Selective Protection/Deprotection in 1-Deoxynojirimycin Scaffold: Regioselective Mono-Benzoylation and Alkylation using TBAB-NaOH Catalytic System

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Copies of ¹H NMR and ¹³C NMR S2-S37

¹H NMR of *N*-benzyloxycarbonyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (3)

^{13}C NMR of *N*-benzyloxycarbonyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (3)

Chemical structure of compound **4** is shown in the top left. The structure is a substituted tetrahydropyran with a methoxy group at C2, a methoxycarbonyl group at C3, and a benzylcarbamoyl group at C4. The anomeric carbon is labeled **4**.

¹H NMR spectrum (CDCl₃) of compound **4** is shown below. The x-axis represents the chemical shift in ppm (f1), ranging from 0.0 to 8.0. The spectrum displays several peaks, with integration values indicated below the baseline.

Chemical shift labels (ppm) are provided at the top of the spectrum:

- Black labels (left): 7.3695, 7.3554, 7.3526, 7.3408, 7.3358, 7.3263, 7.3103, 7.2645.
- Red labels (right): 5.1644, 5.1398, 5.0987, 5.0751, 4.3847, 4.3753, 4.3621, 4.3526, 4.0004, 3.8236, 3.8067, 3.8023, 3.7852, 3.6059, 3.5065, 3.3580, 3.2810, 3.2754, 3.2690, 3.2601, 3.2491, 3.1914, 3.1831, 3.1745, 3.1662, 1.4110.

Integration values (below the baseline) are provided for several peaks:

- 5.27 (peak at ~7.3 ppm)
- 1.00, 1.05 (peak at ~5.1 ppm)
- 1.05 (peak at ~4.4 ppm)
- 1.08, 1.20, 2.12, 3.08, 3.03, 2.13, 1.07 (peaks between 3.0 and 4.5 ppm)
- 3.22, 3.08 (peak at ~1.4 ppm)

^{13}C NMR of *N*-benzyloxycarbonyl-2,3-di-*O*-methyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (4)

Chemical structure of compound **5** is shown in the top left corner. The structure is a bicyclic acetal with an N-benzyl group and two ethoxy groups.

The ^1H NMR spectrum (CDCl₃) shows the following chemical shifts (ppm) and integration values:

Chemical Shift (ppm)	Integration
7.3583, 7.3554, 7.3436, 7.3374, 7.3299, 7.3246, 7.3140, 7.2730	4.50
5.1190, 5.1066, 4.3752, 4.3656, 4.3523, 4.3427	1.65
4.1162, 4.1108, 3.7834, 3.7764, 3.7712, 3.7665, 3.7618, 3.7571, 3.7437, 3.7389, 3.7289, 3.7043, 3.6953, 3.6904, 3.6811, 3.6762, 3.5717, 3.5572, 3.5424, 3.3366, 3.3324, 3.3271, 3.3228, 3.2583, 3.2560, 3.2492, 3.2433, 3.2341, 3.2248	1.24, 1.52, 5.18, 2.51, 2.24, 2.38, 1.71
1.4777, 1.3985, 1.2714, 1.2575, 1.2431, 1.2033, 1.1950, 1.1893, 1.1846, 1.1753, 1.1515, 1.1376, 1.1236	3.76, 3.99, 3.95, 3.71

^{13}C NMR of *N*-benzyloxycarbonyl-2,3-di-*O*-ethyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (5)

CC1(C)OC(C2=CC=CC=C2C(=O)N)C(OC(C)C)C1OC(C)C

6

δ (ppm): 7.3577, 7.3447, 7.3396, 7.3315, 7.3173, 7.2728, 5.1122, 5.1058, 4.3611, 4.3516, 3.7873, 3.7704, 3.7661, 3.7492, 3.7161, 3.7117, 3.6922, 3.6792, 3.6661, 3.6337, 3.6209, 3.6149, 3.5172, 3.5042, 3.4911, 3.4846, 3.4729, 3.4599, 3.4551, 3.3181, 3.3121, 3.2426, 3.2342, 3.2267, 3.2164, 1.5522, 1.5384, 1.5241, 1.5069, 1.4930, 1.4750, 1.4647, 1.3991, 1.3860, 1.3775, 1.3711, 1.3567, 1.3420, 1.3264, 1.2639, 0.9351, 0.9204, 0.9122, 0.9056, 0.8975, 0.8828.

Integration: 5.76, 2.00, 1.12, 1.04, 1.08, 2.24, 1.27, 2.60, 1.98, 2.03, 4.20, 3.05, 3.40, 4.72, 3.22, 3.09.

^{13}C NMR of *N*-benzyloxycarbonyl-2,3-di-*O*-butyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (6)

¹H NMR of *N*-benzyloxycarbonyl-2,3-di-*O*-benzyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (7)

^{13}C NMR of *N*-benzyloxycarbonyl-2,3-di-*O*-benzyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (7)

Chemical structure of compound **8** is shown above the spectrum. The structure is a cyclohexane ring substituted with an N-Cbz group and two NapO groups.

