

Supporting Information

Chemoselective Suzuki Coupling of Diborylmethane for Facile Synthesis of Benzylboronates

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Contents:

| | |
|--|------------|
| 1. General Instruments and Chemicals | S2 |
| 2. DFT Calculations | S3 |
| 3. Physical Properties of New Compounds | S8 |
| 4. NMR spectra | S14 |

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 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.*¹

Instrumentation: IR spectra were recorded as neat liquids or KBr pellets and absorptions are reported in cm^{-1} . NMR spectra were measured on 400 MHz for ^1H and 100 MHz for ^{13}C NMR, using tetramethylsilane as an internal reference and CDCl_3 as a solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of CDCl_3 (δ 7.26). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz: chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of CDCl_3 (δ 77.0). Boron nuclear magnetic resonance spectra (^{11}B NMR) were recorded at 128 MHz: chemical shifts for boron are reported in parts per million (ppm, δ scale) referenced to the boron resonance of $\text{BF}_3\cdot\text{Et}_2\text{O}$ (δ 0). Fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 470 MHz: chemical shifts for fluorine are reported in parts per million (ppm, δ scale) referenced to the fluorine resonance of trifluoroacetic acid (δ 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.²

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

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

2. DFT calculations³

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 B¹–O^H distance in acyclic monoborate is 1.46 Å. In contrast, the B¹–O^H and B²–O^H distances in cyclic monoborate are 1.687 Å and 1.716 Å, respectively. The sp³-hybridized B² atom in cyclic monoborate was observed due to the coordination of the O^H atom. The cyclic monoborate was relatively instable 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–B¹–C¹–B²–O^B–H atoms and O^H–B²–C¹–B¹–O^B–H atoms. The incorporation of two sp³-B atoms in diborate can serve the symmetrical structure; in contrast, the sp²-B² atom in acyclic monoborate prevents the formation of 6-membered cycle through O^H–B¹–C¹–B²–O^B–H atoms due to the strain at the sp²-B atom.

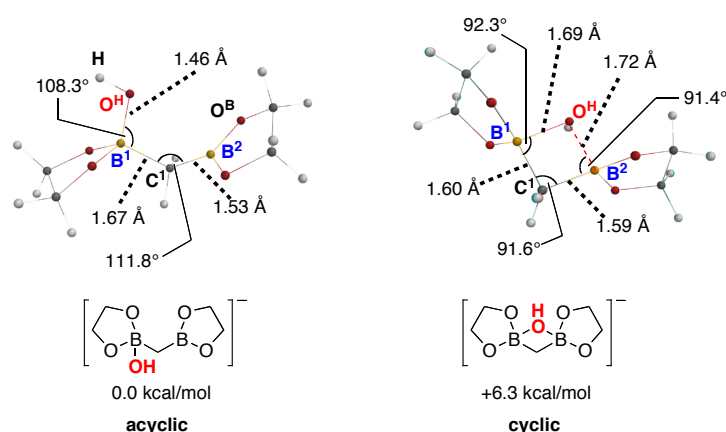


Figure S1. Optimized geometries of borate intermediate (B3LYP/6-311+G**)

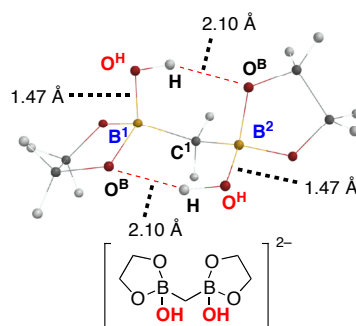
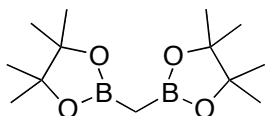


Figure S2. Optimized geometry of diborate intermediate (B3LYP/6-311+G**)

³ 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 OH₂-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

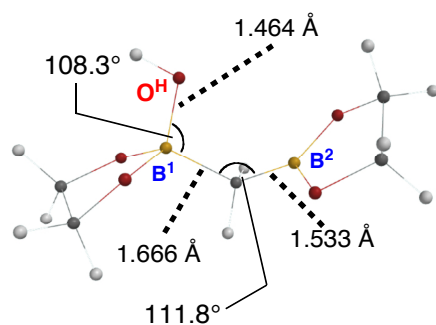
Diborylmethane



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 |

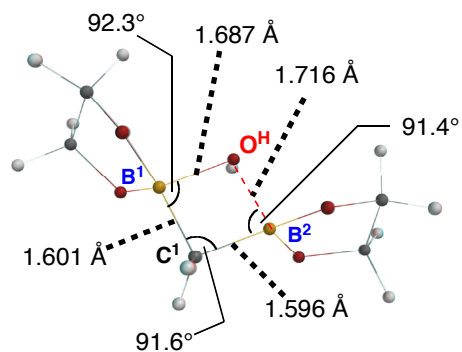
acyclic monoborate



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 |

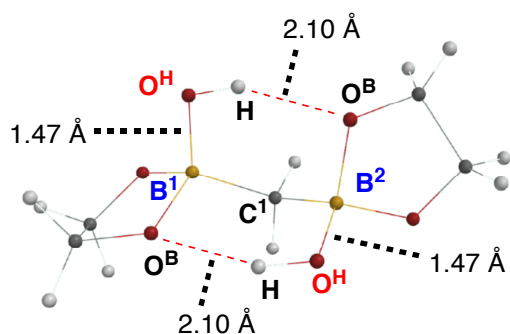
cyclic monoborate



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 |

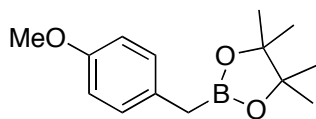
diborate



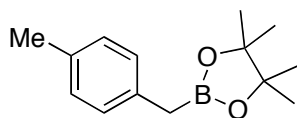
E (B3LYP/6-311+G**) = -699.208217289

| 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 |

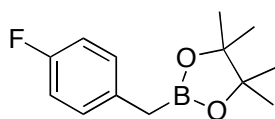
3. Physical Properties of New Compounds



2-(4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)⁴; 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)₃]₂ (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 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).



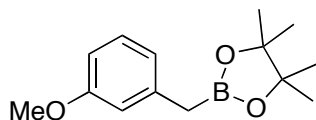
4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (3b)⁴; To a solution of diborylmethane **1a** (80 mg, 0.3 mmol, 2 equiv), 4-bromotoluene (**2b**) (25.7 mg, 0.15 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37 μL, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 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).



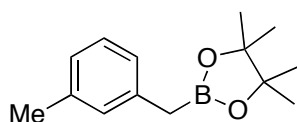
2-(4-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)⁵; To a solution of diborylmethane **1a** (76 mg, 0.28 mmol, 2 equiv), 1-bromo-4-fluorobenzene (**2c**) (25.0 mg, 0.142 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (36 μL, 0.29 mmol, 2 equiv) 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).

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

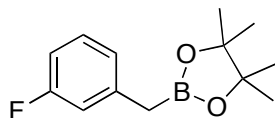
⁵ Falck, J. R.; Bondlela, M.; Ye, J.; Cho, S.-D. *Tetrahedron Lett.* **1999**, *40*, 5647.



2-(3-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)⁶; 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)₃]₂ (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 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).



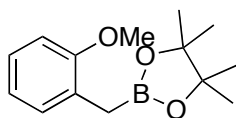
4,4,5,5-tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (3e)⁷; To a solution of diborylmethane **1a** (80 mg, 0.3 mmol, 2 equiv), 3-bromotoluene (**2b**) (25.6 mg, 0.149 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37 μL, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 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).



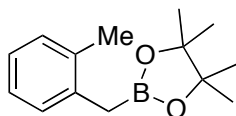
2-(3-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f); To a solution of diborylmethane **1a** (88 mg, 0.33 mmol, 2 equiv), 1-bromo-3-fluorobenzene (**2f**) (28.5 mg, 0.163 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (41 μL, 0.33 mmol, 2 equiv) 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; ¹H NMR (CDCl₃, 400 MHz) δ 7.30–7.17 (m, 1H), 6.95–6.82 (m, 3H), 2.29 (s, 2H), 1.24 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 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; ¹¹B NMR (CDCl₃, 128 MHz) δ 33.2; ¹⁹F NMR (CDCl₃, 470 MHz) δ –114.20; IR (neat, cm^{–1}) 2979, 2932, 1332, 1254, 1145, 766, 748; HRMS (FAB, positive): *m/z* calcd for C₁₃H₉BFO₂ [M + H]⁺ 237.1462, found 237.1463.

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

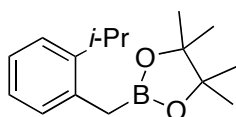
⁷ Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *Synth. Commun.* **2002**, 32, 2513.



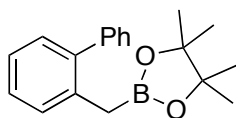
2-(2-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g); To a solution of diborylmethane **1a** (81 mg, 0.3 mmol, 2 equiv), 2-bromoanisole (**2g**) (28 mg, 0.15 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (38 μL, 0.3 mmol, 2 equiv) at room temperature. 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; ¹H NMR (CDCl₃, 400 MHz) δ 7.14–7.11 (m, 2H), 6.86–6.79 (m, 2H), 3.79 (s, 3H), 2.18 (s, 2H), 1.23 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 157.3, 130.6, 128.1, 126.3, 120.6, 109.8, 83.2, 55.1, 24.8; ¹¹B NMR (CDCl₃, 128 MHz) δ 33.9; IR (neat, cm⁻¹) 2979, 2933, 1494, 1379, 1352, 1243, 1144, 750; HRMS (FAB, positive): *m/z* calcd for C₁₄H₂₁BO₃ 248.1584, found 248.1582.



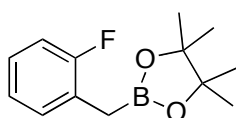
2-(2-methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)⁴; To a solution of diborylmethane **1a** (91 mg, 0.34 mmol, 2 equiv), 2-bromotoluene (**2h**) (29.4 mg, 0.172 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μg, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (43 μL, 0.34 mmol, 2 equiv) at room 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)



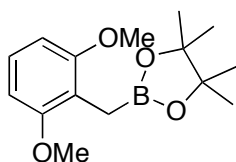
2-(2-isopropylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i); To a solution of diborylmethane **1a** (83 mg, 0.31 mmol, 2 equiv), 1-bromo-2-isopropylbenzene (**2i**) (30.7 mg, 0.154 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (39 μL, 0.31 mmol, 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; ¹H NMR (CDCl₃, 400 MHz) δ 7.23–7.04 (m, 4H), 3.09 (sept, *J* = 6.8 Hz, 1H), 2.31 (s, 2H), 1.22–1.21 (m, 18H); ¹³C NMR (CDCl₃, 100 MHz) δ 146.4, 136.0, 130.1, 125.6 (2C), 125.0, 83.4, 29.4, 24.8, 23.7; ¹¹B NMR (CDCl₃, 128 MHz) δ 33.7; IR (neat, cm⁻¹) 2977, 2931, 1738, 1349, 1330, 1144, 847, 752; HRMS (FAB, positive): *m/z* calcd for C₁₆H₂₅BO₂ 260.1948, found 260.1948.



2-[(1,1'-biphenyl)-2-ylmethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)⁸; 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)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (35 μL, 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)



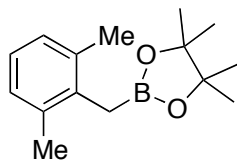
2-(2-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k); To a solution of diborylmethane **1a** (79 mg, 0.29 mmol, 2 equiv), 1-bromo-2-fluorobenzene (**2k**) (25.0 mg, 0.144 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (36 μL, 0.29 mmol, 2 equiv) 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; ¹H NMR (CDCl₃, 400 MHz) δ 7.19–6.97 (m, 4H), 2.25 (s, 2H), 1.24 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 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; ¹¹B NMR (CDCl₃, 128 MHz) δ 33.9; ¹⁹F NMR (CDCl₃, 470 MHz) δ –116.78; IR (neat, cm^{–1}) 2979, 2932, 1737, 1352, 1216, 1144, 847, 751; HRMS (FAB, positive): *m/z* calcd for C₁₃H₁₉BFO₂ [M + H]⁺ 237.1462, found 237.1461.



