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m-Carborane-*C*-carboxylic Acid Esters Derived from Some Terpene Alcohols, Sterols, Plant Phenols, and Oximes of Natural Carbonyl Compounds

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Abstract—Previously unknown esters were synthesized by reaction of *m*-carborane-*C*-carbonyl chloride with natural terpene alcohols, sterols, plant phenols, and oximes in the presence of pyridine.

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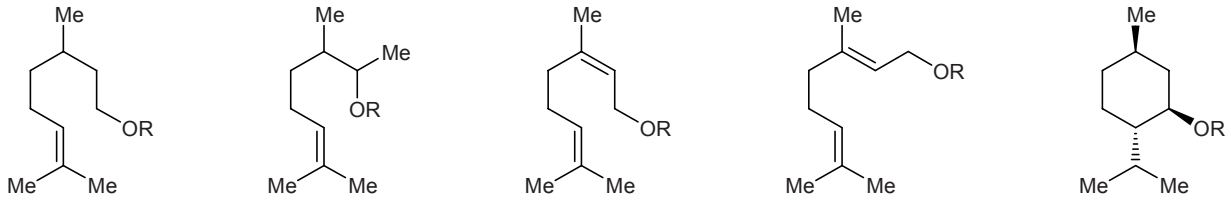
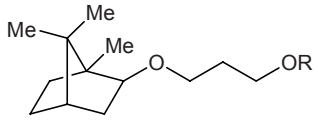
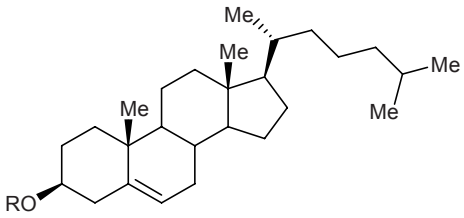
Derivatives of the polyhedral carborane cluster system attract some interest for pharmacokinetic studies in the fields of boron neutron capture therapy of cancer and radionuclide diagnostics and therapy [1]. We previously synthesized esters on the basis of natural hydroxy compounds and 7-isopropyl-*m*-carborane-1-carboxylic acid [2], *m*-carborane-1,7-dicarboxylic acid [3] and *o*-carborane-1-carboxylic acid [4, 5].

The goal of the present study was to synthesize a series of new derivatives of terpene alcohols, sterols, plant phenols, and oximes, namely the corresponding esters **Ib**–**XXVb** with *m*-carborane-1-carboxylic acid, with a view to examine their properties and test them for antitumor activity. The following naturally occurring compounds were used as alcohol component: citronellol (**Ia**), 3,7-dimethyloct-7-en-2-ol (**IIa**), nerol (**IIIa**), geraniol (**IVa**), (–)-menthol (**Va**), 10-hydroxycamphene (**VIa**), borneol (**VIIa**), isoborneol (**VIIIa**), isofenchol (**IXa**), nopol (**Xa**), 3-(isobornyloxy)propan-1-ol (**XIa**), cholesterol (**XIIa**), ergosterol (**XIIIa**), β-sitosterol (**XIVa**), diosgenin (**XVa**), vanillin (**XVIa**), vanillal (**XVIIa**), 2-methoxy-4-(4-methyl-1,3-dioxolan-2-yl)phenol (**XVIIIa**), citral oxime (**XIXa**), menthone (*E*)-oxime (**XXa**), DL-camphor oxime (**XXIa**), 2-methyl-3-(4-tolyl)propionaldehyde oxime (**XXIIa**), cyclamenaldehyde oxime (**XXIIIa**), 3,4-dimethoxy-

