

Supporting Information

Visible-Light-Induced Organocatalytic Borylation of Aryl Chlorides

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1. General Information

Experimental. Air- and moisture-sensitive reactions were carried out in an oven-dried sealed tube (with a Teflon screw cap) or glassware sealed with a rubber septum under an atmosphere of dry argon. Air- and moisture-sensitive liquids and solutions were transferred by syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. Analytical TLC was performed on silica gel GF₂₅₄ plates. The TLC plates were visualized by ultraviolet light ($\lambda = 254$ nm). Purification of products was accomplished by flash column chromatography on silica gel (Innochem SilicaFlashP60, 230-400 mesh).

Chemicals. Reagent grade tetrahydrofuran (THF) and acetonitrile were purified by MBRAUN SPS 800 solvent purification system and were further deoxygenated by three freeze-pump-thaw cycles before use. Other chemicals were purchased from various commercial sources and were used as received. Substrates 1-(allyloxy)-4-chlorobenzene (**4j**)^[1], and *N*-benzyl-5-chloroindole (**4v**)^[2] were synthesized following the published procedures.

Analytical. NMR spectra were recorded on a Bruker AVANCE III HD 400 (¹H at 400 MHz, ¹³C at 100 MHz, ¹¹B at 128 MHz) nuclear magnetic resonance spectrometer. The ¹H NMR were calibrated against the peak of tetramethylsilane (TMS, 0 ppm). The ¹³C NMR were calibrated against the peak of the solvent (77.16 ppm for CDCl₃^[3]). GC analysis was performed on a Shimadzu GC-2010 instrument equipped with a FID detector using nitrogen as the carrier gas. UV-Vis spectrum was obtained from Agilent Cary 8454 UV-Vis Diode Array System. Fluorescence spectrum was obtained from HORIBA FluoroMax-4 spectrometer. TCSPC spectrum was obtained from Hamamatsu Compact Fluorescence lifetime spectrometer C11367. Laser flash photolysis experiments were performed on an Edinburgh LP920 Laser Flash Photolysis Spectrometer.

2. Photochemical Reactions

2.1 Setup of the Instruments

Most photochemical reactions were performed in a 15 mL sealed tube made from borosilicate glass, and the tube was placed onto an aluminum block fitted with a 10 W high-power single LED plate (size: 10×10 mm, $\lambda_{\text{max}} = 400$ or 520 nm), which is driven by a constant current power supply (9-12 V, 900 mA). Another cylindrical aluminum block was utilized to hold the sealed tube. A cooling fan was also employed to keep the reaction at ambient temperature. This reaction setup is detailed in Figure S1A.

Gram-scale reactions were performed in a 50 mL Erlenmeyer flask made from borosilicate glass, and the flask was placed onto a 50 W high-power LED (size: 25×25 mm, $\lambda_{\text{max}} = 400$ nm) which is driven by a constant current power supply (30-34 V, 1500 mA). The 50 W LED was cooled by attaching an aluminum water cooling block which is connected to circulating water cooling pump. This reaction setup is detailed in Figure S1B.

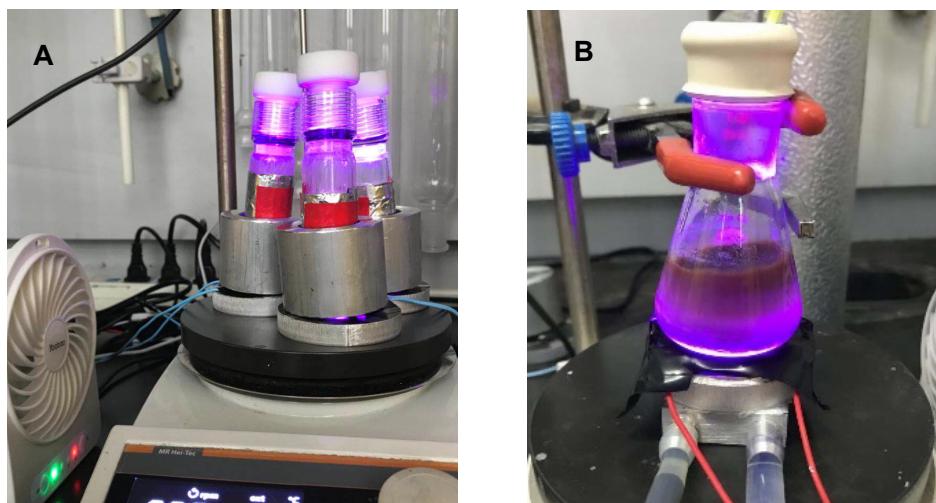


Figure S1. (A) Set up of the photochemical reactors for parallel reactions. (B) Set up of the photochemical reactors for gram-scale reactions.

2.2 Emission Spectra of the LEDs

The emission spectrum of the LED was obtained by an iCCD detector. The maximum emission wavelength of the purple light LED is 400 nm (Figure S2A) and the green light LED is 520 nm (Figure S2B).

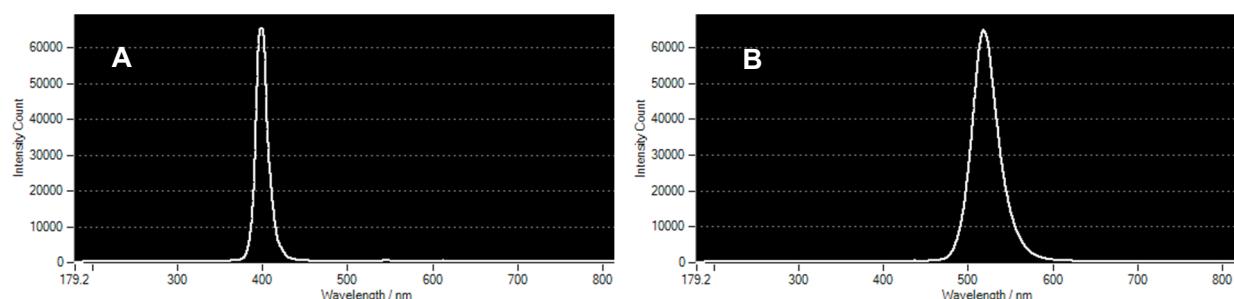


Figure S2. (A) Emission spectrum of a 10 W 400 nm LED. (B) Emission spectrum of a 10 W 520 nm LED.

3. Preliminary Study of the Photoexcited Reaction Mixture

3.1 Fluorescence Study of the Diboron/Methoxide/4-Phenylpyridine System

The fluorescence measurement were performed to estimate the reduction potential of the excited state super electron donors **2** and **3**. In these experiments, a mixture of complexes **2** and **3**, generated *in situ* from the reaction of B_2pin_2 , MeOK, and 4-phenylpyridine at room temperature was used as the sample. Because the lowest energy band in the absorption spectrum of complex **2** is in the 300-500 nm region, and the lowest energy band for complex **3** is in the 500-600 nm region (Figure 1B), we chose 430 and 567 nm as the wavelength of the excitation light for the measurement of fluorescence spectra of complexes **2** and **3**, respectively.

Experimental procedure: A 15 mL reaction tube was charged with a magnetic stir bar, 4-phenylpyridine (31.0 mg, 0.200 mmol), MeOK (14.0 mg, 0.200 mmol), 18-C-6 (52.8 mg, 0.200 mmol), B_2pin_2 (50.8 mg, 0.200 mmol), and 3 mL THF in a glove box. The tube was sealed with a Teflon screw cap and the reaction mixture was stirred at room temperature for 2 h. Solutions for fluorescence study was obtained by diluting this solution ($[\mathbf{2}] \approx 26 \text{ mM}$ in THF) with anhydrous THF to pale purple color. The solutions were introduced to an optical glass sample cuvette. The solution were analyzed using a HORIBA FluoroMax-4 spectrometer.

The absorption and emission spectra of ate complex **2** in THF were summarized in Figure S3A and the spectra of radical anion species **3** in THF were shown in Figure S3B.

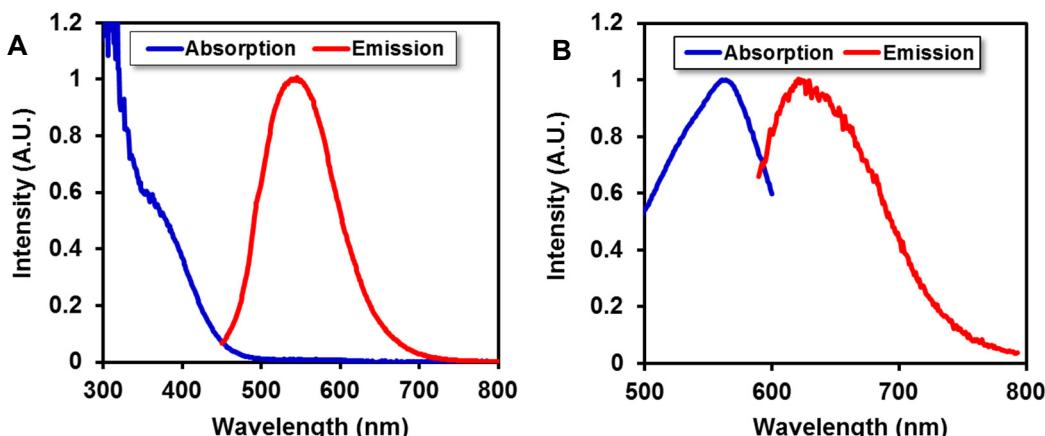


Figure S3. (A) Absorption and emission spectra of ate complex **2**. (B) Absorption and emission spectra of radical anion **3**. The intensity is in arbitrary unit.

3.2 Evaluation of the Excited State Redox Potential

Excited-state redox potential $E^{*1/2}$ was estimated from the following equation:

$$E^{*1/2} = E_{1/2} - E_{0-0}$$

where $E_{1/2}$ is the ground state redox potential; E_{0-0} is the energy difference between 0th vibrational states of ground state and excited state and can be approximated by the crossing point between the absorption spectrum and emission spectrum.

For ate complex **2**, the ground state redox potential, $E_{\text{ox}}(\mathbf{2}^+/\mathbf{2})$, was determined by DPV and CV to be -1.11 V vs Fc^{+0} in our previous work.^[4b] The wavelength of the crossing point is 450 nm (Figure S3A), which translates into an $E_{0-0}(\mathbf{2}^*/\mathbf{2})$ of 2.76 eV. Therefore,

$$E_{\text{ox}}^*(\mathbf{2}^+/\mathbf{2}^*) = E_{\text{ox}}(\mathbf{2}^+/\mathbf{2}) - E_{0-0}(\mathbf{2}^*/\mathbf{2}) = -1.11 \text{ V} - 2.76 \text{ V} = -3.87 \text{ V vs Fc}^{+/0}$$

For radical anion species **3**, the ground state redox potential was not measured because it was difficult to obtain **3** in its pure form. Thus the oxidation potential $E(\mathbf{3}^+/\mathbf{3})$ is assumed to be similar to ate complex **2** and the value -1.11 V was taken as well. The wavelength of the crossing point is 600 nm (Figure S3B), which translates into an $E_{0-0}(\mathbf{3}^*/\mathbf{3})$ of 2.06 eV. Therefore,

$$E_{\text{ox}}^*(\mathbf{3}^+/\mathbf{3}^*) = E_{\text{ox}}(\mathbf{3}^+/\mathbf{3}) - E_{0-0}(\mathbf{3}^*/\mathbf{3}) = -1.11 \text{ V} - 2.06 \text{ V} = -3.17 \text{ V vs Fc}^{+/0}$$

The above estimation indicates that the excited state of complex **2** exhibits superior reduction ability.

3.3 Reactivity of the Diboron/Methoxide/4-Phenylpyridine System under Photoirradiation

Preliminary reactivity evaluation was performed by mixing the diboron/methoxide/4-phenylpyridine super electron donor mixture with haloarenes and irradiated with different LEDs. The results were summarized in Figure 1C.

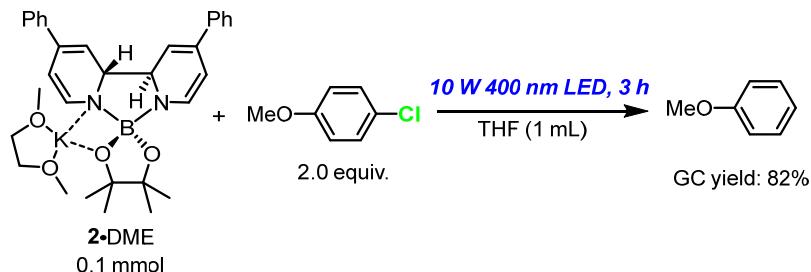
Experimental procedure: A 15 mL reaction tube was charged with a magnetic stir bar, 4-phenylpyridine (31.0 mg, 0.200 mmol), MeOK (14.0 mg, 0.200 mmol), 18-C-6 (52.8 mg, 0.200 mmol), B_2pin_2 (50.8 mg, 0.200 mmol), and 3 mL THF in a glove box. The tube was sealed with a Teflon screw cap and the reaction mixture was stirred at room temperature for 2 h. Substrates 4-bromoanisole or 4-chloroanisole (0.100 mmol) was then added to the mixture in a glove box. The sealed tube was then irradiated with a 10 W LED (400 or 520 nm) for 3 h, and then a standard solution of *n*-dodecane in toluene was added as the internal standard, followed by water. After shaking for 1 min, the organic layer was separated and analyzed by GC to determine the yield of reduction product, anisole.

4. Investigation of the Excited State Ate Complex 2

In these experiments, independently prepared complex **2**·DME^[4b] was employed to investigate the reactivity of complex **2** in a clean reaction system. Due to the lability of complex **2** towards oxygen and water, in some spectroscopic studies requiring the use of a very dilute solution of complex **2**, the data quality may be interfered even though rigorous deoxygenation and drying procedures have been applied to the solvent used.

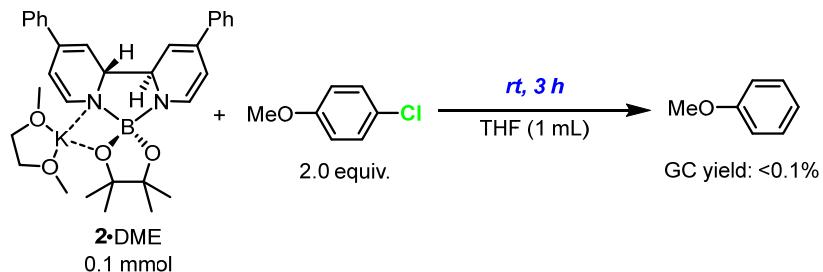
4.1 Reaction of the Excited State Ate Complex **2**·DME with Aryl Chloride

(1) The reaction between **2**·DME and aryl chloride under visible light irradiation



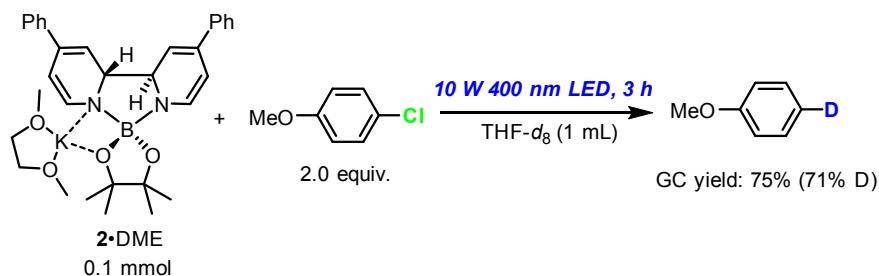
Experimental procedure: In a glove box, to a 15 mL reaction tube charged with a solution of electron donor **2**·DME (56.7 mg, 0.100 mmol) in 1 mL of THF, was added 4-chloroanisole (28.4 mg, 0.200 mmol). The tube was sealed with a Teflon screw cap and the reaction mixture was then irradiated by a 10 W 400 nm LED for 3 h. Then a standard solution of *n*-dodecane in toluene was added as the internal standard, followed by water. After shaking for 1 min, the organic layer was separated and analyzed by GC to obtain the yield of anisole. The result is shown in Figure 1D of the manuscript.

(2) The reaction between **2**·DME and aryl chloride without photoirradiation



Experimental procedure: In a glove box, to a 15 mL reaction tube charged with a solution of electron donor **2**·DME (56.7 mg, 0.100 mmol) in 1 mL of THF, was added 4-chloroanisole (28.4 mg, 0.200 mmol). The tube was sealed with a Teflon screw cap and the reaction mixture was then stirred at room temperature for 3 h. Then a standard solution of *n*-dodecane in toluene was added as the internal standard, followed by water. After shaking for 1 min, the organic layer was separated and analyzed by GC to obtain the yield of anisole.

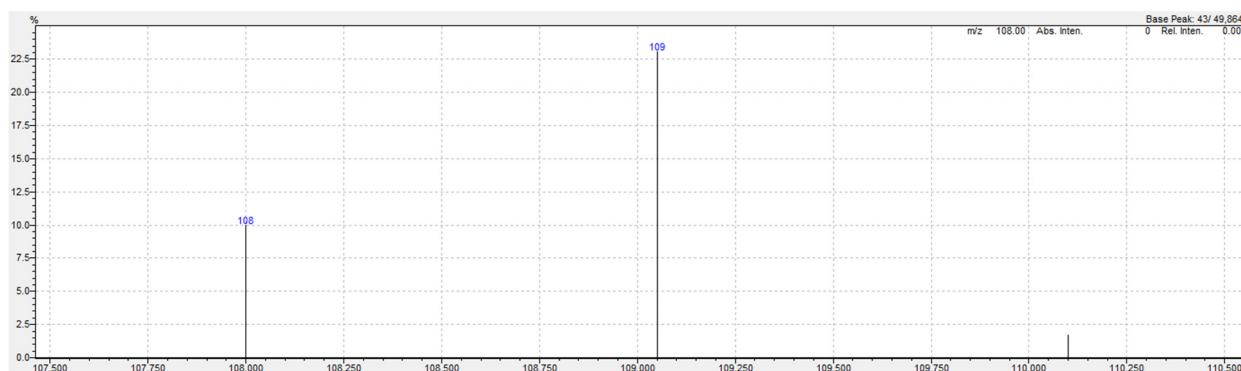
(3) The reaction between **2**·DME and aryl chloride under visible light irradiation in THF-*d*₈



Experimental procedure: In a glove box, to a 15 mL reaction tube charged with a solution of electron donor **2**·DME (56.7 mg, 0.100 mmol) in 1 mL of THF-*d*₈, was added 4-chloroanisole (28.4 mg, 0.200 mmol). The tube was sealed with a Teflon screw cap and the reaction mixture was then irradiated by a 10 W 400 nm LED for 3 h. A solution of *n*-dodecane in toluene was added as the standard, and water was added subsequently. After stirred for 5 min, the organic layer was separated and analyzed by GC and GC-MS.

Deuterium incorporation on C4-position of anisole clearly indicated a hydrogen atom transfer (HAT) process between the aryl radical and the solvent THF-*d*₈. Some HAT product without deuteration was caused by the DME molecule in the electron donor **2**·DME which is also a good hydrogen atom donor for HAT process.

The ratio of deuteration in product anisole was determined by GC-MS employing SIM (selected ions monitoring) mode to detect ions at *m/z* = 108 and 109. If the intensity of the *m/z* = 108 peak is defined as 100%, non-deuterated anisole will contribute 7.6% intensity to the *m/z* = 109 peak according to the natural abundance of ¹³C in anisole. Thus the intensity of the deuterated anisole is $I(109) - 7.6\% \times I(108)$. The ratio of deuterium incorporation is calculated by equation $[I(109) - 7.6\% \times I(108)]/[I(109) + 92.4\% \times I(108)]$. A representative GC-MS spectrum of anisole produced from the reaction employing THF-*d*₈ is shown below.



(4) Trapping of the photochemically generated aryl radical by diboron

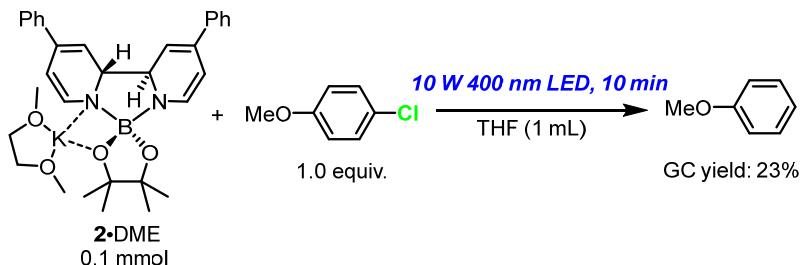


Experimental procedure: In a glove box, to a 15 mL reaction tube charged with a solution of electron donor **2·DME** (85.0 mg, 0.150 mmol) in 1 mL of CH_3CN , was added 4-chloroanisole (14.2 mg, 0.100 mmol) and B_2pin_2 (254.0 mg, 1.00 mmol). The tube was sealed with a Teflon screw cap and the reaction mixture was then irradiated by a 10 W 400 nm LED for 3 h. Then a standard solution of *n*-dodecane in toluene was added as the internal standard, followed by water. After shaking for 1 min, the organic layer was separated and analyzed by GC to obtain the yield of products.

The observation of borylation product in this reaction could further confirm that the aryl radical formed in the photoinduced reaction system could be trapped by diboron to form the arylbronate product.

4.2 Quantum Yield Measurement

In order to measure the quantum yield of this single electron transfer reaction, the photoinduced reaction between **2·DME** and 4-chloroanisole was performed for 10 min. The quantum yield was calculated based on the product yield and the photon flux of the light source as determined by an optical power meter.



Experimental procedure: In a glove box, to a 15 mL reaction tube charged with a solution of electron donor **2·DME** (56.7 mg, 0.100 mmol) in 1 mL of THF, was added 4-chloroanisole (14.2 mg, 0.100 mmol). The tube was sealed with a Teflon screw cap and the reaction mixture was then irradiated by a 10 W 400 nm LED for 10 min. Then a standard solution of *n*-dodecane in toluene was added as the internal standard, followed by water. After shaking for 1 min, the organic layer was separated and analyzed by GC. The conversion of chloroarene was determined to be 24%, and the yield of anisole was determined to be 23%.

The light power of the 10 W 400 nm LED was determined by an optical power meter to be 107.9 mW.

$$\text{photon flux} = \frac{P}{N_A \cdot hc/\lambda} = \frac{107.9 \times 10^{-3}}{6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3 \times 10^8 / (400 \times 10^{-9})} = 3.60 \times 10^{-7} \text{ einstein} \cdot \text{s}^{-1}$$

The quantum yield was determined using the following equation. Assuming that all incident light ($f > 0.999$) is absorbed by the electron donor **2** at the reaction conditions described above, the production of 2.28×10^{-5} mol product (23% yield) in 10 min (600 s) corresponds to a quantum yield of $\Phi = 9.3\%$.

$$\Phi = \frac{\text{mol product}}{\text{photon flux} \cdot t \cdot f} = \frac{2 \times 10^{-5}}{3.60 \times 10^{-7} \times 600 \times 1} = 9.3\%$$

4.3 The Possibility for Donor-Acceptor Complex Formation

In order to investigate whether some electron-donor-acceptor (EDA) complex has been produced when chloroarenes were added, more UV-vis study was carried out. UV-vis spectrum showed that ate complex **2** has an absorption band in visible light region (300-500 nm, Figure S4). Further studies revealed that the addition of 4-chloroanisole did not change the absorption spectra of ate complex **2** (see Figure S4). Therefore, the formation of an EDA complex can be excluded.

(1) UV-Vis of complex **2**·DME

Experimental procedure: A 15 mL reaction tube was charged with complex **2**·DME (3.0 mg, 5.2 μ mol) and 5 mL THF in a glove box. The resulting solution was transferred to the cuvette with 1 cm optical path utilizing an oven-dried glass Pasteur pipette.

(2) UV-Vis of compound **4a**

Experimental procedure: A 15 mL reaction tube was charged with 4-chloroanisole **4a** (0.7 mg, 5.0 μ mol) and 5 mL THF in a glove box. The resulting solution was transferred to the cuvette with 1 cm optical path utilizing an oven-dried glass Pasteur pipette.

(3) UV-Vis of complex **2**·DME and **4a** mixture

Experimental procedure: A 15 mL reaction tube was charged with complex **2**·DME (3.0 mg, 5.2 μ mol) and 5 mL THF in a glove box. After dissolution, 4-chloroanisole **4a** (0.7 mg, 5.0 μ mol) was then added. The solution was transferred to the cuvette with 1 cm optical path utilizing an oven-dried glass Pasteur pipette.

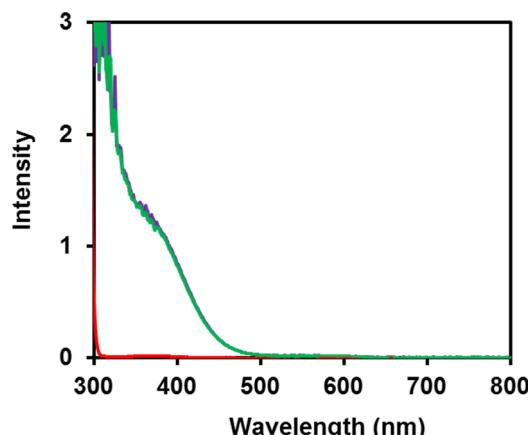


Figure S4. Red line: UV-vis spectrum of 1 mM 4-chloroanisole **4a** in THF. Purple line: UV-vis spectrum of 1 mM ate complex **2**·DME in THF. Green line: UV-vis spectrum of 1 mM 4-chloroanisole **4a** and 1 mM ate complex **2**·DME in THF.

4.4 Stern-Volmer Experiment

In order to figure out how the excited state of complex **2** interacts with the chloroarene substrate, luminescence quenching experiments were performed. In this study, 1 mM of ate complex **2**·DME and variable concentrations of the chloroarene as quencher were used, and degassed anhydrous acetonitrile was used as the solvent. 1,4-Dichlorobenzene (**4w**), which is needle crystal and easily purified, was selected as a suitable quencher. The intensity of the emission peak at 547 nm ($\lambda_{\text{ex}} = 430$ nm) was used as a measure of fluorescence intensity, I . The Stern-Volmer plot for the quenching experiments is given below in Figure S5. A Stern-Volmer constant, K_{SV} , of 8.6 M⁻¹ was obtained.

Experimental procedure: A 15 mL reaction tube was charged with complex **2**·DME (3.0 mg, 5.2 μmol) and 5 mL CH₃CN in a glove box. After dissolution, 1,4-dichlorobenzene **4w** (0.2-1 mmol) was then added. The solution was transferred to the cuvette with 1 cm optical path utilizing an oven-dried glass Pasteur pipette. The sample was then measured by the fluorescence spectrometer immediately.

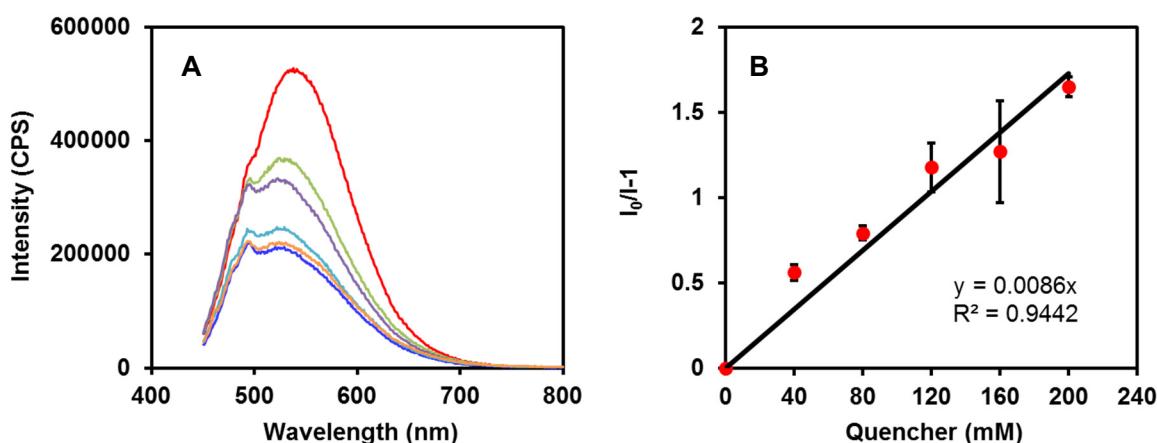


Figure S5. (A) Fluorescence spectra of 1 mM ate complex **2**·DME acetonitrile solution upon adding 0-200 mM quencher. (B) Stern-Volmer plots for 1 mM ate complex **2**·DME acetonitrile solution using 0-200 mM quencher.

4.5 Lifetime of Fluorescence

With the K_{SV} in hand, we performed fluorescence lifetime measurement to estimate the quenching rate coefficient (k_q) between the singlet excited state (S_1) of **2** and the chloroarene. The fluorescence lifetime measurement was carried out by time-correlated single-photon counting (TCSPC). The decay data was collected at 550 nm upon 470 nm excitation.

Experimental procedure: A 15 mL reaction tube was charged with complex **2**·DME (3.0 mg, 5.2 μmol) and 5 mL CH₃CN in a glove box. The resulting solution was transferred to a cuvette with 1 cm optical path utilizing an oven-dried glass Pasteur pipette. The sample was then transferred to the fluorescence lifetime spectrometer immediately.

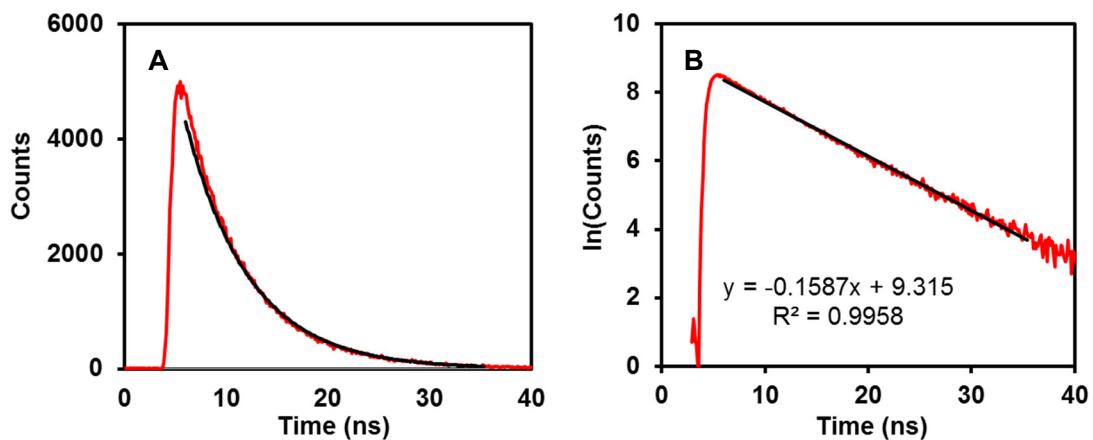


Figure S6. (A) Time-resolved emission intensity decay of ate complex **2**·DME acetonitrile solution shown in red trace. Single exponential fit from 6.0 ns to 35.0 ns is given as black lines, affording $\tau = 6.1 \pm 0.2$ ns. (B) The $\ln(\text{counts})$ versus time plot of time-resolved emission intensity decay for ate complex **2**·DME acetonitrile solution is shown in the red trace with the model shown as the black solid line ($R^2 = 0.9958$).

4.6 Investigation of the T_1 State of Complex **2**

In order to confirm whether or not the triplet excited state of complex **2**, after intersystem crossing from the singlet excited state, could also undergo electron transfer with the chloroarene, we performed a flash laser photolysis (FLP) study of **2**·DME.

General: Sample excitation was provided by Continuum Surelite Laser, delivering ca. 5 ns pulses at 355 nm. Optical parametric oscillator (OPO) was utilized to transform 355 nm laser to 410 nm laser. A continuous tungsten halogen lamp provided analyzing light that was passed through 1×1 cm optical glass sample cuvette in a right-angle configuration. In transient absorption spectra measurement mode, the spectra were measured by an iCCD camera; in kinetic mode, the analyzing light was passed through a monochromator before hitting the LP900 type photomultiplier detector and the PMT signal was converted and digitized using a digital real-time oscilloscope (TDS3012C). Data treatment were performed with the Edinburgh Instruments L900 software.

Experimental procedure: A 15 mL reaction tube was charged with complex **2**·DME (3.0 mg, 5.2 μmol) and 5 mL CH_3CN in a glove box. After dissolution, 4-chloroanisole **4a** (1.5 mmol) was then added. The solution was transferred to the cuvette with 1 cm optical path utilizing an oven-dried glass Pasteur pipette. The sample was then transferred to the LFP instrument immediately.

