# Synthesis of conjugates of *closo*-dodecaborate dianion with cholesterol using a "click" reaction

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The nucleophilic ring-opening reaction of tetrahydropyran derivative of the *closo*-dodecaborate dianion with sodium azide in the presence of tetrabutylammonium bromide led to the novel azido-derivatives of $[B_{12}H_{12}]^{2-}$. A Cu-catalyzed 1,3-dipolar [3+2] cycloaddition reaction of the *closo*-dodecaborate dianion azido-derivatives with alkynyl-cholesterol led to 1,4-disubstituted 1,2,3-triazoles with the *closo*-dodecaborate fragment at position 1. The resulting conjugates are potentially suitable for the development of liposomal drugs to selectively deliver boron into a tumor cell for boron neutron capture therapy of cancer.

**Key words**: *closo*-dodecaborate dianion, cyclic oxonium derivatives of polyhedral boron hydrides, cholesterol, conjugates, lipids, liposomes, boron neutron capture therapy of cancer, "click" reaction.

The prevalence of cancer requires scientists to develop new efficient methods of prevention and intensive therapy. Scientific research is directed on the design of new antitumor agents which have a maximum inhibitory effect on tumor cells with a minimum damage of healthy cells and tissues of the body. At present, boron neutron capture therapy (BNCT),[1,2] a binary method for treating cancer based on the selective accumulation of non-radioactive isotope $^{10}B$ in tumor cells and their subsequent treatment with a flux of thermal neutrons, seems to be a promising method of combating cancer. The irradiation leads to the formation of high-energy fission products ($\alpha$ particles and $^{7}Li$ nuclei), which allows selective destruction of the tumor without affecting the surrounding healthy tissue.[3]

For the successful development of BNCT, it is necessary to have biocompatible nanomolecules containing a large number of boron atoms and capable of being selectively accumulated in malignant cells. One of the high-tech methods for the targeted delivery of drugs to cancer cells is their use in the form of liposomes.[4—6] Due to the high permeability of the walls of blood vessels inside the tumor, liposomes have the property of passive targeting.[7—9] This property is already actively used in medicine for the selective delivery of such anticancer drugs as doxorubicin[10] and paclitaxel.[11] Liposomal transport can also be actively used to deliver into a tumor a wide variety of types of boron polyhedra, which are not able to penetrate through cell membranes by themselves.[12—14] There are examples of producing liposomes based on polyhedral boron hydrides[15,16] containing borane and carborane derivatives both in the aqueous core and in the composition of the lipid bilayer.[17—19] One of the differences between normal and tumor cells is the rate of metabolism of low density lipoproteins. This difference is based on the increased need for tumor cells for cholesterol, which is necessary for the formation of cytoplasmic membranes of new cells. Thus, the design of stable biocompatible boron-containing cholesterol nanostructures for the further creation of liposomal agents containing derivatives of polyhedral boron hydrides is an actual issue which can solve the problem of the selective delivery of boron into tumor cells to carry out BNCT.

Due to its high stability, low toxicity, and good solubility in water in the form of sodium and potassium salts,[20,21] the *closo*-dodecaborate dianion ($[B_{12}H_{12}]^{2-}$) is particularly attractive for researchers, since it can be used as a basis for the development of drugs for boron neutron capture therapy of cancer. It can also be used as a connecting block for introducing a radiohalogen label into biomolecules for radioimmunodiagnostics and radioimmunotherapy.[22]

In the present work, we use the "click" reaction to obtain new conjugates of the *closo*-dodecaborate dianion with cholesterol suitable for the preparation of boron-containing liposomes as potential drugs for boron neutron capture therapy of cancer. The hydrophilic part of such lipids contains an anionic boron cluster, while the lipophilic part contains cholesterol.