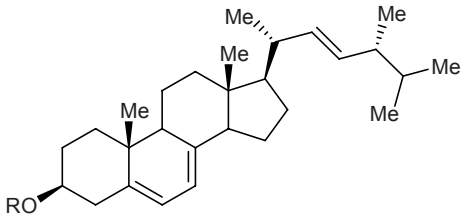




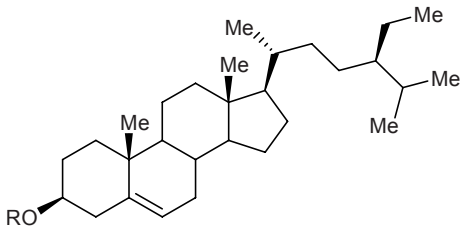
XIa, **XIb**



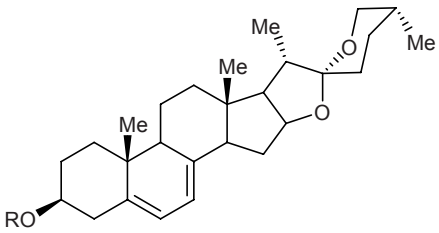
XIIa, **XIIb**



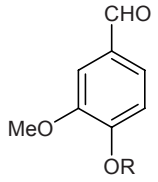
XIIIa, **XIIIb**



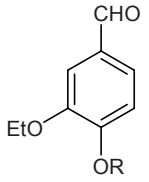
XIVa, **XIVb**



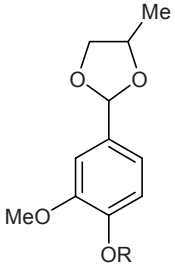
XVa, **XVb**



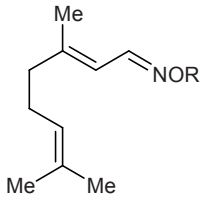
XVIa, **XVIb**



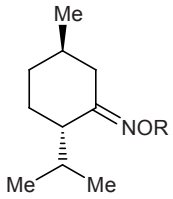
XVIIa, **XVIIb**



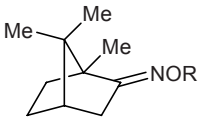
XVIIIa, **XVIIIb**



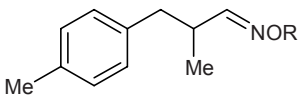
XIXa, **XIXb**



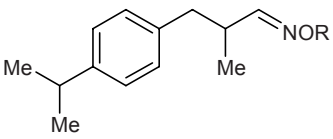
XXa, **XXb**



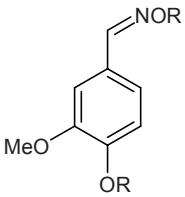
XXIa, **XXIb**



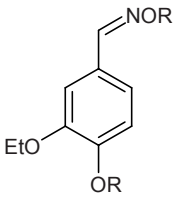
XXIIa, **XXIIb**



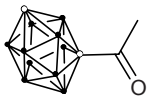
XXIIIa, **XXIIIb**



XXIVa, **XXIVb**



XXVa, **XXVb**

R = H (**a**),  (**b**).

benzaldehyde oxime (**XXIVa**), and 4-ethoxy-3-methoxybenzaldehyde oxime (**XXVa**).

m-Carborane-1-carboxylic acid esters **Ib**–**XXVb** were synthesized by reaction of hydroxy compounds **Ia**–**XXVa** with *m*-carborane-1-carbonyl chloride in anhydrous benzene in the presence of pyridine; the optimal reactant ratio was 1 : 1:1, and the yields of esters **Ib**–**XXVb** were 83–93%. The structure of the products was confirmed by elemental analyses, ^{1}H NMR, IR, and UV spectra, and molecular weight determination by cryoscopy. According to the ^{1}H NMR data, the purity of esters **Ib**–**XXVb** was 98±1%.

EXPERIMENTAL

The IR spectra were recorded on a Nicolet Protegé-460 spectrometer with Fourier transform from samples prepared as thin films (neat) or KBr pellets. The UV spectra were measured on Specord UV-Vis spectrophotometer from 1×10^{-4} M solutions in methanol. The ^{1}H NMR spectra were obtained on a Tesla BS-587A instrument (100 MHz) from 5% solutions in $CDCl_3$ using tetramethylsilane as internal reference. The molecular weights were determined by cryoscopy in benzene. Column chromatography was performed on silica gel L (5–40 μm) using hexane as eluent.

m-Carborane-1-carboxylic acid and the corresponding acid chloride were synthesized according to the procedure described in [6].

***m*-Carborane-1-carboxylic acid esters Ib–XXVb (*general procedure*).** Initial alcohol, phenol, or oxime **Ia**–**XXVa**, 5 mmol, was dissolved in 50 ml of anhydrous benzene, 5 mmol of anhydrous pyridine was added, the mixture was cooled to 10°C, and 5 mmol of *m*-carborane-1-carbonyl chloride was added under shaking. The flask was hermetically capped and was left to stand for 2–3 days at 20–23°C. The precipitate of pyridine hydrochloride was filtered off, the filtrate was thoroughly washed with water and 5% aqueous sodium hydrogen carbonate and dried over calcium chloride, and the solvent was removed under reduced pressure at a temperature not exceeding 30–40°C. The residue was purified by column chromatography on silica gel using hexane as eluent (**Ib**–**Vb**, **Xb**, **XIb**, **XVIIIb**–**XXb**) or by low-temperature crystallization from 96% ethyl alcohol (**VIb**–**IXb**, **XIIb**–**XVIIb**, **XXIb**–**XXVb**).