Analysis: Transient absorption spectra of **2**·DME after the 410 nm laser pulse showed an absorption band around 550 nm, which was tentatively assigned to be the absorption of the T_1 state of complex **2** (Figure S7A). In the kinetic mode, the lifetime of this transient absorption was determined to be as long as 6.6 ms (Figure S7B). However, it was found that the addition of chloroarene **2a** did not change the decaying curve of this absorption, which suggests that the excited T_1 state is not the reactive species (Figure S7C).

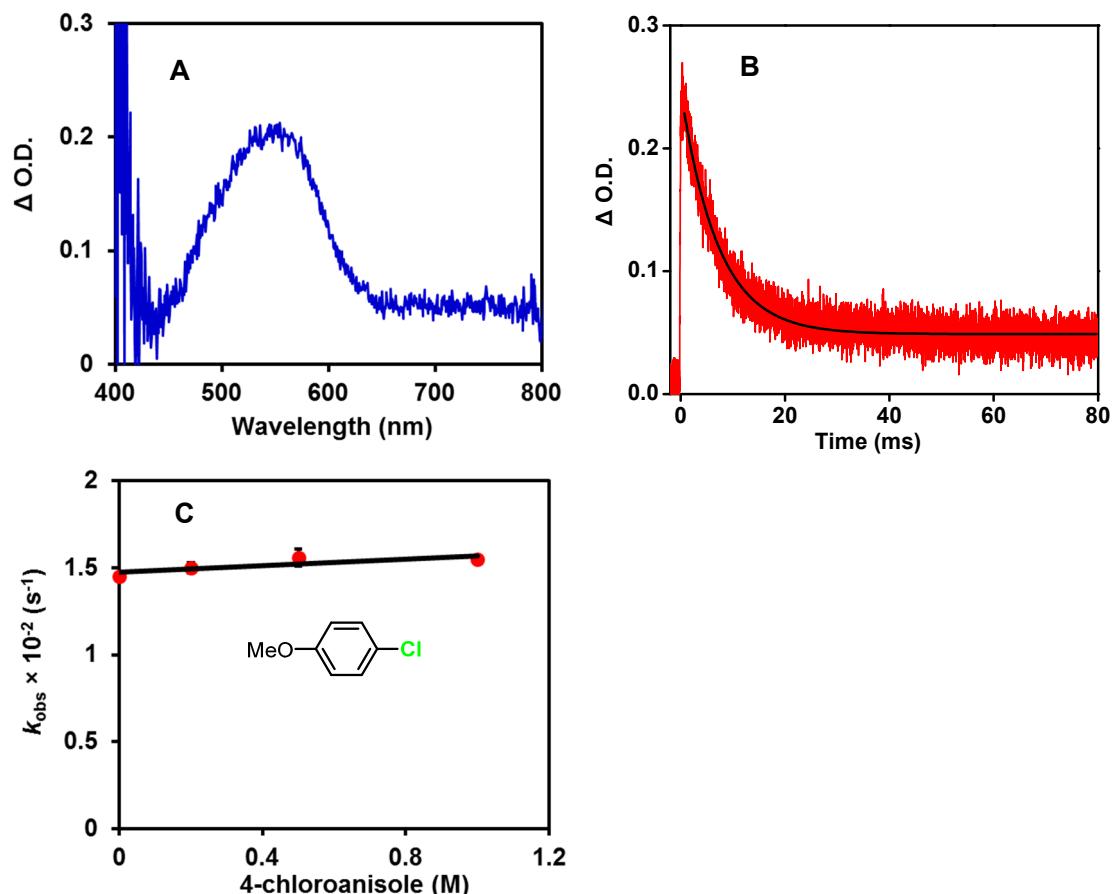


Figure S7. Flash laser photolysis study of **2**·DME in absence and presence of 4-chloroanisole: (A) Transient absorption of **2**·DME in degassed anhydrous MeCN; (B) Transient kinetic trace of **2**·DME monitored at $\lambda = 550$ nm and the pseudo-first order fitting; (C) Plots of k_{obs} versus [4-chloroanisole] (black line).

4.7 UV-Vis Spectroscopic Study of Complexes **2** and **3** in MeCN

Since the optimal solvent for the borylation reaction was found to be MeCN, the UV-vis spectra of the SED complexes were also measured in MeCN to compare with those measured in THF.

(1) UV-vis spectrum of complex **2**·DME in MeCN

Experimental procedure: In a glove box, a 15 mL reaction tube was charged with complex **2**·DME (1.2 mg, 2.1 μmol) and 2 mL MeCN. The resulting solution was transferred to a cuvette with 1 cm optical path using an oven-dried glass Pasteur pipette. The measured UV-vis spectrum of complex **2**·DME is shown in Figure S8A (blue line).

(2) UV-vis spectrum of the in-situ prepared SED mixture in MeCN

Experimental procedure: The SED mixture was prepared by mixing complex $\text{B}_2\text{pin}_2\text{-MeONa}$ (30.8 mg, 0.100 mmol), 4-phenylpyridine (15.5 mg, 0.100 mmol), and MeCN (5 mL) in a reaction tube. The mixture was allowed to react for 10 min under rt. The resulting solution was diluted to pale purple with MeCN and was then transferred to a cuvette with 1 cm optical path using an oven-dried glass Pasteur pipette. The UV-Vis spectrum of the SED mixture is shown in Figure S8A (red line).

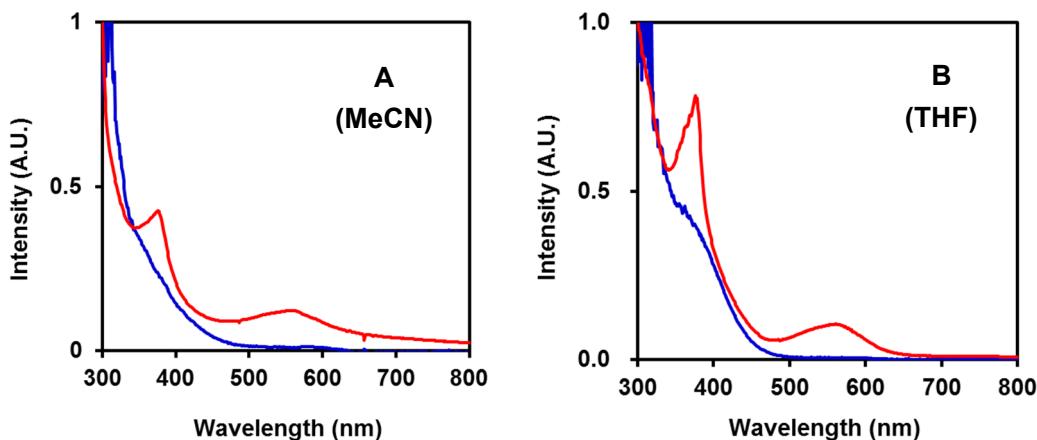


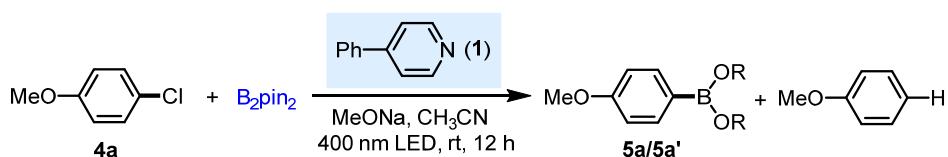
Figure S8. (A) UV-vis spectra in MeCN. Blue line: complex **2**·DME; red line: the SED mixture containing complexes **2** and **3**. (B) UV-vis spectra in THF. Blue line: complex **2**·DME; red line: the SED mixture of complex **2** and complex **3**. The intensity is in arbitrary unit.

By comparison of the spectra measured in MeCN (Figure S8A) and THF (Figure S8B), it was found that these complexes exhibit similar absorption bands in both solvents.

5. Synthetic Studies

5.1 Optimization of the Reaction Conditions

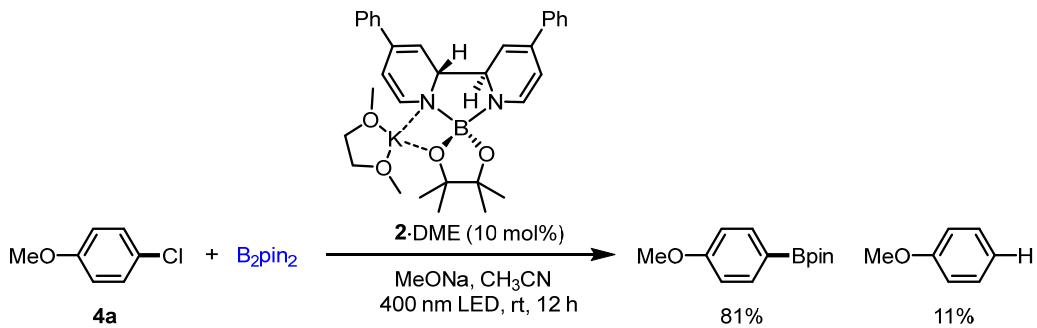
General procedure: A 15 mL reaction tube was charged with a magnetic stir bar, **4a** (71.0 mg, 0.500 mmol), base (0.65 mmol), boron source (1.00 mmol), 4-phenylpyridine (15.5 mg, 0.100 mmol), and 1 mL of solvent in a glove box. The tube was sealed with a Teflon screw cap and then irradiated by a 10 W LED with a certain wavelength for 12 h (the experiment setup is shown in Figure S1A). After then, a standard solution of *n*-dodecane in toluene was added as the internal standard, followed by water. After shaking for 1 min, the organic layer was separated and analyzed by GC to obtain conversion and yield of the reaction. The data were listed in the following table.



Entry	Change from standard conditions	conv. (%)	yield (%)	ArH yield (%)
1	None	99	92	6
2	MeOK instead of MeONa	96	89	5
3	MTBE instead of CH ₃ CN	33	26	4
4	DMSO instead of CH ₃ CN	91	42	9
5	DMAc instead of CH ₃ CN	99	52	30
6	365 nm LED instead of 400 nm LED	40	35	4
7	450 nm LED instead of 400 nm LED	66	53	10
8	254 nm Hg lamp (28 W) instead of 400 nm LED ^b	6	5	<1
9	Without light	<1	<1	<1
10	Without 4-phenylpyridine	<1	<1	<1
11	Reaction set up under air ^c	94	88	5
12	B ₂ hex ₂ instead of B ₂ pin ₂	97	78	16

^a Reaction conditions: **4a** (0.5 mmol, 1 equiv.), **1** (20 mol%), MeONa (1.3 equiv.), diboron reagent (2.0 equiv.) in 1 mL of solvent, irradiated by a 10 W LED at r.t. for 12 h. The conversions and yields were determined by GC using *n*-dodecane as an internal standard. ^b The reaction was performed in a quartz vessel. ^c This reaction was set up under air and performed in a sealed vessel.

It was found that, a catalytic amount of independently prepared complex **2**·DME could also promote the borylation reaction of **4a** efficiently, resulting in a good yield of the borylation product **5a**. This result confirmed that complex **2** could be regenerated after the photoinduced electron transfer process in the presence of B₂pin₂ and methoxide, supporting the proposed reaction mechanism.



Experimental procedure: A 15 mL reaction tube was charged with a magnetic stir bar, **4a** (71.0 mg, 0.500 mmol), MeONa (35.5 mg, 0.650 mmol), B₂pin₂ (254.0 mg, 1.00 mmol), complex **2**·DME (28.4 mg, 0.050 mmol), and 1 mL CH₃CN in a glove box. The tube was sealed with a Teflon screw cap and then irradiated by a 10 W 400 nm LED for 12 h. After then, a standard solution of *n*-dodecane in toluene was added as the internal standard, followed by water. After shaking for 1 min, the organic layer was separated and analyzed by GC to obtain conversion and yield of the reaction.

5.2 General Procedures for the Photoinduced Borylation Reactions

(A) General procedure for small-scale reactions (Table 2 and Scheme 2):

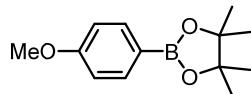
A 15 mL reaction tube was charged with a magnetic stir bar, MeONa (35.5 mg, 0.65 mmol), B₂pin₂ (253.0 mg, 1.00 mmol), 4-phenylpyridine (15.5 mg, 0.100 mmol), 1 mL CH₃CN, and substrate **4** or **6** (0.500 mmol) in a glove box. The tube was sealed with a Teflon screw cap and then irradiated by a 10 W 400 nm LED for 12 h (the experiment setup is shown in Figure S1A). After then, 5 mL of water and 10 mL of ethyl acetate was added. After extraction, the organic layer was separated and to the aqueous phase was added 2 drops of acetic acid to adjust it to a neutral pH. After extraction of the aqueous phase with 3×10 mL ethyl acetate, the combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford the desired borylation product.

(B) Procedure for gram-scale reactions (Table 2, substrates **4b**, **4d**, and **4k**).

A 50 mL Erlenmeyer flask was charged with a magnetic stir bar, B₂pin₂ (5.06 g, 20.0 mmol), MeONa (0.71 g, 13.0 mmol), 4-phenylpyridine (310.0 mg, 2.00 mmol), 20 mL of CH₃CN, and chloroarene substrate **4** (10.0 mmol) in a glove box. A balloon of dry argon was attached after the flask was taken out of the glove box. The flask was then irradiated by a 50 W 400 nm LED for 24 h (the experiment setup is shown in Figure S1B). After then, 20 mL water and 20 mL ethyl acetate were added. The organic layer was separated and to the aqueous phase was added acetic acid to adjust it to a neutral pH. After extraction of the aqueous phase with 3×30 mL ethyl acetate, the combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford the desired borylation product.

5.3 Characterization Data for the Products

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5a**)



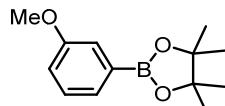
Following procedure A, **5a** was obtained as colorless liquid in 89% yield (104.1 mg) from 4-chloroanisole (**4a**, 71.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 162.4, 136.7, 113.5, 83.7, 55.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

2-(3-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5b**)



Following procedure A, **5b** was obtained as colorless liquid in 83% yield (97.1 mg) from 3-chloroanisole (**4b**, 71.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

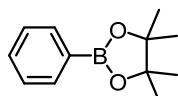
Following procedure B, **5b** was obtained as colorless liquid in 81% yield (1.88 g) from 3-chloroanisole (**4b**, 1.42 g) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 3.0 Hz, 1H), 7.31-7.27 (m, 1H), 7.01 (ddd, *J* = 8.0, 3.0, 1.0 Hz, 1H), 3.83 (s, 3H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 159.2, 129.1, 127.3, 118.9, 118.0, 84.0, 55.4, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

2-(Phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (**5c**)



Following procedure A, **5c** was obtained as colorless liquid in 90% yield (91.8 mg) from chlorobenzene (**4c**, 56.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.0 Hz, 2H), 7.45 (m, 1H), 7.36 (m, 2H), 1.34 (s, 12H).

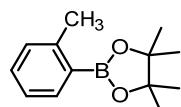
¹³C NMR (100 MHz, CDCl₃) δ 134.9, 131.4, 127.8, 83.9, 25.0. The carbon directly attached to the boron atom

was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

Boronate **5c** was also obtained from fluorobenzene (**8**) following a modified procedure A. A 15 mL reaction tube was charged with a magnetic stir bar, **8** (0.500 mmol), MeONa (70.0 mg, 1.30 mmol), B₂pin₂ (508.0 mg, 2.00 mmol), 4-phenylpyridine (31.0 mg, 0.200 mmol), and 2 mL CH₃CN in a glove box. The tube was sealed with a Teflon screw cap and then irradiated by a 10 W 400 nm LED for 72 h. The reaction mixture was then added a standard solution of *n*-dodecane in toluene as the internal standard, followed by water. Then 2 drops of acetic acid were added to the mixture to adjust pH of solution to ~7. After shaking for 1 min, the organic layer was separated and analyzed by GC.

4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (**5d**)



Following procedure A, **5d** was obtained as colorless liquid in 90% yield (98.1 mg) from 2-chlorotoluene (**4d**, 61.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

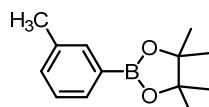
Following procedure B, **5d** was obtained as colorless liquid in 68% yield (1.37 g) from 2-chlorotoluene (**4d**, 1.22 g) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.31 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.18-7.14 (m, 2H), 2.53 (s, 3H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 145.0, 136.0, 130.9, 129.9, 124.8, 83.5, 25.0, 22.3. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

4,4,5,5-Tetramethyl-2-(*m*-tolyl)-1,3,2-dioxaborolane (**5e**)



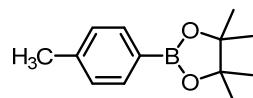
Following procedure A, **5e** was obtained as colorless liquid in 92% yield (100.3 mg) from 3-chlorotoluene (**4e**, 61.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.65-7.58 (m, 2H), 7.30-7.24 (m, 2H), 2.35 (s, 3H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 137.3, 135.5, 132.2, 131.9, 127.8, 83.9, 25.0, 21.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (**5f**)



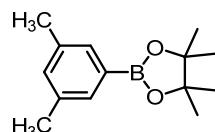
Following procedure A, **5f** was obtained as colorless liquid in 90% yield (98.2 mg) from 4-chlorotoluene (**4f**, 61.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 1.33 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 141.5, 135.0, 128.7, 83.8, 25.0, 21.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5g**)



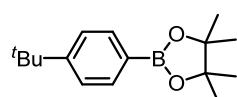
Following procedure A, **5g** was obtained as colorless liquid in 88% yield (102.1 mg) from 1-chloro-3,5-dimethylbenzene (**4g**, 70.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.45-7.42 (m, 2H), 7.11-7.09 (m, 1H), 2.32 (6H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 137.3, 133.1, 132.6, 83.8, 25.0, 21.3. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

2-(4-(Tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5h**)



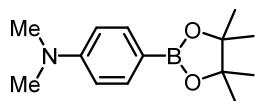
Following procedure A, **5h** was obtained as colorless liquid in 86% yield (111.8 mg) from 1-(*tert*-butyl)-4-chlorobenzene (**4h**, 84.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 2.32 (6H), 1.33 (s, 12H), 1.32 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 154.6, 134.8, 124.8, 83.8, 35.0, 31.4, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[5]

***N,N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (5i)**



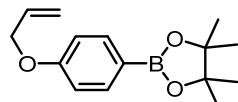
Following procedure A, **5i** was obtained as colorless liquid in 74% yield (91.4 mg) from 4-chloro-*N,N*-dimethylaniline (**4i**, 78.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 2.98 (6H), 1.32 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 152.6, 136.3, 111.4, 83.3, 40.3, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[6]

2-(4-(Allyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5j)



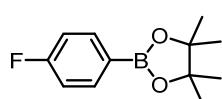
Following procedure A, **5j** was obtained as colorless liquid in 40% yield (51.6 mg) from 1-(allyloxy)-4-chlorobenzene (**4j**, 84.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.74 (m, 2H), 6.90 (m, 2H), 6.05 (ddt, *J* = 17.0, 10.8, 5.6 Hz, 1H), 5.41 (dd, *J* = 17.6, 1.5 Hz, 1H), 5.28 (dd, *J* = 10.8, 1.5 Hz, 1H), 4.56 (dt, *J* = 5.3, 1.5 Hz, 2H), 1.33 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 161.3, 136.6, 133.2, 117.9, 114.4, 83.7, 68.7, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5k)



Following procedure A, **5k** was obtained as colorless liquid in 85% yield (94.2 mg) from 1-chloro-4-fluorobenzene (**4k**, 65.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

Following procedure B, **5k** was obtained as colorless liquid in 78% yield (1.73 g) from 1-chloro-4-fluorobenzene (**4k**, 1.30 g) using 50:1 petroleum ether/EtOAc as eluent.

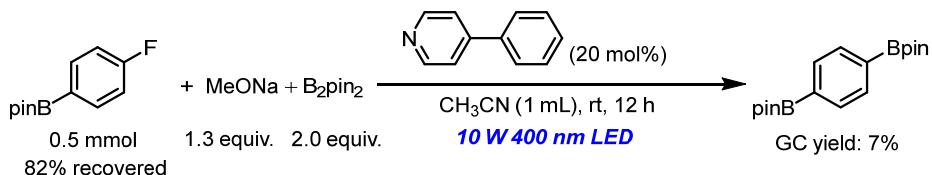
¹H NMR (400 MHz, CDCl₃) δ 7.83-7.76 (m, 2H), 7.08-7.00 (m, 2H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 165.1 (d, *J* = 252.0 Hz), 136.9 (d, *J* = 8.6 Hz), 114.8 (d, *J* = 20.1 Hz), 83.9, 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

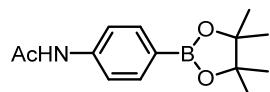
¹⁹F NMR (376 MHz, CDCl₃): δ -108.4.

The NMR data were in consistent with the reported data.^[4]

Trace amount of diborylation product could also be observed in these reactions, a further confirmation experiment was carried out utilizing the separated product of this reaction as substrate, and diborylation product could be observed in 7% yield. These results inspired us to further test the borylation reaction of fluorobenzene.



N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (5l)



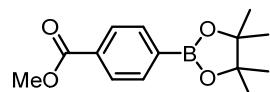
Following procedure A, **5l** was obtained as white solid in 72% yield (94.0 mg) from *N*-(4-chlorophenyl)acetamide (**4l**, 85.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.82 (bs, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 2.16 (s, 3H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 168.7, 140.8, 135.9, 118.5, 83.8, 25.0, 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[7]

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (5m)



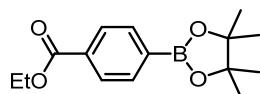
Following procedure A, **5m** was obtained as colorless liquid in 90% yield (117.6 mg) from methyl 4-chlorobenzoate (**4m**, 85.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 7.7 Hz, 2H), 7.86 (d, J = 7.7 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 167.3, 134.8, 132.5, 128.8, 84.3, 52.3, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

Ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (5n)



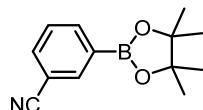
This reaction was carried out at a modified condition of procedure A. A 15 mL reaction tube was charged with a magnetic stir bar, EtONa (44.2 mg, 0.65 mmol), B₂pin₂ (253.0 mg, 1.00 mmol), 4-phenylpyridine (15.5 mg, 0.100 mmol), 1 mL CH₃CN, and substrate **4n** in a glove box. Then following procedure A, **5n** was obtained as colorless liquid in 82% yield (113.1 mg) from ethyl 4-chlorobenzoate (**4n**, 85.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 4.38 (q, *J* = 7.0 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.36 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 166.8, 134.7, 132.8, 128.7, 84.3, 61.1, 25.0, 14.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (5o)



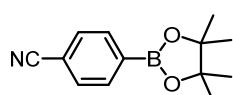
Following procedure A, **5o** was obtained as colorless liquid in 80% yield (92.0 mg) from 3-chlorobenzonitrile (**4o**, 69.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.09 (s), 8.01 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 1.35 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 138.9, 138.5, 134.5, 128.5, 118.9, 112.2, 84.6, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[8]

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (5p)



Following procedure A, **5p** was obtained as white solid in 80% yield (92.2 mg) from 4-chlorobenzonitrile (**4p**, 69.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

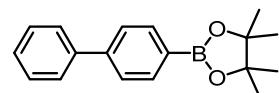
¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 1.35 (m, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 135.3, 131.3, 119.0, 114.8, 84.7, 25.0. The carbon directly attached to the

boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5q)



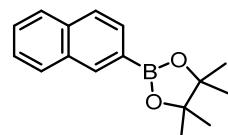
Following procedure A, **5q** was obtained as colorless liquid in 80% yield (112.5 mg) from 4-chloro-1,1'-biphenyl (**4q**, 94.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.65-7.59 (m, 4H), 7.48-7.41 (m, 2H), 7.35 (m, 1H), 1.36 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 144.1, 141.2, 135.4, 128.9, 127.7, 127.4, 126.6, 84.0, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (5r)



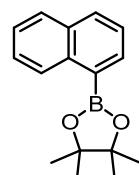
Following procedure A, **5r** was obtained as colorless liquid in 78% yield (99.2 mg) from 2-chloronaphthalene (**4r**, 81 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 7.88 (m, 1H), 7.81-7.85 (m, 3H), 7.47-7.51 (m, 2H), 1.39 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 136.4, 135.2, 133.0, 130.6, 128.8, 127.9, 127.1, 125.9, 84.1, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (5s)



Following procedure A, **5s** was obtained as colorless liquid in 80% yield (101.5 mg) from

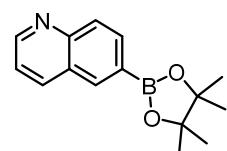
2-chloronaphthalene (**4s**, 81 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.76 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.07 (dd, *J* = 6.8, 1.4 Hz, 1H), 7.93 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.86-7.79 (m, 1H), 7.53 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.50-7.39 (m, 2H), 1.42 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 137.1, 135.8, 133.4, 131.7, 128.6, 128.5, 126.5, 125.6, 125.1, 83.9, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[6]

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (**5t**)



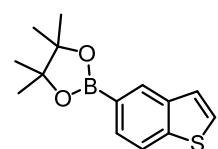
Following procedure A, **5t** was obtained as colorless liquid in 63% yield (79.9 mg) from 6-chloroquinoline (**4t**, 82.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.94 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.35 (s, 1H), 8.19 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.08 (d, *J* = 1.1 Hz, 2H), 7.40 (dd, *J* = 8.2, 4.2 Hz, 1H), 1.40 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 151.5, 150.0, 136.8, 136.3, 134.4, 128.7, 127.9, 121.3, 84.4, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[5]

2-(Benzo[b]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5u**)



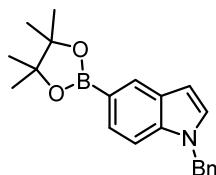
Following procedure A, **5u** was obtained as colorless liquid in 61% yield (79.3 mg) from 5-chlorobenzo[b]thiophene (**4u**, 84.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.31 (s), 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 5.5 Hz, 1H), 7.35 (d, *J* = 5.5 Hz, 1H), 1.37 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 142.9, 139.3, 130.9, 129.9, 126.1, 124.3, 122.0, 84.0, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[6]

1-Benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (5v)



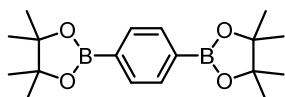
Following procedure A, **5v** was obtained as colorless liquid in 72% yield (120.1 mg) from 1-benzyl-5-chloro-1H-indole (**4v**, 120.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (s), 7.62 (d, *J* = 8.3 Hz, 1H), 7.31-7.20 (m, 4H), 7.12-7.04 (m, 3H), 6.57 (d, *J* = 3.2 Hz, 1H), 5.32 (s, 2H), 1.35 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 138.5, 137.6, 129.1, 128.9 (2C), 128.6, 128.5, 128.0, 127.7, 126.9 (2 C), 109.2, 102.6, 83.6, 50.2, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[9]

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5w)



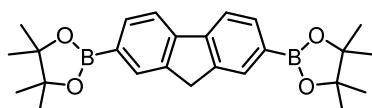
This reaction was carried out following a modified procedure A. A 15 mL sealed tube was added **4w** (73.0mg, 0.500 mmol), MeONa (71.0 mg, 1.30 mmol), B₂pin₂ (508.0 mg, 2.00 mmol), 4-phenylpyridine (15.5 mg, 0.100 mmol) and 1 mL CH₃CN in glove box. Then following procedure A, **5w** was obtained as white solid in 79% yield (130.1 mg) from methyl 1,4-dichlorobenzene (**4w**, 73.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 4H), 1.35 (s, 24H).

¹³C NMR (100 MHz, CDCl₃) δ 134.0, 84.0, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[4]

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene (5x)



This reaction was carried out following a modified procedure A. A 15 mL sealed tube was added **5x** (118.0mg, 0.500 mmol), MeONa (71.0 mg, 1.30 mmol), B₂pin₂ (508.0 mg, 2.00 mmol), 4-phenylpyridine (15.5 mg, 0.100 mmol) and 1 mL CH₃CN in glove box. Then following procedure A, **5x** was obtained as

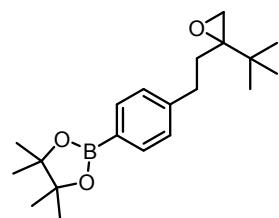
white solid in 62% yield (129.6 mg) from methyl 2,7-dichloro-9*H*-fluorene (**4x**, 118.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 2H), 7.83 (m, 4H), 3.89 (s, 2H), 1.37 (s, 24H).

¹³C NMR (100 MHz, CDCl₃) δ 144.5, 143.3, 133.5, 131.5, 119.9, 83.9, 36.7, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[10]

2-(4-(2-(Tert-butyl)oxiran-2-yl)ethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5y**)**



Following procedure A, **5y** was obtained as white solid in 80% yield (130.8 mg) from 2-(tert-butyl)-2-(4-chlorophenethyl)oxirane (**4y**, 119.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 2.76 (d, *J* = 4.1 Hz, 1H), 2.65 (d, *J* = 4.2 Hz, 1H), 2.57 (ddd, *J* = 13.5, 11.5, 5.1 Hz, 1H), 2.47 (ddd, *J* = 13.5, 11.6, 5.8 Hz, 1H), 2.12 (ddd, *J* = 13.5, 11.5, 5.8 Hz, 1H), 2.00 (ddd, *J* = 13.5, 11.6, 5.2 Hz, 1H), 1.33 (s, 12H), 0.96 (s, 9H).

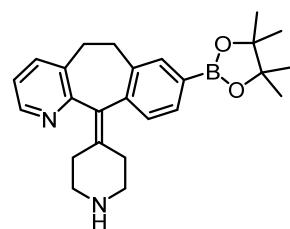
¹³C NMR (100 MHz, CDCl₃) δ 145.8, 135.1, 127.9, 83.8, 77.2, 63.5, 48.1, 34.1, 31.4, 31.0, 26.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

¹¹B NMR (128 MHz, CDCl₃): δ 30.6.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2274, 2177, 2045, 1925, 1608, 1395, 1358, 1321, 1271, 1144, 1089, 857.

HRMS (ESI) calcd. for C₂₀H₃₁BO₃ [M + H]⁺: 331.2439; found: 331.2440.

11-(Piperidin-4-ylidene)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,11-dihydro-5*H*-benzo[5,6]cyclonhepta[1,2-b]pyridine (5z**)**



Following procedure A, **5z** was obtained as red oil in 40% yield (80.2 mg) from desloratadine (**4z**, 155.0 mg) using 10:1 MeOH/DCM as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J* = 4.8 Hz, 1H), 7.65 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0

Hz, 1H), 7.20-7.14 (m, 1H), 7.12-7.05 (m, 1H), 3.45-3.35 (m, 2H), 3.33-3.24 (m, 2H), 3.19-3.06 (m, 2H), 3.19-3.06 (m, 2H), 2.95-2.69 (m, 4H), 2.68-2.54 (m, 2H), 1.33 (s, 12H).

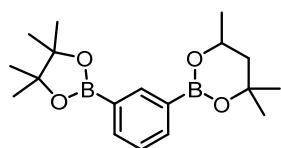
^{13}C NMR (100 MHz, CDCl_3) δ 155.9, 146.8, 141.9, 138.1, 137.8, 137.3, 135.5, 133.9, 132.9, 132.0, 128.1, 122.7, 84.0, 45.2, 32.0, 31.4, 27.9, 27.5, 24.99, 24.93. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

^{11}B NMR (128 MHz, CDCl_3): δ 33.9.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2282, 1606, 1444, 1361, 1276, 1145, 1110, 948, 886, 865, 752.

HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{31}\text{BN}_2\text{O}_2$ $[\text{M} + \text{H}]^+$: 403.2551; found: 403.2551.

4,4,6-Trimethyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,2-dioxaborinane (5ab)



Following procedure A, **5ab** was obtained as colorless oil in 79% yield (130.0 mg) from 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ab**, 119.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

^1H NMR (400 MHz, CDCl_3) δ 8.24 (s, 1H), 7.91 (d, $J = 7.4$ Hz, 1H), 7.85 (d, $J = 7.4$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 2H), 4.39-4.26 (m, 1H), 1.84 (dd, $J = 13.9, 3.0$ Hz, 1H), 1.56 (dd, $J = 13.9, 11.6$ Hz, 1H), 1.37 (s, 3H), 1.36-1.31 (m, 18H).

