Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Metal-Free Borylation of Electron-Rich Aryl(pseudo)halides under Continuous-Flow Photolytic Conditions

Kai Chen,[†] Man Sing Cheung,[‡] Zhenyang Lin*[‡] and Pengfei Li*[†]

[†]Center for Organic Chemistry, Frontier Institute of Science and Technology (FIST). Xi'an Jiaotong University, 99 Yanxiang Road, Xi'an, Shaanxi, 710054, China

[‡]Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, P. R. China

Table of Contents

1. General Reagent Information

Commercial reagents were purchased from J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals, TCI and used as received unless otherwise stated. Acetone and MeCN were purchased from Acros Organics and used directly without further purification. Distilled water was degassed with sonication under vacuum and then backfilled with argon.

The mesylates, triflates, and phosphates used in this work were obtained following known procedures from the corresponding phenols by reaction with the suitable chlorides or anhydrides.[1-6]

2. General Analytical Information

NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents ($CDCl_3$) and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν max) are reported in wavenumbers (cm^{-1}). Melting points were determined with MP300, a laboratory Devices Inc, chinese instrument, and are uncorrected. High resolution mass spectra (HRMS) were obtained on a Bruker Apex IV FTMS spectrometer or an Agilent 6224 LC/MS TOF spectrometer.

3. General Information for Continuous Flow Setup

General Material Information

The equipment configuration that was used for the borylation reaction is depicted in Figures S1 and S2. The dual channels syringe pump (LSP02-1B) was purchased from Baoding Longer Precision Pump Company, which are suitable for high accuracy and small flow rate liquid transferring. The equipped devices (such as: quartz immersion well, 300 W high-pressure mercury lamp and accompanying power supply etc.) were part of the photochemistry instrument XPA-7 (Figures S3) which was purchased from Xujiang electromechanical plant (Nanjing, China). The transparent fluorinated ethylene propylene (FEP) tubing, fluidic connections and the back-pressure regulator were purchased from IDEX Health and Science, formerly Upchurch Scientific. The cooling liquid circulating pump (DLSB-5/10) was purchased from Zhengzhou Changcheng Scientific Industrial and Trade Co. Ltd. The E-series flow chemistry reaction system was a product of Vapourtec, UK.

General setup for the continuous-flow reactor (**Figure S1**)

A 300 W high-pressure mercury lamp is positioned in the center of a jacketed quartz immersion well using the cooling liquid circulating pump to regulate the reaction temperature. One layer of the transparent fluorinated ethylene propylene (FEP) tubing 1.0 m (1.6 mm OD; 1.0 mm ID; the internal volume 0.78 mL) is winded around the central part of the immersion well, and both ends of the tubing are extended with another 0.5 m FEP tubing. The rest part of the quartz immersion well was covered with aluminum foil. The reaction mixture is introduced into the tubing using a syringe pump at controlled flow rates and collected into a cylinder after passing through a 5-psi back pressure regulator.

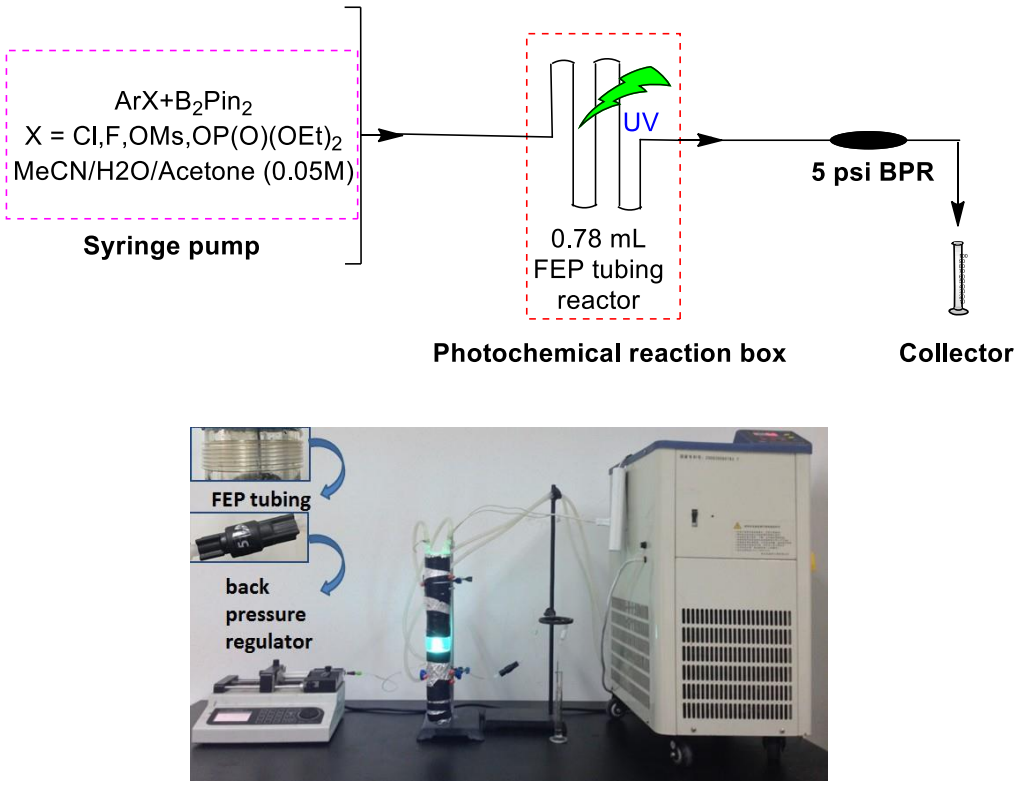


Figure S1. Schematic and pictorial photochemical flow reactor.
(Note: the UV lamp was safely placed in a box to prevent any possible injury.)

General setup for the gram-scale continuous-flow reactor (Figure S2)

A 300 W high-pressure mercury lamp is positioned in the center of a jacketed quartz immersion well using the cooling liquid circulating pump to regulate the reaction temperature. One layer of the transparent fluorinated ethylene propylene (FEP) tubing 1.0 m (1.6 mm OD; 1.0 mm ID; the internal volume 0.78 mL) is winded around the central part of the immersion well, and both ends of the tubing are extended with another 0.5 m FEP tubing. The rest part of the quartz immersion well was covered with aluminum foil. The reaction mixture is introduced into the tubing using the Vapourtec E-series flow chemistry reactor under a 5-psi pressure at controlled flow rates and finally into the collector.

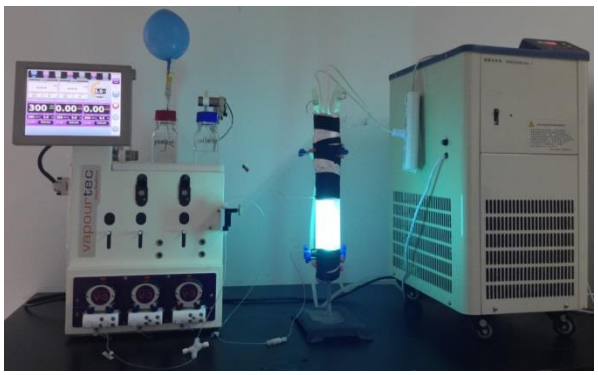


Figure S2. Gram scale photochemical flow reactor with the Vapourtec E-series.
(Note: the UV lamp was safely placed in a box to prevent any possible injury.)

4. Experimental Procedures

Typical batch procedure of the metal-free borylation using the set-up in Figure S3

A solution of the aryl chloride (0.1 mmol), B_2pin_2 (0.1-0.3 mmol), acetone (0.2 mL) and the additive reagents in MeCN and H_2O (4/1 v/v, 2.0 mL) was added into a quartz test tube containing a magnetic stirring bar and the mixture was purged with argon for 10 min. The tube was then capped with a septum. The reaction mixture was irradiated using a 300 W high-pressure mercury lamp through a water-cooled quartz immersion well for 10 h. Then the internal standard 1,3,5-trimethoxybenzene (0.1 mmol) was added into the crude product mixture for the ^{1}H NMR yield study.

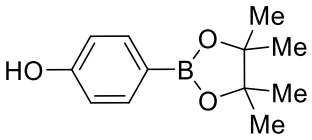
Figure S3. Photochemical batch reactor.

Typical procedure of the continuous metal-free borylation using the set-up in Figure S1

An oven-dried screw capping volumetric flask (10.0 mL) was charged with aryl (pseudo)halide **3** (0.455 mmol, if solid, 1 eq) and B_2pin_2 (0.91 mmol, 2 eq) then capped with a septum. The vessel was evacuated and back-filled with argon (this process was carried out a total of 3 times). **3** (0.455 mmol, if liquid, 1 eq), TMEDA (0.23 mmol, 0.5 eq), TBAF (0.046 mmol, 0.1 eq), acetone (0.9 mL) and H_2O (1.8 mL) were added by syringes and MeCN was added to dissolve the solids and filled up to volume. Before reaction all the solutions were prepared under argon atmosphere and the reactors tubing were purged with MeCN three times at least. After that, all reactors and connecting tubings were filled with MeCN. A 10 mL disposable syringe was used to pump the reaction solution through the continuous-flow reactor at controlled flow rates. A cooling liquid circulating pump is used to maintain the temperature around the tubing is -5 ^{o}C. After reaching steady state, a sample of the reaction mixture

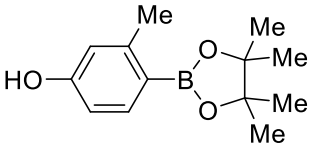
was collected which contained theoretical yield of 0.15 mmol based on flow rate and collecting time. The mixture was concentrated and usual workup and column chromatography produced the target boronate.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (3a).



[1] Following the general procedure for continuous metal-free borylation using the set-up in **Figure S1**, a syringe was loaded with a acetonitrile solution of 4-chlorophenol (58.5 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 30 μL/min. After steady state, a sample solution was collected into a collector for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:50 → EA/PE 1:10 → DCM/PE 1:2) to get the product **3a** (28.1 mg, 85%) as a white solid, mp 108-110 ^oC. [2] The borylation of 4-fluorophenol (51.0 mg, 0.455 mmol); flow rate: 20 μL/min; collecting time: 165 min; Yield: 24.8 mg, 75%. [3] The gram scale borylation of 4-chlorophenol using the set-up in **Figure S2**, Vapourtec E-series flow chemistry reactor was loaded with a solution of 4-chlorophenol (1.28 g, 10.0 mmol), B_2pin_2 (5.08 g, 20.0 mmol), TMEDA (740 μL, 2.5 mmol) and TBAF (1.0 mL, 1.0 mmol) in 200.0 mL MeCN / H_2O = 4/1 and 20.0 mL acetone. The flow rate was 300 μL/min. After steady state, a sample solution was collected into the collector for 9.87 h (177.6 mL, 8.0 mmol). Then the mixture was concentrated in vacuo and extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:50 → EA/PE 1:10 → DCM/PE 1:2) to get the product **3a** (1.53 g, 87%) as a white solid. Spectroscopical data was in accordance with the literature.[7] ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.71 (d, J = 7.6 Hz, 2H), 6.82 (d, J = 7.2 Hz, 2H), 5.14 (s, 1H), 1.33 (s, 12H).^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.1, 137.2, 114.8, 83.6, 24.7. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3367, 2979, 1608, 1360, 1143, 1087.

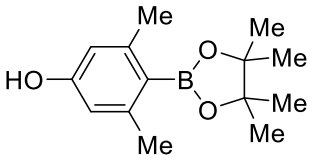
3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (3b).



Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 4-chloro-3-methylphenol (64.9 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:10 → DCM/PE 1:5) to get the product **3b** (25.0 mg, 71%) as a white solid, mp 84-86 ^oC. Spectroscopical data in accordance with the literature.[8] ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.67 (d, J = 7.6 Hz, 1H), 6.63-6.61 (m, 2H), 5.14 (s,

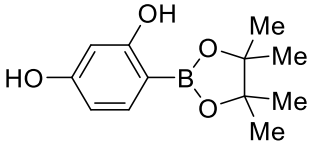
1H), 2.49 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 157.8, 147.6, 138.0, 116.7, 111.8, 83.2, 24.8, 22.2. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3384, 2978, 1603, 1398, 1145, 1063.

3,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (3c).



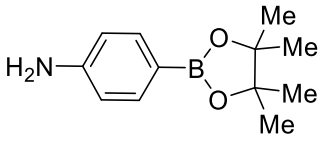
Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 4-chloro-3,5-dimethylphenol (71.3 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:10) to get the product **3c** (19.7 mg, 53%) as a white solid, mp 72-74 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.43 (s, 2H), 4.61 (s, 1H), 2.36 (s, 6H), 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 156.3, 144.7, 113.7, 83.4, 24.9, 22.3. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3384, 2978, 1608, 1333, 1143, 1070. HRMS (ESI^+): Calculated for $C_{14}H_{21}BO_3Na$ $(M+Na)^+$: 271.1481, Found: 271.1471.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,3-diol (3d).



Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 4-chlorobenzene-1,3-diol (65.8 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE (EA/PE 1:10 → EA/PE 1:5 → EA/PE 2:1) to get the product **3d** (21.6 mg, 61%) as a pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.90 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 6.34 (s, 1H), 5.03 (s, 1H), 1.35 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 165.5, 160.5, 137.3, 107.6, 102.1, 84.2, 25.0. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3446, 2981, 1623, 1373, 1144, 1065. HRMS (ESI^-): Calculated for $C_{12}H_{16}BO_4$ $(M-H)^-$: 235.1142, Found: 235.1146

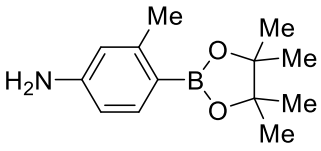
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3e).



[1] Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 4-chloroaniline (58.0 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume.

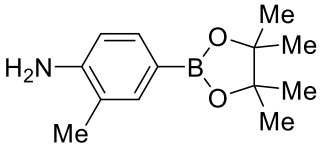
The flow rate was 30 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:50 → EA/PE 1:5 → DCM/PE 1:2) to get the product **3e** (27.6 mg, 84%) as a white solid, mp 134-136 ^{o}C. **[2]** The borylation of 4-fluoroaniline (50.6 mg, 0.455 mmol); flow rate: 20 μL/min; collected time: 165 min; the product **3e** (25.0 mg, 76%). Spectroscopical data in accordance with the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.62 (d, *J* = 7.6 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 2H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 149.2, 136.5, 114.1, 83.3, 25.0. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3450, 2977, 1603, 1360, 1143, 1087.

3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3f)



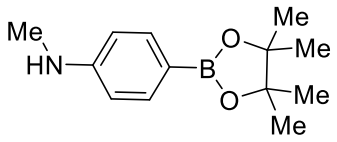
Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 4-chloro-3-methylaniline (64.4 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:10) to get the product **3f** (18.9 mg, 54%) as a white solid, mp 58-60 ^{o}C. Spectroscopical data in accordance with the literature.[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.59 (d, *J* = 8.4 Hz, 1H), 6.48 (s, 2H), 3.74 (s, 2H), 2.45 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.8, 146.9, 137.9, 116.2, 111.3, 82.8, 24.9, 22.3. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3374, 2978, 1603, 1351, 1147, 1061.

2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3g).



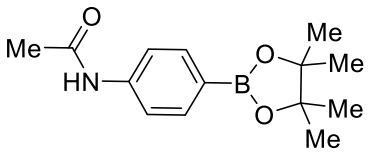
Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 4-chloro-2-methylaniline (64.4 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:10 → DCM/PE 1:5) to get the product **3g** (23.1 mg, 66%) as a white solid, mp 78-80 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.52-7.49 (m, 2H), 6.65 (d, *J* = 7.6 Hz, 1H), 3.79 (s, 2H), 2.16 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 147.6, 137.2, 134.1, 121.1, 113.9, 83.2, 24.8, 17.0. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3379, 2978, 1606, 1356, 1144, 1094. HRMS (ESI^{+}): Calculated for $C_{13}H_{20}BNO_2Na$ $(M+Na)^{+}$: 256.1485, Found: 256.1474

N-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3h).



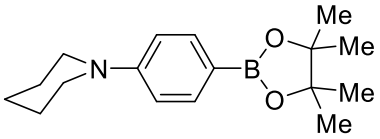
Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 4-chloro-N-methylaniline (64.4 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:20→ EA/PE 1:10→DCM/PE 1:2) to get the product **3h** (19.2 mg, 55%) as a pale yellow viscous liquid. Spectroscopical data in accordance with the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.65 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 3.99 (s, 1H), 2.85 (s, 3H) 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 151.7, 136.3, 111.4, 83.1, 30.3, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3418, 2979, 1607, 1361, 1144, 1048.

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



Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of N-(4-chlorophenyl)acetamide (77.2 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:2) to get the product **3i** (26.2 mg, 67%) as a white solid, mp 188-190 ^{o}C. Spectroscopical data in accordance with the literature.[12]
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.76 (d, *J* = 8.4 Hz, 2H), 7.51(d, *J* = 8.0 Hz, 2H), 7.24 (s, 1H), 2.18 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 168.2, 140.5, 135.8, 118.5, 83.7, 29.7, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3309, 2980, 1595, 1362, 1145, 1091.

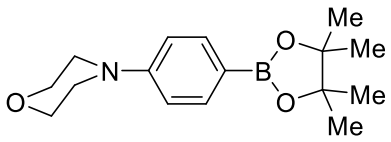
1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperidine (3j).



Following the general continuous borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 1-(4-chlorophenyl)piperidine (89.0 mg, 0.455 mmol), B_2pin_2 (345.7 mg, 1.36 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (455 μL, 0.455 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 30 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:20 → EA/PE 1:10) to get the

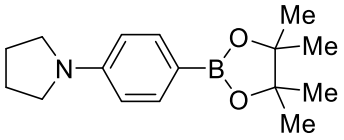
product **3j** (24.1 mg, 56%) as a pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.68 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 3.24 (t, *J* = 4.8, 4H), 1.73 - 1.57 (m, 6H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 153.9, 136.1, 114.5, 83.2, 49.4, 25.5, 24.8, 24.4. Carbon bearing boron not observed. IR (neat, cm^{-1}): 2977, 2936, 1606, 1363, 1145, 1129. HRMS (ESI^+): Calculated for $C_{17}H_{27}BNO_2$ $(M+H)^+$: 288.2135, Found: 288.2118

4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)morpholine (3k).



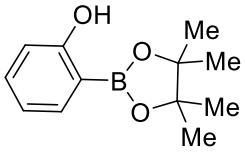
Following the general continuous borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 4-(4-chlorophenyl)morpholine (89.9 mg, 0.455 mmol), B_2pin_2 (345.7 mg, 1.36 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (455 μL, 0.455 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 30 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:20 → EA/PE 1:10) to get the product **3k** (22.1 mg, 51%) as a white solid, mp 101-103 ^{o}C. Spectroscopical data in accordance with the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.72 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.85 (t, *J* = 5.0 Hz, 4H), 3.22 (t, *J* = 4.8 Hz, 4H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 153.3, 136.1, 114.1, 83.4, 66.8, 48.3, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 2977, 2826, 1606, 1363, 1145, 1124.

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



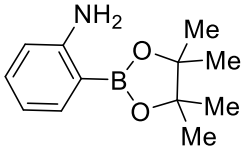
Following the general continuous borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 1-(4-chlorophenyl)pyrrolidine (82.7 mg, 0.455 mmol), B_2pin_2 (345.7 mg, 1.36 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (455 μL, 0.455 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 30 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:20 → EA/PE 1:10) to get the product **3l** (19.3 mg, 47%) as a pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.67 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 3.31 (t, *J* = 6.2 Hz, 4H), 1.99 (t, *J* = 6.6 Hz, 4H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 150.0, 136.2, 110.9, 83.1, 47.3, 25.4, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 2796, 2835, 1605, 1361, 1144, 1091. HRMS (ESI^+): Calculated for $C_{16}H_{25}BNO_2(M+H)^+$: 274.1978, Found: 274.1963

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (3m).



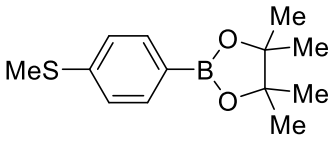
Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 2-chlorophenol (58.5 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:10 → DCM/PE 1:2) to get the product **3m** (12.3 mg, 37%) as a white liquid. Spectroscopical data in accordance with the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.81 (s, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.89 - 6.87 (m, 2H), 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 163.6, 135.7, 133.8, 119.5, 115.4, 84.4, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3447, 2980, 1619, 1357, 1141, 1107.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3n).



Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 2-chloroaniline (58.0 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:50 → EA/PE 1:20 → DCM/PE 1:2) to get the product **3n** (11.5 mg, 35%) as a pale yellow solid, mp 67-69 ^{o}C. Spectroscopical data in accordance with the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 4.73 (s, 2H), 1.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 153.6, 136.8, 132.7, 116.8, 114.7, 83.5, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3446, 2980, 1618, 1358, 1142, 1103.

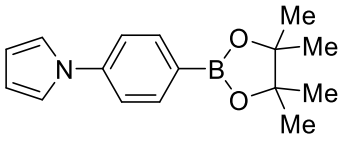
4,4,5,5-tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (3o).



Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of (4-chlorophenyl)(methyl)sulfane (72.2 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:20 → EA/PE 1:10 → DCM/PE 1:5) to get the product **3o** (13.5 mg, 36%) as a pale yellow liquid. Spectroscopical data in accordance with the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.71 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 2.49 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 142.5, 135.1, 125.0,

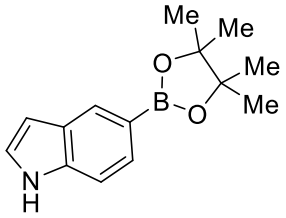
83.7, 24.8, 15.1. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3446, 2979, 1597, 1360, 1144, 1103.

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-pyrrole (3p).



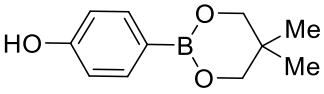
Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 1-(4-chlorophenyl)-1H-pyrrole (80.8 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layers were dried with sodium sulfate, filtered and concentrated in vacuo. The residue was purified by column chromatography (EA/PE 1:10 → DCM/PE 1:3) to get the product **3p** (20.2 mg, 50%) as a white solid, mp 121-123 °C. Spectroscopical data in accordance with the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.86 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.14 (s, 2H), 6.38 (s, 2H), 1.36 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.0, 136.2, 119.2, 119.1, 110.7, 83.9, 25.0. Carbon bearing boron not observed. IR (neat, cm^{-1}): 2979, 2930, 1608, 1362, 1144, 1103.

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (3q).



Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 5-chloro-1H-indole (69.0 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:50 → EA/PE 1:15 → DCM/PE 1:5) to get the product **3q** (9.1 mg, 25%) as a white solid, mp 133-134 °C. Spectroscopical data in accordance with the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.22 (s, 1H), 8.20 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 6.57 (s, 1H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 137.9, 128.6, 128.0, 127.6, 124.2, 110.4, 103.1, 83.5, 24.9. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3419, 2979, 1614, 1356, 1146, 1101.

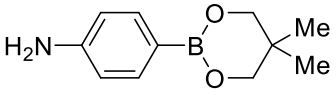
4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenol (3r).



Following the general continuous metal-free borylation procedure using the set-up in **Figure S1**, syringe was loaded with a solution of 4-chlorophenol (58.5 mg, 0.455 mmol),

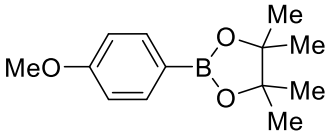
5,5,5',5'-tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (205.6 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 30 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:10) to get the product **3v** (20.1 mg, 65%) as a white solid, mp 125-128 ^{o}C. Spectroscopical data in accordance with the literature.[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.70 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 7.2 Hz, 2H), 4.95 (s, 1H), 3.75 (s, 4H), 1.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 157.8, 135.8, 114.6, 72.2, 31.9, 21.9. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3392, 2962, 1606, 1344, 1171, 1134.

4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)aniline (3s).



Following the general continuous metal-free borylation procedure using the set-up in **Figure S1**, syringe was loaded with a solution of 4-chloroaniline (58.0 mg, 0.455 mmol), 5,5,5',5'-tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (205.6 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 30 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:10) to get the product **3w** (16.9 mg, 55%) as a pale yellow solid, mp 128-130 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.61(d, *J* = 7.6 Hz, 2H), 6.66 (d, *J* = 7.6 Hz, 2H), 3.82 (s, 2H), 3.73 (s, 4H), 1.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.8, 135.4, 114.1, 72.2, 31.9, 21.9. Carbon bearing boron not observed. IR (neat, cm^{-1}): 3471, 3373, 1603, 1344, 1296, 1131. HRMS (ESI^+): Calculated for $C_{11}H_{17}BNO_2$ $(M+H)^+$: 206.1352, Found: 206.1343.

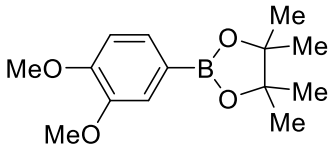
2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t).



[1] Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 1-chloro-4-methoxybenzene (64.9 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:50 → DCM/PE 1:20) to get the product **3t** (14.8 mg, 42%) as a pale yellow liquid. Spectroscopical data in accordance with the literature.[7] **[2]** The borylation of mesylate **1t** (92.0 mg, 0.455 mmol); flow rate: 15 μL/min; collected time: 220 min; the product **3t** (16.2 mg, 46%). **[3]** The borylation of phosphate **1t** (118.4 mg, 0.455 mmol); flow rate: 15 μL/min; collected time: 220 min; the product **3t** (16.8 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.76 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H).

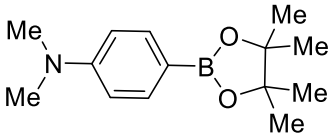
^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 162.3, 137.0, 113.4, 83.5, 55.2, 25.0. Carbon bearing boron not observed. IR (neat, cm^{-1}): 2978, 1605, 1360, 1143, 1091, 1030.

2-(3,4-dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3u).



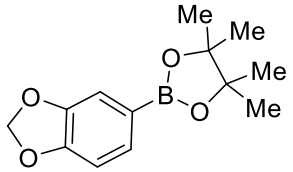
[1] Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of mesylate **1u** (105.7 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 15 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 220 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:50 → DCM/PE 1:20) to get the product **3u** (22.2 mg, 56%) as a pale yellow liquid. Spectroscopical data in accordance with the literature.[15] **[2]** The borylation of phosphate **1u** (132.1 mg, 0.455 mmol); flow rate: 15 μL/min; collected time: 220 min; the product **3u** (22.6 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.42 (d, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 9.2 Hz, 6H), 1.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 151.7, 148.4, 128.6, 116.6, 110.5, 83.6, 55.9, 55.7, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 2978, 1604, 1356, 1141, 1091, 1029.

N,N-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3v).



Following the general continuous borylation procedure using the set-up in Figure S1, a syringe was loaded with an acetonitrile solution of 4-chloro-N,N-dimethylaniline (70.8 mg, 0.455 mmol), B_2pin_2 (345.7 mg, 1.36 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (455 μL, 0.455 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 30 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 110 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:50 → EA/PE 1:10) to get the product **3v** (21.9 mg, 59%) as a white solid, mp 94-96 ^{o}C. Spectroscopical data in accordance with the literature.[8]**[2]** Following the general continuous metal-free borylation procedure using the set-up in Figure S1. The borylation of 4-fluoro-N,N-dimethylaniline (63.3 mg, 0.455 mmol); flow rate: 20 μL/min; collected time: 165 min; the product **3r** (19.7 mg, 53%). **[3]** Following the general continuous metal-free borylation procedure using the set-up in Figure S1. The borylation of mesylate **1r** (97.9 mg, 0.455 mmol); flow rate: 15 μL/min; collected time: 220 min; the product **3r** (16.7 mg, 45%). **[4]** Following the general continuous metal-free borylation procedure using the set-up in Figure S1. The borylation of phosphate **1r** (124.3 mg, 0.455 mmol); flow rate: 15 μL/min; collected time: 220 min; the product **3r** (18.2 mg, 49%) and product **3g** (4.6 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.69 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 2.98 (s, 6H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 152.5, 136.1, 111.2, 83.1, 40.1, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 2978, 1605, 1361, 1247, 1143, 1030.

2-(benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3w).



