

## **Supporting Information**

# **Chemoselective Suzuki Coupling of Diborylmethane for Facile Synthesis of Benzylboronates**

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## 1. General Instruments and Chemicals

**General:** All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator. Thin layer chromatography plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating. Organic solutions were concentrated by rotary evaporation at c.a. 30 mmHg. Flash column chromatography was performed on Kanto Silica gel 60 (spherical, neutral, 140–325 mesh) as described by Still *et al.*<sup>1</sup>

**Instrumentation:** IR spectra were recorded as neat liquids or KBr pellets and absorptions are reported in  $\text{cm}^{-1}$ . NMR spectra were measured on 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$  NMR, using tetramethylsilane as an internal reference and  $\text{CDCl}_3$  as a solvent. Chemical shift values for protons are reported in parts per million (ppm,  $\delta$  scale) downfield from tetramethylsilane and are referenced to residual proton of  $\text{CDCl}_3$  ( $\delta$  7.26). Carbon nuclear magnetic resonance spectra ( $^{13}\text{C}$  NMR) were recorded at 100 MHz: chemical shifts for carbons are reported in parts per million (ppm,  $\delta$  scale) downfield from tetramethylsilane and are referenced to the carbon resonance of  $\text{CDCl}_3$  ( $\delta$  77.0). Boron nuclear magnetic resonance spectra ( $^{11}\text{B}$  NMR) were recorded at 128 MHz: chemical shifts for boron are reported in parts per million (ppm,  $\delta$  scale) referenced to the boron resonance of  $\text{BF}_3\text{:Et}_2\text{O}$  ( $\delta$  0). Fluorine nuclear magnetic resonance spectra ( $^{19}\text{F}$  NMR) were recorded at 470 MHz: chemical shifts for fluorine are reported in parts per million (ppm,  $\delta$  scale) referenced to the fluorine resonance of trifluoroacetic acid ( $\delta$  0). Data are presented as following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers, assignment (*italic*). Mass spectra were measured using TOF-MS spectrometry.

**Chemicals:** All reagents were purchased as commercially available source unless otherwise noted. Arylbromides were purchased as commercially available source or prepared according to the previously reported protocols. Diborylmethane was prepared according to the literature.<sup>2</sup>

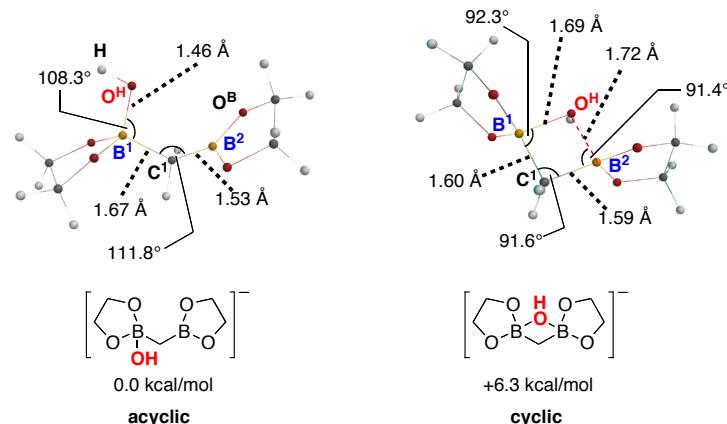
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<sup>1</sup> Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

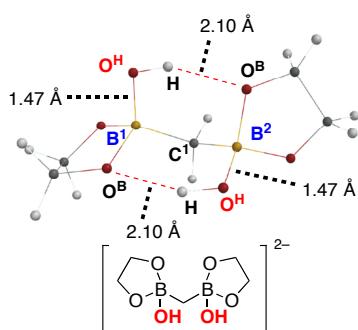
<sup>2</sup> (a) Castle, R. B.; Matteson, D. S. *J. Organomet. Chem.* **1969**, *20*, 19. (b) Matteson, D. S. *Synthesis* **1975**, 147.

## 2. DFT calculations<sup>3</sup>

The optimized geometries of monoborate intermediates were determined by means of DFT calculations at the B3LYP/6-311+G\*\* level of theory (Fig. S1). The  $B^1-O^H$  distance in acyclic monoborate is 1.46 Å. In contrast, the  $B^1-O^H$  and  $B^2-O^H$  distances in cyclic monoborate are 1.687 Å and 1.716 Å, respectively. The  $sp^3$ -hybridized  $B^2$  atom in cyclic monoborate was observed due to the coordination of the  $O^H$  atom. The cyclic monoborate was relatively unstable due to the strain of the 4-membered cycle. The optimized geometry of diborate intermediate in Figure S2 shows the boat type conformation including 6-membered intramolecular hydrogen bonding through  $O^H-B^1-C^1-B^2-O^B-H$  atoms and  $O^H-B^2-C^1-B^1-O^B-H$  atoms. The incorporation of two  $sp^3$ -B atoms in diborate can serve the symmetrical structure; in contrast, the  $sp^2$ - $B^2$  atom in acyclic monoborate prevents the formation of 6-membered cycle through  $O^H-B^1-C^1-B^2-O^B-H$  atoms due to the strain at the  $sp^2$ -B atom.



**Figure S1.** Optimized geometries of borate intermediate (B3LYP/6-311+G\*\*)

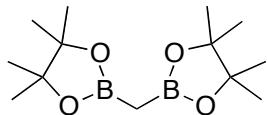


**Figure S2.** Optimized geometry of diborate intermediate (B3LYP/6-311+G\*\*)

<sup>3</sup> The DFT computational calculations were performed using the Spartan'08 suite for Mac (Wave function, Inc.). Zero-point vibrational energies (ZPEs) were calculated and the geometry was verified as true minima using frequency analysis. The optimization of hydrated complex and diborate intermediate did not prefer the formation of 6-membered cycle including hydrogen bonding between OH<sub>2</sub>-OH in hydrated complex or OH-OH in diborate intermediate; the similar geometries to those in Figures S1 and S2 were obtained.

## Cartesian Coordinates of Optimized Geometries

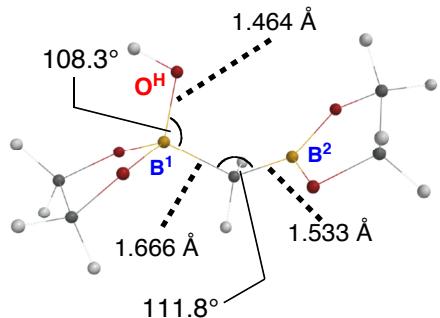
### Diborylmethane



E (B3LYP/6-31G\*\*) = -547.362114613

ATOM	Coordinates (Angstroms)		
	X	Y	Z
1H	-0.039612	1.105789	-1.999917
2C	-0.000451	0.159147	-1.450776
3H	0.028550	-0.662144	-2.175876
4B	1.293559	0.099970	-0.570533
5B	-1.290593	0.031654	-0.570412
6O	2.197187	-0.936055	-0.601530
7O	1.634845	1.083170	0.332601
8O	-2.267716	0.996098	-0.494649
9O	-1.555332	-1.064862	0.220400
10C	3.183650	-0.700529	0.413695
11C	2.902506	0.739032	0.910241
12C	-3.248247	0.571613	0.462786
13C	-2.832987	-0.873137	0.843340
14H	2.837265	0.807731	2.000556
15H	3.061564	-1.446410	1.207663
16H	3.657774	1.454557	0.564249
17H	4.183436	-0.814623	-0.016365
18H	-4.243072	0.620530	0.009049
19H	-3.226079	1.252826	1.320877
20H	-3.533543	-1.624001	0.460159
21H	-2.735223	-1.014604	1.924393

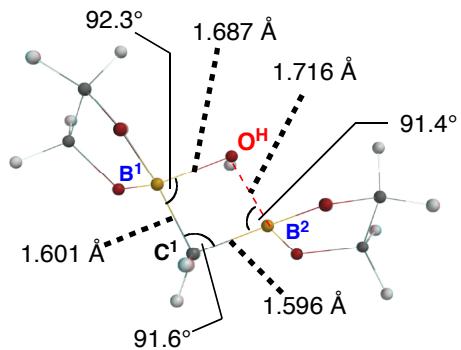
**acyclic monoborate**



$E$  (B3LYP/6-311+G\*\*) = -623.419193881

ATOM	Coordinates (Angstroms)		
	X	Y	Z
1C	0.024309	-0.298949	-1.138558
2H	0.064472	-1.237838	-1.702126
3B	1.146354	-0.430491	0.085791
4B	-1.386818	-0.051056	-0.594473
5O	-2.358307	-1.040991	-0.401041
6O	-1.896797	1.195188	-0.211796
7O	2.449258	-0.964695	-0.481513
8O	1.564731	0.894552	0.669213
9C	-3.243454	1.035258	0.219112
10C	-3.419006	-0.488249	0.369778
11C	3.491336	-0.082013	-0.171661
12C	2.789721	1.258885	0.099238
13O	0.581429	-1.277941	1.137776
14H	1.192191	-1.269436	1.880175
15H	4.217310	-0.021893	-0.998277
16H	3.357871	1.910313	0.780491
17H	4.047274	-0.406859	0.731354
18H	2.648400	1.810297	-0.851207
19H	-3.311250	-0.806716	1.414091
20H	-3.399130	1.575376	1.158447
21H	-3.922027	1.452430	-0.538263
22H	-4.381851	-0.847924	-0.008628
23H	0.356415	0.511673	-1.797912

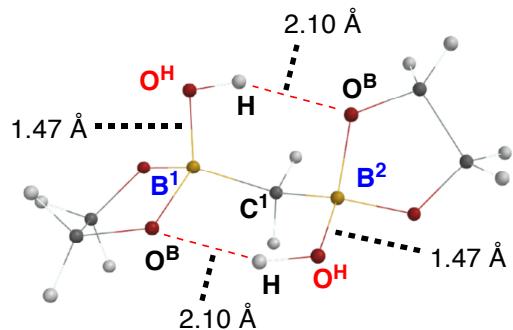
**cyclic monoborate**



$E$  (B3LYP/6-311+G\*\*) = -623.409172841

ATOM	Coordinates (Angstroms)		
	X	Y	Z
1C	-0.806200	1.279490	-0.526482
2H	-1.126683	1.409979	-1.565158
3H	-1.117711	2.153003	0.054788
4B	0.744382	0.908535	-0.381114
5B	-1.246609	-0.120404	0.102074
6O	-1.876386	-1.169229	-0.705265
7O	-1.865442	-0.177879	1.405794
8O	1.585383	0.644772	-1.558496
9O	1.578207	1.627159	0.559742
10C	-2.348916	-1.493782	1.564288
11C	-2.723858	-1.928125	0.134308
12C	2.903104	1.064670	-1.265260
13C	2.911926	1.279082	0.259192
14O	0.390467	-0.609558	0.262686
15H	0.562435	-1.258753	-0.428162
16H	3.128503	2.006102	-1.794349
17H	3.200526	0.349728	0.778183
18H	3.635140	0.311083	-1.589209
19H	3.593302	2.078274	0.577720
20H	-2.573963	-3.004698	-0.029550
21H	-1.565044	-2.150304	1.975780
22H	-3.203131	-1.502661	2.252791
23H	-3.779432	-1.696484	-0.084301

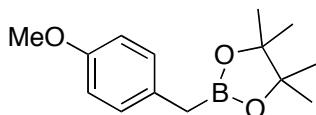
**diborate**



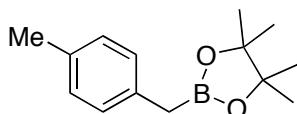
$E$  (B3LYP/6-311+G\*\*) = -699.208217289

ATOM	Coordinates (Angstroms)		
	X	Y	Z
1C	0.004203	-0.012024	-0.973191
2H	-0.294672	-0.834473	-1.648584
3B	1.289778	-0.501226	-0.104677
4B	-1.287860	0.484370	-0.117898
5O	-1.826500	-0.710346	0.733575
6O	-2.542509	0.826009	-0.942262
7O	2.527991	-0.810443	-0.956287
8O	1.841880	0.679165	0.776551
9C	-3.539812	-0.107777	-0.695818
10C	-3.213624	-0.687413	0.692540
11C	3.644146	-0.229356	-0.365132
12C	3.104647	1.035349	0.327408
13O	1.001478	-1.651199	0.759182
14H	4.418130	0.005694	-1.121052
15H	3.756744	1.363259	1.161561
16H	4.114957	-0.894979	0.392428
17H	3.068618	1.871421	-0.407605
18H	-3.645965	-0.029627	1.479006
19H	-4.545453	0.357530	-0.727436
20H	-3.537272	-0.930261	-1.447258
21H	-3.639076	-1.698747	0.837025
22H	0.314482	0.815637	-1.636556
23O	-0.998428	1.649572	0.726958
24H	-0.052713	1.604905	0.924931
25H	0.052682	-1.630985	0.939162

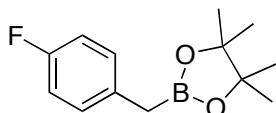
### 3. Physical Properties of New Compounds



**2-(4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)<sup>4</sup>:** To a solution of diborylmethane **1a** (80 mg, 0.3 mmol, 2 equiv), 4-bromoanisole (**2a**) (27.9 mg, 0.149 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37  $\mu$ L, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 1 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **3a** in 0.137 mmol, 92% yield (34.2 mg/36.9 mg).



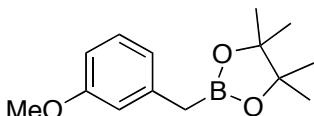
**4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (3b)<sup>4</sup>:** To a solution of diborylmethane **1a** (80 mg, 0.3 mmol, 2 equiv), 4-bromotoluene (**2b**) (25.7 mg, 0.15 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37  $\mu$ L, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 5 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3b** in 0.138 mmol, 92% yield (32 mg/34.8 mg).



