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Synthesis of Substituted 2,3-Dihydro-1*H*-boroles by Transmetalation of Aluminacyclopent-2-enes with $BF_3 \cdot Et_2O$

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Abstract—A procedure was developed for selective synthesis of 4,5-dialkyl-1-fluoro-2,3-dihydro-1*H*-boroles via transmetalation of the corresponding aluminacyclopent-2-enes with $BF_3 \cdot Et_2O$. 4,5-Dialkyl-1-fluoro-2,3-dihydro-1*H*-boroles were isolated as complexes with $BEtF_2$. 4-Alkyl-5-dimethylaminomethyl-1-fluoro-2,3-dihydro-1*H*-boroles were synthesized for the first time.

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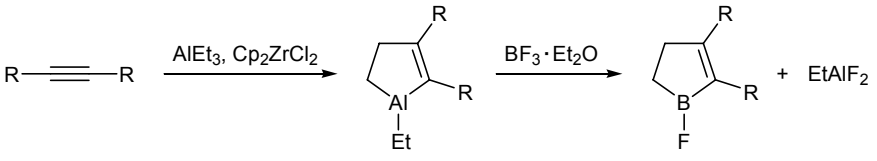
Boron-containing materials exhibit unique optical and structural properties. Three-coordinate boron atom is essentially electron-deficient, which makes boron compounds promising for use as donor–acceptor materials in nonlinear optics [1]. Among known methods of synthesis of cyclic organoboron compounds, important are those based on exchange reactions with participation of organometallic compounds.

We recently reported on the synthesis of 3-substituted 1-fluoroboracyclopentanes by reaction of boron trifluoride–ether complex with 3-substituted 1-ethylaluminacyclopentanes [2]. In continuation of these studies we examined the reaction of $BF_3 \cdot Et_2O$ with 2,3-substituted 1-ethylaluminacyclopent-2-enes [3, 4] which were obtained by reaction of disubstituted acetylenes with Et_3Al in the presence of Cp_2ZrCl_2 as catalyst (Scheme 1).

The reaction of 1-ethyl-2,3-dipropylaluminacyclopent-2-ene (**Ib**) (prepared from oct-4-yne and $AlEt_3$ [4]) with excess $BF_3 \cdot Et_2O$ in hexane at –10°C involved boron–aluminum exchange with formation of compound **IIb**. The ^{27}Al NMR spectra of the reaction mixture showed disappearance of the aluminum signal at δ_{Al} 180 ppm typical of initial compound **Ib** and appearance of a new signal at δ_{Al} –11 ppm which was assigned to $AlEtF_2$. These findings indicated transmetalation leading to replacement of the aluminum atom in **Ib** by boron.

