

Electronic Supplementary Information

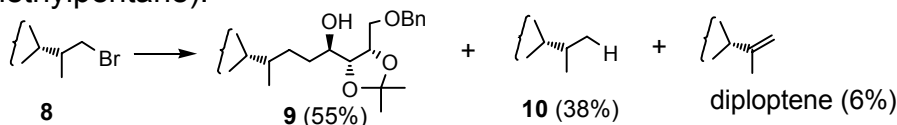
I. Coupling of bromide 8 and epoxide 4.

THF was distilled over Na and benzophenone. Glass syringes were used and magnetic bars were glass-coated. A CaCl₂ trap was placed between the argon source and the reaction flasks. Purity of starting bromide **8** was assessed by elemental analysis before any series of experiments. All other reactants were purchased from Aldrich or Acros without further purification.

Lithium 2-thienyl-cyanocuprate (Solution A): To a solution of thiophene (199 μ L, 2.44 mmol) in dry THF (5 mL) under an argon atmosphere, was added ⁿBuLi (2.5 M in hexane, 0.95 mL, 2.4 mmol) dropwise *via* a syringe at -78°C. Stirring was continued at this temperature for 15 min, then at -20°C for 30 min. The solution was transferred, *via* a cannula, into a suspension of CuCN (218.6 mg, 2.44 mmol) and dry THF (1 mL) at -78°C. Then, the mixture was warmed to -40°C to give a clear, light-tan solution.

Lithium naphthalene (Solution B): To freshly prepared Li^o (26 mg, 3.6 mmol) and naphthalene (312.7 mg, 2.44 mmol), under argon, was added freshly distilled THF (8 mL). The flask was then clamped in an ultrasonic bath, at a position of maximum energy and the irradiation was continued for 5 min at room temperature to afford a bottle-green solution. The reaction mixture was stirred for another 1h at room temperature to give a dark green solution.

Coupling reaction: Lithium naphthalene (Solution B) was transferred into the above freshly prepared lithium 2-thienylcyanocuprate (Solution A) at -78°C *via* a syringe, dropwise over a period of 20 min. Then, the stirring was continued for 30 min at -78°C. A solution of bromohopane **8** (270 mg, 0.549 mmol) in freshly distilled THF (6 mL, containing 0.2 eq. LiDBB), under argon, was added *via* a syringe at -78°C over a period of 10 min. A solution of epoxide **4** (2.8 eq.) in freshly distilled THF (2 mL, containing 0.2 eq. LiDBB) was added, in 2 minutes, by a syringe at -30°C. After stirring at -30°C for 10 min, the reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction mixture was then quenched with an aqueous NH₄Cl solution. The aqueous phase was extracted three times with CH₂Cl₂, the combined organic phases were washed with brine, dried (MgSO₄) and concentrated under reduced pressure. The resulting crude product was purified by silica gel chromatography (2,2,4-trimethylpentane/acetone, 40/1-30/1) to yield alcohol **9** as a white powder (204 mg, 55%, *R_f* 0.30, 2,2,4-trimethylpentane/acetone, 15/1), the protonation product **10** (142 mg, 38%, *R_f* 0.85, 2,2,4-trimethylpentane) and diploptene (22 mg, 6%, *R_f* 0.79, 2,2,4-trimethylpentane).



m.p.: 118-119°C;

[α]²²_D +48.2 (C 1.09, CHCl₃);

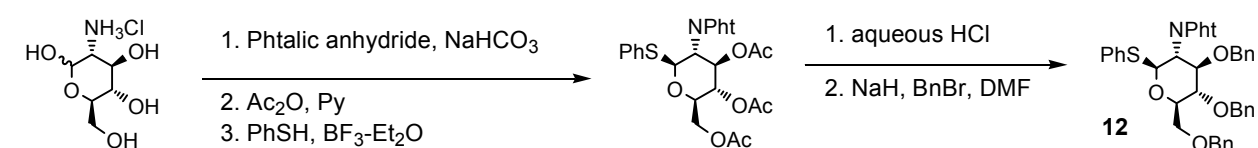
¹H NMR (400 MHz, CDCl₃): δ /ppm = 7.40-7.35 (5H, m, ArH), 4.61 (2H, m, BnCH₂), 4.39 (1H, ddd, *J*_{33,34} = 5.3 Hz, *J*_{34,35a} = 3.6 Hz, *J*_{34,35b} = 9.4 Hz, 34-H), 4.03 (1H, dd, *J*_{32,33} = 9.0 Hz, *J*_{33,34} = 5.3 Hz, 33-H), 3.70 (1H, m, 35-H_b), 3.67 (1H, m, 32-H), 3.59 (1H, d, *J*_{32,32-OH} = 2.8 Hz, 32-OH), 3.47 (1H, dd, *J*_{34,35a} = 3.6 Hz, *J*_{gem} = 9.3 Hz, 35-H_a), 1.39 and 1.36 (6H, d, acetal-Me),