3,7-Dimethyloct-6-en-1-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (Ib). Yield 92%, d_{20}^{20} = 0.9604, n_D^{20} = 1.5155. IR spectrum, ν, cm^{-1}: 3067 (C–H_{carb}); 2964, 2926, 1915, 2873, 2853 (C–H_{aliph}); 2609 (B–H); 1745 (C=O); 1678 (C=C); 1454 (CH_2); 1269, 1000 (C–O); 731, 726 (δC–H_{carb}). UV spectrum: λ_{max} 204 nm (ε = 4000). ^{1}H NMR spectrum, δ, ppm: 0.92 d (3H, 3-CH_3), 1.62 s and 1.69 s (6H, 7-CH_3), 2.96 br.s (1H, 7′-H), 4.17 t (2H, 1-H), 5.09 m (1H, 6-H). Found, %: C 48.13; H 9.35; B 32.79. *M* 319.7. $C_{13}H_{30}B_{10}O_2$. Calculated, %: C 47.82; H 9.26; B 33.11. *M* 326.5.

3,7-Dimethyloct-6-en-2-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (IIb). Yield 86%, d_{20}^{20} = 0.9965, n_D^{20} = 1.5095. IR spectrum, ν, cm^{-1}: 3067 (C–H_{carb}); 2967, 2930, 2878, 2858 (C–H_{aliph}); 2609 (B–H); 1741 (C=O); 1645 (C=C); 1452 (CH_2); 1270, 999 (C–O); 731, 726 (δC–H_{carb}). UV spectrum: λ_{max} 204 nm (ε = 4000). ^{1}H NMR spectrum, δ, ppm: 0.85 m (3H, 3-CH_3), 1.19 m (3H, 1-H), 1.62 s and 1.71 s (6H, 7-CH_3), 3.02 br.s (1H, 7′-H), 4.64 m (1H, 2-H), 5.08 m (1H, 6-H). Found, %: C 48.18; H 9.30; B 32.84. *M* 318.1. $C_{13}H_{30}B_{10}O_2$. Calculated, %: C 47.82; H 9.26; B 33.11. *M* 326.5.

(2*Z*)-3,7-Dimethylocta-2,6-dien-1-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (IIIb). Yield 90%, d_{20}^{20} = 1.0246, n_D^{20} = 1.5280. IR spectrum, ν, cm^{-1}: 3065 (C–H_{carb}); 3030 (=C–H); 2968, 2924, 2856 (C–H_{aliph}); 2609 (B–H); 1744 (C=O); 1667, 1645 (C=C); 1446 (CH_2); 1256, 998 (C–O); 728 (δC–H_{carb}). UV spectrum: λ_{max} 204 nm (ε = 8000). ^{1}H NMR spectrum, δ, ppm: 1.62 s and 1.70 s (3H each, 7-CH_3), 1.78 br.s (3H, 3-CH_3), 2.12 d (4H, 4-H, 5-H), 2.98 br.s (1H, 7′-H), 4.58 m (2H, 1-H), 5.06 m and 5.28 m (1H each, 2-H, 6-H). Found, %: C 48.58; H 8.86; B 33.10. *M* 317.8. $C_{13}H_{28}B_{10}O_2$. Calculated, %: C 48.12; H 8.70; B 33.32. *M* 324.5.

(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (IVb). Yield 84%, d_{20}^{20} = 1.0382, n_D^{20} = 1.5190. IR spectrum, ν, cm^{-1}: 3066 (C–H_{carb}); 3030 (=C–H); 2965, 2926, 2870, 2855 (C–H_{aliph}); 2609 (B–H); 1745 (C=O); 1668, 1647 (C=C); 1452 (CH_2); 1267, 999 (C–O); 731, 726 (δC–H_{carb}). UV spectrum: λ_{max} 205 nm (ε = 8000). ^{1}H NMR spectrum, δ, ppm: 1.50–1.80 m (9H, 7-CH_3, 3-CH_3), 2.08 d (4H, 4-H, 5-H), 2.98 br.s (1H, 7′-H), 4.61 d (2H, 1-H), 5.06 m and 5.26 m (1H each, 2-H, 6-H). Found, %: C 48.44; H 8.81; B 33.16. *M* 318.2. $C_{13}H_{28}B_{10}O_2$. Calculated, %: C 48.12; H 8.70; B 33.32. *M* 324.5.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (Vb). Yield 89%, d_{20}^{20} = 1.0738, n_D^{20} = 1.5140. IR spectrum, ν, cm^{-1}: 3066 (C–H_{carb}); 2958, 2927, 2871 (C–H_{aliph}); 2609 (B–H); 1740 (C=O); 1456 (CH_2); 1265, 999 (C–O); 731, 726 (δC–H_{carb}). UV spectrum, λ_{max}, nm (ε): 206 (300), 220 (150), 243 (100). ^{1}H NMR spectrum, δ, ppm: 0.73 d (5-CH_3), 0.91 d [$(CH_3)_2C$], 2.98 br.s (1H, 7′-H), 4.62 d.t (1H, 1-H). Found, %: C 48.09; H 9.27; B 32.90. *M* 314.7. $C_{13}H_{30}B_{10}O_2$. Calculated, %: C 47.82; H 9.26; B 33.11. *M* 326.5.

