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Synthesis of new *nido*-carborane based carboxylic acids and amines

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ABSTRACT

A series of new *nido*-carborane based carboxylic acids 10-HOOC$(CH_2)_n$(Me)S-7,8-$C_2B_9H_{11}$ (n = 1–4) was prepared by alkylation of tetrabutylammonium salt of 10-methylthio-7,8-dicarba-*nido*-caborane with ω-halogenoalkyl esters or nitriles followed by acid hydrolysis. Likewise *nido*-carborane based amines 10-$H_2N(CH_2)_n$(Me)S-7,8-$C_2B_9H_{11}$ (n = 2, 3) were obtained using ω-bromoalkylphthalimides as alkylating agents followed by removal of the protecting group with hydrazine. Structure of 10-$C_6H_4(CO)_2NCH_2CH_2$(Me)S-7,8-$C_2B_9H_{11}$ was determined by single crystal X-ray diffraction.

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1. Introduction

Boron neutron capture therapy (BNCT) is a binary method for the treatment of cancer, which is based on the nuclear reaction of two essentially nontoxic species, non-radioactive ^{10}B and low-energy thermal neutrons. The neutron-capture reaction by ^{10}B produces α-particle, $^4He^{2+}$, and $^7Li^{3+}$ ion. These high-linear-energy transfer ions dissipate their kinetic energy before traveling one cell diameter (5–9 μm) in biological tissues, ensuring their potential for precise tumor cell-killing and sparing healthy tissues. Clinical interest in BNCT has focused primarily on the treatment of high-grade gliomas, and specifically glioblastoma multiforms, which are extremely resistant to all current forms of therapy, including surgery, chemotherapy, radiotherapy, immunotherapy, and gene therapy [1]. The initial step of development of the BNCT development was connected with use of nuclear reactors as the neutron sources [2,3]. The main advantage of using nuclear reactors is the lack of the need for large financial investments (only modification of the primary spectrum of the neutron beam for medical purposes using an appropriate beam shaping assembly (moderator, thermal neutron and gamma filters and collimator) is required). However, in this case, the medical treatment is strongly dependent on the operating cycle of the reactor and the reactor shutdown results in the stop of BNCT program. Therefore today's efforts to use BNCT as a routine radiotherapy focus on accelerator-based neutron sources which can be placed in a hospital environment [4–6]. At the same time, we should not forget that the accelerators are only one face of the problem and even more important for the BNCT establishment as a routine treatment procedure is development of new BNCT agents and better drug delivery systems [7–10].

Since BNCT is the binary therapy, the selective delivery of sufficiently large amount of ^{10}B nuclei to tumor cells (20–35 μg per gram of tumor tissue) is one of the most important requirements. This problem can be solved with the help of targeted liposomal delivery systems or by the attachment of a large number of boron-containing moieties to various biomolecules which will provide their targeted delivery to the tumor. One of the most widely used methods of modification of biomolecules is the reaction of their amino and carboxy groups with boron-containing acids and amines, respectively, to form an amide bond. Therefore, the synthesis of carborane-containing acids and amines has attracted the attention of researchers for more than fifty years [11]. Earlier we described the synthesis of a series of *nido*-carborane containing acids [12,13] and amines [13,14] with a terminal functional group attached to the carborane cage through sulfur atom. However, introduction of substituent at positions 7 or 9 of the *nido*-carborane cage results in the goal products as enantiomeric [12,14] or diastereomeric [13] mixtures. In this contribution we describe the synthesis of symmetrically substituted *nido*-carborane based carboxylic acids and amines 10-X$(CH_2)_n$(Me)S-7,8-$C_2B_9H_{11}$ (X = COOH, NH_2).

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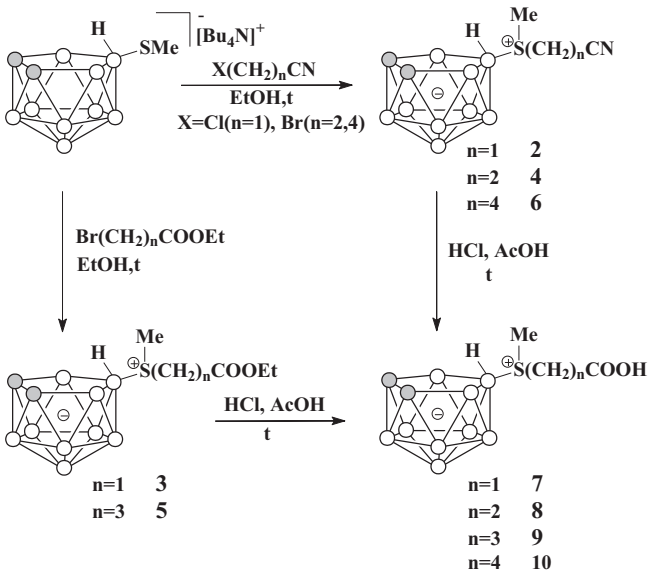
2. Results and discussion

Synthesis of functional derivatives of *closo*-decaborate $[B_{10}H_{10}]^{2-}$ [15–17] and *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$ [15,18] anions by alkylation of their methylsulfide derivatives is well known. These reactions result in chiral BS(Me)R sulfonium derivatives, nevertheless due low activation energy (ΔG_{298} = 0.4–0.8 kcal/mol) the epimerization at sulfur atom was found to proceed much easier than for trialkylsulfonium salts and occurs rather fast at room temperature [19]. However, in some cases, for example in the case of 9-alkyl(methyl)sulfonium derivatives of *nido*-carborane 9-R$(CH_2)_n$(Me)S-7,8-$C_2B_9H_{11}$ [13,20,21], the epimerization barrier is much higher due to strong interaction of the sulfur lone pair electrons with the B(9)–B(10) antibonding orbital of the *nido*-carborane cage [22]. As a result, these derivatives exist as mixtures of diastereomers which are not very suitable for medical applications. To overcome this problem, we synthesized a series of new *nido*-carborane based acids by alkylation of the symmetrical 10-methylsulfide derivative $[10\text{-MeS-7,8-}C_2B_9H_{11}]^-$. The 10-methylsulfide derivative was prepared by partial demethylation of well known 10-dimethylsulfonium derivative [10-Me_2S-7,8-$C_2B_9H_{11}$] [23] with sodium amide in refluxing toluene [24].

