

Supplementary information

# Aerobic Visible Light-Driven Borylation of Heteroarenes in a Gel Nanoreactor

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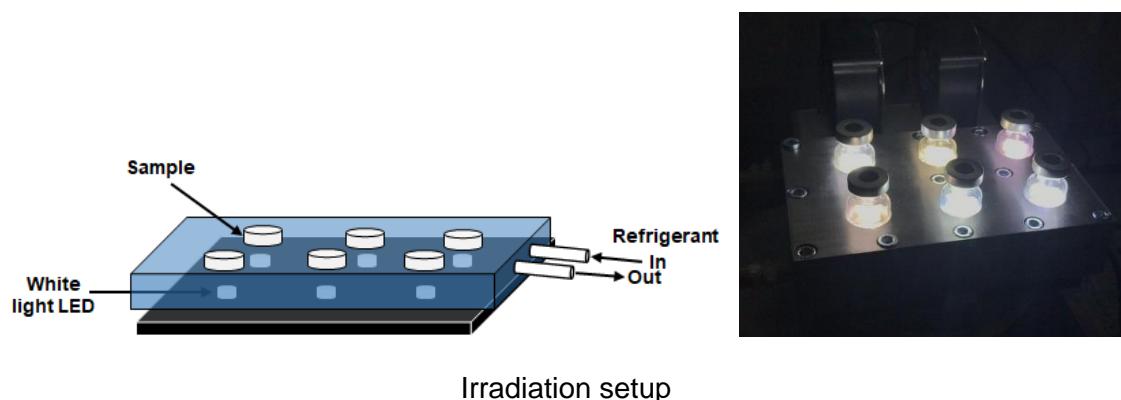
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## **Materials and methods**

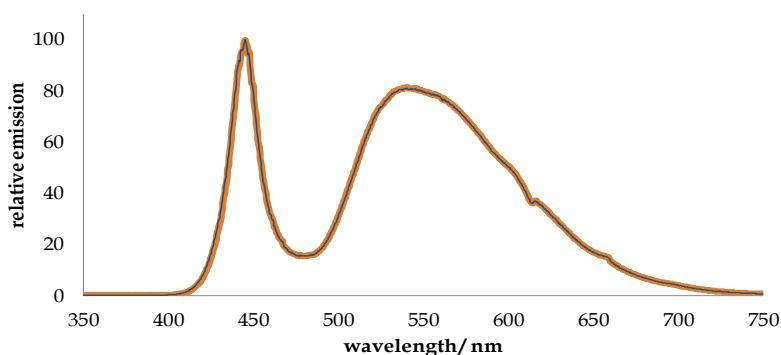
All reagents ( $\geq 97\%$  purity) and solvents ( $\geq 99\%$  purity) were purchased from commercial suppliers (Merck, TCI, Apollo Scientific, Fluorochem, Scharlab) and used as received unless otherwise indicated. Reactions were carried out in Metria®-Crimp Headspace clear vial flat bottom (10 mL, Ø 20 mm) sealed with Metria®-aluminium crimp cap with moulded septum butyl/natural PTFE (Ø 20 mm). Irradiation was performed with a cool white LED (LED Cree MK-R, cold-white, 11.6 V, 700 mA, P = 8.5 W). TLC was performed on commercial SiO<sub>2</sub>-coated aluminium and plastic sheets (DC60 F254, Merck). Visualization was done by UV-light (254nm). Product were isolated materials after TLC on silica gel (Merck, mesh 35-70, 60 Å pore size) and their corresponding yields were determined by quantitative GC-FID measurements on an Agilent 8860 GC-System with N<sub>2</sub> as carrier gas. Dodecanenitrile was used as an internal standard in the GC-FID quantitative measurements; yield products were estimated as: [conversion  $\times$  selectivity]/mass balance. Determination of purity and structure confirmation of the literature known products was performed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and high-resolution mass spectrometry (HRMS) in case of unknown products. NMR spectral data were collected on a Bruker Advance 400 (400 MHz for <sup>1</sup>H and 101 MHz for <sup>13</sup>C) spectrometer at 20 °C. Chemical shifts are reported in  $\delta$ /ppm, coupling constants J are given in Hertz. Solvent residual peaks were used as internal standard for all NMR measurements. The quantification of <sup>1</sup>H cores was obtained from integrations of appropriate resonance signals. Abbreviations used in NMR spectra: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, bs – broad singlet, dd – doublet of doublet, ddd – doublet of doublet of doublet. HRMS was carried out was performed in the mass facility of SCSIE University of Valencia. LRMS was carried out on an HP 6890 Series GC System with Agilent 5973 Network Mass Selective Detector and H<sub>2</sub> as carrier gas.

## General procedure

A vial (10 mL) was charged with the heteroarene derivative (20  $\mu$ mol, 1.0 eq.), diborylates (200  $\mu$ mol, 10.0 eq.) and the correspondent gelator (G1, 10 mg/mL). Acetonitrile/H<sub>2</sub>O (9/1 v/v) mixture (1.0 mL) was poured. Then, DIPEA (24  $\mu$ mol, 1.2 eq.) and dodecanenitrile (20  $\mu$ mol, 1.0 eq.) were added with 10  $\mu$ L Hamilton syringe. Quickly, the vial was sealed with a septum. It was heated to 150 °C for 1.5 minutes with manual stirring until complete clear solution. The vial cooled to room temperature until gel formation was observed. The reaction was irradiated with an external LED through the plain bottom side of the vial at 23 °C during the corresponding time. Then, brine (2 mL) was added, and the aqueous phase was extracted with dichloromethane (1 mL). The reaction was monitored by GC-FID analysis. The organic phase was dried over anhydrous sodium sulfate, filtered from the drying agent, and concentrated in vacuo. After recrystallization of the excess of starting diboron derivative, which is recovered, the crude was purified via TLC plastic sheet using a hexane/ethyl acetate mixture as the mobile phase. Note: The gelator can be easily separated by filtration and reused in subsequent experiments without any detriment of its gelation properties.



**Lamp emission: cold white light LED**



## **Synthesis of Low Molecular Weight Gelators (LMW Gelators)**

### ***N,N'-Bis(octadecyl)-L-Boc-glutamic Diamide (G1).***

Boc-glutamic acid (0.01 mol, 1.0 equiv) and octadecylamine (0.02 mol, 2.0 equiv) in dichloromethane (200 mL) were mixed. Then, 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC·HCl) (0.022 mol, 2.2 equiv) was added to the mixture and stirred at RT for 72 h. The obtained white solid was isolated by filtration and washed three times with dichloromethane. The crude product was dissolved in THF and precipitated by water. A fine white solid was obtained (80%). Following the procedure reported previously *Soft Matter* **2007**, 3, 1312–1317.

<sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ 6.69 (br, 1H), 6.32 (br, 1H), 5.77 (br, 1H), 4.08 (br, 1H), 3.26–3.22 (m, 4H), 2.41–2.27 (m, 2H), 2.06–1.93 (m, 2H), 1.58–1.46 (m, 4H), 1.43 (s, 9H), 1.25 (s, 60H), 0.87 (t, 6H) ppm.

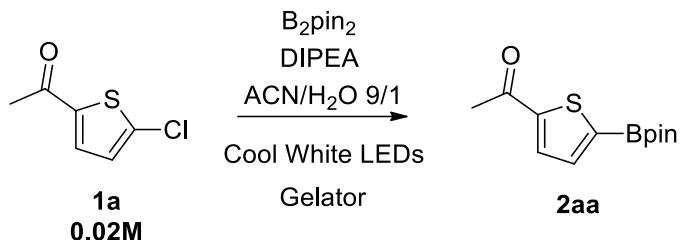
### ***(S,S)-Dodecyl-3-[2(3-dodecyl-ureido)cyclohexyl]urea (G2).***

A solution of dodecylisocyanate (15 mmol, 2.0 equiv) in toluene (20 mL) was slowly added to a solution of (S,S)-1,2-cyclohexyldiamine (7 mmol, 1.0 equiv) in toluene (100 mL). The reaction mixture was stirred for 16 h at RT and 2 h at 100 °C. After cooling to RT, the gel-like reaction mixture was filtered to give a white waxy solid. The waxy solid was further stirred for 16 h with dichloromethane (50 mL) and collected by filtration. This procedure was repeated with diethyl ether. After drying, a white solid was obtained (70%). Following the procedure reported previously *Chem. - Eur. J.* **1999**, 5, 937–950

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.18 (br, 2H), 4.67 (br, 2H), 3.42 (m, 2H), 3.08 (m, 4H), 2.03 (d, 2H), 1.72 (m, 6H), 1.45 (m, 4H), 1.25 (s, 36H), 0.87 (t, 6H) ppm.

## Searching the optimal conditions

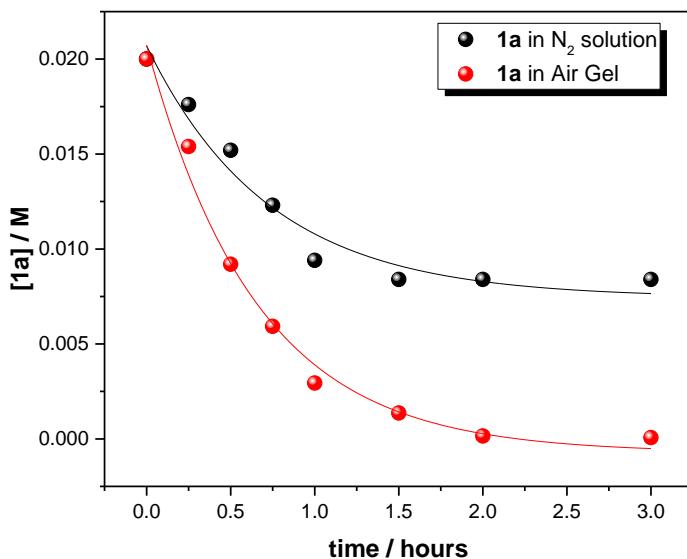
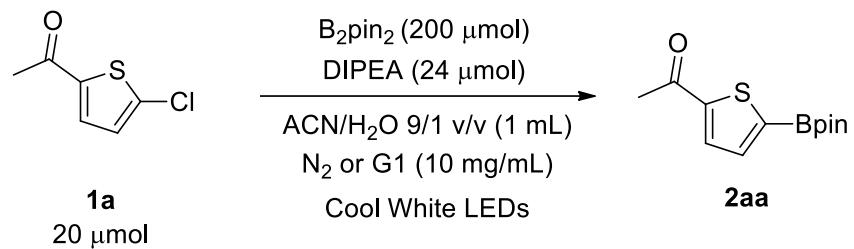
Table S1.



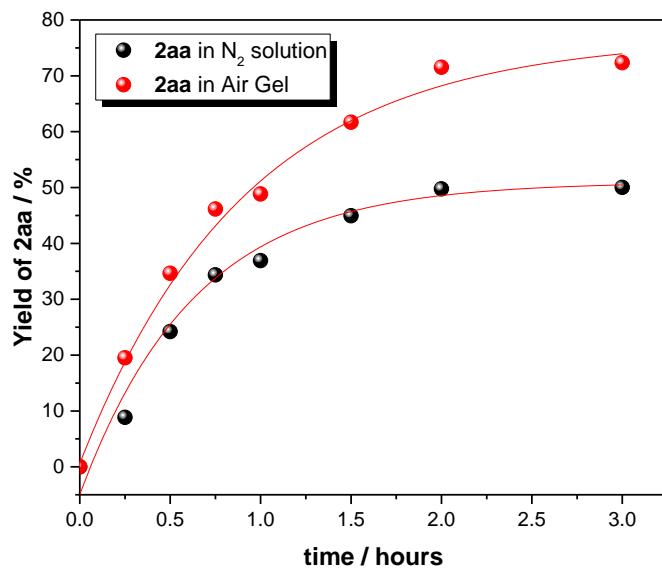
Entry	$B_2pin_2$ (eq)	DIPEA (eq)	G1/solvent	Conv (%)	Yield of <b>2aa</b> (%)
1	3	1.5	21 mg/2mL	100	16
2	5	1.2	10 mg/1mL	92	57
3	5	1.5	21 mg/2mL	100	28
4	15	1.2	10 mg/1mL	26	18
5	10	1.5	21 mg/2mL	100	60
6	20	1.5	21 mg/2mL	92	69
7	10	1	21 mg/2mL	94	62
8	10	1	10 mg/1mL	46	35
9	10	3	21 mg/2mL	100	38
10	10	3	10 mg/1mL	100	58
11	10	1.2	21 mg/2mL	100	64
12	10	1.5	42 mg/4mL	92	40
13	10	1.2	42 mg/4mL	100	53
14	10	1.2	10 mg/1mL	100	72
15	10	1.2	8 mg/1mL	70	43
16	10	1.2	15 mg/1mL	59	37
17	10	1.2	<sup>a</sup> 8.5 mg/1mL	59	38
18	10	1.2	<sup>a</sup> 10 mg/1mL	86	56
19	10	1.2	<sup>a</sup> 5 mg/1mL	55	44
20	10	1.2	Air <sup>b</sup>	-	-
21	10	1.2	N <sub>2</sub> <sup>b</sup>	75	56
22	10	1.2	G1/N <sub>2</sub> <sup>b</sup>	46	34
23	10	-	10 mg/1mL	-	-
24	-	1.2	10 mg/1mL	-	-
25 <sup>c</sup>	10	1.2	10 mg/1mL	-	-
26	10	Et <sub>3</sub> N 1.2	10 mg/1mL	19	11
27	10	DIPA 1.2	10 mg/1mL	29	29
28	10	DBU 1.2	10 mg/1mL	66	45
29	10	DABCO 1.2	10 mg/1mL	15	7.8
30	10	Ph <sub>3</sub> N 1.2	10 mg/1mL	-	-
31	10	1.2	Frozen No G1	-	-
32	10	1.2	Frozen; 10 mg/1mL	35	30
33	10	1.2	<sup>d</sup> N <sub>2</sub> and 10 mg/1mL	73	60

<sup>a</sup>G2 as gelator was used. <sup>b</sup>Solution reaction without gel. <sup>c</sup>Without 1a. <sup>d</sup>Purged with N<sub>2</sub> before gel formation.

## Kinetic studies

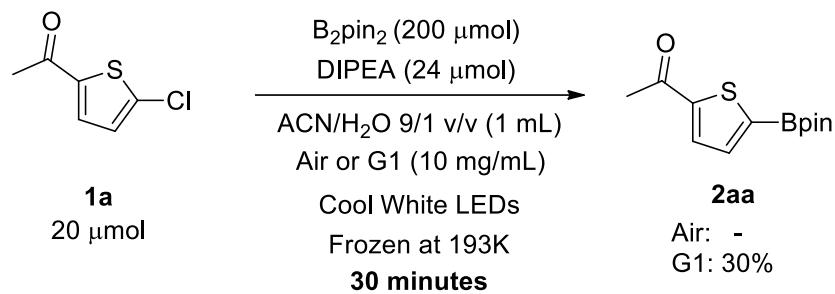


**Figure S1.** Variation of **1a** concentration upon irradiation time in different conditions.



**Figure S2.** Formation of **2aa** upon irradiation time in different conditions.

## Frozen model reaction procedure

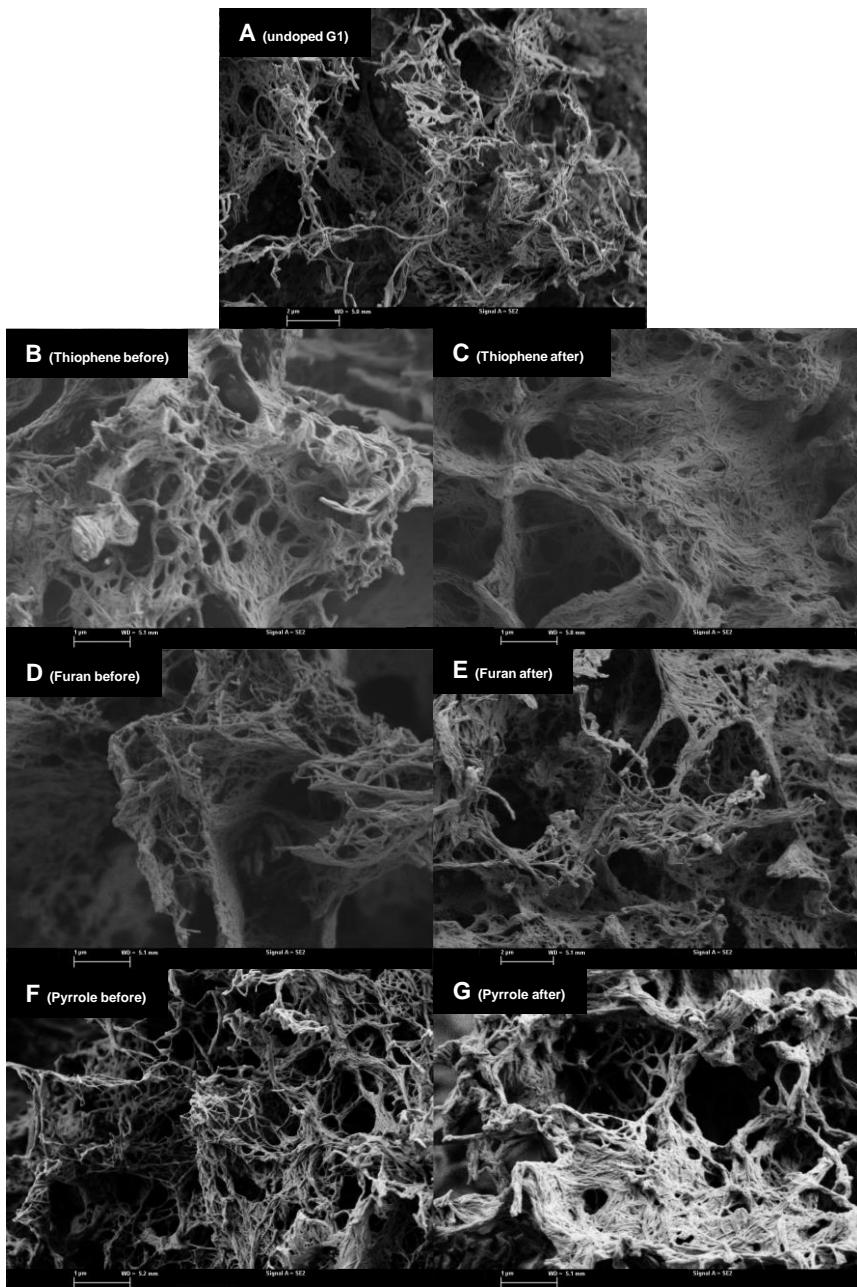


A vial (10 mL) was charged with 1-(5-chlorothiophen-2-yl)ethenone (3.2 mg, 20  $\mu$ mol, 1.0 equiv.), bispinacolato diboron (50 mg, 200  $\mu$ mol, 10.0 equiv.) and the correspondent gelator (G1, 10 mg/mL). Acetonitrile/H<sub>2</sub>O (9/1 v/v) mixture (1.0 mL) was poured, and it was stirred until almost complete solution. Then, DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) were added with 10  $\mu$ L Hamilton syringe. Quickly, the vial was sealed with a septum. It was heated to 150 °C with heatgun for 1.5 minutes with manual stirring until complete clear solution. The vial cooled to room temperature until gel formation was observed. The vial was frozen at 193K for 2 hours. Then, the reaction was irradiated with an external LED through the plain bottom side of the vial at 23 °C for 30 minutes. The reaction was monitored by GC-FID analysis. The gel was broken with dichloromethane (2 mL) and it was clean with brine (6 mL). The organic phase was dried over anhydrous sodium sulfate, filtered from the drying agent, and concentrated in vacuo.

## **Field-emission scanning electron microscopy (FESEM)**

The equipment in operation in the UPV Microscopy Service is the ZEISS ULTRA 55 model, incorporating the following detectors:

- A Secondary Electron Detector (SE2), which provides an SEM topography image of the sample surface with a large depth of field.
- A Secondary Electron In-Lens Detector located inside the electron column, which works with low energy secondary electrons and provides images with a higher resolution.
- A Backscattered Electron Detector (AsB) which is sensitive to the variation of atomic number in the elements present in the sample; therefore, it is used to observe changes in the chemical composition of the specimen.
- A Backscattered Electron In-lens Detector (EsB), independent of the secondary In-lens detector, which provides a pure backscattered signal with no secondary electron contamination and very low acceleration potential.
- An X-Ray Dispersive Energy Detector, EDS, (Oxford Instruments) which receives x-rays from each surface point the electron beam passes over.

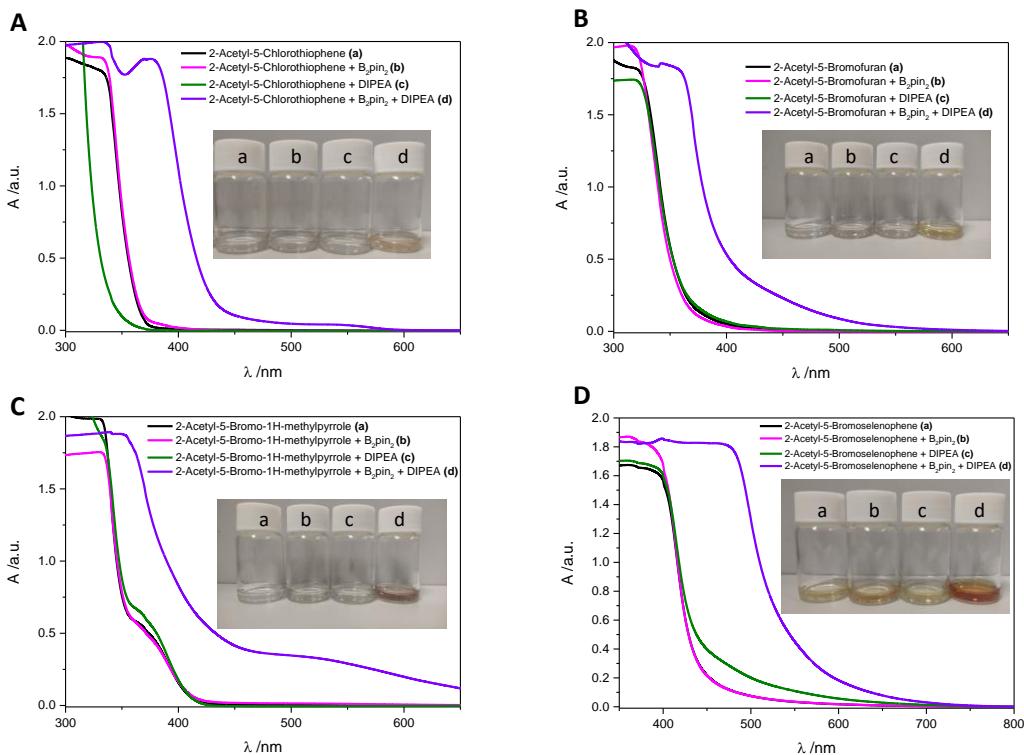


**Figure S3.** Representative field-emission scanning electron microscopy (FESEM) images. **A:** undoped gel of **G1** (10 mg/mL). **B, C:** gel of **G1** (10 mg/mL) doped with 2-acetyl-5-chlorothiophene (3.2 mg),  $B_2pin_2$  (50 mg) and DIPEA (3.1 mg). **D, E:** gel of **G1** (10 mg/mL) doped with 2-acetyl-5-bromofuran (3.8 mg),  $B_2pin_2$  (50 mg) and DIPEA (3.1 mg). **F, G:** gel of **G1** (10 mg/mL) doped with 2-acetyl-5-bromo-1H-methylpyrrole (4.0 mg),  $B_2pin_2$  (50 mg) and DIPEA (3.1 mg).

## **Determination of gel-to-sol transition temperature ( $T_{\text{gel}}$ )**

$T_{\text{gel}}$  values were determined using a custom-made set-up where a sealed vial was placed into a mold of an alumina block and heated up at 1 °C/5 min using an electric heating plate equipped with a temperature control couple as previously described (see for instance, *Chem. Commun.* **2015**, 51, 16848-16851). The temperature at which the gel started to break was defined as  $T_{\text{gel}}$  with an estimated error of  $\pm 2$  °C after several heating-cooling cycles.

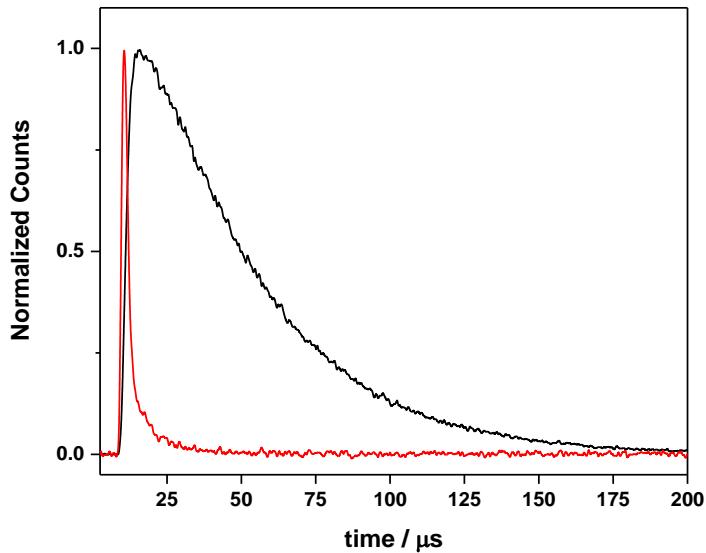
## UV-vis absorption spectra



**Figure S4.** UV-vis absorption spectra. Inset: photographs of different solutions. **A:** 2-Acetyl-5-Chlorothiophene (0.02 mmol), B<sub>2</sub>pin<sub>2</sub> (0.2 mmol) and DIPEA (0.024 mmol) in ACN/H<sub>2</sub>O 9/1 v/v 1 mL. **B:** 2-Acetyl-5-Bromofuran (0.02 mmol), B<sub>2</sub>pin<sub>2</sub> (0.2 mmol) and DIPEA (0.024 mmol) in ACN/H<sub>2</sub>O 9/1 v/v 1 mL. **C:** 2-Acetyl-5-Bromo-1H-methylpyrrole (0.02 mmol), B<sub>2</sub>pin<sub>2</sub> (0.2 mmol) and DIPEA (0.024 mmol) in ACN/H<sub>2</sub>O 9/1 v/v 1 mL. **D:** 2-Acetyl-5-Bromoselenophene (0.02 mmol), B<sub>2</sub>pin<sub>2</sub> (0.2 mmol) and DIPEA (0.024 mmol) in ACN/H<sub>2</sub>O 9/1 v/v 1 mL.

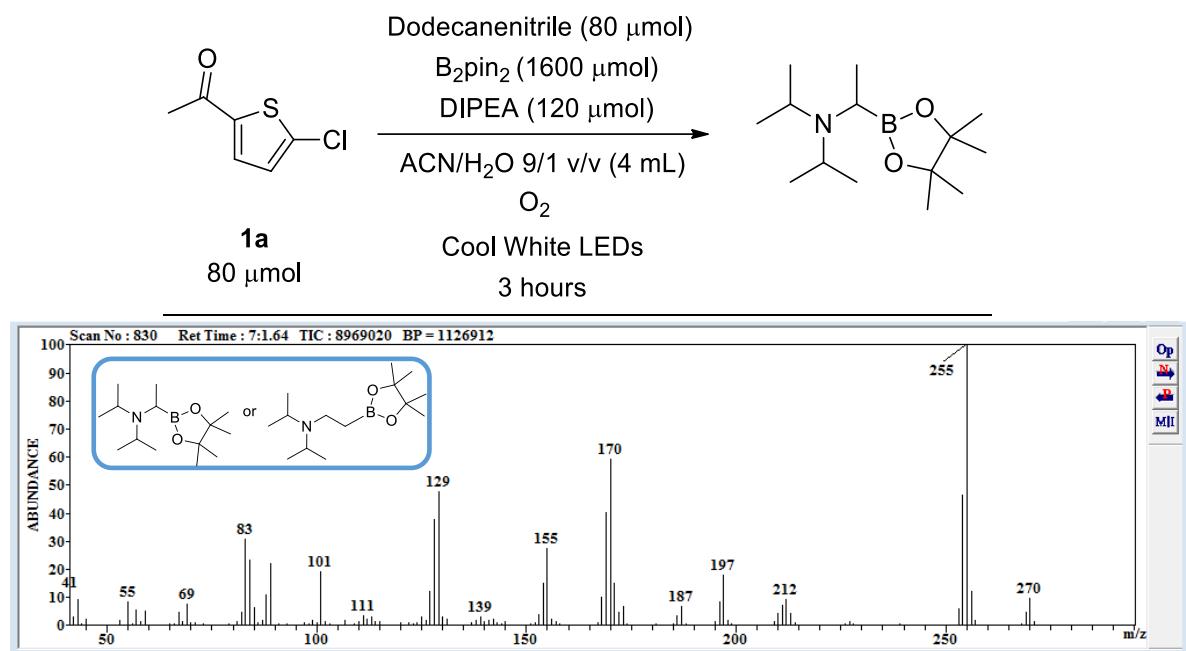
## Singlet Oxygen

Time-resolved measurements of  ${}^1\text{O}_2$  luminiscence were performed in a front face setup in FLS 1000 (Edinburgh Instruments) spectrophotometer by making use of a 450W Xe lamp and a NIR sensitive PMT 1700 detector (H10330C-75, Hamamatsu) in Peltier Cooled Housing.



**Figure S5.** Decay traces of the  ${}^1\text{O}_2$  emission (1275 nm) generated by an aerobic ACN/H<sub>2</sub>O (9/1 v/v) solution of; **black**: Rose Bengal (0.1 mM,  $\lambda_{\text{exc}} = 532$  nm); **red**: 1a+B<sub>2</sub>pin<sub>2</sub>+DIPEA (20 mM, 200 mM and 24 mM, respectively,  $\lambda_{\text{exc}} = 400$  nm).

## GC-MS Byproduct

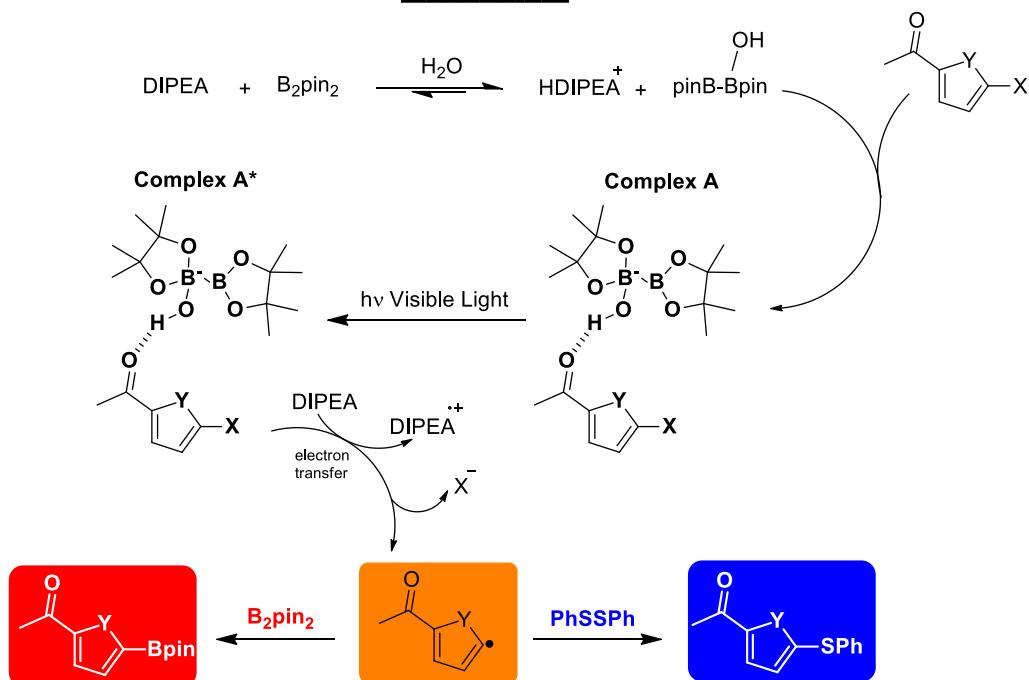


## Trapping reaction

A vial (10 mL) was charged with heteroarene derivative (20  $\mu$ mol, 1.0 equiv.), diborylates (200  $\mu$ mol, 10.0 equiv.), diphenyldisulfide (20  $\mu$ mol, 1.0 equiv.) and the correspondent gelator (G1, 10 mg/mL). Acetonitrile/H<sub>2</sub>O (9/1 v/v) mixture (1.0 mL) was poured, and it was stirred until almost complete solution. Then, DIPEA (24  $\mu$ mol, 1.2 equiv.) and dodecanenitrile (20  $\mu$ mol, 1.0 equiv.) were added with 10  $\mu$ L Hamilton syringe. Quickly, the vial was sealed with a septum. It was heated to 150 °C for 1.5 minutes with manual stirring until complete clear solution. The vial cooled to room temperature until gel formation was observed. The reaction was irradiated with an external LED through the plain bottom side of the vial at 23 °C for 3 hours. Then, brine (6 mL) was added, and the aqueous phase was extracted with dichloromethane (2 mL). The reaction was monitored by GC-FID analysis. The organic phase was dried over anhydrous sodium sulfate, filtered from the drying agent, and concentrated in vacuo. After crystallization of the excess of starting diboron derivative, the crude was purified via TLC plastic sheet using a hexane/ethyl acetate mixture as the mobile phase.

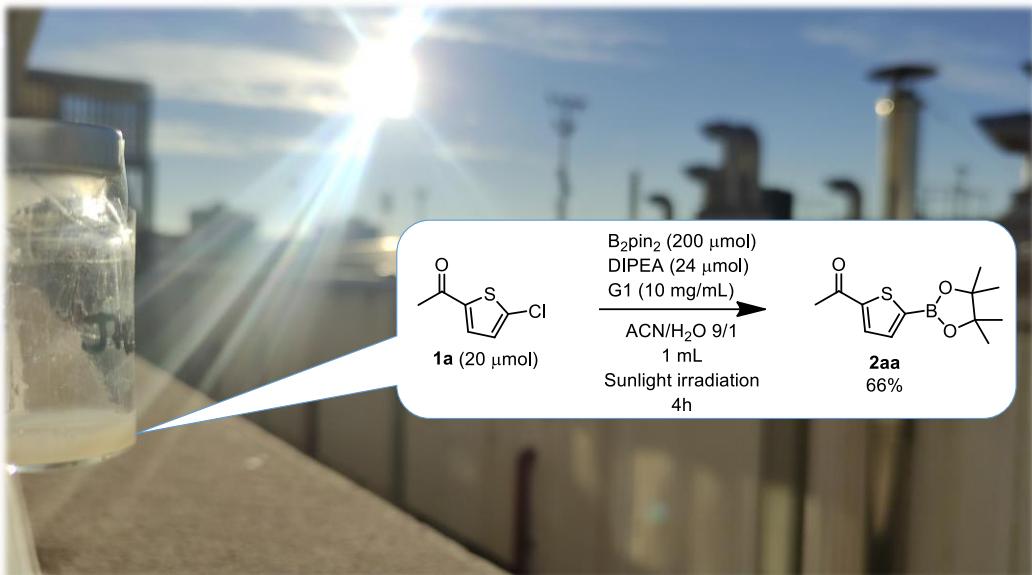
Product distribution			
Y: S X: Cl Y: O X: Br	37%	15%	78%

## Mechanism



## Sunlight irradiation and 1 mmol scale

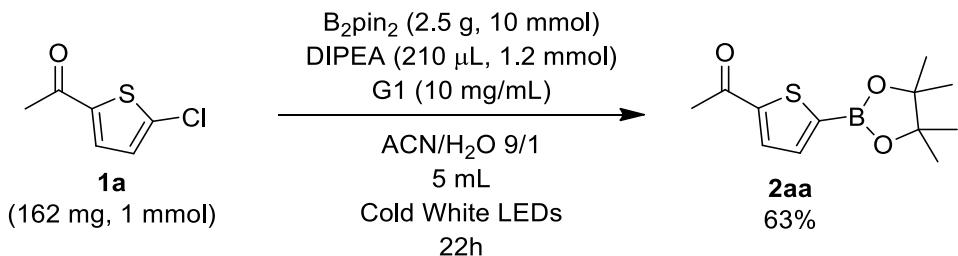
### *Sunlight irradiation*



The compound **2aa** (CAS 942070-32-8) was prepared according to the general procedure using 1-(5-chlorothiophen-2-yl)ethenone (3.2 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated with sunlight for 4 hours, obtaining 66% product yield according to GC-FID analysis.

Location: Camí de Vera S/N, Chemistry Department, Universitat Politècnica de València (UPV), Valencia, Spain (coordinate: 39.482917, -0.341642), temperature: 12-16 °C, from 9:00 to 13:00. Date: 23/12/2020.

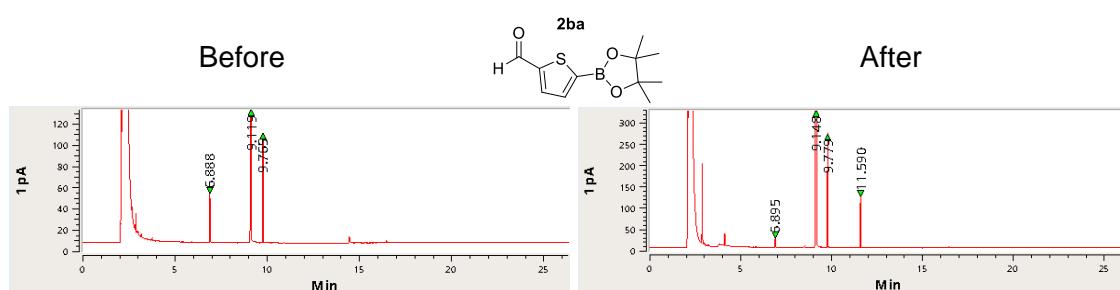
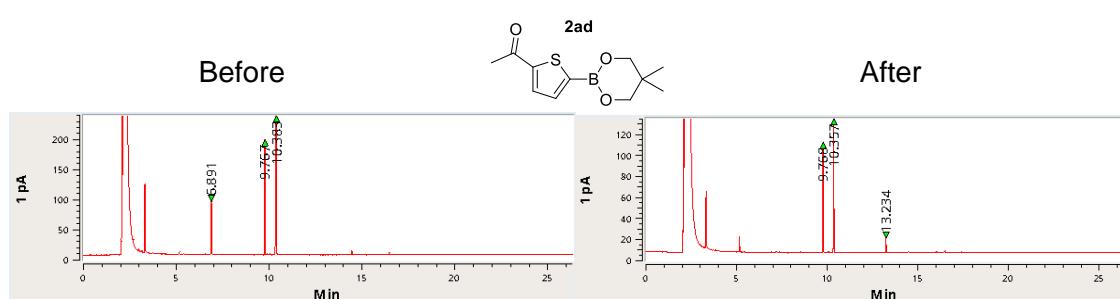
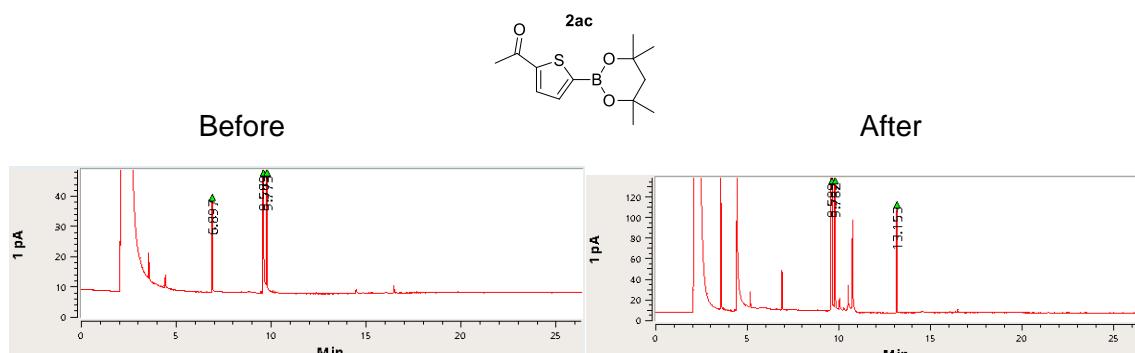
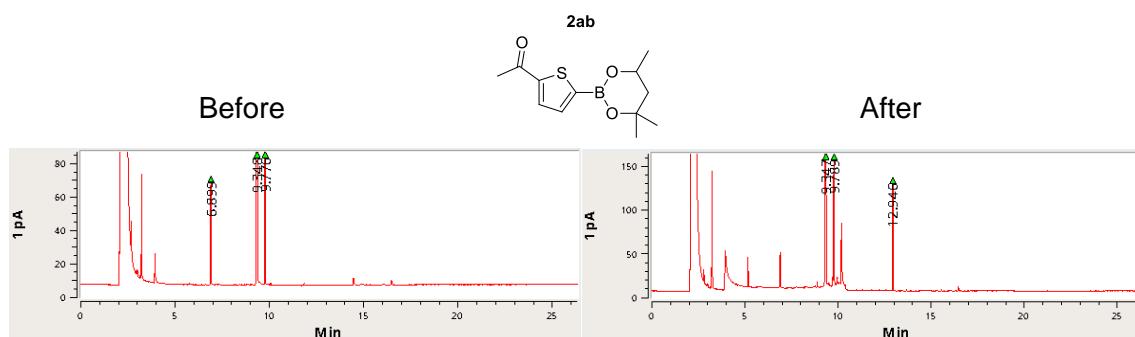
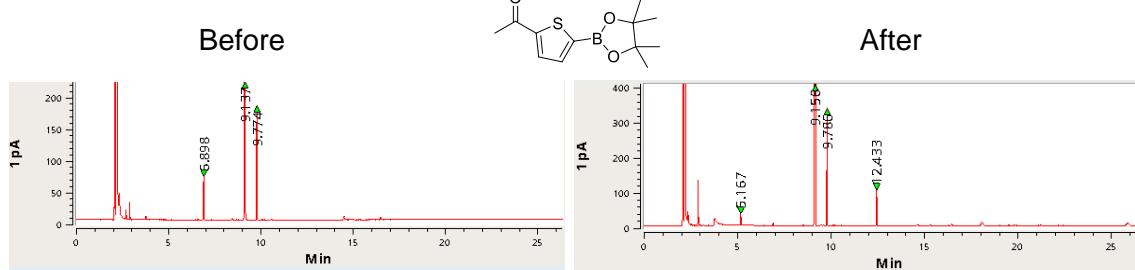
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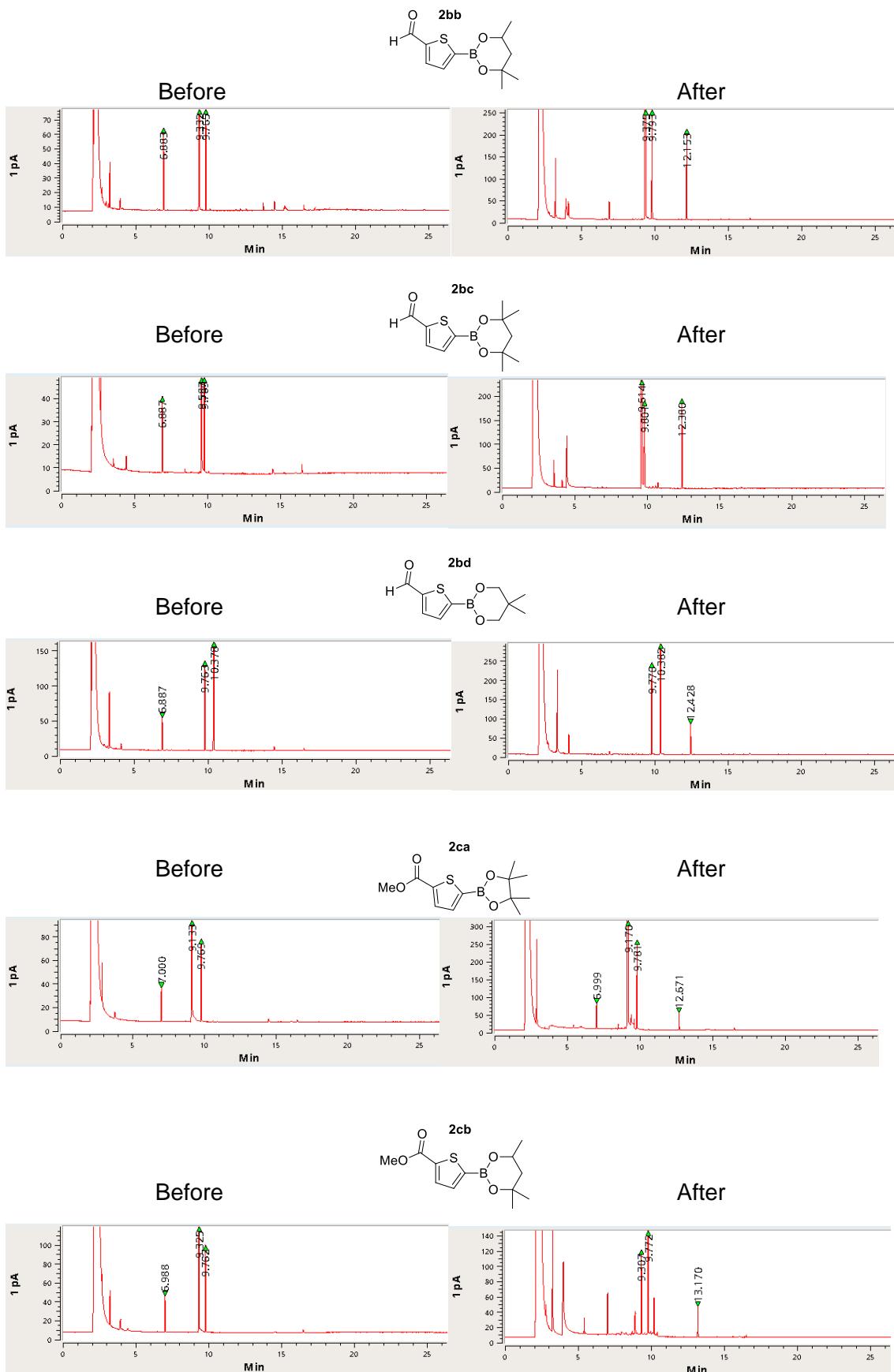


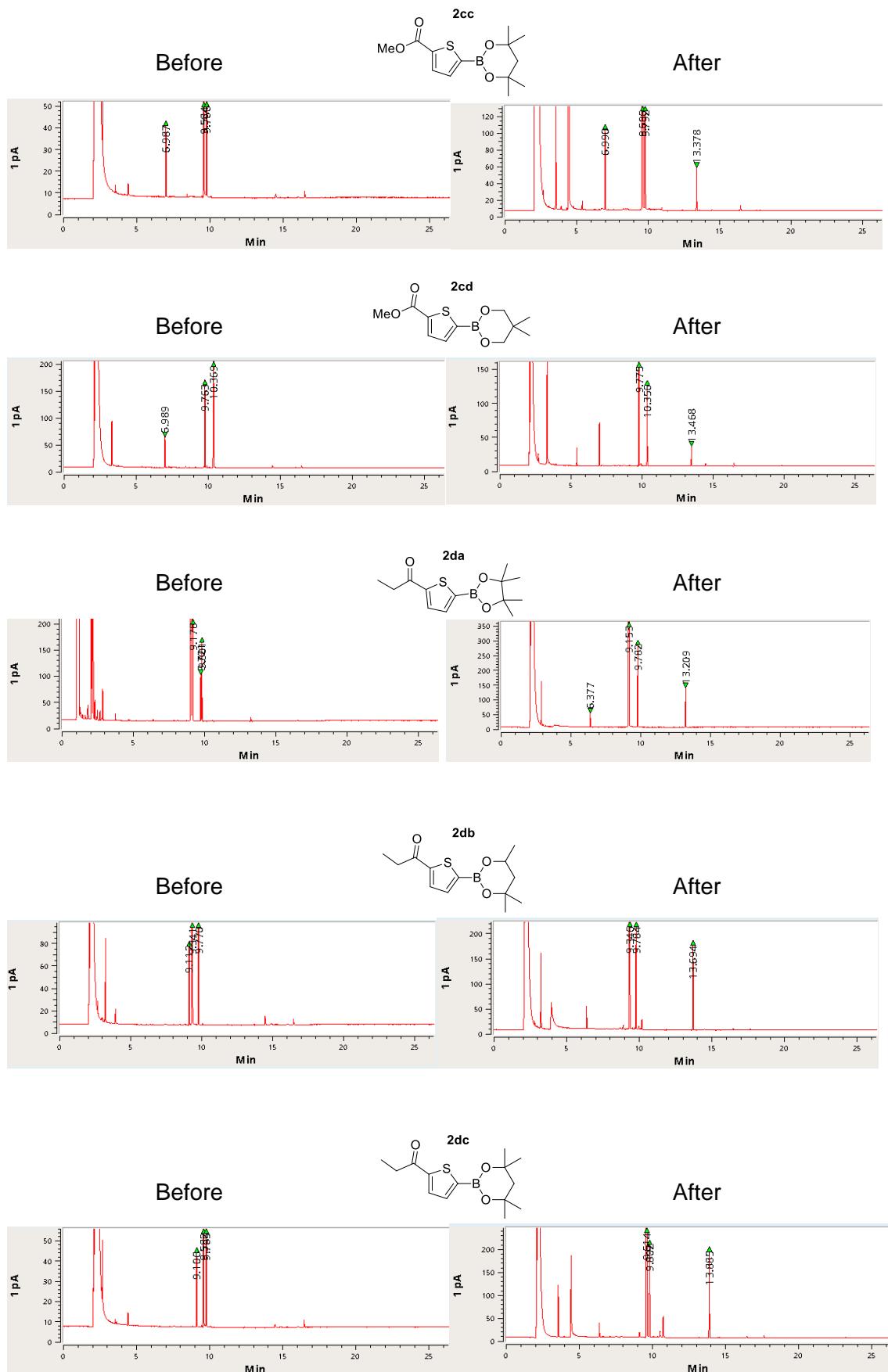
The compound **2aa** (CAS 942070-32-8) was prepared according to the general procedure using 1-(5-chlorothiophen-2-yl)ethenone (162 mg, 1 mmol, 1.0 eq.), bis(pinacolato)diboron (2.5 g, 10 mmol, 10.0 eq.), dodecanenitrile (220  $\mu$ L, 1 mmol, 1.0 equiv.) as internal standard and DIPEA (210  $\mu$ L, 1.2 mmol, 1.2 eq.) and G1 (10 mg/mL) in 5 mL. The reaction mixture was irradiated for 22 hours, obtaining 63% product yield according to GC-FID analysis.

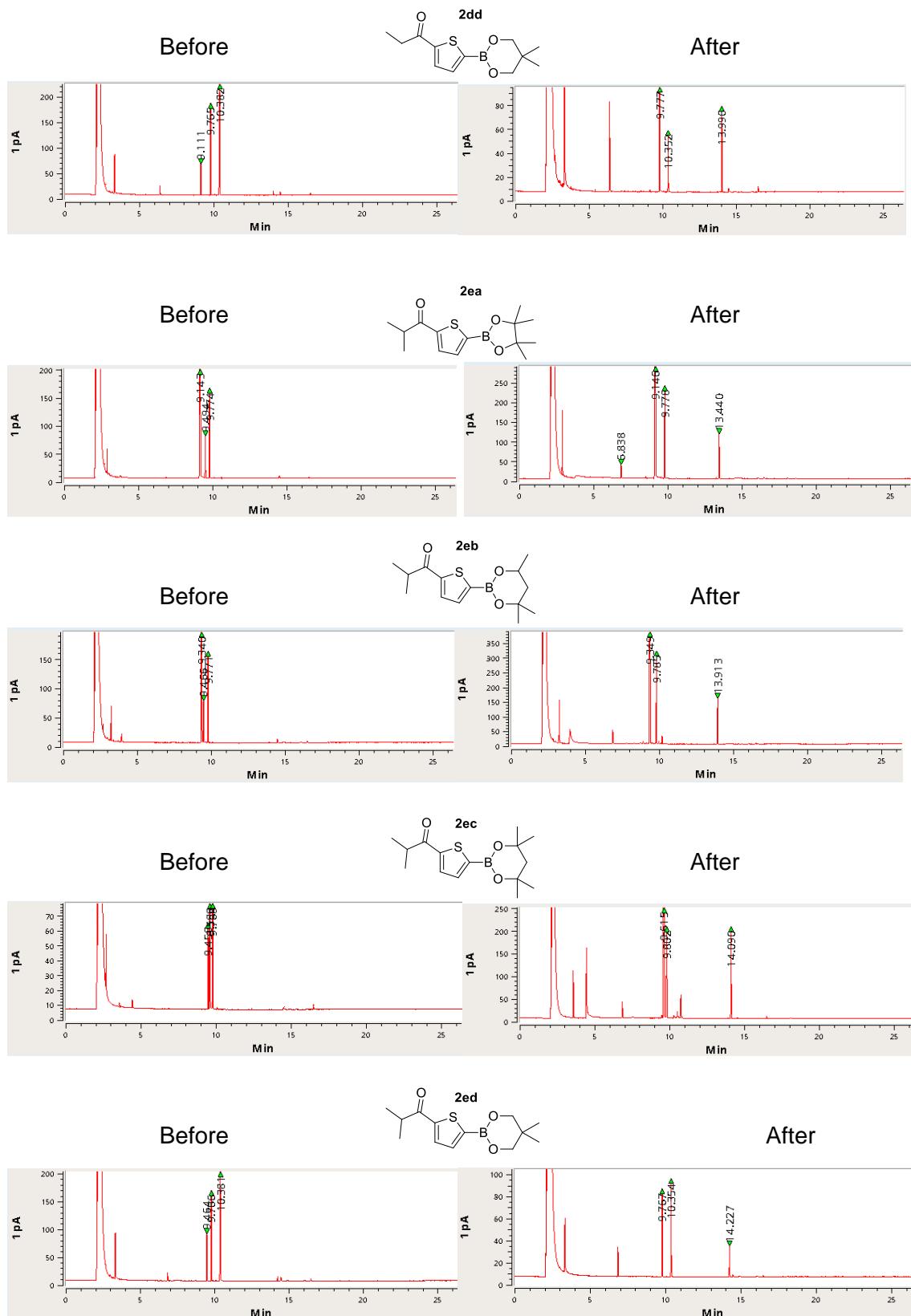
## GC chromatograms

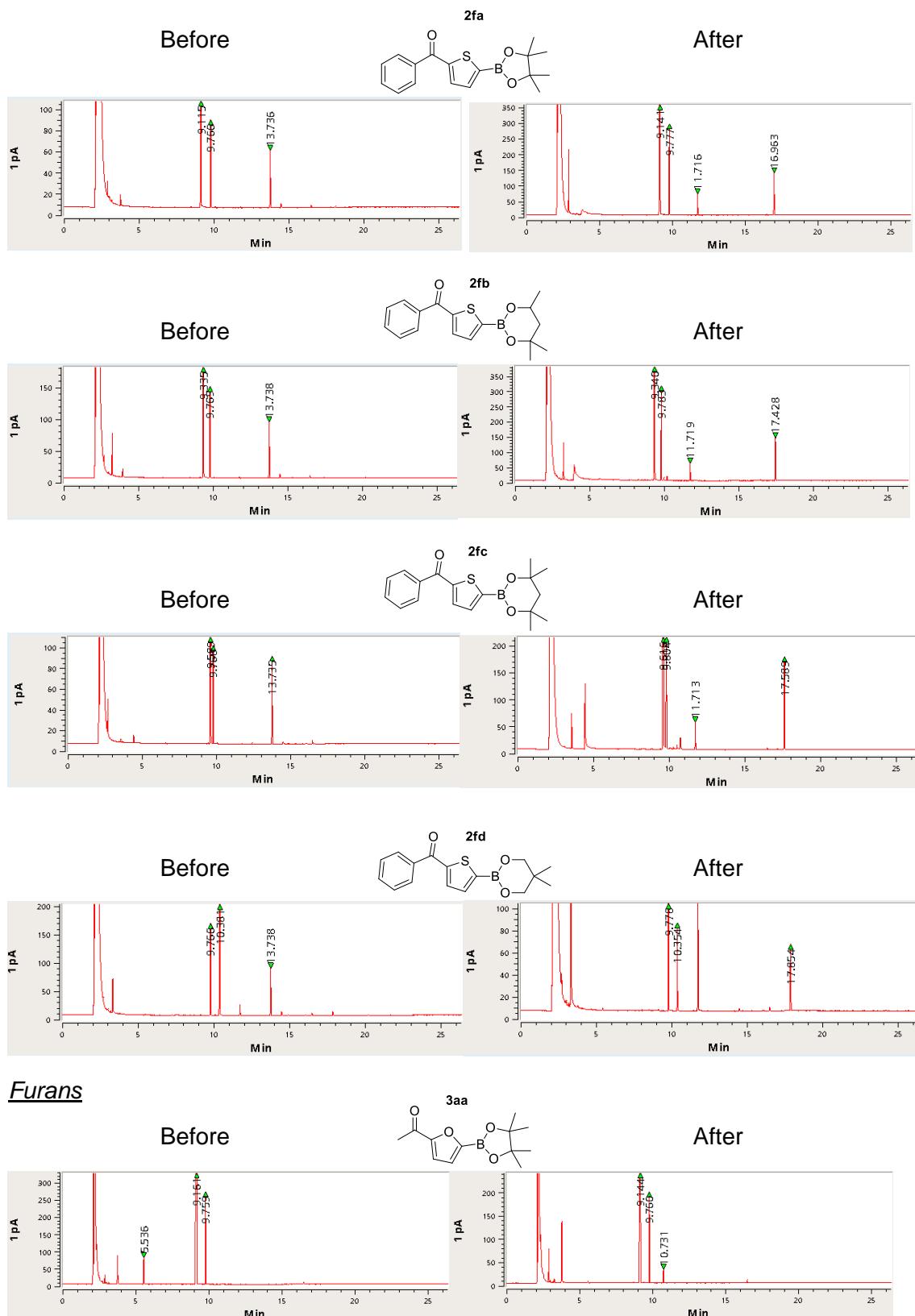
### Thiophenes

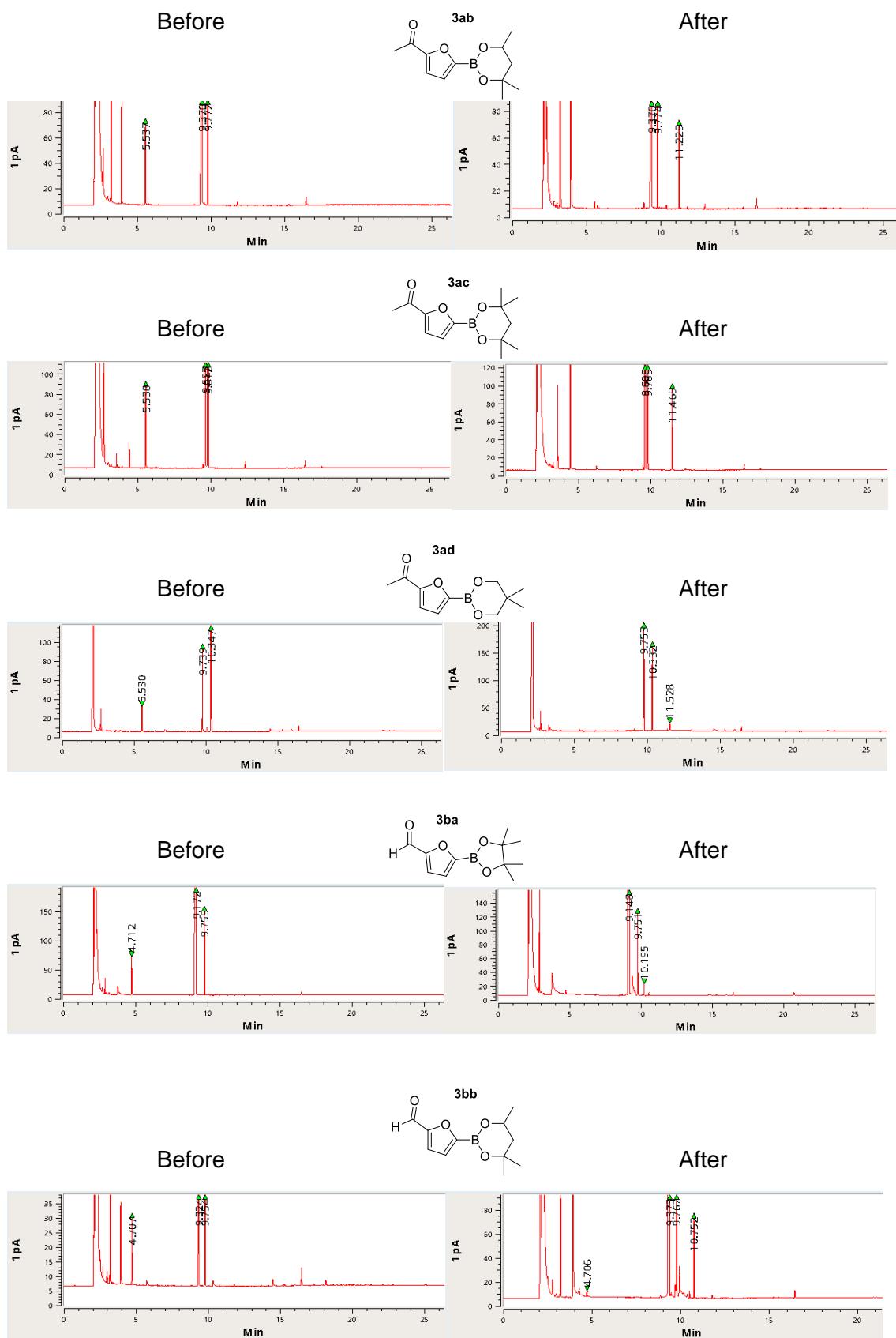


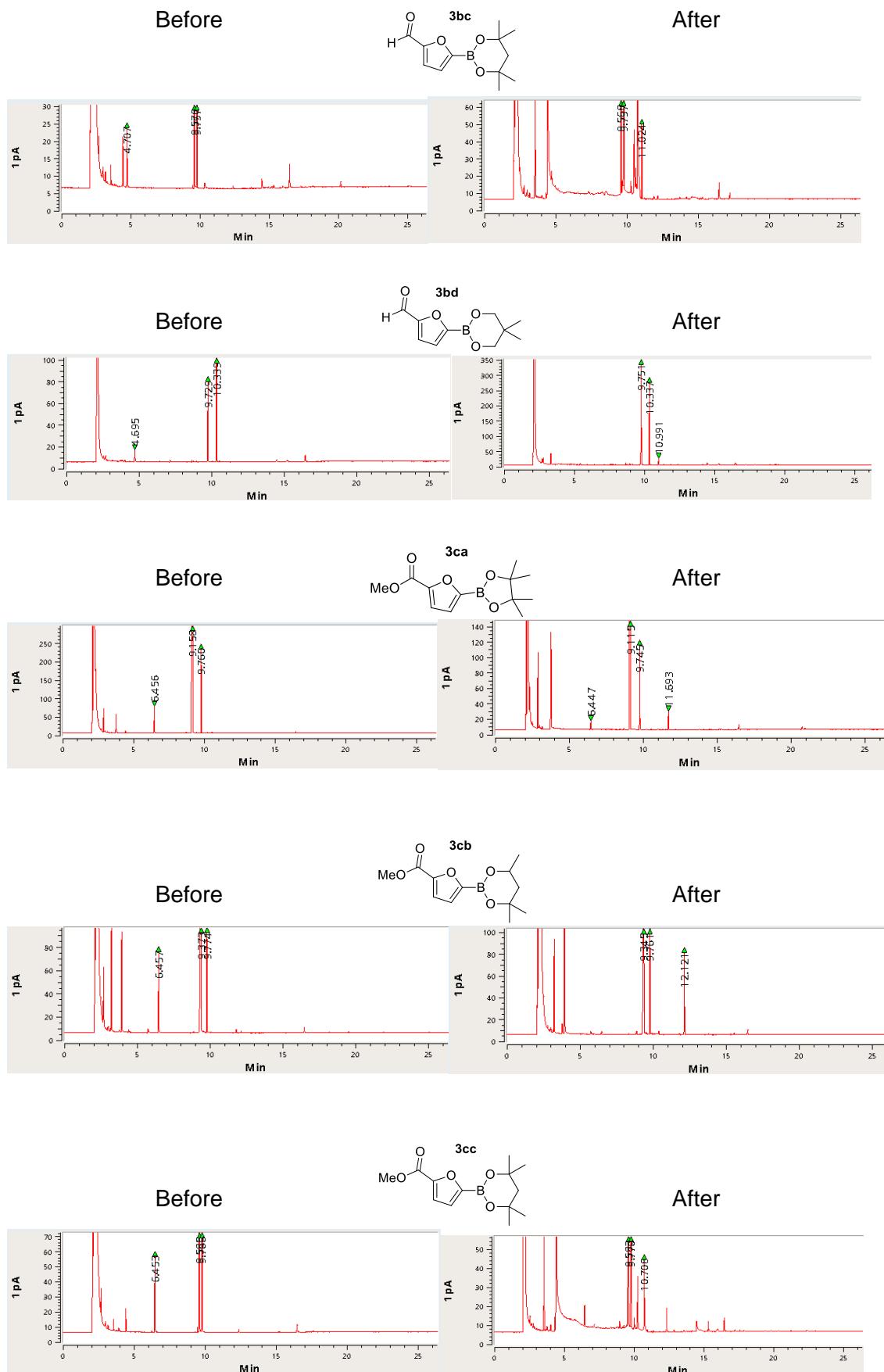


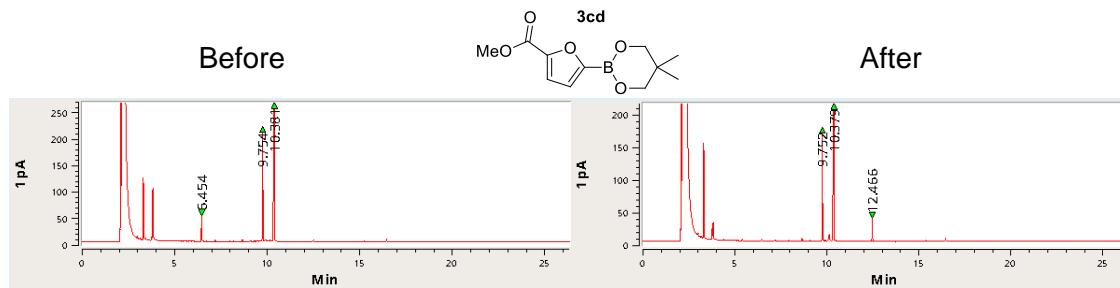




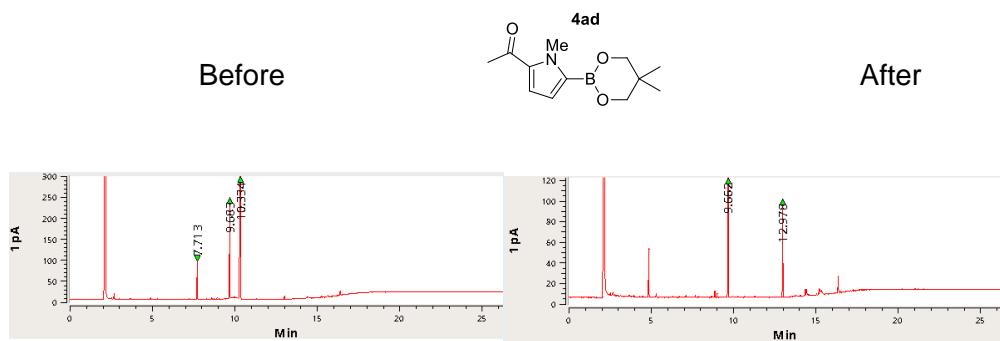
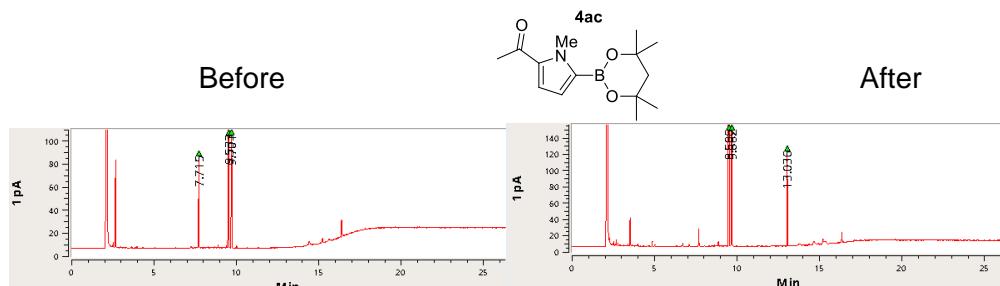
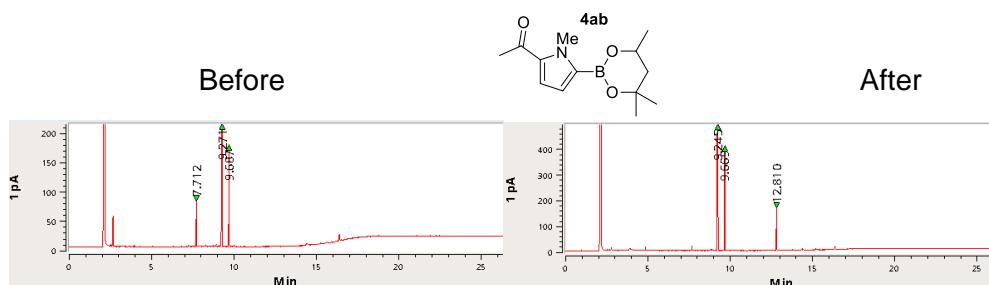
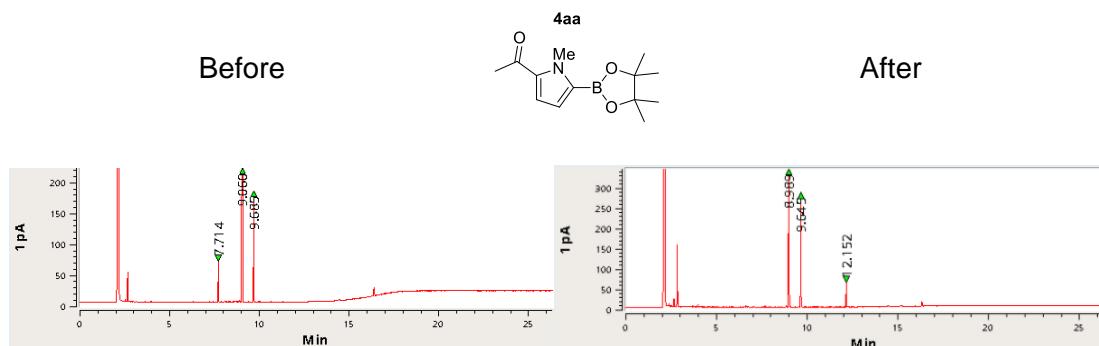