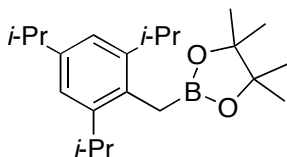
2-(2,6-dimethoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l); To a solution of diborylmethane **1a** (80 mg, 0.3 mmol, 2 equiv), 2-bromo-1,3-dimethoxybenzene (**2l**) (32.0 mg, 0.148 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (37 μL, 0.3 mmol, 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 >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; ¹H NMR (CDCl₃, 400 MHz) δ 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); ¹³C NMR (CDCl₃, 100 MHz) δ 157.9, 125.7, 116.2, 103.7,

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

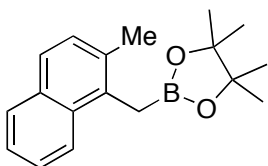
83.0, 55.7, 24.8; ^{11}B NMR (CDCl_3 , 128 MHz) δ 33.8; IR (neat, cm^{-1}) 2978, 2935, 1737, 1473, 1349, 1145, 765, 750; HRMS (FAB, positive): m/z calcd for $\text{C}_{15}\text{H}_{23}\text{BO}_4$ 278.1689, found 278.1697.



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 μmol , 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (36 μL , 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 $^\circ\text{C}$ 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; ^1H NMR (CDCl_3 , 400 MHz) δ 6.81 (s, 3H), 2.23 (s, 6H), 2.20 (s, 2H), 1.20 (s, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 135.6, 133.7, 133.3, 128.5, 83.3, 24.8, 20.8; ^{11}B NMR (CDCl_3 , 128 MHz) δ 33.2; IR (neat, 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.

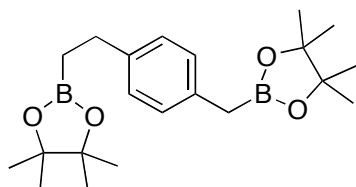


4,4,5,5-tetramethyl-2-(2,4,6-triisopropylbenzyl)-1,3,2-dioxaborolane (3n); To a solution of diborylmethane **1a** (69 mg, 0.26 mmol, 2 equiv), 2-bromo-1,3,5-triisopropylbenzene (**2n**) (36 mg, 0.127 mmol), and $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (3.8 mg, 7.4 μmol , 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (29 μL , 0.24 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 $^\circ\text{C}$ 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; ^1H NMR (CDCl_3 , 400 MHz) δ 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}C NMR (CDCl_3 , 100 MHz) δ 145.9, 145.0, 130.6, 120.6, 83.3, 34.1, 30.1, 24.8, 24.2, 23.9; ^{11}B NMR (CDCl_3 , 128 MHz) δ 33.4; IR (neat, 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.



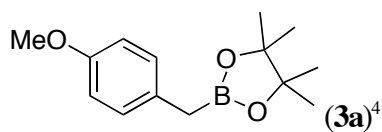
4,4,5,5-tetramethyl-2-[(2-methylnaphthalen-1-yl)methyl]-1,3,2-dioxaborolane (3o); To a solution of diborylmethane **1a** (78 mg, 0.29 mmol, 2 equiv), 1-bromo-2-methylnaphthalene (**2o**) (32.1 mg, 0.145 mmol), and $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (3.8 mg, 7.4 μmol , 5 mol %) in dioxane 1.5 mL was added 8 N KOH aq. (36 μL , 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; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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; ¹¹B NMR (CDCl₃, 128 MHz) δ 34.3; IR (neat, cm⁻¹) 3383, 2977, 2932, 1737, 1372, 1275, 1143, 765, 749; HRMS (FAB, positive): *m/z* calcd for C₁₈H₂₃BO₂ 282.1791, found 282.1778.

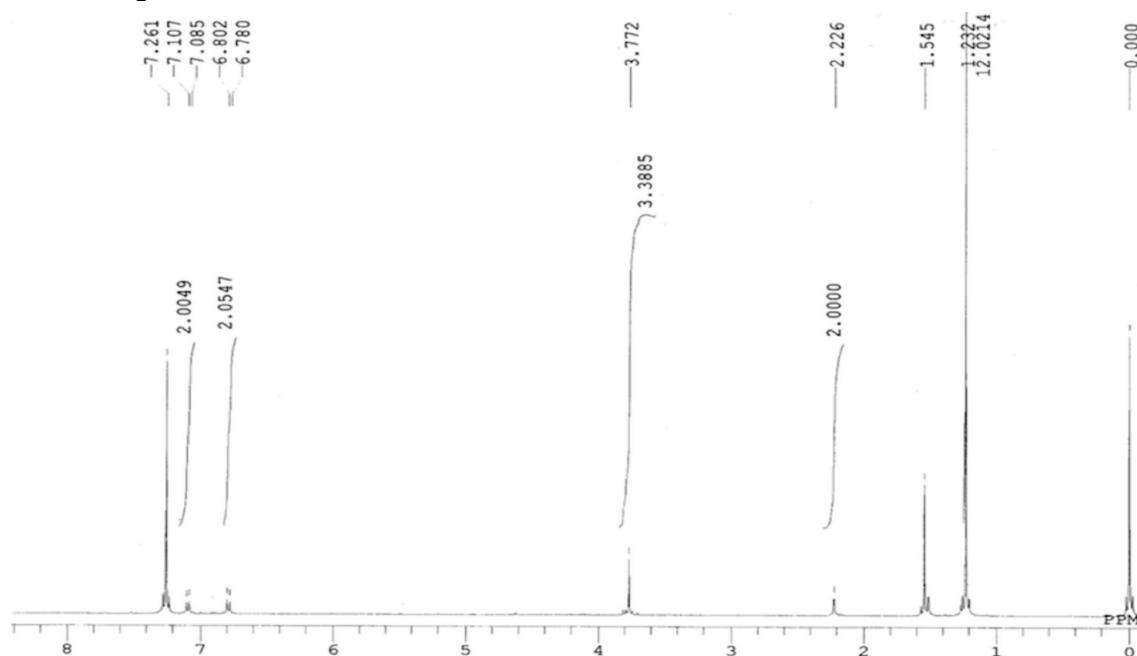


4,4,5,5-tetramethyl-2-{4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzyl}-1,3,2-dioxaborolane (3p): To a solution of diboryl methane **1a** (80 mg, 0.3 mmol, 2 equiv), 2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2p**) (46.6 mg, 0.15 mmol), and Pd[P(*t*-Bu)₃]₂ (3.8 mg, 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; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 100 MHz) δ 140.8, 135.5, 128.9, 128.0, 83.4, 83.1, 29.5, 24.9, 24.8; ¹¹B NMR (CDCl₃, 128 MHz) δ 33.7 (2B); IR (neat, cm⁻¹) 2979, 2933, 1738, 1371, 1355, 1322, 1144, 847, 764, 750; HRMS (FAB, positive): *m/z* calcd for C₂₁H₃₄B₂O₄ 372.2721, found 373.2731.

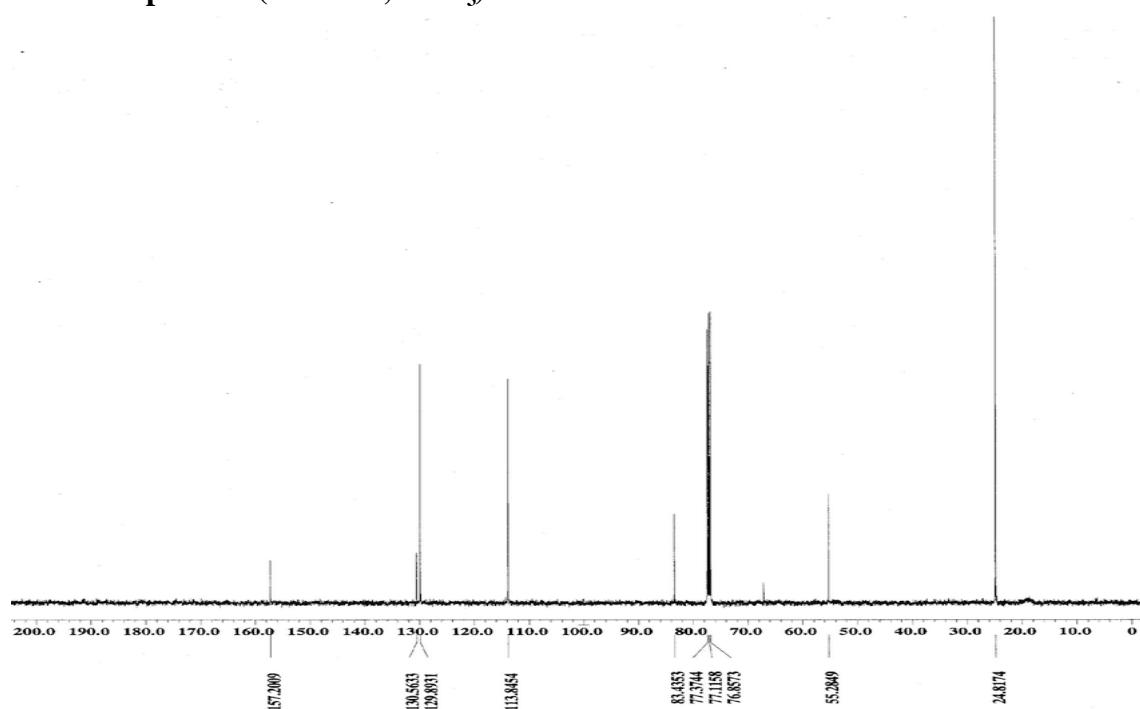
4. NMR spectra

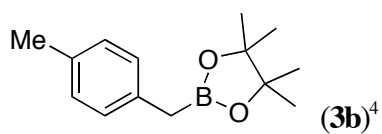


¹H NMR spectrum (400 MHz, CDCl₃)

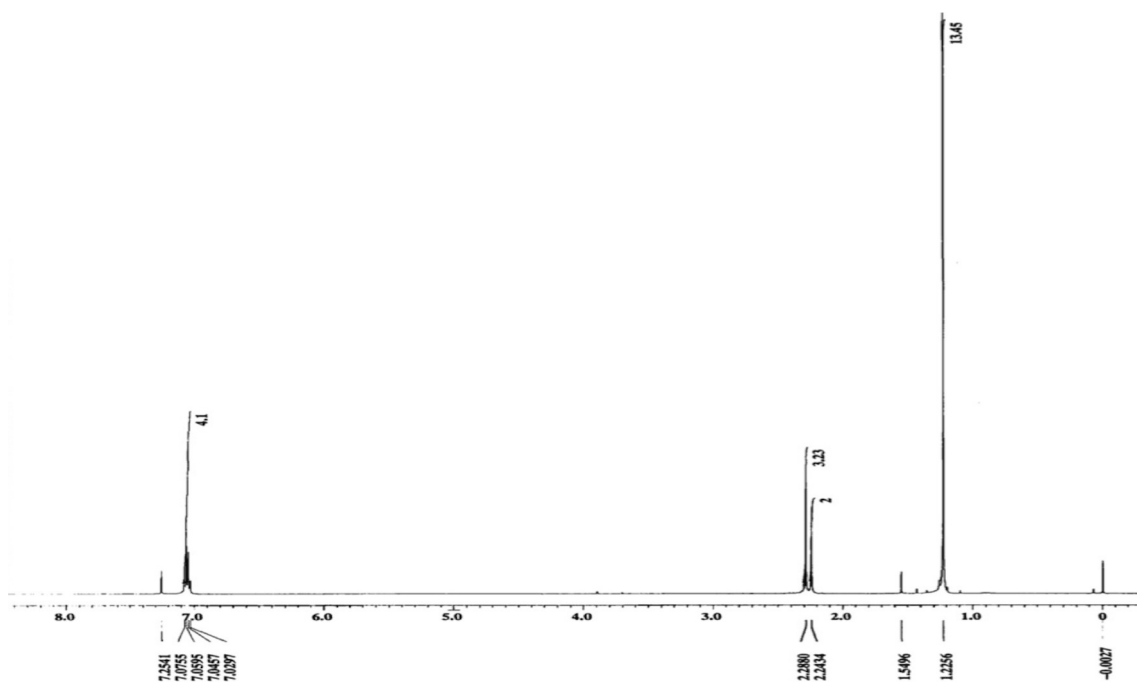


¹³C NMR spectrum (100 MHz, CDCl₃)

