

Supplementary Information

Strain-release enables access to carbonyl conjugated allylic diborons and alkenyl boronates having multiple contiguous stereocenters in a one-pot process

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Table of Contents

General information	3
Experimental Section	4
Compound characterization data	21
X-Ray Studies.....	47
References	51
NMR Spectra.....	52

General information

Materials

All reagents used in chemical reactions were purchased from Sigma-Aldrich, Acros Organics, Thermo Scientific, TCI or BLDPharm. Anhydrous solvents (Sure/Seal™ bottles) were purchased from Sigma-Aldrich and distilled over CaH₂. 2-dram vials were purchased from chem glass (CG-4912-02). Reaction progress was monitored via thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 TLC plates. The TLC plates were visualized under a UV lamp and/or by treatment with KMnO₄ or curcumin stains. Flash column chromatography was performed using a Teledyne-Isco CombiFlash Rf purification system employing silica gel 60 Å (230-400 or 400-632 mesh size). Chromatographic solvent systems are given as volume:volume ratios. Organic solutions were concentrated via rotary evaporation under reduced pressure with a bath temperature of 45 °C unless otherwise mentioned. All reactions were performed in oven-dried glassware under an atmosphere of dry nitrogen/argon unless otherwise mentioned.

Apparatus

¹H and ¹³C NMR spectra were recorded on a Varian-400 (400 MHz, ¹H; 100 MHz, ¹³C; 128 MHz, ¹¹B) or Bruker 500 MHz spectrometer unless otherwise mentioned. The ¹H and ¹³C chemical shifts are reported in parts per million (ppm) and referenced to residual chloroform signal as applicable. ¹¹B chemical shifts are referenced to an external standard of BF₃·Et₂O (δ = 0 ppm). The following abbreviations are used to designate chemical shift multiplicities: s = singlet, d = doublet, dd = doublet of doublets, ddd, doublet of doublet of doublet, dt = doublet of triplet, dtd = double of triplet of doublet, td – triplet of doublet, tdd = triplet of doublet of doublet, t = triplet, m = multiplet, q = quartet, quint = quintet. All ¹³C NMR spectra are proton decoupled. The carbon atoms connected to a boron atom (C-B) were not detected in ¹³C NMR (due to quadrupolar relaxation). NMR spectra were processed using MestReNova software. High resolution mass spectra (HRMS) were obtained at the Center for Mass Spectrometry at Stevens Institute of Technology using a Waters SYNAPT G2 Q-ToF (Atmospheric Solids Analysis Probe (ASAP) mode), unless otherwise mentioned. Melting points were measured on an IA9000 series digital melting point apparatus and are uncorrected. The absorbance was measured with PerkinElmer Lambda 25 UV/Vis spectrophotometer. HPLC analysis was performed on an Agilent 1100 series HPLC instrument using Daicel CHIRALPAK IBN-3 column at 20 °C. 210 nm wavelength DAD detector system was used for HPLC analysis. Photochemical reactions were conducted in a Penn PhD Photoreactor M2 (365 nm LED light source).

Experimental Section

Preparation of VCPs (1a to 1f, Figure 1)

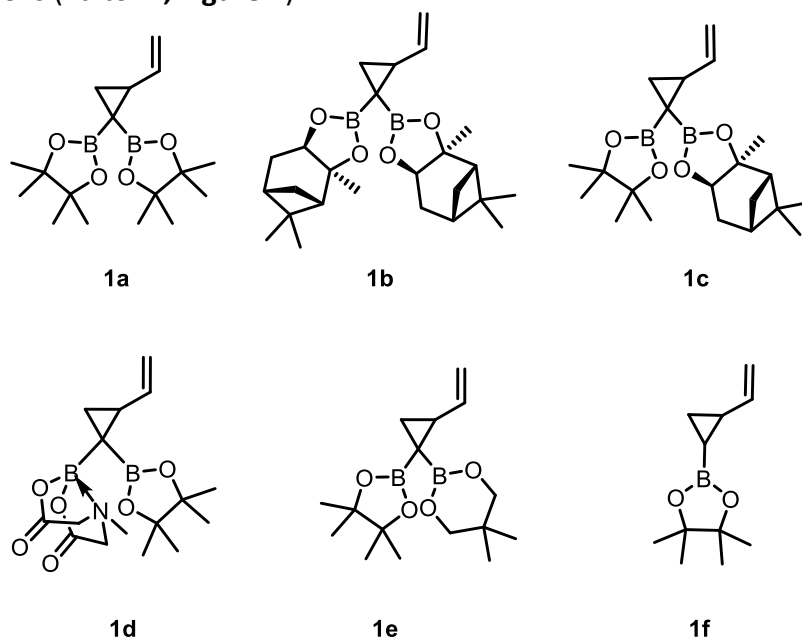
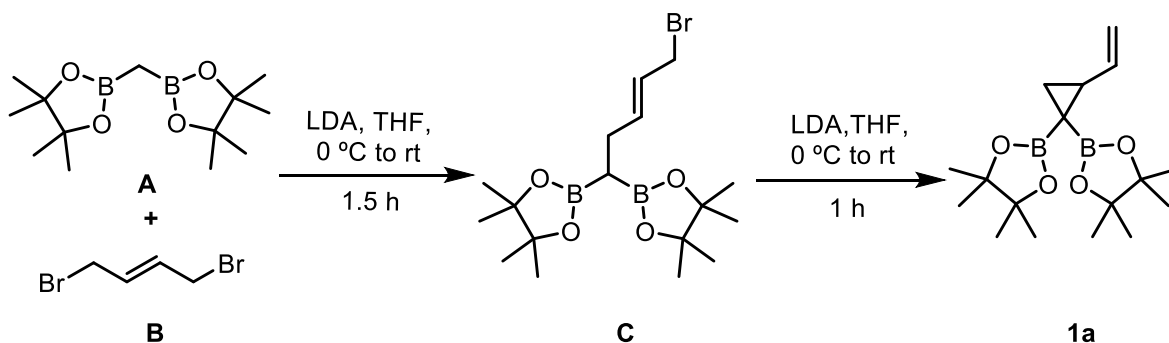


Figure 1. Vinyl cyclopropane diborons used in this study

General procedure A: Synthesis of Vinyl Cyclopropyl Diboron (VCPDB, 1a)



To a solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane **A** (5 gm, 18.65 mmol, 1 equiv.) in tetrahydrofuran (20 mL) in argon atmosphere, LDA (10.3 mL, 2M solution in tetrahydrofuran, 1.1 equiv.) was added at 0 °C. The reaction mixture was stirred at 23 °C until turbid solution/precipitate was observed (usually 20-30 min), this turbid solution was transferred dropwise to the solution of *trans*-1,4-Dibromo-2-butene **B** (1.1 equiv.) in 15 mL tetrahydrofuran at 0 °C. The reaction mixture was further stirred for 1.5 h at room temperature (~23 °C). The reaction mixture was quenched with a saturated aqueous NH₄Cl solution (100 mL), extracted with EtOAc (2 x 200 mL) and combined organic phases were washed with a brine solution, dried over Na₂SO₄ and concentrated in vacuo. The resulting

residue was purified by flash column chromatography (silica gel; EtOAc/hexane, 0:100 to 10:90) to give a pale-yellow oil **C** (65%).

To a solution of (E)-2,2'-(5-bromopent-3-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**C**, 1 equiv) in tetrahydrofuran (40 mL, 0.3 M) in argon atmosphere, LDA (9.4 mL, 2 M solution in tetrahydrofuran, 1.5 equiv.) was added at 0 °C. The reaction mixture was allowed to reach 23 °C while stirring for 1 h. The reaction mixture was quenched with saturated aqueous NH₄Cl solution (100 mL), extracted with EtOAc (2 x 150 mL) and combined organic phases were washed with a brine solution, dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by flash column chromatography (silica gel; EtOAc/hexane, 0:100 to 05:95) to give a colorless oil (**1a**, 74%) (**Note** – pure **1a** may convert into a white solid after keeping for 2-3 days at -20 °C). NMR spectra matched with the reported data.¹

General procedure B: Synthesis of different VCPs from VCPDB (1a)

General procedure B1: Synthesis of unsymmetrical vinyl cyclopropyl diboron **1c**.

In a 2-dram vial, VCPDB (**1a**, 500 mg, 1.55 mmol, 1.0 equiv.) and (+)-Pinediol (528 mg, 3.1 mmol, 2.0 equiv.) was added. After argon purging, 1,4-dioxane (3.1 mL, 0.5 M) was added and the reaction mixture stirred at 80 °C for 15 h. After consumption of **1a** (confirmed by TLC), the reaction mixture was concentrated in vacuo and the crude was purified using flash column chromatography (silica gel; EtOAc/hexanes, 0:100 to 10:90). NMR spectra matched with the reported data.¹

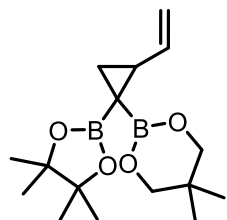
General procedure B2: Synthesis of vinyl cyclopropyl diboron **1d**.

To a stirrer solution of VCPDB (**1a**) (400 mg, 1.25 mmol, 1.0 equiv.) in DMSO (4 mL) triethyl orthoformate (0.6 mL, 3 equiv.), methyliminodiacetic acid (MIDA, 920 mg, 6 equiv.) was added and reaction stirred at 115 °C for 15 h. The reaction mixture was allowed to cool down to rt, filtered through a funnel to recover unreacted MIDA, washed with excess ethyl acetate (150 ml). Filtrate was transferred to a separatory funnel, diluted with more amount of ethyl acetate (50 ml), washed with 100 ml of H₂O, dried over sodium sulfate, concentrated in vacuo and crude was purified using flash column chromatography (silica gel; EtOAc/hexanes, 0:100 to 100:0). NMR spectra matched with the reported data.¹

General procedure B3: Synthesis of unsymmetrical vinyl cyclopropyl diboron **1e**.

In a 2-dram vial, VCPDB (**1a**, 500 mg, 1.55 mmol, 1.0 equiv.) and 2,2-Dimethyl-1,3-propanediol (neopentyl glycol) (4.0 equiv.) was added. After argon purging, 1,4-dioxane (3.1 mL, 0.5 M) was added and the reaction mixture stirred at 80 °C for 15 h. After consumption of **1a** (confirmed by TLC), the reaction mixture was concentrated in vacuo and the crude was purified using flash column chromatography (silica gel; EtOAc/hexanes, 0:100 to 15:85).

5,5-dimethyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-vinylcyclopropyl)-1,3,2-dioxaborinane (1e)



Pale yellow oil, Yield - 68%, (322 mg), dr – 1:0.15

R_f (EtOAc/Hexane, 10:90) = 0.3

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.50 – 5.35 (m, 1H), 5.18 – 5.12 (m, 1H), 4.93 – 4.83 (m, 1H), 3.62 – 3.47 (m, 4H), 1.92 – 1.81 (m, 1H), 1.28 – 1.17 (m, 13H), 1.13 – 1.03 (m, 1H), 0.90 – 0.94 (m, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.9, 113.2, 83.1, 83.0, 72.3, 72.2, 31.8, 26.5, 24.9, 21.9, 16.3.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 33.1.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{16}\text{H}_{29}\text{B}_2\text{O}_4$, calculated 307.2246; observed 307.2260.

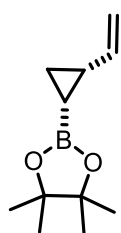
General procedure B4: Synthesis of vinyl cyclopropyl diboron **1b**.

In a 2-dram vial, **1c** (250 mg, 0.73 mmol, 1.0 equiv) and (+)-Pinanediol (497 mg, 2.9 mmol, 4.0 equiv.) was added. After argon purging, 1,4-dioxane (1.5 mL, 0.5 M) was added and reaction mixture stirred at 80 °C for 15 h. After consumption of **1c**, the reaction mixture was concentrated in vacuo and the crude was purified using flash column chromatography (silica gel; EtOAc/hexanes, 0:100 to 5:95). NMR spectra matched with the reported data.¹

General procedure B5: Synthesis of vinyl cyclopropyl monoboron **1f**.

In a 2-dram vial, VCPDB (**1a**, 1 gm, 3.12 mmol, 1.0 equiv.) and sodium *tert*-butoxide (3 equiv.) was added. After argon purging, 1,4-dioxane (6.2 mL, 0.5 M) was added and the reaction mixture was stirred at 80 °C for 15 h. After consumption of **1a** (confirmed by TLC), saturated solution of NH_4Cl was added and organic phase was extracted by diethyl ether (3 x 50 mL). The crude was purified using flash column chromatography (silica gel, DCM/petroleum ether, 0:100 to 10:90). **Note**- The desired compound is volatile and may be lost if subjected to high vacuum condition.

4,4,5,5-tetramethyl-2-(2-vinylcyclopropyl)-1,3,2-dioxaborolane (1f)



Colorless oil; 25% Yield (151 mg)

R_f (EtOAc/Hexane, 10:90) = 0.7

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.64 (dt, $J = 17.1, 10.0$ Hz, 1H), 5.13 (dd, $J = 17.1, 2.0$ Hz, 1H), 4.88 (dd, $J = 10.2, 2.0$ Hz, 1H), 1.74 (td, $J = 8.8, 5.5$ Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.02 (ddd, $J = 9.1, 7.8, 3.8$ Hz, 1H), 0.73 (ddd, $J = 7.5, 5.4, 3.7$ Hz, 1H), 0.23 (td, $J = 9.2, 7.3$ Hz,

1H).

^{13}C NMR (100 MHz, CDCl_3) δ 140.7, 112.9, 83.3, 25.2, 24.7, 21.9, 12.3.

^{11}B NMR (128 MHz, CDCl_3) δ 32.9.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{11}\text{H}_{22}\text{BO}_2$, calculated 195.1551; observed 195.1547.

General procedure C: Synthesis of propiolates

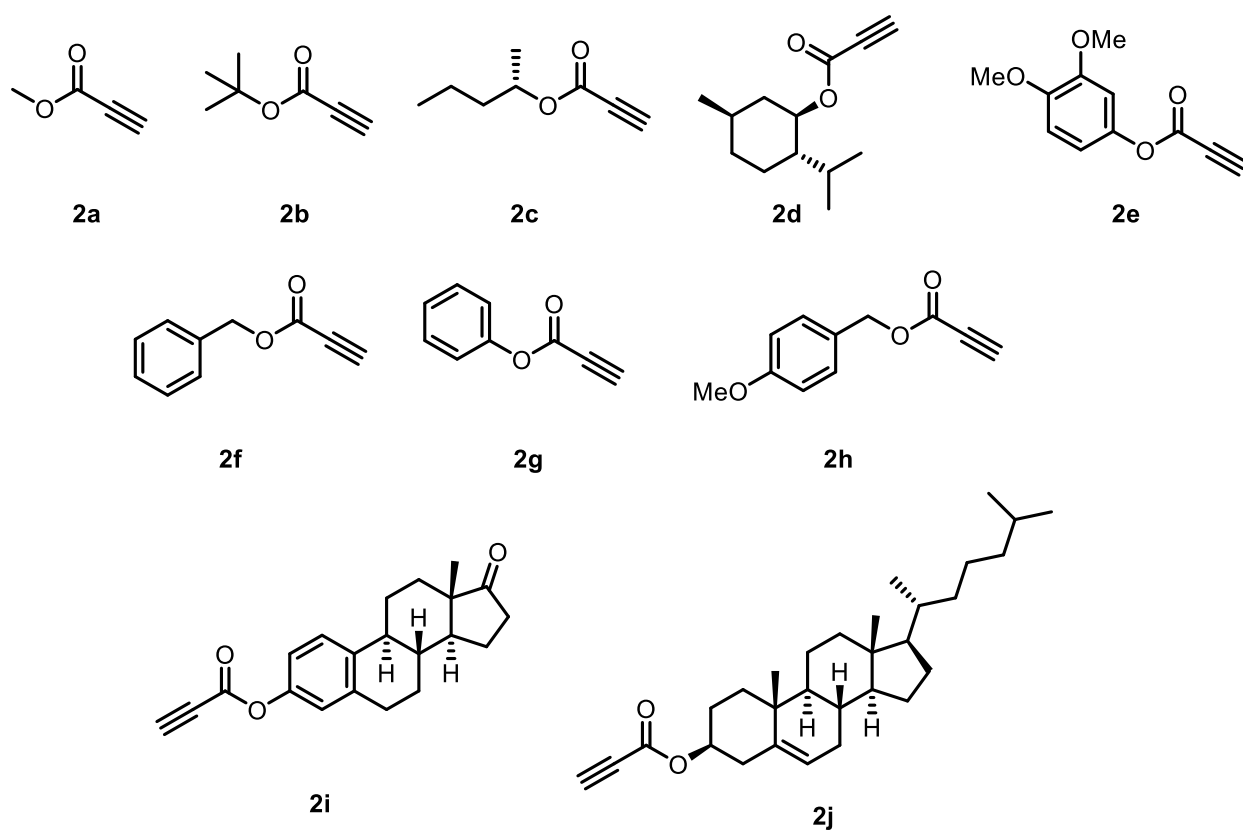
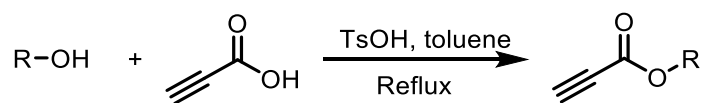


Figure 2. Propiolates

2a and **2b** were purchased commercially.

General procedure C1:

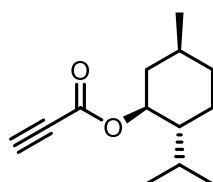
2c and **2d** were prepared by following general procedure C1:



A mixture of propiolic acid (350 mg, 5 mmol, 1.0 equiv.), corresponding alcohol (5.5 mmol, 1.1 equiv.) and *p*-toluenesulfonic acid monohydrate (95 mg, 0.5 mmol, 0.1 equiv.) in toluene (15 mL) were refluxed for 18 h using a Dean-Stark apparatus. The solvent was removed in vacuo and the resultant residue was purified by flash column chromatography on silica gel using EtOAc/Hexane as eluent to afford the title compound **2c** and **2d**. The NMR spectral data of **2c** matched with the reported data.²

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl propiolate (2d)

White solid; 84% yield, Melting Point – 80 – 82 °C



R_f (EtOAc/Hexane, 10:90) = 0.7

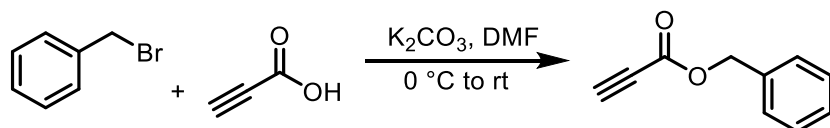
^1H NMR (400 MHz, CDCl_3) δ 4.79 (td, J = 10.9, 4.4 Hz, 1H), 2.87 (s, 1H), 2.07 – 1.98 (m, 1H), 1.92 – 1.88 (m, 1H), 1.74 – 1.64 (m, 2H), 1.46 – 1.42 (m, 2H), 1.06 (dd, J = 13.7, 10.1 Hz, 2H), 0.93 – 0.88 (m, 7H), 0.76 (d, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 76.9, 75.2, 74.3, 46.9, 40.6, 34.2, 31.6, 26.3, 23.5, 22.1, 20.8, 16.3.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{13}\text{H}_{21}\text{O}_2$, calculated 209.1536; observed 209.1547.

General procedure C2:

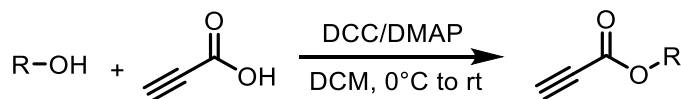
2f was prepared by following general procedure C2:



Propiolic acid (350 mg, 5 mmol, 1 equiv.) was added to a suspension of K_2CO_3 (690 mg, 5 mmol, 1 equiv.) in DMF (10 mL) and the reaction mixture was stirred at 0 °C for 10 min. Benzyl bromide (725 mg, 4.25 mmol, 0.85 equiv.) was added to the above mixture at room temperature, and the resulting solution was continued to stir for another 2 h and then the reaction was quenched with 25 mL water. The resulting solution was extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with brine and dried over Na_2SO_4 . The solvent was removed in vacuo and the resultant residue was purified by flash column chromatography on silica gel using EtOAc/Hexane as eluent to afford final compound **2f** whose NMR spectra matched with the reported data.³

General procedure C3:

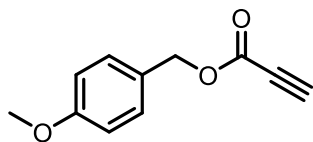
2e, 2h, 2g, 2i and **2j** were prepared by following general procedure C3.



A solution of 4-Dimethylaminopyridine (DMAP) (6 mg, 0.005 mmol, 0.01 equiv.) and *N,N'*-Dicyclohexylcarbodiimide (DCC) (1.03 g, 5 mmol, 1 equiv.) in CH₂Cl₂ (15 mL) was added slowly over 30 min. to a solution of propiolic acid (350 mg, 5 mmol, 1 equiv.) and alcohol or phenol (1.1 equiv.) in CH₂Cl₂ (15 mL) at 0 °C. The mixture was allowed to stir at room temperature until the acid was consumed (determined by TLC). Upon completion, the mixture was filtered through a pad of celite, the filtrate was concentrated in vacuo, and the resultant residue was purified by flash column chromatography on silica gel using EtOAc/Hexane as eluent to afford the propiolates **2e**,⁴ **2g**,³ **2i**,⁵ and **2j**,⁵ matched with the reported data.

4-Methoxybenzyl propiolate (**2h**):

Pale-yellow oil; 89% Yield



R_f (EtOAc/Hexane, 10:90) = 0.6

¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.16 (s, 2H), 3.81 (s, 3H), 2.89 (s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 160.0, 152.7, 130.7, 129.5, 114.1, 75.0, 74.7, 67.9, 55.4.

HRMS (ASAP): *m/z* [M+H]⁺ for C₁₁H₁₁O₃, calculated 191.0703; observed 191.0712.

General procedure D1: Photocatalytic [3+2] cycloaddition of VCPDB with propiolates or alkynes (Formation of vinyl boronates or allylic diborons)

A 2-dram vial (screw cap with Teflon septum) was charged with a small magnetic stir bar, VCPDB **1a** (0.31 mmol, 1 equiv.) and diphenyl disulfide (13.64 mg, 0.062 mmol, 0.2 equiv.). The vial was evacuated and refilled with argon gas. DCE (1.25 mL, 0.25M) followed by the corresponding propiolates **2** (0.41 mmol, 1.3 equiv.) were added and the reaction mixture stirred at 500 rpm in Penn PhD photoreactor M2 using 365 nm LED light source (90% intensity) for 5 h. After consumption of VCPDB (confirmed by TLC or crude NMR), volatiles were removed in vacuo and the crude reaction was purified by flash column chromatography on silica gel (EtOAc/hexanes, 0:100 to 10:90) to afford the monobpin product (**4**). Alternatively, NMR of the crude reaction mixture was taken which confirmed the presence of allylic diboronate as the only product.

General Procedure D2 (for alkyl/aryl acetylenes, **2**):

The above procedure (**D1**) was followed except that 0.37 mmol, 82 mg, 1.2 equiv. of diphenyl disulfide and 0.94 mmol, 3 equiv. with alkyl/aryl acetylene (**5**) were used to afford allylic diboron (**6**).

General Procedure D3 (Base mediated diastereoselective deboronative allylic shift):

A 2-dram screw cap vial (screw cap with Teflon septum) was charged with a small magnetic stir bar, VCPDB **1a** (0.31 mmol, 1 equiv.) and diphenyl disulfide (13.64 mg, 0.062 mmol, 0.2 equiv.). The vial was evacuated and refilled with argon gas. DCE (1.25 mL, 0.25M) followed by the corresponding propiolates **2a** (0.41 mmol, 1.3 equiv.) were added and the reaction mixture stirred at 500 rpm in the photoreactor using 365 nm LED light source (90% intensity) for 5 h. After consumption of VCPDB **1a** (confirmed by TLC or crude NMR), volatiles were removed via positive pressure of argon. Acetonitrile (1.25 mL) and Cs₂CO₃ (0.34 mmol, 1.1 equiv.) were added in the same pot and the reaction mixture was stirred for 1 h at room temperature. The dr ratio was determined by crude analysis. The volatiles were removed in vacuo and the reaction crude was purified by flash column chromatography on silica gel (EtOAc/hexanes, 0:100 to 10:90) to afford the separate diastereomers of deborylation product **4a** (52%, dr = 1:0.12, *trans*-isomer major).

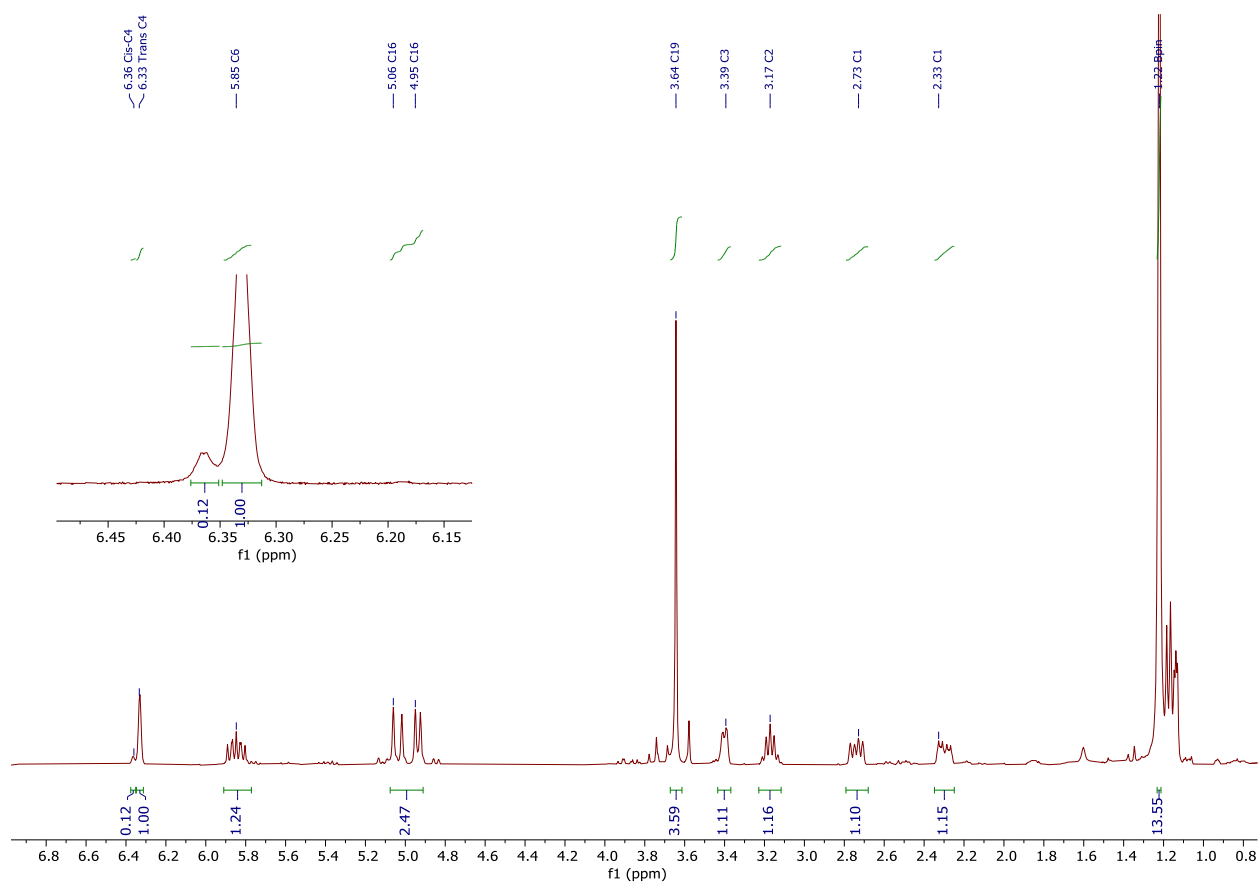
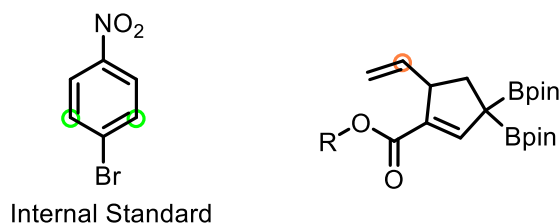


Figure 3. Crude NMR of base-mediated diastereoselective deboronative allylic shift reaction.

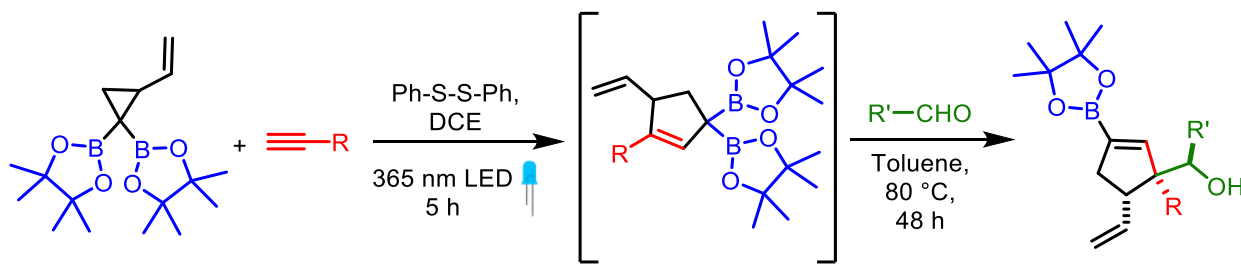
Note: Treatment of pure **4a** (dr = 1:1) with Cs₂CO₃ in acetonitrile for 12 h at rt also improved the dr of **4a** to 1:0.25.

Procedure for NMR yield

A 2-dram vial (screw cap with Teflon septum) was charged with a small magnetic stir bar, VCPDB **1a** (100 mg, 0.312 mmol, 1 equiv.) and diphenyl disulfide (13.64 mg, 0.062 mmol, 0.2 equiv.). DCE (1250 μ L via micropipette, 0.25M) followed by the addition of corresponding propiolates **2** (0.41 mmol, 1.3 equiv.). The reaction mixture was stirred at 500 rpm in Penn PhD photoreactor M2 using 365 nm LED light source (90% intensity) for 5 h. 200 μ L of this reaction mixture was added to 200 μ L of internal standard solution (0.25 M solution of 1-bromo-4-nitrobenzene in DCE) and volatiles were removed in vacuo. The ^1H NMR of resulting material was taken in CDCl_3 , and yield was confirmed by taking a ratio of internal standard 2 protons (highlighted in green color) with terminal alkene CH proton (highlighted in orange color).



General procedure E: One-pot multicomponent [3+2] cycloaddition-allylboration



t = 0 min



t = 5 h
(allyl diboron)



A



B

A - t = 48 h at 80 °C (allyl boration reaction mixture)
B - If the color changes to dark black after 48 h a drastic decrease in the yield was observed

General Procedure E1 (for propiolates (**2**) as substrates):

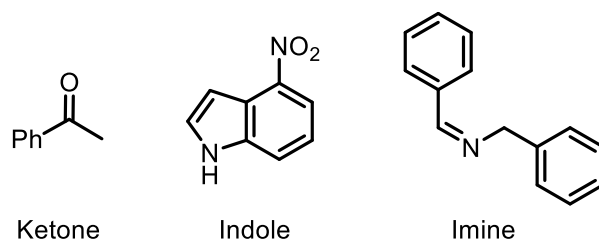
A 2-dram screw cap vial (screw cap with Teflon septum) was charged with a small magnetic stir bar, VCPDB **1a-f** (0.31 mmol, 1 equiv.) and diphenyl disulfide (13.64 mg, 0.062 mmol, 0.2 equiv.). The vial was evacuated and refilled with argon gas. DCE (1.25 mL, 0.25M) followed by the corresponding propiolates **2** (0.41 mmol, 1.3 equiv.) were added and the reaction mixture stirred at 500 rpm in Penn PhD photoreactor M2 using 365 nm LED light source (90% intensity) for 5 h. After consumption of VCPDB (confirmed by TLC or crude NMR), volatiles were removed via positive pressure of argon. Toluene (1.25 mL) and corresponding aldehyde (2 equiv.) were added, and the reaction mixture was stirred for 48 h at 80 °C. The volatiles were removed in vacuo and the reaction crude was purified by flash column chromatography on silica gel (EtOAc/hexanes, 0:100 to 50:50) to afford the allyl boration products (**7, 8** or **9**).

General Procedure E2 (for aryl acetylenes (**5**) as substrates):

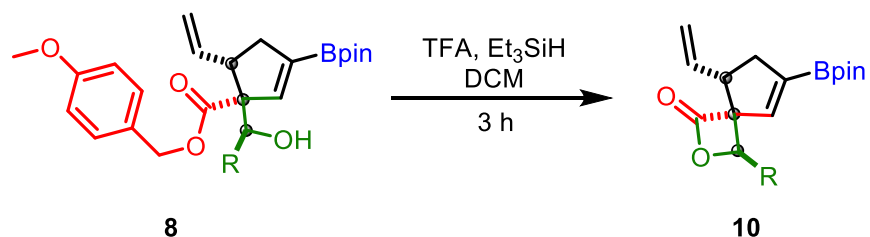
The above procedure (**E1**) was followed except that 0.37 mmol, 82 mg, 1.2 equiv. of diphenyl disulfide and 0.94 mmol, 3 equiv. with aryl acetylene (**5**) were used.

Note – All the allylboration products (**7a** to **7t**, **8a** to **8k**, **9a** and **9c**) show $m/z = [M-17]^+$ peak in HRMS due to loss of water molecule after protonation, which generates stabilized benzylic carbocation.

Unsuccessful substrates for allylboration reaction with **3a/6a**:



General procedure F: Formation of spirolactones (**10**).



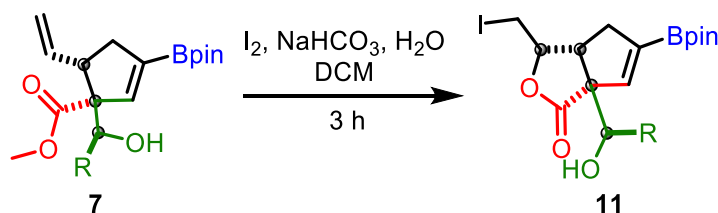
A 2-dram vial with a small magnetic stir bar was charged with **8** (0.25 mmol, 1 equiv.) in dichloromethane (0.25M) followed by addition of triethyl silane (2.5 mmol, 10.0 equiv.) and Trifluoroacetic acid (TFA) (1.25 mmol, 5.0 equiv.). The reaction mixture was stirred for 3 h at

room temperature and after consumption of starting material (confirmed by TLC), volatiles were removed under vacuo and crude was purified by flash column chromatography on silica gel (EtOAc/Hexane, 0:100 to 40:60) to afford the corresponding spiro lactones **10**.

General procedure G: One-pot spiro lactonization from VCPDB (**1a**)

A 2-dram vial (screw cap with Teflon septum) was charged with a small magnetic stir bar, VCPDB **1a** (0.31 mmol, 1 equiv.) and diphenyl disulfide (13.64 mg, 0.062 mmol, 0.2 equiv.) The vial was evacuated and refilled with argon gas. DCE (1.25 mL, 0.25M) followed by the PMB propiolate **2h** (0.41 mmol, 1.3 equiv.) were added and the reaction mixture stirred at 500 rpm in Penn PhD photoreactor M2 using 365 nm LED light source (90% intensity) for 5 h. After consumption of VCPDB **1a** (confirmed by TLC or crude NMR), volatiles were removed via positive pressure of argon. Toluene (1.25 mL) and benzaldehyde (2 equiv.) were added and stirred for 48 h at 80 °C. After conversion of allyldiboron to allylboration product **8b**, (confirmed by TLC) triethyl silane (3.1 mmol, 10.0 equiv.) and TFA (1.55 mmol, 5.0 equiv.) were added to the same pot. The reaction was stirred for 3 h at room temperature. After consumption of allylboration product **8b** (confirmed by TLC), volatiles were removed under vacuo and crude was purified by flash column chromatography on silica gel (EtOAc/Hexane, 0:100 to 40:60) to afford the corresponding spiro lactone **10a**.

General procedure H: Formation of iodo-lactone (**11**).



A 2-dram vial with a small magnetic stir bar was charged with **7** (0.25 mmol, 1 equiv.), Iodine (0.3 mmol, 1.2 equiv.) and NaHCO₃ (0.3 mmol, 1.2 equiv.) in dichloromethane (0.25M) with 200 μL of water. Reaction stirred for 3 h at room temperature. After consumption of starting material (confirmed by TLC), reaction mass was filtered through small pad of celite using dichloromethane as eluent and filtrate were concentrated in vacuo and crude was purified by flash column chromatography on silica gel (EtOAc/hexanes, 0:100 to 40:60) to afford the γ-butyrolactone **11**.

General procedure I: Light “On/Off” experiment

A 2-dram vial (screw cap with Teflon septum) was charged with a small magnetic stir bar, VCPDB **1a** (100 mg, 0.31 mmol, 1 equiv.) and diphenyl disulfide (13.64 mg, 0.062 mmol, 0.2 equiv.). DCE (1250 μL via micropipette, 0.25M) followed by the methyl propiolate **2a** (0.41 mmol, 1.3 equiv.) were added and the reaction mixture stirred at 500 rpm in Penn PhD photoreactor M2 using 365 nm LED light source (90% intensity) for 0.5 min. An aliquot of around 0.1 mL was taken out via syringe and 80 μL was added via a micropipette in a vial

having 0.80 μL of 0.25 M solution of internal standard (1-bromo-4-nitrobenzene in DCE). Volatiles were removed in vacuo. The ^1H NMR of resulting material was taken in CDCl_3 . The yield was calculated using same method as mentioned in NMR yield calculation procedure (Page S11). The reaction mixture was then stirred for 1 min at room temperature without light irradiation. This on/off procedure was repeated few more times, and the NMR yields were determined. The results are shown in Figure 4 below.

Entry	Time (mins)	NMR Yield (%)
1	0	0
2	0.5	31
3	1.5 (off)	31
4	2.5	59
5	3.5 (off)	59
6	5.5	69
7	7.5 (off)	69
8	10	77

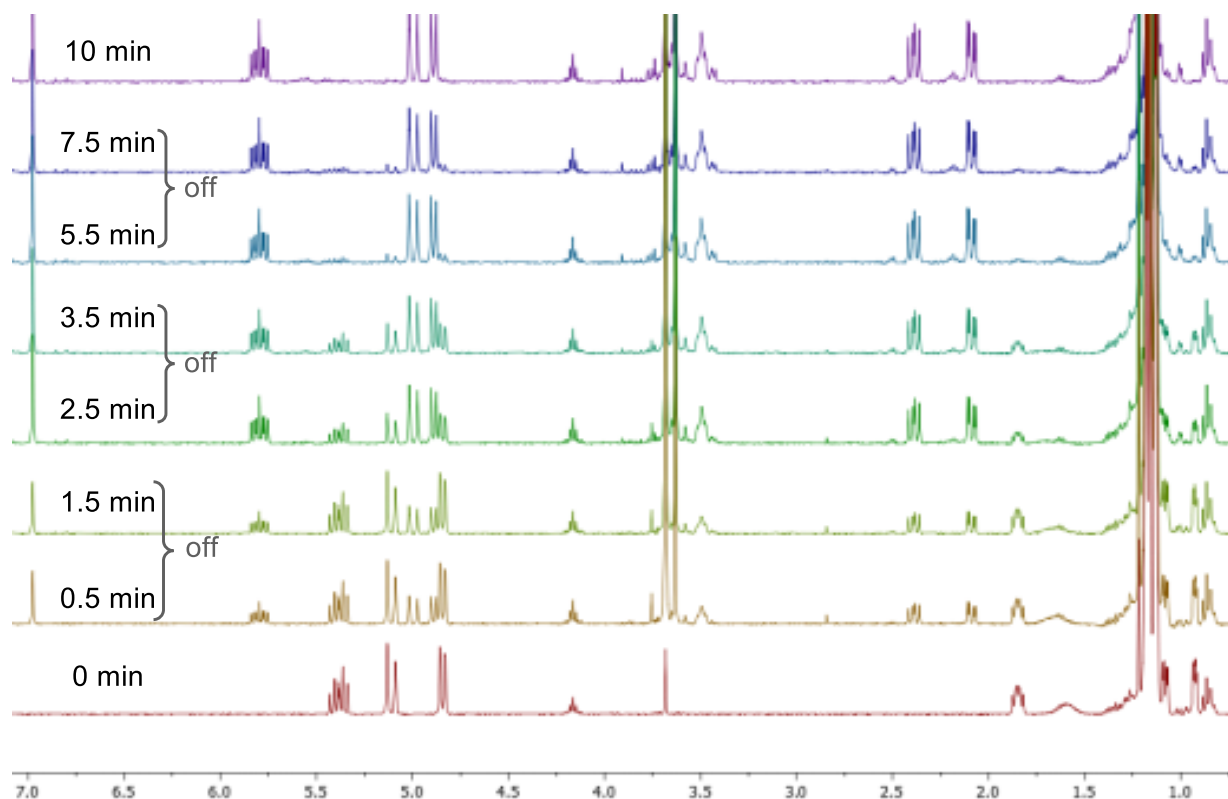
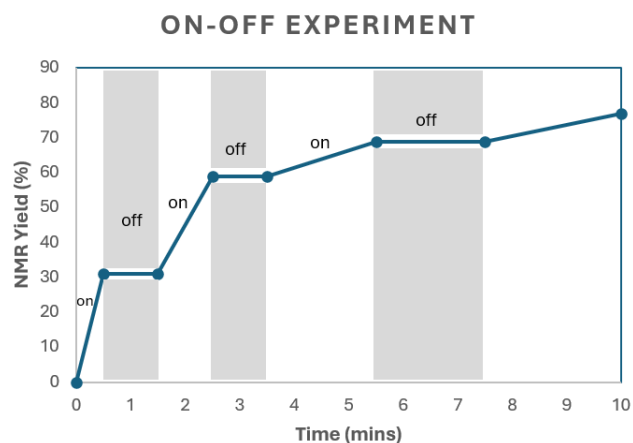
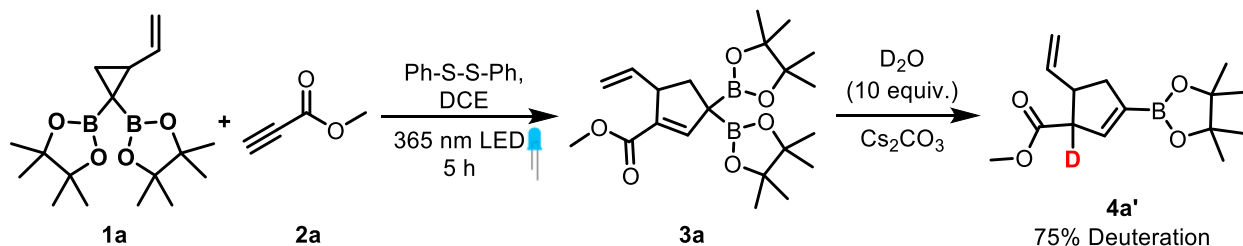


Figure 4. Light On-Off experiment results

General procedure J: Deuterium labeling experiment

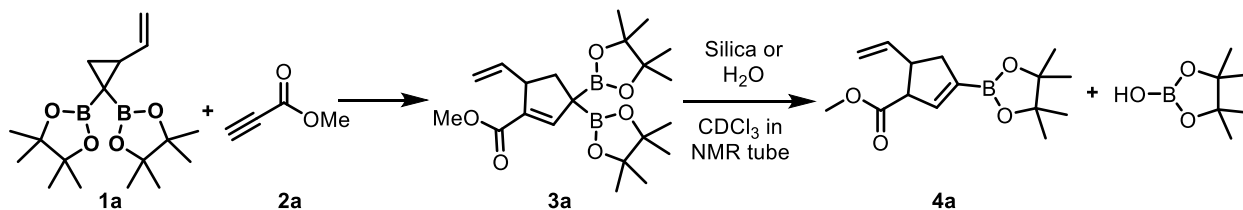


A 2-dram vial (screw cap with Teflon septum) was charged with a small magnetic stir bar, VCPDB **1a** (0.31 mmol, 1 equiv.) and diphenyl disulfide (13.64 mg, 0.062 mmol, 0.2 equiv.). The vial was evacuated and refilled with argon gas. DCE (1.25 mL, 0.25M) followed by the methyl propiolate **2a** (0.41 mmol, 1.3 equiv., 36 μ L) were added and the reaction mixture stirred at 500 rpm in Penn PhD photoreactor M2 using 365 nm LED light source (90% intensity) for 5 h. After consumption of **1a**, cesium carbonate (0.34 mmol, 1.1 equiv.) and D₂O (3.1 mmol, 10 equiv.) was added. The reaction was stirred for 1h at room temperature, volatiles were removed in vacuo and crude was purified by flash column chromatography on silica gel (EtOAc/hexanes, 0:100 to 10:90) to afford corresponding deuterated monobpin product (**4a'**).

NMR of **4a'** - ¹H NMR (400 MHz, CDCl₃) δ 6.39 (q, J = 2.1 Hz, 1H), 5.89 – 5.75 (m, 1H), 5.10 – 5.02 (m, 1H), 4.99 – 4.93 (m, 1H), 3.69 (s, 0.25H), 3.62 (s, 3H), 3.17 (quint, J = 8.3 Hz, 1H), 2.67 – 2.59 (m, 1H), 2.54 – 2.48 (m, 1H), 1.27 (s, 12H).

HRMS (ASAP): m/z [M+H]⁺ for C₁₅H₂₃DBO₄, calculated 280.1825; observed 280.1837.

General procedure K: ¹¹B NMR Study



A 2-dram vial (screw cap with Teflon septum) was charged with a small magnetic stir bar, VCPDB **1a** (0.62 mmol, 1 equiv.) and diphenyl disulfide (27.28 mg, 0.124 mmol, 0.2 equiv.). The vial was evacuated and refilled with argon gas. DCE (2.5 mL, 0.25M) followed by the addition of methyl propiolate (0.82 mmol, 1.3 equiv.) and the reaction mixture stirred at 500 rpm in Penn PhD photoreactor M2 using 365 nm LED light source (90% intensity) for 5 h. The volatiles were removed in vacuo and NMR sample was prepared by adding 0.6 mL of CDCl₃

in the same reaction vial, water (20 μL) or oven dried silica (30 mg) was added directly to NMR tube and ^{11}B NMR recorded at different time intervals ($t = 0 - 200$ minutes for water (Figure 5 in SI) and $t = 0$ to 90 minutes for silica (Figure 2C in the manuscript)).

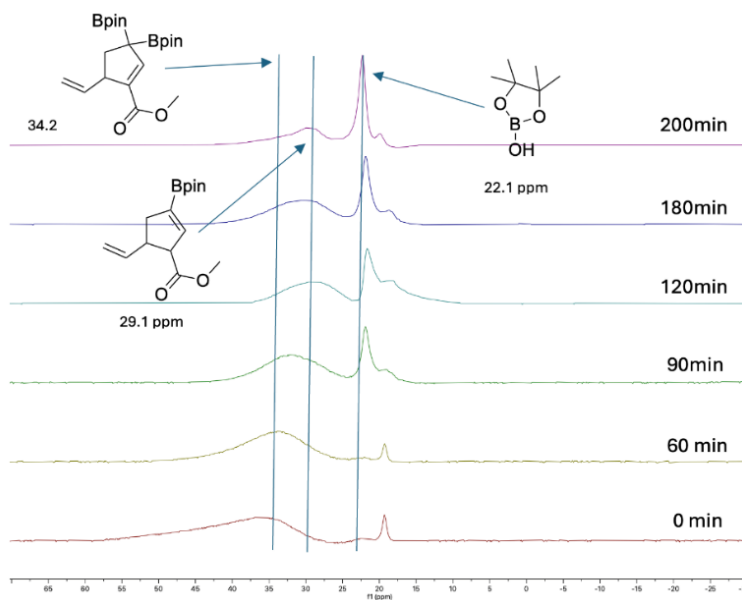
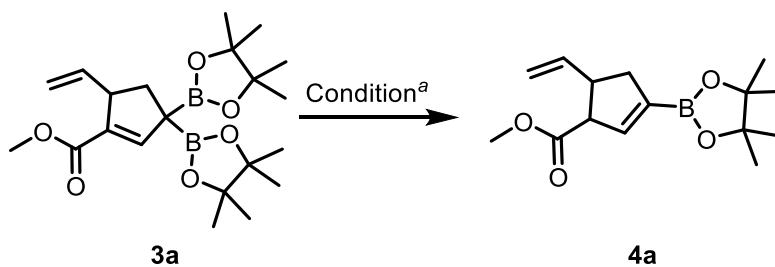


Figure 5. ^{11}B NMR analysis using water as additive.

Table 1. Stability of carbonyl conjugated allylic diborons in different conditions

Entry	(3a) (mmol)	Condition	Solvent (1 mL)	Time (h)	3a/4a (%) ^b
1	20 mg (0.05)	20 mg silica	EtOAc	1	90/10
2	20 mg (0.05)	50 μ L H ₂ O	EtOAc	1	00/100
3	20 mg (0.05)	50 μ L AcOH	EtOAc	1	00/100
4	20 mg (0.05)	1.1 gm oven dried silica	EtOAc	1	00/100
5	20 mg (0.05)	1.1 gm oven dried silica, washed with Et ₃ N	EtOAc	1	00/100
6	20 mg (0.05)	75 °C in water bath	--	1	83/17
7	20 mg (0.05)	65 °C on hot plate	--	12	60/40
8	20 mg (0.05)	Et ₃ N (12 μ L)	EtOAc	1	00/100
9	20 mg (0.05)	Argon	Hexane	1	85/15
10	20 mg (0.05)	Argon	--	12	98/02
11	20 mg (0.05)	Argon	--	24	95/05
12	20 mg (0.05)	Argon	--	72	93/07

^aReaction condition – **3a** (20 mg, 0.05 mmol), stirred for indicated time with given conditions ^bRatio was determined by ¹H NMR analysis

Quantum yield calculation

General Information:

The following procedure was adapted from the literature with slight modifications.⁶⁻⁷ The whole experiment was performed in the dark except when the sample was irradiated.

The samples were irradiated using Penn PhD photoreactor M2 at 365 nm with 25% light intensity.

Photon flux measurement:

- a. Potassium ferrioxalate trihydrate solution
0.15 M aqueous solution of potassium ferrioxalate trihydrate (1.47 g, 3 mmol) in DI water (20 mL) was prepared.

- b. 1,10-Phenanthroline buffer solution
Sodium acetate (2.47 g, 30 mmol) was added to 30 mL DI water. 1,10-phenanthroline (50 mg, 0.27 mmol) and concentrated H₂SO₄ (0.5 mL) were added and diluted with water to 50 mL.

Procedure:

1 mL of the prepared 0.15 M potassium ferrioxalate solution was added in a reaction vial and placed under the photoreactor for 5 sec at 25% intensity. The same process was repeated with 10 sec and 20 sec respectively. After each irradiation, 250 μ L (V_1) of irradiated solution was transferred to another vial, 2.5 mL of 1,10-phenanthroline buffer was added and diluted with 9.75 mL of DI water (total volume $V_2 = 12.5$ mL). The resulting solution were allowed to stirred at rt for 20 min in the dark. 3 mL of resulting solution was transferred to a quartz cuvette. The absorbance was measured at 510 nm. The absorbance value was used to determine the amount of Fe²⁺ which is formed during irradiation and thereby photon flux of the photoreactor. A non-irradiated solution was also prepared and the absorbance at 510 nm was measured as a blank.

Calculation:

Step 1 – Concentration of Fe²⁺

The photolysis gives Fe²⁺ which makes a complex with 1,10-phenanthroline. This complex exhibits a characteristic absorbance peak at 510 nm. ($\epsilon = 11100$ L cm⁻¹ mol⁻¹). The concentration of Fe²⁺ can be calculated using Beer-Lambert Law. (See the table 2 for ΔA)

$$\Delta A = \epsilon l C$$

Where, ϵ = molar absorptivity,

l = path length (1 cm)

C = concentration (cuvette)

$$C = \frac{\epsilon \times l}{\Delta A}$$

$$C = \frac{11100 \times 1}{0.032}$$

$$C = 2.88 \times 10^{-6} M$$

Step 2 – Concentration of Fe²⁺ upon irradiation:

The concentration of Fe²⁺ in irradiated 1 mL solution can be determined by the dilution equation given below.

$$C_1V_1 = C_2V_2$$

$$C_{vial} = \frac{C_{cuvette}V_{cuvette}}{V_{vial}}$$

$$C_{vial} = \frac{2.883 \times 10^{-6} \times 12.5 \times 10^{-3}}{0.25 \times 10^{-3}}$$

$$C_{vial} = 1.44 \times 10^{-4} M$$

Step 3 – Calculation of photon flux:

The moles of incident photons can be approximated using quantum yield of Fe²⁺, previously found to be $\Phi = 1.21$ at 363.8 nm.⁸ Dividing the moles of photons by the time irradiated then gives the photon flux in the units photons per second.

$$Mol\ photons = \frac{C_{vial}V_{vial}}{\Phi_{Fe(II),363.8\ nm}}$$

$$Mol\ photons = \frac{1.44 \times 10^{-4} \times 1 \times 10^{-3}}{1.21}$$

$$Mol\ photons = 1.19 \times 10^{-7} mol$$

$$Photons\ flux = \frac{mol\ photons}{t_{irradiation}}$$

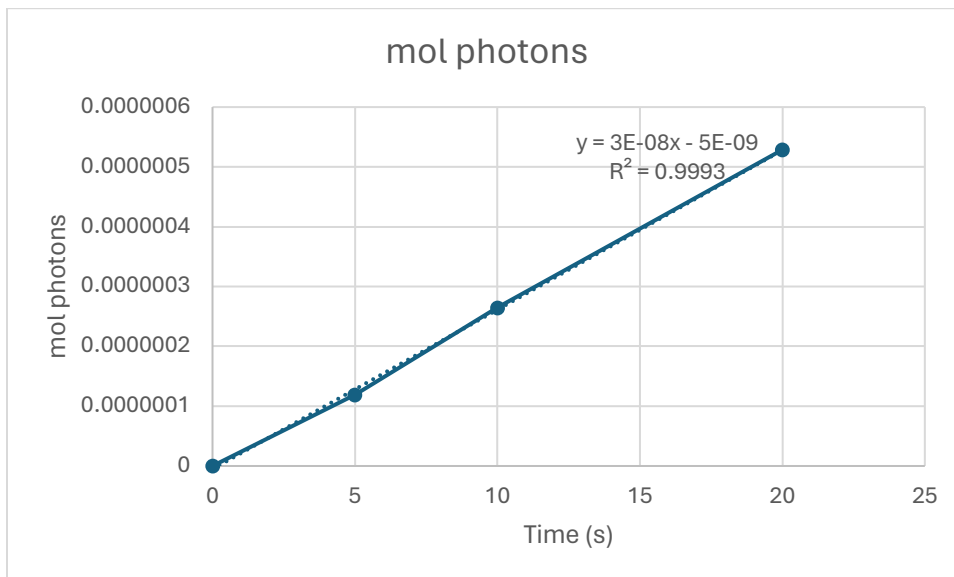
$$Photons\ flux = \frac{1.19 \times 10^{-7}}{5}$$

$$Photons\ flux = 2.38 \times 10^{-8} mol\ s^{-1}$$

Table 2. Determination of photon flux

TIME	ABSORBANCE	ΔA	CONCENTRATION	C OF SAMPLE (AMOUNT 1 mL)	MOL PHOTONS	PHOTON FLUX
0	0.025	0	-	-	-	-
5	0.057	0.032	2.882×10^{-6}	1.441×10^{-4}	1.191×10^{-7}	2.382×10^{-8}
10	0.096	0.071	6.396×10^{-6}	3.198×10^{-4}	2.643×10^{-7}	2.643×10^{-8}
20	0.167	0.142	1.279×10^{-5}	6.396×10^{-4}	5.286×10^{-7}	2.643×10^{-8}

Average photon flux of Penn PhD photoreaction M2 at 25% intensity was found to be $2.55 \times 10^{-8} \text{ mol s}^{-1}$.



Quantum yield calculation

$$\text{Quantum yield } (\Phi) = \frac{\text{mol of product}}{\text{photon flux} \times \text{fraction of light absorbed} \times \text{time of reaction (s)}}$$

Moles of product formed:

The reaction of VCPDB (**1a**) was performed with methyl propiolate (**2a**) at $0.312 \times 10^{-3} \text{ mol}$ scale with 25% light intensity. The crude NMR study showed that 58% yield after 10 min. Therefore, the moles of product formed = 0.18×10^{-3} .

Fraction of light absorbed:

The fraction of light absorbed can be determined by the following equation.

$$f = 1 - 10^{-A(\lambda)}$$

The absorbance of phenyl disulfide solution was determined as $A(365) = 2.43$

$$f = 0.99$$

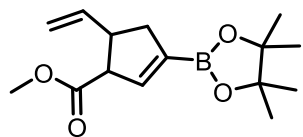
$$\text{Quantum yield } (\Phi) = \frac{0.18 \times 10^{-3}}{2.55 \times 10^{-8} \times 0.99 \times 600}$$

$$\text{Quantum yield } (\Phi) = 11.88$$

Compound characterization data

Compounds **4a** to **4e** were prepared according to general procedure **D1**.

methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (4a)



Colorless oil; 59% Yield (51 mg)

R_f (EtOAc/Hexane, 10:90) = 0.5

Diastereomer 1 (26 mg)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.36 (td, $J = 2.3, 1.5$ Hz, 1H), 5.88 (ddd, $J = 17.4, 10.2, 7.6$ Hz, 1H), 5.07 (dt, $J = 17.1, 1.5$ Hz, 1H), 4.98 – 4.95 (m, 1H), 3.67 (s, 3H), 3.43 (dq, $J = 7.7, 2.5$ Hz, 1H), 3.24 – 3.16 (m, 1H), 2.80 – 2.73 (m, 1H), 2.33 (ddt, $J = 16.4, 7.7, 2.8$ Hz, 1H), 1.25 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.9, 142.8, 140.8, 114.5, 83.6, 58.5, 52.0, 46.8, 40.9, 25.0, 24.9.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.0.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{15}\text{H}_{24}\text{BO}_4$, calculated 279.1762; observed 279.1771.

Diastereomer 2 (25 mg)

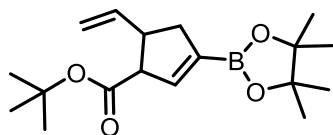
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.39 (q, $J = 2.1$ Hz, 1H), 5.86 – 5.75 (m, 1H), 5.05 (d, $J = 17.1$ Hz, 1H), 4.95 (dd, $J = 10.2, 1.8$ Hz, 1H), 3.69 (dd, $J = 8.6, 2.3$ Hz, 1H), 3.61 (s, 3H), 3.16 (quint, $J = 8.0$ Hz, 1H), 2.67 – 2.59 (m, 1H), 2.49 (ddt, $J = 16.1, 5.8, 2.1$ Hz, 1H), 1.26 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.8, 142.9, 138.4, 115.7, 83.6, 57.1, 51.5, 46.9, 40.3, 25.0.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.9.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{15}\text{H}_{24}\text{BO}_4$, calculated 279.1762; observed 279.1778.

tert-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (4b)



Pale-yellow oil; 54% Yield (54 mg)

R_f (EtOAc/Hexane, 10:90) = 0.5

Diastereomer 1 (27 mg)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.37 (d, $J = 2.5$ Hz, 1H), 5.90 (ddd, $J = 17.4, 10.3, 7.5$ Hz, 1H), 5.07 (dt,

$J = 17.1, 1.4$ Hz, 1H), 4.97 (ddd, $J = 10.2, 1.8, 1.0$ Hz, 1H), 3.34 (dt, $J = 8.4, 2.5$ Hz, 1H), 3.16 (quint, $J = 8.0$ Hz, 1H), 2.76 (dd, $J = 16.3, 8.5$ Hz, 1H), 2.32 (ddt, $J = 16.3, 8.0, 2.9$ Hz, 1H), 1.44 (s, 9H), 1.27 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 143.8, 141.1, 114.3, 83.6, 80.7, 59.6, 46.8, 40.8, 28.3, 25.0, 24.9.

^{11}B NMR (128 MHz, CDCl_3) δ 29.1.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{18}\text{H}_{30}\text{BO}_4$, calculated 321.2232; observed 321.2225.

Diastereomer 2 (27 mg)

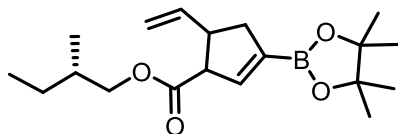
^1H NMR (400 MHz, CDCl_3) δ 6.41 (q, $J = 2.1$ Hz, 1H), 5.88 (ddd, $J = 17.0, 10.2, 8.5$ Hz, 1H), 5.07 (ddd, $J = 17.1, 1.9, 1.0$ Hz, 1H), 5.00 – 4.94 (m, 1H), 3.56 (dq, $J = 8.6, 2.1$ Hz, 1H), 3.20 – 3.08 (m, 1H), 2.62 (ddt, $J = 16.0, 7.7, 1.9$ Hz, 1H), 2.49 (ddt, $J = 16.0, 6.2, 2.1$ Hz, 1H), 1.41 (s, 9H), 1.27 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 143.8, 138.6, 115.5, 83.5, 80.7, 57.7, 47.1, 40.4, 28.3, 25.0, 25.0.

^{11}B NMR (128 MHz, CDCl_3) δ 29.0.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{18}\text{H}_{30}\text{BO}_4$, calculated 321.2232; observed 321.2220.

(S)-2-methylbutyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (4c)



Colorless oil; 52% Yield (53 mg)

R_f (EtOAc/Hexane, 10:90) = 0.4

Diastereomer 1 (26 mg)

^1H NMR (400 MHz, CDCl_3) δ 6.38 (q, $J = 2.1$ Hz, 1H), 5.90 (ddd, $J = 17.5, 10.3, 7.6$ Hz, 1H), 5.08 (dt, $J = 17.2, 1.5$ Hz, 1H), 4.98 (dt, $J = 10.2, 1.3$ Hz, 1H), 3.93 (dtd, $J = 38.5, 10.5, 6.4$ Hz, 2H), 3.44 (dq, $J = 7.8, 2.5$ Hz, 1H), 3.21 (quint, $J = 8.0$ Hz, 1H), 2.78 (ddt, $J = 16.4, 8.5, 1.9$ Hz, 1H), 2.34 (ddt, $J = 16.4, 7.8, 2.8$ Hz, 1H), 1.70 (dq, $J = 13.3, 6.6$ Hz, 1H), 1.41 (tq, $J = 13.3, 6.6$ Hz, 1H), 1.26 (s, 12H), 1.24 – 1.14 (m, 1H), 0.92 – 0.88 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 143.1, 140.9, 114.5, 83.6, 69.5, 58.6, 46.8, 40.9, 34.3, 26.2, 24.9, 16.6, 16.5, 11.4, 11.4.

^{11}B NMR (128 MHz, CDCl_3) δ 28.7

HRMS (ASAP): m/z $[M+H]^+$ for $C_{19}H_{32}BO_4$, calculated 335.2328; observed 335.2335.

Diastereomer 2 (27 mg)

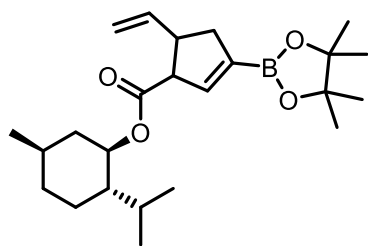
1H NMR (400 MHz, $CDCl_3$) δ 6.42 (q, $J = 2.1$ Hz, 1H), 5.84 (ddd, $J = 17.1, 10.2, 8.5$ Hz, 1H), 5.07 (ddd, $J = 17.1, 2.0, 1.1$ Hz, 1H), 4.97 (ddd, $J = 10.2, 1.9, 0.9$ Hz, 1H), 3.93 – 3.78 (m, 2H), 3.69 (dq, $J = 8.6, 2.1$ Hz, 1H), 3.19 (h, $J = 8.1$ Hz, 1H), 2.64 (ddt, $J = 16.1, 7.7, 1.8$ Hz, 1H), 2.57 – 2.45 (m, 1H), 1.67 (dq, $J = 13.1, 6.6$ Hz, 1H), 1.48 – 1.33 (m, 1H), 1.27 (s, 12H), 1.19 (dd, $J = 14.1, 6.9$ Hz, 1H), 0.92 – 0.86 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 143.3, 143.2, 138.4, 115.8, 83.6, 69.2, 57.2, 47.1, 40.3, 34.2, 26.2, 25.0, 24.9, 16.7, 11.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 28.4

HRMS (ASAP): m/z $[M+H]^+$ for $C_{19}H_{32}BO_4$, calculated 335.2328; observed 335.2321.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (4d)



White semi-solid oil; 45% Yield (57 mg)

R_f (EtOAc/Hexane, 10:90) = 0.6

Diastereomer 1 (29 mg)

1H NMR (400 MHz, $CDCl_3$) δ 6.32 (dq, $J = 3.9, 2.2$ Hz, 1H), 5.85 (dddd, $J = 17.5, 10.3, 7.5, 2.8$ Hz, 1H), 5.02 (dt, $J = 17.1, 1.5$ Hz, 1H), 4.93 (dq, $J = 10.2, 1.4$ Hz, 1H), 4.64 (tdd, $J = 10.9, 4.4, 2.4$ Hz, 1H), 3.36 (dp, $J = 7.7, 2.4$ Hz, 1H), 3.14 (p, $J = 8.2$ Hz, 1H), 2.73 (dddt, $J = 16.3, 8.1, 3.9, 1.9$ Hz, 1H), 2.35 – 2.22 (m, 1H), 1.97 – 1.89 (m, 1H), 1.83 (hd, $J = 6.9, 2.6$ Hz, 1H), 1.63 (t, $J = 7.3$ Hz, 3H), 1.49 – 1.32 (m, 2H), 1.22 (s, 12H), 1.04 – 0.85 (m, 2H), 0.85 – 0.81 (m, 6H), 0.69 (dd, $J = 6.9, 2.5$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.1, 143.3, 140.8, 114.4, 83.6, 74.6, 58.9, 47.5, 47.1, 41.0, 40.8, 34.4, 31.5, 26.2, 25.0, 24.9, 23.5, 22.2, 20.9, 16.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 28.4

HRMS (ASAP): m/z $[M+H]^+$ for $C_{24}H_{40}BO_4$, calculated 403.3014; observed 403.3022.

Diastereomer 2 (28 mg)

1H NMR (400 MHz, $CDCl_3$) δ 6.41 (dq, $J = 6.5, 2.1$ Hz, 1H), 5.86 (dddd, $J = 17.0, 15.2, 10.2, 8.5$ Hz, 1H), 5.07 (ddt, $J = 17.0, 5.7, 1.5$ Hz, 1H), 4.96 (ddd, $J = 10.4, 5.8, 1.9$ Hz, 1H), 4.61 (dtd, $J = 17.3, 10.9, 4.3$ Hz, 1H), 3.63 (ddq, $J = 16.2, 8.5, 2.0$ Hz, 1H), 3.17 (dt, $J = 12.8, 5.3$ Hz, 1H),

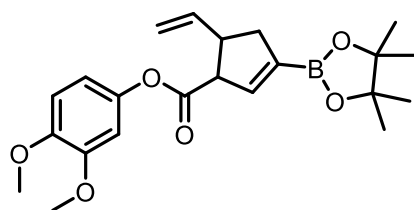
2.69 – 2.44 (m, 2H), 2.02 – 1.82 (m, 2H), 1.65 (d, $J = 6.4$ Hz, 2H), 1.48 – 1.30 (m, 2H), 1.28 – 1.25 (m, 12H), 1.07 – 0.90 (m, 2H), 0.90 – 0.85 (m, 6H), 0.71 (dd, $J = 10.2, 6.9$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) $\delta = 172.0, 143.5, 138.3, 115.9, 83.5, 74.6, 57.5, 47.3, 47.1, 41.1, 40.5, 34.4, 31.5, 25.9, 25.0, 24.9, 23.3, 22.2, 20.9, 16.2$.

^{11}B NMR (128 MHz, CDCl_3) $\delta 28.2$

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{40}\text{BO}_4$, calculated 403.3014; observed 403.3001.

3,4-dimethoxyphenyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (4e)



White semi-solid oil; 53% Yield (57 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

Diastereomer 1 (29 mg)

^1H NMR (400 MHz, CDCl_3) $\delta 6.82$ (dt, $J = 8.3, 1.1$ Hz, 1H), 6.66 – 6.61 (m, 2H), 6.52 (dt, $J = 3.9, 1.9$ Hz, 1H), 5.96 (ddd, $J = 17.5, 10.2, 7.6$ Hz, 1H), 5.16 (dt, $J = 17.1, 1.4$ Hz, 1H), 5.04 (dt, $J = 10.2, 1.3$ Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.67 (dq, $J = 7.8, 2.5$ Hz, 1H), 3.34 (quint, $J = 8.0$ Hz, 1H), 2.85 (ddt, $J = 16.4, 8.6, 1.9$ Hz, 1H), 2.42 (ddt, $J = 16.4, 7.8, 2.8$ Hz, 1H), 1.29 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) $\delta 172.2, 149.4, 146.9, 144.6, 142.2, 140.5, 114.9, 112.9, 111.2, 105.8, 83.7, 58.6, 56.3, 56.1, 46.9, 41.0, 25.0, 24.9$.

^{11}B NMR (128 MHz, CDCl_3) $\delta 28.7$

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{30}\text{BO}_6$, calculated 401.2130; observed 401.2121.

Diastereomer 2 (28 mg)

^1H NMR (400 MHz, CDCl_3) $\delta 6.82 - 6.78$ (m, 1H), 6.61 – 6.57 (m, 2H), 6.53 – 6.50 (m, 1H), 5.98 (ddd, $J = 17.1, 10.2, 8.8$ Hz, 1H), 5.20 (d, $J = 17.1$, 1H), 5.08 (dd, $J = 10.2, 1.9$ Hz, 1H), 3.94 – 3.89 (m, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.38 - 3.28 (m, 1H), 2.73 (ddt, $J = 16.1, 7.6, 2.1$ Hz, 1H), 2.57 (ddt, $J = 16.1, 5.4, 2.0$ Hz, 1H), 1.28 (s, 12H).

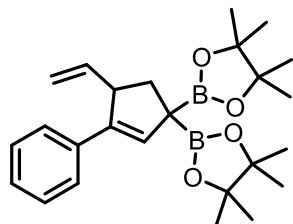
^{13}C NMR (100 MHz, CDCl_3) $\delta = 171.2, 149.3, 146.9, 144.5, 142.4, 138.3, 116.2, 113.1, 111.2, 106.0, 83.7, 56.6, 56.3, 56.0, 47.1, 40.5, 25.0, 24.9$.

^{11}B NMR (128 MHz, CDCl_3) $\delta 28.4$

HRMS (ASAP): m/z $[M+H]^+$ for $C_{22}H_{30}BO_6$, calculated 401.2130; observed 401.2121.

Compounds **6a** to **6e** were prepared according to general procedure **D2**.

2,2'-(3-phenyl-4-vinylcyclopent-2-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6a)



Pale-yellow oil; 43% Yield (57 mg)

R_f (EtOAc/Hexane, 10:90) = 0.5 (Note – SM and Product has almost same R_f)

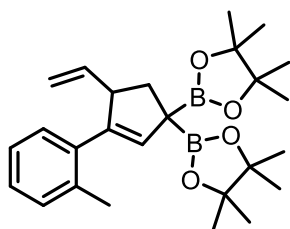
1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.5 Hz, 2H), 7.25 (t, J = 7.7 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 6.42 (s, 1H), 5.85 (ddd, J = 17.4, 10.1, 7.6 Hz, 1H), 5.06 (dt, J = 17.2, 1.5 Hz, 1H), 4.93 (dd, J = 10.2, 1.9 Hz, 1H), 3.77 – 3.67 (m, 1H), 2.53 (dd, J = 12.5, 9.3 Hz, 1H), 2.18 (dd, J = 12.5, 3.4 Hz, 1H), 1.22 (d, J = 2.0 Hz, 24H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.5, 136.7, 130.9, 128.1, 126.24, 126.2, 114.3, 83.53, 83.5, 49.8, 36.5, 24.9, 24.88, 24.7, 24.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.4.

HRMS (ASAP): m/z $[M+H]^+$ for $C_{25}H_{37}B_2O_4$, calculated 423.2872; observed 423.2878.

2,2'-(3-(*o*-tolyl)-4-vinylcyclopent-2-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6b)



Pale-yellow oil; 38% Yield (52 mg)

R_f (EtOAc/Hexane, 10:90) = 0.55

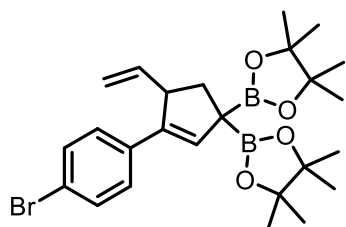
1H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 4H), 5.88 (d, J = 1.7 Hz, 1H), 5.69 (ddd, J = 17.1, 10.1, 7.9 Hz, 1H), 4.92 (ddd, J = 17.1, 2.0, 1.1 Hz, 1H), 4.81 (ddd, J = 10.2, 1.9, 0.9 Hz, 1H), 3.77 – 3.68 (m, 1H), 2.54 (dd, J = 12.4, 8.7 Hz, 1H), 2.34 (s, 3H), 2.11 (dd, J = 12.4, 6.0 Hz, 1H), 1.25 (d, J = 2.3 Hz, 12H), 1.23 (s, 13H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 140.6, 137.7, 136.0, 133.1, 130.3, 129.0, 126.2, 125.2, 113.9, 83.44, 83.4, 53.0, 35.8, 24.84, 24.8, 24.74, 24.7, 21.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.8.

HRMS (ASAP): m/z $[M+H]^+$ for $C_{26}H_{39}B_2O_4$, calculated 437.3029; observed 437.3021.

2,2'-(3-(4-bromophenyl)-4-vinylcyclopent-2-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6c)



Pale-yellow oil; 44% Yield (69 mg)

R_f (EtOAc/Hexane, 10:90) = 0.55

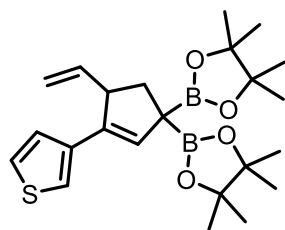
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.32 (m, 2H), 7.29 (d, J = 8.6 Hz, 2H), 6.41 (d, J = 1.1 Hz, 1H), 5.80 (ddd, J = 17.5, 10.1, 7.6 Hz, 1H), 5.02 (dt, J = 17.2, 1.4 Hz, 1H), 4.92 (ddd, J = 10.1, 1.9, 0.8 Hz, 1H), 3.68 – 3.63 (m, 1H), 2.51 (dd, J = 12.5, 9.3 Hz, 1H), 2.15 (dd, J = 12.5, 3.5 Hz, 1H), 1.21 (s, 24H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.5, 138.5, 135.6, 131.9, 131.2, 127.8, 119.9, 114.5, 83.62, 83.6, 49.7, 36.5, 24.9, 24.86, 24.7, 24.65.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 33.9.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{25}\text{H}_{36}\text{B}_2\text{BrO}_4$, calculated 501.1978; observed 501.1986.

2,2'-(3-(thiophen-3-yl)-4-vinylcyclopent-2-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6d)



Pale-yellow oil; 51% Yield (68 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

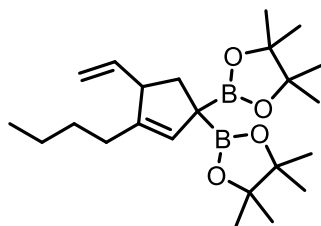
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.27 (dd, J = 5.0, 1.3 Hz, 1H), 7.19 (dd, J = 5.0, 2.9 Hz, 1H), 7.10 (dd, J = 2.9, 1.2 Hz, 1H), 6.24 (s, 1H), 5.86 (ddd, J = 17.0, 10.1, 8.1 Hz, 1H), 5.14 – 5.07 (m, 1H), 4.95 (dd, J = 10.1, 1.9 Hz, 1H), 3.61 (td, J = 8.7, 3.5 Hz, 1H), 2.51 (dd, J = 12.6, 9.3 Hz, 1H), 2.13 (dd, J = 12.6, 3.6 Hz, 1H), 1.22 (s, 24H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.3, 138.7, 135.2, 130.3, 126.6, 124.8, 119.5, 114.2, 83.5, 51.1, 36.4, 24.9, 24.6, 24.6.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 34.1.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{23}\text{H}_{35}\text{B}_2\text{O}_4\text{S}$, calculated 429.2437; observed 429.2442.

2,2'-(3-butyl-4-vinylcyclopent-2-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6e)



Colorless oil; 35% Yield (44 mg)

R_f (EtOAc/Hexane, 10:90) = 0.6

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.64 (ddd, $J = 17.0, 10.0, 8.7$ Hz, 1H), 5.46 (s, 1H), 4.99 (dd, $J = 17.1, 2.2$ Hz, 1H), 4.90 (dd, $J = 10.0, 2.1$ Hz, 1H), 3.13 (q, $J = 8.1$ Hz, 1H), 2.39 (dd, $J = 12.4, 8.5$ Hz, 1H), 2.05 – 1.94 (m, 1H), 1.89 (ddd, $J = 19.3, 9.7, 6.0$ Hz, 2H), 1.37 (tdd, $J = 8.2, 4.8, 2.4$ Hz, 2H), 1.30 – 1.24 (m, 2H), 1.21 (s, 24H), 0.85 (t, $J = 7.2$ Hz, 3H).

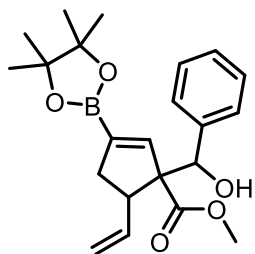
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.5, 141.9, 126.1, 113.7, 83.2, 52.5, 35.9, 29.7, 29.0, 24.9, 24.8, 24.6, 24.6, 22.4, 14.1.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 33.6.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{23}\text{H}_{41}\text{B}_2\text{O}_4$, calculated 403.3185; observed 403.3186.

Compounds **7a** to **7t** were prepared according to general procedure E1.

methyl 1-(hydroxy(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7a)



Pale-yellow oil; 62% Yield (74 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

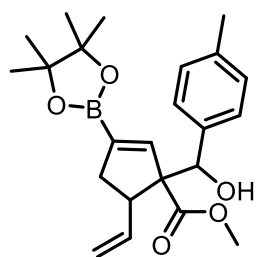
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 – 7.25 (m, 5H), 6.37 (t, $J = 2.0$ Hz, 1H), 5.69 (ddd, $J = 17.1, 10.2, 8.9$ Hz, 1H), 5.08 (ddd, $J = 17.0, 1.9, 1.0$ Hz, 1H), 4.98 (dd, $J = 10.2, 1.8$ Hz, 1H), 4.88 (s, 1H), 3.64 (s, 3H), 3.14 – 3.08 (m, 1H), 2.40 – 2.26 (m, 2H), 1.27 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.7, 144.4, 140.6, 138.4, 128.0, 127.9, 116.0, 83.6, 77.9, 71.3, 51.9, 50.1, 39.9, 25.0, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.9.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{28}\text{BO}_4$, calculated 367.2075; observed 367.2083.

methyl 1-(hydroxy(p-tolyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7b)



Pale-yellow oil; 56% Yield (70 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

Major diastereomer (70 mg)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.14 (d, $J = 7.9$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.37 (s, 1H), 5.68 (ddd, $J = 16.9, 10.1, 8.9$ Hz, 1H), 5.12 – 5.04 (m, 1H), 4.97 (dd, $J = 10.2, 1.8$ Hz, 1H), 4.85 (s, 1H), 3.64 (s, 3H), 3.09 (td, $J = 7.9, 4.9$ Hz, 1H), 2.40 – 2.27 (m, 5H), 1.27 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.8, 144.6, 138.4, 137.7, 137.6, 128.7, 127.8, 116.0, 83.6, 77.7, 71.3, 51.9, 50.1, 39.8, 25.0, 24.8, 24.7, 21.3.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.2.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{30}\text{BO}_5$, calculated 381.2232; observed 381.2242.

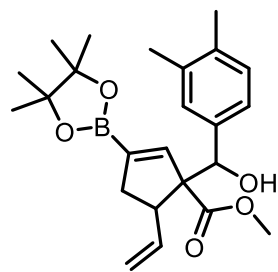
Minor diastereomer (5 mg)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.11 (d, $J = 8.4$ Hz, 2H), 7.05 (d, $J = 8.2$ Hz, 2H), 6.37 – 6.27 (m, 1H), 6.18 (s, 1H), 5.24 – 5.16 (m, 2H), 4.84 (d, $J = 5.2$ Hz, 1H), 3.69 (s, 3H), 3.33 (d, $J = 5.3$ Hz, 1H), 3.16 (q, $J = 7.5$ Hz, 1H), 2.52 (dd, $J = 16.8, 7.2$ Hz, 1H), 2.31 (s, 3H), 2.16 (ddd, $J = 16.0, 8.9, 2.5$ Hz, 1H), 1.26 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 175.2, 146.4, 137.7, 137.5, 137.4, 128.3, 127.9, 117.2, 83.6, 74.7, 68.8, 52.0, 51.1, 38.3, 25.0, 24.8, 21.3.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{30}\text{BO}_5$, calculated 381.2232; observed 381.2218.

methyl 1-((3,4-dimethylphenyl)(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7c)



Yellow oil; 49% Yield (63 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

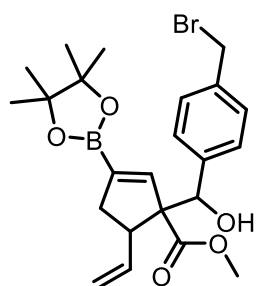
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.06 – 6.95 (m, 3H), 6.41 (s, 1H), 5.68 (ddd, $J = 17.0, 10.1, 8.9$ Hz, 1H), 5.07 (dd, $J = 17.1, 1$ Hz, 1H), 4.97 (dd, $J = 10.1, 2.5$ Hz, 1H), 4.83 (d, $J = 6.6$ Hz, 1H), 3.70 (d, $J = 6.6$ Hz, 1H), 3.64 (s, 3H), 3.07 (td, $J = 7.9, 4.9$ Hz, 1H), 2.39 – 2.25 (m, 2H), 2.22 (s, 6H), 1.27 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.8, 144.8, 138.5, 138.1, 136.2, 136.0, 129.3, 129.2, 125.4, 115.9, 83.5, 77.7, 71.3, 51.8, 50.0, 39.8, 25.1, 24.7, 19.9, 19.6.

^{11}B NMR (128 MHz, CDCl_3) δ 29.0.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{32}\text{BO}_4$, calculated 395.2388; observed 395.2357.

methyl 1-((4-(bromomethyl)phenyl)(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7d)



Yellow oil; 42% Yield (62 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

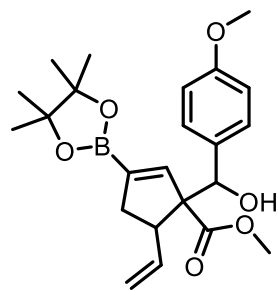
^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 6.33 (s, 1H), 5.68 (ddd, J = 17.1, 10.2, 8.9 Hz, 1H), 5.08 (d, J = 17.0 Hz, 1H), 4.96 (d, J = 10.5 Hz, 1H), 4.86 (d, J = 6.9 Hz, 1H), 4.47 (s, 2H), 3.94 (d, J = 7.0 Hz, 1H), 3.63 (s, 3H), 3.11 (td, J = 7.7, 4.7 Hz, 1H), 2.44 – 2.27 (m, 2H), 1.27 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 144.1, 141.0, 138.2, 137.3, 128.7, 128.4, 116.2, 83.6, 77.5, 71.2, 51.9, 50.1, 39.8, 33.4, 25.0, 24.8. (Note – 1 peak is merging with CDCl_3)

^{11}B NMR (128 MHz, CDCl_3) δ 28.5.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{21}\text{H}_{29}\text{BBrO}_4$, calculated 459.1377; observed 459.1391.

methyl 1-(hydroxy(4-methoxyphenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7e)



Yellow oil; 54% Yield (70 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

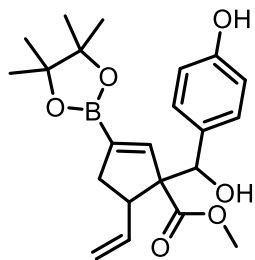
^1H NMR (400 MHz, CDCl_3) δ 7.20 – 7.16 (m, 2H), 6.83 – 6.78 (m, 2H), 6.39 (d, J = 2.0 Hz, 1H), 5.67 (ddd, J = 16.9, 10.1, 8.9 Hz, 1H), 5.30 (s, 1H), 5.06 (ddd, J = 17.1, 1.8, 1.0 Hz, 1H), 4.96 (dd, J = 10.2, 1.8 Hz, 1H), 4.87 (s, 1H), 3.79 (s, 3H), 3.64 (s, 3H), 3.04 (dt, J = 8.7, 6.1 Hz, 1H), 2.29 (dt, J = 5.6, 2.1 Hz, 2H), 1.26 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.8, 159.3, 144.4, 138.4, 132.8, 129.1, 116.0, 113.4, 83.6, 77.5, 71.5, 55.4, 51.9, 50.0, 39.9, 25.0, 24.8. (Note – 1 peak is merging with CDCl_3)

^{11}B NMR (128 MHz, CDCl_3) δ 29.1.

HRMS (ASAP): m/z $[M+H]^+$ for $C_{23}H_{30}BO_5$, calculated 397.2181; observed 397.2199.

methyl 1-(hydroxy(4-hydroxyphenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7f)



Pale-yellow oil; 35% Yield (44 mg)

R_f (EtOAc/Hexane, 40:60) = 0.3

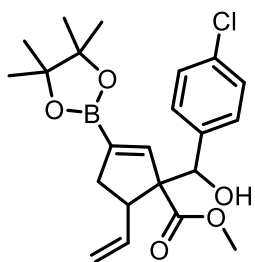
1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.3 Hz, 2H), 6.68–6.64 (m, 2H), 6.38 (d, J = 1.9 Hz, 1H), 5.67 (ddd, J = 17.1, 10.1, 8.8 Hz, 1H), 5.09–5.02 (m, 1H), 4.97 (dd, J = 10.2, 1.8 Hz, 1H), 4.84 (d, J = 4.9 Hz, 1H), 3.88 (d, J = 6.3 Hz, 1H), 3.63 (s, 3H), 3.03 (q, J = 7.0 Hz, 1H), 2.40–2.24 (m, 2H), 1.27 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 155.7, 144.6, 138.3, 132.4, 129.2, 116.1, 114.9, 83.8, 77.5, 71.4, 51.9, 50.1, 39.8, 24.9, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 28.2.

HRMS (ASAP): m/z $[M+H]^+$ for $C_{22}H_{28}BO_5$, calculated 383.2024; observed 383.2012.

methyl 1-((4-chlorophenyl)(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7g)



Yellow oil; 56% Yield (73 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

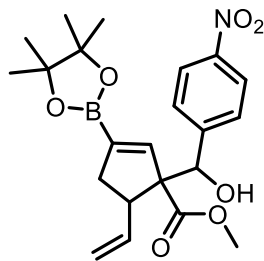
1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 2H), 7.20–7.16 (m, 2H), 6.31 (t, J = 2.0 Hz, 1H), 5.65 (ddd, J = 16.9, 10.1, 8.8 Hz, 1H), 5.10–5.03 (m, 1H), 4.97 (dd, J = 10.1, 1.8 Hz, 1H), 4.85 (s, 1H), 3.62 (s, 3H), 3.04 (td, J = 7.8, 5.1 Hz, 1H), 2.42–2.25 (m, 2H), 1.26 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 143.9, 139.1, 138.0, 133.7, 129.3, 128.1, 116.3, 83.7, 77.1, 71.2, 52.0, 50.0, 39.8, 25.0, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 28.9.

HRMS (ASAP): m/z $[M+H]^+$ for $C_{22}H_{27}BClO_4$, calculated 401.1685; observed 401.1672.

methyl 1-(hydroxy(4-nitrophenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7h)



Light Brown solid; 44% Yield (59 mg), Melting point – 116-118 °C

R_f (EtOAc/Hexane, 20:80) = 0.2

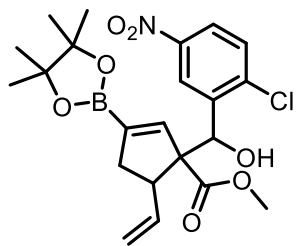
^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 6.26 (s, 1H), 5.67 (ddd, J = 17.1, 10.0, 8.8 Hz, 1H), 5.11 (d, J = 17.4 Hz, 1H), 5.02 (d, J = 10.2 Hz, 1H), 4.95 (d, J = 7.2 Hz, 1H), 4.25 (d, J = 7.2 Hz, 1H), 3.64 (s, 3H), 3.15 – 3.09 (m, 1H), 2.51 – 2.33 (m, 2H), 1.27 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.5, 148.0, 147.7, 143.2, 137.7, 128.9, 123.2, 116.7, 83.8, 76.9, 71.0, 52.1, 50.3, 40.0, 25.1, 24.9.

^{11}B NMR (128 MHz, CDCl_3) δ 29.3.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{27}\text{BNO}_6$, calculated 412.1926; observed 412.1927.

methyl 1-((2-chloro-5-nitrophenyl)(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7i)



Light brown oil; 36% Yield (52 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

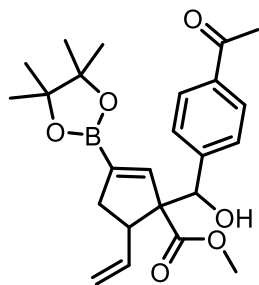
^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, J = 2.8 Hz, 1H), 8.05 (dd, J = 8.8, 2.7 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 6.43 (s, 1H), 5.76 – 5.65 (m, 2H), 5.06 (d, J = 17.3 Hz, 1H), 4.97 (d, J = 10.6 Hz, 1H), 3.98 (d, J = 5.9 Hz, 1H), 3.69 (s, 3H), 2.94 (td, J = 8.2, 4.9 Hz, 1H), 2.34 – 2.17 (m, 2H), 1.24 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.4, 146.5, 142.5, 140.3, 140.1, 137.6, 130.3, 125.5, 123.7, 116.5, 83.8, 72.1, 71.8, 52.3, 49.2, 39.9, 25.1, 24.6.