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## Results and Discussion

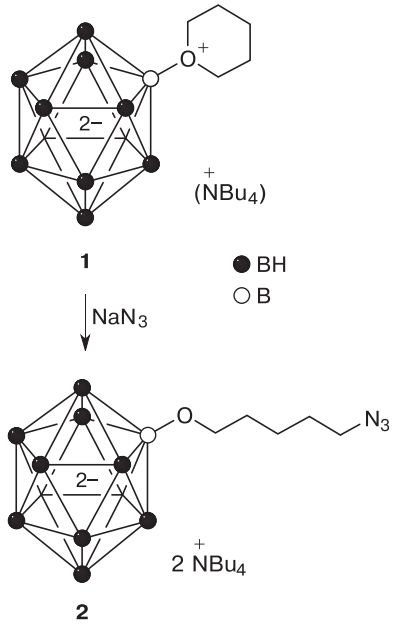
Preparation of biologically active molecules is a very important area of bioorganic chemistry, since these compounds are widely used in medicinal chemistry. In this case, significant limitations are imposed on bioconjugation methods: they should, as a rule, give high yields and do not react with various functional groups of biomolecules. Among these methods, one of the widely used is the Cu-catalyzed 1,3-dipolar [3+2] cycloaddition reaction of alkynes to azides, which proceeds regiospecifically to form the 1,4-isomer of 1,2,3-triazole. Azides and alkynes are inert toward most functional groups of both biomolecules and reagents used in other bioconjugation methods. Earlier, the "click" reaction was successfully used to obtain a wide range of conjugates of polyhedral boron hydrides with various biologically active molecules, for example, nucleosides[23] and chlorine $e_6$;[24] as well as derivatives of cholesterol based on cobalt and iron bis(1,2-dicarbollide) were obtained.[25] In the present work, we synthesize novel conjugates of cholesterol with the *closo*-dodecaborate dianion using the Cu-catalyzed 1,3-dipolar [3+2] cycloaddition reaction of azides to alkynes.

Earlier, our research team suggested an efficient method for the functionalization of *closo*-dodecaborate by nucleophilic ring-opening of its cyclic oxonium derivatives,[26] which allows one to obtain various functional groups or bioorganic molecules.[27—29] This approach was used to obtain the azido derivatives of $[B_{12}H_{12}]^{2-}$. The nucleophilic oxonium ring-opening of **1** with sodium azide in the presence of tetrabutylammonium bromide upon reflux in ethanol for 16 h gave quantitative yield of azide **2** based on the tetrahydropyran derivative of *closo*-dodecaborate dianion (Scheme 1). The structure of the obtained compound was confirmed by $^1$H, $^{11}$B, and $^{13}$C NMR spectra, IR spectroscopy and high resolution mass spectrometry. The $^{11}$B NMR spectrum of compound **2** exhibits four signals in a ratio of 1 : 5 : 5 : 1, which is characteristic of a monosubstituted boron cluster with a B—O bond. The signal of the substituted boron atom B—O at δ 6.5 is upfield shifted by 3 ppm as compared to that of the starting compound **1** (δ ≈ 9.2), which is typical of the transition from the $BO^+R_2$ to the B—OR system[26] and unambiguously confirms the opening of the oxonium ring. The $^1$H NMR spectrum of compound **2** contains the signals of the tetrabutylammonium cation at δ 3.20, 1.57, 1.32, and 0.94. In the IR spectrum, the absorption bands at ν ≈ 2090 cm$^{-1}$ and ν ≈ 2474 cm$^{-1}$ confirm, respectively, the presence of the azide and the BH group in compound **2**.

Azides based on the dioxane and tetrahydrofuran derivative of *closo*-dodecaborate dianion **3—5** were obtained according to the described procedures.[30,31] Azido-derivatives based on the *closo*-dodecaborate dianion **2—5** were used to synthesize new boron-containing cholesterols. The 1,3-dipolar [3+2] cycloaddition reaction of azides to terminal alkynes resulted in the synthesis of a number of 1,2,3-triazoles **7—10** substituted with the *closo*-dodecaborate dianion at position 1 and with cholesterol at position 4 (Scheme 2). The reaction of boron-containing azides **2—5** proceeded in a slight excess of alkynyl-cholesterol **6** in the presence of a CuI catalyst and diisopropylethylamine (DIPEA) as a base in ethanol upon prolonged reflux for 24 h (see Scheme 2). All the target triazoles **7—10** were isolated as cesium salts in 92—94% yield by reprecipitation from a methanol solution of CsF. The reaction progress of obtaining triazole derivatives was monitored by $^1$H NMR spectra, where the signal for the proton of the triazole group appeared and the signal for the proton of the acetylene group disappeared. The structures of conjugates **7—10** were confirmed by $^1$H, $^{13}$C, and $^{11}$B NMR spectra, IR spectroscopy, and high-resolution mass spectrometry.