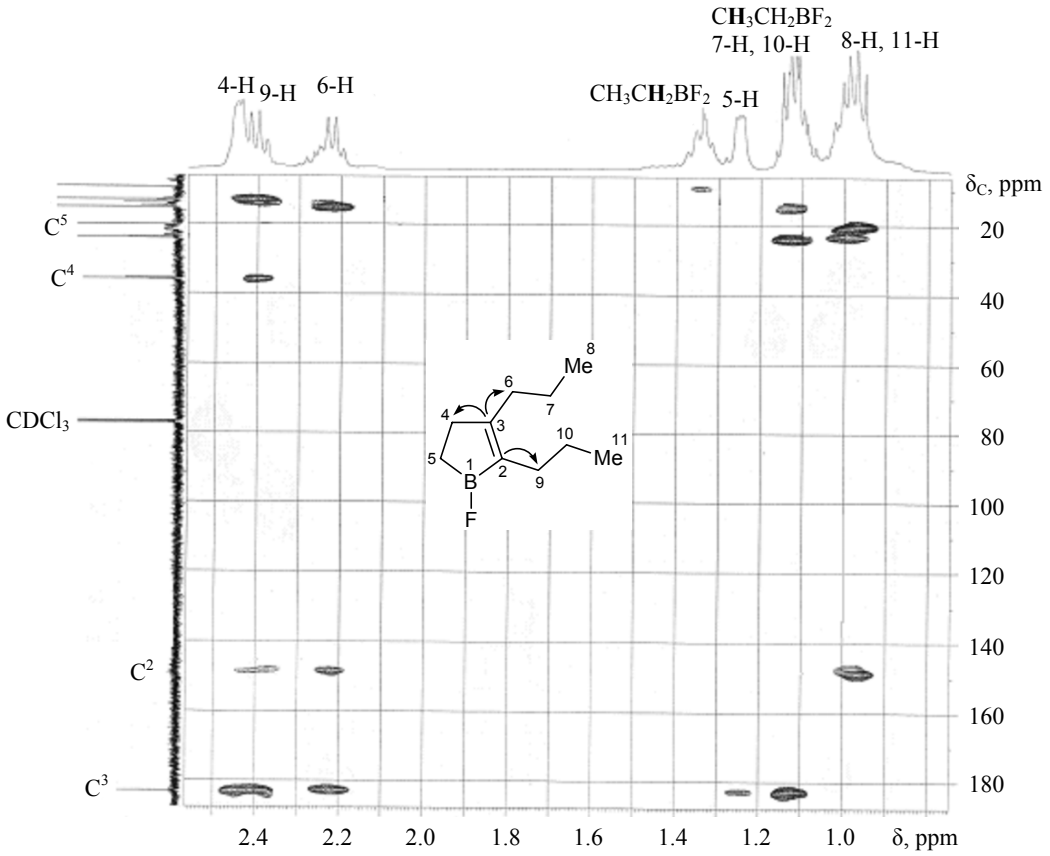
After removal of the solvent and subsequent fractional distillation under reduced pressure in a stream of argon we isolated a transparent liquid which fumed on exposure to air. The product was identified by ^1H, ^{13}C (DEPT 135), and ^{11}B NMR spectroscopy, including one- and two-dimensional techniques (HSQC, HMBC, HH COSY). In the downfield region of the ^{13}C NMR spectrum of the isolated compound we observed two signals which were assigned to double-bonded carbon atoms, C^3 (δ_C 181.82 ppm) and C^2 (δ_C 147.73 ppm, broadened). Signals from the other ring carbon atoms and two nonequivalent propyl groups were reliably assigned on the basis of the HMBC data (see figure). The C^3 signal displayed couplings with protons on C^6 in the propyl group and methylene protons on C^4 (δ_C 36.26, δ 2.42 ppm). Joint analysis of the HSQC and

Scheme 1.



Ia–Ic **IIa–IIc**

R = Et (**a**), Pr (**b**), Bu (**c**).



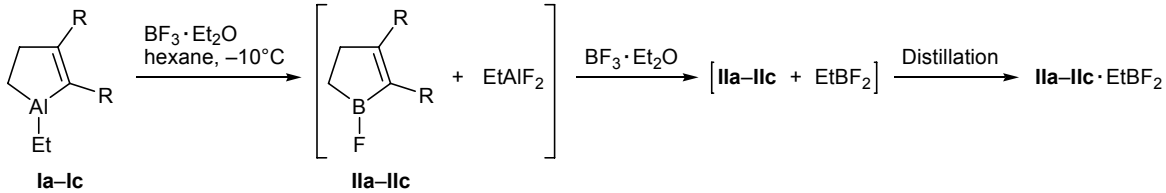
HMBC spectrum of 1-fluoro-4,5-dipropyl-2,3-dihydro-1*H*-borole (**IIb**).

COSY spectra allowed us to unambiguously identify protons on C^5 (δ_C 21.70, δ 1.23 ppm); here, the key correlation was that observed between protons on C^4 and C^5 in the HH COSY experiment. The boron nucleus resonated in the ^{11}B NMR spectrum ($CDCl_3$) at δ_B 81 ppm. The above data are very consistent with the assumed 1-fluoro-4,5-dipropyl-2,3-dihydro-1*H*-borole structure (see figure).