Alkylation of the tetrabutylammonium salt of 10-methylthio-7,8-dicarba-*nido*-caborane $(Bu_4N)^+[10\text{-MeS-7,8-}C_2B_9H_{11}]^-$ (**1**) with ω-halogenoalkyl nitriles or esters in refluxing ethanol gives the corresponding nitriles **2**, **4**, **6** and esters **3**, **5** (Scheme 1). Compounds **2**–**6** were purified by column chromatography on silica with CH_2Cl_2 as eluent. In all cases small amount of the 10-dimethylsulfonium derivative 10-Me_2S-7,8-$C_2B_9H_{11}$ was isolated. The subsequent acidic hydrolysis of nitriles and esters with the mixture of glacial acetic and hydrochloric acids lead to a series of *nido*-carborane based carboxylic acids with different spacer length between the carborane cage and terminal carboxylic group **7**–**10** (Scheme 1).

The synthesized compounds were characterized by ^{1}H, ^{13}C and ^{11}B NMR spectroscopy, IR spectroscopy and mass spectrometry. The ^{1}H NMR spectra of compounds **2**, **3** and **7** demonstrate magnetically non-equivalent signals of the S-CH_2 protons with J_2(H-H) geminal coupling constants ~16 Hz, whereas in the spectra of the compounds with longer spacers these signals are observed as multiplets. The ^{11}B{^{1}H} NMR spectra of compounds **3**–**10** contain a set of signals with 2:2:1:2:1:1 intensity ratio, indicating the expected



Scheme 1. Synthesis of *nido*-carborane based carboxylic acids.

mirror symmetry. However, in the spectrum of 10-N≡CCH_2(Me)S-7,8-$C_2B_9H_{11}$ (**2**) all three pair of signals are splitted giving 1:1:1:2:1:1:1:1 pattern (Fig. 1) that practically exactly (with the measurement error) coincides with the spectrum of the related propargyl derivative 10-HC≡CCH_2(Me)S-7,8-$C_2B_9H_{11}$ [24]. The signals of the B(5) and B(6) atoms in *nido*-carborane derivatives are known to be very sensitive to the position of the "extra" hydrogen atom which can migrate over two bridge positions B(9)–H–B(10) and B(10)–H–B(11) (so-called "μ-H rule") [25]. In the symmetrical dimethylsulfonium derivative 10-Me_2S-7,8-$C_2B_9H_{11}$ the "extra" hydrogen is located equally over the B(9)–H–B(10) and B(10)–H–B(11) positions, that results in the mirror plane passing through the B(1), B(3) and B(10) atoms. In asymmetrical alkylmethylsulfonium derivatives 10-R(Me)S-7,8-$C_2B_9H_{11}$, the presence of nonequivalent substituents at the sulfur atom could shift slightly the equilibrium position, producing in such a way splitting of the B(5/6) signal in the ^{11}B NMR spectra. This splitting (Δ) is incomplete (less than the signal linewidth) and rather small and varies from 0 to 0.8 ppm [24,26]. However, in the case of **2** this splitting arises to 3.3 ppm with simultaneous splitting of the B(9/11) and B(2,4) signals (Δ = 1.1–1.2 ppm) indicating strong shift of the "extra" hydrogen equilibrium resulting in its fixation over one B-B edge of the open pentagonal face of *nido*-carborane ("frozen" migration). The similar pattern was found earlier for the alkyne derivatives RC≡CCH_2(Me)S-7,8-$C_2B_9H_{11}$ (R = H, Ph, $SiMe_3$) where intramolecular B–H···π(C≡C) hydrogen bonding between the BHB hydrogen and alkyne group was revealed by single crystal X-ray diffraction and quantum chemical calculations [24]. Unfortunately, we were unable to obtain good quality crystals of **2**, however it is reasonable to suppose that similar intramolecular interaction between the BHB hydrogen and the nitrile group exists in this case as well.

The reaction of **1** with ω-bromoalkylphthalimides in refluxing ethanol gives the corresponding carboranyl alkylphthalimides **11**–**13**. The subsequent treatment of **12** and **13** with hydrazine hydrate results in the removal of phthalimide protection leading to the corresponding amines **14** and **15** (Scheme 2).

The ^{11}B NMR spectra of compounds **13**–**15** are similar to those of compounds **3**–**10**, whereas the spectra of compounds **11** and **12** were found unexpectedly to display practically the same pattern as in the spectrum of nitrile **2** indicating the "frozen" migration of the "extra" hydrogen. It is worth noting that increase of the spacer length results in the absence of such effect in phthalimide **13** and the removal of the phthalimide protection produces the disappearance of this effect in amine **14**. On the other hand, the presence of carboxyl (carboxyethyl) group in compounds **3**, **5**, **7**–**10** with different spacer length produces no effect in the ^{11}B NMR spectra. This let us to assume that fixation of the "extra" hydrogen is caused by its interaction with the phthalimide group. To clarify the nature of these interactions we performed X-ray diffraction study of compound **12**. However, in the solid state the substituent is oriented outward the carborane cage (the torsion angle B10-S1-C2-C3 is equal to −173.49(9)°) and there are no intramolecular interactions between the "extra" hydrogen atom and the phthalimide group (Fig. 2). Instead of this, numerous intermolecular contacts including intermolecular C–H···O hydrogen bonds and head-to-tail π-stacking between the phthalimide rings which are well known for phthalimide derivatives [27,28] were found. Thus, the formation of numerous weak intermolecular interactions in the solid state is preferable than the formation of one stronger intramolecular hydrogen bond. A similar situation was observed earlier in the case of Me_3SiC≡CCH_2(Me)S-7,8-$C_2B_9H_{11}$ [24].

