Samarium Diiodide/Samarium-Mediated Direct Deoxygenative Hydroborylation of Ketones with Hydroborane Esters

Yongqi Liang,[†] Yilin Ma,[†] Wei Zhou,[†,] Yongmei Cui,*[,†] Michal Szostak,*[,§] and Chengwei Liu*[,†]

[†]*Department of Chemistry, Shanghai University, 99 Shangda Road, Shanghai 200444, China*
[§]*Department of Chemistry, Rutgers University, 73 Warren Street, Newark, NJ 07102, USA*

ymcui@shu.edu.cn; michal.szostak@rutgers.edu; liuchengwei@shu.edu.cn; liuchengwei2024@163.com

Supporting Information

Corresponding Author:

Prof. Dr. Y. Cui
Shanghai University
ymcui@shu.edu.cn

Prof. Dr. M. Szostak
Rutgers University
michal.szostak@rutgers.edu

Prof. Dr. C. Liu
Shanghai University
liuchengwei@shu.edu.cn
liuchengwei2024@163.com

List of Known Compounds/General Methods

Unless stated otherwise, all compounds reported in this manuscript have been previously reported. Spectroscopic data matched literature values. All experiments involving samarium were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on JEOL spectrometers at 400 (^{1}H NMR) and 101 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.27 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5977C inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 45 °C. The injector temperature was 280 °C. The detector temperature was 280 °C. For runs with the initial oven temperature of 45 °C, temperature was increased with a 20 °C/min ramp after 45 °C hold for 2.5 min to a final temperature of 280 °C, then hold at 280 °C for 2 min (splitless mode of injection, total run time of 16.25 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument (for HRMS). Melting point was measured on MeltEMP (laboratory devices). All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Information. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds. ^{11}B NMR are typically not reported for borylation products because ^{11}B NMR is not as characteristic as compared to ^{1}H and ^{13}C NMR.

Experimental Procedures

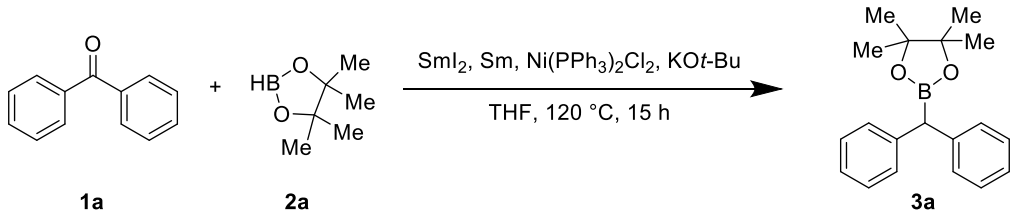
General Procedure for Deoxygenative Hydroborylation of Ketones. An oven-dried Schlenk tube equipped with a stir bar was charged with ketone (neat, 1.0 equiv), pinacolborane (neat, 2.0 equiv), KO*t*-Bu (neat, 2.0 equiv), $Ni(PPh_3)_2Cl_2$ (typically, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. The Schlenk tube was then transferred to the glovebox, samarium (typically, 2.0 equiv) and samarium diiodide (typically, 2.2 equiv, 0.1 M in THF) were added with vigorous stirring at room temperature. The Schlenk tube was then transferred out of the glovebox and placed in a preheated oil bath at 120 °C, which was stirred for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature. The reaction mixture was added ethyl acetate (10 mL) and washed with saturated $NaHCO_3$ solution (2×10 mL). The obtained solution was dried with anhydrous sodium sulfate, filtrated, concentrated to get crude product. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexane/ethyl acetate) afforded the title product. Caution: reactions involving high pressure must be carried out in a well-ventilated hood with appropriate pressure vessels, pressure relief equipment, and/or blast shields.

Representative Procedure for Deoxygenative Hydroborylation of Ketones. An oven-dried Schlenk tube equipped with a stir bar was charged with benzophenone (neat, 36.4 mg, 0.2 mmol, 1.0 equiv), pinacolborane (neat, 51.2 mg, 0.4 mmol, 2.0 equiv), KO*t*-Bu (neat, 44.9 mg, 0.4 mmol, 2.0 equiv), $Ni(PPh_3)_2Cl_2$ (6.18 mg, 0.01 mmol, 0.05 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. The Schlenk tube was then transferred to the glovebox, samarium (60.1 mg, 0.4 mmol, 2.0 equiv) and samarium diiodide (4.4mL, 0.44 mmol, 2.2 equiv, 0.1 M in THF) were added with vigorous stirring at room temperature. The Schlenk tube was then transferred out of the glovebox and placed in a preheated oil bath at 120 °C, which was stirred for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature. The reaction mixture was added ethyl acetate (10 mL) and washed with saturated $NaHCO_3$ solution (2×10 mL). The obtained solution was dried with anhydrous sodium sulfate, filtrated, concentrated to get crude product. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using

internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexane/ethyl acetate) afforded the title product. Yield 68% (40.0 mg, 0.136 mmol). White Solid. Characterization data are included in the section below. Caution: reactions involving high pressure must be carried out in a well-ventilated hood with appropriate pressure vessels, pressure relief equipment, and/or blast shields.

Characterization Data for Deoxygenative Hydroborylation of Ketones

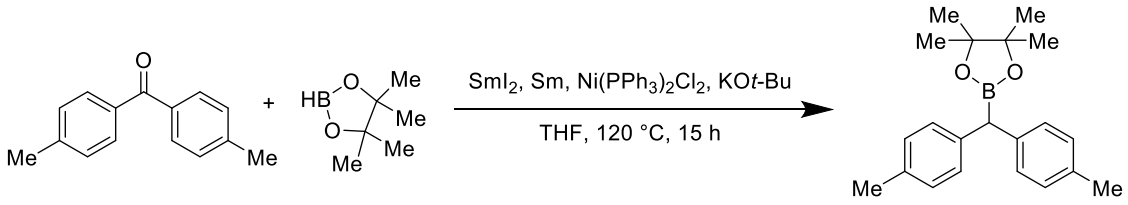
2-(Diphenylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3a)[1]



1a **2a** **3a**

According to the general procedure, the reaction of benzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 68% yield (40.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33-7.25 (m, 1H), 7.21-7.18 (m, 7H), 7.12-7.06 (m, 2H), 3.79 (s, 1H), 1.16 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.04, 128.10, 127.37, 124.58, 82.71, 23.57.

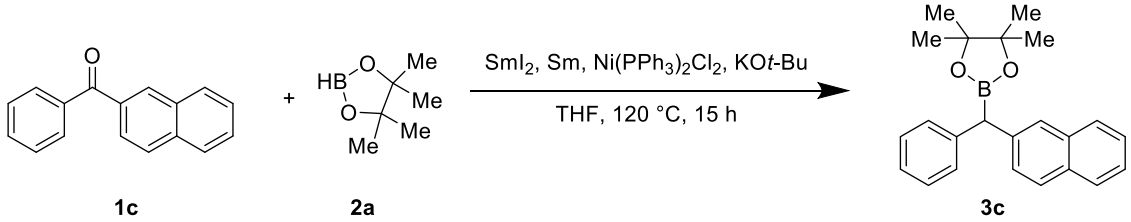
2-[Bis(4-methylphenyl)methyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3b)[1]



1b **2a** **3b**

According to the general procedure, the reaction of 4,4'-dimethylbenzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 31% yield (20.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.06 (d, *J* = 8.0 Hz, 4H), 6.99 (d, *J* = 8.0 Hz, 4H), 3.70 (s, 1H), 2.22 (s, 6H), 1.15 (s, 12H), **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.21, 133.86, 127.88, 125.40, 82.59, 23.58, 19.96.

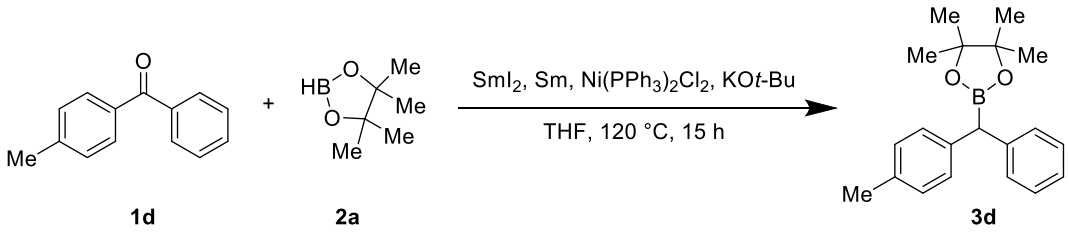
4,4,5,5-Tetramethyl-2-(2-naphthalenylphenylmethyl)-1,3,2-dioxaborolane (Scheme 1, 3c)[2]



1c **2a** **3c**

According to the general procedure, the reaction of 2-benzoylnaphthalene (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 43% yield (29.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.61 (s, 1H), 7.42-7.37 (m, 1H), 7.35-7.32 (m, 3H), 7.25-7.20 (m, 4H), 3.96 (s, 1H), 1.17 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.88, 138.61, 132.70, 130.83, 128.20, 127.41, 127.13, 126.84, 126.65, 126.48, 126.07, 125.69, 124.70, 124.10, 82.80, 23.11.

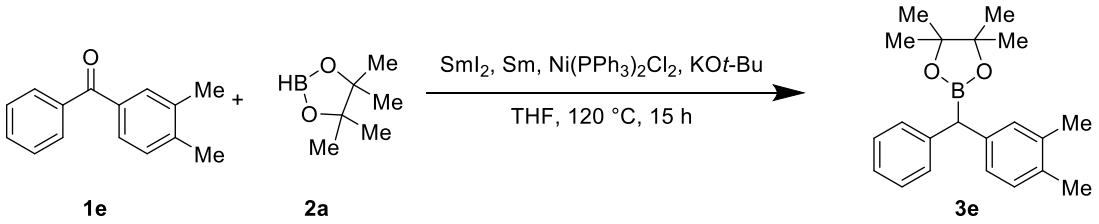
4,4,5,5-Tetramethyl-2-[(4-methylphenyl)phenylmethyl]-1,3,2-dioxaborolane (Scheme 1, 3d)[1]



1d **2a** **3d**

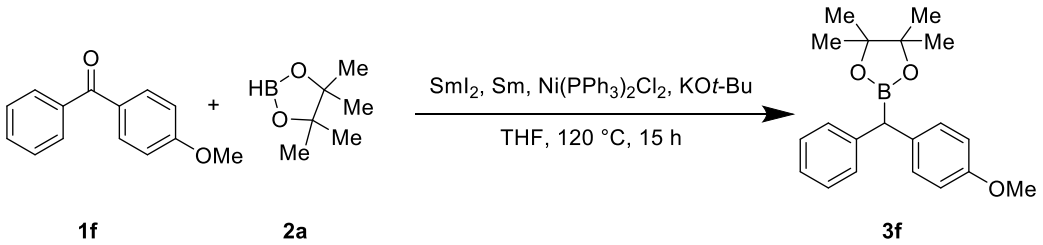
According to the general procedure, the reaction of 4-methylbenzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 54% yield (33.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (t, 1H), 7.20-7.18 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 1H), 2.22 (s, 3H), 1.15 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.33, 137.90, 133.98, 127.98, 127.33, 125.49, 125.41, 124.47, 81.87, 23.57, 19.14.

2-((3,4-Dimethylphenyl)(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3e)[1]



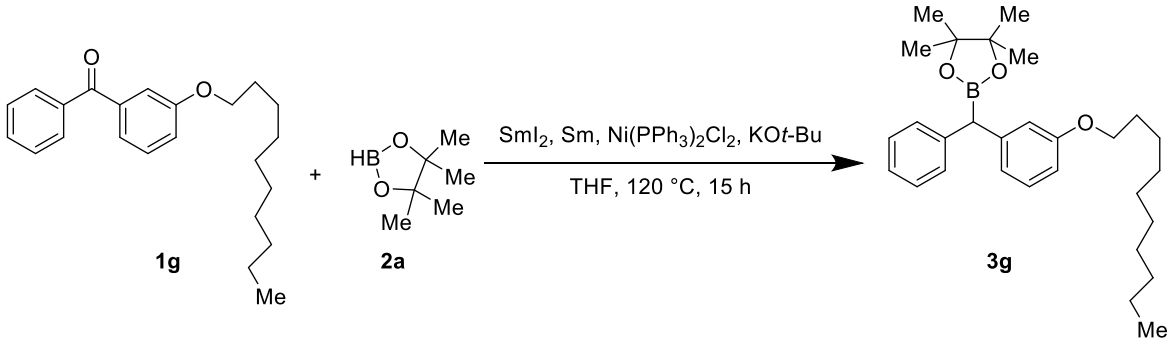
According to the general procedure, the reaction of 3,4-dimethylbenzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 50% yield (32.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 (t, *J* = 8.0 Hz, 1H), 7.20-7.18 (m, 4H), 7.08 (t, *J* = 4.0 Hz, 1H), 6.94 (d, *J* = 4.0 Hz, 2H), 3.72 (s, 1H), 2.13 (s, 6H), 1.16 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.44, 138.27, 135.42, 132.68, 129.50, 128.65, 127.95, 127.31, 125.45, 124.41, 82.62, 23.58, 18.83, 18.28.

2-[(4-Methoxyphenyl)phenylmethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3f)[1]



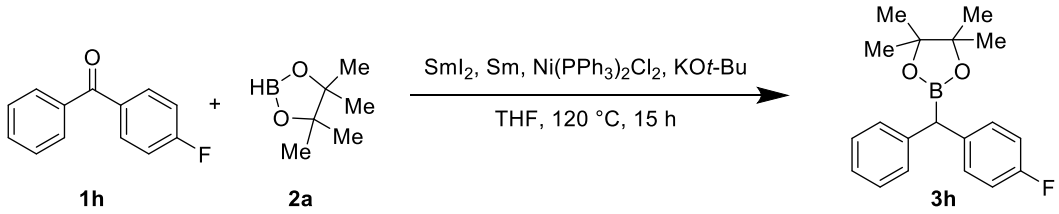
According to the general procedure, the reaction of 4-methoxybenzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 44% yield (28.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20-7.18 (m, 4H), 7.14-7.07 (m, 3H), 6.74 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 1H), 3.70 (s, 3H), 1.15 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.69, 142.68, 134.11, 130.21, 129.00, 128.45, 125.57, 113.92, 83.77, 55.28, 24.68.

2-((3-(Decyloxy)phenyl)(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3g)



According to the general procedure, the reaction of [4-(decyloxy)phenyl]phenylmethanone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 31% yield (27.9 mg). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.25 (m, 1H), 7.16 (t, J = 8.0 Hz, 4H), 7.09 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H), 3.84 (t, J = 6.6 Hz, 2H), 3.72 (s, 1H), 1.71-1.64 (m, 2H), 1.36 (t, J = 8.0 Hz, 2H), 1.21-1.18 (m, 12H), 1.15 (s, 12H), 0.81 (t, J = 6.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.38, 156.17, 141.63, 132.58, 129.06, 128.38, 127.88, 127.31, 124.42, 113.38, 82.63, 66.87, 38.52, 33.43, 30.87, 28.55, 28.40, 28.31, 25.05, 23.57, 21.66, 13.11. **HMRS** calcd for $C_{29}H_{43}BO_3$ (M^+ + H) 451.3379, found 451.3378.

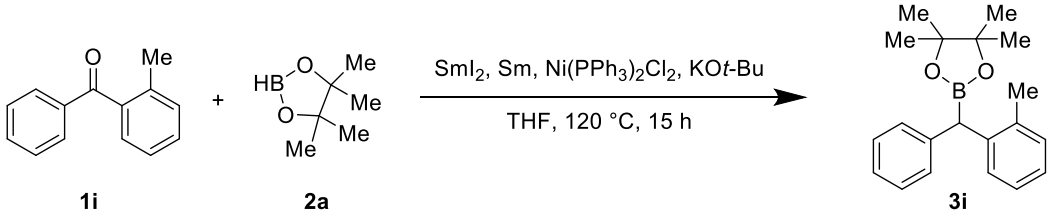
2-[(4-Fluorophenyl)phenylmethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3h)[3]



According to the general procedure, the reaction of 4-fluorobenzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 27% yield (16.9 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.19-7.18 (m, 2H), 7.16 (s, 1H), 7.14-7.13 (m, 2H), 7.09 (t, J = 5.1 Hz, 2H), 6.87 (t, J = 8.0 Hz, 2H) 3.75 (s, 1H), 1.15 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.10 (d, J^F = 10.1 Hz), 137.80, 135.14, 130.57 (d, J^F =

7.1 Hz), 129.14 (d, J^F = 15.2 Hz), 128.53 (d, J^F = 9.1 Hz), 125.76 (d, J^F = 13.1 Hz), 115.21 (d, J^F = 21.2 Hz), 83.91, 24.67. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -118.61.

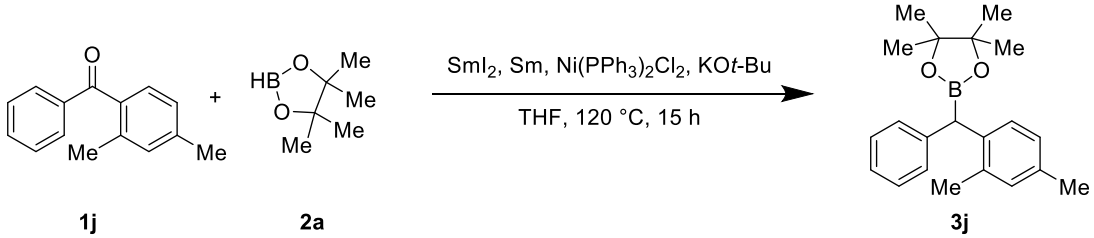
4,4,5,5-Tetramethyl-2-[(2-methylphenyl)phenylmethyl]-1,3,2-dioxaborolane (Scheme 1, 3i)[1]



1i **2a** **3i**

According to the general procedure, the reaction of 2-methylbenzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 64% yield (39.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28-7.25 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.19-7.15 (m, 2H), 7.11 (t, *J* = 4.0 Hz, 1H), 7.09-7.06 (m, 3H), 7.04 (t, *J* = 1.7 Hz, 1H), 3.93 (s, 1H), 2.20 (s, 3H), 1.16 (d, *J* = 2.2 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.73, 140.18, 136.79, 130.49, 129.36, 129.17, 128.41, 126.02, 125.91, 125.51, 83.80, 24.67, 20.22.

2-((2,4-Dimethylphenyl)(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3j)

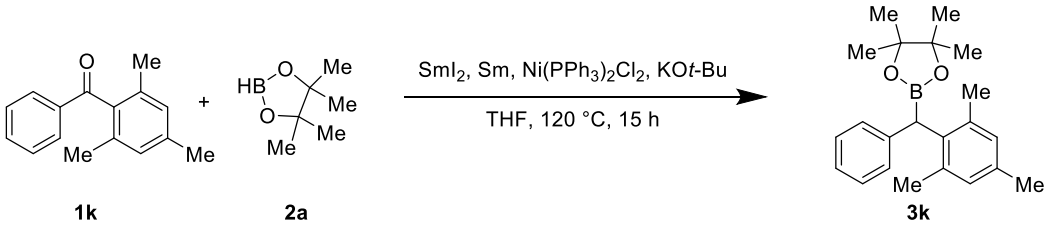


1j **2a** **3j**

According to the general procedure, the reaction of 2,4-dimethylbenzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 44% yield (28.4 mg). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (d, *J* = 4.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 3H), 7.06-7.04 (m, 1H), 6.88 (t, *J* = 8.0 Hz, 2H), 3.88 (s, 1H), 2.21 (s, 3H), 2.15 (s, 3H), 1.15 (d, *J* = 4.0 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.89, 135.93, 135.48, 134.15, 130.27, 128.18, 127.96, 127.26,

125.55, 124.29, 82.62, 23.64, 19.89, 19.00. **HMRS** calcd for $C_{29}H_{43}BO_3$ (M^+ + H) 323.2177, found 323.2197.

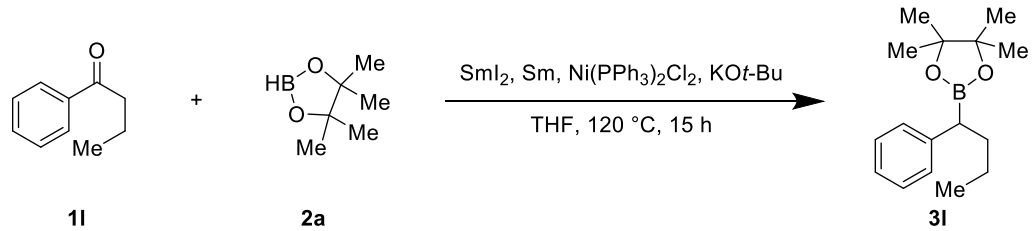
2-(Mesityl(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3k)



1k 2a 3k

According to the general procedure, the reaction of 2,4,6-trimethylbenzophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 62% yield (41.7 mg). *New compound*. Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.12 (t, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 3H), 6.79 (s, 2H), 4.08 (s, 1H), 2.20 (s, 3H), 2.10 (s, 6H), 1.19 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.39, 137.33, 135.47, 135.13, 129.35, 128.41, 127.99, 124.97, 83.62, 25.00, 21.28, 20.99. **HMRS** calcd for $C_{22}H_{29}BO_2$ (M^+ + H) 337.2334, found 337.2333.

