Synthesis of a Glycosylated *ortho*-Carboranyl Amino Acid

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Abstract: The preparation of an *ortho*-carborane derivative bearing both carbohydrate and amino acid substituents is presented; opening of a glucofuranuro-γ-lactone derivative with propargylamines, cycloaddition of decaborane to an acetylenic bond and amidation with a *N*-Fmoc-glutamate derivative are the key-steps in this synthesis.

Key words: amino acids, boron, carbohydrates, carboranes, cycloadditions

ortho-Carboranes are boron-rich clusters,[1] which are of current interest for applications in medicinal chemistry.[2] Conjugation of carboranes to carbohydrates endows these (otherwise very) lipophilic boron cages with aqueous solubility; on the other hand, amino acid units can be grafted to allow carboranes incorporation into peptides.[2] To confer these two properties to a carborane core [3] we have prepared a glycosylated carboranyl amino acid, thus encompassing both carbohydrate and amino acid units, which has been designed (Figure 1) as follows.

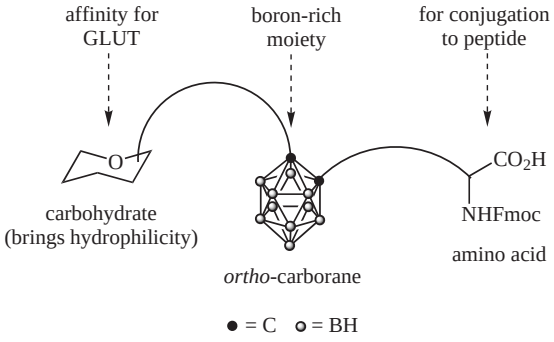

Figure 1

Solid phase peptide assembly of *N*-Fmoc-protected carboranyl amino acids has been shown to proceed efficiently,[4] which led to our choice of a *N*-α-Fmoc amino acid pendant side chain to enable subsequent conjugation. With regard to the carbohydrate unit, D-glucose was selected as it could allow recognition by the glucose transport proteins (GLUTs), provided linkage by a non-binding region (such as the non-reducing end of glucose).[5]

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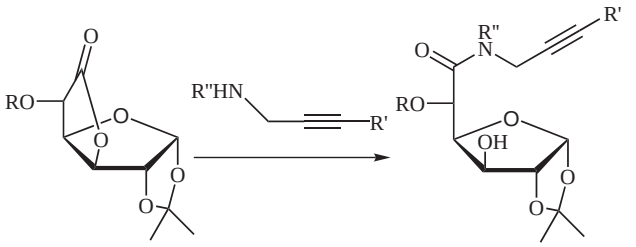
The carborane derivative shown in Figure 1 is unsymmetrical and there are two ways to obtain such C,C′-disubstituted carboranes: either by desymmetrisation of *ortho*-carborane[6] or by cycloaddition of decaborane to an unsymmetrically substituted triple bond.[7] This latter approach was favoured because it avoids the use of the expensive *ortho*-carborane as the starting material but also because formation of the boron cage can be planned at a late stage of the synthesis, thus bringing flexibility.



2 : R = H
3 : R = TBDMS

4 : R = R' = R" = H (100%)
5 : R = TBDMS ; R' = R" =H (62 %)
6 : R = R' = H ; R" = CH_3 (87%)
7 : R = R" = H ; R' = CH_2OH (98%)

Scheme 1

To introduce a glucose unit, advantage was taken of the peculiar reactivity at C-6 of the (readily available) glucofuranurono-γ-lactone acetals **2**[8] or **3**[9] as ring opening by amines is known to occur under particularly mild conditions.[10,11] For this work (Scheme 1) amidation with propargylamine occurred smoothly, which gave **4** and **5**, respectively. Efficient results were also achieved when **2** was treated with *N*-methyl-propargylamine (to give **6**) or 4-hydroxy-but-2-ynamine[12] (to give **7**); interestingly, when treated with 1,4-diamino-but-2-yne,[12] which was followed by acetal formation, **2** gave **8** (Figure 2), which therefore arose from a double condensation.[13]

