Supplementary Information

Enantioselective synthesis of α-aminoboronates by NiH-catalysed asymmetric hydroamidation of alkenyl boronates

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I. Supplementary Methods

1. General Information

Solvents were either purified and dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system or bought from the commercial sources and transferred to the glovebox without exposure to air. Other commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, TCI, Aladdin, J&K, Energy Chemical, Bide Pharmatech Ltd. and were used as received. Deionized water was used after degassing. Flash chromatography was performed using glass columns with silica gel (*SiliaFlash*® P60, particle size 40-63 μm, Silicycle).

$NiCl_2 \cdot 6H_2O$ (CAS 7791-20-0, nickel(II) chloride hexahydrate, *ReagentPlus*®) was purchased from Sigma-Aldrich and stored under nitrogen in glovebox;

$(EtO)_3SiH$ (CAS 2031-62-1, triethoxysilane) was purchased from TCI and stored under nitrogen at –20 °C in glove box;

LiI (CAS 10377-51-2) was purchased from Aladdin or Energy Chemical (99.9% metals basis) and stored under nitrogen in glovebox;

DMA (CAS 127-19-5, *N,N*-dimethylacetamide) was purchased from Acros (99.5%, Extra Dry, *AcroSeal*®) and stored under nitrogen in glovebox.

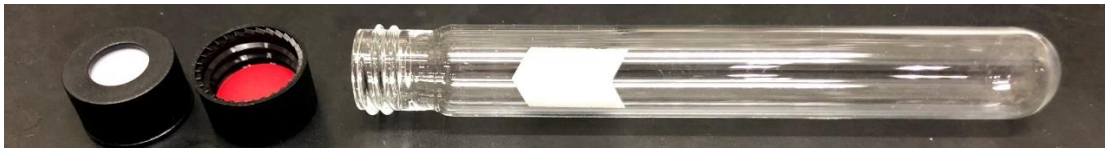
Safety note: MSDS indicates that $(EtO)_3SiH$ is a corrosive and flammable liquid. According to the literatures[1], it may form pyrophoric gas (possibly SiH_4) during the storage or reaction. Although during our reactions, we used $(EtO)_3SiH$ without incident and SiH_4 was not observed, we urge the users of these procedures to be alert to the possibility of SiH_4 formation and possible exotherms and to take suitable precautions (suitable eye protection is also required). $(MeO)_2MeSiH$ could be an alternative hydride source in case of safety consideration.

General analytical information.

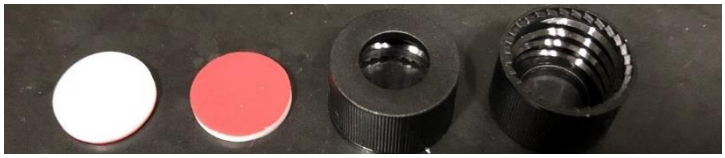
All compounds (starting materials and products) were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and high-resolution mass spectrometry. ^1H NMR spectra were recorded on Bruker 500 MHz spectrometer and are referenced relative to residual

$CDCl_3$ proton signals at δ 7.26 ppm. ^{19}F NMR spectra were recorded on a Bruker 500 MHz spectrometer and are referenced to $CFCl_3$ (δ 0.0 ppm). Data for ^{1}H and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant (Hz). ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer and are referenced to $CDCl_3$ at δ 77.16 ppm. The ^{13}C NMR spectra were obtained with ^{1}H decoupling. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. ^{11}B NMR spectra were recorded on a Bruker 500 MHz spectrometer and are referenced to $BF_3 \cdot Et_2O$ (δ 0.0 ppm), and the broad peaks around -3 ppm were ascribed to NMR tubes. IR spectra were obtained on a Bruker Alpha or Thermo Scientific Nicolet iS10 FT-IR and was reported in terms of frequency of absorption (cm^{-1}). GC analyses were performed on Agilent 7890 or 8890 gas chromatograph with an FID detector using a J&W DB-1 column (10 m, 0.1 mm I.D.). Low Resolution Mass spectra were obtained from on an Agilent 5977A GC-MS. High Resolution Mass spectra were obtained on a Thermo Fisher Q Exactive instrument (ESI). Melting points (m.p.) were obtained on a Mel-Temp capillary melting point apparatus. High pressure liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using Daicel Chiralcel & Chiralpak columns (250 mm). Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm pathlength cell at 589 nm with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL.

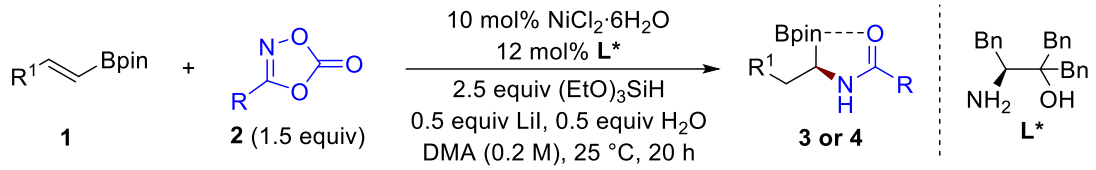
Medium-sized screw-cap test tubes (8 mL) were used for all 0.20 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No. 14-959-35C)



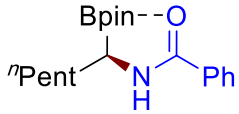
Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)



2. NiH-Catalyzed Asymmetric Hydroamidation of Alkenyl Boronates



<u>General procedure A</u> for NiH-catalyzed asymmetric hydroamidation of alkenyl boronates. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 1,4,2-dioxazol-5-one (0.30 mmol, 1.5 equiv) (if the olefin is a solid, it was also added at this time) and anhydrous DMA (1.0 mL, 0.20 M). The mixture was stirred for 10 min at room temperature, at which time alkenyl boronate (0.20 mmol, 1.0 equiv) (if the 1,4,2-dioxazol-5-one is a liquid, it was added at this time), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv) and $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath for up to 20 h (the mixture was stirred at 800 rpm). After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with Et_2O. The organic layer was concentrated to give the crude product. *n*-Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by flash column chromatography (petroleum ether/EtOAc) for each substrate. The yields reported are the average of at least two experiments, unless otherwise indicated. The enantiomeric excesses (% *ee*) were determined by HPLC analysis using chiral stationary phases.



(*R*)-*N*-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 3, **3a**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A**

using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 71% yield (46.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 2.79 (t, *J* = 6.3 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.61 – 1.52 (m, 1H), 1.49 – 1.37 (m, 2H), 1.34 – 1.28 (m, 4H), 1.26 (s, 12H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 133.1, 128.6, 128.2, 128.1, 81.2, 32.1, 31.3, 27.7, 25.4, 25.2, 22.7, 14.2;

^{11}B NMR (160 MHz, $CDCl_3$) δ 17.8;

HRMS (ESI) calcd. for $C_{19}H_{30}BNNaO_3$ $[M+Na]^+$ m/z 354.2211, found 354.2202;

IR (neat, cm^{-1}) 3079, 2925, 1608, 1530, 1127, 1099, 709;

m.p. 130 – 132 °C;

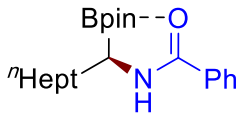
$[\alpha]_D^{25}$ = –35.8 (c = 1.06, $CHCl_3$);

HPLC analysis: the *ee* (95%) was determined using a CHIRALPAK® IE-3 column, 5% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 6.8 min, t_R (minor) = 7.4 min.

From (*Z*)-**1a** (Figure 2, entry 15): (*Z*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*Z*)-**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv) were used. The title compound was prepared following the general procedure A. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 64% yield (42.6 mg).

HPLC analysis: the *ee* (85%) was determined using a CHIRALPAK® IE-3 column, 5% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 6.9 min, t_R (minor) =

7.5 min.



(*R*)-*N*-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)benzamide (Figure 3, **3b**). From (*E*)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (**1b**) (47.6 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 73% yield (52.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 2.86 – 2.77 (m, 1H), 1.74 – 1.66 (m, 1H), 1.60 – 1.53 (m, 1H), 1.47 – 1.35 (m, 2H), 1.33 – 1.20 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 133.1, 128.6, 128.2, 81.2, 32.0, 31.4, 29.9, 29.4, 28.0, 25.4, 25.3, 22.8, 14.3;

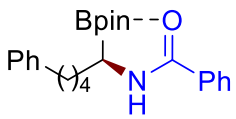
^{11}B NMR (160 MHz, $CDCl_3$) δ 18.3;

HRMS (ESI) calcd. for $C_{21}H_{35}BNO_3$ $[M+H]^+$ m/z 360.2705, found 360.2699;

IR (neat, cm^{-1}) 3196, 2925, 2855, 1610, 1112, 705;

$[\alpha]_D^{25}$ = –36.4 (c = 1.10, $CHCl_3$);

HPLC analysis: the *ee* (95%) was determined using a CHIRALCEL® OD-H column, 8% *i*PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 7.3 min, t_R (major) = 8.0 min.



(*R*)-*N*-(5-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)

benzamide (Figure 3, **3c**). From (*E*)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane (**1c**) (54.4 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 56% yield (44.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.14 (m, 3H), 2.87 – 2.78 (m, 1H), 2.69 – 2.55 (m, 2H), 1.78 – 1.69 (m, 1H), 1.69 – 1.57 (m, 3H), 1.51 – 1.40 (m, 2H), 1.25 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 142.8, 133.2, 128.7, 128.6, 128.4, 128.2, 125.7, 81.3, 35.9, 31.6, 31.2, 27.5, 25.4, 25.3;

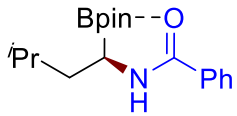
^{11}B NMR (160 MHz, $CDCl_3$) δ 18.2;

HRMS (ESI) calcd. for $C_{24}H_{32}BNNaO_3$ $[M+Na]^+$ m/z 416.2367, found 416.2358;

IR (neat, cm^{-1}) 3193, 2970, 2927, 1610, 1576, 1113, 698, 580;

$[\alpha]_D^{25}$ = –32.4 (c = 0.89, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALPAK® IE-3 column, 10% EtOH in hexane, 0.8 mL/min, 240 nm UV detector, t_R (major) = 7.4 min, t_R (minor) = 7.8 min.



(*R*)-*N*-(3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide (Figure 3, **3d**). From (*E*)-4,4,5,5-tetramethyl-2-(3-methylbut-1-en-1-yl)-1,3,2-dioxaborolane (**1d**) (39.2 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following

the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 68% yield (43.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.64 (s, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 2.95 (t, *J* = 6.8 Hz, 1H), 1.79 – 1.67 (m, 1H), 1.53 – 1.47 (m, 2H), 1.27 (s, 12H), 0.96 (d, *J* = 6.5 Hz, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 133.1, 128.7, 128.4, 128.0, 81.2, 40.6, 26.3, 25.3, 25.3, 23.6, 22.2;

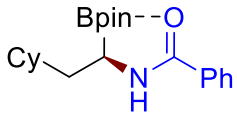
^{11}B NMR (160 MHz, $CDCl_3$) δ 18.6;

HRMS (ESI) calcd. for $C_{18}H_{29}BNO_3$ $[M+H]^+$ m/z 318.2235, found 318.2231;

IR (neat, cm^{-1}) 2958, 1609, 1528, 1113, 1098, 707;

$[\alpha]_D^{25}$ = –37.3 (c = 0.96, $CHCl_3$);

HPLC analysis: the *ee* (92%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (minor) = 4.8 min, t_R (major) = 5.5 min.



(*R*)-*N*-(2-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzamide (Figure 3, **3e**). From (*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1e**) (47.2 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash

column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 70% yield (50.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.71 (s, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 3.00 – 2.92 (m, 1H), 1.91 – 1.81 (m, 1H), 1.76 – 1.63 (m, 4H), 1.60 – 1.51 (m, 1H), 1.51 – 1.45 (m, 1H), 1.43 – 1.36 (m, 1H), 1.27 (s, 12H), 1.22 – 1.11 (m, 3H), 1.01 – 0.84 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 133.2, 128.7, 128.3, 128.1, 81.2, 39.1, 35.8, 34.2, 33.0, 26.8, 26.5, 26.5, 25.3, 25.3;

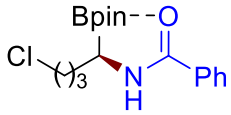
^{11}B NMR (160 MHz, $CDCl_3$) δ 18.6;

HRMS (ESI) calcd. for $C_{21}H_{33}BNO_3$ $[M+H]^+$ m/z 358.2548, found 358.2541;

IR (neat, cm^{-1}) 3066, 2921, 1611, 1122, 705;

$[\alpha]_D^{25}$ = –41.2 (c = 1.08, $CHCl_3$);

HPLC analysis: the *ee* (93%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 254 nm UV detector, t_R (minor) = 6.0 min, t_R (major) = 6.8 min.



(*R*)-*N*-(4-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide (Figure 3, **3f**). From (*E*)-2-(4-chlorobut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1f**) (43.3 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a white solid in 59% yield (37.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.5

Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 3.60 – 3.49 (m, 2H), 2.79 (t, *J* = 6.5 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.86 – 1.77 (m, 1H), 1.77 – 1.68 (m, 1H), 1.27 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 133.5, 128.7, 128.4, 127.2, 81.3, 45.3, 30.7, 28.9, 25.4, 25.3;

^{11}B NMR (160 MHz, $CDCl_3$) δ 16.7;

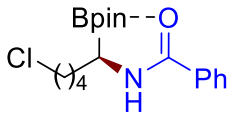
HRMS (ESI) calcd. for $C_{17}H_{26}BClNO_3$ $[M+H]^+$ m/z 338.1689, found 338.1682;

IR (neat, cm^{-1}) 3078, 2966, 1603, 1569, 1532, 1109, 712;

m.p. 53 – 55 °C;

$[\alpha]_D^{25}$ = –53.3 (c = 0.51, $CHCl_3$);

HPLC analysis: the *ee* (95%) was determined using a CHIRALPAK® ID-3 column, 5% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 5.1 min, t_R (minor) = 5.5 min.



(*R*)-*N*-(5-Chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide (Figure 3, **3g**). From (*E*)-2-(5-chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1g**) (46.1 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 55% yield (38.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 3.59 – 3.48 (m, 2H), 2.83 – 2.75 (m, 1H), 1.83 – 1.74 (m, 2H), 1.74 – 1.66 (s, 1H), 1.64 – 1.51 (m, 3H), 1.26 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 133.3, 128.7, 128.3, 127.7, 81.2, 45.2, 32.8, 30.7,

25.5, 25.3, 25.1;

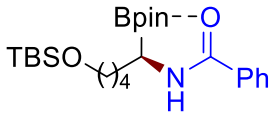
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.6;

HRMS (ESI) calcd. for $C_{18}H_{27}BClNNaO_3$ $[M+Na]^+$ m/z 374.1665, found 374.1656;

IR (neat, cm^{-1}) 3193, 2971, 2929, 1610, 1576, 1111, 734;

$[\alpha]_D^{25}$ = –40.0 (c = 1.08, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (minor) = 7.9 min, t_R (major) = 9.2 min.



(*R*)-*N*-(5-((*tert*-Butyldimethylsilyl)oxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide (Figure 3, **3h**). From (*E*)-*tert*-butyldimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)silane (**1h**) (65.3 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 76% yield (68.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.68 (s, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 3.64 (t, *J* = 6.2 Hz, 2H), 2.92 – 2.83 (m, 1H), 1.78 – 1.67 (m, 1H), 1.68 – 1.44 (m, 5H), 1.27 (s, 6H), 1.26 (s, 6H), 0.88 (s, 9H), 0.04 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 133.2, 128.8, 128.5, 128.0, 81.3, 63.3, 32.9, 31.0, 26.2, 25.4, 25.2, 24.2, 18.5, -5.1;

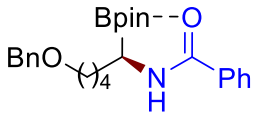
^{11}B NMR (160 MHz, $CDCl_3$) δ 18.9;

HRMS (ESI) calcd. for $C_{24}H_{42}BNNaO_4Si$ $[M+Na]^+$ m/z 470.2868, found 470.2858;

IR (neat, cm^{-1}) 3070, 2928, 2857, 1611, 1096, 706;

[α]$_D^{25}$ = –41.6 (c = 0.98, $CHCl_3$);

HPLC analysis: the *ee* (95%) was determined using a CHIRALPAK® IG-3 column, 5% EtOH in hexane, 0.8 mL/min, 240 nm UV detector, t_R (major) = 4.9 min, t_R (minor) = 5.7 min.



(*R*)-*N*-(5-(Benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide (Figure 3, **3i**). From (*E*)-2-(5-(benzyloxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1i**) (60.4 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 66% yield (55.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 4.50 (s, 2H), 3.51 (t, *J* = 6.3 Hz, 2H), 2.90 – 2.80 (m, 1H), 1.76 – 1.57 (m, 4H), 1.57 – 1.51 (m, 2H), 1.26 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 138.6, 133.2, 128.7, 128.5, 128.1, 127.8, 127.7, 81.1, 73.1, 70.6, 30.9, 29.6, 25.4, 25.2, 24.6;

^{11}B NMR (160 MHz, $CDCl_3$) δ 18.3;

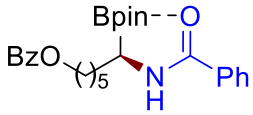
HRMS (ESI) calcd. for $C_{25}H_{34}BNNaO_4$ $[M+Na]^+$ m/z 446.2473, found 446.2462;

IR (neat, cm^{-1}) 3195, 2927, 2856, 1610, 1098, 707;

[α]$_D^{25}$ = –41.6 (c = 1.06, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALPAK® IG-3 column, 5% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, t_R (major) = 8.3 min, t_R (minor) =

11.6 min.



(*R*)-6-Benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate (Figure 3, **3j**). From (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl benzoate (**1j**) (66.0 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 66% yield (59.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.92 (m, 3H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.57 – 7.48 (m, 2H), 7.44 – 7.37 (m, 4H), 4.48 – 4.39 (m, 1H), 4.32 – 4.22 (m, 1H), 2.83 (t, *J* = 5.9 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.78 – 1.67 (m, 2H), 1.66 – 1.57 (m, 1H), 1.56 – 1.39 (m, 4H), 1.26 (s, 6H), 1.25 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 167.2, 133.3, 133.1, 130.5, 129.7, 128.8, 128.5, 128.2, 81.1, 64.7, 31.2, 29.0, 27.1, 25.7, 25.5, 25.2;

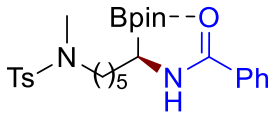
^{11}B NMR (160 MHz, $CDCl_3$) δ 18.2;

HRMS (ESI) calcd. for $C_{26}H_{34}BNNaO_5$ $[M+Na]^+$ m/z 474.2422, found 474.2413;

IR (neat, cm^{-1}) 3050, 2970, 2930, 1716, 1610, 1265, 1117, 734;

$[\alpha]_D^{25}$ = –58.1 (c = 0.98, $CHCl_3$);

HPLC analysis: the *ee* (95%) was determined using a CHIRALPAK® IF-3 column, 10% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, t_R (major) = 6.8 min, t_R (minor) = 7.6 min.



(*R*)-*N*-(6-((*N*,4-Dimethylphenyl)sulfonamido)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 3, **3k**). From (*E*)-*N*,4-dimethyl-*N*-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl)benzenesulfonamide (**1k**) (78.7 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a white solid in 57% yield (58.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.21 – 3.11 (m, 1H), 2.93 – 2.85 (m, 1H), 2.82 – 2.73 (m, 1H), 2.68 (s, 3H), 2.42 (s, 3H), 1.72 – 1.43 (m, 7H), 1.38 – 1.31 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 143.5, 134.4, 133.2, 129.8, 128.7, 128.4, 127.9, 127.4, 80.8, 49.0, 34.5, 30.9, 26.4, 26.0, 25.5, 25.2, 24.8, 21.6;

^{11}B NMR (160 MHz, $CDCl_3$) δ 17.3;

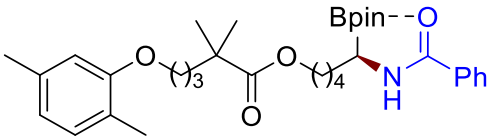
HRMS (ESI) calcd. for $C_{27}H_{39}BN_2NaO_5S$ $[M+Na]^+$ m/z 537.2565, found 537.2556;

IR (neat, cm^{-1}) 3050, 2929, 1610, 1156, 732;

m.p. 123 – 125 °C;

$[\alpha]_D^{25}$ = –25.5 (c = 1.05, $CHCl_3$);

HPLC analysis: the *ee* (97%) was determined using a CHIRALPAK® IG-3 column, 20% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, t_R (major) = 9.7 min, t_R (minor) = 12.3 min.



(*R*)-5-Benzamido-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (Figure 3, **3l**). From (*E*)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**1l**) (88.9 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 60% yield (67.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.59 (s, 1H), 4.07 (t, *J* = 6.1 Hz, 2H), 3.90 (t, *J* = 5.5 Hz, 2H), 2.83 (t, *J* = 6.0 Hz, 1H), 2.29 (s, 3H), 2.16 (s, 3H), 1.79 – 1.61 (m, 7H), 1.61 – 1.53 (m, 1H), 1.53 – 1.41 (m, 2H), 1.28 (s, 6H), 1.27 (s, 6H), 1.20 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 171.1, 157.0, 136.6, 133.3, 130.4, 128.6, 128.3, 127.7, 123.7, 120.8, 112.1, 81.1, 68.1, 64.5, 42.2, 37.2, 31.0, 28.9, 25.4, 25.3, 25.2, 24.1, 21.5, 15.9;

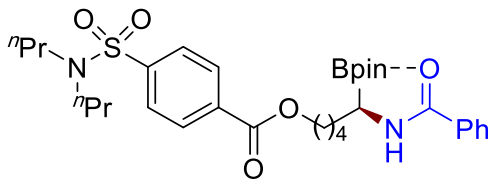
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.9;

HRMS (ESI) calcd. for $C_{33}H_{48}BNNaO_6$ $[M+Na]^+$ m/z 588.3467, found 588.3453;

IR (neat, cm^{-1}) 2925, 1725, 1610, 1151, 1127, 707;

$[\alpha]_D^{25}$ = –30.3 (c = 0.98, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALPAK® AD-H column, 8% *i*PrOH in hexane, 0.8 mL/min, 240 nm UV detector, t_R (minor) = 7.0 min, t_R (major) = 8.1 min.



(*R*)-5-Benzamido-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (Figure 3, **3m**). From (*E*)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**1m**) (95.9 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:3) to provide the title compound as a colorless oil in 60% yield (72.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.52 (s, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 4.37 (t, *J* = 6.5 Hz, 2H), 3.13 – 3.04 (m, 4H), 2.98 – 2.88 (m, 1H), 1.89 – 1.75 (m, 3H), 1.69 – 1.49 (m, 7H), 1.26 (s, 6H), 1.26 (s, 6H), 0.86 (t, *J* = 7.4 Hz, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 165.6, 144.3, 133.8, 133.3, 130.3, 128.8, 128.0, 127.1, 81.5, 65.7, 50.1, 31.1, 28.9, 25.4, 25.2, 24.2, 22.1, 11.3;

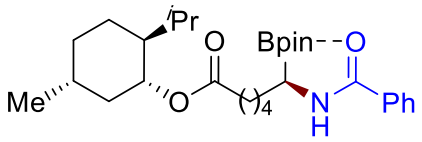
^{11}B NMR (160 MHz, $CDCl_3$) δ 18.0;

HRMS (ESI) calcd. for $C_{31}H_{45}BN_2NaO_7S$ $[M+Na]^+$ m/z 623.2933, found 623.2923;

IR (neat, cm^{-1}) 2967, 2932, 1721, 1609, 1272, 1155, 1087, 601;

$[\alpha]_D^{25}$ = –30.7 (c = 1.04, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALPAK® ID-3 column, 15% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, t_R (major) = 9.2 min, t_R (minor) = 13.5 min.



(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*R*)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, **3n**). From (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (**1n**) (75.7 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 58% yield (58.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 4.69 (td, *J* = 10.9, 4.3 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.43 – 2.22 (m, 2H), 2.00 – 1.92 (m, 1H), 1.90 – 1.80 (m, 1H), 1.78 – 1.62 (m, 5H), 1.62 – 1.54 (m, 1H), 1.54 – 1.41 (m, 3H), 1.41 – 1.32 (m, 1H), 1.27 (s, 6H), 1.27 (s, 6H), 1.10 – 0.92 (m, 2H), 0.89 (d, *J* = 3.9 Hz, 3H), 0.89 – 0.81 (m, 4H), 0.76 (d, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 171.2, 133.3, 128.7, 128.3, 127.8, 81.0, 74.5, 47.1, 41.1, 34.4, 34.3, 31.6, 30.0, 27.1, 26.4, 25.4, 25.2, 24.0, 23.6, 22.2, 20.8, 16.4;

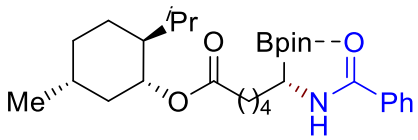
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.2;

HRMS (ESI) calcd. for $C_{29}H_{46}BNNaO_5$ $[M+Na]^+$ m/z 500.3542, found 500.3531;

IR (neat, cm^{-1}) 2957, 2928, 1724, 1610, 1113;

$[\alpha]_D^{25}$ = –59.2 (c = 1.01, $CHCl_3$);

HPLC analysis: the *dr* (98:2) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 5.7 min, t_R (minor) = 8.6 min.



(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*S*)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, **3n'**). From (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (**1n**) (75.7 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), *ent*-**L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 55% yield (55.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 4.71 (td, *J* = 10.9, 4.4 Hz, 1H), 2.94 – 2.86 (m, 1H), 2.43 – 2.22 (m, 2H), 2.02 – 1.92 (m, 1H), 1.87 – 1.78 (m, 1H), 1.79 – 1.62 (m, 5H), 1.62 – 1.54 (m, 1H), 1.54 – 1.40 (m, 3H), 1.40 – 1.32 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.11 – 0.93 (m, 2H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.88 – 0.81 (m, 4H), 0.73 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 171.2, 133.3, 128.7, 128.3, 127.8, 81.0, 74.6, 47.1, 41.1, 34.4, 34.3, 31.6, 30.0, 27.1, 26.4, 25.4, 25.1, 23.9, 23.6, 22.2, 20.9, 16.5;

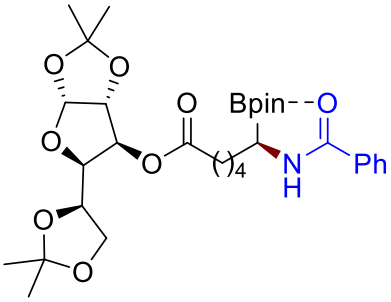
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.2;

HRMS (ESI) calcd. for $C_{29}H_{46}BNNaO_5$ $[M+Na]^+$ m/z 500.3542, found 500.3532;

IR (neat, cm^{-1}) 2954, 2926, 1711, 1603, 1106;

$[\alpha]_D^{25}$ = +7.1 (c = 0.98, $CHCl_3$);

HPLC analysis: the *dr* (2:98) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (minor) = 5.7 min, t_R (major) = 8.6 min.



(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (*R*)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, **3o**). From (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (**1o**) (96.5 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 58% yield (70.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 5.87 (d, *J* = 3.6 Hz, 1H), 5.30 (d, *J* = 2.7 Hz, 1H), 4.49 (d, *J* = 3.7 Hz, 1H), 4.23 – 4.14 (m, 2H), 4.10 – 4.04 (m, 1H), 4.02 – 3.96 (m, 1H), 2.92 – 2.84 (m, 1H), 2.47 – 2.32 (m, 2H), 1.80 – 1.56 (m, 4H), 1.56 – 1.41 (m, 5H), 1.34 (s, 3H), 1.30 (s, 3H), 1.29 – 1.24 (m, 15H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 171.2, 133.4, 128.8, 128.3, 127.7, 112.4, 109.5, 105.2, 83.5, 81.1, 80.1, 76.2, 72.6, 67.4, 34.0, 30.3, 26.9, 26.9, 26.4, 25.4, 25.4, 25.1, 23.9;

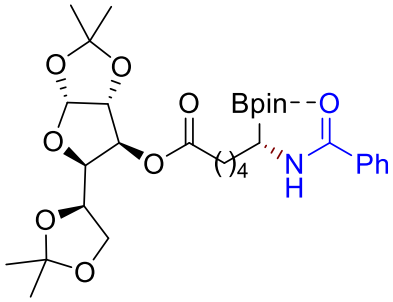
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.7;

HRMS (ESI) calcd. for $C_{31}H_{46}BNNaO_{10}$ $[M+Na]^+$ m/z 626.3107, found 626.3105;

IR (neat, cm^{-1}) 2986, 2933, 1745, 1610, 1373, 1155;

[α]$_D^{25}$ = –46.6 (c = 1.00, $CHCl_3$);

HPLC analysis: the *dr* (97:3) was determined using a CHIRALPAK® IF-3 column, 12% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 6.8 min, t_R (minor) = 7.5 min.



(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (*S*)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, **3o'**). From (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (**1o**) (96.5 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), ***ent*-L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 61% yield (73.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 5.87 (d, *J* = 3.7 Hz, 1H), 5.28 (d, *J* = 2.0 Hz, 1H), 4.47 (d, *J* = 3.7 Hz, 1H), 4.24 – 4.17 (m, 2H), 4.11 – 4.05 (m, 1H), 4.04 – 3.98 (m, 1H), 2.91 – 2.82 (m, 1H), 2.49 – 2.30 (m, 2H), 1.80 – 1.56 (m, 4H), 1.55 – 1.42 (m, 5H), 1.39 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 1.27 (s, 6H), 1.26 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 171.2, 133.4, 128.8, 128.3, 127.8, 112.4, 109.5,

105.2, 83.6, 81.1, 79.9, 76.3, 72.5, 67.4, 33.9, 30.2, 27.0, 27.0, 26.9, 26.4, 25.4, 25.4, 25.1, 24.0;

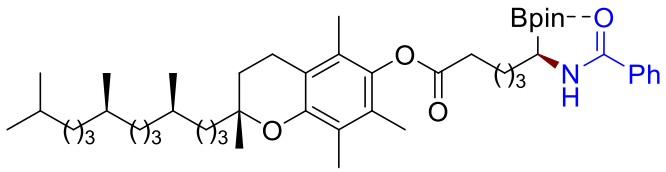
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.5;

HRMS (ESI) calcd. for $C_{31}H_{46}BNNaO_{10}$ $[M+Na]^+$ m/z 626.3107, found 626.3109;

IR (neat, cm^{-1}) 2987, 2934, 1746, 1610, 1373, 1157;

$[\alpha]_D^{25}$ = +14.1 (c = 1.00, $CHCl_3$);

HPLC analysis: the *dr* (3:97) was determined using a CHIRALPAK® IF-3 column, 12% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (minor) = 6.7 min, t_R (major) = 7.5 min.



(*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl (*R*)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, **3p**). From (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (**1p**) (130.6 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 5:2) to provide the title compound as a colorless oil in 57% yield (88.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 2.91 – 2.82 (m, 1H), 2.73 – 2.51 (m, 4H), 2.08 (s, 3H), 2.02 – 1.84 (m, 7H), 1.84 – 1.65 (m, 5H), 1.64 – 1.47 (m, 5H), 1.45 – 1.33 (m, 4H), 1.32 – 1.18 (m, 23H), 1.17 – 1.01 (m, 6H), 0.90 – 0.79 (m, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 171.2, 149.5, 140.6, 133.3, 128.7, 128.3, 127.6,

126.7, 124.9, 123.1, 117.5, 80.9, 75.2, 39.5, 37.6, 37.6, 37.4, 33.9, 32.9, 32.8, 31.2, 30.3, 28.1, 27.2, 25.4, 25.2, 24.9, 24.6, 24.2, 22.9, 22.8, 21.2, 20.7, 19.9, 19.8, 13.2, 12.3, 12.0;

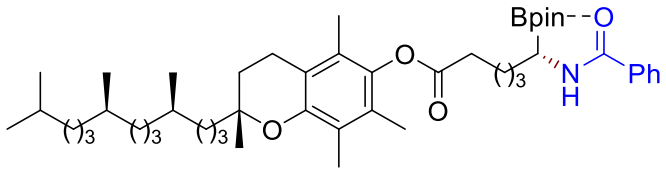
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.2;

HRMS (ESI) calcd. for $C_{48}H_{76}BNNaO_6$ $[M+Na]^+$ m/z 796.5658, found 796.5652;

IR (neat, cm^{-1}) 2925, 2866, 1751, 1610, 1110;

$[\alpha]_D^{25}$ = –19.2 (c = 1.01, $CHCl_3$);

HPLC analysis: the *dr* (98:2) was determined using a CHIRALPAK® ID-3 column, 10% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 4.9 min, t_R (minor) = 5.7 min.



(*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl (*S*)-6-benzamido-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (Figure 3, **3p'**). From (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (**1p**) (130.6 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), *ent*-**L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 5:2) to provide the title compound as a colorless oil in 58% yield (90.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 2.90 – 2.82 (m, 1H), 2.72 – 2.51 (m, 4H), 2.08 (s, 3H), 2.03 – 1.84 (m, 7H), 1.84 – 1.65 (m, 5H), 1.63 –1.46 (m, 5H), 1.44 – 1.32 (m, 4H),

1.31 – 1.20 (m, 23H), 1.16 – 1.03 (m, 6H), 0.89 – 0.81 (m, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 171.2, 149.5, 140.6, 133.3, 128.6, 128.3, 127.5, 126.7, 124.9, 123.1, 117.5, 80.9, 75.2, 39.5, 37.6, 37.6, 37.4, 33.9, 32.9, 32.8, 31.2, 30.3, 28.1, 27.2, 25.4, 25.2, 24.9, 24.6, 24.2, 22.9, 22.8, 21.2, 20.7, 19.9, 19.8, 13.2, 12.3, 12.0;

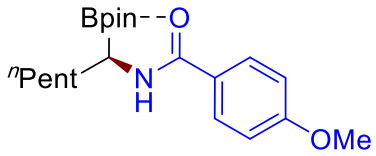
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.1;

HRMS (ESI) calcd. for $C_{48}H_{76}BNNaO_6$ $[M+Na]^+$ m/z 796.5658, found 796.5654;

IR (neat, cm^{-1}) 2926, 2867, 1750, 1610, 1110;

$[\alpha]_D^{25}$ = +26.7 (c = 1.07, $CHCl_3$);

HPLC analysis: the *dr* (2:98) was determined using a CHIRALPAK® ID-3 column, 10% EtOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 4.9 min, t_R (minor) = 5.7 min.



(*R*)-4-Methoxy-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl) benzamide (Figure 4, **4b**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (**2b**) (57.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a white solid in 72% yield (51.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.78 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 2.69 (t, *J* = 6.6 Hz, 1H), 1.72 – 1.63 (m, 1H), 1.58 – 1.48 (m, 1H), 1.47 – 1.36 (m, 2H), 1.35 – 1.27 (m, 4H), 1.26 (s, 6H), 1.25 (s, 6H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 163.6, 130.5, 119.4, 113.8, 80.7, 55.5, 32.2, 31.4, 27.7, 25.5, 25.3, 22.7, 14.3;

^{11}B NMR (160 MHz, $CDCl_3$) δ 15.8;

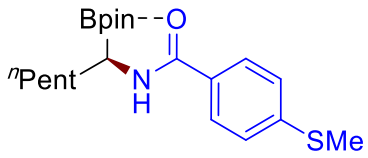
HRMS (ESI) calcd. for $C_{20}H_{33}BNO_4$ $[M+H]^+$ m/z 362.2497, found 362.2489;

IR (neat, cm^{-1}) 3064, 2925, 2854, 1609, 1497, 1260, 1108;

m.p. 166 – 168 °C;

$[\alpha]_D^{25}$ = –59.2 (c = 0.98, $CHCl_3$);

HPLC analysis: the *ee* (95%) was determined using a CHIRALPAK® IG-3 column, 5% EtOH in hexane, 1.0 mL/min, 254 nm UV detector, t_R (major) = 7.2 min, t_R (minor) = 8.1 min.



(*R*)-4-(Methylthio)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 4, **4c**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(4-(methylthio)phenyl)-1,4,2-dioxazol-5-one (**2c**) (62.8 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 61% yield (46.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 2.73 (t, *J* = 6.5 Hz, 1H), 2.47 (s, 3H), 1.74 – 1.63 (m, 1H), 1.59 – 1.49 (m, 1H), 1.48 – 1.37 (m, 2H), 1.35 – 1.27 (m, 4H), 1.27 (s, 12H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 146.2, 128.7, 124.9, 123.2, 81.0, 32.2, 31.4, 27.6, 25.4, 25.3, 22.7, 14.8, 14.2;

^{11}B NMR (160 MHz, $CDCl_3$) δ 16.6;

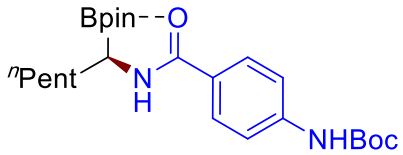
HRMS (ESI) calcd. for $C_{20}H_{33}BNO_3S$ $[M+H]^+$ m/z 378.2269, found 378.2260;

IR (neat, cm^{-1}) 3205, 2969, 2929, 1602, 1547, 1115, 733;

m.p. 166 – 167 °C;

$[\alpha]_D^{25}$ = –59.5 (c = 1.16, $CHCl_3$);

HPLC analysis: the *ee* (93%) was determined using a CHIRALPAK® IE-3 column, 5% EtOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (major) = 9.7 min, t_R (minor) = 10.8 min.



tert*-Butyl (*R*)-(4-((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamoyl)phenyl)carbamate** (Figure 4, **4d**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and *tert*-butyl (4-(5-oxo-1,4,2-dioxazol-3-yl)phenyl)carbamate (**2d**) (83.5 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 67% yield (59.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 2.77 – 2.67 (m, 1H), 1.76 – 1.65 (m, 1H), 1.56 – 1.38 (m, 12H), 1.36 – 1.24 (m, 16H), 0.85 (t, *J* = 6.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 153.2, 143.7, 129.4, 120.3, 117.7, 81.2, 80.6, 32.1, 31.4, 28.5, 28.1, 25.5, 25.4, 22.7, 14.2;

^{11}B NMR (160 MHz, $CDCl_3$) δ 15.5;

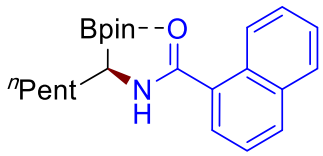
HRMS (ESI) calcd. for $C_{24}H_{39}BN_2NaO_5$ $[M+Na]^+$ m/z 469.2844, found 469.2834;

IR (neat, cm^{-1}) 3224, 2929, 1733, 1605, 1520, 1154, 1096, 737;

m.p. 204 – 205 °C;

[α]$_D^{25}$ = –37.7 (c = 1.10, $CHCl_3$);

HPLC analysis: the *ee* (94%) was determined using a CHIRALPAK® IF-3 column, 5% EtOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (major) = 5.7 min, t_R (minor) = 6.3 min.



(*R*)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-naphthamide (Figure 4, **4e**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(naphthalen-1-yl)-1,4,2-dioxazol-5-one (**2e**) (64.0 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 4:1) to provide the title compound as a white solid in 60% yield (45.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.67 (d, *J* = 6.9 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.46 – 7.41 (m, 1H), 6.88 (s, 1H), 3.17 – 3.09 (m, 1H), 1.82 – 1.73 (m, 1H), 1.70 – 1.60 (m, 1H), 1.50 – 1.39 (m, 2H), 1.39 – 1.32 (m, 4H), 1.30 (s, 12H), 0.89 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 133.7, 132.0, 130.4, 130.0, 128.5, 127.6, 126.7, 126.4, 125.5, 124.7, 82.4, 32.0, 31.3, 27.6, 25.3, 25.2, 22.7, 14.2;

^{11}B NMR (160 MHz, $CDCl_3$) δ 23.9;

HRMS (ESI) calcd. for $C_{23}H_{33}BNO_3$ $[M+H]^+$ m/z 382.2548, found 382.2542;

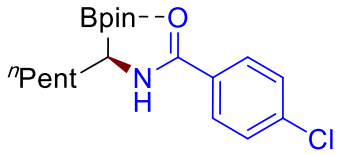
IR (neat, cm^{-1}) 3176, 3065, 2931, 1579, 1532, 1191, 1127, 779;

m.p. 53 – 55 ° Ç

[α]$_D^{25}$ = –34.4 (c = 0.62, $CHCl_3$);

HPLC analysis: the *ee* (84%) was determined using a CHIRALPAK® ID-3 column, 5%

EtOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 4.7 min, t_R (minor) = 5.1 min.



(*R*)-4-Chloro-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 4, **4f**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(4-chlorophenyl)-1,4,2-dioxazol-5-one (**2f**) (59.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 62% yield (45.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 2.85 – 2.78 (m, 1H), 1.77 – 1.64 (m, 1H), 1.62 – 1.51 (m, 1H), 1.46 – 1.36 (m, 2H), 1.35 – 1.28 (m, 4H), 1.26 (s, 12H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 139.6, 129.7, 128.9, 126.6, 81.7, 32.1, 31.3, 27.5, 25.3, 25.2, 22.7, 14.2;

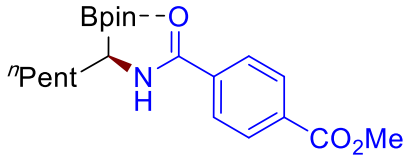
^{11}B NMR (160 MHz, $CDCl_3$) δ 19.1;

HRMS (ESI) calcd. for $C_{19}H_{29}BClNNaO_3$ $[M+Na]^+$ m/z 388.1821, found 388.1811;

IR (neat, cm^{-1}) 3066, 2969, 2927, 1606, 1485, 1092;

$[\alpha]_D^{25}$ = –47.6 (c = 1.09, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALPAK® AS-H column, 3% *i*PrOH in hexane, 0.4 mL/min, 254 nm UV detector, t_R (minor) = 9.3 min, t_R (major) = 10.3 min.



Methyl (*R*)-4-((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamoyl)benzoate (Figure 4, **4g**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and methyl 4-(5-oxo-1,4,2-dioxazol-3-yl)benzoate (**2g**) (66.4 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), MeOH (4.0 μL, 0.10 mmol, 0.50 equiv, instead of H_2O), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 62% yield (48.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 3H), 3.00 – 2.91 (m, 1H), 1.77 – 1.68 (m, 1H), 1.65 – 1.53 (m, 1H), 1.48 – 1.37 (m, 2H), 1.35 – 1.24 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 166.1, 133.8, 133.3, 129.8, 128.1, 82.1, 52.6, 32.1, 31.2, 27.4, 25.3, 25.2, 22.7, 14.2;

^{11}B NMR (160 MHz, $CDCl_3$) δ 21.8;

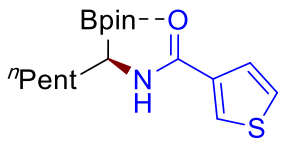
HRMS (ESI) calcd. for $C_{21}H_{33}BNO_5$ $[M+H]^+$ m/z 390.2446, found 390.2436;

IR (neat, cm^{-1}) 2925, 2856, 1730, 1603, 1278, 1107, 725;

m.p. 116 – 118 °C;

$[\alpha]_D^{25}$ = –27.8 (c = 1.01, $CHCl_3$);

HPLC analysis: the *ee* (93%) was determined using two connected CHIRALCEL® OD-H columns, 3% *i*PrOH in hexane, 0.8 mL/min, 254 nm UV detector, t_R (major) = 15.7 min, t_R (minor) = 18.7 min.



(*R*)-*N*-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)thiophene-3-carboxamide (Figure 4, **4h**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(thiophen-3-yl)-1,4,2-dioxazol-5-one (**2h**) (50.7 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 74% yield (49.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.09 (dd, *J* = 2.9, 1.0 Hz, 1H), 7.44 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.21 (dd, *J* = 5.1, 3.0 Hz, 1H), 2.76 (t, *J* = 5.9 Hz, 1H), 1.74 – 1.63 (m, 1H), 1.60 – 1.48 (m, 1H), 1.48 – 1.36 (m, 2H), 1.35 – 1.27 (m, 4H), 1.26 (s, 12H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 132.3, 130.5, 126.6, 126.6, 81.3, 32.1, 31.3, 27.5, 25.3, 25.2, 22.7, 14.2;

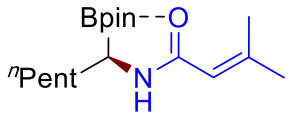
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.3;

HRMS (ESI) calcd. for $C_{17}H_{28}BNNaO_3S$ $[M+Na]^+$ m/z 360.1775, found 360.1765;

IR (neat, cm^{-1}) 3119, 2965, 2925, 1594, 1098;

$[\alpha]_D^{25}$ = –51.0 (c = 1.01, $CHCl_3$);

HPLC analysis: the *ee* (98%) was determined using a CHIRALCEL® OD-H column, 2% *i*PrOH in hexane, 1.0 mL/min, 254 nm UV detector, t_R (minor) = 6.1 min, t_R (major) = 8.4 min.



(*R*)-3-Methyl-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)but-2-enamide (Figure 4, **4i**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(2-methylprop-1-en-1-yl)-

1,4,2-dioxazol-5-one (**2i**) (42.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 3:2) to provide the title compound as a colorless oil in 63% yield (39.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 5.74 (s, 1H), 2.40 – 2.33 (m, 1H), 2.18 (s, 3H), 1.87 (s, 3H), 1.60 – 1.51 (m, 1H), 1.47 – 1.39 (m, 1H), 1.36 – 1.24 (m, 6H), 1.21 (s, 6H), 1.19 (s, 6H), 0.87 (t, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 158.2, 112.1, 80.2, 32.2, 31.5, 28.3, 28.0, 25.5, 25.1, 22.8, 21.0, 14.3;

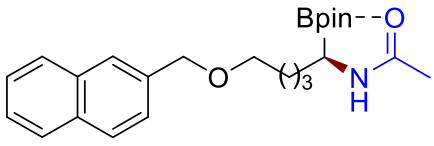
^{11}B NMR (160 MHz, $CDCl_3$) δ 14.1;

HRMS (ESI) calcd. for $C_{17}H_{33}BNO_3$ $[M+H]^+$ m/z 310.2548, found 310.2543;

IR (neat, cm^{-1}) 3176, 2965, 2927, 1665, 1573, 1156, 1107;

$[\alpha]_D^{25}$ = –79.0 (c = 1.00, $CHCl_3$);

HPLC analysis: the *ee* (97%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 5.2 min, t_R (minor) = 7.2 min.



(*R*)-*N*-(5-(Naphthalen-2-ylmethoxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)acetamide (Figure 4, **4j**). From (*E*)-4,4,5,5-tetramethyl-2-(5-(naphthalen-2-ylmethoxy)pent-1-en-1-yl)-1,3,2-dioxaborolane (**1t**) (70.5 mg, 0.20 mmol, 1.0 equiv) and 3-methyl-1,4,2-dioxazol-5-one (**2j**) (30.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA

(1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (CH_2Cl_2/MeOH = 10:1) to provide the title compound as a colorless oil in 47% yield (38.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.84 – 7.78 (m, 3H), 7.75 (s, 1H), 7.49 – 7.41 (m, 3H), 4.63 (s, 2H), 3.56 – 3.47 (m, 2H), 2.55 – 2.46 (m, 1H), 1.94 (s, 3H), 1.74 – 1.56 (m 3H), 1.56 – 1.37 (m, 3H), 1.17 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 136.1, 133.4, 133.1, 128.3, 128.0, 127.8, 126.6, 126.3, 126.0, 126.0, 80.7, 73.2, 70.6, 30.8, 29.6, 25.4, 25.2, 24.8, 18.1;

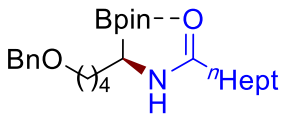
^{11}B NMR (160 MHz, $CDCl_3$) δ 16.6;

HRMS (ESI) calcd. for $C_{24}H_{34}BNNaO_4$ $[M+Na]^+$ m/z 434.2473, found 434.2461;

IR (neat, cm^{-1}) 3053, 2969, 2927, 1609, 1557, 1154, 1097;

$[\alpha]_D^{25}$ = –59.4 (c = 1.04, $CHCl_3$);

HPLC analysis: the *ee* (97%) was determined using a CHIRALCEL® OD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 254 nm UV detector, t_R (minor) = 10.0 min, t_R (major) = 12.1 min.



(*R*)-*N*-(5-(Benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)octanamide (Figure 4, **4k**). From (*E*)-2-(5-(benzyloxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1i**) (60.4 mg, 0.20 mmol, 1.0 equiv) and 3-heptyl-1,4,2-dioxazol-5-one (**2k**) (55.6 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 63% yield (56.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.35 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H),

4.48 (s, 2H), 3.53 – 3.43 (m, 2H), 2.60 – 2.52 (m, 1H), 2.27 – 2.14 (m, 2H), 1.71 – 1.52 (m, 5H), 1.52 – 1.38 (m, 3H), 1.32 – 1.22 (m, 8H), 1.20 (s, 12H), 0.87 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.1, 138.6, 128.5, 127.8, 127.7, 80.8, 73.1, 70.6, 31.9, 31.7, 30.8, 29.6, 29.2, 28.9, 25.3, 25.1, 25.1, 24.8, 22.7, 14.2;

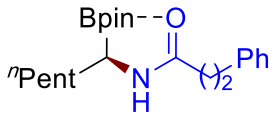
^{11}B NMR (160 MHz, $CDCl_3$) δ 16.6;

HRMS (ESI) calcd. for $C_{26}H_{44}BNNaO_4$ $[M+Na]^+$ m/z 468.3256, found 468.3246;

IR (neat, cm^{-1}) 2963, 2925, 1603, 1155, 1099;

$[\alpha]_D^{25}$ = –50.0 (c = 1.08, $CHCl_3$);

HPLC analysis: the *ee* (97%) was determined using a CHIRALCEL® OD-H column, 8% *i*PrOH in hexane, 0.5 mL/min, 210 nm UV detector, t_R (major) = 9.6 min, t_R (minor) = 10.6 min.



(*R*)-3-Phenyl-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)propanamide (Figure 4, **4l**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-phenethyl-1,4,2-dioxazol-5-one (**2l**) (57.4 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:3) to provide the title compound as a colorless oil in 61% yield (43.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.30 – 7.24 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.64 – 2.51 (m, 3H), 1.61 – 1.51 (m, 1H), 1.39 – 1.32 (m, 1H), 1.31 – 1.22 (m, 6H), 1.21 (s, 12H), 0.87 (t, *J* = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 139.8, 128.8, 128.4, 126.7, 81.1, 34.1, 32.0, 31.2, 31.2, 27.8, 25.4, 25.2, 22.7, 14.2;

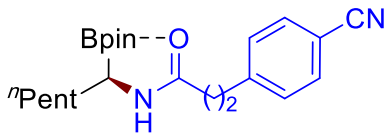
^{11}B NMR (160 MHz, $CDCl_3$) δ 19.2;

HRMS (ESI) calcd. for $C_{21}H_{35}BNO_3$ $[M+H]^+$ m/z 360.2705, found 360.2696;

IR (neat, cm^{-1}) 3168, 2961, 2926, 1604, 1550, 1155, 1109;

$[\alpha]_D^{25}$ = –43.0 (c = 0.91, $CHCl_3$);

HPLC analysis: the *ee* (97%) was determined using a CHIRALCEL® OD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 210 nm UV detector, t_R (minor) = 5.7 min, t_R (major) = 6.5 min.



(*R*)-3-(4-Cyanophenyl)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)propanamide (Figure 4, **4m**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 4-(2-(5-oxo-1,4,2-dioxazol-3-yl)ethyl)benzonitrile (**2m**) (64.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:3) to provide the title compound as a colorless oil in 48% yield (36.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.41 (s, 1H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.83 – 2.74 (m, 1H), 2.62 – 2.48 (m, 2H), 1.61 – 1.51 (m, 1H), 1.44 – 1.35 (m, 1H), 1.31 – 1.24 (m, 6H), 1.23 (s, 12H), 0.87 (t, *J* = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 145.9, 132.5, 129.4, 119.0, 110.6, 82.2, 34.9, 31.9, 31.4, 31.1, 27.4, 25.2, 25.1, 22.7, 14.2;

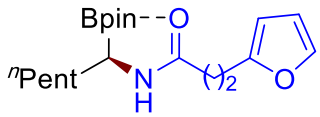
^{11}B NMR (160 MHz, $CDCl_3$) δ 23.7;

HRMS (ESI) calcd. for $C_{22}H_{34}BN_2O_3$ $[M+H]^+$ m/z 385.2657, found 385.2648;

IR (neat, cm^{-1}) 3173, 2964, 2927, 2229, 1606, 1155, 1109;

$[\alpha]_D^{25}$ = –19.1 (c = 0.58, $CHCl_3$);

HPLC analysis: the *ee* (95%) was determined using a CHIRALPAK® AD-H column, 10% *i*PrOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (major) = 4.1 min, t_R (minor) = 5.0 min.



(*R*)-3-(Furan-2-yl)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)propanamide (Figure 4, **4n**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(2-(furan-2-yl)ethyl)-1,4,2-dioxazol-5-one (**2n**) (54.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a yellow oil in 58% yield (40.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 6.26 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.04 (d, *J* = 2.7 Hz, 1H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.69 – 2.55 (m, 3H), 1.62 – 1.52 (m, 1H), 1.43 – 1.35 (m, 1H), 1.33 – 1.23 (m, 6H), 1.21 (s, 12H), 0.87 (t, *J* = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 153.3, 141.6, 110.5, 106.2, 81.3, 32.0, 31.3, 31.2, 27.7, 25.3, 25.1, 23.7, 22.7, 14.2;

^{11}B NMR (160 MHz, $CDCl_3$) δ 19.9;

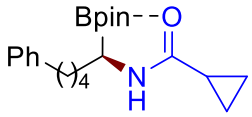
HRMS (ESI) calcd. for $C_{19}H_{33}BNO_4$ $[M+H]^+$ m/z 350.2497, found 350.2491;

IR (neat, cm^{-1}) 3168, 2964, 2926, 1605, 1552, 1154, 1109, 729;

$[\alpha]_D^{25}$ = –37.7 (c = 1.04, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALPAK® AD-H column,

5% *i*PrOH in hexane, 0.8 mL/min, 220 nm UV detector, t_R (major) = 5.6 min, t_R (minor) = 7.5 min.



(*R*)-*N*-(5-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)cyclopropanecarboxamide (Figure 4, **4o**). From (*E*)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane (**1c**) (54.4 mg, 0.20 mmol, 1.0 equiv) and 3-cyclopropyl-1,4,2-dioxazol-5-one (**2o**) (38.1 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 55% yield (39.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.28 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 2.67 – 2.53 (m, 2H), 2.52 – 2.45 (m, 1H), 1.70 – 1.52 (m, 4H), 1.52 – 1.32 (m, 3H), 1.31 – 1.21 (m, 1H), 1.16 (s, 6H), 1.15 (s, 6H), 1.12 – 1.06 (m, 1H), 0.95 – 0.85 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 142.8, 128.5, 128.4, 125.8, 80.5, 36.0, 31.7, 31.3, 27.9, 25.5, 25.1, 10.9, 8.6;

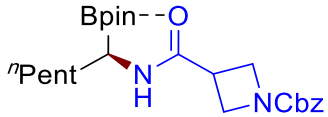
^{11}B NMR (160 MHz, $CDCl_3$) δ 16.2;

HRMS (ESI) calcd. for $C_{21}H_{33}BNO_3$ $[M+H]^+$ m/z 358.2548, found 358.2538;

IR (neat, cm^{-1}) 3206, 3062, 2929, 1603, 1548, 1154, 1115, 734;

$[\alpha]_D^{25}$ = –61.3 (c = 0.97, $CHCl_3$);

HPLC analysis: the *ee* (98%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (major) = 4.3 min, t_R (minor) = 6.4 min.



Benzyl (*R*)-3-((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamoyl)azetidine-1-carboxylate (Figure 4, **4p**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and benzyl 3-(5-oxo-1,4,2-dioxazol-3-yl)azetidine-1-carboxylate (**2p**) (82.9 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (CH_2Cl_2/MeOH = 30:1) to provide the title compound as a colorless oil in 47% yield (42.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 5H), 6.14 (s, 1H), 5.08 (s, 2H), 4.24 – 4.14 (m, 2H), 4.11 (t, *J* = 8.5 Hz, 2H), 3.29 – 3.20 (m, 1H), 3.06 – 2.96 (m, 1H), 1.67 – 1.56 (m, 1H), 1.54 – 1.42 (m, 1H), 1.33 – 1.26 (m, 6H), 1.24 (s, 6H), 1.24 (s, 6H), 0.87 (t, *J* = 6.6 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 156.4, 136.6, 128.6, 128.2, 128.1, 83.2, 66.9, 52.0, 32.5, 31.9, 31.0, 27.1, 25.1, 25.1, 22.6, 14.1;

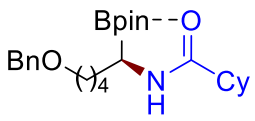
^{11}B NMR (160 MHz, $CDCl_3$) δ 27.9;

HRMS (ESI) calcd. for $C_{24}H_{37}BN_2NaO_5$ $[M+Na]^+$ m/z 467.2688, found 467.2678;

IR (neat, cm^{-1}) 3210, 2959, 2829, 1711, 1605, 1352, 1132;

$[\alpha]_D^{25}$ = –13.4 (c = 0.95, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALCEL® OD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 210 nm UV detector, t_R (minor) = 9.9 min, t_R (major) = 11.7 min.



(*R*)-*N*-(5-(Benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)pentyl)cyclohexanecarboxamide (Figure 4, **4q**). From (*E*)-2-(5-(benzyloxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1i**) (60.4 mg, 0.20 mmol, 1.0 equiv) and 3-cyclohexyl-1,4,2-dioxazol-5-one (**2q**) (50.8 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 65% yield (55.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 7.10 (s, 1H), 4.48 (s, 2H), 3.49 (t, *J* = 6.3 Hz, 2H), 2.59 – 2.50 (m, 1H), 2.25 – 2.15 (m, 1H), 1.89 – 1.81 (m, 2H), 1.81 – 1.71 (m, 2H), 1.70 – 1.56 (m, 4H), 1.50 –1.39 (m, 3H), 1.39 – 1.29 (m, 2H), 1.29 – 1.21 (m, 3H), 1.19 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 180.9, 138.6, 128.5, 127.8, 127.7, 80.6, 73.1, 70.6, 40.5, 30.8, 29.6, 28.9, 28.8, 25.6, 25.4, 25.4, 25.4, 25.1, 24.8;

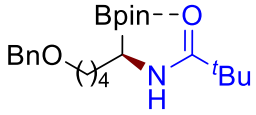
^{11}B NMR (160 MHz, $CDCl_3$) δ 16.0;

HRMS (ESI) calcd. for $C_{25}H_{40}BNNaO_4$ $[M+Na]^+$ m/z 452.2943, found 452.2933;

IR (neat, cm^{-1}) 3198, 2930, 2855, 1599, 1098, 733;

$[\alpha]_D^{25}$ = –55.7 (c = 1.05, $CHCl_3$);

HPLC analysis: the *ee* (94%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (major) = 4.6 min, t_R (minor) = 8.4 min.



(*R*)-*N*-(5-(Benzyloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)pivalamide (Figure 4, **4r**). From (*E*)-2-(5-(benzyloxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1i**) (60.4 mg, 0.20 mmol, 1.0 equiv) and 3-(*tert*-butyl)-1,4,2-dioxazol-5-one (**2r**) (42.9 mg, 0.30 mmol, 1.5 equiv), the title

compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 53% yield (42.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 6.85 (s, 1H), 4.49 (s, 2H), 3.49 (t, *J* = 6.3 Hz, 2H), 2.59 – 2.51 (m, 1H), 1.72 – 1.56 (m, 3H), 1.51 – 1.38 (m, 3H), 1.21 – 1.16 (m, 21H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 183.9, 138.6, 128.5, 127.8, 127.7, 80.4, 73.1, 70.5, 35.7, 30.9, 29.6, 26.9, 25.4, 25.2, 24.8;

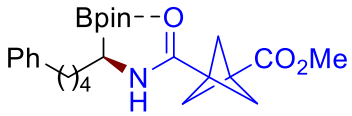
^{11}B NMR (160 MHz, $CDCl_3$) δ 15.8;

HRMS (ESI) calcd. for $C_{23}H_{39}BNO_4$ $[M+H]^+$ m/z 404.2967, found 404.2956;

IR (neat, cm^{-1}) 3204, 2970, 2931, 1581, 1097, 732;

$[\alpha]_D^{25}$ = –49.9 (c = 0.99, $CHCl_3$);

HPLC analysis: the *ee* (83%) was determined using a CHIRALCEL® OD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (major) = 5.3 min, t_R (minor) = 8.2 min.



Methyl (*R*)-3-((5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamoyl)bicyclo[1.1.1]pentane-1-carboxylate (Figure 4, **4s**). From (*E*)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane (**1c**) (54.4 mg, 0.20 mmol, 1.0 equiv) and methyl 3-(5-oxo-1,4,2-dioxazol-3-yl)bicyclo[1.1.1]pentane-1-carboxylate (**2s**) (63.4 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction

mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 53% yield (46.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 6.15 (s, 1H), 3.69 (s, 3H), 2.89 – 2.80 (m, 1H), 2.65 – 2.56 (m, 2H), 2.28 (s, 6H), 1.70 – 1.59 (m, 3H), 1.56 – 1.43 (m, 1H), 1.37 – 1.29 (m, 2H), 1.21 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ171.5, 169.6, 142.6, 128.6, 128.4, 125.8, 82.4, 52.6, 52.0, 37.6, 37.5, 35.8, 31.3, 31.0, 27.0, 25.2, 25.1;

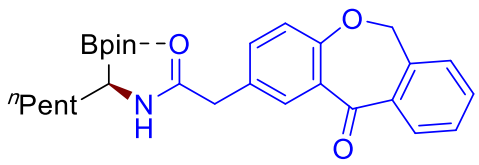
^{11}B NMR (160 MHz, $CDCl_3$) δ 24.5;

HRMS (ESI) calcd. for $C_{25}H_{36}BNNaO_5$ $[M+Na]^+$ m/z 464.2579, found 464.2567;

IR (neat, cm^{-1}) 2929, 1732, 1598, 1202, 1141;

$[\alpha]_D^{25}$ = –29.1 (c = 0.99, $CHCl_3$);

HPLC analysis: the *ee* (97%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (major) = 5.2 min, t_R (minor) = 6.0 min.