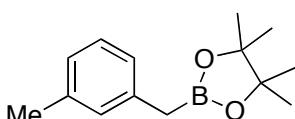
**2-(4-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)<sup>5</sup>:** To a solution of diborylmethane **1a** (76 mg, 0.28 mmol, 2 equiv), 1-bromo-4-fluorobenzene (**2c**) (25.0 mg, 0.142 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (36  $\mu$ L, 0.29 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 2 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 90% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **3c** in 0.118 mmol, 83% yield (28.0 mg/33.5 mg).

<sup>4</sup> Pintaric, C.; Olivero, S.; Gimbert, Y.; Chavant, P.-Y.; Duñach, E. *J. Am. Chem. Soc.* **2010**, *132*, 11825.

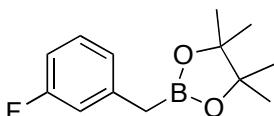
<sup>5</sup> Falck, J. R.; Bondlela, M.; Ye, J.; Cho, S.-D. *Tetrahedron Lett.* **1999**, *40*, 5647.



**2-(3-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)<sup>6</sup>:** To a solution of diborylmethane **1a** (107 mg, 0.4 mmol, 2 equiv), 3-bromoanisole (**2d**) (28.5 mg, 0.152 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37  $\mu$ L, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 3 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 97% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **3d** in 0.134 mmol, 88% yield (33.1 mg/37.7 mg).



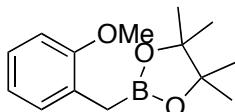
**4,4,5,5-tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (3e)<sup>7</sup>:** To a solution of diborylmethane **1a** (80 mg, 0.3 mmol, 2 equiv), 3-bromotoluene (**2b**) (25.6 mg, 0.149 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37  $\mu$ L, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 3 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 91% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3e** in 0.124 mmol, 83% yield (28.4 mg/34.5 mg).



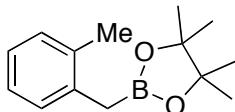
**2-(3-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f):** To a solution of diborylmethane **1a** (88 mg, 0.33 mmol, 2 equiv), 1-bromo-3-fluorobenzene (**2f**) (28.5 mg, 0.163 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (41  $\mu$ L, 0.33 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 3 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 82% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3f** in 0.113 mmol, 69% yield (26.6 mg/38.4 mg); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.30–7.17 (m, 1H), 6.95–6.82 (m, 3H), 2.29 (s, 2H), 1.24 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  162.9 (d, *J* = 244 Hz), 141.3 (d, *J* = 8.3 Hz), 129.6 (d, *J* = 8.4 Hz), 124.8, 115.9 (d, *J* = 21.4 Hz), 111.8 (d, *J* = 20.3 Hz), 83.7, 24.8; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz)  $\delta$  33.2; <sup>19</sup>F NMR (CDCl<sub>3</sub>, 470 MHz)  $\delta$  -114.20; IR (neat, cm<sup>-1</sup>) 2979, 2932, 1332, 1254, 1145, 766, 748; HRMS (FAB, positive): *m/z* calcd for C<sub>13</sub>H<sub>19</sub>BFO<sub>2</sub> [M + H]<sup>+</sup> 237.1462, found 237.1463.

<sup>6</sup> Pintaric, C.; Laza, C.; Olivero, S.; Duñach, E. *Tetrahedron Lett.* **2004**, 45, 8031.

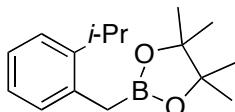
<sup>7</sup> Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *Synth. Commun.* **2002**, 32, 2513.



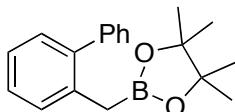
**2-(2-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g);** To a solution of diborylmethane **1a** (81 mg, 0.3 mmol, 2 equiv), 2-bromoanisole (**2g**) (28 mg, 0.15 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (38  $\mu$ L, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 3 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3g** in 0.131 mmol, 87% yield (32.3 mg/37.1 mg); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.14–7.11 (m, 2H), 6.86–6.79 (m, 2H), 3.79 (s, 3H), 2.18 (s, 2H), 1.23 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  157.3, 130.6, 128.1, 126.3, 120.6, 109.8, 83.2, 55.1, 24.8; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz)  $\delta$  33.9; IR (neat, cm<sup>-1</sup>) 2979, 2933, 1494, 1379, 1352, 1243, 1144, 750; HRMS (FAB, positive): *m/z* calcd for C<sub>14</sub>H<sub>21</sub>BO<sub>3</sub> 248.1584, found 248.1582.



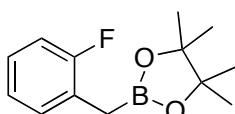
**2-(2-methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)<sup>4</sup>;** To a solution of diborylmethane **1a** (91 mg, 0.34 mmol, 2 equiv), 2-bromotoluene (**2h**) (29.4 mg, 0.172 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ g, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (43  $\mu$ L, 0.34 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 3 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 93% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3h** in 0.152 mmol, 88% yield (35.5 mg/39.9 mg)



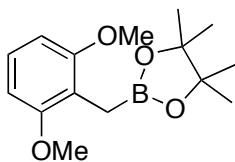
**2-(2-isopropylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i);** To a solution of diborylmethane **1a** (83 mg, 0.31 mmol, 2 equiv), 1-bromo-2-isopropylbenzene (**2i**) (30.7 mg, 0.154 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (39  $\mu$ L, 0.31 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 3 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 79% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3i** in 0.986 mmol, 64% yield (25.8 mg/40 mg); yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.23–7.04 (m, 4H), 3.09 (sept, *J* = 6.8 Hz, 1H), 2.31 (s, 2H), 1.22–1.21 (m, 18H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  146.4, 136.0, 130.1, 125.6 (2C), 125.0, 83.4, 29.4, 24.8, 23.7; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz)  $\delta$  33.7; IR (neat, cm<sup>-1</sup>) 2977, 2931, 1738, 1349, 1330, 1144, 847, 752; HRMS (FAB, positive): *m/z* calcd for C<sub>16</sub>H<sub>25</sub>BO<sub>2</sub> 260.1948, found 260.1948.



**2-[(1,1'-biphenyl)-2-ylmethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)**<sup>8</sup>: To a solution of diborylmethane **1a** (71 mg, 0.27 mmol, 2 equiv), 2-bromo-1,1'-biphenyl (**2j**) (31.4 mg, 0.135 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (35  $\mu$ L, 0.28 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 94% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3j** in 0.116 mmol, 86% yield (34 mg/39.7 mg)



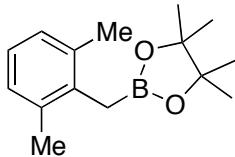
**2-(2-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)**: To a solution of diborylmethane **1a** (79 mg, 0.29 mmol, 2 equiv), 1-bromo-2-fluorobenzene (**2k**) (25.0 mg, 0.144 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (36  $\mu$ L, 0.29 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 3 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 77% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3k** in 0.893 mmol, 62% yield (21 mg/33.8 mg); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.19–6.97 (m, 4H), 2.25 (s, 2H), 1.24 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  161.1 (d, *J* = 244 Hz), 131.4 (d, *J* = 4.8 Hz), 126.7 (d, *J* = 8.4 Hz), 126.1 (d, *J* = 7.9 Hz), 123.9 (d, *J* = 3.6 Hz), 115.0 (d, *J* = 21.5 Hz), 83.6, 24.8; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz)  $\delta$  33.9; <sup>19</sup>F NMR (CDCl<sub>3</sub>, 470 MHz)  $\delta$  -116.78; IR (neat, cm<sup>-1</sup>) 2979, 2932, 1737, 1352, 1216, 1144, 847, 751; HRMS (FAB, positive): *m/z* calcd for C<sub>13</sub>H<sub>19</sub>BFO<sub>2</sub> [M + H]<sup>+</sup> 237.1462, found 237.1461.



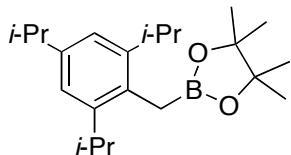
**2-(2,6-dimethoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)**: To a solution of diborylmethane **1a** (80 mg, 0.3 mmol, 2 equiv), 2-bromo-1,3-dimethoxybenzene (**2l**) (32.0 mg, 0.148 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4  $\mu$ mol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37  $\mu$ L, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 7/1) gave the product **3l** in 0.138 mmol, 93% yield (38.2 mg/41.2 mg); white solid; mp 88 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.07 (t, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 6H), 2.17 (s, 2H), 1.23 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  157.9, 125.7, 116.2, 103.7,

<sup>7</sup> Varela, J. A.; Peña, D.; Goldfuss, B.; Denisenko, D.; Kulhanek, J.; Polbom, K.; Knochel, P. *Chem. Eur. J.* **2004**, *10*, 4252–4264.

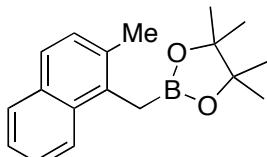
83.0, 55.7, 24.8;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz)  $\delta$  33.8; IR (neat,  $\text{cm}^{-1}$ ) 2978, 2935, 1737, 1473, 1349, 1145, 765, 750; HRMS (FAB, positive):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{23}\text{BO}_4$  278.1689, found 278.1697.



**2-(2,6-dimethylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m):** To a solution of diborylmethane **1a** (79 mg, 0.29 mmol, 2 equiv), 2-bromo-1,3-dimethylbenzene (**2m**) (26.7 mg, 0.145 mmol), and  $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$  (3.8 mg, 7.4  $\mu\text{mol}$ , 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (36  $\mu\text{L}$ , 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 2 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3m** in 0.125 mmol, 86% yield (30.4 mg/35.7 mg); colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  6.81 (s, 3H), 2.23 (s, 6H), 2.20 (s, 2H), 1.20 (s, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  135.6, 133.7, 133.3, 128.5, 83.3, 24.8, 20.8;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz)  $\delta$  33.2; IR (neat,  $\text{cm}^{-1}$ ) 2977, 1737, 1471, 1340, 1277, 1144, 788, 765; HRMS (FAB, positive):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{23}\text{BO}_2$  246.1791, found 246.1785.

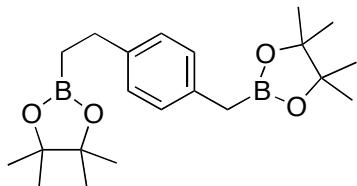


**4,4,5,5-tetramethyl-2-(2,4,6-triisopropylbenzyl)-1,3,2-dioxaborolane (3n):** To a solution of diborylmethane **1a** (69 mg, 0.26 mmol, 2 equiv), 2-bromo-1,3,5-triisopropylbenzene (**2n**) (36 mg, 0.127 mmol), and  $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$  (3.8 mg, 7.4  $\mu\text{mol}$ , 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (29  $\mu\text{L}$ , 0.24 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 60% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3n** in 0.073 mmol, 57% yield (25 mg/43.7 mg); yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  6.94 (s, 2H), 3.09 (sept,  $J$  = 6.8 Hz, 2H), 2.85 (sept, 7.2 Hz, 1H), 2.32 (s, 2H), 1.22 (m, 30H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  145.9, 145.0, 130.6, 120.6, 83.3, 34.1, 30.1, 24.8, 24.2, 23.9;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz)  $\delta$  33.4; IR (neat,  $\text{cm}^{-1}$ ) 2961, 2869, 1738, 1461, 1325, 1144, 765, 750; HRMS (FAB, positive):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{37}\text{BO}_2$  344.2887, found 344.2879.



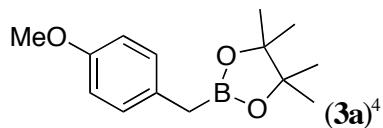
**4,4,5,5-tetramethyl-2-[(2-methylnaphthalen-1-yl)methyl]-1,3,2-dioxaborolane (3o):** To a solution of diborylmethane **1a** (78 mg, 0.29 mmol, 2 equiv), 1-bromo-2-methylnaphthalene (**2o**) (32.1 mg, 0.145 mmol), and  $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$  (3.8 mg, 7.4  $\mu\text{mol}$ , 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (36  $\mu\text{L}$ , 0.29 mmol, 2 equiv) at room temperature. The

mixture was stirred at 25 °C for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 88% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave the product **3o** in 0.11 mmol, 76% yield (31.2 mg/40.9 mg); yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.0 (d, *J* = 9.9 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.40–7.38 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 2.69 (s, 2H), 2.49 (s, 3H), 1.18 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 132.9, 132.7, 132.6, 132.5, 129.2, 128.4, 125.5, 125.1, 124.3, 124.2, 83.4, 24.8, 21.2; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz) δ 34.3; IR (neat, cm<sup>-1</sup>) 3383, 2977, 2932, 1737, 1372, 1275, 1143, 765, 749; HRMS (FAB, positive): *m/z* calcd for C<sub>18</sub>H<sub>23</sub>BO<sub>2</sub> 282.1791, found 282.1778.