Protection of the free hydroxyl groups of **4** and **5** needed to be performed as exchangeable protons are know to have adverse effects against the cycloaddition of decaborane to acetylenic bonds.[14] When masked as acetates (from compound **4**) or as silyl ethers (from compound **5**) complex mixtures were observed after reaction with decaborane but when protected together as a benzylidene acetal,[15] carborane formation was effective. However, to avoid introduction of a new stereocenter, an isopropylidene

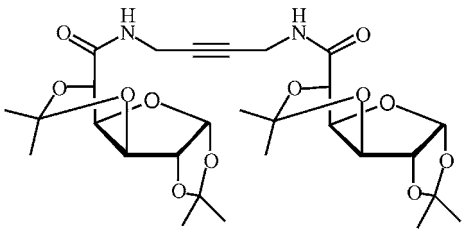


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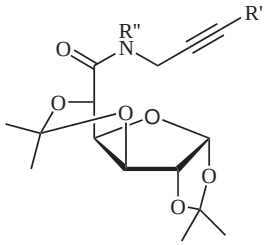
Figure 2

acetal seemed preferable. Using 2,2-dimethoxypropane/acetone under acidic catalysis, an acetalation procedure,[16] which consistently gave good results in this work, compounds **9** and **10** were obtained from **4** and **6**, respectively(Figure 3). Remarkably, when reacting **7** under those conditions, the mixed acetal **11** arising from a reaction of the primary hydroxyl group,[17] was formed. Compound **11** was selectively deprotected (without isolation) to give the desired alcohol **12**[18] that was subsequently converted to mesylate **13**.[19] Thus, **13** was obtained in 4 steps (86% overall yield) from **2** (Figure 3).



9 : R' = R" = H (81%)
10 : R' = H ; R" = CH_3 (87%)
11 : R' = CH_2O-CH(OCH_3)CH_3 ; R" =H
12: R' = CH_2OH ; R" = H (90%, 2 steps)
13: R' = $CH_2OSO_2CH_3$; R" = H (98%)

Figure 3

Substitution of **13** with cysteine was next attempted so as to link an amino acid moiety in a straightforward manner (Scheme 2). Deprotonation of the thiol group of cysteine with sodium ethoxide has been shown to occur without racemisation,[20] which allowed ligation of cysteine to mesylate **13** to afford **14**. Subsequent orthogonal protections of the amine and of the carboxylic groups (see Scheme 2) were performed as, here again, these functional groups needed to be protected before reaction with decaborane. However, despite such masking of exchangeable protons, no formation of carborane could be observed. This result was unexpected as thiopropargylic derivatives are known to react with decaborane uneventfully.[21] In case that the sulfur atom of **14** acted itself as a ligand of decaborane, thus inhibiting the process, the reaction was next attempted in the presence of an excess of diethyl sulfide but without success. Therefore, **13** was next converted to **15**[22] and condensed with FmocGlu(OH)OBn, which yielded **16**.[23] Reaction of **16** with decaborane proceeded then satisfactorily to give **17**.[24]

Thus, a glucosyl-carborane bearing a pendant *N*-Fmoc amino-acid side-chain, **17**, was obtained in 7 steps (31% overall yield from **2**). This boron cluster is of interest not only because its preparation provides a methodology for assembling carbohydrates and amino acids to a carborane core, but also because solid phase peptide assembly could enable its auto assembly towards the preparation of hydrophilic polycarboranes oligomers. This could be of interest for conveying large quantities of boron-10[25] to targets before Boron Neutron Capture Therapy (BNCT) treatments.[26]