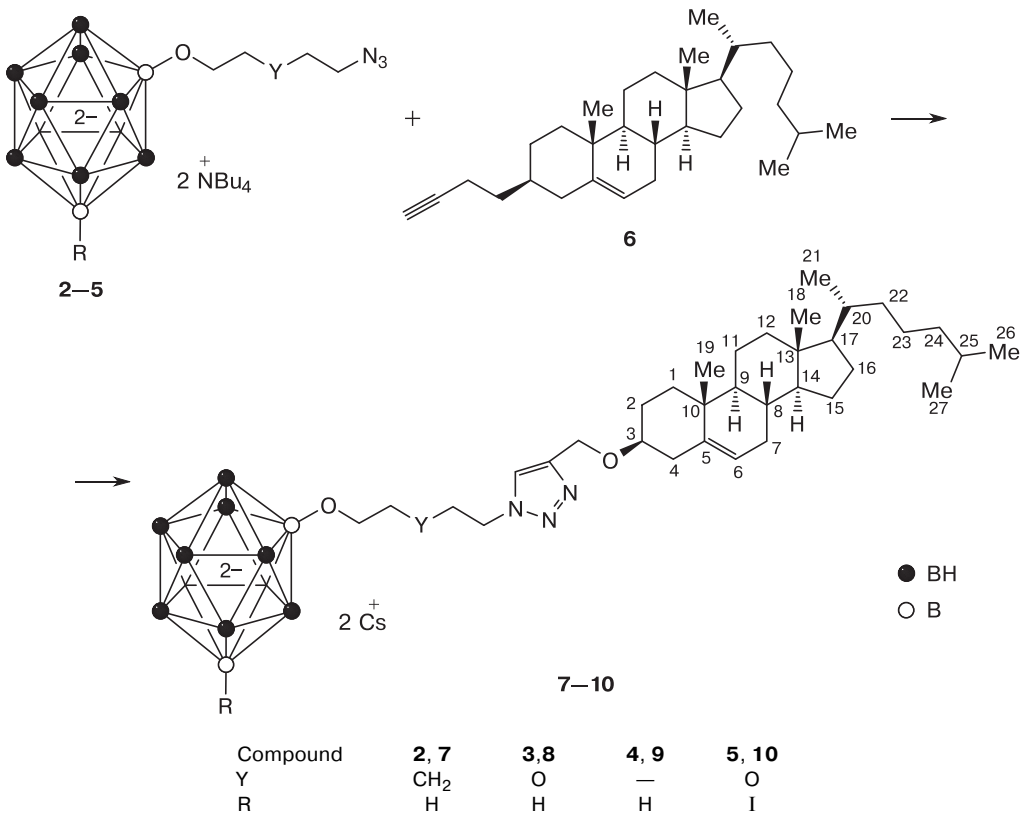
The $^1$H NMR spectra of complexes **7—10** contain signals for the protons of the triazole group at δ 8.04—8.12. A characteristic signal for the CH proton of the cholesterol fragment of the conjugates (at the double bond of the steroid fragment) is observed in the region of δ 5.3. The $^{13}$C NMR spectra of 1,2,3-triazoles exhibit signals for two carbon atoms of the triazole fragment in the region of δ 144 (the "nodal" atom) and in the region of δ 124—125. In the $^{11}$B NMR spectrum of compounds **7—10**, the signal for the B—O (B(1)) atom, as expected, is present at δ 6.2—6.4. The IR spectra of compounds **7—10** exhibit absorption bands characteristic of the BH groups (ν ≈ 2480 and 2475, 2488 and 2497 cm$^{-1}$, respectively) and the triazole ring (ν ≈ 1674, 1655, 1683, and 1658 cm$^{-1}$, respectively).

