New carborane-containing amino acids and their derivatives. Crystal structures of *N*-protected carboranylalaninates

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New alanine derivatives containing both the carboranyl and trifluoromethyl groups were synthesized by the reaction of organometallic derivatives of *o*-carborane with methyl trifluoropyruvate imines. When using the 1*R*-(−)-menthoxycarbonyl protecting group at the nitrogen atom, one of diastereomers was isolated and characterized. Trifluoromethylcarboranylalanine methyl esters containing different protecting groups at the nitrogen atom were studied by X-ray diffraction. Both complete and partial deprotection of the amino and carboxy groups was performed.

Key words: amino acids, alanine, organofluorine compounds, imines, carboranes, X-ray diffraction study.

Boron neutron capture therapy (BNCT) of cancer would be one of possible applications of carborane-containing amino acids.[1,2] This expectation is based on the fact that *p*-dihydroxyborylphenylalanine (BPA) is used in clinical practice as a reagent for BNCT. It should be taken into account that normal cells fundamentally differ from cancer cells in that the latter are characterized by high growth and division rates, *i.e.*, cancer cells absorb much higher amounts of substances necessary for their replication. Because of this, compounds serving as cell building blocks (in particular, amino acids and peptides) or their analogs should be absorbed predominantly by cancer cells, which opens possibilities for selective delivery of ^{10}B to tumors.

It is also known that the introduction of fluorine and fluoroalkyl substituents into amino acids sometimes leads to an increase in their biological activity.[3] In peptide and amino acid chemistry, β-fluorine-substituted α-amino acids are of particular interest because they serve as irreversible enzyme inhibitors.[4,5] These acids have a broad spectrum of biological activities, including antiviral and antitumor activities.[3]

In the present study, we synthesized amino acids and their derivatives containing both the carboranyl group and the trifluoromethyl fragment and established their structures. We believe that this combination of fragments imparts unusual biological properties to the resulting compounds. We have synthesized α- and β-carboranyl-α-amino acid esters containing the trifluoromethyl group by the reactions of organometallic derivatives of carboranes with highly electrophilic methyl trifluoropyruvate imines[6—8] (see the preliminary communication[9]).

Results and Discussion

The reaction of *o*-carboranylmethylmagnesium bromide with imines $(CF_3)(CO_2Me)C{=}NR$ (R = SO_2Ph, $COCF_3$, or CO_2Bu^t) in diethyl ether at −78 °C produced β-carboranyl-α-trifluoromethyl-α-amino acid esters (**1—3**), in which the amino group is protected by the benzenesulfonyl, trifluoroacetyl, or *tert*-butoxycarbonyl (Boc) group (Scheme 1).

Free amino acid was prepared by deprotection, which was carried out for compound **3** in two steps. The Boc group was removed by the reaction with trifluoroacetic acid in dichloromethane at room temperature followed by hydrolysis of the ester group. The intermediate solid compound (methyl ester **4**) was refluxed in 6 *M* HCl until the precipitate was completely dissolved (~8 h) to prepare amino acid **5** as hydrochloride. Compound **5** · HCl was obtained as a water-soluble white crystalline compound.

Hydrolysis of the ester group without deprotection of nitrogen was performed for compound **1** by the reaction with lithium hydroxide in a water—THF system giving rise to *N*-protected acid **6**. This acid is potentially suitable for peptide synthesis.

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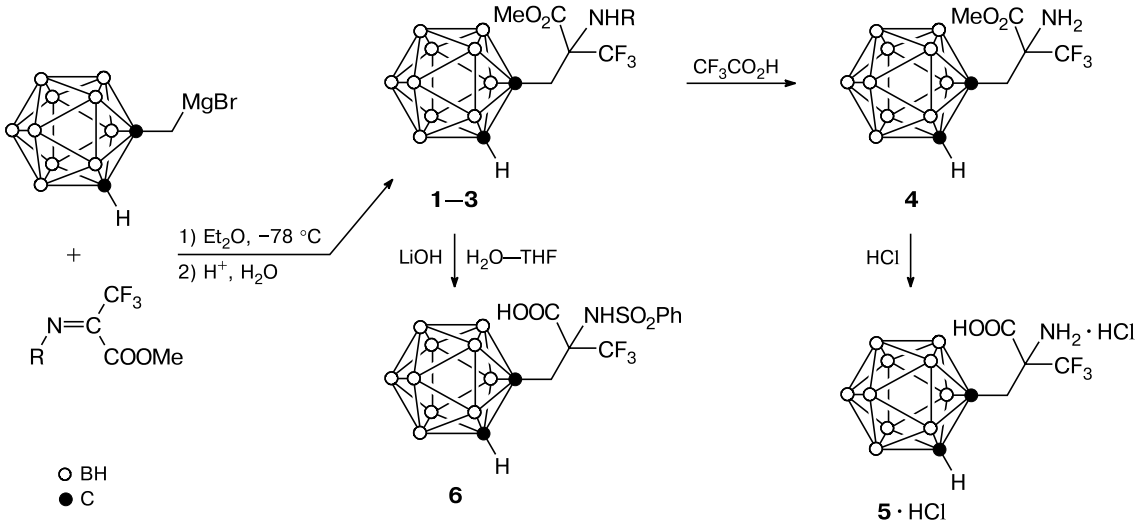
Scheme 1



