Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Photocatalyzed Borylation Using Water Soluble Quantum Dots

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General consideration

Reagent Information. Unless otherwise stated, all reactions were carried out in screw cap reaction tubes, commercially available blue LED strips (λ_{ex} = 455 ± 15 nm) were used. All the solvents were bought from commercial sources and were used without further purification. Bis-pinacalotodiboron and anilines were purchased from Alfa Aesar and Aldrich. Silica gel (100–200 mesh) obtained from SRL Co. was used for column chromatography. A gradient elution using petroleum ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel $60F_{254)}$.

Cadmium acetate dihydrate ($Cd(OAC)_2.2H_2O$, Merck India, 98%), selenium powder (Sigma Aldrich, 99.5%), silver nitrate ($AgNO_3$, Sigma Aldrich, 98%), tetrabutyl ammonium perchlorate (TBAP, TCI), 1-octadecene (Sigma Aldrich, technical grade, 90%), oleic acid (OA, Sigma Aldrich, technical grade, 90%), trioctylphosphine (Sigma Aldrich, 90%), 3-mercaptopropionic acid (3-MPA, Sigma Aldrich, 99%), chloroform (Emplura, Merck India), hexane (Emplura, Merck India), acetonitrile (HPLC grade, Merck India) and ethanol (Absolute, Changshu Yangyuan, China) were used without further purification.

Analytical Information All compounds are characterized by ^{1}H NMR, ^{13}C NMR, ^{11}B NMR spectroscopy, and GC-MS. Copies of the ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra can be found in the Supporting Information. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 500 MHz / 400 MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to deuterochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. All the optimizations and yield calculations were done with Agilent 7890A GC system with an FID detector using a J & W DB–1 column (10 m, 0.1 mm I.D.) using *n*-decane as the internal standard.

The powder XRD measurements were performed with a Rigaku powder X-ray diffractometer having Cu Kα = 1.54059 Å radiation. TEM images were recorded with the DST-FIST facility, IISER Kolkata, JEOL, JEM-2100F. UV-Vis absorbance spectra of the QD dispersion were recorded using Jasco V-670 spectrophotometer. Room temperature PL spectra were recorded with Horiba Jobin Yovon Fluorolog using a Xe lamp as the excitation source with an excitation wavelength of 402 nm. PL decay measurements of QDs dispersed in chloroform were carried out using time correlated single-photon counting spectrofluorimeter from HORIBA Jobin Yvon IBH using a 402 nm laser as an excitation source and the curves were fitted with an iterative fitting program provided by IBH to calculate the fluorescence lifetime. The Fourier transform infrared measurements were performed with a Perkin Elmer spectrum RX1 with KBr pellets. Zeta potential measurement was carried out with Horiba Scientific nano partica Nano Particle Analyzer SZ-100. CV plots of all the QDs were recorded by using a three electrode setup electrochemical workstation having a scan rate 100 mV/s by using a potentiostat from Biologic.

Glassy carbon, platinum and Ag/0.01 M $AgNO_3$ + 0.1 M TBAP in acetonitrile were used as working, counter and the reference electrodes, respectively. To record the CVs, few drops of the diluted QD solution were drop casted onto the surface of the glassy carbon electrode and dried in air. 0.1 M TBAP dissolved into acetonitrile was used as the supporting electrolyte.

Description of Reaction Tube:

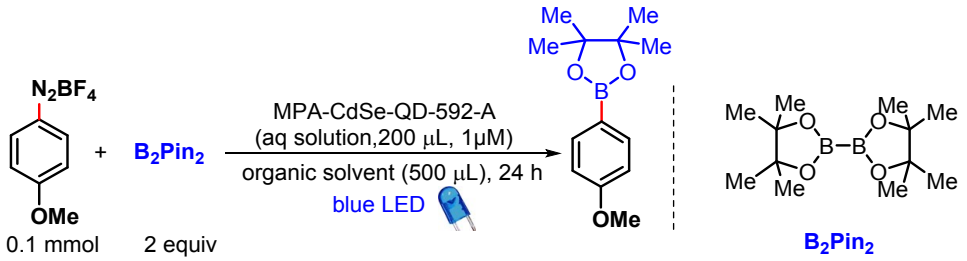
Figure S1. Pictorial description of reaction tube for borylation: Fisher brand Disposable Borosilicate Glass Tubes (16*125mm) with Threaded End (Fisher Scientific Order No.1495935A) [left]; Kimble Black Phenolic Screw Thread Closures with Open Tops (Fisher Scientific Order No. 033407E) [middle]; Thermo Scientific National PTFE/Silicone Septa for Sample Screw Thread Caps (Fisher Scientific Order No. 03394A) [right].

LED System used:

The reaction mixture was irradiated with commercially available blue LED strips (λ_{ex} = 455 ± 15 nm) throughout the experiment.

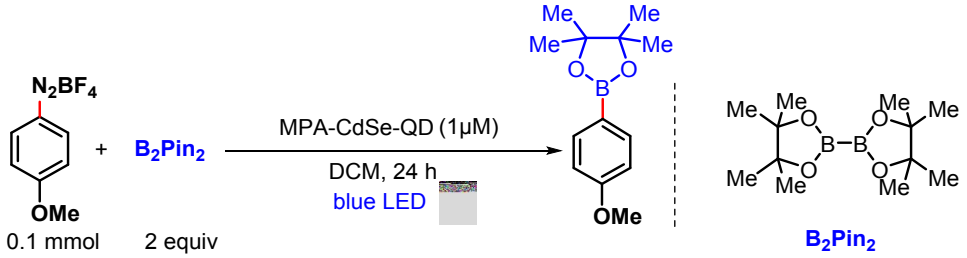
Optimization details

O.1 Optimization of solvents



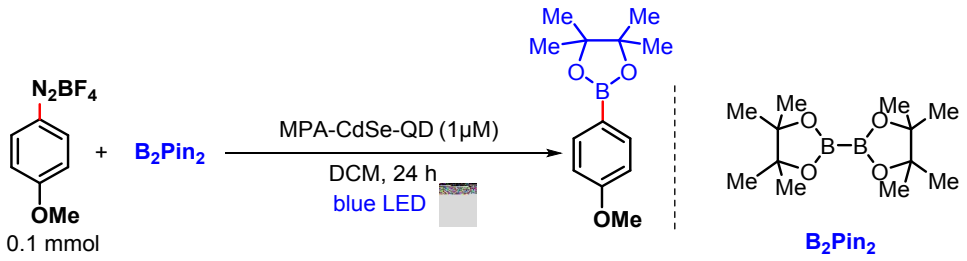
Entry	Solvent	GC-Yield (%)
1	Dichloromethane(DCM)	90
2	Acetone	67
3	Diethylether	43
4	Ethanol	40
5	Trifluorotoluene(TFT)	24
6	Acetonitrile(MeCN)	21
7	Toluene	17
8	Tertiarybutyl alcohol(^{t}Bu-OH)	16
9	Dimethylformamide(DMF)	11
10	Benzene	06
11	Water	08

O.2 Optimization of QD photocatalyst



Entry	λmax (nm)	GC-Yield (%)
QD-A	592	90
QD-B	534	61
QD-C	530	51
QD-D	512	45
QD-E	542	68
QD-F	602	72
QD-OA	592	32

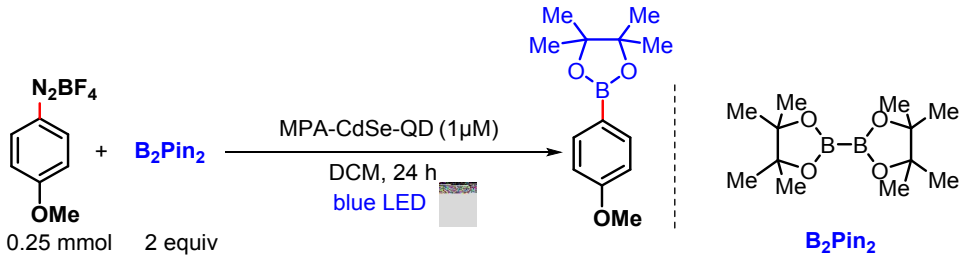
O.3 B_2pin_2 Equivalence Optimization



Concentration ($QD+H_2O$)	B_2pin_2 (in Eq)	GC-Yield (%)
200 µL	2.0	90
200 µL	1.5	52
200 µL	1.0	24
200 µL	0.5	11

General Procedures

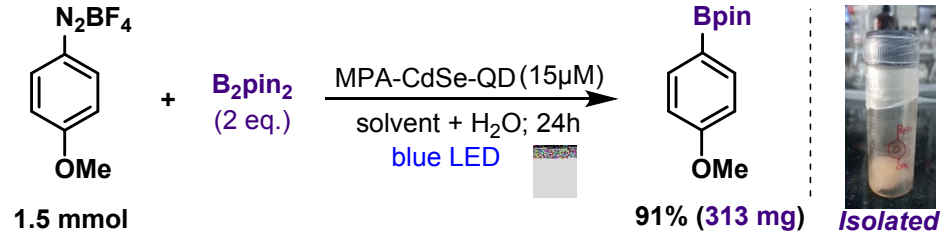
G.1 General procedure for the borylation of Aryldiazonium salts



Briefly, a typical procedure consisted of irradiating with blue LED strip lights of wavelength λ_{ex} = 455 ± 15 nm a stirred solution of an aryldiazonium tetrafloroboronate (0.25 mm), bis-pinacolatodiboron (B_2pin_2) (2.0eq), MPA-capped CdSe QDs (2 μM), 200 μL of water and dichloromethane (1.mL). Following the completion of the reaction after 20-24h, the mixture was diluted and extracted with ethyl acetate. The combined organic fraction was dried over anhydrous sodium sulphate and purified by column chromatography.

G.2 Scalability of the reaction

The scalability of the reaction was successfully tested in 1.5 mmol scale with 91% yield.



G.3 Synthesis of aryl diazonium tetraflouroborate salts

Arylamine (5 mmol) was dissolved in a mixture of 3.0 mL of distilled water and 3.0 mL of 45% hydrofluoroboric acid. After cooling the reaction mixture to 0 °C using ice bath and the sodium nitrite (0.35 g in 1 mL distilled water) was added dropwise over 5 mins. The resulting mixture was stirred for 1h and the precipitate was collected by filtration and re-dissolved in minimum amount of acetone. Diethyl ether was added until precipitation of aryl diazonium tetrafluoroborate, which is filtered, washed several times with diethyl ether and dried under vacuum**.**

G.4 Synthesis of CdSe QDs

The QDs were prepared as per a literature reported method with some modifications.[1] In a typical synthesis protocol, 0.5 mmol $Cd(OAc)_2.2H_2O$, 10 mL 1-octadecene and 2.5 mL oleic acid were loaded in a three necked round bottomed flask. The reaction mixture was cycled between

vacuum and N_2 three times at 80°C. Thereafter the temperature was increased to 220°C and allowed to stand for 15 min to form a clear and colourless Cd-oleate complex solution. The temperature was further increased to 270°C, whereby TOP:Se solution was swiftly injected into the Cd-oleate complex solution. The reaction temperature immediately dropped to 240°C and the colour of the solution changed from yellow to orange to red due to particle growth. The flask was allowed to cool down to the room temperature and the product was isolated by precipitation with ethanol followed by centrifugation. The resulting precipitates were washed multiple times with ethanol to remove unreacted precursors and finally dispersed in chloroform for further use. The diameter of the QDs was varied either by cooling the QD solution by ice quenching or by altering the reaction temperature from 270^{o}C to 285^{o}C.

TOP:Se precursor solution was prepared by dissolving 2mmol Se powder in 2 mL TOP under N_2 atmosphere

G.5 Preparation of water soluble MPA-capped CdSe QDs

The water soluble MPA capped QDs were prepared by replacing the long chain hydrophobic oleic acid group with short chain bi-functional linker molecules e.g. MPA by following our previous literature reported method.[2] At first, MPA solution was prepared by adding 100 µL MPA into a methanol and water mixture (3:1) followed by adjusting pH 12 by 5 M NaOH. To carry out the ligand exchange, the chloroform dispersion of QDs and MPA-methanol solution were taken into a container and stirred for 4 h. Post stirring, the mixture was washed with acetone to remove free MPA molecules and the product was re-dispersed in water for further use.

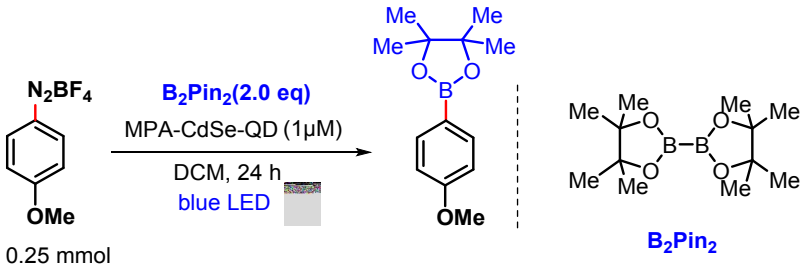
G.6 Control experiments

a) Borylation reaction

In a Fisher brand Disposable Borosilicate Glass Tubes (16*125mm) with Threaded End, Kimble Black Phenolic Screw Thread Closures with Open Tops equipped with magnetic stirring bar, solution of an aryldiazonium tetrafloroboronate (0.25 mm), bis-pinacolatodiboron (B_2pin_2) (2.0eq), MPA-capped CdSe QDs (2 µM), 200 µL of water, TEMPO (1.0 equivalent), BHT (ButylatedHydroxyPhenol 1.0 equivalent), $CuCl_2$ (1.0 equivalent) and dichloromethane (1.mL). The vial was irradiated using 450 nm blue LEDs with a cooling device maintaining a temperature around 25 °C. Following the completion of the reaction, the mixture was diluted and extracted with ethyl acetate. The combined organic fraction was dried over anhydrous sodium sulphate (Na_2SO_4). The crude product was analyzed by Mass Spectrometry.

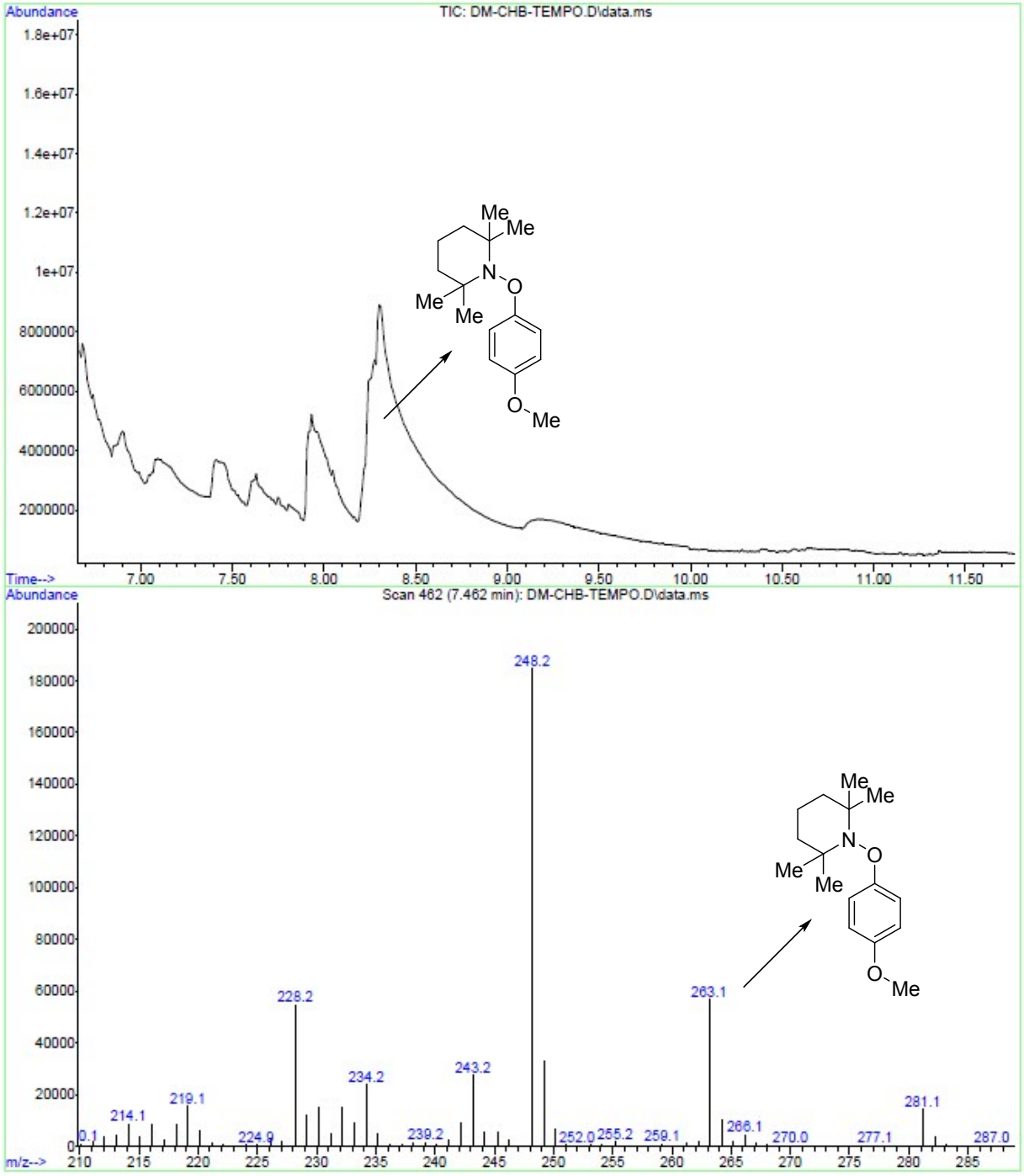
Note: Three batch of the reaction conducted individually using scavengers (TEMPO (1.0 equivalent), BHT (Butylatedhydroxyphenol 1.0 equivalent) and $CuCl_2$ (1.0 equivalent)

respectively) during the trapping experiment. TEMPO and BHT trapped adducts support the proposed radical pathway of the catalytic cycle.

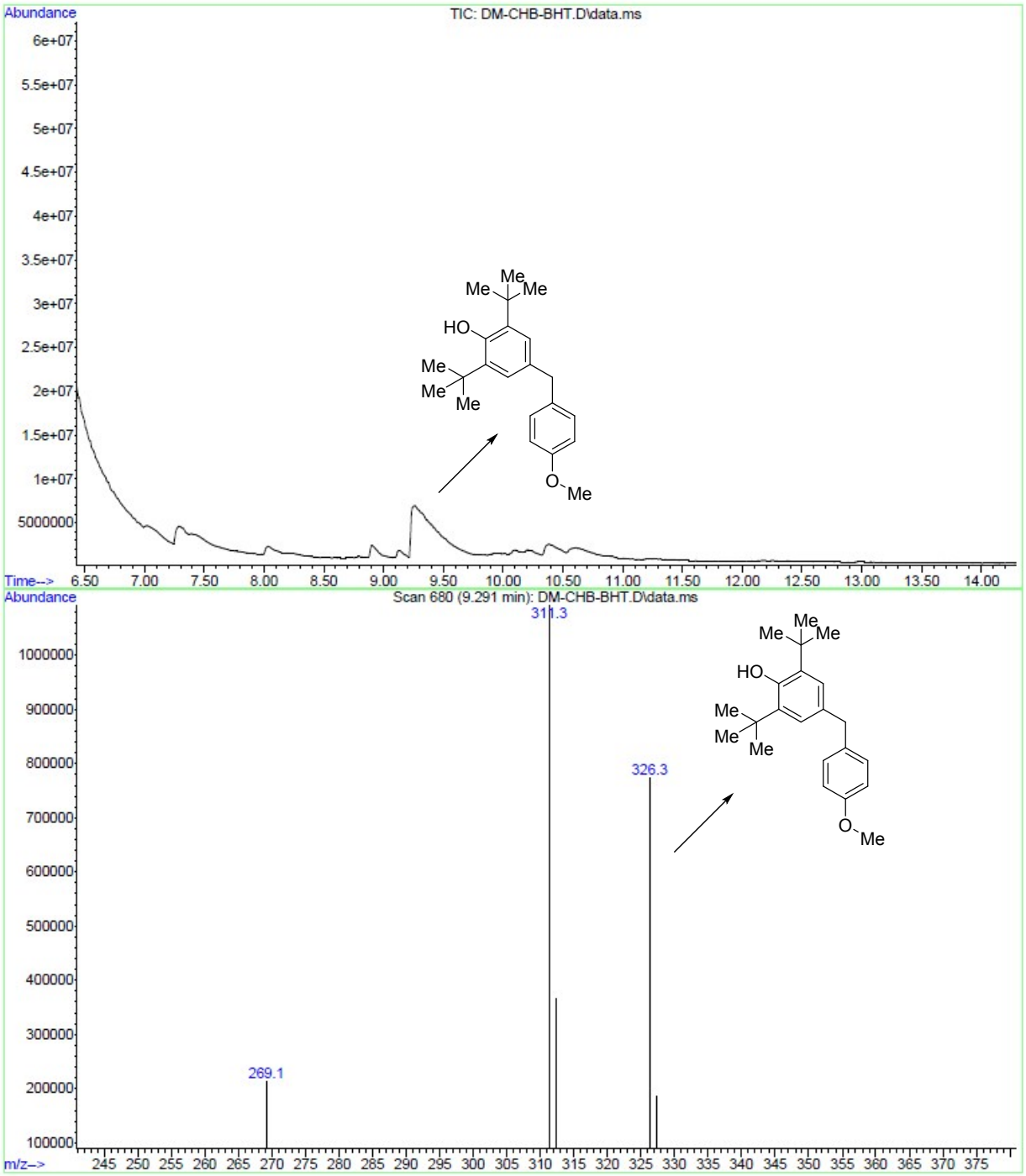


Entry	Conditions	GC-Yield (%)
1	Standard	90
2	Absence of QD	2
3	Absence of light	3
4	Absence of light and QD	4
5	TEMPO	2
6	BHT	5
7	$CuCl_2$	0

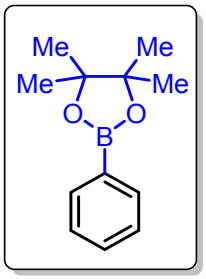
A. GCMS data of TEMPO-trapped aryl radical complex (263.1)



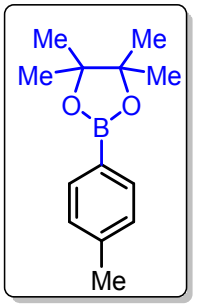
B. GCMS data of BHT-trapped aryl radical complex (326.3)



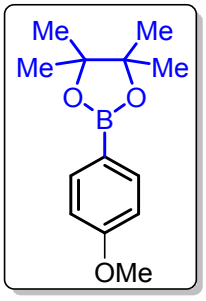
4. Spectral Details



4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (1a): Compound 1a was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **78%** (41 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.88 - 7.80 (m, 2H), 7.48 (d, *J* = 0.7 Hz, 2H), 7.42 - 7.37 (m, 1H), 1.37 (s, 12H) ppm **^{13}C NMR (126 MHz, $CDCl_3$) δ** 134.86, 131.37, 127.82, 83.87, 77.41, 77.16, 76.91, 24.98 ppm. **GCMS** (m/z) – 204.13

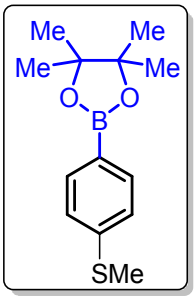


4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (1b): Compound 1b was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **68%** (48 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 2.38 (s, 3H), 1.35 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.52, 134.93, 128.64, 83.74, 77.41, 77.16, 76.91, 24.97, 21.84.
GCMS (m/z) – 218.14

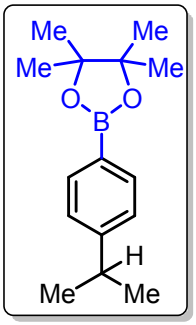


2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c): Compound 1c was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **90%** (53 mg). Isolated by column chromatography of the crude reaction mixture (silica gel,

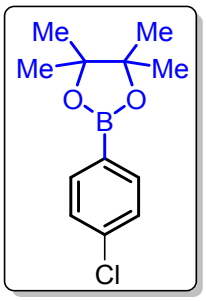
mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 – 7.73 (m, 2H), 6.94 – 6.87 (m, 2H), 3.82 (s, 3H), 1.34 (s, 12H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.27, 136.63, 113.43, 83.66, 77.48, 77.16, 76.84, 55.19, 24.97. **GCMS** (m/z) – 234.14



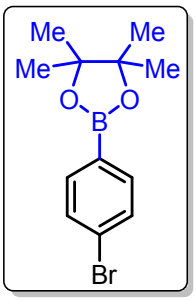
4,4,5,5-tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (1d) : Compound 1d was synthesized by following the general procedure (G.1).. Pure product was obtained as yellow oil in **65%** (40 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 2.48 (s, 3H), 1.34 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.69, 135.18, 125.11, 83.83, 77.41, 77.16, 76.91, 24.95, 15.15. **GCMS** (m/z) – 250.11



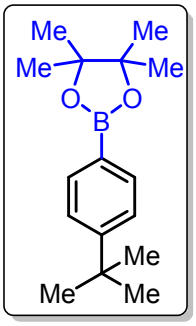
2-(4-isopropylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1e) : Compound 1e was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **69%** (43 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.37 (s, 12H), 1.29 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.41, 135.06, 126.02, 83.69, 77.41, 77.16, 76.91, 34.46, 24.95, 23.96. **GCMS** (m/z) – 246.17



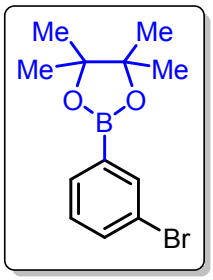
2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1f): Compound 1f was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **80%** (47.6 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 1.34 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.62, 136.24, 128.09, 84.08, 77.41, 77.16, 76.91, 24.94. **GCMS** (m/z) – 238.09



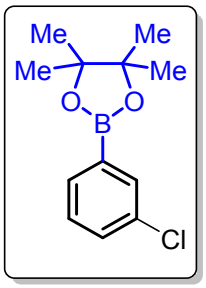
2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1g): Compound 1g was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **76%** (53.5 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 1.34 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.42, 131.05, 126.33, 84.12, 77.41, 77.16, 76.91, 24.95. **GCMS** (m/z) – 282.04



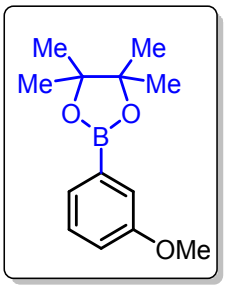
2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1h) : Compound 1h was synthesized by following the general procedure (G.1). Pure product was obtained as transparent solid in **61%** (40 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 1.36 (s, 12H), 1.35 (s, 9H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.61, 134.83, 124.82, 83.72, 77.41, 77.16, 76.91, 35.01, 31.33, 24.96. **GCMS** (m/z) – 260.19



2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1i): Compound 1i was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **61%** (43 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 0.8 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 1.34 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.58, 134.29, 133.21, 129.61, 122.55, 77.41, 77.16, 76.91, 24.96. **GCMS** (m/z) – 282.04

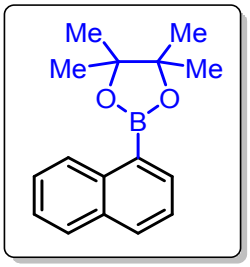


2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j): Compound 1j was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **60%** (37 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 1.1 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.42 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 1.35 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 134.68, 134.15, 132.78, 131.38, 129.31, 84.25, 77.41, 77.16, 76.91, 24.97.**GCMS** (m/z) – 238.09

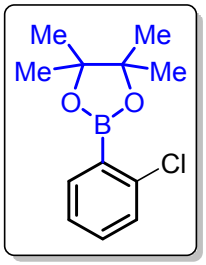


2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1k): Compound 1k was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **68%** (40 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 (d, *J* =

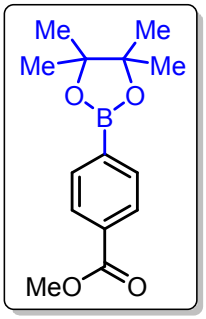
7.2 Hz, 1H), 7.40 (d, *J* = 2.6 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.12 – 7.05 (m, 1H), 3.91 (s, 3H), 1.42 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.16, 129.07, 127.31, 118.81, 118.04, 83.96, 77.48, 77.16, 76.84, 55.36, 24.98. **GCMS** (m/z) – 234.14



4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (1l) : Compound 1l was synthesized by following the general procedure (G.1). Pure product was obtained as yellow oil in **52%** (34 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 6.8 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.51 – 7.46 (m, 2H), 1.44 (s, 12H) **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.07, 135.78, 133.35, 131.74, 128.55, 128.48, 126.46, 125.61, 125.10, 83.87, 77.48, 77.16, 76.84, 25.10.**GCMS** (m/z) – 254.14

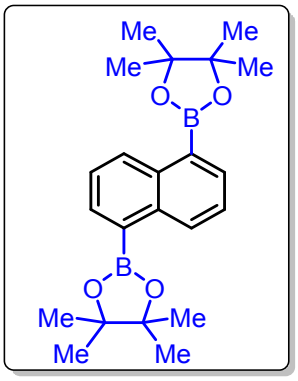


2-(2-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1m) Compound 1m was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **58%** (34.5 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (t, *J* = 5.8 Hz, 1H), 7.25 – 7.21 (m, 3H), 1.37 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.54, 131.98, 129.52, 125.95, 84.31, 77.41, 77.16, 76.91, 24.94. **GCMS** (m/z) – 238.09

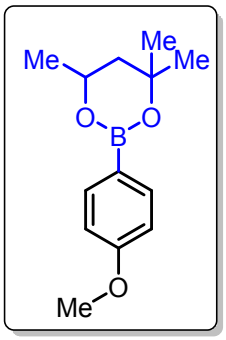


methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (1n) : Compound 1n was synthesized by following the general procedure (G.1). Pure product was obtained as white solid

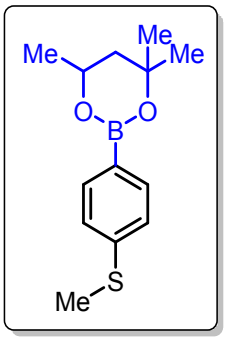
in **40%** (27 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 1.34 (s, 12H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.22, 134.76, 132.40, 128.69, 84.27, 77.48, 77.16, 76.84, 52.22, 24.97. **GCMS** (m/z) – 262.13



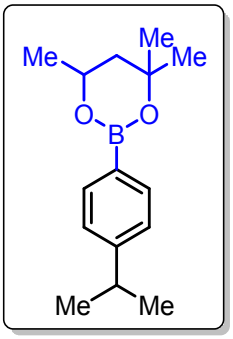
1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (1o) : Compound 1o was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **65%** (62 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.91 (d, *J* = 8.6 Hz, 2H), 8.09 (d, *J* = 6.1 Hz, 2H), 7.54 (dd, *J* = 8.3, 6.9 Hz, 2H), 1.45 (s, 24H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.73, 135.30, 131.97, 125.42, 83.70, 24.98. **GCMS** (m/z) – 380.23



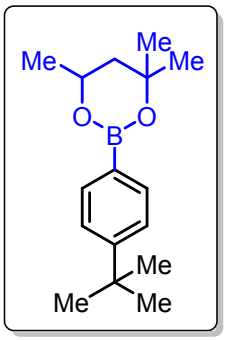
2-(4-methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2a) : Compound 2a was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **84%** (49 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.32 (dqd, *J* = 12.3, 6.2, 3.0 Hz, 1H), 3.82 (s, 3H), 1.85 (dd, *J* = 13.9, 2.9 Hz, 1H), 1.57 (d, *J* = 4.6 Hz, 1H), 1.36 (d, *J* = 4.5 Hz, 6H), 1.33 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.64, 135.56, 113.14, 77.48, 77.16, 76.84, 70.94, 64.99, 55.20, 46.22, 31.49, 28.31, 23.42. **GCMS** (m/z) – 234.14



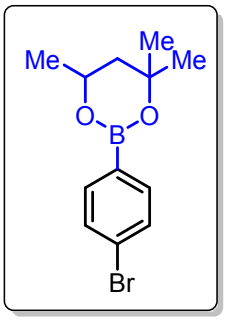
4,4,6-trimethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborinane (2b) Compound 2b was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **69%** (43 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 4.33 (dqd, *J* = 12.3, 6.2, 2.9 Hz, 1H), 2.48 (s, 3H), 1.85 (dd, *J* = 13.9, 2.9 Hz, 1H), 1.56 (d, *J* = 11.4 Hz, 1H), 1.36 (d, *J* = 4.5 Hz, 6H), 1.33 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.16, 134.31, 125.28, 77.48, 77.16, 76.84, 71.12, 65.11, 46.19, 31.44, 28.31, 23.36, 15.49.**GCMS** (m/z) – 250.11



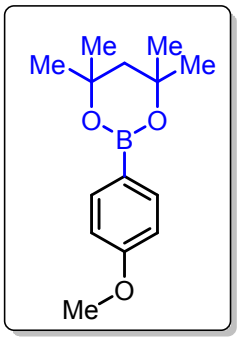
2-(4-isopropylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2c) : Compound **2c** was synthesized by following the general procedure (G.1). Pure product was obtained as yellow oil in **62%** (62.5 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 4.34 (dqd, *J* = 12.2, 6.1, 3.0 Hz, 1H), 2.96 – 2.85 (m, 1H), 1.86 (dd, *J* = 13.8, 2.9 Hz, 1H), 1.56 (d, *J* = 14.3 Hz, 1H), 1.37 (d, *J* = 7.3 Hz, 6H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 6H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.37, 134.03, 125.76, 77.41, 77.16, 76.91, 70.95, 65.01, 46.24, 34.39, 31.46, 28.28, 24.06, 24.05, 23.41.**GCMS** (m/z) – 246.17



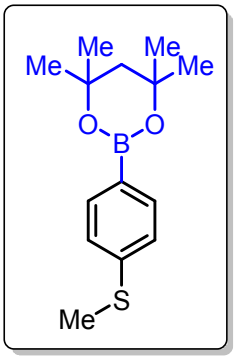
2-(4-(tert-butyl)phenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2d) : Compound 2d was synthesized by following the general procedure (G.1). Pure product was obtained as yellow oil in **68%** (44 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 4.36 (dqd, *J* = 12.2, 6.1, 3.0 Hz, 1H), 1.87 (dd, *J* = 13.9, 2.9 Hz, 1H), 1.57 (d, *J* = 13.5 Hz, 1H), 1.38 (d, *J* = 6.5 Hz, 9H), 1.34 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.45, 133.84, 124.50, 77.41, 77.16, 76.91, 70.76, 49.15, 34.86, 31.97, 31.40. **GCMS** (m/z) – 260.19



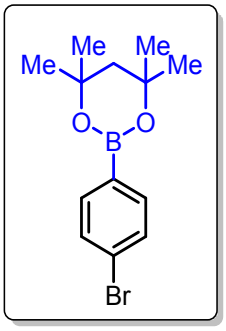
2-(4-bromophenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2e) : Compound 2e was synthesized by following the general procedure (G.1). Pure product was obtained as yellow oil in **70%** (50 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 4.33 (dqd, *J* = 12.2, 6.2, 2.9 Hz, 1H), 1.86 (dd, *J* = 13.9, 2.9 Hz, 1H), 1.57 (d, *J* = 13.9 Hz, 1H), 1.37 (d, *J* = 6.4 Hz, 6H), 1.34 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.59, 130.73, 125.30, 77.48, 77.16, 76.84, 71.33, 65.24, 46.10, 31.37, 29.84, 28.28, 23.29. **GCMS** (m/z) – 282.04



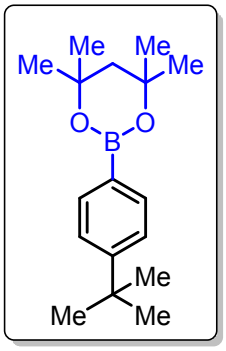
2-(4-methoxyphenyl)-4,4,6,6-tetramethyl-1,3,2-dioxaborinane (3a) : Compound 3a was synthesized by following the general procedure (G.1). Pure product was obtained as yellow oil in **90%** (56 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 1.90 (s, 1H), 1.42 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.63, 135.62, 113.12, 77.48, 77.16, 76.84, 70.76, 55.20, 49.16, 31.99. **GCMS** (m/z) – 248.15



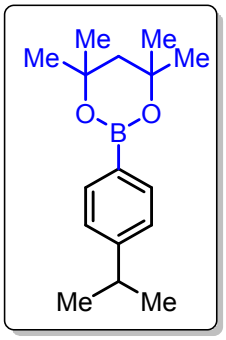
2-(4-methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (3b) : Compound 3b was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **60%** (39.6 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 2.48 (s, 3H), 1.90 (s, 2H), 1.41 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.08, 134.38, 125.34, 77.48, 77.36, 77.16, 76.84, 70.94, 49.15, 31.97, 29.85, 22.84, 15.57. **GCMS** (m/z) – 264.13



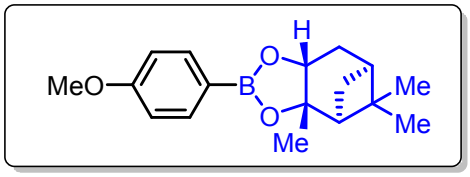
2-(4-bromophenyl)-4,4,6,6-tetramethyl-1,3,2-dioxaborinane (3c) : Compound 3c was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **68%** (50.4 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 1.91 (s, 2H), 1.42 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.65, 130.70, 125.24, 77.48, 77.16, 76.84, 71.16, 49.06, 31.9
GCMS (m/z) – 296.05



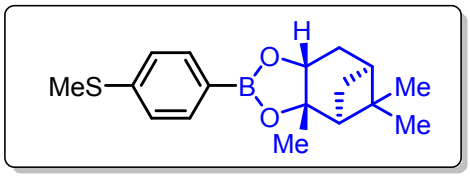
2-(4-(tert-butyl)phenyl)-4,4,6,6-tetramethyl-1,3,2-dioxaborinane (3d) : Compound 3d was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **72%** (49.3 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 (dd, *J* = 4.4, 3.7 Hz, 2H), 7.46 – 7.35 (m, 2H), 1.92 (s, 2H), 1.44 (s, 12H), 1.35 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.33, 134.09, 125.74, 77.41, 77.16, 76.91, 70.79, 49.17, 34.41, 31.98, 24.08. **GCMS** (m/z) – 274.21



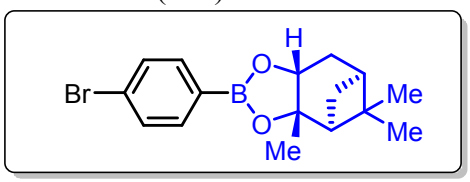
2-(4-isopropylphenyl)-4,4,6,6-tetramethyl-1,3,2-dioxaborinane (3e) : Compound 3e was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **73%** (47.4 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.95 – 2.84 (m, 1H), 1.90 (s, 2H), 1.41 (s, 12H), 1.24 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.33, 134.09, 125.74, 77.41, 77.16, 76.91, 70.79, 49.17, 34.41, 31.98, 24.08. **GCMS** (m/z) – 260.19



(3aS,4S,6S,7aR)-2-(4-methoxyphenyl)-3a,5,5-trimethylhexahydro-4,6 methanobenzo[d][1,3,2]dioxaborole (4a) : Compound 4a was synthesized by following the general procedure (G.1). Pure product was obtained as yellow thick liquid in **92%** (65.8 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.44 (dd, *J* = 8.8, 1.8 Hz, 1H), 3.83 (s, 3H), 2.42 (ddt, *J* = 11.2, 8.7, 2.2 Hz, 1H), 2.23 (dtd, *J* = 8.3, 6.0, 2.0 Hz, 1H), 2.15 (t, *J* = 5.5 Hz, 1H), 2.05 – 1.88 (m, 2H), 1.48 (s, 3H), 1.32 (s, 3H), 1.23 (d, *J* = 10.9 Hz, 1H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.23, 136.65, 113.49, 86.16, 78.26, 77.48, 77.16, 76.84, 55.19, 51.61, 39.69, 38.31, 35.76, 28.86, 27.24, 26.62, 24.17. **GCMS** (m/z) – 286.17

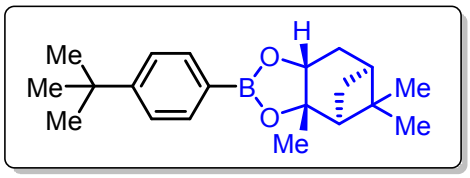


(3aS,4S,6S,7aR)-3a,5,5-trimethyl-2-(4-(methylthio)phenyl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (G.1). Compound 4b was synthesized by following the general procedure (v). Pure product was obtained as white solid in **65%** (49 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.44 (d, *J* = 8.4 Hz, 1H), 2.49 (s, 3H), 2.26 – 2.19 (m, 1H), 2.14 (t, *J* = 5.5 Hz, 1H), 1.95 (dd, *J* = 12.3, 9.9 Hz, 2H), 1.48 (s, 3H), 1.31 (s, 3H), 1.20 (d, *J* = 10.9 Hz, 1H), 0.89 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.25, 125.20, 86.39, 78.36, 77.16, 51.56, 39.66, 38.35, 35.71, 28.84, 27.25, 26.63, 24.20, 15.20. **GCMS** (m/z) – 302.15

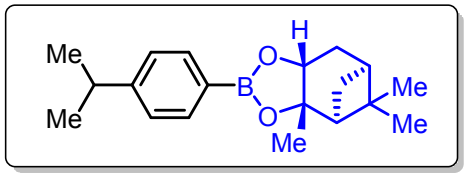


(3aS,4S,6S,7aR)-2-(4-bromophenyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (4c) : Compound 4c was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **76%** (63.4 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2).

