

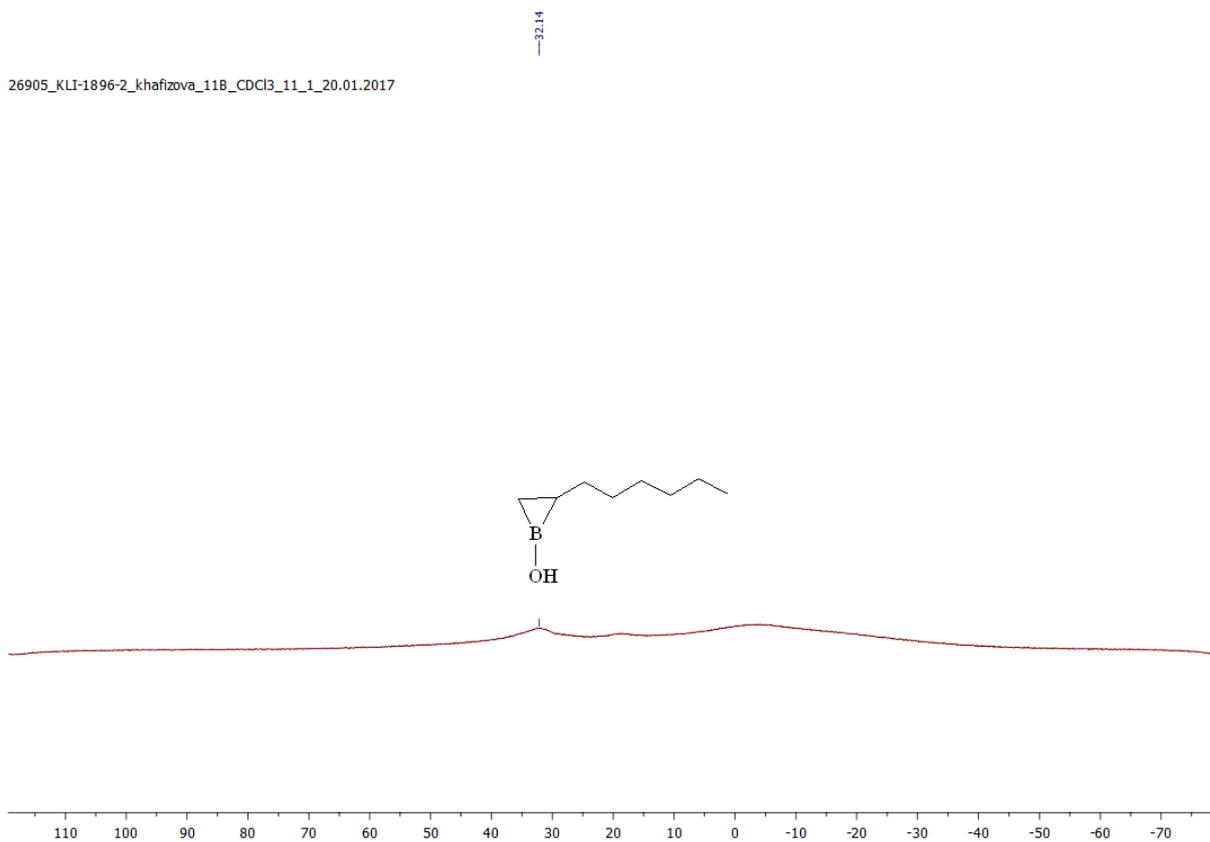
## An original catalytic synthesis of boriran-1-ols

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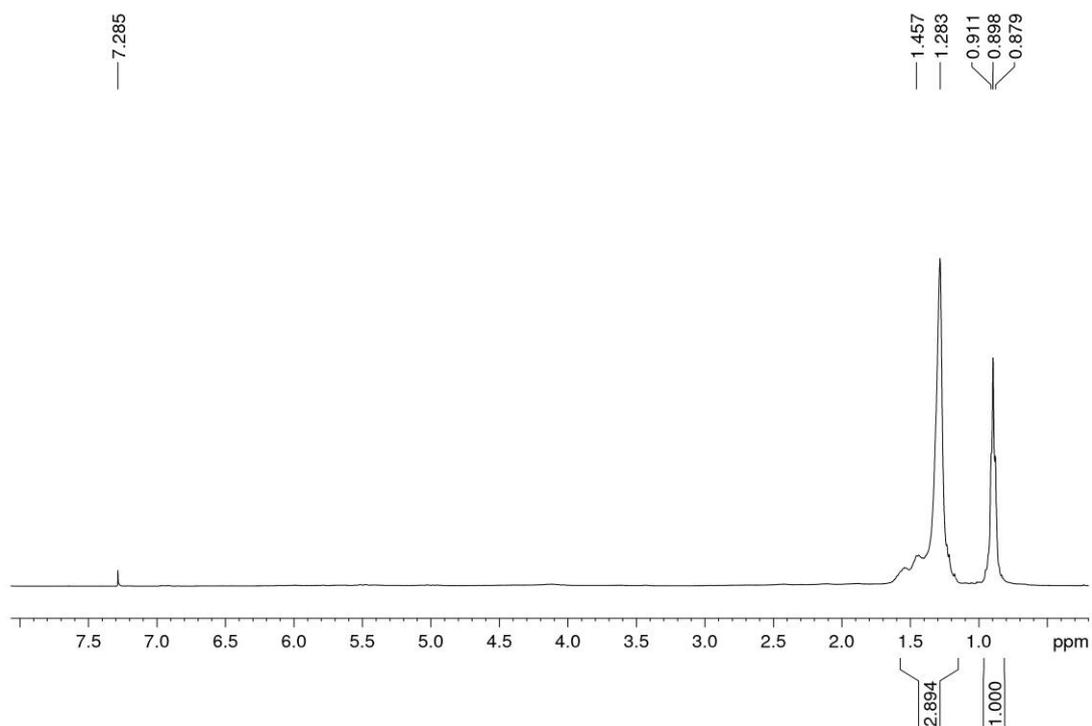
$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$  NMR spectra were measured in  $\text{CDCl}_3$  on a Bruker Avance-400 spectrometer [400.13 ( $^1\text{H}$ ), 100.62 ( $^{13}\text{C}$ ), 128.33 ( $^{11}\text{B}$ ) MHz]. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  ( $^{11}\text{B}$ ) and the coupling constants ( $J$ ) in Hz. Mass spectra were obtained on Shimadzu GCMS-QP2010 Ultra, capillary column Supelco PTE-5 (60 m  $\times$  0.25 mm, carrier gas helium, ramp from 40 to 280  $^\circ\text{C}$  at a rate 8 deg  $\text{min}^{-1}$ , ionizing electrons energy 70 eV, injector temperature 260  $^\circ\text{C}$ , ion source temperature 200  $^\circ\text{C}$ ). The IR spectra were recorded on a Bruker Vertex 70v spectrometer from liquid films. The molecular weights of organoboron compounds were determined by cryoscopy in benzene under argon according to literature (Refs. [6a,b] of the main text) with the use of a three-necked glass cell equipped with a Beckmann thermometer (accuracy  $\pm 0.005$   $^\circ\text{C}$ ). The  $\text{H}_2\text{O}_2$  oxidation of 2-alkylboriran-1-ols **3a,b** was done under alkaline conditions as described in Refs. [1,4] of the main text. Spectral and physical characteristics of compounds (**4–6a,b**) have been reported in Refs. [5a-f] of the main text.