(*R*)-2-(11-Oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)acetamide (Figure 4, **4t**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-((11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)methyl)-1,4,2-dioxazol-5-one (**2t**) (92.8 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 50% yield (47.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.2 Hz, 1H), 7.92 – 7.82 (m, 1H), 7.59 – 7.53 (m, 1H), 7.51 – 7.44 (m, 1H), 7.40 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.47 (s, 1H), 5.18 (s, 2H), 3.64 (s, 2H), 2.76 – 2.68 (m, 1H), 1.61 – 1.51 (m, 1H), 1.44 – 1.34 (m, 1H), 1.29 – 1.17 (m, 18H), 0.82 (t, *J* = 6.7 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 174.2, 160.9, 140.4, 136.4, 135.6, 133.1, 132.7, 129.6, 129.5, 128.0, 127.1, 125.5, 121.8, 81.8, 73.8, 39.3, 31.9, 31.1, 27.4, 25.3, 25.1, 22.6, 14.1;

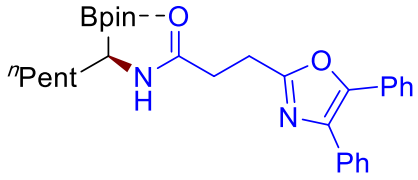
^{11}B NMR (160 MHz, $CDCl_3$) δ 22.4;

HRMS (ESI) calcd. for $C_{28}H_{36}BNNaO_5$ $[M+Na]^+$ m/z 500.2579, found 500.2569;

IR (neat, cm^{-1}) 3055, 2927, 1660, 1613, 1265, 735;

$[\alpha]_D^{25}$ = –20.5 (c = 1.01, $CHCl_3$);

HPLC analysis: the *ee* (97%) was determined using a CHIRALPAK® AD-H column, 10% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 6.3 min, t_R (minor) = 7.7 min.



(*R*)-3-(4,5-Diphenyloxazol-2-yl)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)propanamide (Figure 4, **4u**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-(2-(4,5-diphenyloxazol-2-yl)ethyl)-1,4,2-dioxazol-5-one (**2u**) (100.3 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 51% yield (51.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.64 – 7.56 (m, 4H), 7.41 – 7.33 (m 6H),

3.28 – 3.18 (m, 2H), 2.97 – 2.88 (m, 2H), 2.81 – 2.73 (m, 1H), 1.63 – 1.54 (m, 1H), 1.50 – 1.39 (m, 1H), 1.34 – 1.25 (m, 4H), 1.25 – 1.20 (m, 14H), 0.84 (t, *J* = 6.7 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 162.1, 146.0, 134.6, 131.7, 129.0, 128.9, 128.8, 128.5, 128.0, 126.9, 126.7, 81.5, 31.9, 31.0, 29.6, 27.8, 25.2, 25.1, 23.8, 22.6, 14.2;

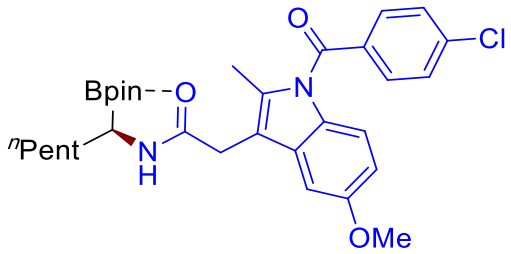
^{11}B NMR (160 MHz, $CDCl_3$) δ 20.8;

HRMS (ESI) calcd. for $C_{30}H_{40}BN_2O_4$ $[M+H]^+$ m/z 503.3076, found 503.3068;

IR (neat, cm^{-1}) 3198, 3056, 2927, 1606, 1156, 1110, 763, 693;

$[\alpha]_D^{25}$ = –21.1 (c = 0.92, $CHCl_3$);

HPLC analysis: the *ee* (97%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 0.8 mL/min, 240 nm UV detector, t_R (major) = 6.2 min, t_R (minor) = 7.5 min.



(*R*)-2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-*N*-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)acetamide (Figure 4, **4v**). From (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv) and 3-((1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)-1,4,2-dioxazol-5-one (**2v**) (119.6 mg, 0.30 mmol, 1.5 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv), $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:3) to provide the title compound as a light yellow solid in 46% yield (52.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.88 – 6.83 (m, 2H), 6.69 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.37 (s, 1H), 3.81 (s, 3H), 3.74 (s, 2H),

2.73 – 2.63 (m, 1H), 2.34 (s, 3H), 1.60 – 1.49 (m, 1H), 1.41 – 1.31 (m, 1H), 1.22 (s, 12H), 1.20 – 1.11 (m, 6H), 0.80 (t, *J* = 6.7 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 168.4, 156.5, 139.9, 136.9, 133.6, 131.3, 131.0, 130.0, 129.4, 115.3, 112.9, 111.0, 100.6, 81.7, 55.9, 31.9, 31.2, 29.0, 27.4, 25.3, 25.1, 22.6, 14.1, 13.5;

^{11}B NMR (160 MHz, $CDCl_3$) δ 21.9;

HRMS (ESI) calcd. for $C_{31}H_{40}BClN_2NaO_5$ $[M+Na]^+$ m/z 589.2611, found 589.2596;

IR (neat, cm^{-1}) 3249, 2928, 1678, 1603, 1323, 1146;

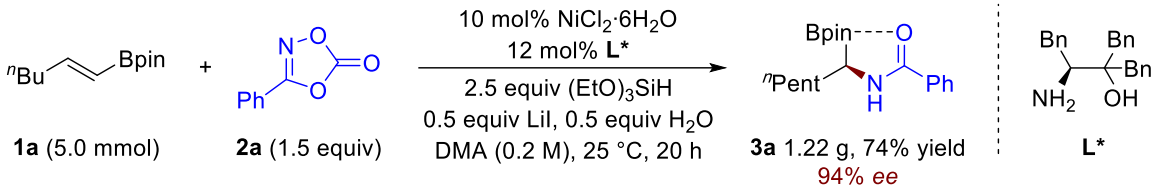
m.p. 150 – 151 °C;

$[\alpha]_D^{25}$ = –34.5 (c = 0.65, $CHCl_3$);

HPLC analysis: the *ee* (98%) was determined using a CHIRALPAK® AD-H column, 10% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 5.7 min, t_R (minor) = 6.7 min.

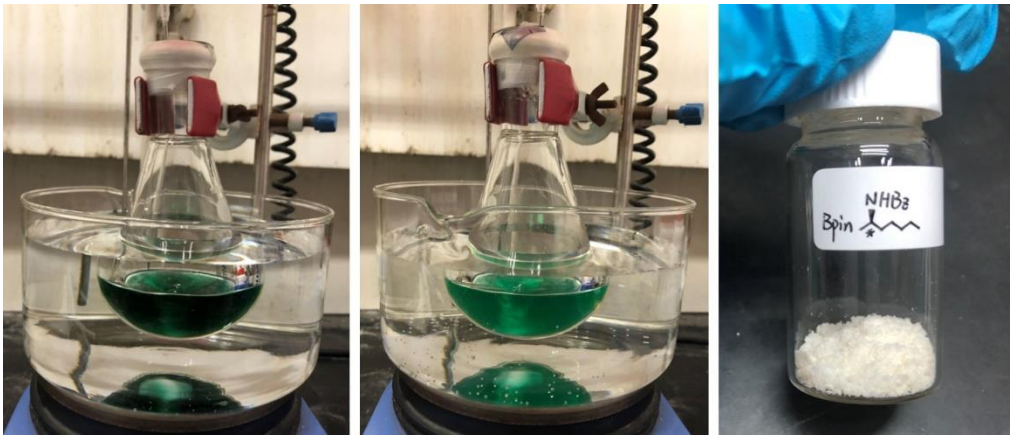
3. Synthetic Application

a. Gram-Scale Experiment



1a (5.0 mmol) **2a** (1.5 equiv) **3a** 1.22 g, 74% yield, 94% *ee* **L***

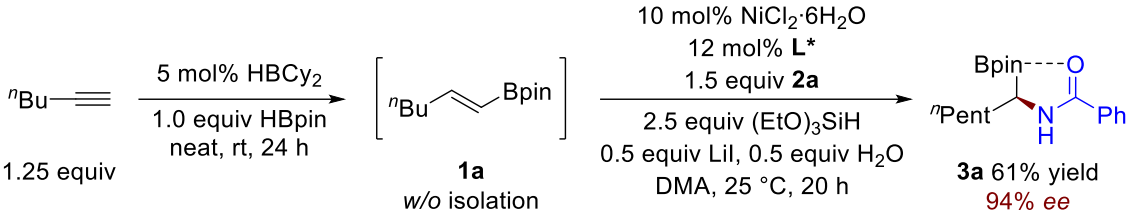
In a nitrogen-filled glove box, to an oven-dried 100 mL round bottom flask equipped with a magnetic stir bar was added $NiCl_2 \cdot 6H_2O$ (118.8 mg, 10 mol%), **L*** (198.9 mg, 12 mol%), LiI (334.6 mg, 2.5 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (1.224 g, 7.5 mmol, 1.5 equiv). The flask was sealed with a rubber stopper, removed from the glove box and equipped with a N_2 balloon, and anhydrous DMA (25 mL, 0.20 M) was added via syringe and the mixture was stirred for 10 min at 25 °C (water bath), at which time (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (1.051g, 5.0 mmol, 1.0 equiv), H_2O (45 μL, 2.5 mmol, 0.50 equiv) were added via syringe and the mixture was stirred for 5 min and then $(EtO)_3SiH$ (2.053 g, 12.5 mmol, 2.5 equiv) was added to the resulting mixture. The mixture was stirred at 25 °C for up to 20 h. After the reaction was complete, *n*-dodecane (500 μL) was added as an internal standard for GC analysis, and the reaction was quenched upon the addition of H_2O (150 mL). The mixture was extracted with Et_2O. The organic layer was concentrated. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide **3a** as a white solid in 74% yield (1.220 g). The *ee* (94%) was determined via chiral HPLC analysis.



Supplementary Figure 1: (Left) All the reagents were added and stirred at 25 °C for 10 min. (a

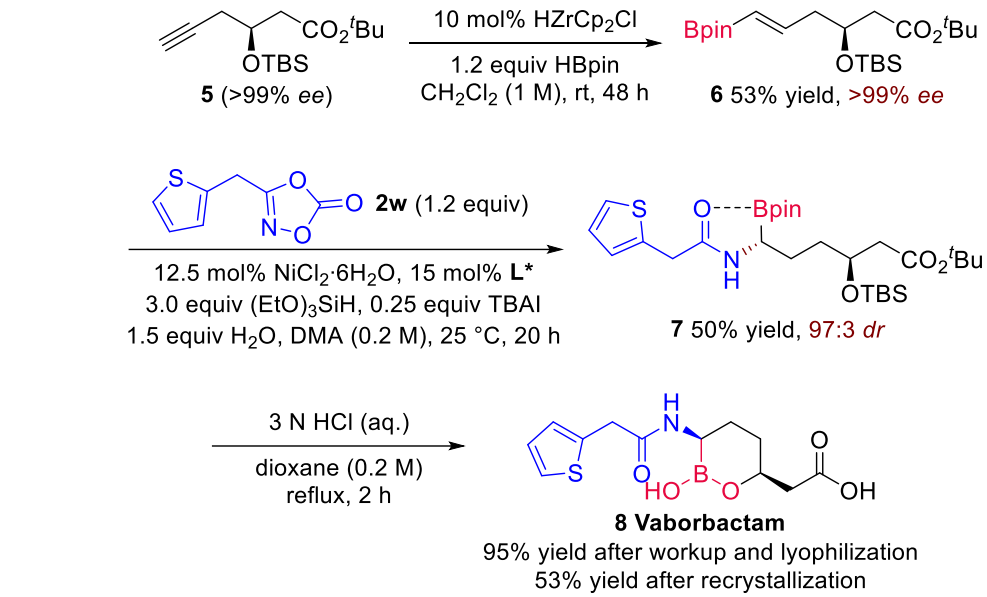
dark green homogeneous mixture) **(Center)** The mixture was stirred at 25 °C for 20 h. (a light green homogeneous mixture) **(Right)** Purified product **3a**. (A white solid (1.220 g) was obtained after purification by column chromatography.).

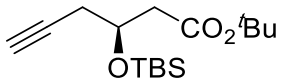
b. One-pot asymmetric hydroamidation *w/o* isolation of alkenyl boronate



The procedure was modified from the previous literature[7]. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added freshly prepared dicyclohexylborane (3.6 mg, 5 mol%), 1-hexyne (41.1 mg, 0.5 mmol, 1.25 equiv) and pinacolborane (58 μL, 0.4 mmol, 1.0 equiv). The reaction mixture was stirred for 18 hours. Afterwards, the volatile materials were removed under reduced pressure at room temperature for 1 h. The vial was refilled with N_2 and transferred to the nitrogen-filled glove box. $NiCl_2 \cdot 6H_2O$ (9.6 mg, 10 mol%), **L*** (16.0 mg, 12 mol%), LiI (26.8 mg, 0.20 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (97.8 mg, 0.60 mmol, 1.5 equiv) and anhydrous DMA (2.0 mL, 0.20 M) were added to the vial. The mixture was stirred for 10 min at room temperature, at which time H_2O (3.6 μL, 0.20 mmol, 0.50 equiv) and $(EtO)_3SiH$ (184 μL, 1.0 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath for up to 20 h (the mixture was stirred at 1000 rpm). After the reaction was complete, *n*-dodecane (40 μL) was added as an internal standard for GC analysis, and the reaction was quenched upon the addition of H_2O. The mixture was extracted with Et_2O. The organic layer was concentrated. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide **3a** as a white solid in 61% yield (80.6 mg). The *ee* (94%) was determined via chiral HPLC analysis.

c. Concise Synthetic Route to Vaborbactam





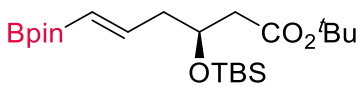
***tert*-Butyl (*S*)-3-((*tert*-butyldimethylsilyl)oxy)hex-5-ynoate** (Figure 5, **5**). The title compound was prepared according to the known literature method[2]. Spectral data match the previously reported.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29 – 4.17 (m, 1H), 2.58 (dd, *J* = 15.4, 4.8 Hz, 1H), 2.45 (dd, *J* = 15.4, 7.1 Hz, 1H), 2.40 (dd, *J* = 6.1, 2.7 Hz, 2H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.45 (s, 9H), 0.87 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 81.0, 80.6, 70.6, 68.1, 43.1, 28.3, 27.5, 25.9, 18.1, -4.5, -4.7;

HRMS (ESI) calcd. for $C_{16}H_{30}NaO_3Si$ $[M+Na]^+$ m/z 321.1856, found 321.1847;

$[\alpha]_D^{25}$ = +28.9 (c = 1.02, $CHCl_3$), >99% *ee*;



***tert*-Butyl (*S,E*)-3-((*tert*-butyldimethylsilyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate** (Figure 5, **6**). Under N_2 atmosphere, to an oven-dried round bottom flask equipped with a stir bar, Schwartz's reagent (0.351 g, 10 mol%), CH_2Cl_2 (13 mL) and *tert*-butyl (*S*)-3-((*tert*-butyldimethylsilyl)oxy)hex-5-ynoate (**5**)

(4.060 g, 13.6 mmol, 1.0 equiv) were added and stirred for 5 minutes. At 0 °C, pinacolborane (2.089 g, 16.3 mmol, 1.2 equiv) was added dropwise to the mixture. Then, the mixture was allowed to warm to rt and stirred for 48 hours. The reaction was quenched with H_2O carefully, extracted with Et_2O, and concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford the titled (*E*)-alkenyl boronate as a colorless oil in 53% yield (3.068 g).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (dt, *J* = 17.9, 7.0 Hz, 1H), 5.47 (d, *J* = 17.9 Hz, 1H), 4.22 – 4.13 (m, 1H), 2.40 – 2.32 (m, 4H), 1.43 (s, 9H), 1.25 (s, 12H), 0.86 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 150.1, 83.2, 80.4, 68.9, 44.4, 43.7, 28.3, 26.0, 24.9, 24.9, 18.2, -4.3, -4.6;

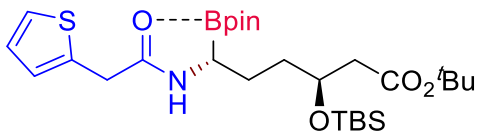
^{11}B NMR (160 MHz, $CDCl_3$) δ 29.9;

HRMS (ESI) calcd. for $C_{22}H_{43}BNaO_5Si$ $[M+Na]^+$ m/z 449.2865, found 449.2853;

IR (neat, cm^{-1}) 2978, 2930, 1730, 1640, 1361, 1142, 832;

$[\alpha]_D^{25}$ = +13.8 (c = 1.09, $CHCl_3$);

HPLC analysis: the *ee* (>99%) was determined using a CHIRALPAK® IF-3 column, 0.5% *i*PrOH in hexane, 1.0 mL/min, 220 nm UV detector, t_R (minor) = 6.9 min, t_R (major) = 8.8 min.



tert*-Butyl (3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(2-(thiophen-2-yl)acetamido)hexanoate** (Figure 5, **7**). From *tert*-butyl (*S*,*E*)-3-((*tert*-butyldimethylsilyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (**6**) (85.3 mg, 0.20 mmol, 1.0 equiv) and 3-(thiophen-2-ylmethyl)-1,4,2-dioxazol-5-one (**2w**) (44.0 mg, 0.24 mmol, 1.2 equiv), the title compound was prepared following the general procedure **A** using $NiCl_2 \cdot 6H_2O$ (5.9 mg, 12.5 mol%), **L (12.0 mg, 15 mol%), TBAI (18.5 mg, 0.050 mmol, 0.25 equiv, instead

of LiI), H_2O (5.4 μL, 0.30 mmol, 1.5 equiv), $(EtO)_3SiH$ (110 μL, 0.60 mmol, 3.0 equiv), anhydrous DMA (1.0 mL). The reaction mixture was stirred for 20 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound as a yellow oil in 50% yield (56.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.93 (d, *J* = 3.1 Hz, 1H), 6.58 (s, 1H), 4.08 – 3.97 (m, 1H), 3.87 (s, 2H), 2.76 – 2.66 (m, 1H), 2.39 – 2.26 (m, 2H), 1.65 – 1.55 (m, 1H), 1.55 – 1.44 (m, 3H), 1.41 (s, 9H), 1.22 (s, 12H), 0.84 (s, 9H), 0.02 (s, 3H), 0.02 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 171.3, 133.9, 128.2, 127.7, 126.2, 81.7, 80.5, 68.9, 43.6, 35.0, 34.1, 28.3, 26.4, 26.0, 25.3, 25.1, 18.1, -4.4, -4.6;

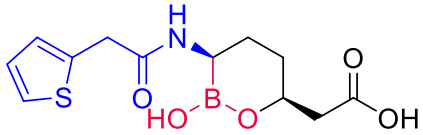
^{11}B NMR (160 MHz, $CDCl_3$) δ 21.8;

HRMS (ESI) calcd. for $C_{28}H_{50}BNNaO_6SSi$ $[M+Na]^+$ m/z 590.3113, found 590.3103;

IR (neat, cm^{-1}) 2968, 2929, 1729, 1607, 1149, 834;

$[\alpha]_D^{25}$ = –20.2 (c = 1.00, $CHCl_3$);

HPLC analysis: the *dr* (97:3) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (major) = 4.3 min, t_R (minor) = 6.5 min.



2-((3*R*,6*S*)-2-Hydroxy-3-(2-(thiophen-2-yl)acetamido)-1,2-oxaborinan-6-yl)acetic acid[3] (Figure 5, **8**). The title compound was prepared according to a known method with a similar substrate[3]. To a solution of *tert*-butyl (3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(2-(thiophen-2-yl)acetamido)hexanoate (**7**) (398 mg, 0.70 mmol) in 1,4-dioxane (2 mL) was added 2 mL of 3 N HCl (aq.). The reaction mixture was heated at reflux for 2 h, after which the cooled reaction mixture was diluted with water (2 mL) and extracted with Et_2O (3 × 6 mL). The aqueous layer was concentrated to afford a sticky residue which was azeotroped with MeCN (3 × 8 mL), dissolved in 20% dioxane-water, and

lyophilized to afford a white powder (198 mg, 95%).

The crude product (150 mg) was suspended in EtOAc (3 mL). Water (0.5 mL) was added, and most of the compound appeared to go into the water layer. After sonicating for about 30 min, a white precipitate formed. The solid was collected by filtration, washed with Et_2O and hexane. The solid was dissolved in 20% dioxane-water, and lyophilized to provide the title compound as a white solid in 53% yield (79.2 mg).

^{1}H NMR (500 MHz, CD_3OD) δ 7.34 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.09 – 7.02 (m, 1H), 7.00 (dd, *J* = 5.2, 3.5 Hz, 1H), 4.14 – 4.04 (m, 1H), 3.97 (s, 2H), 2.66 – 2.57 (m, 1H), 2.37 (dd, *J* = 15.0, 7.3 Hz, 1H), 2.25 (dd, *J* = 15.0, 5.8 Hz, 1H), 1.78 – 1.68 (m, 1H), 1.68 – 1.52 (m, 2H), 1.11 – 0.97 (m, 1H);

^{13}C NMR (126 MHz, CD_3OD) δ 177.8, 175.6, 135.2, 128.8, 128.2, 126.7, 70.5, 44.4, 32.6, 28.5, 27.6;

^{11}B NMR (160 MHz, CD_3OD) δ 11.7;

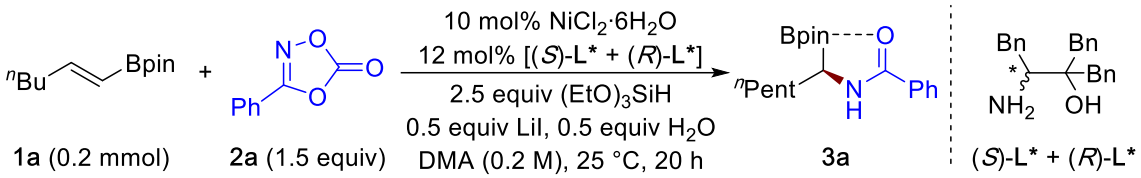
HRMS (ESI) calcd. for $C_{12}H_{15}BNO_4S$ $[M–H_2O+H]^+$ m/z 280.0809, found 280.0802;

IR (neat, cm^{-1}) 3511, 2941, 1718, 1607, 1225, 1183, 701;

$[\alpha]_D^{25}$ = –6.1 (c = 0.85, CH_3OH).

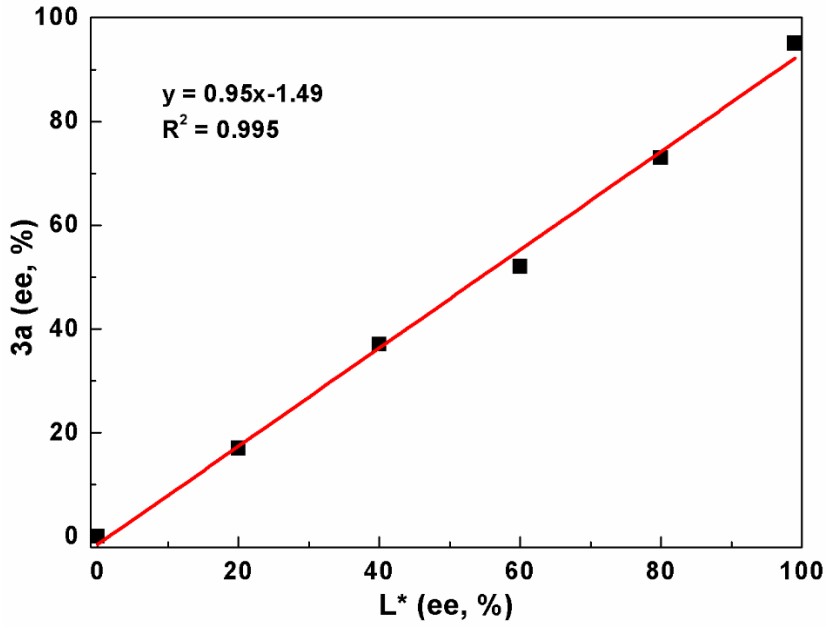
4. Mechanistic Experiments

a. Nonlinear effect study



Supplementary Table 1: Nonlinear effect study

Entry	*ee* (%) of mixed L*	(*S*)-L* (mg)	(*R*)-L* (mg)	*ee* (%) of 3a
1	20	4.8	3.2	17
2	40	5.6	2.4	37
3	60	6.4	1.6	52
4	80	7.2	0.8	73
5	99	8.0	0	95

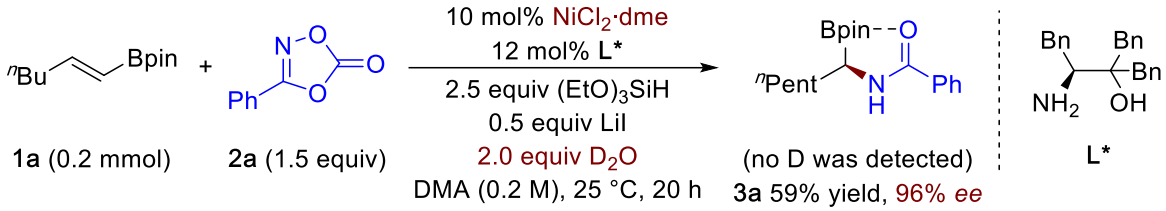


5 parallel reactions at 0.20 mmol scale were performed following general procedure **A**. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiCl_2·6H_2O$ (4.8 mg, 10 mol%), specified amount of (*S*)-**L*** and (*R*)-**L*** (to provide the enantiomeric composition of **L***) as listed in Supplementary Table 1, LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv) and anhydrous DMA (1.0 mL,

0.20 M). The mixture was stirred for 10 min at room temperature, at which time (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv) and $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath (the mixture was stirred at 800 rpm). The reactions were stopped at the indicated reaction time, quenched upon the addition of H_2O and extracted with Et_2O. *n*-Dodecane (20 μL) was added as an internal standard for GC analysis. The organic layer was concentrated to give the crude product. The product was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) for each substrate. The enantiomeric excesses (% *ee*) were determined by HPLC analysis using chiral stationary phases.

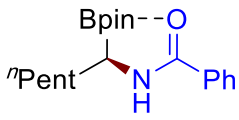
Note: A linear correlation between the *ee* value of the ligand **L*** and that of the product **3a** was observed, consistent with the monomeric nature of the active catalyst.

b. Isotopic labelling experiments



Following the general procedure **A**, in a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiCl_2$·dme (4.4 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv) and anhydrous DMA (1.0 mL, 0.20 M) were added, and the mixture was stirred for 10 min at 25 °C, at which time (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv), D_2O (7.2 μL, 0.40 mmol, 2.0 equiv) and $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C for up to 20 h (the mixture was stirred at 800 rpm). The reaction was quenched upon the addition of H_2O, and the mixture was extracted with Et_2O. The organic layer was concentrated to give the crude product. *n*-Dodecane (20 μL) was added as an internal standard for GC analysis. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide **3a** as a colorless liquid in 57% yield (37.7 mg). The *ee* (96%) of **3a** was determined via HPLC analysis.

Note: Althought 2 equiv D_2O was added, no deuterium incorporation was observed in the product (**3a**), eliminating the possibility of a protic reagent as the hydride source.



(no D was detected)

(*R*)-*N*-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (Figure 6, **3a**, no D was detected).

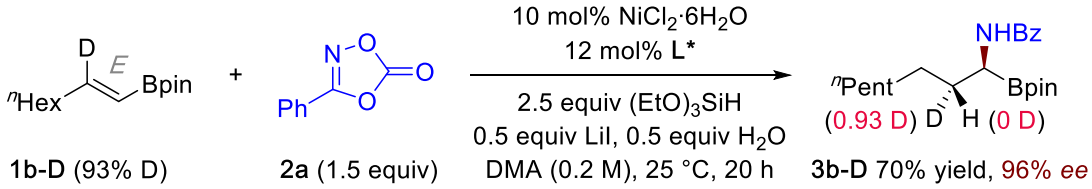
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 6.5 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.61 –

1.52 (m, 1H), 1.49 – 1.37 (m, 2H), 1.34 – 1.28 (m, 4H), 1.26 (s, 12H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 133.1, 128.6, 128.3, 127.9, 81.2, 32.1, 31.3, 27.6, 25.4, 25.2, 22.7, 14.2;

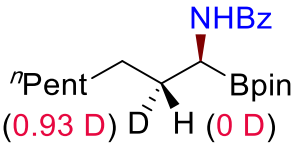
^{11}B NMR (160 MHz, $CDCl_3$) δ 17.6;

^{2}H NMR (92 MHz, $CHCl_3$) no D was detected.



Following the general procedure **A**, in a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiCl_2·6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv) and anhydrous DMA (1.0 mL) were added, and the mixture was stirred for 10 min at 25 °C, at which time (*E*)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl-2-d)-1,3,2-dioxaborolane (**1b-D**, 93% D) (47.8 mg, 0.20 mmol, 1.0 equiv), H_2O (1.8 μL, 0.50 equiv) and $(EtO)_3SiH$ (92 μL, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C for up to 20 h (the mixture was stirred at 800 rpm). The reaction was quenched upon the addition of H_2O, and the mixture was extracted with Et_2O. The organic layer was concentrated to give the crude product. *n*-Dodecane (20 μL) was added as an internal standard for GC analysis. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide **3b-D** as a colorless liquid in 70% yield (50.1 mg). The *ee* (96%) of **3b-D** was determined via HPLC analysis.

Note: Diastereomerically pure **3b-D** was obtained from this reaction, indicating that *syn*-hydronickellation is involved in the enantio-determining step.



***N*-((1*S*,2*R*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)octyl-2-d)benzamide** (Figure 6, **3b-D**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 2.79 (d, *J* = 6.8 Hz, 1H), 1.74 – 1.66 (m, 0.07H), 1.58 – 1.51 (m, 1H), 1.46 – 1.36 (m, 2H), 1.33 – 1.20 (m, 20H), 0.87 (t, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 133.1, 128.6, 128.3, 128.0, 81.2, 32.0, 31.0 (t, *J* = 18.9 Hz), 29.9, 29.4, 27.9, 25.4, 25.2, 22.8, 14.3;

^{11}B NMR (160 MHz, $CDCl_3$) δ 18.0;

^{2}H NMR (92 MHz, $CHCl_3$) δ 1.68 (corresponding to the missing 0.93H);

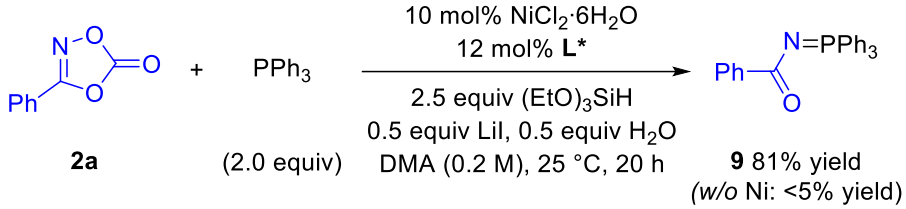
HRMS (ESI) calcd. for $C_{21}H_{33}DBNNaO_3$ $[M+Na]^+$ m/z 383.2587, found 383.2576;

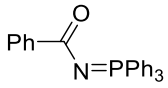
IR (neat, cm^{-1}) 3196, 2923, 2854, 1610, 1154, 1111, 706;

$[\alpha]_D^{25}$ = –38.3 (c = 1.00, $CHCl_3$);

HPLC analysis: the *ee* (96%) was determined using a CHIRALCEL® OD-H column, 8% *i*PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 7.3 min, t_R (major) = 7.9 min (see Supplementary Figure 192).

c. Capture of metal-nitrenoid intermediate





N*-(Triphenyl-λ^5-phosphaneylidene)benzamide** (Figure 6, **9**). In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiCl_2·6H_2O$ (4.8 mg, 10 mol%), **L (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 1,4,2-dioxazol-5-one (32.6 mg, 0.20 mmol, 1.0 equiv), PPh_3 (104.9 mg, 0.40 mmol, 2.0 equiv), anhydrous DMA (1.0 mL, 0.20 M) were added and the mixture was stirred for 10 min at room temperature. H_2O (1.8 μL, 0.10 mmol, 0.50 equiv) and $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath for up to 20 h (the mixture was stirred at 800 rpm). After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with EtOAc. The organic layer was concentrated to give the crude product. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 4:1) to provide the title compound as a white solid in 81% yield (61.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.94 – 7.78 (m, 6H), 7.60 – 7.53 (m, 3H), 7.53 – 7.37 (m, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 138.6, 133.3 (d, *J* = 9.9 Hz), 132.4, 130.8, 129.6, 128.8 (d, *J* = 12.3 Hz), 127.8;

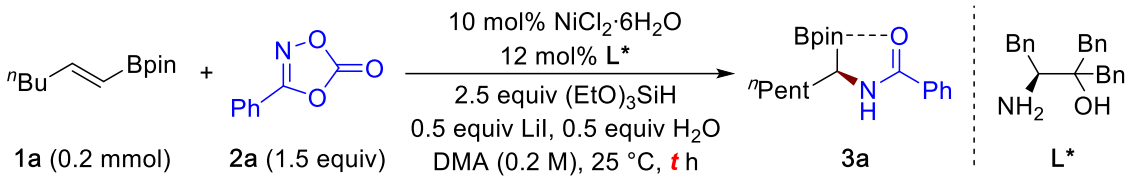
^{31}P NMR (202 MHz, $CDCl_3$) δ 20.7;

HRMS (ESI) calcd. for $C_{25}H_{20}NNaOP$ $[M+Na]^+$ m/z 404.1175, found 404.1163;

IR (neat, cm^{-1}) 3057, 1594, 1557, 1328, 1106, 719, 690, 515;

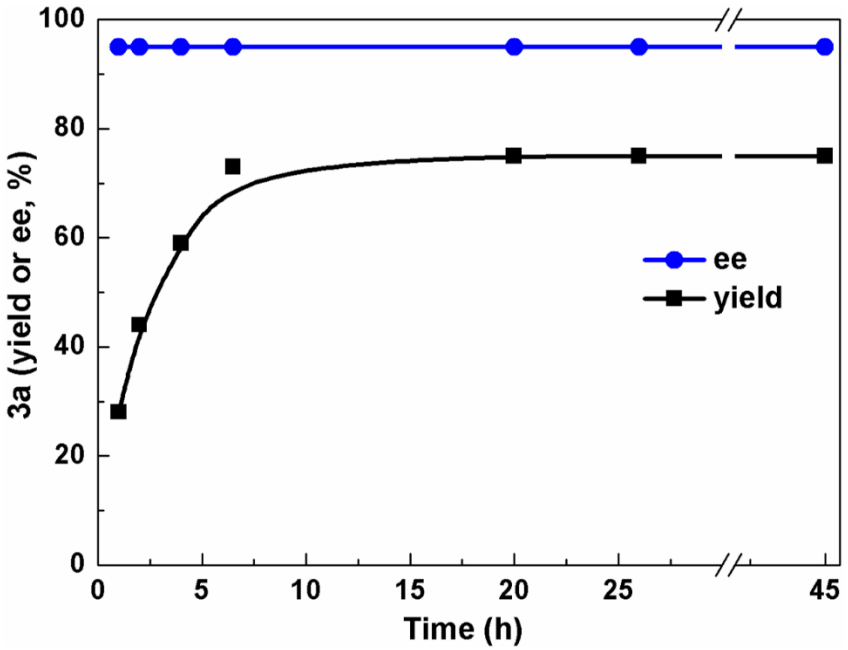
m.p. 198 – 199 °C.

d. Monitoring of the Reaction Progress



Supplementary Table 2: Yield and *ee* of **3a** as a function of time

Entry	*t* (h)	yield (%)	*ee* (%)
1	1	28	95
2	2	44	95
3	4	59	95
4	6.5	75	95
5	20	75	95
6	26	75	95
7	45	75	95

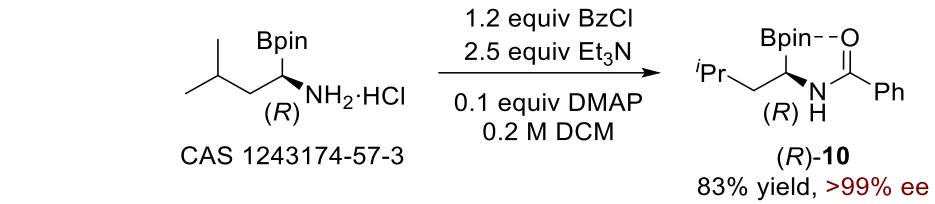


7 parallel reactions at 0.20 mmol scale were performed following general procedure **A**. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiCl_2·6H_2O$ (4.8 mg, 10 mol%), **L*** (8.0 mg, 12 mol%), LiI (13.4 mg, 0.10 mmol, 0.50 equiv), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (48.9 mg, 0.30 mmol, 1.5 equiv) and anhydrous DMA (1.0 mL, 0.20 M). The mixture was stirred

for 10 min at room temperature, at which time (*E*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) (42.0 mg, 0.20 mmol, 1.0 equiv), H_2O (1.8 μL, 0.10 mmol, 0.50 equiv) and $(EtO)_3SiH$ (92 μL, 0.50 mmol, 2.5 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C water bath (the mixture was stirred at 800 rpm). The reactions were stopped at the indicated reaction time, quenched upon the addition of H_2O and extracted with Et_2O. *n*-Dodecane (20 μL) was added as an internal standard for GC analysis. The organic layer was concentrated to give the crude product. The product was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) for each substrate. The enantiomeric excesses (% *ee*) were determined by HPLC analysis using chiral stationary phases.

Note: During the entire reaction, the *ee* of the product remained unchanged.

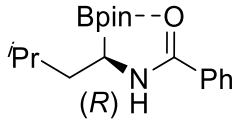
5. Determination of the Absolute Configuration



CAS 1243174-57-3

(*R*)-**10**

83% yield, >99% ee



(*R*)-*N*-(3-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)benzamide ((*R*)-**10**). To a stirred solution of (*R*)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-amine hydrochloride (CAS 1243174-57-3, commercial available optically pure compound) (49.9 mg, 0.20 mmol, 1.0 equiv), dimethylaminopyridine (DMAP, 2.4 mg, 0.020 mmol, 0.10 equiv) in dry CH_2Cl_2 (15 mL) at 0 °C was added Et_3N (70 μL, 0.5 mmol, 2.5 equiv). After 10 minutes, benzoyl chloride (33.7 mg, 0.24 mmol, 1.2 equiv) were added. The resulting reaction mixture was allowed to warm to rt and the stirring was continued for overnight. After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with EtOAc. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography (petroleum ether/EtOAc = 2:1) to provide the title compound **10** as a white solid in 83% yield (52.4 mg), and the spectral data match **3d**.

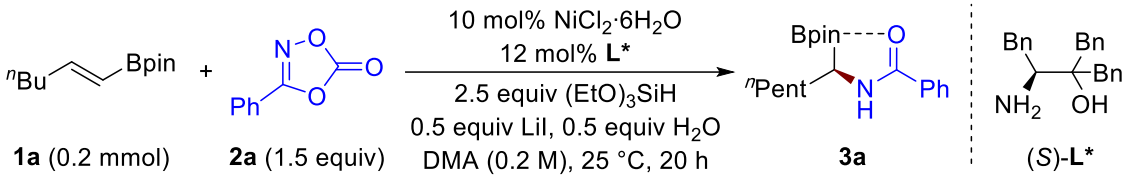
$[\alpha]_D^{25}$ = –40.9 (c = 0.94, $CHCl_3$);

HPLC analysis: the *ee* (>99%) was determined using a CHIRALPAK® AD-H column, 5% *i*PrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (minor) = 4.8 min, t_R (major) = 5.6 min, (*R*) configuration (see Supplementary Figure 197).

Note: The absolute configuration of **3d** was determined to be (*R*) by comparison of the optical rotation and HPLC peak of the title compound with **3d** ($[\alpha]_D^{25}$ = –37.3 (c = 0.96, $CHCl_3$); HPLC analysis: the *ee* (92%) of **3d** was determined using a CHIRALPAK® AD-H column, 5% iPrOH in hexane, 1.0 mL/min, 240 nm UV detector, t_R (minor) = 4.8 min, t_R (major) = 5.5 min.).

6. Conditions Optimization

Supplementary Table 3: Effect of reaction parameters[a].



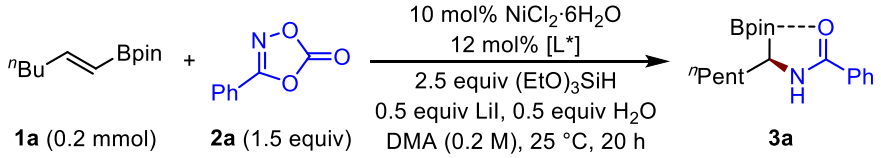
1a (0.2 mmol) **2a** (1.5 equiv) **3a** (*S*)-**L***

Entry	Variation from the standard conditions	Yield (%)	*ee* (%)
1	None	75 (71)	95
2	w/o Ni	0	-
3	w/o **L***	13	nd
4	$NiCl_2$·dme instead of $NiCl_2·6H_2O$	63	86
5	$NiBr_2·3H_2O$ instead of $NiCl_2·6H_2O$	58	61
6	$NiCl_2$ instead of $NiCl_2·6H_2O$	<5	nd
7	$Ni(NO_3)_2·6H_2O$ instead of $NiCl_2·6H_2O$	<5	nd
8	NiI_2 instead of $NiCl_2·6H_2O$	8	nd
9	$NiI_2·xH_2O$ instead of $NiCl_2·6H_2O$	8	nd
10	w/o LiI	46	97
11	NaI instead of LiI	67	94
12	TBAI instead of LiI	72	95
13	DMMS instead of $(EtO)_3SiH$	69	96
14	DEMS instead of $(EtO)_3SiH$	20	94
15	$(MeO)_3SiH$ instead of $(EtO)_3SiH$	67	95
16	PMHS instead of $(EtO)_3SiH$	<5	nd
17	w/o H_2O	58	81
18	MeOH instead of H_2O	73	89
19	EtOH instead of H_2O	72	88
20	^{i}PrOH instead of H_2O	72	85
21	^{t}BuOH instead of H_2O	64	80
22	DMF instead of DMAc	11	nd
23	DMPU instead of DMAc	13	nd
24	NMP instead of DMAc	49	96
25	THF instead of DMAc	12	nd
26	DCE instead of DMAc	<5	nd
27	10 °C instead of 25 °C	59	97

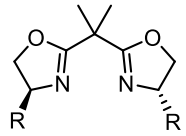
28	40 °C instead of 25 °C	74	85
29	under air in a closed vial	68	94
30	2 equiv H_2O	70	96

[a] Yields determined by GC using *n*-dodecane as the internal standard, the yield in parentheses is the isolated yield (0.20 mmol scale). Enantioselectivities were determined by chiral HPLC analysis.

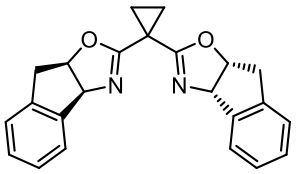
Supplementary Table 4: Effect of Ligands[a].



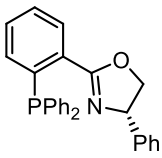
1a (0.2 mmol) **2a** (1.5 equiv) **3a**



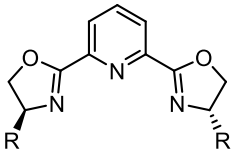
L4, R = Ph, 18% yield, 56% *ee*
L7, R = ^{i}Pr, 6% yield



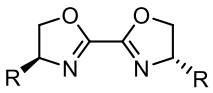
L8, 0% yield



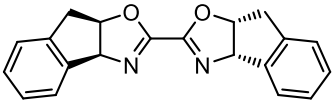
L9, 18% yield, 0% *ee*



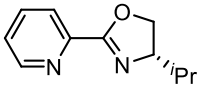
L10, R = Ph, 6% yield
L11, R = ^{i}Pr, 0% yield



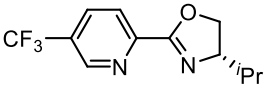
L12, R = Ph, 67% yield, 0% *ee*
L13, R = ^{i}Pr, 80% yield, 10% *ee*
L5, R = Bn, 74% yield, 44% *ee*



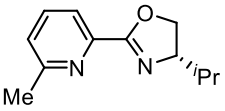
L14, 41% yield, 7% *ee*



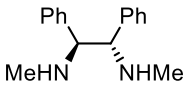
L15, 16% yield, 8% *ee*



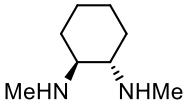
L16, 38% yield, 8% *ee*



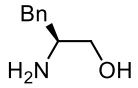
L6, 75% yield, 16% *ee*



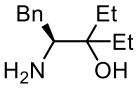
L17, 0% yield



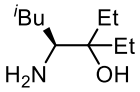
L18, 0% yield



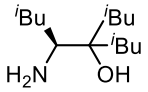
L3, 14% yield, 13% *ee*



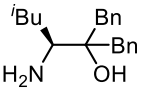
L2, 57% yield, 85% *ee*



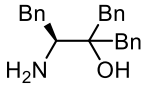
L19, 38% yield, 75% *ee*



L20, 51% yield, 85% *ee*



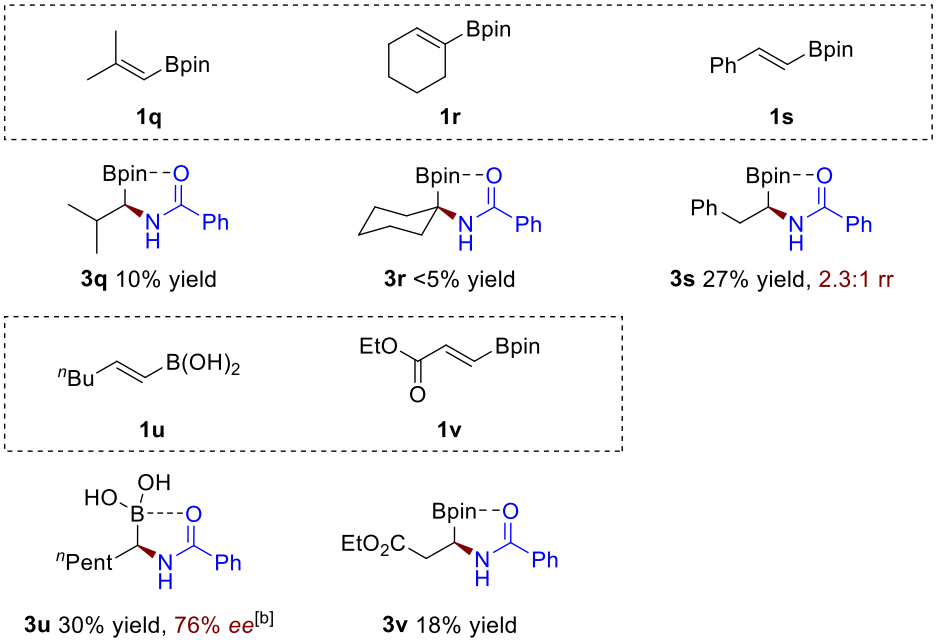
L21, 67% yield, 93% *ee*



L*, 75% yield, 95% *ee*

[a] Yields determined by GC using *n*-dodecane as the internal standard, the yield in parentheses is the isolated yield (0.20 mmol scale). Enantioselectivities were determined by chiral HPLC analysis.

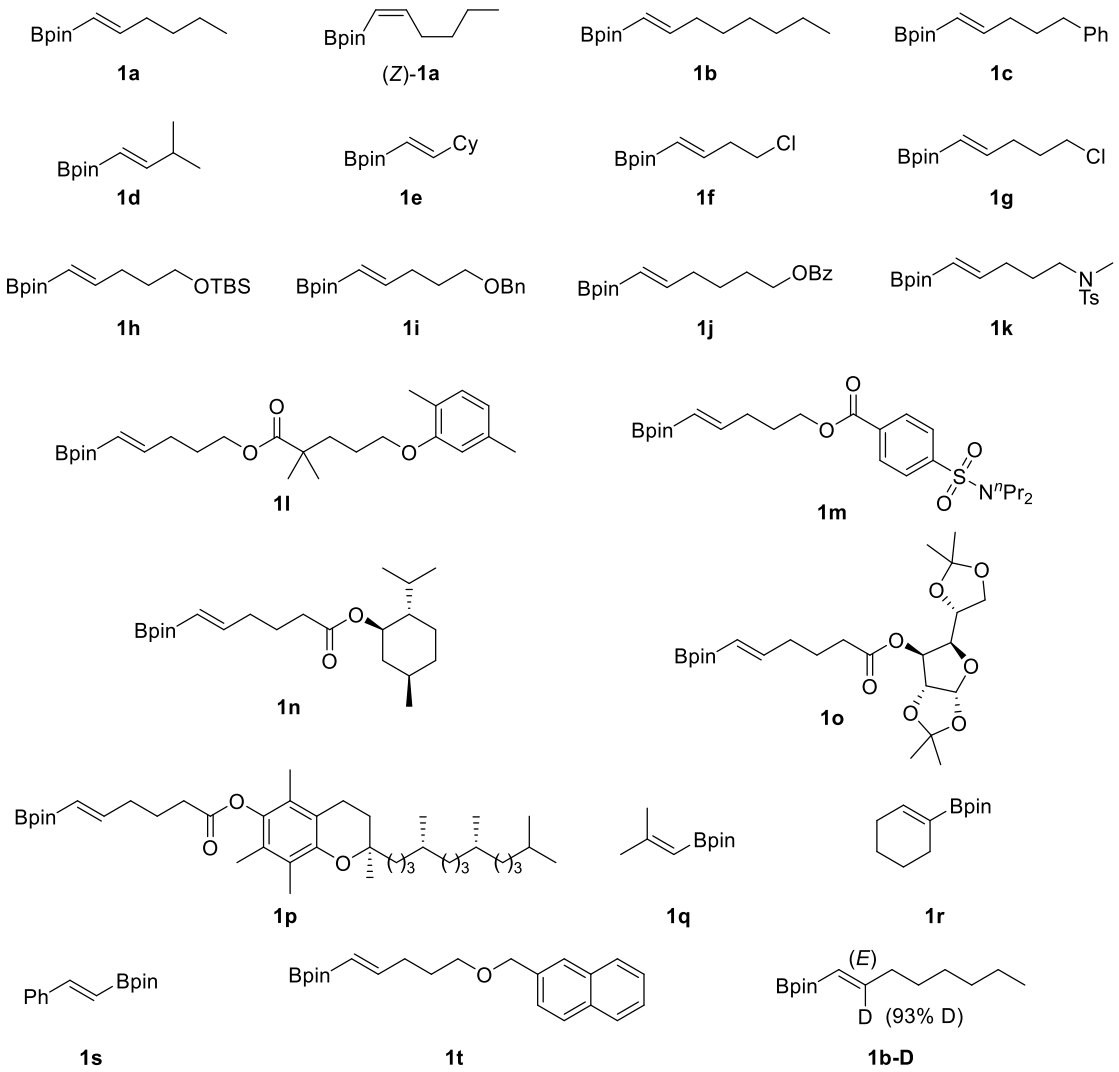
Supplementary Table 5: Effect of other olefins under standard conditions[a].



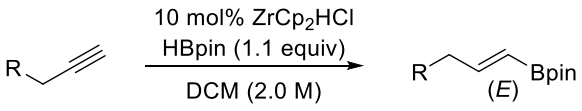
[a] reaction conditons were the same as **Figure 3**; [b] $(MeO)_2MeSiH$ was used instead of $(EtO)_3SiH$, the product was isolated as **3a** after treatment with pinacol.

7. Preparation of Substrates

a. Preparation of alkenyl boronates

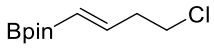


Compounds **1a**, **1e**, **1q**, **1r**, **1s** are commercially available. Compounds (*Z*)-**1a**[4], **1b**[5], **1c**[7], **1d**[6], **1g**[5], **1h**[8], **1i**[9], **1j**[7],**1k**[5],and **1b-D**[10] were prepared according to the previously reported procedures.



General procedure B for the synthesis of (*E*)-alkenyl boronates[11]. Under N_2 atmosphere, to an oven-dried round bottom flask equipped with a stir bar, Schwartz's reagent (10 mol%), CH_2Cl_2 (2.0 M) and alkyne (1.0 equiv) were added and stirred for 5 minutes. At 0 °C, pinacolborane (1.1 equiv) was added dropwise to the mixture. Then,

the mixture was allowed to warm to 30 °C and stirred for 24 hours. The reaction was quenched with H_2O, extracted with Et_2O, and concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (petroleum ether/EtOAc) to afford the (*E*)-alkenyl boronates.



(*E*)-2-(4-chlorobut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Figure 3, **1f**). From the 4-chlorobut-1-yne (0.89 g, 10.0 mmol), the title compound was prepared following the general procedure **B**. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless oil in 59% yield (1.27 g).

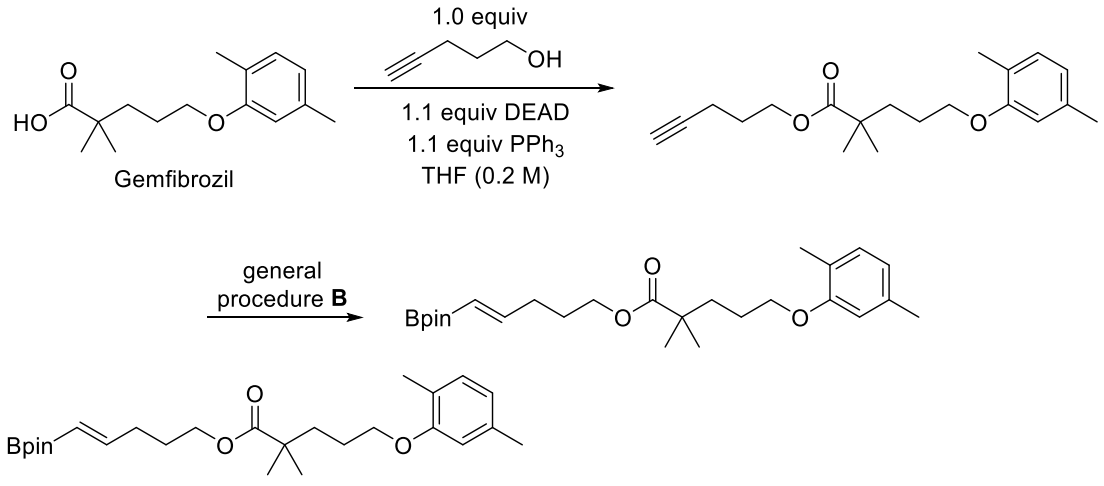
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.55 (dt, *J* = 18.0, 1.4 Hz, 1H), 3.57 (t, *J* = 7.0 Hz, 2H), 2.65 – 2.58 (m, 2H), 1.27 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 83.4, 43.0, 38.8, 24.9;

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.7;

HRMS (ESI) calcd. for $C_{10}H_{18}BClNaO_2$ $[M+Na]^+$ m/z 239.0981, found 239.0978;

IR (neat, cm^{-1}) 2977, 1638, 1360, 1318, 1139, 1005.



(*E*)-5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (Figure 3, **1l**). To an anhydrous THF (40 mL) solution of gemfibrozil (10.0 mmol, 1.0 equiv, CAS 25812-30-0), pent-4-yn-1-ol

(0.84 g, 10 mmol, 1.0 equiv) and triphenylphosphine (PPh_3, 2.89 g, 11.0 mmol, 1.1 equiv) was slowly added a THF solution (20 mL) of diethyl azodicarboxylate (DEAD, 1.92 g, 11.0 mmol, 1.1 equiv) over 30 min at 0 °C. The resulting mixture was then stirred at rt overnight. The reaction was quenched with brine and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a yellow oil in 68% yield (2.15 g).

From the resulting alkyne (1.90 g, 6.0 mmol), the title compound was prepared following the general procedure **B**. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless oil in 53% yield (1.41 g).

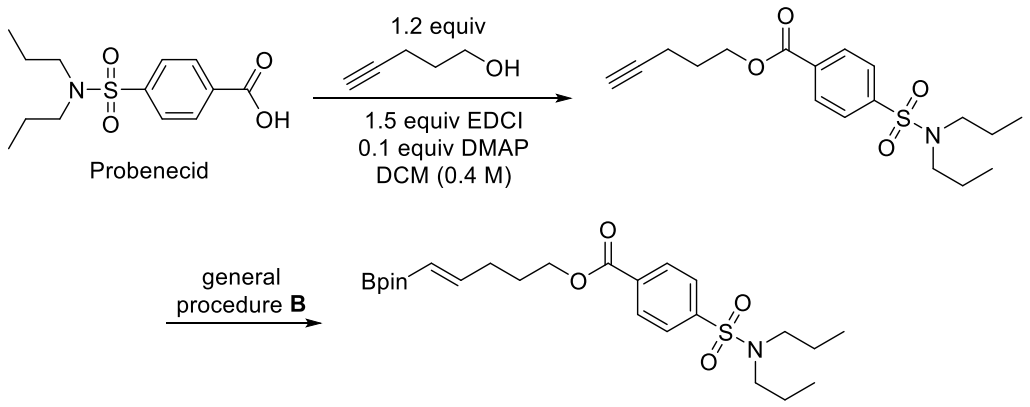
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.5 Hz, 1H), 6.70 – 6.54 (m, 3H), 5.47 (dt, *J* = 17.9, 1.5 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.96 – 3.87 (m, 2H), 2.30 (s, 3H), 2.27 – 2.19 (m, 2H), 2.30 (s, 3H), 1.80 – 1.68 (m, 6H), 1.26 (s, 12H), 1.21 (s, 6H);

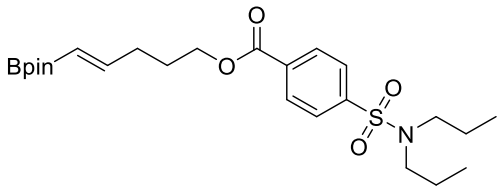
^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 157.1, 152.9, 136.5, 130.4, 123.7, 120.8, 112.1, 83.2, 68.1, 63.9, 42.2, 37.3, 32.2, 27.4, 25.3, 24.9, 21.5, 15.9;

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.9;

HRMS (ESI) calcd. for $C_{26}H_{41}BNaO_5$ $[M+Na]^+$ m/z 467.2939, found 467.2926;

IR (neat, cm^{-1}) 2977, 1726, 1639, 1363, 1142.





(*E*)-5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (Figure 3, **1m**). The probenecid (2.85 g, 10 mmol, 1.0 equiv, CAS 57-66-9) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI, 2.88 g, 15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol, 0.10 equiv) in CH_2Cl_2 (25 mL) at 0 °C. Pent-4-yn-1-ol (1.01 g, 12 mmol, 1.2 equiv) was then added. The reaction mixture was allowed to warm to rt overnight. The solution was diluted with CH_2Cl_2 and washed with 1 M HCl (aq.), saturated $NaHCO_3$ (aq.) and brine sequentially. The organic layer was dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a yellow oil in 84% yield (2.95 g).

From the resulting alkyne (2.81 g, 8.0 mmol), the title compound was prepared following the general procedure **B**. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 10:1) to provide the title compound as a white solid in 55% yield (2.10 g).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 6.65 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.50 (dt, *J* = 17.9, 1.5 Hz, 1H), 4.36 (t, *J* = 6.5 Hz, 2H), 3.12 – 3.06 (m, 4H), 2.37 – 2.28 (m, 2H), 1.97 – 1.87 (m, 2H), 1.60 – 1.48 (m, 4H), 1.26 (s, 12H), 0.87 (t, *J* = 7.4 Hz, 6H);

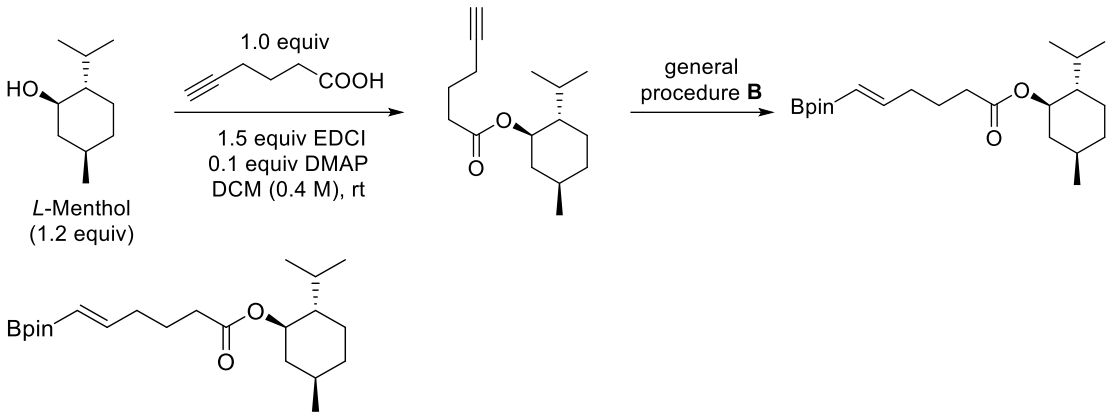
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 152.5, 144.3, 133.8, 130.3, 127.1, 83.3, 65.2, 50.1, 32.2, 27.3, 24.9, 22.1, 11.3;

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3;

HRMS (ESI) calcd. for $C_{24}H_{38}BNNaO_6S$ $[M+Na]^+$ m/z 502.2405, found 502.2392;

IR (neat, cm^{-1}) 2975, 1720, 1643, 1275, 1142, 601;

m.p. 63 – 65 °C.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (Figure 3, **1n**). The hex-5-ynoic acid (1.12 g, 10 mmol, 1.0 equiv) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI, 2.88 g, 15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol, 0.10 equiv) in CH_2Cl_2 (25 mL) at 0 °C. *L*-Menthol (1.88 g, 12 mmol, 1.2 equiv, CAS 2216-51-5) was then added. The reaction mixture was allowed to warm to rt overnight. The solution was diluted with CH_2Cl_2 and washed with 1 M HCl (aq.), saturated $NaHCO_3$ (aq.) and brine sequentially. The organic layer was dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a colorless oil in 80% yield (2.01 g).

From the resulting alkyne (1.88 g, 7.5 mmol), the title compound was prepared following the general procedure **B**. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless oil in 62% yield (1.76 g).