Acknowledgement

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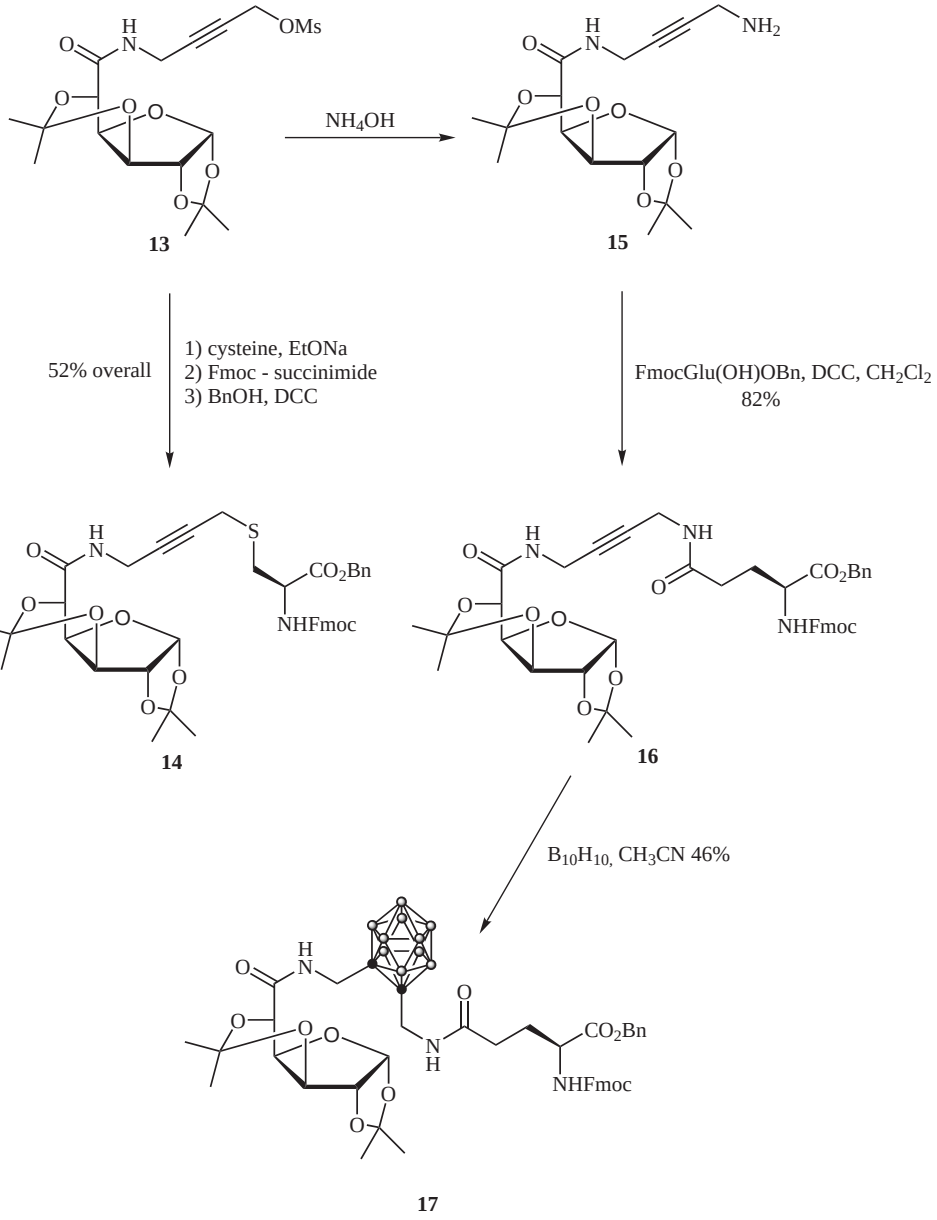
(11) General procedure for opening of lactone **2** with amines (5–15 mmole scale): To a solution of lactone in acetonitrile (10 mL/mmole) was added an excess of amine (2–4 equiv) and the mixture was stirred overnight after which time volatiles were removed. Compound **4** was obtained quantitatively without purification while isolation of pure **6** (87%) and **7** (98%) was performed by flash chromatography on silica gel (eluent:CH_2Cl_2/CH_3OH, 95:5).
4: ^{1}H NMR (300 MHz,, $CDCl_3$): 7.38 (t, J = 5.4 Hz, 1 H, NH); 5.97 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1); 4.84–4.07 (m, 8 H); 2.32 (t, $J_{1',3'}$ = 2.5 Hz, 1 H, H-3′); 1.48 (s, 3 H, CH_3); 1.31 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 172.3 (C-6); 112.2 (C-1); 105.2 [$C(CH_3)_2$]; 85.1; 80.8; 79.1 (C-3′); 75.2; 72.0