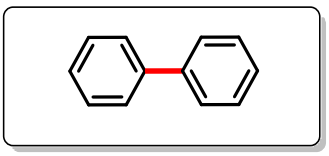
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 4.45 (dd, *J* = 8.7, 1.7 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.28 – 2.19 (m, 1H), 2.14 (t, *J* = 5.5 Hz, 1H), 1.96 (dt, *J* = 8.6, 3.5 Hz, 2H), 1.48 (s, 3H), 1.32 (s, 3H), 1.18 (d, *J* = 11.0 Hz, 1H), 0.89 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.49, 131.14, 126.30, 86.65, 78.53, 77.48, 77.16, 76.84, 51.51, 39.64, 38.34, 35.62, 28.80, 27.22, 26.61, 24.18.
GCMS (m/z) – 334.07



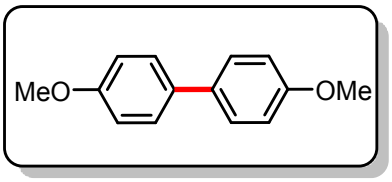
(3aS,4S,6S,7aR)-2-(4-(tert-butyl)phenyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (4d) Compound 4d was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **76%** (63 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 4.45 (dd, *J* = 8.8, 1.4 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.22 (ddd, *J* = 8.0, 6.2, 3.2 Hz, 1H), 2.16 (t, *J* = 5.5 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.47 (s, 3H), 1.33 (s, 9H), 1.31 (s, 3H), 1.22 (d, *J* = 10.9 Hz, 1H), 0.89 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.56, 134.86, 124.89, 86.24, 78.30, 77.41, 77.16, 76.91, 51.57, 39.70, 38.34, 35.80, 35.03, 31.34, 28.88, 27.26, 26.65, 24.21. **GCMS** (m/z) – 312.22



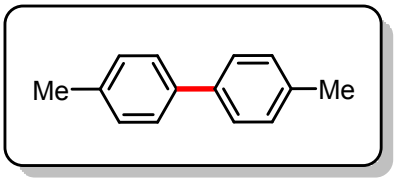
(3aS,4S,6S,7aR)-2-(4-isopropylphenyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (4e) Compound 4e was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **70%** (52.8 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 6.2 Hz, 2H), 4.44 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.92 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.27 – 2.18 (m, 1H), 2.17 – 2.13 (m, 1H), 1.95 (ddd, *J* = 12.2, 5.4, 2.9 Hz, 2H), 1.48 (s, 3H), 1.31 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.22 (d, *J* = 10.8 Hz, 1H), 0.89 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.38, 135.10, 126.11, 86.24, 78.30, 77.41, 77.16, 76.91, 51.57, 39.69, 38.34, 35.79, 34.48, 28.87, 27.26, 26.64, 24.21, 23.99, 23.97. **GCMS** (m/z) – 298.21



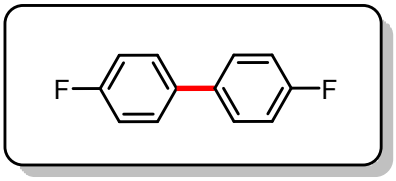
1,1'-biphenyl (5a) Compound 5a was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **87%** (35 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 – 7.64 (m, 4H), 7.51 (dd, *J* = 10.6, 4.8 Hz, 4H), 7.41 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR (126 MHz, CDCl3)** δ 141.36, 128.88, 127.38, 127.29, 77.41, 77.16, 76.91. **GCMS** (m/z) – 157.07



4,4'-dimethoxy-1,1'-biphenyl (5b) Compound 5b was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **90%** (48 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50 (d, J = 8.8 Hz, 4H), 6.98 (d, J = 8.8 Hz, 4H), 3.86 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.80, 133.59, 127.85, 114.28, 77.41, 77.16, 76.91, 55.45. **GCMS** (m/z) – 214.09



4,4'-dimethyl-1,1'-biphenyl (5c) Compound 5c was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **91%** (41.4 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 (d, J = 8.0 Hz, 4H), 7.24 (d, J = 7.9 Hz, 4H), 2.39 (s, 6H).
13C NMR (126 MHz, $CDCl_3$) δ 138.45, 136.84, 129.57, 126.96, 77.41, 77.16, 76.91, 21.21.**GCMS** (m/z) – 182.10



4,4'-difluoro-1,1'-biphenyl (5d) Compound 5d was synthesized by following the general procedure (G.1). Pure product was obtained as white solid in **59%** (28 mg). Isolated by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.52 – 7.47 (m, 4H), 7.13 (t, J = 8.6 Hz, 4H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.54, 161.58, 136.53, 136.51, 128.74, 128.67, 115.90, 115.73, 77.41, 77.16, 76.91.
GCMS (m/z) – 190.05

5. Characterization data of Quantum Dots (QDs)

D.1 Structural and Optical characterization of QDs

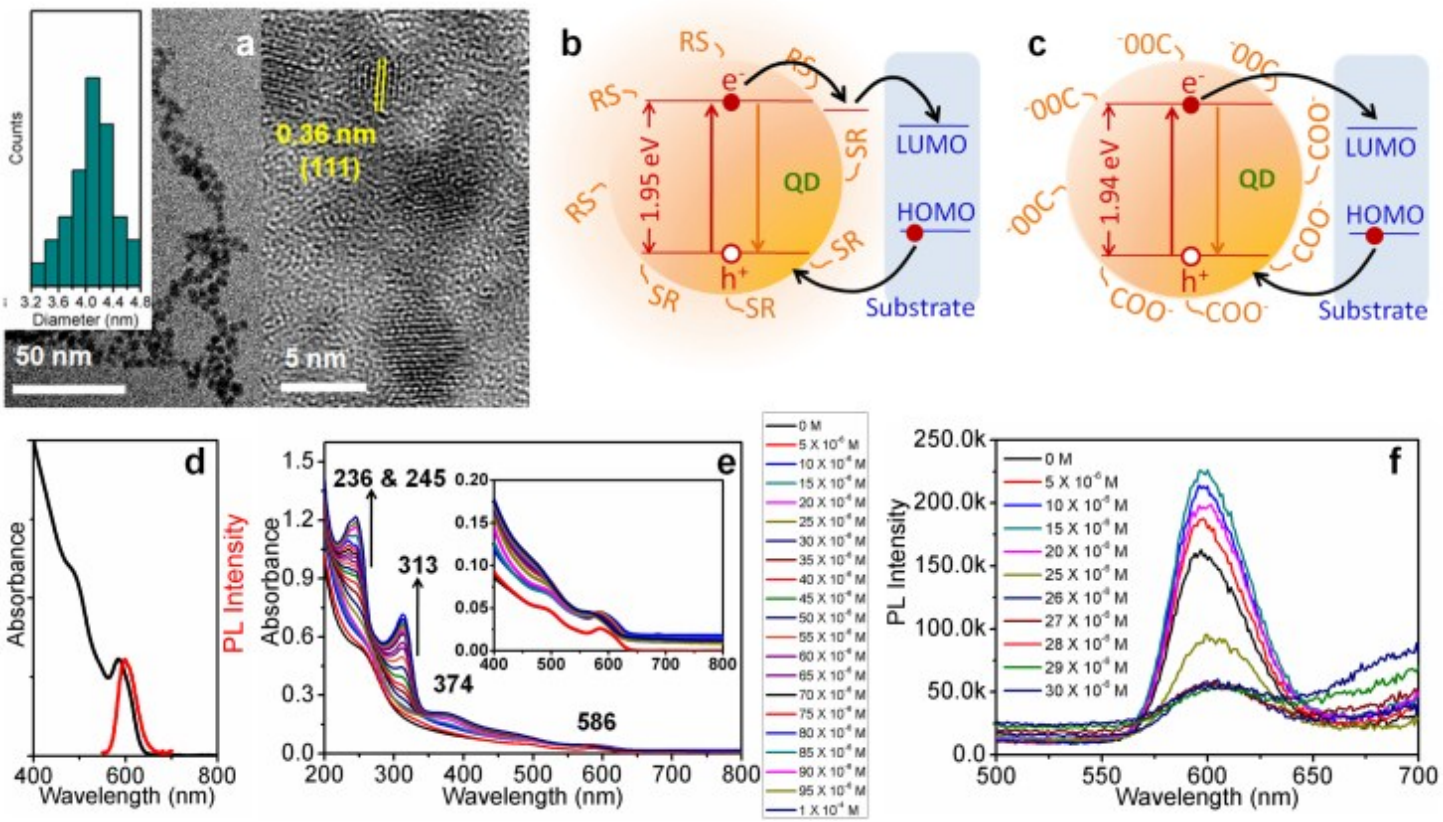


Figure 1. (a) Low and high resolution transmission electron micrographs (TEM) images of QD-592-MPA with diameter histogram in the inset. Schematics of electron transfer with (b) QD-592-MPA and (c) QD-592-OA. (d) Absorption and emission spectra of QD-592-MPA. Intensity variation of (e) absorbance and (f) emission bands of QD-592-MPA with changing substrate concentration. Inset (e) shows the enlarged view of the 586 nm emission band

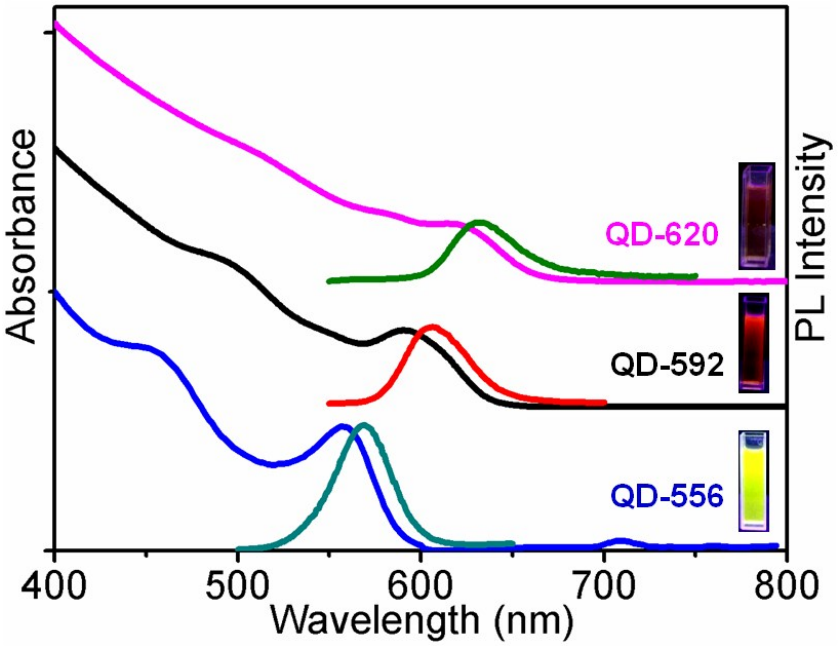


Figure S1: UV and PL spectra of OA-capped QDs with different sizes. Insets show the digital photographs of the QDs in presence of UV light.

OA-capped QDs show a broad light harvesting ability from UV to visible region and the excitonic bands depend on the cooling procedures of the reaction bath. The QDs prepared at 270^{o}C and cooled by ice quenching have an excitonic band at 556 nm, while those cooled normally from 270^{o}C and 285^{o}C show bands at 592 and 620 nm, respectively. Thereby the QDs are designated as QD-556, QD-592 and QD-620, which have photoluminescence (PL) emission maxima at 569, 605 and 632 nm, respectively. The QD size calculated from the absorbance spectra are 3.2, 4.2 and 5.6 nm, respectively.

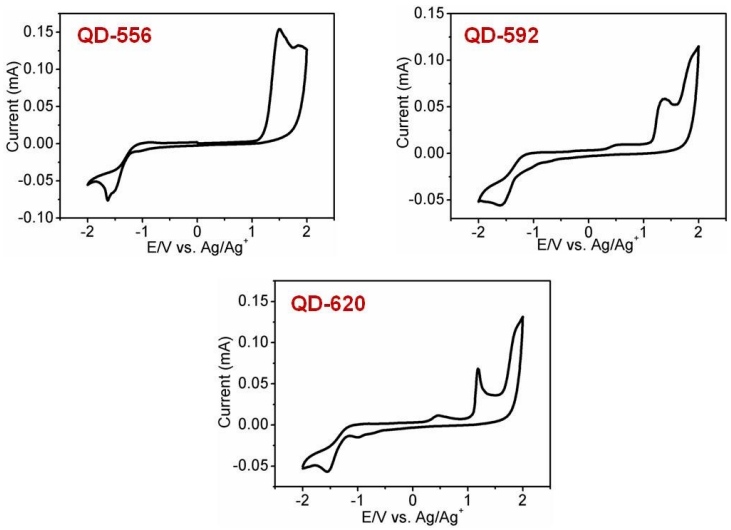


Figure S2: Cyclic voltammograms of differently sized QDs.

Table S1: Band position calculation from cyclic voltammetry

Sample Code	E_{OX} (onset) (V)	E_{VB} (eV)	E_g (UV) (eV)	E_{CB} (eV)
QD-556	1.25	-5.96	2.11	-3.85
QD-592	1.17	-5.88	1.94	-3.94
QD-620	1.12	-5.83	1.87	-3.96

The position of the valence band (VB) and conduction band (CB) energy levels of the QDs were calculated according to the following equations:

$$E_{HOMO} = -(E_{OX} + 4.71)\, eV \quad \text{(S1)}$$

$$E_{LUMO} = (E_{HOMO} + E_g)\, eV \quad \text{(S2)}$$

The calculated band gaps are 2.11, 1.94 and 1.87 eV for QD-556, QD-592 and QD-620, respectively.

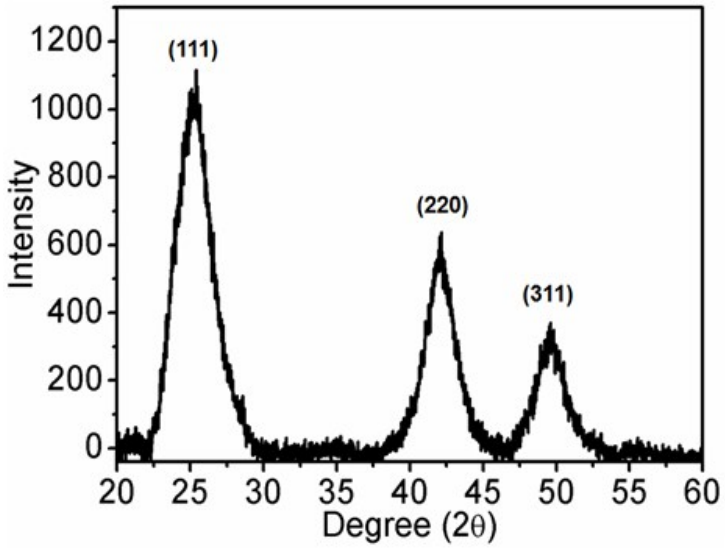


Figure S3: Powder XRD pattern of CdSe QDs.

The QDs crystallize in zinc blende crystal structure with space group $F\bar{4}3m$ according to the JCPDS pattern 01-088-2346.

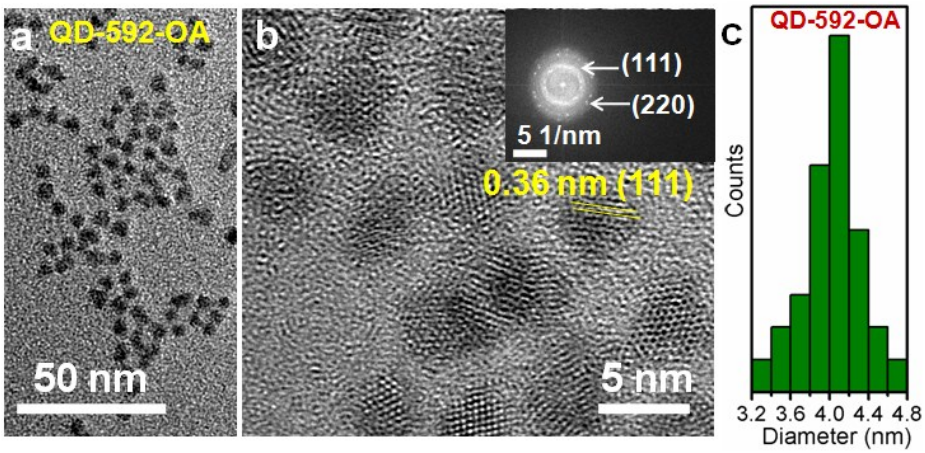


Figure S4: (a) Low and (b) high resolution TEM images of QD-592-OA. Inset of (b) shows the SAED pattern of the QDs. (c) Diameter histograms of QD-592-OA.

Both the OA-capped QD-592-OA (Figure S4) and MPA-capped QD-592-MPA (Figure 1a) crystalline QDs have an average diameter of ~4 nm and are highly monodisperse.

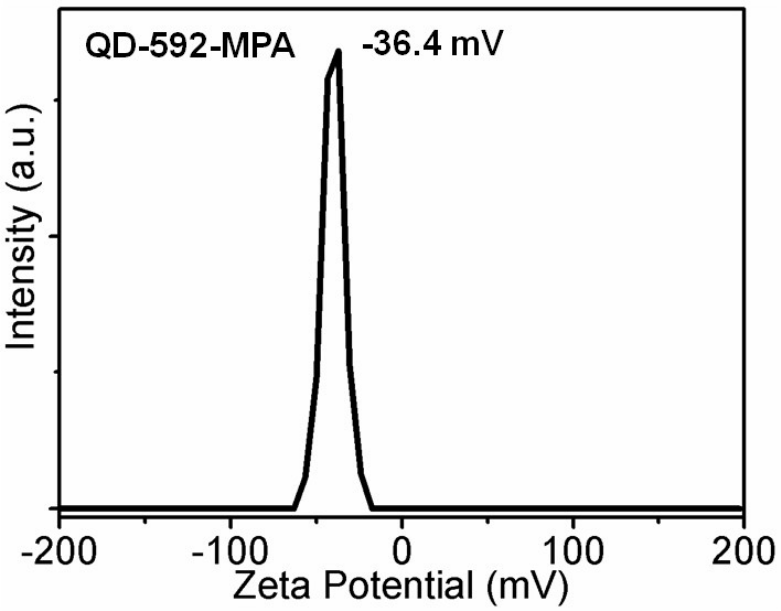


Figure S5: Zeta potential of QD-592-MPA.

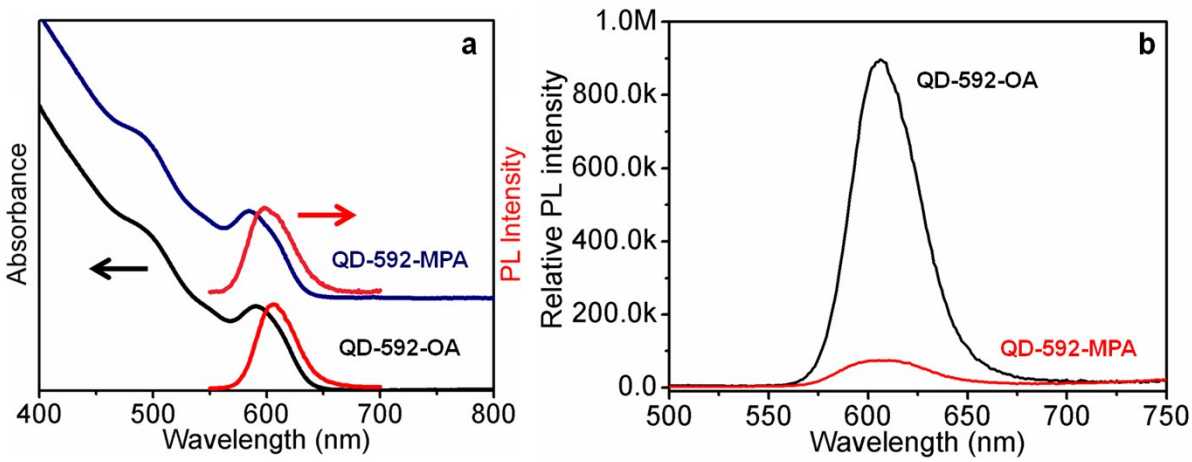


Figure S6: (a) UV and PL spectra of CdSe-592 QDs before (QD-592-OA) and after ligand exchange (QD-592-MPA). (b) Relative PL intensity plot of QD-592 before and after ligand exchange.

MPA ligand exchange results in a blue shift of both absorption and PL spectra (Figure S6a) due to redistribution of electron density. This is well validated from the transfer of excited electrons from QD conduction band (CB) to the MPA shell resulting in PL intensity quenching as compared to the OA-capped QDs (Figure S6b), and thereby the quantum yield of QD-592-OA and QD-592-MPA QDs are 4.1% and 0.003%, respectively.

D.2 Quantum Yield (QY) Measurement

Calculation of QY of QD-592-OA and QD-592-MPA using Rhodamine 6GG as the standard

QY was measured with the help of a standard dye rhodamine 6G and calculated according to the following formula:

$$(QY)_S = (QY)_R \frac{\eta_S^2 I_S A_S}{\eta_R^2 A_R I_R}$$

Here,

$(QY)_S$ = QY of the sample

$(QY)_R$ = QY of the reference

η_S = Refractive Index of the sample

η_R = Refractive Index of the reference

I_R = Integrated fluorescence Intensity of the reference

I_S = Integrated fluorescence Intensity of the sample

A_R = Absorbance of reference at the excitation wavelength

A_S = Absorbance of sample at the excitation wavelength

D.2 IR spectral data

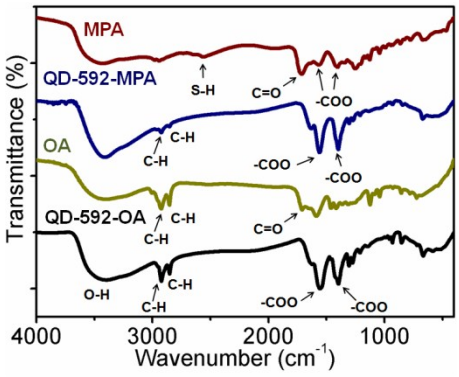


Figure S7: Infrared (IR) spectra of OA, MPA, QD-592-OA and QD-592-MPA.

IR spectral data indicates the attachment surface ligand to the surface of QDs through their sulfur atoms and also confirms the replacement of OA with MPA to the QD surface through the absence of ν_{S-H} at ~ 2553 cm^{-1} in MPA-capped QDs (Figure S7 and Table S2).

Table S2: IR stretching frequencies of different functional groups

Wave Number (cm^{-1})	**Functional Groups**
2553	S-H
1718	C=O stretching
~3400	O-H stretching
1556-1585	COO- (Asymmetric stretching)
1402	COO- (symmetric stretching)
2925	C-H (Asymmetric stretching)
2849	C-H (symmetric stretching)

D.3 Absorbance Measurements

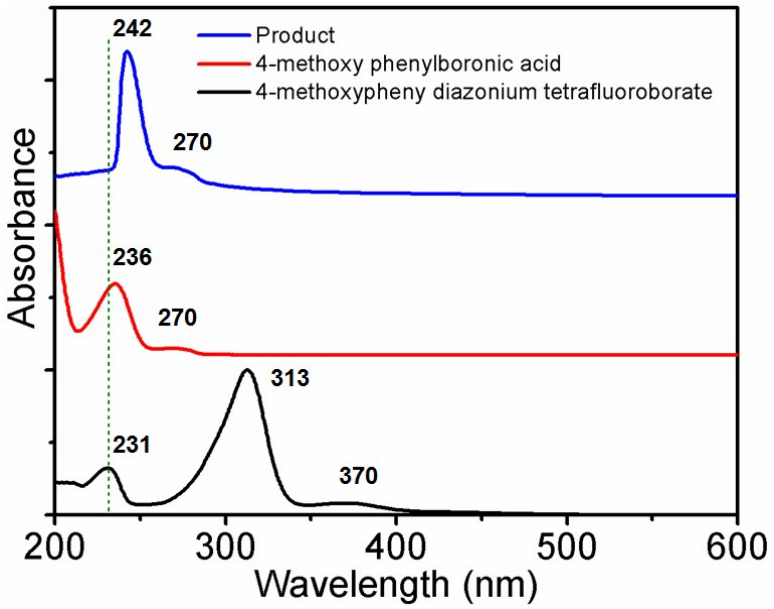


Figure S8: Absorbance spectra of 4-methoxy phenyl diazonium tetrafluoroborate salt (substrate), 4-methoxy phenyl boronic acid and the product.

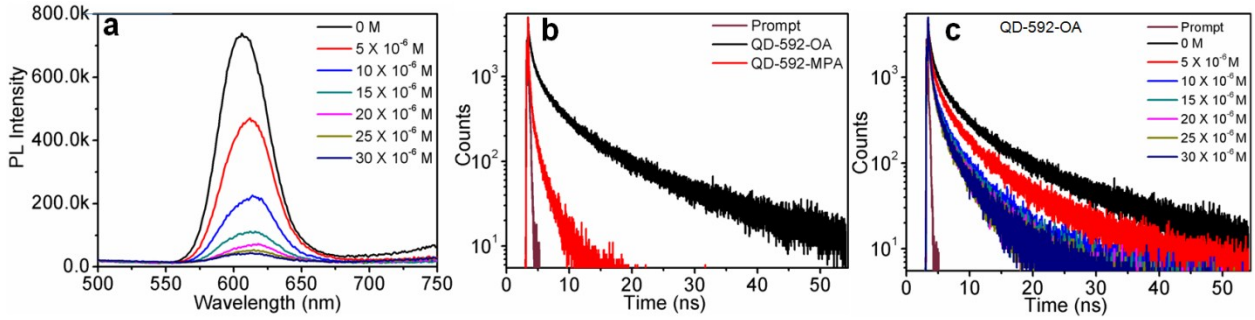


Figure S9: (a) PL spectra of QD-592-OA by varying concentration of 4-methoxy phenyl diazonium tetrafluoroborate salt. PL lifetime decay plots of (b) QD-592-OA and QD-592-MPA, and (c) QD-592-OA at different substrate concentration. In case of QD-592-OA, PL intensity rapidly decreases with increasing substrate concentration due to electron transfer from CdSe CB to the LUMO of substrate.

The PL decay curves were fitted with the following tri-exponential equation:

$$I(t) = A_1 exp\left(-\frac{t}{\tau_1}\right) + A_2 exp\left(-\frac{t}{\tau_2}\right) + A_3 exp\left(-\frac{t}{\tau_3}\right) \quad \text{(S3)}$$

The average lifetime was calculated by the following equation:

$$< \tau_{ava} >= \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3} \quad \text{(S4)}$$

Here, A_1, A_2 and A_3 denote the contribution of τ_1, τ_2 and τ_3 components; respectively.

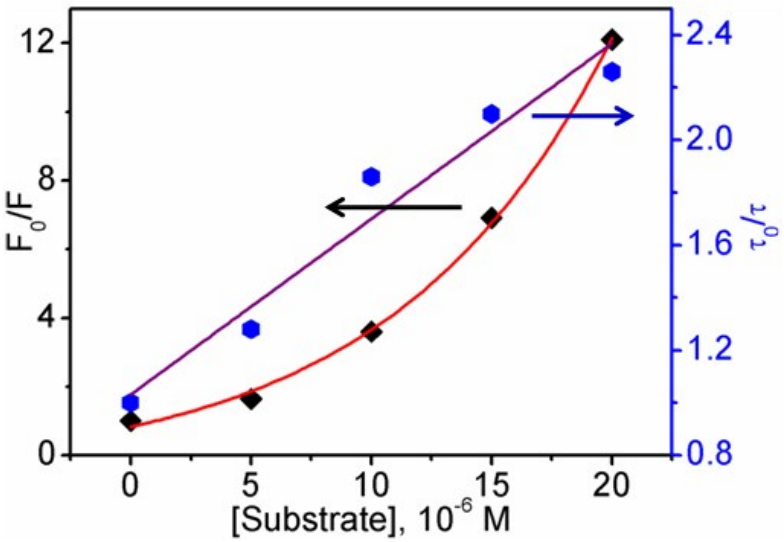


Figure S10: Stern-Volmer plot of QD-592-OA at different substrate concentration.

Table S3. PL deacy parameters of QD-592-OA and QD-592-MPA.

QD-592-OA								
Substrate conc.	**A_1**	**τ_1 (ns)**	**A_2**	**τ_2 (ns)**	**A_3**	**τ_3 (ns)**	**χ^2**	**$<\tau_{ave}>$ (ns)**
0 M	35.33	2.34	51.59	10.74	13.08	0.35	1.24	9.58
5 X 10^{-6} M	40.50	1.97	43.33	8.74	16.17	0.28	1.24	7.49
10 X 10^{-6} M	41.45	1.43	37.13	6.20	21.42	0.22	1.26	5.14
15 X 10^{-6} M	40.24	1.25	36.54	5.51	23.23	0.21	1.28	4.57
20 X 10^{-6} M	39.65	1.17	35.30	5.15	25.05	0.21	1.21	4.24
25 X 10^{-6} M	39.32	1.16	33.53	5.11	27.14	0.21	1.16	4.17
30 X 10^{-6} M	40.61	1.27	30.37	5.39	29.02	0.26	1.24	4.26
QD-592-MPA								
0 M	39.10	0.42	32.12	2.26	28.77	0.05	1.10	1.89

d)Transient absorption experiments

From the Ti:Sapphire oscillator (Vitesse, Coherent, USA) operating at 80 MHz repetition rate, train of modelocked femtosecond laser pulses are generated which acts as seed pulse. Second harmonic Q-Switched Nd:YLF laser (Evolution, Coherent, USA) with a repetition rate of 1 kHz is used as pump pulse to amplify the seed light using a regenerative amplifier (Coherent, Libra, USA) based on chirped pulse amplification. Libra output of 800 nm of 4 mJ/ pulse light with 1 kHz repetition rate and 100 fs pulse duration is used as the pump-probe source for transient absorption. The amplified output is divided into two parts using a beam splitter to generate pump and probe pulse. One part of the red light (1.6 W) is passed through the Optical Parametric Amplifier (OPA - TOPAS, Light Conversion, Lithuania) to get the desired wavelength for pumping the sample. Here, to generate 400 nm pump beam, BBO crystal is used as for the second harmonic generation of the 800 nm light. Another part of the red light is focused on CaF_2 crystal to produce a white light continuum (WLC) (370 - 750 nm) probe as a recognition of the pump-induced absorbance changes. In order to vary the time delay between the pump and probe pulses, amplified output for white light generation is directed through an optical delay line, which consists of a retroreflector mounted on a computer-controlled high-precision motorized translation stage. After generating WLC, it is divided into two parts; one acts as reference and another is the probe pulse. Reference beam is there to account for the intensity fluctuation present in white light continuum. The pump (400 nm) and probe pulses are focused and spatially overlapped on the water soluble CdSe quantum dots, kept in a rotating cell with a path length of 1 mm. Before that, pump pulse is passed through mechanical chopper which is synchronized so that it can block every alternative excitation pulse. So there is a situation in alternative moments when sample is not excited which denotes the “without pump” sample. In this way, difference of the absorption spectra is monitored for pumped and without pumped sample in terms of the intensity of the probe beam through detector diode array. The reference and transmitted probe beam are sent to multichannel detector diode arrays. Any effect of rotational diffusion is

corrected by adjusting the polarization between pump and probe to the magic angle (54.7°). Absorbance of samples before and after transient absorption experiment is compared in order to monitor the extent of degradation of sample. All recorded data are fitted using Surface Minor Pro version 4.0 software and subsequently chirp is corrected to remove the group velocity dispersion (GVD).

Femtosecond pump-probe spectroscopy is a tool where ultrashort pump pulse is used to excite the sample and broadband less intense white light generated by CaF_2 crystal acts as probe to monitor transient absorption. With the help of detected probe intensity, difference of the absorption spectra (ΔA) in the presence and absence of pump light is monitored. To get the idea of electron transfer, ground state bleach recovery at 584 nm is examined in the presence and absence of quencher. In Fig.**S11**, in the presence of quencher, there is fast recovery of the ground state bleach dynamics may be due to the electron transfer from quantum dot to 4-methoxy phenyl boronic acid.

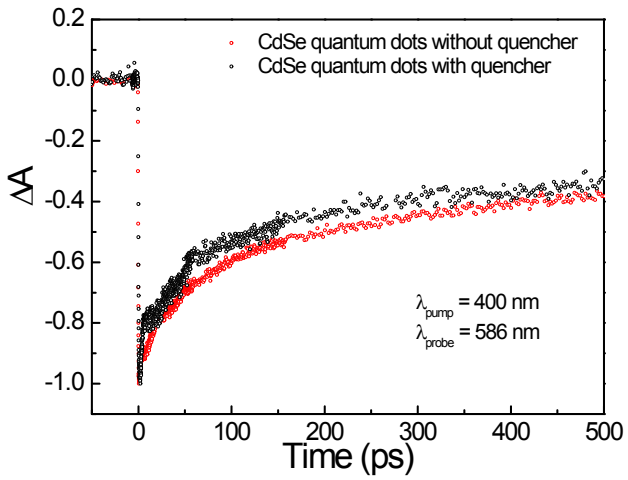


Figure S11. In the transient absorption experiments, ground state bleach recovery dynamics at 584 nm in the presence (red) and absence (black) of quencher

CdSe	a_1	T_1 (ps)	a_2	T_2 (ps)	a_2	T_2 (ns)
Absence Of Quencher	0.29	38.5	0.39	328	0.32	>2

With Quencher	0.35	36.9	0.41	506	0.23	>2

Table S4. Temporal parameters from Transient absorption of CdSe quantum dots in the presence and absence of quencher, λ_{ex} = 400 nm

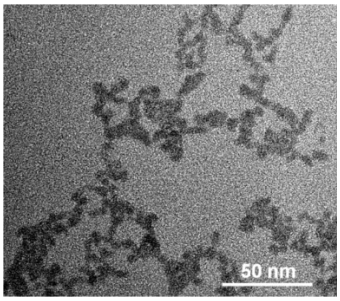
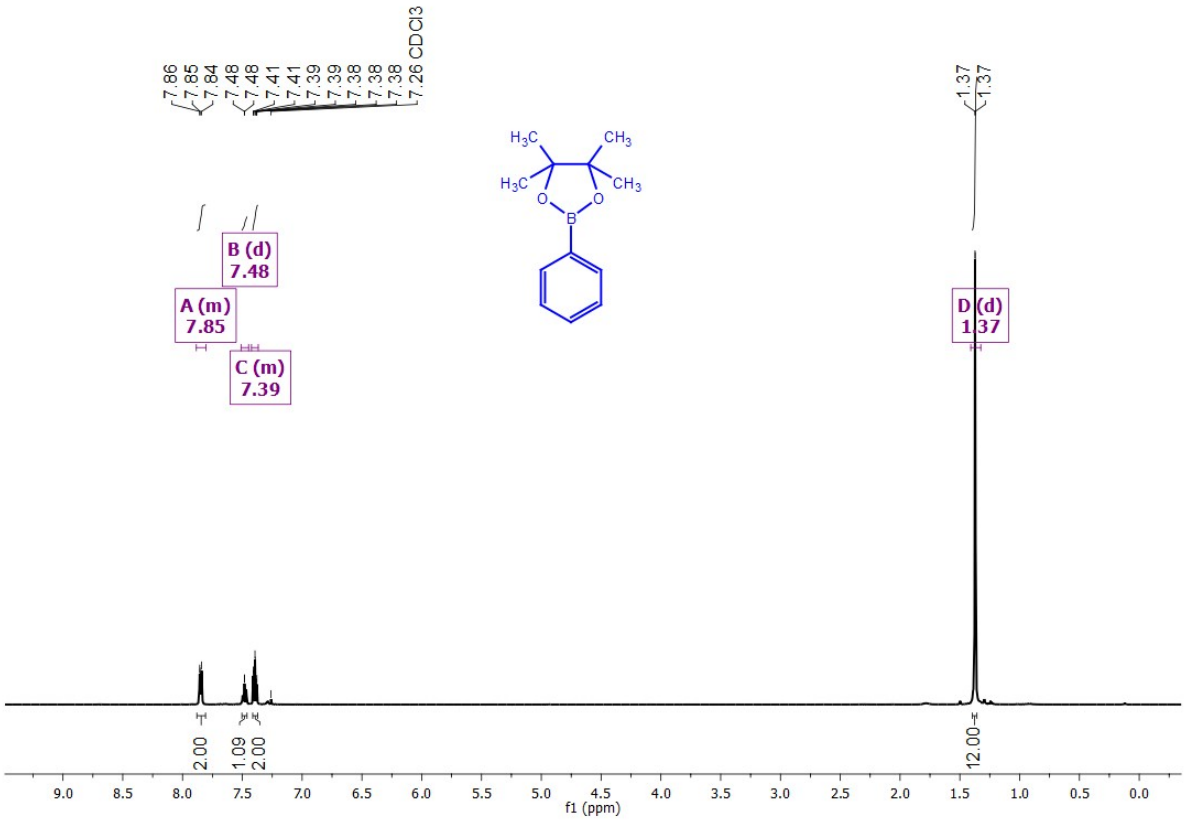
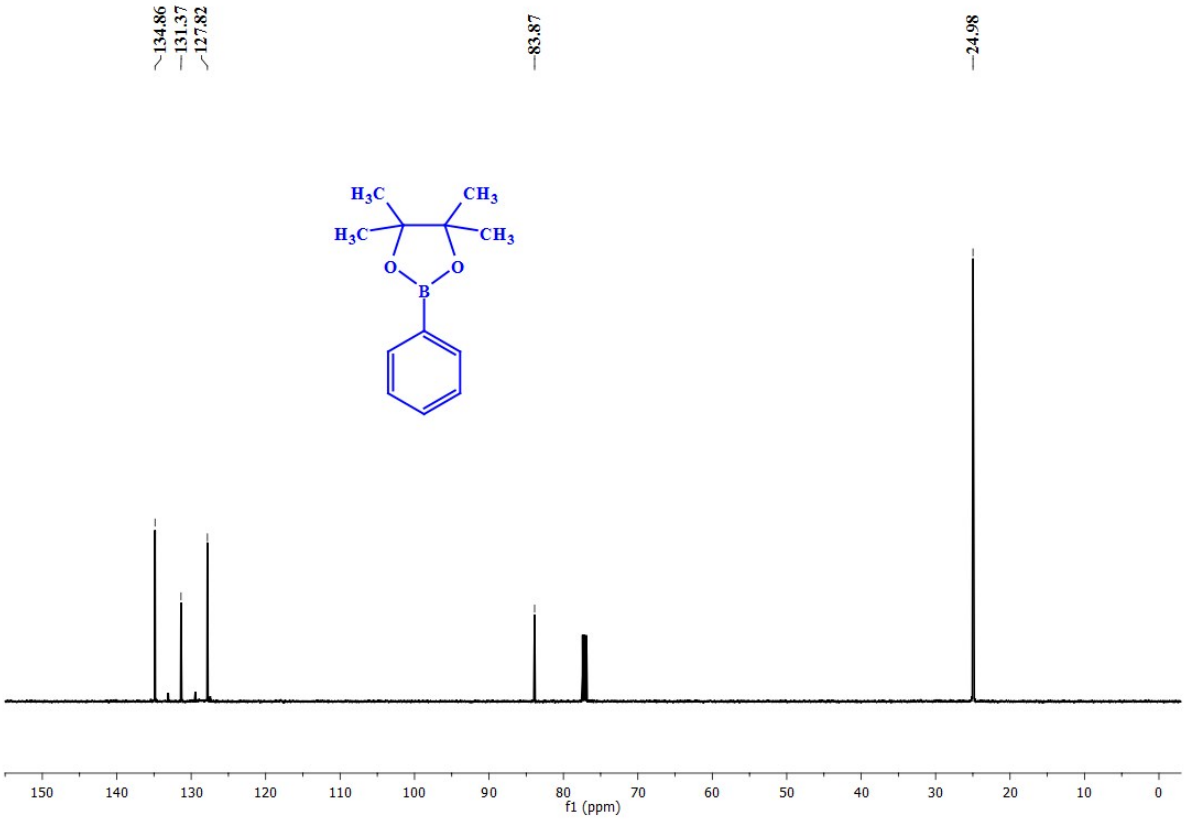
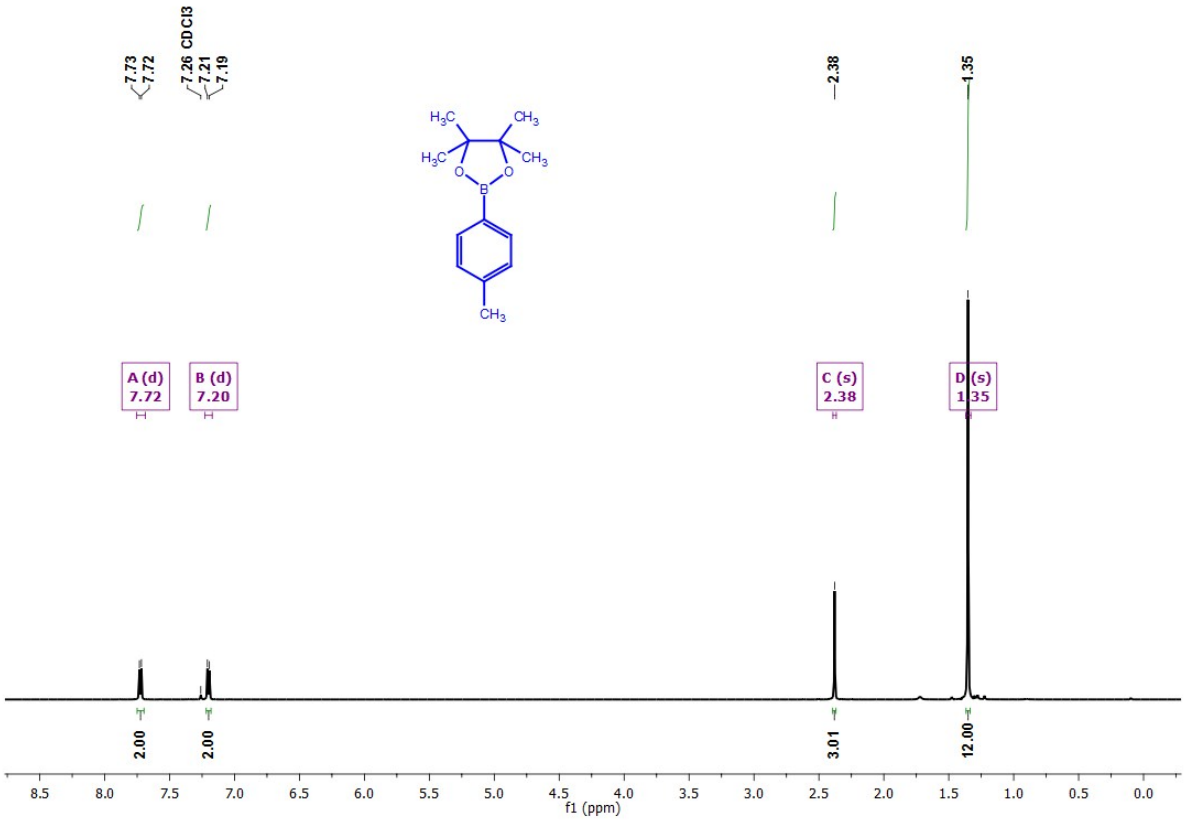


Figure S12: TEM image of QD-592-MPA post reaction.