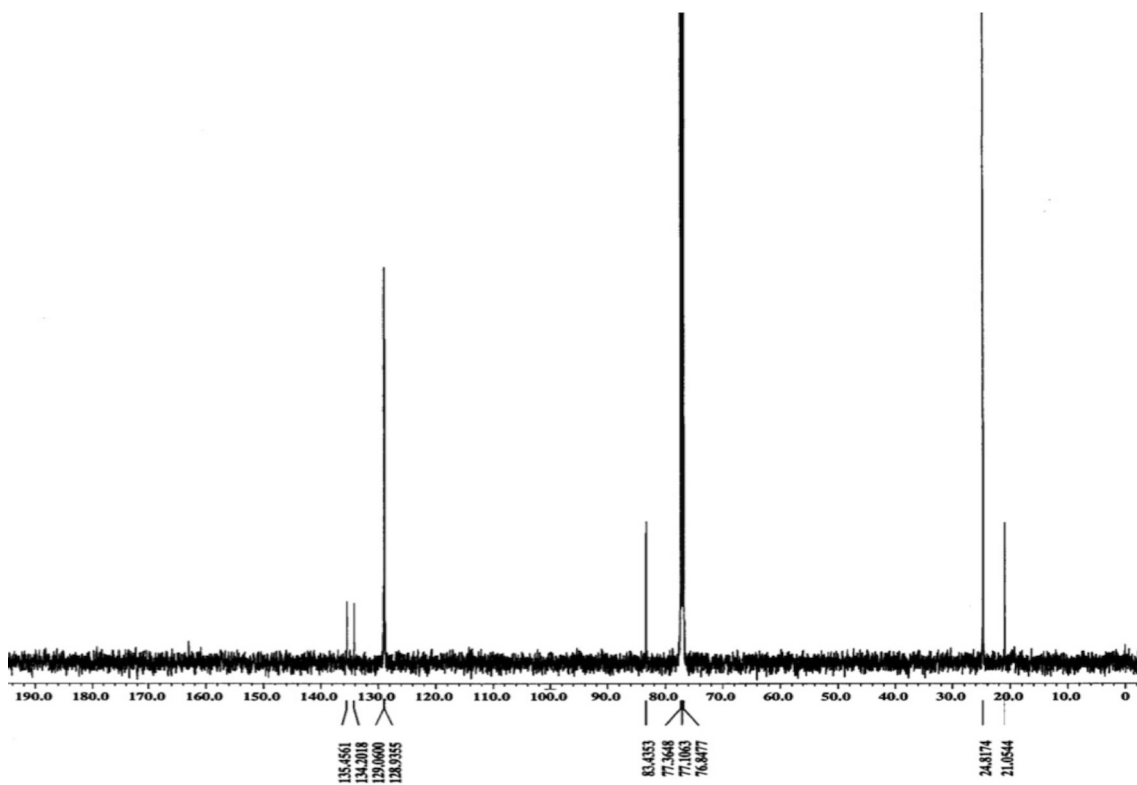


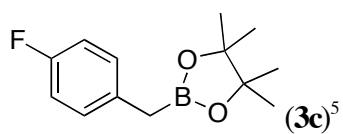


¹H NMR spectrum (400 MHz, CDCl₃)

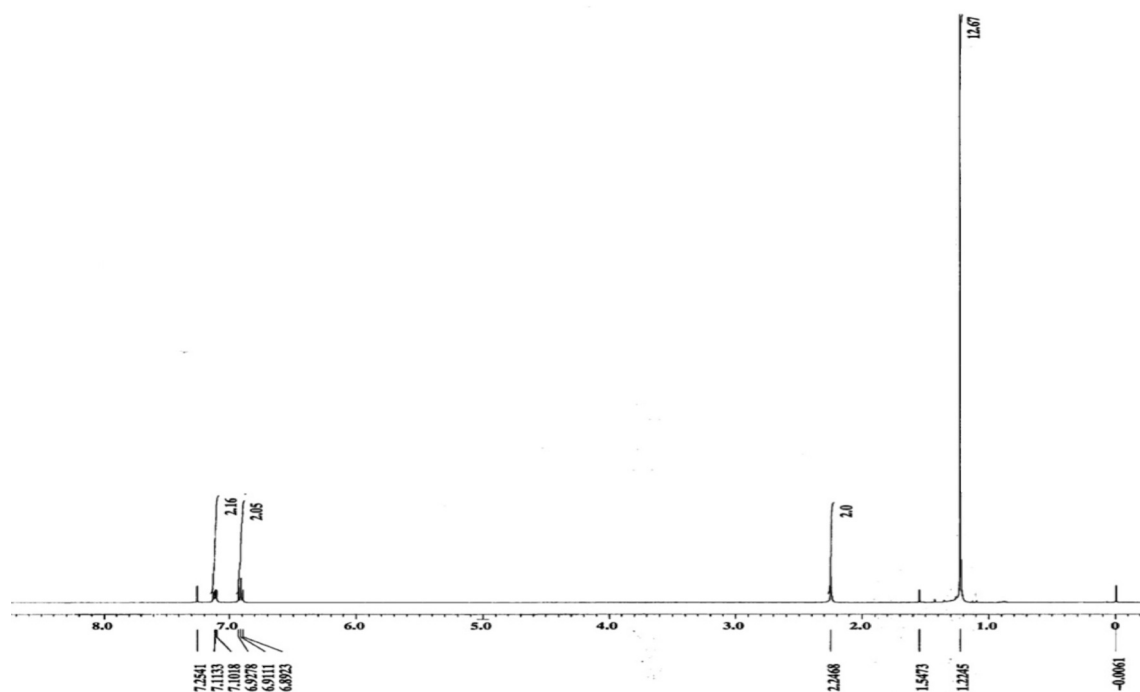


¹³C NMR spectrum (100 MHz, CDCl₃)

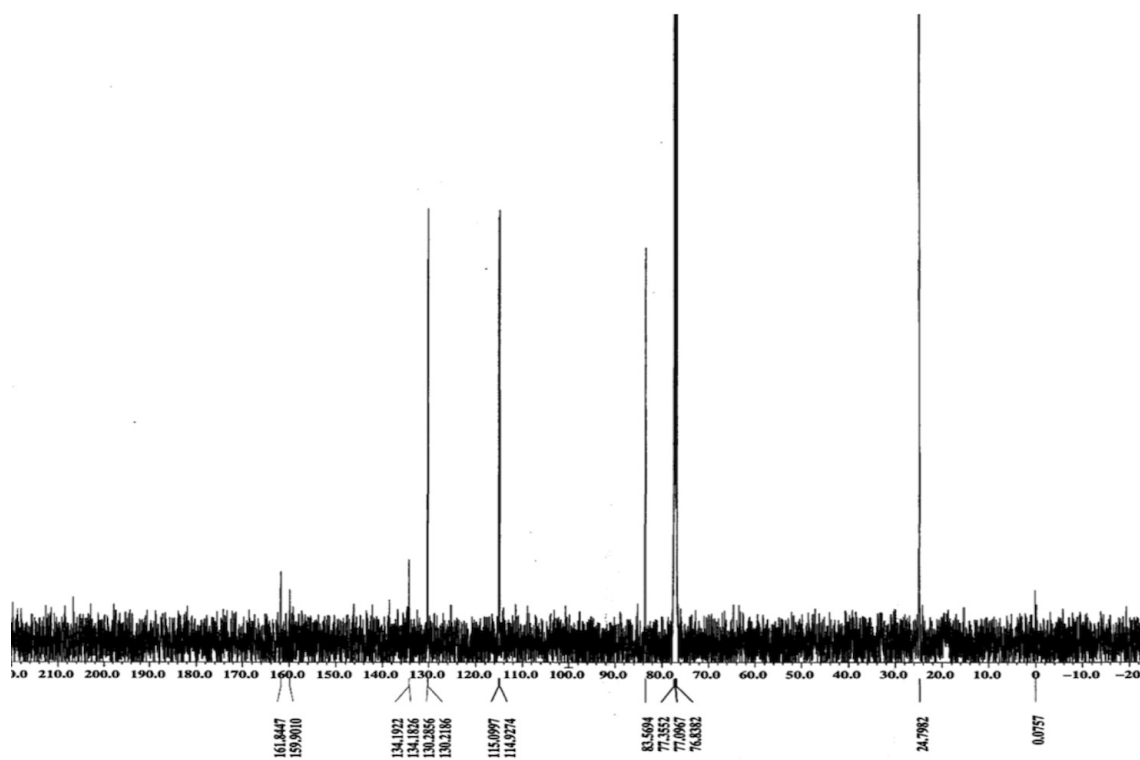


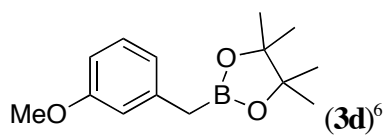


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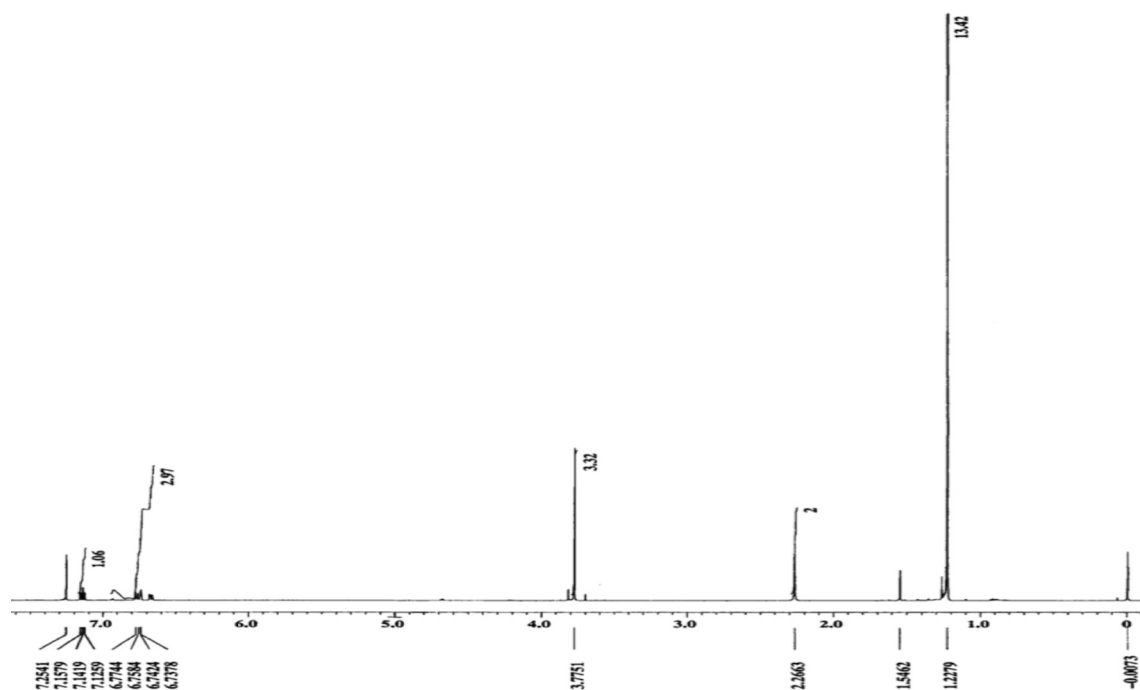


¹³C NMR spectrum (125 MHz, CDCl₃)