$^{11}\text{B}$ NMR ( $\text{CDCl}_3$ , 128.33 MHz), 2-hexylboriran-1-ol <b>3a</b> .....	S2
$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400.13 MHz), 2-hexylboriran-1-ol <b>3a</b> .....	S2
$^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100.62 MHz), 2-hexylboriran-1-ol <b>3a</b> .....	S3
$^{11}\text{B}$ NMR ( $\text{CDCl}_3$ , 128.33 MHz), 2-octylboriran-1-ol <b>3b</b> .....	S3
$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400.13 MHz), 2-octylboriran-1-ol <b>3b</b> .....	S4
$^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100.62 MHz), 2-octylboriran-1-ol <b>3b</b> .....	S4
$^{11}\text{B}$ NMR ( $\text{CDCl}_3$ , 128.33 MHz), 1,1'-oxybis(2-hexylborirane) <b>7a</b> .....	S5
$^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400.13 MHz), 1,1'-oxybis(2-hexylborirane) <b>7a</b> .....	S5
$^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100.62 MHz), 1,1'-oxybis(2-hexylborirane) <b>7a</b> .....	S6
$^{11}\text{B}$ NMR ( $\text{CDCl}_3$ , 128.33 MHz), 1,1'-oxybis(2-octylborirane) <b>7b</b> .....	S6

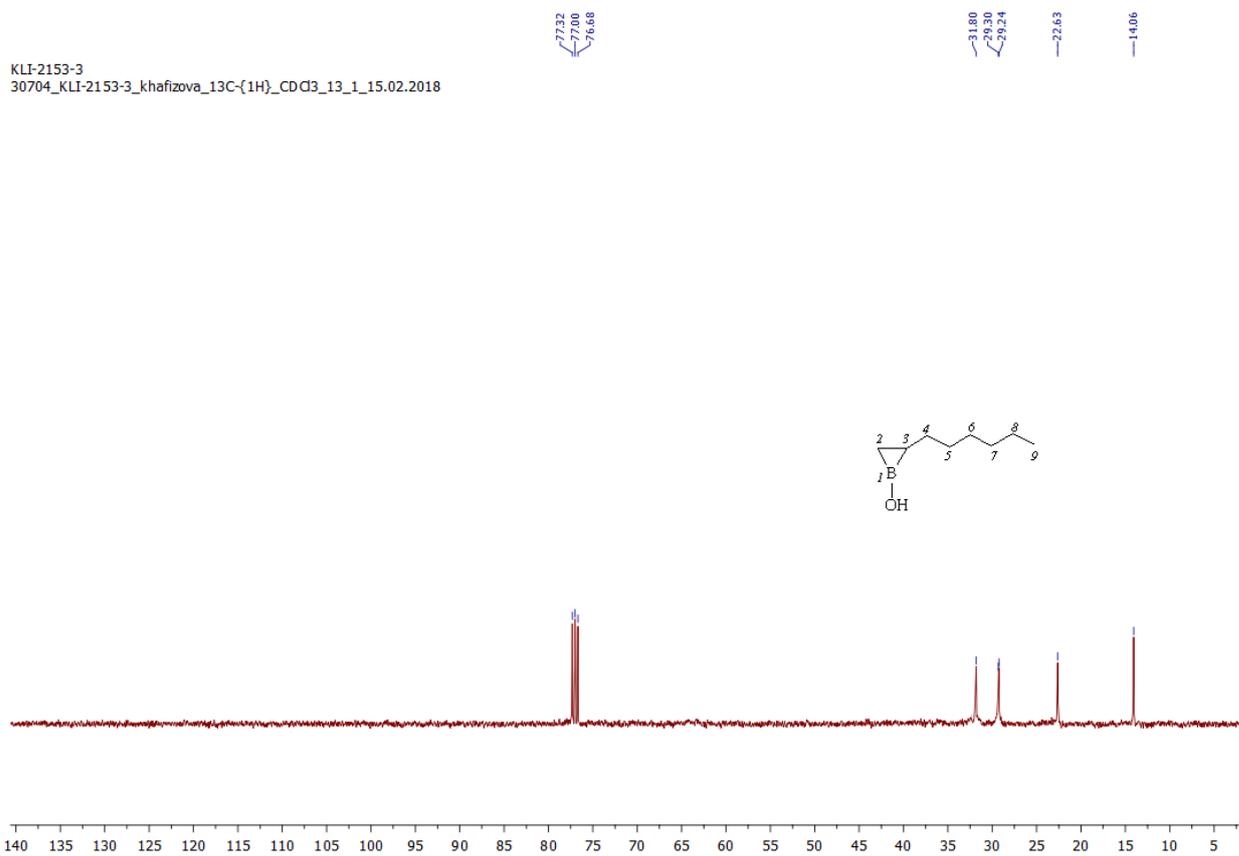
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128.33 MHz), 2-hexylboriran-1-ol **3a**.



