Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Materials for

Direct Borylation of Benzyl Alcohol and Its Analogues in the Absence of Base

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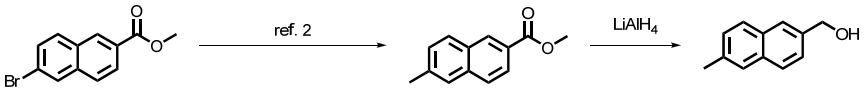
(I) General information

All the reactions were carried out under nitrogen atmosphere using standard Schlenk technique in the oil bath. The catalyst $Pd(OAc)_2$ was purchased from Acros without further purification, $Ni(COD)_2$ was purchased from Sigma-Alderich. Ligands DCyPF was purchased from Energy Chemical without further purification, IAd was purchased from Fluorochem without further purification. THF, benzene and Et_2O was freshly distilled over sodium under N_2 with the use of diphenyl ketone as an indicator; B_2pin_2 was prepared by strict recrystallization before being used as the borylation reagent. ^{1}H NMR (400 MHz)/^{13}C NMR (100 MHz) were registered on Bruker 400 M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. ^{11}B NMR (500 MHz)/ ^{13}C NMR (125 MHz) were obtained on a Bruker 500 M spectrometer equipped with the appropriate decoupling accessories. All ^{11}B NMR chemical shifts were referenced to an external $BF_3{\cdot}OEt_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad), coupling constant *J* (Hz) and integration. The ^{13}C signal of the carbon bonded to boron was not observed in some cases due to quadrupolar relaxation. Column chromatography was performed on silica gel 200-300 meshes. MS and HRMS were performed by the State-authorized Analytical Center in Peking University.

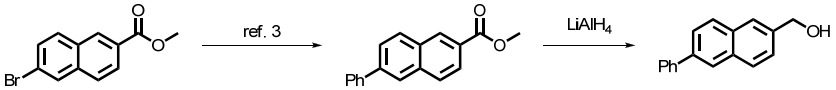
(II) Preparation of benzyl alcohols and phenols

Benzyl alcohols **1a**, **1d**, **1e**, **1f**, **1i**, **1k**, **1l**, **1m** were prepared from corresponding aryl aldehydes or ketones,[1] **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, **1t**, **1u, 1v, 1w** were purchased from J&K without further purification.

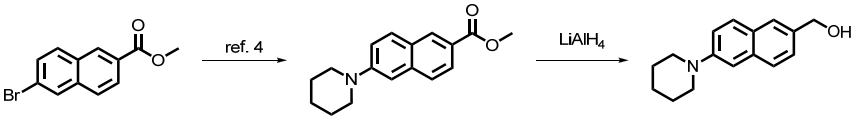
Benzyl alcohol **1b** was prepared via the following method, [2]



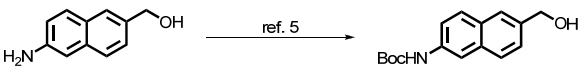
Benzyl alcohol **1c** was prepared via the following method,[3]



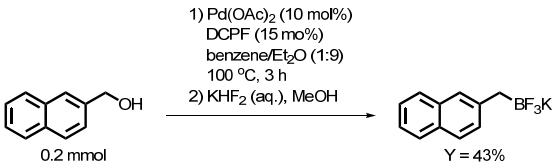
Benzyl alcohol **1g** was prepared via the following method,[4]



Benzyl alcohol **1h** was prepared via the following method,[5]



(III) Synthesis of benzylic trifluoroborates



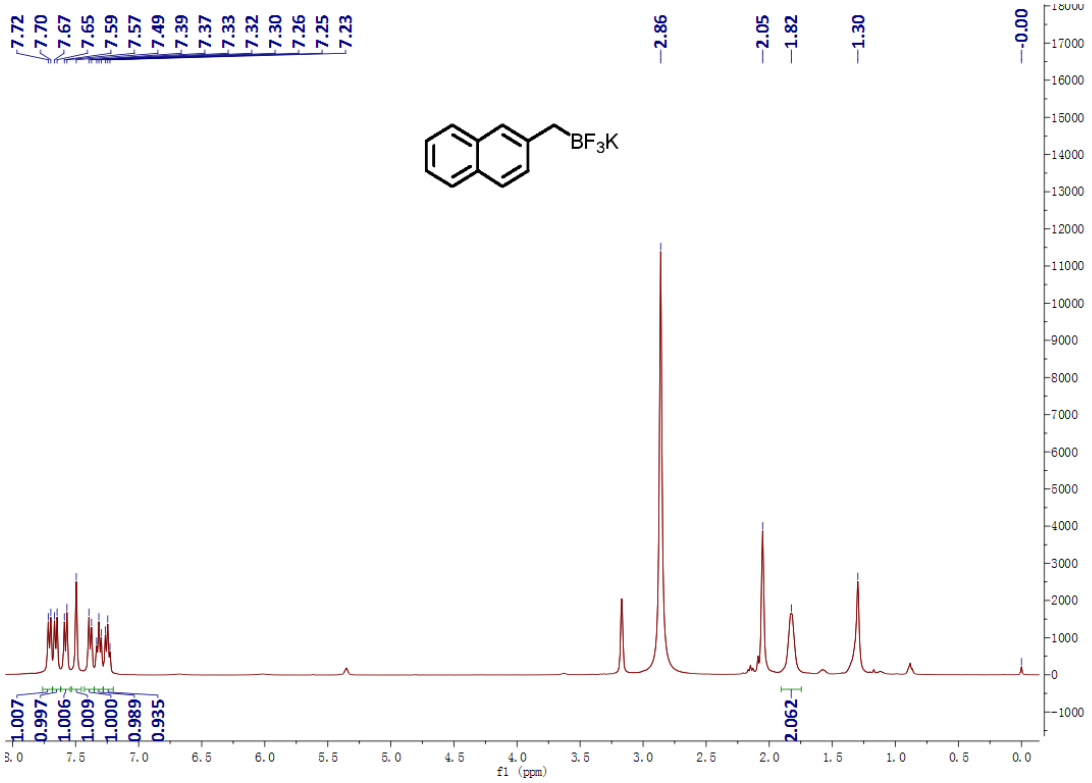
An oven dried sealed tube containing a stirbar was charged with benzyl alcohols (31.7 mg, 0.20 mmol), B_2pin_2 (76.2 mg, 0.30 mmol), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg) and ligand DCPF (0.03 mmol, 17.4 mg) and then the tube was degassed and refilled with N_2 for 3 times. The mixed solvent Et_2O/benzene (0.9 mL/0.1 mL) were added by syringe (the process completed in a glovebox is better), and reacted in a 100 °C oil bath for 3 h. The red mixture was concentrated to near dryness and then diluted with MeOH (HPLC grade, 0.8 mL) under 0 °C, and sat. KHF_2 (0.4 mL, 1.8 mmol, 9 equiv., in water) was added dropwise. The resultant suspension was concentrated under reduced pressure. Then hot acetone (2 mL * 3) was added and filtered. The filtrate was concentrated to near dryness and Et_2O (5 mL) was added to yield a white precipitate. The precipitate was isolated by filtration, washed by CH_2Cl_2 (0.5 mL), to afford the desired benzylic trifluoroborate in 43% yield, this result is concord with the reported yield[6].

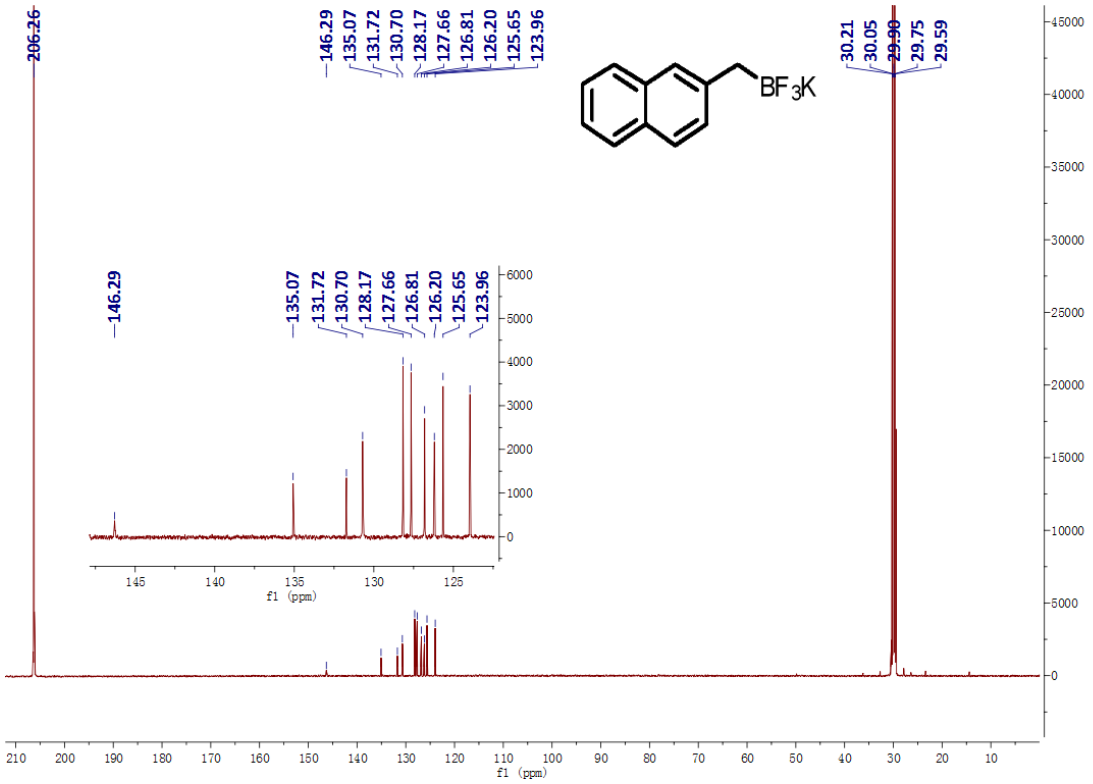
Potassium Trifluoro(naphthalen-2-ylmethyl)borate[6]

^{1}H NMR (400 MHz, Acetone) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.49 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.20 (m, 2H), 1.82 (s, 2H).

^{13}C NMR (126 MHz, Acetone) δ 146.29, 135.07, 131.72, 130.70, 128.17, 127.66, 126.81, 126.20, 125.65, 123.96.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 209.07459, Found: 209.07514.

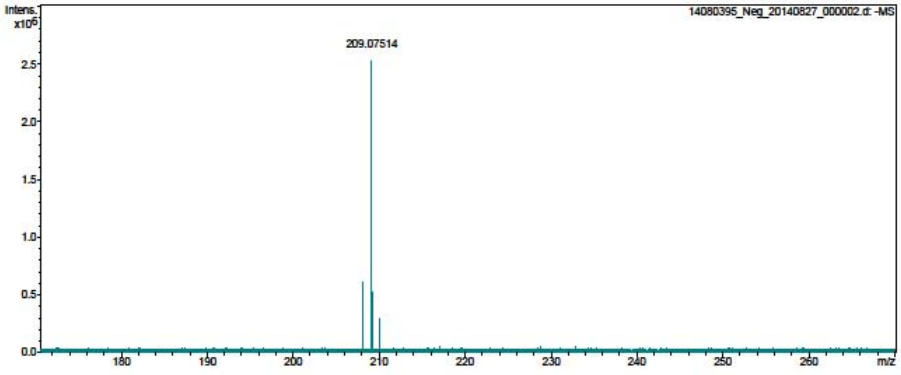




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	14080395_Neg_20140827_000002.d	Acquisition Date	8/27/2014 11:34:57 AM
Sample	czc-04-TFB-mass	Instrument	Bruker Apex IV FTMS
Comment	ESI Negative	Operator	Peking University



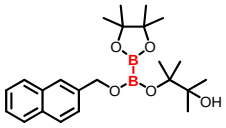
Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
209.07514	2613165	C 11 H 9 B F 3	209.07459	-0.55	-2.6	3.9	6.5	even	Ok

Bruker Compass DataAnalysis 4.0 printed: 8/27/2014 11:38:45 AM Page 1 of 1

(IV) Detection of Possible Boronic Ester Intermediates

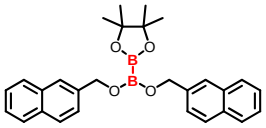
The mixture of naphthmethanol (0.1 mmol, 15.8 mg) and B_2pin_2 (0.15 mmol, 38.1 mg) was detected ESI-HRMS after heated at 100 ^oC with benzene as solvent for 3 h. From the corresponding HRMS, we failed to get the peak value of the following possible boronic esters.

Possible esters



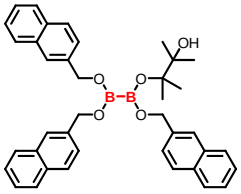
Chemical Formula: $C_{23}H_{34}B_2O_5$
Exact Mass: 412.25924

A



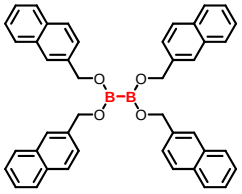
Chemical Formula: $C_{28}H_{30}B_2O_4$
Exact Mass: 452.23302

B



Chemical Formula: $C_{39}H_{40}B_2O_5$
Exact Mass: 610.30619

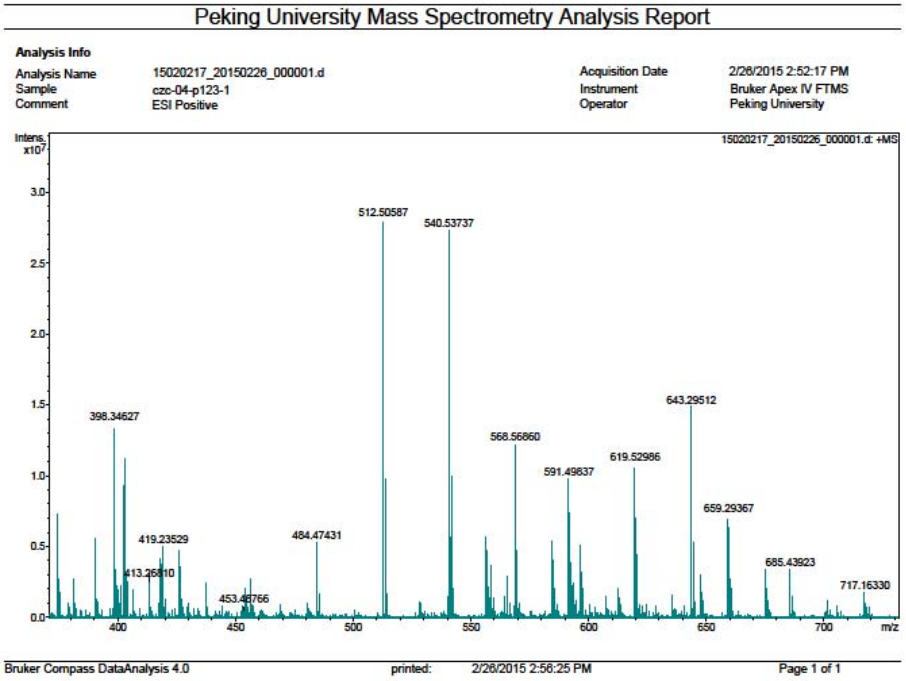
C



Chemical Formula: $C_{44}H_{36}B_2O_4$
Exact Mass: 650.27997

D

All possible intermediates are excluded!

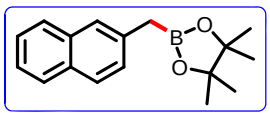


(V) General Procedure of the Miyaura Borylation

General Procedure A: An oven-dried sealed tube containing a stirbar was charged with benzyl alcohols (0.2 mmol), B_2pin_2 (76.2mg, 0.3 mmol), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg) and ligand DCPF (0.03 mmol, 17.4 mg) and then the tube was degassed and refilled with N_2 for 3 times, the mixed solvent Et_2O/benzene were added via syringe (the process completed in a glovebox is better), and reacted in an 100 ^oC oil bath for an indicated time. Then the mixture was cooled to room temperature and quenched by EtOAc (1 mL). The solvent was removed by rotavapor, the yield was determined by NMR and the product was purified by flash silica gel column chromatography.

General Procedure B: An oven-dried sealed tube containing a stirbar was charged with benzyl alcohols (0.2 mmol), B_2pin_2 (76.2mg, 0.3 mmol), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg) and ligand DCPF (0.03 mmol, 17.4 mg). The tube was degassed and refilled with N_2 for 3 times, the solvent benzene (1 mL) were added via syringe (the process completed in a glovebox is better), and then $Ti(O^iPr)_4$ (0.75 eq., 45 uL) was added, and reacted in an 100 ^oC oil bath for an indicated time. Then the mixture was cooled to room temperature and quenched by EtOAc (1 mL). The solvent was removed by rotavapor, the NMR yields and isolated yields were reported and the product was purified by flash silica gel column chromatography. [Notes: the desired products were easily decomposed in the silica gel due to their instability, the isolated yields are lower than the NMR yields.]

(VI) Synthesis and Analytical Data for The Products



4,4,5,5-tetramethyl-2-(naphthalen-2-ylmethyl)-1,3,2-dioxaborolane (**2a**).[7]

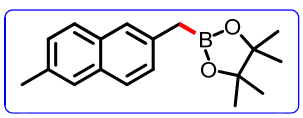
Procedure: This desired product was obtained as white solid in 58% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 3H), 7.61 (s, 1H), 7.44 – 7.29 (m, 3H), 2.45 (s, 2H), 1.22 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.31, 133.81, 131.49, 128.22, 127.63, 127.52, 127.23, 126.59, 125.64, 124.65, 83.47, 24.71. [Due to quadrupolar relaxation, the carbon attached to the boron atom was not detected]

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.86.

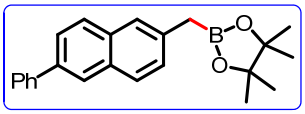
HRMS (ESI) Anal. Calcd. ($M+H^+$) 269.17104, Found: 269.17127.



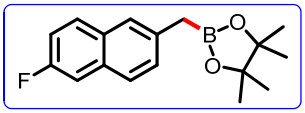
4,4,5,5-tetramethyl-2-((6-methylnaphthalen-2-yl)methyl)-1,3,2-dioxaborolane (**2b**)

Procedure: This desired product was obtained as white solid in 46% isolated yield *via* the general procedure A and Et_2O/benzene (1.0 mL/0.1 mL) was used as the solvent.