¹H NMR spectrum (CDCl₃) of compound **8**. The x-axis represents the chemical shift in ppm (f1), ranging from 0.5 to 8.5. The spectrum shows several multiplets in the aromatic region (7.0-8.5 ppm) and aliphatic region (1.0-4.5 ppm). Integration values are provided below the peaks.

Chemical shift values (ppm) listed above the spectrum:

- 7.9186, 7.9068, 7.9013, 7.8897, 7.8726, 7.8645, 7.8597, 7.8418, 7.7744, 7.5640, 7.5612, 7.5552, 7.5462, 7.3895, 7.3802, 5.2223, 5.1977, 5.1443, 5.1198, 5.0620, 5.0382, 4.9656, 4.9417, 4.8511, 4.8270, 4.7754, 4.7518, 4.5271, 4.5179, 4.5043, 4.4951, 4.2353, 4.0826, 4.0669, 4.0622, 4.0458, 3.9176, 3.8909, 3.7345, 3.7223, 3.4596, 3.4503, 3.4388, 3.4294, 1.6191, 1.5620.

Integration values listed below the spectrum:

- 9.13, 5.51, 4.98, 1.00, 1.00, 1.01, 1.11, 1.14, 1.05, 1.01, 1.09, 1.16, 2.05, 1.02, 1.06, 3.14, 3.05.

¹³C NMR of *N*-benzyloxycarbonyl-2,3-di-*O*-naphthyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (8)

^1H NMR of 2,3-di-*O*-methyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (9)

^{13}C NMR of 2,3-di-*O*-methyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (9)

^{13}C NMR of 2,3-di-*O*-ethyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (10)

¹H NMR of 2,3-di-*O*-butyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (11)

^{13}C NMR of 2,3-di-*O*-butyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (11)

¹H NMR of 2,3-di-*O*-benzyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (12)

^{13}C NMR of 2,3-di-*O*-benzyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (12)

^{13}C NMR of 2,3-di-*O*-naphthyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (13)

¹H NMR of *N*-benzyloxycarbonyl-2-*O*-benzoyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (14a)

^{13}C NMR of *N*-benzyloxycarbonyl-2-*O*-benzoyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (14a)

¹H NMR of *N*-benzyloxycarbonyl-3-*O*-benzoyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (14b)

^{13}C NMR of *N*-benzyloxycarbonyl-3-*O*-benzoyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (14b)

¹H NMR of *N*-benzyloxycarbonyl-2,3-di-*O*-benzoyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (14c)

^{13}C NMR of *N*-benzyloxycarbonyl-2,3-di-*O*-benzoyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (14c)

Chemical structure of **15a** is shown above the spectrum. The structure is a bicyclic molecule with a hydroxyl group (HO), a benzyloxy group (OBn), and a carbamate group (NCbz).

¹H NMR spectrum (CDCl₃) of **15a**. The x-axis is labeled f1 (ppm) and ranges from 0.0 to 7.5. The y-axis represents intensity. The spectrum shows several peaks, with chemical shifts labeled above them and integration values below them.

Chemical shifts (ppm): 7.3510, 7.3365, 7.3324, 7.3288, 7.3195, 7.3046, 7.3006, 7.2955, 7.2890, 7.2780, 7.2720, 7.2684, 7.2649, 7.2574, 7.2435, 5.0881, 5.0636, 5.0584, 5.0338, 4.6433, 4.3277, 4.3218, 4.3168, 4.1554, 3.6227, 3.6100, 3.6037, 3.4153, 3.4092, 3.4056, 3.4006, 3.3970, 3.3912, 3.1144, 3.1065, 3.0950, 2.9218, 2.9030, 2.8949, 1.8752, 1.4722, 1.4050.

Integration values: 1.30, 2.03, 2.02, 2.23, 1.14, 2.08, 1.07, 1.00, 1.10, 3.81, 3.18.

Chemical structure of **15a** is shown above the spectrum. The structure is a substituted furanose derivative with a benzylidene acetal protecting group and a benzylidene ether protecting group.

The ¹³C NMR spectrum (CDCl₃) shows the following chemical shifts (ppm):

- 154.2
- 137.0
- 135.1
- 127.7
- 127.5
- 127.3
- 127.1
- 126.9
- 126.8
- 126.7
- 124.7
- 98.3
- 75.1
- 72.3
- 71.2
- 66.5
- 61.2
- 53.8
- 45.6
- 28.8
- 28.5
- 28.3

15a

¹H NMR of *N*-benzyloxycarbonyl-3-*O*-benzyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (15b)

^{13}C NMR of *N*-benzyloxycarbonyl-3-*O*-benzyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (15b)

¹H NMR of *N*-benzyloxycarbonyl-2-*O*-naphthyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (16a)

^{13}C NMR of *N*-benzyloxycarbonyl-2-*O*-naphthyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (16a)

¹H NMR of *N*-benzyloxycarbonyl-3-*O*-naphthyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (16b)

^{13}C NMR of *N*-benzyloxycarbonyl-3-*O*-naphyl-1,5-dideoxy-1,5-imino-4,6-*O*-isopropylidene-D-glucitol (16b)