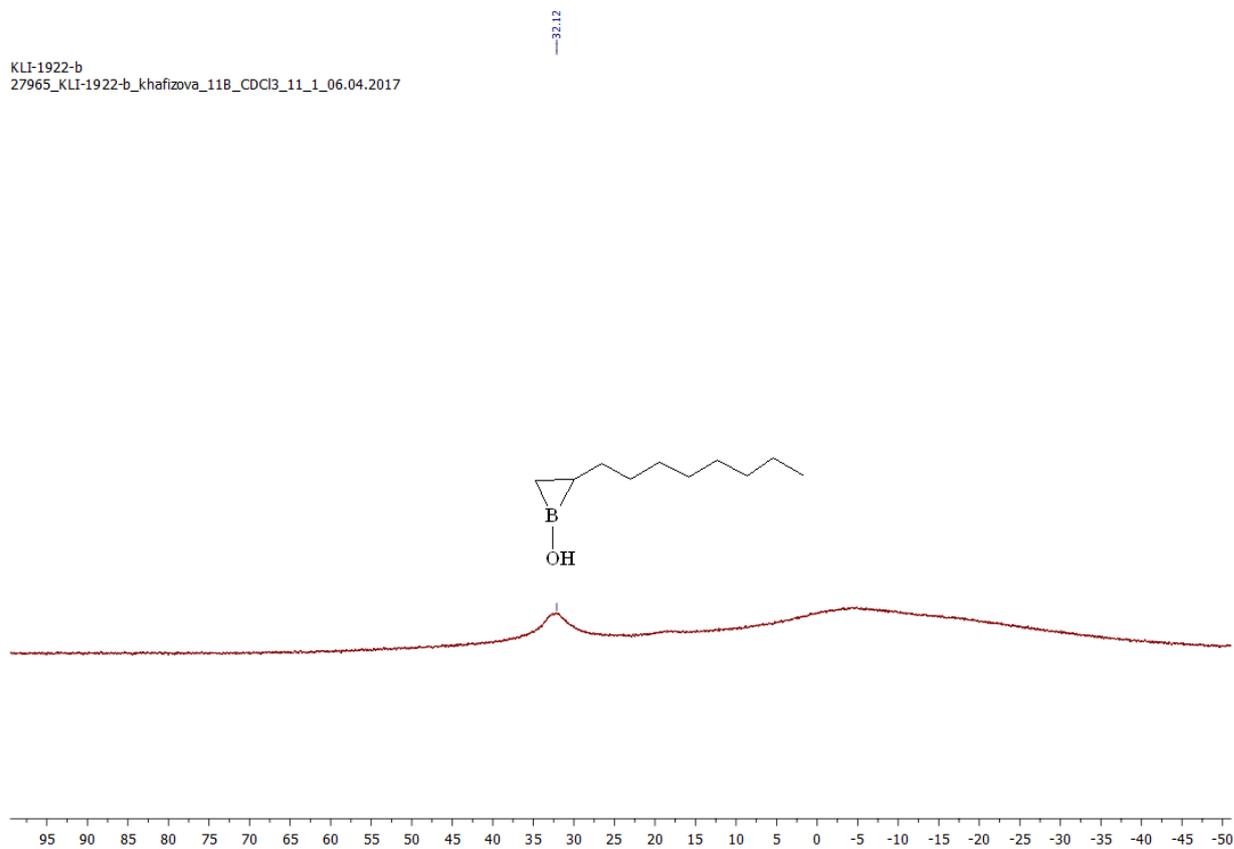
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz), 2-hexylboriran-1-ol **3a**.