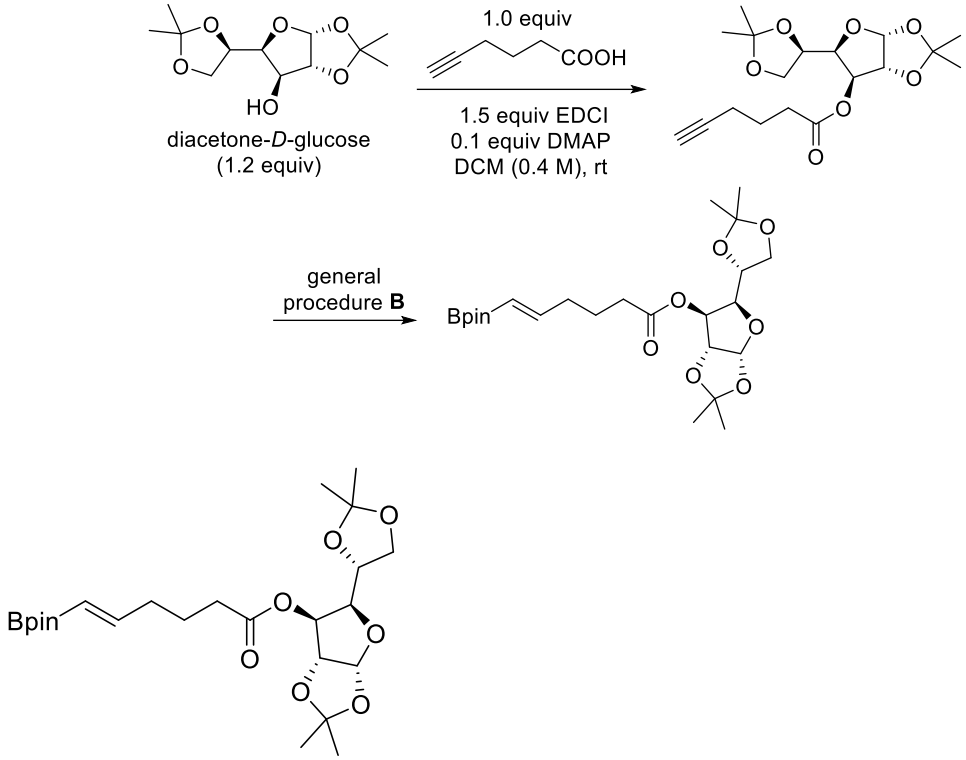
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.45 (dt, *J* = 17.9, 1.5 Hz, 1H), 4.67 (td, *J* = 10.9, 4.4 Hz, 1H), 2.32 – 2.24 (m, 2H), 2.22 – 2.14 (m, 2H), 2.00 – 1.93 (m, 1H), 1.90 – 1.80 (m, 1H), 1.79 – 1.71 (m, 2H), 1.71 – 1.63 (m, 2H), 1.54 – 1.42 (m, 1H), 1.39 – 1.31 (m, 1H), 1.26 (s, 12H), 1.10 – 0.99 (m, 1H), 0.99 – 0.90 (m, 1H), 0.91 – 0.81 (m, 7H), 0.75 (d, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 153.2, 83.2, 74.1, 47.2, 41.1, 35.2, 34.4, 34.3, 31.5, 26.4, 24.9, 23.8, 23.6, 22.2, 20.9, 16.4;

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.9;

HRMS (ESI) calcd. for $C_{22}H_{39}BNaO_4$ $[M+Na]^+$ m/z 401.2834, found 401.2823;

IR (neat, cm^{-1}) 2955, 2929, 1728, 1639, 1362, 1143.



(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydro furo[2,3-*d*][1,3]dioxol-6-yl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (Figure 3, **1o**). The hex-5-ynoic acid (1.12 g, 10 mmol, 1.0 equiv) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI, 2.88 g, 15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol, 0.10 equiv) in CH_2Cl_2 (25 mL) at 0 °C. Diacetone-*D*-glucose (3.12 g, 12 mmol, 1.2 equiv, CAS 582-52-5) was then added. The reaction mixture was allowed to warm to rt overnight. The solution was diluted with CH_2Cl_2 and washed with 1 M HCl (aq.), saturated $NaHCO_3$ (aq.) and brine sequentially. The organic layer was dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a colorless oil in 86% yield (3.05 g).

From the resulting alkyne (3.01 g, 8.5 mmol), the title compound was prepared following the general procedure **B**. The crude material was purified by flash column

chromatography (petroleum ether/EtOAc = 5:1) to provide the title compound as a colorless oil in 57% yield (2.33 g).

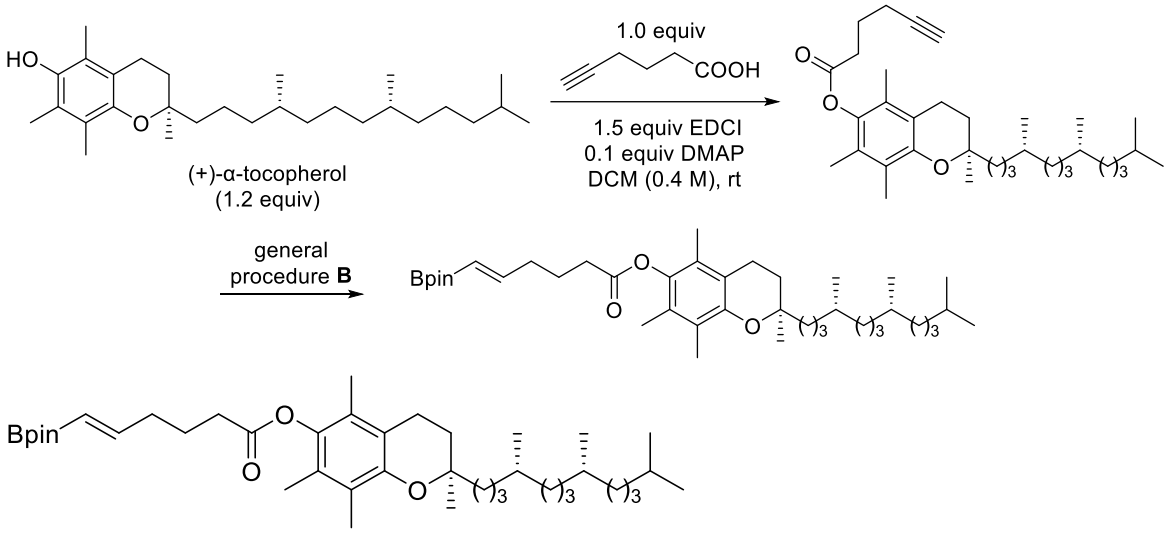
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.86 (d, *J* = 3.7 Hz, 1H), 5.45 (dt, *J* = 17.9, 1.5 Hz, 1H), 5.26 (d, *J* = 1.9 Hz, 1H), 4.46 (d, *J* = 3.7 Hz, 1H), 4.23 – 4.16 (m, 2H), 4.11 – 4.05 (m, 1H), 4.03 – 3.98 (m, 1H), 2.41 – 2.30 (m, 2H), 2.24 – 2.15 (m, 2H), 1.82 – 1.73 (m, 2H), 1.51 (s, 3H), 1.40 (s, 3H), 1.32 – 1.29 (m, 6H), 1.26 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 152.8, 112.4, 109.5, 105.2, 83.5, 83.3, 80.0, 76.1, 72.6, 67.5, 34.9, 33.7, 27.0, 26.9, 26.4, 25.4, 24.9, 23.4;

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.0;

HRMS (ESI) calcd. for $C_{24}H_{39}BNaO_9$ $[M+Na]^+$ m/z 505.2579, found 505.2577;

IR (neat, cm^{-1}) 2981, 2936, 1745, 1638, 1363, 1142, 1073.



(*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (Figure 3, **1p**). The hex-5-ynoic acid (1.12 g, 10 mmol, 1.0 equiv) was added to a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI, 2.88 g, 15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol, 0.10 equiv) in CH_2Cl_2 (25 mL) at 0 °C. (+)-α-Tocopherol (5.16 g, 12 mmol, 1.2 equiv, CAS 59-02-9) was then added. The reaction mixture was allowed to warm to rt overnight. The solution was diluted with CH_2Cl_2 and washed with 1 M HCl (aq.), saturated $NaHCO_3$ (aq.) and brine

sequentially. The organic layer was dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude material was purified by flash column chromatography to provide the corresponding alkyne as a colorless oil in 87% yield (4.57 g).

From the resulting alkyne (4.46 g, 8.5 mmol), the title compound was prepared following the general procedure **B**. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless oil in 68% yield (3.78 g).

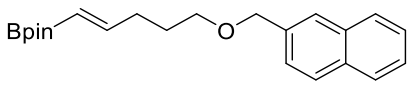
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.64 (dt, *J* = 17.9, 6.5 Hz, 1H), 5.50 (dt, *J* = 17.9, 1.4 Hz, 1H), 2.64 – 2.55 (m, 4H), 2.35 – 2.27 (m, 2H), 2.08 (s, 3H), 2.00 (s, 3H), 1.98 – 1.89 (m, 5H), 1.85 – 1.70 (m, 2H), 1.58 – 1.48 (m, 3H), 1.46 – 1.32 (m, 4H), 1.33 – 1.21 (s, 23H), 1.17 – 1.02 (m, 6H), 0.90 – 0.82 (m, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 153.0, 149.5, 140.6, 126.8, 125.0, 123.1, 117.5, 83.3, 75.2, 39.5, 37.6, 37.6, 37.4, 35.3, 33.7, 33.0, 32.9, 31.3, 28.1, 25.0, 24.9, 24.6, 23.9, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.1, 12.3, 12.0;

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.9;

HRMS (ESI) calcd. for $C_{41}H_{69}BNaO_5$ $[M+Na]^+$ m/z 675.5130, found 675.5128;

IR (neat, cm^{-1}) 2926, 2868, 1753, 1638, 1362, 1133.



(*E*)-4,4,5,5-Tetramethyl-2-(5-(naphthalen-2-ylmethoxy)pent-1-en-1-yl)-1,3,2-dioxaborolane (Figure 4, **1t**). From 2-((pent-4-yn-1-yloxy)methyl)naphthalene (1.35 g, 6.0 mmol), the title compound was prepared following the general procedure **B**. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless oil in 64% yield (1.35 g).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.1 Hz, 3H), 7.77 (s, 1H), 7.49 – 7.43 (m, 3H), 6.65 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.47 (dt, *J* = 17.9, 1.5 Hz, 1H), 4.66 (s, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.32 – 2.23 (m, 2H), 1.82 – 1.74 (m, 2H), 1.26 (s, 12H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 136.2, 133.4, 133.1, 128.3, 128.0, 127.8, 126.4,

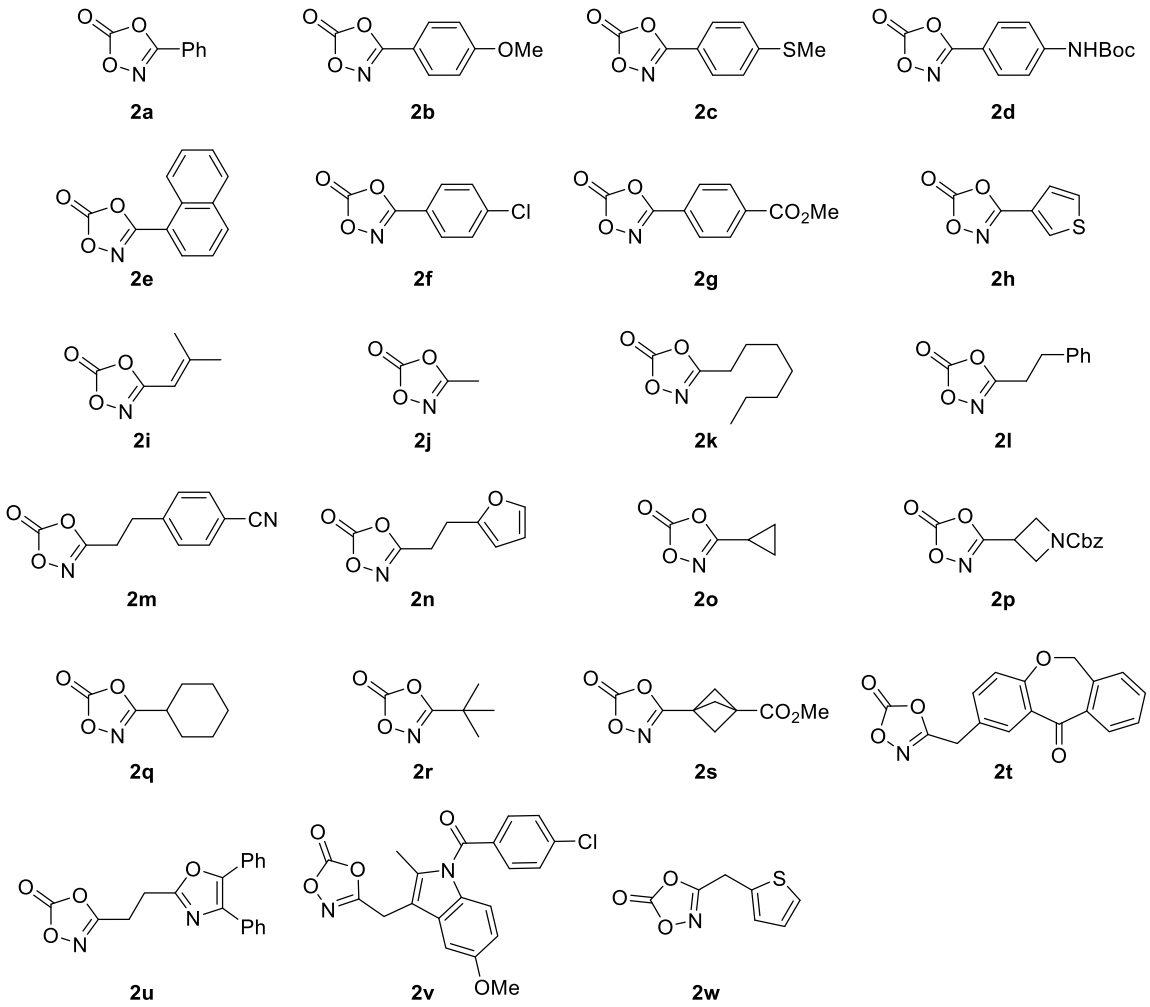
126.2, 125.9, 83.2, 73.1, 69.9, 32.5, 28.4, 24.9;

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.0;

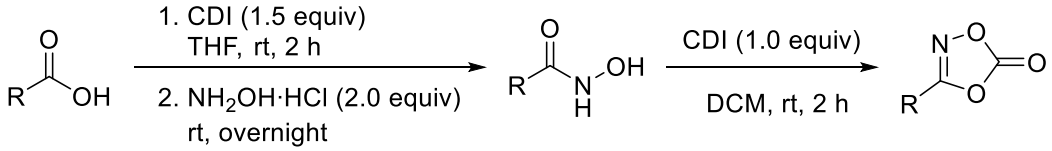
HRMS (ESI) calcd. for $C_{22}H_{29}BNaO_3$ $[M+Na]^+$ m/z 375.2102, found 375.2093;

IR (neat, cm^{-1}) 2978, 2935, 2856, 1639, 1362, 1143.

b. Preparation of 1,4,2-dioxazol-5-ones



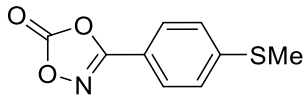
Compounds **2a**, **2b**, **2f**, **2k**, **2l**, **2s**, **2t** and **2v** were prepared according to reference 12. Compounds **2g**, **2j**, **2o**, **2q** and **2r** were prepared according to reference 13.



General procedure C for the synthesis of 1,4,2-dioxazol-5-ones[12-14]. 1,1'-Carbonyldiimidazole (CDI, 1.5 equiv) was added to a mixture of carboxylic acid (1.0 equiv.) in dry tetrahydrofuran (THF, 1.0 M) at rt. The reaction mixture was stirred for 2 hours. Afterward, hydroxylamine hydrochloride (2.0 equiv) was added. The resulting mixture was stirred overnight. The reaction mixture was diluted with 5% $KHSO_4$ (aq) and extracted with EtOAc. The combined organic layer was washed with water and

brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude hydroxamic acid was used for next step without further purification.

To a stirred solution of hydoxamic acid (1.0 equiv) in freshly distilled dichloromethane, 1,1′-carbonyldiimidazole (1.0 equiv) was added in one portion at rt. After being stirred for 2 hours, the reaction mixture was quenched with 1 N HCl (aq.), and extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified quickly by short silica pad (PE/EA = 10:1 ~ 5:1) to give the desired 1,4,2-dioxazol-5-ones.



3-(4-(Methylthio)phenyl)-1,4,2-dioxazol-5-one (Figure 4, **2c**). From 4-(methylthio)benzoic acid (1.68 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 10:1) to provide the title compound as a white solid in 58% yield (1.21 g).

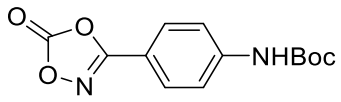
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 2.54 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 154.0, 147.4, 126.8, 125.8, 115.9, 14.9;

HRMS (ESI) calcd. for C_8H_7NNaOS $[M–CO_2+Na]^+$ m/z 116.0321, found 116.0317;

IR (neat, cm^{-1}) 1824, 1605, 1360, 1097, 996, 750;

m.p. 115 – 116 °C.



***tert*-Butyl (4-(5-oxo-1,4,2-dioxazol-3-yl)phenyl)carbamate** (Figure 4, **2d**). From 4-((*tert*-butoxycarbonyl)amino)benzoic acid (2.37 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 8:1) to provide the title compound as a

white solid in 47% yield (1.31 g).

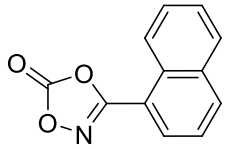
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 8.9 Hz, 2H), 6.77 (s, 1H), 1.53 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 154.1, 152.1, 143.7, 128.0, 118.4, 114.0, 81.9, 28.4;

HRMS (ESI) calcd. for $C_{12}H_{14}N_2NaO_3$ $[M–CO_2+Na]^+$ m/z 257.0897, found 257.0893;

IR (neat, cm^{-1}) 3355, 1860, 1698, 1613, 1502, 1155, 757;

m.p. 159 – 160 °C.



3-(naphthalen-1-yl)-1,4,2-dioxazol-5-one (Figure 4, **2e**). From 1-naphthoic acid (3.44 g, 20 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 8:1) to provide the title compound as a white solid in 27% yield (1.15 g).

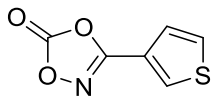
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 – 8.71 (m, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.06 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.67 – 7.56 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 153.6, 134.9, 133.9, 129.6, 129.5, 129.3, 129.1, 127.4, 125.5, 124.9, 116.7;

HRMS (ESI) calcd. for $C_{11}H_8NO$ $[M–CO_2+H]^+$ m/z 170.0601, found 170.0596;

IR (neat, cm^{-1}) 1809, 1321, 1002, 759;

m.p. 53 – 54 °C.

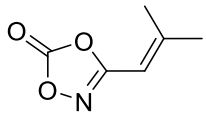


3-(Thiophen-3-yl)-1,4,2-dioxazol-5-one (Figure 4, **2h**). From thiophene-3-carboxylic acid (1.28 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 8:1) to provide the title compound as a white solid in 72% yield (1.22

g). Spectral data match those previously reported[15].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 1H), 7.56 – 7.45 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 153.7, 130.6, 128.7, 124.8, 121.1.



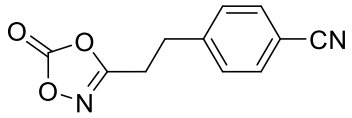
3-(2-Methylprop-1-en-1-yl)-1,4,2-dioxazol-5-one (Figure 4, **2i**). From 3-methylbut-2-enoic acid (1.00 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 10:1) to provide the title compound as a yellow liquid in 55% yield (0.78 g).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 – 5.74 (m, 1H), 2.13 (d, *J* = 0.9 Hz, 3H), 2.04 (d, *J* = 1.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 156.6, 154.0, 104.8, 27.8, 21.8;

HRMS (ESI) calcd. for C_5H_8NO $[M–CO_2+H]^+$ m/z 98.0601, found 98.0602;

IR (neat, cm^{-1}) 1830, 1656, 1284, 1154, 984, 761.



4-(2-(5-Oxo-1,4,2-dioxazol-3-yl)ethyl)benzonitrile (Figure 4, **2m**). From 3-(4-cyanophenyl)propanoic acid (1.75 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 5:1) to provide the title compound as a white solid in 79% yield (1.71 g).

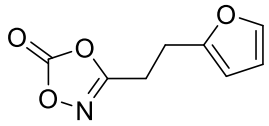
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 3.02 – 2.93 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 153.8, 143.4, 132.9, 129.2, 118.6, 111.5, 30.4, 26.2;

HRMS (ESI) calcd. for $C_{10}H_8N_2NaO$ $[M–CO_2+Na]^+$ m/z 195.0529, found 195.0524;

IR (neat, cm^{-1}) 2231, 1826, 1637, 1148, 989, 756, 558;

m.p. 82 – 83 °C.



3-(2-(Furan-2-yl)ethyl)-1,4,2-dioxazol-5-one (Figure 4, **2n**). From 3-(furan-2-yl)propanoic acid (1.40 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 5:1) to provide the title compound as a white solid in 72% yield (1.30 g).

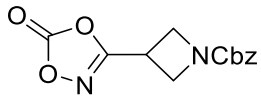
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 1.8, 0.6 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.15 – 6.06 (m, 1H), 3.08 (t, *J* = 7.3 Hz, 2H), 3.03 – 2.94 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 154.1, 151.4, 142.2, 110.6, 106.8, 24.1, 23.3;

HRMS (ESI) calcd. for $C_7H_7NNaO_2$ $[M–CO_2+Na]^+$ m/z 160.0369, found 160.0365;

IR (neat, cm^{-1}) 1819, 1641, 1152, 983, 758;

m.p. 50 – 51 °C.



Benzyl 3-(5-oxo-1,4,2-dioxazol-3-yl)azetidine-1-carboxylate (Figure 4, **2p**). From 1-((benzyloxy)carbonyl)azetidine-3-carboxylic acid (2.35 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 3:1) to provide the title compound as a white solid in 63% yield (1.74 g).

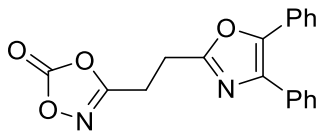
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 5.12 (s, 2H), 4.37 (t, *J* = 9.0 Hz, 2H), 4.26 (dd, *J* = 9.1, 6.0 Hz, 2H), 3.84 – 3.73 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 156.0, 153.6, 136.1, 128.7, 128.5, 128.3, 67.4, 51.3, 24.7;

HRMS (ESI) calcd. for $C_{12}H_{12}N_2NaO_3$ $[M–CO_2+Na]^+$ m/z 255.0740, found 255.0733;

IR (neat, cm^{-1}) 1820, 1708, 1356, 1131, 990, 760, 732;

m.p. 110 – 111 °C.



3-(2-(4,5-Diphenyloxazol-2-yl)ethyl)-1,4,2-dioxazol-5-one (Figure 4, **2u**). From 3-(4,5-diphenyloxazol-2-yl)propanoic acid (2.93 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 81% yield (2.71 g).

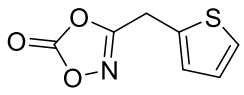
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.59 – 7.54 (m, 2H), 7.41 – 7.31 (m, 6H), 3.35 – 3.21 (m, 4H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 159.5, 154.0, 146.2, 135.4, 132.1, 128.9, 128.9, 128.8, 128.7, 128.4, 128.0, 126.7, 23.1, 22.5;

HRMS (ESI) calcd. for $C_{18}H_{14}N_2NaO_2$ $[M–CO_2+Na]^+$ m/z 313.0948, found 313.0941;

IR (neat, cm^{-1}) 1869, 1829, 1157, 991, 757, 694;

m.p. 76 – 77 °C.



3-(Thiophen-2-ylmethyl)-1,4,2-dioxazol-5-one (Figure 5, **2w**). From 2-(thiophen-2-yl)acetic acid (1.42 g, 10 mmol), the title compound was prepared following the general procedure **C**. The crude material was purified quickly by short silica pad (petroleum ether/EtOAc = 8:1) to provide the title compound as a orange solid in 62% yield (1.14 g).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.08 – 6.97 (m, 2H), 4.17 (s, 2H);

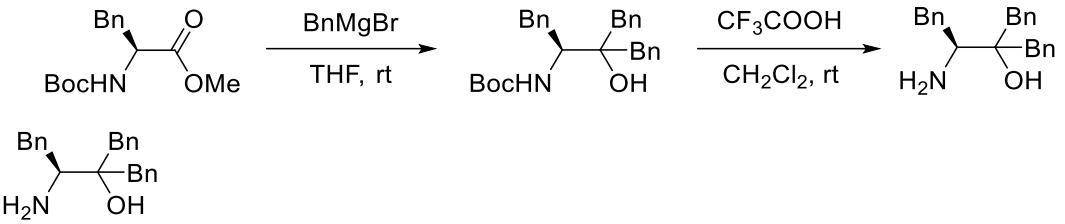
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 153.8, 131.0, 128.4, 127.7, 126.6, 25.7;

HRMS (ESI) calcd. for C_6H_6NOS $[M–CO_2+H]^+$ m/z 140.0165, found 140.0161;

IR (neat, cm^{-1}) 1817, 1632, 1341, 1150, 988, 712;

m.p. 51 – 52 °C.

c. Preparation of L*



(*S*)-3-Amino-2-benzyl-1,4-diphenylbutan-2-ol (**L***).

Under N_2 atmosphere, methyl (*tert*-butoxycarbonyl)-*L*-phenylalaninate (2.23 g, 8.0 mmol, 1.0 equiv) was dissolved in THF (10 mL). The solution was cooled to 0 °C, and benzylmagnesium chloride (40 mL, 1.0 M in THF, 5.0 equiv) was added dropwise over 15 min. The resulting mixture was warmed to rt and stirred for 24 h at rt. Completion of the reaction was monitored by TLC. The solution was cooled to 0 °C again and carefully quenched with a saturated aqueous solution of NH_4Cl. The mixture was extracted with Et_2O and washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide *tert*-butyl (*S*)-(3-benzyl-3-hydroxy-1,4-diphenylbutan-2-yl)carbamate as a sticky oil or white solid in 38% yield (1.31 g).

CF_3COOH (2.0 mL) was added to a solution of *tert*-butyl (*S*)-(3-benzyl-3-hydroxy-1,4-diphenylbutan-2-yl)carbamate (1.31 g, 3.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL), and the mixture was stirred at rt. Completion of the reaction was monitored by TLC. The solution was cooled to 0 °C, and saturated aqueous $NaHCO_3$ was added carefully. The mixture was extracted with Et_2O and washed with saturated aqueous K_2CO_3, brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. After recrystallization (petroleum ether/EtOAc), (*S*)-3-amino-2-benzyl-1,4-diphenylbutan-2-ol was obtained as a white solid in 85% yield (0.85 g).

^{1}H NMR (500 MHz, CD_3CN) δ 7.40 – 7.14 (m, 13H), 7.09 – 7.03 (m, 2H), 3.90 (s, 1H),

3.23 (d, *J* = 12.5 Hz, 1H), 2.95 (d, *J* = 13.3 Hz, 1H), 2.90 – 2.78 (m, 2H), 2.68 (d, *J* = 13.3 Hz, 1H), 2.52 – 2.38 (m, 2H), 1.04 (s, 2H);

^{13}C NMR (126 MHz, CD_3CN) δ 141.6, 139.4, 139.3, 132.2, 131.9, 130.1, 129.3, 128.8, 128.7, 127.1, 127.0, 126.9, 76.2, 59.4, 42.4, 42.3, 39.6;

HRMS (ESI) calcd. for $C_{23}H_{26}NO$ $[M+H]^+$ m/z 332.2009, found 332.2000;

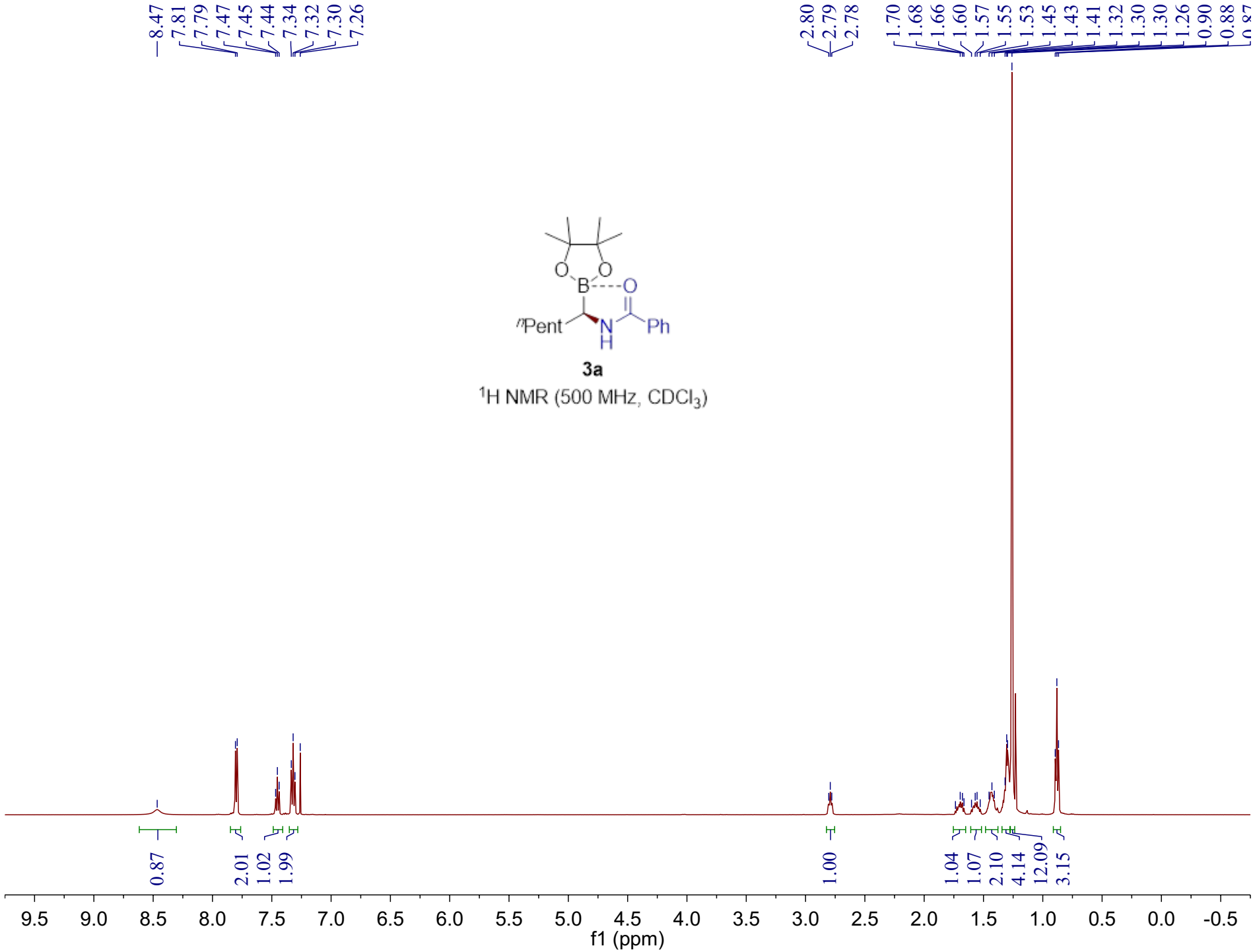
IR (neat, cm^{-1}) 3377, 3317, 3026, 2937, 1493, 752, 696;

m.p. 133 – 135 °C;

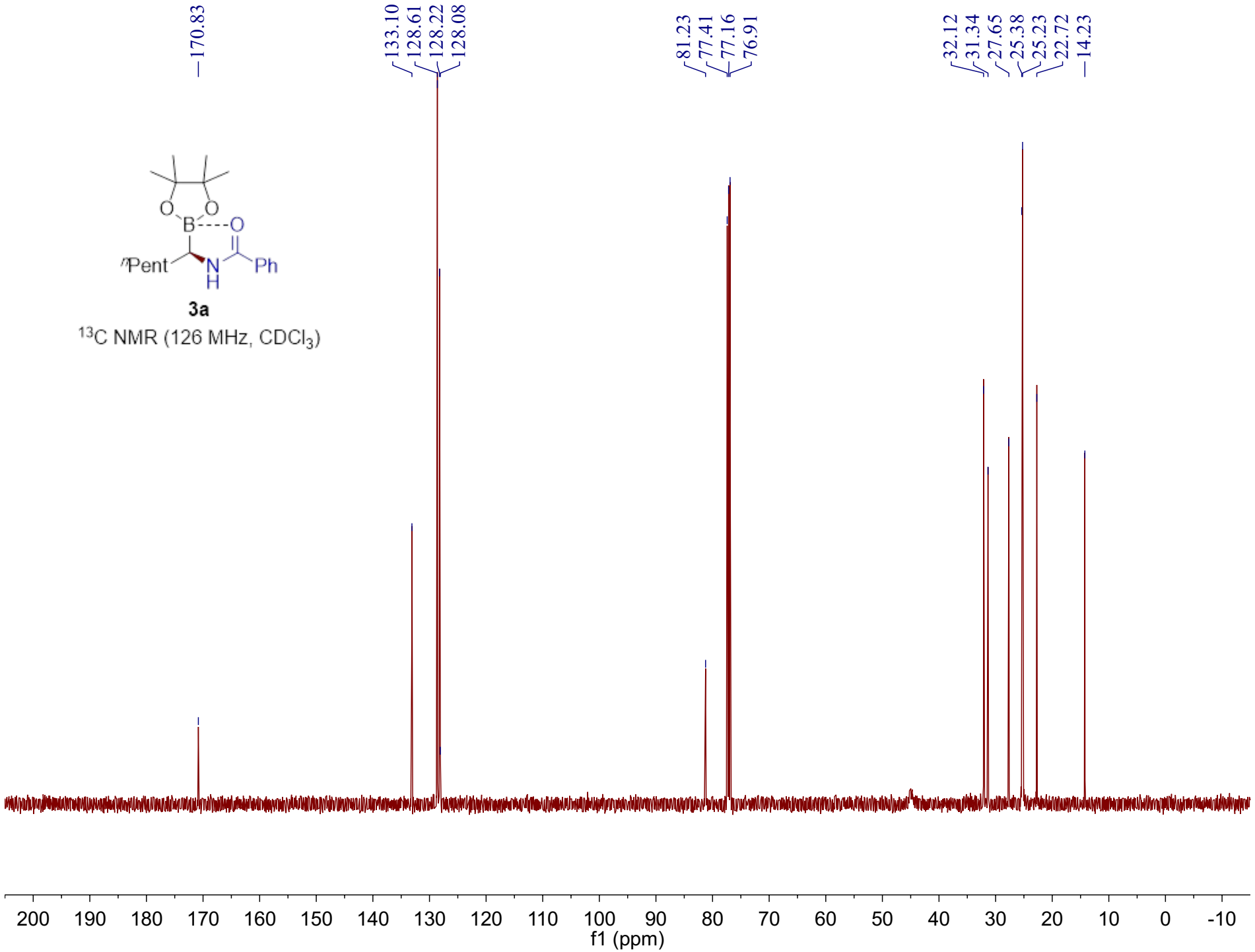
$[\alpha]_D^{23}$ = +17.1 (c = 0.79, $CHCl_3$).

II. Supplementary Figures

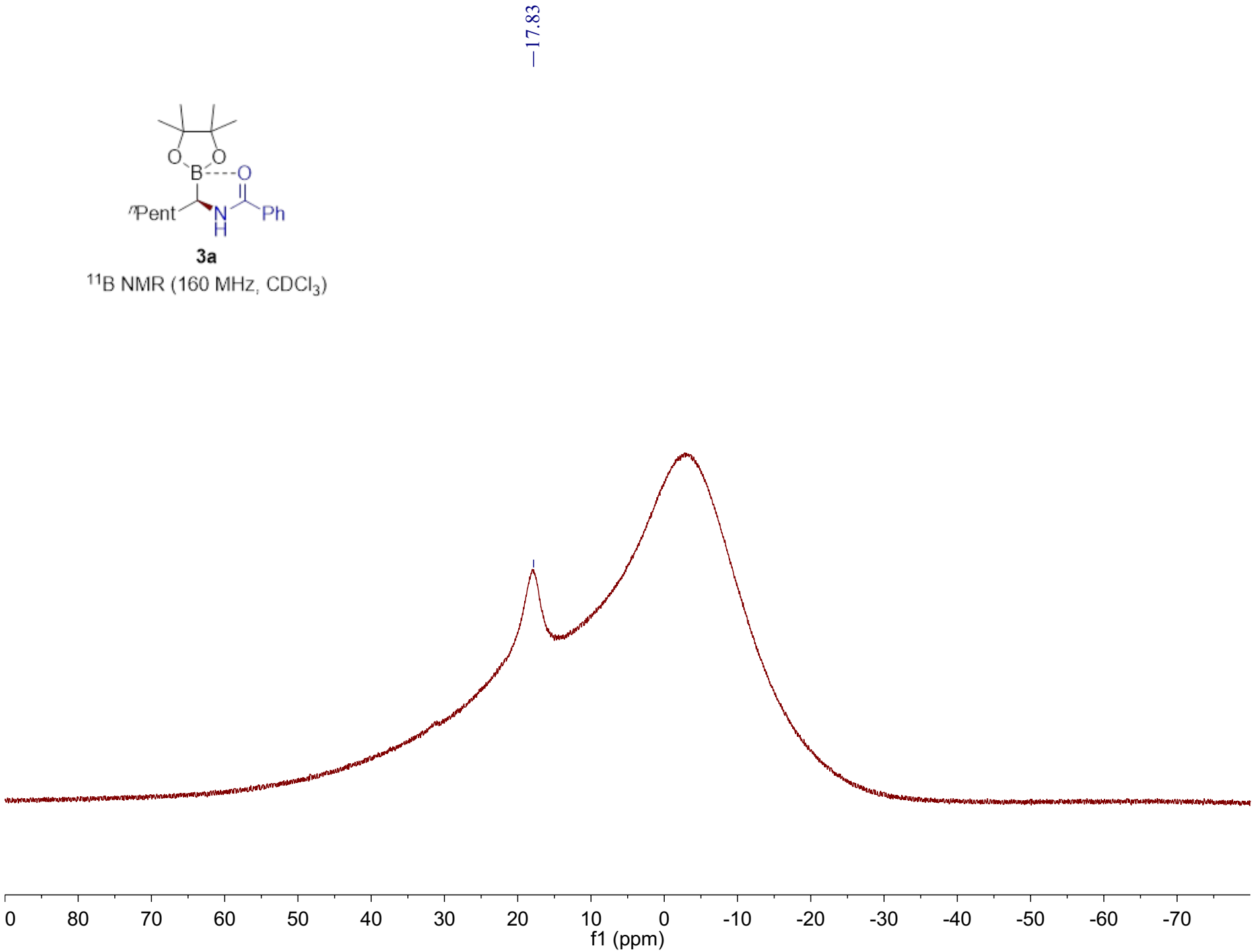
1. NMR Spectroscopic Data



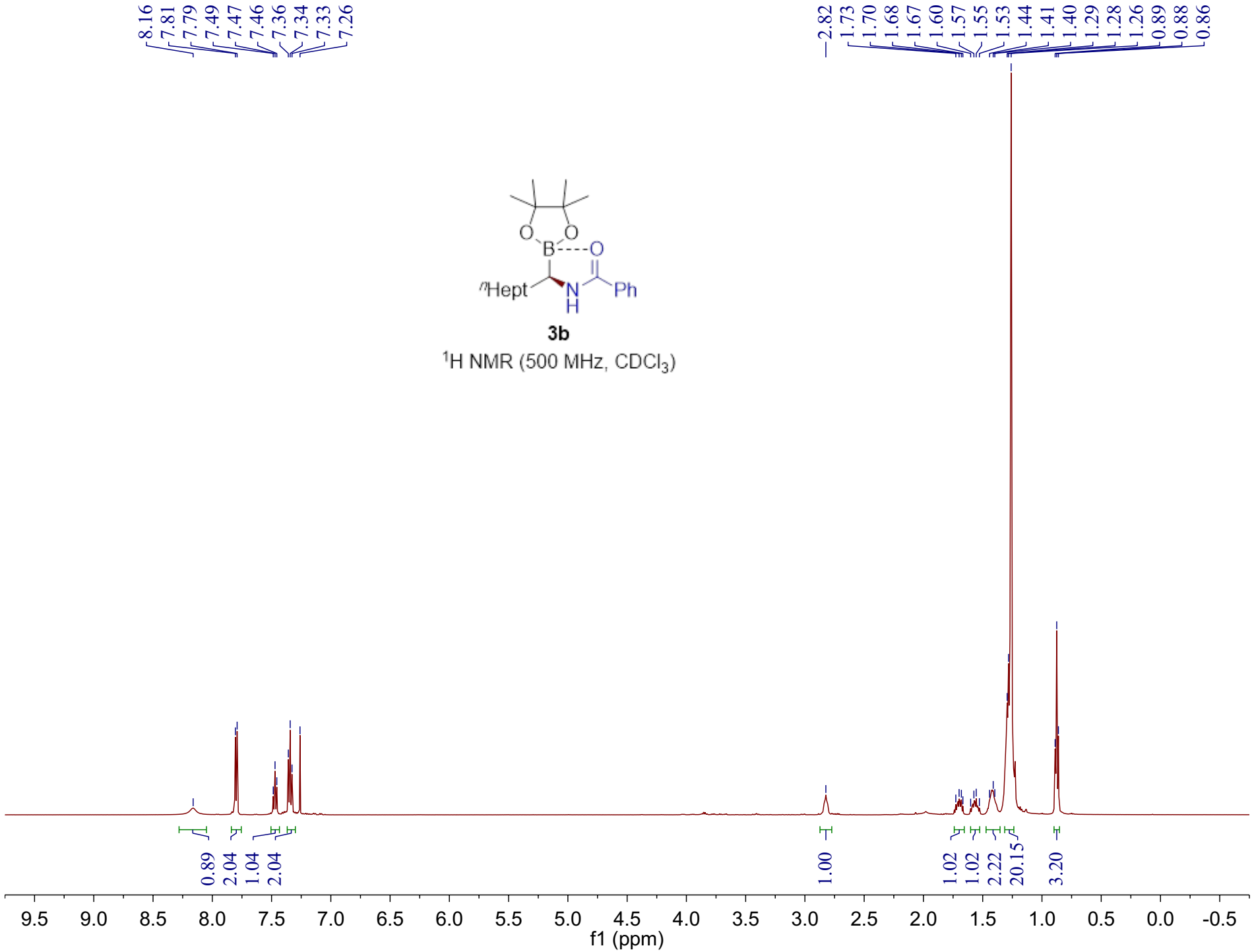
Supplementary Figure 2: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3a**.



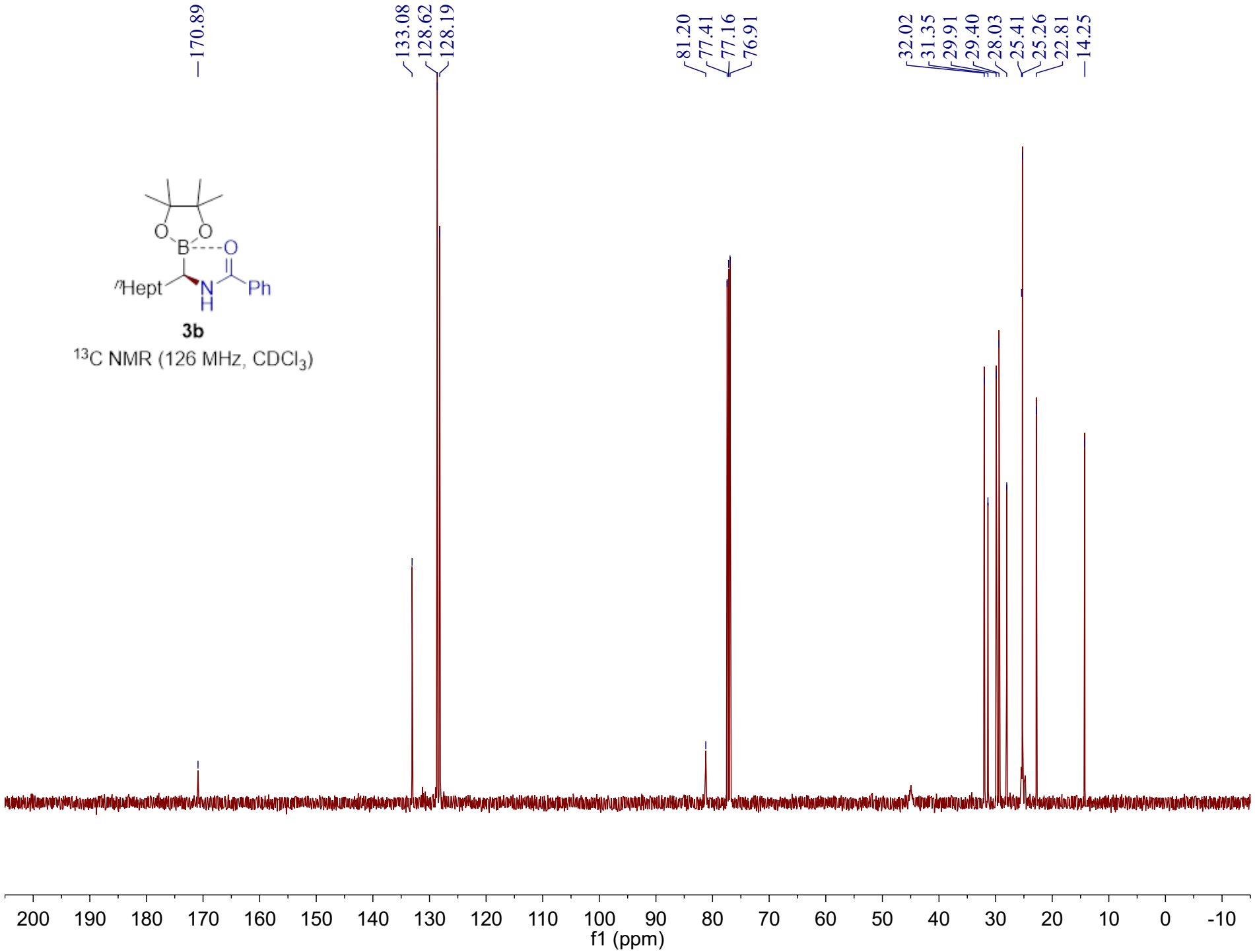
Supplementary Figure 3: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3a**.



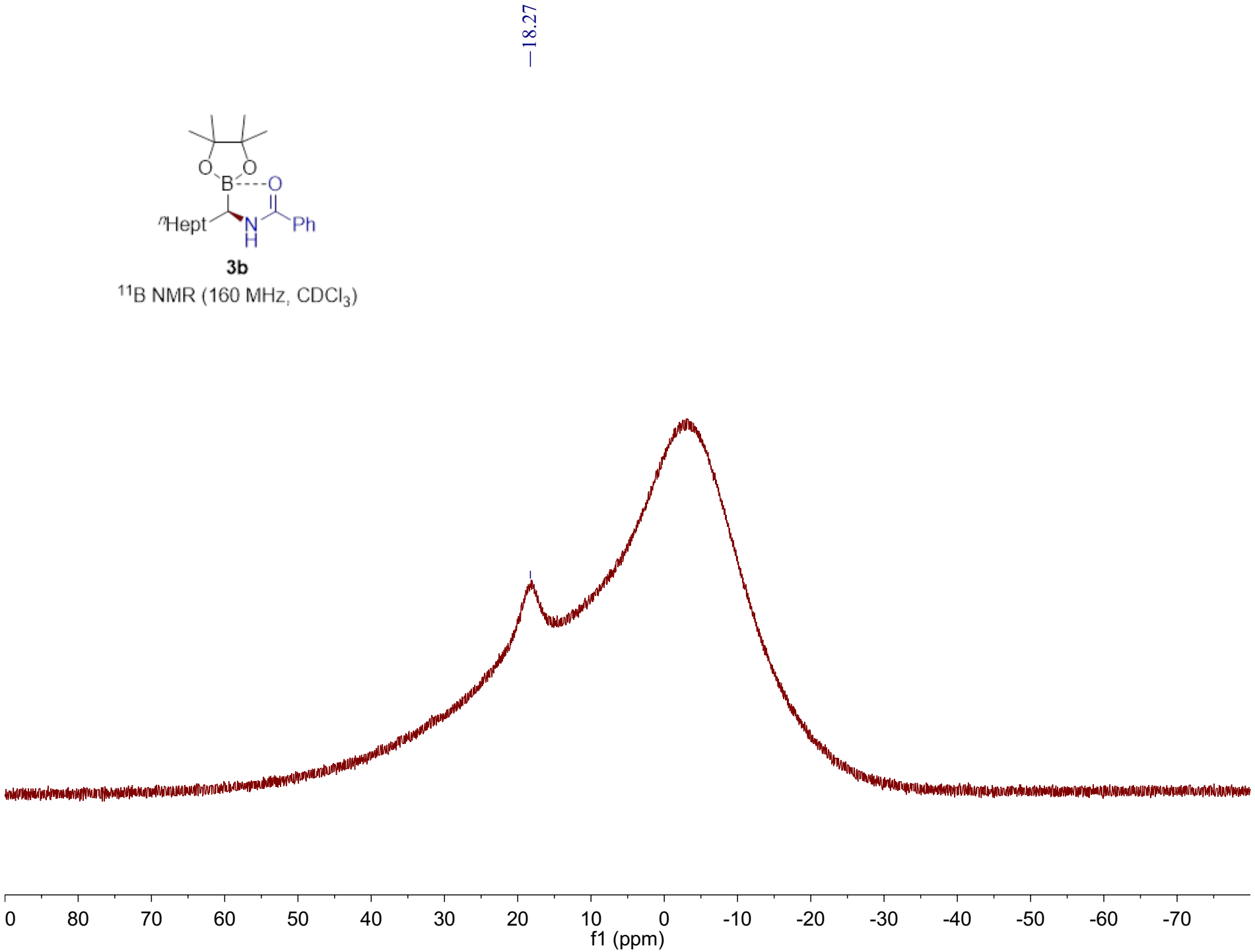
Supplementary Figure 4: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3a**.



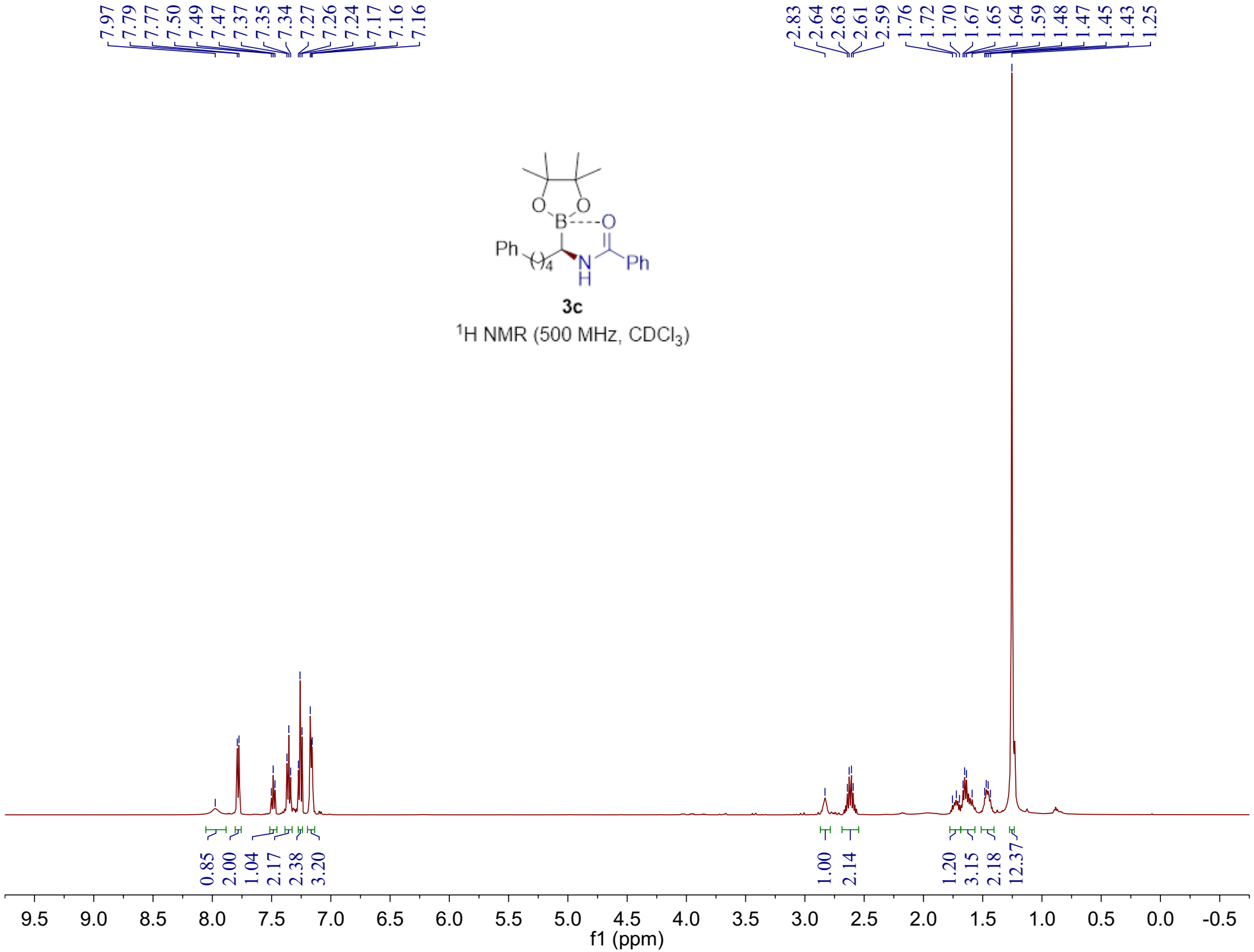
Supplementary Figure 5: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3b**.



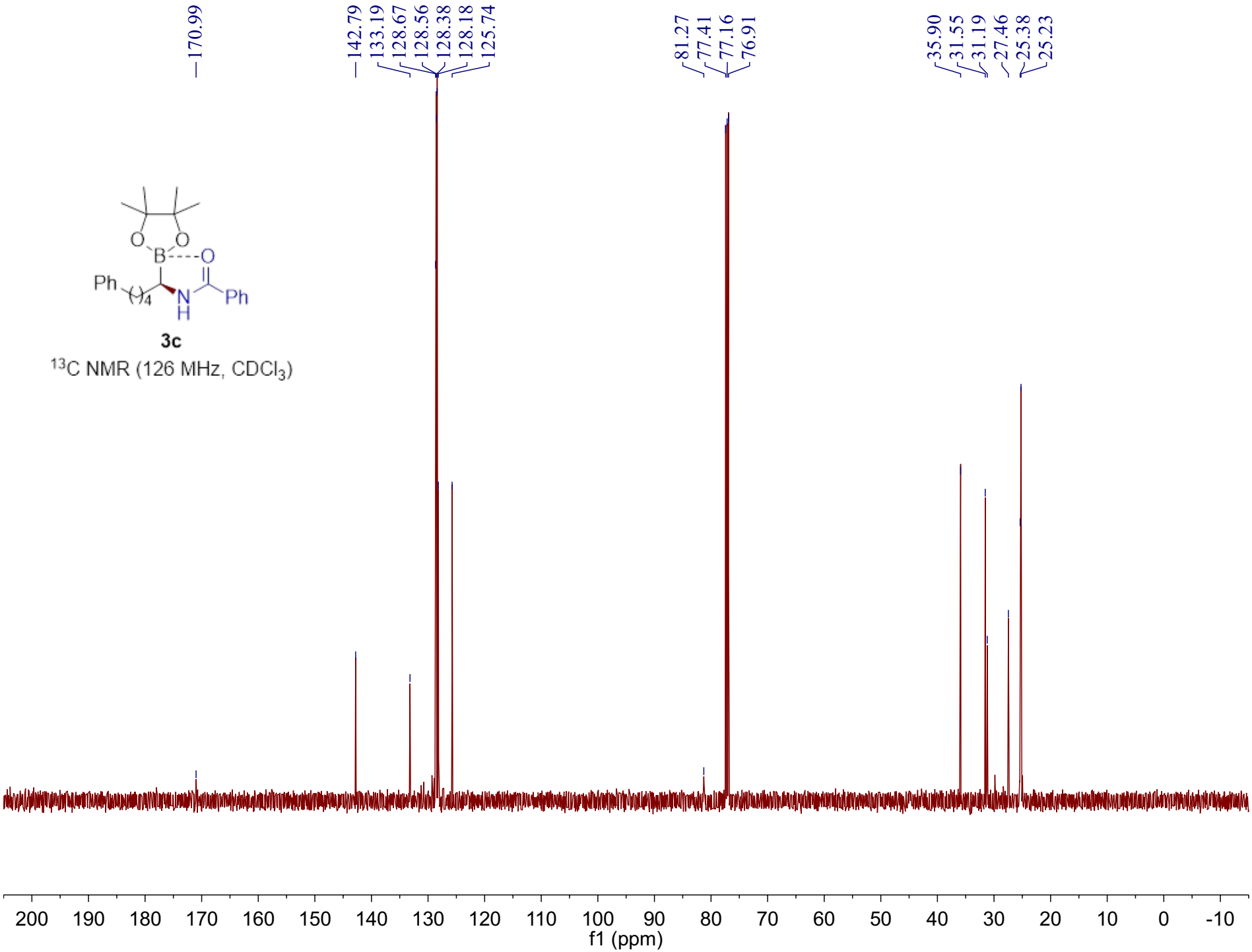
Supplementary Figure 6: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3b**.



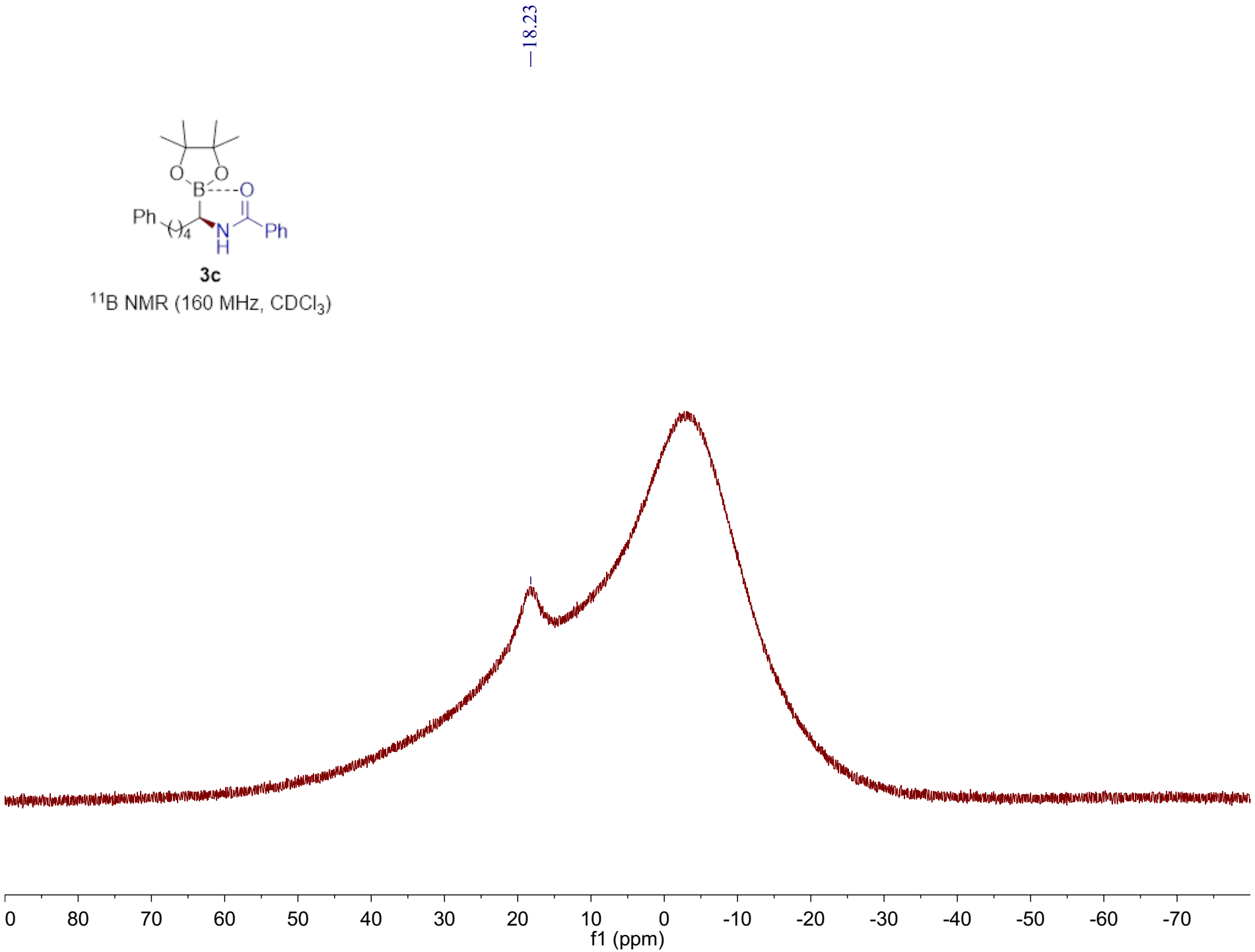
Supplementary Figure 7: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3b**.



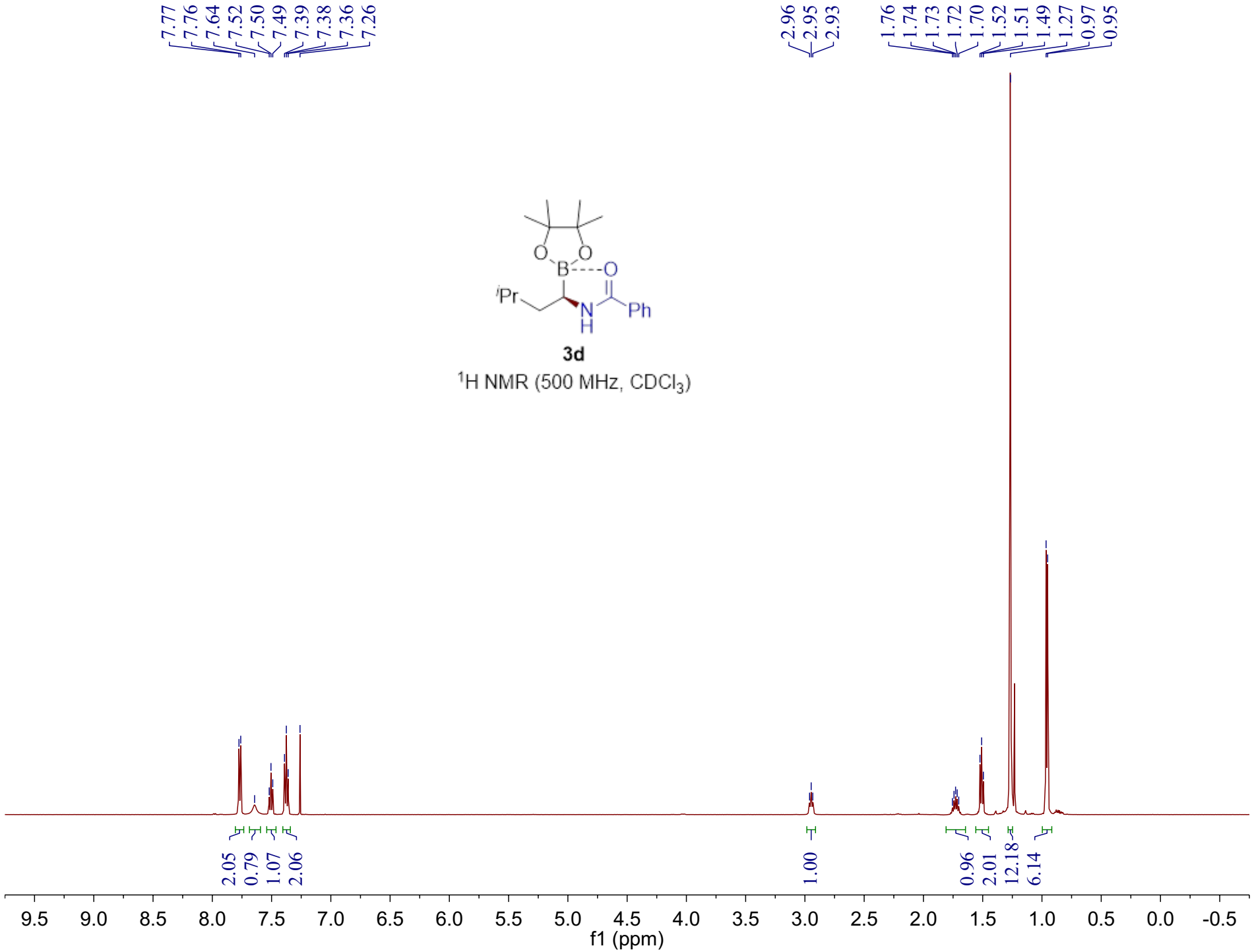
Supplementary Figure 8: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3c**.