[1] Following the general continuous metal-free borylation procedure using the set-up in Figure S1, syringe was loaded with a solution of 5-chlorobenzo[d][1,3]dioxole (71.2 mg, 0.455 mmol), B_2pin_2 (231.3 mg, 0.91 mmol), TMEDA (35 μL, 0.23 mmol) and TBAF (46 μL, 0.046 mmol, 1M in THF) in 10.0 mL volume. The flow rate was 20 μL/min. After steady state, a sample solution was collected into a graduated cylinder for 165 min (3.3 mL, 0.15 mmol). Then 0.5 mL brine was added, the mixture was extracted with ethyl acetate. The combined organic layer were dried with sodium sulfate, filtered and concentrated in vacuo then purified by column chromatography (EA/PE 1:10 → DCM/PE 1:10) to get the product **3s** (25.3 mg, 68%) as a pale yellow liquid. Spectroscopical data in accordance with the literature.[9] **[2]** The borylation of mesylate **1s** (98.4 mg, 0.455 mmol); flow rate: 15 μL/min; collected time: 220 min; the product **3s** (20.1 mg, 54%). **[3]** The borylation of phosphate **1s** (124.8 mg, 0.455 mmol); flow rate: 15 μL/min; collected time: 220 min; the product **3s** (16.7 mg, 45%). **[4]** The borylation of triflate **1s** (122.9 mg, 0.455 mmol); flow rate: 15 μL/min; collected time: 220 min; the product **3s** (8.2 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.36 (d, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 2H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 150.1, 147.2, 129.7, 113.9, 108.2, 100.7, 83.7, 24.8. Carbon bearing boron not observed. IR (neat, cm^{-1}): 2979, 1605, 1356, 1144, 1106, 1039.

5. DFT Computational Details

All molecular geometries were optimized without constraints via density functional theory (DFT) calculations using the UBecke3LYP (UB3LYP) functional.[16] The effective core potentials (ECPs) of Hay and Wadt with the double-ζ valence basis sets (LanL2DZ)[17] were used to describe Cl. The 6-311G* Pople basis set[18] was used for B and those C atoms involved in the bond breaking and making processes, while the standard 6-31G basis set[19] was used for all other atoms. Polarization functions were added for Cl (ζ_d = 0.640).[20] Frequency calculations were carried out to confirm all of the optimized structures are either minima (zero imaginary frequency) or transition-states (one imaginary frequency) as specified, and to provide free energies at 298.15 K including entropy contributions. Calculations of intrinsic reaction coordinates (IRC)[21] were also performed to confirm that all the transition-states indeed connect two relevant minima. All of the calculations mentioned were performed with the Gaussian 09 software package.[22]

Photolytic borylation of electron-rich aryl halides involve state crossing between triplet and singlet states. Reactants normally have a triplet ground state, while products are usually in a singlet state. We employed a code developed by Harvey and co-workers to optimize the geometry of minimum energy crossing points (MECPs) between potential energy surfaces of different spin states.[23]

To consider solvent effects, we employed a continuum medium to perform single-point energy

calculations for all optimized species using UAKS radii on the conductor-like polarizable continuum model (CPCM).[24] Acetonitrile was used as solvent, corresponding to the experimental conditions.

Because of the entropic contributions, the relative free energies and relative electronic energies are significantly different in cases where the numbers of reactant and product molecules are not equal. Gas-phase calculations often overestimate the entropic contribution, and therefore we applied corrections to the calculated gas-phase free energies.[25] A correction of -2.6 (or 2.6) kcal/mol at T = 298.15 K was made for two-to-one (or one-to-two) transformations as employed in a number of earlier theoretical studies.[26]

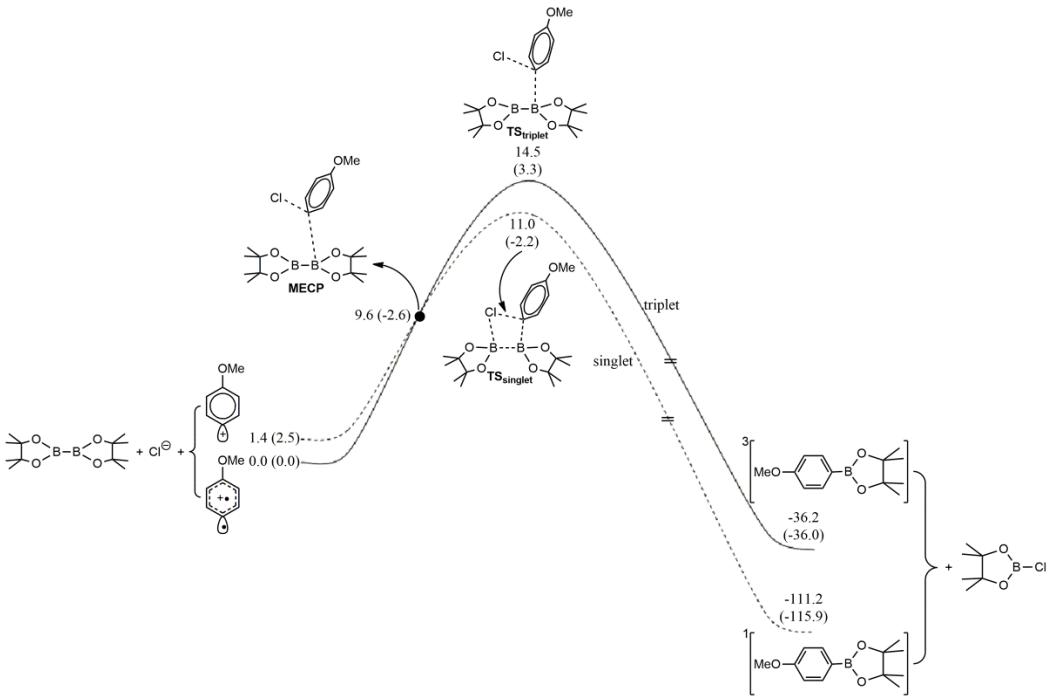


Figure S4. Energy profiles calculated for borylation of the singlet and triplet aryl cations. The relative solvation- and entropy-corrected free energies and solvation-corrected electronic energies (in parentheses) are given in kcal/mol.

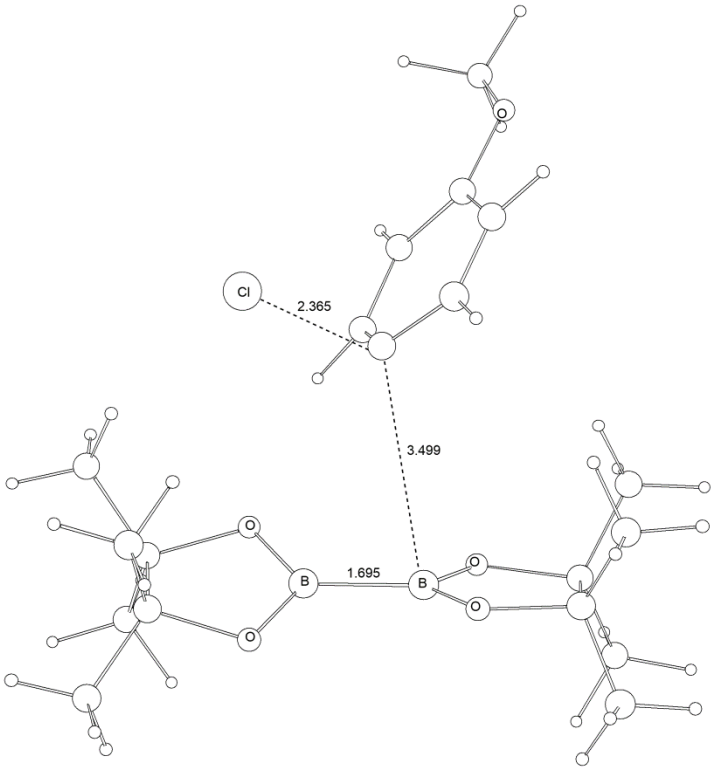


Figure S5. Structure calculated for the minimum energy crossing point (**MECP**). Selected bond distances are given in Å.

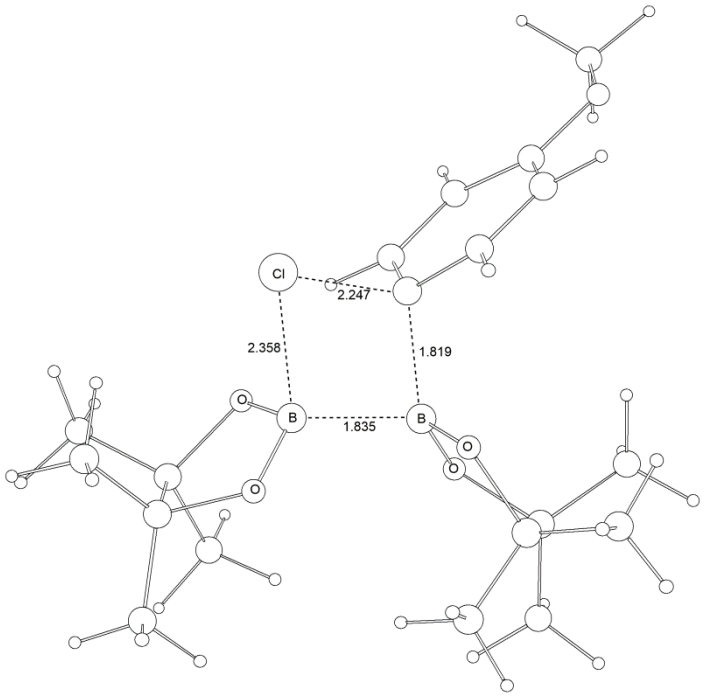


Figure S6. Structure calculated for $\mathbf{TS_{singlet}}$. Selected bond distances are given in Å.

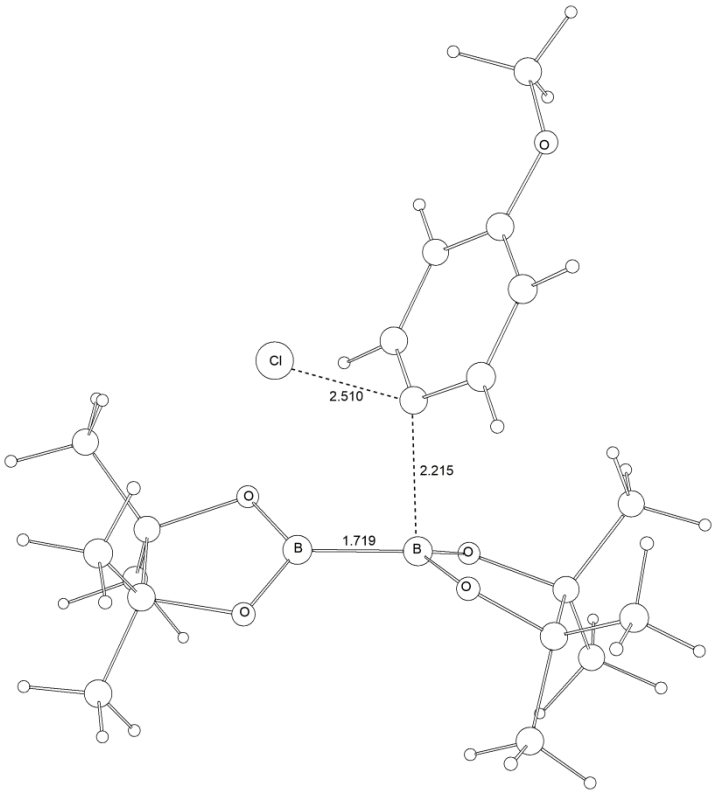


Figure S7. Structure calculated for $\mathbf{TS_{triplet}}$. Selected bond distances are given in Å.

6. References

[1] A. M. Echavarren, J. K. Stille, *J. Am. Chem. Soc*. **1987**, *109*, 5478.

[2] D. A. Wilson, C. J. Wilson, C. Moldoveanu, A. M. Resmerita, P. Corcoran, L. M. Hoang, B. M. Rosen, V. Percec, *J. Am. Chem. Soc*. **2010**, *132*, 1800.

[3] R. K. Crossland, K. L. Servis, *J. Org. Chem*. **1970**, *35*, 3195.

[4] G. A. Molander, F. Beaumard, *Org. Lett.* **2011**, *13*, 3948.

[5] D. E. Frantz, D. G. Weaver, J. P. Carey, M. H. Kress, U. H. Dolling, *Org. Lett.* **2002**, *4*, 4717.

[6] A. Mori, T. Mizusaki, T. Ikawa, T. Maegawa, Y. Monguchi, H. Sajiki, *Tetrahedron*. **2007**, *63*, 1270.

[7] K. L. Billingsley, T. E. Barder, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2007**, *46*, 5359.

[8] J. Lu, Z. Guan, J. Gao, Z. Zhang, Appl. Organometal. Chem. **2011**, *25*, 537.

[9] D. Qiu, L. Jin, Z. Zheng, H. Meng, F. Mo, X. Wang, Y. Zhang, J. Wang, *J. Org. Chem.* **2013**, *78*, 1923.

[10] D. Qiu, S. Wang, S. Tang, H. Meng, L. Jin, F. Mo, Y. Zhang, J. Wang, *J. Org. Chem*. **2014**, *79*, 1979.

[11] M. Miki, S. Tomoko, W. Shinji, M. Yuzuru, *Synlett*. **2006**, *12*, 1867.

[12] F. Mo, Y. Jiang, D. Qiu, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 1846.

[13] T. Yamamoto, T. Morita, J. Takagi, T. Yamakawa, *Org. Lett.* **2011**, *13*, 5766.

[14] C. Moldoveanu, D. A. Wilson, C. J. Wilson, P. Corcoran, B. M. Rosen, V, Percec, *Org. Lett.* **2009**, *11*, 4974.

[15] N. R. Anastasi, J. F. Hartwig, *J. Am. Chem. Soc*. **2002**, *124*, 390.

[16] (a) A. D. Becke, *J. Chem. Phys*, **1993**, *98*, 5648. (b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200. (c) C. Lee, W. Yang, G. Parr, *Phys. Rev. B* **1988**, *37*, 785. (d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, *J. Phys. Chem.* **1994**, *98*, 11623.

[17] (a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270. (b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284. (c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

[18] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650.

[19] (a) M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163. (b) P. C. Hariharan, J. A.Pople, *Theor. Chim. Acta* **1973**, *28*, 213. (c) R. C. Binning, L. A. Curtiss, *J. Comput. Chem.* **1990**, *11*, 1206.

[20] A. Höllwarth, H. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 237.

[21] (a) K. Fukui, *J. Phys. Chem.* **1970**, *74*, 4161. (b) K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363.

[22] M. J. Frisch, et al. *Gaussian 09, revision D.01*; Gaussian, Inc., Pittsburgh, PA, **2009**.

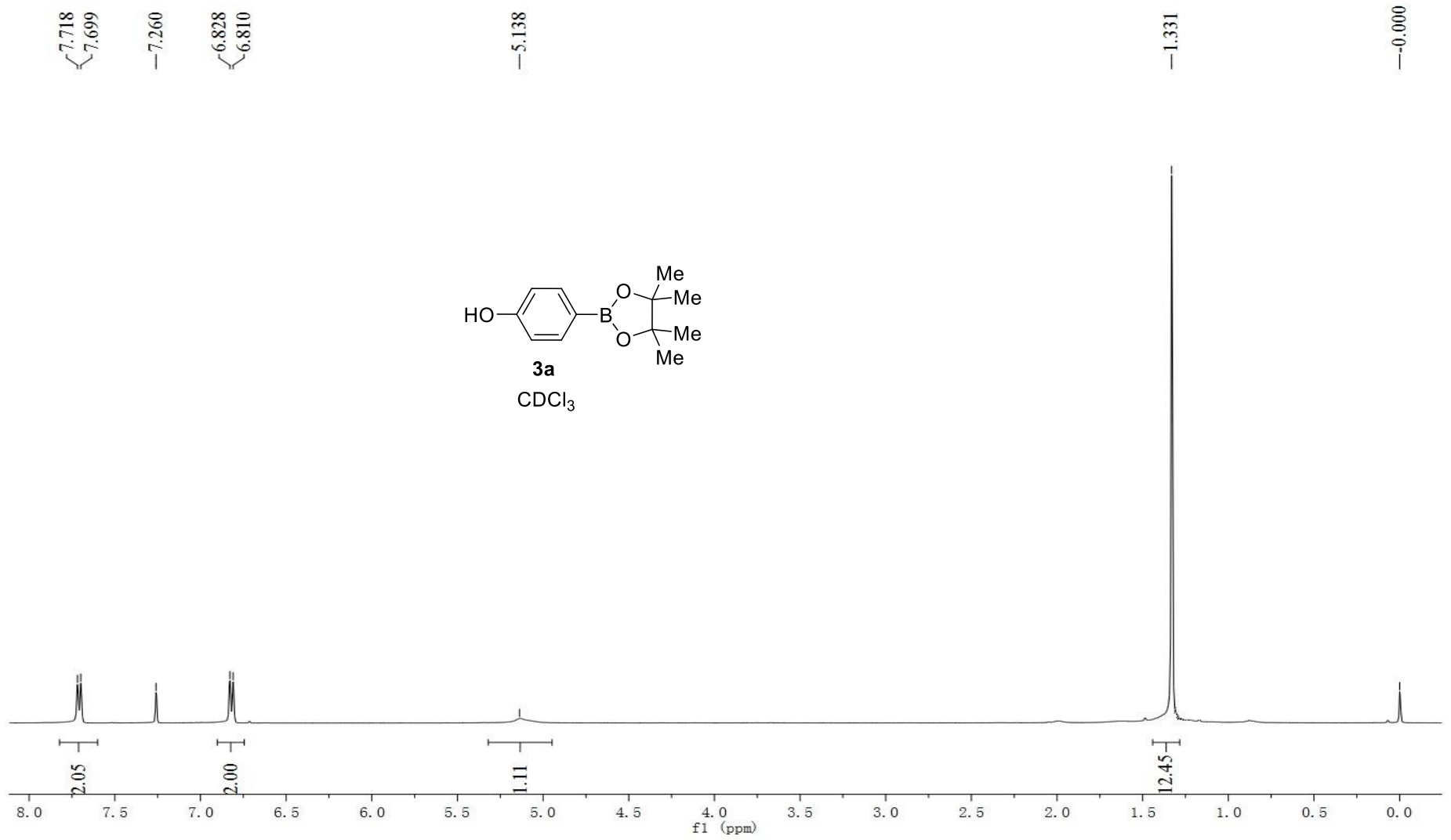
[23] (a) J. N. Harvey, M. Aschi, H. Schwarz, W. Koch, *Theor. Chem. Acc.* **1998**, *99*, 95. (b) J. N. Harvey, M. Aschi, *Phys. Chem. Chem. Phys.* **1999**, *1*, 5555.

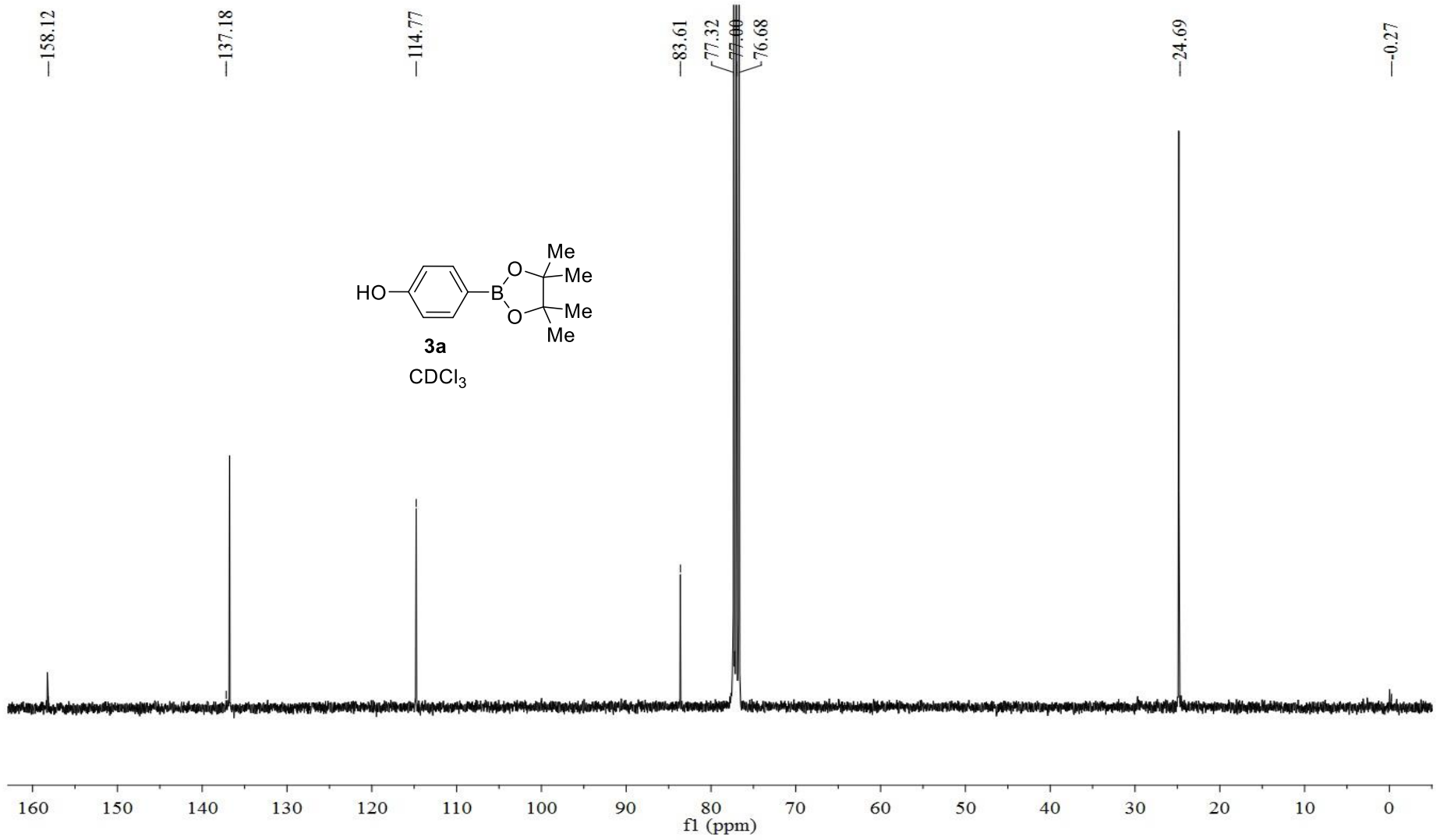
[24] (a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995. (b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669.

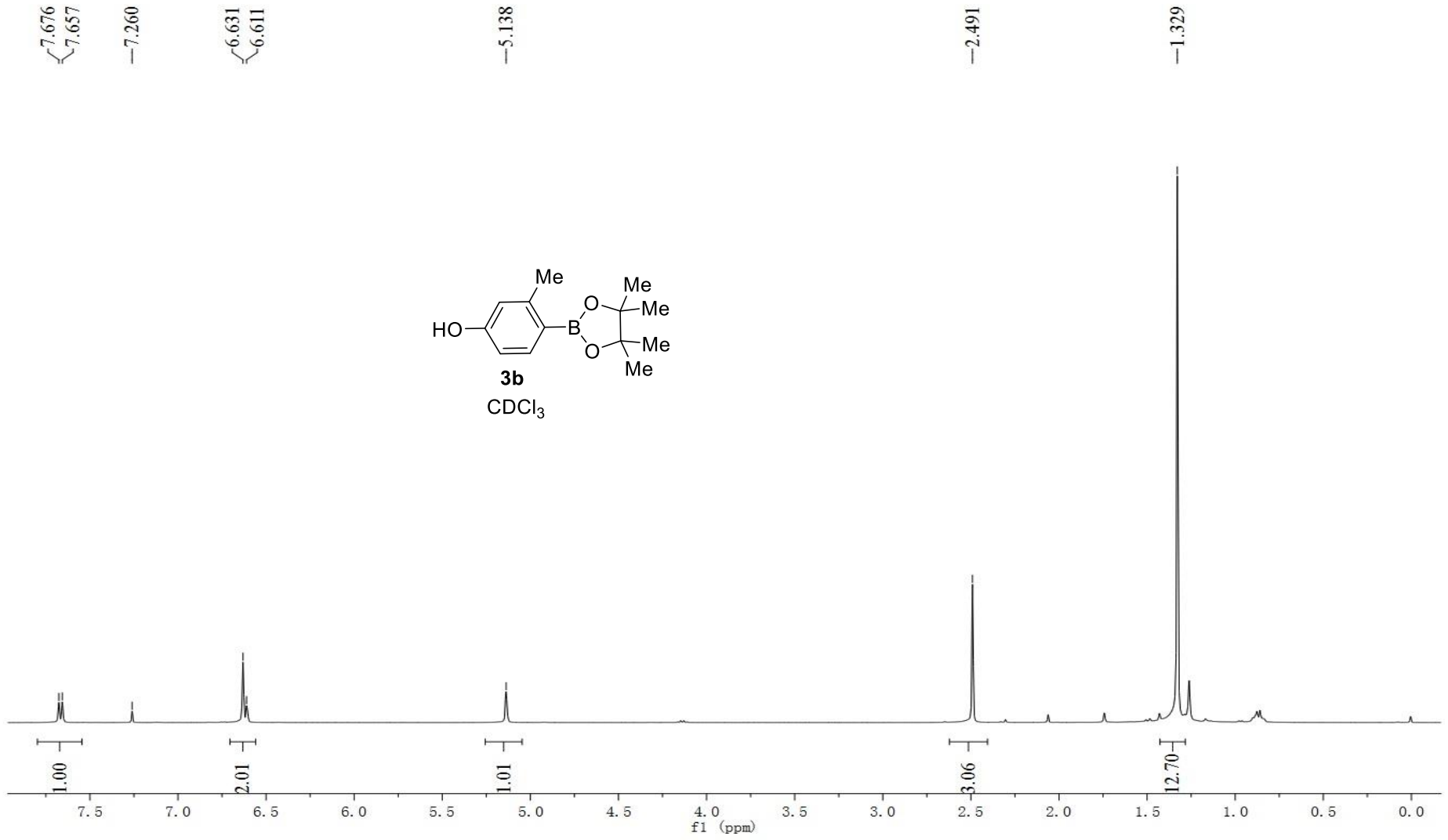
[25] S. W. Benson, *The Foundations of Chemical Kinetics*; Krieger: Malabar, FL, 1982.

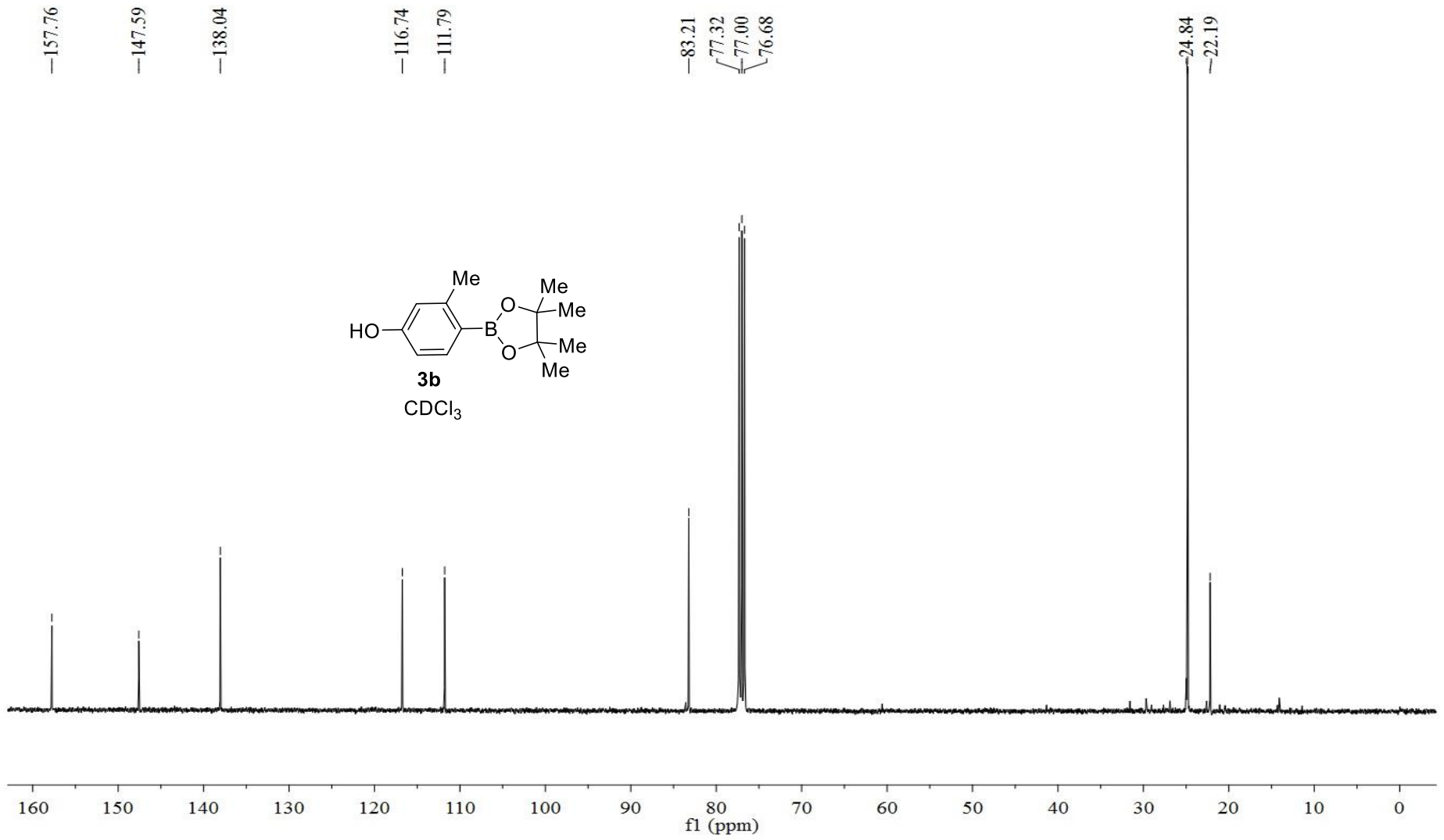
[26] (a) Y. Okuno, *Chem. Eur. J.* **1997**, *3*, 212. (b) D. Ardura, R. López, T. L. Sordo, *J. Phys. Chem. B.* **2005**, *109*, 23618. (c) F. Schoenebeck, K. N. Houk, *J. Am. Chem. Soc.* **2010**, *132*, 2496. (d) Q. Liu, Y. Lan, J. Liu, G. Li, Y. D. Wu, A. Lei, *J. Am. Chem. Soc.* **2009**, *131*, 10201. (e) A. Ariafard, N. J. Brookes, R. Stanger, B. F. Yates, *Organometallics* **2011**, *30*, 1340. (f) M. Y. Wang, T. Fan, Z. Y. Lin, *Organometallics* **2012**, *31*, 560.