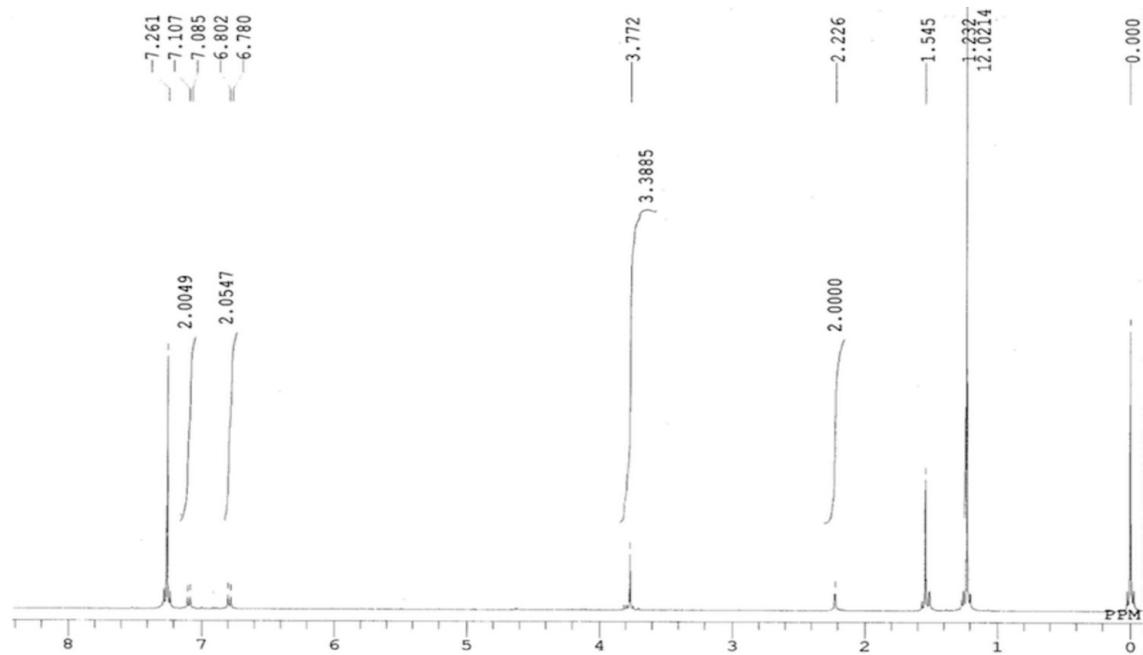


**4,4,5,5-tetramethyl-2-{4[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzyl}-1,3,2-dioxaborolane (3p):** To a solution of diborylmethane **1a** (80 mg, 0.3 mmol, 2 equiv), 2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2p**) (46.6 mg, 0.15 mmol), and Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> (3.8 mg, 7.4 µmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37 µL, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 89% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **3p** in 0.123 mmol, 82% yield (45.9 mg/55.8 mg); colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.08 (s, 4H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 2H), 1.24–1.22 (m, 24H), 1.12 (t, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 140.8, 135.5, 128.9, 128.0, 83.4, 83.1, 29.5, 24.9, 24.8; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz) δ 33.7 (2B); IR (neat, cm<sup>-1</sup>) 2979, 2933, 1738, 1371, 1355, 1322, 1144, 847, 764, 750; HRMS (FAB, positive): *m/z* calcd for C<sub>21</sub>H<sub>34</sub>B<sub>2</sub>O<sub>4</sub> 372.2721, found 373.2731.

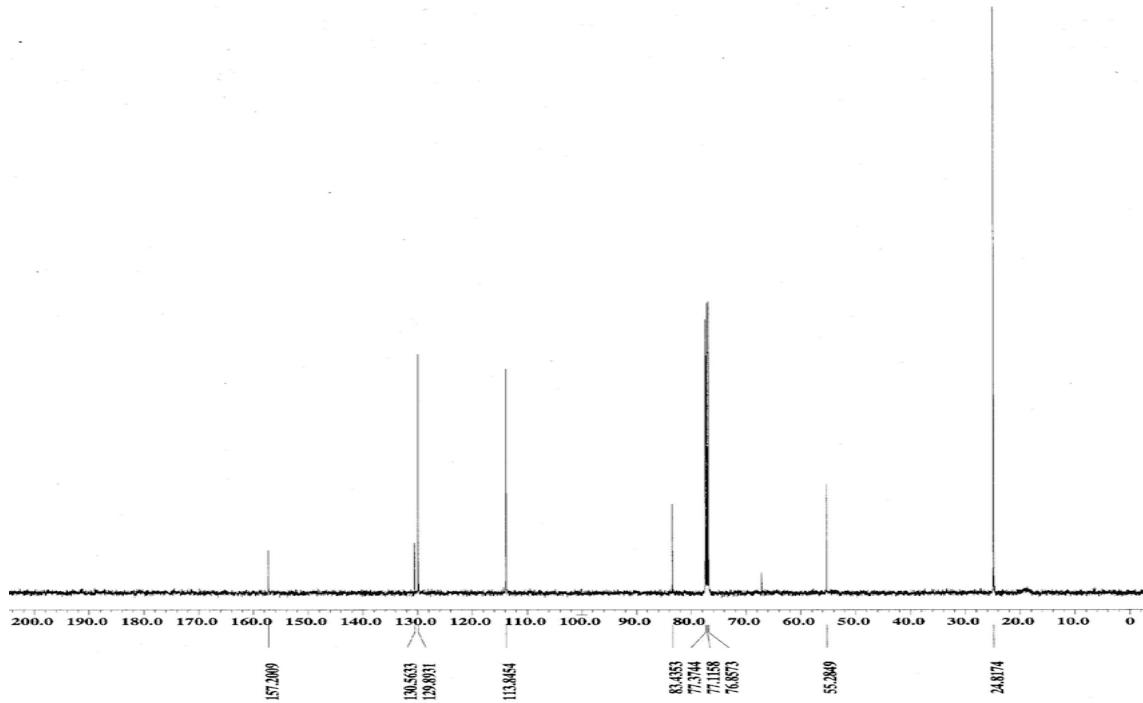
#### 4. NMR spectra

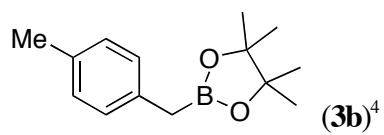


$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ )

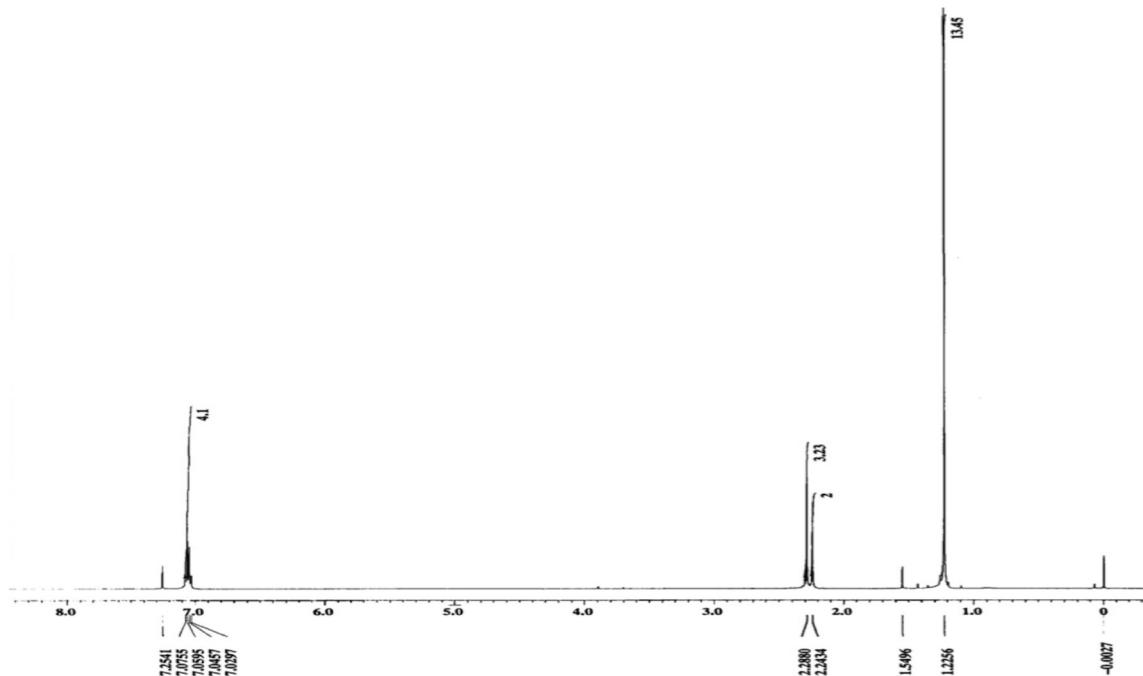


$^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ )

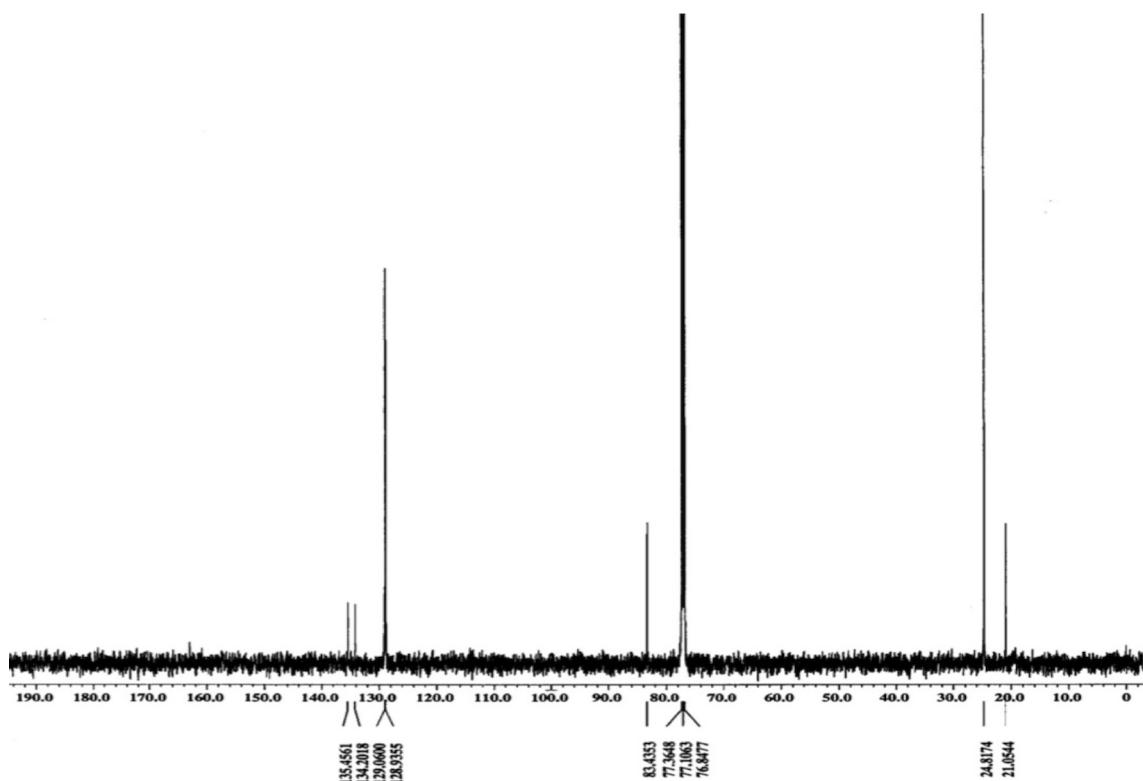


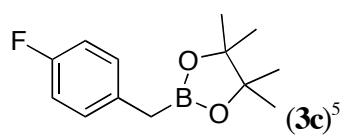


<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)

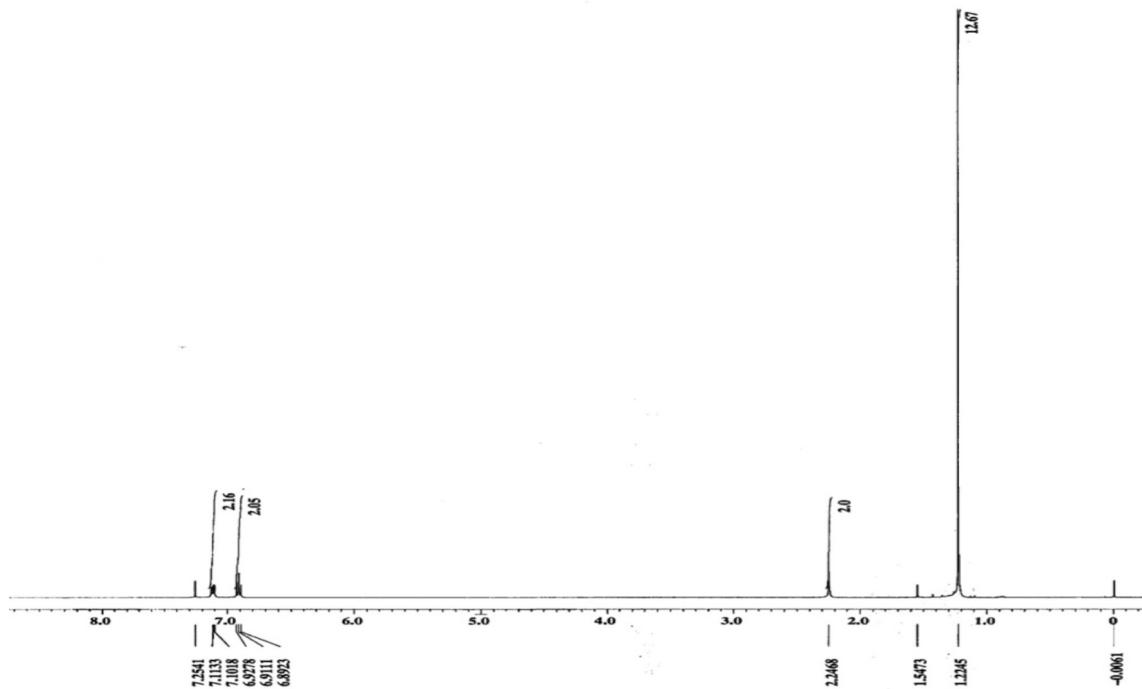


<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)