**Scheme 1**




**Reagents and conditions:** $NBu_4Br$, EtOH, reflux, 16 h.

**Scheme 2**




| Compound | **2**, **7** | **3**,**8** | **4**, **9** | **5**, **10** |
|---|---|---|---|---|
| Y | $CH_2$ | O | — | O |
| R | H | H | H | I |

**Reagents and conditions:** 1) CuI, DIPEA, EtOH, reflux, 24 h; 2) CsF, MeOH.

In conclusion, we have successfully applied the 1,3-dipolar [3+2] cycloaddition reaction of azides to terminal alkynes to obtain derivatives based on the *closo*-dodecaborate dianion. We found the optimal conditions allowing us to synthesize boron-containing cholesterols in higher than 90% yields. The resulting boron-containing lipids can be used as liposome precursors for the selective delivery of boron into tumor cells for boron neutron capture therapy of cancer.

## Experimental

The compounds $[B_{12}H_{11}O(CH_2)_5][NBu_4]$ (**1**),[26] $[B_{12}H_{11}O(CH_2)_2O(CH_2)_2N_3][(NBu_4)_2]$ (**3**),[30,31] $[B_{12}H_{11}O(CH_2)_4N_3][(NBu_4)_2]$ (**4**),[30] $[B_{12}H_{10}IO(CH_2)_2O(CH_2)_2N_3][(NBu_4)_2]$ (**5**),[32] alkynyl-cholesterol (**6**)[33] were obtained according to the described procedures. Reaction progress was monitored by thin layer chromatography on Kieselgel 60 F245 plates (Merck), visualization with a 0.5% solution of $PdCl_2$ in a 1% solution of HCl in the mixture of MeOH—$H_2O$ (10 : 1). $^1H$, $^{13}C$, $^{11}B$, and $^{11}B\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are given relative to $Me_4Si$ (for $^1H$ and $^{13}C$ NMR spectra) and $BF_3 \cdot Et_2O$ (for $^{11}B$ NMR spectra). The splitting patterns of signals of boron polyhedra were determined based on the $^{11}B$ NMR spectra. Electrospray ionization (ESI) mass spectra of negative ions were recorded on a MicroOTOF II mass spectrometer (Bruker Daltonics) operating in the mass range of $m/z$ 50—3000.

**Bis(tetrabutylammonium) (5-azidopentoxy)-*closo*-dodecaborate (2).** A mixture of compound **1** (500 mg, 1.07 mmol), $NaN_3$ (280 mg, 4.26 mmol), and $NBu_4Br$ (350 mg, 1.07 mmol) was refluxed in 96% EtOH (15 mL) for 16 h. The reaction mixture was cooled to room temperature, EtOH was evaporated, and water (10 mL) was added to the residue. The precipitate formed was collected by filtration, washed with water (5 mL), and dried in air. The yield of product **2** was 750 mg (93 %), a white powder. $^1H$ NMR (DMSO-$d_6$), δ: 3.28 (m, 4 H, O—C$\underline{H}_2$—$(CH_2)_3$—C$\underline{H}_2N_3$); 3.20 (m, 16 H, $\{^+N—[C\underline{H}_2—(CH_2)_2—CH_3]_4\}_2$); 1.57 (m, 20 H, $[^+N—(CH_2—C\underline{H}_2—CH_2—CH_3)_4]_2$, O—$CH_2$—C$\underline{H}_2$—$CH_2$—C$\underline{H}_2$—$CH_2N_3$); 1.32 (m, 18 H, $\{^+N—[(CH_2)_2—C\underline{H}_2—CH_3]_4\}_2$, O—$(CH_2)_2$—C$\underline{H}_2$—$(CH_2)_2N_3$); 0.94 (m, 24 H, $\{^+N—[(CH_2)_3—C\underline{H}_3]_4\}_2$). $^{13}C$ NMR (DMSO-$d_6$), δ: 68.2 (O—$\underline{C}H_2$—$(CH_2)_4N_3$); 58.0 ($\{^+N—[\underline{C}H_2—(CH_2)_2—CH_3]_4\}_2$); 51.3 [O—$(CH_2)_4$—$\underline{C}H_2N_3$]; 32.0 (O—$CH_2$—$\underline{C}H_2$—$CH_2$—$\underline{C}H_2$—$CH_2N_3$); 28.9 [O—$(CH_2)_2$—$\underline{C}H_2$—$(CH_2)_2N_3$]; 23.6 ($[^+N—(CH_2—\underline{C}H_2—CH_2—CH_3)_4]_2$); 19.7 ($\{^+N—[(CH_2)_2—\underline{C}H_2—CH_3]_4\}_2$); 14.0 ($\{^+N—[(CH_2)_3—\underline{C}H_3]_4\}]_2$). $^{11}B$ NMR (DMSO-$d_6$, δ: 6.5 (s, 1 B, $\underline{B}$—O); –16.8 (d, 5 B, $J$ = 128 Hz); –18.3 (d, 5 B, $J$ = 131 Hz); –23.1 (d, 1 B, $J$ = 129 Hz). IR, ν/$cm^{-1}$: 2474 (BH), 2090 ($N_3$). MS (ESI), found $m/z$: 511.5735[M]$^-$, calculated for $[C_5H_{21}B_{12}N_3O]^{2-}[NBu_4]^+$ 511.5740.