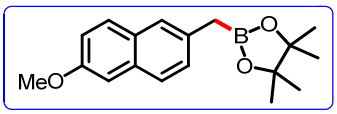
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.55 (d, *J* = 11.4 Hz, 2H), 7.34 – 7.19 (m, 2H), 2.47 (s, 3H), 2.42 (s, 2H), 1.22 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 135.26, 134.11, 132.04, 131.67, 128.23, 127.90, 127.05, 126.99, 126.49, 126.34, 83.42, 24.70, 21.57.
^{11}B NMR (160 MHz, $CDCl_3$) δ 32.70.
HRMS (ESI) Anal. Calcd. ($M+H^+$) 283.18671, Found: 283.18726.



4,4,5,5-tetramethyl-2-((6-phenylnaphthalen-2-yl)methyl)-1,3,2-dioxaborolane (**2c**)
Procedure: This desired product was obtained as white solid in 64% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.83 – 7.74 (m, 2H), 7.73 – 7.65 (m, 3H), 7.63 (s, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.31 (m, 2H), 2.47 (s, 2H), 1.23 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.34, 137.41, 136.54, 132.99, 131.69, 128.84, 128.76, 128.68, 127.97, 127.74, 127.36, 127.30, 127.07, 126.34, 125.50, 125.39, 83.49, 24.71.
^{11}B NMR (160 MHz, $CDCl_3$) δ 33.29.
HRMS (ESI) Anal. Calcd. ($M+H^+$) 345.20244, Found: 345.20191.



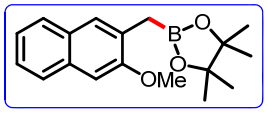
2-((6-fluoronaphthalen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**)
Procedure: This desired product was obtained as white solid in 58% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 9.0, 5.7 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.60 (s, 1H), 7.42 – 7.32 (m, 2H), 7.24 – 7.14 (m, 1H), 2.43 (s, 2H), 1.23 (s, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.01 (d, *J* = 244.0 Hz), 135.56 (d, *J* = 2.6 Hz), 131.98 (d, *J* = 9.0 Hz), 130.78, 129.48 (d, *J* = 8.8 Hz), 129.26 (s), 127.00 (d, *J* = 5.3 Hz), 126.60 (d, *J* = 0.7 Hz), 115.95 (d, *J* = 25.3 Hz), 110.50 (d, *J* = 20.2 Hz), 83.53, 24.72.
^{11}B NMR (160 MHz, $CDCl_3$) δ 32.94.
HRMS (ESI) Anal. Calcd. ($M+H^+$) 287.16132, Found: 287.16124.



2-((6-methoxynaphthalen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**)
Procedure: This desired product was obtained as white solid in 52% isolated yield *via* the general procedure A and Et_2O/benzene (0.7 mL/0.3 mL) was used as the solvent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.54 (s, 1H), 7.30 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.12 – 7.04 (m, 2H), 3.89 (s, 3H), 2.41 (s, 2H), 1.23 (s, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.82, 133.81, 132.37, 129.30, 128.72, 128.67, 126.54, 126.48, 118.38, 105.60, 83.41, 55.23, 24.70.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.60.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 299.18162, Found: 299.18152.



2-((3-methoxynaphthalen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**)

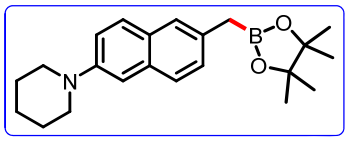
Procedure: This desired product was obtained as white solid in 34% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H), 7.56 (s, 1H), 7.39 – 7.26 (m, 2H), 7.05 (s, 1H), 3.91 (s, 3H), 2.34 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.38, 133.17, 129.99, 129.12, 128.46, 126.88, 126.24, 125.05, 123.31, 104.30, 83.19, 55.06, 24.67.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.31.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 299.18162, Found: 299.18166.



1-(6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)naphthalen-2-yl)piperidine (**2g**)

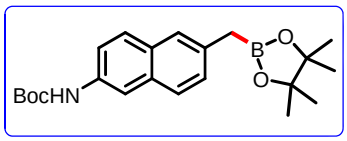
Procedure: This desired product was obtained as white solid in 61% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 15.4, 8.7 Hz, 2H), 7.48 (s, 1H), 7.25 – 7.18 (m, 2H), 7.08 (d, J = 2.1 Hz, 1H), 3.23 – 3.13 (m, 4H), 2.39 (s, 2H), 1.94 – 1.62 (m, 6H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.44, 133.37, 132.54, 128.82, 128.40, 127.84, 126.55, 126.23, 120.29, 110.57, 83.37, 51.34, 25.95, 24.71, 24.36.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.12.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 352.24463, Found: 352.24341.



tert-butyl 6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)naphthalen-2-ylcarbamate (**2h**)

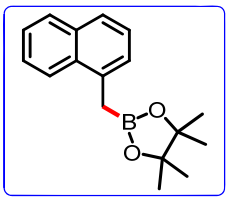
Procedure: This desired product was obtained as white solid in 50% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.64 (dd, J = 8.6, 3.6 Hz, 2H), 7.53 (s, 1H), 7.32 – 7.26 (m, 2H), 6.56 (s, 1H), 2.41 (s, 2H), 1.54 (s, 9H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.88, 134.86, 134.79, 131.94, 130.45, 128.82, 128.04, 127.18, 126.30, 119.08, 114.55, 83.46, 80.51, 28.38, 24.71.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.33.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 401.26100, Found: 401.26123.



4,4,5,5-tetramethyl-2-(naphthalen-1-ylmethyl)-1,3,2-dioxaborolane (**2i**)

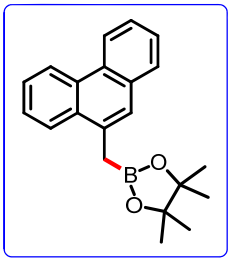
Procedure: This desired product was obtained as white solid in 38% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.87 – 7.76 (m, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.29 (m, 4H), 2.68 (s, 2H), 1.19 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.59, 133.76, 132.44, 128.48, 126.43, 125.74, 125.33, 125.30, 124.51, 83.51, 29.69, 24.65.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.02.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 269.17104, Found: 269.17180.



4,4,5,5-tetramethyl-2-(phenanthren-9-ylmethyl)-1,3,2-dioxaborolane (**2k**)

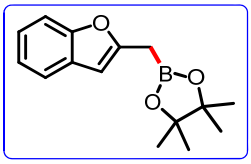
Procedure: This desired product was obtained as white solid in 41% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.67 (m, 1H), 8.64 – 8.59 (m, 1H), 8.11 – 8.03 (m, 1H), 7.80 – 7.75 (m, 1H), 7.63 – 7.58 (m, 3H), 7.57 – 7.49 (m, 2H), 2.72 (s, 2H), 1.18 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.92, 132.27, 132.02, 130.58, 129.44, 127.83, 126.53, 126.41, 126.21, 126.02, 125.48, 125.08, 122.96, 122.35, 83.58, 24.64.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.29.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 319.18676, Found: 319.18679.



2-(benzofuran-2-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2l**)

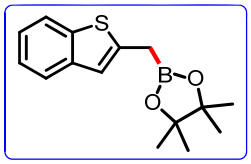
Procedure: This desired product was obtained as white solid in 62% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.34 (m, 2H), 7.23 – 7.09 (m, 2H), 6.44 (s, 1H), 2.45 (s, 2H), 1.29 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.06, 154.65, 129.48, 122.68, 122.20, 119.94, 110.54, 102.38, 83.90, 24.75.

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.10.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 259.15027, Found: 259.15006.



2-(benzo[b]thiophen-2-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2m**)

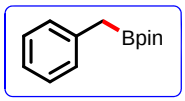
Procedure: This desired product was obtained as white solid in 57% isolated yield *via* the general procedure A and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.26 (m, 1H), 7.24 – 7.16 (m, 1H), 7.01 (s, 1H), 2.56 (s, 2H), 1.28 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.73, 140.66, 139.61, 123.84, 123.00, 122.42, 121.84, 121.18, 83.88, 24.75.

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.13.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 269.17104, Found: 269.17180.



2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2n**)

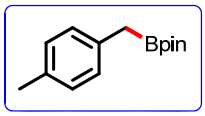
Procedure: This desired product was obtained as colorless oil in 56% isolated yield *via* the general procedure B and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.07 (m, 5H), 2.29 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.65, 128.99, 128.22, 124.80, 83.39, 24.71.

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.73.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 241.13727, Found: 241.13697.



4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (**2o**)

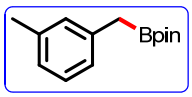
Procedure: This desired product was obtained as colorless oil in 59% isolated yield *via* the general procedure B and Et_2O/benzene (0.9 mL/0.1 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.06 (m, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 2.29 (s, 3H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.38, 134.08, 128.95, 128.84, 83.33, 24.72, 20.93.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.15.

HRMS (ESI) Anal. Calcd. ($M+Na^+$) 255.15293, Found: 255.15268.



4,4,5,5-tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (**2p**)

Procedure: This desired product was obtained as colorless oil in 56% isolated yield *via* the

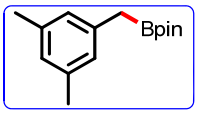
general procedure B and benzene (1.0 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.90 (m, 3H), 2.30 (s, 3H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.44, 137.69, 129.83, 128.10, 125.94, 125.57, 83.35, 24.69, 21.38.

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.73.

HRMS (ESI) Anal. Calcd. ($M+Na^+$) 255.15293, Found: 255.15268.



2-(3,5-dimethylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2q**)

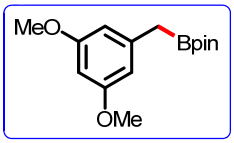
Procedure: This desired product was obtained as colorless oil in 64% isolated yield *via* the general procedure B and benzene (1.0 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 6.76 (s, 1H), 2.26 (s, 6H), 2.21 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.31, 137.58, 126.83, 126.54, 83.32, 24.69, 21.25.

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.71.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 247.18666, Found: 247.18611.



2-(3,5-dimethoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2r**)

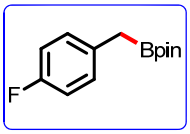
Procedure: This desired product was obtained as colorless oil in 74% isolated yield *via* the general procedure B and benzene (1.0 mL) was used as the solvent, while 1.0 eq. $Ti(O^iPr)_4$ was used.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, *J* = 2.2 Hz, 2H), 6.25 (t, *J* = 2.2 Hz, 1H), 3.76 (s, 6H), 2.24 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.62, 140.90, 107.10, 97.31, 83.41, 55.15, 24.71.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.15.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 279.17649, Found: 279.17624.



2-(4-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2s**)

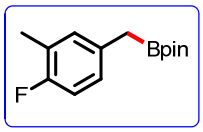
Procedure: This desired product was obtained as colorless oil in 44% isolated yield *via* the general procedure B and benzene (1.0 mL) was used as the solvent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.01 – 6.79 (m, 2H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.82 (d, *J* = 242.0 Hz), 134.12 (d, *J* = 3.1 Hz), 130.17 (d, *J* = 7.6 Hz), 114.92 (d, *J* = 21.1 Hz), 114.92 (d, *J* = 21.1 Hz), 83.48 (s), 24.71 (s).

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.75.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 259.12785, Found: 259.12756.



2-(4-fluoro-3-methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2t**)

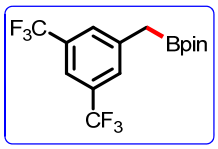
Procedure: This desired product was obtained as colorless oil in 63% isolated yield *via* the general procedure B and benzene (1.0 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.91 (m, 2H), 6.89 – 6.81 (m, 1H), 2.22 (d, *J* = 1.9 Hz, 5H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.30 (d, *J* = 240.9 Hz), 133.69 (d, *J* = 3.6 Hz), 131.80 (d, *J* = 4.8 Hz), 127.37 (d, *J* = 7.7 Hz), 124.19 (d, *J* = 17.1 Hz), 114.56 (d, *J* = 22.0 Hz), 83.43 (s), 24.68 (s), 14.51 (d, *J* = 3.6 Hz).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.26.

HRMS (ESI) Anal. Calcd. ($M+Na^+$) 273.14351, Found: 273.14290.



2-(3,5-bis(trifluoromethyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2u**)

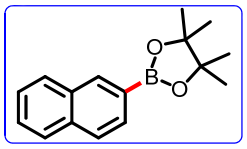
Procedure: This desired product was obtained as colorless oil in 53% isolated yield *via* the general procedure B and benzene (1.0 mL) was used as the solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 3H), 2.42 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.31 (s), 131.22 (q, *J* = 32.8 Hz), 129.16 (s), 123.51 (q, *J* = 272.4 Hz), 118.99 (q, *J* = 3.9 Hz), 83.97 (s), 24.67 (s).

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.85.

HRMS (ESI) Anal. Calcd. ($M+H^+$) 355.13013, Found: 355.12998.



4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (**2w**)[8]

Procedure: This desired product was obtained as white solid in 45% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.98 – 7.67 (m, 4H), 7.64 – 7.31 (m, 2H), 1.38 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.22, 135.01, 132.80, 130.38, 128.62, 127.68, 126.94, 125.76, 83.88, 24.90.

MS (EI) m/z: 258 (M^+)

References:

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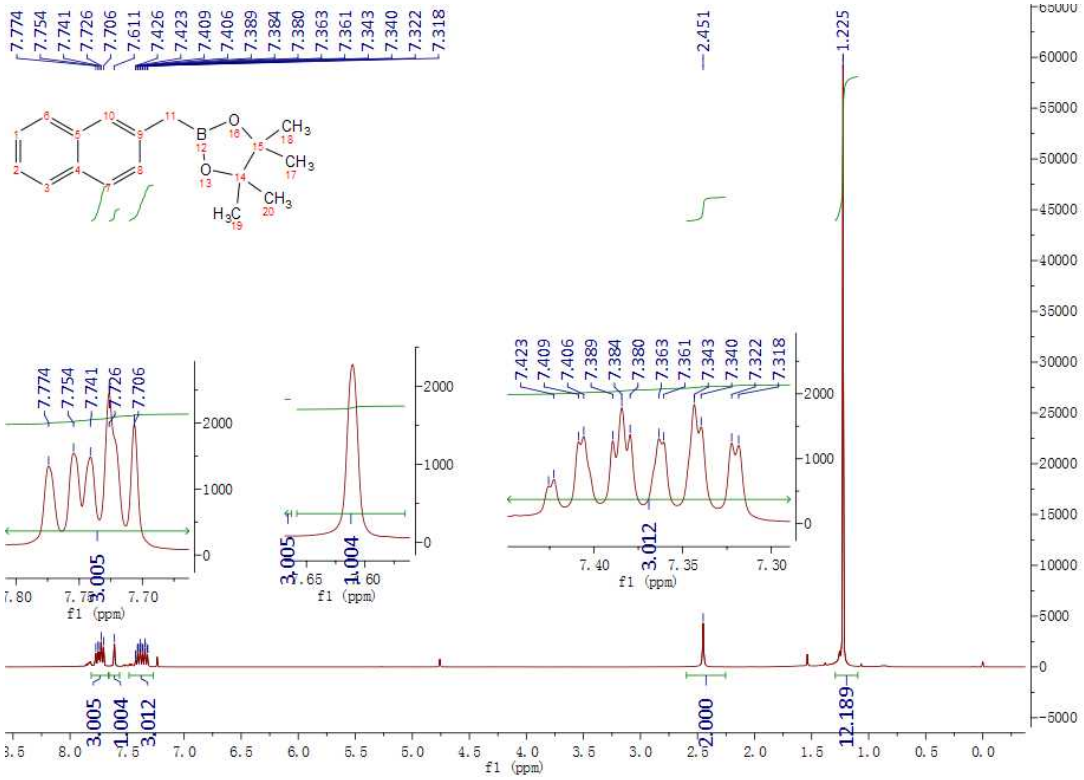
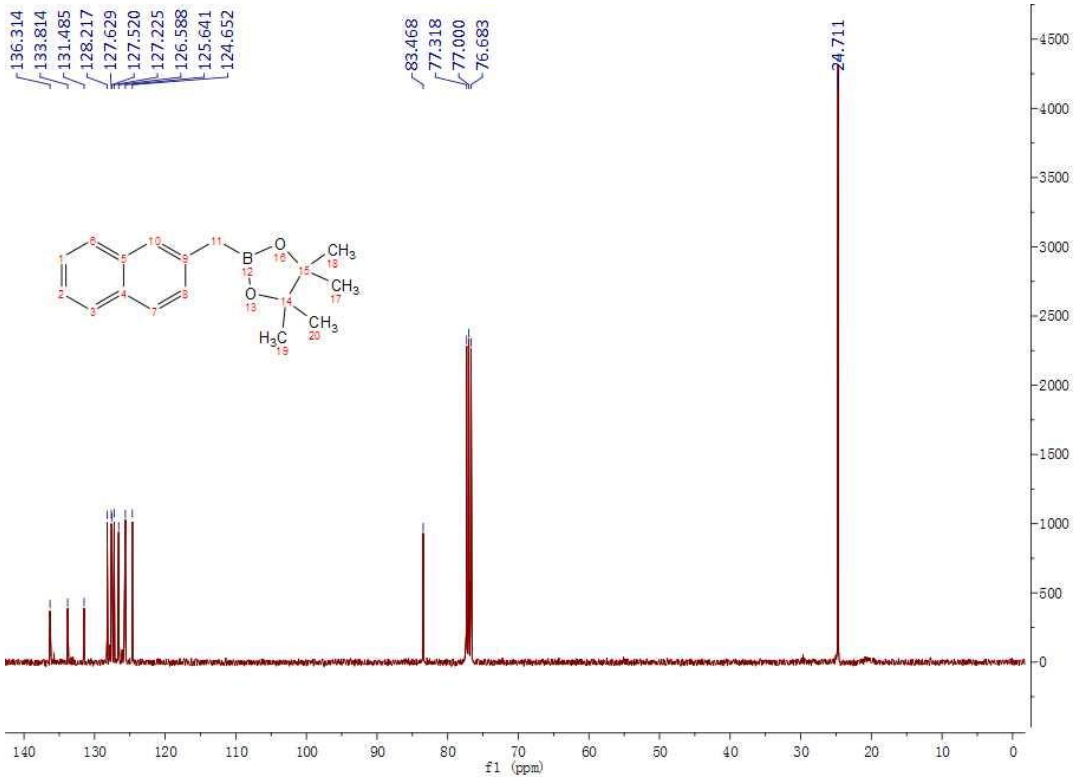
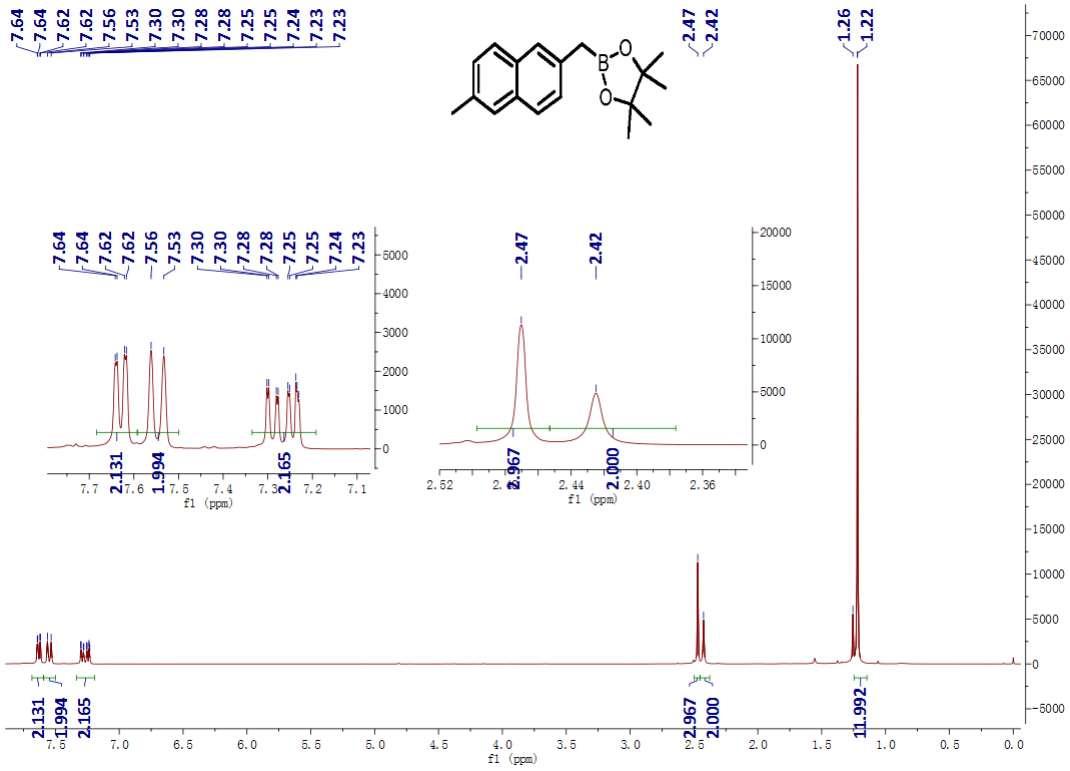
(VII) Spectral Data for Compounds