3,3-Dimethylbicyclo[2.2.1]hept-*exo*-2-ylmethyl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (VIb). Yield 93%, mp 156–157°C. IR spectrum, ν, cm^{-1}: 3065 (C–H_{carb}); 2959, 2925, 2875, 2868 (C–H_{aliph}); 2608 (B–H); 1741 (C=O); 1460, 1450

(CH_2); 1278, 1257, 1000 (C–O); 731, 725 (δC–H_{carb}). UV spectrum, λ_{max}, nm (ε): 206 (300), 220 (150), 245 (100). ^{1}H NMR spectrum, δ, ppm: 1.01 s and 1.03 s (3H each, 3-CH_3), 2.94 br.s (1H, 2-H), 2.97 br.s (1H, 7′-H), 4.57 d (2H, 2-CH_2). Found, %: C 48.29; H 8.83; B 33.11. *M* 317.6. $C_{13}H_{28}B_{10}O_2$. Calculated, %: C 48.12; H 8.70; B 33.32. *M* 324.5.

1,7,7-Trimethylbicyclo[2.2.1]hept-*endo*-2-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (VIIb). Yield 90%, mp 162–163°C. IR spectrum, ν, cm^{-1}: 3064 (C–H_{carb}); 2957, 2924, 2885, 2872 (C–H_{aliph}); 2609 (B–H); 1739 (C=O); 1454 (CH_2); 1303, 1287, 1013, 1000 (C–O); 731, 724 (δCH_{carb}). UV spectrum, λ_{max}, nm (ε): 206 (300), 220 (150), 244 (100). ^{1}H NMR spectrum, δ, ppm: 0.82 s (2H, 1-CH_3), 0.88 s (6H, 7-CH_3), 3.03 br.s (1H, 7′-H), 4.88 m (1H, 2-H). Found, %: C 48.35; H 8.87; B 33.17. *M* 320.4. $C_{13}H_{28}B_{10}O_2$. Calculated, %: C 48.12; H 8.70; B 33.32. *M* 324.5.

1,7,7-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (VIIIb). Yield 89%, mp 167–168°C. IR spectrum, ν, cm^{-1}: 3064 (C–H_{carb}); 2955, 2933, 2876 (C–H_{aliph}); 2609 (B–H); 1737 (C=O); 1455 (CH_2); 1265, 1001 (C–O); 731, 724 (δC–H_{carb}). UV spectrum, λ_{max}, nm (ε): 206 (300), 220 (150), 245 (100). ^{1}H NMR spectrum, δ, ppm: 0.83 s (3H, 1-CH_3), 0.90 s and 1.01 s (3H each, 7-CH_3), 3.03 br.s (1H, 7′-H), 4.78 m (1H, 2-H). Found, %: C 48.50; H 8.79; B 33.05. *M* 319.0. $C_{13}H_{28}B_{10}O_2$. Calculated, %: C 48.12; H 8.70; B 33.32. *M* 324.5.

1,5,5-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (IXb). Yield 87%, mp 112–113°C. IR spectrum, ν, cm^{-1}: 3065 (C–H_{carb}); 2958, 2927, 2870 (C–$H_{a;oph}$); 2609 (B–H); 1740 (C=O); 1453 (CH_2); 1280, 1268, 1007 (C–O); 731, 724 (C–H_{carb}). UV spectrum, λ_{max}, nm (ε): 206 (300), 220 (150), 245 (100). ^{1}H NMR spectrum, δ, ppm: 0.93 s (3H, 1-CH_3), 1.02 s (6H, 5-CH_3), 2.15–2.45 m (1H, 4-H), 2.97 br.s (1H, 7′-H), 4.47 m (1H, 2-H). Found, %: C 48.43; H 8.88; B 32.97. *M* 318.3. $C_{13}H_{28}B_{10}O_2$. Calculated, %: C 48.12; H 8.70; B 33.32. *M* 324.5.