0.99 (9H, m, 22-, 8 β - and 14 α -Me), 0.89 (3H, s, 4 α -Me), 0.85 (3H, s, 10 β -Me), 0.83 (3H, s, 4 β -Me), 0.75 (3H, s, 18 α -Me), 1.12-1.92 (29H, m, hopane), 0.72-0.97 (3H, m, hopane);

^{13}C NMR (101 MHz, CDCl_3): δ /ppm = 136.7, 128.6, 128.4, 128.2, 128.1, 108.4 (acetal-C), 80.8 (C-33), 75.4 (C-34), 73.9 (BnCH $_2$), 69.2 (C-32), 68.5 (C-35), 56.1 (C-5), 54.5 (C-17), 50.4 (C-9), 49.3 (C-13), 46.3 (C-21), 44.4 (C-18), 42.1 (C-3), 41.8 (C-14), 41.7 (C-8), 41.6 (C-19), 40.3 (C-1), 37.4 (C-10), 36.9 (C-22), 33.7 (C-15), 33.4 (C-24), 33.3 and 33.2 (C-4 and C-7), 31.1 (C-30), 30.9 (C-20), 28.1 (acetal-Me), 27.7 (C-31), 25.4 (acetal-Me), 24.0 (C-12), 22.8 (C-16), 21.6 (C-23), 20.9 (C-11), 20.0 (C-29), 18.7 (C-2 and C-6), 16.6 and 16.5 (C-26 and C-27), 15.9 (C-25 and C-28);

HRMS (DCI): m/z 694.5766 [$\text{M}+\text{NH}_4^+$], calcd for $\text{C}_{45}\text{H}_{76}\text{O}_4\text{N}$: 694.5774.

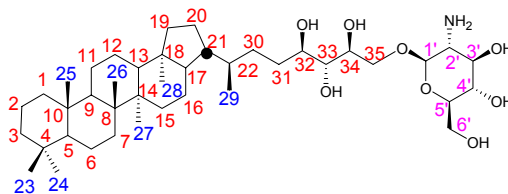
II. Thioglycoside 12 synthetic scheme.



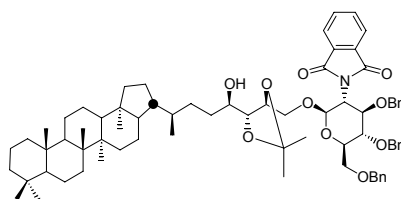
D-glucosamine
hydrochloride

III. Analytical data of final molecules.

Molecule numbering:



Protected glycoside (11).



^1H NMR (400 MHz, CDCl_3): δ 6.90-7.69 (19H, m, ArH), 5.28 (1H, d, $J_{1',2'} = 8.5$ Hz, 1'-H), 4.43-4.87 (6H, m, ArCH $_2$), 4.35 (1H, dd, $J_{2',3'} = 10.7$ Hz, $J_{3',4'} = 8.6$ Hz, 3'-H), 4.30 (1H, m, 34-H), 4.23 (1H, dd, $J_{1',2'} = 8.5$ Hz, $J_{2',3'} = 10.7$ Hz, 2'-H), 3.88 (1H, dd, $J_{34,35a} = 3.3$ Hz, $J_{\text{gem}} = 9.6$ Hz, 35-H $_a$), 3.85 (1H, m, 4'-H), 3.82 (2H, m, 6'-H $_a$ and 6'-H $_b$), 3.81 (1H, m, 33-H), 3.69 (1H, m, 5'-H), 3.62 (1H, m, 35-H $_b$), 3.33 (1H, m, 32-H), 2.62 (1H, d, $J_{32,32\text{-OH}} = 3.0$ Hz, 32-OH), 1.29 and 1.27 (6H, 2s, acetal-Me), 0.99 and 0.98 (6H, 2s, 26- and 27-Me), 0.89 (3H, s, 24-Me), 0.86 (3H, s, 25-Me), 0.84 (3H, s, 23-Me), 0.80 (3H, d, $J_{22,29} = 6.4$ Hz, 29R-Me), 0.70 (3H, s, 28-Me), 1.05-1.75 (27H, m, hopane), 0.63-0.95 (3H, m, hopane);