R = SO_2Ph (**1**), $COCF_3$ (**2**), CO_2Bu^t (**3**)

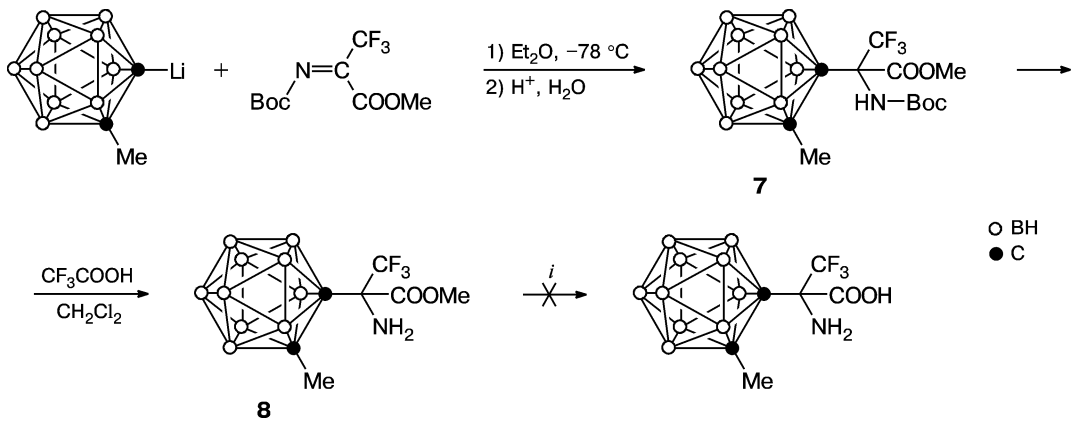
Compounds **1—6** were characterized by ^1H NMR spectroscopy and elemental analysis. The structures of compounds **1** and **2** were established by X-ray diffraction.

The reaction of (methyl-*o*-carboranyl)lithium with imine produces *N*-Boc-protected α-carboranyl-α-trifluoromethyl-α-amino acid methyl ester **7** (Scheme 2). The reaction affords the target product in virtually quantitative yield already at −78 °C. The protecting group at the nitrogen atom was removed by the reaction with trifluoroacetic acid giving rise to the corresponding amino acid methyl ester **8**. Compounds **7** and **8** are colorless crystals soluble in most of organic solvents. An attempt to synthesize the corresponding free amino acid by acid hydrolysis of the ester group with the use of hydrochloric acid failed. Alkali hydrolysis leads to degradation of the carborane cage and the formation of, apparently, a *nido* structure.

With the aim of synthesizing optically active trifluoromethylcarboranylalanine, we performed the reaction of the lithium derivative of methyl-*o*-carborane with chiral trifluoropyruvate imine containing the (1*R*)-menthoxycarbonyl group at the nitrogen atom (Scheme 3).

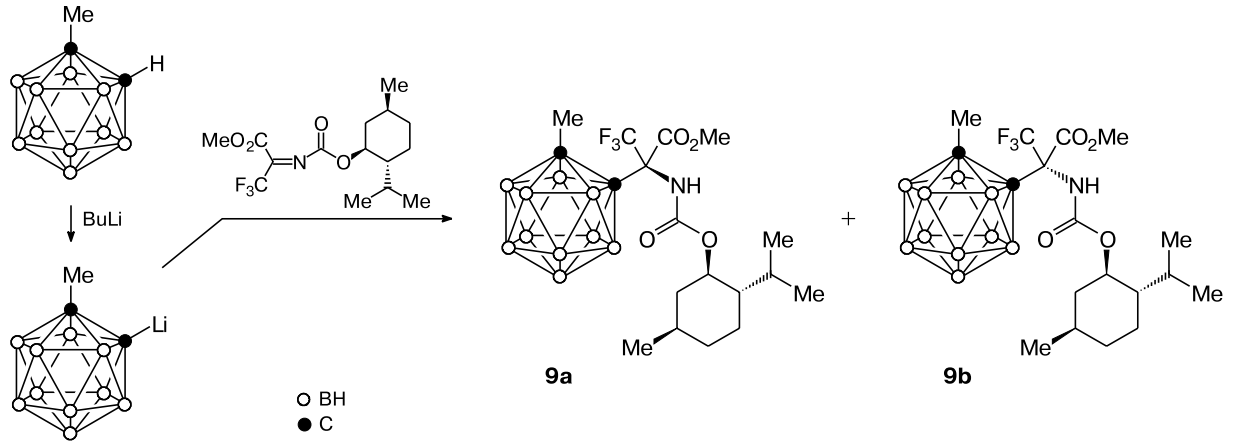
Unfortunately, we failed to achieve the expected stereoselectivity and obtained diastereomers **9a** and **9b** in a ratio of ~1 : 1. Nevertheless, we succeeded in isolating methyl 3,3,3-trifluoro-2-(1′-methyl-*o*-carboranyl)-*N*-({[(1*S*,2*R*,5S)-2-isopropyl-5-methylcyclohexyl]oxy}carbonyl)-D-alaninate (**9a**) by crystallization from chloroform. The structure of **9a** was established by X-ray diffraction.