**Dicesium 4-[({(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-[(17*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,**

**14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl}-oxy)methyl]-1-[4-(decahydro-*closo*-dodecaborate)pentyl]-1*H*-1,2,3-triazole (7).** A mixture of compound **2** (300 mg, 0.40 mmol), alkynyl-cholesterol **6** (200 mg, 0.72 mmol), DIPEA (1 mL), and CuI (8 mg, 0.04 mmol) was refluxed in 96% EtOH (15 mL) for 16 h. The reaction progress was monitored by thin layer chromatography. Then, the reaction mixture was cooled to room temperature and passed through a layer of silica gel (2—3 cm) on a Schott filter. The system was washed with EtOH until the product ceased to be detected by thin layer chromatography. The solvent was removed on a rotary evaporator. The residue was dissolved in MeOH and an excess of a solution of CsF in MeOH was added. The precipitate formed was washed with MeOH (20 mL) and dried. The yield of product **7** was 350 mg (92%), a white powder. $^1$H NMR (DMSO-$d_6$), δ: 8.05 (s, 1 H, $CHCN_3$); 5.31 (s, 1 H, $C_{st}(6)H$);* 4.51 (s, 2 H, $CHCN_3$—C$\underline{H}_2$O—(3)); 4.30 (m, 2 H, $CH_2O$); 3.22 (m, 3 H, $CH_2N$, $C_{st}(3)H$); 2.35 (m, 1 H); 2.10 (m, 1 H); 1.94 (m, 4 H); 1.77 (m, 4 H); 1.49 (m, 6 H); 1.35 (m, 9 H); 1.09 (m, 10 H); 0.94 (s, 3 H, $C_{st}(19)H_3$); 0.88 (s, 3 H, $C_{st}(21)H_3$); 0.83 (s, 6 H, $C_{st}(26)H_3$, $C_{st}(27)H_3$); 0.64 (s, 3 H, $C_{st}(18)H_3$). $^{13}$C NMR (DMSO-$d_6$), δ: 144.8 (CH$\underline{C}N_3$), 140.9 ($C_{st}(5)$), 124.0 ($\underline{C}HCN_3$), 121.6 ($C_{st}(6)$), 78.1 ($C_{st}(3)$), 68.2 (O—$\underline{C}H_2$), 61.0 (O—$\underline{C}H_2$), 56.6 ($C_{st}(14)$), 56.0 ($C_{st}(17)$), 50.0 (N$\underline{C}H_2$), 49.9 ($C_{st}(9)$), 42.3 ($C_{st}(4)$), 39.0 ($C_{st}(13)$), 37.2 ($C_{st}(24)$), 36.7 ($C_{st}(1)$), 36.1 ($C_{st}(10)$), 35.7 ($C_{st}(22)$), 31.9 ($C_{st}(20)$), 31.8 ($C_{st}(8)$), 31.6 ($C_{st}(2)$), 30.3 ($CH_2$), 28.4 ($CH_2$), 28.3 ($C_{st}(7)$), 27.9 ($C_{st}(16)$), 24.3 ($C_{st}(25)$), 23.7 ($C_{st}(15)$), 23.3 ($C_{st}(23)$), 23.1 ($C_{st}(26)$), 22.9 ($C_{st}(27)$), 21.1 ($C_{st}(11)$, $C_{st}(12)$), 19.5 ($C_{st}(19)$), 19.0 ($C_{st}(21)$), 12.1 ($C_{st}(18)$). $^{11}$B NMR (DMSO-$d_6$), δ: 6.3 (s, 1 B, $\underline{B}$—O); −16.8 (d, 5 B, $J$ = 142 Hz); −18.3 (d, 5 B, $J$ = 151 Hz); −23.0 (d, 1 B, $J$ = 120 Hz). IR, ν/cm$^{-1}$: 2480 (BH), 1674 (triazole). MS (ESI), found *m/z*: 346.8279 [M]$^-$, calculated for $[C_{35}H_{69}B_{12}N_3O_2]^{2-}$ 346.8305.