Assuming that intramolecular interactions between the "extra" hydrogen atom and the phthalimide group can exist in solution, we calculated dependence of conformational energy upon rotation of the heterocyclic fragment around the S1-C2 bond (from 0 to 360°

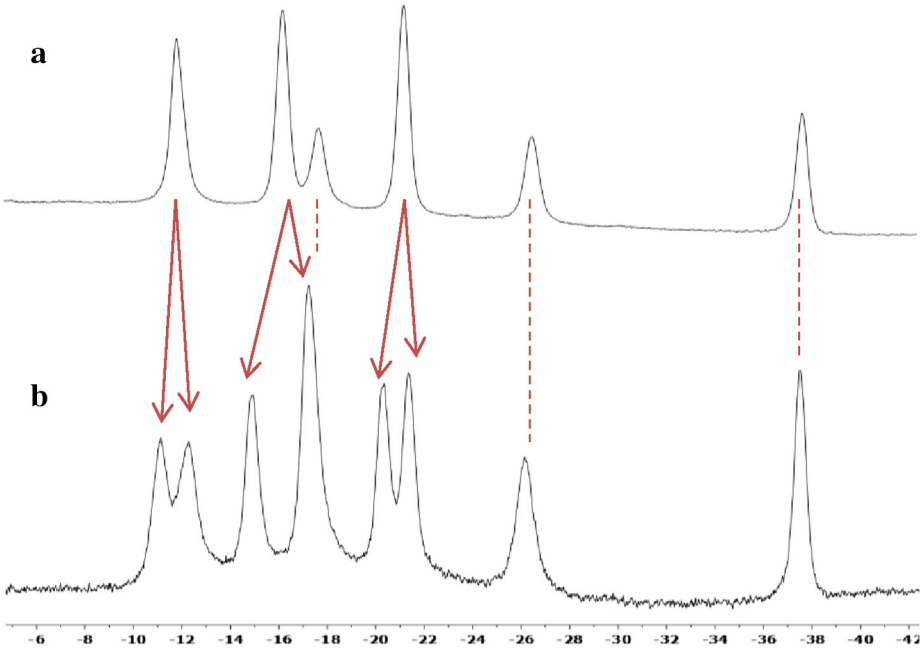
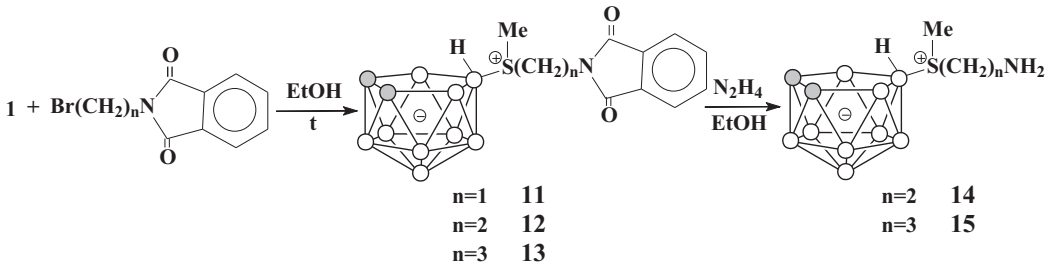


Fig. 1. $^{11}B\{^1H\}$ NMR spectra of compounds **4** (a) and **2** (b).



Scheme 2. Scheme of synthesis of *nido*-carborane based amines.

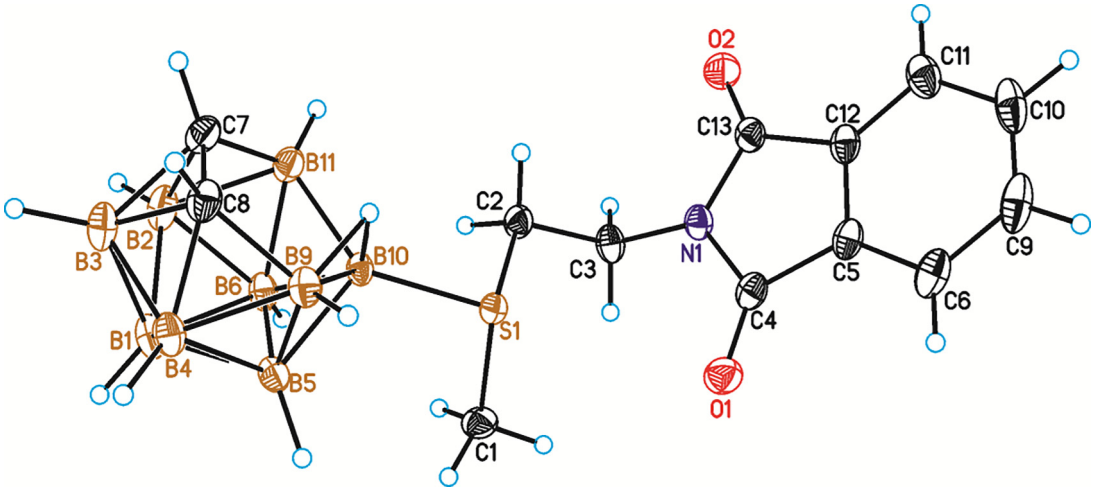


Fig. 2. General view of molecular structure of compound **12** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

with a step of 5°) using the GAUSSIAN program [29]. The PBE0/6-311G(df,pd) level of approximation was used in the present study being suitable for reliable estimation of both geometry and electron density distribution [21,24,30]. The results demonstrate the presence of three minima on potential energy curve (see ESI, Fig. S1). The global minimum corresponds to experimentally observed structure with the torsion angle of −175°. Two local minima were found at 95 and −60°. For all three structures, an additional optimization without torsion angle constraint was carried out. The corresponding torsion angles appeared to be equal to 94.4, −176.6, and −67.1° for local minimum 1, global minimum, and local minimum 2, respectively. Differences in energy between

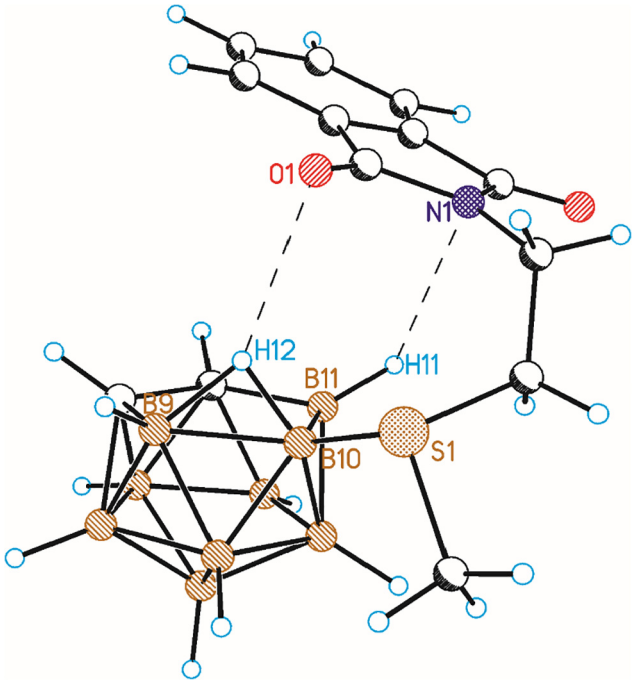


Fig. 3. Molecular structure of compound **12** in the conformation at local minimum 1.

global and local minima (2.2 and 3.0 kcal/mol for local minima 1 and 2, respectively) as well as the transition barriers (4.0 and 5.9 kcal/mol for transition from global min to local minima 1 and 2, respectively) are rather small that allows to suppose an existence of all conformers in solution. For both local minima conformers, topological analysis of calculated electron density within AIM theory [31] was carried out using the AIMALL program [32]. It was found that local minimum 1 corresponds to conformation with two nonbonded attractive intramolecular contacts H11…N1 and H12…O1 between the open face of carborane and the π-system of the substituent (Fig. 3).