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7.24
7.23
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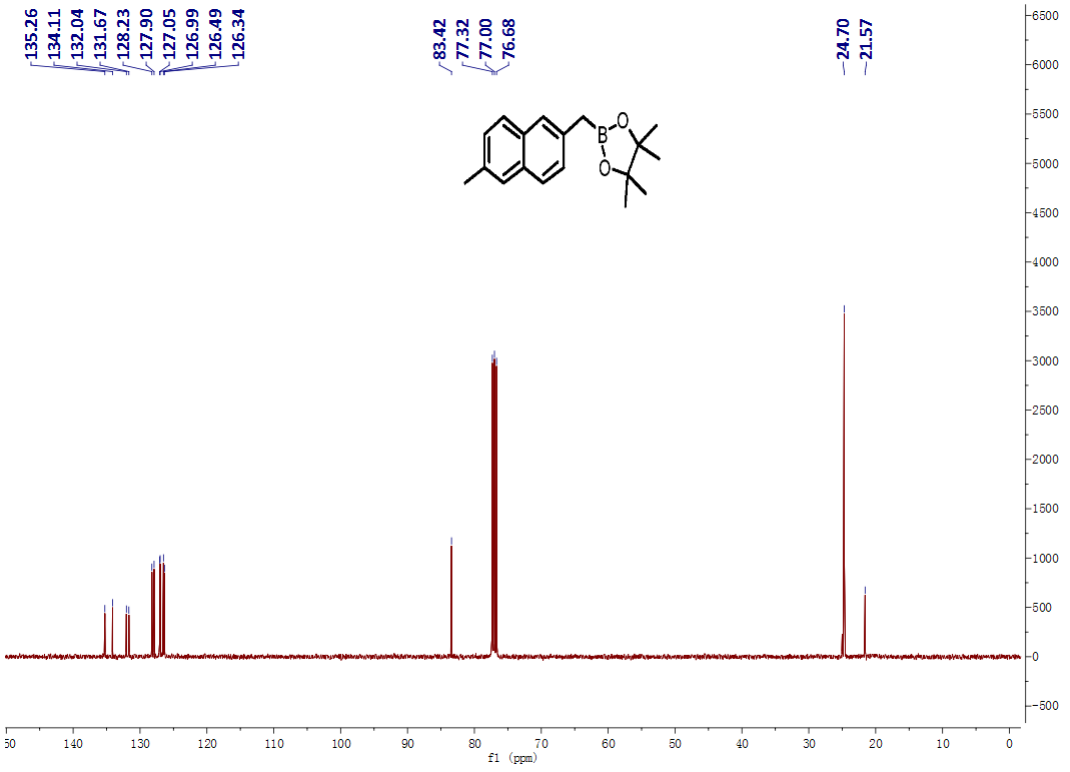
11.992
f1 (ppm)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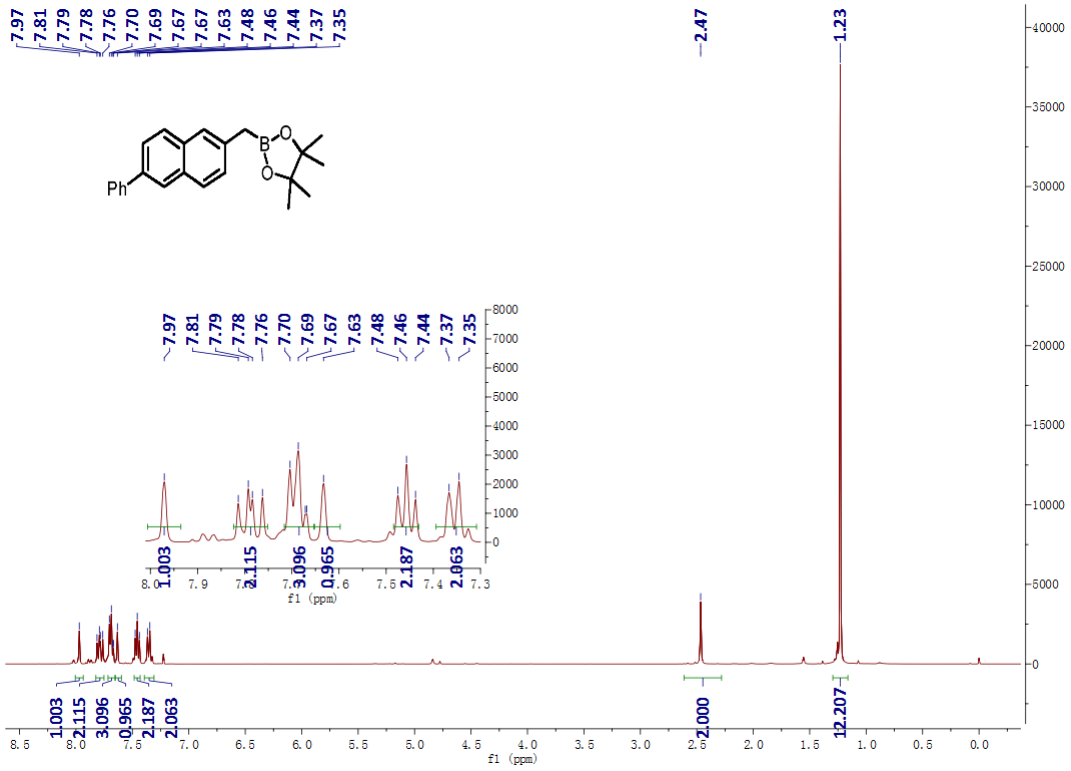
f1 (ppm)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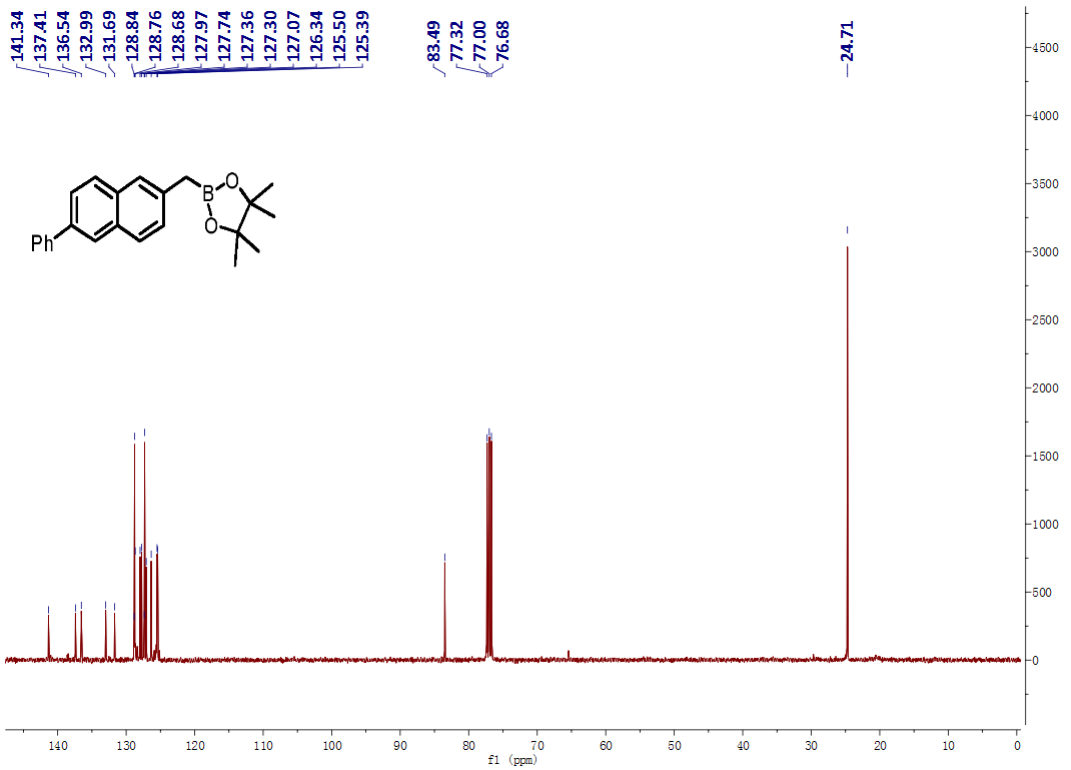
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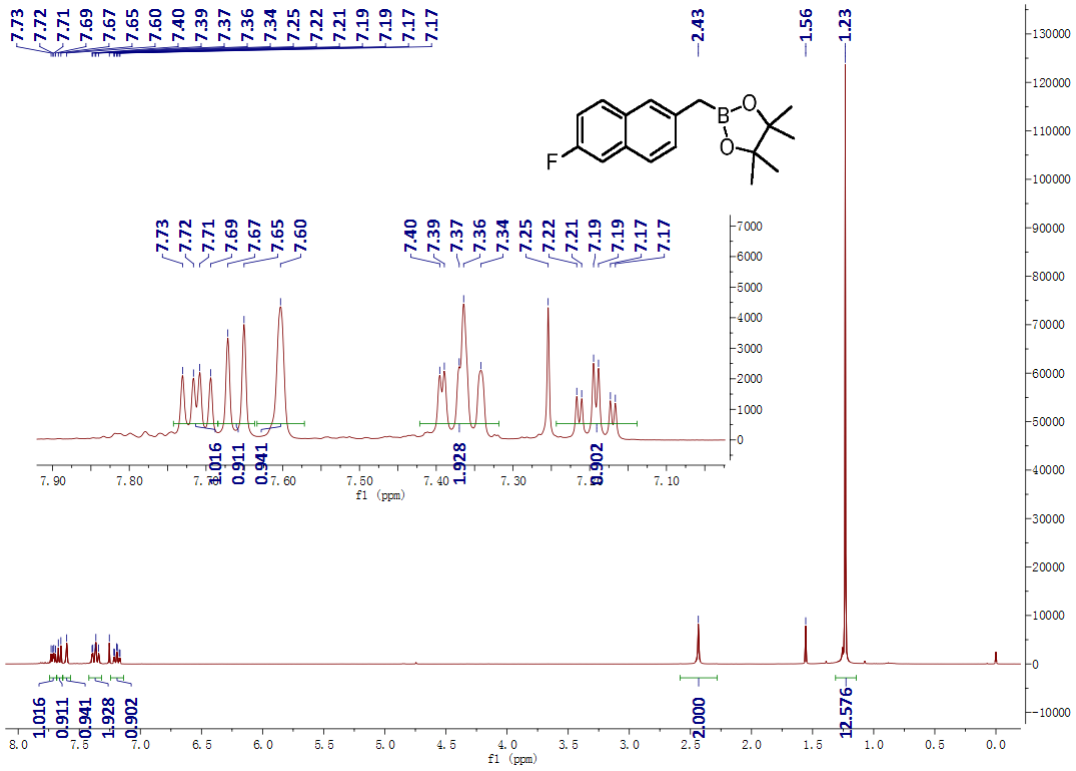
f1 (ppm)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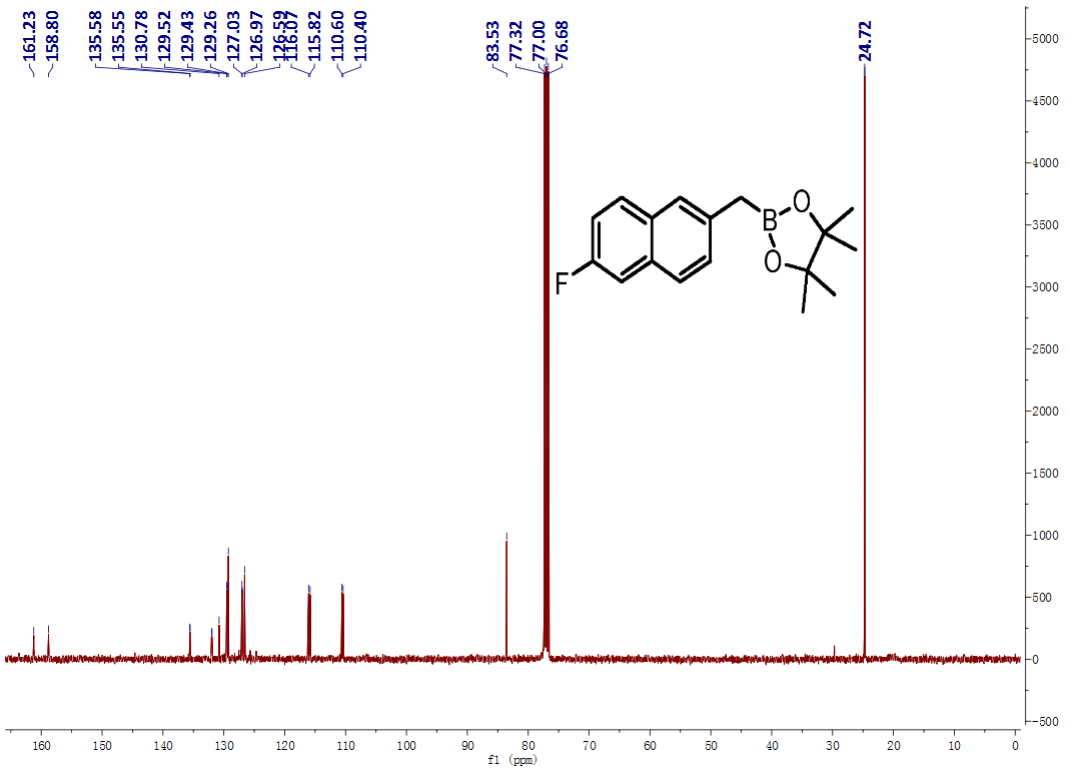
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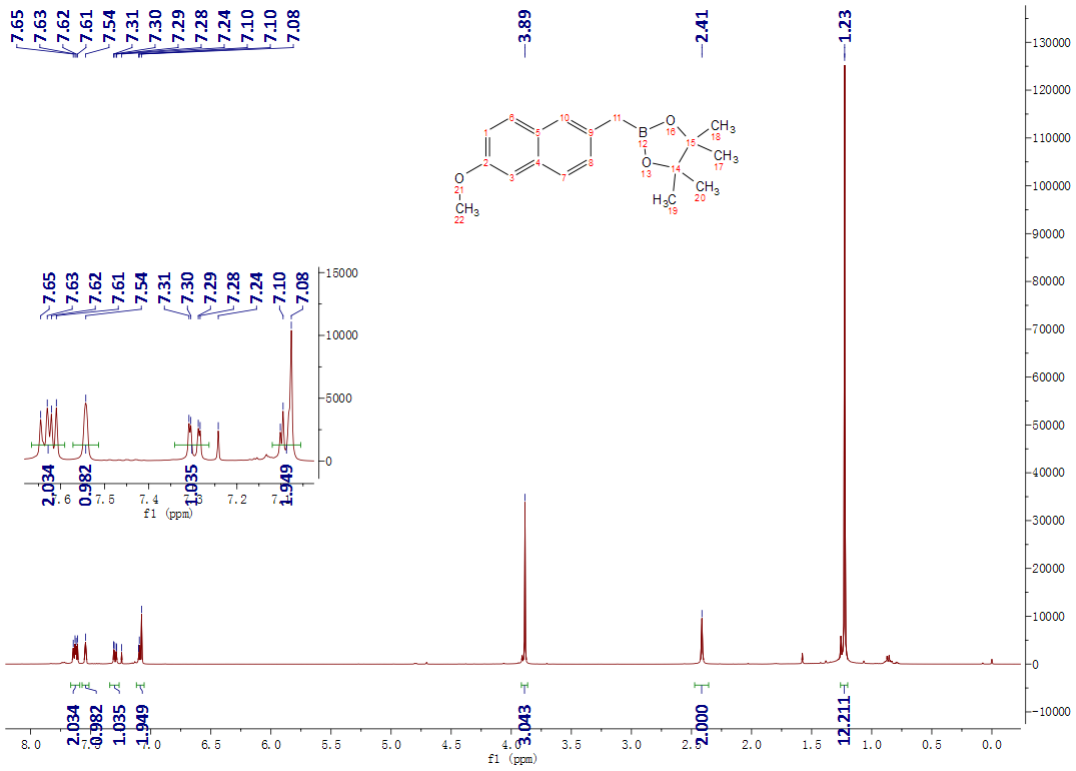
B
O
O
f1 (ppm)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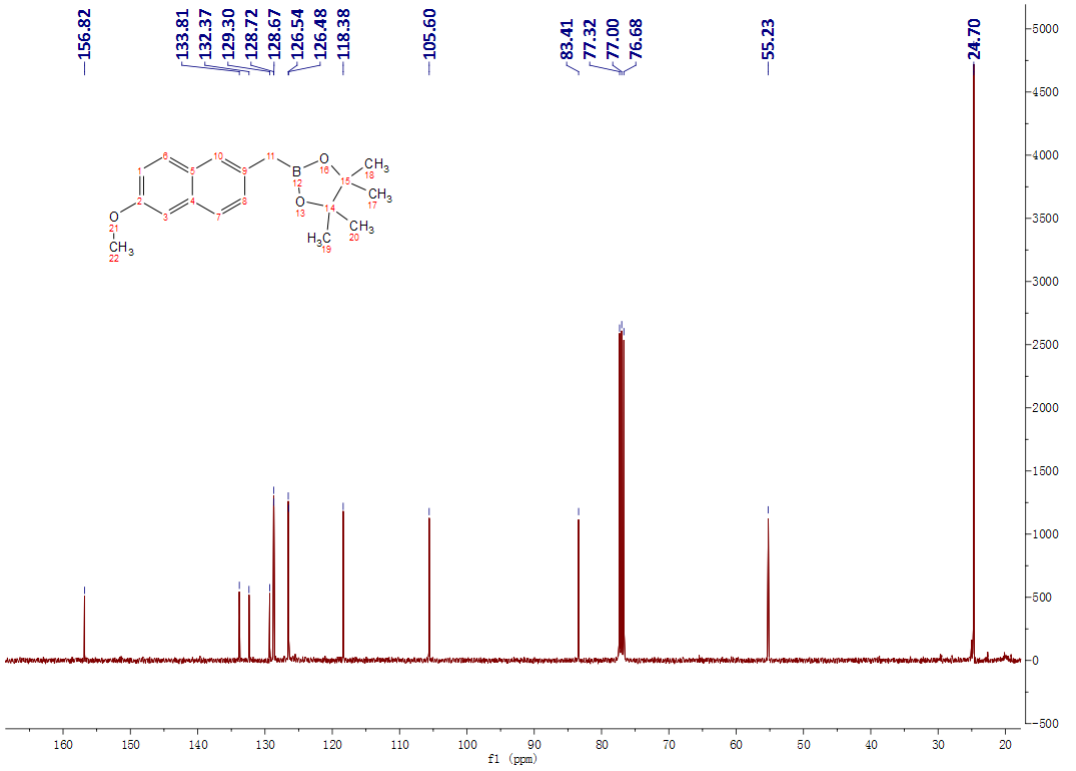
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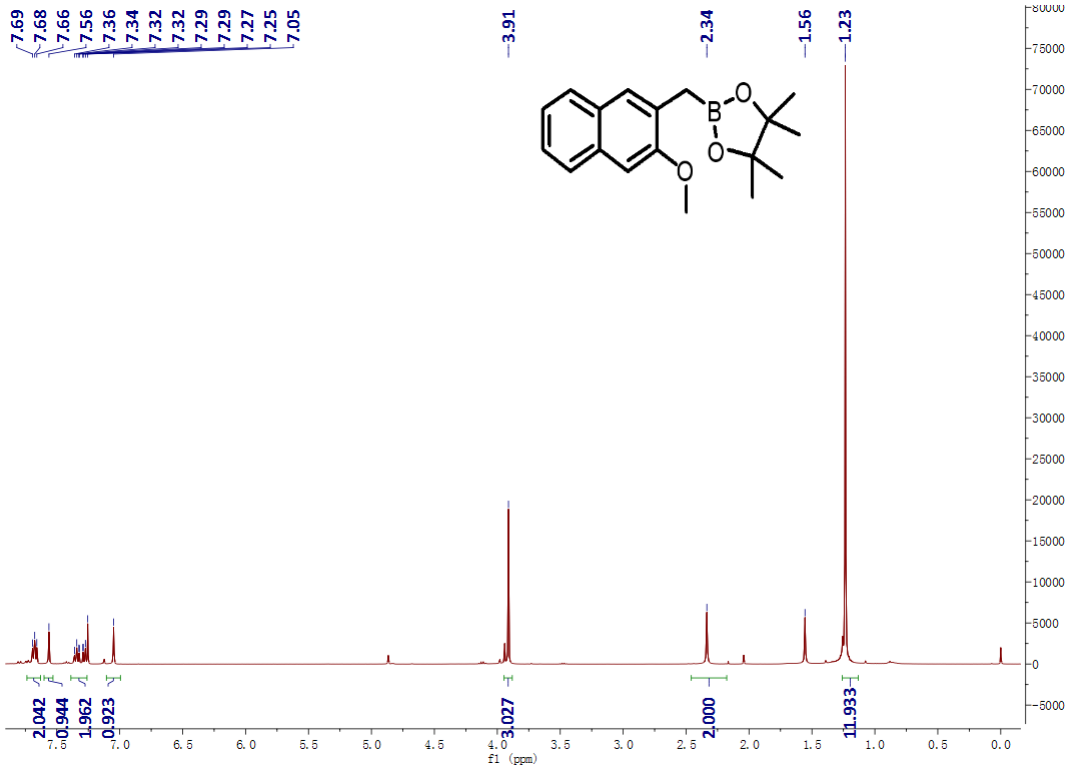
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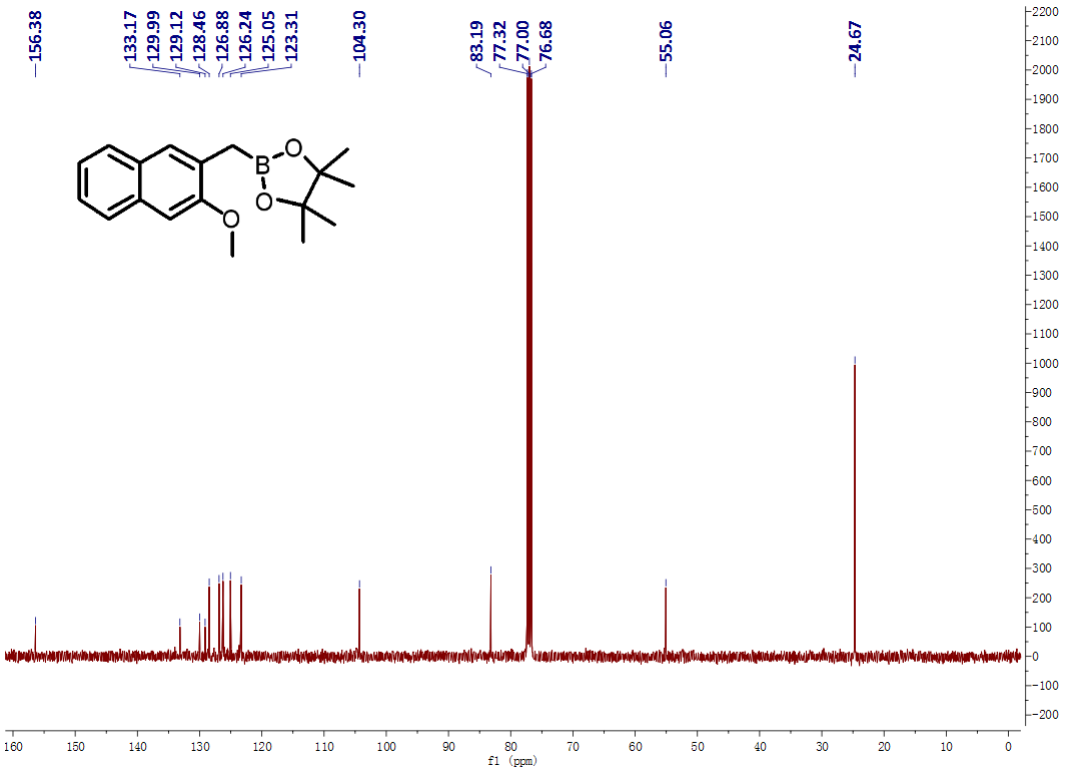
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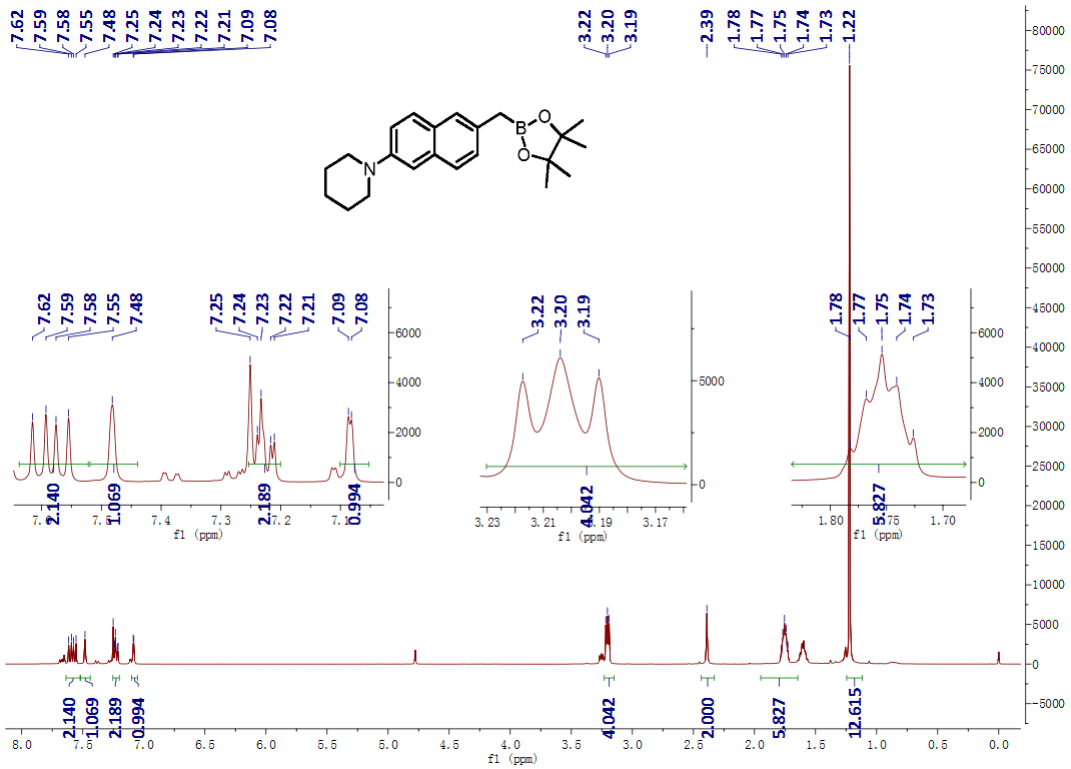
B
O
O
O
f1 (ppm)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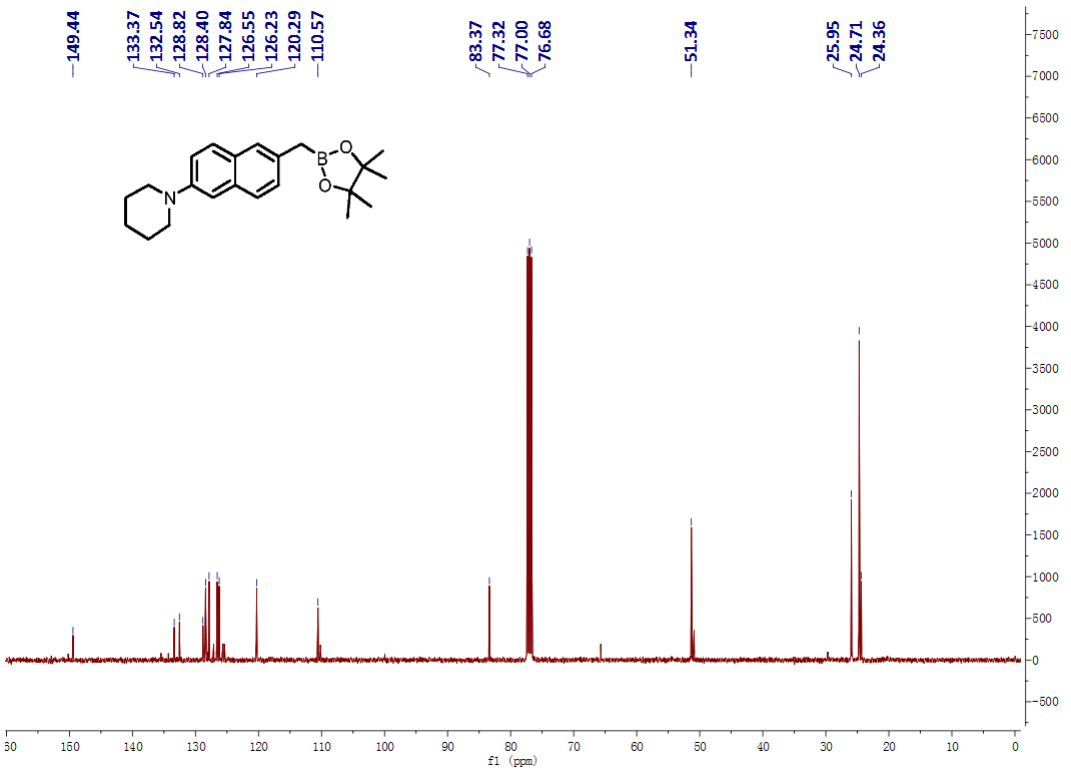
7.59
7.58
7.55
7.48
7.25
7.24
7.23
7.22
7.21
7.09
7.08
3.22
3.20
3.19
2.39
1.78
1.77
1.75
1.74
1.73
1.22
2.140
1.069
2.189
0.994
4.042
2.000
5.827
12.615
f1 (ppm)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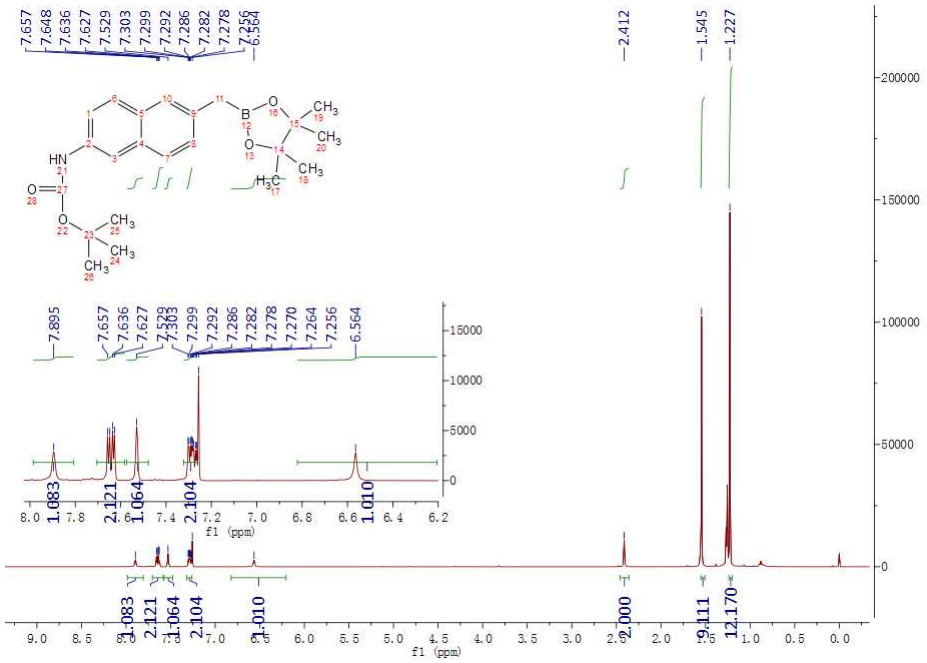
133.37
132.54
128.82
128.40
127.84
126.55
126.23
120.29
110.57
83.37
77.32
77.00
76.68
51.34
25.95
24.71
24.36
f1 (ppm)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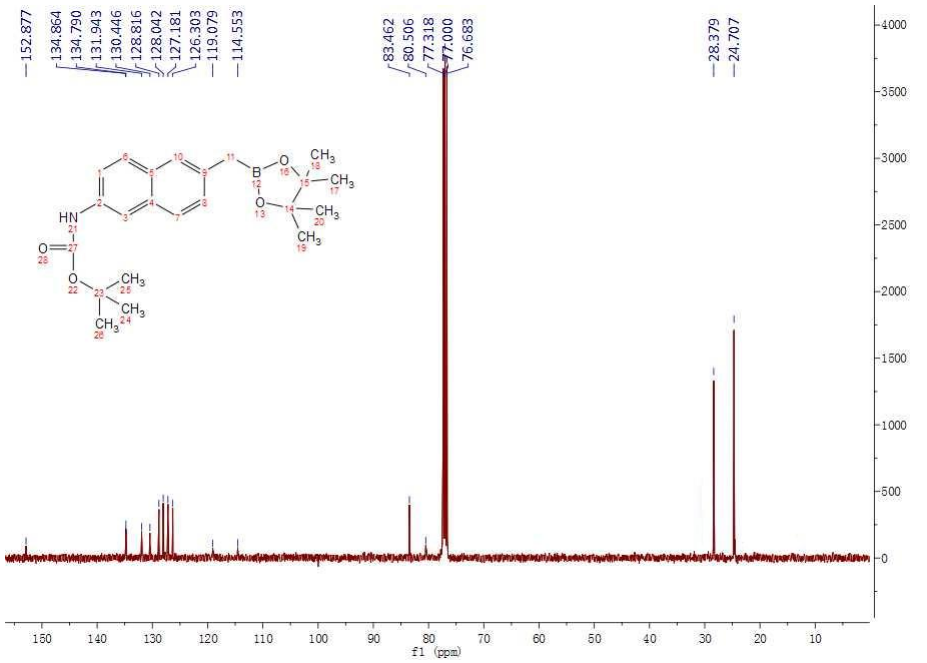
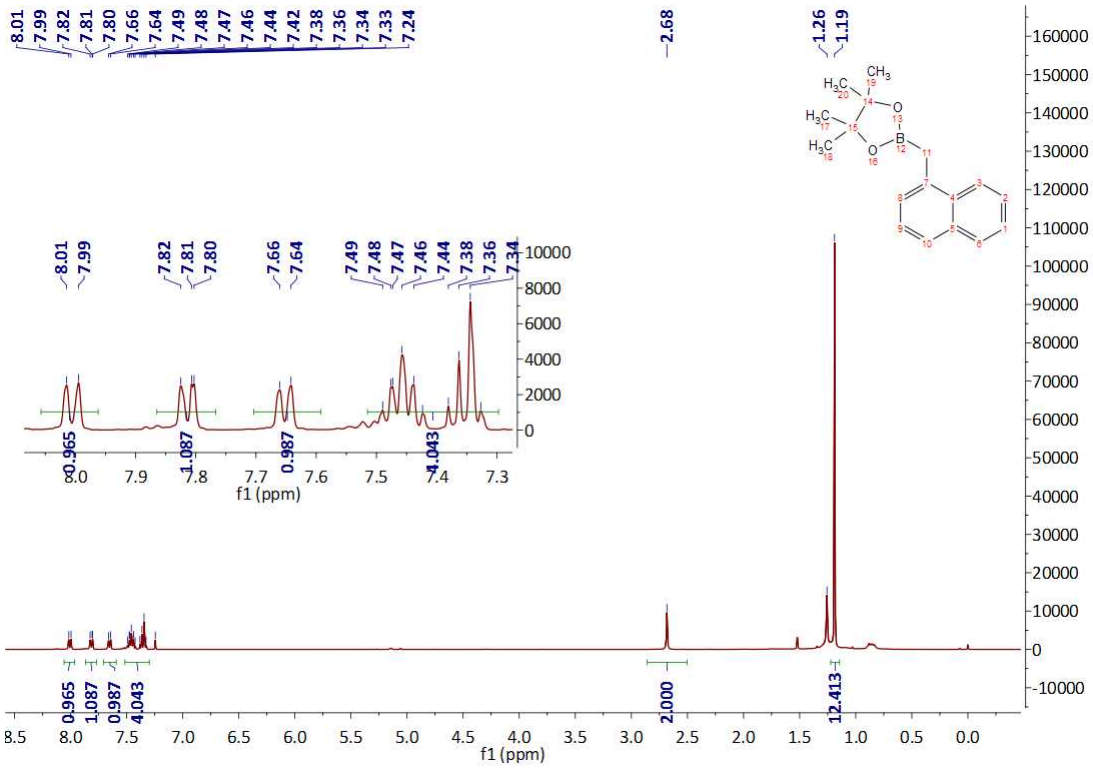
7.648
7.636
7.627
7.529
7.303
7.299
7.292
7.286
7.282
7.278
7.256
6.564
2.412
1.545
1.227
7.895
1.083
2.121
1.064
2.104
1.010
2.000
9.111
12.170
f1 (ppm)