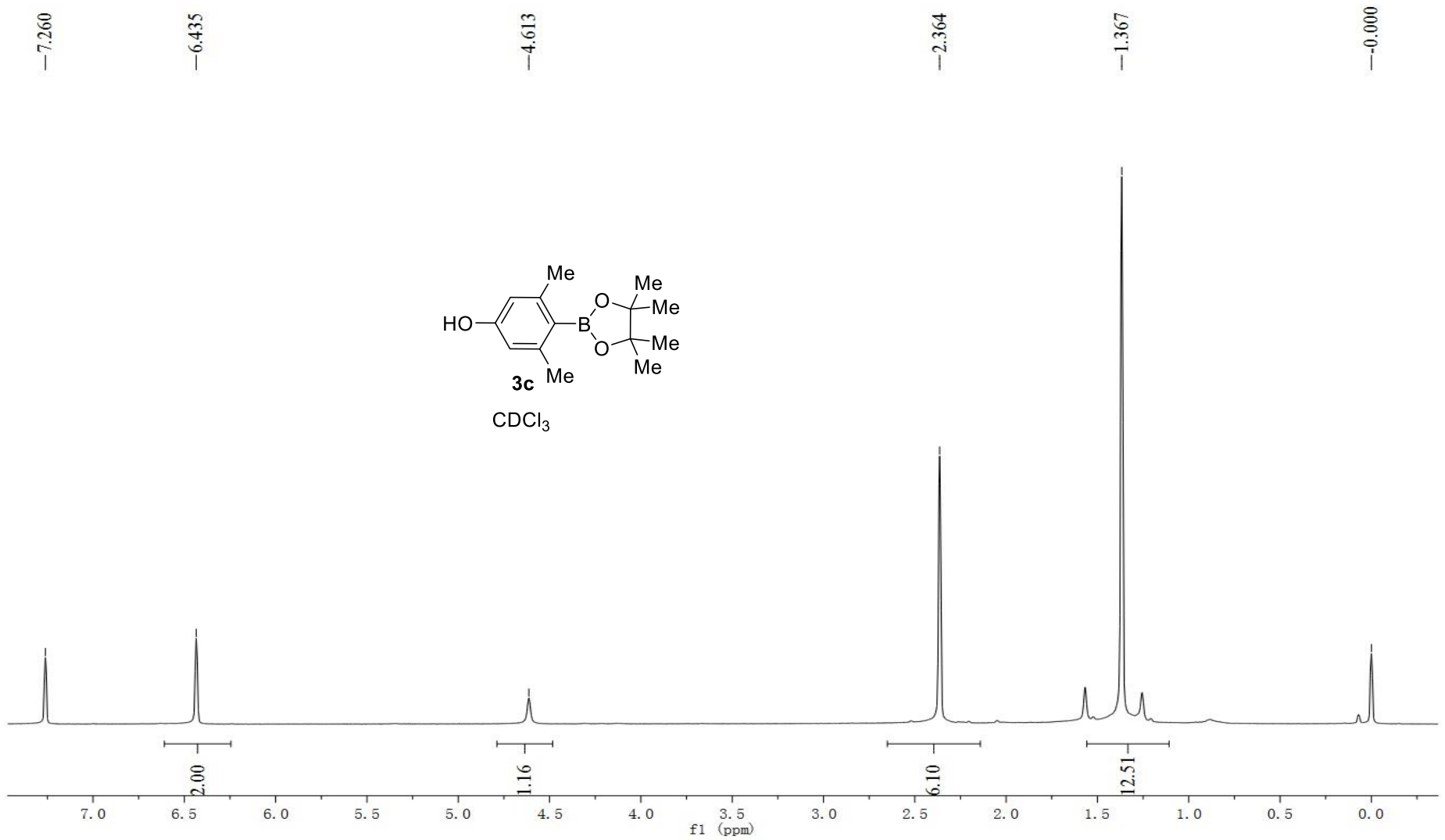
7. ^{1}H NMR and ^{13}C NMR spectra

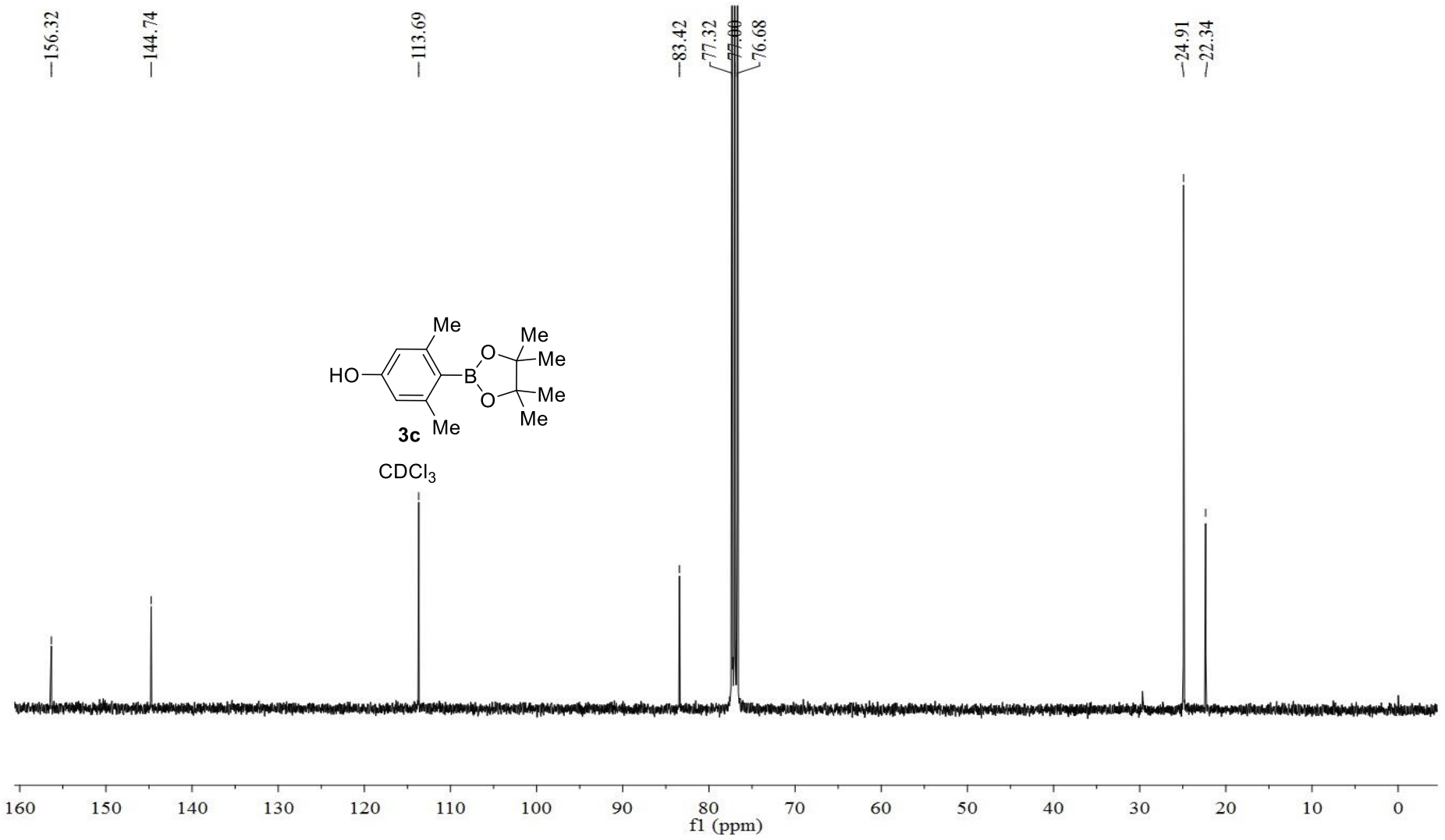

7.718
7.699
7.260
6.828
6.810
5.138
1.331
0.000
HO
B
O
O
Me
Me
Me
Me
3a
CDCl3
2.05
2.00
1.11
12.45
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

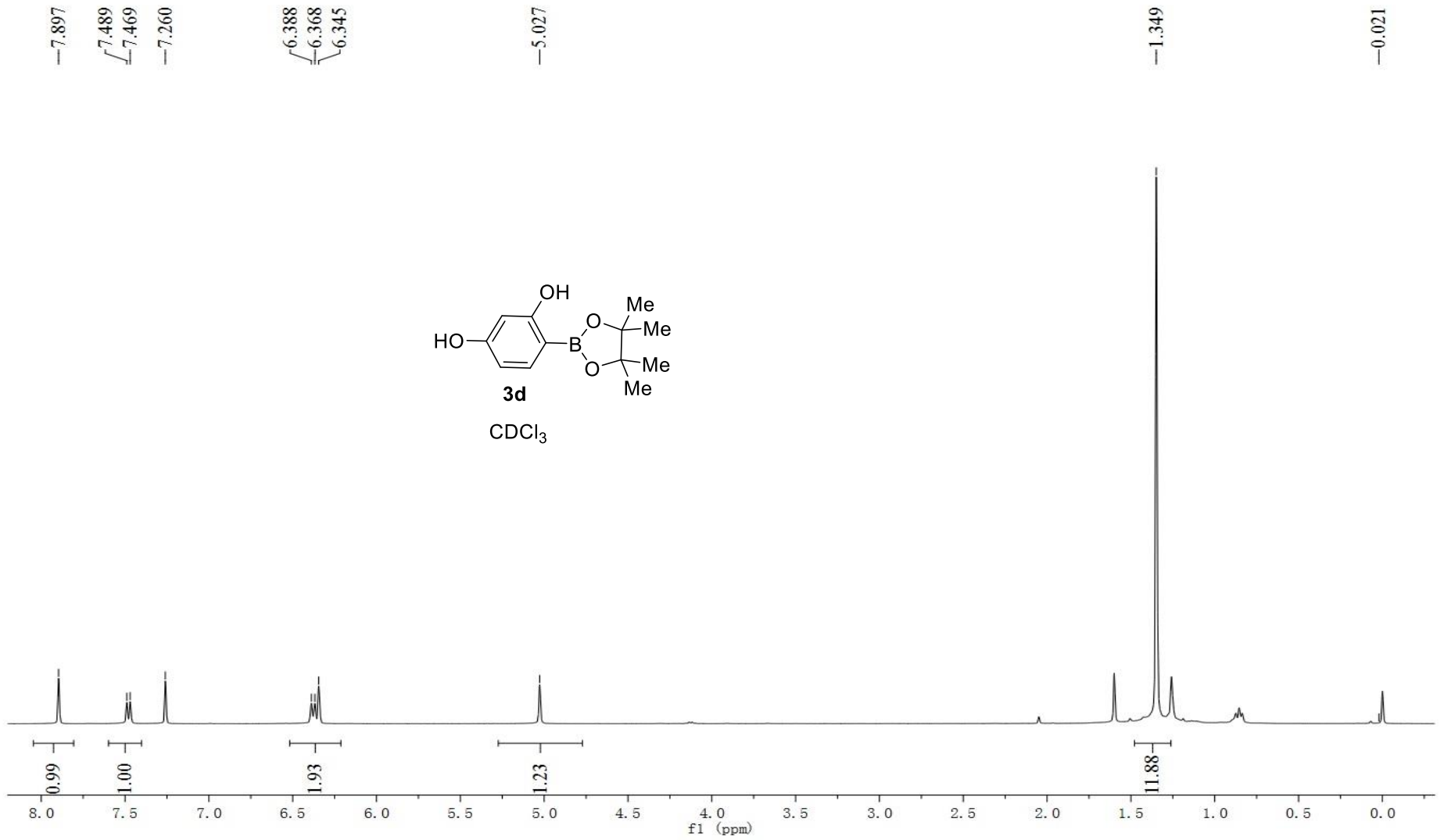

158.12
137.18
114.77
83.61
77.32
77.00
76.68
24.69
-0.27
HO
B
O
O
Me
Me
Me
Me
3a
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

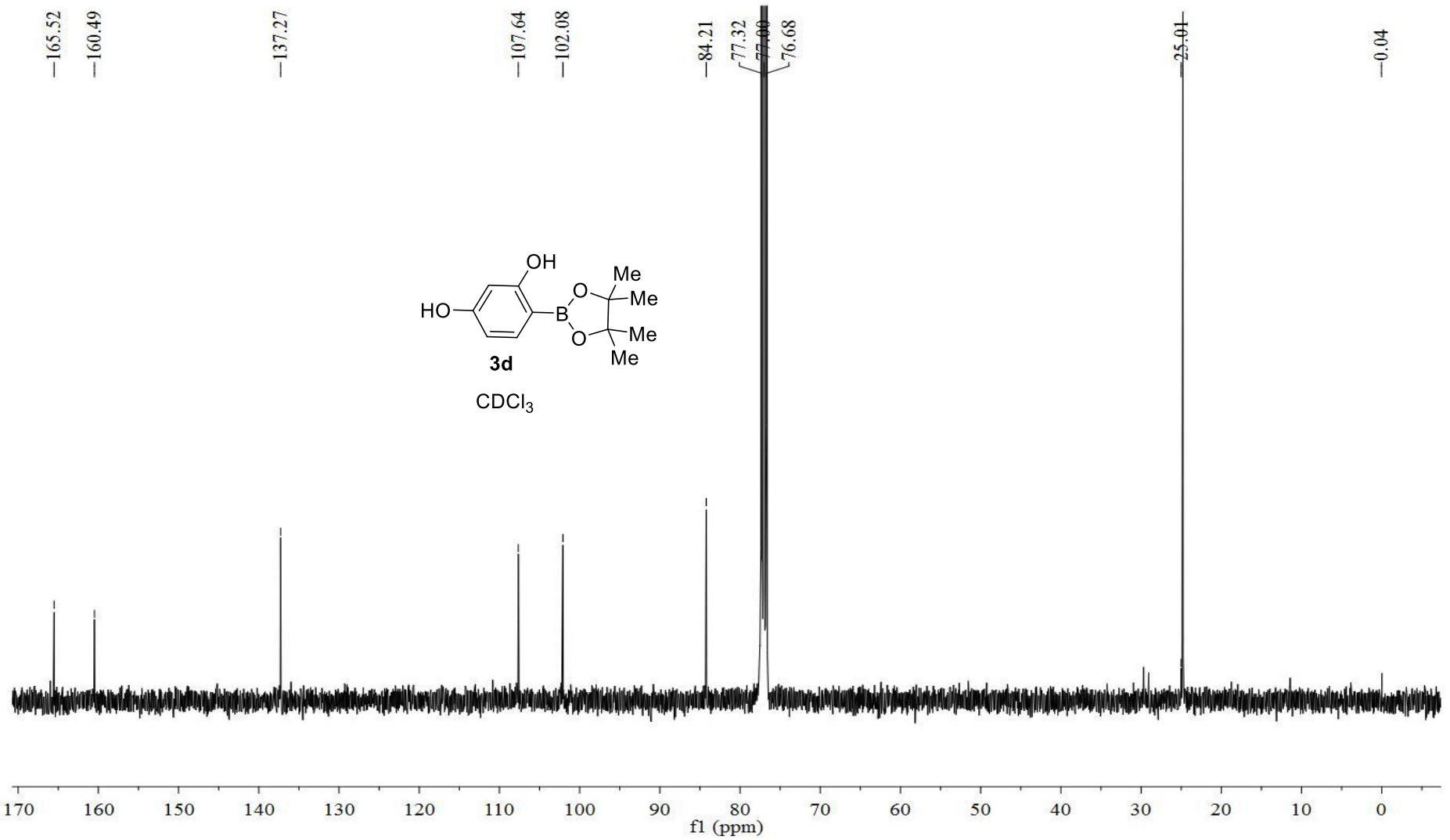

7.676
7.657
7.260
6.631
6.611
5.138
2.491
1.329
Me
HO
B
O
O
Me
Me
Me
Me
3b
CDCl3
1.00
2.01
1.01
3.06
12.70
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

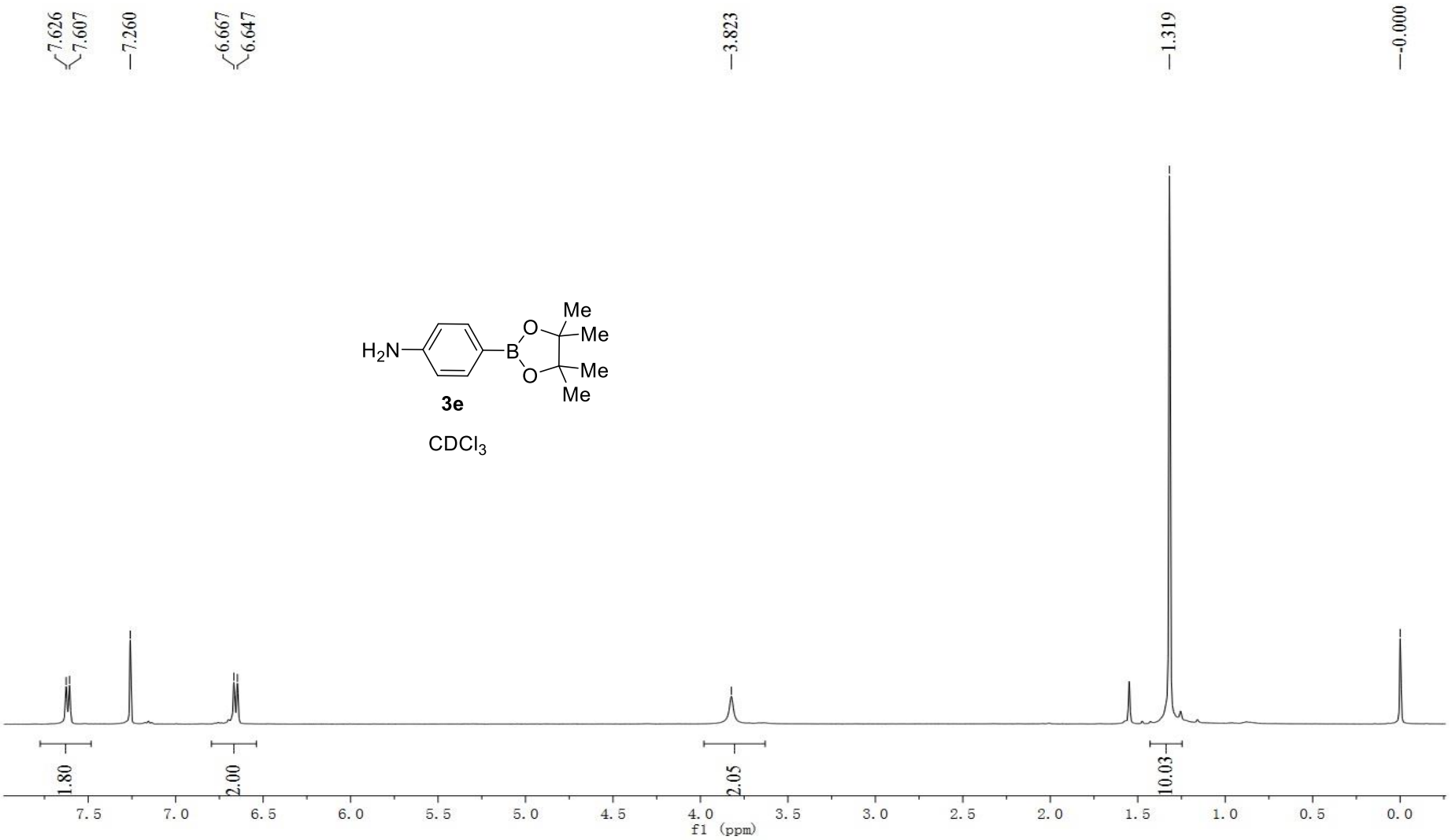

157.76
147.59
138.04
116.74
111.79
83.21
77.32
77.00
76.68
24.84
22.19
Me
HO
B
O
O
Me
Me
Me
Me
3b
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

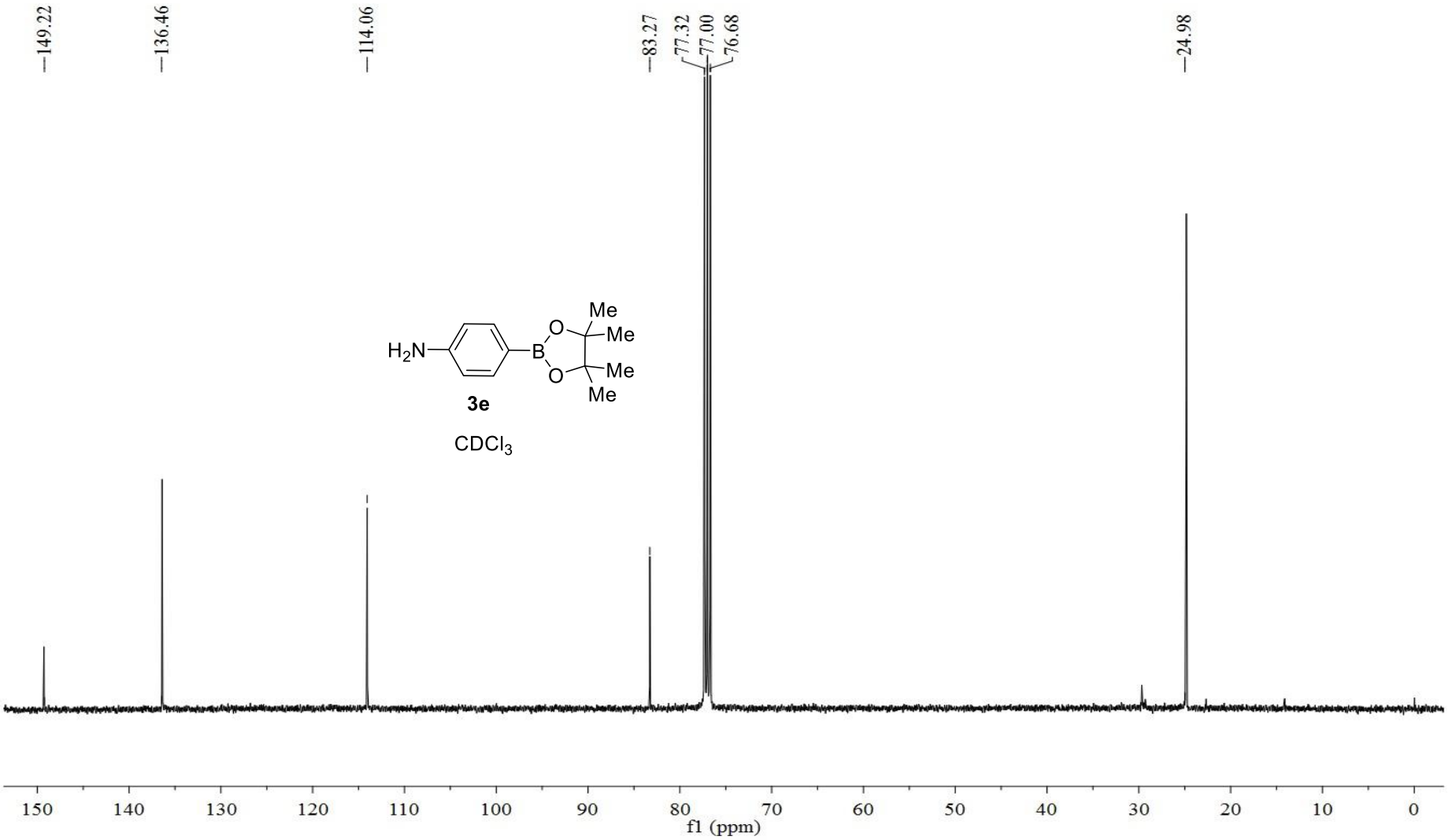

7.260
6.435
4.613
2.364
1.367
0.000
HO
Me
Me
Me
Me
Me
Me
O
O
B
3c
CDCl3
2.00
1.16
6.10
12.51
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

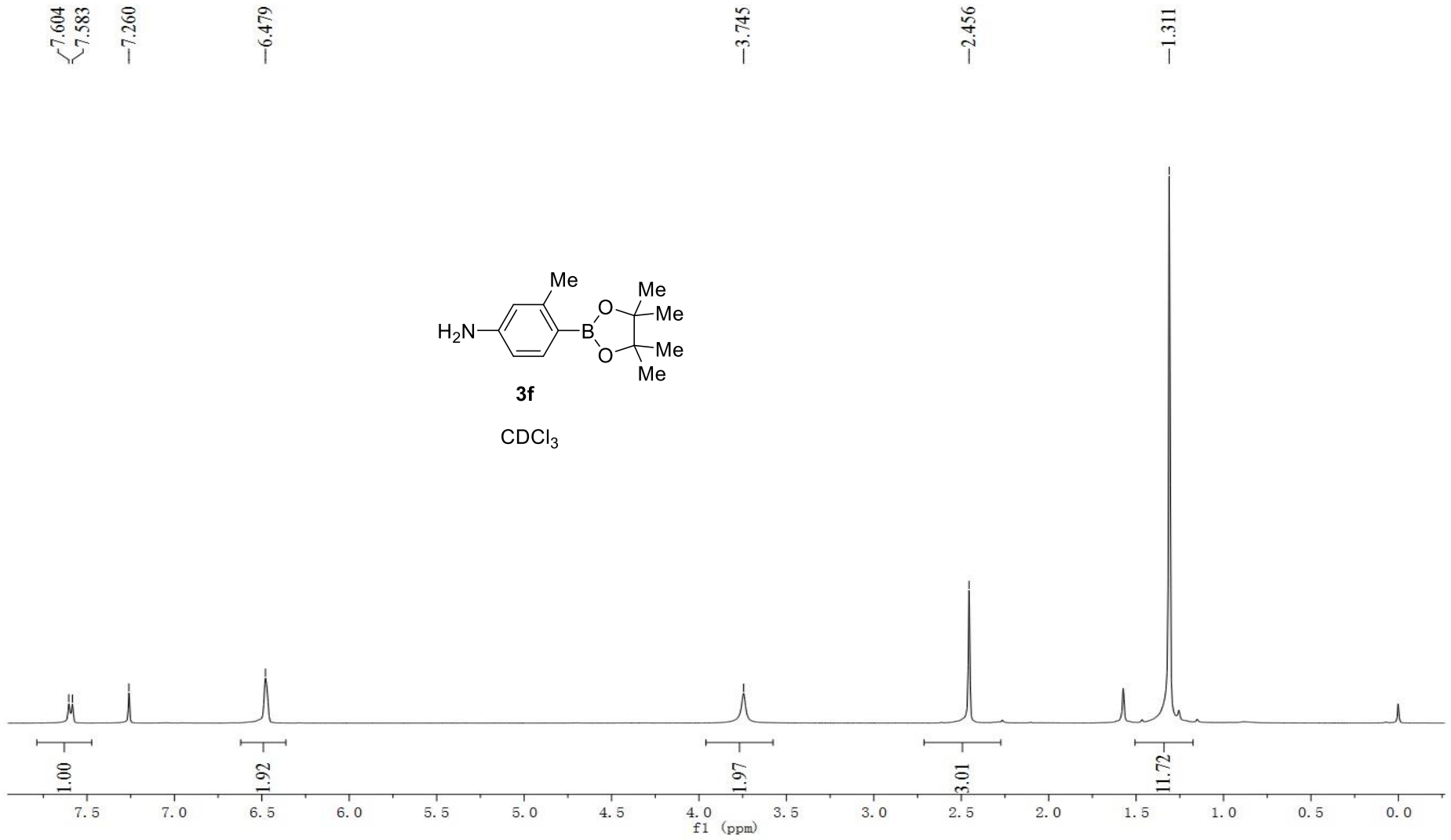

156.32
144.74
113.69
83.42
77.32
77.00
76.68
24.91
22.34
HO
B
O
O
Me
Me
Me
Me
Me
Me
3c
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