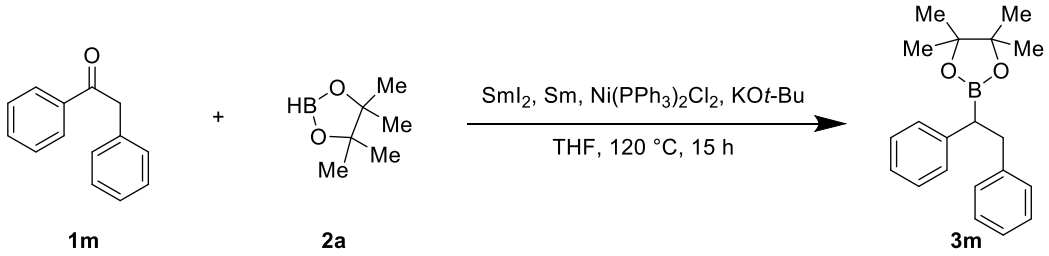
4,4,5,5-Tetramethyl-2-(1-phenylbutyl)-1,3,2-dioxaborolane (Scheme 2, 3l)[1]



1l 2a 3l

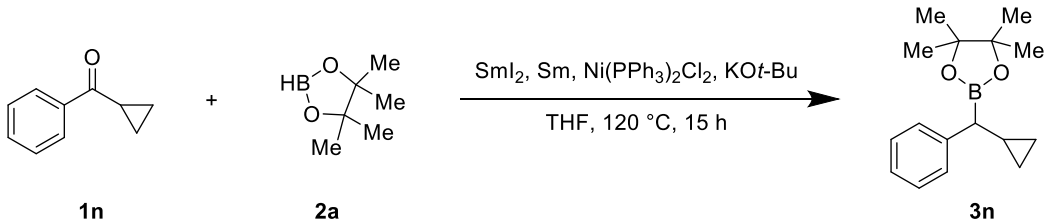
According to the general procedure, the reaction of butyrophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 78% yield (40.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.14-7.12 (m, 2H), 7.07-7.03 (m, 1H), 2.24 (t, *J* = 8.0 Hz, 1H), 1.79-1.70 (m, 1H), 1.59-1.53 (m, 1H), 1.21 (dd, *J* = 16, 4.0 Hz, 2H), 1.12 (d, *J* = 4.0 Hz, 12H), 0.82 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.54, 128.46, 128.31, 124.69, 83.31, 34.89, 24.66, 22.46, 14.21.

2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 2, 3m)[4]



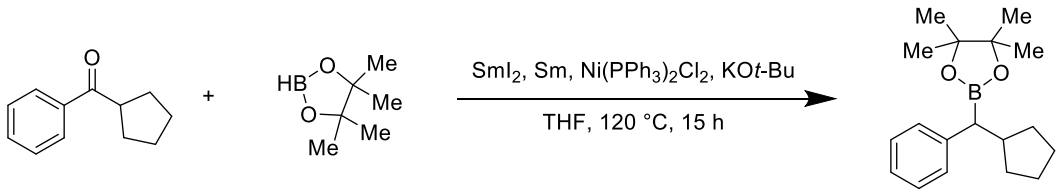
According to the general procedure, the reaction of 2-phenylacetophenone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 67% yield (41.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30-7.20 (m, 1H), 7.18 (t, *J* = 1.9 Hz, 2H), 7.16-7.10 (m, 5H), 7.09-7.04 (m, 2H), 3.11-3.05 (m, 1H), 2.91-2.86 (m, 1H), 2.63-2.59 (m, 1H), 1.03 (d, *J* = 4.0 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.64, 141.82, 128.97, 128.49, 128.43, 128.13, 125.85, 125.49, 85.74, 38.00, 24.66.

2-(Cyclopropylphenylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 2, 3n)[5]



According to the general procedure, the reaction of benzoylcyclopropane (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 51% yield (26.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.16-7.13 (m, 4H), 7.07-7.02 (m, 1H), 2.29-2.18 (m, 1H), 2.02 (d, *J* = 12 Hz, 1H), 1.89-1.81 (m, 1H), 1.60-1.55 (m, 1H), 1.43-1.33 (m, 2H), 1.12 (d, *J* = 8.0 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.94, 128.80, 128.21, 125.13, 82.81, 43.03, 33.32, 25.27, 24.67.

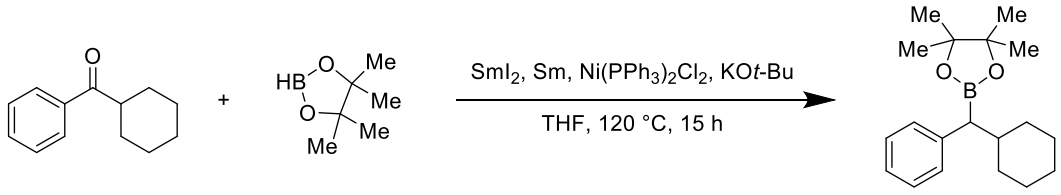
2-(Cyclopentylphenylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 2, 3o)[4]



1o **2a** **3o**

According to the general procedure, the reaction of cyclopentyl phenyl ketone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 75% yield (42.9 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.17-7.13 (m, 4H), 7.07-7.03 (m, 1H), 2.27-2.20 (m, 1H), 2.01 (d, *J* = 12 Hz, 1H), 1.89-1.81 (m, 1H), 1.60-1.55 (m, 2H), 1.49-1.33 (m, 5H), 1.12 (s, *J* = 8.0 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.08, 128.80, 128.21, 125.13, 83.28, 43.03, 32.78, 32.49, 25.27, 24.67.

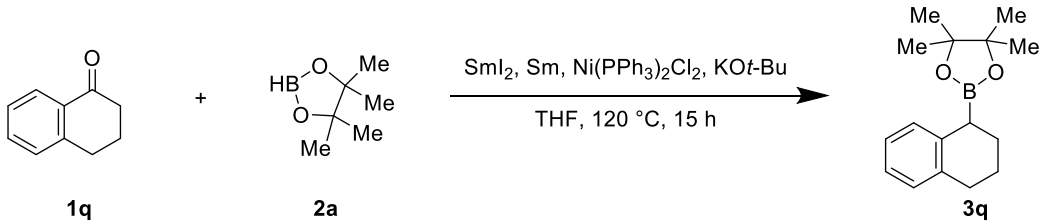
2-(Cyclohexylphenylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 2, 3p)[4]



1p **2a** **3p**

According to the general procedure, the reaction of cyclohexyl phenyl ketone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 52% yield (31.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (d, *J* = 8.0 Hz, 2H), 7.13-7.11 (m, 2H), 7.07-7.03 (m, 1H), 1.97 (d, *J* = 12 Hz, 1H), 1.78-1.62 (m, 5H), 1.39 (d, *J* = 12 Hz, 1H), 1.28-1.16 (m, 2H), 1.11(d, *J* = 4.0 Hz, 12H), 1.08-1.01 (m, 2H), 0.98-0.94 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.84, 129.27, 128.14, 125.17, 85.26, 40.93, 33.33, 31.43, 26.68, 26.41, 24.75.

4,4,5,5-Tetramethyl-2-(1,2,3,4-tetrahydro-1-naphthalenyl)-1,3,2-dioxaborolane (Scheme 2, 3q)[5]

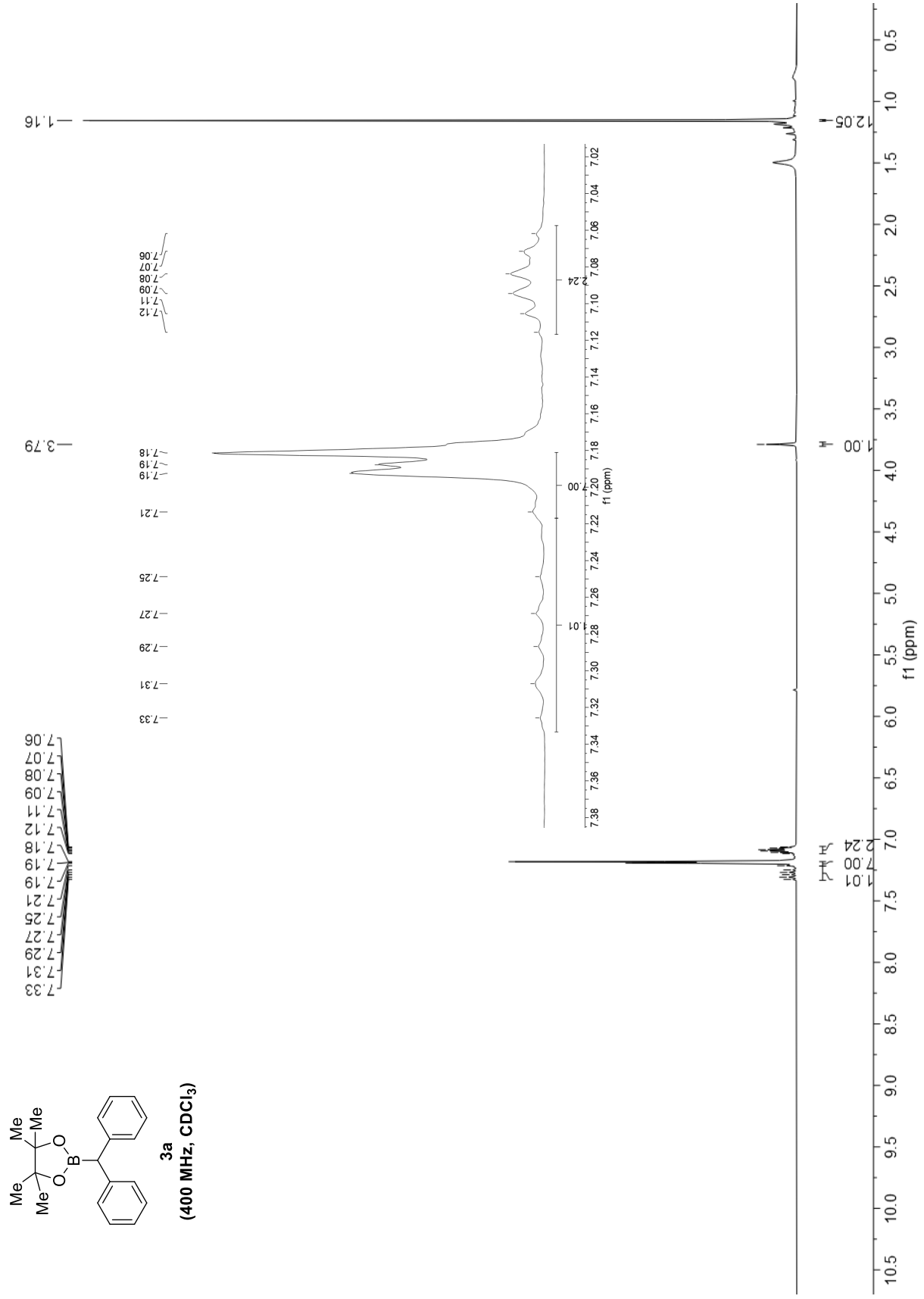


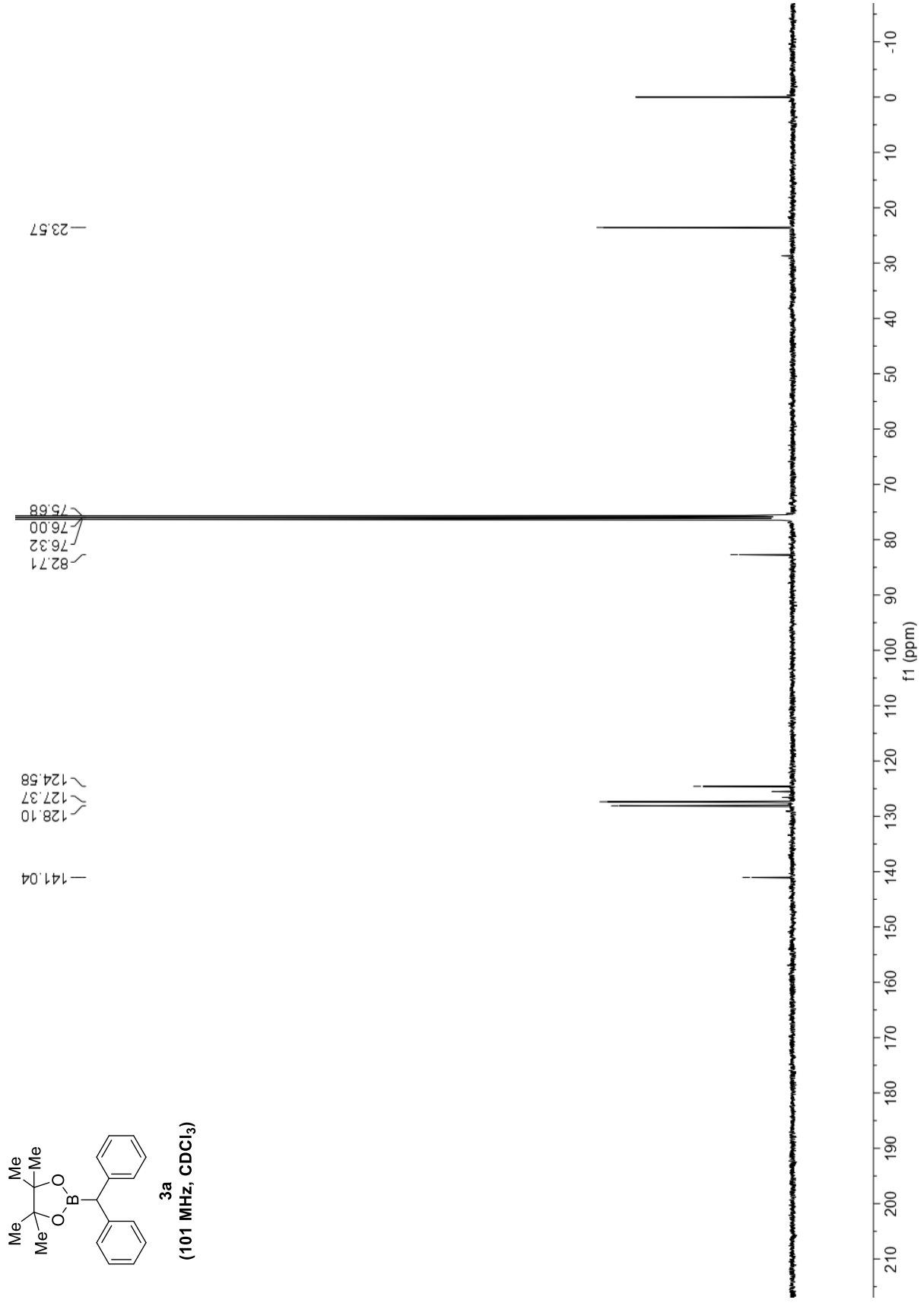
1q **2a** **3q**

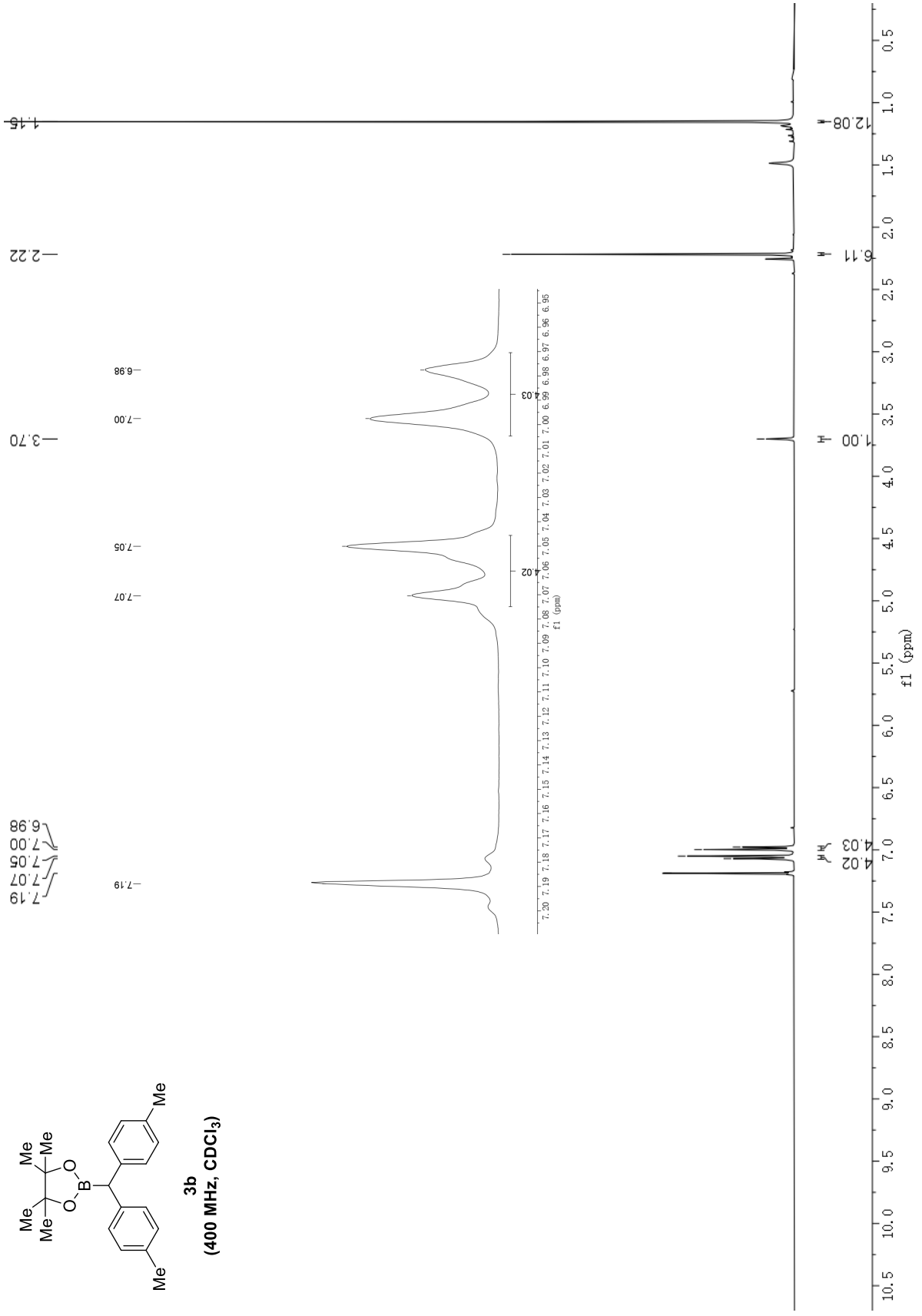
According to the general procedure, the reaction of 1-tetralone (0.20 mmol, 1.0 equiv), pinacolborane (2.0 equiv), SmI_2 (2.2 equiv), Sm (2.0 equiv), KO*t*-Bu (2.0 equiv) and $Ni(PPh_3)_2Cl_2$ (5 mol%) in THF (0.1 M) for 15 h at 120 °C, afforded after work-up and chromatography the title compound in 48% yield (24.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.01-6.96 (m, 4H), 2.68 (s, 2H), 2.51 (s, 1H), 1.80 (s, 3H), 1.67 (s, 1H), 1.16 (d, *J* = 8.0 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.71, 136.74, 129.43, 129.39, 125.37, 124.84, 83.39, 29.80, 25.16, 24.76, 22.75.