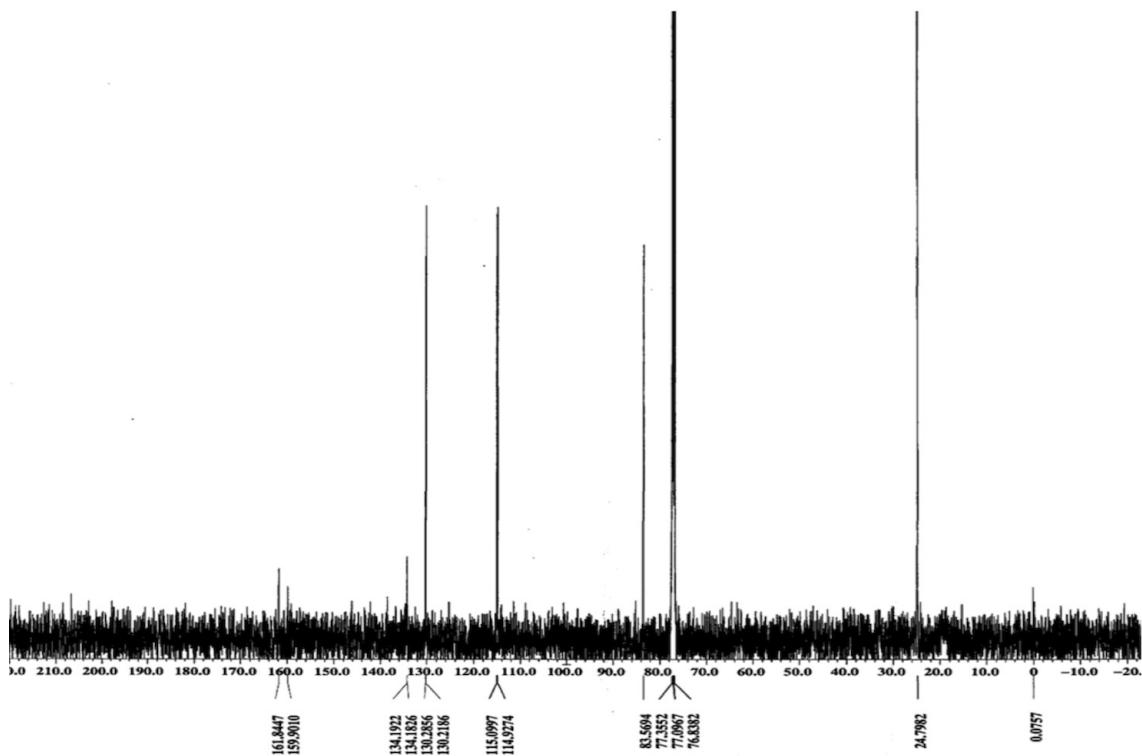


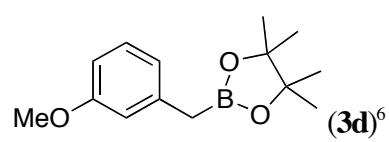


<sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>)

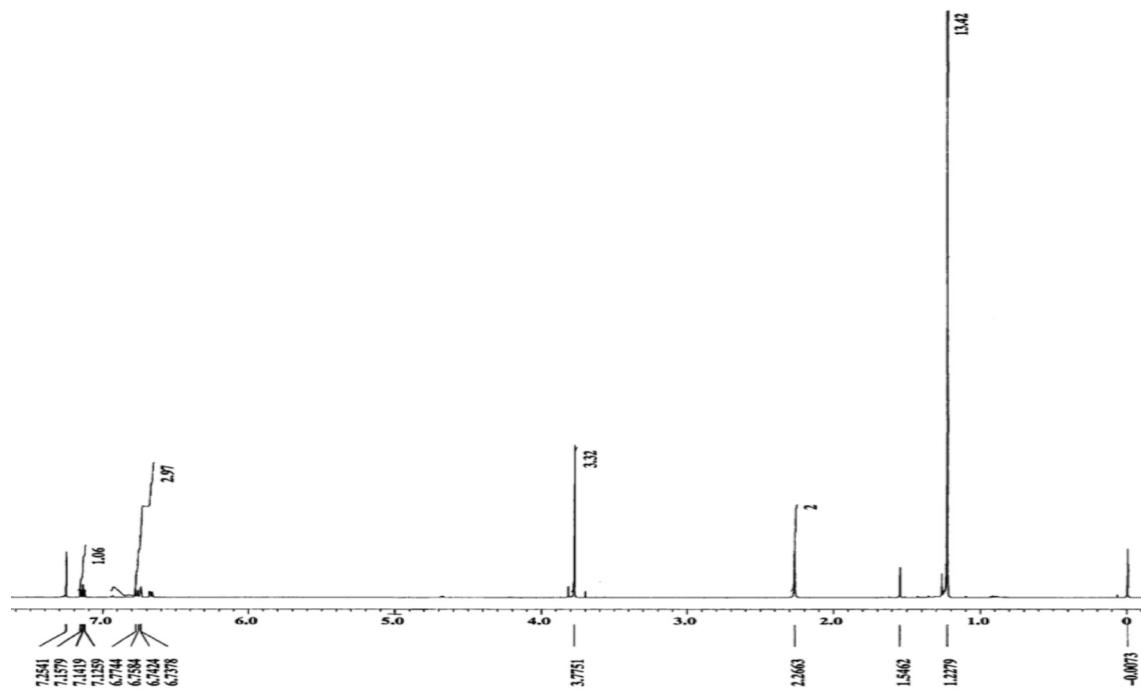


<sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>)

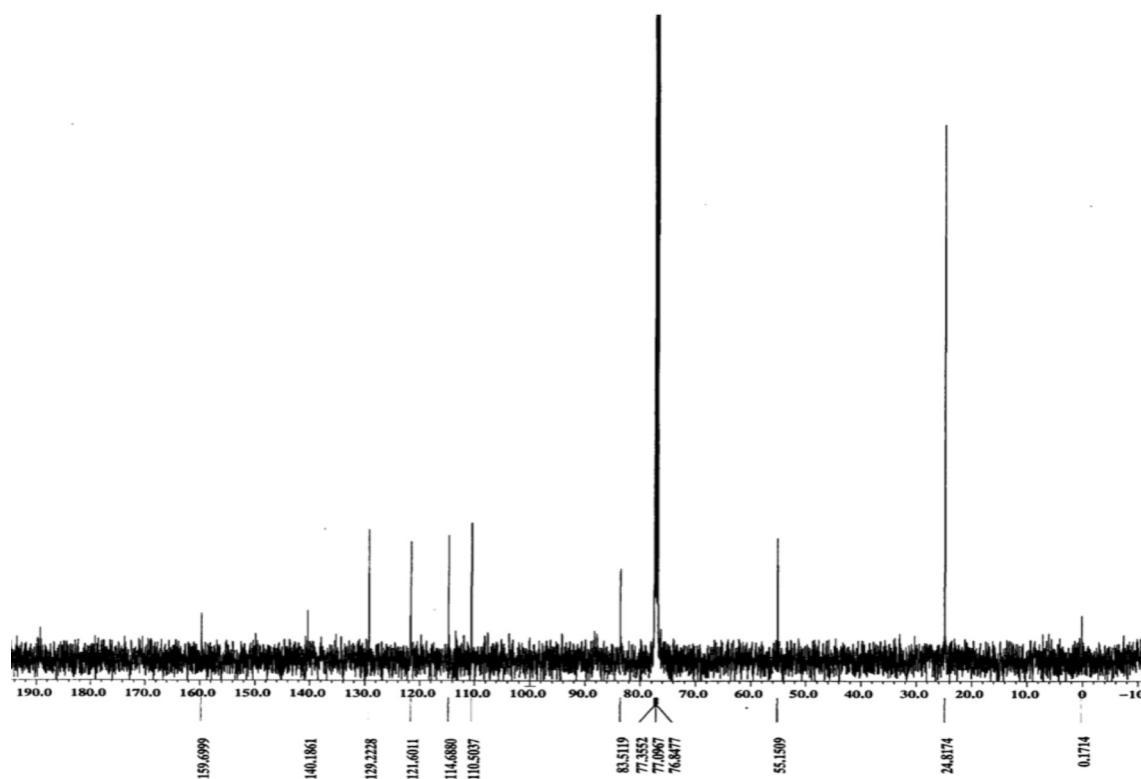


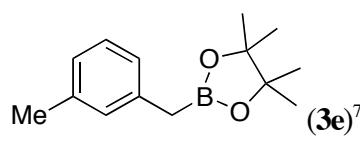


<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)

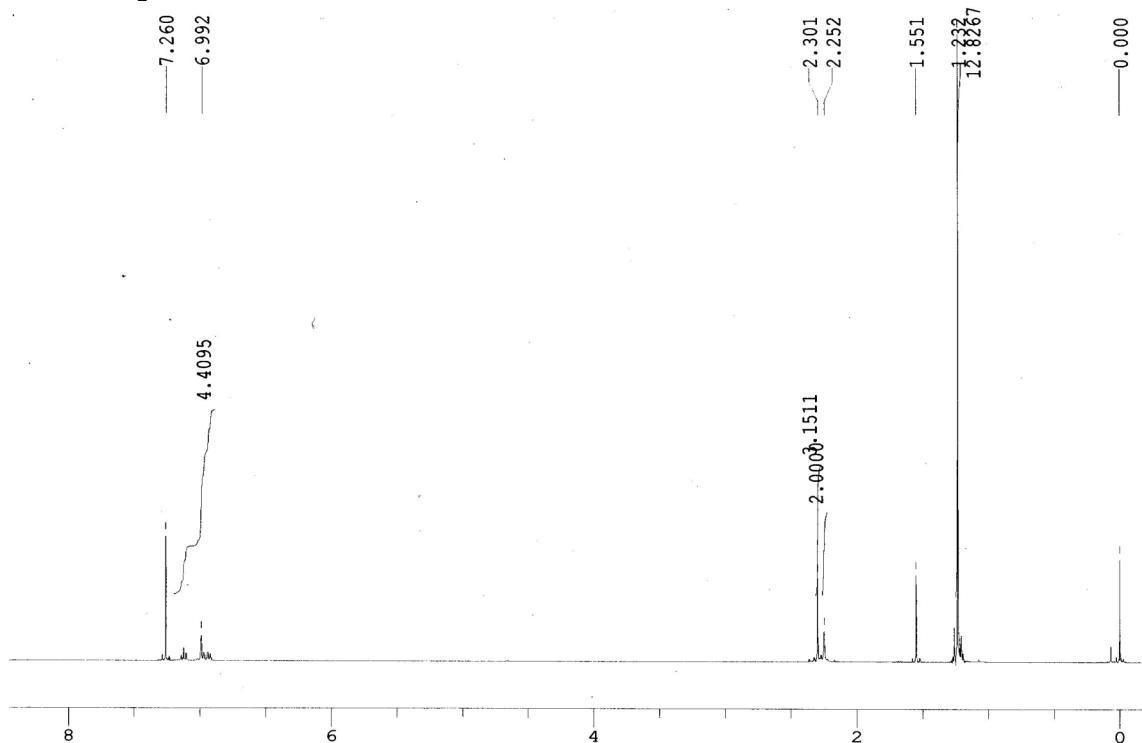


<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)

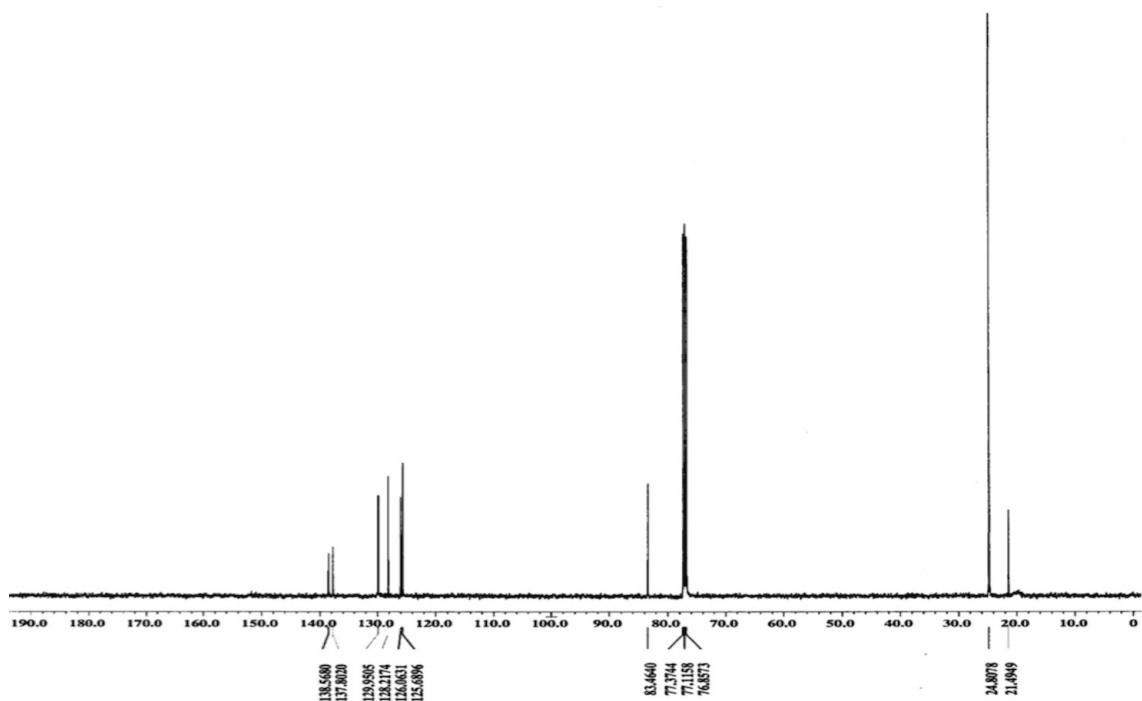


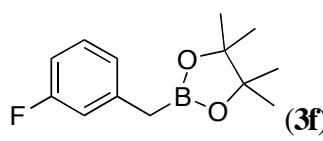


$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ )

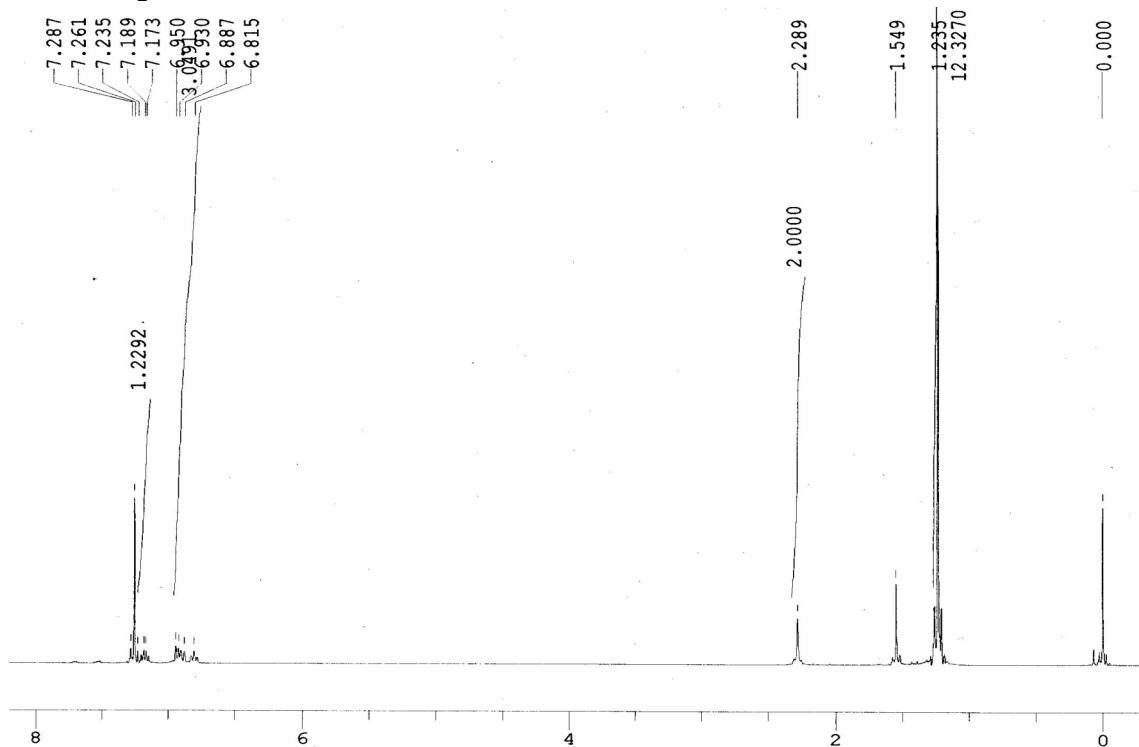


$^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ )

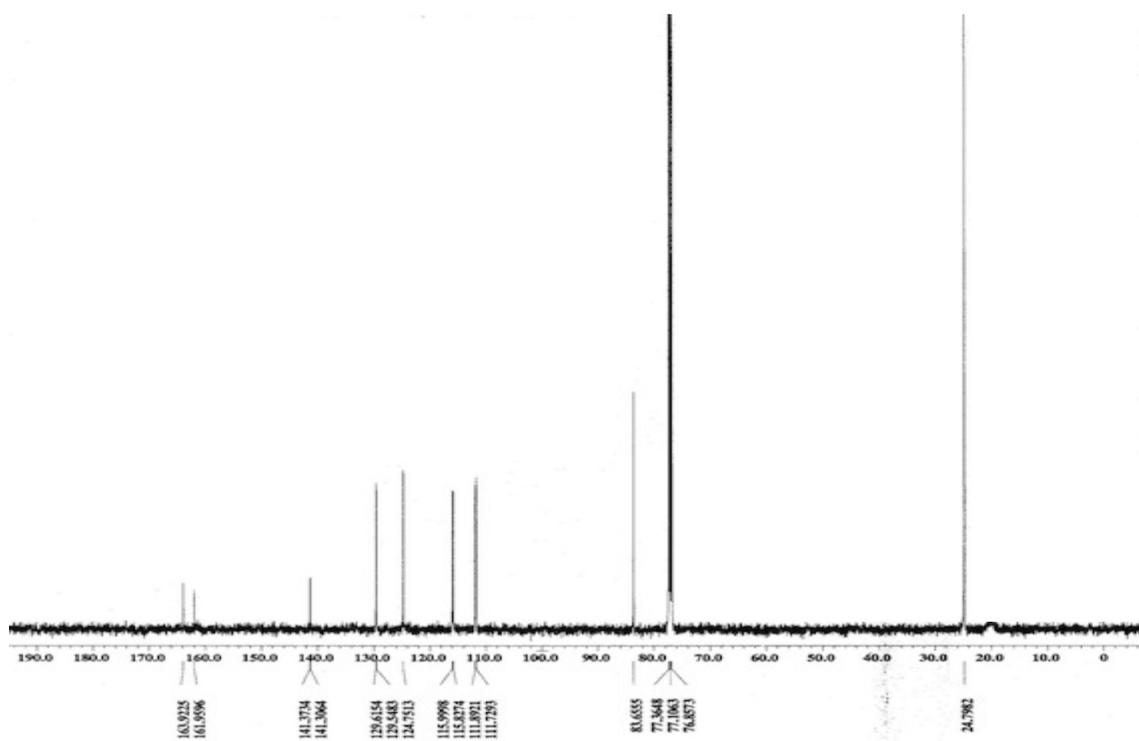


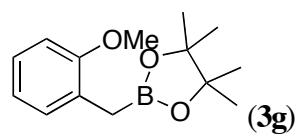


<sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>)

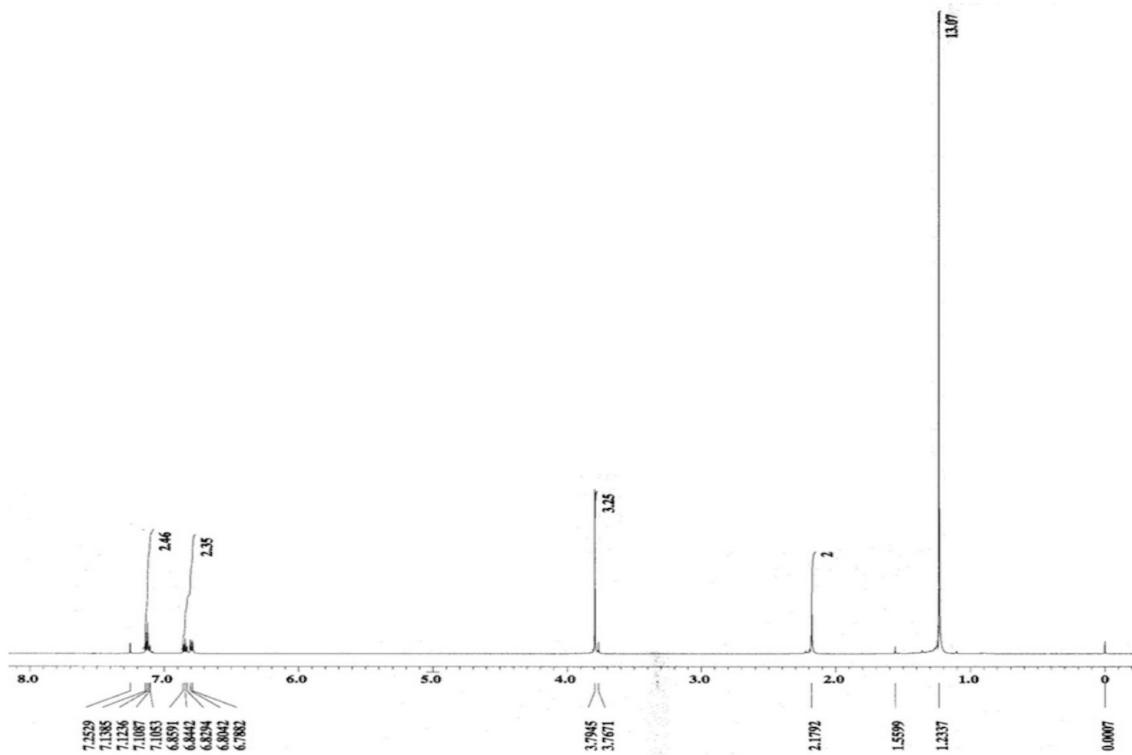


<sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>)

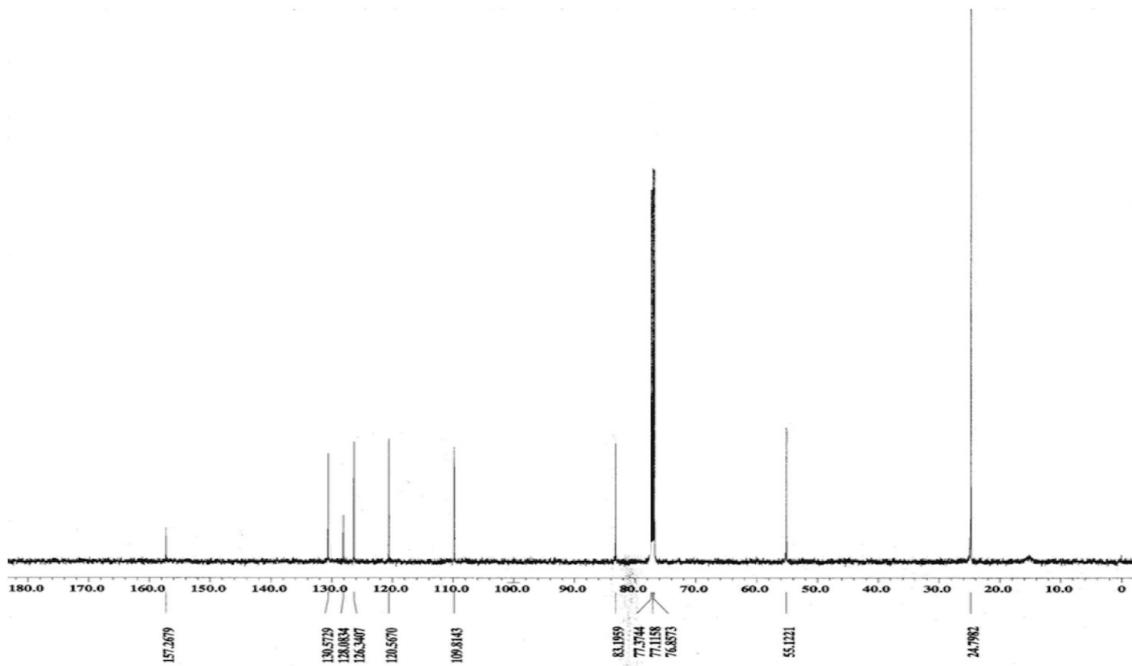


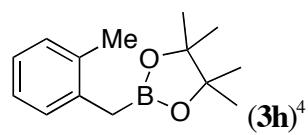


<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)

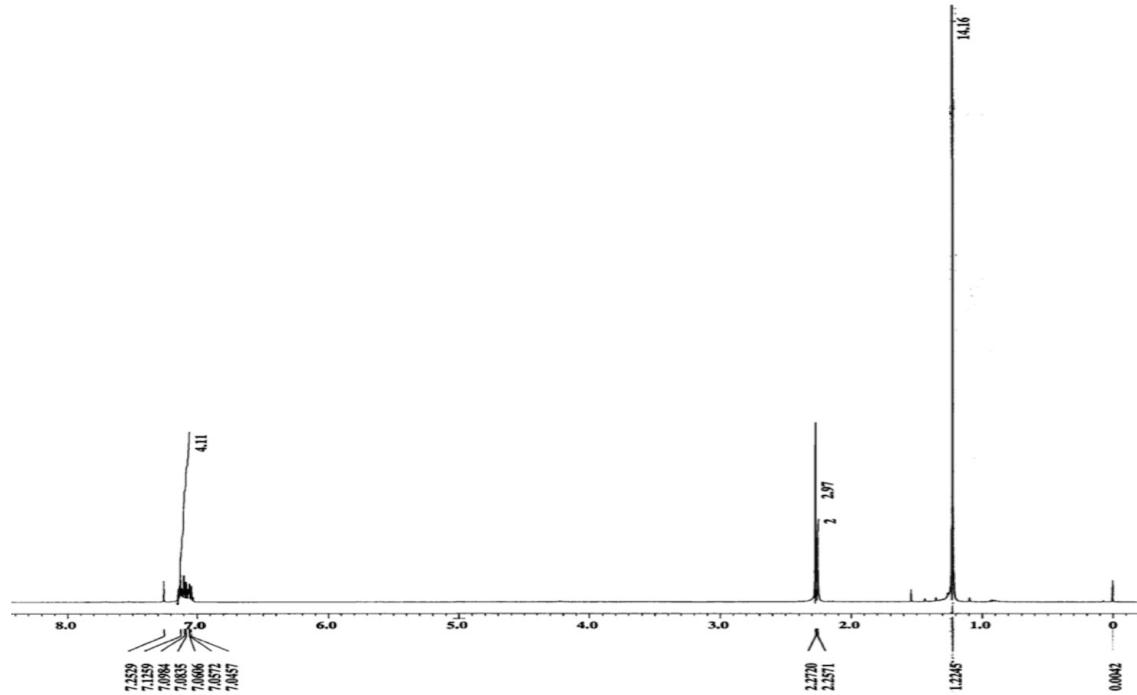


<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)