7.86
7.85
7.84
7.48
7.48
7.41
7.41
7.39
7.39
7.38
7.38
7.38
7.26 CDCl3
1.37
1.37
B (d)
7.48
A (m)
7.85
C (m)
7.39
D (d)
1.37
2.00
1.09
2.00
12.00
f1 (ppm)


134.86
131.37
127.82
83.87
24.98
f1 (ppm)


7.73
7.72
7.26 CDCl3
7.21
7.19
2.38
1.35
A (d)
7.72
B (d)
7.20
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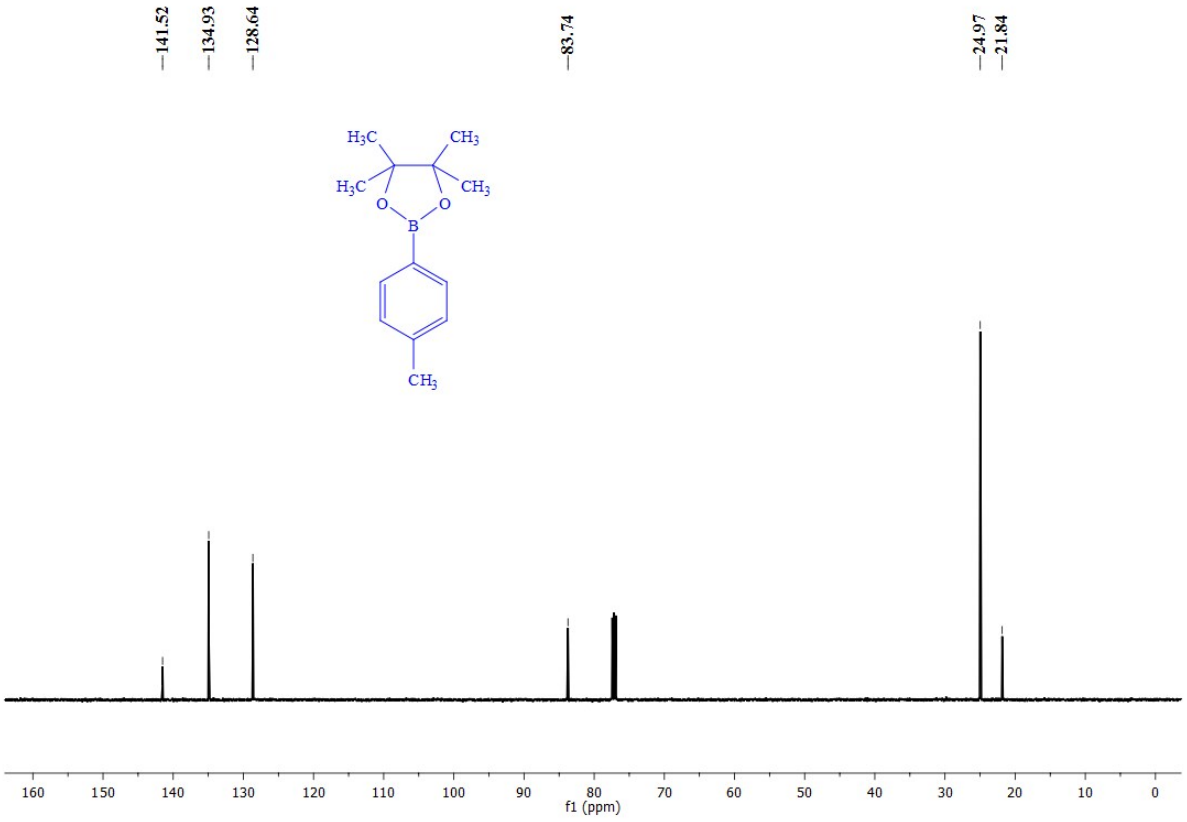
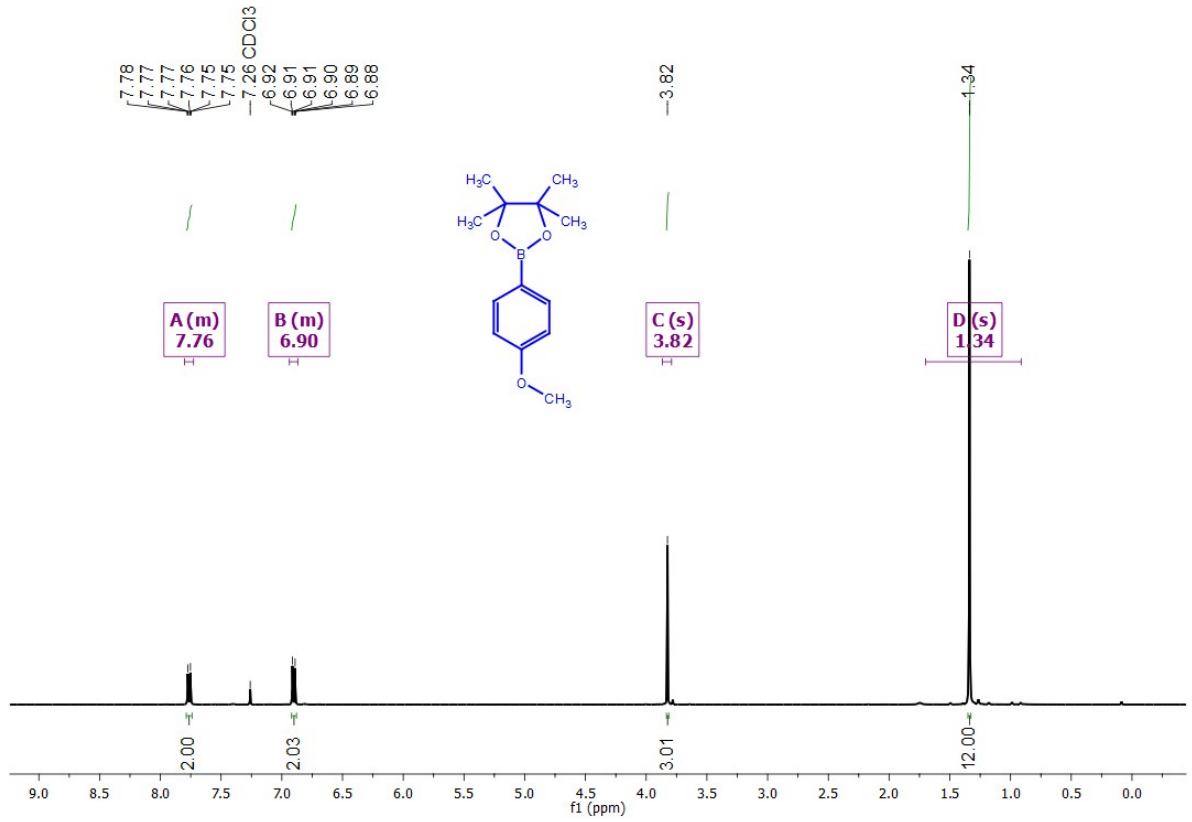
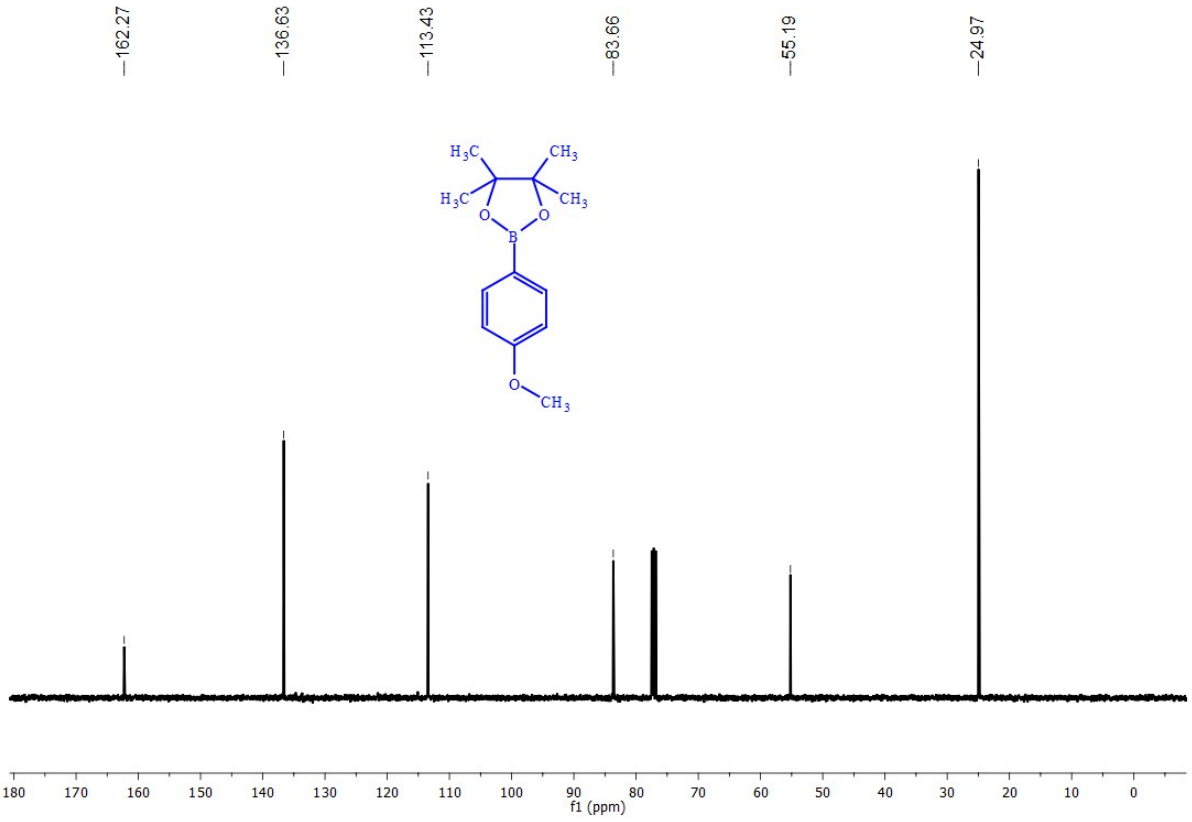
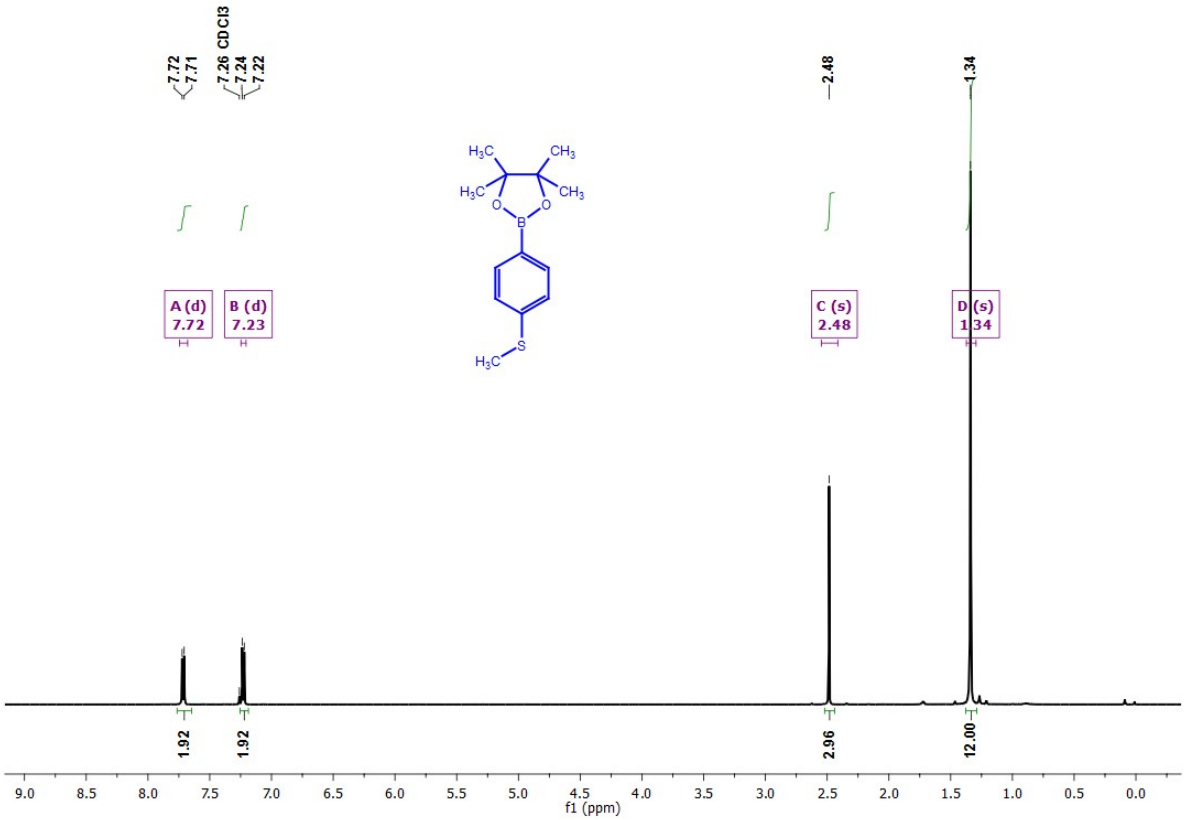
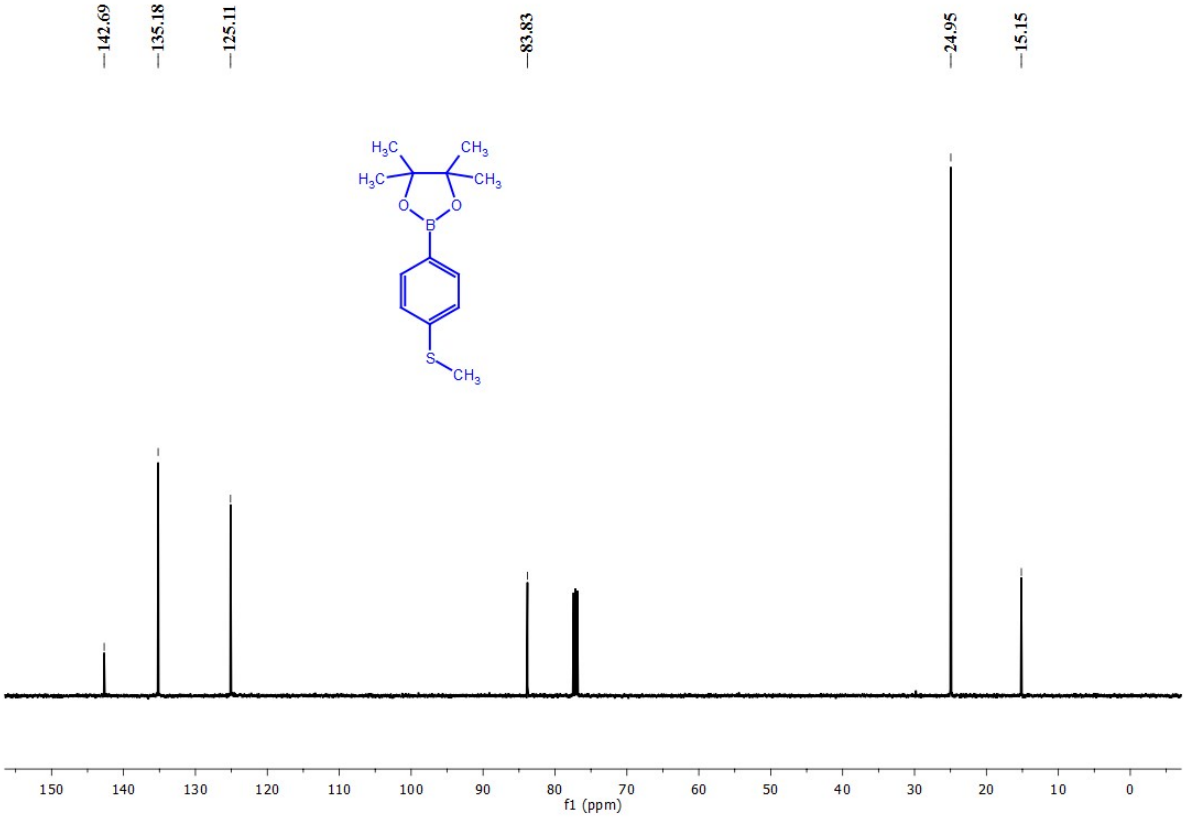
2.00
3.01
12.00
f1 (ppm)

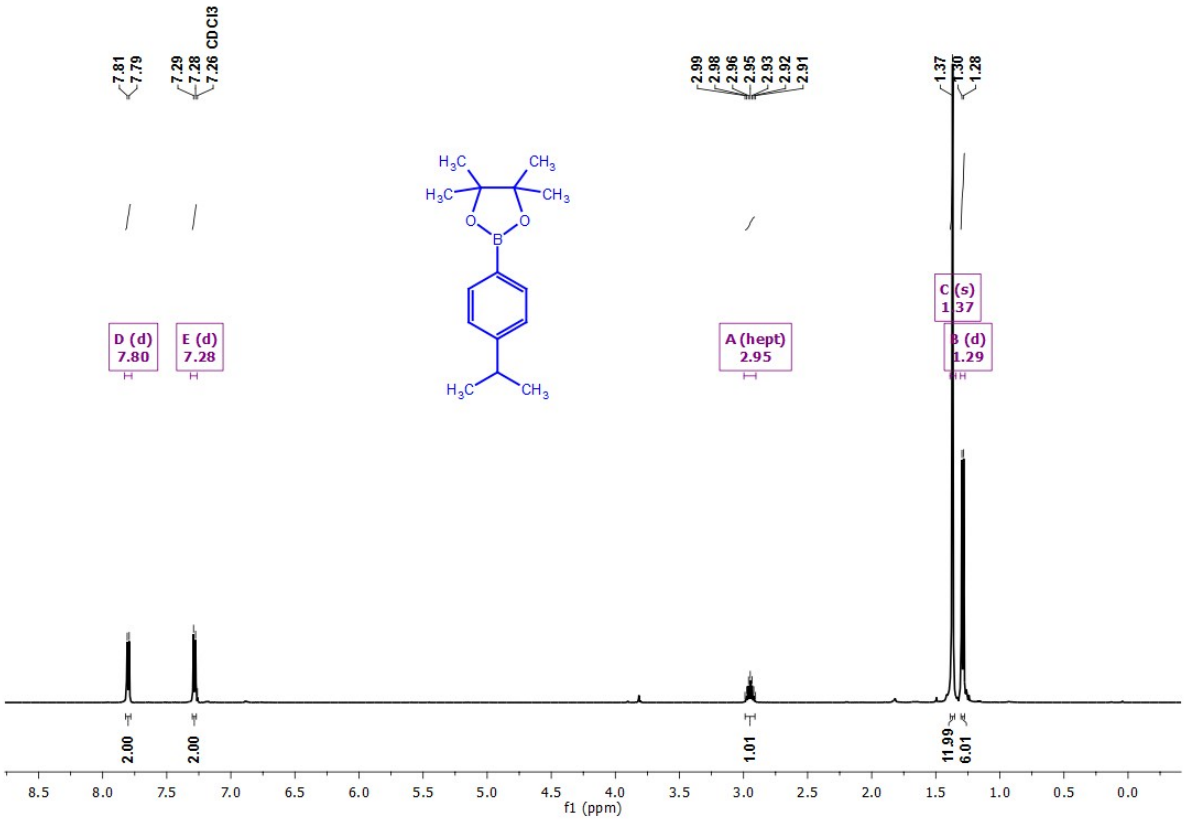

141.52
134.93
128.64
83.74
24.97
21.84
f1 (ppm)

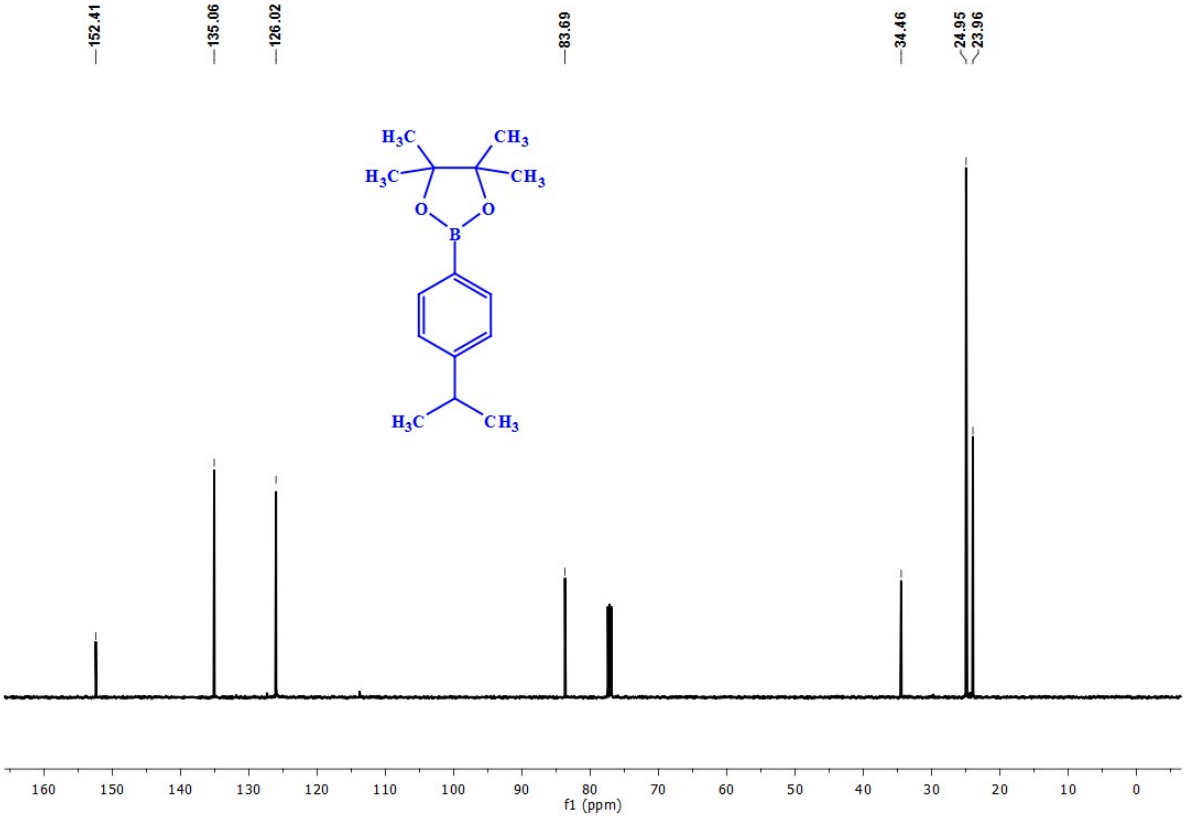

7.78
7.77
7.77
7.76
7.75
7.75
7.26 CDCl3
6.92
6.91
6.91
6.90
6.89
6.88
3.82
1.34
A (m)
7.76
B (m)
6.90
C (s)
3.82
D (s)
1.34
2.00
2.03
3.01
12.00
f1 (ppm)

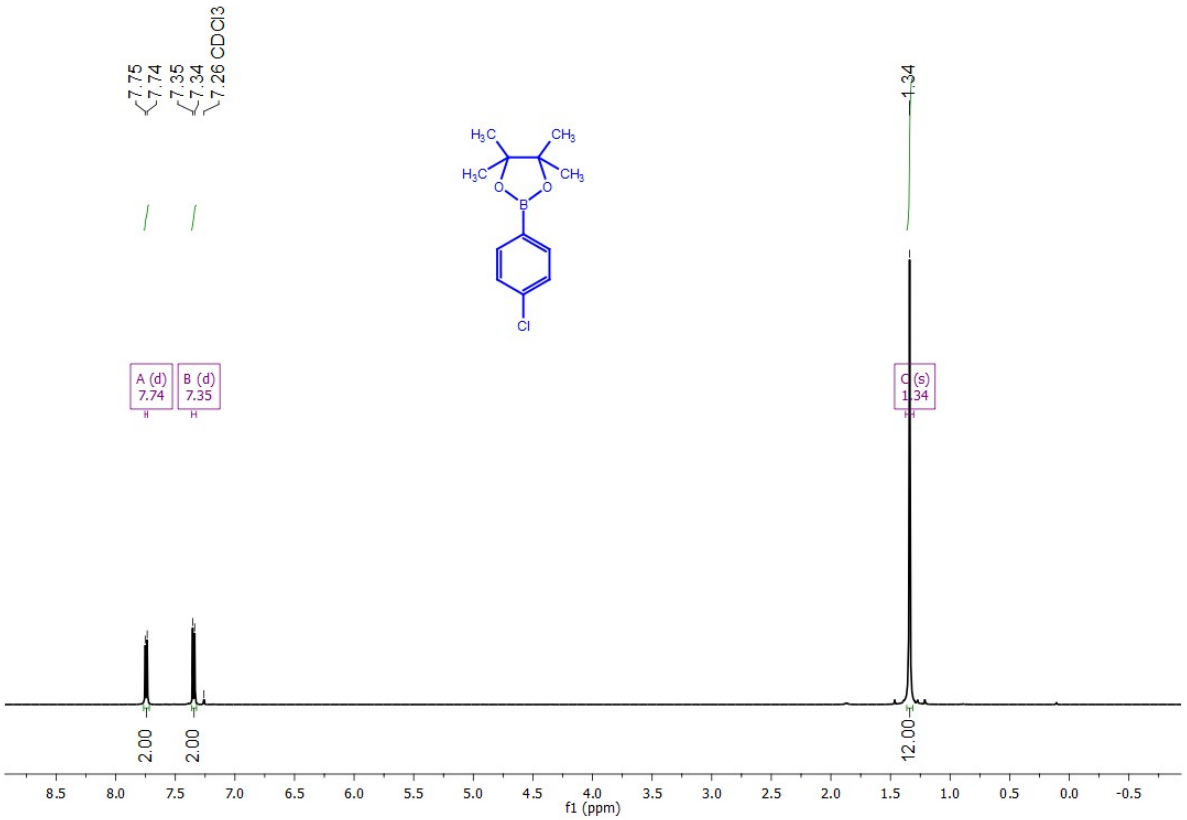

162.27
136.63
113.43
83.66
55.19
24.97
f1 (ppm)

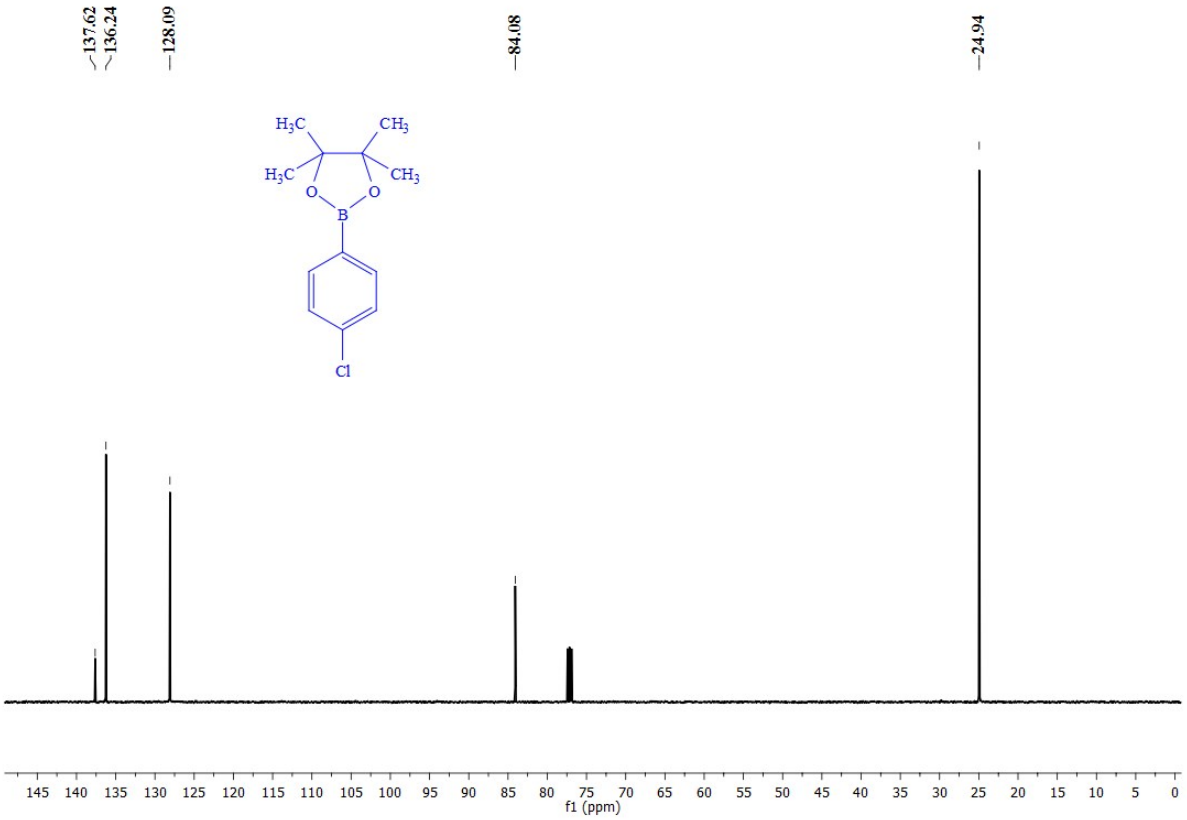

7.72
7.71
7.26 CDCl3
7.24
7.22
2.48
1.34
A (d)
7.72
B (d)
7.23
C (s)
2.48
D (s)
1.34
1.92
1.92
2.96
12.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

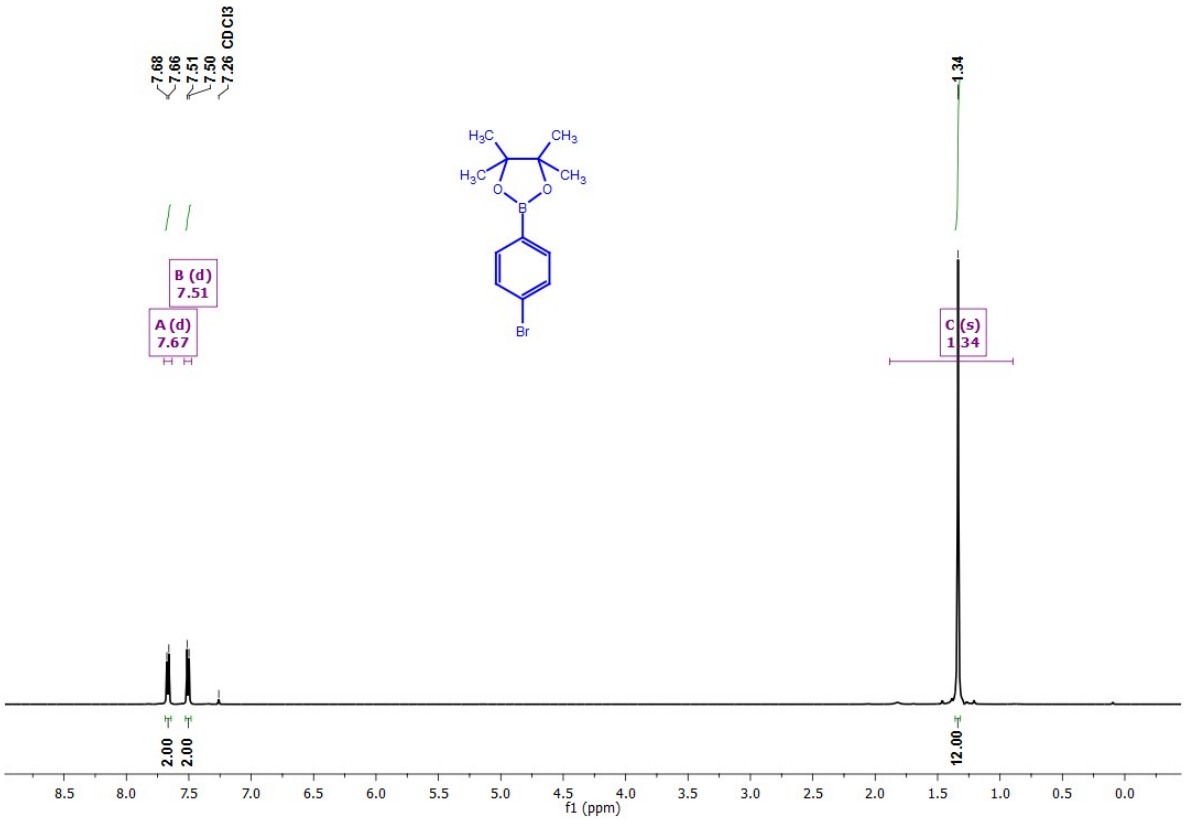

142.69
135.18
125.11
83.83
24.95
15.15
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

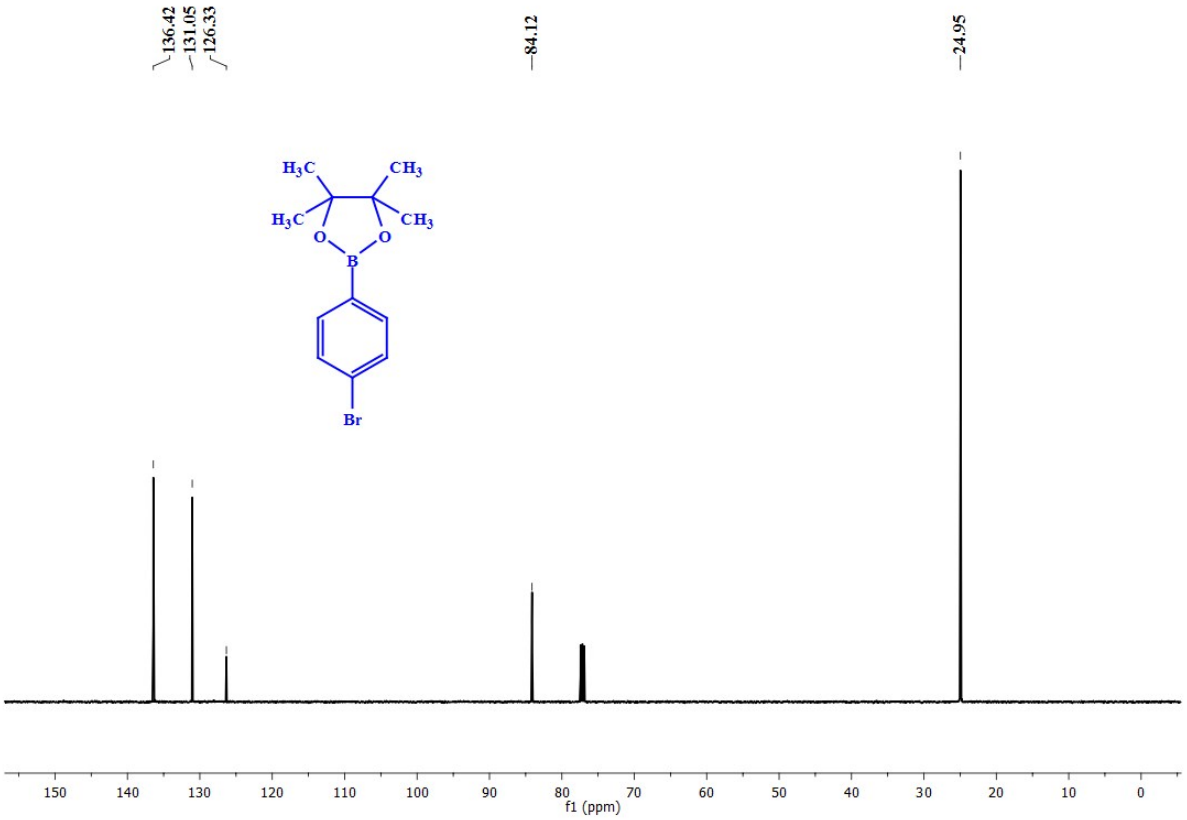

7.81
7.79
7.29
7.28
7.26 CDCl3
2.99
2.98
2.96
2.95
2.93
2.92
2.91
1.37
1.30
1.28
D (d)
7.80
E (d)
7.28
A (hept)
2.95
C (s)
1.37
B (d)
1.29
2.00
2.00
1.01
11.99
6.01
f1 (ppm)