Scheme 2



i. KOH or HCl.

Scheme 3



Therefore, we developed a simple and efficient procedure for the synthesis of fluorine-containing carboranylalaninates, which are potential reagents for BNCT. The synthesis of optically active representatives of this class and the peptide synthesis based on these compounds will be the subject of further investigation.

The structures of **1** and **2** each contain two crystallographically independent molecules. The structure of one of two independent molecules **1** is shown in Fig. 1; one independent molecule **2**, in Fig. 2. In both crystal structures, two independent molecules differ by a small rotation of the $\{B_9C_2\}$ cage about the C(1)—C(3) bond (the C(2)—C(1)—C(3)—C(4) torsion angles in independent molecules are 97.8(2) and 116.9(2)°) and in the orientation of the Ph rings relative to the S(1)N(1)C(4) plane (the corresponding dihedral angles are 68.5 and 76.0°). In the crystal structure of **2**, the rotation of the $\{B_9C_2\}$ cage about the C(1)—C(3) bond in two independent molecules is characterized by the torsion angles of 160(1) and 169(1)°; the C(4)—N(1)—C(7)—C(8) torsion angles char-

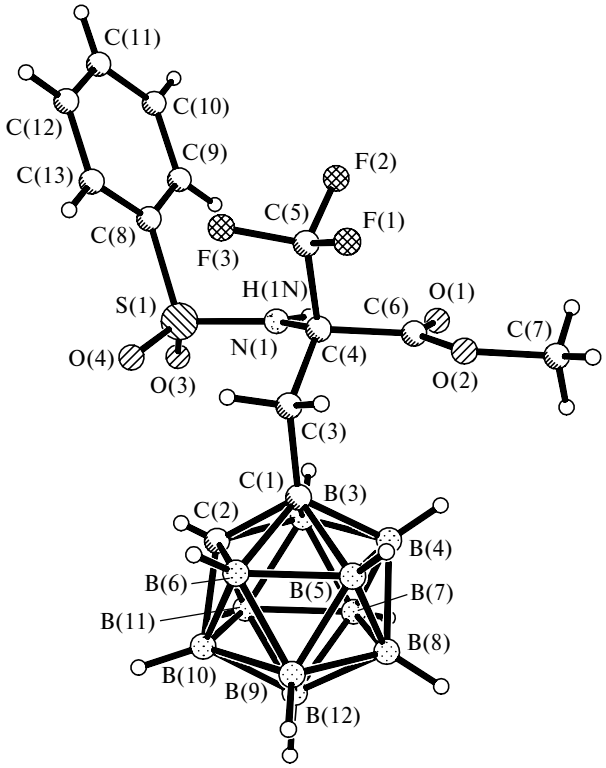


Fig. 1. Molecular structure of **1**.

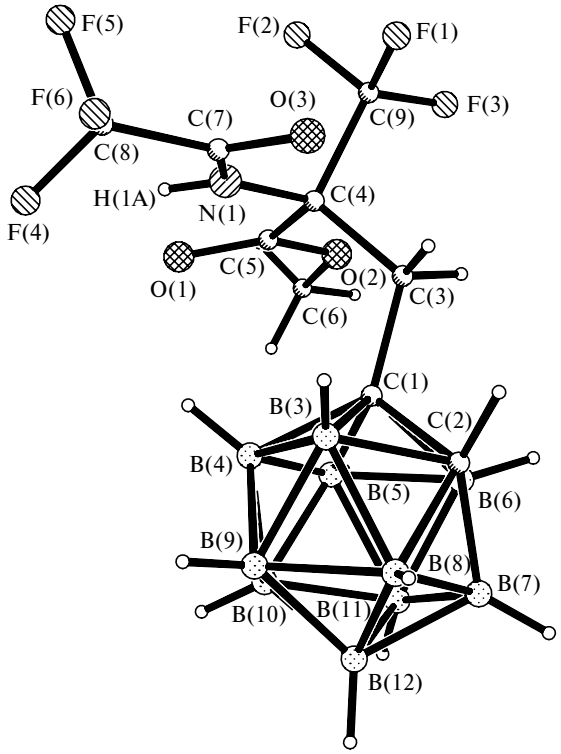


Fig. 2. Molecular structure of **2**.