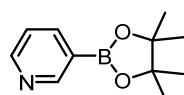
^{13}C NMR (100 MHz, CDCl_3) δ 140.2, 137.0, 136.9, 83.7, 71.1, 65.1, 46.3, 31.5, 28.3, 25.00, 24.97, 23.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

^{11}B NMR (128 MHz, CDCl_3): δ 30.8, 26.7.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1602, 1580, 1385, 1361, 1294, 1272, 1145, 1081, 964, 864, 709.

HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{29}\text{B}_2\text{O}_4$ $[\text{M} + \text{H}]^+$: 331.2264; found: 331.2270.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (7a)



Following procedure A, **7a** was obtained as white solid in 48% yield (49.6 mg) from 3-bromopyridine (**6a**, 79.0 mg) using 10:1 petroleum ether/EtOAc as eluent.

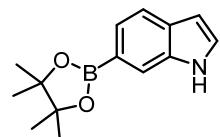
^1H NMR (400 MHz, CDCl_3) δ 8.95 (s, 1H), 8.70-8.64 (m, 1H), 8.08-8.02 (m, 1H), 7.31-7.26 (m, 1H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 152.2, 142.3, 123.2, 84.4, 25.0. The carbon directly attached to the

boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[5]

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (7b)



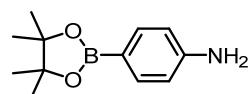
Following procedure A, **7b** was obtained as colorless liquid in 56% yield (68.1 mg) from 6-bromo-1*H*-indole (**6b**, 98.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (bs, 1H), 7.90 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.29 (s, 1H), 6.56 (s, 1H), 1.37 (s, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 135.7, 130.5, 125.8, 125.7, 120.2, 118.2, 102.9, 83.7, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[11]

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (7c)



Following procedure A, **7c** was obtained as white solid in 78% yield (85.8 mg) from 4-bromoaniline (**6c**, 86.0 mg) using 50:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.0, 2H), 3.84 (bs, 2H), 1.32 (s, 12H).

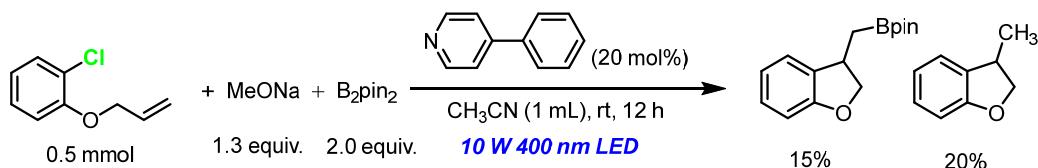
¹³C NMR (100 MHz, CDCl₃) δ 149.4, 136.6, 114.2, 83.4, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

The NMR data were in consistent with the reported data.^[7]

6. Mechanism of the Borylation Reaction

6.1 Probe Substrate

Performing this borylation reaction utilizing a typical radical cyclization substrate could produce 5-exo-trig product, indicating intramolecular trapping of the aryl radical by the olefin moiety, followed by coupling with the borylation reagent. This results indicate the intermediacy of an aryl radical in this borylation reaction.



Experimental procedure: A 15 mL reaction tube charged with a magnetic stir bar, MeONa (35.5 mg, 0.65 mmol), B_2pin_2 (254.0 mg, 1.00 mmol), and 1 mL CH_3CN was added 1-(allyloxy)-2-chlorobenzene (84.0 mg, 0.500 mmol) in a glove box. The tube was sealed with a Teflon screw cap and then irradiated by a 10 W 400 nm LED for 12 h. The reaction mixture was then added a standard solution of *n*-dodecane in toluene as the internal standard, followed by water. Then 2 drops of acetic acid were added to the mixture to adjust pH of solution to ~7. After shaking for 1 min, the organic layer was separated and analyzed by GC.

6.2 On-Off Experiment

In order to better understand the effect of light in this radical borylation reaction. On-off experiment was carried out. No product formation was observed during the dark periods in this experiment. In recent work reported by Yoon, they demonstrated that conversion ceases during dark periods could not exclude radical chain mechanism since typical lifetimes for radical chain processes can often be on the second or subsecond timescale which terminate faster than the timescale of the analytical measurement used.^[12] Nevertheless, this experiment still demonstrate that light is important for this borylation reaction.

Experimental procedure: A 15 mL reaction tube charged with a magnetic stir bar, MeONa (70.0 mg, 1.30 mmol), B_2pin_2 (508.0 mg, 2.00 mmol), and 2 mL CH_3CN was added 4-chlorofluorobenzene (130.0 mg, 1.00 mmol) and dodecane (80.0 mg, internal standard) in a glove box. The tube was sealed with a Teflon screw cap and then irradiated by a 10 W 400 nm LED. Aliquots (ca. 0.1 mL) were taken from the reaction mixture in glove box. After then, it was added water and ethyl acetate to dilute the organic phase. After shaking for 1 min, the organic layer was separated and analyzed by GC.

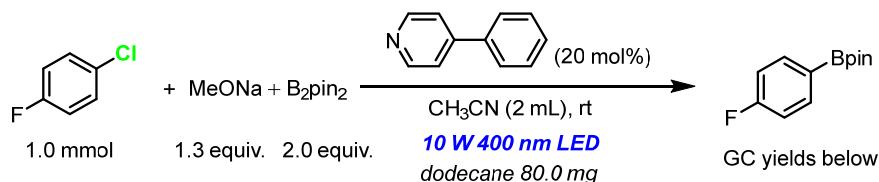


Table S1. Raw data of GC yields in on-off experiment.

Time/h	0	2	4	6	8	10	16	20	26	32	42
Yield/%	0	4	4	18	18	45	45	70	70	83	83

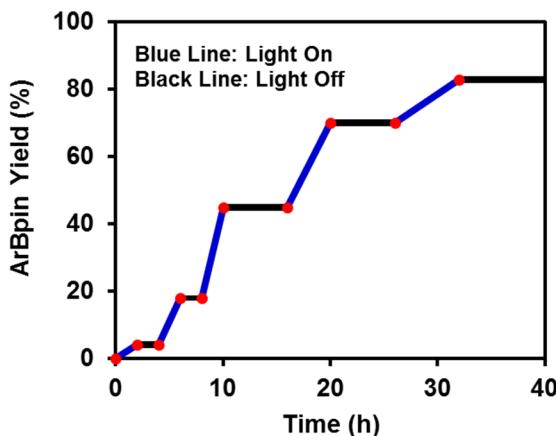


Figure S9. On-off experiment kinetic profile.

6.3 Borylation Mechanism

Based on our previous study on the mechanism of pyridine-catalyzed radical borylation reaction^[4] and the mechanistic study of the excited state ate complex in this work, the following borylation mechanism is proposed (Figure S10). First, ate complex **2** was formed after pyridine- and methoxide-promoted heterolytic cleavage of diboron and followed nucleophilic addition reaction. Stern-Volmer experiments results suggest ate complex **2** could be excited under visible light and the excited singlet state of ate complex **2** could undergo single electron transfer process with arylchlorides to form an aryl radical. The produced aryl radical could react with diboron to form the arylboronate. Mechanism after the electron transfer process was also taken into consideration: pyridine stabilized boryl radical **A** was produced after SET process, which would dimerize to afford compound **B**,^[4] which is the precursor of super electron donor **2** upon treatment with base.

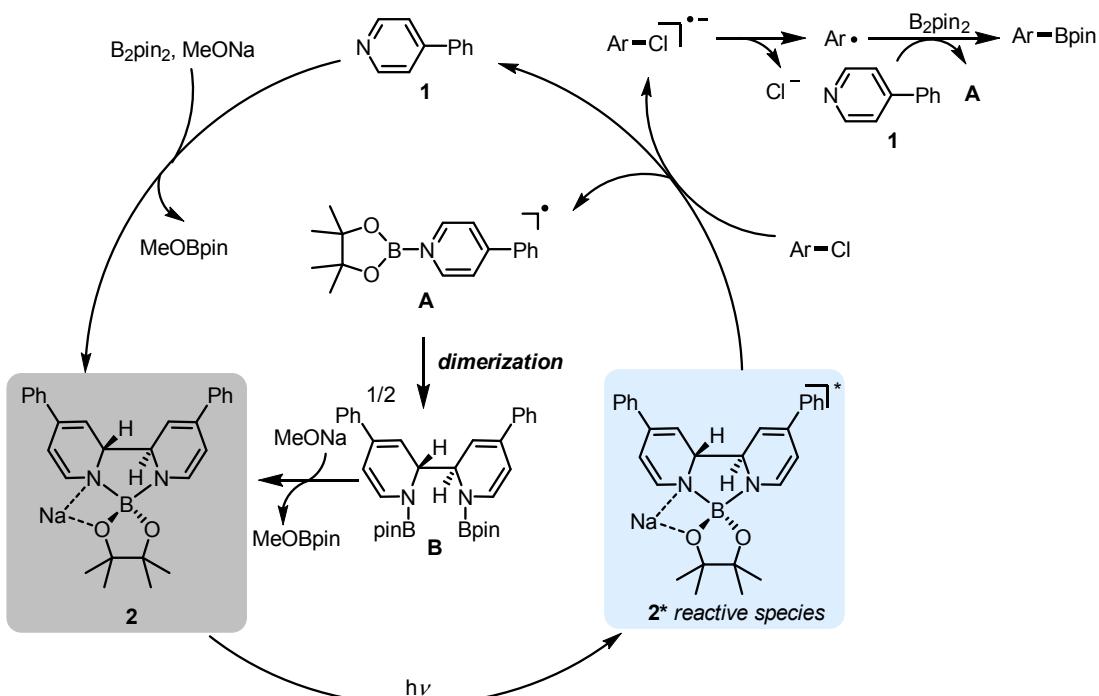
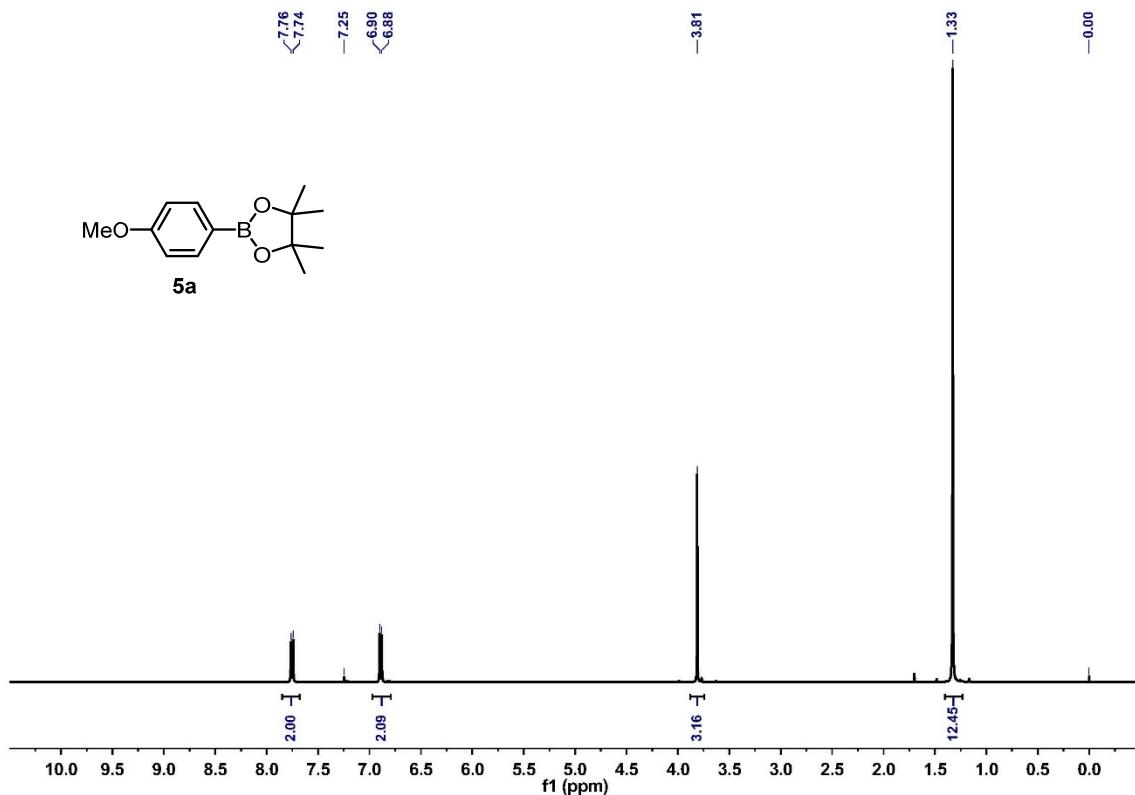
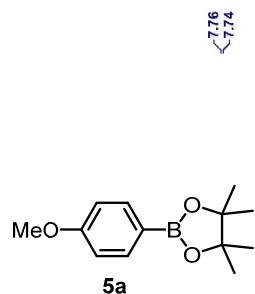


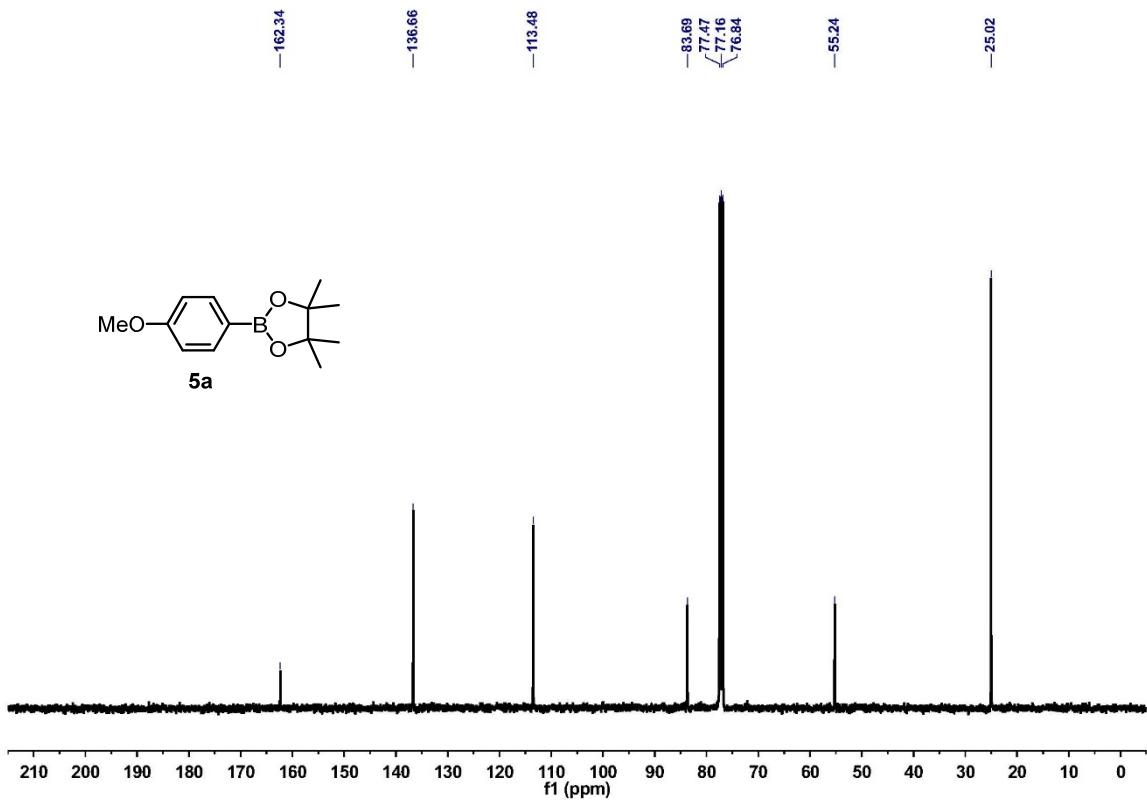
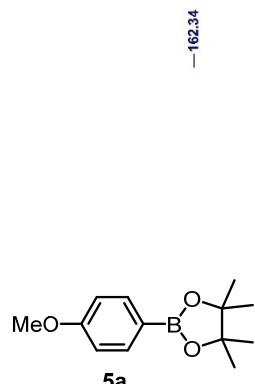
Figure S10. Borylation mechanism of aryl chlorides.

7. NMR Spectra

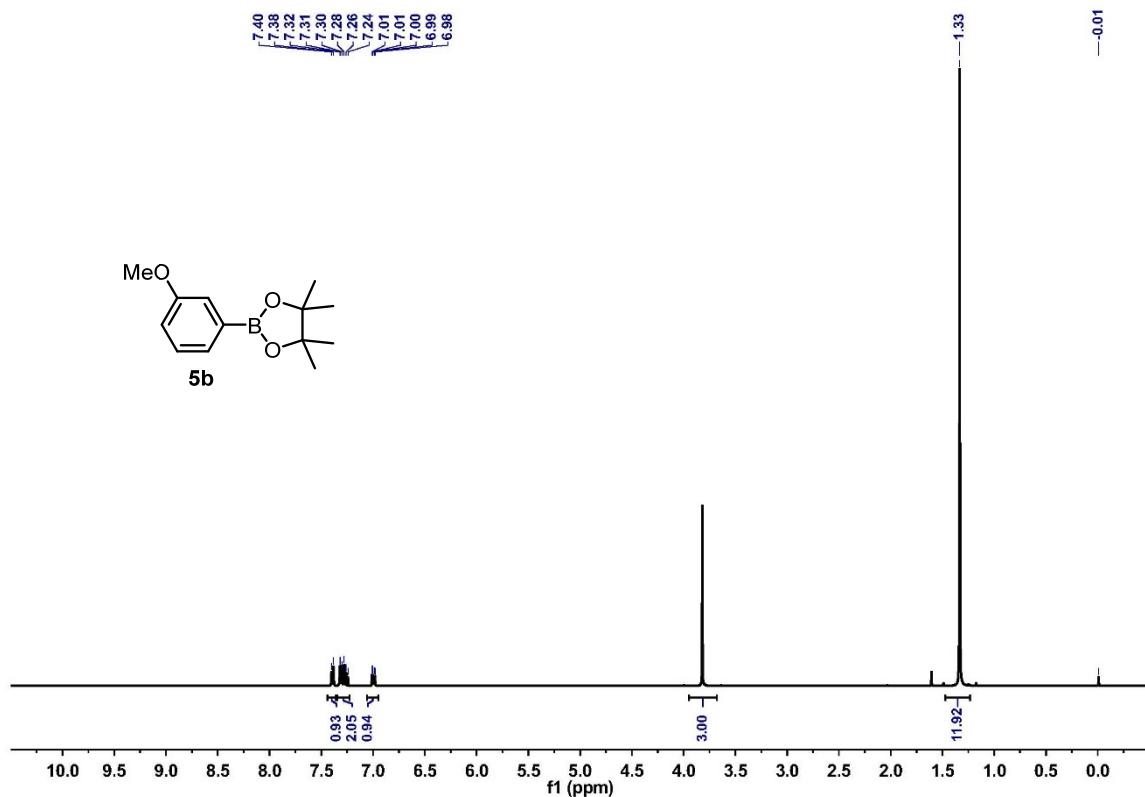
¹H NMR:



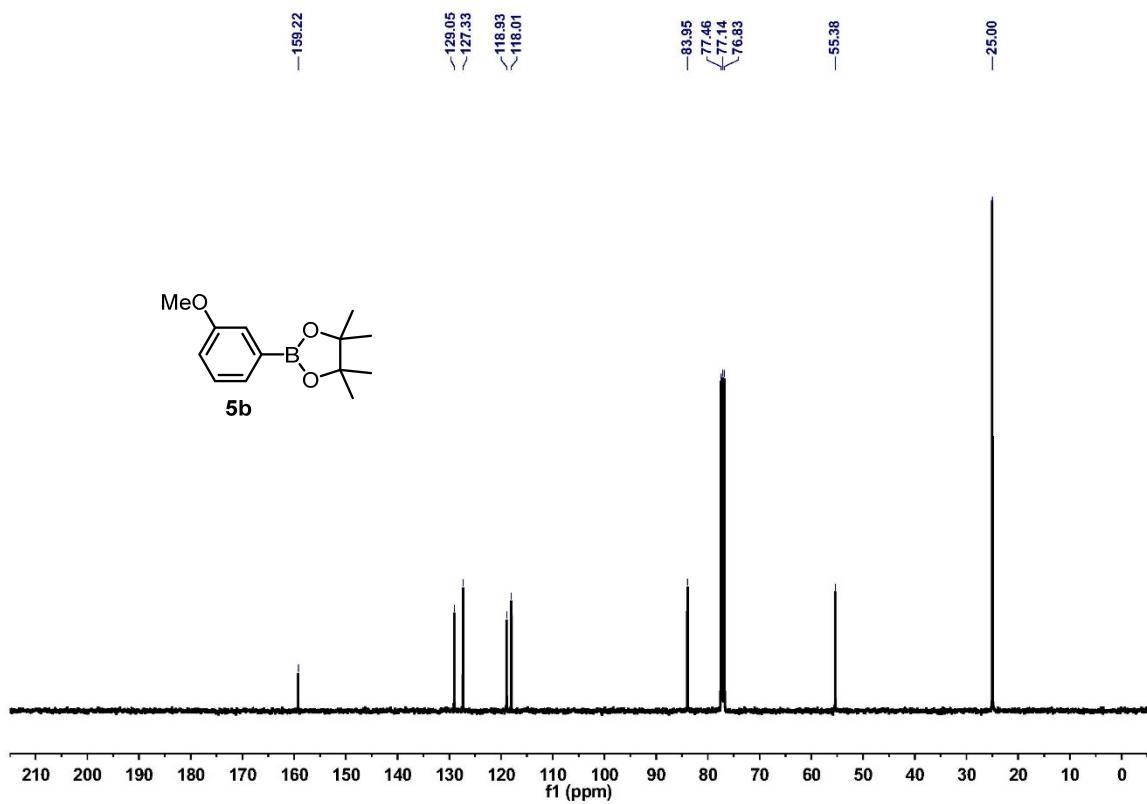
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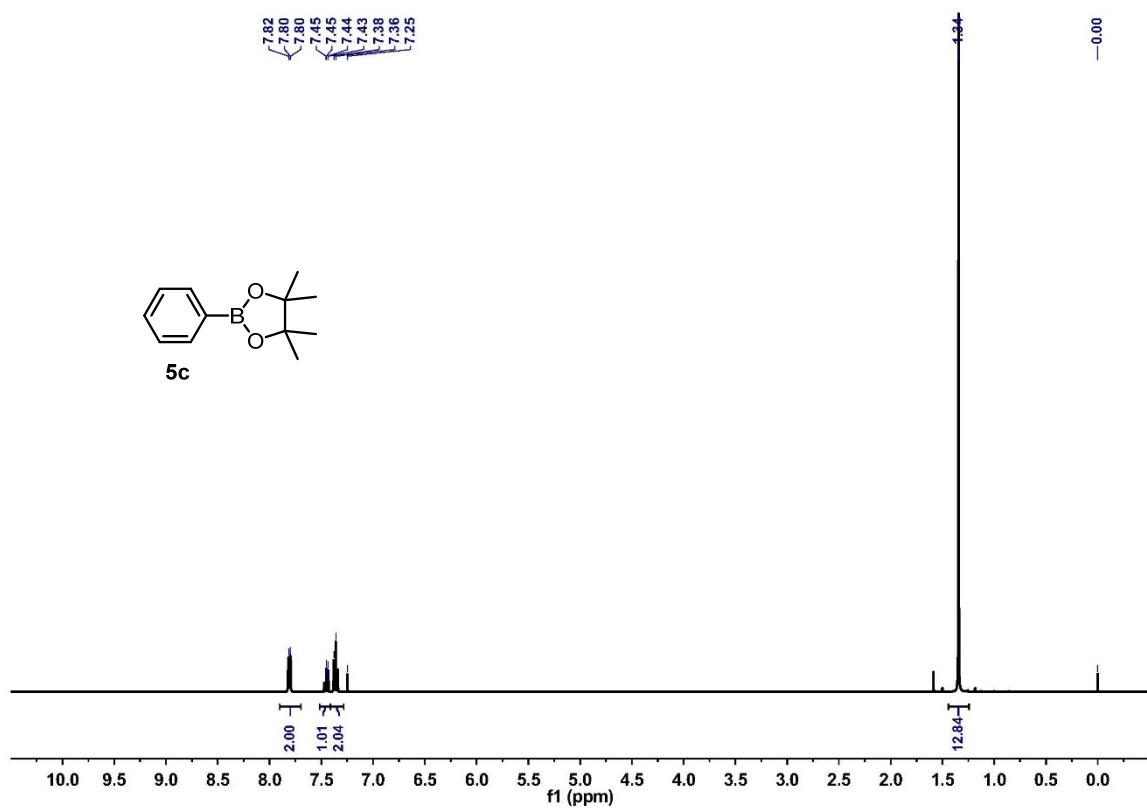
¹H NMR:



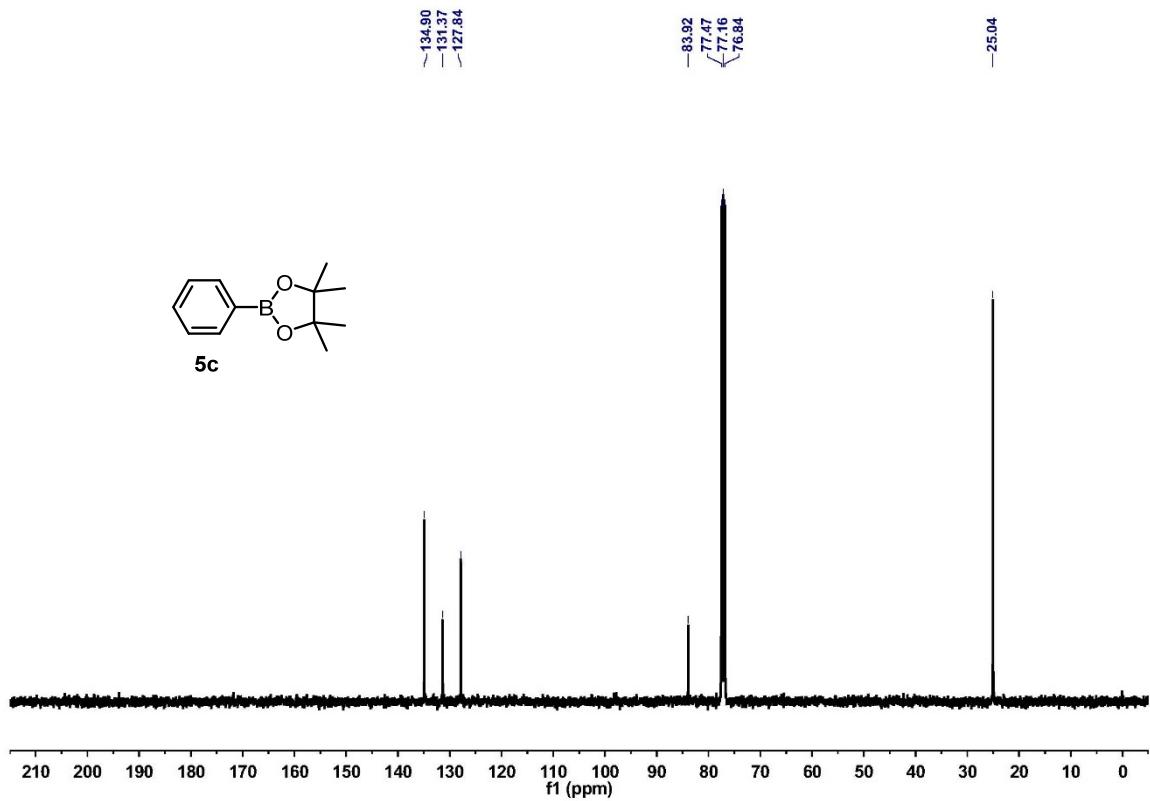
¹³C NMR:



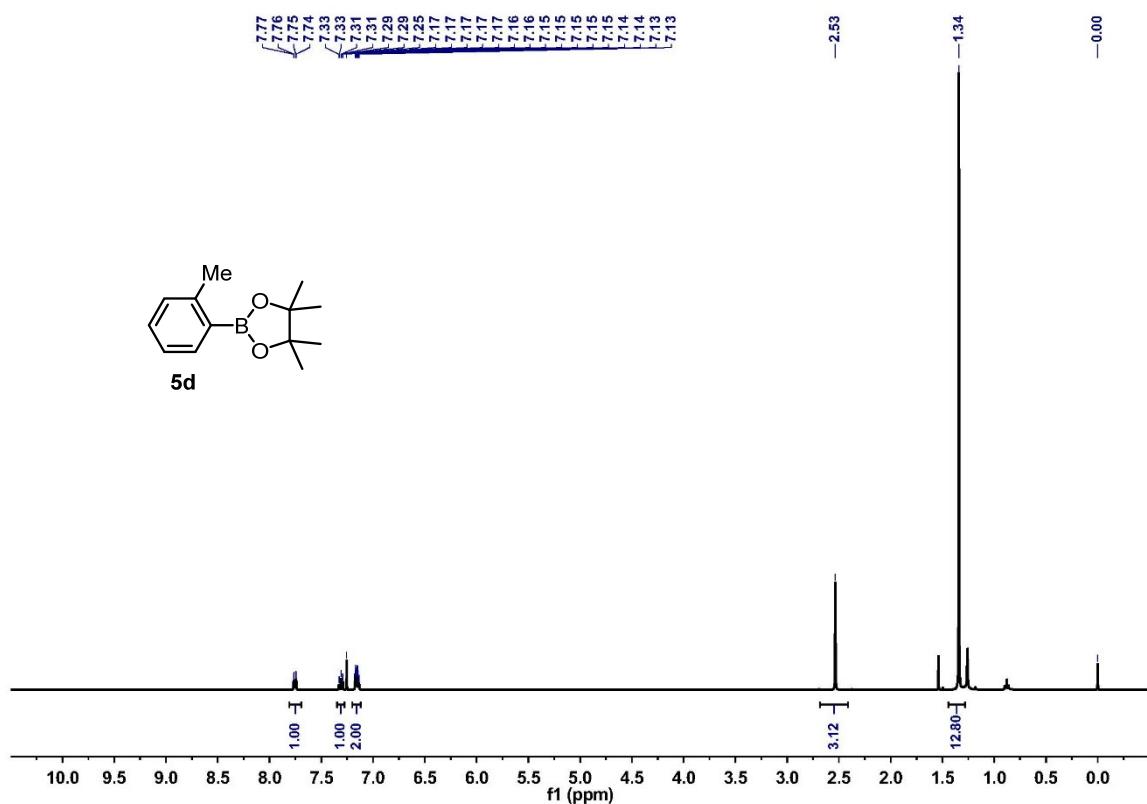
¹H NMR:



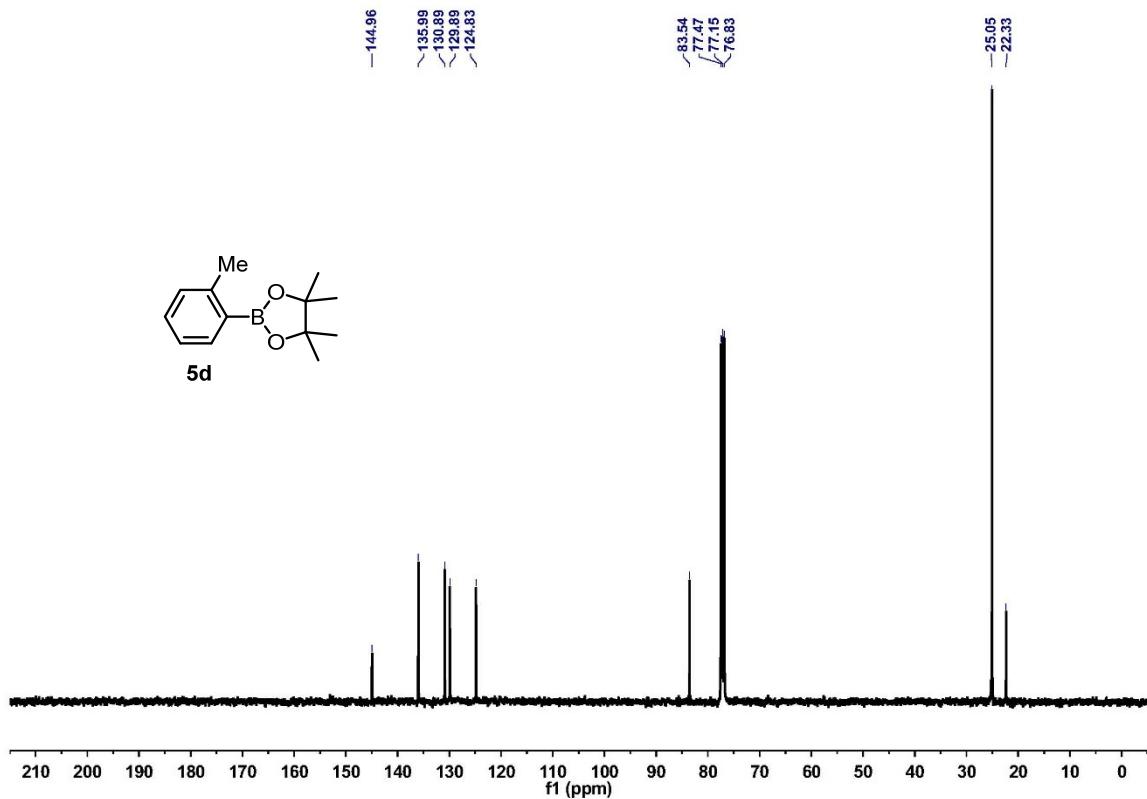
¹³C NMR:



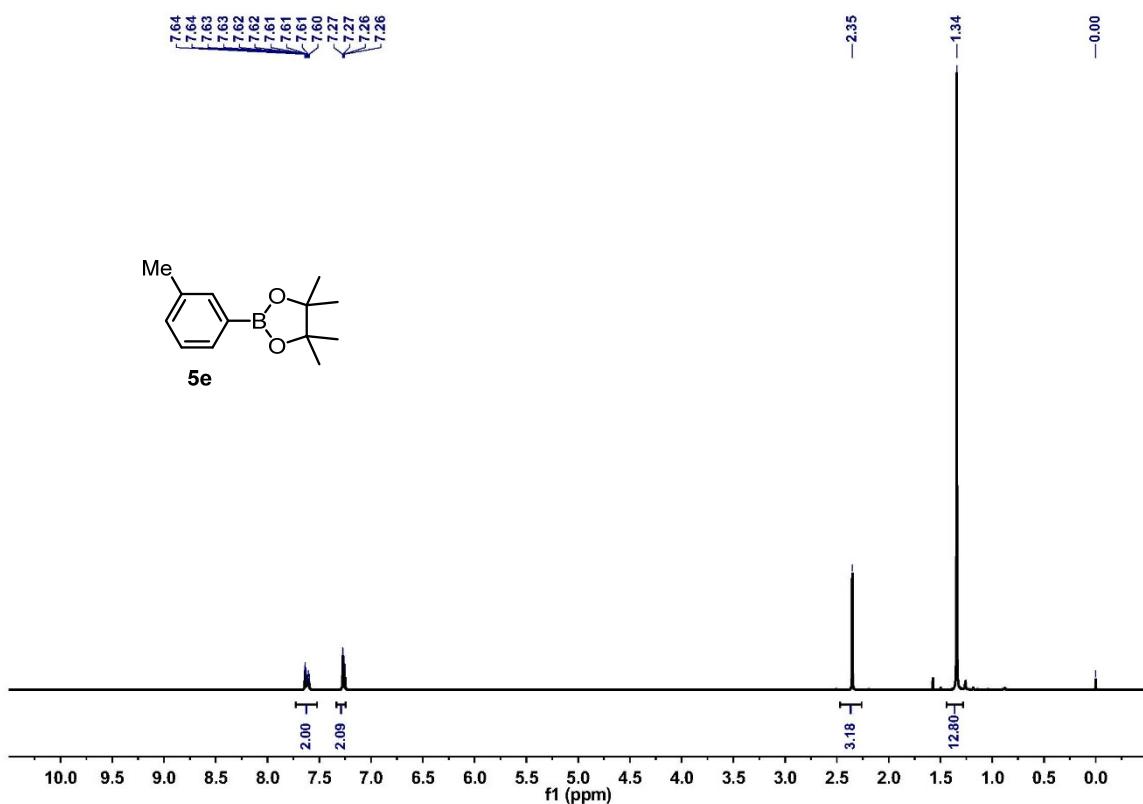
¹H NMR:



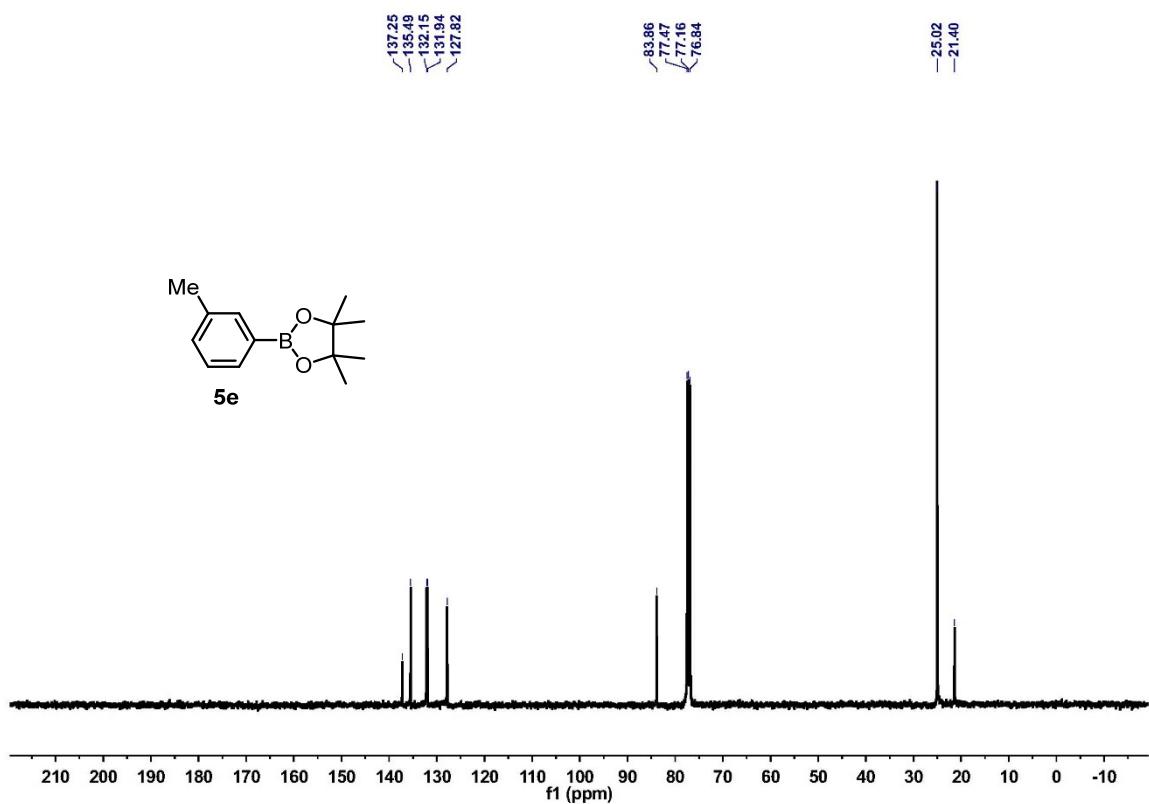
¹³C NMR:



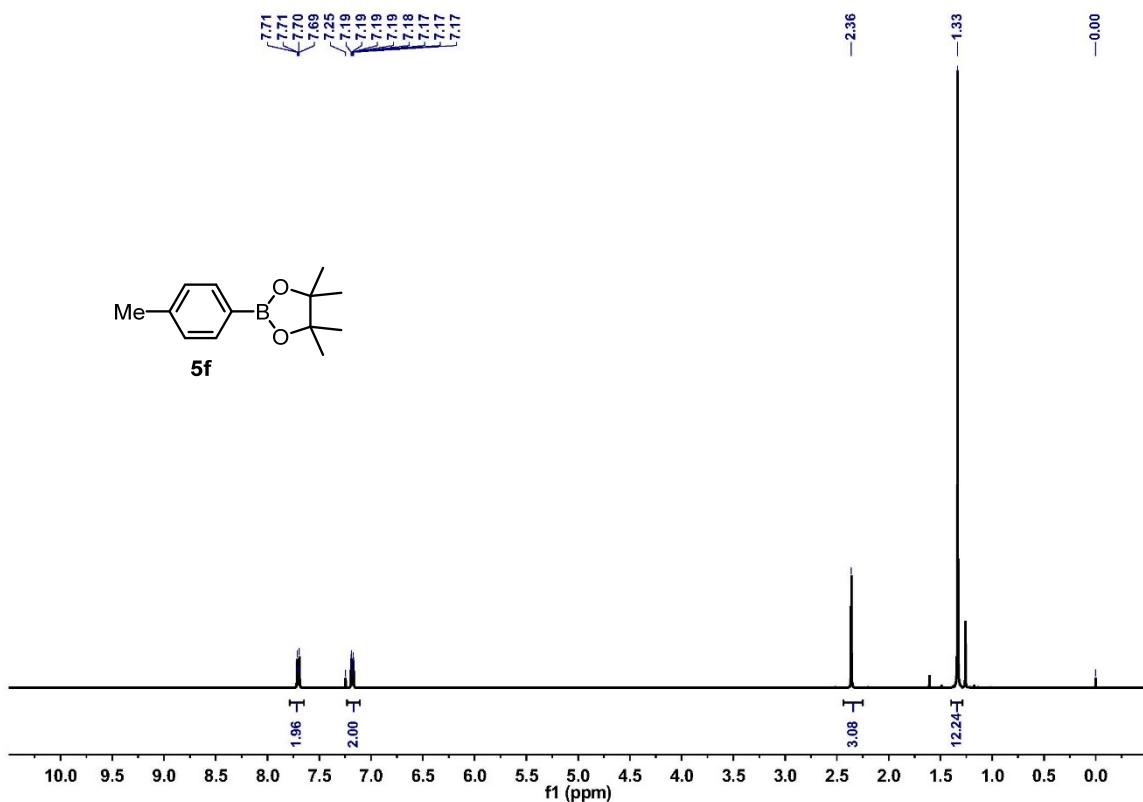
¹H NMR:



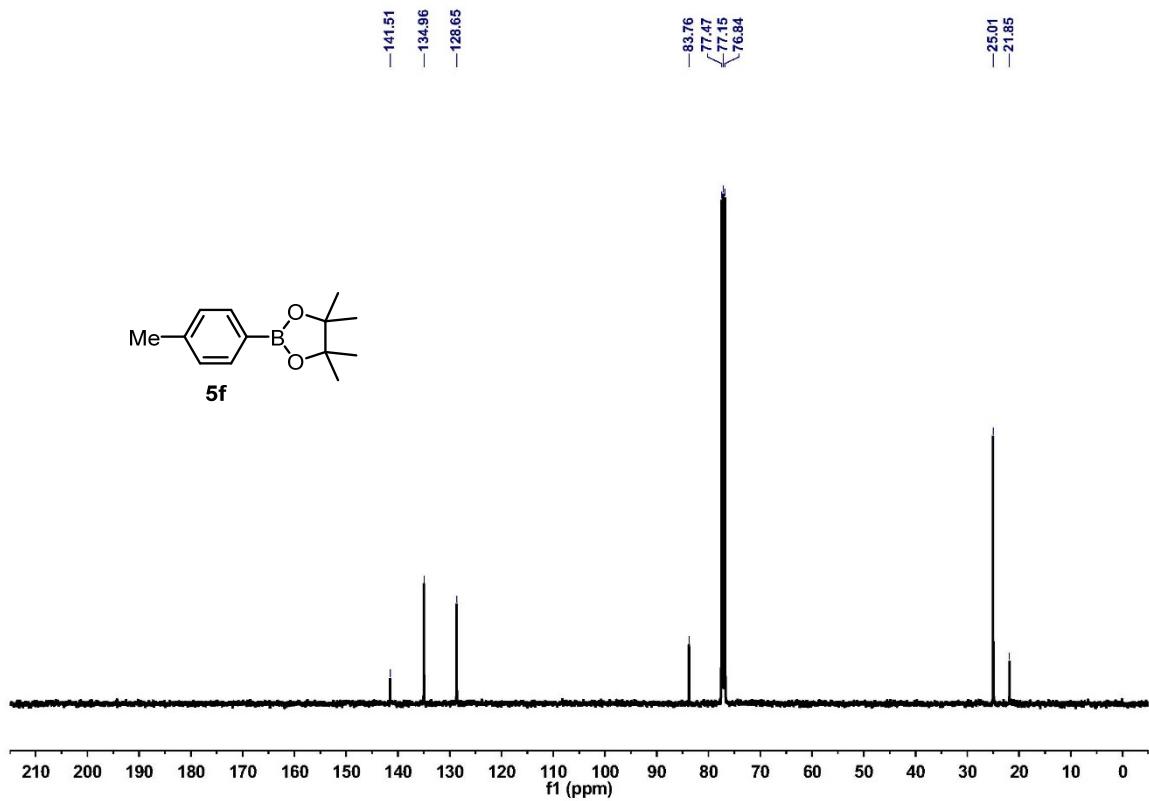
¹³C NMR:



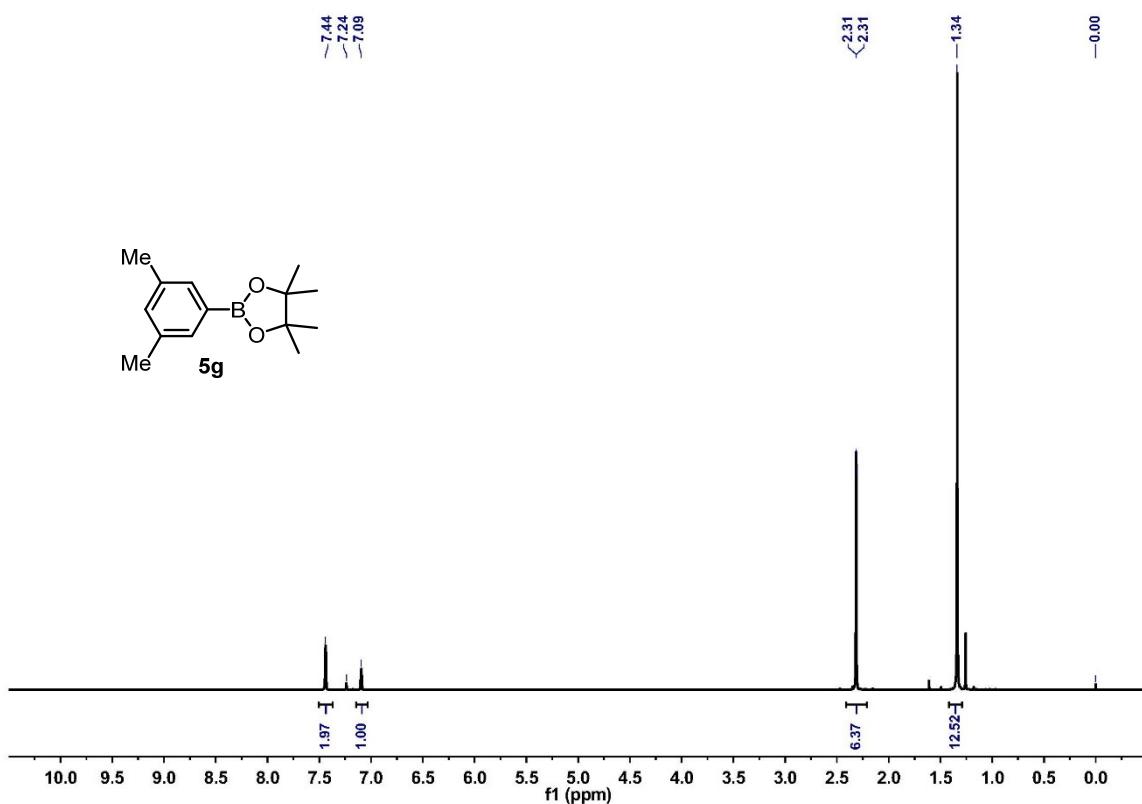
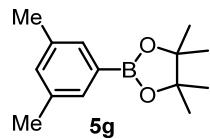
¹H NMR:



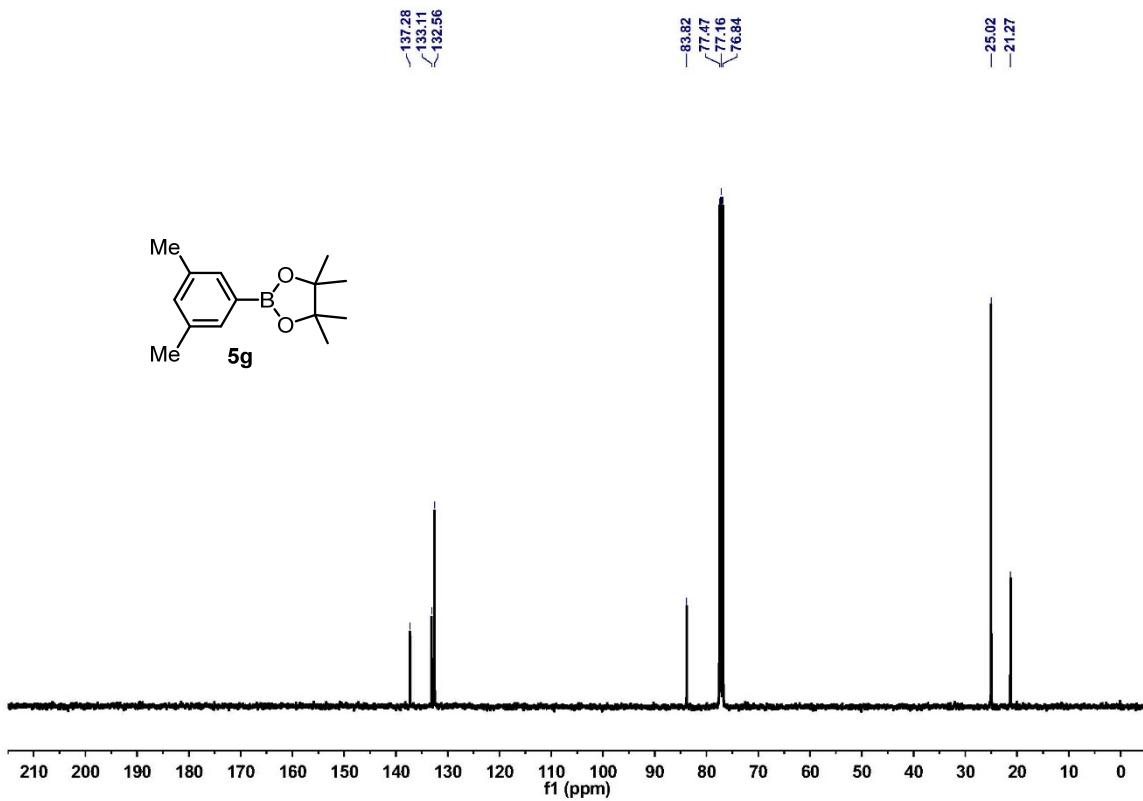
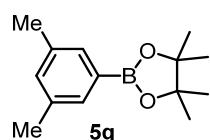
¹³C NMR:



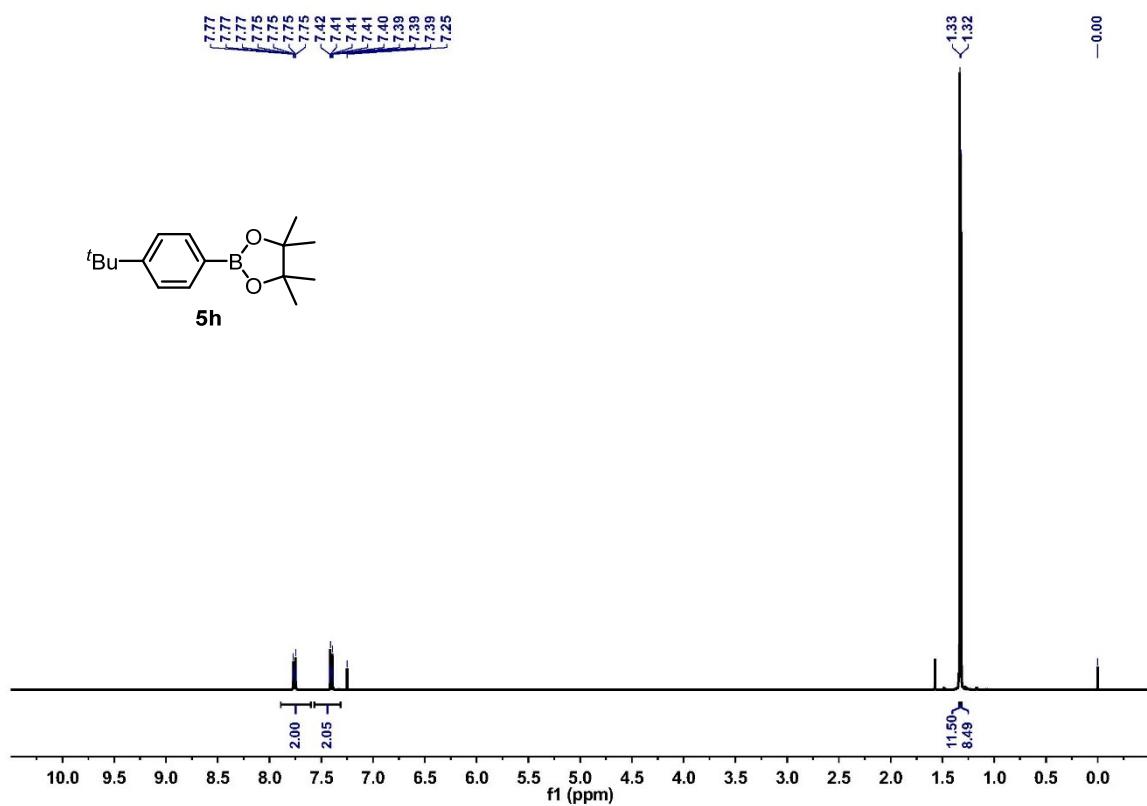
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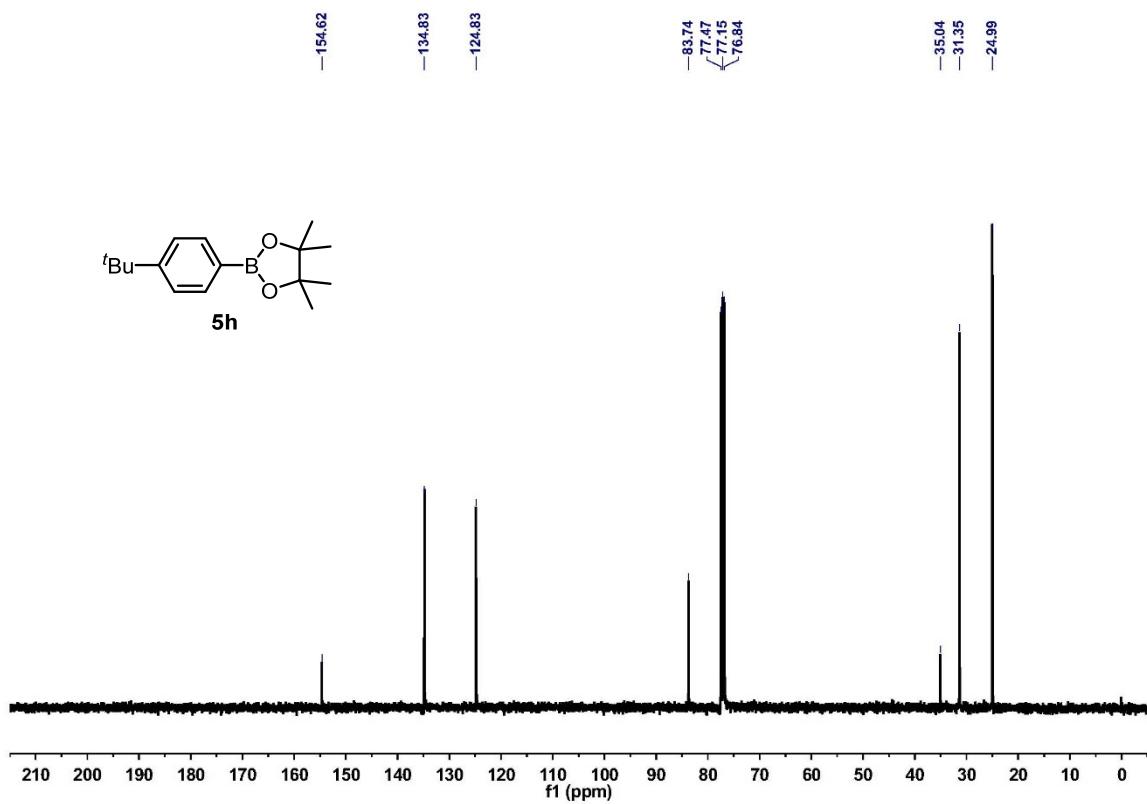
¹³C NMR:



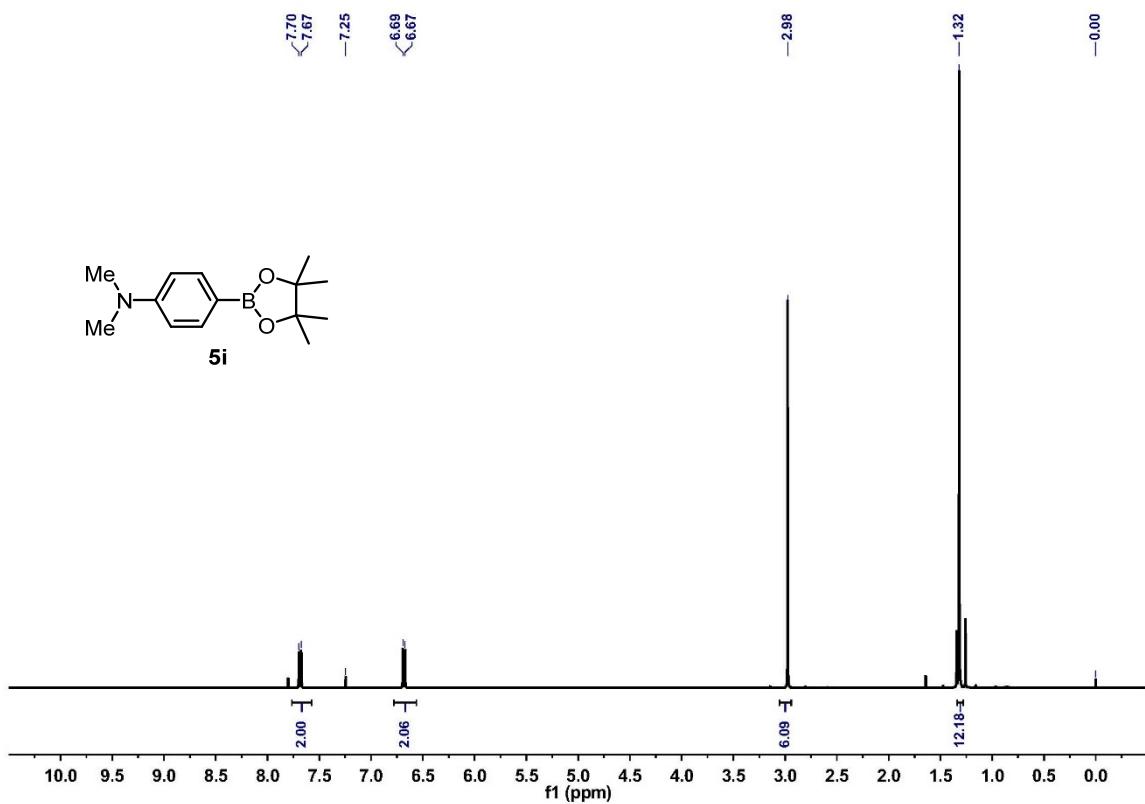
¹H NMR:



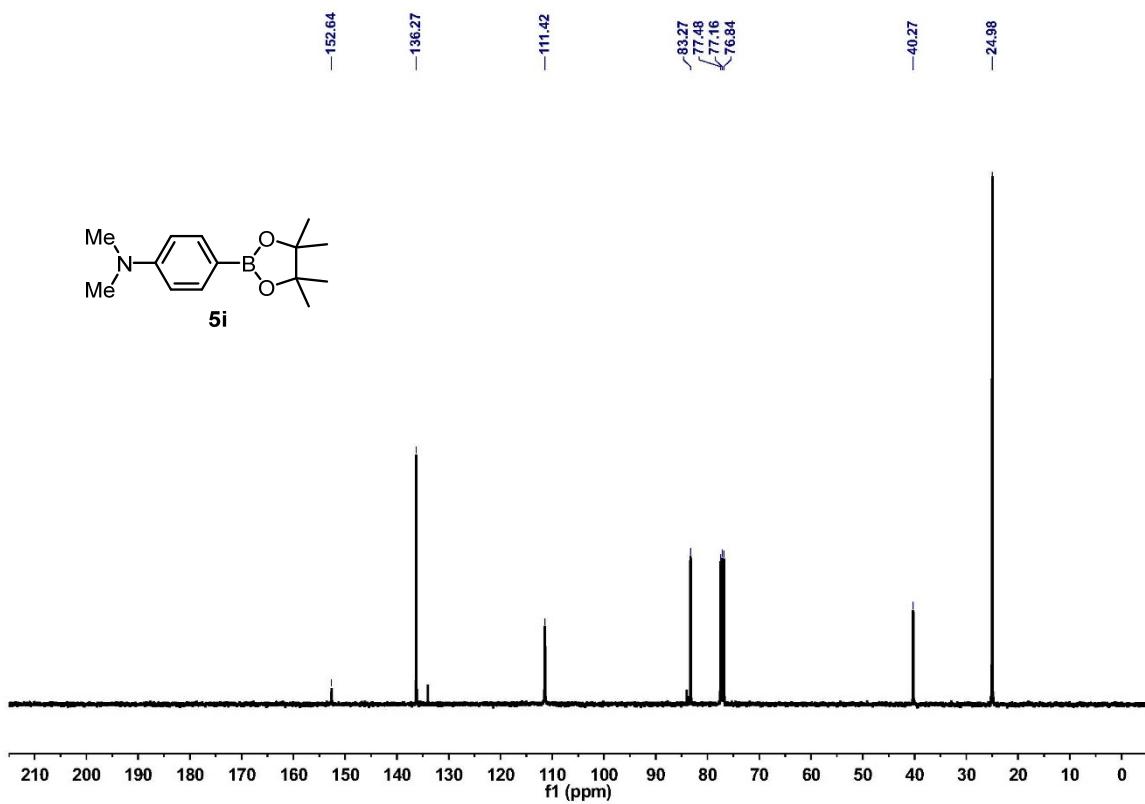
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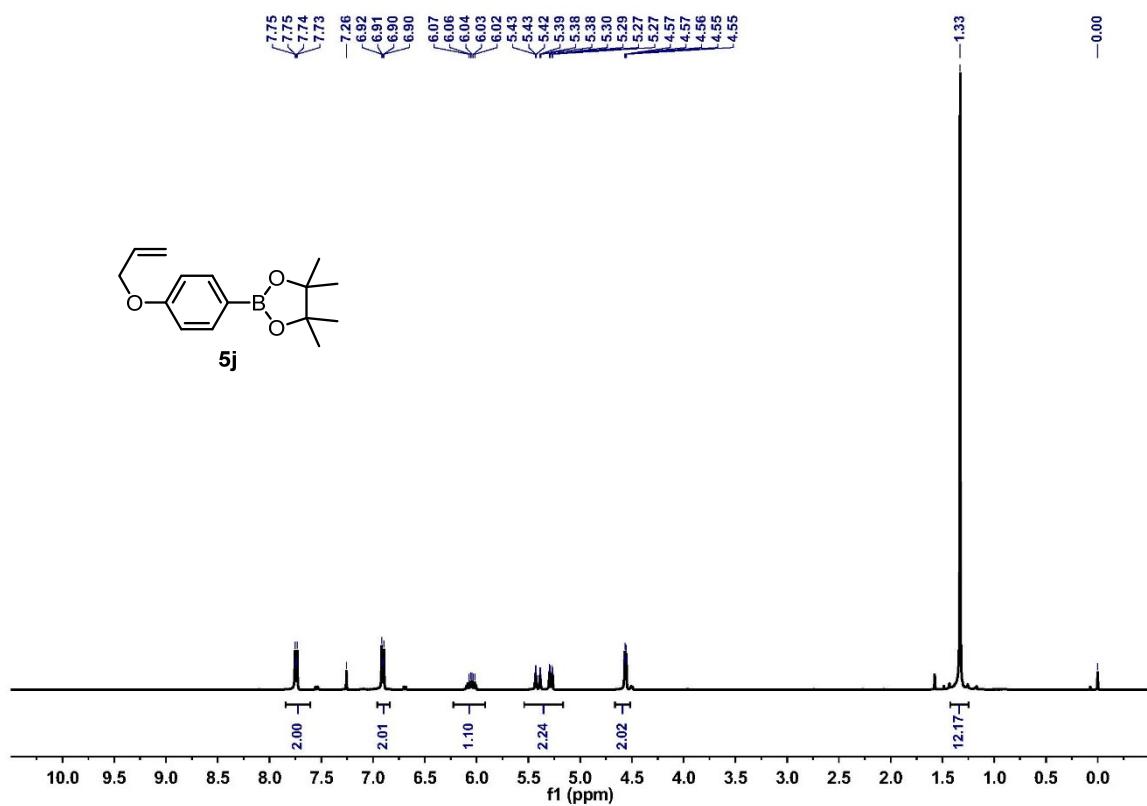
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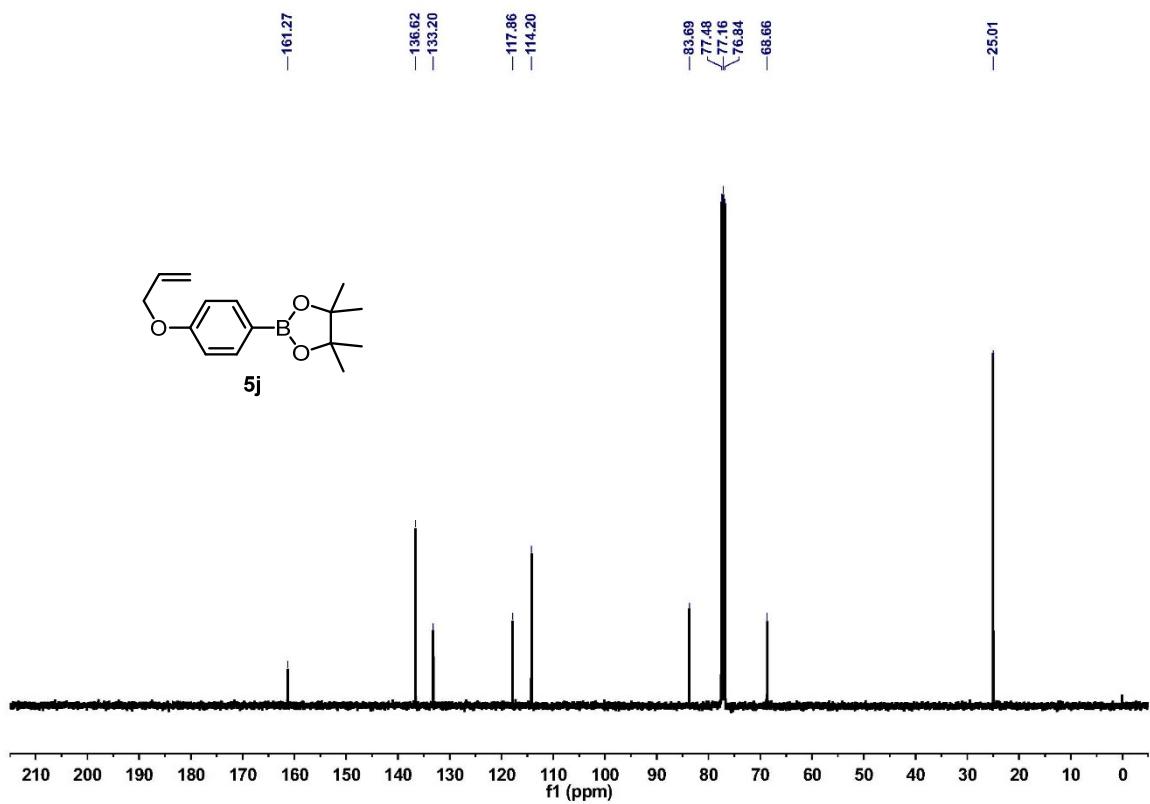
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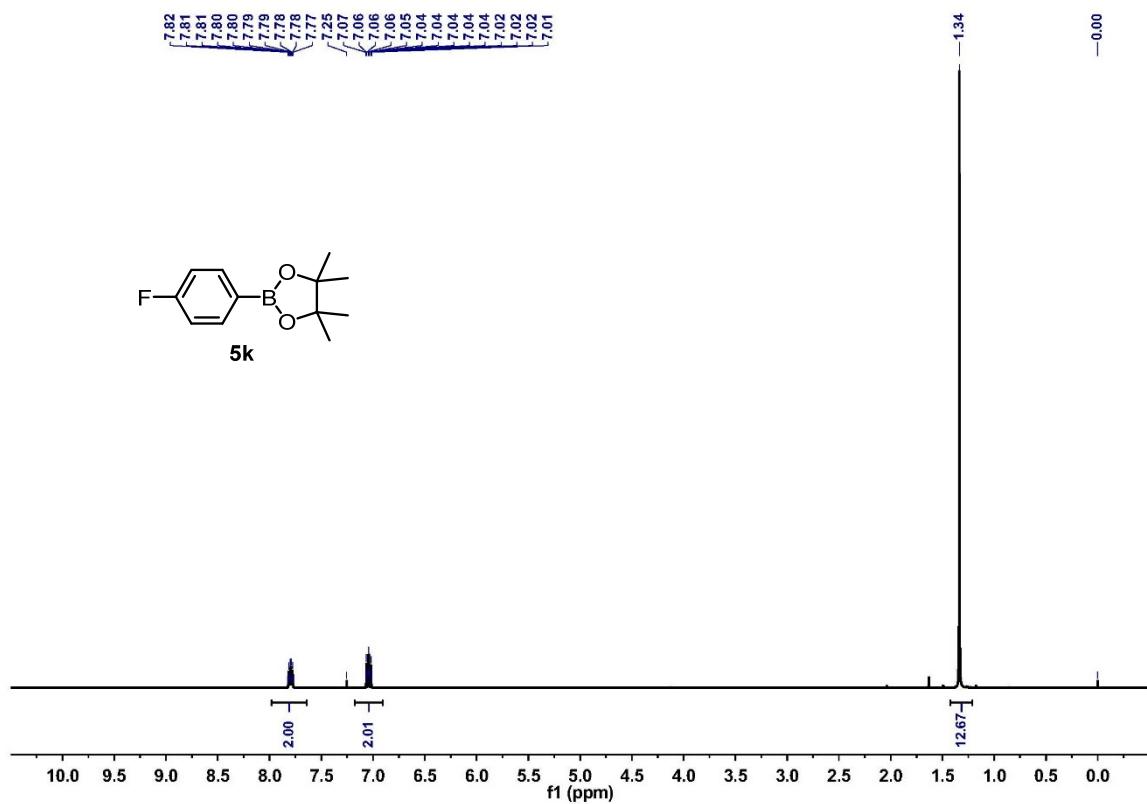
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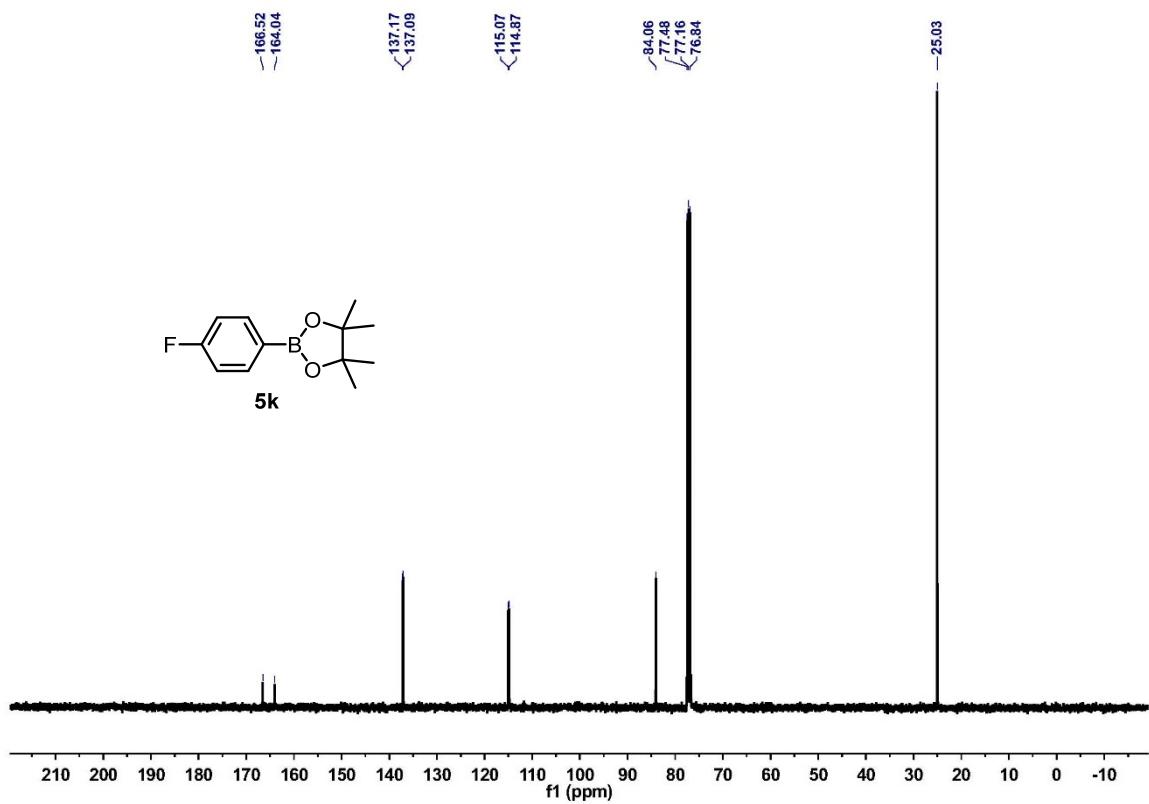
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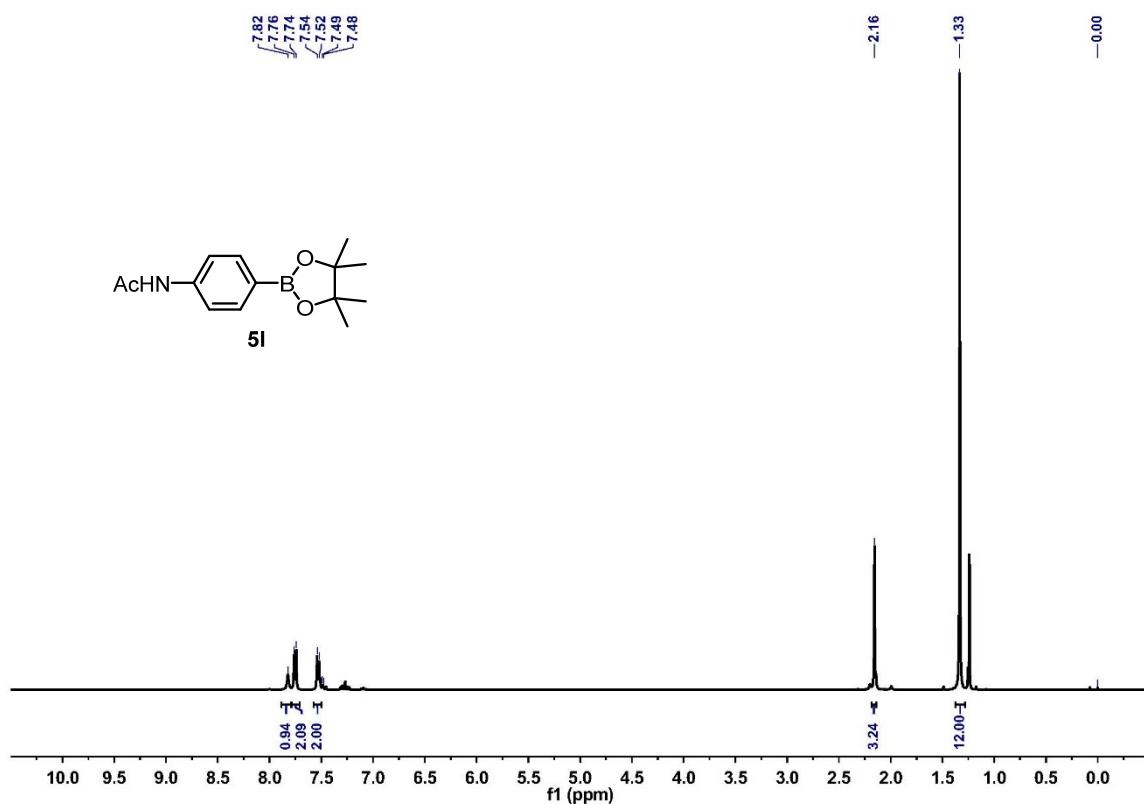
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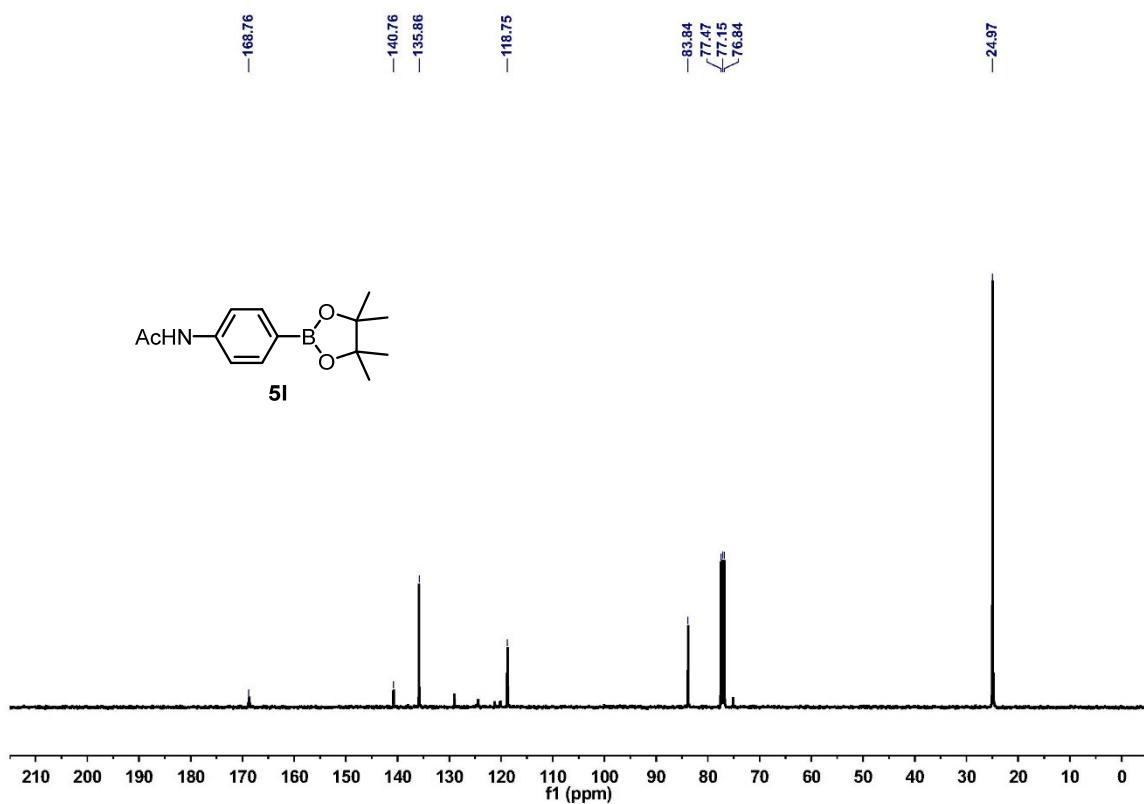
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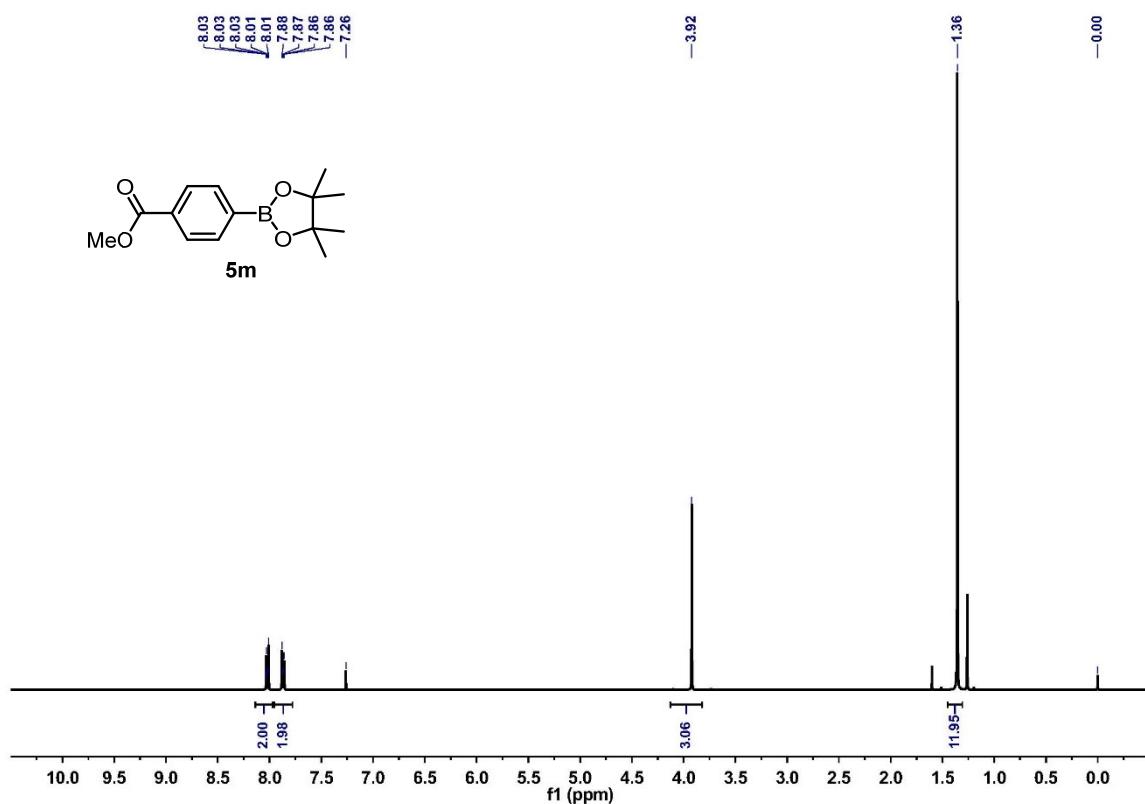
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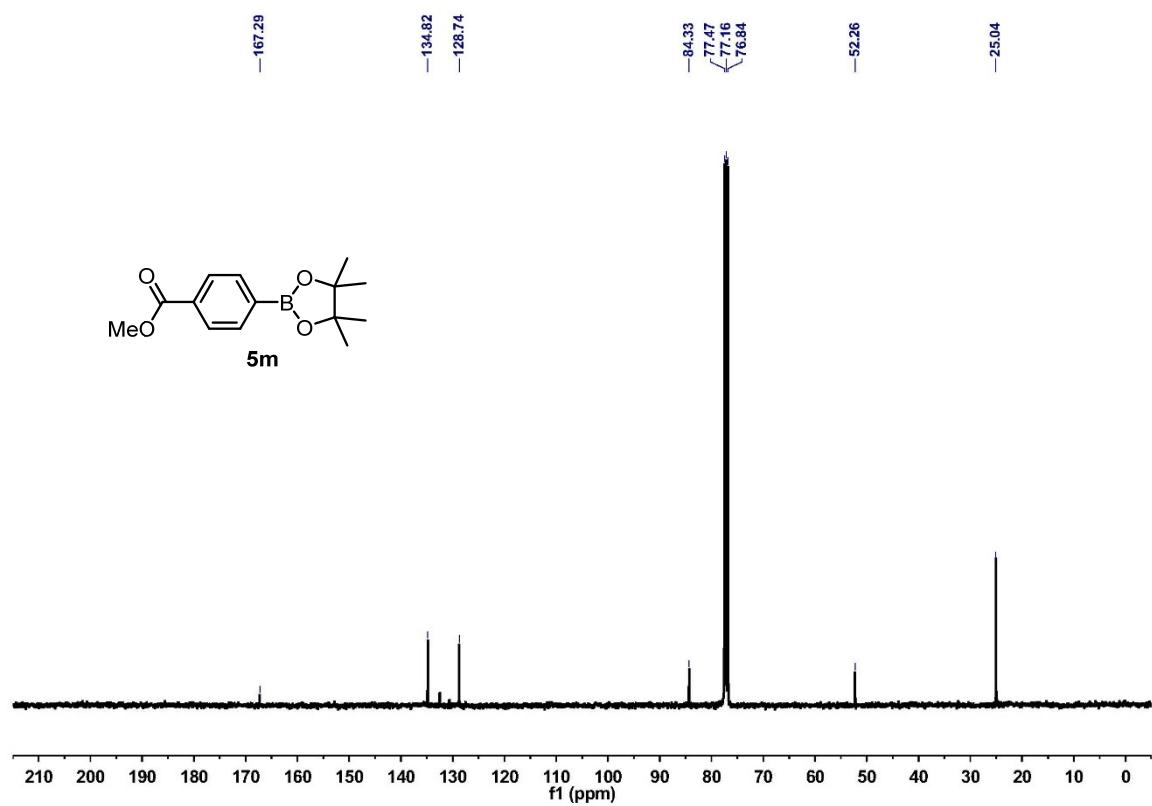
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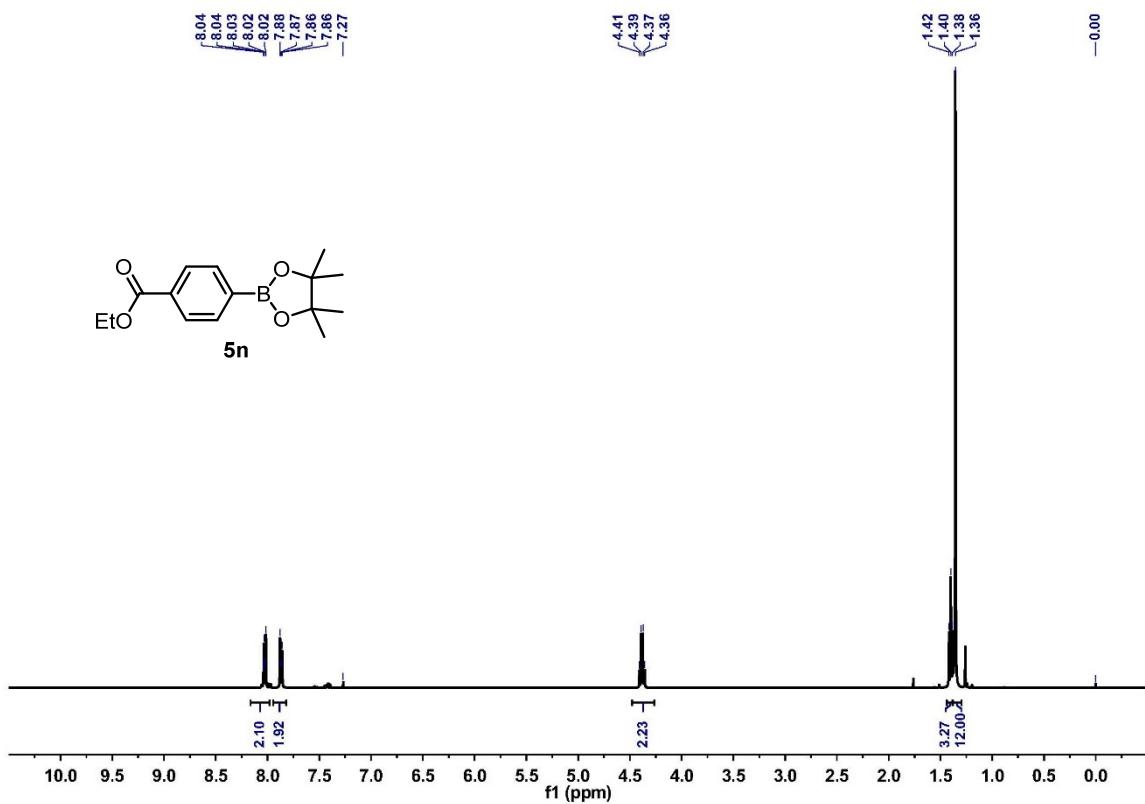
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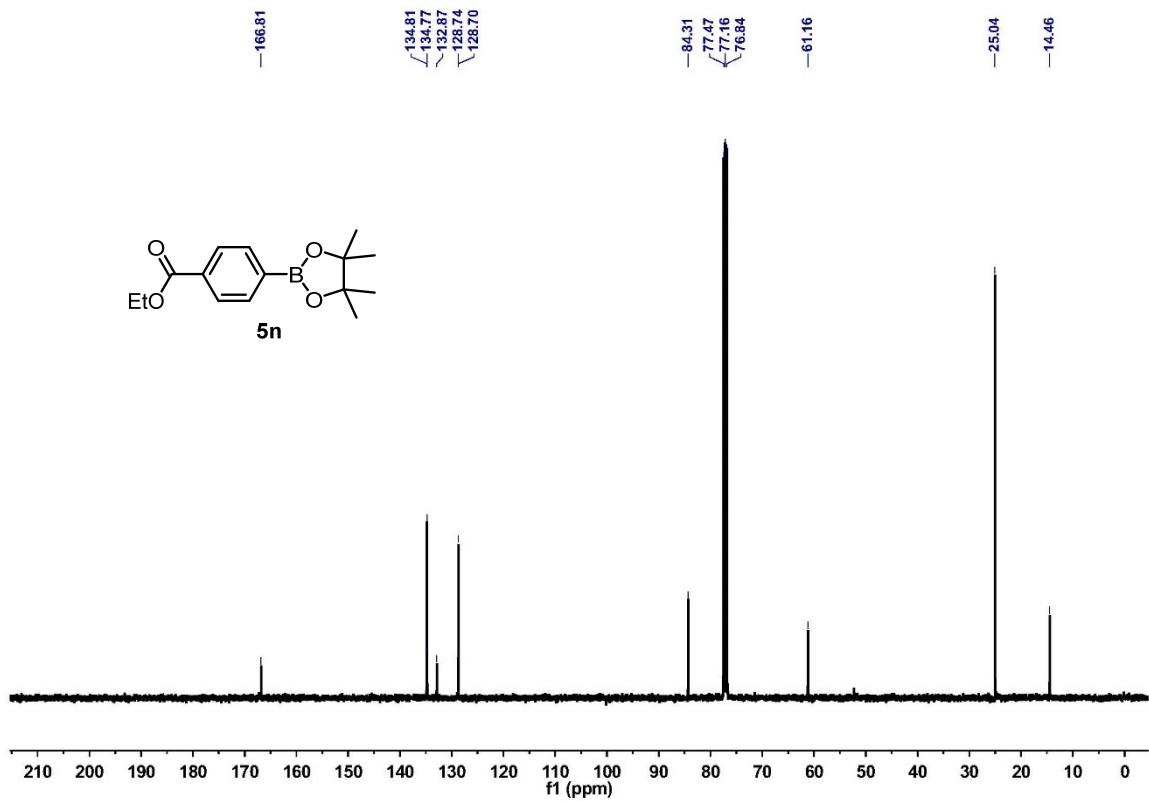
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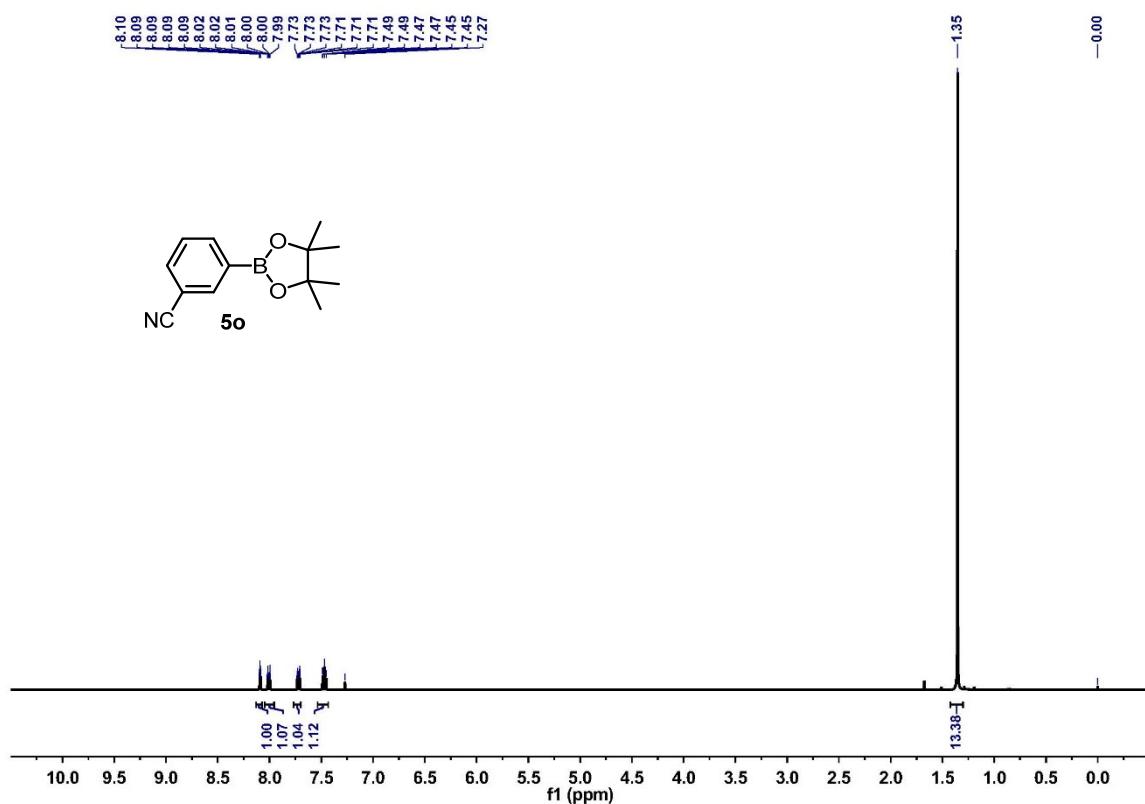