References

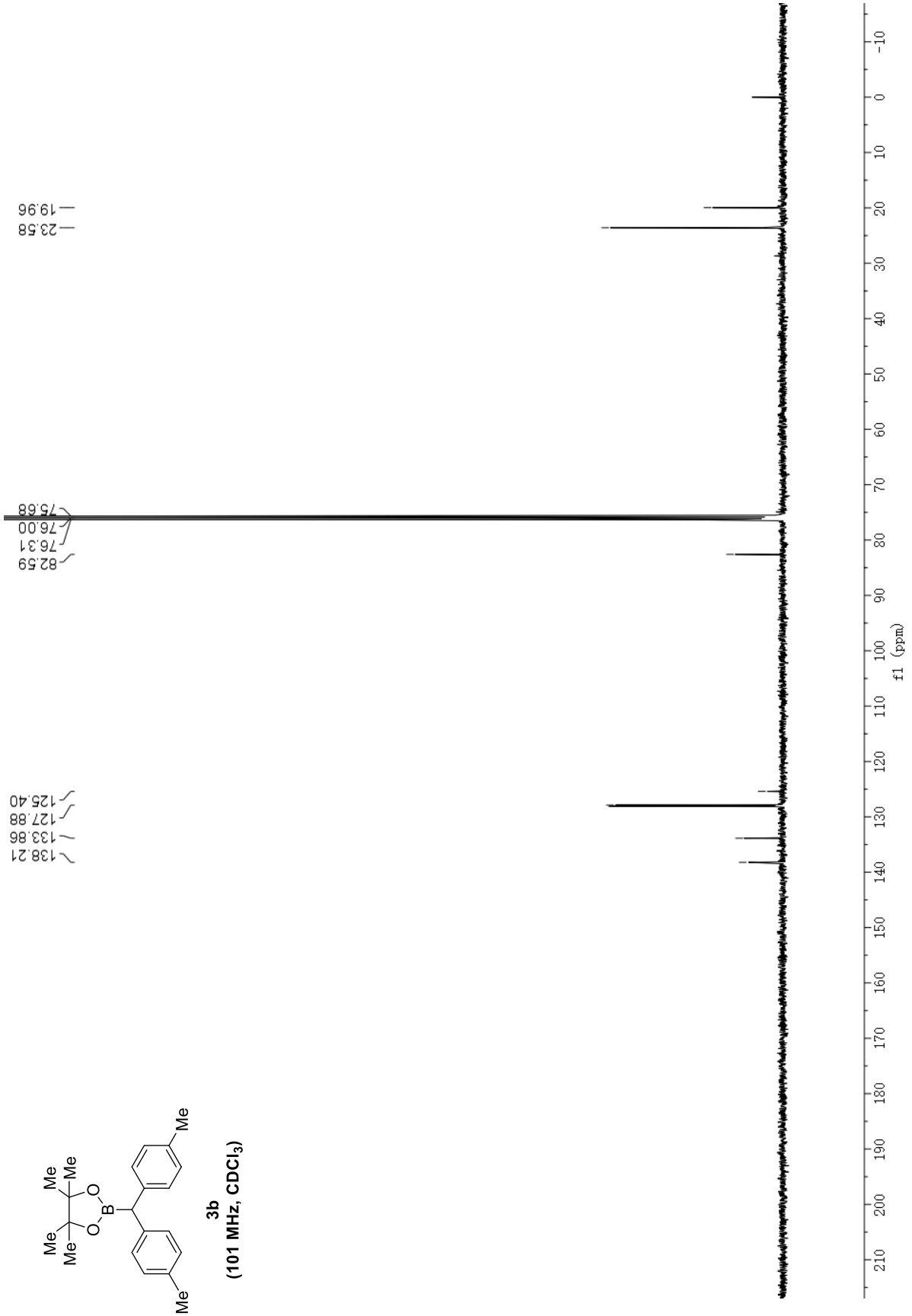
1. Liu, L.; Zhang, B.; Liu, Y.; Zhao, J.; Li, T.; Zhao, W. Cobalt-Catalyzed Deoxygenative Borylation of Diaryl Ketones. *Chin*. *Chem*. *Lett*. **2024**, *35*, 108631.
2. Maekawa, Y.; Ariki, Z. T.; Nambo, M.; Crudden, C. M. Pyridine-Catalyzed Desulfonative Borylation of Benzyl Sulfones. *Org*. *Biomol*. *Chem*. **2019**, *17*, 7300-7303.
3. Cho, S. H.; Hartwig, J. F. Iridium-Catalyzed Diborylation of Benzylic C–H Bonds Directed by A Hydrosilyl Group: Synthesis of 1,1-Benzyldiboronate Esters. *Chem*. *Sci*. **2014**, *5*, 694-698.
4. Jin, H.; Han, J.; Liu, X.; Feng, C.; Zhan, M. Access to Diverse Organoborons by α-Deprotonation and Functionalization of Benzylboronates. *Org*. *Lett*. **2023**, *25*, 4168-4172.
5. Grayson, J. D.; Partridge, B. M. Mild Cu-Catalyzed Oxidation of Benzylic Boronic Esters to Ketones. *ACS Catal*. **2019**, *9*, 4296-4301.


Me
Me
Me
Me
O
O
B
3a
(400 MHz, CDCl3)
f1 (ppm)

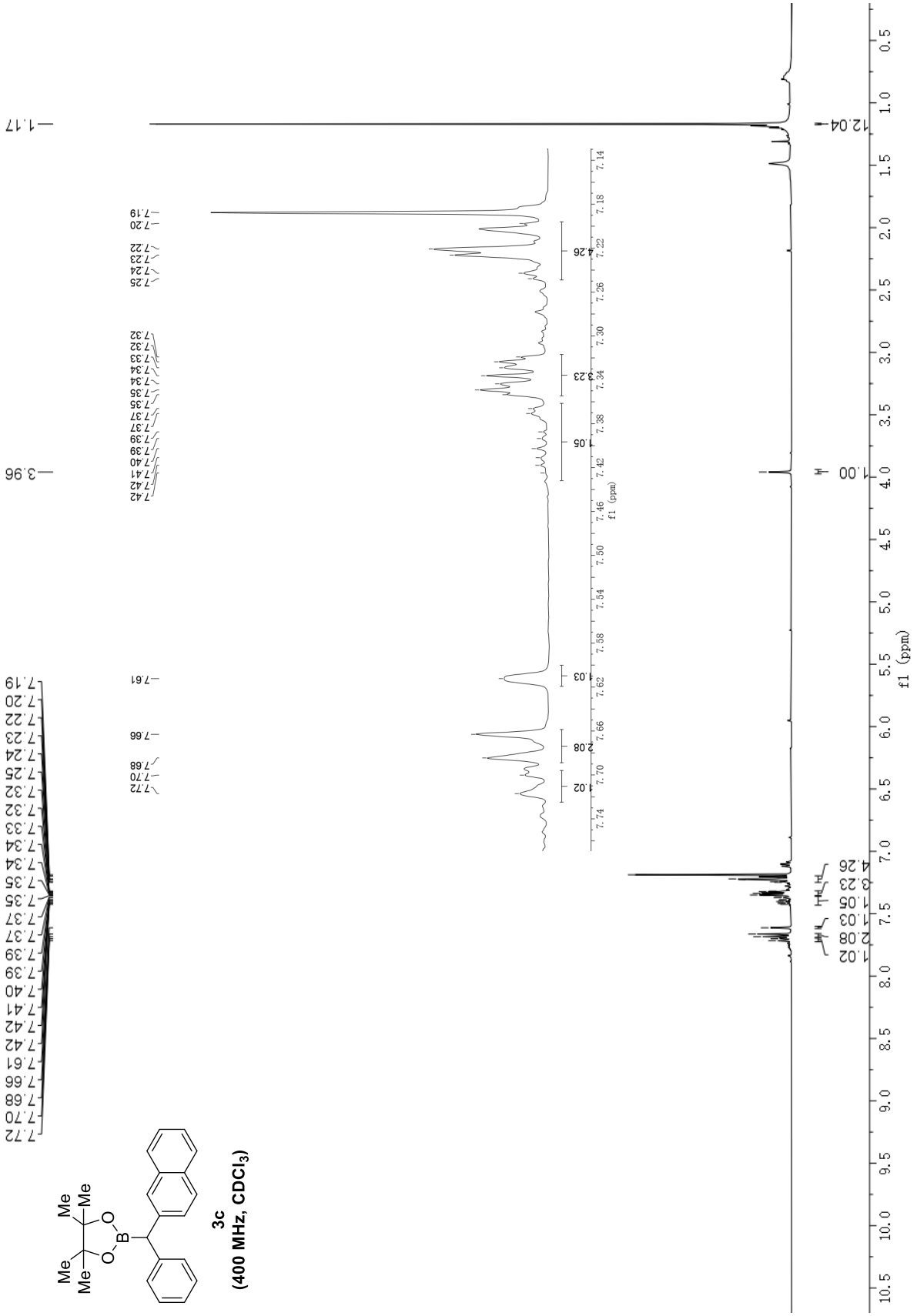

23.57
75.68
76.00
76.32
82.71
124.58
127.37
128.10
141.04
f1 (ppm)
Me
Me
Me
Me
O
O
B
3a
(101 MHz, CDCl3)

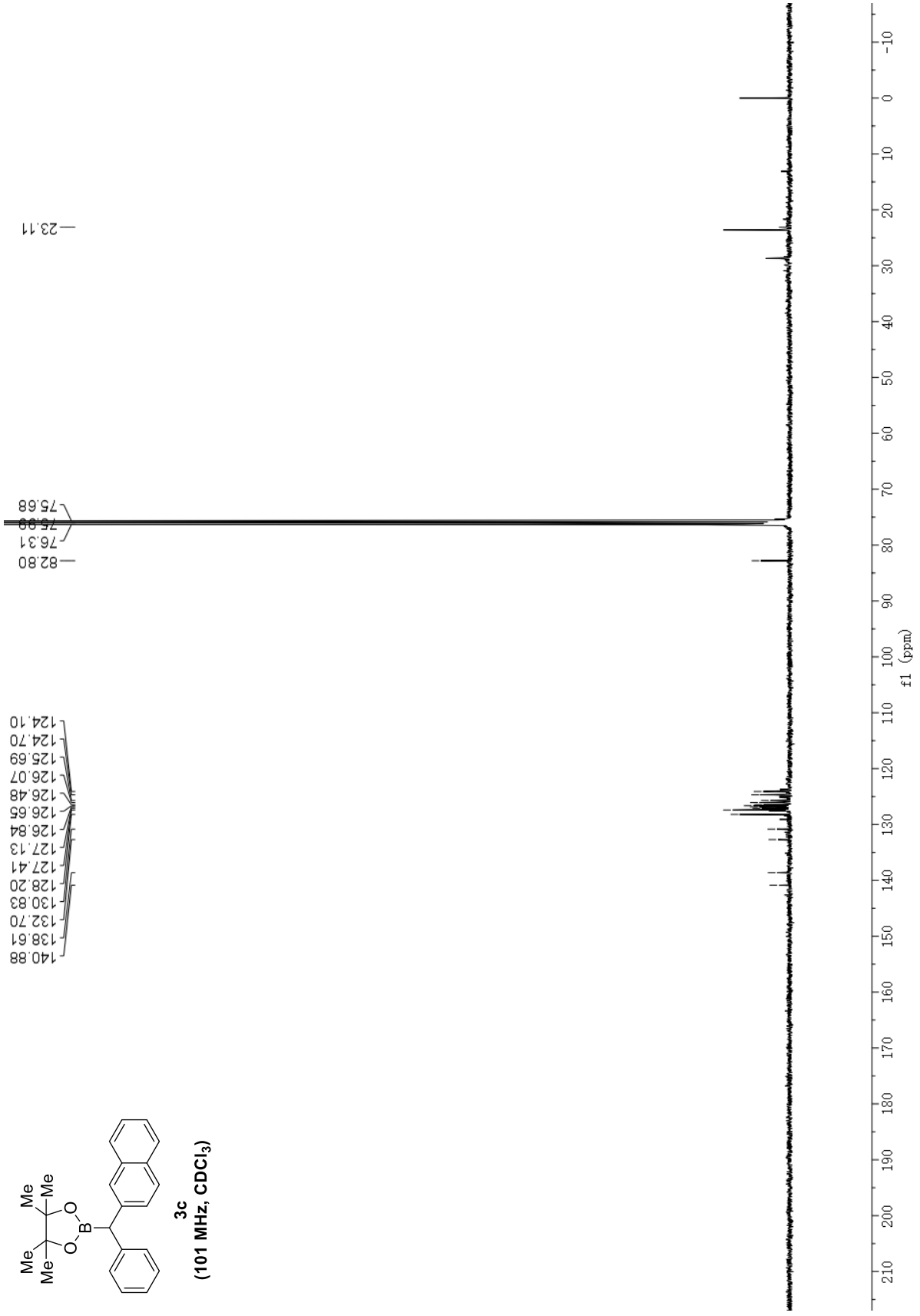


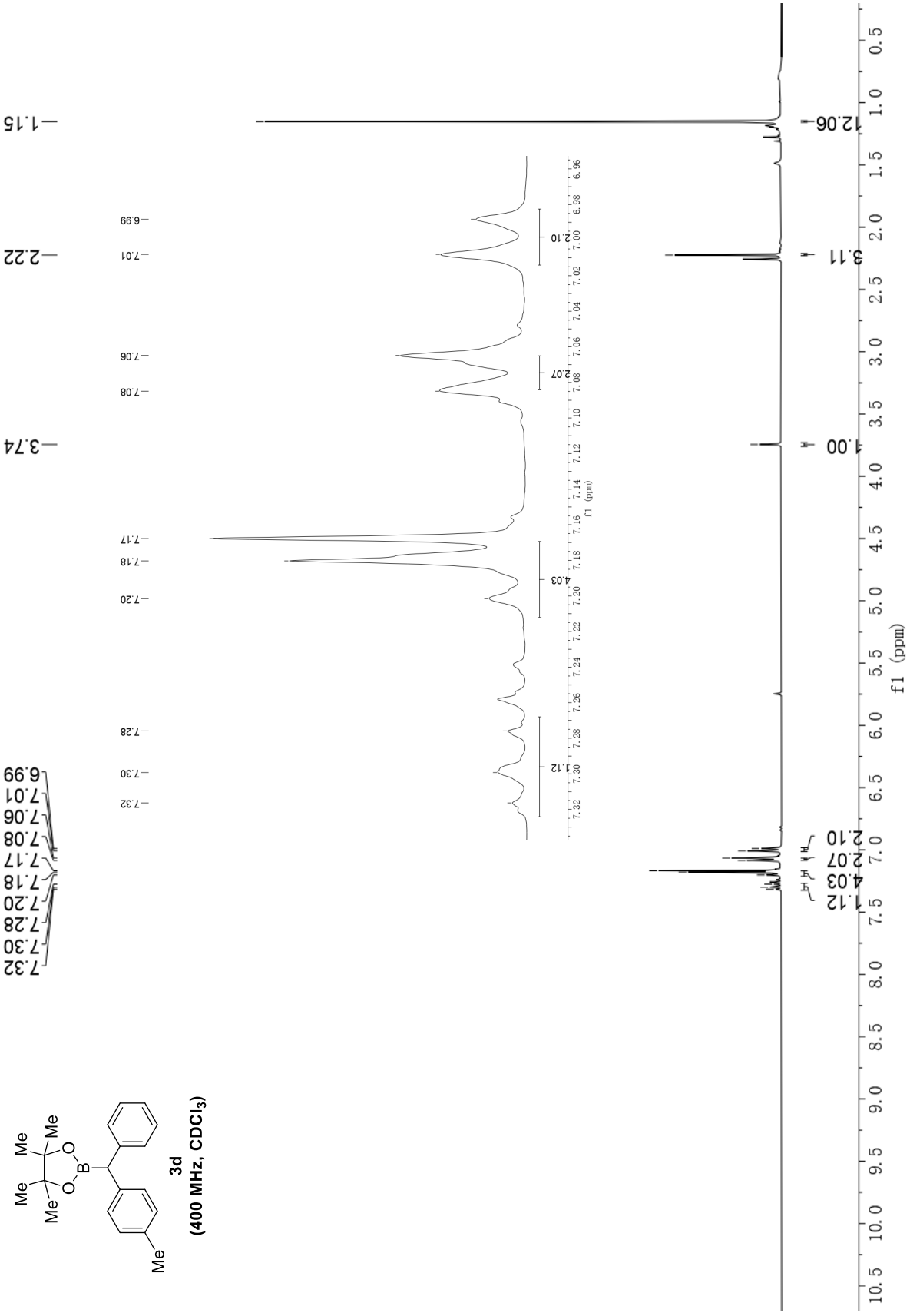
3b
(400 MHz, $CDCl_3$)

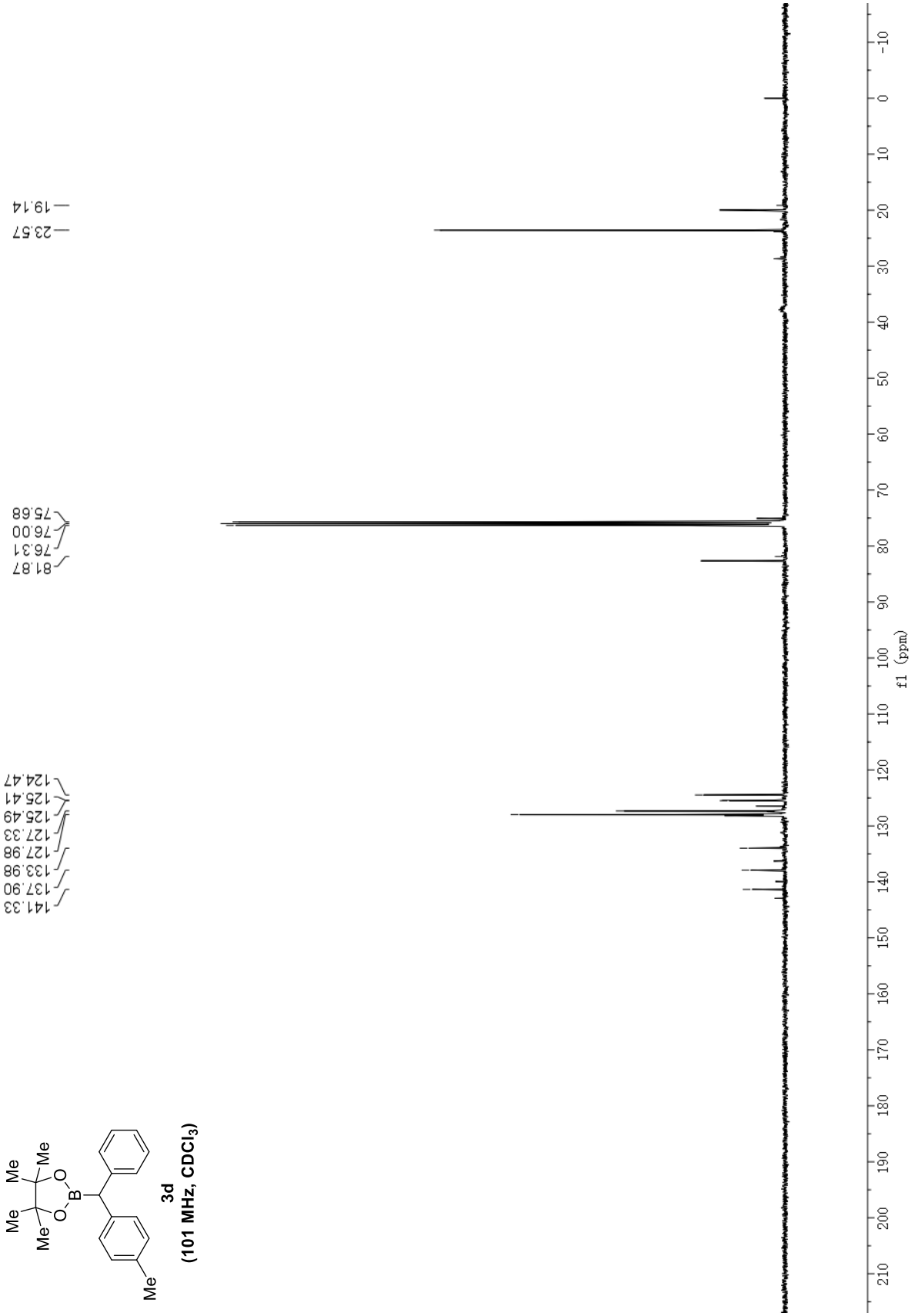


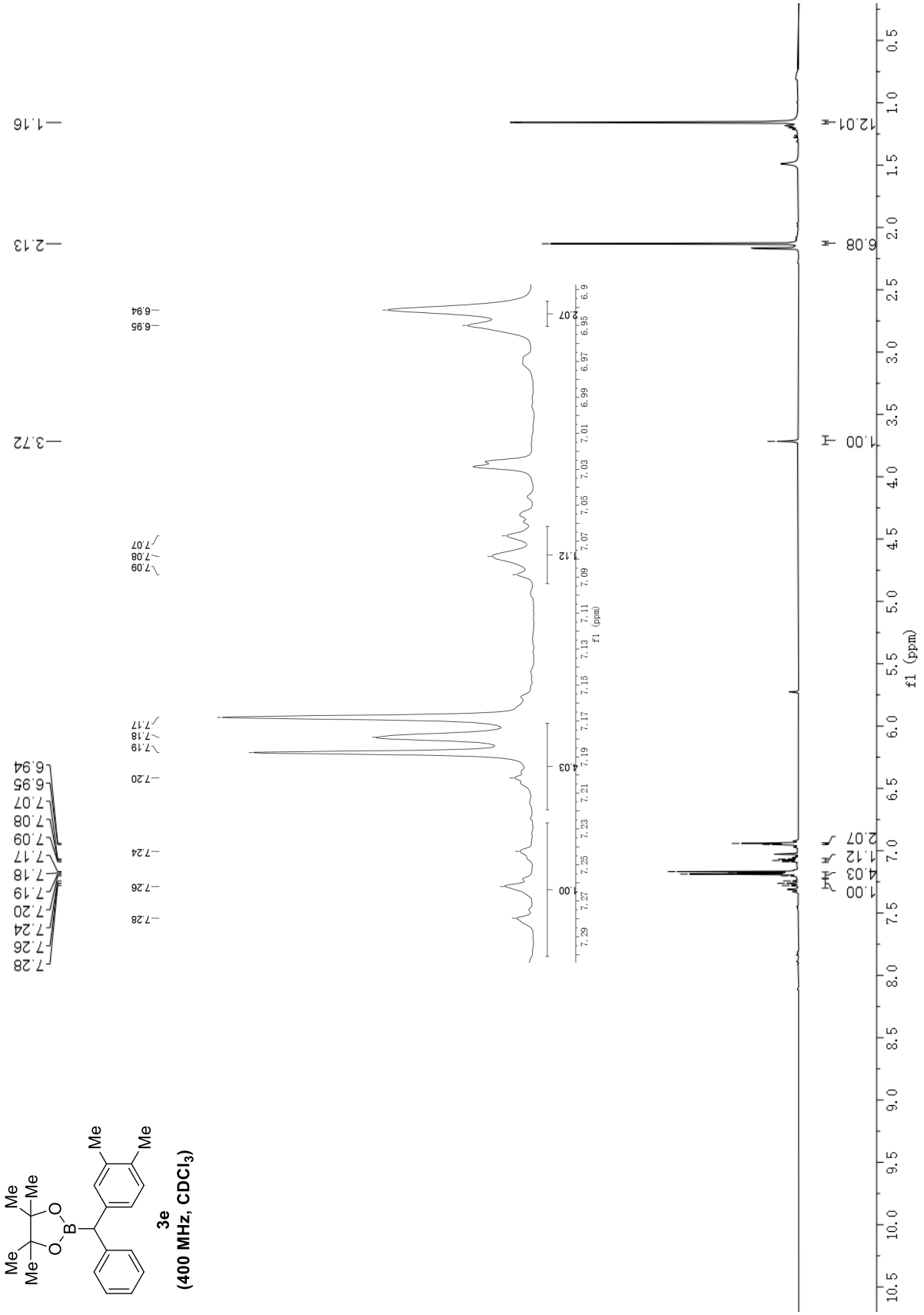
3b
(101 MHz, $CDCl_3$)