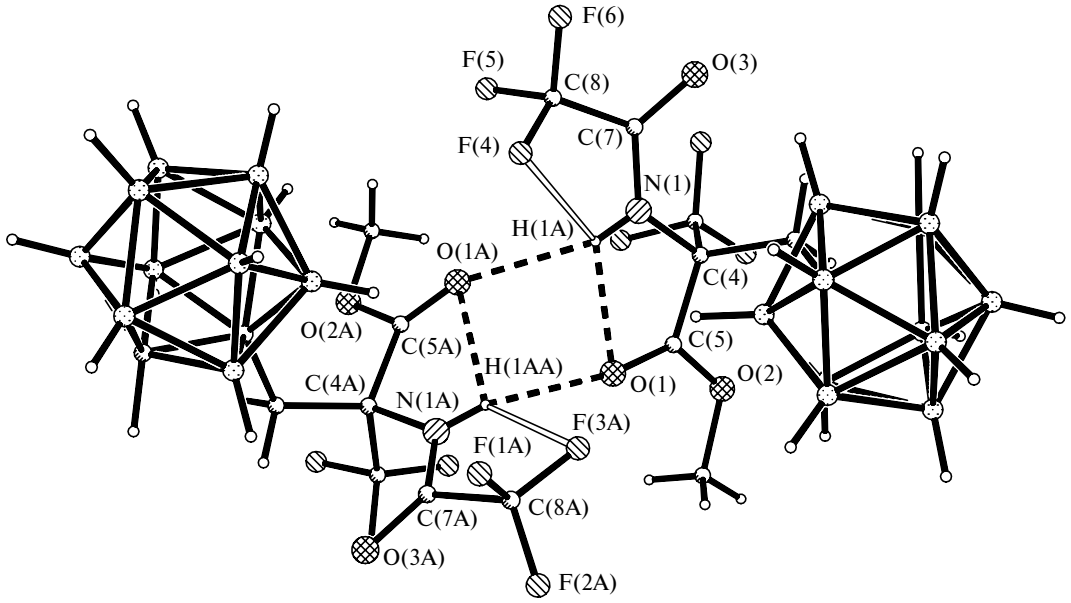


Fig. 3. Structure of the hydrogen-bonded dimer in the crystal structure of **2**.

acterizing rotation of the NH—CO—CF_3 fragment about the N(1)—C(4) bond are 175(1) and 171(1)°.

The bond lengths and bond angles in molecules **1**, **2**, and **9a** have standard values.

The presence of different substituents R in similar molecules **1** and **2** (SO_2Ph and $COCF_3$, respectively) results in the different involvement of the NH group in hydrogen binding. Only the intramolecular N—H...O(1) hydrogen bond with one of the oxygen atoms of the SO_2 group (H...O, 2.16 and 2.29 Å; N...O, 2.618(2) and 2.631(2) Å; N—H..... 113, 118°) is formed in molecules **1**.

The IR spectrum of solid compound **1** shows ν_{NH} absorption bands at 3300, 3288, and 3251 cm^{-1}. In the ν_{CO} region, the corresponding absorption bands are observed at 1751 and 1765 cm^{-1}. The IR spectrum of a solution of compound **1** has a ν_{NH} band at 3319 cm^{-1} and a ν_{CO} band at 1756 cm^{-1}, which can be assigned to NH and CO groups involved in intramolecular hydrogen binding.

In the crystal structure of **2**, the H(N) atoms are involved not only in intramolecular but also in intermolecular hydrogen bonds. Independent molecules are linked