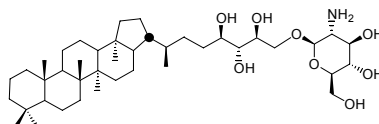
^{13}C NMR (101 MHz): δ 137.8, 137.7, 133.6, 128.4, 128.0, 127.9, 127.8, 127.4, 123.3, 108.3 (acetal-C), 97.9 (C-1'), 80.5 (C-4'), 79.4 (C-33), 79.0 (C-3'), 75.1 (C-5'), 75.0 (ArCH₂), 74.9 (C-34), 74.8 (ArCH₂), 73.6 (ArCH₂), 69.0 (C-32), 68.4 (C-6'), 67.3 (C-35), 56.1 (C-5), 55.5 (C-2'), 54.4 (C-17), 50.4 (C-9), 49.3 (C-13), 45.7 (C-21), 44.4 (C-18), 42.1 (C-3), 41.8 (C-14), 41.7 (C-8), 41.6 (C-19), 40.3 (C-1), 37.4 (C-10), 36.7 (C-22), 33.7 (C-15), 33.4 (C-23), 33.24 and 33.22 (C-4 and C-7), 30.4 (C-30), 30.2 (C-20), 28.1 and 25.4 (acetal-Me), 27.6 (C-31), 24.0 (C-12), 22.8 (C-16), 21.6 (C-23), 21.0 (C-11), 20.1 (C-29), 18.7 (C-2 and C-6), 16.6 and 16.5 (C-26 and C-27), 15.9 (C-25 and C-28);

HRMS(FAB): m/z 1170.7003 [$\text{M}+\text{Na}^+$], calcd for C₇₃H₉₇O₁₀NNa: 1170.7010;

m.p.: 154.5-155°C;

$[\alpha]_D^{22} +33.0$ (C 0.58, CHCl₃).

Final Molecule (2).



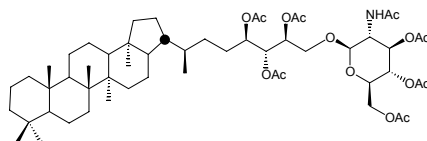
^1H NMR (400 MHz, Pyridine-*d*₅): δ 4.89 (1H, d, $J_{1',2'} = 7.9$ Hz, 1'-H), 4.67 (1H, m, 34-H), 4.66 (1H, m, 35-H_a), 4.58 (1H, m, 35-H_b), 4.49 (1H, dd, $J_{5',6'a} = 2.2$ Hz, $J_{\text{gem}} = 11.7$ Hz, 6'-H_a), 4.41 (1H, m, 32-H), 4.35 (1H, dd, $J_{5',6'b} = 5.2$ Hz, $J_{\text{gem}} = 11.7$ Hz, 6'-H_b), 4.29 (1H, m, 33-H), 4.20 (1H, dd, $J_{3',4'} = 9.2$ Hz, $J_{4',5'} = 8.9$ Hz, 4'-H), 4.00 (1H, dd, $J_{2',3'} = 8.9$ Hz, $J_{3',4'} = 9.2$ Hz, 3'-H), 3.89 (1H, m, 5'-H), 3.30 (1H, brdd, $J_{1',2'} = 7.9$ Hz, $J_{2',3'} = 8.9$ Hz, 2'-H), 1.06 (3H, d, $J_{22,29} = 5.5$ Hz, 29R-Me), 0.95 and 0.94 (6H, 2s, 26- and 27-Me), 0.87 (3H, s, 24-Me), 0.81 (6H, 2s, 25- and 23-Me), 0.70 (3H, s, 28-Me), 1.08-2.20 (27H, m, hopane), 0.70-0.91 (3H, m, hopane);

^{13}C NMR (101 MHz, Pyridine-*d*₅): δ 105.4 (C-1'), 78.5 (C-5'), 77.9 (C-3'), 75.3 (C-33), 73.6 (C-32), 73.3 (C-34), 73.1 (C-35), 71.5 (C-4'), 62.3 (C-6'), 58.5 (C-2'), 56.1 (C-5), 54.4 (C-17), 50.4 (C-9), 49.3 (C-13), 46.5 (C-21), 44.3 (C-18), 42.0 (C-3), 41.7 (C-14), 41.6 (C-8 and C-19), 40.2 (C-1), 37.3 (C-10), 37.0 (C-22), 33.7 (C-15), 33.3 (C-24), 33.1 (C-4 and C-7), 32.2 (C-30), 29.8 (C-20), 27.7 (C-31), 23.9 (C-12), 22.8 (C-16), 21.5 (C-23), 20.9 (C-11), 20.3 (C-29), 18.7 (C-2 and C-6), 16.5 and 16.4 (C-26 and C-27), 15.8 (C-25 and C-28);