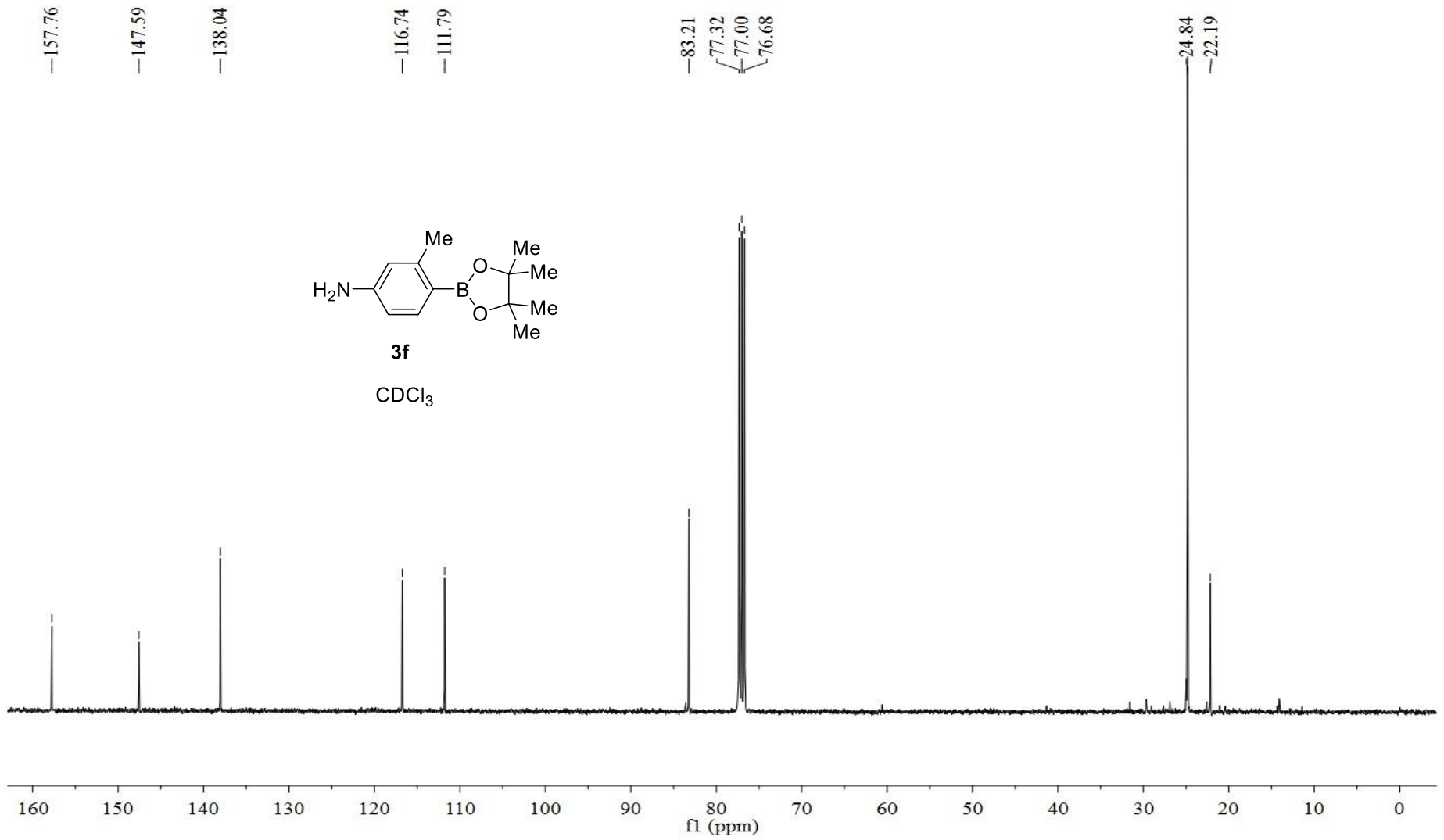

7.897
7.489
7.469
7.260
6.388
6.368
6.345
5.027
1.349
0.021
OH
HO
B
O
O
Me
Me
Me
Me
3d
CDCl3
0.99
1.00
1.93
1.23
11.88
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

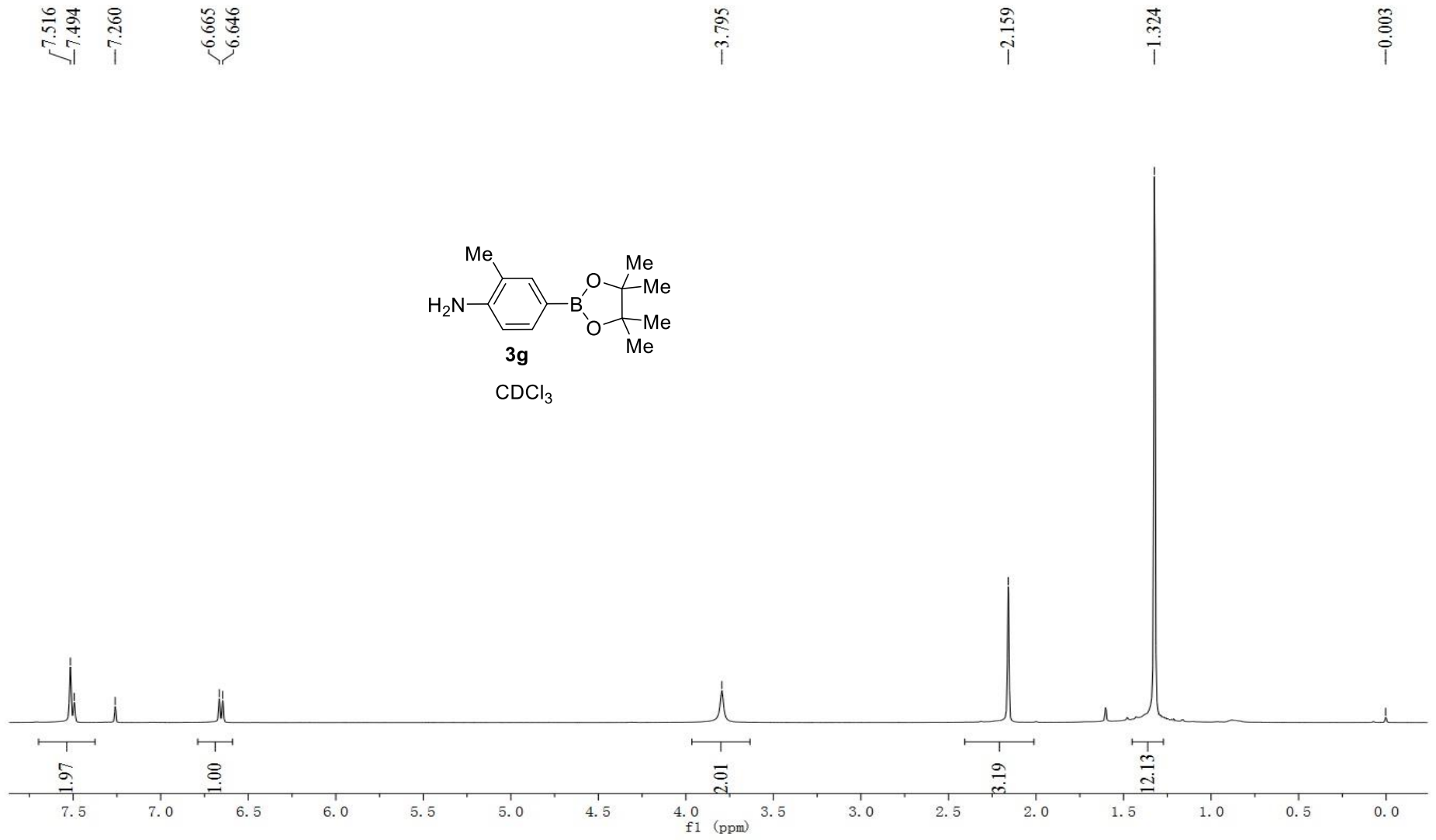

165.52
160.49
137.27
107.64
102.08
84.21
77.32
77.00
76.68
25.01
0.04
OH
HO
B
O
O
Me
Me
Me
Me
3d
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

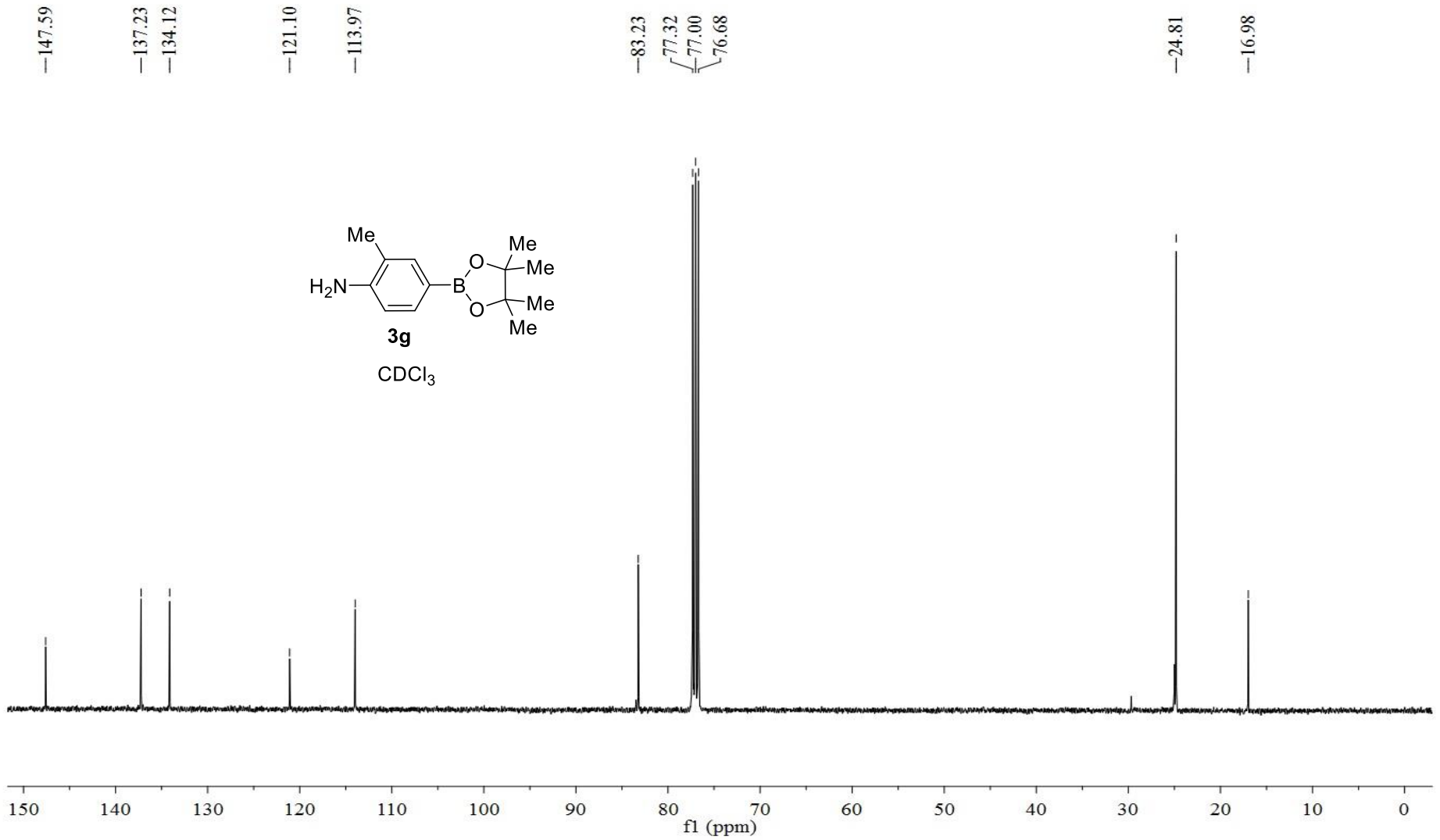

7.626
7.607
7.260
6.667
6.647
3.823
1.319
0.000
H2N
B
O
O
Me
Me
Me
Me
3e
CDCl3
1.80
2.00
2.05
10.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

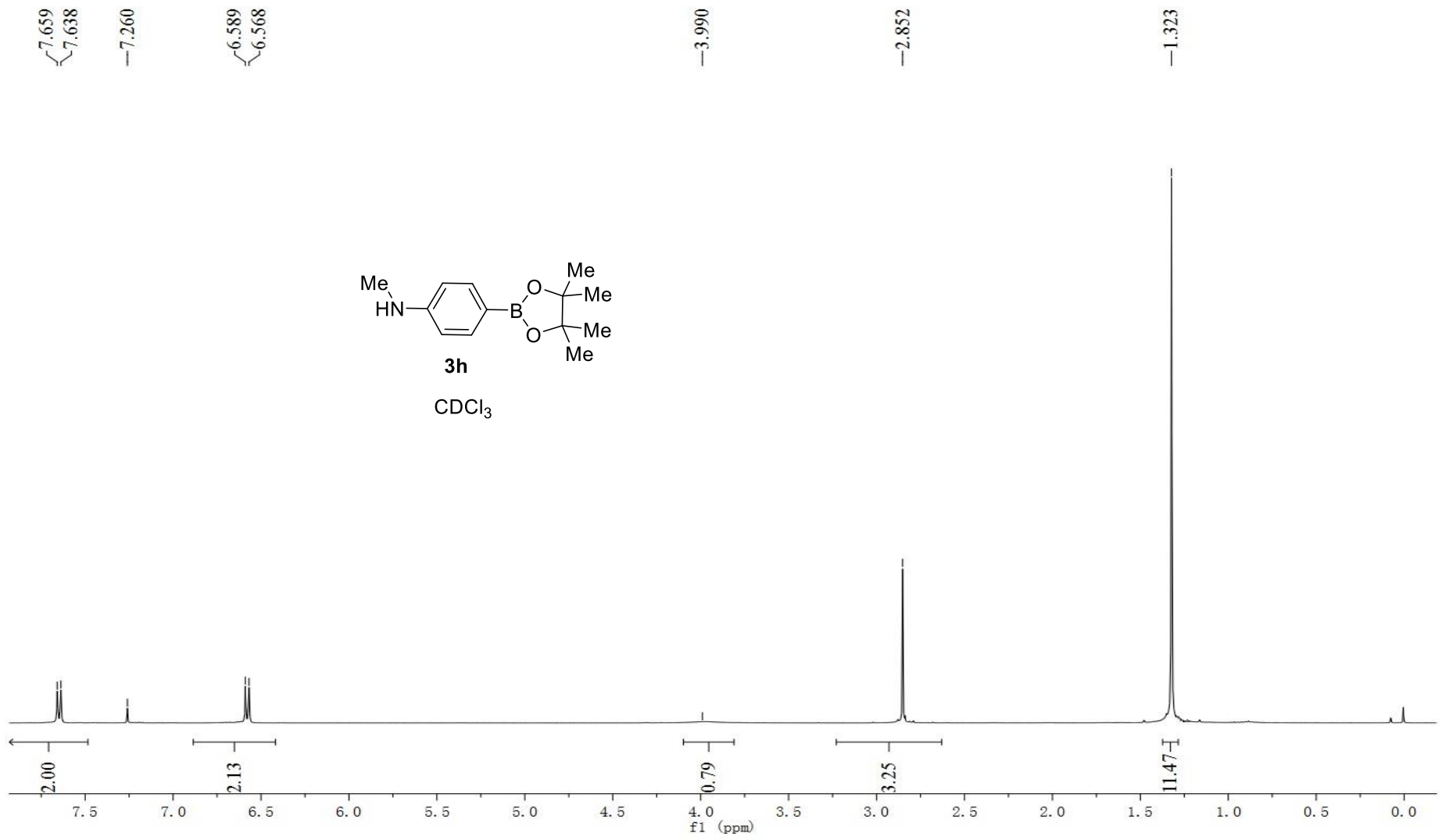

149.22
136.46
114.06
83.27
77.32
77.00
76.68
24.98
H2N
B
O
O
Me
Me
Me
Me
3e
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

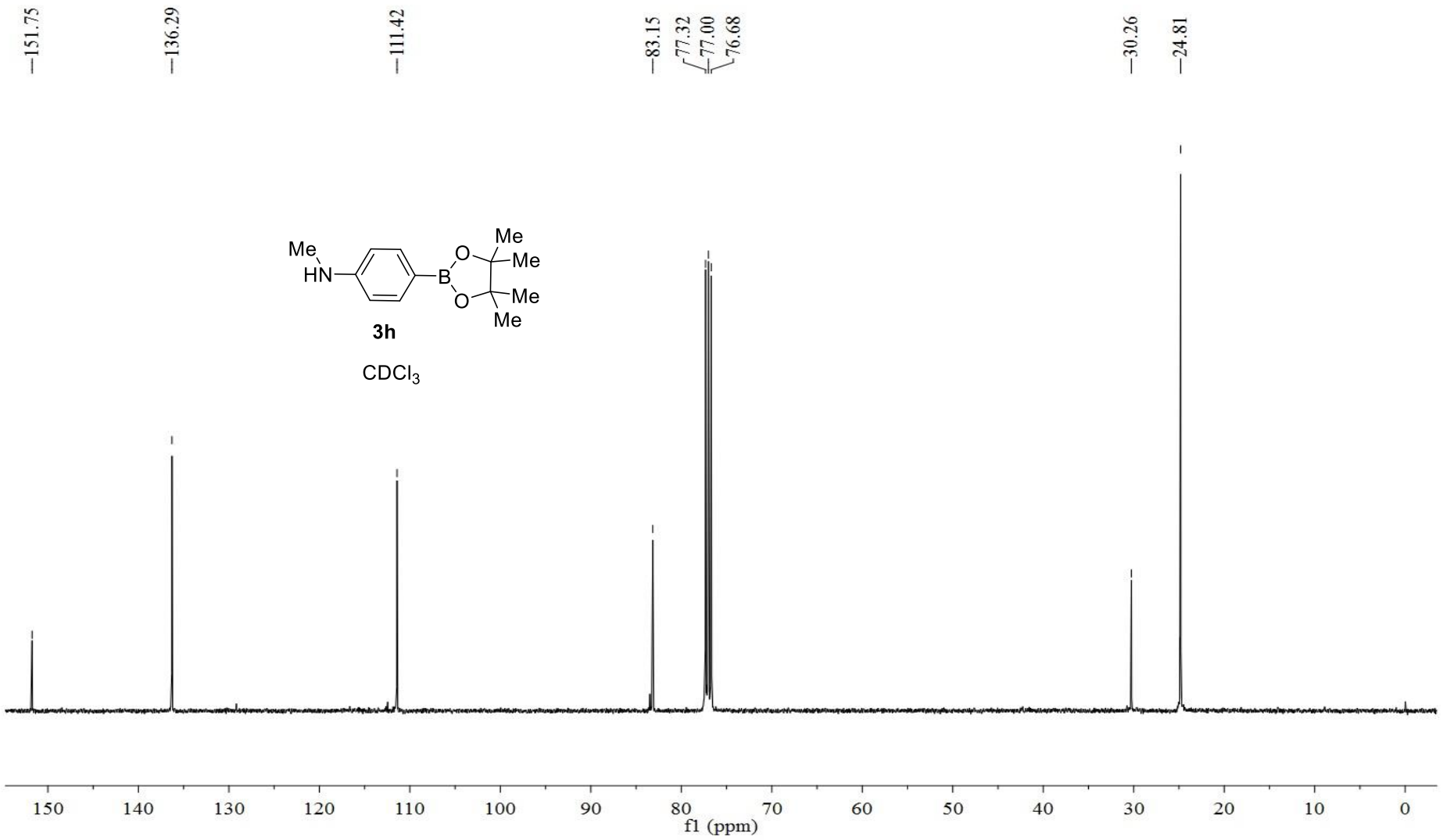

7.604
7.583
7.260
6.479
3.745
2.456
1.311
Me
H2N
B
O
O
Me
Me
Me
Me
3f
CDCl3
1.00
1.92
1.97
3.01
11.72
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

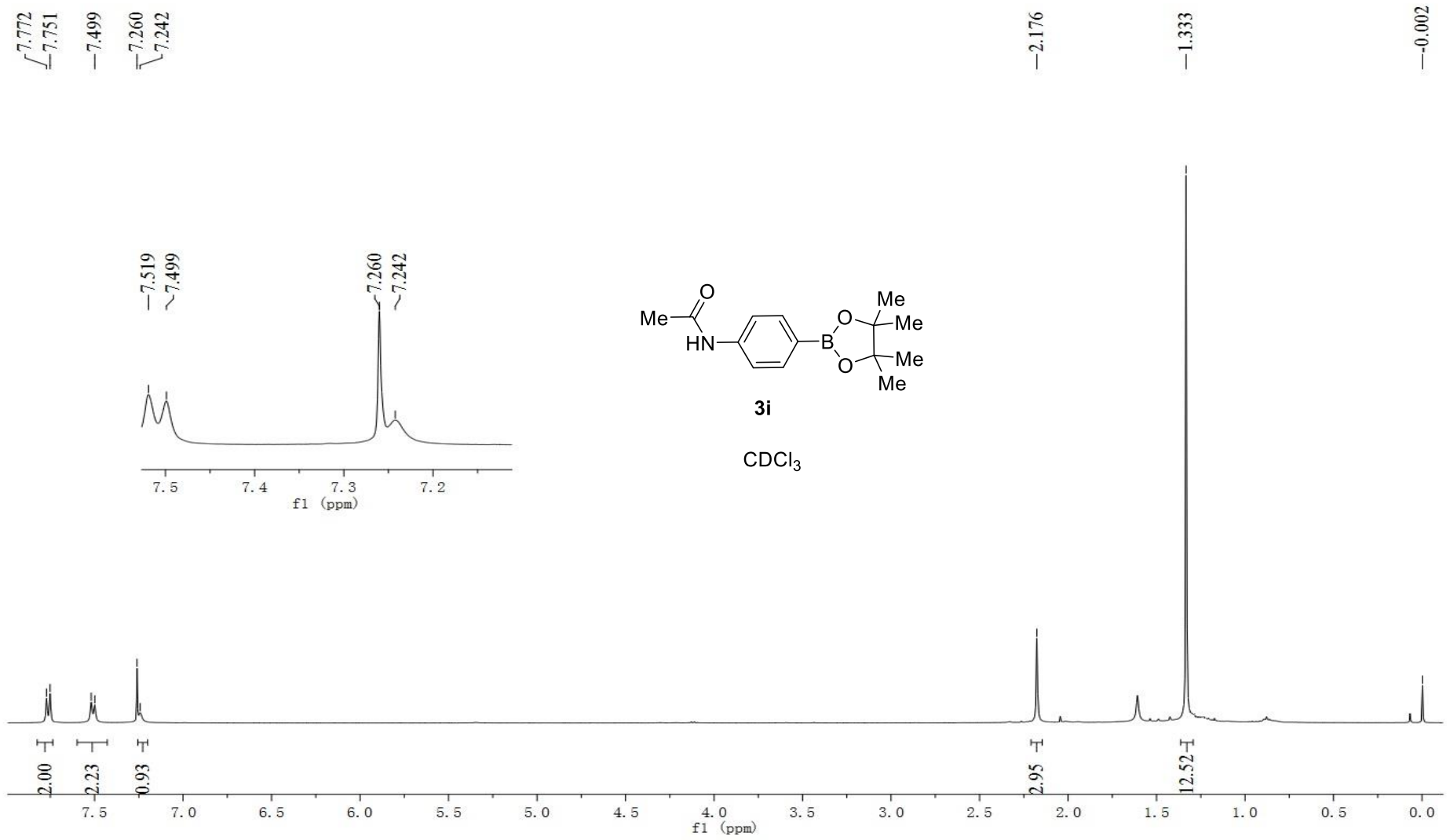

157.76
147.59
138.04
116.74
111.79
83.21
77.32
77.00
76.68
24.84
22.19
Me
Me
Me
Me
Me
H_2N
B
O
O
3f
$CDCl_3$
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

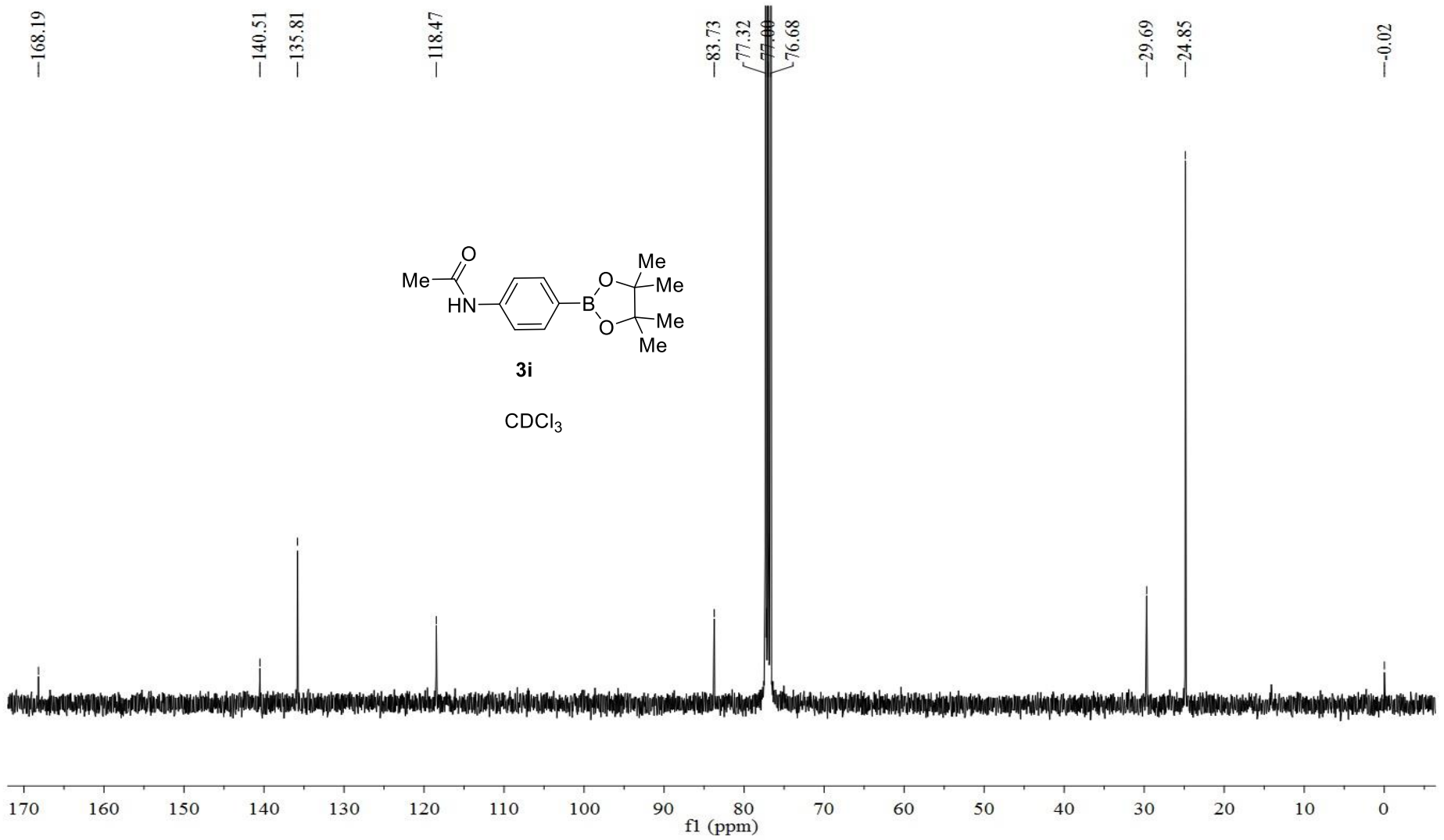

7.516
7.494
7.260
6.665
6.646
3.795
2.159
1.324
0.003
Me
H2N
B
O
O
Me
Me
Me
Me
3g
CDCl3
1.97
1.00
2.01
3.19
12.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