Their energies were estimated by correlation between energy and energy density function V(r) at the bond critical point (BCP), Eint = ½V(r) [33] that was successfully used for energetical analysis of different types of nonbonded interactions [34–37]. The observed interactions are formed by the H11 and H12 hydrogen atoms of the open face of carborane with the π-system of the cyclic fragment of the substituent. The interaction energies were found to be −1.2 and −1.1 kcal/mol for H12…O1 and H11…N1 contacts, respectively, that can induce an asymmetry in the carborane cage and result in the splitting signals in the ^{11}B NMR spectrum.

It is worth noting that the synthesized *nido*-carborane acids **7**–**10** are stable both in the solid state and in solution, whereas amines **14** and **15** slowly decompose in the solid state and faster in solutions.

In summary, we have prepared and characterized a series of new *nido*-carborane based acids 10-HOOC$(CH_2)_n$(Me)S-7,8-$C_2B_9H_{11}$ (n = 1–4) and amines 10-$H_2N(CH_2)_n$(Me)S-7,8-$C_2B_9H_{11}$ (n = 2,3). The synthesized acids can be used for conjugation with tumor seeking biomolecules or for preparation of boron containing nanoparticles that have potential appliance in cancer diagnostics and therapy.

3. Experimental

The tetrabutylammonium salt of 10-methylthio-7,8-dicarba-*nido*-caborane [1] was prepared according to the literature procedure [24]. All reactions were carried out in air. The reaction progress was monitored by thin-layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5% $PdCl_2$ in 1% HCl in aq. MeOH (1:10). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B) and 100.0 MHz (^{13}C) in acetone d_6 were recorded with a Bruker Avance-400 spectrometer. The residual signal of the NMR solvent relative to tetramethylsilane was taken as the internal reference for ^{1}H and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced using BF_3Et_2O as external standard. Infrared spectra were recorded on an IR Prestige-21 (SHIMADZU) instrument. The electron ionization mass spectra were obtained with a Kratos MS 890 instrument operating in a mass range of m/z 50–800. Elemental analyses were performed at the Laboratory of Microanalysis of the Institute of Organoelement Compounds.

3.1. Synthesis of 10-NCCH$_2$(Me)S-7,8-C$_2$B$_9$H$_{11}$ (**2**)

To a solution of the tetrabutylammonium salt of 10-methylthio-7,8-dicarba-*nido*-caborane [1] (0.40 g, 0.95 mmol) in ethanol (10 ml) chloroacetonitrile (0.06 ml, 0.95 mmol) was added. After stirring for 15 min, *r.t.*, the mixture was heated under reflux for about 15 h and the solvent was evaporated under reduced pressure. The column chromatography on silica gel was used for the purification of the substance with CH_2Cl_2 as an eluent. Finally the solvent was removed in a vacuum to yield white solid (0.14 g, 68% yield). ^{1}H NMR (ppm): δ 4.58 (d, 1H, J = 16.6 Hz, SCH*H*), 4.47 (d, 1H, J = 16.6 Hz, SCH*H*), 2.92 (s, 3H, SCH_3), 2.26 (s, 2H, CH_{carb}), 2.6 ÷ (−0.2) (br s, 9H, B*H*).^{13}C NMR (ppm): δ 112.0 (CH_2CN), 48.7 (SCH_2-CN), 44.7 (CH_{carb}), 22.9 (SCH_3). ^{11}B NMR (ppm): δ −11.1 (d, J = 139 Hz, 1B), −12.3 (d, J = 147 Hz, 1B), −13.9 (d, J = 148 Hz, 1B), −17.2 (d, J = 138 Hz, 2B), −19.9 (d, J = 163 Hz, 1B), −21.0 (d, J = 142 Hz, 1B), −26.7 (s, 1B), −37.3 (d, J = 155 Hz, 1B). IR (Nujol, cm^{-1}): 2584 (br, ν_{B-H}), 2542 (br, ν_{B-H}), 2530 (br, ν_{B-H}), 2263 (ν_{CN}). MS (EI): m/z for $C_5H_{16}B_9NS$: calcd 220.2 [M]$^+$, obsd 220.0 [M]$^+$.

3.2. Synthesis of 10-C$_2$H$_5$O(O)CCH$_2$(Me)S-7,8-C$_2$B$_9$H$_{11}$ (**3**)

The procedure was analogous to that described for synthesis of **2** using (Bu_4N)[**1**] (0.40 g, 0.95 mmol) in ethanol (10 ml) and $BrCH_2C(O)OC_2H_5$ (0.10 ml, 0.95 mmol). The column chromatography on silica gel was used for the purification of the substance with CH_2Cl_2 as an eluent. Finally the solvent was removed in a vacuum to yield white solid (0.19 g, 75% yield). ^{1}H NMR (ppm): δ 4.30 (dq, 2H, J = 7.1 Hz, J = 1.4 Hz, OCH_2CH$_3$), 4.28 (d, 1H, J = 16.3 Hz, SCH*H*), 4.17 (d, 1H, J = 16.3 Hz, SC*H*H), 2.79 (s, 3H, SCH_3), 2.22 (s, 2H, CH_{carb}), 1.31 (t, 3H, J = 7.1 Hz, OCH$_2$CH_3), 2.5 ÷ 0.1 (br s, 8H, B*H*), −1.0 (br s, 1H, B*H*B). ^{13}C NMR (ppm): δ 164.9 (*C*(O)OCH$_2$CH$_3$), 62.3 (C(O)OCH$_2$CH$_3$), 45.3 (*C*H$_{carb}$), 43.9 (SCH$_2$), 23.1 (SCH$_3$), 13.3 (C(O)OCH$_2$CH$_3$). ^{11}B NMR (ppm): δ −11.4 (d, J = 143 Hz, 2B), −15.9 (d, J = 147 Hz, 2B), −17.3 (d, J = 184 Hz, 1B), −20.9 (d, J = 154 Hz, 2B), −26.4 (s, 1B), −37.5 (d, J = 144 Hz, 1B). IR (Nujol, cm^{-1}): 2557 (br, ν_{B-H}), 1734 ($\nu_{C=O}$). MS (EI): m/z for $C_7H_{21}B_9O_2S$: calcd 266.6 [M]$^+$, obsd 266.9 [M]$^+$.