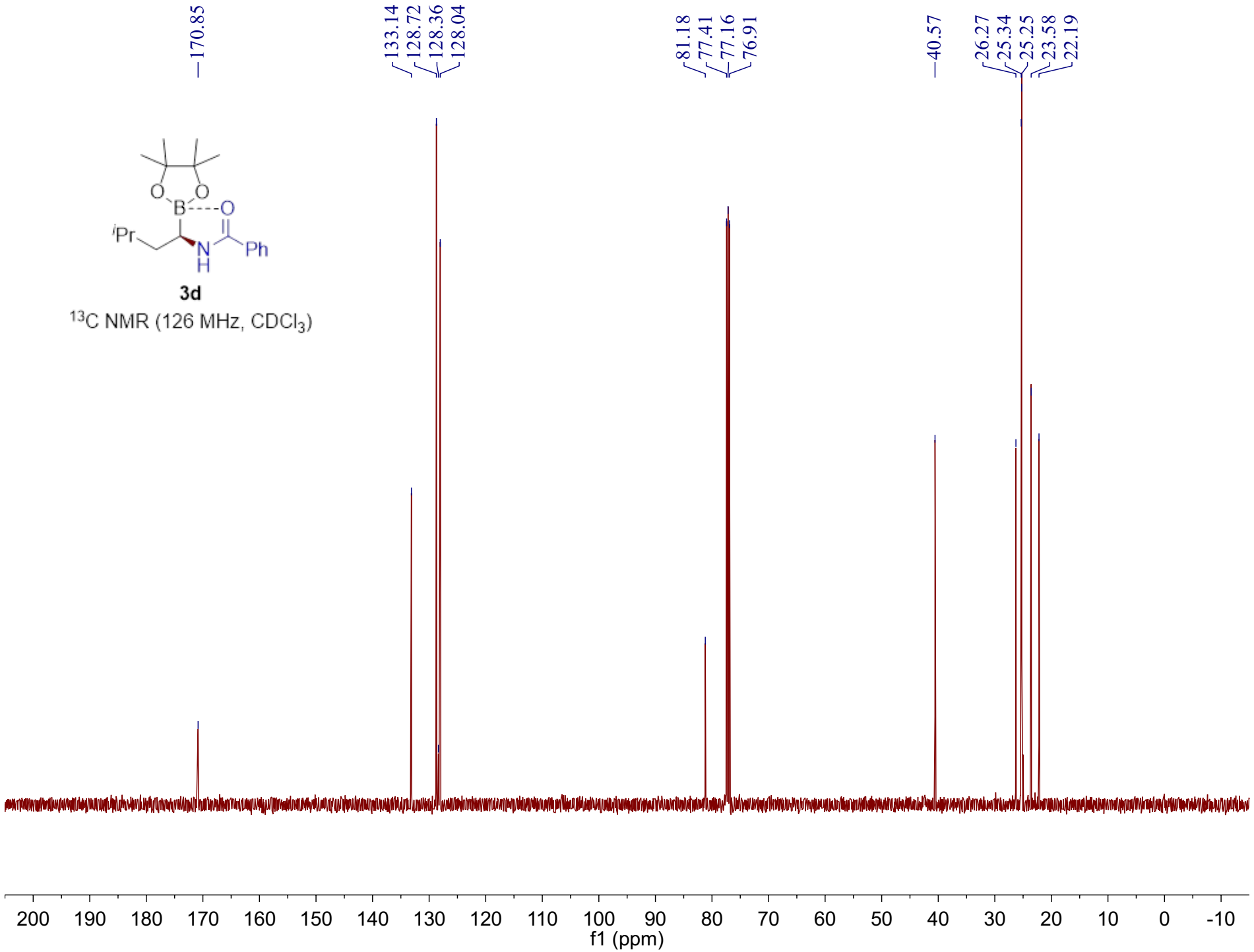
Supplementary Figure 9: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3c**.



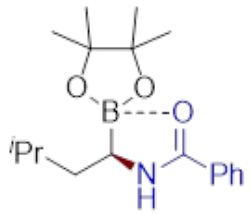
Supplementary Figure 10: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3c**.



Supplementary Figure 11: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3d**.



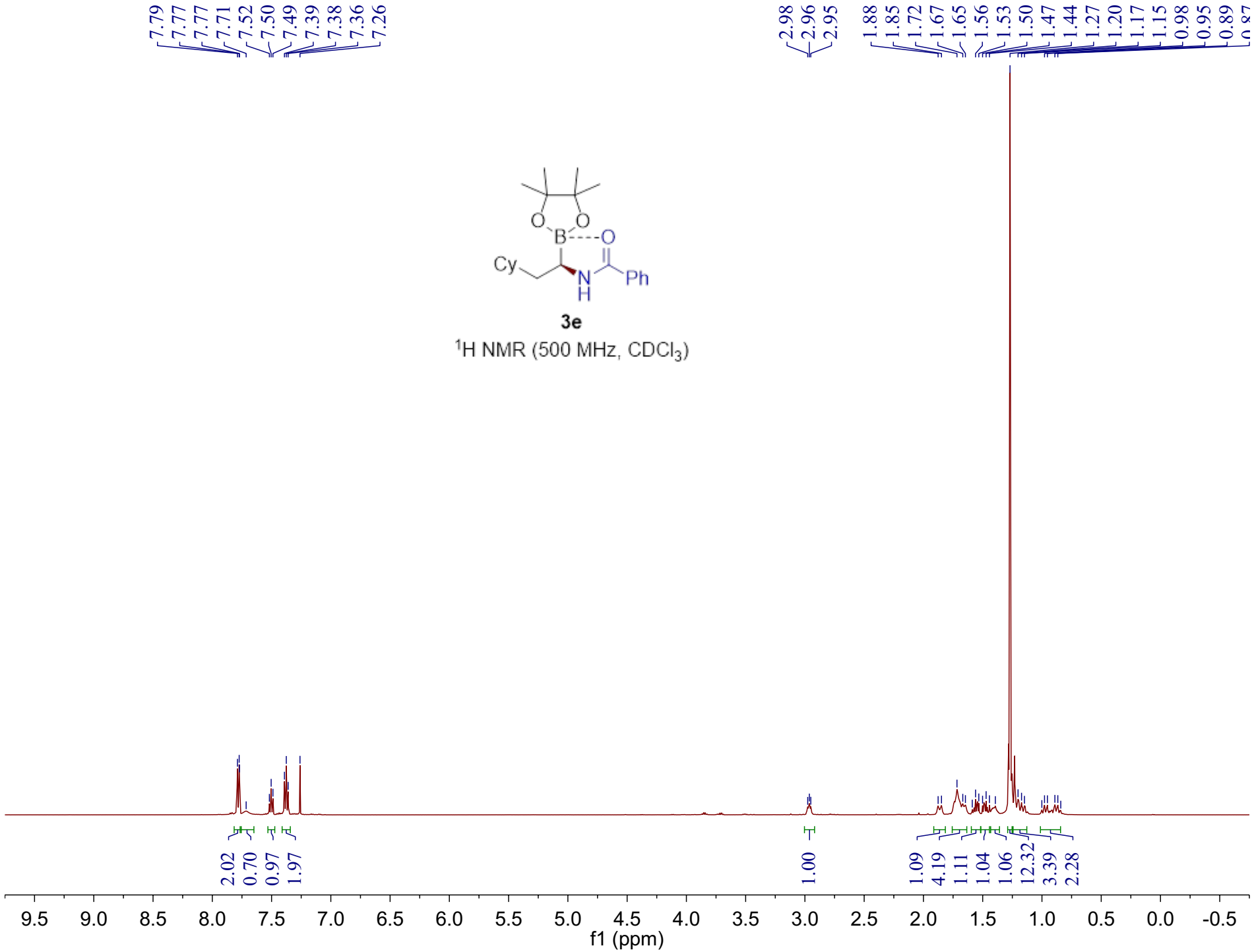
Supplementary Figure 12: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3d**.



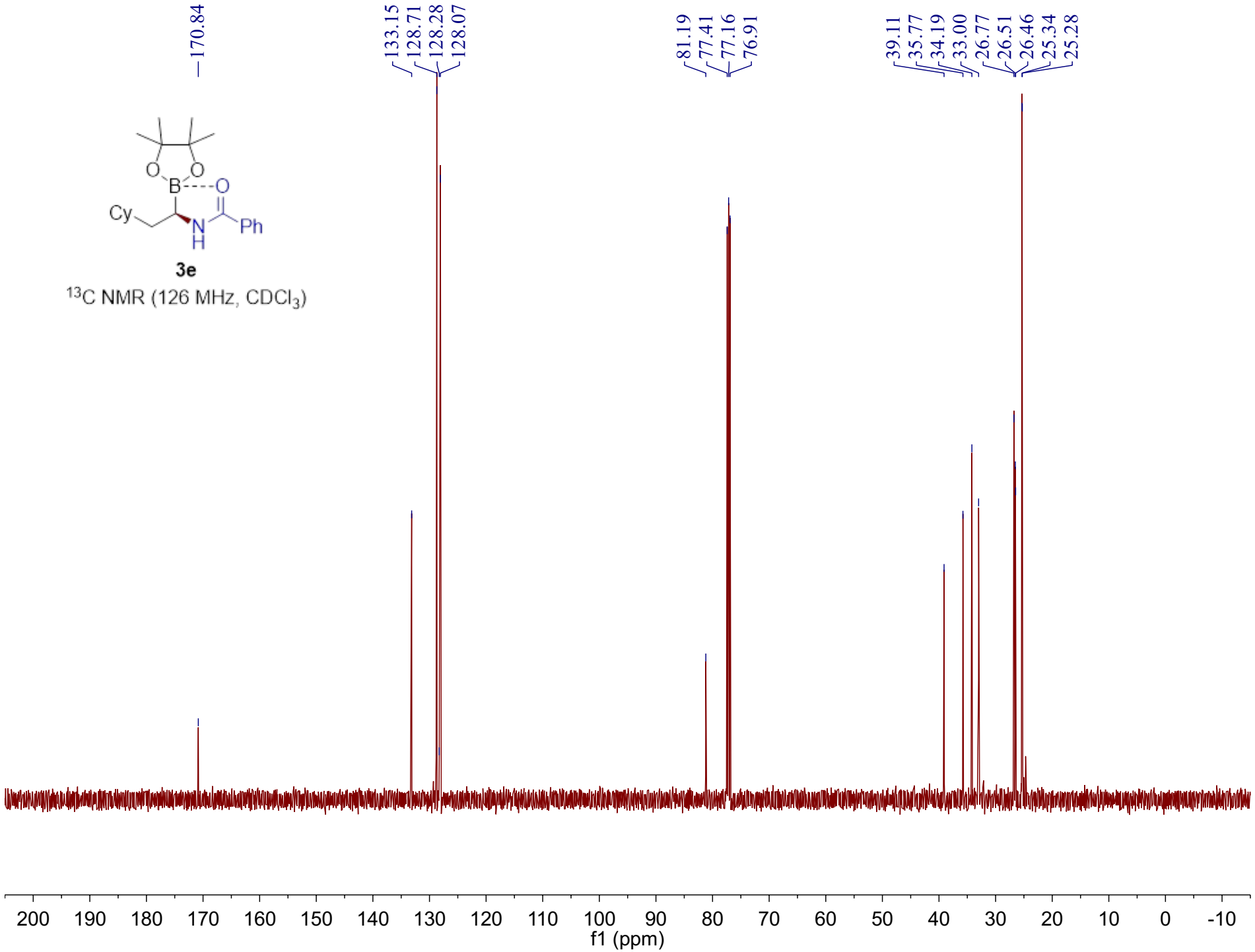
3d

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

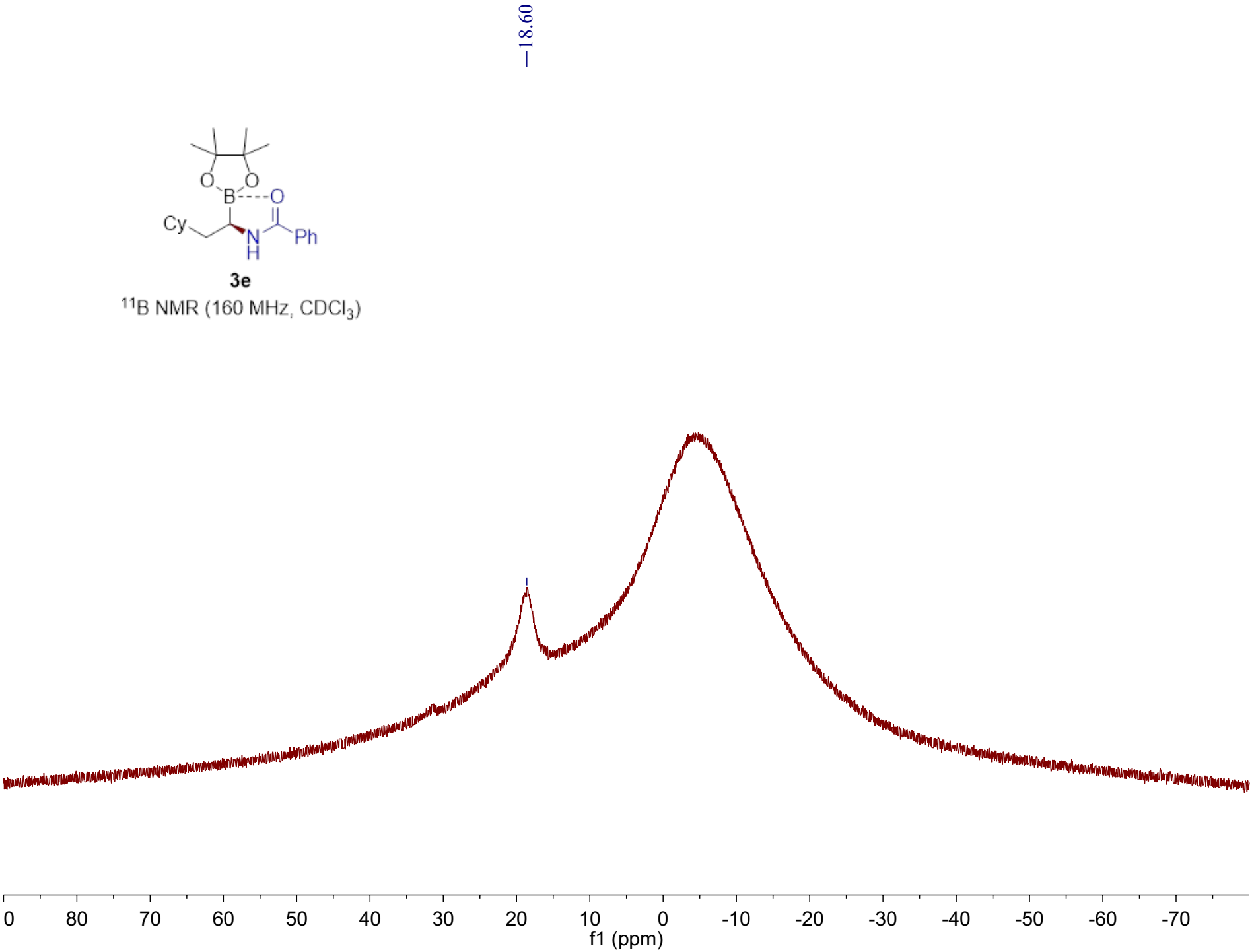
Supplementary Figure 13: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3d**.



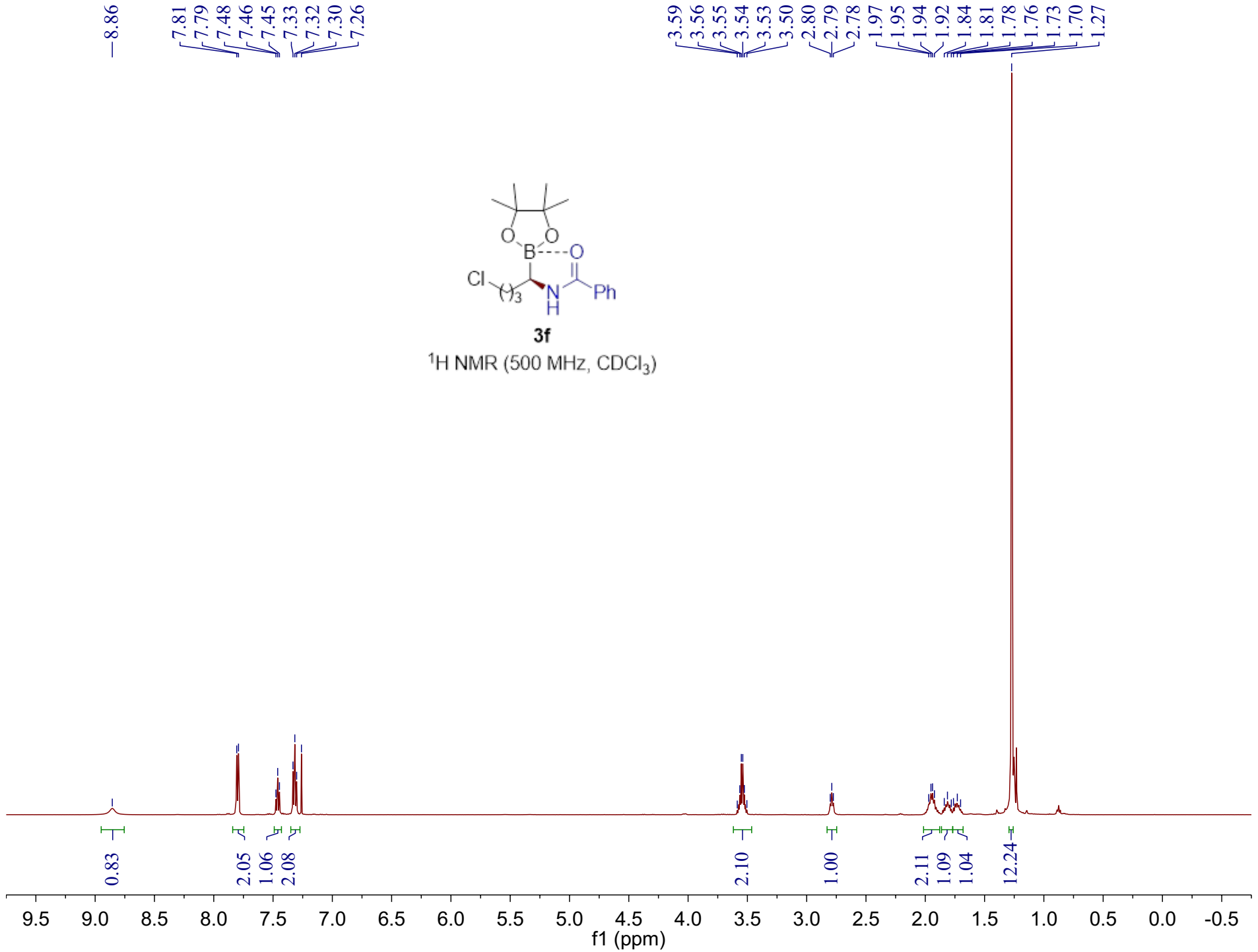
Supplementary Figure 14: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3e**.



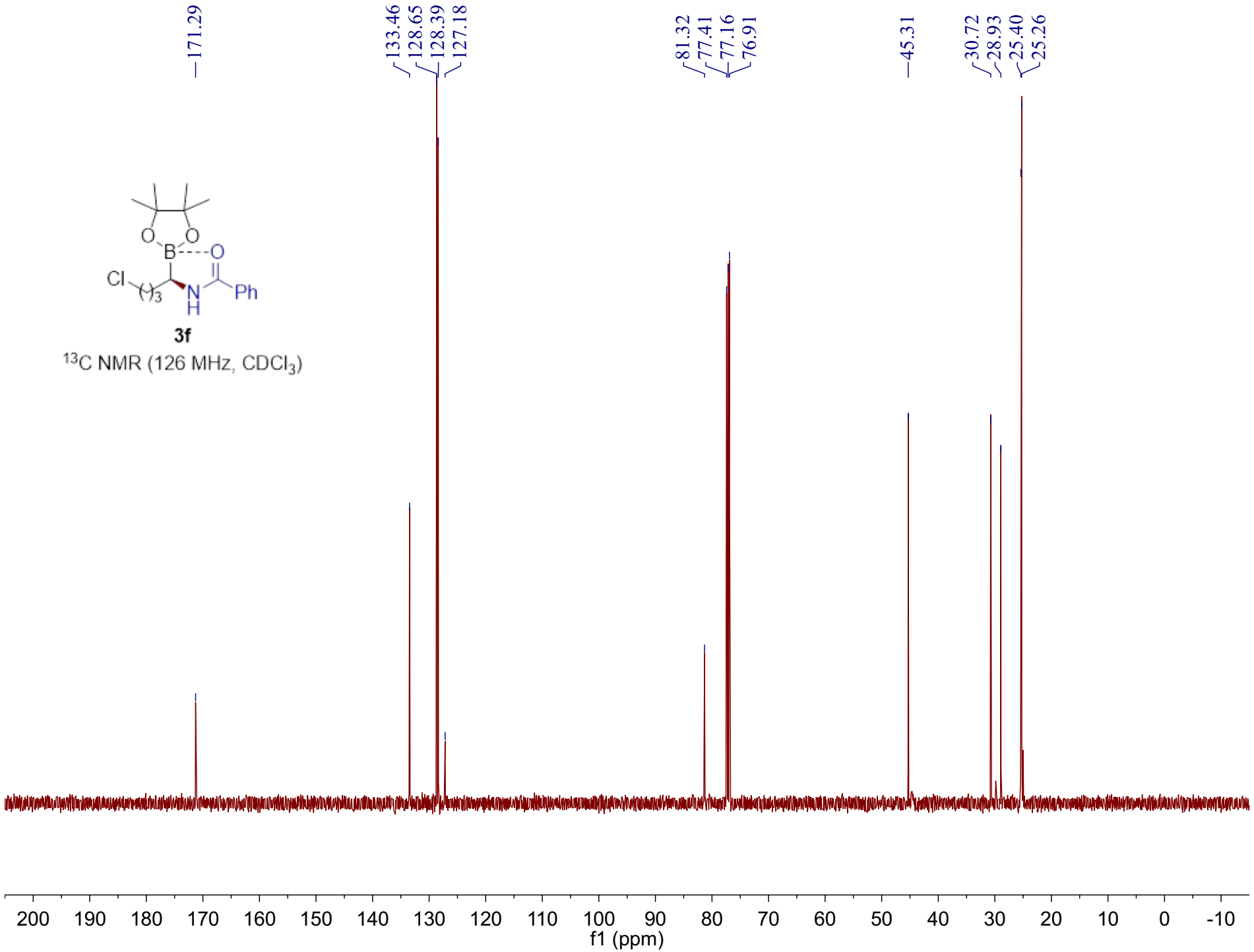
Supplementary Figure 15: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3e**.



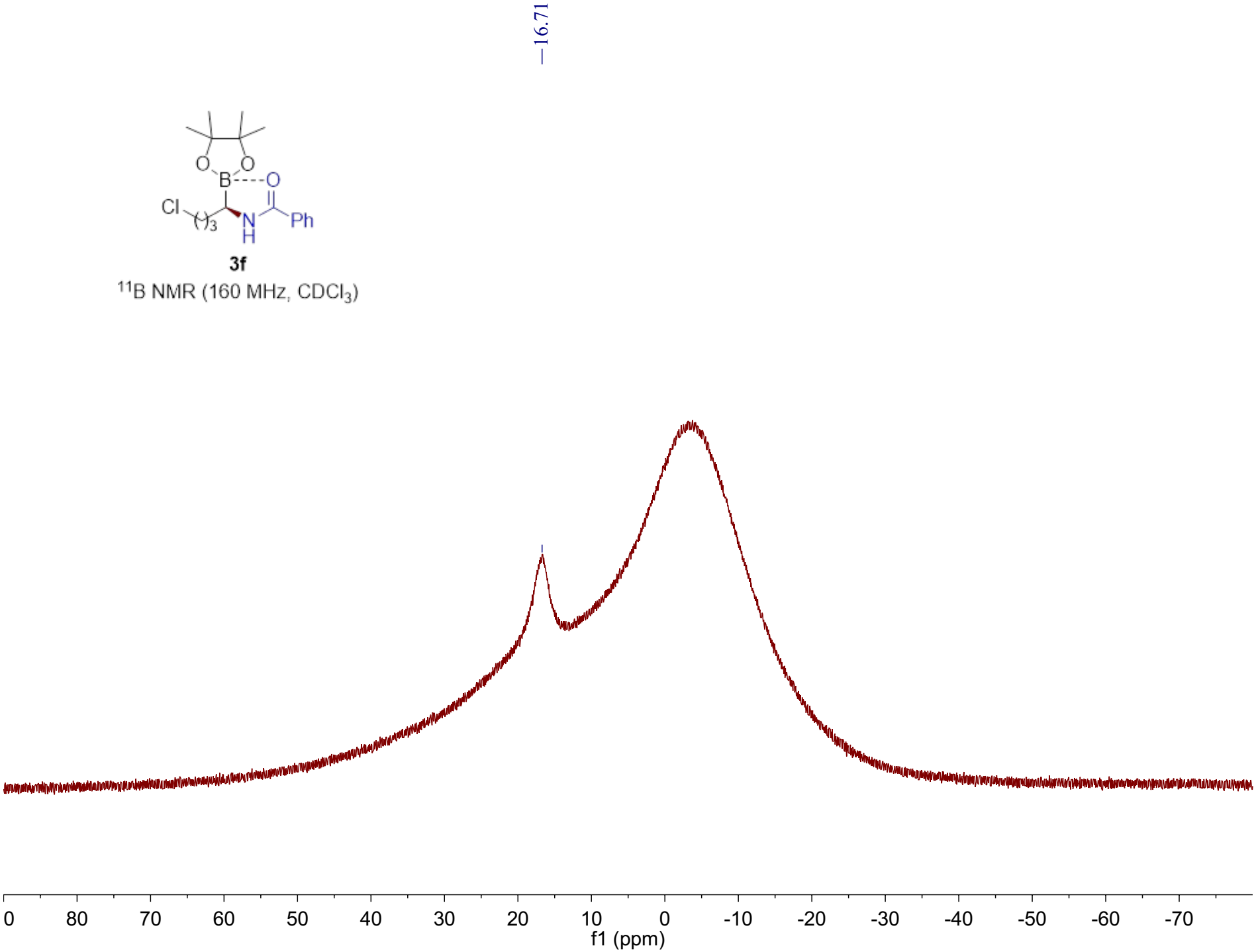
Supplementary Figure 16: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3e**.



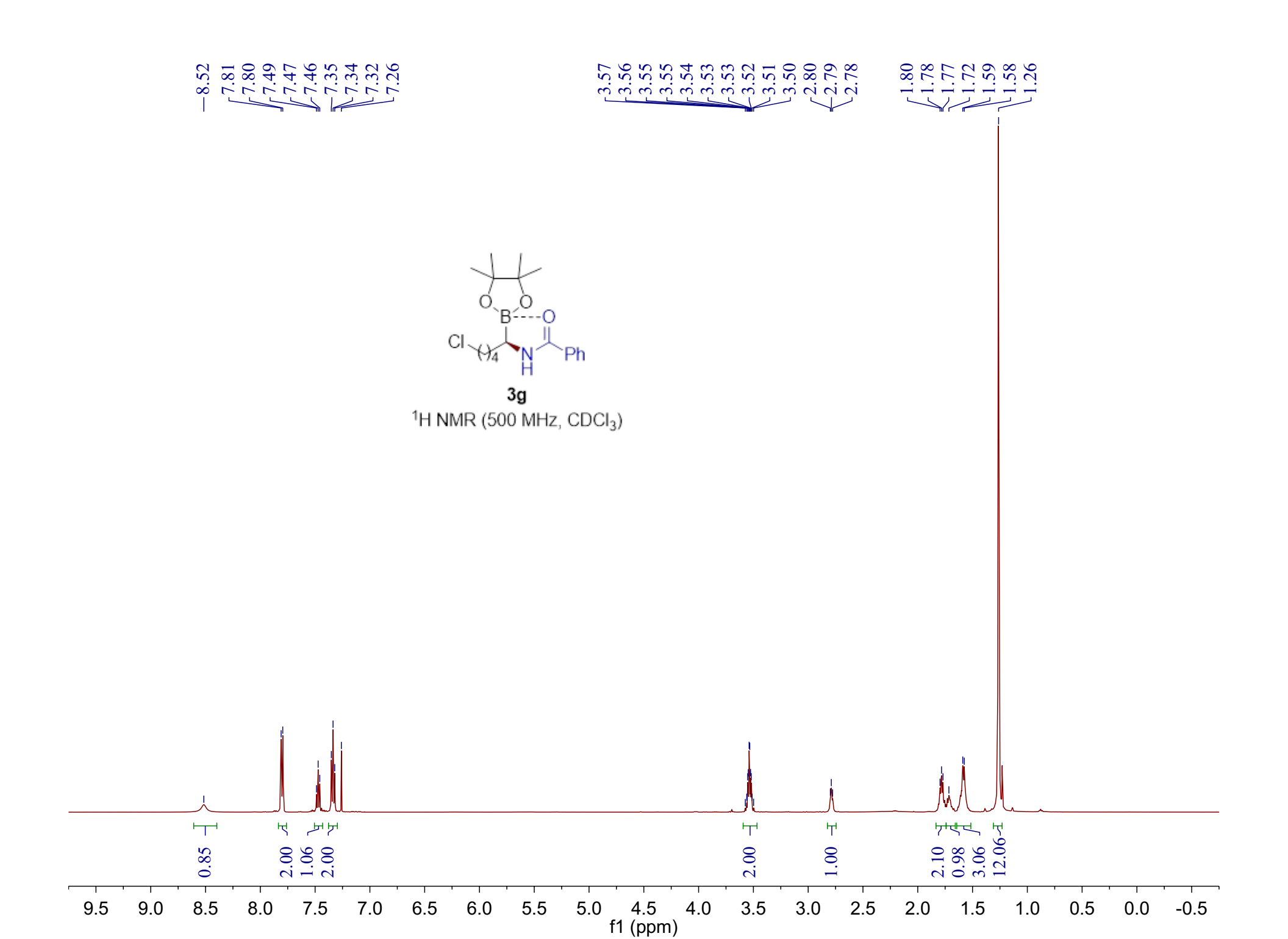
Supplementary Figure 17: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3f**.



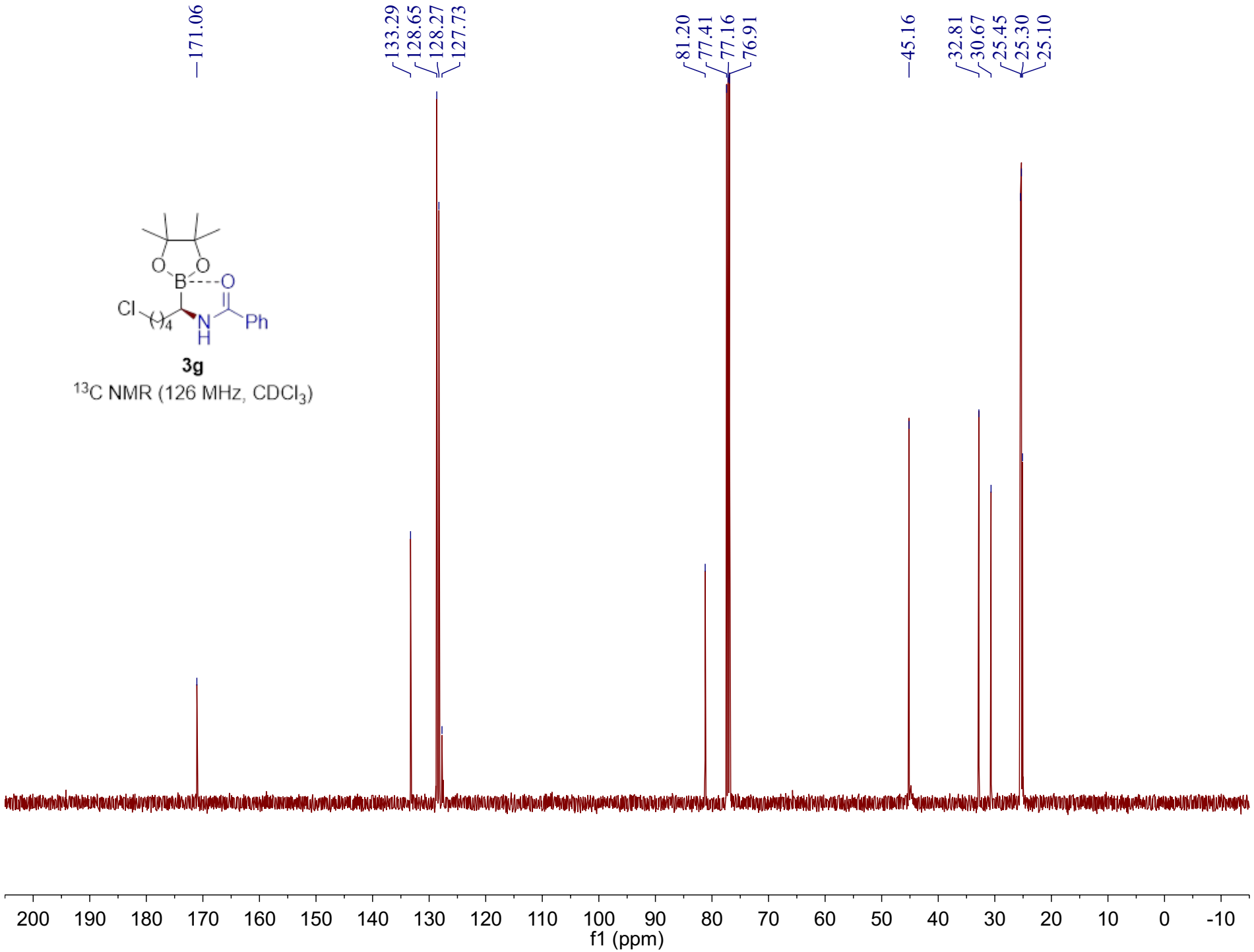
Supplementary Figure 18: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3f**.



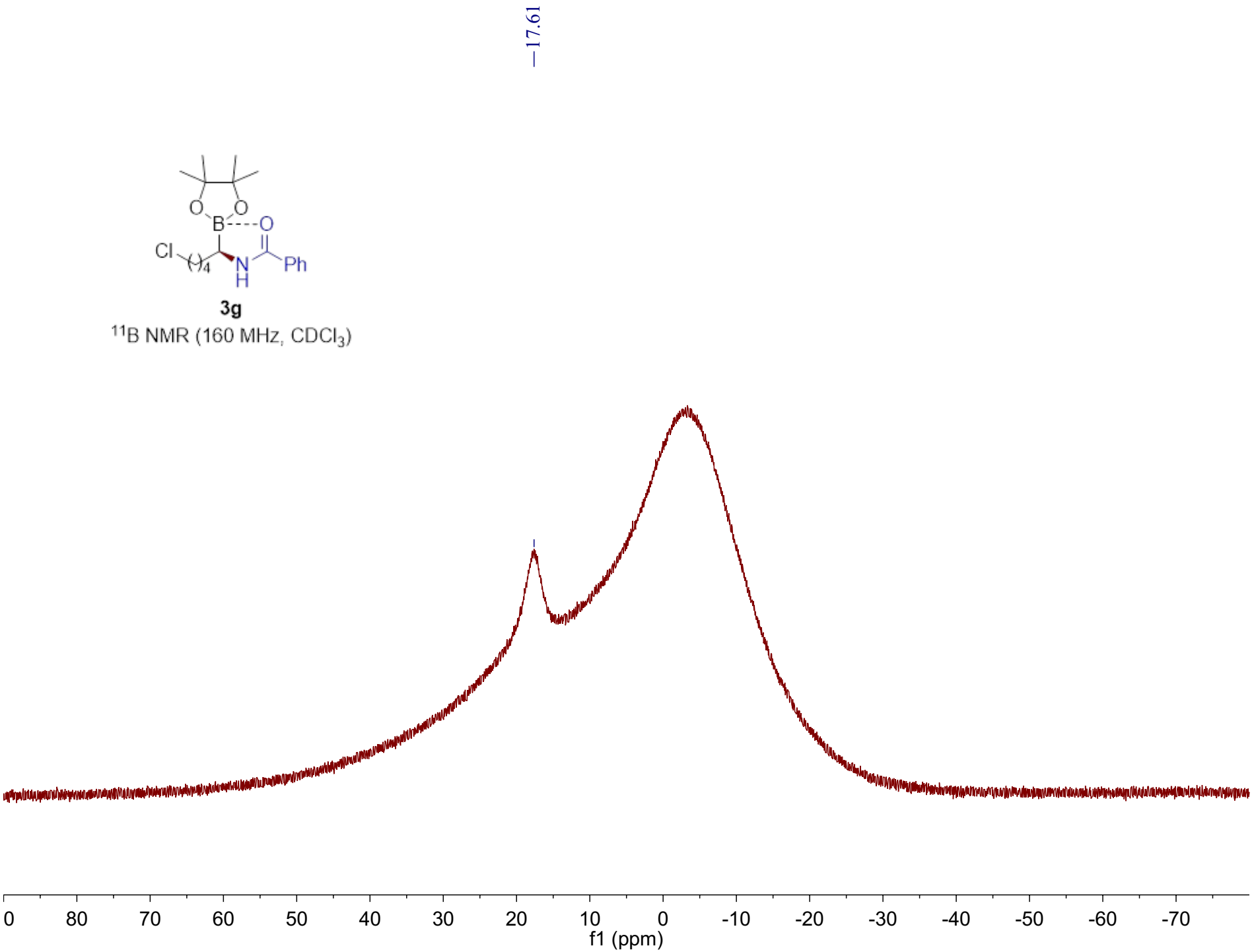
Supplementary Figure 19: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3f**.



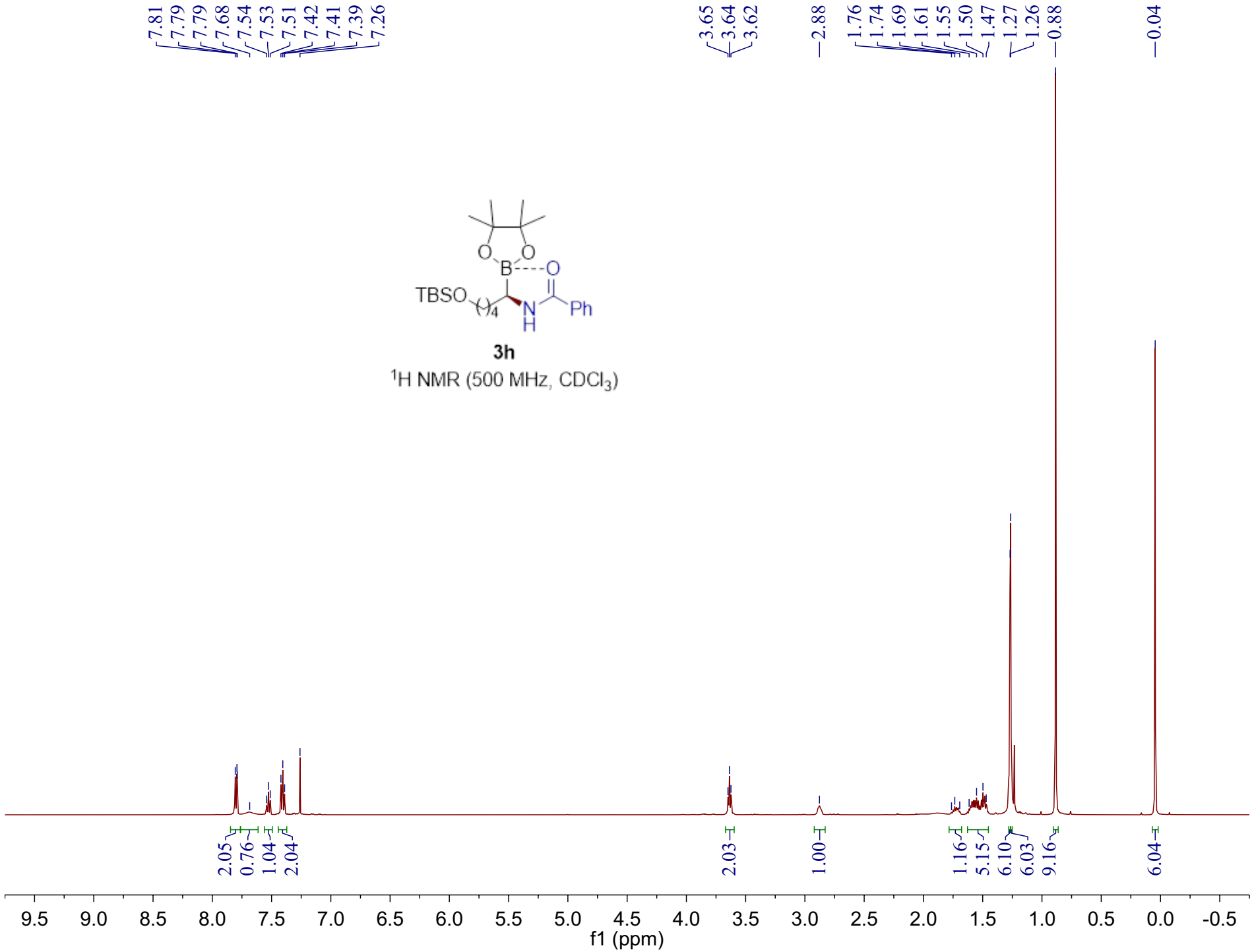
Supplementary Figure 20: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3g**.



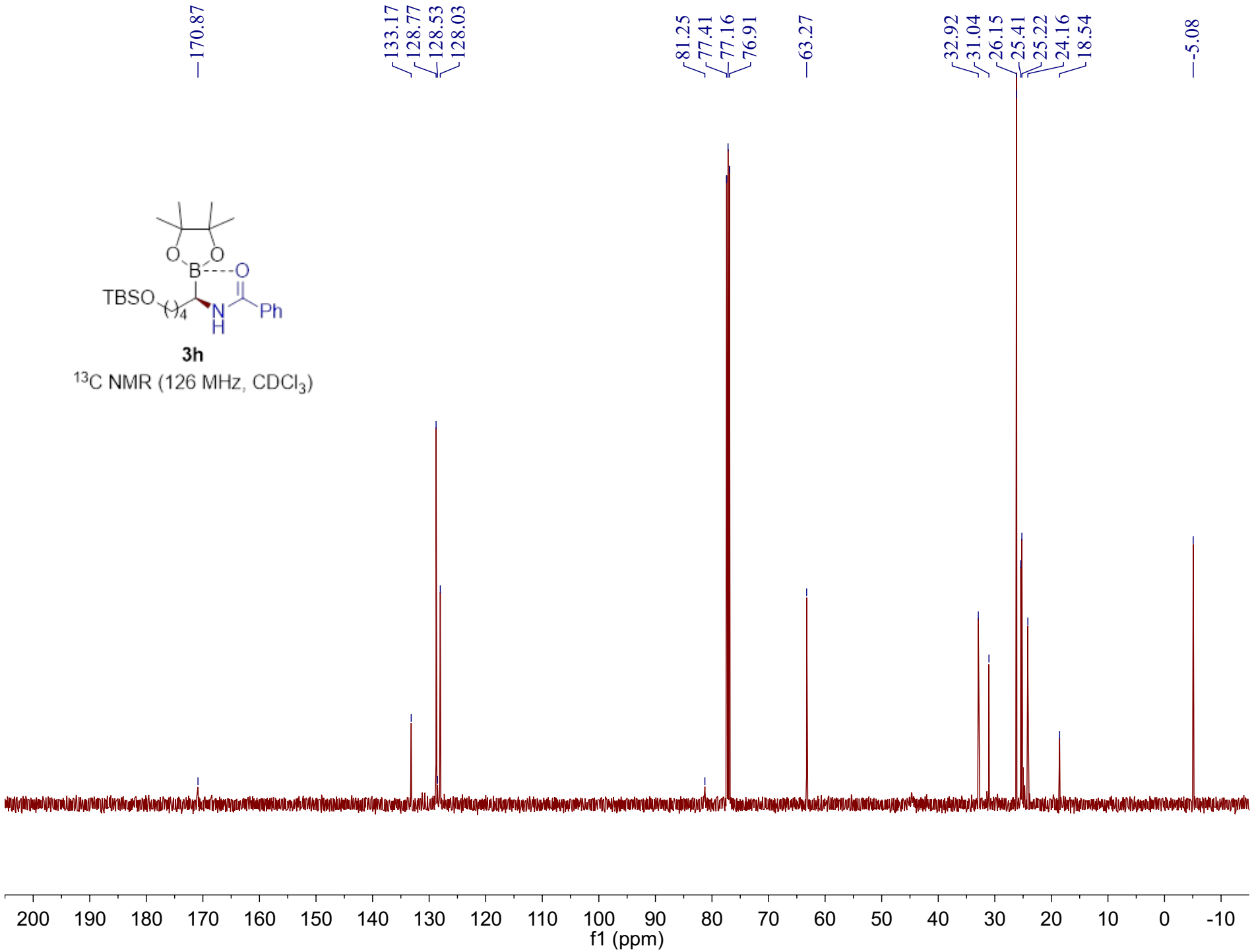
Supplementary Figure 21: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3g**.



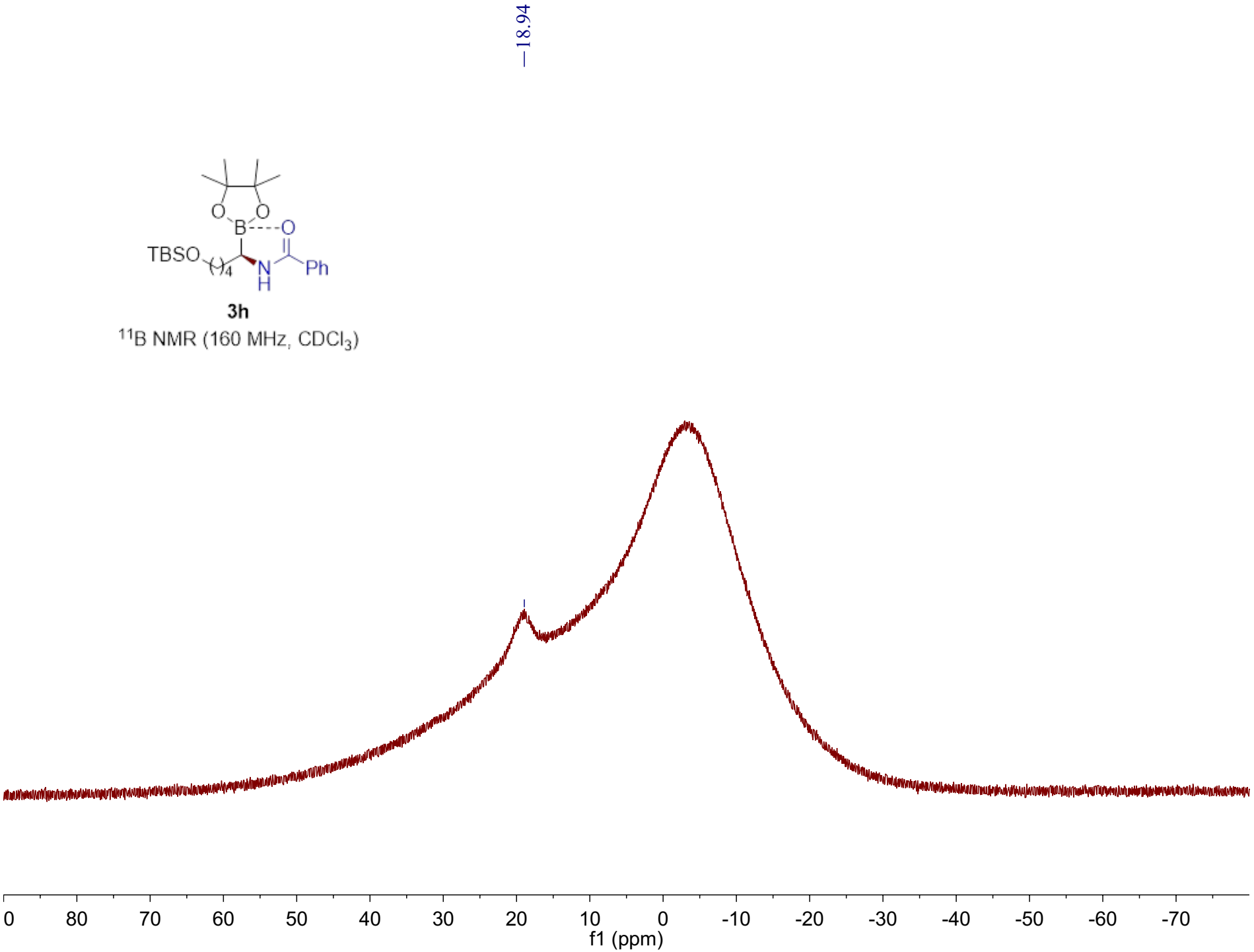
Supplementary Figure 22: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3g**.



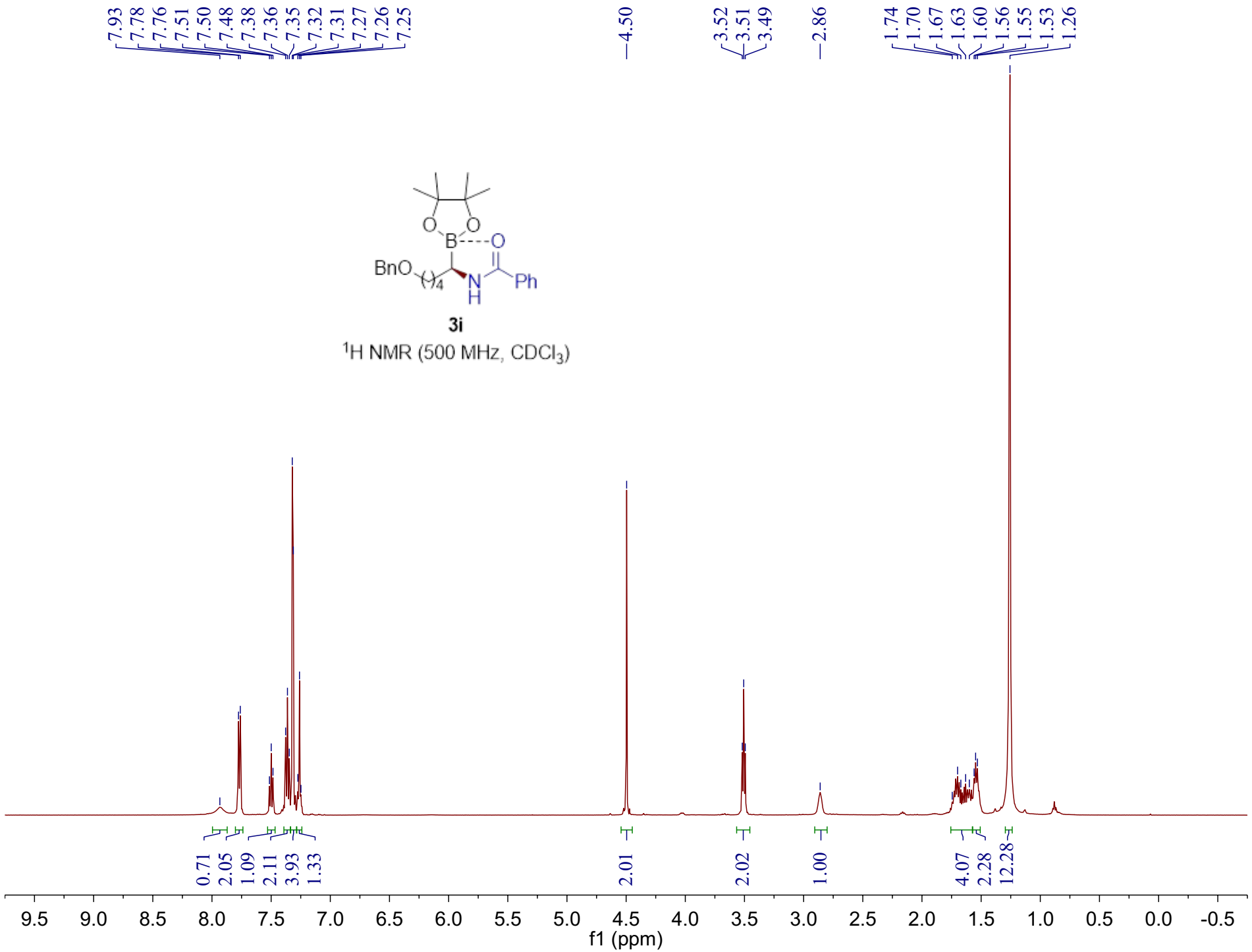
Supplementary Figure 23: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3h**.



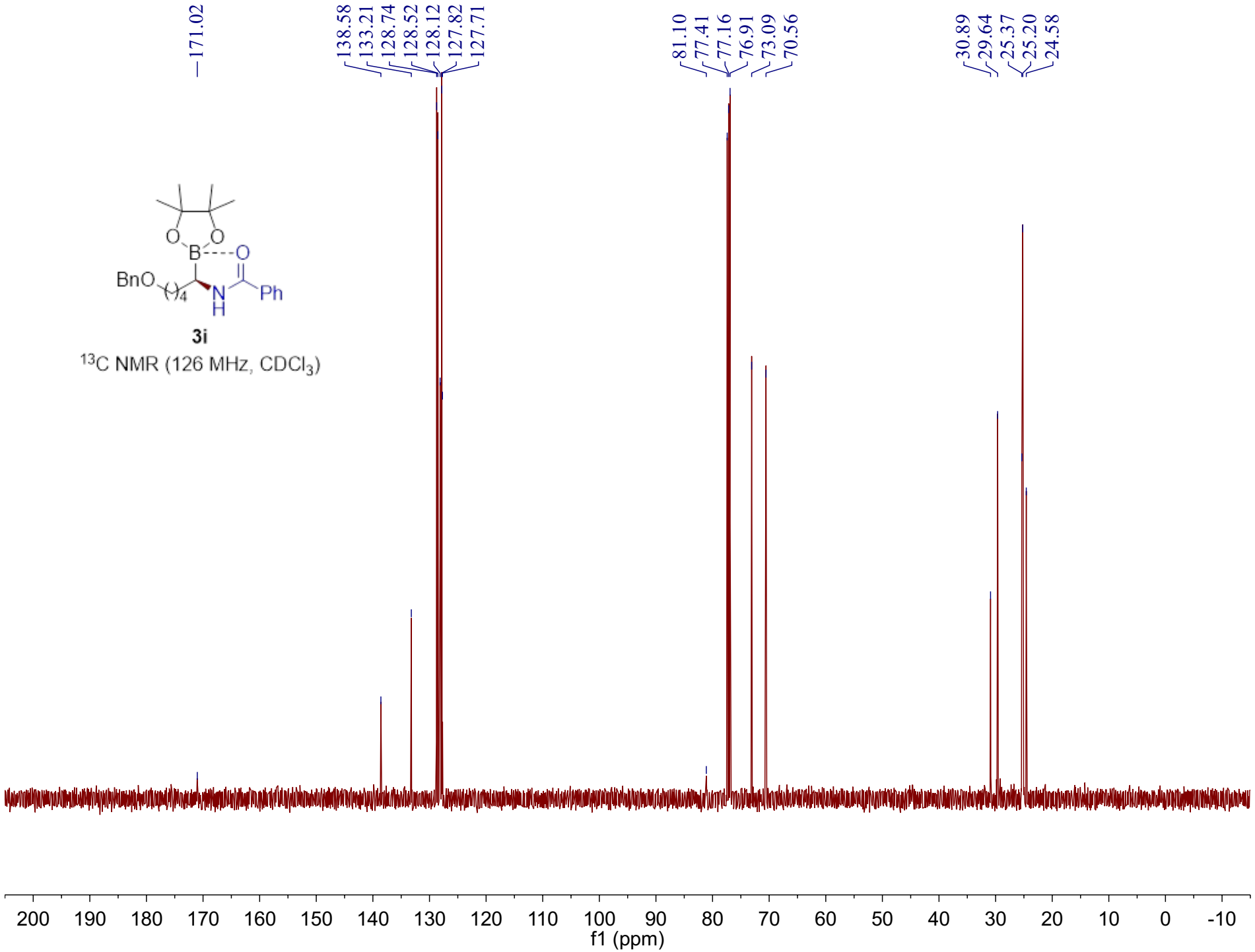
Supplementary Figure 24: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3h**.



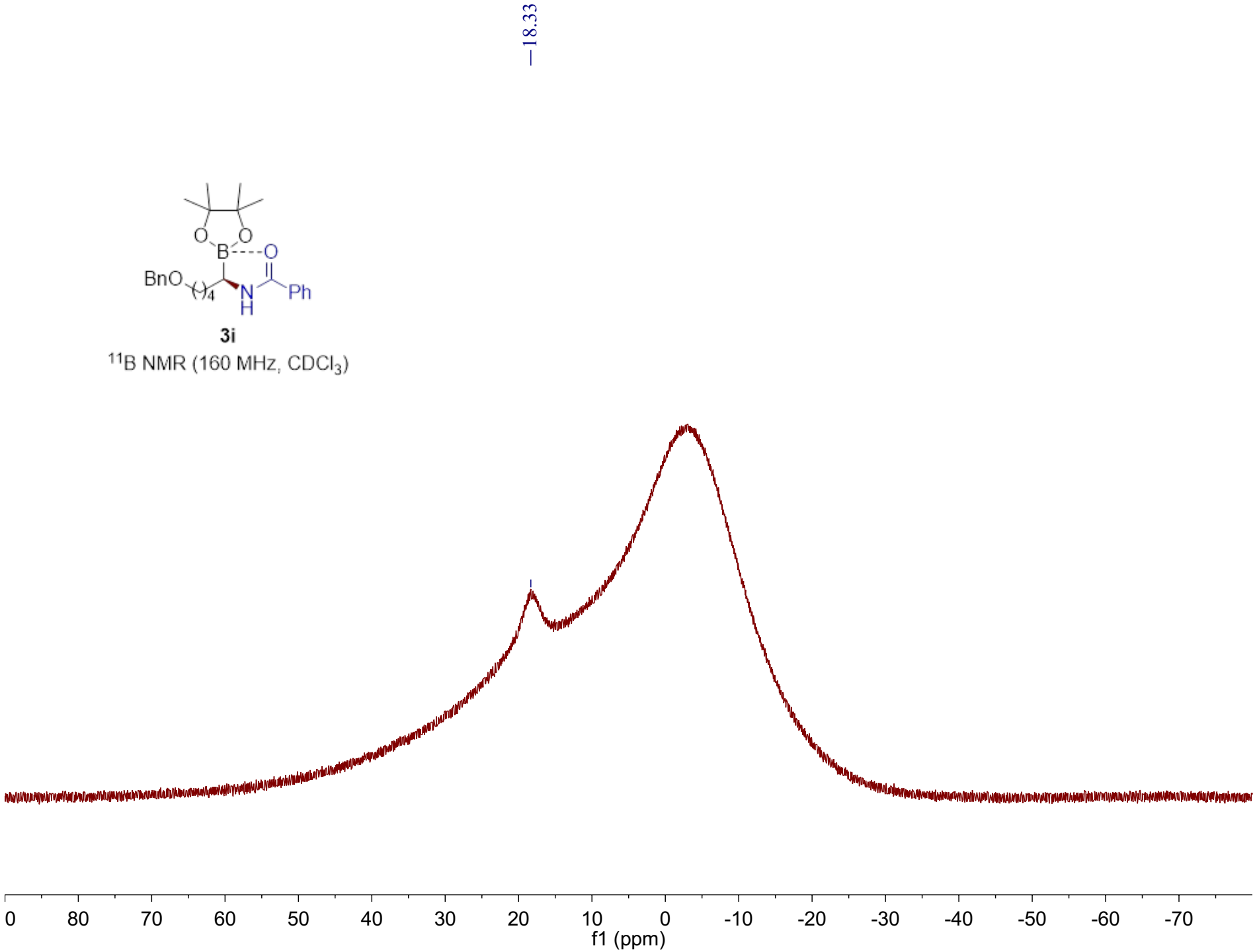
Supplementary Figure 25: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3h**.