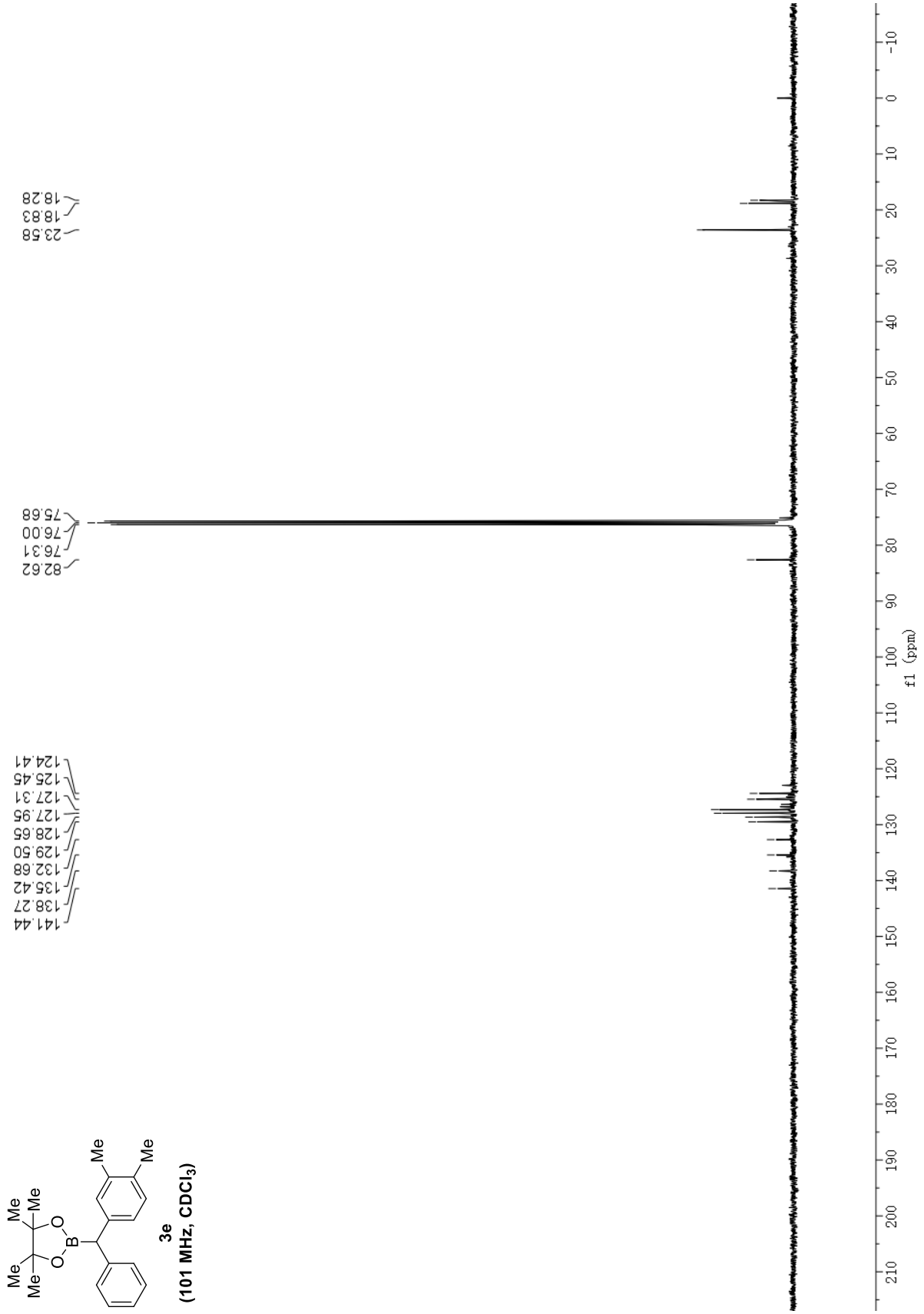

Me
Me
Me
Me
O
O
B
3c
(400 MHz, CDCl3)
f1 (ppm)

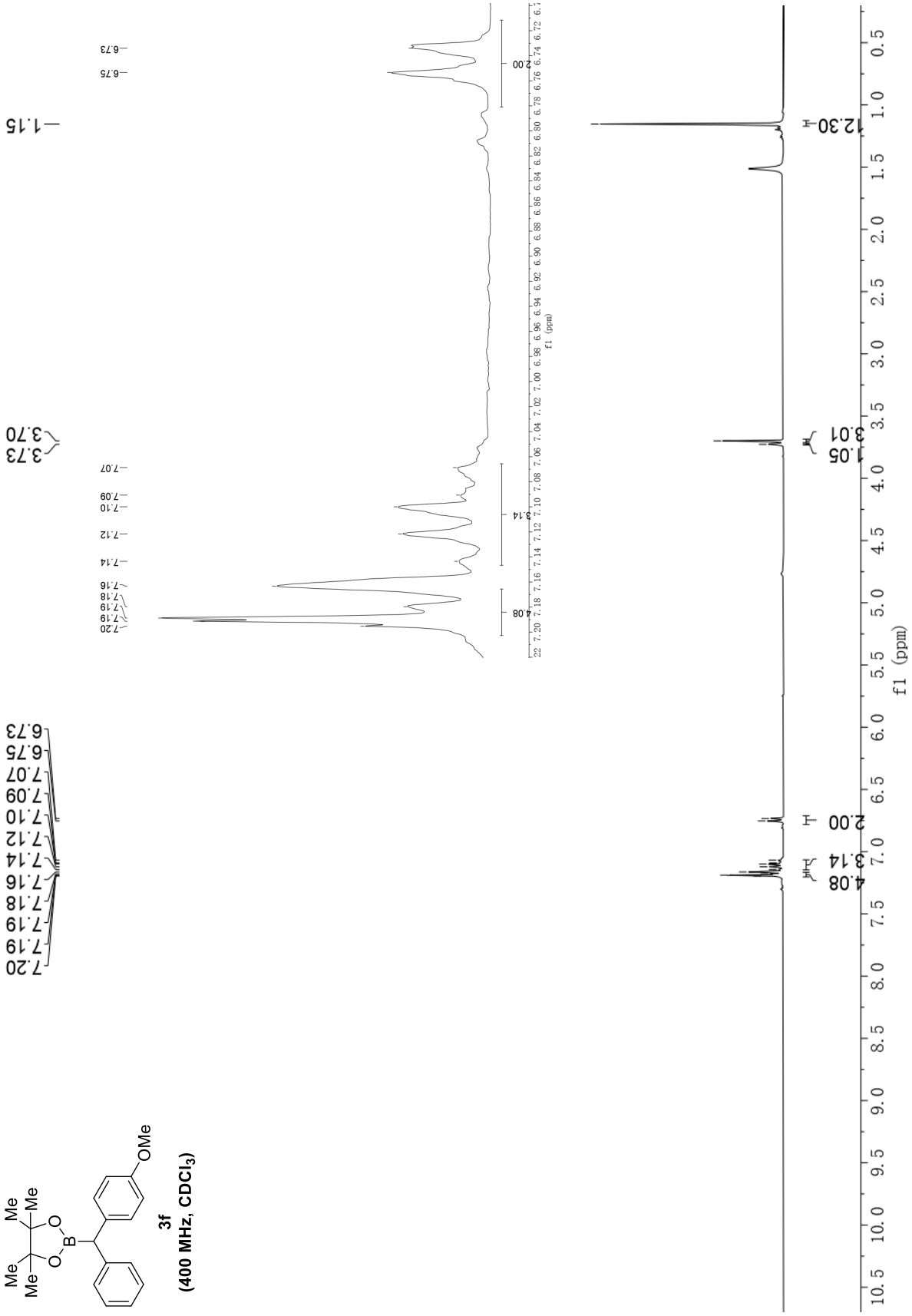

23.11
75.68
76.99
76.31
82.80
124.10
124.70
125.69
126.07
126.48
126.65
126.84
127.13
127.41
128.20
130.83
132.70
138.61
140.88
f1 (ppm)
Me
Me
Me
Me
O
O
B
3c
(101 MHz, CDCl3)

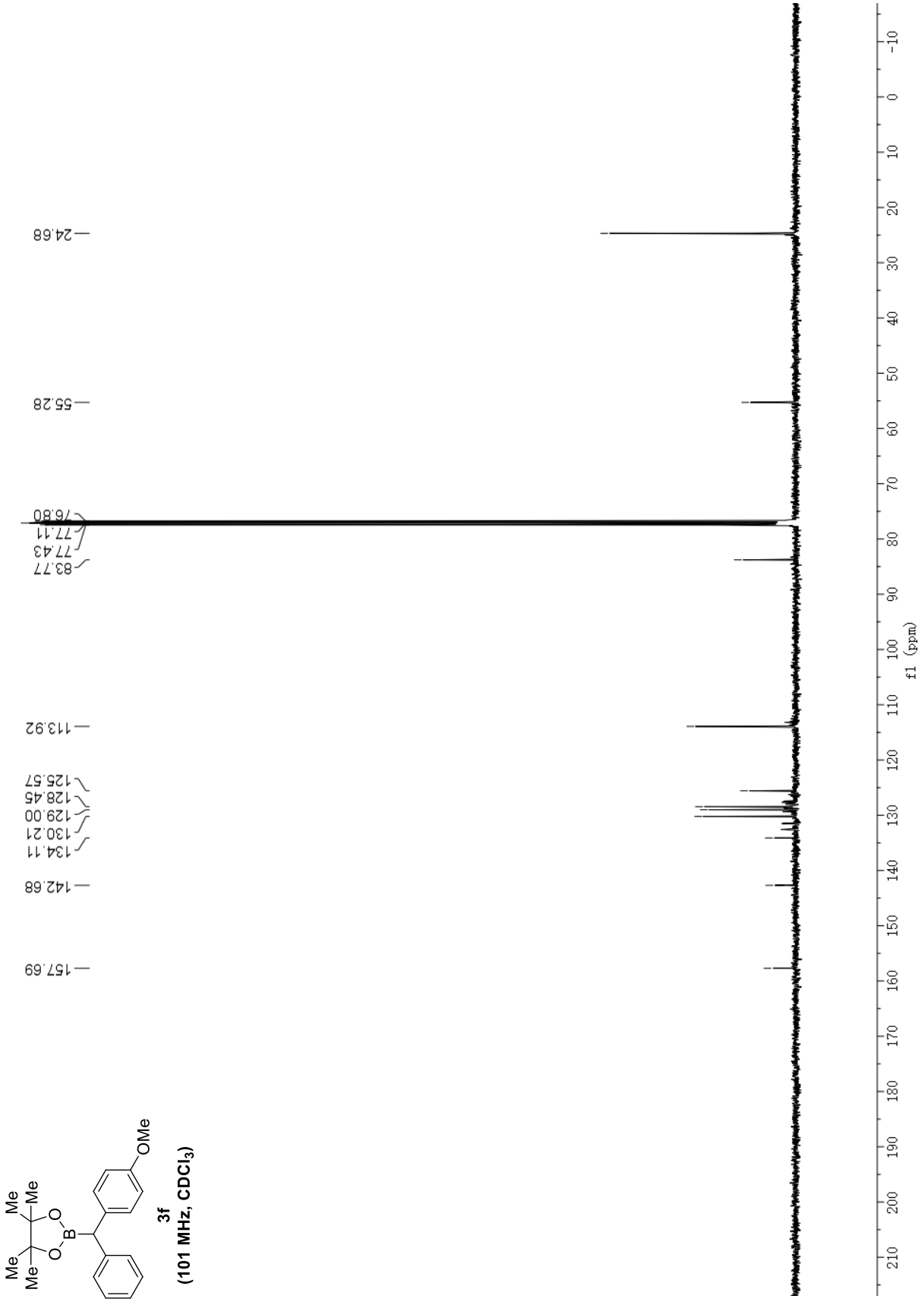

Me
Me
Me
Me
O
O
B
Me
3d
(400 MHz, $CDCl_3$)
f1 (ppm)

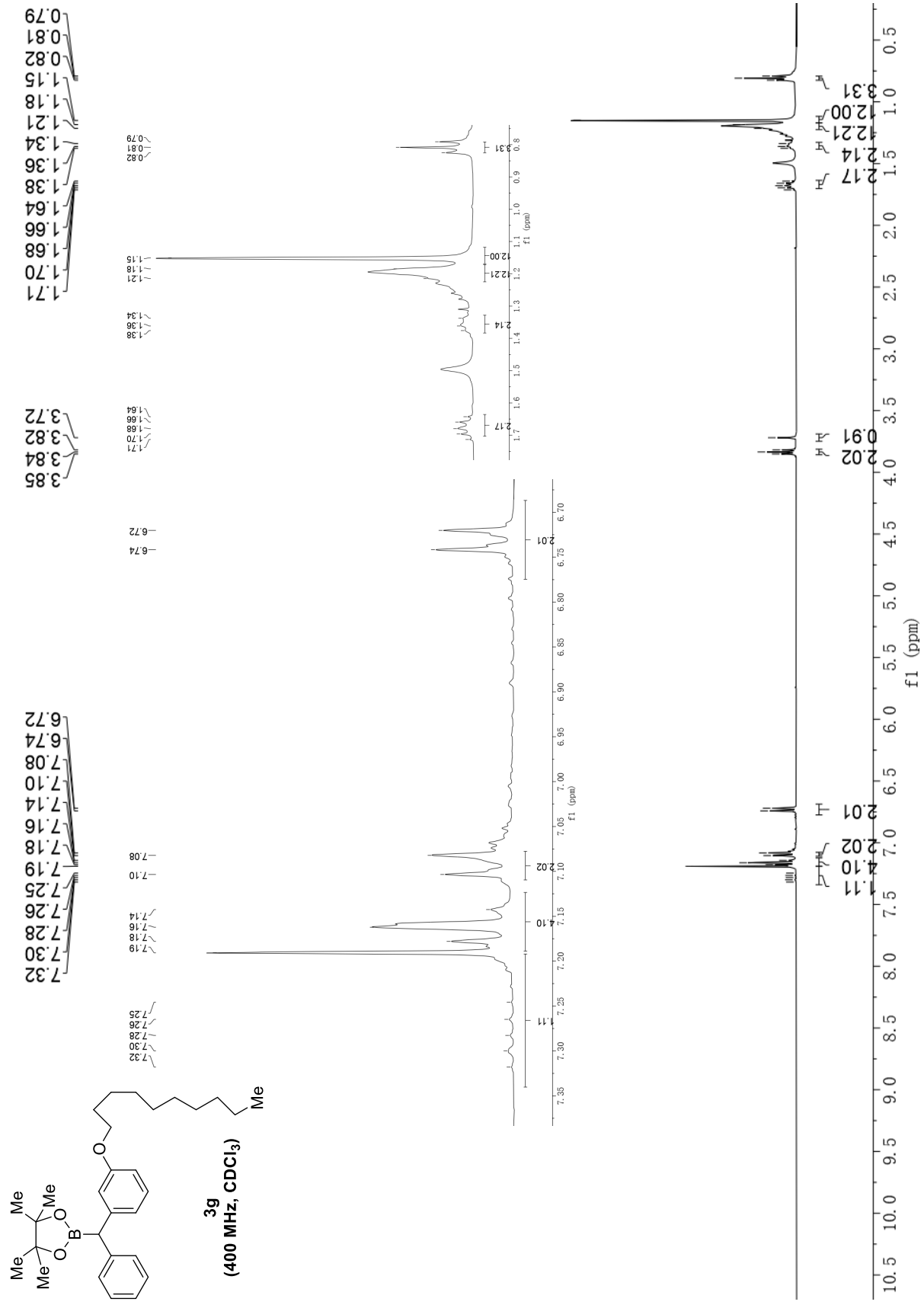

19.14
23.57
75.68
76.00
76.31
81.87
124.47
125.41
125.49
127.33
127.98
133.98
137.90
141.33
f1 (ppm)
Me
Me
Me
Me
O
O
B
Me
3d
(101 MHz, CDCl3)

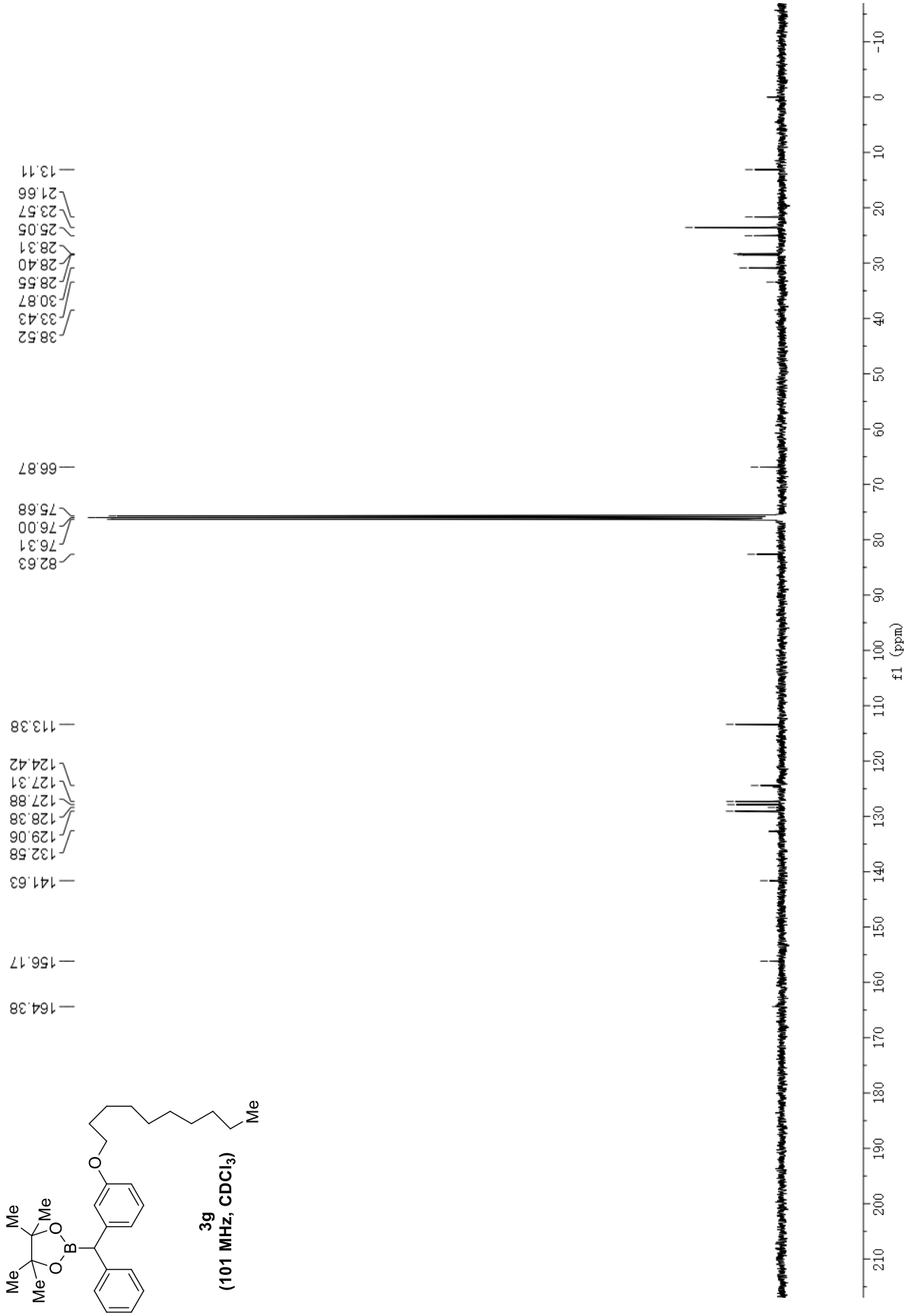

Me
Me
Me
Me
O
O
B
Me
Me
3e
(400 MHz, CDCl3)
f1 (ppm)

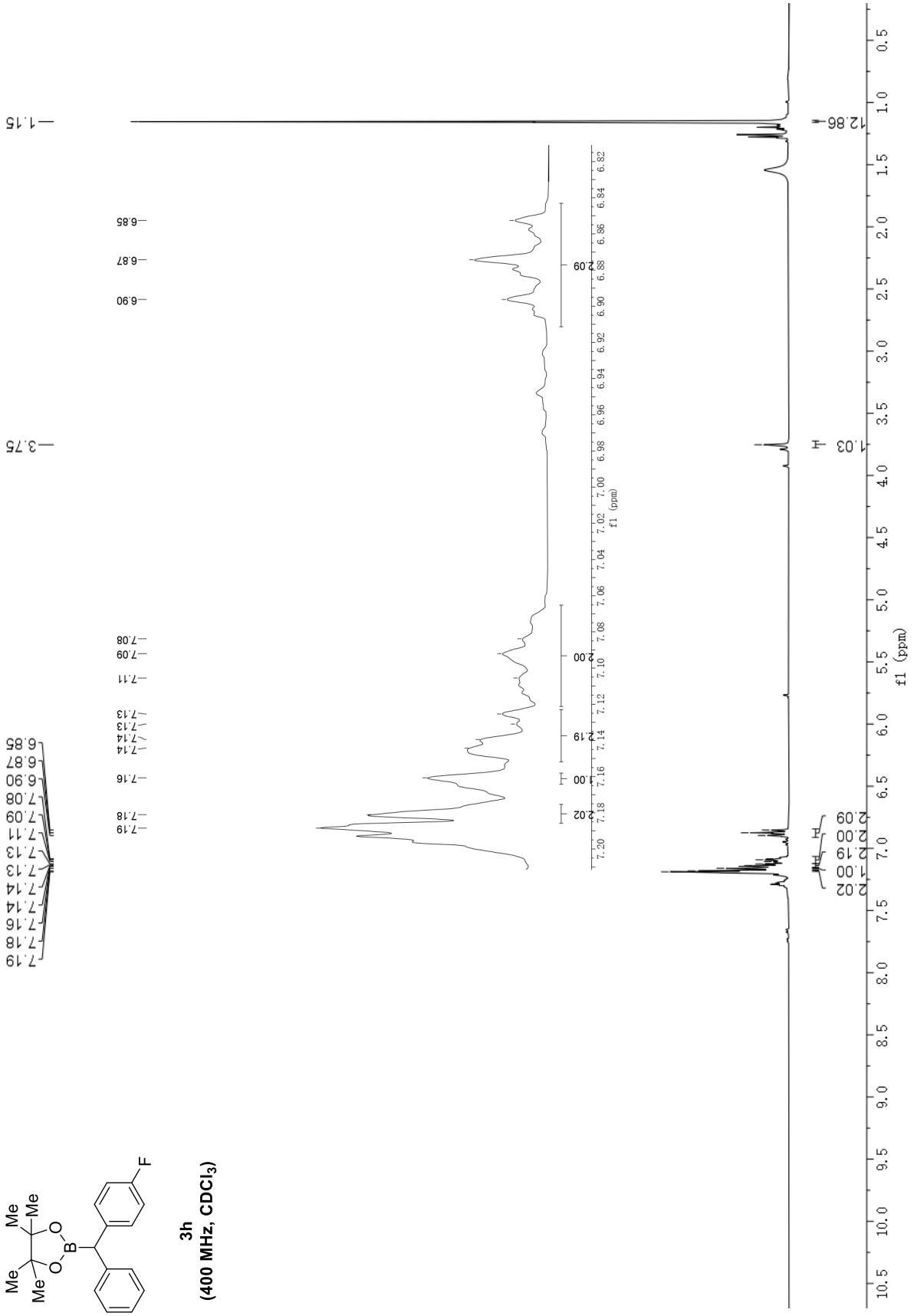

23.58
18.83
18.28
82.62
76.31
76.00
75.68
141.44
138.27
135.42
132.68
129.50
128.65
127.95
127.31
125.45
124.41
f1 (ppm)
Me
Me
Me
Me
O
O
B
Me
Me
3e
(101 MHz, CDCl3)

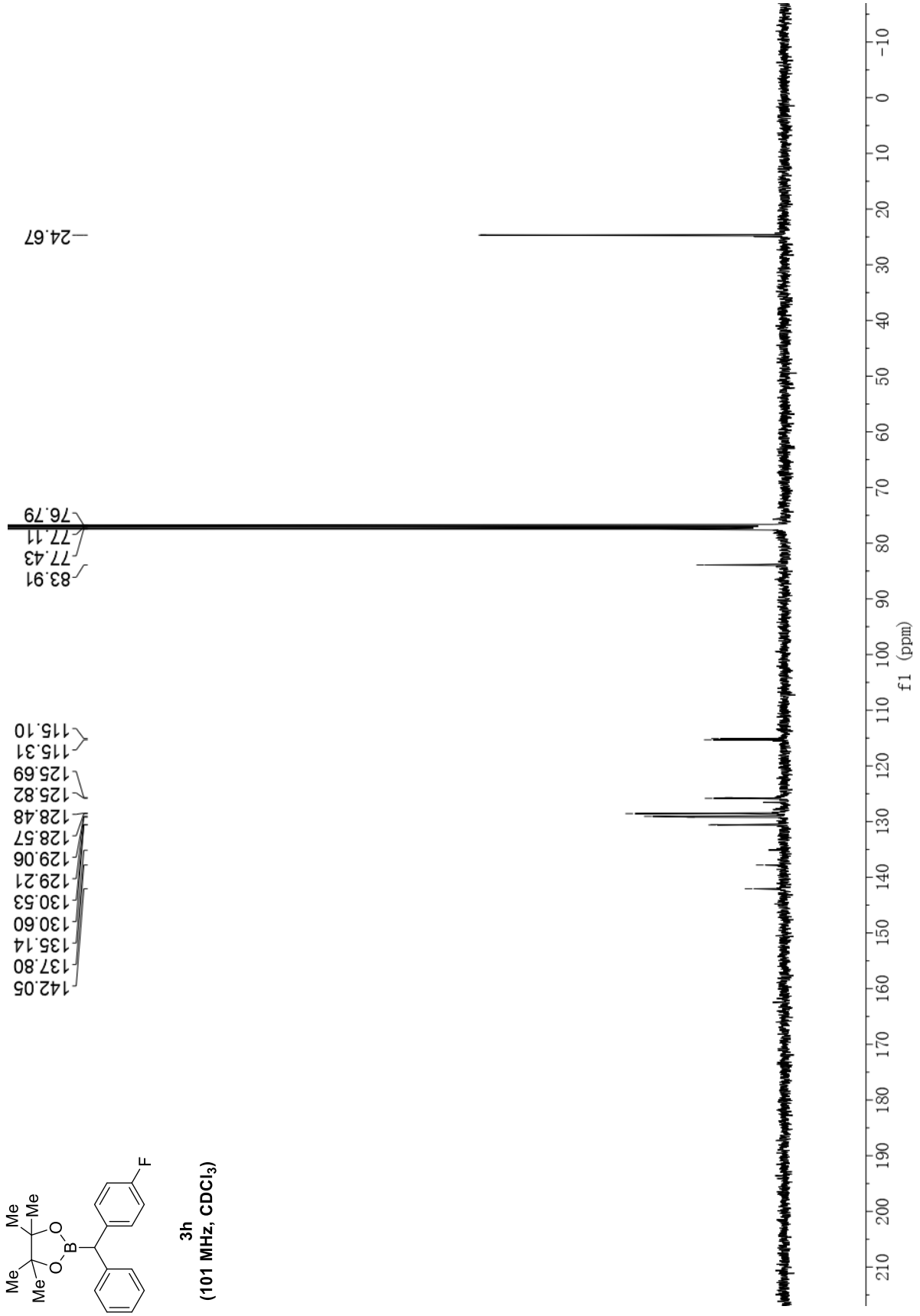

Me
Me
Me
Me
O
O
B
OMe
3f
(400 MHz, CDCl3)
f1 (ppm)

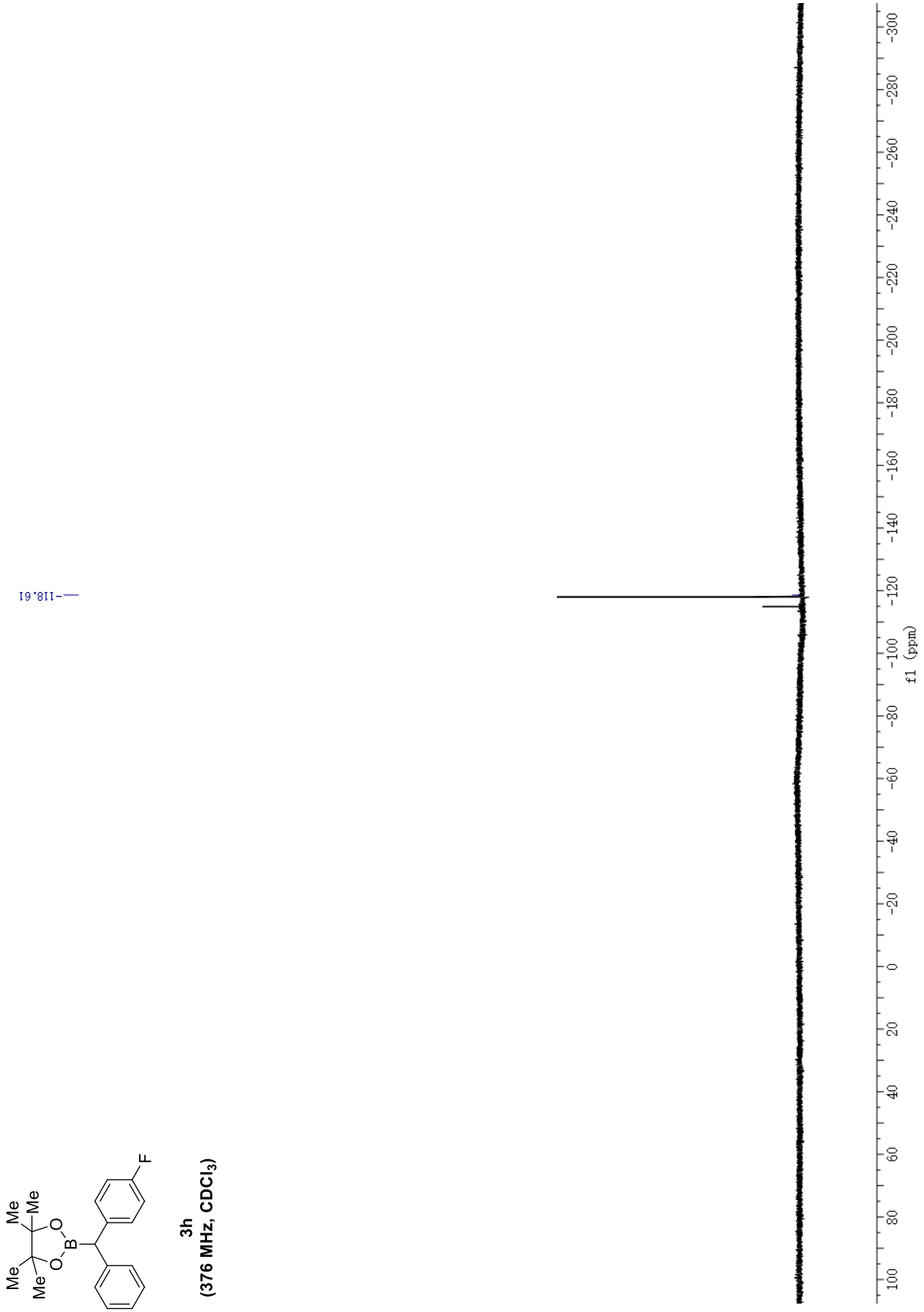

24.68
55.28
76.80
77.11
77.43
83.77
113.92
125.57
128.45
129.00
130.21
134.11
142.68
157.69
f1 (ppm)
Me
Me
Me
Me
O
O
B
OMe
3f
(101 MHz, CDCl3)

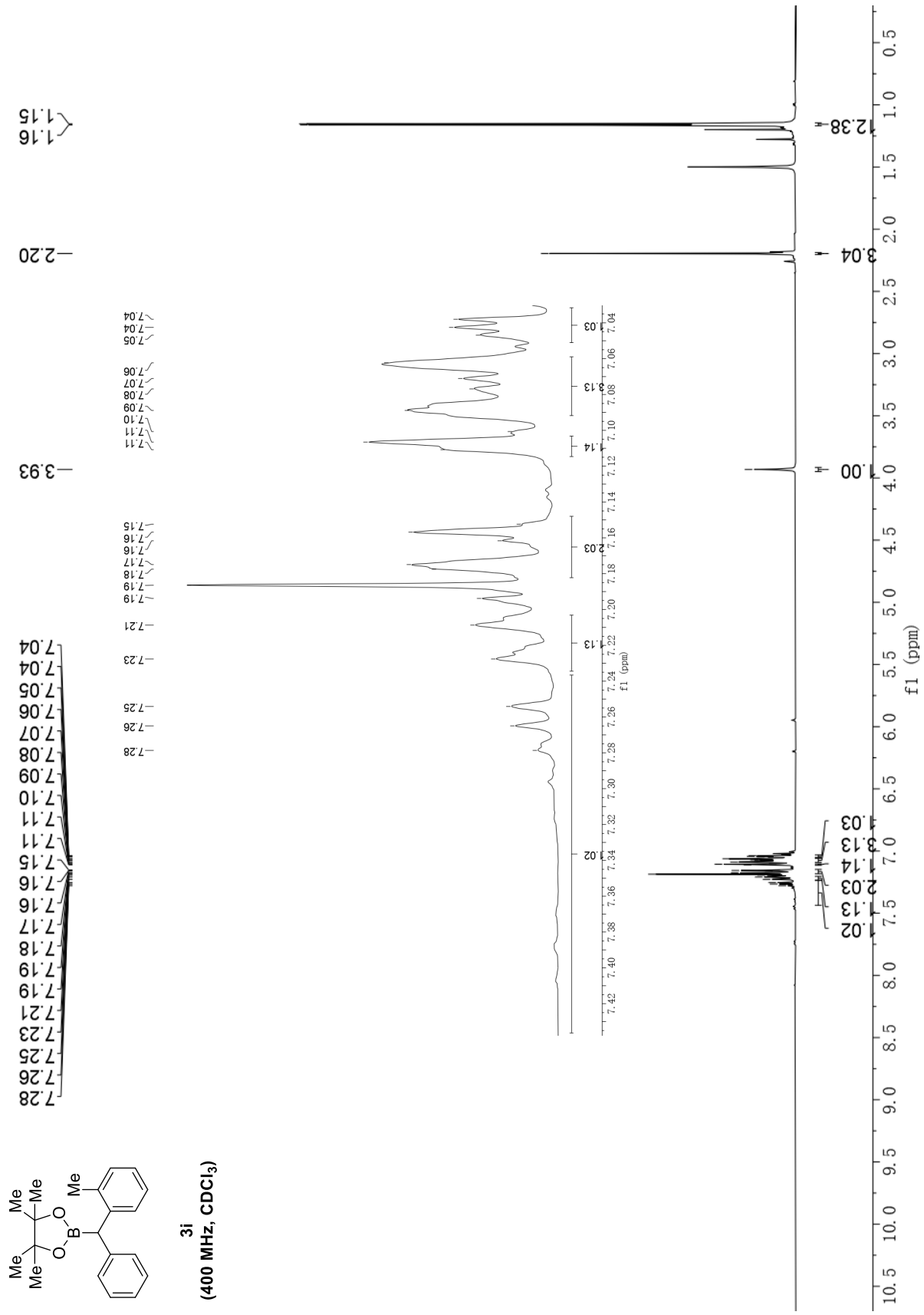

Me
Me
Me
Me
O
B
O
O
Me
3g
(400 MHz, CDCl3)
f1 (ppm)

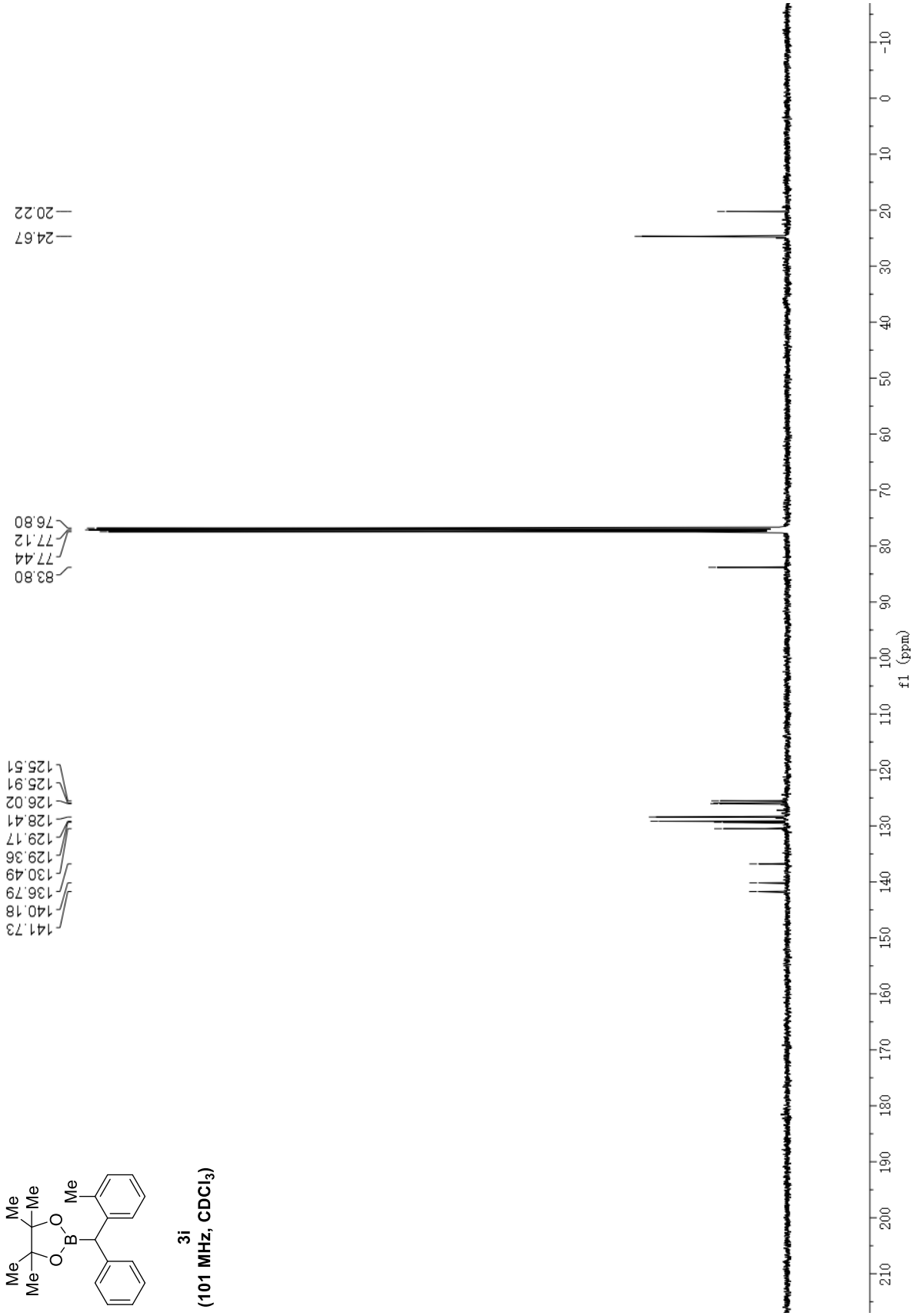

13.11
21.66
23.57
25.05
28.31
28.40
28.55
30.87
33.43
38.52
66.87
75.68
76.00
76.31
82.63
113.38
124.42
127.31
127.88
128.38
129.06
132.58
141.63
156.17
164.38
f1 (ppm)
Me
Me
Me
Me
O
O
B
O
Me
3g
(101 MHz, CDCl3)


Me
Me
Me
Me
O
O
B
F
3h
(400 MHz, CDCl3)
f1 (ppm)


24.67
76.79
77.11
77.43
83.91
115.10
115.31
125.69
125.82
128.48
128.57
129.06
129.21
130.53
130.60
135.14
137.80
142.05
f1 (ppm)
Me
Me
Me
Me
O
O
B
F
3h
(101 MHz, CDCl3)

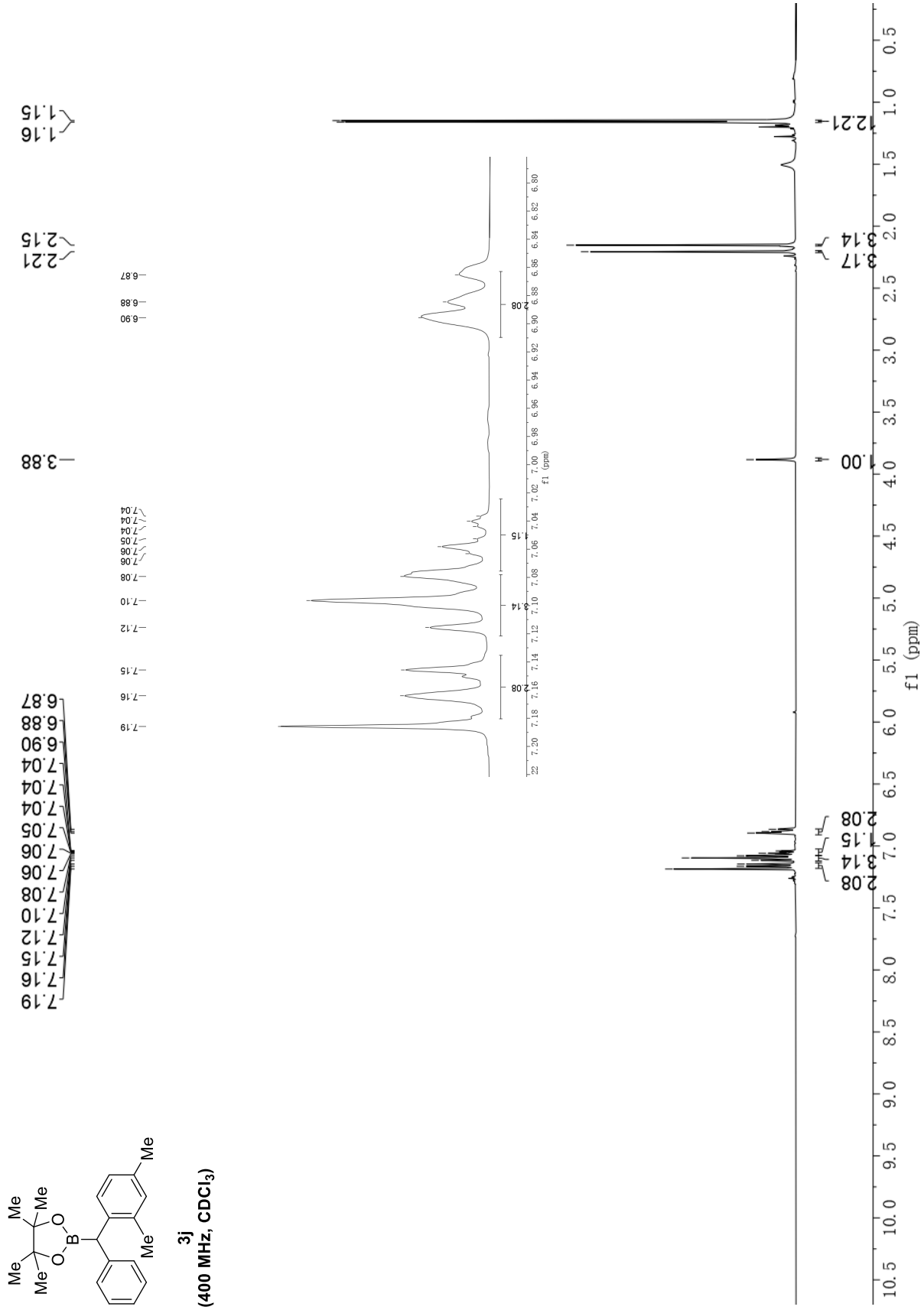

-118.61
f1 (ppm)
-300
-280
-260
-240
-220
-200
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20
40
60
80
100
Me
Me
Me
Me
O
O
B
F
3h
(376 MHz, CDCl3)


Me
Me
Me
Me
O
O
B
3i
(400 MHz, CDCl3)
f1 (ppm)

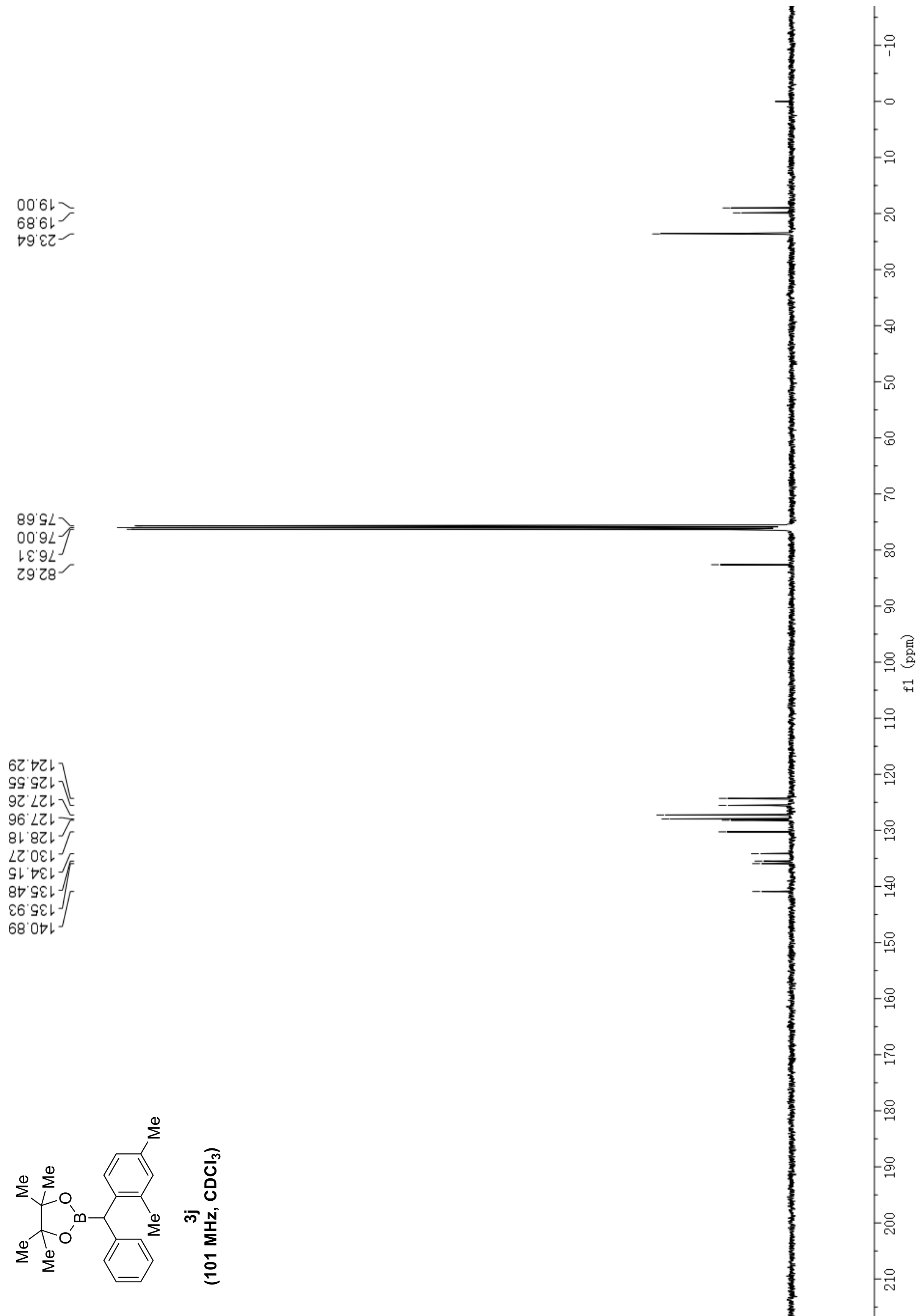


3i

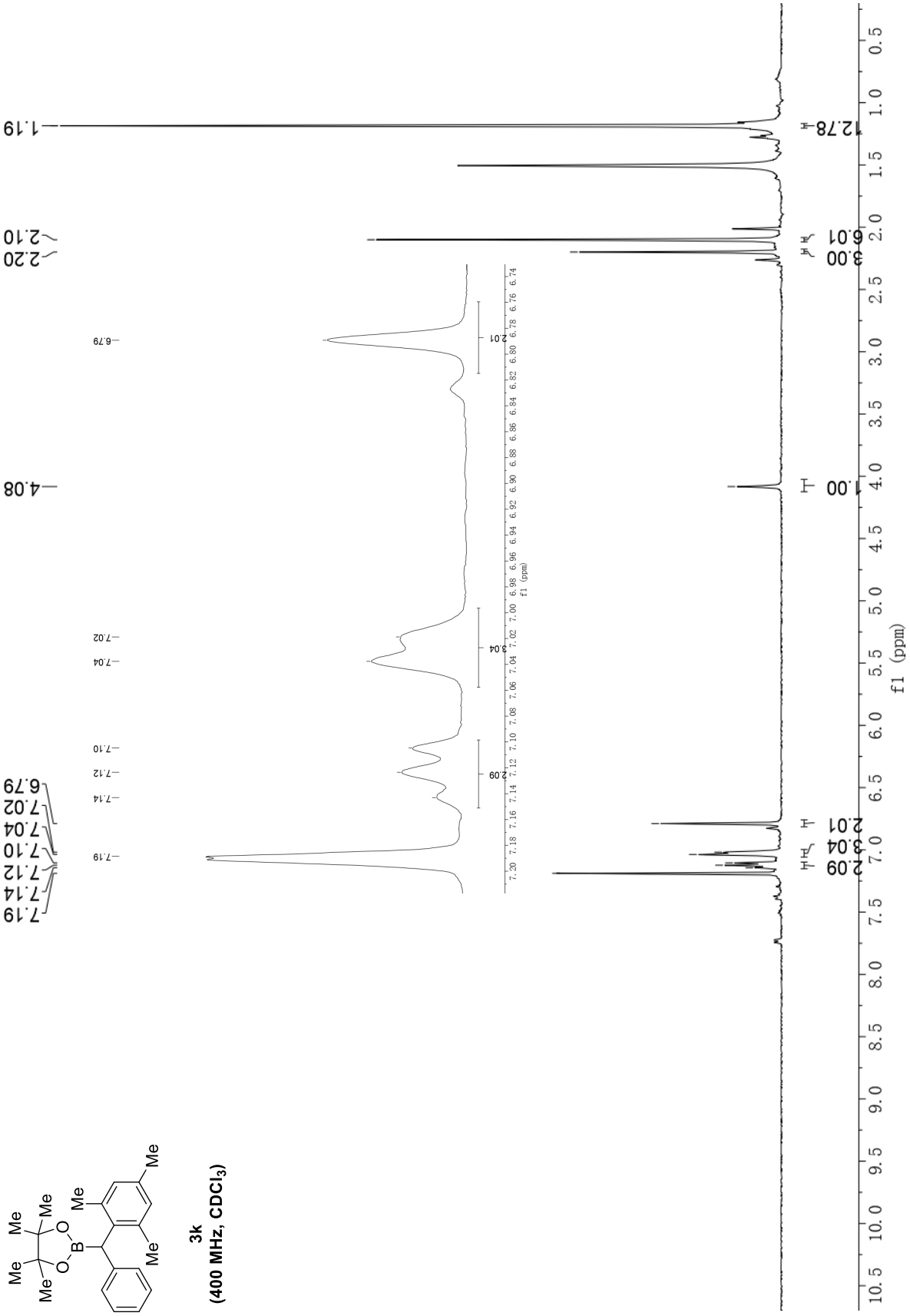
(101 MHz, $CDCl_3$)

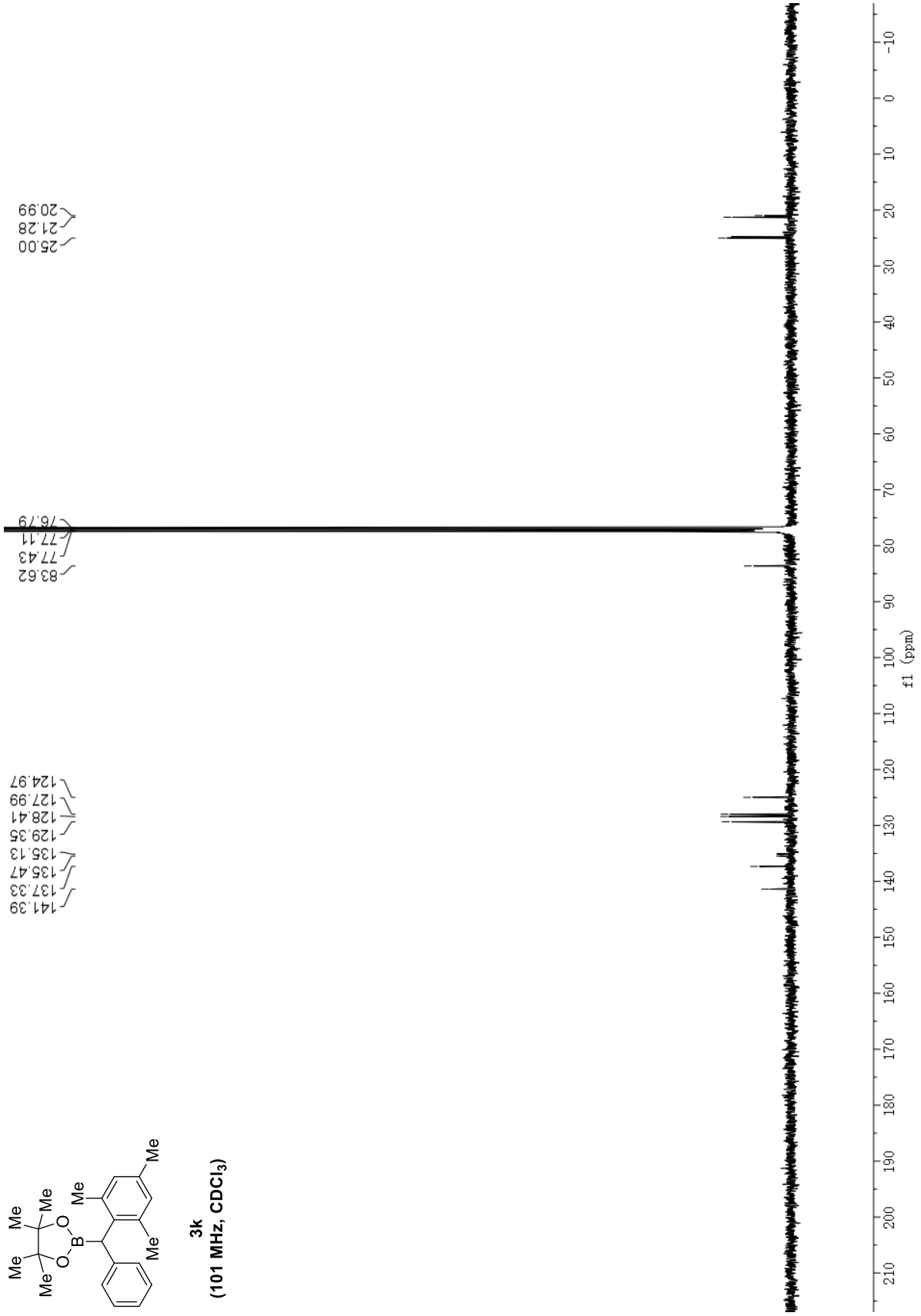


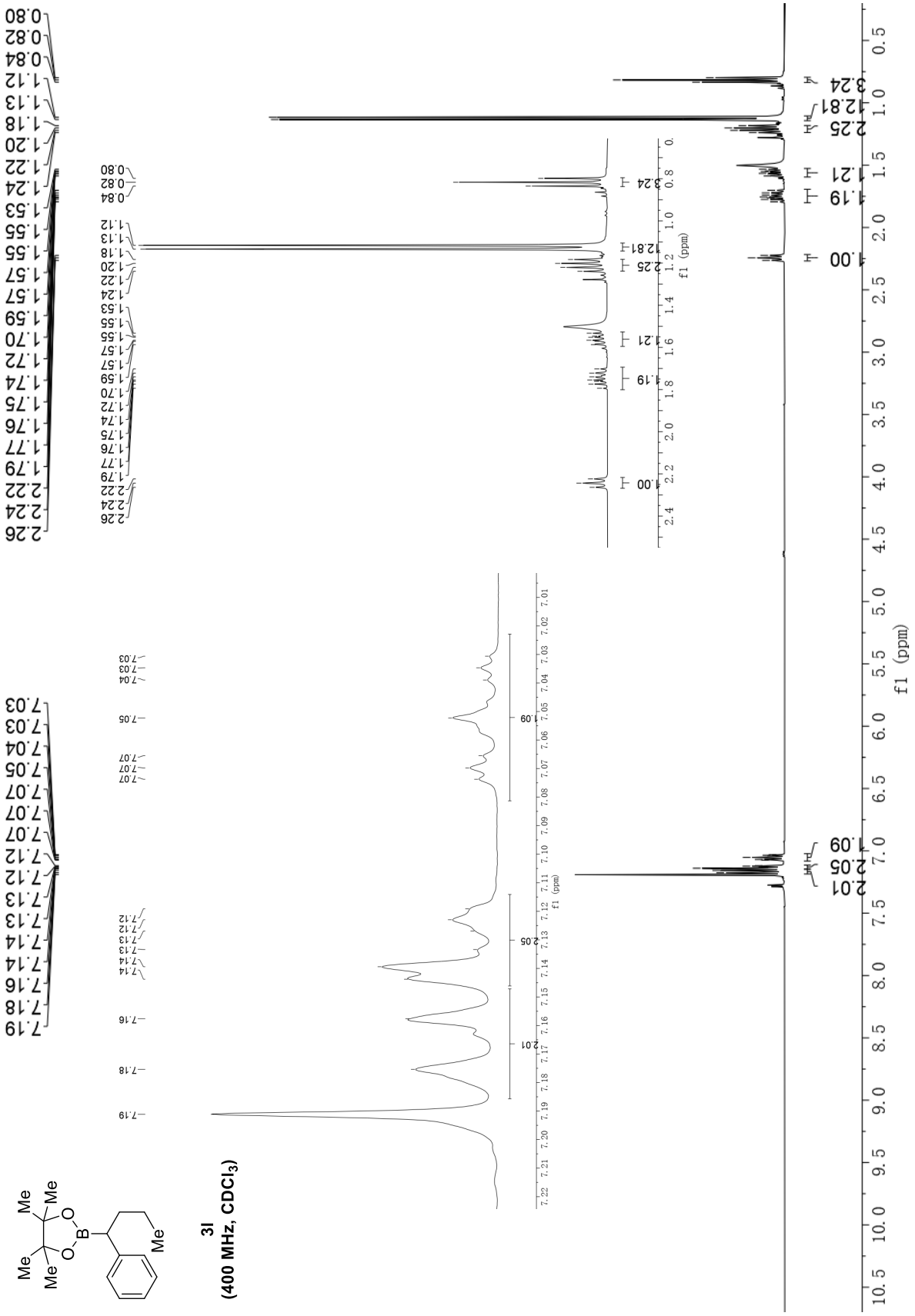
3j
(400 MHz, $CDCl_3$)

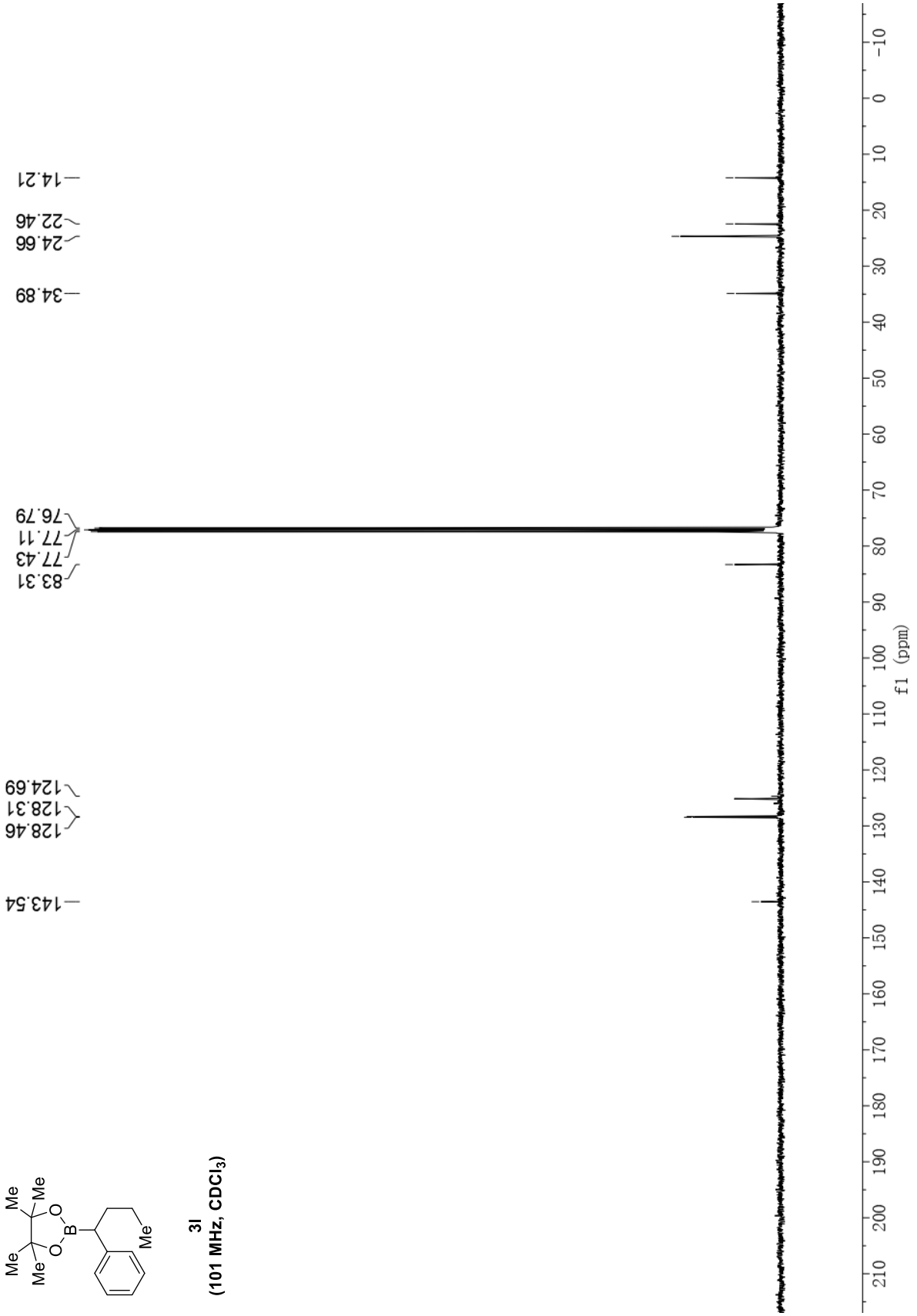


3j
(101 MHz, $CDCl_3$)

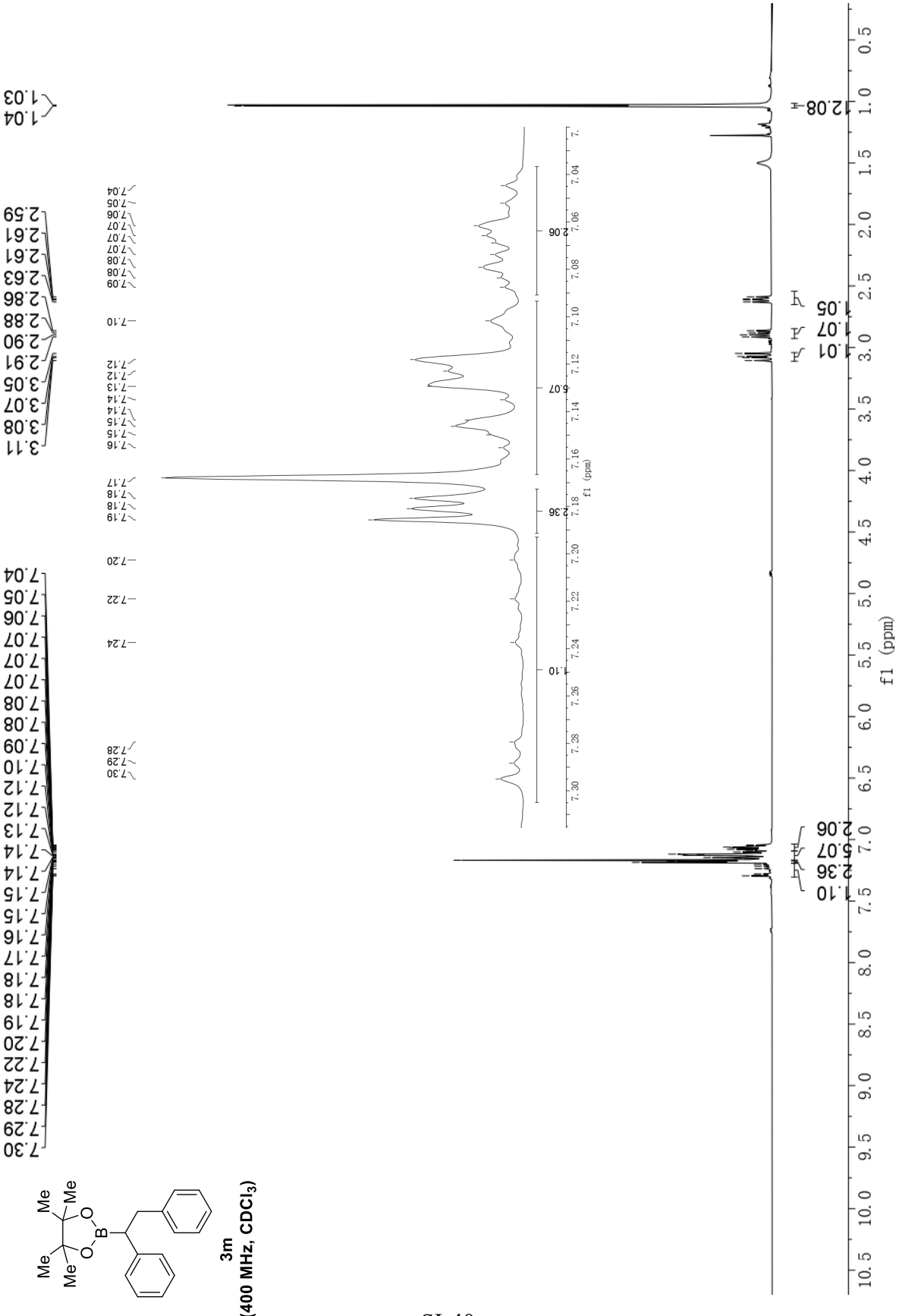

1.19
2.10
2.20
4.08
6.79
7.02
7.04
7.10
7.12
7.14
7.19
12.78
6.01
3.00
1.00
2.01
3.04
2.09
f1 (ppm)
Me
Me
Me
Me
Me
Me
O
O
B
3k
(400 MHz, CDCl3)

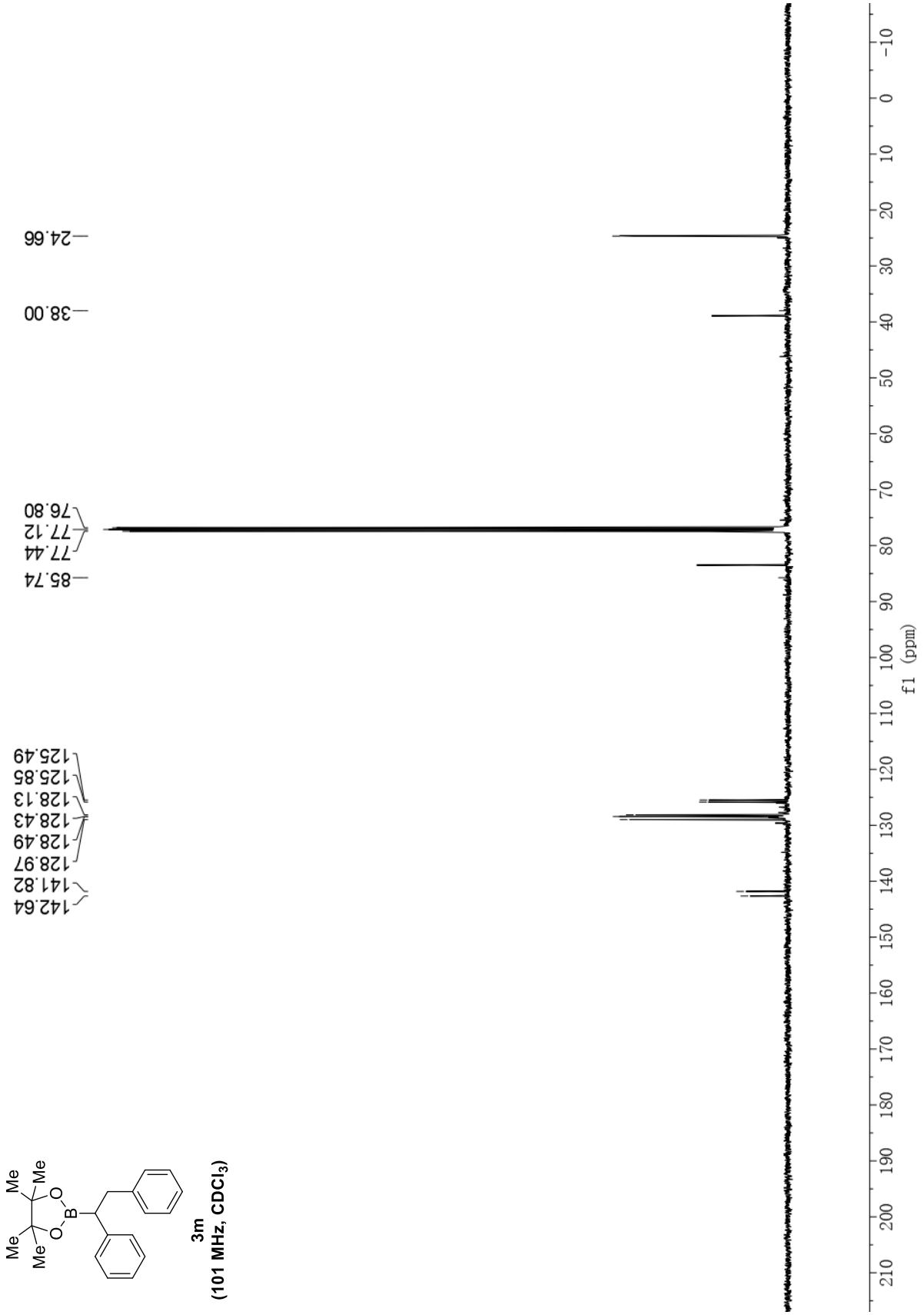

20.99
21.28
25.00
76.79
77.11
77.43
83.62
124.97
127.99
128.41
129.35
135.13
135.47
137.33
141.39
f1 (ppm)
Me
Me
Me
Me
Me
Me
O
O
B
3k
(101 MHz, CDCl3)

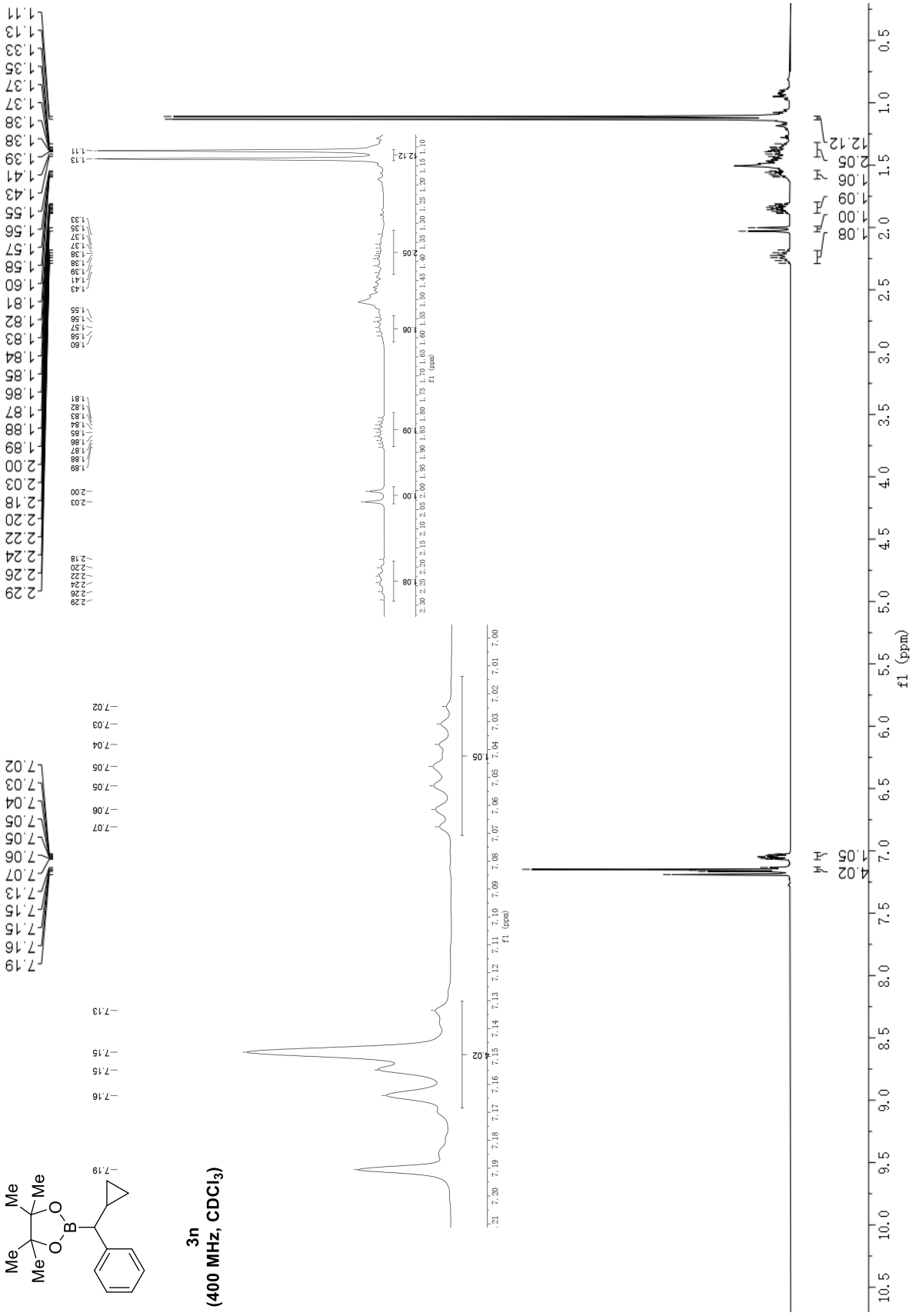

Me
Me
Me
Me
O
O
B
Me
3l
(400 MHz, CDCl3)
f1 (ppm)

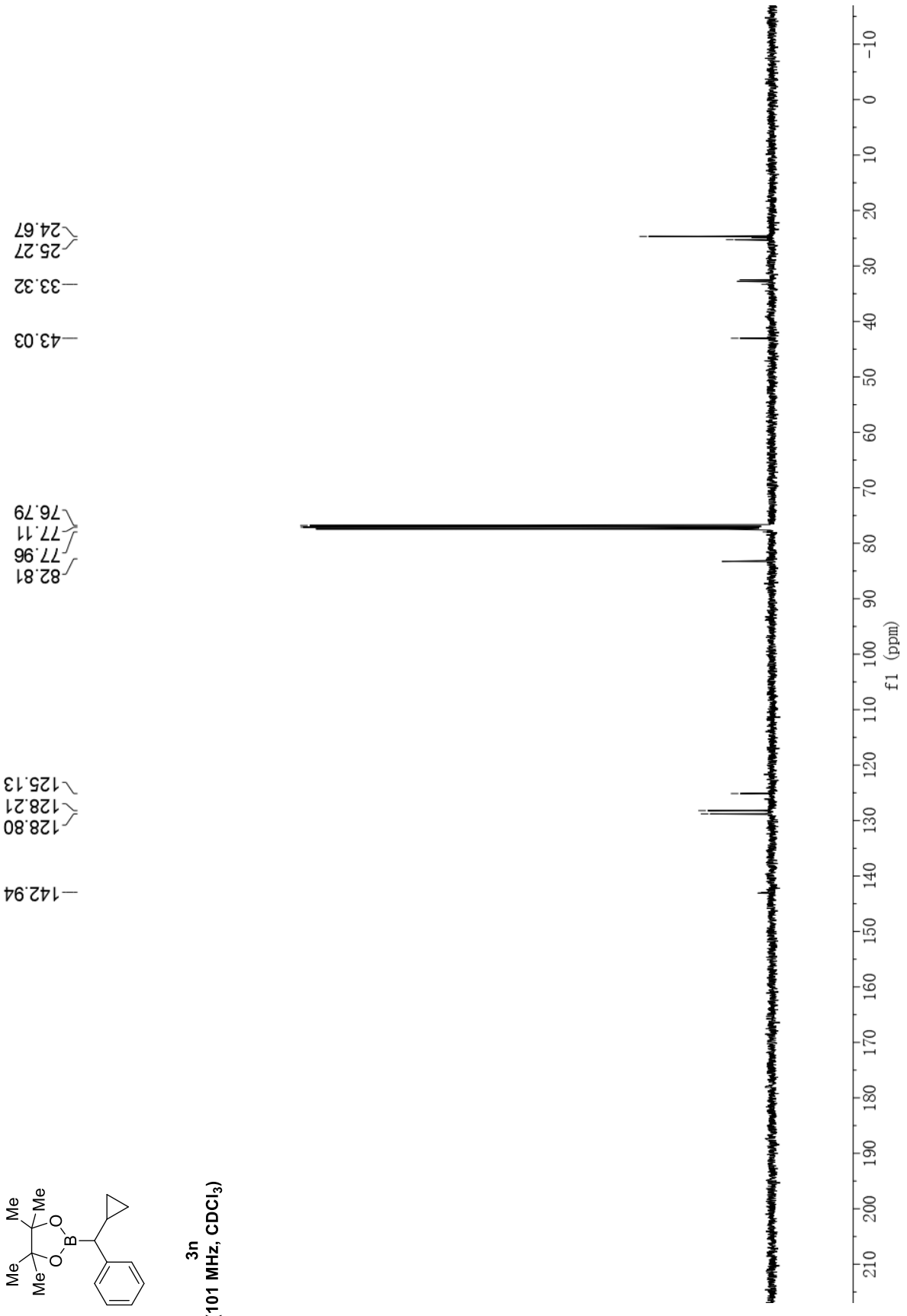


3l
(101 MHz, $CDCl_3$)

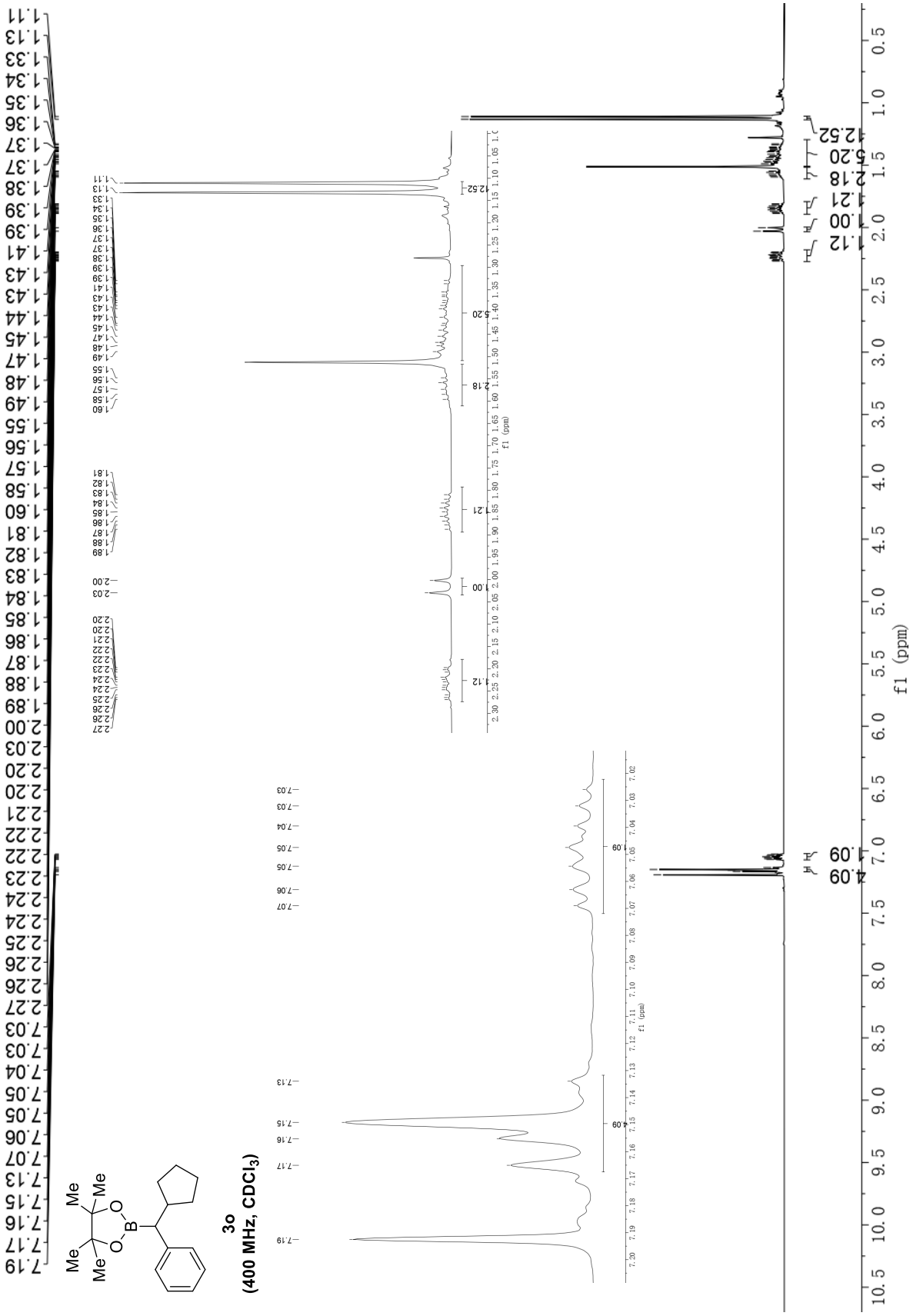

Me
Me
Me
Me
O
O
B
3m
(400 MHz, CDCl3)
f1 (ppm)

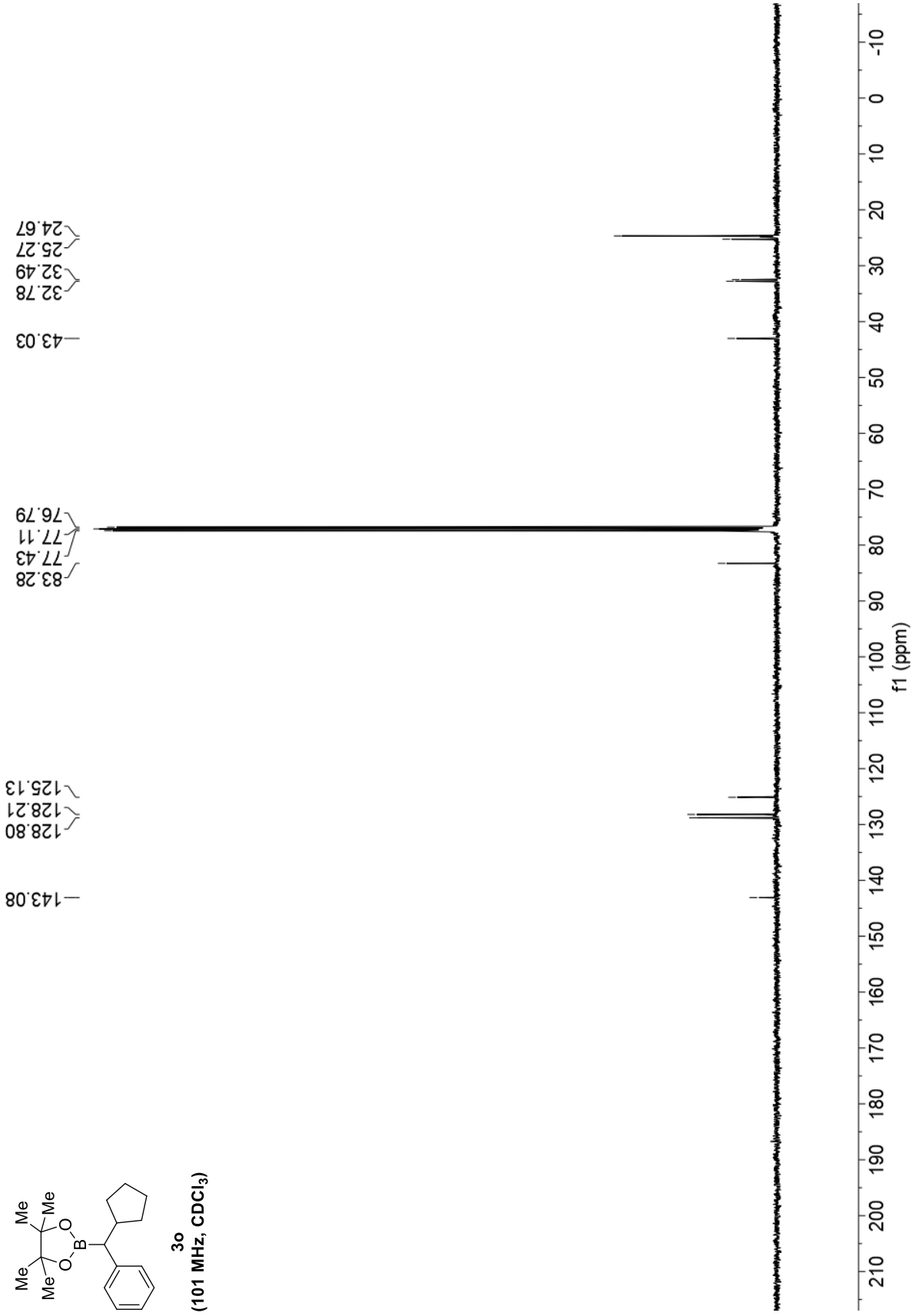

24.66
38.00
76.80
77.12
77.44
85.74
125.49
125.85
128.13
128.43
128.49
128.97
141.82
142.64
f1 (ppm)
Me
Me
Me
Me
O
O
B
3m
(101 MHz, CDCl3)

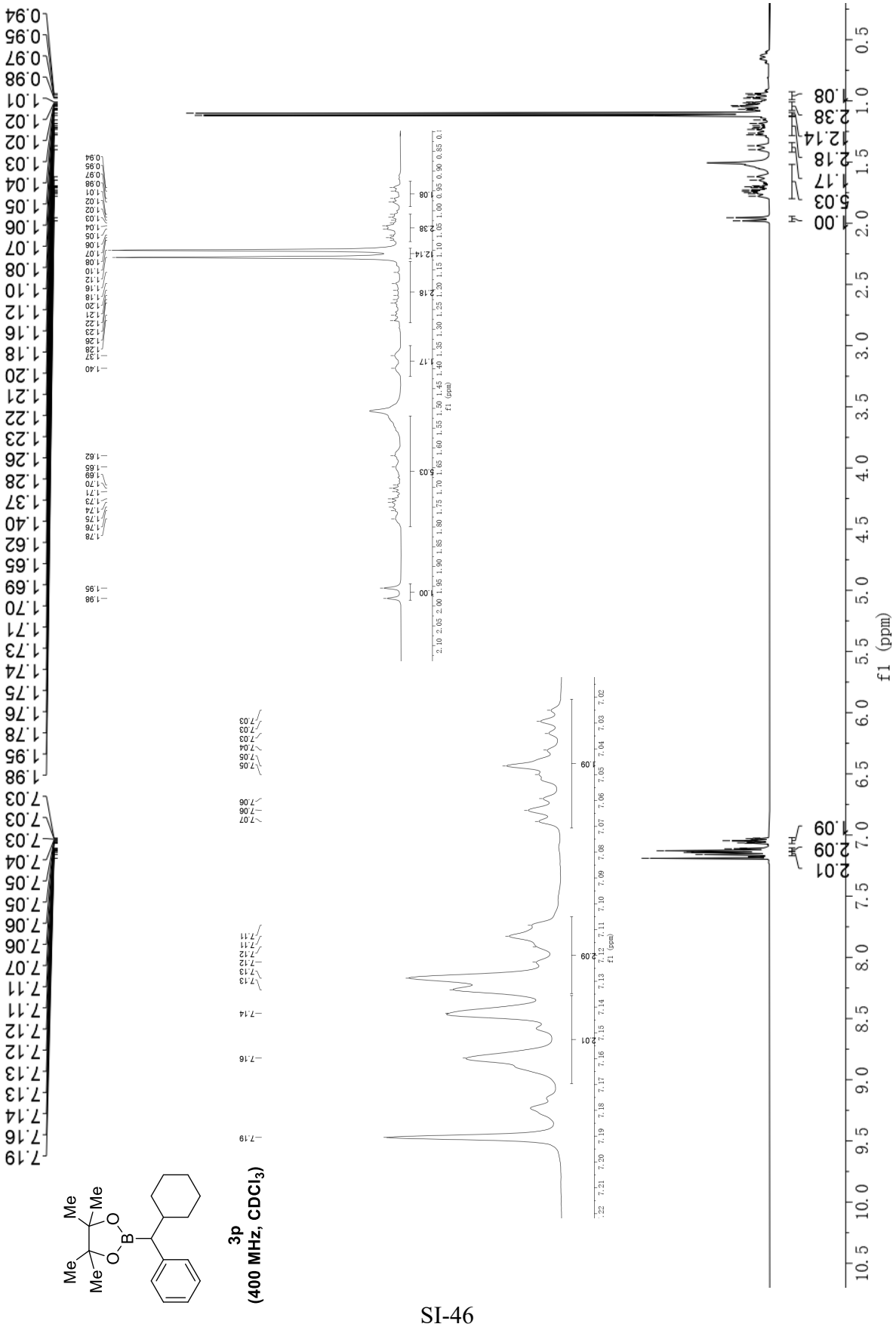

Me
Me
Me
Me
O
O
B
3n
(400 MHz, CDCl3)
f1 (ppm)

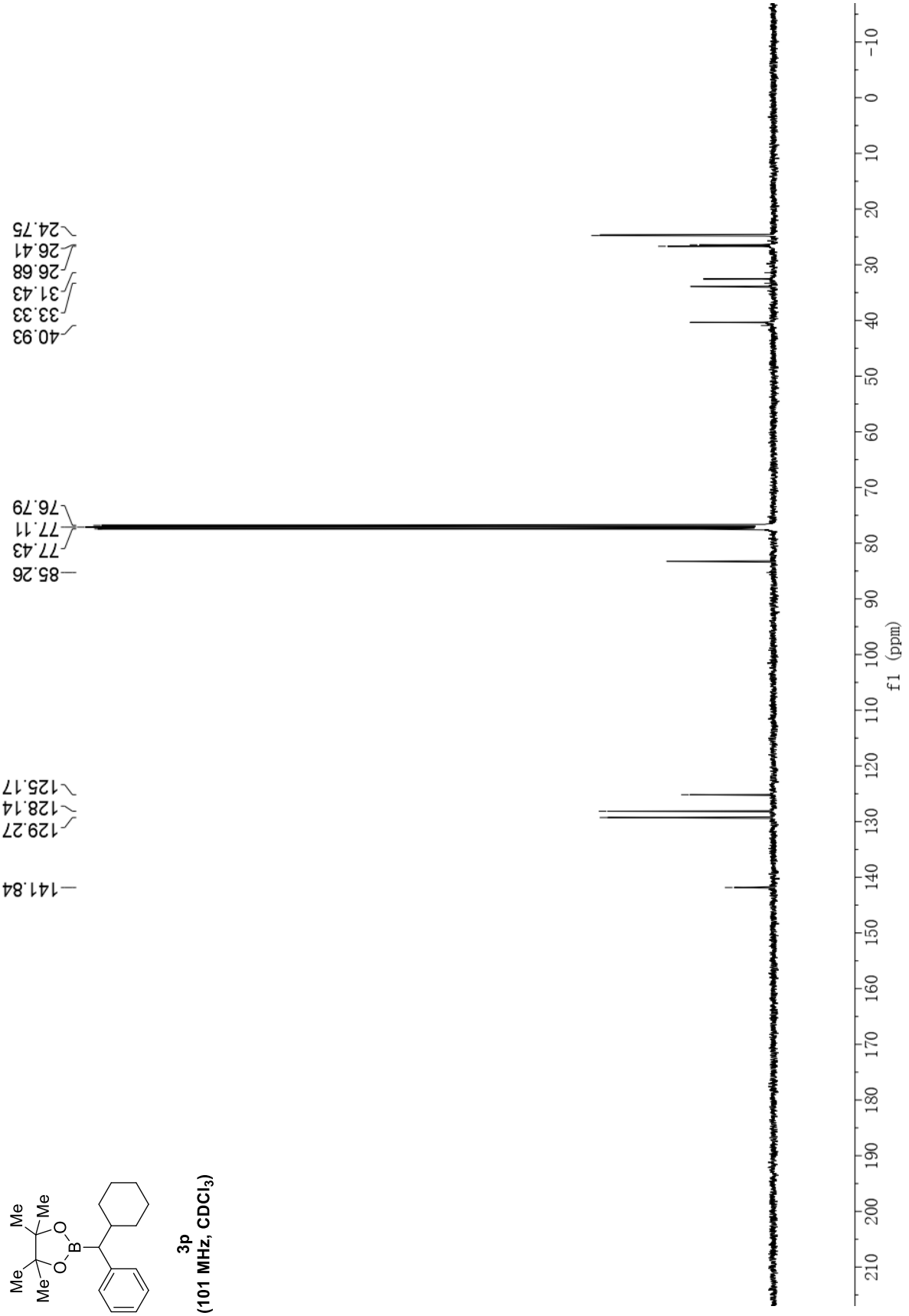


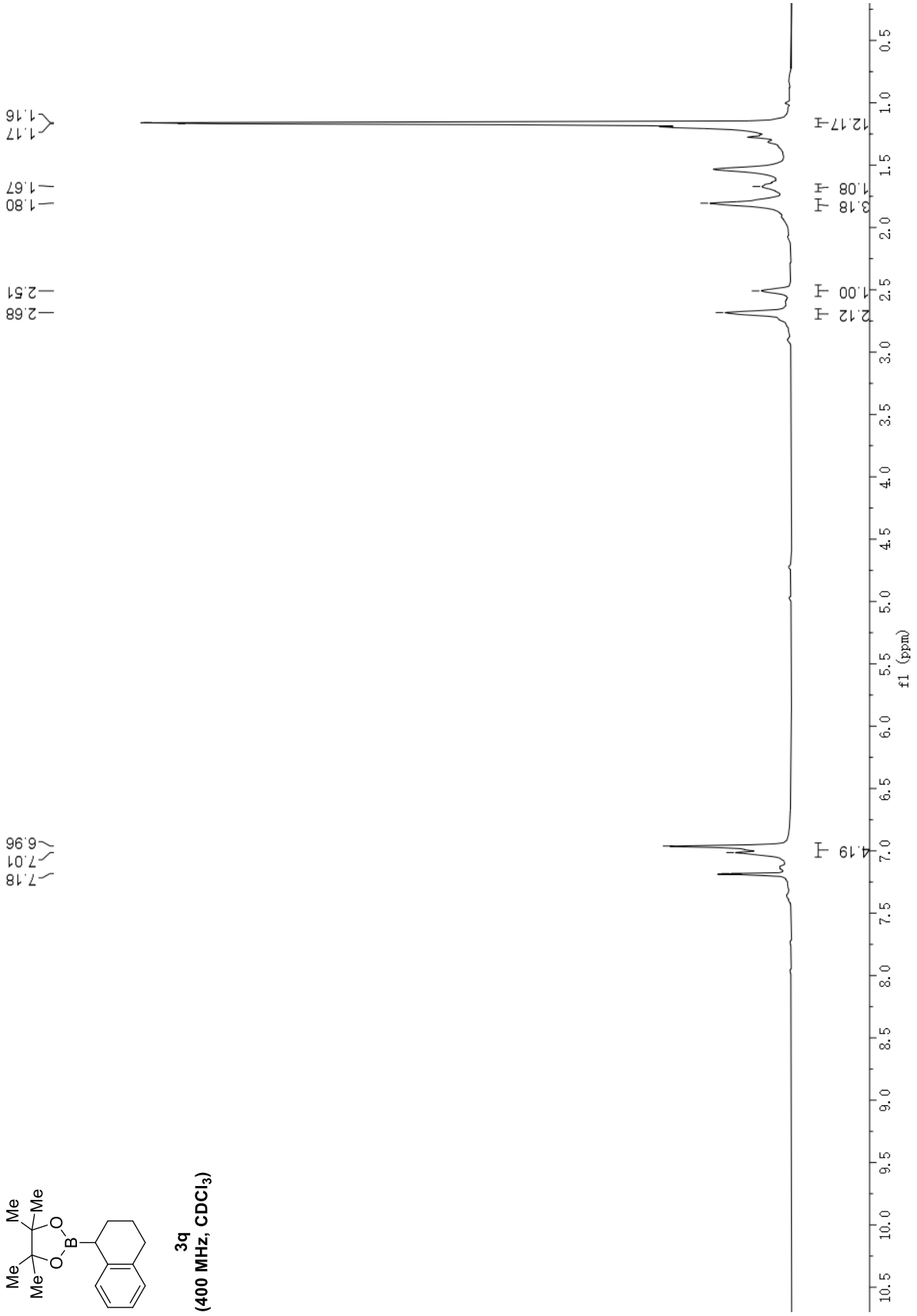
3n
(101 MHz, $CDCl_3$)


Me
Me
Me
Me
O
O
B
3o
(400 MHz, CDCl3)
f1 (ppm)

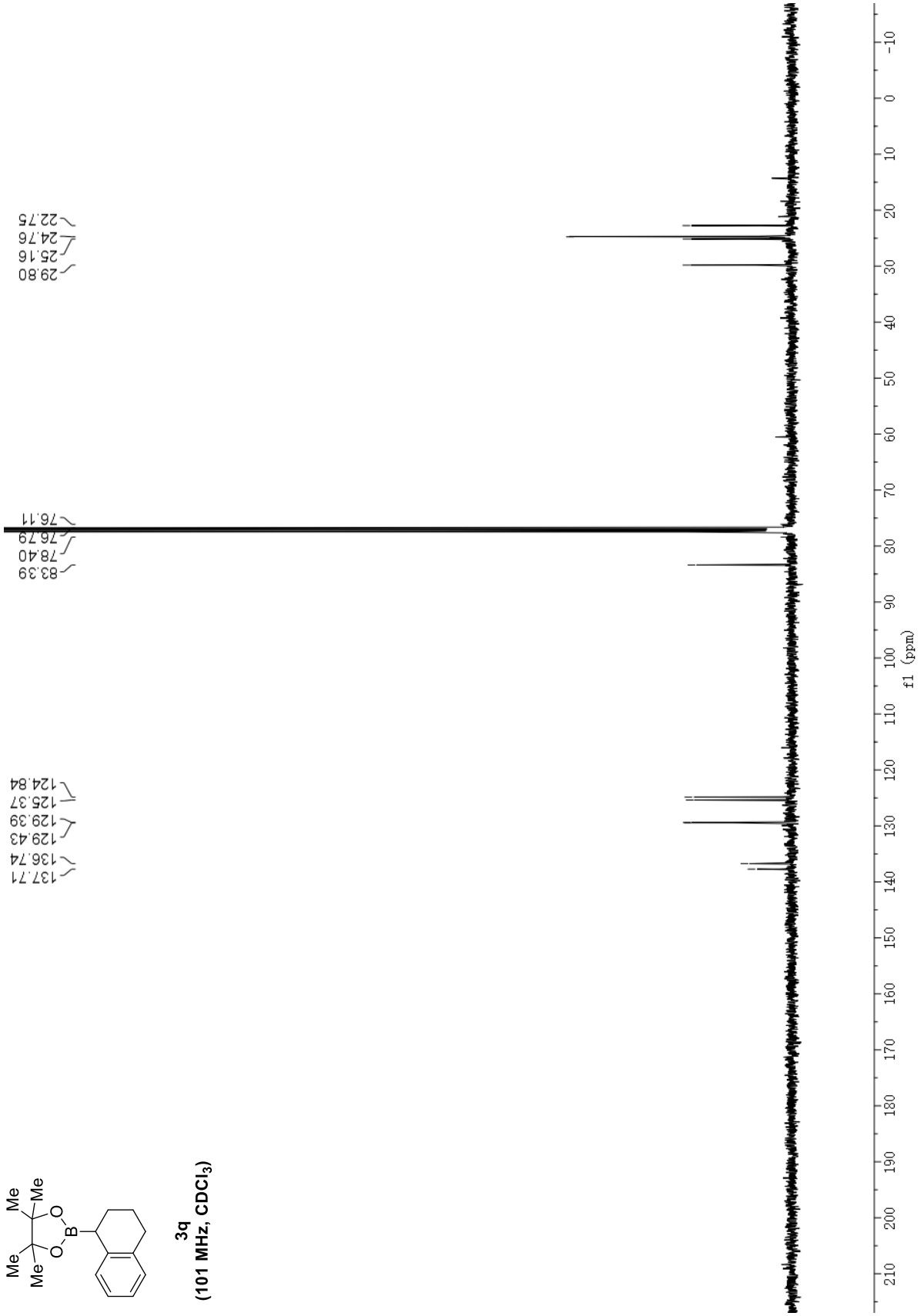

24.67
25.27
32.49
32.78
43.03
76.79
77.11
77.43
83.28
125.13
128.21
128.80
143.08
f1 (ppm)
Me
Me
Me
Me
O
O
B
3o
(101 MHz, CDCl3)


Me
Me
Me
Me
O
O
B
3p
(400 MHz, CDCl3)
f1 (ppm)


24.75
26.41
26.68
31.43
33.33
40.93
76.79
77.11
77.43
85.26
125.17
128.14
129.27
141.84
f1 (ppm)
Me
Me
Me
Me
O
O
B
3p
(101 MHz, CDCl3)



3q
(400 MHz, $CDCl_3$)



3q
(101 MHz, $CDCl_3$)