3.3. Synthesis of 10-NCCH$_2$CH$_2$(Me)S-7,8-C$_2$B$_9$H$_{11}$ (**4**)

The procedure was analogous to that described for synthesis of **2** using (Bu_4N)[**1**] (0.40 g, 0.95 mmol) in ethanol (10 ml) and $BrCH_2CH_2CN$ (0.08 ml, 0.95 mmol). The column chromatography on silica gel was used for the purification of the substance with CH_2Cl_2 as an eluent. Finally the solvent was removed in a vacuum to yield white solid (0.17 g, 77% yield). ^{1}H NMR (ppm): δ 3.57 (m, 2H, SCH_2), 3.27 (t, 2H, J = 7.0 Hz, CH_2CN), 2.85 (s, 3H, SCH_3), 2.23 (s, 2H, CH_{carb}), 2.5 ÷ 0.2 (br s, 8H, B*H*), −1.0 (br s, 1H, B*H*B). ^{13}C

NMR (ppm): δ 117.1 (CH_2CN), 45.2 (CH_{carb}), 37.7 (SCH_2), 22.7 (SCH_3), 14.8 (CH_2CN). ^{11}B NMR (ppm): δ −11.4 (d, J = 143 Hz, 2B), −15.9 (d, J = 150 Hz, 2B), −17.2 (d, J = 178 Hz, 1B), −20.8 (d, J = 154 Hz, 2B), −26.4 (s, 1B), −37.4 (d, J = 146 Hz, 1B). IR (Nujol, cm^{-1}): 2580 (br, ν_{B-H}), 2553 (br, ν_{B-H}), 2530 (br, ν_{B-H}), 2254 (ν_{CN}). MS (EI): m/z for $C_6H_{18}B_9NS$: calcd 234.2 $[M]^+$, obsd 233.9 $[M]^+$.

3.4. Synthesis of 10-$C_2H_5O(O)CCH_2CH_2CH_2(Me)S$-7,8-$C_2B_9H_{11}$ (**5**)

The procedure was analogous to that described for synthesis of **2** using (Bu_4N)[**1**] (0.40 g, 0.95 mmol) in ethanol (10 ml) and $BrCH_2CH_2CH_2C(O)OC_2H_5$ (0.14 ml, 0.95 mmol). The column chromatography on silica gel was used for the purification of the substance with CH_2Cl_2 as an eluent. Finally the solvent was removed in a vacuum to yield white solid (0.17 g, 61% yield). ^{1}H NMR (ppm): δ 4.12 (q, 2H, J = 7.1 Hz, OCH_2CH_3), 3.22 (m, 2H, SCH_2), 2.70 (s, 3H, SCH_3), 2.56 (t, 2H, J = 7.1 Hz, $CH_2C(O)OCH_2CH_3$), 2.20 (s, 2H, CH_{carb}), 2.13 (m, 2H, $CH_2CH_2CH_2$), 1.23 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 2.8 ÷ 0.2 (br s, 9H, B*H*). ^{13}C NMR (ppm): δ 171.6 ($C(O)OCH_2CH_3$), 60.1 ($C(O)OCH_2CH_3$), 45.1 (CH_{carb}), 41.6 (SCH_2), 31.7 ($CH_2C(O)OCH_2CH_3$), 22.4 (SCH_3), 21.1 ($CH_2CH_2CH_2$), 13.6 ($C(O)OCH_2CH_3$). ^{11}B NMR (ppm): δ −11.7 (d, J = 140 Hz, 2B), −15.8 (d, J = 150 Hz, 2B), −17.3 (d, J = 183 Hz, 1B), −20.8 (d, J = 151 Hz, 2B), −26.1 (s, 1B), −37.5 (d, J = 138 Hz, 1B). IR (Nujol, cm^{-1}): 2581 (br, ν_{B-H}), 2553 (br, ν_{B-H}), 2528 (br, ν_{B-H}), 1734 ($\nu_{C=O}$). MS (EI): m/z for $C_9H_{25}B_9O_2S$: calcd 295.2 $[M]^+$, obsd 295.1 $[M]^+$.

3.5. Synthesis of 10-$NCCH_2CH_2CH_2CH_2(Me)S$-7,8-$C_2B_9H_{11}$ (**6**)

The procedure was analogous to that described for synthesis of **2** using (Bu_4N)[**1**] (0.50 g, 1.19 mmol) in ethanol (15 ml) and $BrCH_2CH_2CH_2CH_2CN$ (0.14 ml, 1.19 mmol). The column chromatography on silica gel was used for the purification of the substance with CH_2Cl_2 as an eluent. Finally the solvent was removed in a vacuum to yield white solid (0.24 g, 77% yield). ^{1}H NMR (ppm): δ 3.24 (m, 2H, SCH_2), 2.70 (s, 3H, SCH_3), 3.61 (t, 2H, J = 7.1 Hz, CH_2CN), 2.20 (s, 2H, CH_{carb}), 2.02 (m, 2H, SCH_2CH_2), 1.89 (m, 2H, CH_2CH_2CN), 2.4 ÷ 0.2 (br s, 9H, B*H*). ^{13}C NMR (ppm): δ 119.4 (CH_2CN), 45.2 (CH_{carb}), 41.5 (SCH_2), 24.8 (SCH_3), 24.1 (CH_2CN), 22.5 (SCH_2CH_2), 15.9 (CH_2CH_2CN). ^{11}B NMR (ppm): δ −11.4 (d, J = 142 Hz, 2B), −15.9 (d, J = 147 Hz, 2B), −17.3 (d, J = 180 Hz, 1B), −20.9 (d, J = 155 Hz, 2B), −26.2 (s, 1B), −37.5 (d, J = 147 Hz, 1B). IR (Nujol, cm^{-1}): 2583 (br, ν_{B-H}), 2561 (br, ν_{B-H}), 2541 (br, ν_{B-H}), 2528 (br, ν_{B-H}), 2254 (ν_{CN}). MS (EI): m/z for $C_8H_{22}B_9NS$: calcd 262.2 $[M]^+$, obsd 261.9 $[M]^+$.