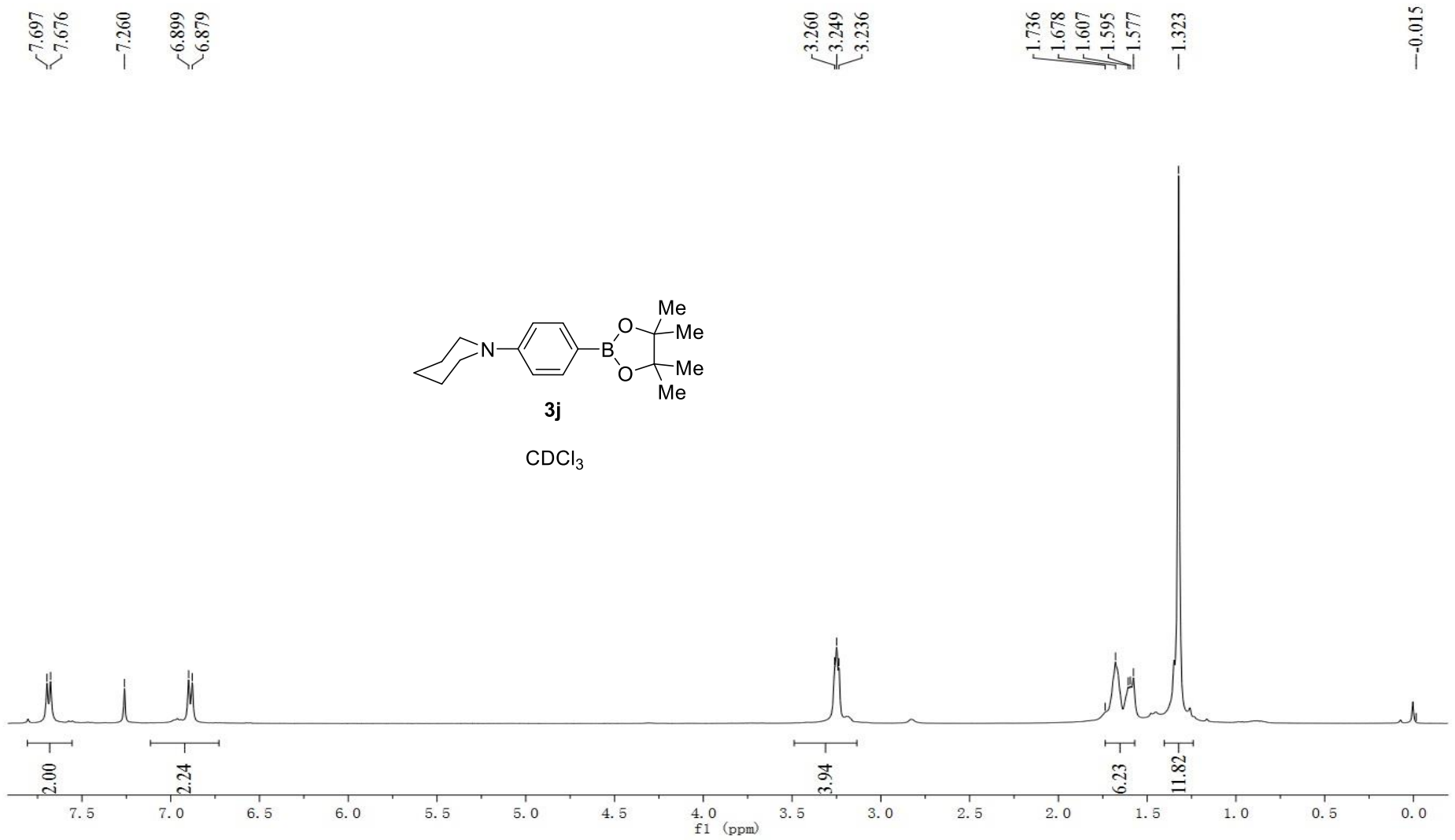

147.59
137.23
134.12
121.10
113.97
83.23
77.32
77.00
76.68
24.81
16.98
Me
H2N
B
O
O
Me
Me
Me
Me
3g
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

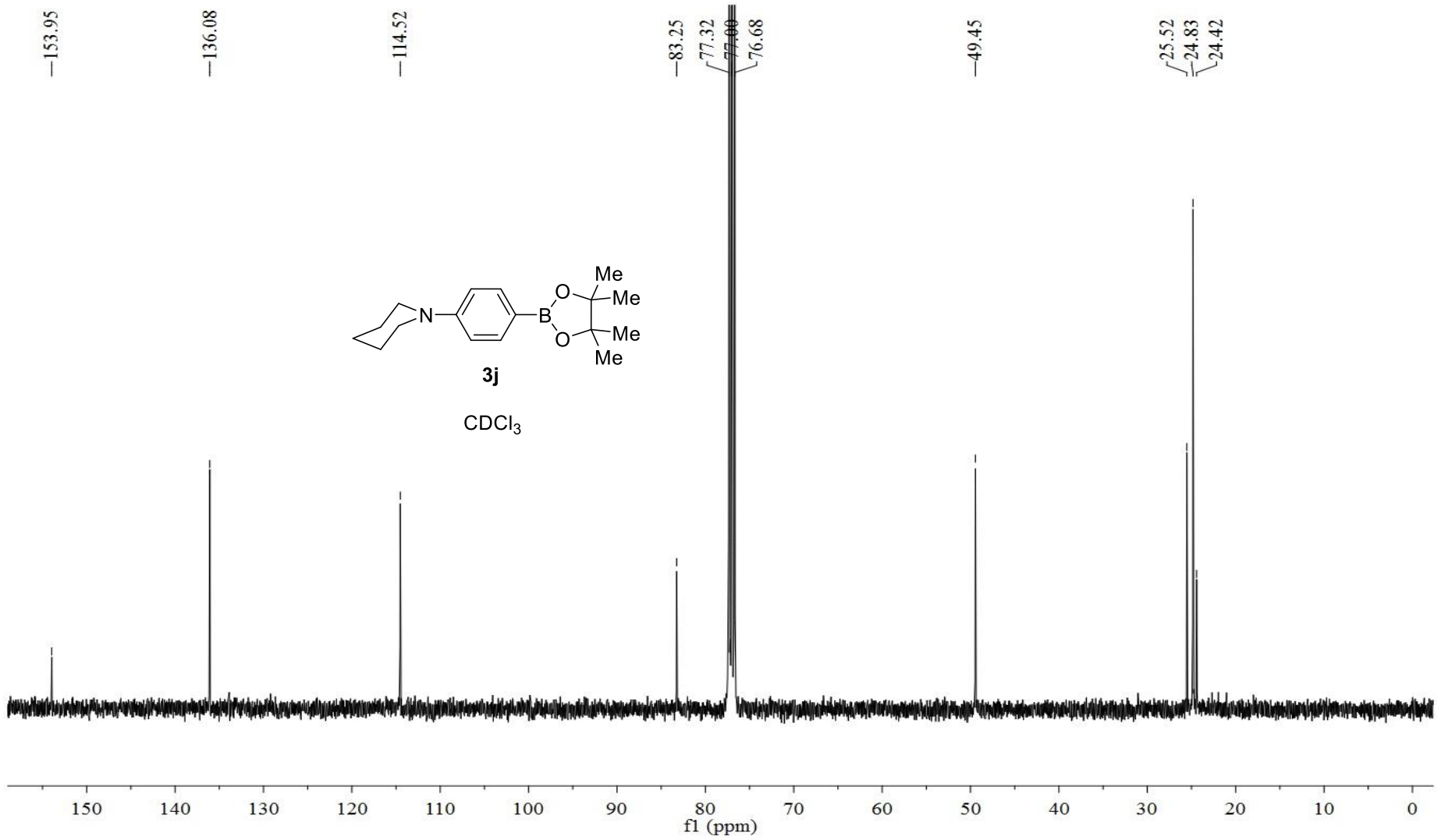

7.659
7.638
7.260
6.589
6.568
3.990
2.852
1.323
Me
HN
B
O
O
Me
Me
Me
Me
3h
CDCl3
2.00
2.13
0.79
3.25
11.47
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

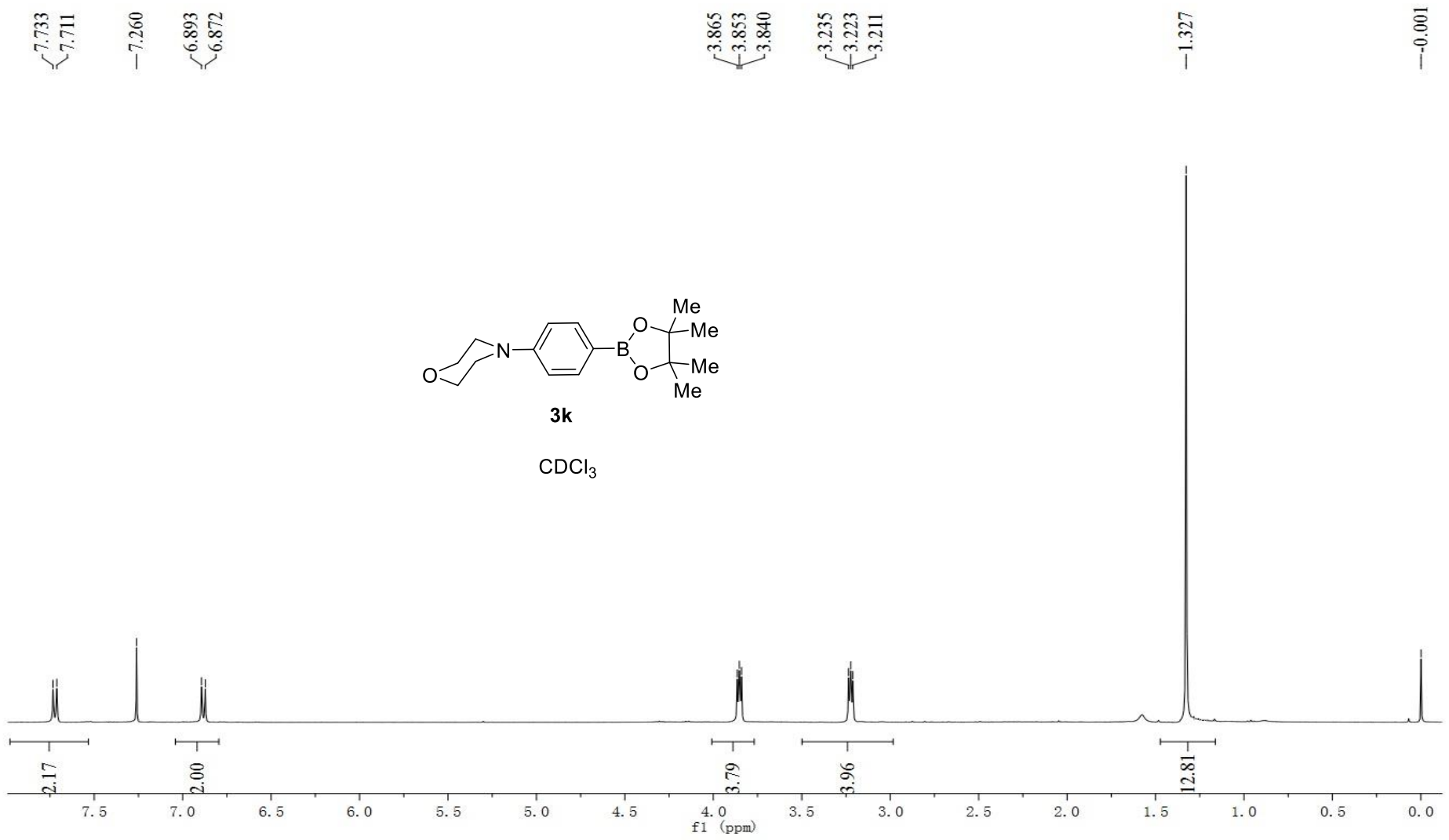

151.75
136.29
111.42
83.15
77.32
77.00
76.68
30.26
24.81
Me
HN
B
O
O
Me
Me
Me
Me
3h
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

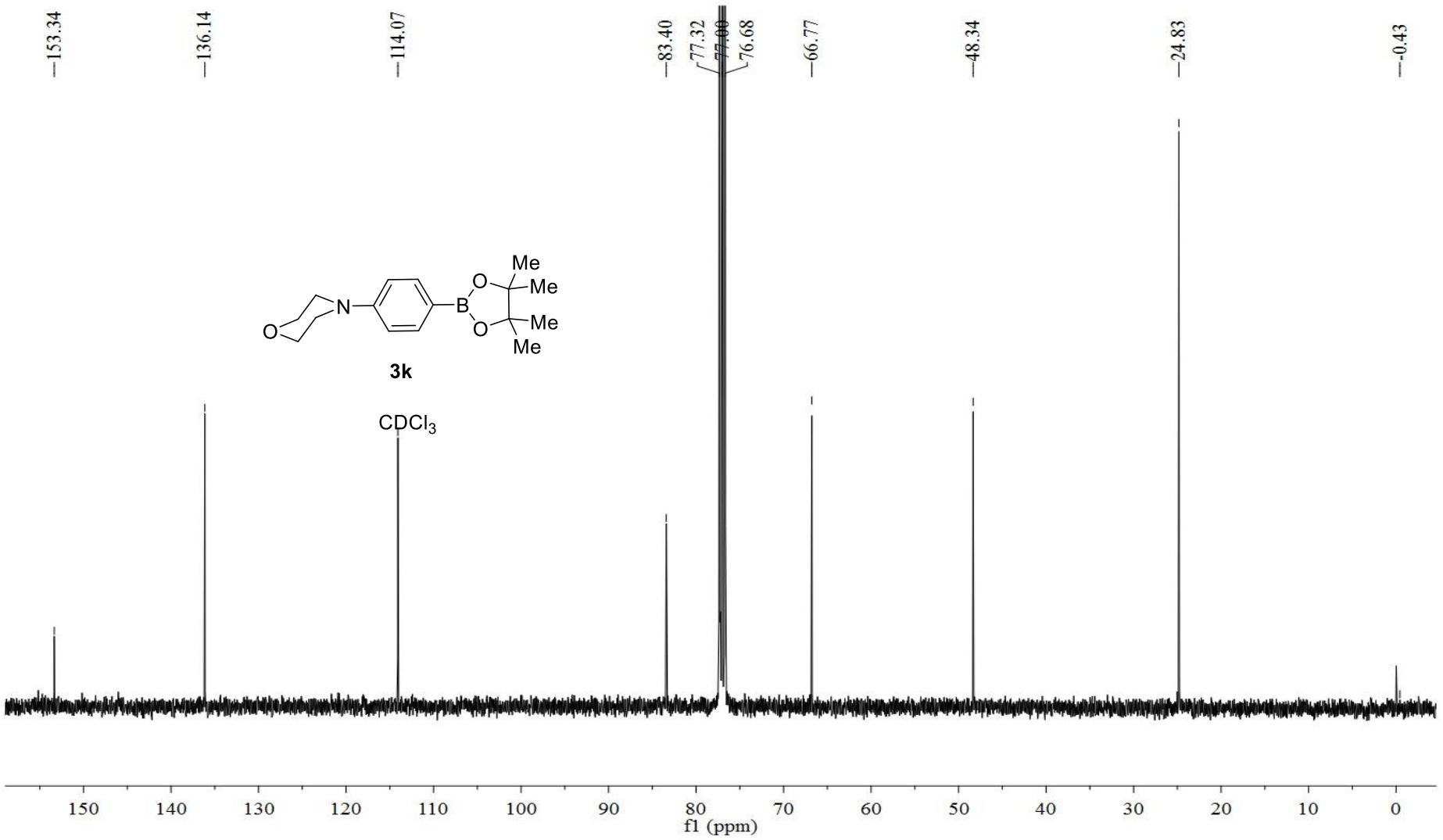

7.772
7.751
7.499
7.260
7.242
2.176
1.333
0.002
7.519
7.499
7.260
7.242
7.5
7.4
7.3
7.2
f1 (ppm)
Me
HN
O
B
O
Me
Me
Me
Me
3i
CDCl3
2.00
2.23
0.93
2.95
12.52
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

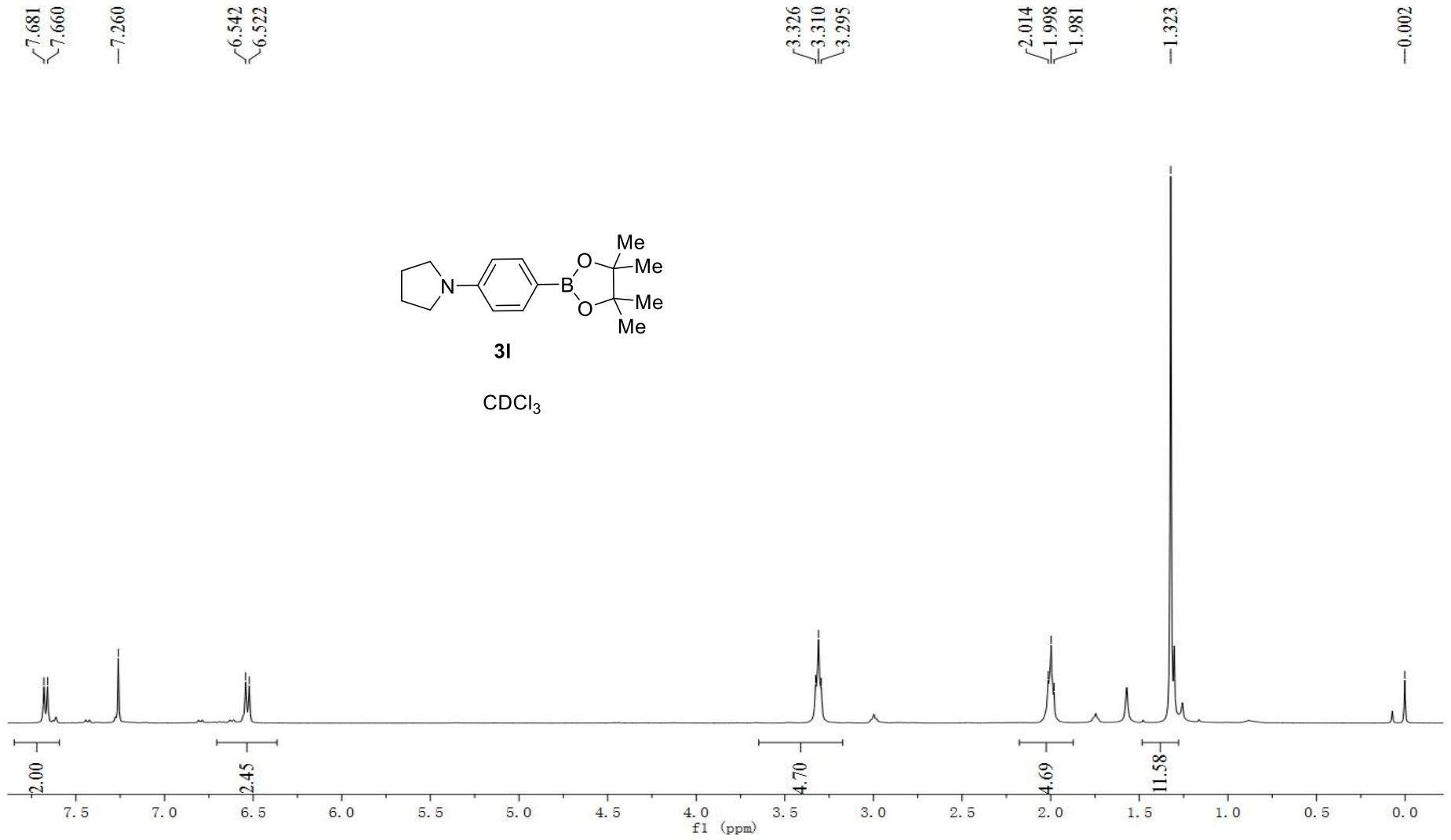

168.19
140.51
135.81
118.47
83.73
77.32
77.00
76.68
29.69
24.85
-0.02
Me
O
HN
B
O
Me
Me
Me
Me
3i
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

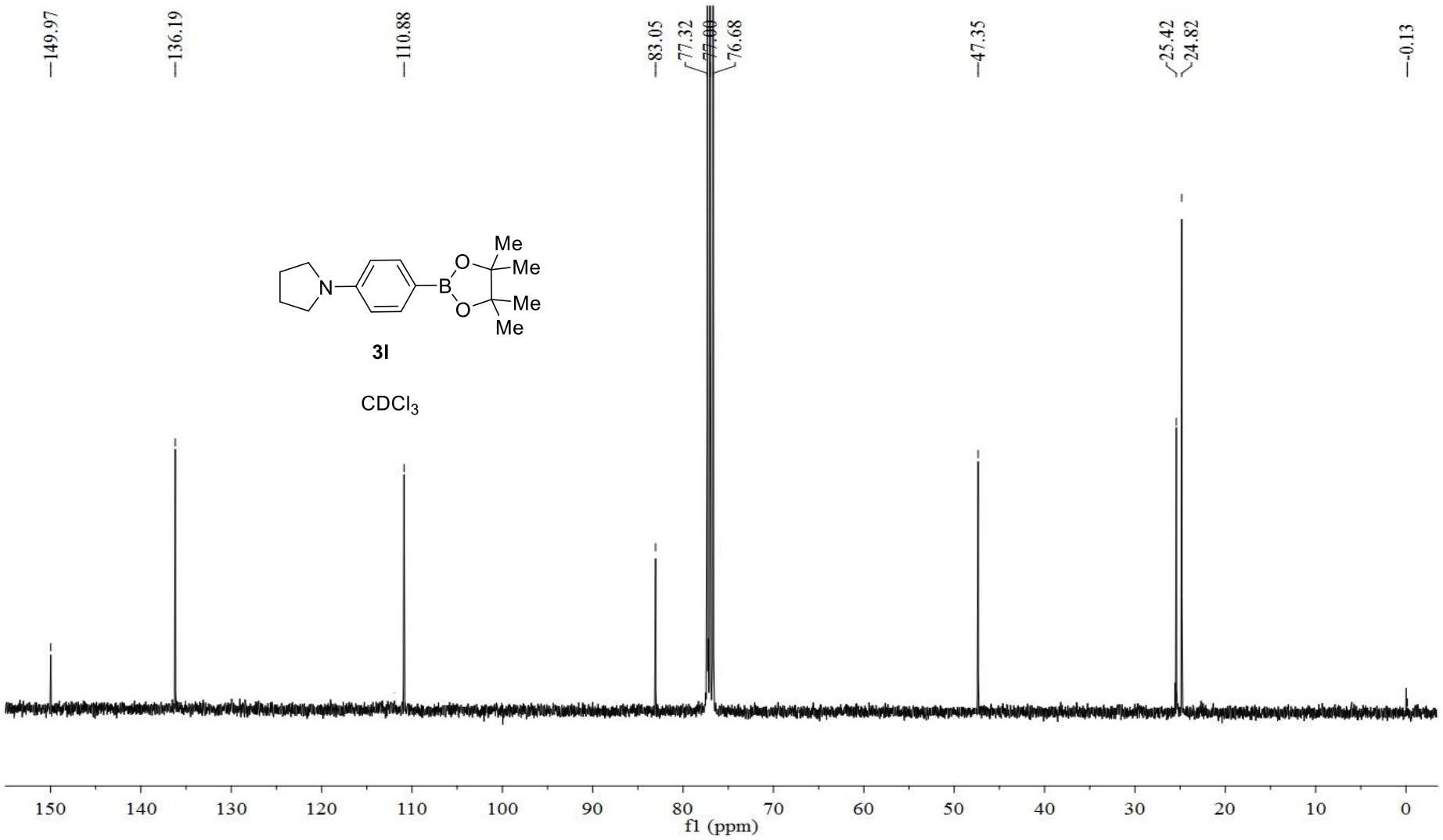

7.697
7.676
7.260
6.899
6.879
3.260
3.249
3.236
1.736
1.678
1.607
1.595
1.577
1.323
-0.015
Me
Me
Me
Me
N
B
O
O
3j
CDCl3
2.00
2.24
3.94
6.23
11.82
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

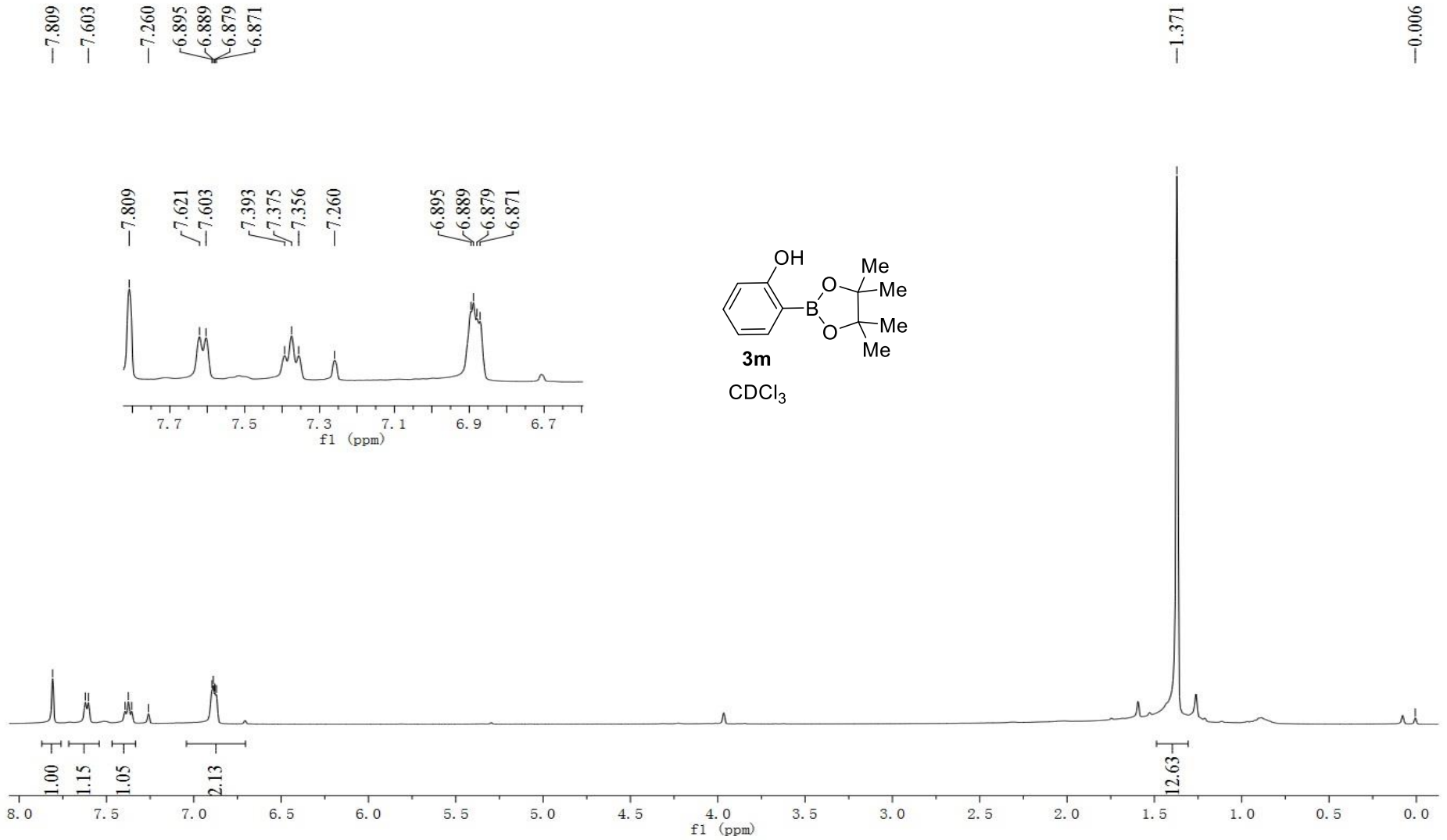

153.95
136.08
114.52
83.25
77.32
77.00
76.68
49.45
25.52
24.83
24.42
Me
Me
Me
Me
O
O
B
N
3j
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

