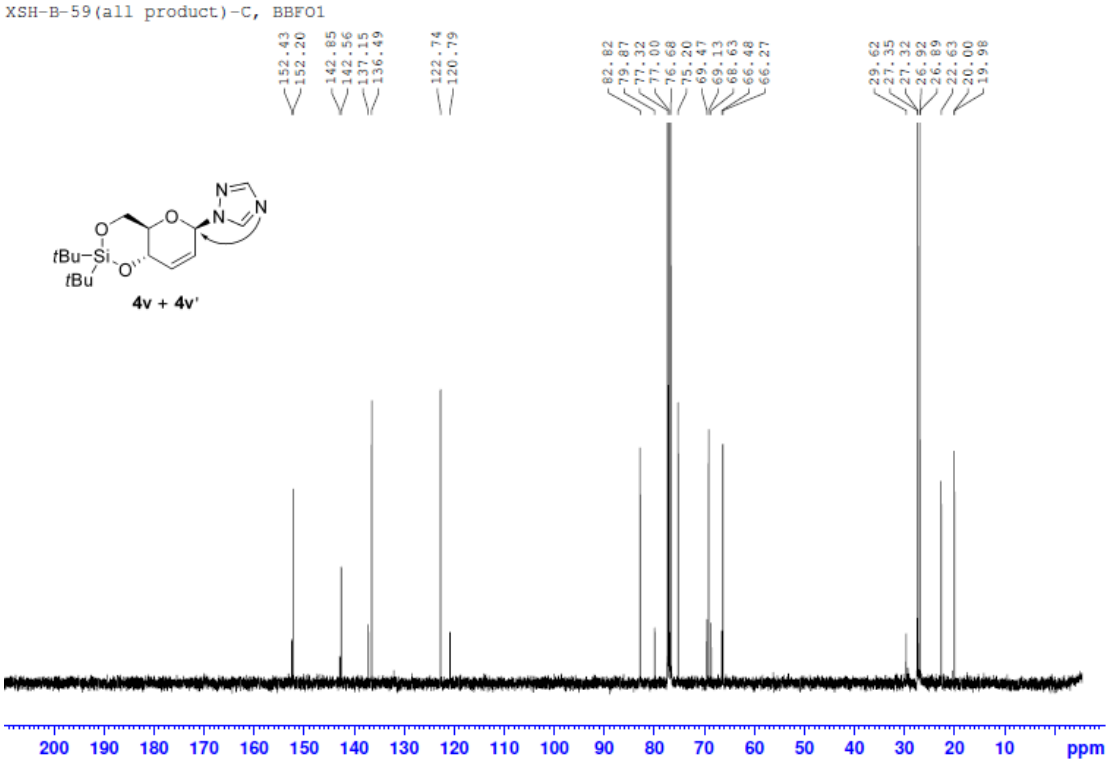

XSHD-39-purine-Cbz-5, bbfo1, CDCl3, 20131129
NHCbz
PMP
4t + 4t'
ppm


XSHD-39-purine-Cbz-5-C, bbfo1, CDCl3, 20131129
NHCbz
PMP
4t + 4t'
ppm

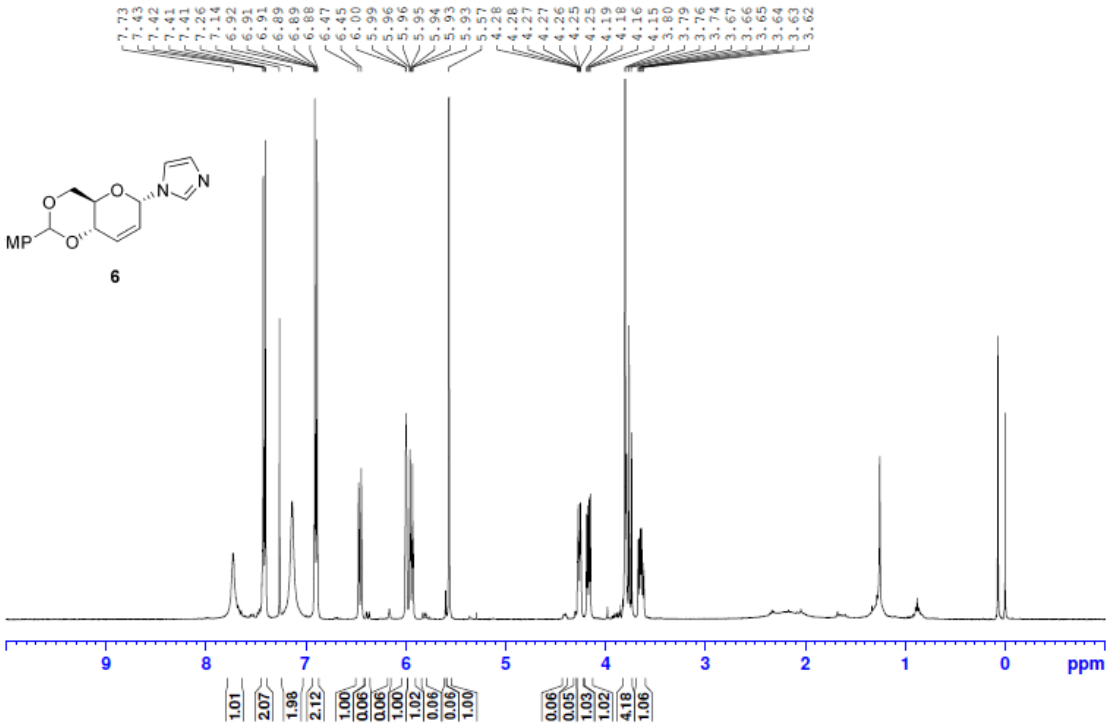