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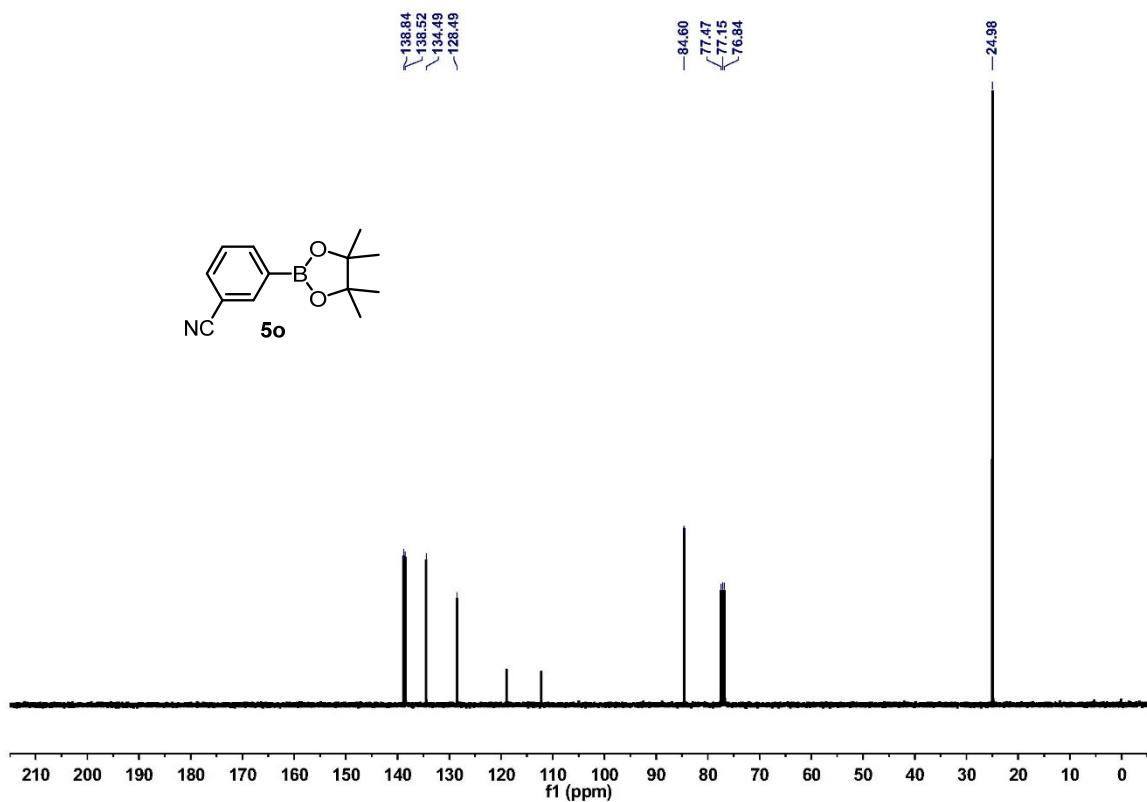
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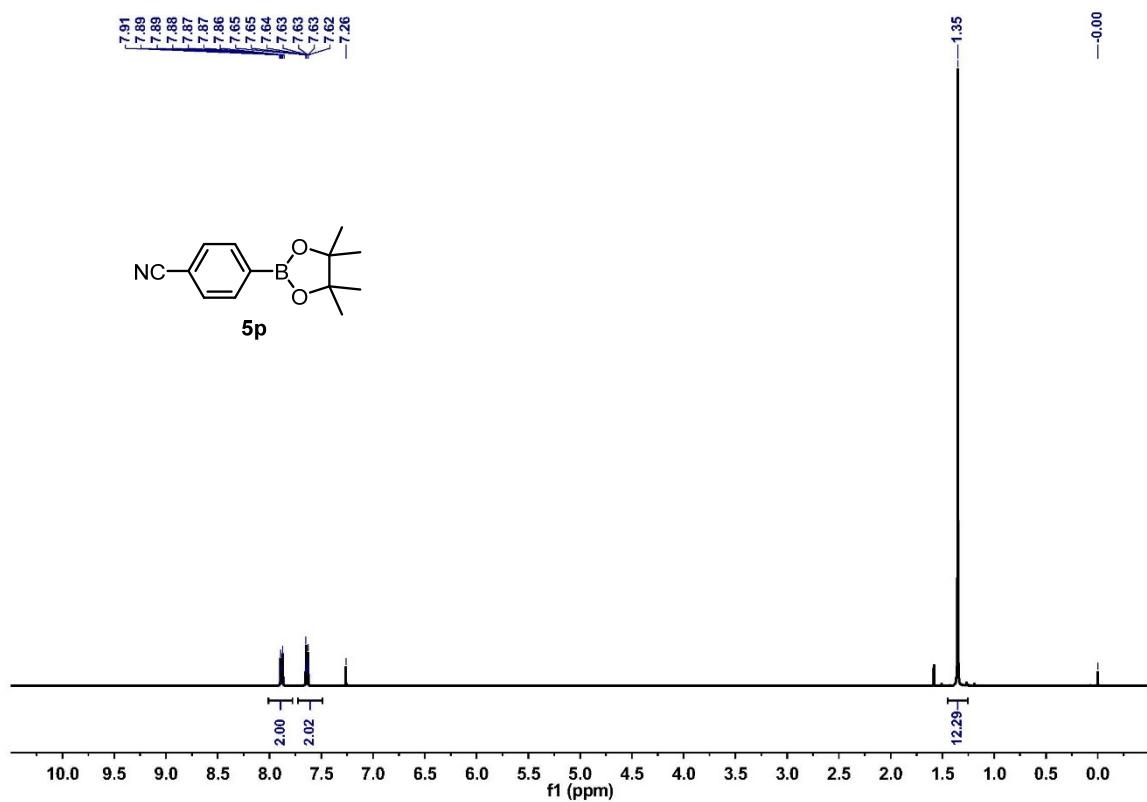
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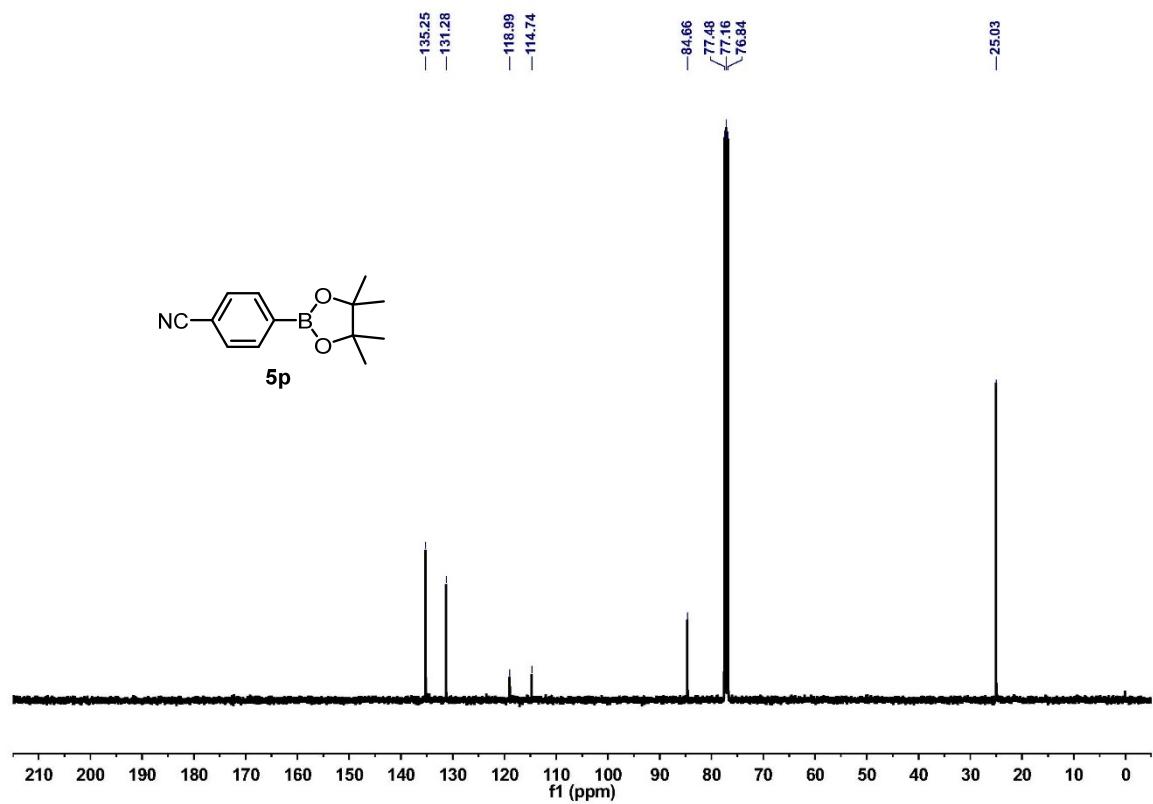
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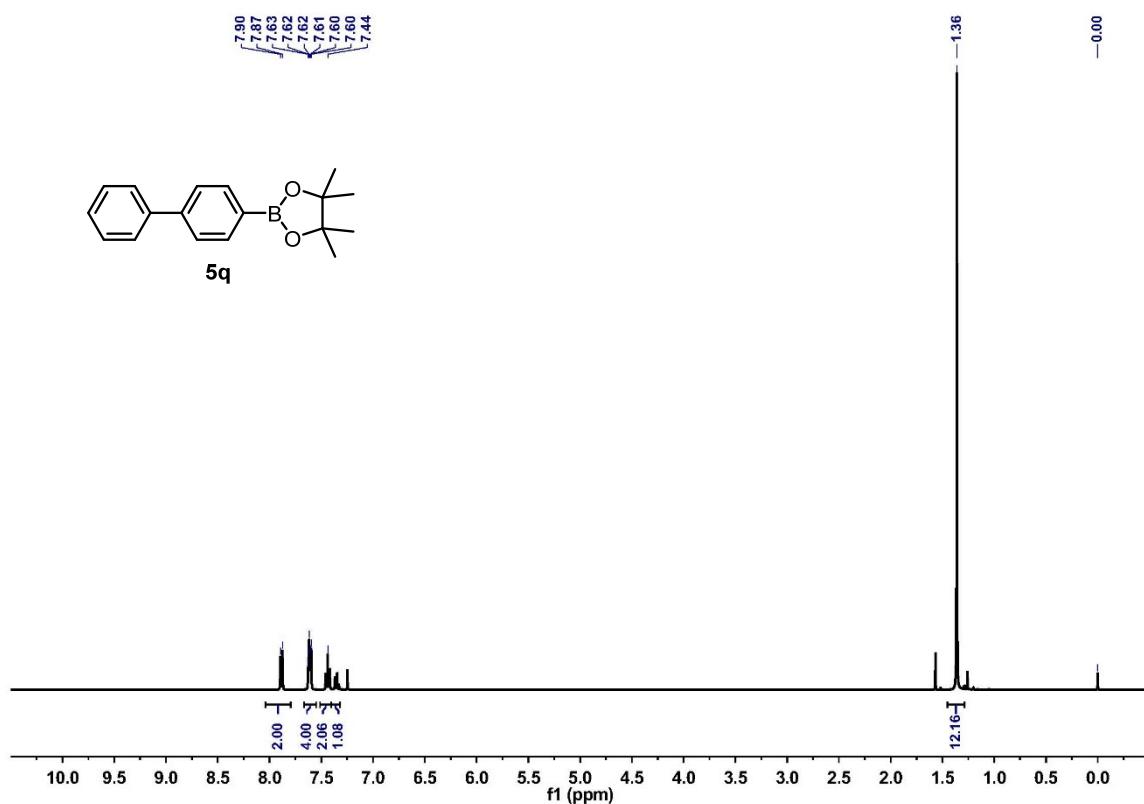
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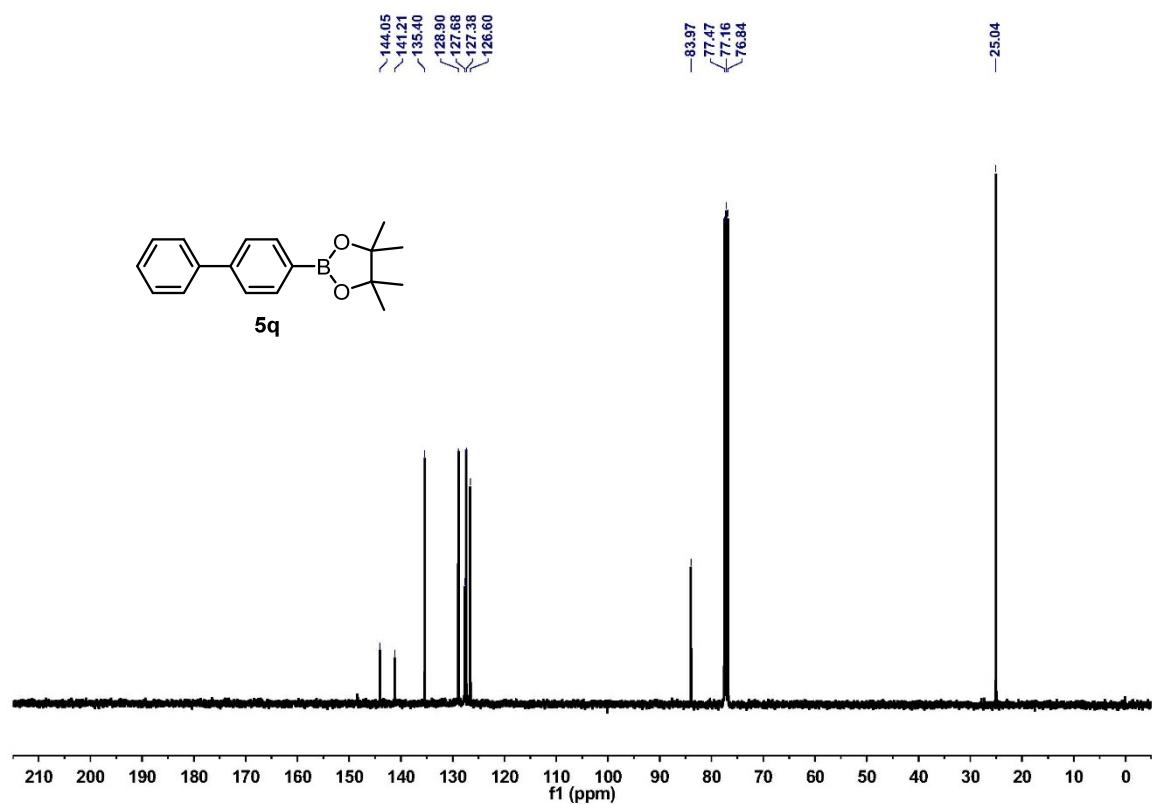
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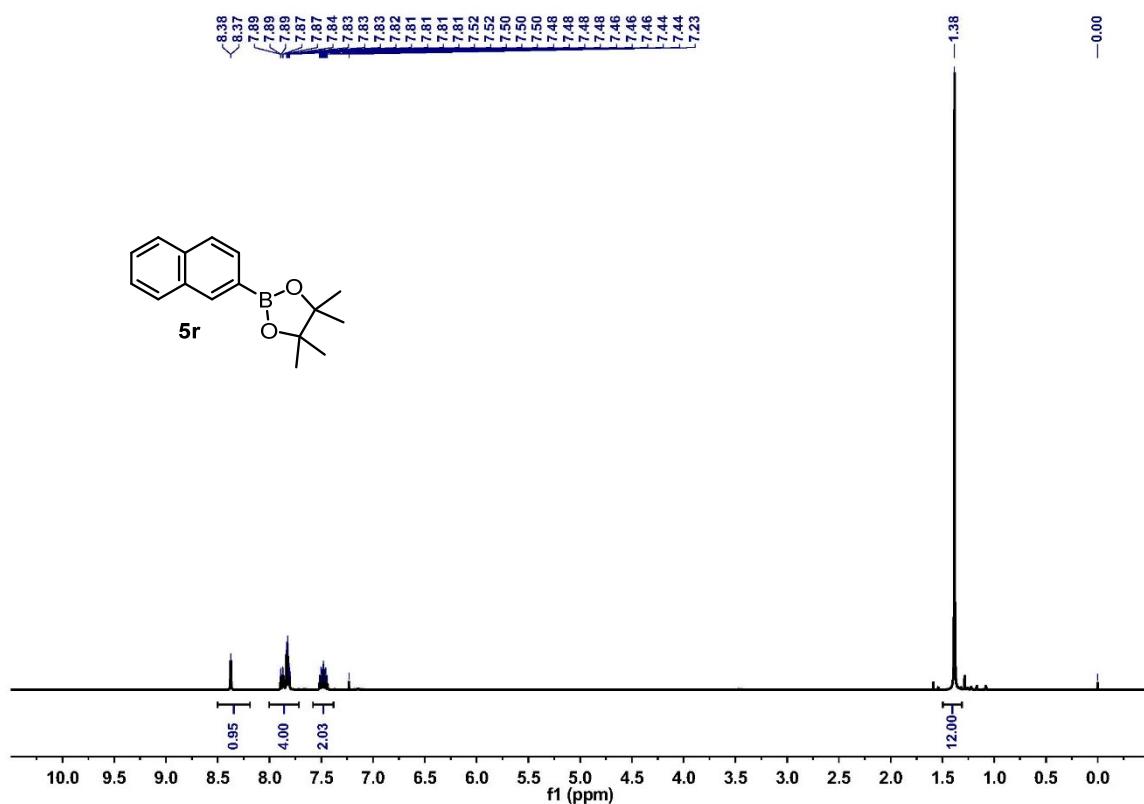
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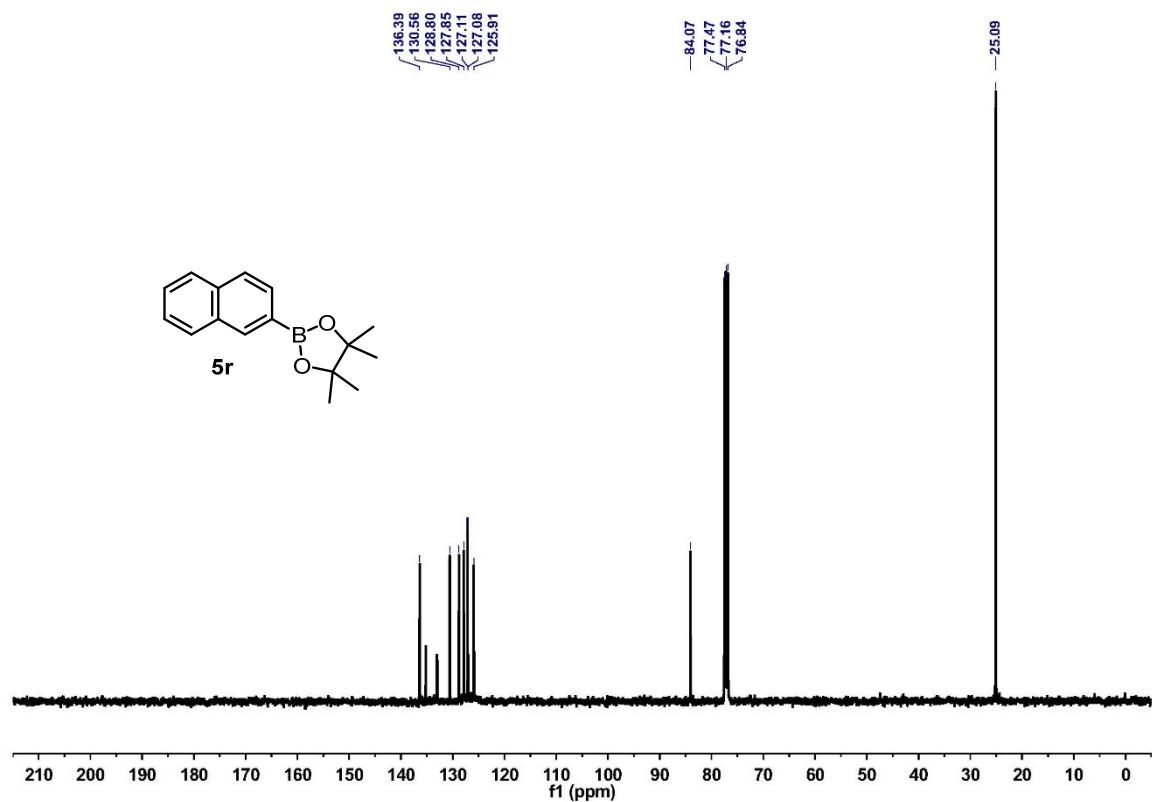
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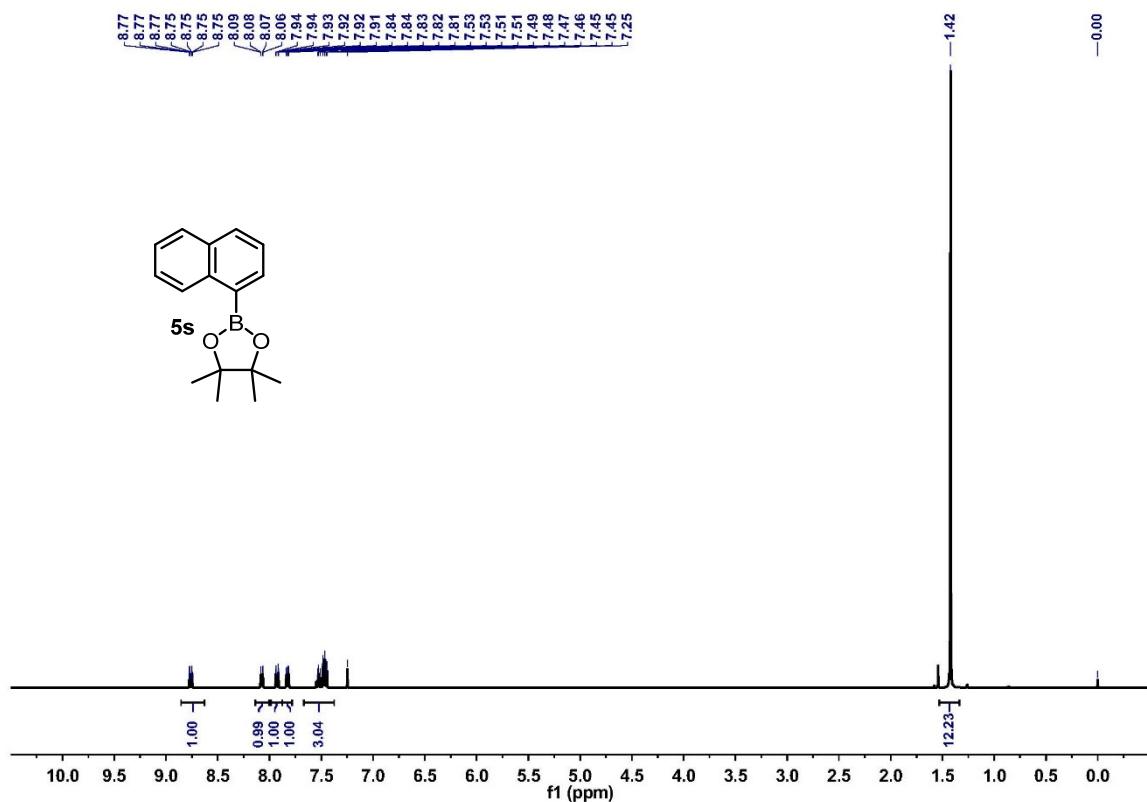
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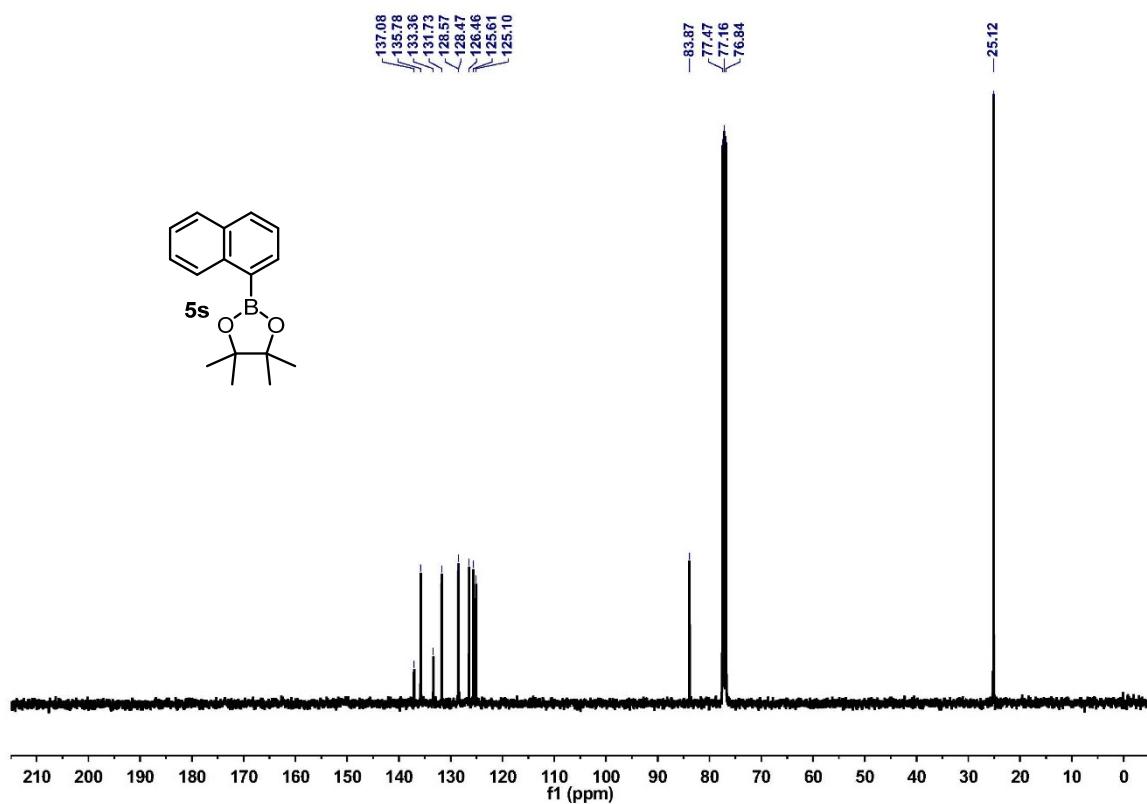
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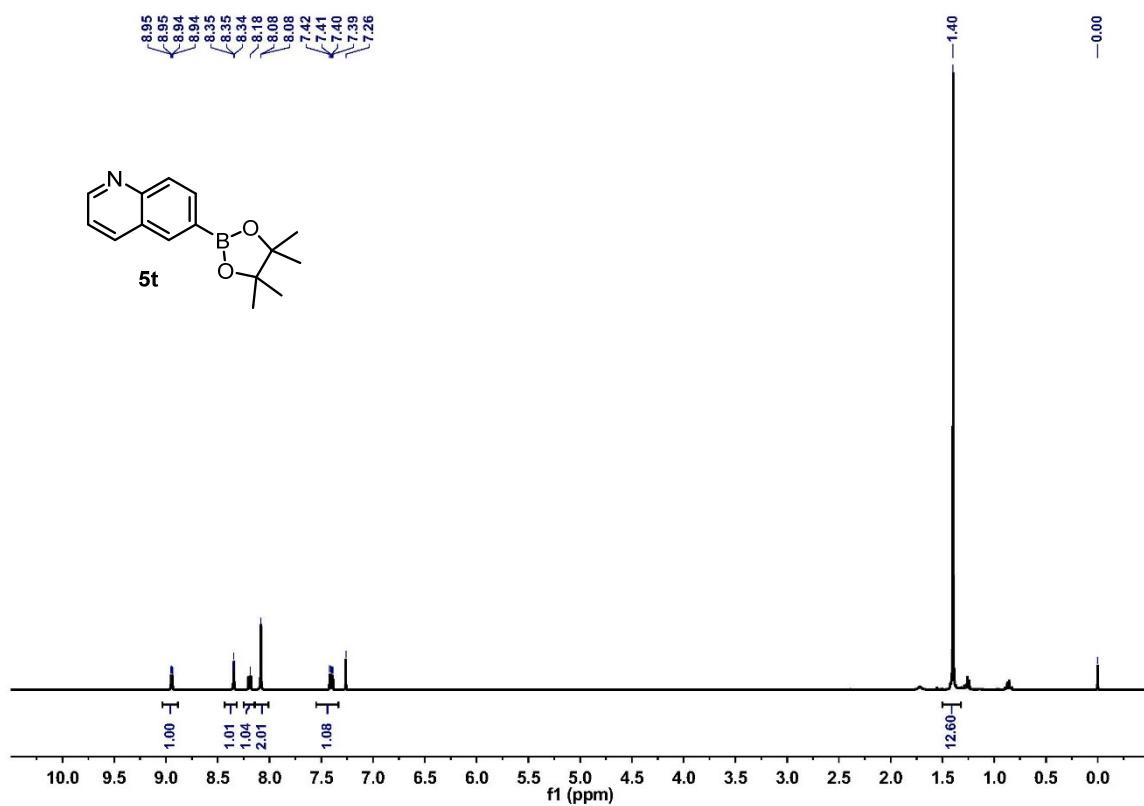
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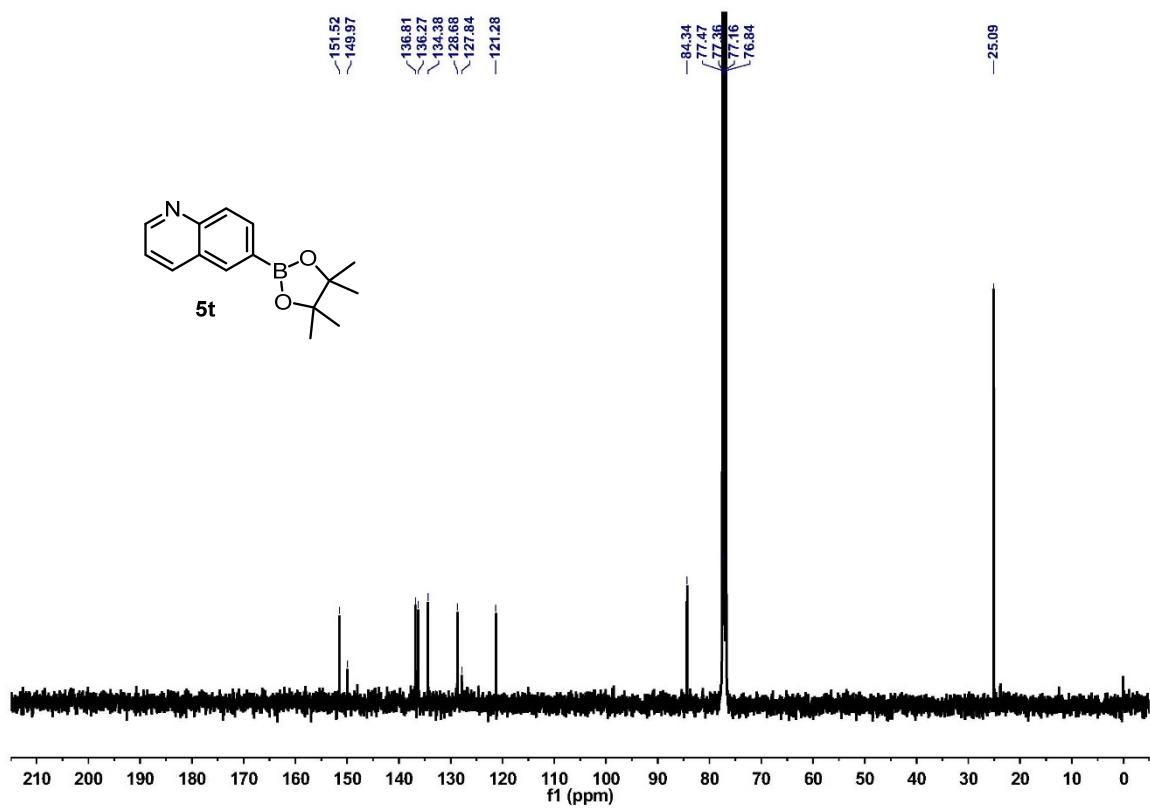
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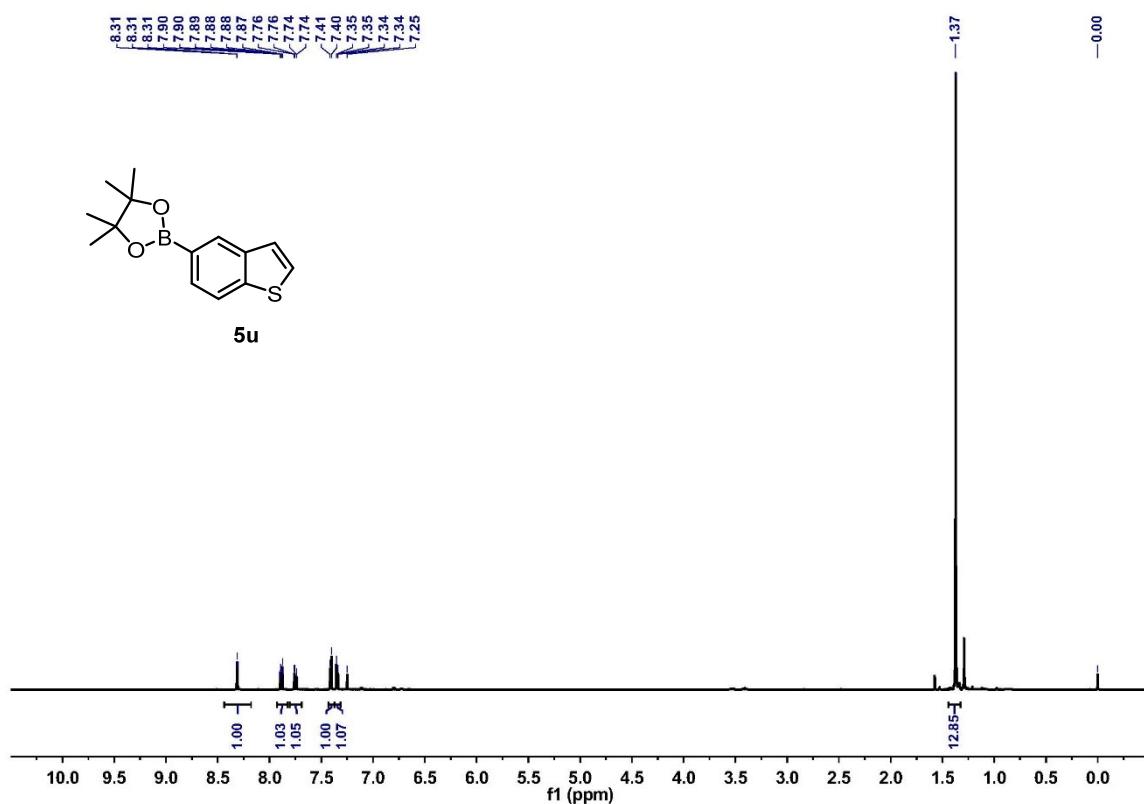