152.877
134.864
134.790
131.943
130.446
128.816
128.042
127.181
126.303
119.079
114.553
83.462
80.506
77.318
77.000
76.683
28.379
24.707
f1 (ppm)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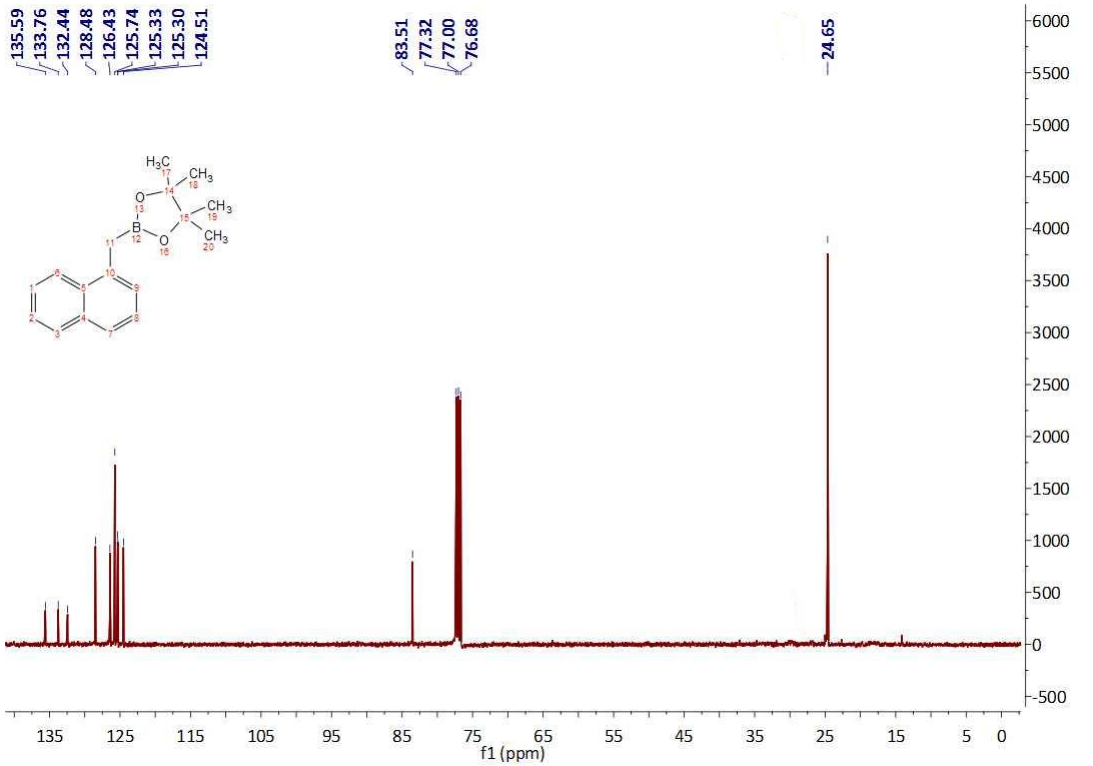
7.99
7.82
7.81
7.80
7.66
7.64
7.49
7.48
7.47
7.46
7.44
7.42
7.38
7.36
7.34
7.33
7.24
2.68
1.26
1.19
0.965
1.087
0.987
4.043
2.000
12.413
f1 (ppm)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133.76
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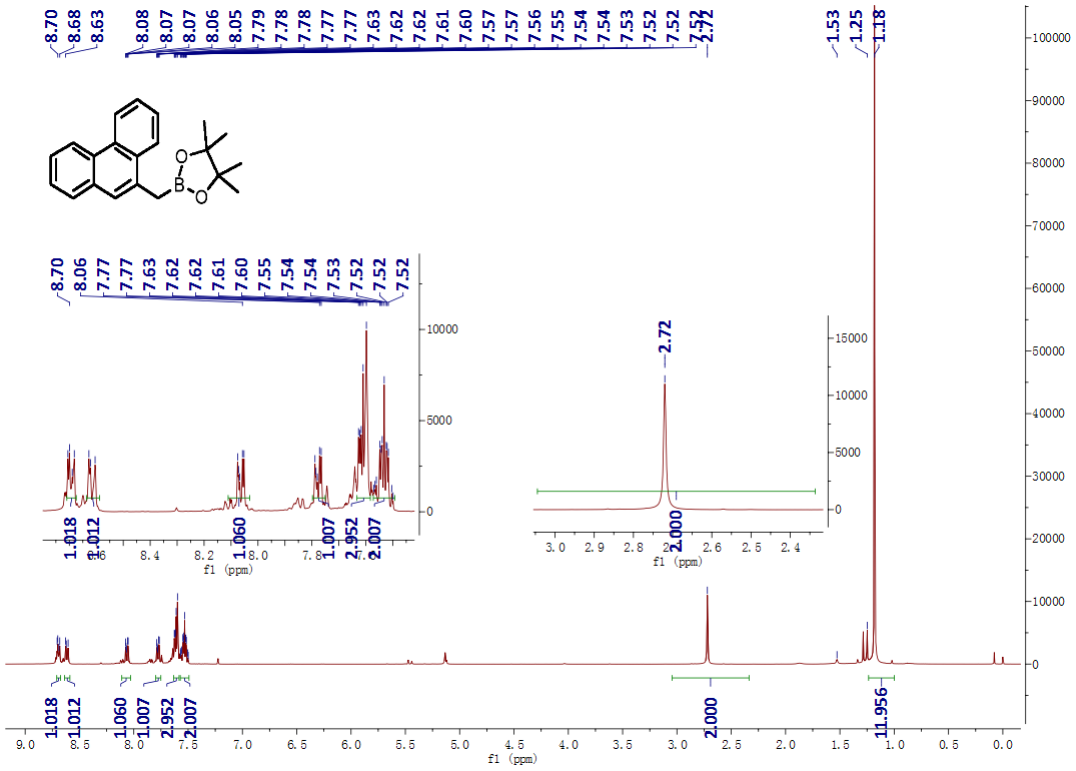
125.33
125.30
124.51
83.51
77.32
77.00
76.68
24.65
f1 (ppm)