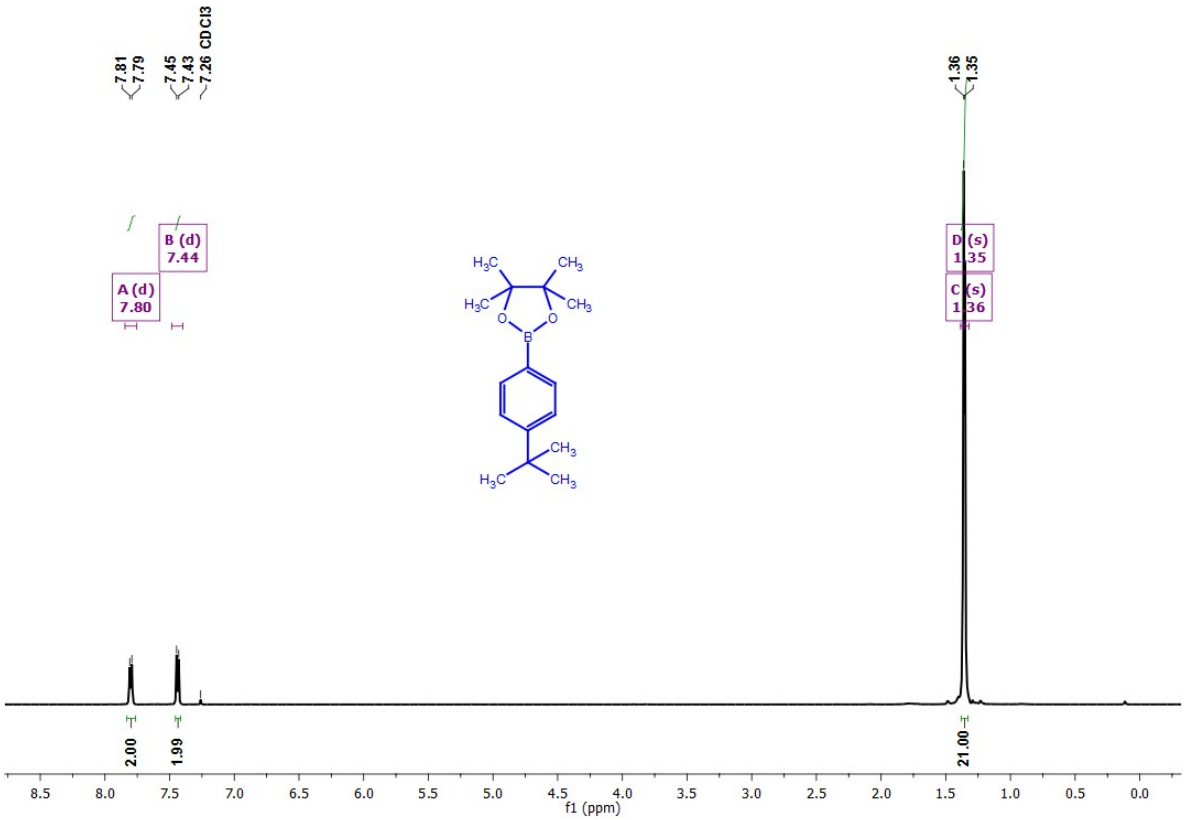

152.41
135.06
126.02
83.69
34.46
24.95
23.96
f1 (ppm)

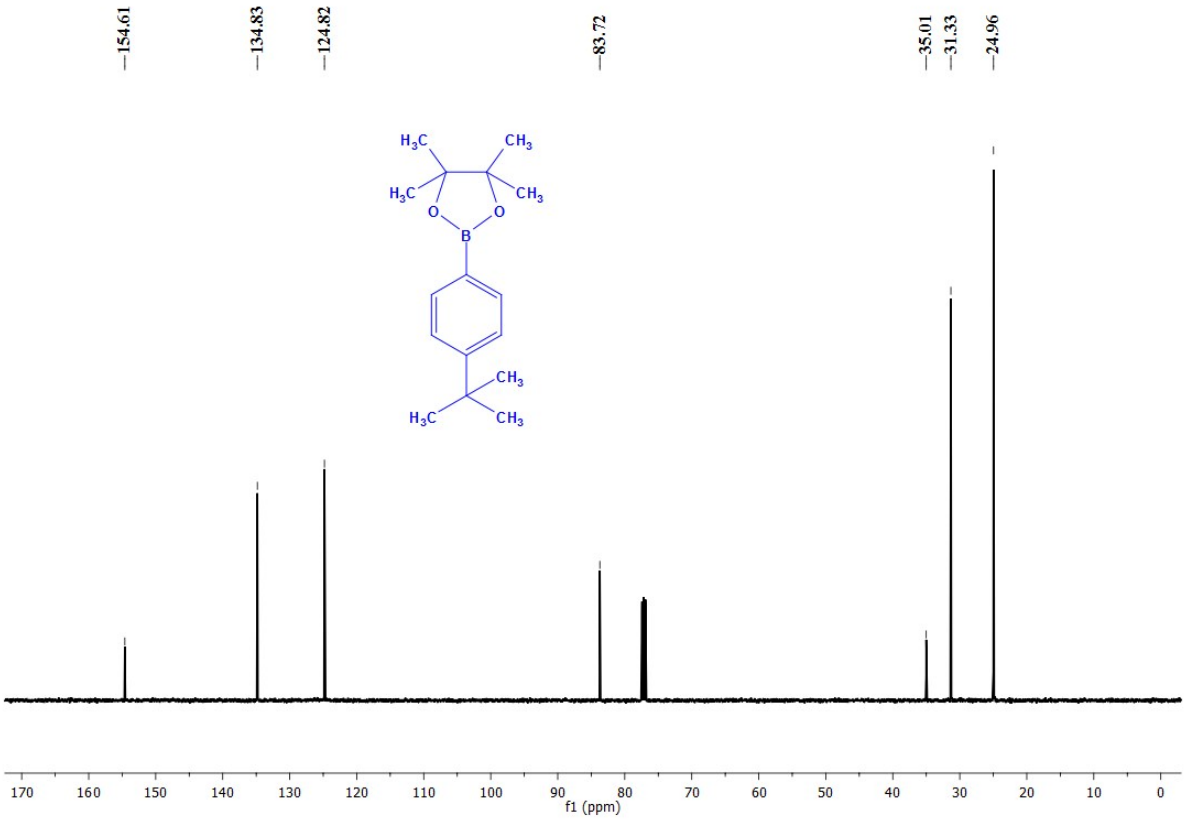

7.75
7.74
7.35
7.34
7.26 CDCl3
1.34
A (d) 7.74
B (d) 7.35
C (s) 1.34
2.00
2.00
12.00
f1 (ppm)

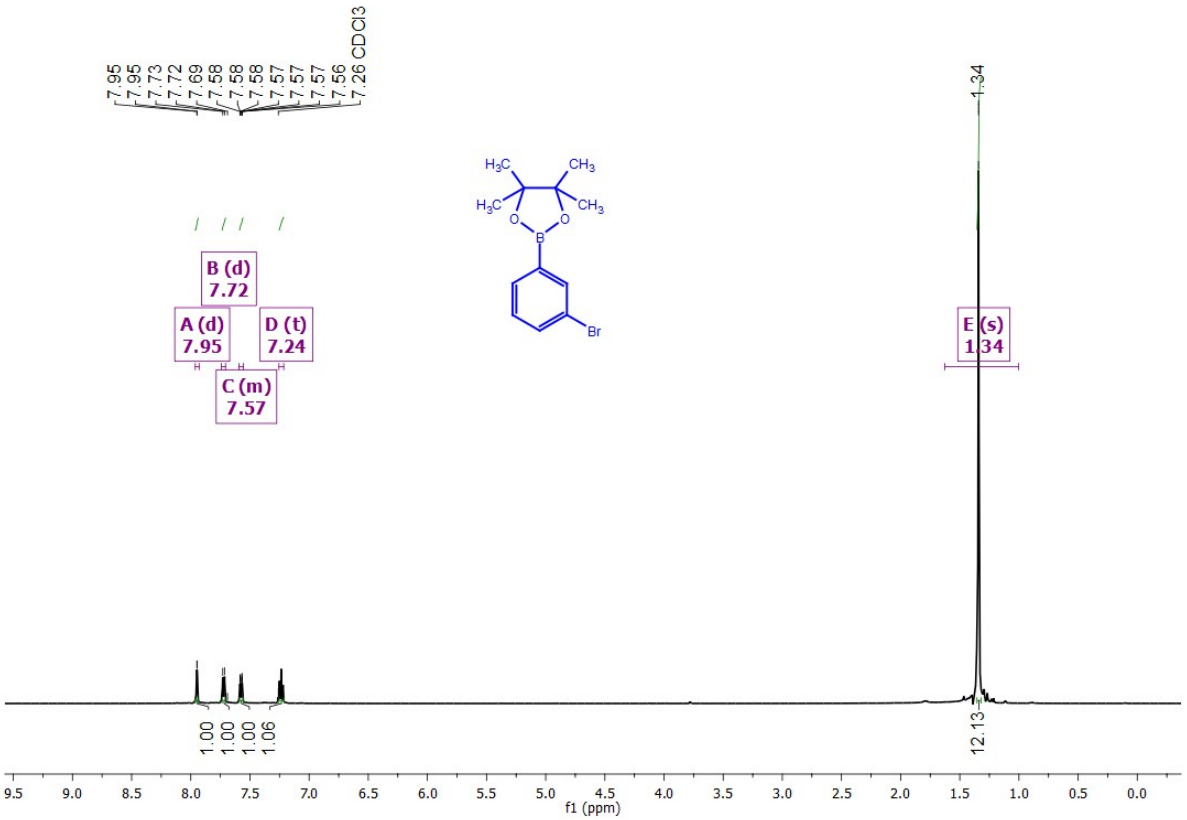

137.62
136.24
128.09
84.08
24.94
f1 (ppm)

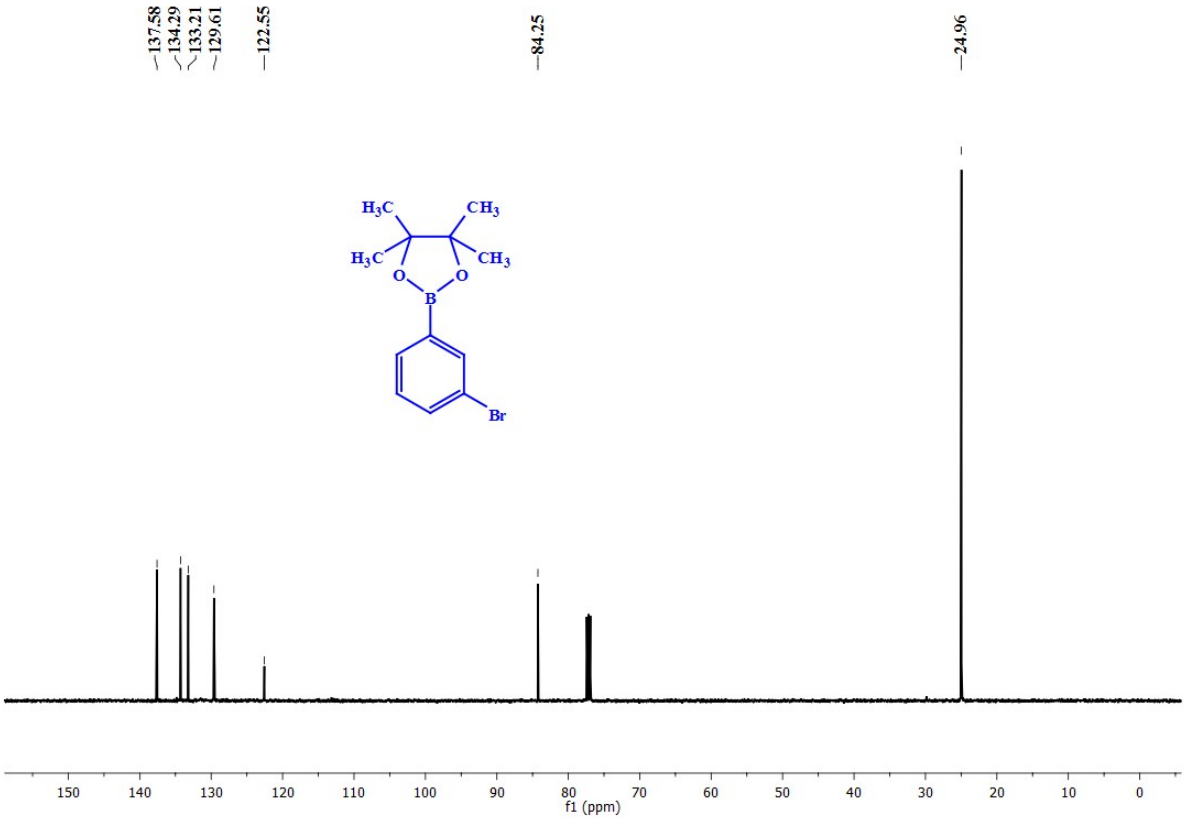

7.68
7.66
7.51
7.50
7.26 CDCl3
1.34
B (d)
7.51
A (d)
7.67
C (s)
1.34
2.00
2.00
12.00
f1 (ppm)


136.42
131.05
126.33
84.12
24.95
f1 (ppm)


7.81
7.79
7.45
7.43
7.26 CDCl3
1.36
1.35
B (d)
7.44
A (d)
7.80
D (s)
1.35
C (s)
1.36
2.00
1.99
21.00
f1 (ppm)


154.61
134.83
124.82
83.72
35.01
31.33
24.96
f1 (ppm)


7.95
7.95
7.73
7.72
7.69
7.58
7.58
7.58
7.57
7.57
7.57
7.56
7.26 CDCl3
1.34
B (d)
7.72
A (d)
7.95
D (t)
7.24
C (m)
7.57
E (s)
1.34
1.00
1.00
1.00
1.06
12.13
f1 (ppm)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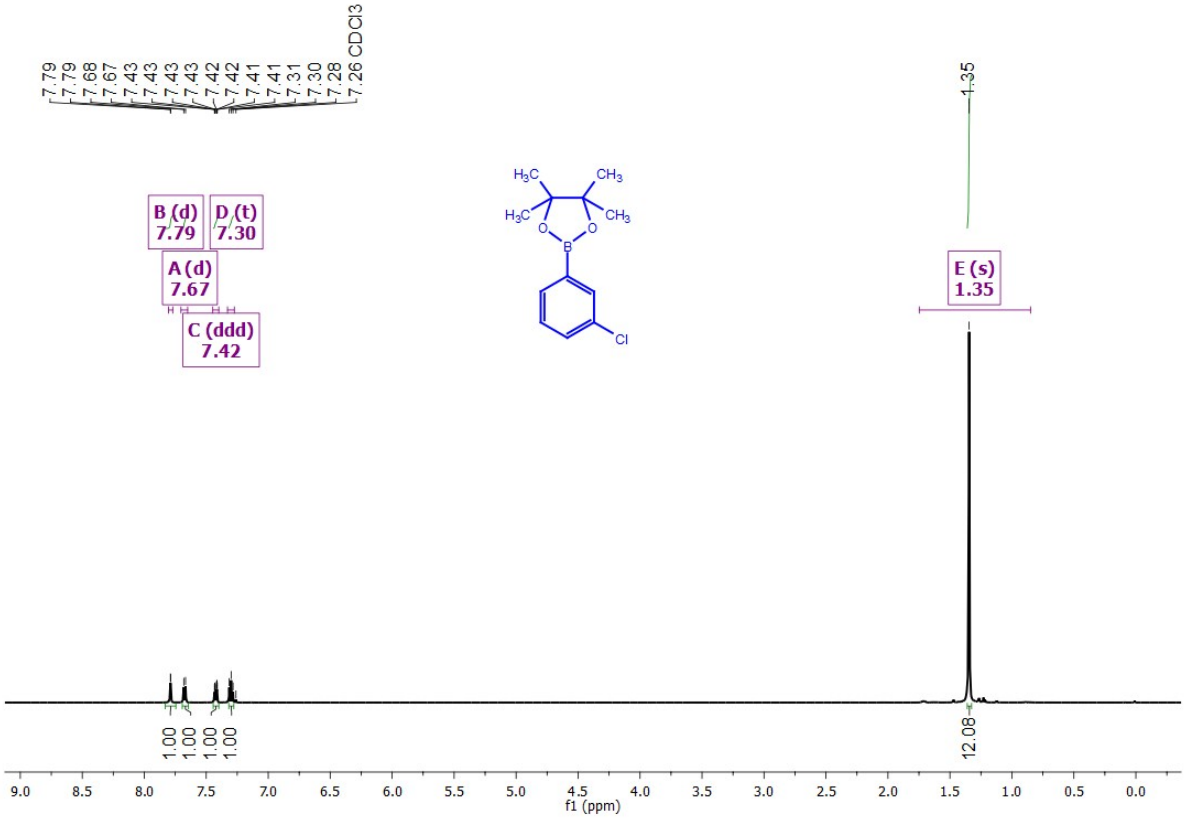
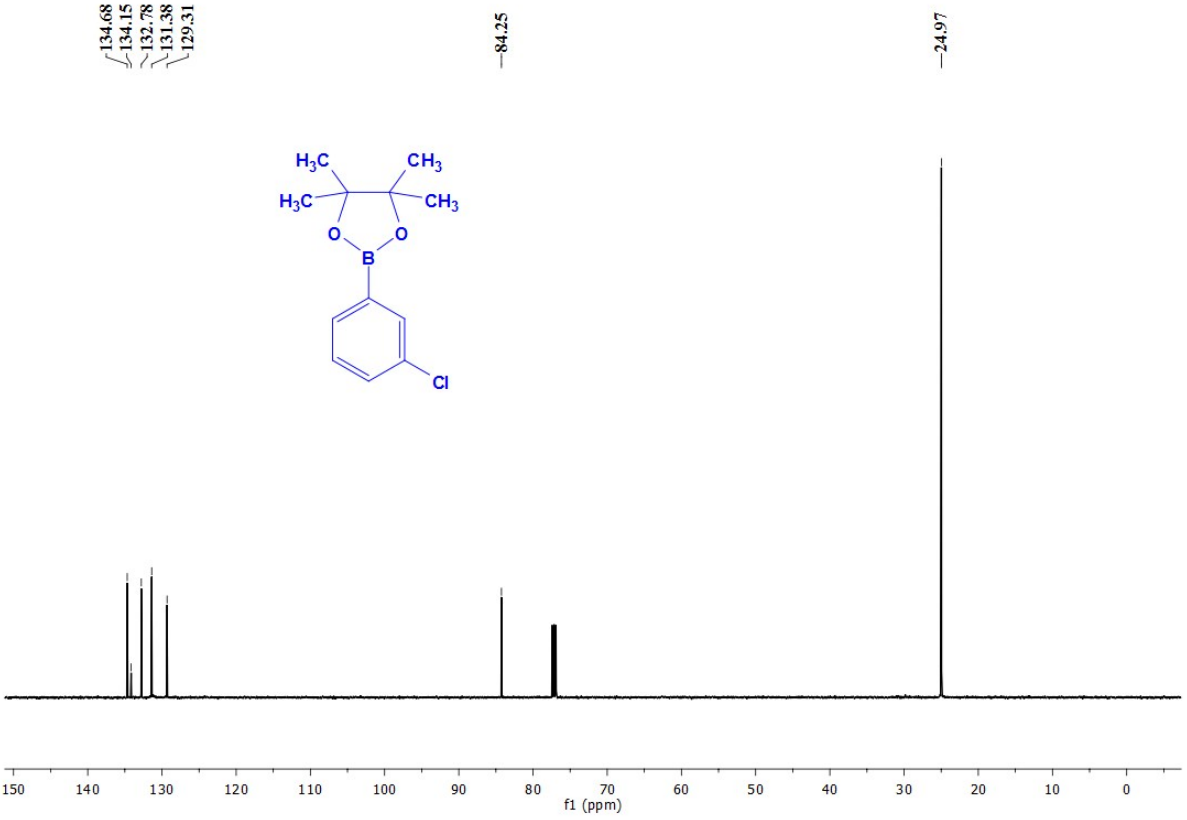
134.29
133.21
129.61
122.55
84.25
24.96
f1 (ppm)


7.79
7.79
7.68
7.67
7.43
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.31
7.30
7.28
7.26 CDCl3
B (d) 7.79
D (t) 7.30
A (d) 7.67
C (ddd) 7.42
1.35
E (s) 1.35
1.00
1.00
1.00
1.00
12.08
f1 (ppm)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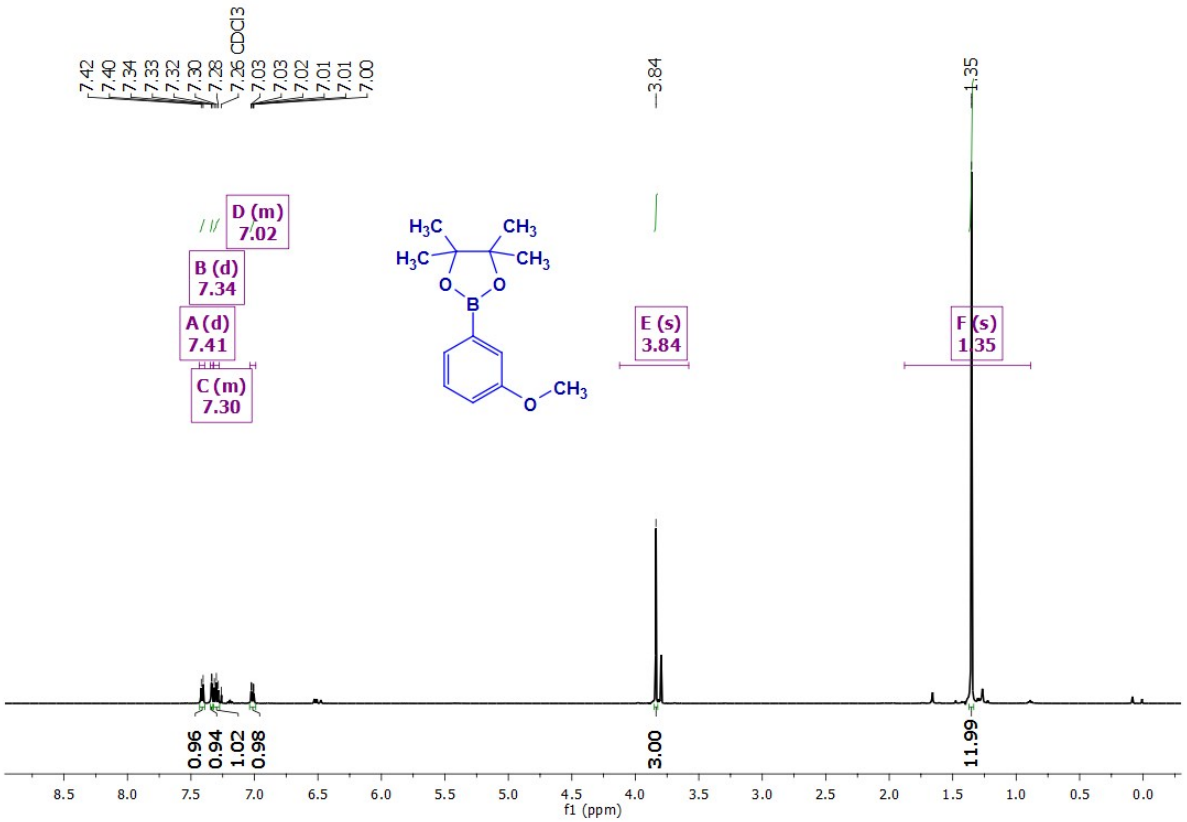
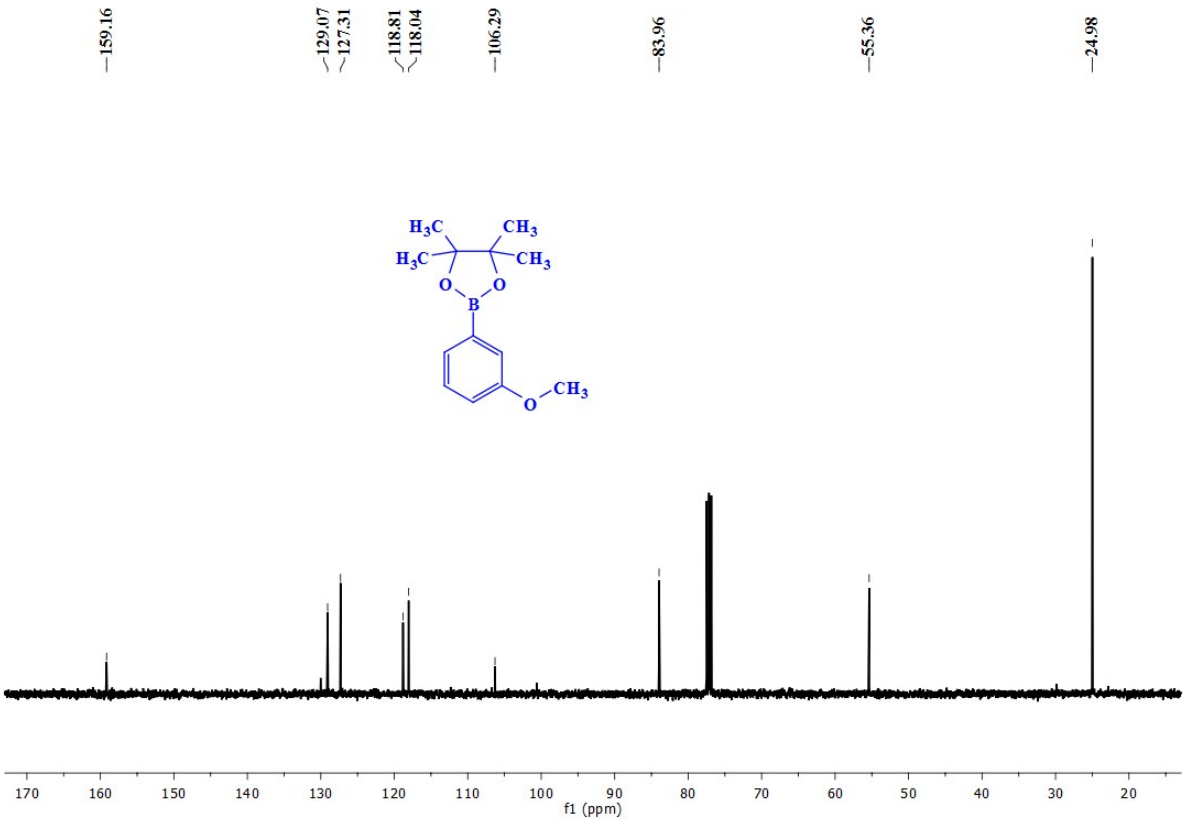
132.78
131.38
129.31
84.25
24.97
f1 (ppm)


7.42
7.40
7.34
7.33
7.32
7.30
7.28
7.26 CDCl3
7.03
7.03
7.02
7.01
7.01
7.00
3.84
1.35
D (m) 7.02
B (d) 7.34
A (d) 7.41
C (m) 7.30
E (s) 3.84
F (s) 1.35
0.96
0.94
1.02
0.98
3.00
11.99
f1 (ppm)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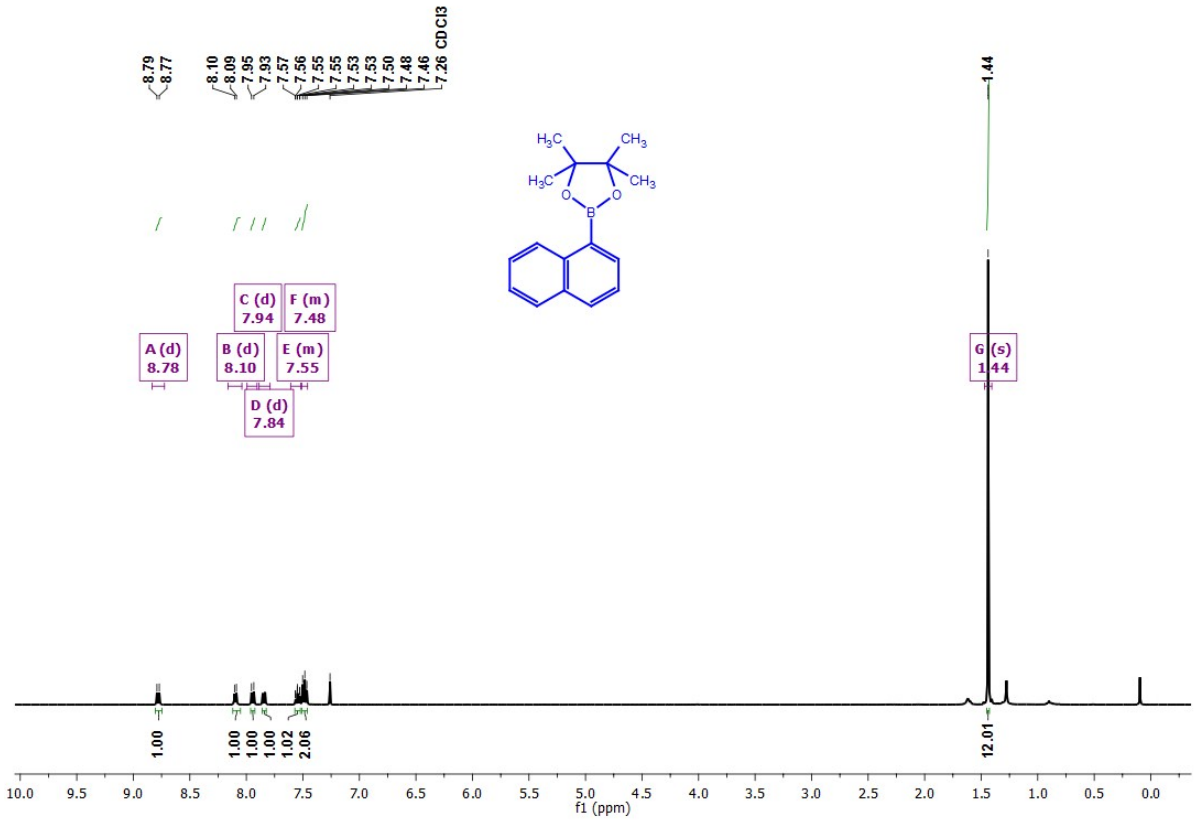
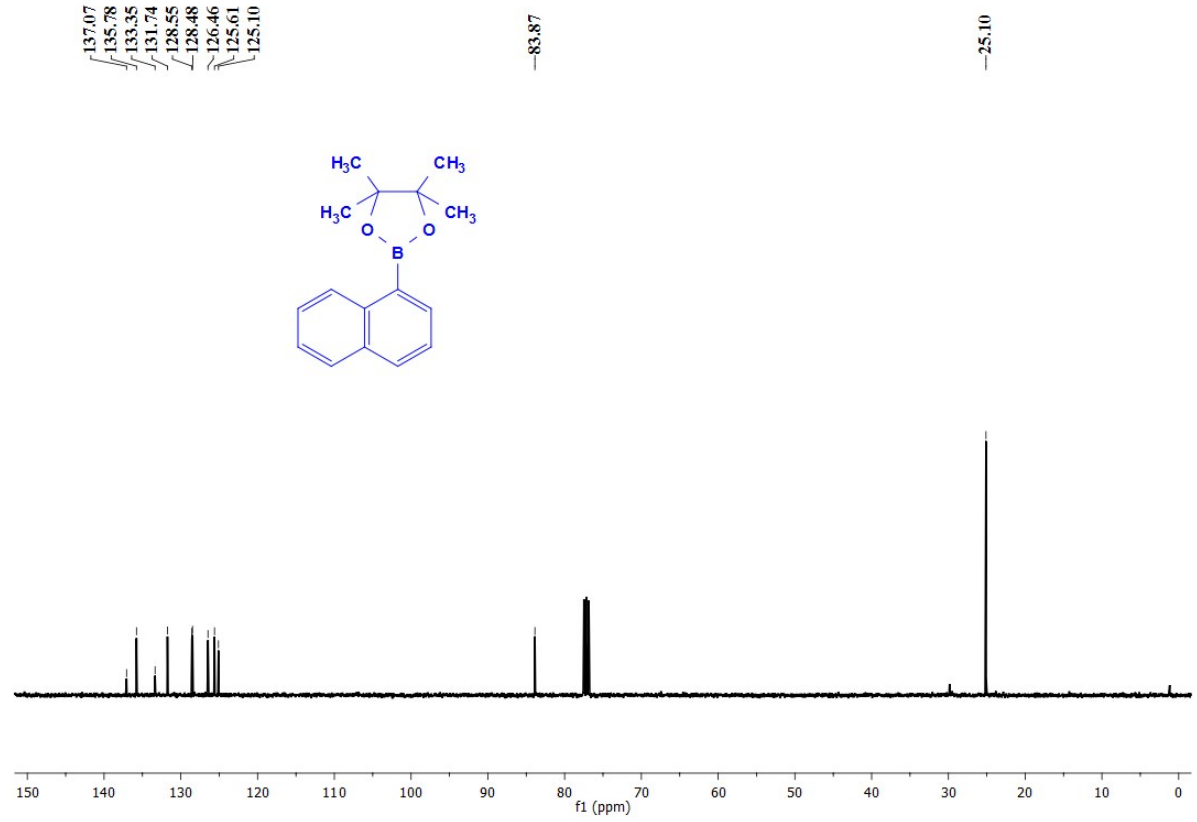
129.07
127.31
118.81
118.04
106.29
83.96
55.36
24.98
f1 (ppm)


8.79
8.77
8.10
8.09
7.95
7.93
7.57
7.56
7.55
7.55
7.53
7.53
7.50
7.48
7.46
7.26 CDCl3
1.44
A (d) 8.78
B (d) 8.10
C (d) 7.94
D (d) 7.84
E (m) 7.55
F (m) 7.48
G (s) 1.44
1.00
1.00
1.00
1.00
1.02
2.06
12.01
f1 (ppm)


137.07
135.78
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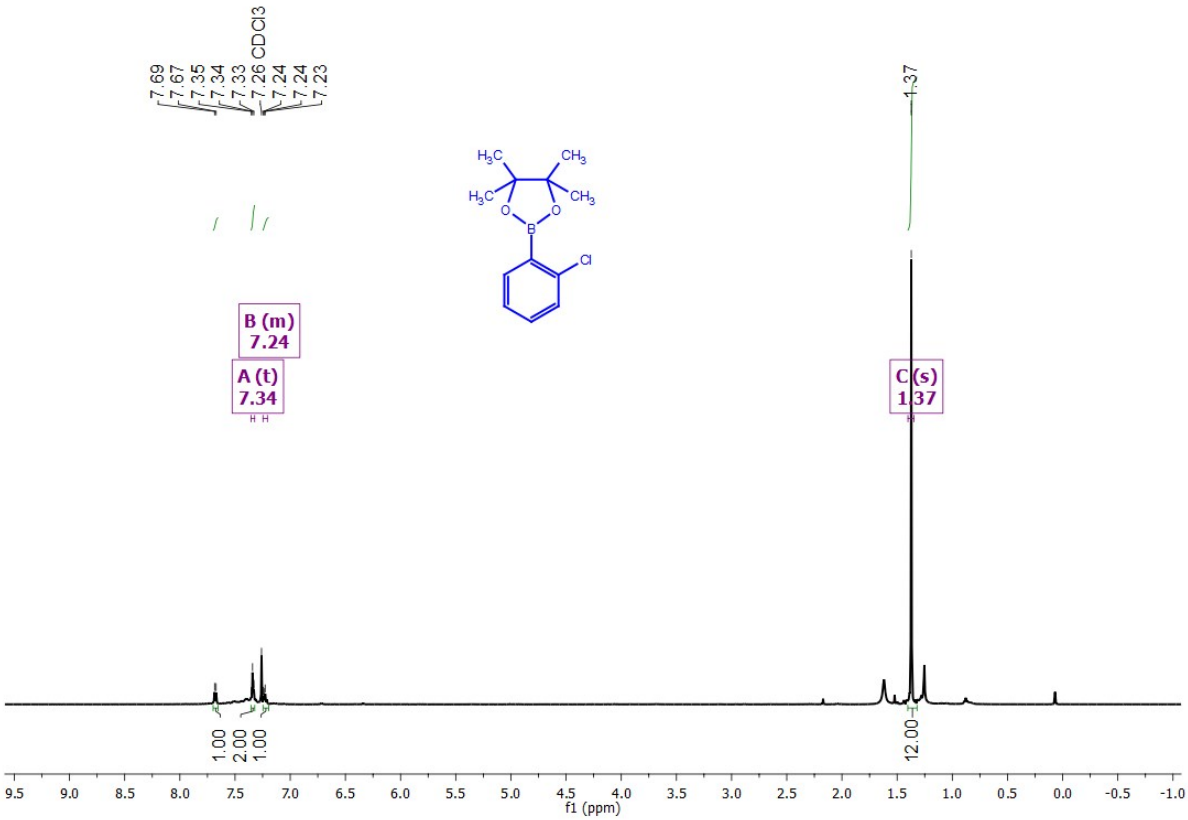
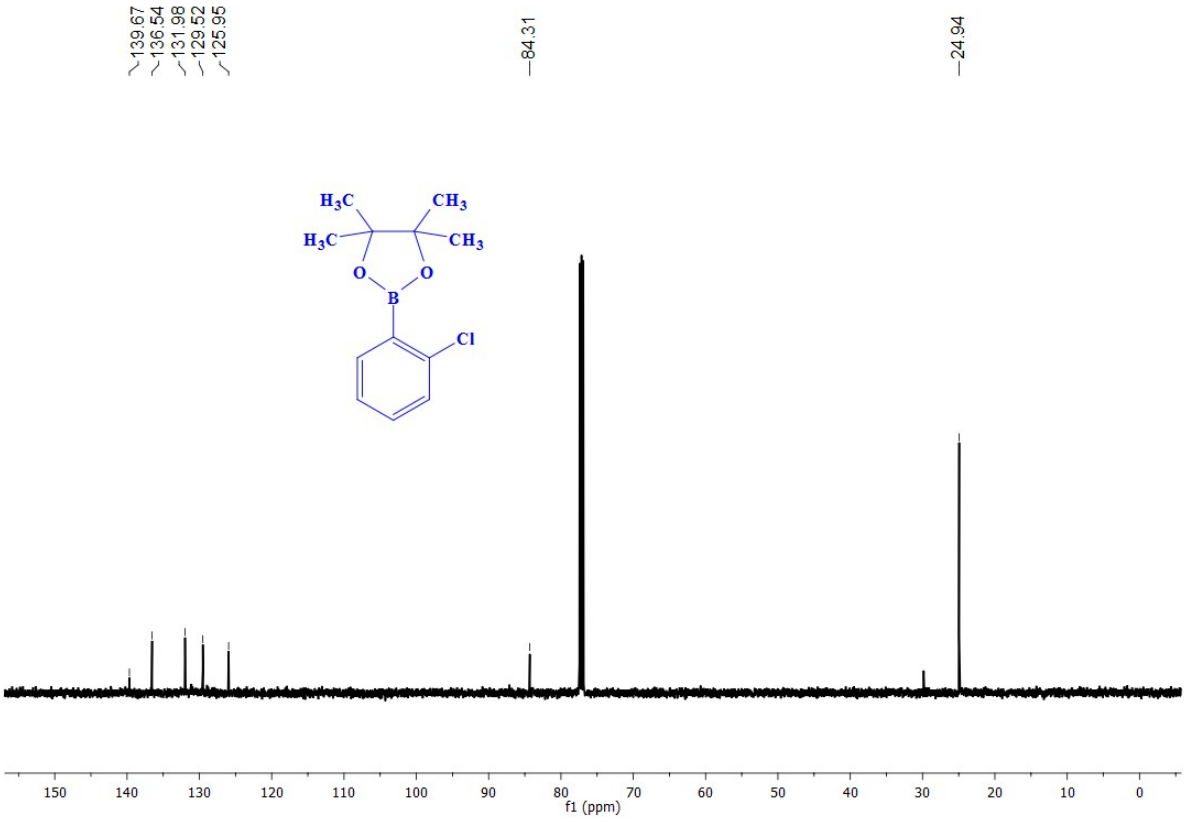
131.74
128.55
128.48
126.46
125.61
125.10
83.87
25.10
f1 (ppm)