The molecular weight of the isolated compound estimated by cryoscopy was 238.29 which differs from 168.06 calculated for 1-fluoro-4,5-dipropyl-2,3-dihydro-1*H*-borole but approaches the molecular weight calculated for the complex of 1-fluoro-4,5-dipropyl-2,3-dihydro-1*H*-borole with $BEtF_2$ (245.93). Furthermore, the ^{13}C NMR spectrum of the product, apart from signals assigned to 1-fluoro-4,5-dipropyl-2,3-dihydro-1*H*-borole, contained additional signals at δ_C 9.48 and 14.98 ppm, the latter being broadened. These signals were assigned to the ethyl group in $BEtF_2$ molecule formed as a result of reaction of $AlEtF_2$ with $BF_3 \cdot Et_2O$ (Scheme 2). Analogous results were obtained in the reactions of $BF_3 \cdot Et_2O$ with substituted aluminacyclopent-2-enes **Ia** and **Ic**; the latter were synthesized from hex-3-yne and dec-5-yne, respectively.

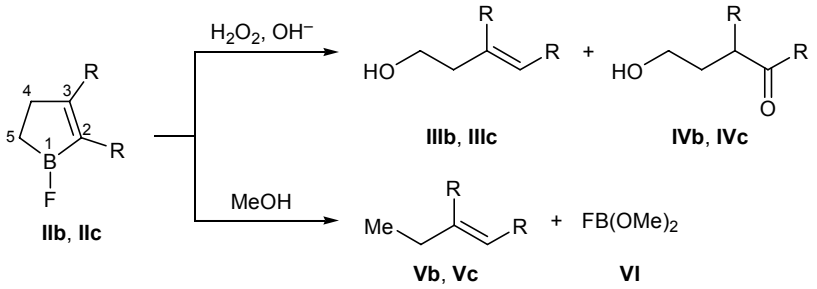
Thus the reaction of 2,3-dialkyl-1-ethylaluminacyclopent-2-enes **Ia**–**Ic** with $BF_3 \cdot Et_2O$ yields 4,5-dialkyl-1-fluoro-2,3-dihydro-1*H*-boroles **IIa**–**IIc** as

Scheme 2.



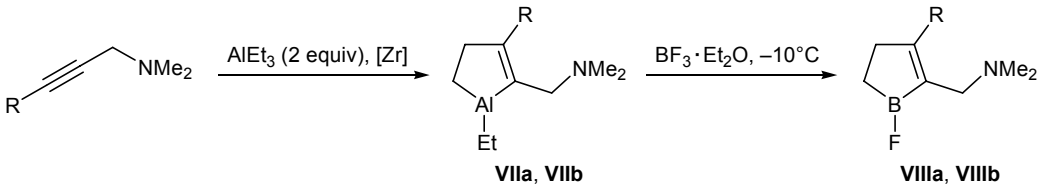
R = Et (**a**), Pr (**b**), Bu (**c**).

Scheme 3.



R = Pr (**b**), Bu (**c**).

Scheme 4.



R = Bu (**a**), C_5H_{11} (**b**).

complexes with $BEtF_2$ (Scheme 2), as in reactions of 3-substituted 1-ethylaluminacyclopentanes with $BF_3 \cdot Et_2O$ [2].

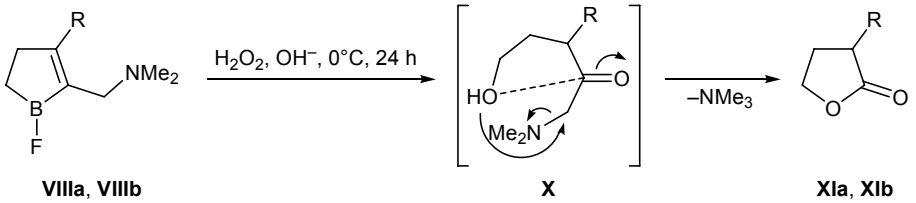
The structure of 4,5-dialkyl-1-fluoro-2,3-dihydro-1*H*-boroles was additionally confirmed by their oxidation with hydrogen peroxide in alkaline medium in accordance with known methods of oxidation of organoboron compounds [5–7]. As a result, we isolated unsaturated alcohols **IIIb** and **IIIc** and hydroxy ketones **IVb** and **IVc** at a ratio of 1:3. The reaction of **IIb** and **IIc** with methanol afforded 1,2-dialkylbut-1-enes **Vb** and **Vc** together with an equimolar amount of $BF(OMe)_2$ (**VI**) via protolytic cleavage of both B–C bonds (Scheme 3).