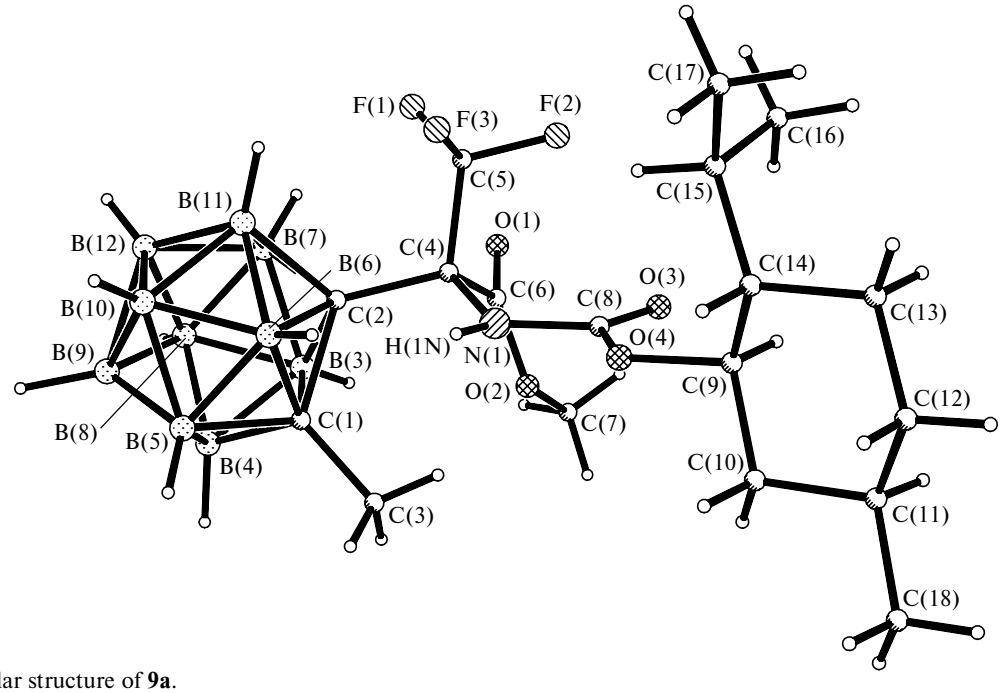


Fig. 4. Molecular structure of **9a**.

by the latter bonds to form isolated hydrogen-bonded dimers (Fig. 3). The hydrogen bond parameters are as follows: N(1)...O(1), 2.61(1) Å; N(1)...O(1A), 3.08(1) Å; N(1A)...O(1), 3.12(1) Å; N(1A)...O(1A), 2.66(1) Å; H(1A)...O(1), 2.17 Å; H(1A)...O(1A), 2.32 Å; H(1AA)...O(1), 2.33 Å; H(1AA)...O(1A), 2.13 Å; N(1)—H(1A)...O(1), 112°; N(1)—H(1A)...O(1A), 148°; N(1A)—H(1AA)...O(1A), 118°; N(1A)—H(1AA)...O(1), 153°. In addition, the H(N) atoms in all molecules form short intramolecular contacts with the fluorine atoms (H(1A)...F(4), 2.46 Å; H(1AA)...F(3A), 2.24 Å). These contacts are indicative of the presence of specific directed interactions;[10] all other H...F contacts are substantially longer (2.66—2.95 Å).

The IR spectrum of a solid sample of compound **2** shows bands at 3337 and 3309 cm^{-1} assigned to bonded NH groups. In the ν_{CO} region, there are bands at 1738 cm^{-1} (belonging to stretching vibrations of the hydrogen-bonded C=O group) and 1762 cm^{-1} (the free C=O group). In the spectrum of a solution of compound **2**, the position of the high-frequency band ν_{CO} remains unchanged, whereas the band of the bonded C=O group (1738 cm^{-1}) is shifted to higher frequencies, which may be indicative of the cleavage of the intermolecular hydrogen bond. In the ν_{NH} region, weak bands are observed at 3314 and 3362 cm^{-1}, which can be assigned to the NH group involved in an intramolecular hydrogen bond.

An interesting feature of the structure of **9a** (Fig. 4) is the presence of shortened intramolecular F...H—B contacts (F(1)...H(7)—B(7) and F(3)...H(11)—B(11); the F(1)...H(7) and the F(3)...H(11) distances are 2.43 Å). However, these contacts are apparently forced because the rather strong intramolecular C(3)—H(3c)...N(1) hydrogen bond (the C(3)...N(1) and H(3c)...N(1) distances are 3.002 and 2.24 Å, respectively, and the C(3)—H(3c)...N(1) angle is 136°) fixes the orientation of the N substituent and, as a consequence, the orientations of other substituents.

Experimental

Starting methyl trifluoropyruvate imines were synthesized according to procedures described earlier.[6,7]

The ^1H and ^{19}F NMR spectra were measured on Bruker-Avance-400 (400.13 MHz for ^1H) and Bruker-Avance-300 (282.4 MHz for ^{19}F) spectrometers. The chemical shifts (δ) for ^1H are given relative to Me_4Si. The IR spectra were recorded on an Infralyum FT-801 Fourier-transform spectrometer in dichloromethane in CaF_2 cells (d = 0.04—0.22 cm). The mass spectra were obtained on a Finnigan Polaris instrument (EI, 70 eV). The elemental analysis was carried out in the Laboratory of Microanalysis of A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

Reactions of imines with *o*-carboranylmethylmagnesium bromide. A solution of the corresponding methyl trifluoropyruvate imine (3.2 mmol) in diethyl ether (25 mL) was added dropwise at −70 °C to an ethereal solution of the Grignard reagent, which was prepared from bromomethyl-*o*-carborane (3 mmol) and magnesium (4 mmol). The reaction mixture was stirred at −70 °C for 1 h, slowly warmed to 20 °C, and stirred for 6 h. Then the reaction mixture was treated with a saturated NH_4Cl solution and extracted with diethyl ether (2×20 mL). The combined ethereal extracts were dried with sodium sulfate, the solvent was removed, and the product was finally purified on a silica gel column using a hexane—ethyl acetate mixture as the eluent.