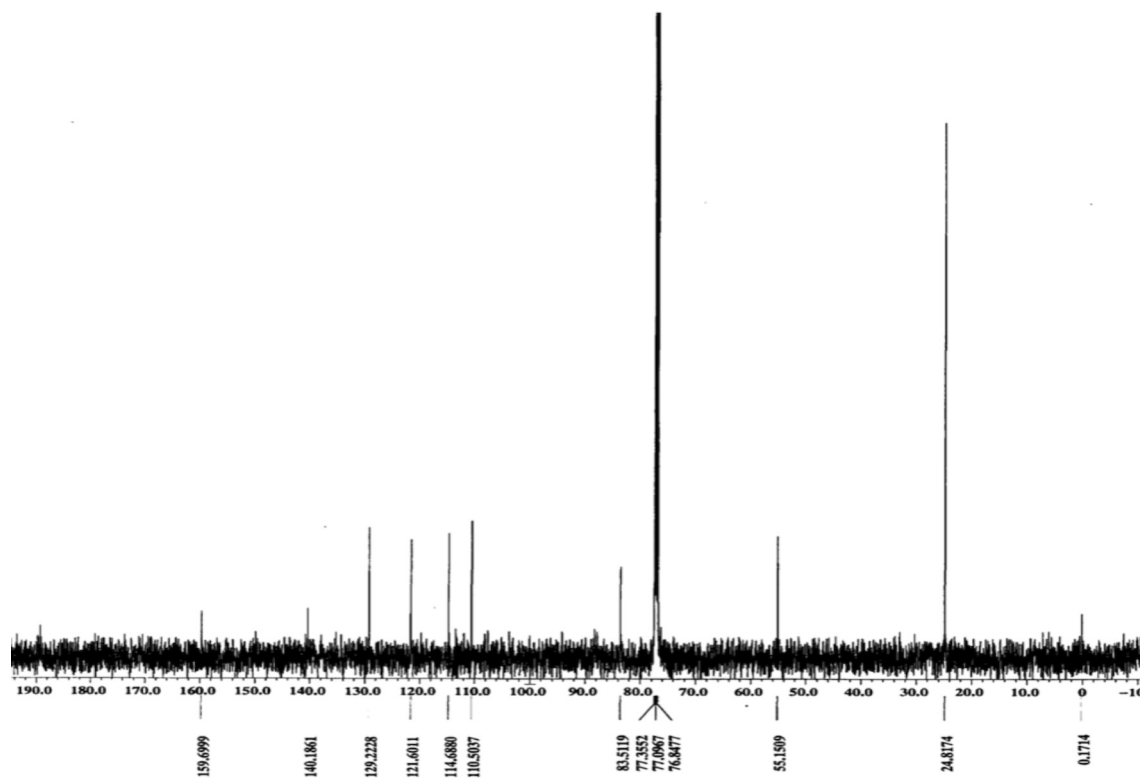


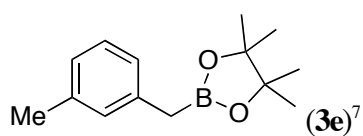


¹H NMR spectrum (400 MHz, CDCl₃)

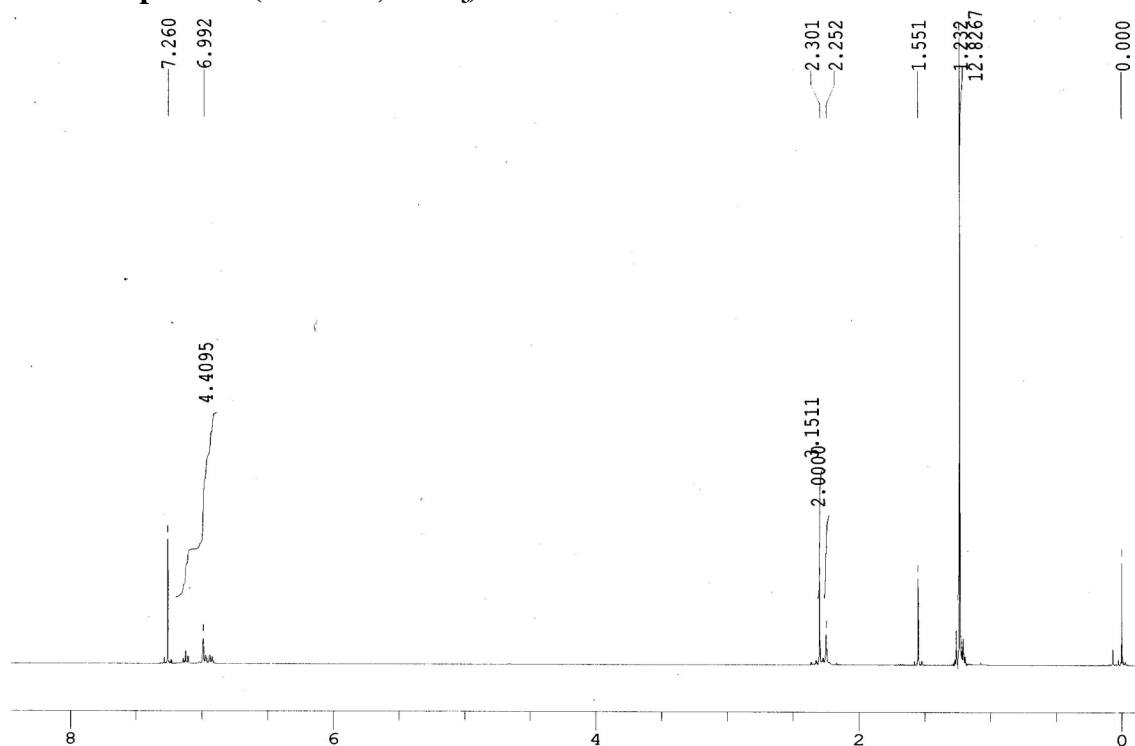


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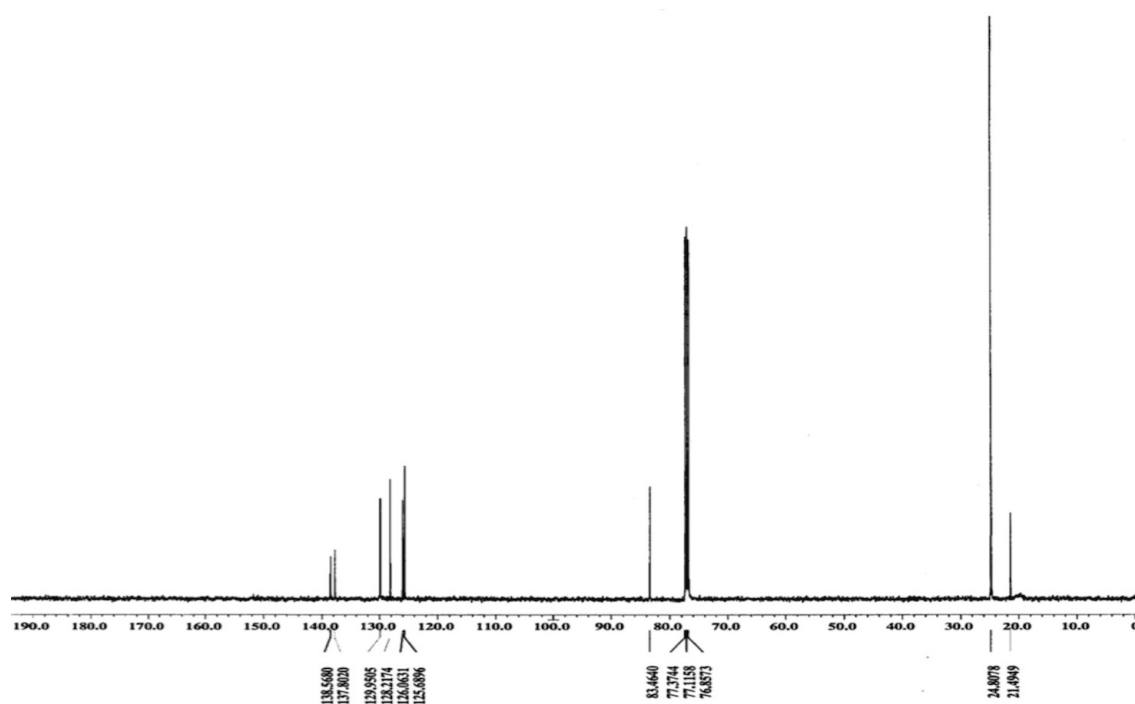


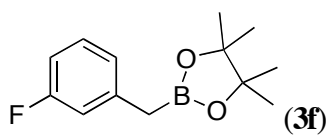


¹H NMR spectrum (400 MHz, CDCl₃)

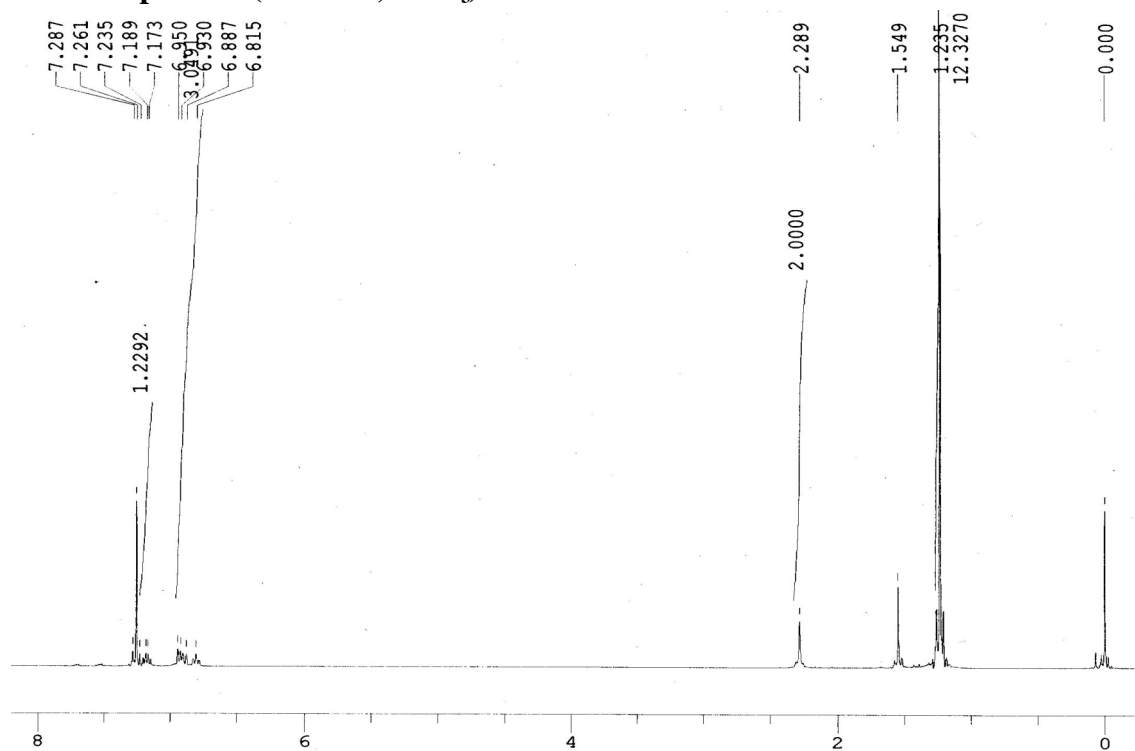


¹³C NMR spectrum (100 MHz, CDCl₃)

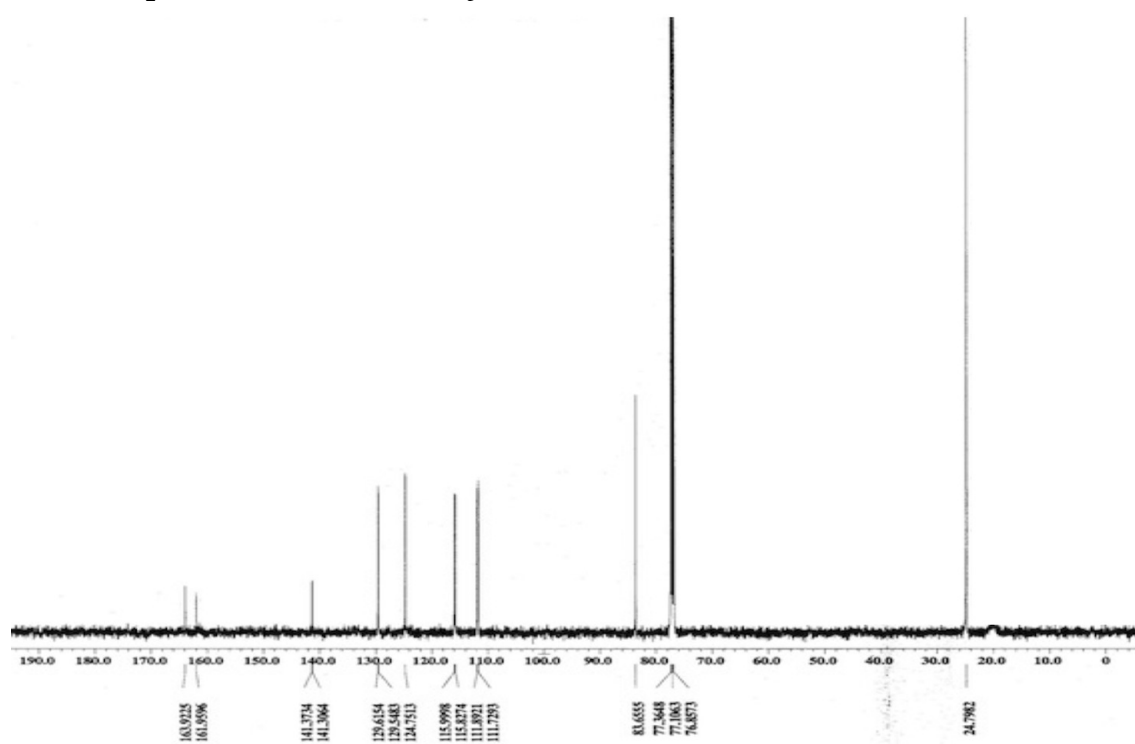


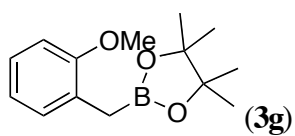


^1H NMR spectrum (500 MHz, CDCl_3)