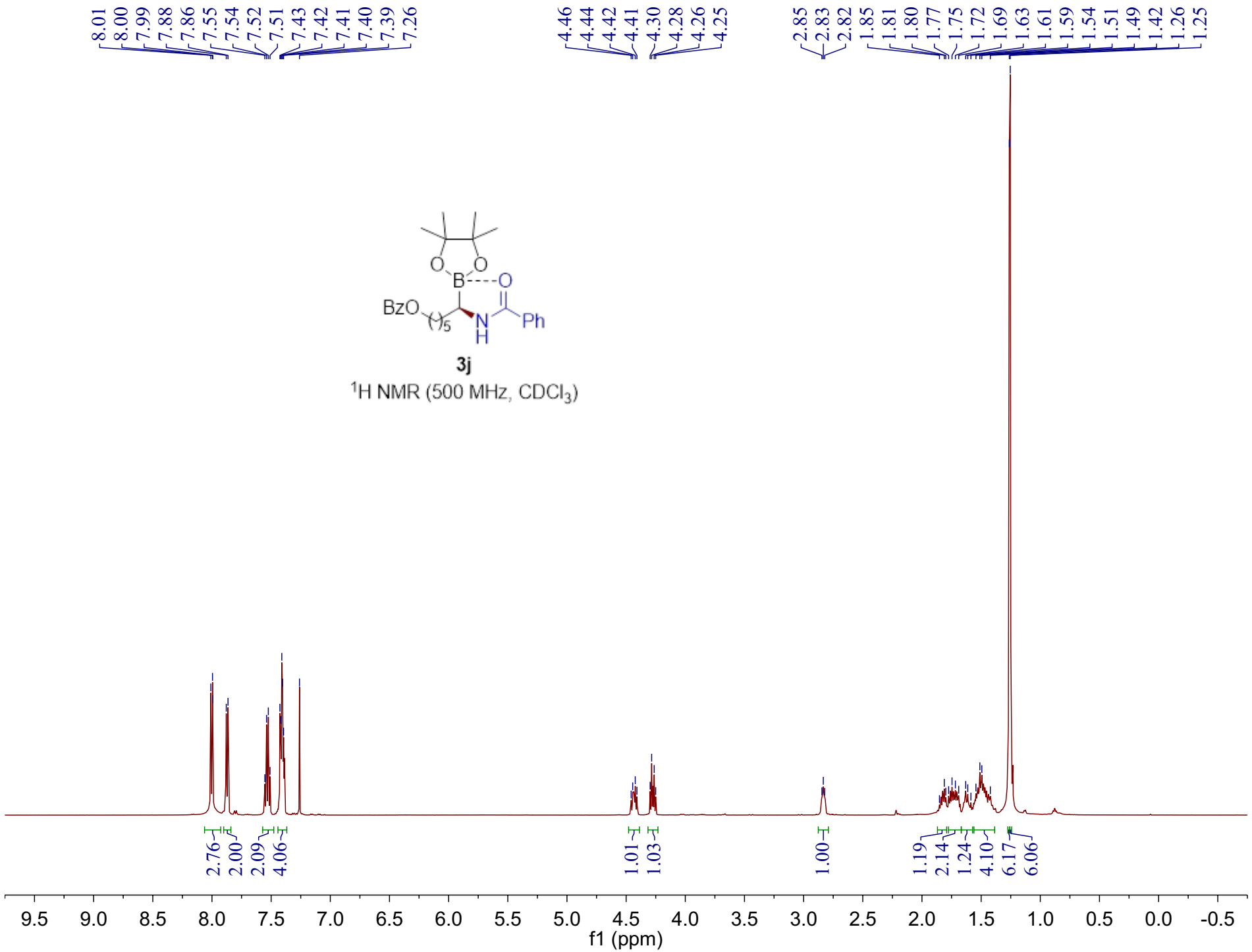
Supplementary Figure 26: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3i**.



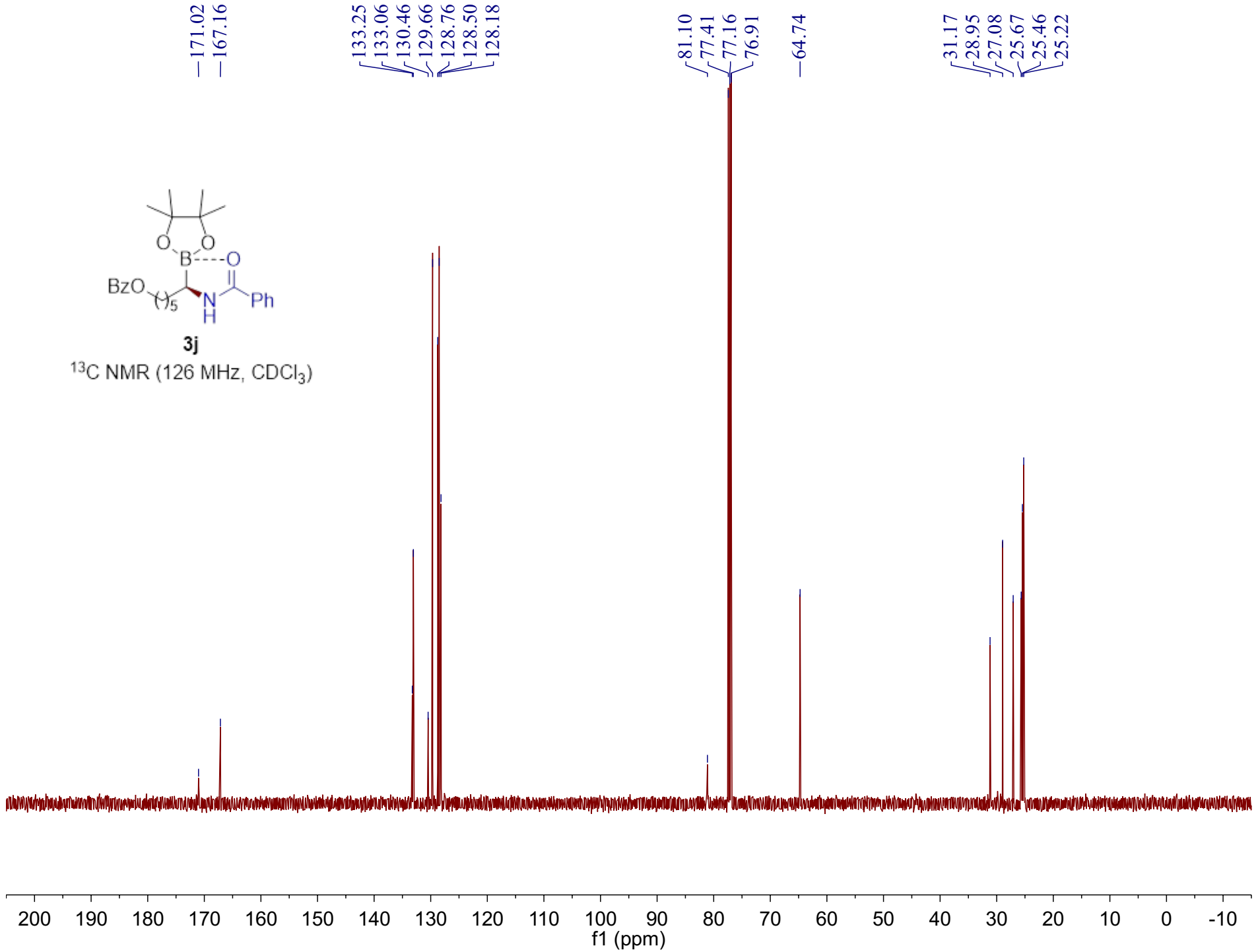
Supplementary Figure 27: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3i**.



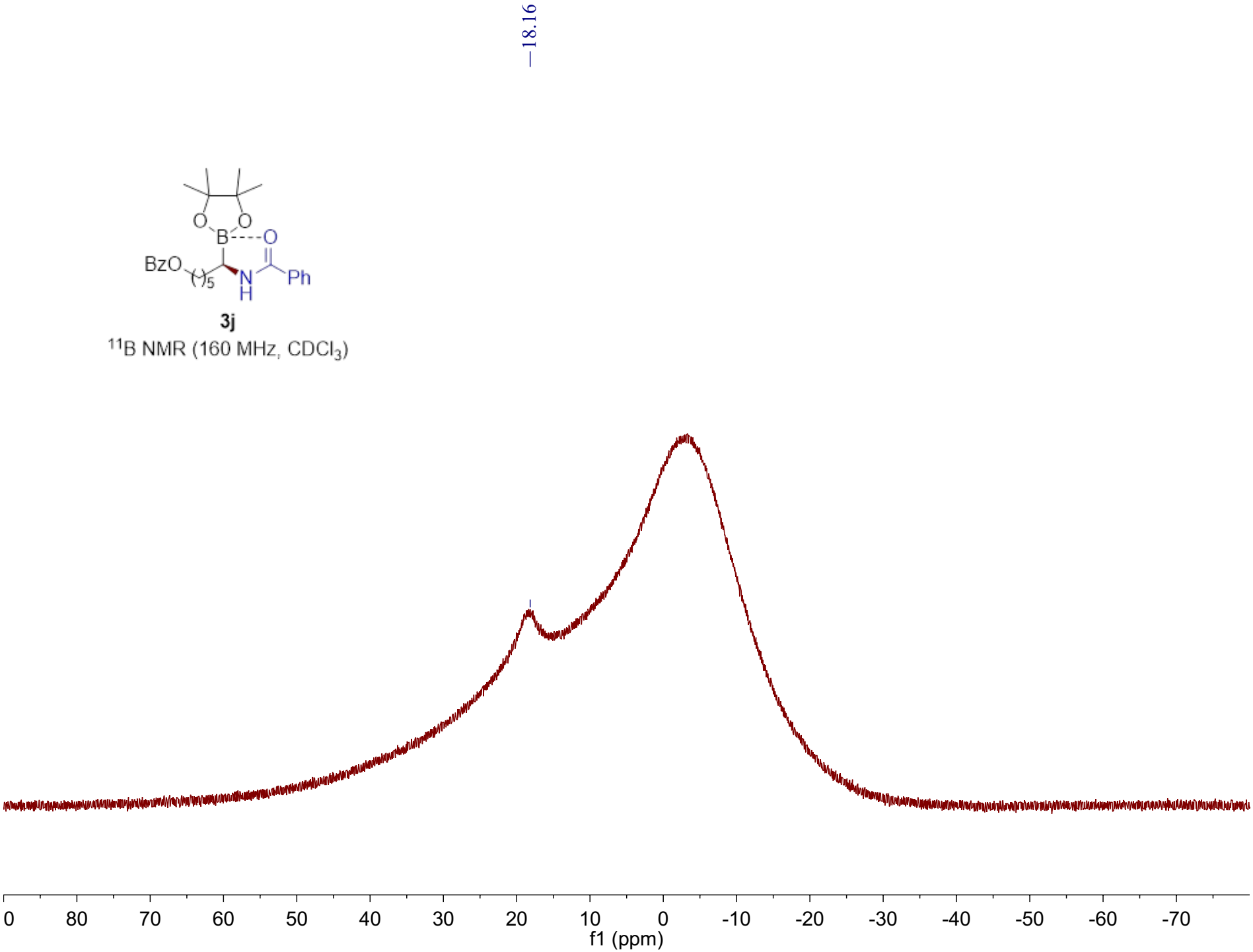
Supplementary Figure 28: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3i**.



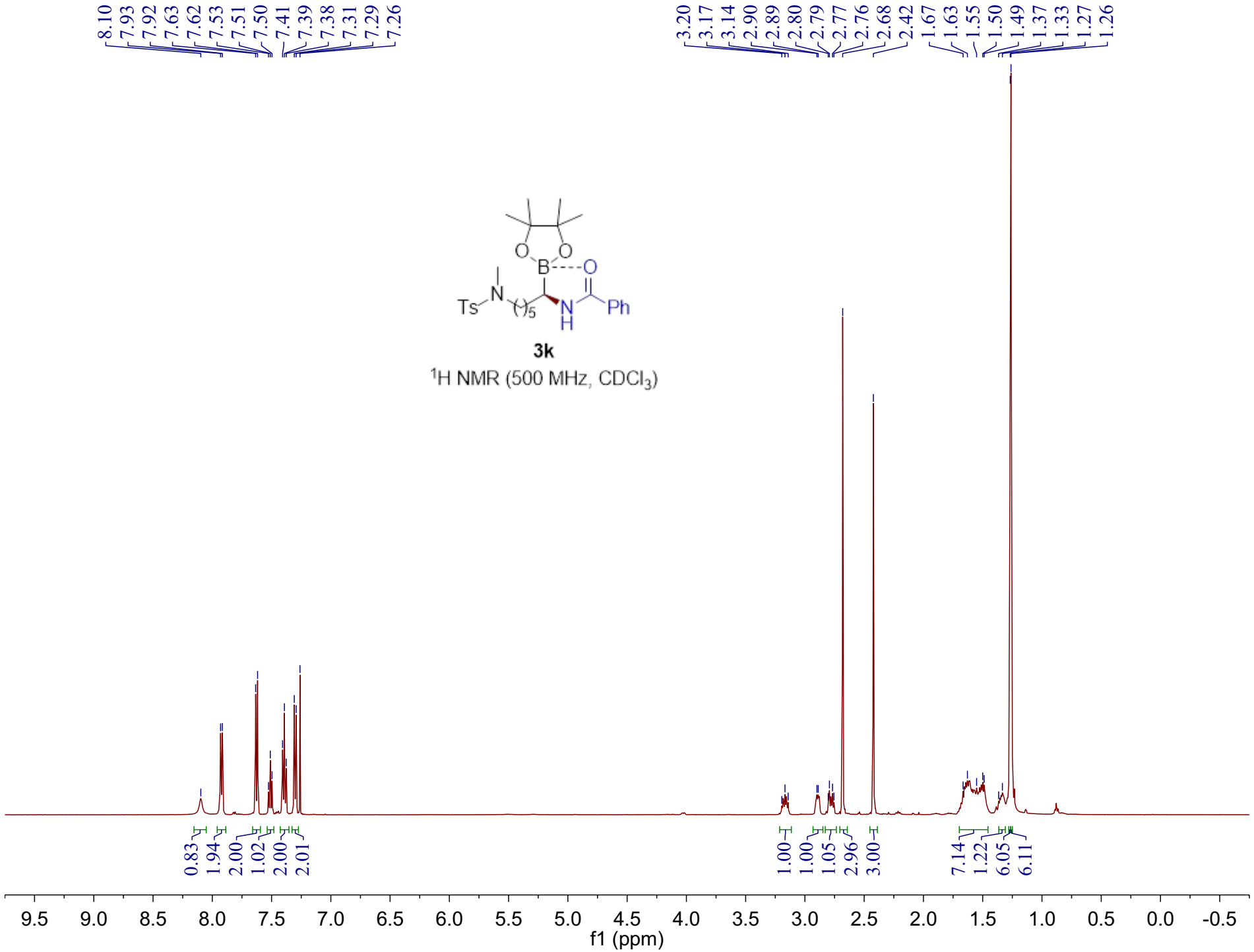
Supplementary Figure 29: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3j**.



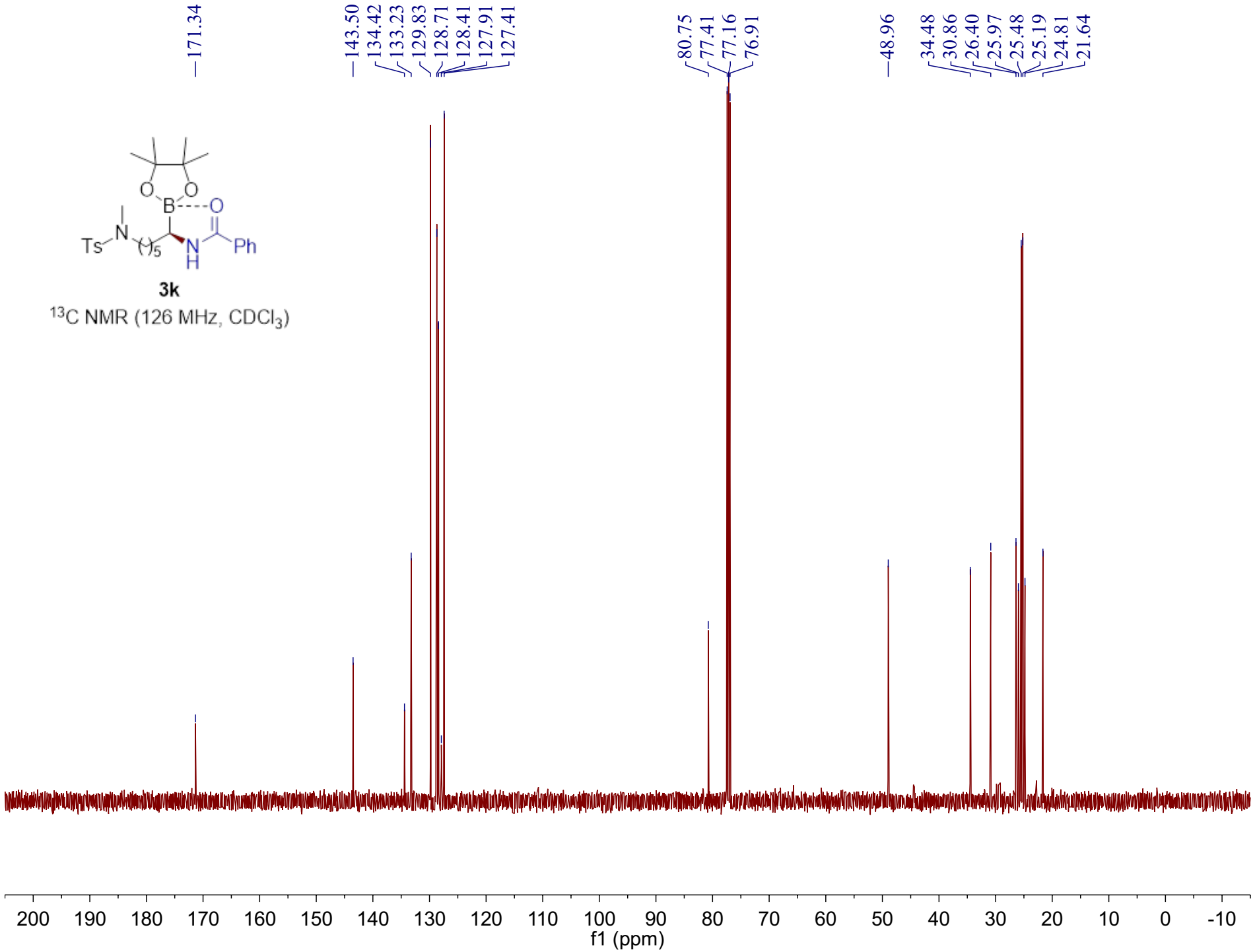
Supplementary Figure 30: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3j**.



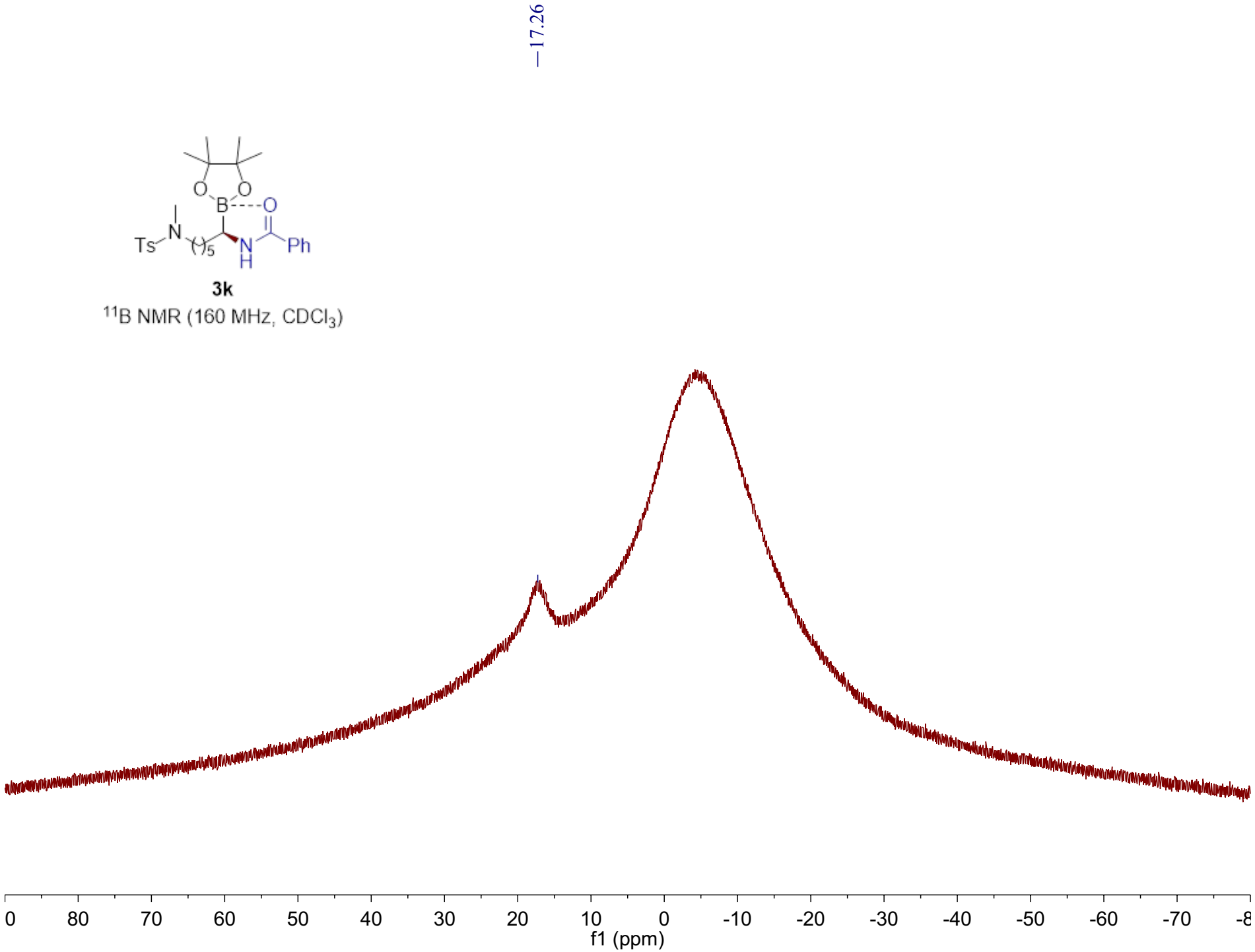
Supplementary Figure 31: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3j**.



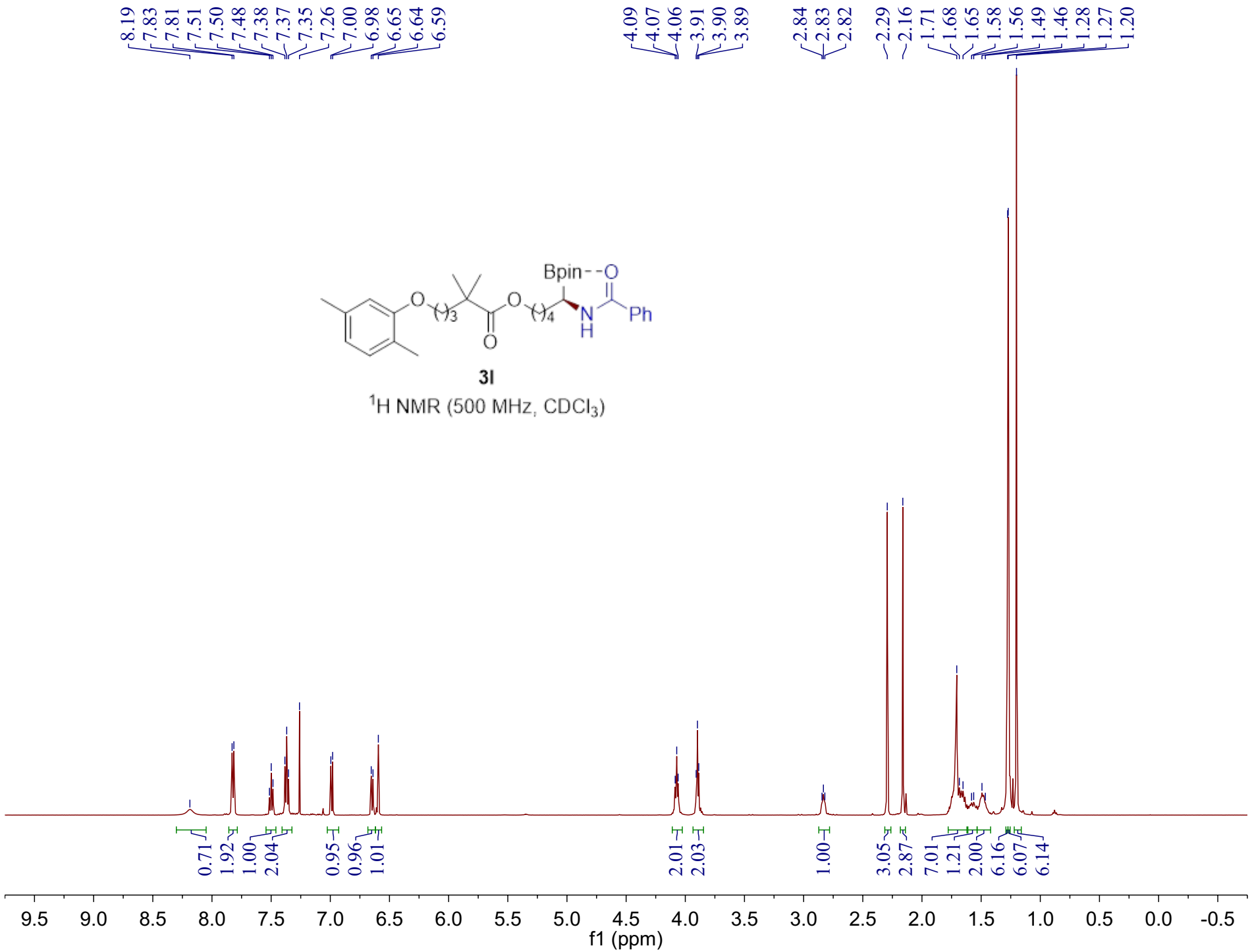
Supplementary Figure 32: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3k**.



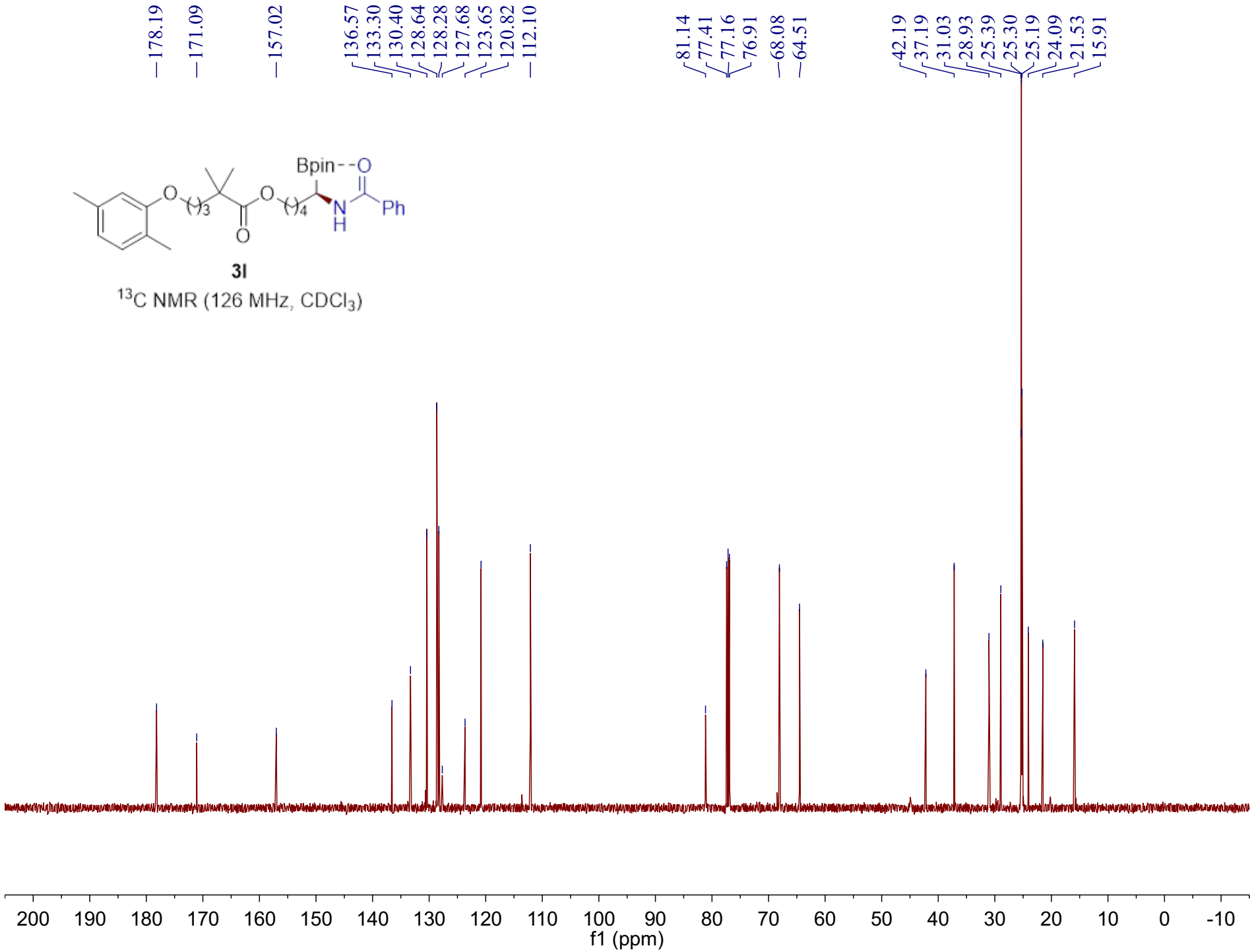
Supplementary Figure 33: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3k**.



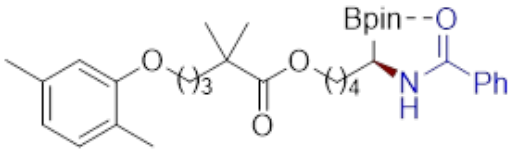
Supplementary Figure 34: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3k**.



Supplementary Figure 35: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3l**.



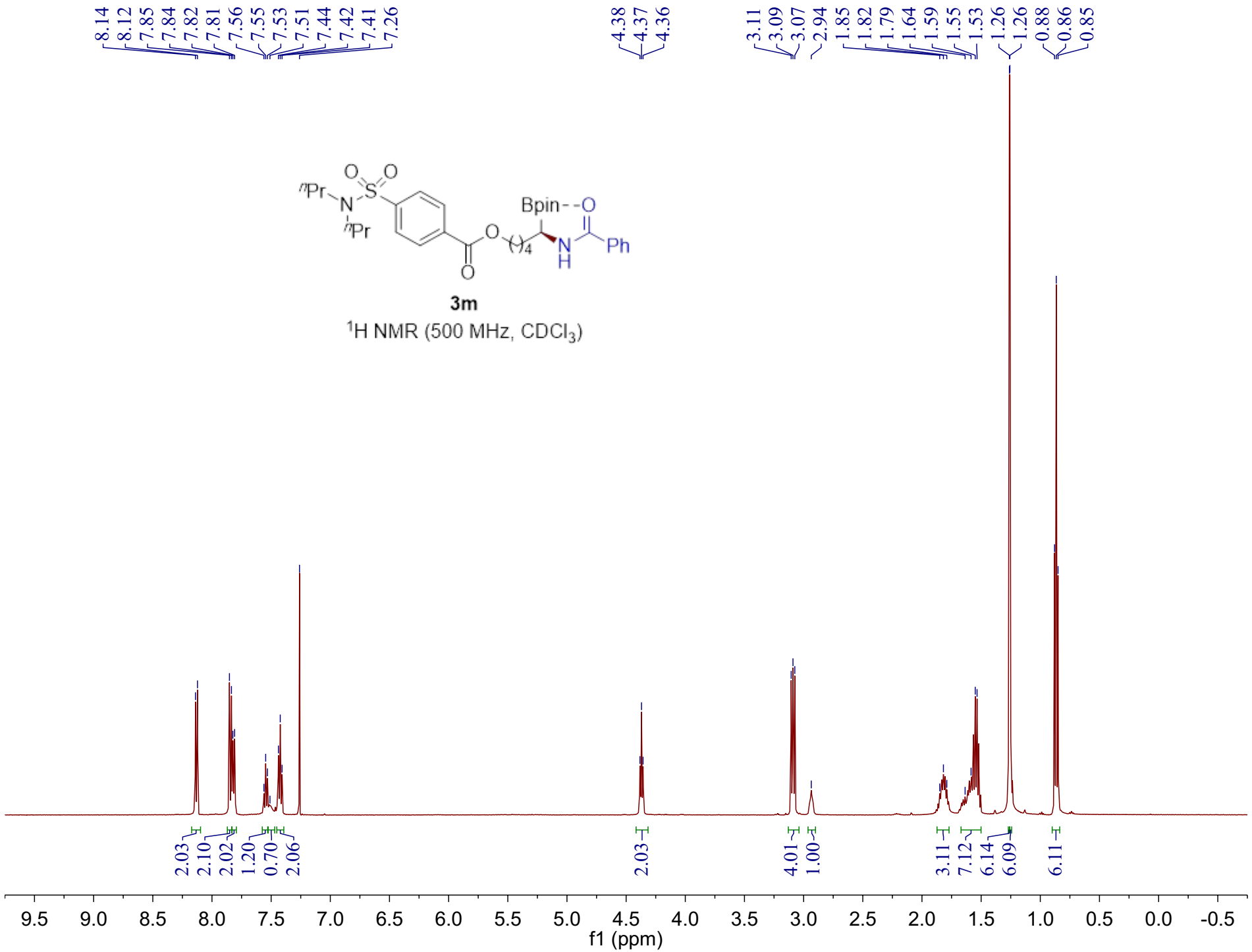
Supplementary Figure 36: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3l**.



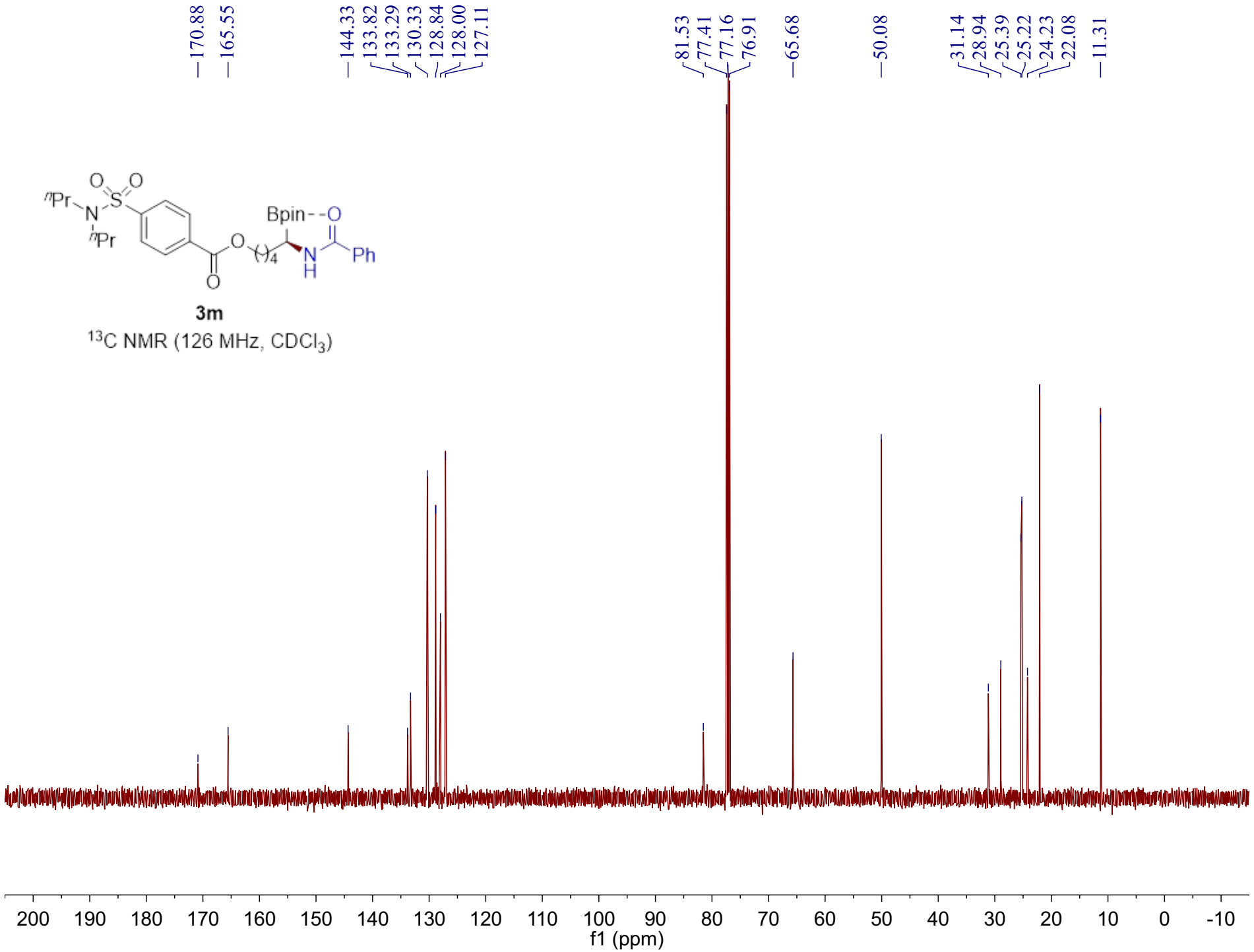
3l

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

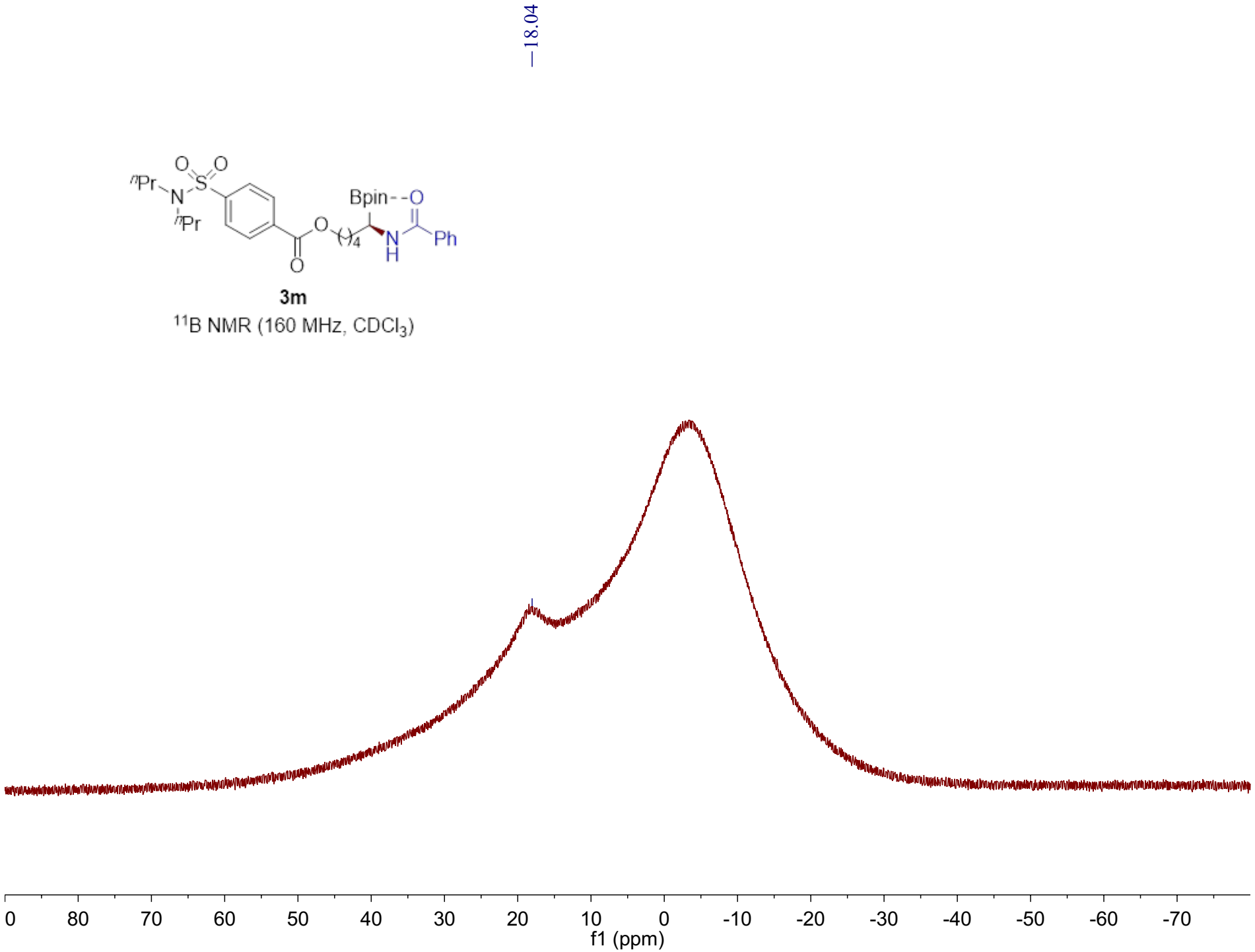
Supplementary Figure 37: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3l**.



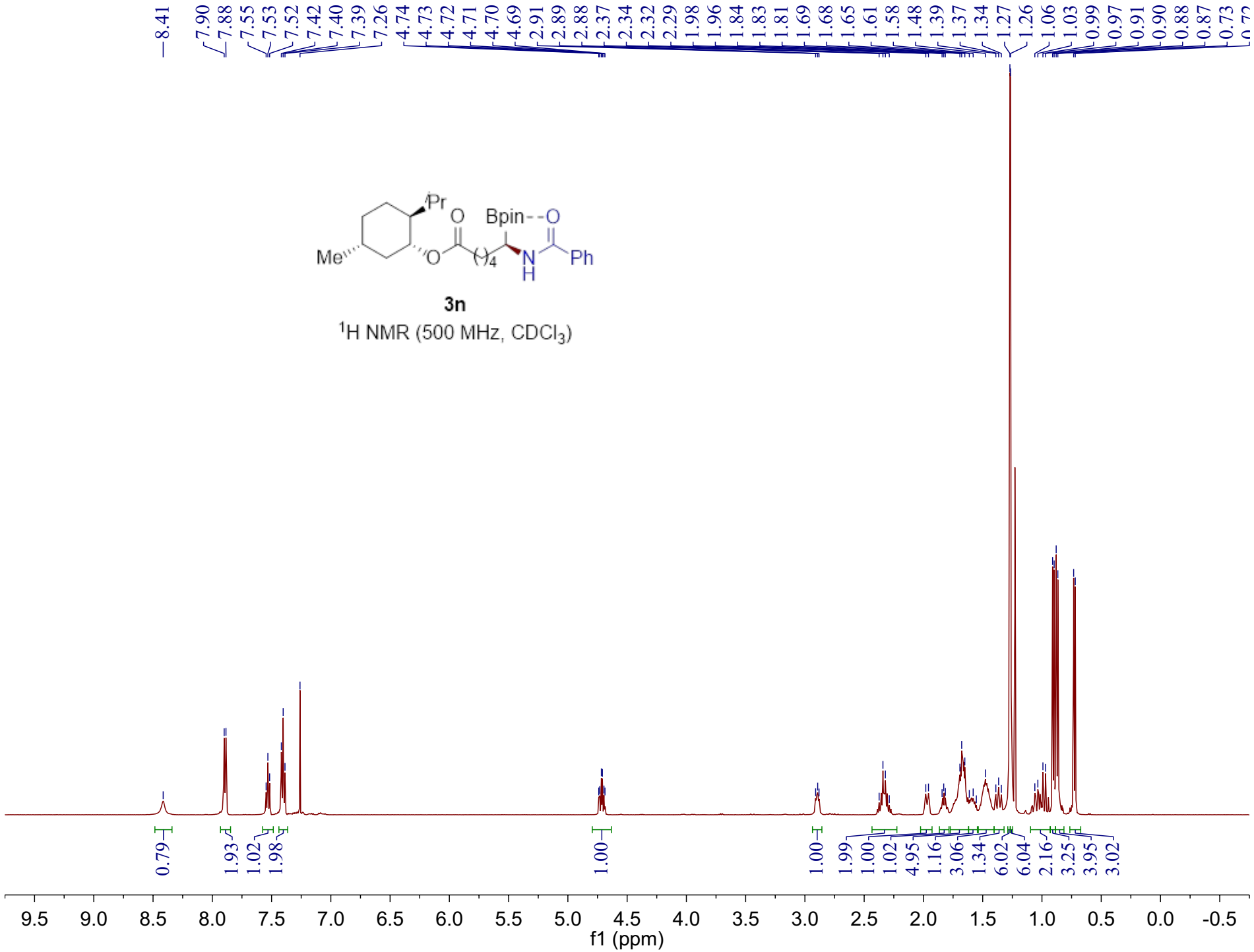
Supplementary Figure 38: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3m**.



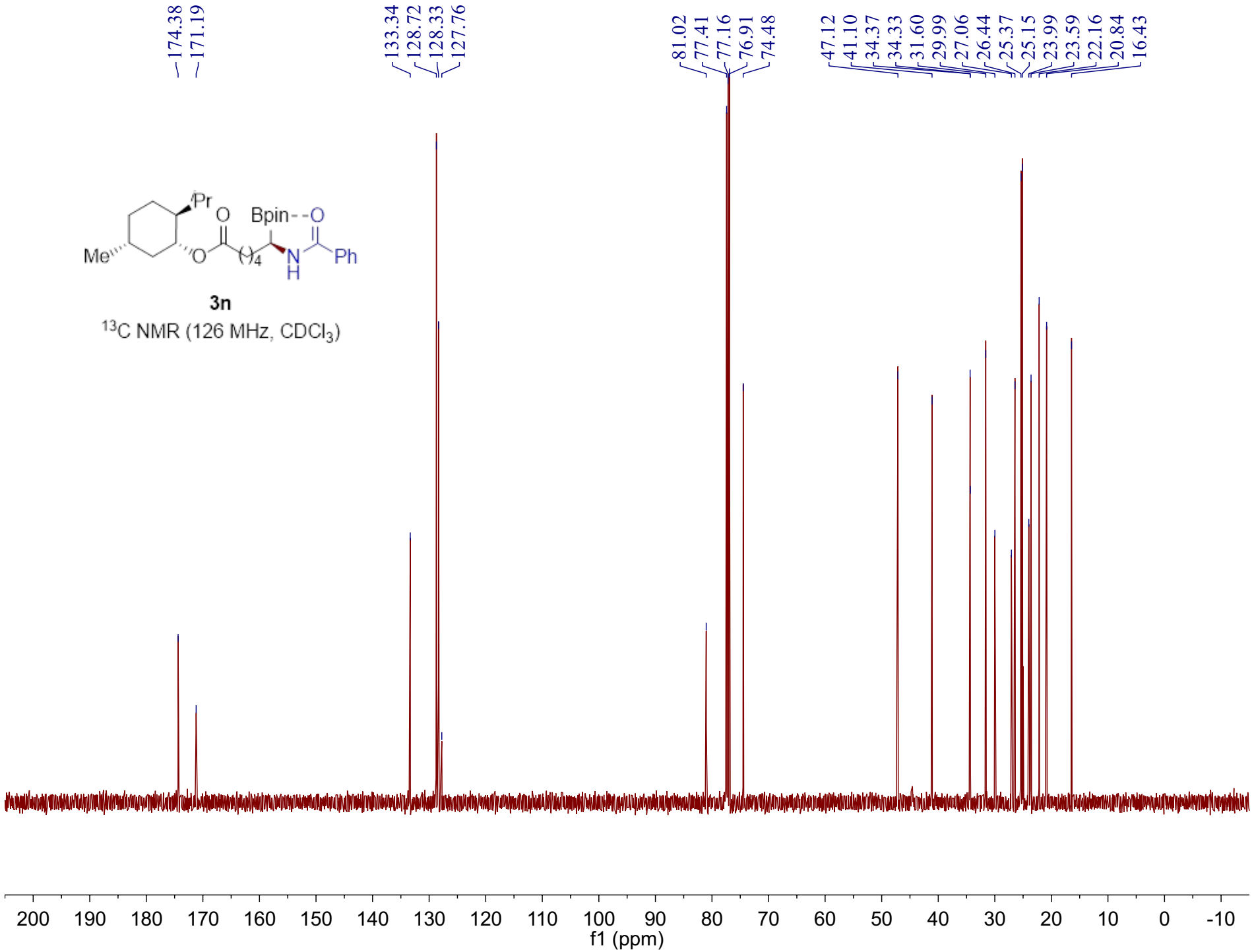
Supplementary Figure 39: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3m**.



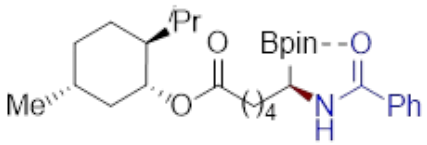
Supplementary Figure 40: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3m**.



Supplementary Figure 41: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3n**.



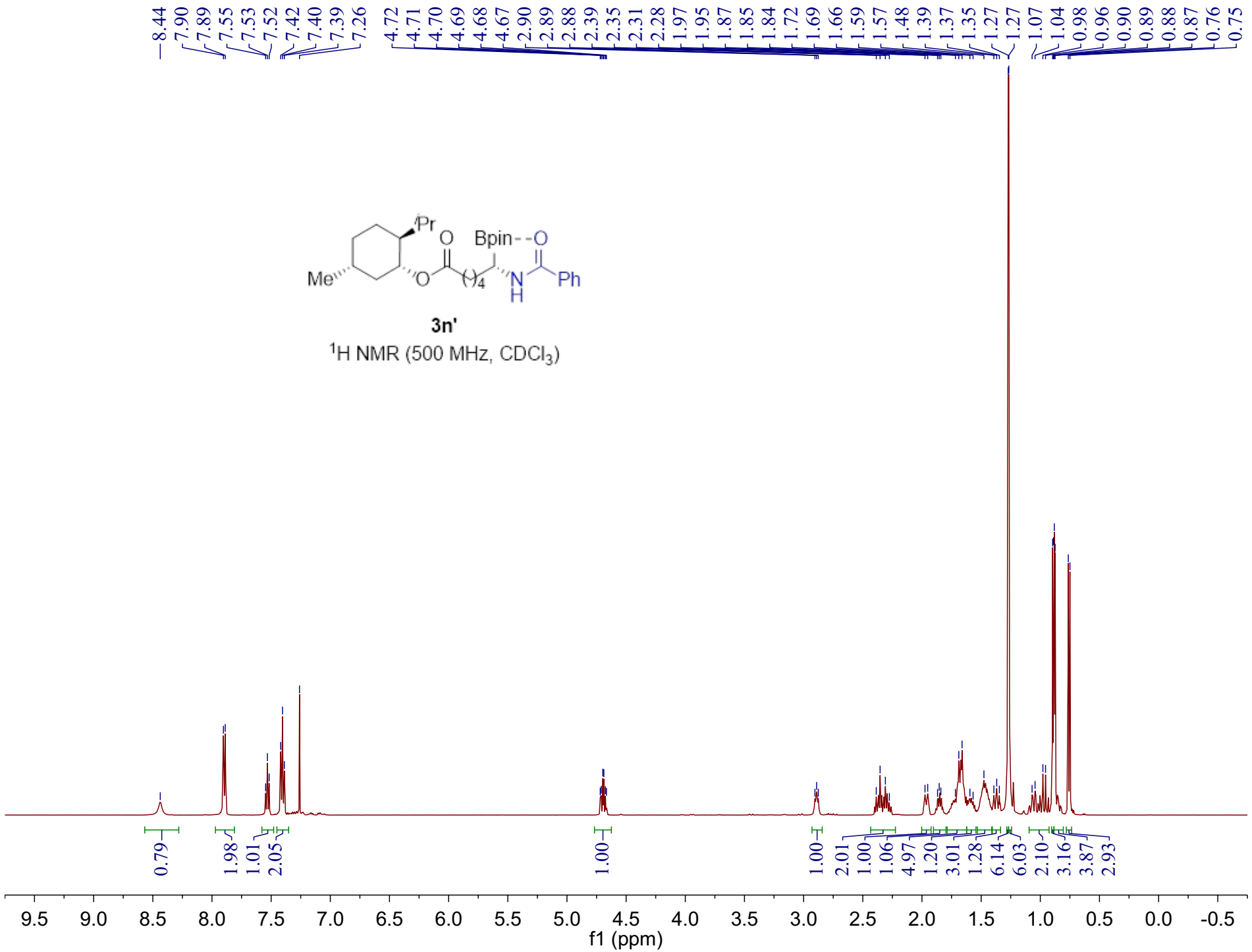
Supplementary Figure 42: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3n**.



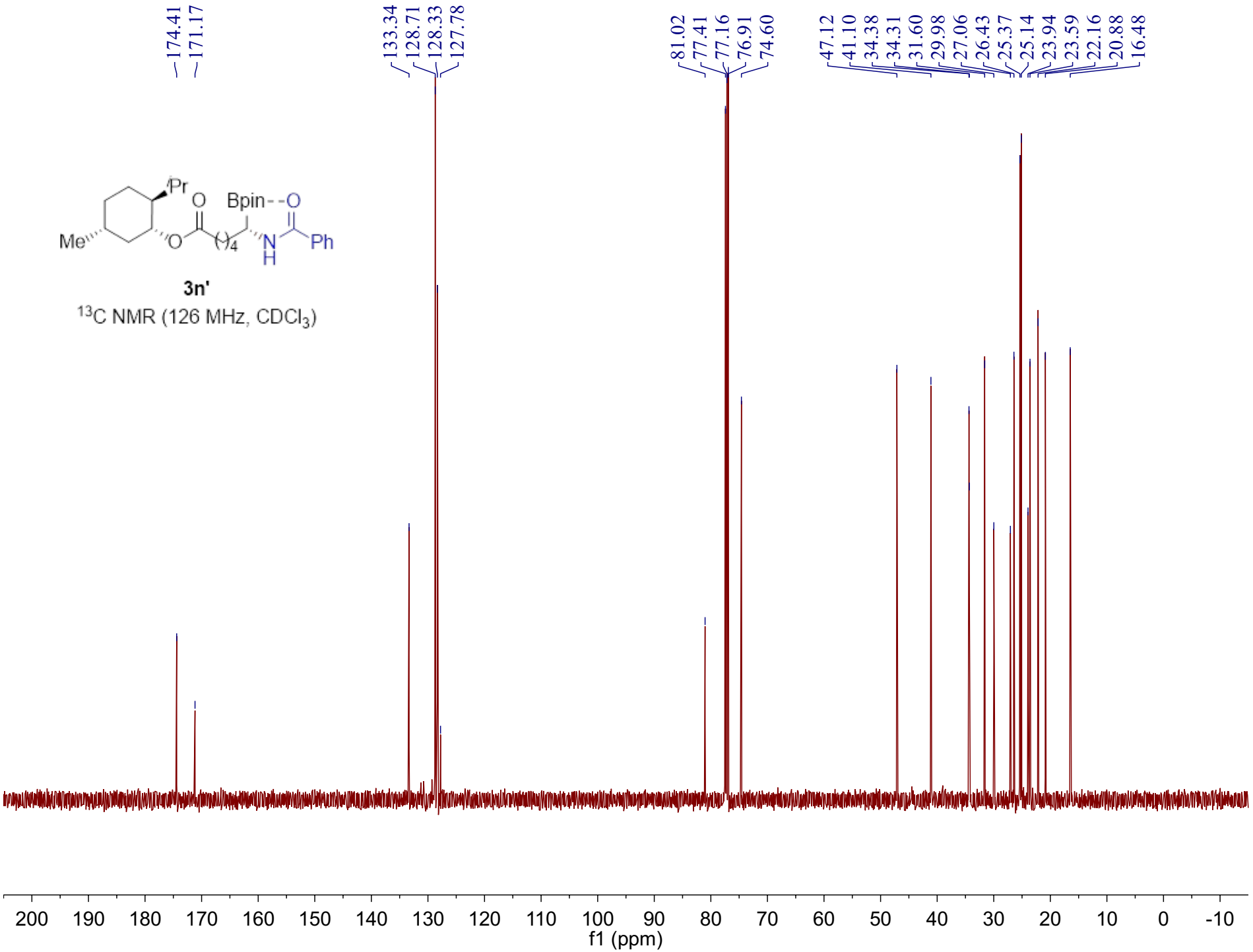
3n

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

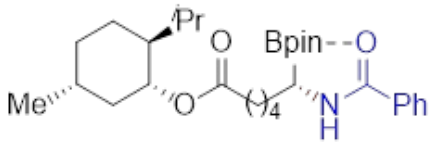
Supplementary Figure 43: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3n**.



Supplementary Figure 44: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3n'**.



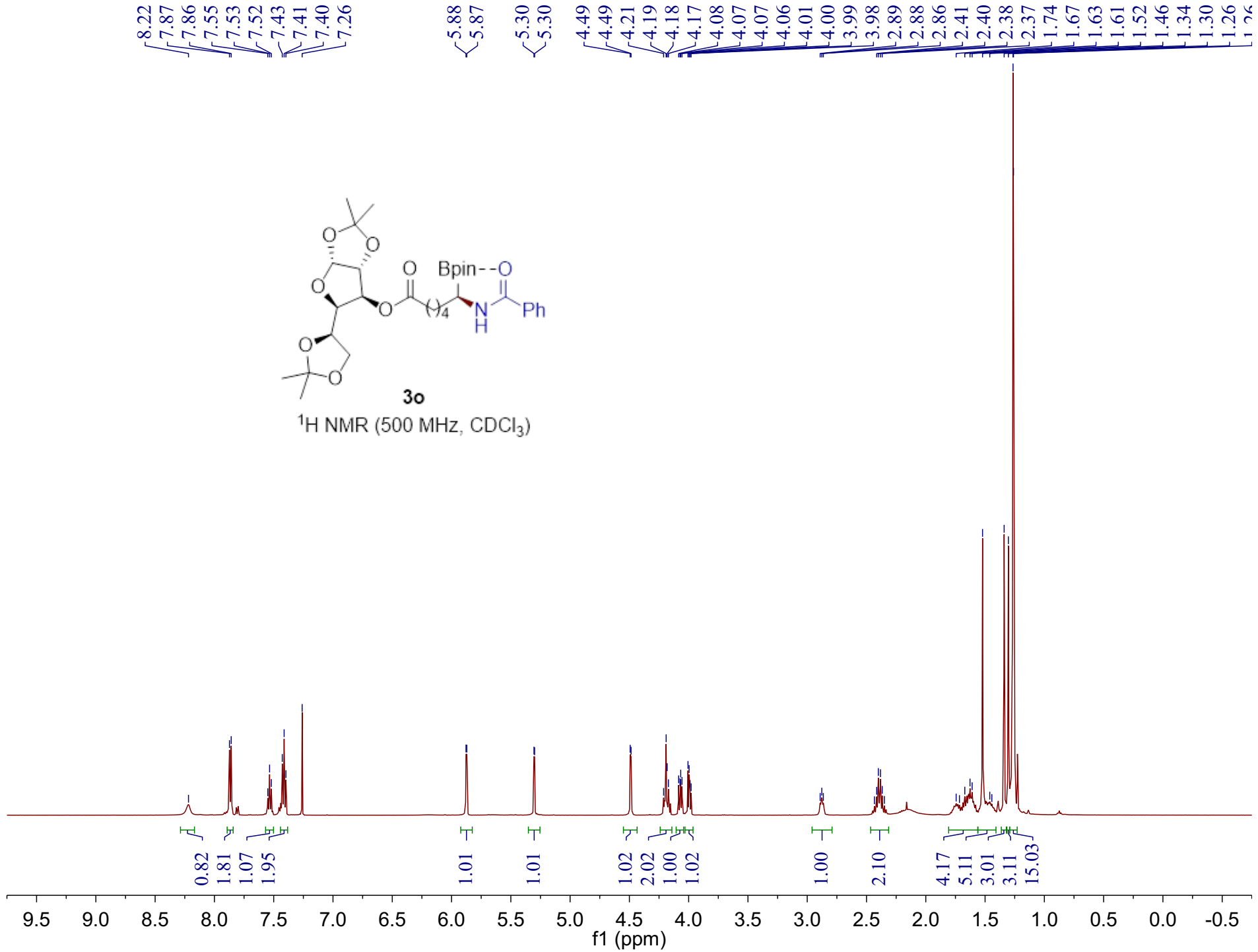
Supplementary Figure 45: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3n'**.



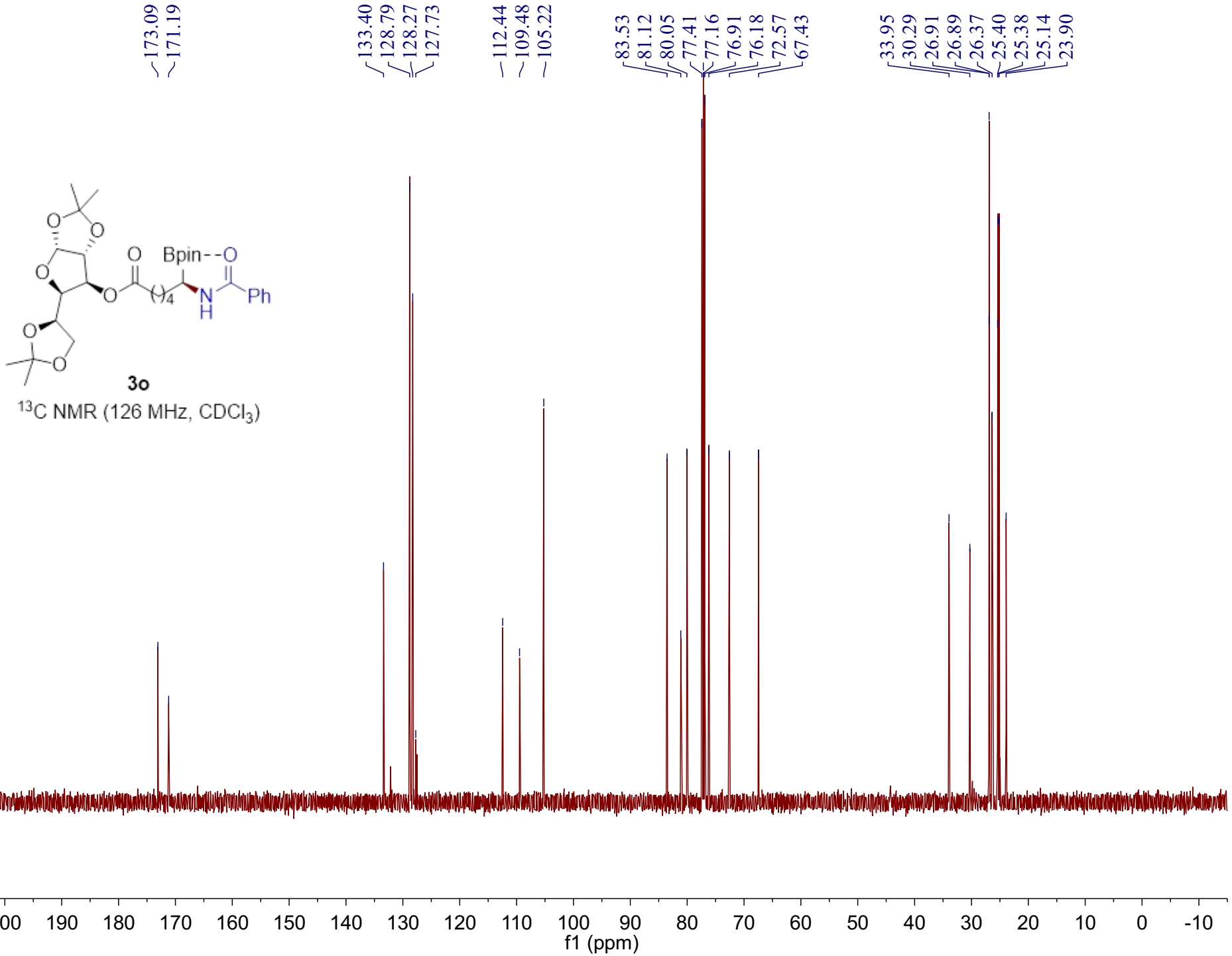
3n'

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

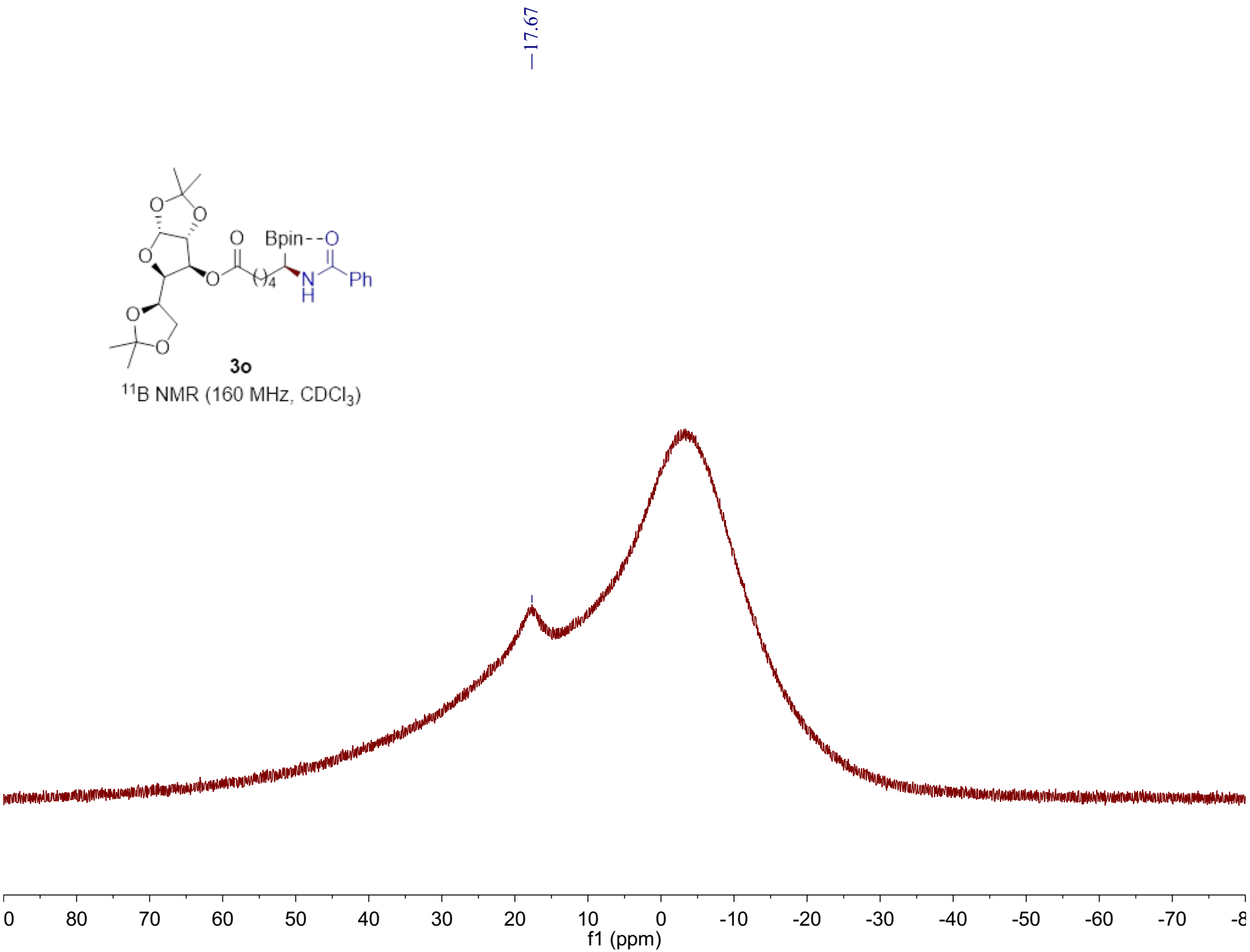
Supplementary Figure 46: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3n'**.