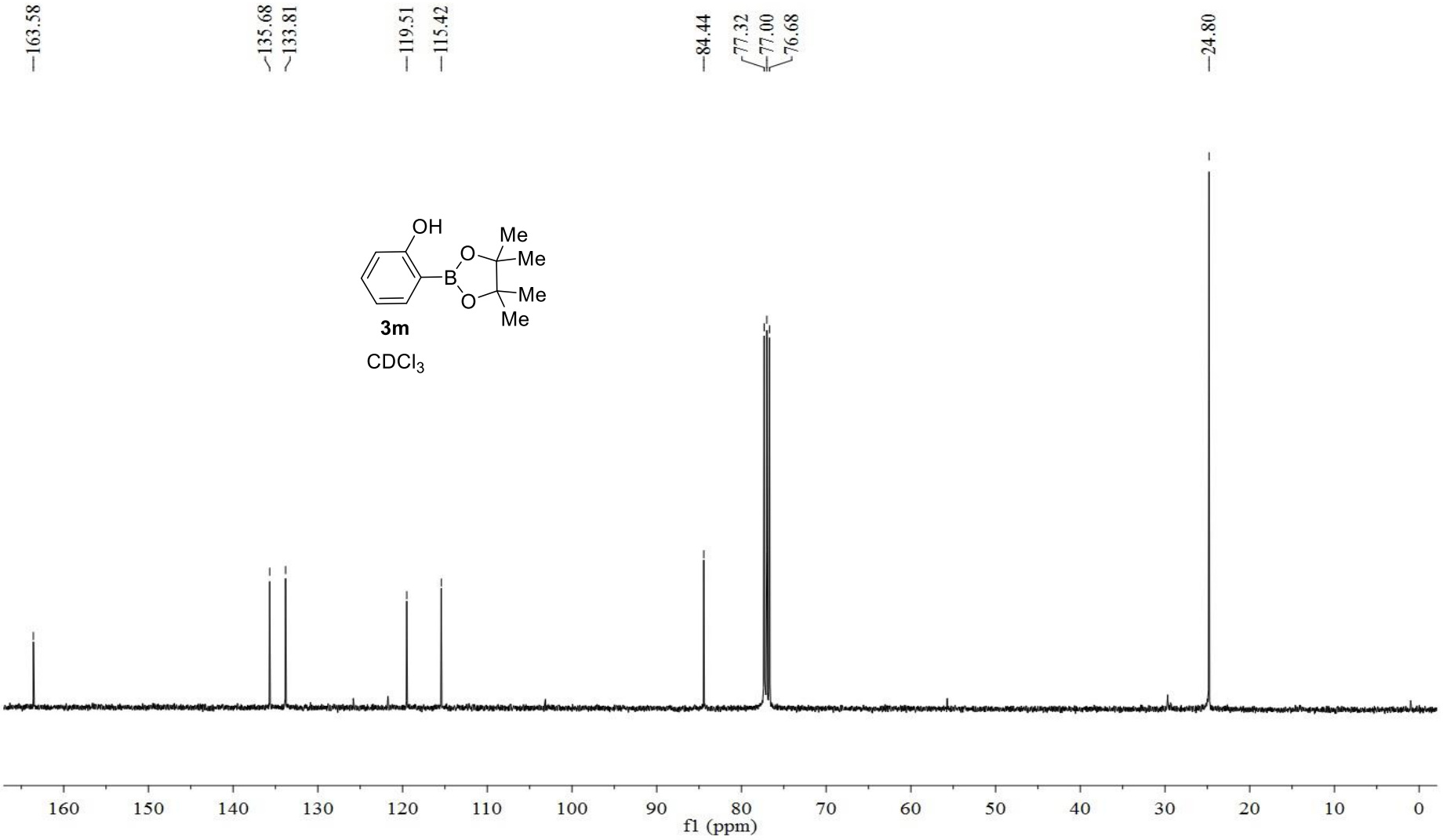

7.733
7.711
7.260
6.893
6.872
3.865
3.853
3.840
3.235
3.223
3.211
1.327
0.001
Me
Me
Me
Me
O
N
O
B
O
3k
CDCl3
2.17
2.00
3.79
3.96
12.81
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

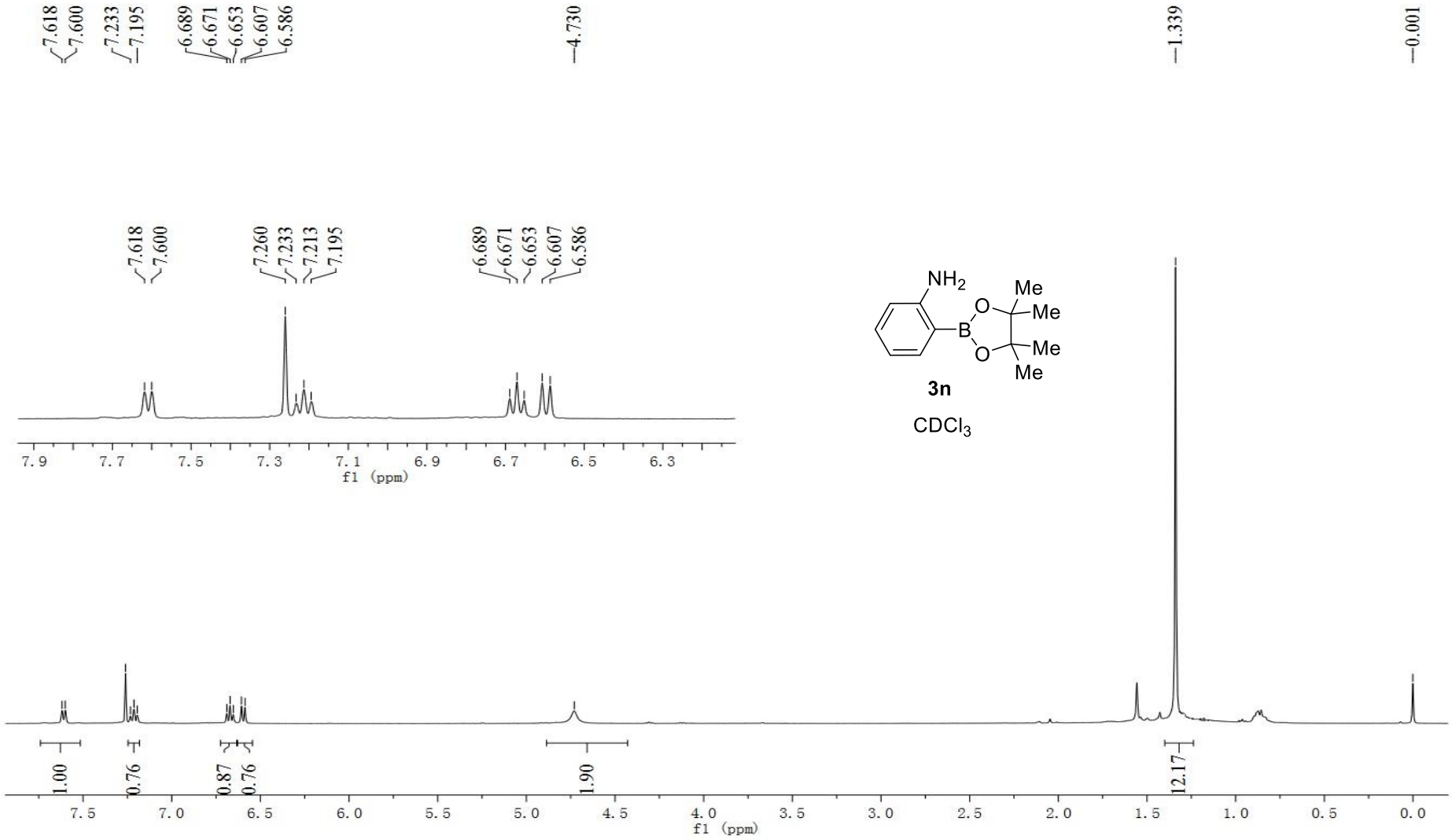

153.34
136.14
114.07
83.40
77.32
77.00
76.68
66.77
48.34
24.83
0.43
Me
Me
Me
Me
O
N
B
O
O
3k
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

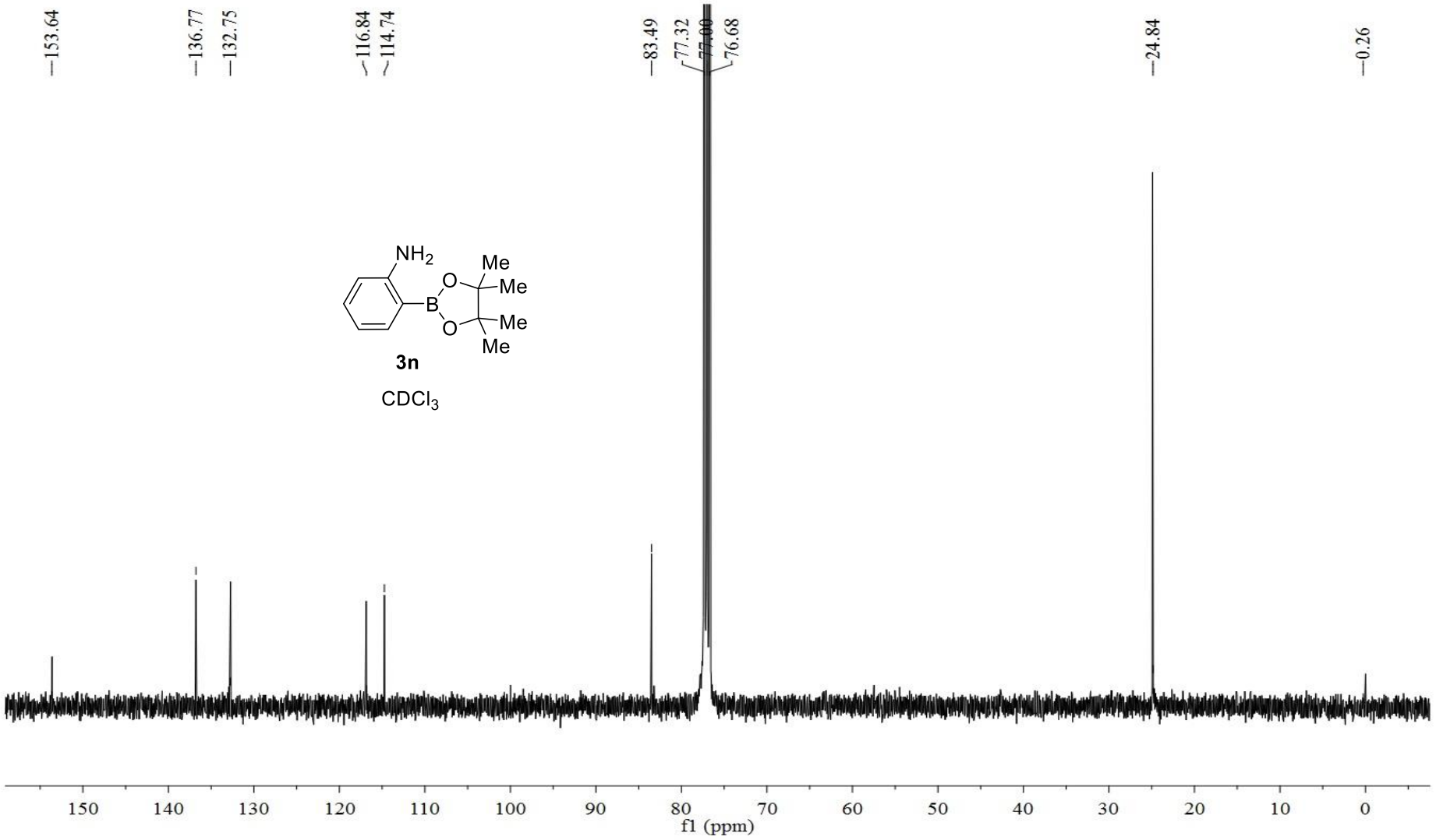

7.681
7.660
7.260
6.542
6.522
3.326
3.310
3.295
2.014
1.998
1.981
1.323
0.002
Me
Me
Me
Me
O
O
B
N
3l
CDCl3
2.00
2.45
4.70
4.69
11.58
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

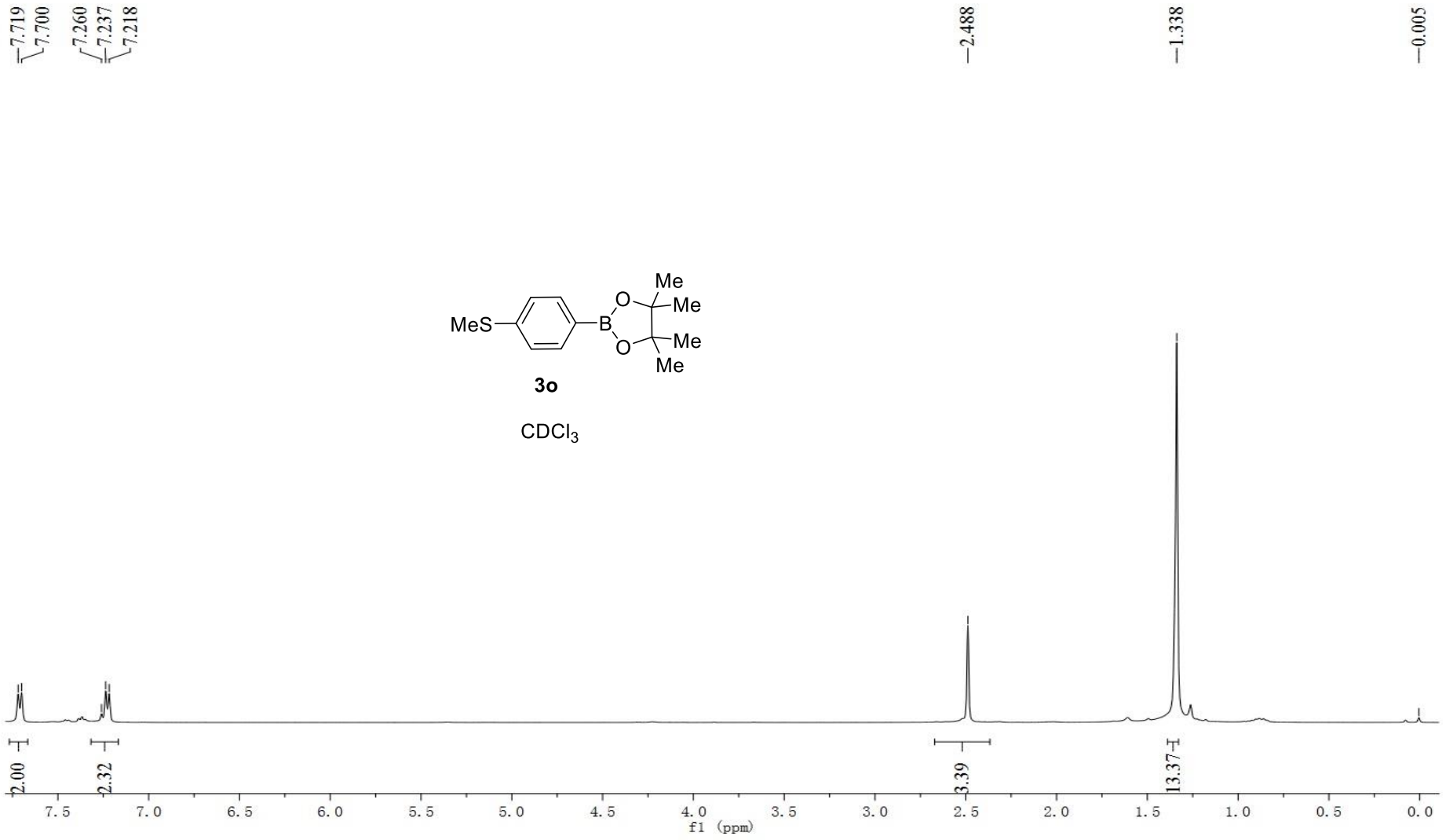

149.97
136.19
110.88
83.05
77.32
77.00
76.68
47.35
25.42
24.82
-0.13
Me
Me
Me
Me
O
O
B
N
3l
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

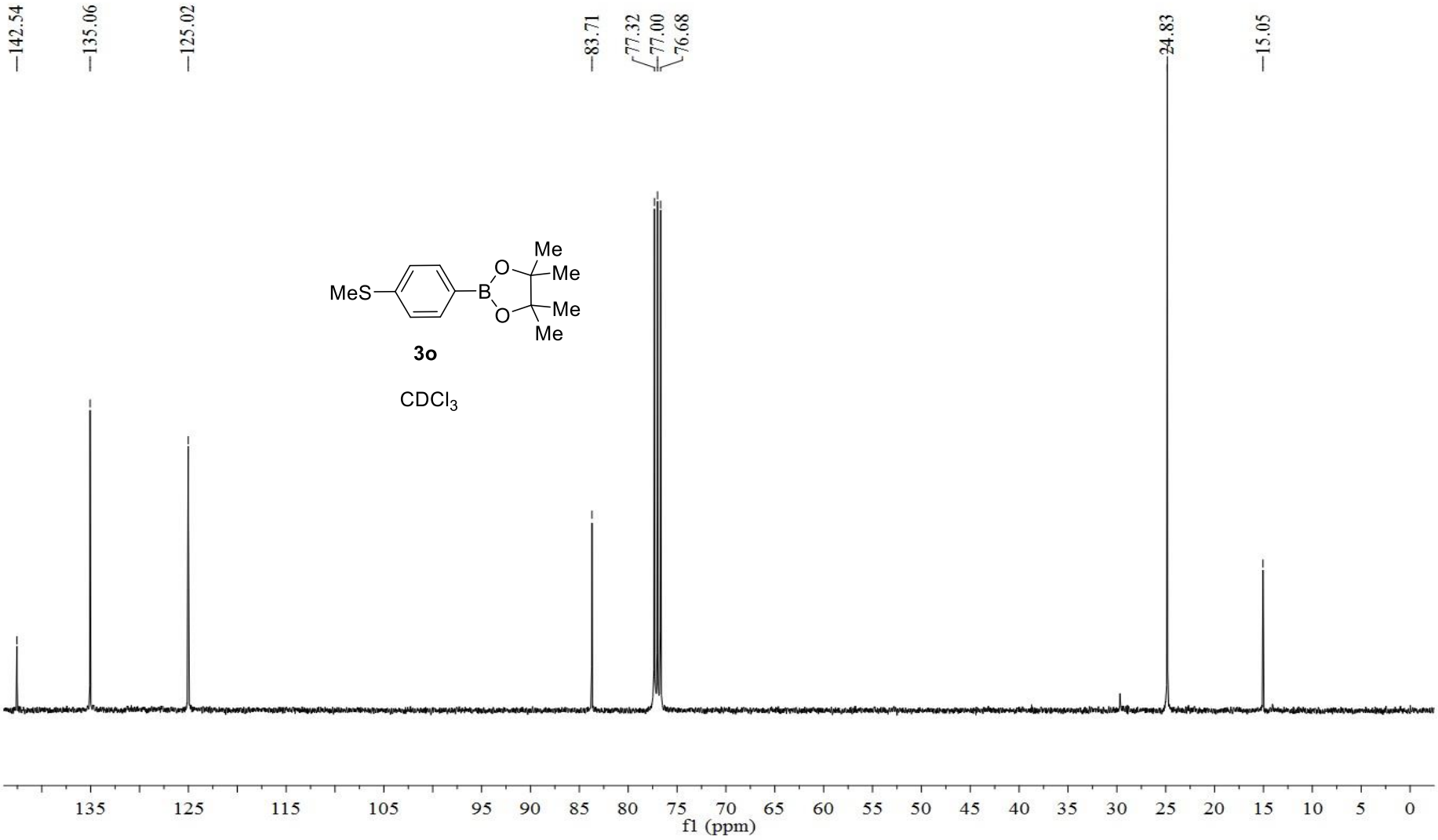

7.809
7.603
7.260
6.895
6.889
6.879
6.871
1.371
0.006
7.809
7.621
7.603
7.393
7.375
7.356
7.260
6.895
6.889
6.879
6.871
7.7
7.5
7.3
7.1
6.9
6.7
f1 (ppm)
OH
Me
Me
Me
Me
B
O
O
3m
CDCl3
1.00
1.15
1.05
2.13
12.63
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

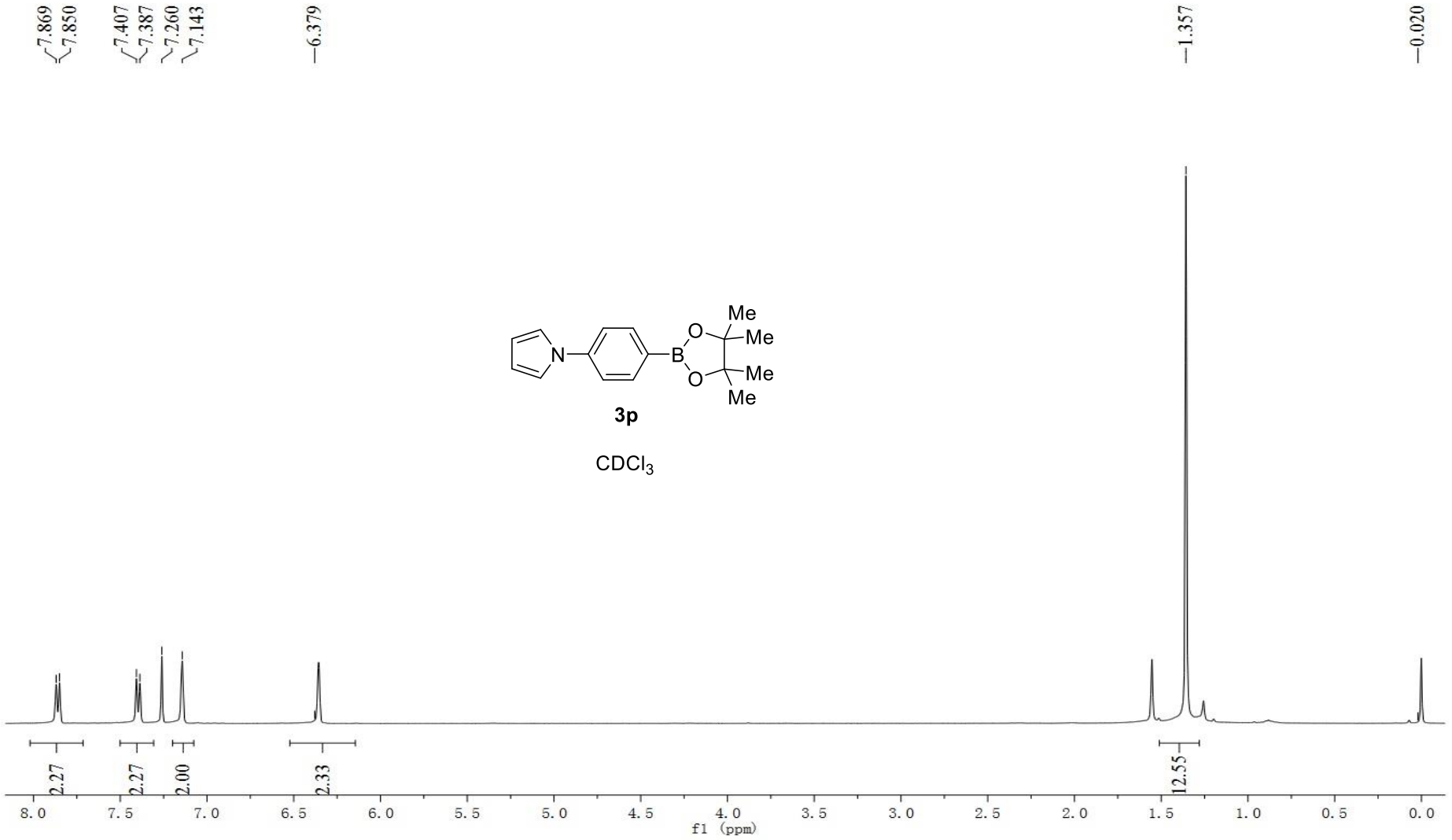

163.58
135.68
133.81
119.51
115.42
84.44
77.32
77.00
76.68
24.80
OH
Me
Me
Me
Me
O
O
B
3m
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

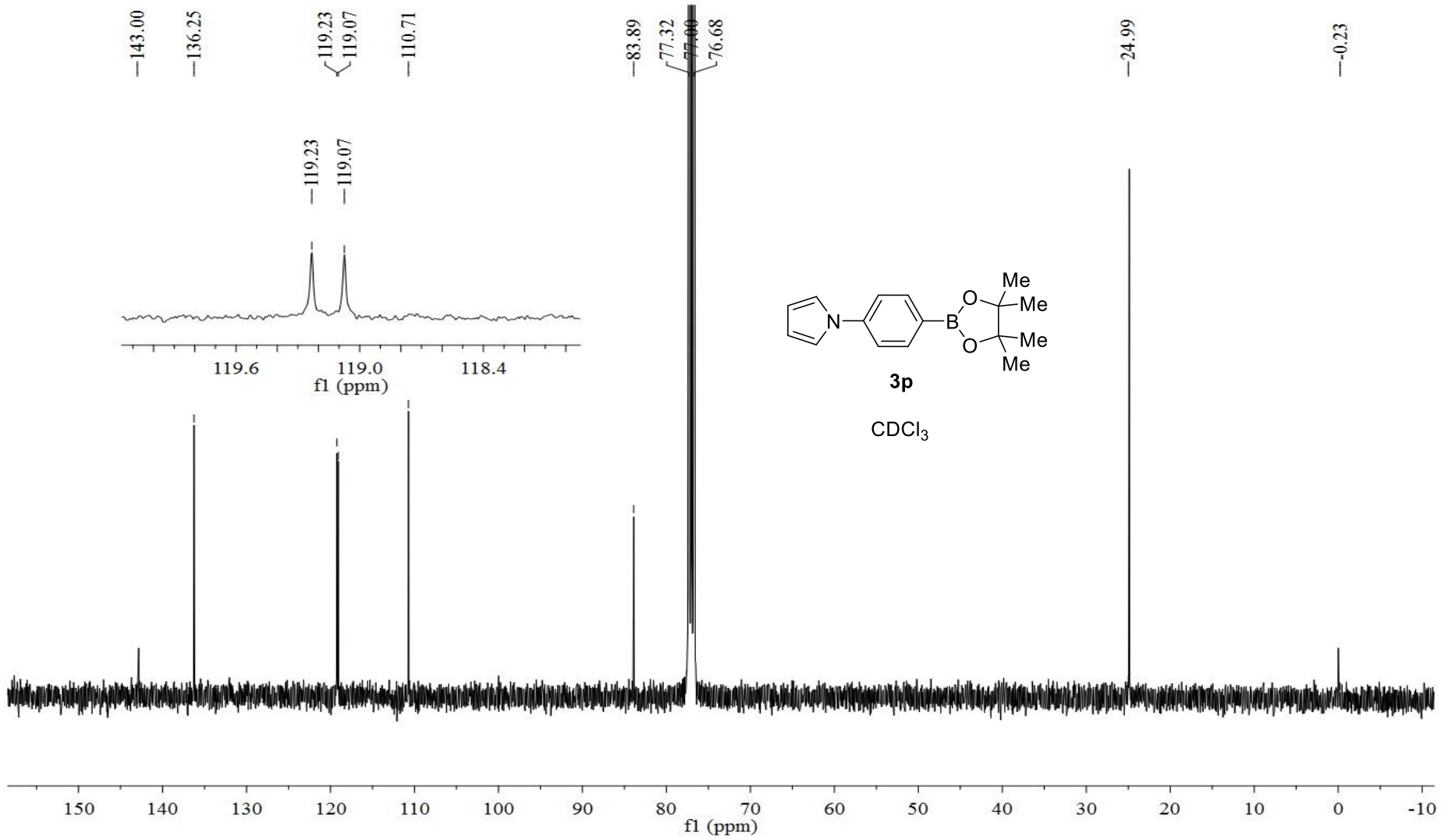

7.618
7.600
7.233
7.195
6.689
6.671
6.653
6.607
6.586
4.730
1.339
0.001
7.260
7.213
NH2
Me
Me
Me
Me
O
O
B
3n
CDCl3
1.00
0.76
0.87
0.76
1.90
12.17
f1 (ppm)