We also tried to perform transmetalation of more complex functionally substituted aluminacyclopent-2-enes. For this purpose, boron trifluoride–ether complex was brought into reaction with 3-alkyl-1-ethyl-2-(*N*,*N*-dimethylaminomethyl)aluminacyclopent-2-enes **VIIa** and **VIIb** which were synthesized from *N*,*N*-dimethylalk-2-yn-1-amines and $AlEt_3$ in the presence of Cp_2ZrCl_2 [8]. These reactions gave 2,3-dihydro-1*H*-boroles **VIIIa** and **VIIIb** having a dimethylaminomethyl group on C^2 (Scheme 4).

Compounds **VIIIa** and **VIIIb** were isolated by distillation, and their structure was confirmed by NMR spectroscopy and determination of molecular weights by cryoscopy. In the ^{13}C NMR spectra of **VIIIa** and **VIIIb** ($CDCl_3$) signals from the double-bonded carbon atoms were displaced by ~7–12 ppm relative to those of dihydro-1*H*-boroles **IIa**–**IIc**. The boron signal was located in the ^{11}B NMR spectra at δ_B 5.2 ppm, which is typical of three-coordinate boron atom [9]. Presumably, the heteroatoms in **VIIIa** and **VIIIb** are involved in intra- and intermolecular interactions in nonpolar solvent. Multiple signal splitting was observed in the ^{13}C NMR spectra, whereas no signals assignable to the secondary exchange product ($BEtF_2$) were present.

Thus aluminacyclopent-2-enes having nitrogen-containing substituents successfully undergo transmetalation by the action of $BF_3 \cdot Et_2O$ with formation

Scheme 5.



of the corresponding *N*,*N*-dimethyl-3-alkyl-1-fluoro-4,5-dihydro-1*H*-borol-2-ylmethanamines.

The oxidation of **VIIIa** and **VIIIb** with hydrogen peroxide in alkaline medium gave no unsaturated alcohols and hydroxy ketones like **III** and **IV** (Scheme 3) but produced lactones **XIa** and **XIb** (Scheme 5). The latter were likely to be formed via intramolecular rearrangement of intermediate hydroxy ketone **X** with simultaneous elimination of trimethylamine.

To conclude, we were the first to accomplish transmetalation of aluminacyclopent-2-enes, including functionally substituted derivatives, with boron trifluoride–ether complex to obtain dihydro-1*H*-boroles. The described reaction opens a simple and efficient one-pot synthetic route to five-membered unsaturated organoboron compounds starting from acetylenes, organoaluminum compounds, and $BF_3 \cdot Et_2O$.

EXPERIMENTAL

All reactions with organometallic reagents were carried out under argon. Commercially available 98% $AlEt_3$, 48% $BF_3 \cdot Et_2O$, and symmetrically substituted acetylenes were used without additional purification. Alkynylamines were synthesized by aminomethylation of the corresponding terminal alkynes [10]. Hexane was distilled over Al(*i*-Bu)$_3$. The IR spectra were recorded from thin films on a Bruker Vertex 70 spectrometer. The ^{1}H, ^{13}C, ^{27}Al, and ^{11}B NMR spectra, including homo- (COSY) and heteronuclear (HSQC, HMBC) correlation spectra, were measured from solutions in $CDCl_3$ on a Bruker Avance 400 spectrometer at 400.13 (^{1}H), 100.62 (^{13}C), 128.33 (^{11}B), and 104.22 MHz (^{27}Al); the ^{1}H and ^{13}C chemical shifts were determined relative to tetramethylsilane, ^{11}B, relative to $BF_3 \cdot Et_2O$, and ^{27}Al, relative to $AlCl_3$ in D_2O. The molecular weights of organoboron compounds were determined by cryoscopy in benzene according to the procedure described in [11]. The elemental compositions were determined on a Carlo Erba 1106 analyzer.