7,7-Dimethylbicyclo[3.1.1]hept-2-ylmethyl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (Xb). Yield 90%, d_{20}^{20} = 1.0268, n_D^{20} = 1.5375. IR spectrum, ν, cm^{-1}: 3066 (C–H_{carb}); 2986, 2951, 2917, 2880, 2832 (C–H_{aliph}); 2609 (B–H); 1745 (C=O); 1467 (CH_2); 1271, 1001 (C–O); 731, 726 (δC–H_{carb}). UV spectrum, λ_{max}, nm (ε): 205 (300), 220 (150), 244 (100). ^{1}H NMR spectrum, δ, ppm: 0.82 s (3H, CH_3), 1.28 s (3H, CH_3), 2.97 br.s (1H, 7′-H), 4.14 t (2H, 2-H). Found, %: C 48.23; H 8.76; B 33.08. *M* 317.1. $C_{13}H_{28}B_{10}O_2$. Calculated, %: C 48.12; H 8.70; B 33.32. *M* 324.5.

3-(1,7,7-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-propyl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (XIb). Yield 89%, d_{20}^{20} = 1.0598, n_D^{20} = 1.5210. IR spectrum, ν, cm^{-1}: 3066 (C–H_{carb}); 2989, 2951, 2927, 2876 (C–H_{aliph}); 2609 (B–H); 1747 (C=O); 1475, 1453 (CH_2); 1268, 1119, 1078, 1001 (C–O); 731, 726 (δC–H_{carb}). UV spectrum, λ_{max}, nm (ε): 204 (300), 220 (150), 245 (120). ^{1}H, δ, ppm: 0.81 s (3H, 1-CH_3), 0.87 s and 0.94 s (3H each, 7-CH_3), 1.87 t (2H, CH_2O), 3.03 br.s (1H, 7′-H), 3.13 m (1H, 2-H), 3.42 m (2H, CH_2), 4.22 t (2H, CH_2O). Found, %: C 50.41; H 9.03; B 27.96. *M* 374.4. $C_{16}H_{34}B_{10}O_3$. Calculated, %: C 50.23; H 8.96; B 28.26. *M* 382.6.

Cholest-5-en-3β-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (XIIb). Yield 93%, mp 162–163°C. IR spectrum, ν, cm^{-1}: 3065 (C–H_{carb}); 2960, 2935, 2901, 2890, 2866, 2855 (C–H_{aliph}); 2608 (B–H); 1739 (C=O); 1635 (C=C); 1470, 1440 (CH_2); 1267, 997 (C–O); 731, 726 (δC–H_{carb}). UV spectrum: λ_{max} 204 nm (ε = 4000). ^{1}H NMR spectrum, δ, ppm: 0.69 s (3H, $C^{18}H_3$), 1.02 s (3H, $C^{19}H_3$), 3.02 br.s (1H, 7′-H), 4.71 m (1H, 3-H), 5.38 m (1H, 6-H). Found, %: C 64.96; H 10.19; B 19.09. *M* 532.8. $C_{30}H_{56}B_{10}O_2$. Calculated, %: C 64.70; H 10.14; B 19.41. *M* 556.9.

Ergosta-5,7,22-trien-3β-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (XIIIb). Yield 87%, mp 104–105°C. IR spectrum, ν, cm^{-1}: 3064 (C–H_{carb}); 3040 (=C–H); 2955, 2930, 2870, 2852 (C–H_{aliph}); 2613 (B–H); 1740 (C=O); 1684, 1640 (C=C); 1458 (CH_2); 1273, 998 (C–O); 730 (δC–H_{carb}). UV spectrum, λ_{max}, nm (ε): 205 (12000), 242 (5000), 265 (9000). ^{1}H NMR spectrum, δ, ppm: 0.64 s (3H, $C^{18}H_3$), 1.03 s (3H, $C^{19}H_3$), 3.02 br.s (1H, 7′-H), 4.74 m (1H, 3-H), 5.05–5.75 m (4H, 6-H, 7-H, 22-H, 23-H). Found, %: C 66.04; H 9.73; B 18.87. *M* 551.3. $C_{31}H_{54}B_{10}O_2$. Calculated, %: C 65.68; H 9.60; B 19.07. *M* 566.9.