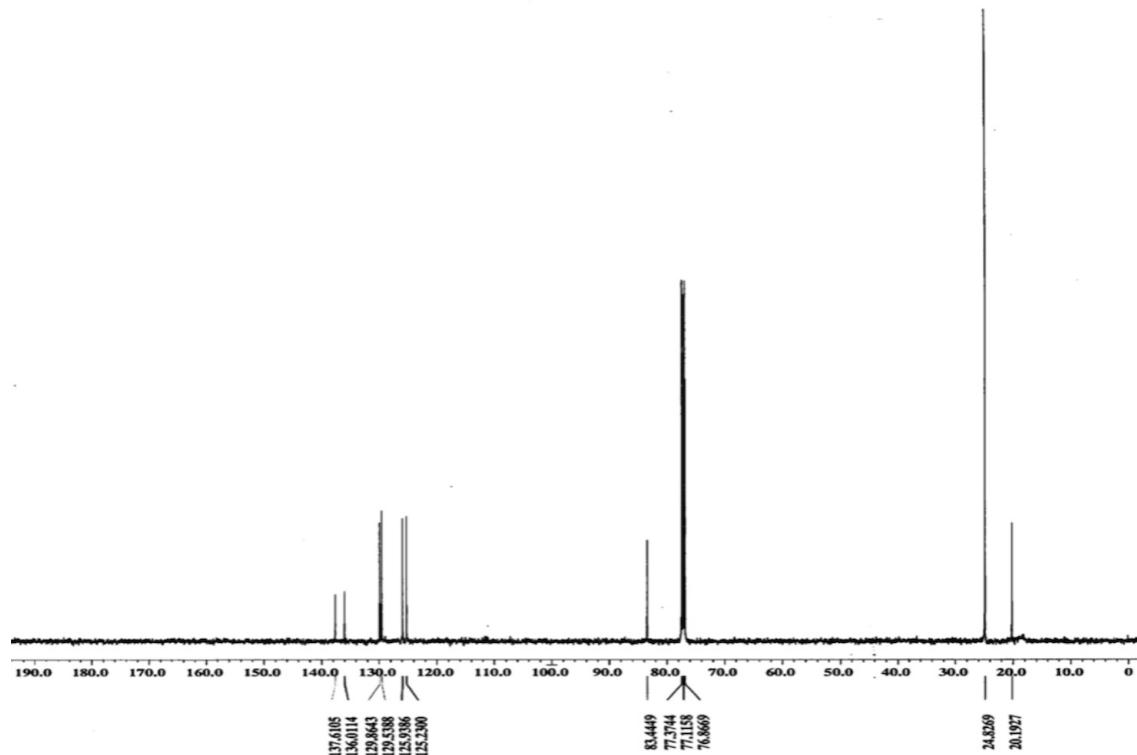


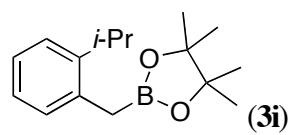


<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)

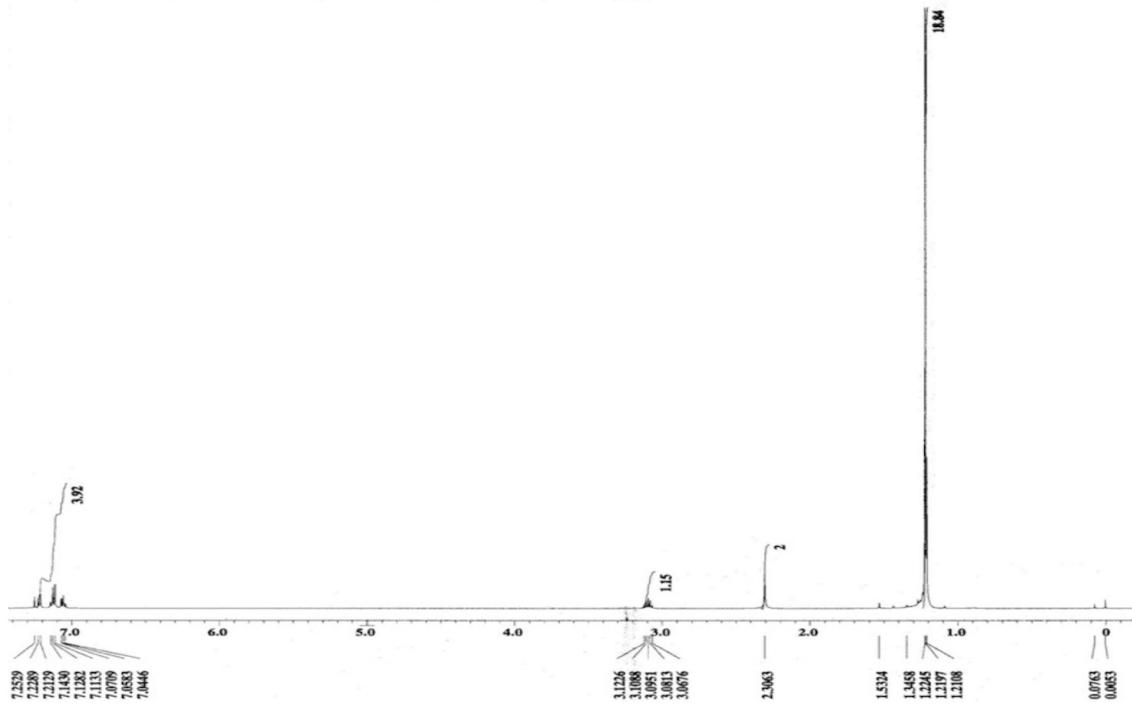


<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)

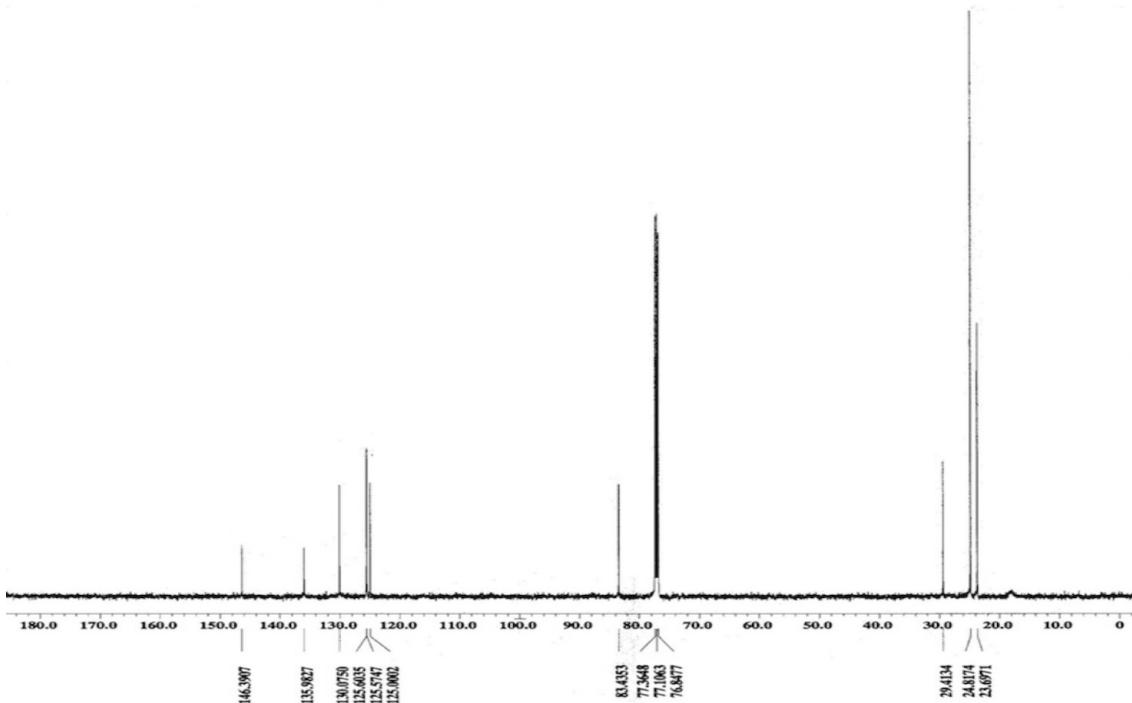


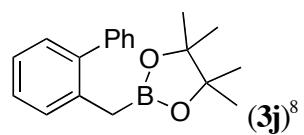


<sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>)

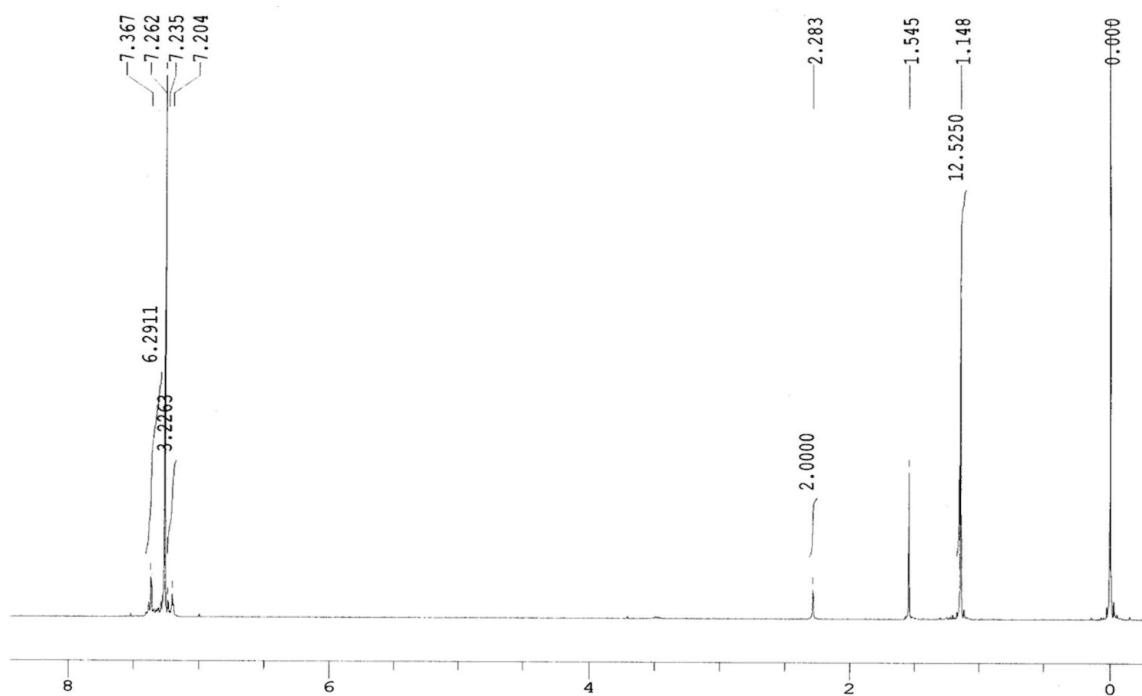


<sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>)

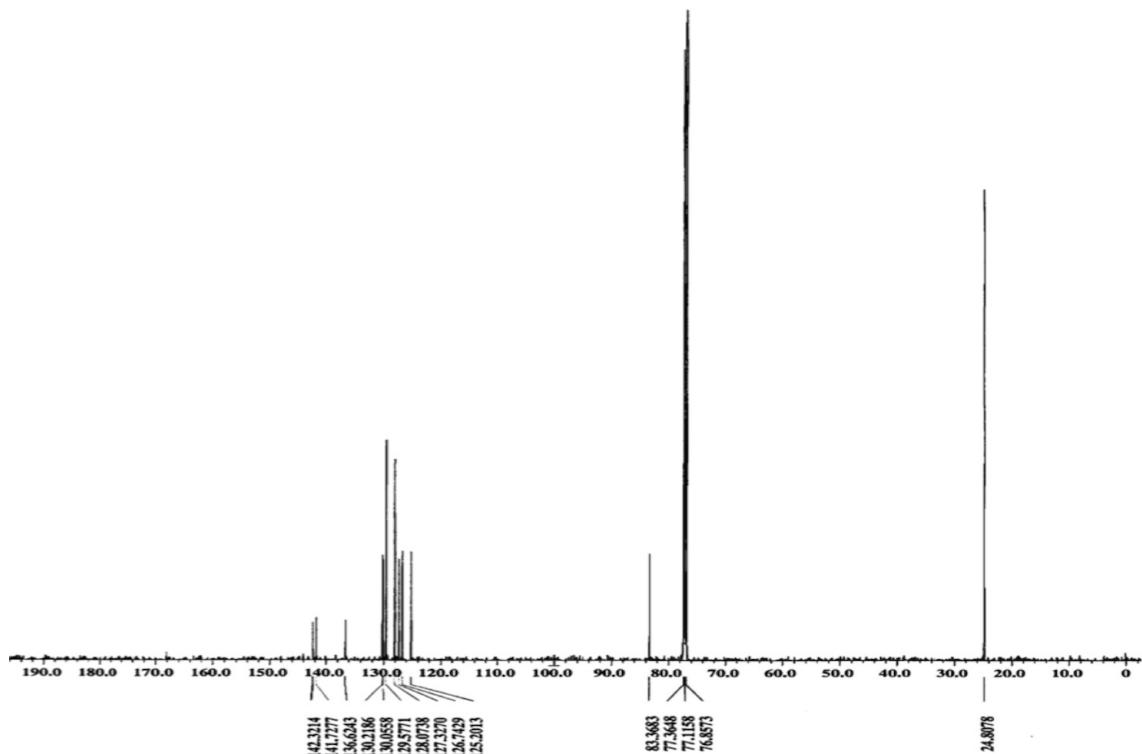


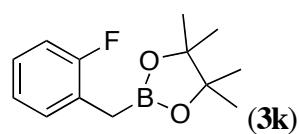


$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ )

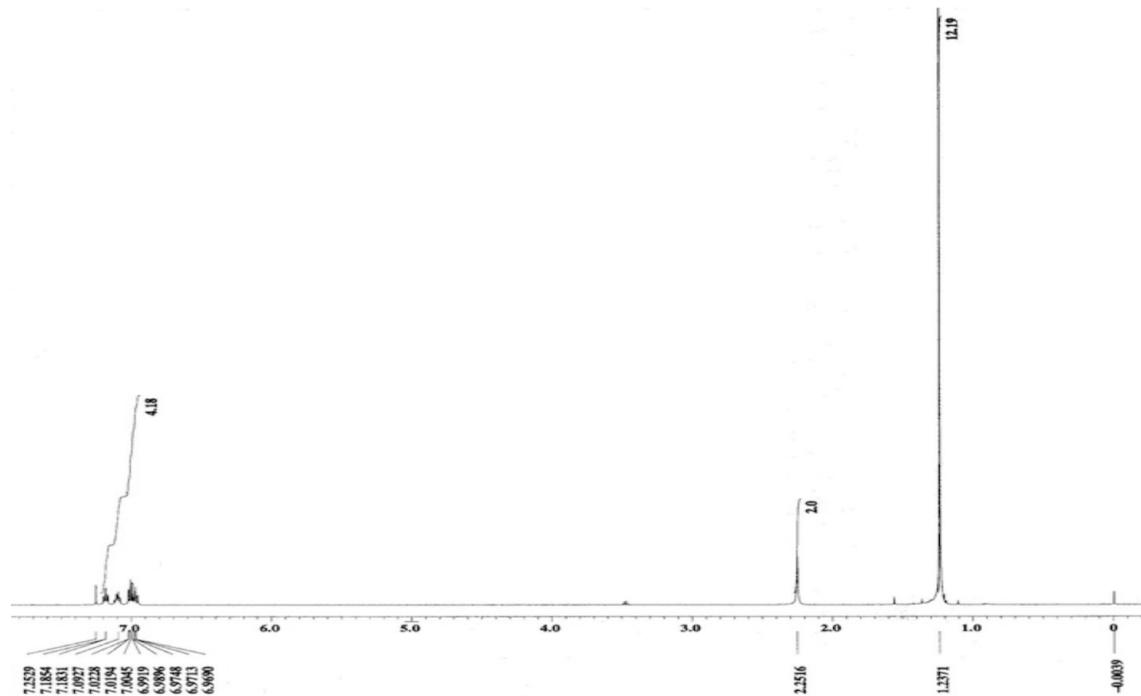


$^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ )

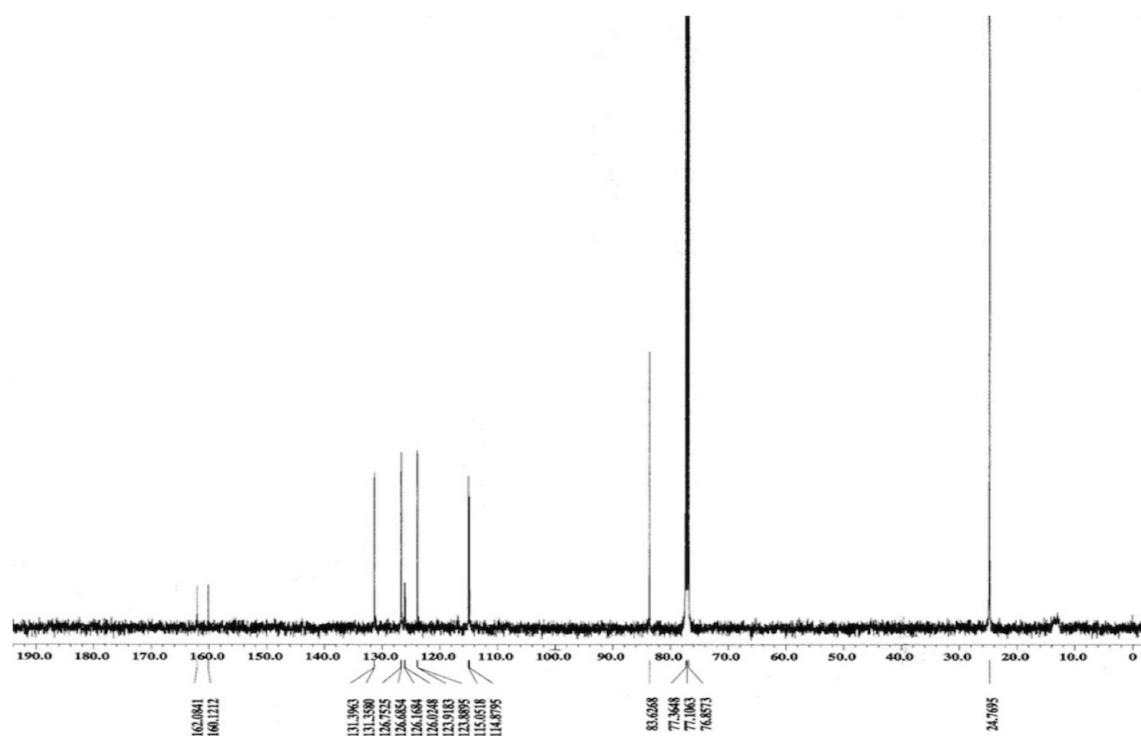


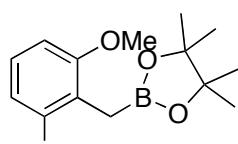


<sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>)



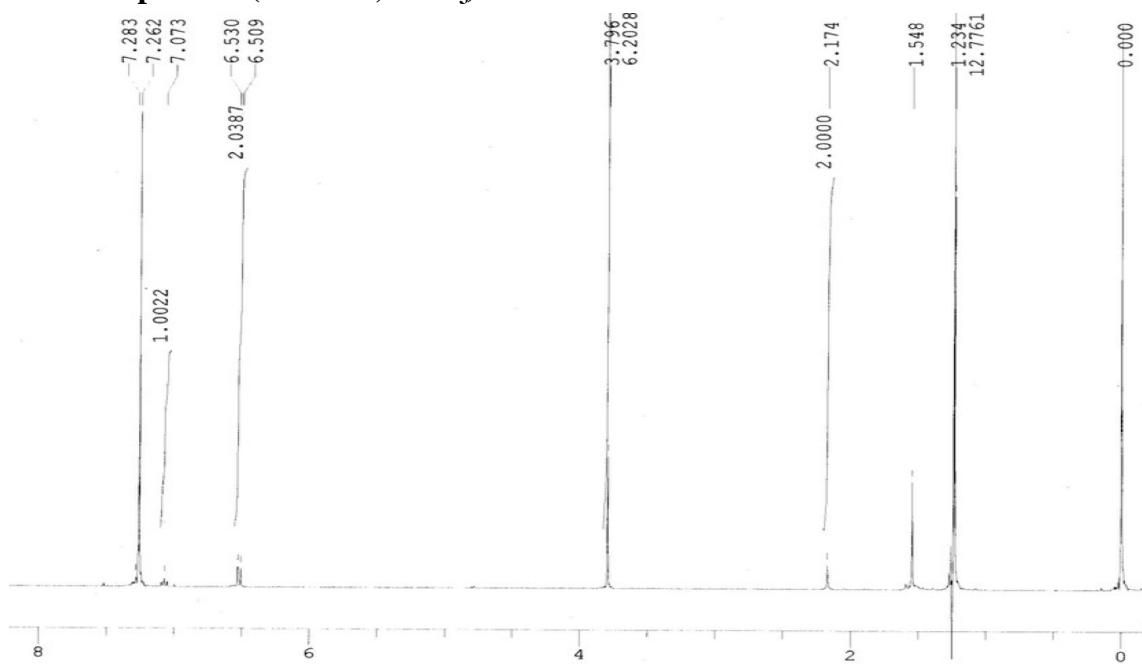
<sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>)



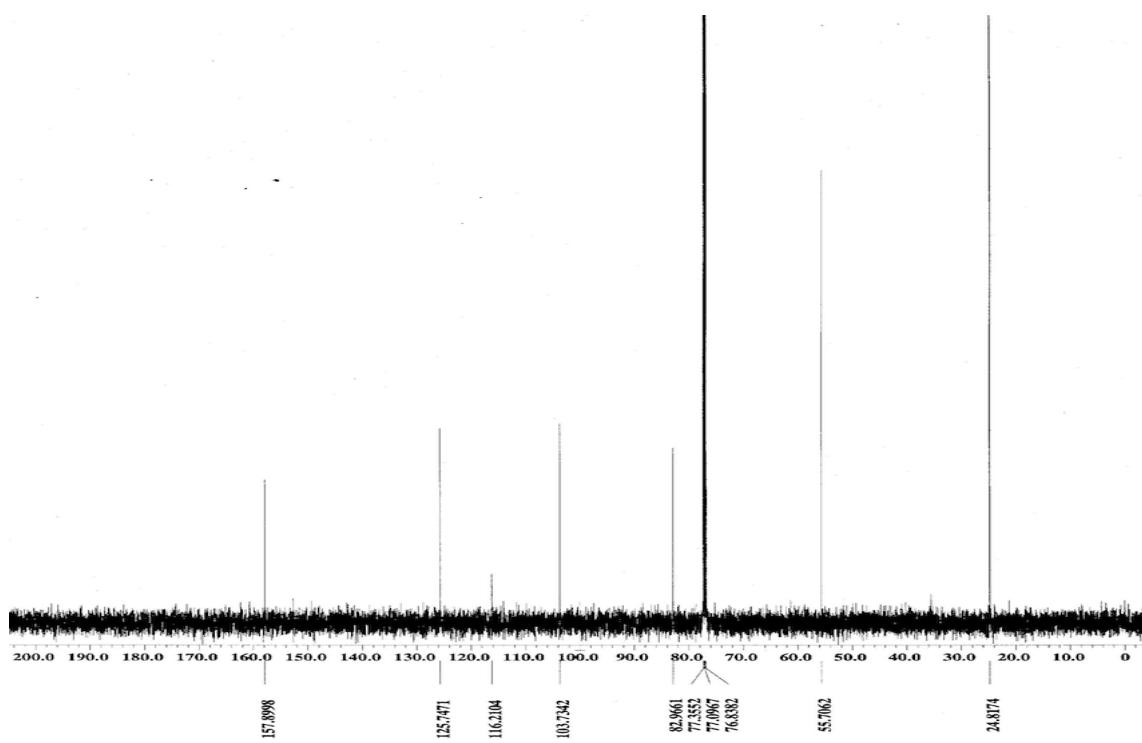


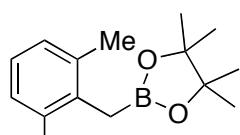
(3l)

<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)



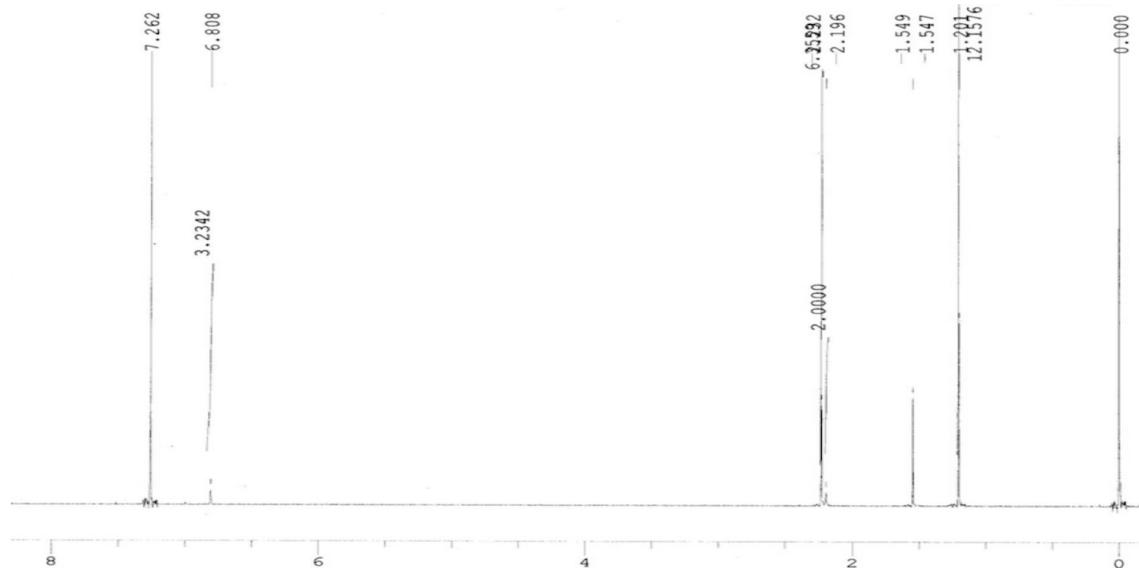
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)



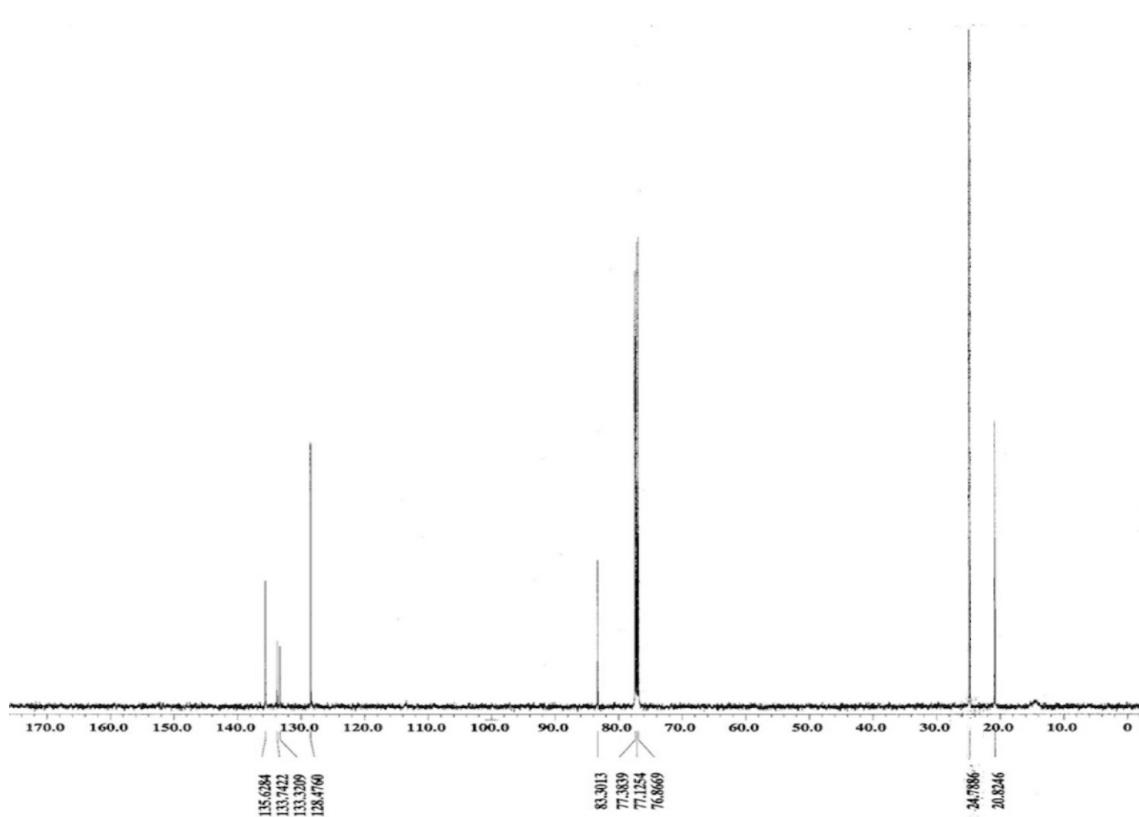


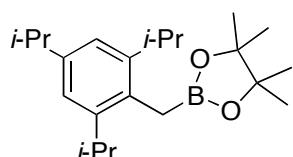
(3m)