XSHB-53-3,BBFO1,20130107
PMP
4u + 4u'
ppm


XSHB-53-4-C,BBFO1,20130107
PMP
4u + 4u'
ppm


XSH-B-59(all product), BBFO1
4v + 4v'

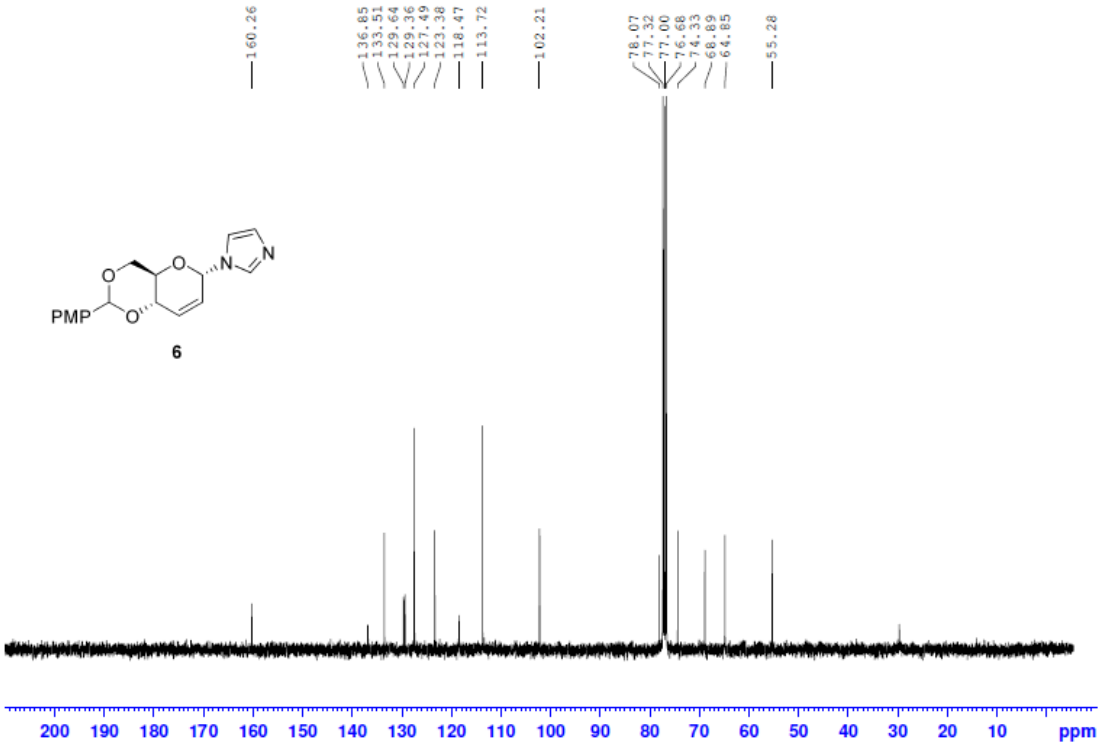

XSH-B-59(all product)-C, BBFO1
4v + 4v'