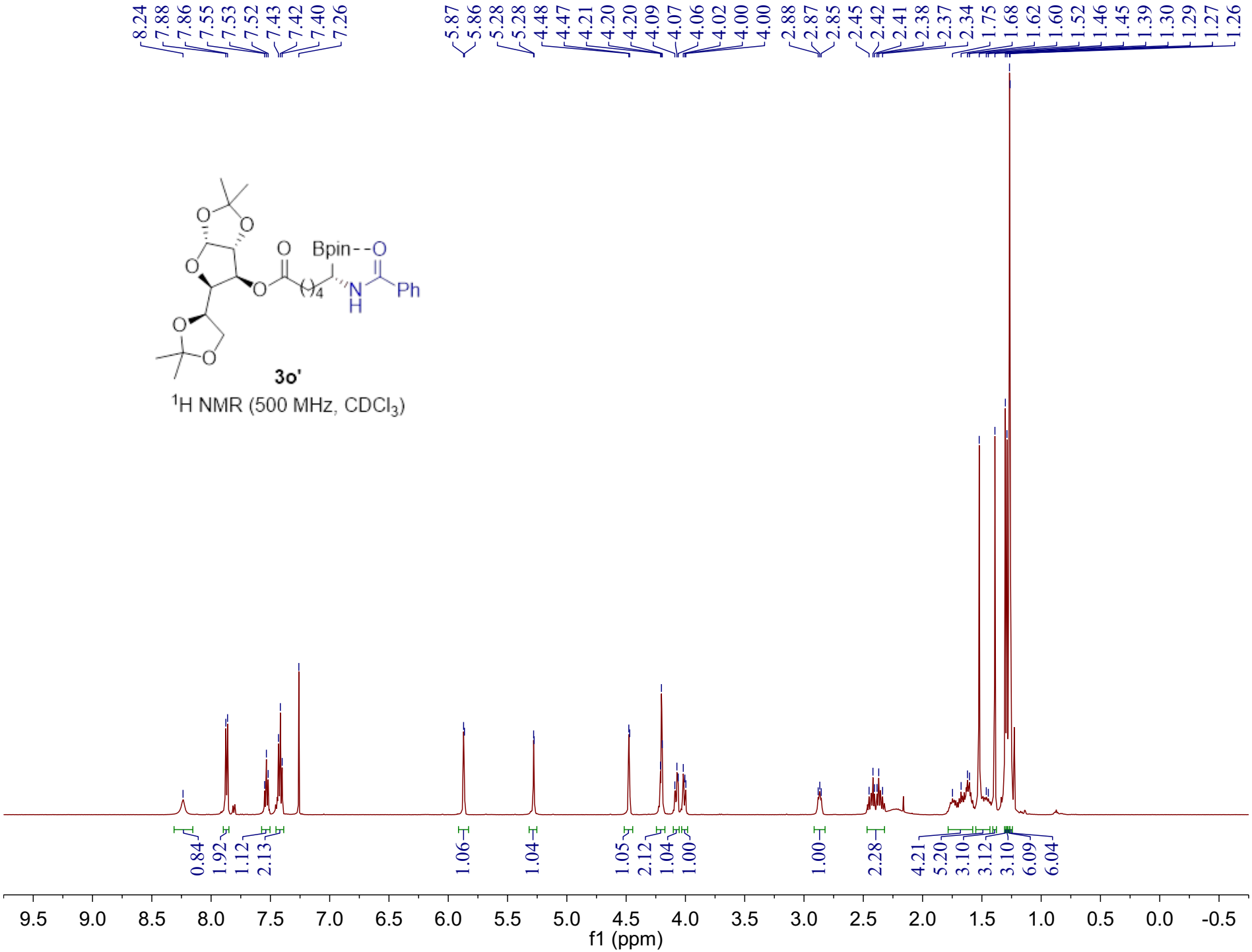
Supplementary Figure 47: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3o**.



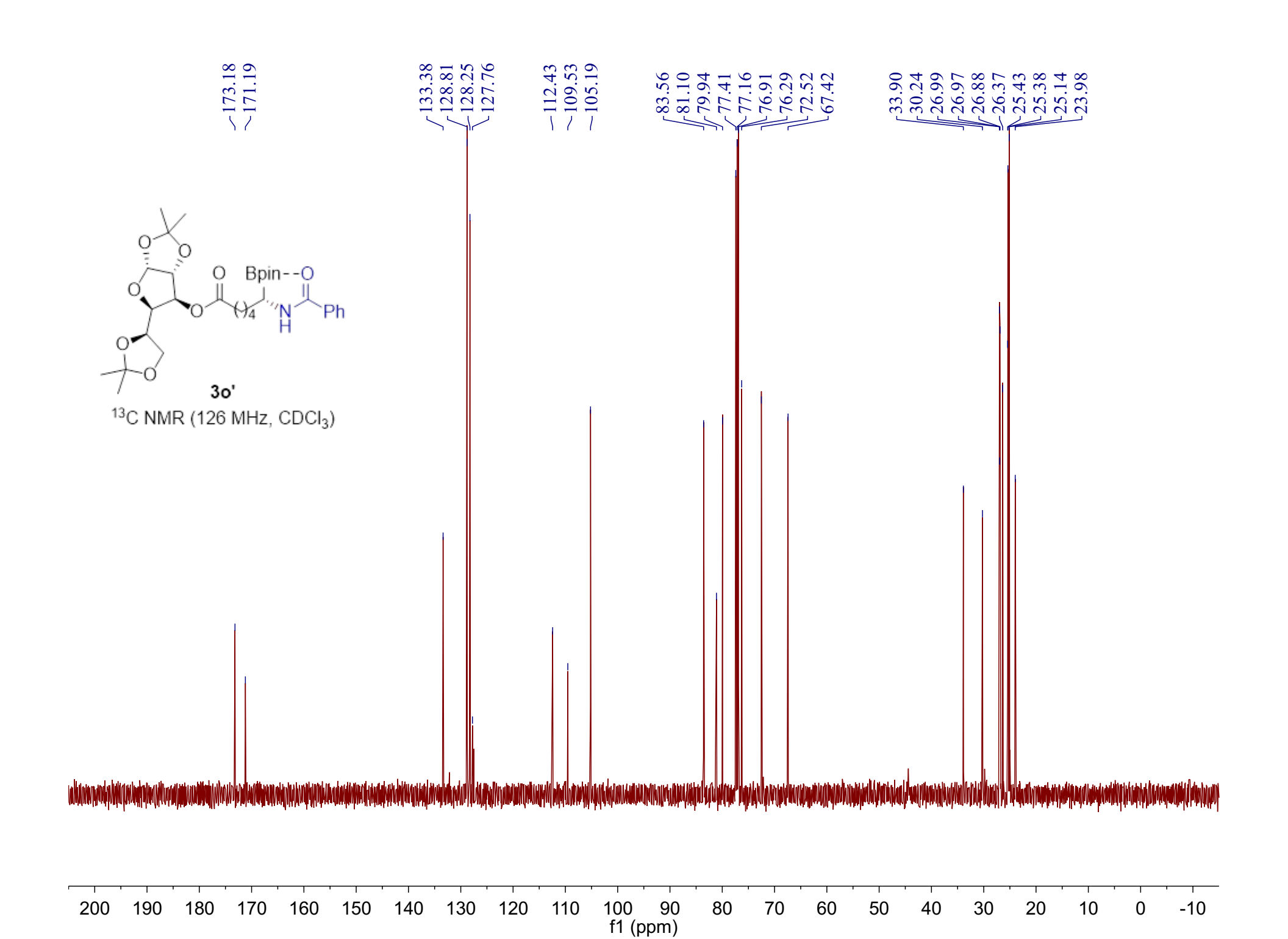
Supplementary Figure 48: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3o**.



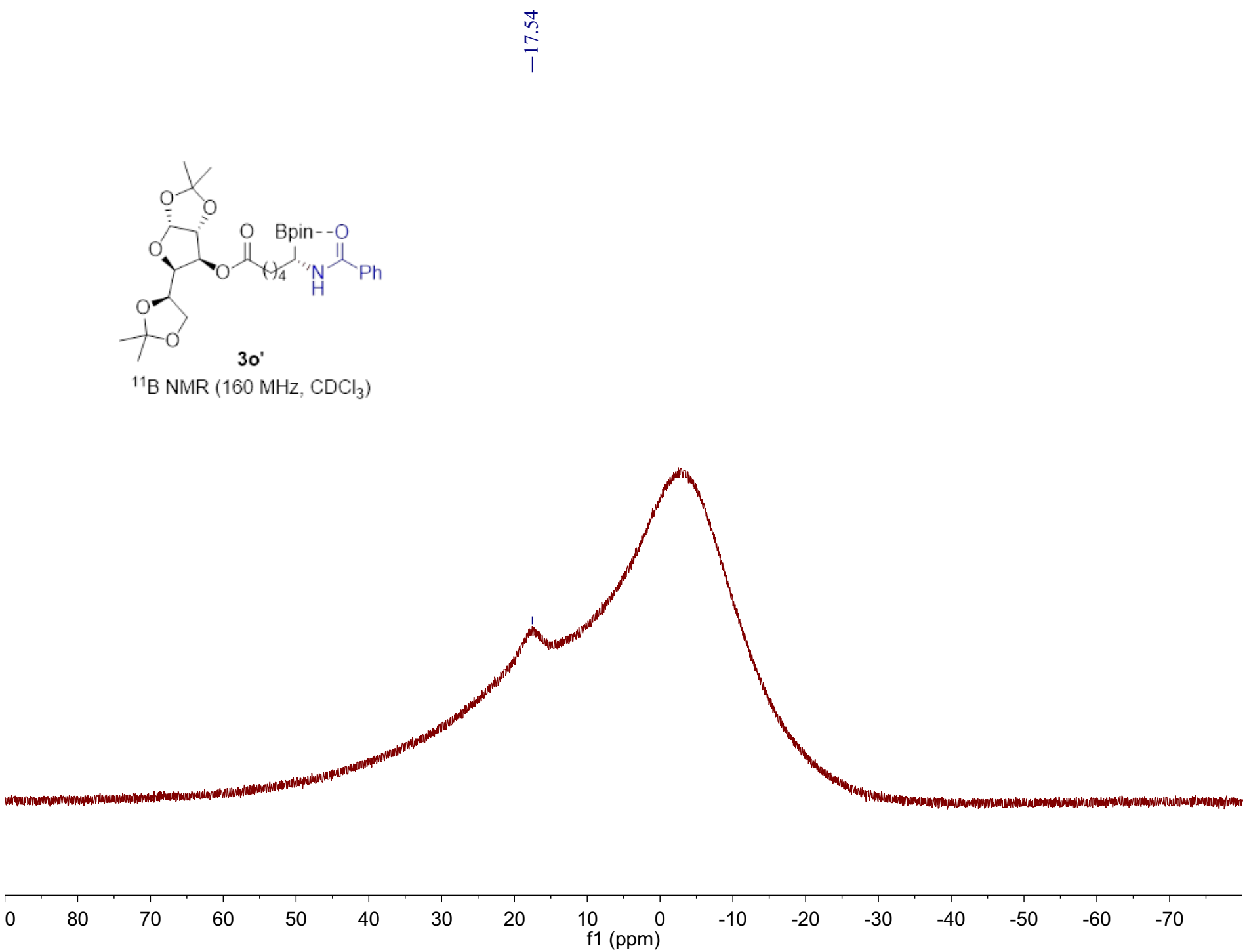
Supplementary Figure 49: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3o**.



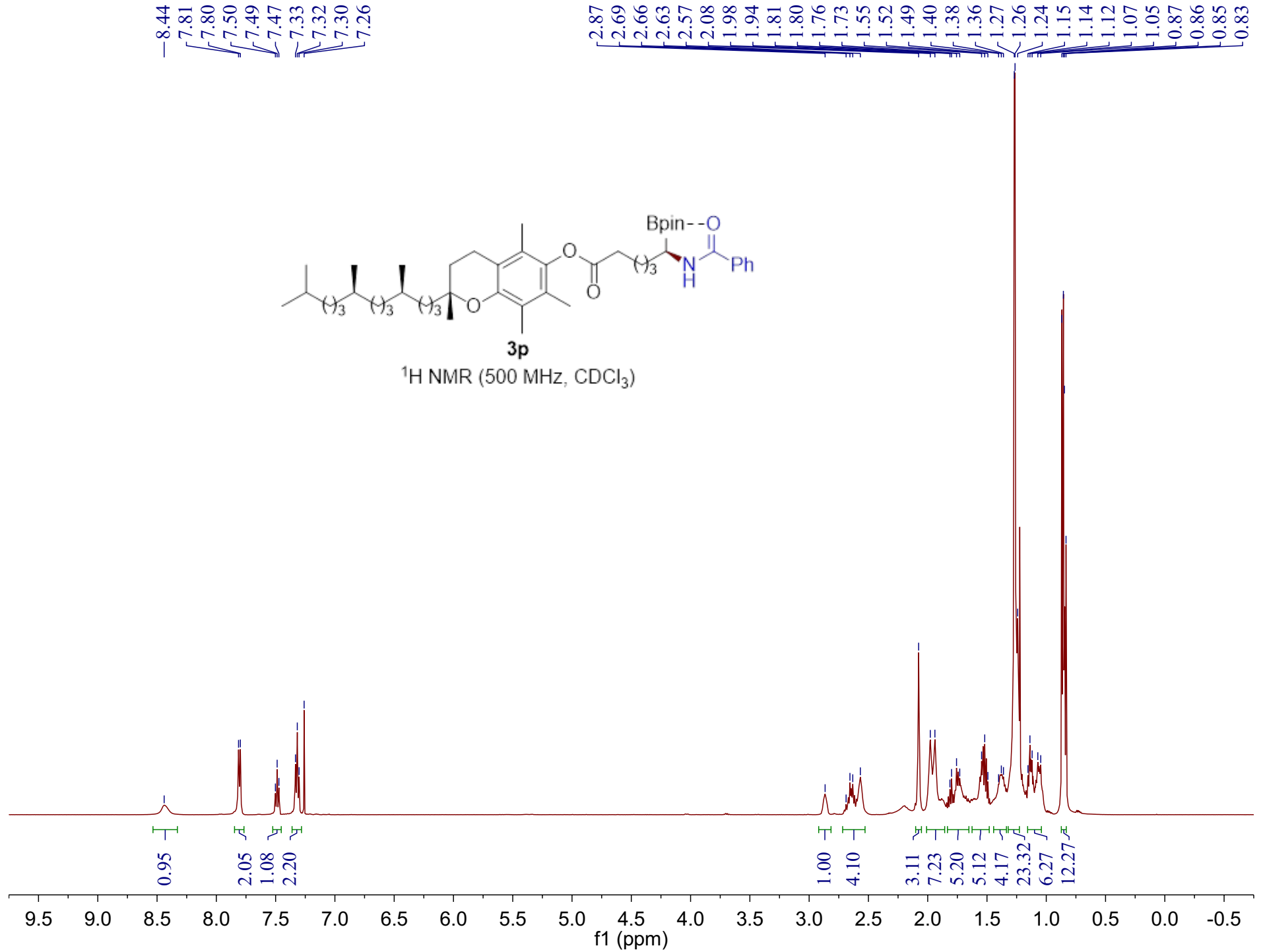
Supplementary Figure 50: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3o'**.



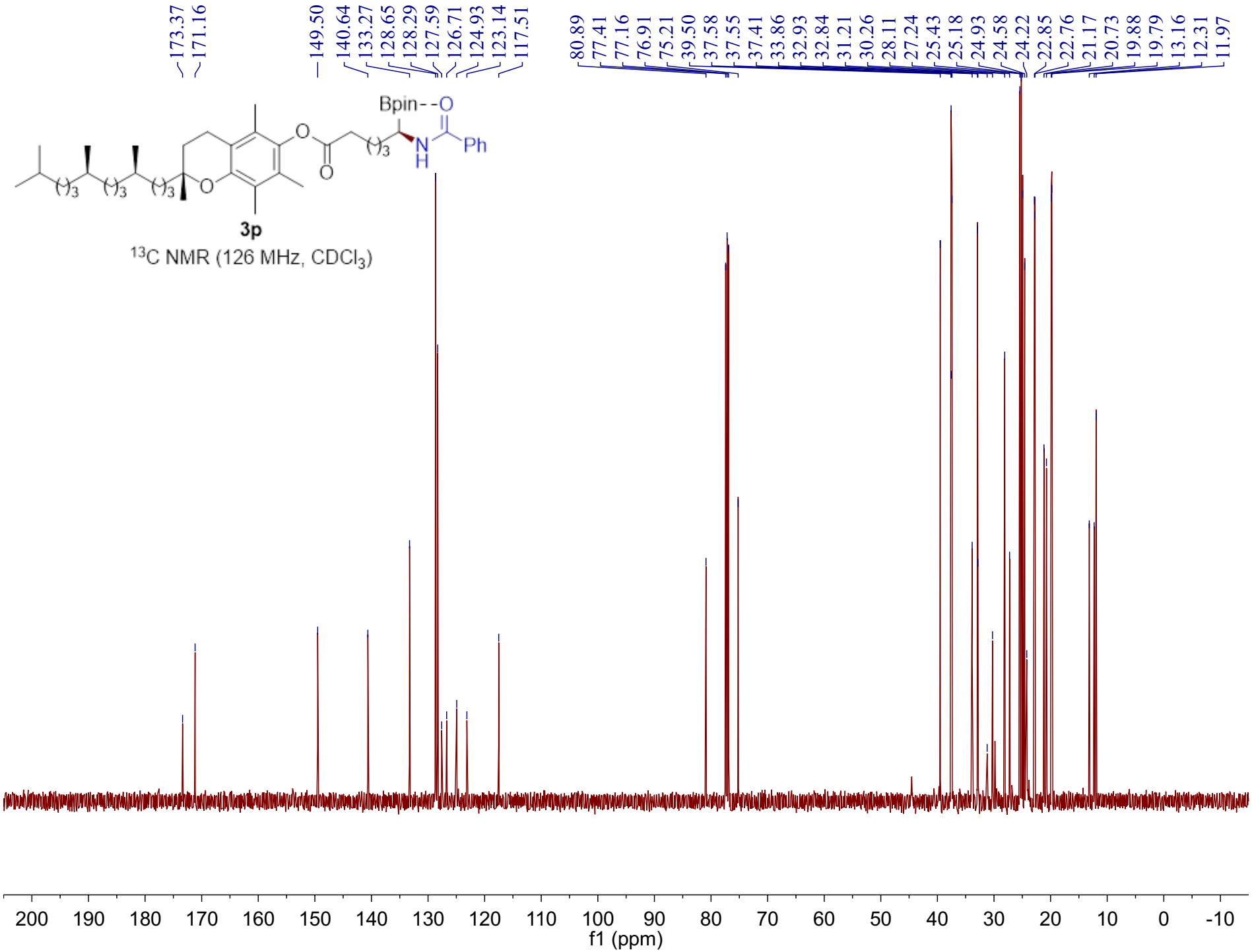
Supplementary Figure 51: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3o'**.



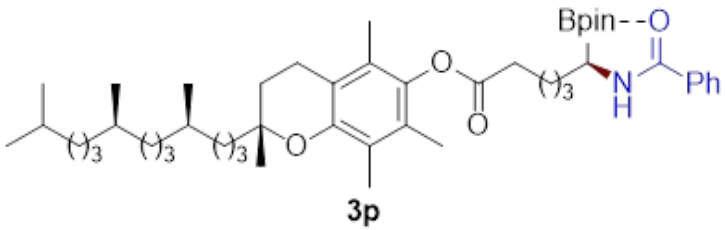
Supplementary Figure 52: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3o'**.



Supplementary Figure 53: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3p**.



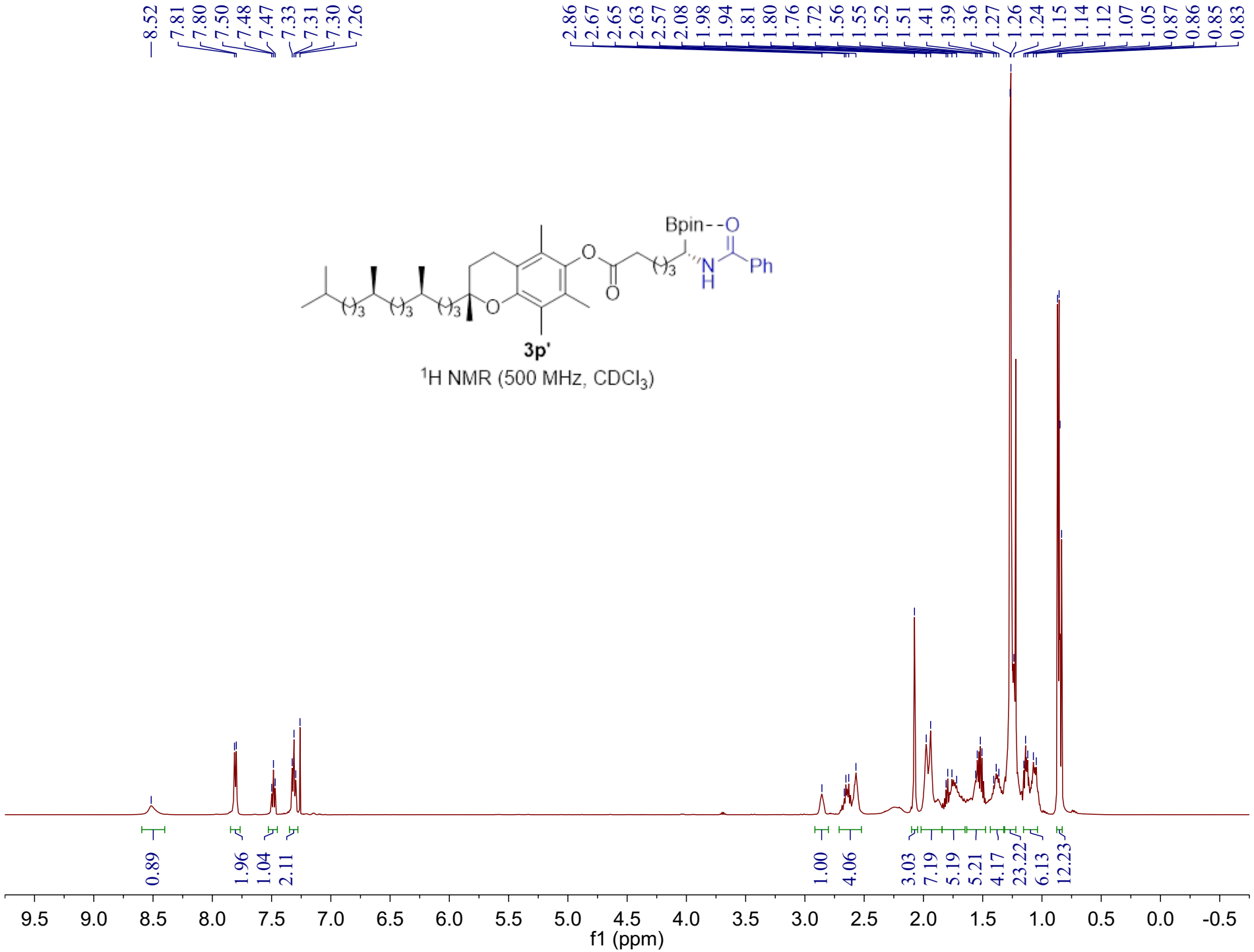
Supplementary Figure 54: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3p**.



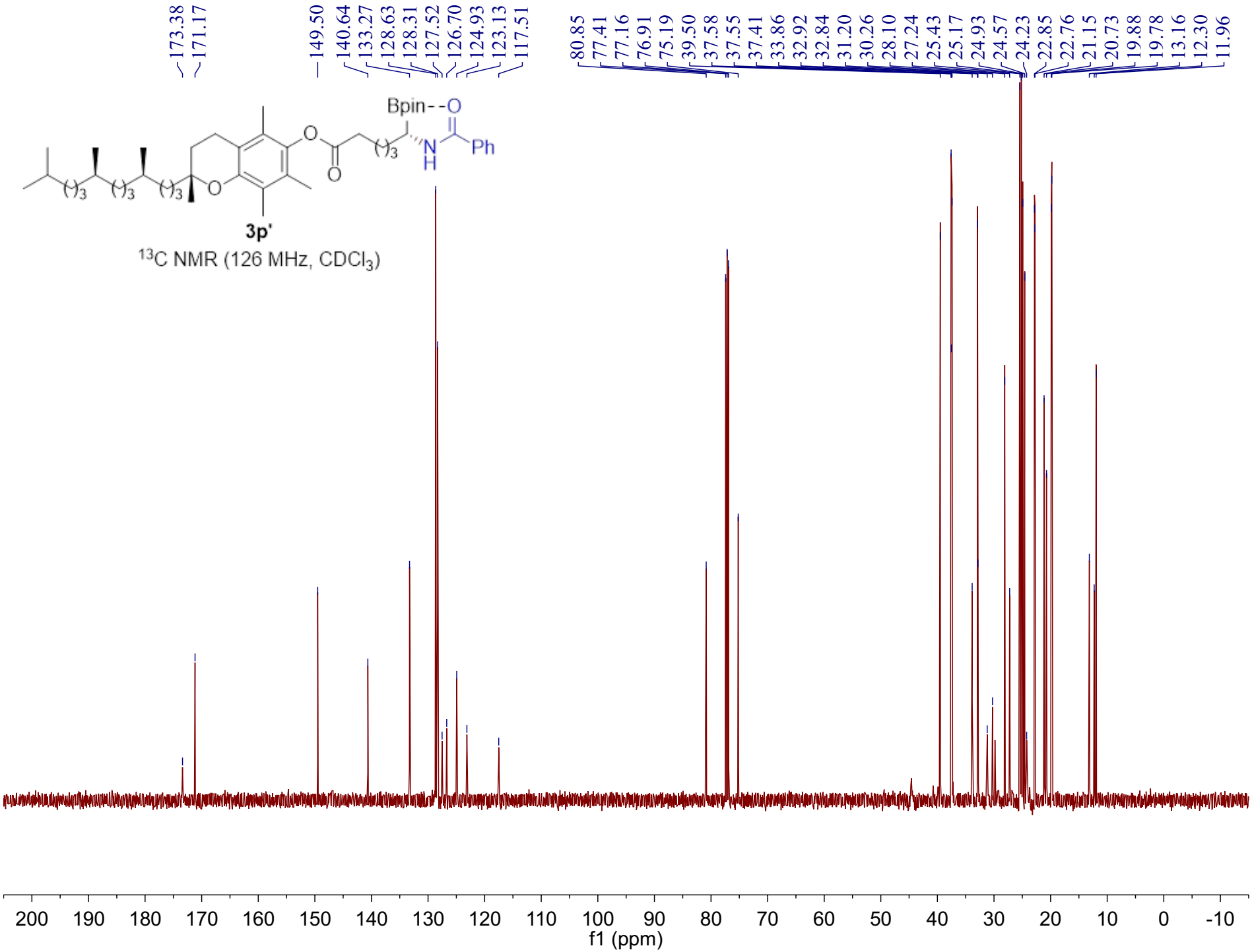
3p

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

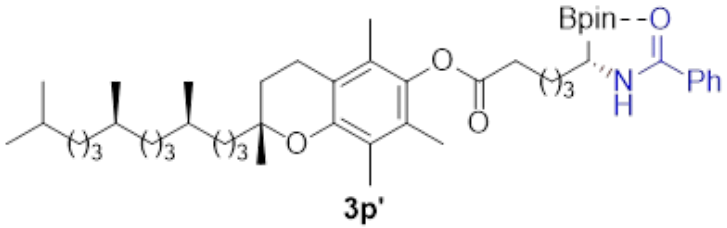
Supplementary Figure 55: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3p**.



Supplementary Figure 56: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3p'**.



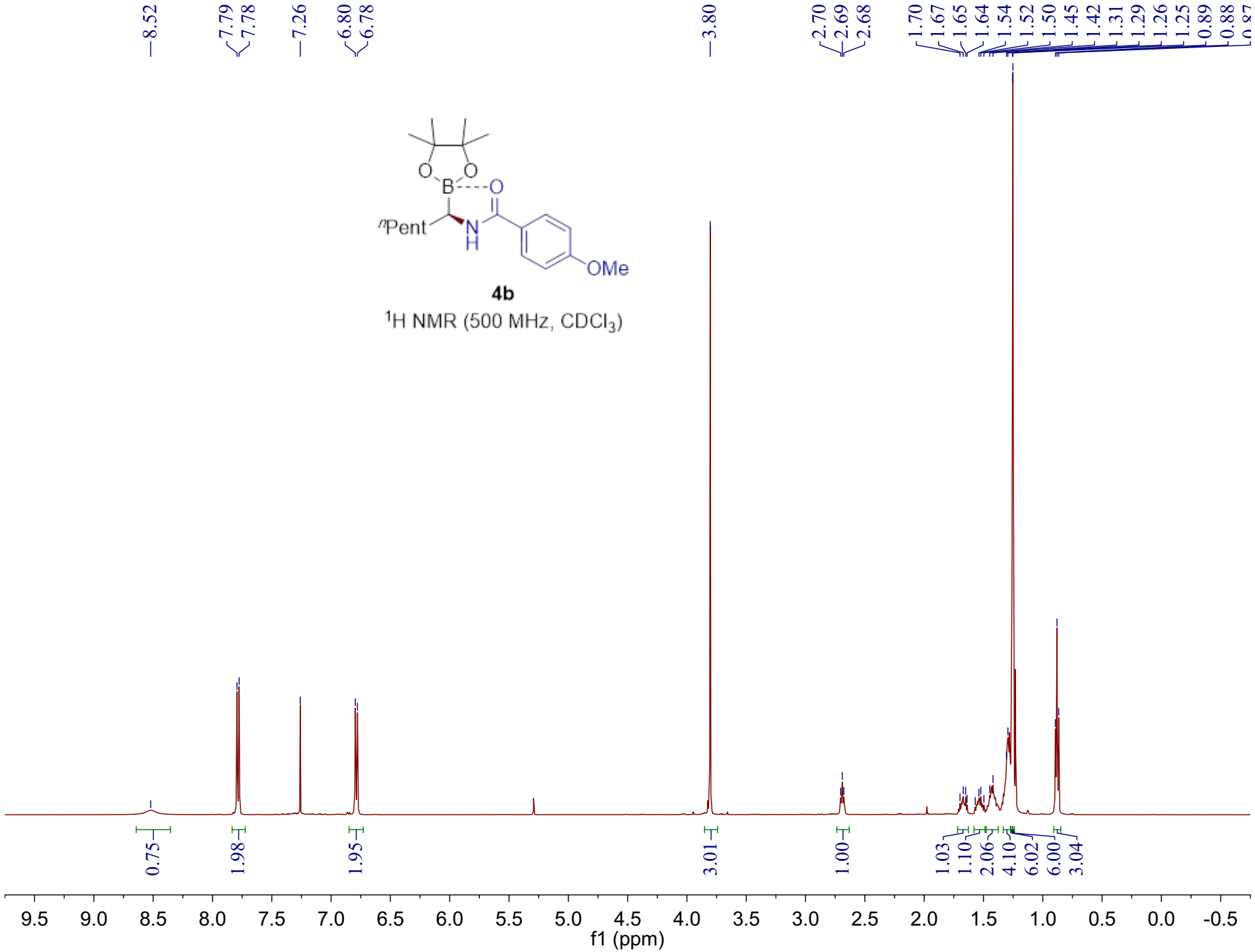
Supplementary Figure 57: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3p'**.



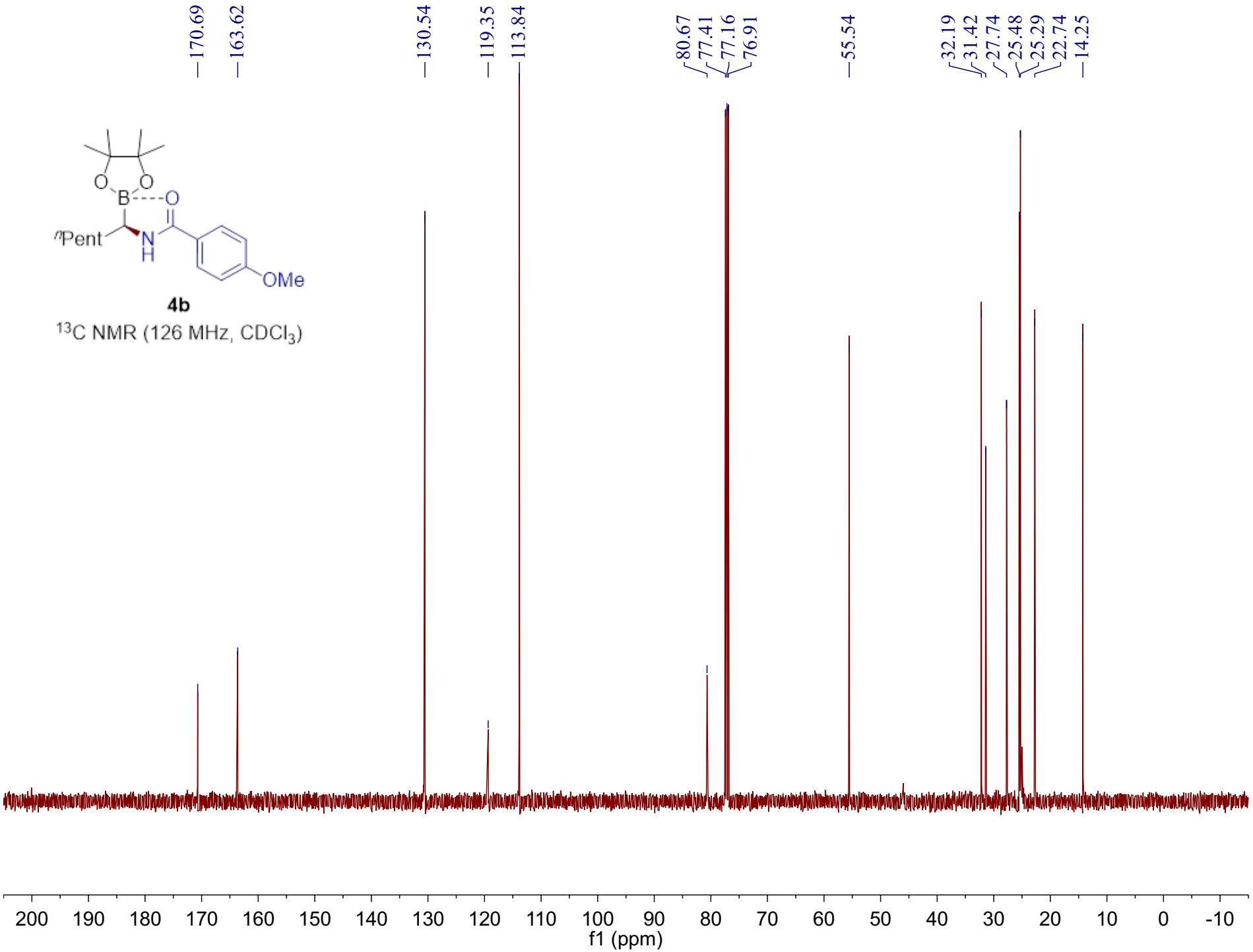
3p'

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

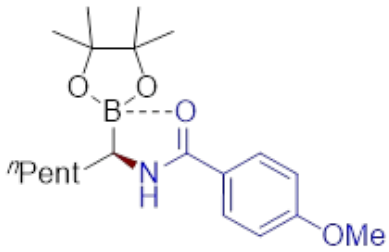
Supplementary Figure 58: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3p'**.



Supplementary Figure 59: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4b**.



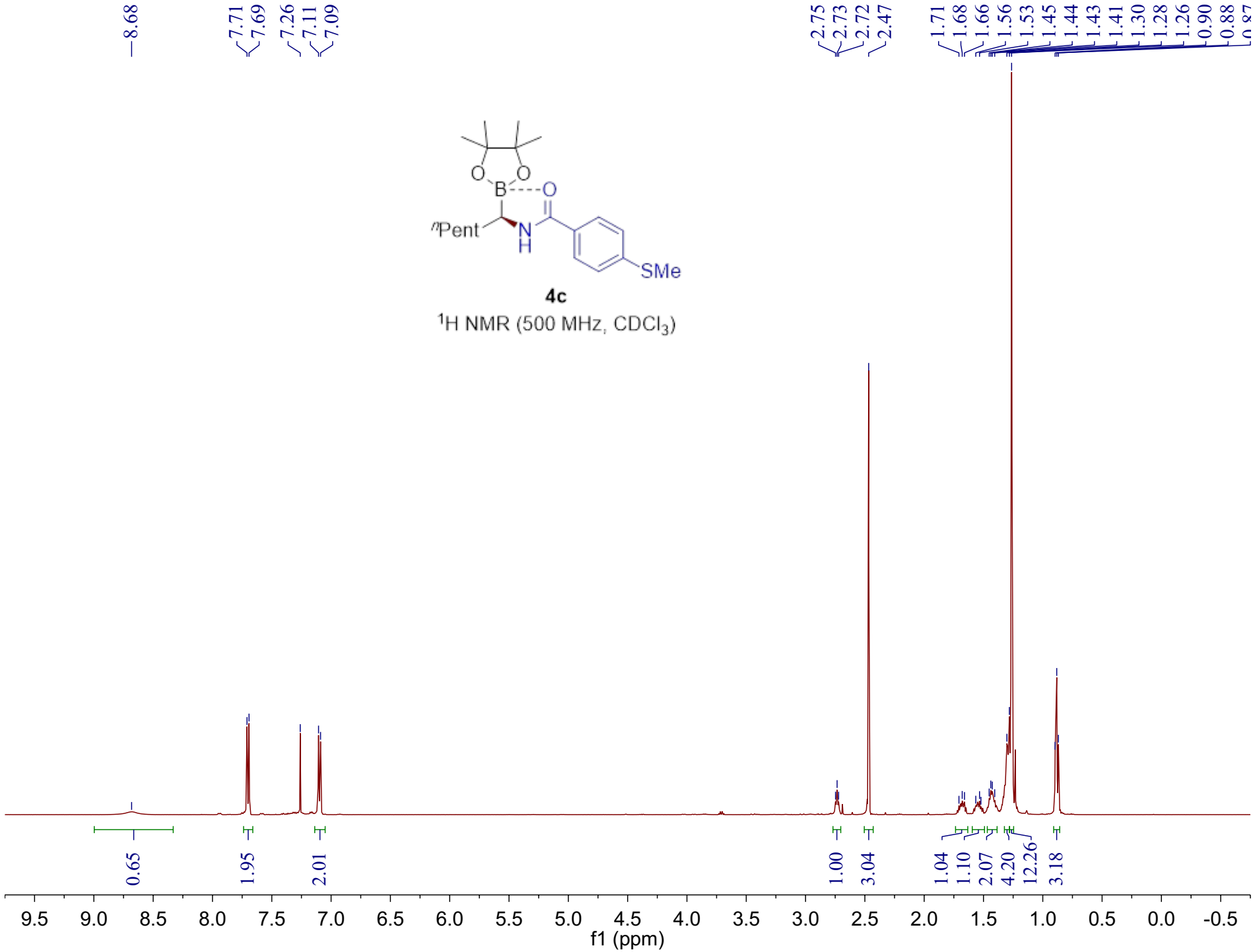
Supplementary Figure 60: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4b**.



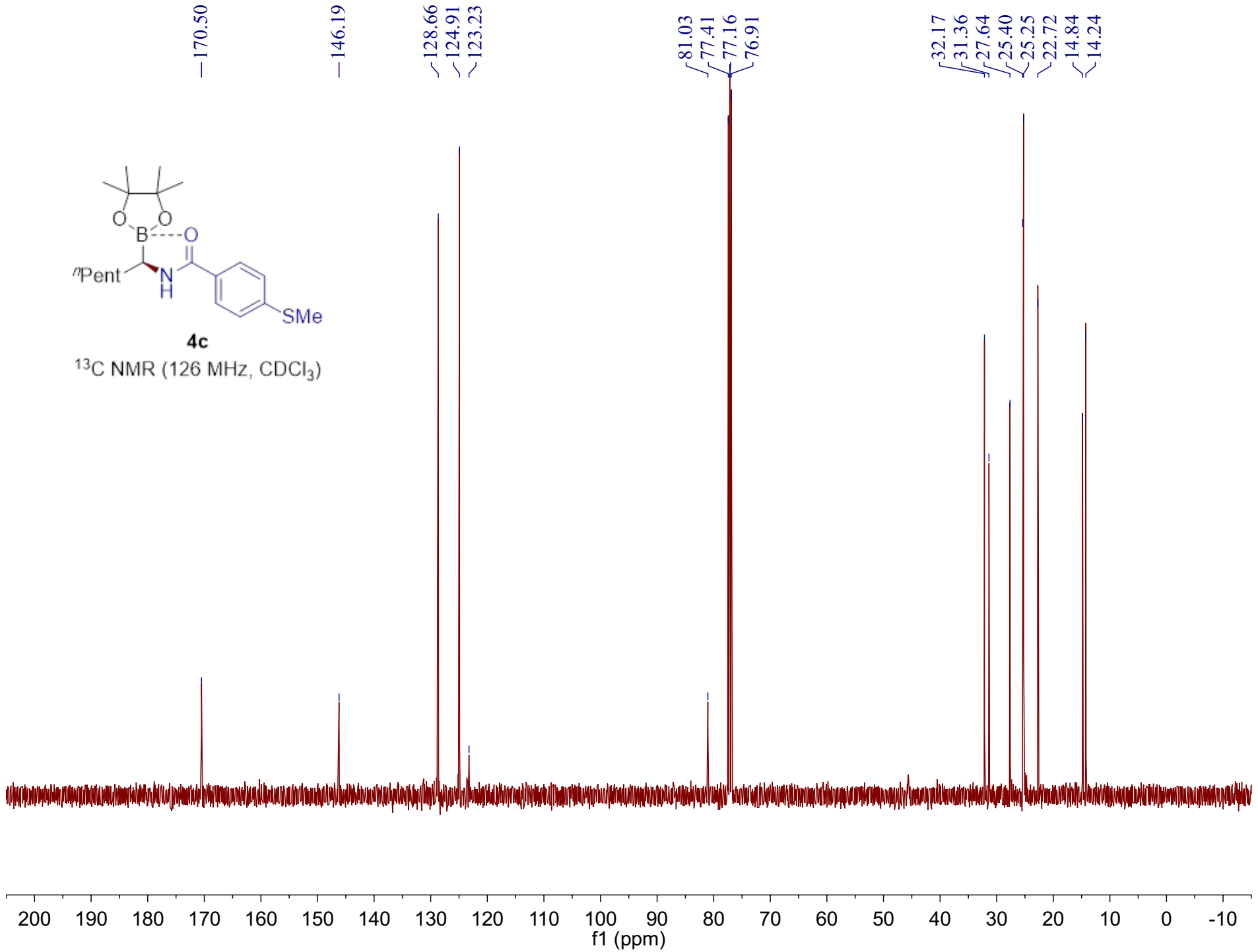
4b

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

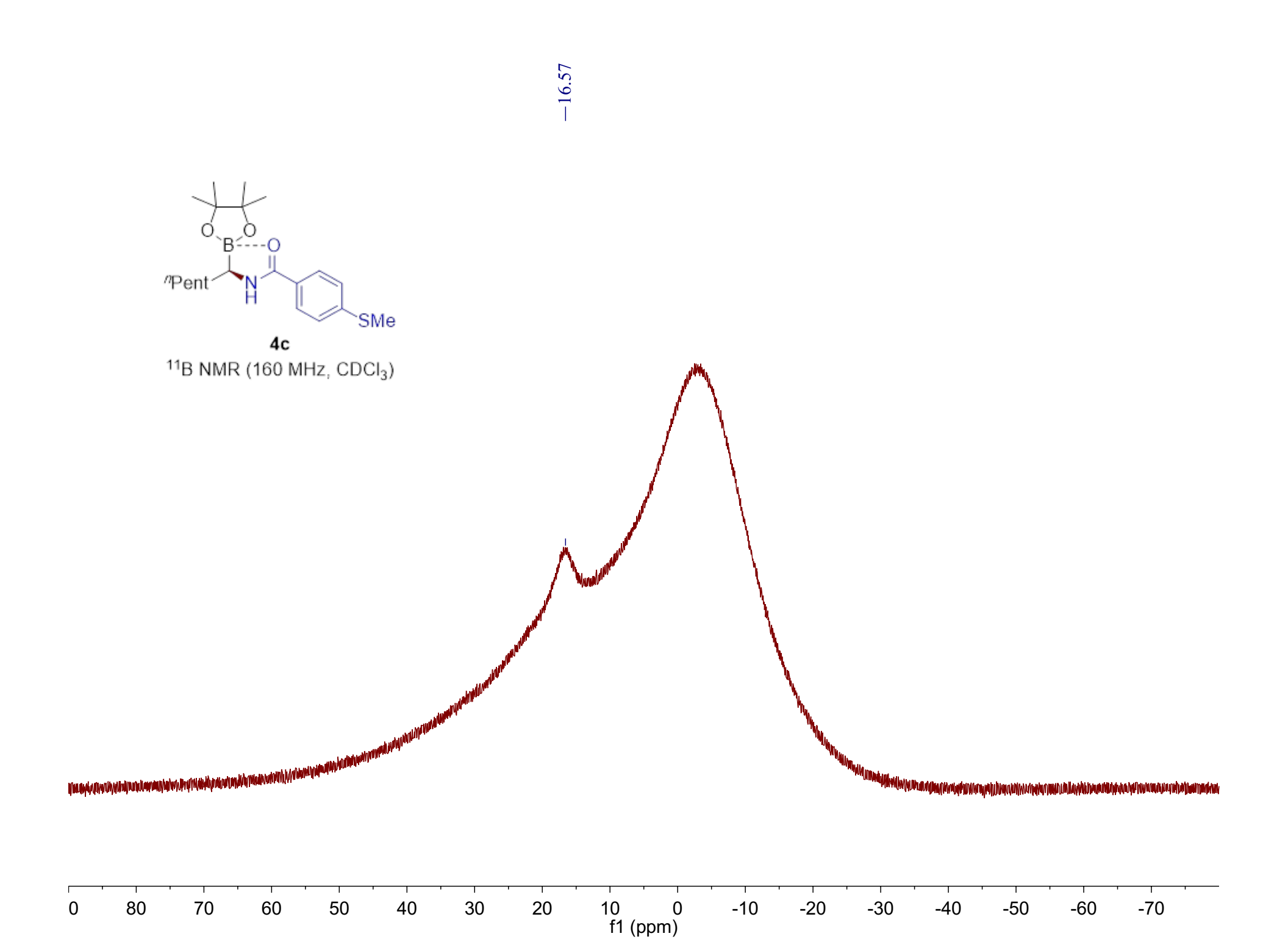
Supplementary Figure 61: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4b**.



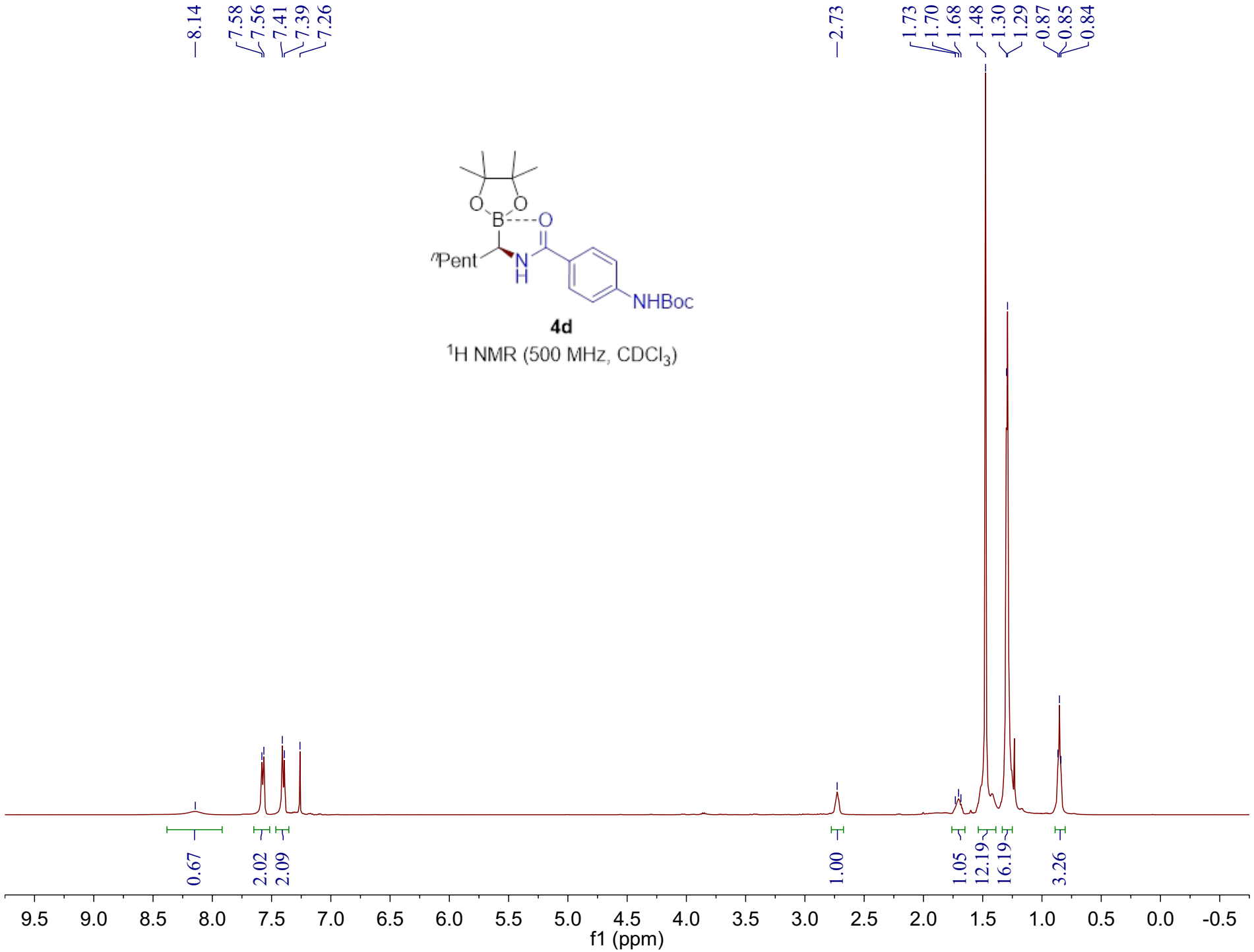
Supplementary Figure 62: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4c**.



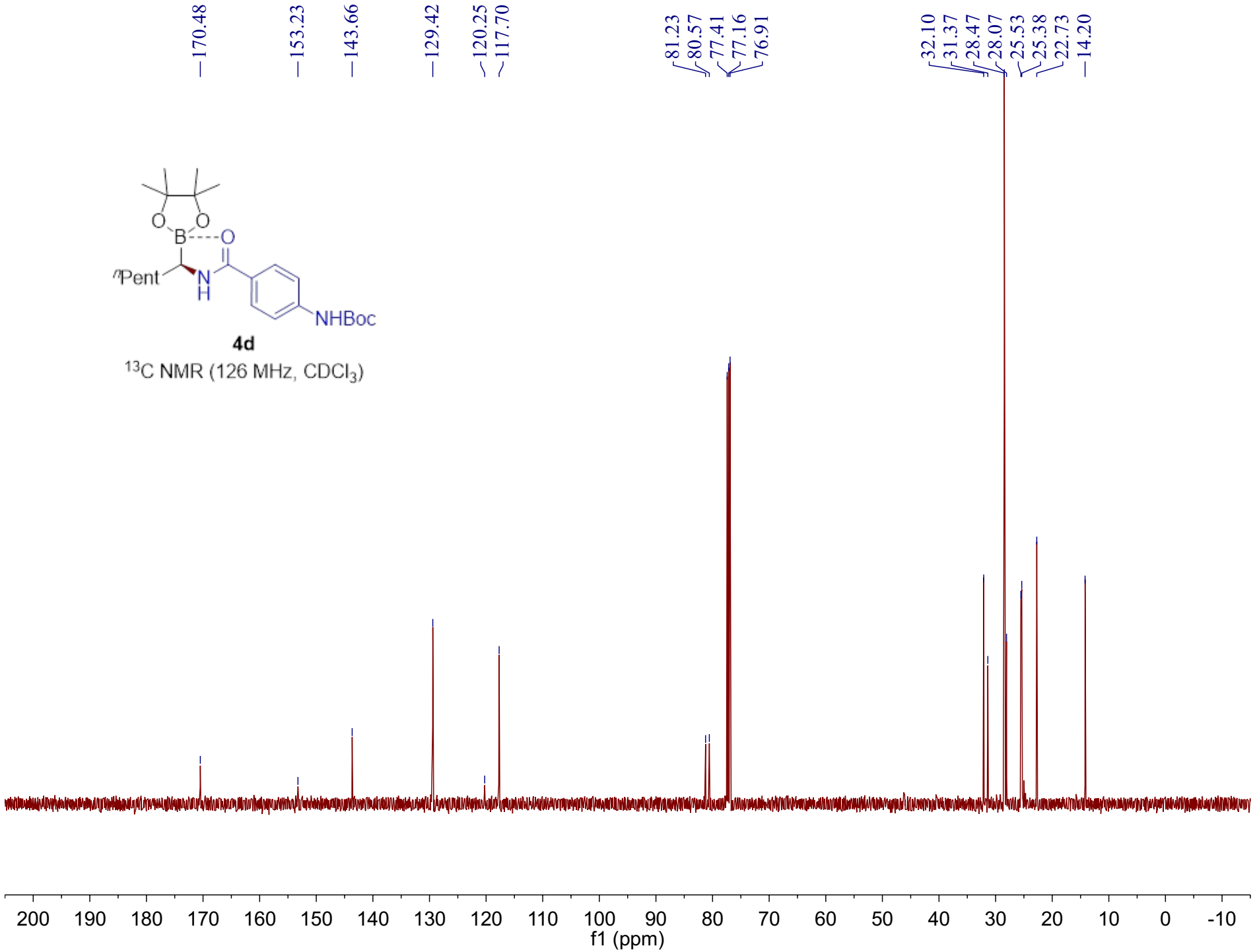
Supplementary Figure 63: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4c**.



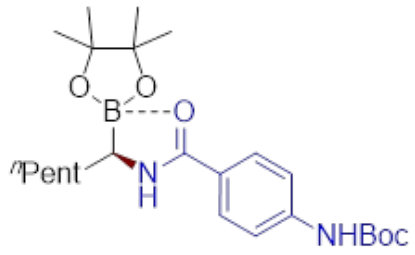
Supplementary Figure 64: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4c**.



Supplementary Figure 65: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4d**.



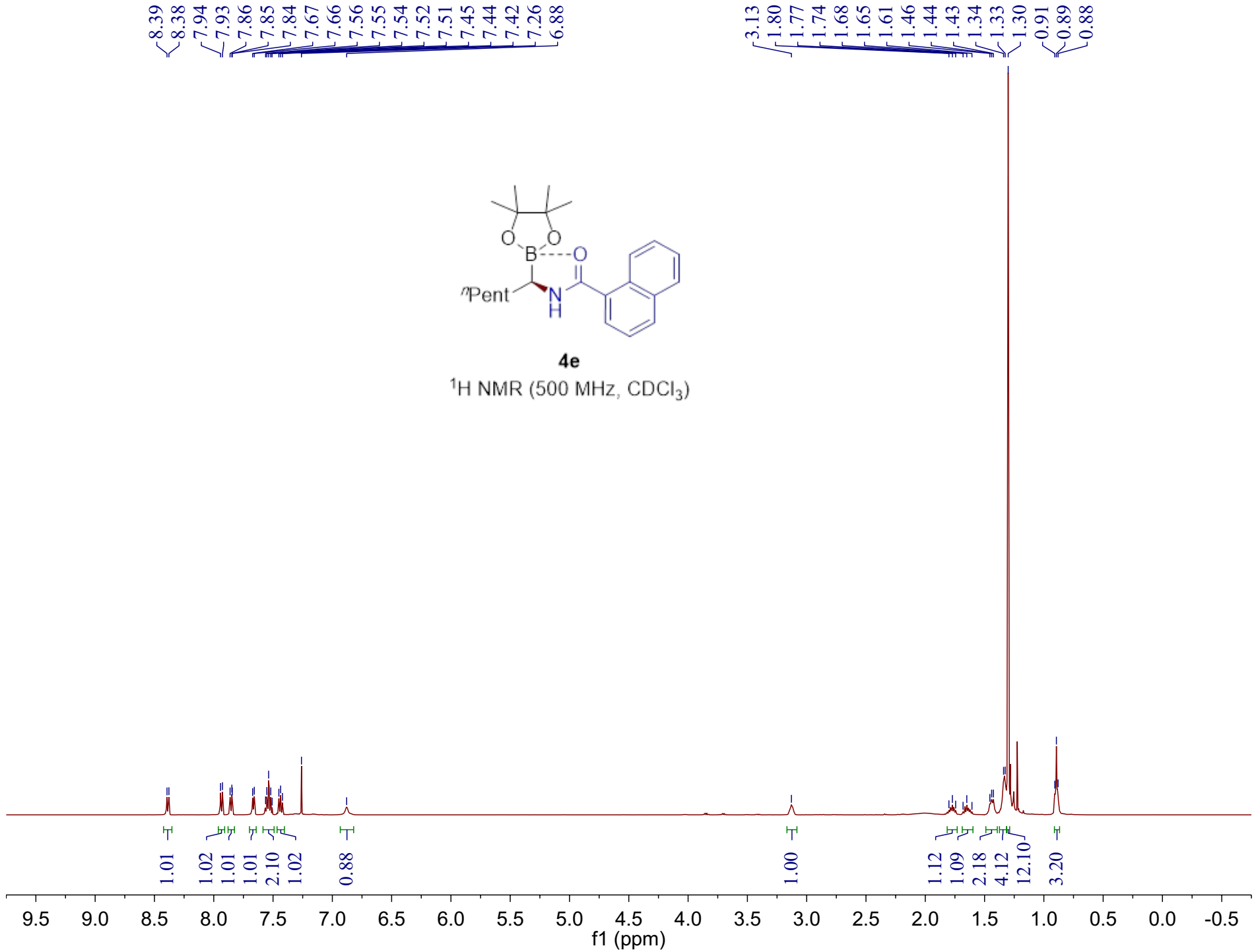
Supplementary Figure 66: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4d**.