**Dicesium 4-[({(3*S*,8S,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-[(17*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl}oxy)methyl]-1-{2-[2-(decahydro-*closo*-dodecaborate)etoxy]-ethyl}-1*H*-1,2,3-triazole (8).** The synthesis was carried out similarly to the procedure described above using compound **3** (200 mg, 0.27 mmol), alkynyl-cholesterol **6** (140 mg, 0.32 mmol), DIPEA (1 mL), and CuI (5 mg, 0.04 mmol). The yield of product **8** was 240 mg (94%), a white powder. $^1$H NMR (DMSO-$d_6$), δ: 8.11 (s, 1 H, $CHCN_3$); 5.33 (s, 1 H, $C_{st}(6)H$); 4.51 (m, 4 H, $CH_2O$); 3.76 (m, 2 H, $CH_2O$); 3.56 (m, 1 H, $C_{st}(3)H$); 3.24 (m, 2 H, C$\underline{H}_2$N); 2.37 (m, 1 H); 2.10 (m, 1 H); 1.92 (m, 4 H); 1.79 (m, 3 H); 1.50 (m, 6 H); 1.34 (m, 9 H); 1.10 (m, 10 H); 0.95 (s, 3 H, $C_{st}(19)H_3$); 0.89 (d, 3 H, $C_{st}(21)H_3$, $J$ = 6.6 Hz); 0.85 (s, 3 H, $C_{st}(26)H_3$); 0.83 (s, 3 H, $C_{st}(27)H_3$); 0.65 (s, 3 H, $C_{st}(18)H_3$). $^{13}$C NMR (DMSO-$d_6$), δ: 144.7 (CH$\underline{C}N_3$), 140.9 ($C_{st}(5)$), 125.0 ($\underline{C}HCN_3$), 121.6 ($C_{st}(6)$), 78.1 ($C_{st}(3)$), 72.4 (O—$\underline{C}H_2$), 69.0 (O—$\underline{C}H_2$), 67.7 (O—$\underline{C}H_2$), 60.9 (O—$\underline{C}H_2$), 56.7 ($C_{st}(14)$), 56.0 ($C_{st}(17)$), 50.1 (N$\underline{C}H_2$), 49.8 ($C_{st}(9)$), 42.3 ($C_{st}(4)$), 40.4 ($C_{st}(13)$), 39.4 ($C_{st}(12)$), 39.0 ($C_{st}(24)$), 37.2 ($C_{st}(1)$), 36.8 ($C_{st}(10)$), 36.1 ($C_{st}(22)$), 35.7 ($C_{st}(20)$) 31.9 ($C_{st}(8)$), 28.4 ($C_{st}(2)$), 28.3 ($C_{st}(7)$), 27.9 ($C_{st}(16)$), 24.3 ($C_{st}(25)$), 23.7 ($C_{st}(15)$), 23.1 ($C_{st}(23)$), 22.9 ($C_{st}(26)$), 21.1 ($C_{st}(27)$), 19.5 ($C_{st}(11)$), 19.0 ($C_{st}(19)$), 14.0 ($C_{st}(21)$), 12.2 ($C_{st}(18)$). $^{11}$B NMR (DMSO-$d_6$), δ: 6.2 (s, 1 B); −16.8 (d, 5 B, $J$ = 142 Hz); −18.1 (d, 5 B, $J$ = 151 Hz); −22.7 (d, 1 B, $J$ = 110 Hz). IR, ν/cm$^{-1}$: 2475 (BH), 1655 (triazole). MS (ESI), found *m/z:* 347.8200 [M]$^-$, calculated for $[C_{34}H_{67}B_{12}N_3O_3]^2$ 347.8201.