Complexes IIa–IIc of 4,5-dialkyl-1-fluoro-2,3-dihydro-1*H*-boroles with $BEtF_2$ (*general procedure*). A glass reactor was charged under dry argon with 5 ml of hexane, 0.5 mmol of Cp_2ZrCl_2, 10 mmol of the corresponding alkyne, and 12 mmol of $AlEt_3$ were added in succession under stirring at 0°C, and the mixture was stirred for 8 h at 20–22°C. The mixture was then diluted with 10 ml of hexane, cooled to –10°C, and 24 mmol of $BF_3 \cdot Et_2O$ was gradually added dropwise. The mixture was allowed to warm up to room temperature, stirred for 30 min, and evaporated, and the residue was distilled under reduced pressure in a stream of argon.

4,5-Diethyl-1-fluoro-2,3-dihydro-1*H*-borole–ethyldifluoroborane (1/1) (IIa). Yield 1.05 g (48%), colorless liquid, bp 70°C (11 mm). IR spectrum, ν, cm^{-1}: 2962, 2932, 2874, 1606, 1583, 1460, 1374, 1348, 1317, 1246, 1205, 1173, 1064, 912, 844, 785. ^{1}H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, J = 7.6 Hz), 1.08–1.11 m (3H, C**H**$_3$CH$_2$BF$_2$), 1.12 t (3H, CH_3, J = 7.6 Hz), 1.24–1.29 m (2H, 5-H), 1.30–1.37 m (2H, CH_2BF_2), 2.22 q (2H, CH_2, J = 7.6 Hz), 2.40 q (2H, CH_2, J = 7.6 Hz), 2.44 m (2H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 9.44 (**C**H$_3$CH$_2$BF$_2$), 13.18, 14.72 (CH$_3$**C**H$_2$BF$_2$), 15.29, 20.38, 21.65 (C^5), 23.95, 35.81 (C^4), 145.37 (C^2), 182.90 (C^3). ^{11}B NMR spectrum, δ_B, ppm: 34.6 ($BEtF_2$, $W_{1/2}$ = 2.8 kHz), 81.19 ($W_{1/2}$ = 1.6 kHz). Found, %: C 54.86; H 8.55. *M* 198.21. $C_{10}H_{19}B_2F_3$. Calculated, %: C 55.03; H 8.78. *M* 217.87.

1-Fluoro-4,5-dipropyl-2,3-dihydro-1*H*-borole–ethyldifluoroborane (1/1) (IIb). Yield 1.18 g (48%), colorless liquid, bp 80°C (13 mm). ^{1}H NMR spectrum, δ, ppm: 0.90–1.00 m (6H, CH_3), 1.10 t (3H, C**H**$_3$CH$_2$-BF$_2$, J = 7.6 Hz), 1.23 m (2H, 5-H), 1.30–1.38 m (4H, CH_2, CH$_3$C**H**$_2$BF$_2$), 1.55 sext (2H, CH_2, J = 7.6 Hz), 2.18 t (2H, CH_2, J = 7.6 Hz), 2.36 t (2H, CH_2, J = 7.6 Hz), 2.42 m (2H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 9.48 (**C**H$_3$CH$_2$BF$_2$), 14.26, 14.38, 14.95 (CH$_3$-**C**H$_2$BF$_2$), 21.61 (C^5), 21.85, 24.05, 29.85, 33.30, 36.26 (C^4), 148.84 (C^2), 183.13 (C^3). ^{11}B NMR spectrum, δ_B, ppm: 35.16 ($EtBF_2$, $W_{1/2}$ = 1.6 kHz), 80.76 ($W_{1/2}$ = 1.2 kHz). Found, %: C 58.32; H 9.21. *M* 238.29. $C_{12}H_{23}B_2F_3$. Calculated, %: C 58.51; H 9.42. *M* 245.93.