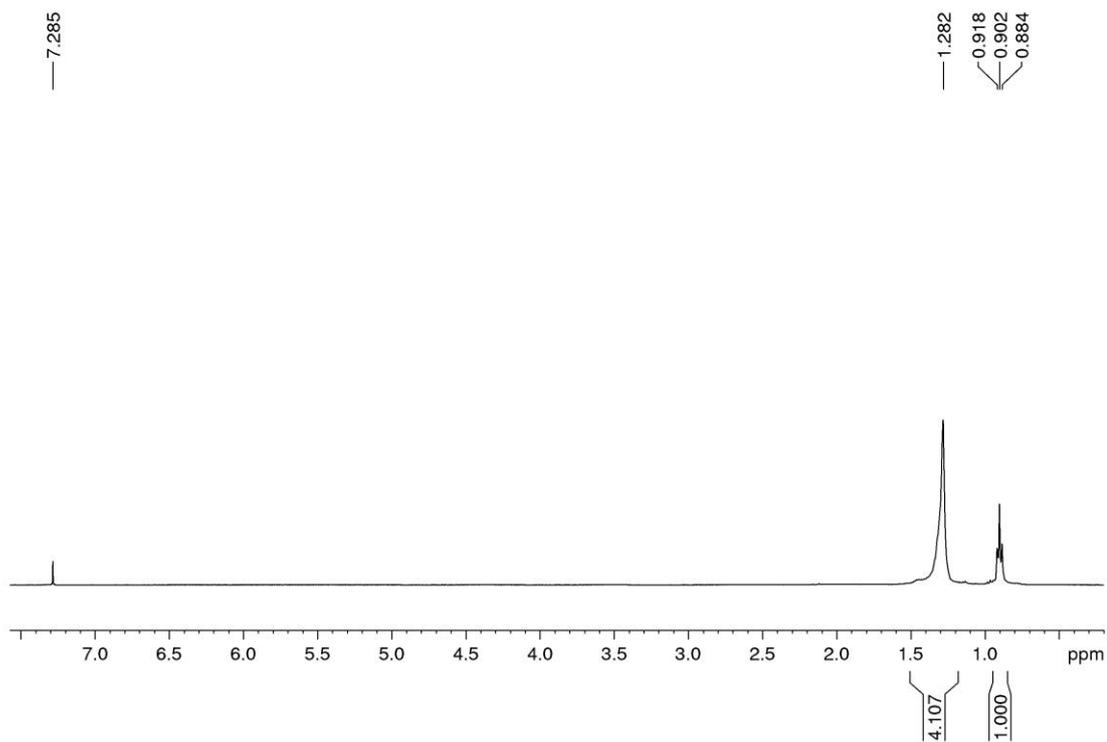
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.62 MHz), 2-hexylboriran-1-ol **3a**.



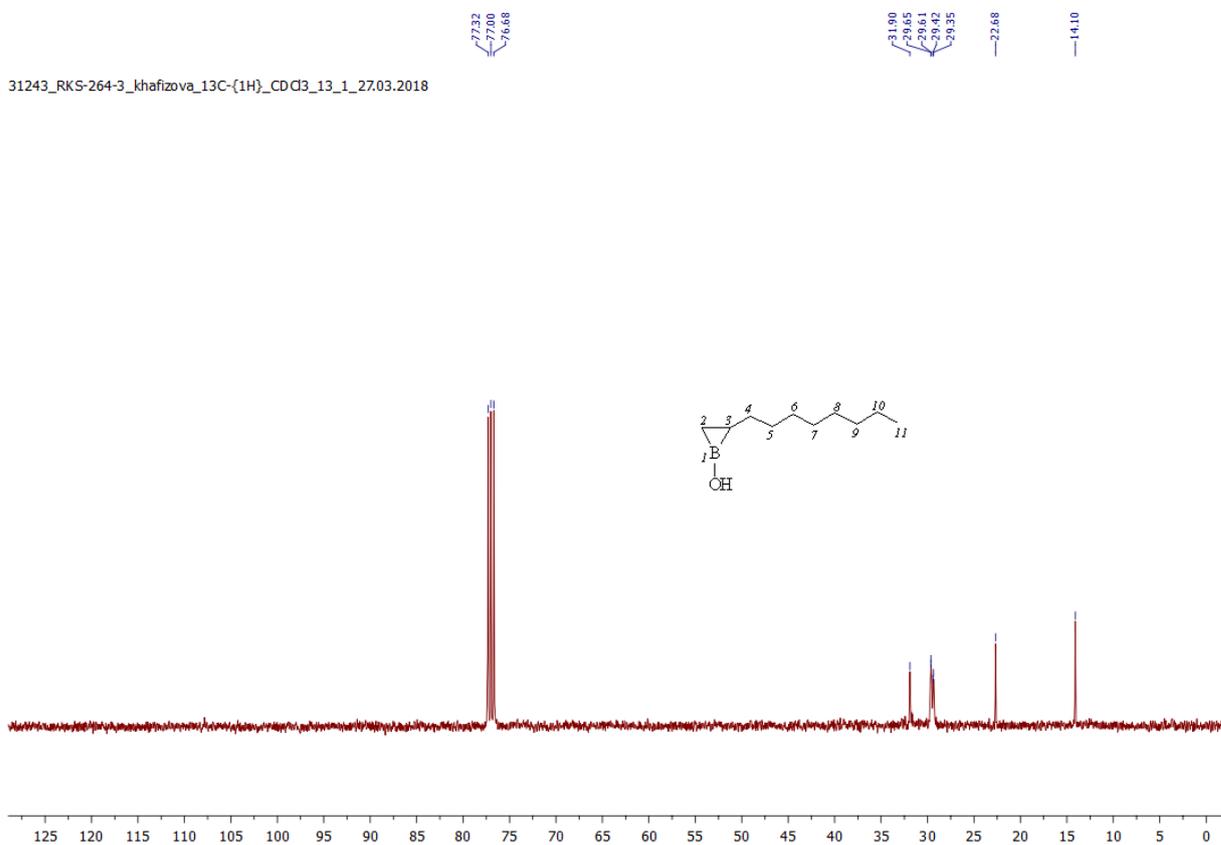
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128.33 MHz), 2-octylboriran-1-ol **3b**.



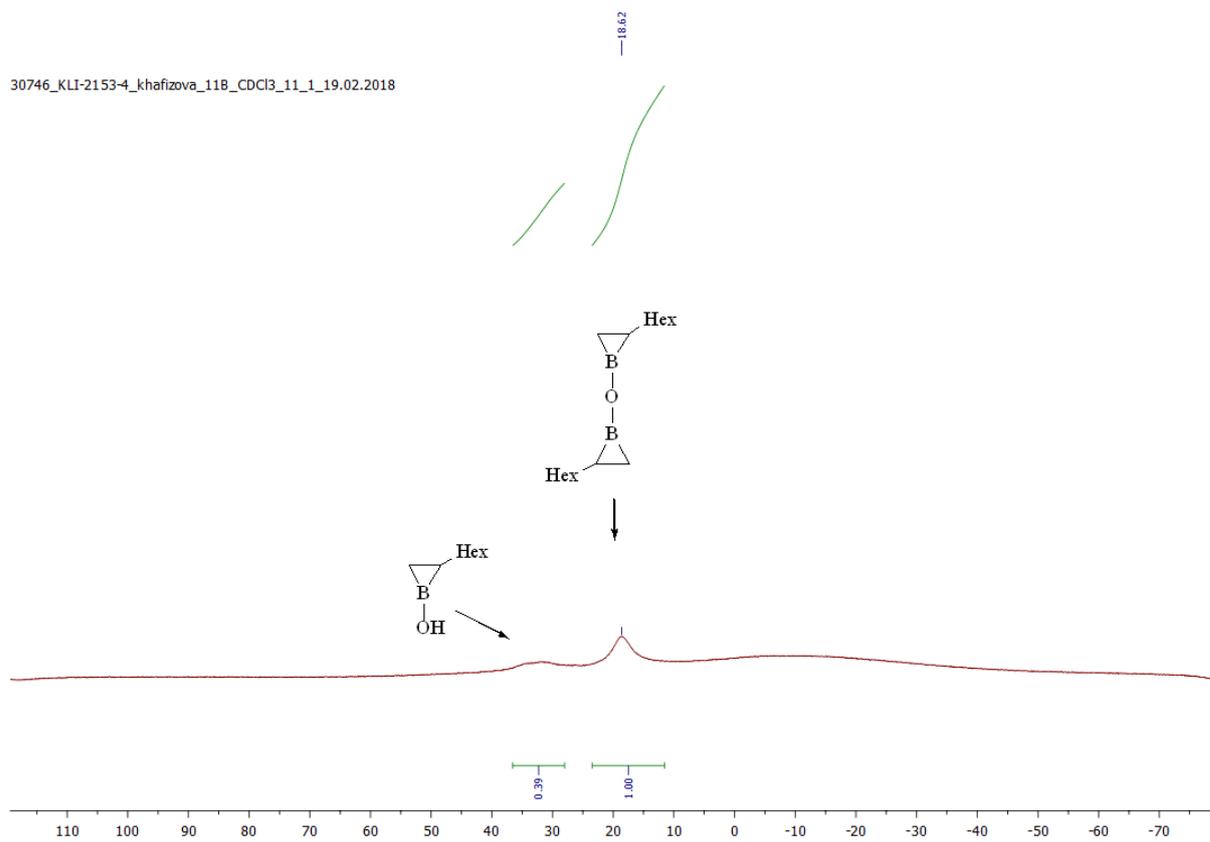
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz), 2-octylboriran-1-ol **3b**.



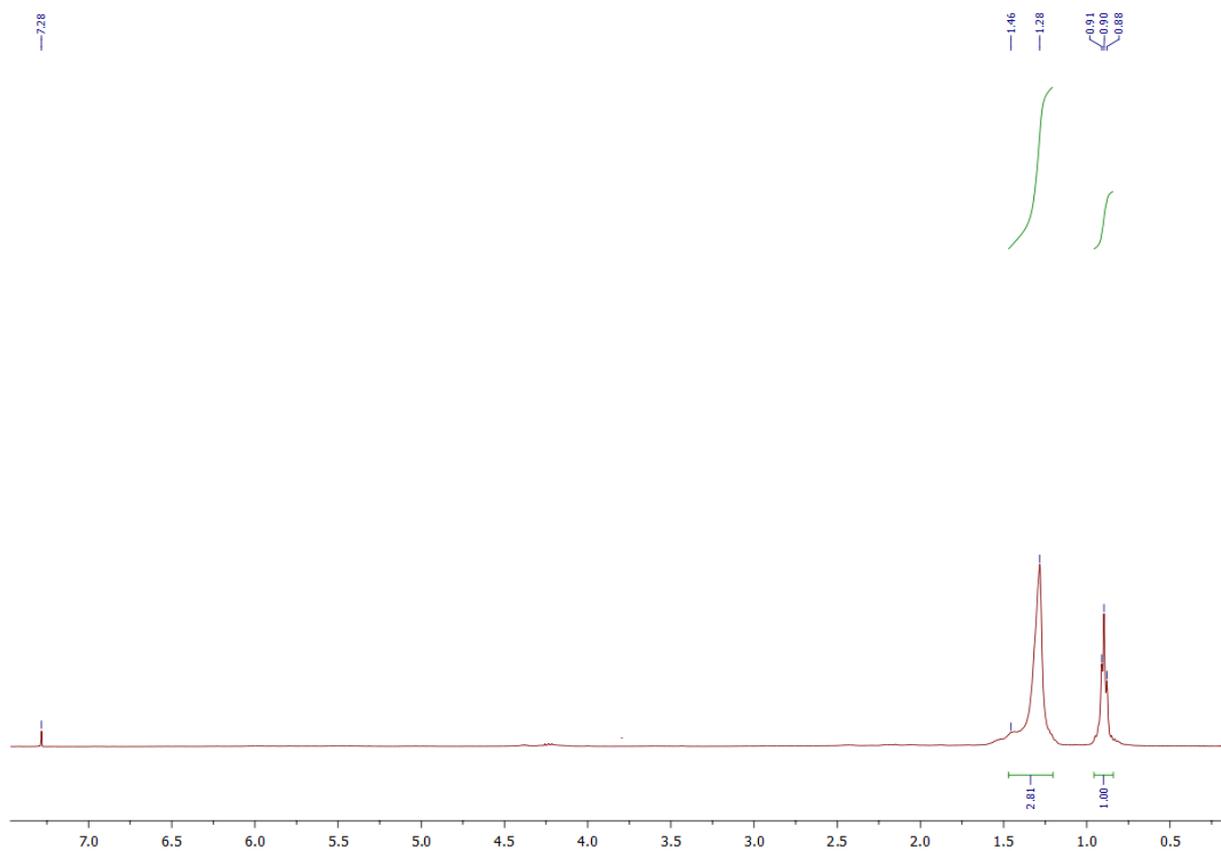
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.62 MHz), 2-octylboriran-1-ol **3b**.



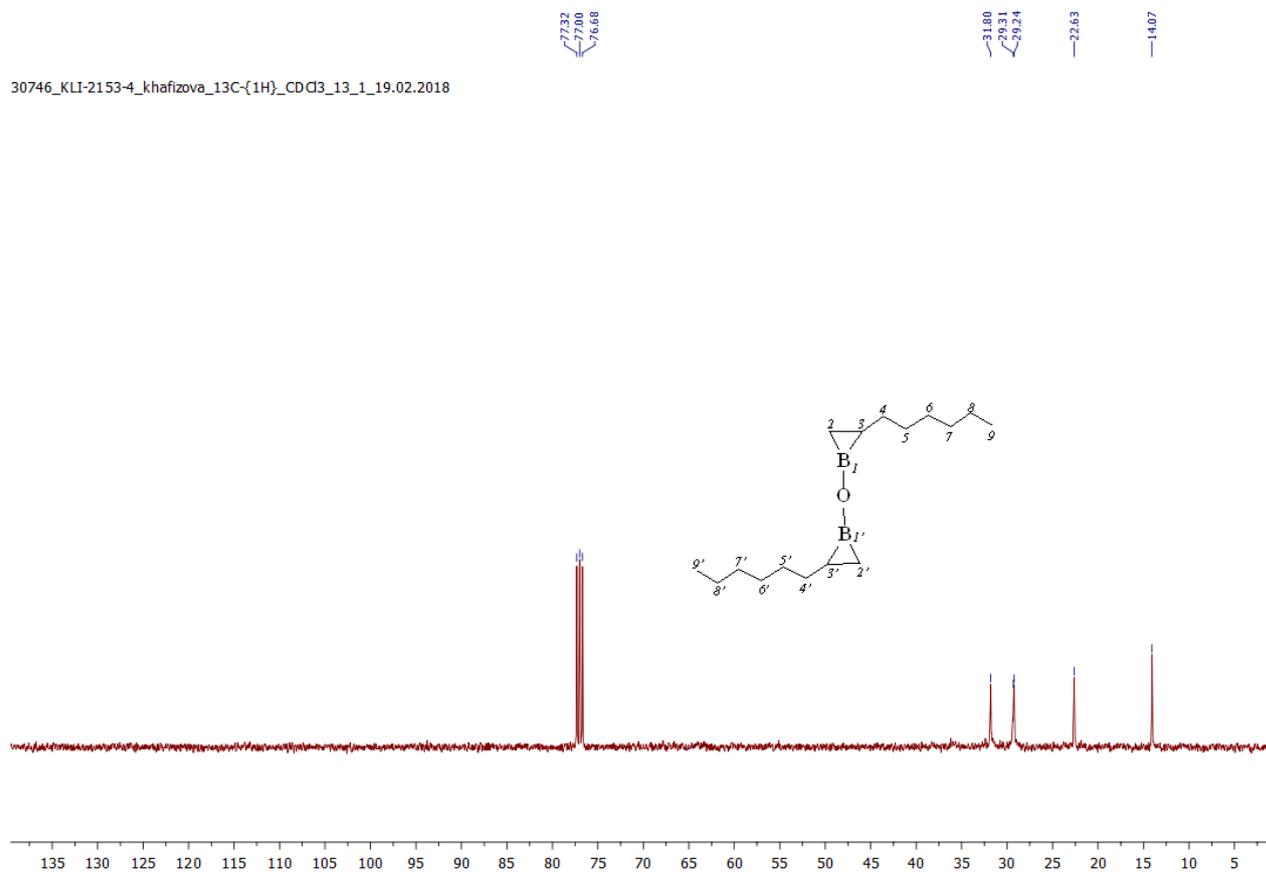
$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128.33 MHz), 1,1'-oxybis(2-hexylborirane) **7a**.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz), 1,1'-oxybis(2-hexylborirane) **7a**.



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.62 MHz), 1,1'-oxybis(2-hexylborirane) **7a**.



$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128.33 MHz), 1,1'-oxybis(2-octylborirane) **7b**.