HRMS (FAB⁺): m/z 730.5232 [$\text{M}+\text{Na}^+$], calcd for C₄₁H₇₃O₈NNa: 730.5234;

$[\alpha]_D^{22} +8.4$ (C 0.38, THF/H₂O 4/1).

Final molecule's peracetate



^1H NMR (400 MHz, CDCl₃): δ 5.89 (1H, d, $J_{2',\text{NHAc}} = 8.3$ Hz, NHAc), 5.48 (1H, dd, $J_{2',3'} = 10.5$ Hz, $J_{3',4'} = 9.4$ Hz, 3'-H), 5.28 (1H, t, $J_{32,33} = J_{33,34} = 5.1$ Hz, 33-H), 5.20 (1H, q, $J_{33,34} = J_{34,35a} = J_{34,35b} = 5.1$ Hz, 34-H), 5.09 (1H, dd, $J_{3',4'} = 9.4$ Hz, $J_{4',5'} = 10.0$ Hz, 4'-H), 4.98 (1H, m, 32-H), 4.84 (1H, d, $J_{1',2'} = 8.3$ Hz, 1'-H), 4.31 (1H, dd, $J_{5',6'a} = 4.5$ Hz, $J_{\text{gem}} = 12.3$ Hz, 6'-H_a), 4.16 (1H, dd, $J_{5',6'b} = 2.2$ Hz, $J_{\text{gem}} = 12.3$ Hz, 6'-H_b), 3.90 (2H, d, $J_{34,35a} = J_{34,35b} = J_{\text{gem}} = 5.1$ Hz, 35-H_a and 35-H_b), 3.76 (1H, ddd, $J_{4',5'} = 10.0$ Hz, $J_{5',6'a} = 4.5$ Hz, $J_{5',6'b} = 2.2$ Hz, 5'-H), 3.66 (1H, dt, $J_{1',2'} = J_{2',\text{NHAc}} = 8.3$ Hz, $J_{2',3'} = 10.5$ Hz, 2'-H), 2.12, 2.11, 2.11, 2.11, 2.06, 2.05 and 1.99 (21H, 7s, Ac), 0.97 (6H, s, 26- and 27-Me), 0.93 (3H, d, $J_{22,29} = 6.5$ Hz, 29R-Me), 0.88 (3H, s, 24-Me), 0.84 (3H, s, 25-Me), 0.82 (3H, s, 23-Me), 0.71 (3H, s, 28-Me), 0.99-1.85 (27H, m, hopane), 0.71-0.95 (3H, m, hopane);

¹³C NMR (101 MHz, CDCl₃): δ 170.8, 170.7, 170.6, 170.5, 170.2, 169.7 and 169.5 (Ac-C=O), 99.2 (C-1'), 72.1 (C-3'), 72.0 (C-32), 71.8 (C-5'), 71.3 (C-33), 69.9 (C-34), 68.6 (C-4'), 66.5 (C-35), 61.9 (C-6'), 56.1 (C-5), 55.0 (C-2'), 54.3 (C-17), 50.4 (C-9), 49.2 (C-13), 45.9 (C-21), 44.3 (C-18), 42.1 (C-3), 41.8 (C-14), 41.6 (C-8), 41.5 (C-19), 40.3 (C-1), 37.4 (C-10), 36.1 (C-22), 33.6 (C-15), 33.4 (C-24), 33.2 (C-4 and C-7), 30.7 (C-30), 27.6 (C-20), 25.9 (C-31), 23.9 (C-12), 23.2 (CH₃CONH), 22.8 (C-16), 21.6 (C-23), 21.1 and 20.94 (CH₃CO), 20.9 (C-11), 20.8, 20.74, 20.68 and 20.63 (CH₃CO), 19.8 (C-29), 18.7 (C-2 and C-6), 16.6 and 16.5 (C-26 and C-27), 15.9 and 15.8 (C-25 and C-28);

Mass (DCI-NH₃): m/z 1001.6 [M⁺];

m.p. 192-193 °C;

[α]_D²² +9.0 (C 0.71, CHCl₃).