<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)



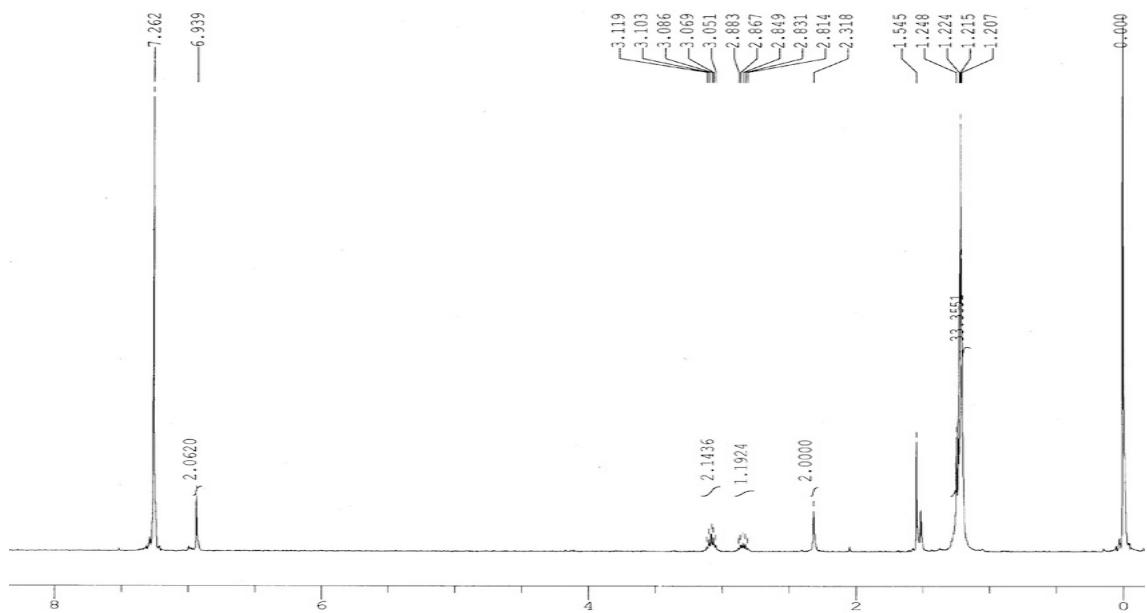
<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)



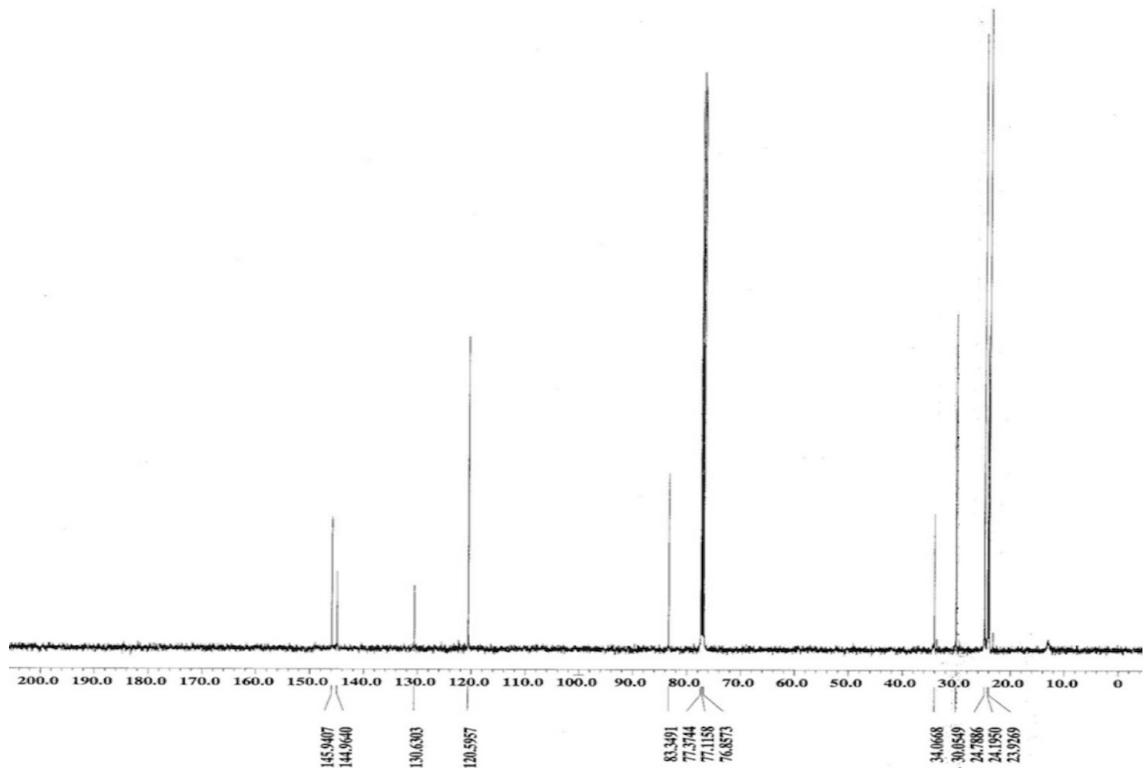


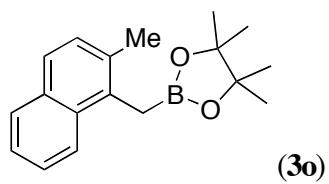
(3n)

<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)

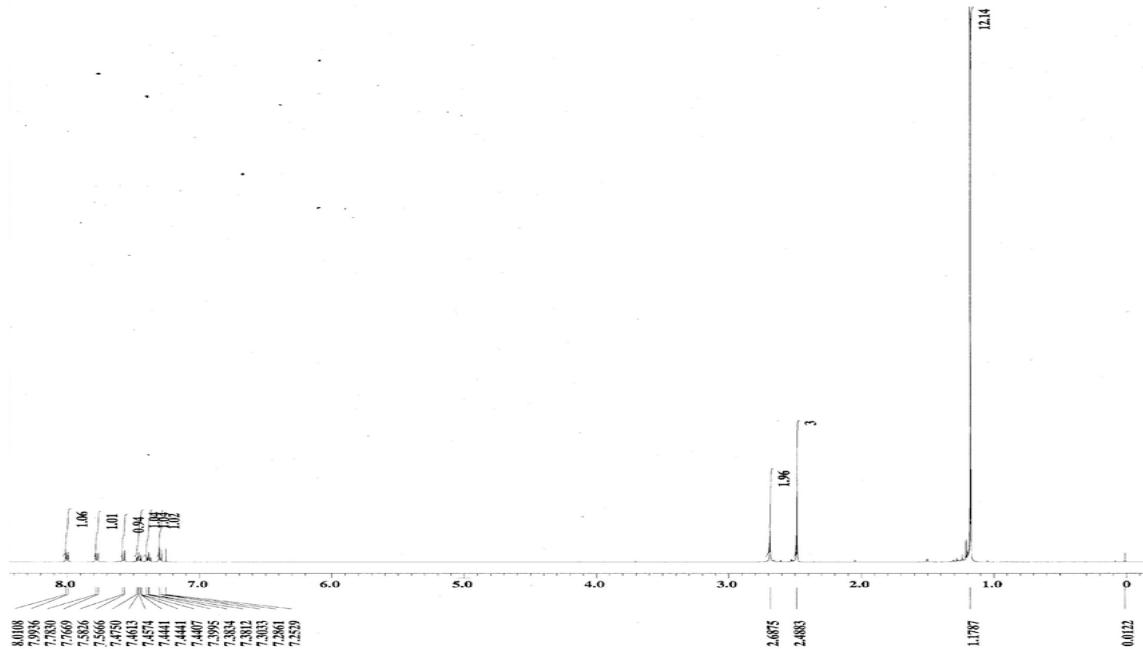


<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)

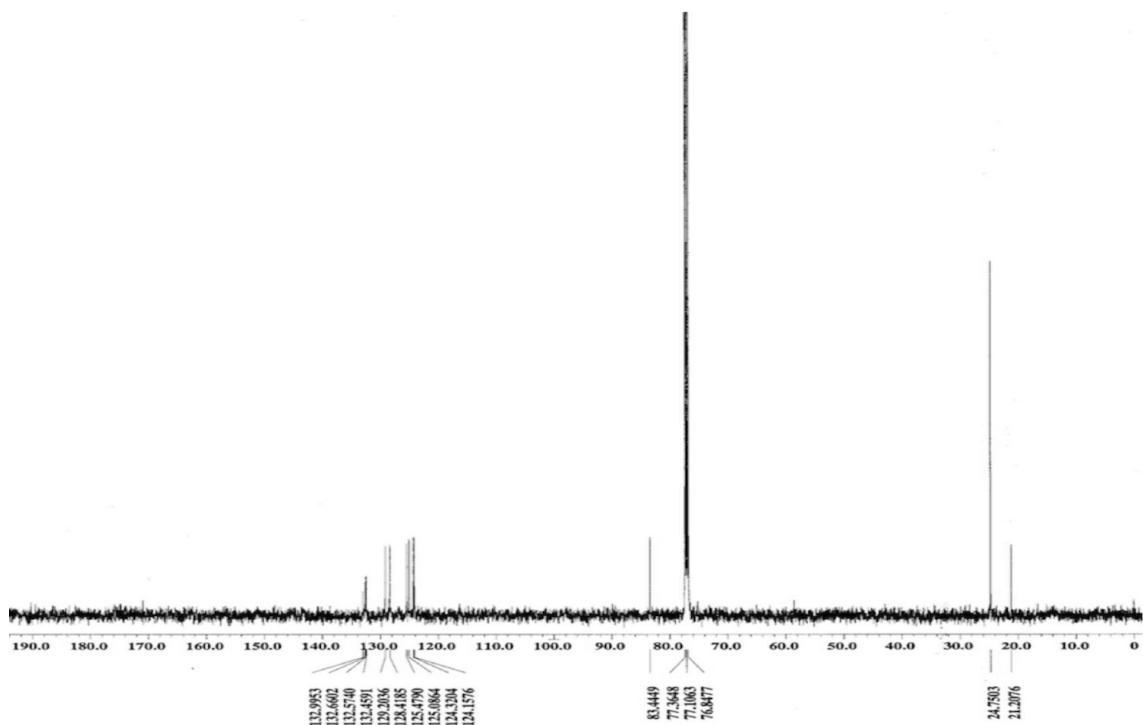


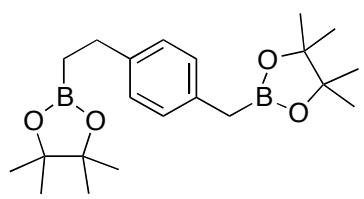


**<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)**



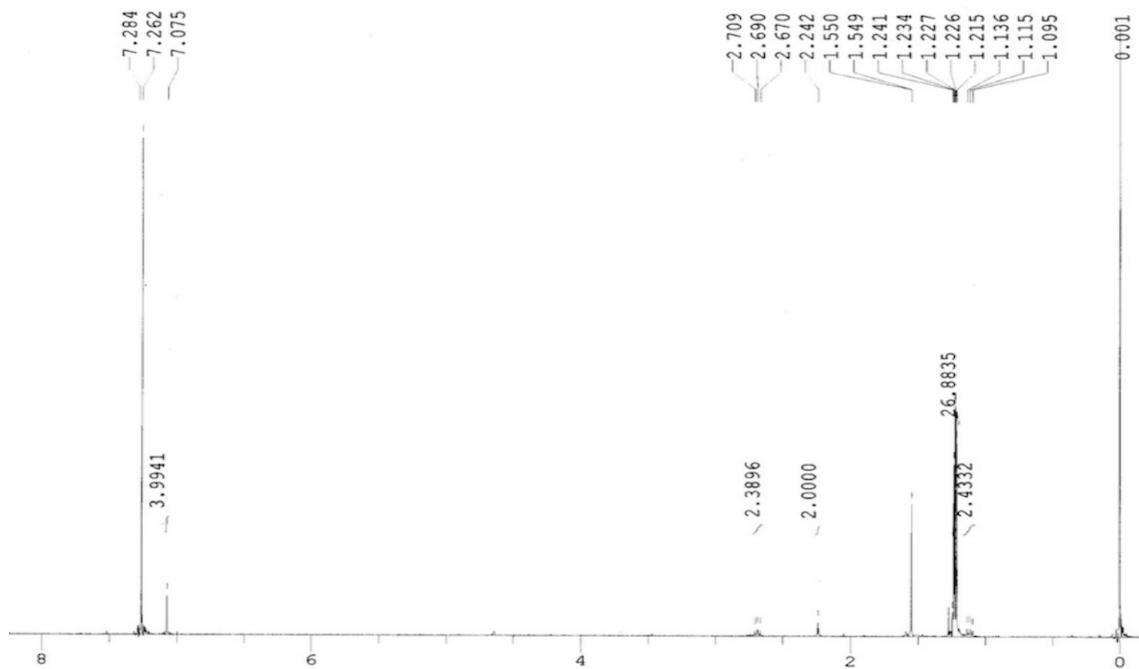
**<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)**





(3p)

<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>)