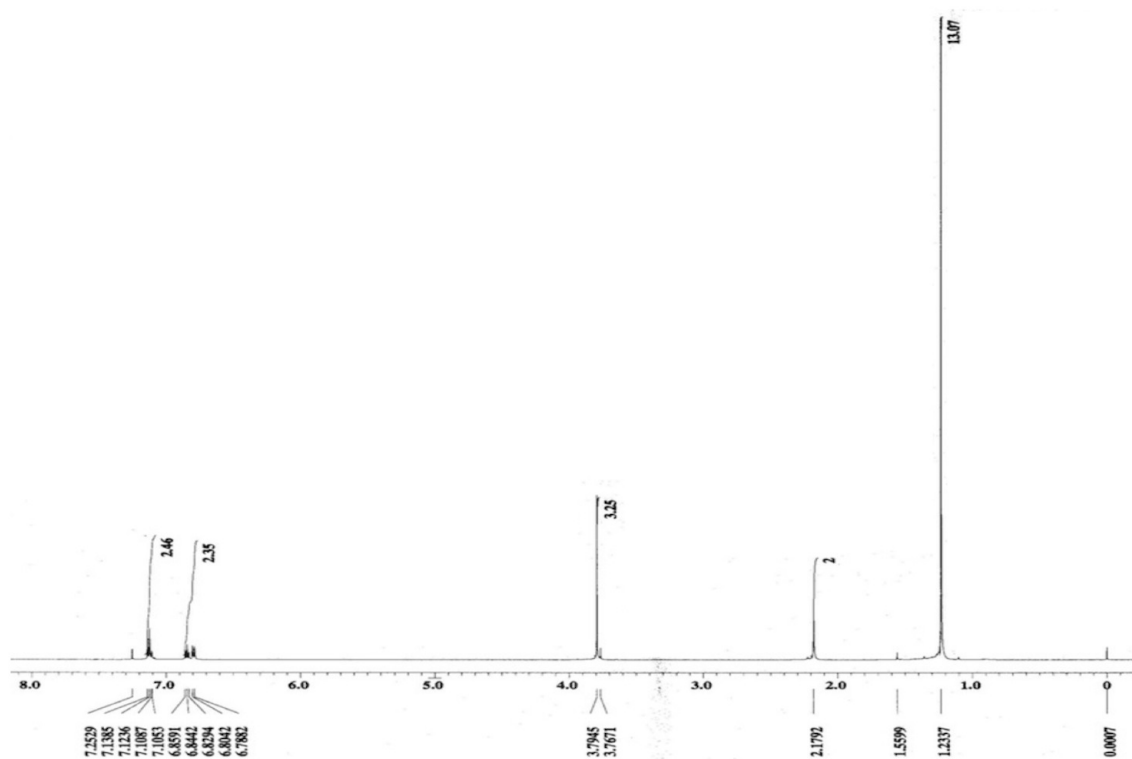


^{13}C NMR spectrum (125 MHz, CDCl_3)

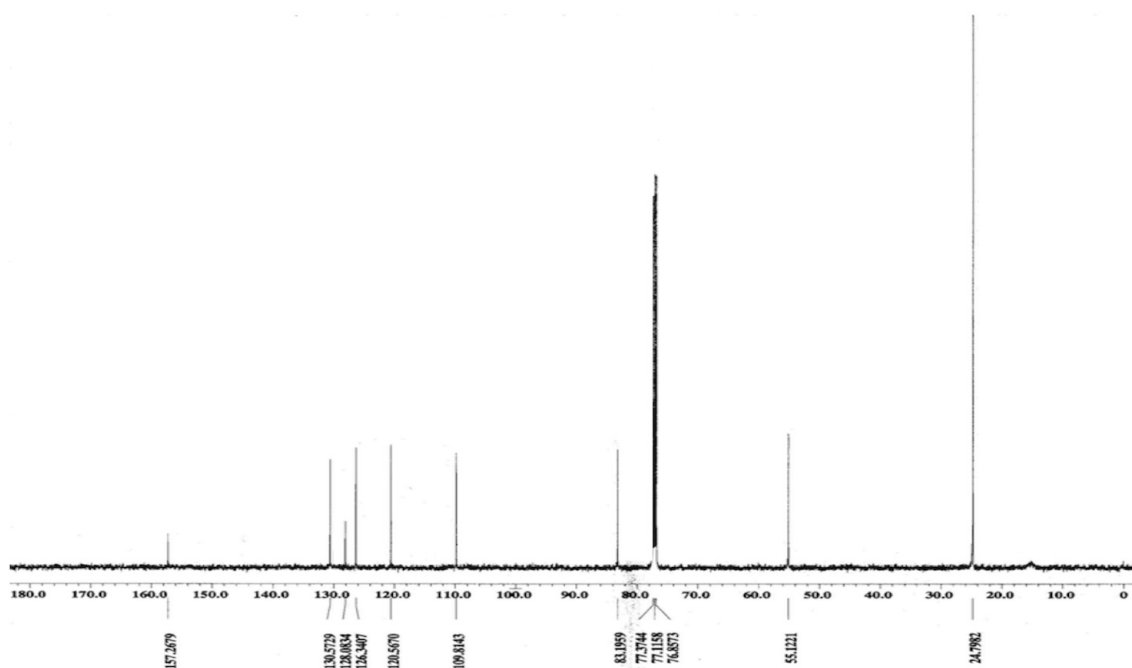


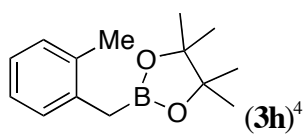


^1H NMR spectrum (400 MHz, CDCl_3)

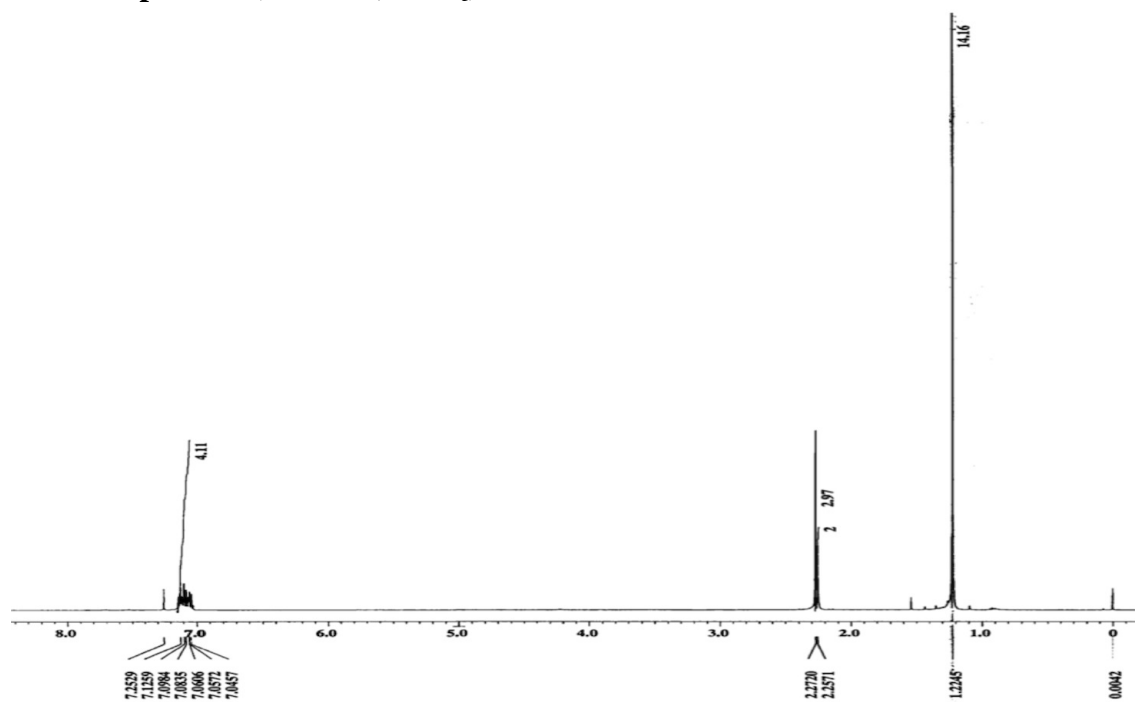


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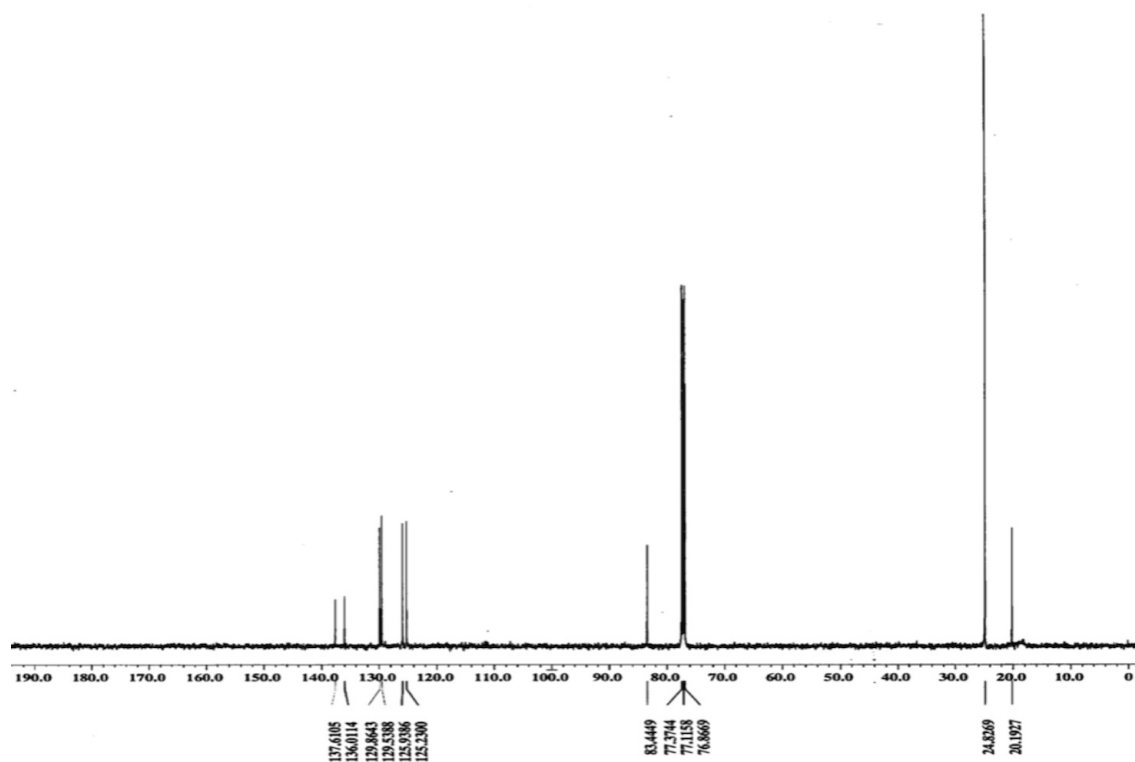


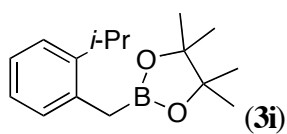


¹H NMR spectrum (400 MHz, CDCl₃)