4,5-Dibutyl-1-fluoro-2,3-dihydro-1*H*-borole–ethyldifluoroborane (1/1) (IIc). Yield 1.27 g (47%), colorless liquid, bp 120°C (14 mm). IR spectrum, ν, cm^{-1}: 2958, 2928, 2859, 1603, 1582, 1460, 1376, 1348, 1209, 1104, 1074, 1039, 996, 909, 844, 774, 728. ^{1}H NMR spectrum, δ, ppm: 0.90–1.00 m (6H, CH_3), 1.09 t (3H, C**H**$_3$CH$_2$BF$_2$, J = 7.6 Hz), 1.23 m (2H, 5-H), 1.27–1.42 m (10H, CH_2, CH$_3$C**H**$_2$BF$_2$), 2.20 t and 2.38 t (2H each, 4-CH_2, 5-CH_2, J = 7.6 Hz), 2.42 m (2H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 9.48 (**C**H$_3$CH$_2$BF$_2$), 13.98, 14.08, 14.98 (CH$_3$**C**H$_2$BF$_2$), 21.70 (C^5), 23.07, 27.27, 30.86, 30.94, 33.13, 36.32 (C^4), 147.76 (C^2), 181.88 (C^3). ^{11}B NMR spectrum, δ_B, ppm: 35.16 ($EtBF_2$, $W_{1/2}$ = 1.6 kHz), 81.57 ($W_{1/2}$ = 1.2 kHz). Found, %: C 61.17; H 9.68. *M* 270.15. $C_{14}H_{27}B_2F_3$. Calculated, %: C 61.29; H 9.92. *M* 273.98.

Oxidation of 4,5-dialkyl-1-fluoro-2,3-dihydro-1*H*-boroles IIb and IIc with hydrogen peroxide in

alkaline medium (*genral procedure*). Compound **IIb** or **IIc** was dissolved in 10 ml of hexane, 6 ml of 20% aqueous sodium hydroxide was added at 0°C, and 2 ml of 30% hydrogen peroxide was then added dropwise. The mixture was stirred for 6 h, the organic phase was separated, the aqueous phase was extracted with diethyl ether (2×30 ml), the extracts were combined with the organic phase, dried over $CaCl_2$, and concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel (40–100 mesh, 30 cm×12 mm) using ethyl acetate–hexane (1:50) as eluent.

3-Propylhept-3-en-1-ol (IIIb). Yield 31%, R_f 0.62 (ethyl acetate–hexane, 1:5). ^{1}H NMR spectrum, δ, ppm: 0.91 t (6H, CH_3, J = 7.2 Hz), 1.32–1.45 m (4H, CH_2), 1.98–2.04 m (4H, CH_2), 2.25 t (2H, C**H**$_2$CH=C, J = 6.2 Hz), 3.64 m (2H, C**H**$_2$OH), 5.23 t (1H, CH=C, J = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.86, 14.09, 21.64, 23.13, 29.89, 31.80, 39.93, 60.42, 128.51, 135.38. Found, %: C 76.77; H 12.79. $C_{10}H_{20}O$. Calculated, %: C 76.86; H 12.90.

3-Butyloct-3-en-1-ol (IIIc). Yield 29%, R_f 0.62 (ethyl acetate–hexane, 1:5). ^{1}H NMR spectrum, δ, ppm: 0.92 t (6H, CH_3, J = 7.0 Hz), 1.32–1.38 m (8H, CH_2), 2.01–2.05 m (4H, CH_2), 2.27 t (2H, CH_2, J = 6.2 Hz), 3.66 t (2H, C**H**$_2$OH, J = 6.4 Hz), 5.24 t (1H, CH=C, J = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.96, 13.99, 22.42, 22.79, 27.47, 29.49, 30.76, 32.24, 39.98, 60.40, 128.50, 135.42. Found, %: C 77.95; H 13.02. $C_{12}H_{24}O$. Calculated, %: C 78.19; H 13.13.