Scheme 2

(C-2′); 69.7; 29.2 (C-1′); 26.8 (CH_3); 26.2 (CH_3). **6:** ^{1}H NMR (300 MHz,, $CDCl_3$): 5.96 (d, $J_{1,2}$ = 3.5 Hz, 1 H, H-1); 4.76–4.43 (m, 4 H); 4.10–3.82 (m, 3 H); 3.40–3.10 (m); 3.16 (s, H-1″); 3.09 (s, H-1); 2.32 (t, $J_{1'\text{-}3'}$ = 2.4 Hz, H-3′); 2.26 (t, $J_{1'\text{-}3'}$ = 2.4 Hz, H-3′); 1.46 (s, 3 H, CH_3); 1.31 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 172.9 and 172.8 (C-6); 112.1 [$C(CH_3)_2$]; 112.0 [$C(CH_3)_2$]; 105.6 (C-1); 84.5; 82.7*; 77.9; 75.7; 75.6; 73,3; 72.7; 65.9; 39.0 (C-1′); 37.6 (C-1′); 34.6 (C-1″); 34.1 (C-1′); 26.9 (CH_3); 26.3 (CH_3). **7** ^{1}H NMR (300 MHz, CD_3OD): 5.90 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1); 4.47 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-2); 4.34–4.37 (d_{app}, J_{app} = 6.0 Hz, 1 H,); 4.26–4.16 (m, 4 H); 4.08–4.05 (t_{app}, J_{app} = 1.9 Hz, 2 H,); 1.44 (s, 3 H, CH_3); 1.29 (s, 3 H,CH_3). ^{13}C NMR (75 MHz, CD_3OD): 174.3 (C-6); 112.9 [$C(CH_3)_2$]; 106.4 (C-1); 86.4; 82.3; 81.9; 81.3; 75.9; 71.0; 50.7 (C-4′); 29.6 (C-1′); 271 (CH_3); 264 (CH_3). $[\alpha]^{20}_D$ –13 (c 6; MeOH).

(12) (a) 4-Hydroxy-but-2-ynamine was prepared by overnight stirring of a solution of 4-tosyloxybut-2-yn-1-ol in ammonium hydroxide, followed by evaporation and treatment of the crude solid with Dowex 1X8 $R_3N^+Cl^-$ pre-washed with 4% NaOH aq solution. The brown oil thus obtained should be used without delay. (b) For more information on 4-hydroxy-but-2-ynamine, see: Marszak-Fleury, A.; Laroche, J. *Bull. Soc. Chim. Fr.* **1963**, 1270. (c) For more information on synthetic procedure, see:Dumez, E.; Faure, R.; Dulcere, J.-P. *Eur. J. Org. Chem.* **2001**, 2577. (d) Analytical data for the tosylate salt: mp 94–96 °C. ^{1}H NMR (300 MHz, D_2O) 7.60 (d, 2 H, *J* = 7.1 Hz, ArH), 7.27 (d, 2 H, *J* = 7.1 Hz, ArH), 4.18 (s, 2 H, H-4), 3.77 (s, 2 H, H-1), 2.30 (s, 3 H, CH_3). ^{13}C NMR 140.0 (Cquat Ar), 137.9 (Cquat Ar); 127.2 (CH Ar), 123.1 (CH Ar), 82.5 and 73.8 (C-2, C-3), 47.1 and 27.0 (C-1, C-4), 18.3 (CH_3). (e) Similarly, but-2-yn-1,4-diamine was prepared from 1,4-bis-mesyloxy-but-2-yne, see: Haslinger, H.; Soloway, A. H. *J. Med. Chem.* **1966**, *9*, 792. (f) Analytical data for its bis mesylate salt: mp 160 (dec.) ^{1}H NMR (300 MHz, D_2O) 3.77 (s, 4 H, H-1/H-4), 2.58 (s, 6 H, CH_3). ^{13}C NMR 79.1 (C-2/C-3), 39.2 (CH_3), 29.8 (C-1/C-4).