8.70
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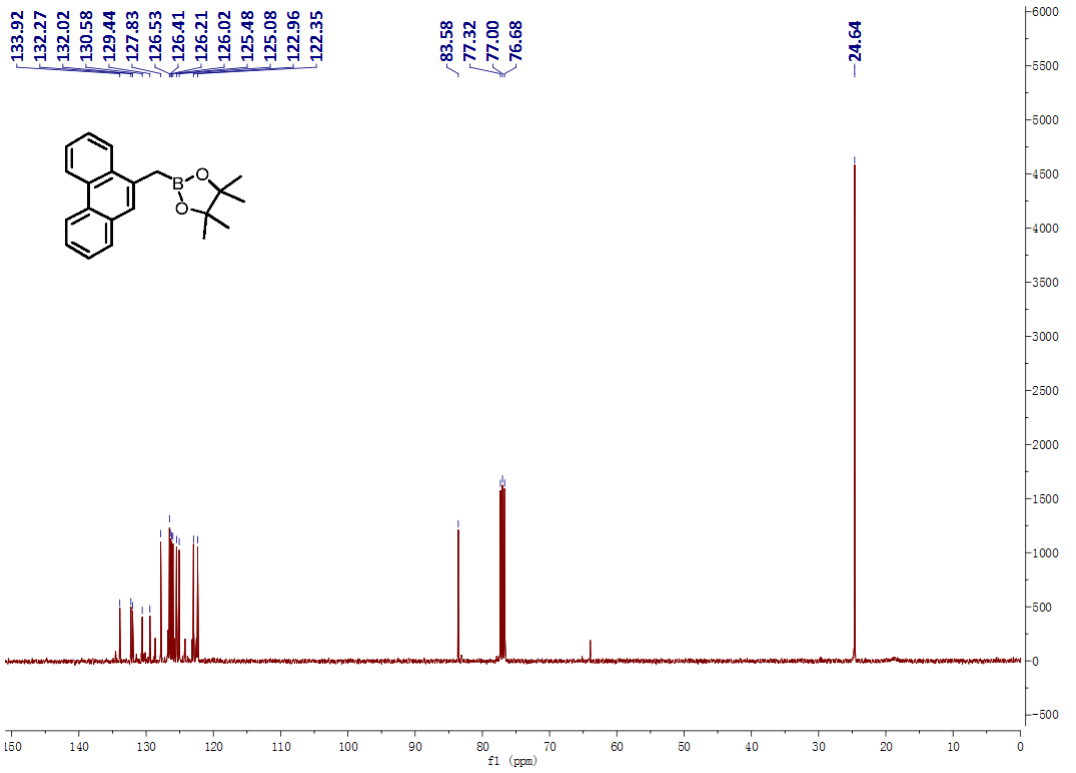
8.63
8.08
8.07
8.07
8.06
8.05
7.79
7.78
7.78
7.77
7.77
7.63
7.62
7.62
7.61
7.60
7.57
7.57
7.56
7.55
7.54
7.53
7.52
7.52
7.52
7.52
1.53
1.25
1.18
2.72
1.018
1.012
1.060
1.007
2.952
2.007
2.000
11.956
f1 (ppm)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132.27
132.02
130.58
129.44
127.83
126.53
126.41
126.21
126.02
125.48
125.08
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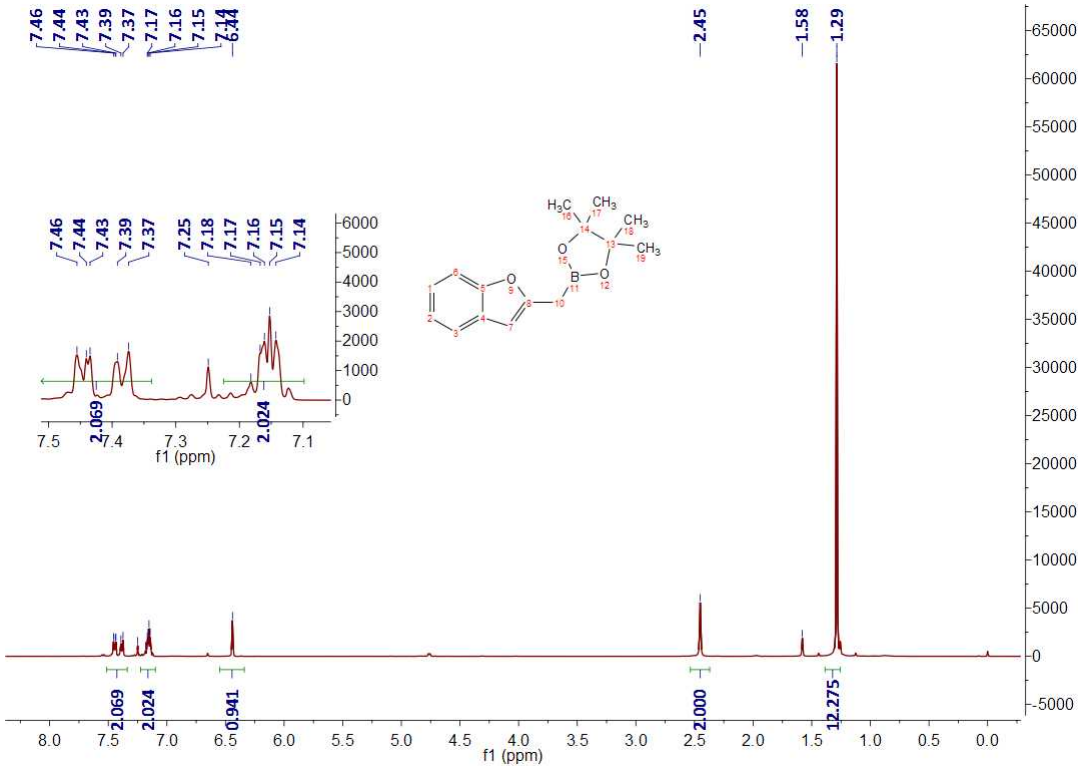
122.35
83.58
77.32
77.00
76.68
24.64
f1 (ppm)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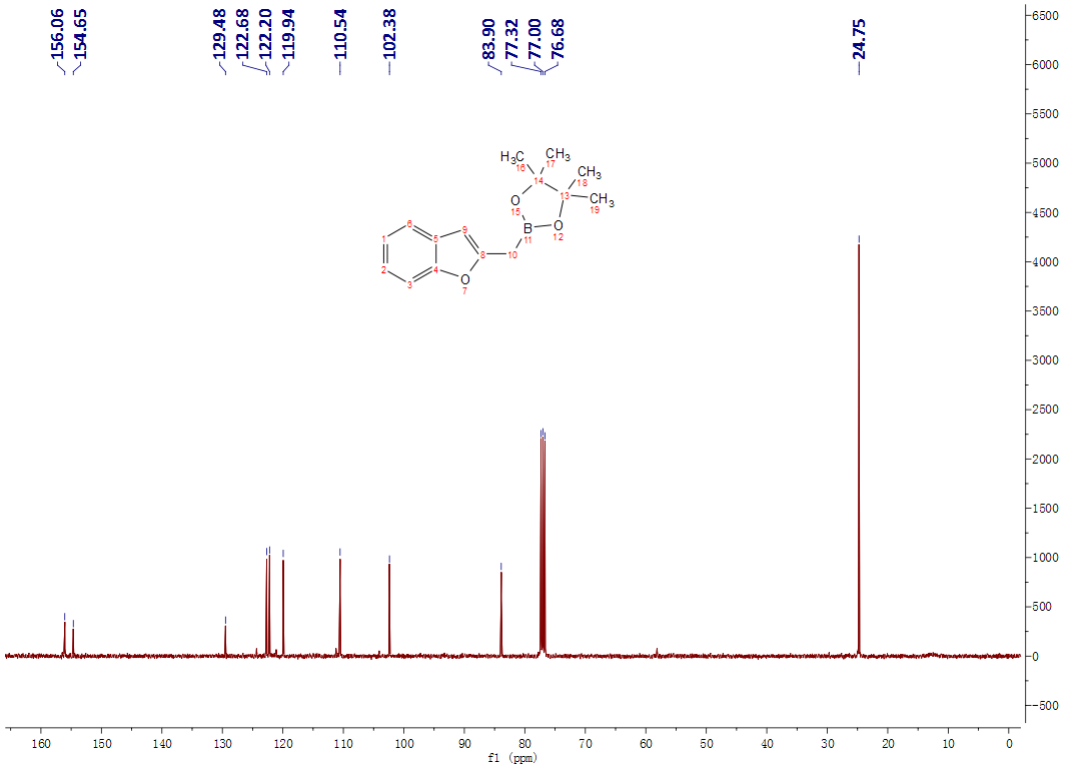
7.44
7.43
7.39
7.37
7.17
7.16
7.15
7.14
2.45
1.58
1.29
7.25
7.18
2.069
2.024
f1 (ppm)
2.069
2.024
0.941
2.000
12.275
f1 (ppm)