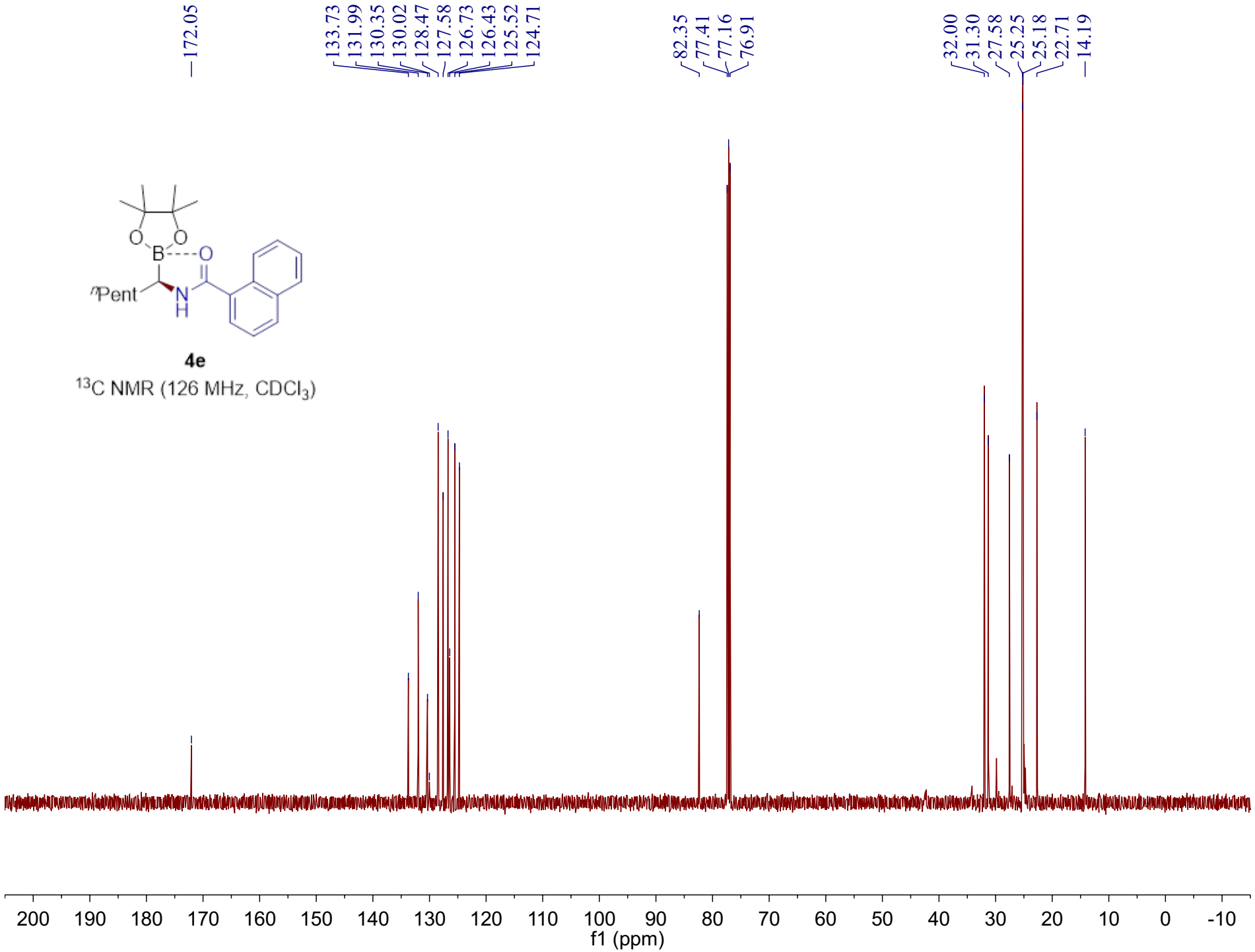
4d

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

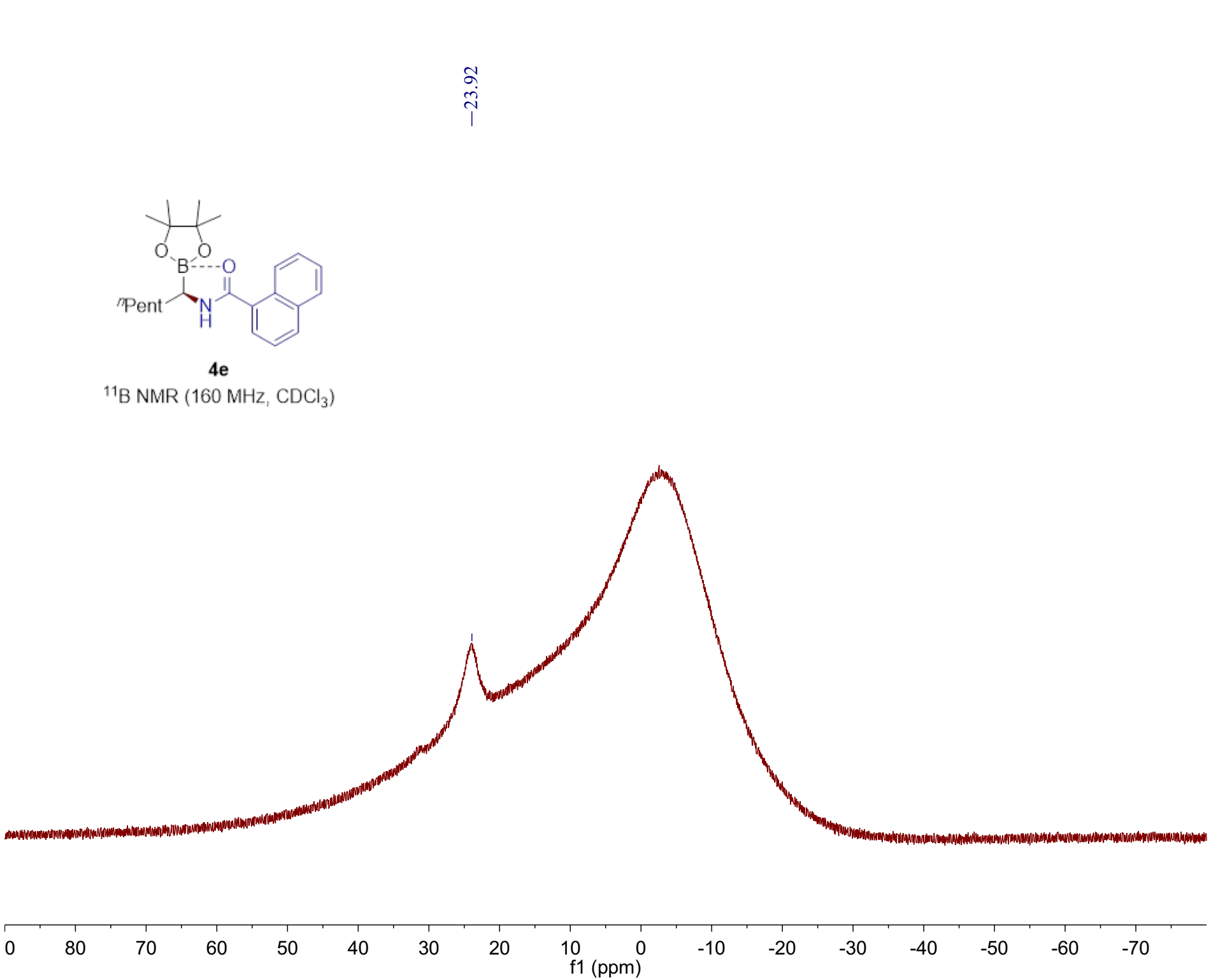
Supplementary Figure 67: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4d**.



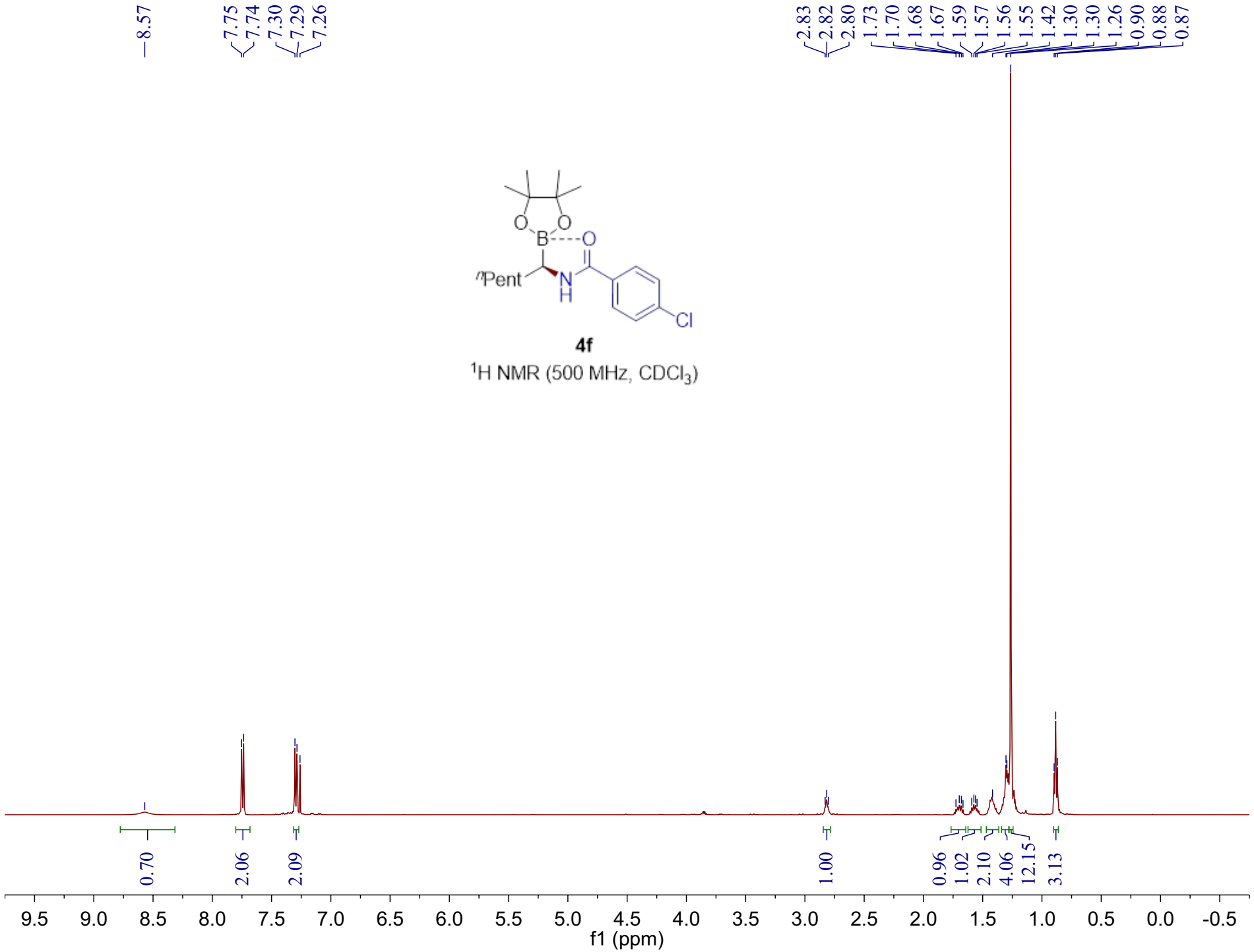
Supplementary Figure 68: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4e**.



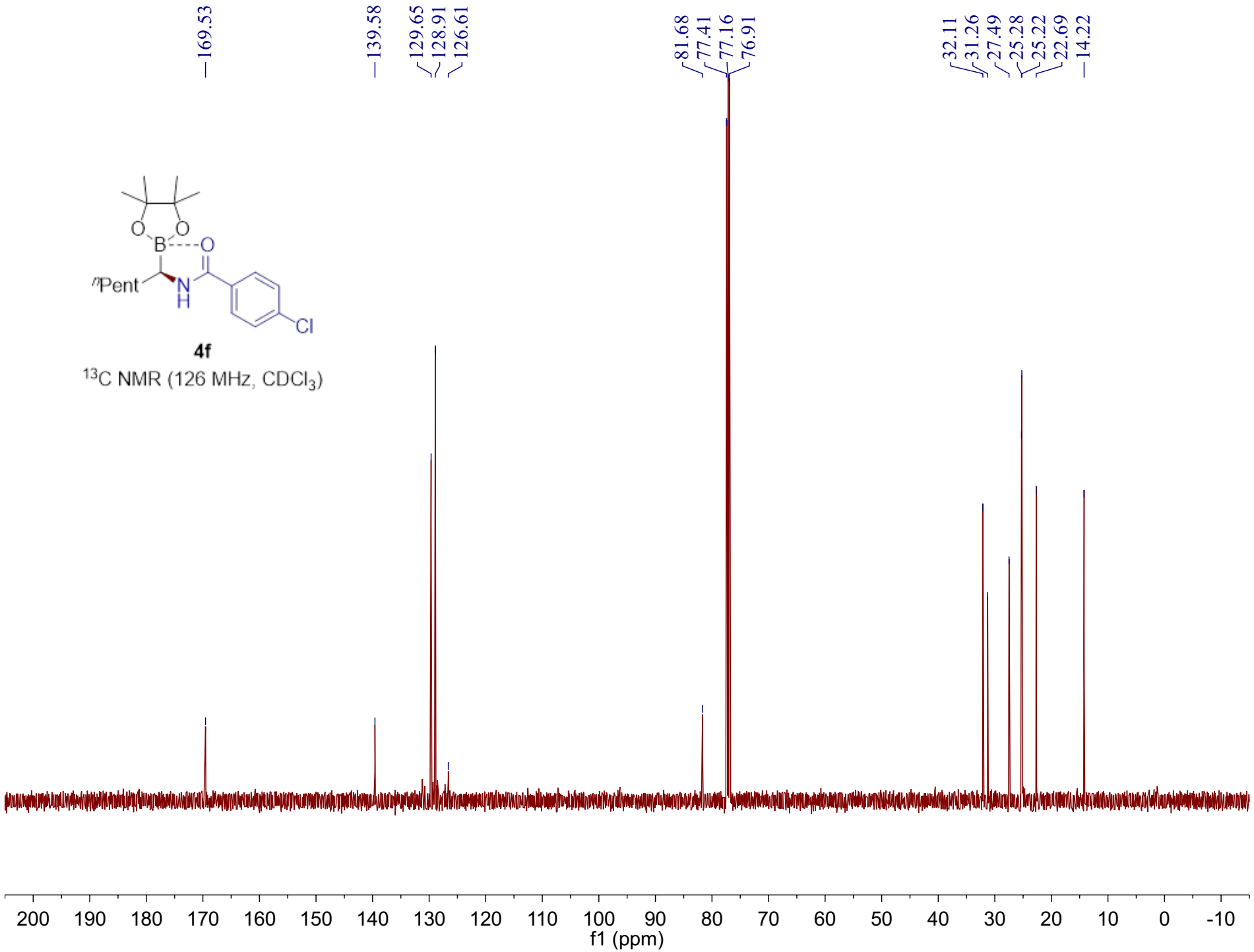
Supplementary Figure 69: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4e**.



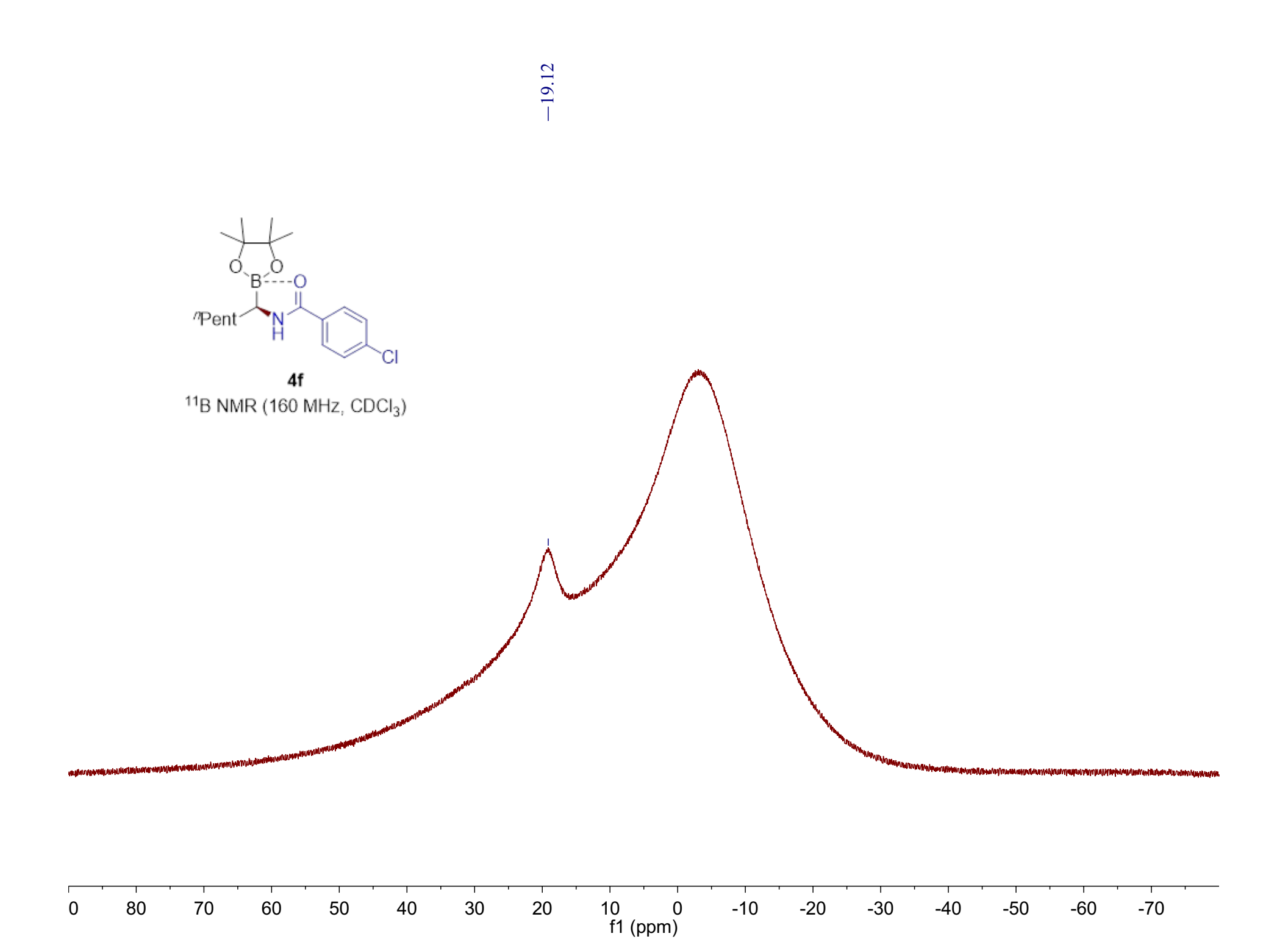
Supplementary Figure 70: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4e**.



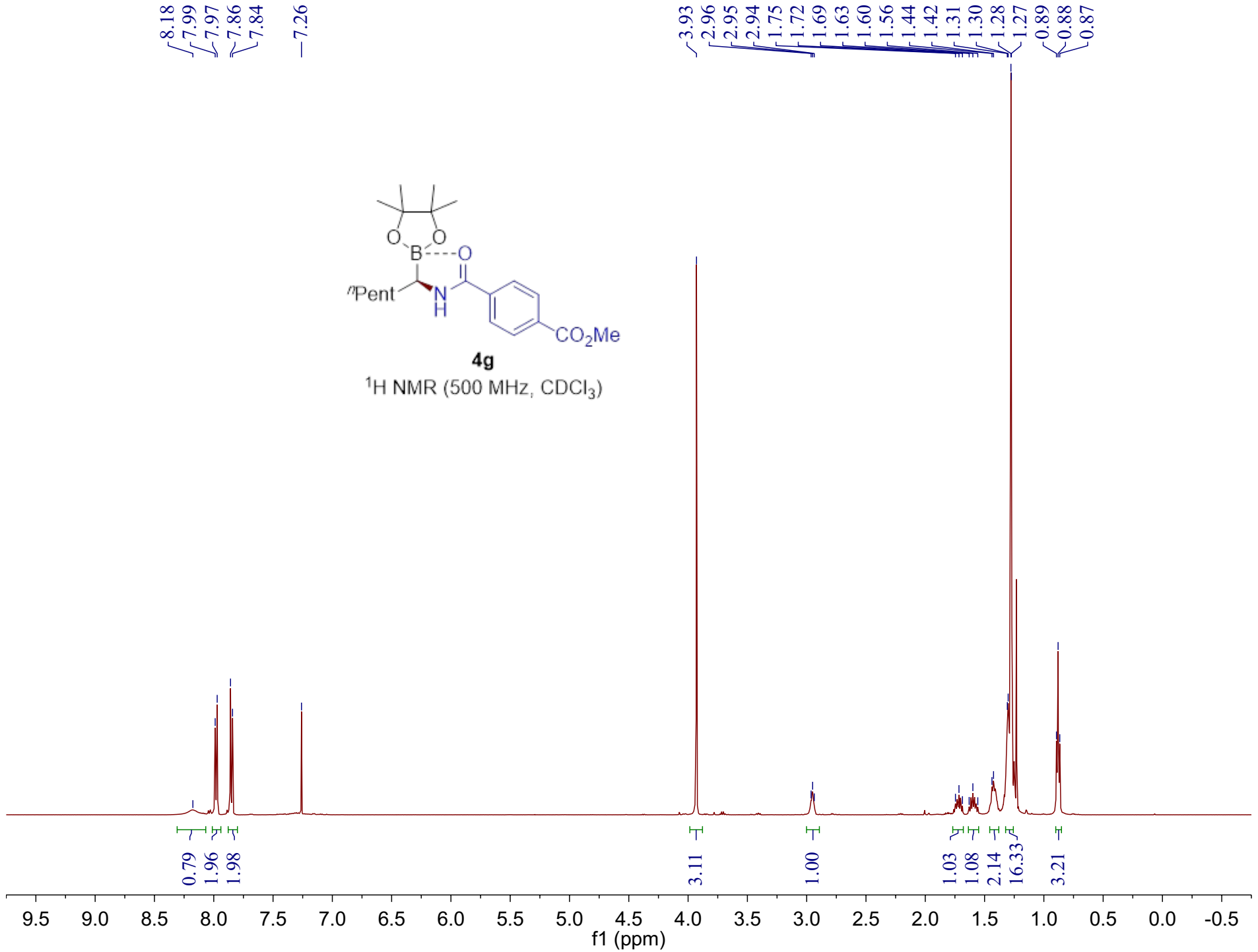
Supplementary Figure 71: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4f**.



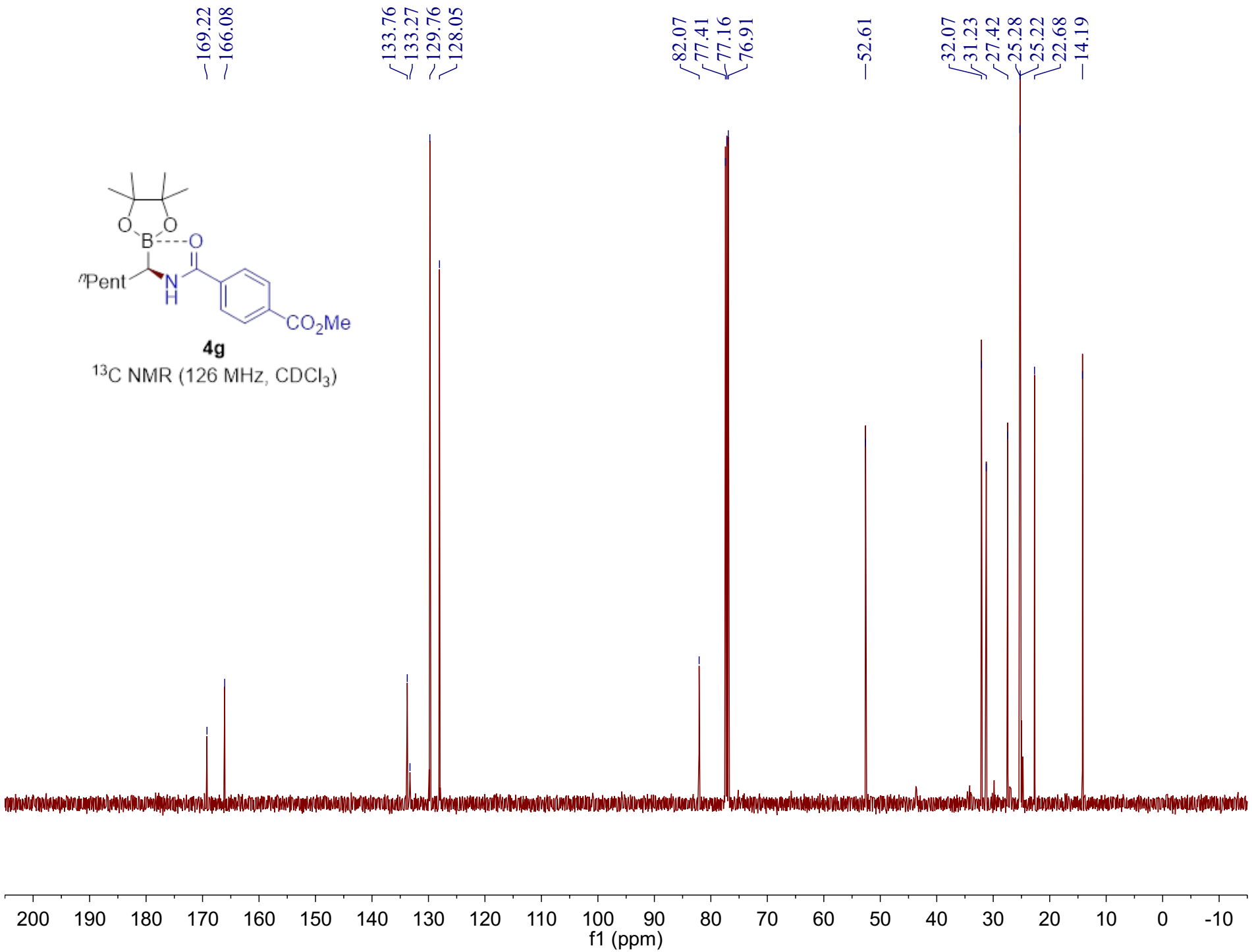
Supplementary Figure 72: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4f**.



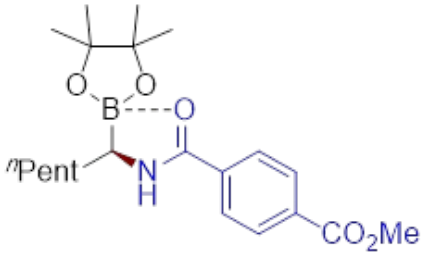
Supplementary Figure 73: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4f**.



Supplementary Figure 74: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4g**.



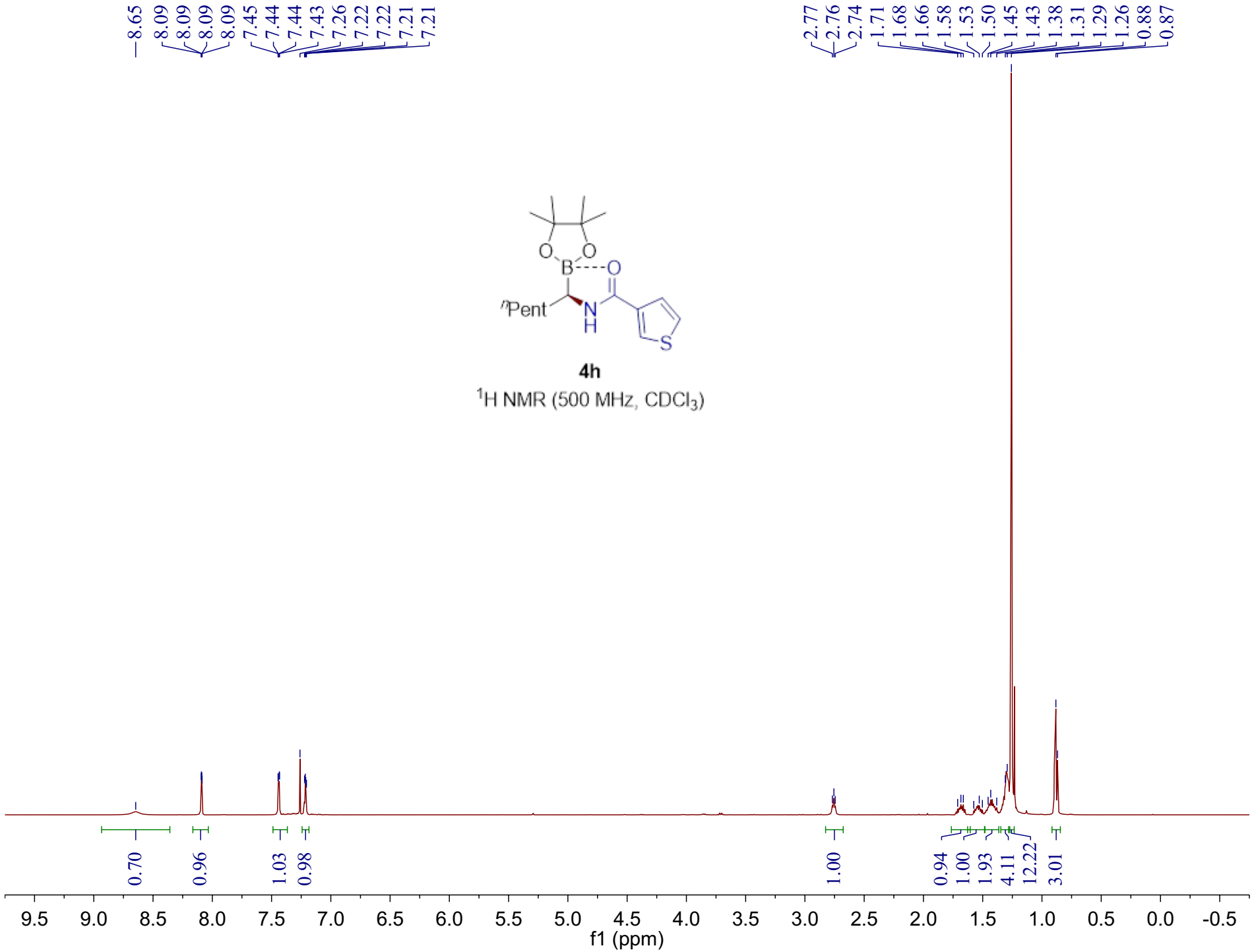
Supplementary Figure 75: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4g**.



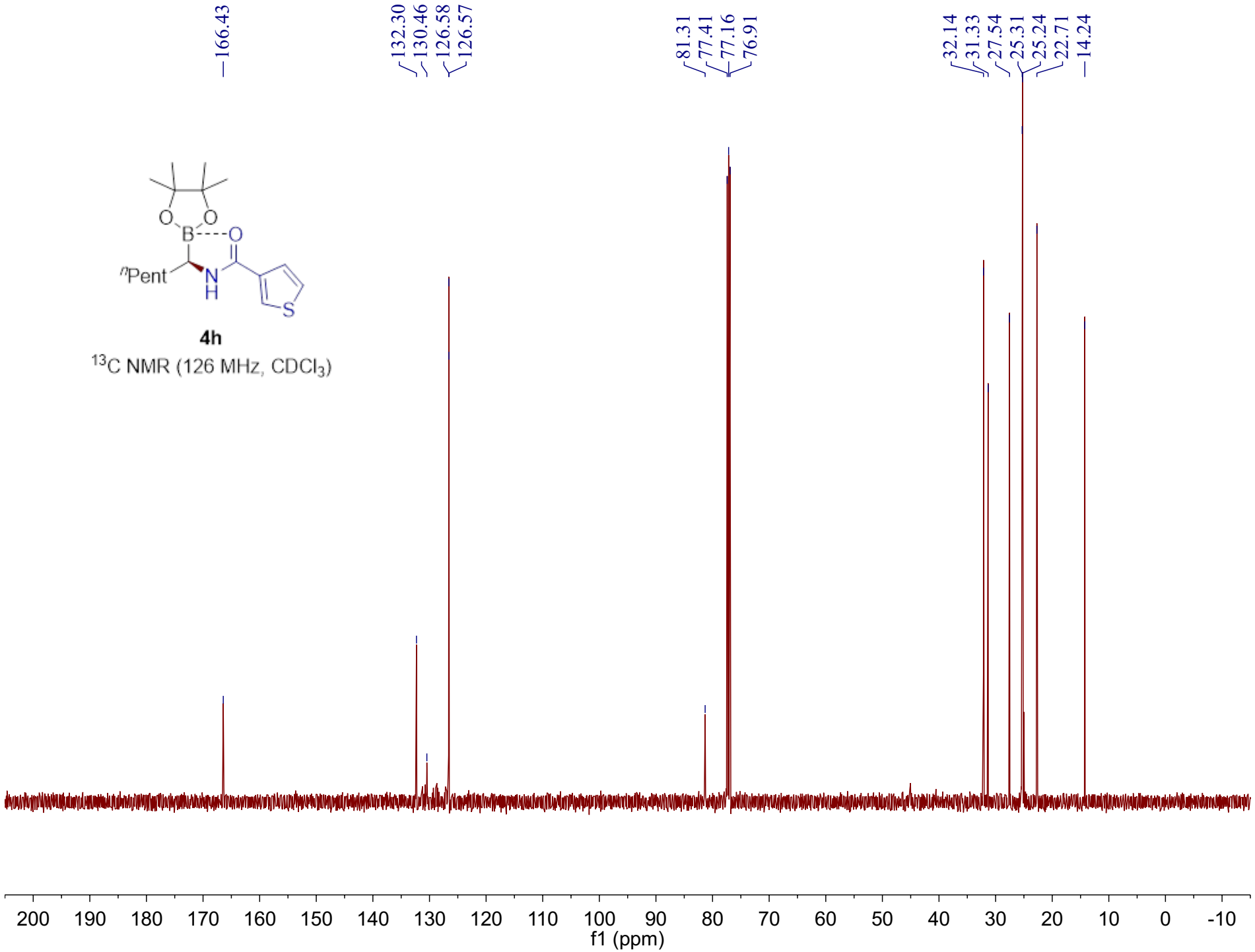
4g

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

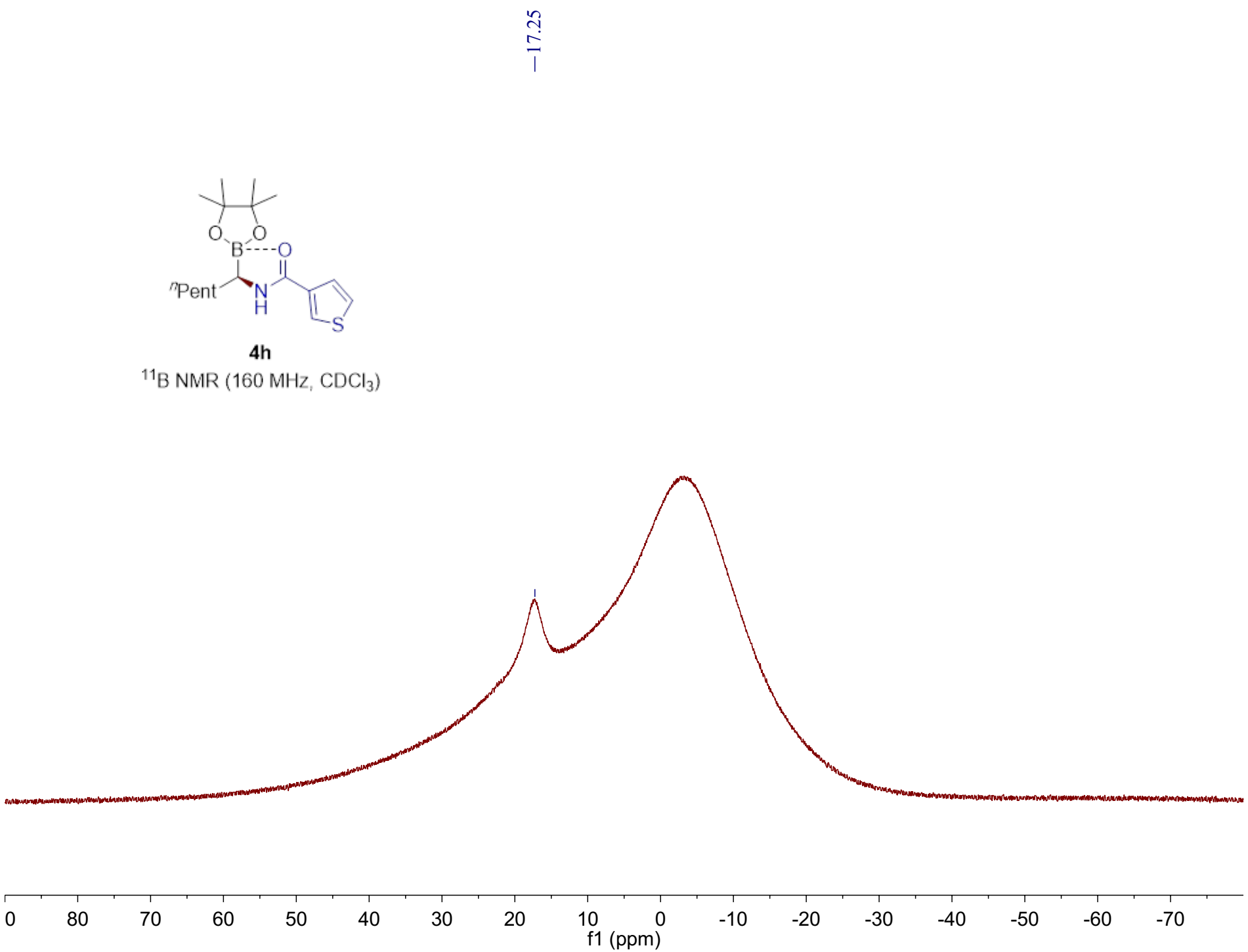
Supplementary Figure 76: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4g**.



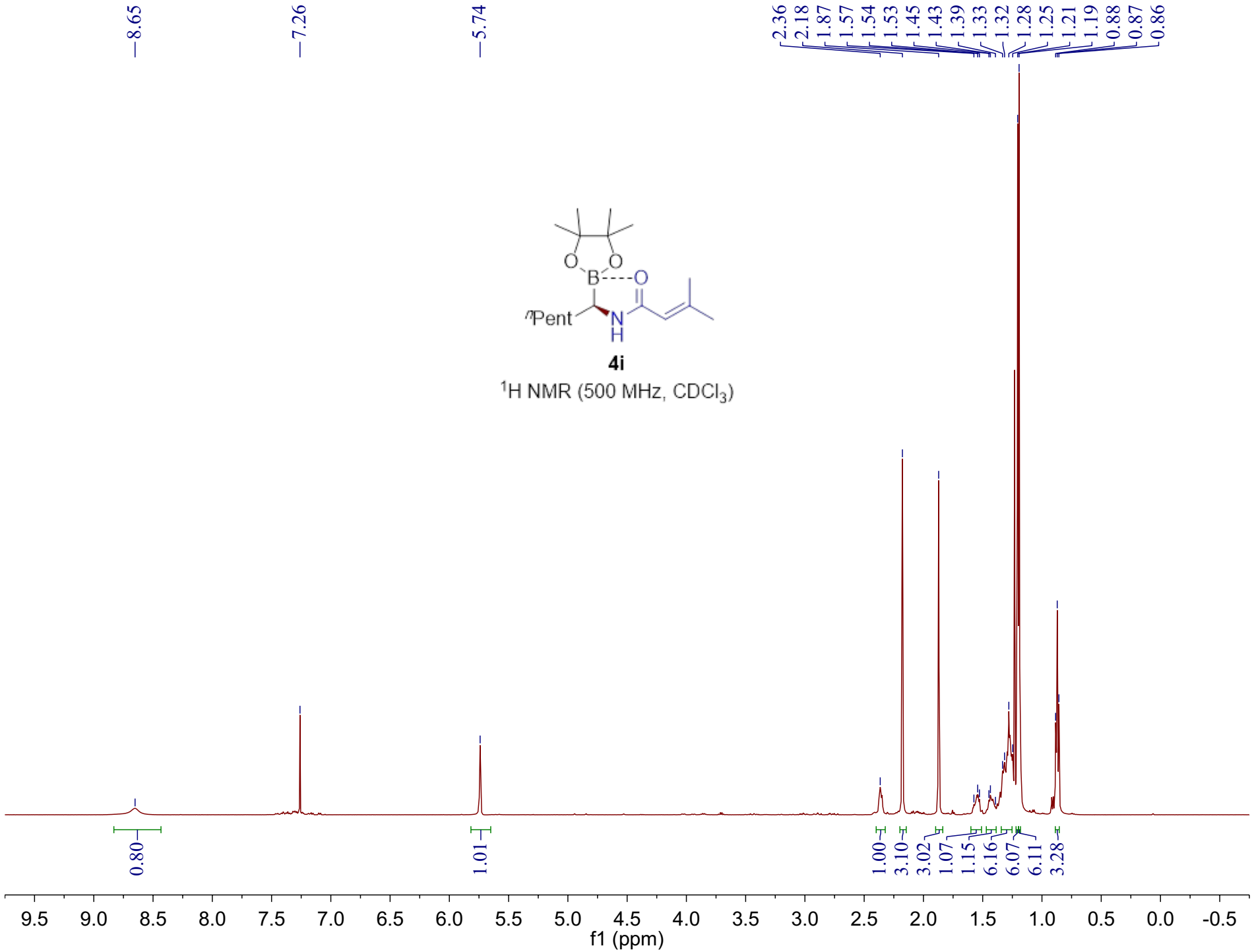
Supplementary Figure 77: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4h**.



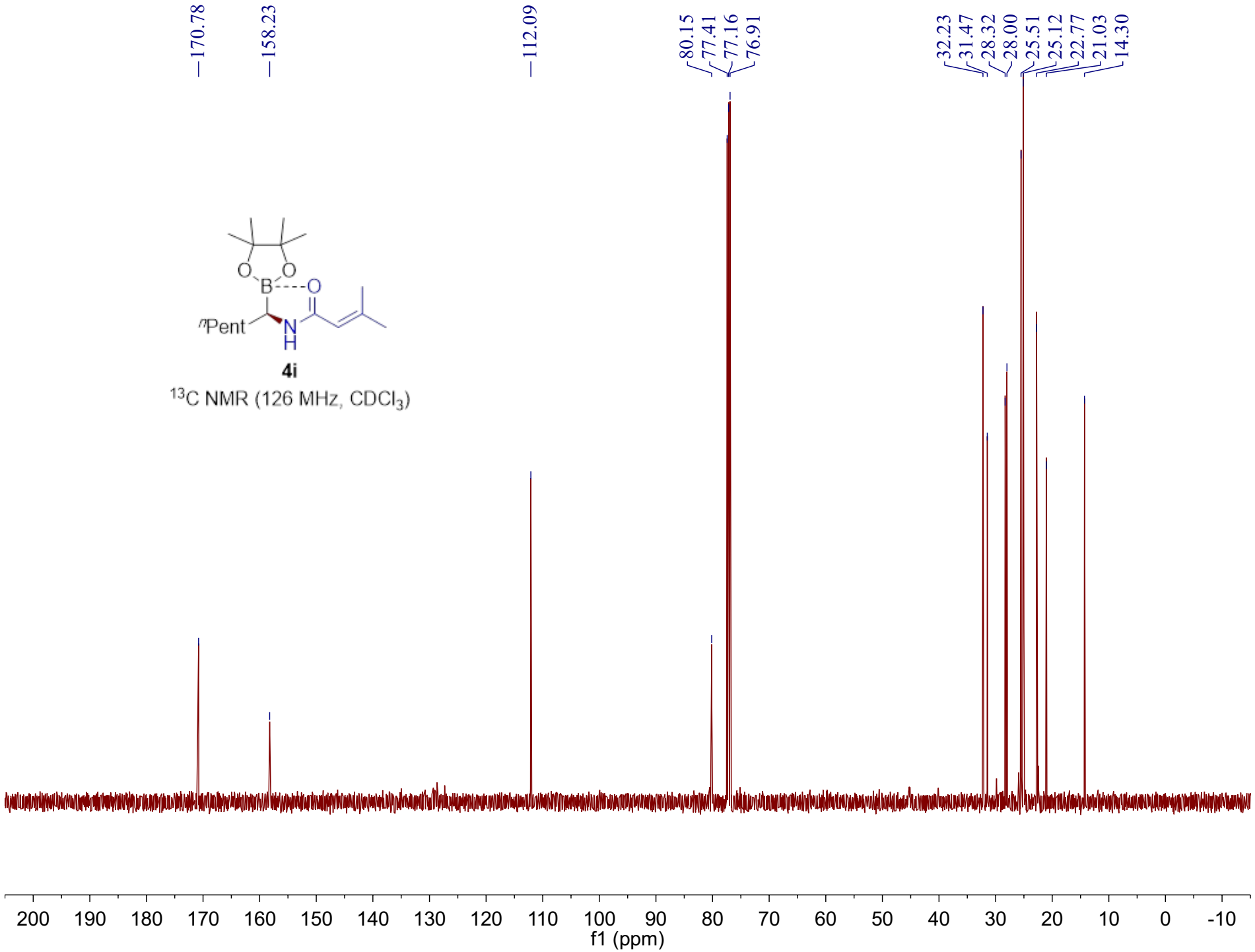
Supplementary Figure 78: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4h**.



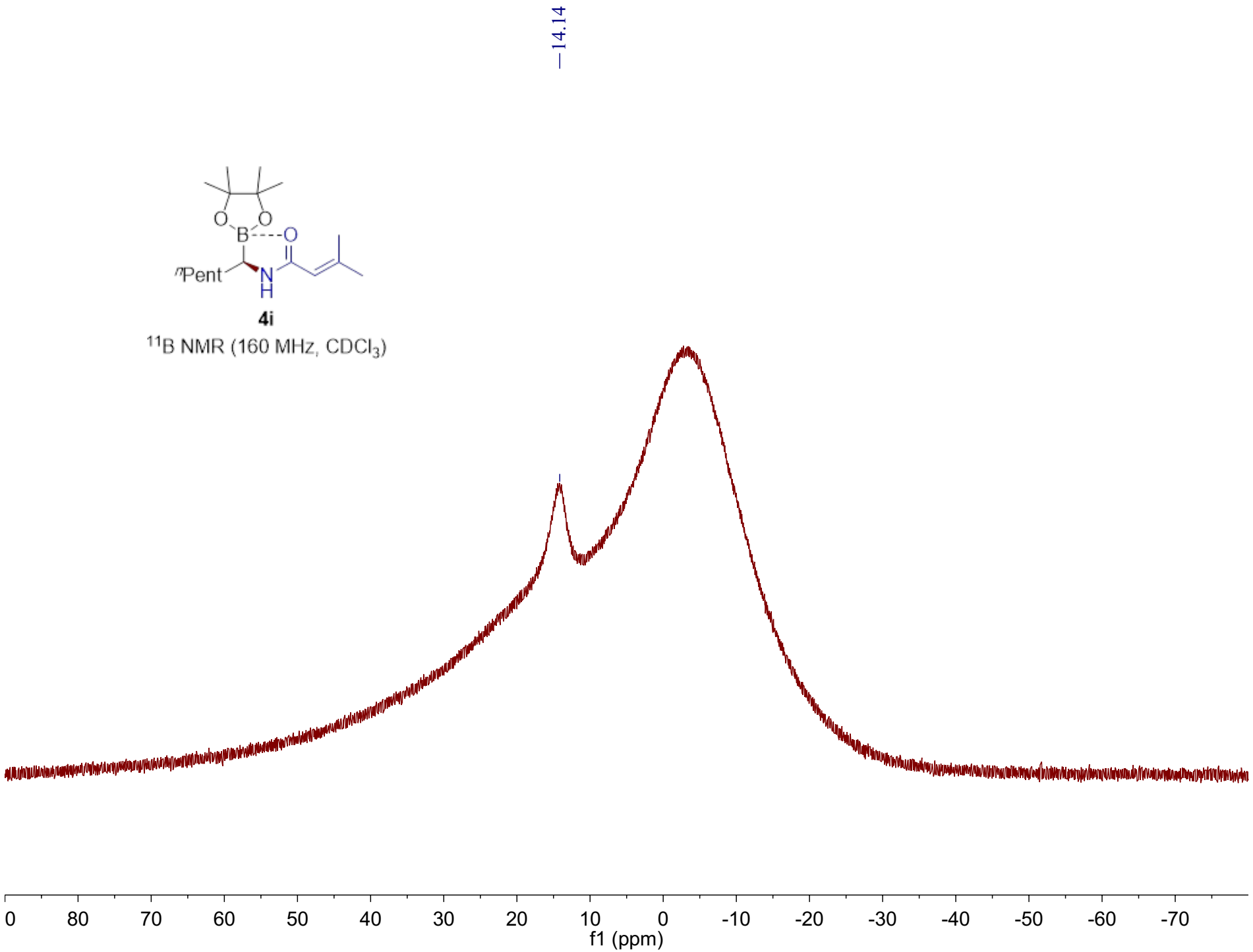
Supplementary Figure 79: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4h**.



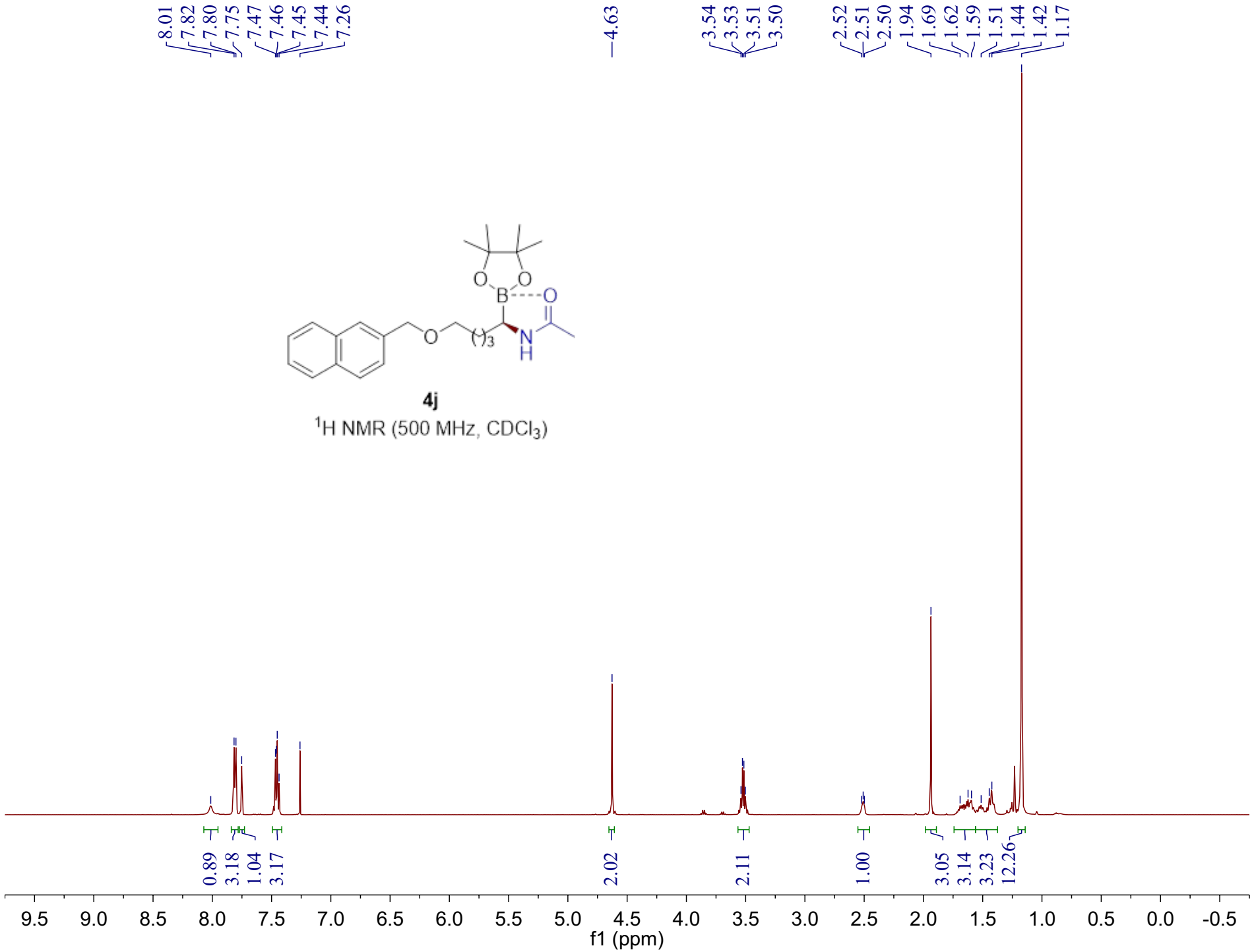
Supplementary Figure 80: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4i**.



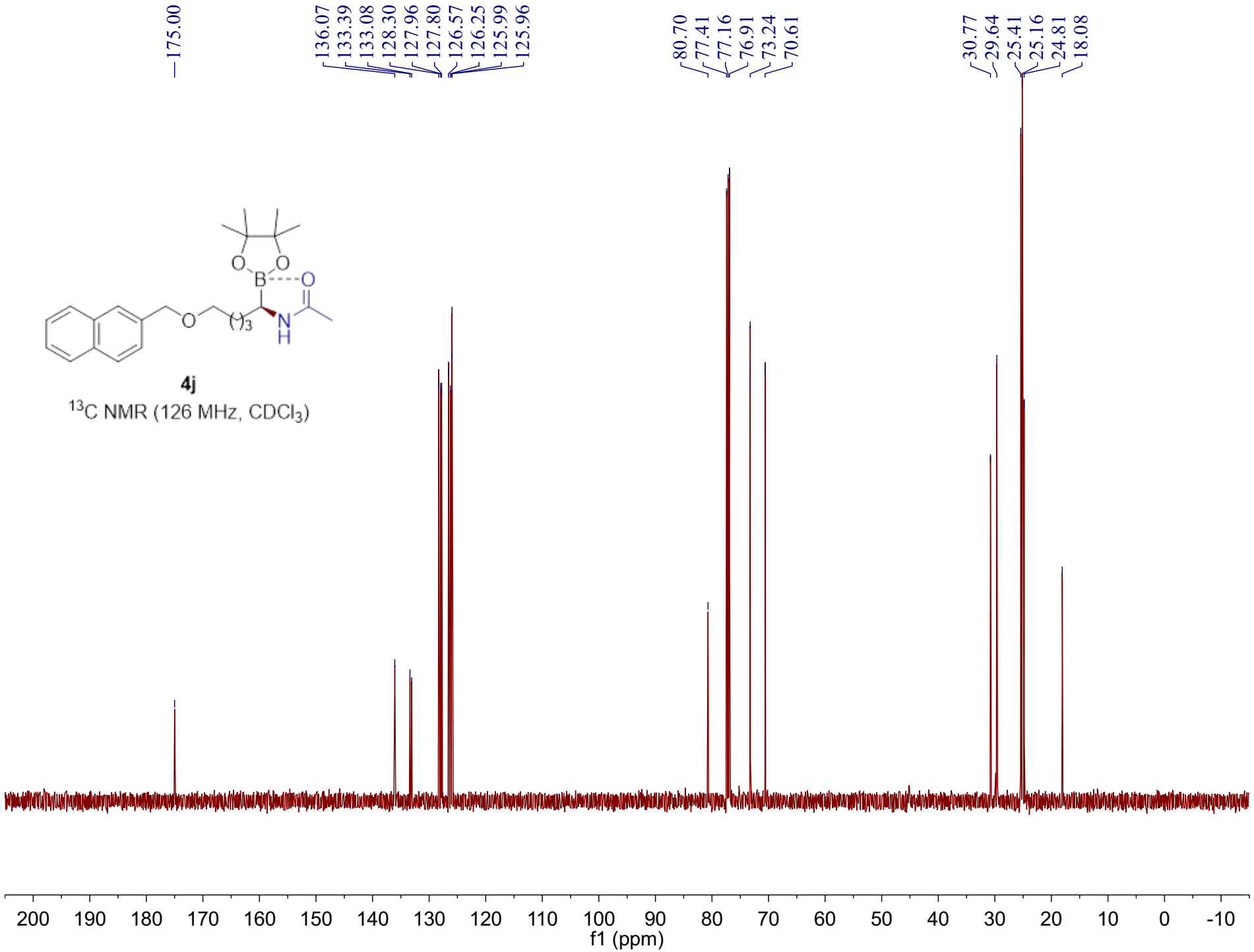
Supplementary Figure 81: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4i**.



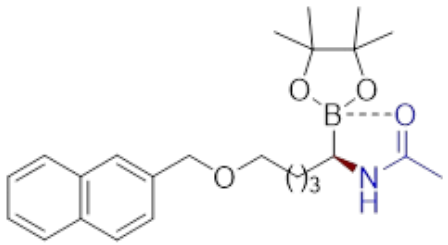
Supplementary Figure 82: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4i**.



Supplementary Figure 83: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4j**.

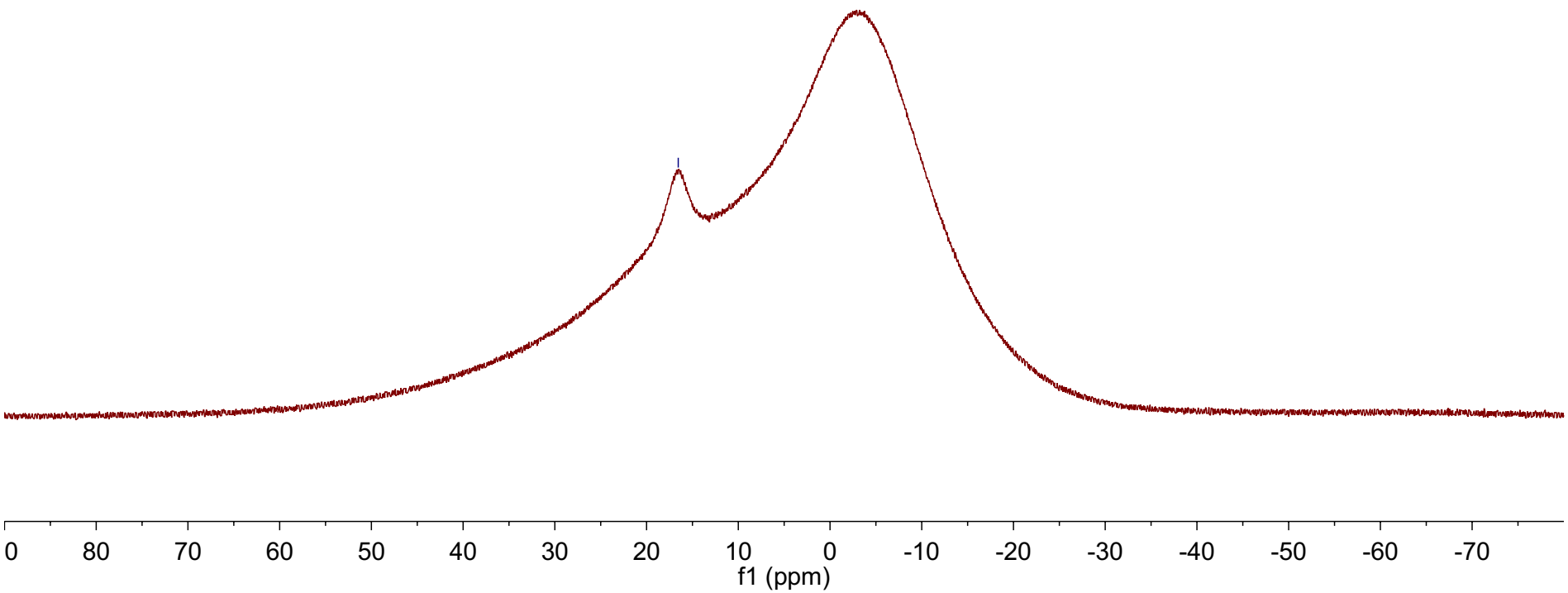


Supplementary Figure 84: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4j**.