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(18) To a solution of **7** (1g; 3.3 mmol) in acetone (30 mL) were added under stirring 2,2- dimethoxypropane (20 mL, 164 mmol; 50 equiv) and camphorsulfonic acid (77 mg, 0.33 mmol; 0.1 equiv). After 24 h stirring, $NaHCO_3$ (2 g) was added and after further 15 min stirring the mixture was filtered on celite. The oil (crude **11**) obtained after evaporation of the volatiles was dissolved in methanol (50 mL) containing AcOH (170 μL of 60% aqueous solution) and stirred at 50 °C for 80 min then cooled rapidly to r.t. Sodium hydrogen carbonate (2 g) was added and the solution was stirred for 15 min before filtration. Compound **12** (1.010 g, 3 mmol 90%) was obtained pure after column chromatography (silica gel, CH_2Cl_2/CH_3OH: 95/5) as a white foam ^1H NMR (300 MHz, $CDCl_3$): 6.57 (l s, 1 H, NH); 6.04 (d, $J_{1,2}$ = 3.7 Hz, 1 H, H-1); 4.60-4.50 (m, 2 H); 4.30–4.11 (m, 6 H); 1.49 (s, 3 H, CH_3); 1.42 (s, 3 H, CH_3); 1.39 (s, 3 H, CH_3); 1.32 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 169.3 (C-6); 112.1 [$C(CH_3)_2$)]; 107.8 (C-1); 101.0 [$C(CH_3)_2$]; 83.0; 82.2; 80.3 (C-2′, C-3′); 78.6; 74.2; 71.2; 50.3 (C-4′); 28.8 (C-1′); 26.5 (CH_3); 26.0 (CH_3); 23.9 (CH_3); 23.2 (CH_3).
(19) Mesylate **13** was obtained conventionally (triethylamine, mesyl chloride, 2.2 equiv each, in CH_2Cl_2, 2 h, 98%). ^1H NMR (300 MHz, $CDCl_3$): 6.53 (s l, 1 H, NH); 6.04 (d, $J_{1,2}$ = 3.7 Hz, 1 H, H-1); 4.90–4.85 (m, 2 H, $W_{1/2}$ = 33 Hz); 4.60–4.50 (m, 2 H); 4.10–4.25 (m, 4 H); 3.12 (s, 3 H, H-1″); 1.49 (s, 3 H, CH_3); 1.43 (s, 3 H, CH_3); 1.40 (s, 3 H, CH_3); 1.32 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 169.8 (C-6); 112.4 [$C(CH_3)_2$]; 106.5 (C-1); 101.3 [$C(CH_3)_2$]; 85.6 (CCH_2); 83.6; 79.3; 75.6 (CCH_2); 74.9; 71.9; 57.6 (C-4′); 39.1 (C-1″); 28.9 (C-1′); 27.2 (CH_3); 26.6 (CH_3); 24.6 (CH_3); 23.9 (CH_3).
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(22) Amine **15** was obtained by reaction of mesylate **13** with 25% aq. ammonia/dioxane (5/1) 35 °C, 80 min Yield: 95%. ^1H NMR (300 MHz, $CDCl_3$): 6.56 (s l, 1 H, NH); 6.04 (d, J_{1-2} = 3.7 Hz, 1 H, H-1); 4.59–4.55 (m, 2 H); 4.24–4.08 (m, 4 H); 3.46–3.44 (m, 2 H, J_{app} = 2 Hz); 1.70 (s l, 2 H, NH_2); 1.48 (s, 3 H, CH_3); 1.43 (s, 3 H, CH_3); 1.39 (s, 3 H, CH_3); 1.32 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 169.5 (C-6); 112.3 [$C(CH_3)_2$]; 106.4 (C-1); 101.1 [$C(CH_3)_2$]; 84.3; 83.6; 79.1; 74.8; 71.8 (C-2, C-3, C-4, C-5); 67,1; 31.6 (C-4′); 29.1 (C-1′); 27.1 (CH_3); 26.6 (CH_3); 24.6 (CH_3); 23.8 (CH_3).