7.69
7.67
7.35
7.34
7.33
7.26 CDCl3
7.24
7.24
7.23
1.37
B (m)
7.24
A (t)
7.34
C (s)
1.37
1.00
2.00
1.00
12.00
f1 (ppm)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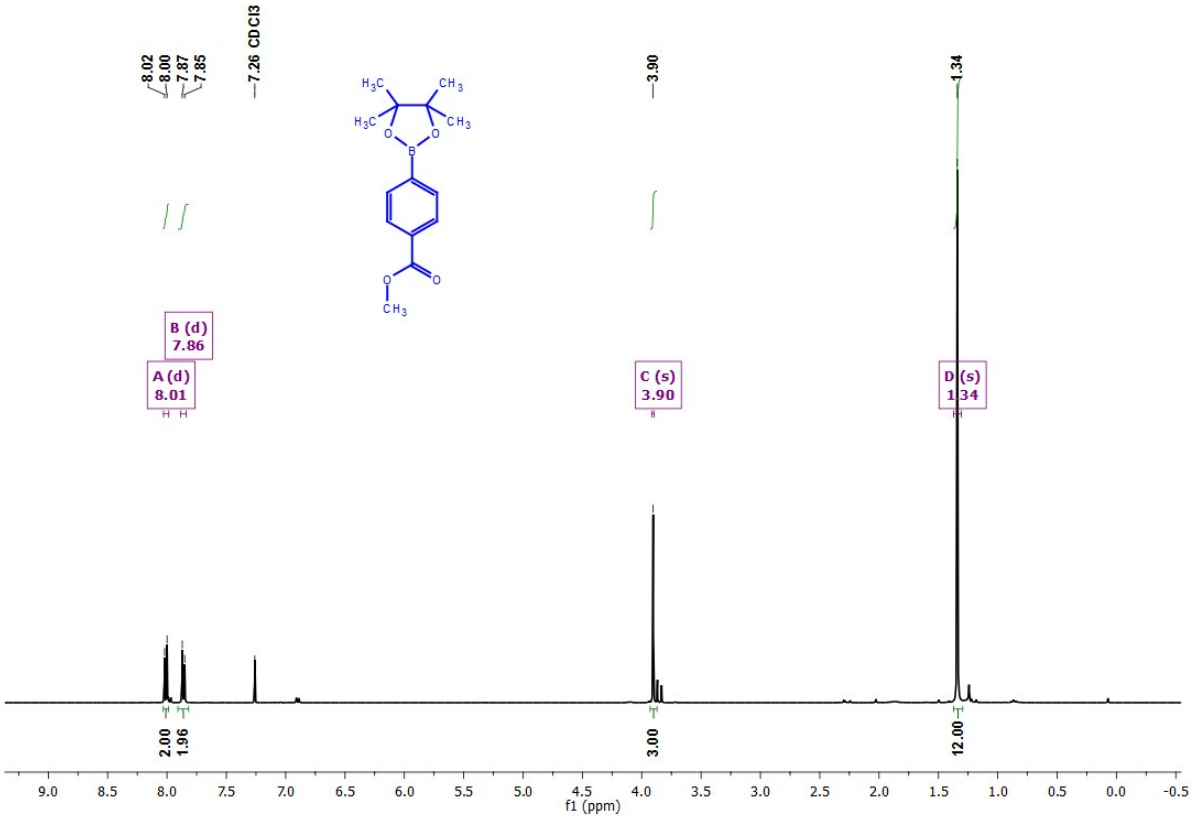
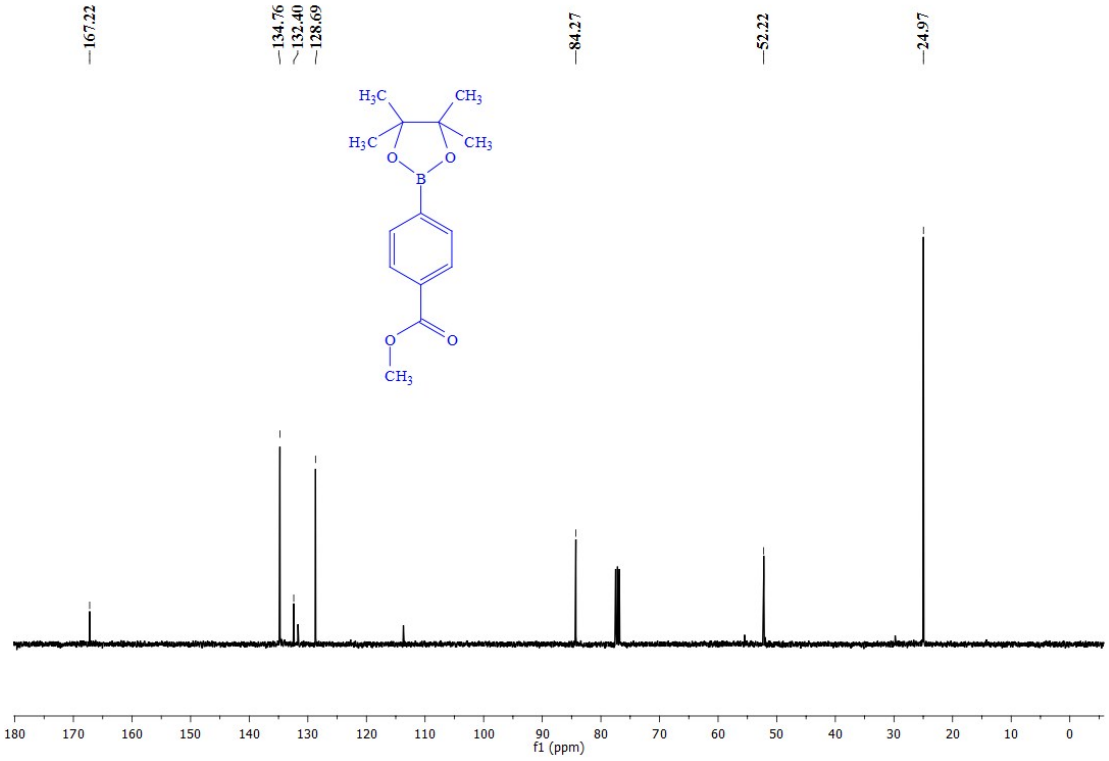
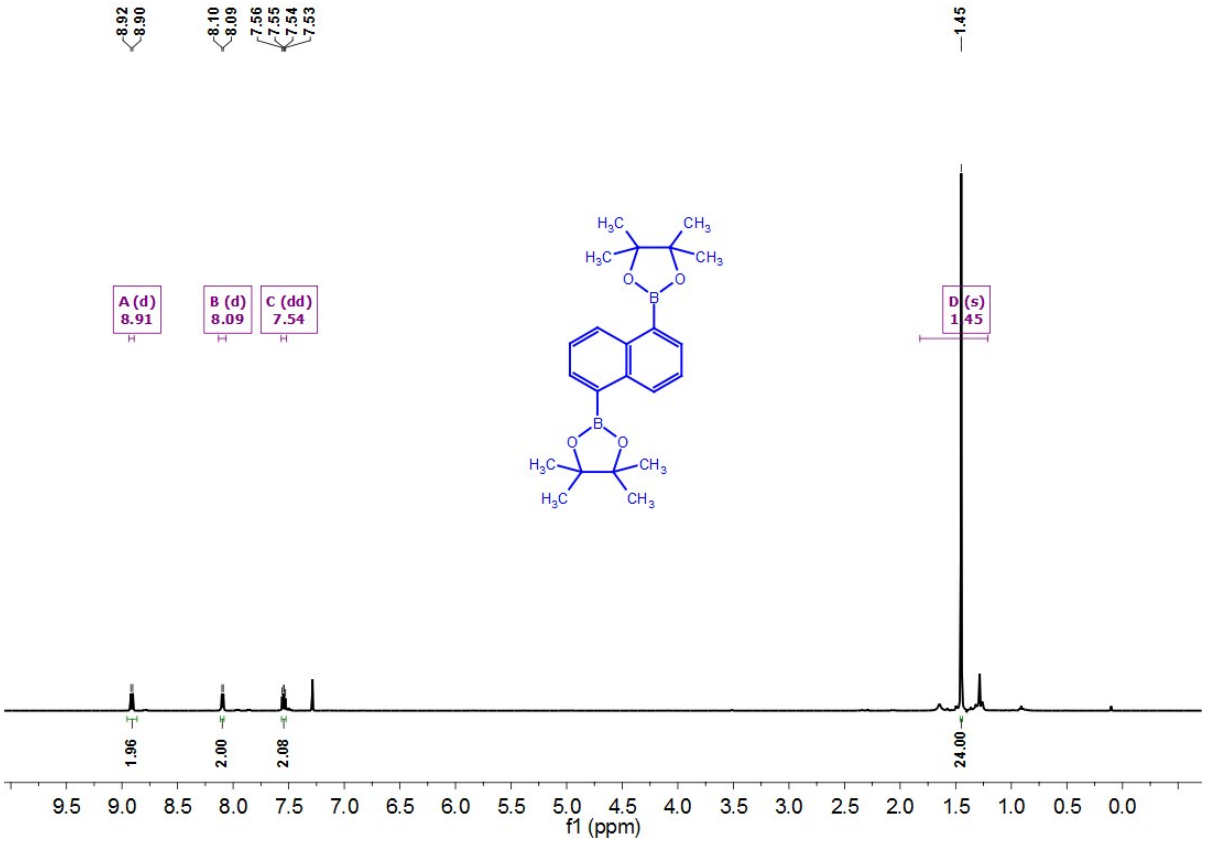
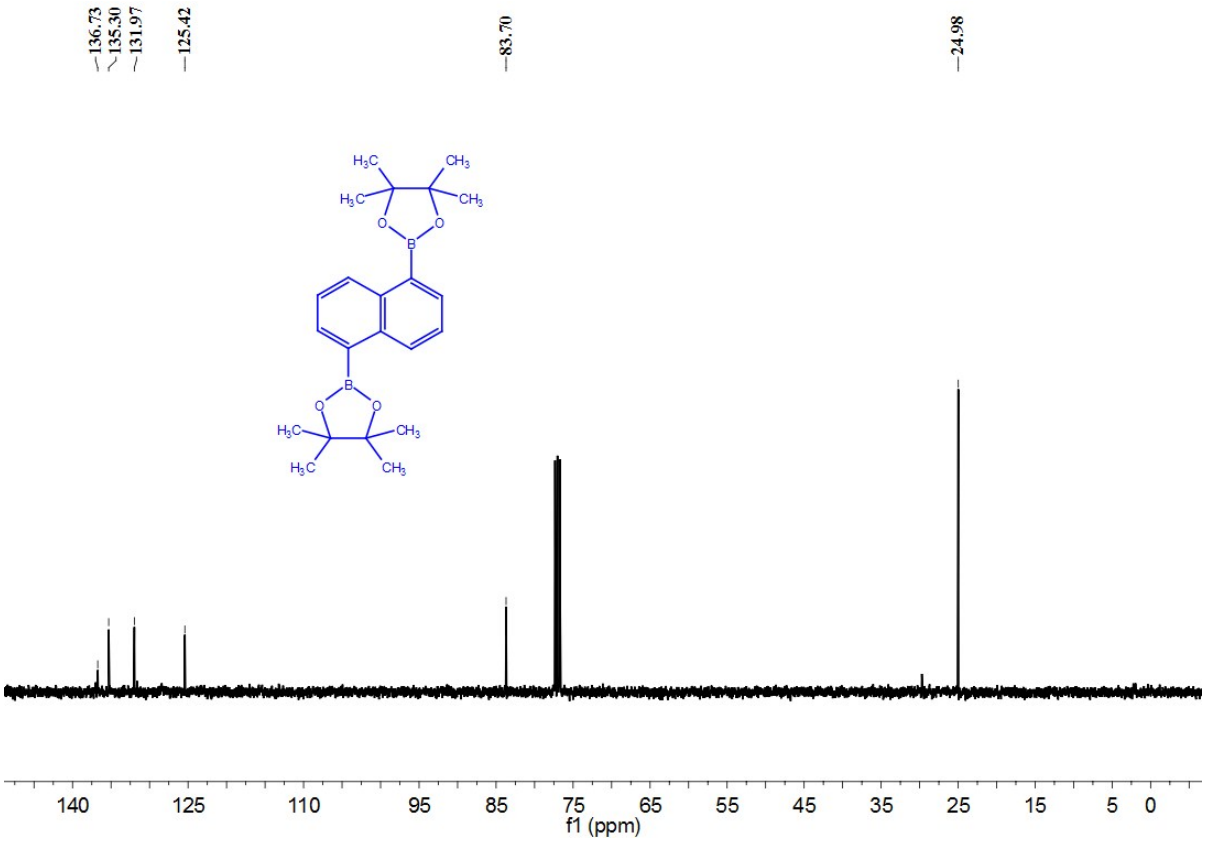
129.52
125.95
84.31
24.94
f1 (ppm)


8.02
8.00
7.87
7.85
7.26 CDCl3
3.90
1.34
B (d)
7.86
A (d)
8.01
C (s)
3.90
D (s)
1.34
2.00
1.96
3.00
12.00
f1 (ppm)


167.22
134.76
132.40
128.69
84.27
52.22
24.97
f1 (ppm)


8.92
8.90
8.10
8.09
7.56
7.55
7.54
7.53
1.45
A (d)
8.91
B (d)
8.09
C (dd)
7.54
D (s)
1.45
1.96
2.00
2.08
24.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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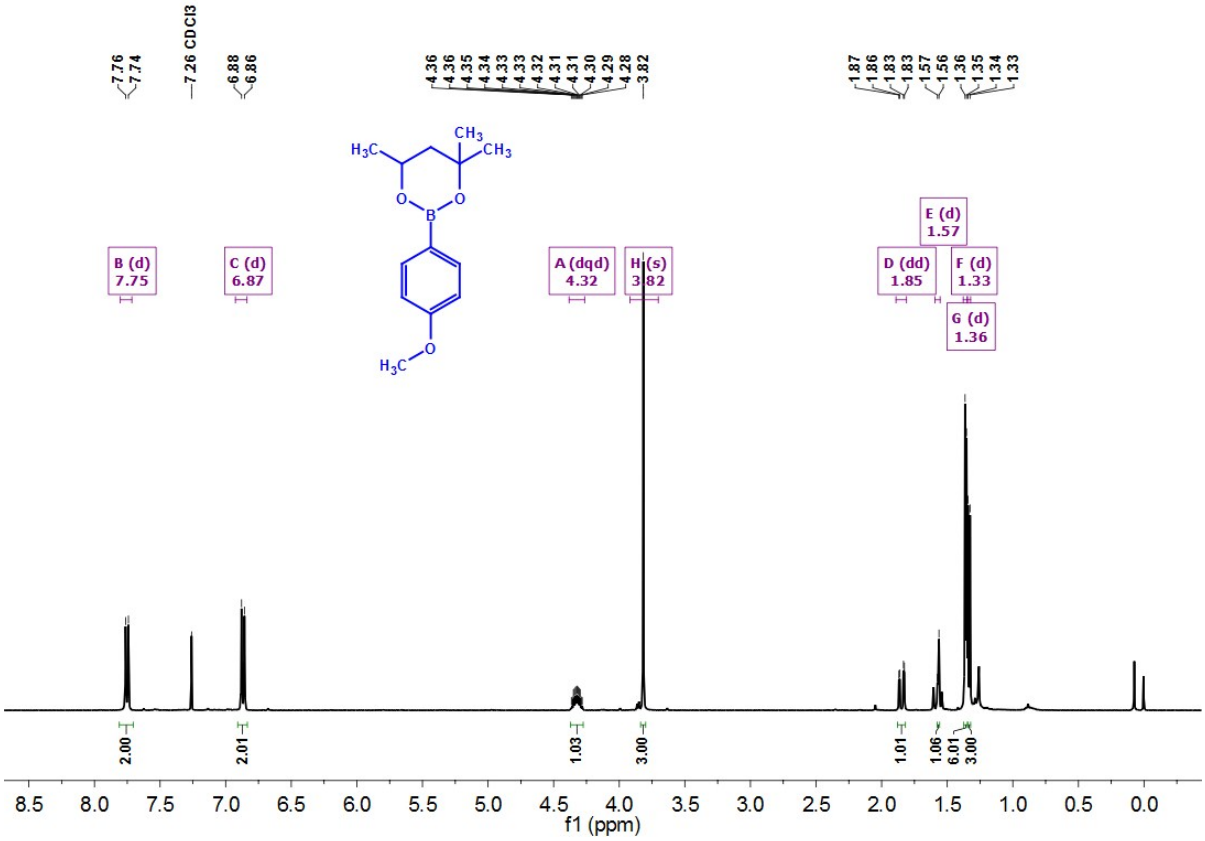
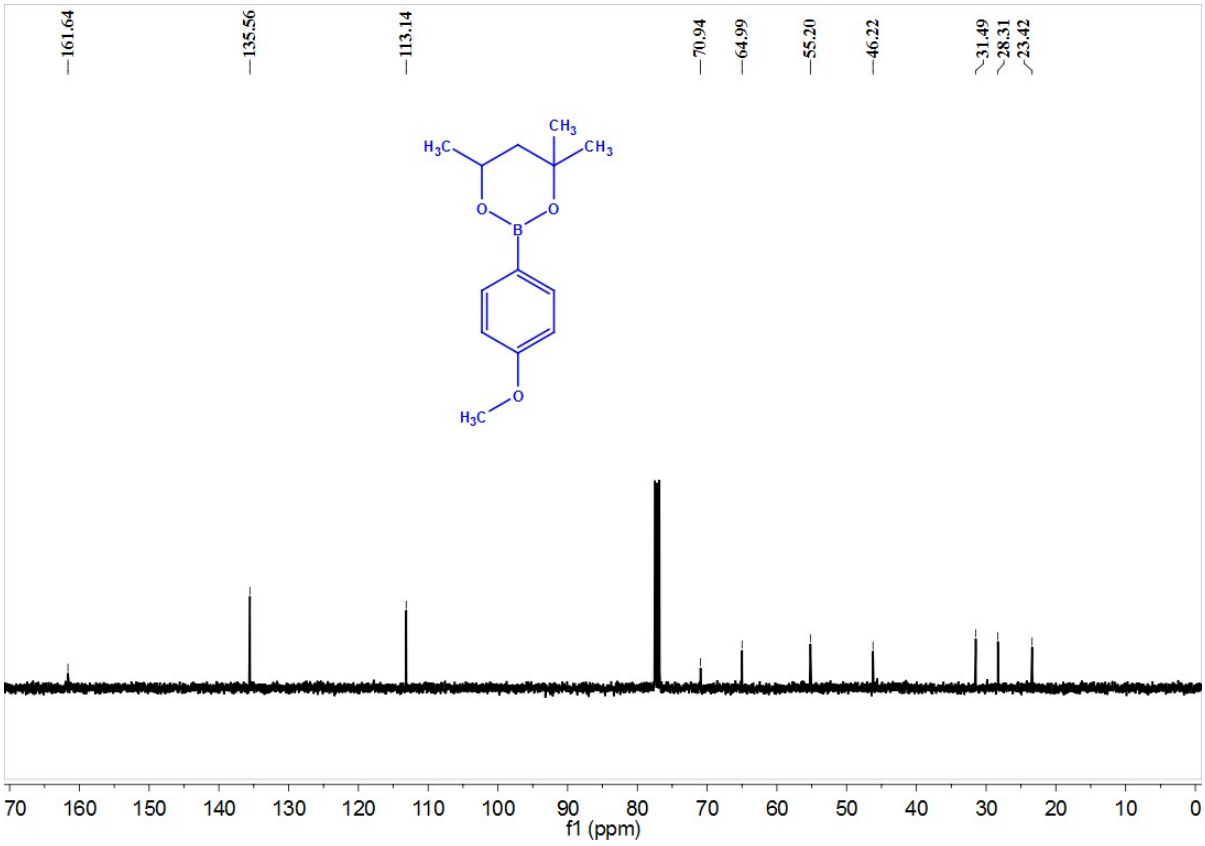
135.30
131.97
125.42
83.70
24.98
140 125 110 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)


7.76
7.74
7.26 CDCl3
6.88
6.86
4.36
4.36
4.35
4.34
4.33
4.33
4.32
4.31
4.31
4.30
4.29
4.28
3.82
1.87
1.86
1.83
1.83
1.57
1.56
1.36
1.35
1.34
1.33
B (d) 7.75
C (d) 6.87
A (dqd) 4.32
H (s) 3.82
D (dd) 1.85
E (d) 1.57
F (d) 1.33
G (d) 1.36
2.00
2.01
1.03
3.00
1.01
1.06
6.01
3.00
f1 (ppm)


161.64
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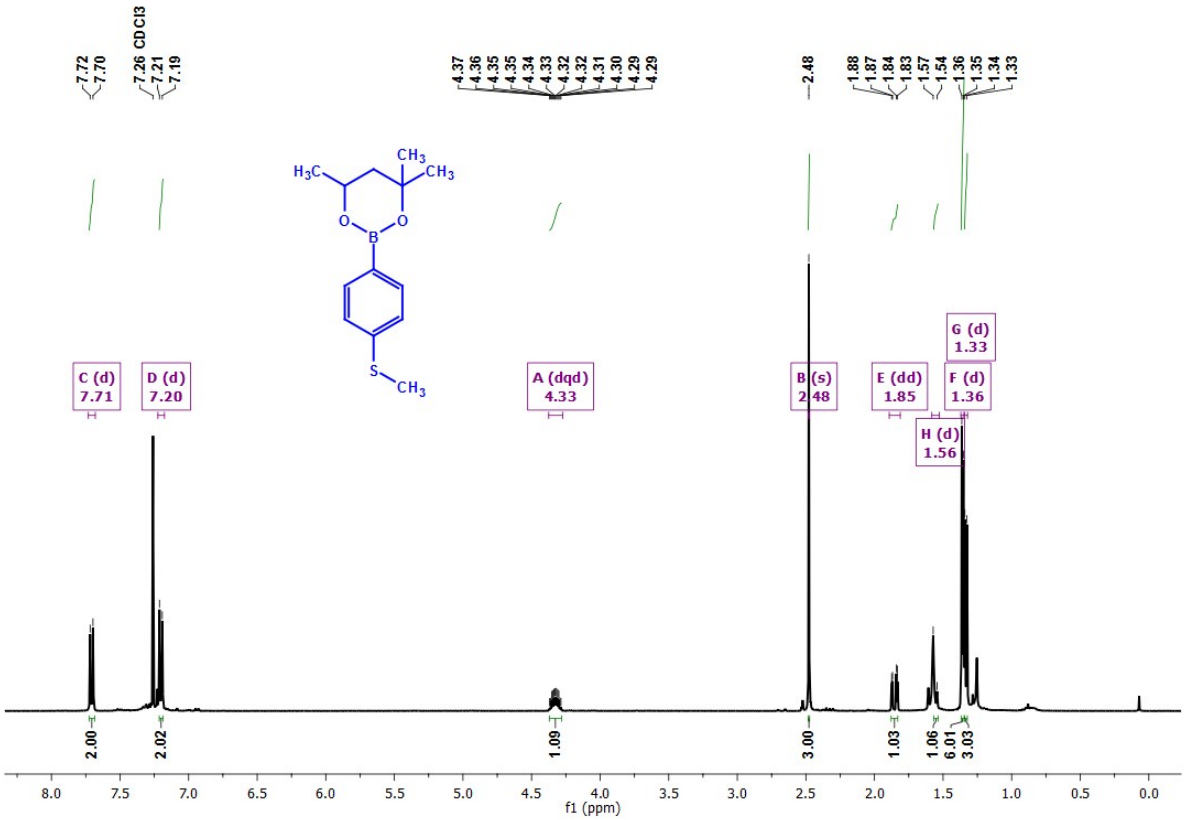
64.99
55.20
46.22
31.49
28.31
23.42
f1 (ppm)


7.72
7.70
7.26 CDCl3
7.21
7.19
4.37
4.36
4.35
4.35
4.34
4.33
4.32
4.32
4.31
4.30
4.29
4.29
2.48
1.88
1.87
1.84
1.83
1.57
1.54
1.36
1.35
1.34
1.33
C (d) 7.71
D (d) 7.20
A (dqd) 4.33
B (s) 2.48
E (dd) 1.85
F (d) 1.36
G (d) 1.33
H (d) 1.56
2.00
2.02
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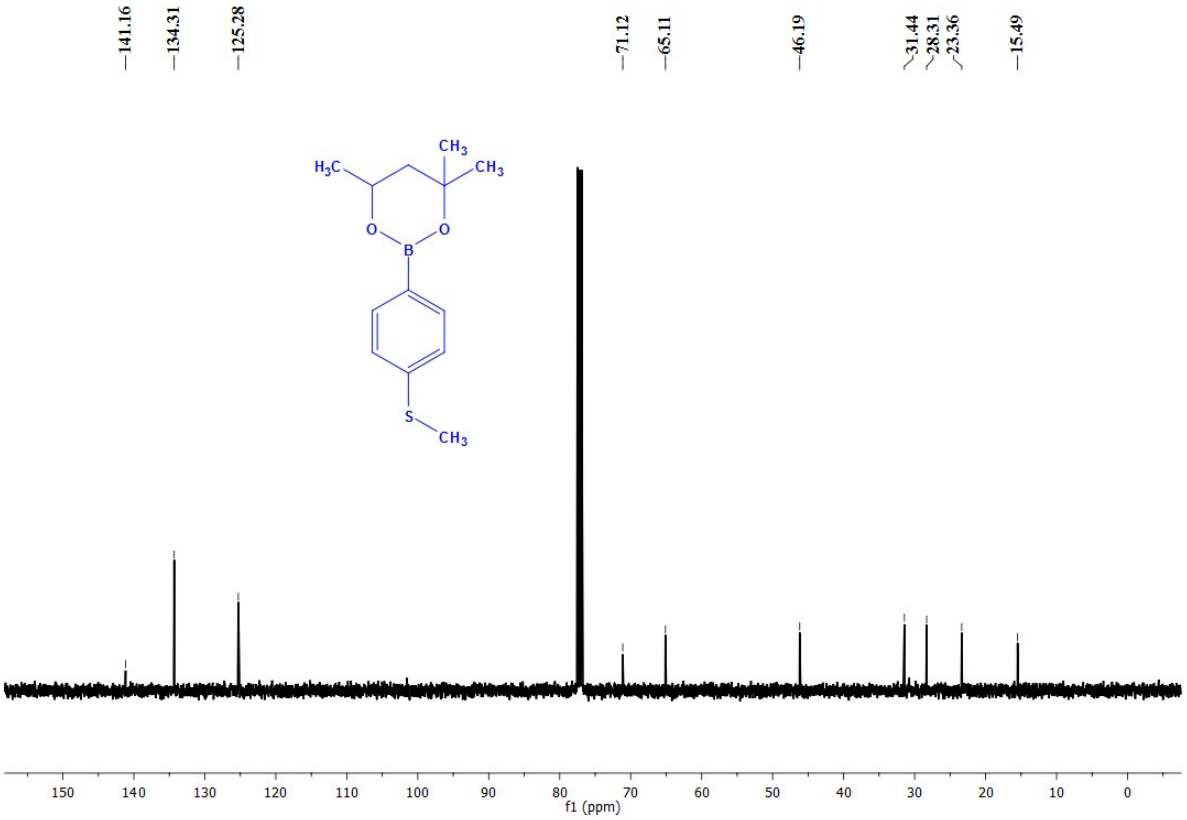
1.03
1.06
6.01
3.03
f1 (ppm)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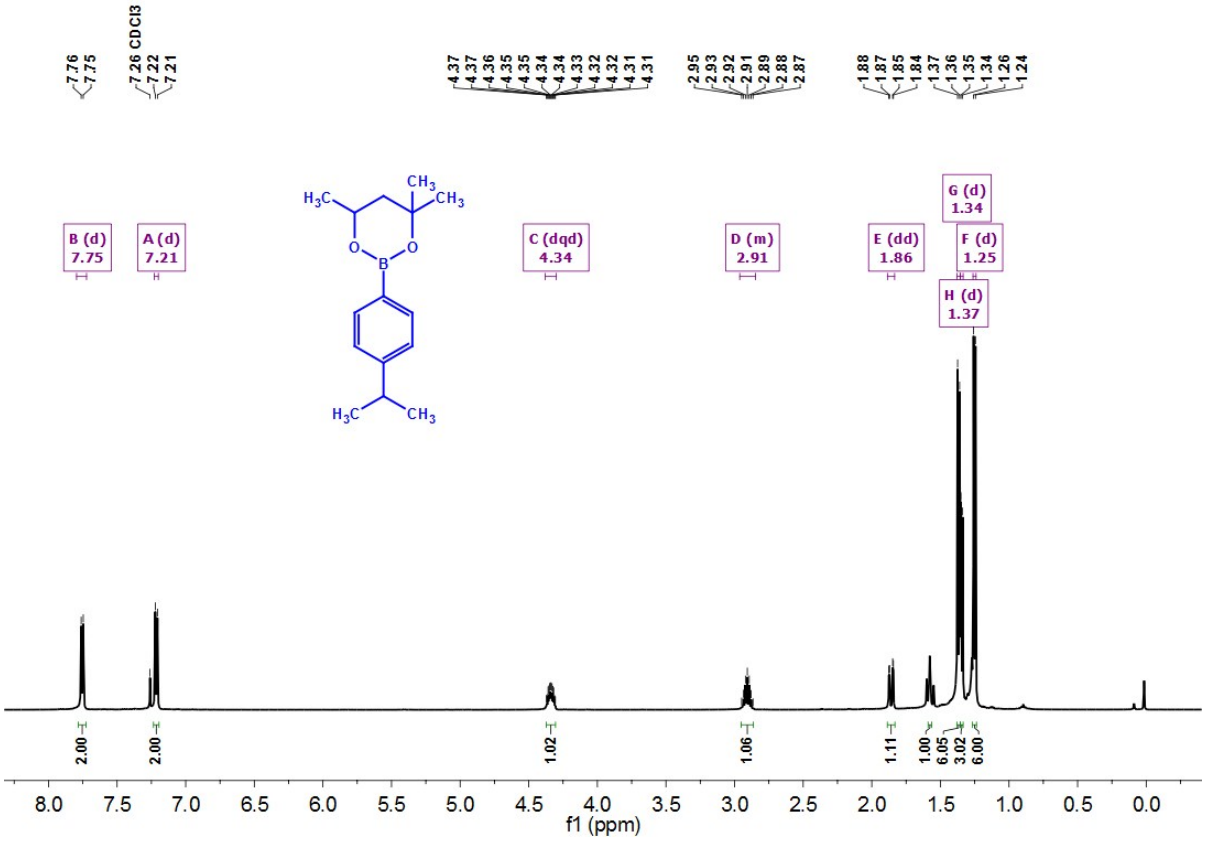
125.28
71.12
65.11
46.19
31.44
28.31
23.36
15.49
f1 (ppm)


7.76
7.75
7.26 CDCl3
7.22
7.21
4.37
4.37
4.36
4.35
4.35
4.34
4.34
4.33
4.32
4.32
4.31
4.31
2.95
2.93
2.92
2.91
2.89
2.88
2.87
1.88
1.87
1.85
1.84
1.37
1.36
1.35
1.34
1.26
1.24
B (d)
7.75
A (d)
7.21
C (dqd)
4.34
D (m)
2.91
E (dd)
1.86
G (d)
1.34
F (d)
1.25
H (d)
1.37
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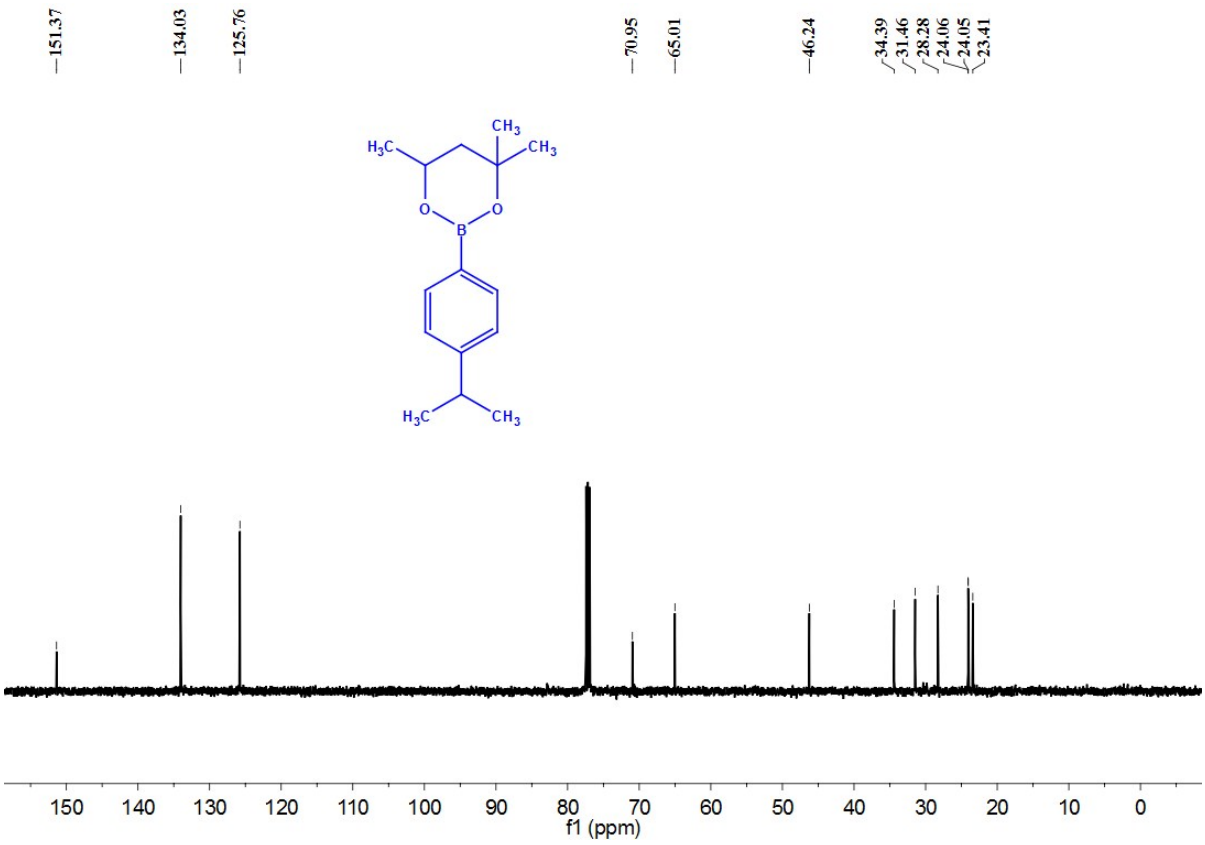
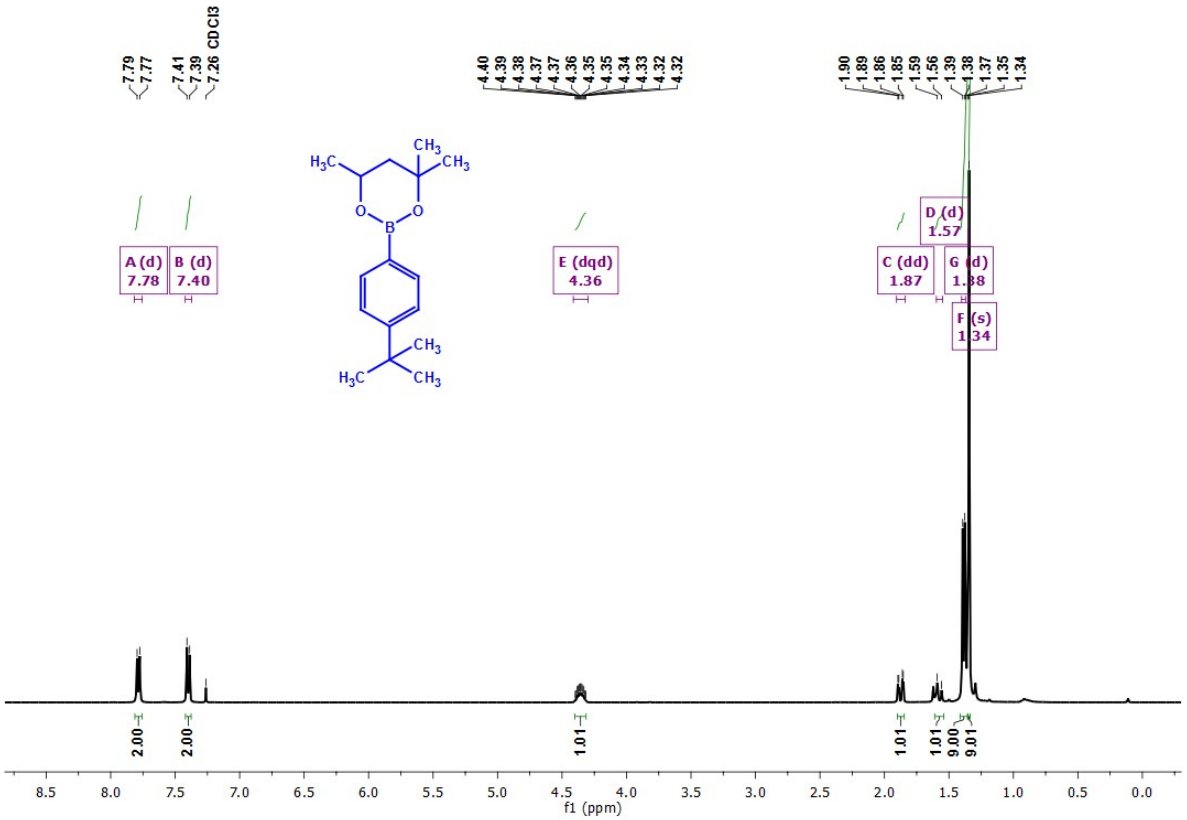
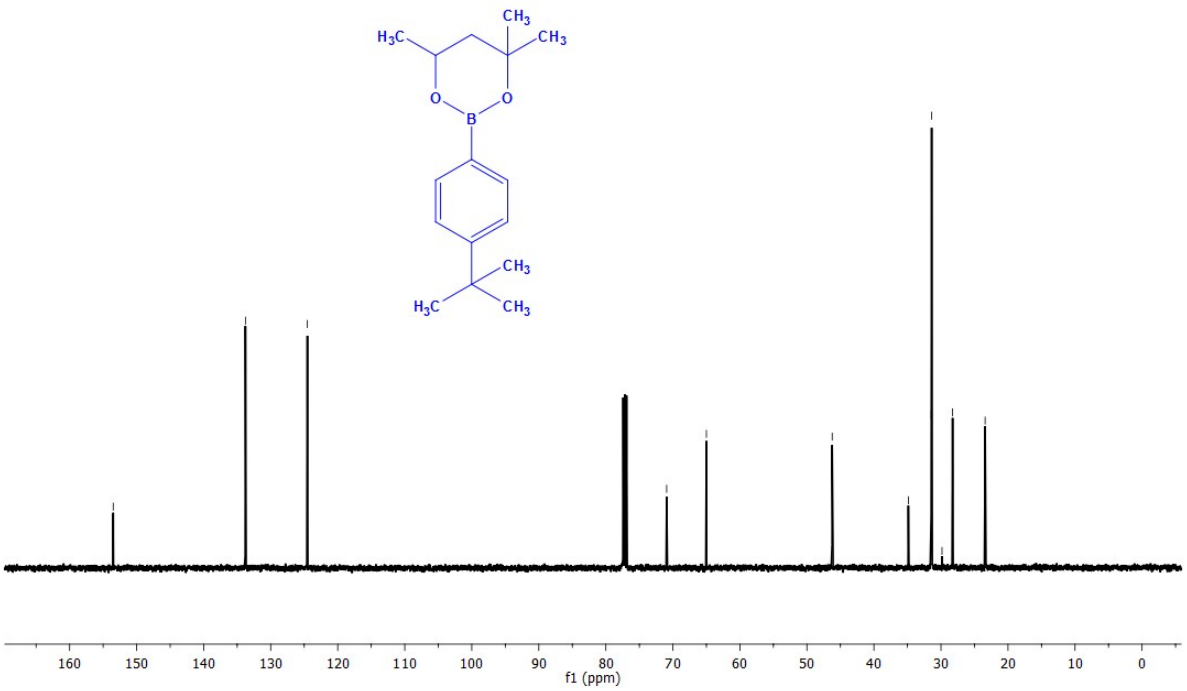
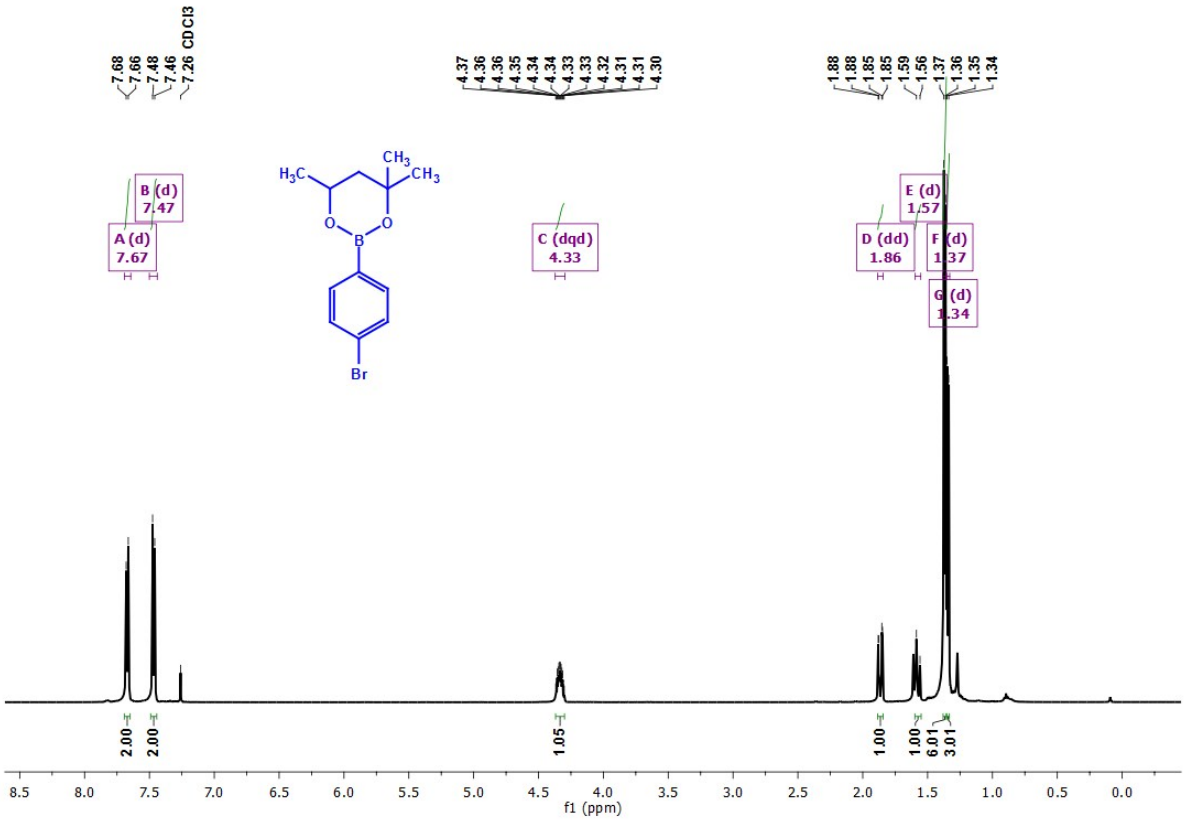
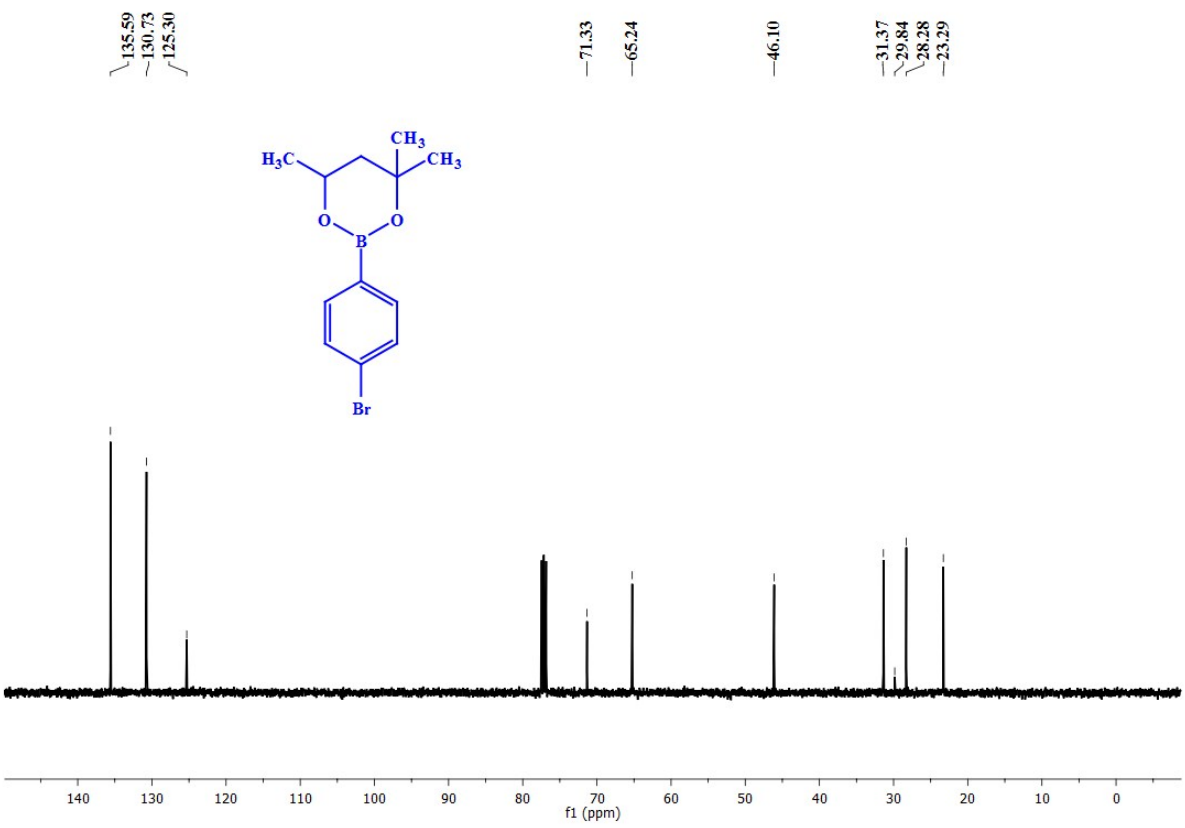
2.00
1.02
1.06
1.11
1.00
6.05
3.02
6.00
f1 (ppm)