156.06
154.65
129.48
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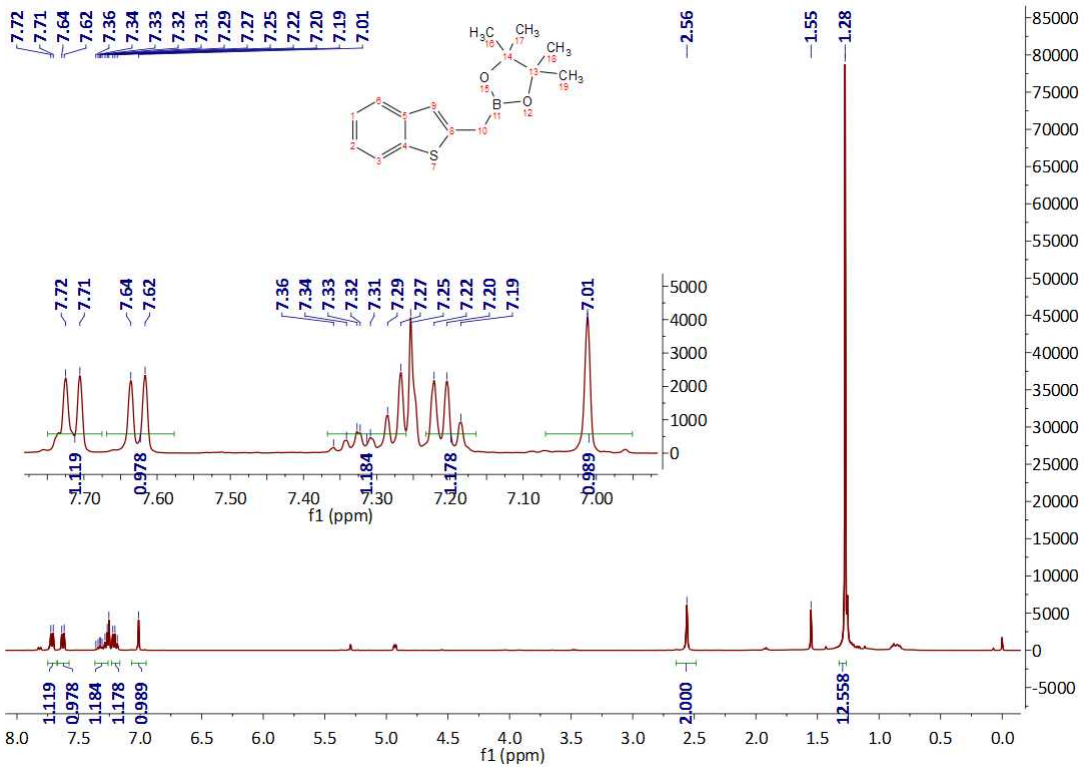
119.94
110.54
102.38
83.90
77.32
77.00
76.68
24.75
f1 (ppm)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7.71
7.64
7.62
7.36
7.34
7.33
7.32
7.31
7.29
7.27
7.25
7.22
7.20
7.19
7.01
2.56
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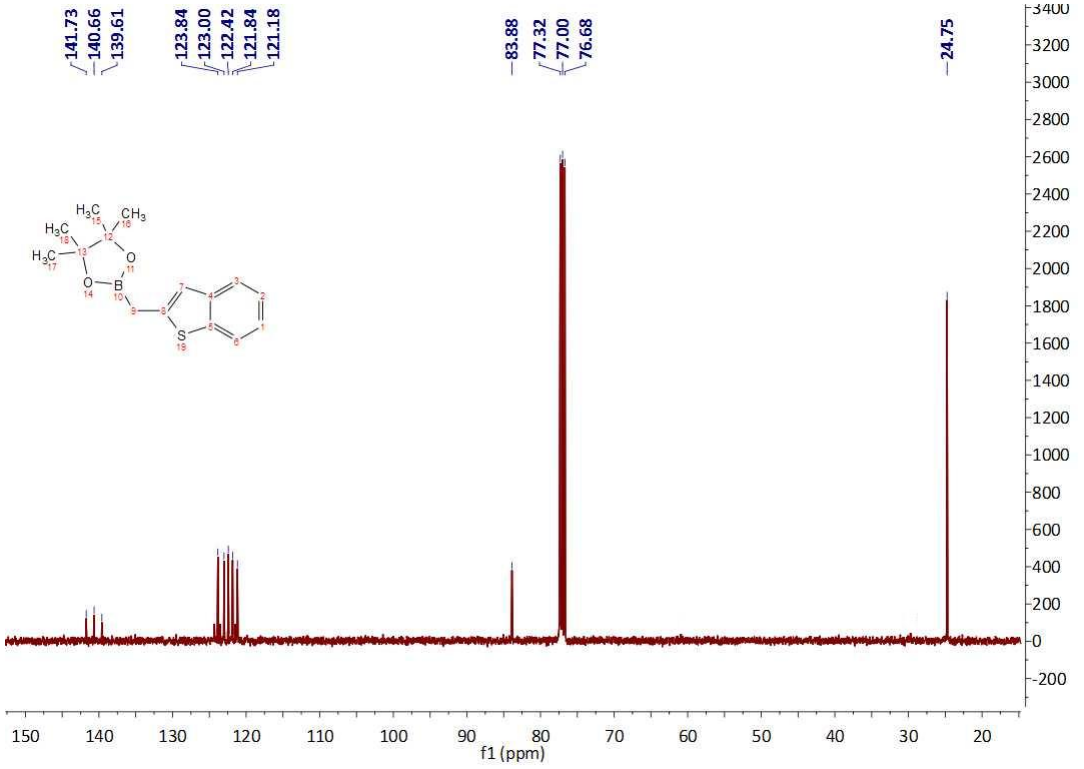
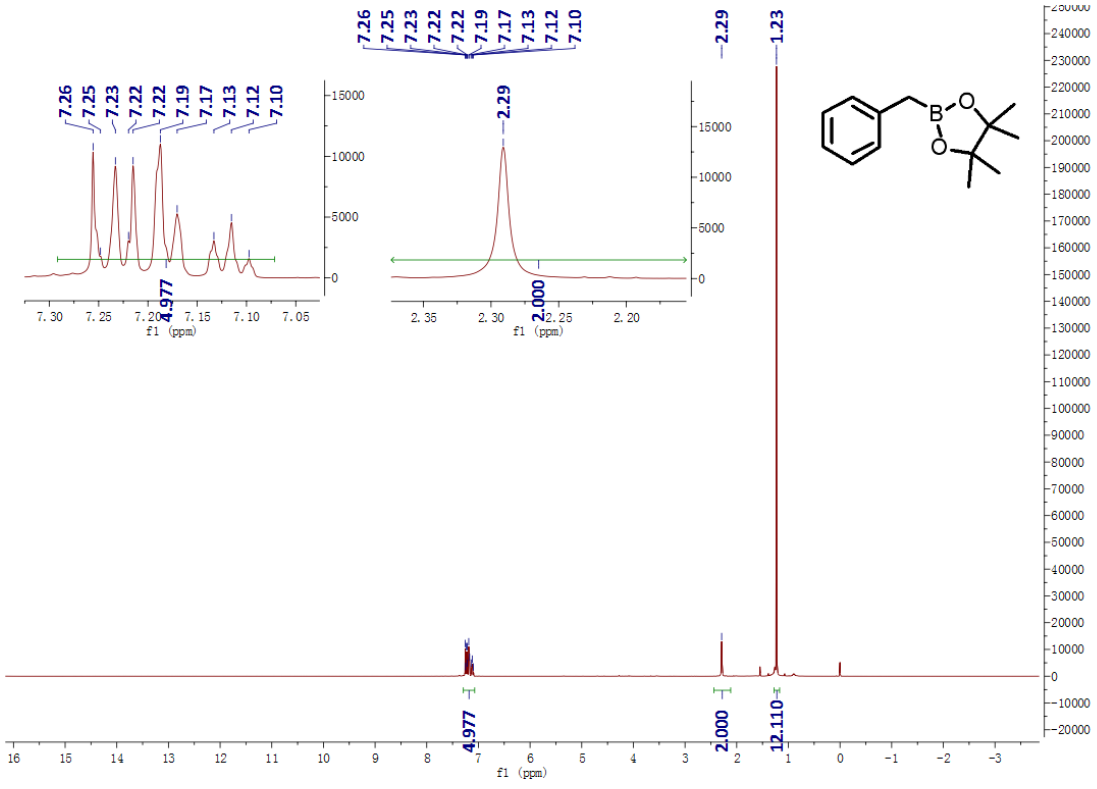
1.28
1.119
0.978
1.184
1.178
0.989
2.000
12.558
f1 (ppm)