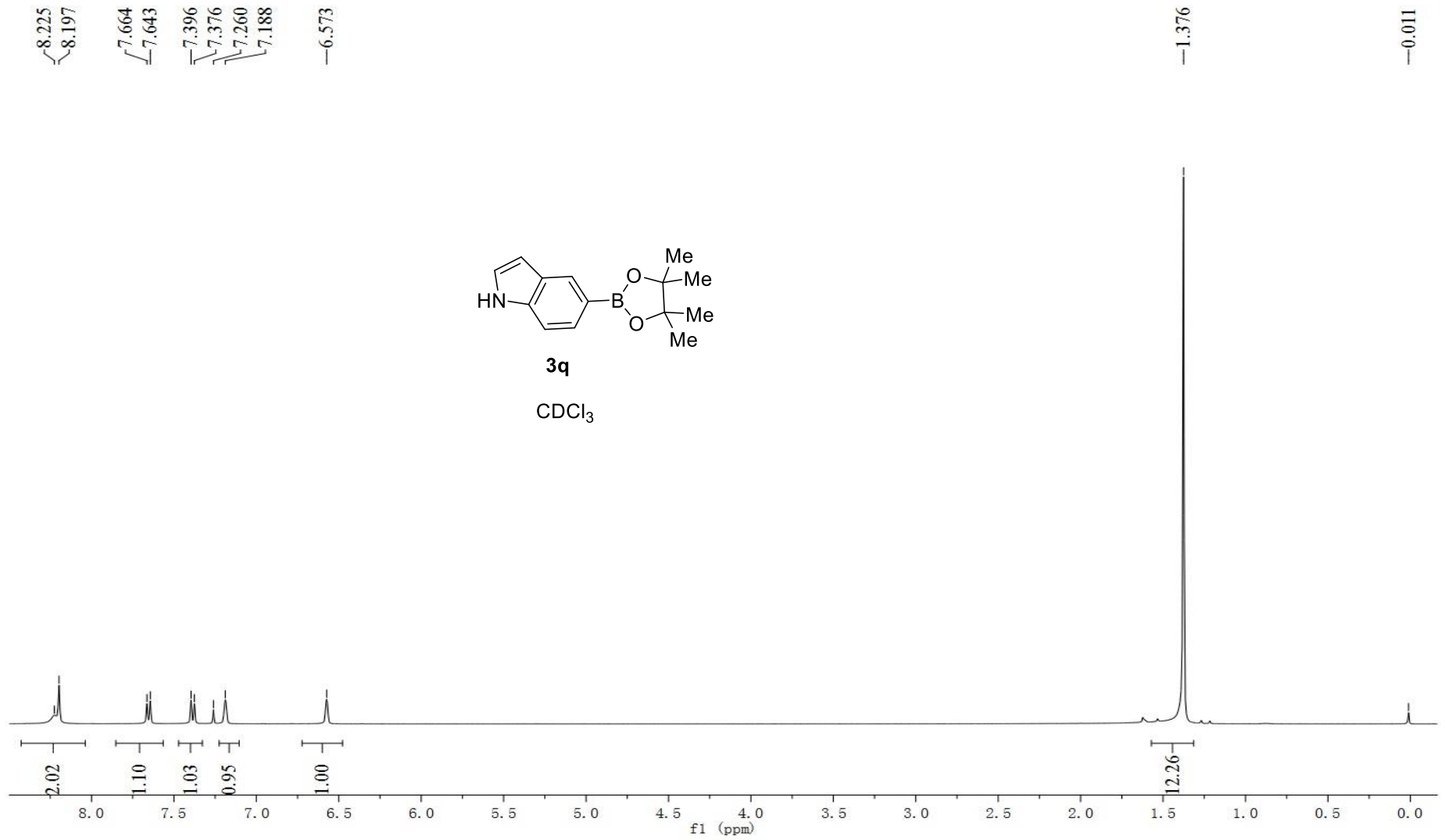

153.64
136.77
132.75
116.84
114.74
83.49
77.32
77.00
76.68
24.84
0.26
NH2
Me
Me
Me
Me
O
O
B
3n
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

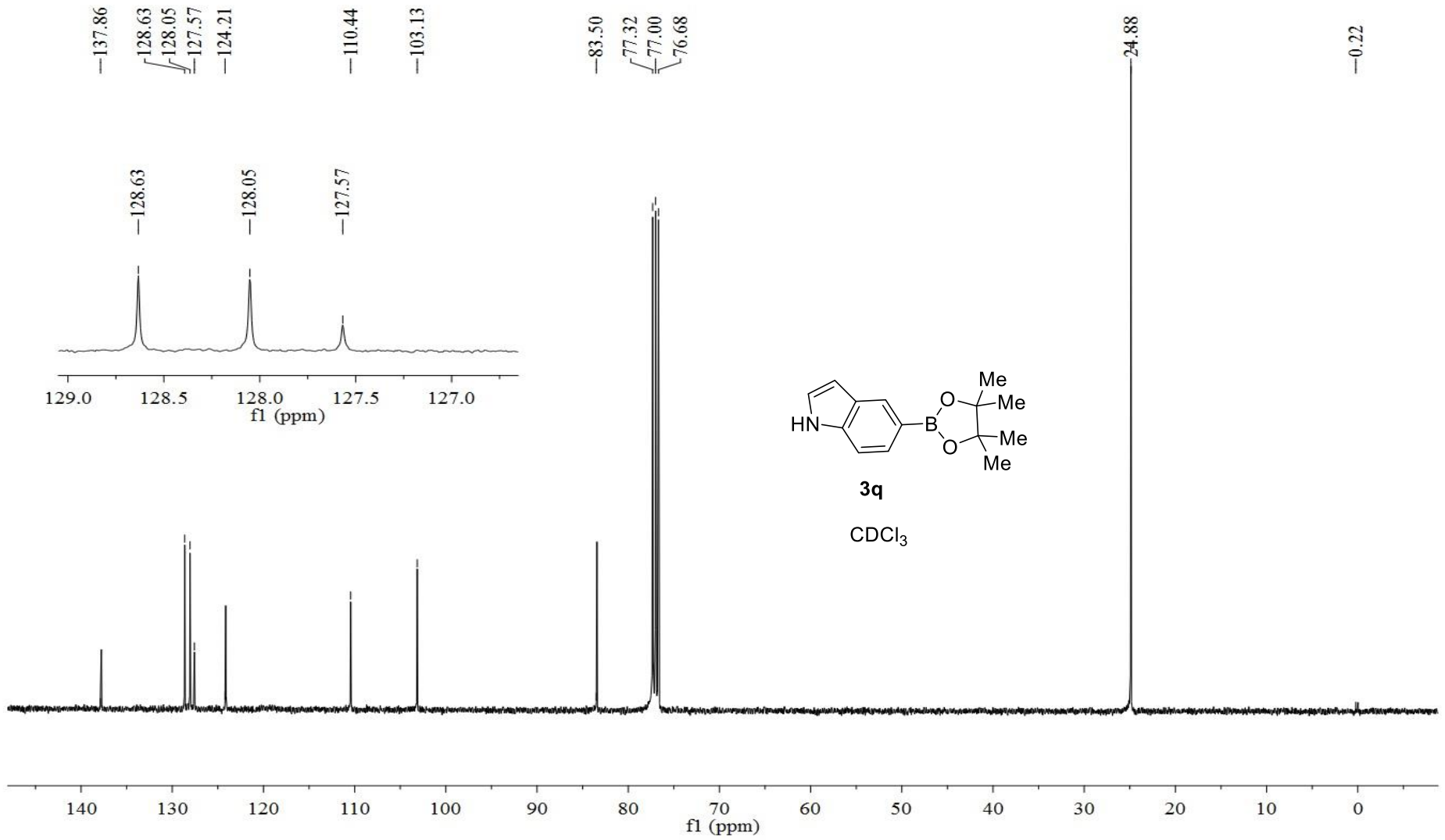

7.719
7.700
7.260
7.237
7.218
2.488
1.338
0.005
MeS
B
O
O
Me
Me
Me
Me
3o
CDCl3
2.00
2.32
3.39
13.37
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

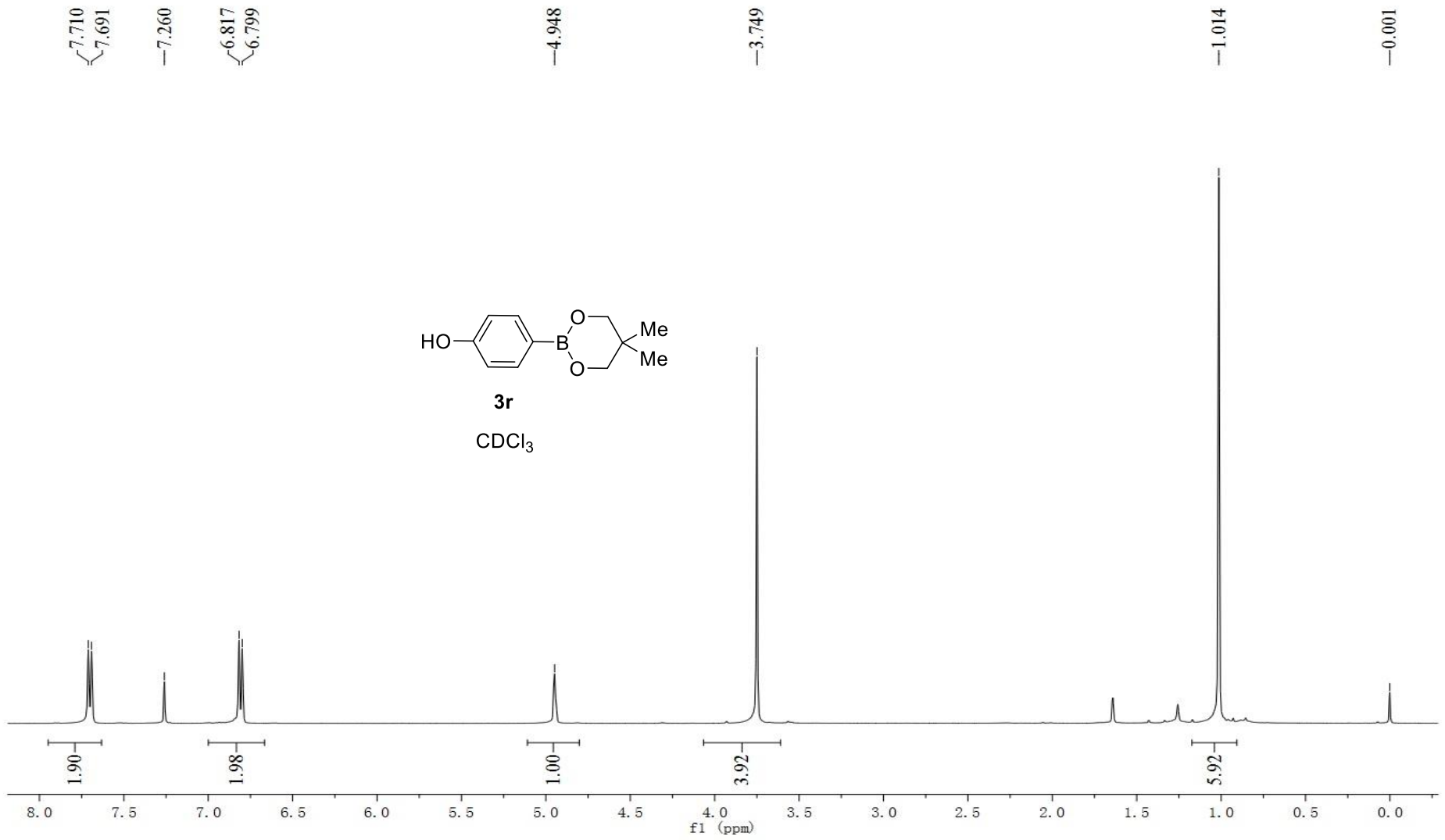

142.54
135.06
125.02
83.71
77.32
77.00
76.68
24.83
15.05
MeS
B
O
O
Me
Me
Me
Me
3o
CDCl3
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

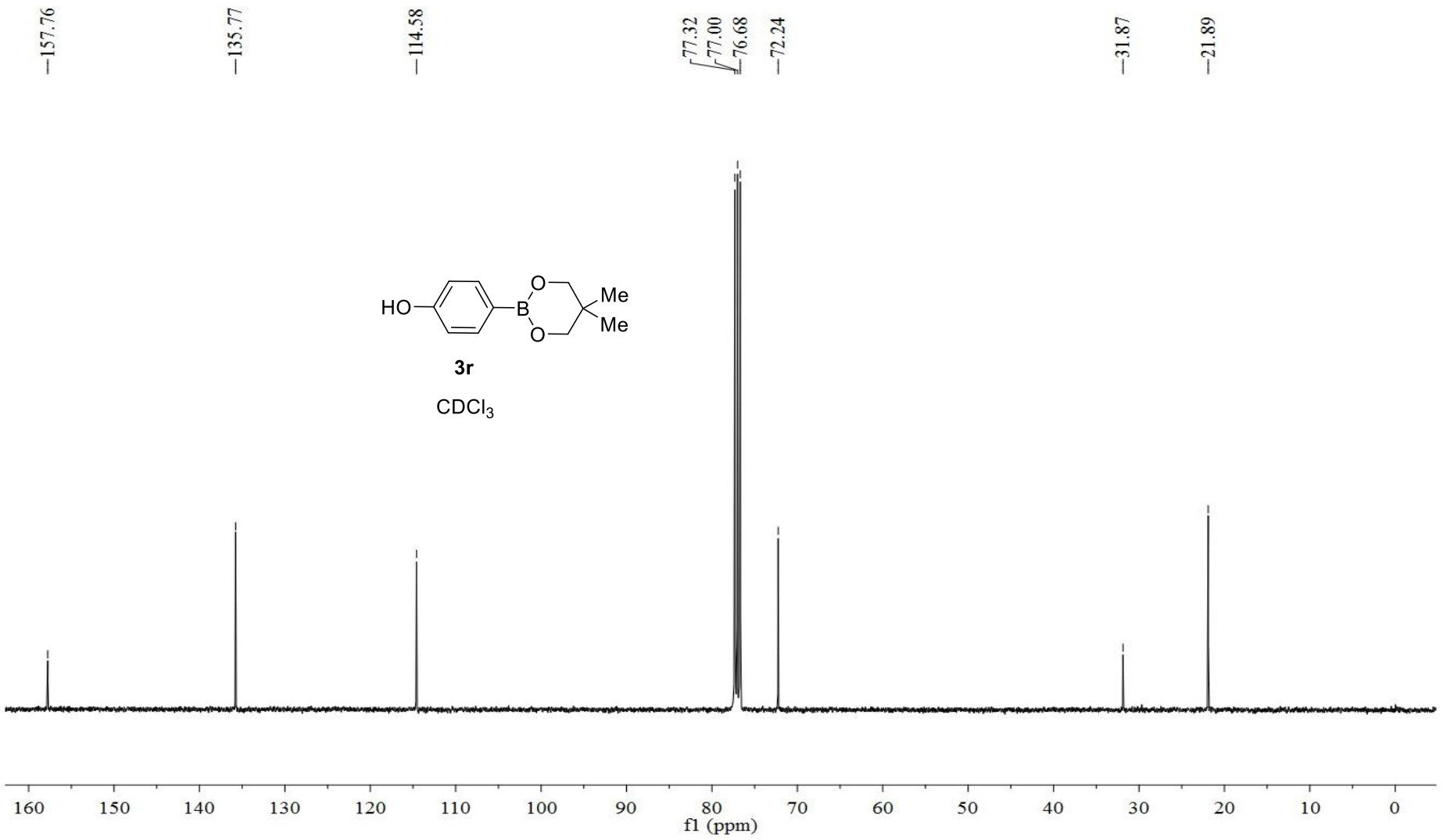

7.869
7.850
7.407
7.387
7.260
7.143
6.379
1.357
0.020
Me
Me
Me
Me
O
O
B
N
3p
CDCl3
2.27
2.27
2.00
2.33
12.55
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

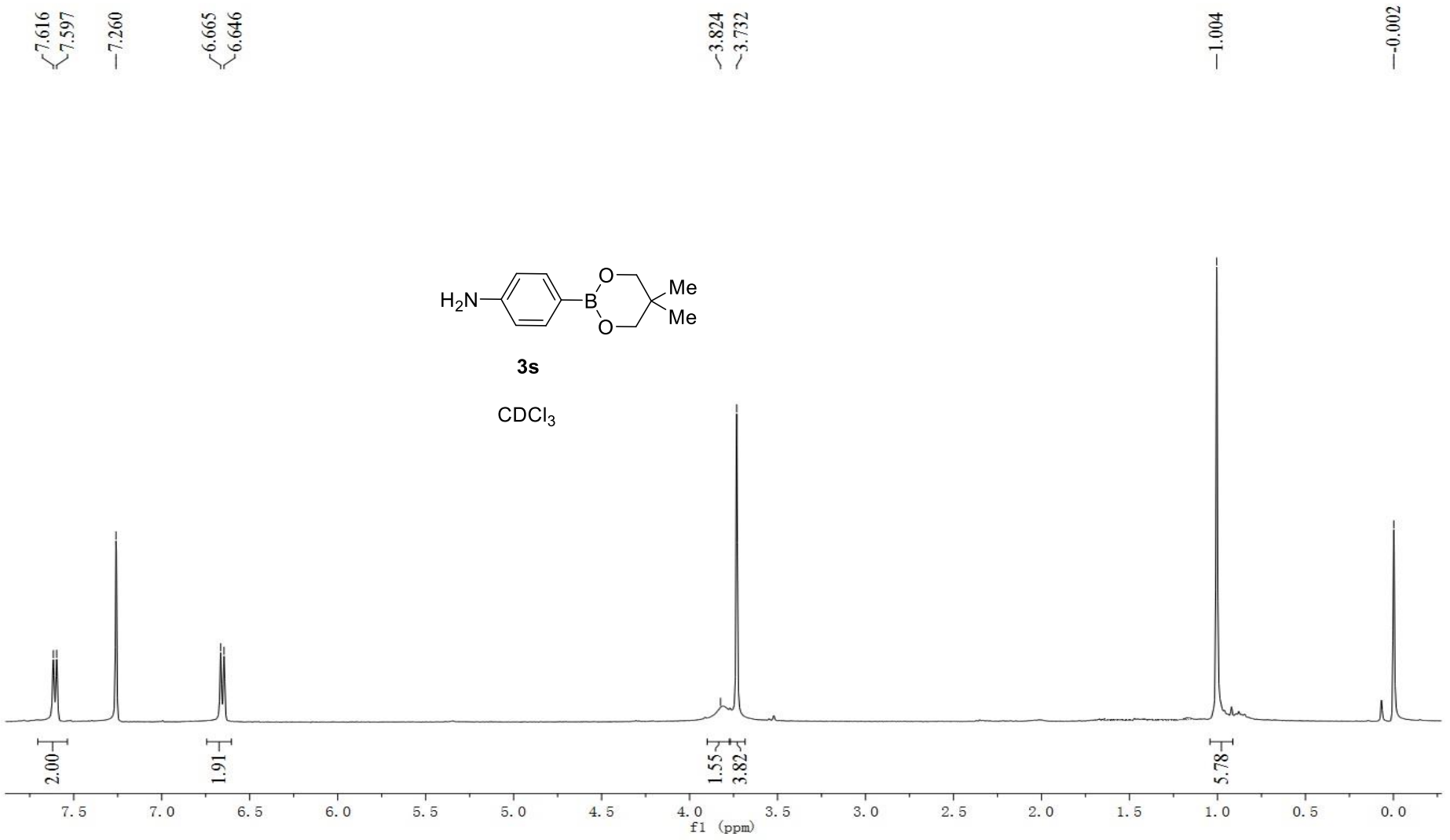

143.00
136.25
119.23
119.07
110.71
83.89
77.32
77.00
76.68
24.99
0.23
119.23
119.07
119.6
119.0
118.4
f1 (ppm)
Me
Me
Me
Me
O
O
B
N
3p
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

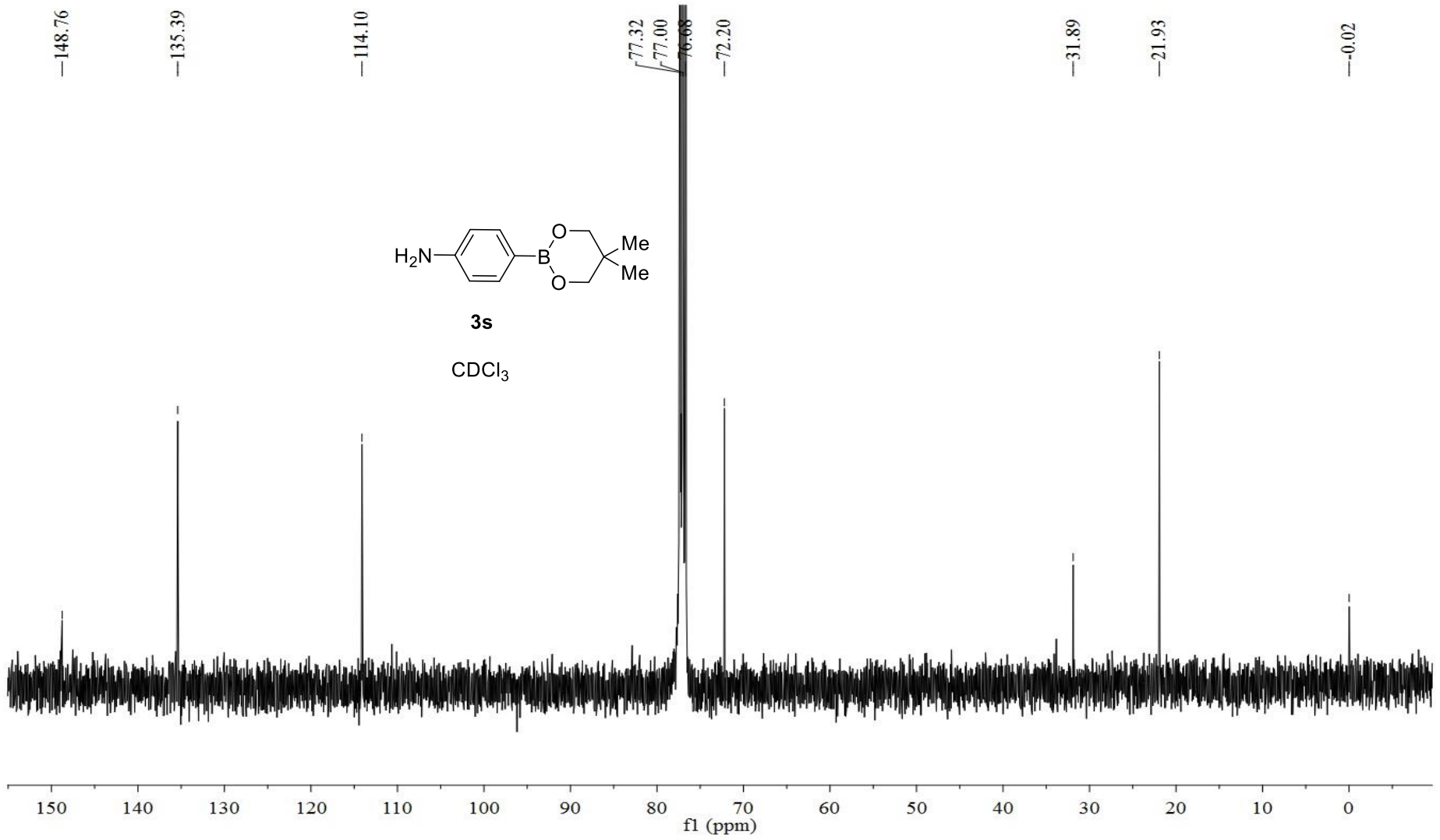

8.225
8.197
7.664
7.643
7.396
7.376
7.260
7.188
6.573
1.376
0.011
HN
B
O
O
Me
Me
Me
Me
3q
CDCl3
2.02
1.10
1.03
0.95
1.00
12.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

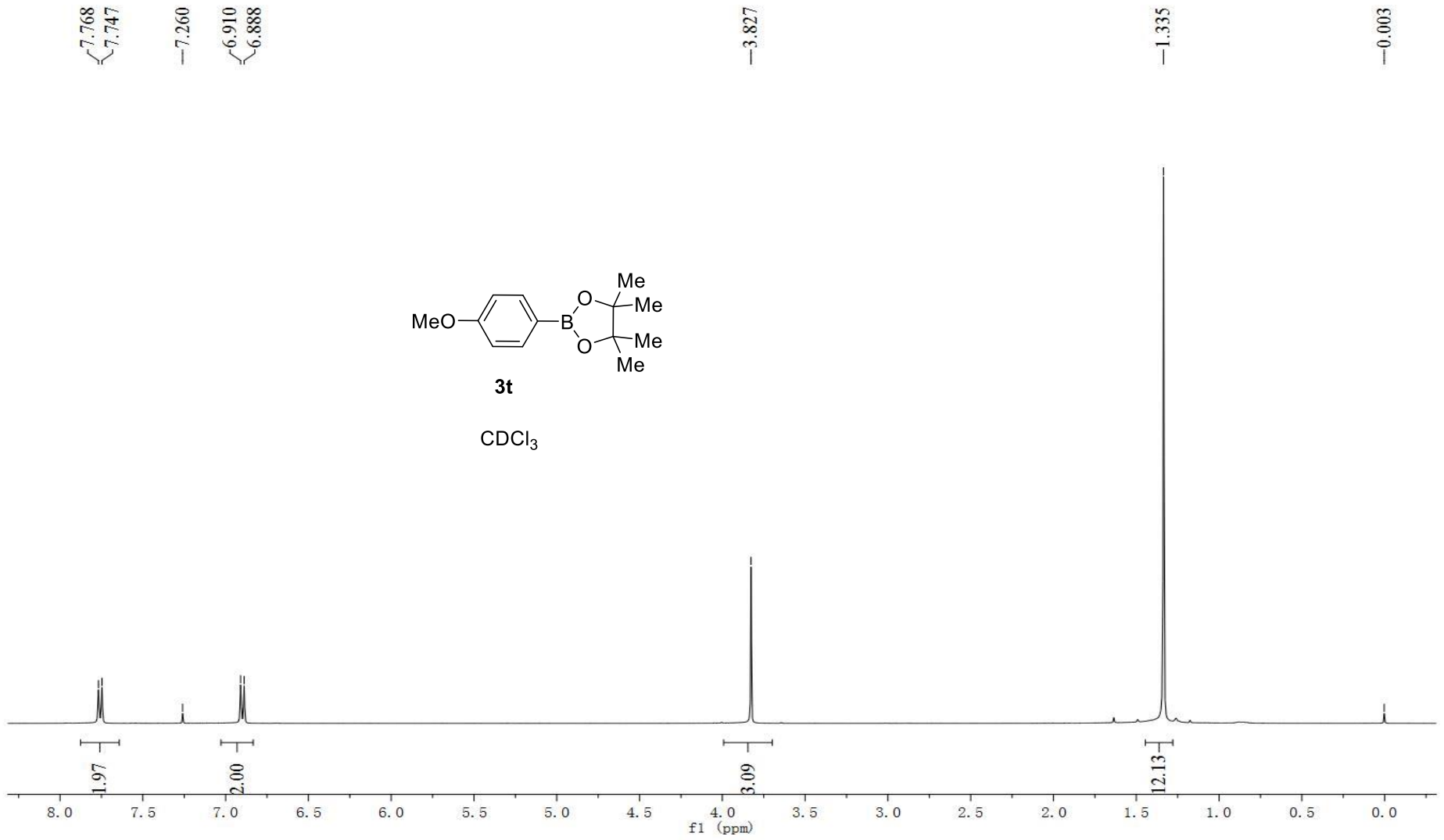

137.86
128.63
128.05
127.57
124.21
110.44
103.13
83.50
77.32
77.00
76.68
24.88
0.22
128.63
128.05
127.57
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
HN
B
O
O
Me
Me
Me
Me
3q
CDCl3
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