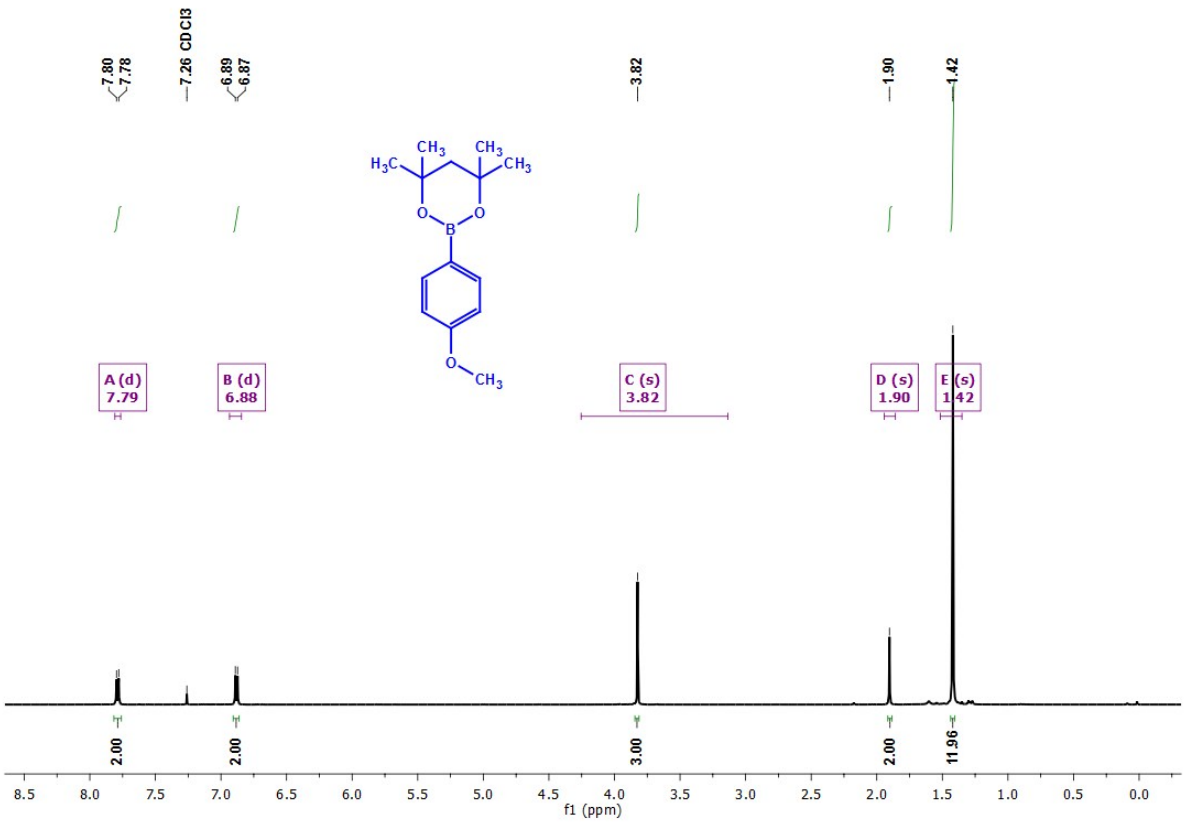

151.37
134.03
125.76
70.95
65.01
46.24
34.39
31.46
28.28
24.06
24.05
23.41
f1 (ppm)

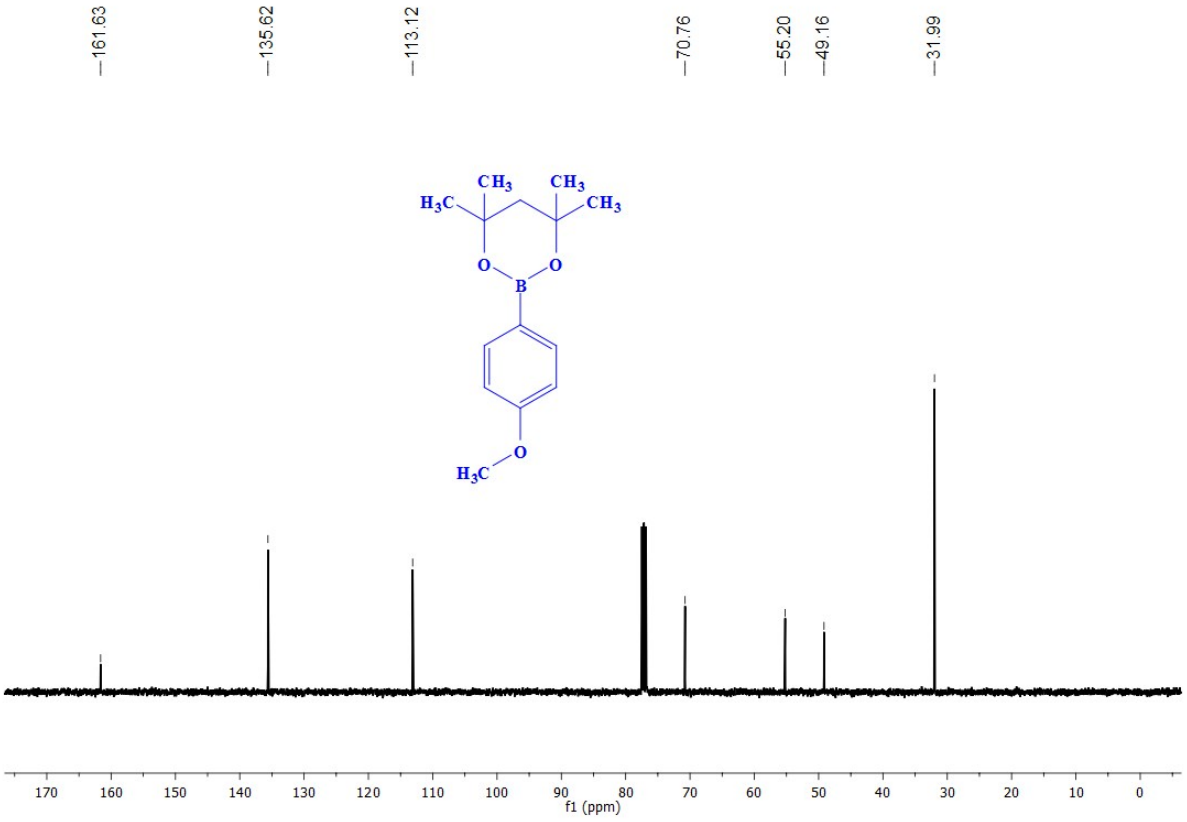

7.79
7.77
7.41
7.39
7.26 CDCl3
4.40
4.39
4.38
4.37
4.37
4.36
4.35
4.35
4.34
4.33
4.32
4.32
1.90
1.89
1.86
1.85
1.59
1.56
1.39
1.38
1.37
1.35
1.34
A (d) 7.78
B (d) 7.40
E (dqd) 4.36
C (dd) 1.87
D (d) 1.57
G (d) 1.38
F (s) 1.34
2.00
2.00
1.01
1.01
1.01
9.00
9.01
f1 (ppm)

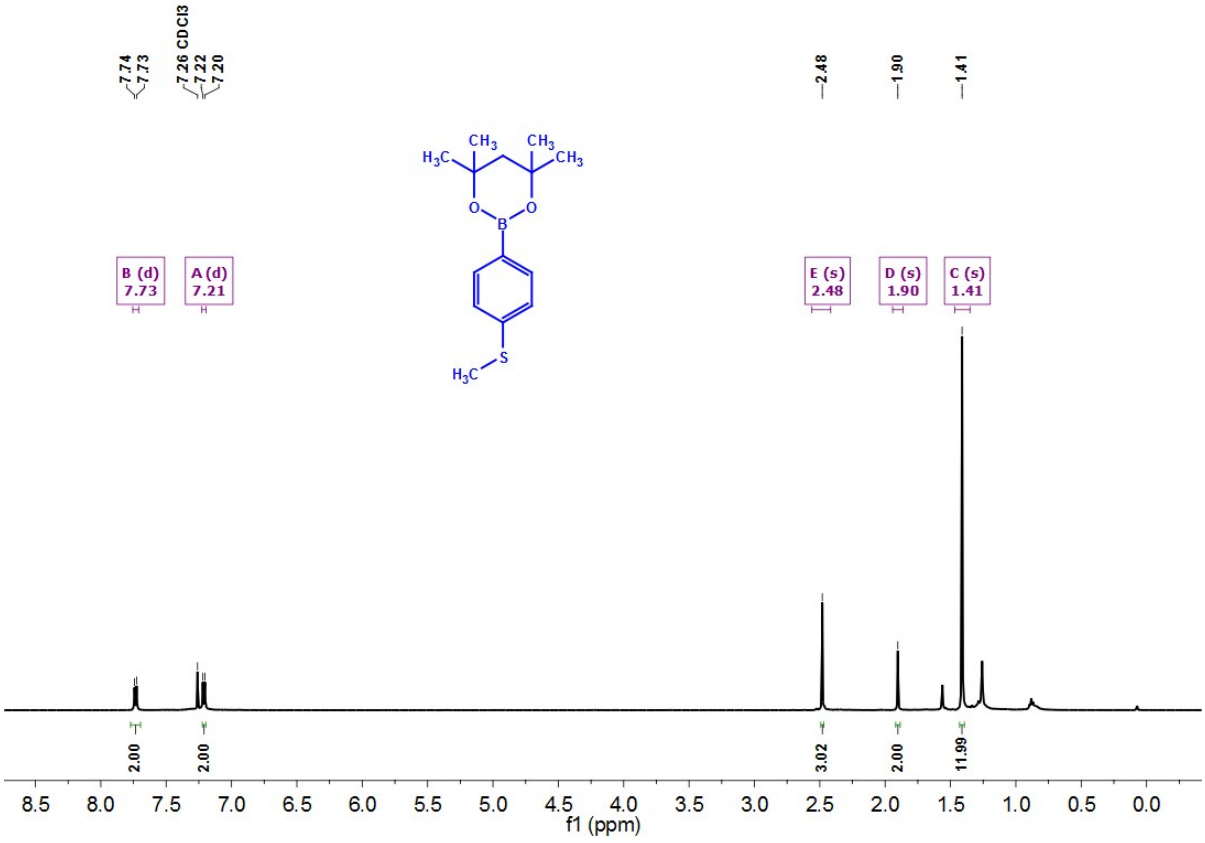

153.50
133.77
124.53
70.92
65.00
46.23
34.86
31.45
31.39
29.84
28.26
23.41
f1 (ppm)

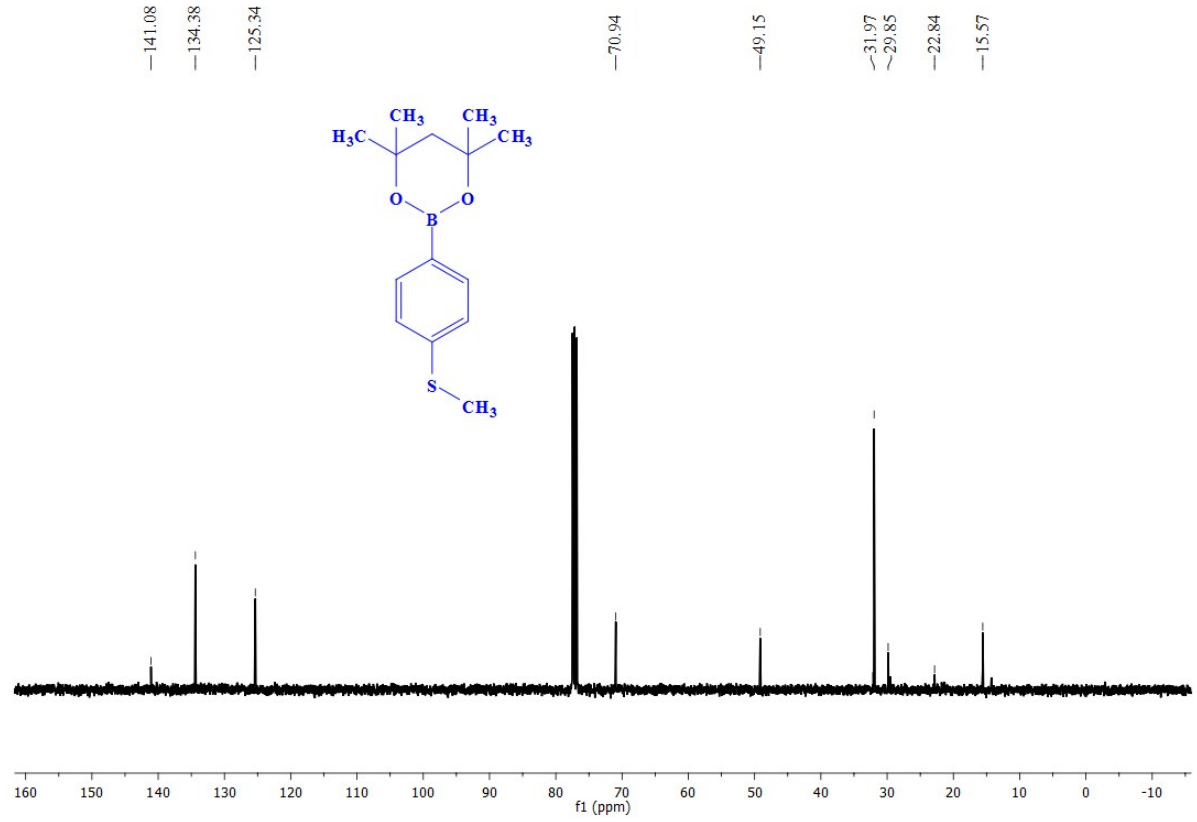

7.68
7.66
7.48
7.46
7.26 CDCl3
4.37
4.36
4.36
4.35
4.34
4.34
4.33
4.33
4.32
4.31
4.31
4.30
1.88
1.88
1.85
1.85
1.59
1.56
1.37
1.36
1.35
1.34
A (d)
7.67
B (d)
7.47
C (dqd)
4.33
D (dd)
1.86
E (d)
1.57
F (d)
1.37
G (d)
1.34
Br
2.00
2.00
1.05
1.00
1.00
6.01
3.01
f1 (ppm)

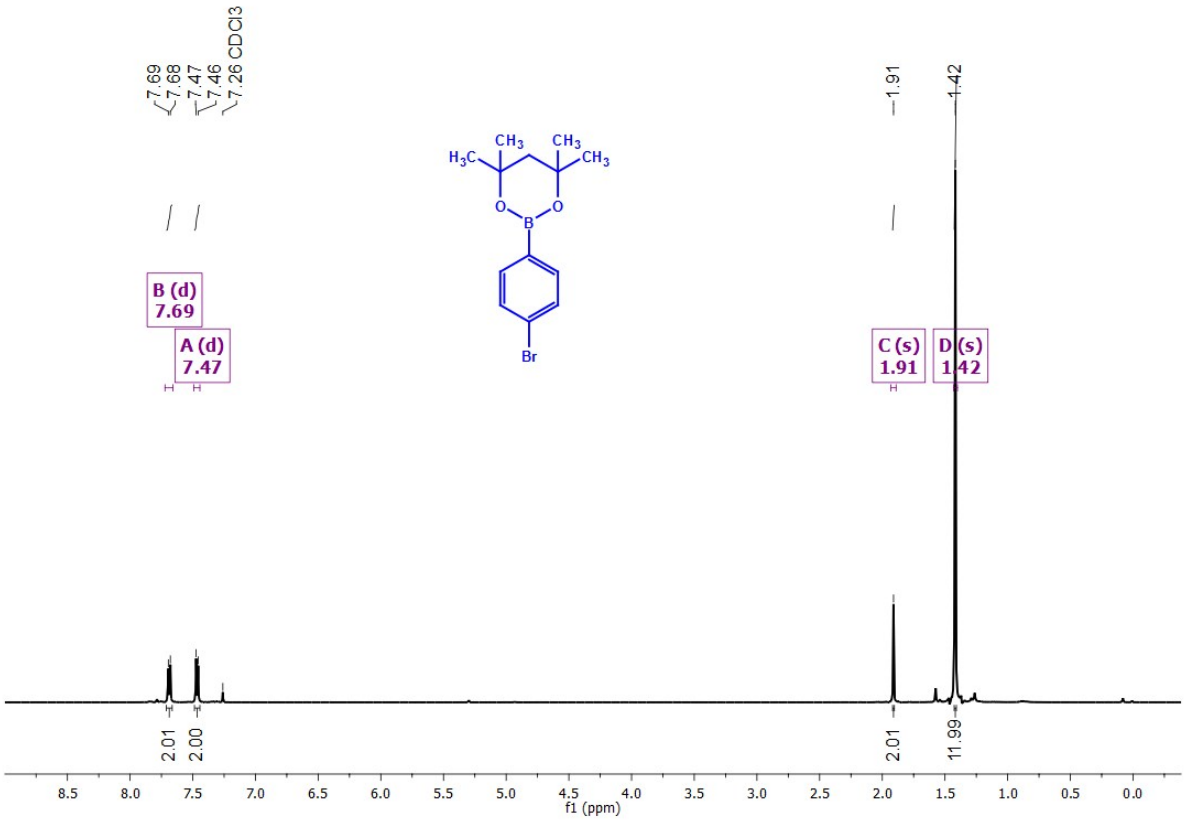

135.59
130.73
125.30
71.33
65.24
46.10
31.37
29.84
28.28
23.29
Br
f1 (ppm)

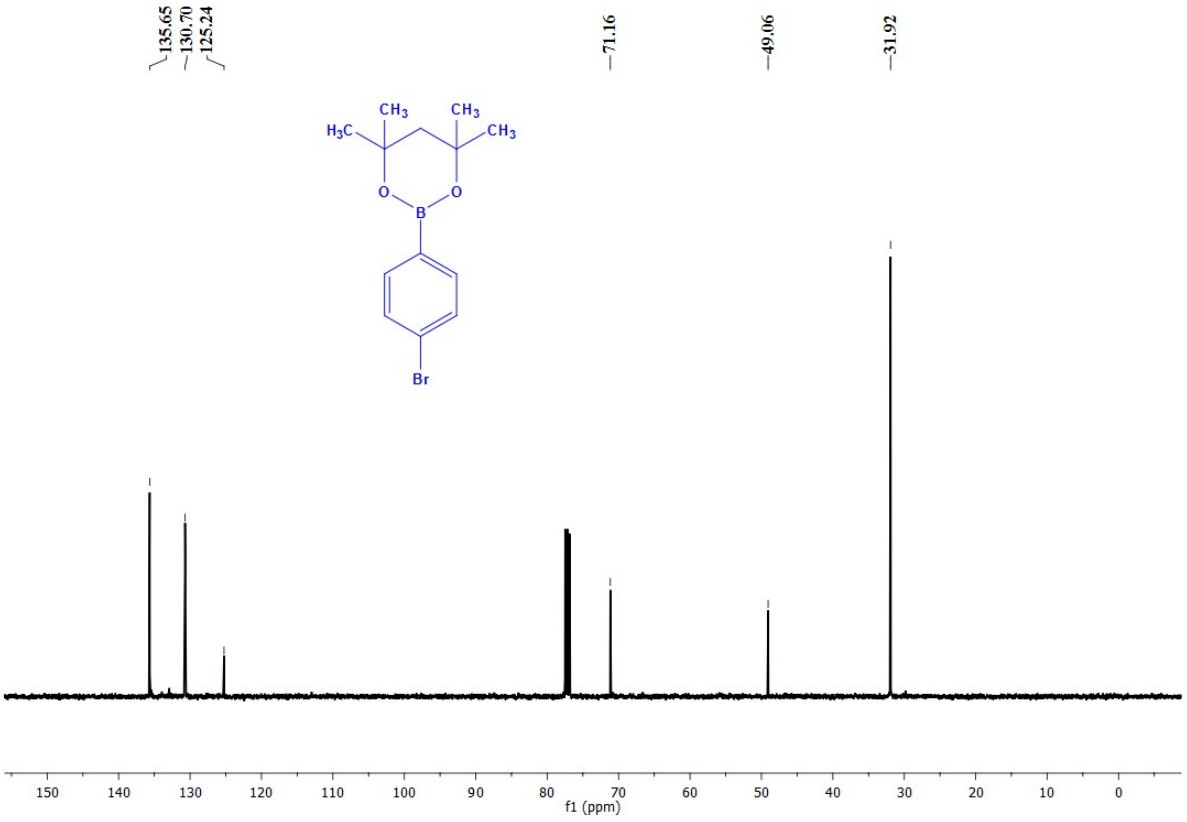

7.80
7.78
7.26 CDCl3
6.89
6.87
3.82
1.90
1.42
A (d)
7.79
B (d)
6.88
C (s)
3.82
D (s)
1.90
E (s)
1.42
2.00
2.00
3.00
2.00
11.96
f1 (ppm)

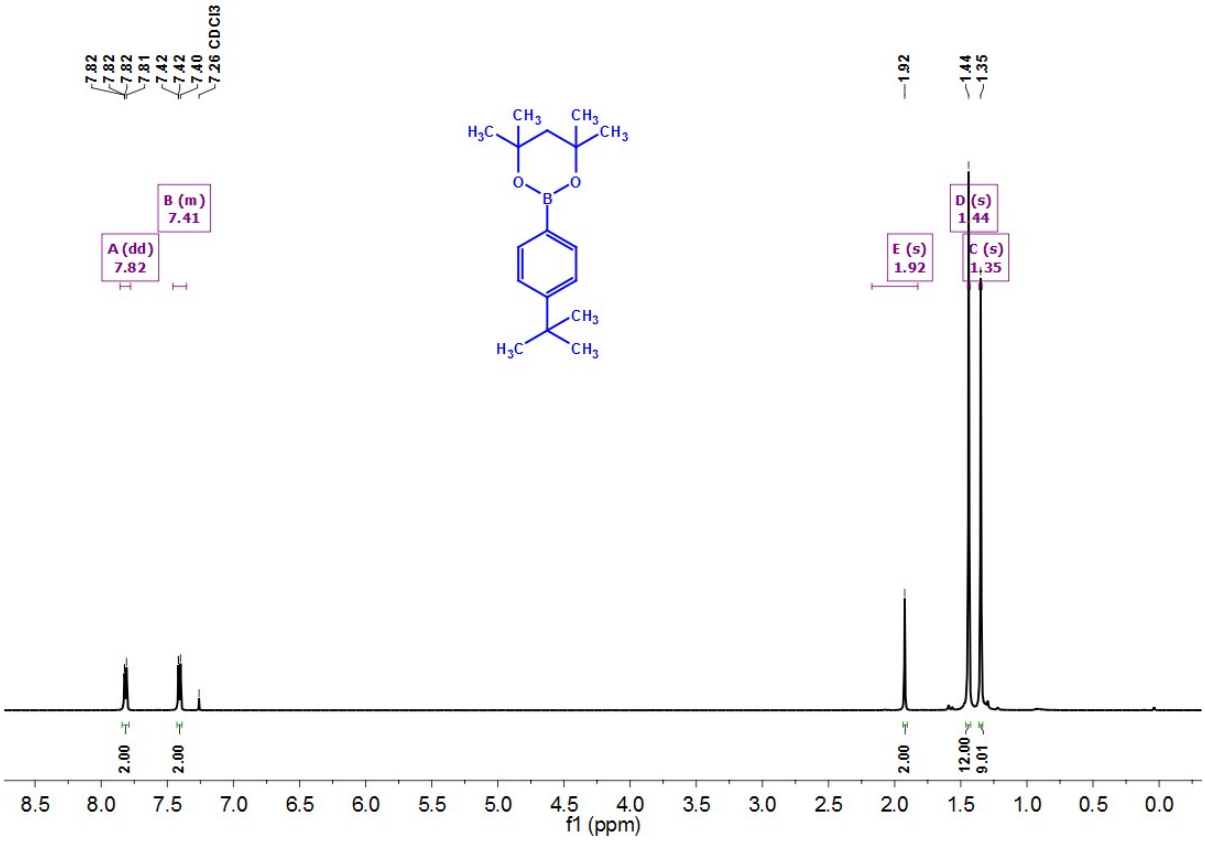

161.63
135.62
113.12
70.76
55.20
49.16
31.99
f1 (ppm)

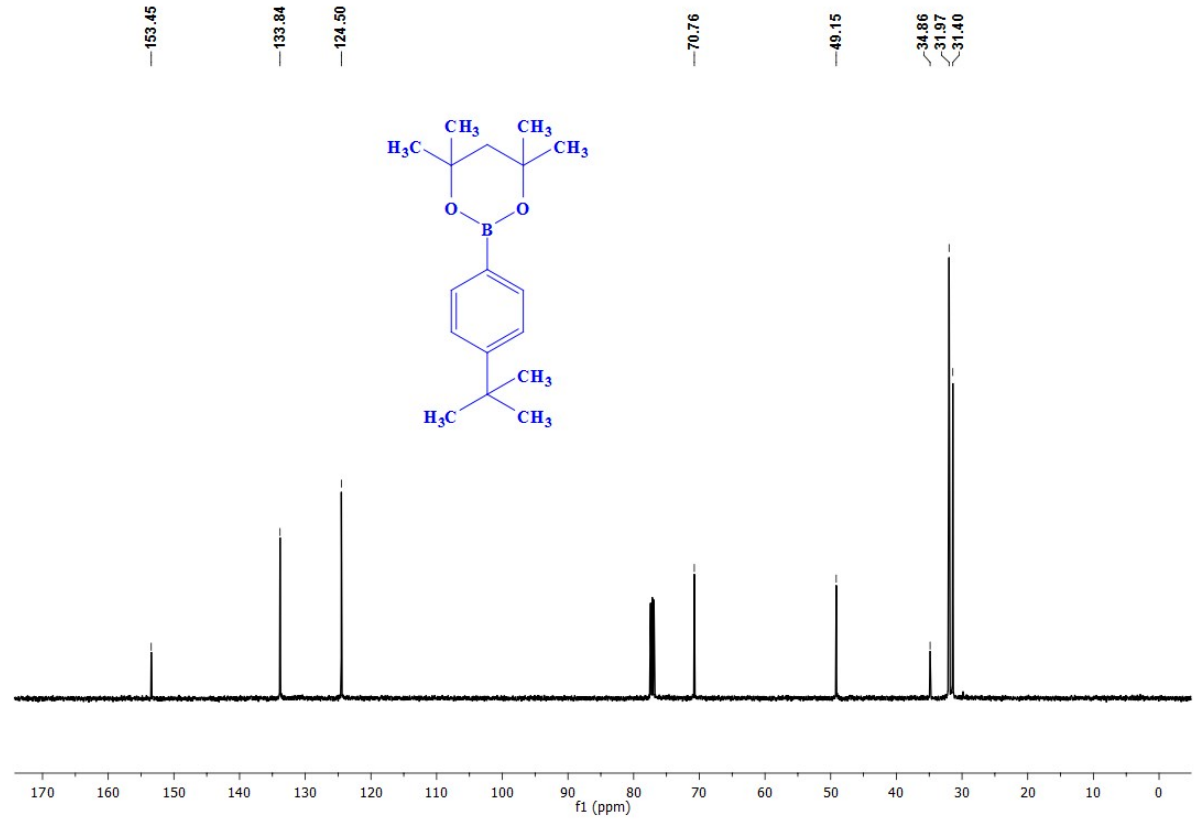

7.74
7.73
7.26 CDCl3
7.22
7.20
2.48
1.90
1.41
B (d) 7.73
A (d) 7.21
E (s) 2.48
D (s) 1.90
C (s) 1.41
2.00
2.00
3.02
2.00
11.99
f1 (ppm)

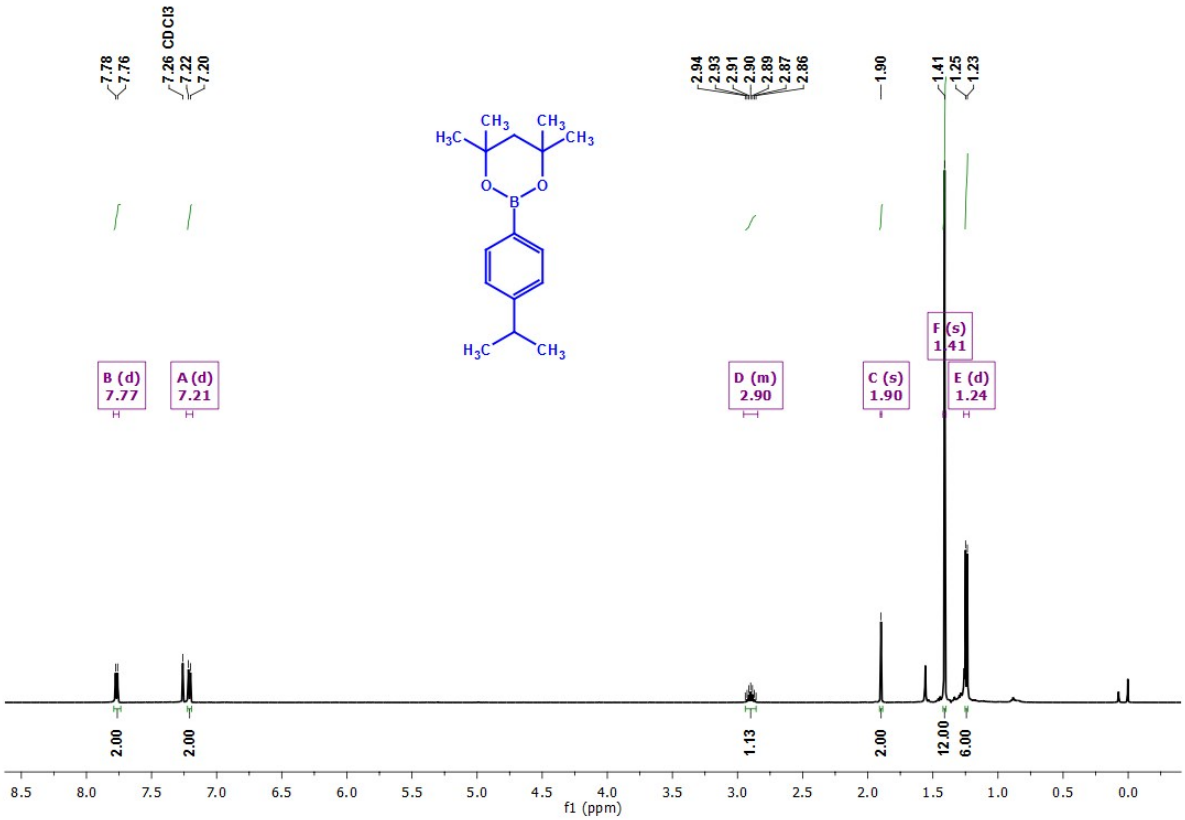

141.08
134.38
125.34
70.94
49.15
31.97
29.85
22.84
15.57
f1 (ppm)

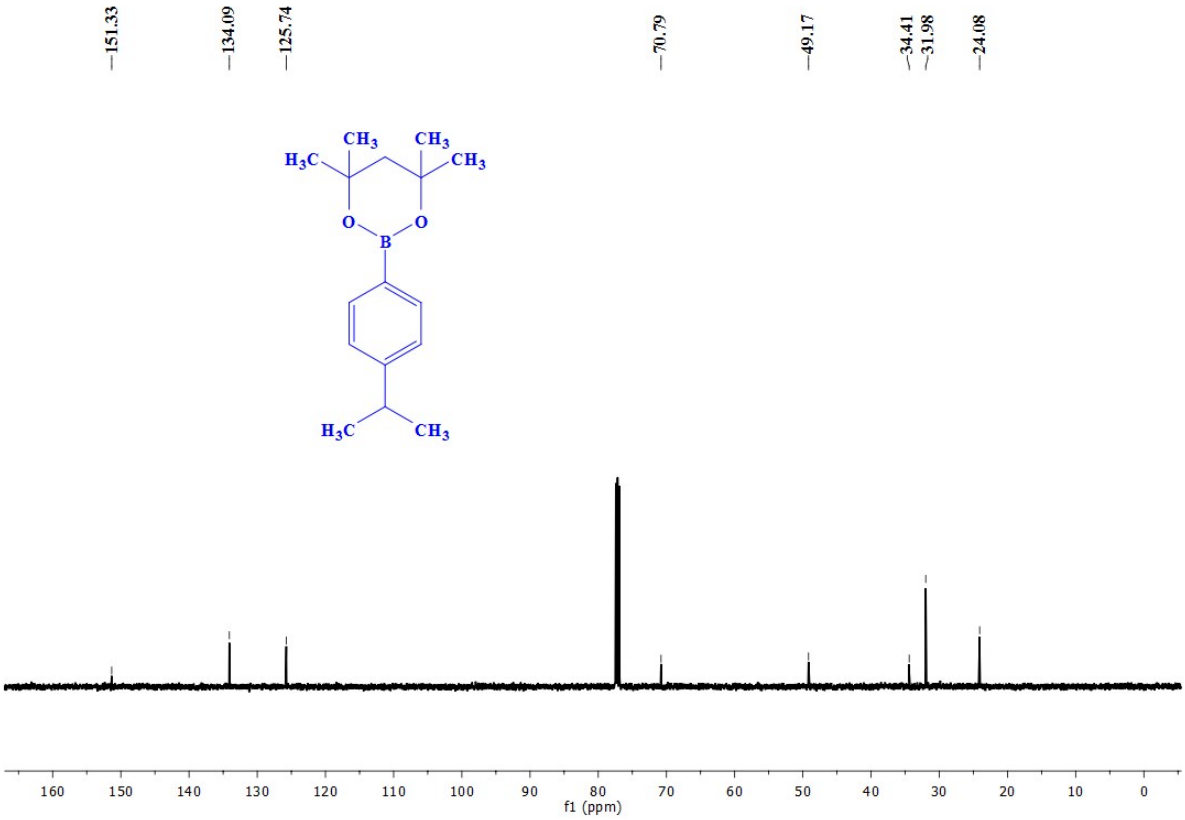

7.69
7.68
7.47
7.46
7.26 CDCl3
1.91
1.42
B (d) 7.69
A (d) 7.47
C (s) 1.91
D (s) 1.42
2.01
2.00
2.01
11.99
f1 (ppm)