3.6. Synthesis of 10-$HOOCCH_2(Me)S$-7,8-$C_2B_9H_{11}$ (**7**)

a. Compound **2** (0.12 g, 0.56 mmol) was dissolved in glacial acetic acid (8 ml) forming a colorless solution. After stirring for 15 min, *r.t.*, concentrated hydrochloric acid (4 ml) was added. The reaction mixture was refluxed for 4 h. and then was cooled and evaporated under reduced pressure. The column chromatography on silica gel was used for the purification of the substance with ethyl acetate as an eluent. Finally the solvent was removed in a vacuum to yield white solid (0.10 g, 74% yield).

b. The procedure was analogous to method **a**, using **3** (0.15 g, 0.56 mmol), glacial acetic acid (8 ml) and concentrated hydrochloric acid (4 ml) to yield white solid (0.11 g, 82% yield).

^{1}H NMR (ppm): δ 4.23 (d, 1H, J = 16.5 Hz, SCH*H*), 4.14 (d, 1H, J = 16.5 Hz, SCH*H*), 2.76 (s, 3H, SCH_3), 2.20 (s, 2H, CH_{carb}), 2.5 ÷ (−0.2) (br s, 8H, B*H*), −1.0 (br s, 1H, B*H*B). ^{13}C NMR (ppm): δ 166.3 (*C*OOH), 45.0 (CH_{carb}), 44.0 (SCH_2COOH), 22.9 (SCH_3). ^{11}B NMR (ppm): δ −11.6 (d, J = 134 Hz, 2B), −15.7 (d, J = 135 Hz, 1B), −16.1 (d, J = 134 Hz, 1B), −17.4 (d, J = 160 Hz, 1B), −20.8 (d, J = 146 Hz, 2B), −26.3 (s, 1B), −37.5 (d, J = 144 Hz, 1B). IR (Nujol, cm^{-1}): 2557 (br, ν_{B-H}), 2553 (br, ν_{B-H}), 1701 ($\nu_{C=O}$). MS (EI): m/z for $C_5H_{17}B_9O_2S$: calcd 239.1 $[M]^+$, obsd 239.0 $[M]^+$. *Anal.* Calc. for $C_5H_{17}B_9O_2S$: C, 25.18; H, 7.18; B 40.79. Found: C, 25.11, H, 7.20, B, 40.63.

3.7. Synthesis of 10-$HOOCCH_2CH_2(Me)S$-7,8-$C_2B_9H_{11}$ (**8**)

The procedure was analogous to that described for synthesis of **7** using **4** (0.13 g, 0.56 mmol), glacial acetic acid (8 ml) and concentrated hydrochloric acid (4 ml) to yield white solid (0.11 g, 80% yield). ^{1}H NMR (ppm): δ 3.40 (m, 1H, SCH*H*), 3.31 (m, 1H, SCH*H*), 2.98 (t, 2H, J = 7.1 Hz CH_2COOH), 2.74 (s, 3H, SCH_3), 2.21 (s, 2H, CH_{carb}), 2.5 ÷ 0.3 (br s, 8H, B*H*), −1.1 (br s, 1H, B*H*B). ^{13}C NMR (ppm): δ 170.9 (*C*OOH), 44.7 (CH_{carb}), 37.5 (SCH_2), 29.7 (CH_2COOH), 22.9 (SCH_3). ^{11}B NMR (ppm): δ −11.4 (d, J = 143 Hz, 2B), −15.8 (d, J = 147 Hz, 2B), −17.3 (d, J = 181 Hz, 1B), −20.9 (d, J = 154 Hz, 2B), −26.2 (s, 1B), −37.4 (d, J = 145 Hz, 1B). IR (Nujol, cm^{-1}): 2561 (br, ν_{B-H}), 2537 (br, ν_{B-H}), 2507(br, ν_{B-H}), 1702 ($\nu_{C=O}$). MS (EI): m/z for $C_6H_{19}B_9O_2S$: calcd 253.2 $[M]^+$, obsd 253.0 $[M]^+$. *Anal.* Calc. for $C_6H_{19}B_9O_2S$: C, 28.53; H, 7.58; B 38.52. Found: C, 28.26, H, 7.73, B, 38.33.

3.8. Synthesis of 10-$HOOCCH_2CH_2CH_2(Me)S$-7,8-$C_2B_9H_{11}$ (**9**)

The procedure was analogous to that described for synthesis of **7** using **5** (0.14 g, 0.47 mmol), glacial acetic acid (6 ml) and concentrated hydrochloric acid (3 ml) to yield white solid (0.09 g, 72% yield). ^{1}H NMR (ppm): δ 3.22 (m, 2H, SCH_2), 2.71 (s, 3H, SCH_3), 2.54 (t, 2H, J = 7.1 Hz CH_2COOH), 2.21 (s, 2H, CH_{carb}), 2.14 (m, 2H, $CH_2CH_2CH_2$), 2.5 ÷ 0.1 (br s, 9H, B*H*). ^{13}C NMR (ppm): δ 172.9 (*C*OOH), 45.2 (CH_{carb}), 41.5 (SCH_2), 31.4 (CH_2COOH), 24.1 (SCH_3), 22.4 ($CH_2CH_2CH_2$). ^{11}B NMR (ppm): δ −11.7 (d, J = 144 Hz, 2B), −15.8 (d, J = 146 Hz, 2B), −17.4 (d, J = 182 Hz, 1B), −20.8 (d, J = 155 Hz, 2B), −26.1 (s, 1B), −37.5 (d, J = 141 Hz, 1B). IR (Nujol, cm^{-1}): 2553 (br, ν_{B-H}), 2538 (br, ν_{B-H}), 2518 (br, ν_{B-H}), 1704 ($\nu_{C=O}$). MS (EI): m/z for $C_7H_{21}B_9O_2S$: calcd 267.2 $[M]^+$, obsd 267.1 $[M]^+$. *Anal.* Calc. for $C_7H_{21}B_9O_2S$: C, 31.54; H, 7.94; B 36.49. Found: C, 31.60, H, 7.98, B, 36.23.