^{11}B NMR (128 MHz, CDCl_3) δ 29.4.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{26}\text{BClNO}_6$, calculated 446.1536; observed 446.1540.

methyl 1-((4-acetylphenyl)(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7j)



Pale-yellow oil; 58% Yield (77 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

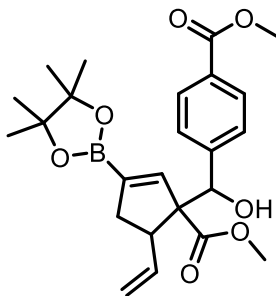
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 6.29 (s, 1H), 5.65 (ddd, $J = 17.2, 10.1, 8.8$ Hz, 1H), 5.06 (d, $J = 16.7$ Hz, 1H), 4.96 (d, $J = 10.5$ Hz, 1H), 4.90 (d, $J = 7.0$ Hz, 1H), 4.16 (d, $J = 7.0$ Hz, 1H), 3.61 (s, 3H), 3.09 (td, $J = 7.9, 4.8$ Hz, 1H), 2.57 (s, 3H), 2.41 – 2.27 (m, 2H), 1.25 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.8, 174.4, 145.9, 143.7, 137.9, 136.5, 128.0, 127.8, 116.9, 83.5, 76.7, 70.9, 51.8, 49.9, 39.7, 26.6, 24.9, 24.7.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.3.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{30}\text{BO}_5$, calculated 409.2181; observed 409.2202.

methyl 4-(hydroxy(1-(methoxycarbonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-en-1-yl)methyl)benzoate (7k)



Yellow oil; 62% Yield (85 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

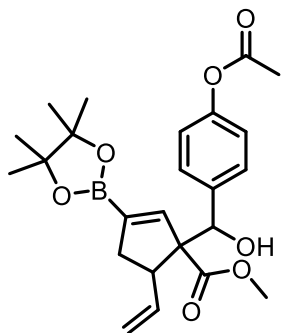
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 6.30 (s, 1H), 5.66 (ddd, $J = 17.0, 10.1, 8.8$ Hz, 1H), 5.05 (d, $J = 17.3$ Hz, 1H), 4.96 (d, $J = 11.2$ Hz, 1H), 4.90 (s, 1H), 4.11 (brs, 1H), 3.89 (s, 3H), 3.61 (s, 3H), 3.09 (td, $J = 7.9, 4.9$ Hz, 1H), 2.41 – 2.27 (m, 2H), 1.25 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.4, 166.9, 145.6, 143.7, 137.8, 129.5, 129.1, 127.8, 116.2, 83.5, 76.7, 70.9, 52.0, 51.8, 49.9, 39.7, 24.9, 24.6.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.1.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{30}\text{BO}_6$, calculated 425.2130; observed 425.2114.

methyl 1-((4-acetoxyphenyl)(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7l)



Yellow oil; 55% Yield (76 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

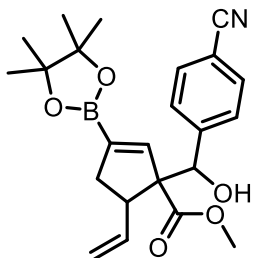
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.24 (d, $J = 8.6$ Hz, 2H), 6.99 (d, $J = 8.6$ Hz, 2H), 6.34 (t, $J = 1.9$ Hz, 1H), 5.66 (ddd, $J = 17.4, 10.2, 8.8$ Hz, 1H), 5.05 (dd, $J = 17.1, 1.7$ Hz, 1H), 4.96 (dd, $J = 10.2, 1.8$ Hz, 1H), 4.86 (d, $J = 5.8$ Hz, 1H), 3.88 (d, $J = 6.7$ Hz, 1H), 3.61 (d, $J = 1.2$ Hz, 3H), 3.07 (td, $J = 7.9, 5.0$ Hz, 1H), 2.41 – 2.24 (m, 5H), 1.24 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.7, 169.4, 150.3, 144.1, 138.23, 138.2, 129.0, 121.0, 116.2, 83.6, 77.3, 71.2, 51.9, 50.1, 39.9, 25.0, 24.8, 21.3.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.2.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{30}\text{BO}_6$, calculated 425.2130; observed 443.2240.

methyl 1-((4-cyanophenyl)(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7m)



Light brown oil; 43% Yield (55 mg)

R_f (EtOAc/Hexane, 20:80) = 0.4

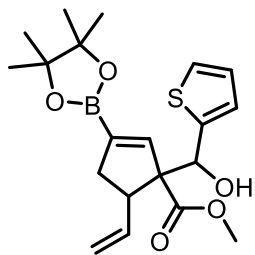
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 6.26 (t, $J = 1.9$ Hz, 1H), 5.65 (ddd, $J = 17.3, 10.2, 8.8$ Hz, 1H), 5.07 (dd, $J = 17.0, 1.6$ Hz, 1H), 4.99 (dd, $J = 10.1, 1.6$ Hz, 1H), 4.90 (s, 1H), 3.62 (s, 3H), 3.11 – 3.02 (m, 1H), 2.43 – 2.30 (m, 2H), 1.26 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.4, 146.0, 143.3, 137.7, 131.7, 128.7, 118.8, 116.6, 111.8, 83.8, 77.1, 71.0, 52.1, 50.1, 39.9, 25.0, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.4.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{23}\text{H}_{27}\text{BNO}_4$, calculated 392.2028; observed 395.2035.

methyl 1-(hydroxy(thiophen-2-yl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7n)



Orange oil; 45% Yield (55 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

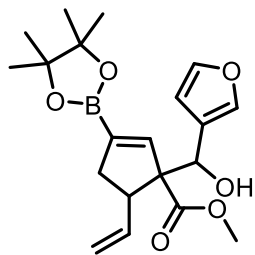
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22 (dd, $J = 4.9, 1.3$ Hz, 1H), 6.96 – 6.91 (m, 2H), 6.38 (d, $J = 2.1$ Hz, 1H), 5.69 (dt, $J = 17.0, 9.5$ Hz, 1H), 5.12 – 4.95 (m, 3H), 3.67 (s, 3H), 3.19 (td, $J = 8.3, 5.5$ Hz, 1H), 2.58 (ddd, $J = 16.6, 7.6, 2.0$ Hz, 1H), 2.40 (ddd, $J = 16.5, 5.7, 1.9$ Hz, 1H), 1.27 (s, 13H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.7, 144.3, 144.0, 138.1, 126.4, 126.2, 125.5, 116.3, 83.7, 74.1, 71.0, 52.0, 50.4, 39.9, 25.0, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.6.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{20}\text{H}_{26}\text{BO}_4\text{S}$, calculated 373.1639; observed 373.1648.

methyl 1-(furan-3-yl(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7o)



Yellow oil; 47% Yield (54 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

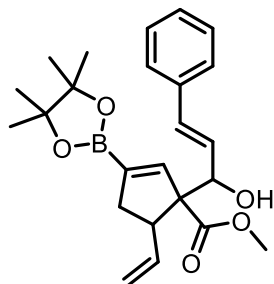
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.29 (m, 2H), 6.36 – 6.32 (m, 2H), 5.69 (ddd, $J = 17.0, 10.2, 8.7$ Hz, 1H), 5.04 (d, $J = 16.8$ Hz, 1H), 4.95 (d, $J = 11.79$ Hz, 1H), 4.70 (d, $J = 8.1$ Hz, 1H), 3.92 (d, $J = 8.2$ Hz, 1H), 3.64 (s, 3H), 3.19 (td, $J = 8.1, 5.2$ Hz, 1H), 2.62 (ddd, $J = 16.5, 7.6, 2.1$ Hz, 1H), 2.41 (ddd, $J = 16.5, 5.1, 2.0$ Hz, 1H), 1.27 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.9, 144.3, 142.9, 140.4, 138.3, 125.7, 116.1, 109.8, 83.7, 70.8, 70.6, 51.9, 50.2, 39.9, 25.0, 24.9.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.1.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{20}\text{H}_{26}\text{BO}_5$, calculated 357.1868; observed 357.1880.

methyl (E)-1-(1-hydroxy-3-phenylallyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7p)



Pale-yellow oil; 61% Yield (78 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

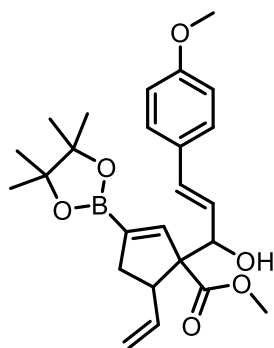
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39 – 7.21 (m, 5H), 6.64 (d, J = 15.9 Hz, 1H), 6.44 (s, 1H), 6.18 (dd, J = 15.8 Hz, 6.9 Hz, 1H), 5.73 (ddd, J = 17.1, 10.2, 8.6 Hz, 1H), 5.08 (d, J = 17.0 Hz, 1H), 4.98 (d, J = 10.3 Hz, 1H), 4.34 (t, J = 7.3 Hz, 1H), 3.64 (s, 3H), 3.47 (d, J = 7.9 Hz, 1H), 3.27 – 3.22 (m, 1H), 2.73 (ddd, J = 16.5, 7.7, 2.0 Hz, 1H), 2.46 (ddd, J = 16.6, 5.4, 2.0 Hz, 1H), 1.26 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.4, 144.1, 138.4, 136.8, 133.0, 128.7, 128.4, 127.9, 126.8, 116.1, 83.7, 76.6, 70.5, 51.8, 50.1, 40.0, 25.0, 24.98.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.62

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{30}\text{BO}_4$, calculated 393.2232; observed 393.2229.

methyl (E)-1-(1-hydroxy-3-(4-methoxyphenyl)allyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7q)



Pale-yellow oil; 62% Yield (80 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

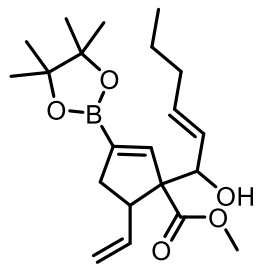
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 15.8 Hz, 1H), 6.44 (s, 1H), 6.03 (dd, J = 15.9, 7.2 Hz, 1H), 5.73 (dt, J = 17.5, 9.4 Hz, 1H), 5.08 (d, J = 17.1 Hz, 1H), 4.98 (d, J = 10.6 Hz, 1H), 4.33 (t, J = 7.4 Hz, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 3.39 (d, J = 7.7 Hz, 1H), 3.25 – 3.18 (m, 1H), 2.76 – 2.67 (m, 1H), 2.45 (dd, J = 16.6, 5.2 Hz, 1H), 1.29 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.4, 159.5, 144.2, 138.4, 132.6, 129.6, 128.0, 126.1, 116.1, 114.1, 83.7, 76.7, 70.6, 55.4, 51.8, 50.1, 40.0, 25.0, 24.97.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.4.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{25}\text{H}_{32}\text{BO}_5$, calculated 423.2337; observed 423.2349.

methyl (E)-1-(1-hydroxyhex-2-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7r)



Pale-yellow oil; 52% Yield (61 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

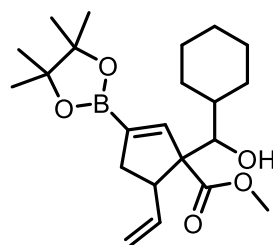
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.37 (t, $J = 2.0$ Hz, 1H), 5.75 – 5.65 (m, 2H), 5.42 (ddt, $J = 15.3, 7.2, 1.5$ Hz, 1H), 5.04 (ddd, $J = 17.1, 1.9, 1.1$ Hz, 1H), 4.95 (ddd, $J = 10.1, 1.9, 0.8$ Hz, 1H), 4.14 – 4.11 (m, 1H), 3.63 (s, 3H), 3.19 – 3.12 (m, 1H), 2.70 (ddd, $J = 16.4, 7.7, 2.0$ Hz, 1H), 2.42 (ddd, $J = 16.4, 5.3, 2.0$ Hz, 1H), 2.03 – 1.97 (m, 2H), 1.38 (h, $J = 7.3$ Hz, 2H), 1.28 (s, 12H), 0.88 (t, $J = 7.4$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.5, 144.5, 138.6, 134.8, 128.9, 115.9, 83.7, 76.5, 70.5, 51.7, 49.9, 40.0, 34.5, 25.03, 25.0, 22.4, 13.7.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.9.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{21}\text{H}_{32}\text{BO}_4$, calculated 359.2388; observed 359.2379.

methyl 1-(cyclohexyl(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7s)



Colorless oil; 44% Yield (53 mg)

R_f (EtOAc/Hexane, 10:90) = 0.35

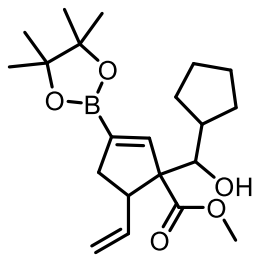
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.35 (dd, $J = 2.6, 1.3$ Hz, 1H), 5.65 (dt, $J = 17.0, 9.8$ Hz, 1H), 5.04 (dd, $J = 17.1, 1.9$ Hz, 1H), 4.91 (dd, $J = 10.1, 2.0$ Hz, 1H), 3.61 (d, $J = 1.4$ Hz, 3H), 3.42 – 3.32 (m, 1H), 3.29 (s, 1H), 2.77 (ddd, $J = 16.6, 7.2, 2.5$ Hz, 1H), 2.33 (dd, $J = 16.7, 2.5$ Hz, 1H), 1.71 (d, $J = 11.7$ Hz, 2H), 1.60 (d, $J = 11.3$ Hz, 1H), 1.47 – 1.38 (m, 4H), 1.29 (d, $J = 1.5$ Hz, 13H), 1.25 – 1.08 (m, 5H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 175.6, 144.8, 138.7, 115.9, 83.7, 79.6, 68.4, 51.7, 51.2, 41.2, 39.5, 31.4, 26.7, 26.4, 26.36, 26.3, 25.01, 25.0.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.2.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{34}\text{BO}_4$, calculated 373.2545; observed 373.2548.

methyl 1-(cyclopentyl(hydroxy)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (7t)



Pale-yellow oil; 49% Yield (57 mg)

R_f (EtOAc/Hexane, 10:90) = 0.35

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.41 (s, 1H), 5.64 (ddd, $J = 17.1, 10.1, 9.3$ Hz, 1H), 5.04 (d, $J = 16.0$ Hz, 1H), 4.91 (d, $J = 10.1$ Hz, 1H), 3.78 (d, $J = 10.4$ Hz, 1H), 3.62 (s, 3H), 3.52 – 3.46 (m, 1H), 3.42 – 3.36 (m, 1H), 2.76 (ddd, $J = 16.6, 7.1, 2.6$ Hz, 1H), 2.36 – 2.30 (m, 1H), 1.99 – 1.86 (m, 1H), 1.65 – 1.52 (m, 4H), 1.49 – 1.42 (m, 4H), 1.27 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 175.2, 145.3, 138.7, 115.8, 83.7, 76.7, 69.8, 51.8, 50.7, 43.7, 39.3, 30.6, 26.2, 25.0, 24.95.

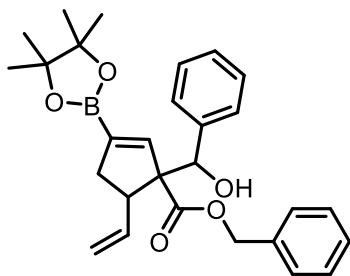
$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.5.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{21}\text{H}_{32}\text{BO}_4$, calculated 359.2388; observed 359.2379.

Alkyne Scope (Allylboration) 8a to 8k

Compounds **8a** to **8d** were prepared according to general procedure E1.

benzyl 1-(hydroxy(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (8a)



Pale-yellow oil; 51% Yield (73 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

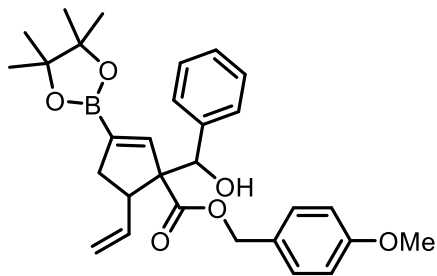
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.26 (m, 10H), 6.44 (s, 1H), 5.68 (dt, $J = 16.3, 9.5$ Hz, 1H), 5.18 – 5.05 (m, 3H), 4.92 (d, $J = 10.3$ Hz, 2H), 3.16 – 3.09 (m, 1H), 2.41 – 2.29 (m, 2H), 1.28 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.0, 144.4, 140.5, 138.2, 135.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.9, 116.2, 83.6, 77.7, 71.2, 66.6, 50.1, 39.9, 25.0, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.5.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{28}\text{H}_{32}\text{BO}_4$, calculated 443.2388; observed 443.2375.

4-methoxybenzyl 1-(hydroxy(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (8b)



Pale-yellow oil; 56% Yield (86 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

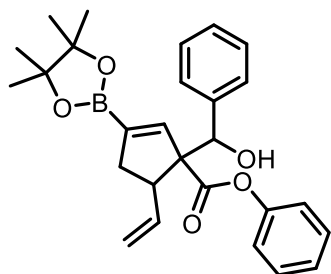
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21 (ddd, $J = 8.5, 6.6, 2.6$ Hz, 7H), 6.86–6.83 (m, 2H), 6.38 (t, $J = 2.0$ Hz, 1H), 5.63 (ddd, $J = 17.1, 10.1, 8.9$ Hz, 1H), 5.07–5.02 (m, 3H), 4.92–4.83 (m, 2H), 3.86 (d, $J = 7.0$ Hz, 1H), 3.81 (d, $J = 1.0$ Hz, 3H), 3.11 (q, $J = 7.2$ Hz, 1H), 2.42–2.24 (m, 2H), 1.26 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.1, 159.7, 144.6, 144.4, 140.6, 138.2, 130.2, 128.0, 127.9, 116.1, 114.0, 113.8, 83.6, 71.1, 66.5, 55.4, 50.1, 39.9, 25.0, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.2.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{29}\text{H}_{34}\text{BO}_5$, calculated 473.2494; observed 473.2505.

phenyl 1-(hydroxy(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (8c)



Pale-yellow oil; 53% Yield (74 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

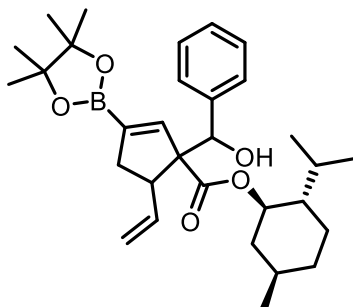
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37–7.30 (m, 7H), 7.24–7.19 (m, 1H), 7.01–6.93 (m, 2H), 6.54 (t, $J = 2.0$ Hz, 1H), 5.92 (ddd, $J = 17.1, 10.2, 8.8$ Hz, 1H), 5.21 (ddd, $J = 17.1, 1.7, 1.0$ Hz, 1H), 5.11 (ddd, $J = 10.2, 1.8, 0.7$ Hz, 1H), 5.00 (s, 1H), 3.26 (dt, $J = 8.8, 5.8$ Hz, 1H), 2.41 (d, $J = 2.0$ Hz, 1H), 2.39 (d, $J = 2.0$ Hz, 1H), 1.28 (d, $J = 1.6$ Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.0, 150.7, 144.1, 140.5, 138.2, 129.5, 128.1, 128.0, 126.1, 121.8, 116.6, 83.7, 78.0, 71.1, 50.2, 39.9, 25.0, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.7.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{27}\text{H}_{30}\text{BO}_4$, calculated 429.2232; observed 429.2219.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 1-(hydroxy(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (8d)



Pale-yellow oil; 49% Yield (75 mg)

R_f (EtOAc/Hexane, 25:75) = 0.3

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.25 – 7.18 (m, 5H), 6.27 (q, J = 2.2 Hz, 1H), 5.69 (ddt, J = 17.0, 12.4, 9.5 Hz, 1H), 5.12 – 5.02 (m, 1H), 4.93 (ddd, J = 14.3, 10.1, 1.8 Hz, 1H), 4.74 (dd, J = 7.5, 3.4 Hz, 1H), 4.62 (dtd, J = 37.4, 10.8, 4.3 Hz, 1H), 4.35 (dd, J = 93.9, 7.5 Hz, 1H), 3.17 (qd, J = 8.5, 4.5 Hz, 1H), 2.49 (tdd, J = 16.8, 7.3, 2.2 Hz, 1H), 2.30 (dddd, J = 30.4, 16.5, 4.6, 1.7 Hz, 1H), 1.92 – 1.78 (m, 1H), 1.63 – 1.59 (m, 1H), 1.56 (dd, J = 6.3, 3.0 Hz, 1H), 1.43 (ddd, J = 19.3, 9.7, 5.3 Hz, 2H), 1.24 (d, J = 2.4 Hz, 12H), 0.85 – 0.81 (m, 3H), 0.78 (d, J = 6.9 Hz, 2H), 0.73 – 0.58 (m, 6H).

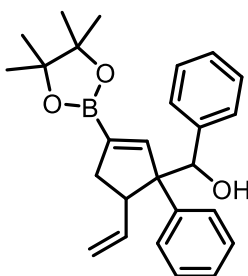
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.4, 145.3, 140.9, 138.2, 128.0, 127.9, 127.8, 127.7, 116.4, 83.5, 78.1, 75.8, 70.8, 50.4, 46.8, 40.7, 40.0, 34.3, 31.6, 25.9, 25.0, 24.95, 24.9, 24.8, 23.2, 22.2, 20.9, 16.1.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.2.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{31}\text{H}_{44}\text{BO}_4$, calculated 491.3327; observed 491.3319.

Compounds **8g** to **8i** were prepared according to general procedure E2.

phenyl(1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-en-1-yl)methanol (8g)



Dark yellow oil; 40% Yield (50 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

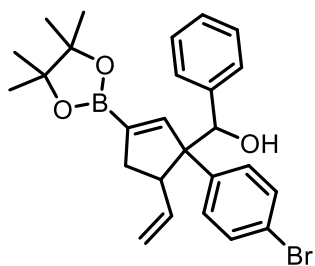
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.24 (m, 10H), 6.87 – 6.84 (m, 1H), 5.24 – 5.13 (m, 2H), 4.94 – 4.88 (m, 1H), 4.77 – 4.72 (m, 1H), 2.96 – 2.89 (m, 1H), 2.12 – 1.96 (m, 2H), 1.28 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.9, 141.0, 140.8, 139.7, 129.2, 128.9, 128.3, 127.9, 127.6, 126.9, 114.3, 83.5, 79.6, 67.8, 50.7, 40.7, 25.1, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.5.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{26}\text{H}_{30}\text{BO}_2$, calculated 385.2333; observed 385.2344.

(1-(4-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-en-1-yl)(phenyl)methanol (8h)



Orange oil; 39% Yield (58 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

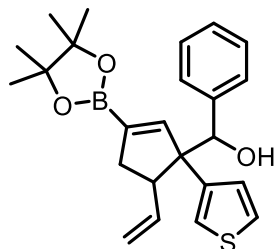
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (d, J = 8.7 Hz, 2H), 7.30 – 7.22 (m, 7H), 6.80 (s, 1H), 5.24 – 5.10 (m, 2H), 4.95 (dd, J = 17.0, 2.5 Hz, 1H), 4.80 (dd, J = 10.0, 2.2 Hz, 1H), 3.04 – 2.96 (m, 1H), 2.18 (dd, J = 17.3, 8.4 Hz, 1H), 2.05 (dd, J = 15.4, 6.9 Hz, 1H), 1.94 (brs, 1H), 1.30 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.4, 140.7, 138.9, 131.1, 128.6, 128.0, 127.7, 120.8, 114.7, 83.5, 79.4, 67.3, 50.7, 40.7, 25.1, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.9.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{26}\text{H}_{29}\text{BBrO}_2$, calculated 463.1438; observed 463.1429

phenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-3-yl)-5-vinylcyclopent-2-en-1-yl)methanol (8i)



Brown oil; 45% Yield (57 mg)

R_f (EtOAc/Hexane, 20:80) = 0.2

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (dd, J = 5.0, 3.0 Hz, 1H), 7.29 – 7.25 (m, 5H), 7.13 (dd, J = 5.1, 1.4 Hz, 1H), 7.04 (dd, J = 3.0, 1.3 Hz, 1H), 6.76 (s, 1H), 5.39 – 5.29 (m, 1H), 5.09 (s, 1H), 4.99 (dd, J = 16.6 Hz, 1.7 Hz, 1H), 4.86 (dd, J = 10.1 Hz, 2.2 Hz, 1H), 2.91 – 2.83 (m, 1H), 2.30 – 2.22 (m, 1H), 2.16 – 2.08 (m, 2H), 2.09 (brs, 1H), 1.28 (s, 12H).

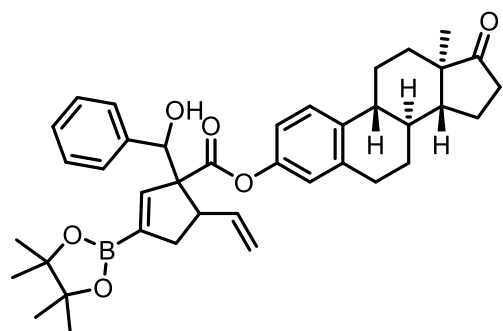
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.5, 140.7, 140.67, 140.5, 128.6, 128.3, 127.9, 127.8, 125.3, 123.3, 114.8, 83.5, 79.5, 65.8, 51.0, 40.3, 25.0, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.9.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{24}\text{H}_{28}\text{BO}_2\text{S}$, calculated 391.1898; observed 391.1886.

Compounds **8j** and **8k** were prepared according to general procedure E1.

(8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 1-(hydroxy(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (8j**)**



White solid; 38% Yield (74 mg), Melting point – 135-137 °C

R_f (EtOAc/Hexane, 20:80) = 0.2

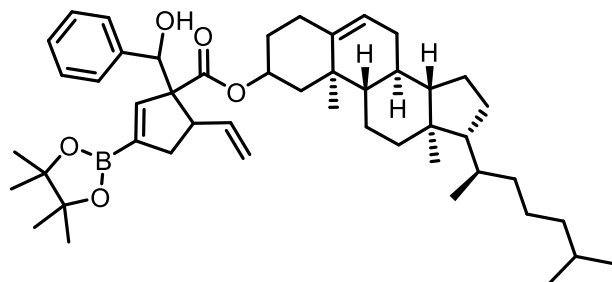
¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.19 (m, 6H), 6.70 (dt, *J* = 8.5, 2.5 Hz, 1H), 6.65 (d, *J* = 2.6 Hz, 1H), 6.49 (q, *J* = 1.8 Hz, 1H), 5.86 (ddd, *J* = 17.1, 10.1, 8.8 Hz, 1H), 5.19 – 5.12 (m, 1H), 5.06 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.94 (d, *J* = 1.3 Hz, 1H), 3.25 – 3.15 (m, 1H), 2.87 – 2.80 (m, 2H), 2.50 – 2.32 (m, 4H), 2.24 – 1.91 (m, 5H), 1.63 – 1.34 (m, 7H), 1.23 (s, 12H), 0.86 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 220.9, 173.2, 148.5, 144.2, 140.5, 138.1, 138.1, 137.6, 128.1, 128.0, 126.4, 121.7, 118.9, 116.6, 83.6, 77.9, 71.0, 50.6, 50.2, 48.1, 44.3, 39.9, 38.1, 36.0, 31.7, 29.5, 26.4, 25.9, 25.0, 24.8, 21.7, 13.9.

¹¹B NMR (128 MHz, CDCl₃) δ 29.0.

HRMS (ESI): *m/z* [M+H]⁺ for C₃₉H₄₆BO₅, calculated 605.3433; observed 605.3425.

(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-2-yl 1-(hydroxy(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (8k**)**



White solid; 43% Yield (99 mg), Melting point – 120-122 °C

R_f (EtOAc/Hexane, 20:80) = 0.2

¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 2.9 Hz, 5H), 6.32 (d, *J* = 2.1 Hz, 1H), 5.79 – 5.67 (m, 1H), 5.36 (s, 1H), 5.10 (dd, *J* = 17.2, 3.1 Hz, 1H), 4.97 (ddd, *J* = 10.1, 5.2, 1.8 Hz, 1H), 4.80 (s, 1H), 4.68 – 4.59 (m, 1H), 3.19 (s, 1H), 2.52 – 2.41 (m, 1H), 2.33 (dd, *J* = 16.5, 4.1 Hz, 1H), 2.28 (d, *J* = 8.2 Hz, 1H), 2.18 (t, *J* = 7.4 Hz, 1H), 2.01 (d, *J* = 13.1 Hz, 2H), 1.95 (s, 1H), 1.81 (d, *J* = 4.9 Hz, 2H), 1.61 – 1.32 (m, 12H), 1.28 (s, 13H), 1.25 – 0.97 (m, 17H), 0.92 (d, *J* = 6.5 Hz, 4H), 0.87 (dd, *J* = 6.6, 1.8 Hz, 7H), 0.68 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 173.7, 145.0, 140.9, 139.7, 138.4, 127.9, 127.8, 122.9, 116.1,

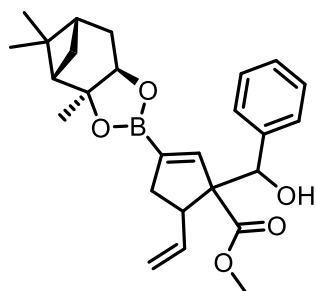
83.6, 77.7, 75.1, 70.6, 56.8, 56.3, 50.2, 50.0, 42.5, 39.9, 39.7, 38.3, 38.1, 37.1, 36.7, 36.3, 35.9, 32.0, 28.4, 28.2, 28.0, 27.8, 25.0, 24.8, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0.

^{11}B NMR (128 MHz, CDCl_3) δ 29.3.

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{48}\text{H}_{72}\text{BO}_3$, calculated 707.5569; observed 707.5561.

Compounds **9a** and **9c** were prepared according to general procedure E1.

methyl 1-(hydroxy(phenyl)methyl)-3-((3aS,4S,6S,7aR)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)-5-vinylcyclopent-2-ene-1-carboxylate (9a)



Pale yellow oil, 41% yield, 56 mg

R_f (EtOAc/Hexane, 20:80) = 0.2

^1H NMR (400 MHz, CDCl_3) δ 7.26 (s, 5H), 6.38 (dt, J = 3.8, 1.9 Hz, 1H), 5.68 (dt, J = 16.8, 9.5 Hz, 1H), 5.08 (d, J = 17.0 Hz, 1H), 4.97 (dt, J = 10.1, 1.7 Hz, 1H), 4.90 (d, J = 3.2 Hz, 1H), 4.30 (d, J = 8.7 Hz, 1H), 3.64 (s, 3H), 3.09 (q, J = 6.8 Hz, 1H), 2.38 – 2.28 (m, 3H), 2.26 – 2.18 (m, 1H), 2.06 (dt, J = 8.8, 5.5 Hz, 1H), 1.94 – 1.81 (m, 2H), 1.40 (d, J = 1.9 Hz, 3H), 1.31 – 1.23 (m, 4H), 1.11 (dd, J = 10.9, 8.1 Hz, 1H), 0.84 (s, 3H).

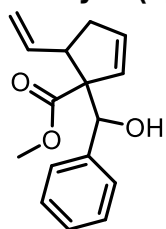
^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 144.2, 140.6, 138.3, 128.0, 128.0, 127.9, 116.0, 86.1, 78.1, 77.9, 71.4, 51.9, 51.4, 50.0, 39.9, 39.7, 38.3, 35.6, 28.7, 27.2, 26.6, 24.1.

^{11}B NMR (128 MHz, CDCl_3) δ 29.7.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{26}\text{H}_{32}\text{BO}_4$, calculated 419.2388; observed 419.2402.

Note: Chiral HPLC of this compound indicated it to be a racemic mixture.

methyl 1-(hydroxy(phenyl)methyl)-5-vinylcyclopent-2-ene-1-carboxylate (9c)



Colorless oil; 52% Yield (42 mg)

R_f (EtOAc/Hexane, 20:80) = 0.3

^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.24 (m, 5H), 6.35 (ddd, J = 16.4, 10.8, 8.0 Hz, 1H), 5.91 – 5.86 (m, 1H), 5.45 – 5.41 (m, 1H), 5.26 (t, J = 1.0 Hz, 1H), 5.26 – 5.21 (m, 1H), 4.84 (s, 1H), 3.72 (s, 3H), 3.20 (q, J = 8.2 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.22 – 2.13 (m, 1H), 1.28 (d, J = 4.0 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 175.6, 140.9, 137.5, 132.4, 132.0, 128.0, 127.8, 127.7, 117.3, 75.1, 67.0, 52.1, 50.6, 36.6.

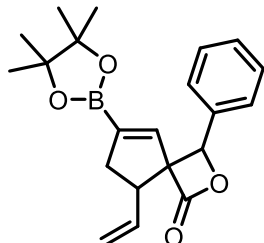
HRMS (ASAP): m/z $[M+H]^+$ for $C_{16}H_{17}O_2$, calculated 241.1223; observed 241.1231.

Lactones

Compounds **10a** to **10e** were prepared according to general procedure F.

3-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-vinyl-2-oxaspiro[3.4]oct-5-en-1-one (**10a**)

Yellow semi solid; 64% Yield (56 mg)



R_f (EtOAc/Hexane, 50:50) = 0.3

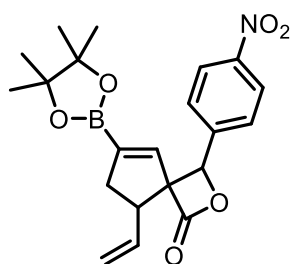
1H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 5H), 6.44 (t, J = 2.0 Hz, 1H), 5.79 (ddd, J = 17.0, 10.1, 8.9 Hz, 1H), 5.11 (dt, J = 17.1, 1.3 Hz, 1H), 5.02 (dd, J = 10.1, 1.8 Hz, 1H), 4.96 (s, 1H), 3.06 – 2.99 (m, 1H), 2.38 – 2.25 (m, 2H), 1.25 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 143.9, 140.1, 138.0, 128.2, 128.1, 128.1, 116.6, 83.7, 77.6, 71.1, 50.2, 40.0, 25.0, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.3.

HRMS (ASAP): m/z $[M+H]^+$ for $C_{21}H_{26}BO_4$, calculated 353.1919; observed 353.1937.

3-(4-nitrophenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-vinyl-2-oxaspiro[3.4]oct-5-en-1-one (**10b**)



Light brown solid, 59% Yield (59 mg), Melting point – 160-162 °C

R_f (EtOAc/Hexane, 50:50) = 0.3

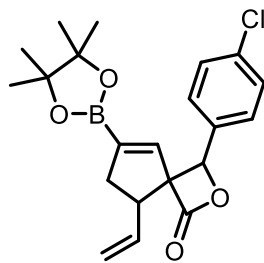
1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 6.42 (s, 1H), 5.78 (dt, J = 17.9, 9.5 Hz, 1H), 5.16 – 5.03 (m, 3H), 2.97 (q, J = 7.3 Hz, 1H), 2.35 (qd, J = 16.6, 6.5 Hz, 2H), 1.26 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 147.8, 147.4, 142.7, 137.3, 129.1, 123.2, 117.2, 83.9, 76.5, 70.9, 50.1, 40.2, 25.0, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2.

HRMS (ASAP): m/z $[M+H]^+$ for $C_{21}H_{25}BNO_6$, calculated 398.1769; observed 398.1754.

3-(4-chlorophenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-vinyl-2-oxaspiro[3.4]oct-5-en-1-one (10c)



Yellow semi solid; 61% Yield (59 mg)

R_f (EtOAc/Hexane, 50:50) = 0.3

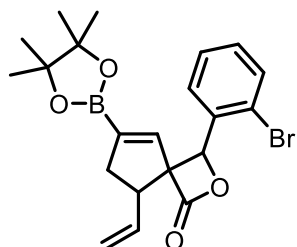
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 – 7.22 (m, 4H), 6.41 (s, 1H), 5.78 (dt, J = 18.0, 9.4 Hz, 1H), 5.11 (d, J = 17.1 Hz, 1H), 5.03 (d, J = 10.1 Hz, 1H), 4.96 (s, 1H), 2.97 (d, J = 7.8 Hz, 1H), 2.36 (s, 2H), 1.26 (s, 13H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 177.3, 143.4, 138.6, 137.7, 134.0, 129.5, 128.3, 116.9, 83.8, 71.0, 50.2, 40.1, 25.0, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.8.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{21}\text{H}_{25}\text{BClO}_4$, calculated 387.1529; observed 387.1510.

3-(2-bromophenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-vinyl-2-oxaspiro[3.4]oct-5-en-1-one (10d)



White solid; 62% Yield (67 mg), Melting point – 170 – 172 °C

R_f (EtOAc/Hexane, 50:50) = 0.3

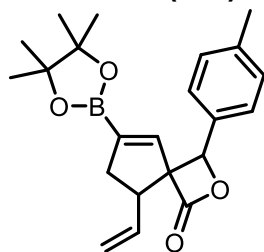
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (ddd, J = 18.4, 8.0, 1.5 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.09 (td, J = 7.6, 1.7 Hz, 1H), 6.36 (t, J = 2.0 Hz, 1H), 5.82 (ddd, J = 17.1, 10.2, 8.3 Hz, 1H), 5.59 (s, 1H), 5.12 (d, J = 17.0 Hz, 1H), 5.00 (d, J = 10.2 Hz, 1H), 3.07 (q, J = 7.0 Hz, 1H), 2.34 – 2.27 (m, 2H), 1.22 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 177.7, 143.1, 139.5, 137.9, 132.9, 130.0, 129.7, 127.3, 124.3, 116.5, 83.7, 74.8, 71.5, 49.5, 39.8, 25.0, 24.7.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 29.1.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{21}\text{H}_{25}\text{BBrO}_4$, calculated 431.1024; observed 431.1032.

6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)-8-vinyl-2-oxaspiro[3.4]oct-5-en-1-one (10e)



Yellow semi solid; 72% Yield (66 mg)

R_f (EtOAc/Hexane, 50:50) = 0.3

^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, J = 30.9 Hz, 5H), 6.42 (s, 1H), 5.79 (s, 1H), 5.11 (d, J = 16.6 Hz, 1H), 5.02 (d, J = 10.2 Hz, 1H), 4.92 (s, 1H), 3.02 (s, 1H), 2.33 (s, 6H), 1.25 (s, 13H).

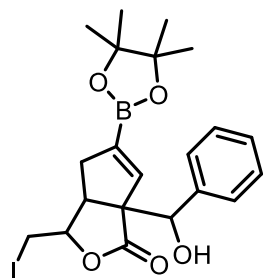
^{13}C NMR (100 MHz, CDCl_3) δ 178.0, 144.0, 138.0, 137.9, 137.1, 128.8, 127.9, 116.6, 83.7, 77.4, 71.1, 50.2, 40.0, 25.0, 24.8, 21.3.

^{11}B NMR (128 MHz, CDCl_3) δ 29.0.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{22}\text{H}_{28}\text{BO}_4$, calculated 367.2075; observed 367.2089.

Compounds **11a** and **11b** were prepared according to general procedure H.

6a-(hydroxy(phenyl)methyl)-3-(iodomethyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3a,4,6a-tetrahydro-1H-cyclopenta[c]furan-1-one (11a)



White semi-solid; 66% Yield (82 mg)

R_f (EtOAc/Hexane, 50:50) = 0.3

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.34 (m, 2H), 7.32 – 7.28 (m, 3H), 6.51 (s, 1H), 5.20 (s, 1H), 3.92 (td, J = 6.6, 4.5 Hz, 1H), 3.11 (dd, J = 10.5, 4.2 Hz, 1H), 2.78 (dd, J = 10.5, 7.0 Hz, 1H), 2.70 (t, J = 6.6 Hz, 1H), 2.28 (d, J = 17.6 Hz, 1H), 2.12 (ddd, J = 17.6, 7.5, 2.7 Hz, 1H), 1.27 (s, 6H), 1.26 (s, 6H).

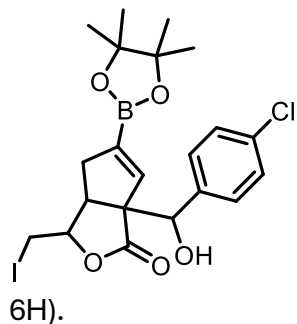
^{13}C NMR (100 MHz, CDCl_3) δ 177.0, 141.4, 138.4, 128.5, 128.1, 127.4, 84.1, 77.5, 77.4, 77.2, 76.8, 75.3, 71.9, 46.7, 41.8, 25.0, 24.8, 7.2.

^{11}B NMR (128 MHz, CDCl_3) δ 27.1.

HRMS (ASAP): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{21}\text{H}_{25}\text{BIO}_4$, calculated 479.0885; observed 479.0862.

6a-(hydroxy(phenyl)methyl)-3-(iodomethyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3a,4,6a-tetrahydro-1H-cyclopenta[c]furan-1-one (11b)

White solid; 61% Yield (81 mg), Melting point – 70-72 °C



R_f (EtOAc/Hexane, 50:50) = 0.3

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34–7.24 (m, 5H), 6.49–6.44 (m, 1H), 5.12 (d, J = 1.4 Hz, 1H), 3.87 (tdd, J = 6.4, 4.4, 1.2 Hz, 1H), 3.20 (ddd, J = 10.6, 4.0, 1.3 Hz, 1H), 3.00 (ddd, J = 10.6, 6.6, 1.3 Hz, 1H), 2.62 (t, J = 6.7 Hz, 1H), 2.28 (d, J = 17.6 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.26 (s, 6H), 1.25 (s,

6H).

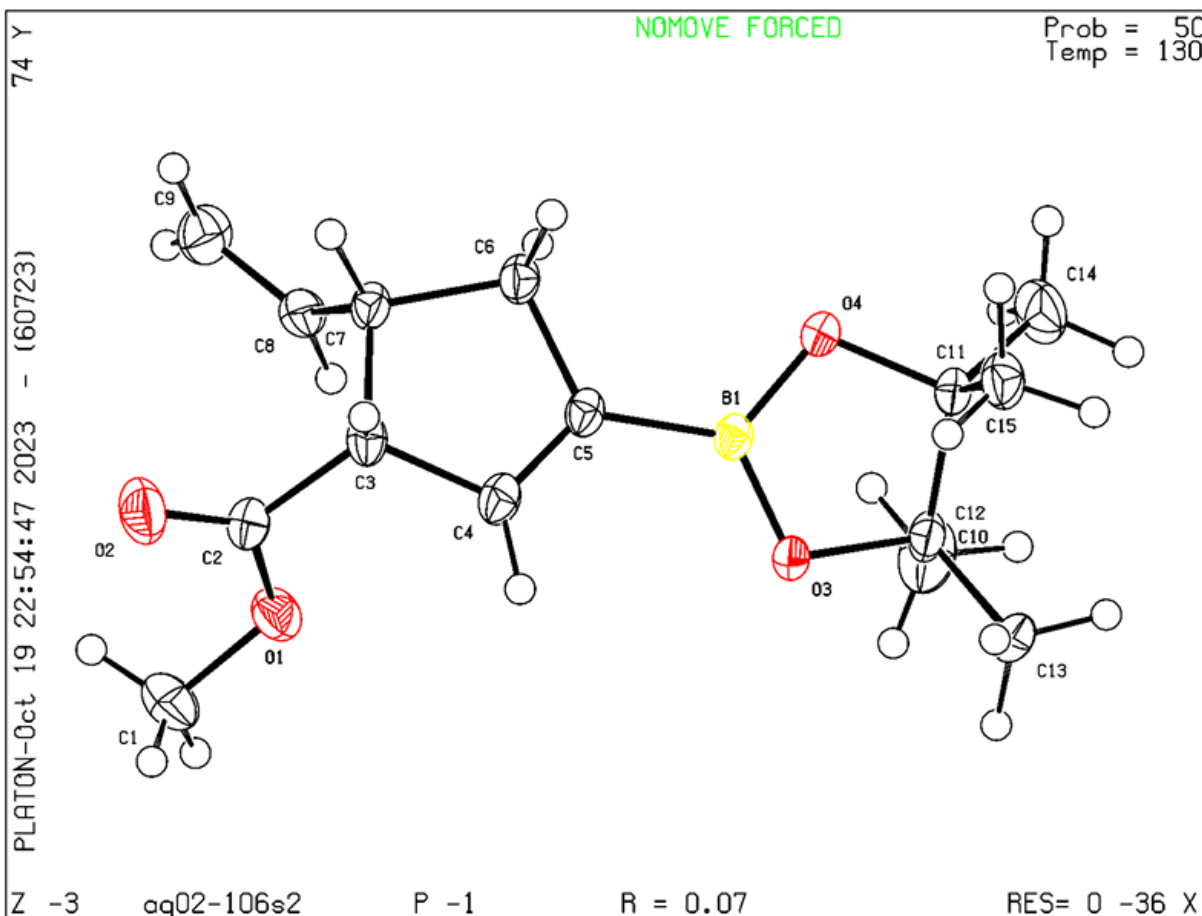
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 176.9, 141.0, 136.8, 134.3, 128.8, 128.2, 84.1, 83.6, 77.5, 77.2, 76.8, 74.9, 71.3, 47.1, 41.4, 24.9, 24.8, 7.5.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 28.6.

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ for $\text{C}_{21}\text{H}_{24}\text{BClIO}_4$, calculated 513.0495; observed 513.0489.

X-Ray Studies

Crystal data of **4a** (CCDC deposition number: 2377383)



The compound crystallized in a centrosymmetric space group, so it is a racemic mixture.

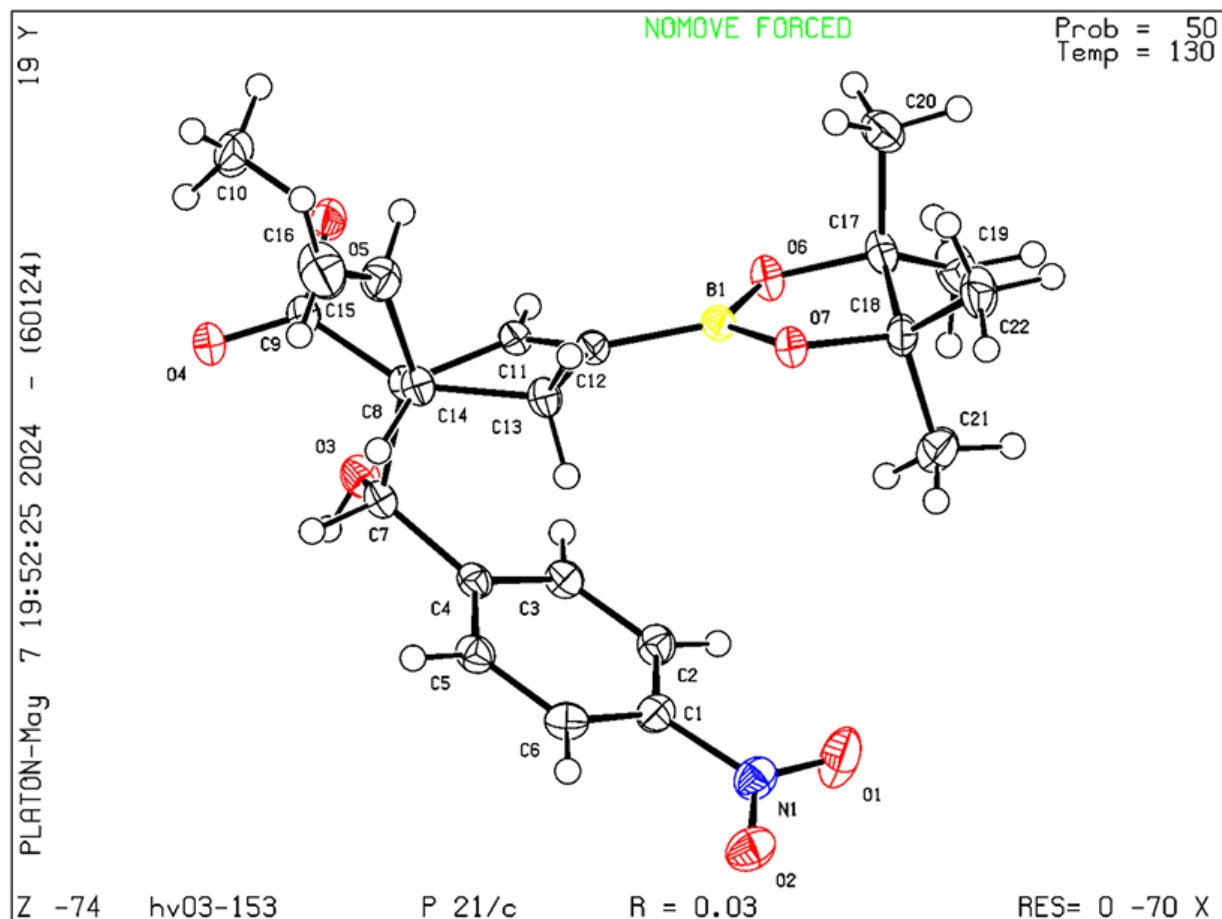
X-ray Structure Determination

X-ray diffraction data were collected on a Bruker D8 VENTURE diffractometer using Cu $K\alpha$ radiation. Crystal data, data collection and refinement parameters are summarized in Table 3. The structure was solved using a dual-space method and standard difference map techniques and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2019/1).⁹⁻¹⁰ All hydrogen atoms were placed in calculated positions and refined with a riding model [$U_{\text{iso}}(\text{H}) = 1.2-1.5U_{\text{eq}}(\text{C})$].

Table 3. **Crystal, intensity collection, and refinement data.**

lattice	Triclinic
formula	$C_{15}H_{23}BO_4$
formula weight	278.14
space group	<i>P</i> -1
<i>a</i> /Å	9.1472(4)
<i>b</i> /Å	9.2824(4)
<i>c</i> /Å	9.3217(4)
α /°	97.6080(10)
β /°	94.6020(10)
γ /°	101.3770(10)
<i>V</i> /Å ³	764.48(6)
<i>Z</i>	2
temperature (K)	130(2)
radiation (λ , Å)	1.54178
ρ (calcd.) g cm ⁻³	1.208
μ (Cu K α), mm ⁻¹	0.686
θ max, deg.	74.324
no. of data collected	16111
no. of data	3016
no. of parameters	186
R_1 [$I > 2\sigma(I)$]	0.0698
wR_2 [$I > 2\sigma(I)$]	0.1839
R_1 [all data]	0.0704
wR_2 [all data]	0.1843
GOF	1.089
R_{int}	0.0456

Crystal data of compound **7h**. (CCDC deposition number: 2377384)



The compound crystallized in a centrosymmetric space group, so it is a racemic mixture.

X-ray Structure Determination

X-ray diffraction data were collected on a Bruker D8 VENTURE diffractometer using Cu $K\alpha$ radiation. Crystal data, data collection and refinement parameters are summarized in Table 4. The structure was solved using a dual-space method and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2019/1).⁹⁻¹⁰ All hydrogen atoms bound to carbon were placed in calculated positions and refined with a riding model [$U_{\text{iso}}(\text{H}) = 1.2-1.5U_{\text{eq}}(\text{C})$], while the hydrogen bound to oxygen was located on the difference map and freely refined.

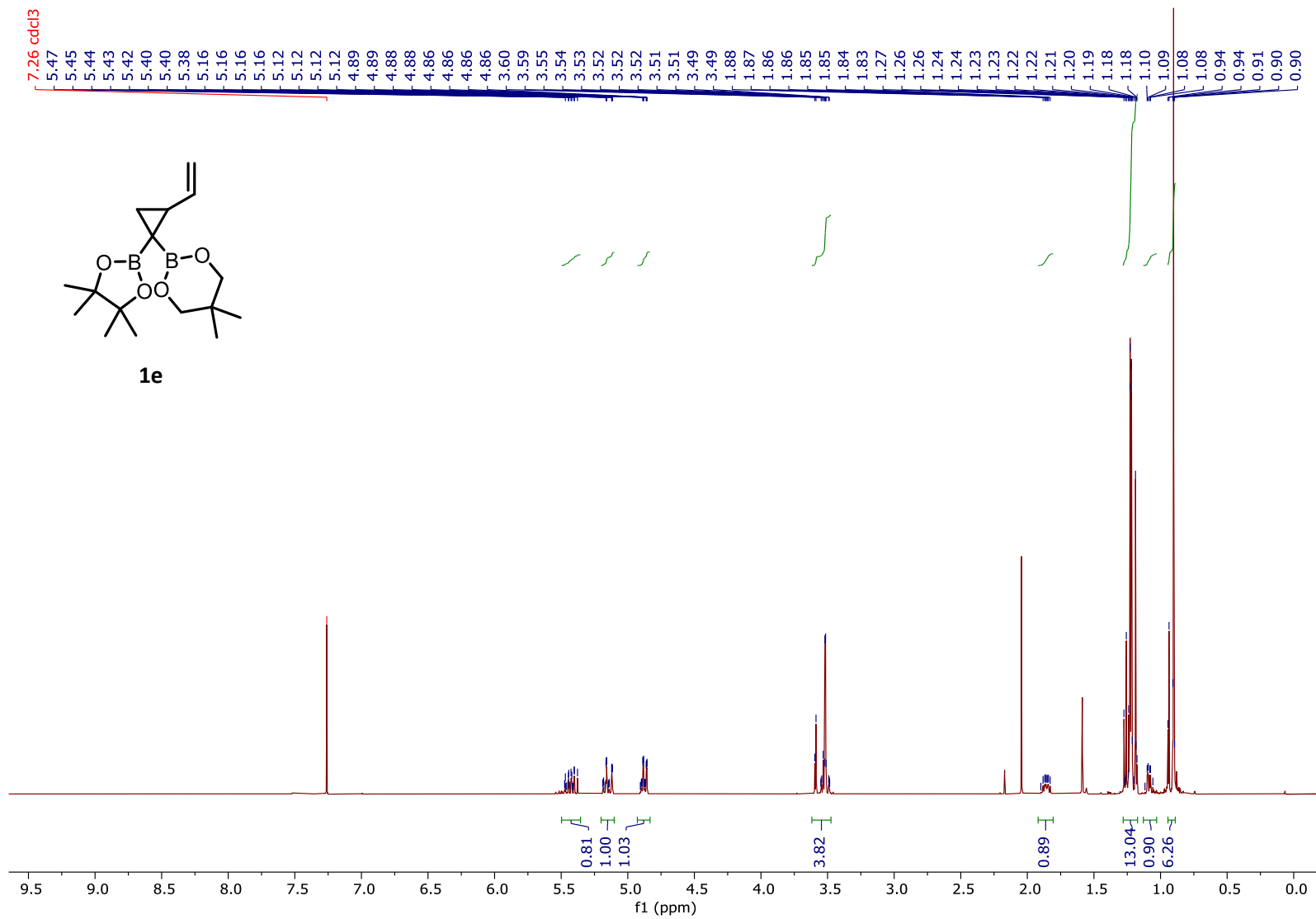
Table 4. **Crystal, intensity collection, and refinement data.**

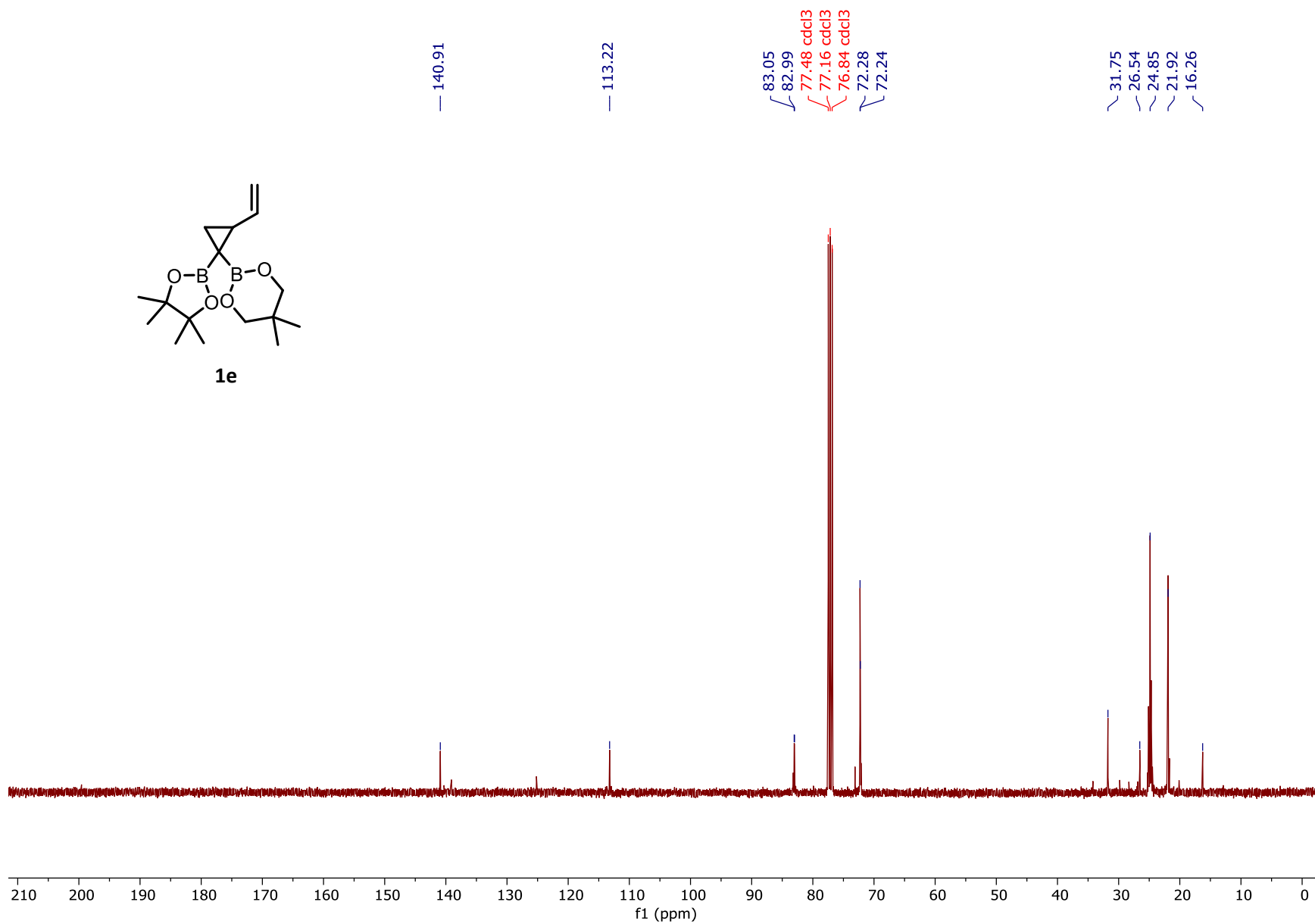
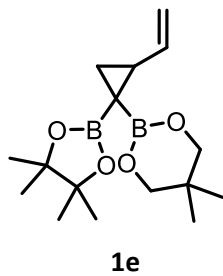
	Compound 7h
Lattice	Monoclinic
formula	C ₂₂ H ₂₈ BNO ₇
formula weight	429.26
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	17.4121(8)
<i>b</i> /Å	10.4286(5)
<i>c</i> /Å	13.1111(6)
α /°	90
β /°	109.670(2)
γ /°	90
<i>V</i> /Å ³	2241.84(18)
<i>Z</i>	4
temperature (K)	130(2)
radiation (λ , Å)	1.54178
ρ (calcd.) g cm ⁻³	1.272
μ (Cu K α), mm ⁻¹	0.774
θ max, deg.	74.515
no. of data collected	60423
no. of data	4575
no. of parameters	289
R_1 [$I > 2\sigma(I)$]	0.0346
wR_2 [$I > 2\sigma(I)$]	0.0897
R_1 [all data]	0.0364
wR_2 [all data]	0.0907
GOF	1.034
R_{int}	0.0384

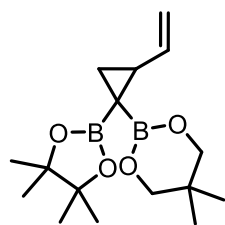
References

1. H. Vyas, A. J. Gangani, A. Mini, S. Lin, J.-M. Chu, C. O. Agee, J. Gabriel, R. T. Williamson, Y. Zhang and A. Sharma, *Chem. Eur. J.*, 2024, **30**, e202303175.
2. Y. Yoshida, Y. Mawatari, T. Sasaki, T. Hiraoki, M. Wagner, K. Müllen and M. Tabata, *Macromolecules*, 2017, **50**, 1291–1301.
3. Y. Tang, M. Huang, L. Jiang, X. Zhang, S. Zheng, Y. Yang and X. Y. Chen, *Chem. Eur. J.* 2023, **29**, e202302249.
4. A. Cervi, Y. Vo, C. L. L. Chai, M. G. Banwell, P. Lan and A. C. Willis, *J. Org. Chem.*, 2021, **86**, 178-198.
5. J. Chen, J. Han, J. Zhang, L. Li, Z. Zhang, Y. Yang and Y. Jiang, *ACS Catal.*, 2022, **12**, 14748–14753.
6. E. Skolia, P. L. Gkizis, N. F. Nikitas and C. G. Kokotos, *Green Chem.*, 2022, **24**, 4108-4118.
7. D. M. Kitcatt, E. Pogacar, L. Mi, S. Nicolle and A.-L. Lee, *J. Org. Chem.*, 2024, **89**, 16055-16059.
8. J. N. Demas, W. D. Bowman, E. F. Zalewski and R. A. Velapoldi, *J. Phys. Chem.*, 1981, **85**, 2766-2771.
9. Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.
10. Sheldrick, G. M., *Acta Cryst.*, **2015**, A71, 3-8.

NMR Spectra

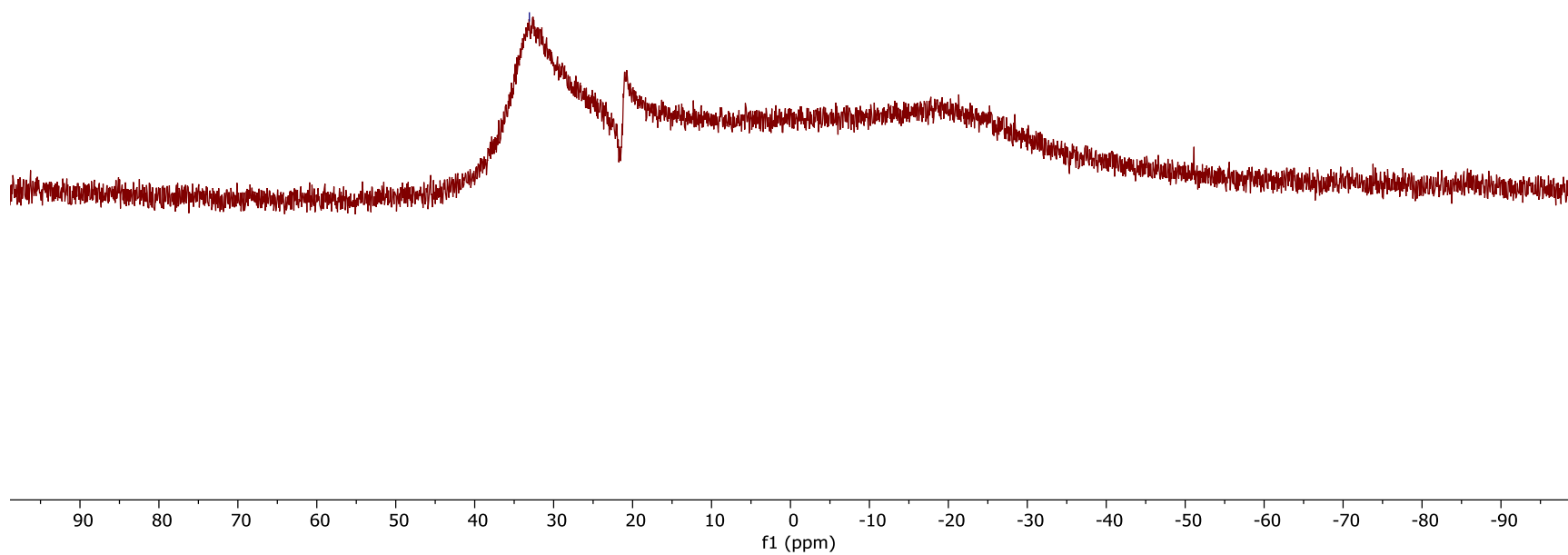


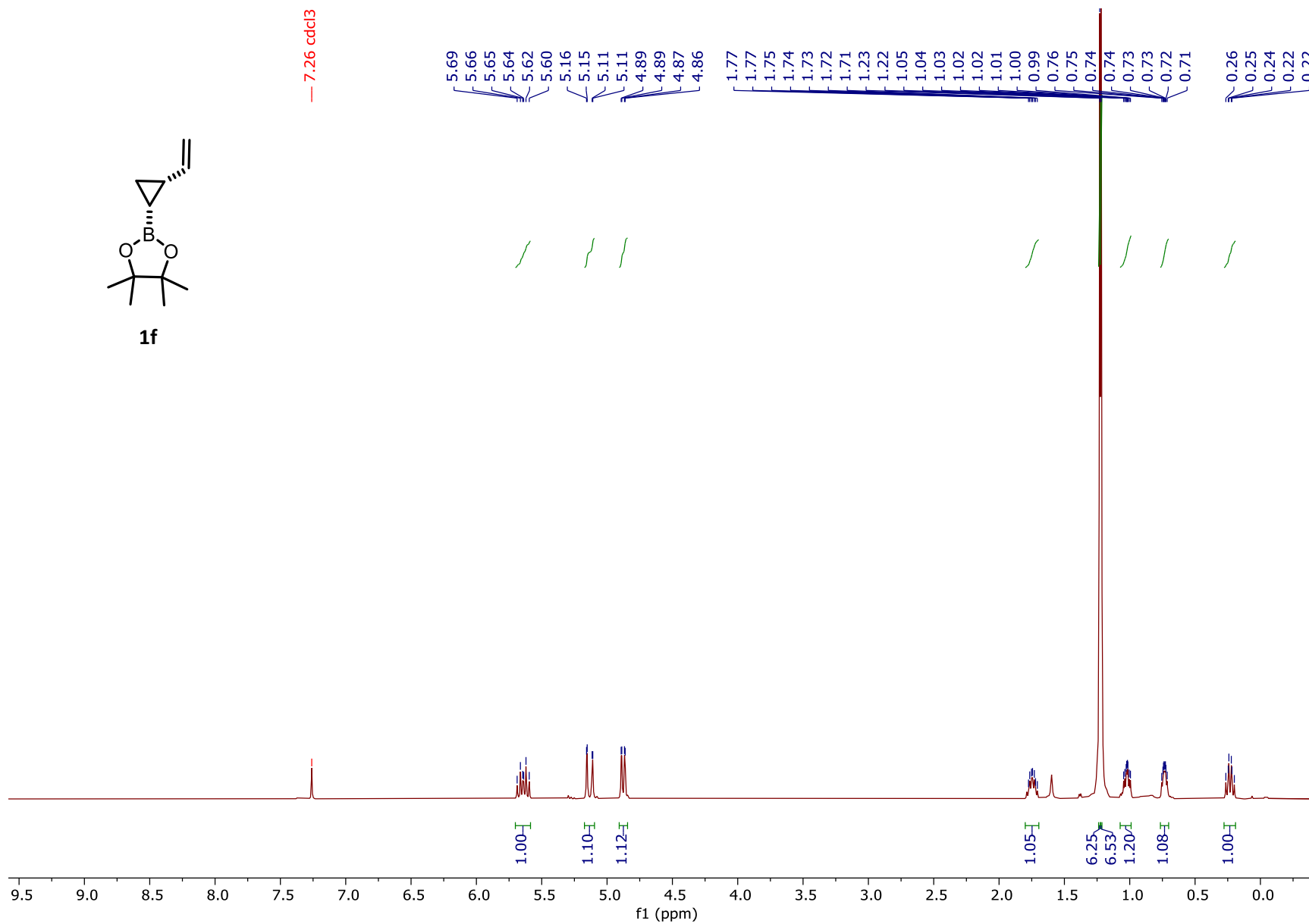
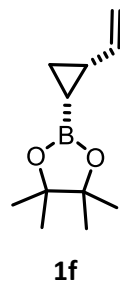


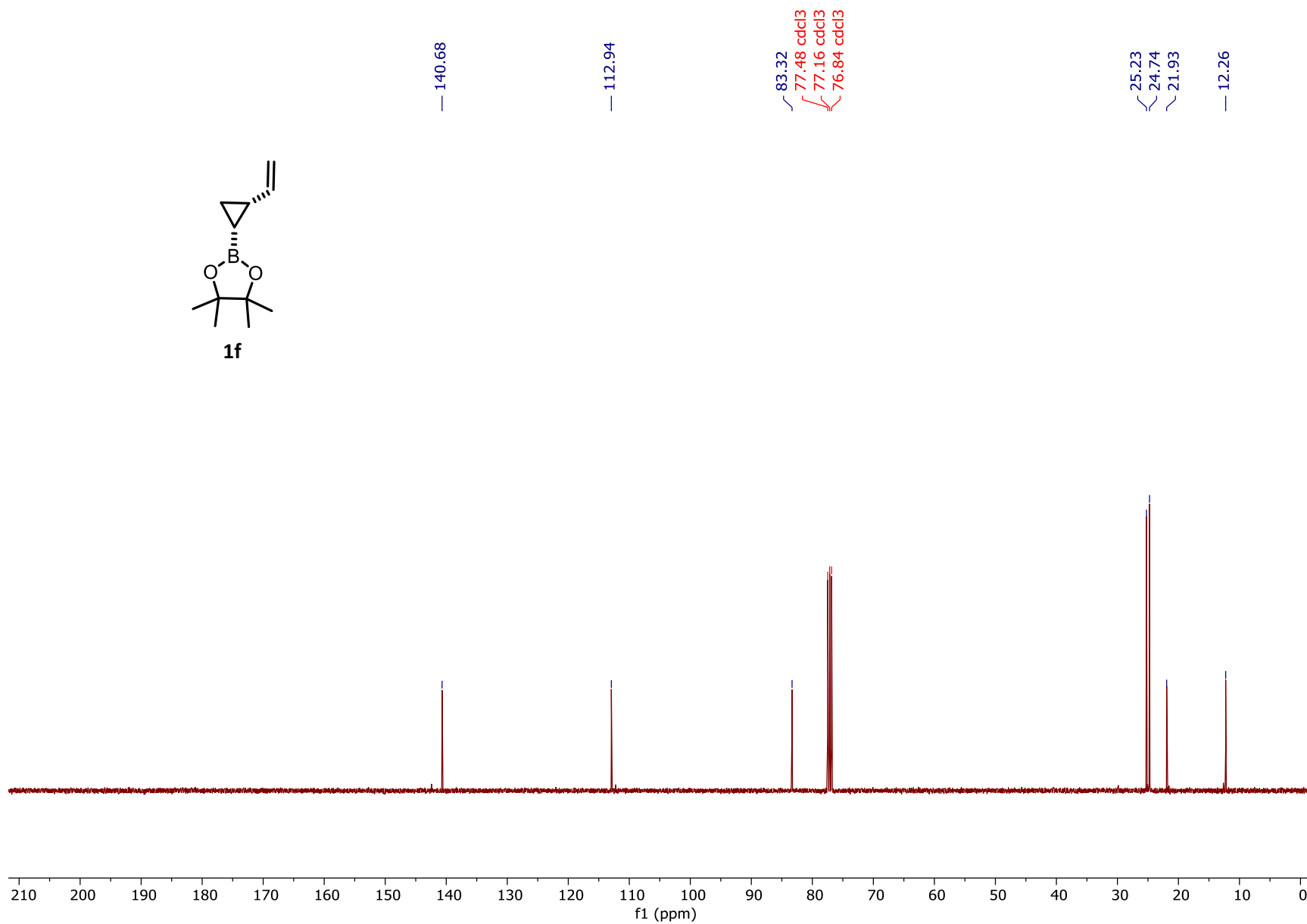
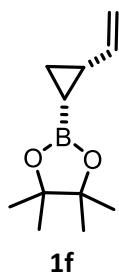


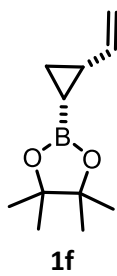
1e

— 33.07

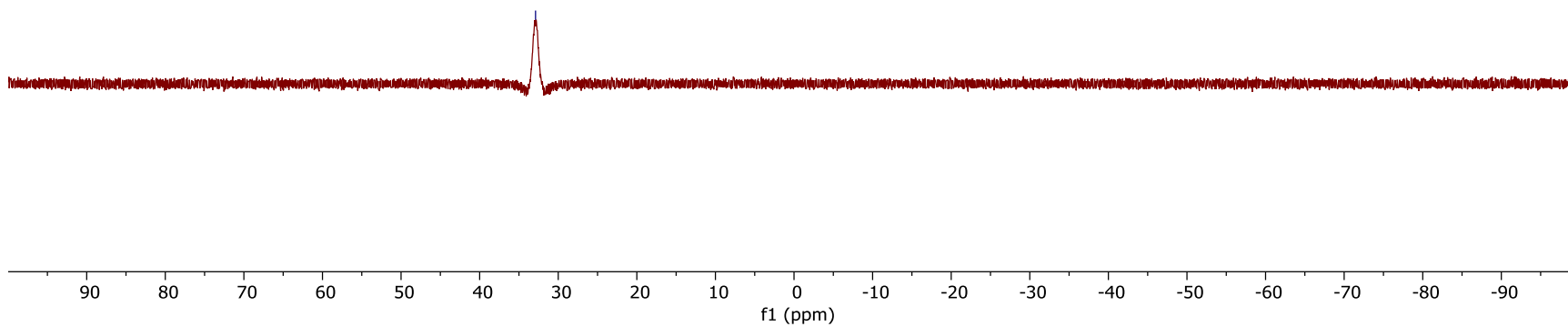


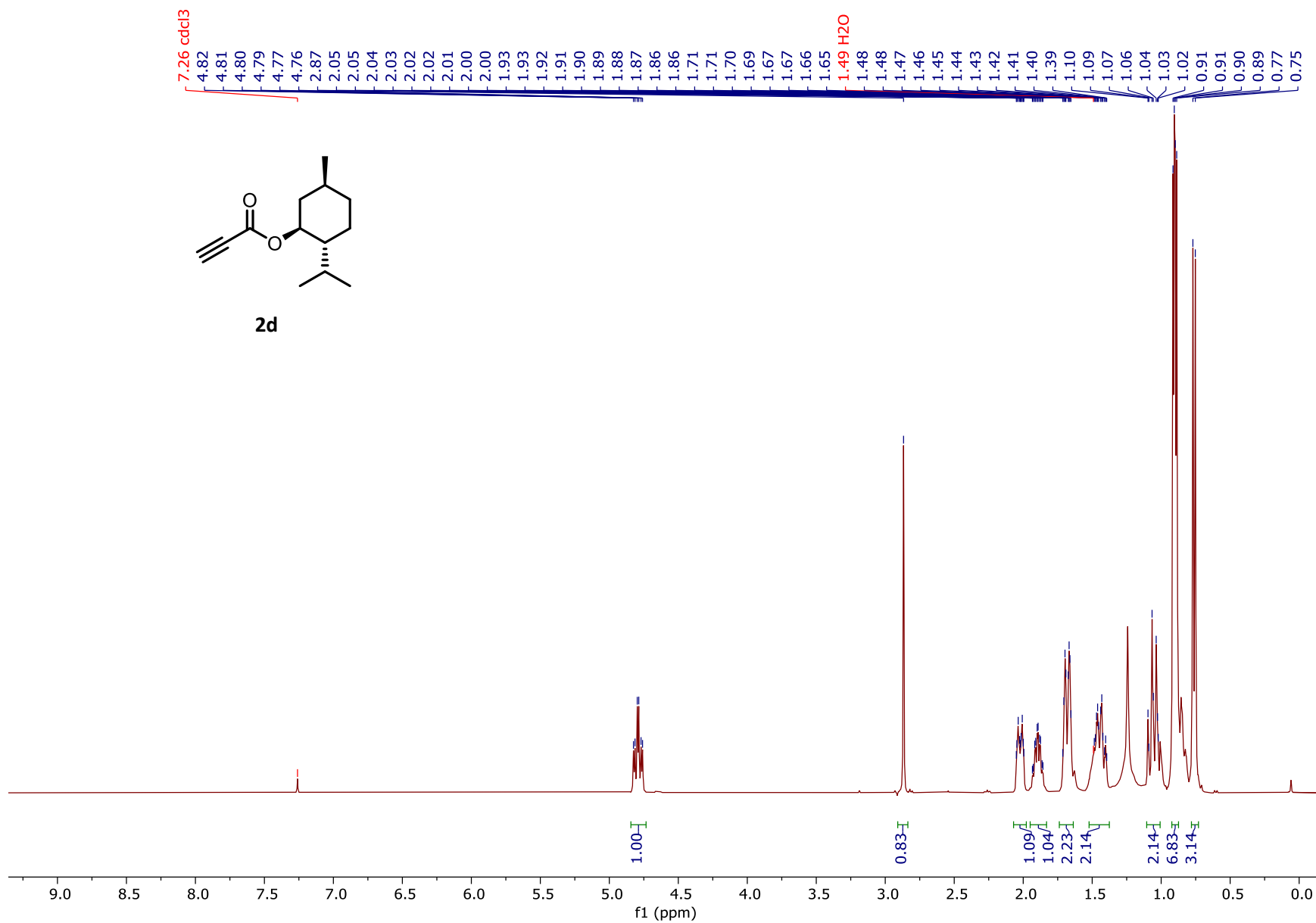


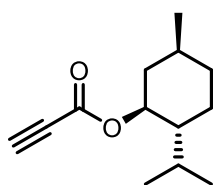




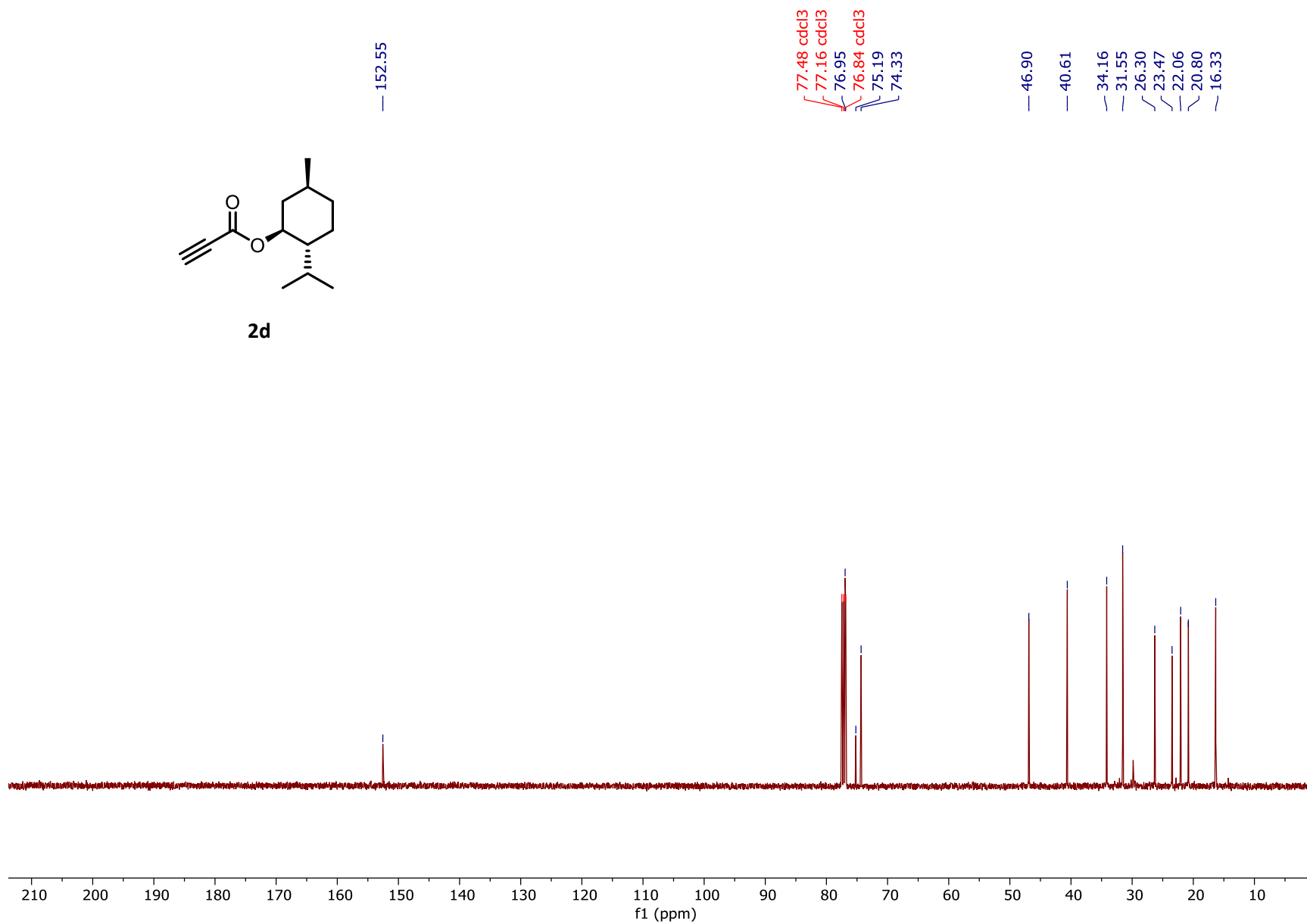
— 32.89

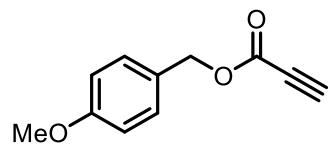




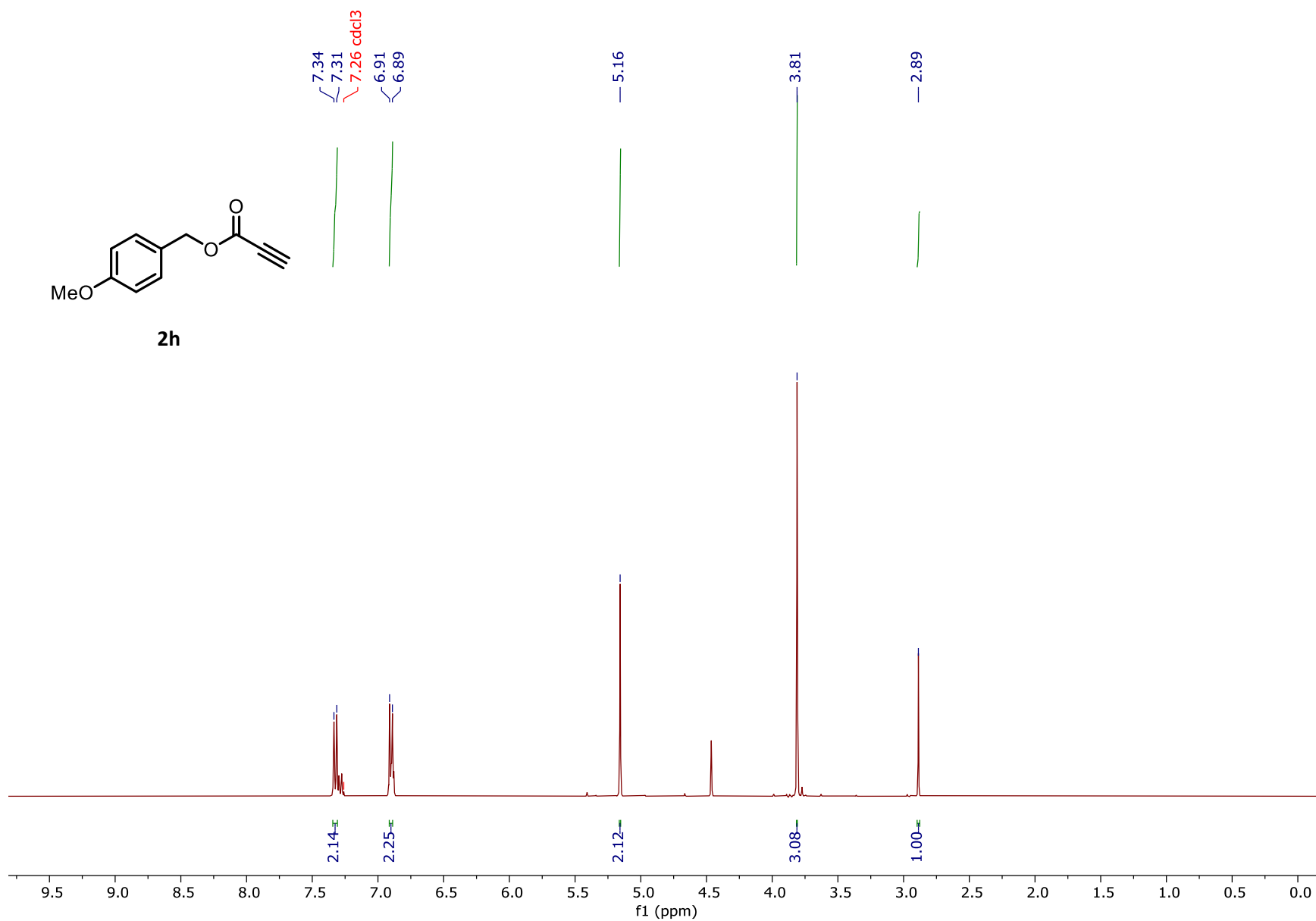


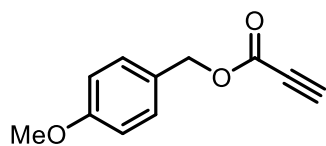
2d



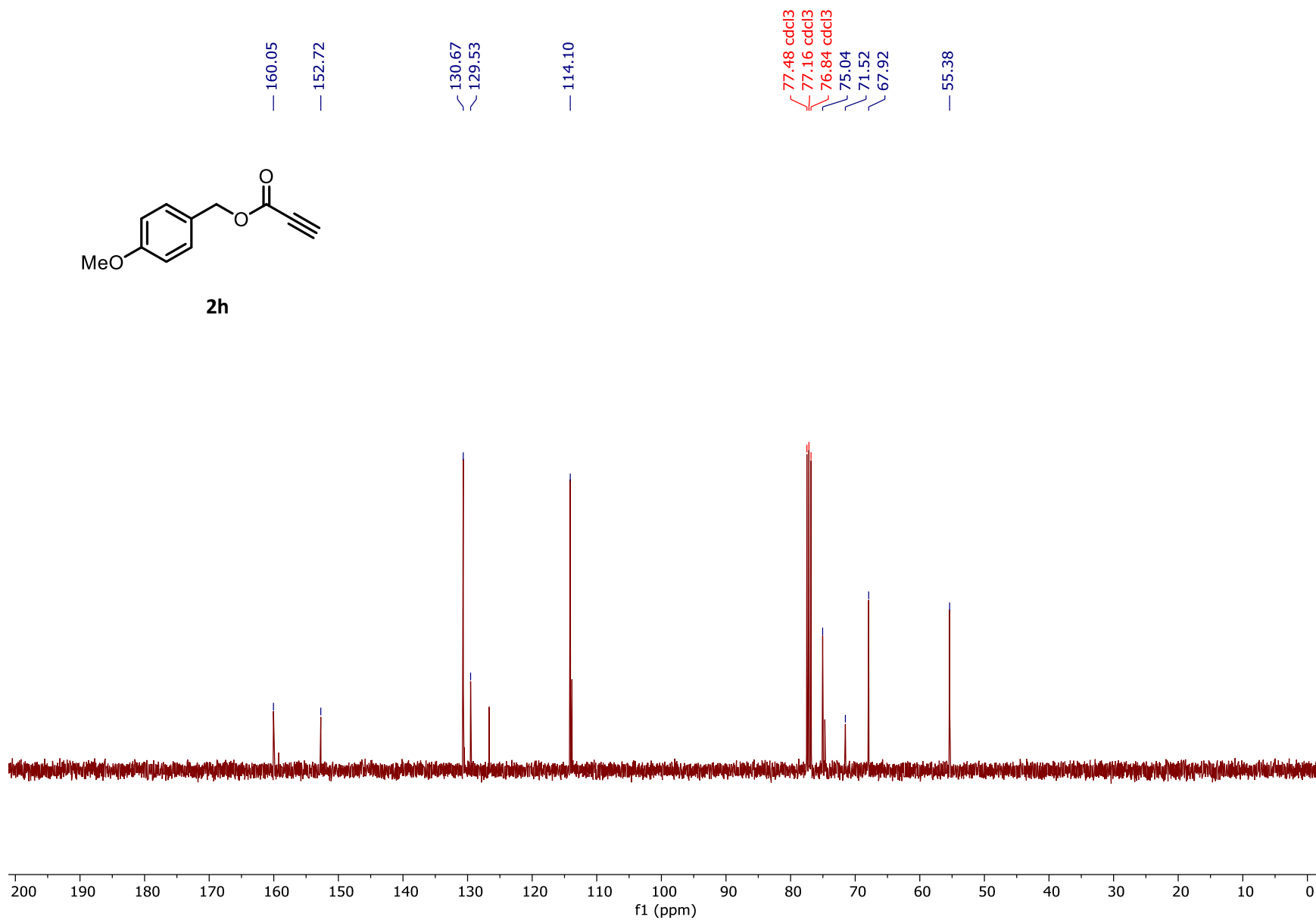


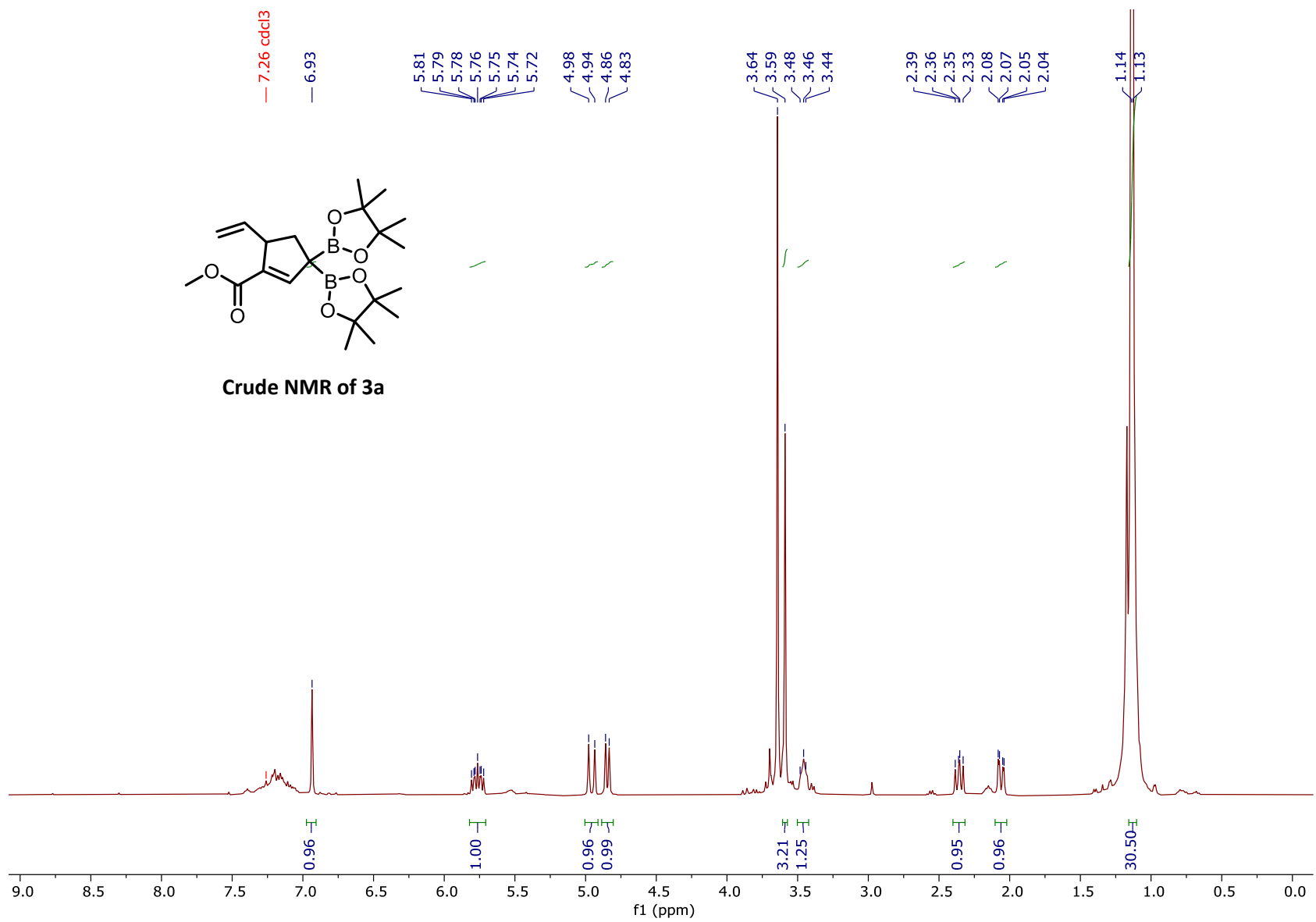
2h



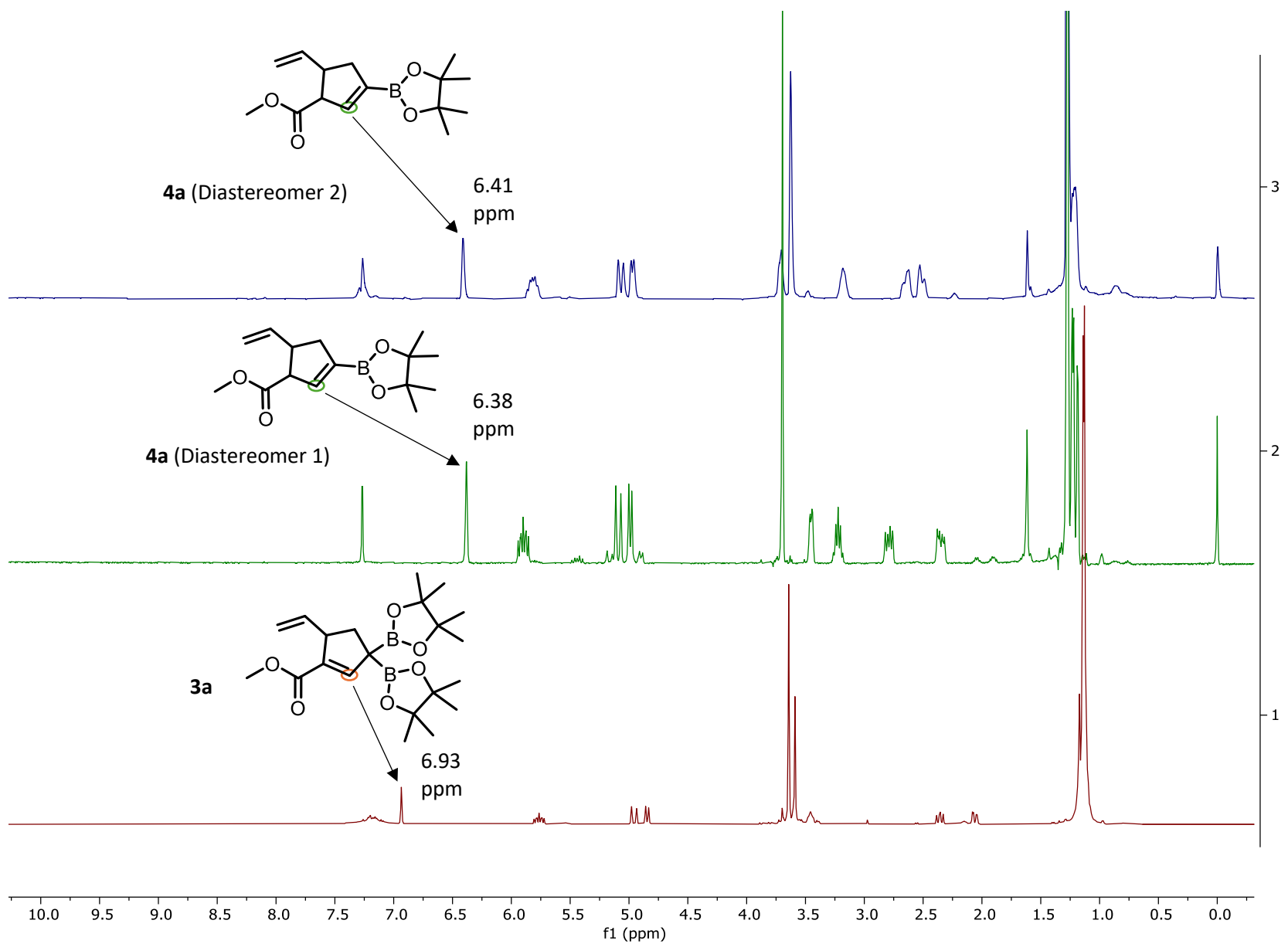


2h

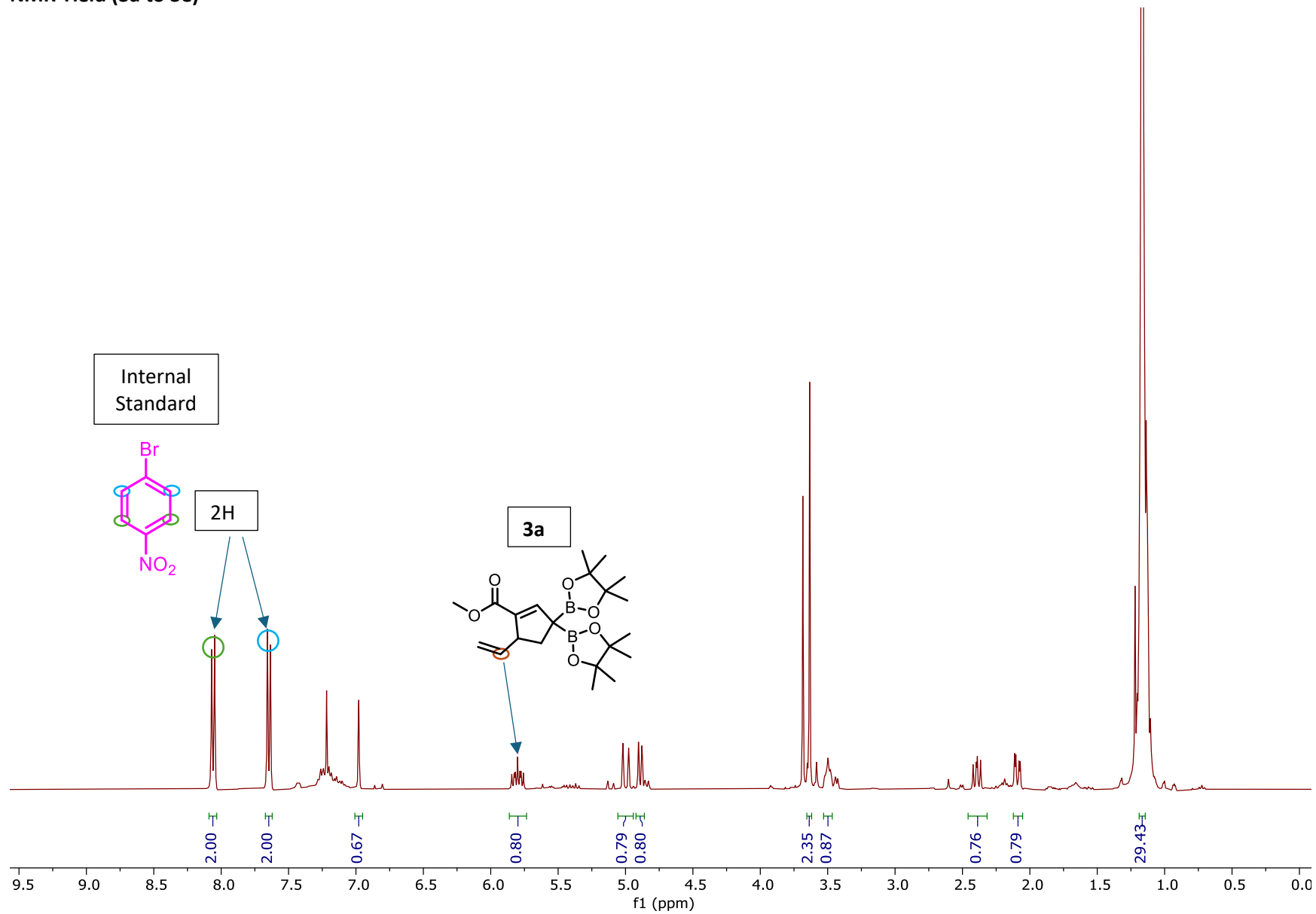


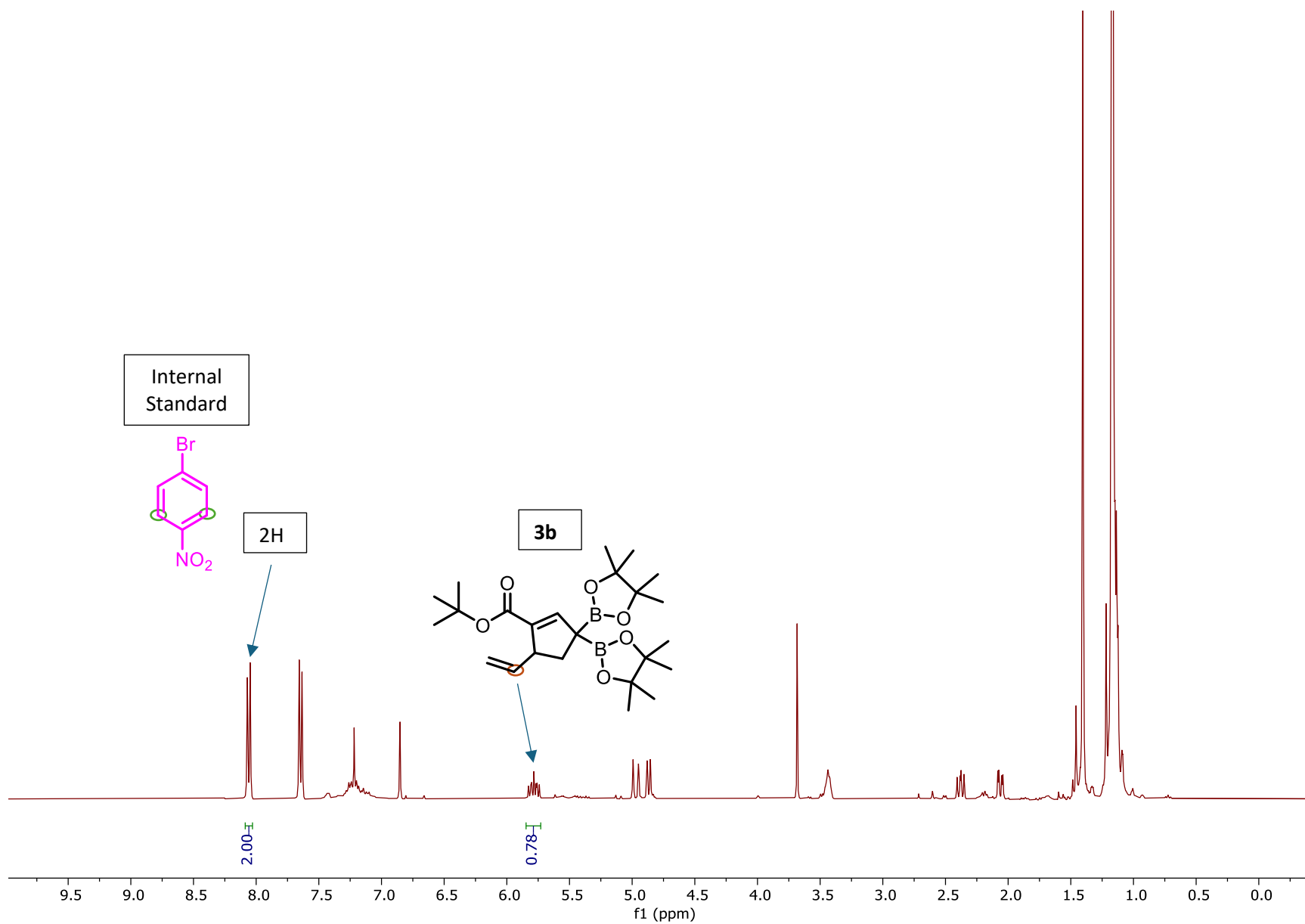


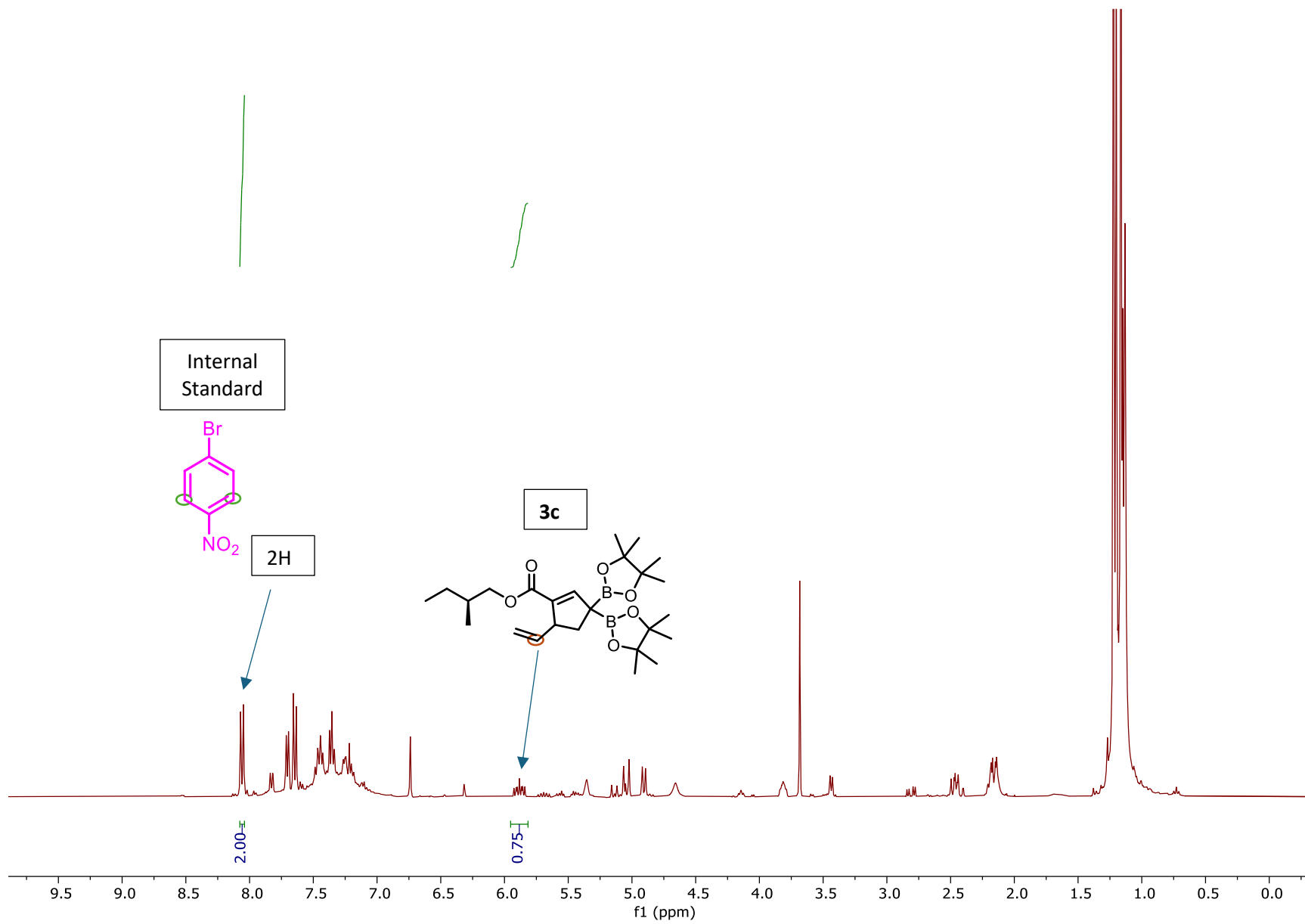
NMR comparison of 3a and diastereomers of 4a

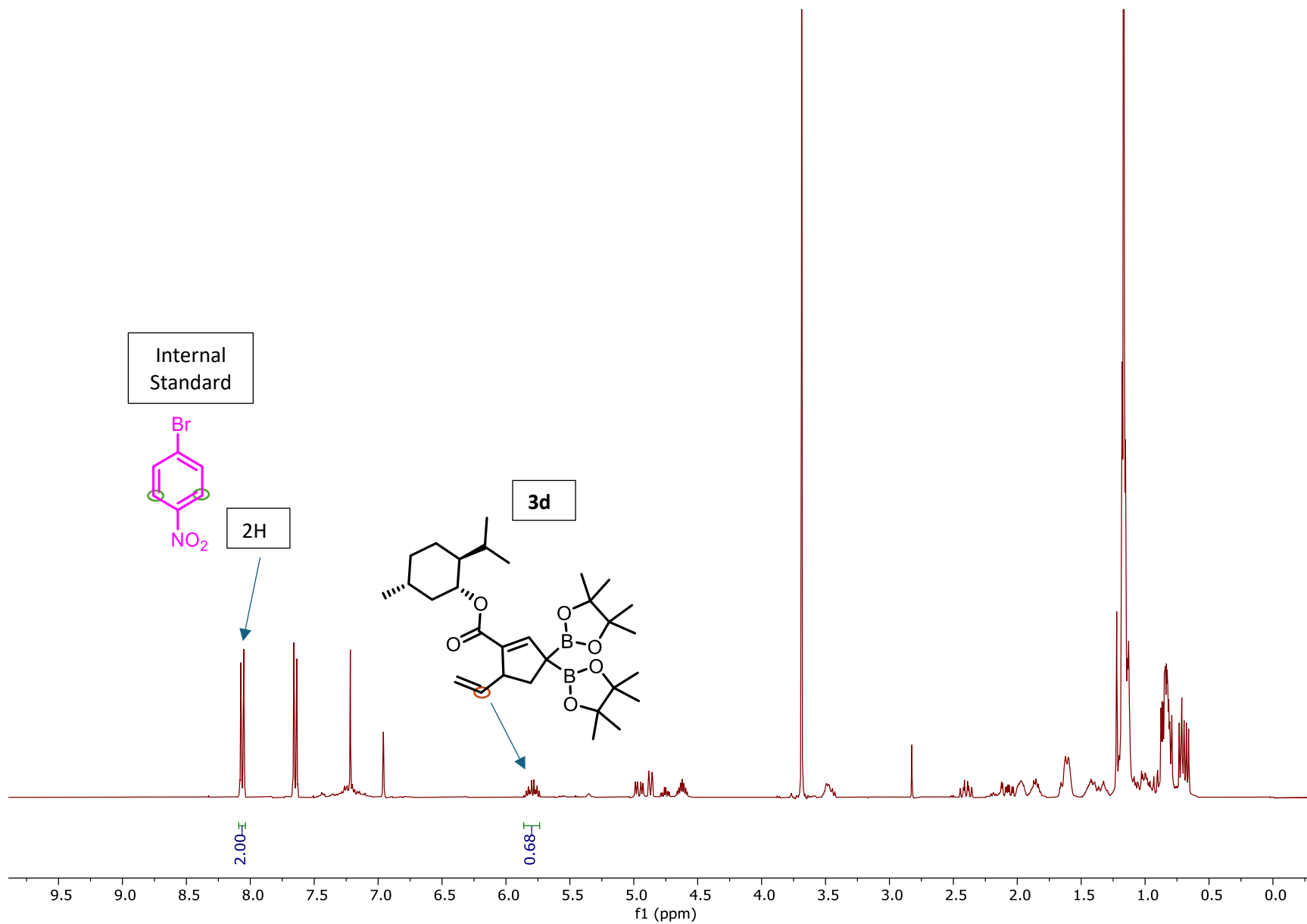


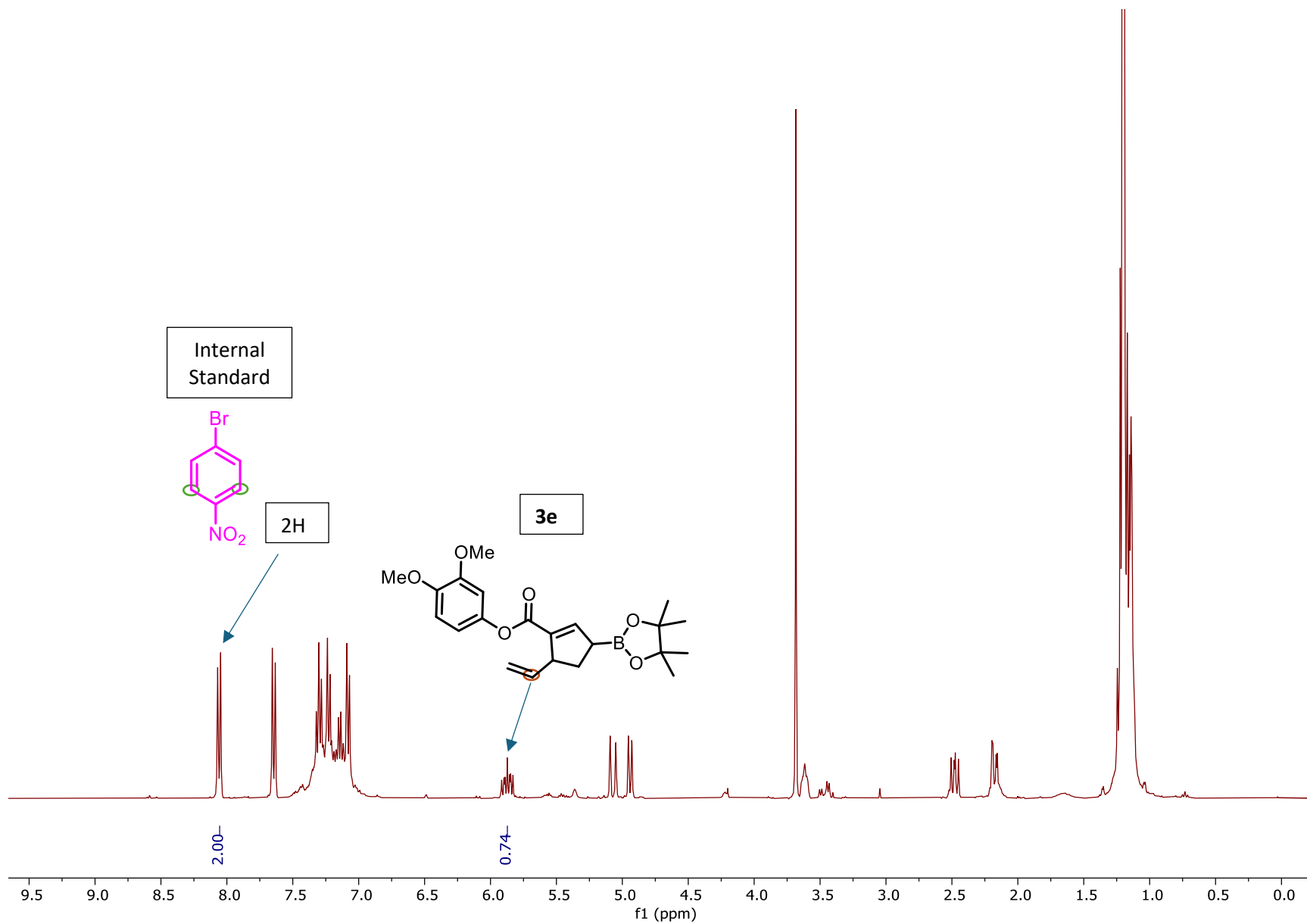
NMR Yield (3a to 3e)

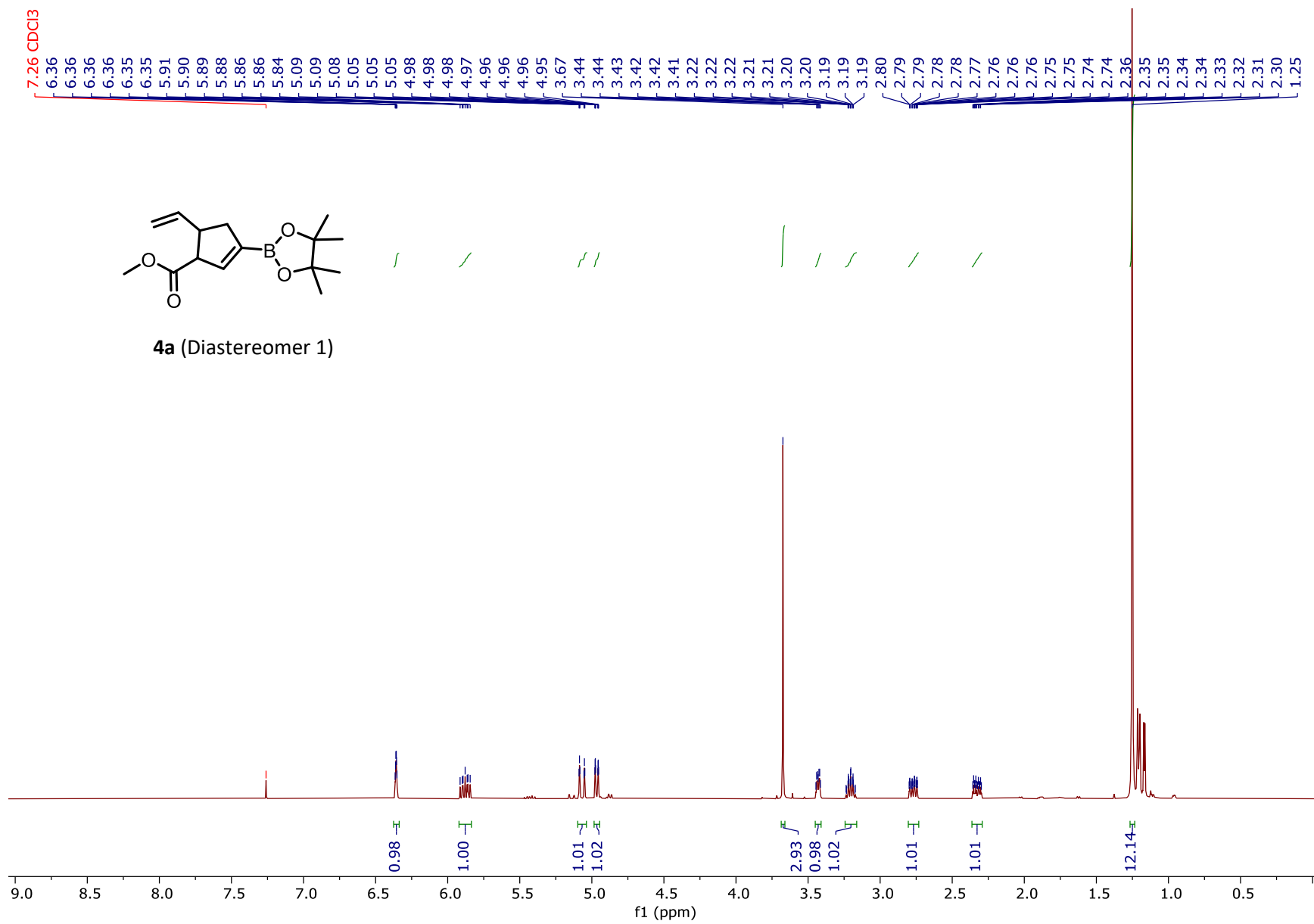


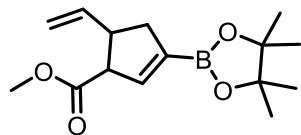




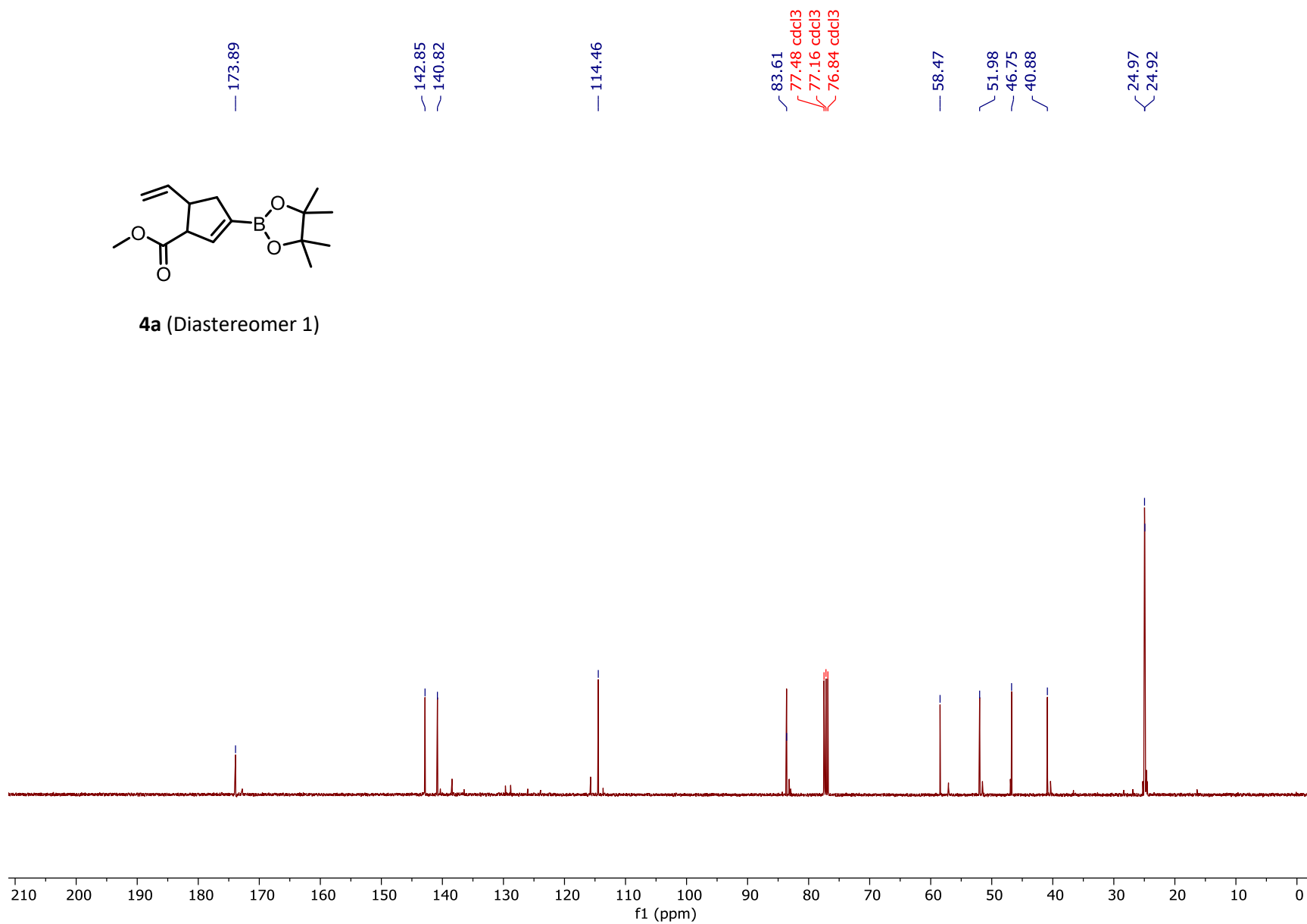


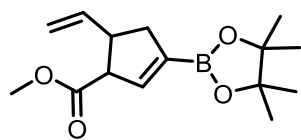






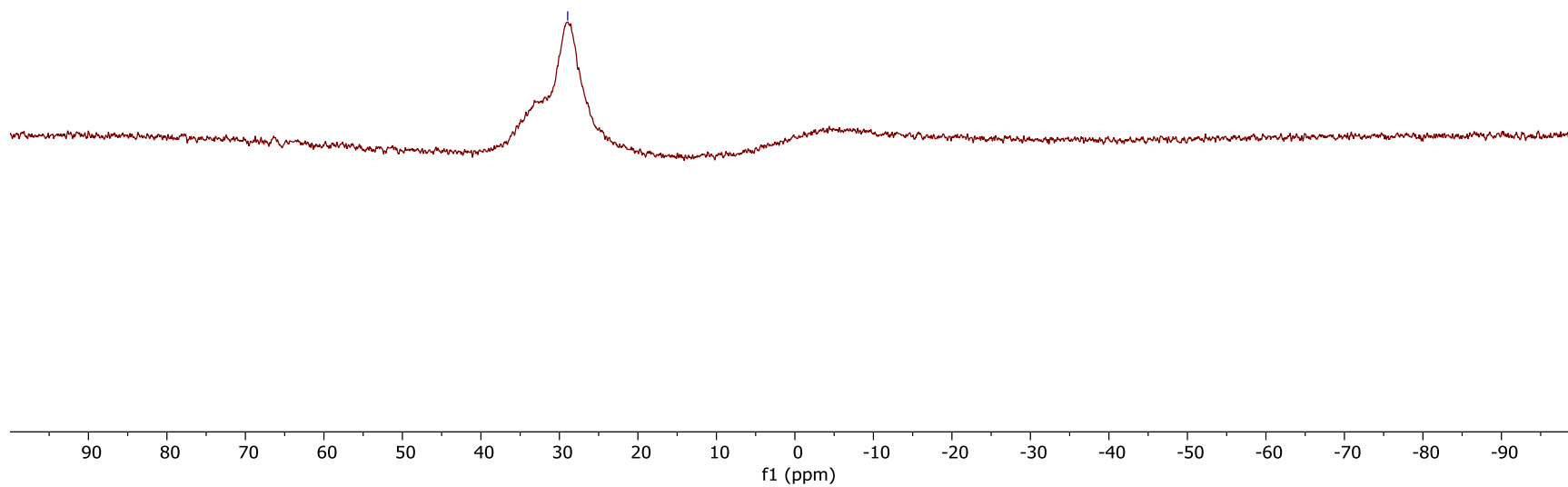
4a (Diastereomer 1)

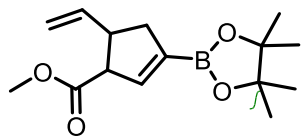




4a (Diastereomer 1)

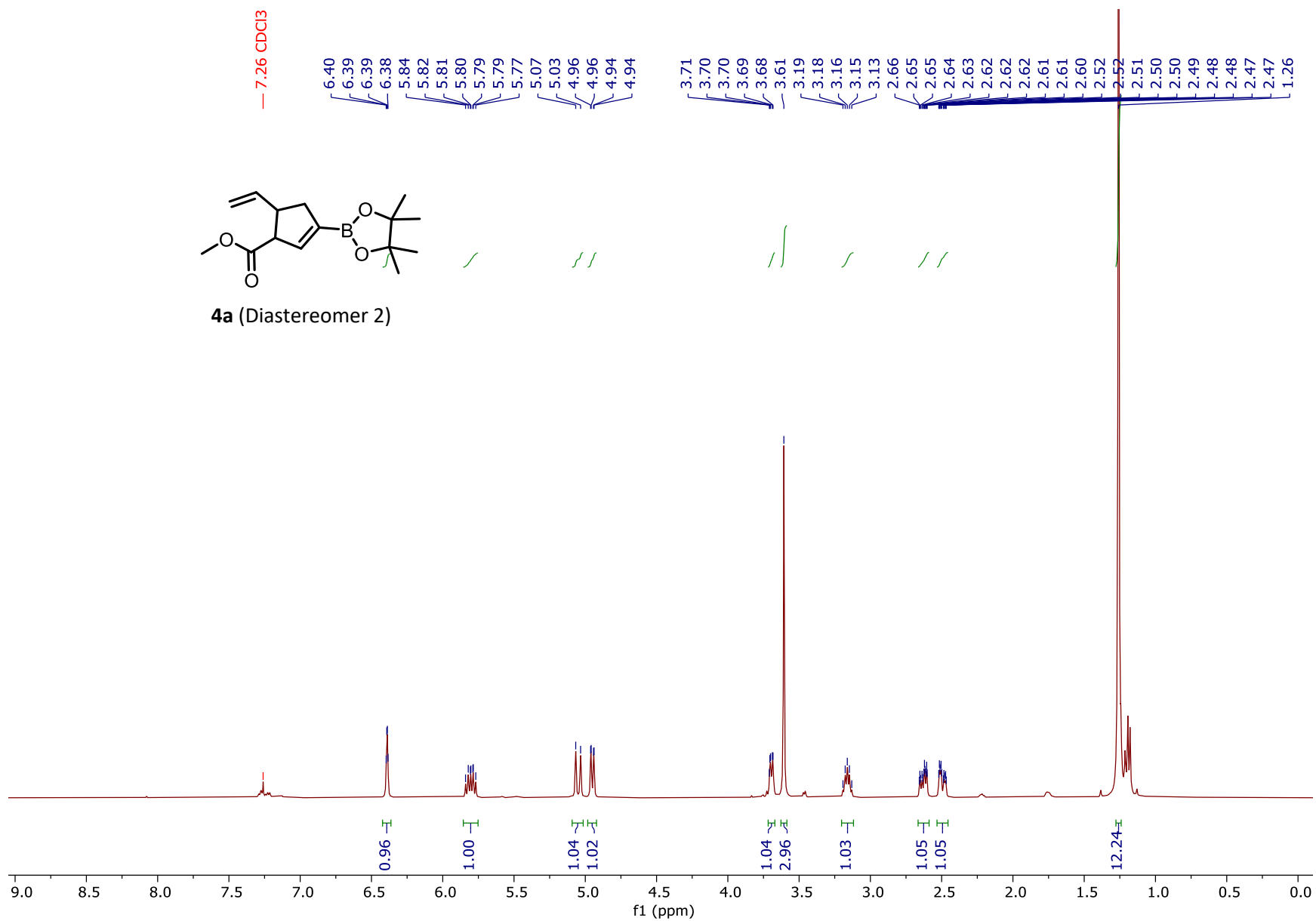
— 28.95

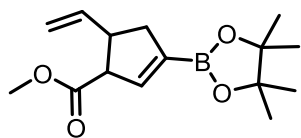




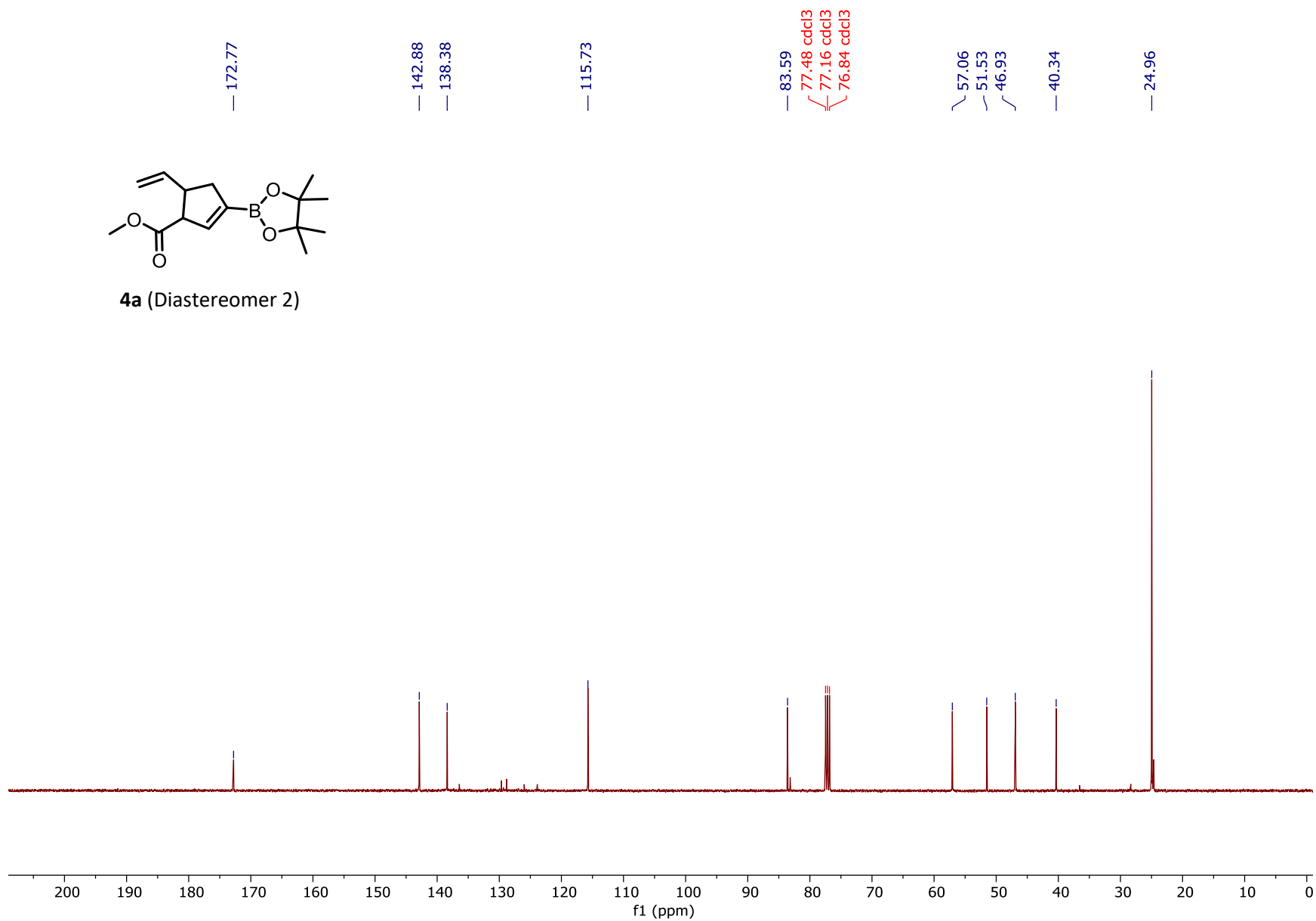
4a (Diastereomer 2)

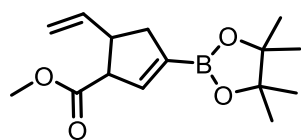
— 7.26 CDCl₃





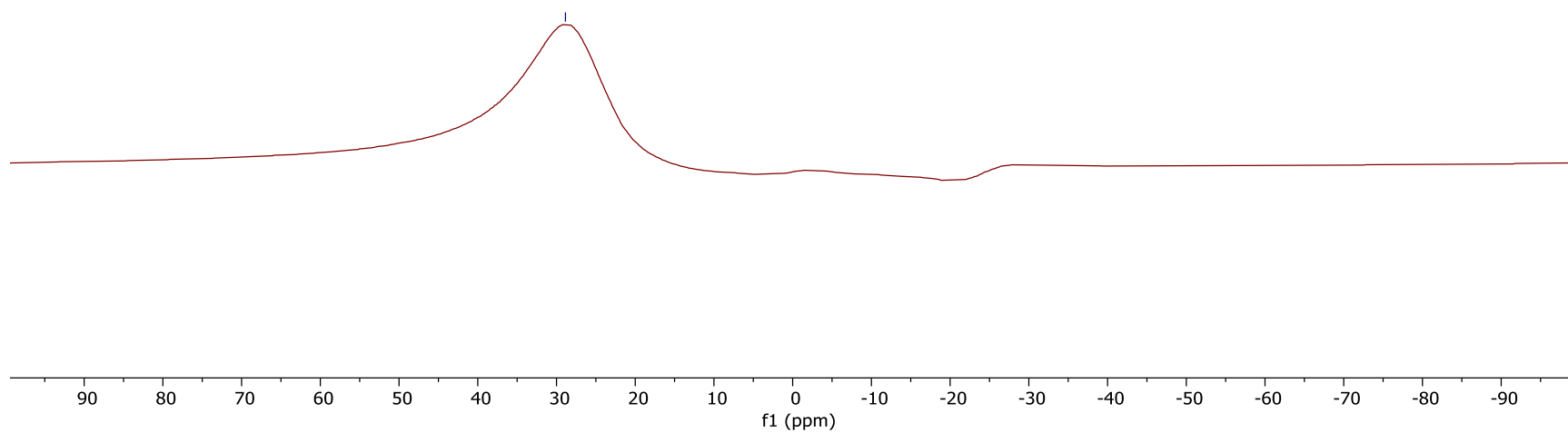
4a (Diastereomer 2)

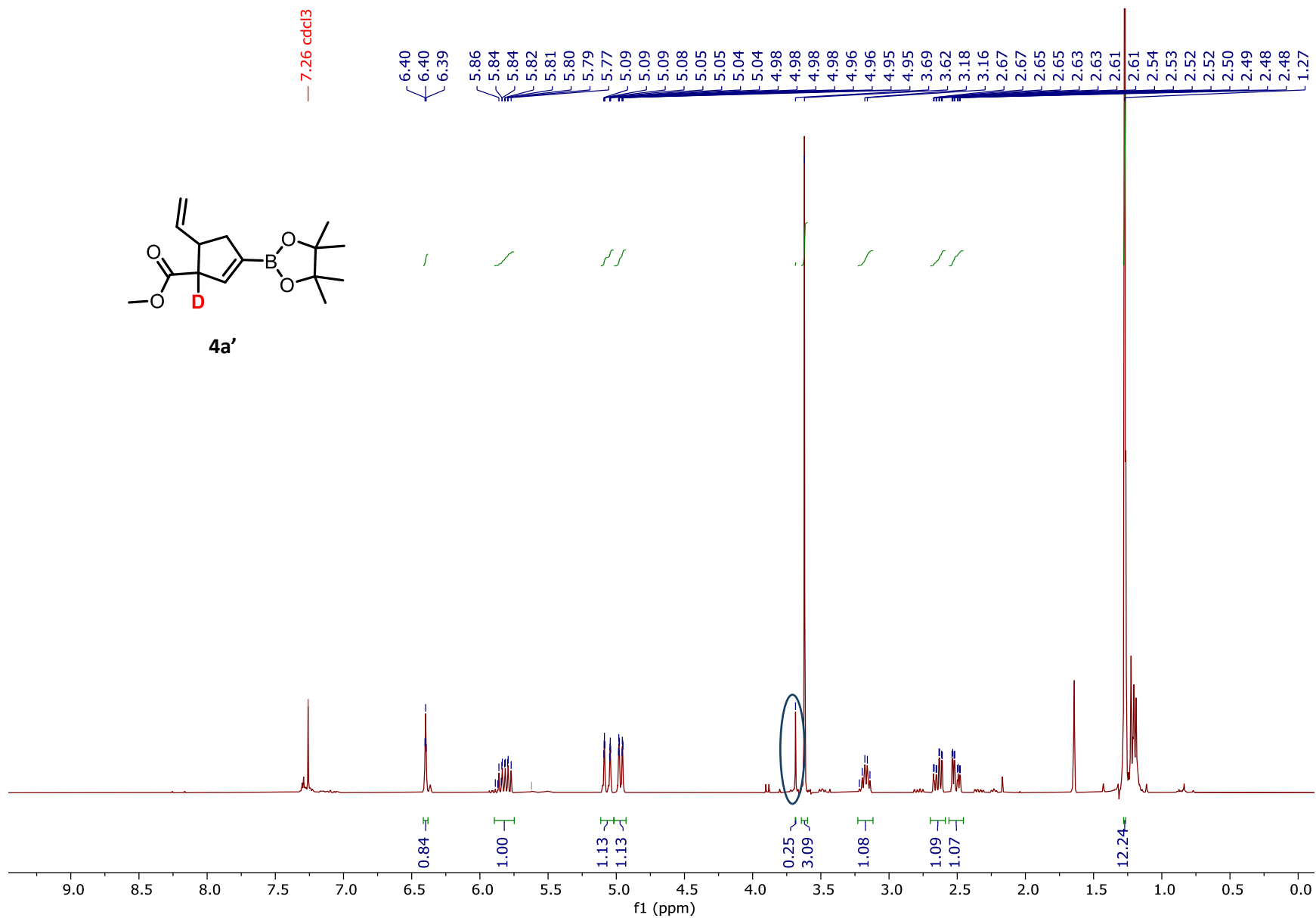


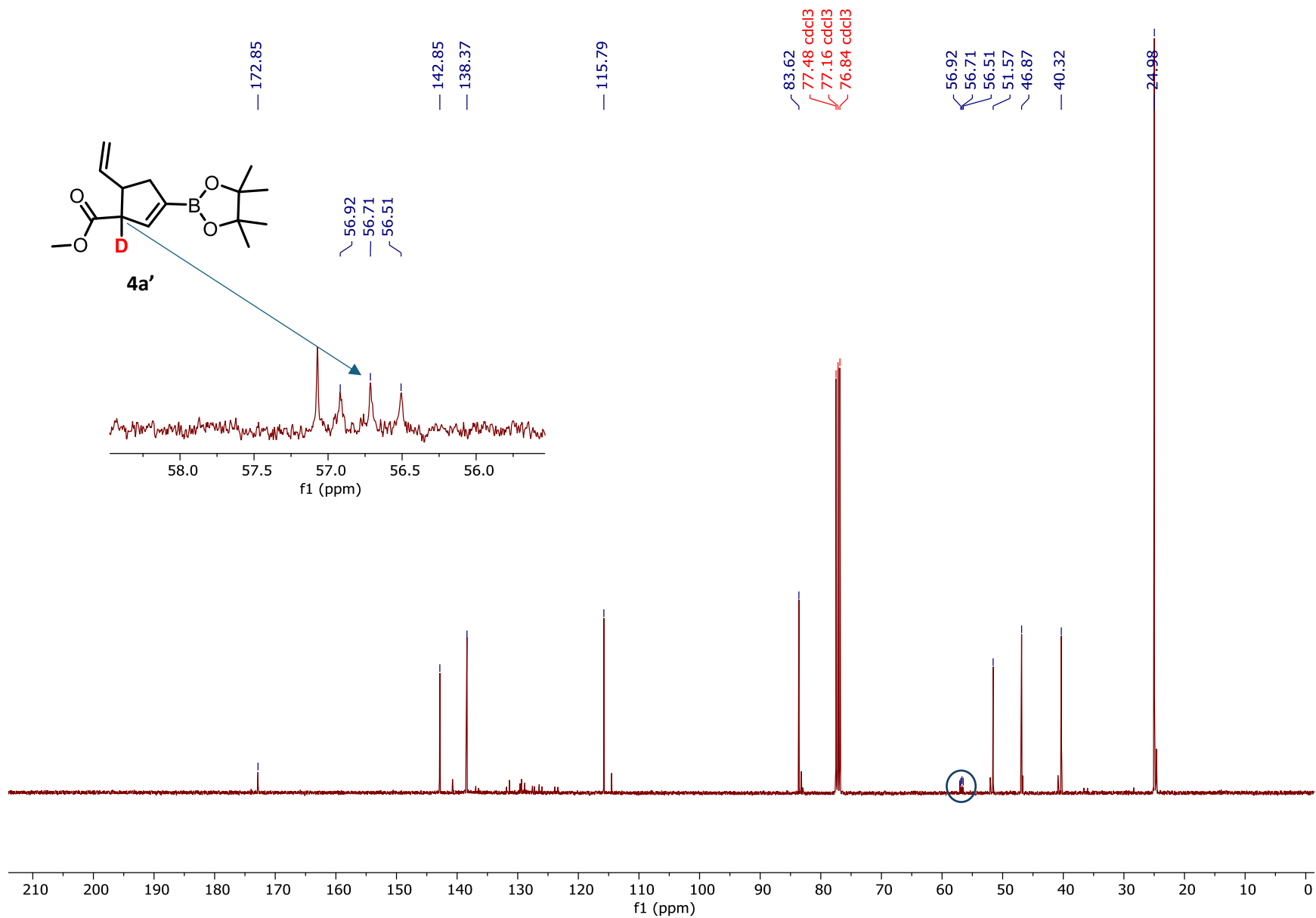


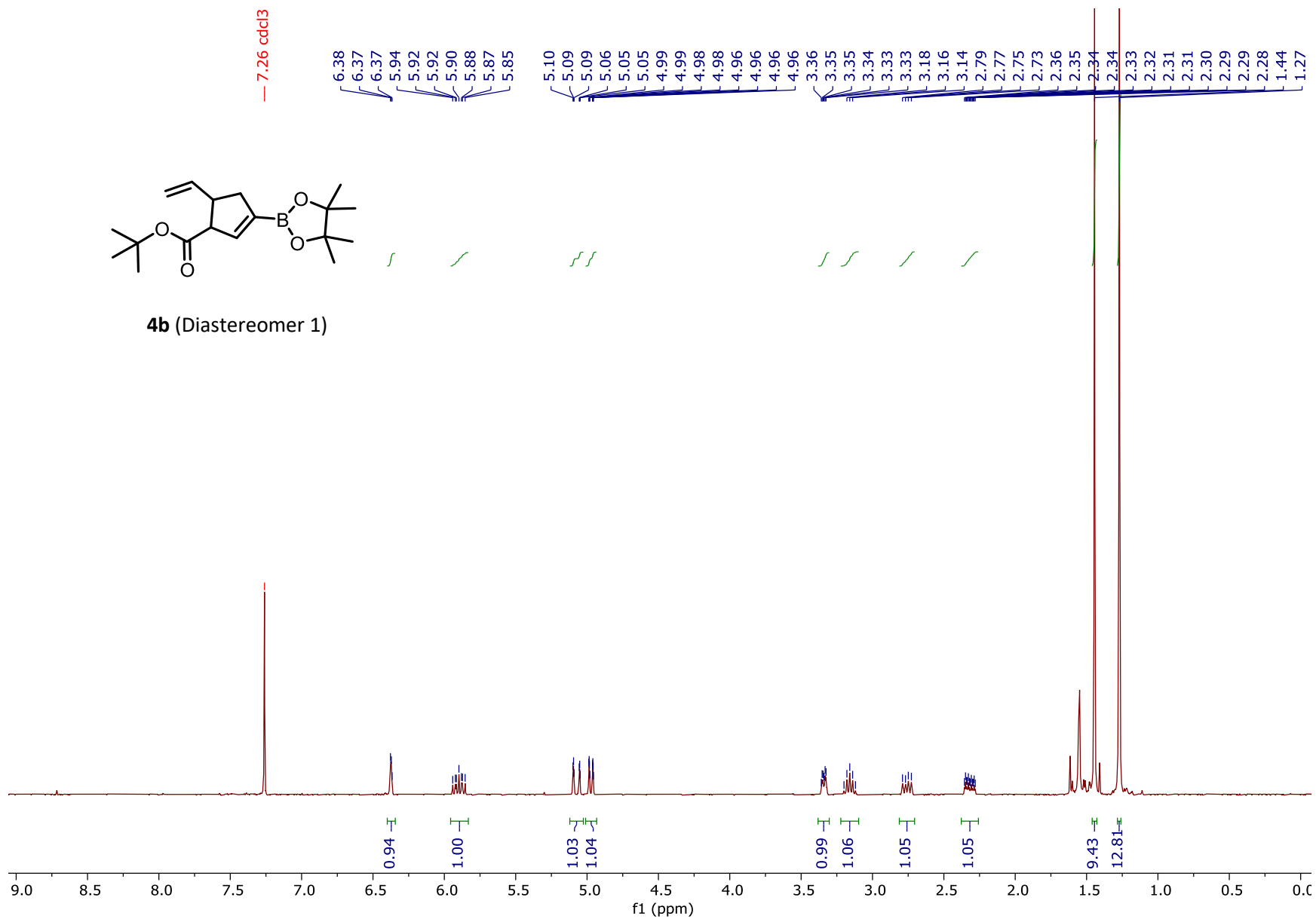
4a (Diastereomer 2)

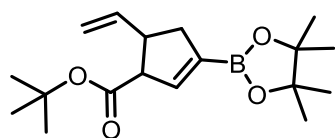
— 28.86



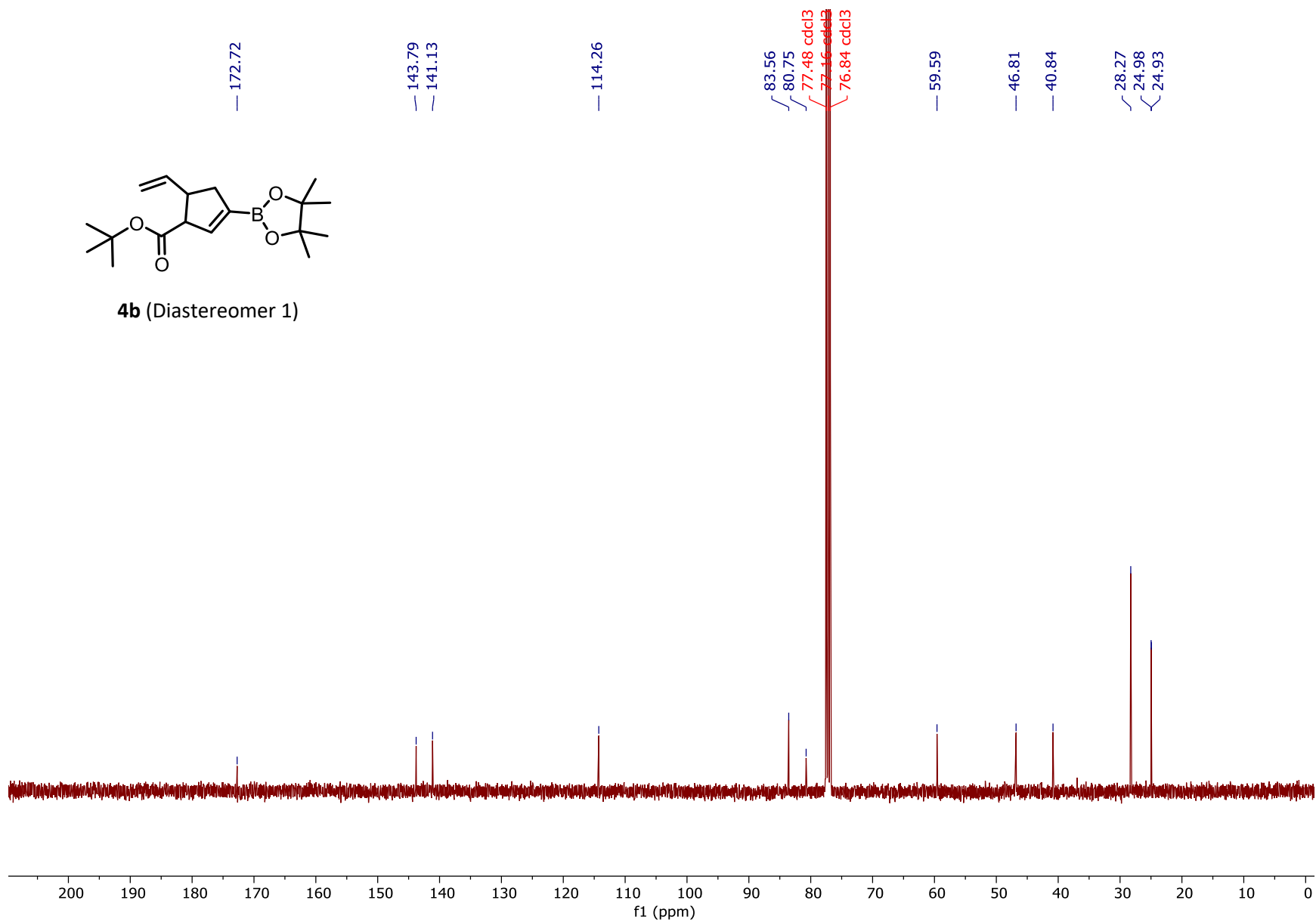




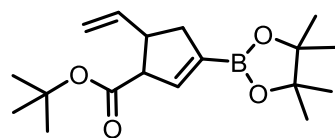




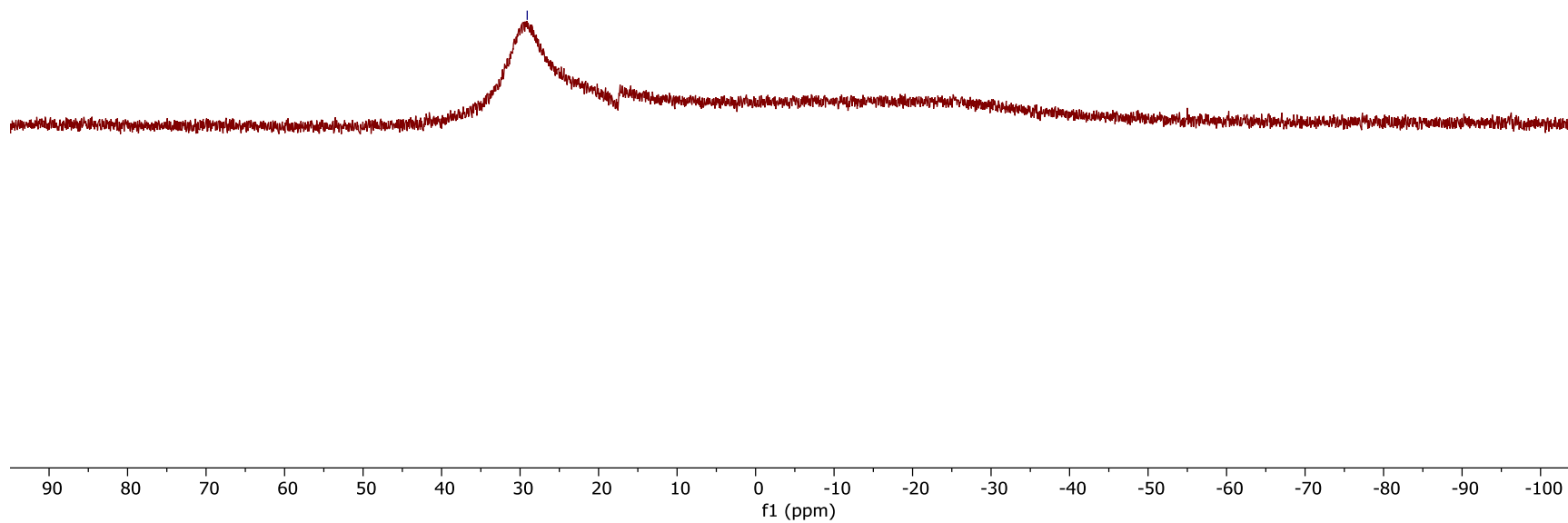
4b (Diastereomer 1)

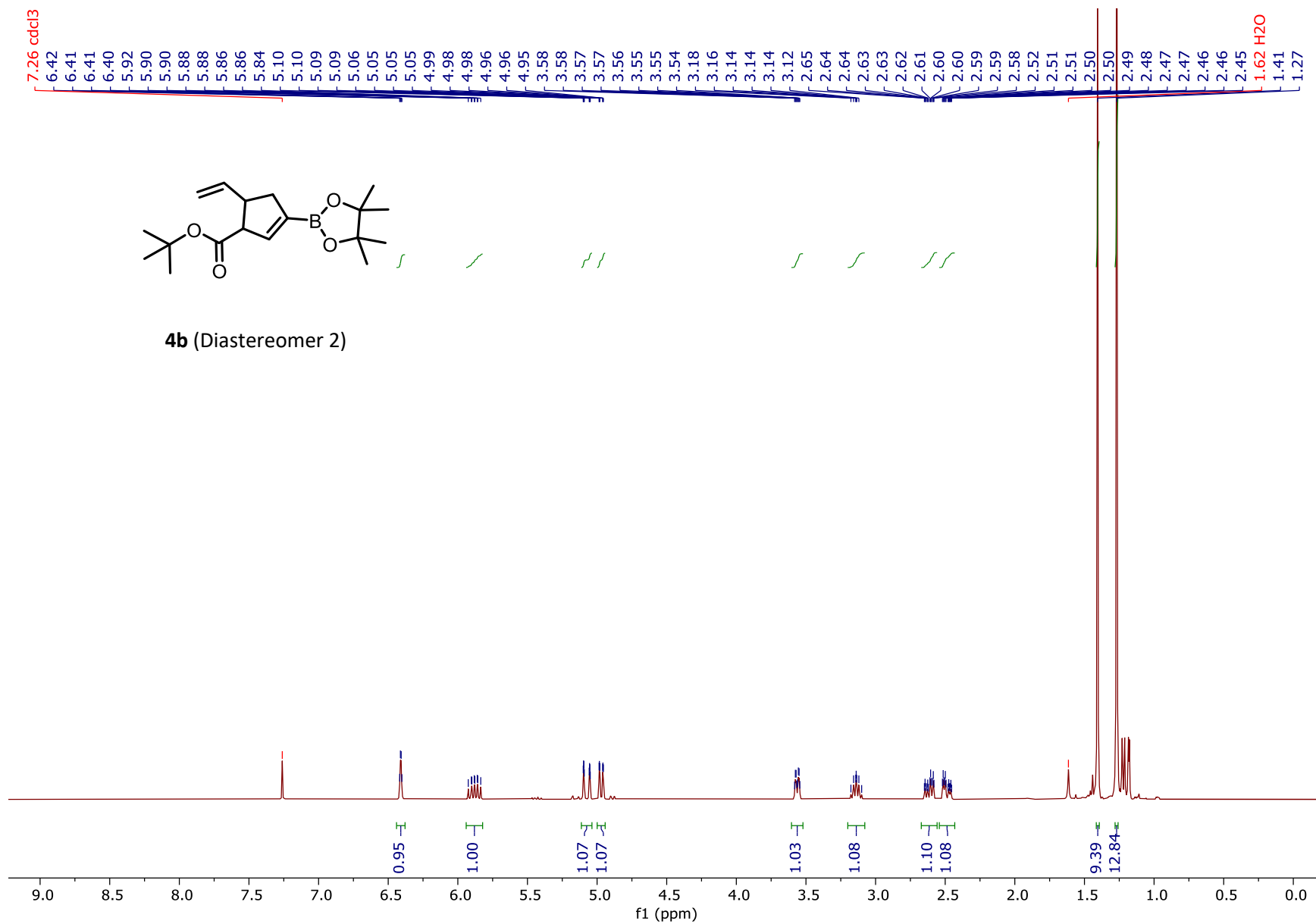


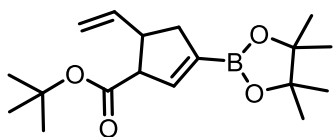
— 29.09



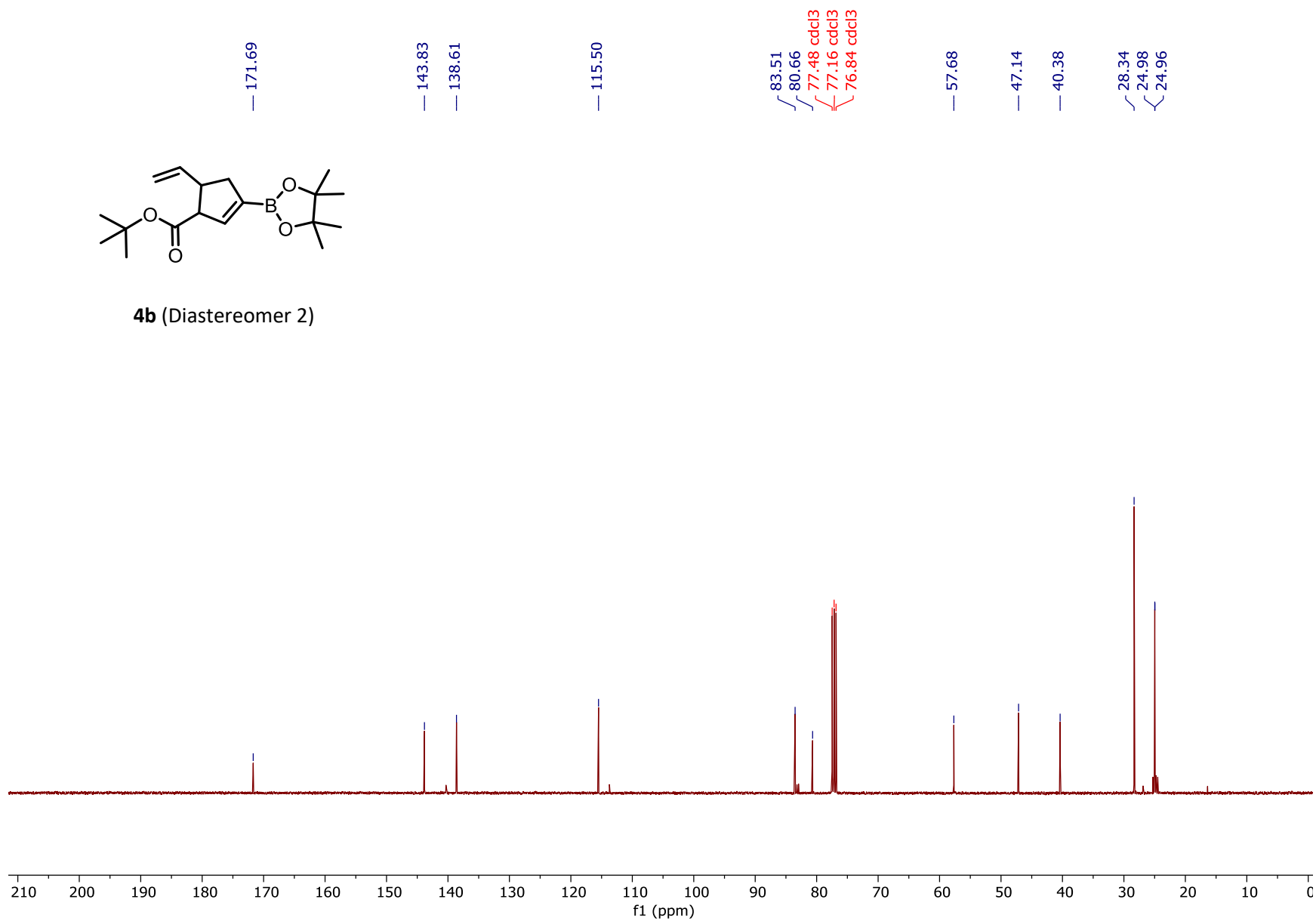
4b (Diastereomer 1)

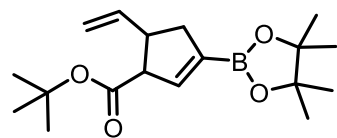






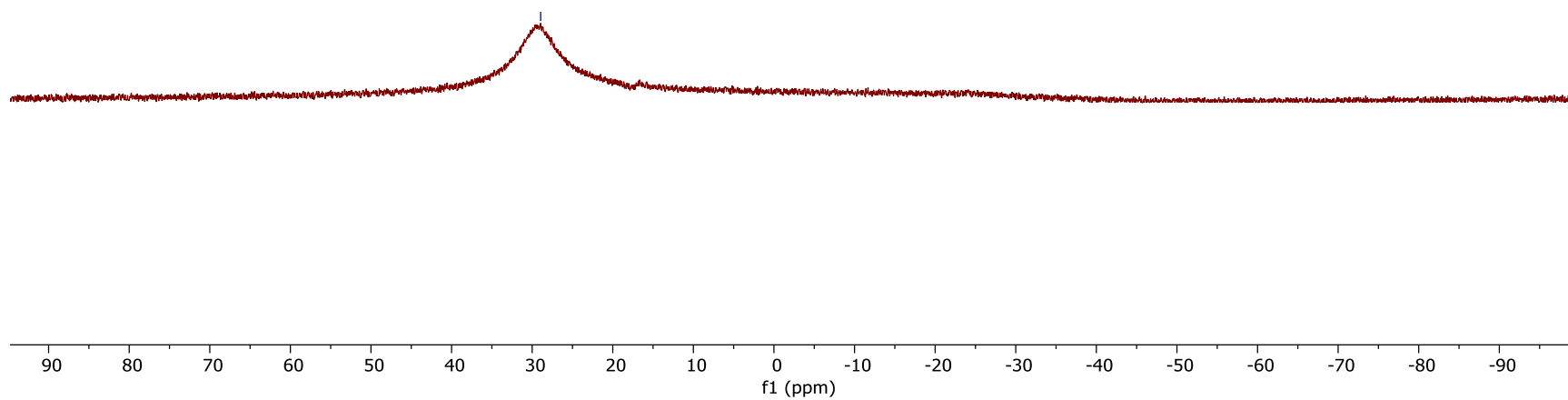
4b (Diastereomer 2)

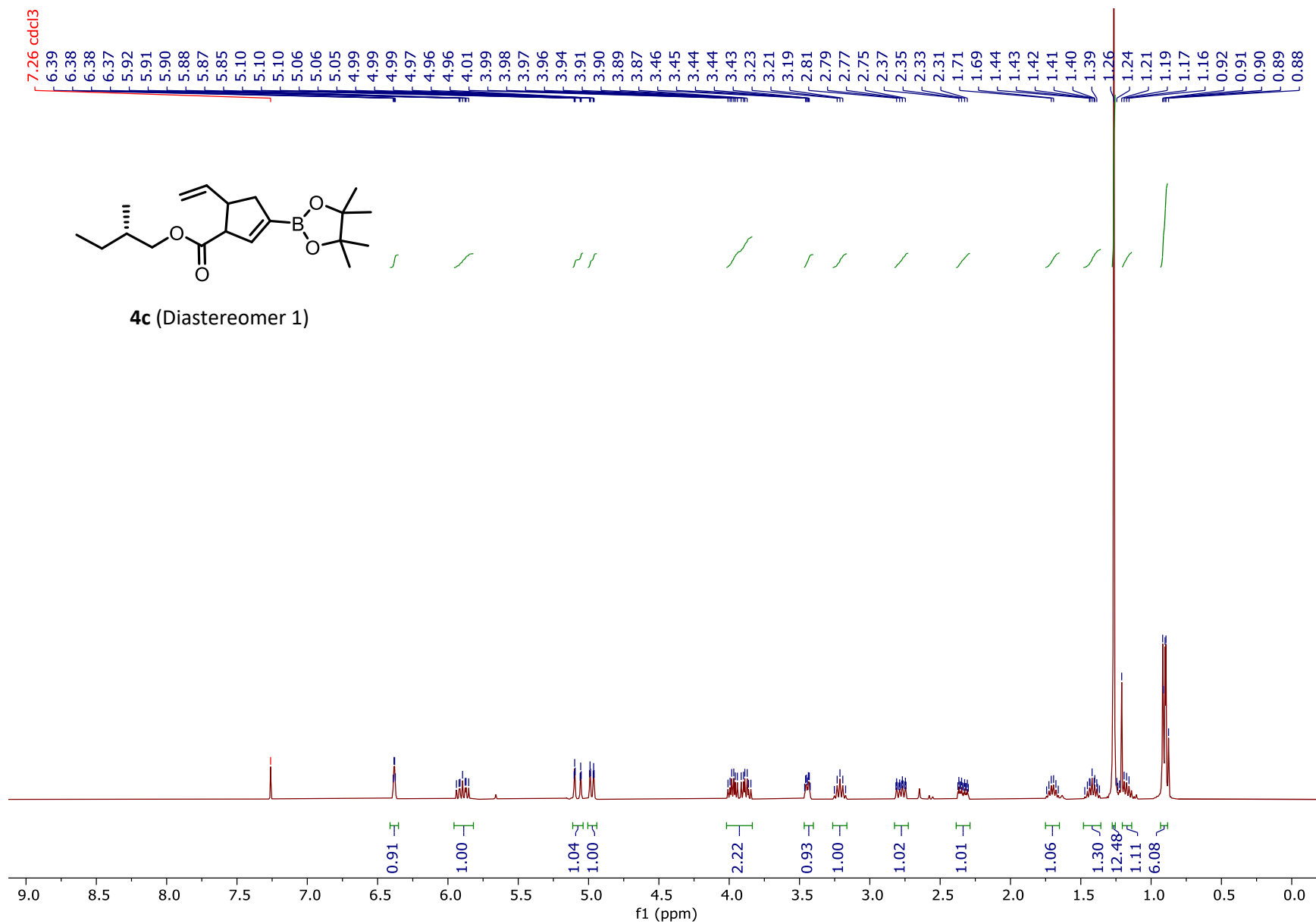


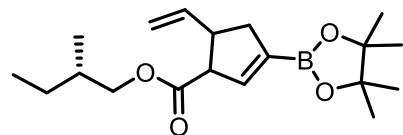


4b (Diastereomer 2)

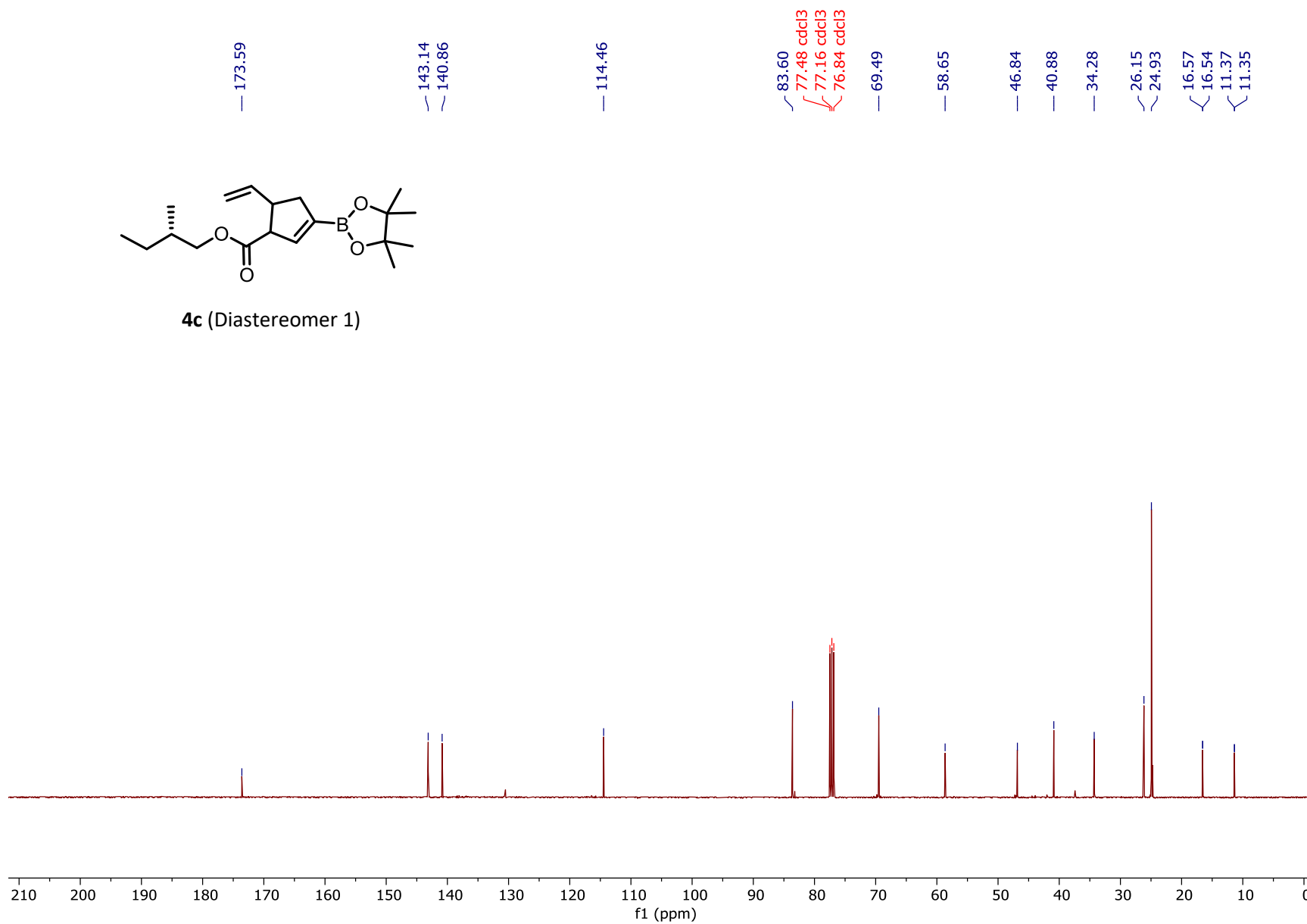
— 28.95

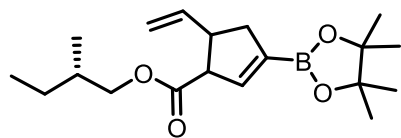






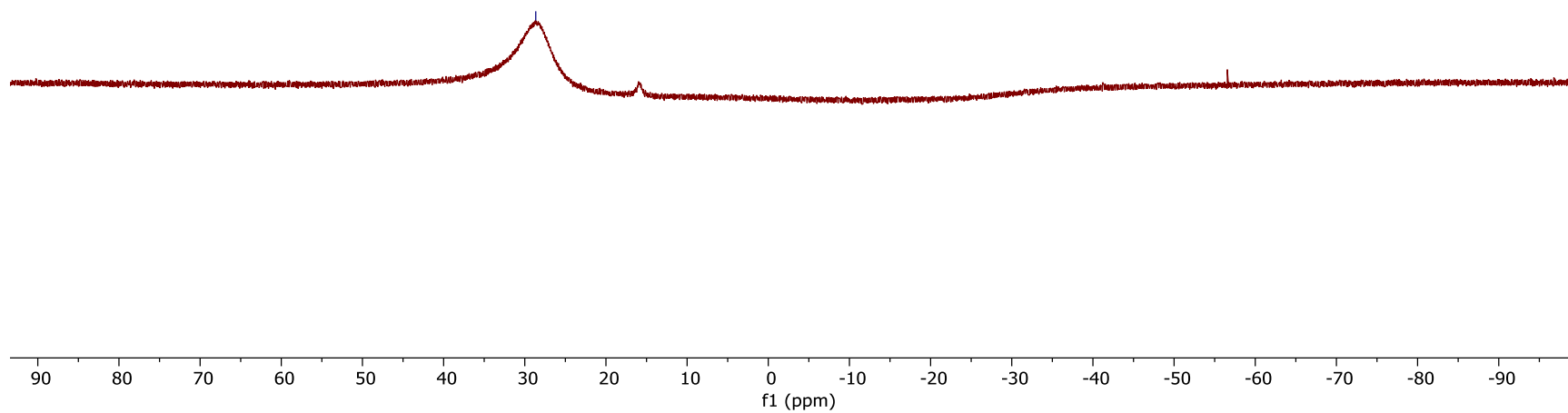
4c (Diastereomer 1)

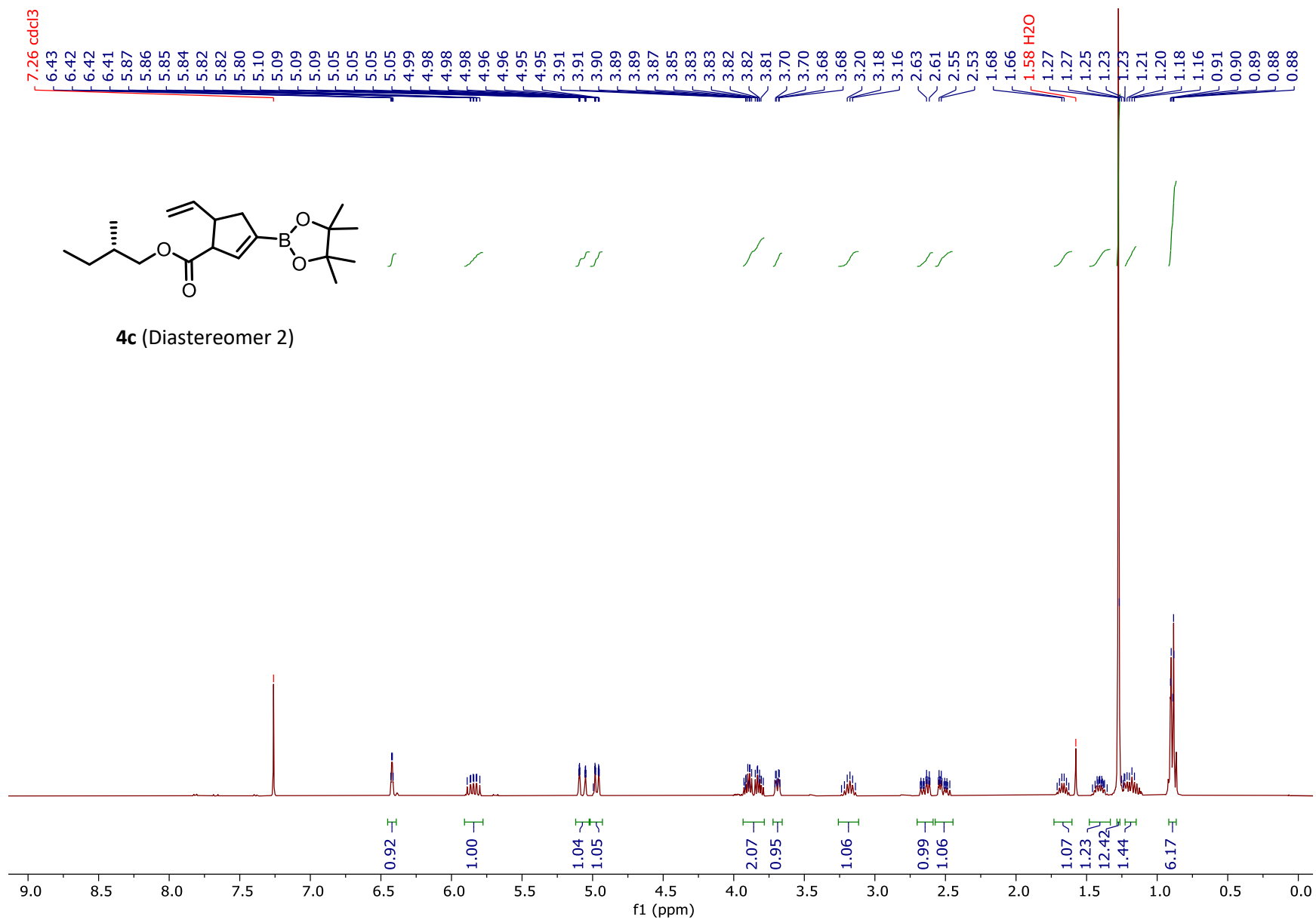


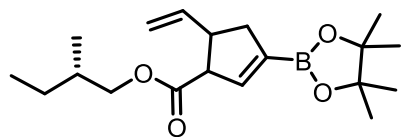


4c (Diastereomer 1)

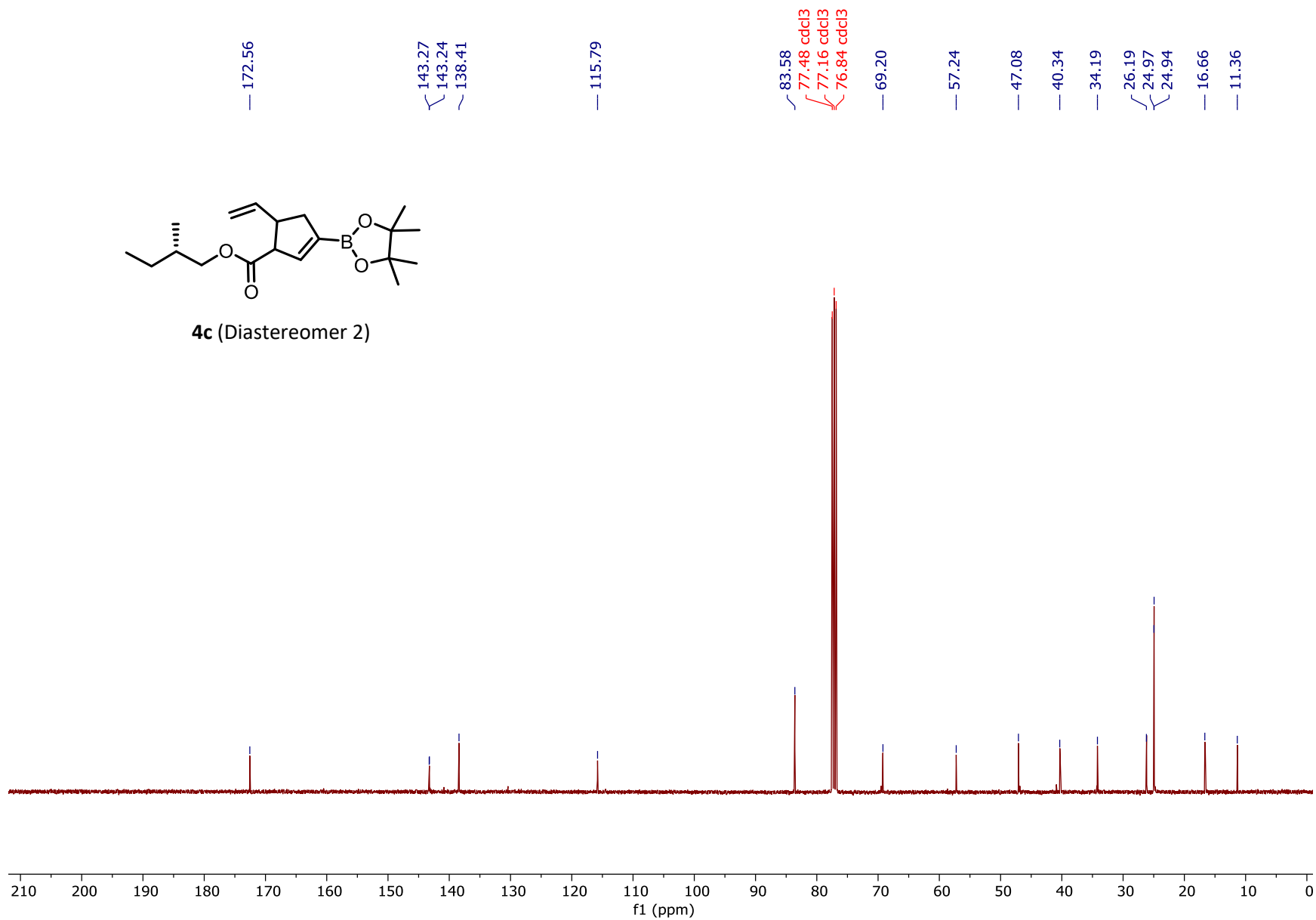
— 28.65

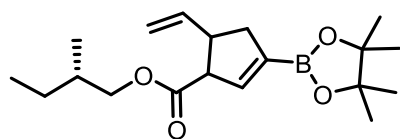






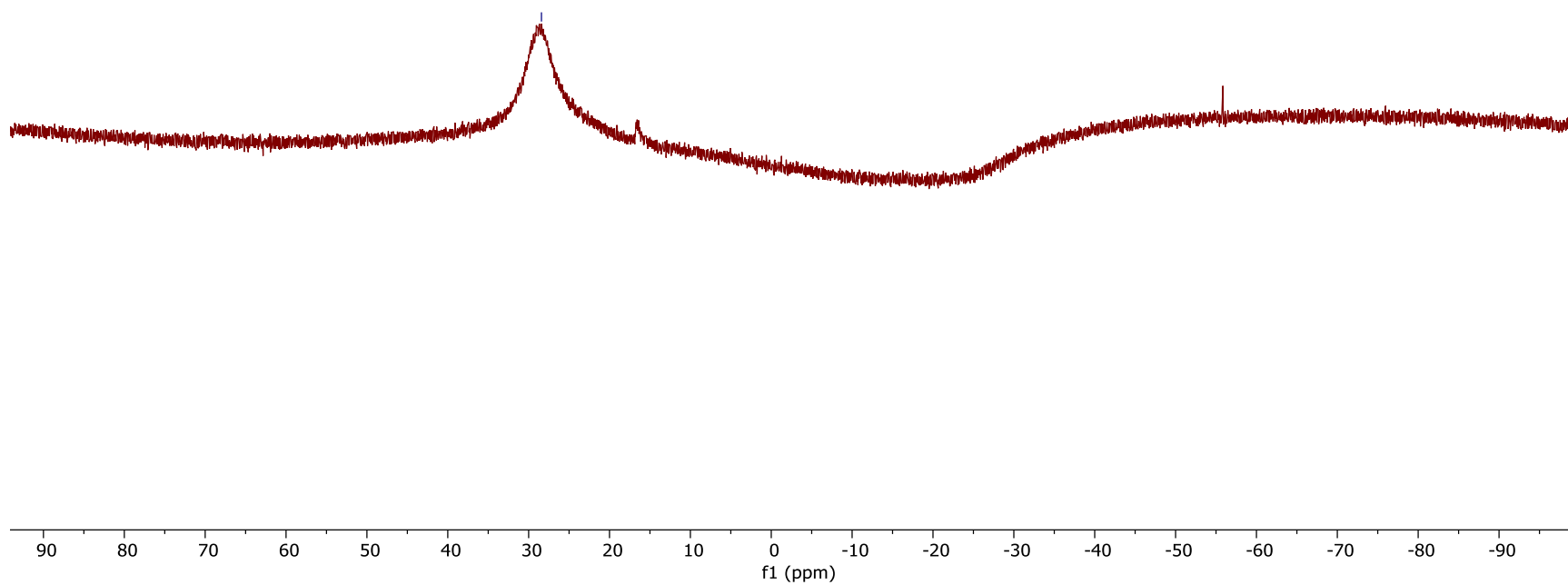
4c (Diastereomer 2)

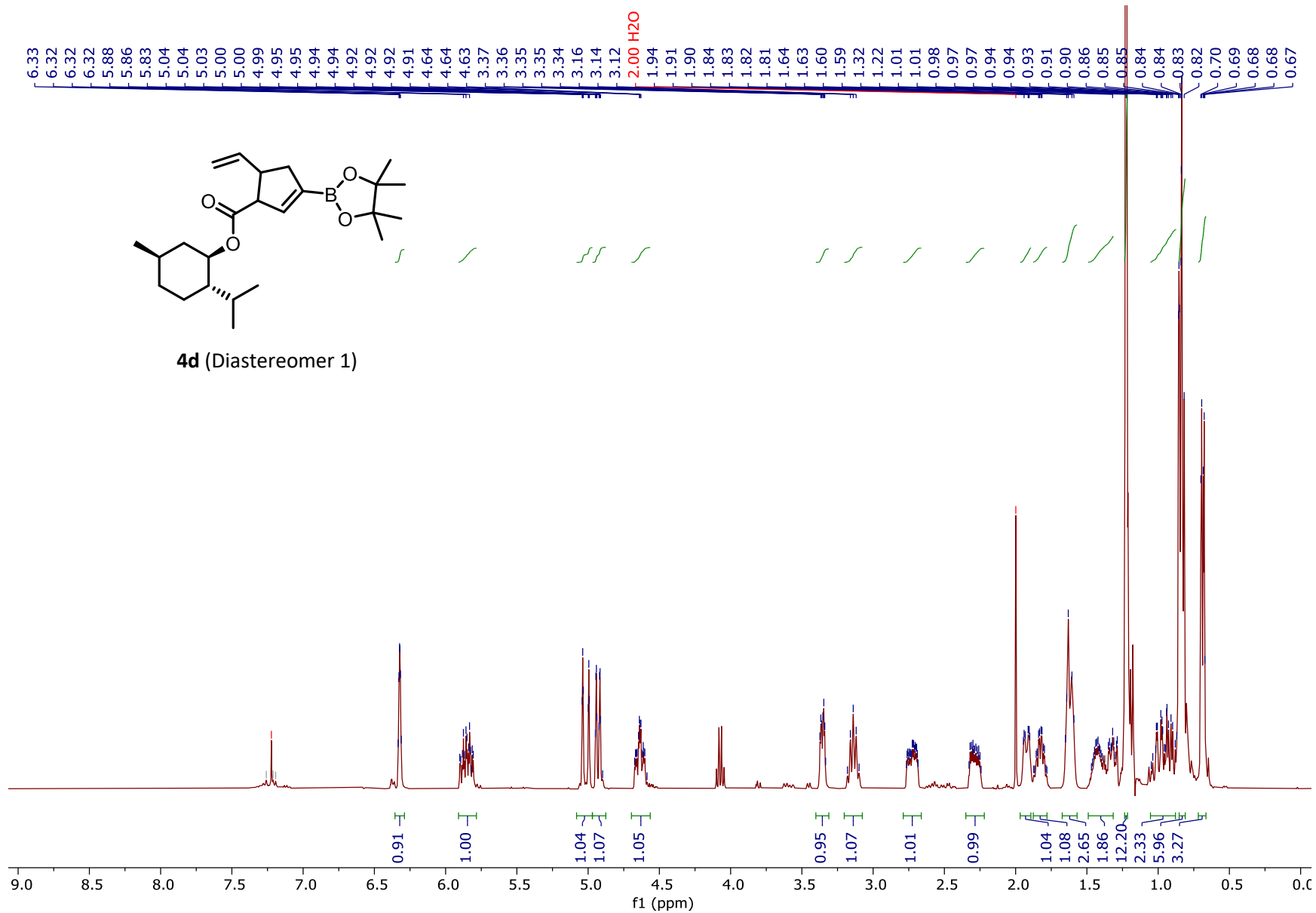


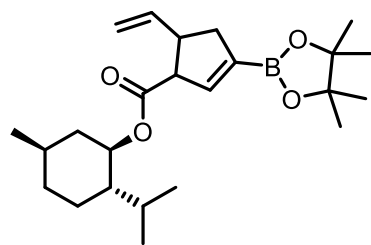


4c (Diastereomer 2)

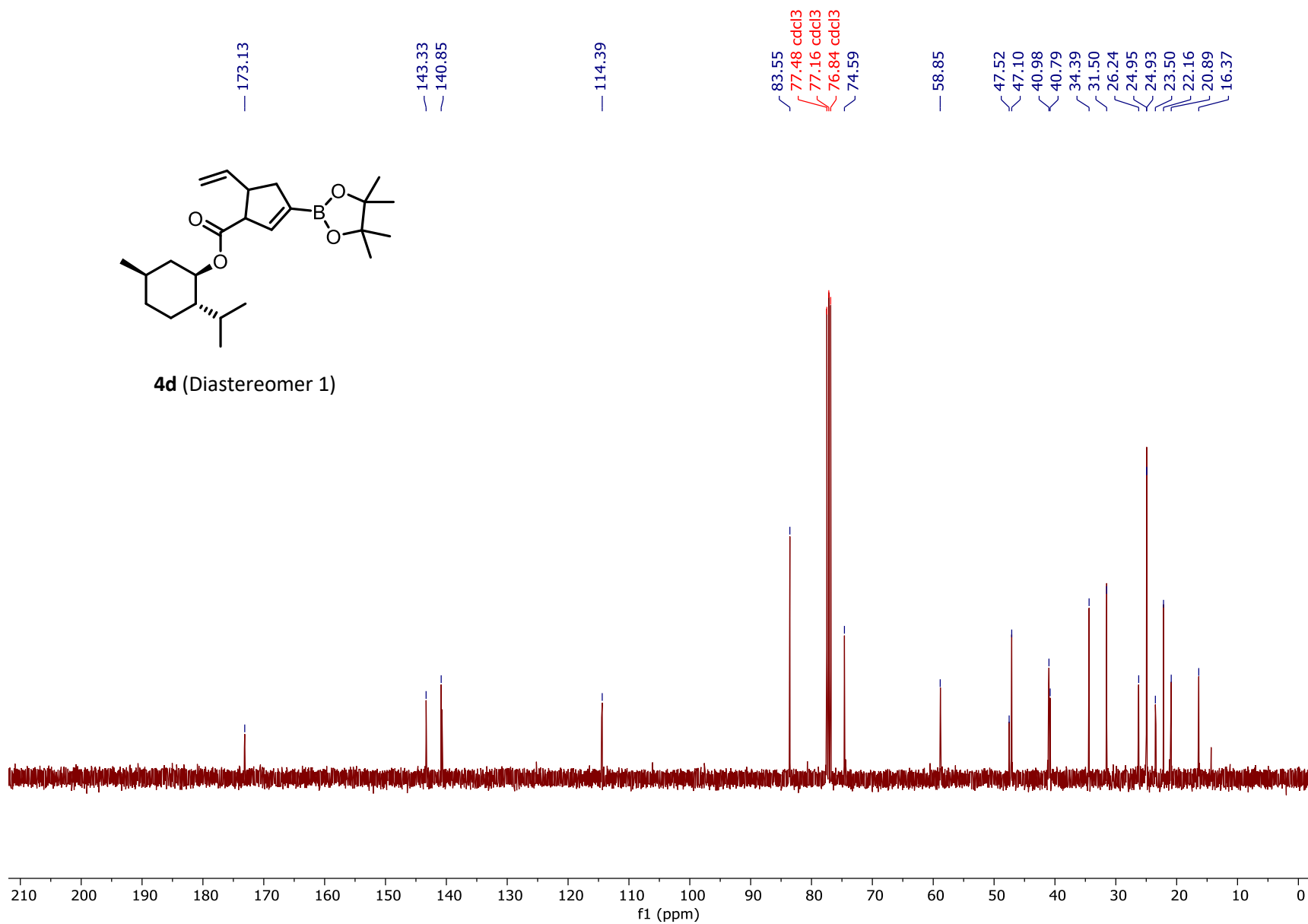
— 28.42

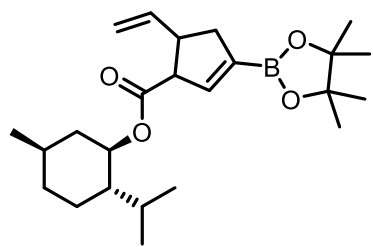






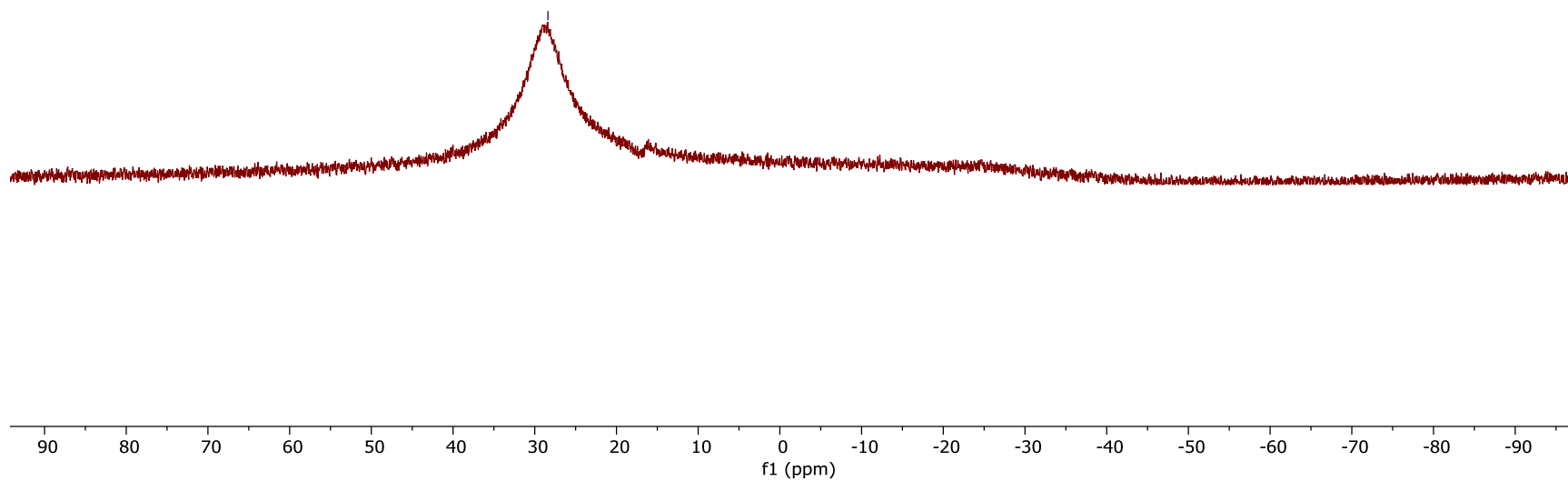
4d (Diastereomer 1)

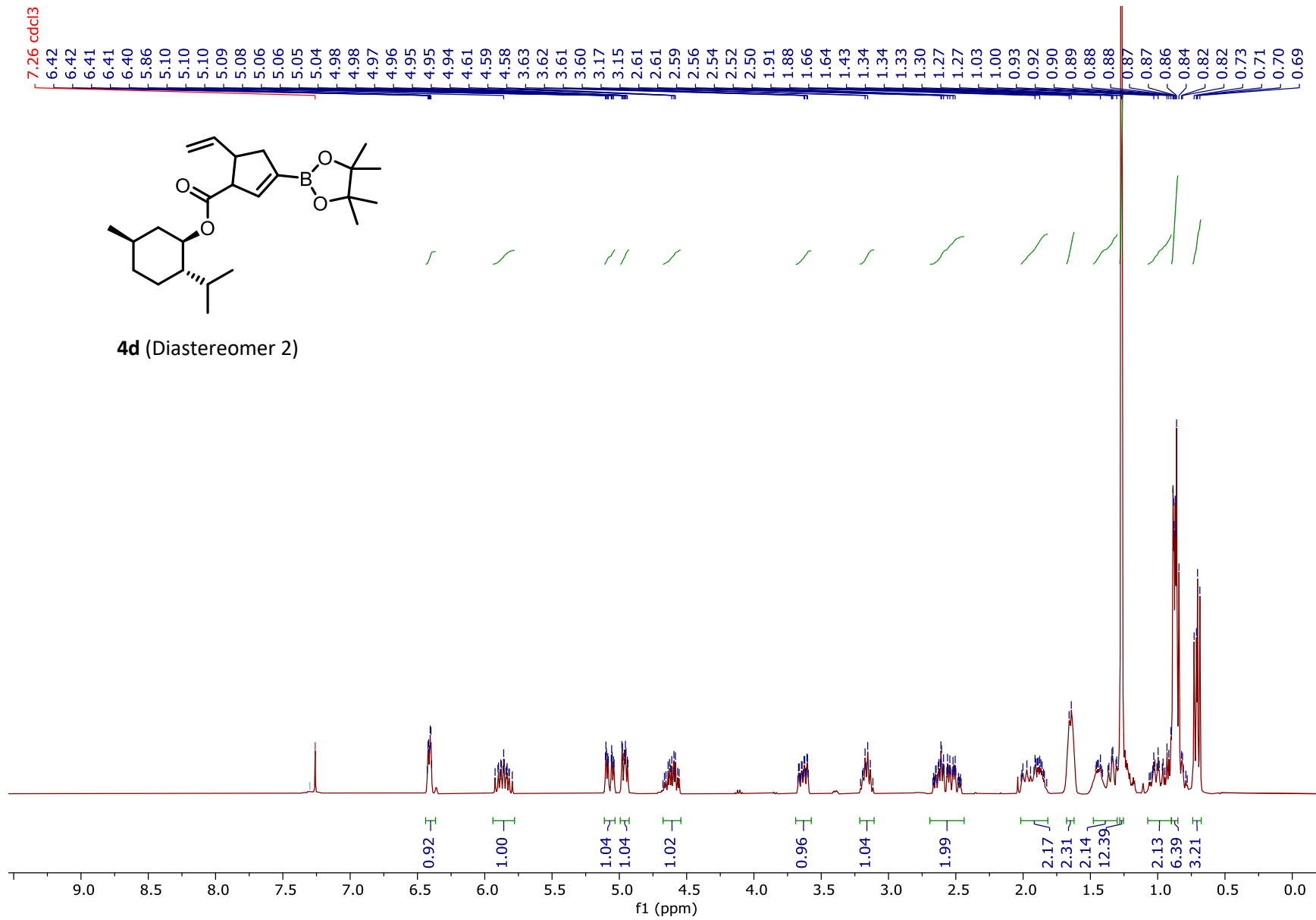


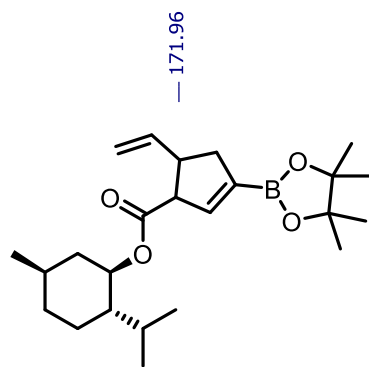


4d (Diastereomer 1)

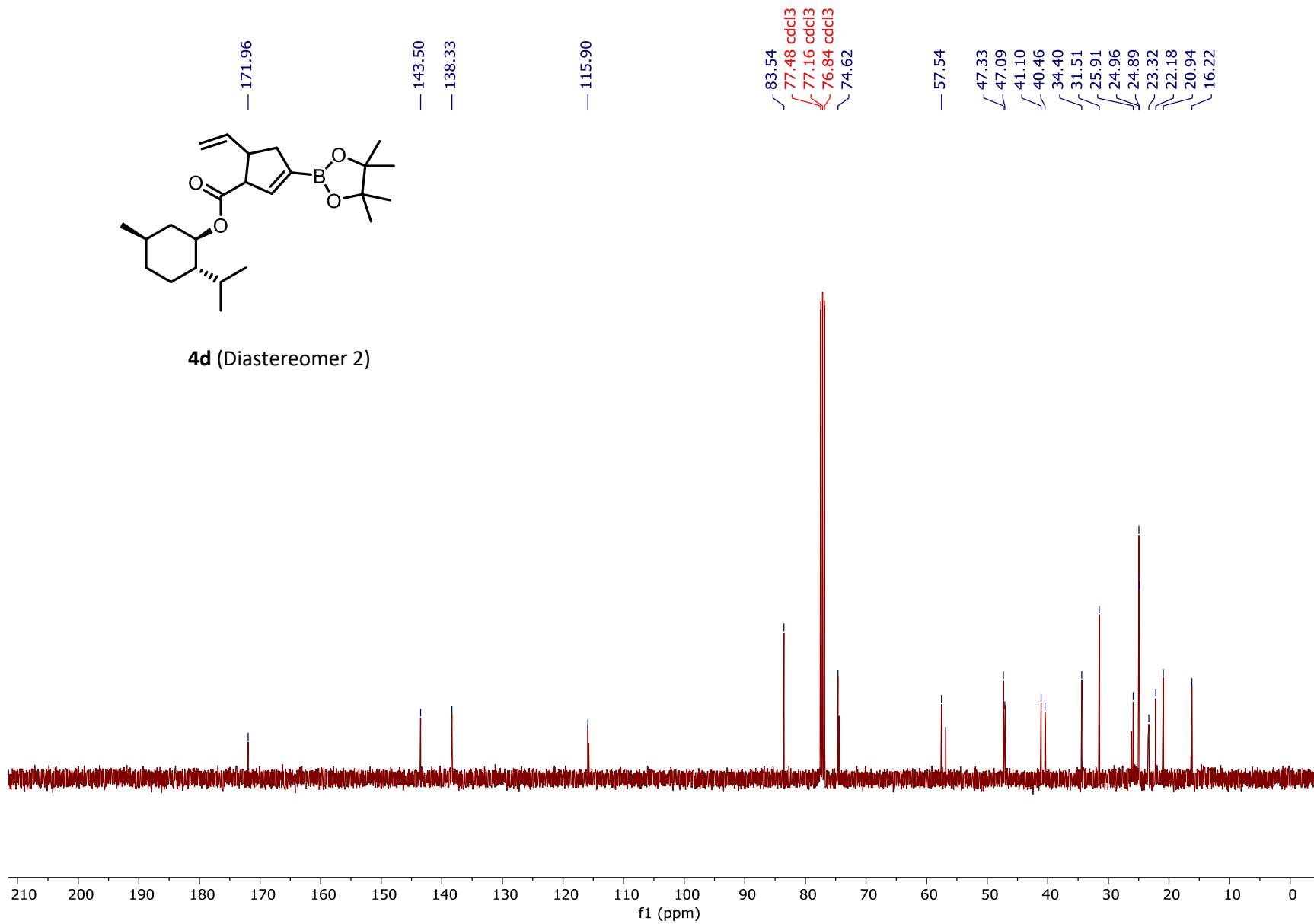
— 28.38

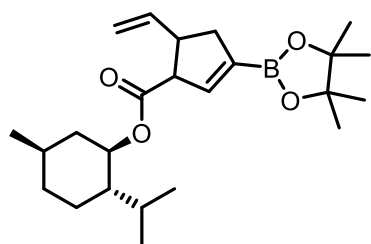






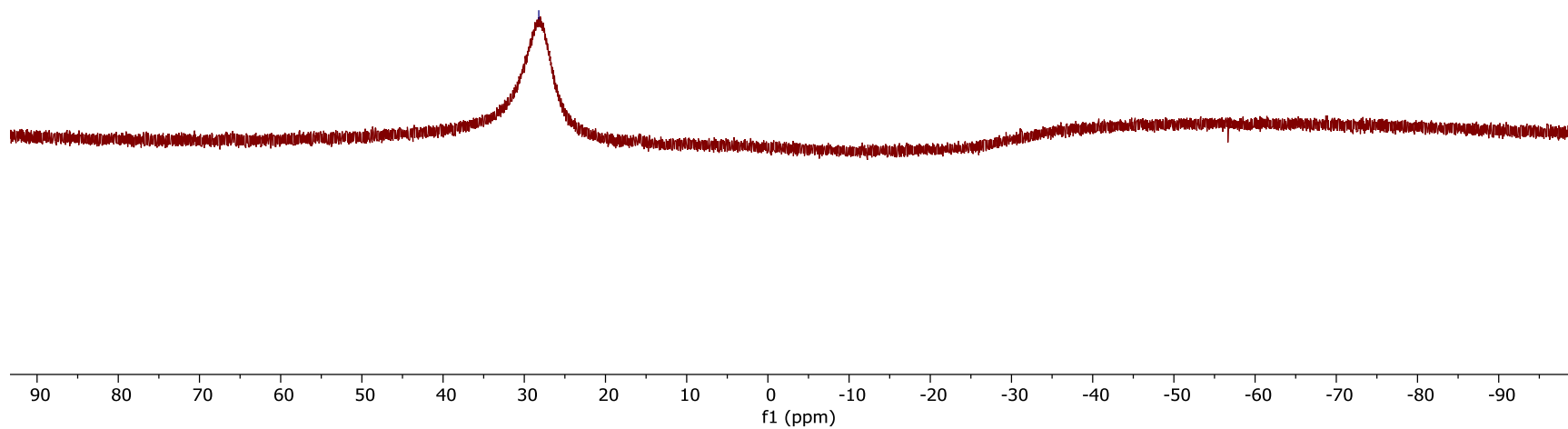
4d (Diastereomer 2)

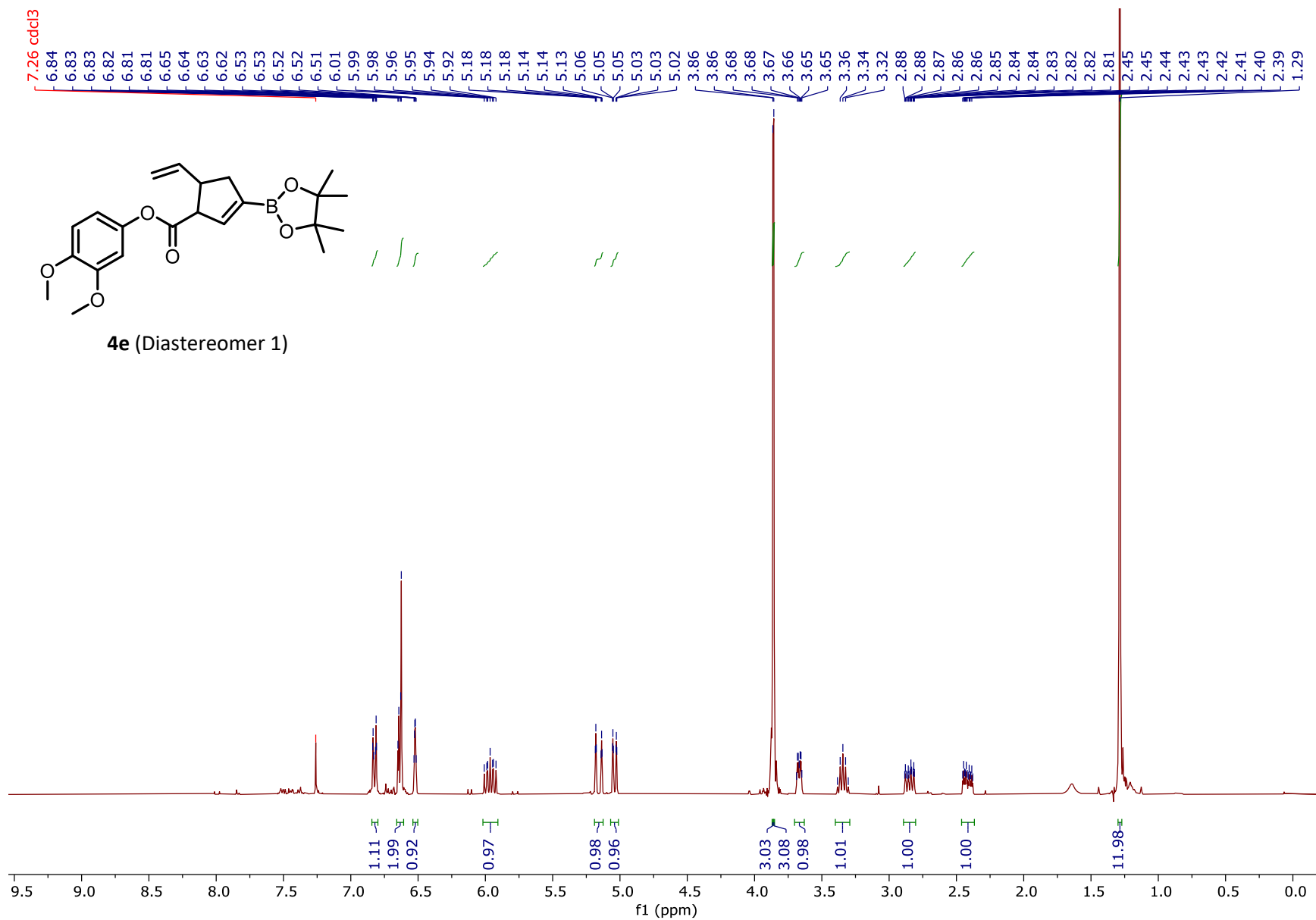


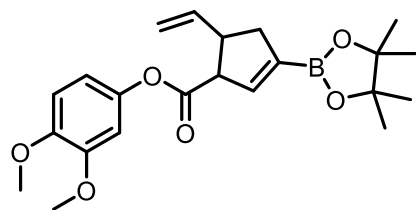


4d (Diastereomer 2)

— 28.22







4e (Diastereomer 1)

— 172.21

∩ 149.45
∩ 146.92
∩ 144.59
∩ 142.25
∩ 140.54

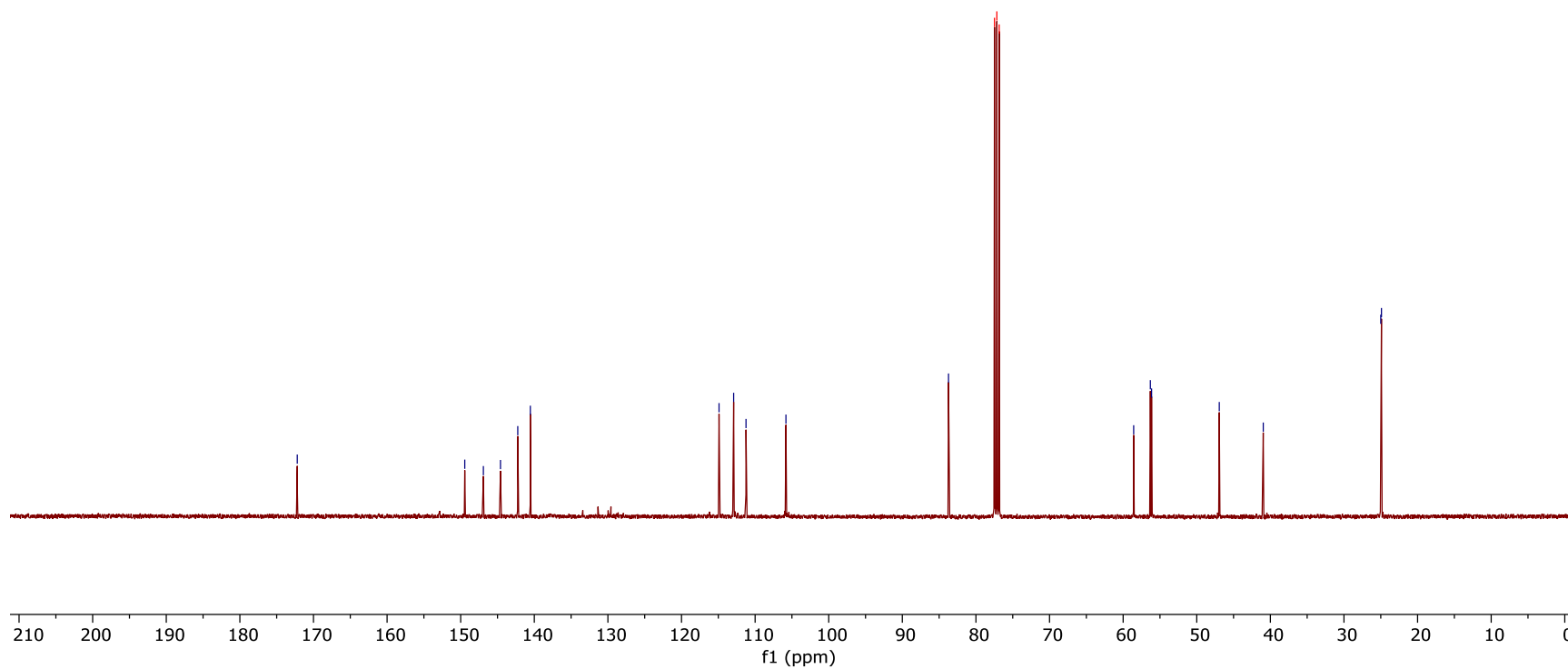
— 114.90
∩ 112.92
∩ 111.24
— 105.81

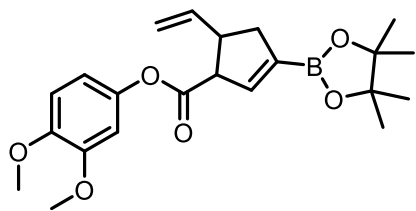
— 83.73
∩ 77.48 cdd13
∩ 77.16 cdd13
∩ 76.84 cdd13

∩ 58.57
∩ 56.31
∩ 56.14

— 46.94
— 40.96

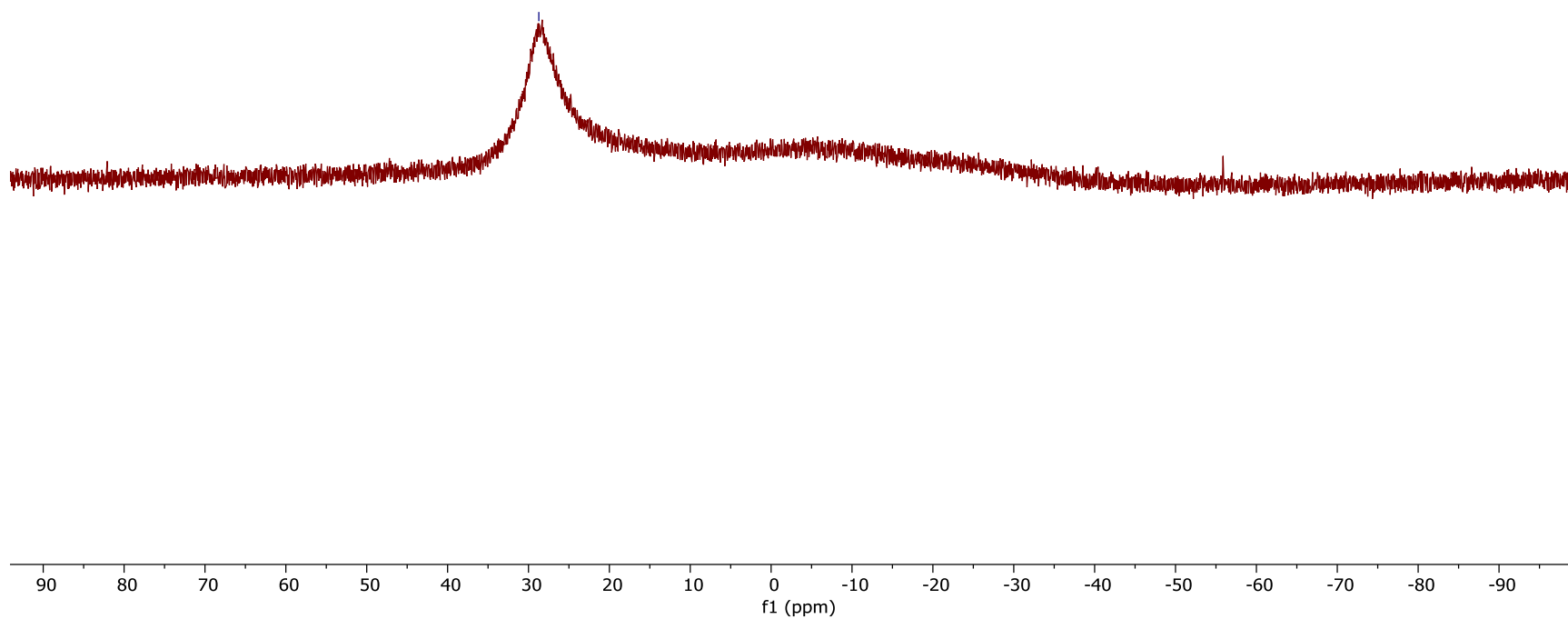
∩ 25.00
∩ 24.91

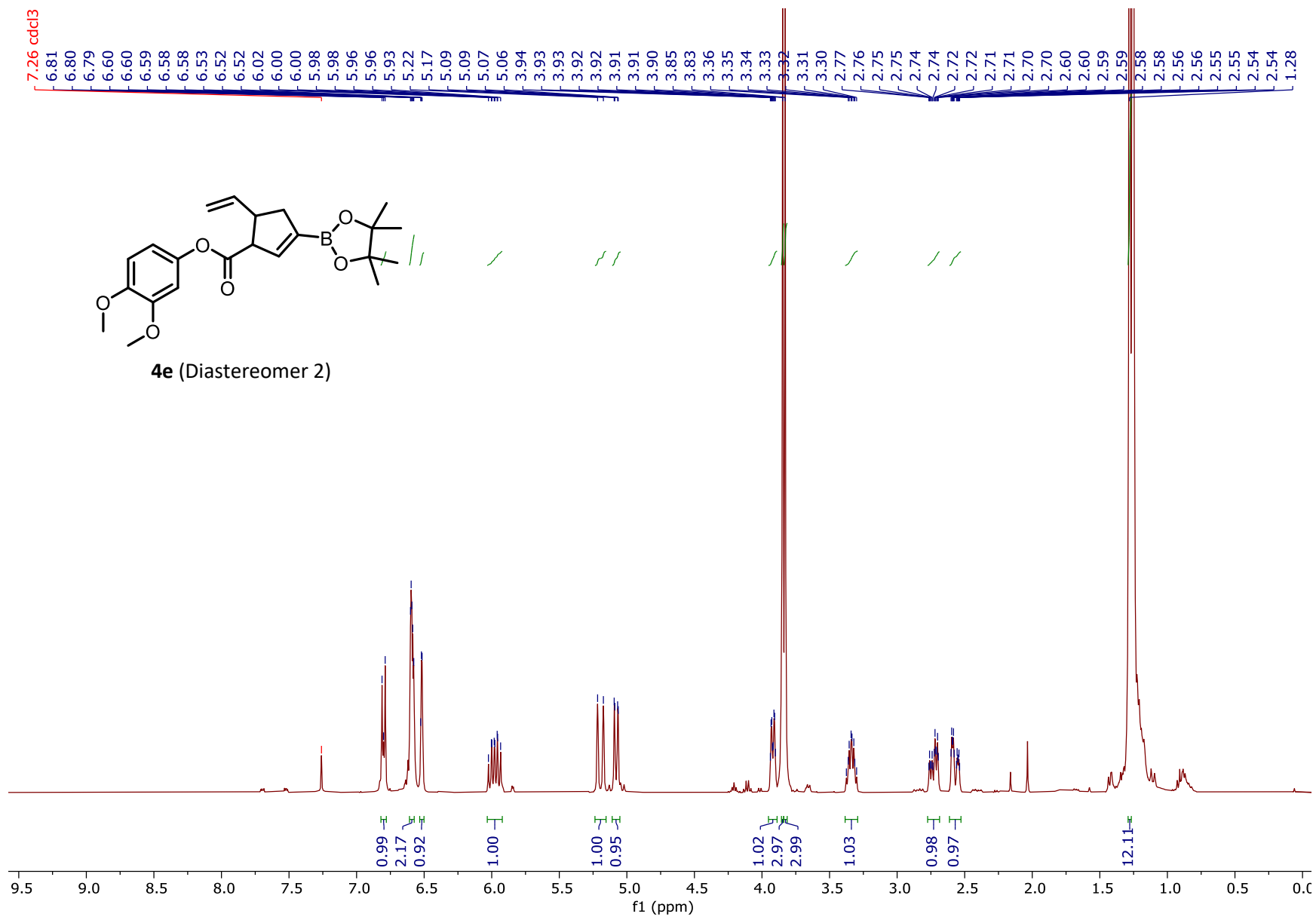


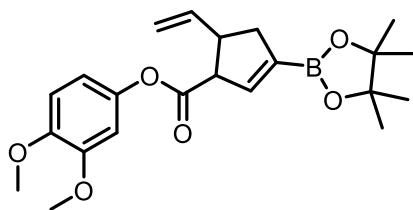


4e (Diastereomer 1)

— 28.72







4e (Diastereomer 2)

— 171.22

~ 149.34
 ~ 146.86
 ~ 144.48
 ~ 142.36
 ~ 138.32

~ 116.16
 ~ 113.05
 ~ 111.18
 ~ 105.96

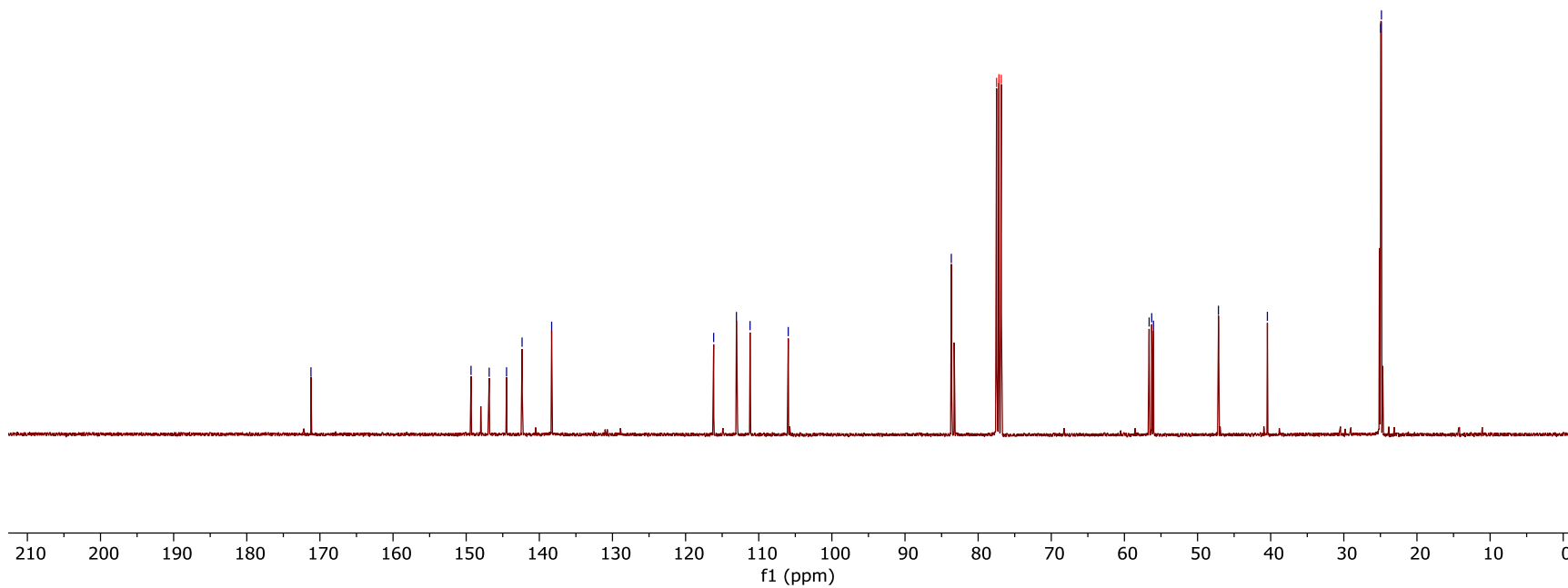
~ 83.67
 77.48 cdc13
 77.16 cdc13
 76.84 cdc13

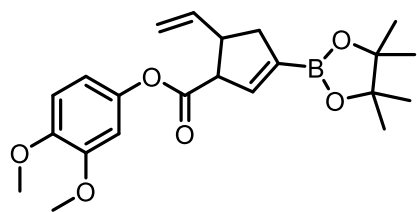
56.62
 56.27
 56.02

— 47.14

— 40.45

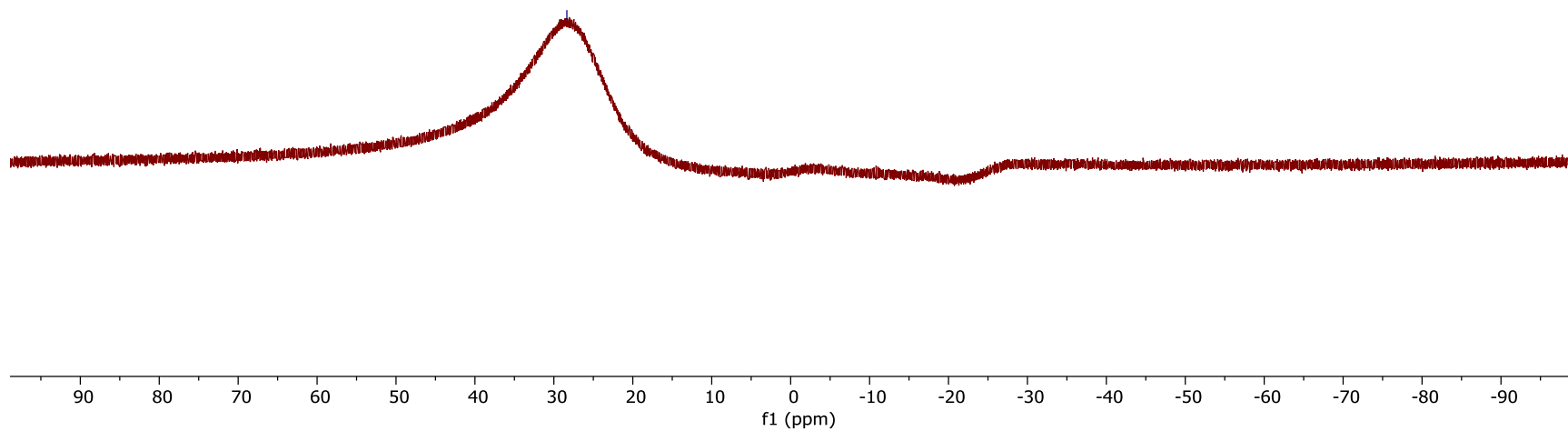
~ 24.96
 ~ 24.86

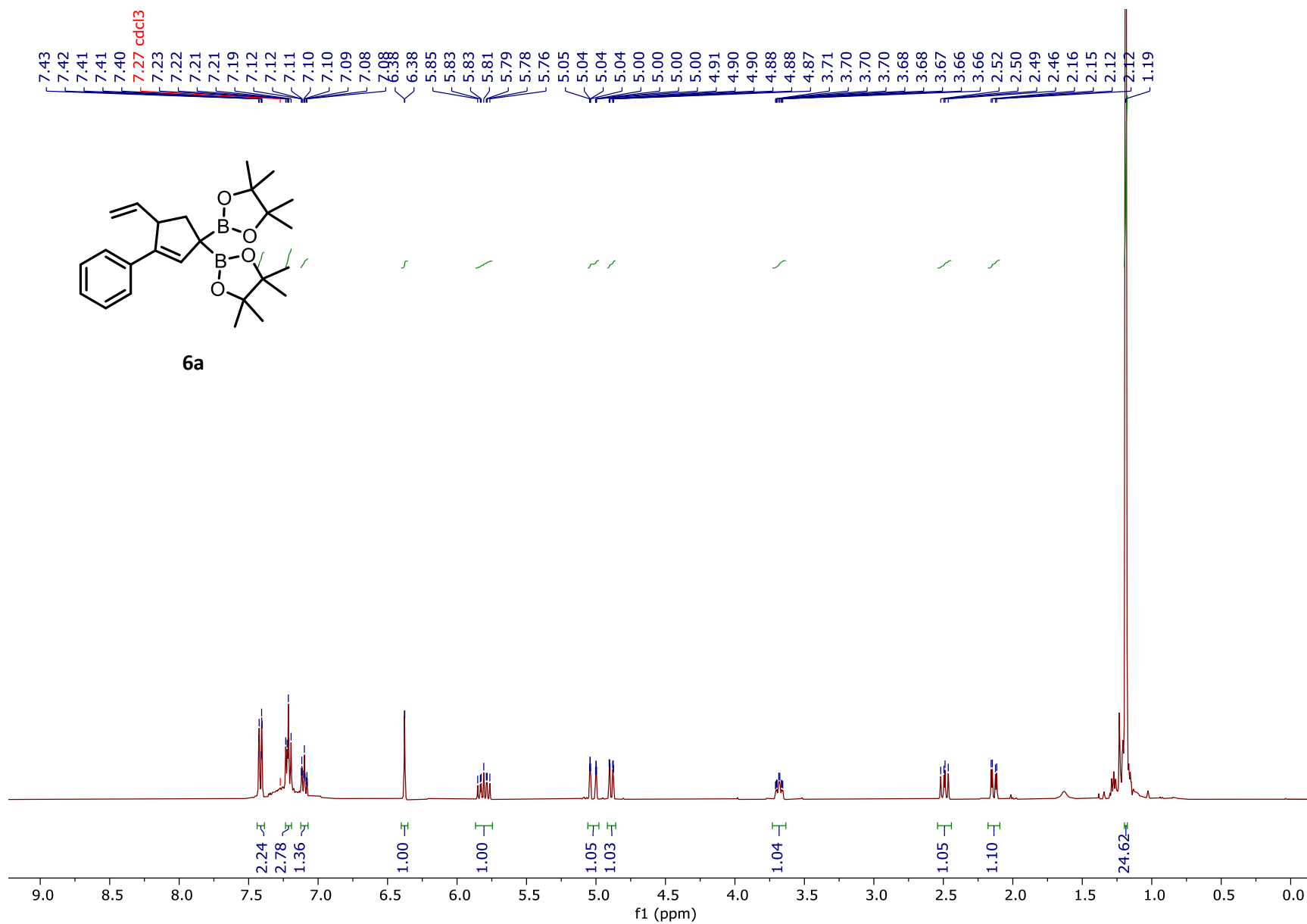


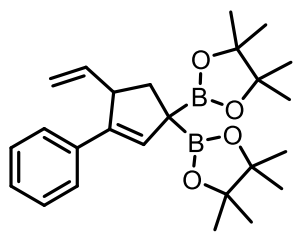


4e (Diastereomer 2)

— 28.35







6a

141.88
139.47
136.67
130.94
128.13
126.24
126.19

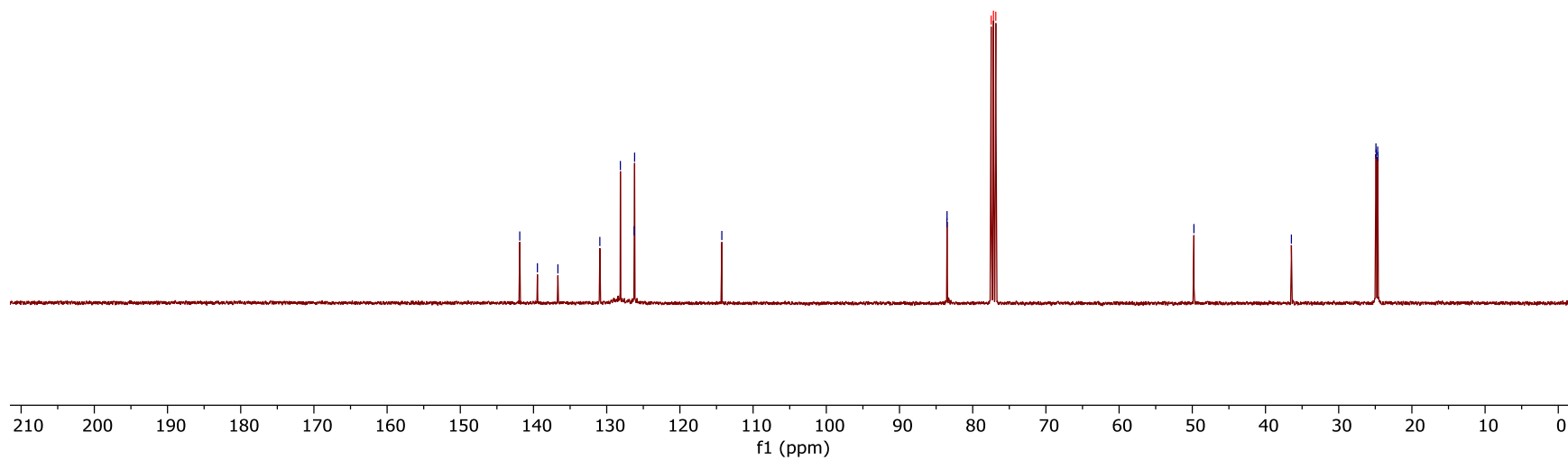
114.27

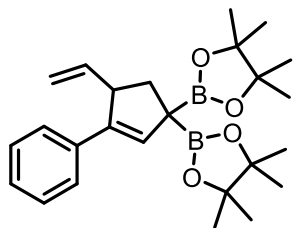
83.53
83.50
77.48 cdc13
77.16 cdc13
76.84 cdc13

49.78

36.46

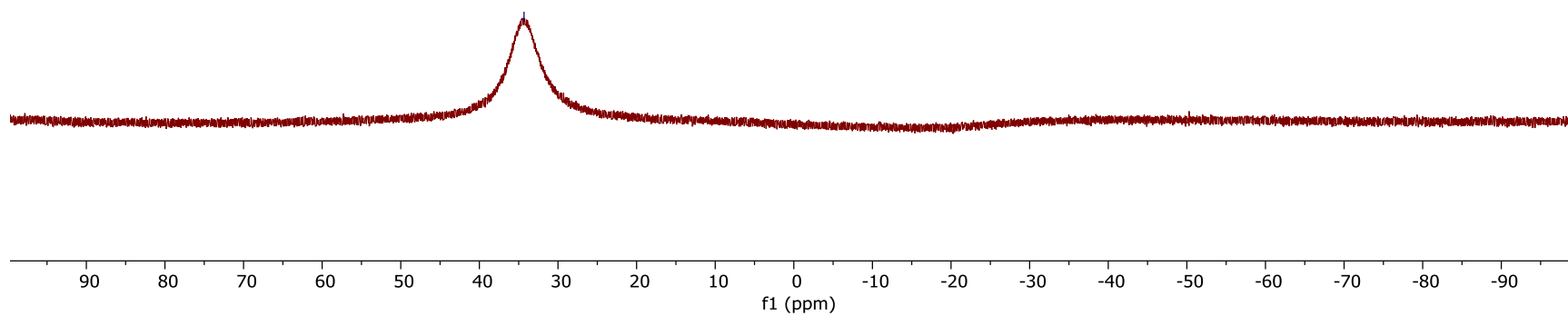
24.91
24.88
24.67
24.63

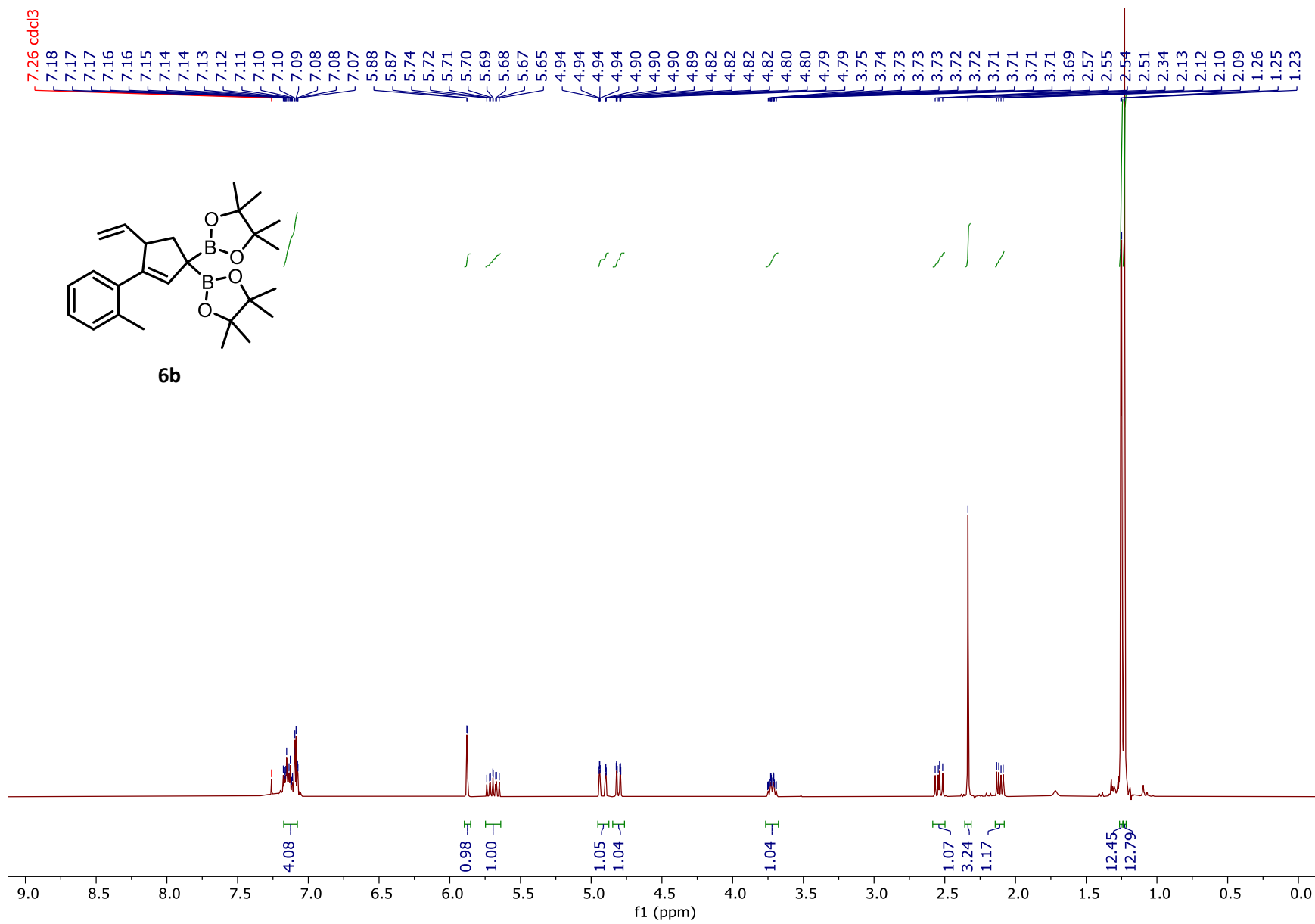


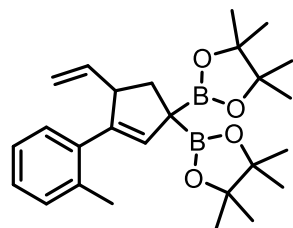


6a

— 34.32







6b

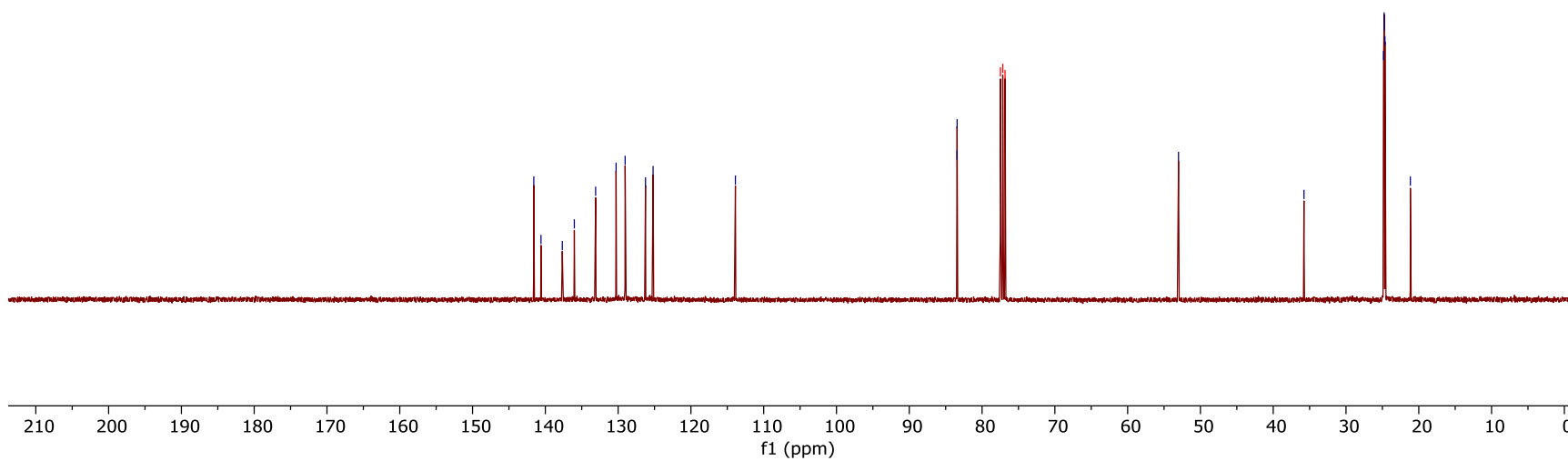
141.58
 140.60
 137.67
 136.02
 133.09
 130.28
 129.04
 126.24
 125.20
 — 113.89

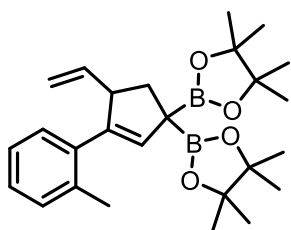
83.44
 83.43
 77.48 cdc13
 77.16 cdc13
 76.84 cdc13

— 53.01

— 35.77

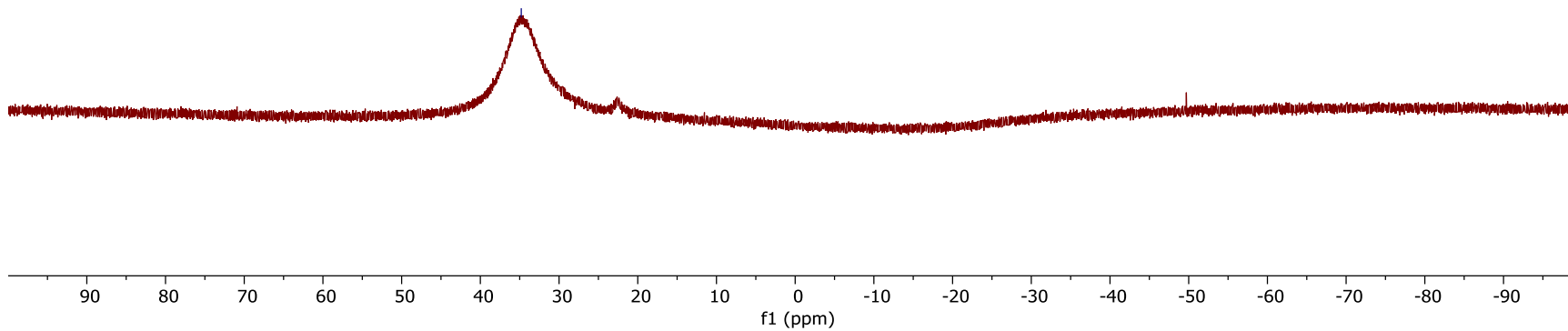
24.84
 24.76
 24.74
 24.65
 21.16

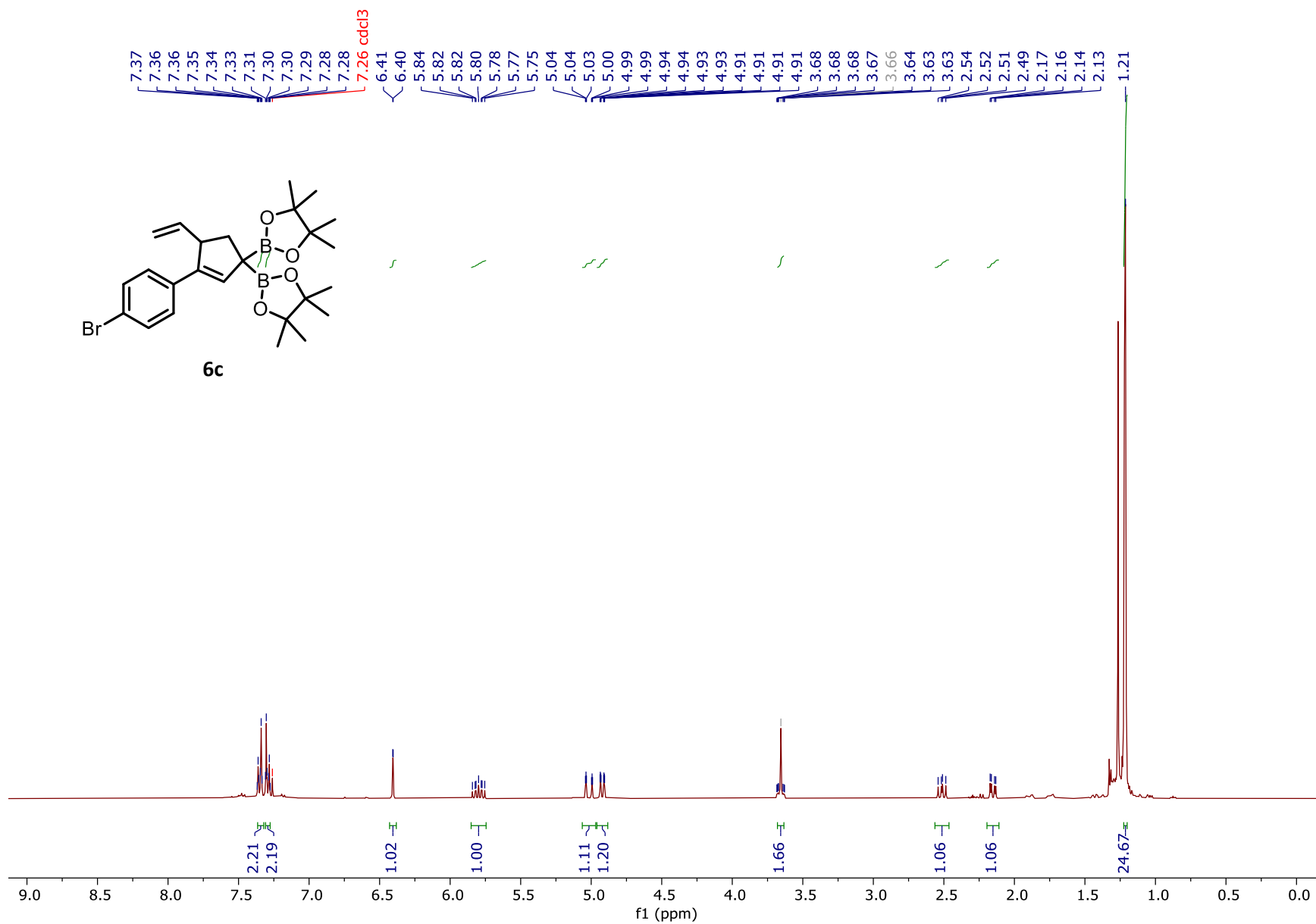


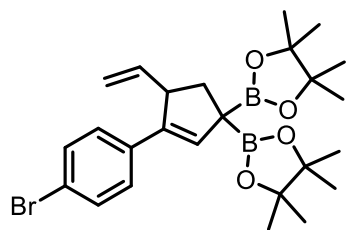


6b

— 34.80







6c

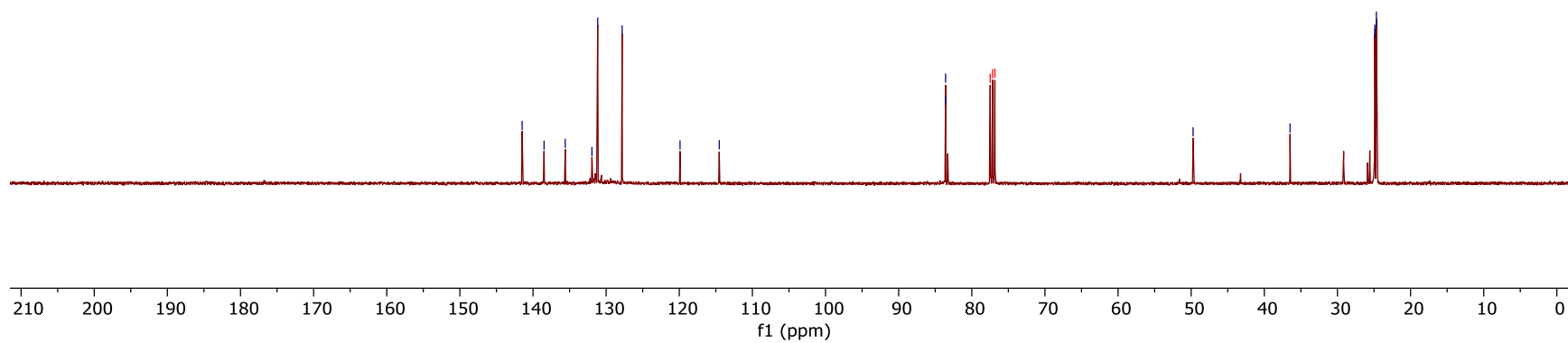
141.49
138.49
135.59
131.95
131.16
127.81
119.90
114.53

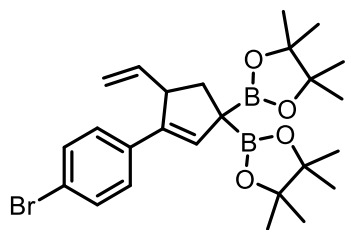
83.62
83.58
77.48 cdc13
77.16 cdc13
76.84 cdc13

49.74

36.48

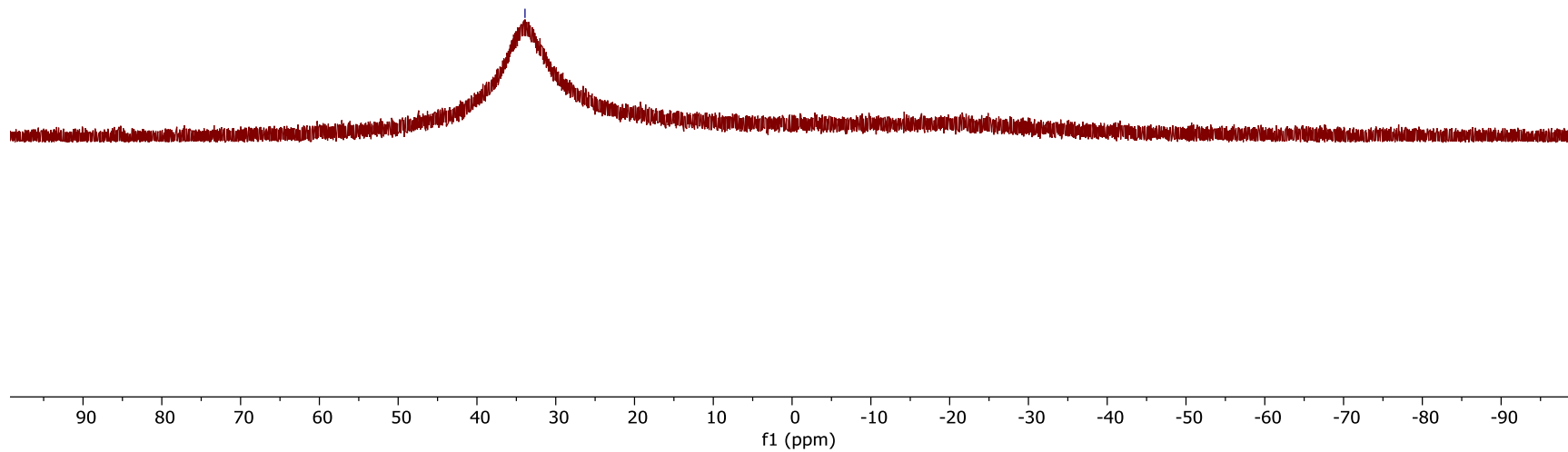
24.89
24.86
24.68
24.65

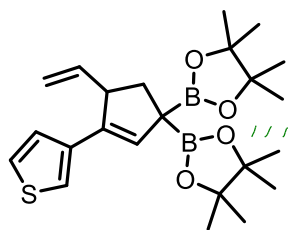




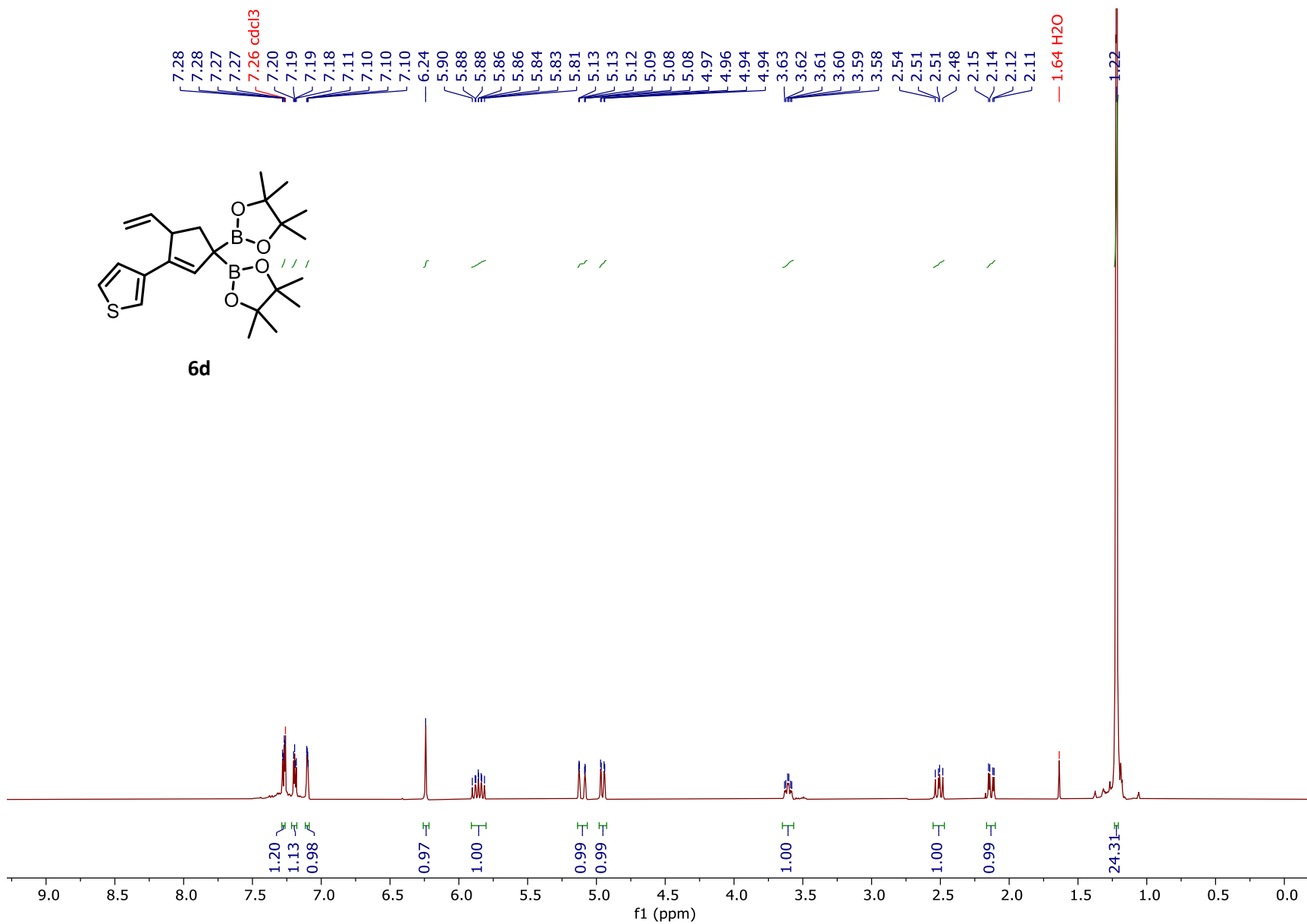
6c

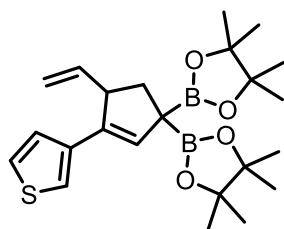
— 33.90





6d





6d

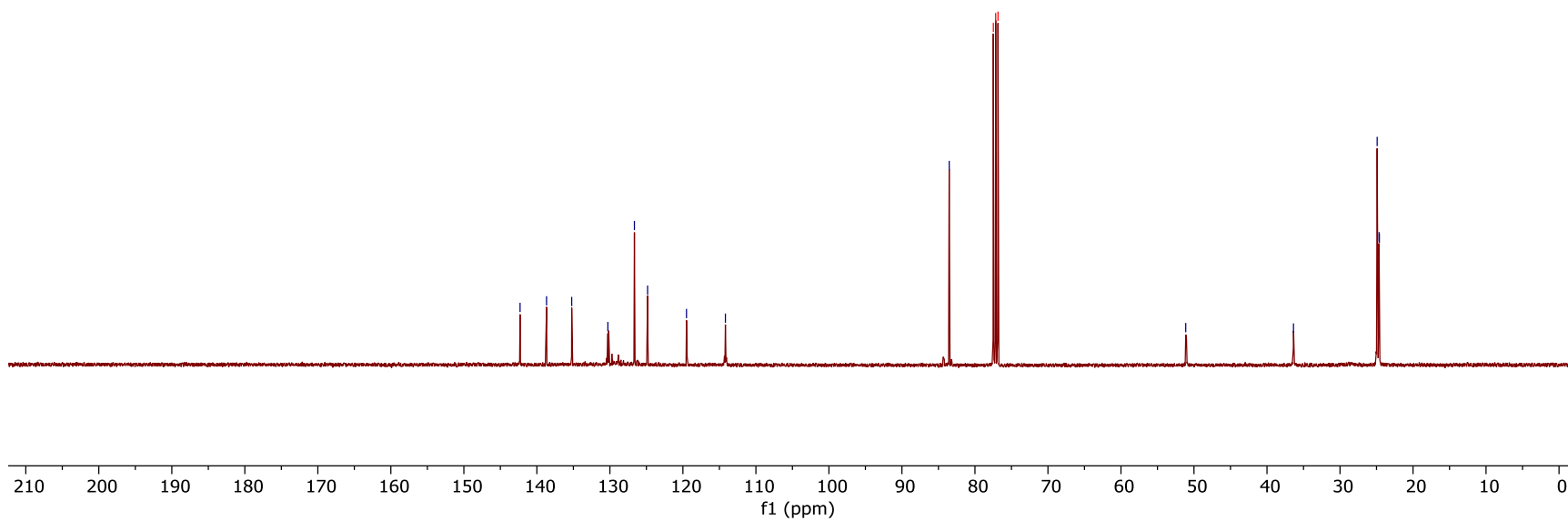
142.30
138.67
135.23
130.28
126.64
124.84
119.51
114.18

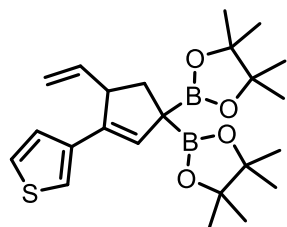
83.52
77.48 cdc13
77.16 cdc13
76.84 cdc13

51.13

36.37

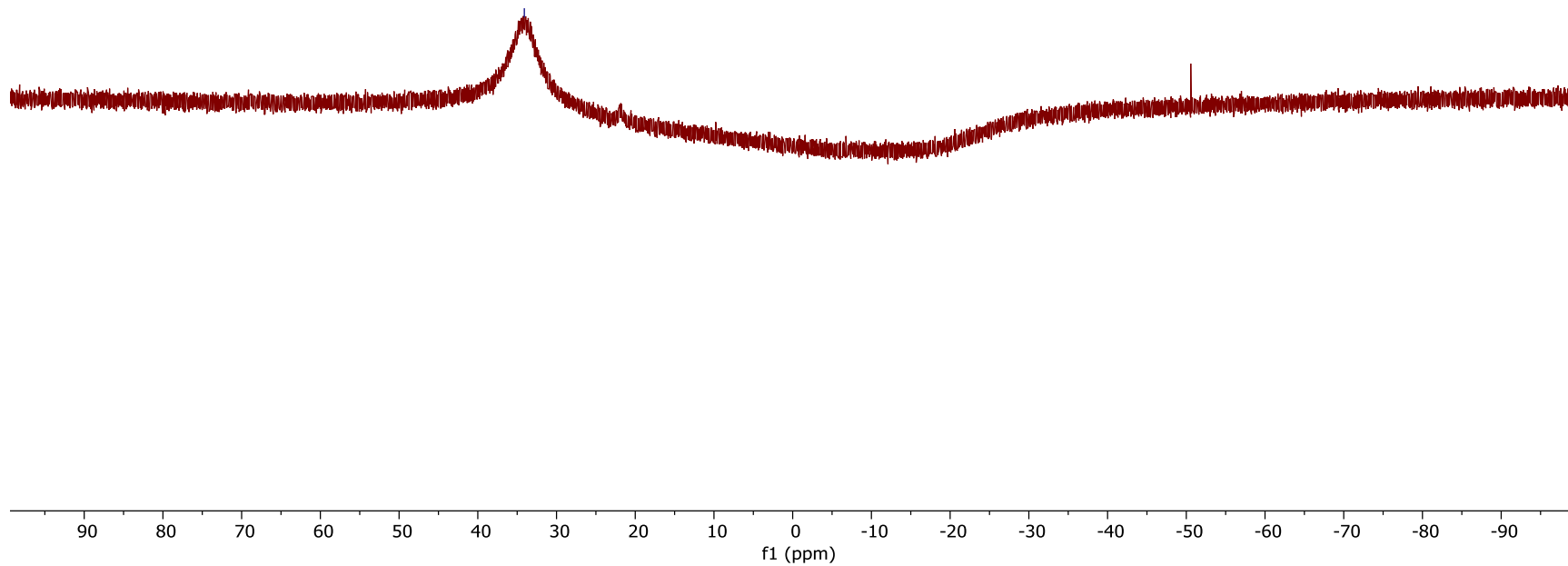
24.91
24.65
24.61

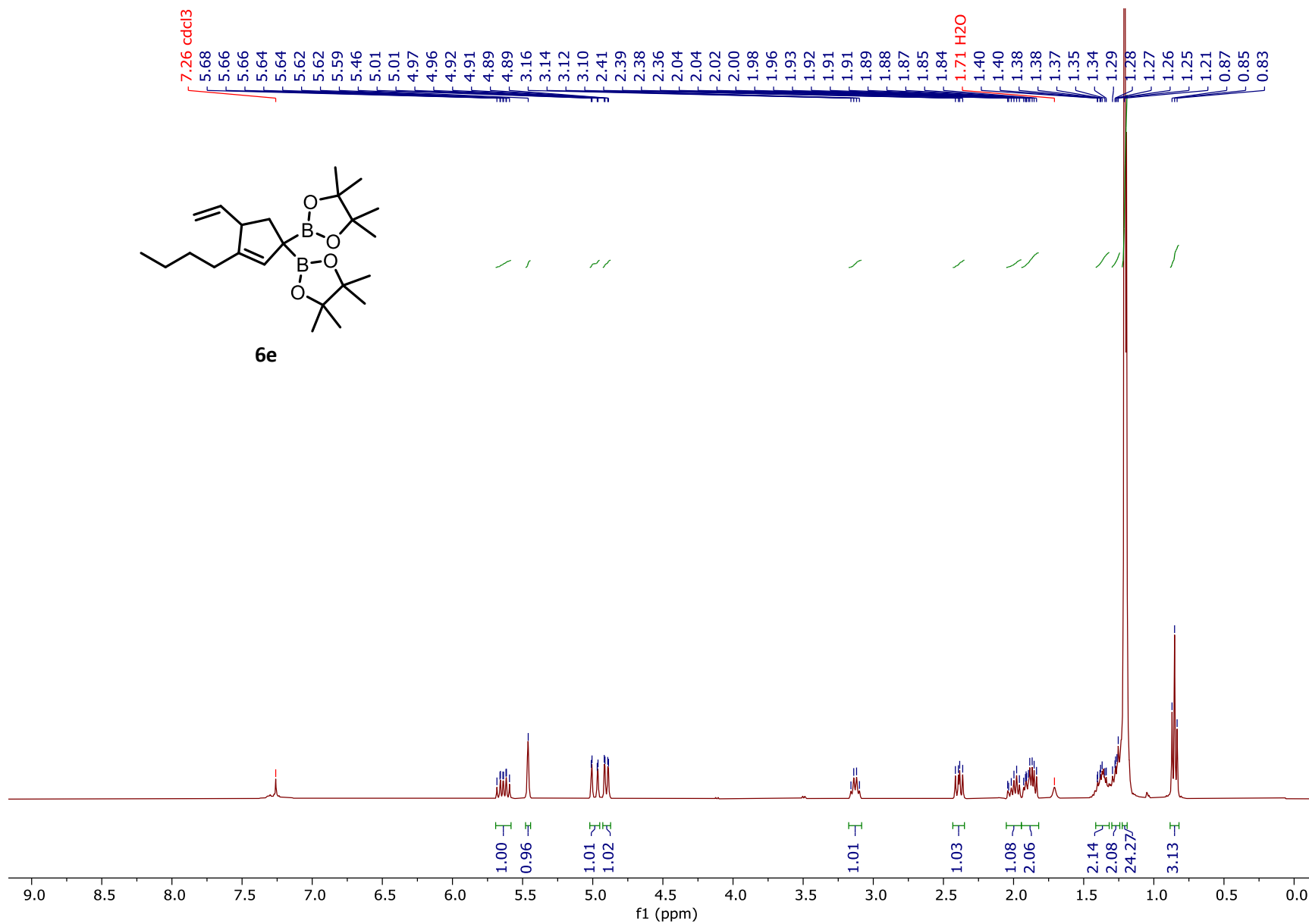


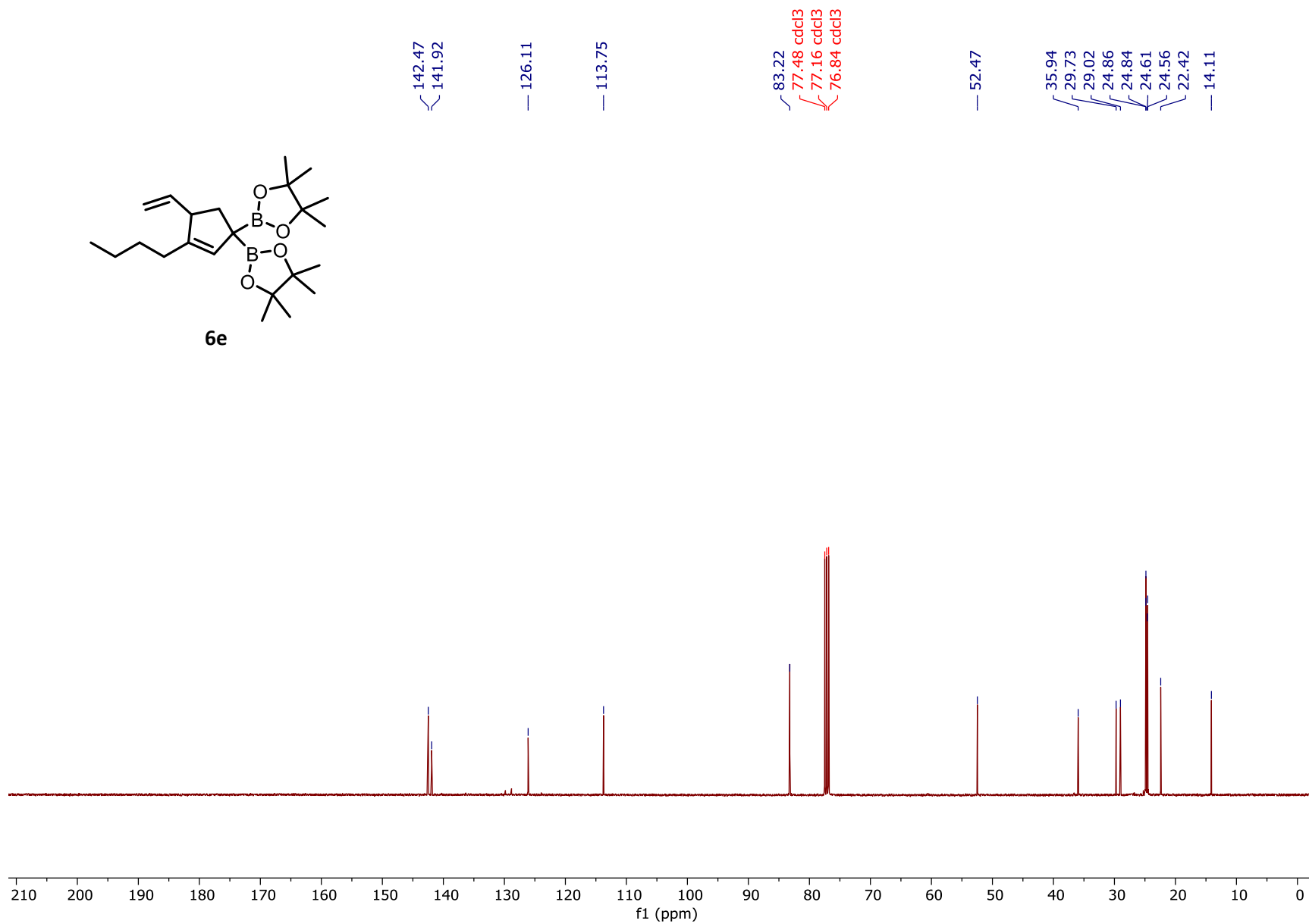
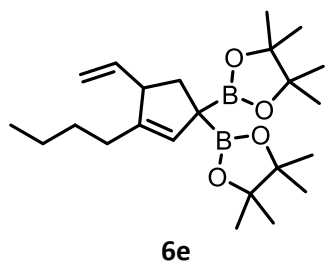


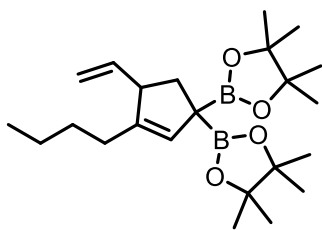
6d

— 34.09



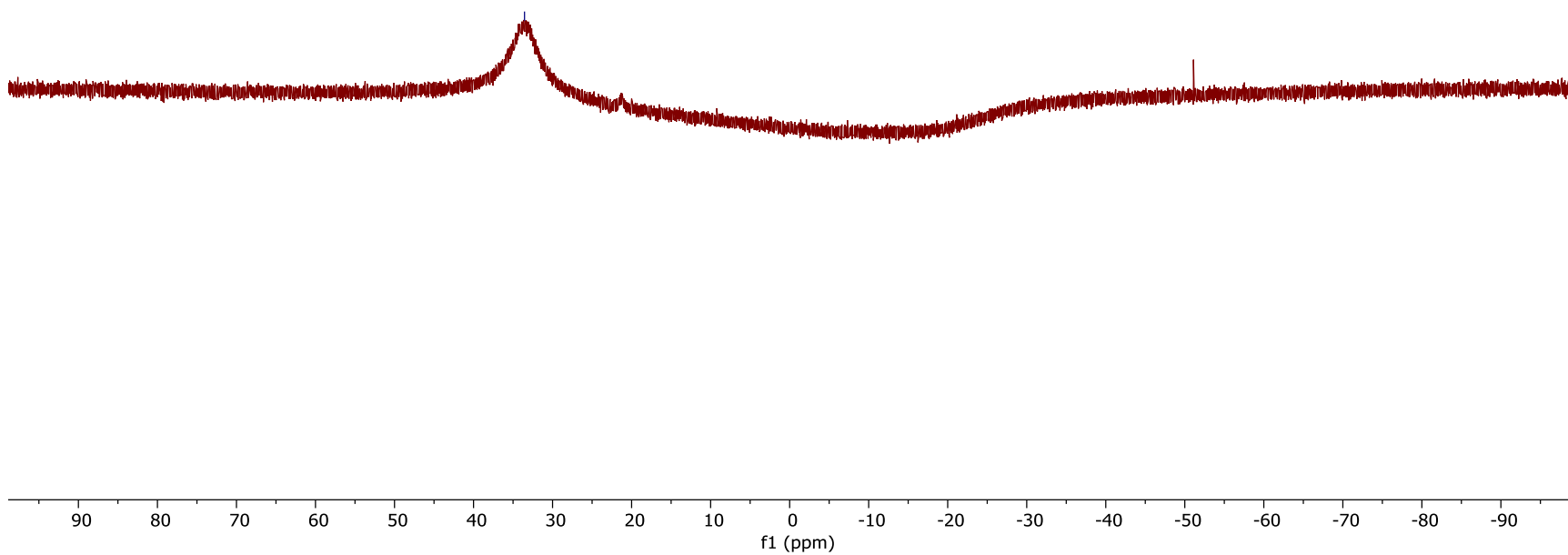


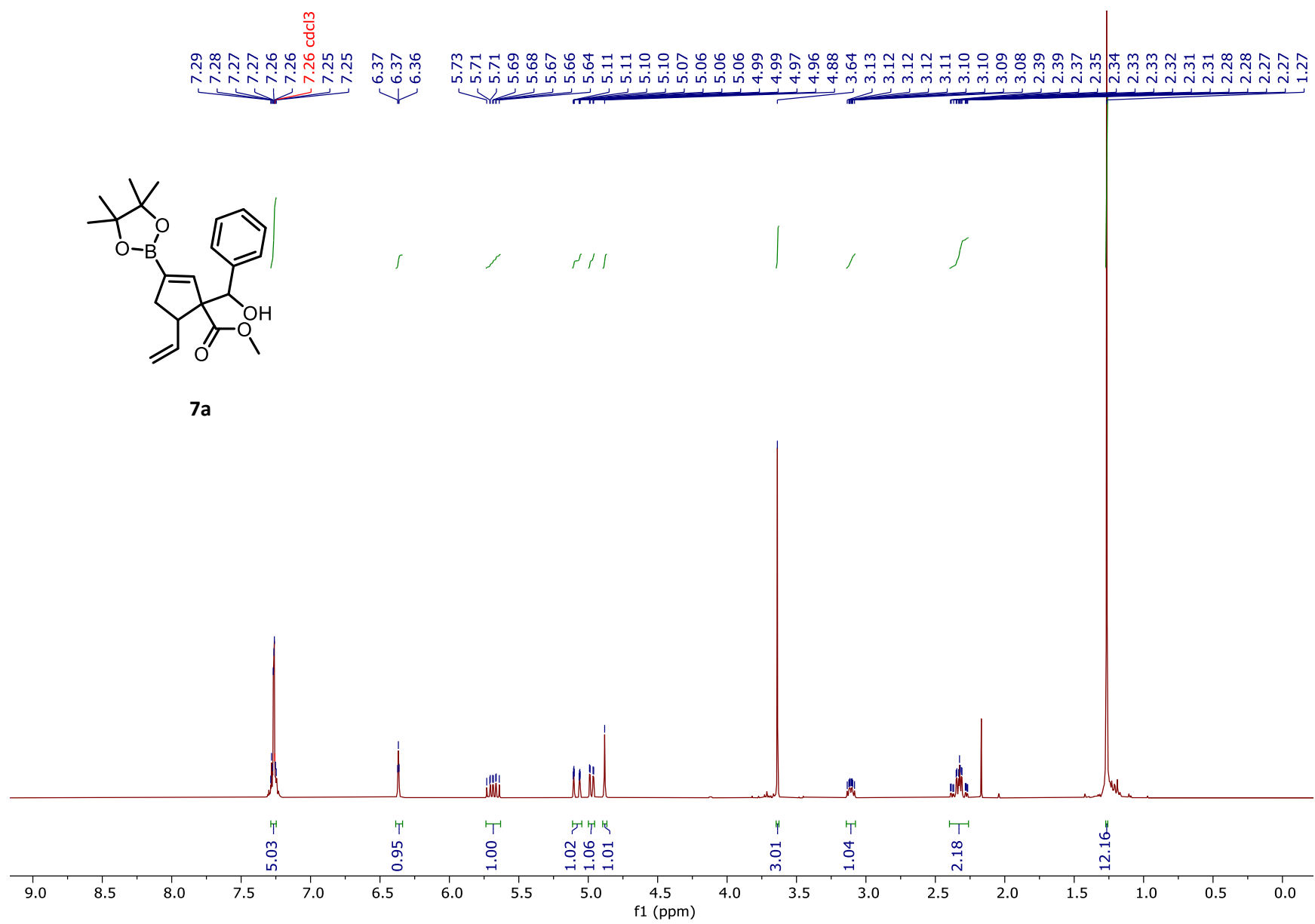
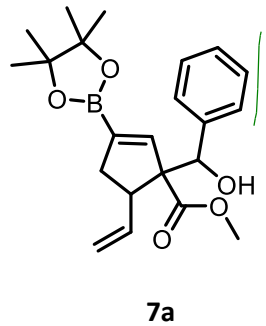


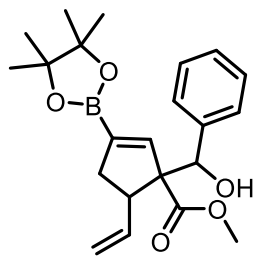


6e

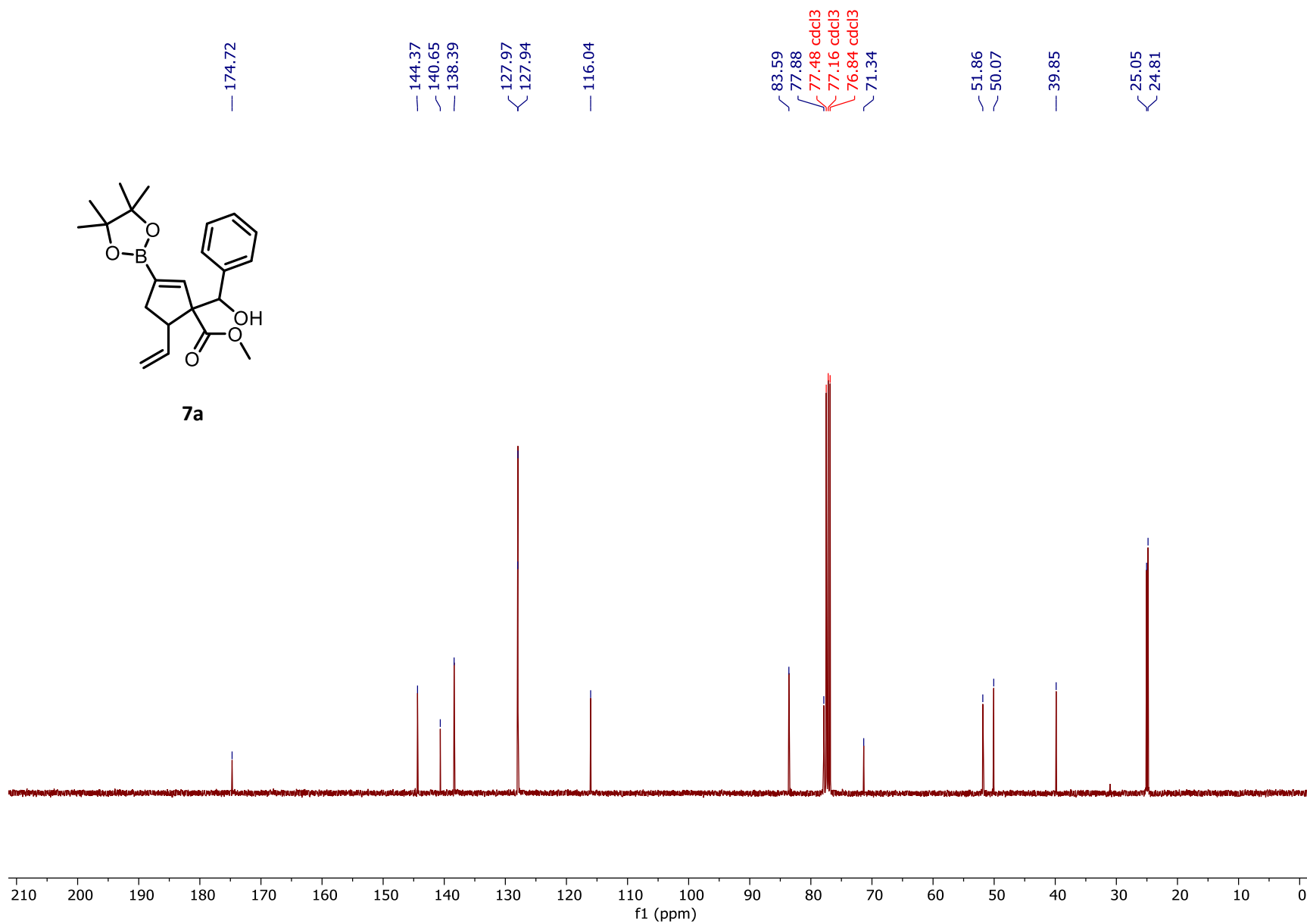
— 33.55

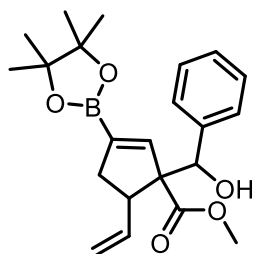






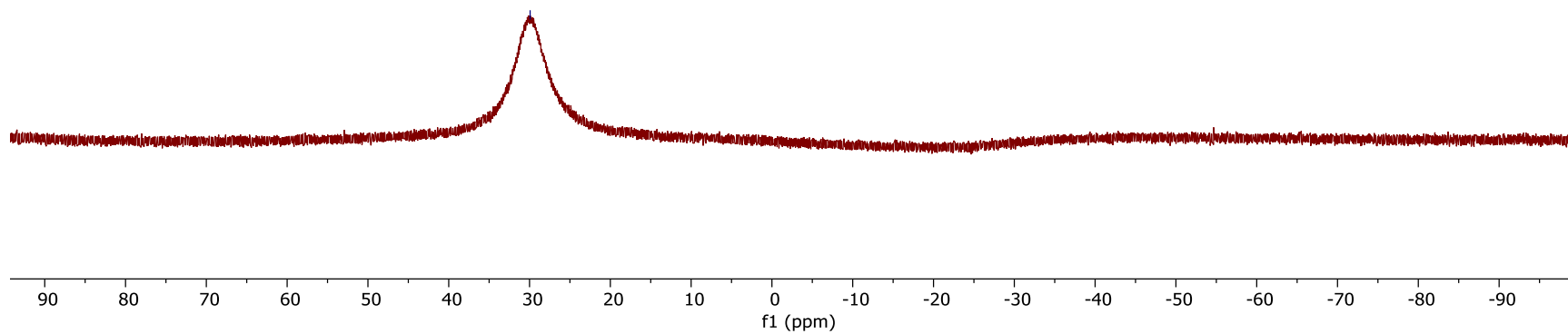
7a

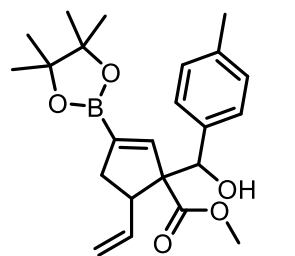




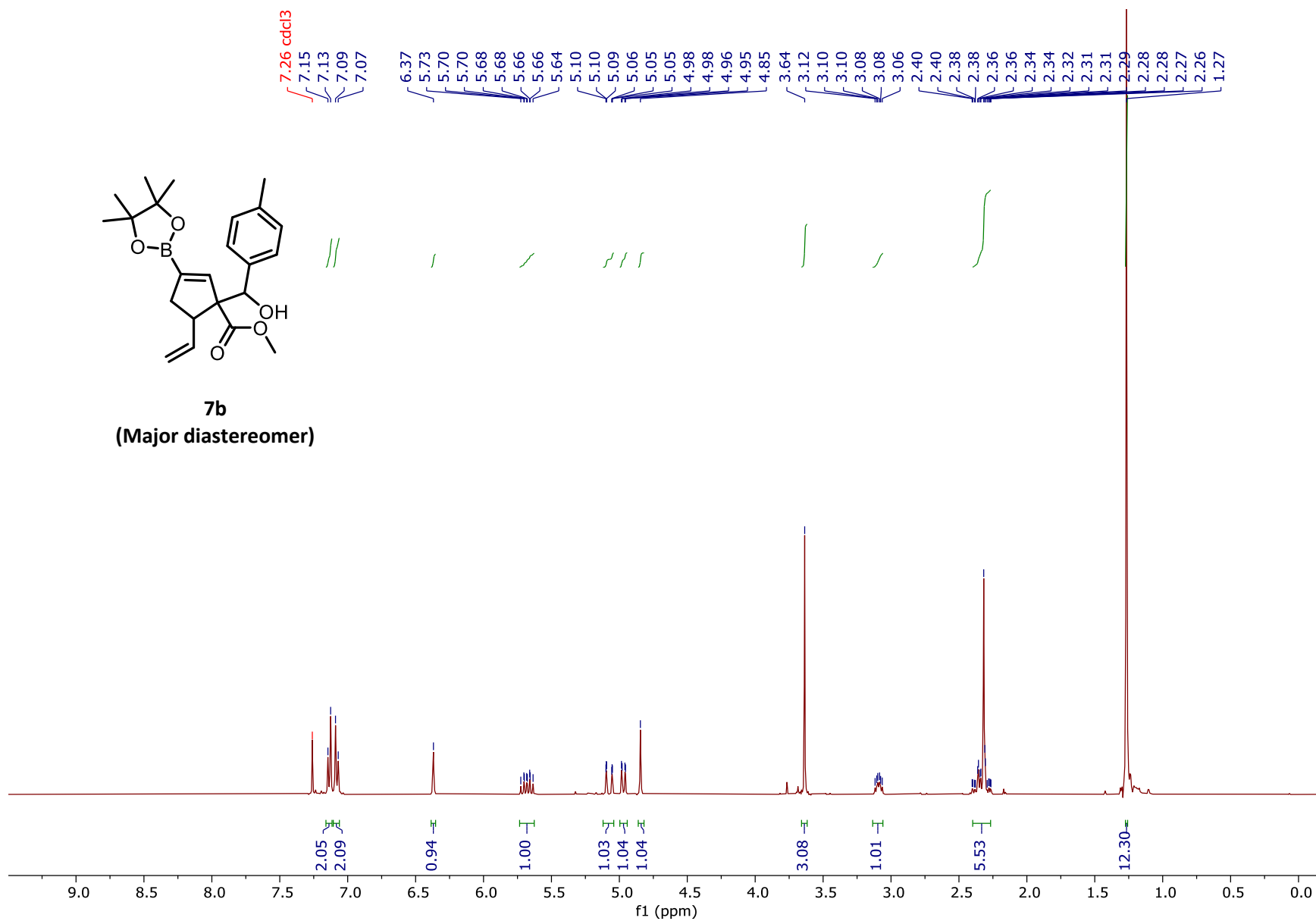
7a

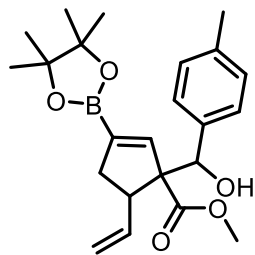
— 29.92



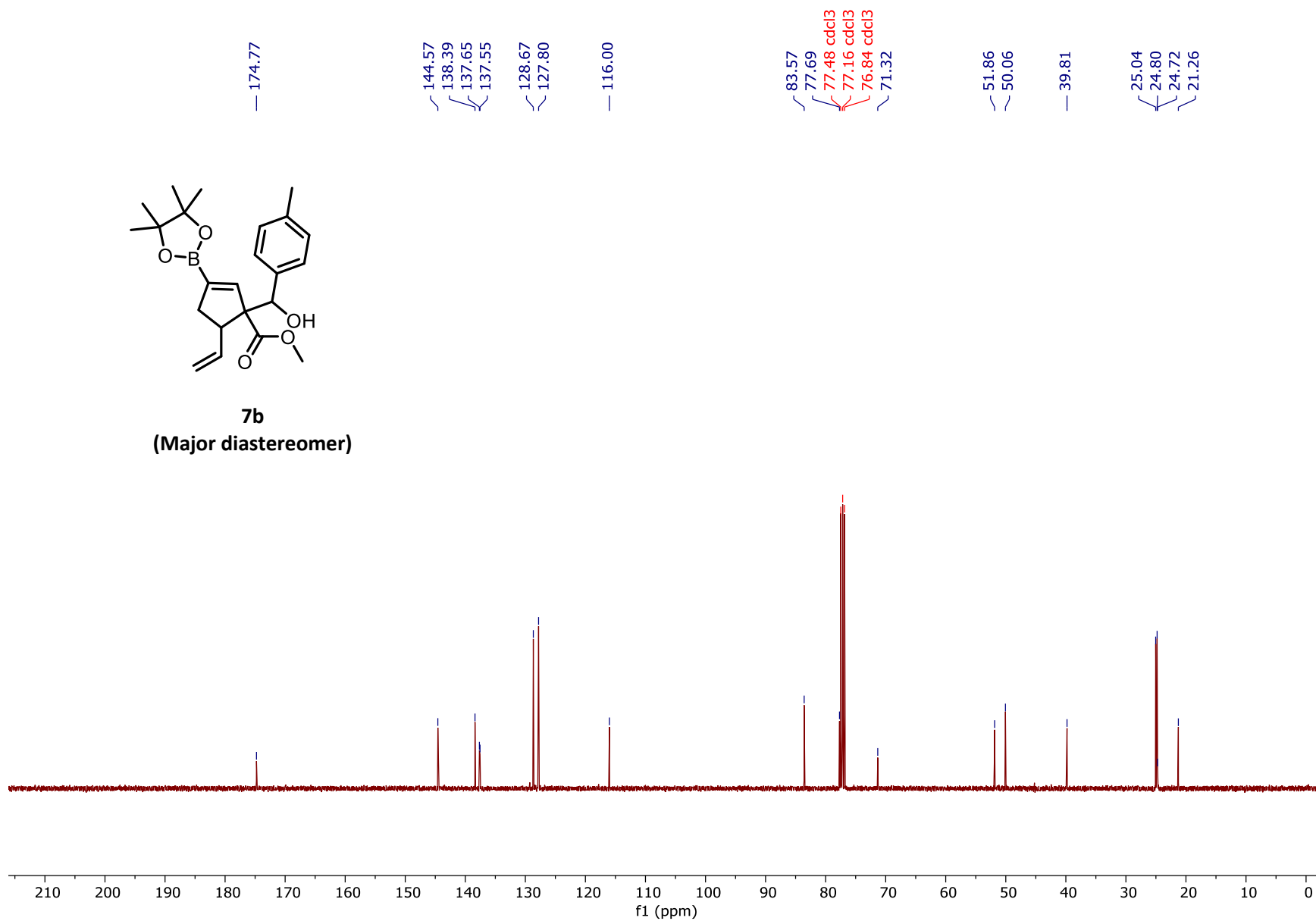


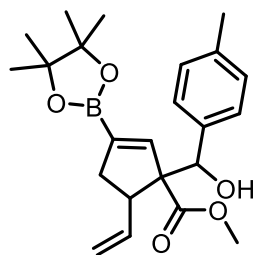
7b
(Major diastereomer)





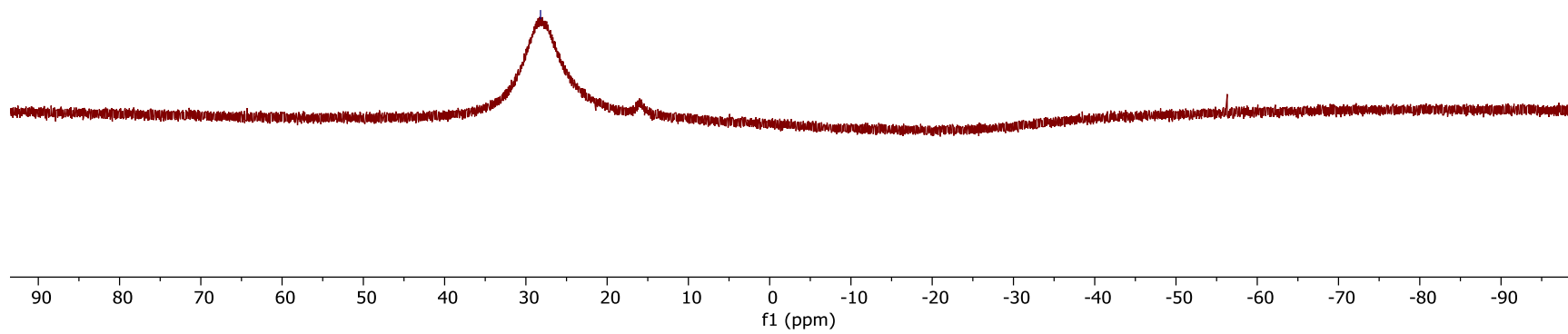
7b
(Major diastereomer)

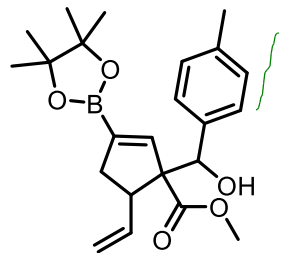




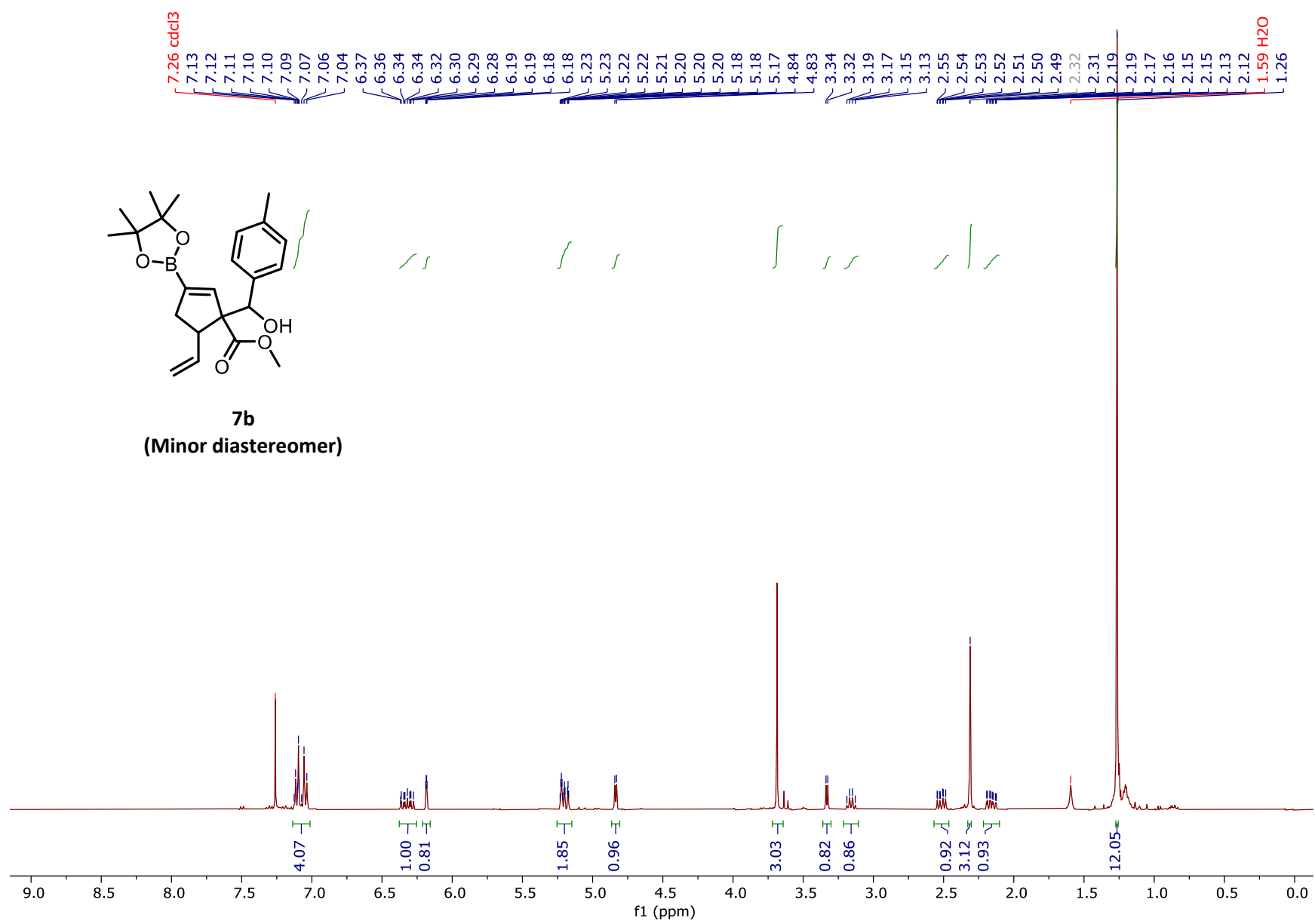
7b
(Major diastereomer)

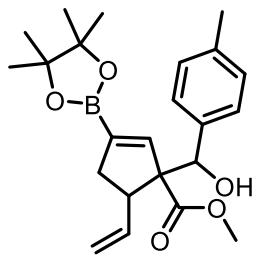
— 28.20



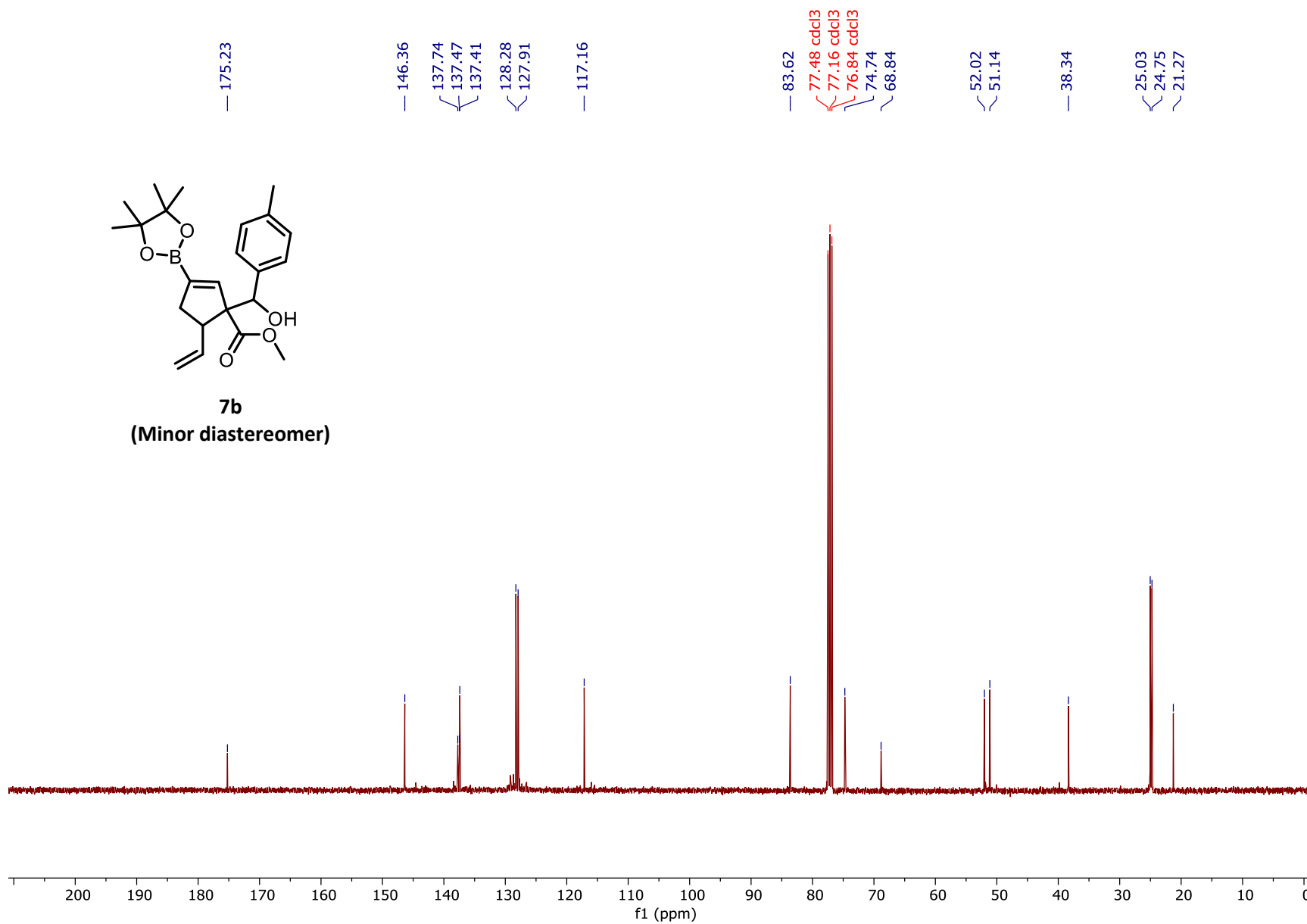


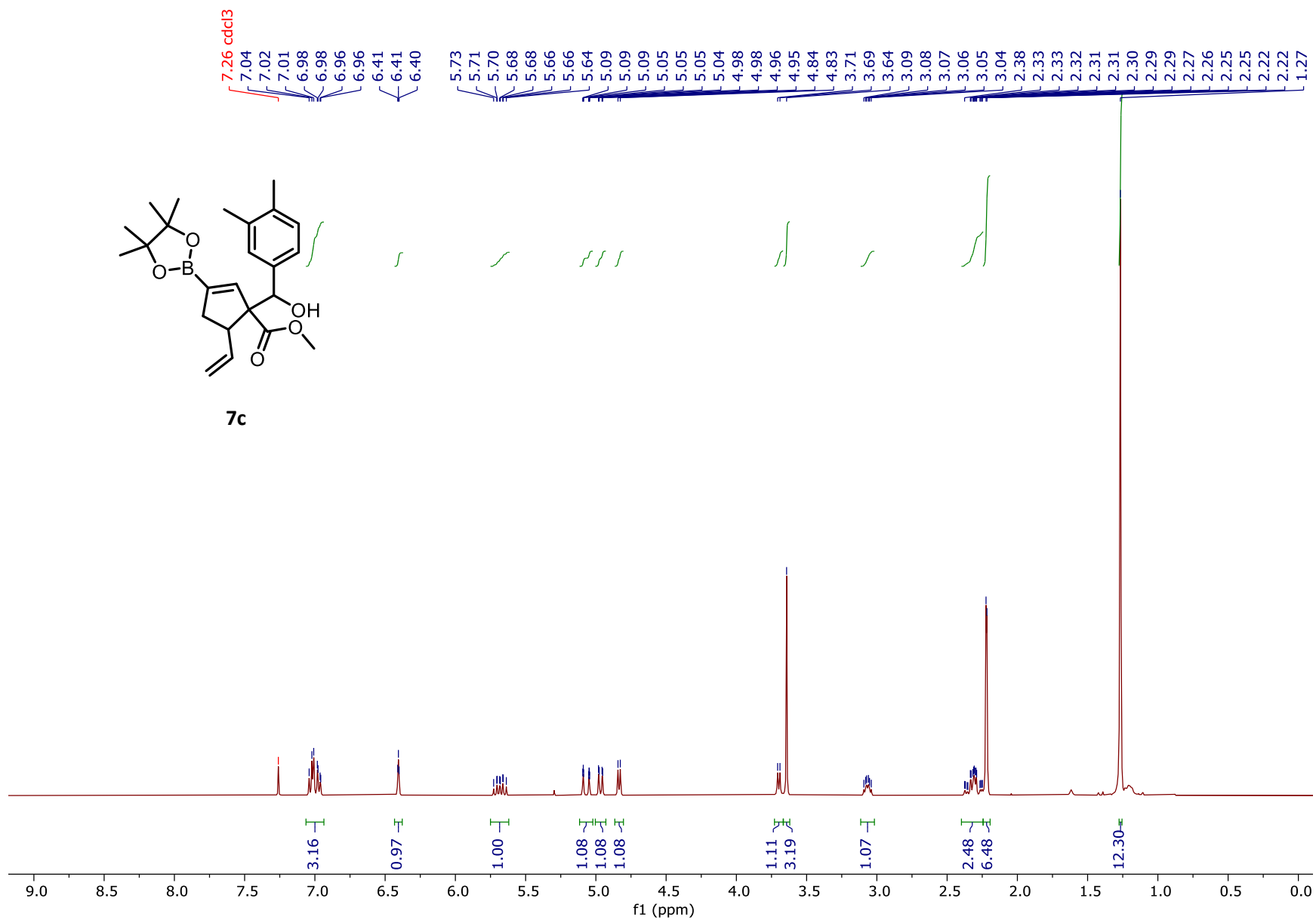
7b
(Minor diastereomer)

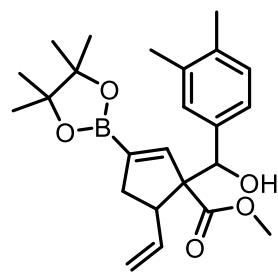




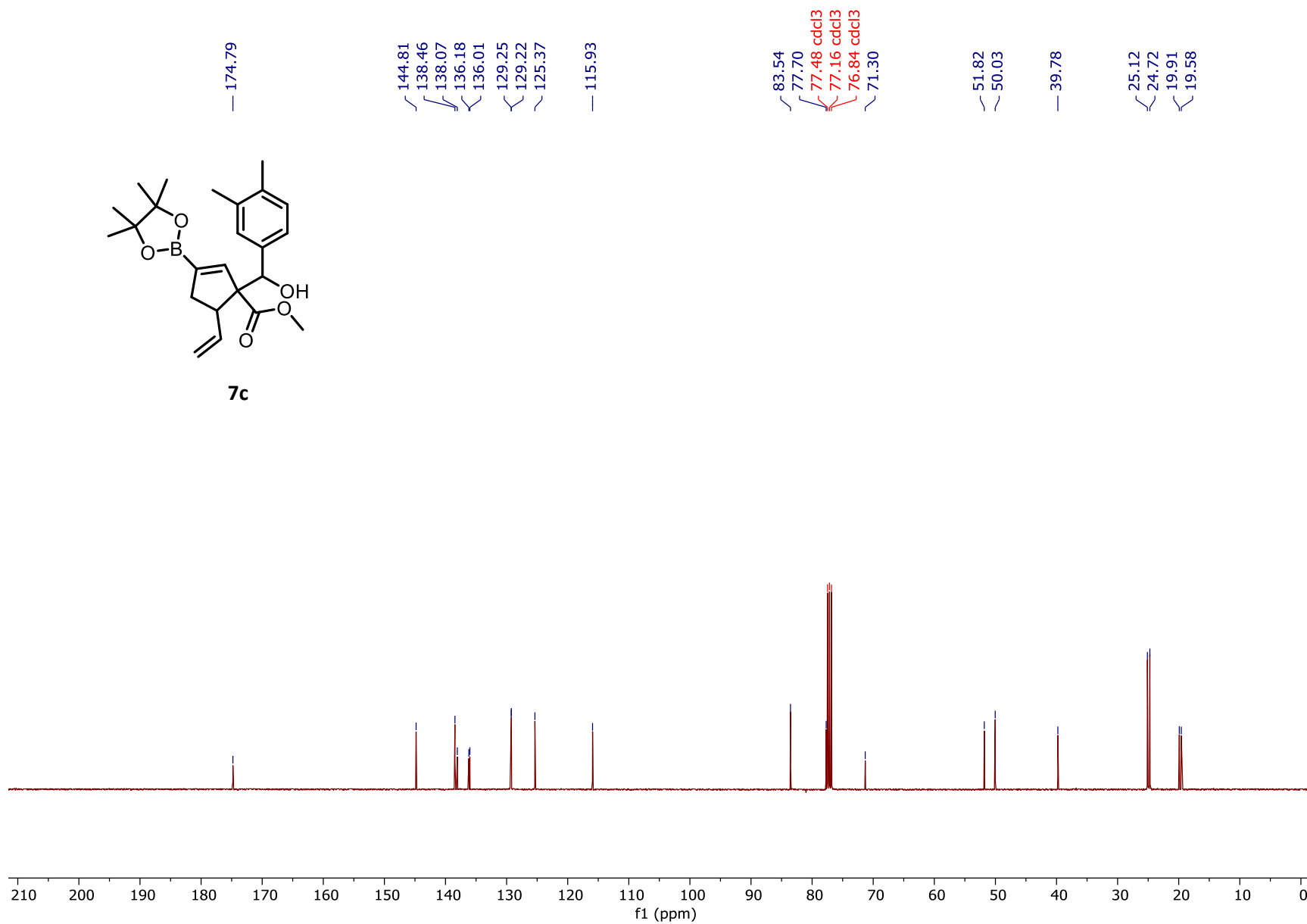
7b
(Minor diastereomer)

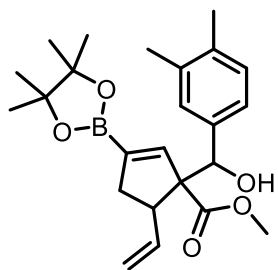






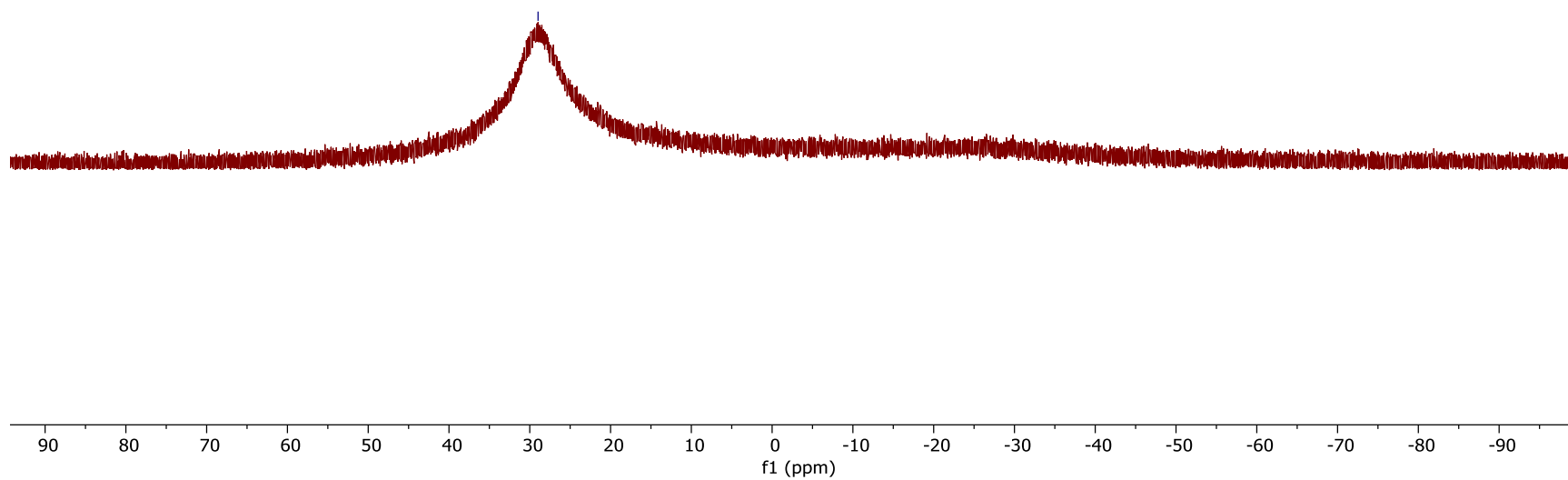
7c

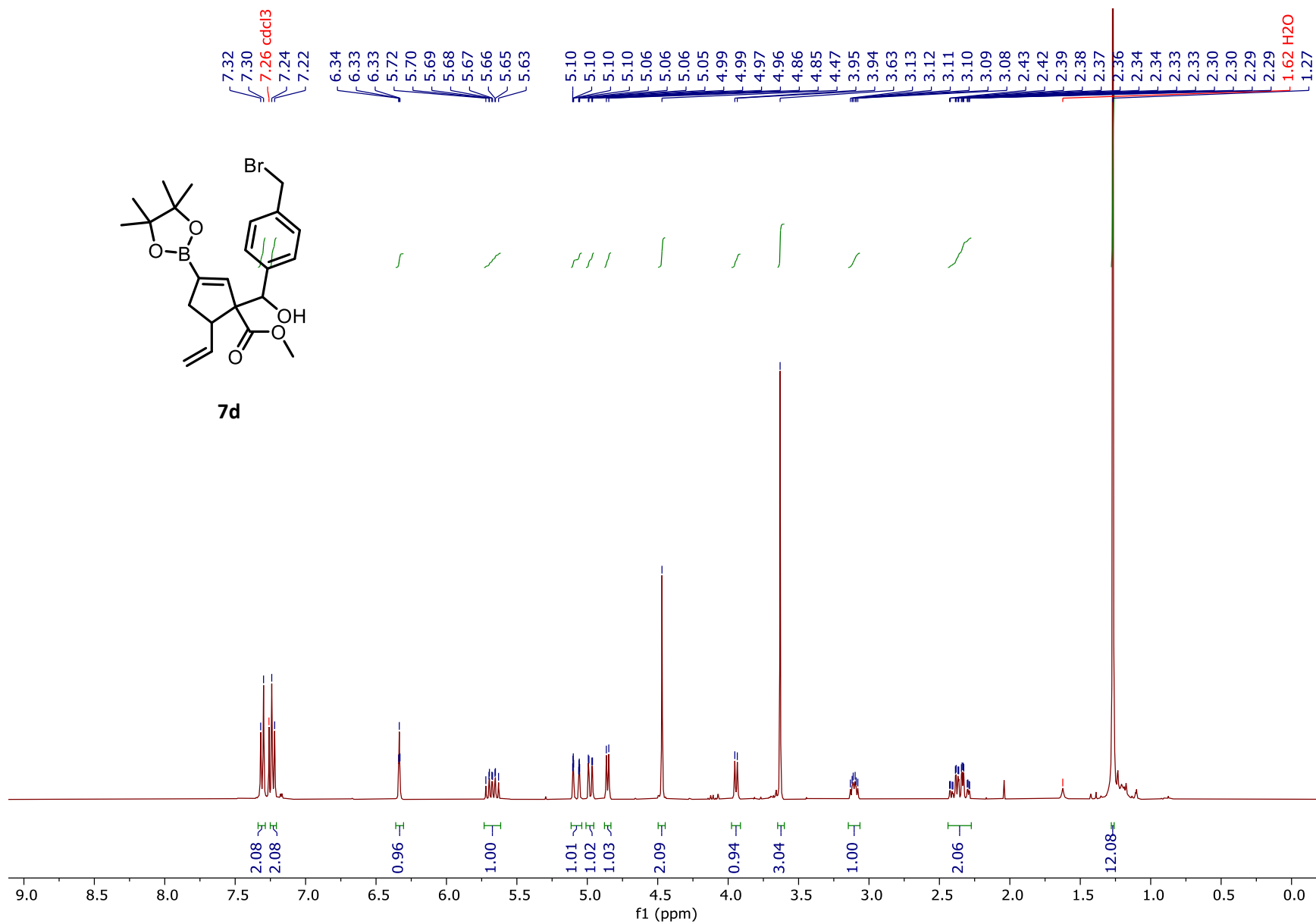


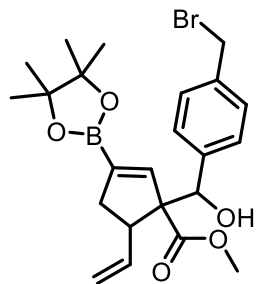


7c

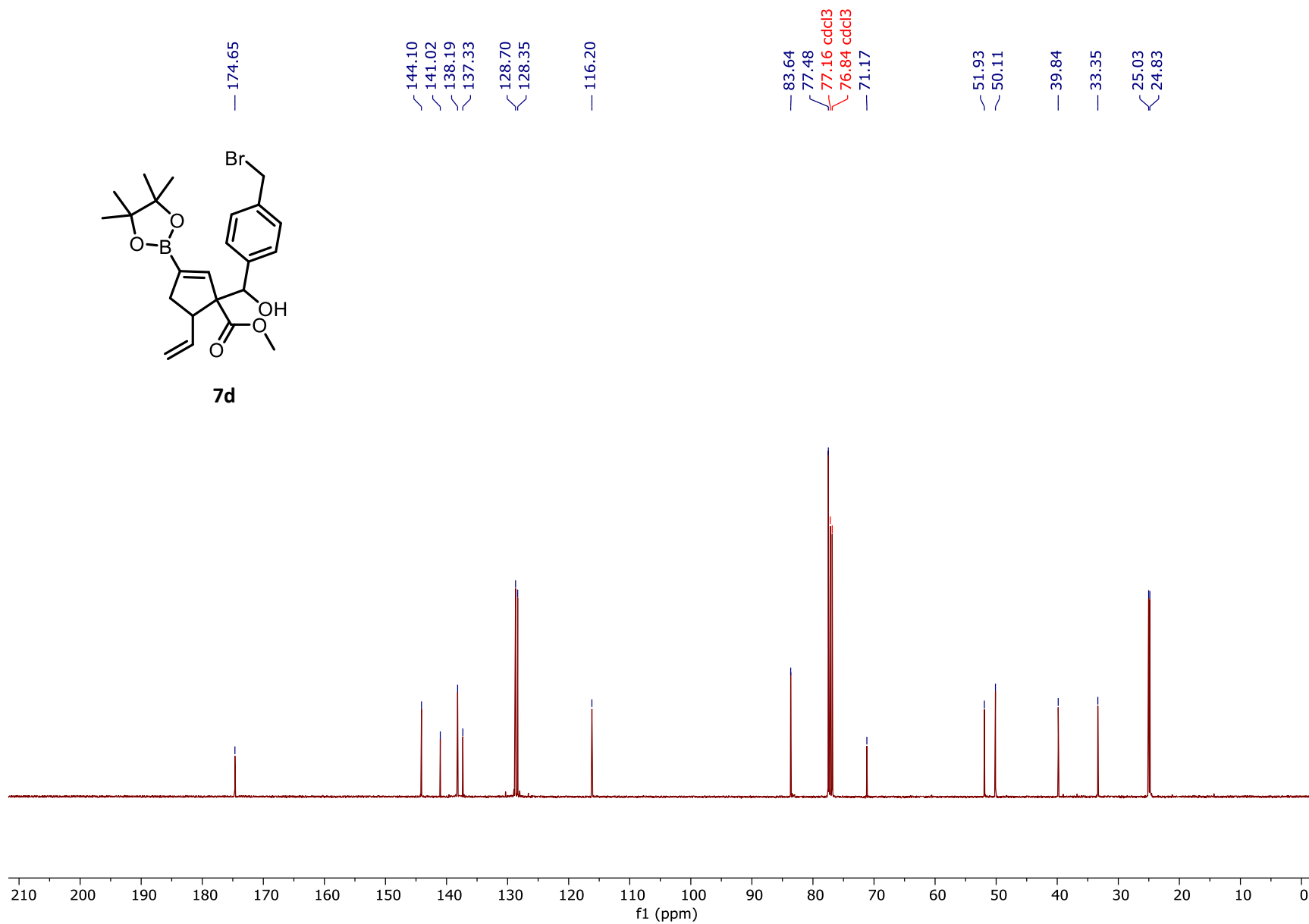
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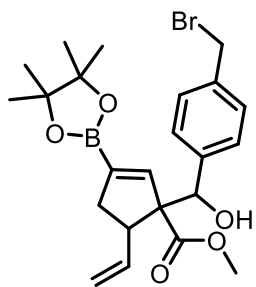






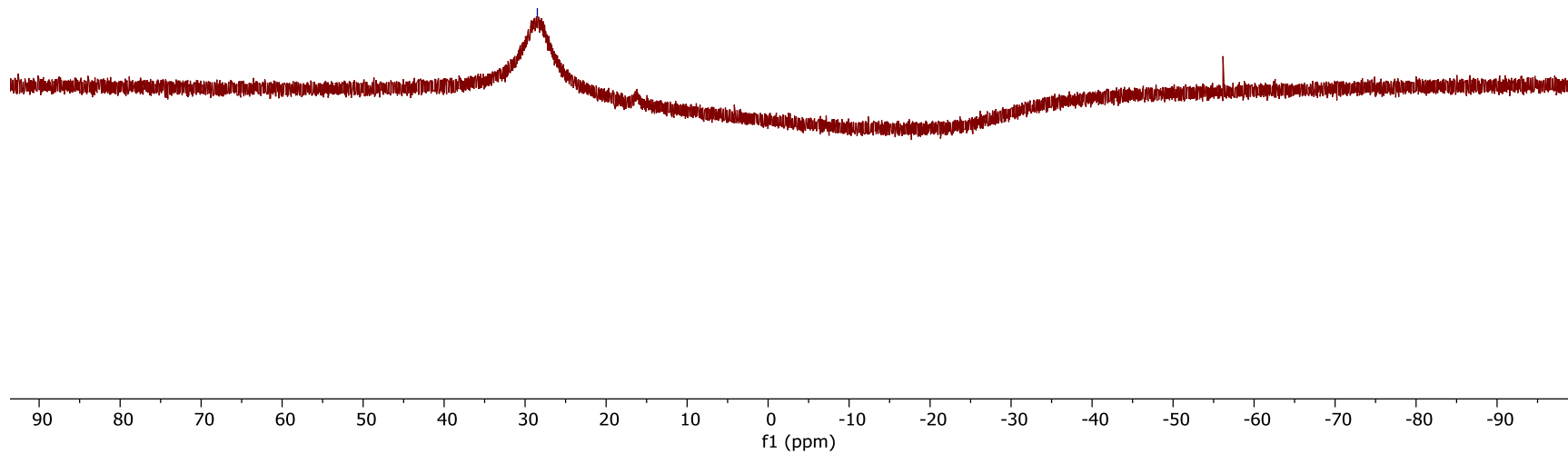
7d

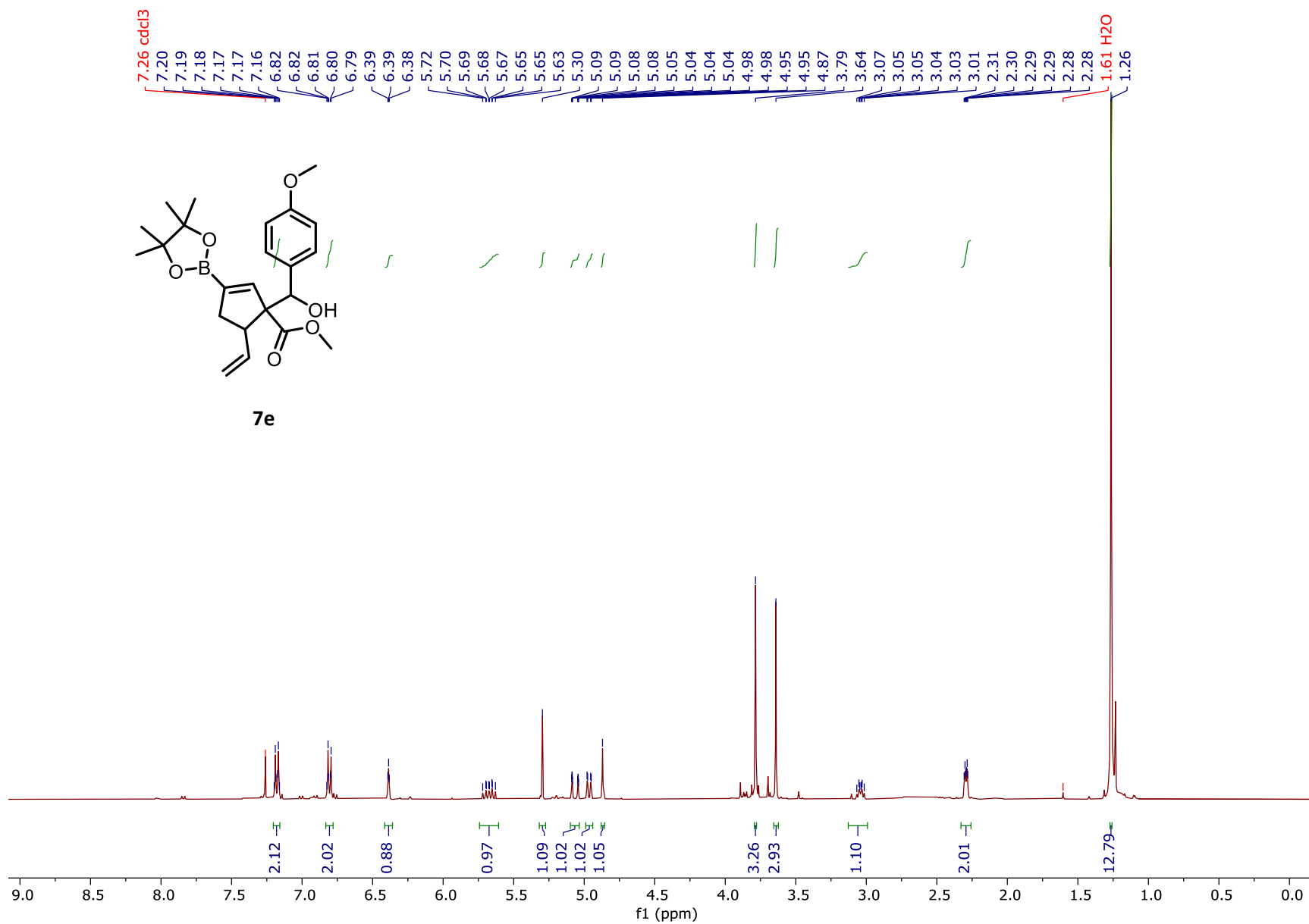


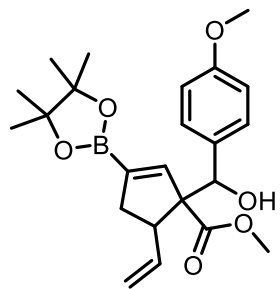


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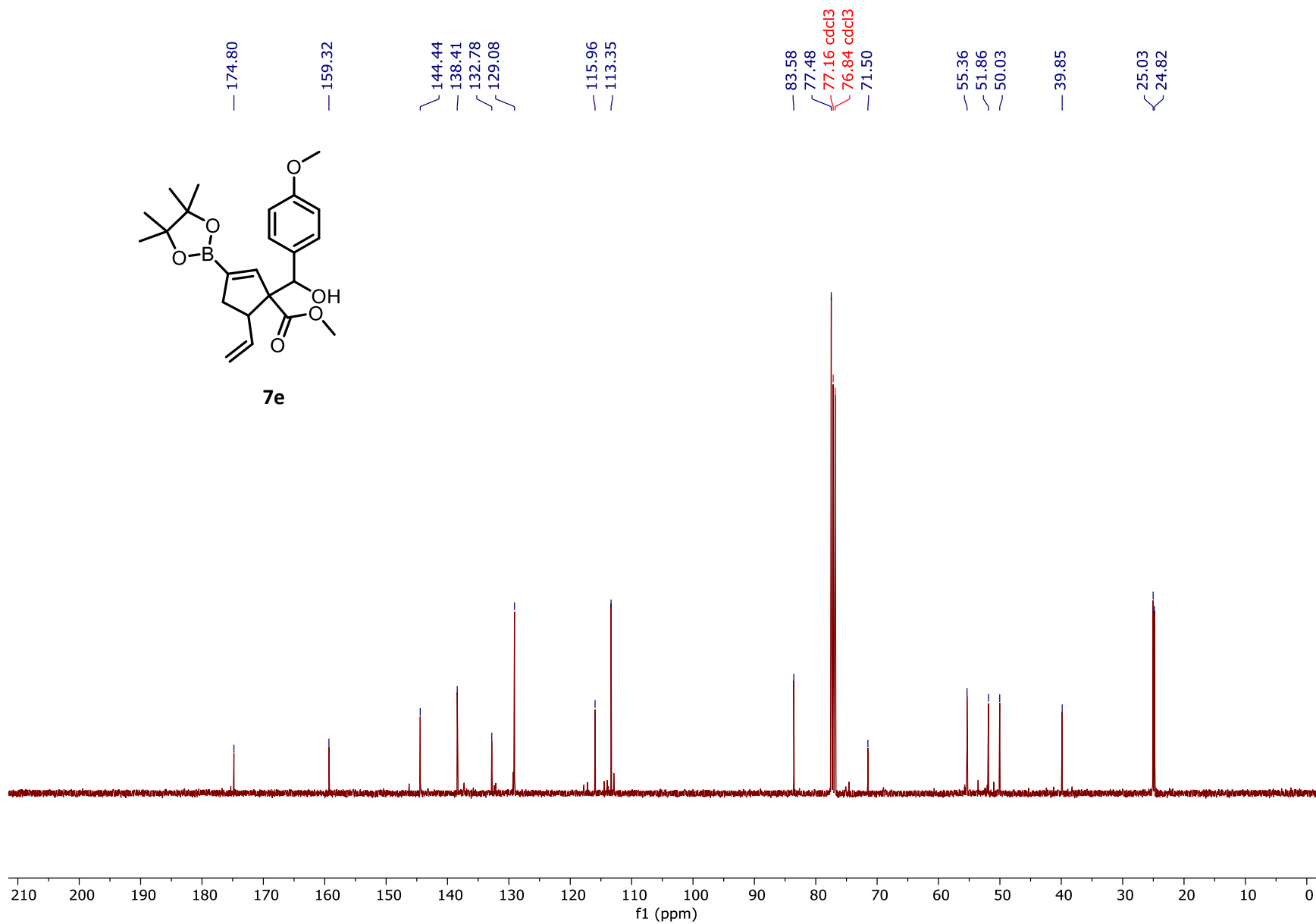
— 28.49

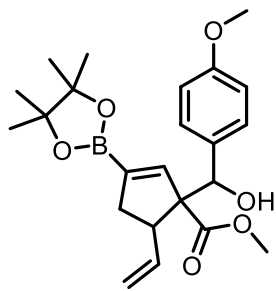






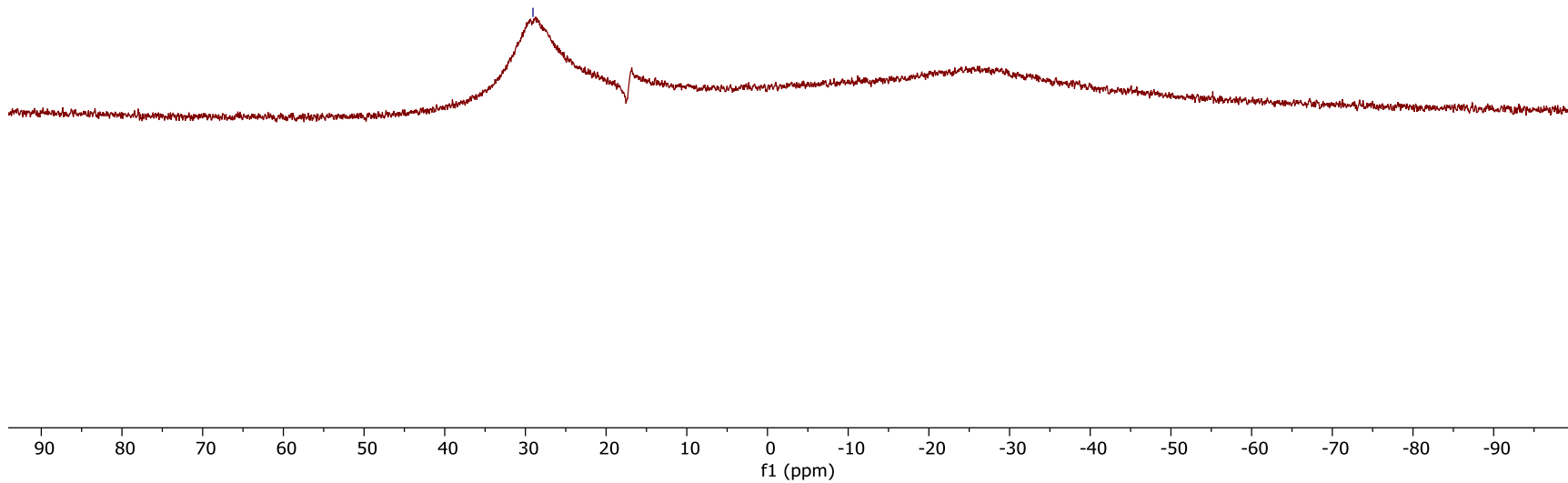
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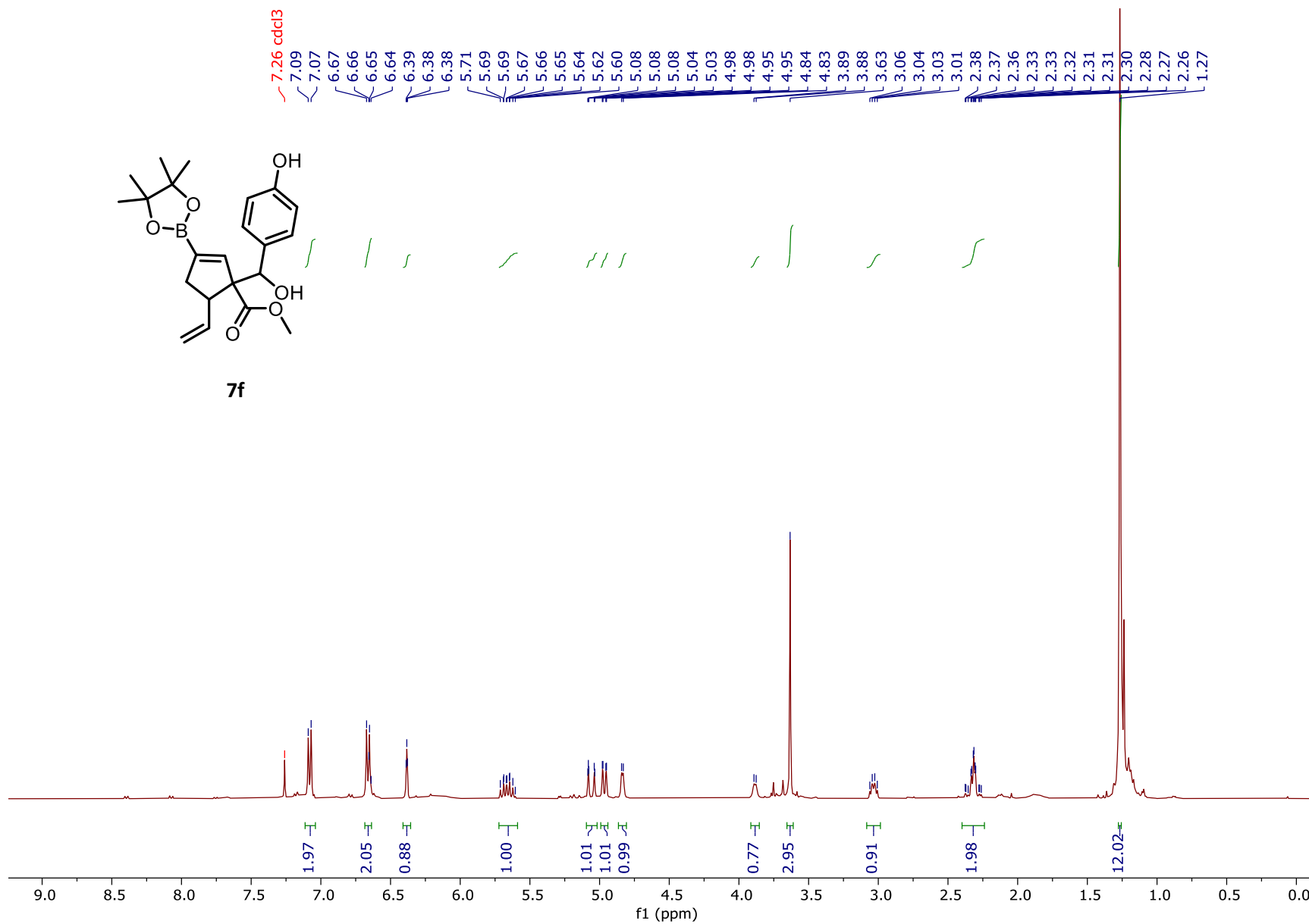


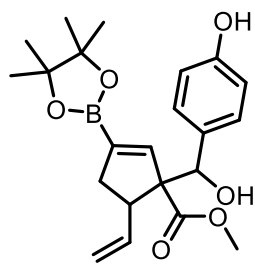


7e

— 29.06







7f

— 174.89

— 155.72

— 144.55

— 138.27

— 132.35

— 129.22

— 116.08

— 114.91

— 83.75

— 77.52

— 77.48 cdc13

— 77.16 cdc13

— 76.84 cdc13

— 71.42

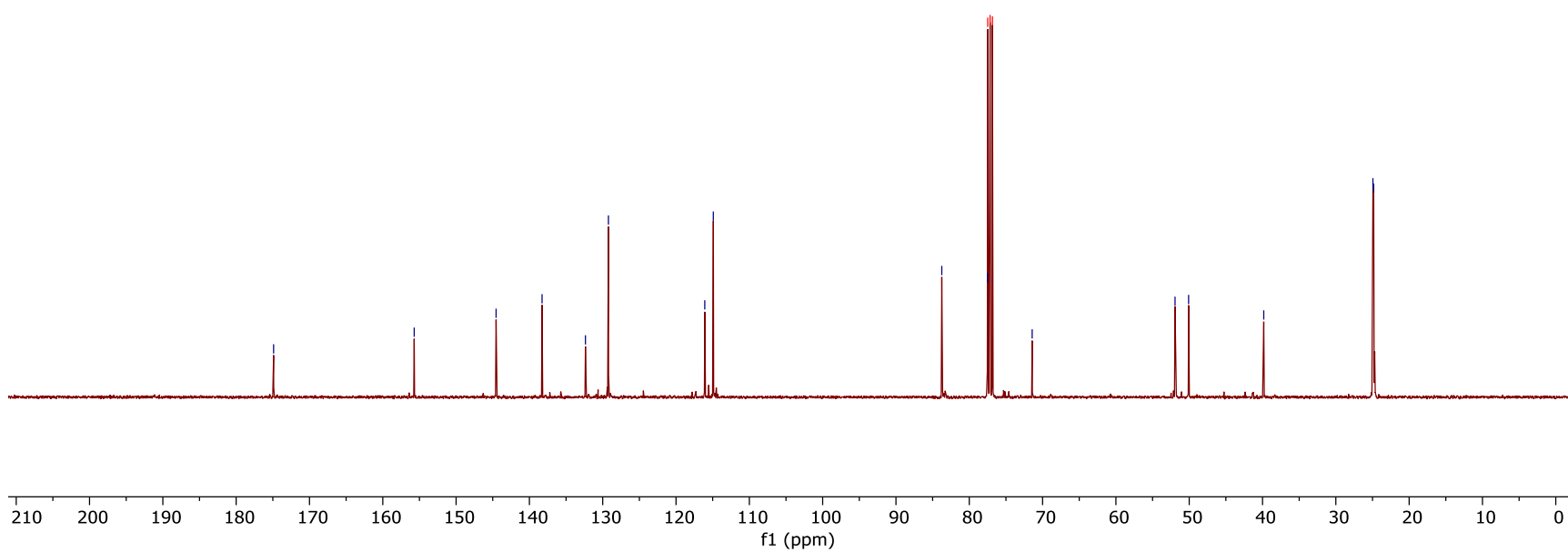
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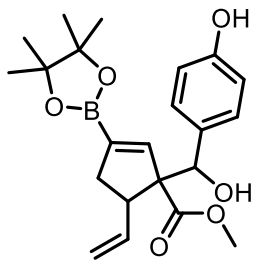
— 50.08

— 39.83

— 24.94

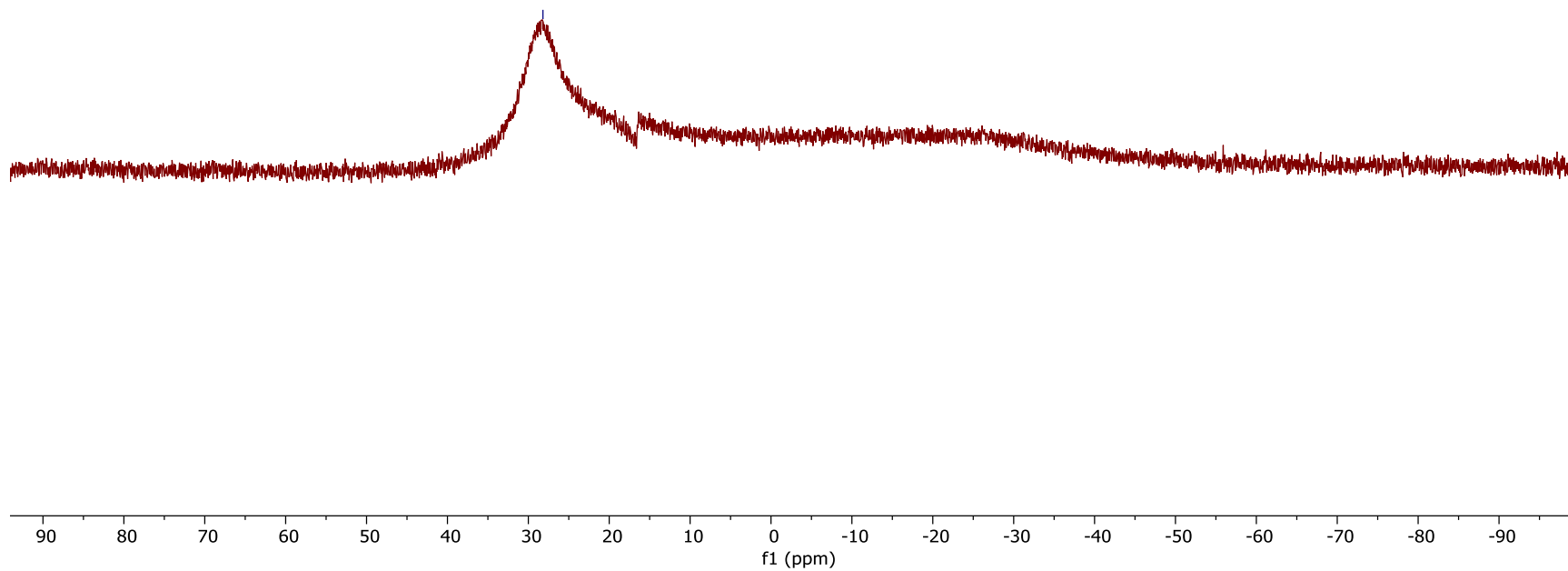
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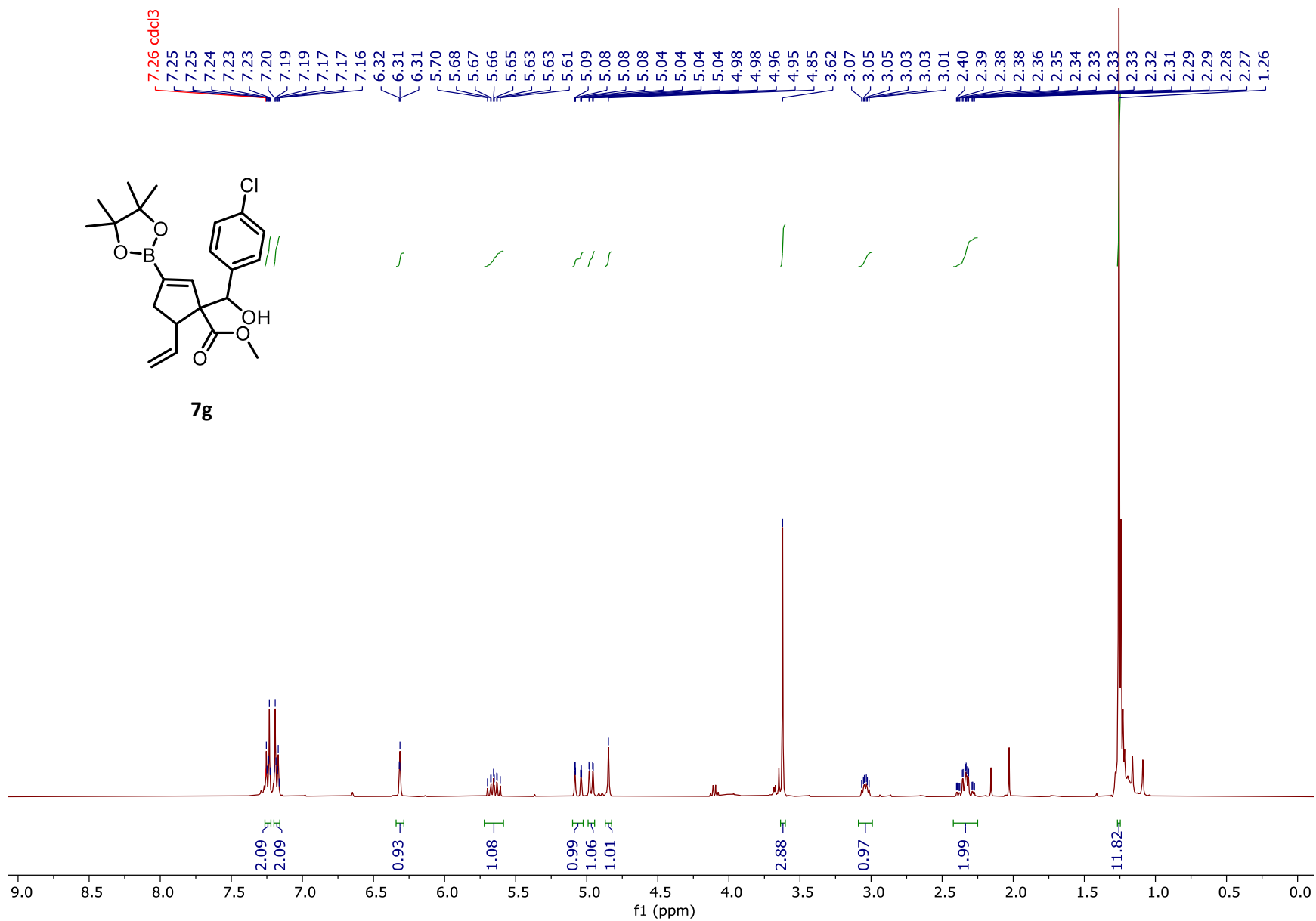


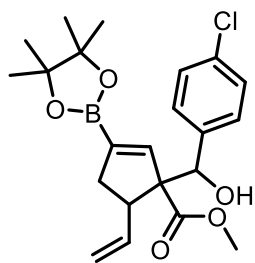


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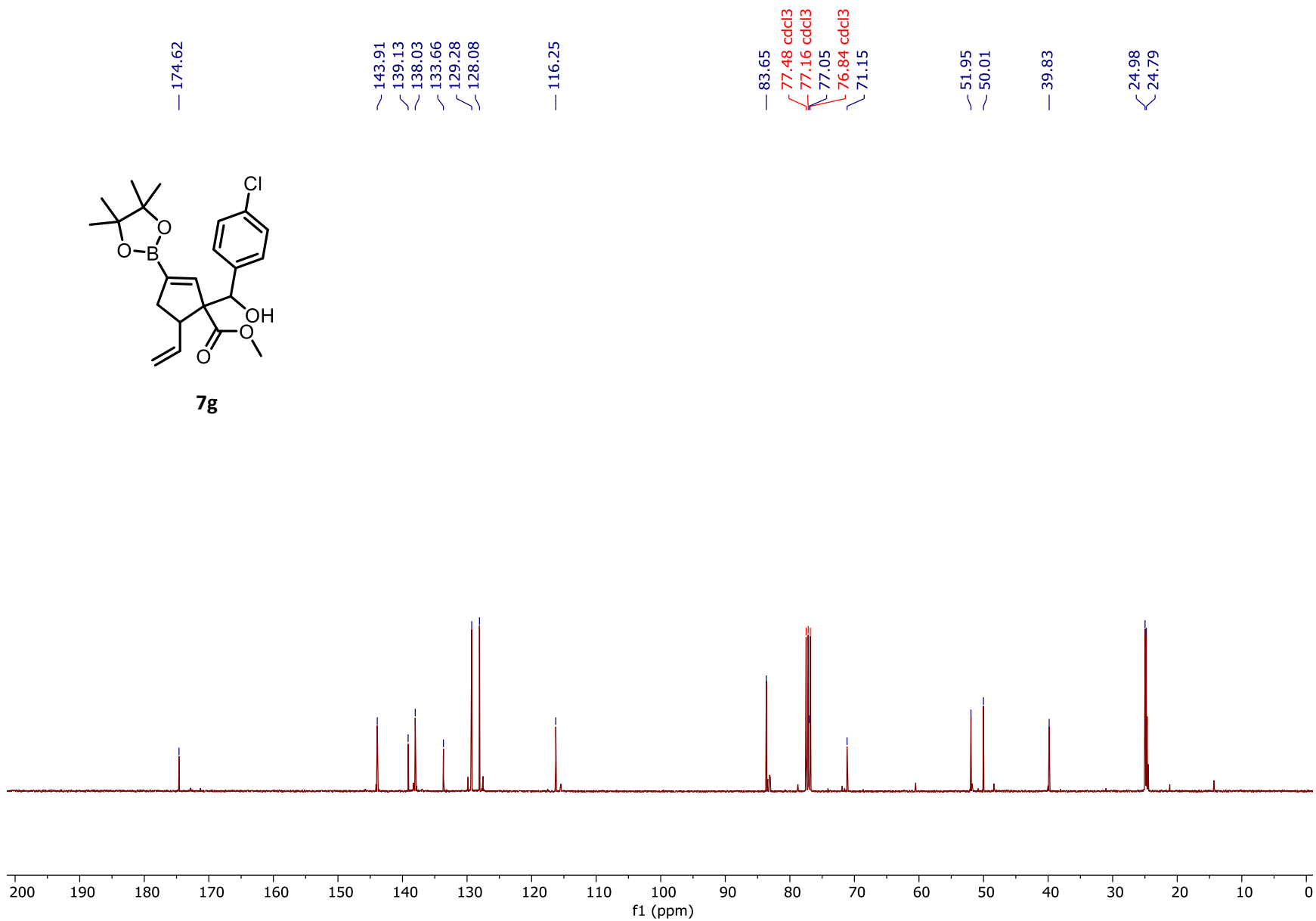
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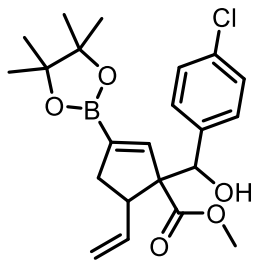






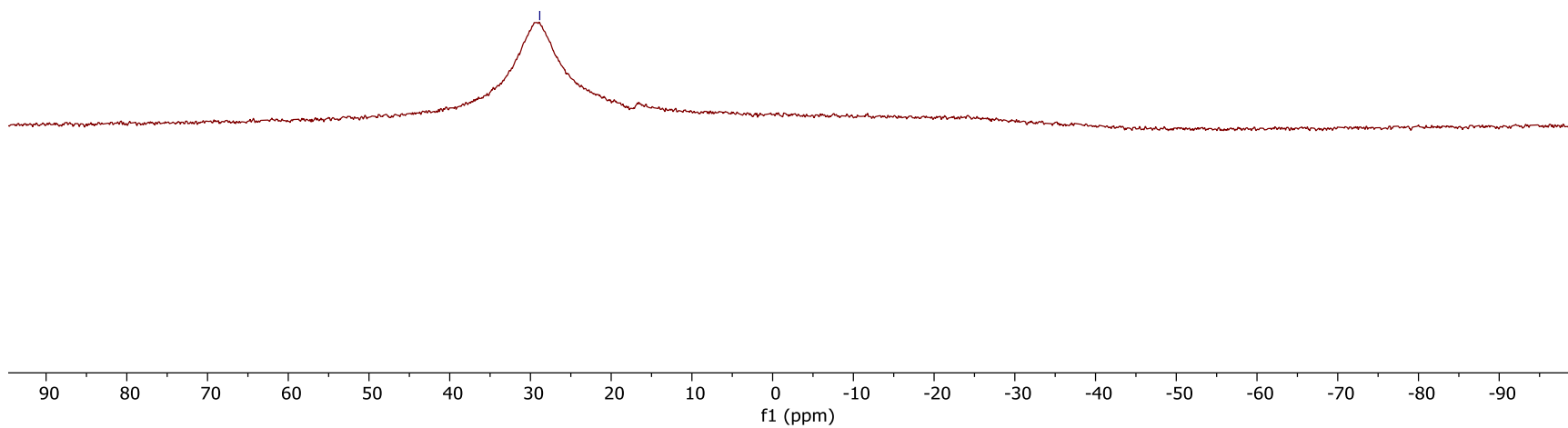
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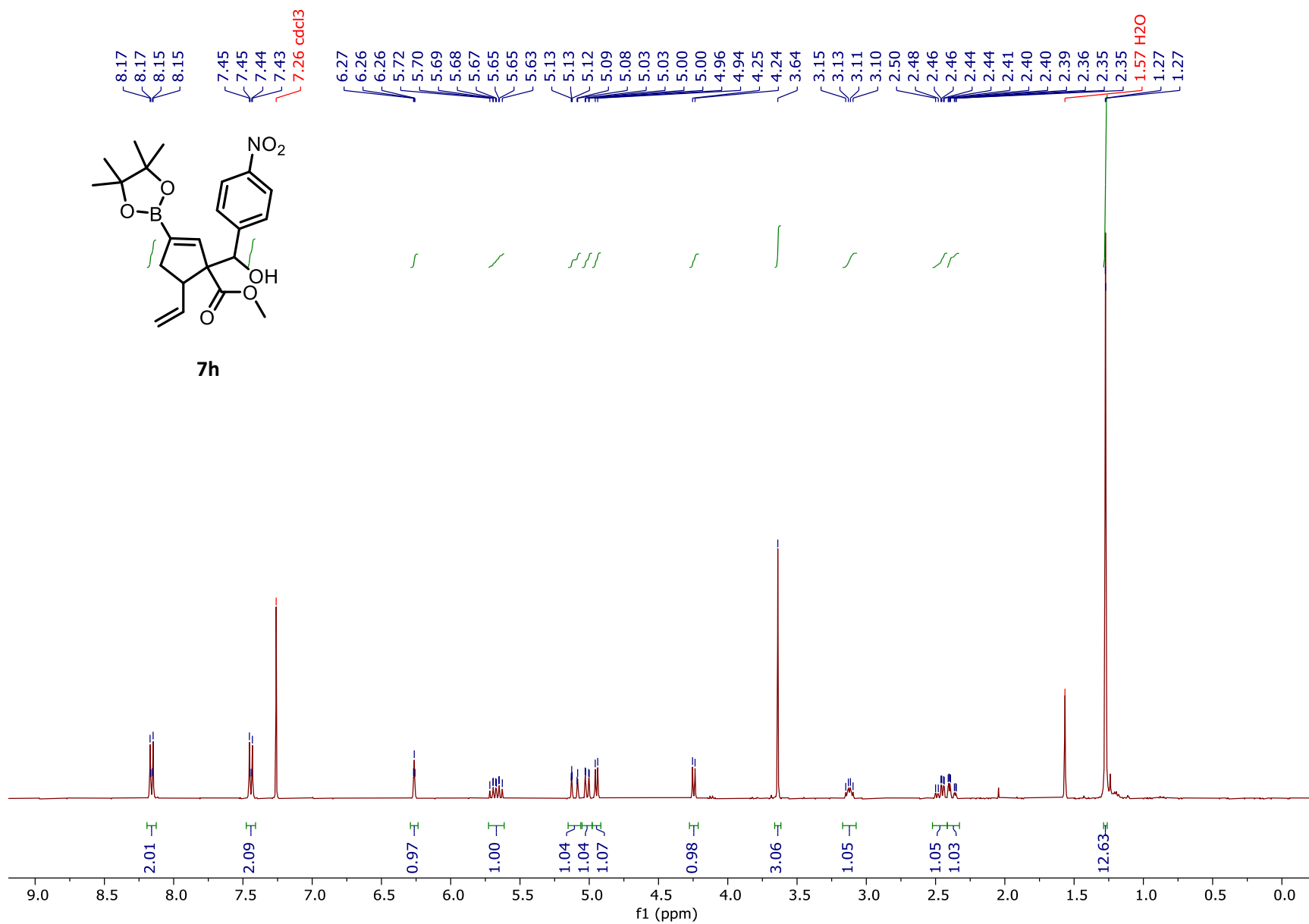


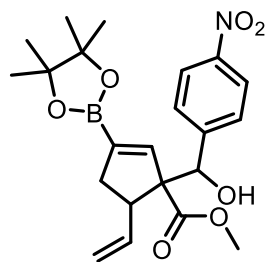


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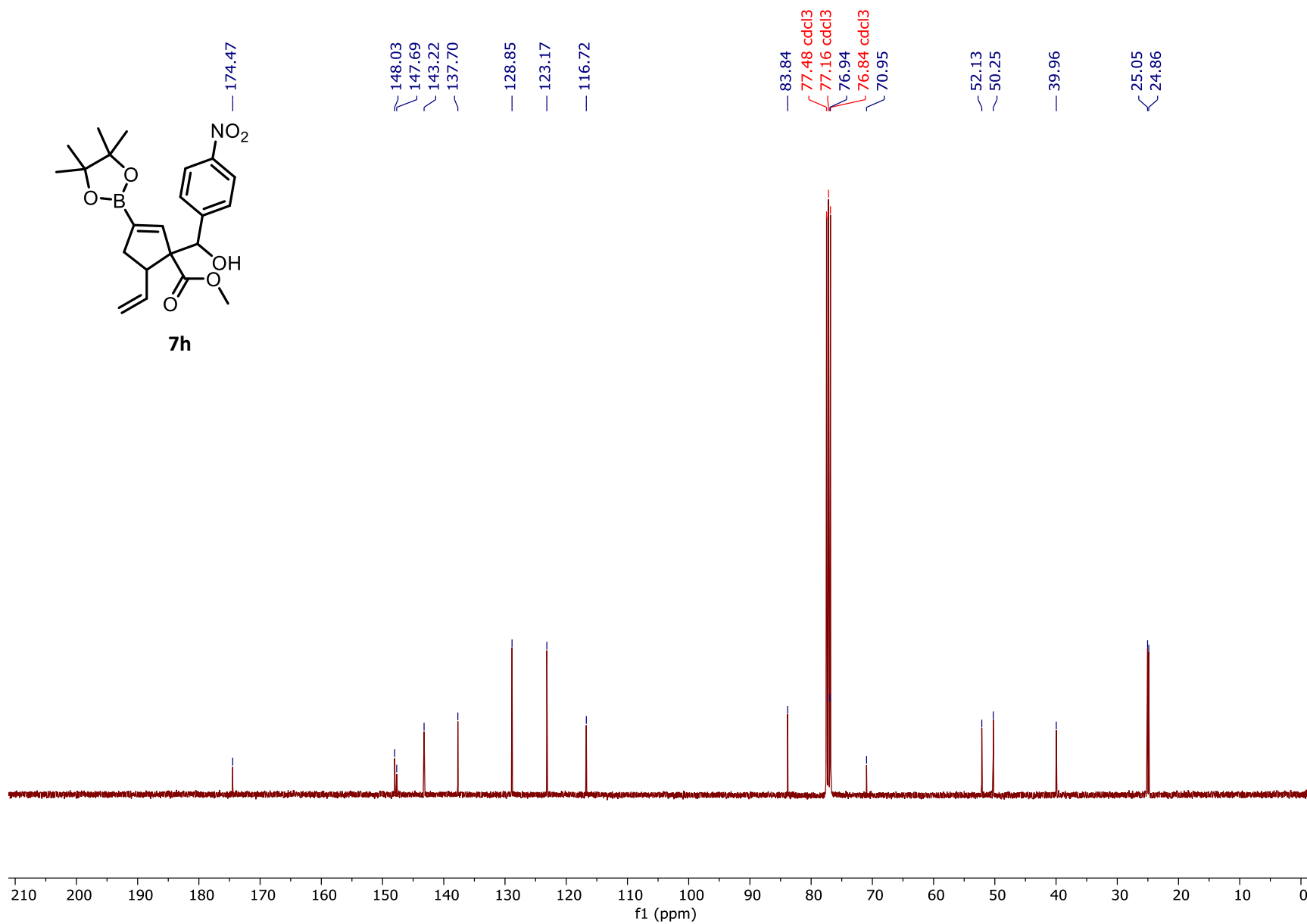
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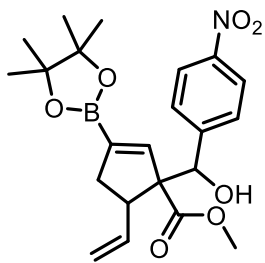






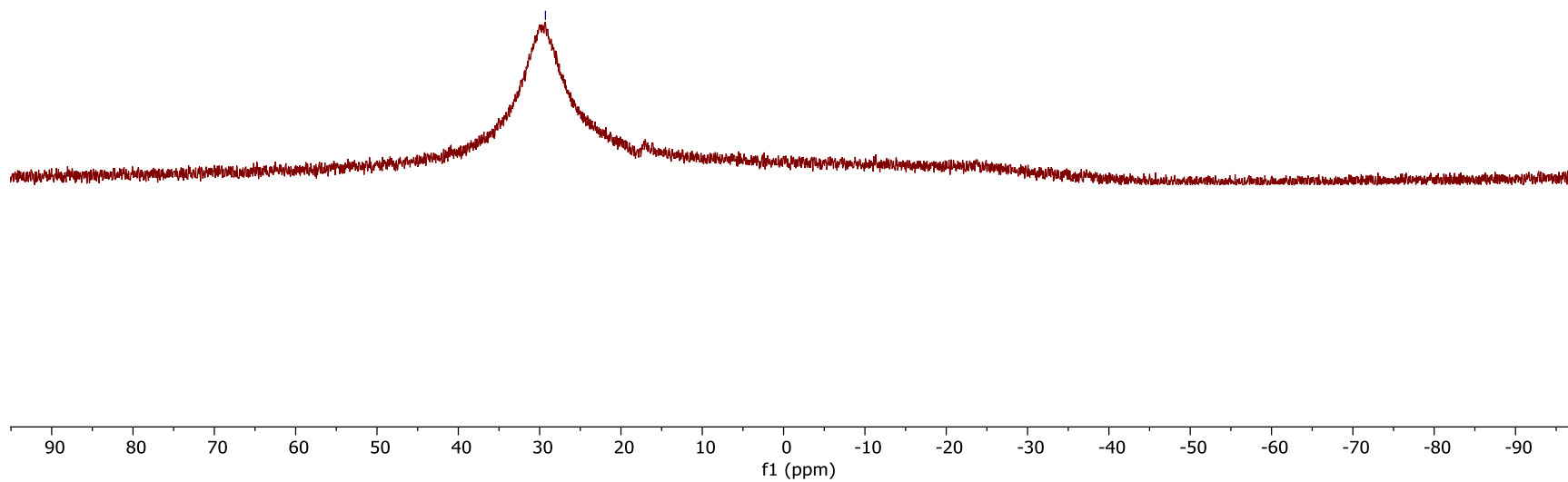
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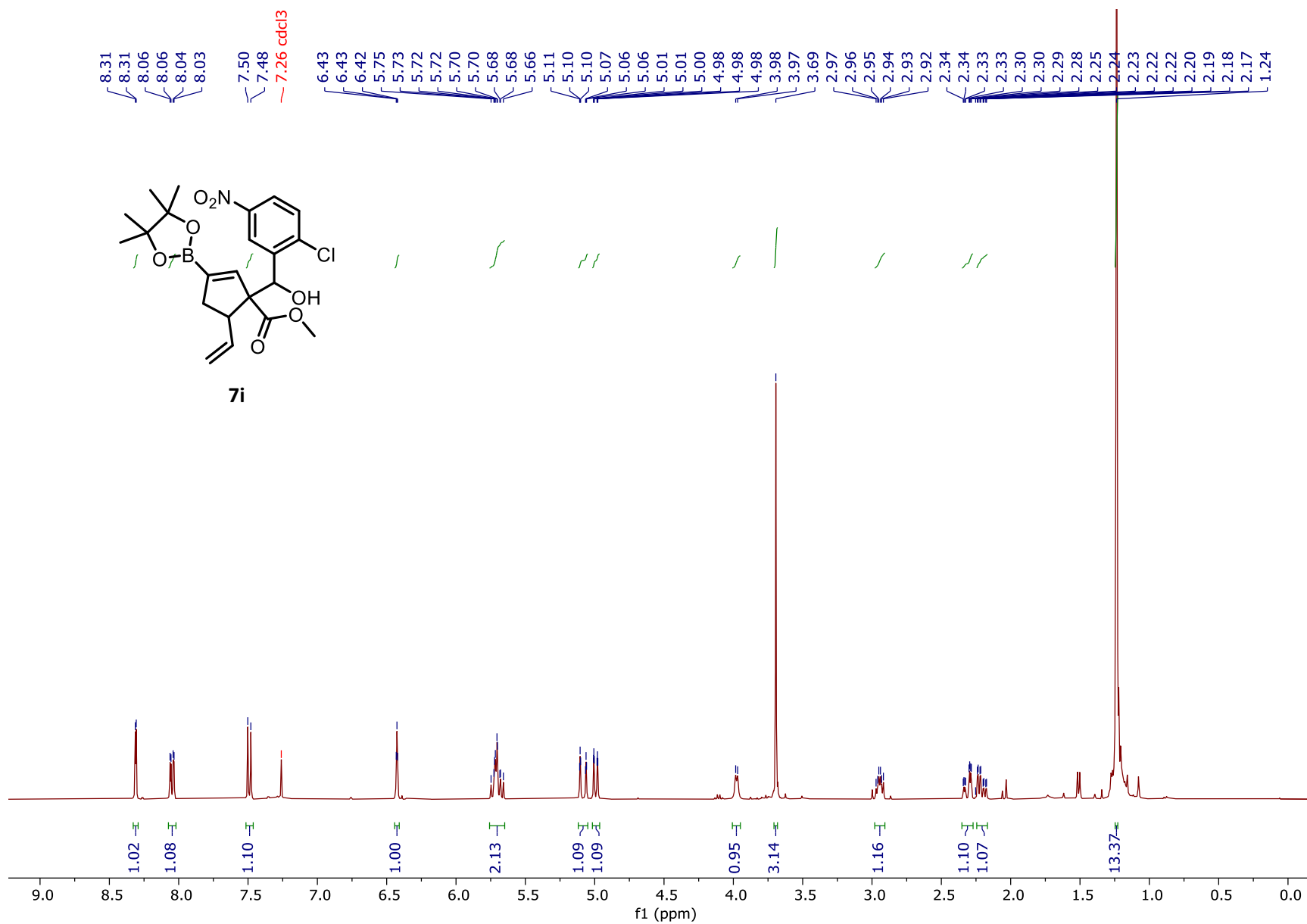


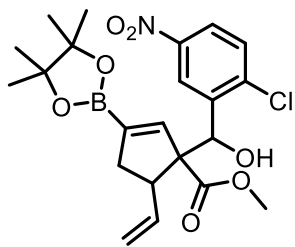


7h

— 29.28







7i

— 174.35

146.48

142.46

140.31

140.09

137.64

130.26

125.46

123.73

— 116.46

— 83.80

77.48 cdc13

77.16 cdc13

76.84 cdc13

72.10

71.78

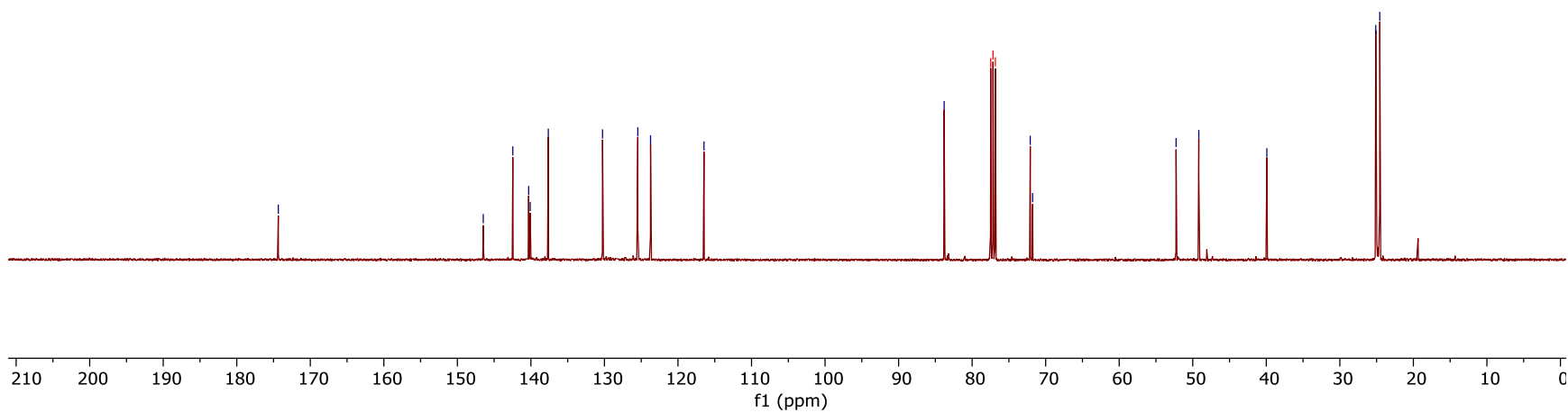
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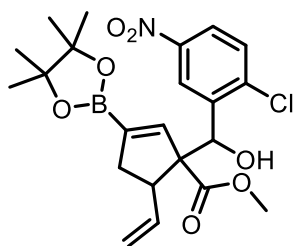
— 49.18

— 39.92

25.11

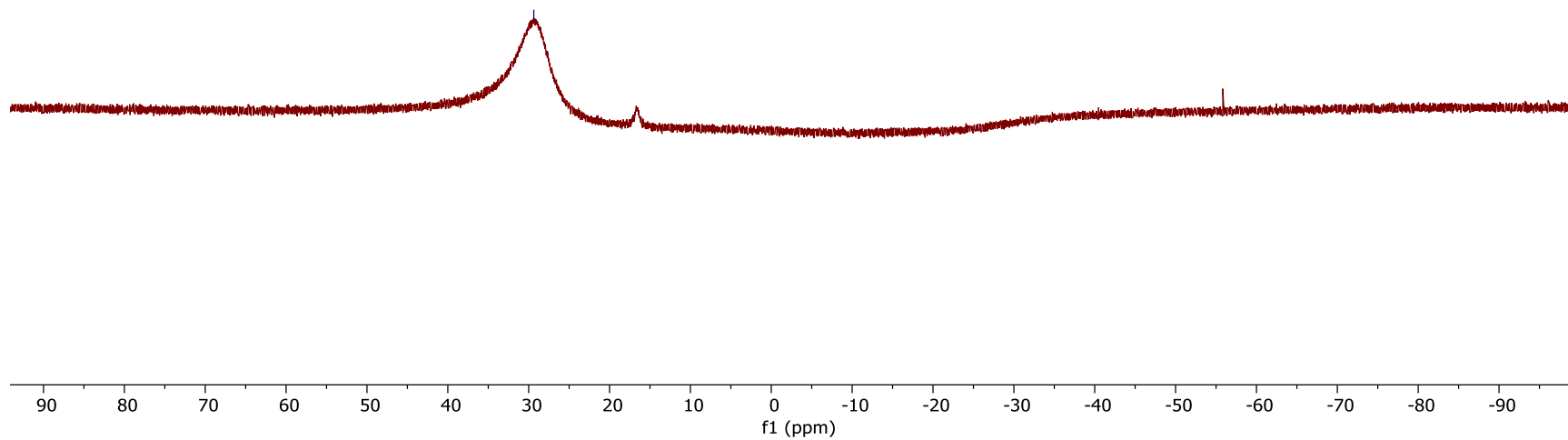
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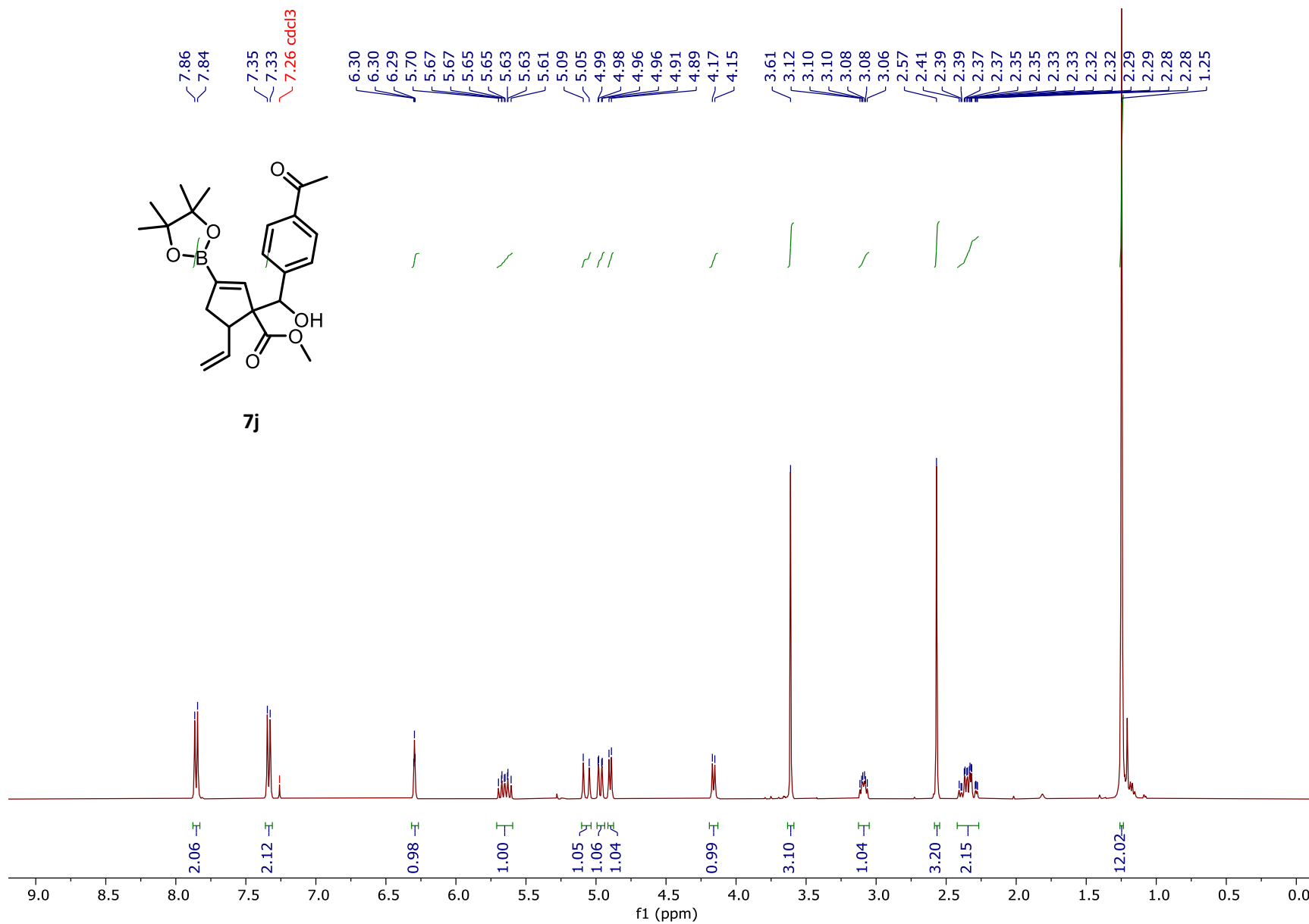




7i

— 29.37





— 197.94

— 174.48

— 146.00

— 143.81

— 137.98

— 136.65

— 128.11

— 127.95

— 116.31

83.66

77.48 cdc13

77.29

77.16 cdc13

76.84 cdc13

71.07

51.94

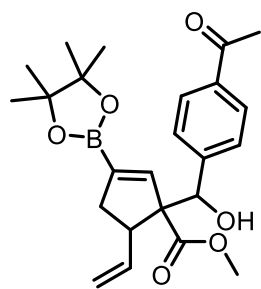
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39.82

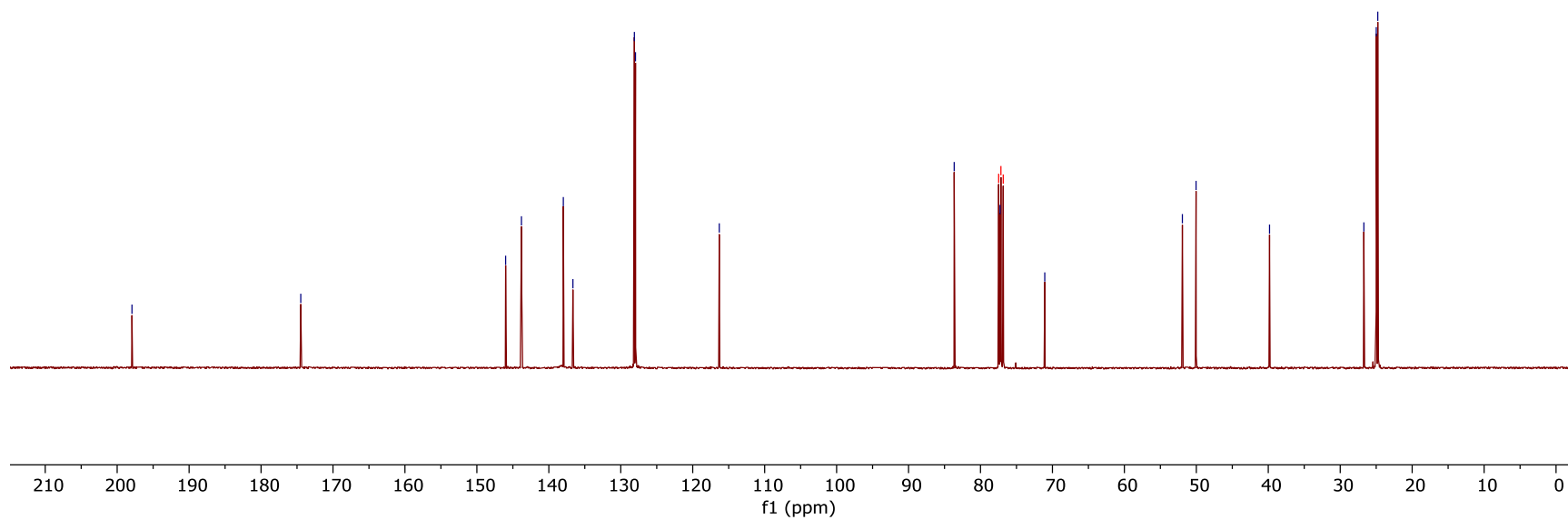
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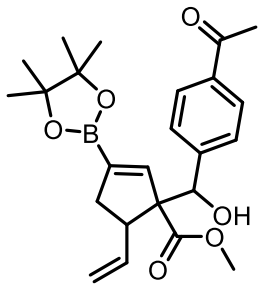
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24.78



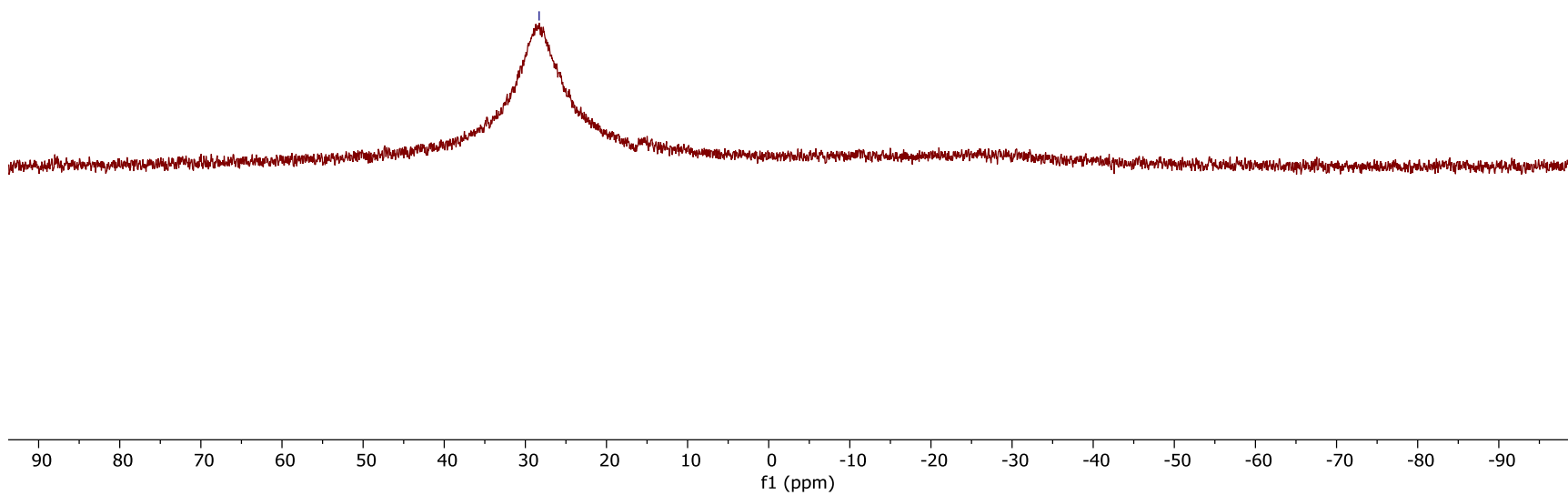
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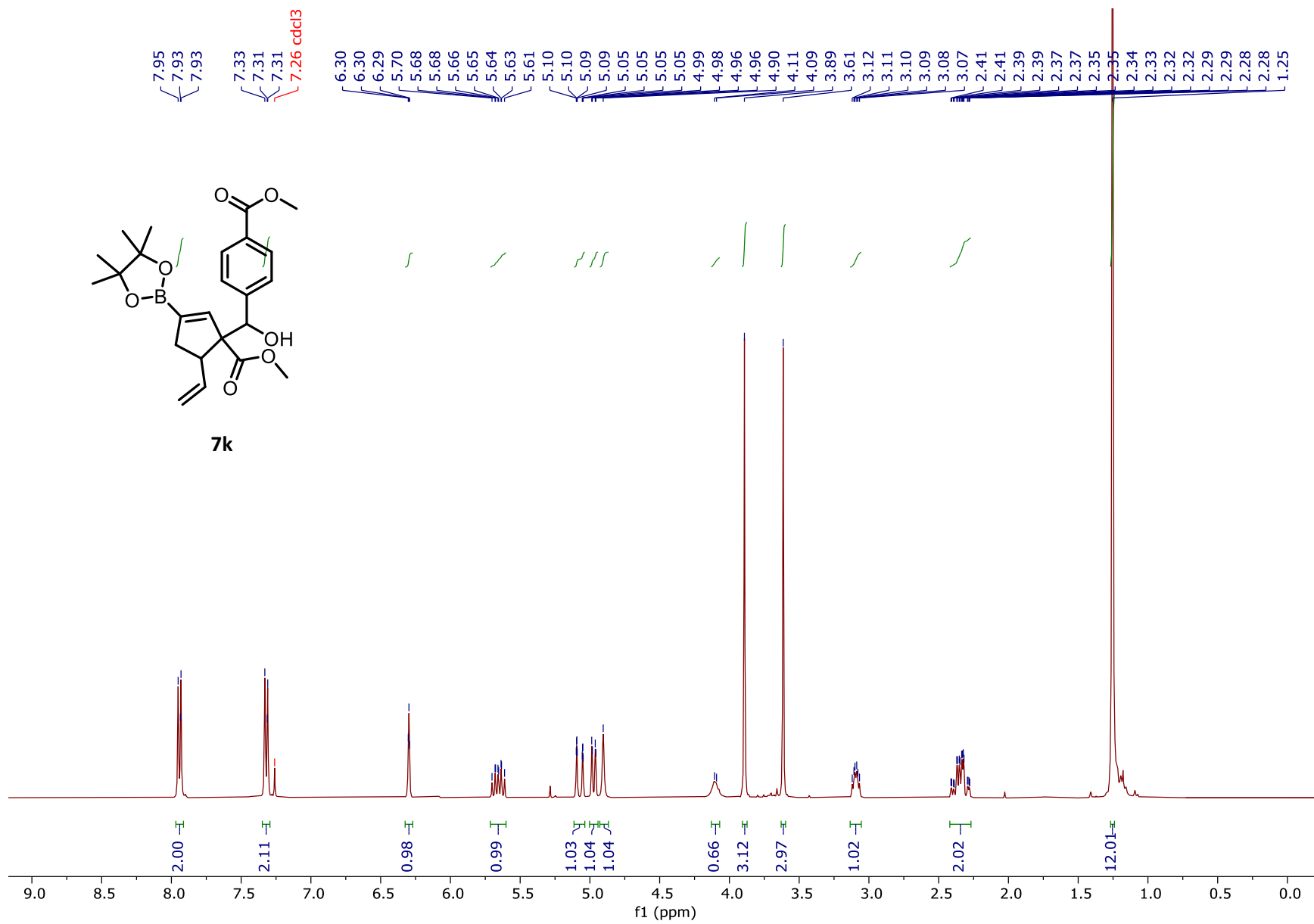


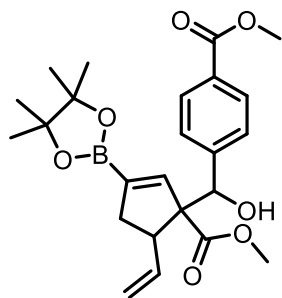


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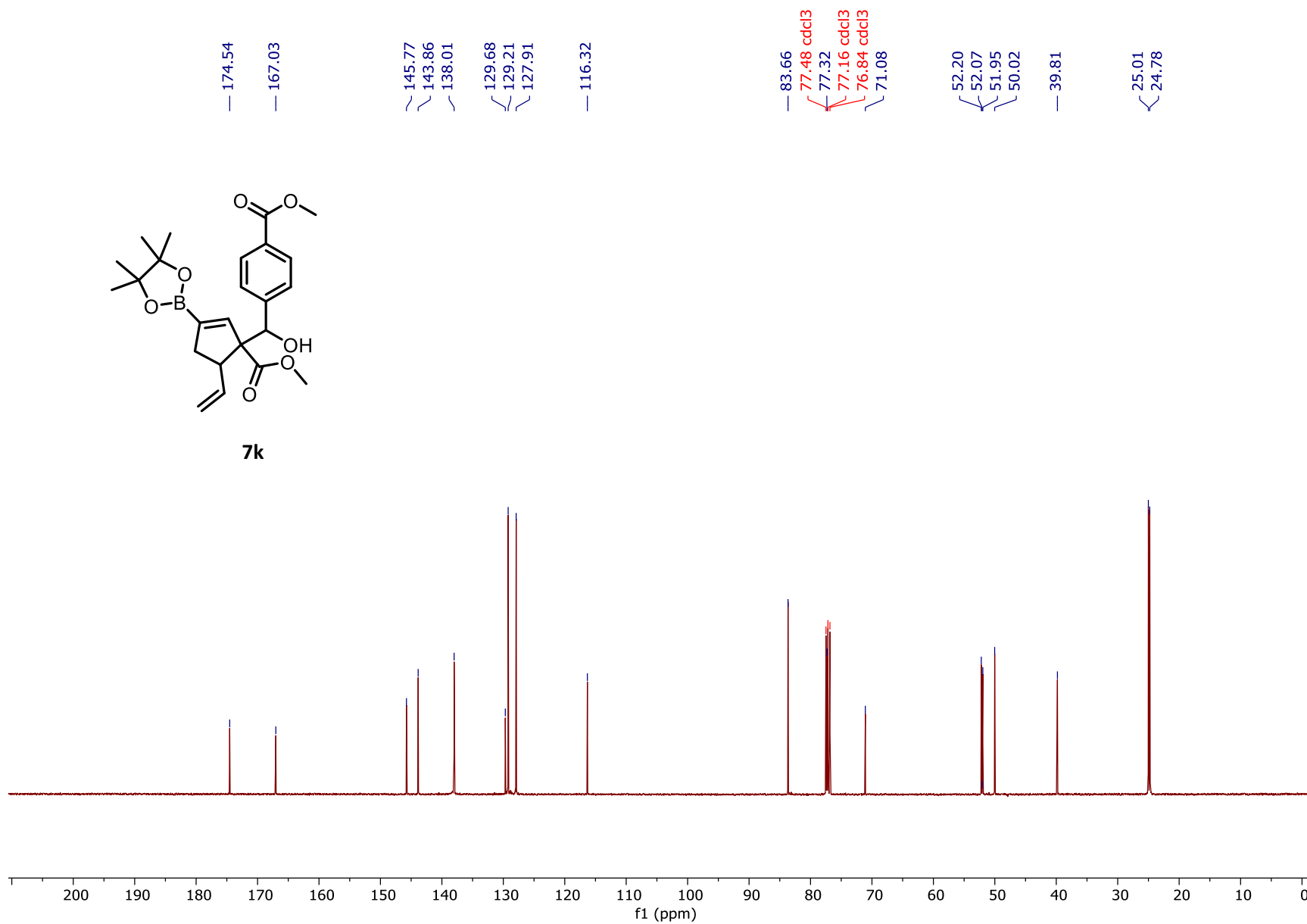
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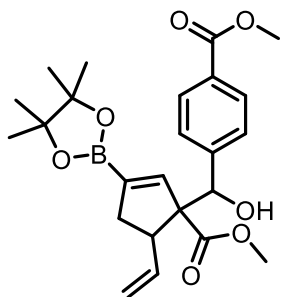






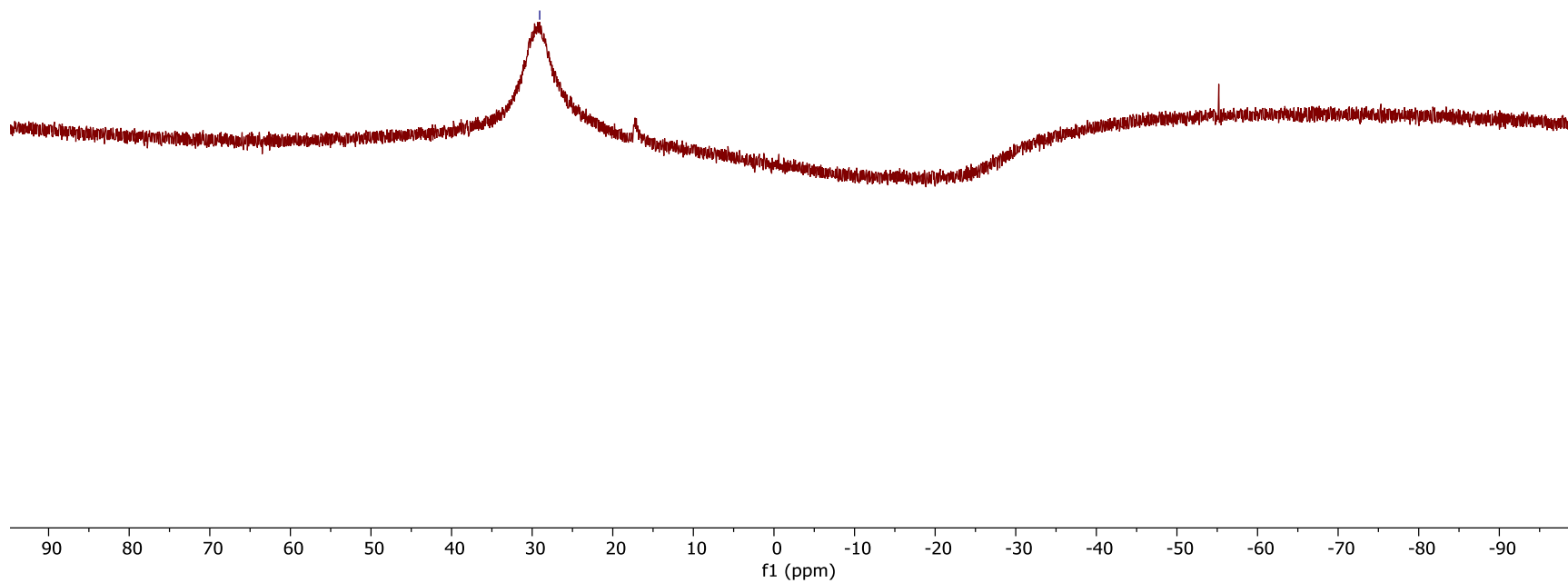
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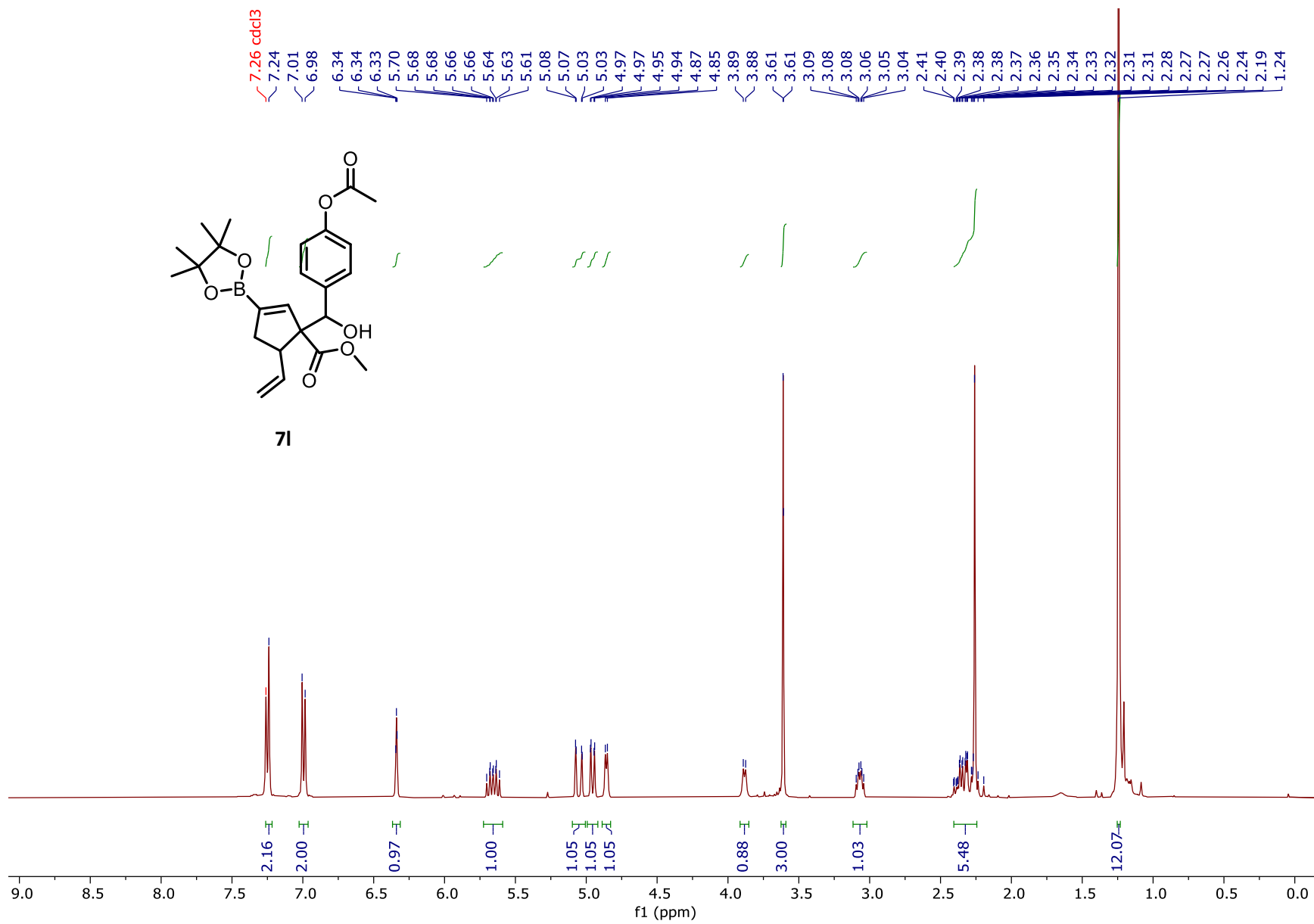


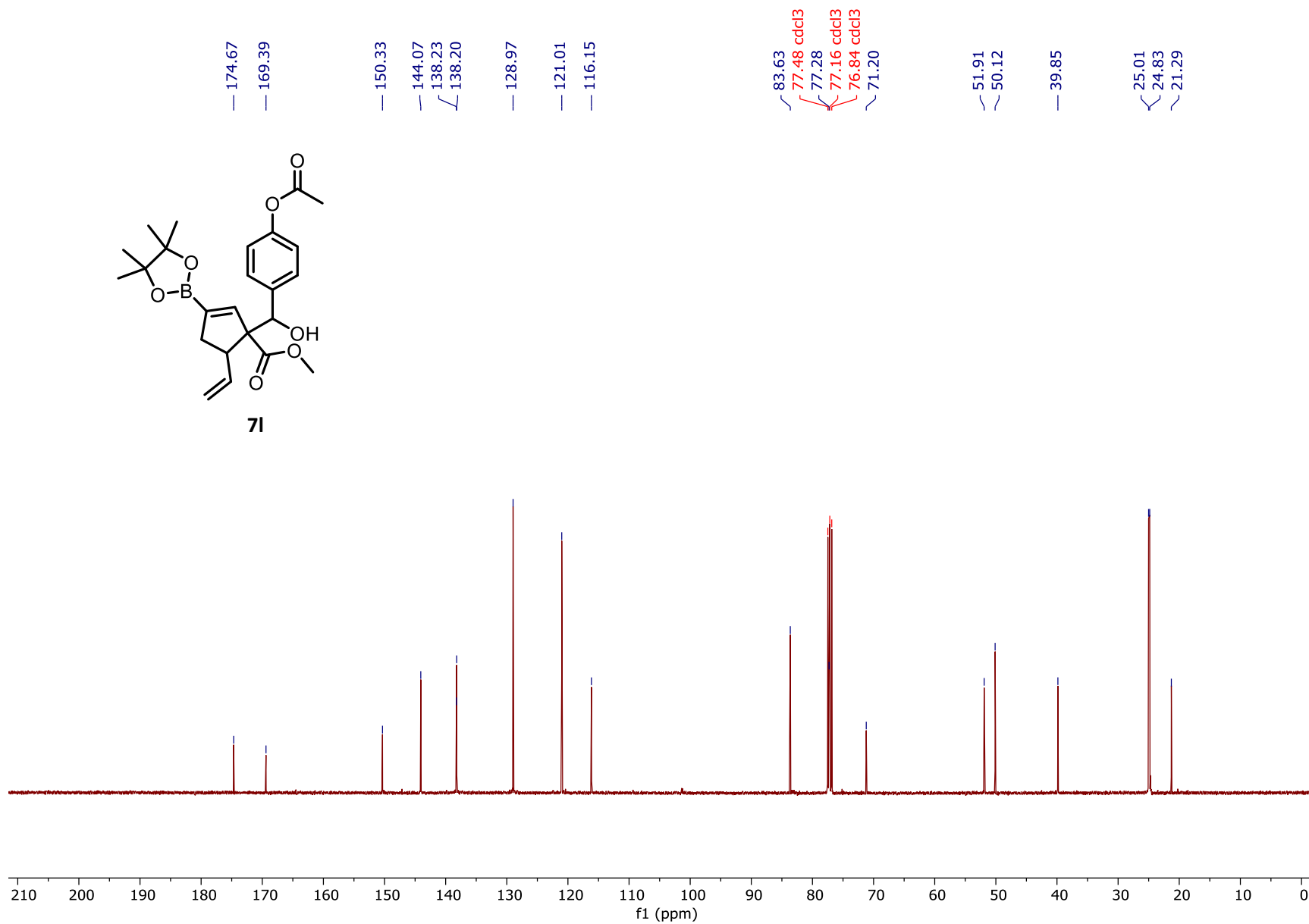
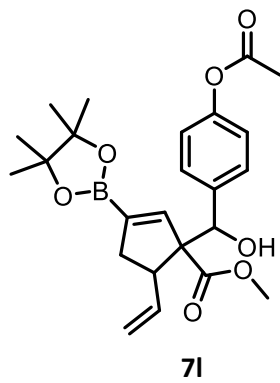


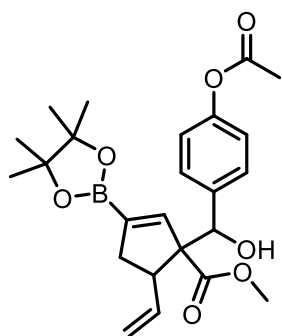
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— 29.07



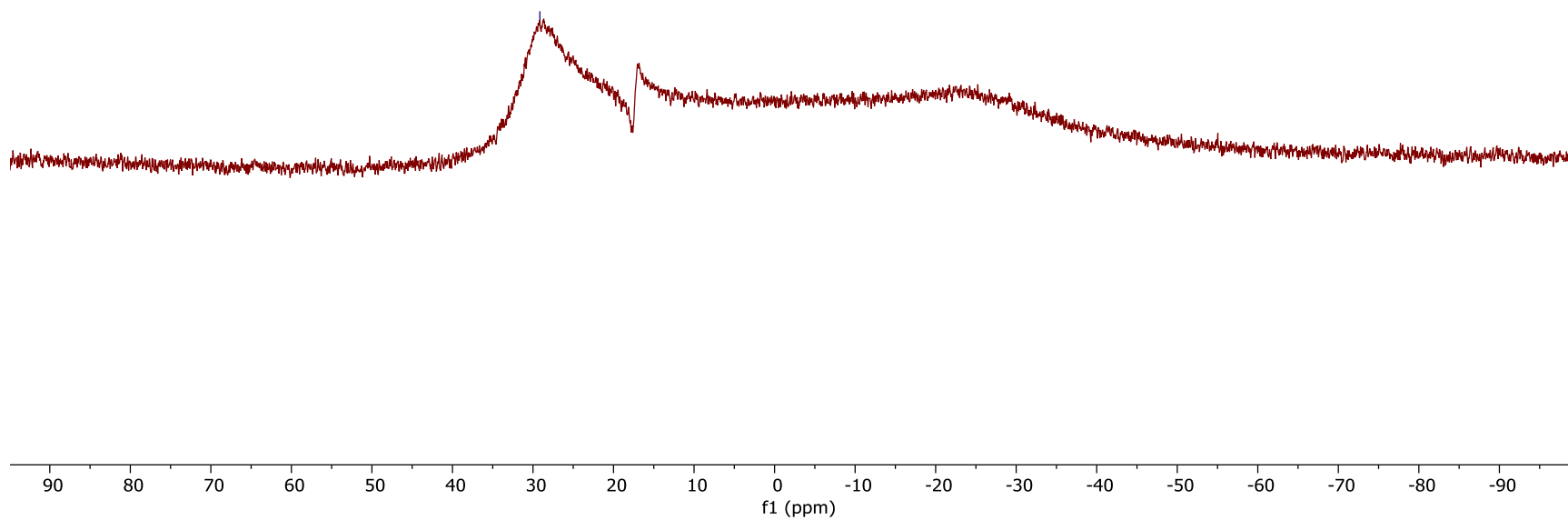


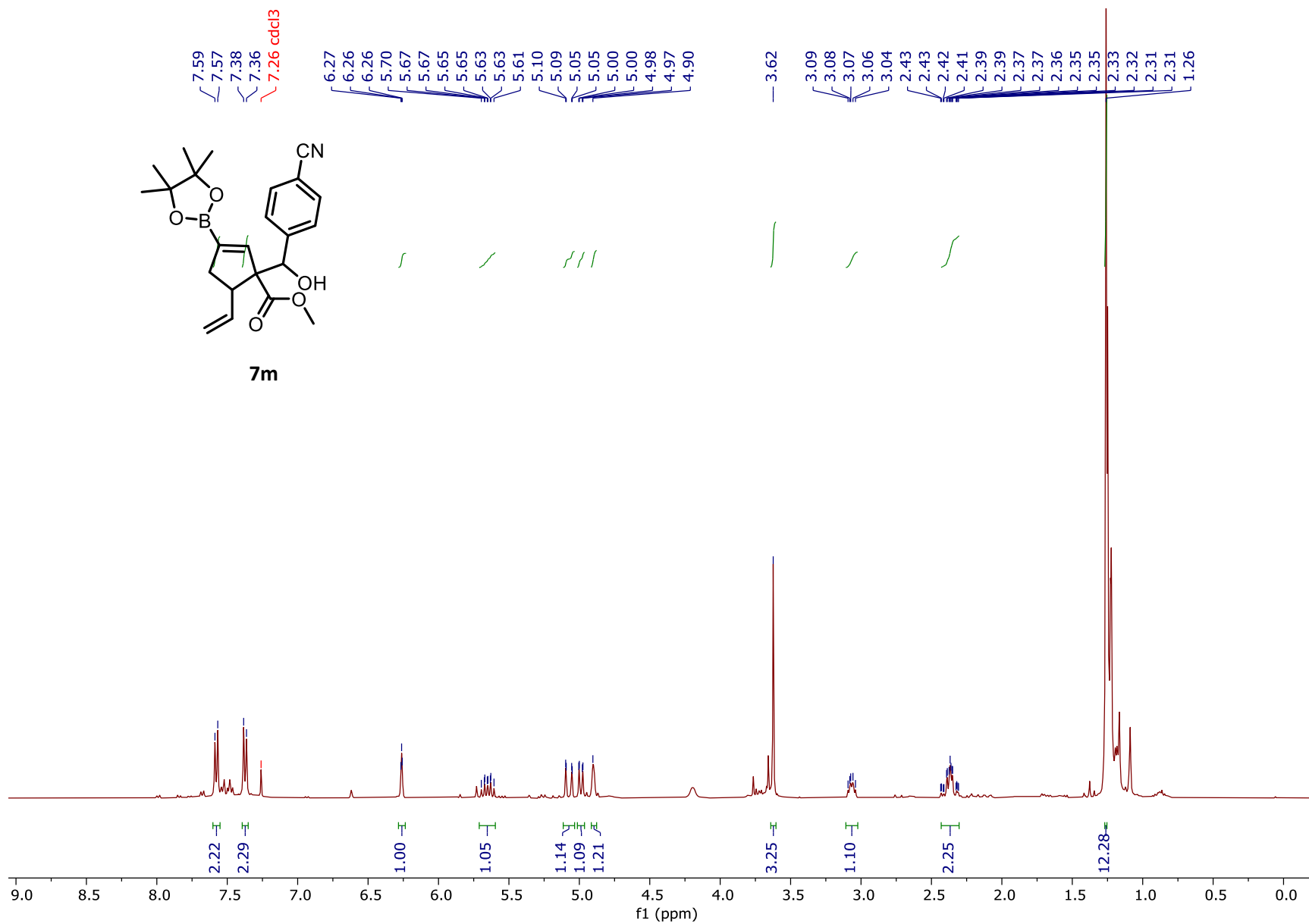


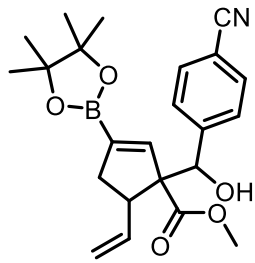


71

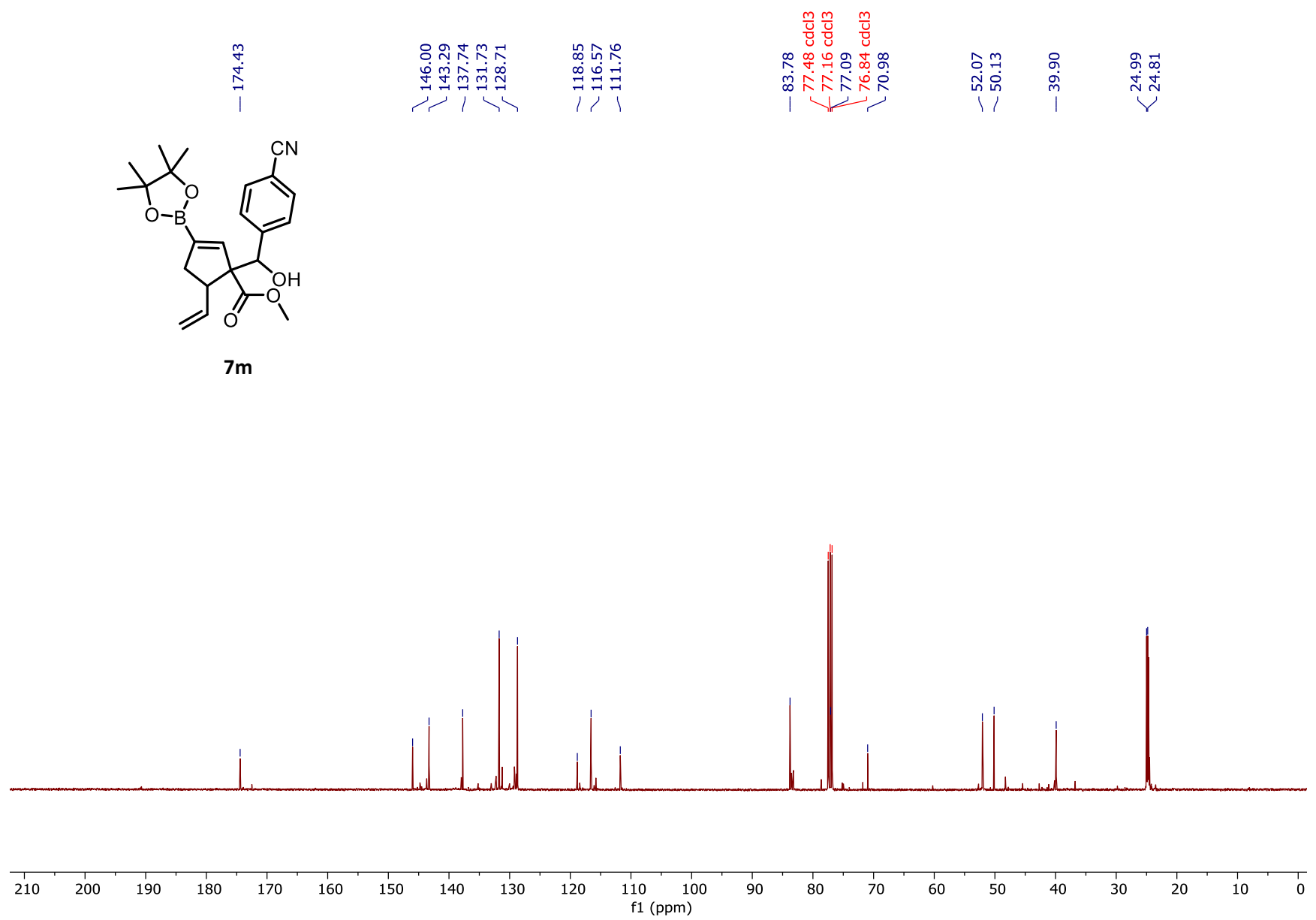
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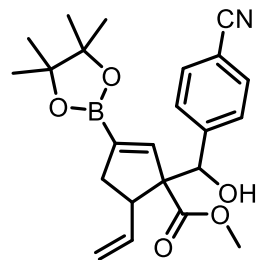






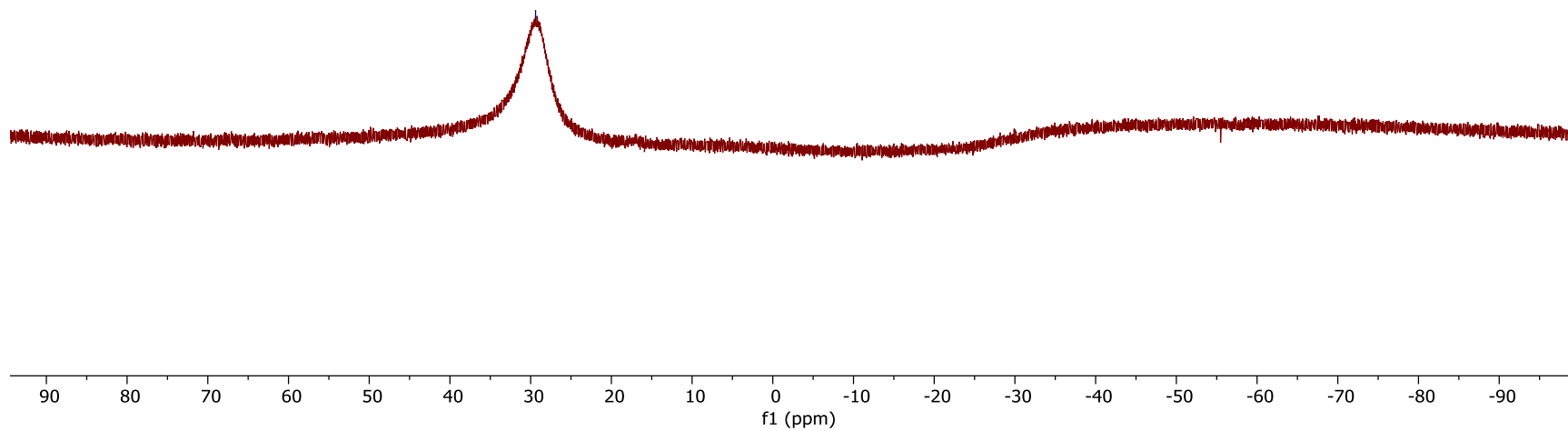
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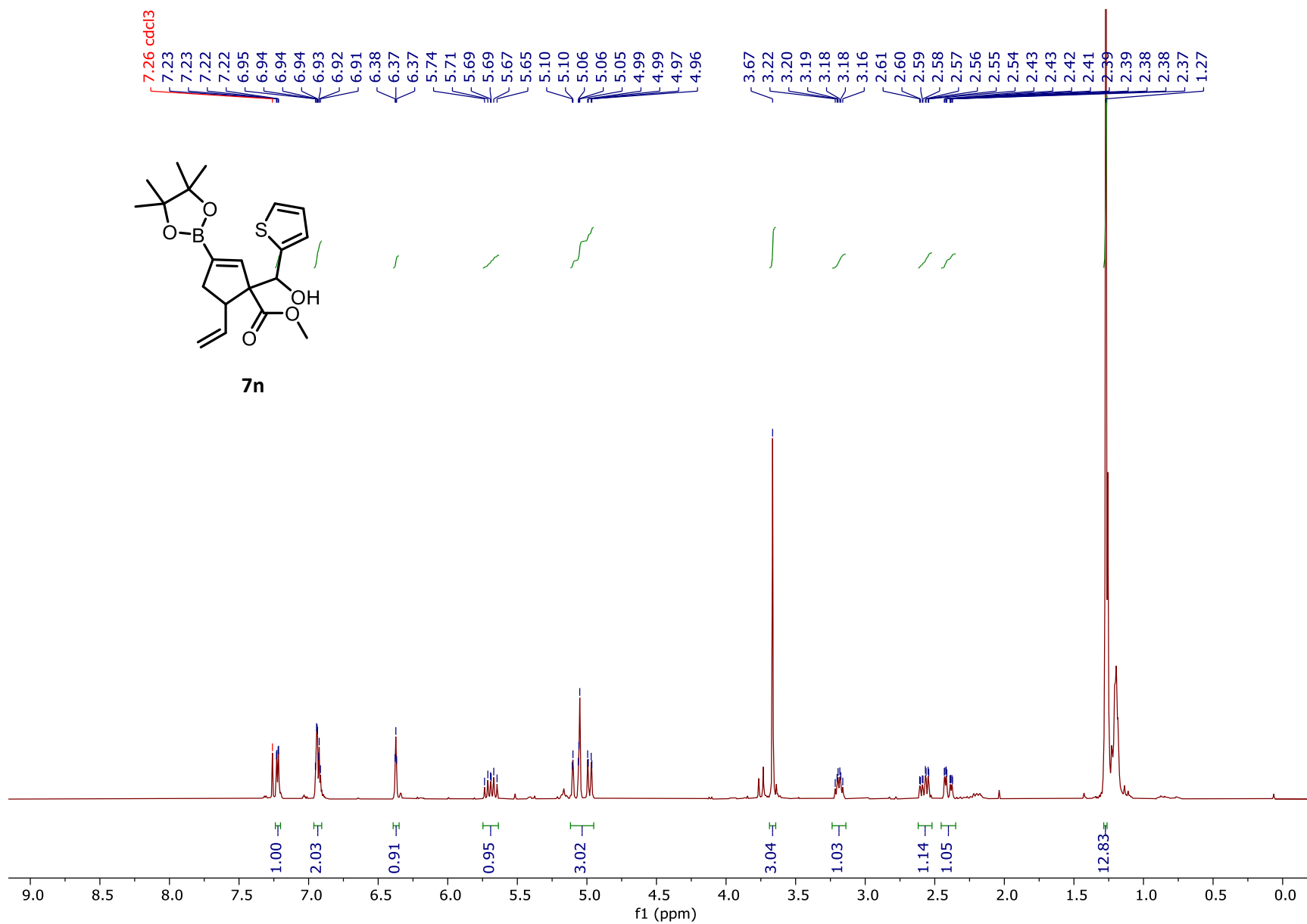


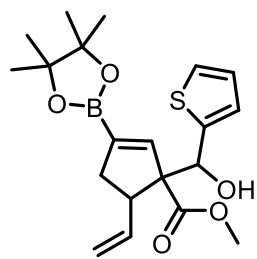


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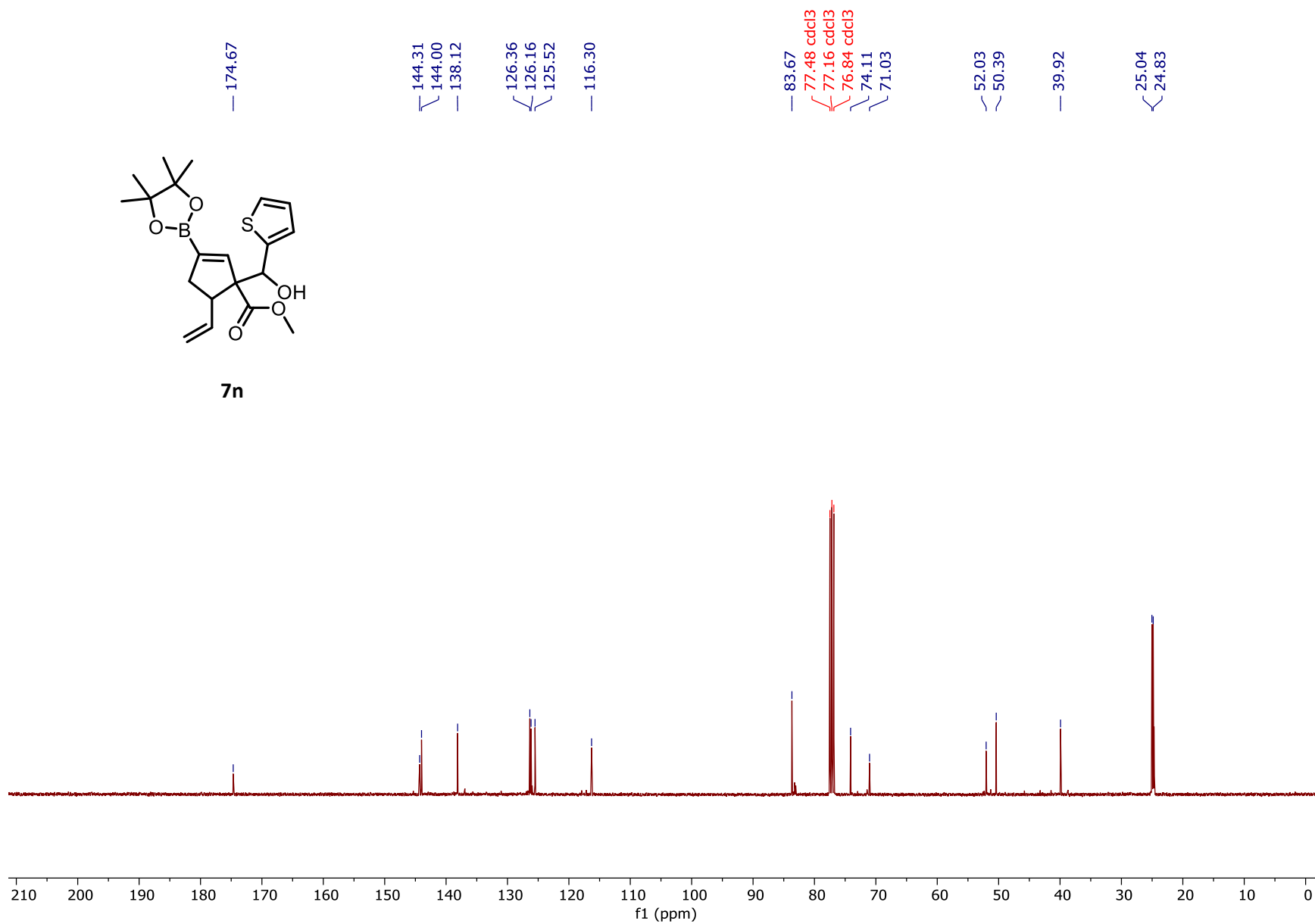
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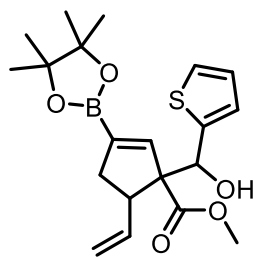






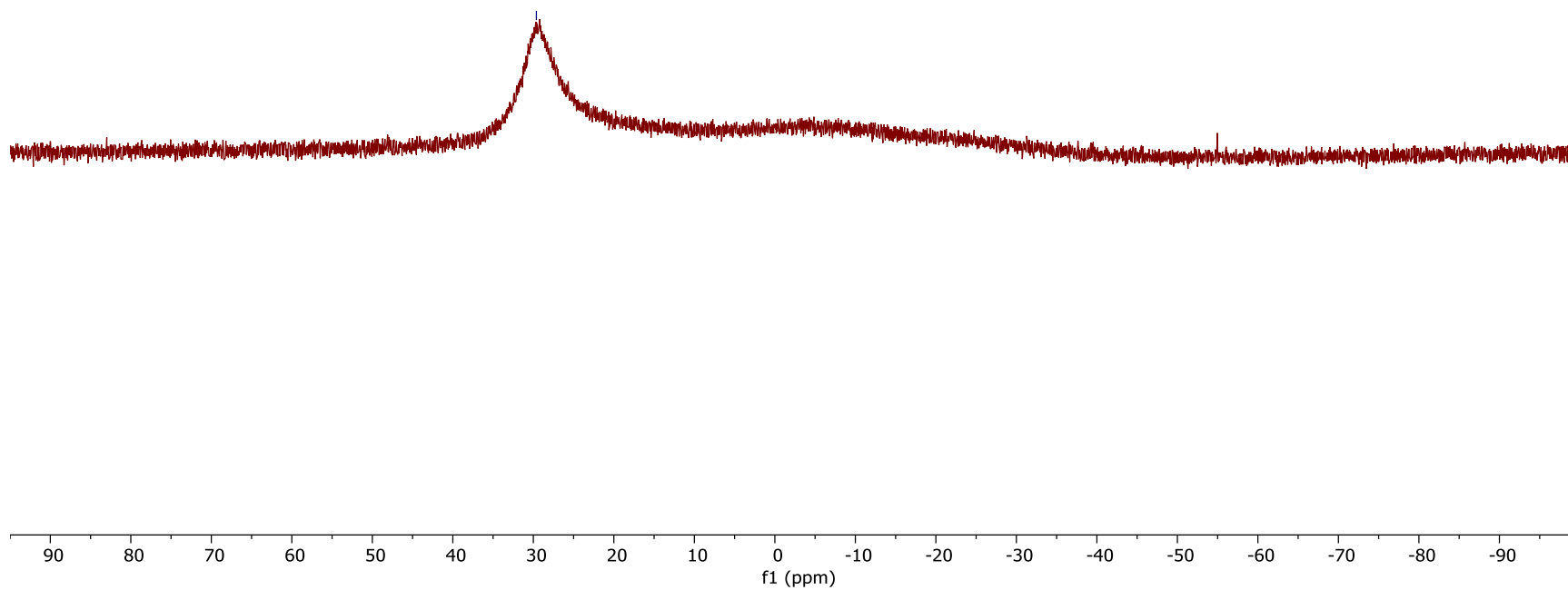
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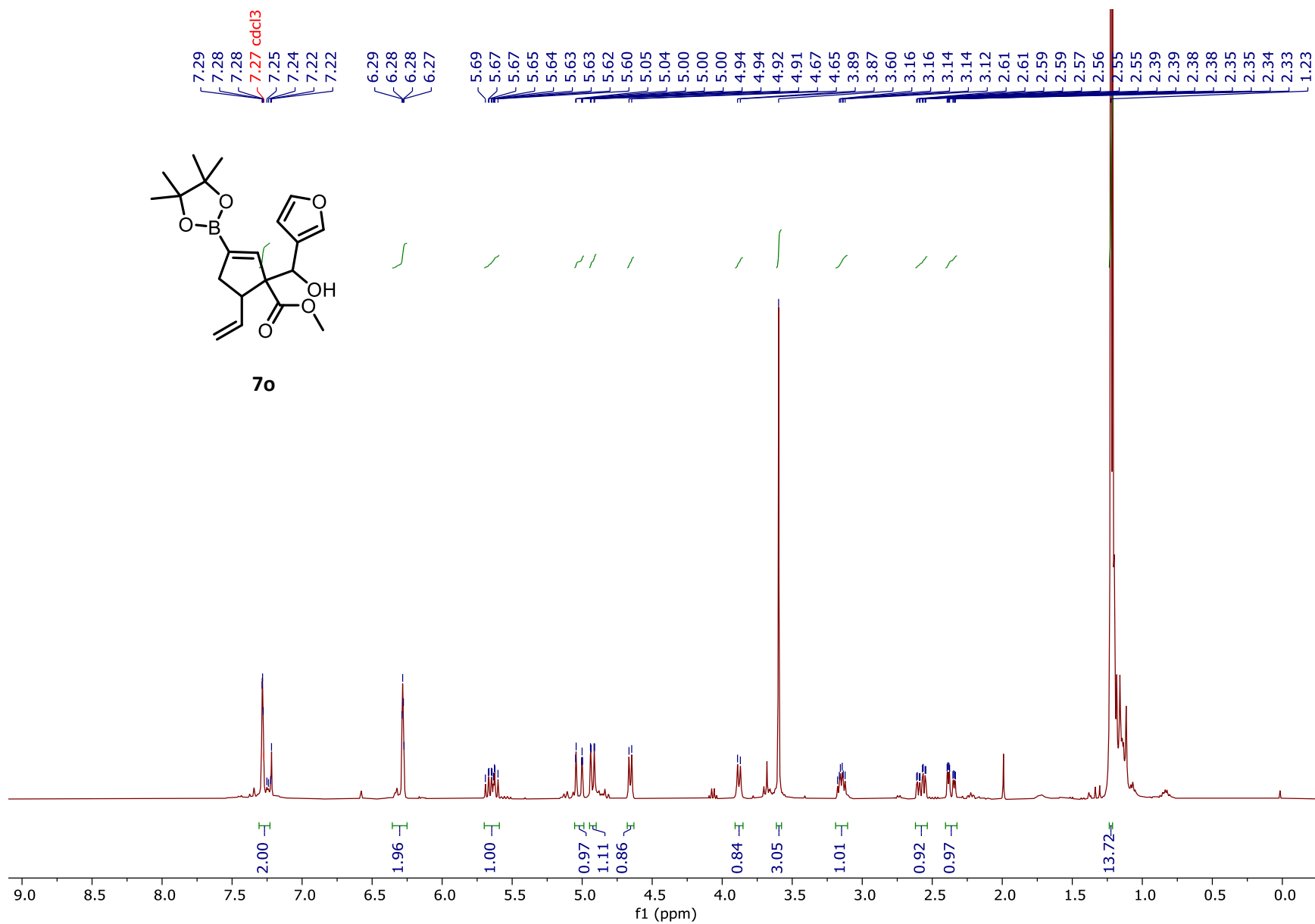


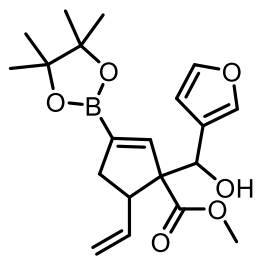


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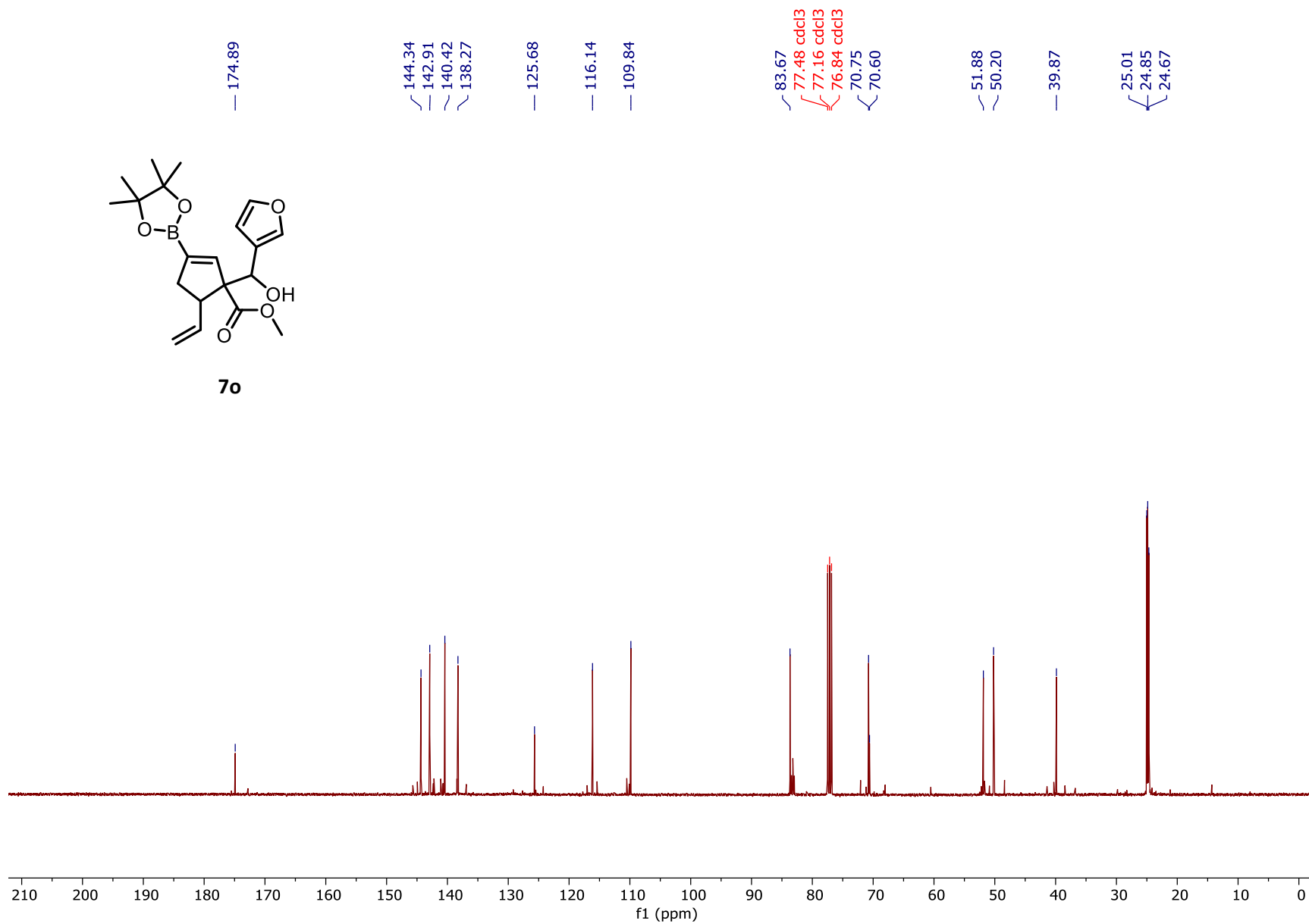
— 29.62

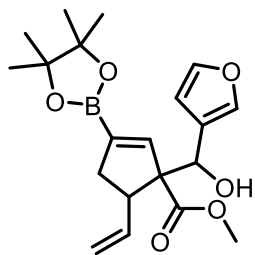






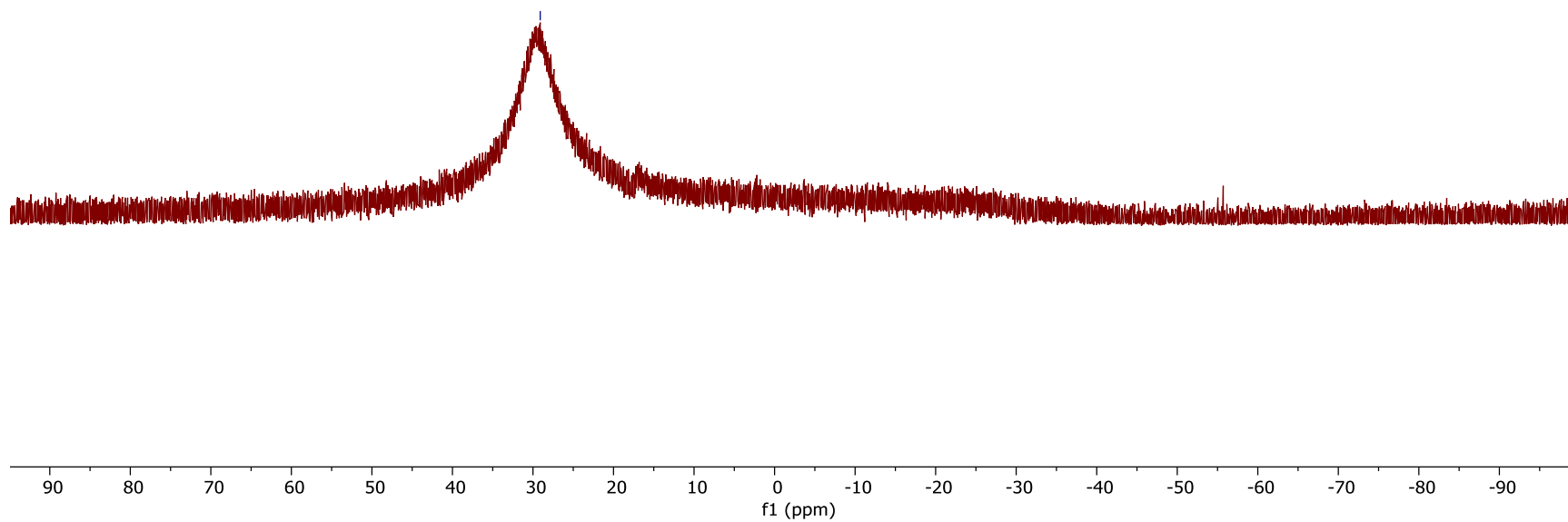
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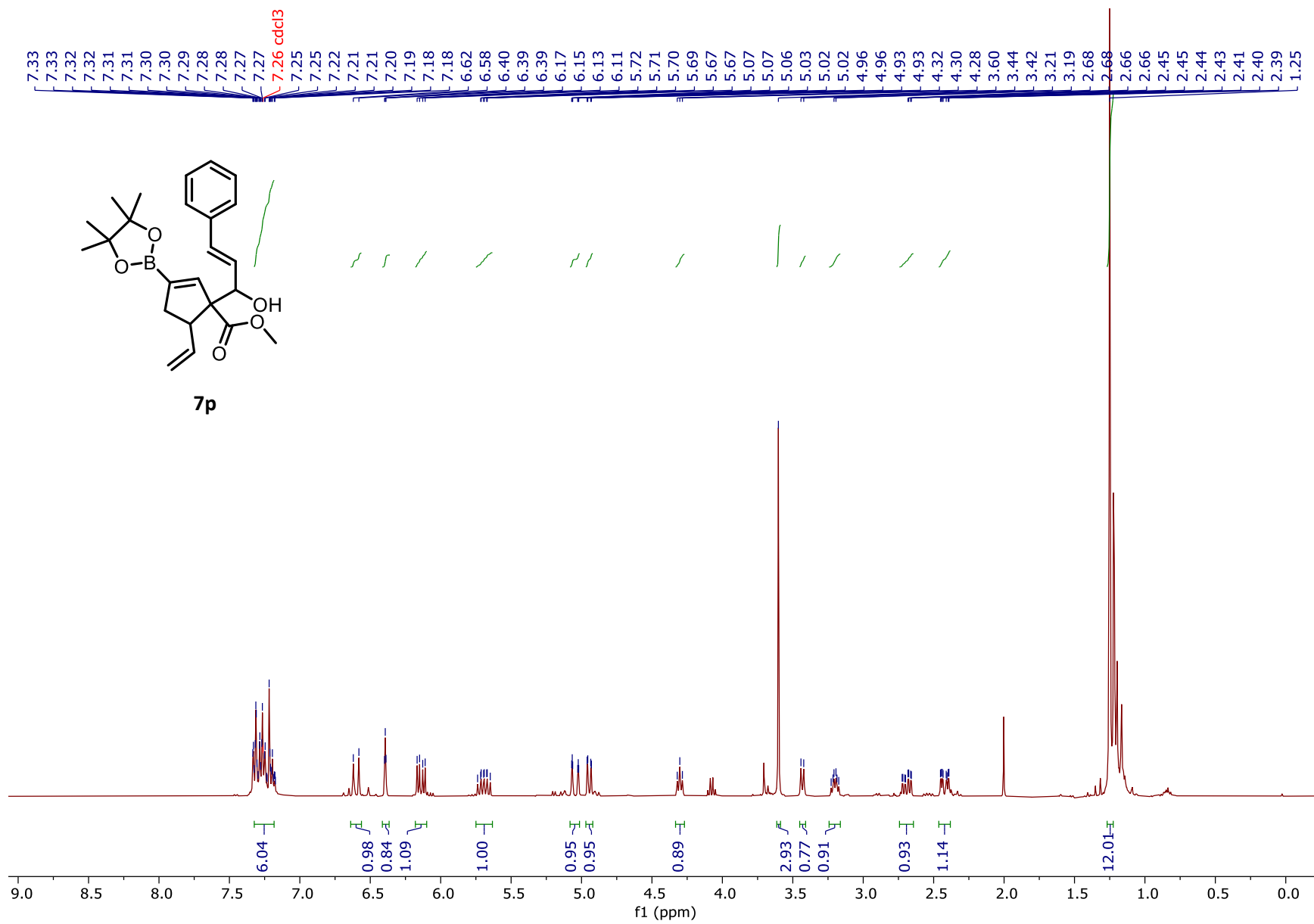


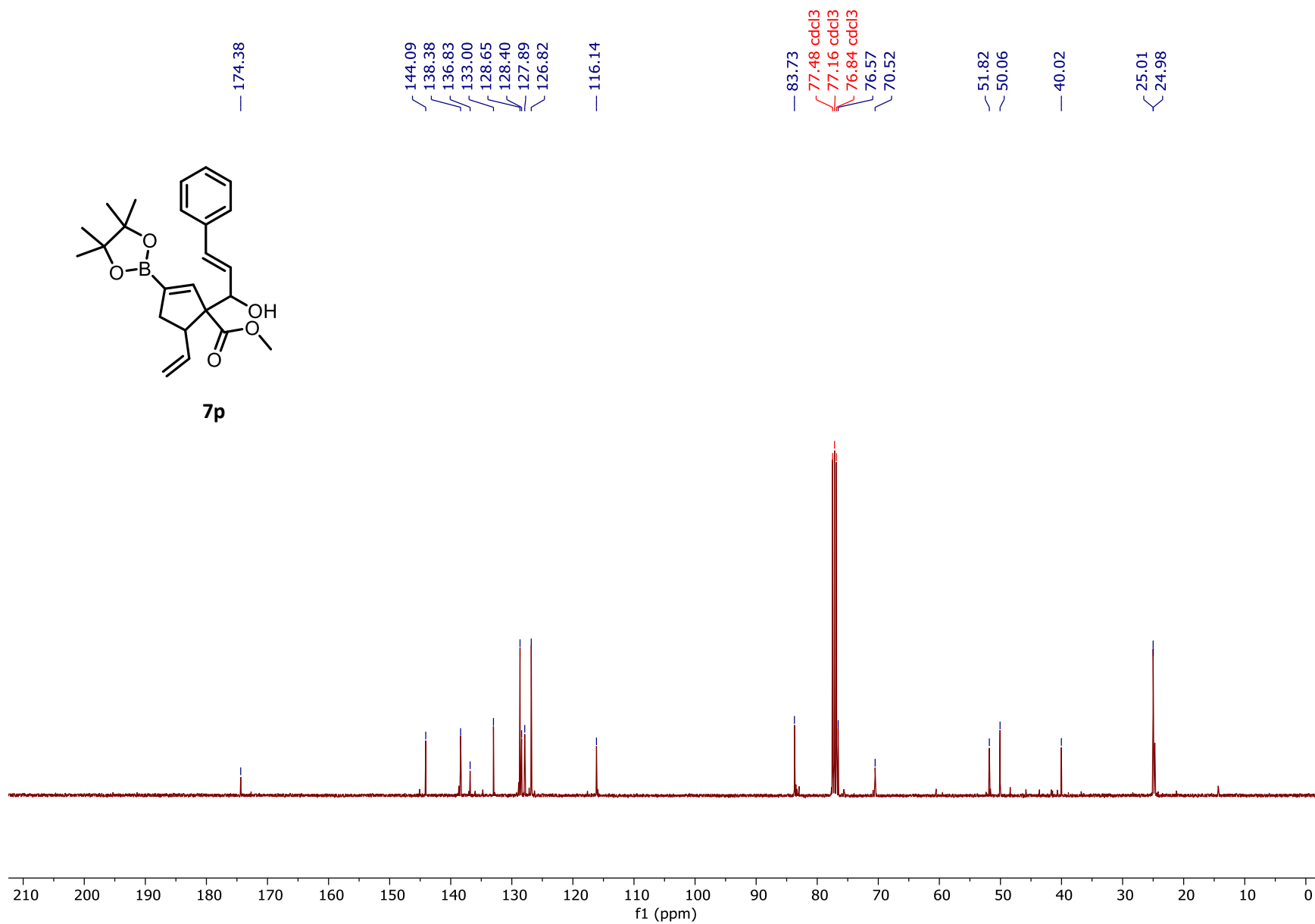
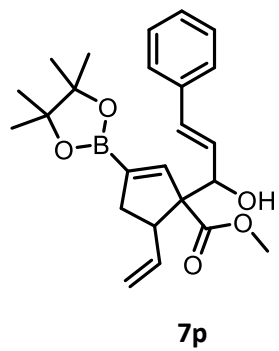


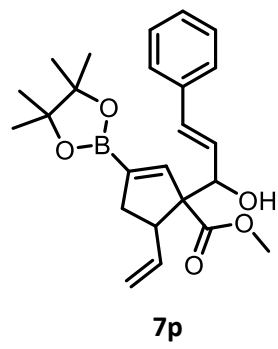
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— 29.10

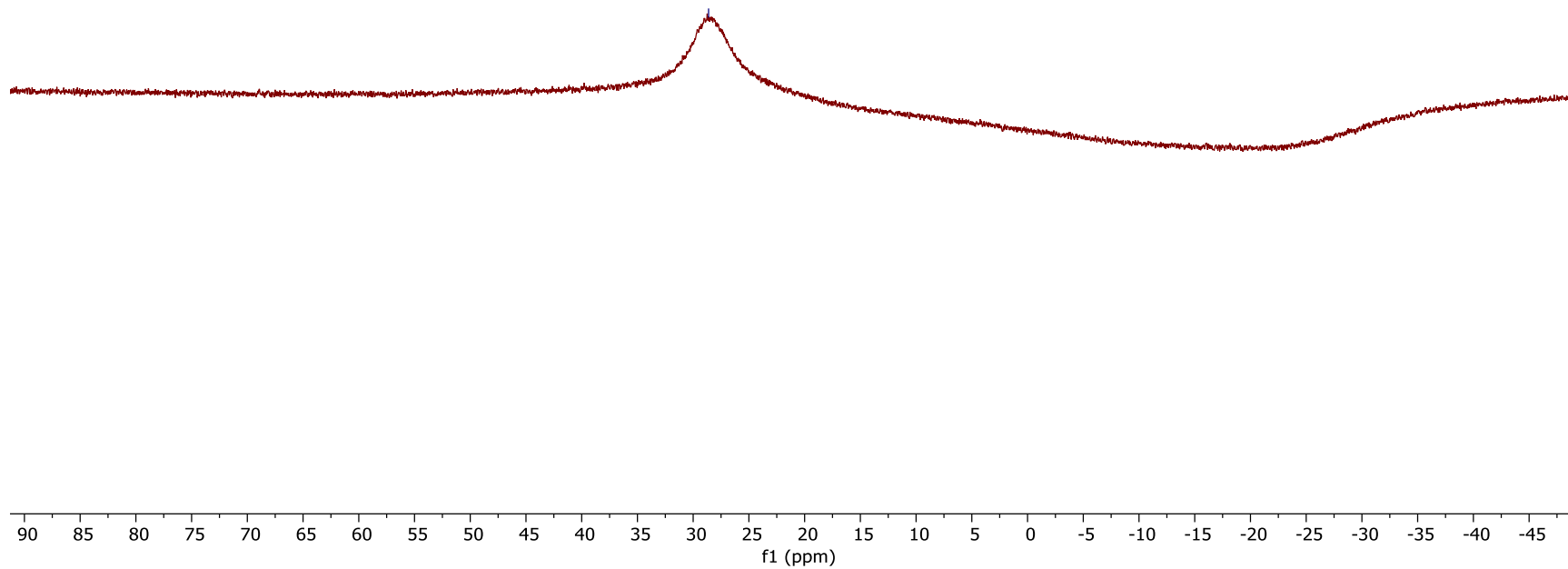


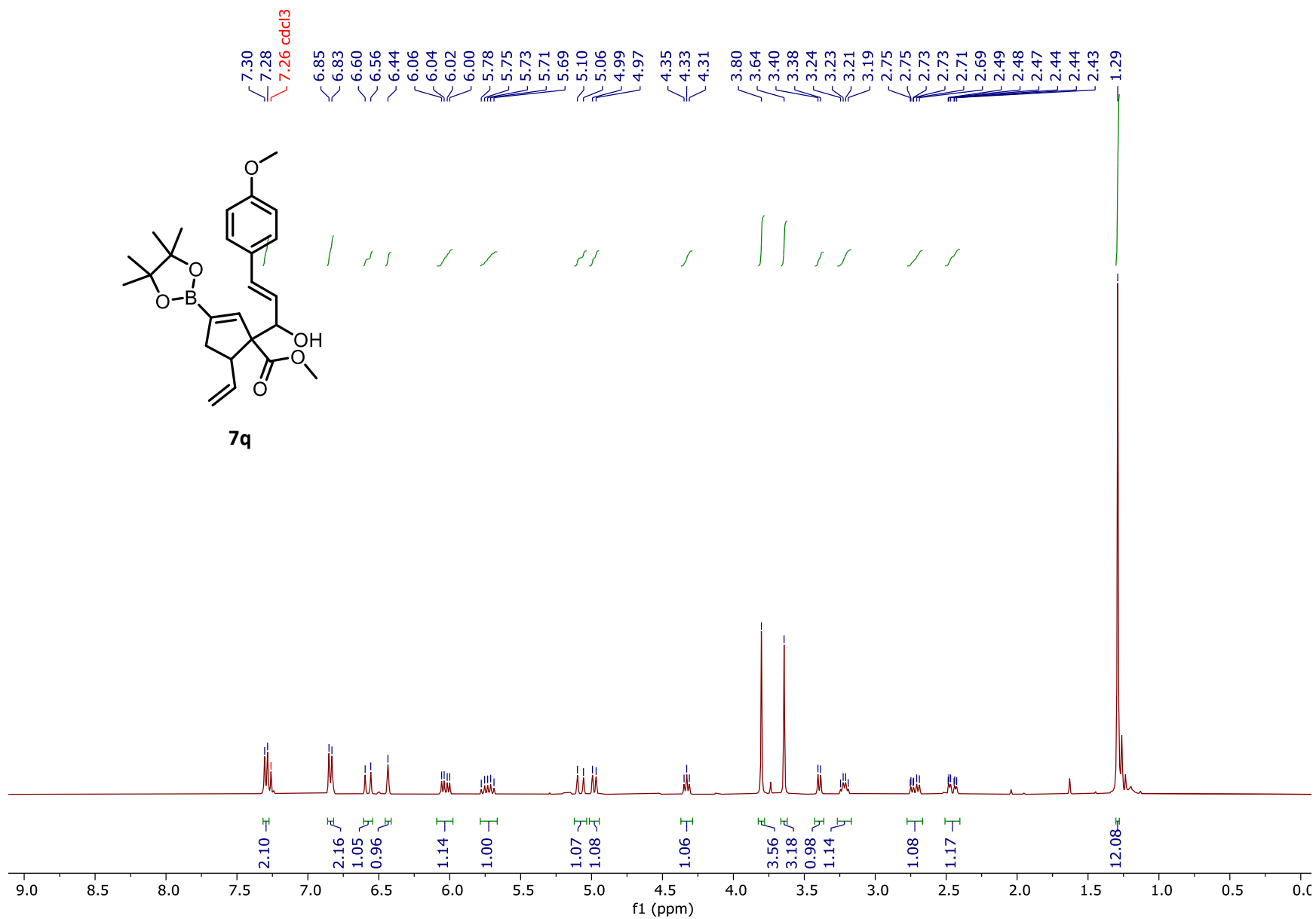


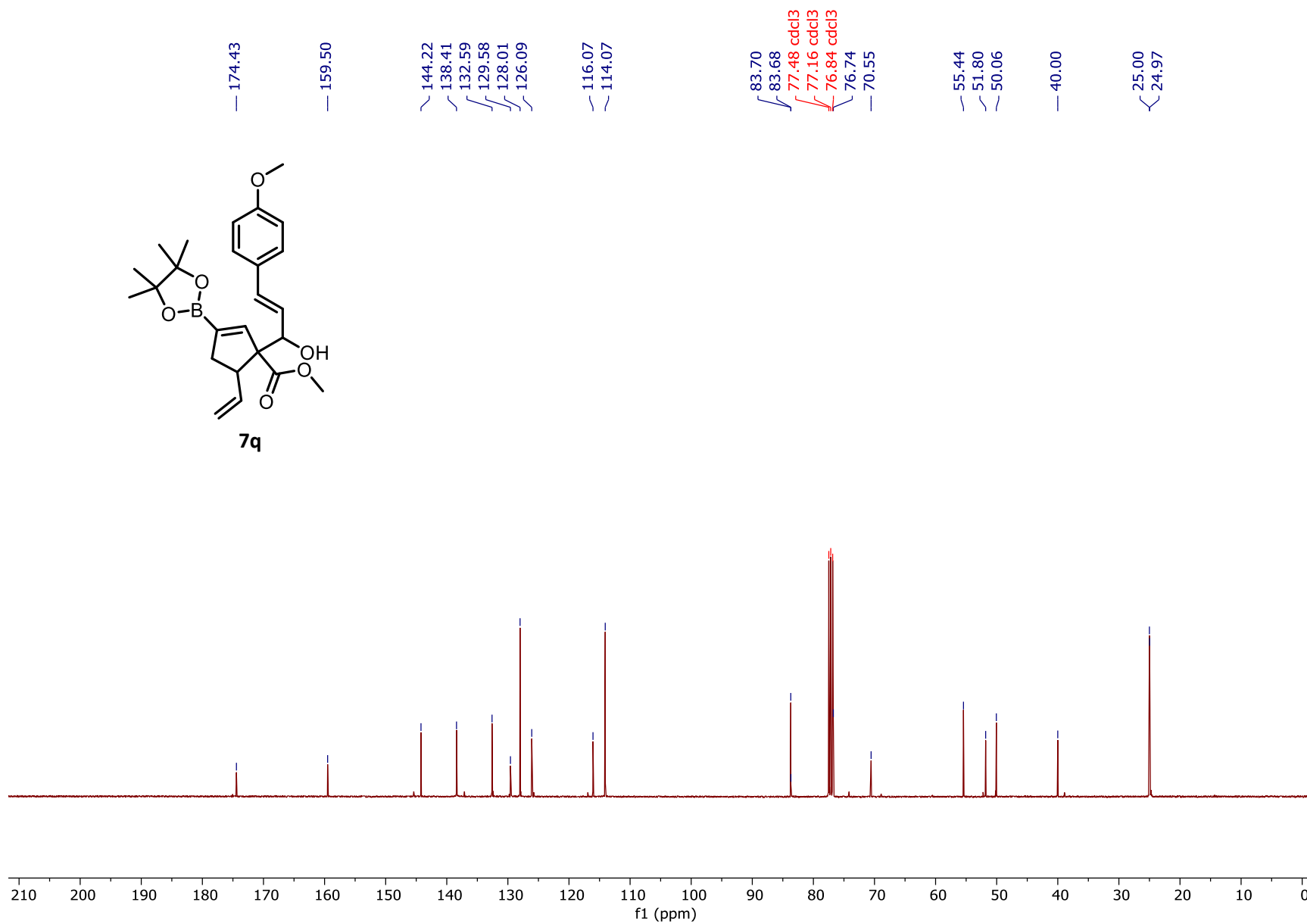
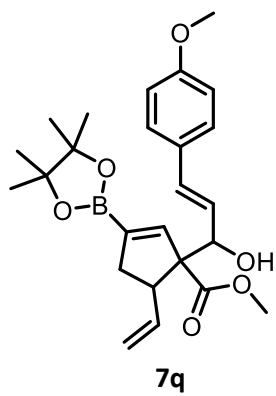


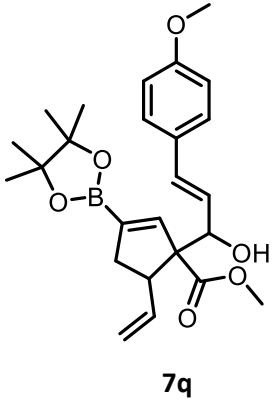


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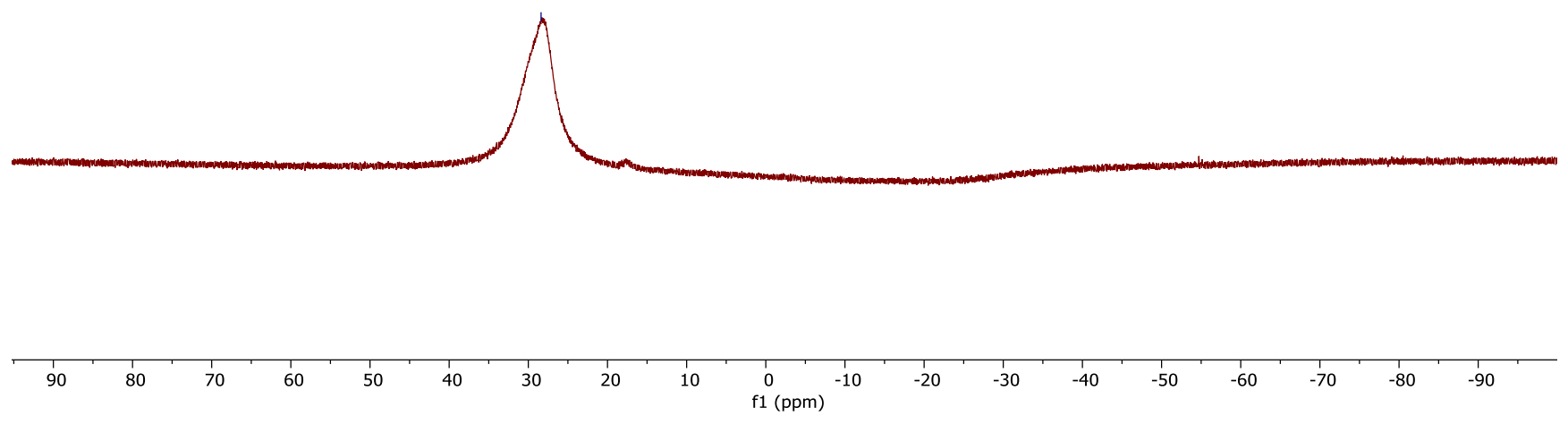


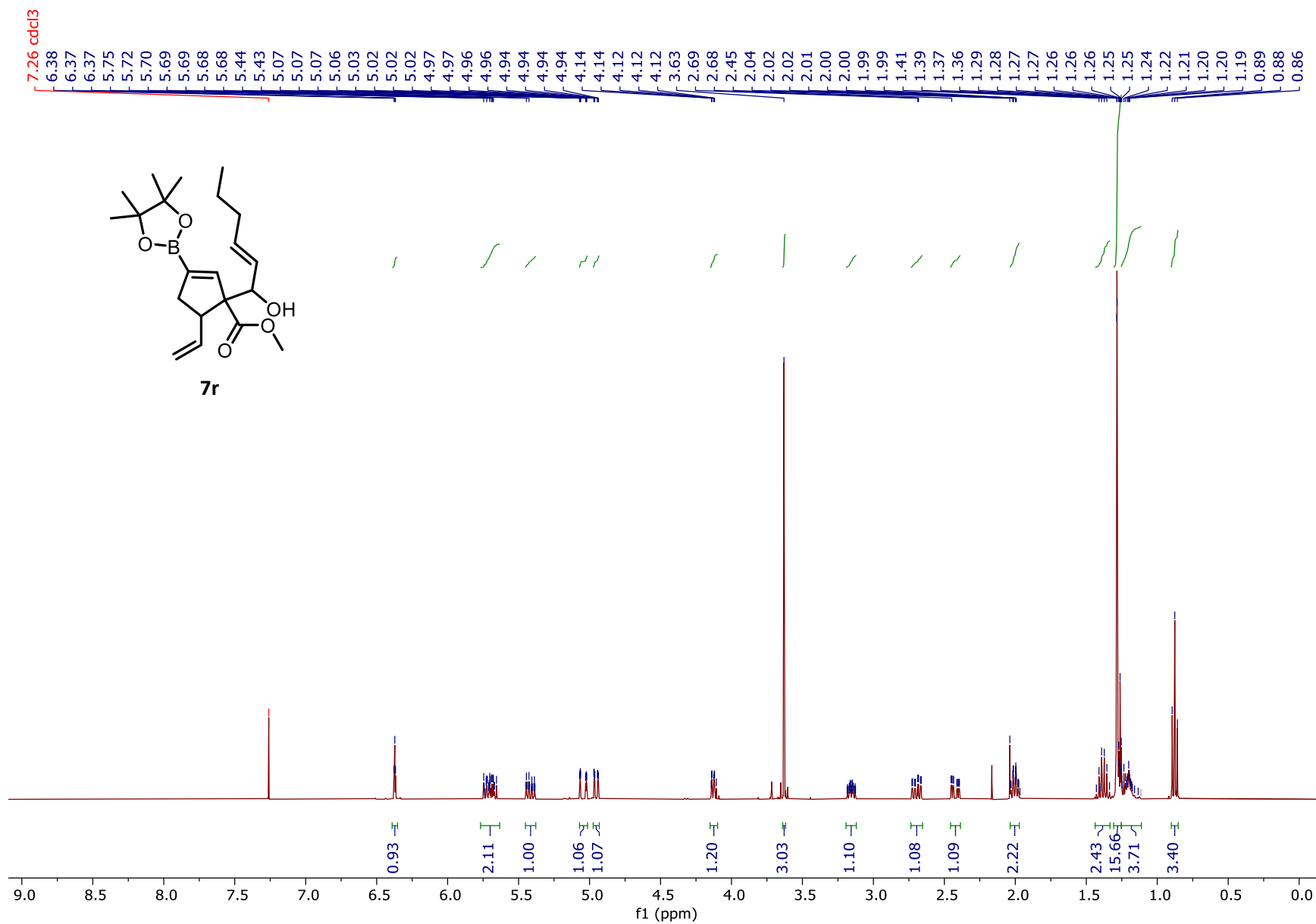


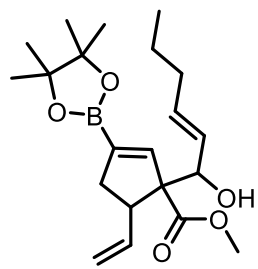




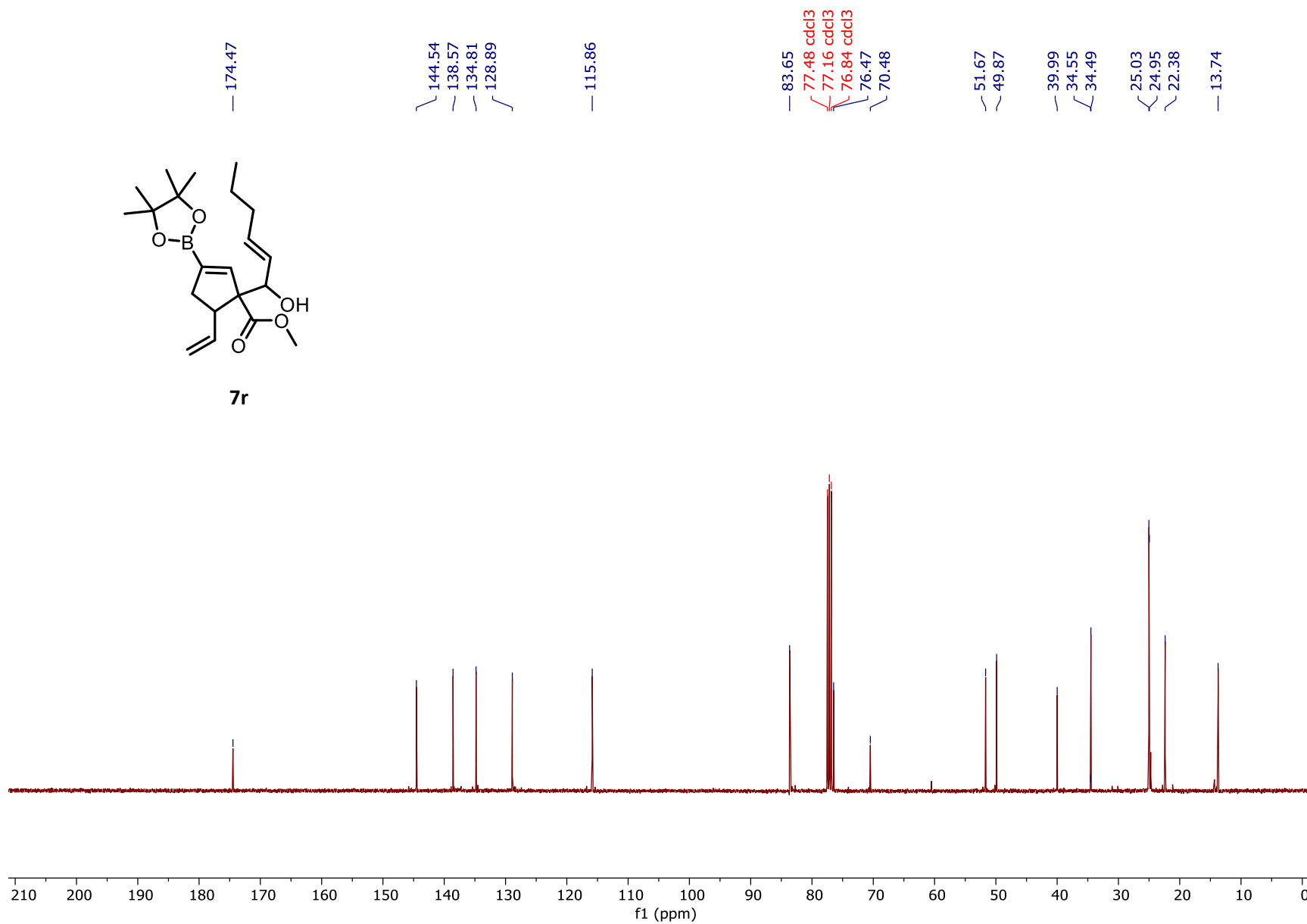
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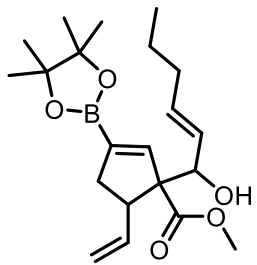






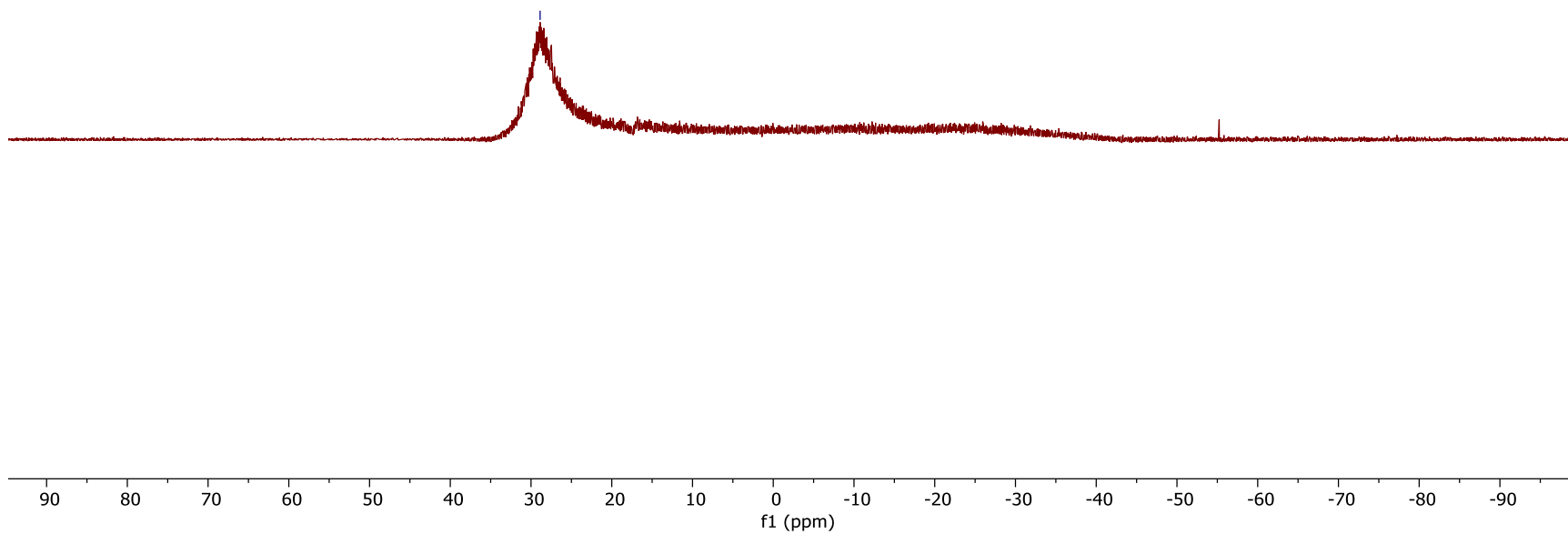
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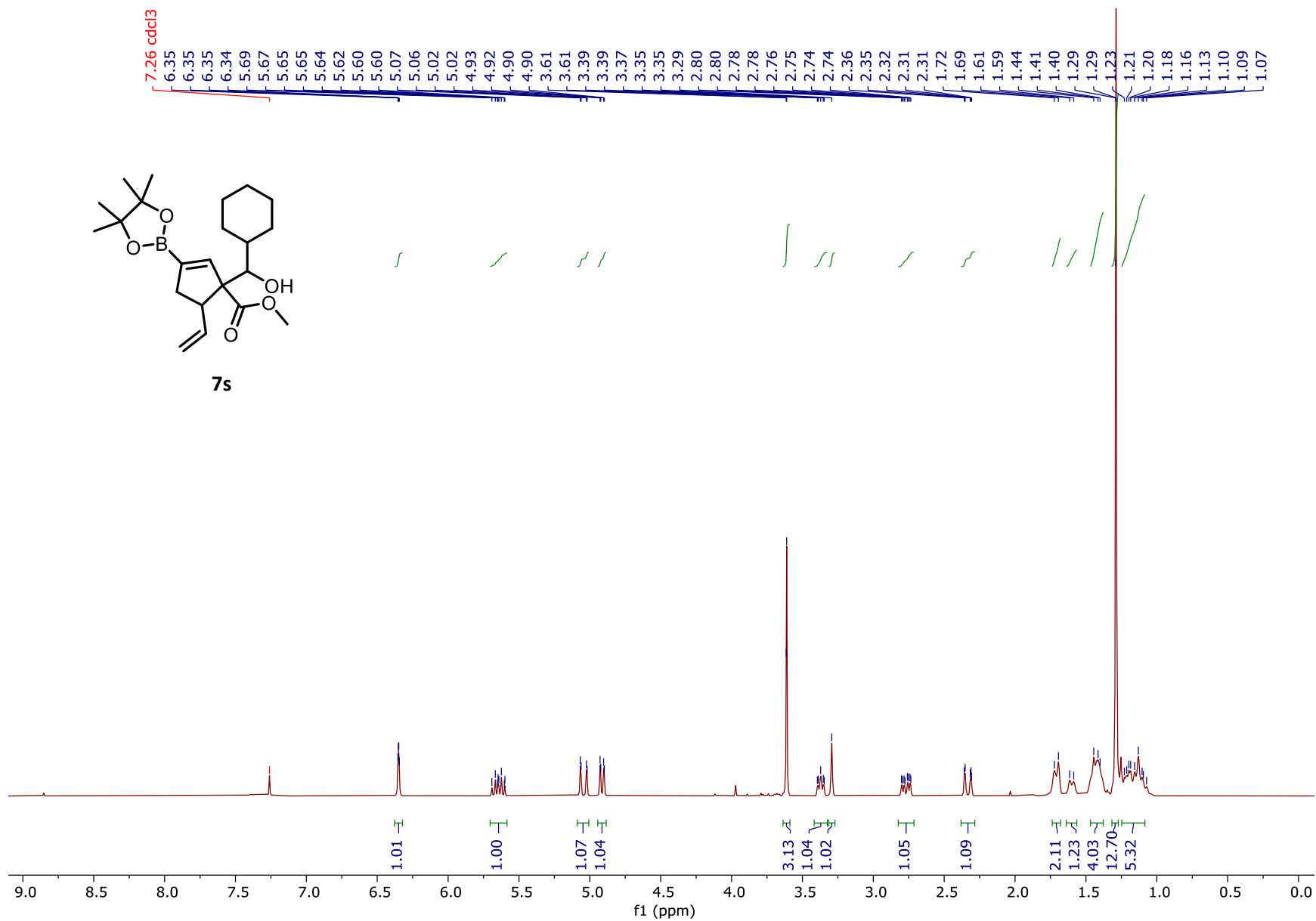


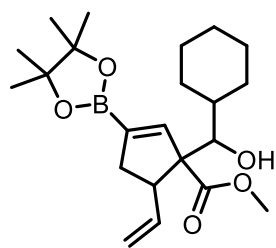


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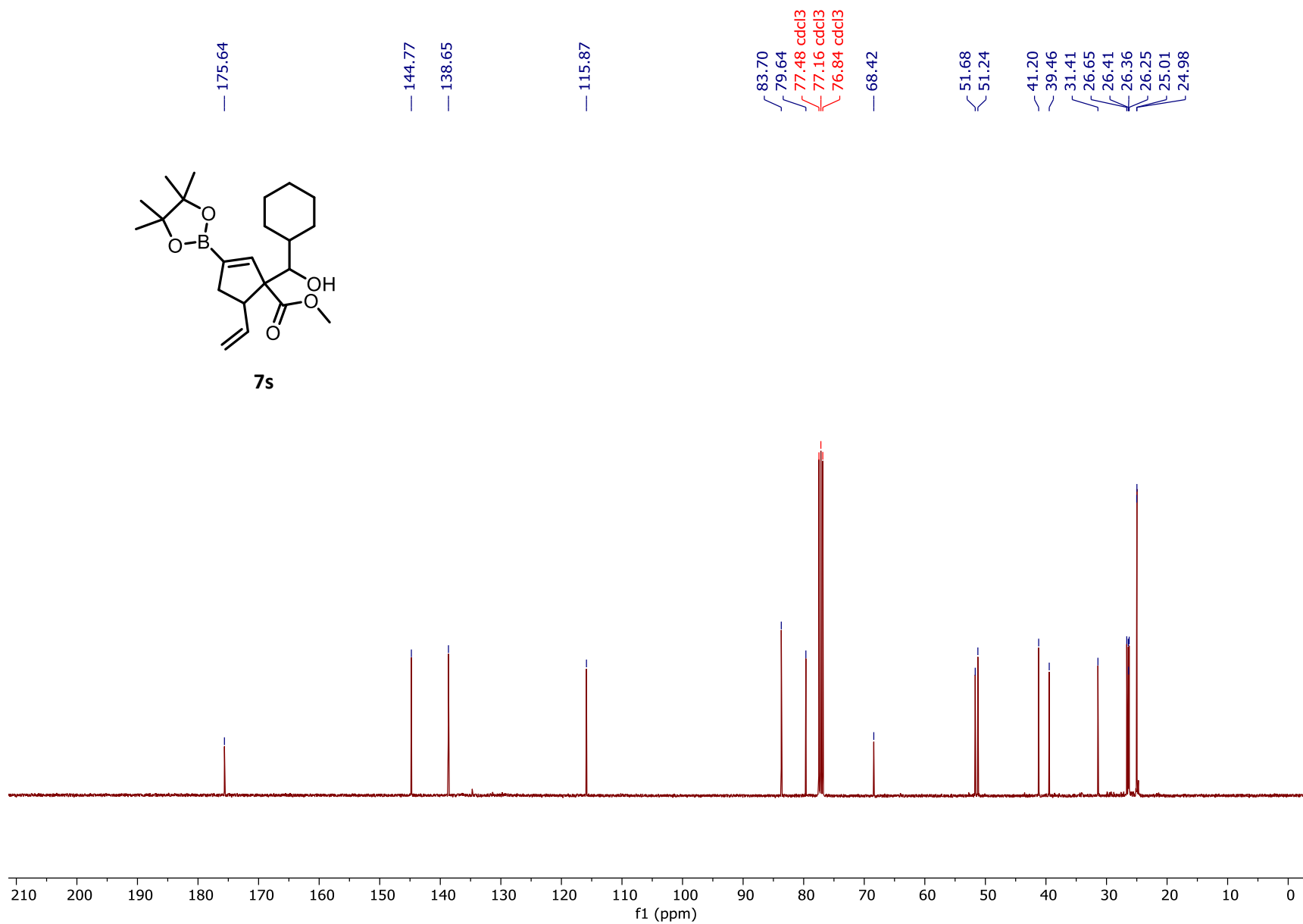
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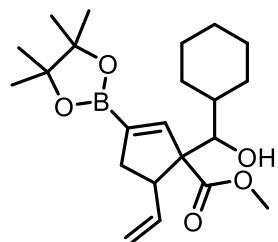






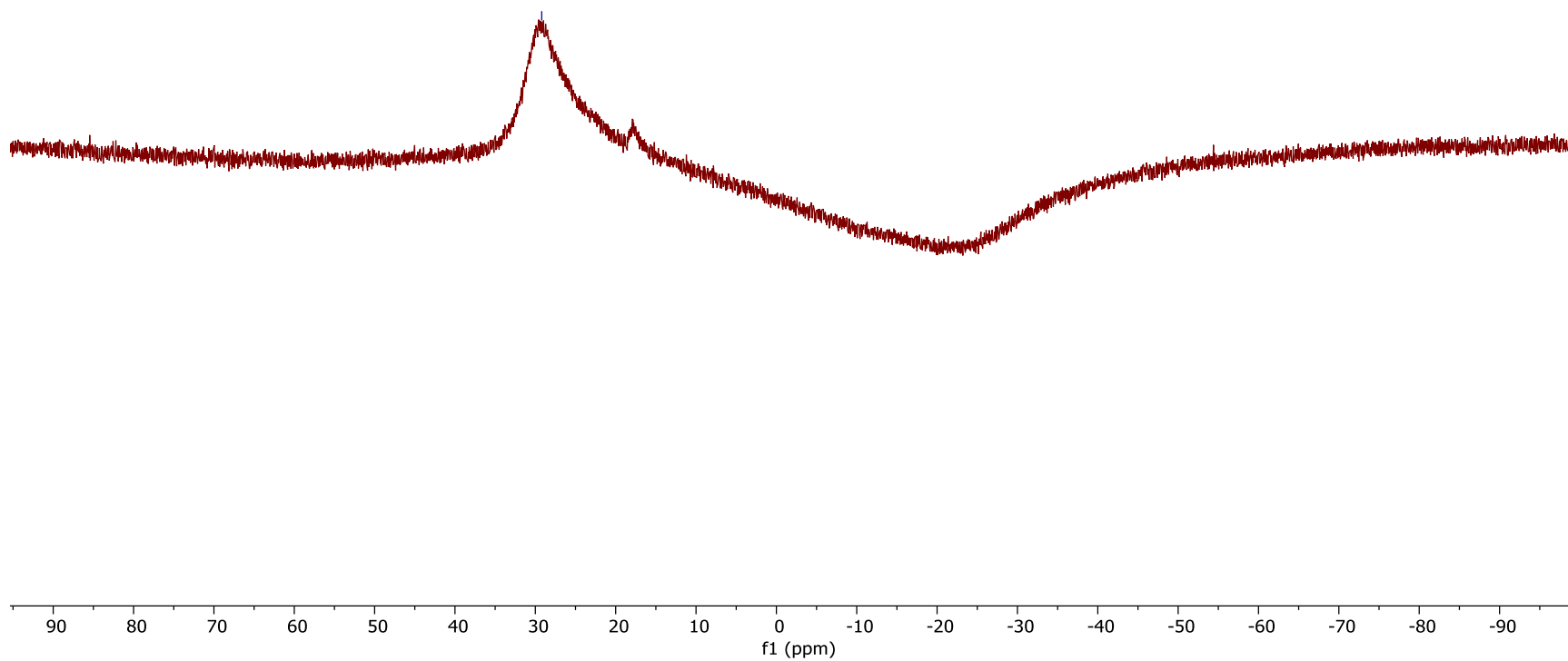
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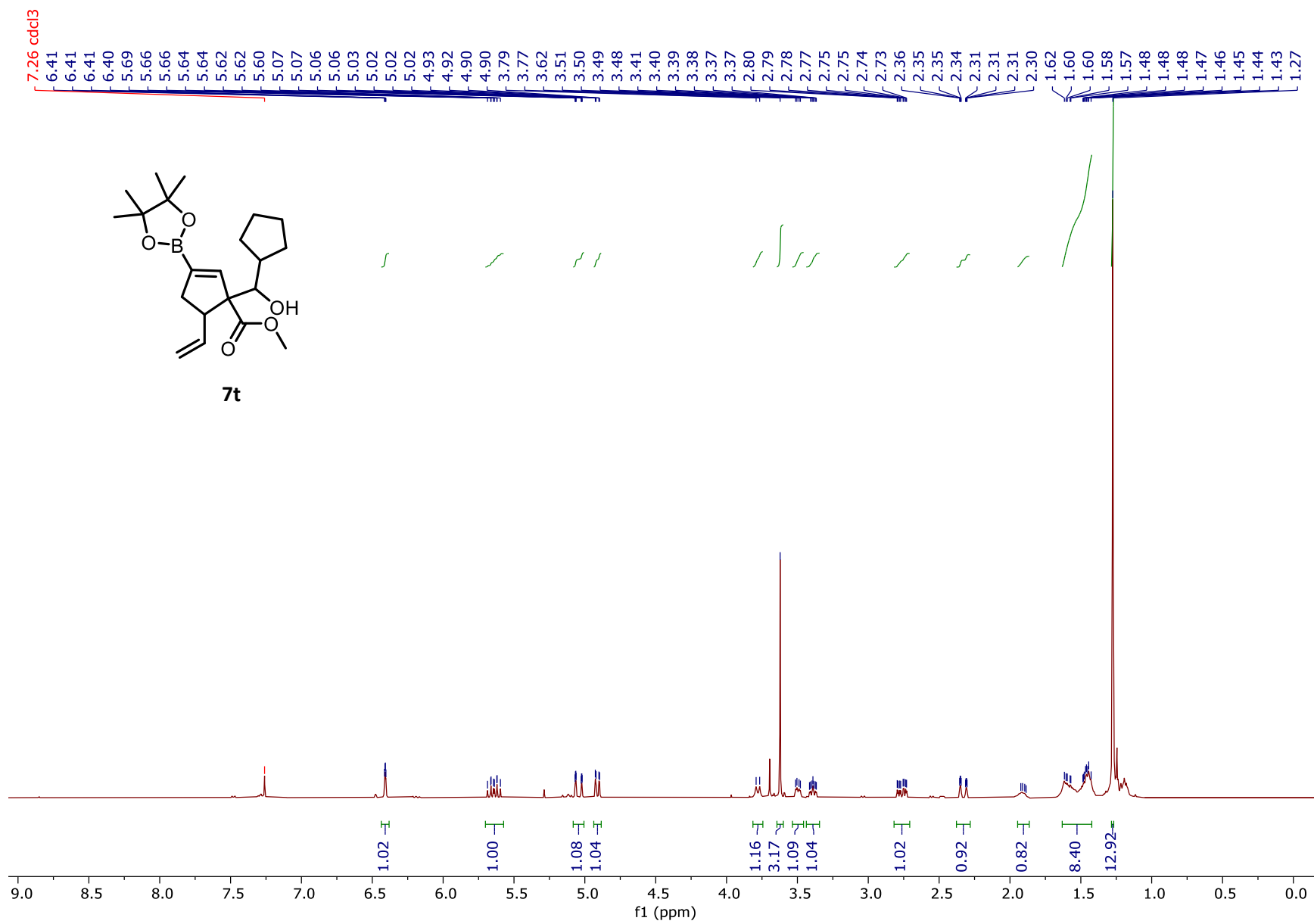


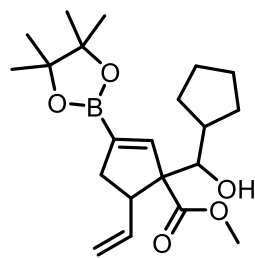


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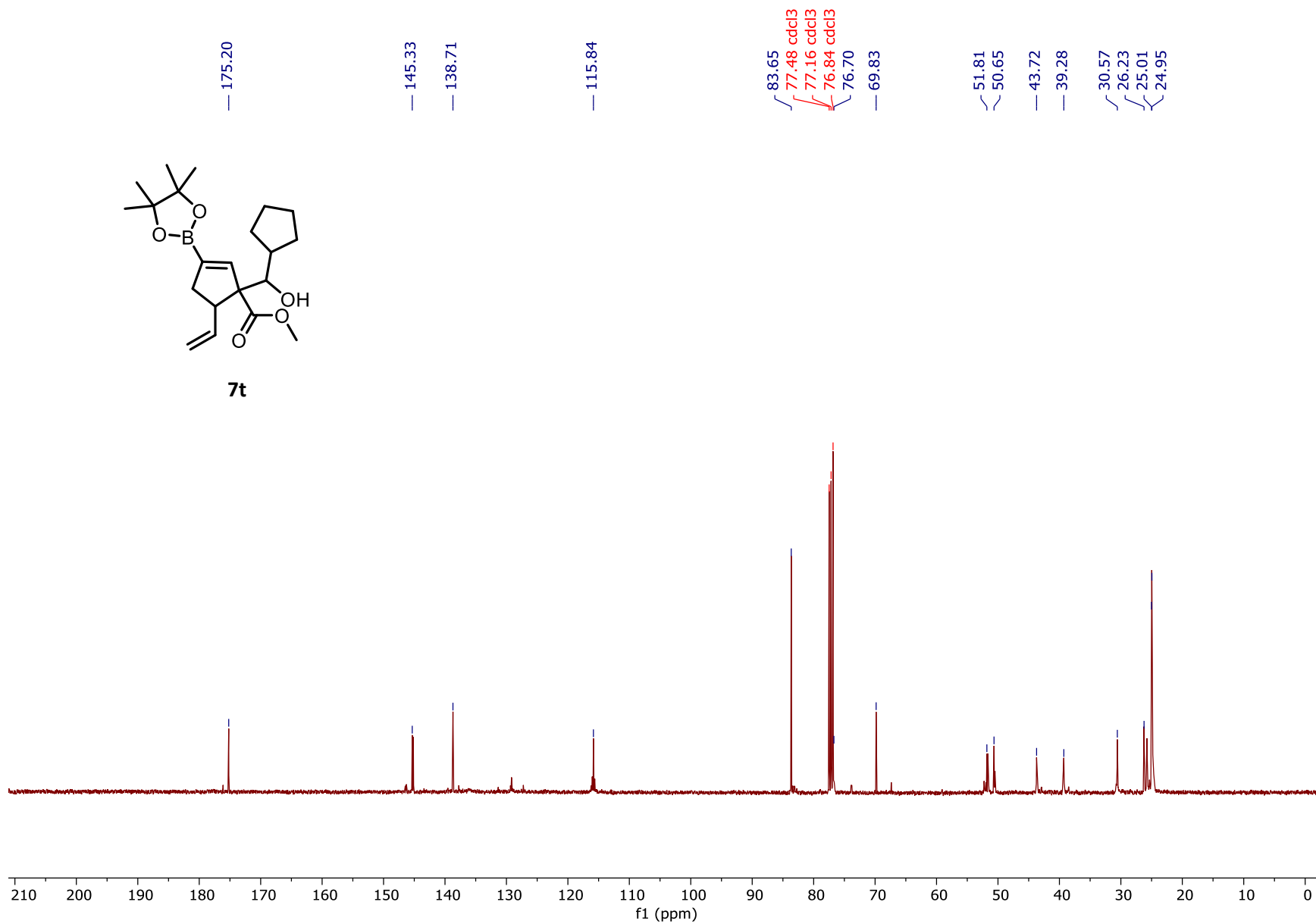
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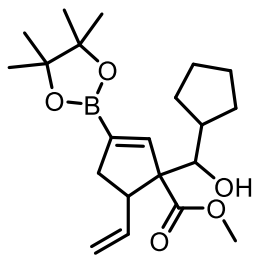






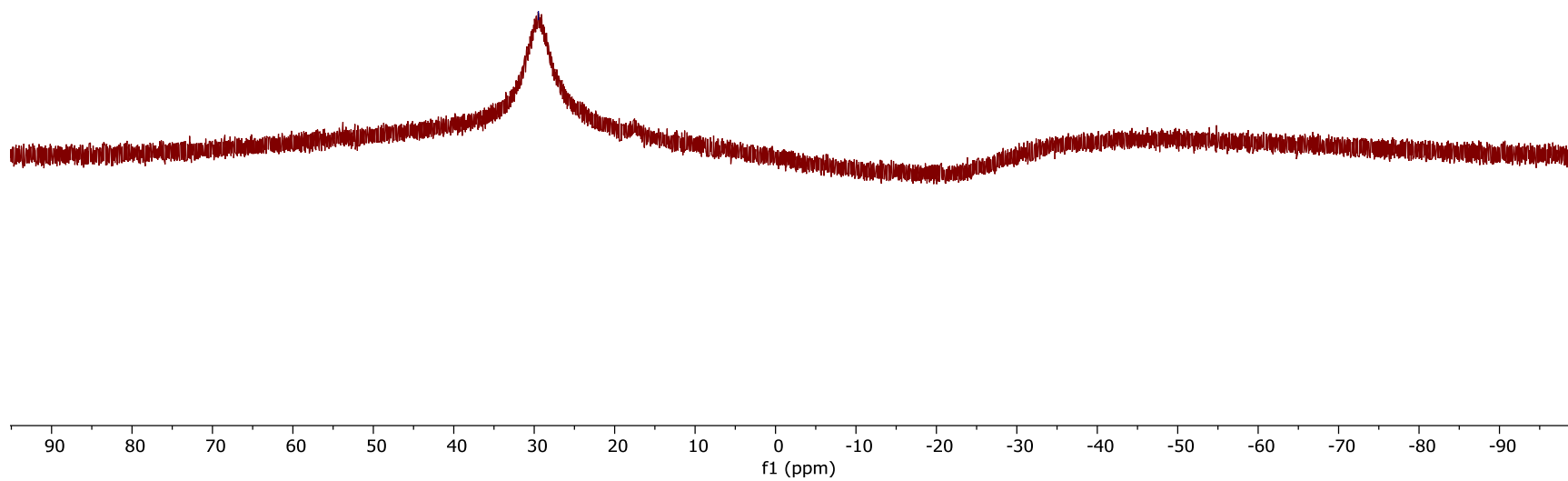
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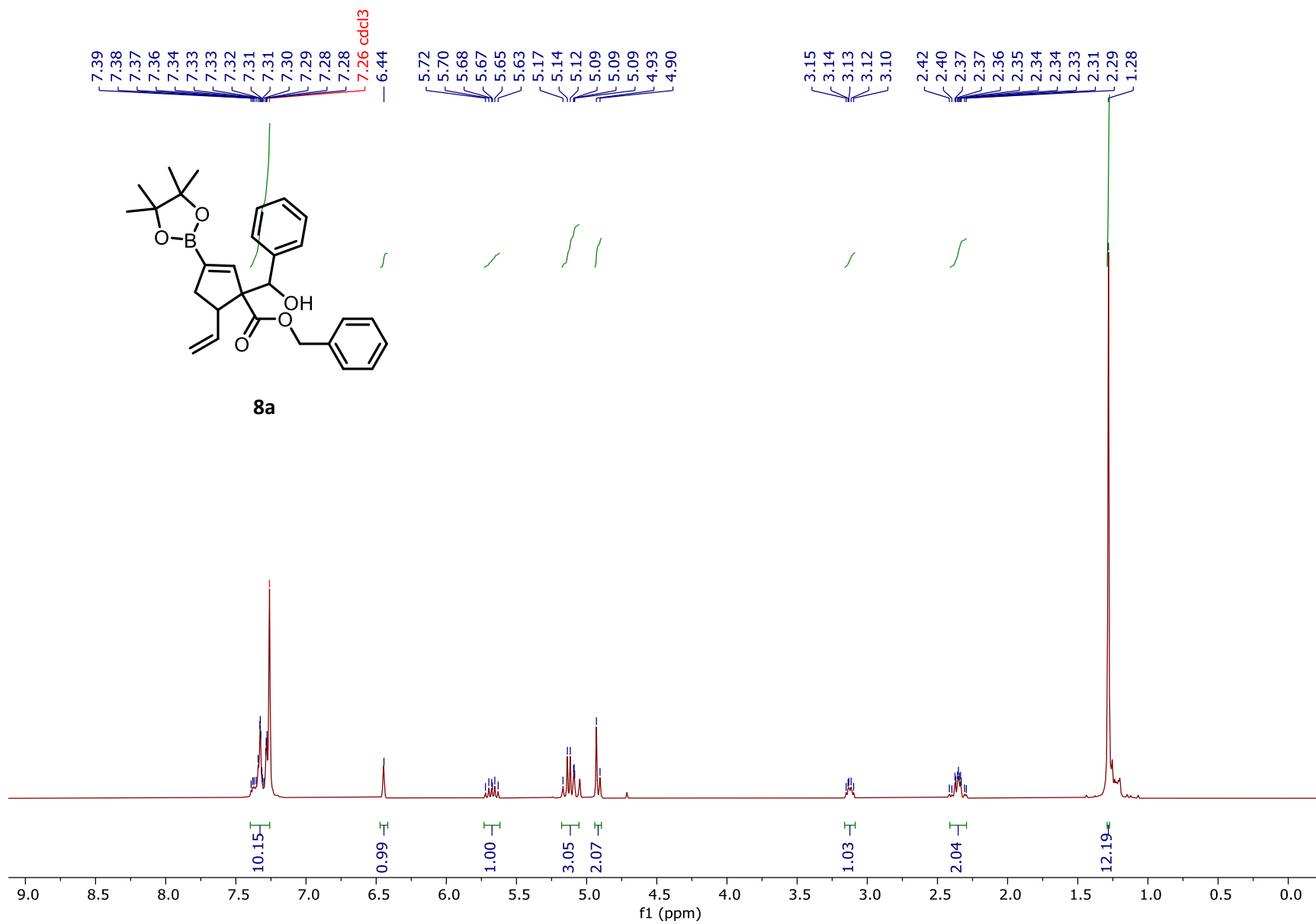


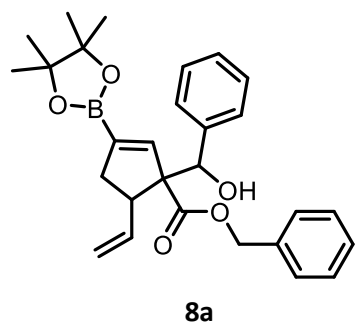


7t

— 29.48







— 174.05

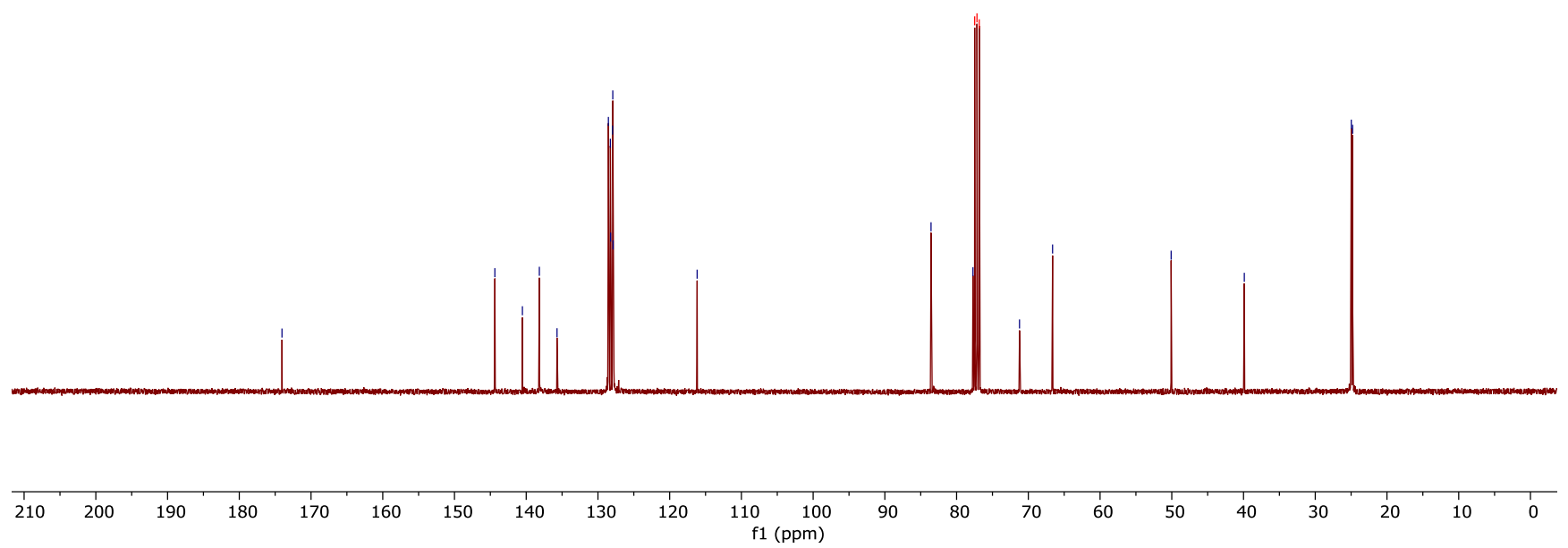
— 144.37
 — 140.53
 — 138.17
 — 135.70
 — 128.54
 — 128.27
 — 128.23
 — 127.97
 — 127.93
 — 127.89
 — 116.17

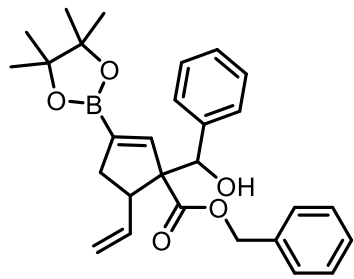
— 83.56
 — 77.72
 — 77.48 cdc13
 — 77.16 cdc13
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 — 71.23
 — 66.62

— 50.09

— 39.89

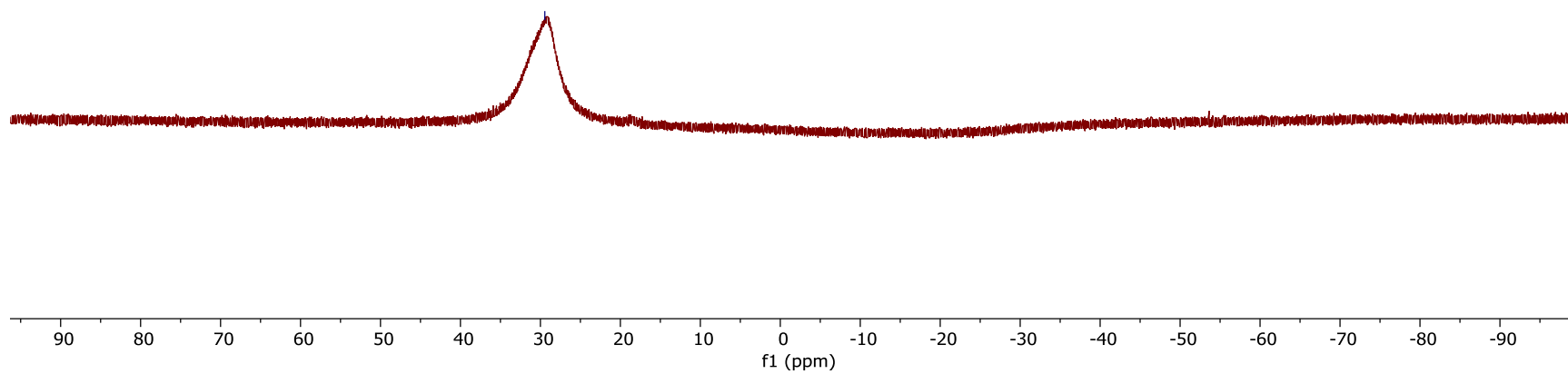
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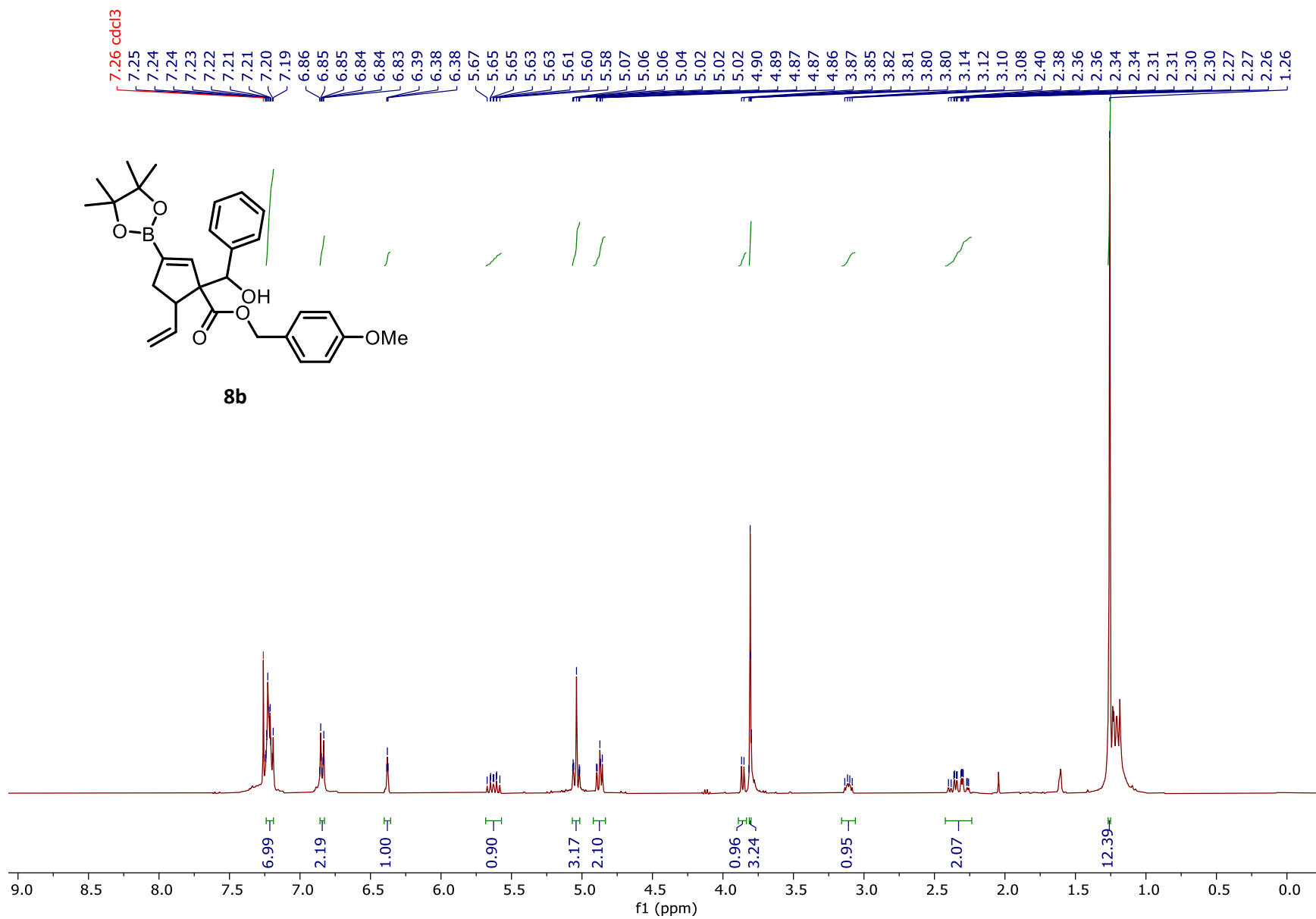


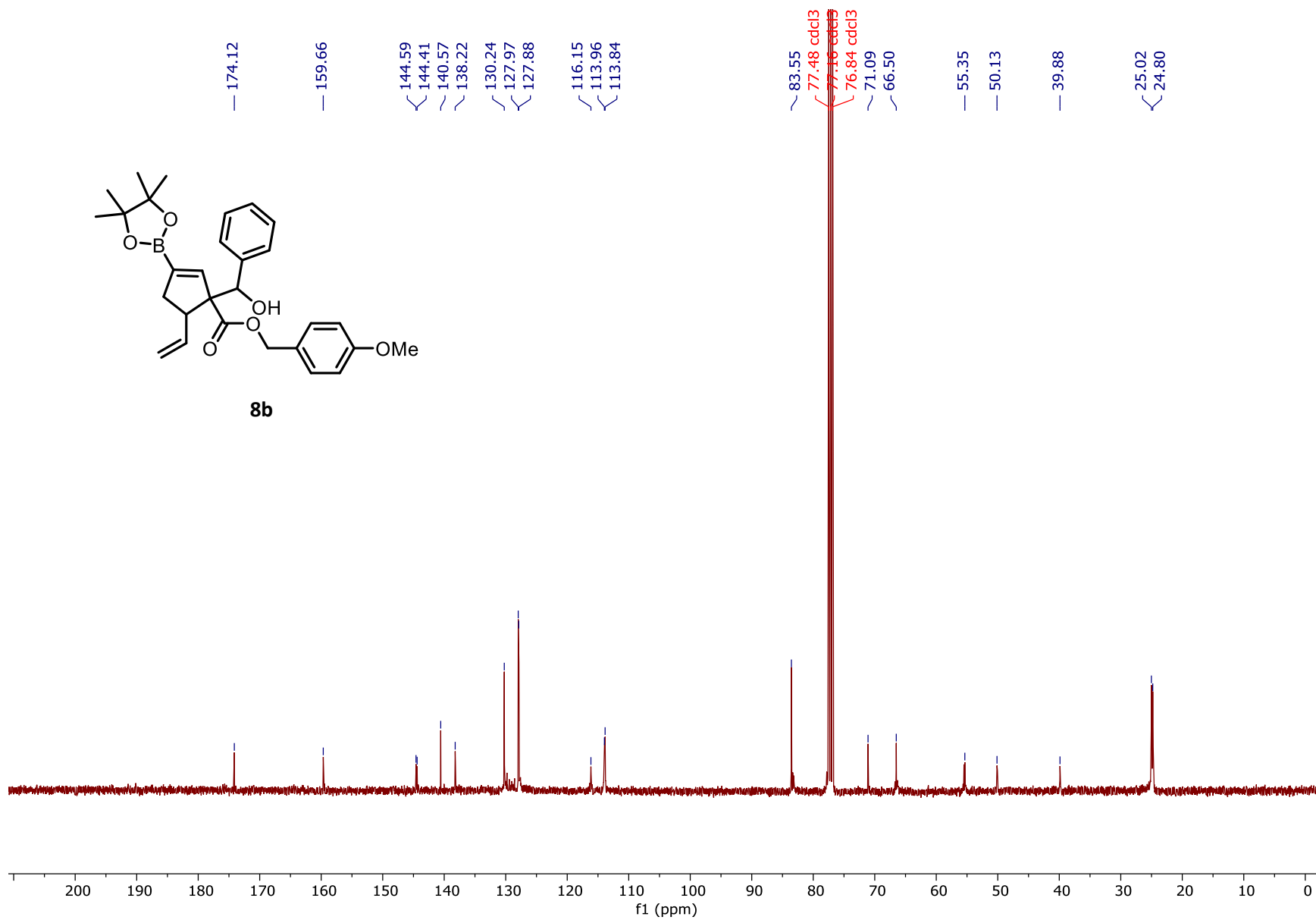


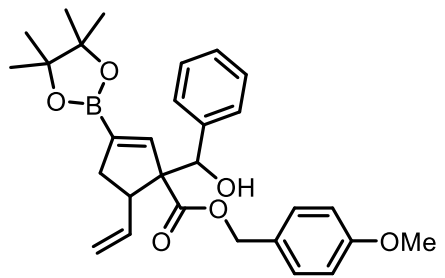
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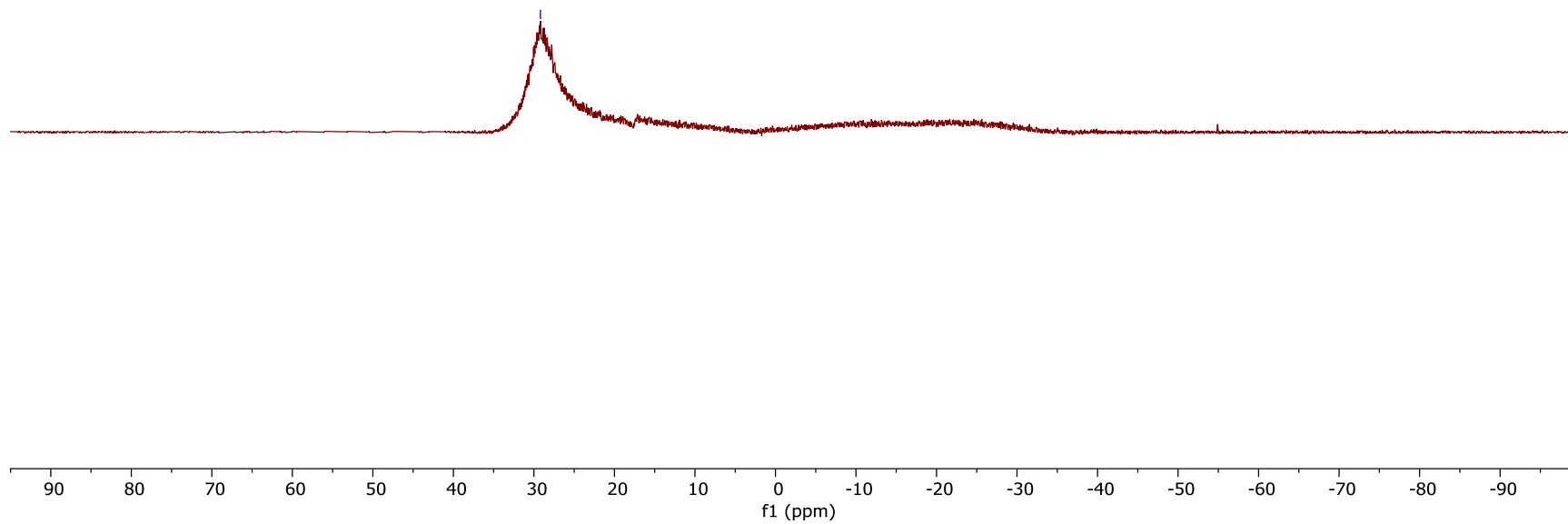


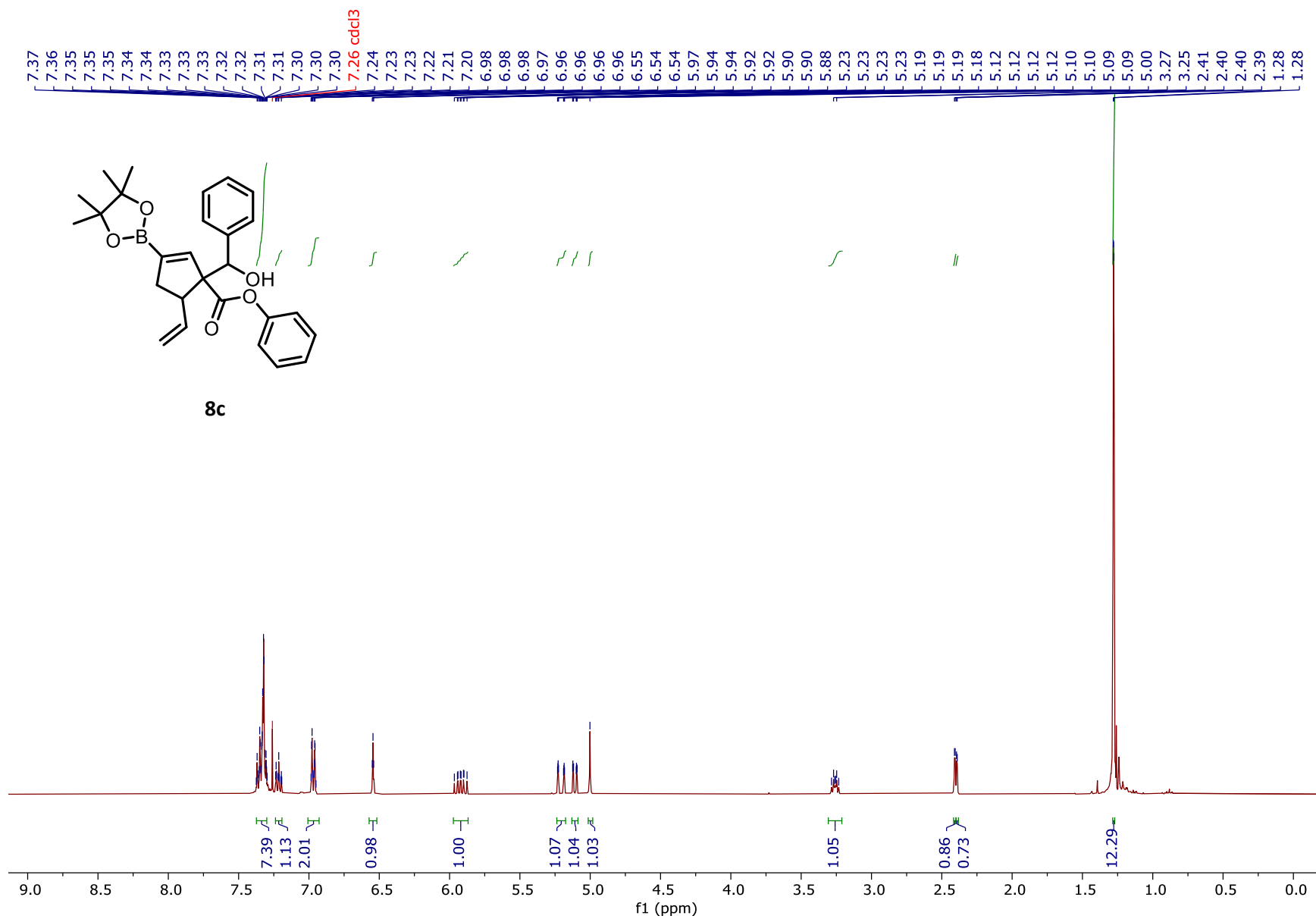


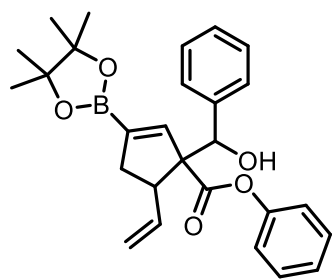


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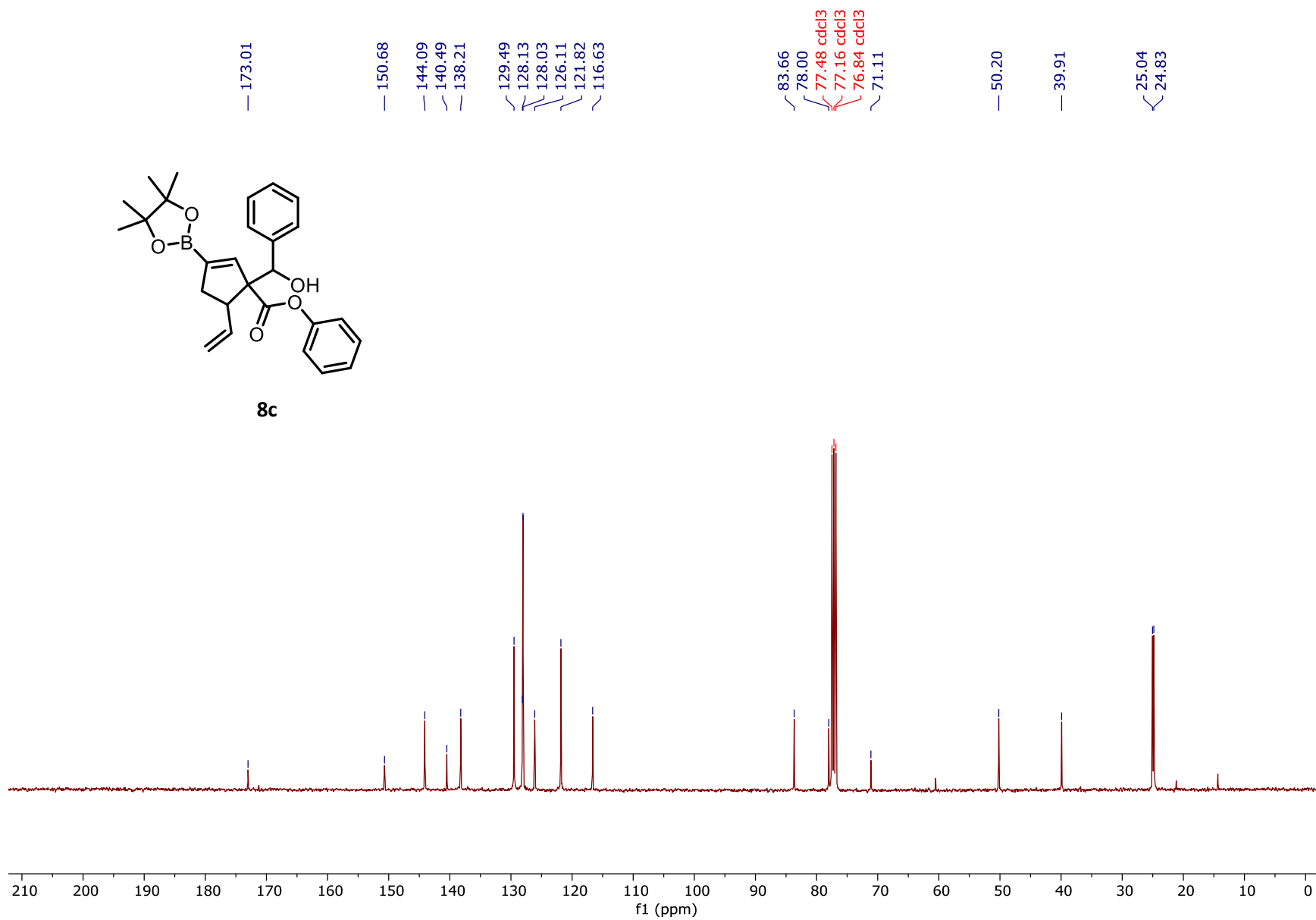
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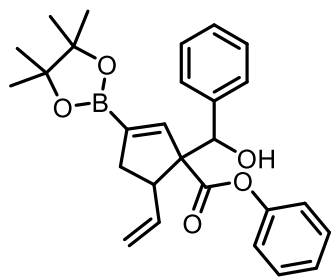






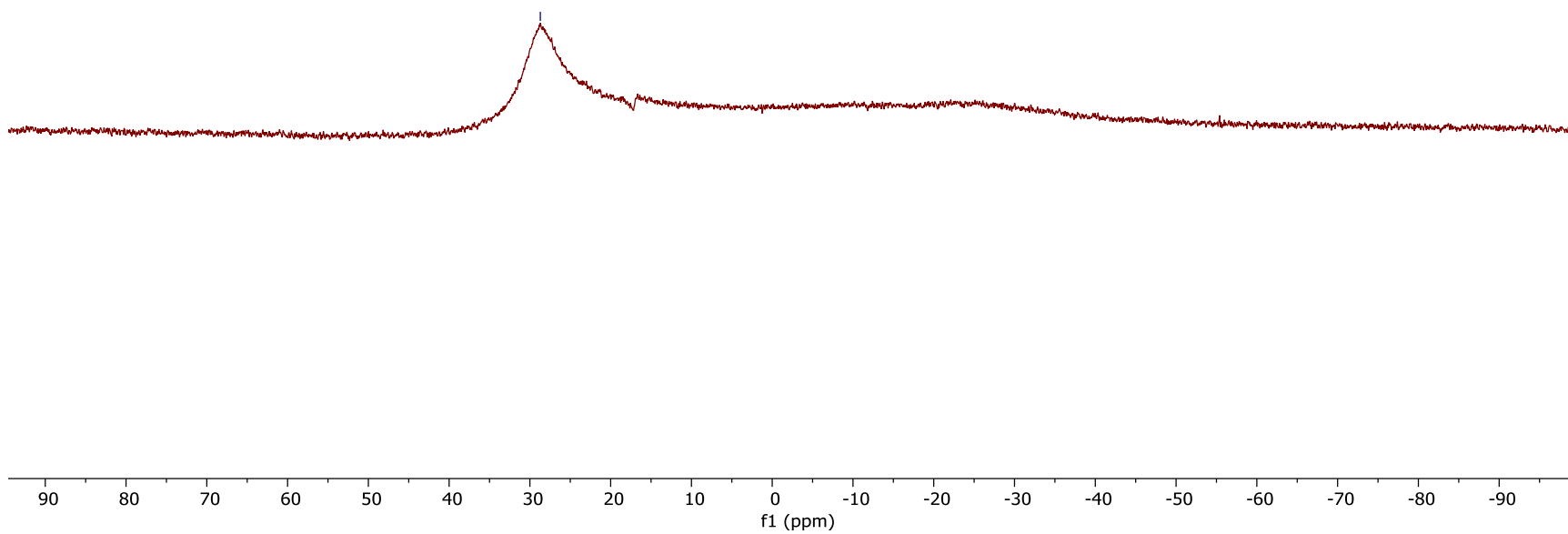
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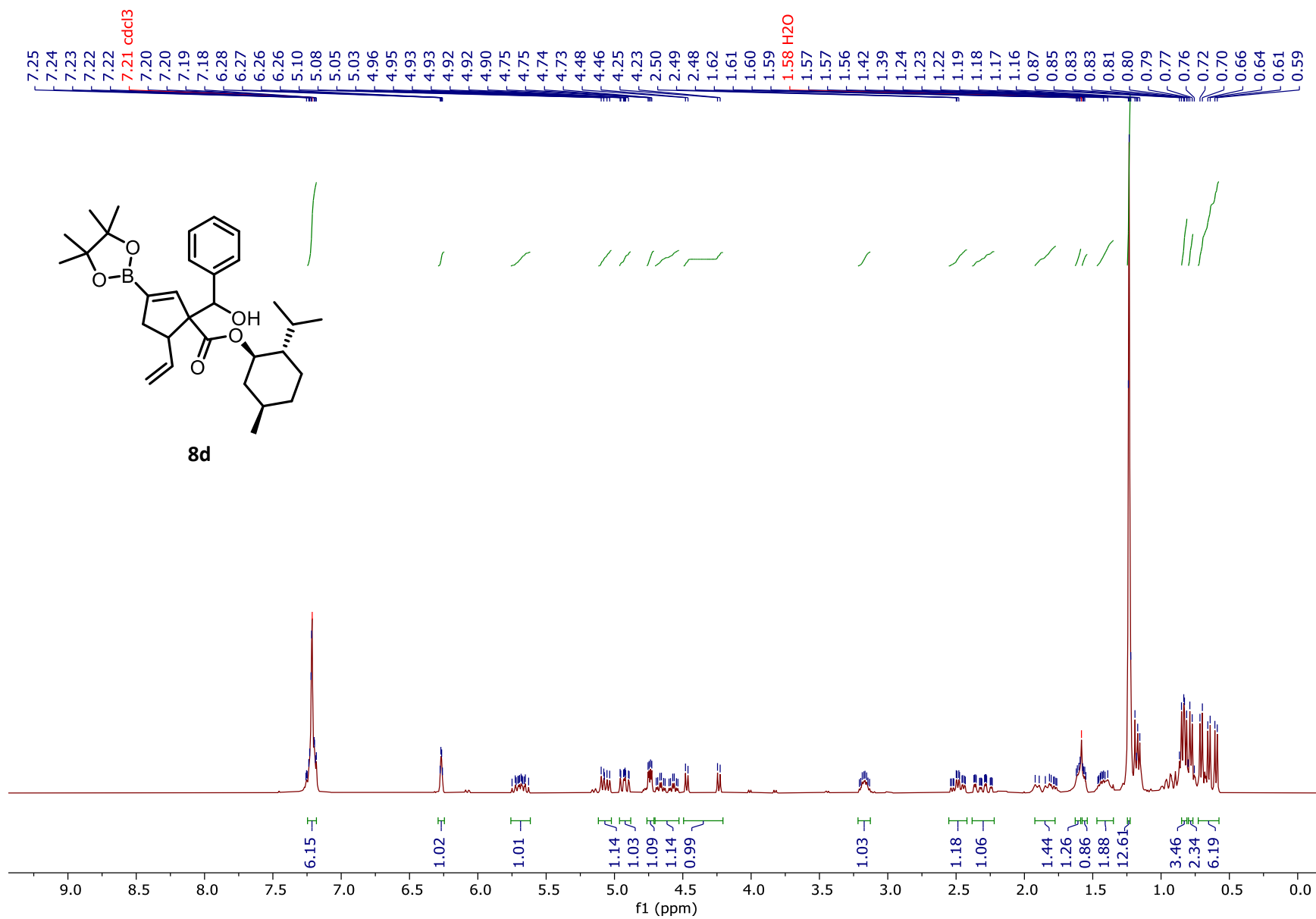


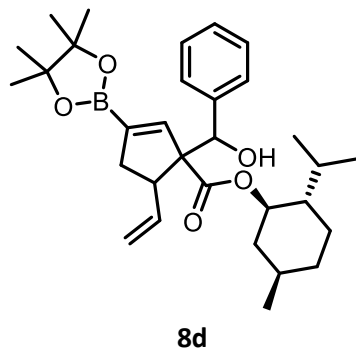


8c

— 28.71





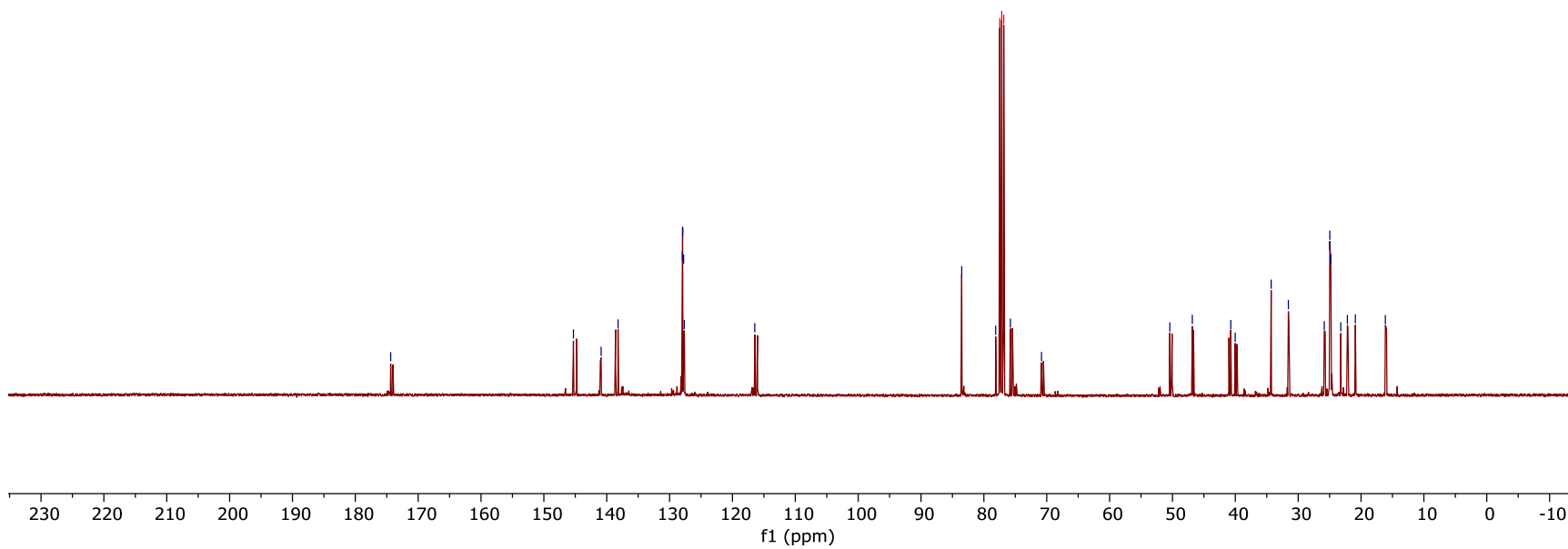


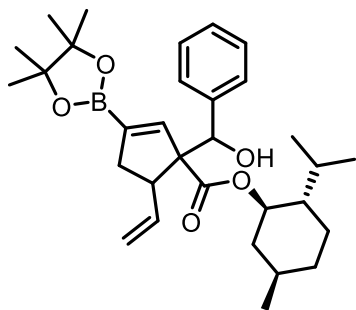
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— 145.30
 — 140.89
 — 138.20
 { 127.97
 { 127.93
 { 127.77
 { 127.66
 — 116.45

{ 83.53
 { 78.13
 { 77.48 cdcl3
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 { 75.78
 { 70.84

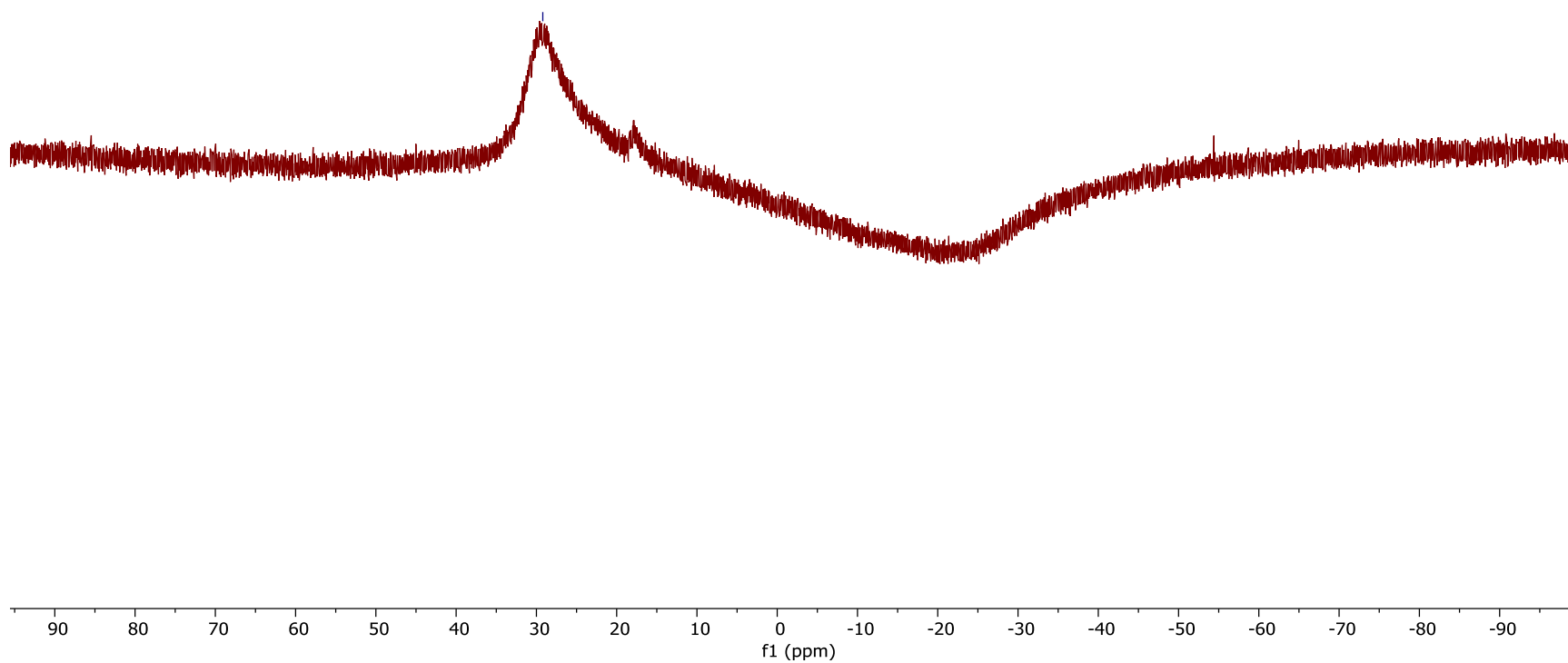
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 { 20.90
 { 16.13

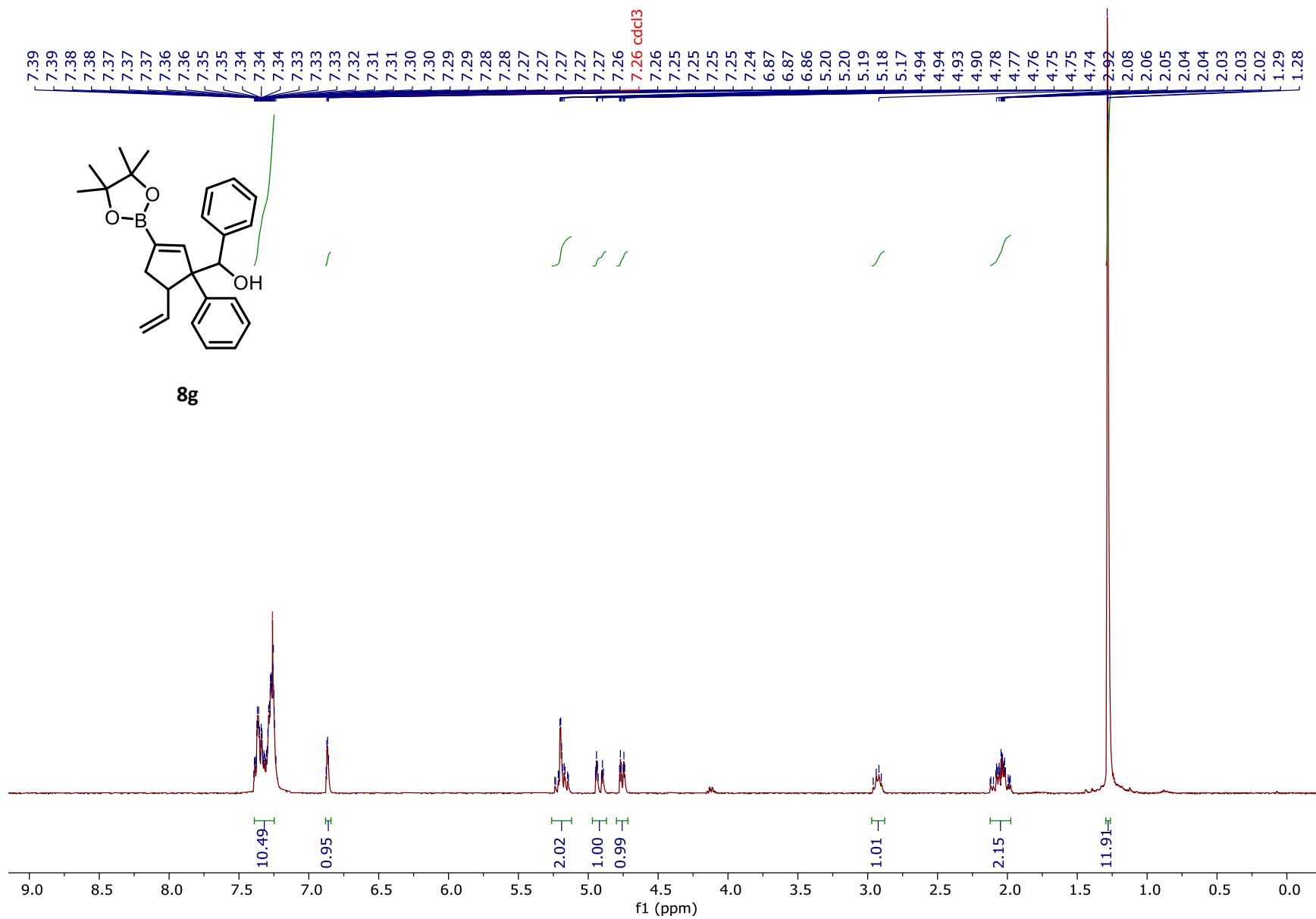


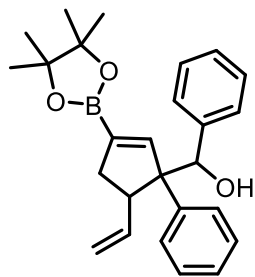


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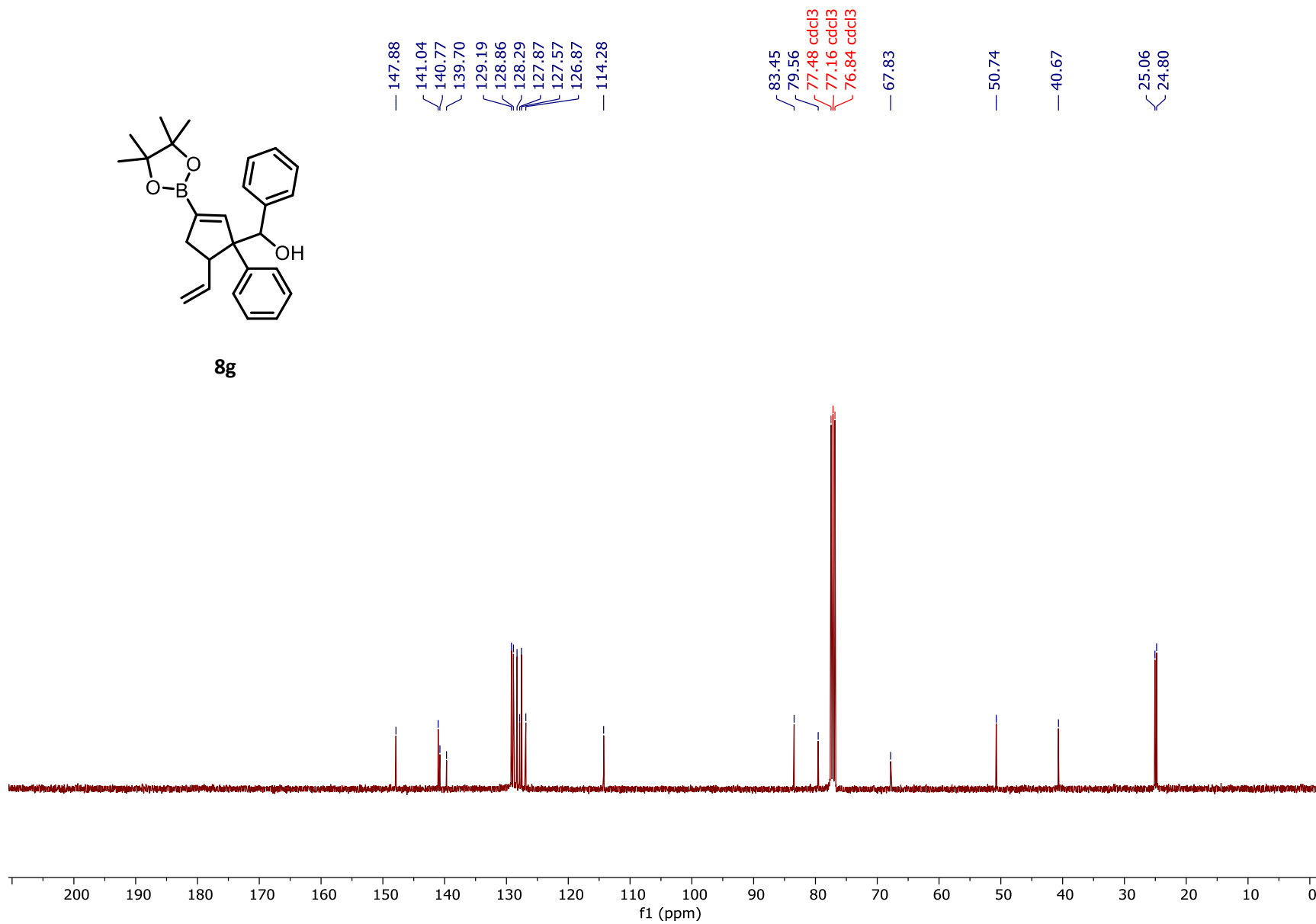
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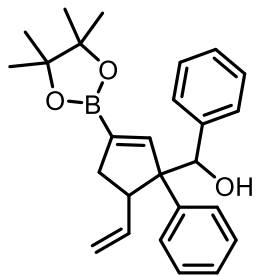






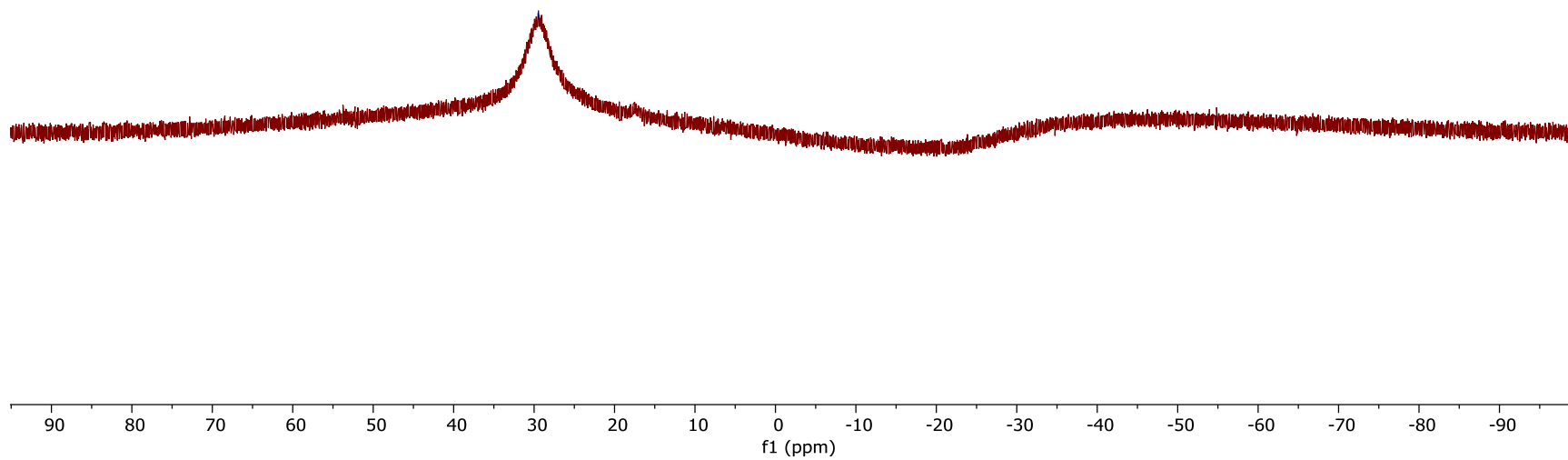
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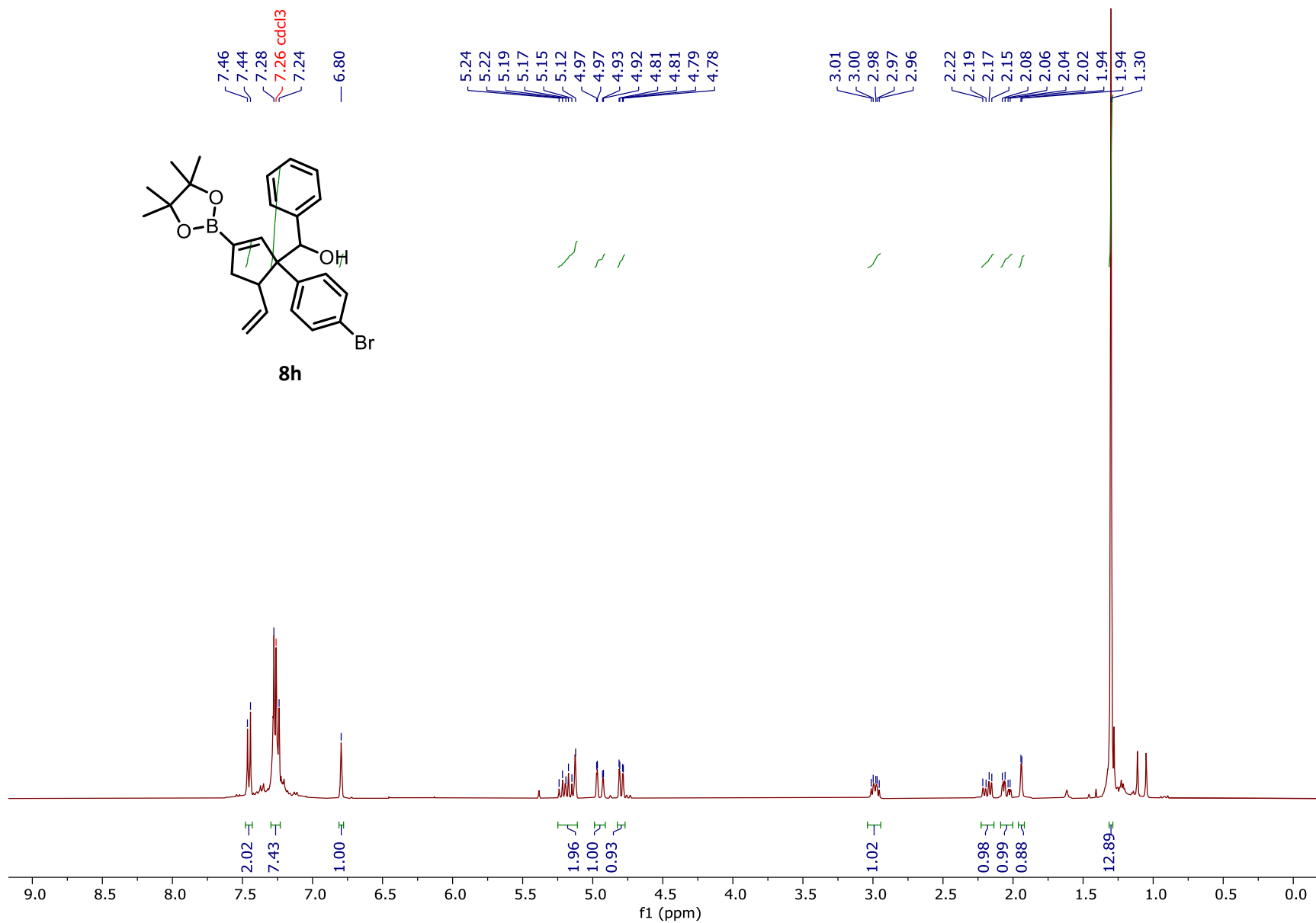
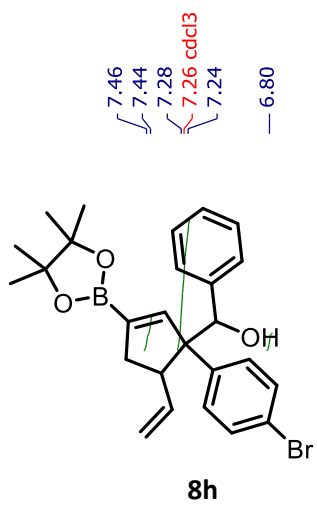


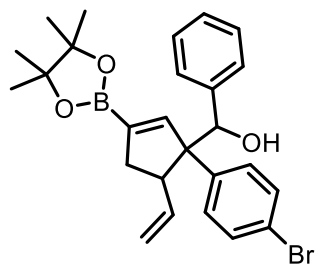


8g

— 29.46







8h

— 147.37
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— 138.93
— 131.10
— 128.64
— 128.00
— 127.68
— 120.80
— 114.68

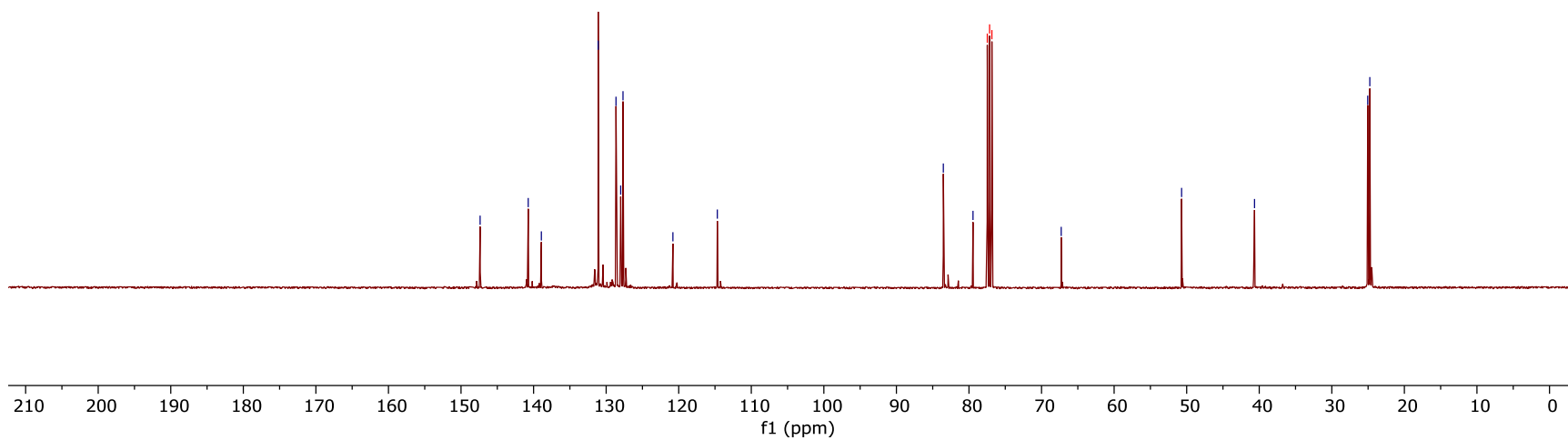
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— 77.48 cdc13
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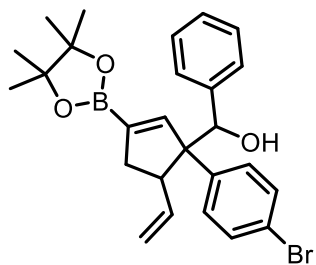
— 67.29

— 50.70

— 40.65

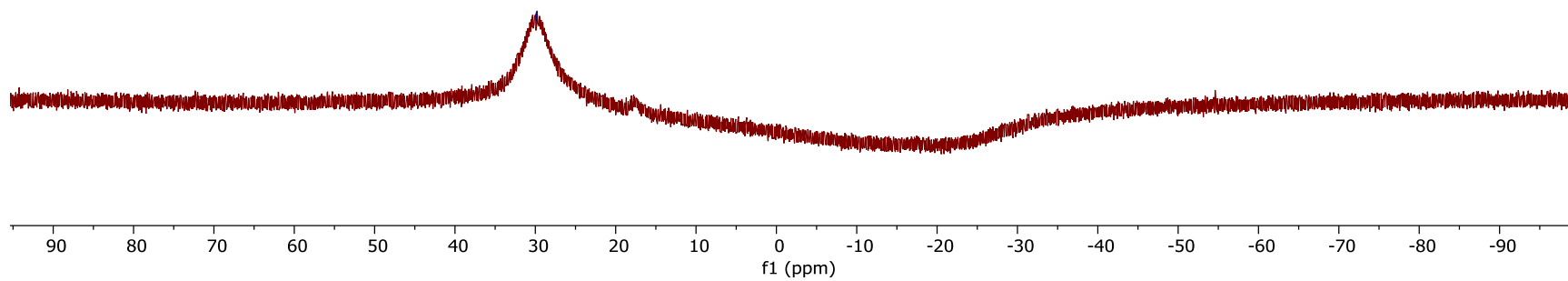
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— 24.77

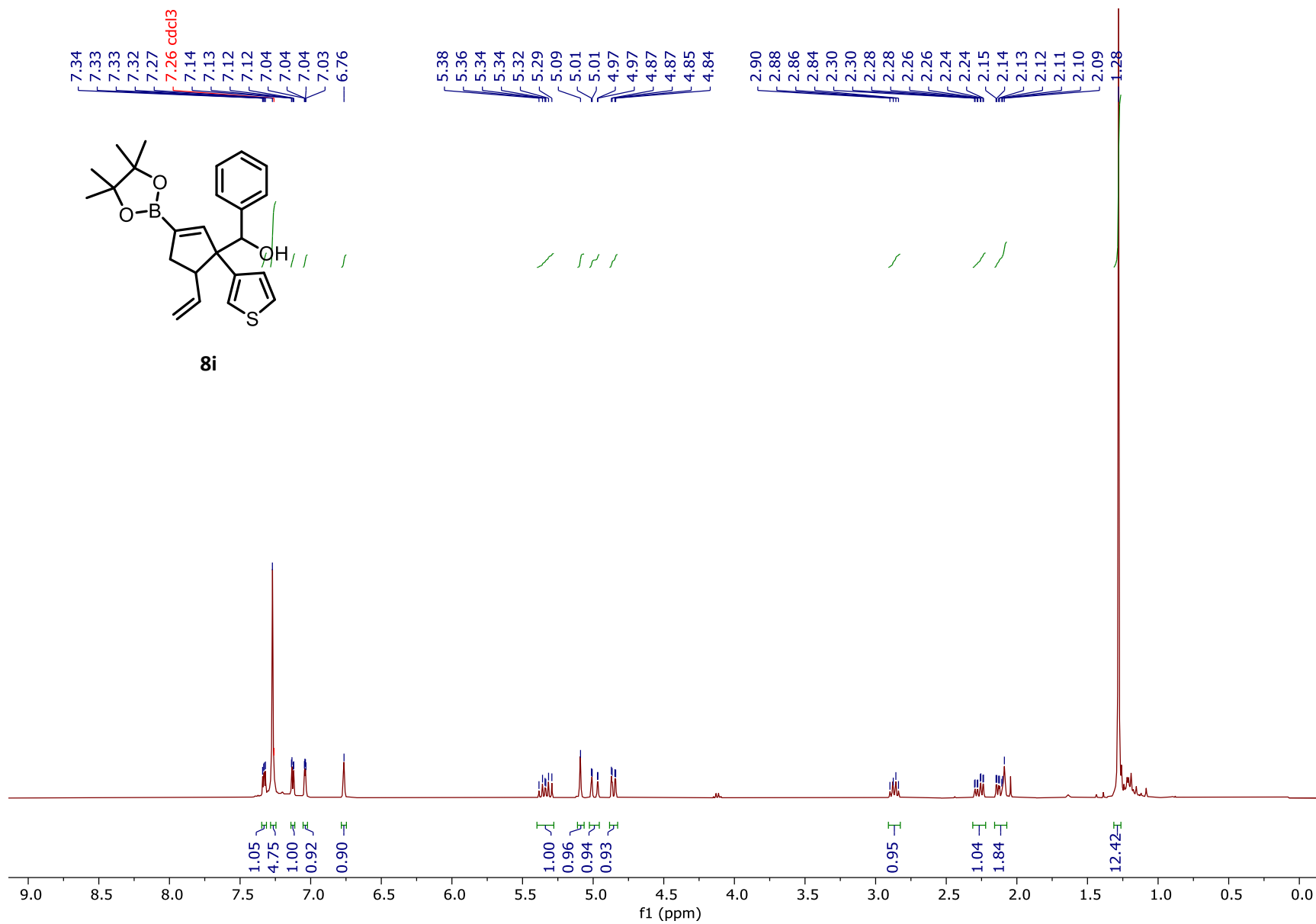


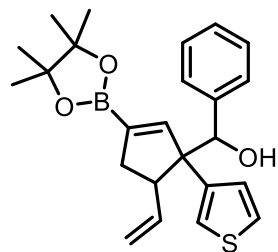


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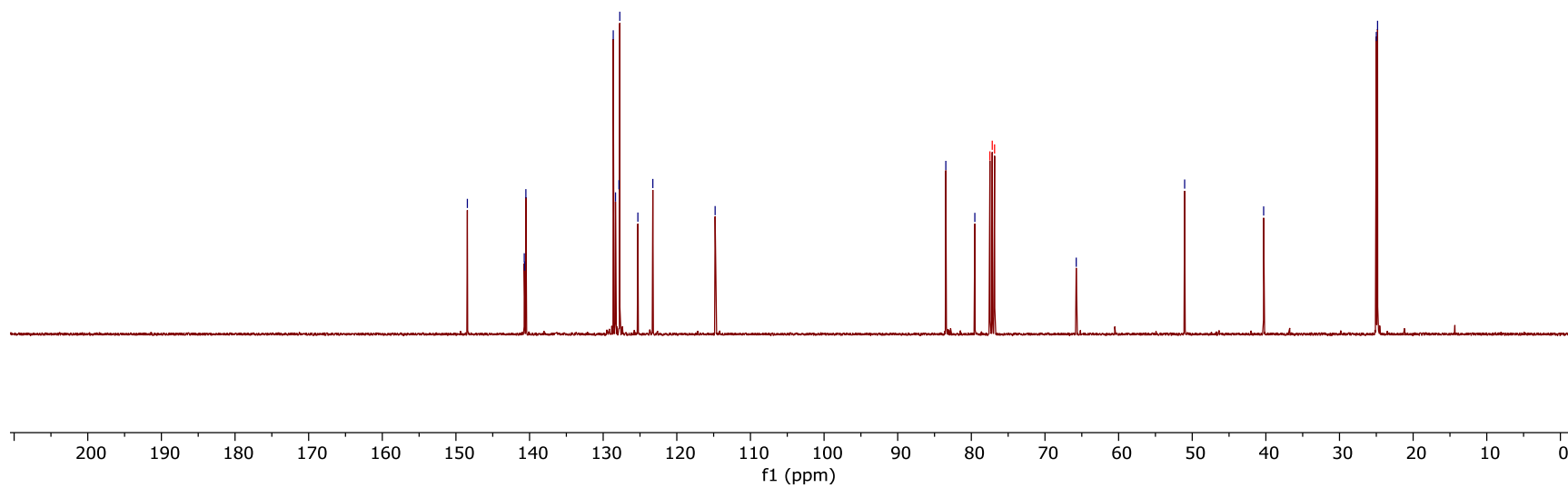
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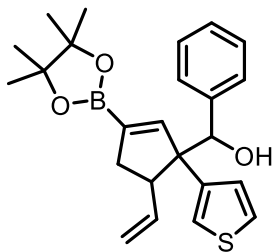






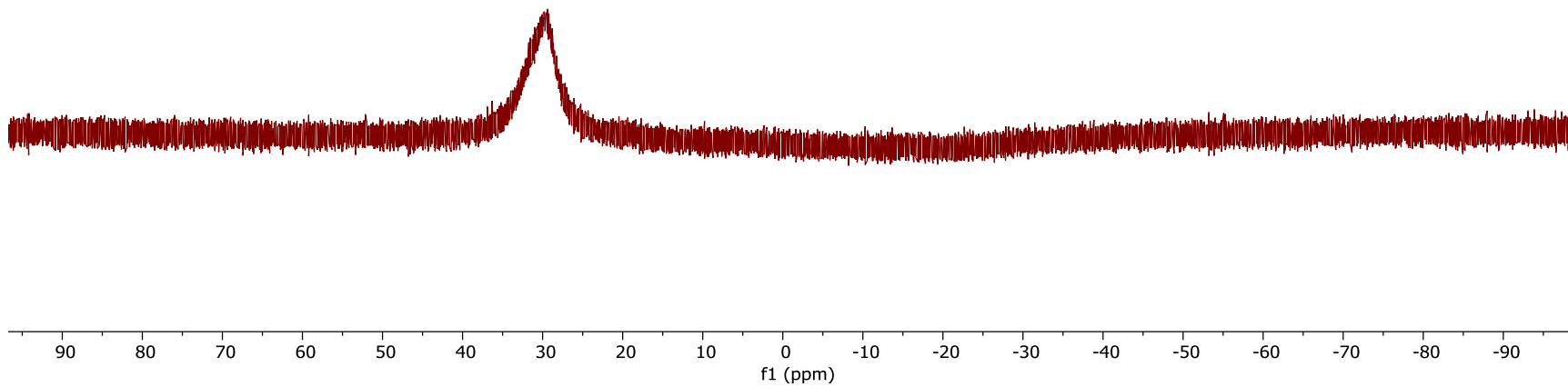
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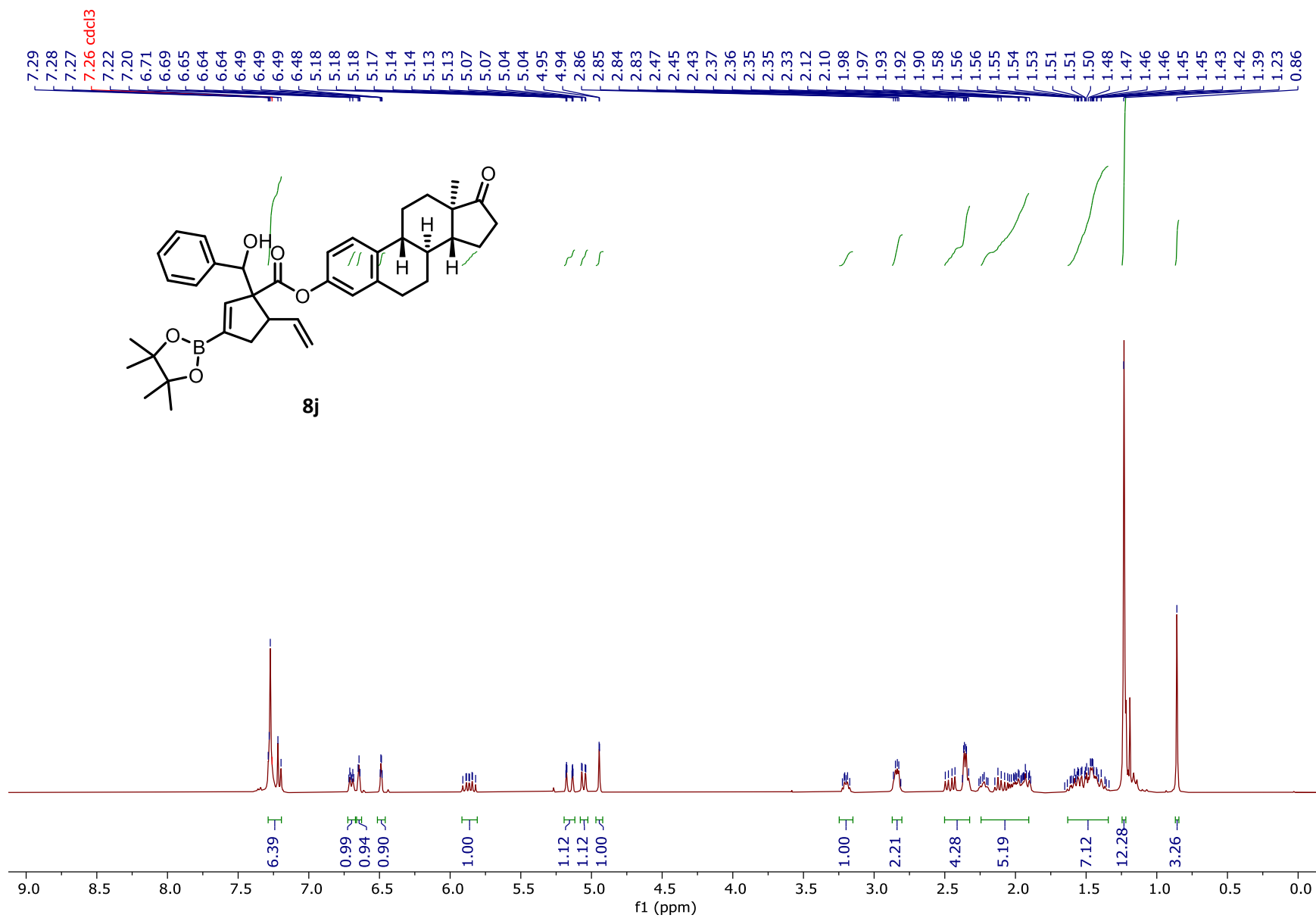




8i

— 29.87





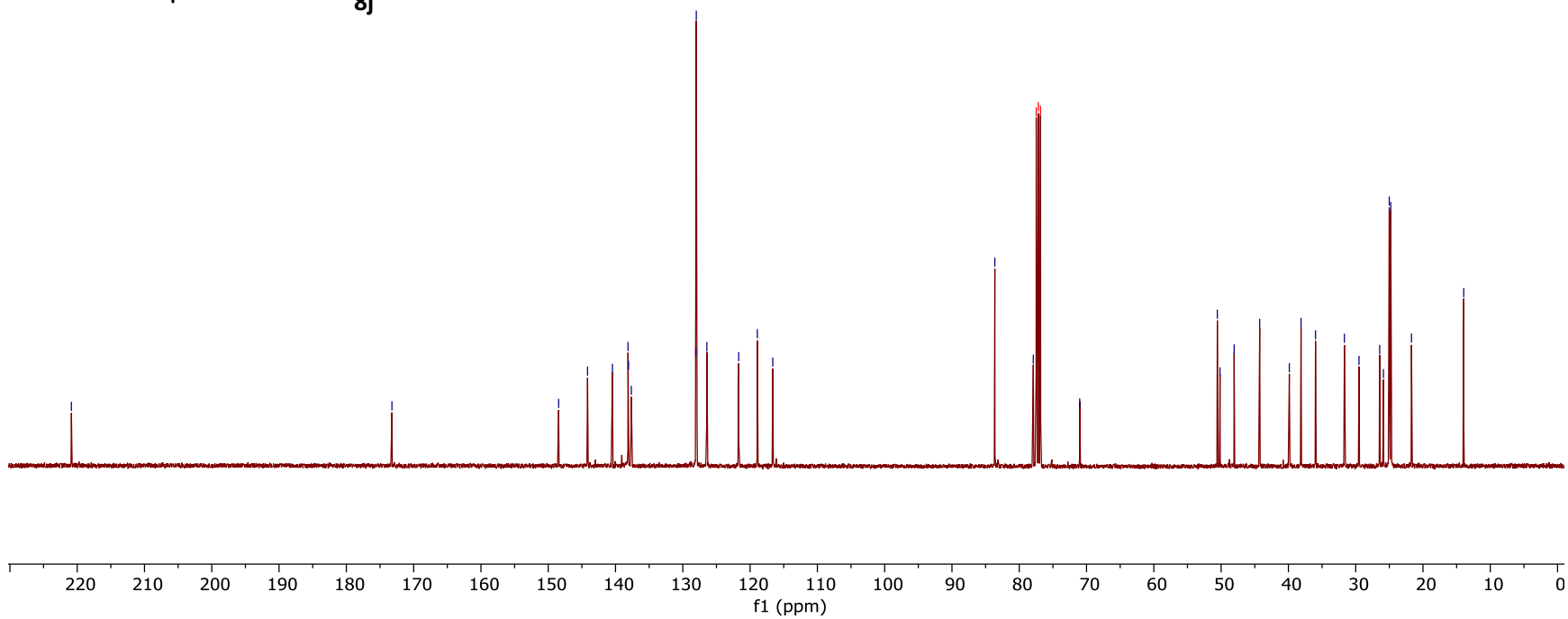
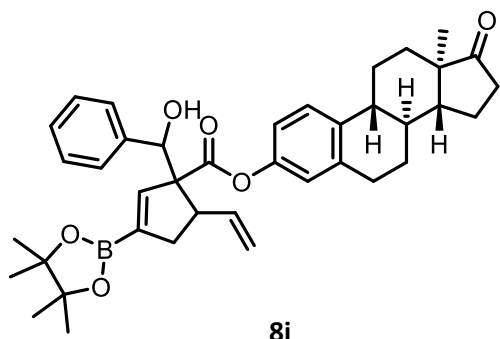
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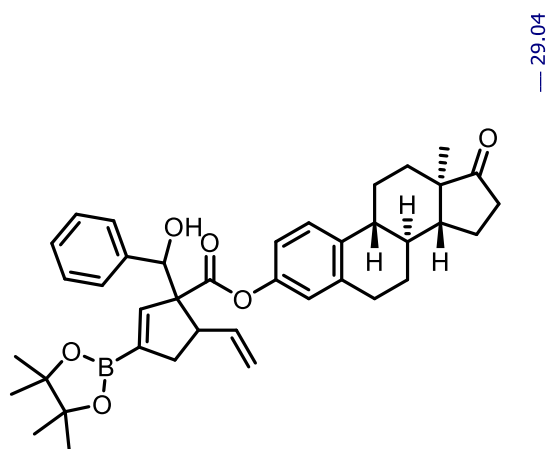
— 173.23

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144.16
140.46
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138.07
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128.07
127.99
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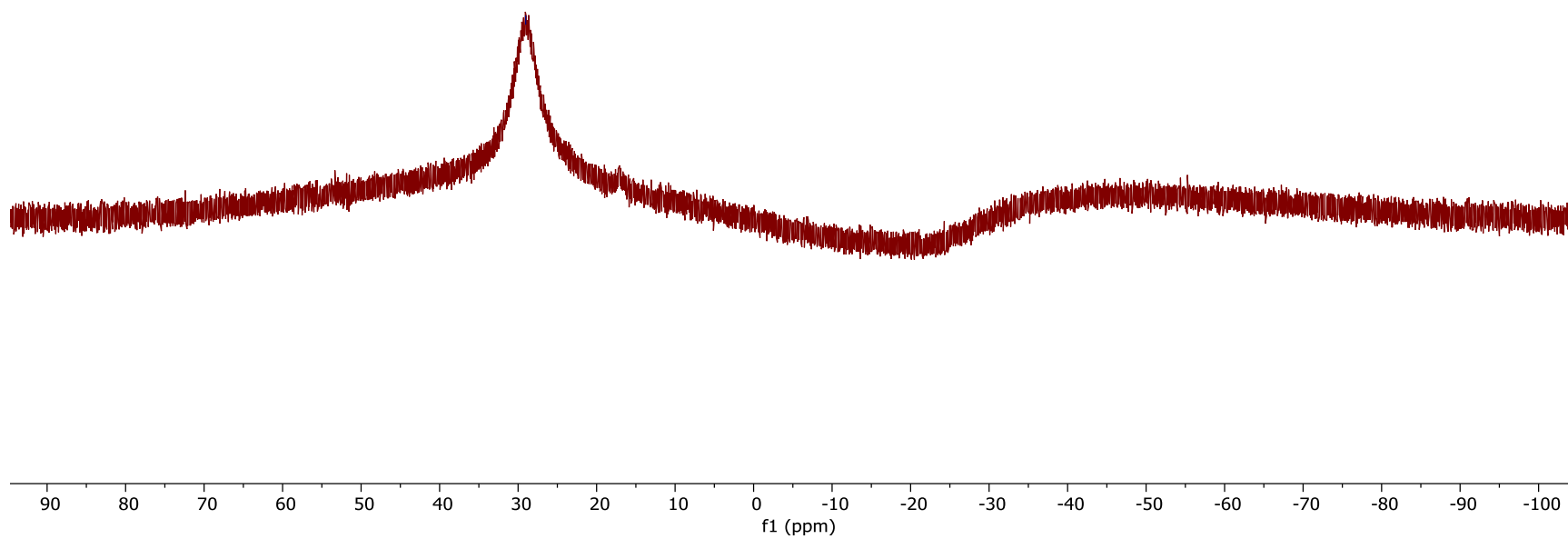
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25.01
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21.71
— 13.95

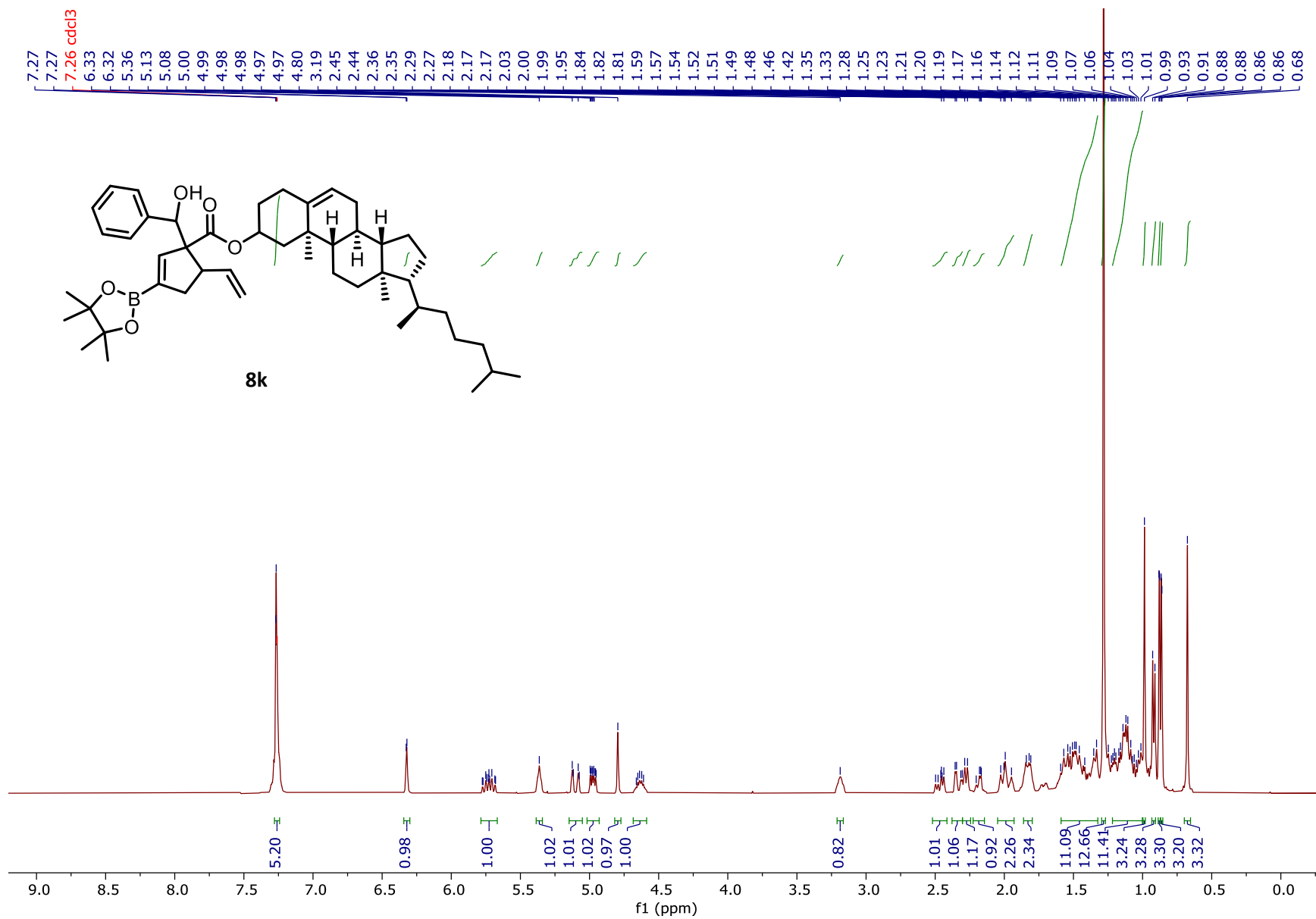


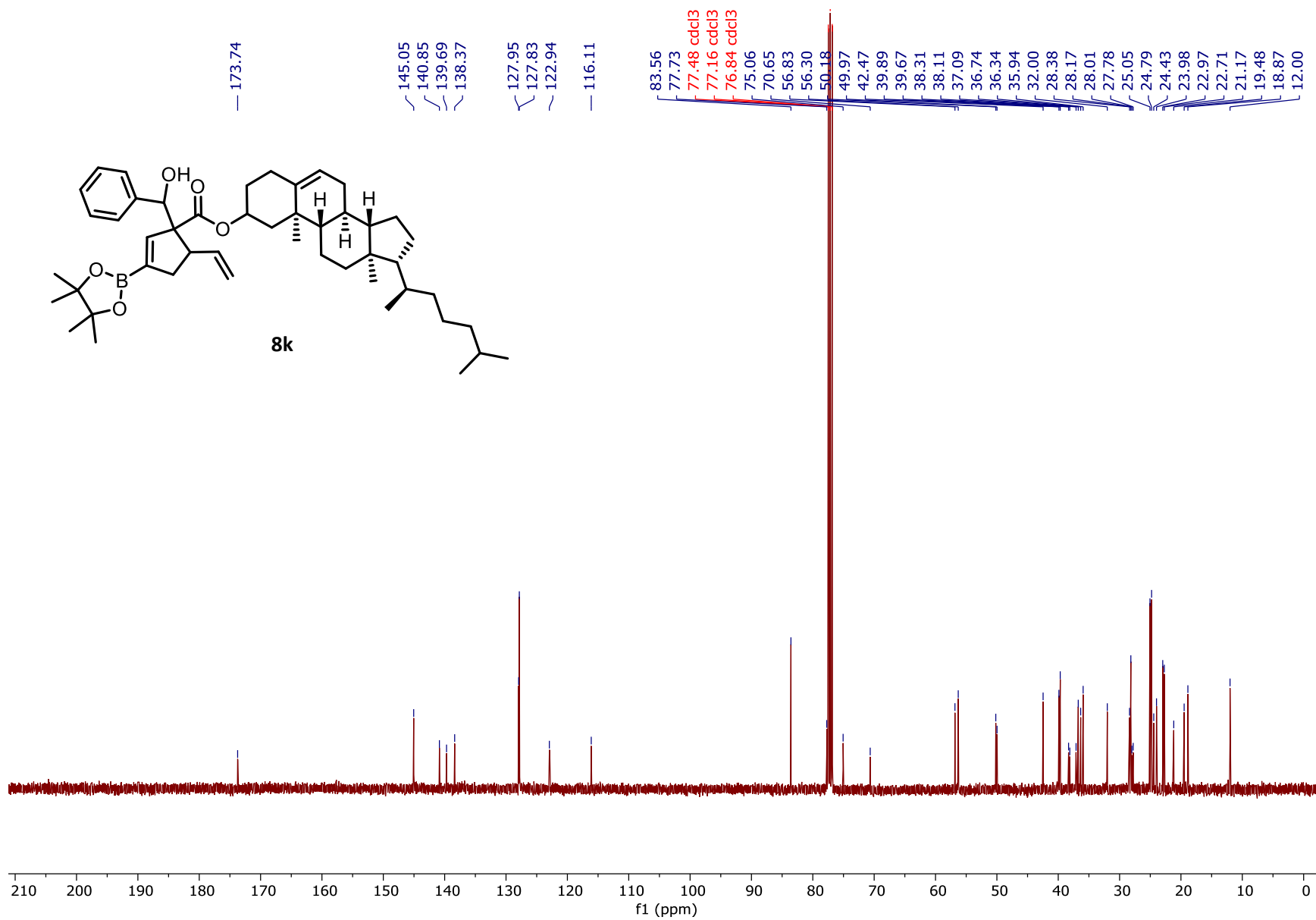


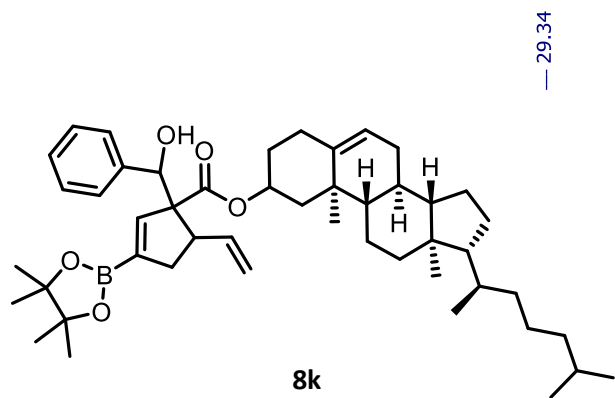
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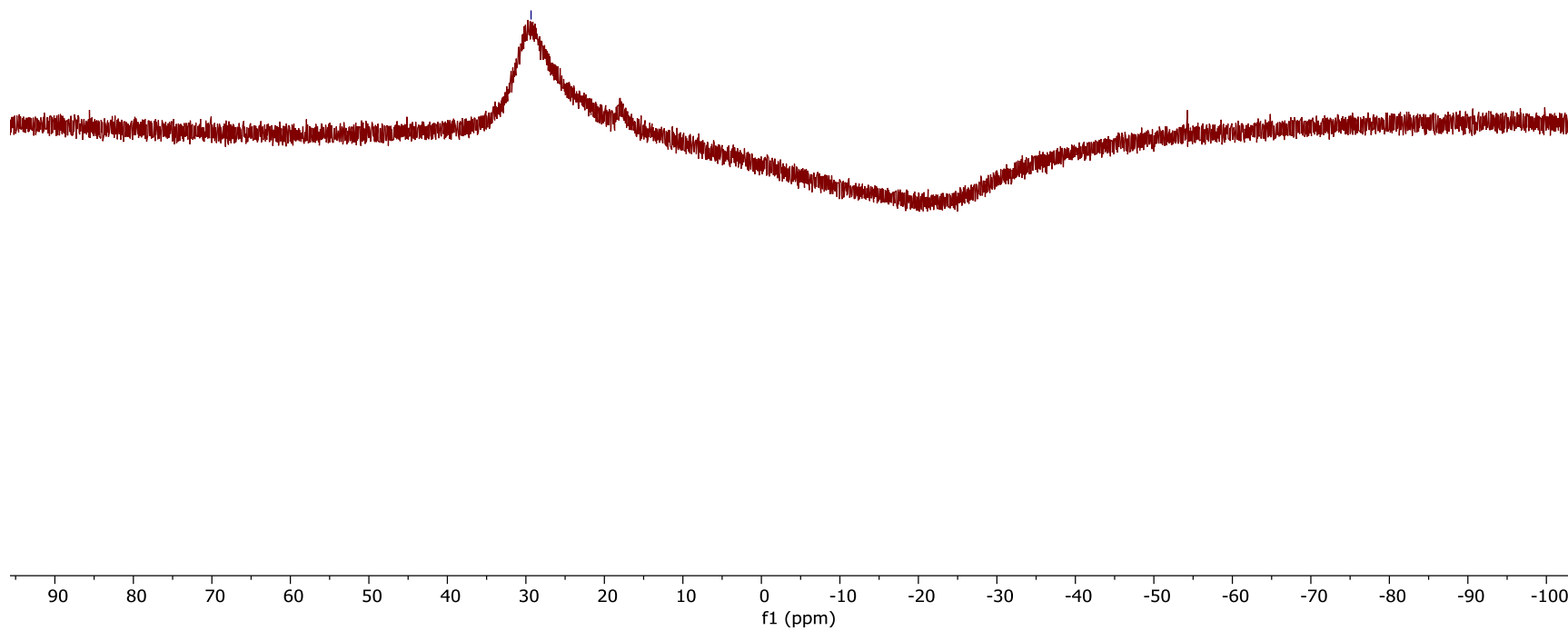


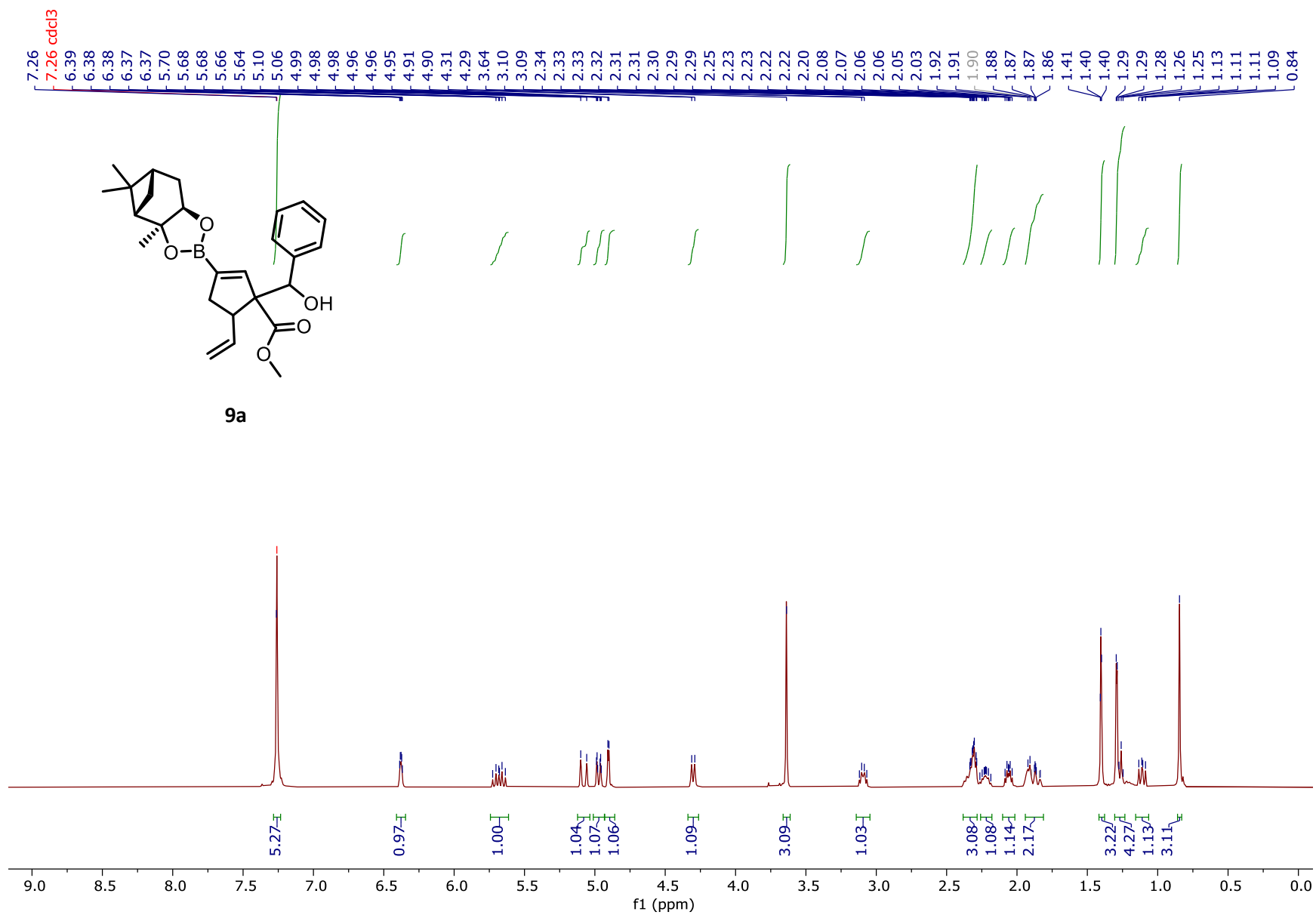


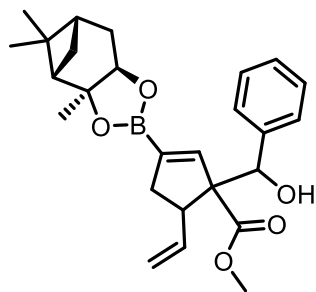




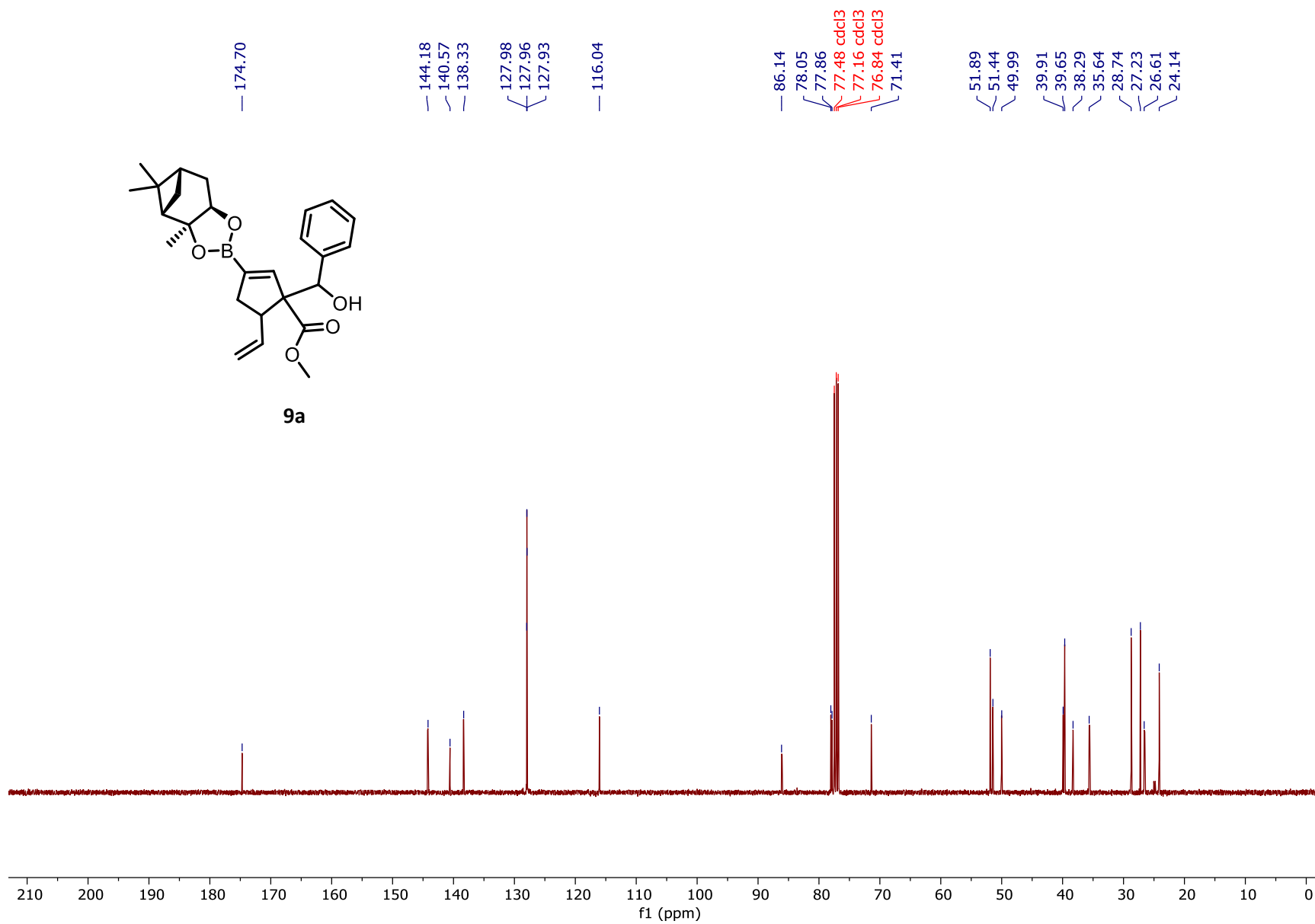
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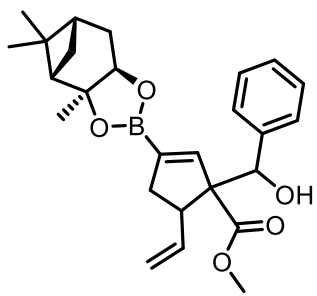






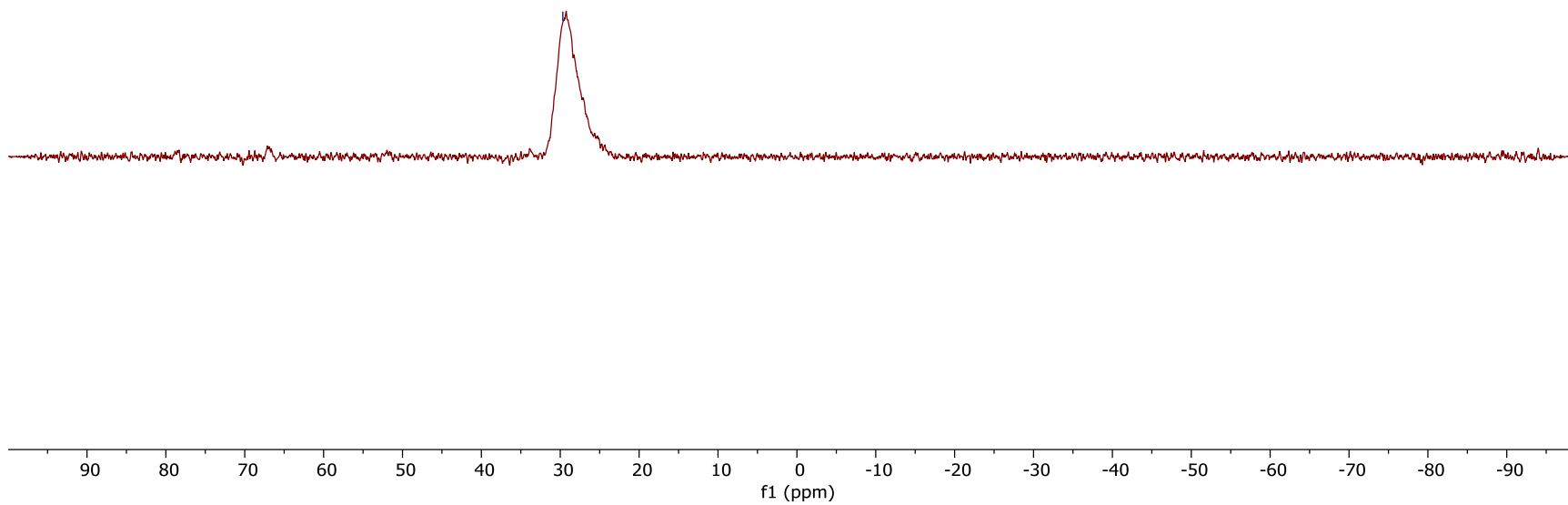
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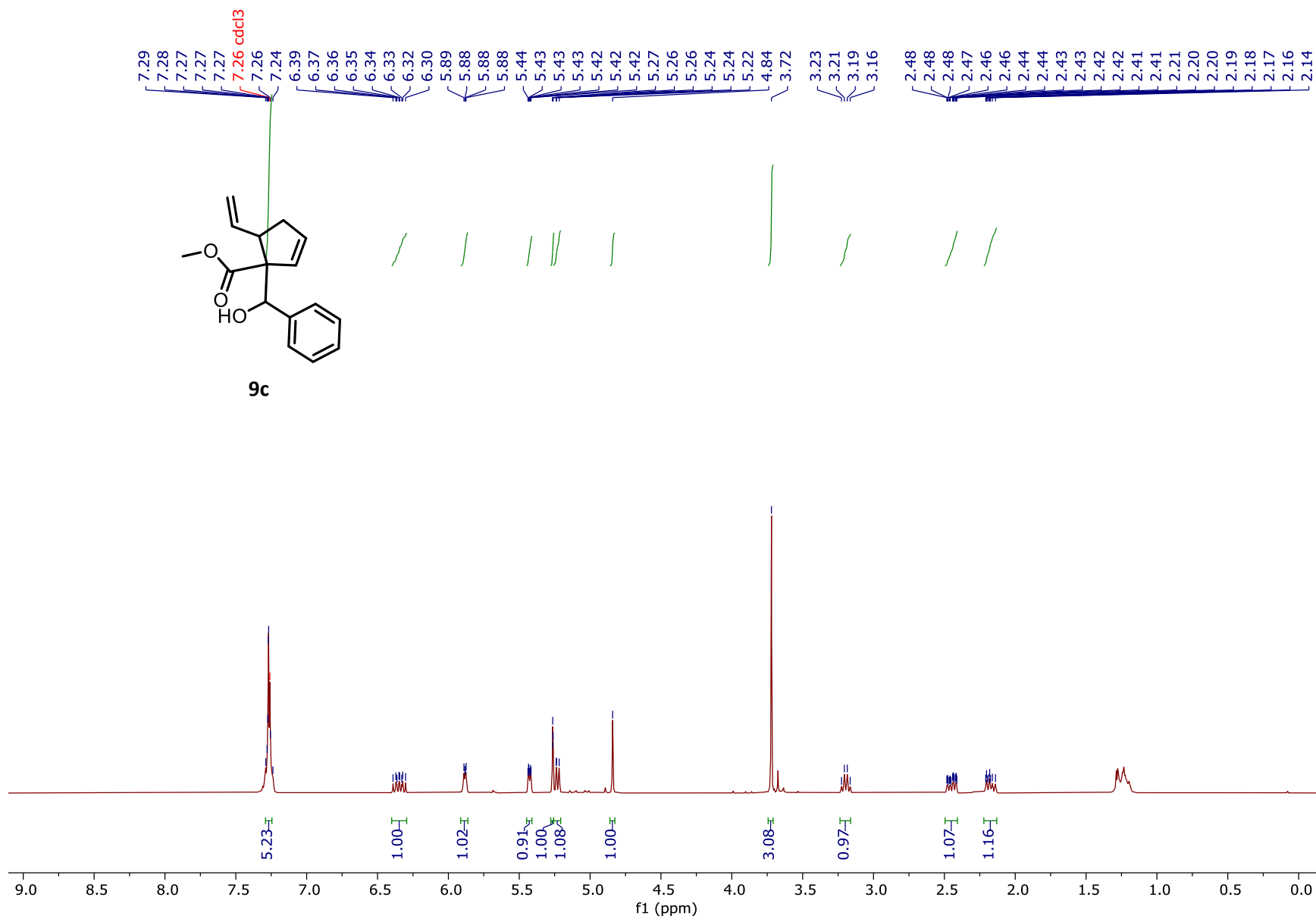


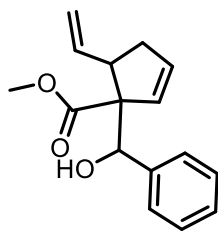


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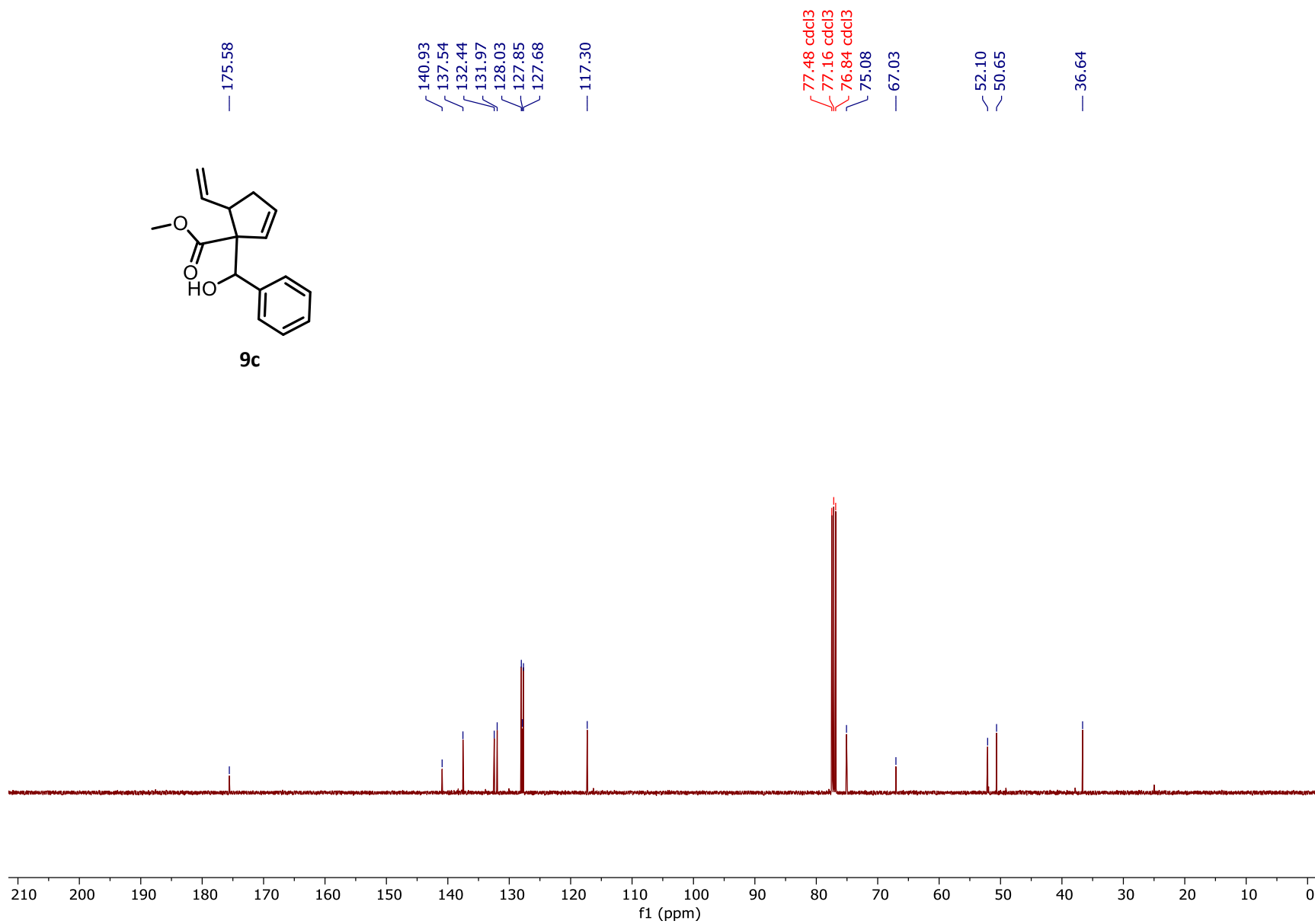
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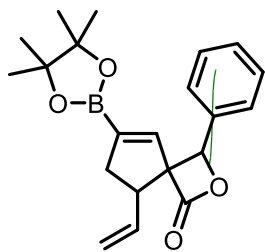




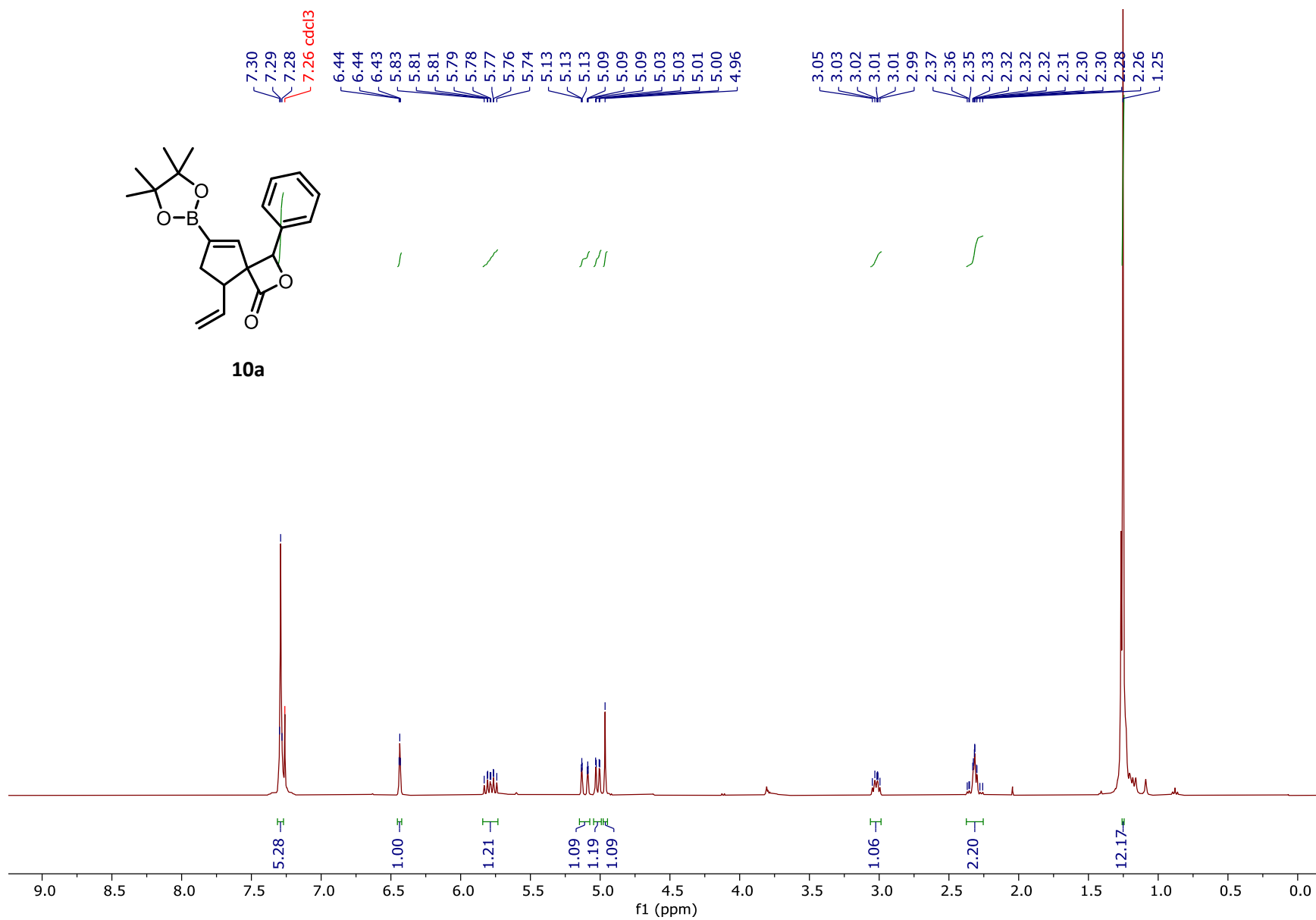


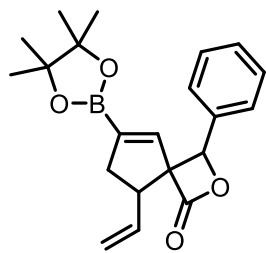
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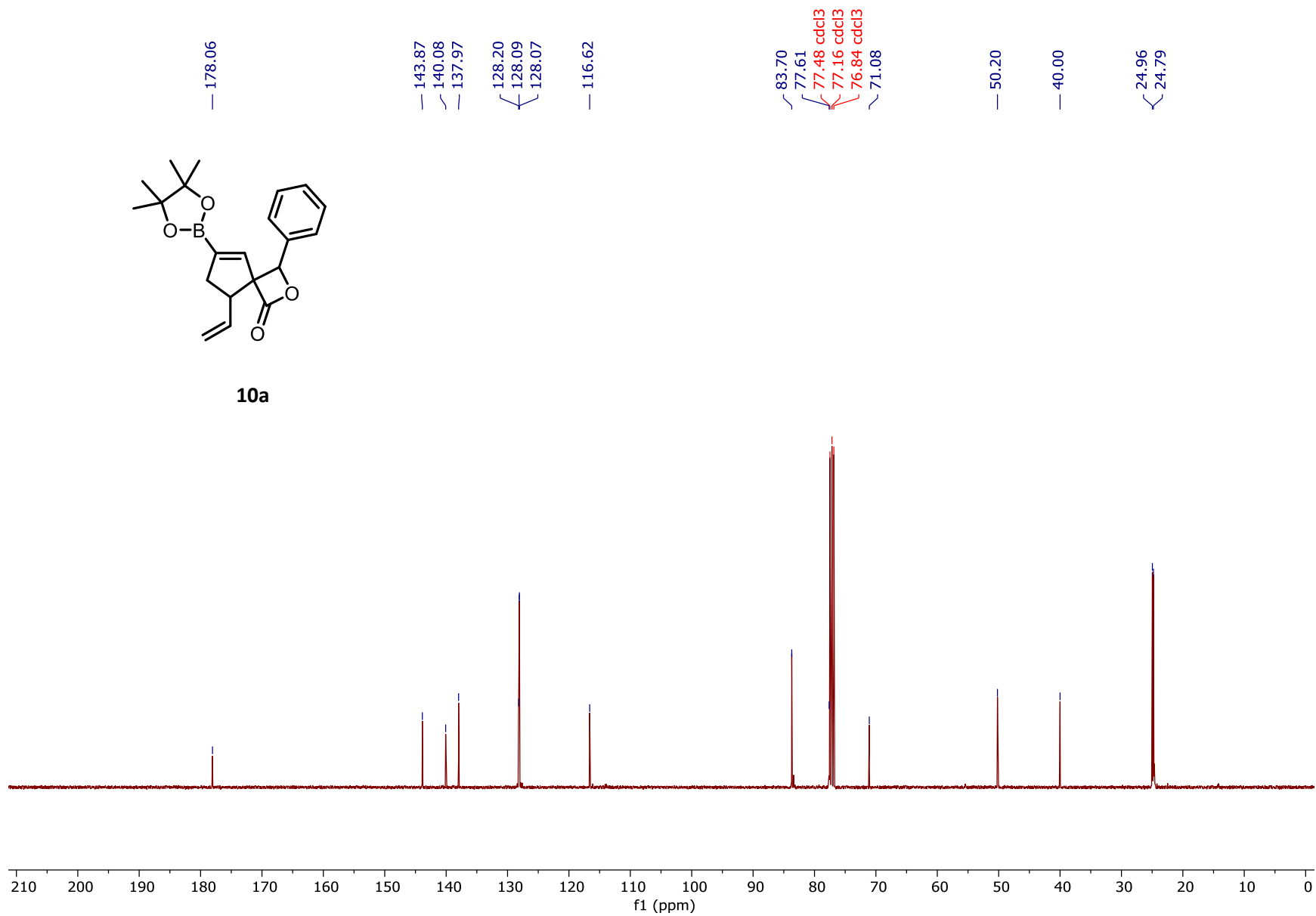


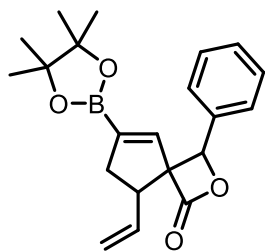
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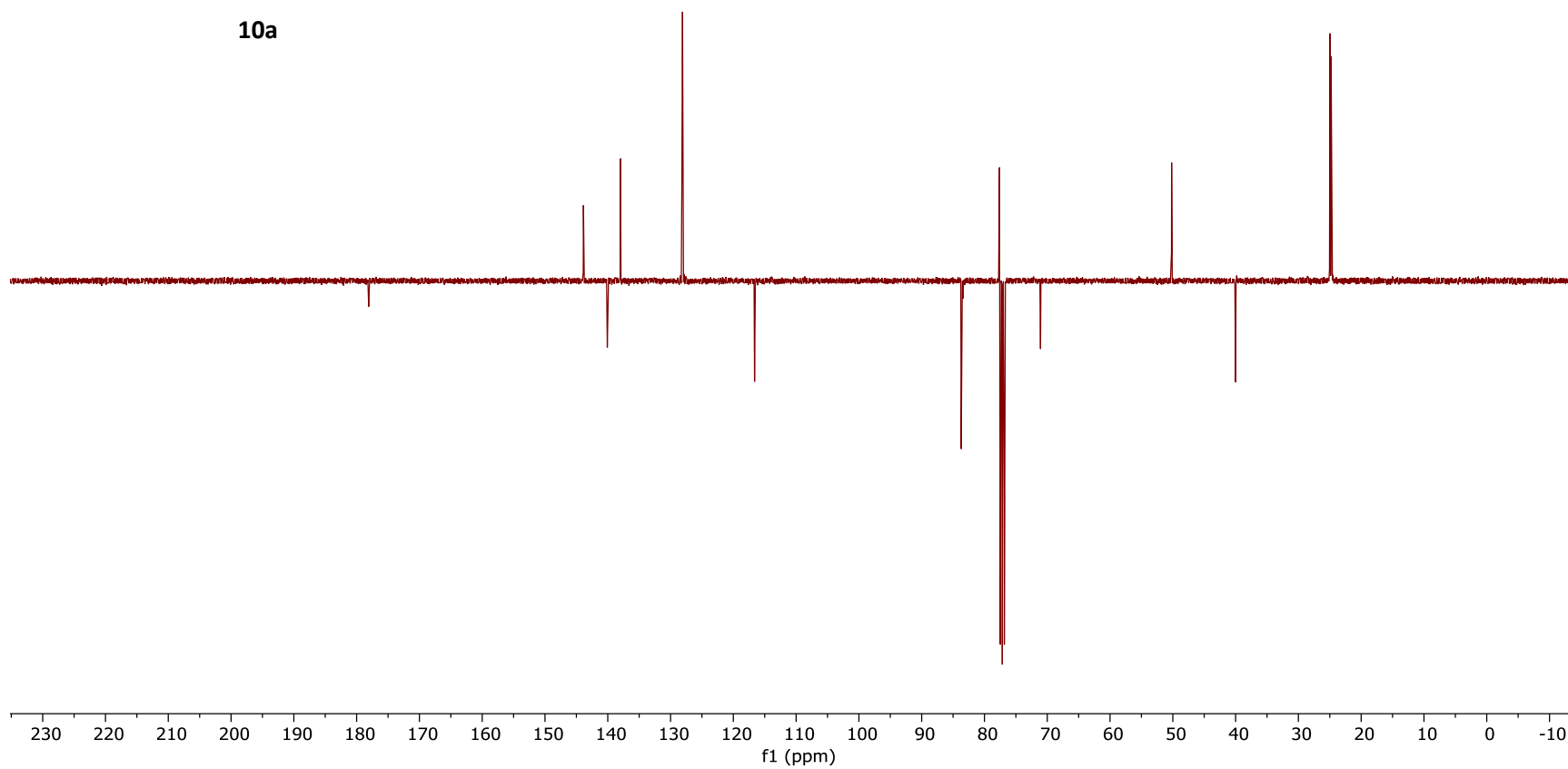
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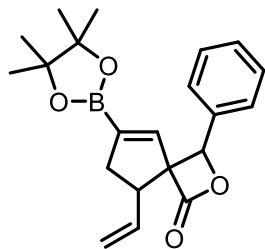




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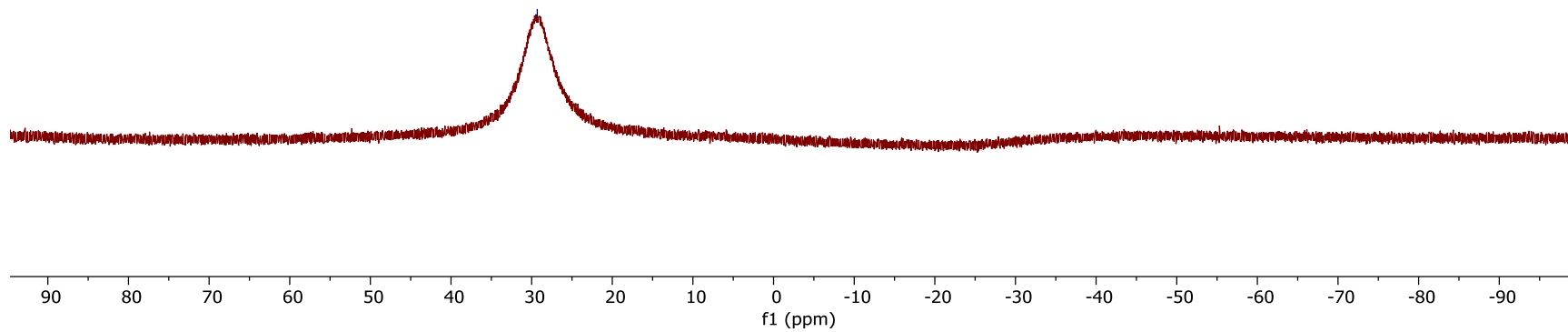
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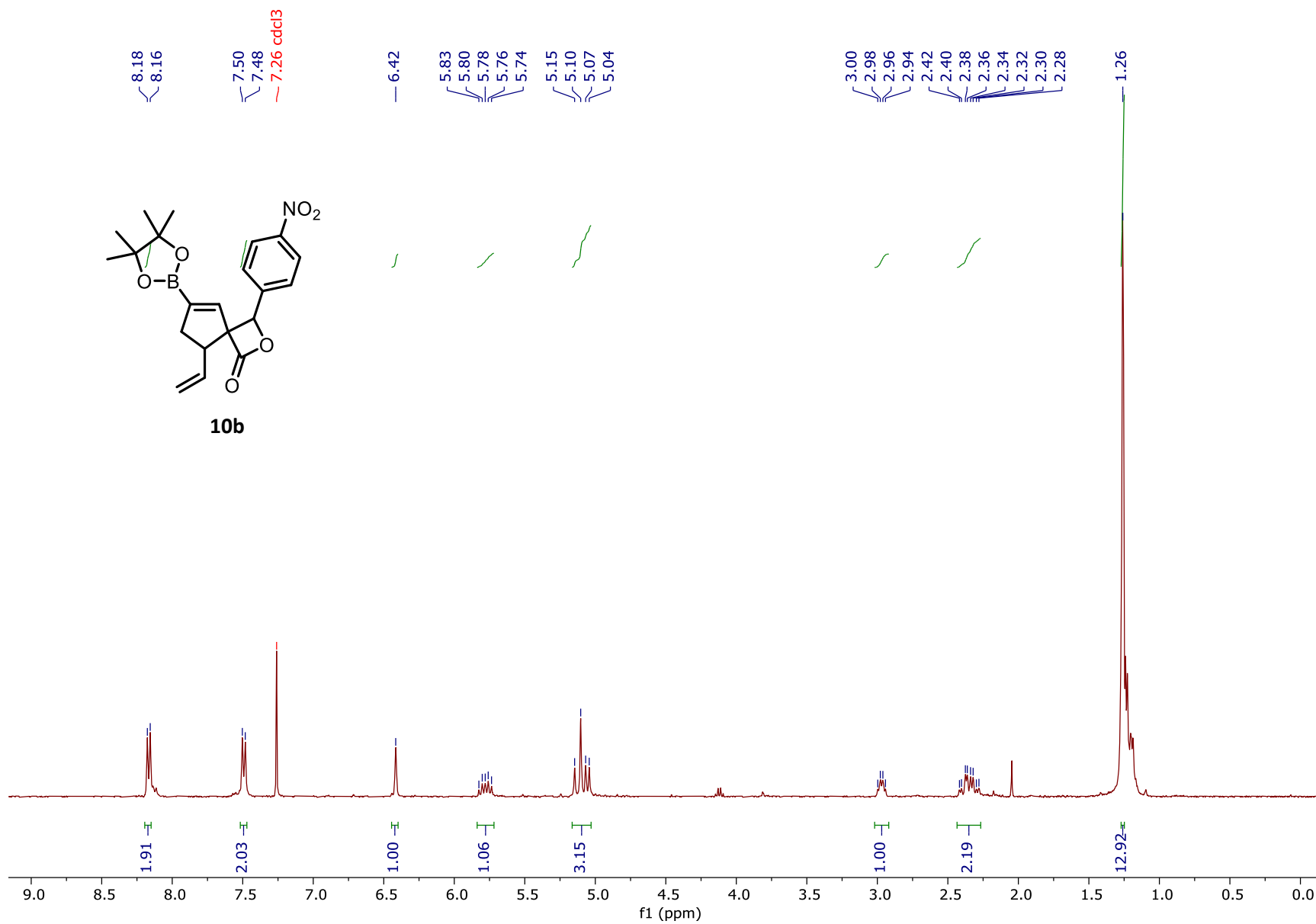


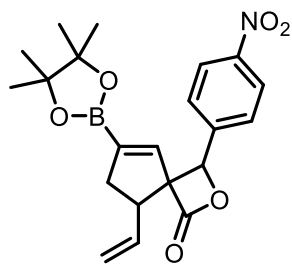


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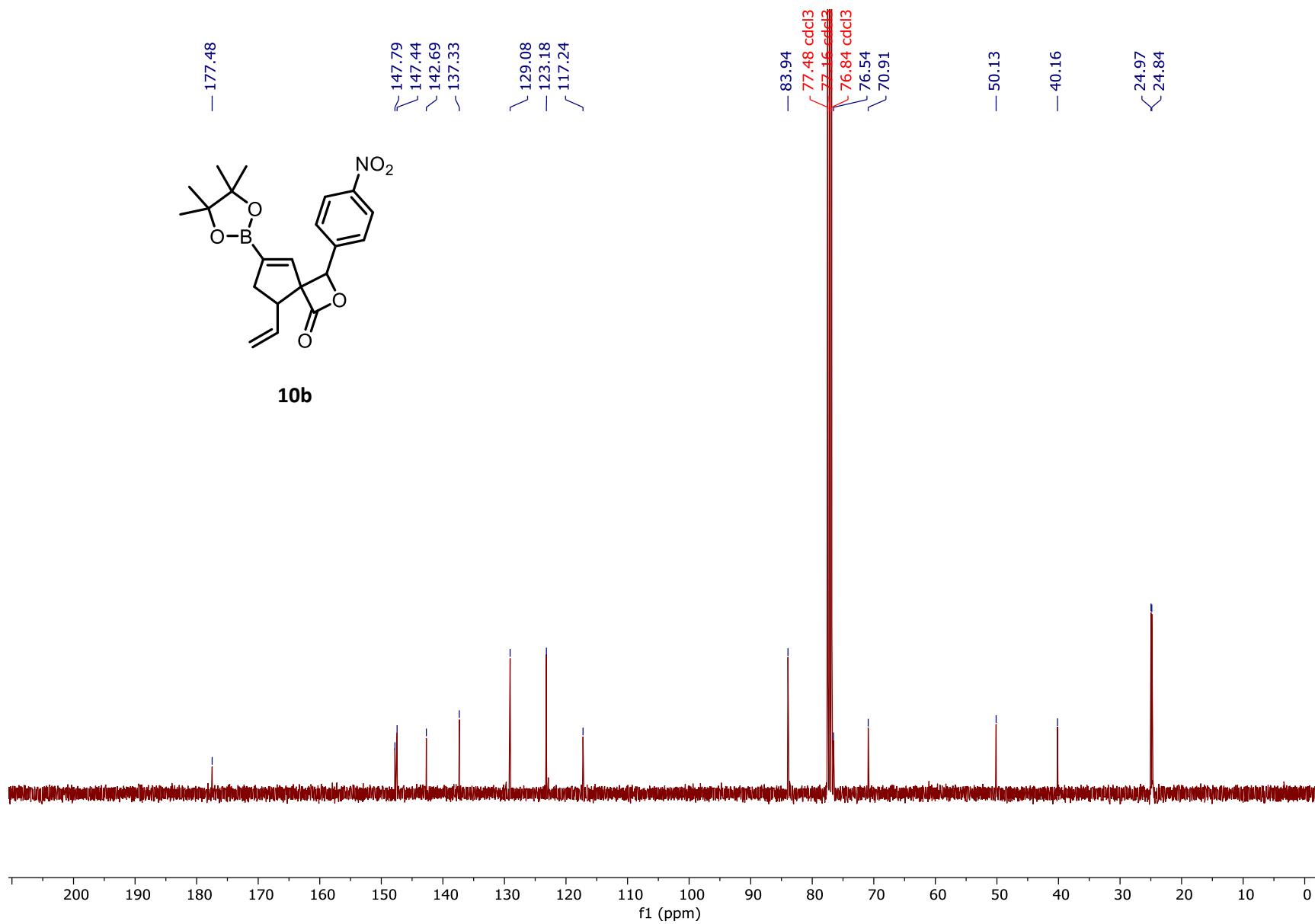
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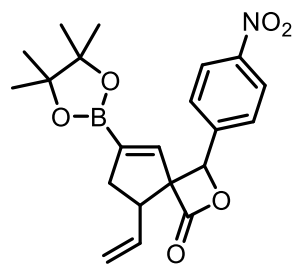






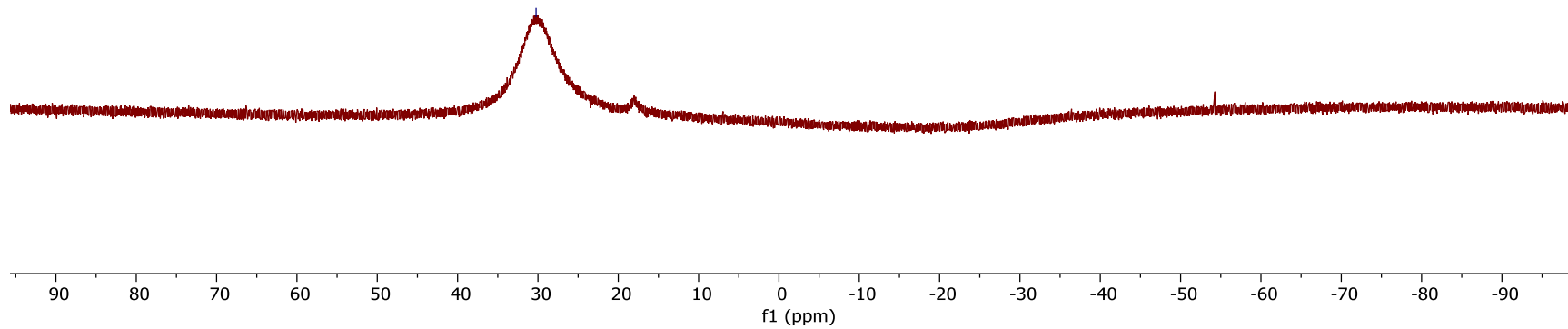
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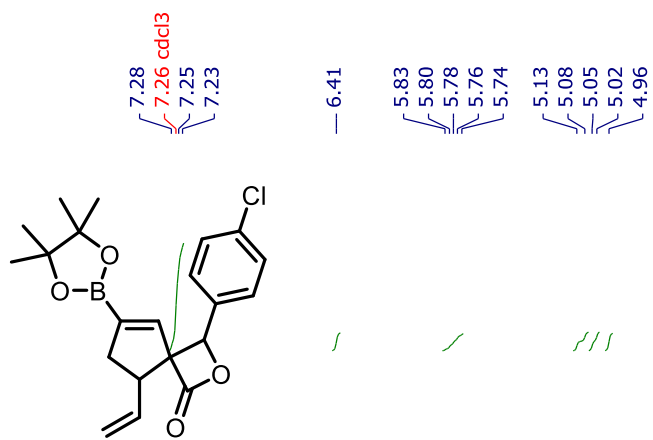




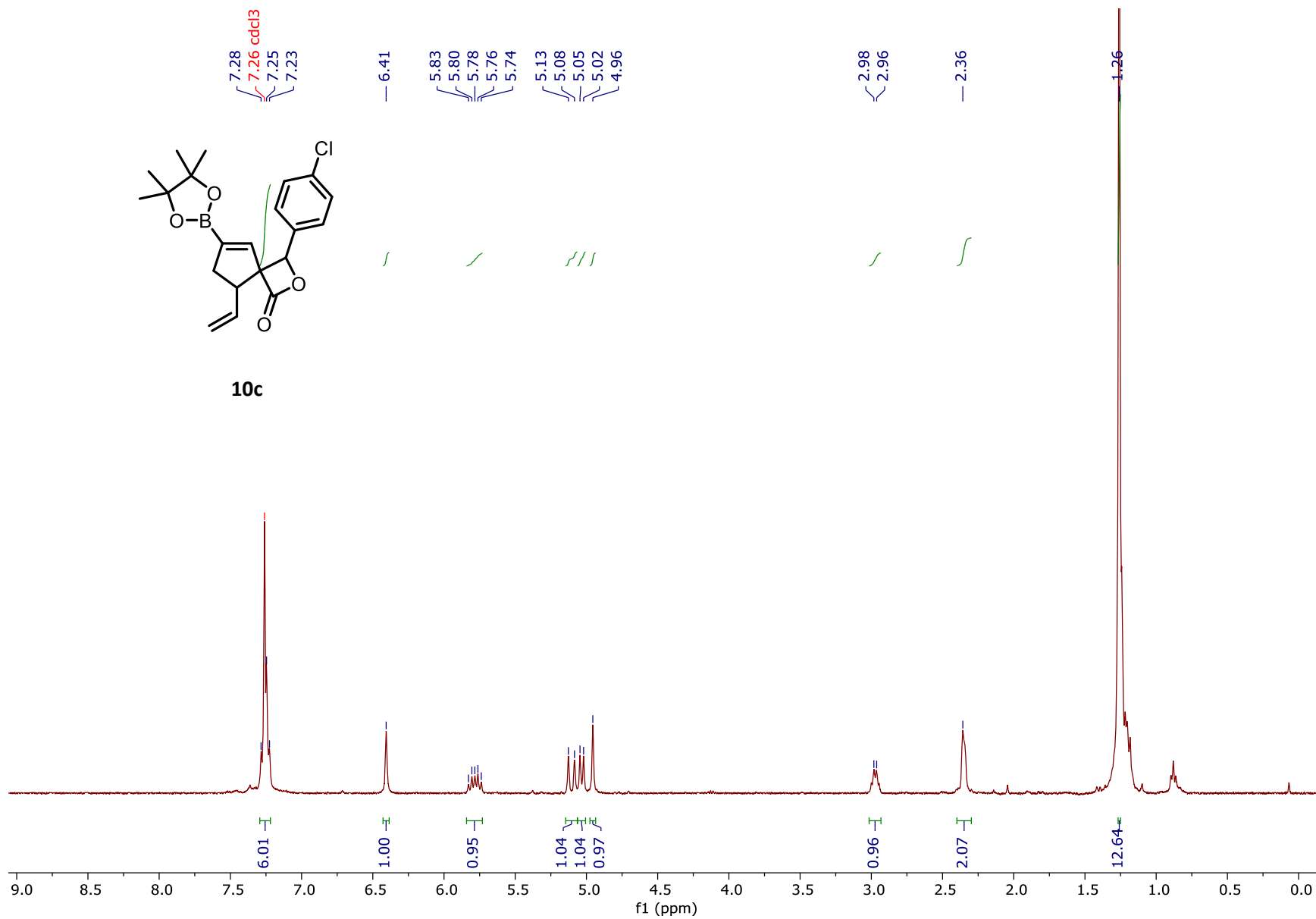
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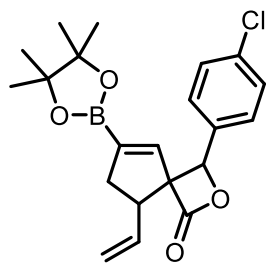
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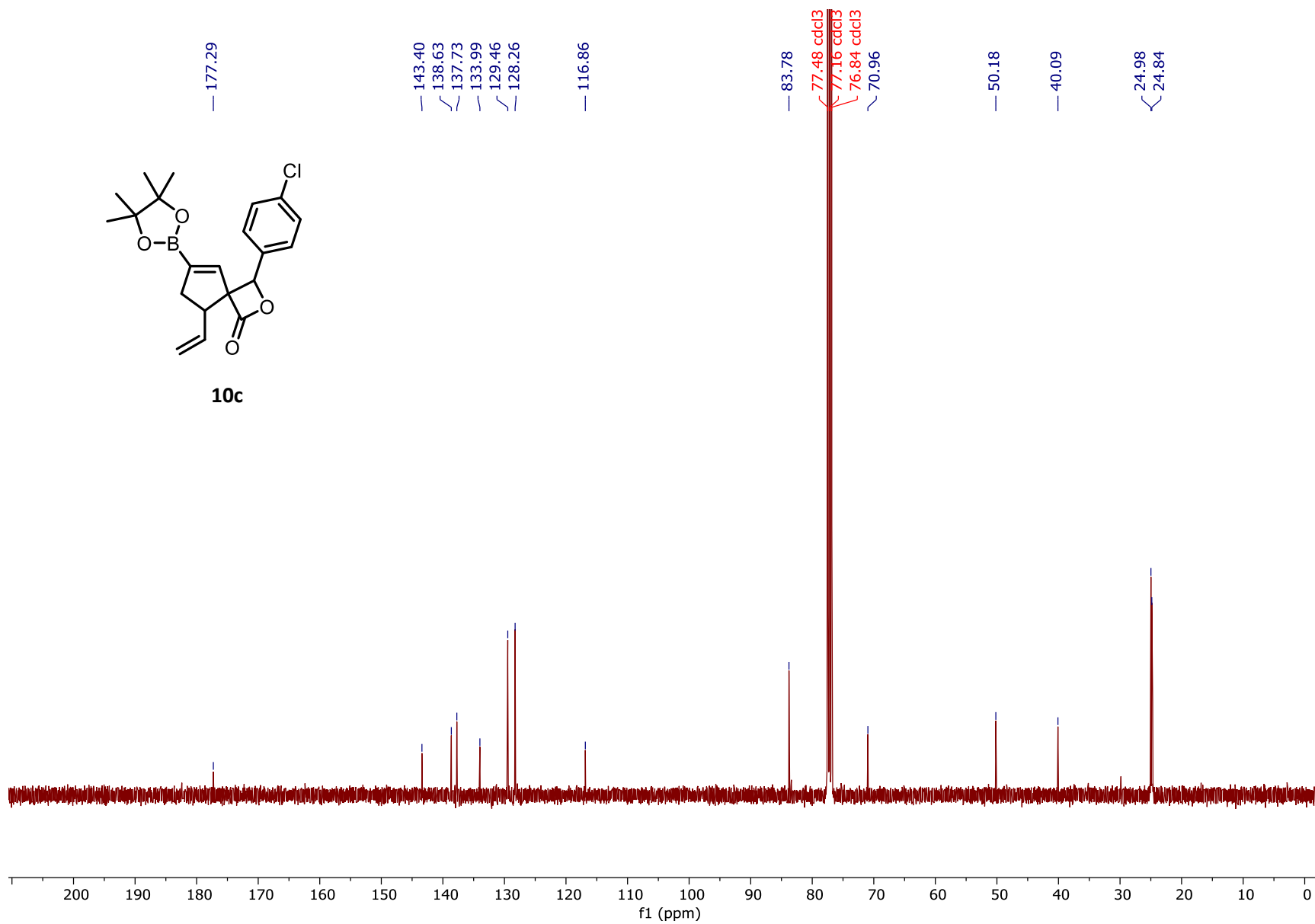


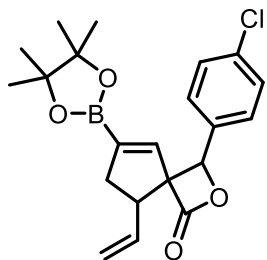
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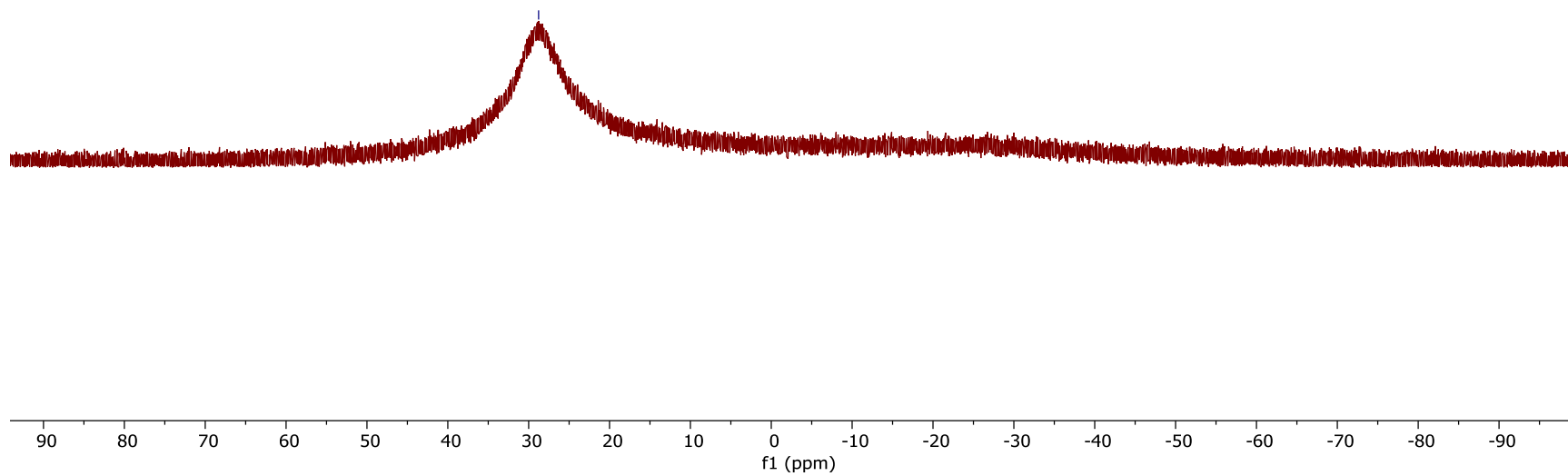
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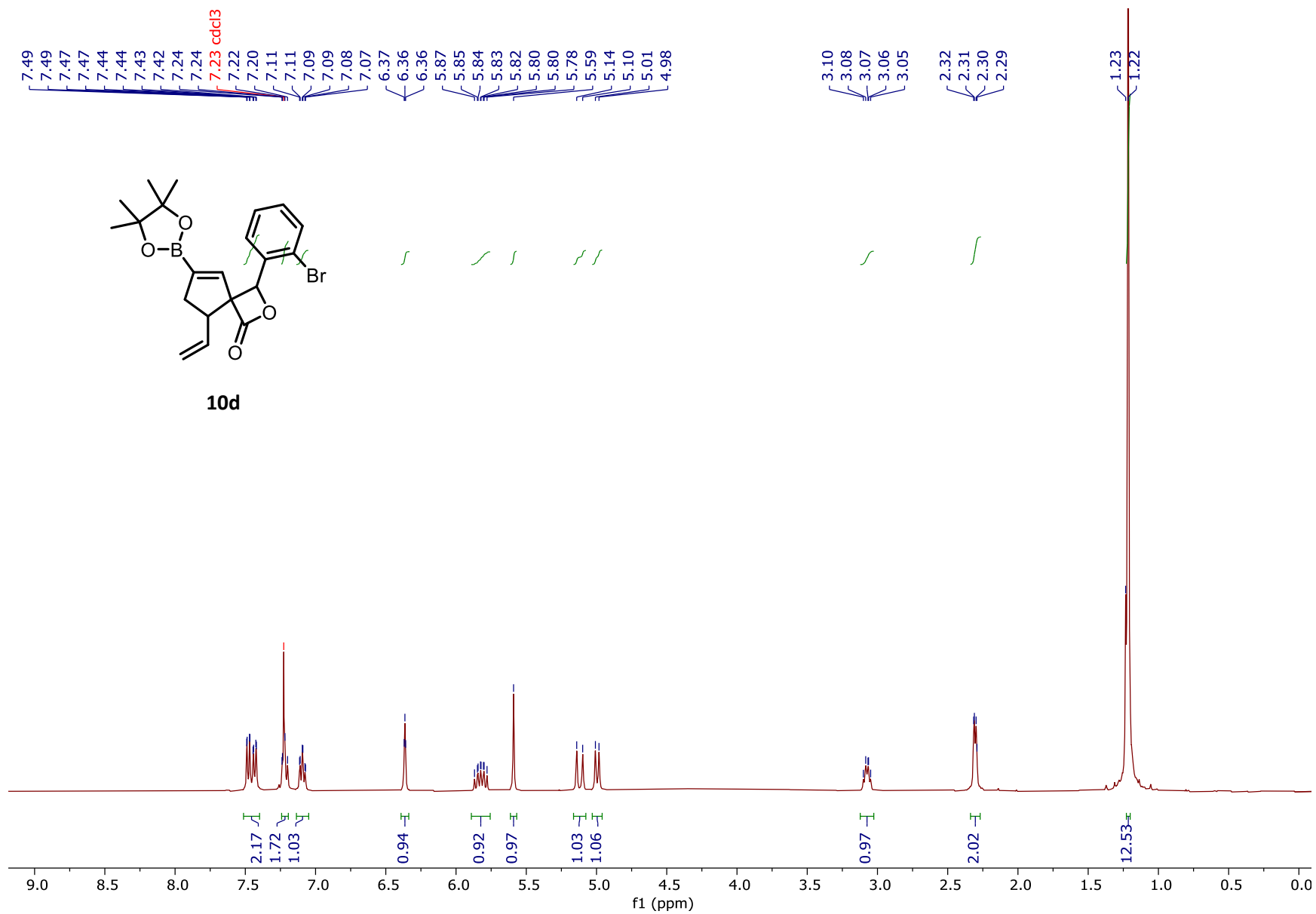


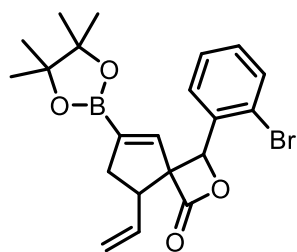


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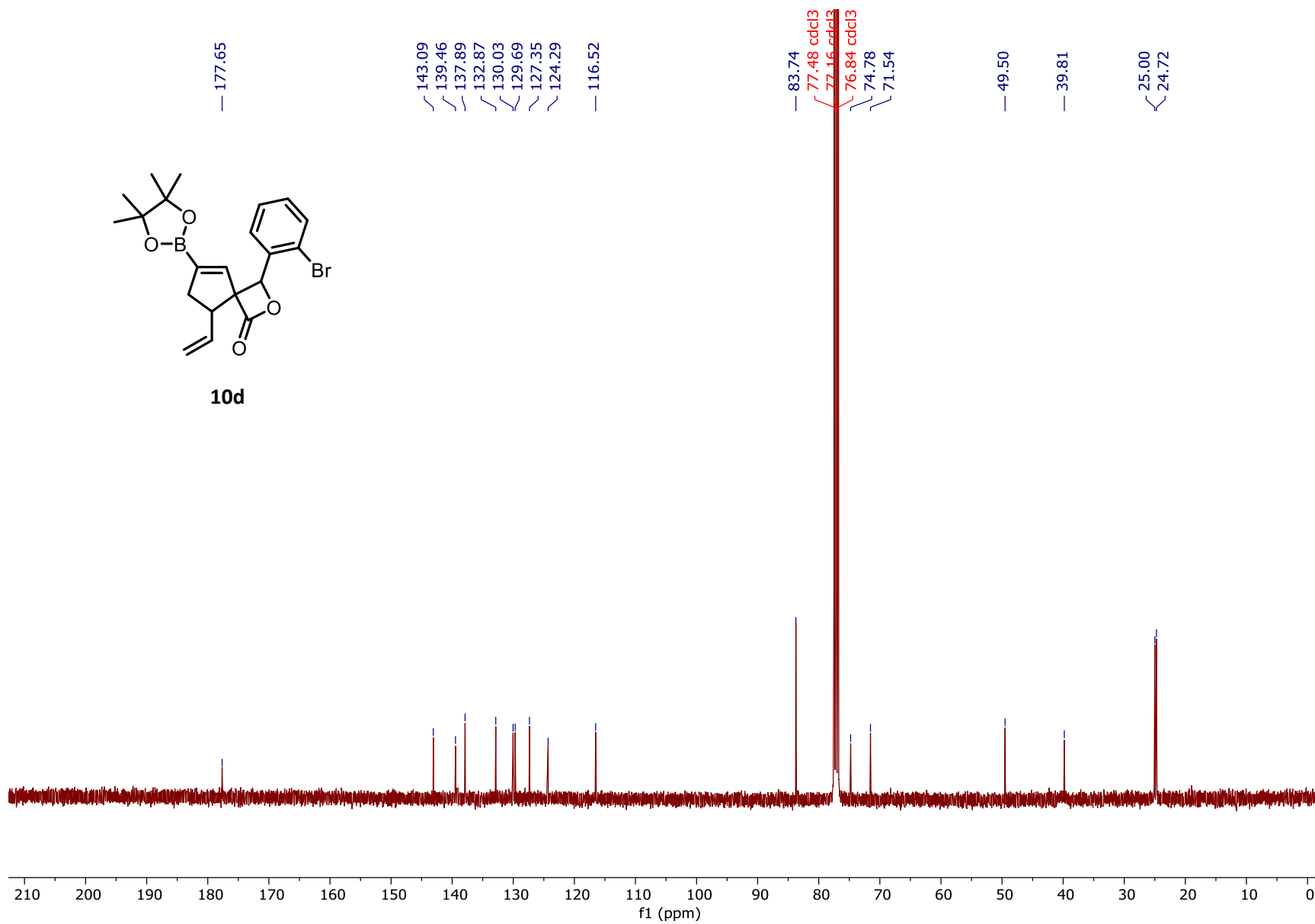
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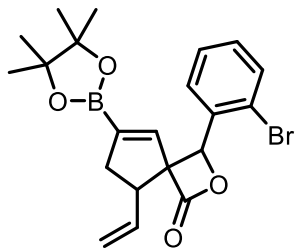






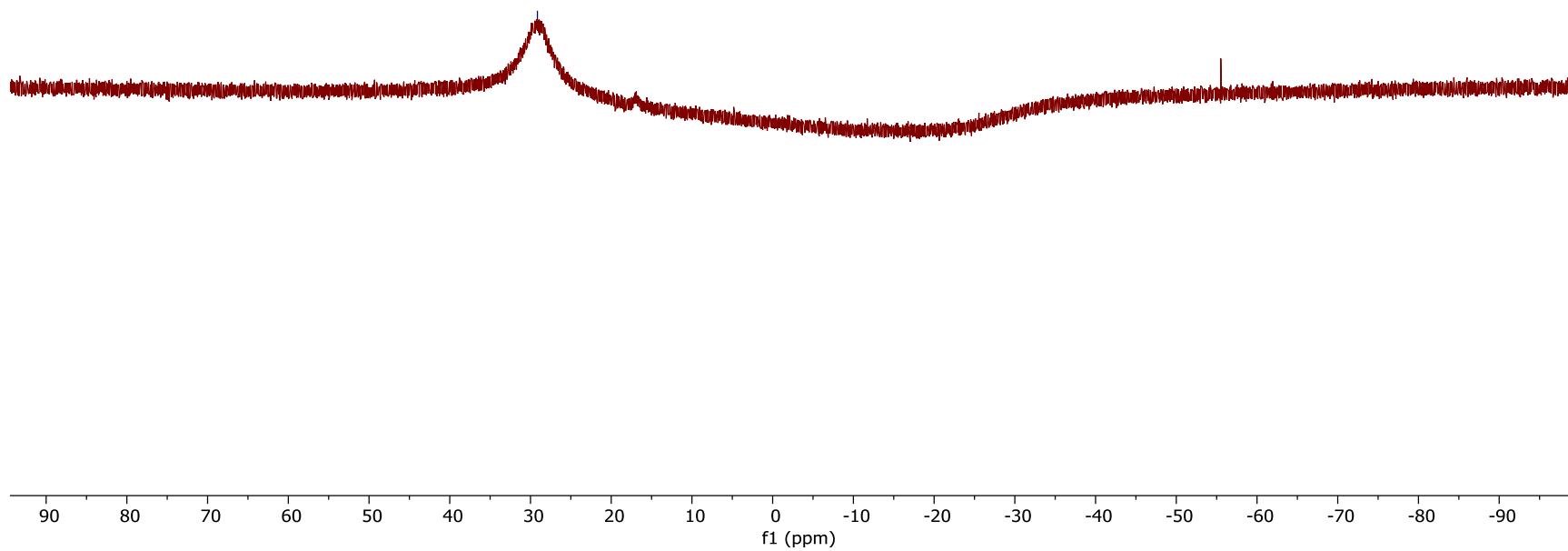
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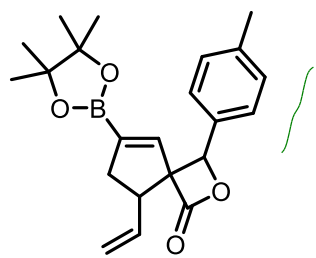




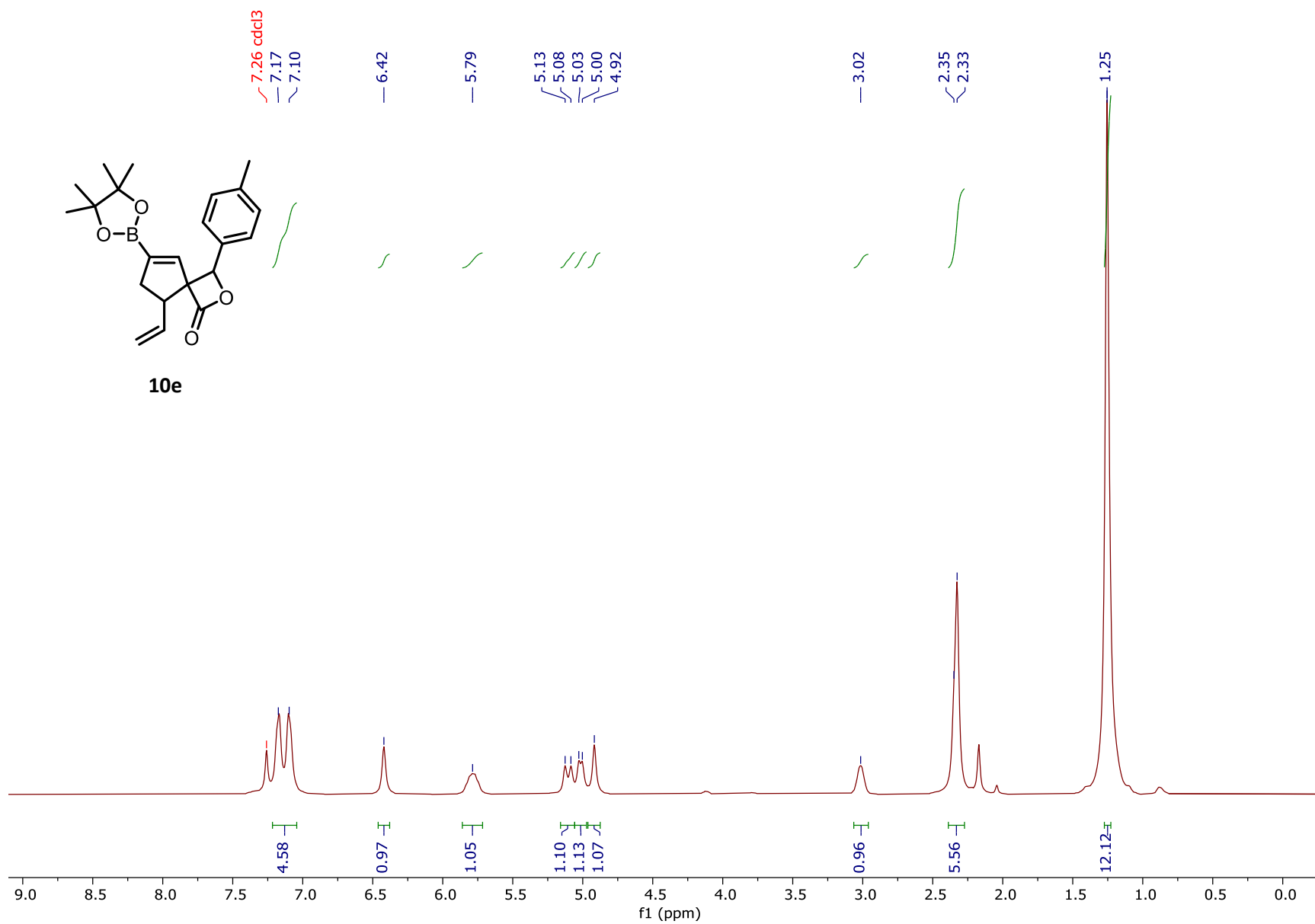
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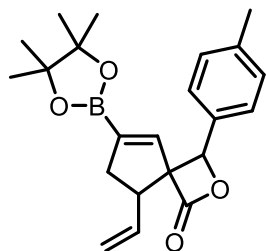
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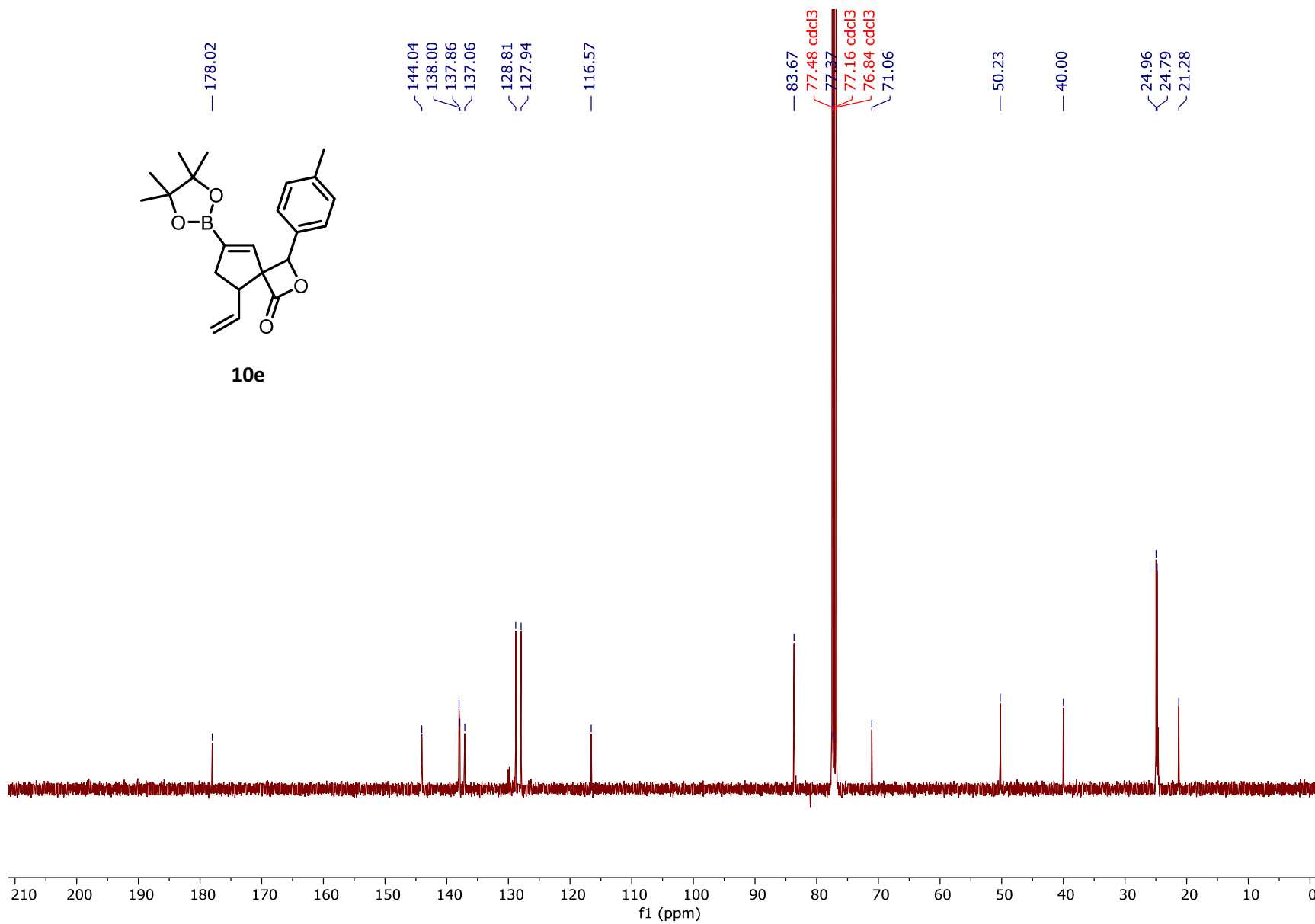


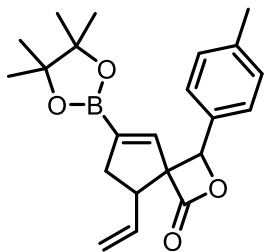
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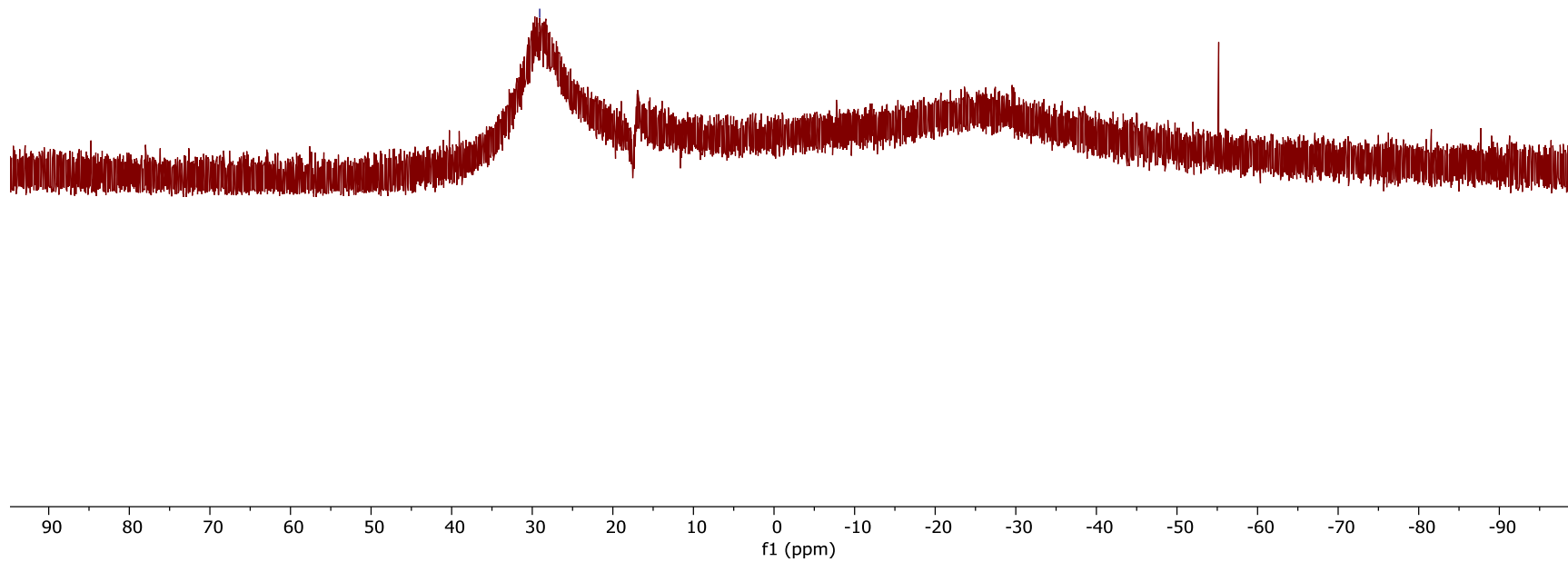
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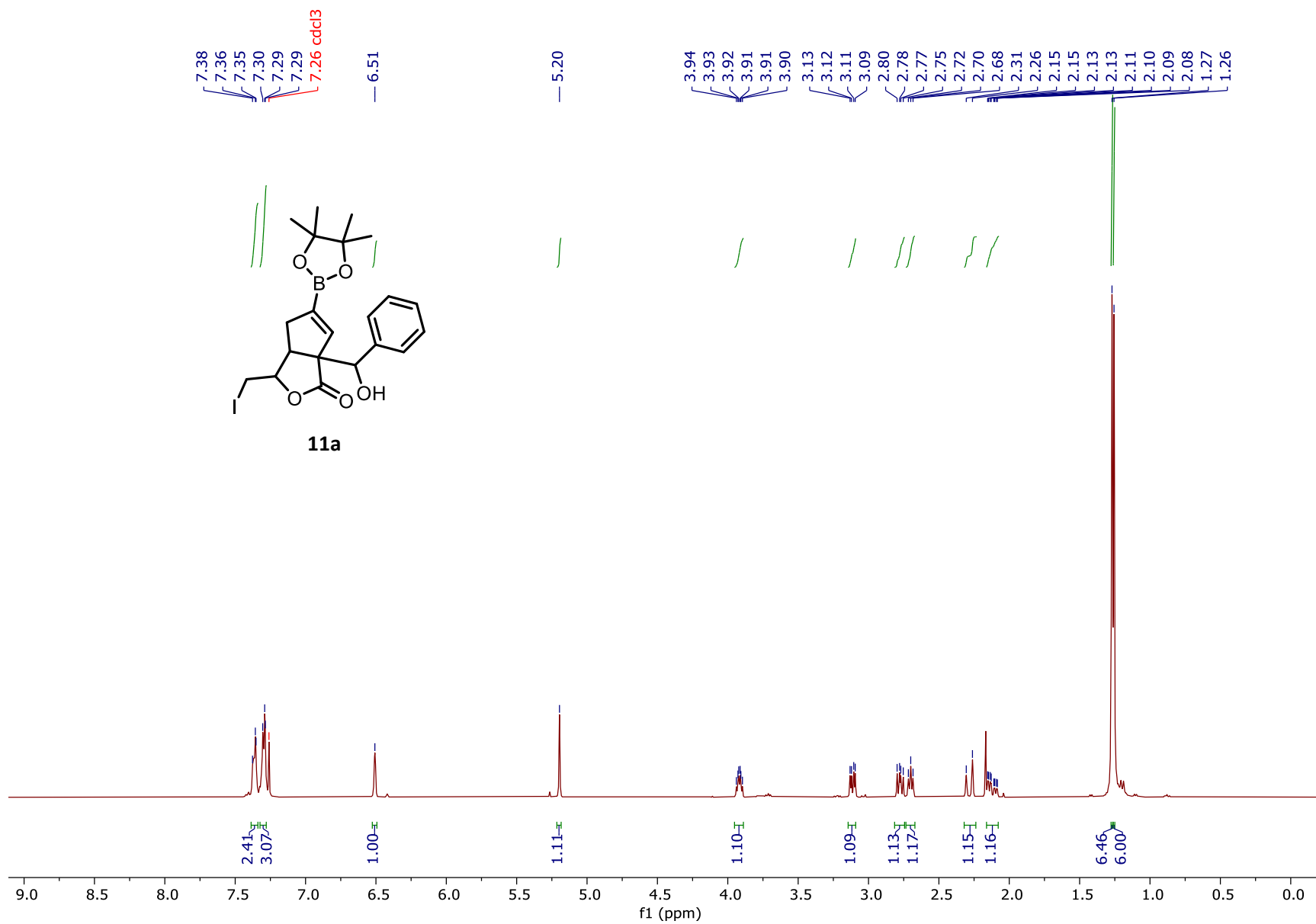


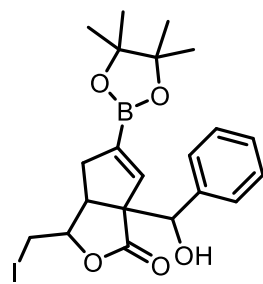


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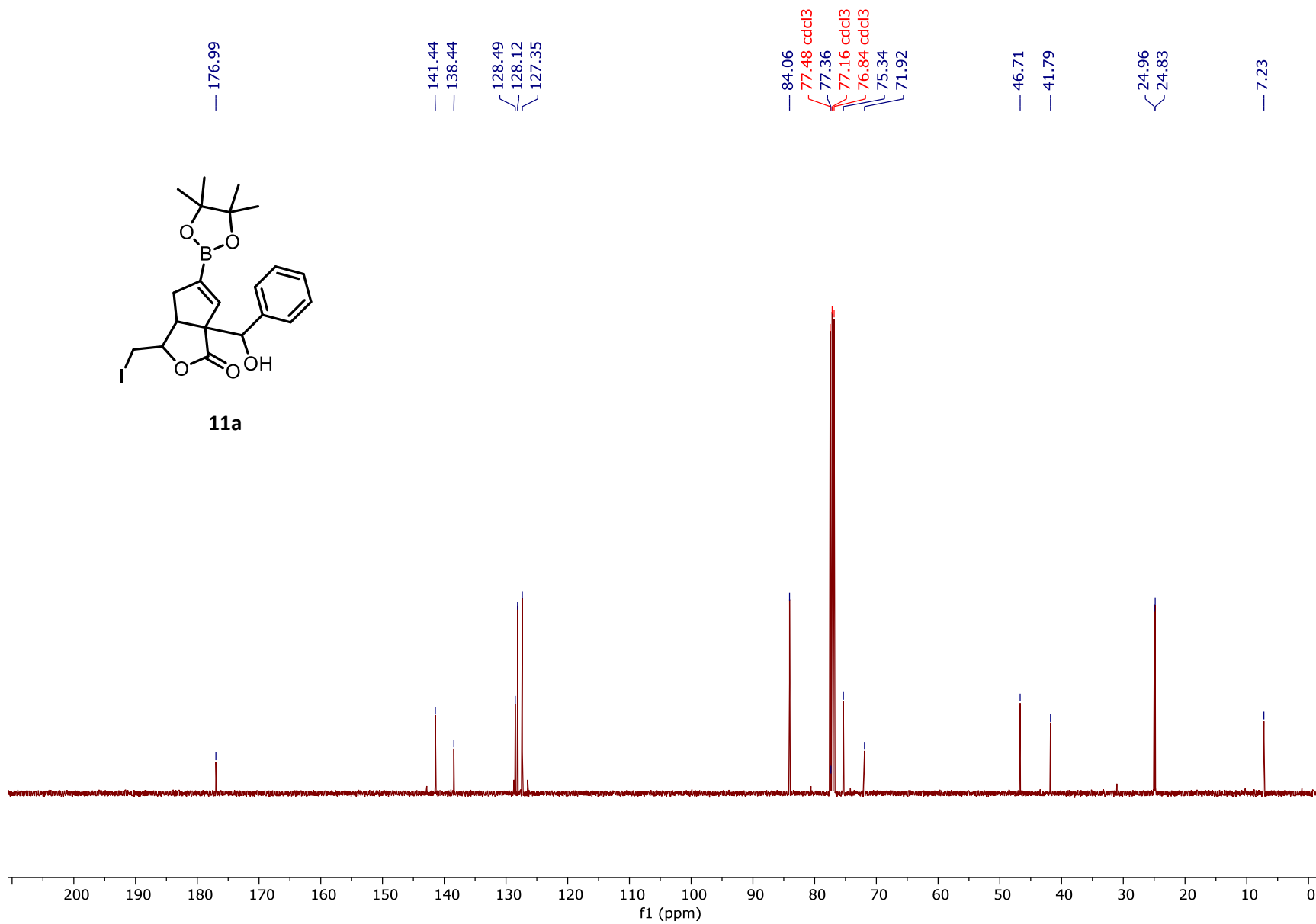
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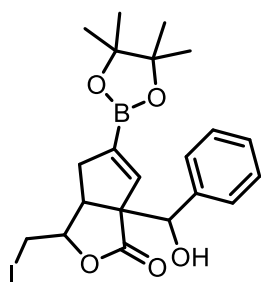






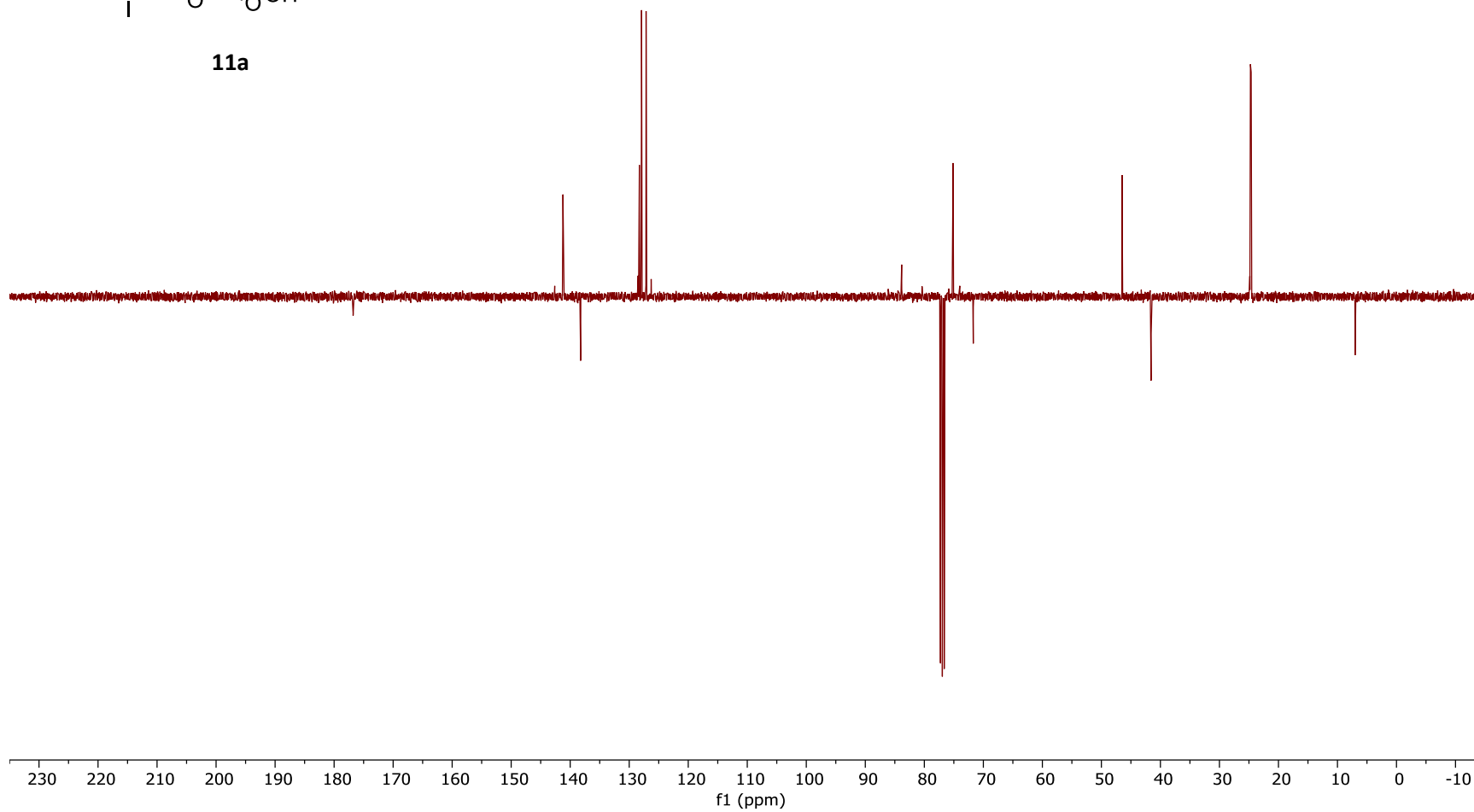
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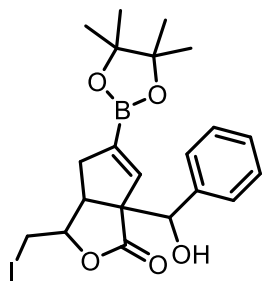




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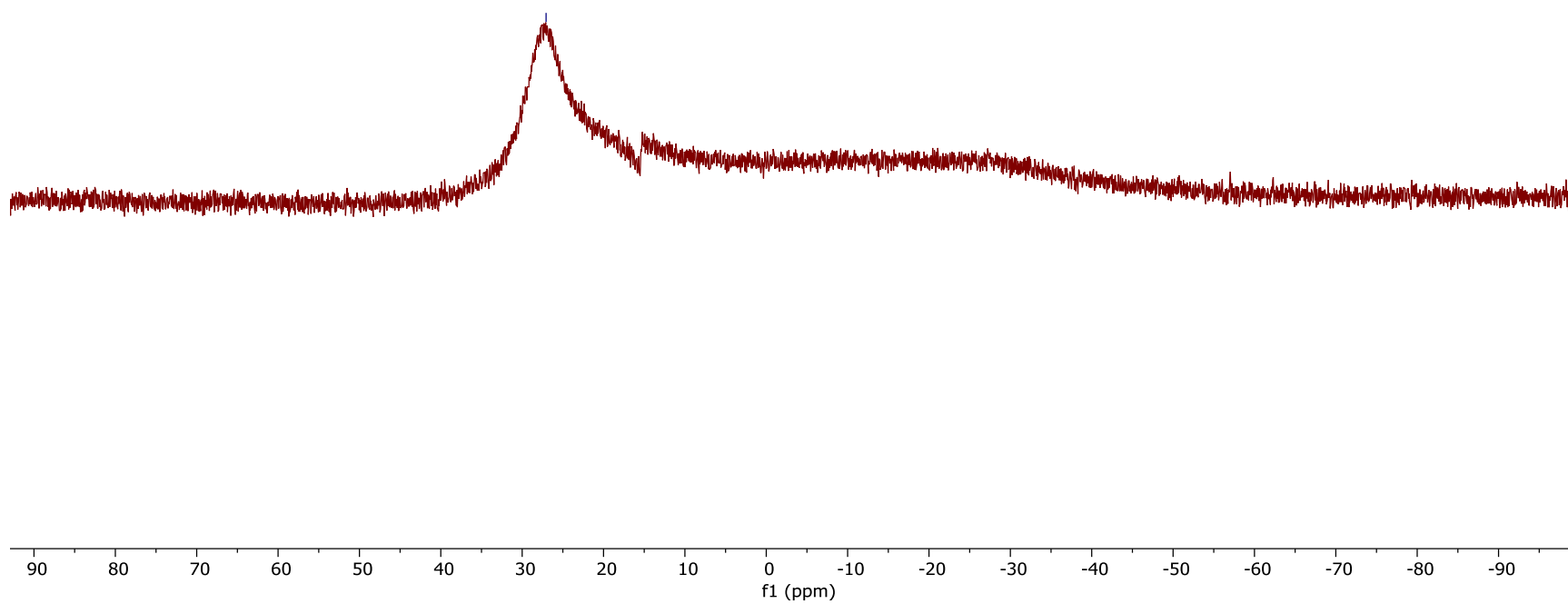
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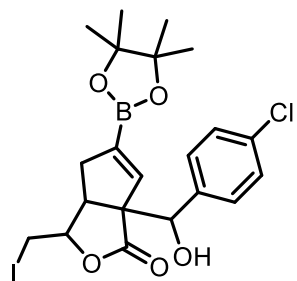




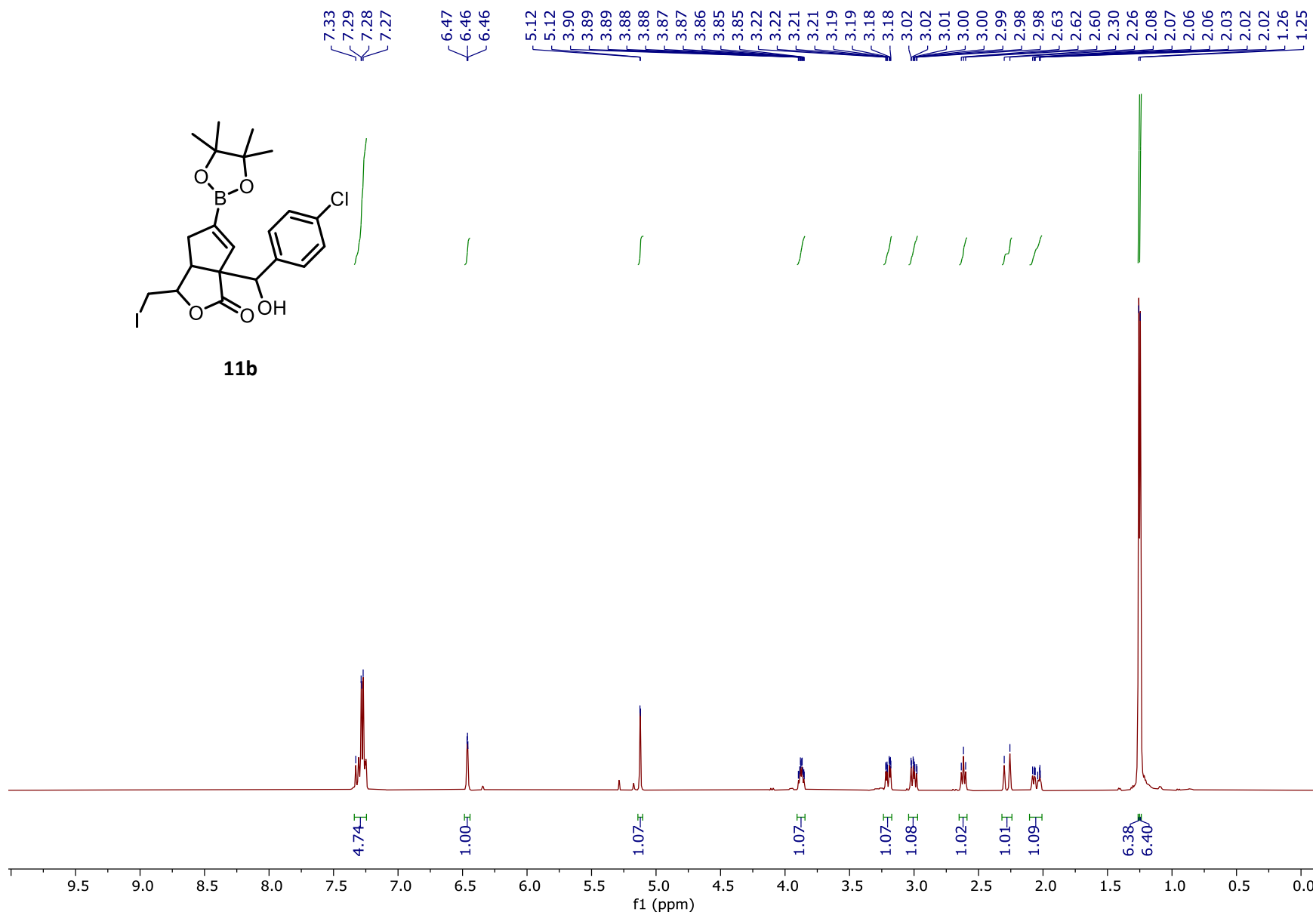
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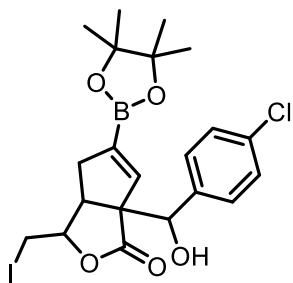
— 27.06





11b





11b