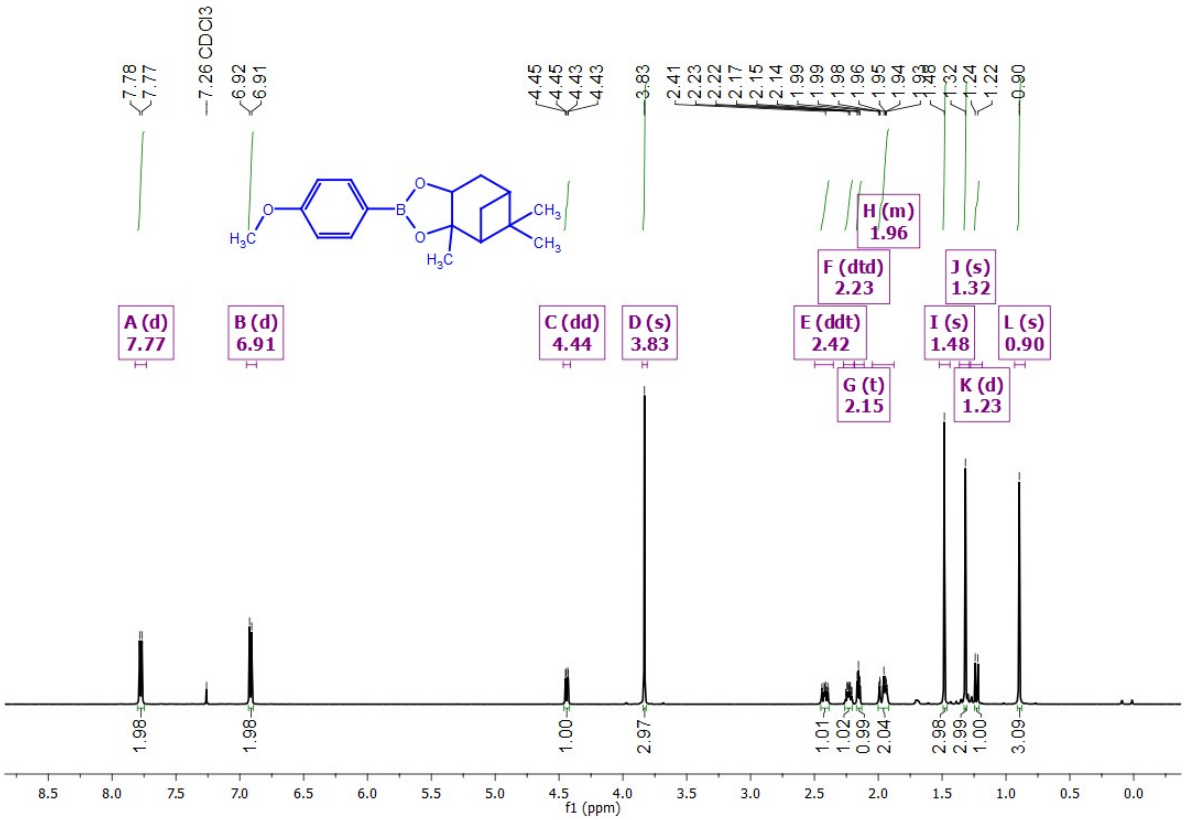

135.65
130.70
125.24
71.16
49.06
31.92
f1 (ppm)

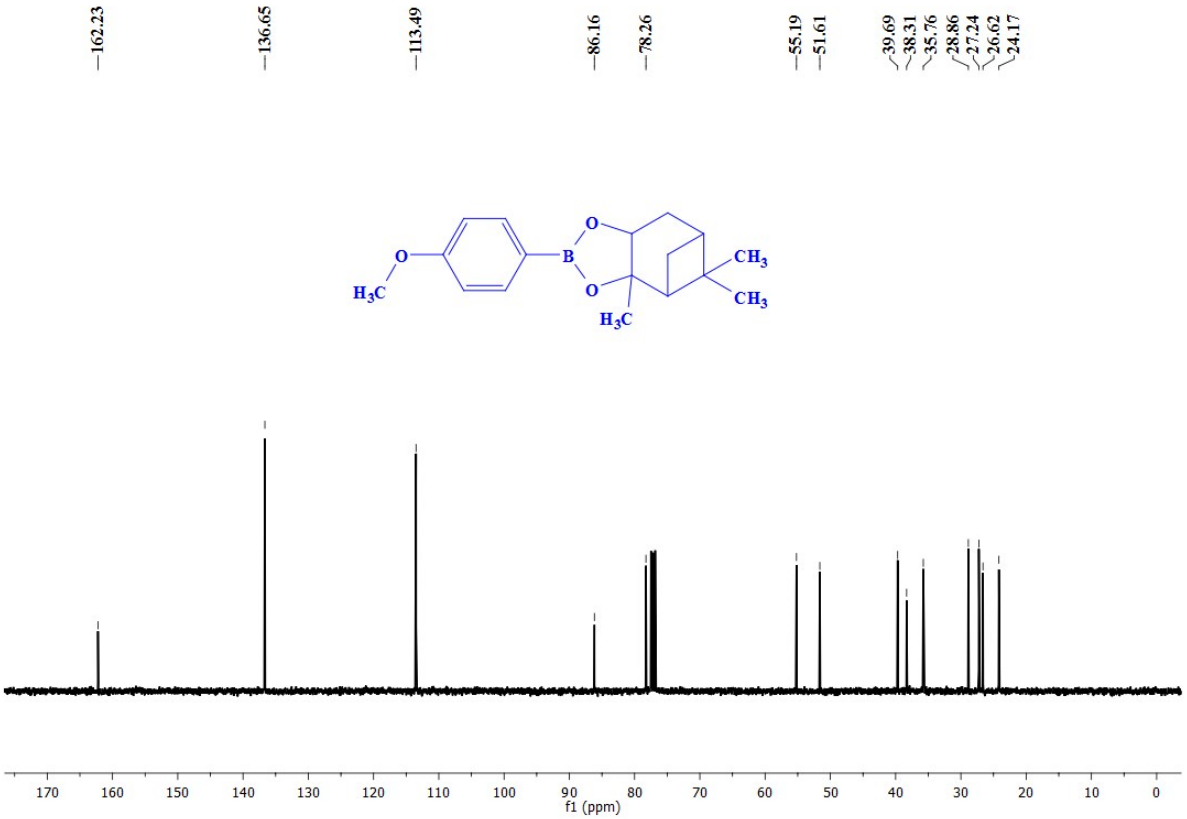

7.82
7.82
7.82
7.81
7.42
7.42
7.40
7.26 CDCl3
1.92
1.44
1.35
B (m)
7.41
A (dd)
7.82
E (s)
1.92
D (s)
1.44
C (s)
1.35
2.00
2.00
2.00
12.00
9.01
f1 (ppm)

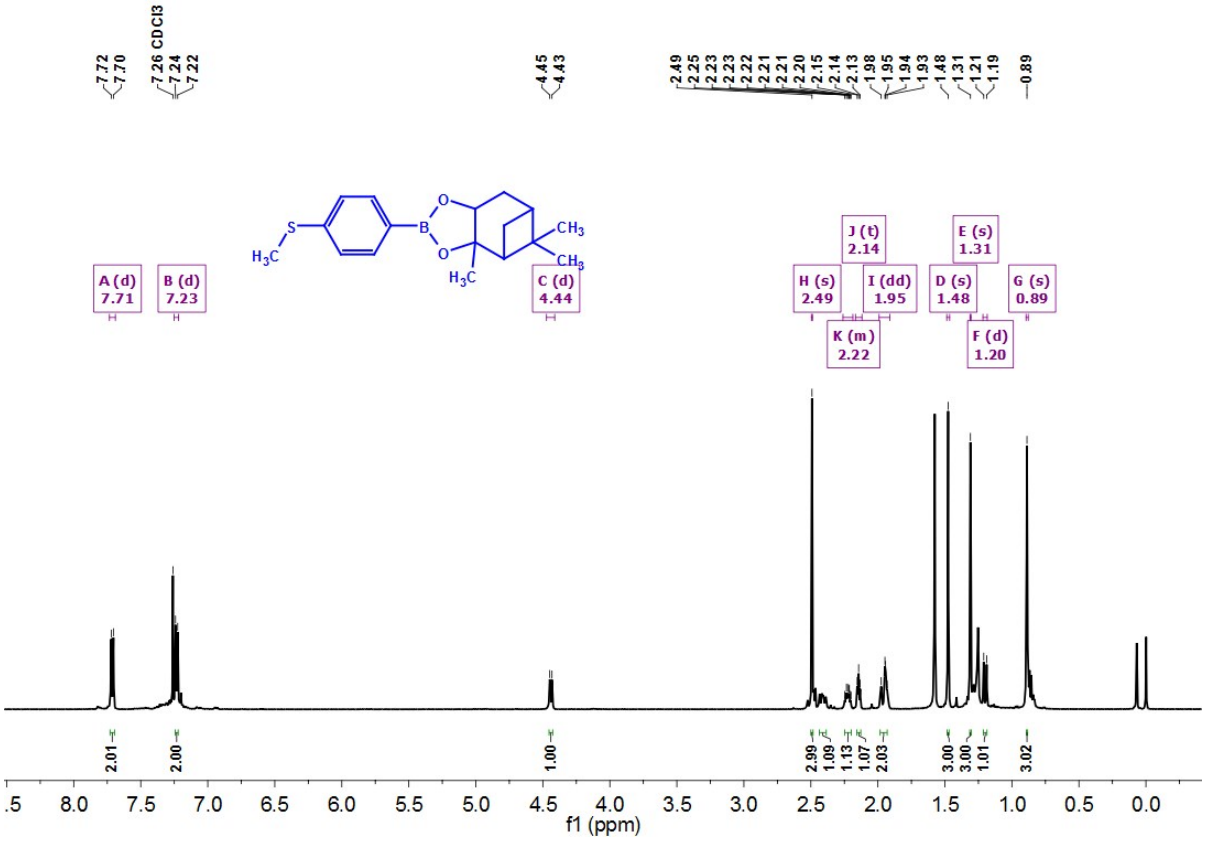

153.45
133.84
124.50
70.76
49.15
34.86
31.97
31.40
f1 (ppm)

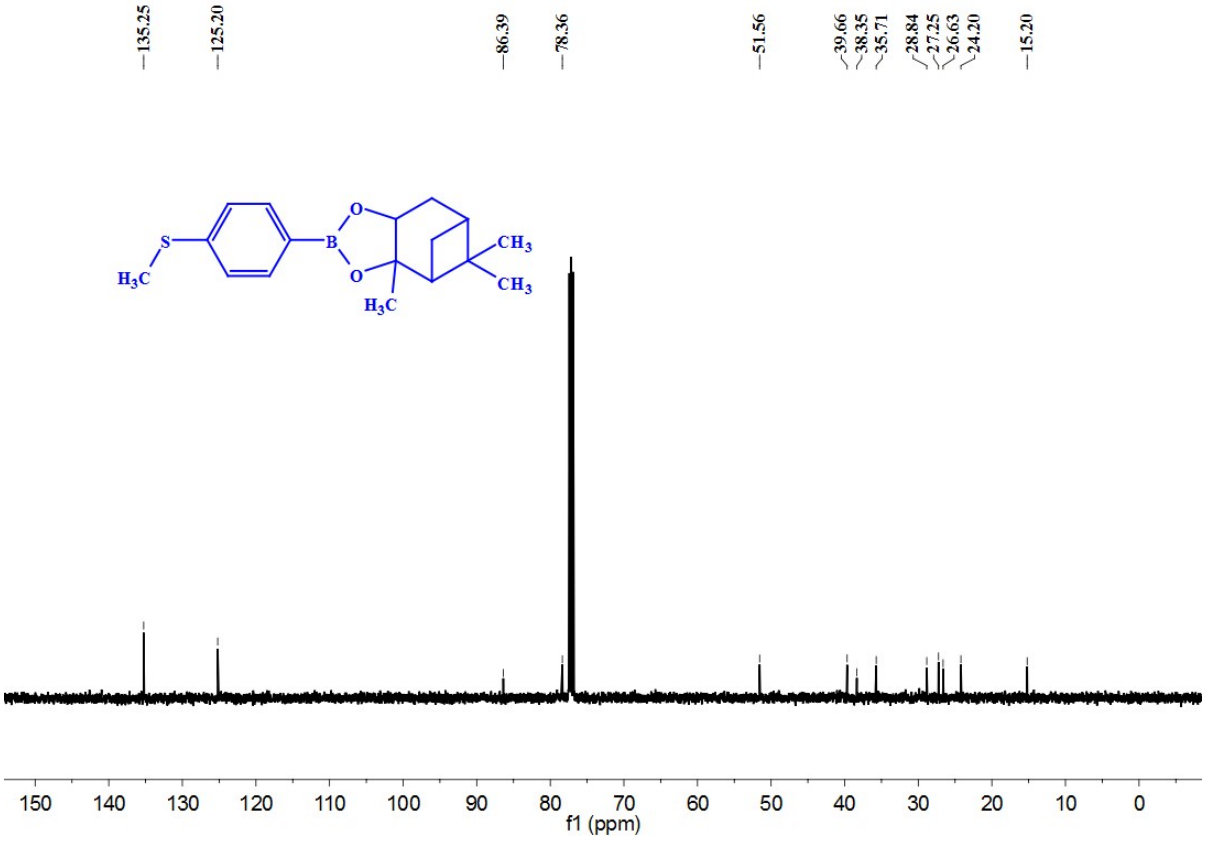

7.78
7.76
7.26 CDCl3
7.22
7.20
2.94
2.93
2.91
2.90
2.89
2.87
2.86
1.90
1.41
1.25
1.23
B (d) 7.77
A (d) 7.21
D (m) 2.90
C (s) 1.90
F (s) 1.41
E (d) 1.24
2.00
2.00
1.13
2.00
12.00
6.00
f1 (ppm)

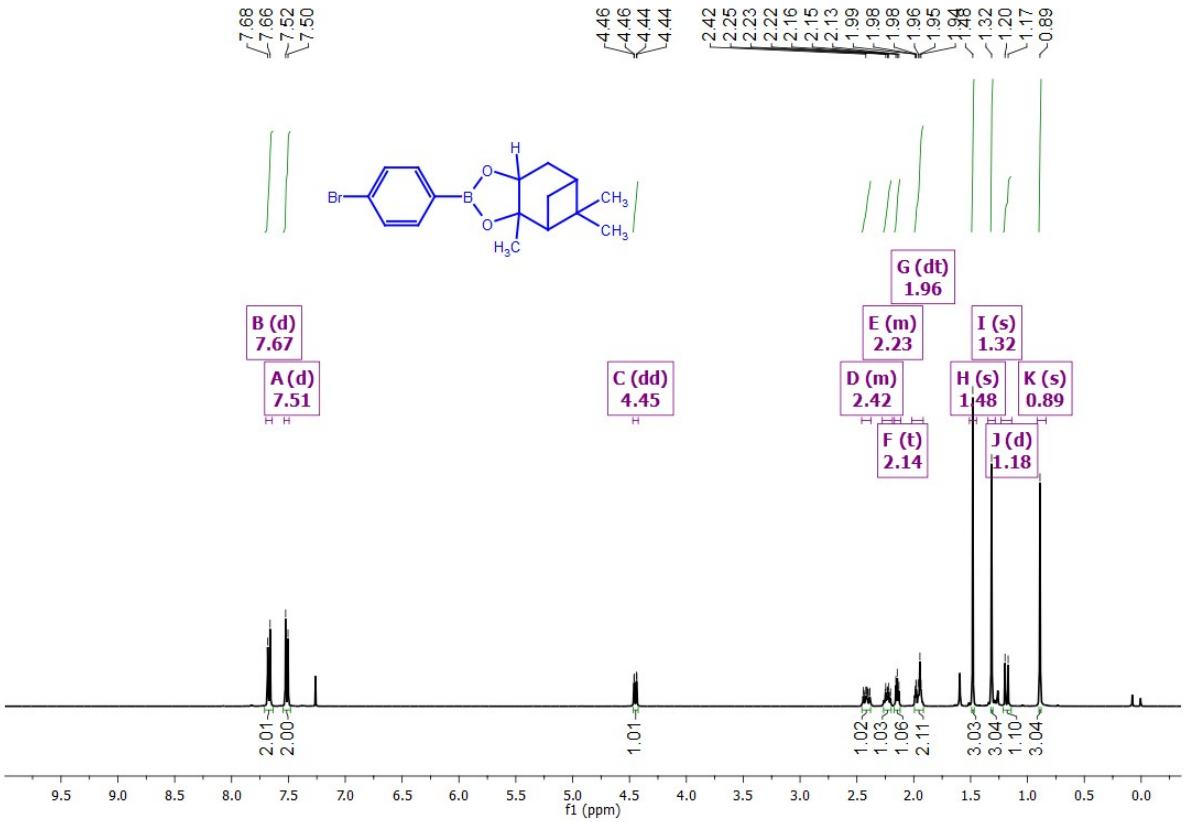

151.33
134.09
125.74
70.79
49.17
34.41
31.98
24.08
f1 (ppm)

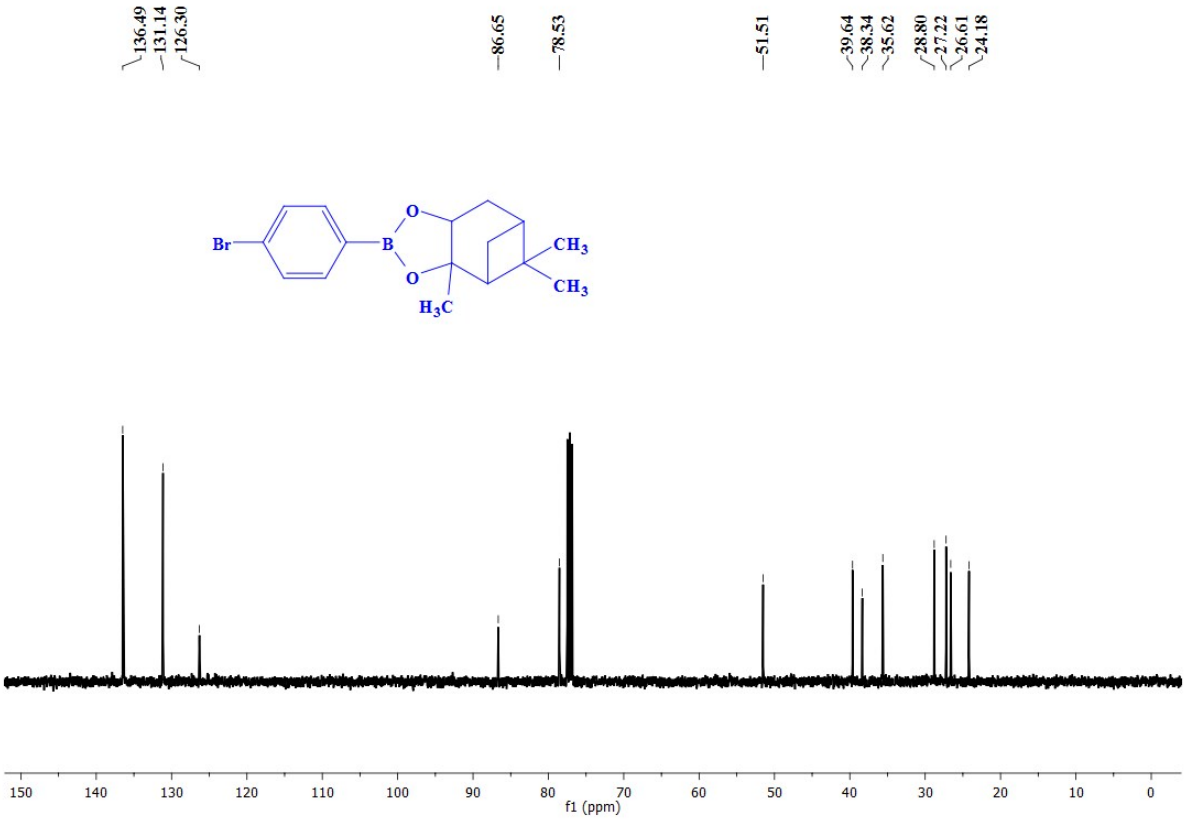

7.78
7.77
7.26 CDCl3
6.92
6.91
4.45
4.45
4.43
4.43
3.83
2.41
2.23
2.22
2.17
2.15
2.14
1.99
1.99
1.98
1.96
1.95
1.94
1.32
1.24
1.22
0.90
A (d) 7.77
B (d) 6.91
C (dd) 4.44
D (s) 3.83
E (ddt) 2.42
F (dtd) 2.23
G (t) 2.15
H (m) 1.96
I (s) 1.48
J (s) 1.32
K (d) 1.23
L (s) 0.90
1.98
1.98
1.00
2.97
1.01
1.02
0.99
2.04
2.98
2.99
1.00
3.09
f1 (ppm)

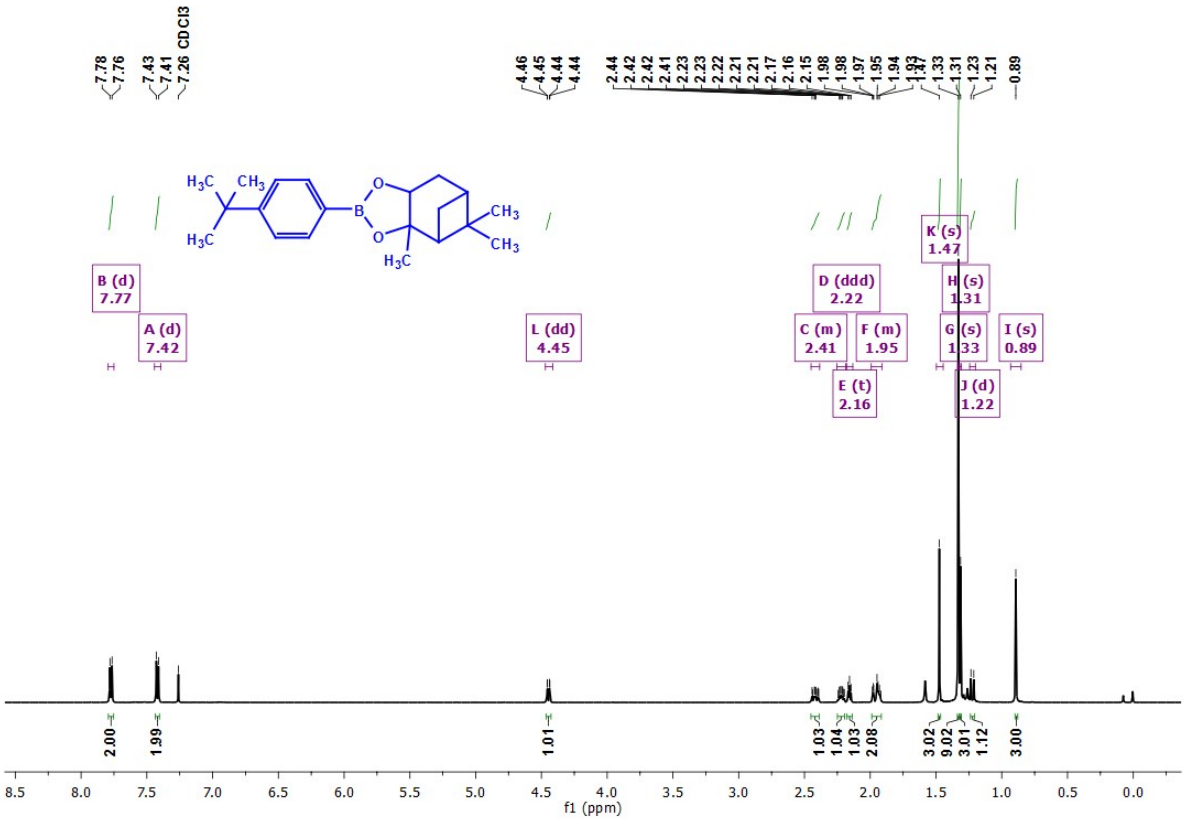

162.23
136.65
113.49
86.16
78.26
55.19
51.61
39.69
38.31
35.76
28.86
27.24
26.62
24.17
f1 (ppm)

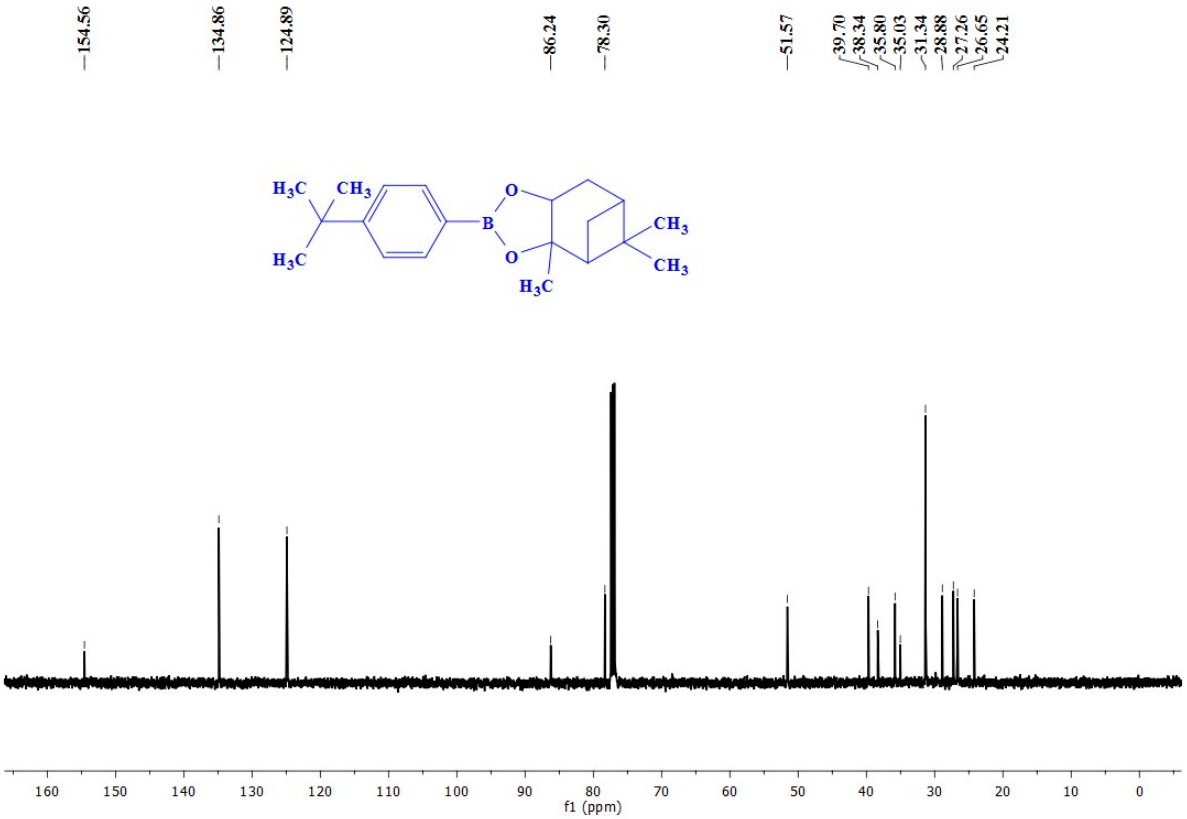

7.72
7.70
7.26 CDCl3
7.24
7.22
4.45
4.43
2.49
2.25
2.23
2.23
2.22
2.21
2.21
2.20
2.15
2.14
2.13
1.98
1.95
1.94
1.93
1.48
1.31
1.21
1.19
0.89
A (d) 7.71
B (d) 7.23
C (d) 4.44
J (t) 2.14
E (s) 1.31
H (s) 2.49
I (dd) 1.95
D (s) 1.48
G (s) 0.89
K (m) 2.22
F (d) 1.20
2.01
2.00
1.00
2.99
1.09
1.13
1.07
2.03
3.00
3.00
1.01
3.02
f1 (ppm)

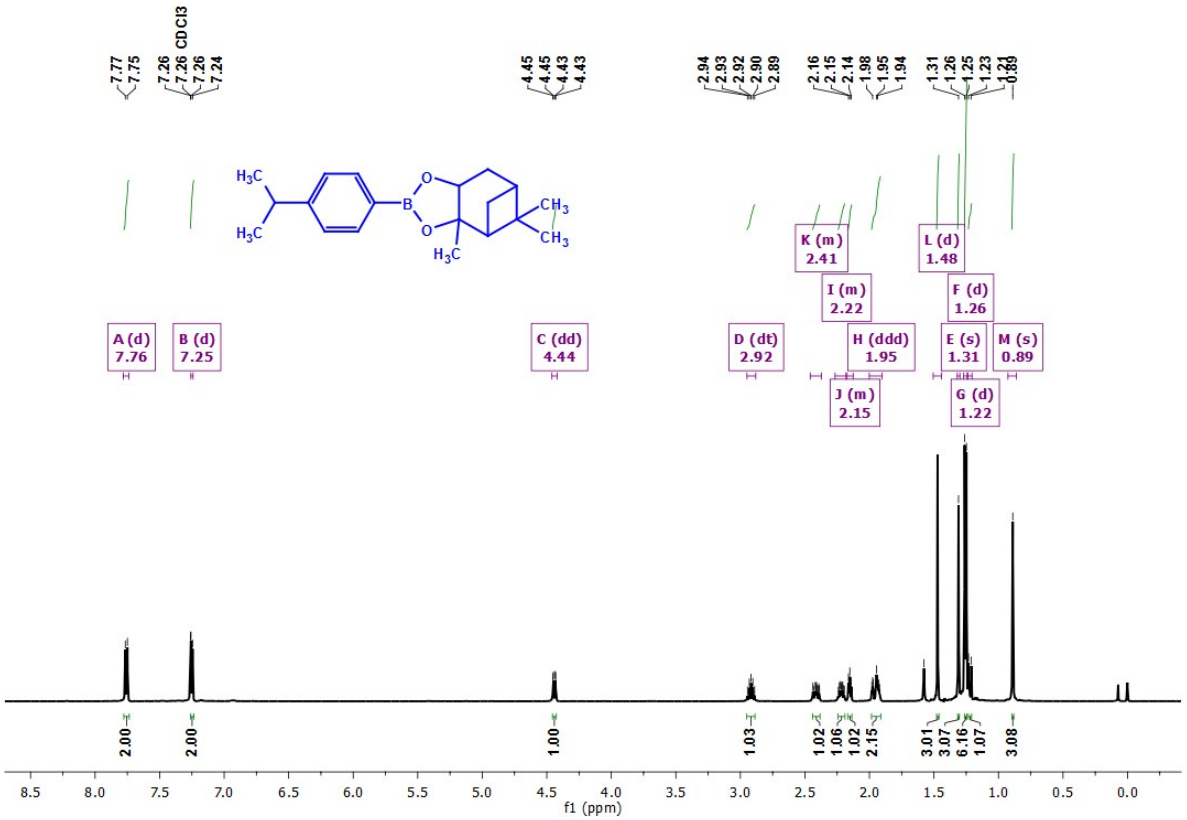

135.25
125.20
86.39
78.36
51.56
39.66
38.35
35.71
28.84
27.25
26.63
24.20
15.20
f1 (ppm)

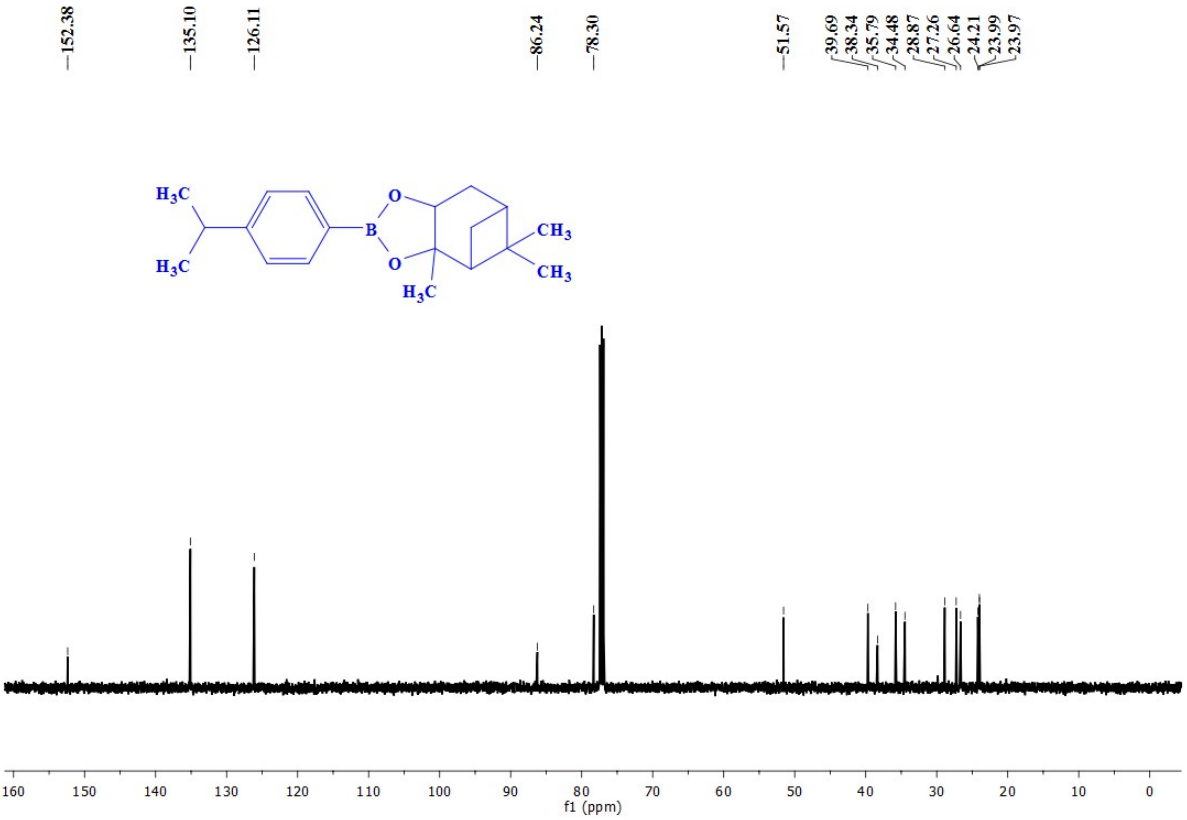

7.68
7.66
7.52
7.50
4.46
4.46
4.44
4.44
2.42
2.25
2.23
2.22
2.16
2.15
2.13
1.99
1.98
1.98
1.96
1.95
1.94
1.48
1.32
1.20
1.17
0.89
Br
B
O
O
H
H3C
CH3
CH3
B (d) 7.67
A (d) 7.51
C (dd) 4.45
G (dt) 1.96
E (m) 2.23
D (m) 2.42
F (t) 2.14
I (s) 1.32
H (s) 1.48
K (s) 0.89
J (d) 1.18
2.01
2.00
1.01
1.02
1.03
1.06
2.11
3.03
3.04
1.10
3.04
f1 (ppm)

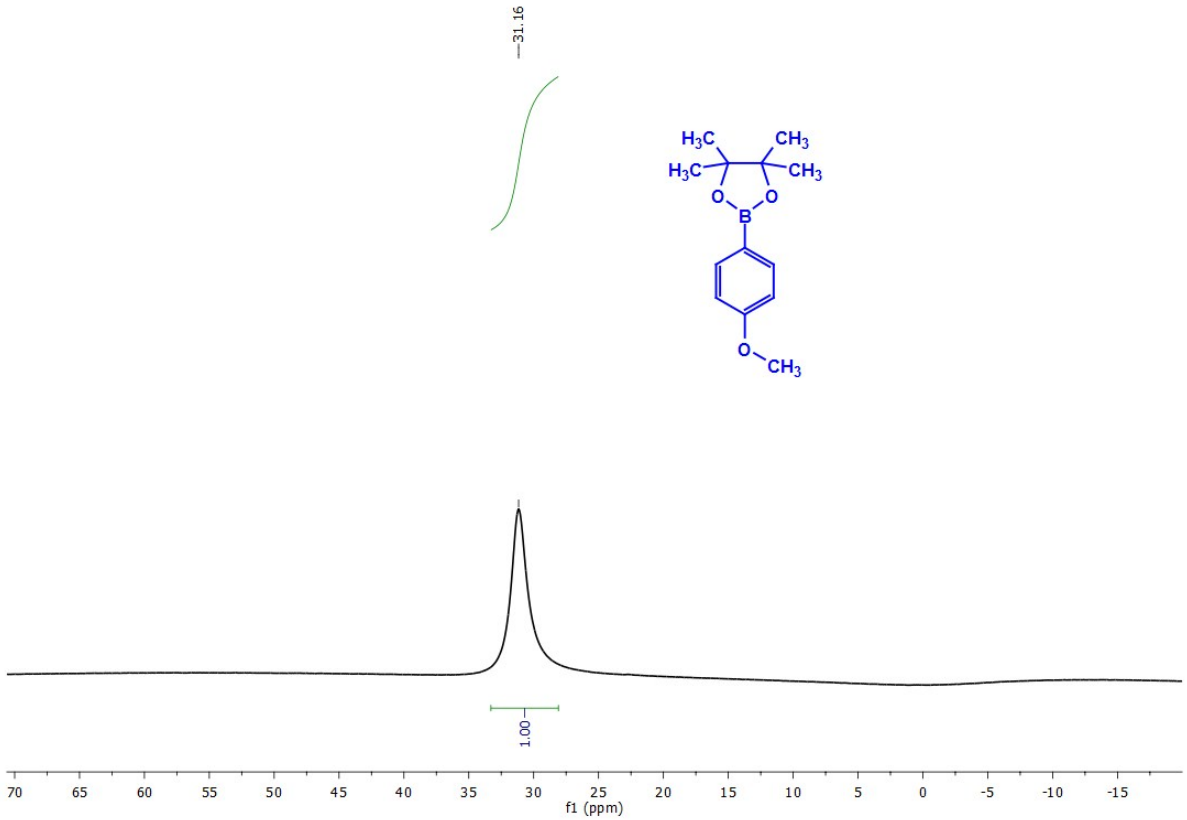

136.49
131.14
126.30
86.65
78.53
51.51
39.64
38.34
35.62
28.80
27.22
26.61
24.18
Br
B
O
O
H3C
CH3
CH3
f1 (ppm)