3.9. Synthesis of 10-$HOOCCH_2CH_2CH_2CH_2(Me)S$-7,8-$C_2B_9H_{11}$ (**10**)

The procedure was analogous to that described for synthesis of **7** using **6** (0.19 g, 0.73 mmol), glacial acetic acid (10 ml) and concentrated hydrochloric acid (5 ml) to yield white solid (0.18 g, 88% yield). ^{1}H NMR (ppm): δ 3.17 (m, 2H, SCH_2), 2.67 (s, 3H, SCH_3), 2.40 (t, 2H, J = 7.0 Hz CH_2COOH), 2.19 (s, 2H, CH_{carb}), 1.94 (m, 2H, SCH_2CH_2), 1.77 (m, 2H, CH_2CH_2COOH), 2.3 ÷ 0.3 (br s, 8H, B*H*), −1.1 (br s, 1H, B*H*B). ^{13}C NMR (ppm): δ 173.7 (*C*OOH), 45.3 (CH_{carb}), 42.1 (SCH_2), 32.5 (CH_2COOH), 25.0 (SCH_3), 23.1 (SCH_2CH_2), 22.6 (CH_2CH_2COOH). ^{11}B NMR (ppm): δ −11.4 (d, J = 143 Hz, 2B), −15.8 (d, J = 142 Hz, 2B), −17.3 (d, J = 181 Hz, 1B), −20.9 (d, J = 153 Hz, 2B), −26.2 (s, 1B), −37.5 (d, J = 144 Hz, 1B). IR (Nujol, cm^{-1}): 2603 (br, ν_{B-H}), 2538 (br, ν_{B-H}), 2524 (br, ν_{B-H}), 1706 ($\nu_{C=O}$). MS (EI): m/z for $C_8H_{23}B_9O_2S$: calcd 281.3 $[M]^+$, obsd 281.2 $[M]^+$. *Anal.* Calc. for $C_8H_{23}B_9O_2S$: C, 34.24; H, 8.26; B 34.67. Found: C, 34.21, H, 8.43, B, 36.07.

3.10. Synthesis of 10-$C_6H_4(CO)_2NCH_2(Me)S$-7,8-$C_2B_9H_{11}$ (**11**)

The procedure was analogous to that described for synthesis of **2** using (Bu_4N)[**1**] (0.30 g, 0.71 mmol) in ethanol (10 ml) and $BrCH_2(CO)_2C_6H_4$ (0.17 g, 0.71 mmol). The column chromatography on silica gel was used for the purification of the substance with $CHCl_3$ as an eluent. Finally the solvent was removed in a vacuum to yield white solid (0.18 g, 73% yield). ^{1}H NMR (ppm): δ 7.98

(m, 4H, Ar*H*), 5.40 (d, 1H, *J* = 13.2 Hz, SCH*H*), 5.28 (d, 1H, *J* = 13.2 Hz, SC*H*H), 2.87 (s, 3H, SCH_3), 2.25 (s, 2H, CH_{carb}), 2.5 ÷ 0.3 (br s, 8H, B*H*), −1.0 (br s, 1H, B*H*B). ^{13}C NMR (ppm): δ 166.6 (*C*O), 135.2 (*o*-C_{Ar}), 131.8 (*ipso*-C_{Ar}), 123.9 (*m*-C_{Ar}), 48.1 (SCH_2), 46.3 (CH_{carb}), 22.9 (SCH_3). ^{11}B NMR (ppm): δ −11.4 (d, *J* = 142 Hz, 1B), −12.5 (d, *J* = 146 Hz, 1B), −14.3 (d, *J* = 142 Hz, 1B), −17.0 (d, *J* = 143 Hz, 2B), −20.0 (d, *J* = 125 Hz, 1B), −20.9 (d, *J* = 134 Hz, 1B), −26.9 (s, 1B), −37.5 (d, *J* = 143 Hz, 1B). IR (Nujol, cm^{-1}): 2580 (br, ν_{B-H}), 2564 (br, ν_{B-H}), 2545 (br, ν_{B-H}), 2536 (br, ν_{B-H}), 1730 ($\nu_{C=O}$). MS (EI): *m*/*z* for $C_{12}H_{20}B_9NO_2S$: calcd 340.2 $[M]^+$, obsd 340.2 $[M]^+$.

3.11. Synthesis of 10-$C_6H_4(CO)_2NCH_2CH_2(Me)$S-7,8-$C_2B_9H_{11}$ (**12**)

To a solution of the tetrabutylammonium salt of 10-methylthio-7,8-dicarba-*nido*-caborane [1] (0.40 g, 0.95 mmol) in ethanol (10 ml) $BrCH_2CH_2(CO)_2C_6H_4$ (0.24 g, 0.95 mmol) was added. After stirring for 15 min, *r.t.*, the mixture was heated under reflux for about 15 h and the mixture was left for cooling at 0 °C. The precipitate formed was filtrated to give white solid (0.33 g, 98% yield). ^{1}H NMR (ppm): δ 7.92 (m, 4H, Ar*H*), 4.24 (m, 2H, CH_2N), 3.51 (m, 2H, SCH_2), 2.77 (s, 3H, SCH_3), 2.15 (s, 2H, CH_{carb}), 2.5 ÷ 0.2 (br s, 9H, B*H*). ^{13}C NMR (ppm): δ 167.5 (*C*O), 134.6 (*o*-C_{Ar}), 132.0 (*ipso*-C_{Ar}), 123.3 (*m*-C_{Ar}), 48.6 (SCH_2), 45.0 (CH_{carb}), 33.5 (CH_2N), 22.3 (SCH_3). ^{11}B NMR (ppm): δ −11.1 (d, *J* = 150 Hz, 1B), −12.3 (d, *J* = 140 Hz, 1B), −14.9 (d, *J* = 137 Hz, 1B), −17.2 (d, *J* = 135 Hz, 2B), −20.3 (d, *J* = 146 Hz, 1B), −21.4 (d, *J* = 136 Hz, 1B), −26.2 (s, 1B), −37.5 (d, *J* = 155 Hz, 1B). IR (Nujol, cm^{-1}): 2568 (br, ν_{B-H}), 2510 (br, ν_{B-H}), 1717 ($\nu_{C=O}$). MS (EI): *m*/*z* for $C_{13}H_{22}B_9NO_2S$: calcd 354.2 $[M]^+$, obsd 354.2 $[M]^+$.