**Dicesium 4-[({(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-[(17*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl}oxy)methyl]-1-[4-(decahydro-*closo*-dodecaborate)butyl]-1*H*-1,2,3-triazole (9).** The synthesis was carried out similarly to the procedure described above using compound **4** (300 mg, 0.41 mmol), alkynyl-cholesterol **6** (210 mg, 0.49 mmol), DIPEA (1 mL), and CuI (8 mg, 0.04 mmol). The yield of product **9** was 360 mg (93%), a white powder. $^1$H NMR (DMSO-$d_6$), δ: 8.04 (s, 1 H, $CHCN_3$); 5.32 (s, 1 H, $C_{st}(6)H$); 4.51 (s, 2 H, C$\underline{H}_2$O—$C_{st}(3)H$); 3.34 (t, 2 H, $CH_2O$, $J$ = 7.2 Hz); 3.29 (t, 2 H, $CH_2N$, $J$ = 6.1 Hz); 3.22 (m, 1 H, $C_{st}(3)H$); 2.36 (m, 1 H); 2.10 (m, 1 H); 1.94 (m, 4 H); 1.77 (m, 5 H); 1.49 (m, 6 H); 1.29 (m, 14 H); 1.09 (m, 10 H); 0.94 (s, 3 H); 0.89 (d, 3 H, $C_{st}(21)H_3$, $J$ = 6.3 Hz); 0.84 (s, 3 H, $C_{st}(26)H_3$); 0.82 (s, 3 H, $C_{st}(27)H_3$); 0.64 (s, 3 H, $C_{st}(18)H_3$). $^{13}$C NMR (DMSO-$d_6$), δ: 144.7 (CH$\underline{C}N_3$), 140.9 ($C_{st}(5)$), 124.2 ($\underline{C}HCN_3$), 121.6 ($C_{st}(6)$), 78.1 ($C_{st}(3)$), 67.8 (O$\underline{C}H_2$), 61.0 (O$\underline{C}H_2$), 56.7 ($C_{st}(14)$), 56.0 ($C_{st}(17)$), 50.1 (N$\underline{C}H_2$), 49.8 ($C_{st}(9)$), 42.3 ($C_{st}(4)$), 39.0 ($C_{st}(13)$), 37.2 ($C_{st}(24)$), 36.8 ($C_{st}(1)$), 36.1 ($C_{st}(10)$), 35.7 ($C_{st}(22)$), 31.9 ($C_{st}(20)$), 31.9 ($C_{st}(8)$), 28.7($C_{st}(2)$), 28.4 ($CH_2$), 28.3 ($C_{st}(7)$), 28.1 ($C_{st}(16)$), 27.9 ($C_{st}(25)$), 24.3 ($C_{st}(15)$), 23.7 ($C_{st}(23)$), 23.1 ($C_{st}(26)$), 22.9 ($C_{st}(27)$), 21.1 ($C_{st}(11)$, $C_{st}(12)$), 19.5 ($C_{st}(19)$), 19.0 ($C_{st}(21)$), 12.2 ($C_{st}(18)$). $^{11}$B NMR (DMSO-$d_6$), δ: 6.4 (s, 1 B); −16.8 (d, 5 B, $J$ = 135 Hz); −18.2 (d, 5 B, $J$ = 176 Hz); −23.0 (d, 1 B, $J$ = 128 Hz). IR, ν/cm$^{-1}$: 2488 (BH), 1683 (triazole). MS (ESI), found *m/z*: 339.8209 [M]$^-$, calculated for $[C_{34}H_{67}B_{12}N_3O_2]^{2-}$ 339.8227.