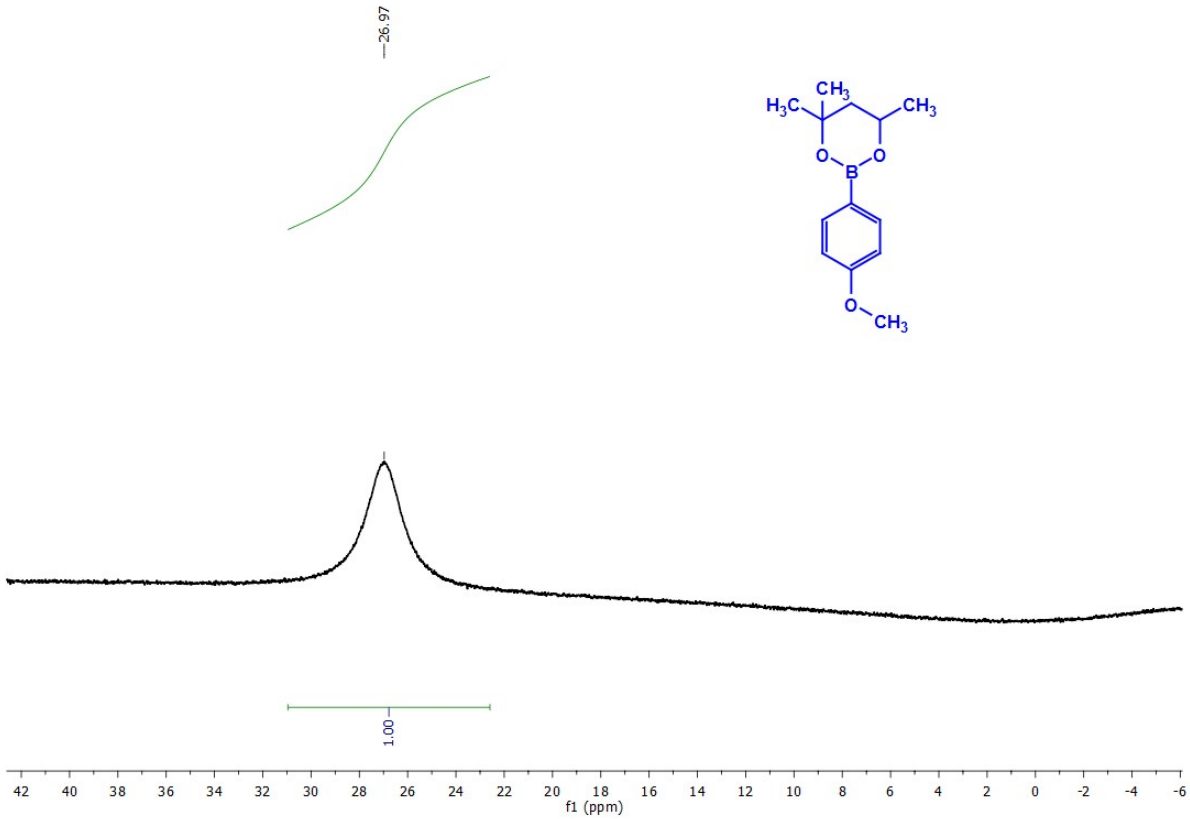

7.78
7.76
7.43
7.41
7.26 CDCl3
4.46
4.45
4.44
4.44
2.44
2.42
2.42
2.41
2.23
2.23
2.22
2.21
2.21
2.17
2.16
2.15
1.98
1.98
1.97
1.95
1.94
1.33
1.31
1.23
1.21
0.89
B (d) 7.77
A (d) 7.42
L (dd) 4.45
D (ddd) 2.22
C (m) 2.41
F (m) 1.95
E (t) 2.16
K (s) 1.47
H (s) 1.31
G (s) 1.33
I (s) 0.89
J (d) 1.22
2.00
1.99
1.01
1.03
1.04
1.03
2.08
3.02
9.02
3.01
1.12
3.00
f1 (ppm)

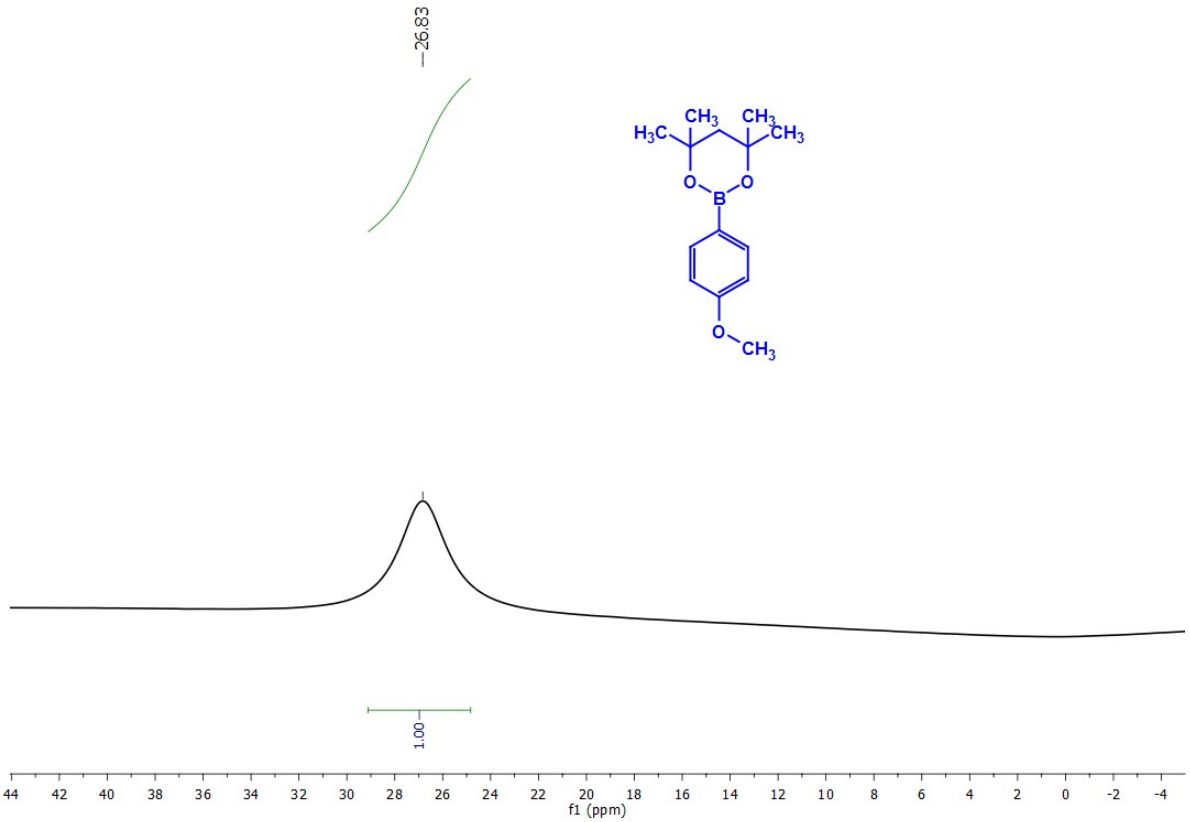

154.56
134.86
124.89
86.24
78.30
51.57
39.70
38.34
35.80
35.03
31.34
28.88
27.26
26.65
24.21
f1 (ppm)

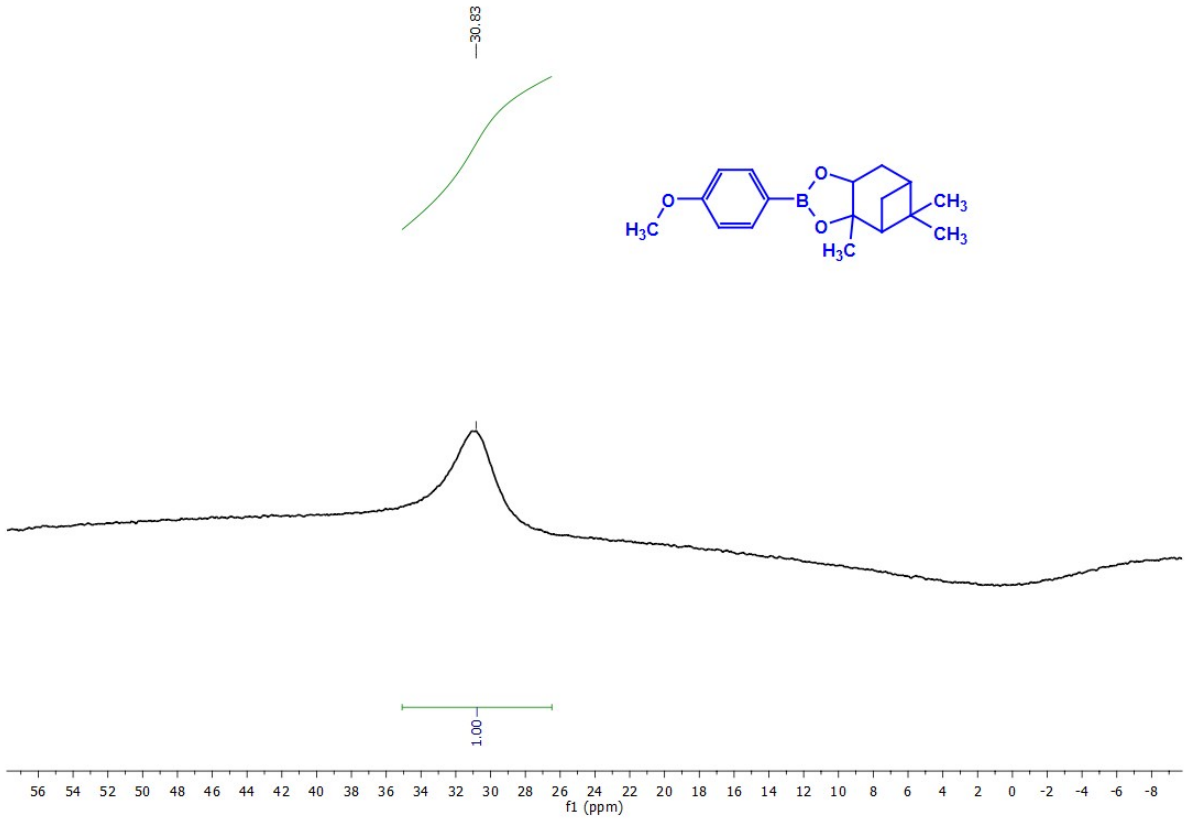

7.77
7.75
7.26 CDCl3
7.26
7.24
4.45
4.45
4.43
4.43
2.94
2.93
2.92
2.90
2.89
2.16
2.15
2.14
1.98
1.95
1.94
1.31
1.26
1.25
1.23
1.21
0.89
A (d) 7.76
B (d) 7.25
C (dd) 4.44
D (dt) 2.92
I (m) 2.22
K (m) 2.41
H (ddd) 1.95
J (m) 2.15
L (d) 1.48
F (d) 1.26
E (s) 1.31
G (d) 1.22
M (s) 0.89
2.00
2.00
1.00
1.03
1.02
1.06
1.02
2.15
3.01
3.07
6.16
1.07
3.08
f1 (ppm)

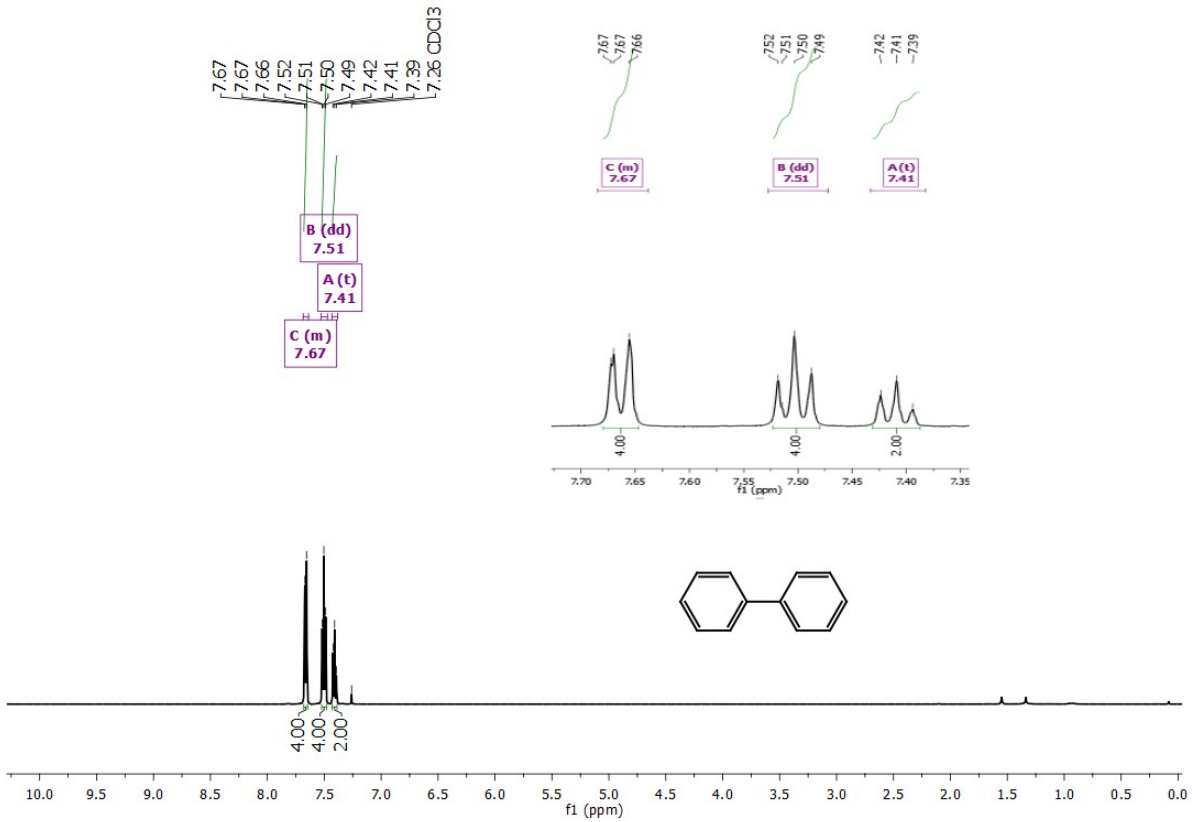

152.38
135.10
126.11
86.24
78.30
51.57
39.69
38.34
35.79
34.48
28.87
27.26
26.64
24.21
23.99
23.97
f1 (ppm)

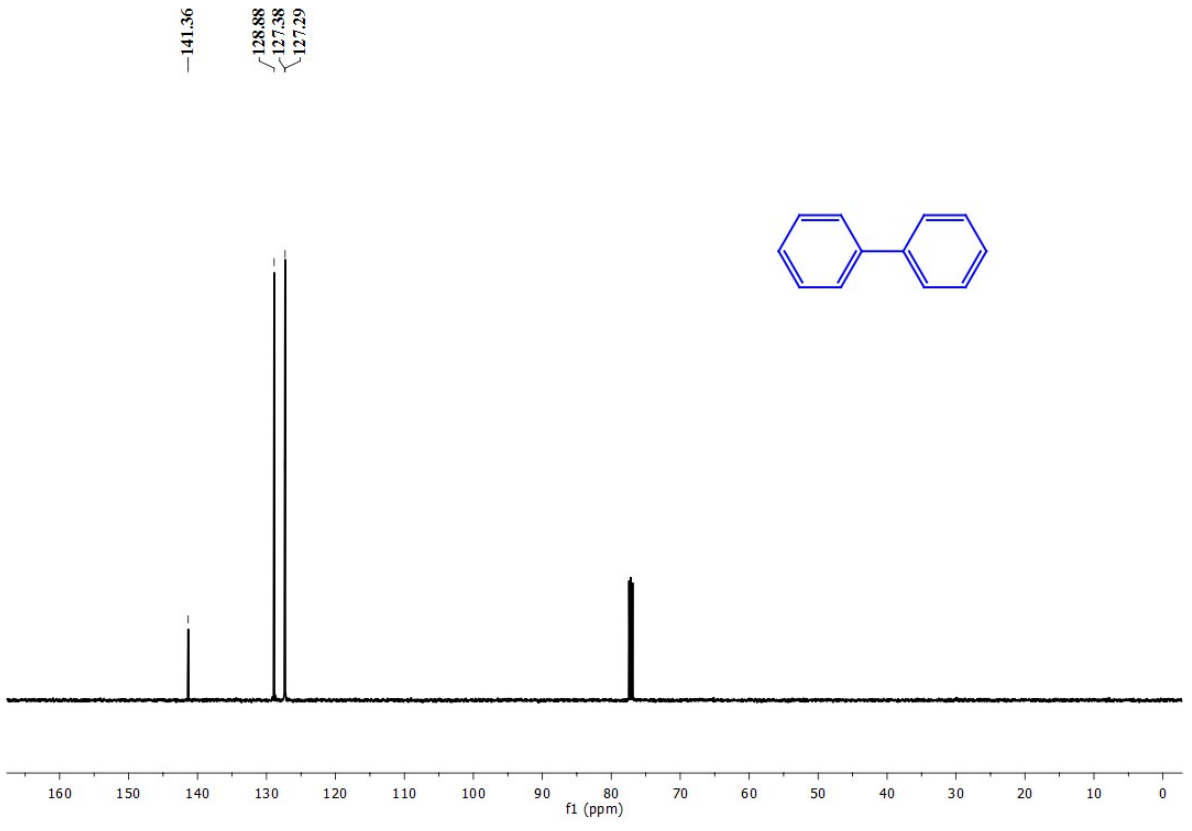

31.16
H3C
CH3
H3C
CH3
O
O
B
O
CH3
1.00
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

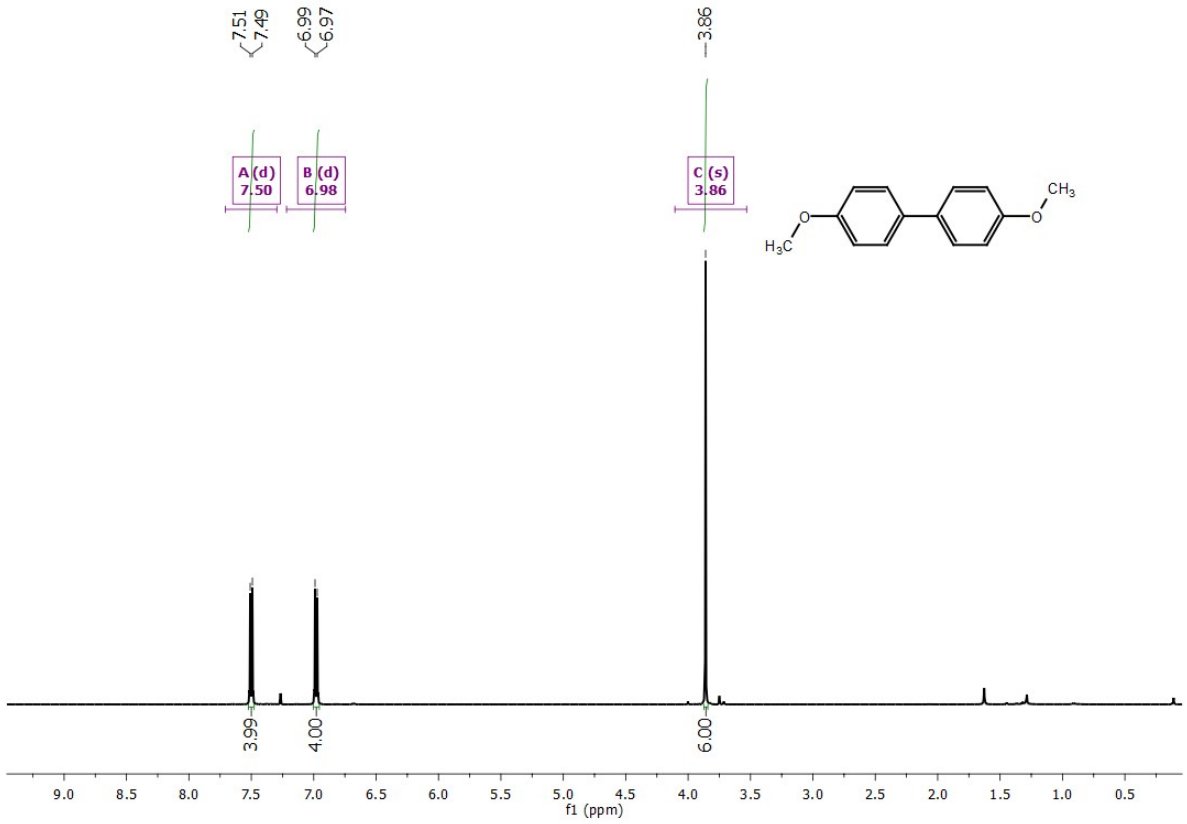

26.97
CH3
H3C
CH3
O
O
B
O
CH3
1.00
42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6
f1 (ppm)

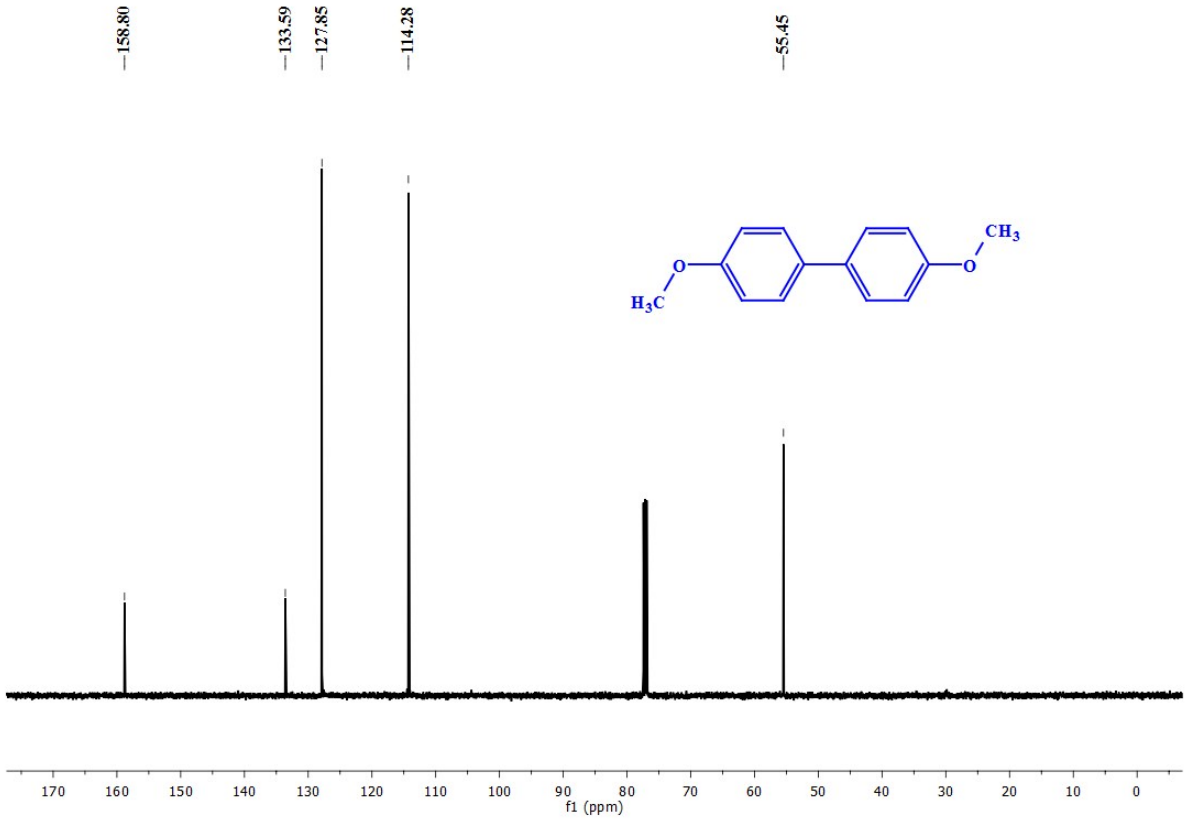

26.83
1.00
44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4
f1 (ppm)

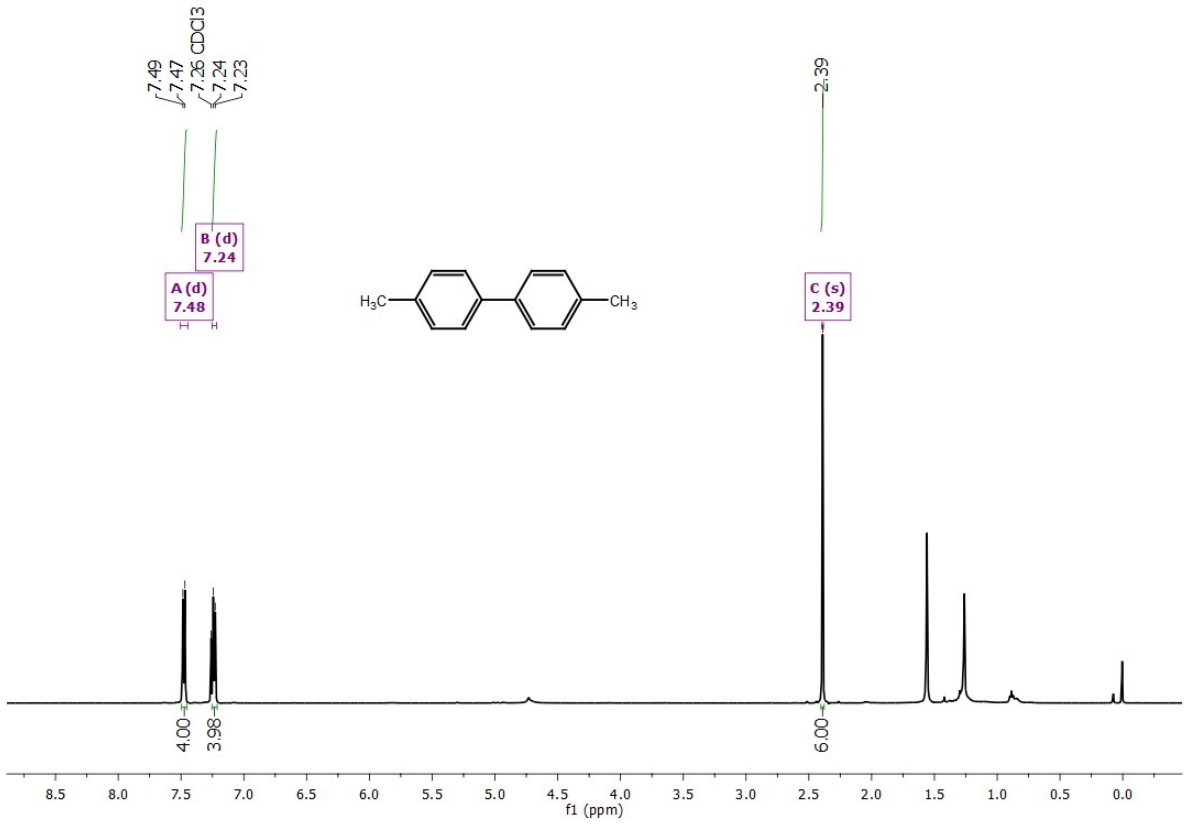

30.83
1.00
56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8
f1 (ppm)

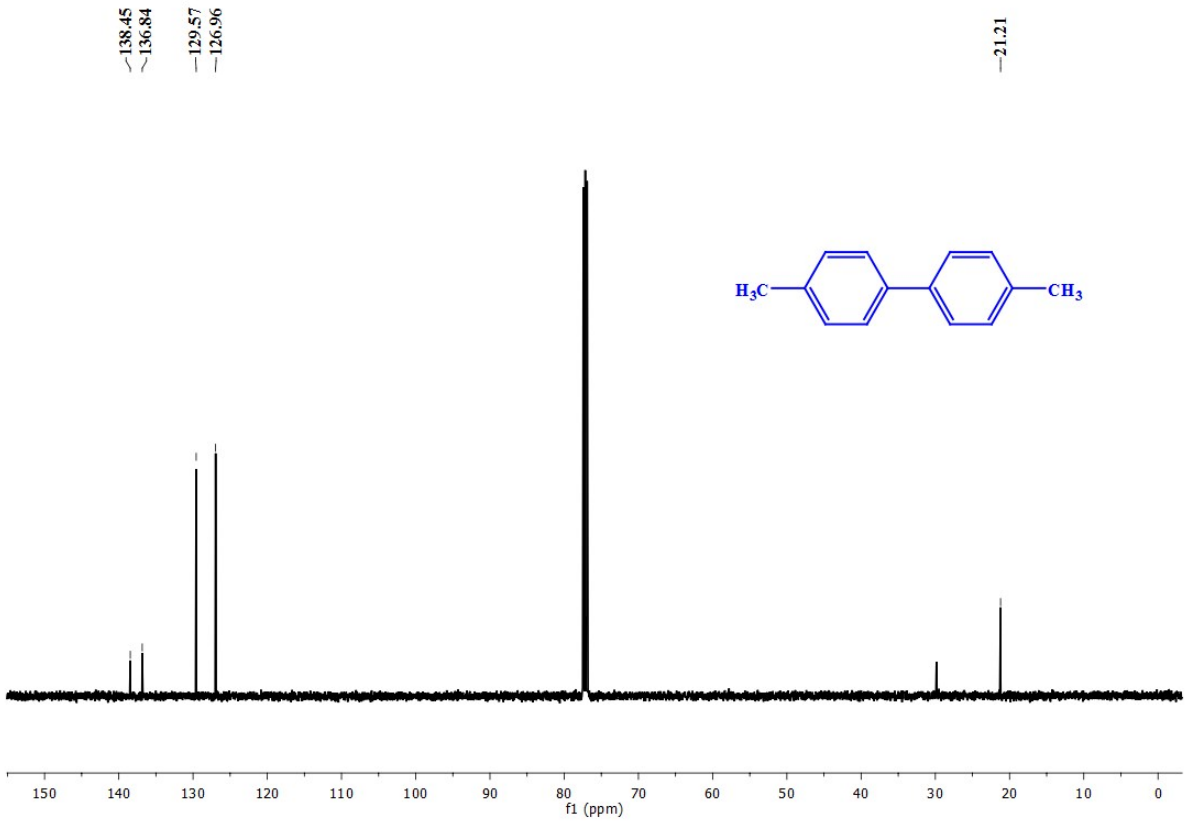

7.67
7.67
7.66
7.52
7.51
7.50
7.49
7.42
7.41
7.39
7.26 CDCl3
B (dd) 7.51
A (t) 7.41
C (m) 7.67
4.00
4.00
2.00
f1 (ppm)

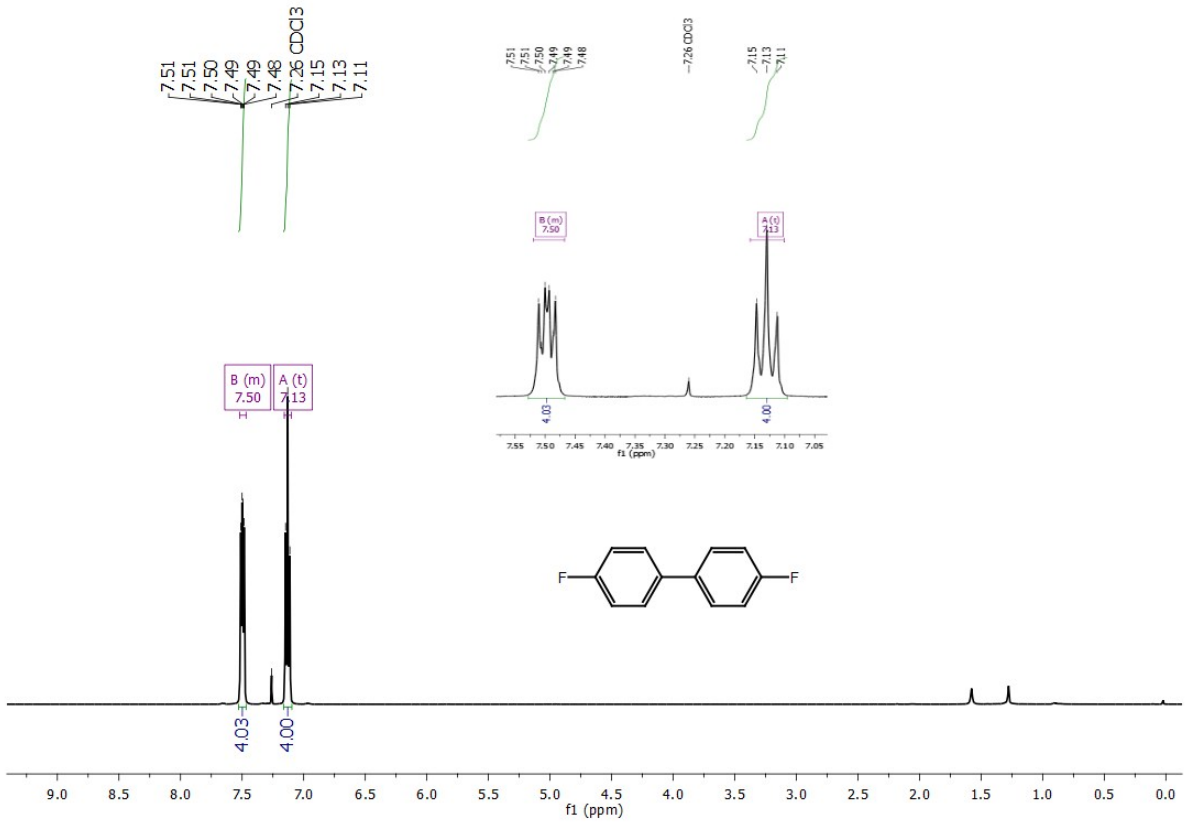

141.36
128.88
127.38
127.29
f1 (ppm)

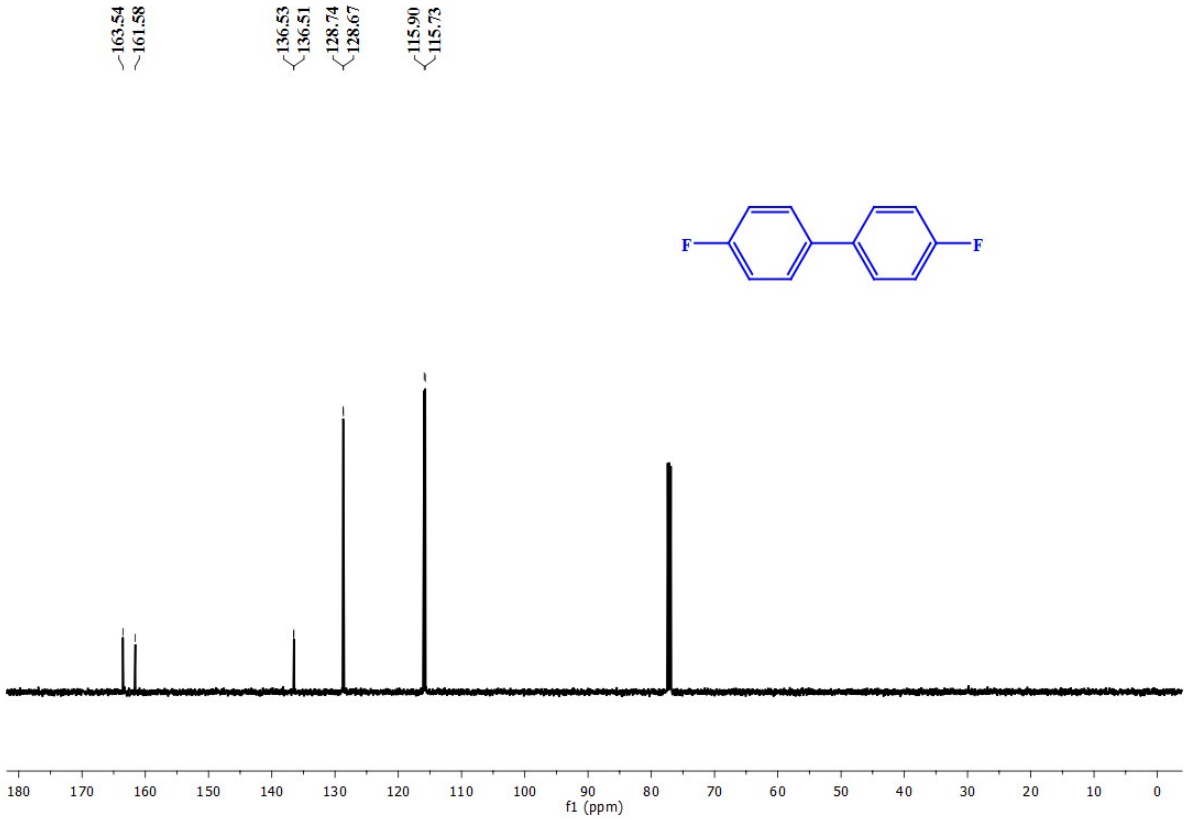

7.51
7.49
6.99
6.97
3.86
A (d)
7.50
B (d)
6.98
C (s)
3.86
3.99
4.00
6.00
f1 (ppm)

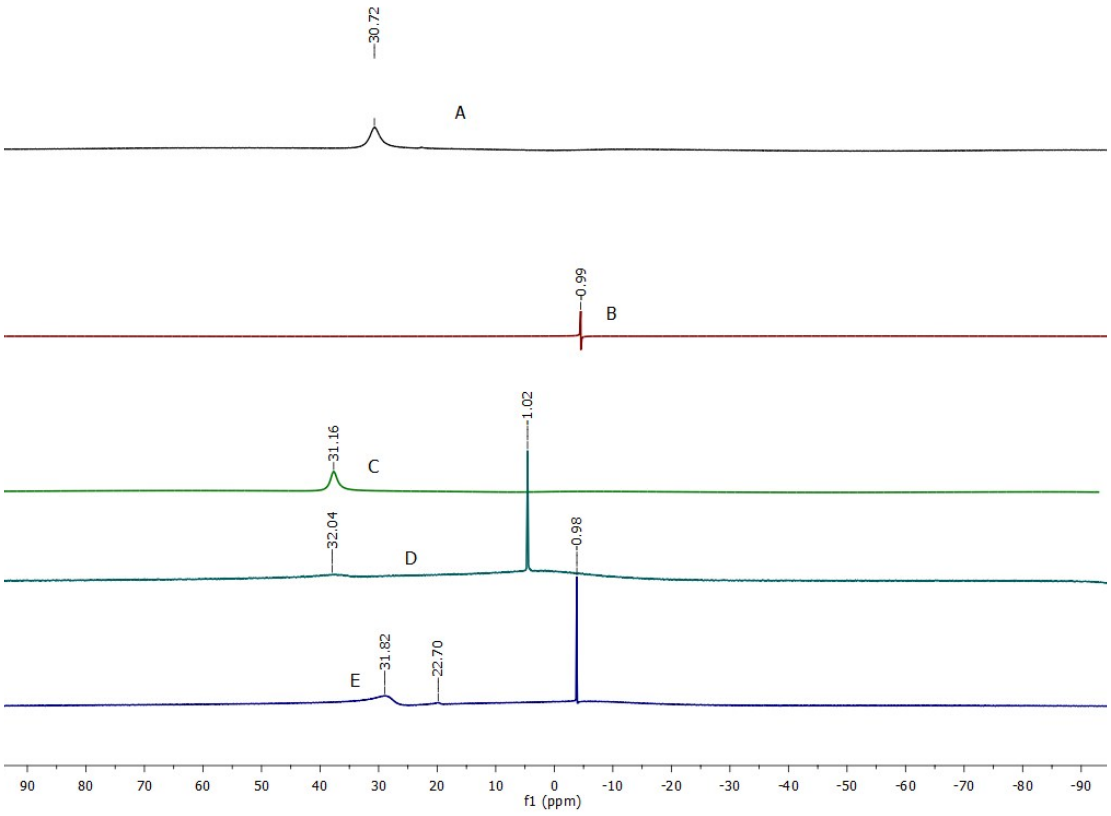

158.80
133.59
127.85
114.28
55.45
f1 (ppm)


7.49
7.47
7.26 CDCl3
7.24
7.23
2.39
B (d)
7.24
A (d)
7.48
H3C
CH3
C (s)
2.39
4.00
3.98
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.45
136.84
129.57
126.96
21.21
H3C
CH3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.51
7.51
7.50
7.49
7.49
7.48
7.26 CDCl3
7.15
7.13
7.11
B (m)
7.50
A (t)
7.13
4.03
4.00
F
F
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.54
161.58
136.53
136.51
128.74
128.67
115.90
115.73
F
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



References

(1) Caputo, J. A.; Frenette, L. C.; Zhao, N.; Sowers, K. L.; Krauss, T. D.; Weix, D. J. General and Efficient C-C Bond Forming Photoredox Catalysis With Semiconductor Quantum Dots. *J. Am. Chem. Soc.* **2017**, *139*, 4250–4253.

(2) Halder, G.; Bhattacharyya, S. Zinc-Diffused Silver Indium Selenide Quantum Dot Sensitized Solar Cells with Enhanced Photo-conversion Efficiency. *J. Mater. Chem. A* **2017**, *5*, 11746−11755.