Poriferast-5-en-3β-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (XIVb). Yield 88%, mp 111–112°C. IR spectrum, ν, cm^{-1}: 3064 (C–H_{carb}); 3040 (=C–H); 2959, 2934, 2868, 2852 (C–H_{aliph}); 2607 (B–H); 1737 (C=O); 1634 (C=C); 1466, 1447 (CH_2); 1277, 1002 (C–O); 731, 726 (δC–H_{carb}). UV spectrum: λ_{max} 204 nm (ε = 4000). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, $C^{18}H_3$), 1.03 s (3H, $C^{19}H_3$), 3.02 br.s (1H,

7′-H), 4.72 m (1H, 3-H), 5.38 m (1H, 6-H). Found, %: C 65.93; H 10.48; B 18.16. *M* 562.8. $C_{32}H_{60}B_{10}O_2$. Calculated, %: C 65.71; H 10.34; B 18.48. *M* 584.9.

16,22:22α,27-Diepoxycholest-5-en-3-β-yl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (XVb). Yield 87%, mp 142–143°C. IR spectrum, ν, cm^{-1}: 3066 (C–H_{carb}); 3040 (=C–H); 2948, 2940, 2906, 2872, 2853 (C–H_{aliph}); 2609 (B–H); 1740 (C=O); 1630 (C=C); 1455 (CH_2); 1269, 1257, 1052, 1001, 981 (C–O); 730 (C–H_{carb}). UV spectrum: λ_{max} 204 nm (ε = 4000). ^{1}H NMR spectrum, δ, ppm: 0.80 s (3H, $C^{18}H_3$), 1.04 s (3H, $C^{19}H_3$), 3.02 br.s (1G, 7′-H, 4.40 m (1H, 3-H), 5.40 m (1H, 6-H). Found, %: C 61.87; H 9.05; B 18.19. *M* 569.3. $C_{30}H_{52}B_{10}O_4$. Calculated, %: C 61.61; H 8.96; B 18.49. *M* 584.9.

4-Formyl-2-methoxyphenyl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (XVIb). Yield 89%, mp 84–85°C. IR spectrum, ν, cm^{-1}: 3071, 3007 (C–H_{carb}, C–H_{arom}); 2974, 2939, 2927, 2875, 2848 (C–H_{aliph}); 2610 (B–H); 1772 (C=O); 1701 (CHO); 1604, 1506, 1465, 1425, 1385, 1324 (C–C_{arom}); 1289, 1249, 1197, 1154, 1110, 1058, 1028, 994 (C–O); 860, 802, 781, 731, 710 (δC–H_{carb}, δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 206 (9000), 225 (12000), 260 (8000), 308 (4000). ^{1}H NMR spectrum, δ, ppm: 3.05 br.s (1H, 7′-H), 3.91 s (3H, CH_3O), 7.04–7.60 m (3H, H_{arom}), 9.96 s (1H, CHO). Found, %: C 41.20; H 5.81; B 33.26. *M* 312.6. $C_{11}H_{18}B_{10}O_4$. Calculated, %: C 40.98; H 5.63; B 33.54. *M* 322.4.

2-Ethoxy-4-formylphenyl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (XVIIb). Yield 90%, mp 96–97°C. IR spectrum, ν, cm^{-1}: 3067 (C–H_{carb}, C–H_{arom}); 2988, 2938, 2927, 2902, 2860, 2840 (C–H_{aliph}); 2612 (B–H); 1771 (C=O); 1696 (CHO); 1602, 1499, 1480, 1436, 1390, 1325 (C–C_{arom}); 1292, 1280, 1248, 1195, 1157, 1117, 1037, 994 (C–O); 801, 790, 743, 728, 712. UV spectrum, λ_{max}, nm (ε): 206 (9000), 224 (13000), 260 (8000), 310 (4000). ^{1}H NMR spectrum, δ, ppm: 1.45 t (3H, CH_3), 3.05 br.s (1H, 7′-H), 4.08 q (2H, OCH_2), 7.04–7.55 m (3H, H_{arom}), 9.94 s (1H, CHO). Found, %: C 43.07; H 6.12; B 31.87. *M* 329.0. $C_{12}H_{20}B_{10}O_4$. Calculated, %: C 42.85; H 5.99; B 32.14. *M* 336.4.