XSH-B-57, 1H, BBOF01, 400Hz, CDCl3



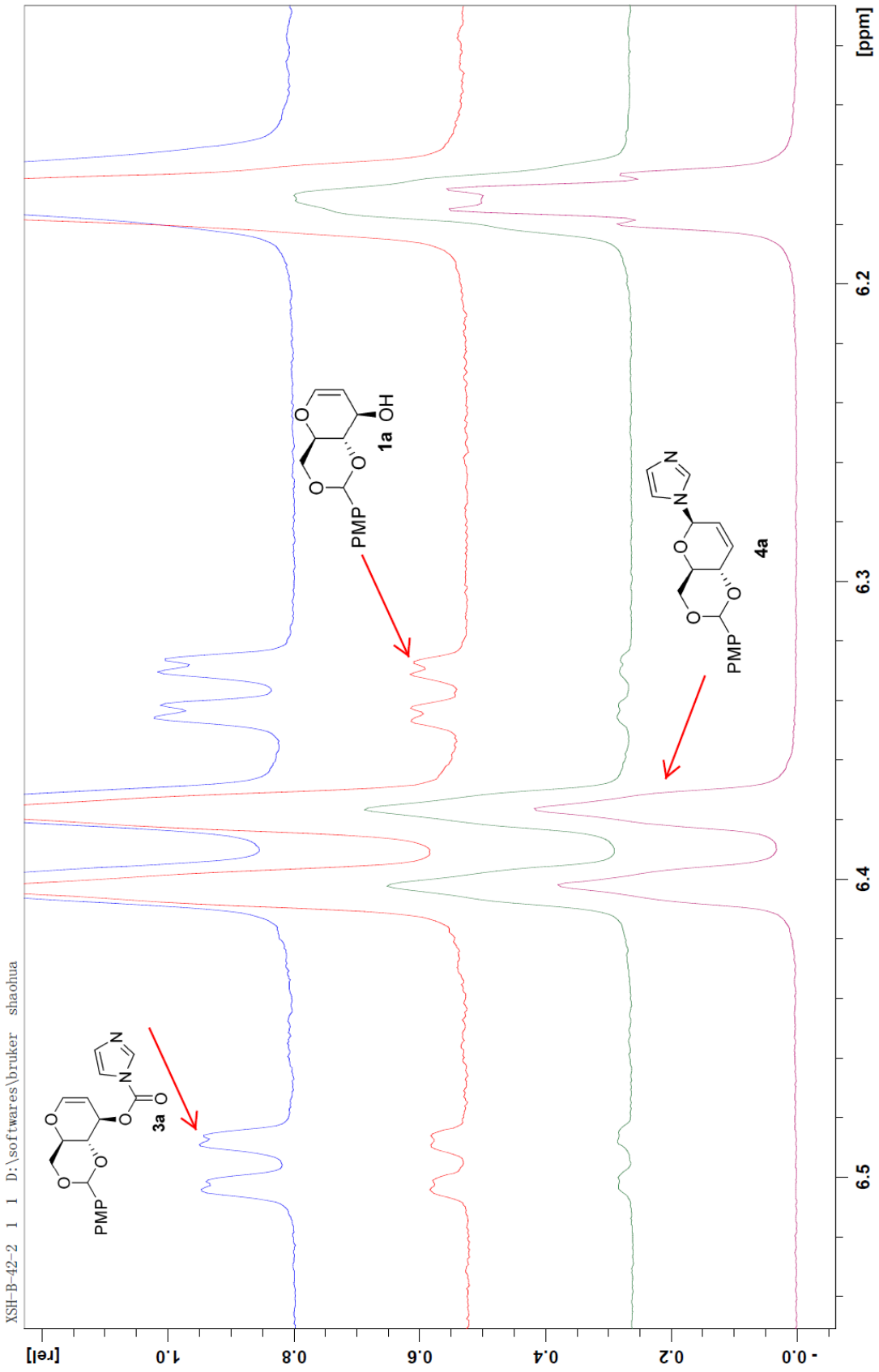
6

XSHB-53-2-C,400MHz,BBFO1,20130104

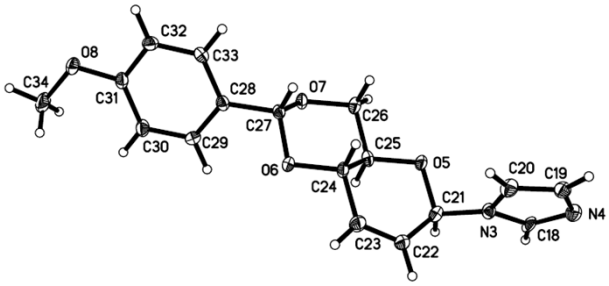


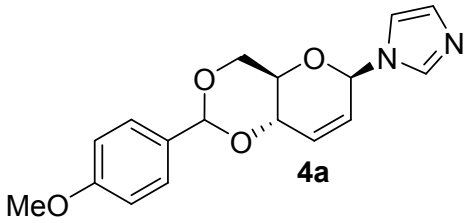
6

Reaction progress of compound 1a as monitored by ^{1}H NMR



The X-ray structure of compound **4a** (CCDC number: 957218)



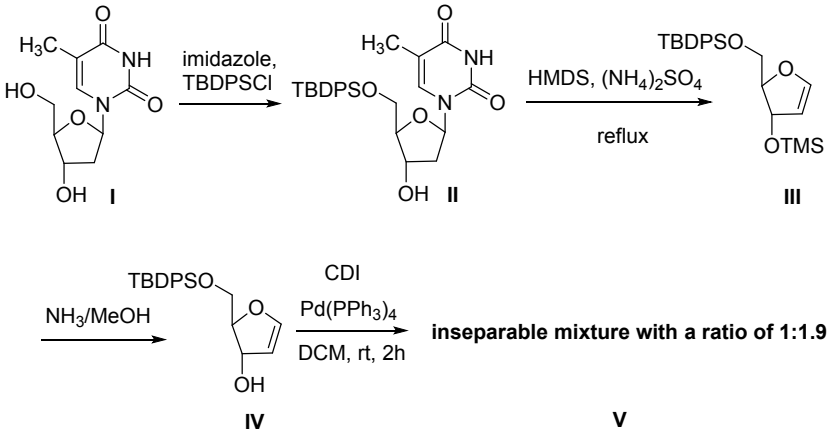


4a

Crystal data and structure refinement for compound **4a**

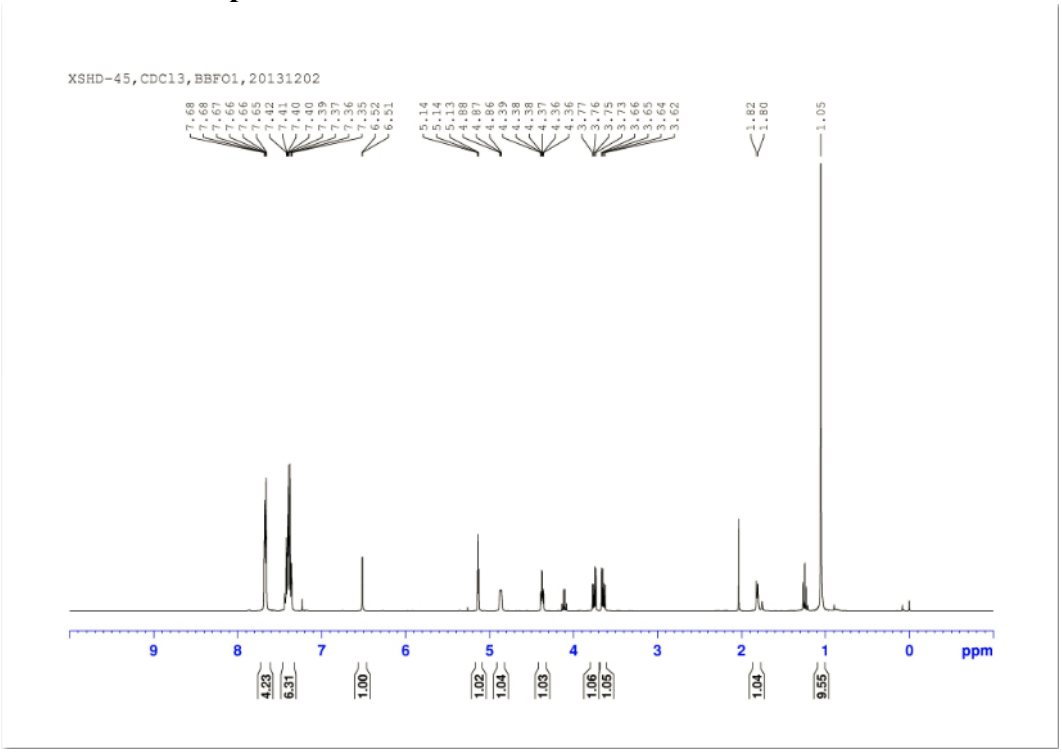
Empirical formula	C17 H18 N2 O4	
Formula weight	314.33	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 7.1797(6) Å	α= 103.804(3)°.
	b = 9.6308(10) Å	β= 93.978(3)°.
	c = 11.5304(12) Å	γ = 95.999(5)°.
Volume	766.34(13) $Å^3$	
Z	2	
Density (calculated)	1.362 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	332	
Crystal size	0.40 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.83 to 29.54°.	
Index ranges	-9<=h<=9, -13<=k<=13, -15<=l<=15	
Reflections collected	9961	
Independent reflections	4224 [R(int) = 0.0307]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9903 and 0.9618	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4224 / 3 / 417	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1017	
R indices (all data)	R1 = 0.0552, wR2 = 0.1221	
Largest diff. peak and hole	0.308 and -0.377 $e.Å^{-3}$	