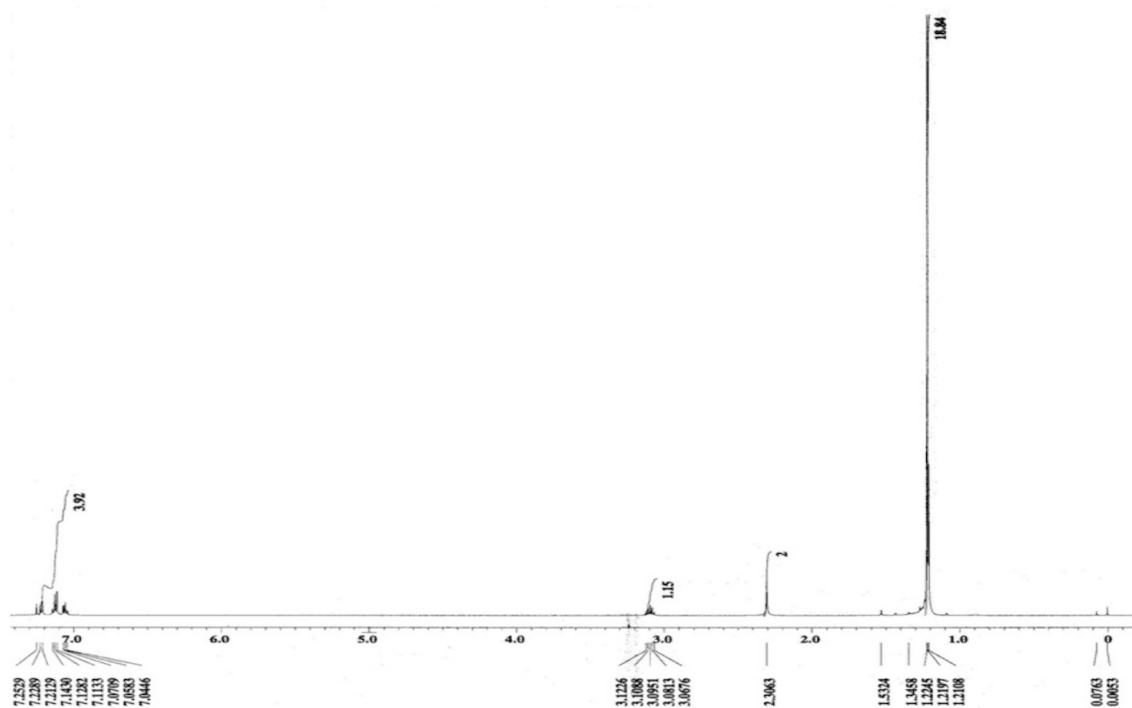


¹³C NMR spectrum (100 MHz, CDCl₃)

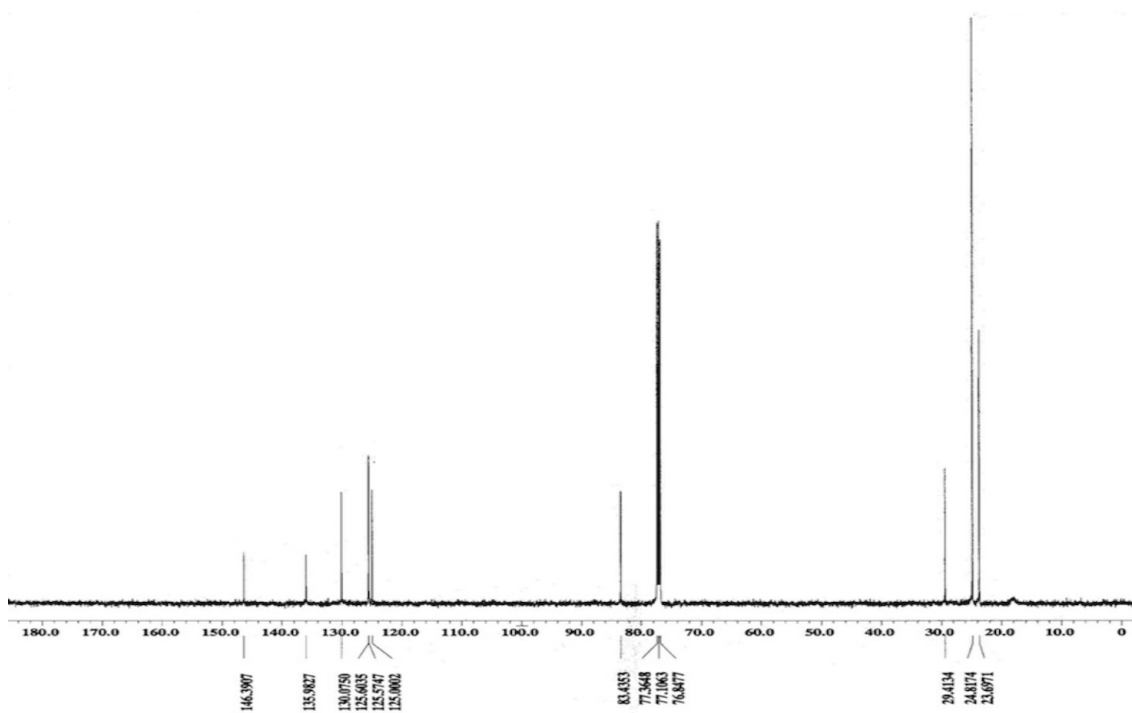


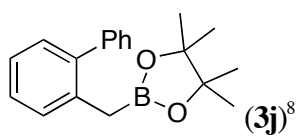


^1H NMR spectrum (500 MHz, CDCl_3)

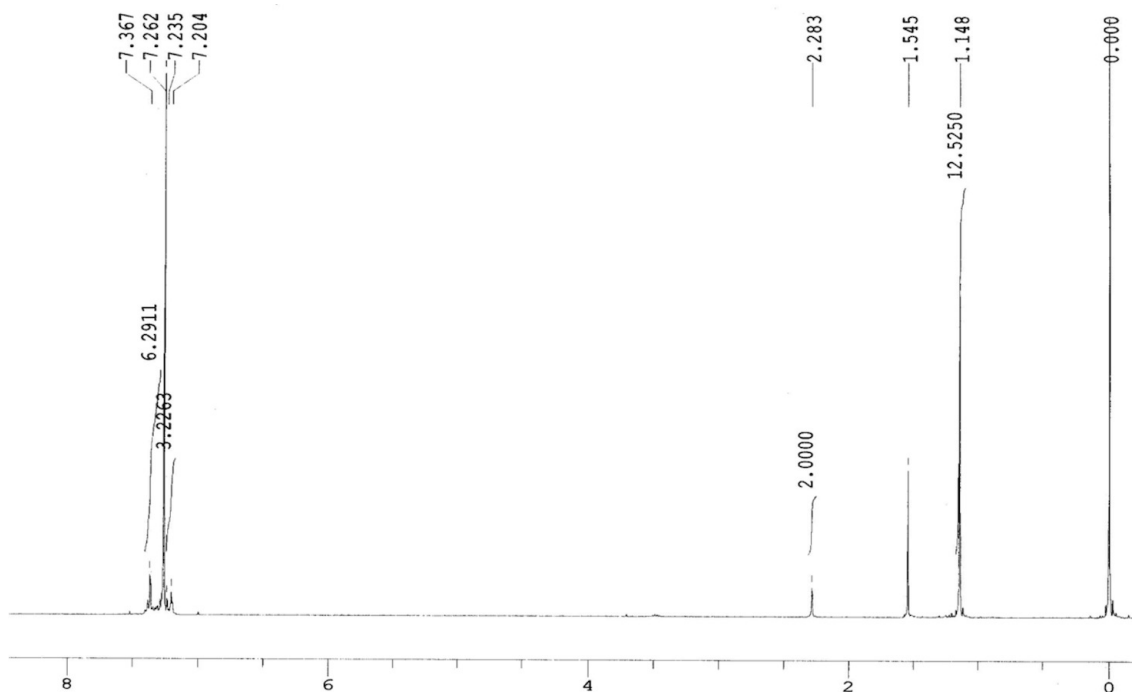


^{13}C NMR spectrum (125 MHz, CDCl_3)

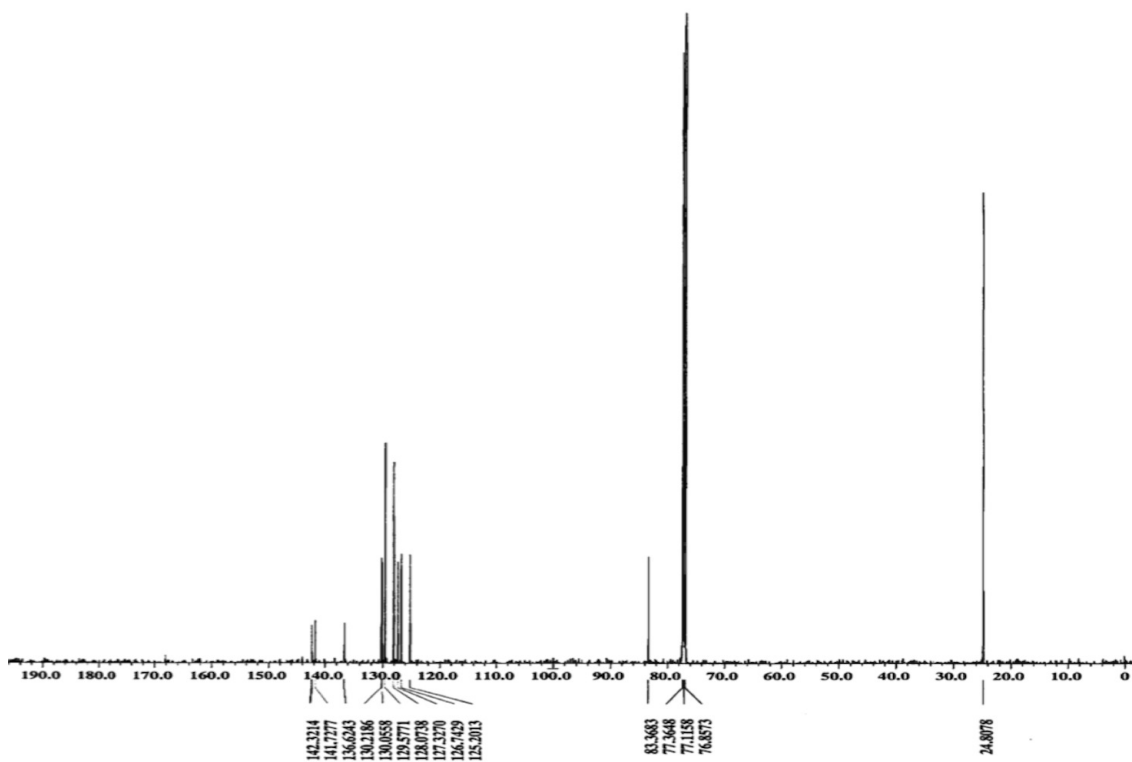


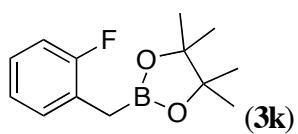


¹H NMR spectrum (400 MHz, CDCl₃)