3.12. Synthesis of 10-$C_6H_4(CO)_2NCH_2CH_2CH_2(Me)$S-7,8-$C_2B_9H_{11}$ (**13**)

The procedure was analogous to that described for synthesis of **12** using (Bu_4N)[**1**] (0.20 g, 0.47 mmol) in ethanol (8 ml) and $BrCH_2CH_2CH_2(CO)_2C_6H_4$ (0.13 g, 0.47 mmol) to give white solid (0.16 g, 93% yield). ^{1}H NMR (ppm): δ 7.88 (m, 4H, Ar*H*), 4.24 (t, 2H, *J* = 6.4 Hz, CH_2N), 3.08 (m, 2H, SCH_2), 2.68 (s, 3H, SCH_3), 2.29 (q, 2H, *J* = 6.9 Hz, $CH_2CH_2CH_2$), 2.17 (s, 2H, CH_{carb}), 2.5 ÷ 0.3 (br s, 8H, B*H*), −1.1 (br s, 1H, B*H*B). ^{13}C NMR (ppm): δ 168.0 (*C*O), 134.1 (*o*-C_{Ar}), 132.3 (*ipso*-C_{Ar}), 123.0 (*m*-C_{Ar}), 48.6 (SCH_2), 45.5 (CH_{carb}), 35.9 (CH_2N), 25.1 ($CH_2CH_2CH_2$), 22.3 (SCH_3). ^{11}B NMR (ppm): δ −11.5 (d, *J* = 130 Hz, 2B), −15.8 (d, *J* = 144 Hz, 2B), −17.4 (d, *J* = 180 Hz, 1B), −20.9 (d, *J* = 163 Hz, 2B), −26.3 (s, 1B), −37.4 (d, *J* = 153 Hz, 1B). IR (Nujol, cm^{-1}): 2579 (br, ν_{B-H}), 2539 (br, ν_{B-H}), 1706 ($\nu_{C=O}$). MS (EI): *m*/*z* for $C_{14}H_{24}B_9NO_2S$: calcd 368.2 $[M]^+$, obsd 368.1 $[M]^+$.

3.13. Synthesis of 10-$H_2NCH_2CH_2(Me)$S-7,8-$C_2B_9H_{11}$ (**14**)

To a solution of **12** (0.20 g, 0.56 mmol) in ethanol (8 ml), N_2H_4·H_2O (0.28 ml, 5.6 mmol) was added. The mixture was heated under reflux for about 2 h until the disappearing of started product (monitored by TLC in CH_2Cl_2). The solvent was removed in a vacuum and the residue was treated with diethyl ether (20 ml) and water (20 ml). The organic layer was separated, washed with water (2 x 20 ml), dried over Na_2SO_4 and evaporated in vacuum to yield white solid (0.08 g, 64% yield). ^{1}H NMR (ppm): δ 3.74 (t, 2H, *J* = 6.2 Hz, CH_2N), 3.44 (m, 1H, SCH*H*), 3.37 (m, 1H, SC*H*H), 2.73 (s, 3H, SCH_3), 2.19 (s, 2H, CH_{carb}), 2.4 ÷ 0.2 (br s, 9H, B*H*). ^{13}C NMR (ppm): 48.7 (CH_2N), 44.1 (CH_{carb}), 42.3 (SCH_2), 23.0 (SCH_3). ^{11}B NMR (ppm): δ −11.7 (d, *J* = 144 Hz, 2B), −15.8 (d, *J* = 138 Hz, 2B), −17.4 (d, *J* = 180 Hz, 1B), −20.8 (d, *J* = 152 Hz, 2B), −25.8 (s, 1B), −37.6 (d, *J* = 137 Hz, 1B). MS (EI): *m*/*z* for $C_5H_{20}B_9NS$: calcd 224.2 $[M]^+$, obsd 224.1 $[M]^+$.

3.14. Synthesis of 10-$H_2NCH_2CH_2CH_2(Me)$S-7,8-$C_2B_9H_{11}$ (**15**)

The procedure was analogous to that described for synthesis of **14** using **13** (0.10 g, 0.27 mmol) in ethanol (7 ml) and N_2H_4·H_2O (0.13 ml, 2.7 mmol) to give white solid (0.04 g, 62% yield). ^{1}H NMR (ppm): δ 3.35 (t, 2H, *J* = 6.4 Hz, CH_2N), 3.22 (m, 2H, SCH_2), 2.68 (s, 3H, SCH_3), 2.19 (s, 2H, CH_{carb}), 2.14 (m, 2H, $CH_2CH_2CH_2$), 2.5 ÷ 0.2 (br s, 9H, B*H*). ^{13}C NMR (ppm): 48.7 (CH_2N), 44.9 (CH_{carb}), 40.8 (SCH_2), 26.8 ($CH_2CH_2CH_2$), 22.6 (SCH_3). ^{11}B NMR (ppm): δ −11.7 (d, *J* = 142 Hz, 2B), −15.8 (d, *J* = 143 Hz, 2B), −17.4 (d, *J* = 180 Hz, 1B), −20.8 (d, *J* = 154 Hz, 2B), −26.0 (s, 1B), −37.6 (d, *J* = 144 Hz, 1B). MS (EI): *m*/*z* for $C_6H_{22}B_9NS$: calcd 238.2 $[M]^+$, obsd 237.9 $[M]^+$.

3.15. X-ray diffraction study

Single crystal X-ray study was carried out with SMART APEX II CCD diffractometer (λ(Mo Kα) = 0.71073 A, graphite monochromator, ω-scans) at 120 K. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms.

Crystallographic data for **12**: $C_{13}H_{22}B_9NO_2S$ are monoclinic, space group *P*21/*n*: *a* = 9.8298(4) Å, *b* = 6.6476(3) Å, *c* = 27.8135 (10) Å, = 90.6761(8)°, *V* = 1817.33(13) Å^3, *Z* = 4, *M* = 353.66, d_{cryst} = 1.293 g cm^{-3}. *wR*2 = 0.1061 calculated on F2hkl for all 5341 independent reflections with 2 < 30.0, (GOF = 1.041, *R* = 0.0283 calculated on Fhkl for 4448 reflections with *I* > 2(*I*)). Crystallographic data (excluding structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 1846133.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.poly.2018.07.009.

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