Methyl *N*-(phenylsulfonyl)-α-(trifluoromethyl)-*o*-carboranylalaninate (1, R = SO_2Ph), m.p. 94—95 °C, the yield was 75%. Found (%): B, 23.84. $C_{13}H_{22}B_{10}F_3NO_4S$. Calculated (%): B, 23.84. ^1H NMR ($CDCl_3$), δ: 7.80 (m, 5 H, Ph); 6.24 (s, 1 H, NH); 4.37 (s, 1 H, CH_{carb}); 3.95 (s, 3 H, OMe); 3.72 (d, 1 H, CH_2, J = 16.0 Hz); 3.22 (d, 1 H, CH_2, J = 16.0 Hz); 3.10—1.00 (br.s, 10 H, BH). ^{19}F NMR ($CDCl_3$, CF_3COOH as the standard), δ: 5.33 (s, 3 F, CF_3). IR (KBr pellets), ν/cm^{-1}: 3300, 3288, 3251 (N—H); 1751, 1765 (C=O). IR (CH_2Cl_2), ν/cm^{-1}: 3319 (N—H); 1756 (C=O).

Methyl *N*-(trifluoroacetyl)-α-(trifluoromethyl)-*o*-carboranylalaninate (2, R = $COCF_3$), m.p. 81—82 °C, the yield was 76%. Found (%): C, 24.35; H, 4.30. $C_8H_{17}B_{10}F_6NO_3$. Calculated (%): C, 24.18; H, 4.31. ^1H NMR ($CDCl_3$), δ: 7.59 (s, 1 H, NH); 4.11 (d, 1 H, CH_2, J = 16.0 Hz); 4.04 (s, 3 H, OMe); 3.70 (s, 1 H, CH_{carb}); 3.35 (s, 1 H, CH_2, J = 16.0 Hz); 3.00—1.50 (br.s, 10 H, BH). ^{19}F NMR ($CDCl_3$, CF_3COOH as the standard), δ: 3.60 (s, 3 F, CF_3); 1.62 (s, 3 F, CF_3). IR (sol.), ν/cm^{-1}: 3337, 3309 (N—H); 1738, 1762 (C=O). IR (CH_2Cl_2), ν/cm^{-1}: 3414, 3362, 3292 (N—H); 1747, 1763 (C=O).

Methyl *N*-(*tert*-butoxycarbonyl)-α-(trifluoromethyl)-*o*-carboranylalaninate (3, R = Boc), m.p. 164—165 °C, the yield was 72%. Found (%): C, 34.89; H, 6.33; B, 26.42. $C_{12}H_{26}B_{10}F_3NO_4$. Calculated (%): C, 34.86; H, 6.34; B, 26.15. ^1H NMR ($CDCl_3$), δ: 5.91 (s, 1 H, NH); 4.92 (s, 1 H, CH_{carb}); 4.06 (d, 1 H, CH_2, J = 20.0 Hz); 3.95 (s, 3 H, OMe); 3.23 (d, 1 H, CH_2, J = 20.0 Hz); 3.10—1.30 (br.s, 10 H, BH); 1.48 (s, 9 H, Bu^t). ^{19}F NMR ($CDCl_3$, CF_3COOH as the standard), δ: 2.39 (s, 3 F, CF_3).

Methyl α-(trifluoromethyl)-*o*-carboranylalaninate (4). Compound **3** (0.2 g, 0.48 mmol) was dissolved in trifluoroacetic acid (5 mL) at ~20 °C and the mixture was stirred until gas evolution ceased (~3 h). Then the reaction mixture was concentrated, and compound **4** was obtained in a yield of 0.15 g. Found (%): B, 34.39. $C_7H_{18}B_{10}F_3NO_2$. Calculated (%): B, 34.50. ^1H NMR ($CDCl_3$), δ: 4.67 (s, 1 H, CH_{carb}); 4.91 (s, 3 H, NH_3); 3.40 (s, 3 H, OMe); 3.20 (s, CH_2, J = 16 Hz); 2.68 (d, CH_2, J = 16.0 Hz); 2.60—1.40 (br.s, 10 H, BH). ^{19}F NMR ($CDCl_3$, $CFCl_3$ as the standard), δ: −79.43 (s, 3 F, CF_3).

α-(Trifluoromethyl)-*o*-carboranylalanine hydrochloride (5). Compound **4** (0.15 g, 0.47 mmol) was refluxed in 12 *M* HCl (8 mL) until complete dissolution (~8 h). Then the reaction mixture was concentrated, and compound **5** was obtained in a yield of 0.1 g. ^1H NMR (acetone-d_6), δ: 5.14 (s, 1 H, CH_{carb}); 2.93 (d, CH_2, J = 16.0 Hz)*. ^{19}F NMR ($CDCl_3$, $CFCl_3$ as the standard), δ: 79.39 (s, 3 F, CF_3). MS (EI, 70 eV), m/z (I_{rel} (%)): 298 $[M]^+$ (1.7).

* The second doublet of CH_2 overlaps with a signal of water present in acetone.