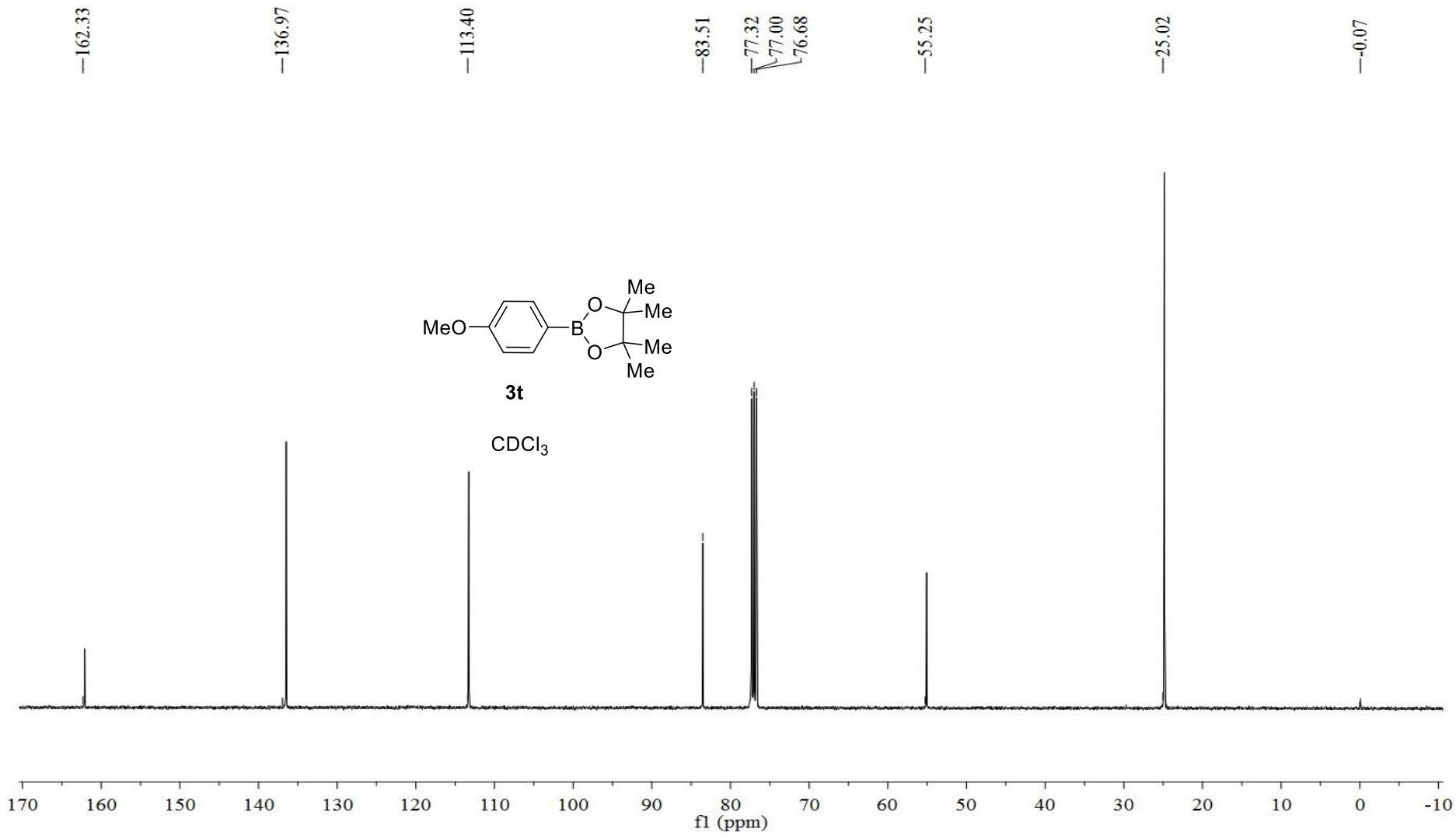

7.710
7.691
7.260
6.817
6.799
4.948
3.749
1.014
0.001
HO
B
O
O
Me
Me
3r
CDCl3
1.90
1.98
1.00
3.92
5.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

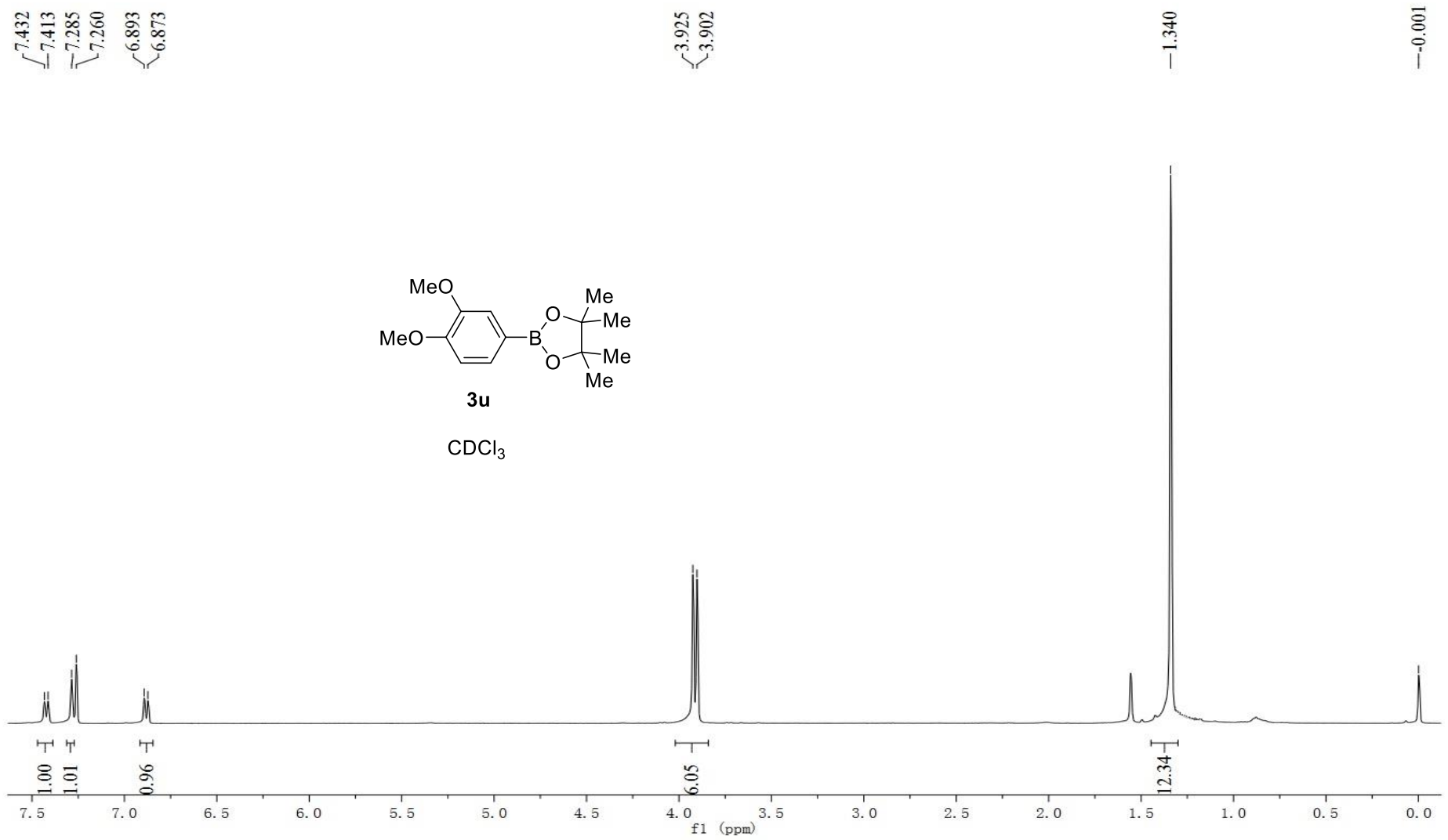

157.76
135.77
114.58
77.32
77.00
76.68
72.24
31.87
21.89
HO
B
O
O
Me
Me
3r
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

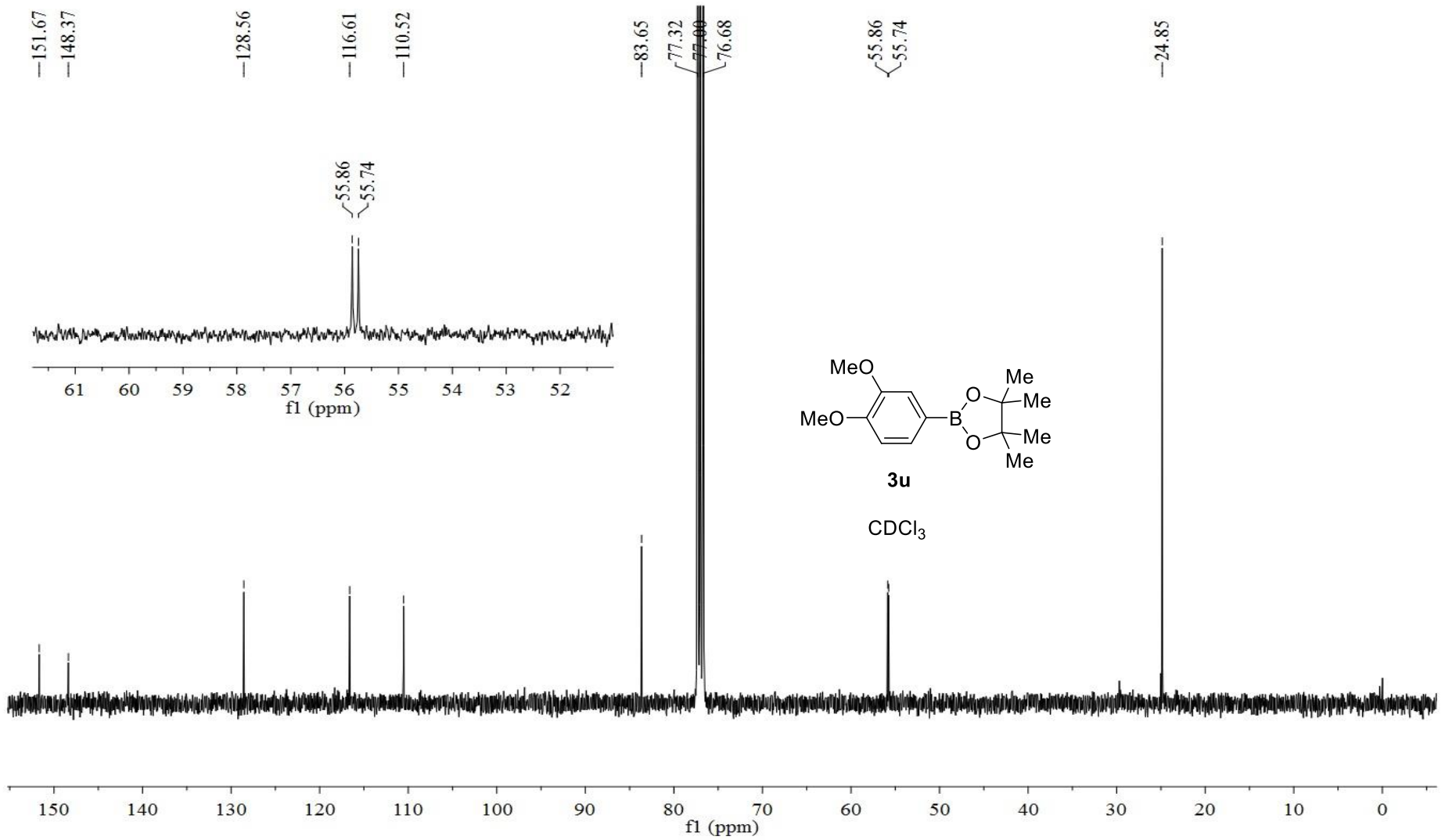

7.616
7.597
7.260
6.665
6.646
3.824
3.732
1.004
0.002
H2N
B
O
O
Me
Me
3s
CDCl3
2.00
1.91
1.55
3.82
5.78
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

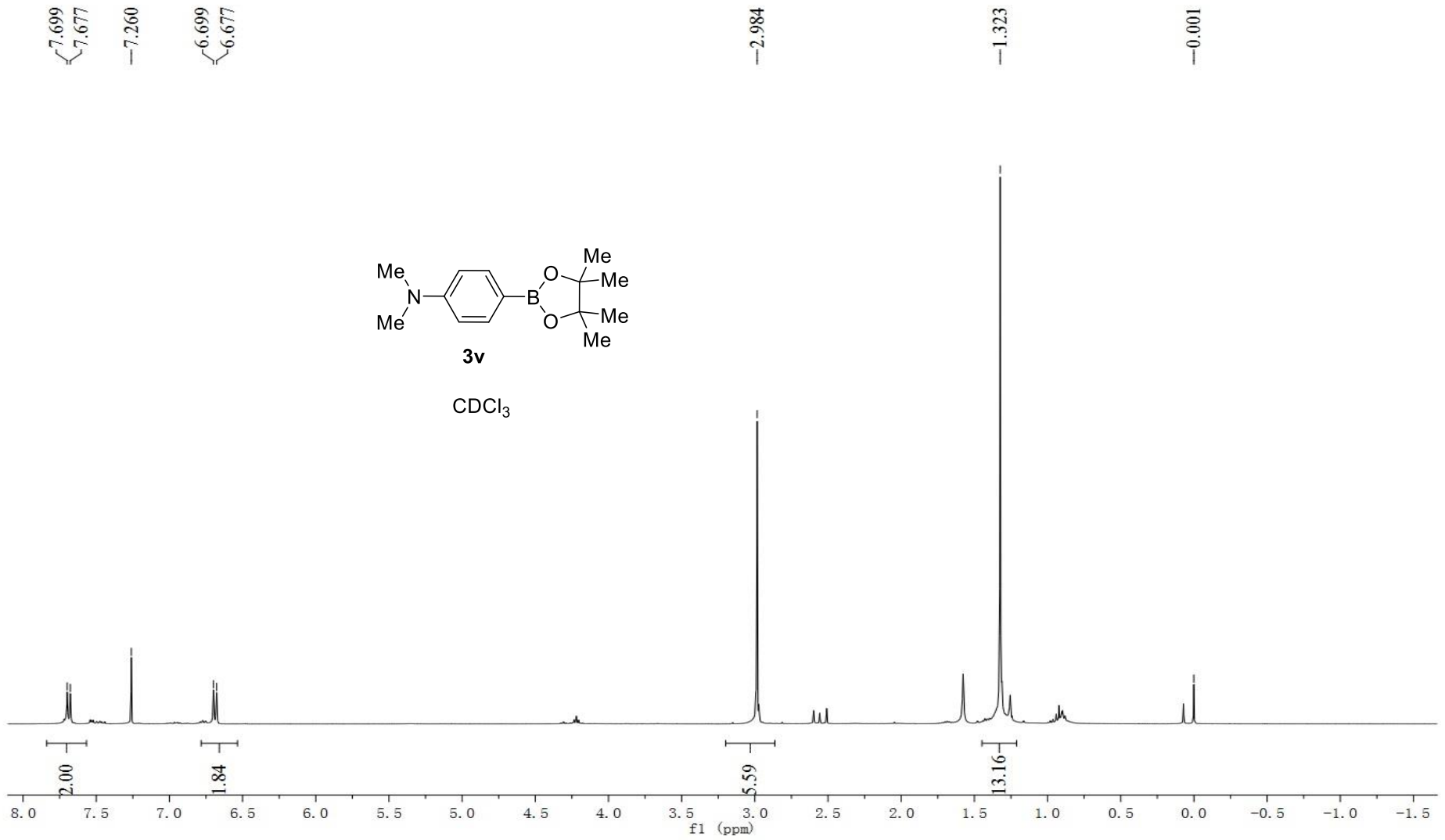

148.76
135.39
114.10
77.32
77.00
76.68
72.20
31.89
21.93
-0.02
H2N
B
O
O
Me
Me
3s
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

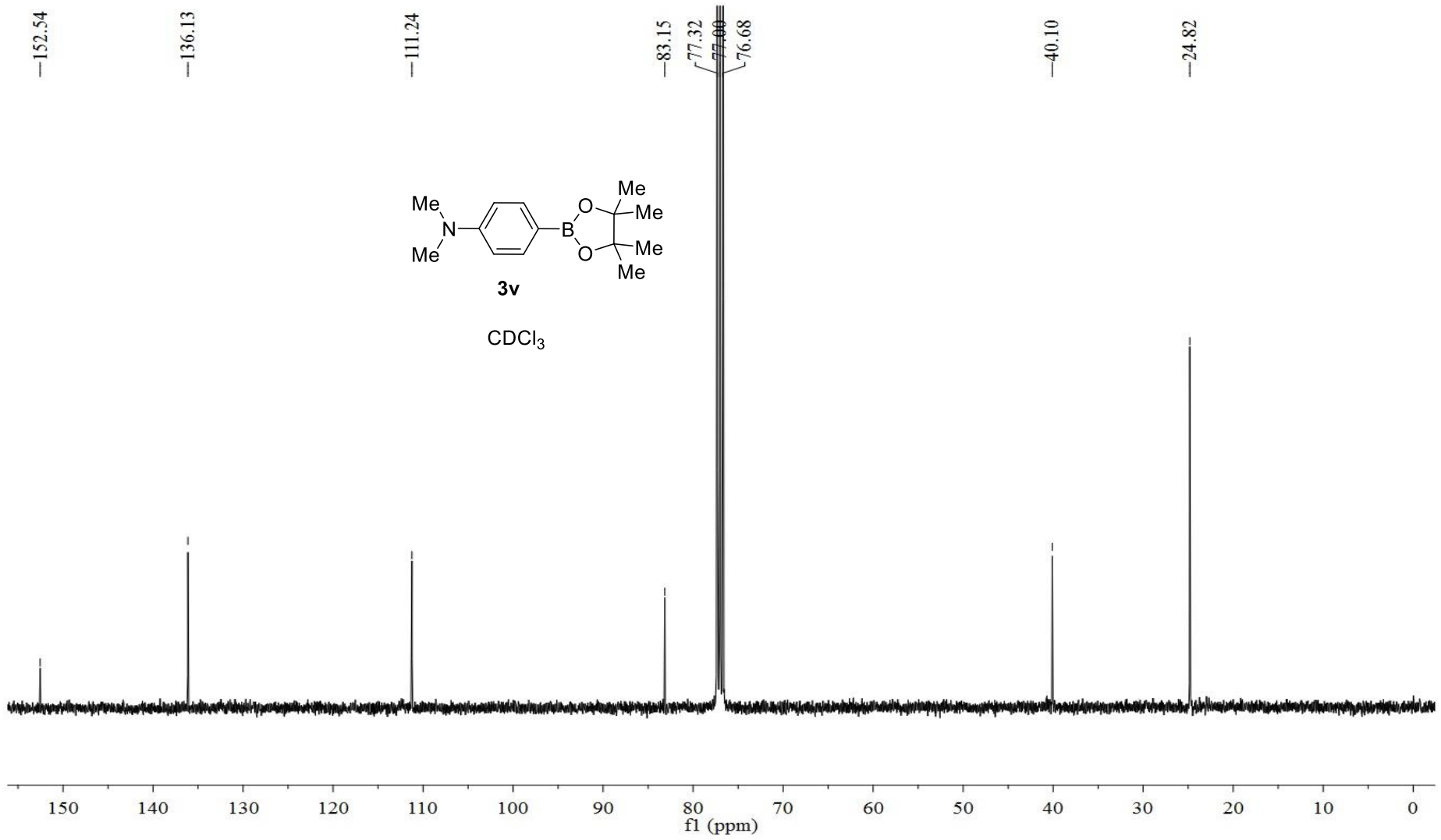

7.768
7.747
7.260
6.910
6.888
3.827
1.335
0.003
MeO
B
O
O
Me
Me
Me
Me
3t
CDCl3
1.97
2.00
3.09
12.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

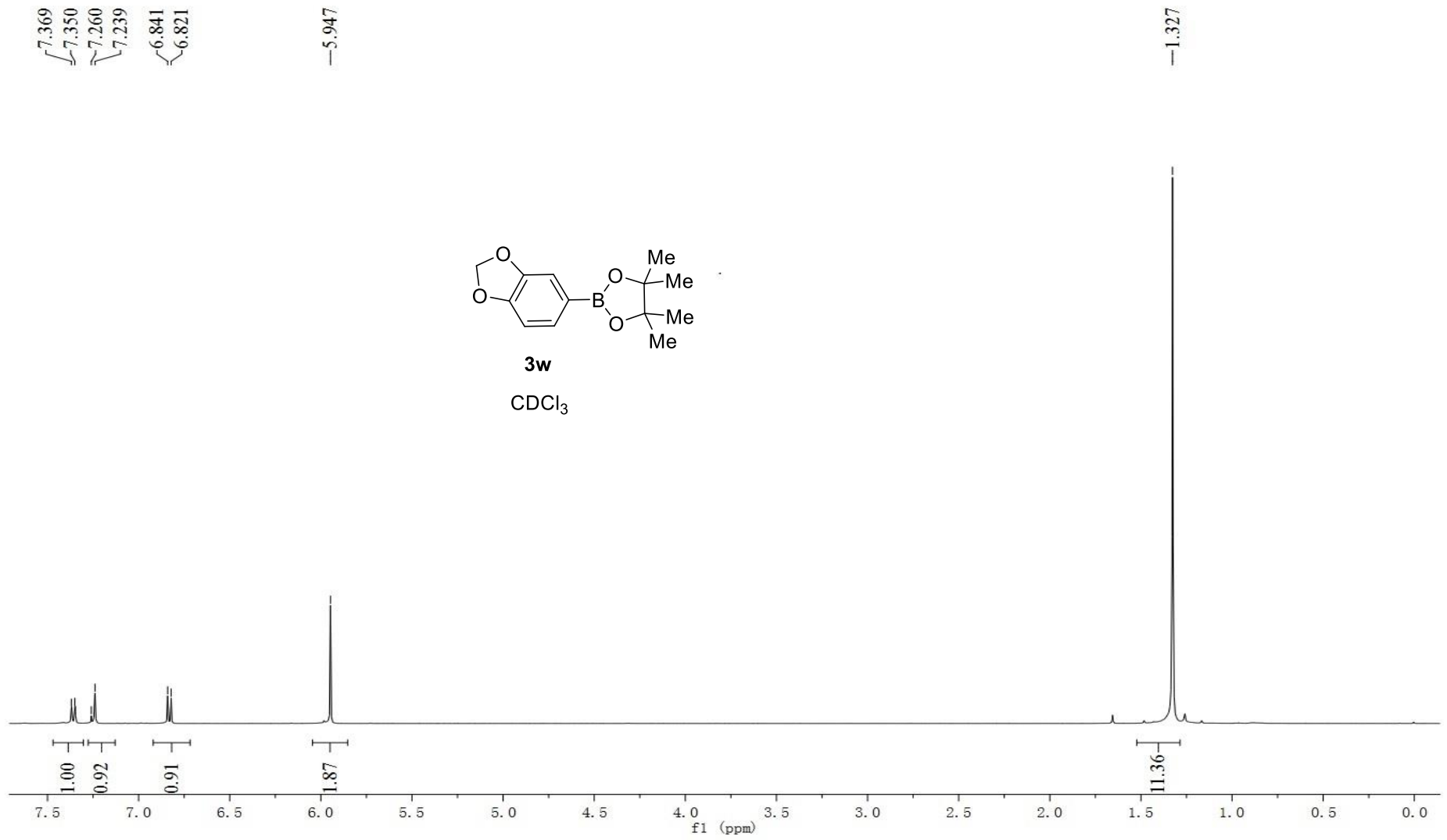

162.33
136.97
113.40
83.51
77.32
77.00
76.68
55.25
25.02
-0.07
MeO
B
O
O
Me
Me
Me
Me
3t
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

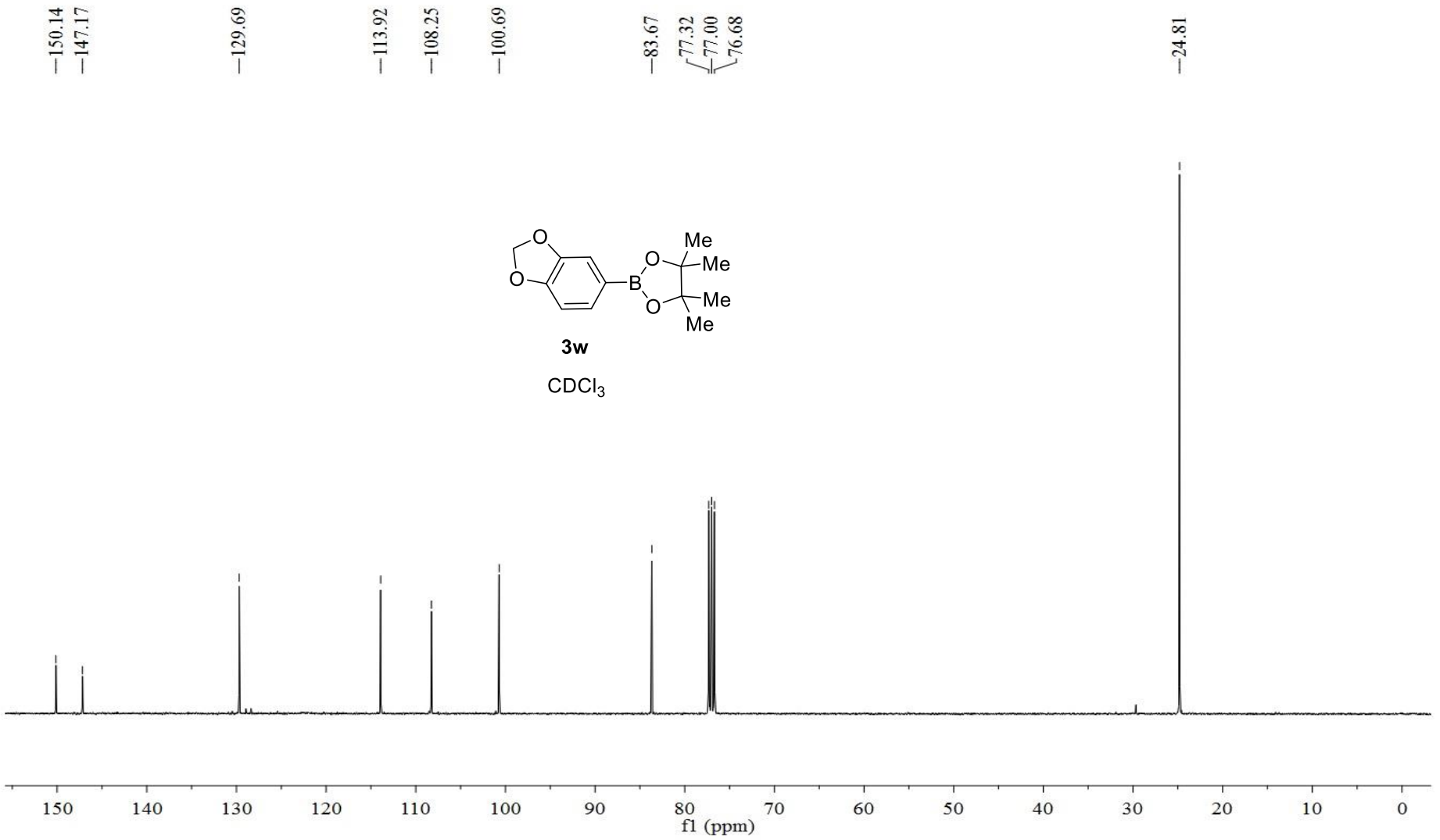

7.432
7.413
7.285
7.260
6.893
6.873
3.925
3.902
1.340
0.001
MeO
MeO
B
O
O
Me
Me
Me
Me
3u
CDCl3
1.00
1.01
0.96
6.05
12.34
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.67
148.37
128.56
116.61
110.52
83.65
77.32
77.00
76.68
55.86
55.74
24.85
55.86
55.74
61 60 59 58 57 56 55 54 53 52
f1 (ppm)
MeO
MeO
B
O
O
Me
Me
Me
Me
3u
CDCl3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.699
7.677
7.260
6.699
6.677
2.984
1.323
0.001
Me
N
Me
B
O
O
Me
Me
Me
Me
3v
CDCl3
2.00
1.84
5.59
13.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


152.54
136.13
111.24
83.15
77.32
77.00
76.68
40.10
24.82
Me
N
Me
B
O
O
Me
Me
Me
Me
3v
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.369
7.350
7.260
7.239
6.841
6.821
5.947
1.327
O
O
O
B
O
Me
Me
Me
Me
3w
CDCl3
1.00
0.92
0.91
1.87
11.36
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.14
147.17
129.69
113.92
108.25
100.69
83.67
77.32
77.00
76.68
24.81
O
O
O
B
O
Me
Me
Me
Me
3w
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)