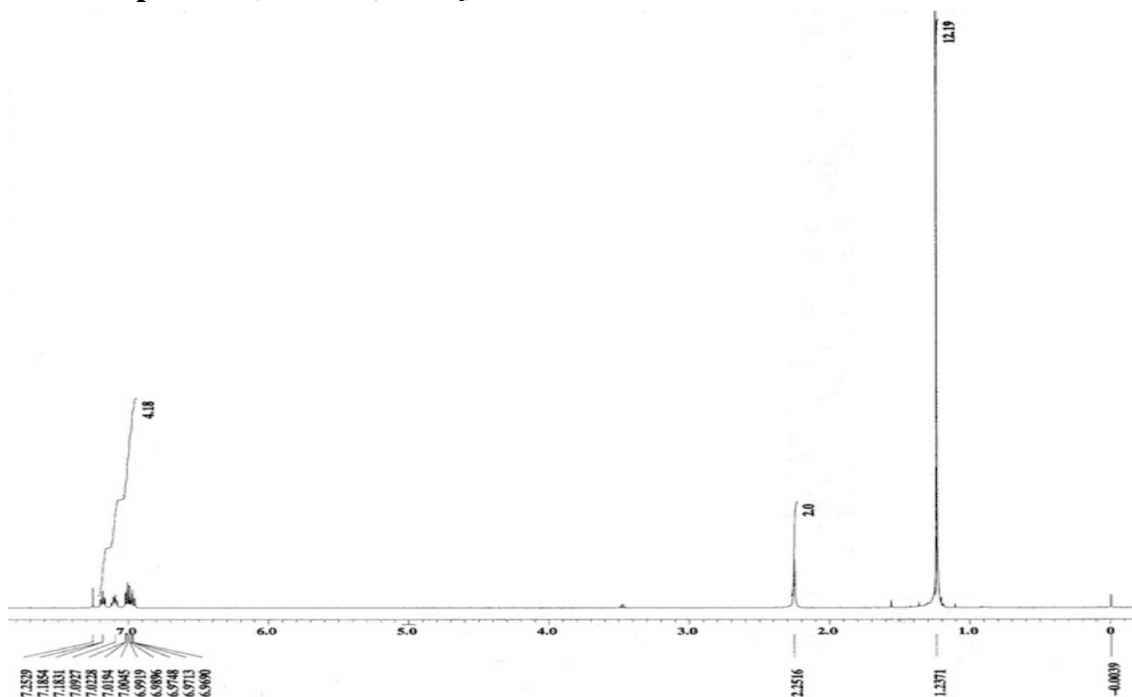


¹³C NMR spectrum (100 MHz, CDCl₃)

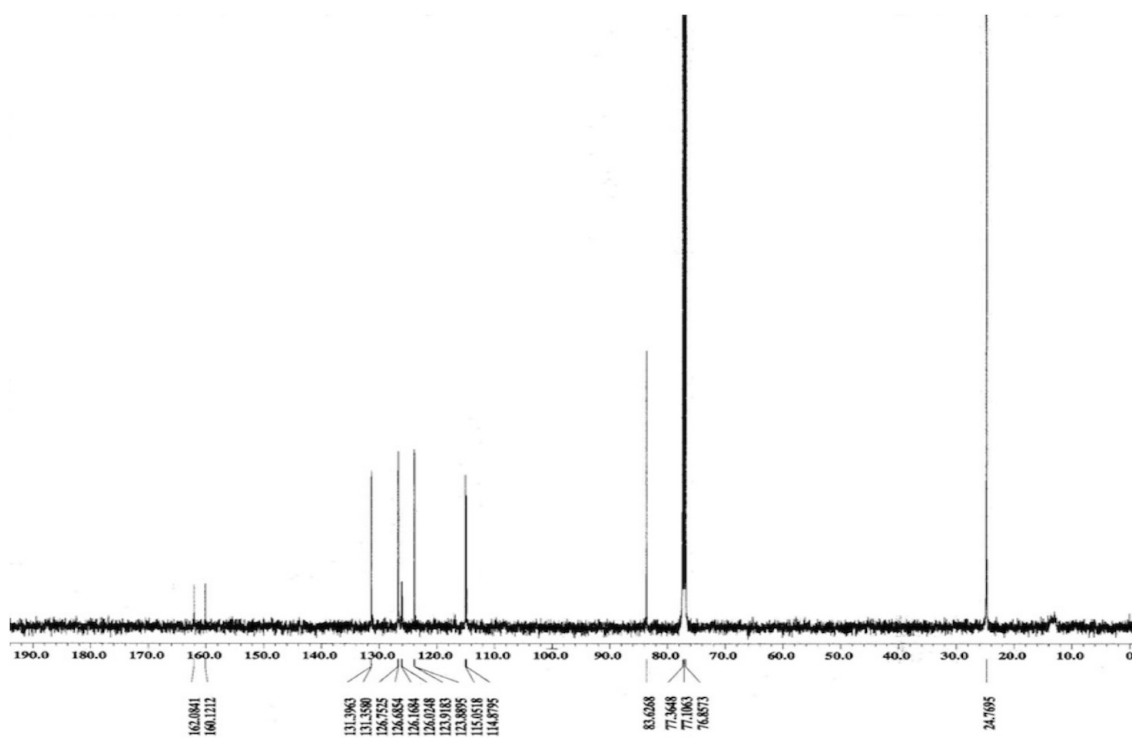


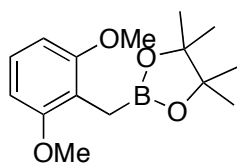


^1H NMR spectrum (500 MHz, CDCl_3)



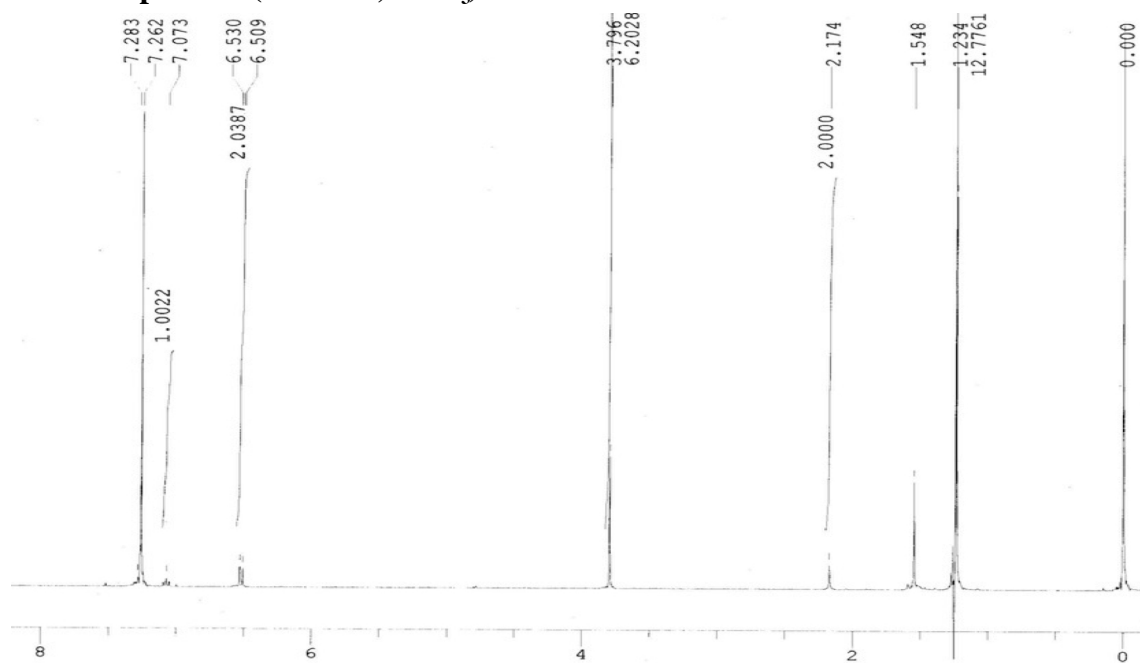
^{13}C NMR spectrum (125 MHz, CDCl_3)



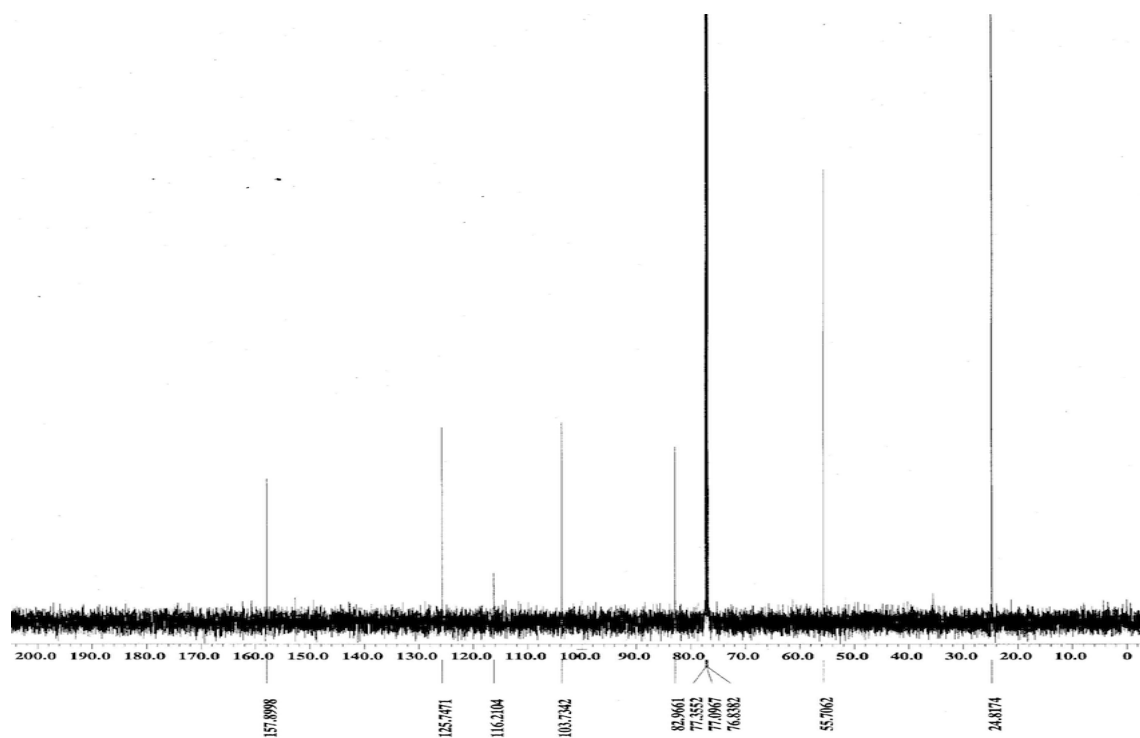


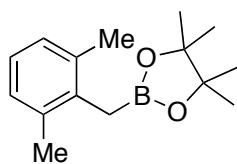
(31)

^1H NMR spectrum (400 MHz, CDCl_3)



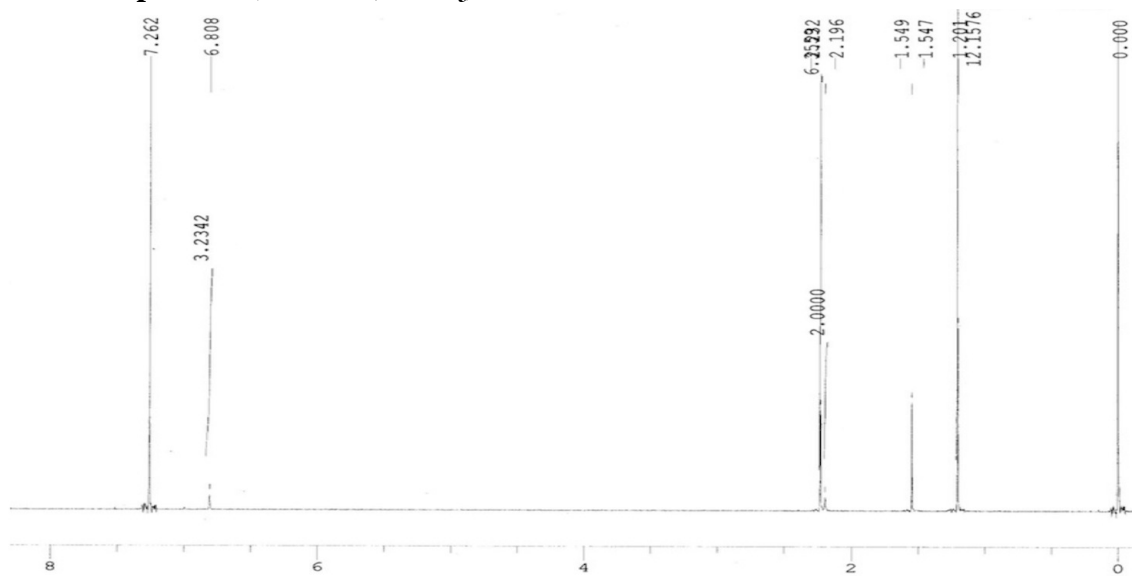
^{13}C NMR spectrum (100 MHz, CDCl_3)