***N*-(Phenylsulfonyl)-α-(trifluoromethyl)-*o*-carboranylalanine (6).** Compound **1** (0.3 g, 0.66 mmol) was added to a solution of lithium hydroxide (0.07 g, 2.29 mmol) in a mixture of THF (12 mL) and water (6 mL). The reaction mixture was stirred at 20 °C for 4 days and extracted with benzene (2×20 mL). Then 1 *M* HCl (4 mL) was added to the aqueous layer. The precipitate that formed was extracted with diethyl ether and dried with anhydrous sodium sulfate. After removal of the solvent, compound **6** was obtained in a yield of 0.17 g. ^{1}H NMR (DMSO-d_6), δ: 7.52 (m, 5 H, Ph); 5.29 (s, 1 H, NH); 4.92 (s, 1 H, CH_{carb}). MS (EI, 70 eV), m/z (I_{rel} (%)): 375 $[M]^+$ (2.3).

Methyl *N*-(*tert*-butoxycarbonyl)-3,3,3-trifluoro-2-(2-methyl-*o*-carboranyl)alaninate (7). A 1.6 *M* butyllithium solution in hexane (3.95 mL) was added dropwise to a solution of methyl-*o*-carborane (1.0 g, 6.3 mmol) in diethyl ether (30 mL) at 0 °C. The temperature of the reaction mixture was slowly raised to ~20 °C. Then the mixture was refluxed for 30 min and cooled to −78 °C. A solution of the corresponding imine (1.6 g, 6.3 mmol) in diethyl ether (5 mL) was added. The temperature of the reaction mixture was slowly raised to ~20 °C, and the mixture was kept at this temperature for 16 h. Then the reaction mixture was treated with 1 *M* HCl (50 mL). The organic layer was separated and dried with magnesium sulfate. After drying, the solvent was removed, and the residue was finally purified on a silica gel column using a hexane—ethyl acetate mixture as the eluent. The yield of compound **7** was 89%. Found (%): C, 34.89; H, 6.33; B, 25.42; N, 3.19. $C_{12}H_{26}B_{10}F_3NO_4$. Calculated (%): C, 34.85; H, 6.29; B, 25.10; N, 3.38. ^{1}H NMR ($CDCl_3$), δ: 5.27 (s, 1 H, NH); 3.89 (s, 3 H, OMe); 3.50—1.30 (br.s, 10 H, BH); 2.26 (s, 3 H, Me); 1.42 (s, 9 H, Bu^t). ^{19}F NMR ($CDCl_3$, CF_3COOH as the standard), δ: 9.02 (s, 3 F, CF_3).

Methyl 3,3,3-trifluoro-2-(2-methyl-*o*-carboranyl)alaninate (8). Trifluoroacetic acid (10 mL) was added to a solution of compound **7** (1.0 g) in dichloromethane (20 mL). The reaction mixture was stirred at room temperature for 6 h and concentrated. The residue (oil) was dissolved in ethyl acetate and treated with a saturated Na_2CO_3 solution (20 mL). The organic layer was separated, the aqueous layer was extracted with ethyl acetate (2×30 mL), the combined extracts were dried with magnesium sulfate, the solvent was removed, and the residue was purified on a silica gel column using a hexane—ethyl acetate mixture as the eluent. The yield of compound **8** was 82%. Found (%): C, 25.94; H, 5.76; B, 35.39; N, 4.17. $C_7H_{18}B_{10}F_3NO_2$. Calculated (%): C, 25.36; H, 5.43; B, 34.50; N, 4.22. ^{1}H NMR ($CDCl_3$), δ: 3.92 (s, 3 H, OMe); 3.10—1.25 (br.s, 10 H, BH); 2.37 (br.s, 2 H, NH_2); 2.29 (s, 3 H, CH_3). ^{19}F NMR ($CDCl_3$, CF_3COOH as the standard), δ: 7.65 (br.s, 3 F, CF_3).

Methyl 3,3,3-trifluoro-*N*-menthoxycarbonyl-2-(2′-methyl-*o*-carboranyl)alaninate (9). A 2.5 *M* butyllithium solution in hexane (1.83 mL) was added dropwise to a solution of methyl-*o*-

Table 1. X-ray data collection and refinement statistics for compounds **1**, **2**, and **9a**