7-Hydroxy-5-propylheptan-4-one (IVb). Yield 62%, R_f 0.67 (ethyl acetate–hexane, 1:5). ^{1}H NMR spectrum, δ, ppm: 0.89 m (6H, CH_3), 1.27–1.45 m (2H, CH_2), 1.35 m (2H, CH_2), 1.55 m (2H, CH_2), 1.60 m (1H, CH_2), 1.76 m (1H, CH_2), 2.42 m (2H, CH_2), 2.64 m (1H, CH), 3.56 t (2H, C**H**$_2$OH, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.70, 13.73, 16.81, 20.52, 34.00, 34.06, 44.34, 48.75, 60.67, 215.30. Found, %: C 69.61; H 11.61. $C_{10}H_{20}O_2$. Calculated, %: C 69.72; H 11.70.

6-Butyl-8-hydroxyoctan-5-one (IVc). Yield 58%, R_f 0.67 (ethyl acetate–hexane, 1:5). ^{1}H NMR spectrum, δ, ppm: 0.93 m (6H, CH_3), 1.27–1.48 m (6H, CH_2), 1.35 m (2H, CH_2), 1.56 m (2H, CH_2), 1.58 m (1H, CH_2), 1.78 m (1H, CH_2), 2.44 m (2H, CH_2), 2.66 m (1H, CH), 3.63 t (2H, C**H**$_2$OH, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.06, 14.12, 22.38, 22.78, 25.65, 29.70, 31.56, 34.01, 42.15, 49.06, 61.02, 215.39. Found, %: C 71.83; H 12.00. $C_{12}H_{24}O_2$. Calculated, %: C 71.95; H 12.08.

Reaction of 4,5-dialkyl-1-fluoro-2,3-dihydro-1*H*-boroles IIb and IIc with methanol (*general procedure*). A solution of 5 mmol of compound **IIb** or **IIc** in 10 ml of hexane was cooled to 0°C, 20 mmol of methanol was added, and the mixture was stirred for 1 h. The solvent and excess methanol were removed under reduced pressure, and the residue was distilled in a vacuum. The spectral parameters and physical constants of **Vb** and **Vc** were reported in [12, 13].

(3-Alkyl-1-fluoro-4,5-dihydro-1*H*-borol-2-yl)-*N*,*N*-dimethylmethanamines VIIIa and VIIIb (*general procedure*). A glass reactor was charged under argon with 50 ml of hexane, 2.0 mmol of Cp_2ZrCl_2, 10 mmol of the corresponding alkynylamine, and 20 mmol of $AlEt_3$ were added in succession, and the mixture was stirred for 3 h at 40°C. The mixture was then cooled to –10°C, 40 mmol of $BF_3 \cdot Et_2O$ was gradually added dropwise, the mixture was allowed to warm up to room temperature, stirred for 30 min, and evaporated, and the residue was distilled under reduced pressure in a stream of argon.

(3-Butyl-1-fluoro-4,5-dihydro-1*H*-borol-2-yl)-*N*,*N*-dimethylmethanamine (VIIIa). Yield 1.22 g (62%), yellow oily liquid, bp 101°C (10 mm). IR spectrum, ν, cm^{-1}: 2961, 2952, 2853, 1487, 1458, 1419, 1374, 1337, 1220, 1053, 765, 724. ^{1}H NMR spectrum, δ, ppm: 0.90 br.m (3H, CH_3), 1.22–1.43 br.m (4H, CH_2), 1.45–1.54 br.m (2H, 5-H), 2.36–2.58 br.m (10H, CH_2, CH_3N), 3.71 br.s (2H, CH_2N). ^{13}C NMR spectrum, δ_C, ppm: 13.97, 14.06, 14.43 (CH_3); 23.28, 23.65 (C^8); 28.85 (C^5); 31.26, 31.29, 31.32 (C^7); 32.71, 32.77 (C^6); 32.56 (C^4); 42.35, 42.79 (NCH_3); 51.06 (CH_2N), 135.20 (C^2), 195.16 (C^3). ^{11}B NMR spectrum: δ_B 5.2 ppm ($W_{1/2}$ = 1.6 kHz). Found, %: C 66.54; H 10.41; N 6.97. M 184.33. $C_{11}H_{21}BFN$. Calculated, %: C 66.96; H 10.73; N 7.10. M 197.10.