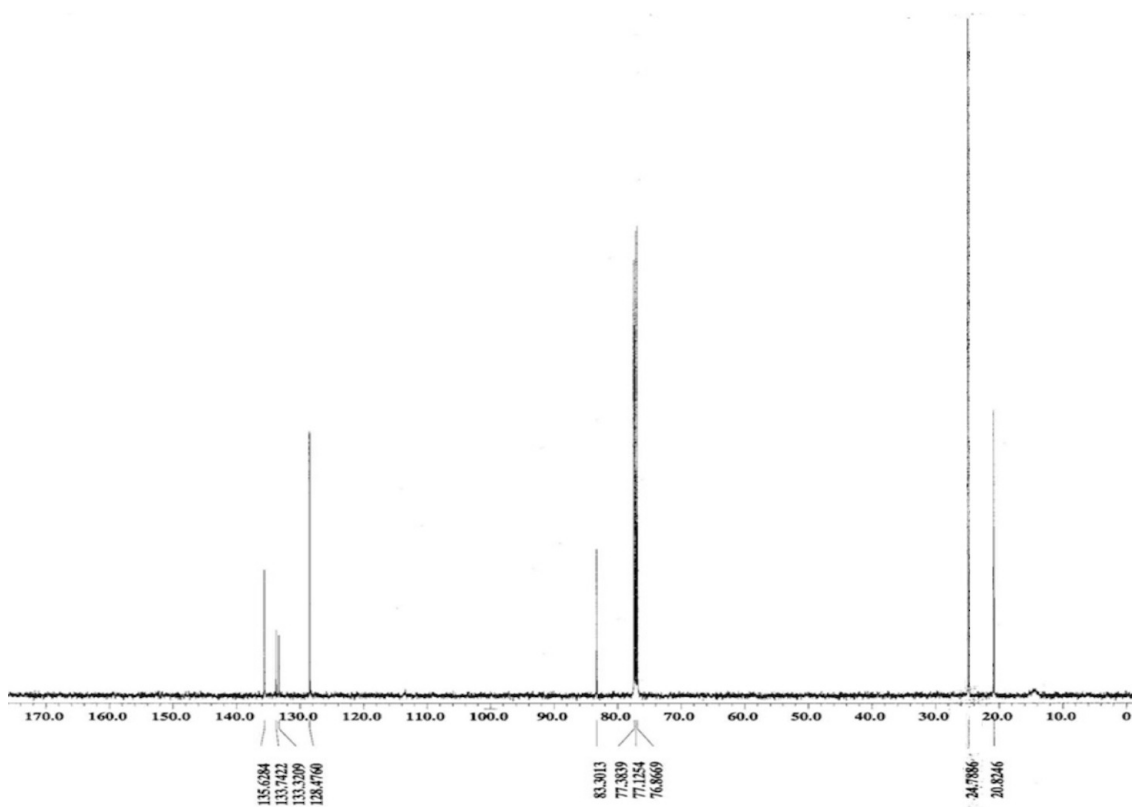


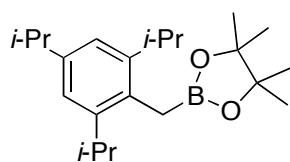
(3m)

^1H NMR spectrum (400 MHz, CDCl_3)



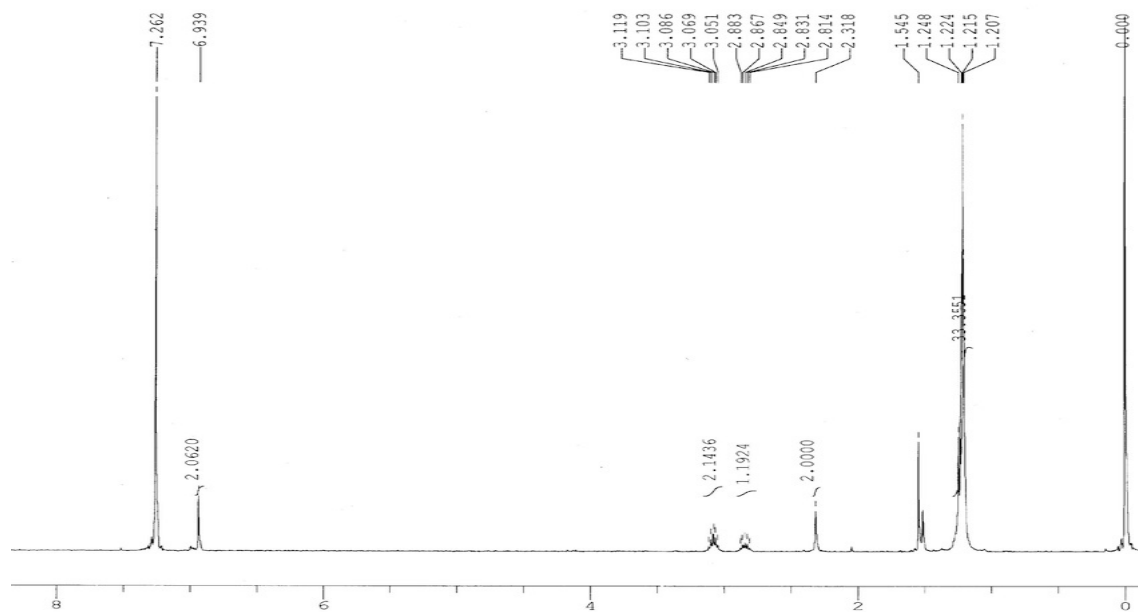
^{13}C NMR spectrum (100 MHz, CDCl_3)



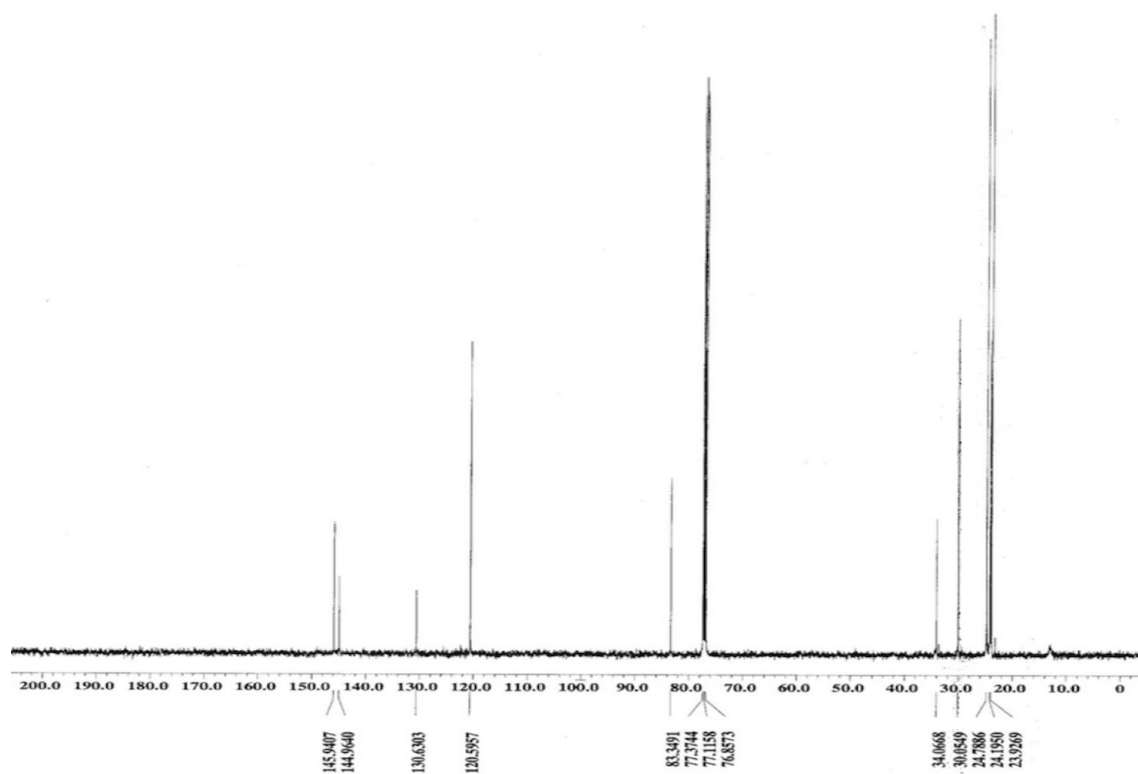


(3n)

^1H NMR spectrum (400 MHz, CDCl_3)



^{13}C NMR spectrum (100 MHz, CDCl_3)

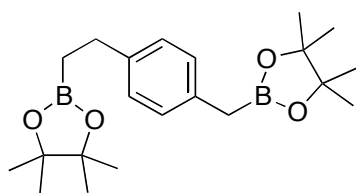




¹H NMR spectrum (CDCl₃) of compound 10a. The spectrum displays a complex multiplet in the aromatic region (7.2–8.0 ppm) with integration values of 1.06, 1.01, 0.94, and 1.02. A doublet at 2.65 ppm has an integration of 1.06, and a singlet at 2.48 ppm has an integration of 3. A reference peak for TMS is at 0.01 ppm. The x-axis is labeled from 0 to 8.0 ppm.

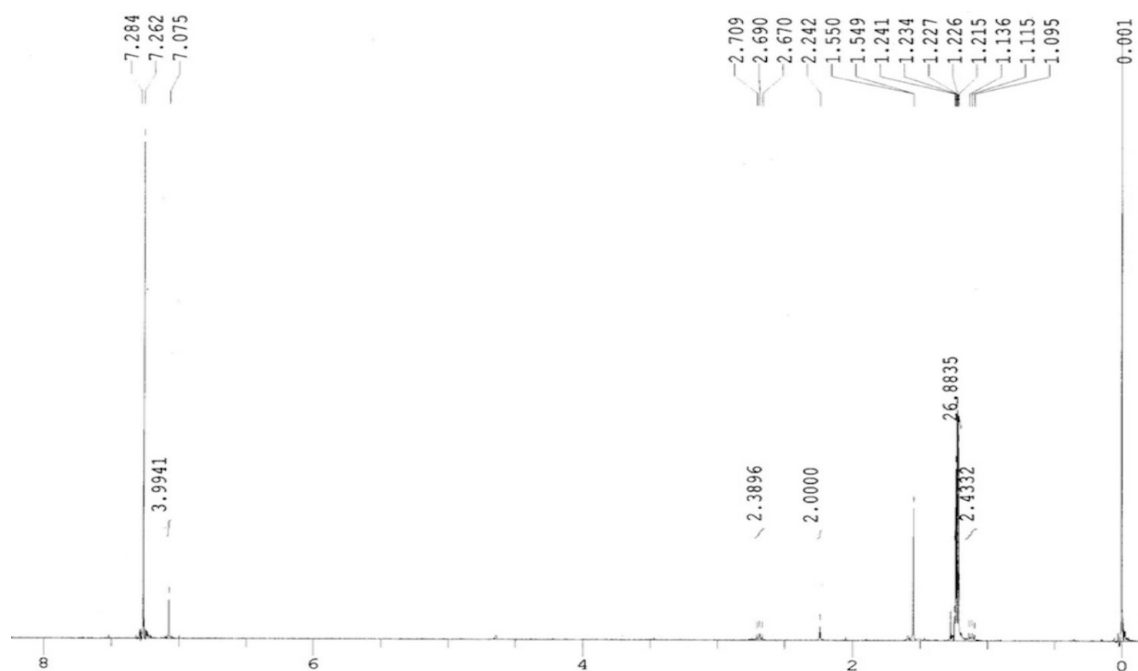
Mass spectrum of compound 10. The x-axis represents the mass-to-charge ratio (m/z) from 10 to 200. The y-axis represents relative intensity from 0 to 100. The base peak is at m/z 77. Other significant peaks are labeled with their m/z values.

| m/z | Relative Intensity (%) |
|----------|------------------------|
| 132.0953 | ~10 |
| 133.6602 | ~10 |
| 133.5740 | ~10 |
| 132.4591 | ~10 |
| 129.2036 | ~10 |
| 128.4185 | ~10 |
| 125.4790 | ~10 |
| 125.0064 | ~10 |
| 124.3304 | ~10 |
| 124.1576 | ~10 |
| 83.4449 | ~10 |
| 77.3648 | 100 |
| 77.1063 | ~10 |
| 76.8477 | ~10 |
| 24.7503 | ~10 |
| 21.2076 | ~10 |



(3p)

^1H NMR spectrum (400 MHz, CDCl_3)



^{13}C NMR spectrum (100 MHz, CDCl_3)