Parameter	**1**	**2**	**9a**
Molecular formula	$C_{13}H_{22}B_{10}F_3NO_4S$	$C_9H_{17}B_{10}F_3NO_3$	$C_{18}H_{36}B_{10}F_3NO_4$
Molecular weight	453.48	409.34	495.58
Space group	$C2/c$	$P\bar{1}$	$P2_1$
a/Å	24.197(4)	11.420(4)	6.786(2)
b/Å	13.754(2)	11.986(4)	17.501(4)
c/Å	27.524(4)	15.406(5)	11.342(2)
α/deg	90.0	95.66(2)	90.0
β/deg	110.032(6)	107.27(2)	96.342(2)
γ/deg	90.0	104.17(2)	90.0
V/Å^3	8606(2)	1919(1)	1337.6(5)
Z	16	4	2
d_{calc}/g cm^{-3}	1.400	1.417	1.230
Crystal color and shape	Colorless prism	Colorless plate	Colorless plate
Crystal dimensions/mm	0.50×0.35×0.30	0.35×0.25×0.20	0.55×0.35×0.25
Radiation		Mo-Kα (λ = 0.71073 Å)	
μ/cm^{-1}	1.98	1.26	0.90
Absorption correction	SADABS	—	—
T_{min}/T_{max}	0.604/0.802	—	—
Scan mode	φ/ω		θ/2θ
$2\theta_{max}$/deg	56.0	42.0	56.0
Total number of reflections	12586	4163	3586
Number of independent reflections (R_{int})	10240 (0.0579)	3930 (0.1081)	3290 (0.0226)
R_1 (based on F^2 for reflections with $I > 2\sigma(I)$)	0.0525 (6561 refl.)	0.1397 (2381 refl.)	0.443 (2172 refl.)
wR_2 (based on F^2 for all reflections)	0.1136	0.2628	0.0863
Number of parameters in refinement	579	523	325
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, где $P = 1/3(F_o^2 + 2F_c^2)$		
a	0.0357	0.0050	0.0103
b	10.950	20.602	—
GOOF	1.015	1.140	0.994
F(000)	3712	824	520

carborane (0.72 g, 4.64 mmol) in diethyl ether (30 mL) at −10 °C. The temperature of the reaction mixture was slowly raised to room temperature, and the mixture was refluxed for 30 min. After cooling to −78 °C, a solution of the corresponding imine (1.54 g, 4.54 mmol) in diethyl ether (5 mL) was added. The temperature of the reaction mixture was slowly raised to ~20 °C, and the mixture was kept at this temperature for 16 h. Then the mixture was treated with a solution of ammonium chloride (6 g) in water (10 mL). The organic layer was separated. The aqueous layer was extracted with diethyl ether (2×10) and dried with magnesium sulfate. After removal of the solvent, a mixture of diastereomers was obtained in a yield of 1.5 g (66%). Crystallization of this mixture from chloroform afforded 3,3,3-trifluoro-2-(1-methyl-*o*-carboranyl)-*N*-({[(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl]oxy}carbonyl)-D-alanine methyl ester (**9a**). ^{1}H NMR of a mixture of diastereomers ($CDCl_3$), δ: 5.37 (s, 1 H, NH); 4.54 (m, 1 H, OCH); 3.9 (s, 3 H, OMe); 2.28 (s, 3 H, MeC_{carb}); 1.93 (m, 2 H, $OCC\underline{H}_2CHMe$); 1.81 (m, 1 H, $MeC\underline{H}Me$); 1.67 (m, 2 H, $CHCHC\underline{H}_2CH_2$); 1.54, (m, 2 H, $CHCH_2C\underline{H}_2CH$); 0.89 (m, 9 H, $C\underline{H}_3CHC\underline{H}_3$, $CHC\underline{H}_3$). ^{19}F NMR ($CDCl_3$, $CFCl_3$ as the standard), δ: 67.28 (s, 3 F, CF_3).

X-ray diffraction study. Single crystals of **1**, **2**, and **9a** were grown by crystallization from a dichloromethane—hexane mixture.

X-ray diffraction data sets were collected on a Bruker SMART CCD area detector diffractometer at 120 K (**1**) and a Syntex $P2_1$ diffractometer at 183 K (**2**) and 193 K (**9a**). The X-ray reflections were processed using the SAINTPlus[11] and SADABS programs[12] for **1** and the P3 and XDISK programs[13] for **2** and **9a**.

The structures were solved by direct methods. All non-hydrogen atoms were located in difference electron density maps and refined anisotropically based on F^2_{hkl}. The hydrogen atoms of the carborane fragments and the NH groups were located in difference electron density maps and refined isotropically using a riding model. Other hydrogen atoms were positioned geometrically and refined using a riding model with $U(H) = nU(C)$, where $U(C)$ are the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are attached, $n = 1.2$ (for CH_2 and CH groups) and $n = 1.5$ for Me groups.

Crystals of compound **2**, which were grown after numerous attempts to perform crystallization from different solvents, were twins and had a very weak reflection ability. X-ray diffraction data were collected from a small chip in the 2θ angle range < 42°. The X-ray data set contained an admixture of a twin component, which is responsible for high values of R_1 and wR_2. Nevertheless, the established molecular structure of compound **2** is reliable, although high errors in bond lengths (0.01—0.02 Å) and bond angles (0.8—1°) did not allow us to perform a correct comparative analysis.

All calculations were carried our using the SHELXTL PLUS 5 program package.[14] The X-ray data collection and refinement statistics are given in Table 1. The atomic coordinates, thermal parameters, and geometric characteristics were deposited with the Cambridge Structural Database (CCDC 231182, 231183, and 601913).

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