141.73
140.66
139.61
123.84
123.00
122.42
121.84
121.18
83.88
77.32
77.00
76.68
24.75
f1 (ppm)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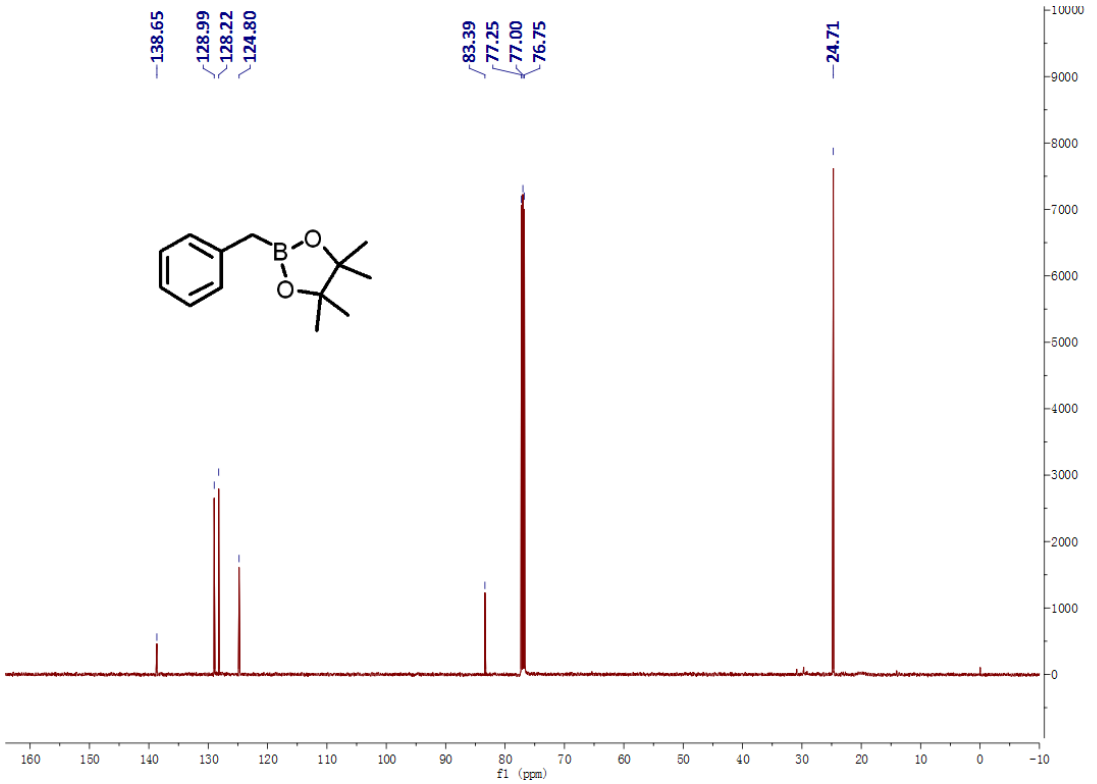
7.25
7.23
7.22
7.22
7.19
7.17
7.13
7.12
7.10
2.29
1.23
4.977
2.000
12.110
f1 (ppm)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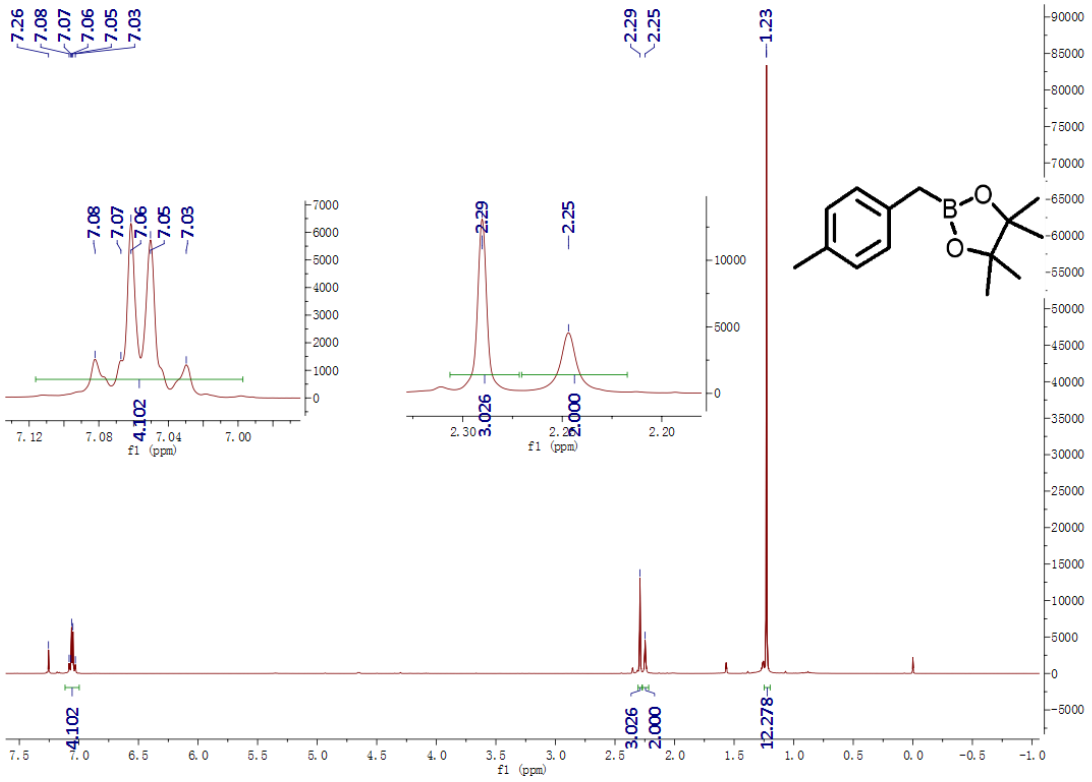
128.22
124.80
83.39
77.25
77.00
76.75
24.71
f1 (ppm)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7.08
7.07
7.06
7.05
7.03
2.29
2.25
1.23
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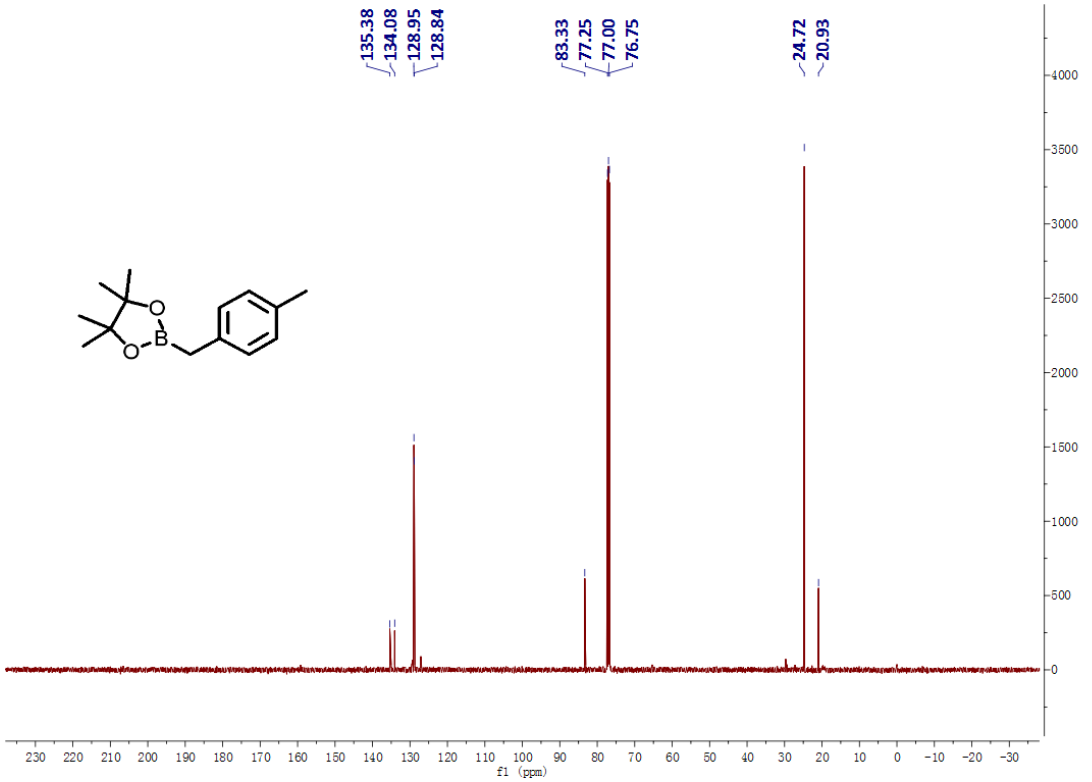
3.026
2.000
12.278
f1 (ppm)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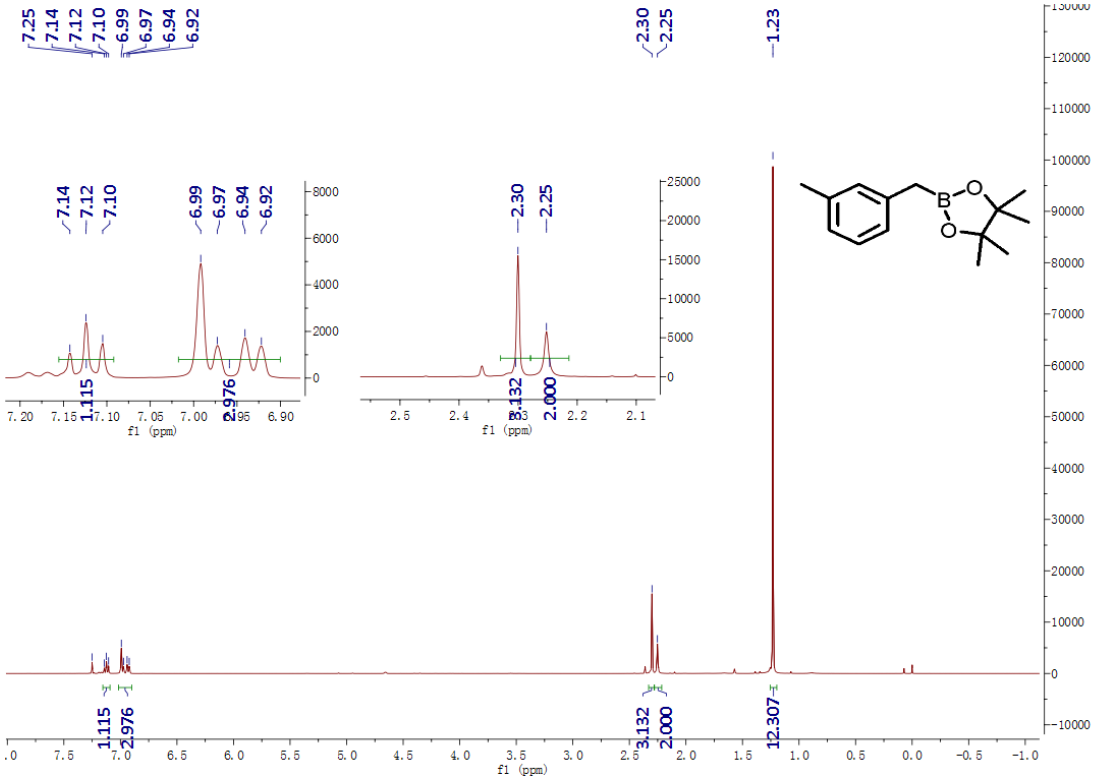
134.08
128.95
128.84
83.33
77.25
77.00
76.75
24.72
20.93
f1 (ppm)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7.14
7.12
7.10
6.99
6.97
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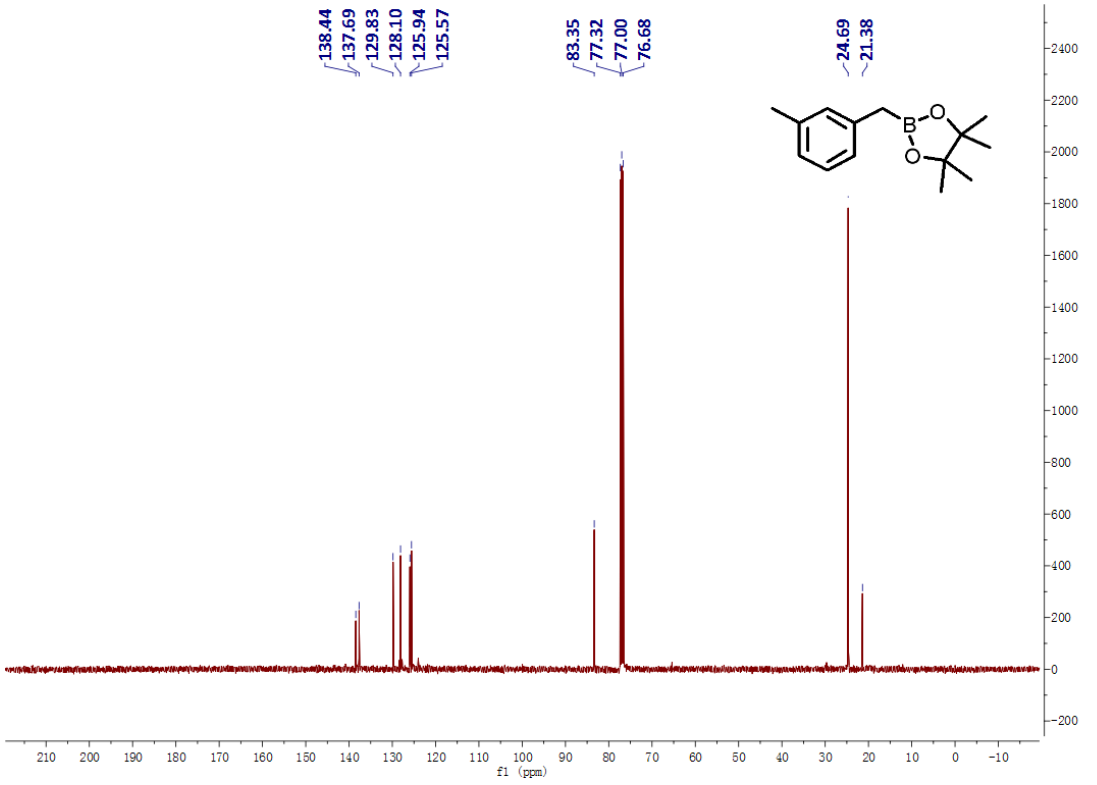
6.92
2.30
2.25
1.23
1.115
2.976
3.132
2.000
12.307
f1 (ppm)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137.69
129.83
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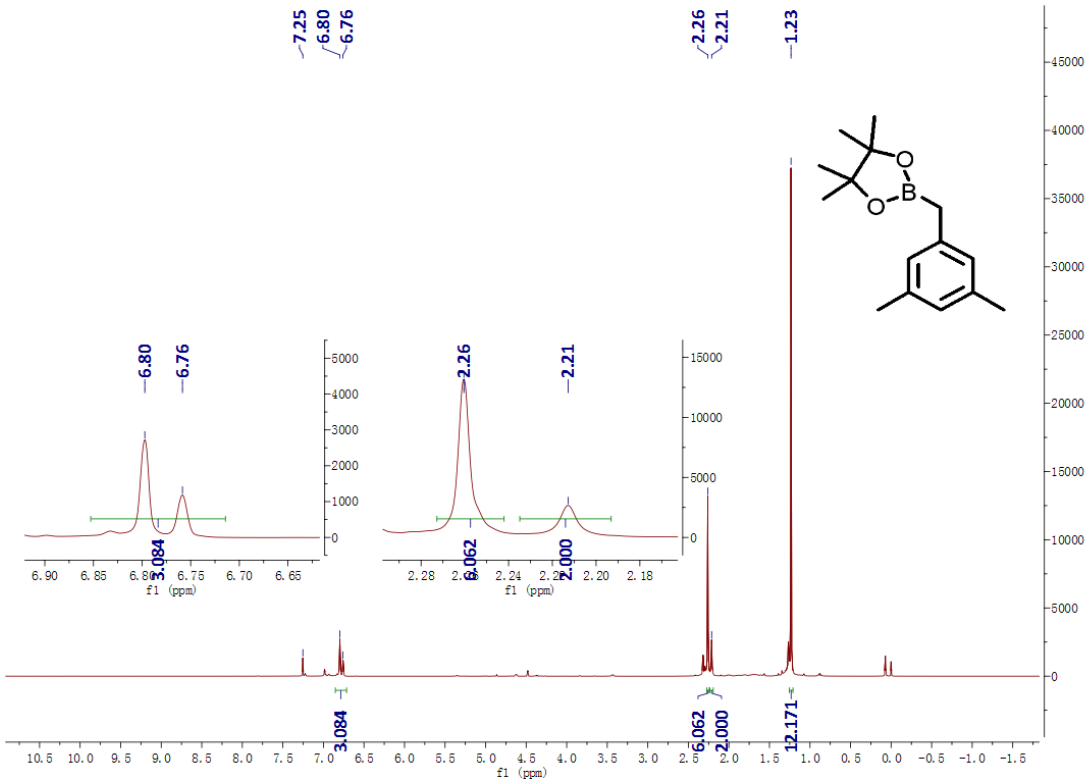
125.94
125.57
83.35
77.32
77.00
76.68
24.69
21.38
f1 (ppm)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2.21
1.23
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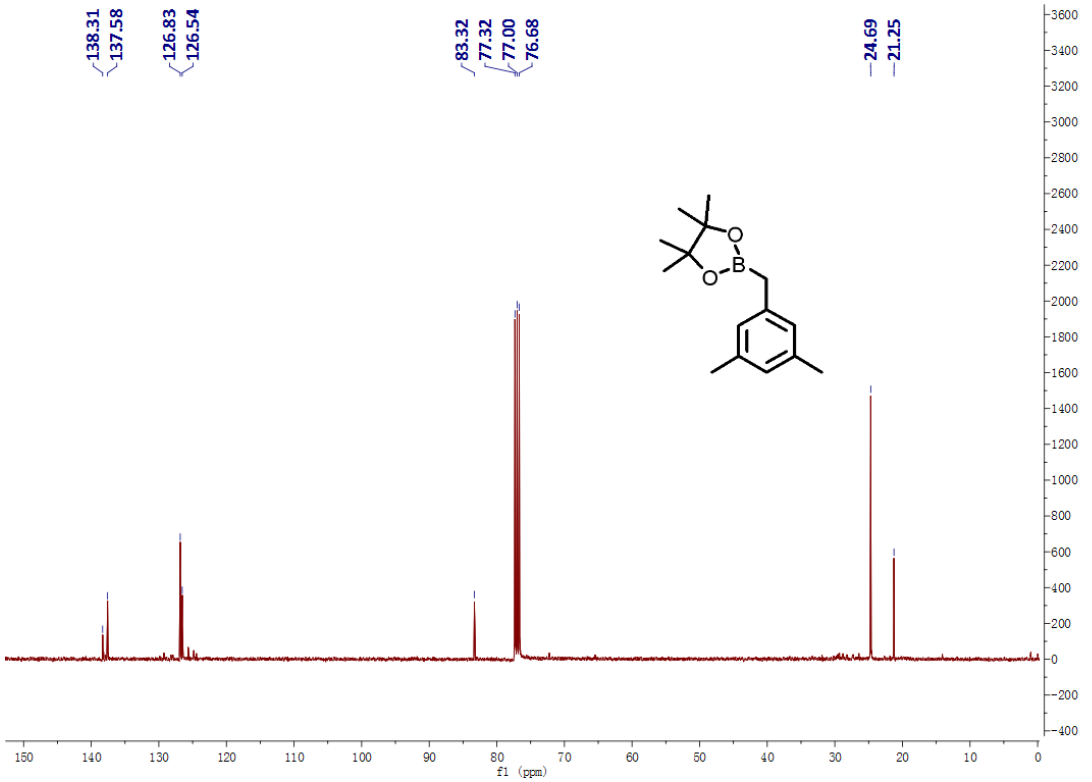
6.062
2.000
12.171
f1 (ppm)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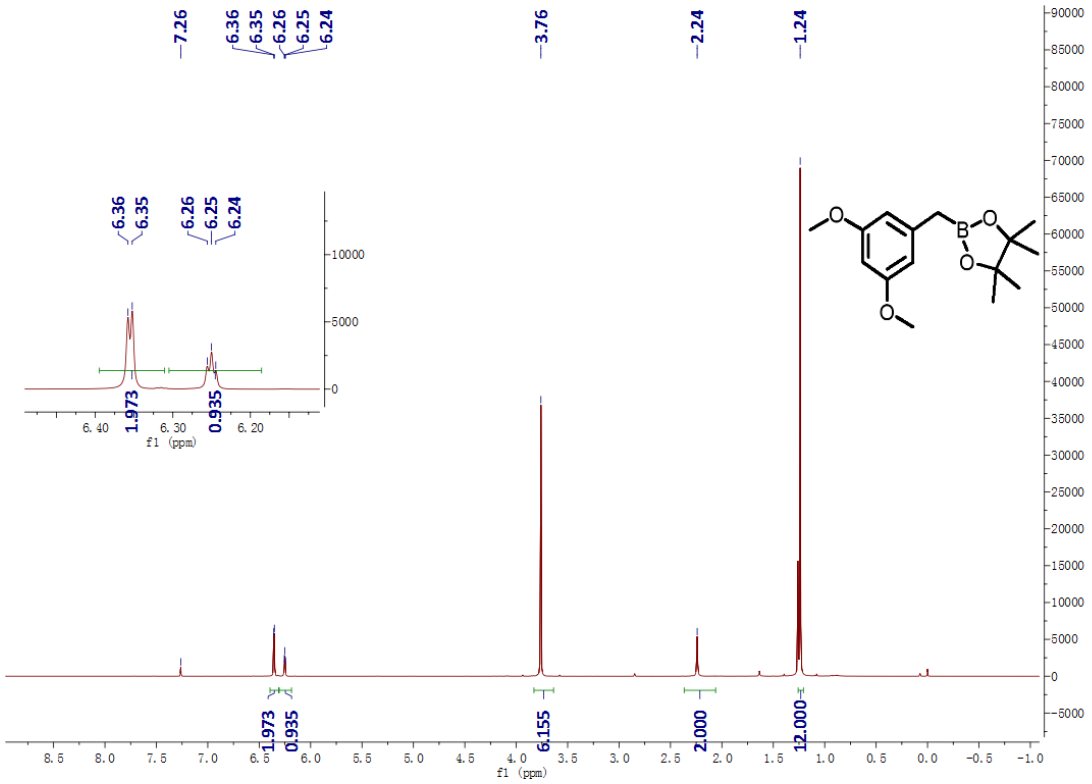
137.58
126.83
126.54
83.32
77.32
77.00
76.68
24.69
21.25
f1 (ppm)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6.35
6.26
6.25
6.24
3.76
2.24
1.24
1.973
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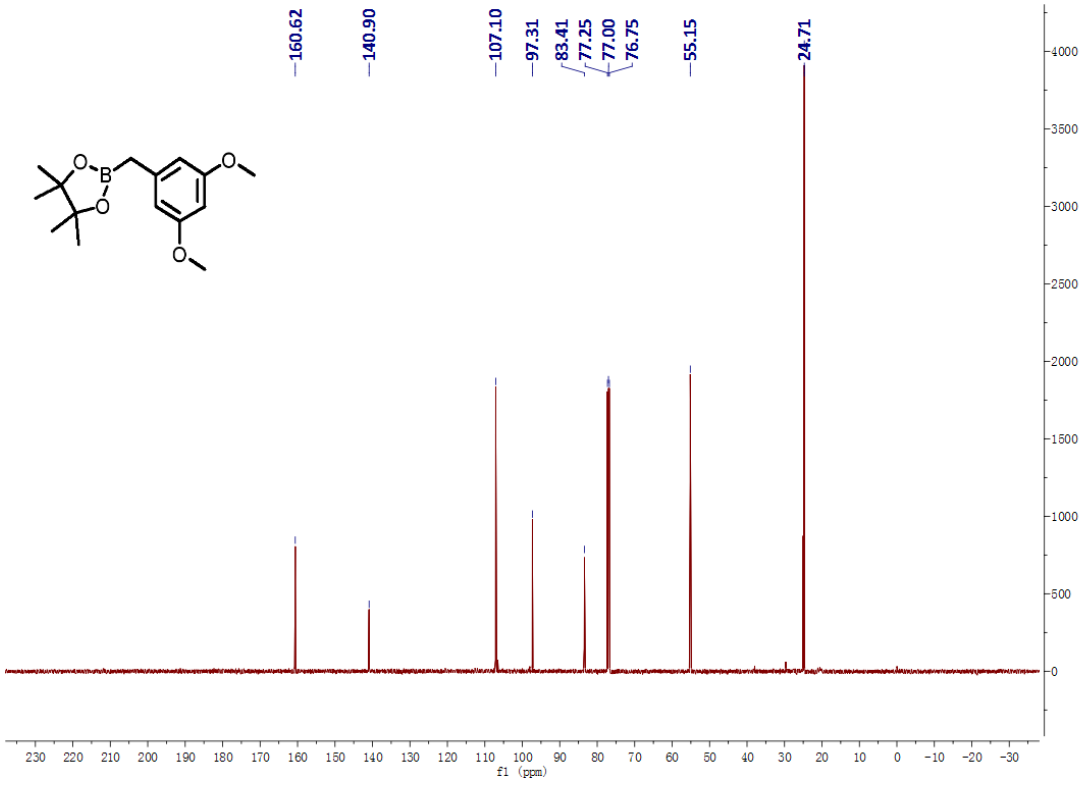
6.155
2.000
12.000