(23) *N*-Fmoc amino acid **16**: Condensation of amine **15** in CH_2Cl_2 with commercially available benzyl ester of *N*-Fmoc glutamic acid in the presence of 1 equiv of DCC: 82%. ^1H NMR (300 MHz, $CDCl_3$): 7.75–7.26 (m, 13 H, H_{ar}); 6.71 (s l, 1 H, NH); 6.59 (s l, 1 H, NH); 6.04 (d_{app}, J_{app} = 7.95 Hz, NH); 6.00 (d_{app}, J_{app} = 3.7 Hz, 1 H, H-1); 5.15 [s, 2 H, CH_2 (Bn)];.4.58–3.98 (m, 12 H); 2.50–1.50 (m l, 4 H); 1.44 (s, CH_3); 1.38 (s, CH_3); 1.34 (s, CH_3); 1.29 (s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 171.9 (C-5″); 169.7 (C-6); 156.3 [OC(O)NH]; 143.9, 143.7, 141.3 (C_{quat} Fmoc); 135.2 (OCH_2C); 128.6; 128.5; 128.3; 127.7; 127.1; 125.1; 120.0; 112.3 [$C(CH_3)_2$]; 106.3 (C-1); 101.2 [$C(CH_3)_2$]; 83.5; 79.4; 79.3; 78.2; 77.6; 74.8; 71.8; 67,.2 (OCH_2CH); 67.0 (OCH_2CH); 53.7 (C-2″); 47.1 (OCH_2CH); 32.0; 29.2; 28.9; 27.9; 27.0 (CH_3); 26.5 (CH_3); 24.4 (CH_3); 23.7 (CH_3).
(24) Carborane **17**: Under argon, a solution of decaborane (20 mg; 0.17 mmol, 1.3 equiv) in toluene (2 mL) and acetonitrile (68 μL; 1.3 mmol, 10 equiv) was heated at 110 °C for 1 h then cooled to r.t. before the addition of **16** (100 mg; 0.13 mmol). The mixture was stirred at reflux for 5 h and methanol (0.5 mL) was added to destroy the excess of decaborane. After evaporation of the volatiles, column chromatography on silica gel (CH_2Cl_2/EtOAc: 8.5/1.5) gave carborane **17** (50 mg, 46%) as a white powder. ^1H NMR (300 MHz, $CDCl_3$): 7.74 (d_{app}, J_{app} = 7.5 Hz, 2 H); 7.58 (d_{app}, J_{app} = 7.2 Hz, 2 H); 7.5–7.2 (m, 11 H); 6.00 (d, *J* = 3.6 Hz, 1 H, H-1); 5.87 (d, *J* = 7.9 Hz, 1 H, NH); 5.17 (s l, 2 H, CCH_2O); 4.55–4.08 (m, 12 H); 2.28–2.02 (m); 1.44 (s, CH_3); 1.39 (s, CH_3); 1.36 (s, CH_3); 1.28 (s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 172.4 (C-1″); 171.7 (NHCO); 170;6 (NHCO); 156.6 [OC(O)NH]; 143.9; 143.7; 141.4 (C_{quat} Fmoc); 135.2 (OCH_2C); 128.7; 128.6; 128.4; 127.8; 127.2; 125.2; 120.1; 112.6 [$C(CH_3)_2$]; 106.5 (C-1); 101.6 [$C(CH_3)_2$]; 83.5; 81.0 (CB); 79.7; 78.2; 75.1; 71.8; 67.5 (OCH_2CH); 67.2 (OCH_2CH); 53.6 (C-2″); 47.2 (OCH_2CH); 42.0 (CH_2N); 41.1 (CH_2N); 32.0; 28.4; 27.1 (CH_3); 26.6 (CH_3); 24.2 (CH_3); 23.7 (CH_3). Anal. $C_{43}H_{57}B_{10}N_3O_{11}$–0.25 CH_2Cl_2. Calcd.: C 56.39, H 6.29, B 11.73, N 4.56; found C 56.48, H 6.35, B 11.75, N 4.55. MS (electrospray): $(M + Na)^+$ centered at *m/z* = 923.5 (cluster from *m/z* = 919.5 to 926.5 with relative intensities matching the calculated spectrum for $C_{43}H_{57}B_{10}N_3O_{11}$).
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