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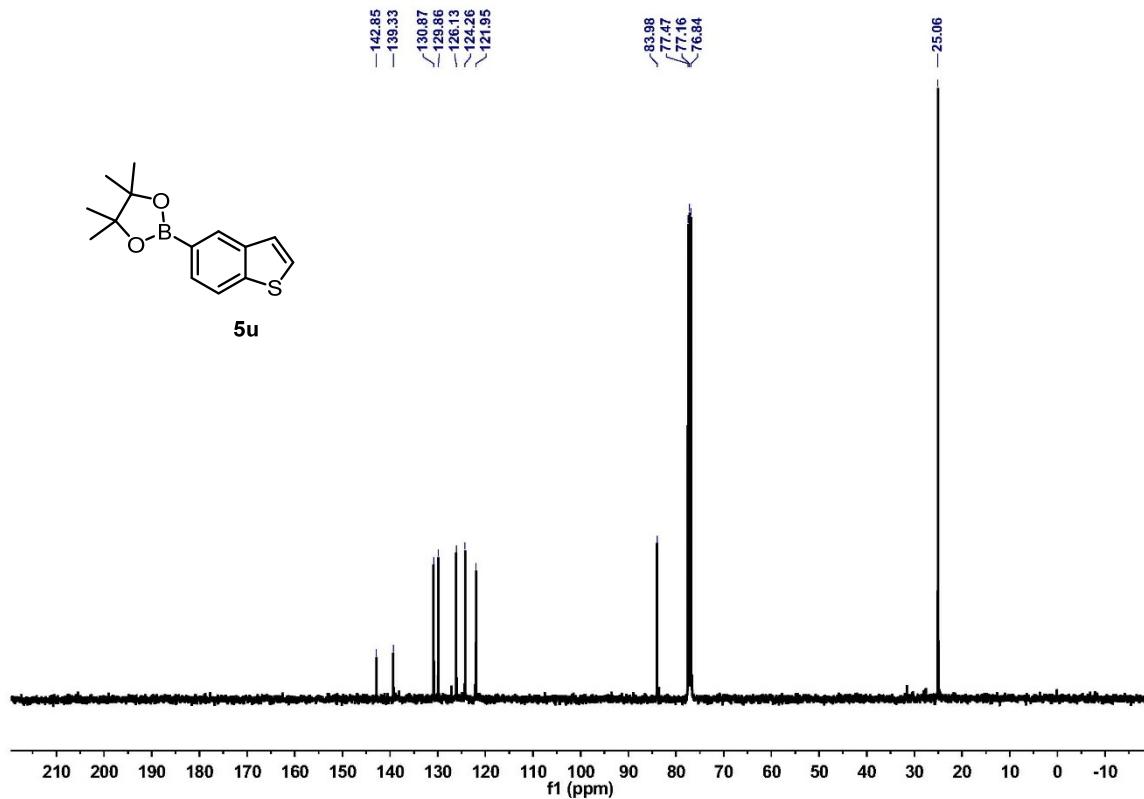
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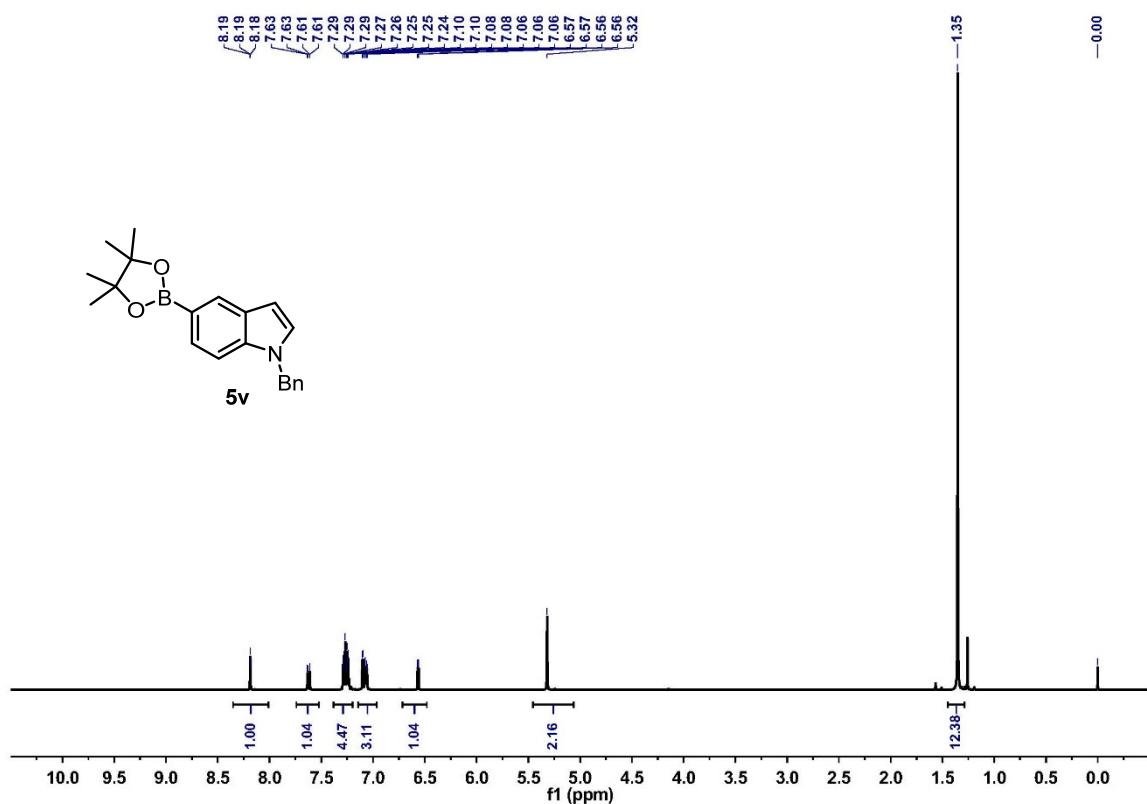
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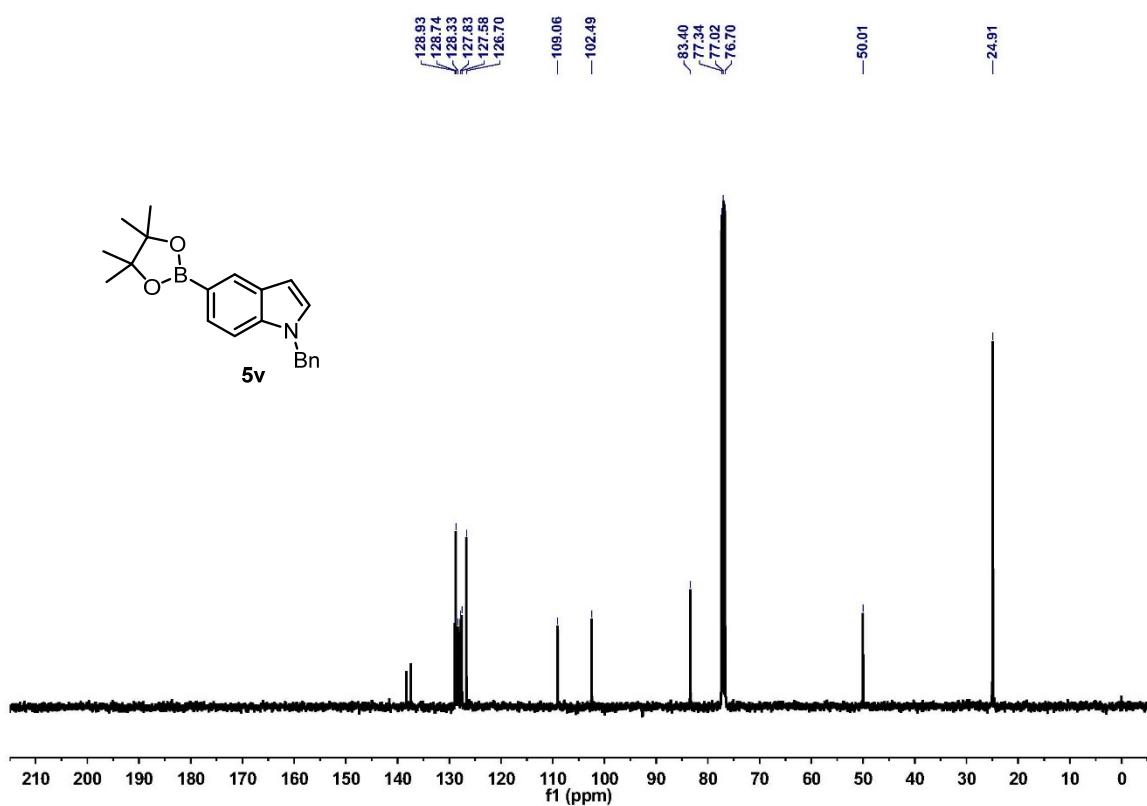
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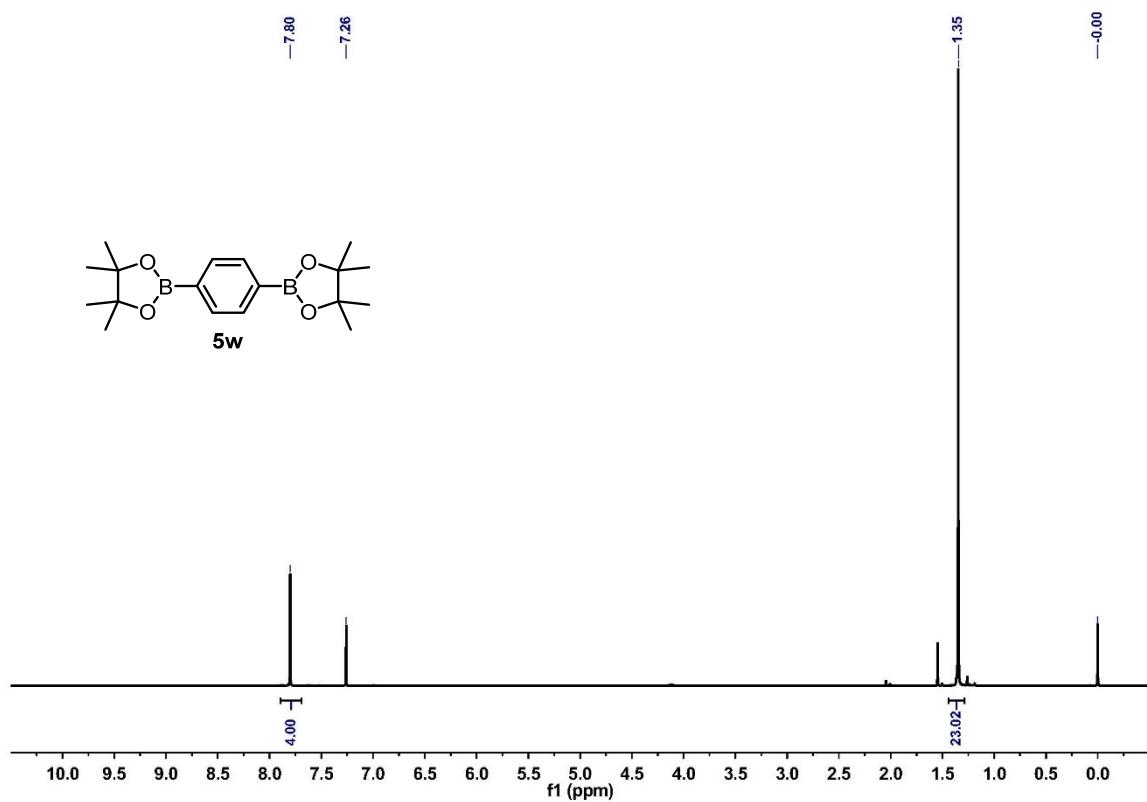
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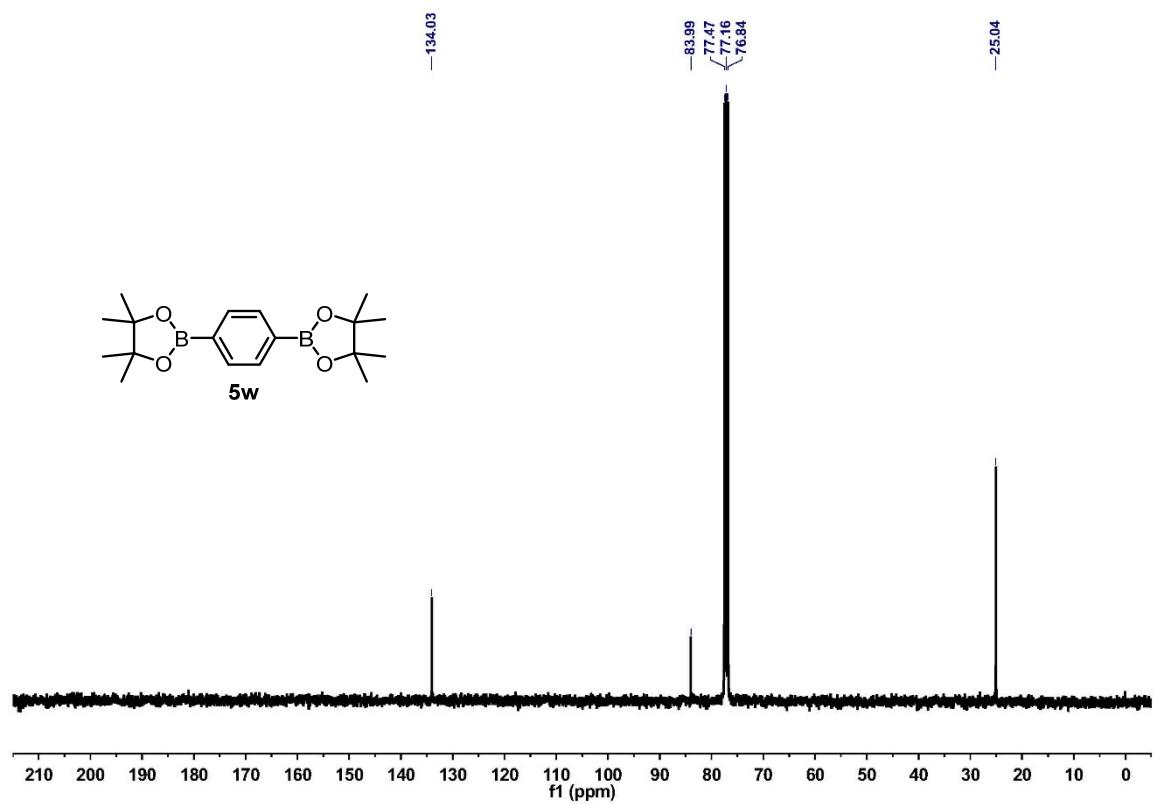
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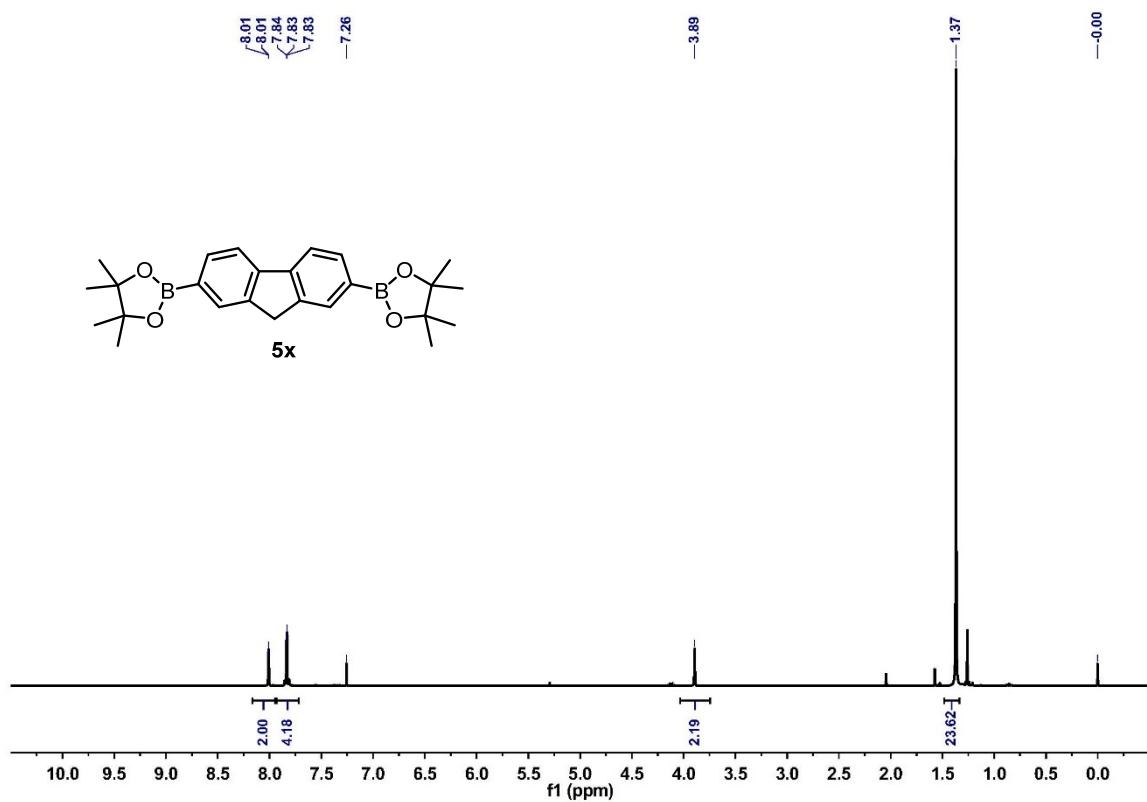
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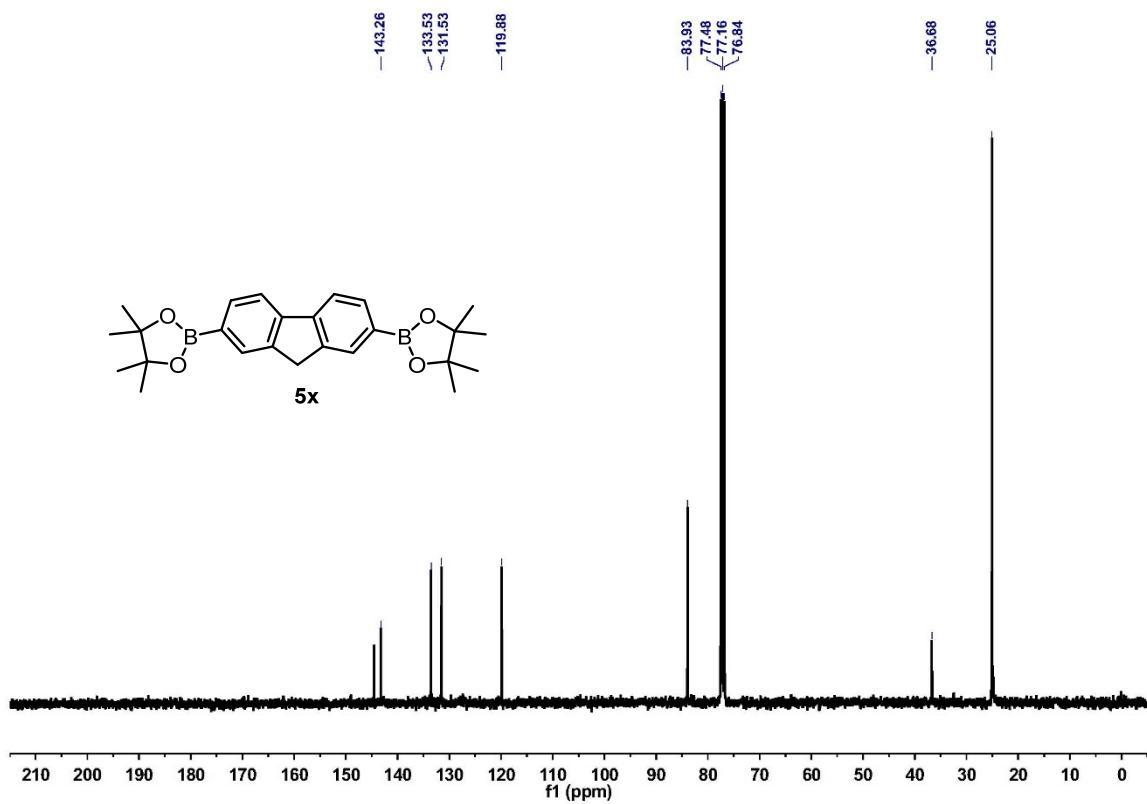
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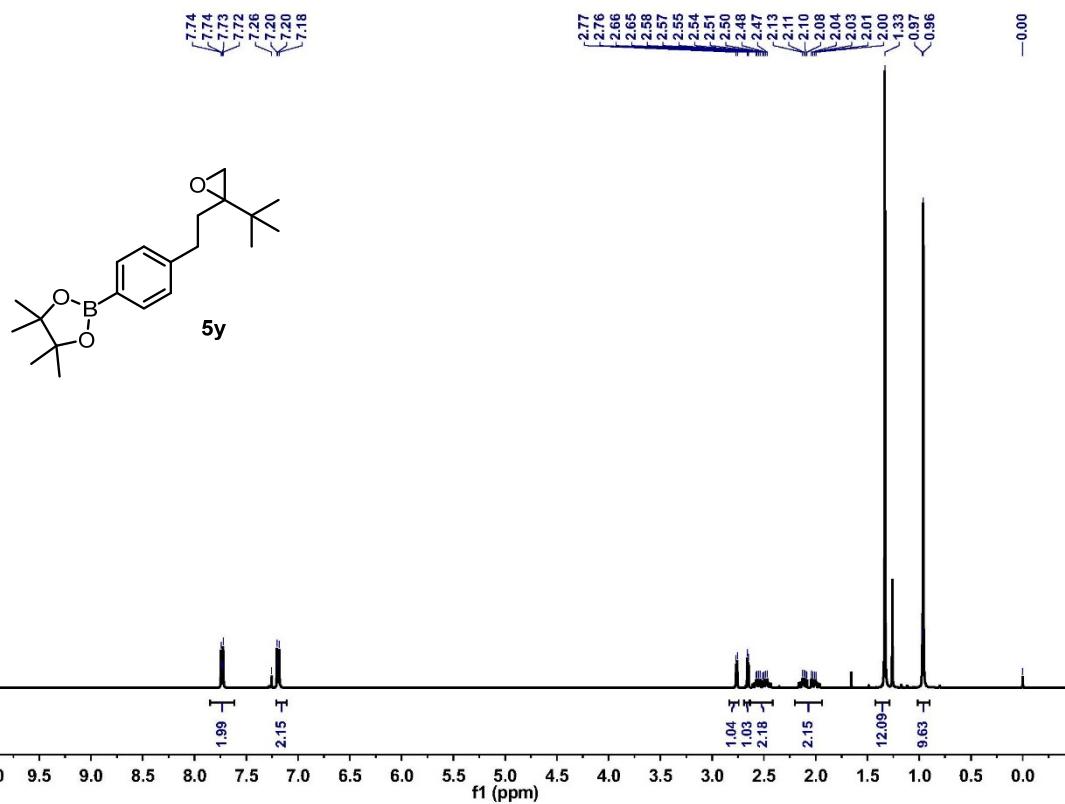
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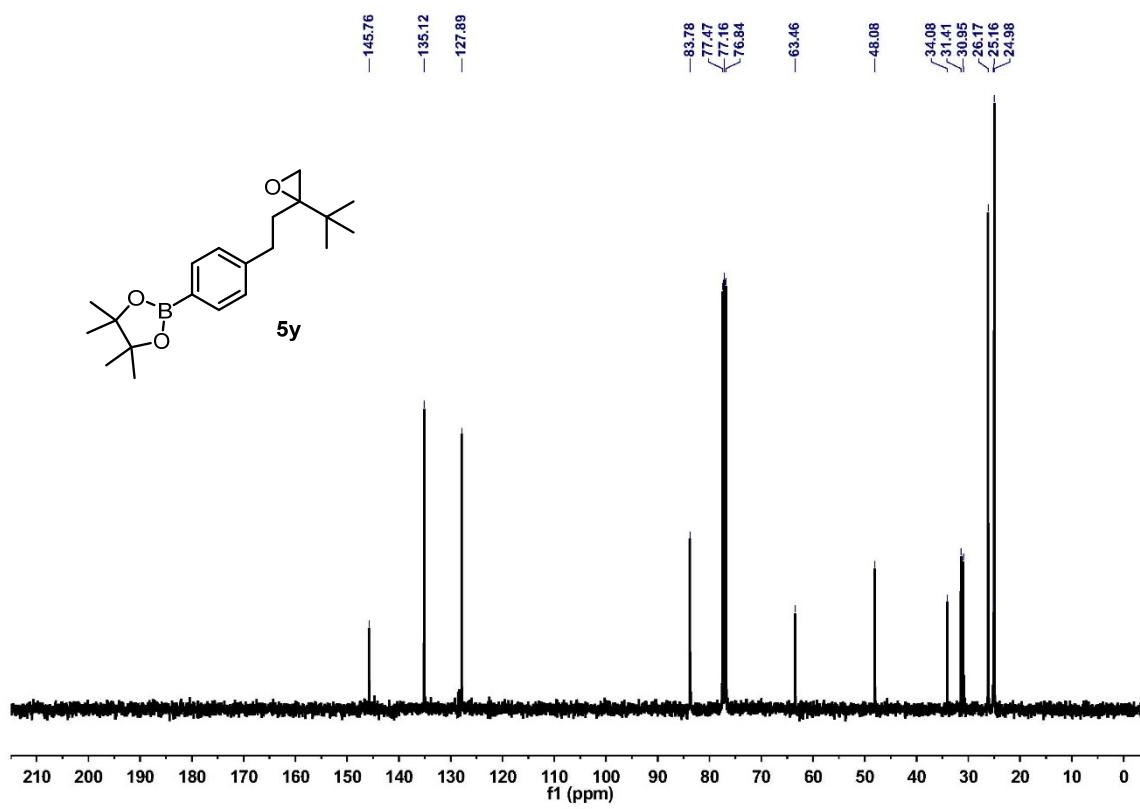
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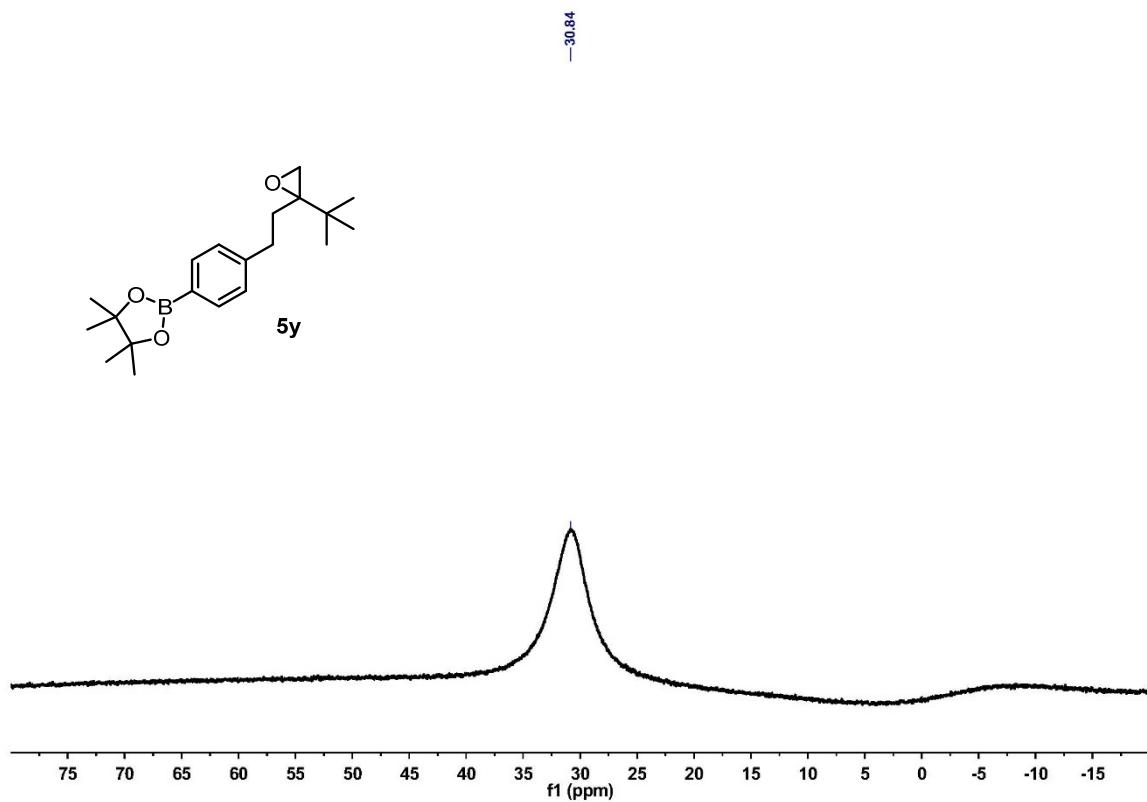
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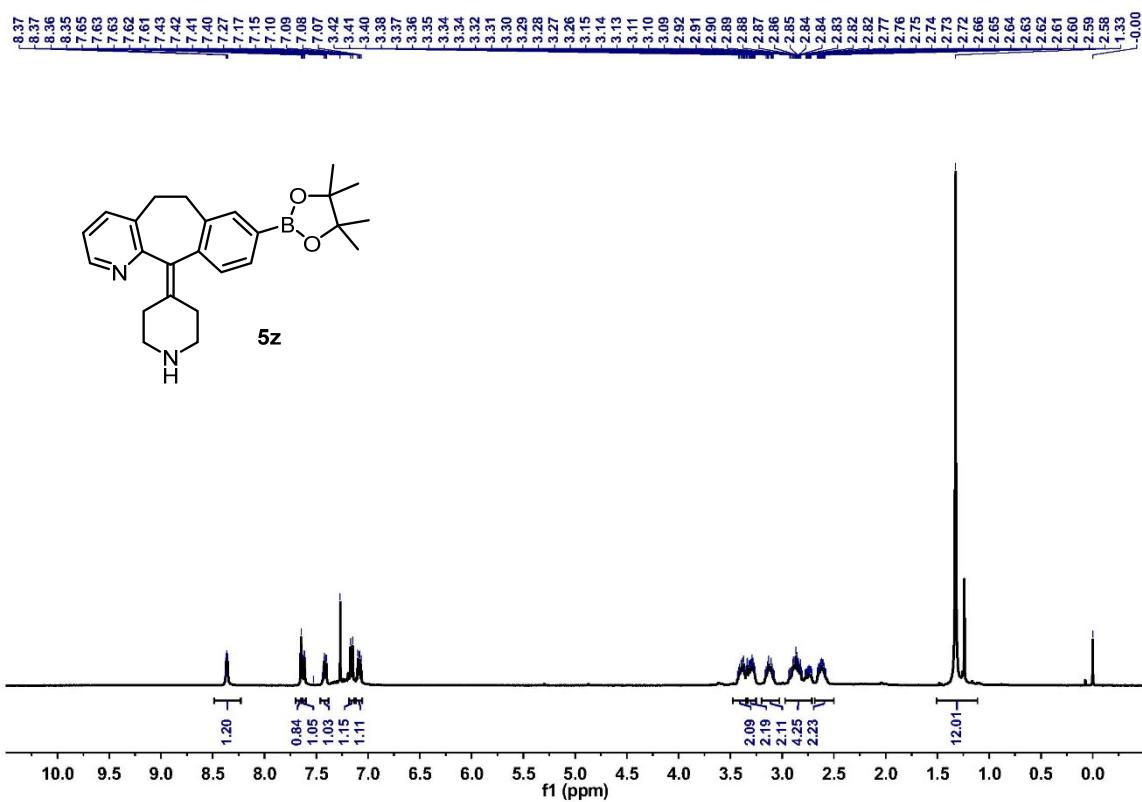