f1 (ppm)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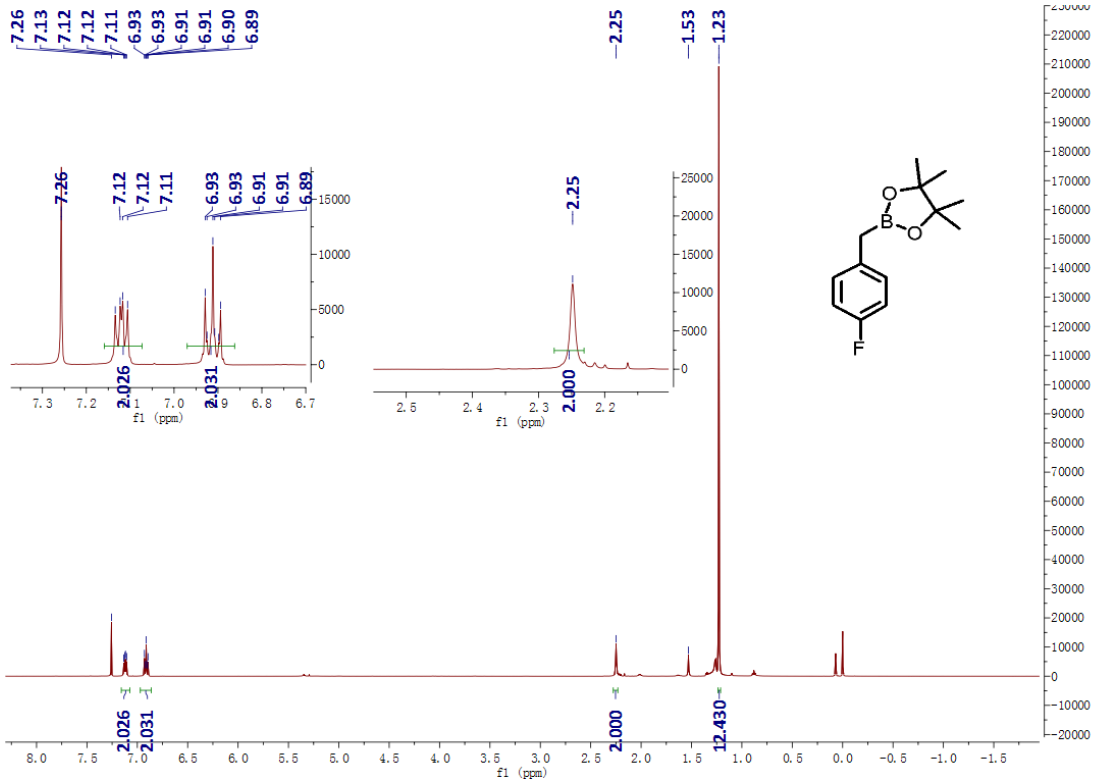
77.25
77.00
76.75
55.15
24.71
f1 (ppm)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7.13
7.12
7.12
7.11
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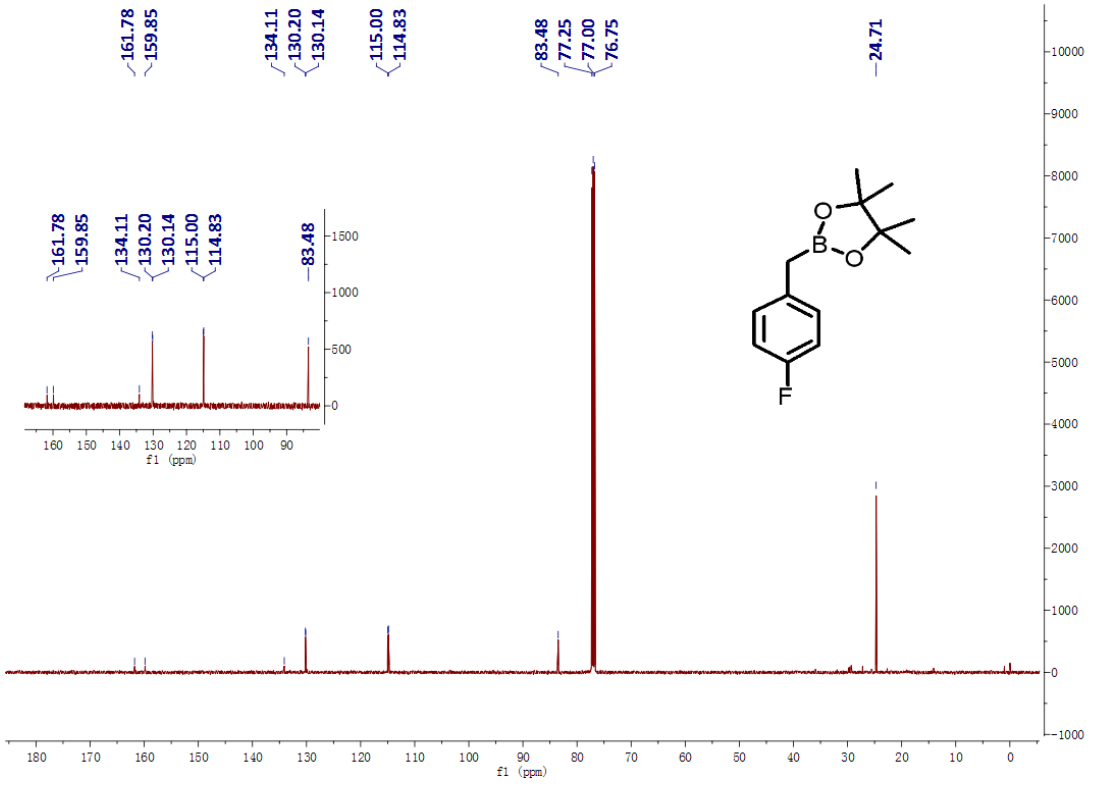
6.93
6.91
6.91
6.90
6.89
2.25
1.53
1.23
2.026
2.031
2.000
12.430
f1 (ppm)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130.14
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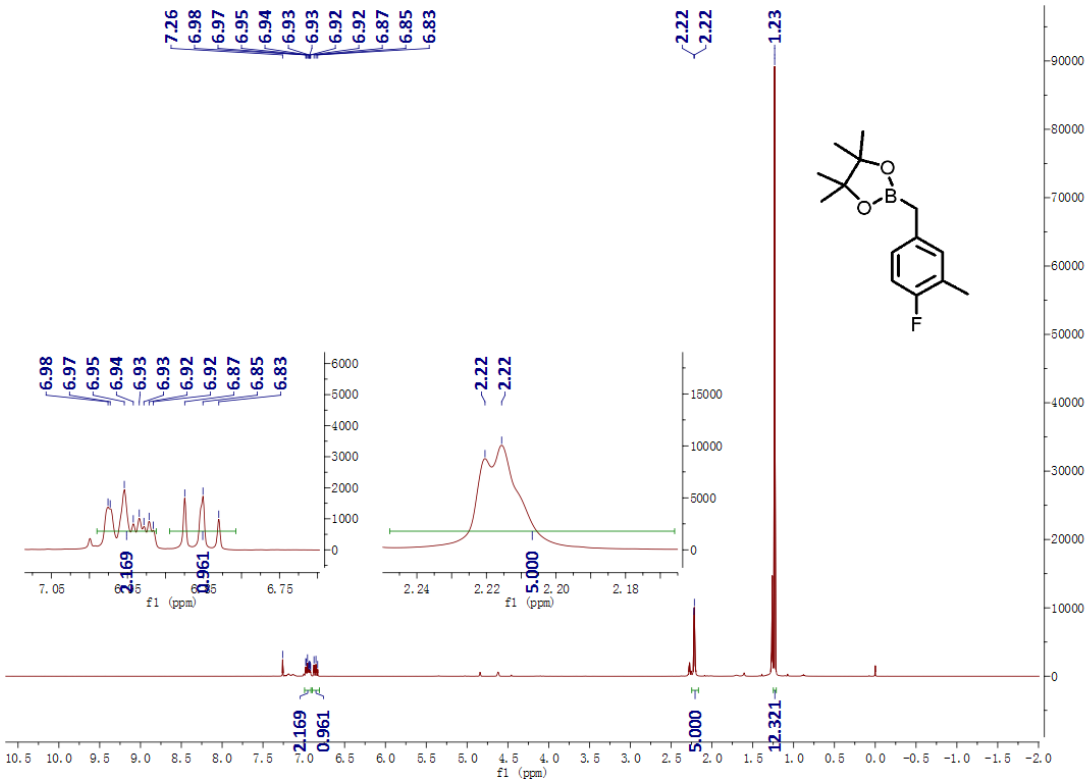
114.83
83.48
77.25
77.00
76.75
24.71
f1 (ppm)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6.95
6.94
6.93
6.93
6.92
6.92
6.87
6.85
6.83
2.22
2.22
1.23
F
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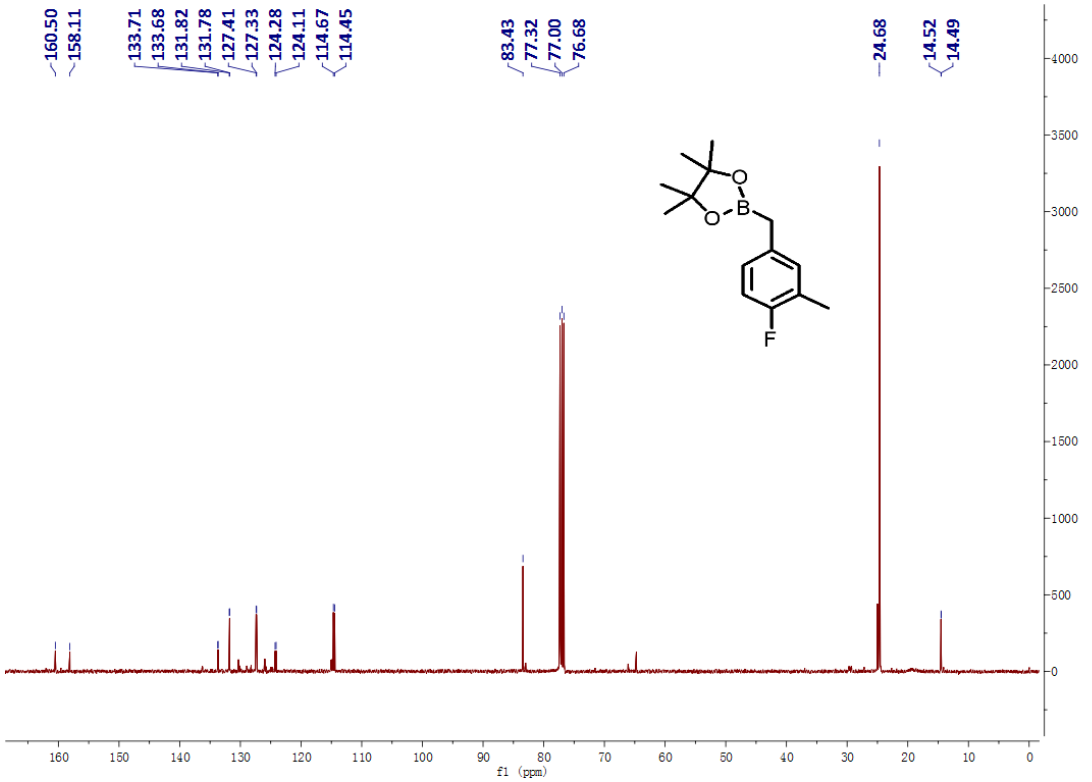
5.000
12.321
f1 (ppm)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133.71
133.68
131.82
131.78
127.41
127.33
124.28
124.11
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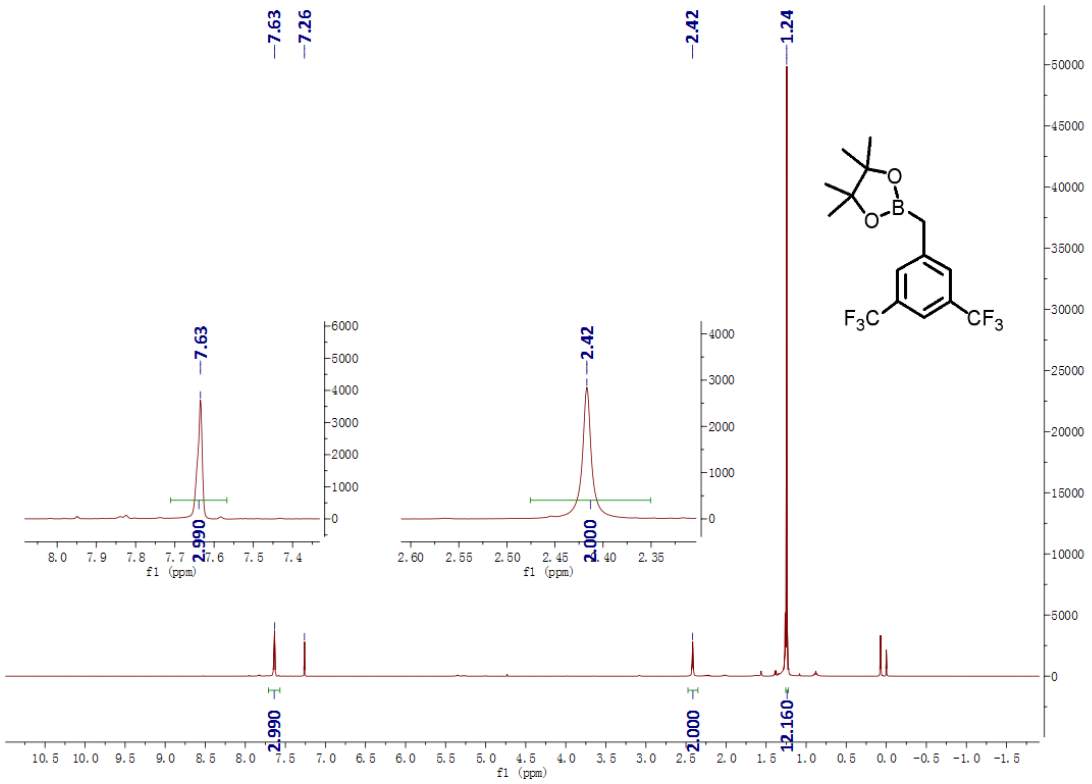
76.68
24.68
14.52
14.49
F
f1 (ppm)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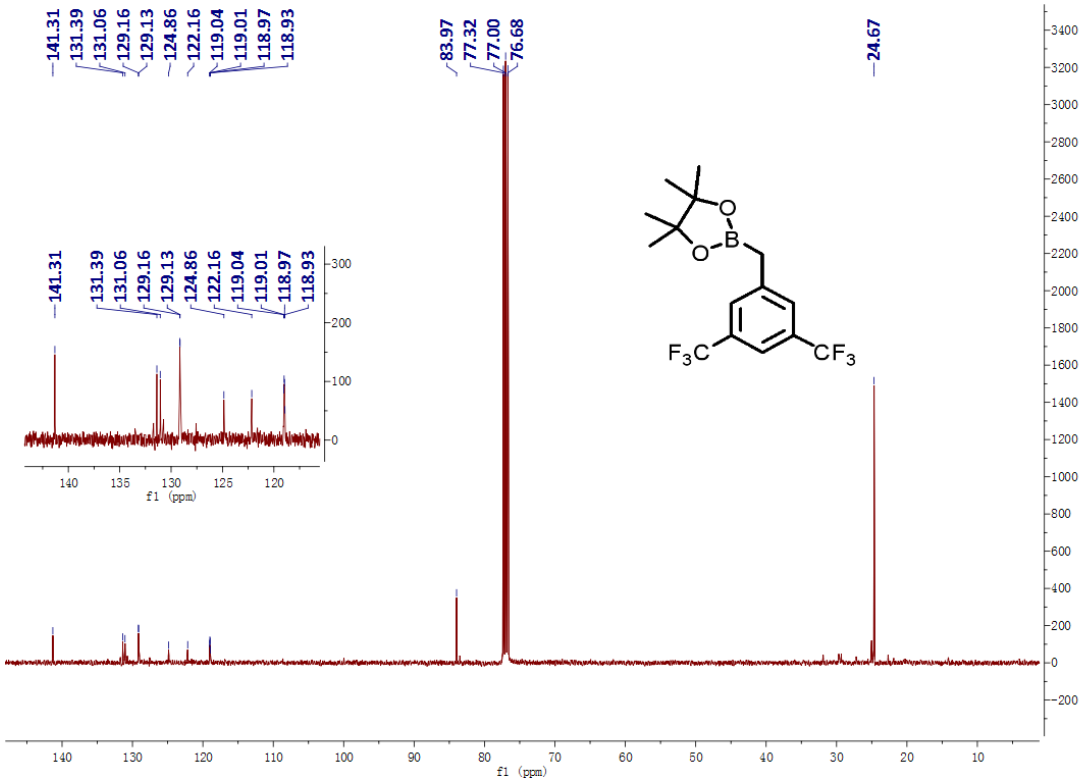
12.160
f1 (ppm)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131.39
131.06
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124.86
122.16
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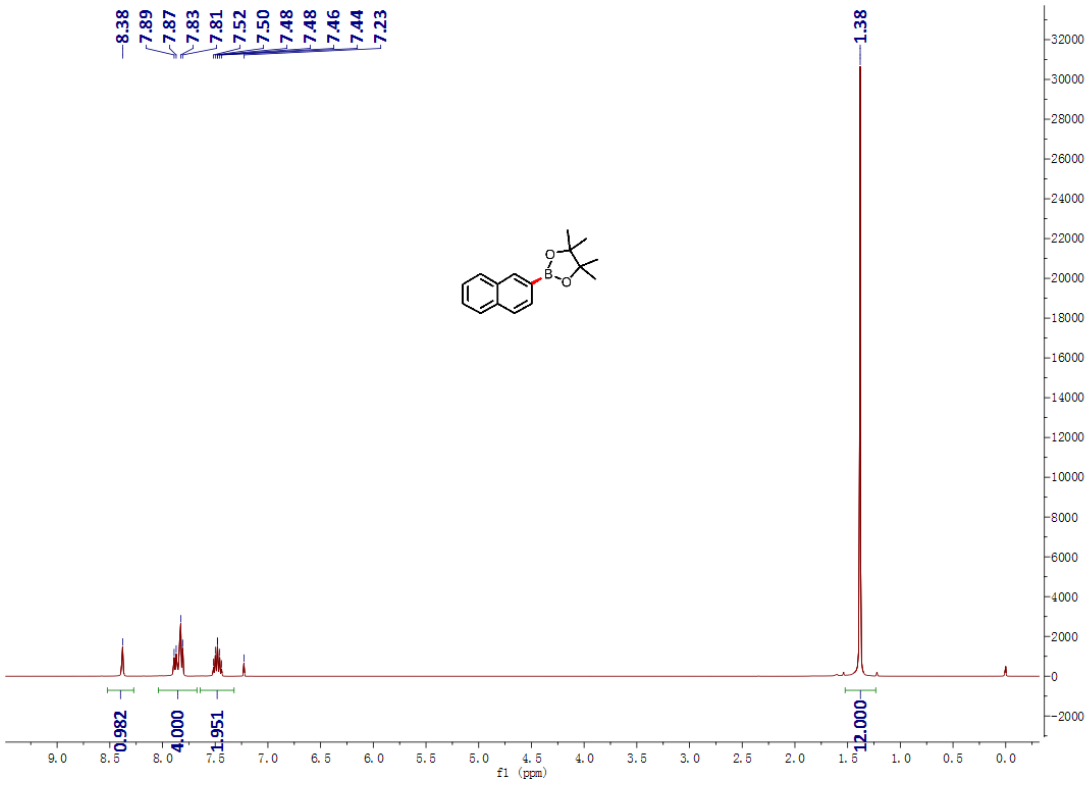
118.93
83.97
77.32
77.00
76.68
24.67
f1 (ppm)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7.52
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7.46
7.44
7.23
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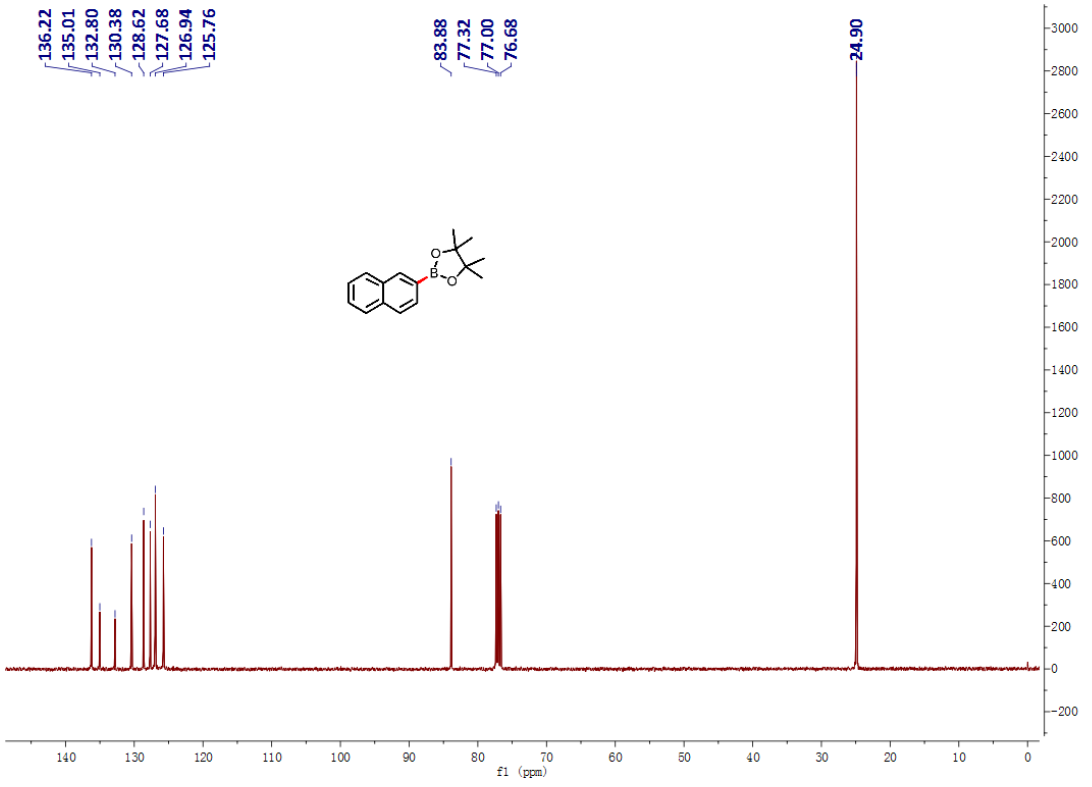
4.000
1.951
12.000
f1 (ppm)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130.38
128.62
127.68
126.94
125.76
83.88
77.32
77.00
76.68
24.90
f1 (ppm)