**Dicesium 4-[({(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-[(17*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl}oxy)methyl]-1-{2-[2-(1-iodo-7-decahydro-*closo*-dodecaborate)ethoxy]ethyl}-1*H*-1,2,3-triazole (10).** The synthesis was carried out similarly to the procedure described above using compound **5** (110 mg, 0.12 mmol), alkynyl-cholesterol **6** (60 mg, 0.14 mmol), DIPEA (1 mL), and CuI (2 mg, 0.01 mmol). The yield of product **10** was 120 mg (93%), a white powder. $^1$H NMR (DMSO-$d_6$), δ: 8.12 (s, 1 H, $CHCN_3$); 5.33 (br.s, 1 H, $C_{st}(6)H$); 4.54 (s, 2 H, C$\underline{H}_2$O—$C_{st}(3)H$); 4.50 (m, 2 H, $CH_2O$); 3.76 (t, 2 H, $CH_2O$, $J$ = 5.3 Hz); 3.56 (m, 1 H, $C_{st}(3)H$); 3.24 (m, 2 H, $CH_2N$); 2.37 (m, 1 H); 2.10 (m, 1 H); 1.92 (m, 4 H); 1.79 (m, 3 H); 1.50 (m, 6 H); 1.35 (m, 9 H); 1.10 (m, 10 H); 0.95 (m, 6 H, $C_{st}(19)H_3$); 0.90 (d, 3 H, $C_{st}(21)H_3$, $J$ = 6.3 Hz); 0.85 (d, 3 H, $C_{st}(26)H_3$, $J$ = 2.0 Hz); 0.84 (d, 3 H, $C_{st}(27)H_3$, $J$ = 2.1 Hz); 0.65 (s, 3 H, $C_{st}(18)H_3$). $^{13}$C NMR (DMSO-$d_6$), δ: 144.7 (CH$\underline{C}N_3$), 141.0 ($C_{st}(5)$), 125.0 ($\underline{C}HCN_3$), 121.6 ($C_{st}(6)$), 78.0 ($C_{st}(3)$), 72.2 (O—$\underline{C}H_2$), 69.0 (O—$\underline{C}H_2$), 67.9 (O—$\underline{C}H_2$), 60.8 (O—$\underline{C}H_2$), 56.6 ($C_{st}(14)$), 56.0 ($C_{st}(17)$), 50.0 (N$\underline{C}H_2$), 49.8 ($C_{st}(9)$), 42.3 ($C_{st}(4)$), 40.4 ($C_{st}(13)$), 39.4 ($C_{st}(12)$), 39.0 ($C_{st}(24)$), 37.2 ($C_{st}(1)$), 36.8 ($C_{st}(10)$), 36.1 ($C_{st}(22)$), 35.7 ($C_{st}(20)$), 31.9 ($C_{st}(8)$), 28.4 ($C_{st}(2)$), 28.3 ($C_{st}(7)$), 27.9 ($C_{st}(16)$), 24.3 ($C_{st}(25)$), 23.7 ($C_{st}(15)$), 23.1 ($C_{st}(23)$), 22.9 ($C_{st}(26)$), 21.1 ($C_{st}(27)$), 19.6 ($C_{st}(11)$), 19.0 ($C_{st}(19)$), 12.2 ($C_{st}(18)$). $^{11}$B NMR (DMSO-$d_6$), δ: 6.2 (s, 1 B), −15.2 (d, 1 B, $J$ = 193 Hz); −16.6 (d, 4 B, $J$ = 168 Hz); −18.2 (d, 4 B, $J$ = 151 Hz); −21.4 (m, 2 B). IR, ν/cm$^{-1}$: 2497 (BH), 1658 (triazole). MS (ESI), found *m/z*: 410.7708 [M]$^-$, calculated for $[C_{34}H_{66}B_{12}IN_3O_3]^{2-}$ 410.7685.

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* Hereinafter st is a steroid fragment.

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