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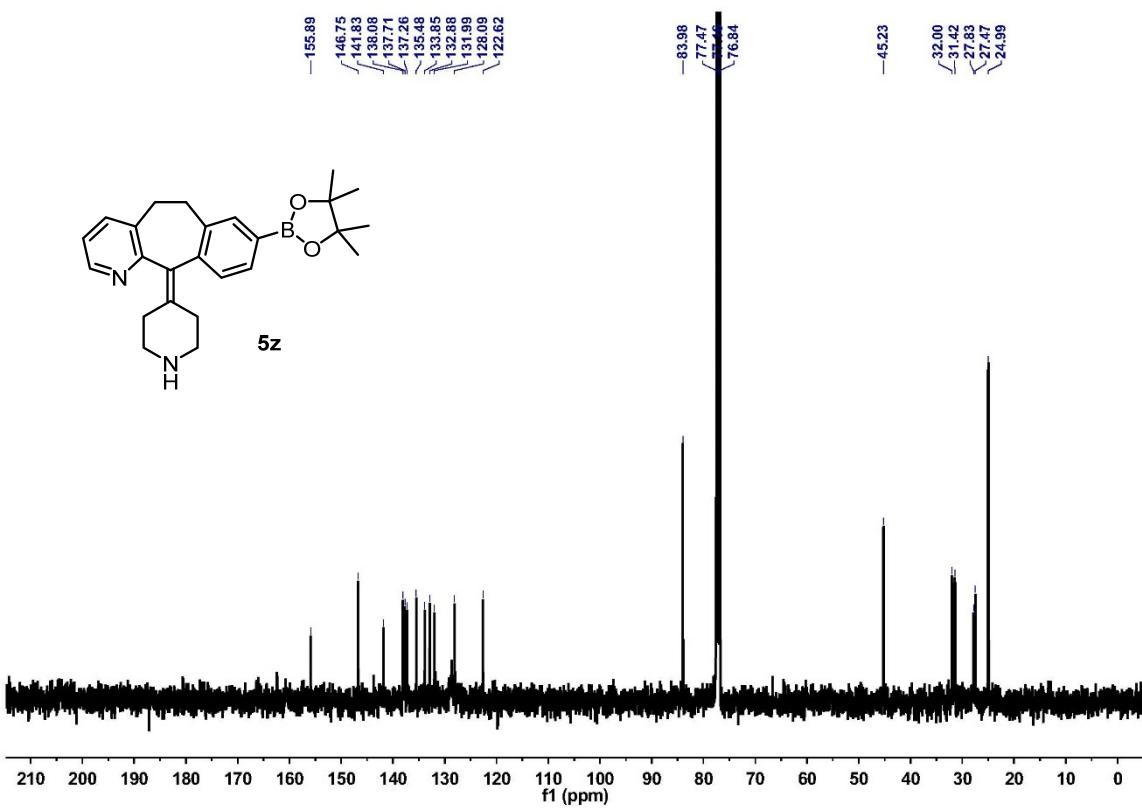
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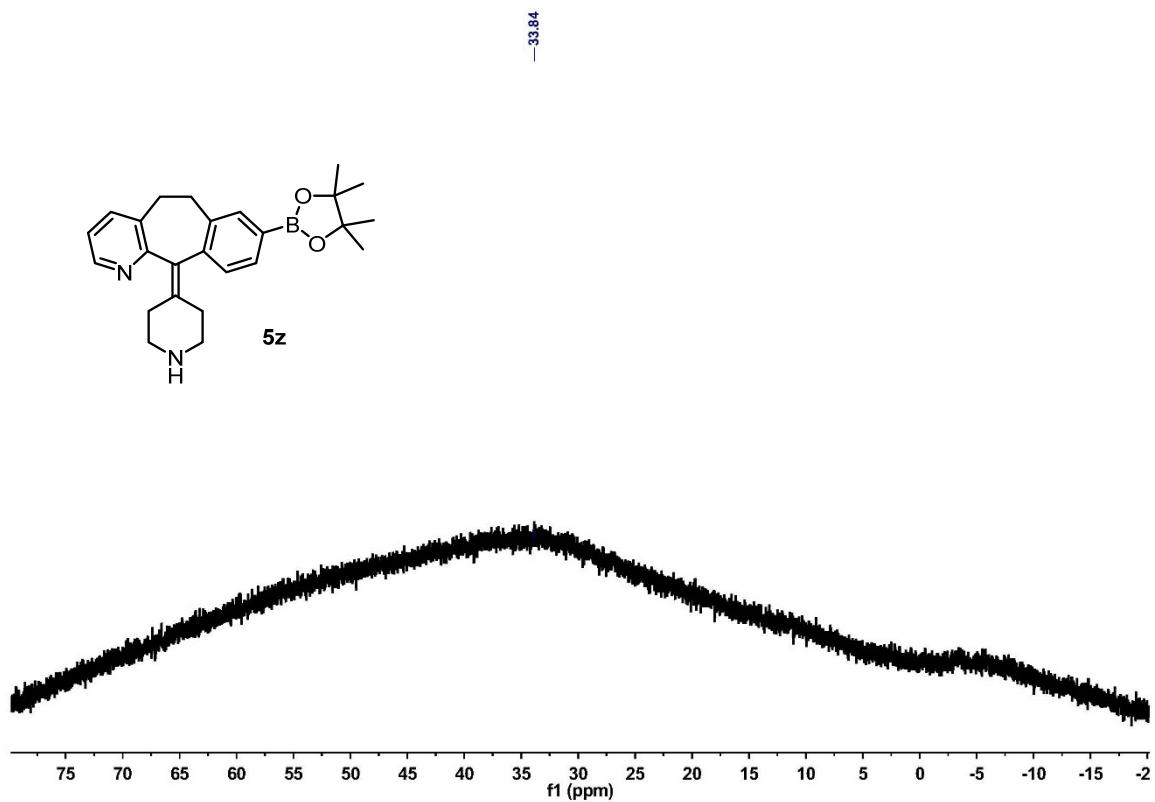
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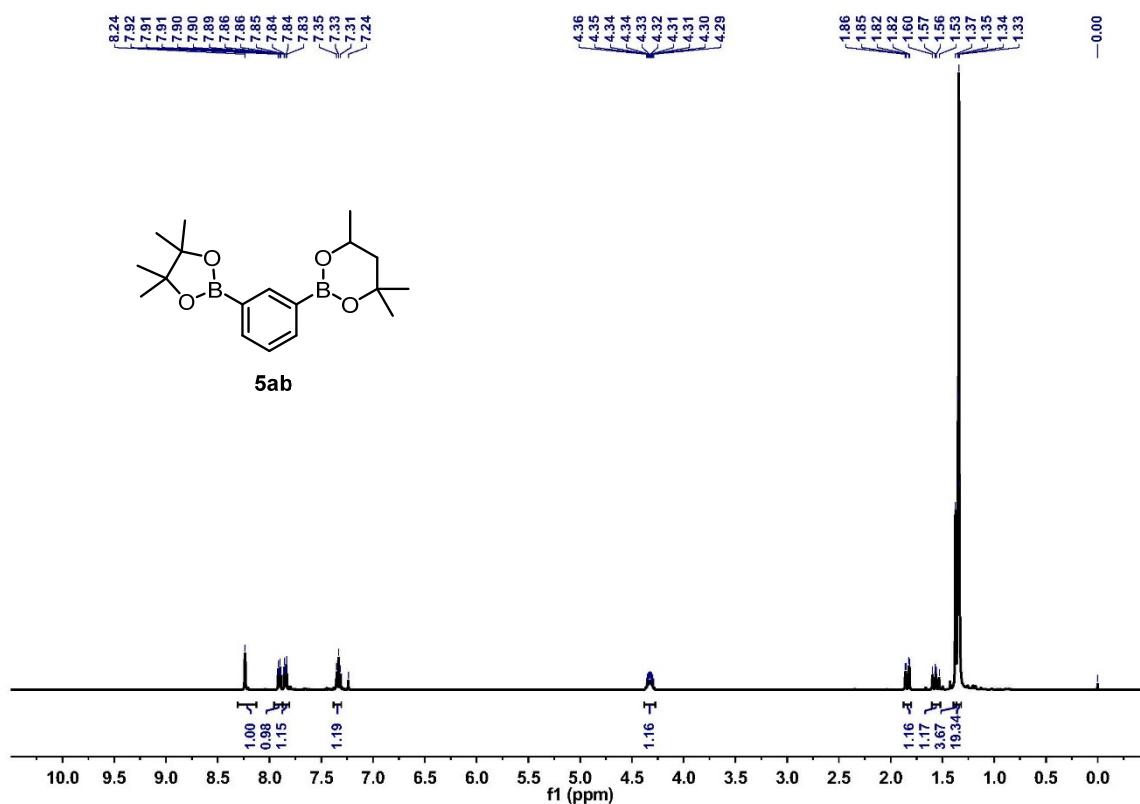
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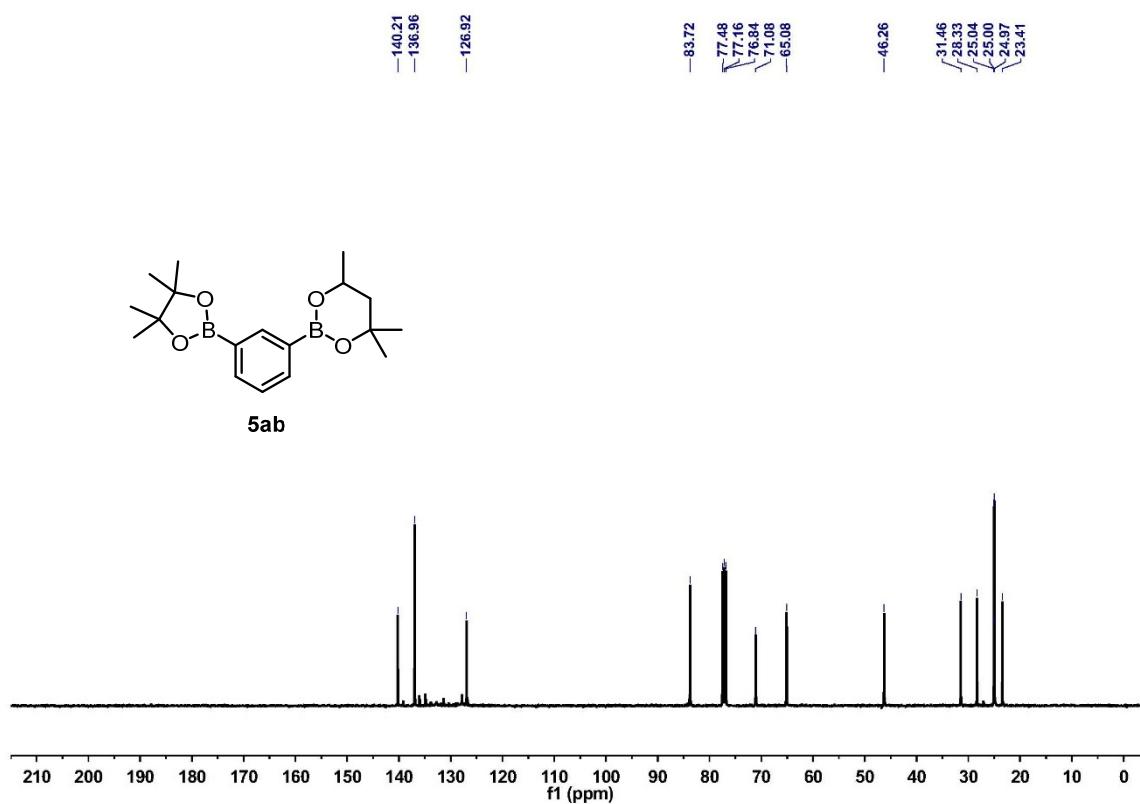
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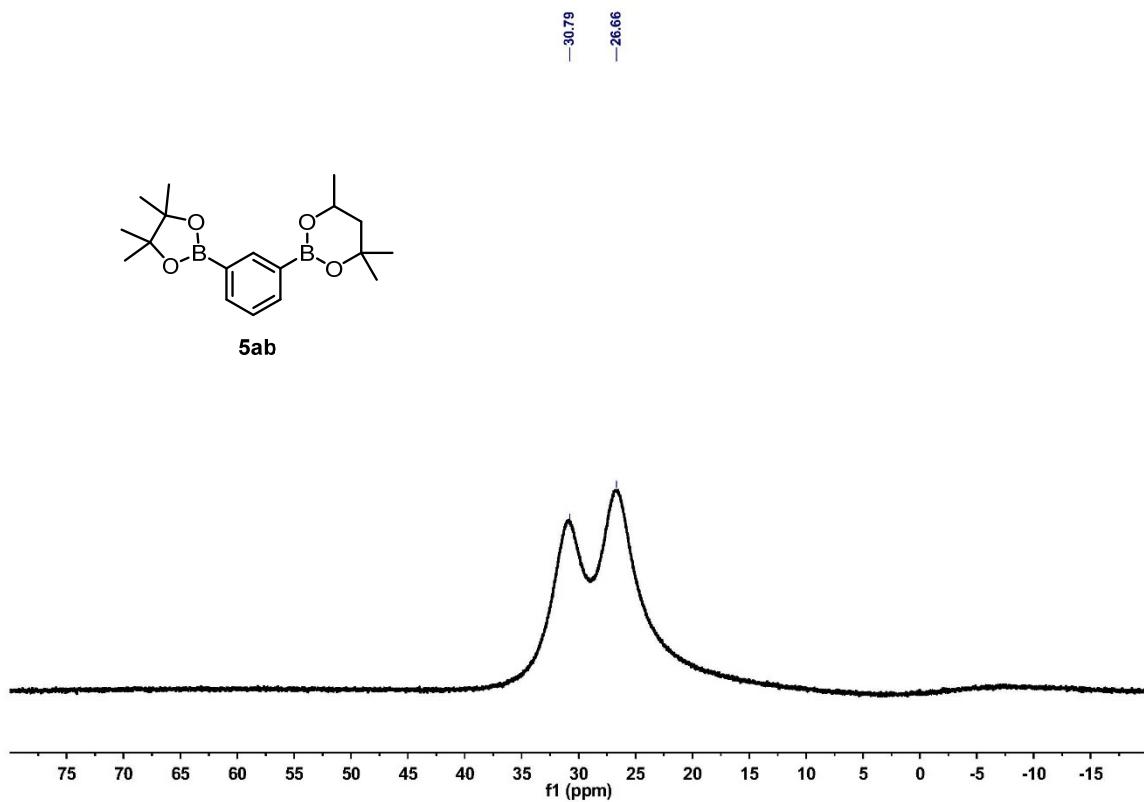
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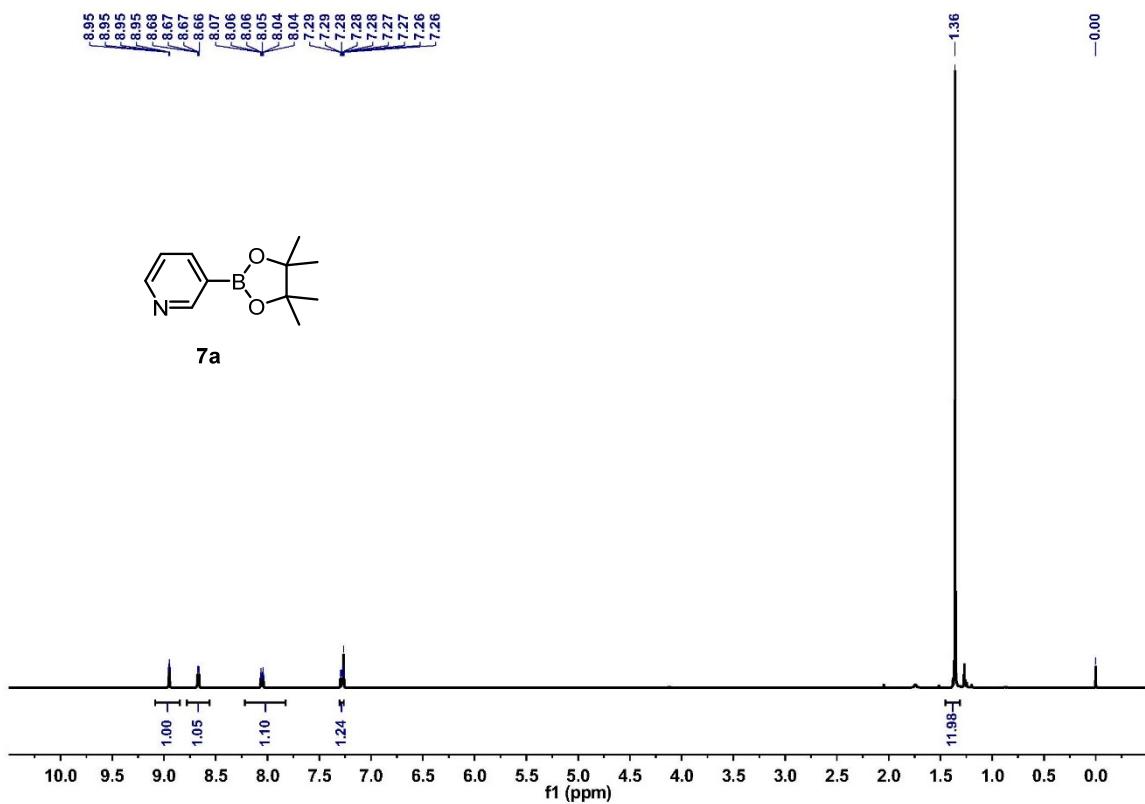
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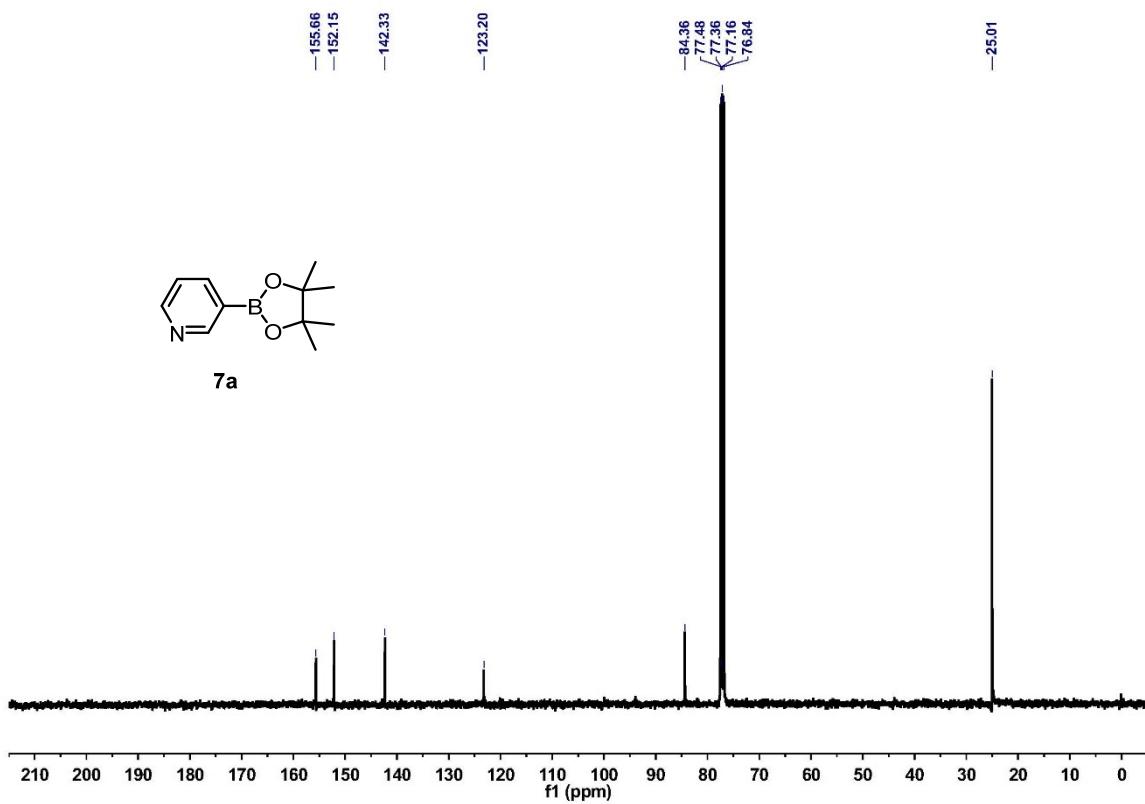
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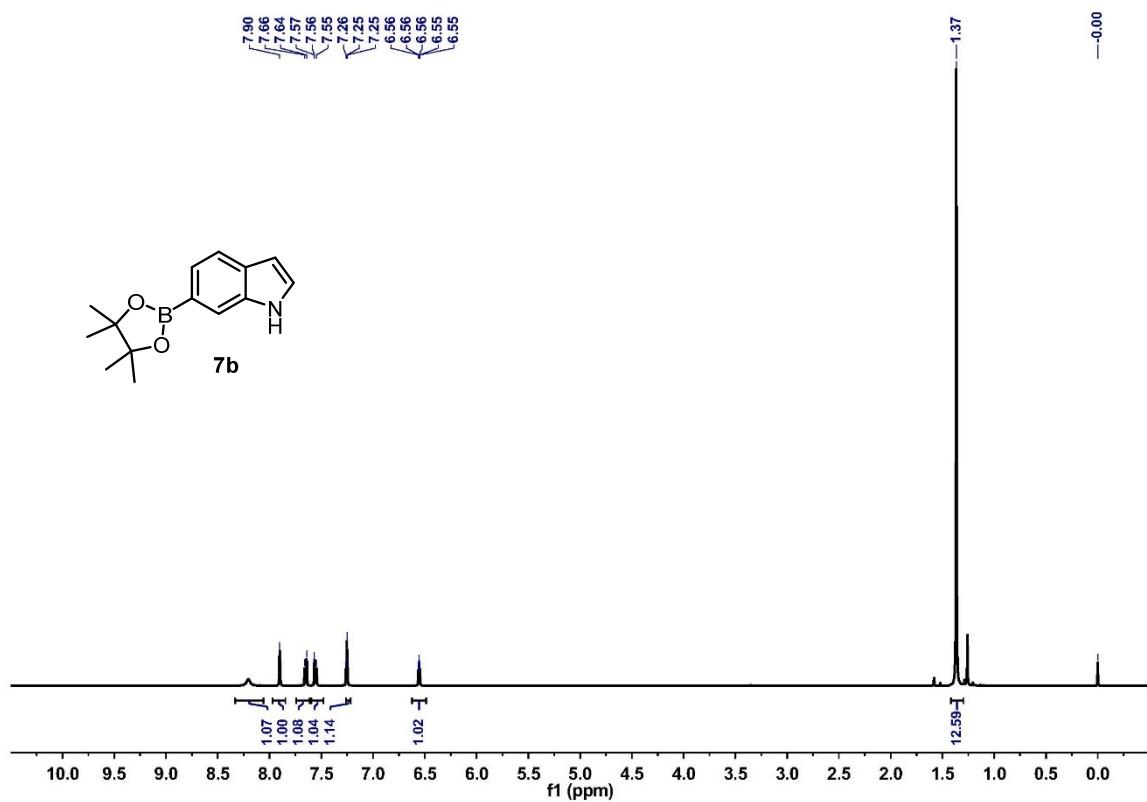
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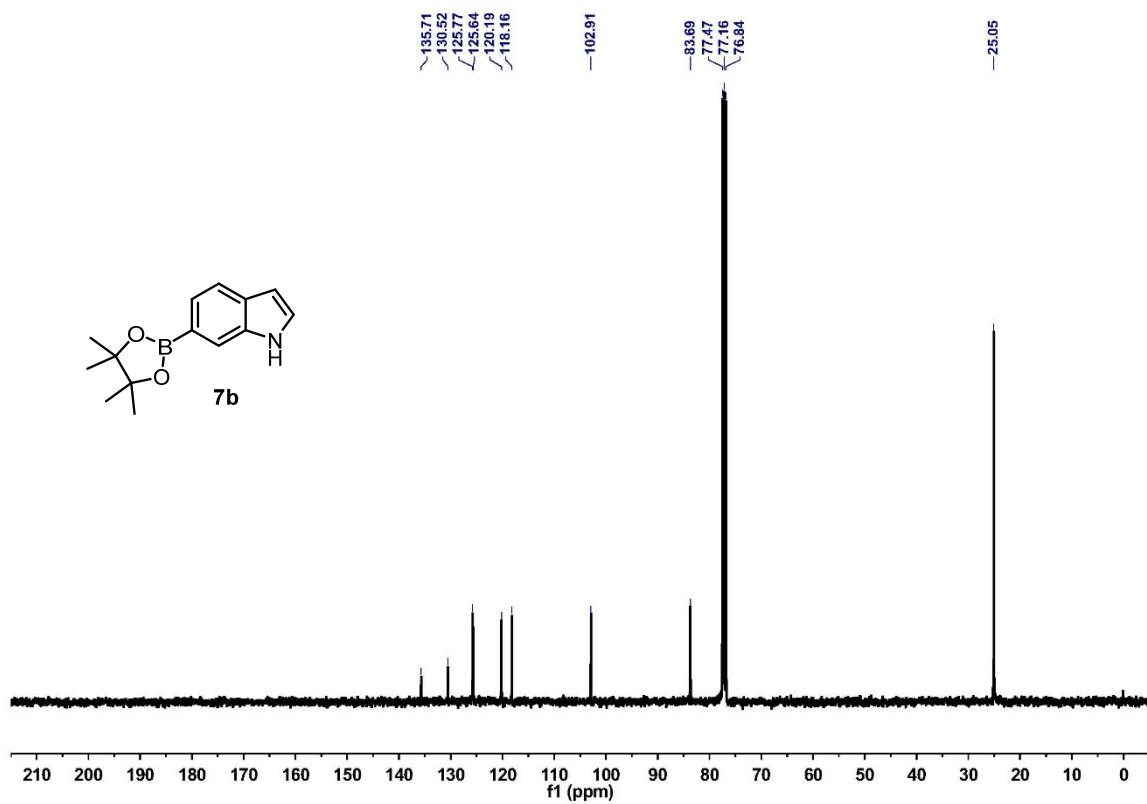
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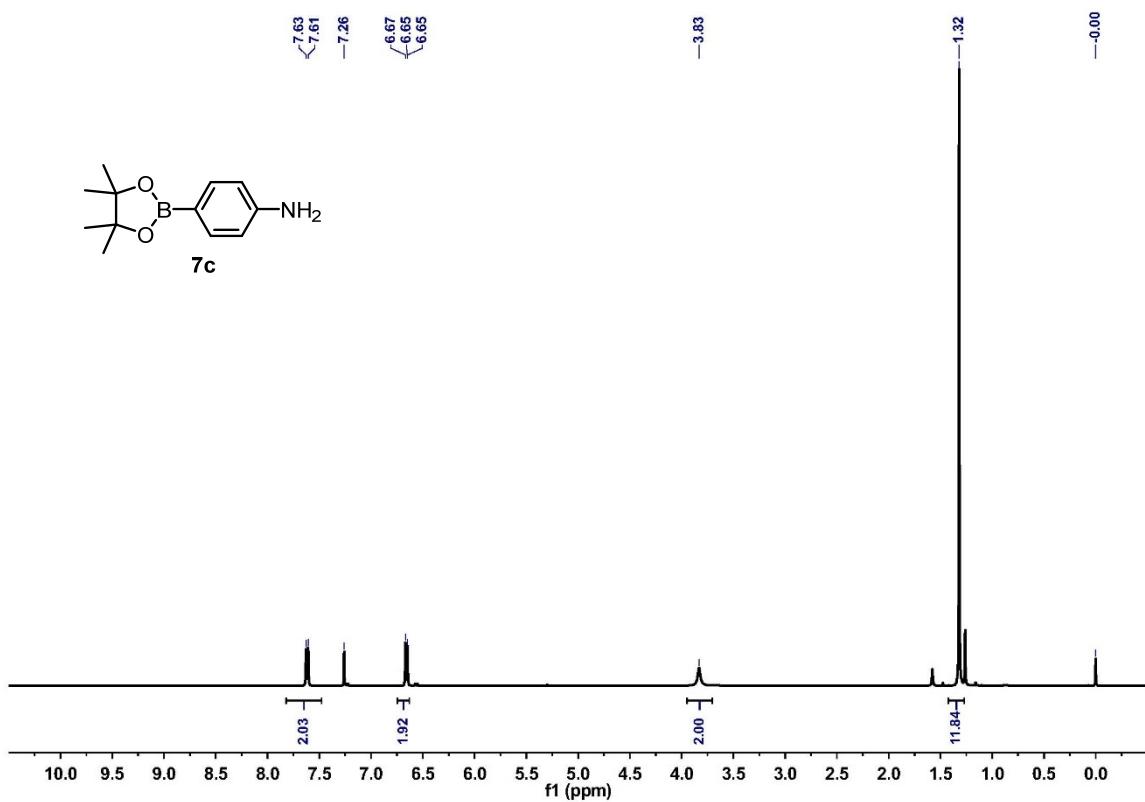
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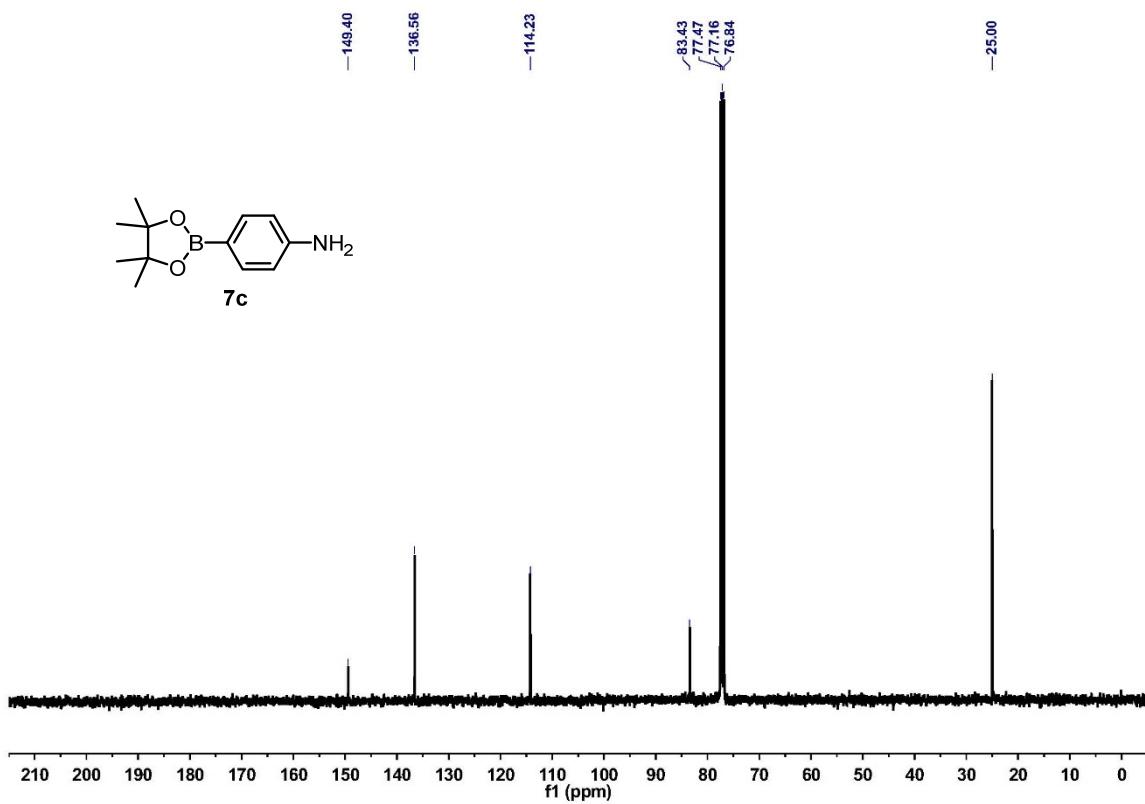
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