The preparation of furanosyl glycal and the corresponding furanosyl *N*-glycoside

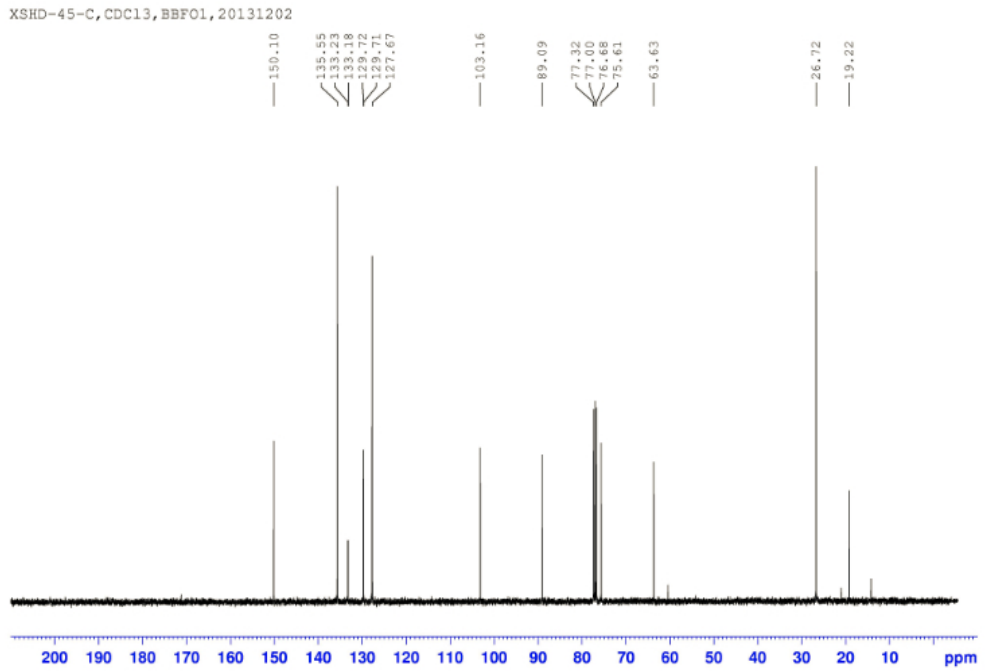


The glycal IV was prepared according to Pedersen's method (Synthesis, 1994, 1037 ; Monatshefte Fur Chemie, 2005, 136, 1641). The Spectra of compound IV and V are attached below.

^{1}H NMR of Compound IV:



^{13}C NMR of Compound IV:



^{1}H NMR of Compound V: