

**Supporting Information for**  
**Formation of Pinacol Boronate Esters via Pyridine Iodoborane Hydroboration**

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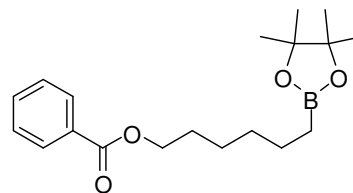
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General Experimental	S2
Known compounds	S2
6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate <b>15</b>	S2
<sup>1</sup> H and <sup>13</sup> C NMR spectra ( <b>5, 6</b> , Table 1 entries 4/5, <b>10, 15</b> )	S4

**General Experimental.** All reactions involving air and moisture sensitive reagents or solvents were performed in flame-dried glassware under a nitrogen atmosphere. Tetrahydrofuran and dichloromethane were passed through an activated alumina column immediately before use. All organic reagents were used as purchased unless otherwise noted. Pyridine borane was purified by filtration through a plug of silica gel (1:1 hexanes:Et<sub>2</sub>O).  $\alpha$ -Methylstyrene,  $\beta$ -methylstyrene, decene, cyclohexene, norbornene, dodecene, and 1-phenyl cyclohexene were distilled before use. Flash chromatography was performed using 32 – 63  $\mu$ m silica gel with the indicated solvent systems.

Nuclear magnetic resonance experiments were performed on 500 MHz and 400 MHz spectrometers. Both of the  $\alpha$ -methylstyrene and  $\beta$ -methylstyrene pinacolate derivatives are known, but NMR spectra have not been published previously and are appended below.<sup>1</sup> The pinacolboronates derived from styrene,<sup>2</sup> decene, cyclohexene, norbornene,<sup>3</sup> dodecene,<sup>4</sup> and 1-phenylcyclohexene<sup>5</sup> were identified by comparison with published NMR data.

**6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate (Table 2, Entries 4 and 5).**



IR (CDCl<sub>3</sub>) 1719 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.05

(m, 2H), 7.55 (m, 1H), 7.44 (m, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.79 (m, 2H), 1.48 (m, 4H),

1.39 (m, 2H), 1.24 (m, 12H), 0.80 (t, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$

166.6, 132.7, 129.5, 128.8, 128.3, 82.8, 65.1, 32.0, 28.6, 25.8, 24.8, 23.9, C on B not

<sup>1</sup> Cipot, J.; Vogels, C. M.; McDonald, R.; Westcott, S. A.; Stradiotto, M. *Organometallics* **2006**, *25*, 5965-5968.

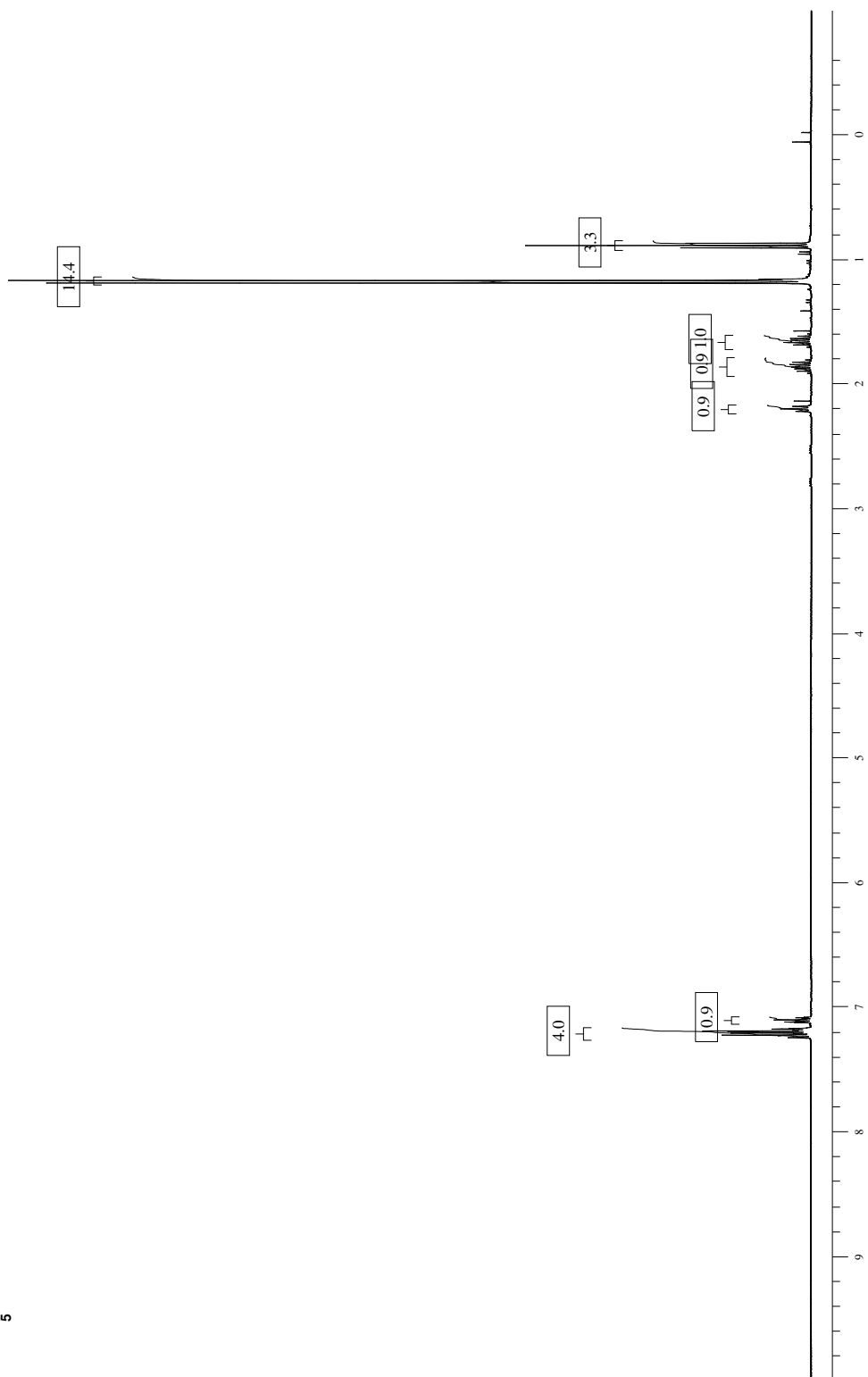
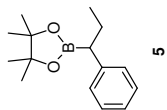
<sup>2</sup> Yamamoto, Y.; Fujikawa, R.; Umemoto, T.; Miyaura, N. *Tetrahedron*, **2004**, *60*, 10695-10700.

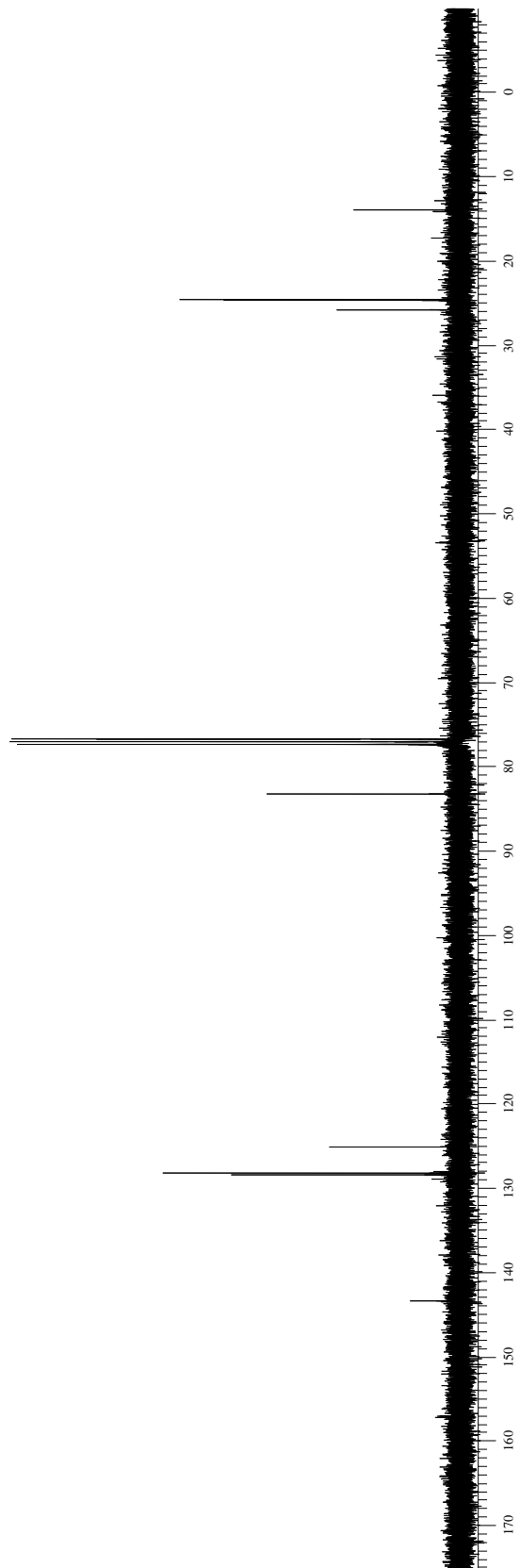
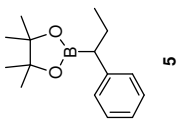
<sup>3</sup> Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482-3485.

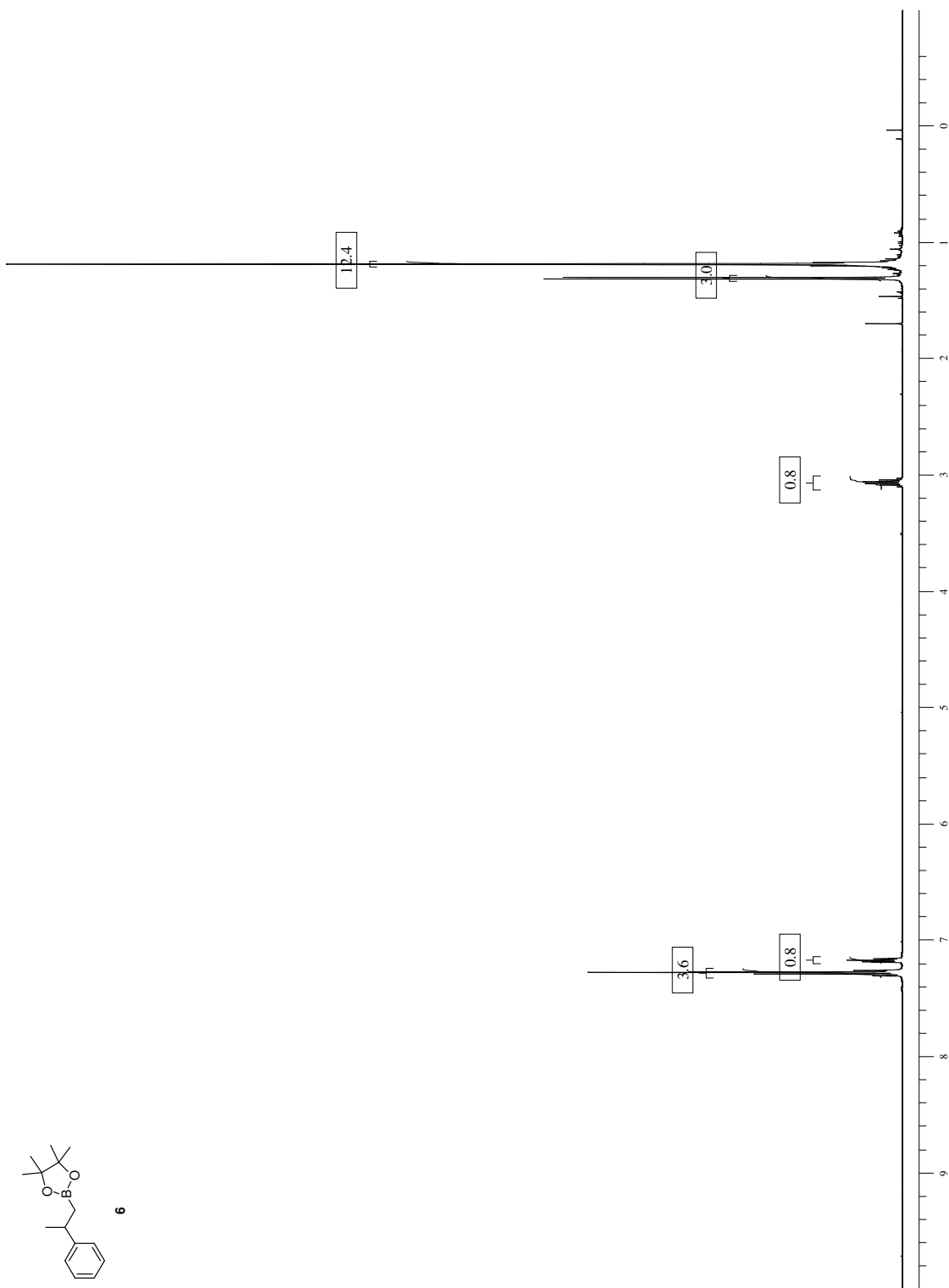
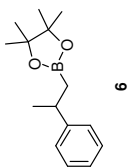
<sup>4</sup> Garrett, C. E.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 3224-3225.

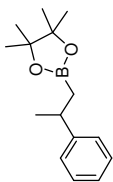
<sup>5</sup> Hupe, E.; Marek, I.; Knochel, P. *Org. Lett.* **2002**, *4*, 2861-2863.

observed;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  34.7; ESMS  $m/z$  (relative intensity) 355.2 (M + Na, 100%); HRMS calcd for  $\text{C}_{19}\text{H}_{29}\text{BO}_4$  (M + Na) 355.2057, found 355.2058.

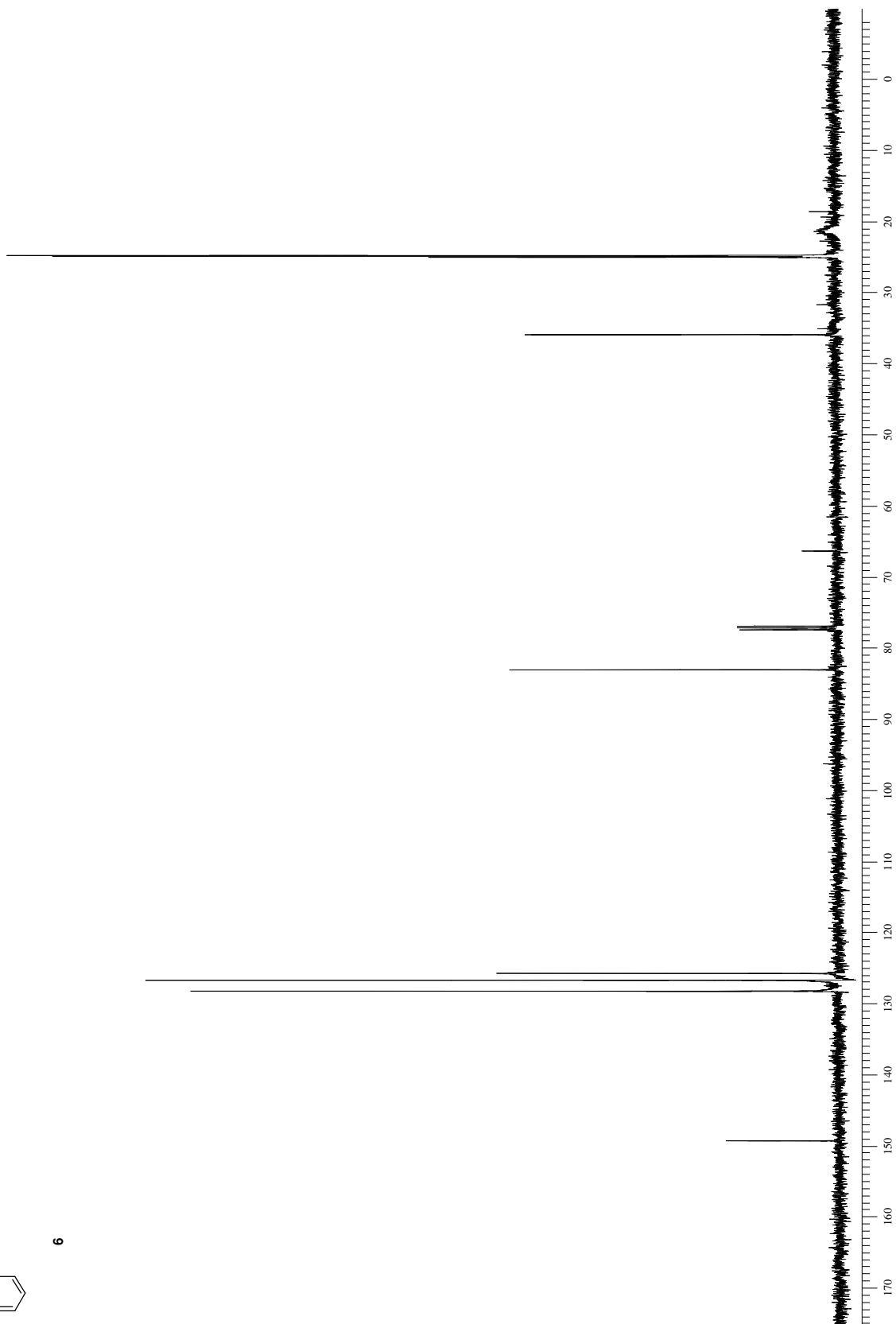


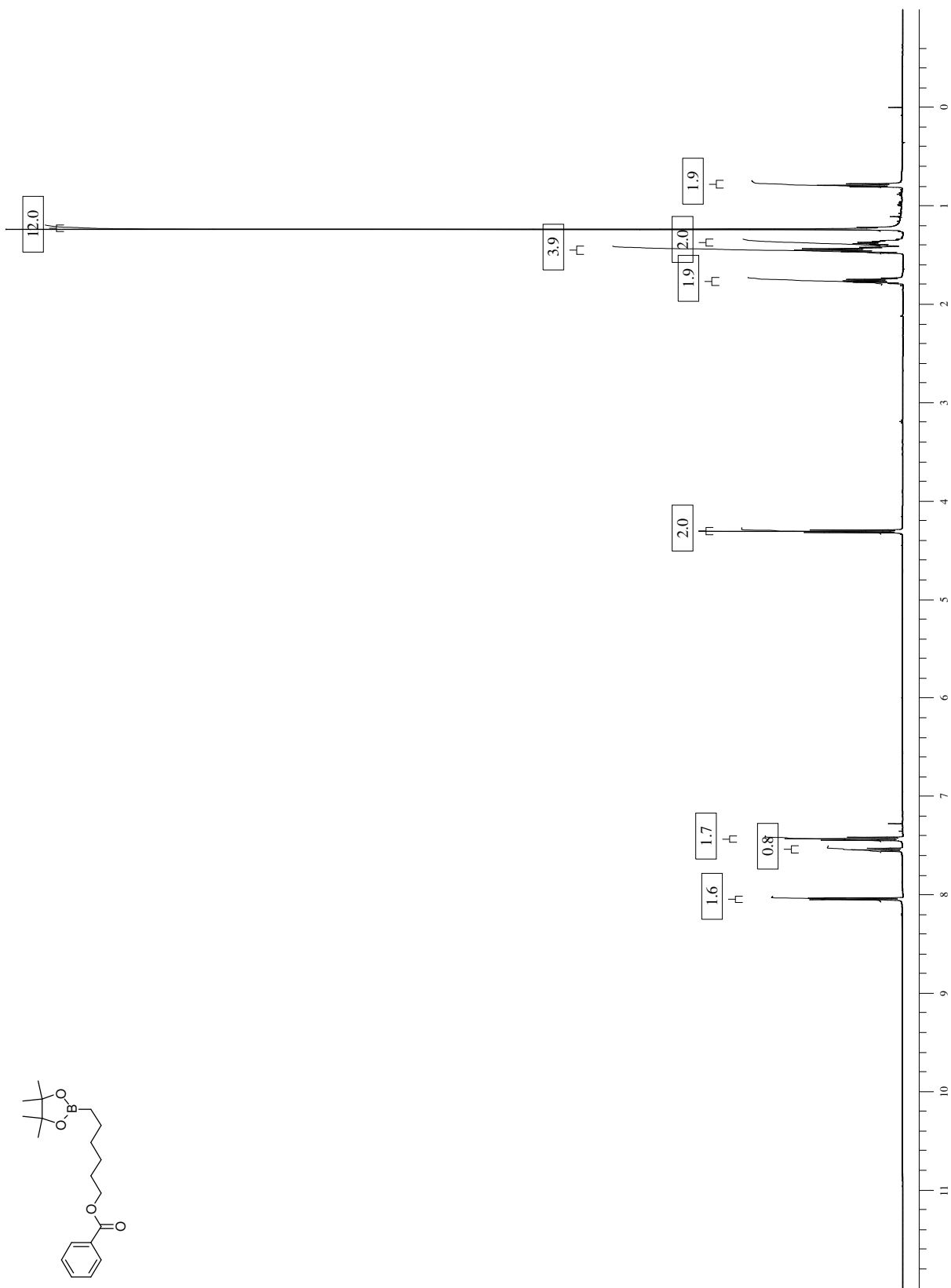
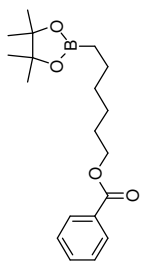




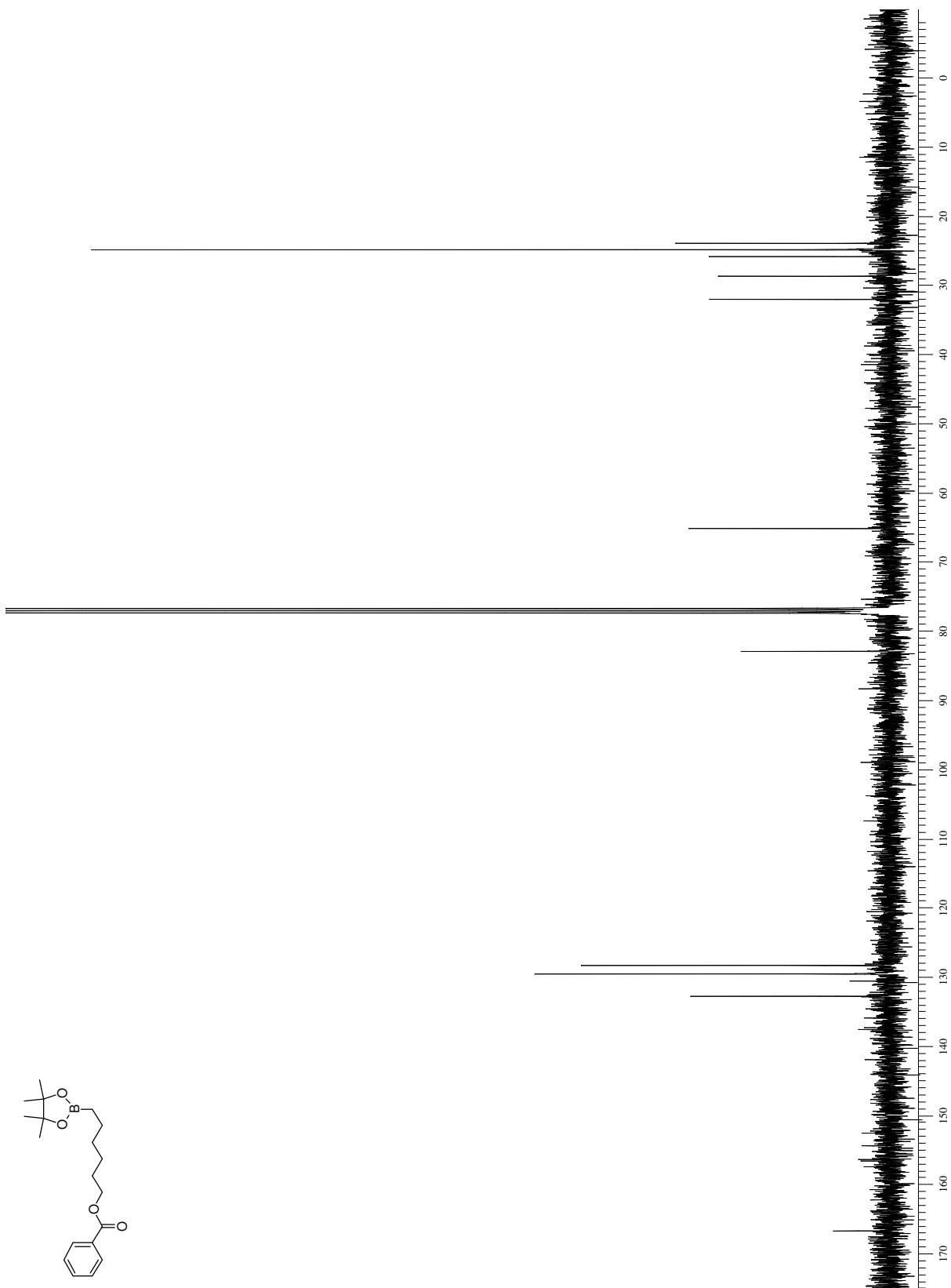


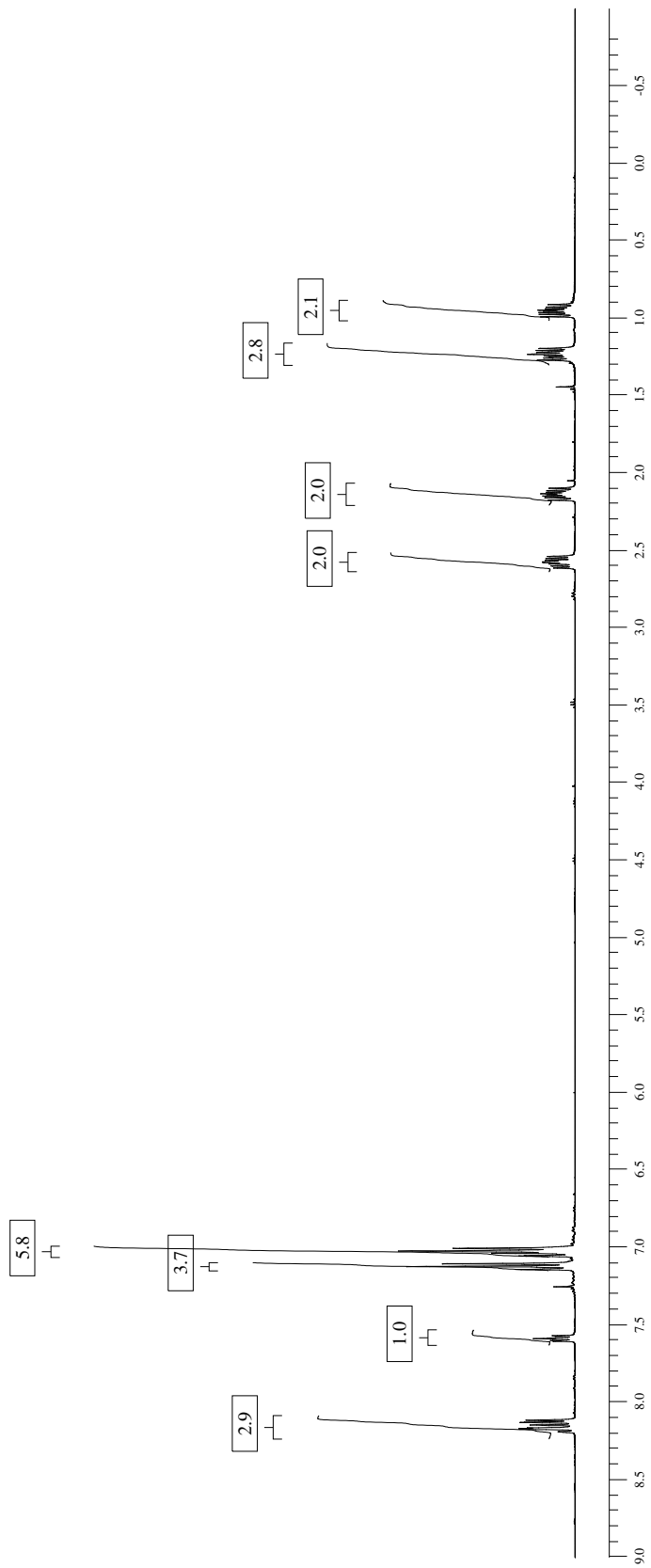
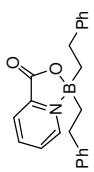
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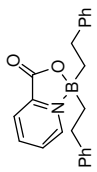












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