(1-Fluoro-3-pentyl-4,5-dihydro-1*H*-borol-2-yl)-*N*,*N*-dimethylmethanamine (VIIIb). Yield 1.27 g (60%), yellow oily liquid, bp 75°C (2 mm). IR spectrum, ν, cm^{-1}: 2959, 2963, 2858, 1491, 1416, 1382, 1338, 1225, 1048, 763, 731. ^{1}H NMR spectrum, δ, ppm: 0.90 br.m (3H, CH_3), 1.20–1.40 br.m (6H, CH_2), 1.45–1.55 br.m (2H, 5-H), 2.37–2.60 br.m (10H, CH_2, CH_3N), 3.73 br.s (2H, CH_2N). ^{13}C NMR spectrum, δ_C, ppm: 13.89, 13.97, 14.06 (CH_3); 22.56, 22.62 (C^9); 28.04, 28.07 (C^7); 28.80 (C^5); 31.04, 31.11, 31.97, 32.05 (C^8); 32.47 (C^4); 36.52, 36.79 (C^6); 42.31, 42.79 (NCH_3); 51.00 (CH_2N), 135.00 (C^2), 194.56 (C^3). ^{11}B NMR spectrum: δ_B 5.2 ppm ($W_{1/2}$ = 1.6 kHz). Found, %: C 67.85; H 10.69; N 6.47. M 233.45.

$C_{12}H_{23}BFN$. Calculated, %: C 68.20; H 10.97; N 6.63. *M* 211.12.

Oxidation of (3-alkyl-1-fluoro-4,5-dihydro-1*H*-borol-2-yl)-*N*,*N*-dimethylmethanamines VIIIa and VIIIb (*general procedure*). A solution of 5 mmol of compound **VIIIa** or **VIIIb** in 10 ml of hexane was cooled to 0°C, 6 ml of 20% aqueous sodium hydroxide was added, and 2 ml of 30% hydrogen peroxide was then slowly added dropwise. The mixture was stirred for 24 h, the organic phase was separated, the aqueous phase was extracted with diethyl ether (2×30 ml), the extracts were combined with the organic phase, dried over $CaCl_2$, and concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (50:1) as eluent.

3-Butyltetrahydrofuran-2-one (XIa). Yield 62%, R_f 0.52 (ethyl acetate–hexane, 1:5). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* = 7.0 Hz), 1.20–1.51 m (4H, CH_2), 1.87–2.00 m (2H, CH_2), 2.36–2.44 m (2H, CH_2), 2.49–2.64 m (1H, CH), 4.20 m and 4.35 m (1H each, CH_2O). ^{13}C NMR spectrum, δ_C, ppm: 13.87, 22.44, 28.63, 29.48, 30.03, 39.23, 66.44, 179.62. Found, %: C 67.46; H 9.85. $C_8H_{14}O_2$. Calculated, %: C 67.57; H 9.92

3-Pentyltetrahydrofuran-2-one (XIb). Yield 62%, R_f 0.52 (ethyl acetate–hexane, 1:5). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, *J* = 6.8 Hz), 1.25–1.48 m (6H, CH_2), 1.87–2.00 m (2H, CH_2), 2.35–2.43 m (2H, CH_2), 2.47–2.55 m (1H, CH), 4.18 m (1H, CH_2O), 4.33 m (1H, CH_2O). ^{13}C NMR spectrum, δ_C, ppm: 13.95, 22.42, 26.97, 28.61, 30.26, 31.50, 39.23, 66.49, 179.63. Found, %: C 69.10; H 10.24. $C_9H_{16}O_2$. Calculated, %: C 69.19; H 10.32.

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