2-Methoxy-4-(4-methyl-1,3-dioxolan-2-yl)phenyl 1,7-dicarba-*closo*-dodecaborane(12)-1-carboxylate (XVIIIb). Yield 83%, d_{20}^{20} = 1.2637, n_D^{20} = 1.5520. IR spectrum, ν, cm^{-1}: 3063, 3010 (C–H_{carb}, C–H_{arom}); 2972, 2938, 2878, 2855 (C–H_{aliph}); 2608 (B–H); 1763 (C=O); 1593, 1510, 1465, 1433, 1400, 1380 (C–C_{arom}); 1283, 1254, 1196, 1161, 1120, 1033, 996 (C–O); 803, 780, 745, 730 (δC–H_{carb}, δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 206 (9000), 220 (10000), 260 (4000), 280 (3000). ^{1}H NMR spectrum, δ, ppm: 1.20–1.45 m (3H, CH_3), 3.04 br.s (1H, 7′-H), 3.30–4.60 m (2H, CH_2), 3.82 s (3H, CH_3O), 5.81 s (1H, 2″-H), 6.80–7.60 m (3H, H_{arom}). Found, %: C 44.48; H 6.43; B 28.10. *M* 363.2. $C_{14}H_{24}B_{10}O_5$. Calculated, %: C 44.20; H 6.36; B 28.42. *M* 380.5.

(2*Z*)-3,7-Dimethylocta-2,6-dienal *O*-[1,7-dicarba-*closo*-dodecaborane(12)-1-carbonyl]oxime (XIXb). Yield 88%, d_{20}^{20} = 1.0632, n_D^{20} = 1.5190. IR spectrum, ν, cm^{-1}: 3062 (C–H_{carb}, =C–H); 2970, 2929, 2857 (C–H_{aliph}); 2609 (B–H); 1744 (C=O); 1660, 1625 (C=C); 1630 (C=N); 1441 (CH_2); 1231, 997 (C–O); 732, 710 (δC–H_{carb}). UV spectrum: λ_{max} 208 nm (ε = 12000). ^{1}H NMR spectrum, δ, ppm: 1.62 s and 1.70 s (3H each, 7-CH_3), 2.08 d (3H, 3-CH_3), 3.05 br.s (1H, 7′-H), 5.08 m and 6.05 m (1H each, 2-H, 6-H). Found, %: C 46.45; H 8.09; B 31.82; N 3.90. *M* 325.3. $C_{13}H_{27}B_{10}NO_2$. Calculated, %: C 46.27; H 8.06; B 32.04; N 4.15. *M* 337.5.

(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexanone (*E*)-*O*-[1,7-dicarba-*closo*-dodecaborane(12)-1-carbonyl]oxime (XXb). Yield 88%, d_{20}^{20} = 1.1705, n_D^{20} = 1.5280. IR spectrum, ν, cm^{-1}: 3063 (C–H_{carb}); 2959, 2929, 2871 (C–H_{aliph}); 2610 (B–H); 1765 (C=O); 1634 (C=N); 1456 (CH_2); 1240, 998 (C–O); 731 (δC–H_{carb}). UV spectrum: λ_{max} 208 nm (ε = 4000). ^{1}H NMR spectrum, δ, ppm: 0.75–1.08 m (9H, CH_3), 3.04 br.s (1H, 7′-H). Found, %: C 46.27; H 8.69; B 31.47; N 3.86. *M* 327.4. $C_{13}H_{29}B_{10}NO_2$. Calculated, %: C 45.99; H 8.61; B 31.85; N 4.13. *M* 339.5.

1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one (*E*)-*O*-[1,7-dicarba-*closo*-dodecaborane(12)-1-carbonyl]oxime (XXIb). Yield 91%, mp 153–154°C. IR spectrum, ν, cm^{-1}: 3064 (C–H_{carb}); 2964, 2932, 2890, 2873 (C–H_{aliph}); 2610 (B–H); 1764 (C=O); 1659 (C=N); 1448 (CH_2); 1238, 997 (C–O); 732 (δC–H_{carb}). UV spectrum: λ_{max} 209 nm (ε = 4000). ^{1}H NMR spectrum, δ, ppm: 0.82 s (3H, 1-CH_3), 0.94 s and 1.09 s (3H each, 7-CH_3), 2.17 s (1H, 4-H), 3.04 br.s (1H, 7′-H). $C_{13}H_{27}B_{10}NO_2$. Calculated, %: C 46.27; H 8.06; B 32.04; N 4.15. *M* 337.5.