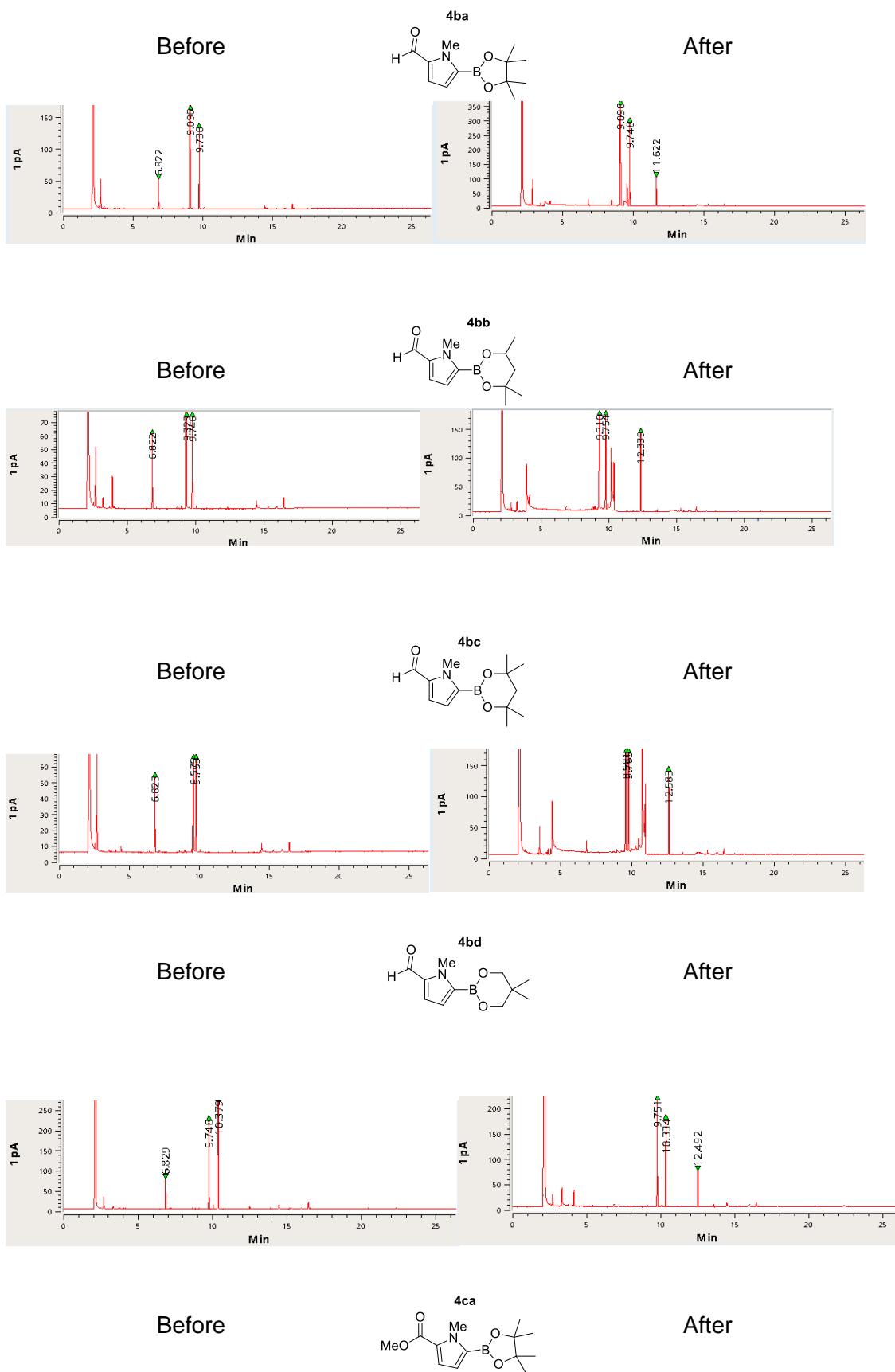


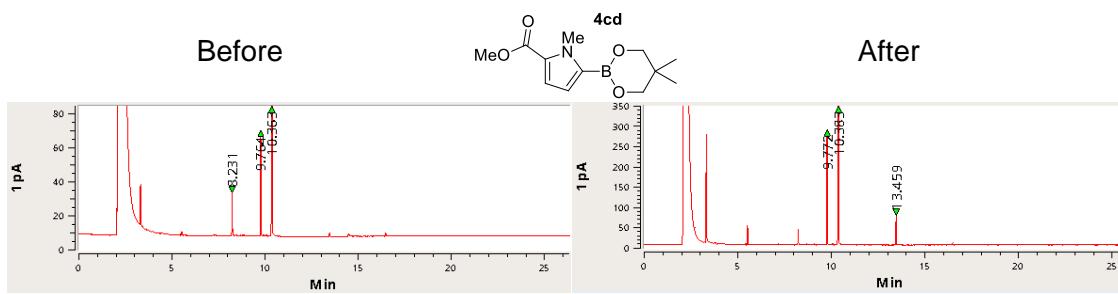
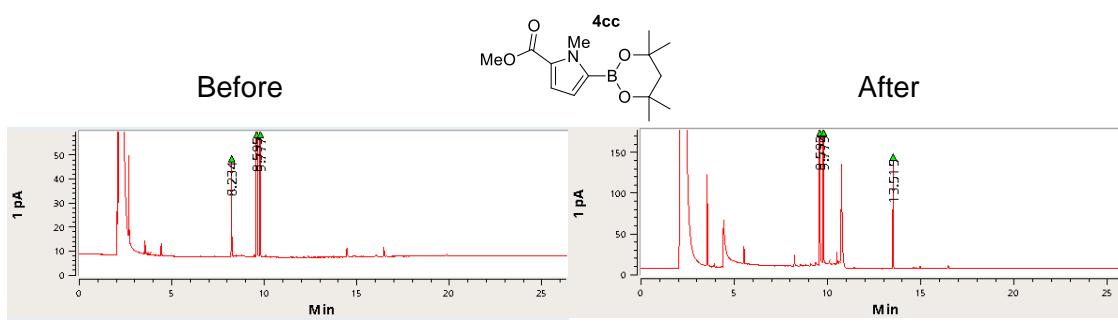
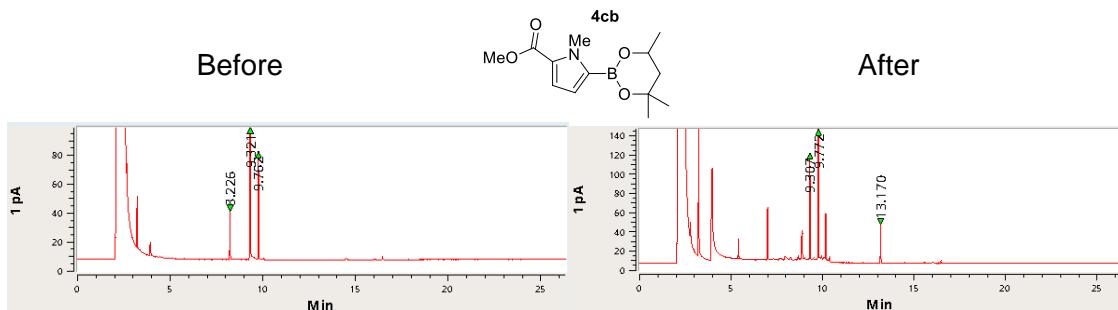
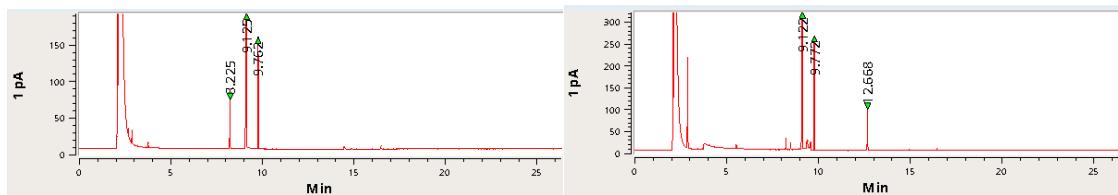




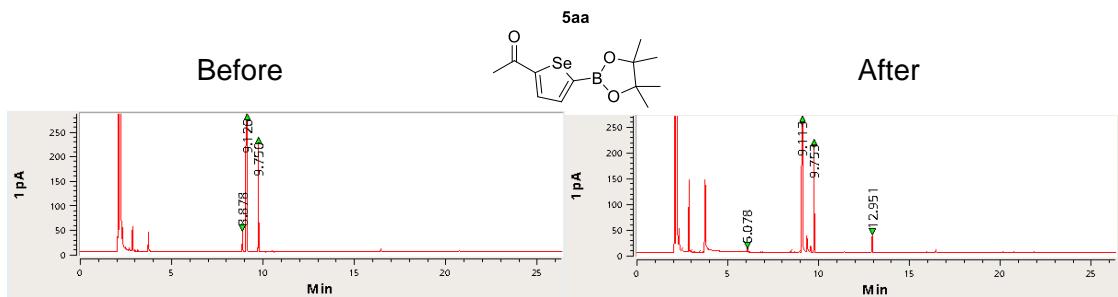
Pyrroles

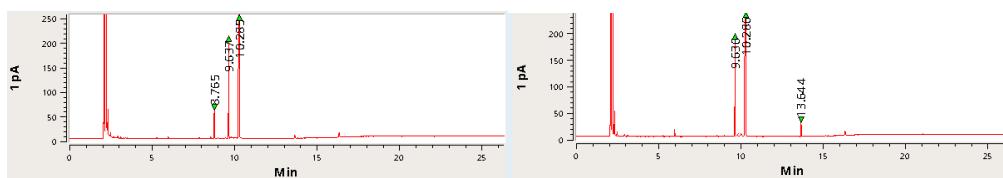
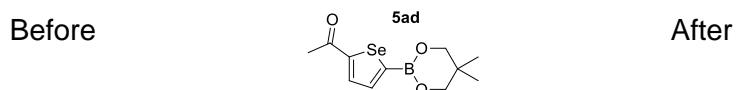
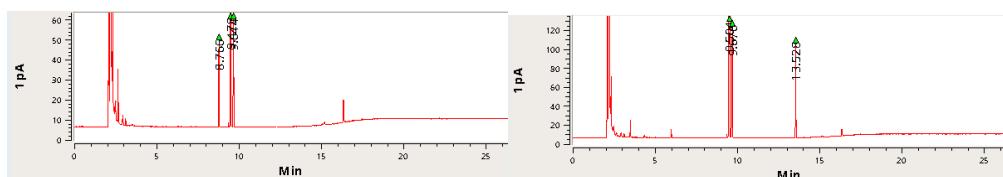
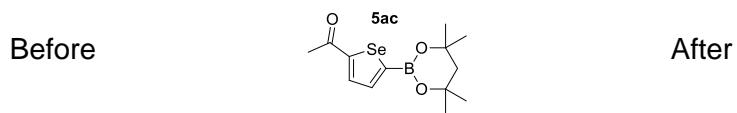
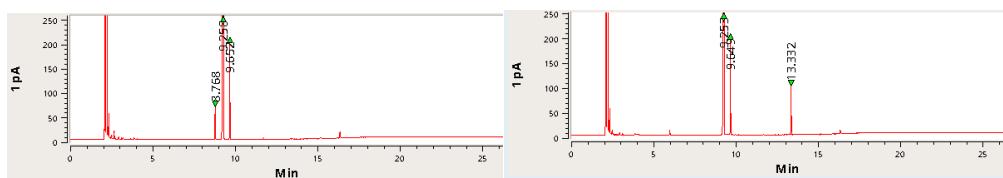
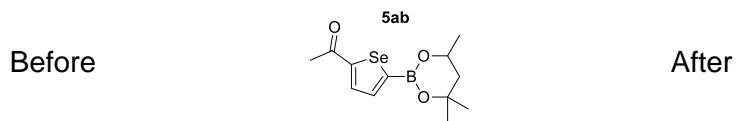






### Selenophenes

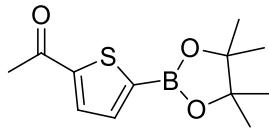




## Characterization of compounds

### THIOPHENES

#### **2aa. 1-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)ethenone**



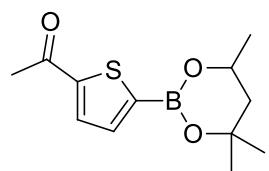
The compound (CAS 942070-32-8) was prepared according to the general procedure using 1-(5-chlorothiophen-2-yl)ethenone (3.2 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 2 hours, obtaining 72% product yield according to GC-FID analysis (63% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J$  = 3.7 Hz, 1H), 7.58 (d,  $J$  = 3.7 Hz, 1H), 2.57 (s, 3H), 1.35 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8 (C), 149.6 (C), 137.4 (CH), 132.8 (CH), 84.8 (C), 27.6 ( $\text{CH}_3$ ), 24.9 ( $\text{CH}_3$ ).

Spectral data were consistent with literature.<sup>1</sup>

#### **2ab. 1-(5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)ethenone**



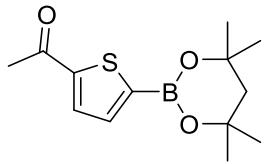
The compound (CAS 2414250-10-3) was prepared according to the general procedure using 1-(5-chlorothiophen-2-yl)ethenone (3.2 mg, 20  $\mu$ mol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 4 hours, obtaining 61% product yield according to GC-FID analysis (50% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J$  = 3.7 Hz, 1H), 7.43 (d,  $J$  = 3.7 Hz, 1H), 4.29 (ddd,  $J$  = 11.6, 6.1, 2.9 Hz, 1H), 2.50 (s, 3H), 1.82 (dd,  $J$  = 14.0, 2.9 Hz, 1H), 1.56 (dd,  $J$  = 13.9, 11.7 Hz, 1H), 1.31 (s, 6H), 1.28 (d,  $J$  = 6.2 Hz, 3H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8 (C), 148.2 (C), 135.5 (CH), 132.7 (CH), 72.1 (C), 65.8 (CH), 45.6 ( $\text{CH}_2$ ), 31.1 ( $\text{CH}_3$ ), 28.0 ( $\text{CH}_3$ ), 27.7 ( $\text{CH}_3$ ), 23.0 ( $\text{CH}_3$ ) ppm.

Spectral data were consistent with literature.<sup>1</sup>

#### **2ac. 1-(5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)ethenone**



The compound (CAS 2414250-15-8) was prepared according to the general procedure using 1-(5-chlorothiophen-2-yl)ethenone (3.2 mg, 20  $\mu$ mol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 63% product yield according to GC-FID analysis (50% isolated yield as white powder).

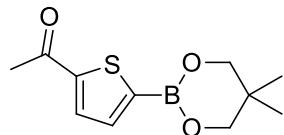
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J$  = 3.7 Hz, 1H), 7.50 (d,  $J$  = 3.7 Hz, 1H), 2.55 (s, 3H), 1.92 (s, 2H), 1.41 (s, 12H) ppm.

<sup>1</sup> J. C. Herrera-Luna, D. Sampedro, M. C. Jiménez and R. Pérez-Ruiz, *Organic Letters*, 2020, **22**, 3273-3278.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.0 (C), 148.3 (C), 135.5 (CH), 132.8 (CH), 71.9 (C), 49.1 (CH<sub>2</sub>), 31.8 (CH<sub>3</sub>), 27.5 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

#### 2ad. 1-(5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)ethenone



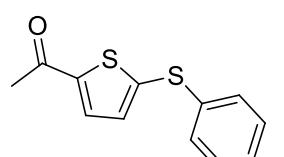
The compound (CAS 2414250-20-5) was prepared according to the general procedure using 1-(5-chlorothiophen-2-yl)ethenone (3.2 mg, 20 μmol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 50% product yield according to GC-FID analysis (45% isolated yield as white powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 3.7 Hz, 1H), 7.50 (d, *J* = 3.7 Hz, 1H), 3.75 (s, 4H), 2.55 (s, 3H), 1.01 (s, 6H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 190.9 (C), 148.7 (C), 135.9 (CH), 132.9 (CH), 73.1 (CH<sub>2</sub>), 32.1 (C), 27.5 (CH<sub>3</sub>), 21.9 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

#### 1-(5-(phenylthio)thiophen-2-yl)ethenone



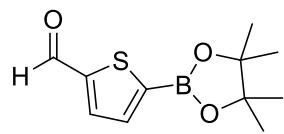
The compound (CAS: 90680-26-5) was prepared according to the general procedure using 1-(5-chlorothiophen-2-yl)ethenone (3.2 mg, 20 μmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 μmol, 10.0 equiv.), diphenyldisulfide (4.4 mg, 80 μmol, 1.0 equiv.) dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 3 hours, obtaining 78% product yield according to GC-FID analysis.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 3.9 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.36 – 7.28 (m, 3H), 7.10 (d, *J* = 3.9 Hz, 1H), 2.50 (s, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 190.0 (C), 146.3 (C), 145.7 (C), 135.2 (C), 132.8 (CH), 132.1 (CH), 130.9 (CH), 129.6 (CH), 128.2 (CH), 26.6 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

#### 2ba. 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbaldehyde



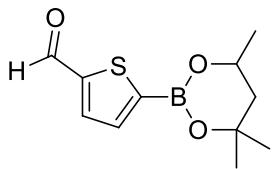
The compound (CAS 1040281-83-1) was prepared according to the general procedure using 5-bromothiophene-2-carbaldehyde (2.5 μL, 20 μmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 66% product yield according to GC-FID analysis (52% isolated yield as white powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.97 (s, 1H), 7.79 (d, *J* = 3.7 Hz, 1H), 7.65 (d, *J* = 3.7 Hz, 1H), 1.35 (s, 12H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 183.1 (C), 149.1 (C), 137.4 (CH), 136.2 (CH), 85.0 (C), 24.9 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

### 2bb. 5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)thiophene-2-carbaldehyde



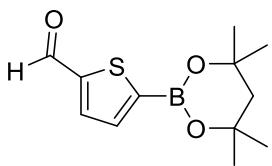
The compound (CAS 2414250-11-4) was prepared according to the general procedure using 5-bromothiophene-2-carbaldehyde (2.5  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 62% product yield according to GC-FID analysis (49% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.87 (s, 1H), 7.69 (d,  $J$  = 3.7 Hz, 1H), 7.49 (d,  $J$  = 3.7 Hz, 1H), 4.29 (ddd,  $J$  = 11.6, 6.1, 2.9 Hz, 1H), 1.82 (dd,  $J$  = 14.1, 2.9 Hz, 1H), 1.60 – 1.51 (m, 1H), 1.30 (s, 6H), 1.27 (d,  $J$  = 6.2 Hz, 3H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  183.1 (C), 147.8 (C), 136.2 (CH), 135.5 (CH), 71.9 (C), 65.7 (CH), 45.6 (CH<sub>2</sub>), 31.0 (CH<sub>3</sub>), 27.7 (CH<sub>3</sub>), 22.9 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

### 2bc. 5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)thiophene-2-carbaldehyde



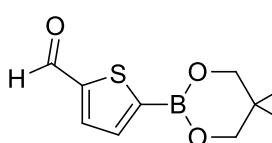
The compound (CAS 2414250-16-9) was prepared according to the general procedure using 5-bromothiophene-2-carbaldehyde (2.5  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), 4,4,4',4',6,6,6,6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 5 hours, obtaining 89% product yield according to GC-FID analysis (73% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.93 (s, 1H), 7.75 (d,  $J$  = 3.6 Hz, 1H), 7.57 (d,  $J$  = 3.6 Hz, 1H), 1.92 (s, 2H), 1.41 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  183.3 (C), 147.9 (C), 136.3 (CH), 135.5 (CH), 72.0 (C), 49.1 (CH<sub>2</sub>), 31.7 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

### 2bd. 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)thiophene-2-carbaldehyde



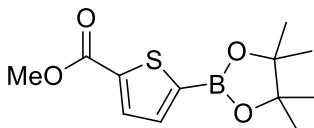
The compound (CAS 2414250-21-6) was prepared according to the general procedure using 5-bromothiophene-2-carbaldehyde (2.5  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 2 hours, obtaining 56% product yield according to GC-FID analysis (41% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.96 (s, 1H), 7.78 (d,  $J$  = 3.7 Hz, 1H), 7.59 (d,  $J$  = 3.7 Hz, 1H), 3.78 (s, 4H), 1.03 (s, 6H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  183.3 (C), 148.3 (C), 136.4 (CH), 136.0 (CH), 72.7 (CH<sub>2</sub>), 32.2 (C), 22.0 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

### 2ca. Methyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxylate



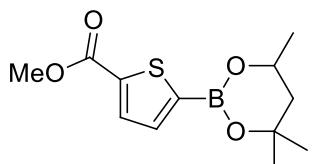
The compound (CAS 916138-13-1) was prepared according to the general procedure using methyl 5-bromothiophene-2-carboxylate (2.6  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 20 hours, obtaining 26% product yield according to GC-FID analysis (19% isolated yield as white powder).

Spectral data were consistent with literature.<sup>2</sup>

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J$  = 3.7 Hz, 1H), 7.54 (d,  $J$  = 3.6 Hz, 1H), 3.88 (s, 3H), 1.34 (s, 12H) ppm.

**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (C), 139.5 (C), 137.0 (CH), 134.1 (CH), 84.7 (C), 52.4 (O-CH<sub>3</sub>), 24.9 (CH<sub>3</sub>) ppm.

### 2cb. Methyl 5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)thiophene-2-carboxylate



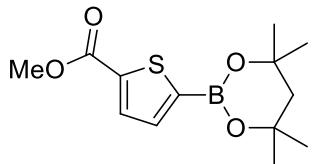
The compound was prepared according to the general procedure using methyl 5-bromothiophene-2-carboxylate (2.6  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 19 hours, obtaining 30% product yield according to GC-FID analysis (25% isolated yield as white powder).

**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J$  = 3.6 Hz, 1H), 7.47 (d,  $J$  = 3.6 Hz, 1H), 4.35 (ddd,  $J$  = 11.6, 6.0, 2.9 Hz, 1H), 3.87 (s, 3H), 1.87 (dd,  $J$  = 14.0, 2.9 Hz, 1H), 1.56 – 1.44 (m, 1H), 1.36 (s, 6H), 1.33 (d,  $J$  = 6.2 Hz, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1 (C), 138.0 (C), 135.2 (CH), 134.0 (CH), 72.0 (C), 65.7 (CH), 52.2 (O-CH<sub>3</sub>), 46.1 (CH<sub>2</sub>), 31.05 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>), 21.18 (CH<sub>3</sub>) ppm.

**GC-MS (EI):** m/z (relative intensity): 268.1 (40) [M+ $\bullet$ ], 253.1 (35), 237.1 (20), 169.0 (20), 137.0 (20), 43.1 (100).

### 2cc. Methyl 5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)thiophene-2-carboxylate



The compound was prepared according to the general procedure using methyl 5-bromothiophene-2-carboxylate (2.6  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 5 hours, obtaining 23% product yield according to GC-FID analysis (15% isolated yield as white powder).

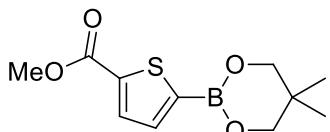
**<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J$  = 3.6 Hz, 1H), 7.48 (d,  $J$  = 3.6 Hz, 1H), 3.87 (s, 3H), 1.92 (s, 2H), 1.41 (s, 12H) ppm.

**<sup>13</sup>C NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.03 (C), 137.96 (C), 135.18 (CH), 134.00 (CH), 119.97 (C), 71.81 (C), 52.17 (O-CH<sub>3</sub>), 49.14 (CH<sub>2</sub>), 31.76 (CH<sub>3</sub>) ppm.

<sup>2</sup> Ghayoor A. Chotana, Venkata A. Kallepalli, Robert E. Maleczka Jr., Milton R. Smith III. *Tetrahedron* 2008, 64, 6103–6114.

**GC-MS (EI):** m/z (relative intensity): 282.1 (100) [M+•], 267.1 (100), 251.1 (30), 183.0 (50), 169.0 (50), 137.0 (60), 99.1 (40), 56.1 (80), 43.1 (80).

**2cd. Methyl 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)thiophene-2-carboxylatecarboxylate**



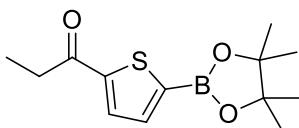
The compound was prepared according to the general procedure using methyl 5-bromothiophene-2-carboxylate (2.6  $\mu$ L, 80  $\mu$ mol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 5 hours, obtaining 24% product yield according to GC-FID analysis (16% isolated yield as rose-pale powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 3.6 Hz, 1H), 7.49 (d,  $J$  = 3.6 Hz, 1H), 3.88 (s, 3H), 3.76 (s, 4H), 1.03 (s, 6H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3 (C), 135.7 (C), 134.1 (CH), 129.2 (CH), 72.6 ( $\text{CH}_2$ ), 52.3 ( $\text{O-CH}_3$ ), 32.2 (C), 22.0 ( $\text{CH}_3$ ) ppm.

**GC-MS (EI):** m/z (relative intensity): 254.1 (40) [M+•], 223.1 (100), 136.9 (25), 111.0 (20), 70.1 (20), 61.0 (20), 43.1 (100).

**2da. 1-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)propan-1-one**



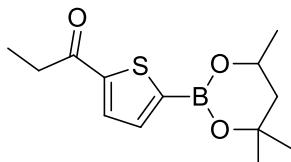
The compound (CAS 2414250-08-9) was prepared according to the general procedure using 1-(5-bromothiophen-2-yl)propan-1-one (4.4 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 74% product yield according to GC-FID analysis (62% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J$  = 3.7 Hz, 1H), 7.55 (d,  $J$  = 3.7 Hz, 1H), 2.92 (q,  $J$  = 7.3 Hz, 2H), 1.32 (s, 12H), 1.21 – 1.17 (t, 3H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.9 (C), 149.2 (C), 137.3 (CH), 132.0 (CH), 84.7 (C), 33.2 ( $\text{CH}_2$ ), 24.6 ( $\text{CH}_3$ ), 8.5 ( $\text{CH}_3$ ) ppm.

Spectral data were consistent with literature.<sup>1</sup>

**2db. 1-(5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)propan-1-one**



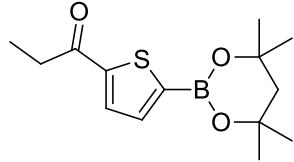
The compound (CAS 2414250-12-5) was prepared according to the general procedure using 1-(5-bromothiophen-2-yl)propan-1-one (4.4 mg, 20  $\mu$ mol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 81% product yield according to GC-FID analysis (69% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J$  = 3.7 Hz, 1H), 7.48 (d,  $J$  = 3.7 Hz, 1H), 4.33 (dqd,  $J$  = 12.4, 6.2, 2.9 Hz, 1H), 2.92 (q,  $J$  = 7.3 Hz, 2H), 1.86 (dd,  $J$  = 14.0, 2.9 Hz, 1H), 1.60 (dd,  $J$  = 13.9, 11.7 Hz, 1H), 1.35 (s, 6H), 1.32 (d,  $J$  = 6.2 Hz, 3H), 1.19 (t,  $J$  = 7.3 Hz, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.1 (C), 148.0 (C), 135.5 (CH), 132.0 (CH), 72.0 (C), 65.7 (CH), 46.1 (CH<sub>2</sub>), 33.1 (CH<sub>2</sub>), 31.2 (CH<sub>3</sub>), 28.1 (CH<sub>3</sub>), 8.6 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

#### 2dc. 1-(5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)propan-1-one



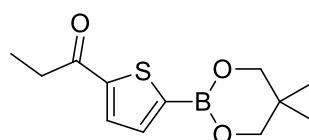
The compound (CAS 2414250-17-0) was prepared according to the general procedure using 1-(5-bromothiophen-2-yl)propan-1-one (4.4 mg, 20 µmol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 82% product yield according to GC-FID analysis (67% isolated yield as white powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 3.7 Hz, 1H), 7.51 (d, *J* = 3.7 Hz, 1H), 2.94 (d, *J* = 7.3 Hz, 2H), 1.93 (s, 2H), 1.42 (s, 12H), 1.22 (t, *J* = 7.3 Hz, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.2 (C), 147.9 (C), 135.5 (CH), 132.1 (CH), 71.9 (C), 49.2 (CH<sub>2</sub>), 33.2 (CH<sub>3</sub>), 8.7 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

#### 2dd. 1-(5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)propan-1-one



The compound (CAS 2414250-22-7) was prepared according to the general procedure using 1-(5-bromothiophen-2-yl)propan-1-one (4.4 mg, 20 µmol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 4 hours, obtaining 58% product yield according to GC-FID analysis (43% isolated yield as white powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 3.7 Hz, 1H), 7.51 (d, *J* = 3.7 Hz, 1H), 3.76 (s, 4H), 2.94 (q, *J* = 7.3 Hz, 2H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.03 (s, 6H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 194.1 (C), 148.4 (C), 135.9 (CH), 132.1 (CH), 72.6 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 32.2 (C), 22.0 (CH<sub>3</sub>), 8.6 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

#### 2ea. 2-methyl-1-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)propan-1-one



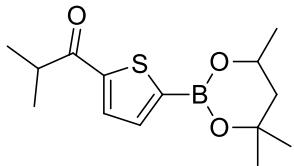
The compound (CAS 2414250-09-0) was prepared according to the general procedure using 1-(5-bromothiophen-2-yl)-2-methylpropan-1-one (3.2 µL, 20 µmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 77% product yield according to GC-FID analysis (61% isolated yield as white powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 3.7 Hz, 1H), 7.58 (d, *J* = 3.7 Hz, 1H), 3.36 (dp, *J* = 13.7, 6.8 Hz, 1H), 1.34 (s, 12H), 1.23 (t, *J* = 4.4 Hz, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 197.6 (C), 148.7 (C), 137.4 (CH), 132.2 (CH), 84.8 (C), 38.0 (CH), 24.9 (CH<sub>3</sub>), 19.5 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

**2eb. 2-methyl-1-(5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)propan-1-one**

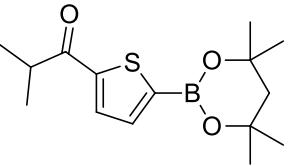


The compound (CAS 2414250-13-6) was prepared according to the general procedure using 1-(5-bromothiophen-2-yl)-2-methylpropan-1-one (3.2  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 78% product yield according to GC-FID analysis (66% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J$  = 3.7 Hz, 1H), 7.46 (d,  $J$  = 3.7 Hz, 1H), 4.30 (ddd,  $J$  = 11.6, 6.1, 2.9 Hz, 1H), 3.33 (dt,  $J$  = 13.7, 6.8 Hz, 1H), 1.83 (dd,  $J$  = 14.0, 2.9 Hz, 1H), 1.57 (dd,  $J$  = 13.9, 11.7 Hz, 1H), 1.32 (s, 6H), 1.29 (d,  $J$  = 6.2 Hz, 3H), 1.17 – 1.12 (m, 6H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.5 (C), 147.3 (C), 135.5 (CH), 132.0 (CH), 71.9 (C), 65.6 (CH), 46.0 (CH<sub>2</sub>), 37.7 (CH), 31.1 (CH<sub>3</sub>), 28.1 (CH<sub>3</sub>), 23.0 (CH<sub>3</sub>), 19.4 (CH<sub>3</sub>) ppm. Spectral data were consistent with literature.<sup>1</sup>

**2ec. 2-methyl-1-(5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)propan-1-one**

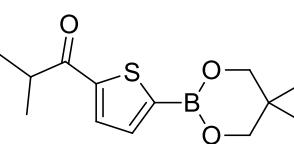


The compound (CAS 2414250-18-1) was prepared according to the general procedure using 1-(5-bromothiophen-2-yl)-2-methylpropan-1-one (3.2  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 82% product yield according to GC-FID analysis (66% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J$  = 3.7 Hz, 1H), 7.52 (d,  $J$  = 3.7 Hz, 1H), 3.38 (dt,  $J$  = 13.7, 6.8 Hz, 1H), 1.93 (s, 2H), 1.42 (s, 12H), 1.23 (d,  $J$  = 6.8 Hz, 6H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8 (C), 147.4 (C), 135.6 (CH), 132.2 (CH), 71.9 (C), 49.2 (CH<sub>2</sub>), 37.8 (CH), 31.8 (CH<sub>3</sub>), 19.6 (CH<sub>3</sub>) ppm. Spectral data were consistent with literature.<sup>1</sup>

**2ed. 1-(5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)-2-methylpropan-1-one**



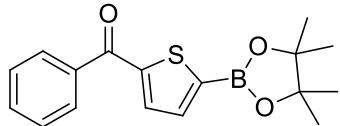
The compound (CAS 2414250-23-8) was prepared according to the general procedure using 1-(5-bromothiophen-2-yl)-2-methylpropan-1-one (3.2  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 2 hours, obtaining 54% product yield according to GC-FID analysis (40% isolated yield as white powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J$  = 3.7 Hz, 1H), 7.52 (d,  $J$  = 3.7 Hz, 1H), 3.77 (s, 4H), 3.43 – 3.25 (m, 1H), 1.23 (d,  $J$  = 6.8 Hz, 6H), 1.03 (s, 6H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 197.7 (C), 147.8 (C), 136.0 (CH), 132.3 (C), 72.6 (CH<sub>2</sub>), 37.9 (CH), 32.2 (C), 22.0 (CH<sub>3</sub>), 19.5 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

**2fa. Phenyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)methanone**



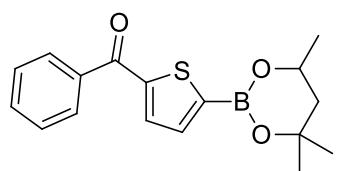
The compound (CAS 1220107-42-5) was prepared according to the general procedure using (5-bromothiophen-2-yl)(phenyl)methanone (5.5 mg, 20 μmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 68% product yield according to GC-FID analysis (51% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.84 (m, 2H), 7.70 (d, *J* = 3.7 Hz, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 1.35 (s, 12H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 188.8 (C), 148.6 (C), 138.4 (C), 137.1 (CH), 135.0 (CH), 132.5 (CH), 129.4 (2xCH), 128.5 (2xCH), 84.8 (C), 24.7 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

**2fb. Phenyl(5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)methanone**



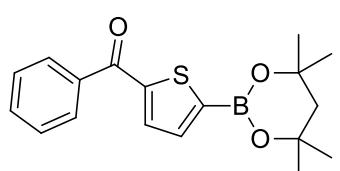
The compound (CAS 2414250-14-7) was prepared according to the general procedure using (5-bromothiophen-2-yl)(phenyl)methanone (5.5 mg, 20 μmol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 75% product yield according to GC-FID analysis (61% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 3.6 Hz, 1H), 7.49 (t, *J* = 7.1 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 4.35 – 4.21 (m, 1H), 1.81 (dd, *J* = 14.0, 2.7 Hz, 1H), 1.59 – 1.49 (m, 1H), 1.29 (s, 6H), 1.26 (d, *J* = 6.2 Hz, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 188.0 (C), 147.1 (C), 138.3 (CH), 135.2 (CH), 134.8 (CH), 132.1 (CH), 129.1 (2xCH), 128.2 (2xCH), 71.8 (C), 65.5 (CH), 45.6 (CH<sub>2</sub>), 31.0 (CH<sub>3</sub>), 27.6 (CH<sub>3</sub>), 22.9 (CH<sub>3</sub>) ppm.

Spectral data were consistent with literature.<sup>1</sup>

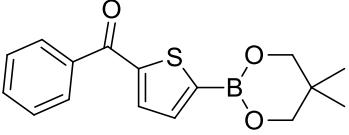
**2fc. Phenyl(5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)methanone**



The compound (CAS 2414250-19-2) was prepared according to the general procedure using (5-bromothiophen-2-yl)(phenyl)methanone (5.5 mg, 20 μmol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 81% product yield according to GC-FID analysis (70% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.84 (m, 2H), 7.67 (d, J = 3.7 Hz, 1H), 7.57 (dd, J = 12.3, 5.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 1.94 (s, 2H), 1.43 (s, 12H) ppm.  
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 188.5 (C), 147.3 (C), 138.7 (C), 135.3 (CH), 132.3 (CH), 129.4 (2xCH), 128.5 (2xCH), 71.9 (C), 49.2 (CH<sub>2</sub>), 31.8 (CH<sub>3</sub>) ppm.  
Spectral data were consistent with literature.<sup>1</sup>

#### 2fd. (5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)(phenyl)methanone

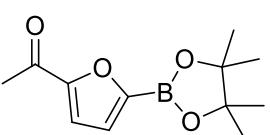
 The compound (CAS 2414250-24-9) was prepared according to the general procedure using (5-bromothiophen-2-yl)(phenyl)methanone (5.5 mg, 20 μmol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 2 hours, obtaining 42% product yield according to GC-FID analysis (35% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 7.4 Hz, 2H), 7.69 (d, J = 3.7 Hz, 1H), 7.57 (dd, J = 12.0, 5.5 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 3.78 (s, 4H), 1.04 (s, 6H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 188.4 (C), 147.7 (C), 138.5 (C), 135.7 (CH), 135.2 (CH), 132.4 (CH), 129.4 (CH), 128.5 (CH), 72.7 (CH<sub>2</sub>), 32.2 (C), 22.0 (CH<sub>3</sub>) ppm.  
Spectral data were consistent with literature.<sup>1</sup>

### FURANS

#### 3aa. 1-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-yl)ethanone

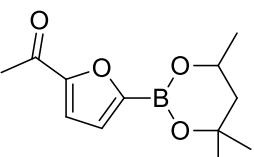
 The compound was prepared according to the general procedure using 1-(5-bromofuran-2-yl)ethanone (3.8 mg, 20 μmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 22 hours, obtaining 56% product yield according to GC-FID analysis (45% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.17 (d, J = 3.5 Hz, 1H), 7.09 (d, J = 3.5 Hz, 1H), 2.54 (s, 3H), 1.36 (s, J = 5.3 Hz, 12H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 188.6 (C), 163.2 (C), 124.5 (CH), 116.5 (CH), 84.9 (C), 26.6 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for C<sub>12</sub>H<sub>18</sub>BO<sub>4</sub>: 237.1293, found: 237.1297.

#### 3ab. 1-(5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)furan-2-yl)ethanone

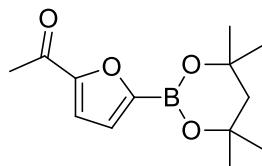
 The compound was prepared according to the general procedure using 1-(5-bromofuran-2-yl)ethanone (3.8 mg, 20 μmol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 6 hours, obtaining 85% product yield according to GC-FID analysis (63% isolated yield as white powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.14 (d, J = 3.5 Hz, 1H), 6.97 (d, J = 3.5 Hz, 1H), 4.36 (ddd, J = 11.6, 6.1, 2.9 Hz, 1H), 2.52 (s, 3H), 1.88 (dd, J = 14.1, 2.9 Hz, 1H), 1.65-1.59 (m, 1H), 1.37 (d, J = 2.4 Hz, 6H), 1.35 (d, J = 6.2 Hz, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 187.8 (C), 155.8 (C), 122.6 (CH), 117.0 (CH), 72.2 (C), 65.8 (CH), 46.2 (CH<sub>2</sub>), 31.2 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>), 23.1 (CH<sub>3</sub>) ppm.

**HRMS (EI):** m/z (M+H)<sup>+</sup> = calcd. for C<sub>12</sub>H<sub>17</sub>BO<sub>4</sub>: 236.0706, found: 236.0711.

### 3ac. 1-(5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)furan-2-yl)ethanone



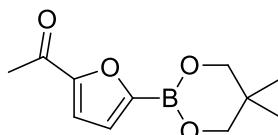
The compound was prepared according to the general procedure using 1-(5-bromofuran-2-yl)ethanone (3.8 mg, 80 μmol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 6 hours, obtaining 73% product yield according to GC-FID analysis (60% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.10 (d, J = 3.5 Hz, 1H), 6.93 (d, J = 3.5 Hz, 1H), 2.46 (s, 3H), 1.88 (s, 2H), 1.37 (s, 12H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 187.7 (C), 155.6 (C), 122.4 (CH), 117.0 (CH), 71.8 (C), 49.2 (CH<sub>2</sub>), 31.6 (CH<sub>3</sub>), 26.3 (CH<sub>3</sub>) ppm.

**GC-MS (EI):** m/z (relative intensity): 250.1 (20) [M+•], 235.1 (30), 251.1 (30), 151.1 (20), 137.0 (20), 70.1 (20), 61.1 (20), 56.1 (10), 43.1 (100).

### 3ad. 1-(5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)furan-2-yl)ethanone



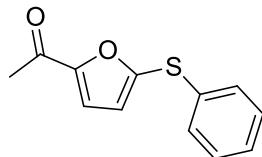
The compound was prepared according to the general procedure using 1-(5-bromofuran-2-yl)ethanone (3.8 mg, 80 μmol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200 μmol, 10.0 equiv.), dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 20 hours, obtaining 51% product yield according to GC-FID analysis (39% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.15 (d, J = 3.5 Hz, 1H), 7.00 (d, J = 3.5 Hz, 1H), 3.77 (s, 4H), 2.53 (s, 3H), 1.03 (s, 6H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 187.7 (C), 156.0 (C), 123.0 (CH), 116.8 (CH), 72.5 (C), 32.1 (CH<sub>2</sub>), 26.5 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>) ppm.

**HRMS (EI):** m/z (M+H)<sup>+</sup> = calcd. for C<sub>11</sub>H<sub>15</sub>BO<sub>4</sub>: 223.1117, found: 223.1125.

### 1-(5-(phenylthio)furan-2-yl)ethanone



The compound (CAS: 28569-36-0) was prepared according to the general procedure using 1-(5-bromofuran-2-yl)ethanone (3.8 mg, 80 μmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 μmol, 10.0 equiv.), diphenyldisulfide (4.4 mg, 80 μmol, 1.0 equiv.) dodecanenitrile (4.4 μL, 20 μmol, 1.0 equiv.) as internal standard and DIPEA (4.2 μL, 24 μmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 3 hours, obtaining 78% product yield according to GC-FID analysis (54% isolated yield as brown-yellow powder).

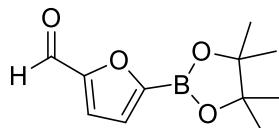
This compound is commercially available, and the spectral data were consistent with the commercial one. Please find this compound in Merck:

<https://www.sigmaaldrich.com/catalog/product/aldrich/t119652?lang=es&region=ES>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.31 (m, 5H), 7.17 (d, J = 3.5 Hz, 1H), 6.63 (d, J = 3.5 Hz, 1H), 2.45 (s, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 186.5 (C), 155.1 (C), 150.6 (C), 133.2 (C), 130.3 (CH), 129.6 (CH), 127.9 (CH), 118.6 (CH), 118.3 (CH), 26.1 (CH<sub>3</sub>) ppm.

### 3ba. 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-carbaldehyde

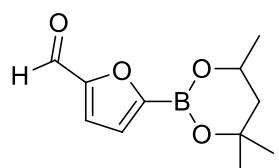


The compound (CAS 273731-82-1) was prepared according to the general procedure using 5-bromofuran-2-carbaldehyde (3.6 mg, 20 µmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 5 hours, obtaining 35% product yield according to GC-FID analysis (23% isolated yield as yellow-pale powder). Spectral data were consistent with literature.<sup>3</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.80 (s, 1H), 7.23 (d, J = 3.6 Hz, 1H), 7.13 (d, J = 3.6 Hz, 1H), 1.35 (s, 12H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 179.4 (C), 156.4 (C), 124.5 (CH), 118.5 (CH), 85.1 (C), 24.9 (CH<sub>3</sub>) ppm.

### 3bb. 5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)furan-2-carbaldehyde



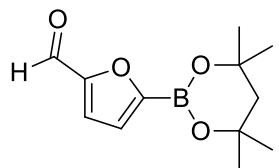
The compound (CAS 1603976-11-9) was prepared according to the general procedure using methyl 5-bromo-2-furaldehyde (3.6 mg, 80 µmol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 20 hours, obtaining 54% product yield according to GC-FID analysis (45% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.77 (s, 1H), 7.21 (d, J = 3.6 Hz, 1H), 7.03 (d, J = 3.5 Hz, 1H), 4.37 (m, J = 12.3, 6.2, 2.8 Hz, 1H), 1.90 (dd, J = 14.1, 2.9 Hz, 1H), 1.65 (d, J = 12.0 Hz, 1H), 1.39 (d, J = 2.9 Hz, 6H), 1.36 (d, J = 6.2 Hz, 3H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 179.4 (C), 155.8 (C), 122.6.1 (CH), 119.5 (CH), 72.4 (C), 65.9 (CH), 46.3 (CH<sub>2</sub>), 31.2 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>), 23.1 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for C<sub>11</sub>H<sub>16</sub>BO<sub>4</sub>: 223.1136, found: 223.1139.

### 3bc. 5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)furan-2-carbaldehyde



The compound was prepared according to the general procedure using methyl 5-bromo-2-furaldehyde (3.6 mg, 80 µmol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinanane) (56.4 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 20 hours, obtaining 66% product yield according to GC-FID analysis (58% isolated yield yellow-pale powder).

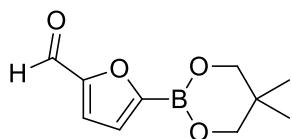
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.77 (s, 1H), 7.22 (d, J = 3.5 Hz, 1H), 7.04 (d, J = 3.5 Hz, 1H), 1.95 (s, 2H), 1.44 (s, 12H) ppm.

<sup>3</sup> Akitake Yamaguchi, Sherif J. Kaldas, Solomon D. Appavoo, Diego B. Diaz and Andrei K. Yudi. *Chem. Commun.*, 2019, 55, 10567-10570.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 179.4 (C), 155.8 (C), 126.7 (CH), 119.6 (CH), 72.1 (C), 49.3 (CH<sub>2</sub>), 31.8 (CH<sub>3</sub>) ppm.

HRMS (EI): m/z (M+H)<sup>+</sup> = calcd. for C<sub>12</sub>H<sub>17</sub>BO<sub>4</sub>: 237.1293, found: 237.1299.

### 3bd. 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)furan-2-carbaldehyde



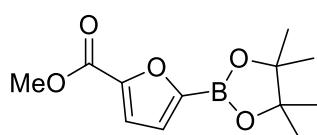
The compound (CAS 1218791-07-1) was prepared according to the general procedure using 5-bromofuran-2-carbaldehyde (3.6 mg, 80 µmol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 20 hours, obtaining 80% product yield according to GC-FID analysis (62% isolated yield as yellow-pale powder).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.78 (s, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.05 (d, J = 3.6 Hz, 1H), 3.78 (s, 4H), 1.03 (s, 6H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 179.2 (C), 156.0 (C), 123.0 (CH), 119.0 (CH), 72.6 (C), 32.3 (CH<sub>2</sub>), 22.0 (CH<sub>3</sub>) ppm.

HRMS (EI): m/z (M+H)<sup>+</sup> = calcd. for C<sub>10</sub>H<sub>14</sub>BO<sub>4</sub>: 209.0985, found: 209.0982.

### 3ca. Methyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-carboxylate



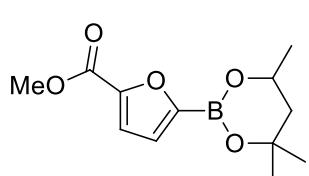
The compound (CAS 676501-87-4) was prepared according to the general procedure using methyl 5-bromofuran-2-carboxylate (4.1 mg, 20 µmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 22 hours, obtaining 60% product yield according to GC-FID analysis (51% isolated yield as yellow-pale powder).

Spectral data were consistent with literature.<sup>4</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 (dd, J = 13.5, 3.5 Hz, 1H), 7.07 (d, J = 3.5 Hz, 1H), 3.88 (s, 3H), 1.33 (s, 12H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.3 (C), 148.5 (C), 124.3 (C), 118.1 (C), 84.9 (C), 52.1 (O-CH<sub>3</sub>), 24.2 (CH<sub>3</sub>) ppm.

### 3cb. Methyl 5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)furan-2-carboxylate



The compound (CAS 1451144-93-6) was prepared according to the general procedure using methyl 5-bromofuran-2-carboxylate (4.1 mg, 80 µmol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 20 hours, obtaining 74% product yield according to GC-FID analysis (61% isolated yield as white powder).

Spectral data were consistent with literature.<sup>5</sup>

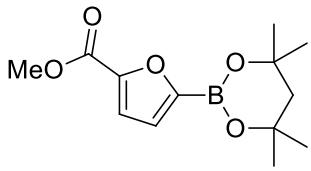
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.11 (d, J = 3.4 Hz, 1H), 6.92 (d, J = 3.4 Hz, 1H), 4.31 (dtd, J = 12.4, 6.2, 2.9 Hz, 1H), 3.85 (s, 3H), 1.84 (dd, J = 14.0, 2.9 Hz, 1H), 1.63 – 1.52 (m, 1H), 1.33 (d, J = 3.8 Hz, 6H), 1.31 (d, J = 6.2 Hz, 3H) ppm.

<sup>4</sup> Neely, Jamie M.; Bezdek, Mate J.; Chirik, Paul J. *ACS Central Science* **2016**, 2, (12), 935-942.

<sup>5</sup> Liskey, Carl W.; Hartwig, John F. *Synthesis* **2013**, 45(13), 1837-1842.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 159.4 (C), 147.5 (C), 122.0 (C), 118.0 (CH), 116.4 (CH), 72.0 (C), 65.7 (CH), 51.9 (O-CH<sub>3</sub>), 46.2 (CH<sub>2</sub>), 31.0 (CH<sub>3</sub>), 28.1 (CH<sub>3</sub>), 23.0 (CH<sub>3</sub>) ppm.

**3cc. Methyl 5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)furan-2-carboxylate**



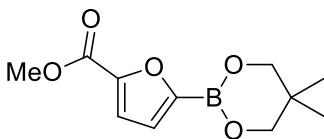
The compound was prepared according to the general procedure using methyl 5-bromofuran-2-carboxylate (4.1 mg, 80 µmol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 20 hours, obtaining 75% product yield according to GC-FID analysis (64% isolated yield as white powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.11 (d, J = 3.4 Hz, 1H), 6.93 (d, J = 3.4 Hz, 1H), 3.85 (s, 3H), 1.88 (s, 2H), 1.39 (s, 12H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 159.5 (C), 147.4 (C), 122.1 (CH), 118.1 (CH), 71.8 (C), 51.9 (O-CH<sub>3</sub>), 49.3 (CH<sub>2</sub>), 31.7 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for C<sub>13</sub>H<sub>20</sub>BO<sub>5</sub>: 267.1188, found: 267.1183.

**3cd. Methyl 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)furan-2-carboxylate**



The compound was prepared according to the general procedure using methyl 5-bromofuran-2-carboxylate (4.1 mg, 80 µmol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 20 hours, obtaining 72% product yield according to GC-FID analysis (60% isolated yield as white powder).

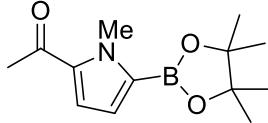
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.17 (d, J = 3.5 Hz, 1H), 6.98 (d, J = 3.5 Hz, 1H), 3.89 (s, 3H), 3.76 (s, 4H), 1.02 (s, 6H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 159.4 (C), 147.9 (C), 122.5 (CH), 118.2 (CH), 73.1 (C), 52.1 (O-CH<sub>3</sub>), 32.2 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for C<sub>11</sub>H<sub>15</sub>BO<sub>5</sub>: 239.1085, found: 239.1078.

**PYRROLES**

**4aa. 1-(1-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrol-2-yl)ethanone**



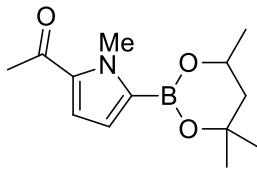
The compound was prepared according to the general procedure using 5-bromo-1-methyl-1H-pyrrole-2-carbaldehyde (4.0 mg, 20 µmol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200 µmol, 10.0 equiv.), dodecanenitrile (4.4 µL, 20 µmol, 1.0 equiv.) as internal standard and DIPEA (4.2 µL, 24 µmol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 22 hours, obtaining 91% product yield according to GC-FID analysis (72% isolated yield as yellow-pale powder).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.92 (d, J = 4.1 Hz, 1H), 6.70 (d, J = 4.0 Hz, 1H), 4.12 (s, 3H), 2.46 (s, 3H), 1.33 (s, 12H) ppm.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 189.6 (C), 168.7 (C), 120.3 (CH), 119.0 (CH), 84.0 (C), 36.7 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>), 24.9 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for C<sub>13</sub>H<sub>20</sub>BNO<sub>3</sub>: 250.1609, found: 250.1604.

**4ab. 1-(1-Methyl-5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1H-pyrrol-2-yl)ethanone**



The compound was prepared according to the general procedure using 5-bromo-1-methyl-1H-pyrrole-2-carbaldehyde (4.0 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L).

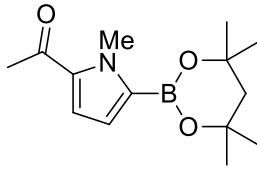
The reaction mixture was irradiated for 20 hours, obtaining 83% product yield according to GC-FID analysis (61% isolated yield as yellow powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.90 (d,  $J$  = 4.0 Hz, 1H), 6.63 (d,  $J$  = 4.0 Hz, 1H), 4.33 (m, 1H), 4.12 (s, 3H), 2.43 (s, 3H), 1.86 (dd,  $J$  = 14.0, 2.9 Hz, 1H), 1.57 (t,  $J$  = 13.9 Hz, 1H), 1.35 (s, 6H), 1.32 (d,  $J$  = 6.1 Hz, 3H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.4 (C), 165.7 (C), 119.1 (CH), 119.0 (CH), 71.8 (C), 65.5 (CH), 46.2 (CH<sub>2</sub>), 36.4 (CH<sub>3</sub>), 31.5 (CH<sub>3</sub>), 28.3 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>), 23.3 (CH<sub>3</sub>) ppm.

**GC-MS (EI):** m/z (relative intensity): 249.2 (30) [M+•], 234.1 (50), 134.1 (30), 70.1 (15), 61.0 (20), 56.1 (5), 43.1 (100).

**4ac. 1-(1-Methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1H-pyrrol-2-yl)ethanone**



The compound was prepared according to the general procedure using 5-bromo-1-methyl-1H-pyrrole-2-carbaldehyde (4.0 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L).

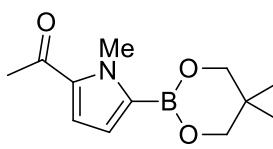
The reaction mixture was irradiated for 20 hours, obtaining 85% product yield according to GC-FID analysis (63% isolated yield as yellow-pale powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (d,  $J$  = 4.0 Hz, 1H), 6.64 (d,  $J$  = 4.0 Hz, 1H), 4.14 (s, 3H), 2.44 (s, 3H), 1.91 (s, 2H), 1.41 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.4 (C), 134.8 (C), 119.1 (CH), 119.0 (CH), 71.5 (C), 49.0 (CH<sub>2</sub>), 36.3 (CH<sub>3</sub>), 31.9 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>) ppm.

**GC-MS (EI):** m/z (relative intensity): 263.1 (5) [M+•], 248.1 (5), 149.0 (5), 88.1 (10), 70.1 (20), 61.1 (30), 43.0 (100).

**4ad. 1-(5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1H-pyrrol-2-yl)ethanone**



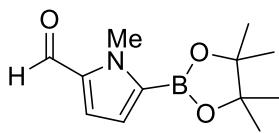
The compound was prepared according to the general procedure using 5-bromo-1-methyl-1H-pyrrole-2-carbaldehyde (4.0 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 20 hours, obtaining 65% product yield according to GC-FID analysis (44% isolated yield as yellow powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (d,  $J$  = 3.7 Hz, 1H), 6.64 (d,  $J$  = 3.8 Hz, 1H), 4.11 (s, 3H), 3.74 (s, 4H), 2.44 (s, 3H), 1.01 (s, 6H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.5 (C), 135.0 (C), 119.3 (CH), 119.1 (CH), 73.1 (C), 36.4 (CH<sub>3</sub>), 32.0 (CH<sub>2</sub>), 28.2 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>) ppm.

**GC-MS (EI):** m/z (relative intensity): 235.1 (15) [M+•], 220.1 (40), 192.0 (5), 148.9 (5), 134.0 (10), 105.9 (5), 88.0 (10), 70.0 (20), 61.0 (20), 52.9 (5), 43.1 (100).

**4ba. 1-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole-2-carbaldehyde**



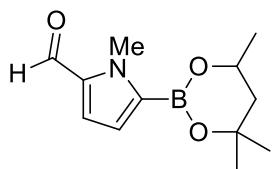
The compound was prepared according to the general procedure using 5-bromo-1-methyl-1H-pyrrole-2-carbaldehyde (3.8 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 20 hours, obtaining 72% product yield according to GC-FID analysis (56% isolated yield as reddish to black powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.56 (s, 1H), 6.81 (d,  $J$  = 4.0 Hz, 1H), 6.67 (d,  $J$  = 4.0 Hz, 1H), 4.05 (s, 3H), 1.25 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.3 (C), 136.0 (C), 123.1 (CH), 112.6 (CH), 84.0 (C), 36.5 ( $\text{CH}_3$ ), 24.0 ( $\text{CH}_3$ ) ppm.

**HRMS** (EI): m/z ( $\text{M}+\text{H}$ ) $^+$  = calcd. for  $\text{C}_{12}\text{H}_{18}\text{BNO}_3$ : 236.0725, found: 236.0713.

**4bb. 1-Methyl-5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1H-pyrrole-2-carbaldehyde**



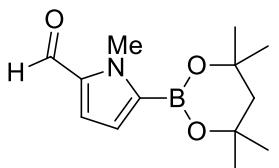
The compound was prepared according to the general procedure using 5-bromo-1-methyl-1H-pyrrole-2-carbaldehyde (3.8 mg, 80  $\mu$ mol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 14 hours, obtaining 81% product yield according to GC-FID analysis (65% isolated yield as reddish to black powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.61 (s, 1H), 6.86 (d,  $J$  = 4.0 Hz, 1H), 6.69 (d,  $J$  = 4.0 Hz, 1H), 4.34 (ddd,  $J$  = 11.6, 6.1, 2.9 Hz, 1H), 4.13 (s, 3H), 1.88 (dd,  $J$  = 14.0, 2.9 Hz, 1H), 1.60 (t,  $J$  = 12.7 Hz, 1H), 1.37 (s, 6H), 1.33 (d,  $J$  = 6.2 Hz, 3H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  180.3 (C), 135.9 (C), 123.5 (CH), 120.0 (CH), 109.7 (CH), 71.9 (C), 65.6 (CH), 46.1 ( $\text{CH}_2$ ), 35.5 ( $\text{CH}_3$ ), 31.3 ( $\text{CH}_3$ ), 28.3 ( $\text{CH}_3$ ), 23.2 ( $\text{CH}_3$ ) ppm.

**HRMS** (EI): m/z ( $\text{M}+\text{H}$ ) $^+$  = calcd. for  $\text{C}_{12}\text{H}_{18}\text{BNO}_3$ : 236.1453, found: 236.1445.

**4bc. 1-Methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1H-pyrrole-2-carbaldehyde**



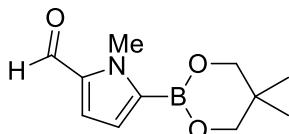
The compound was prepared according to the general procedure using 5-bromo-1-methyl-1H-pyrrole-2-carbaldehyde (3.8 mg, 80  $\mu$ mol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinan-2-yl) (56.4 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 20 hours, obtaining 74% product yield according to GC-FID analysis (59% isolated yield as reddish to black powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.59 (s, 1H), 6.85 (d,  $J$  = 4.0 Hz, 1H), 6.68 (d,  $J$  = 4.0 Hz, 1H), 4.13 (s, 3H), 1.91 (s, 2H), 1.40 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.7 (C), 135.8 (C), 123.4 (CH), 109.6 (CH), 71.6 (C), 49.0 ( $\text{CH}_2$ ), 35.5 ( $\text{CH}_3$ ), 31.8 ( $\text{CH}_3$ ) ppm.

**HRMS** (EI): m/z ( $\text{M}+\text{H}$ ) $^+$  = calcd. for  $\text{C}_{13}\text{H}_{20}\text{BNO}_3$ : 250.1609, found: 250.1604.

**4bd. 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1H-pyrrole-2-carbaldehyde**



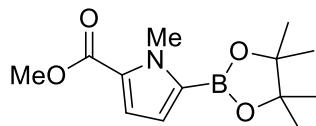
The compound was prepared according to the general procedure using 5-bromo-1-methyl-1H-pyrrole-2-carbaldehyde (3.8 mg, 80  $\mu$ mol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10 g/L). The reaction mixture was irradiated for 14 hours, obtaining 64% product yield according to GC-FID analysis (51% isolated yield reddish to black powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ) 9.59 (s, 1H), 6.85 (d,  $J$  = 4.0 Hz, 1H), 6.68 (d,  $J$  = 4.0 Hz, 1H), 4.11 (s, 3H), 3.73 (s, 4H), 1.00 (s, 6H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.7 (C), 132.2 (C), 124.3 (CH), 109.6 (CH), 73.0 (C), 36.4 (CH<sub>3</sub>), 32.1 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for  $\text{C}_{11}\text{H}_{16}\text{BNO}_3$ : 223.0944, found: 223.0956.

**4ca. Methyl 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole-2-carboxylate**



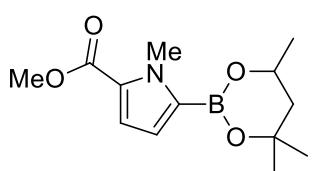
The compound (CAS 2377607-43-5) was prepared according to the general procedure using methyl 5-bromo-1-methyl-1H-pyrrole-2-carboxylate (4.4 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 18 hours, obtaining 69% product yield according to GC-FID analysis (55% isolated yield as yellow-pale oil).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (d,  $J$  = 4.0 Hz, 1H), 6.70 (d,  $J$  = 4.0 Hz, 1H), 4.13 (s, 3H), 3.81 (s, 3H), 1.32 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.91 (C), 127.49 (C), 120.41 (CH), 117.29 (CH), 83.85 (C), 51.27 (O-CH<sub>3</sub>), 35.92 (CH<sub>3</sub>), 24.92 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for  $\text{C}_{13}\text{H}_{21}\text{BNO}_4$ : 266.1559, found: 266.1564.

**4cb. Methyl 1-methyl-5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1H-pyrrole-2-carboxylate**



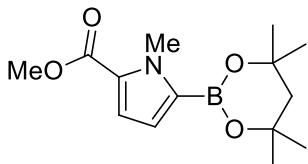
The compound was prepared according to the general procedure using methyl 5-bromo-1-methyl-1H-pyrrole-2-carboxylate (4.4 mg, 80  $\mu$ mol, 1.0 equiv.), bis(hexyleneglycolato)diboron (53.0 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 19 hours, obtaining 76% product yield according to GC-FID analysis (62% isolated yield as yellow-pale oil).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.89 (d,  $J$  = 3.9 Hz, 1H), 6.64 (d,  $J$  = 3.9 Hz, 1H), 4.32 (ddd,  $J$  = 11.7, 6.0, 3.0 Hz, 1H), 4.12 (s, 3H), 3.80 (s, 3H), 1.85 (dd,  $J$  = 13.9, 2.9 Hz, 1H), 1.63 – 1.52 (m, 1H), 1.36 (s, 6H), 1.32 (d,  $J$  = 6.2 Hz, 3H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1 (C), 126.7 (C), 119.1 (CH), 117.1 (CH), 71.6 (C), 65.4 (CH), 51.1 (O-CH<sub>3</sub>), 46.1 (CH<sub>2</sub>), 35.5 (CH<sub>3</sub>), 31.4 (CH<sub>3</sub>), 28.3 (CH<sub>3</sub>), 23.3 (CH<sub>3</sub>) ppm.

**GC-MS** (EI): m/z (relative intensity): 265.1 (60) [M+•], 233.9 (30), 206.8 (20), 166.0 (50), 152.0 (20), 134.1 (40), 108.0 (30), 72.1 (20), 43.1 (100).

**4cc. Methyl 1-methyl-5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)-1H-pyrrole-2-carboxylate**



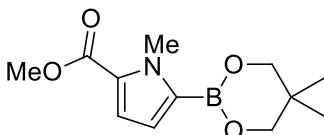
The compound was prepared according to the general procedure using methyl 5-bromo-1-methyl-1H-pyrrole-2-carboxylate (4.4 mg, 80  $\mu$ mol, 1.0 equiv.), 4,4,4',4',6,6,6',6'-octamethyl-2,2'-bi(1,3,2-dioxaborinane) (56.4 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 15 hours, obtaining 77% product yield according to GC-FID analysis (63% isolated yield as yellow-pale oil).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.89 (d,  $J$  = 3.9 Hz, 1H), 6.65 (d,  $J$  = 3.9 Hz, 1H), 4.14 (s, 3H), 3.80 (s, 3H), 1.91 (s, 2H), 1.41 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2 (C), 120.0 (C), 119.1 (CH), 117.1 (CH), 71.4 (C), 51.1 (O-CH<sub>3</sub>), 49.1 (CH<sub>2</sub>), 35.6 (CH<sub>3</sub>), 31.9 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for  $\text{C}_{14}\text{H}_{22}\text{BNO}_4$ : 280.1715, found: 280.1710.

**4cd. Methyl 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1H-pyrrole-2-carboxylate**



The compound was prepared according to the general procedure using methyl 5-bromo-1-methyl-1H-pyrrole-2-carboxylate (4.4 mg, 80  $\mu$ mol, 1.0 equiv.), bis(neopentylglycolato)diboron (45.2 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 19 hours, obtaining 44% product yield according to GC-FID analysis (36% isolated yield as yellow-pale oil).

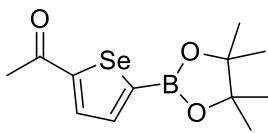
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.90 (d,  $J$  = 3.9 Hz, 1H), 6.65 (d,  $J$  = 3.9 Hz, 1H), 4.12 (s, 3H), 3.80 (s, 3H), 3.74 (s, 4H), 1.02 (s, 6H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1 (C), 119.4 (C), 117.2 (CH), 111.8 (CH), 73.1 (CH<sub>2</sub>), 51.2 (O-CH<sub>3</sub>), 35.8 (CH<sub>3</sub>), 32.1 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for  $\text{C}_{12}\text{H}_{19}\text{BNO}_4$ : 252.1402, found: 252.1406.

**SELENOPHENES**

**5aa. 1-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)selenophen-2-yl)ethenone**



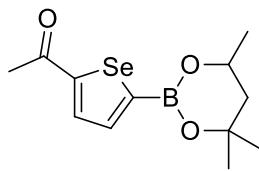
The compound was prepared according to the general procedure using 1-(5-bromoselenophen-2-yl)ethanone (5.0 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 16 hours, obtaining 84% product yield according to GC-FID analysis (70% isolated yield as yellow-brown powder).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J$  = 3.9 Hz, 1H), 7.90 (d,  $J$  = 3.9 Hz, 1H), 2.58 (s, 3H), 1.34 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2 (C), 156.8 (C), 140.0 (CH), 135.6 (CH), 84.8 (C), 26.9 (CH<sub>3</sub>), 24.9 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for  $\text{C}_{12}\text{H}_{17}\text{BO}_3\text{Se}$ : 301.0509, found: 301.0515.

**5ab. 1-(5-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)selenophen-2-yl)ethanone**



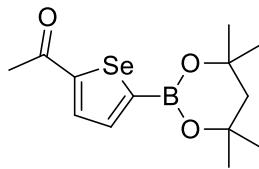
The compound was prepared according to the general procedure using 1-(5-bromoselenophen-2-yl)ethanone (5.0 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 16 hours, obtaining 86% product yield according to GC-FID analysis (73% isolated yield as yellow oil).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J$  = 3.8 Hz, 1H), 7.81 (d,  $J$  = 3.9 Hz, 1H), 4.34 (dtt,  $J$  = 12.2, 6.1, 3.1 Hz, 1H), 2.56 (s, 3H), 1.87 (dd,  $J$  = 14.0, 2.9 Hz, 1H), 1.67 – 1.56 (m, 1H), 1.36 (s, 6H), 1.33 (d,  $J$  = 6.2 Hz, 3H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.3 (C), 155.1 (C), 137.9 (CH), 135.7 (CH), 72.1 (C), 65.8 (CH), 46.1 (CH<sub>2</sub>), 31.2 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>), 26.8 (CH<sub>3</sub>), 23.2 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for  $\text{C}_{12}\text{H}_{17}\text{BO}_3\text{Se}$ : 301.0509, found: 301.0502.

**5ac. 1-(5-(4,4,6,6-tetramethyl-1,3,2-dioxaborinan-2-yl)selenophen-2-yl)ethanone**



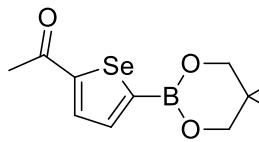
The compound was prepared according to the general procedure using 1-(5-bromoselenophen-2-yl)ethanone (5.0 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 16 hours, obtaining 88% product yield according to GC-FID analysis (69% isolated yield as yellow oil).

**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J$  = 3.9 Hz, 1H), 7.83 (d,  $J$  = 3.9 Hz, 1H), 2.57 (s, 3H), 1.92 (s, 2H), 1.42 (s, 12H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.3 (C), 155.0 (C), 137.8 (CH), 135.7 (CH), 71.9 (C), 49.1 (CH<sub>2</sub>), 31.8 (CH<sub>3</sub>), 26.8 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for  $\text{C}_{13}\text{H}_{19}\text{BO}_3\text{Se}$ : 315.0665, found: 315.0658.

**5ad. 1-(5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)selenophen-2-yl)ethanone**



The compound was prepared according to the general procedure using 1-(5-bromoselenophen-2-yl)ethanone (5.0 mg, 20  $\mu$ mol, 1.0 equiv.), bis(pinacolato)diboron (50.6 mg, 200  $\mu$ mol, 10.0 equiv.), dodecanenitrile (4.4  $\mu$ L, 20  $\mu$ mol, 1.0 equiv.) as internal standard and DIPEA (4.2  $\mu$ L, 24  $\mu$ mol, 1.2 equiv.) and G1 (10g/L). The reaction mixture was irradiated for 22 hours, obtaining 68% product yield according to GC-FID analysis (51% isolated yield as yellow oil).

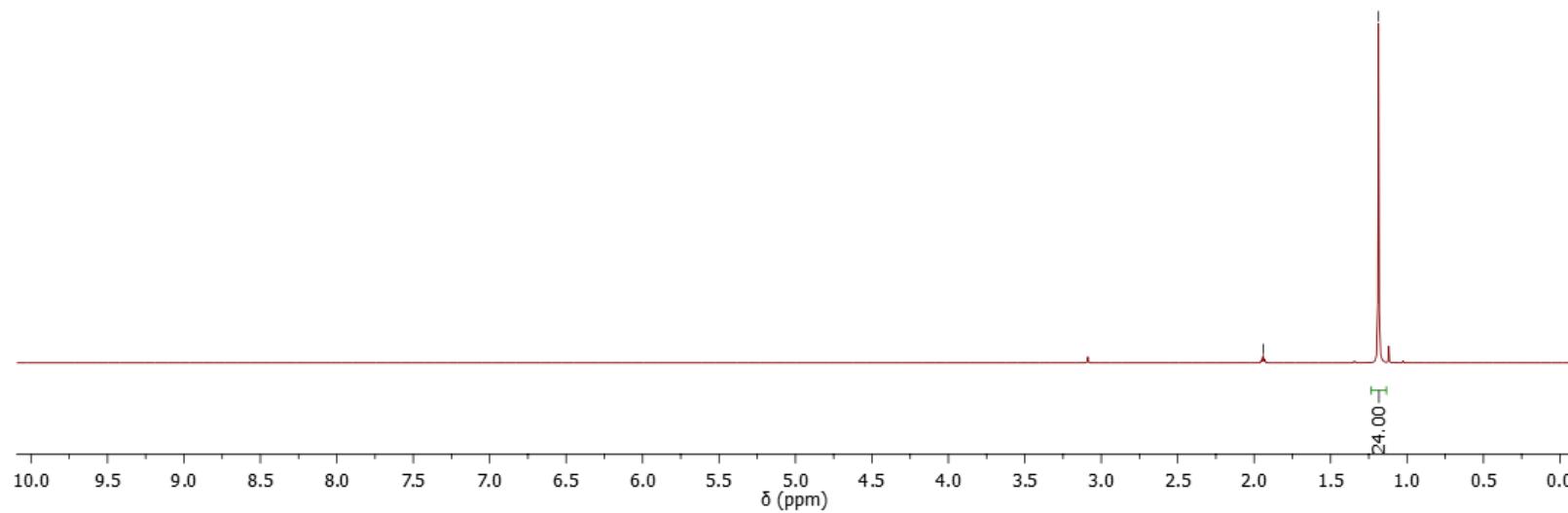
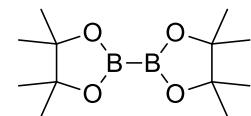
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J$  = 3.9 Hz, 1H), 7.84 (d,  $J$  = 3.9 Hz, 1H), 3.76 (s, 4H), 2.58 (s, 3H), 1.03 (s, 6H) ppm.

**$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.1 (C), 155.1 (C), 138.4 (CH), 135.8 (CH), 72.7 (C), 31.1 (CH<sub>2</sub>), 26.8 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>) ppm.

**HRMS** (EI): m/z (M+H)<sup>+</sup> = calcd. for  $\text{C}_{11}\text{H}_{15}\text{BO}_3\text{Se}$ : 285.0060, found: 285.2277.

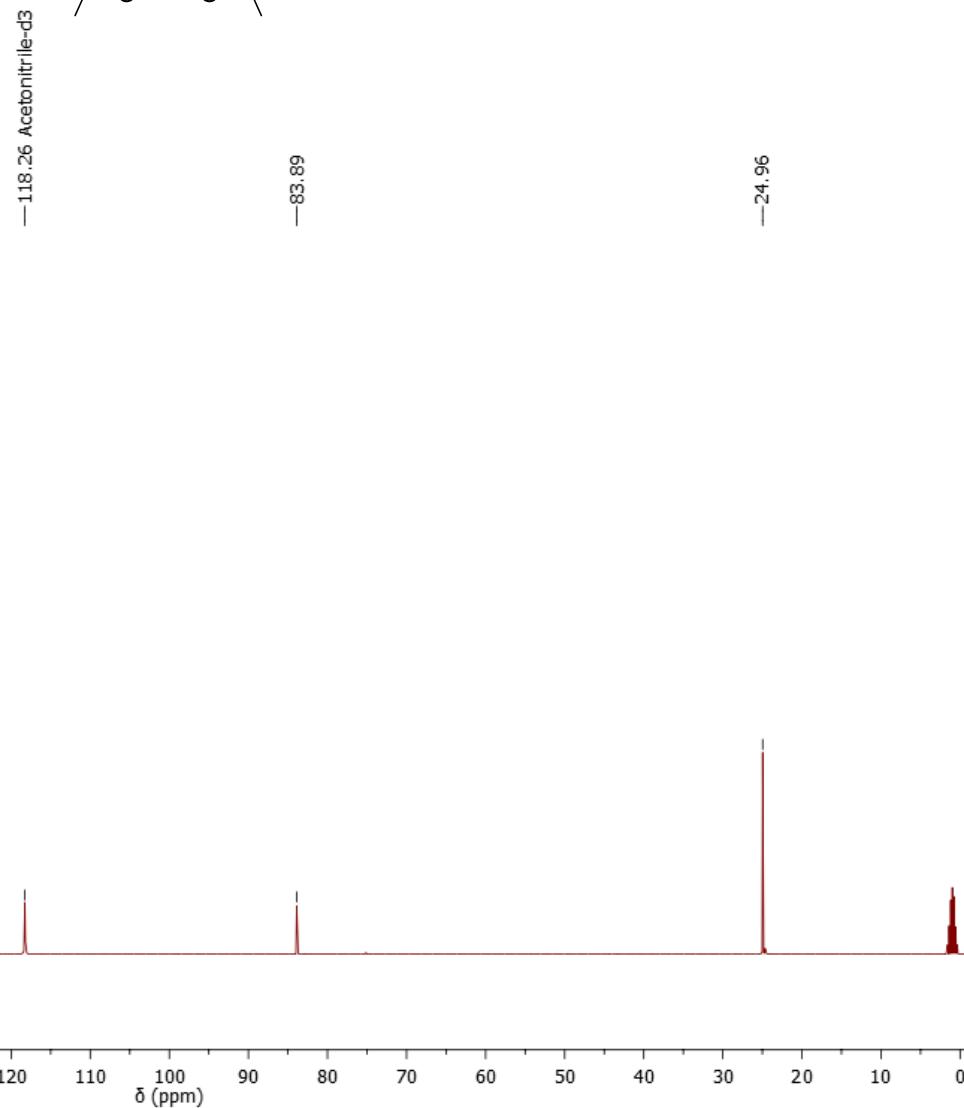
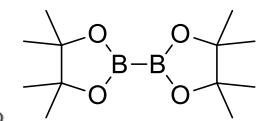
**NMR Spectra**

$^1\text{H}$  400MHz, ACN-d3



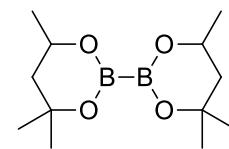
## Diboron esters

$^{13}\text{C}$  101MHz

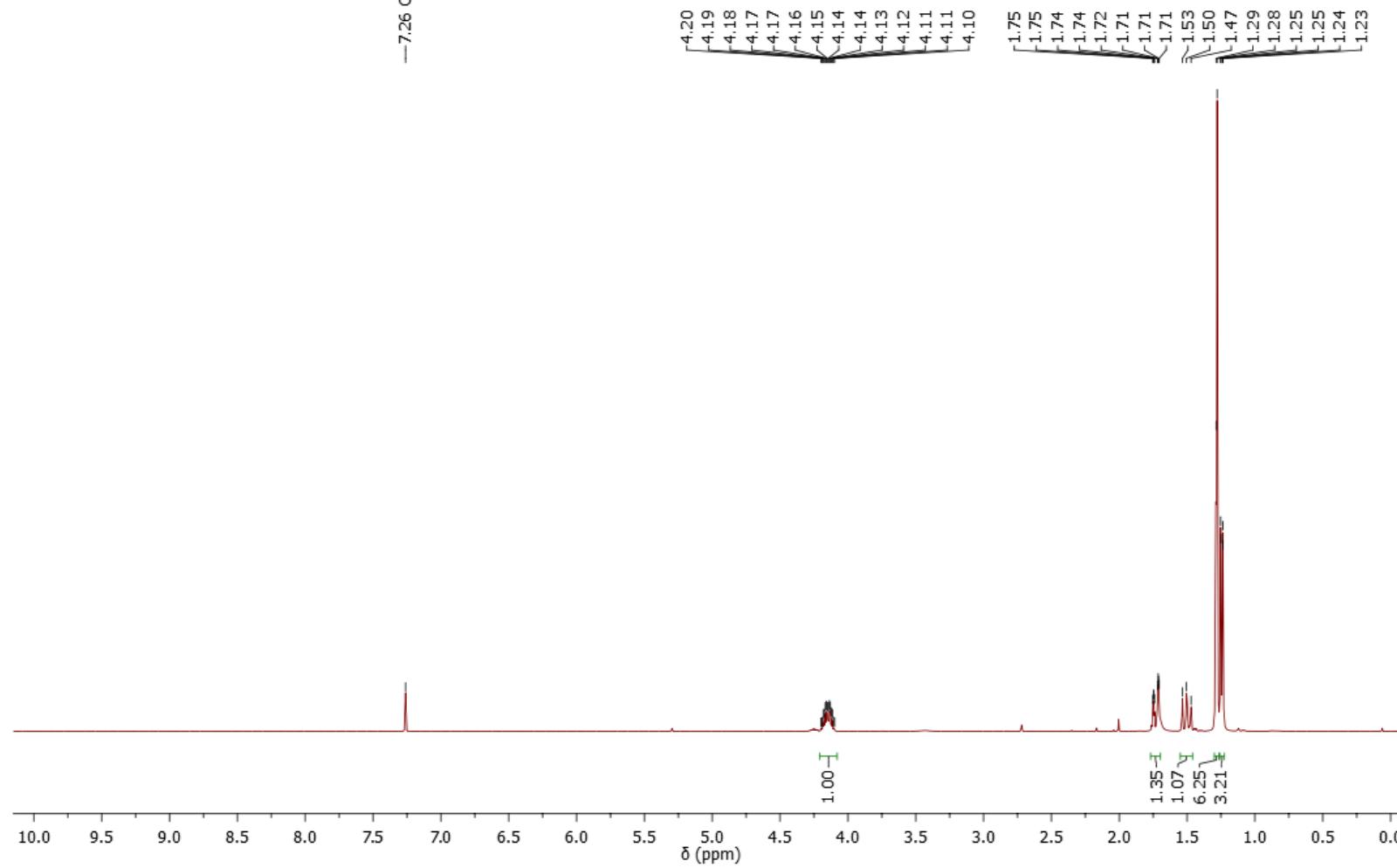


## Diboron esters

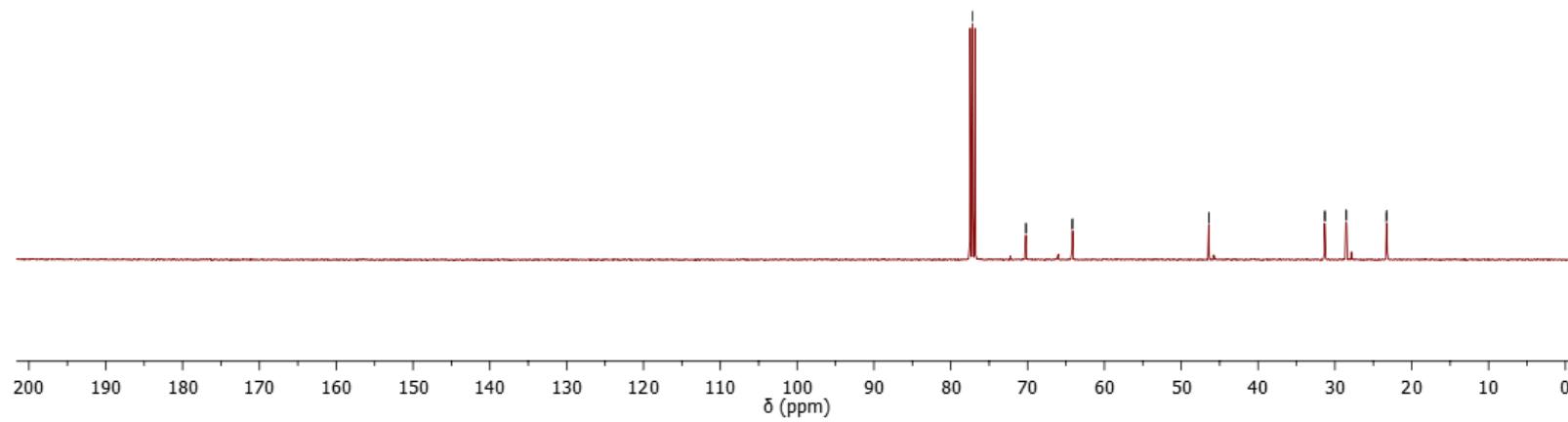
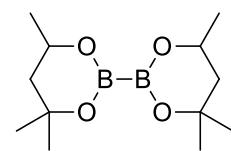
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



— 7.26 Chloroform-d

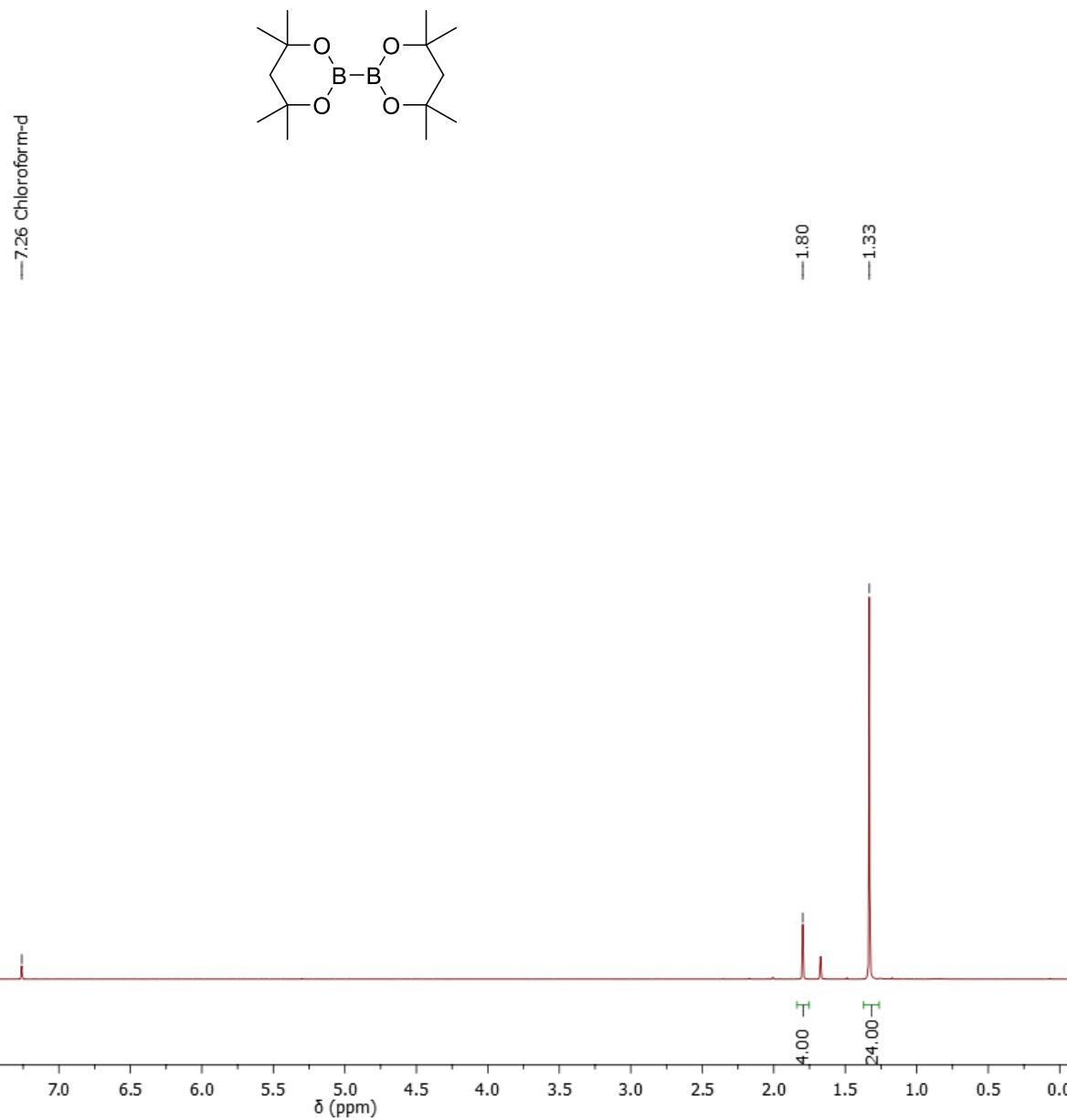


<sup>13</sup>C 101MHz



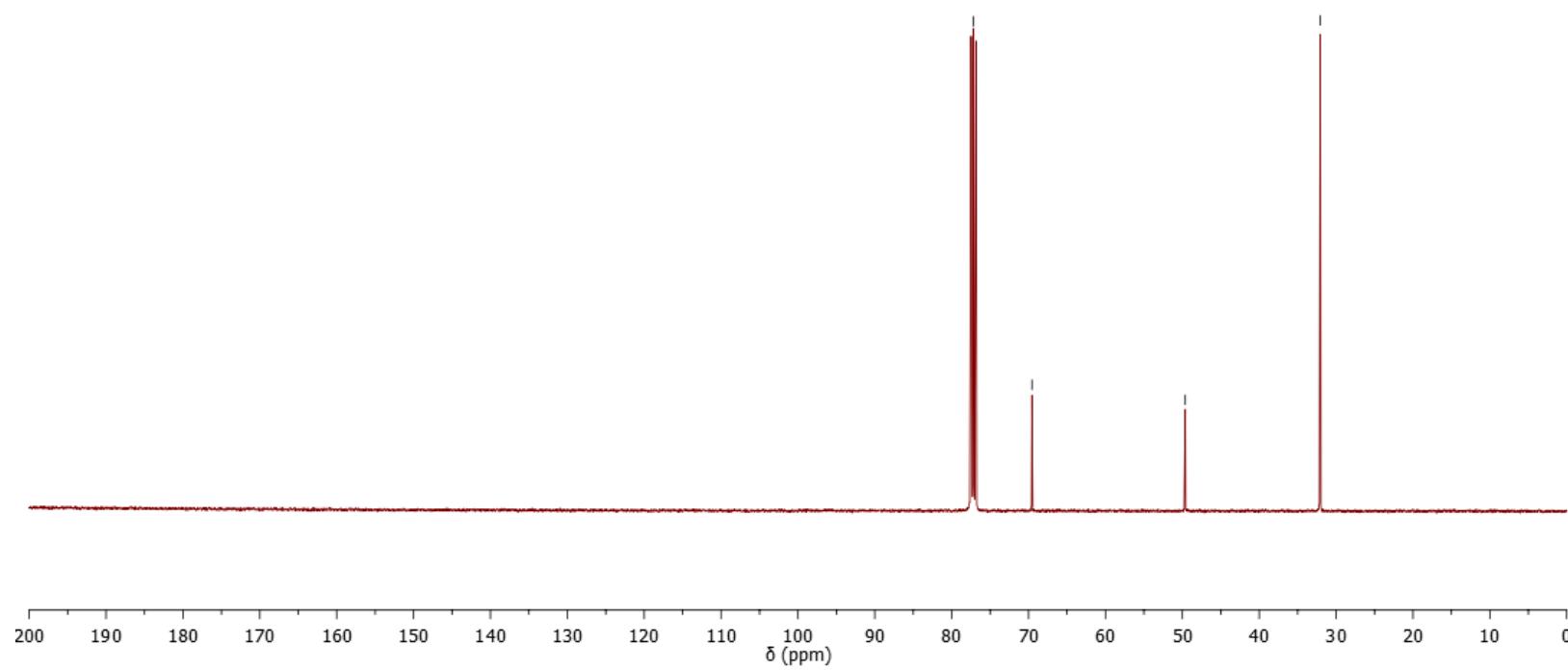
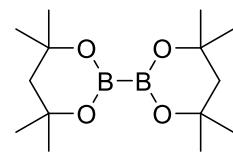
## Diboron esters

$^1\text{H}$  400MHz,  $\text{CDCl}_3$



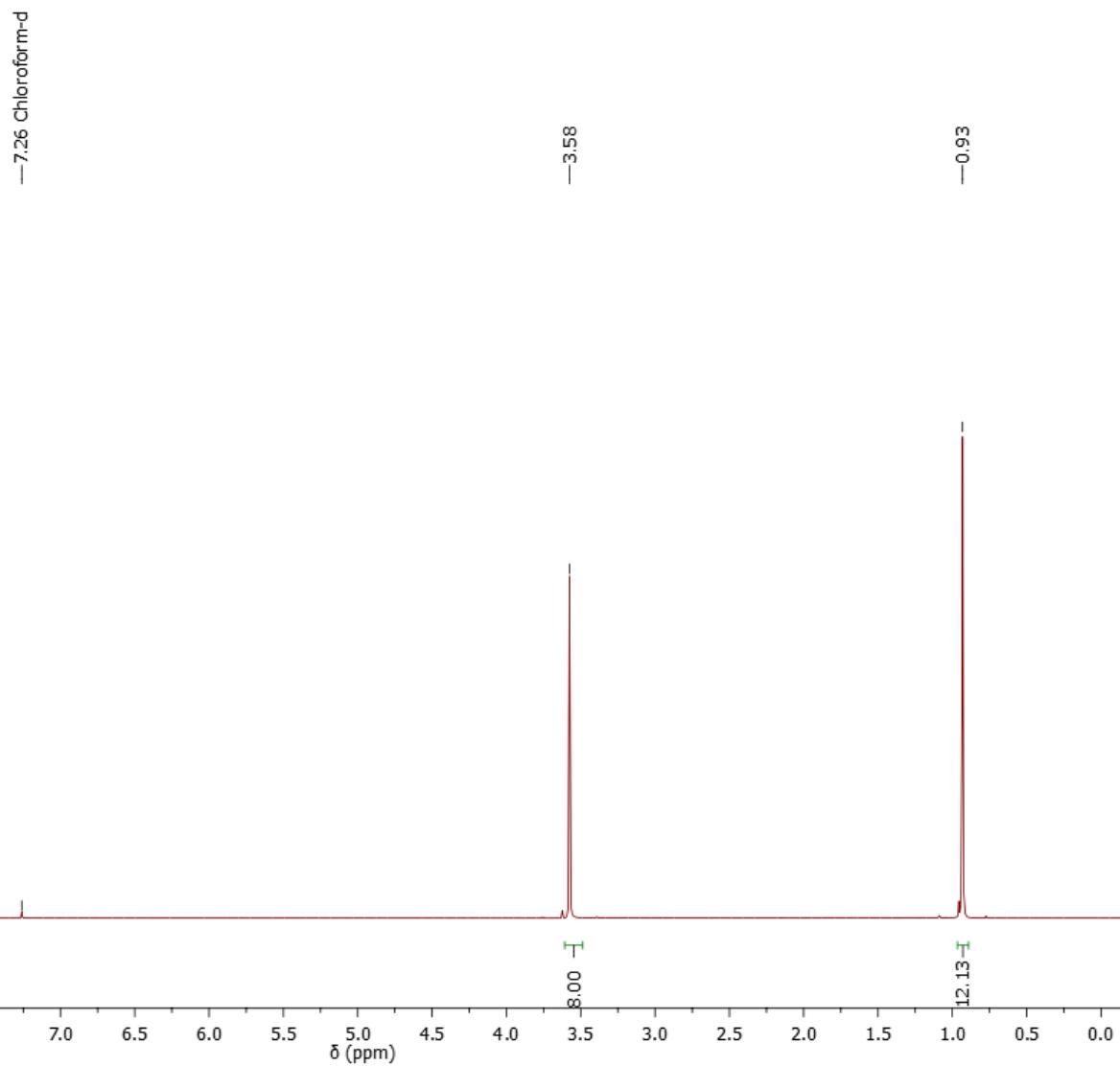
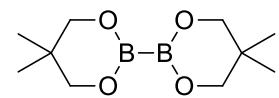
## Diboron esters

$^{13}\text{C}$  101MHz



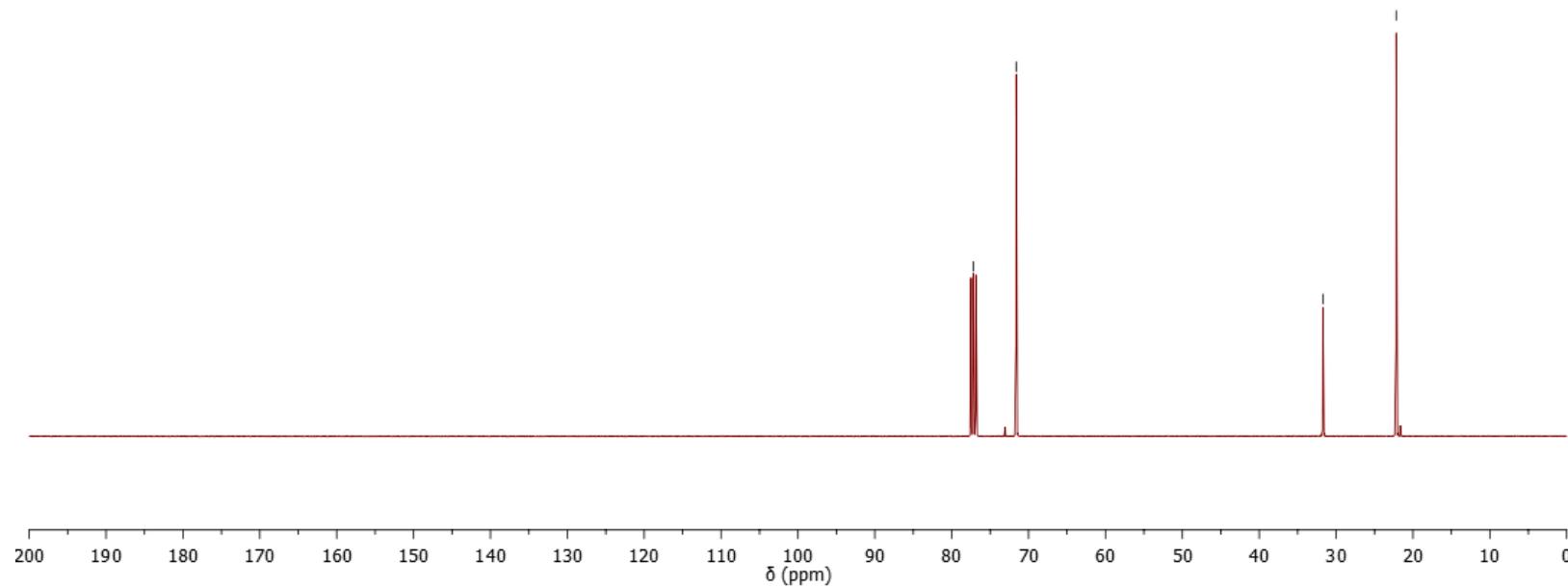
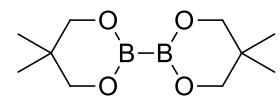
## Diboron esters

$^1\text{H}$  400MHz,  $\text{CDCl}_3$



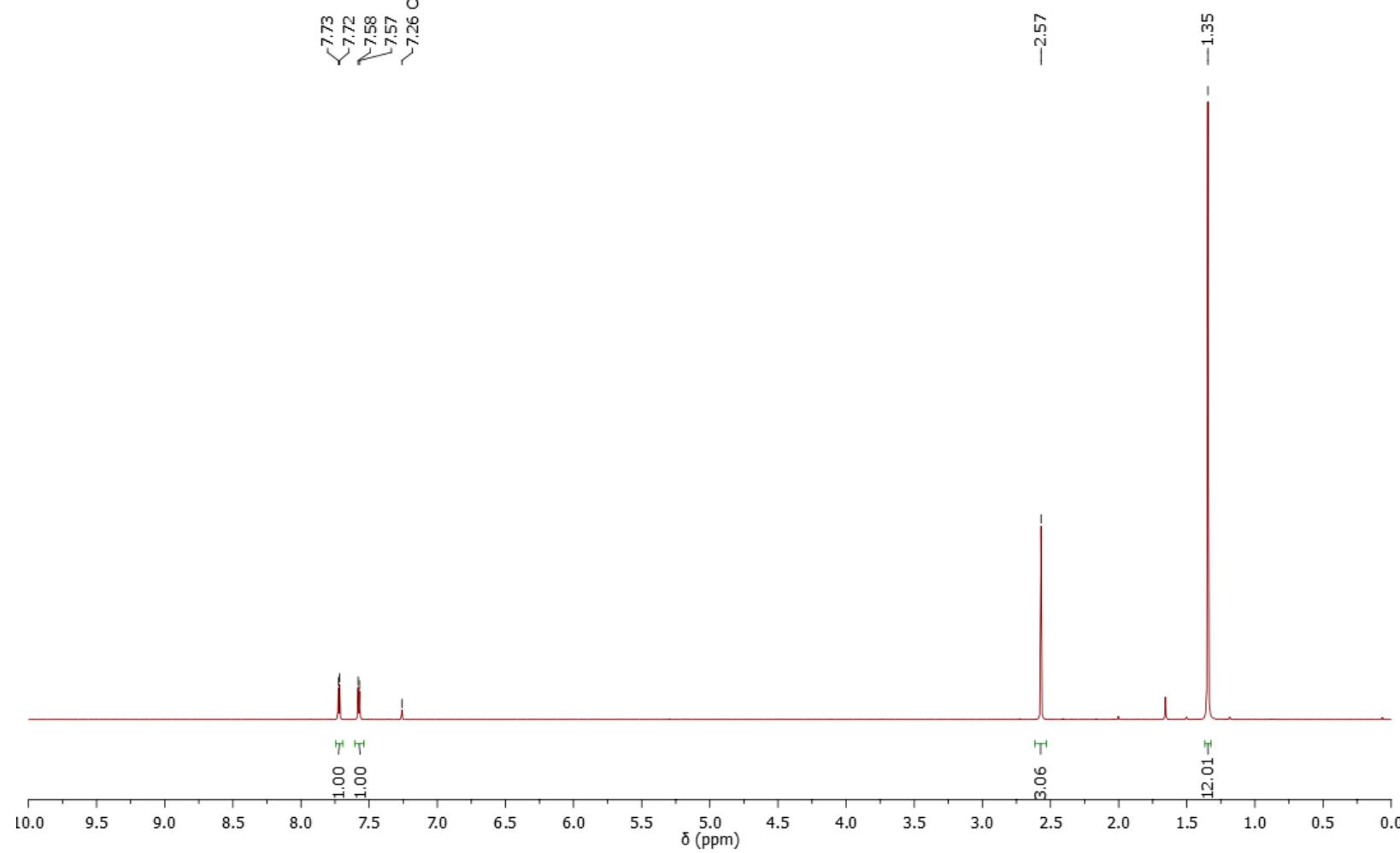
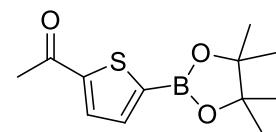
## Diboron esters

$^{13}\text{C}$  101MHz



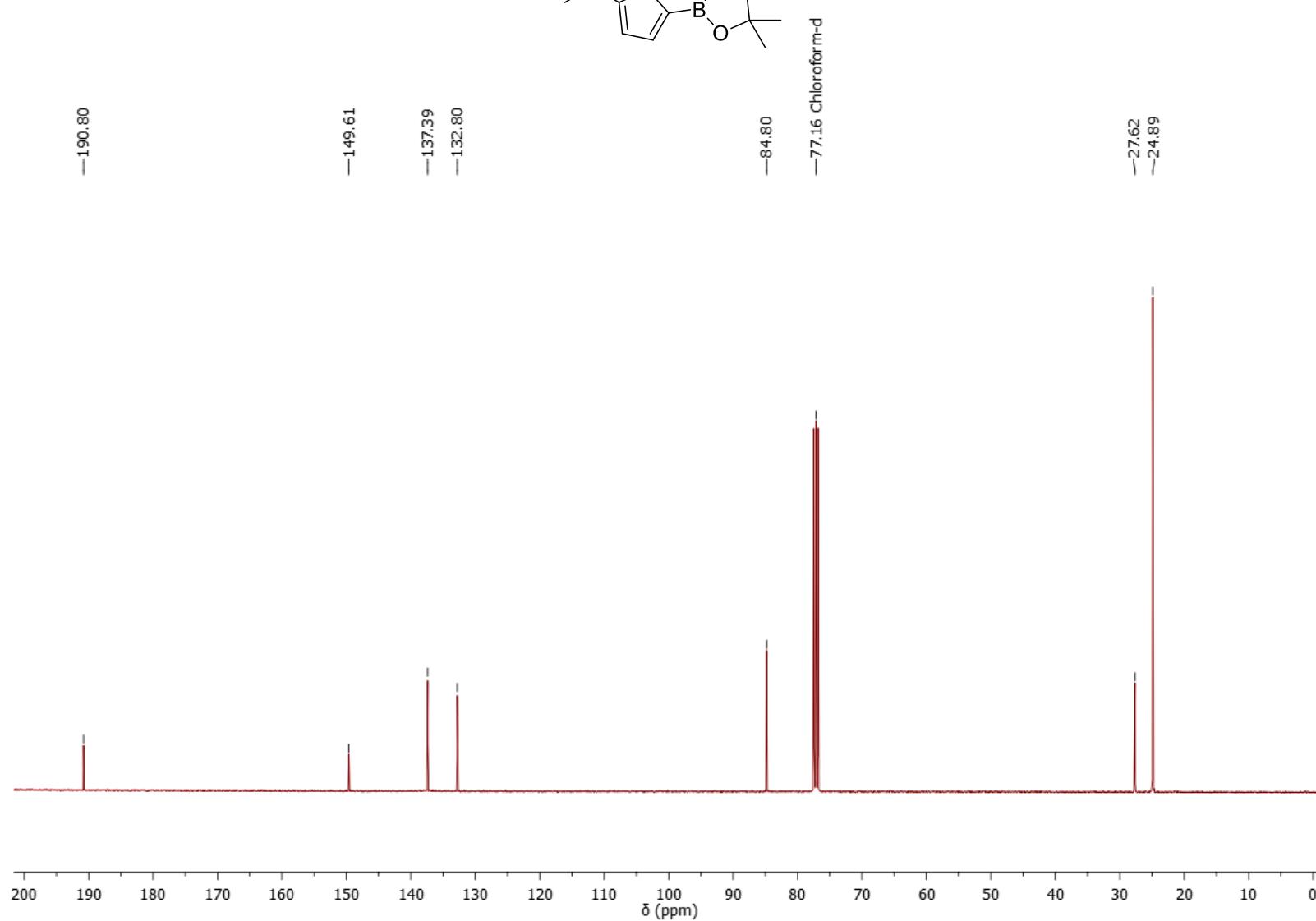
$^1\text{H}$  400MHz,  $\text{CDCl}_3$

**2aa**



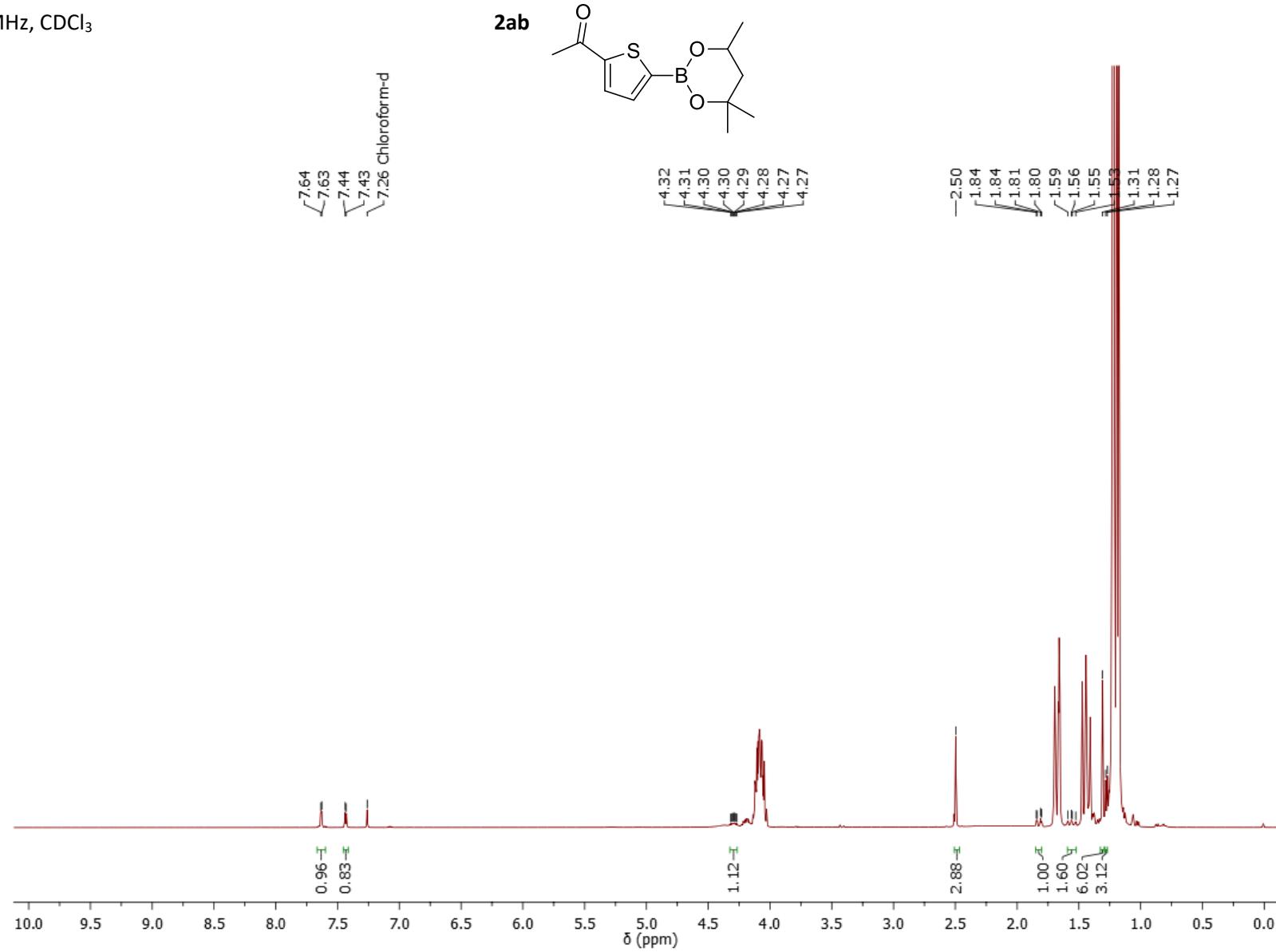
**Thiophene boronate esters**

$^{13}\text{C}$  101MHz



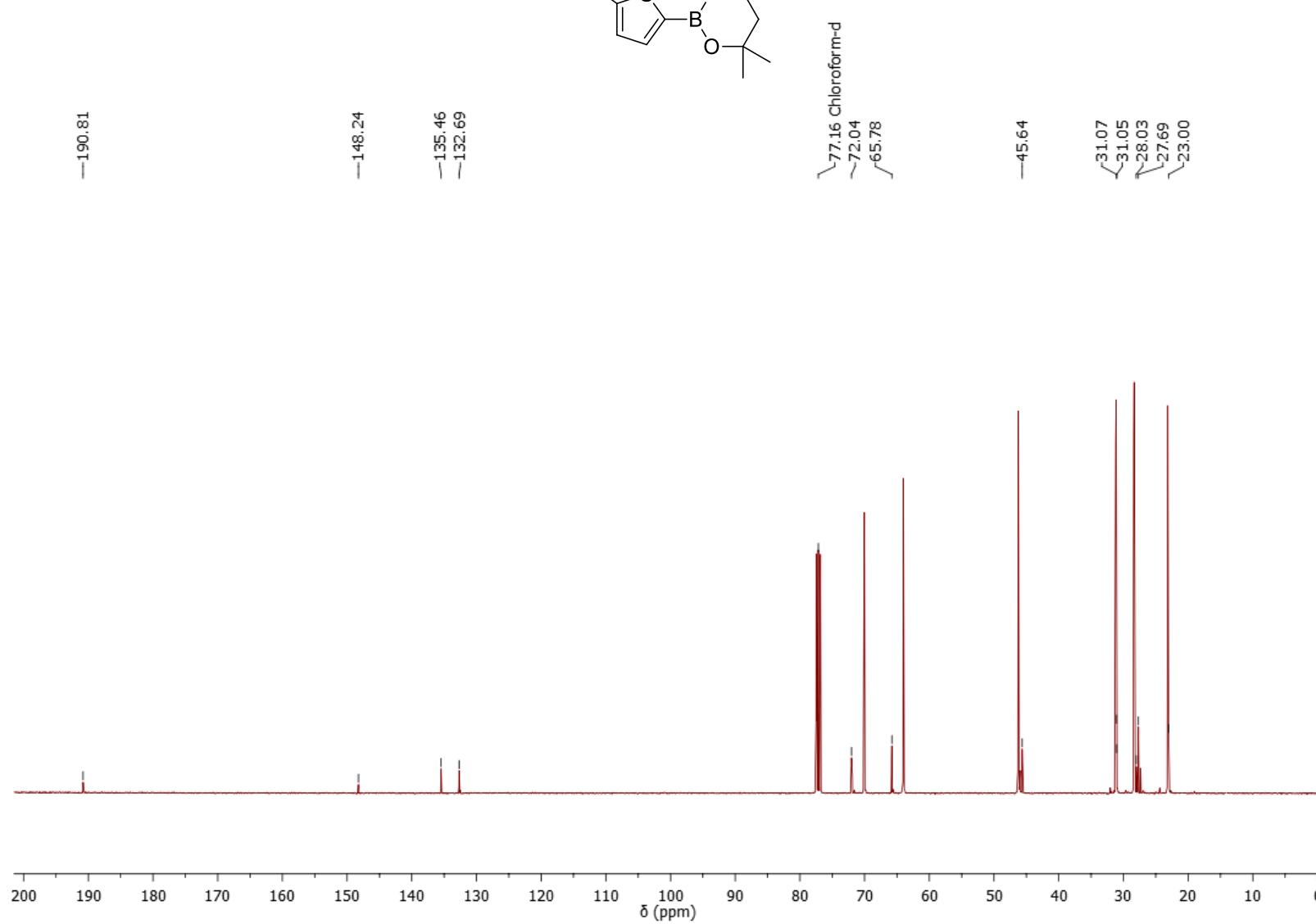
## Thiophene boronate esters

$^1\text{H}$  400MHz,  $\text{CDCl}_3$

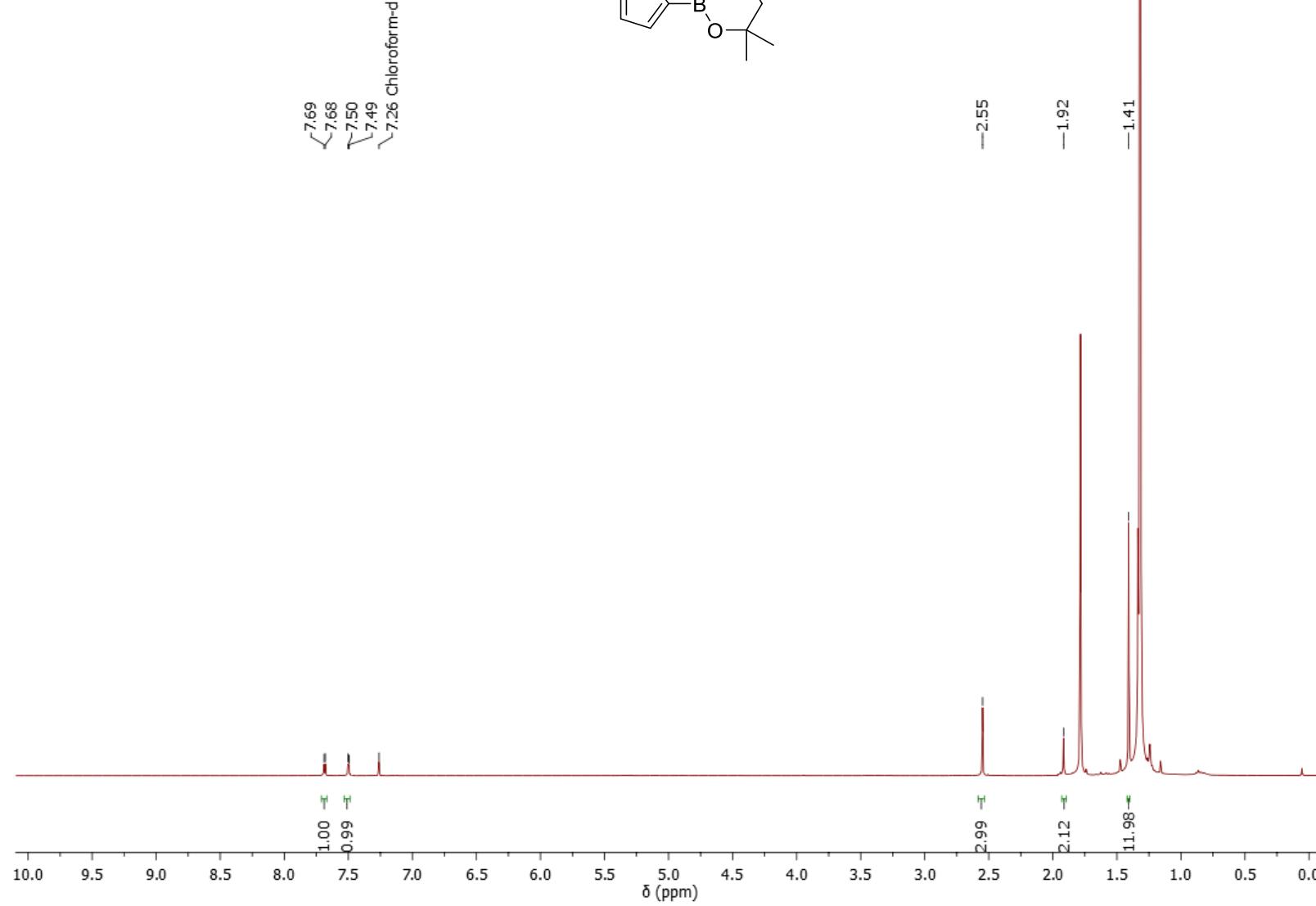
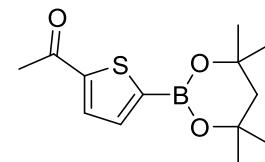


## Thiophene boronate esters

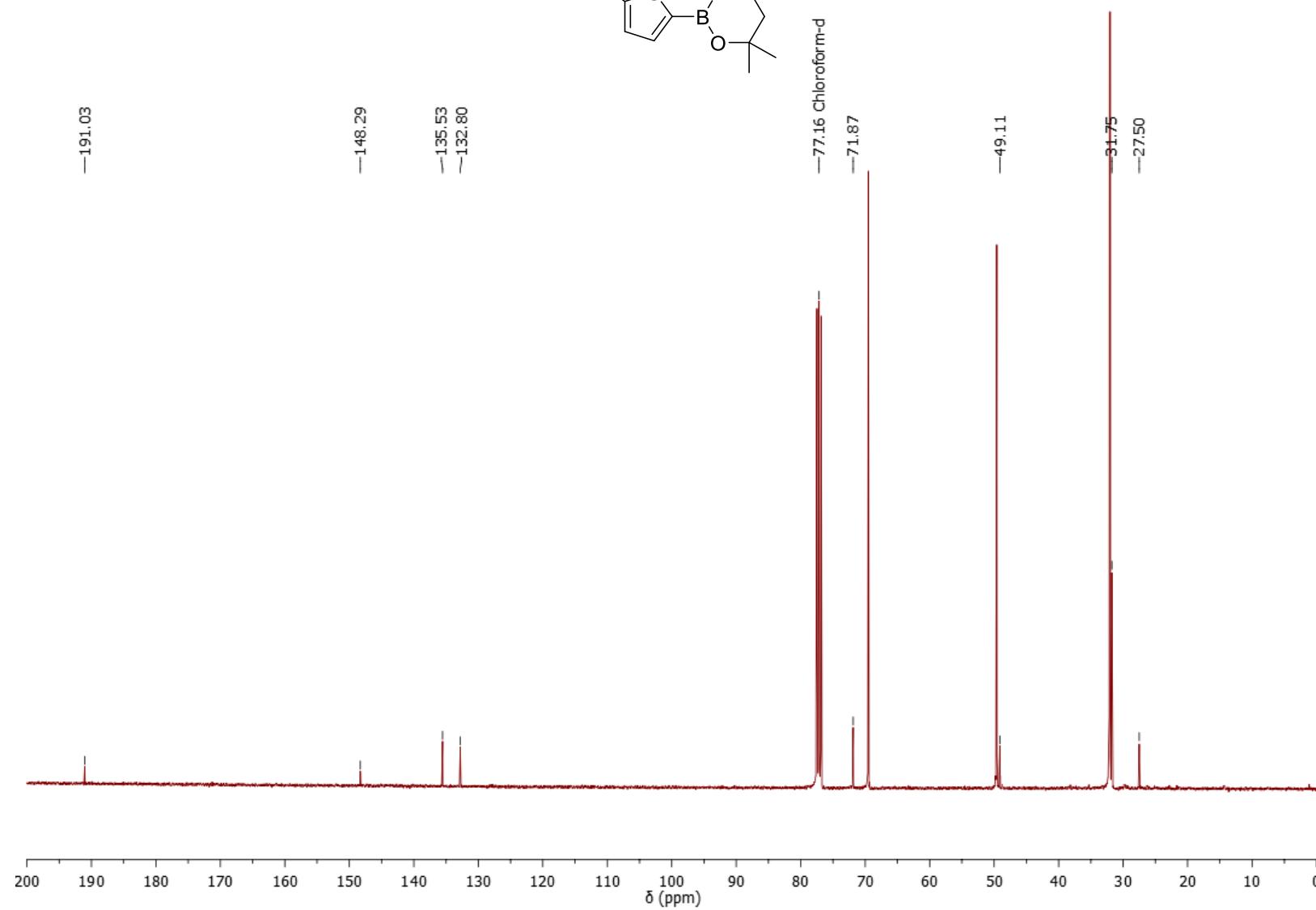
<sup>13</sup>C 101MHz



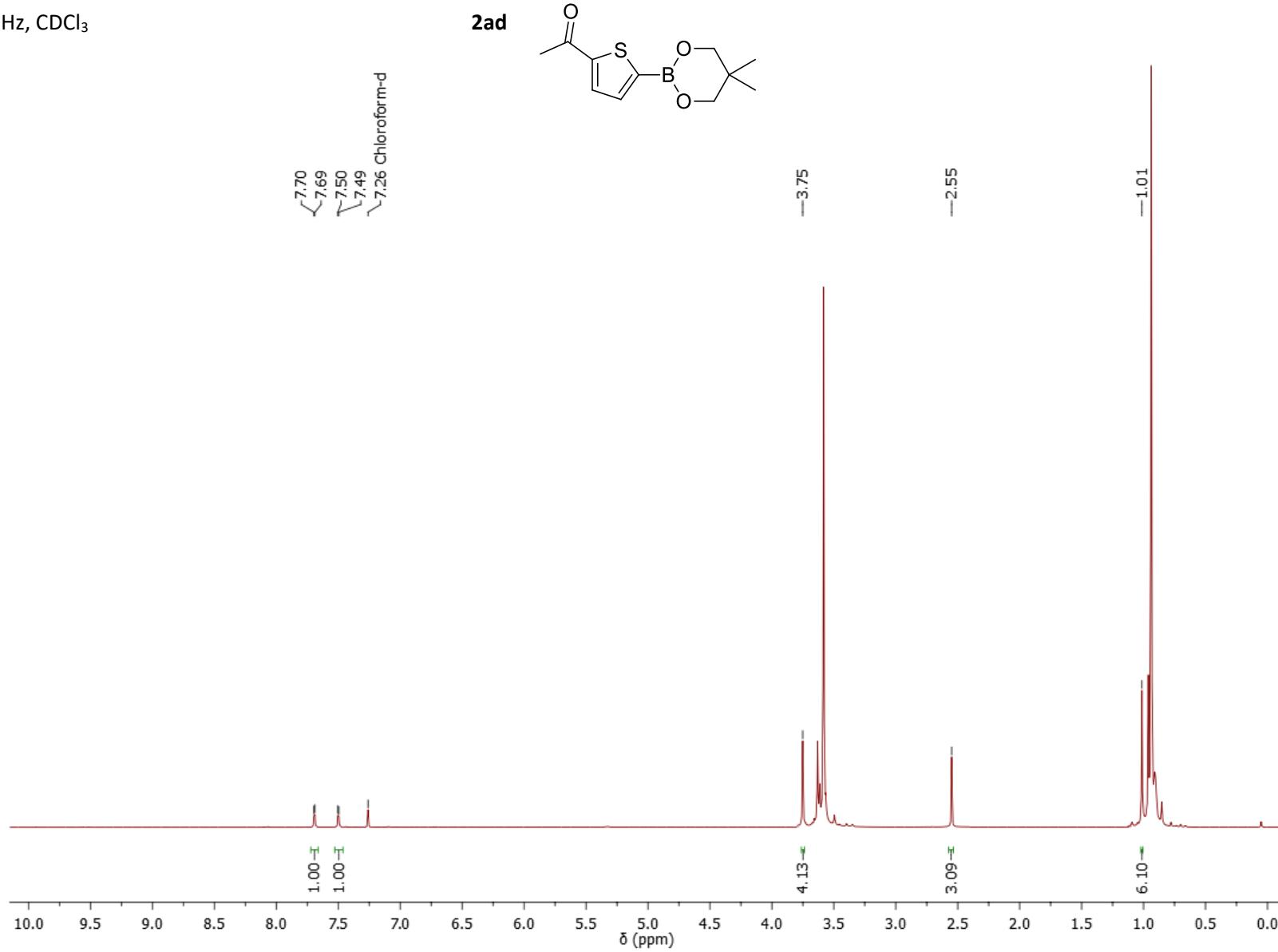
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



<sup>13</sup>C 101MHz



$^1\text{H}$  400MHz,  $\text{CDCl}_3$



## Thiophene boronate esters

$^{13}\text{C}$  101MHz

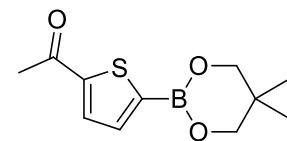
—190.93

—148.70

—135.93

—132.87

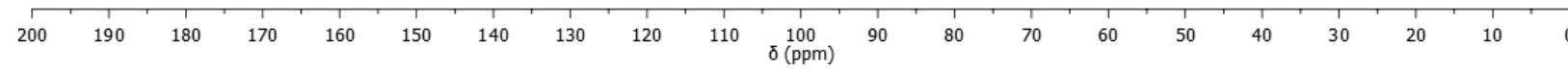
**2ad**



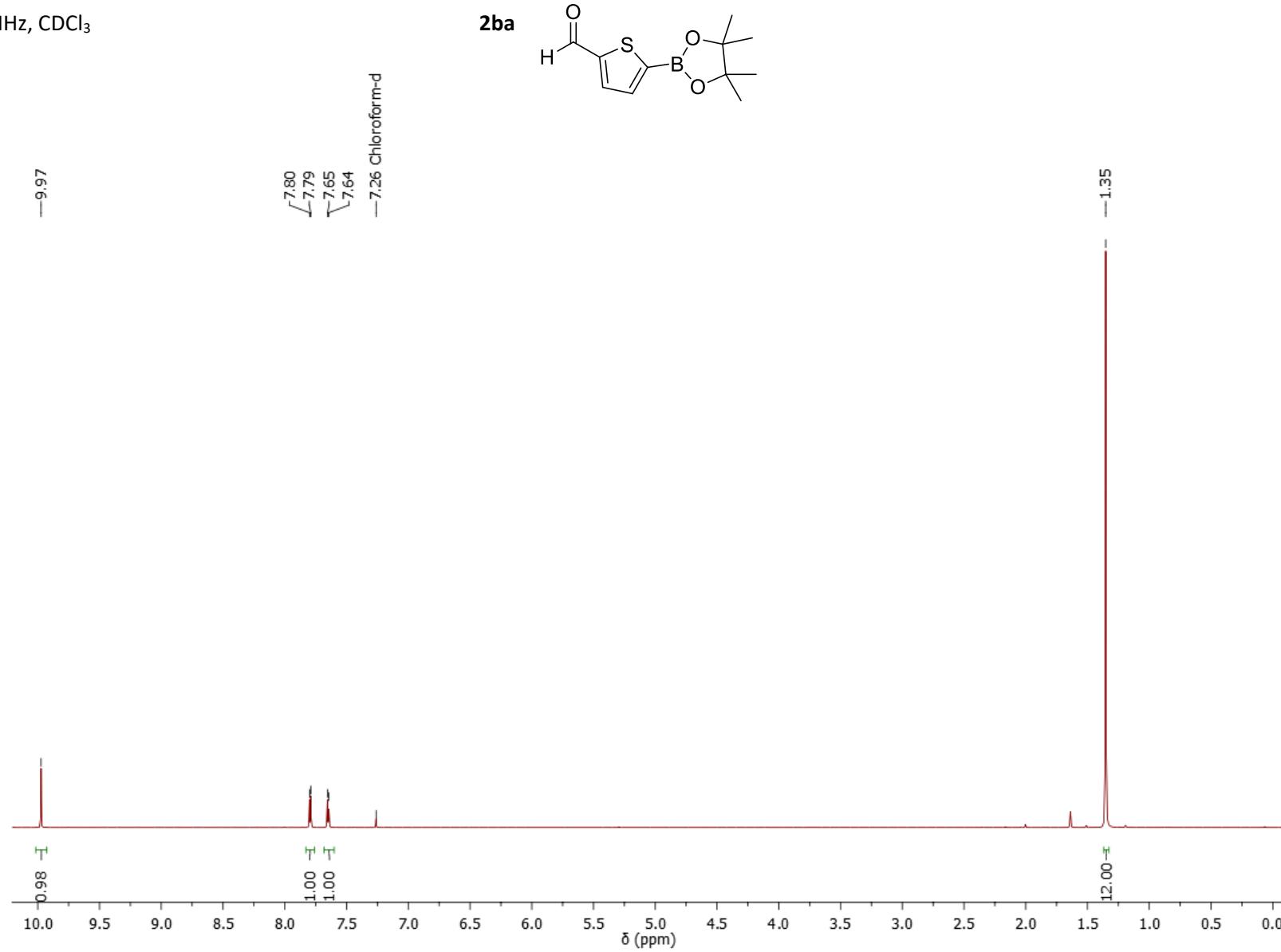
—77.16 Chloroform-d

—73.06

—32.13  
—27.49  
—21.64

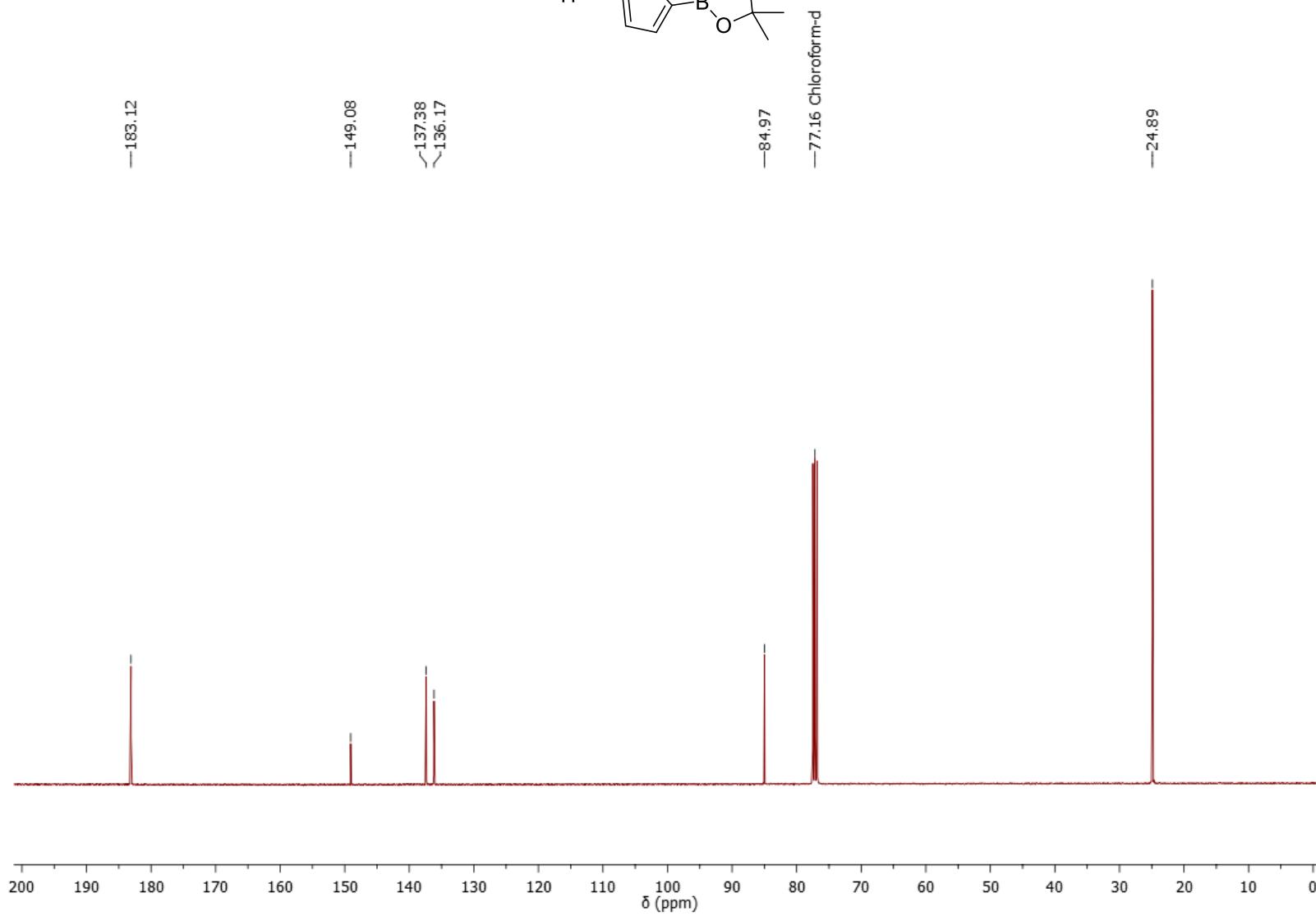


$^1\text{H}$  400MHz,  $\text{CDCl}_3$

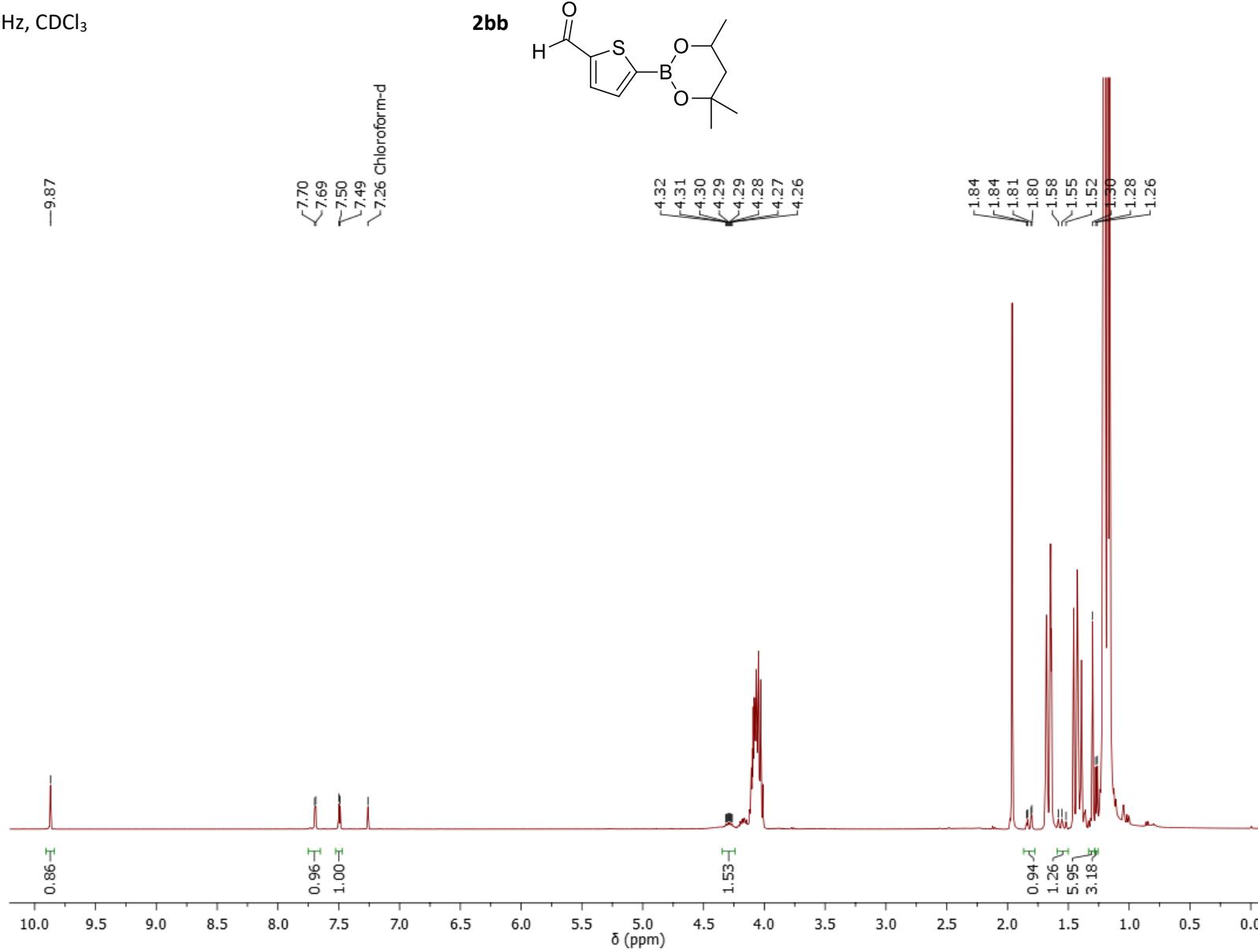


## Thiophene boronate esters

<sup>13</sup>C 101MHz

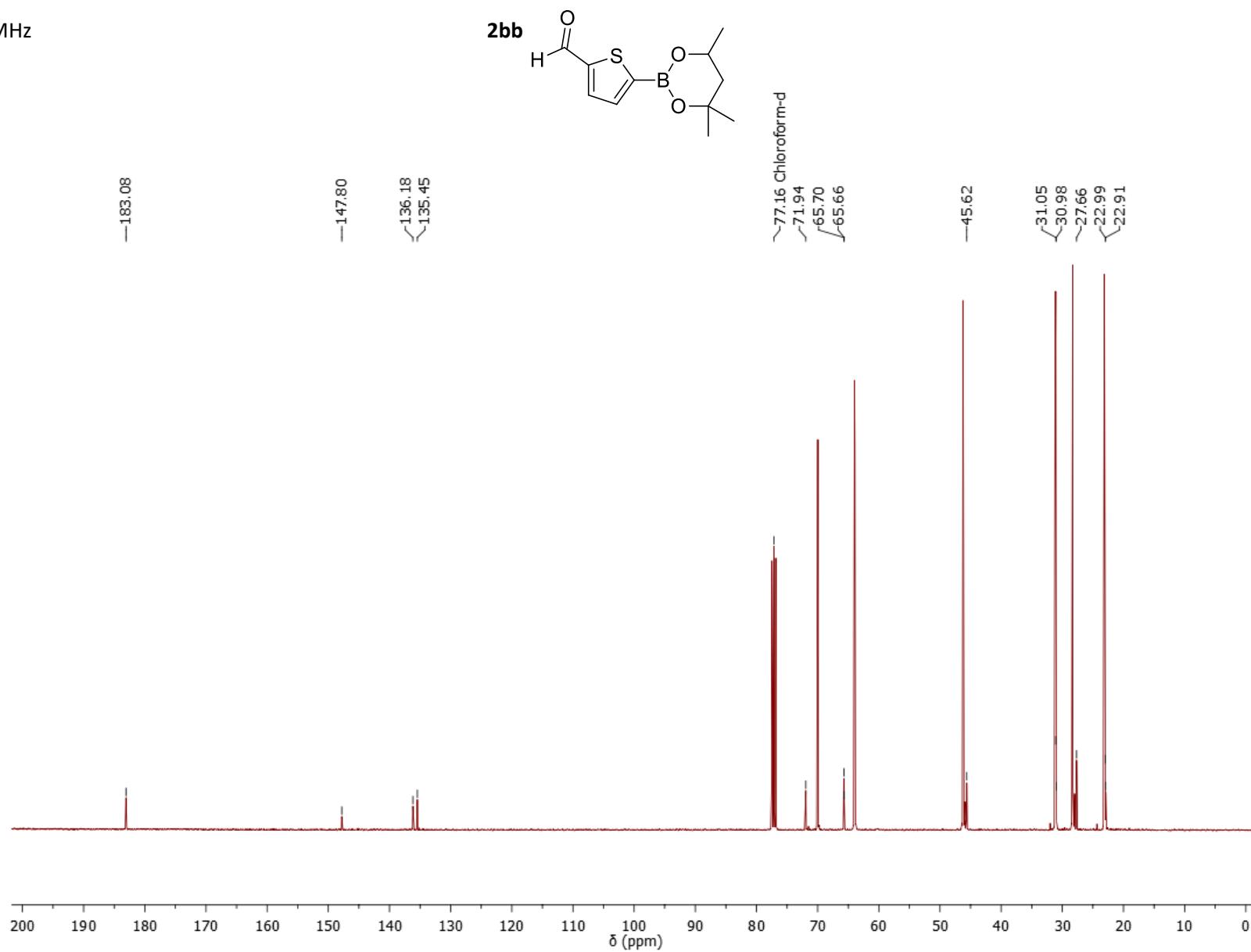


$^1\text{H}$  400MHz,  $\text{CDCl}_3$



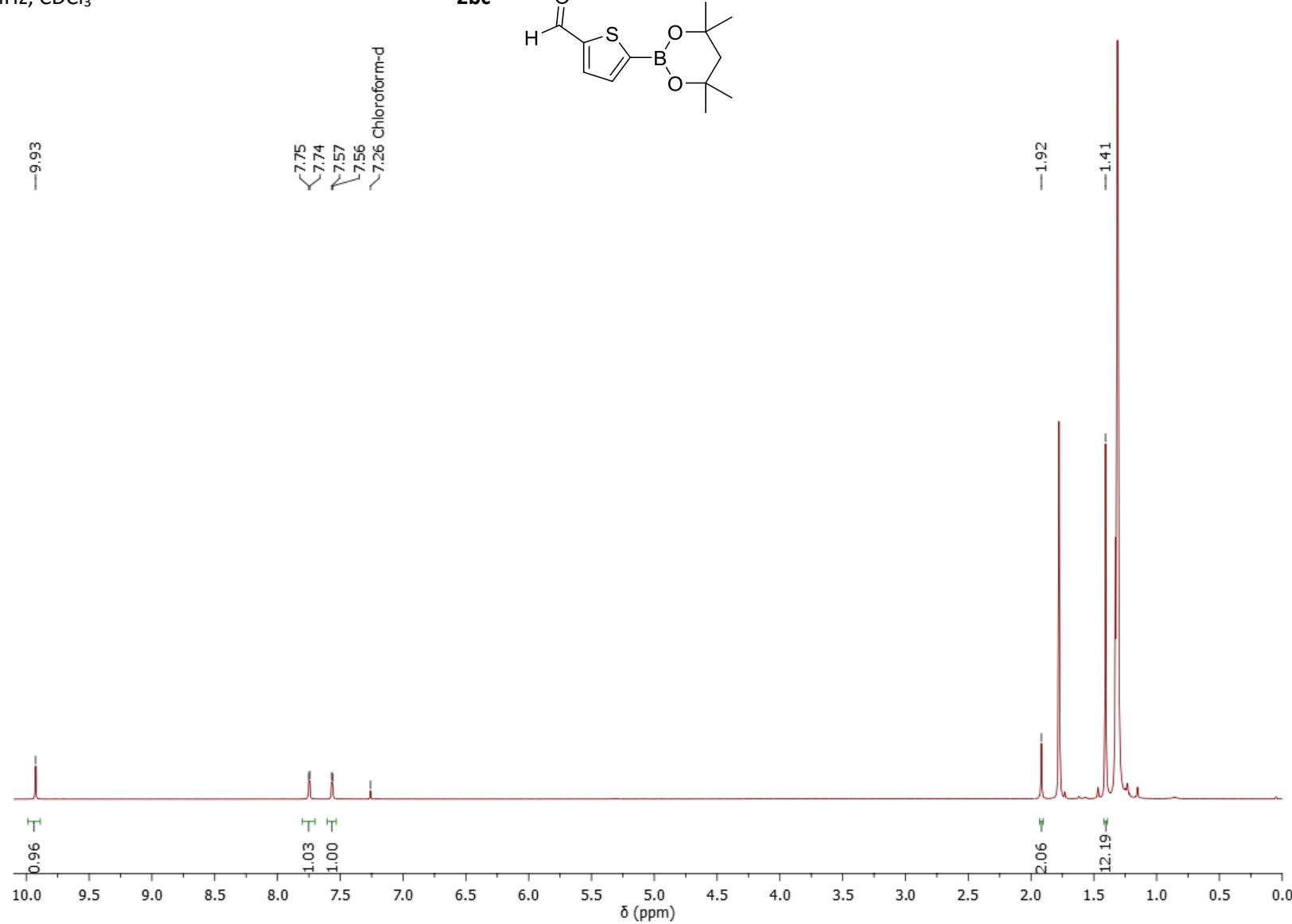
## Thiophene boronate esters

<sup>13</sup>C 101MHz



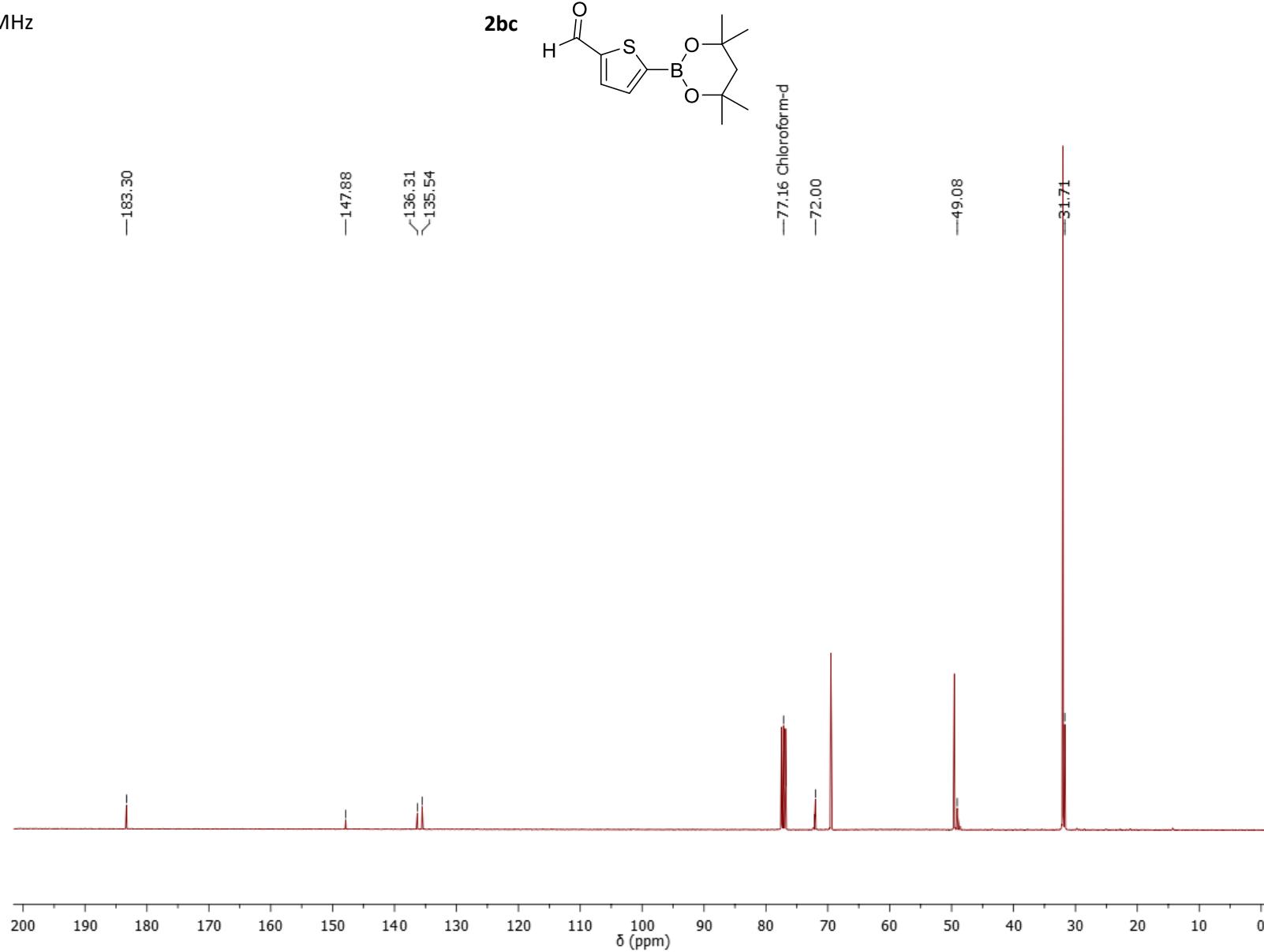
## Thiophene boronate esters

$^1\text{H}$  400MHz,  $\text{CDCl}_3$



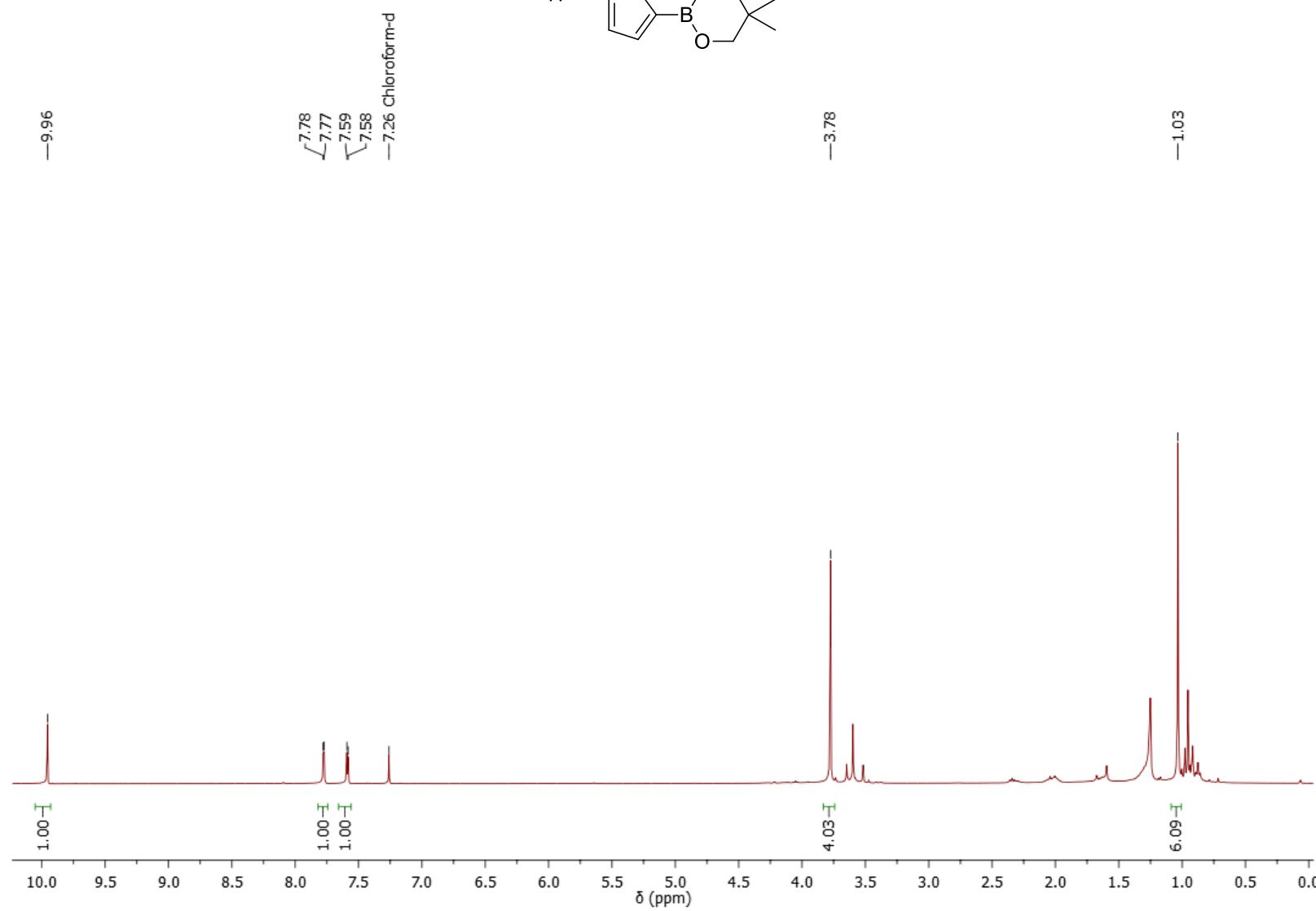
## Thiophene boronate esters

<sup>13</sup>C 101MHz



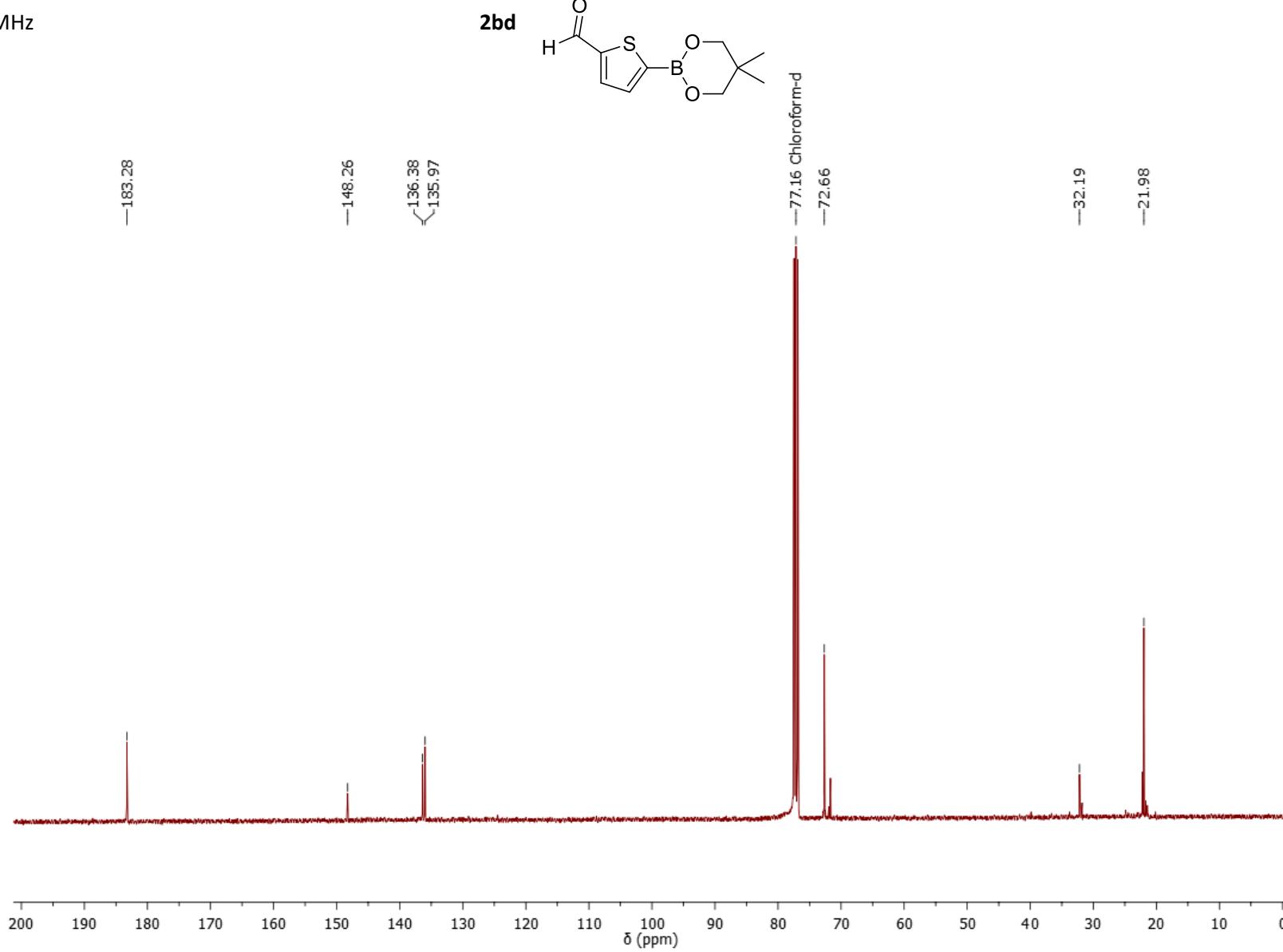
## Thiophene boronate esters

$^1\text{H}$  400MHz,  $\text{CDCl}_3$



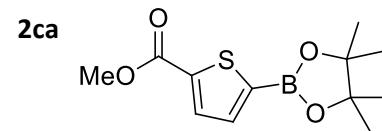
## Thiophene boronate esters

<sup>13</sup>C 101MHz

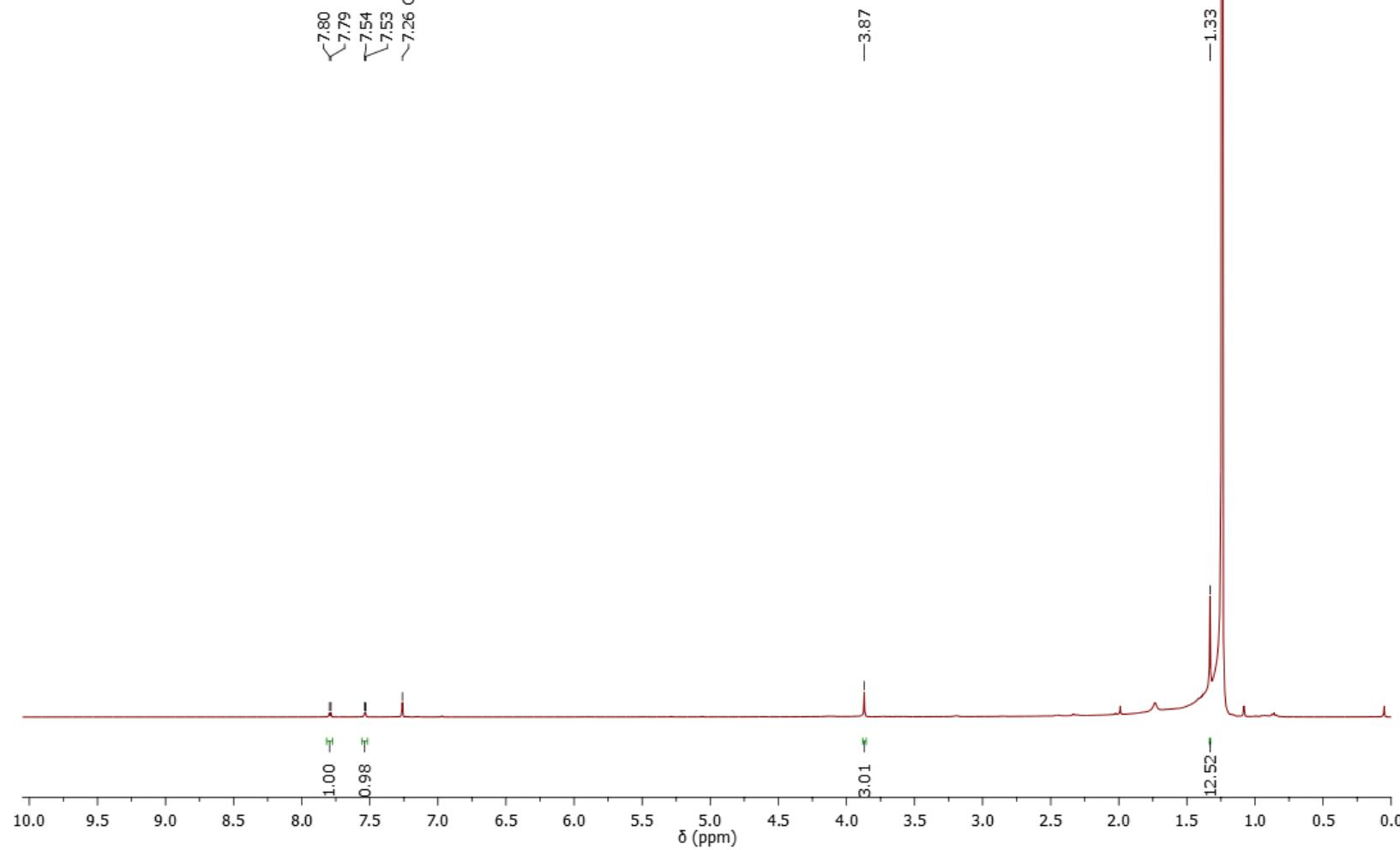


## Thiophene boronate esters

<sup>1</sup>H 400MHz, CDCl<sub>3</sub>

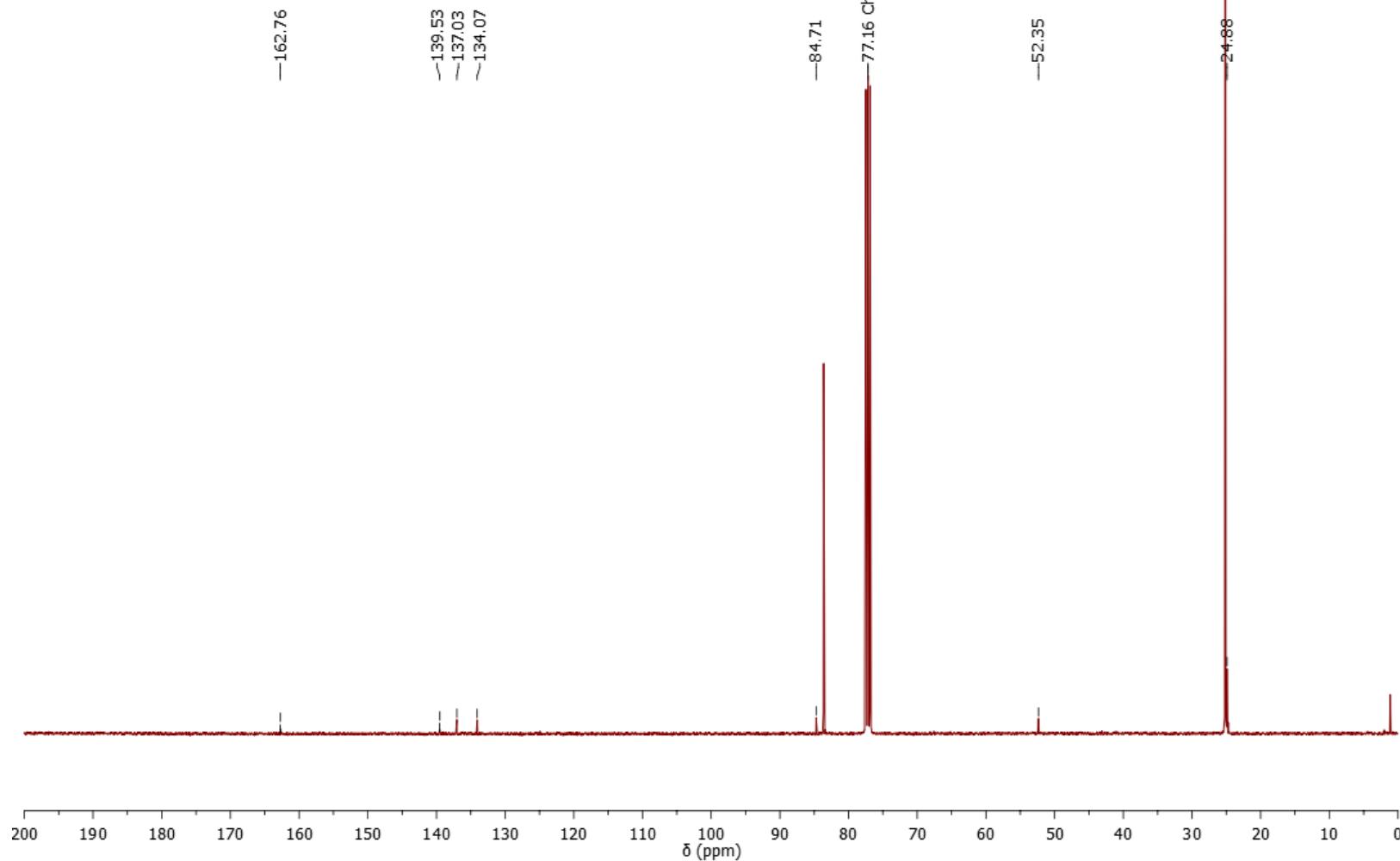
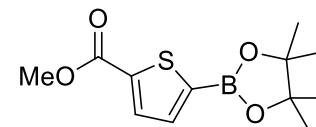


7.80  
7.79  
7.54  
7.53  
7.26 Chloroform-d

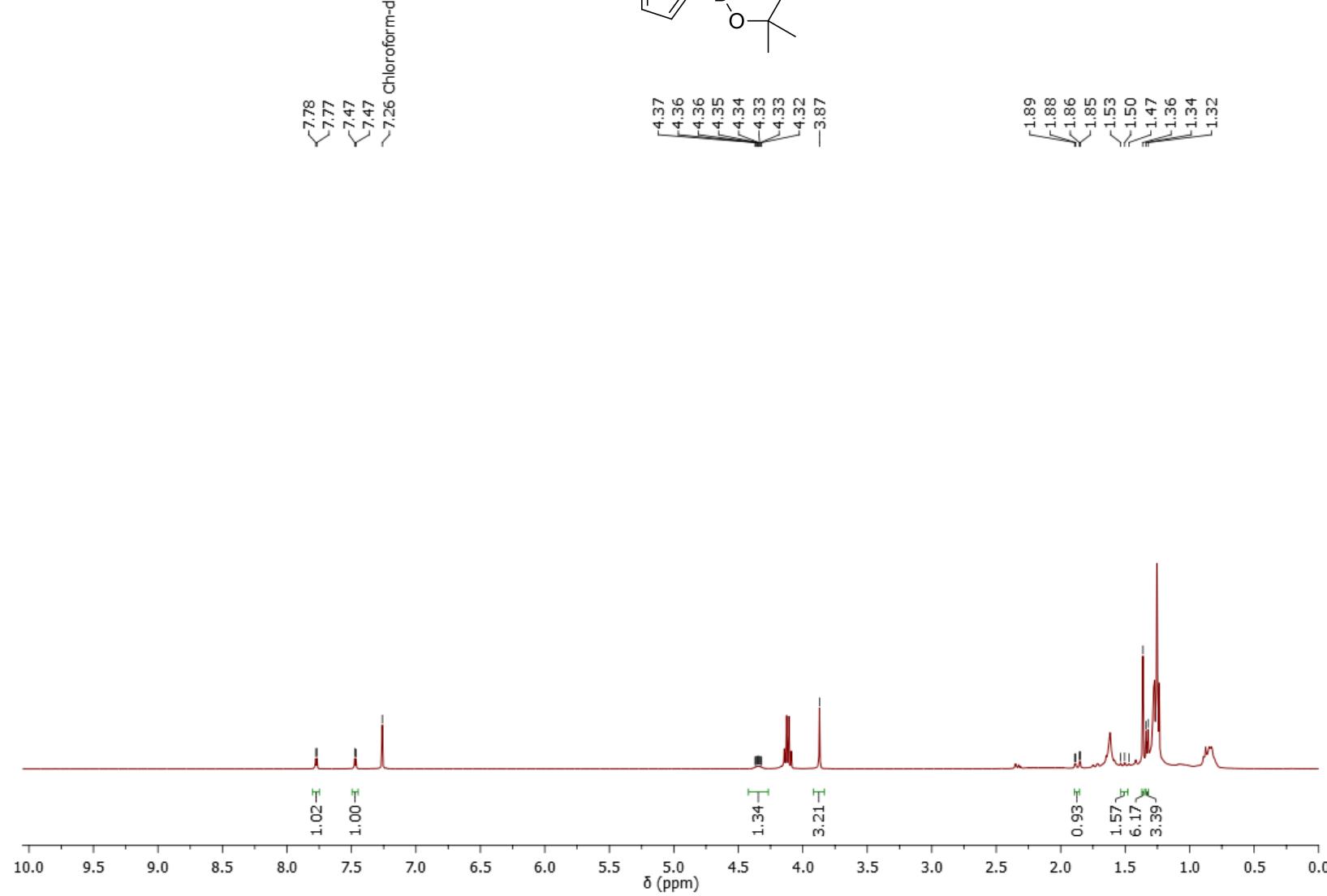
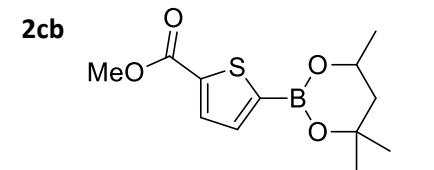


$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$

**2ca**

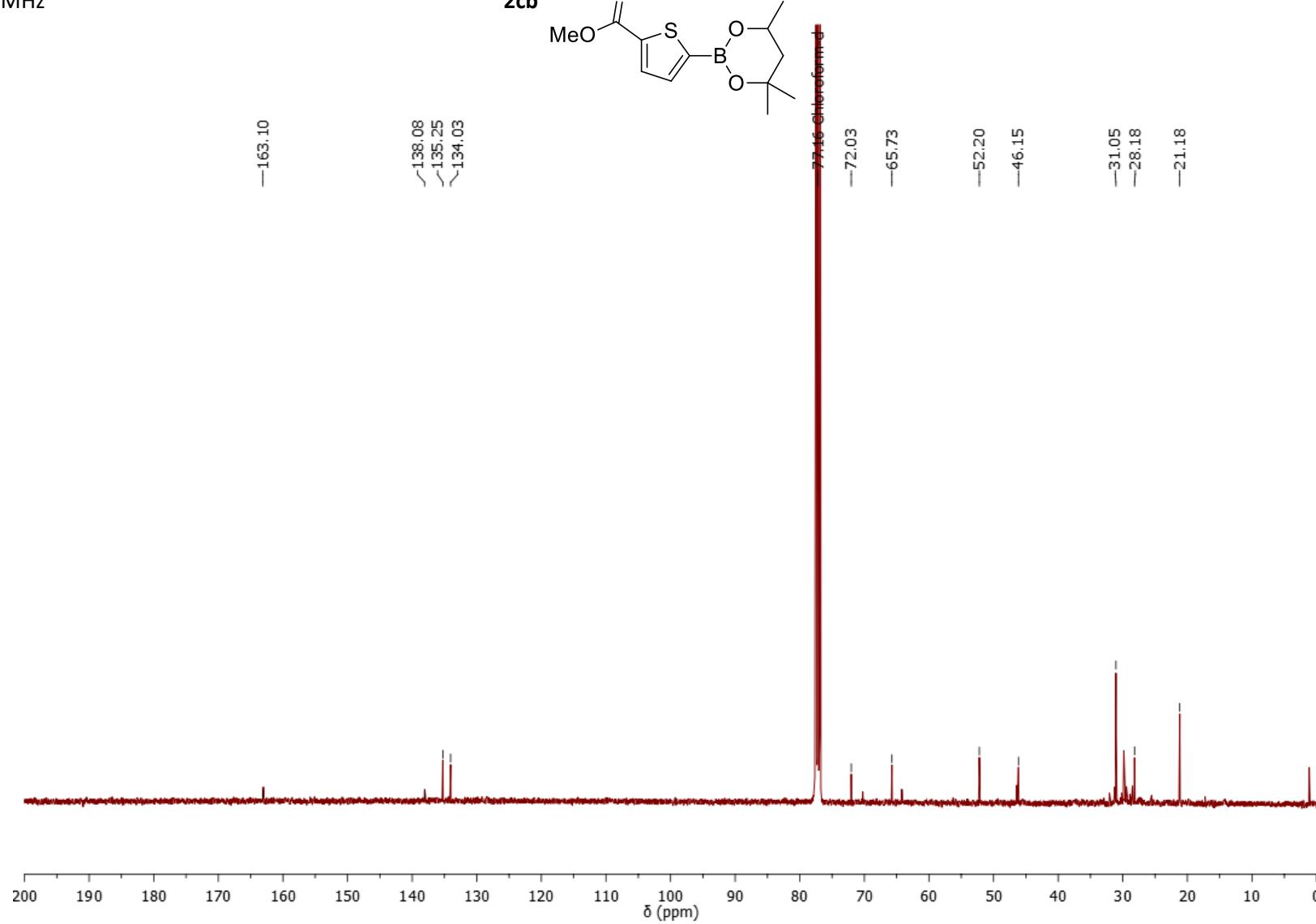


<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



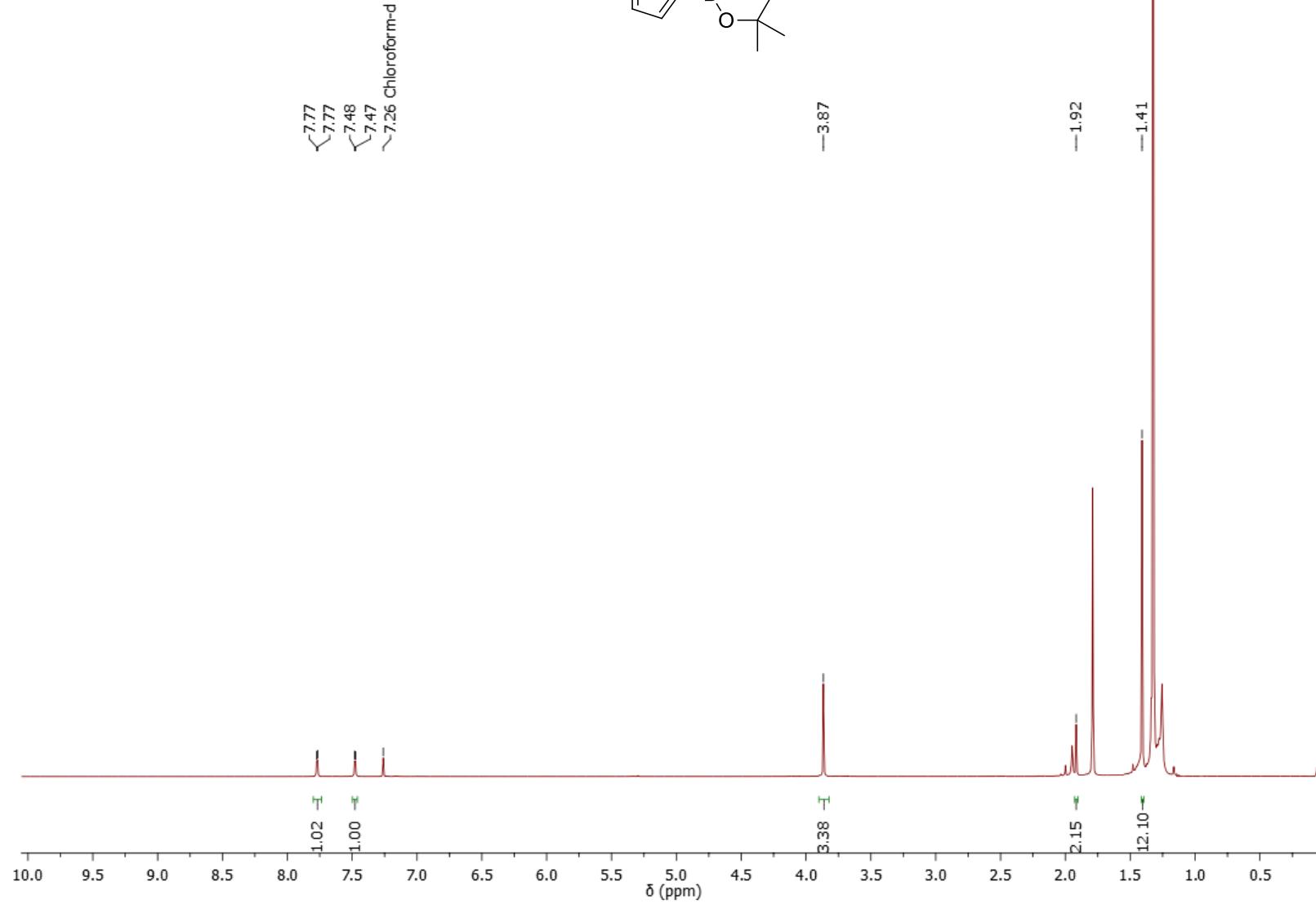
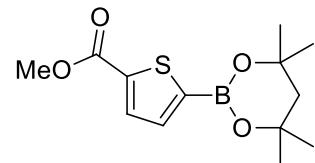
## Thiophene boronate esters

<sup>13</sup>C 101MHz



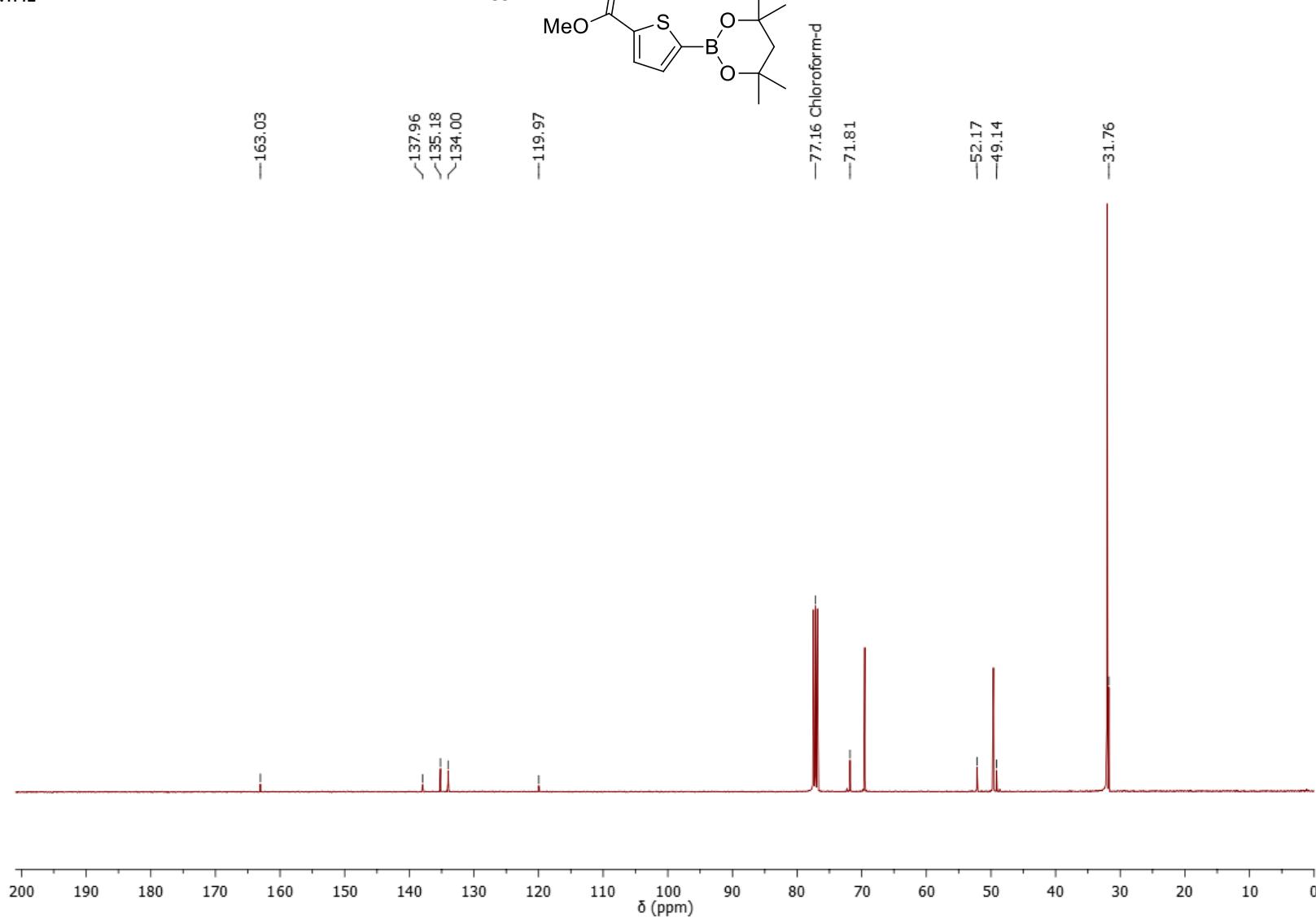
$^1\text{H}$  400MHz,  $\text{CDCl}_3$

**2cc**



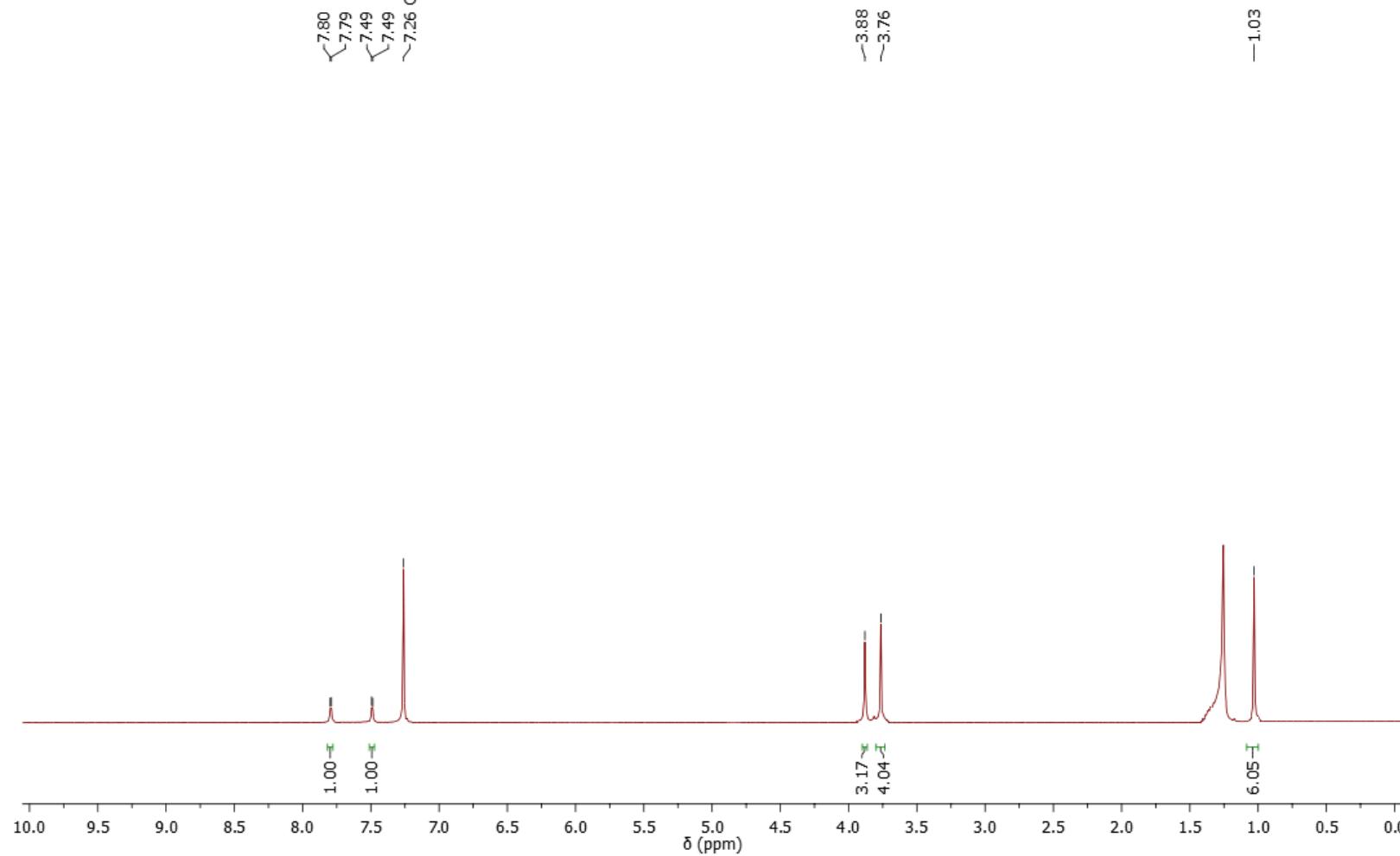
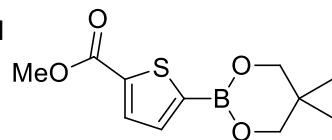
Thiophene boronate esters

<sup>13</sup>C 101MHz



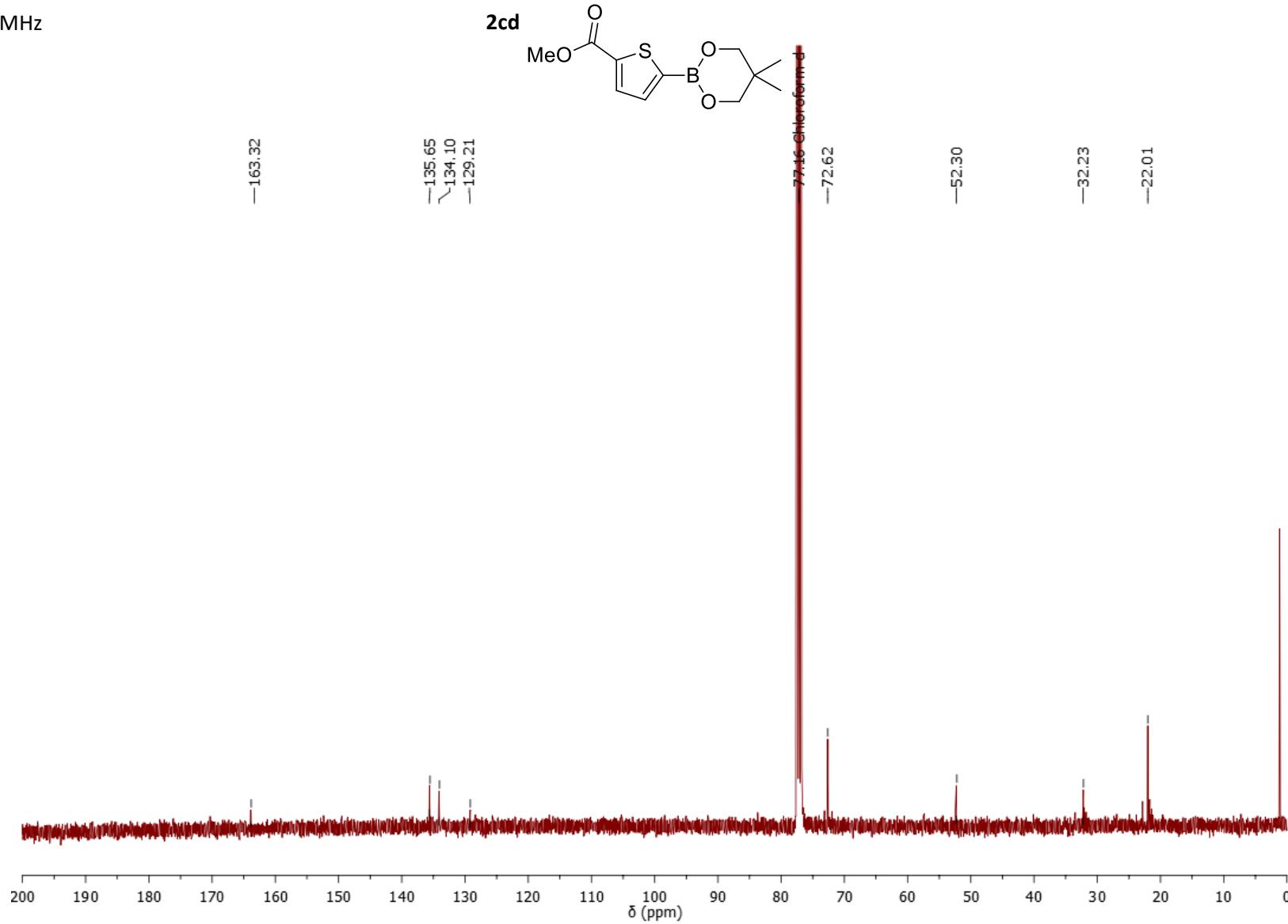
$^1\text{H}$  400MHz,  $\text{CDCl}_3$

**2cd**

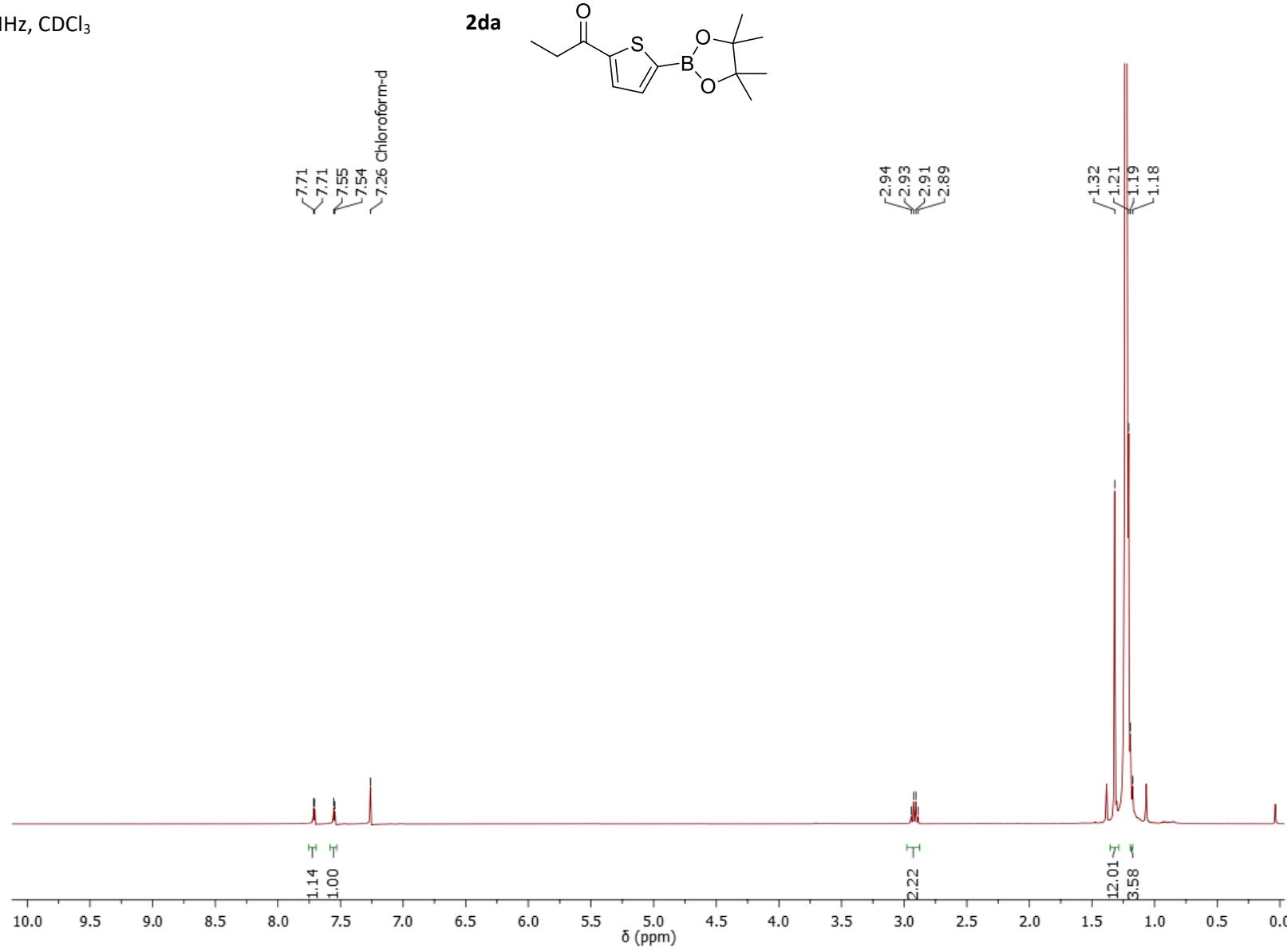


## Thiophene boronate esters

<sup>13</sup>C 101MHz



$^1\text{H}$  400MHz,  $\text{CDCl}_3$



## Thiophene boronate esters

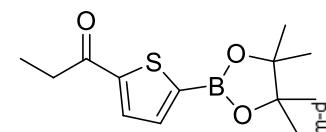
$^{13}\text{C}$  101MHz

—193.86

—149.19

—137.29

—132.00



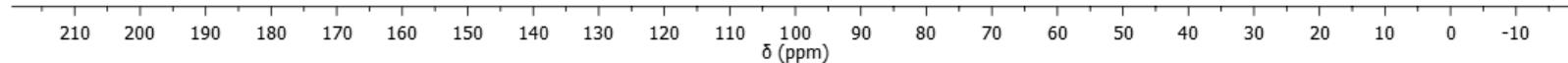
—84.70

—77.16 Chloroform-d

—33.21

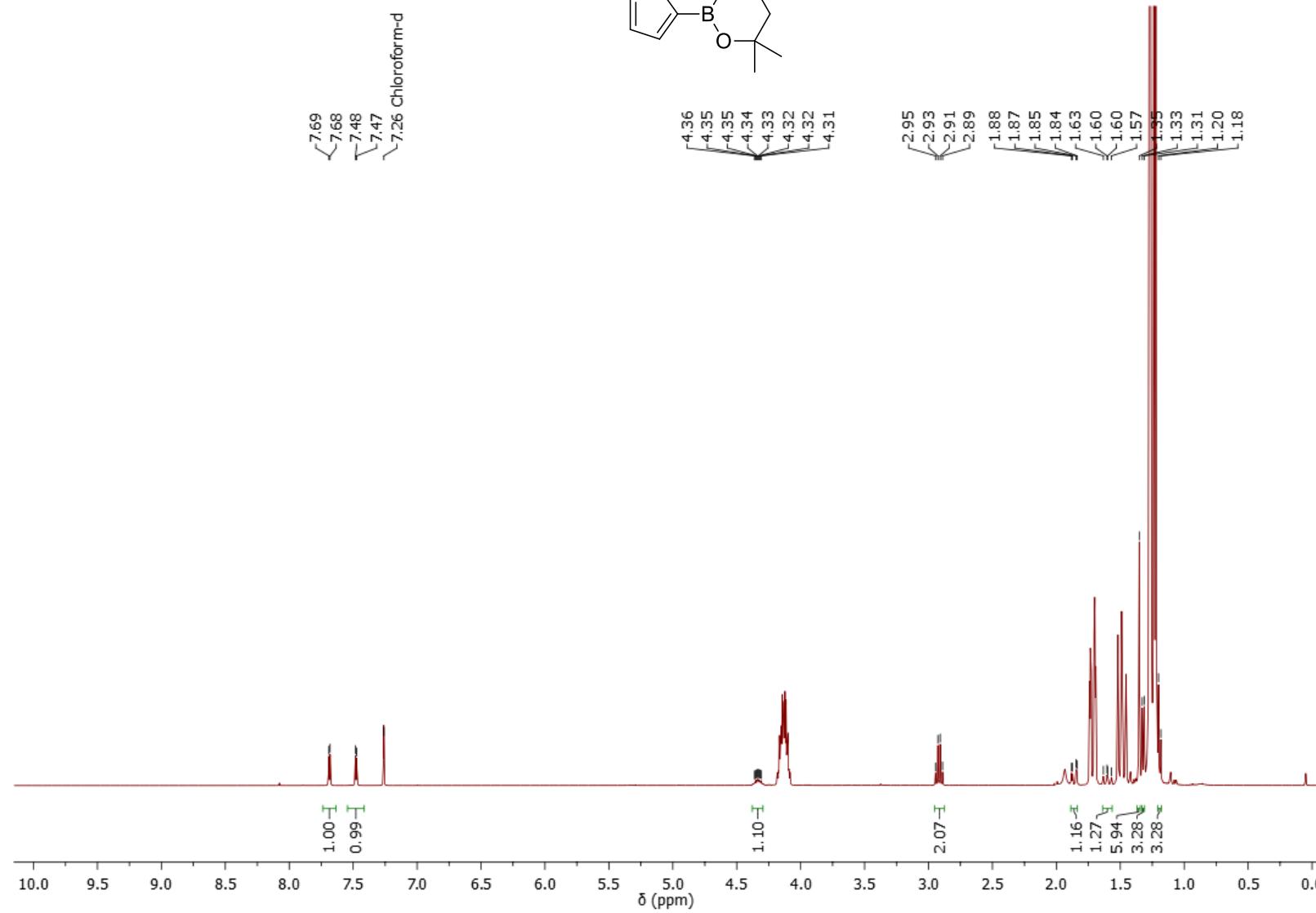
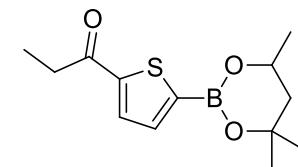
—24.61

—8.49

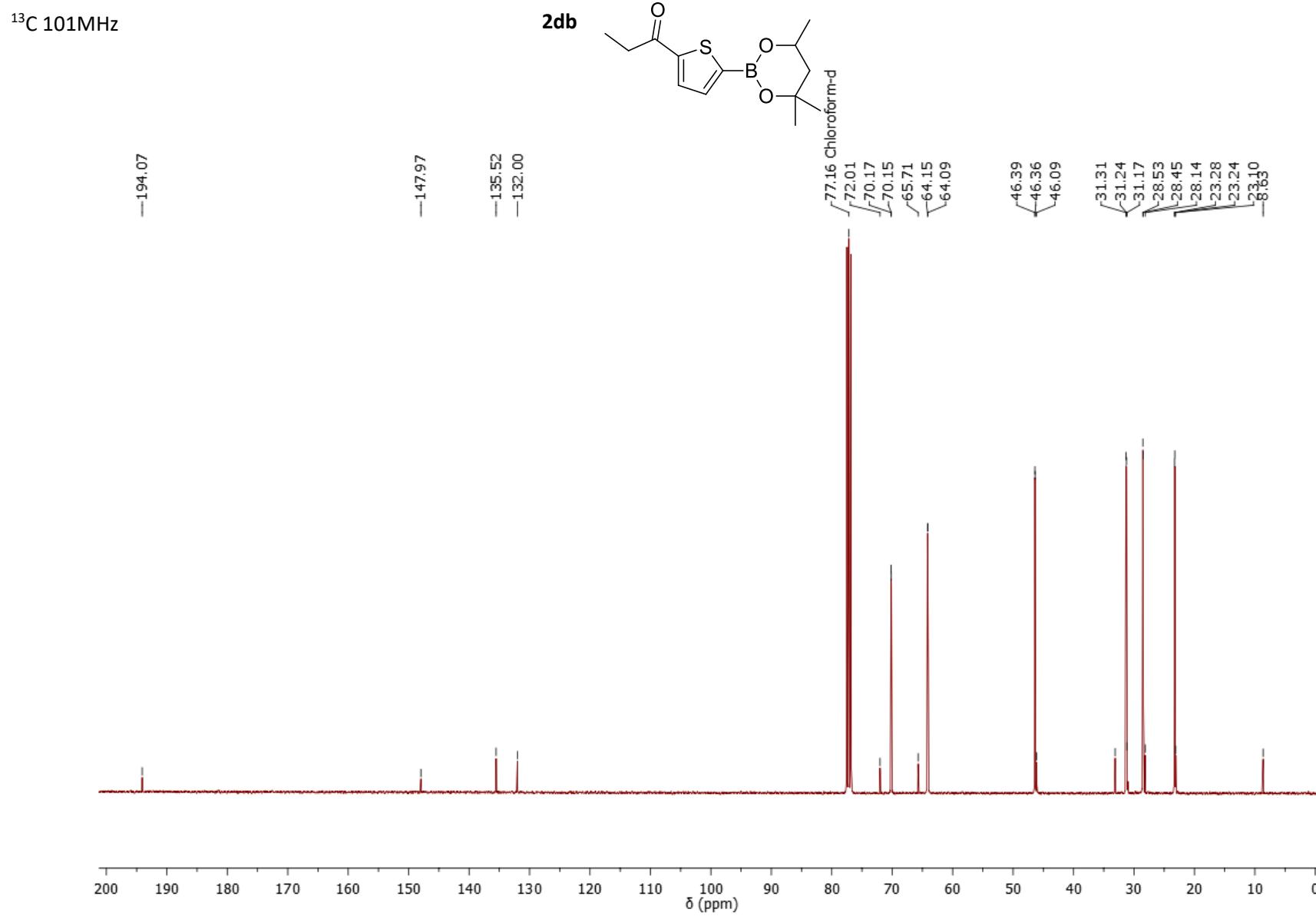


## Thiophene boronate esters

<sup>1</sup>H 400MHz, CDCl<sub>3</sub>

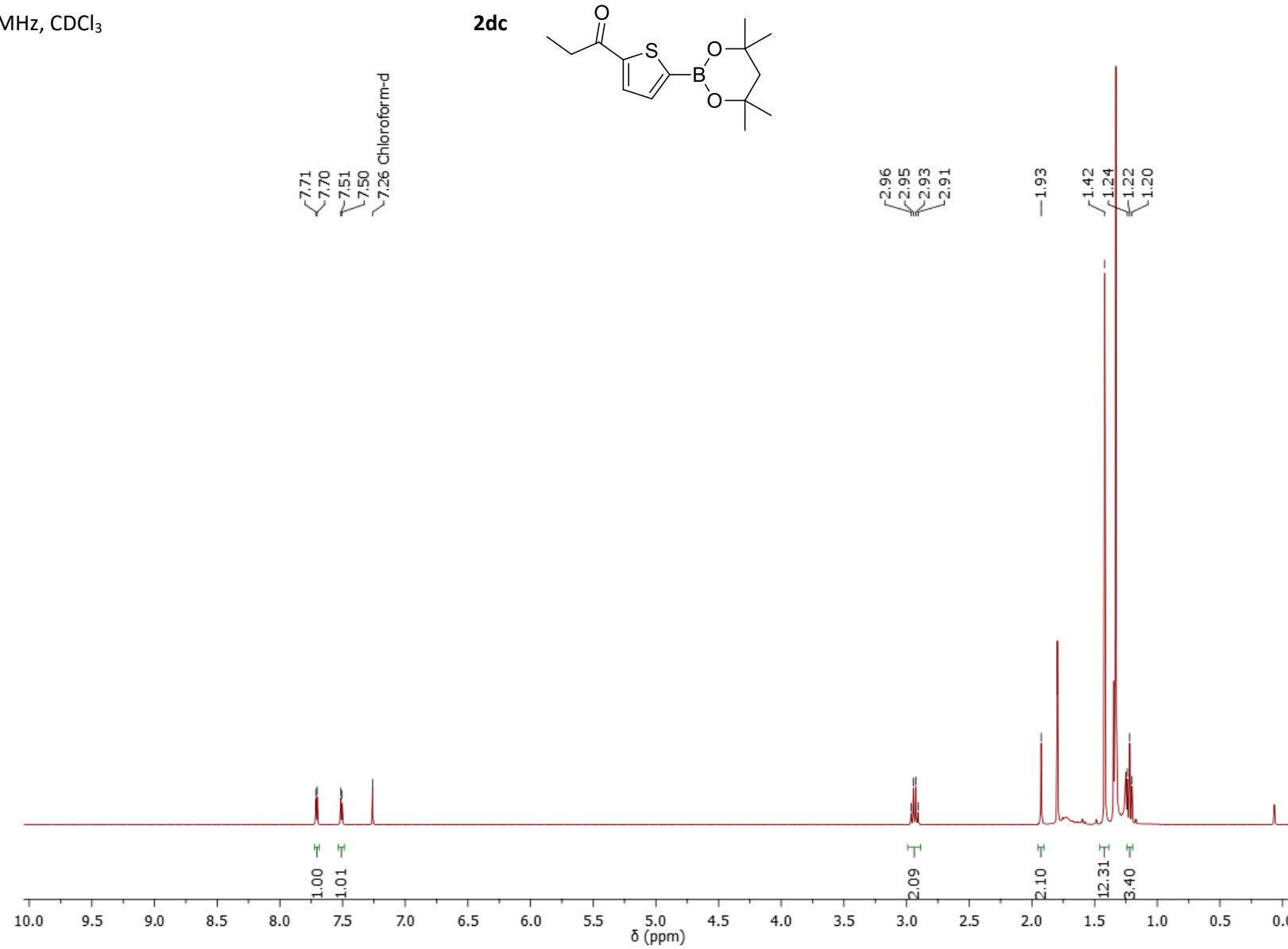


## Thiophene boronate esters



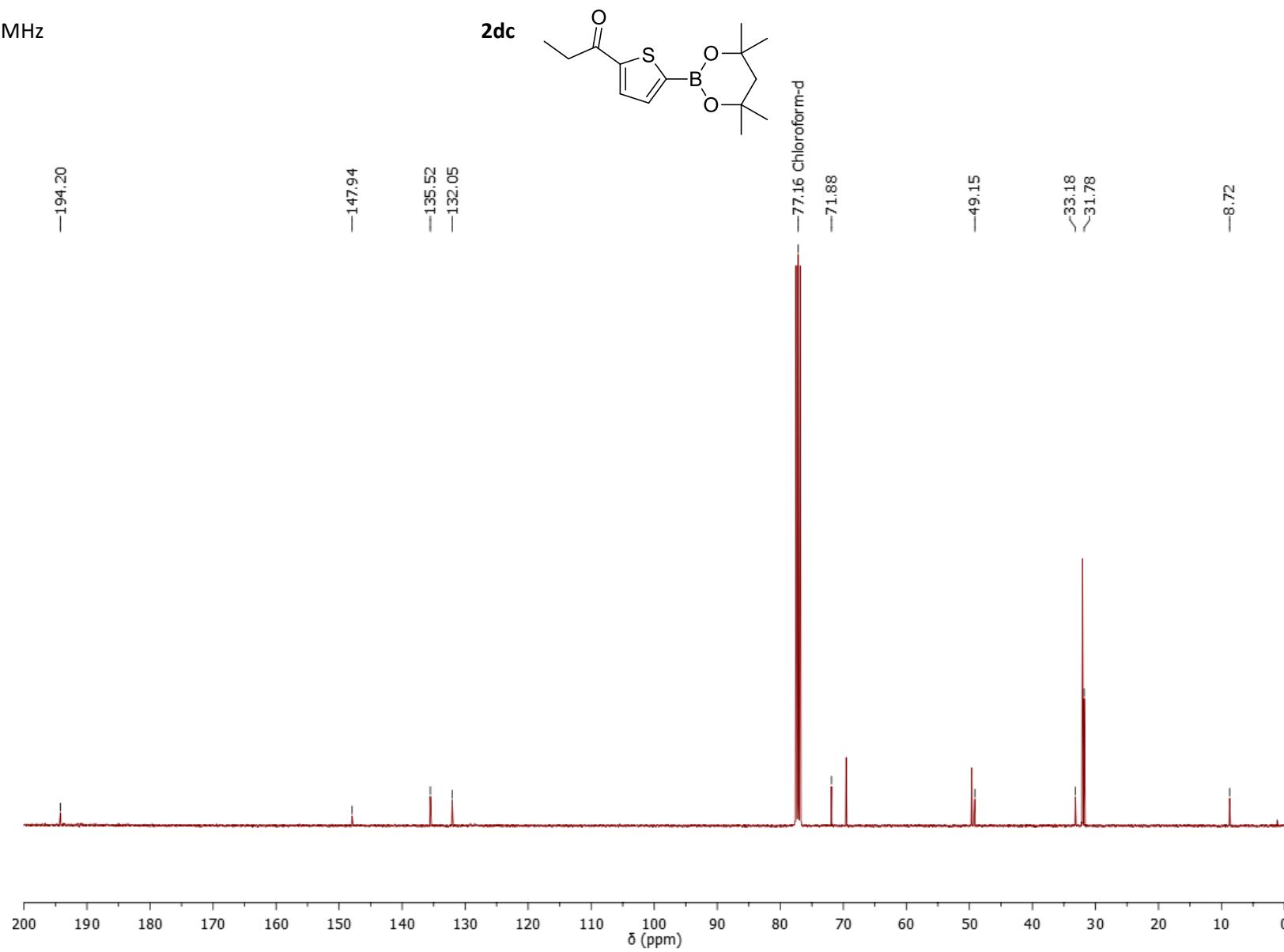
## Thiophene boronate esters

$^1\text{H}$  400MHz,  $\text{CDCl}_3$



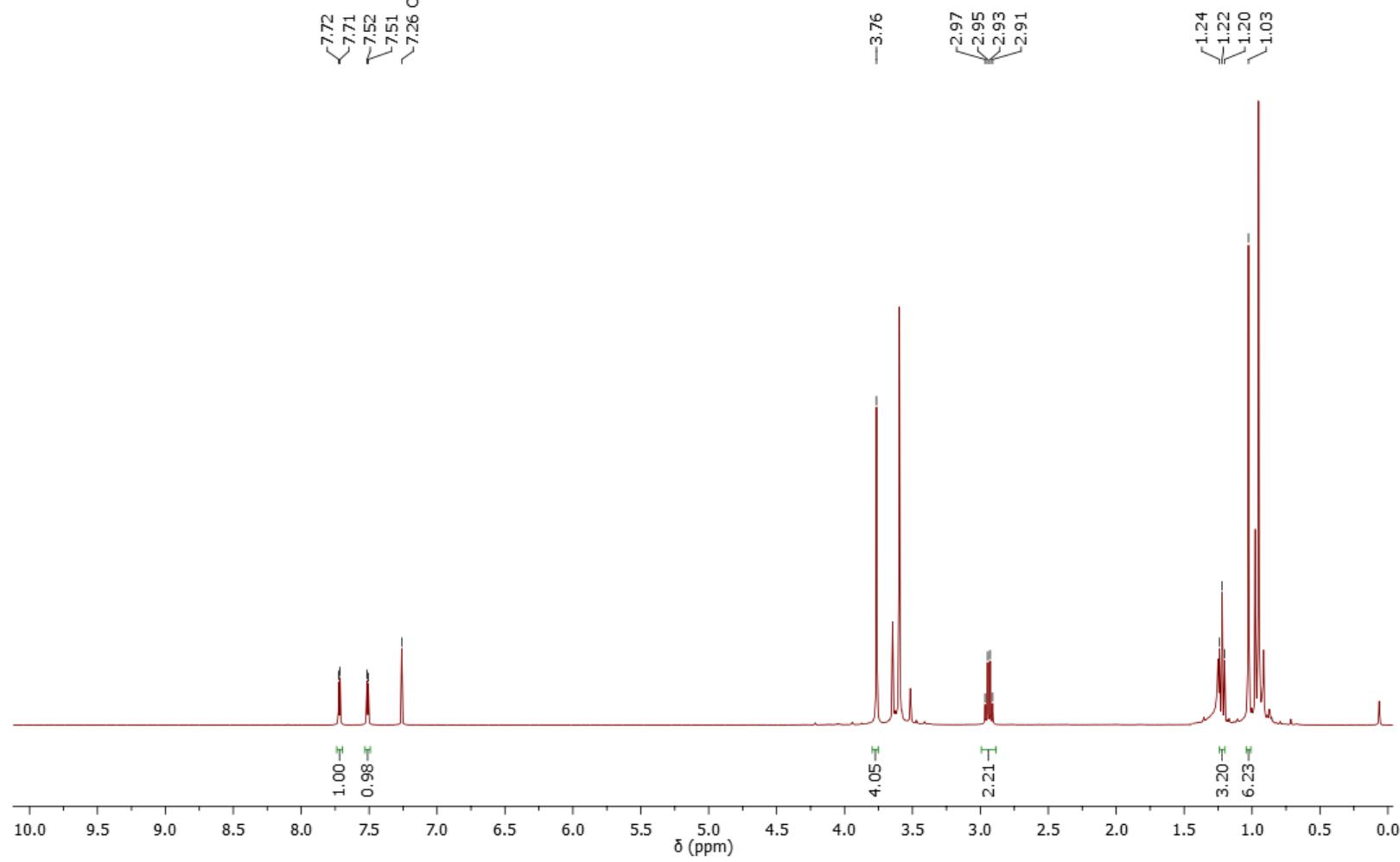
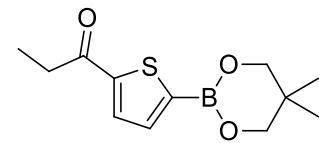
## Thiophene boronate esters

<sup>13</sup>C 101MHz



$^1\text{H}$  400MHz,  $\text{CDCl}_3$

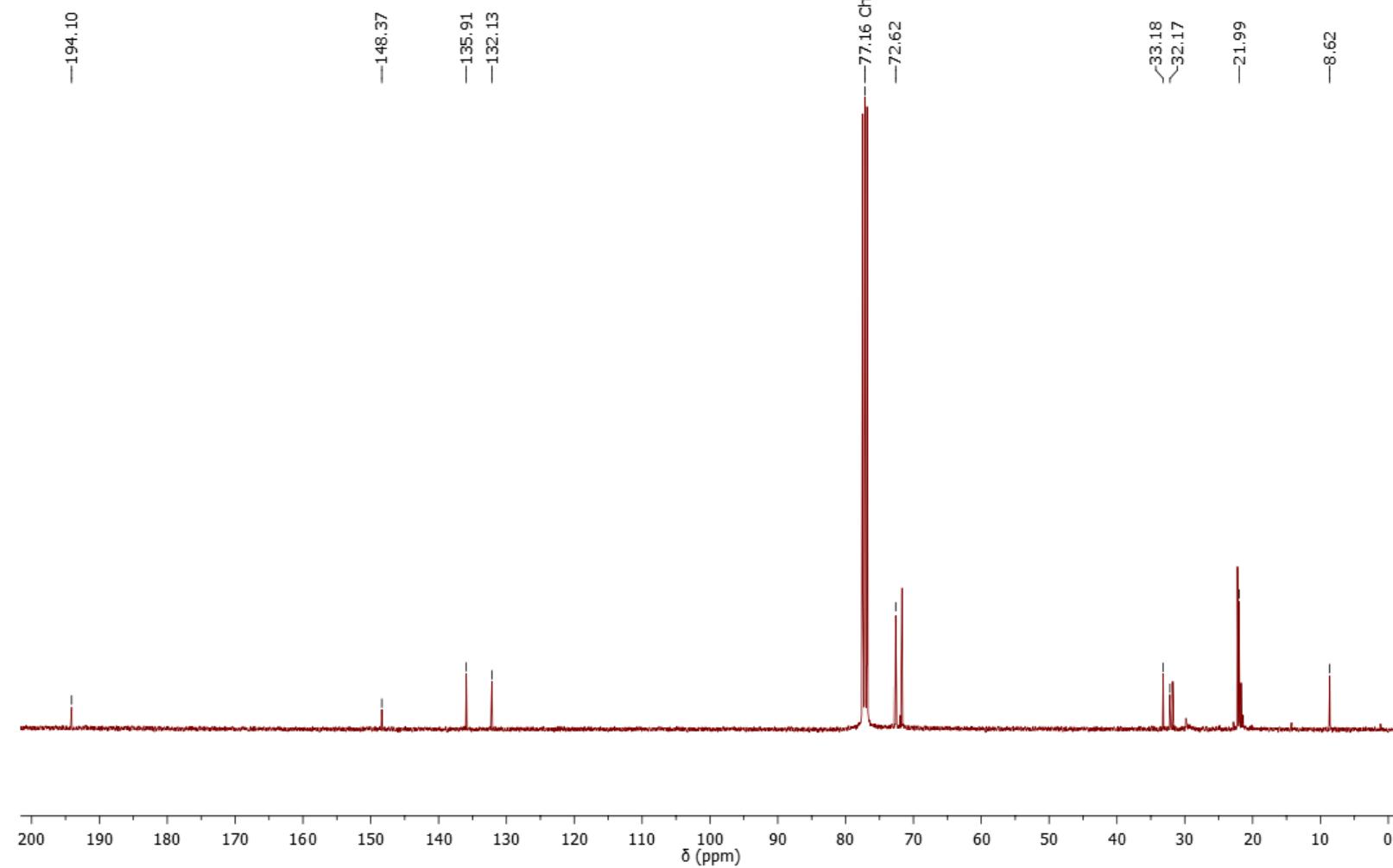
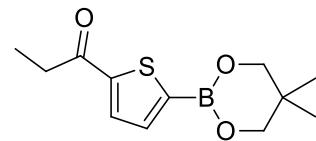
2dd



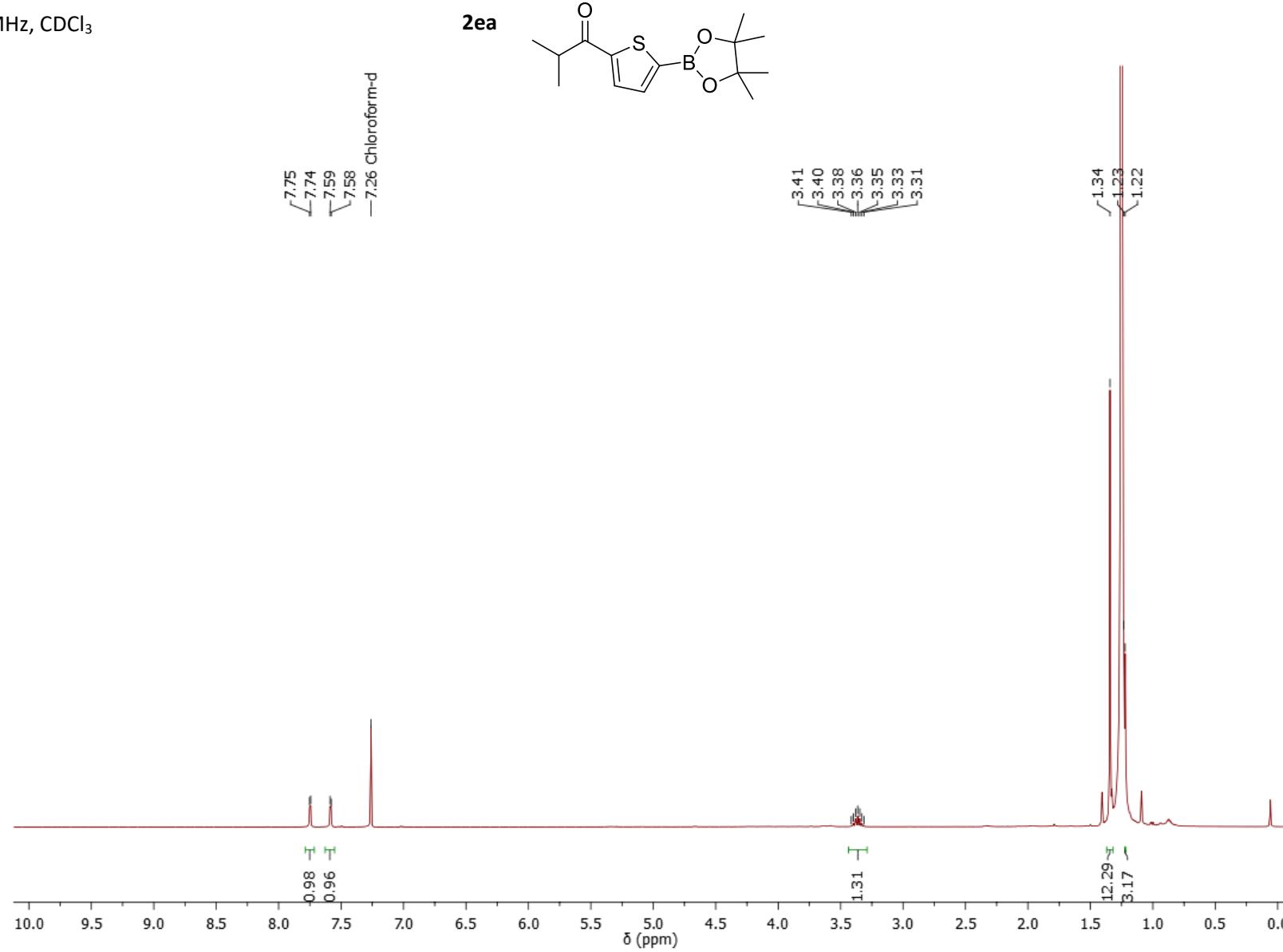
Thiophene boronate esters

$^{13}\text{C}$  101MHz

**2dd**



$^1\text{H}$  400MHz,  $\text{CDCl}_3$



<sup>13</sup>C 101MHz

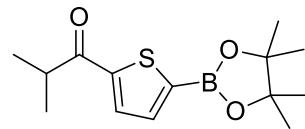
—197.57

—148.66

—137.39

—132.20

**2ea**



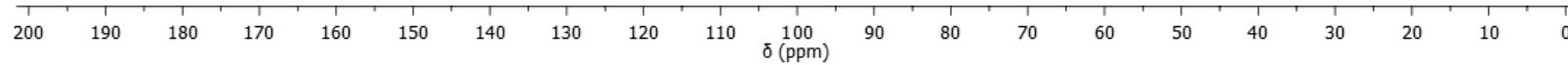
—84.76

77.15 Chloroform

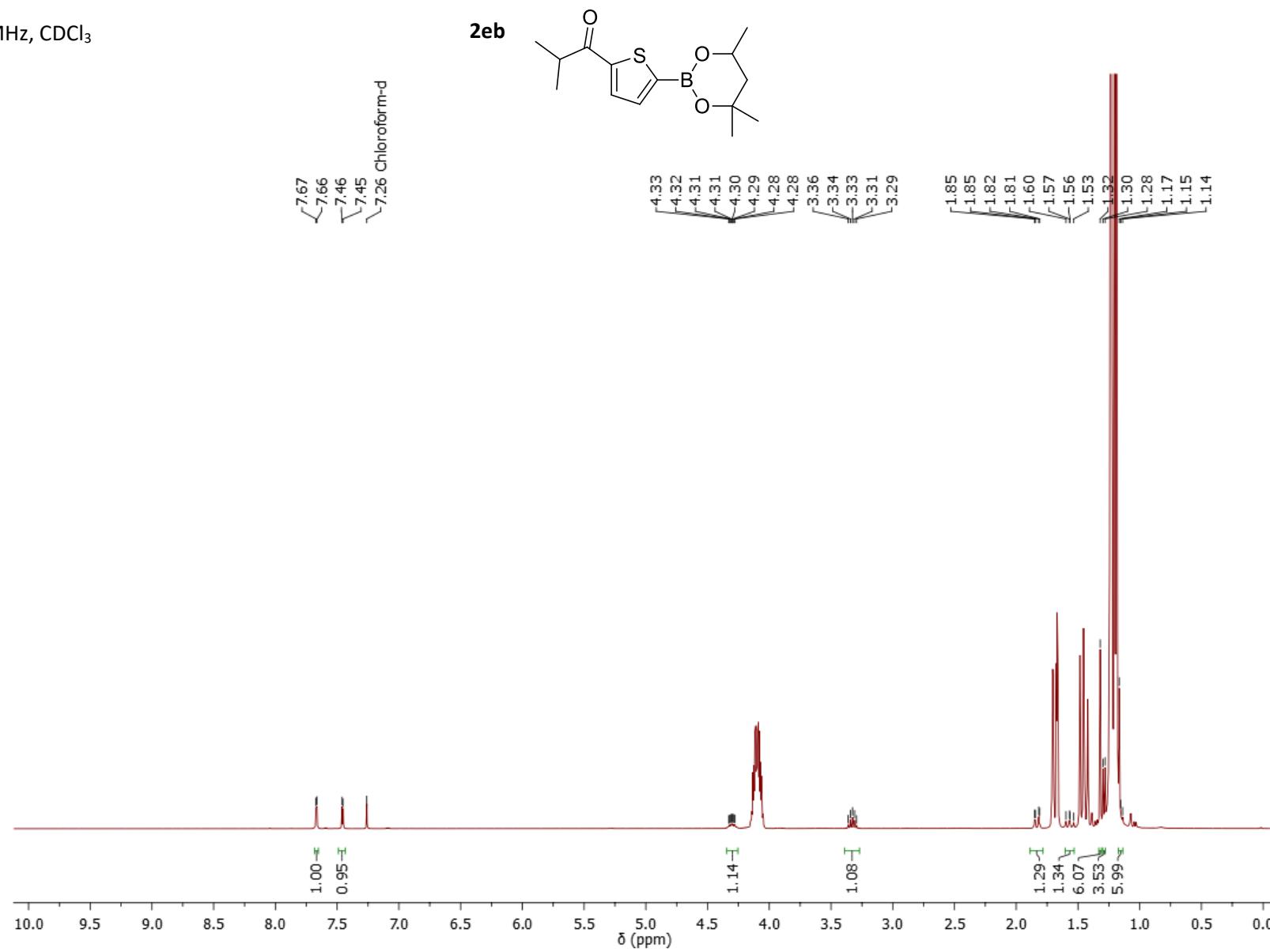
—37.99

—24.88

—19.48

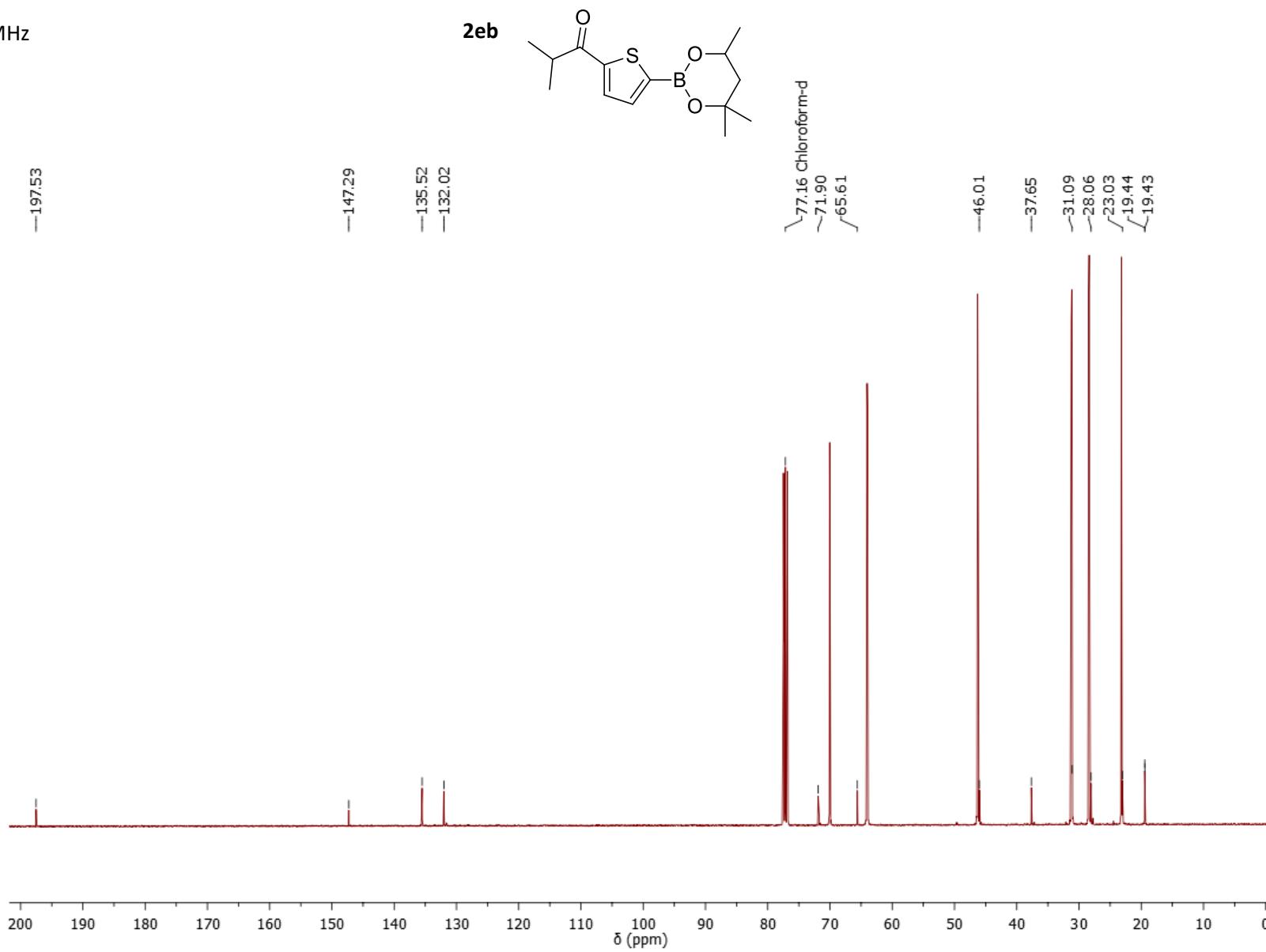


<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



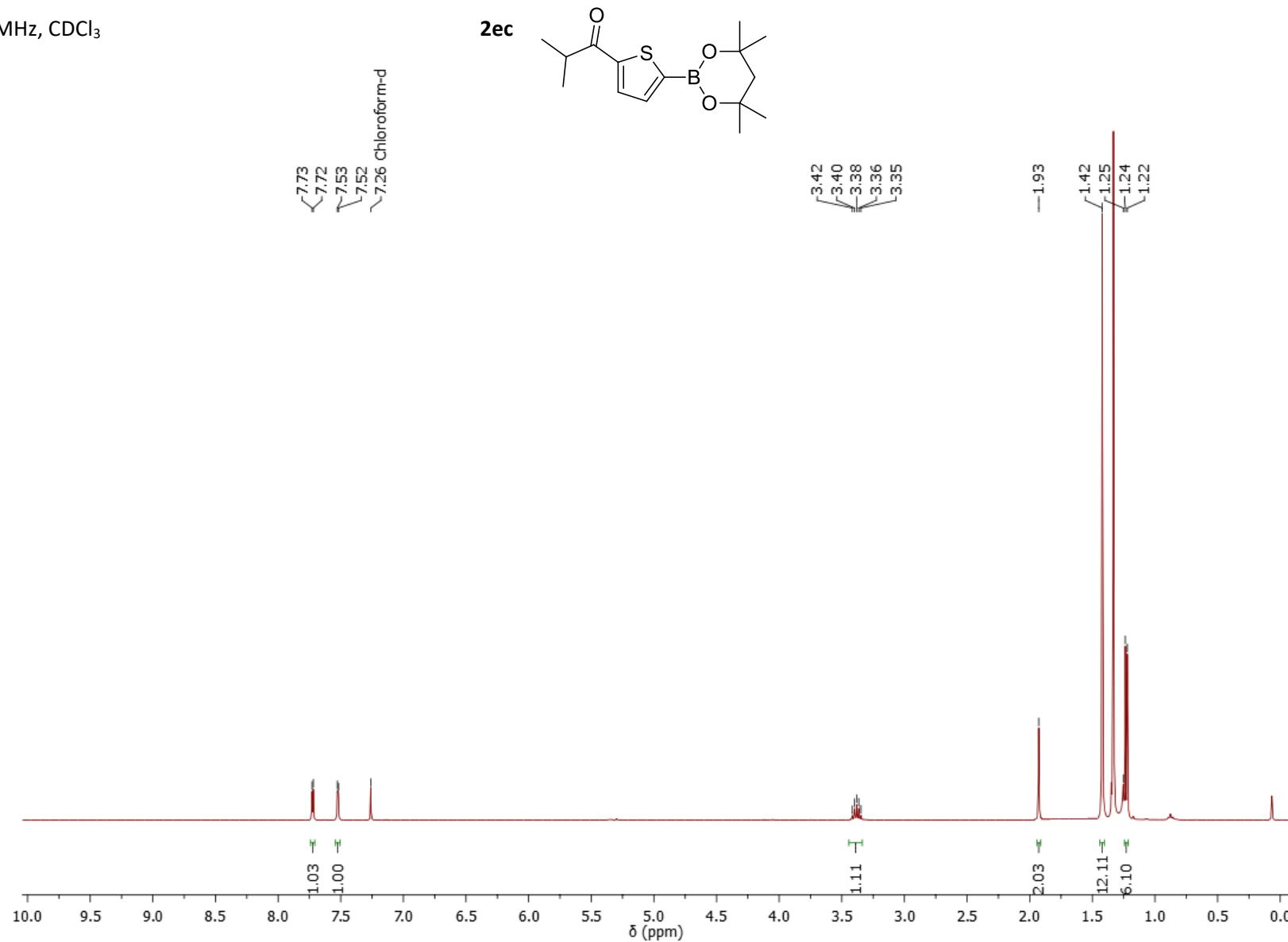
## Thiophene boronate esters

<sup>13</sup>C 101MHz



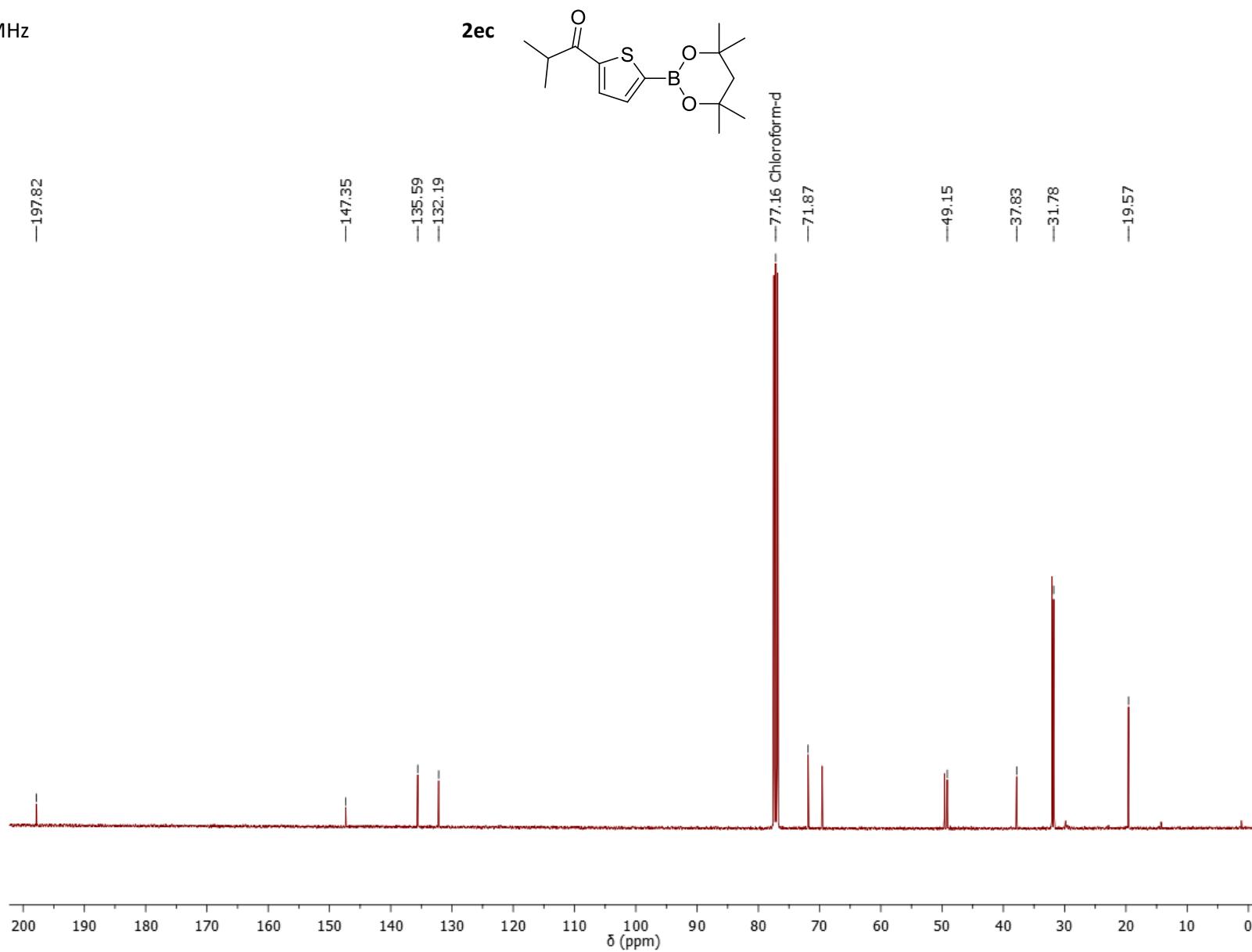
## Thiophene boronate esters

$^1\text{H}$  400MHz,  $\text{CDCl}_3$



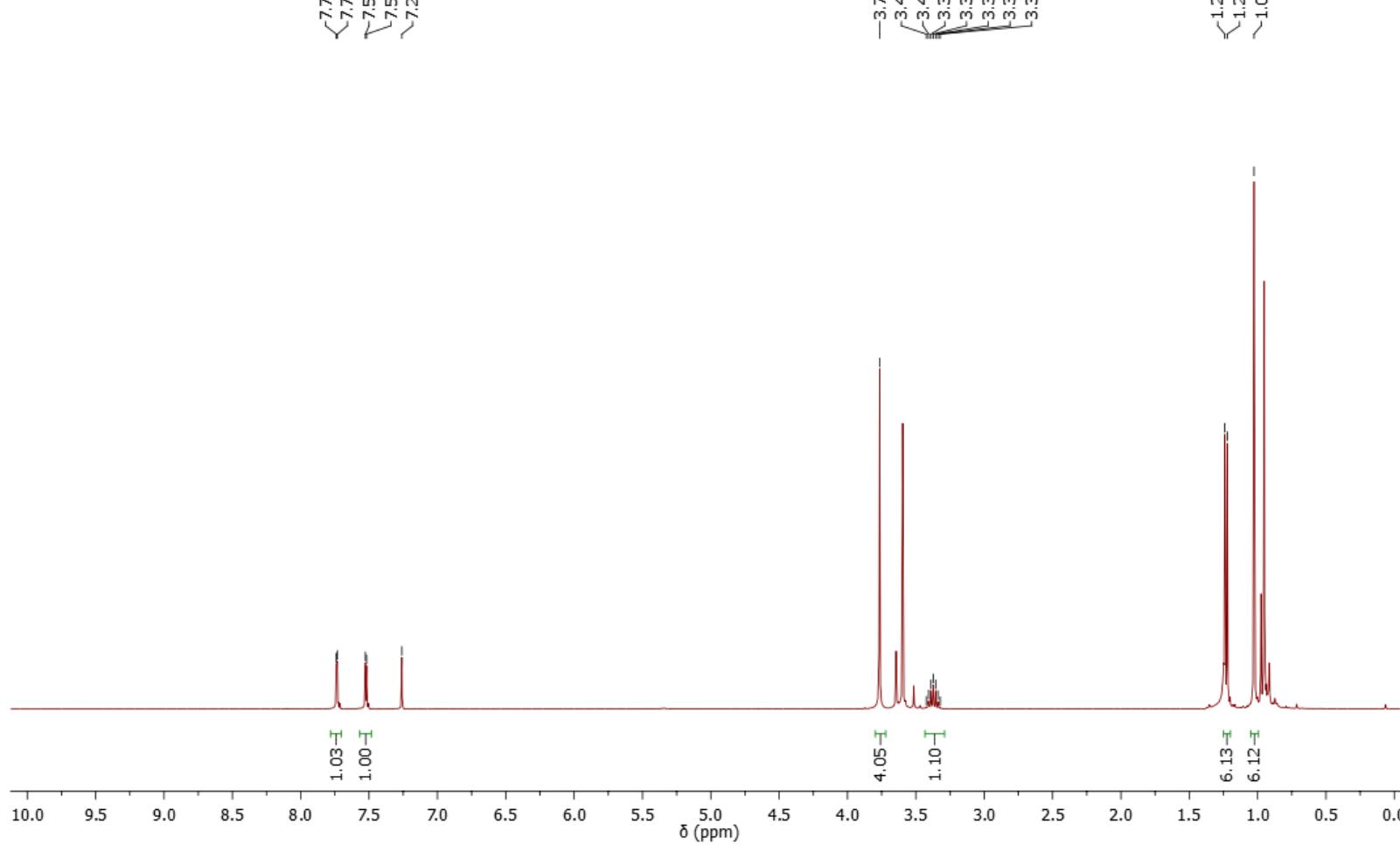
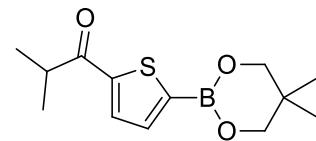
## Thiophene boronate esters

<sup>13</sup>C 101MHz



$^1\text{H}$  400MHz,  $\text{CDCl}_3$

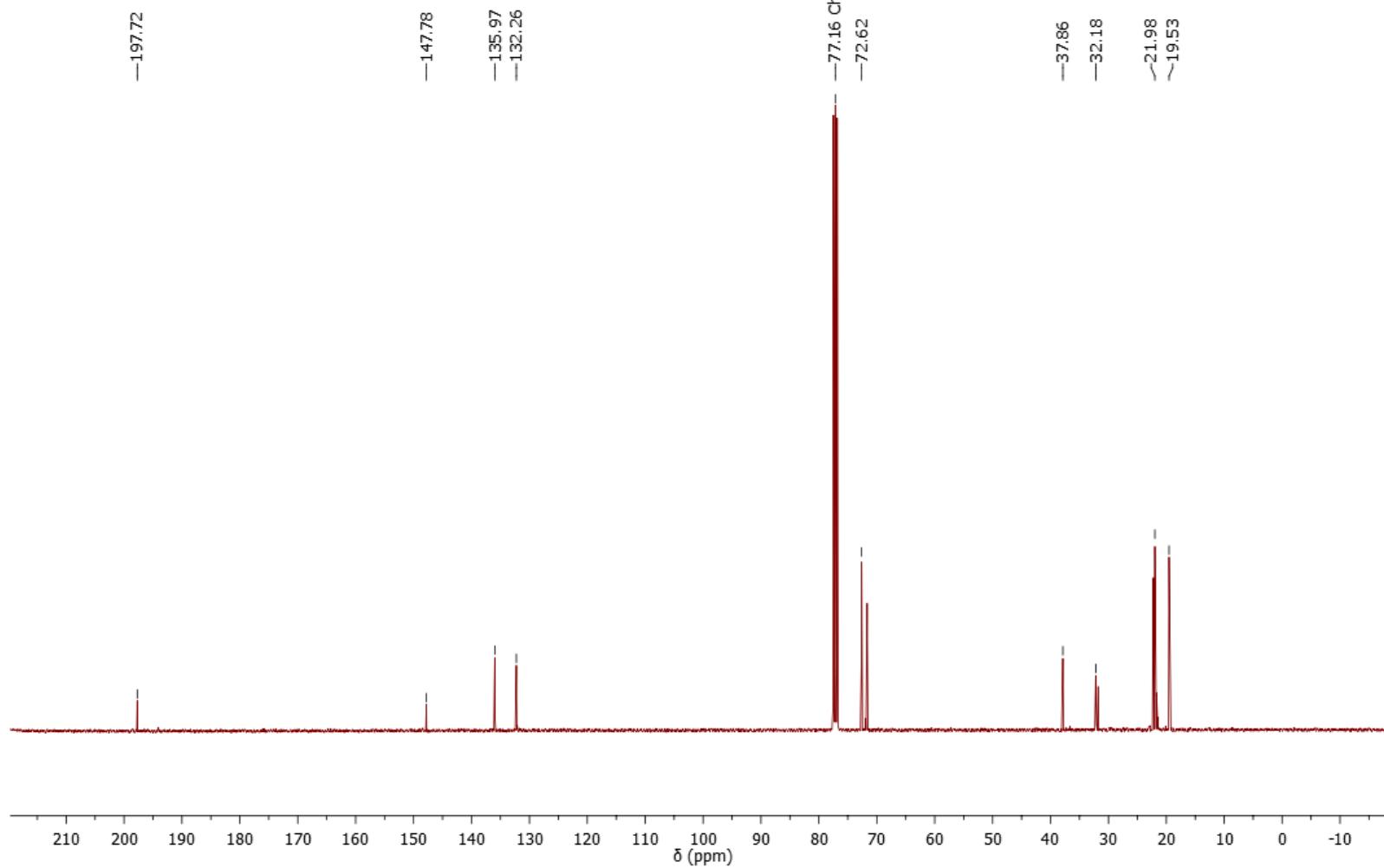
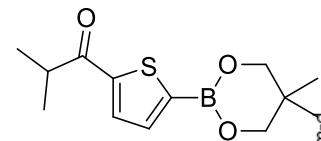
**2ed**



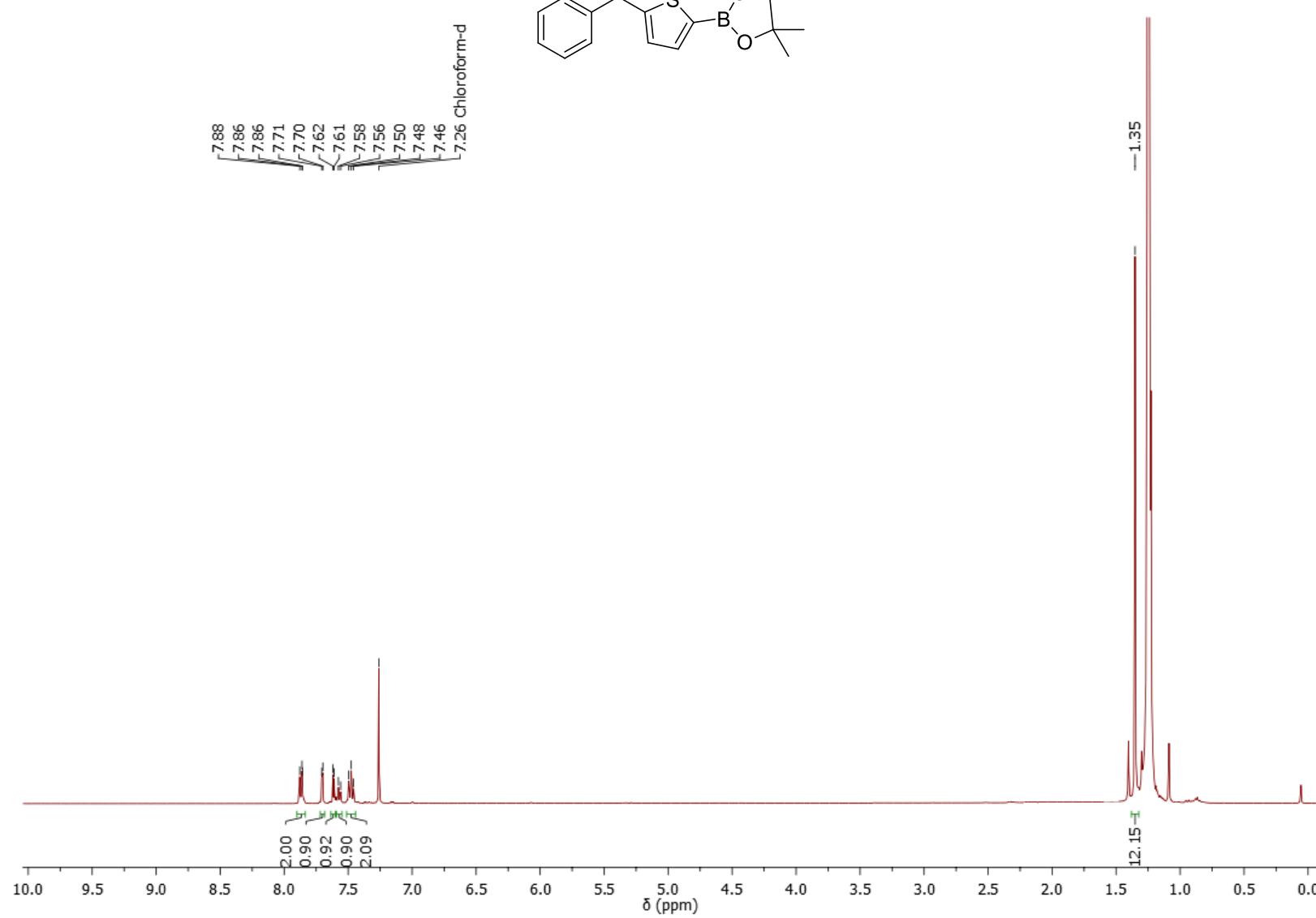
Thiophene boronate esters

<sup>13</sup>C 101MHz

2ed



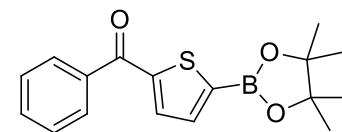
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



<sup>13</sup>C 101MHz

—188.22

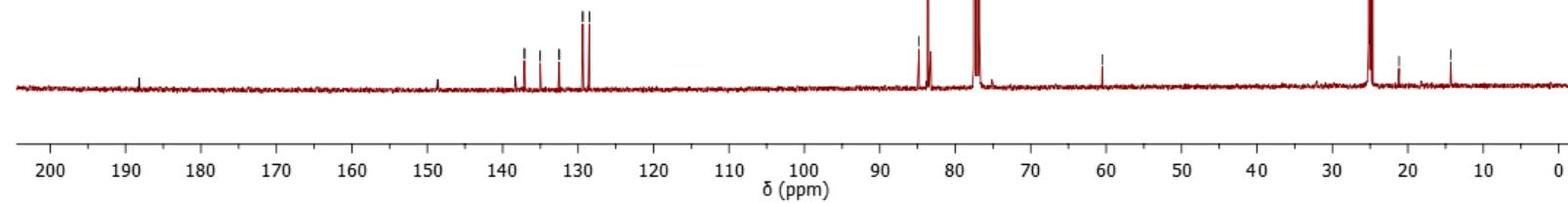
**2fa**



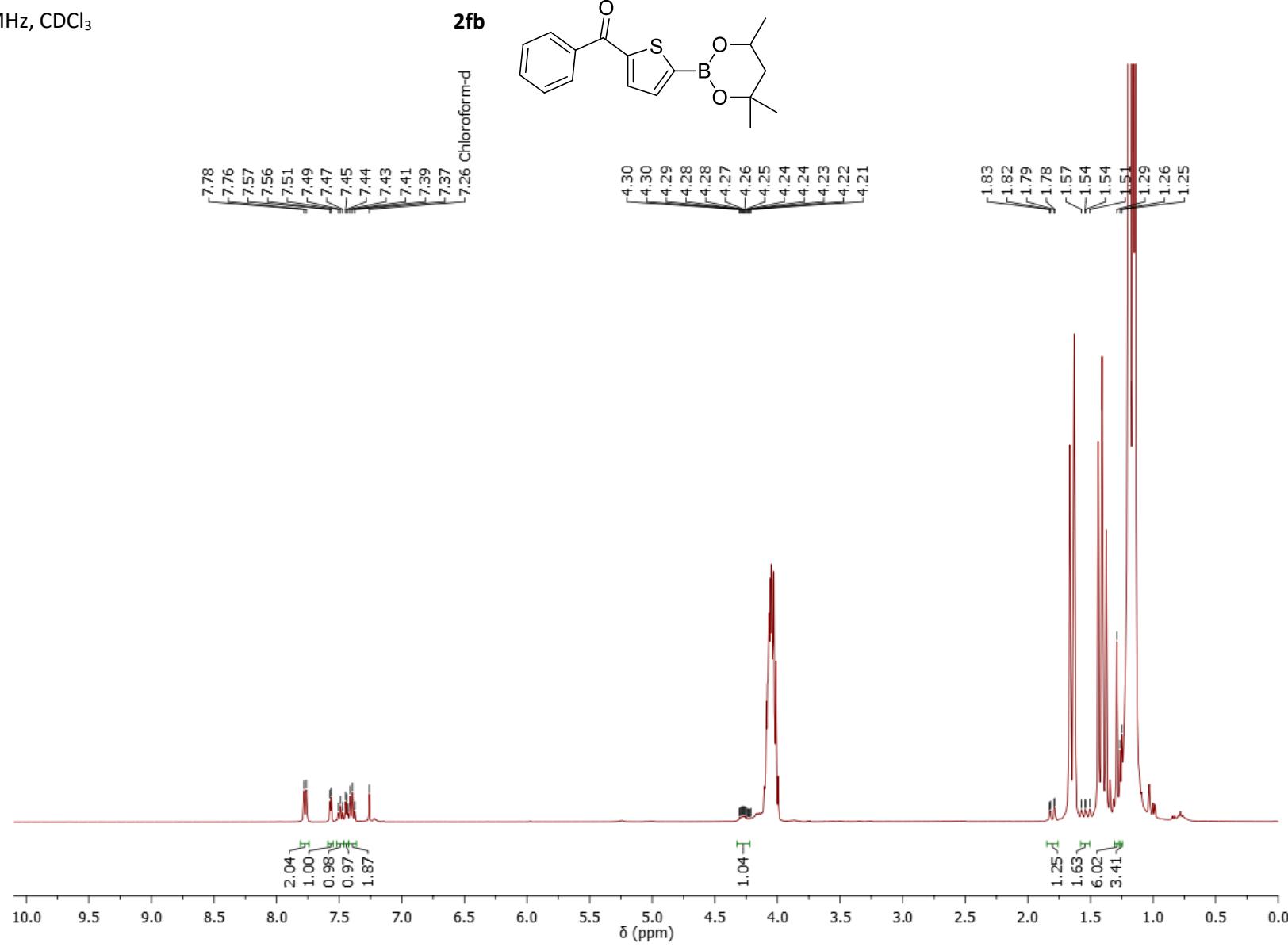
—84.81  
—77.48  
—77.35 *Chloroform*  
—76.84

—60.51

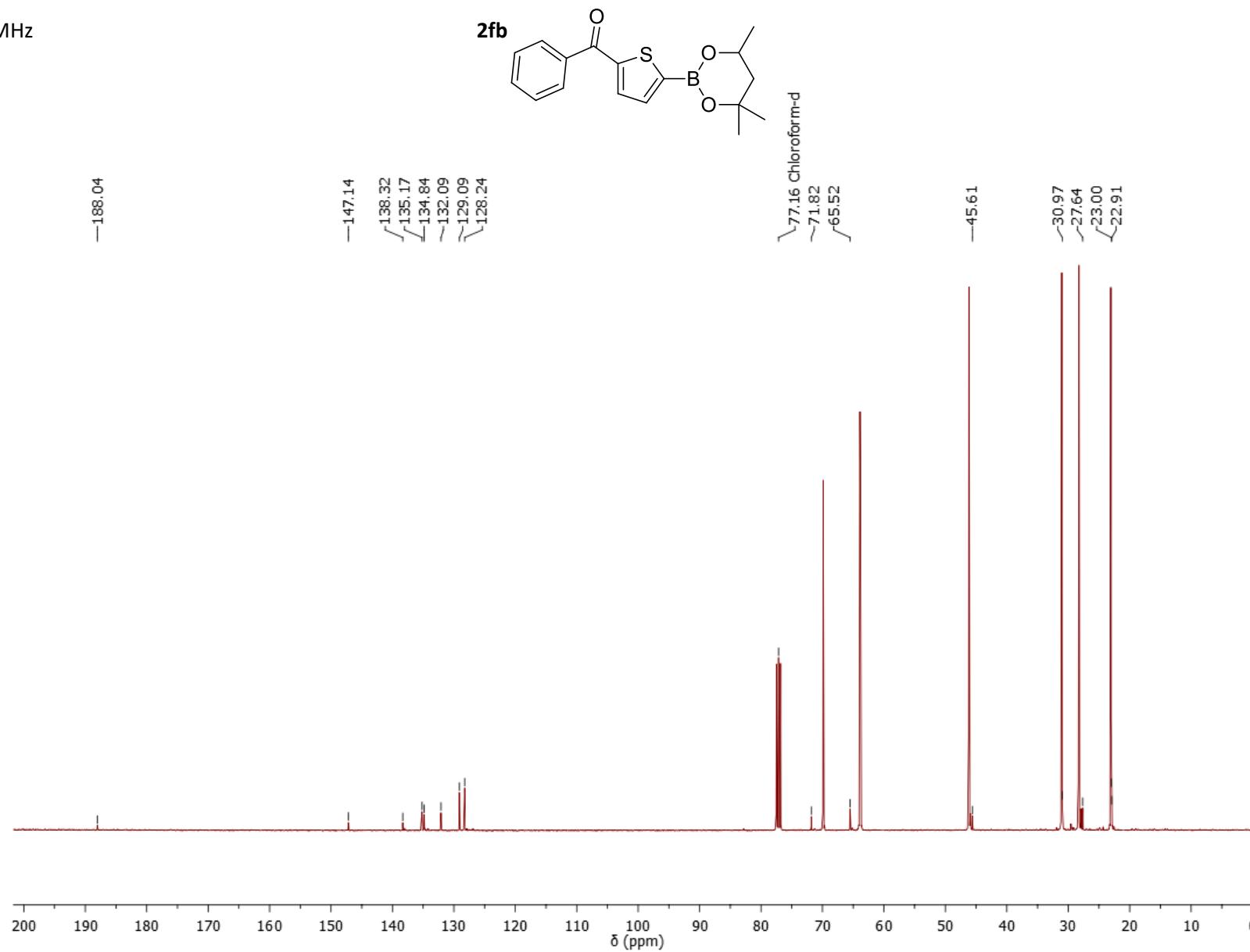
—24.68  
—21.17  
—14.31



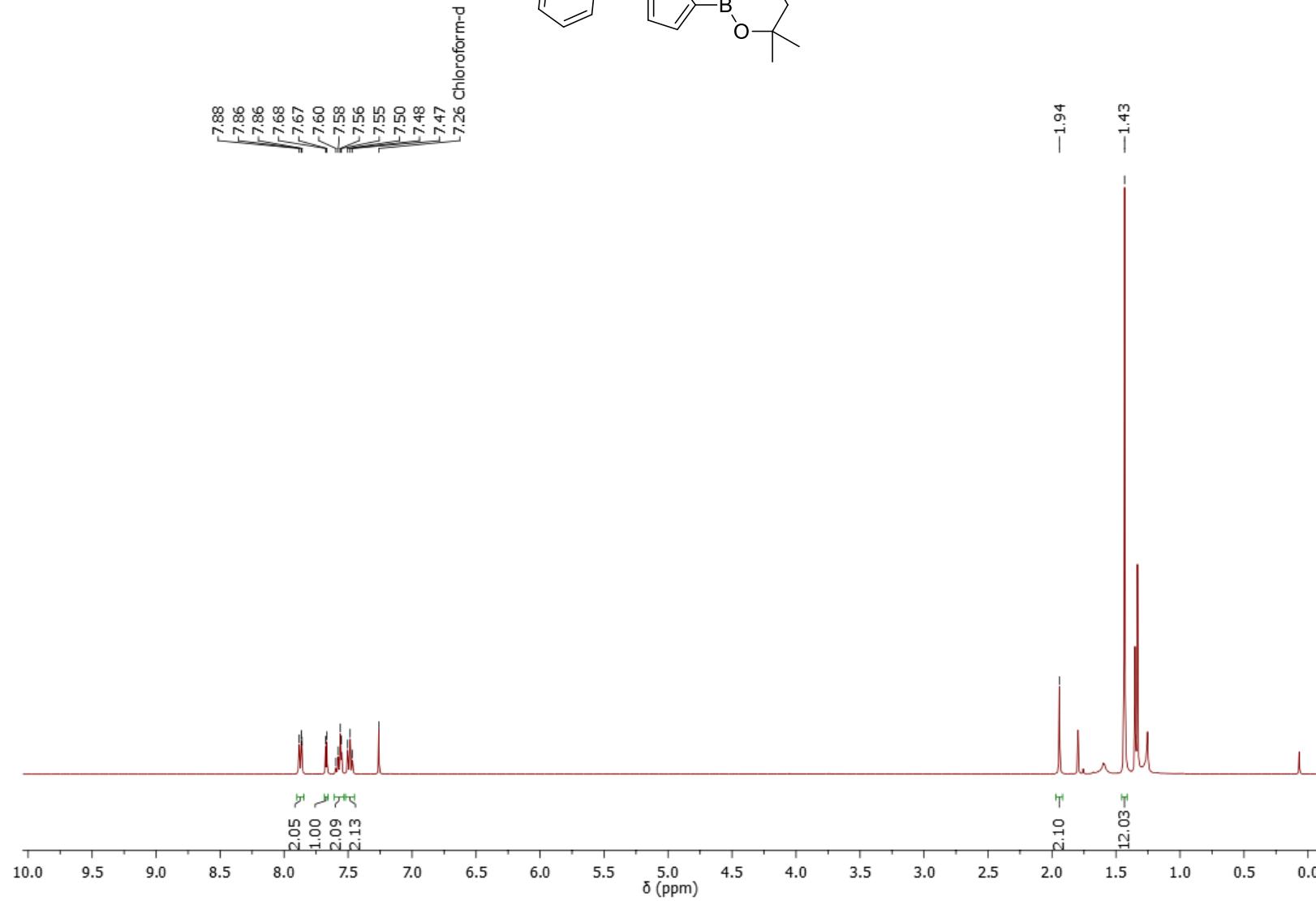
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



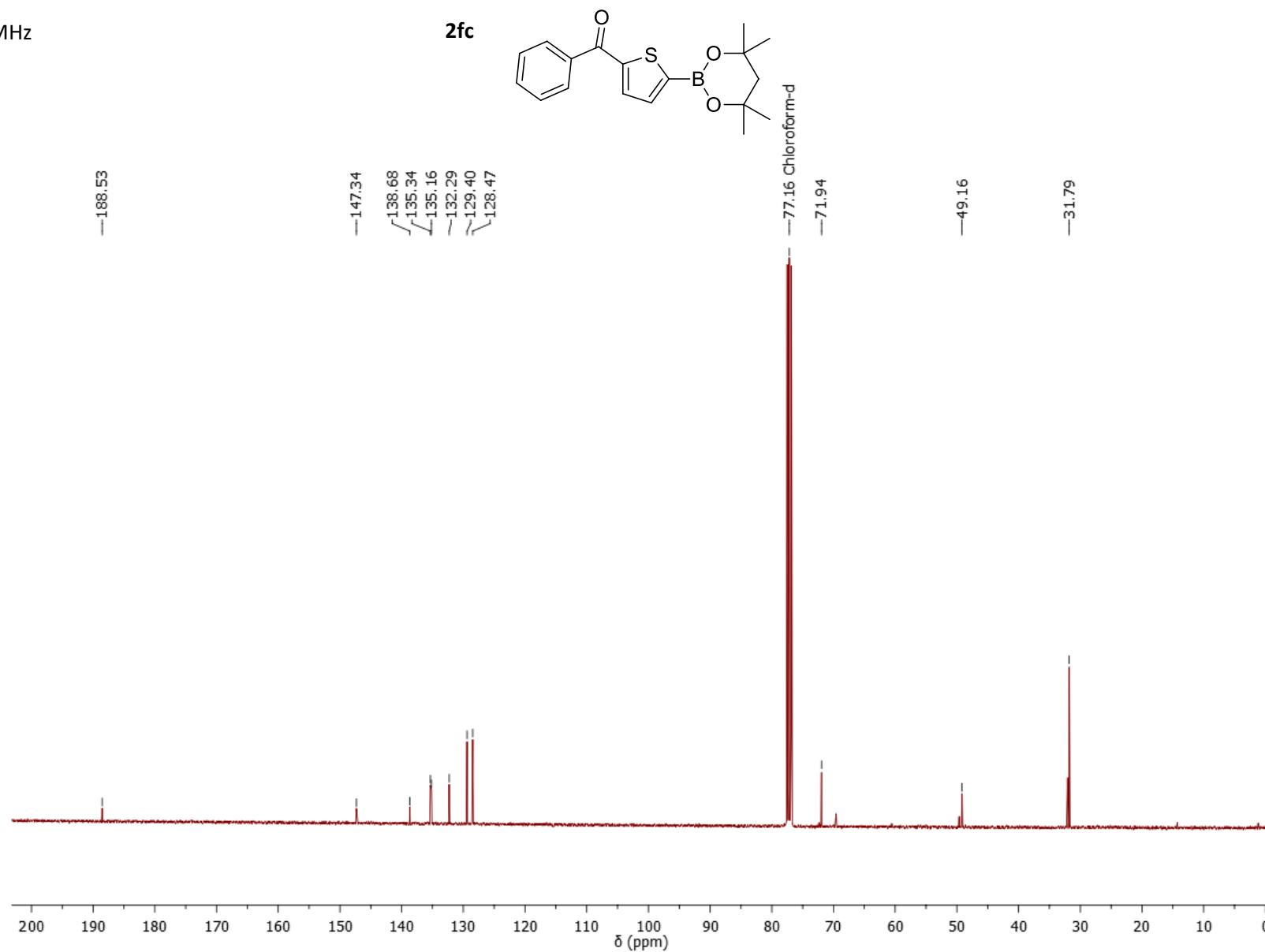
<sup>13</sup>C 101MHz



$^1\text{H}$  400MHz,  $\text{CDCl}_3$

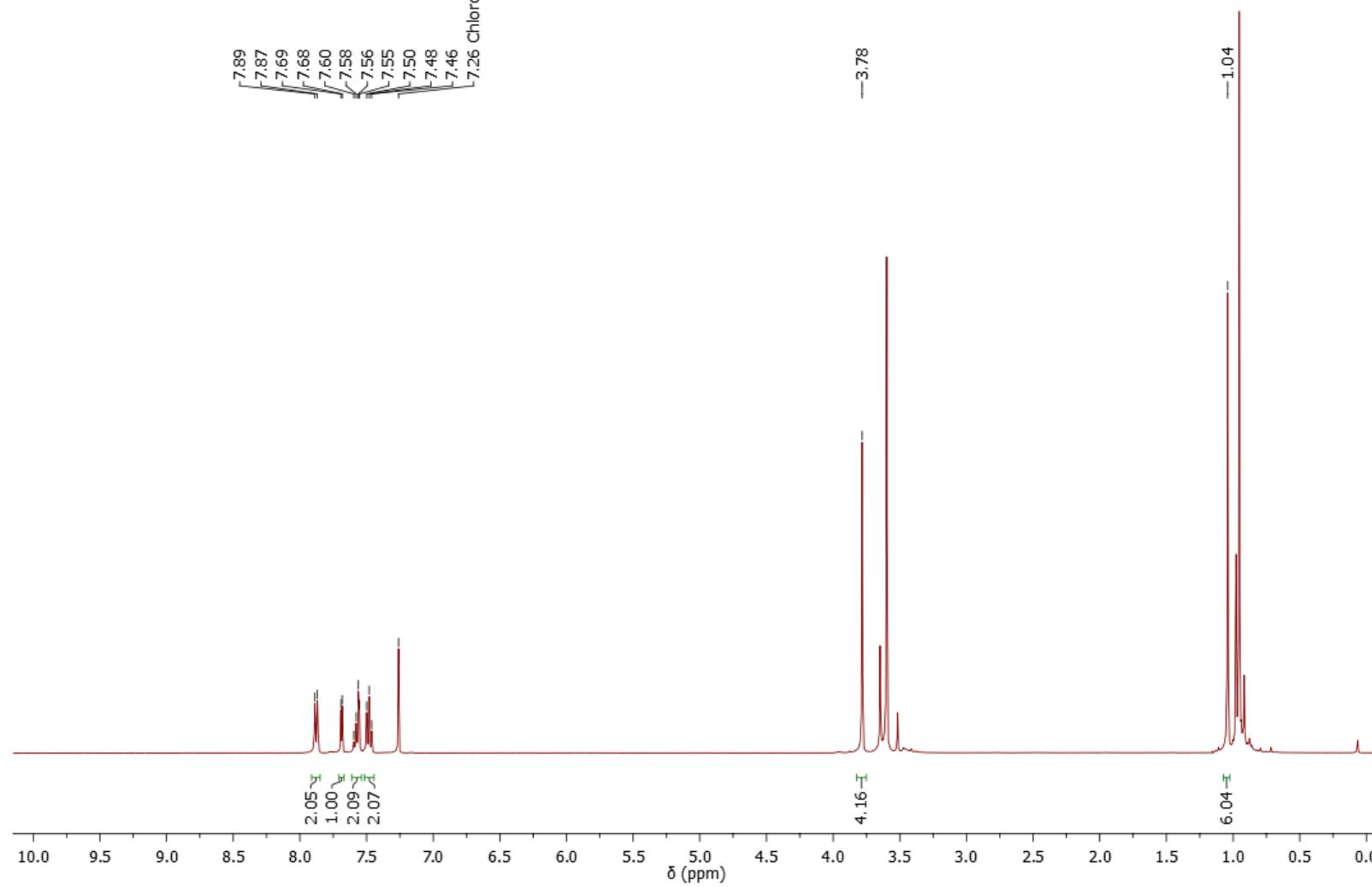
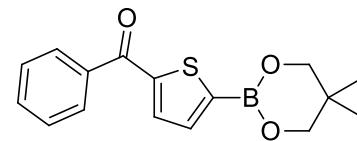


<sup>13</sup>C 101MHz



$^1\text{H}$  400MHz,  $\text{CDCl}_3$

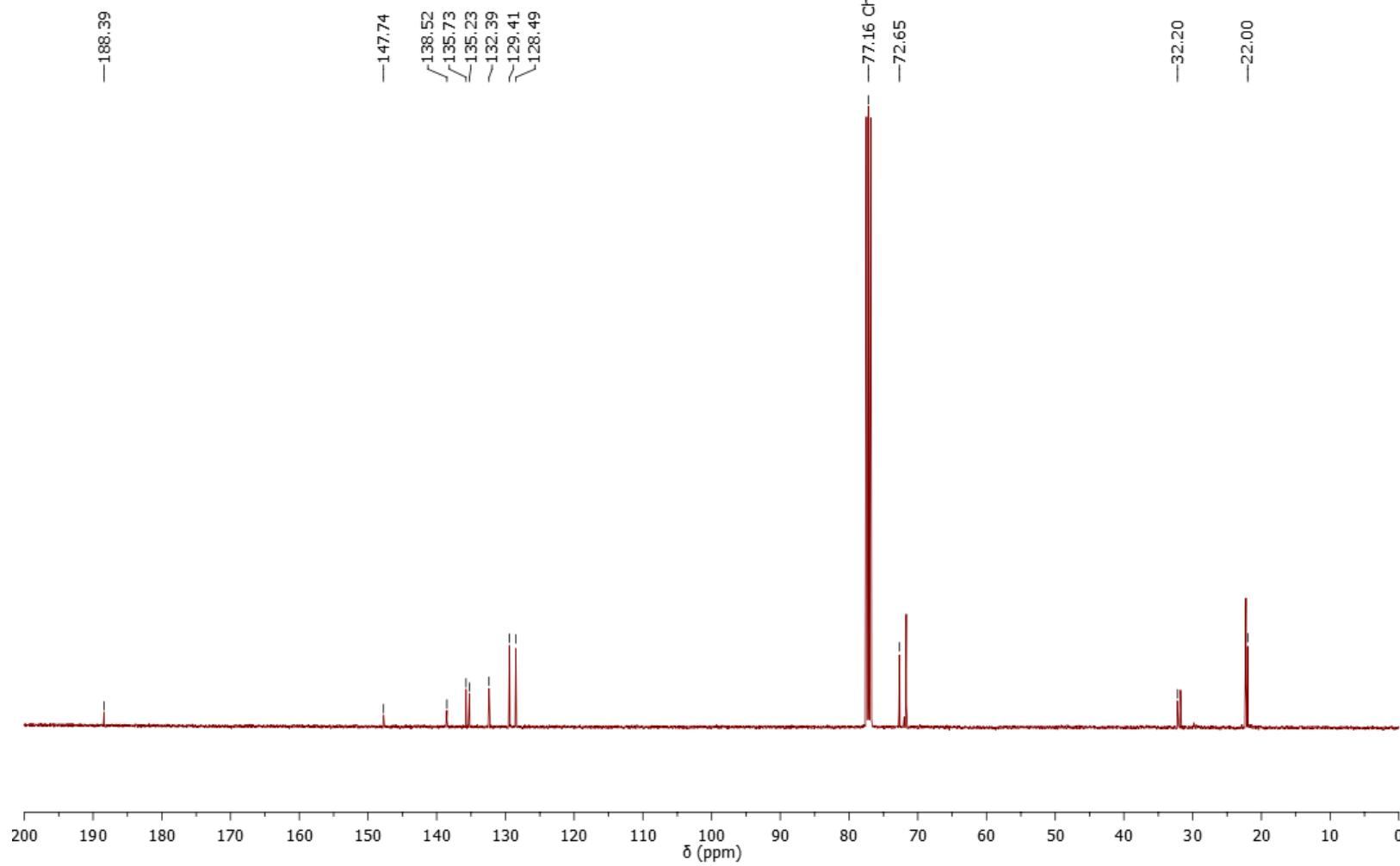
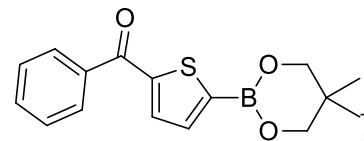
2fd



## Thiophene boronate esters

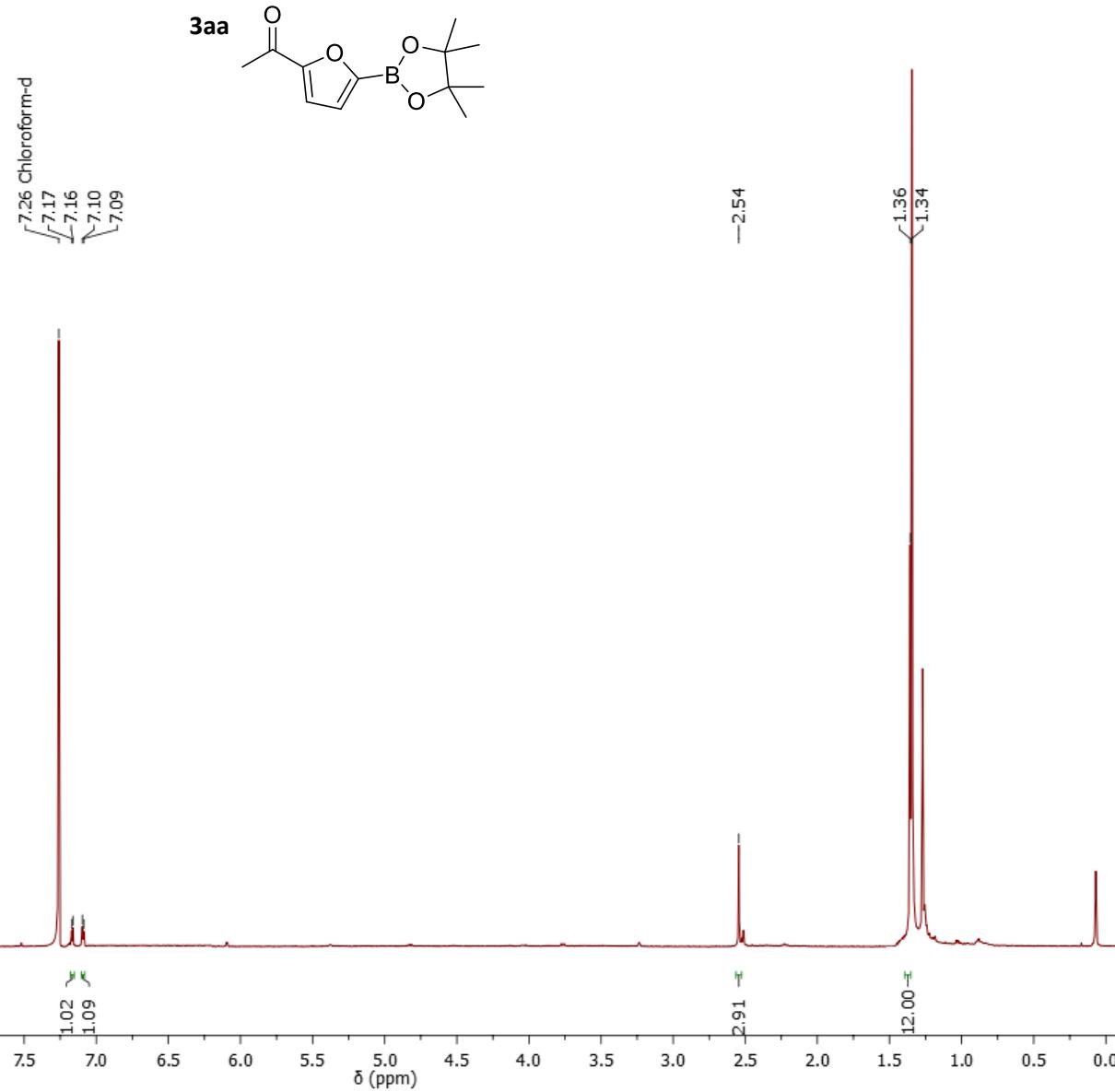
<sup>13</sup>C 101MHz

2fd

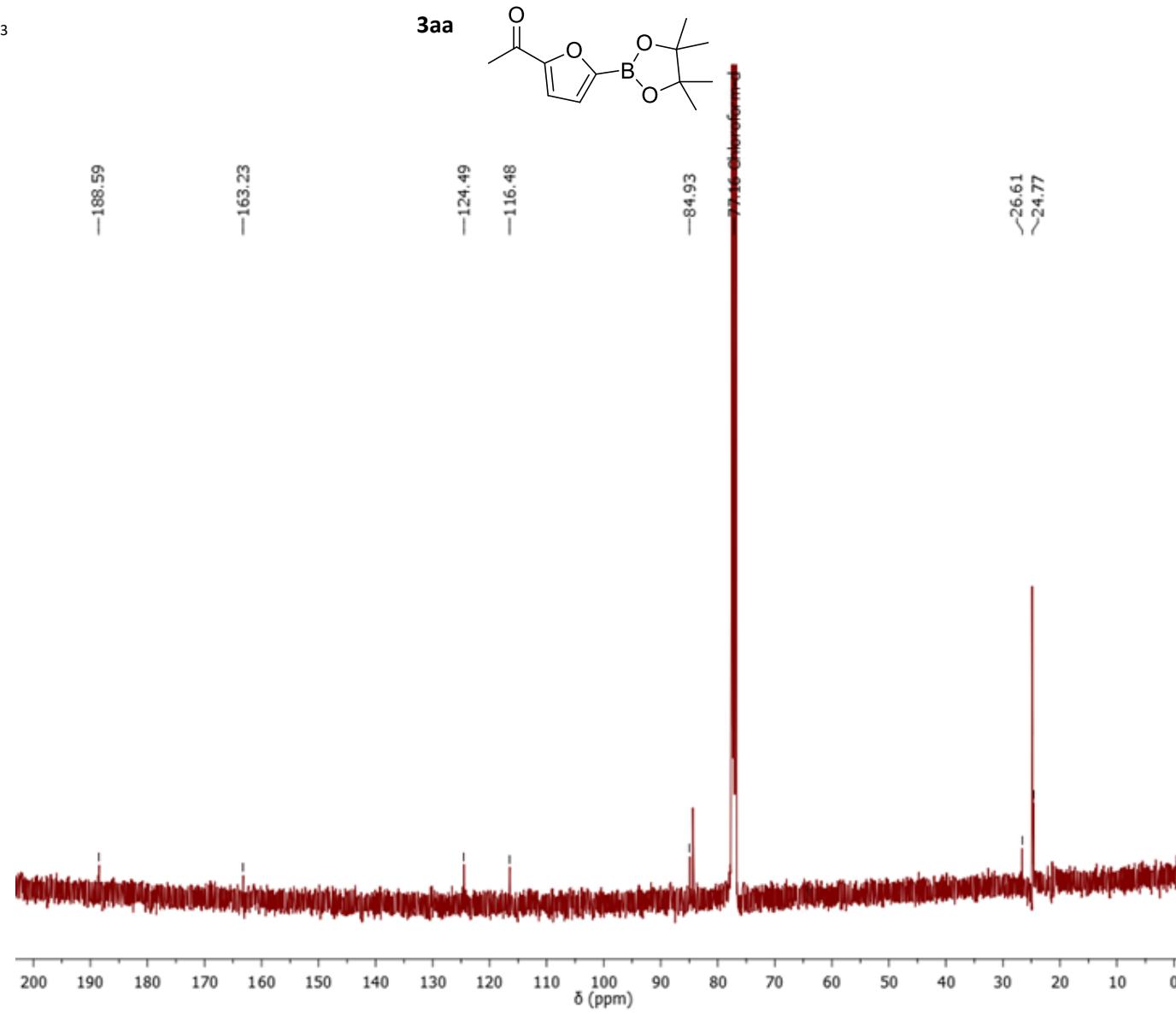


S100

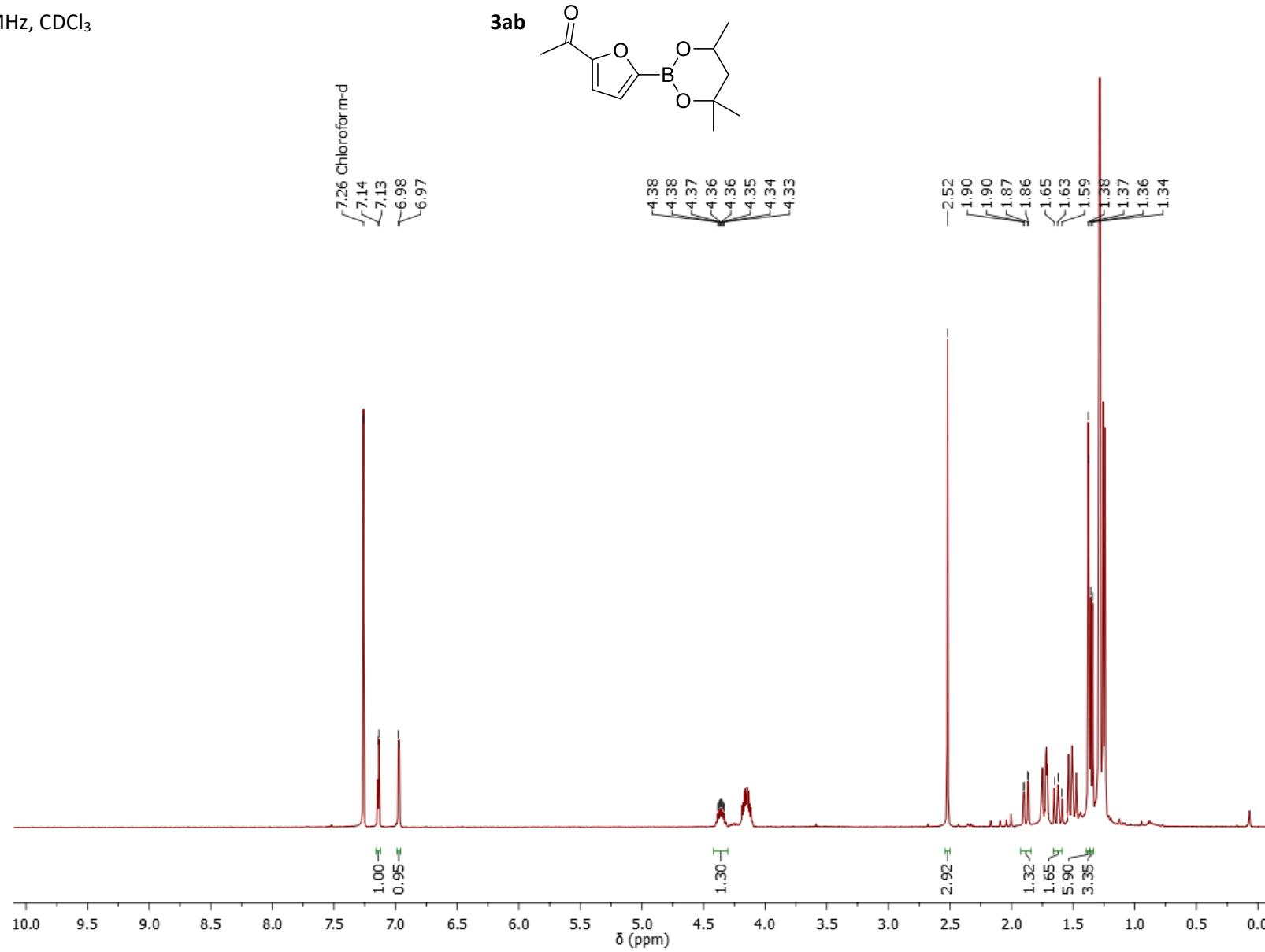
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



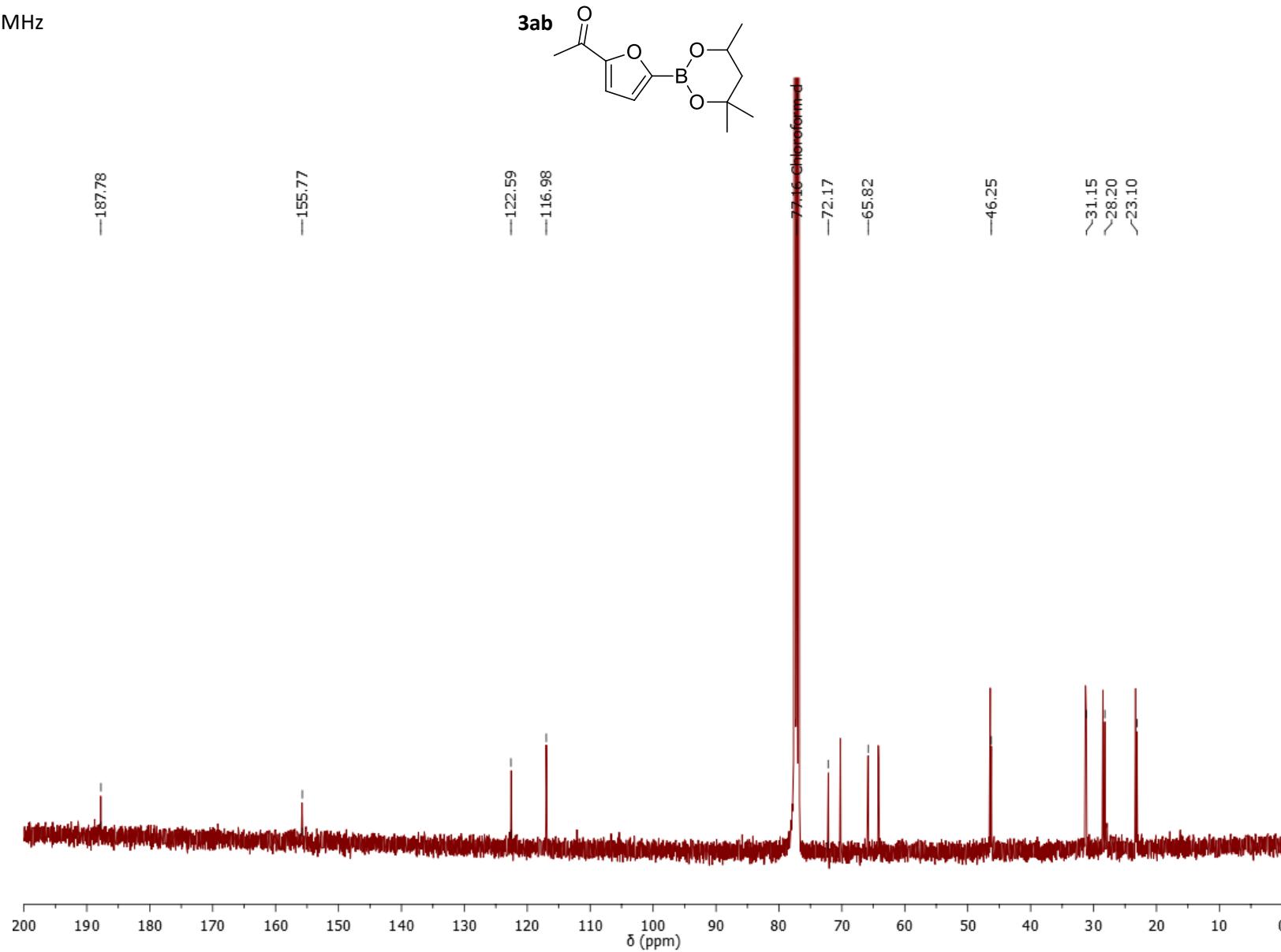
$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$



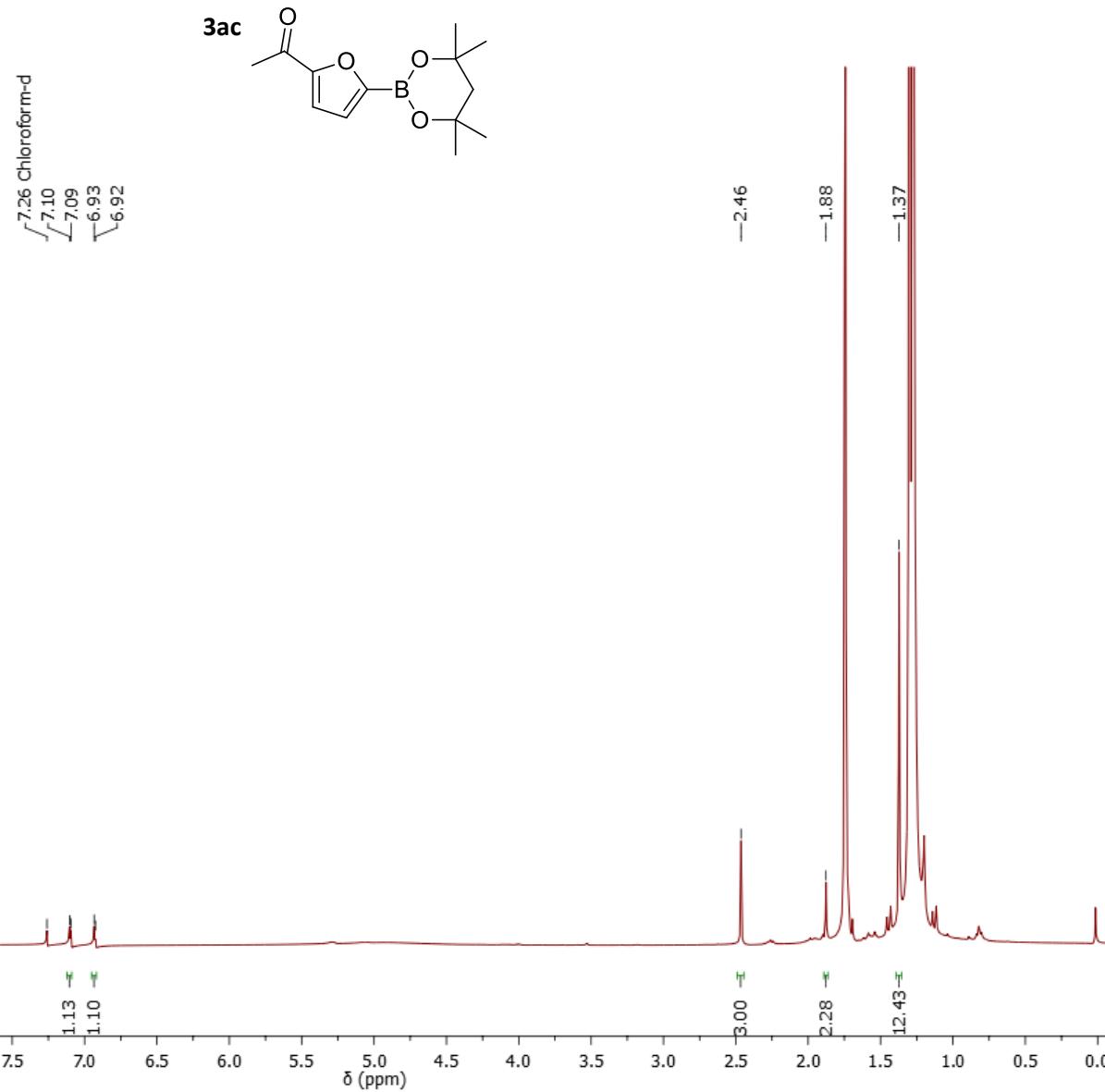
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



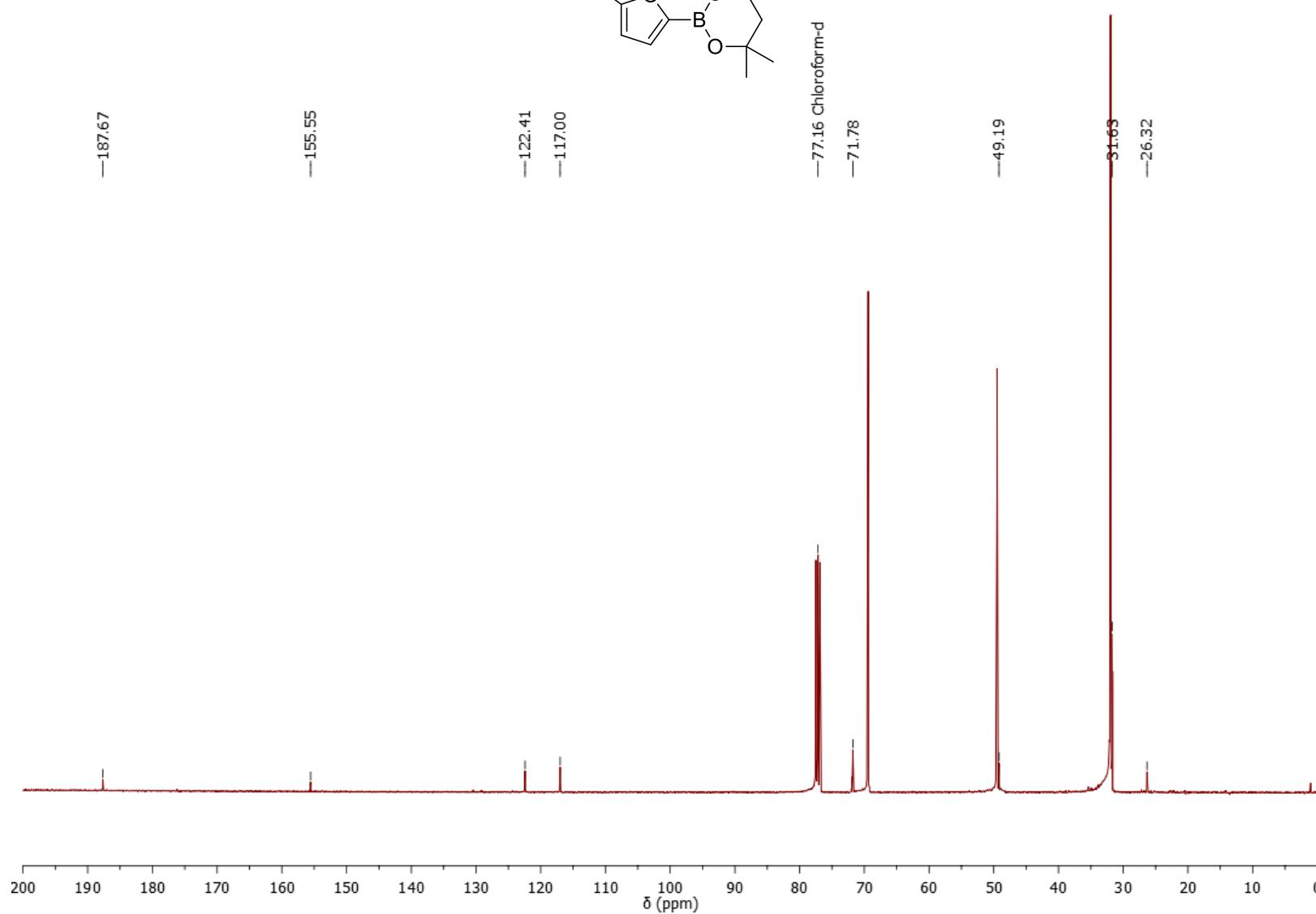
$^{13}\text{C}$  101MHz



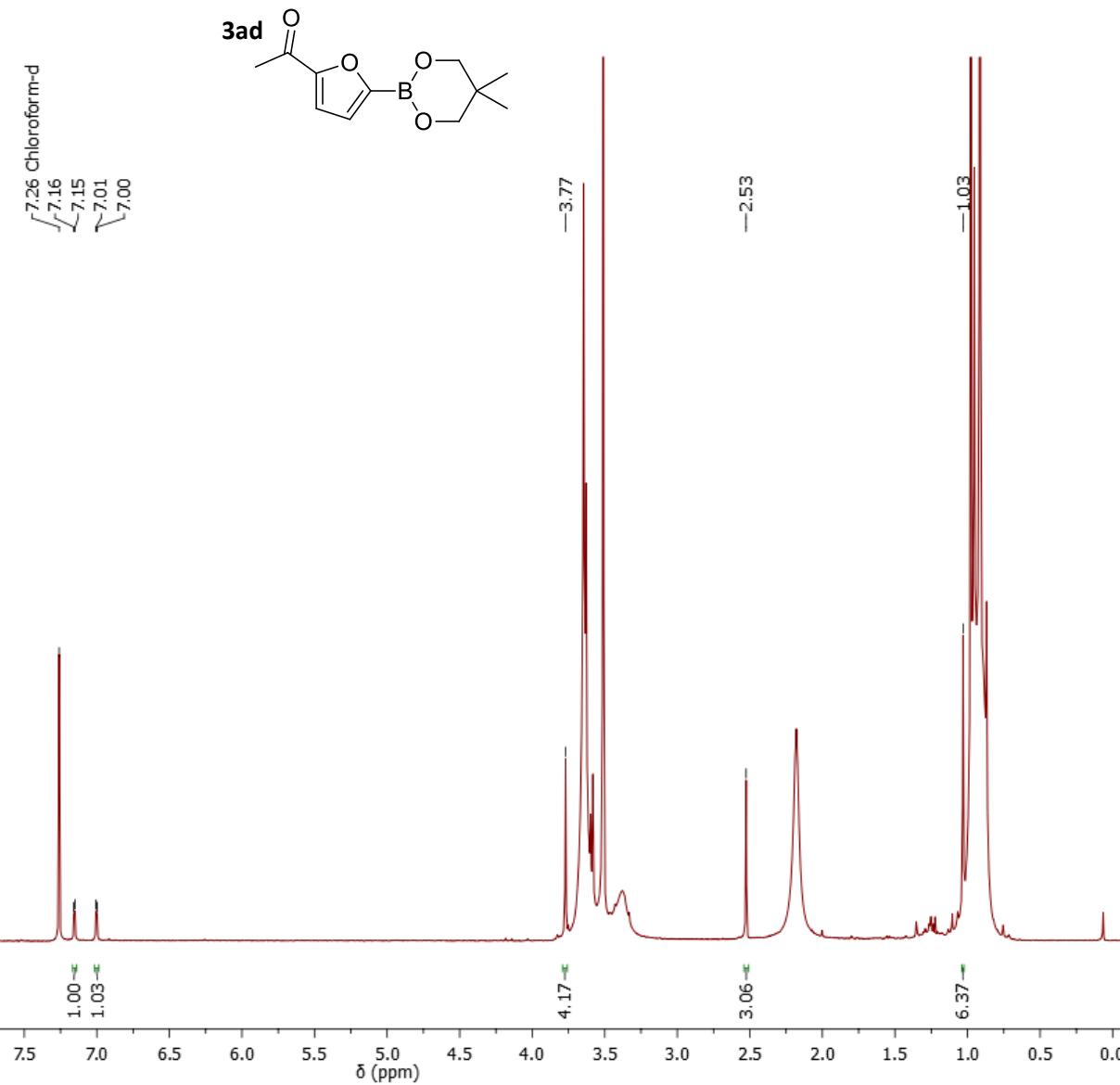
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



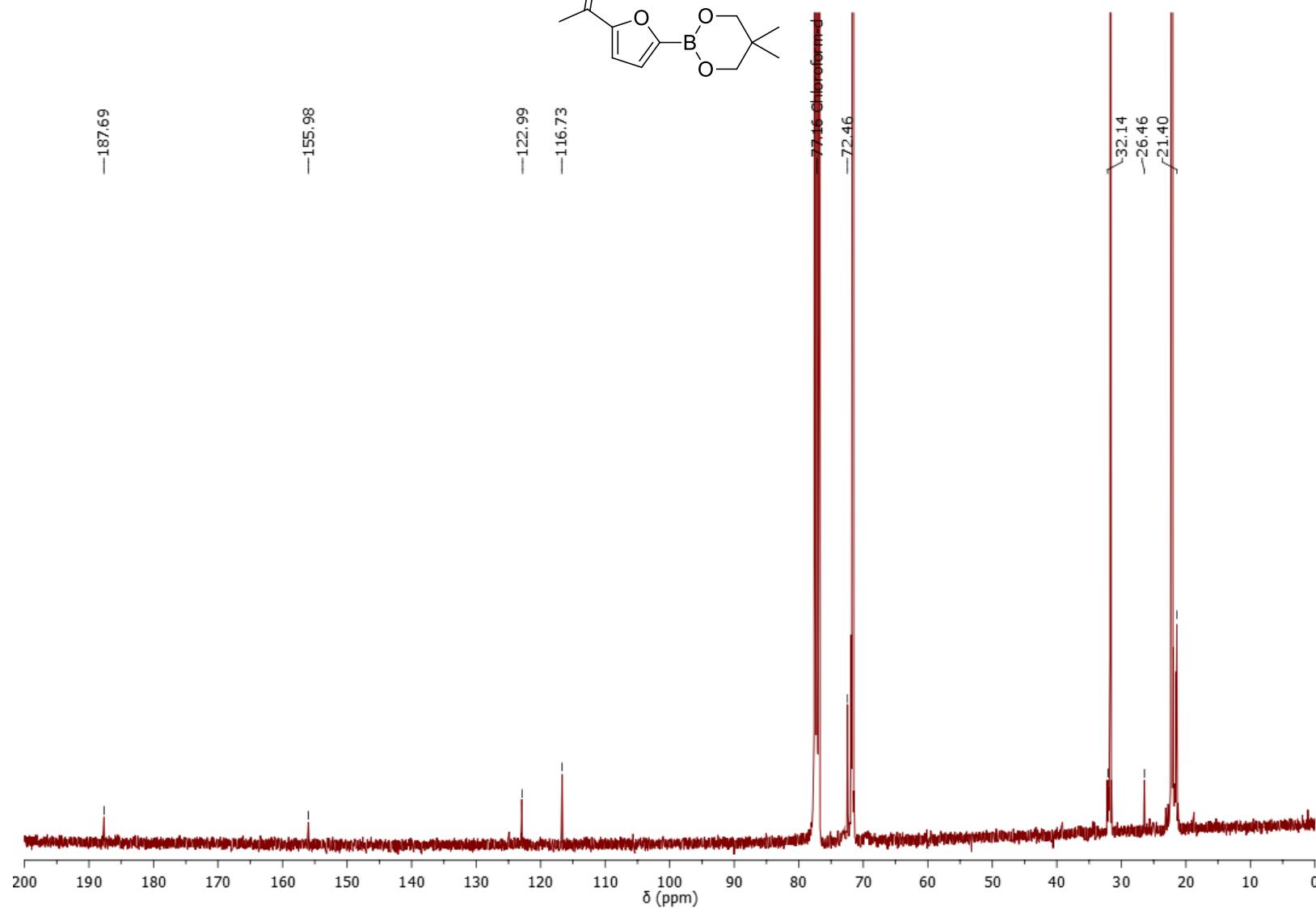
<sup>13</sup>C 101MHz



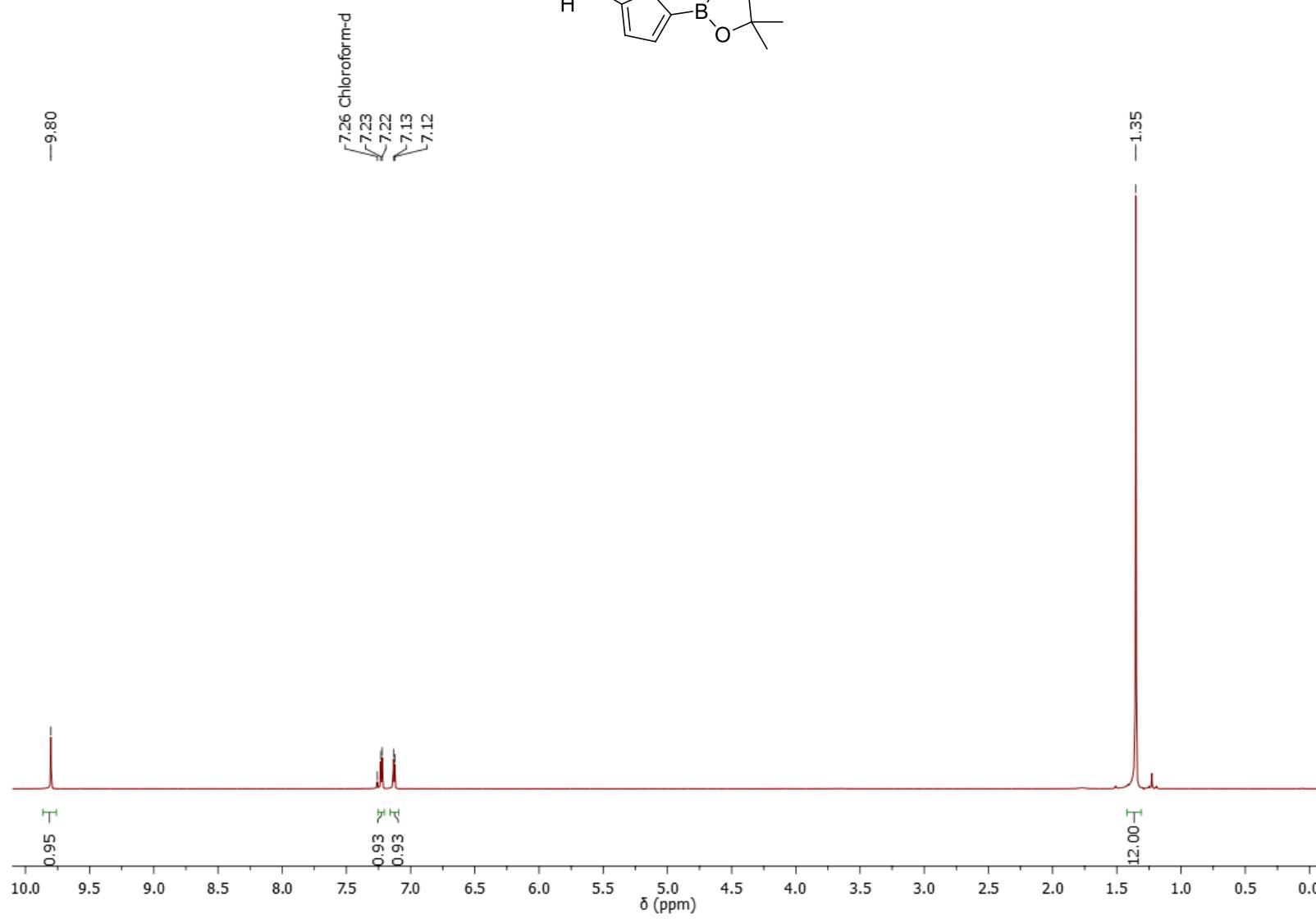
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



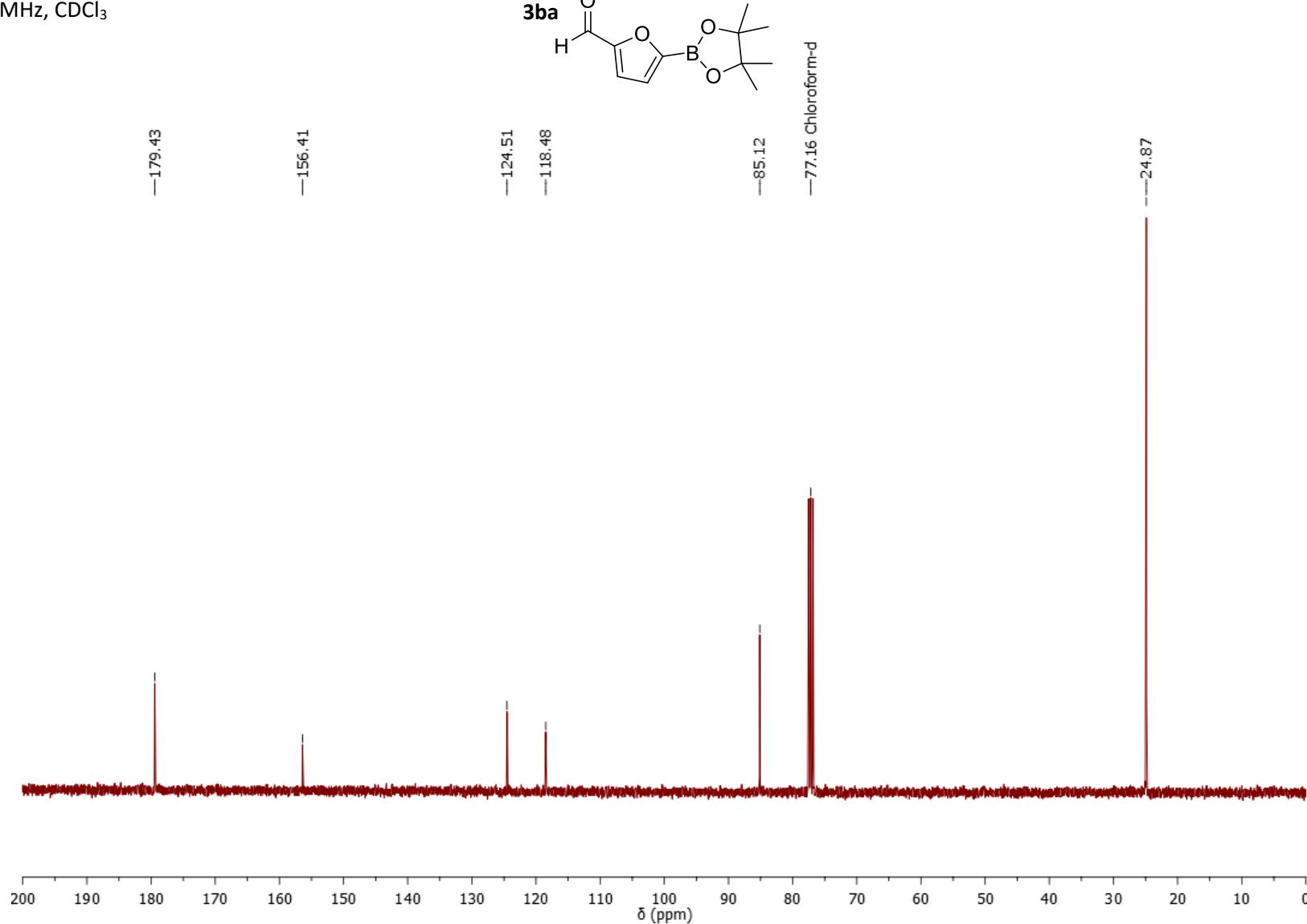
<sup>13</sup>C 101MHz



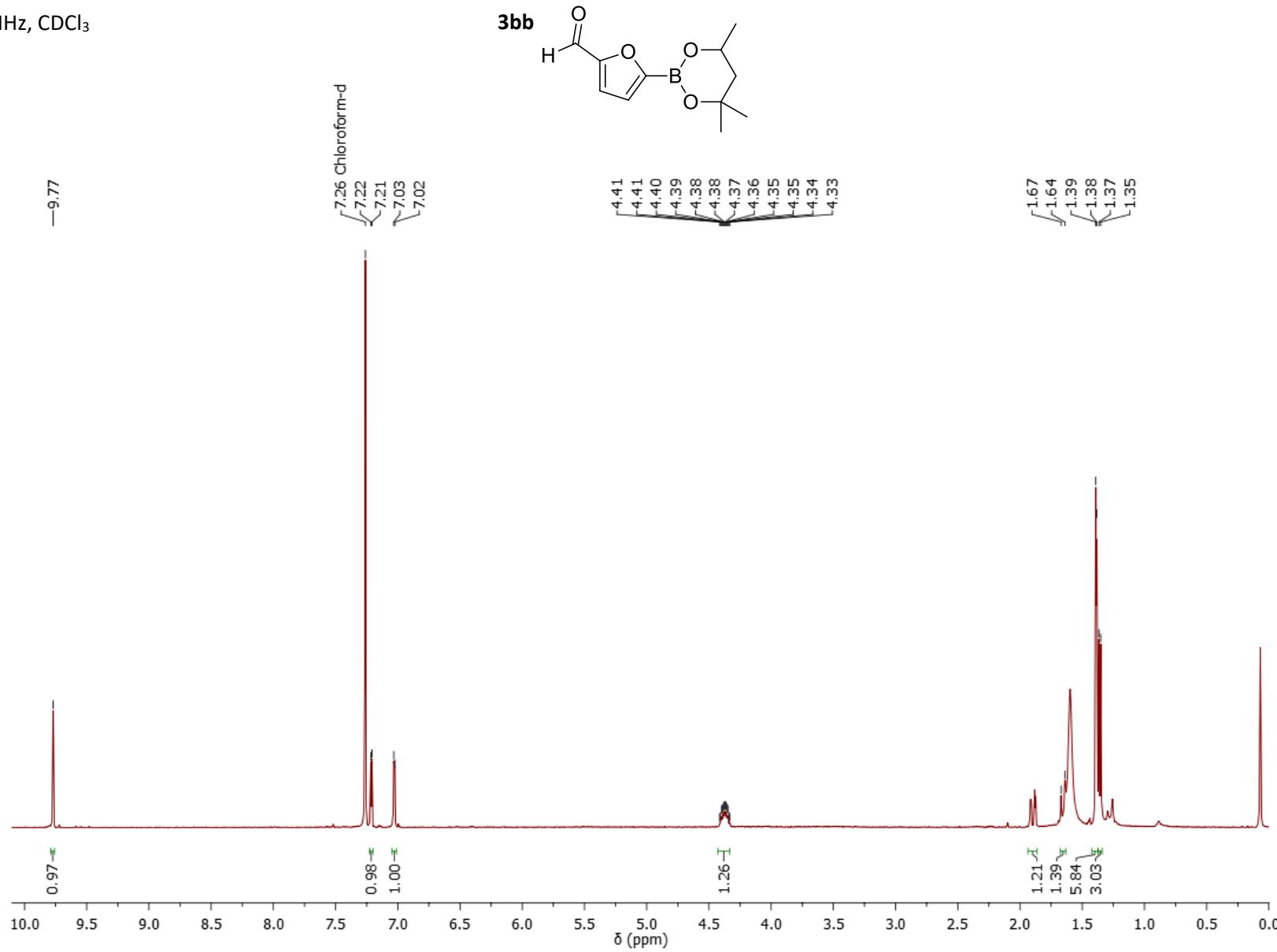
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$

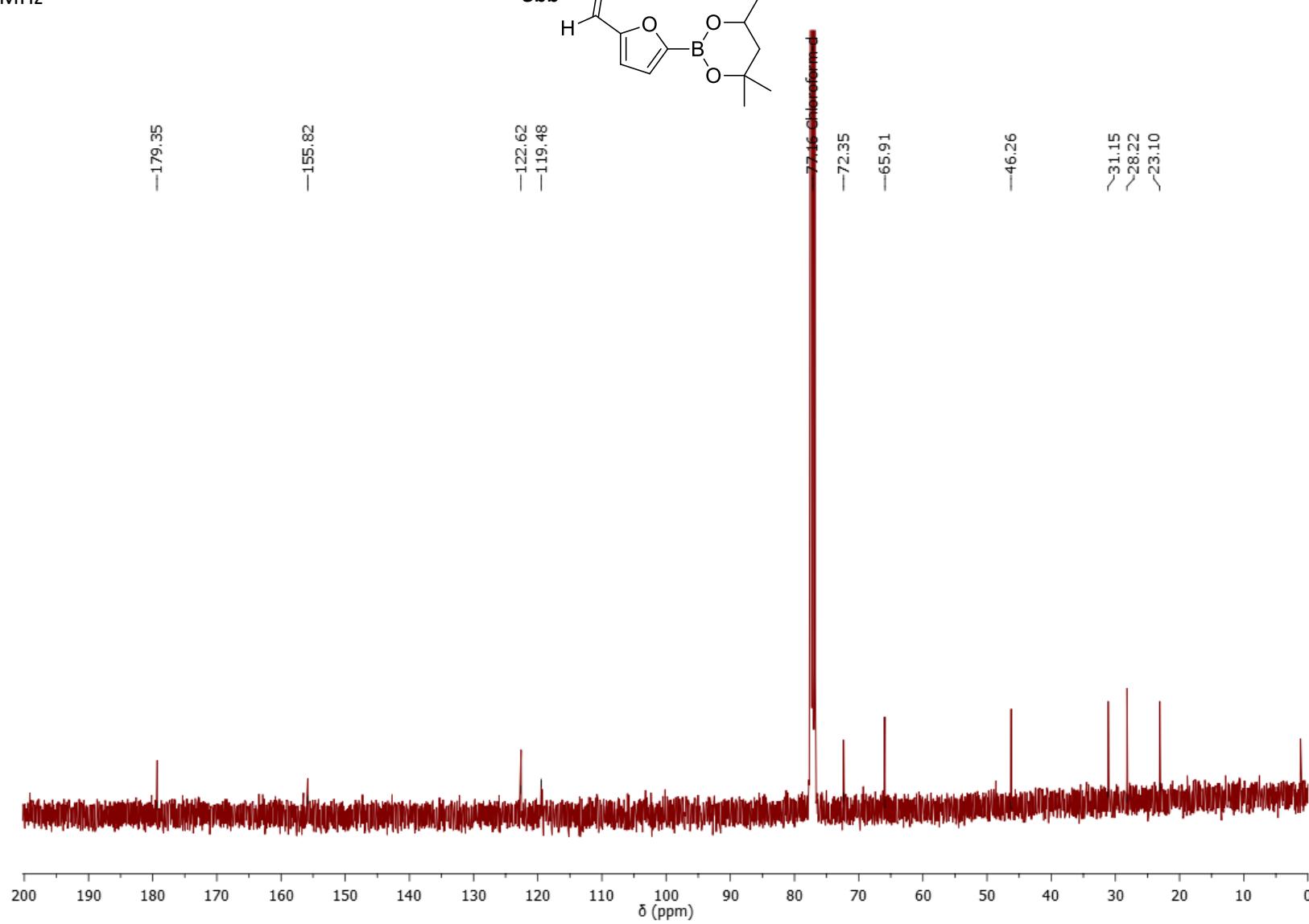


<sup>1</sup>H 400MHz, CDCl<sub>3</sub>

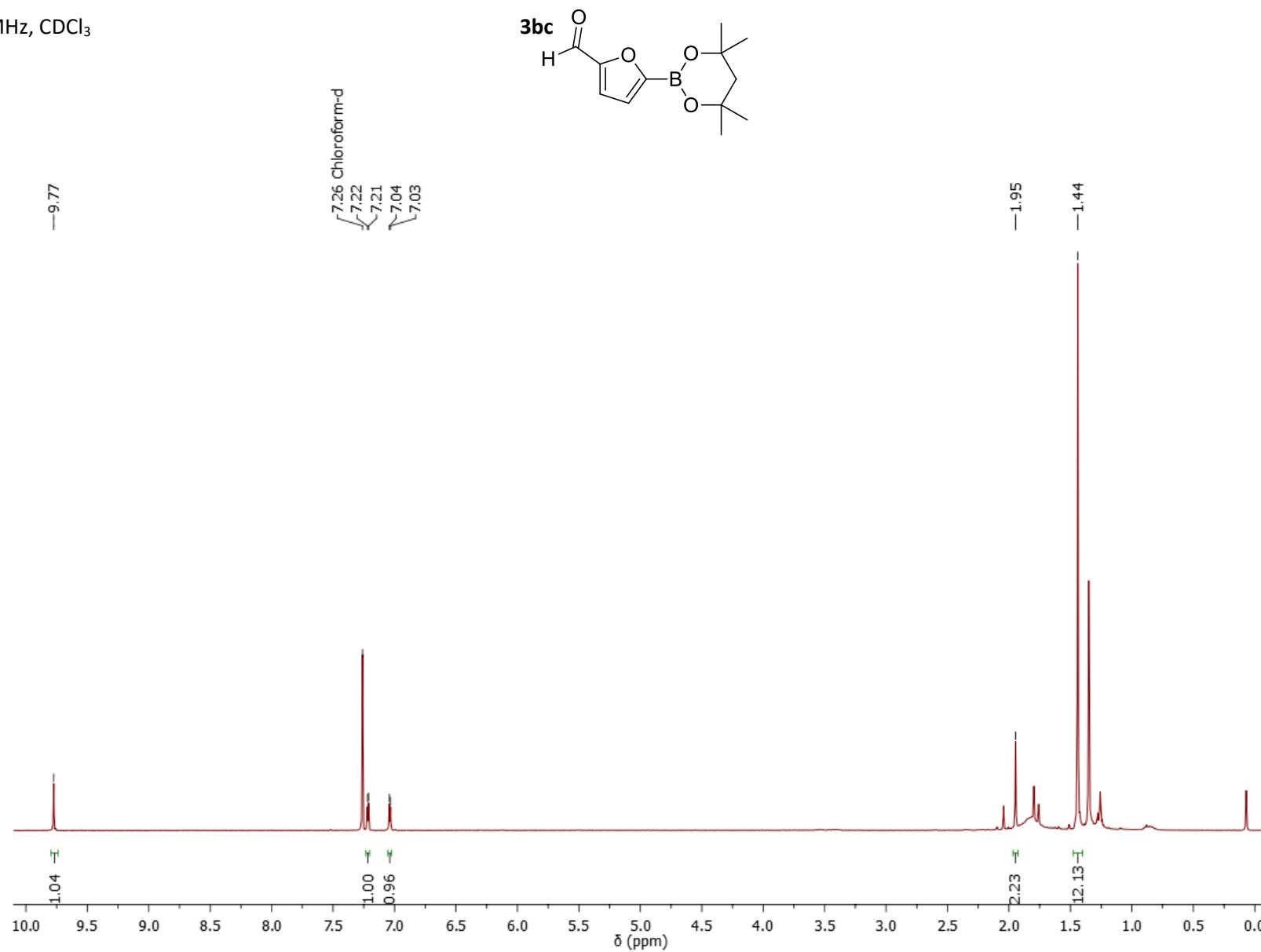


## Furan boronate esters

<sup>13</sup>C 101MHz



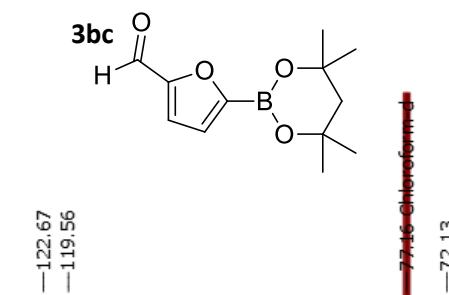
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



$^{13}\text{C}$  101MHz

—179.40

—155.84

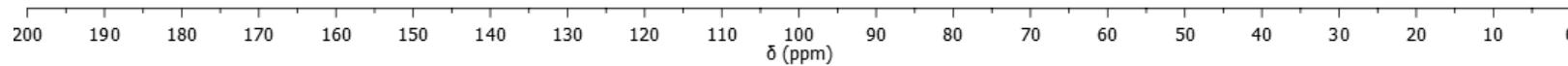


77.16 Chloroform

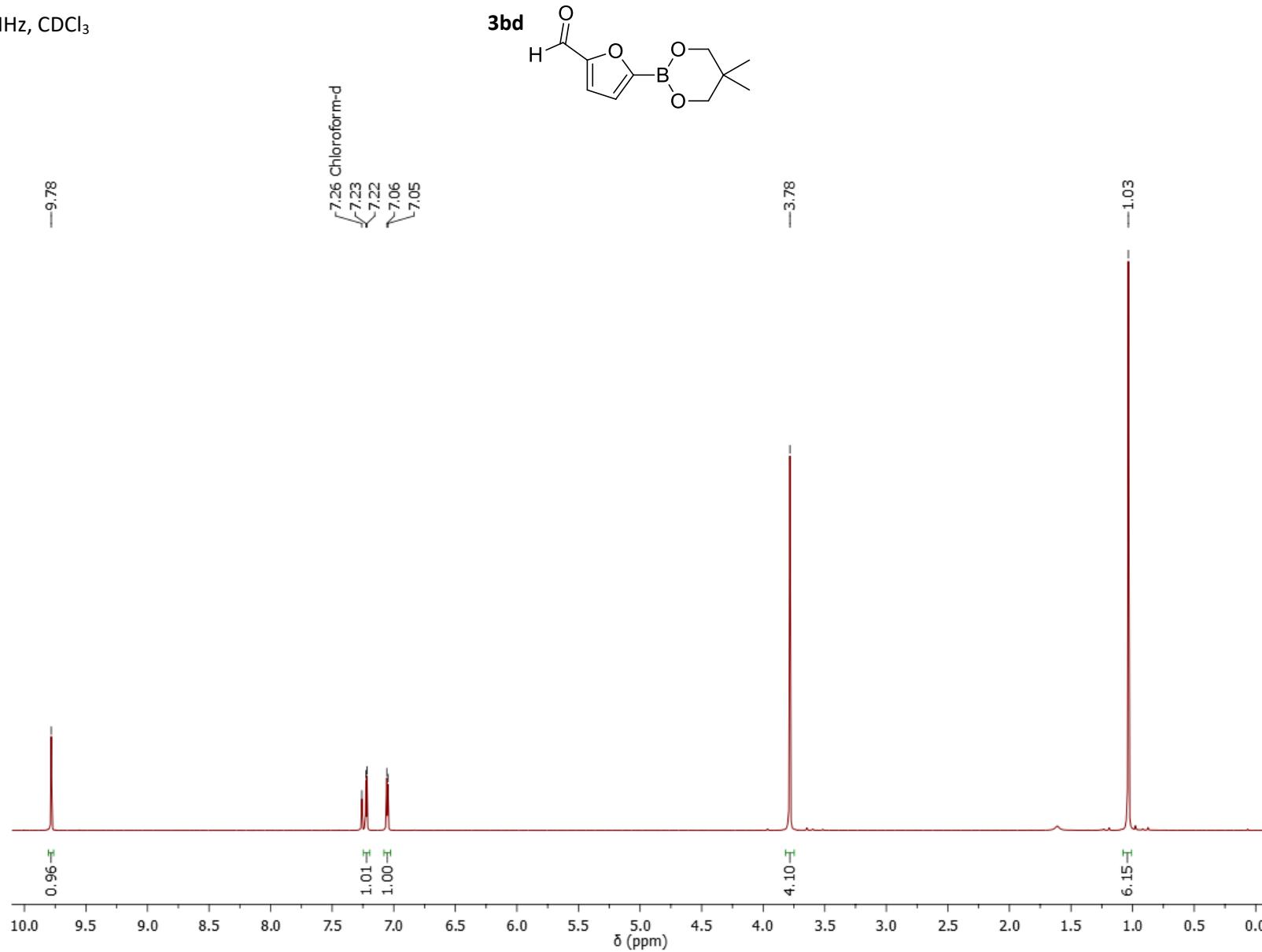
—72.13

—49.32

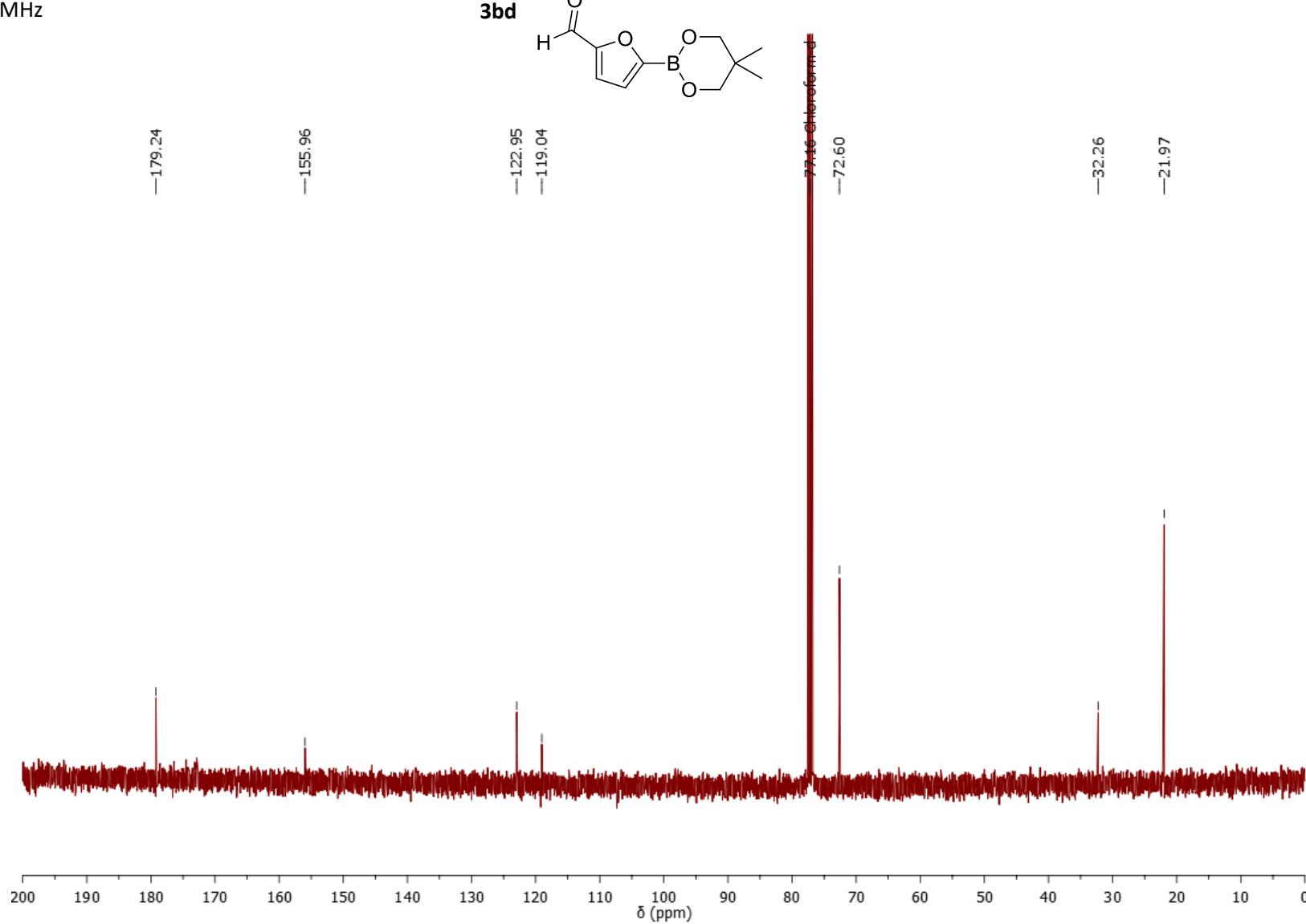
—31.75



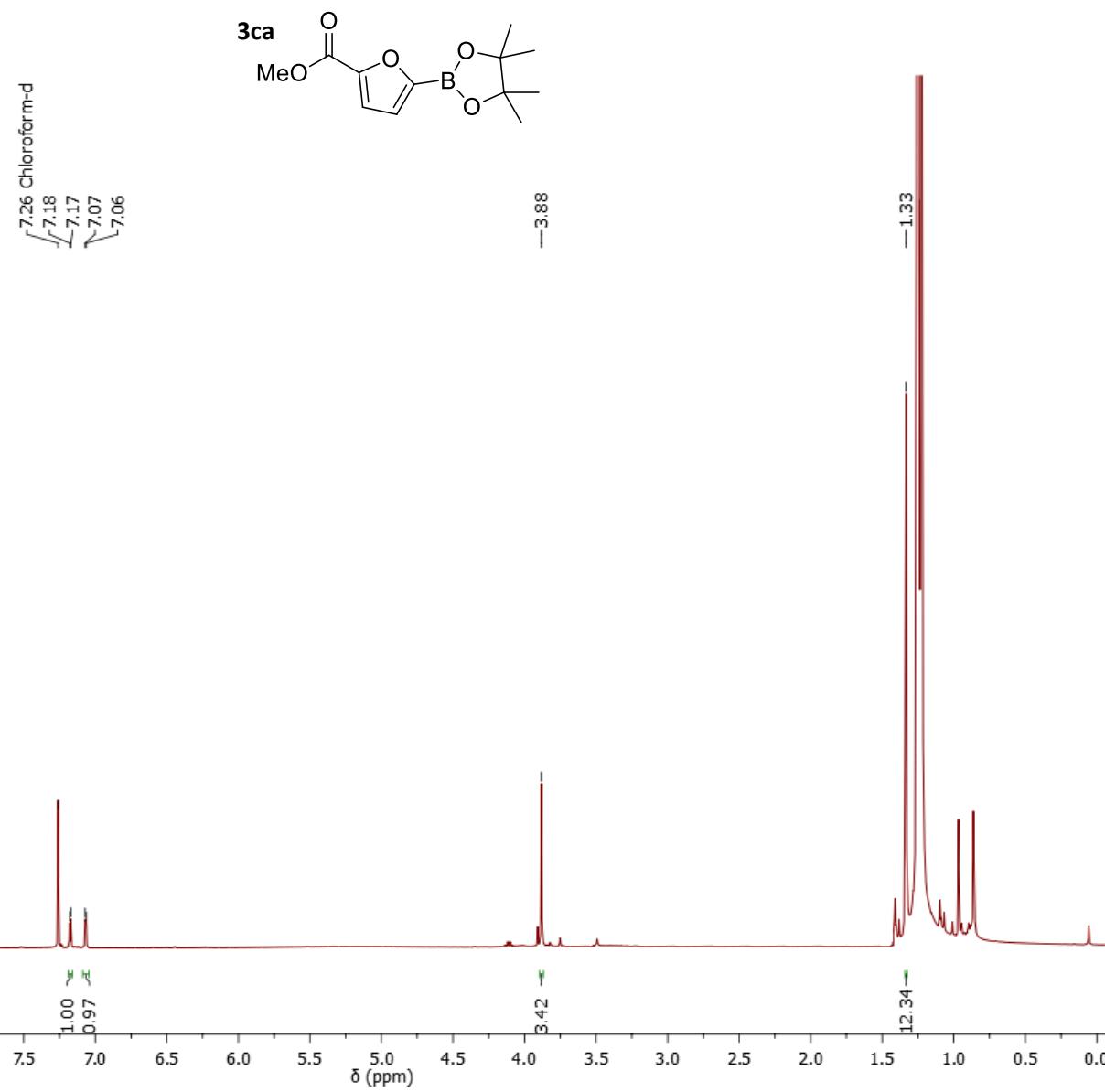
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



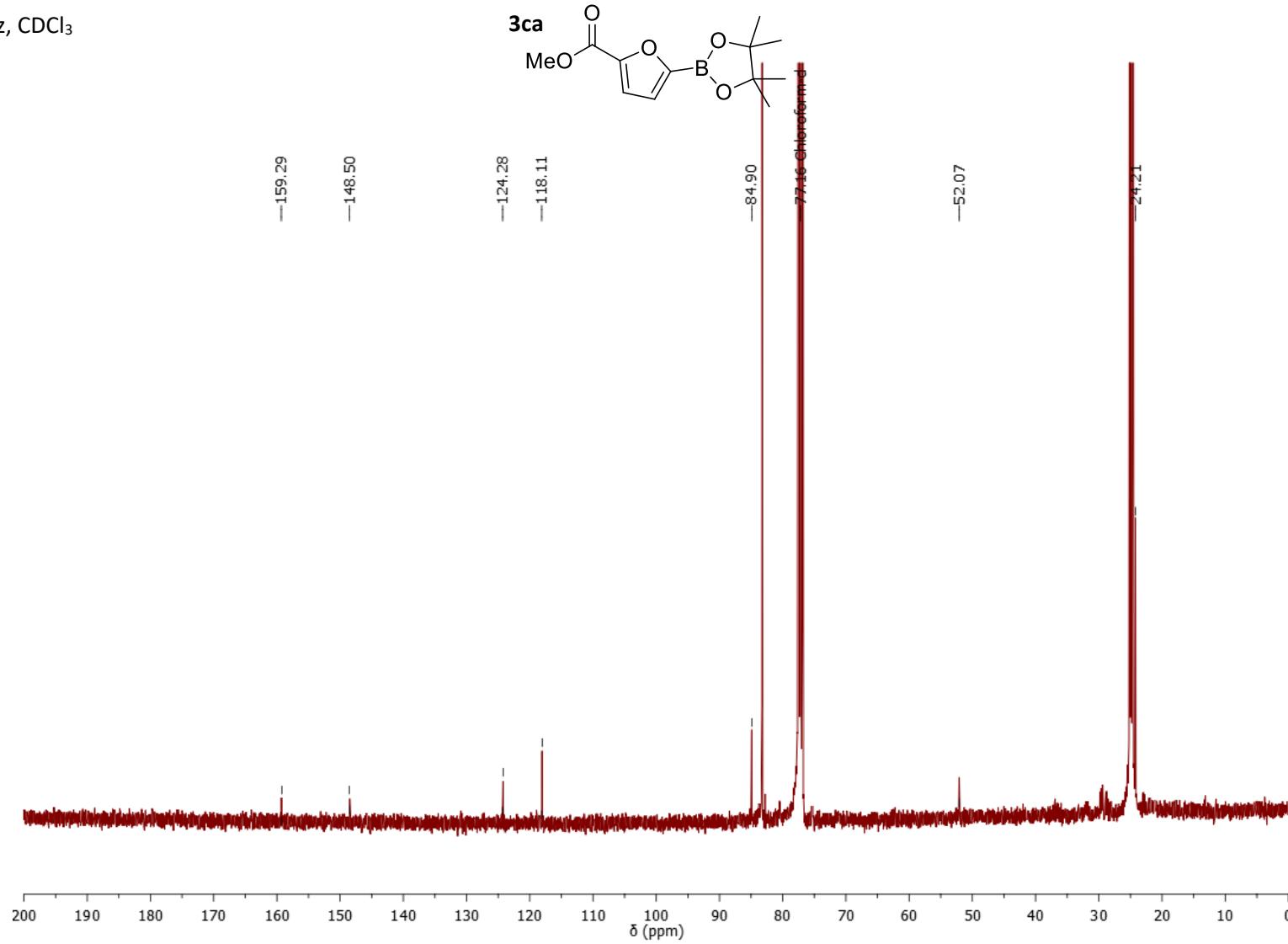
<sup>13</sup>C 101MHz



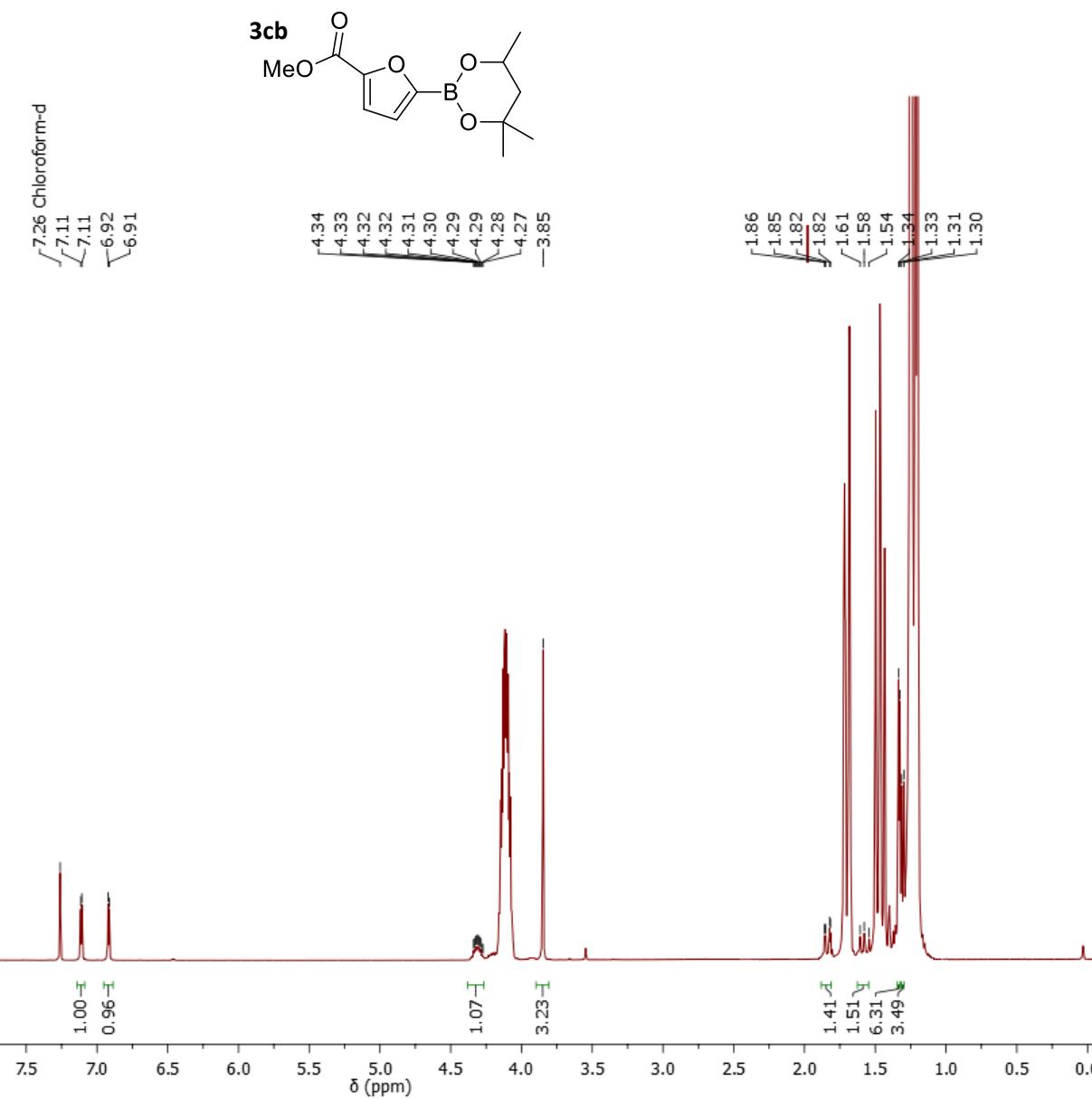
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



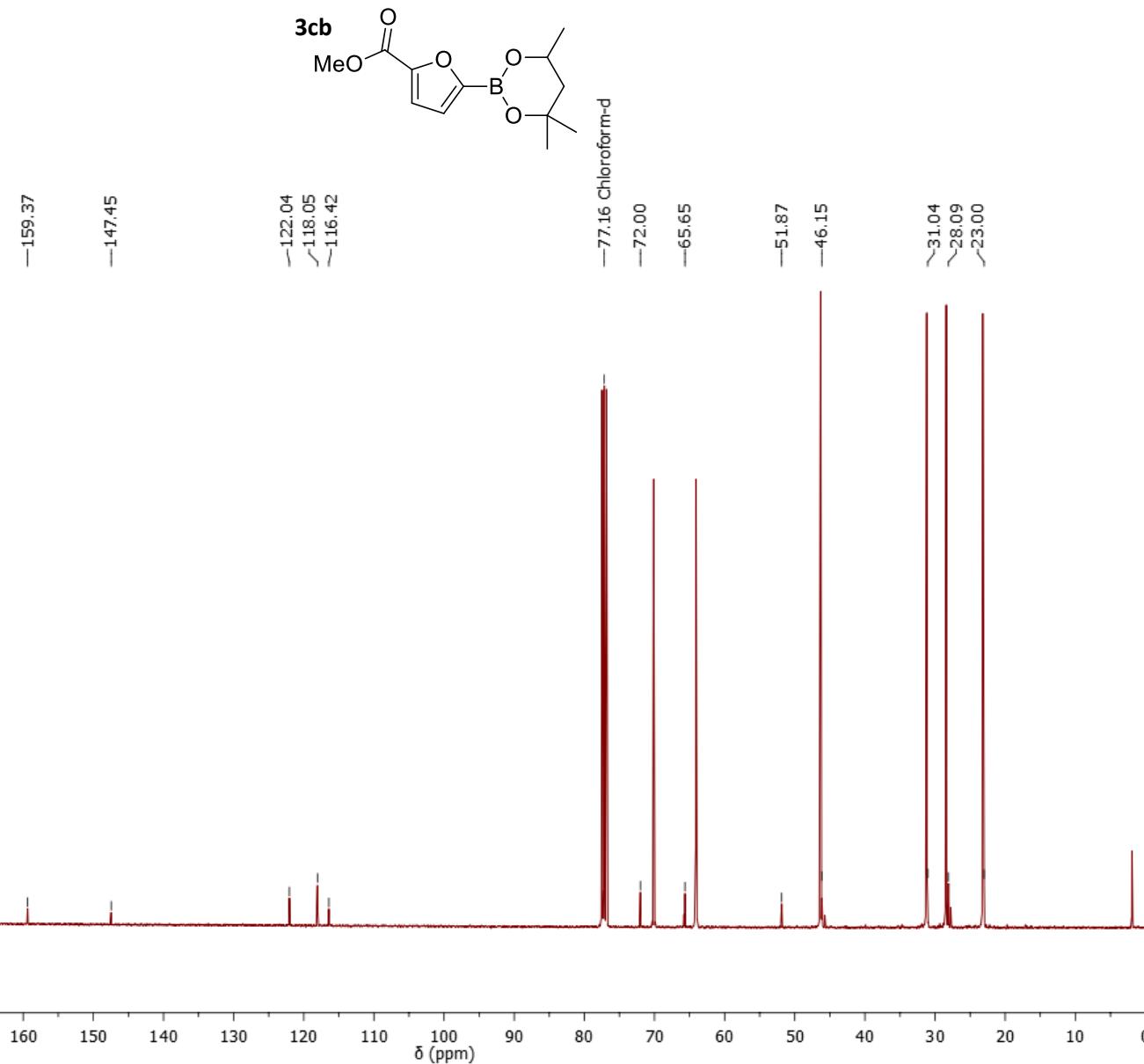
$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$



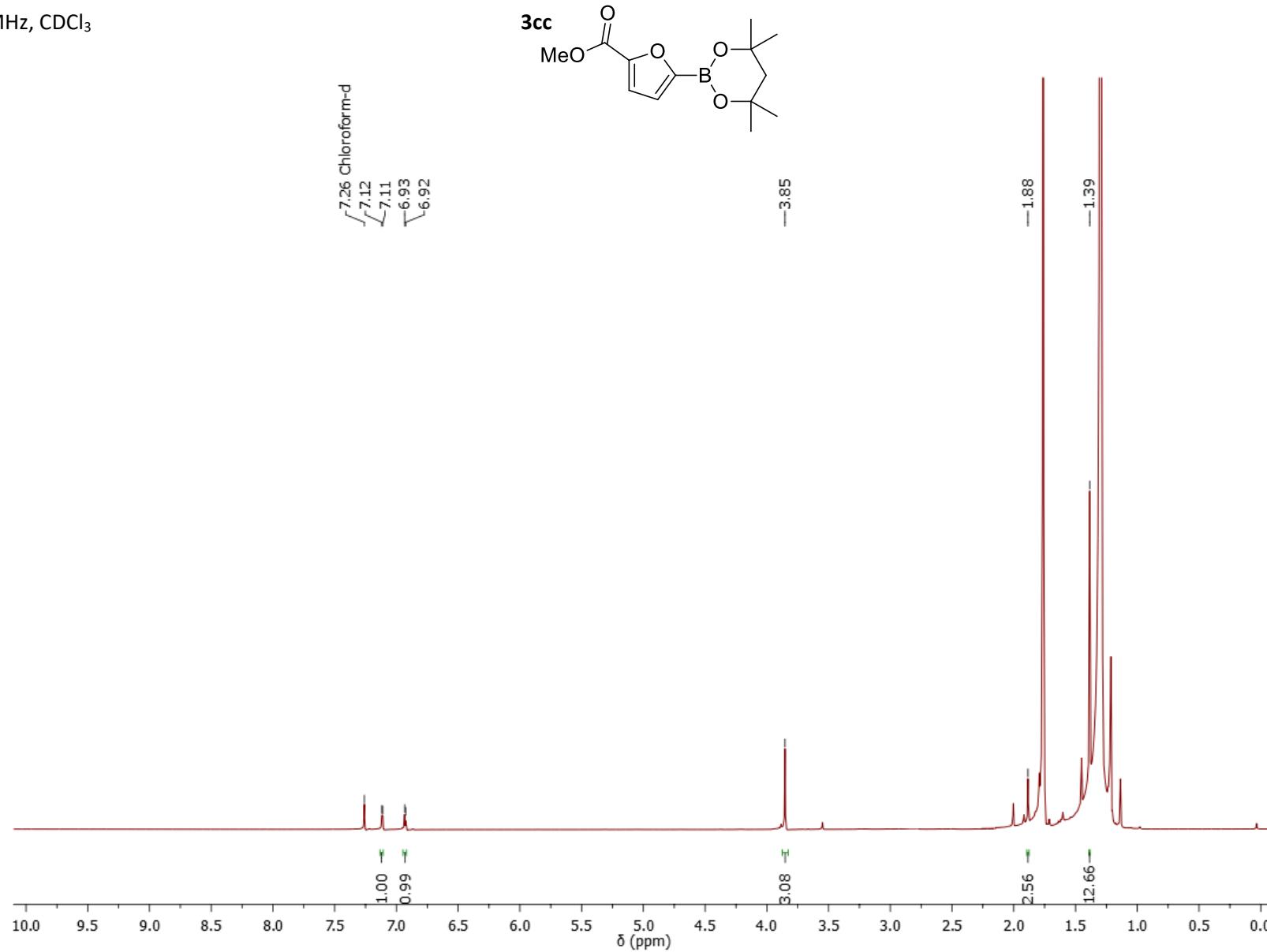
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



<sup>13</sup>C 101MHz

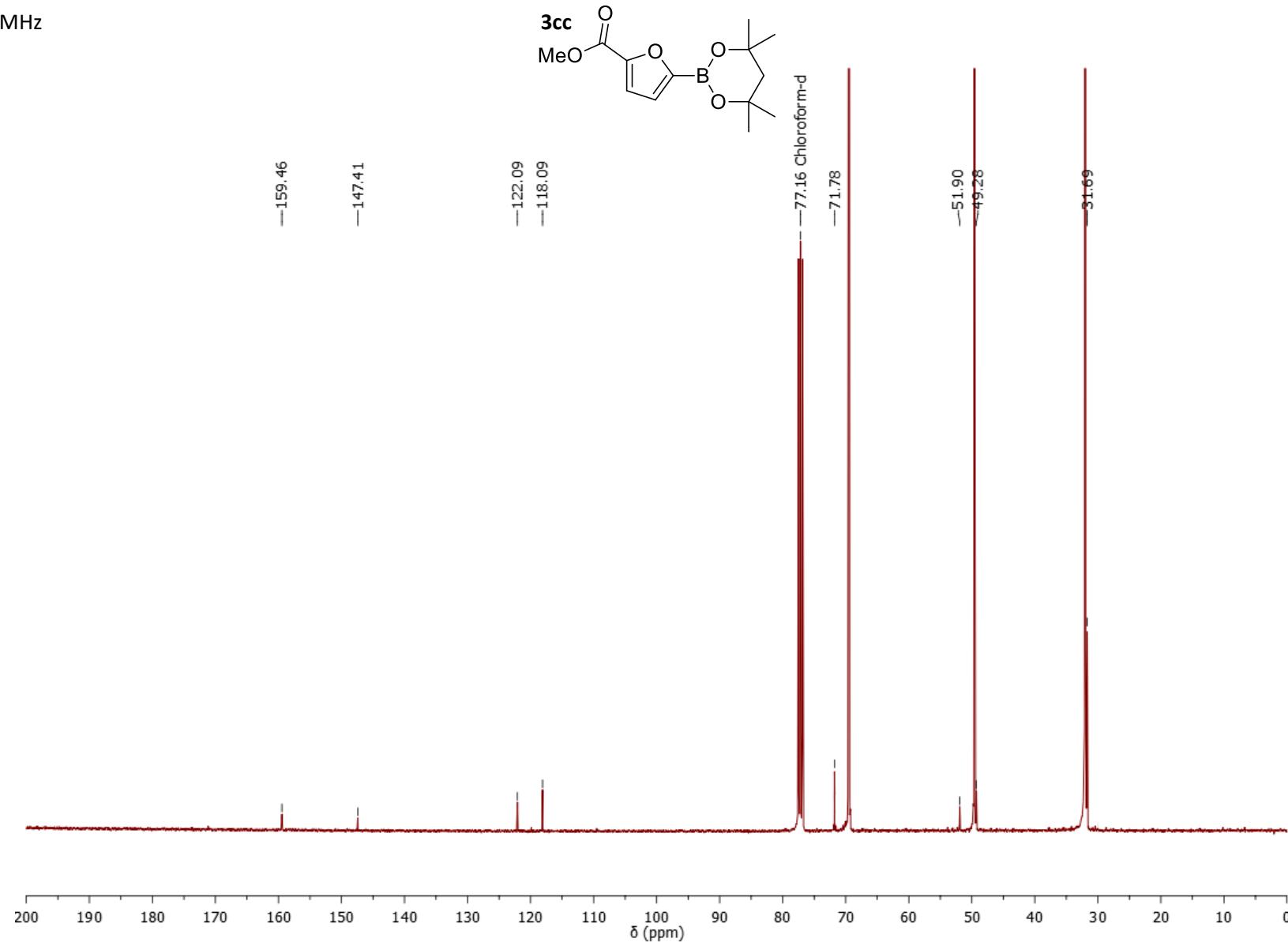


<sup>1</sup>H 400MHz, CDCl<sub>3</sub>

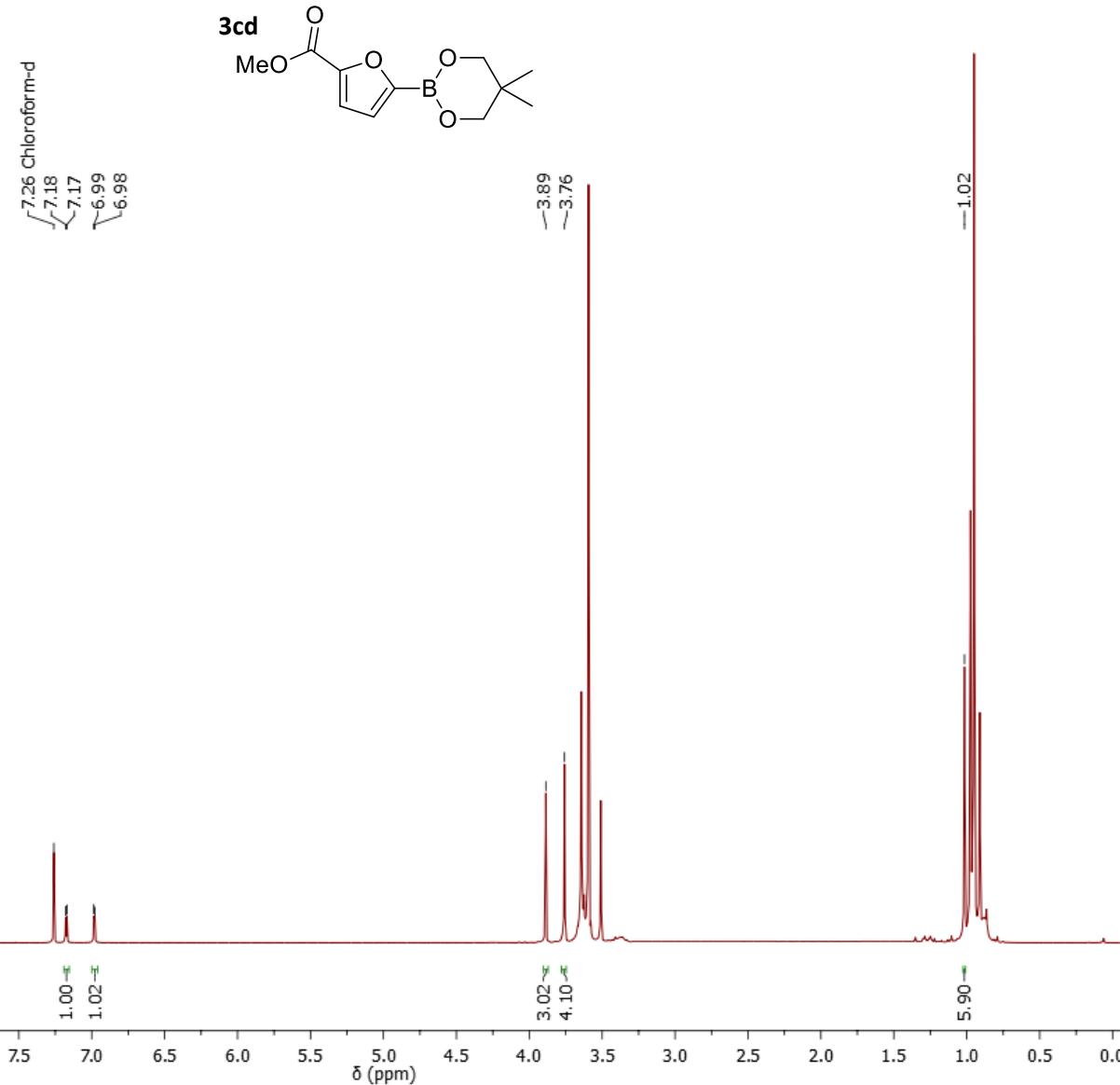


## Furan boronate esters

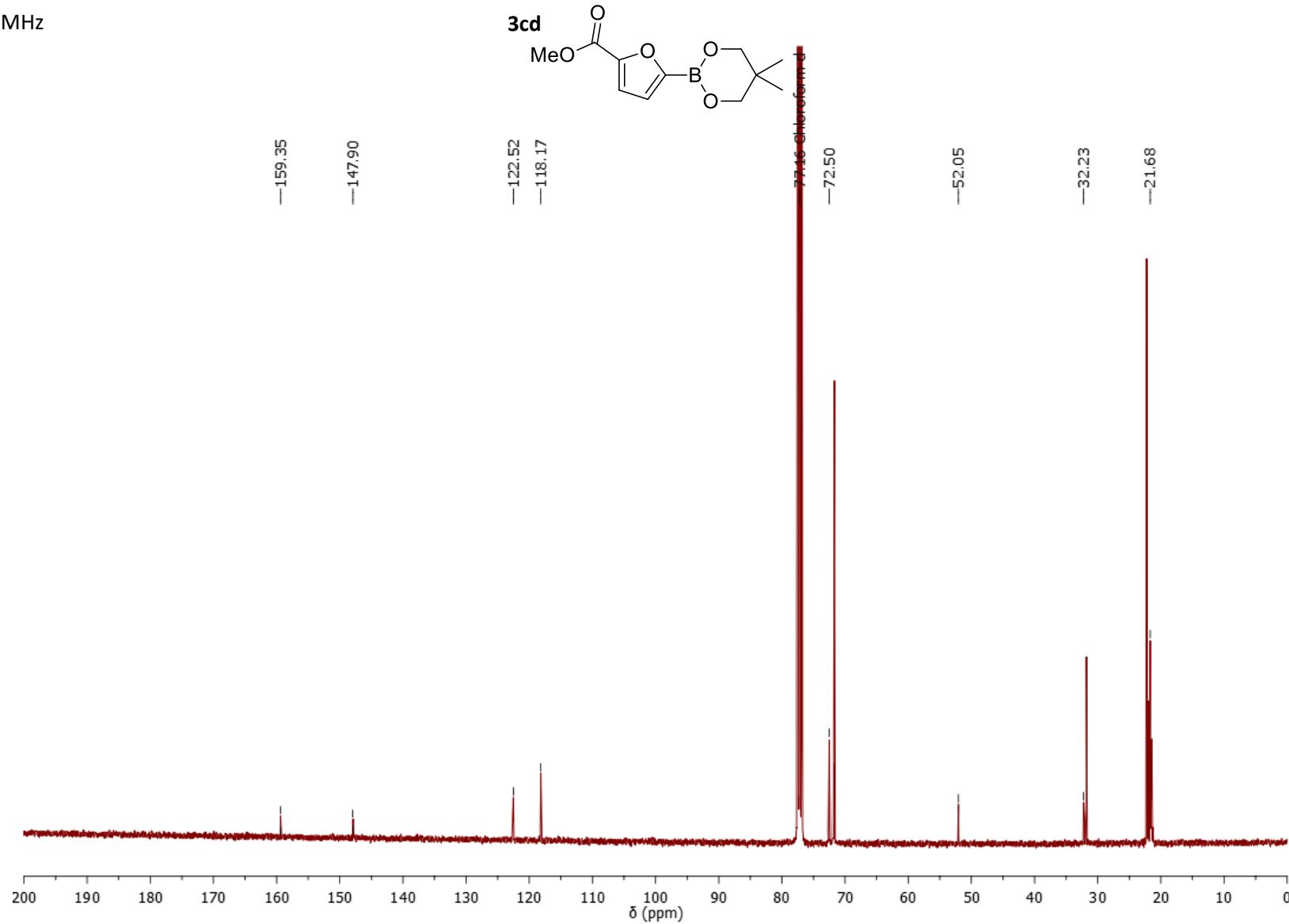
<sup>13</sup>C 101MHz



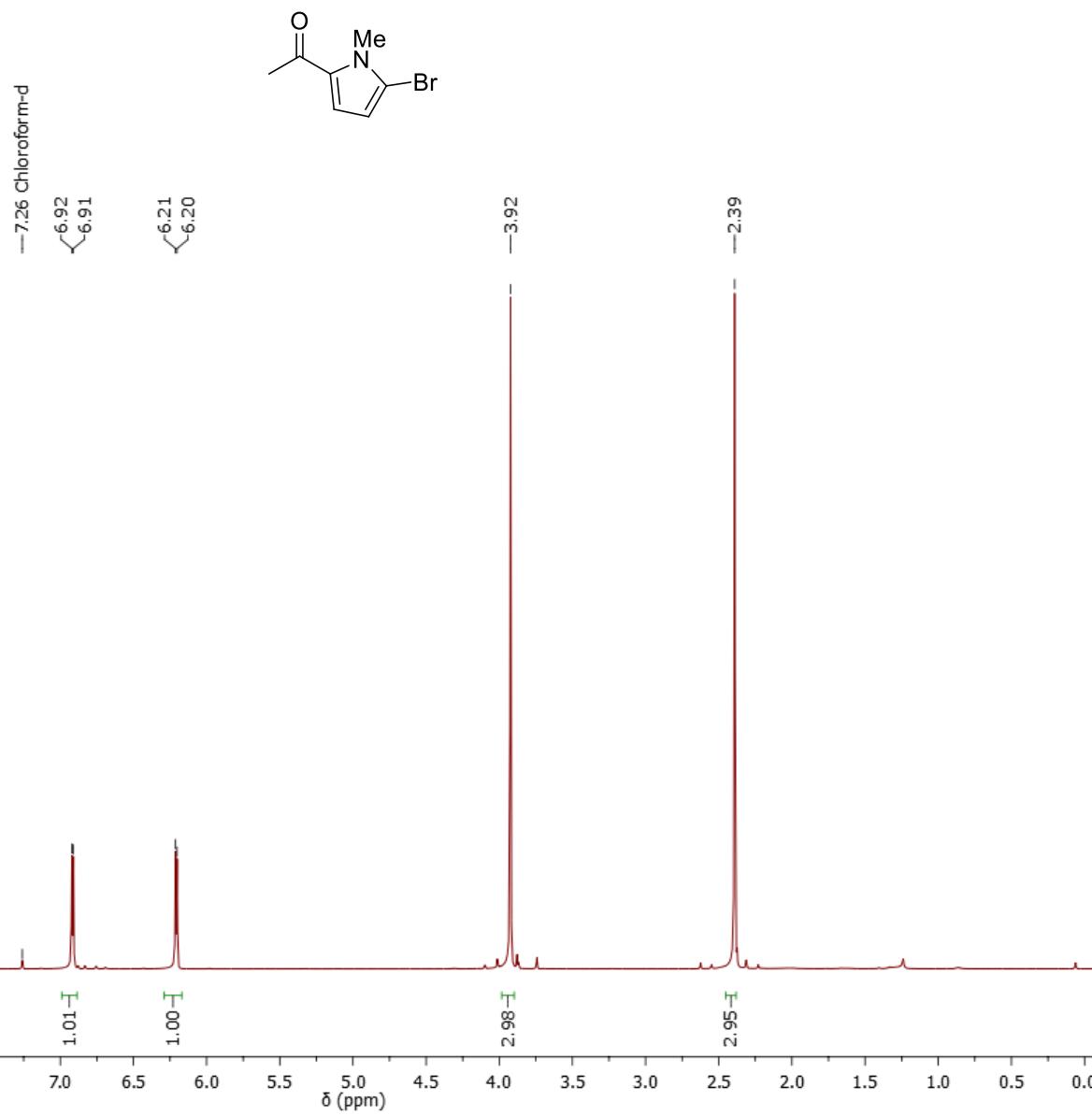
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



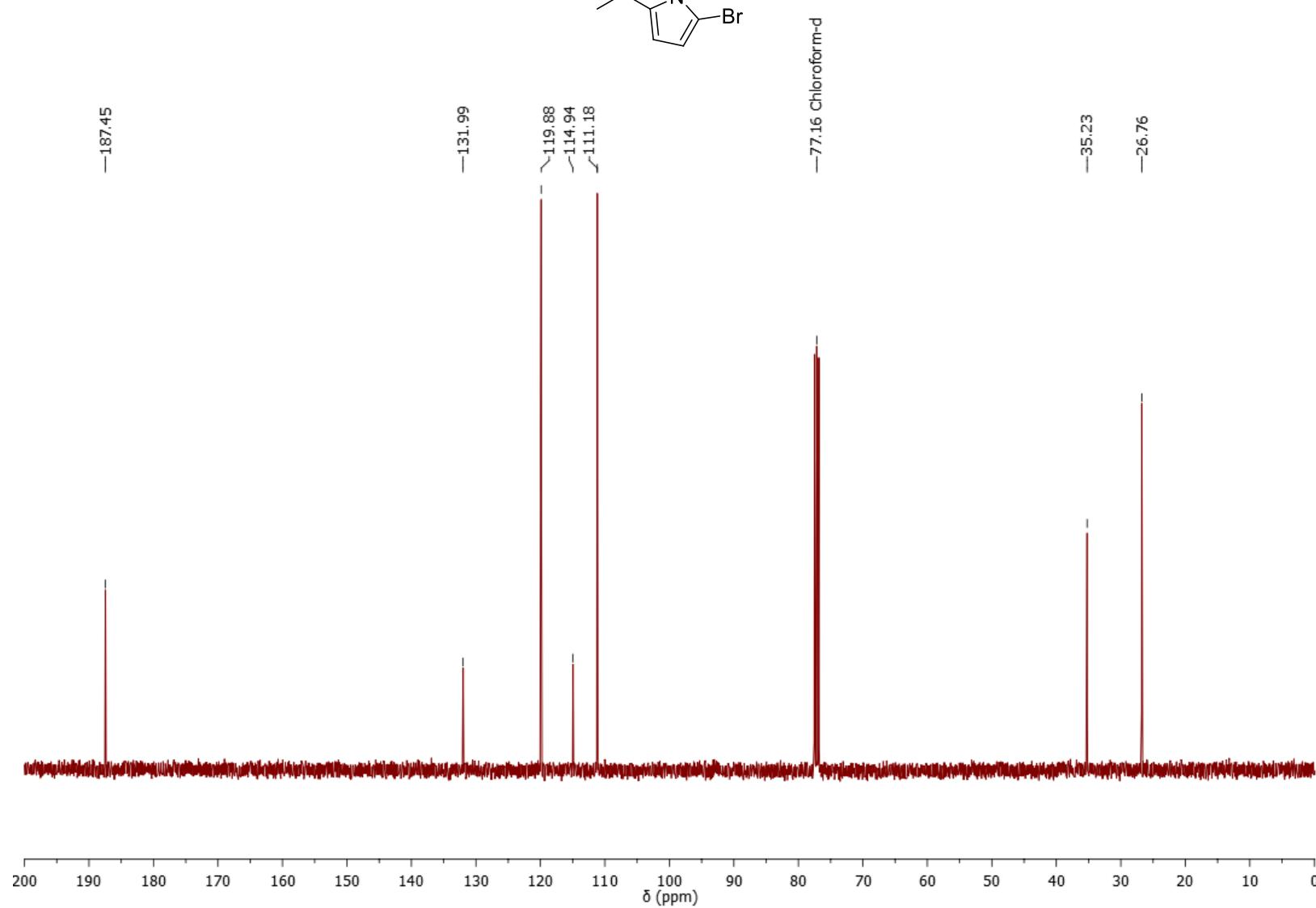
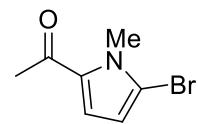
$^{13}\text{C}$  101MHz



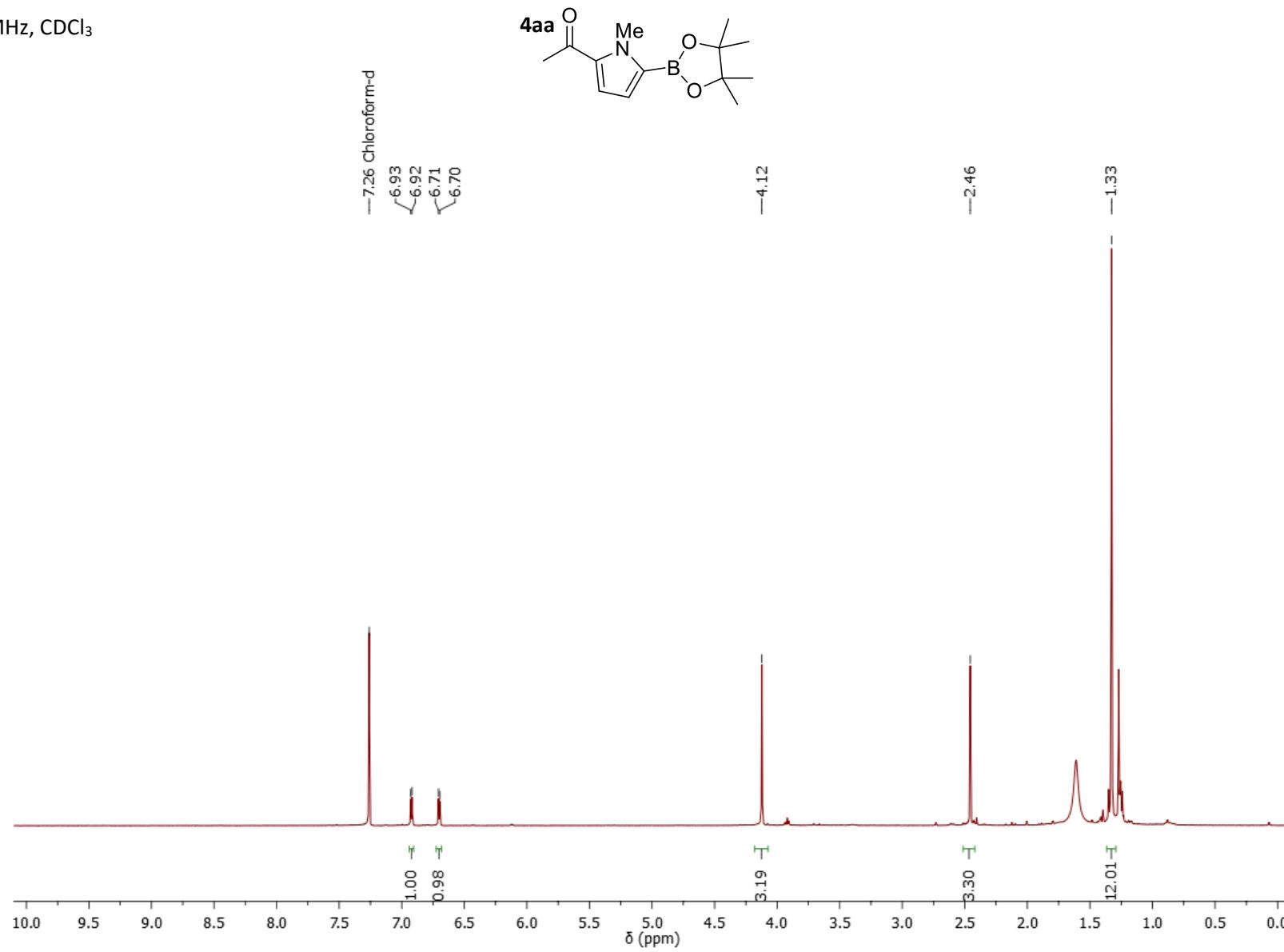
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



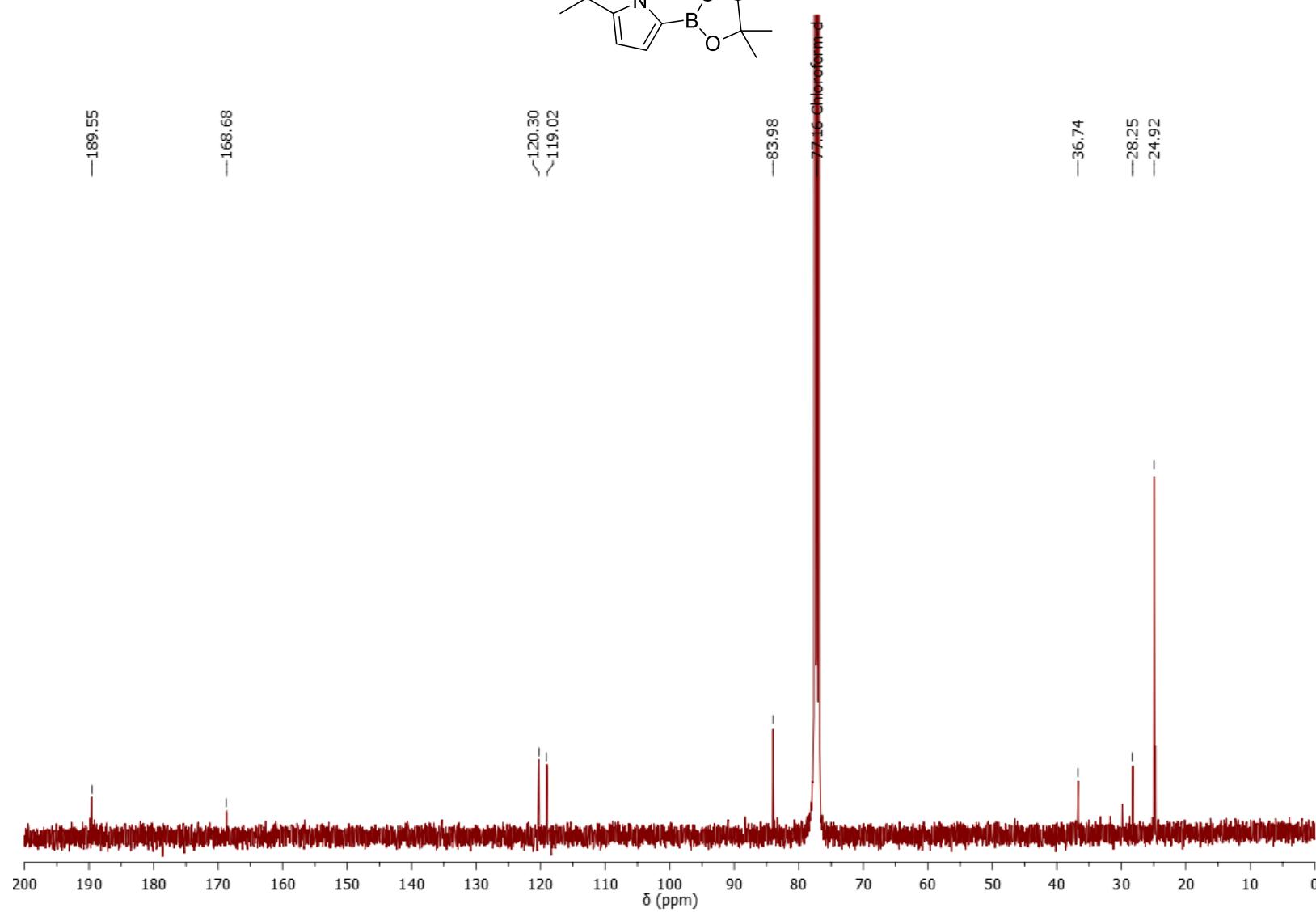
$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$



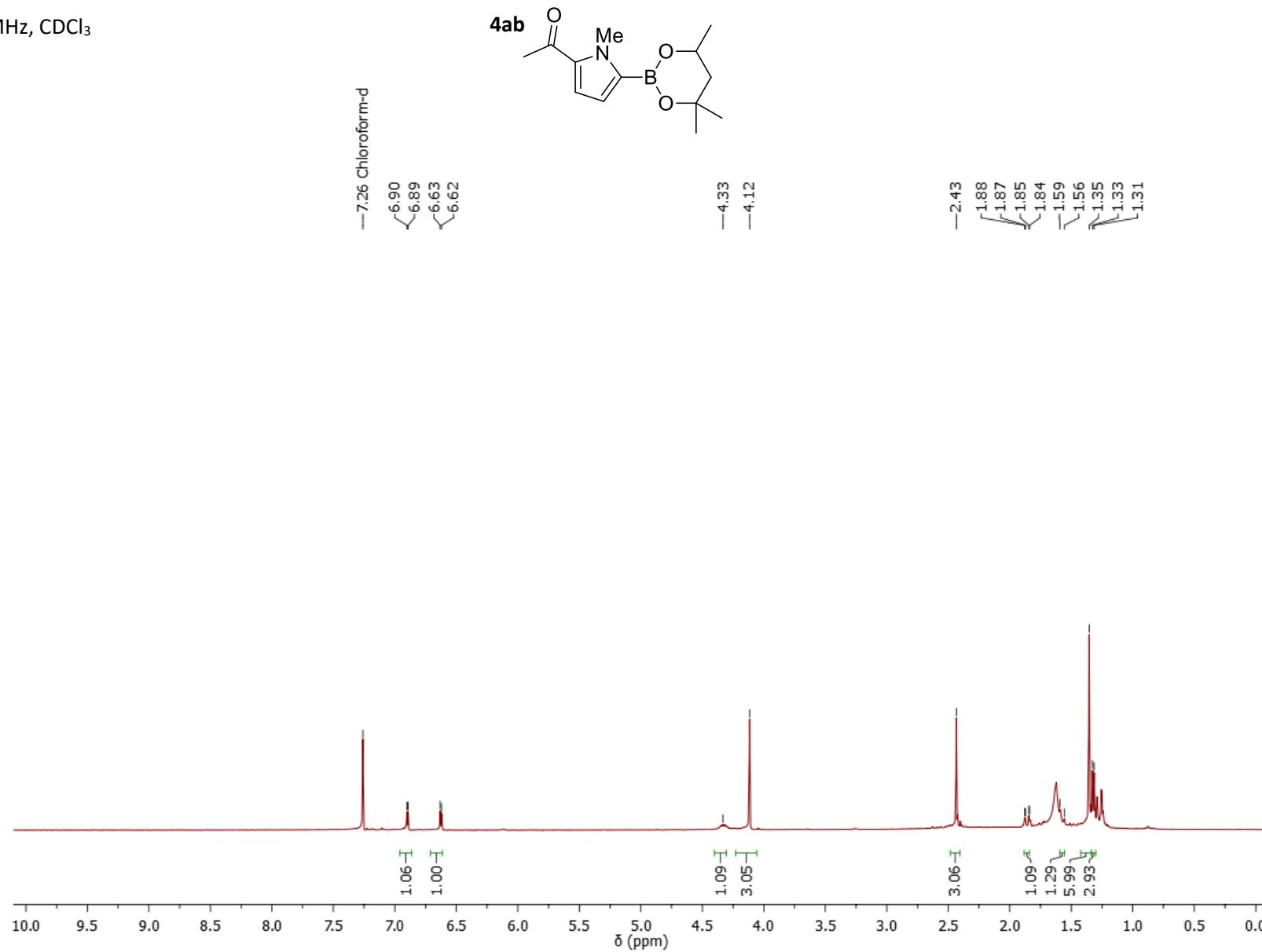
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$

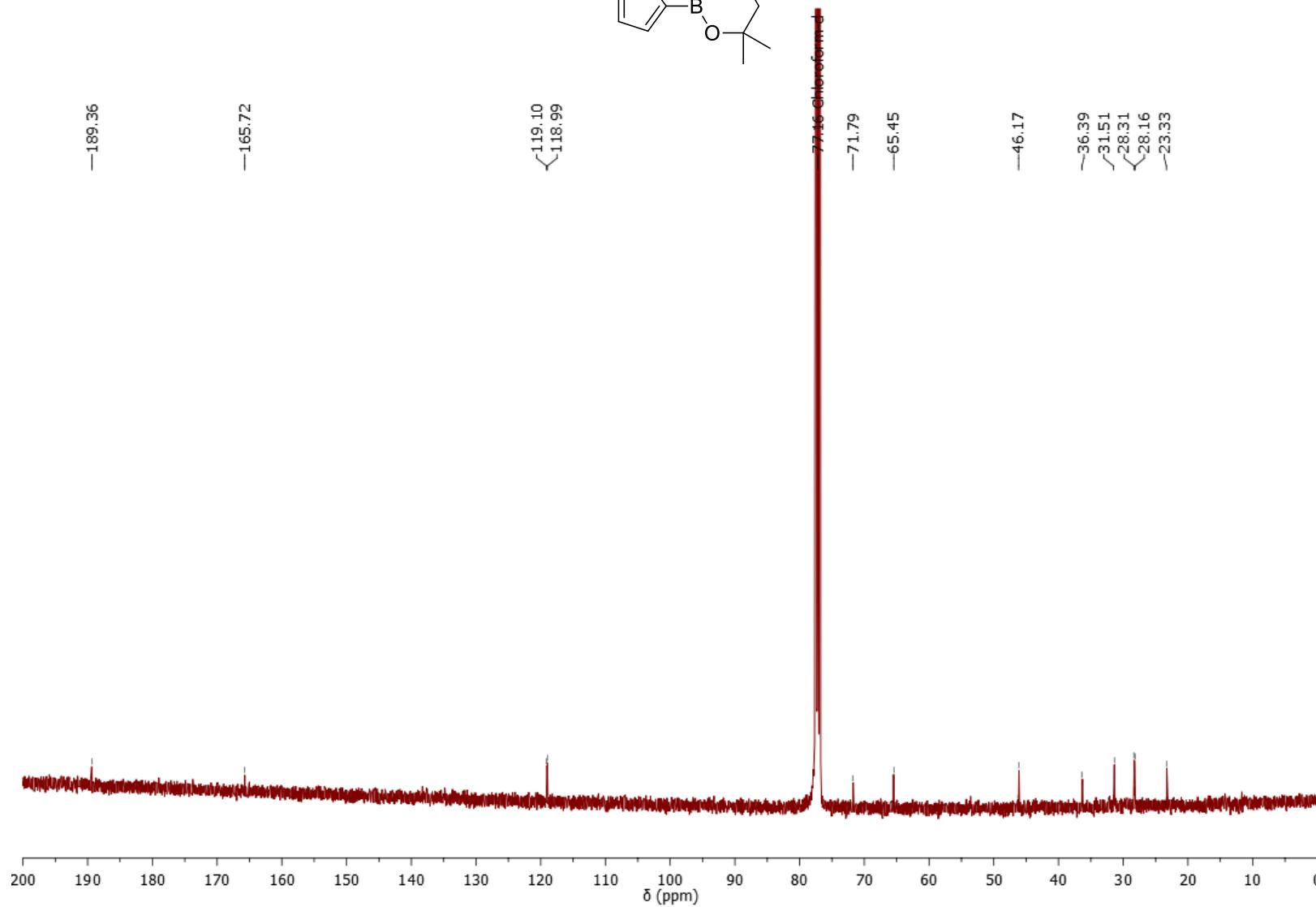


<sup>1</sup>H 400MHz, CDCl<sub>3</sub>

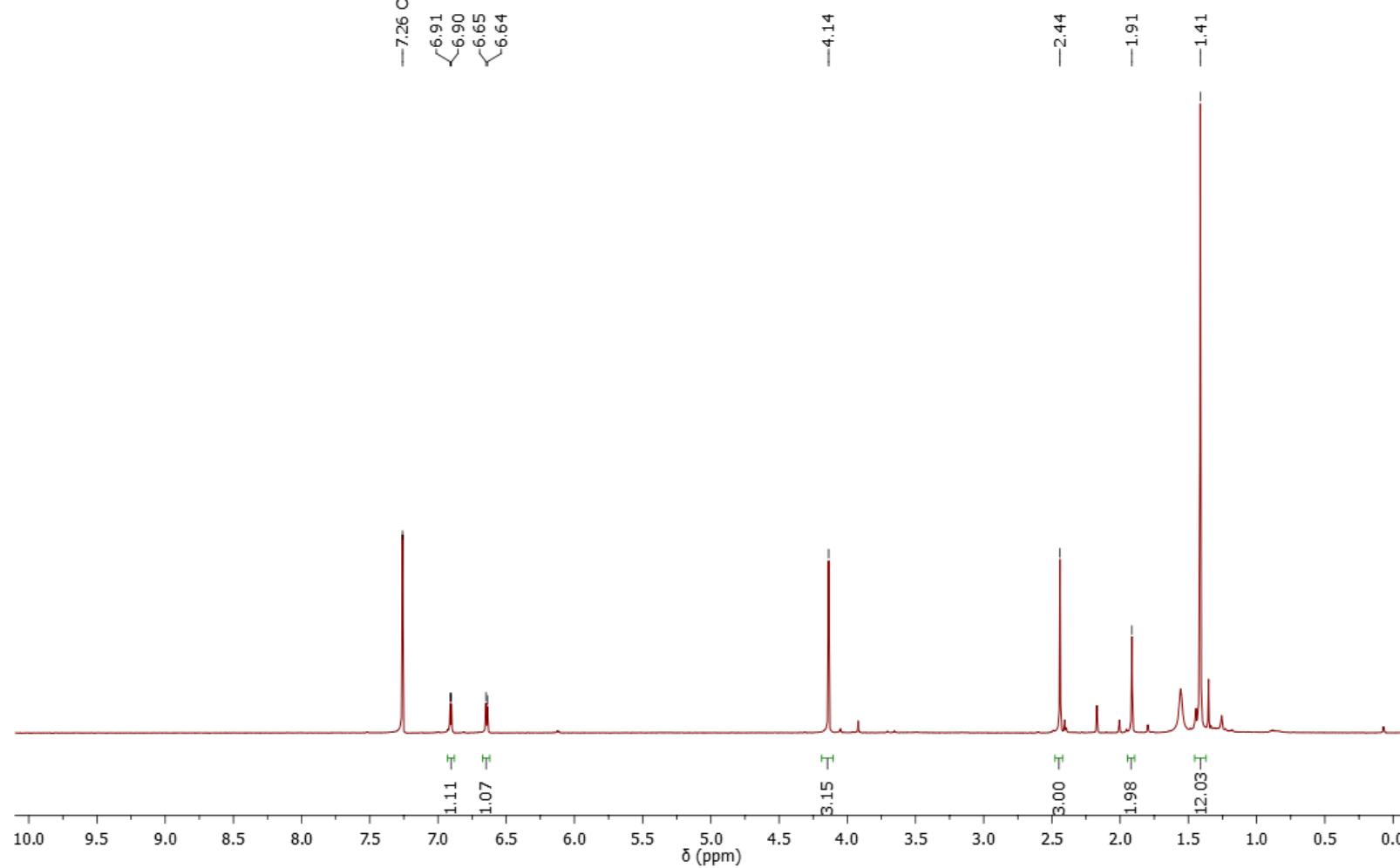
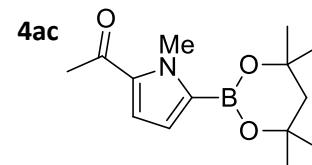


**Selenophene boronate esters**

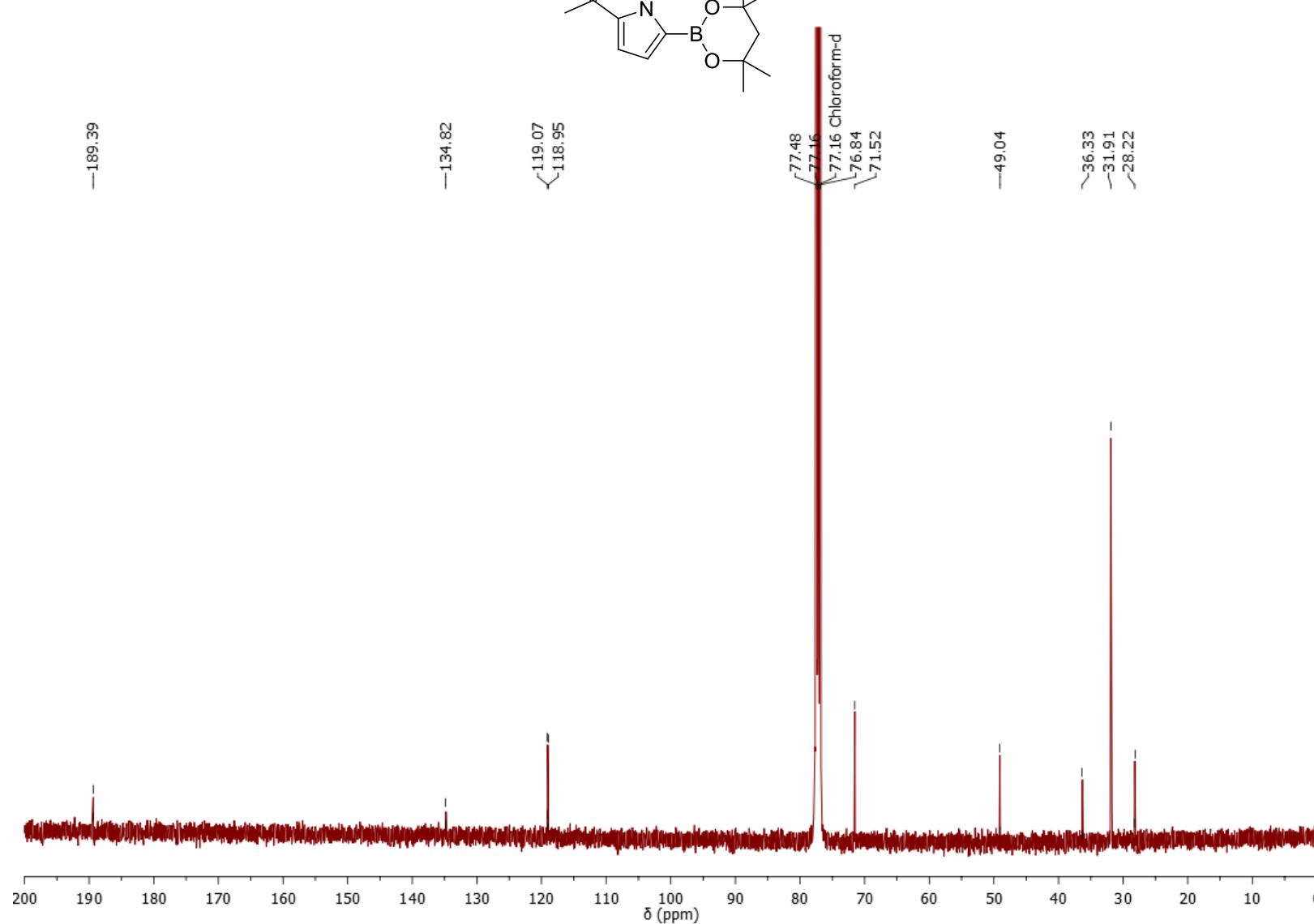
$^{13}\text{C}$  101MHz



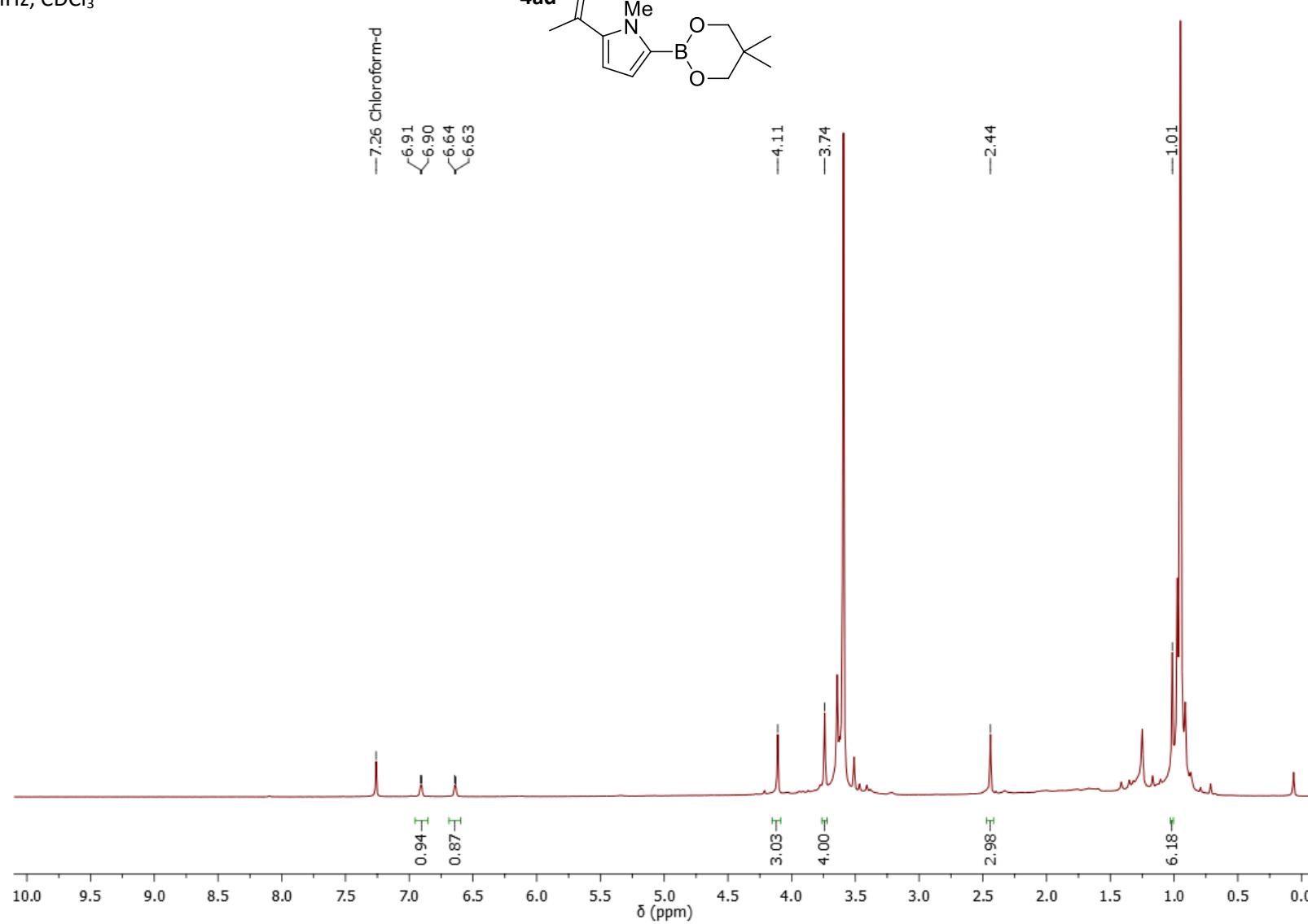
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



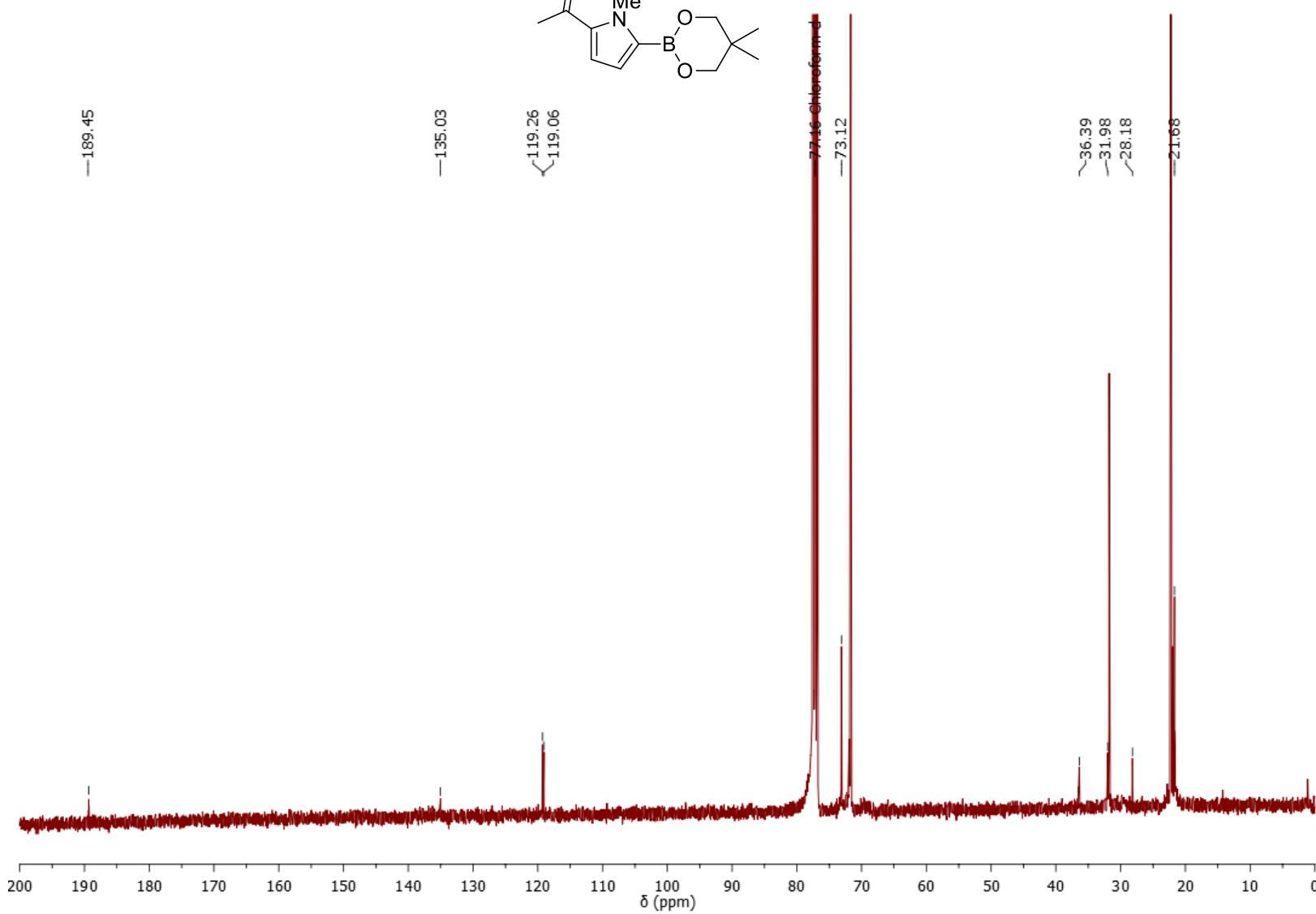
<sup>13</sup>C 101MHz



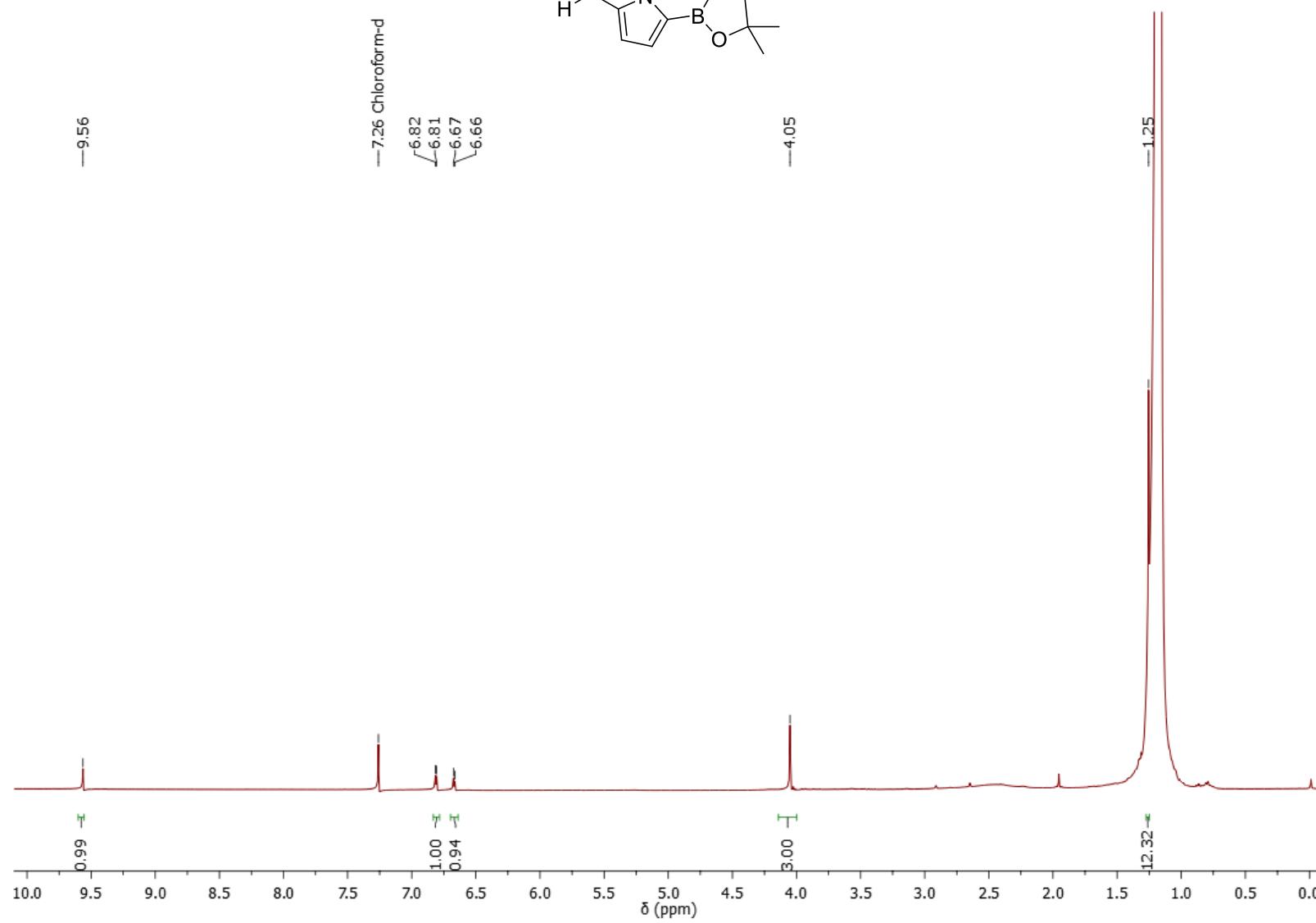
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



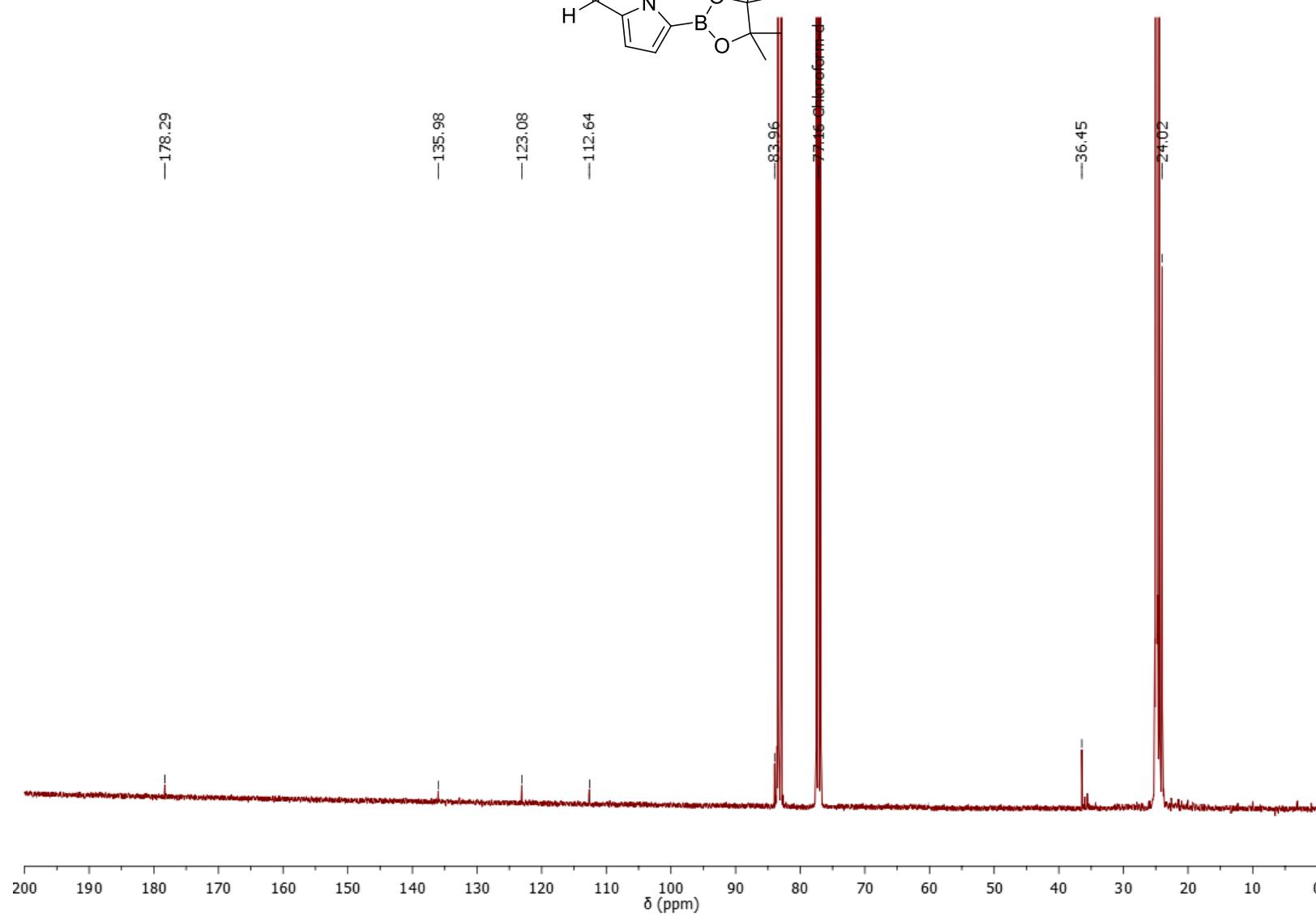
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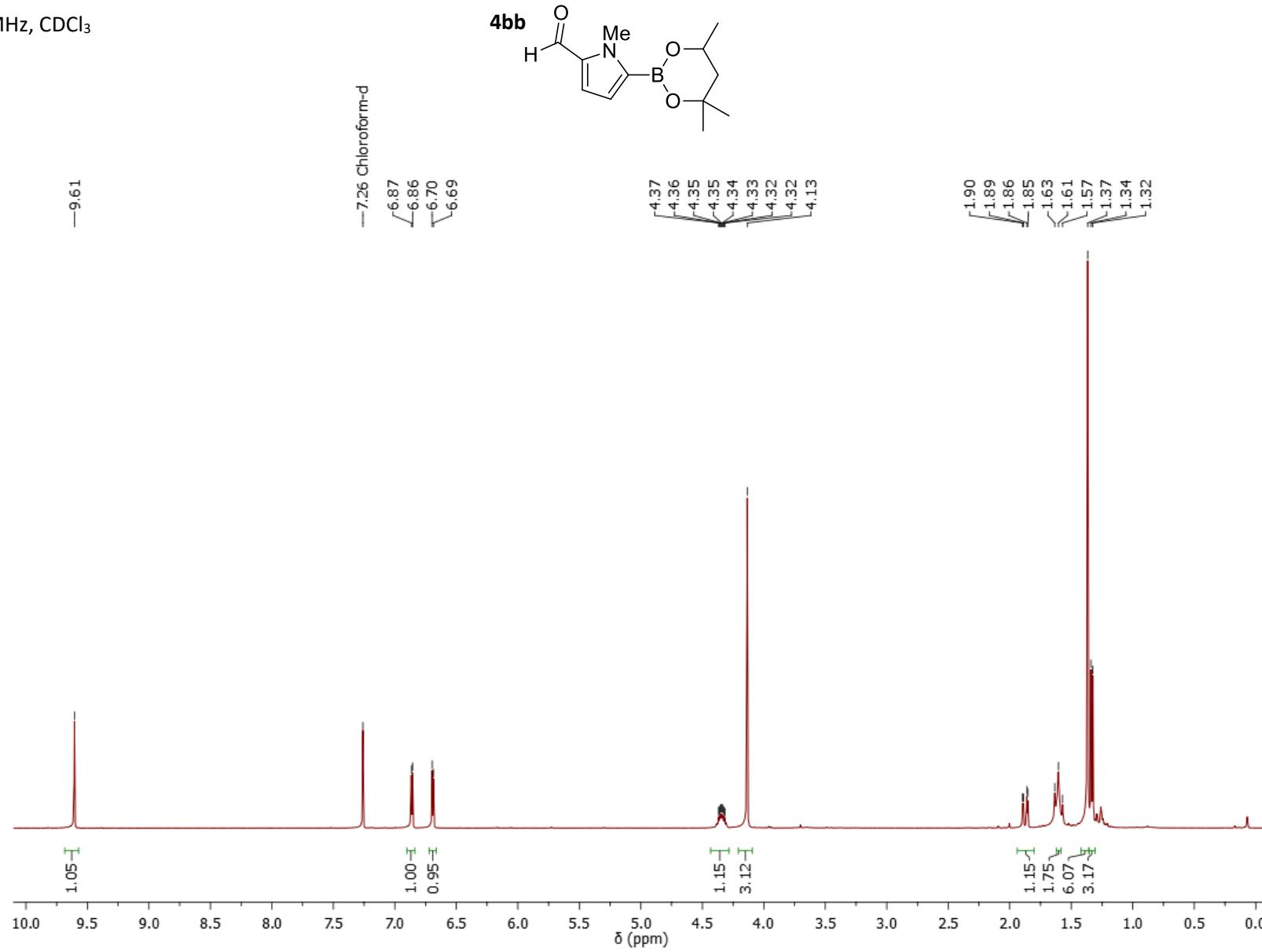
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



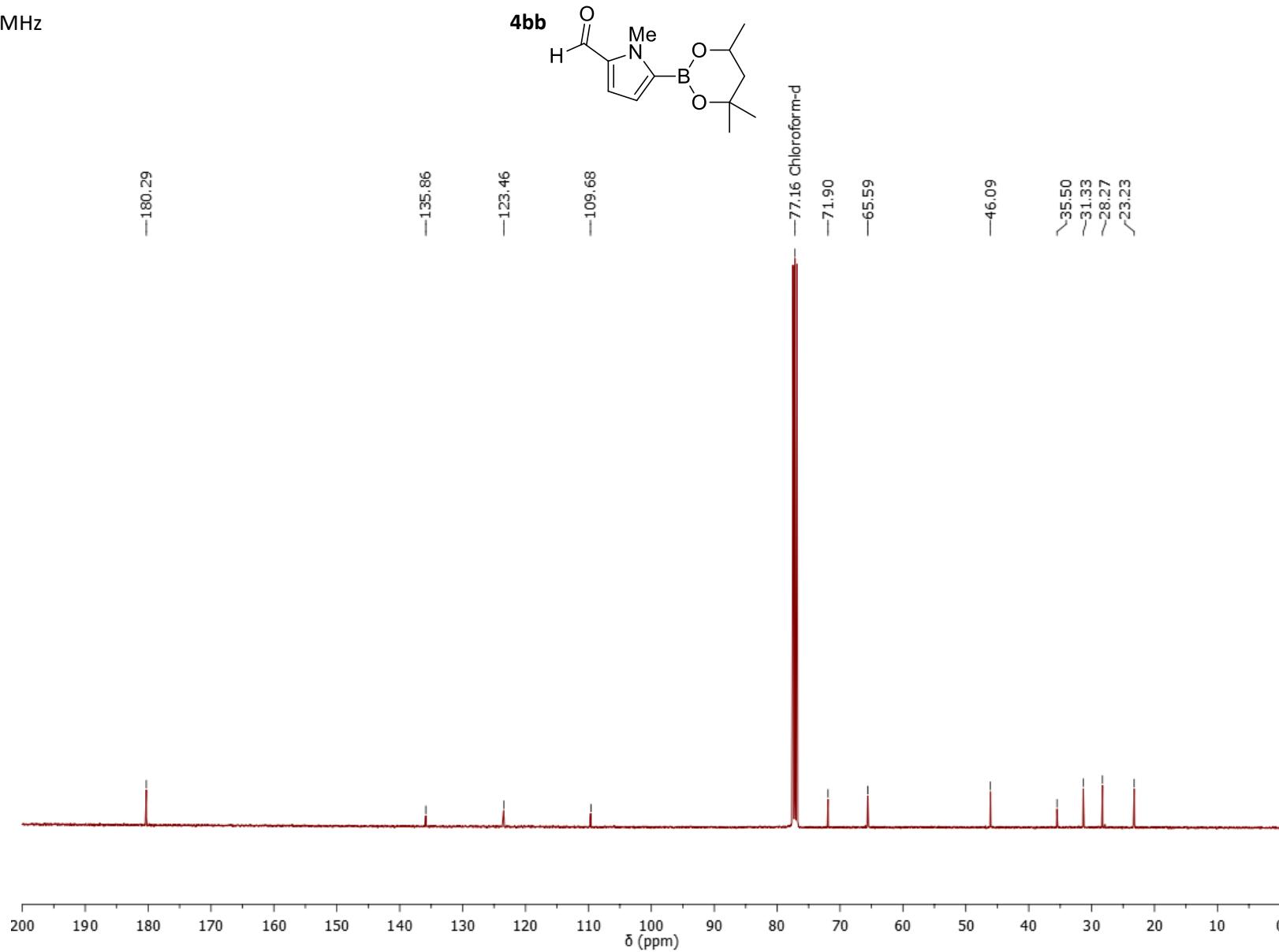
$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$



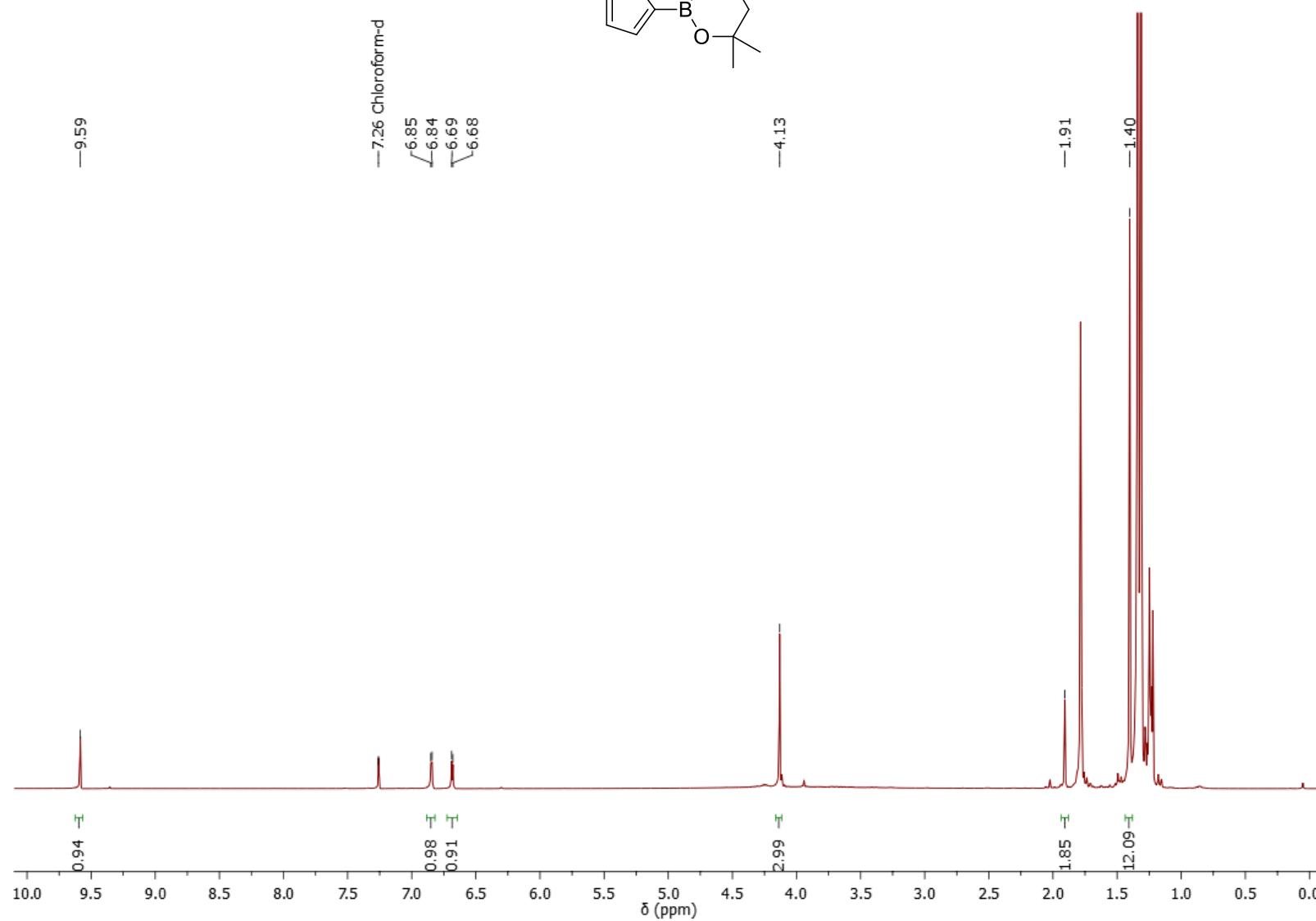
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



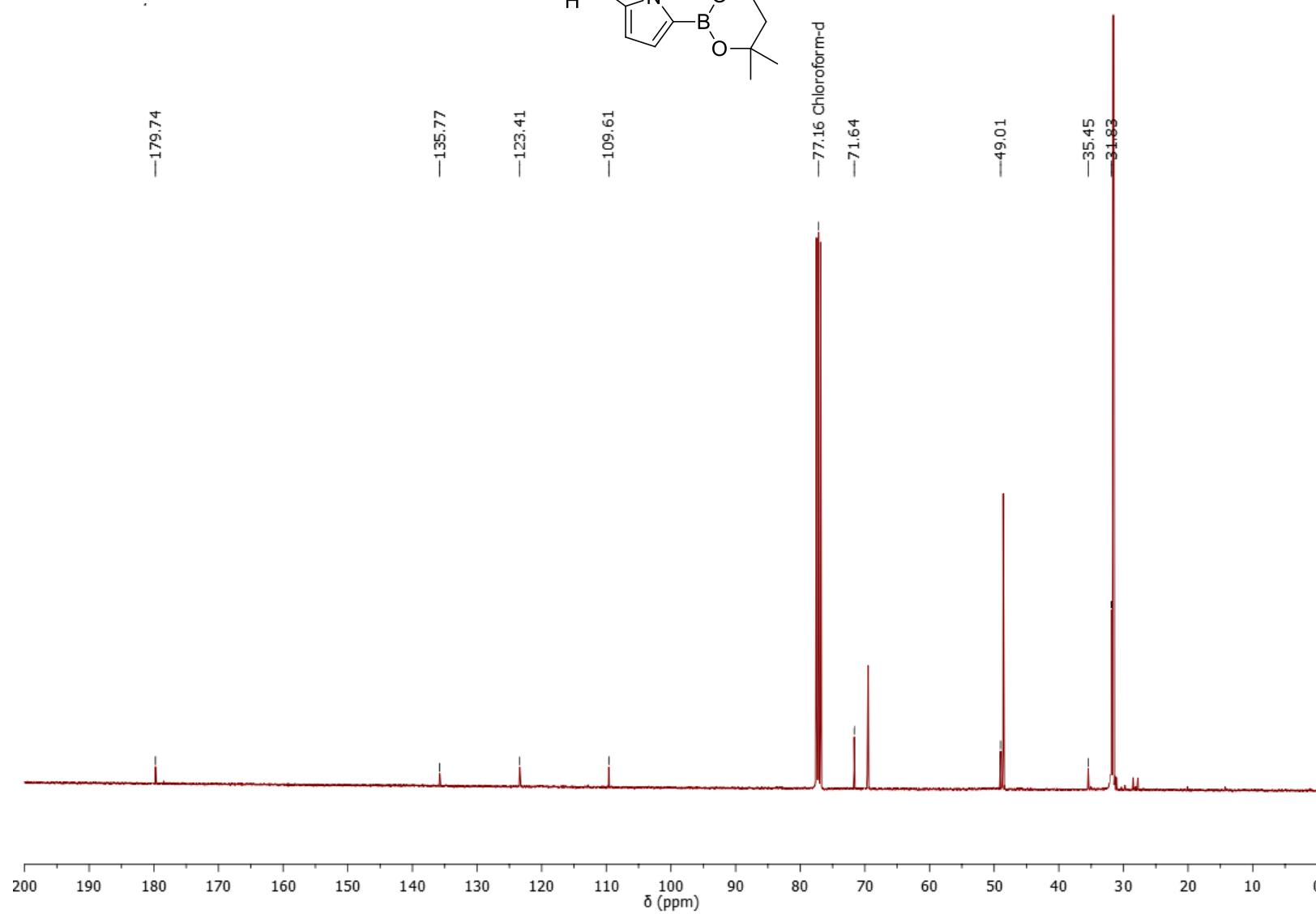
<sup>13</sup>C 101MHz



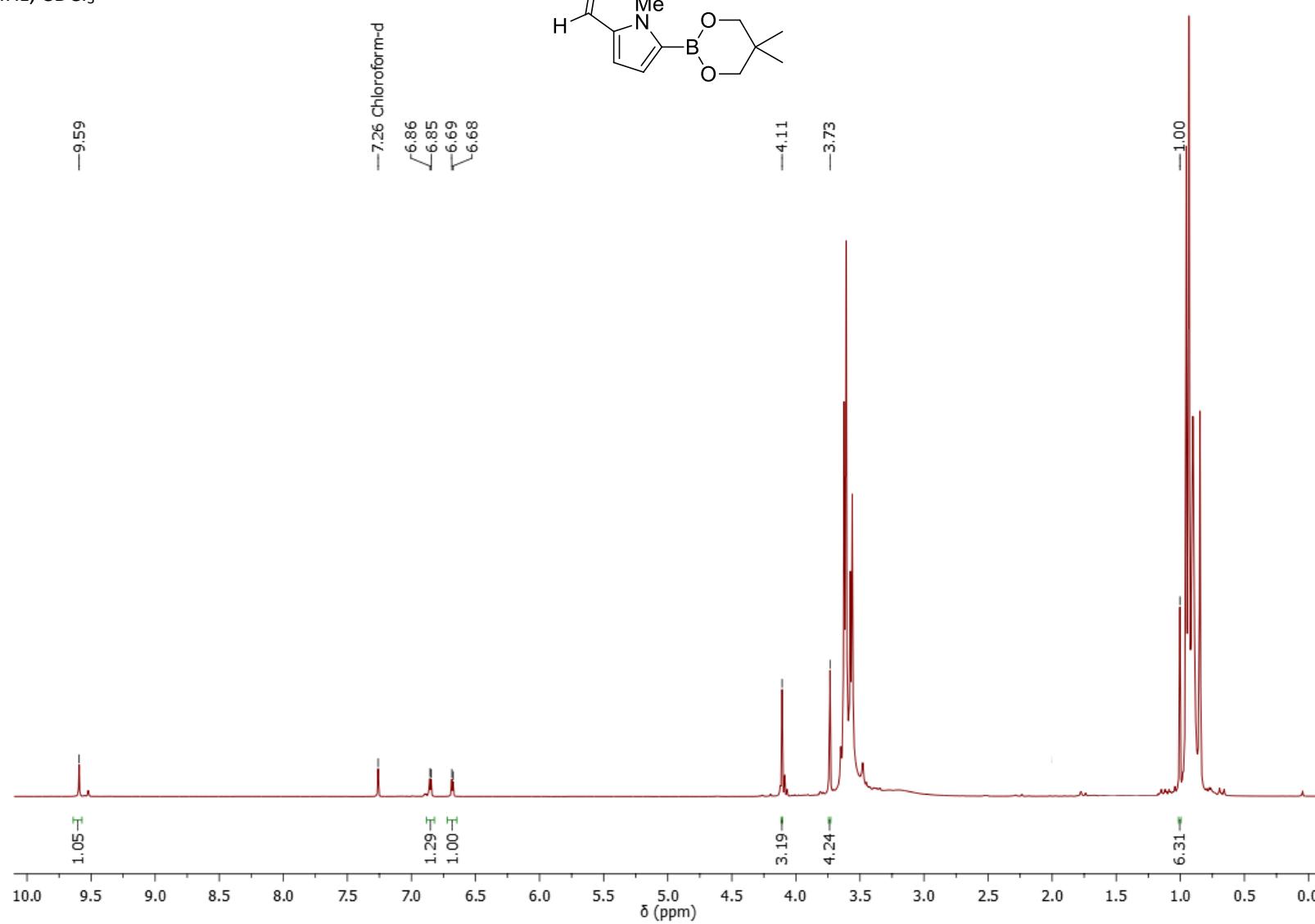
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



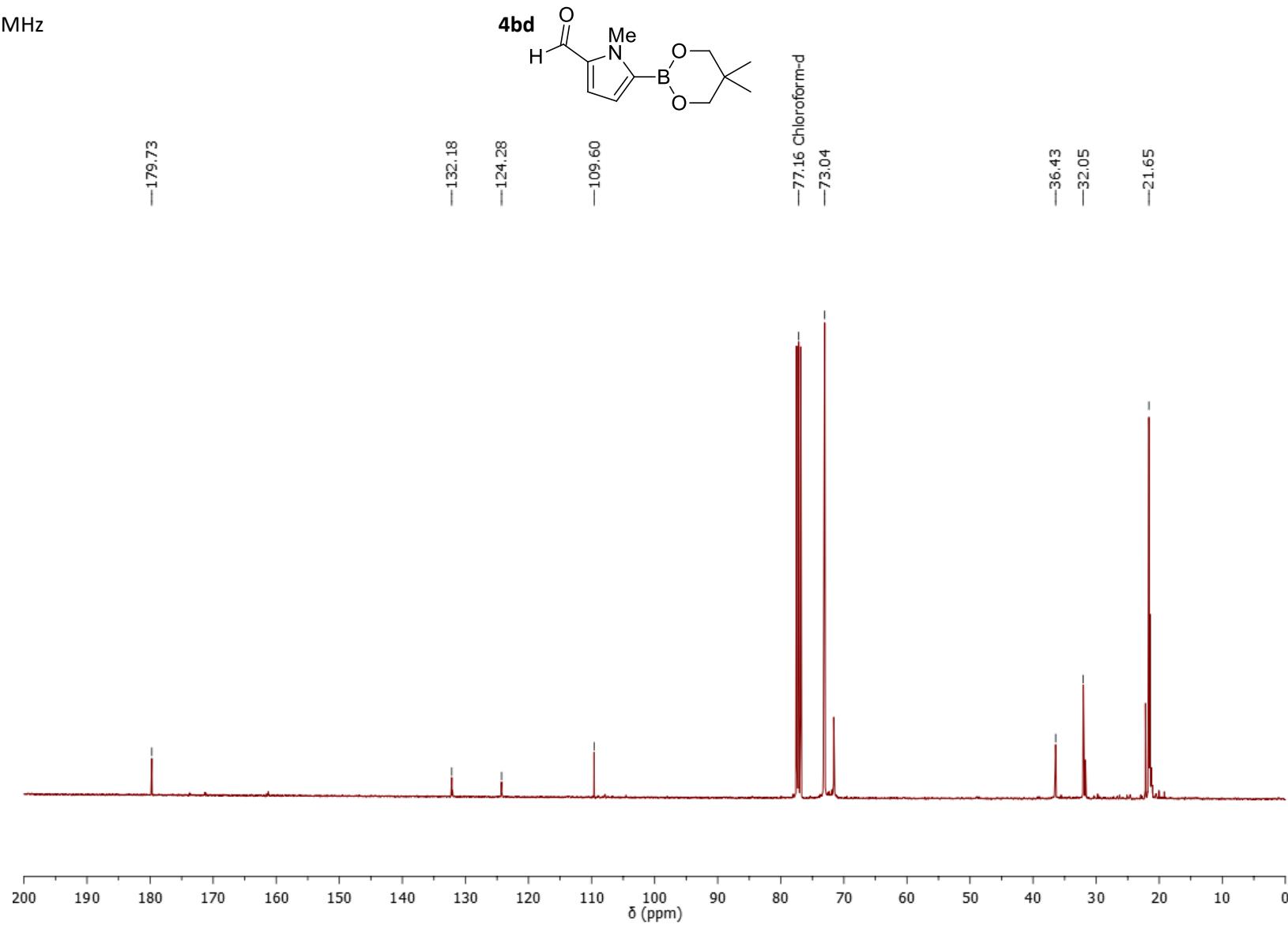
<sup>13</sup>C 101MHz



$^1\text{H}$  400MHz,  $\text{CDCl}_3$

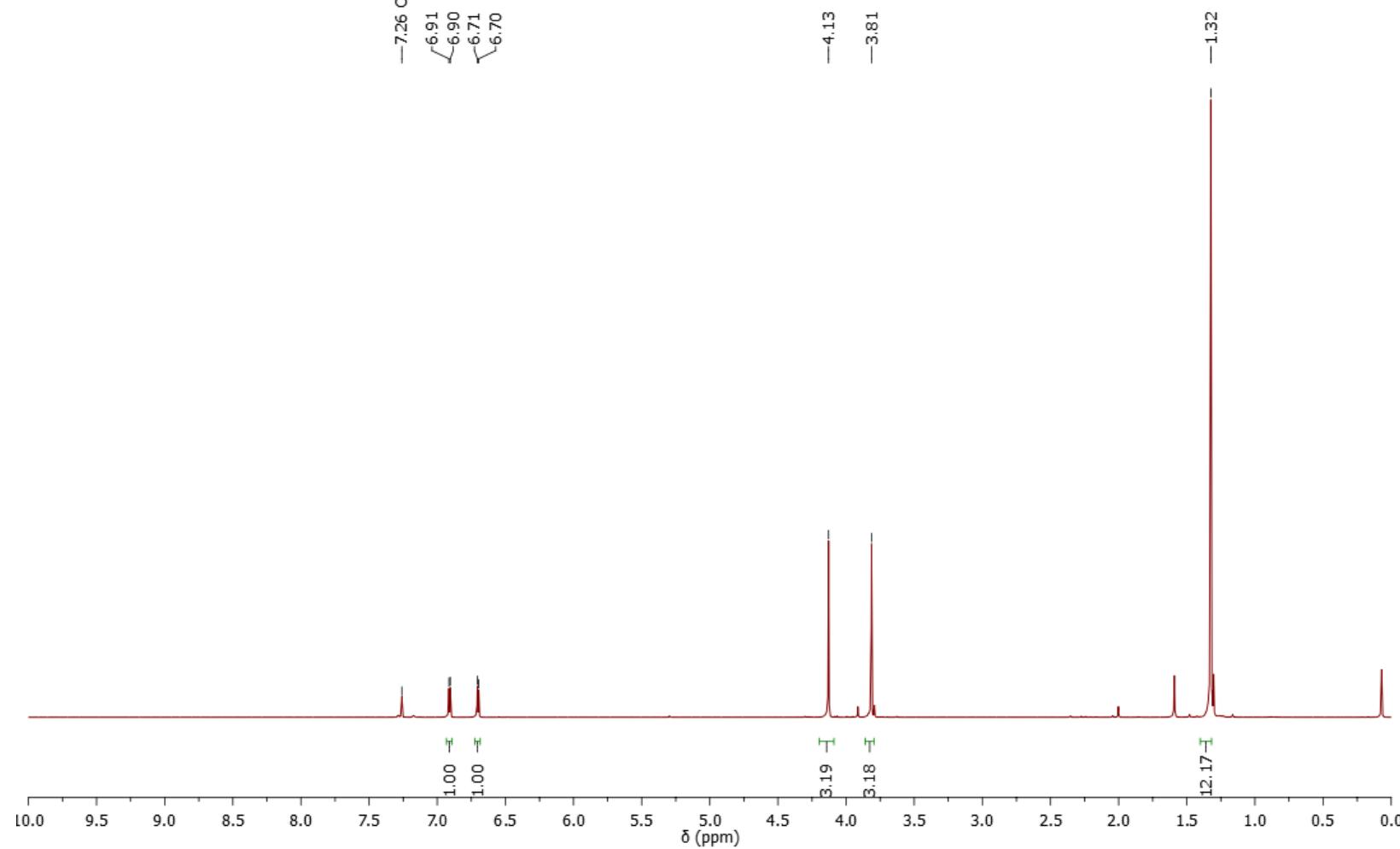
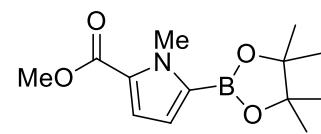


<sup>13</sup>C 101MHz

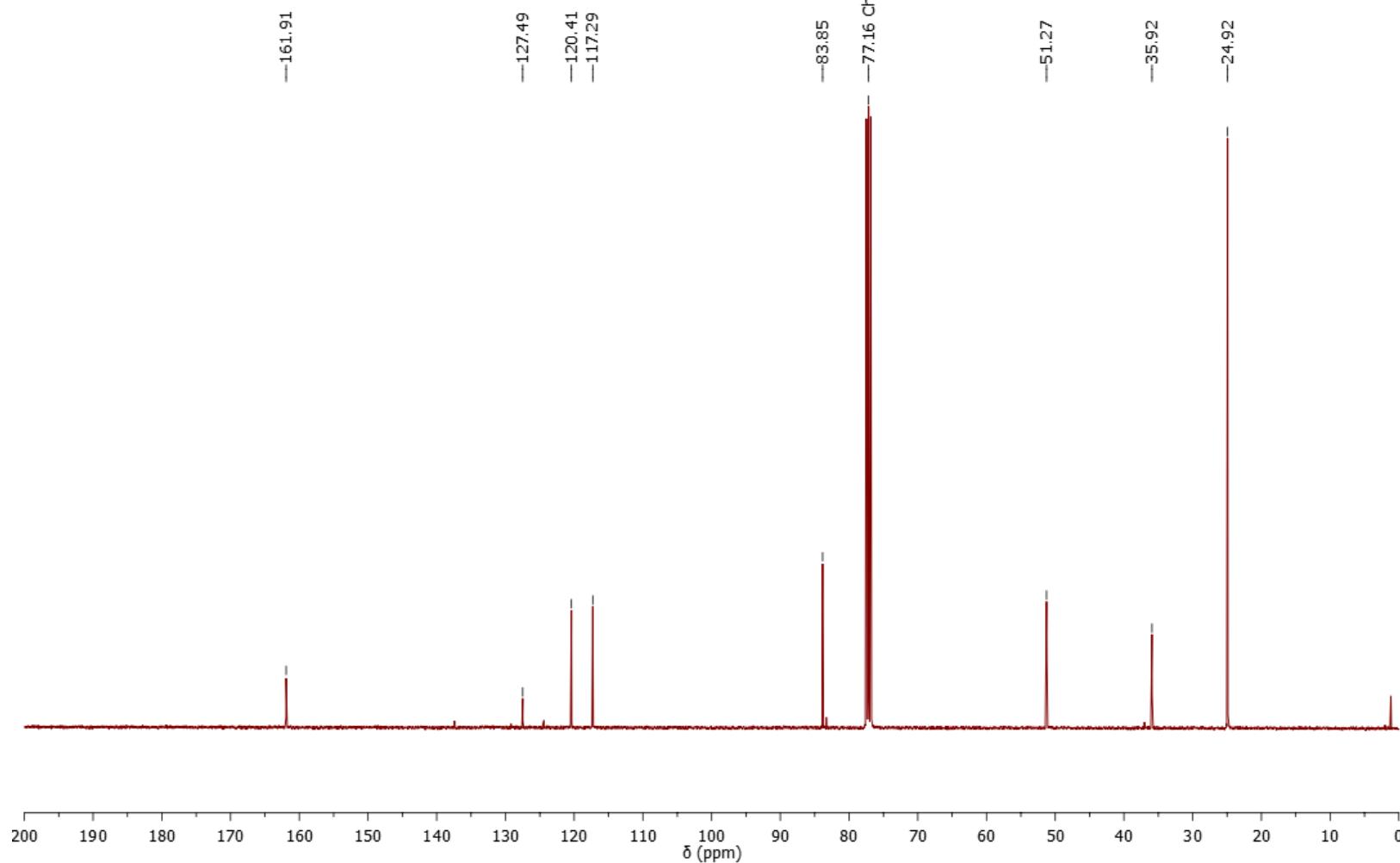
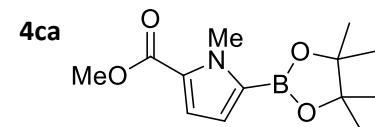


$^1\text{H}$  400MHz,  $\text{CDCl}_3$

**4ca**

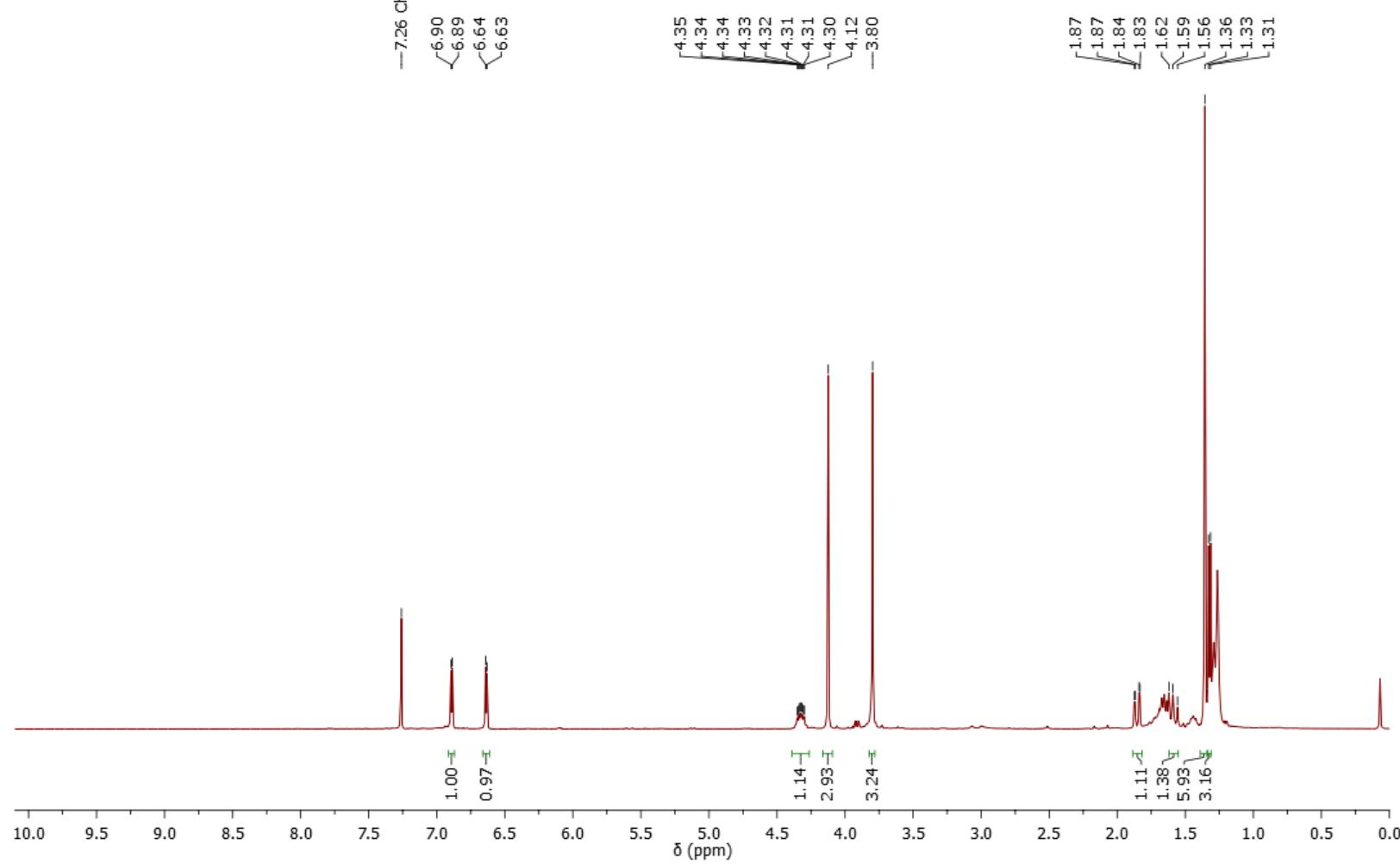
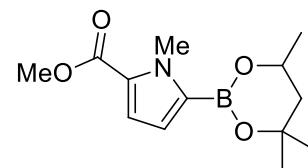


$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$

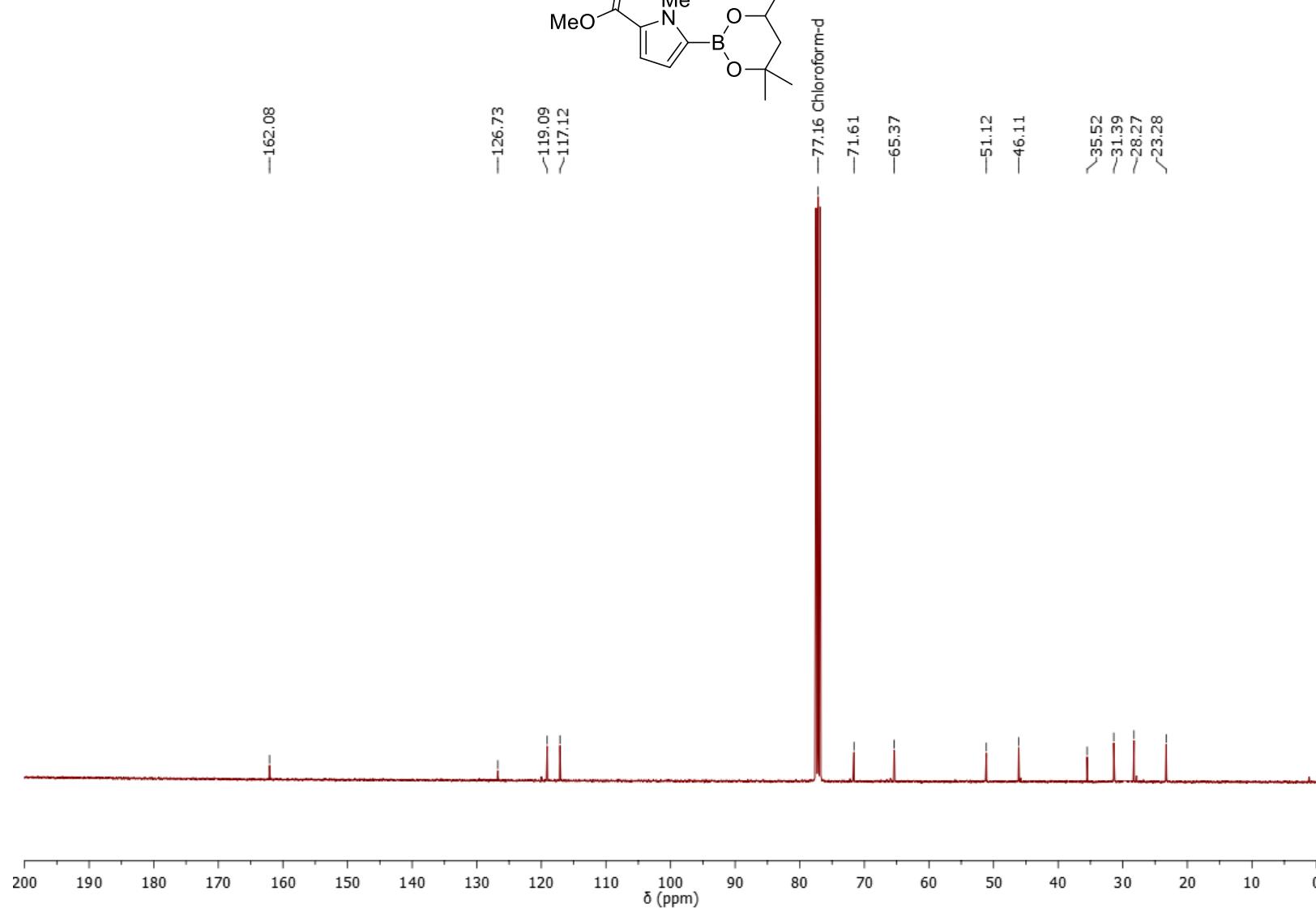


<sup>1</sup>H 400MHz, CDCl<sub>3</sub>

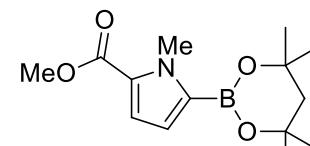
**4cb**



<sup>13</sup>C 101MHz



<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



-4.14

—7.26 Chloroform

6.90

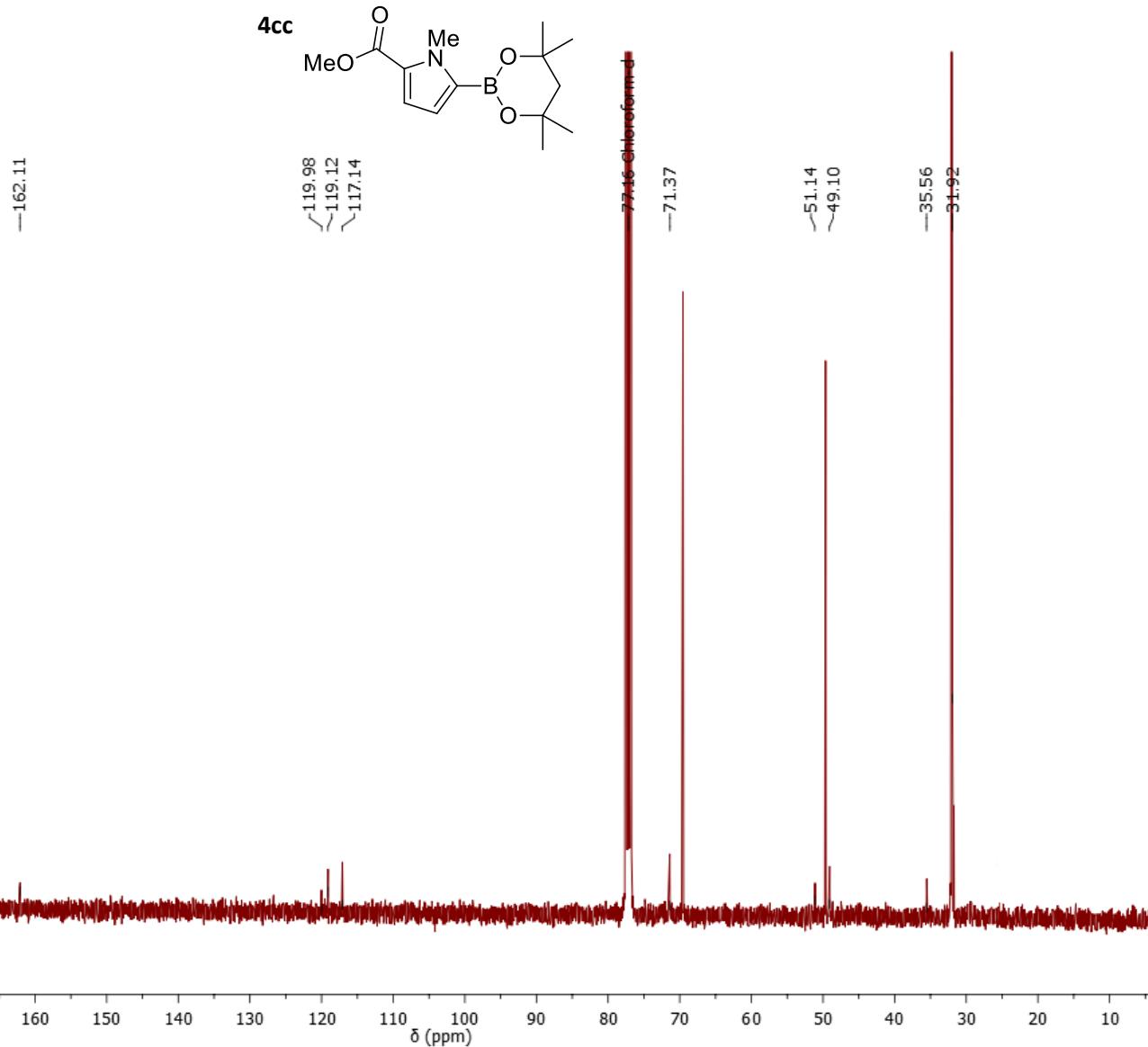
6.89

6.64

Chemical shift scale (ppm) for NMR spectra, ranging from 10.0 to 0.5 ppm.

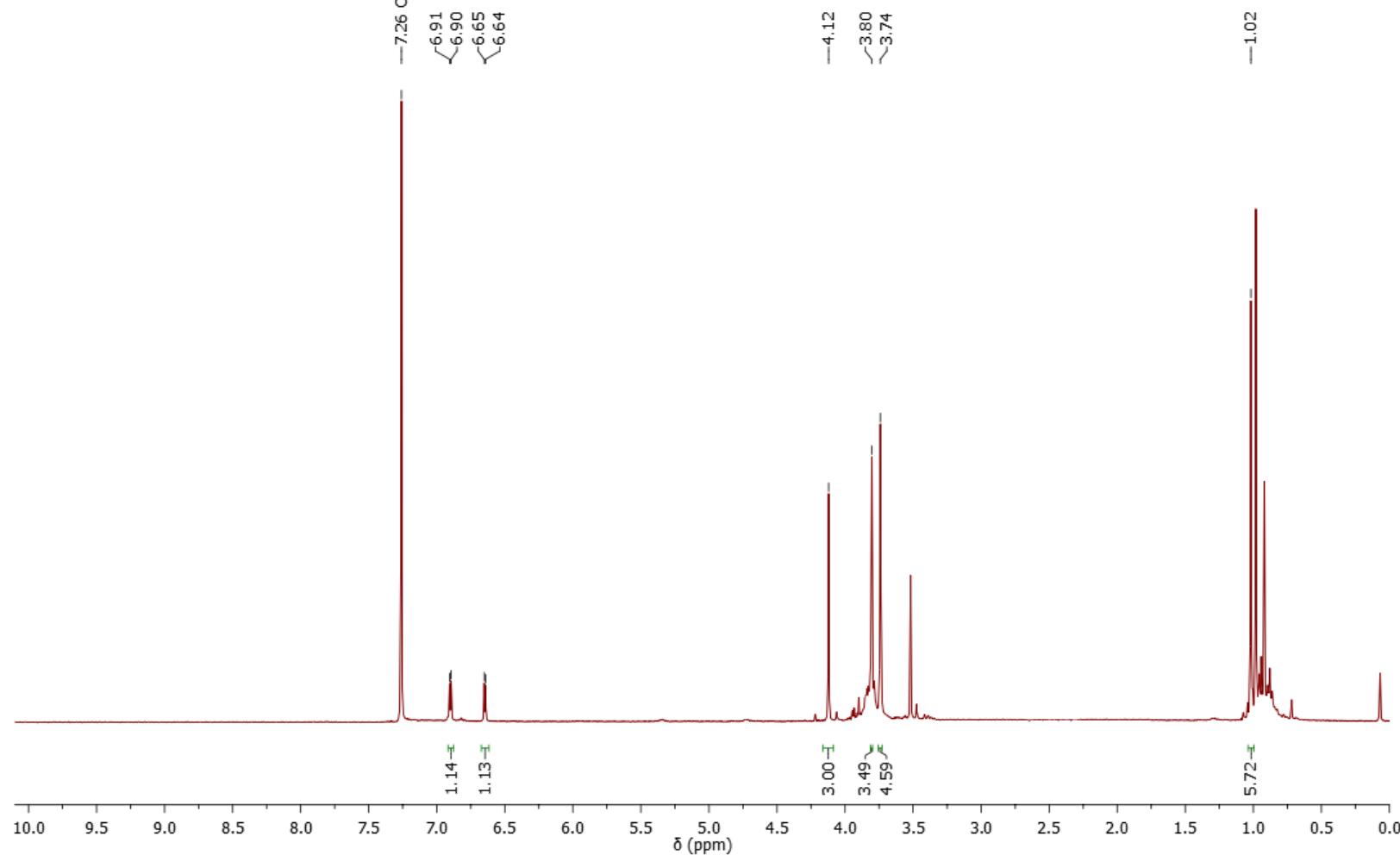
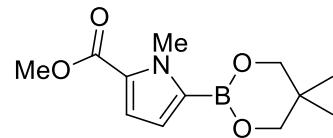
S147

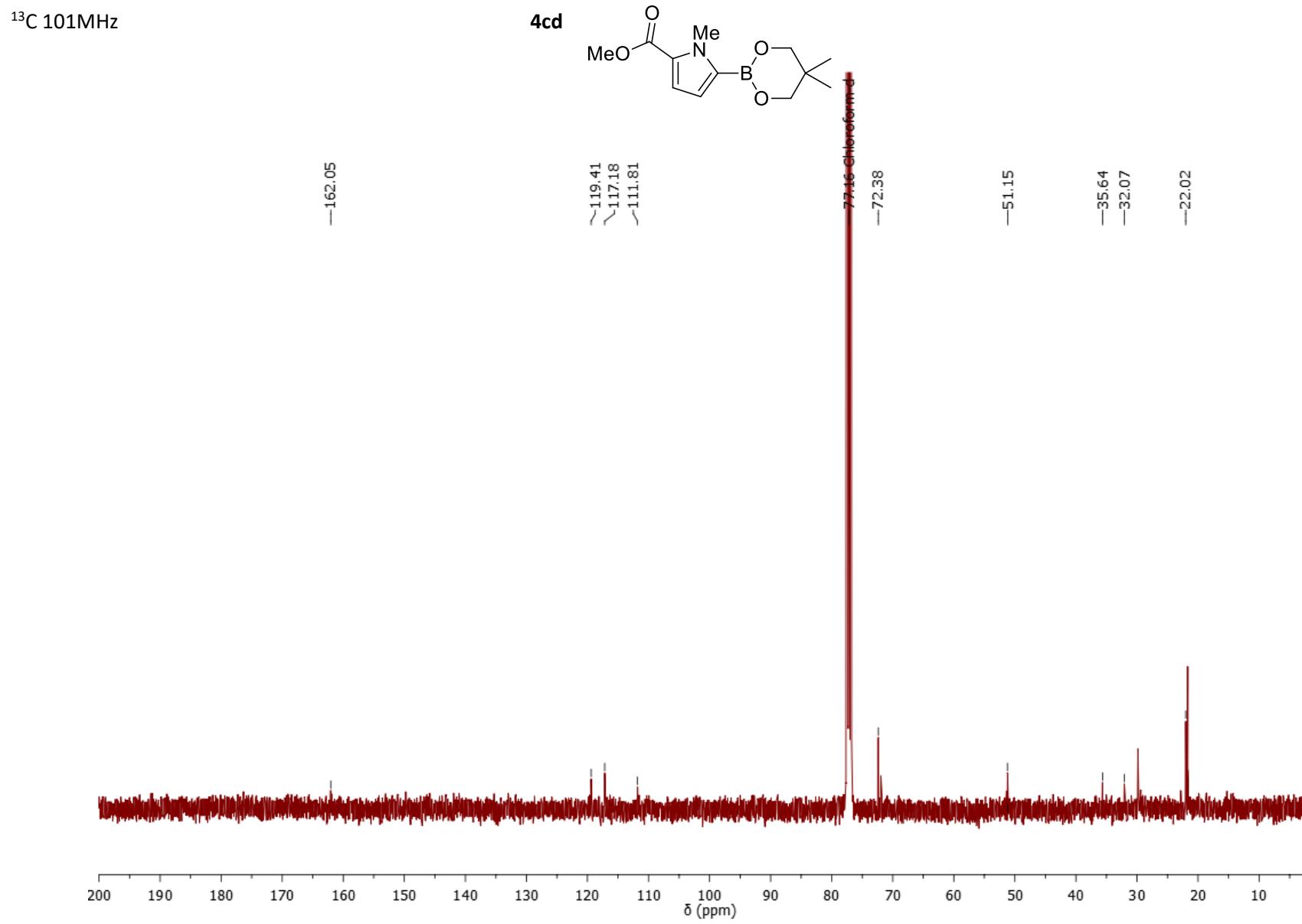
<sup>13</sup>C 101MHz



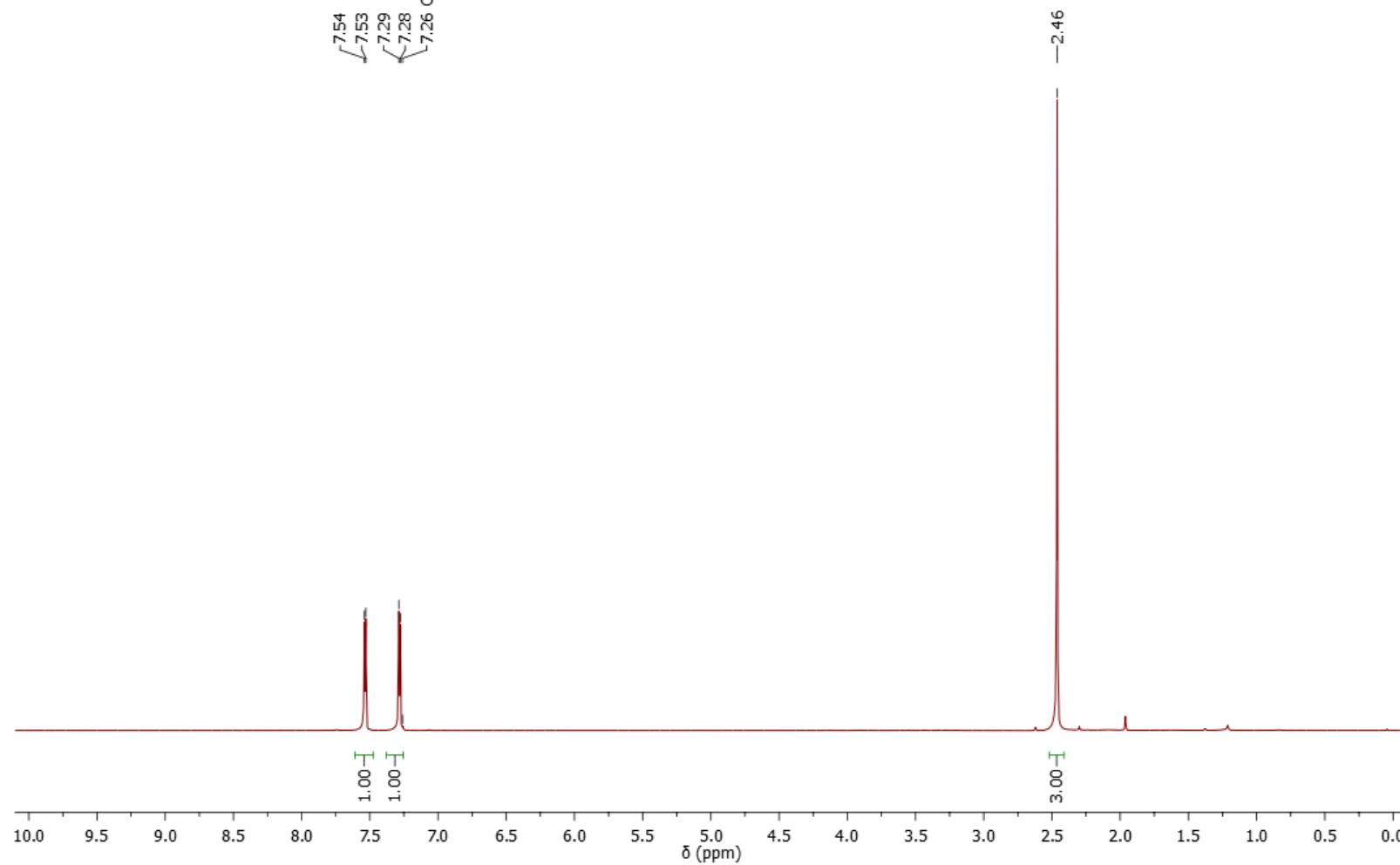
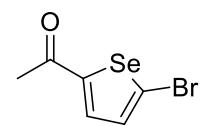
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>

**4cd**



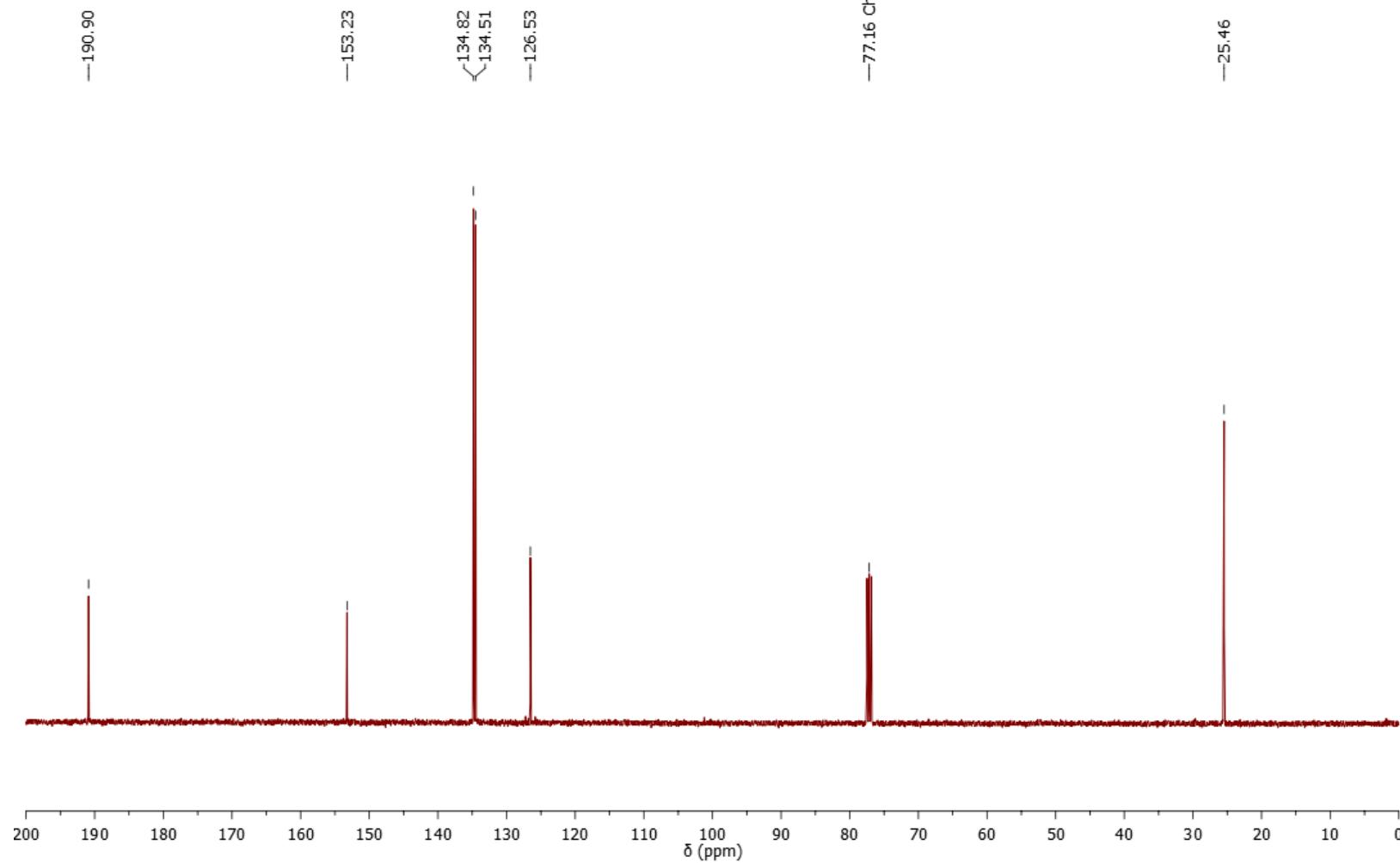
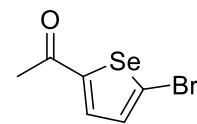


$^1\text{H}$  400MHz,  $\text{CDCl}_3$

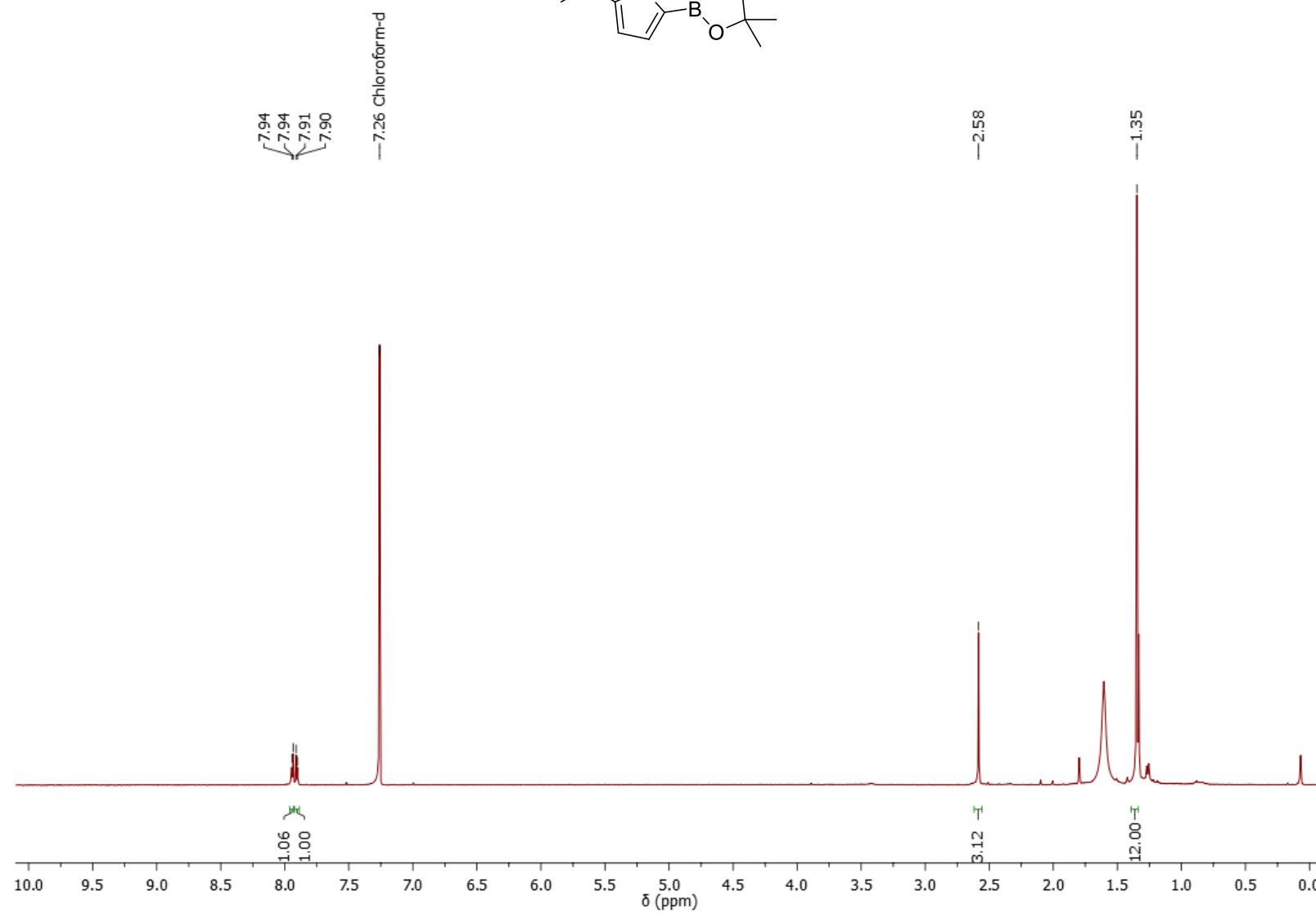
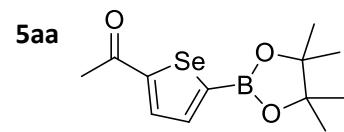


## Selenophene boronate esters

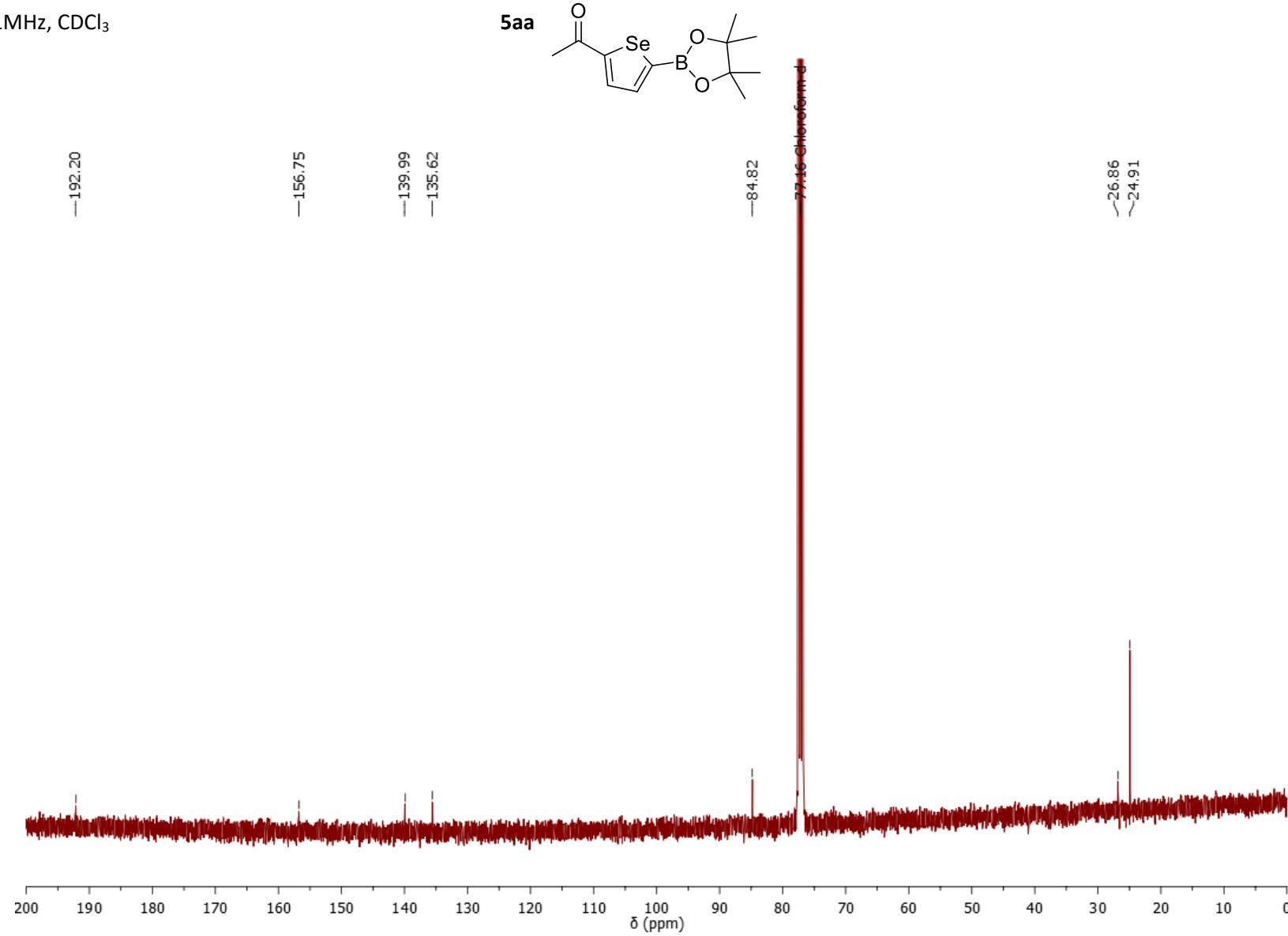
$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$



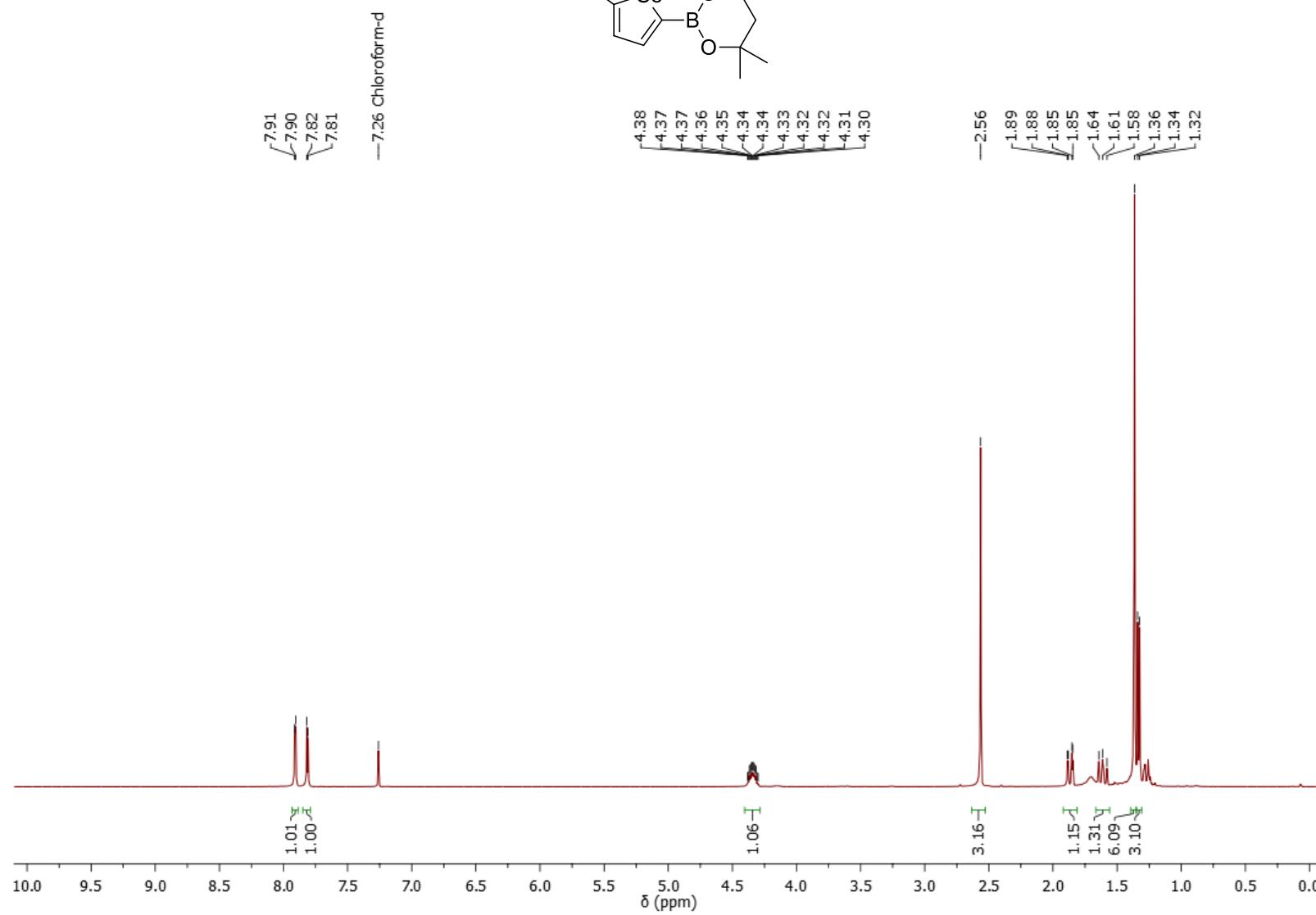
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



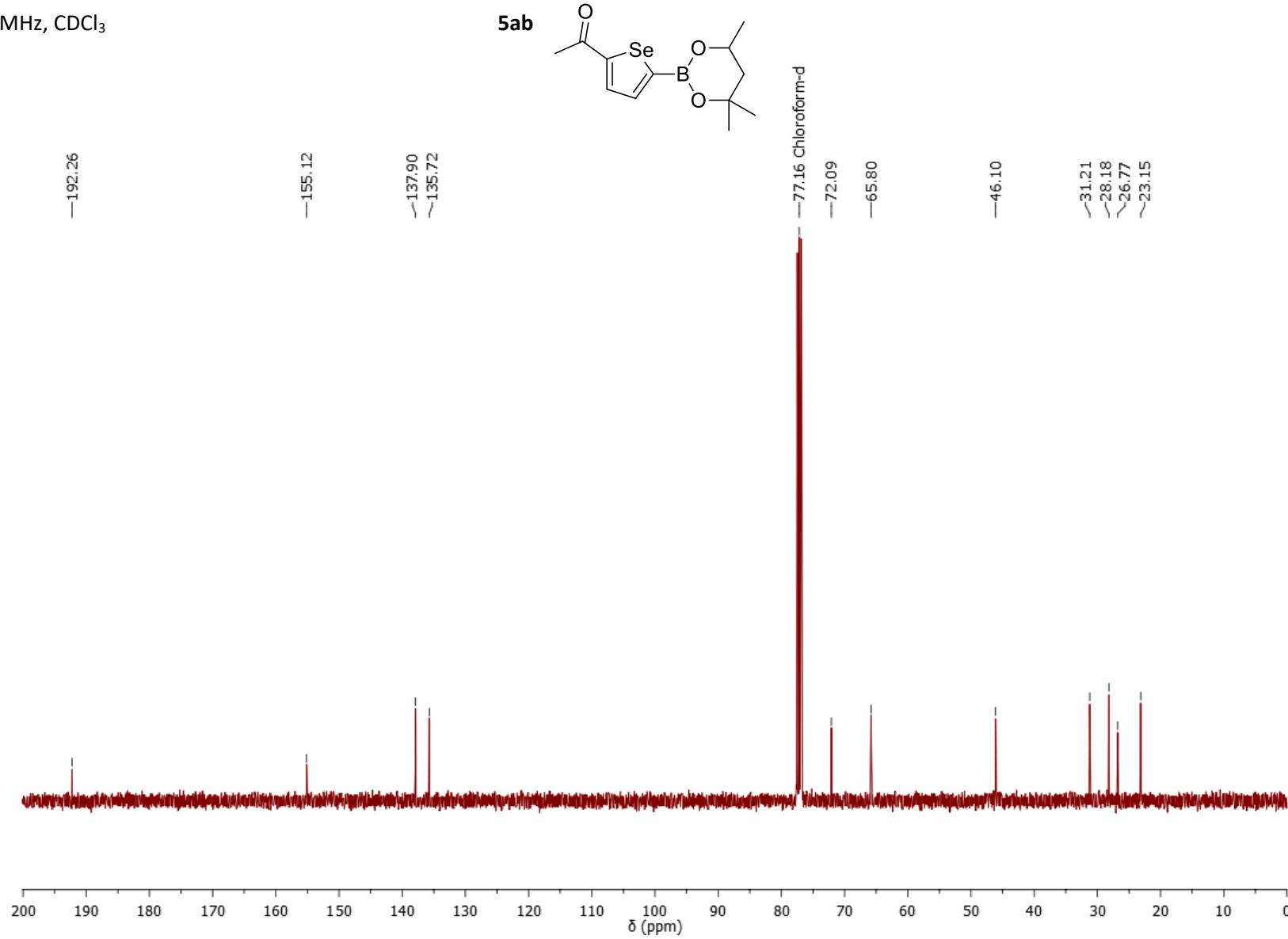
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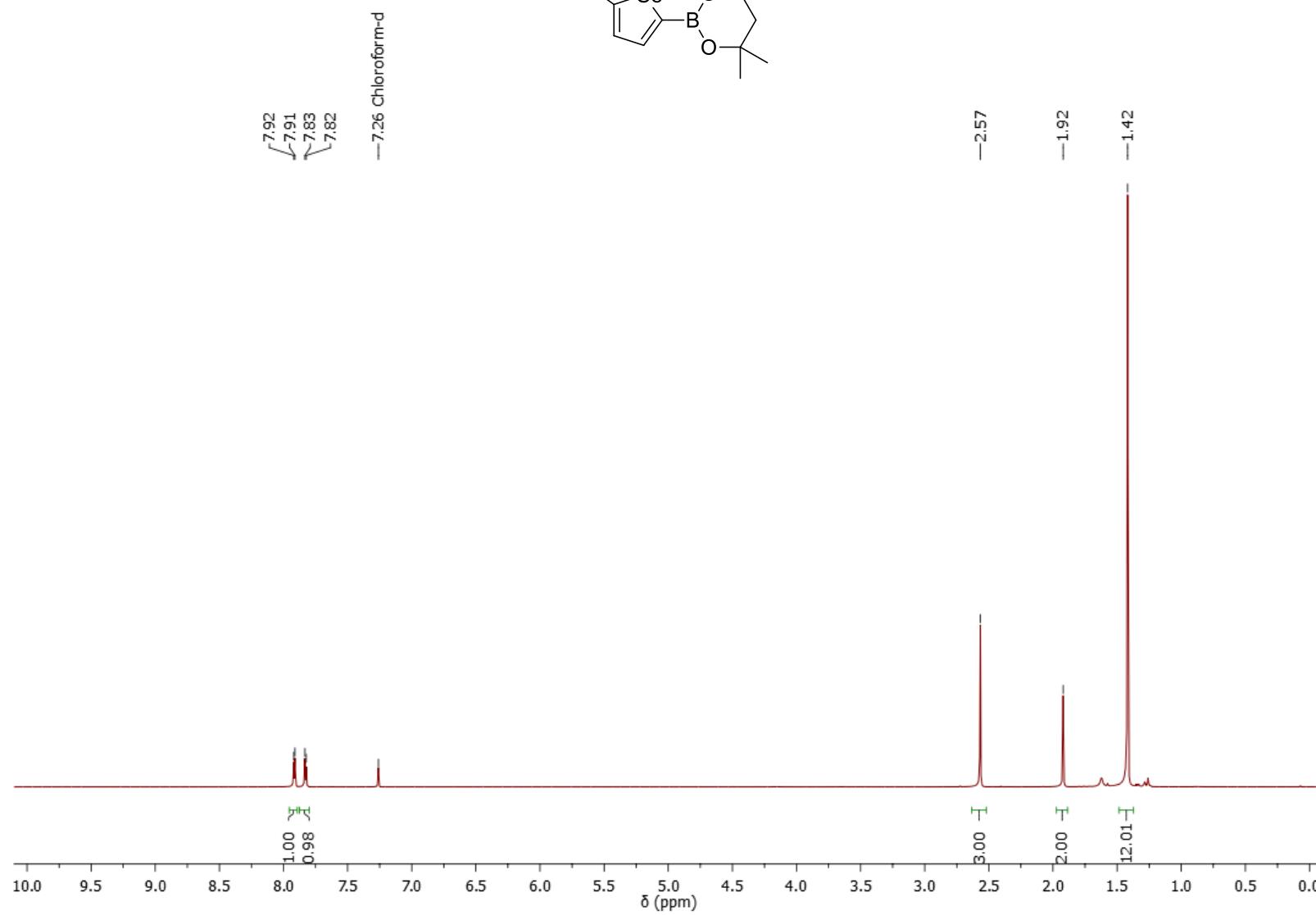
<sup>1</sup>H 400MHz, CDCl<sub>3</sub>



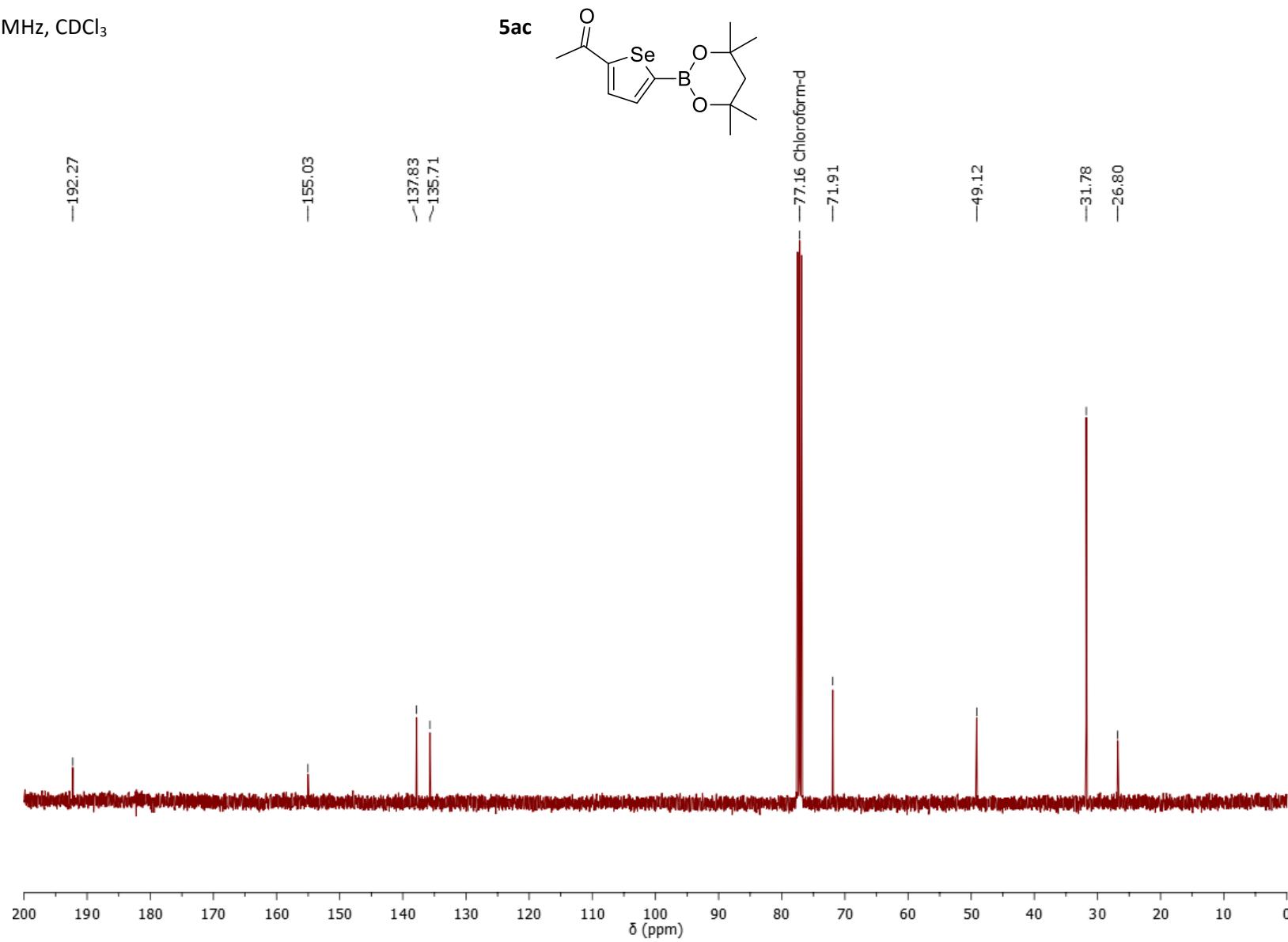
$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$



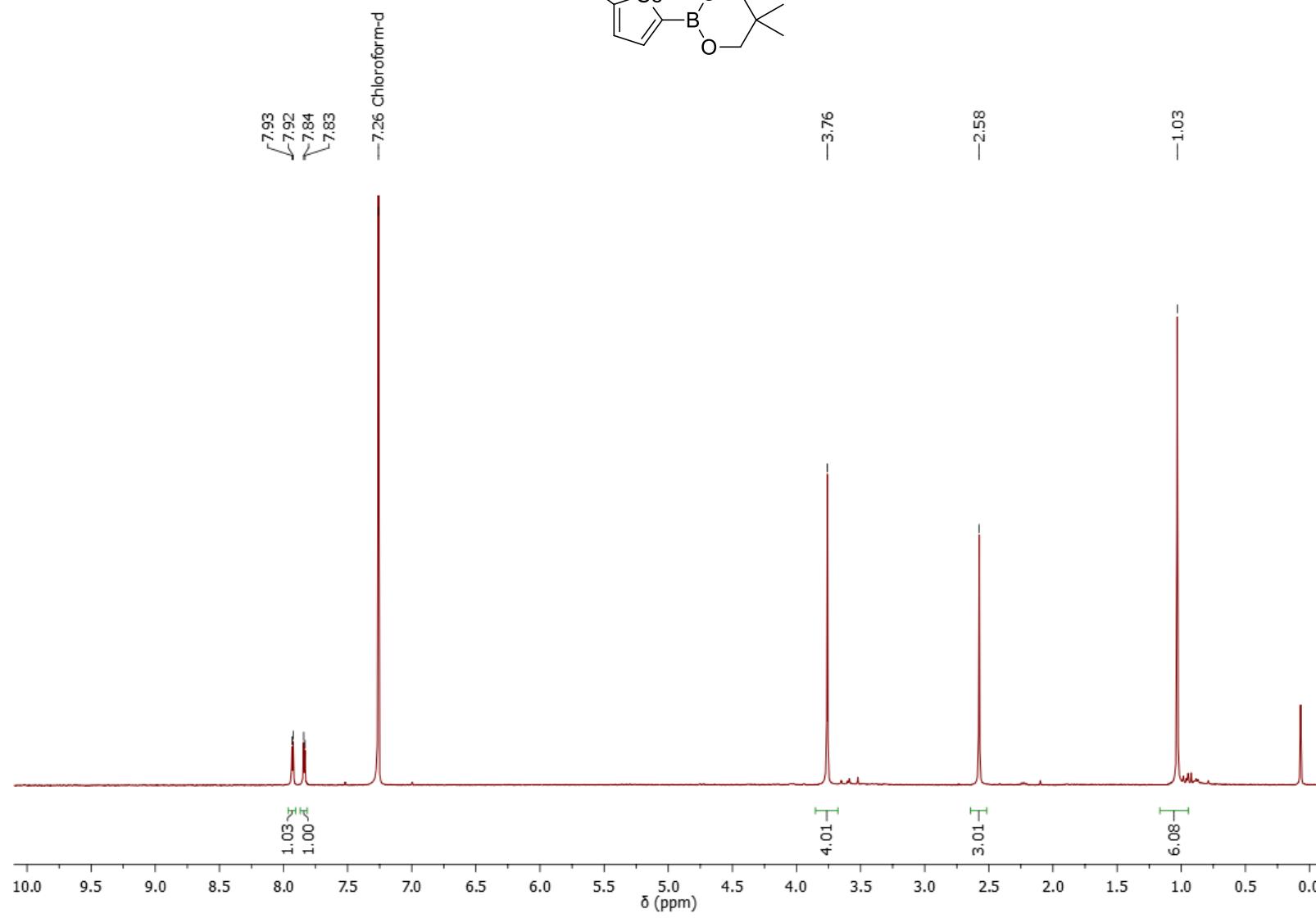
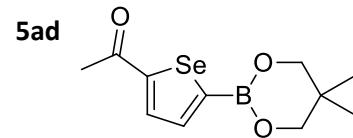
$^1\text{H}$  400MHz,  $\text{CDCl}_3$



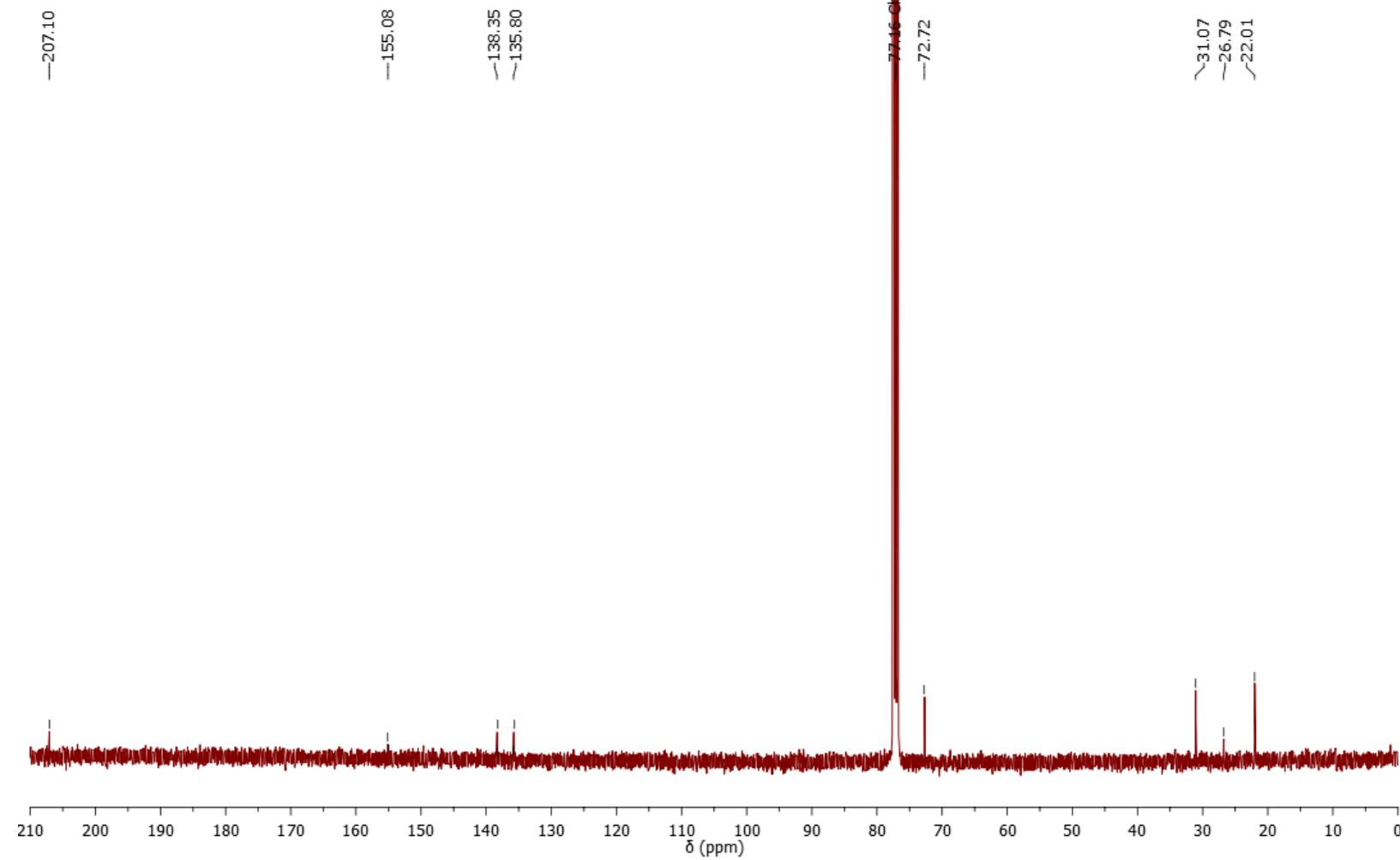
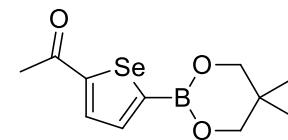
$^{13}\text{C}$  101MHz,  $\text{CDCl}_3$



<sup>1</sup>H 400MHz, CDCl<sub>3</sub>

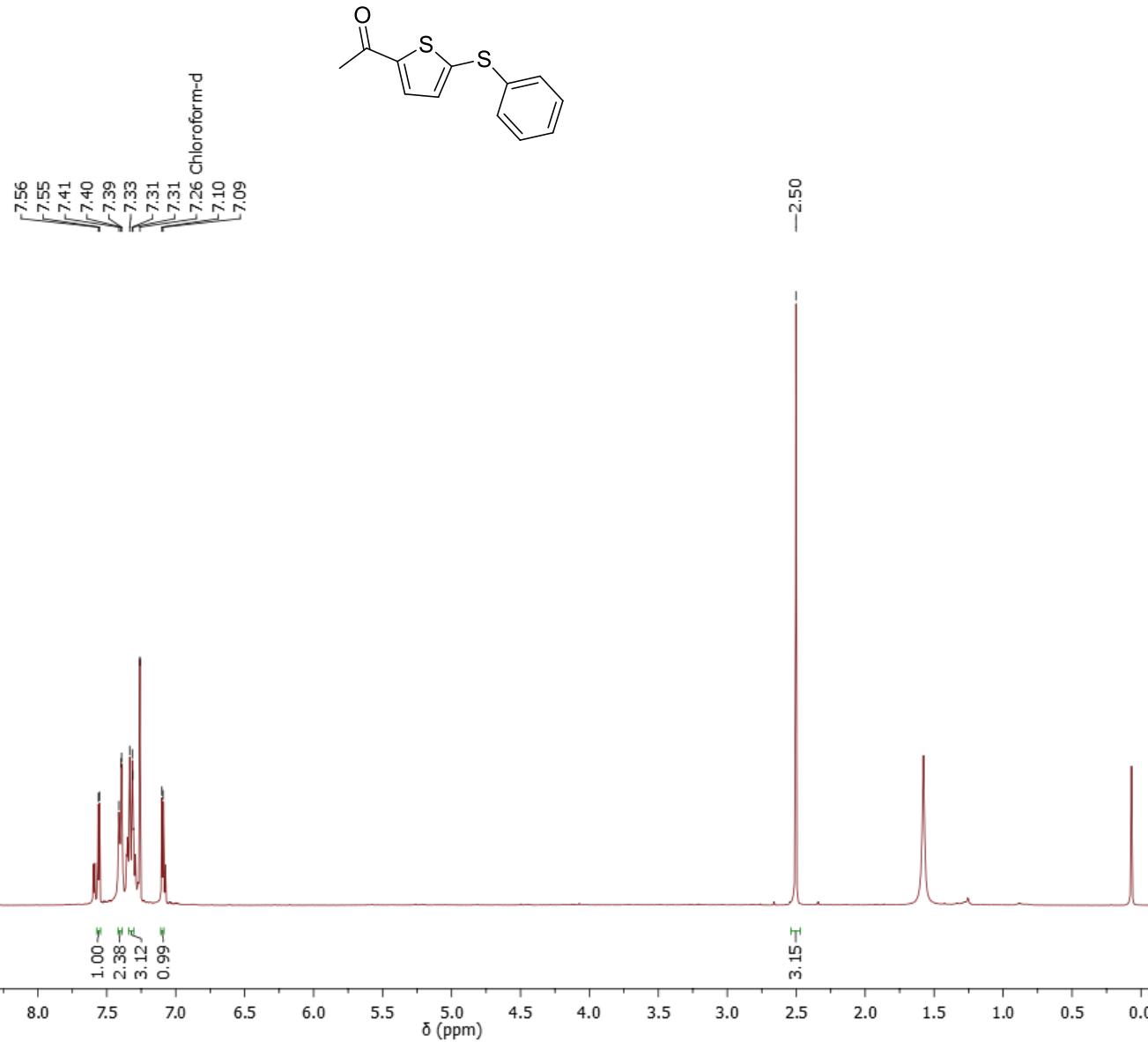


<sup>13</sup>C 101MHz, CDCl<sub>3</sub>



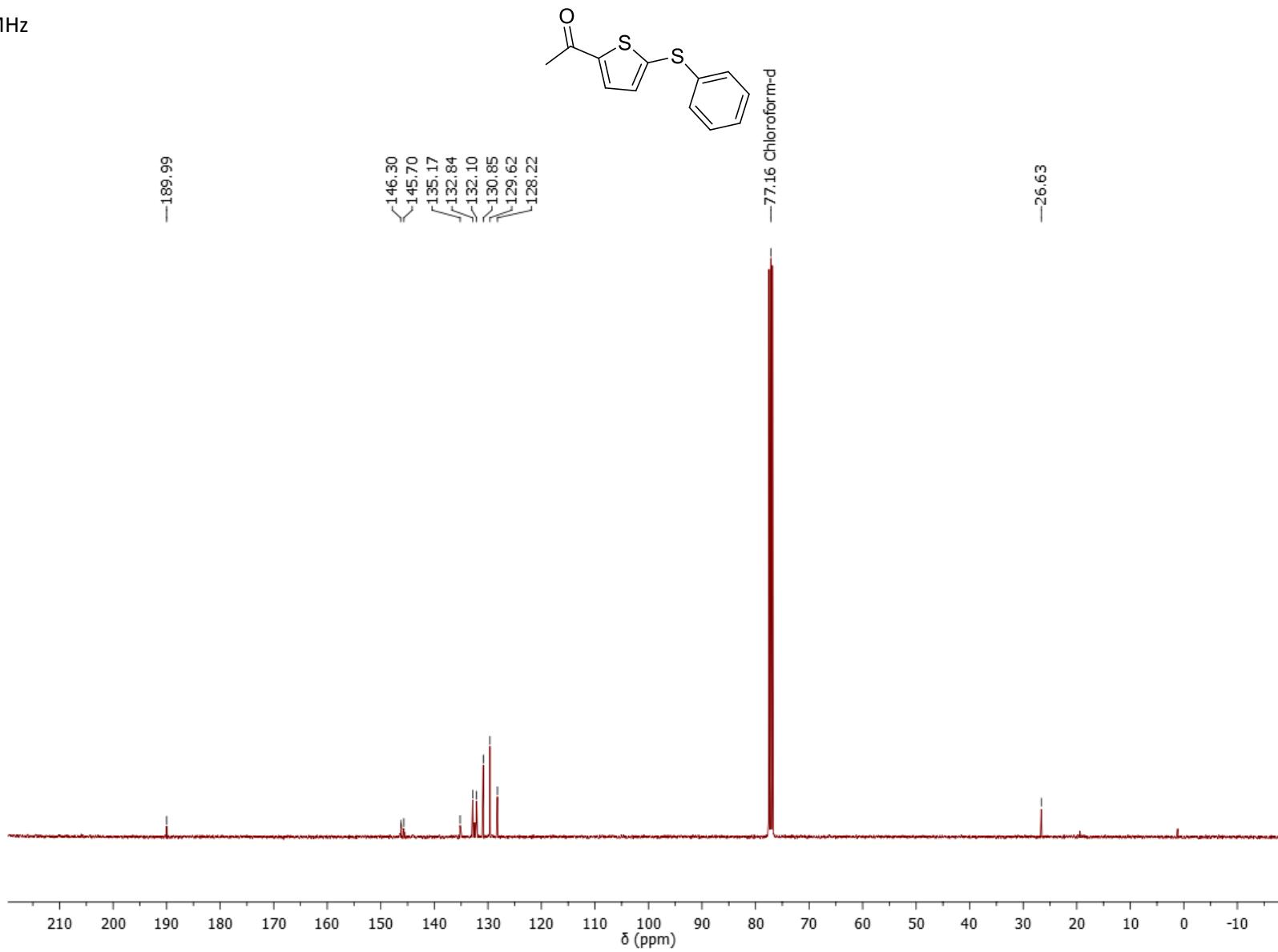
Thiophene thioether

$^1\text{H}$  400MHz,  $\text{CDCl}_3$



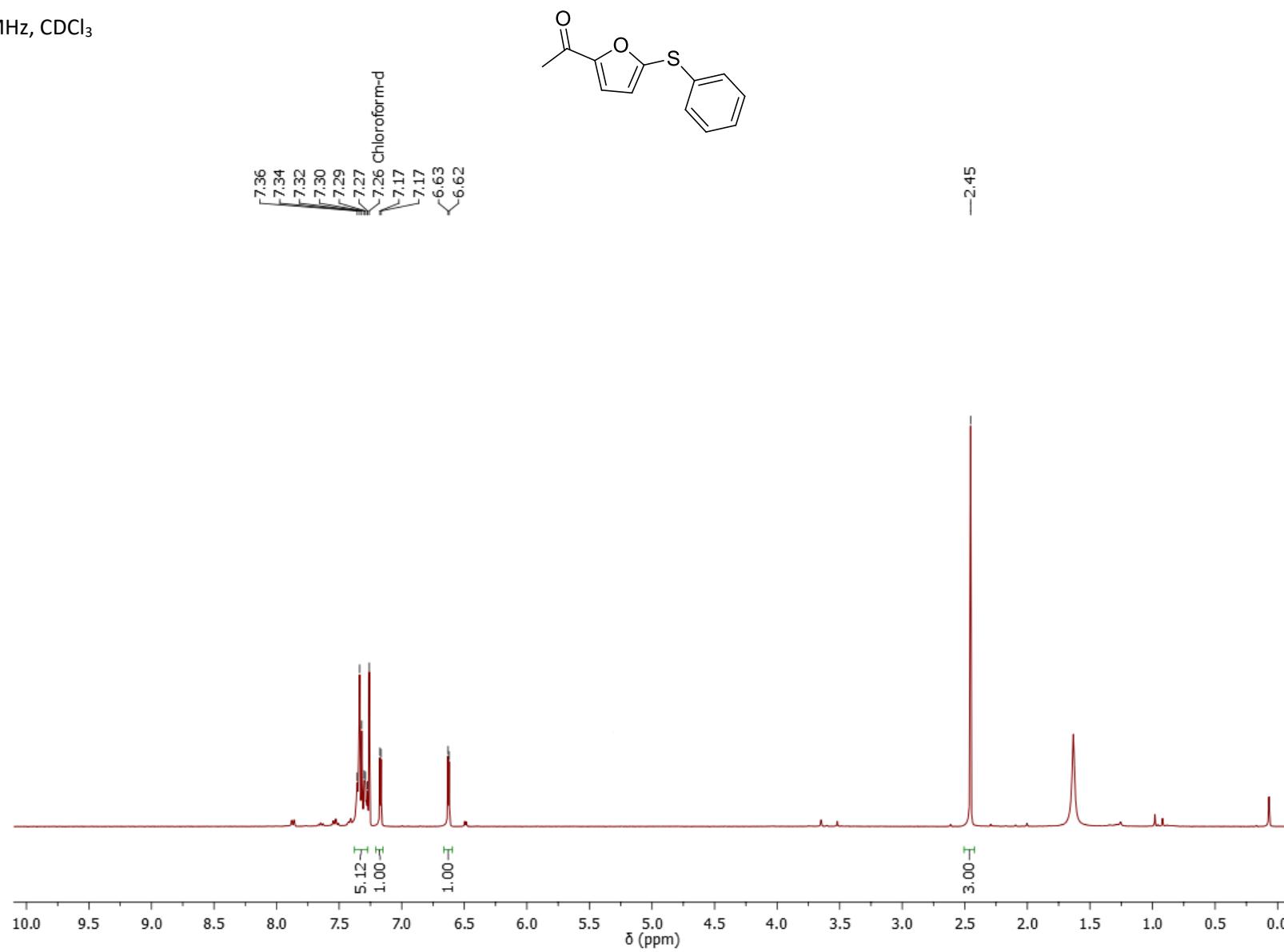
Thiophene thioether

<sup>13</sup>C 101MHz



**Furan thioether**

$^1\text{H}$  400MHz,  $\text{CDCl}_3$



**Furan thioether**

<sup>13</sup>C 101MHz