2-Methyl-3-(4-tolyl)propanal *O*-[1,7-dicarba-*closo*-dodecaborane(12)-1-carbonyl]oxime (XXIIb). Yield 88%, mp 29–30°C. IR spectrum, ν, cm^{-1}: 3094, 3059, 3025, 3004 (C–H_{carb}, C–H_{arom}); 2983, 2925, 2879, 2861 (C–H_{aliph}); 2612 (B–H); 1745 (C=O); 1640 (C=N); 1515, 1421, 1380 (C–C_{arom}); 1455 (CH_2);

1288, 997 (C–O); 825, 790, 747, 735, 729, 705 (δC–H_{carb}, δC–H_{arom}). UV spectrum: λ_{max} 216 nm (ε = 5000). ^{1}H NMR spectrum, δ, ppm: 1.32 m (3H, CH_3), 2.34 s (3H, CH_3), 2.70–2.90 m (3H, CH_2, CH), 3.06 br.s (1H, 7′-H), 7.14 s (4H, H_{arom}). Found, %: C 48.51; H 7.38; B 30.83; N 3.75. *M* 334.9. $C_{14}H_{25}B_{10}NO_2$. Calculated, %: C 48.39; H 7.25; B 31.11; N 4.03. *M* 347.5.

3-(4-Isopropylphenyl)-2-methylpropanal *O*-[1,7-dicarba-*closo*-dodecaborane(12)-1-carbonyl]-oxime (XXIIIb). Yield 89%, mp 24–25°C. IR spectrum, ν, cm^{-1}: 3095, 3063, 3025, 3008 (C–H_{carb}, C–H_{arom}); 2959, 2927, 2872, 2852 (C–H_{aliph}); 2611 (B–H); 1744 (C=O); 1640 (C=N); 1515, 1422, 1378, 1312 (C–C_{arom}); 1463 (CH_2); 1286, 998 (C–O); 810, 737, 725 (δC–H_{carb}, δC–H_{arom}). UV spectrum: λ_{max} 216 nm (ε = 5000). ^{1}H NMR spectrum, δ, ppm: 1.30 m (3H, CH_3), 1.36 d [6H, $(CH_3)_2C$], 2.55–3.00 m (4H, CH, CH, CH_2), 3.05 br.s (1H, 7′-H), 7.16 s (4H, H_{arom}). Found, %: C 51.46; H 7.84; B 28.52; N 3.61. *M* 362.8. $C_{16}H_{29}B_{10}NO_2$. Calculated, %: C 51.18; H 7.78; B 28.79; N 3.73. *M* 375.5.

3,4-Dimethoxybenzaldehyde *O*-[1,7-dicarba-*closo*-dodecaborane(12)-1-carbonyl]oxime (XXIVb). Yield 90%, mp 45–46°C. IR spectrum, ν, cm^{-1}: 3059, 3010 (C–H_{carb}, C–H_{arom}); 2963, 2937, 2920, 2840 (C–H_{aliph}); 2611 (B–H); 1767 (C=O); 1600, 1576, 1514, 1464, 1421, 1336 (C–C_{arom}); 1270, 1241, 1166, 1140, 1106, 1060, 1023, 1001, 976 (C–O); 805, 760, 747, 732, 707 (δC–H_{carb}, δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 207 (12000), 225 (12000), 262 (8000), 310 (4000). ^{1}H NMR spectrum, δ, ppm: 3.05 br.s (1H, 7′-H), 3.94 s (3H, OCH_3), 3.97 s (3H, OCH_3), 6.80–7.50 m (3H, H_{arom}), 8.40 s (1H, N=CH). Found, %: C 40.84; H 5.93; B 30.39; N 3.60. *M* 340.2. $C_{12}H_{21}B_{10}NO_4$. Calculated, %: C 41.01; H 6.02; B 30.77; N 3.99. *M* 351.4.

3-Ethoxy4-methoxybenzaldehyde *O*-[1,7-dicarba-*closo*-dodecaborane(12)-1-carbonyl]oxime (XXVb). Yield 91%, mp 35–36°C. IR spectrum, ν, cm^{-1}: 3059, 3014 (C–H_{carb}, C–H_{arom}); 2981, 2936, 2918, 2885, 2840 (C–H_{aliph}); 2612 (B–H); 1766 (C=O); 1599, 1574, 1514, 1480, 1440, 1340 (C–C_{arom}); 1267, 1241, 1173, 1141, 1105, 1055, 1026, 995 (C–O); 810, 754, 735, 705 (δC–H_{carb}, δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 208 (13000), 224 (12000), 264 (8000), 310 (4000). ^{1}H NMR spectrum, δ, ppm: 1.45 t (3H, CH_3), 3.05 br.s (1H, 7′-H), 3.90 s (3H, CH_3O), 4.20 q (2H, OCH_2), 6.78–7.50 m (3H, H_{arom}), 8.39 s (1H, N=CH). Found, %: C 43.07; H 6.38; B 29.25; N .51. *M* 352.7. $C_{13}H_{23}B_{10}NO_4$. Calculated, %: C 42.73; H 6.34; B 29.58; N 3.83. *M* 365.4.

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