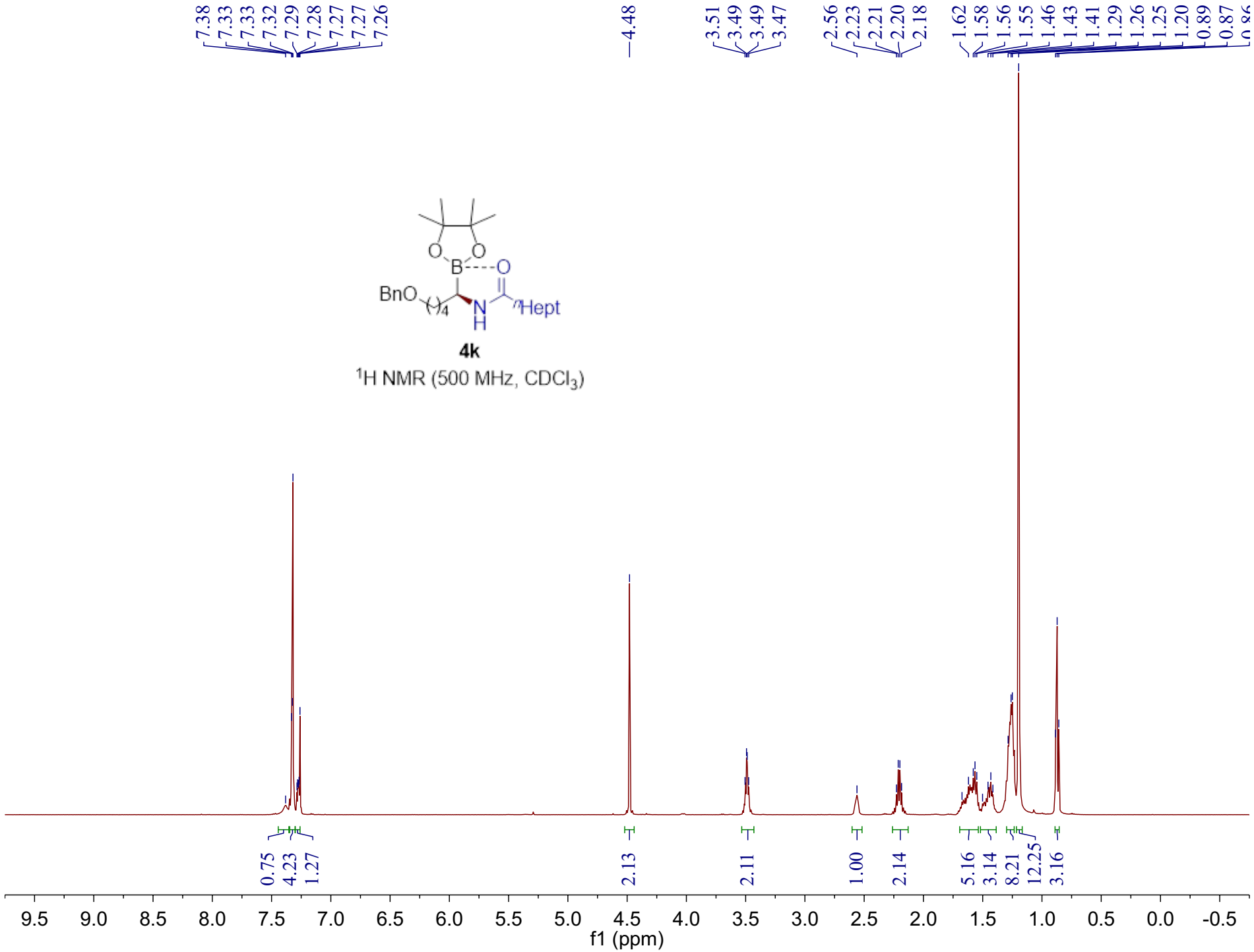


4j

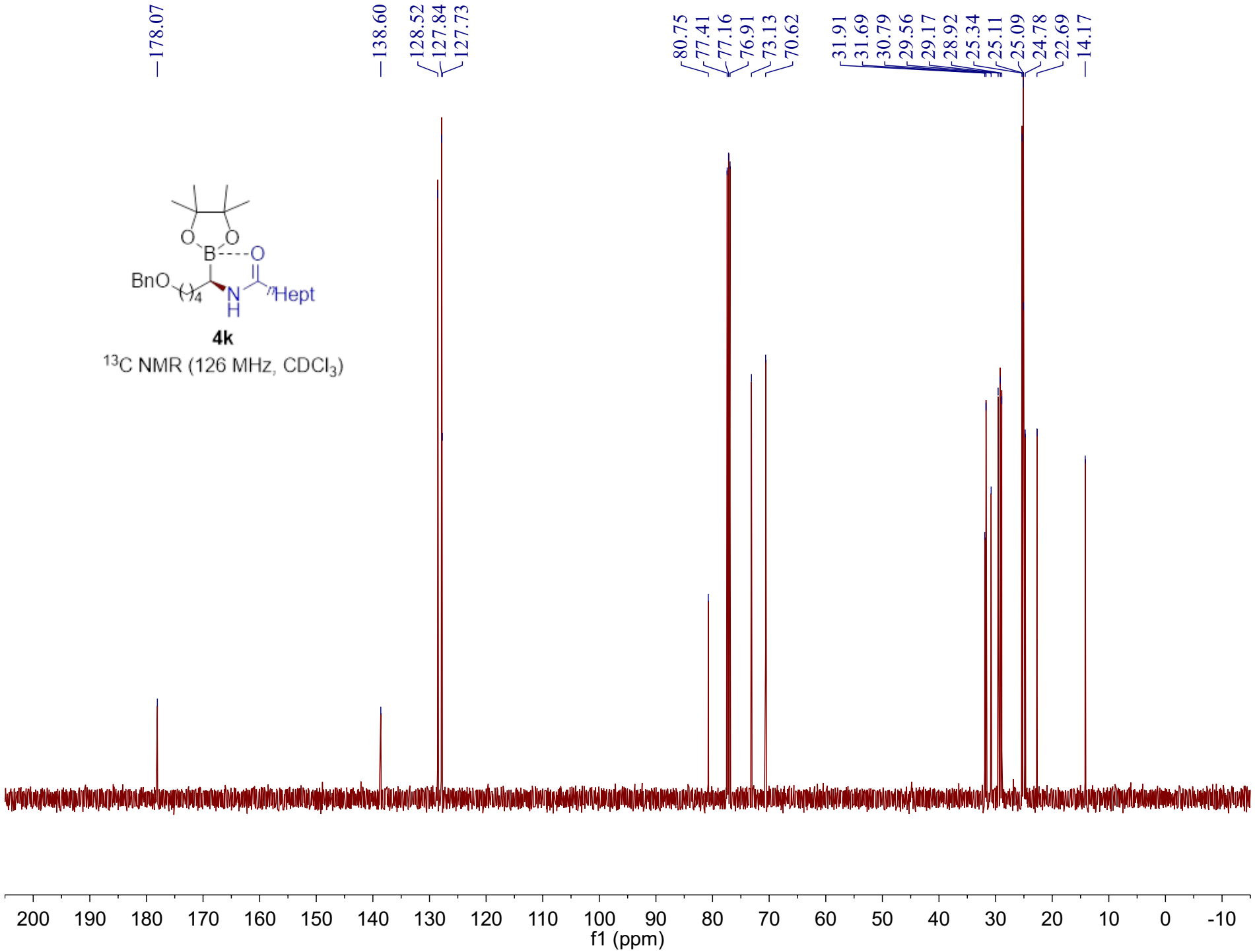
^{11}B NMR (160 MHz, $CDCl_3$)



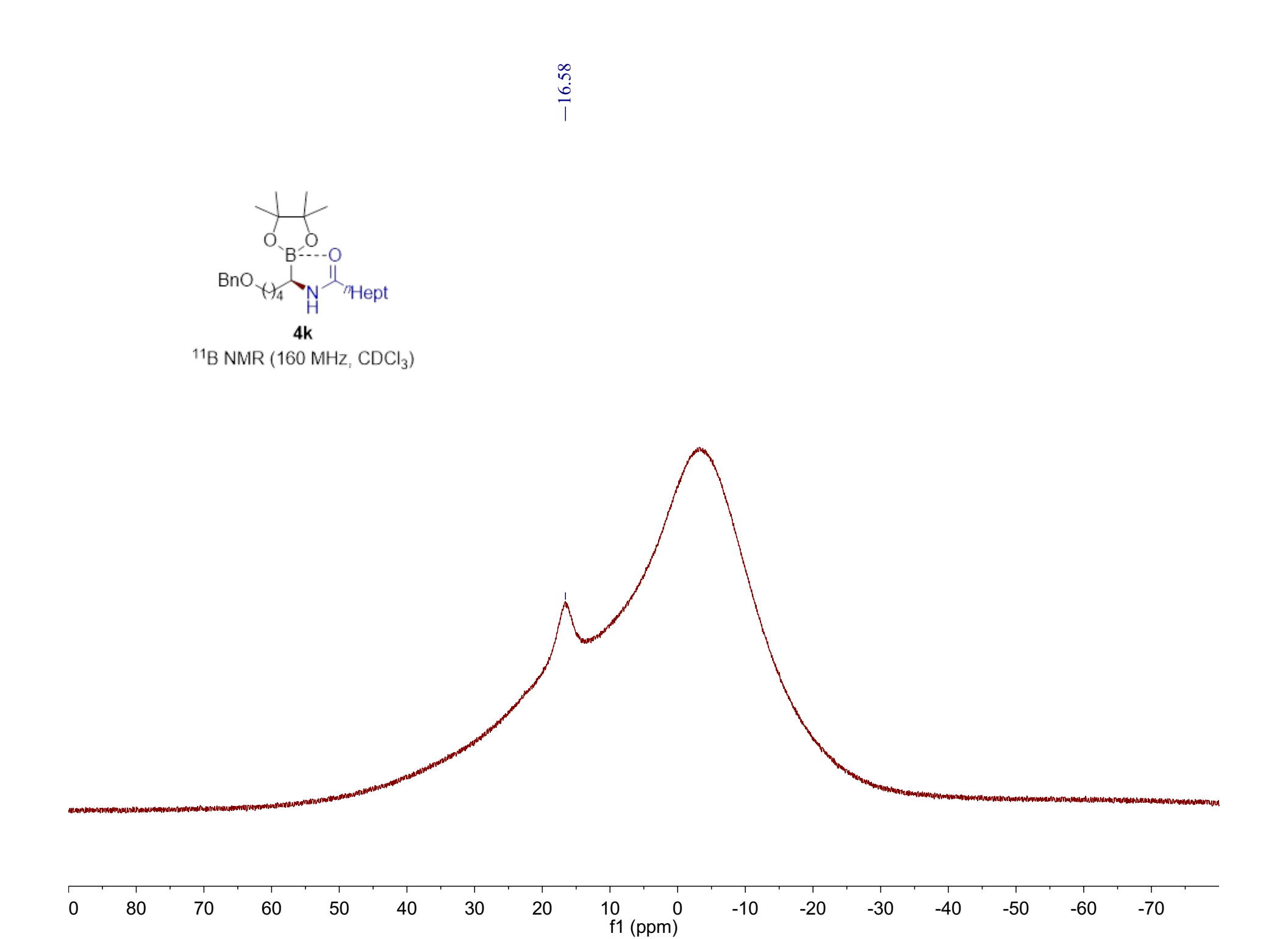
Supplementary Figure 85: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4j**.



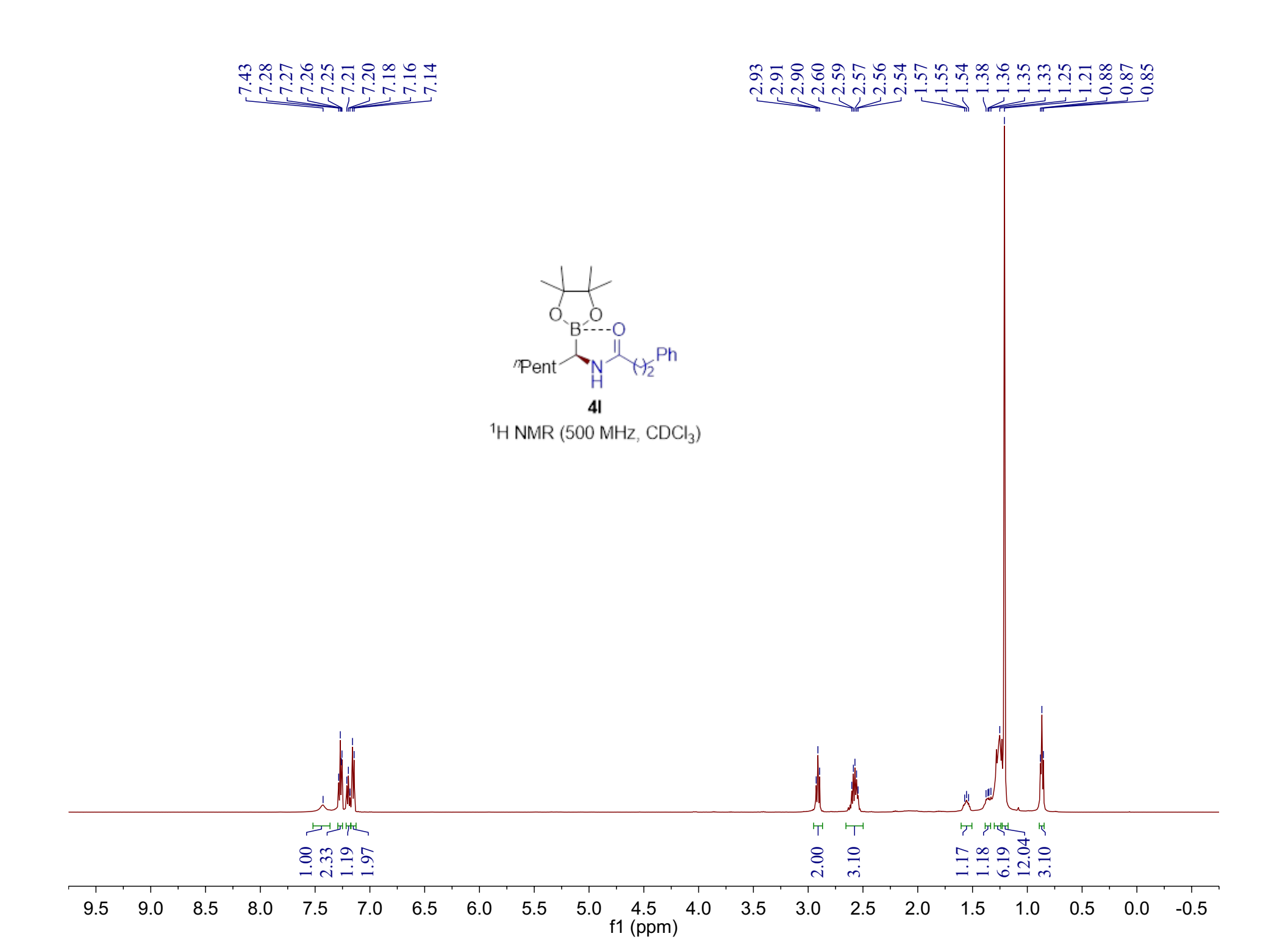
Supplementary Figure 86: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4k**.



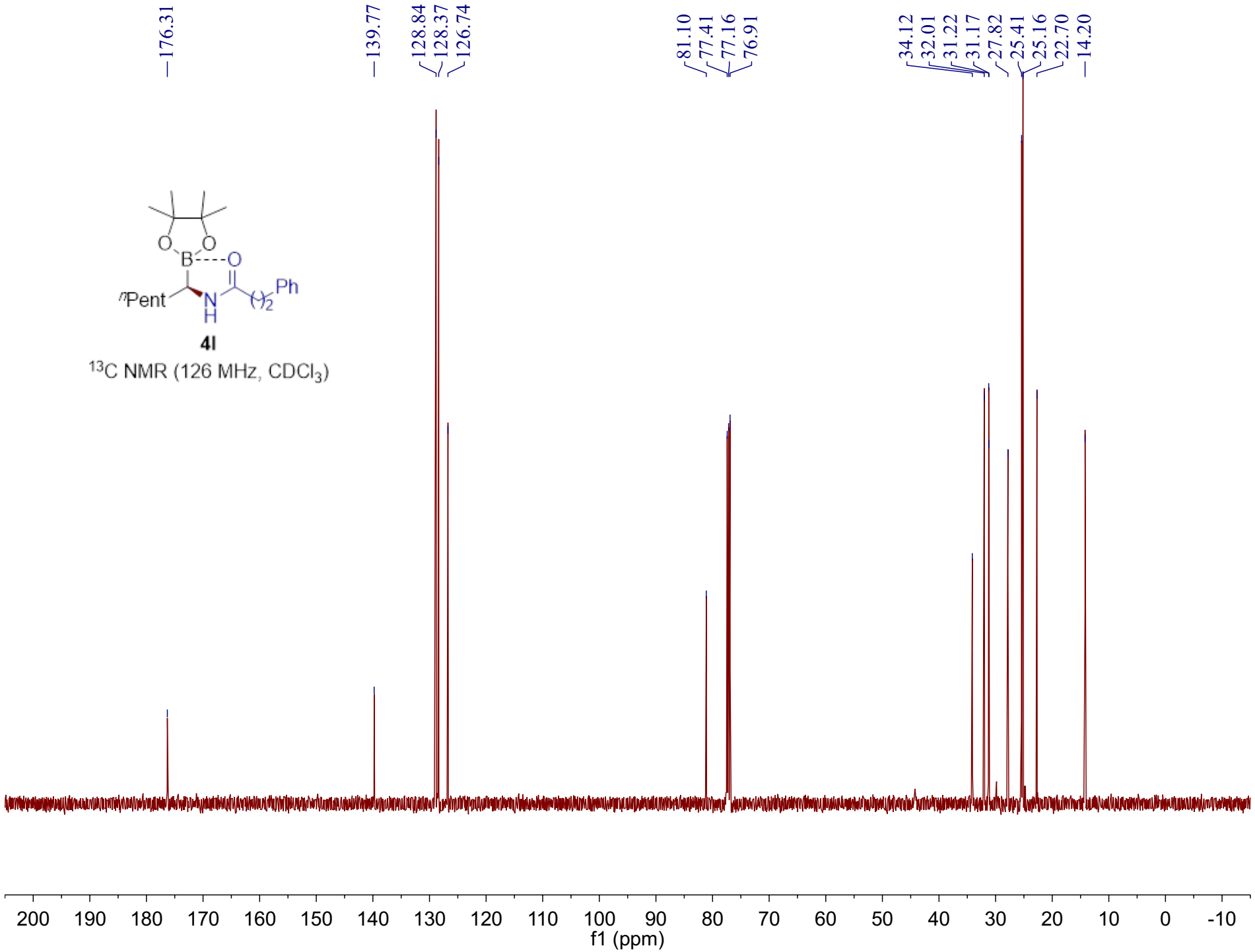
Supplementary Figure 87: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4k**.



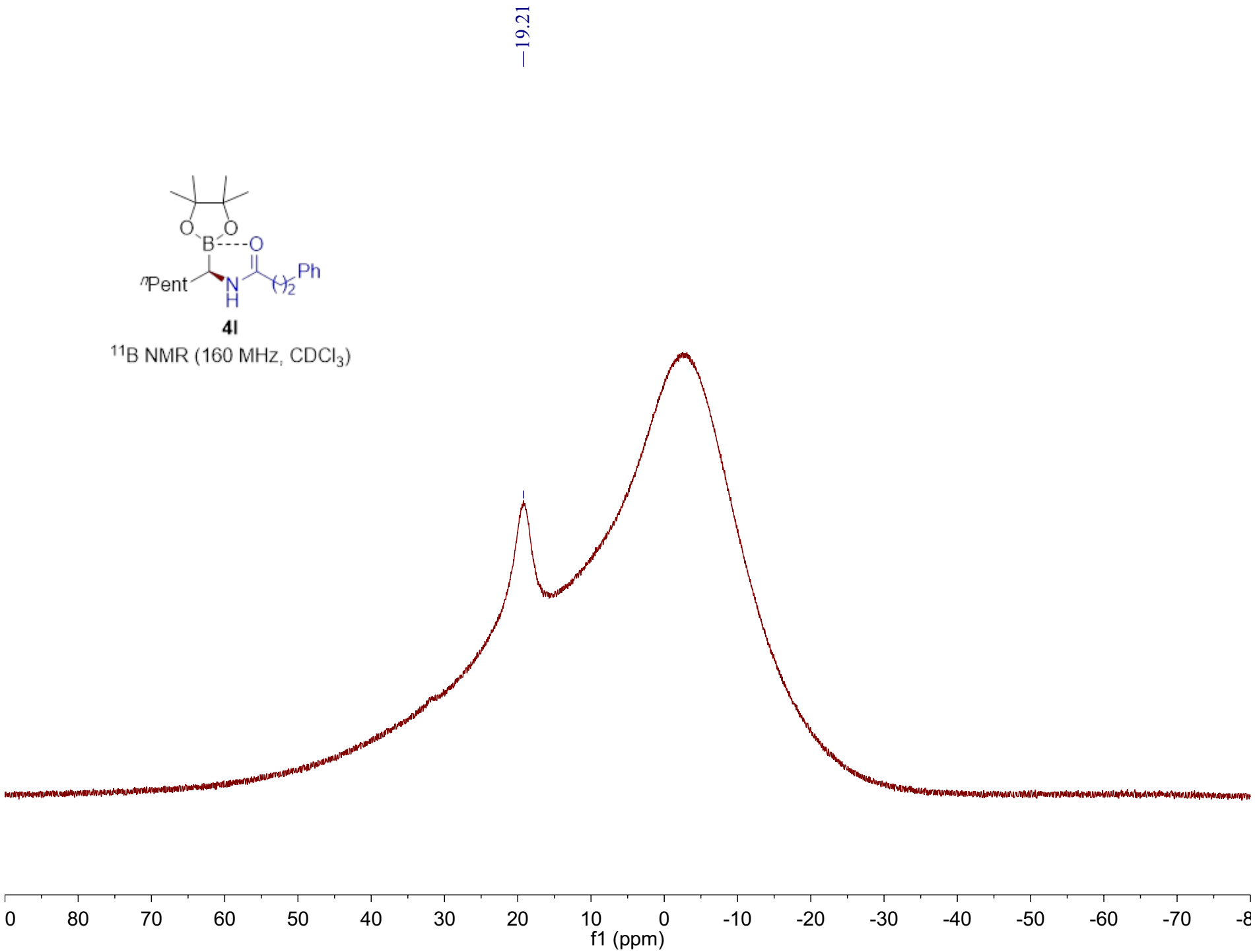
Supplementary Figure 88: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4k**.



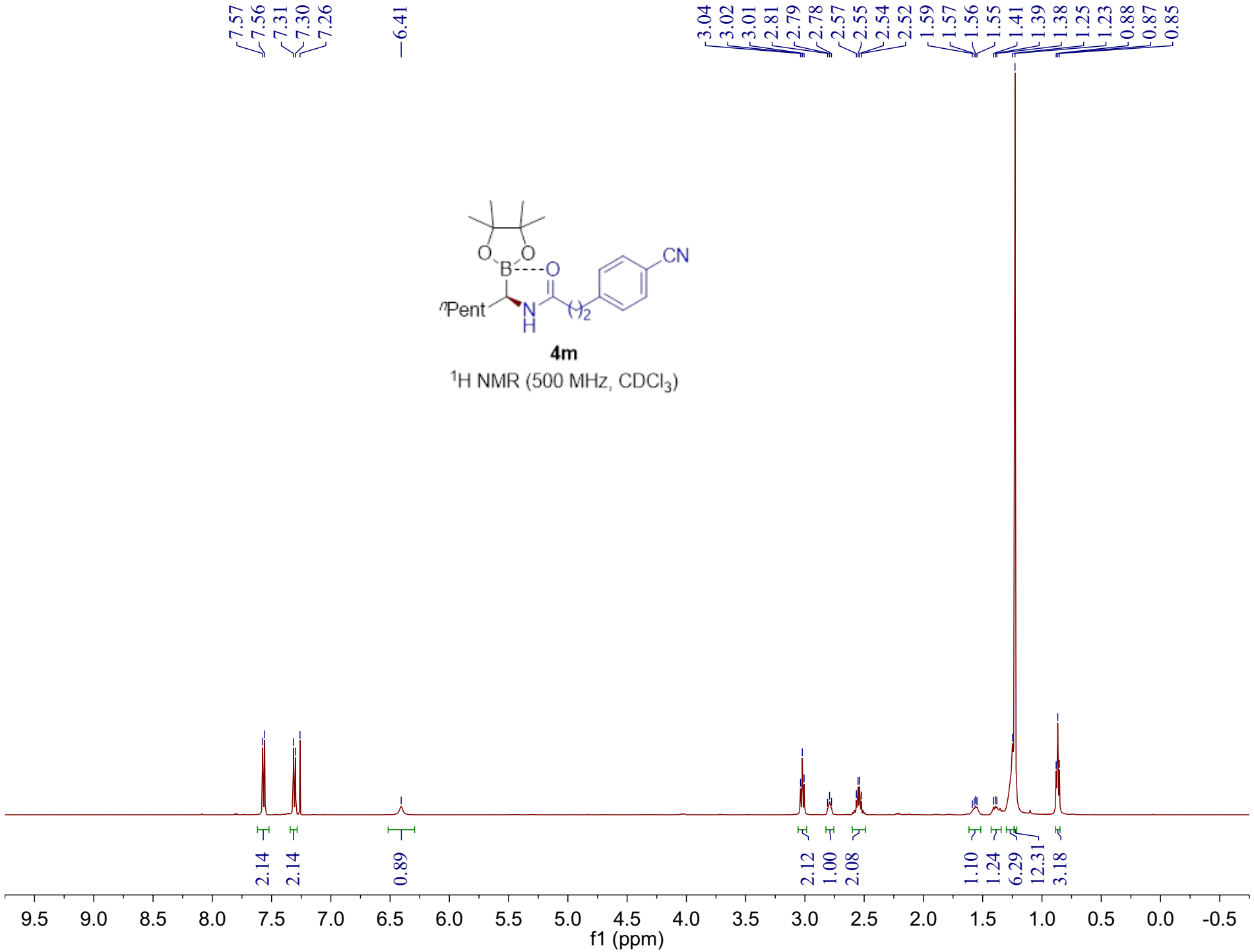
Supplementary Figure 89: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4l**.



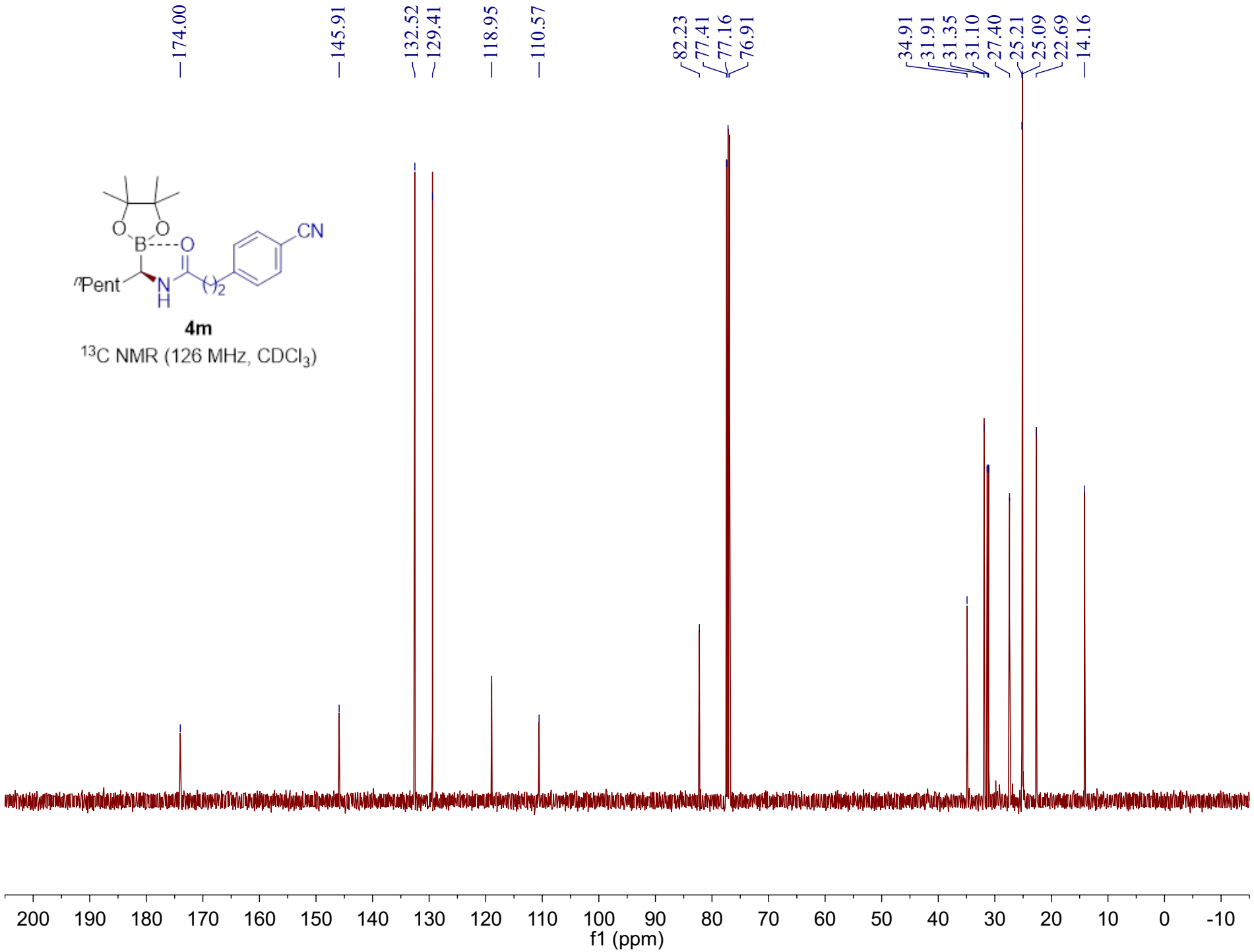
Supplementary Figure 90: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4l**.



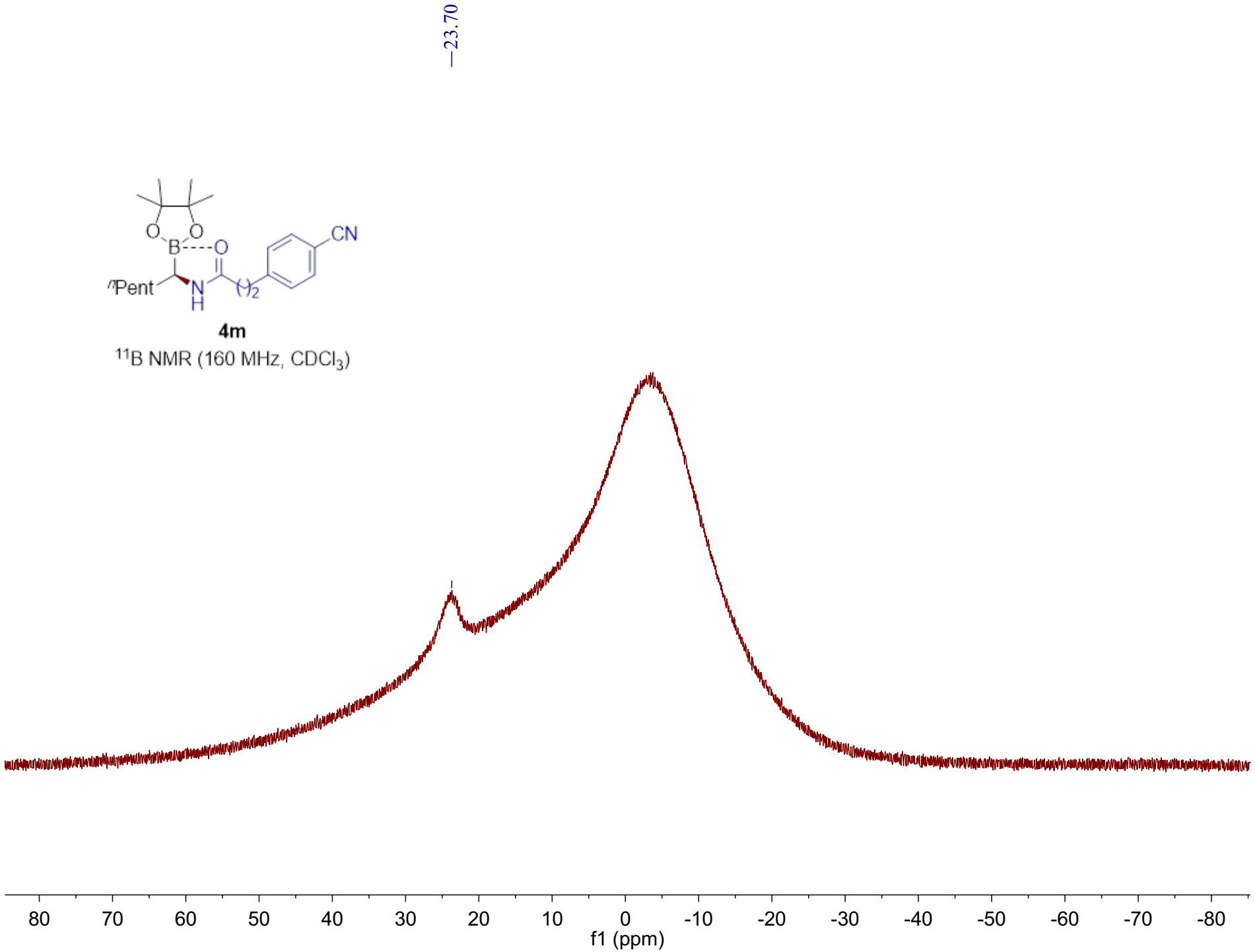
Supplementary Figure 91: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4l**.



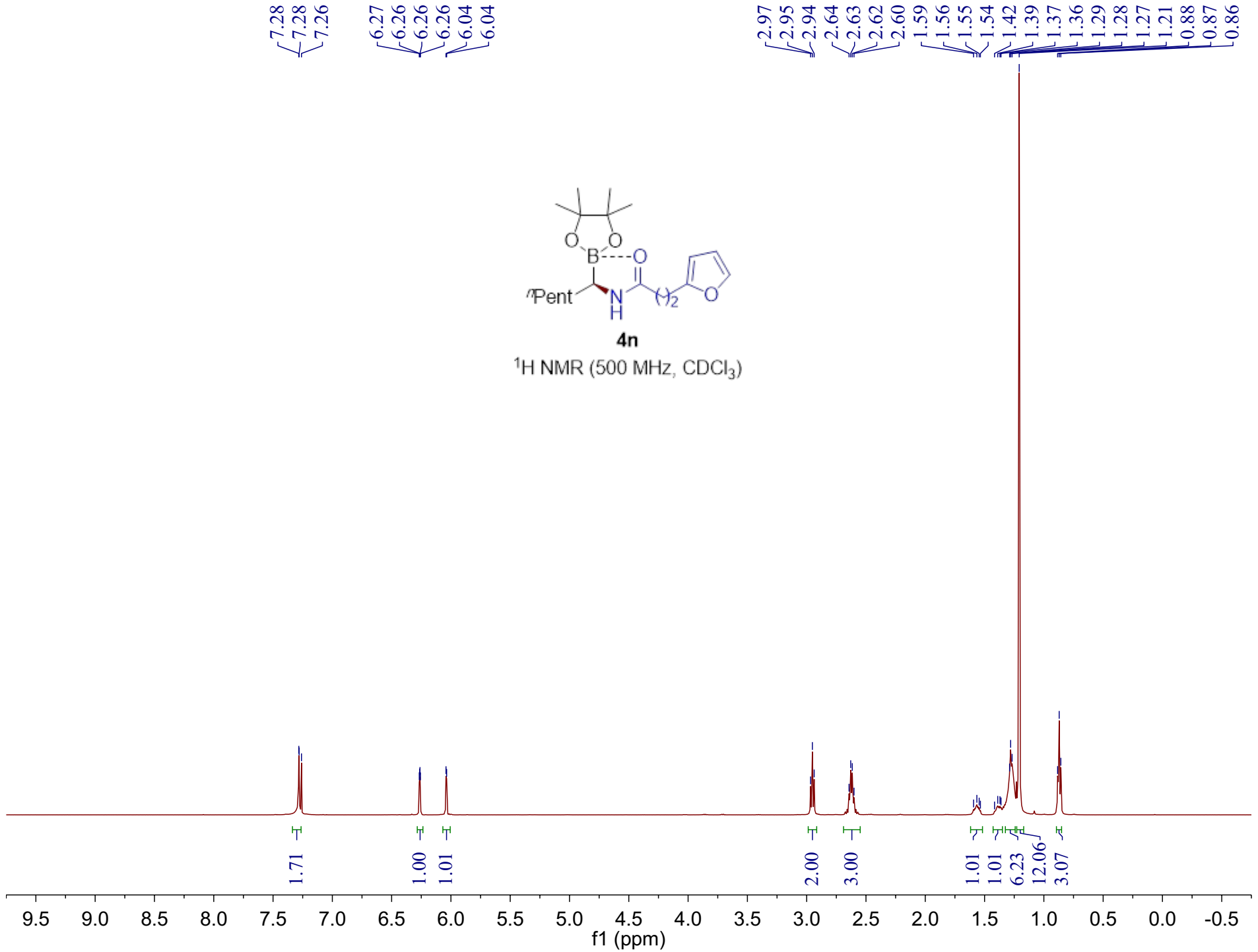
Supplementary Figure 92: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4m**.



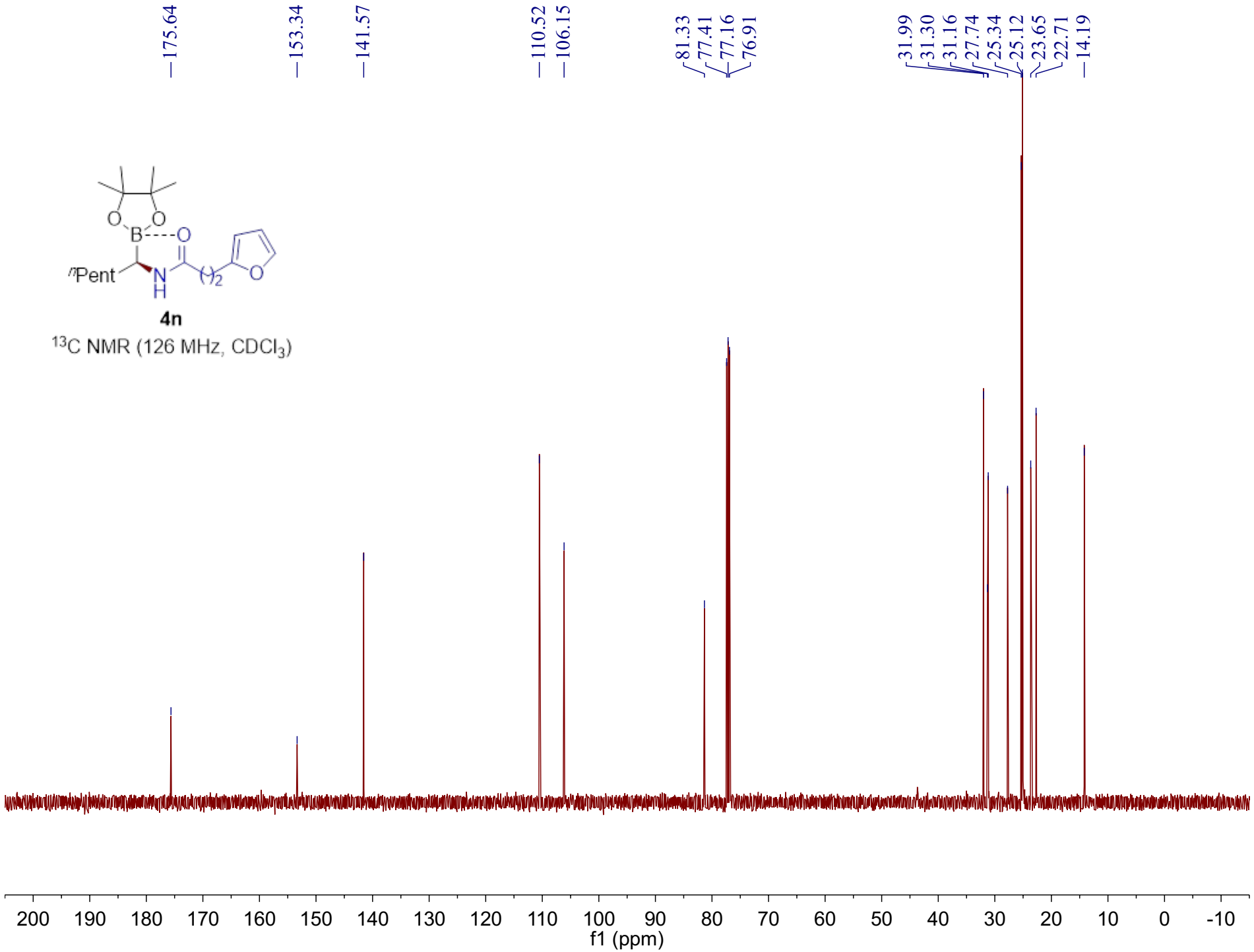
Supplementary Figure 93: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4m**.



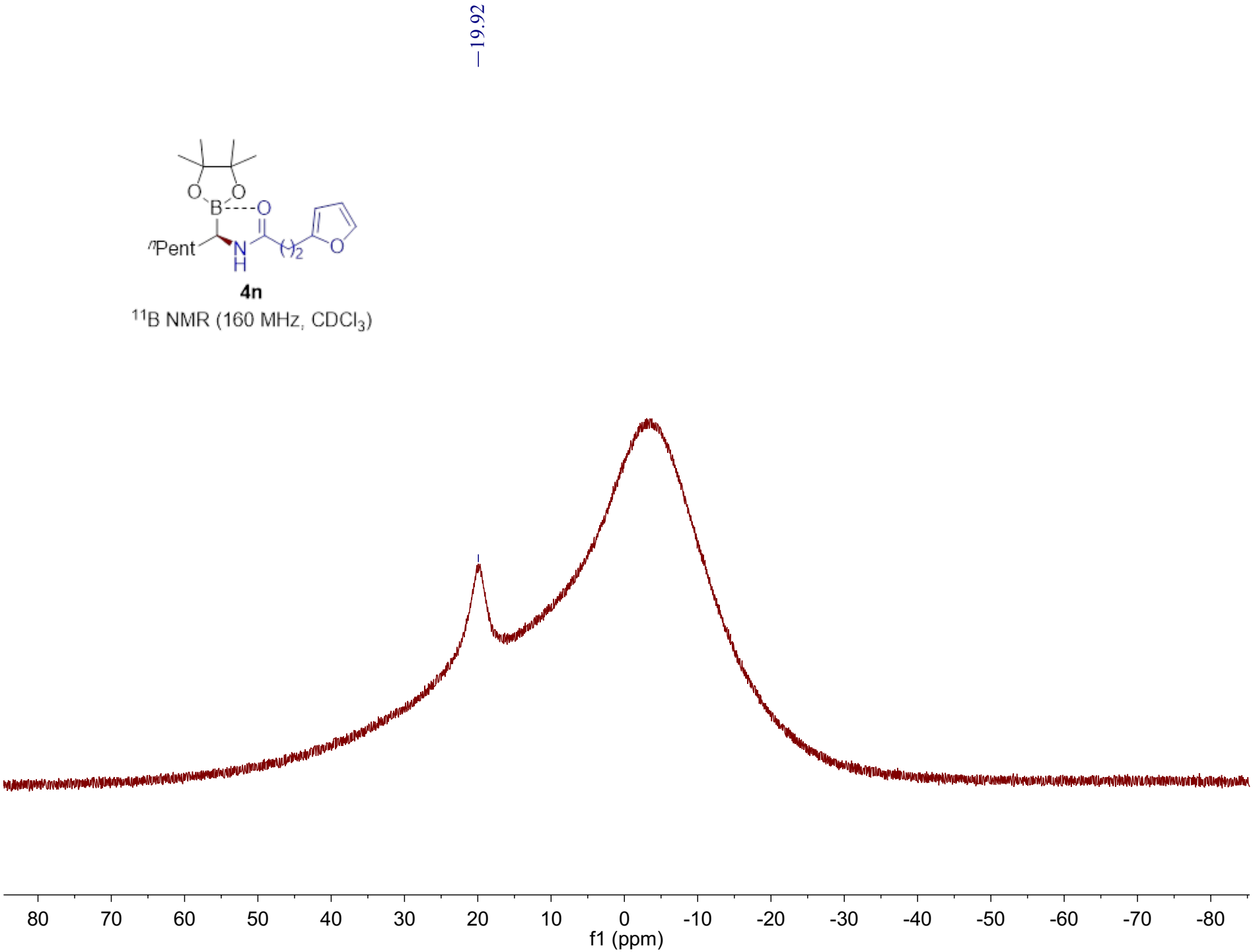
Supplementary Figure 94: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4m**.



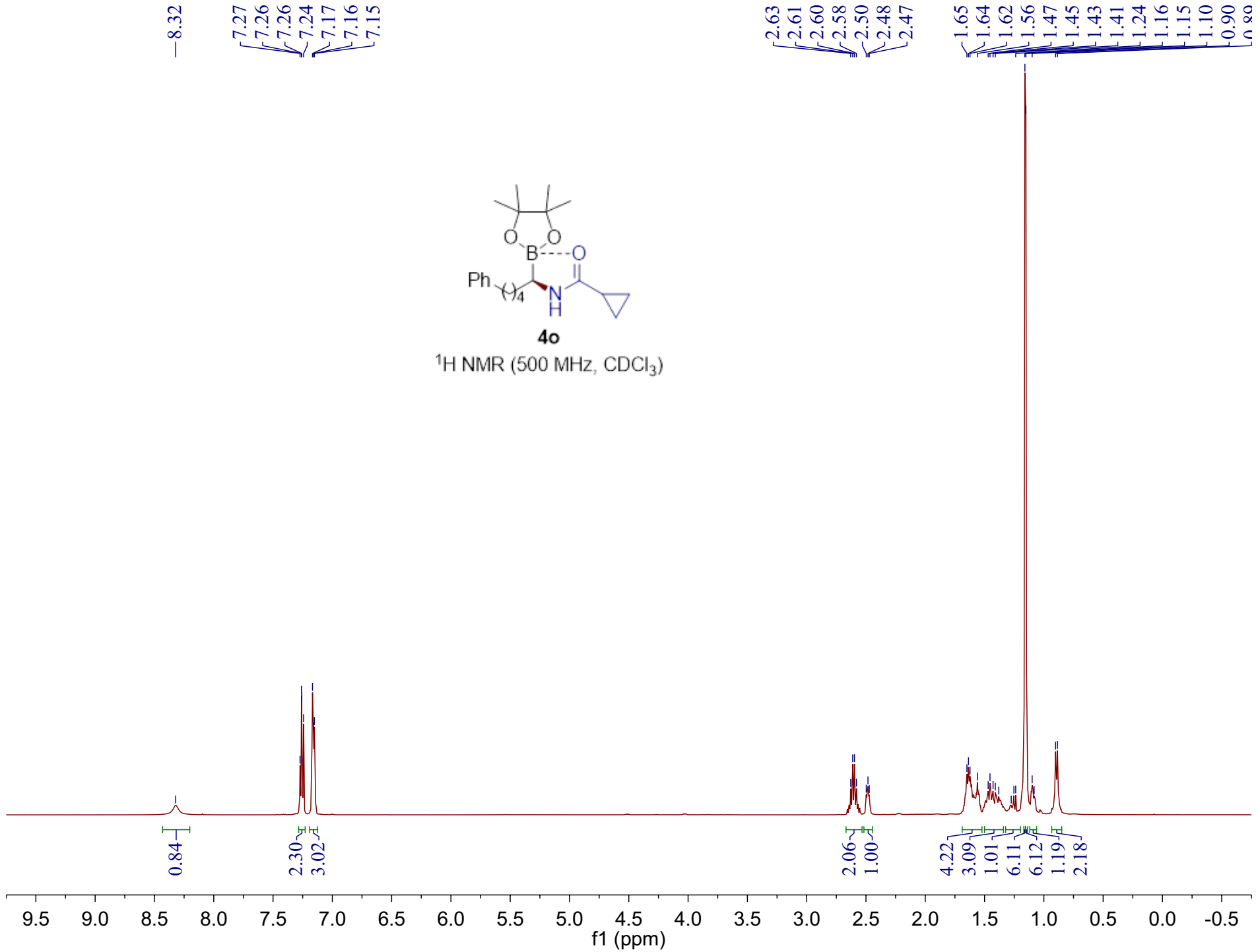
Supplementary Figure 95: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4n**.



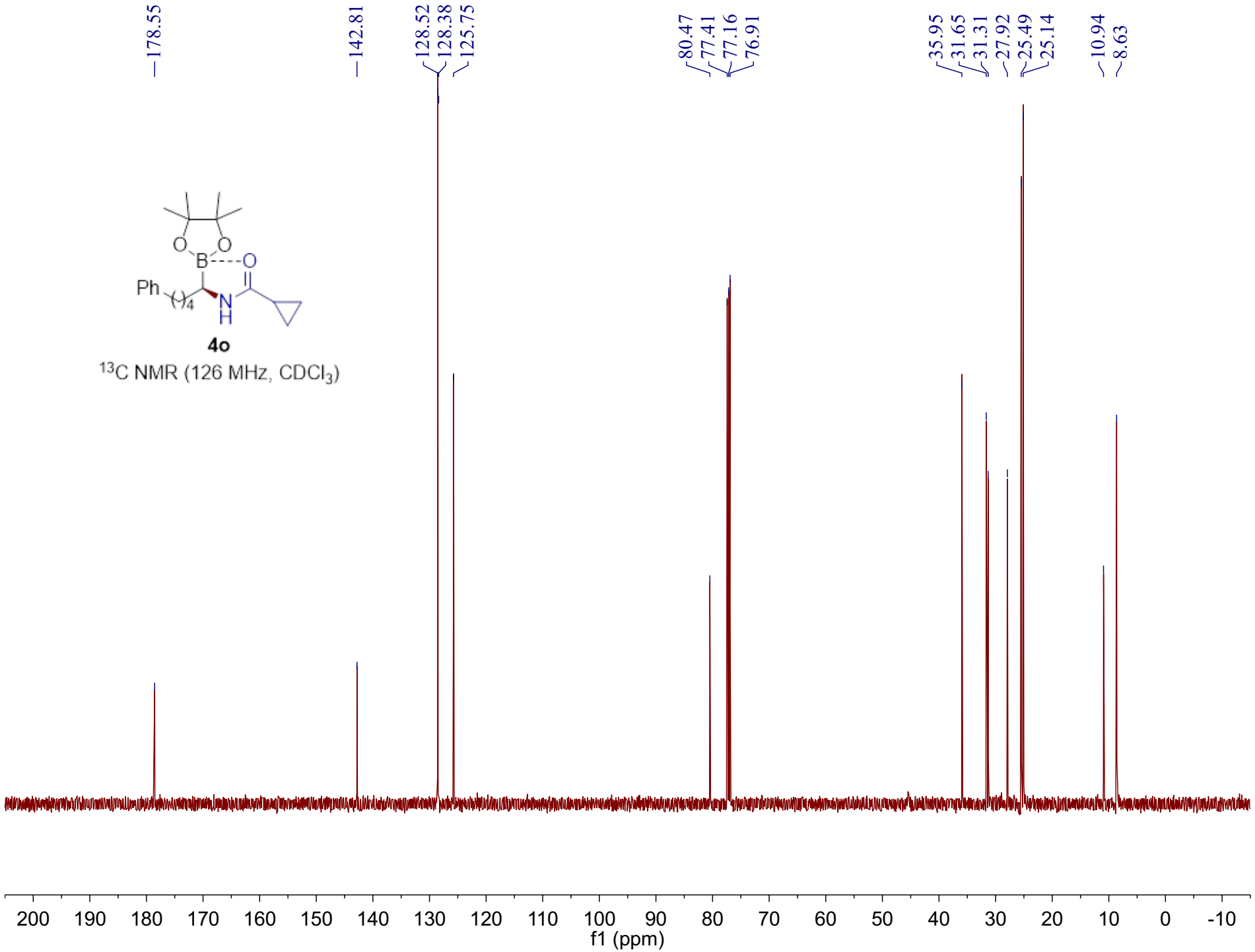
Supplementary Figure 96: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4n**.



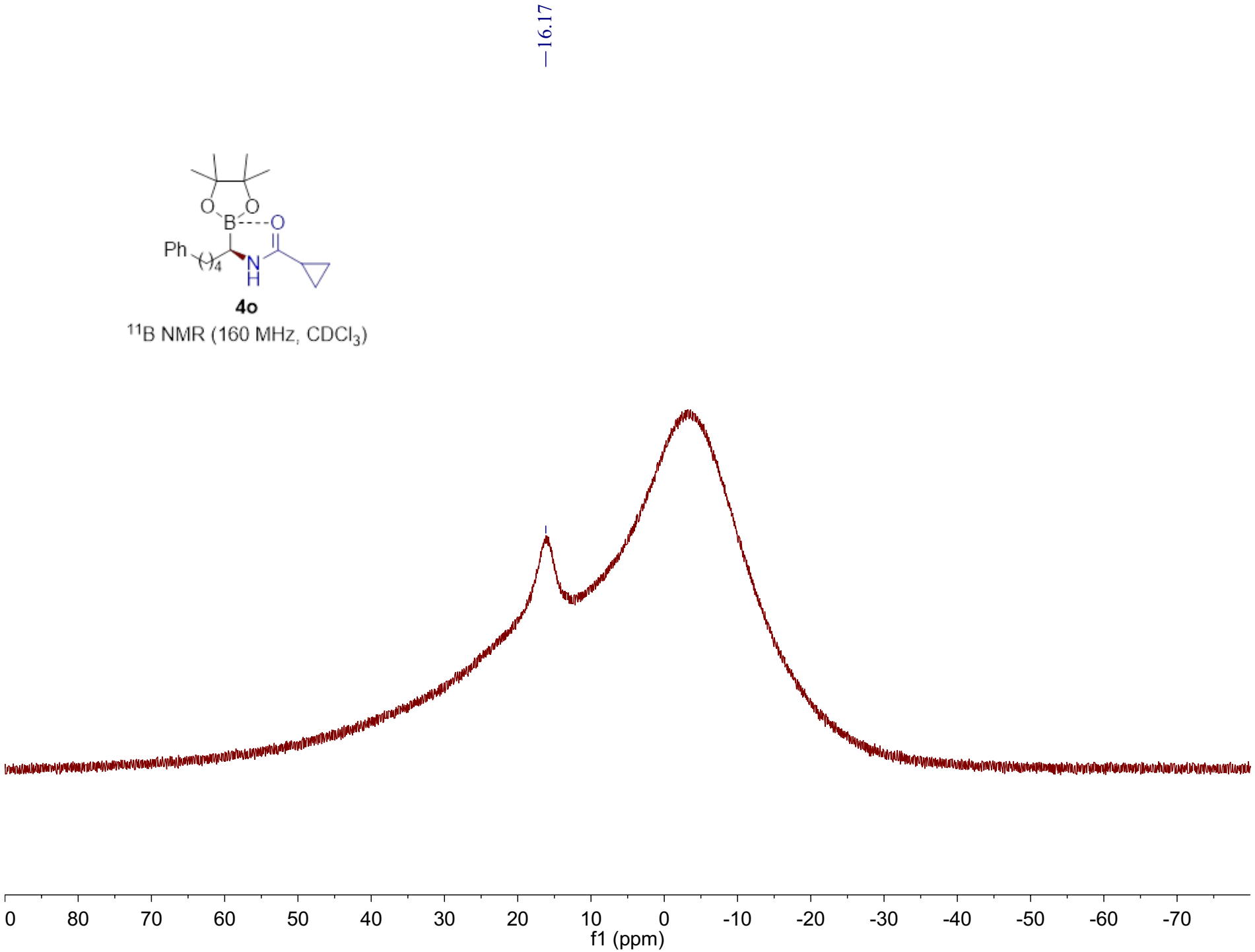
Supplementary Figure 97: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4n**.



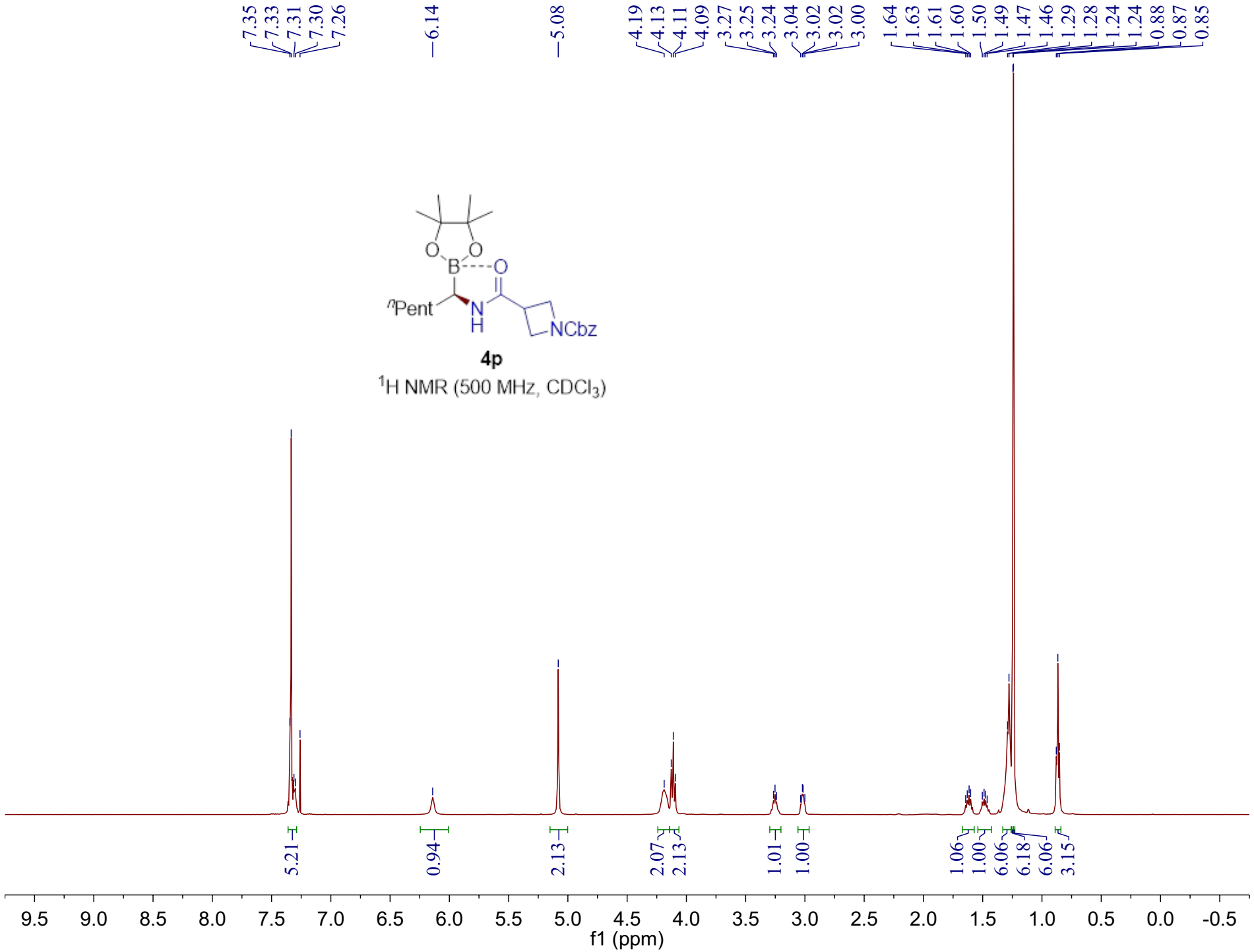
Supplementary Figure 98: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4o**.



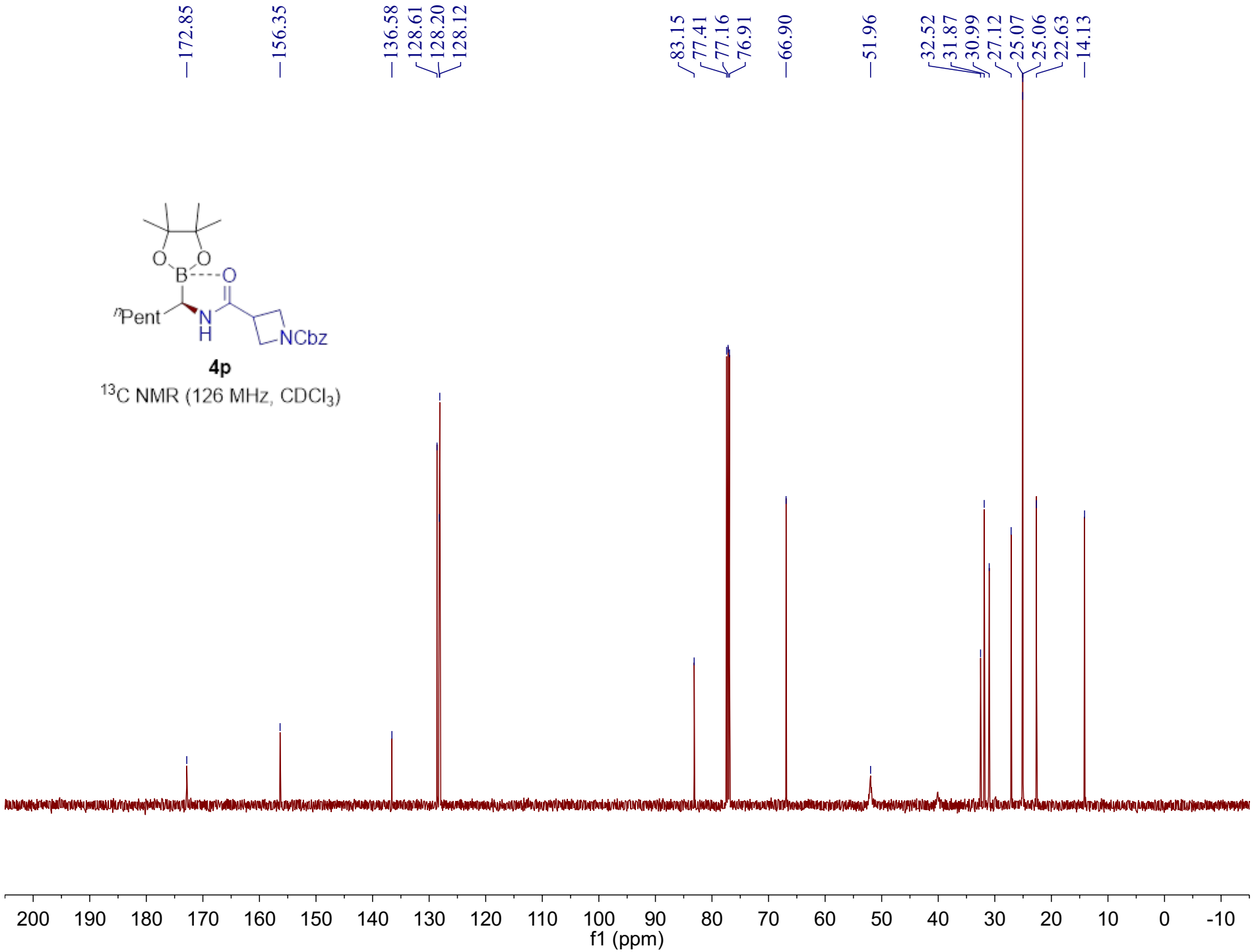
Supplementary Figure 99: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4o**.



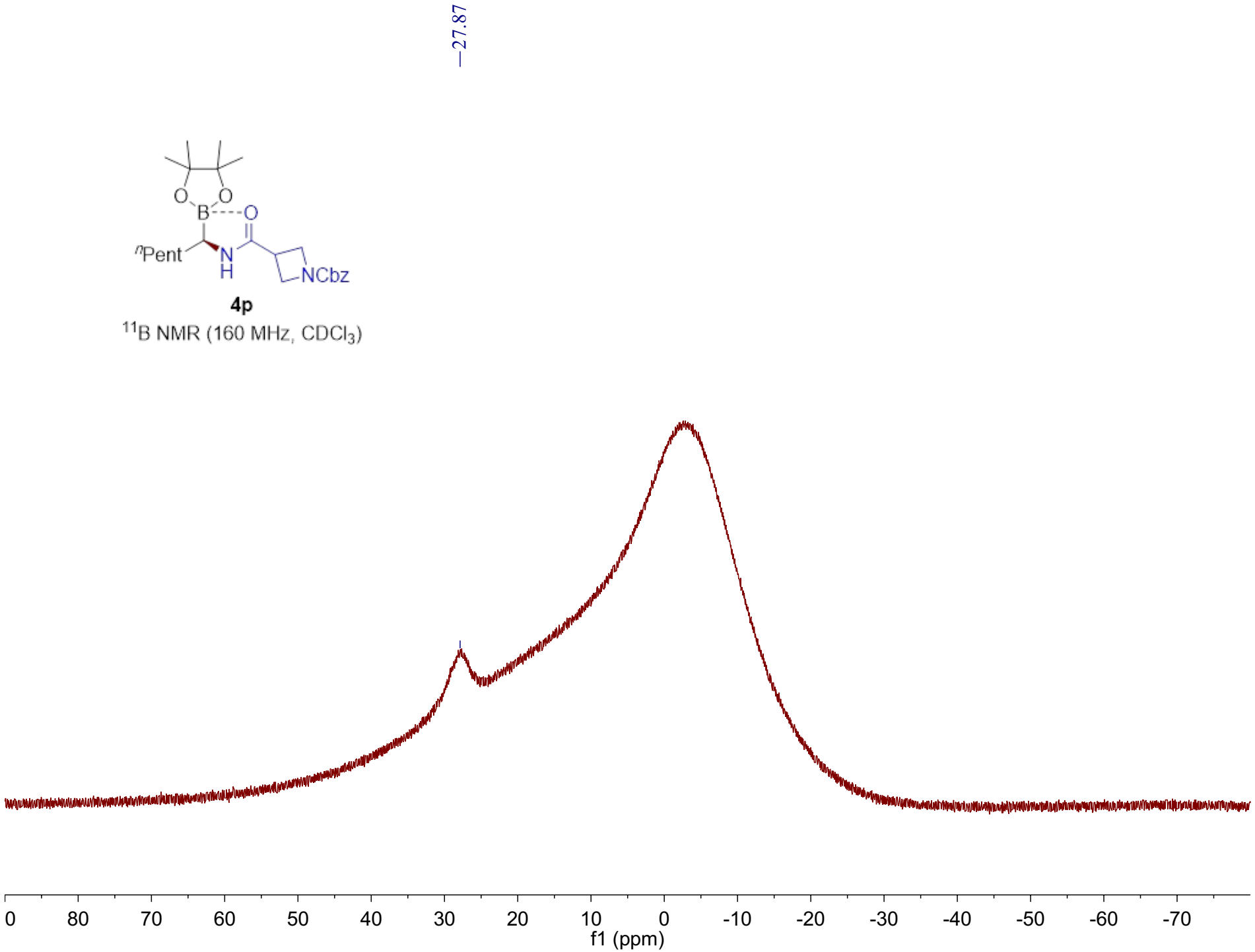
Supplementary Figure 100: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4o**.



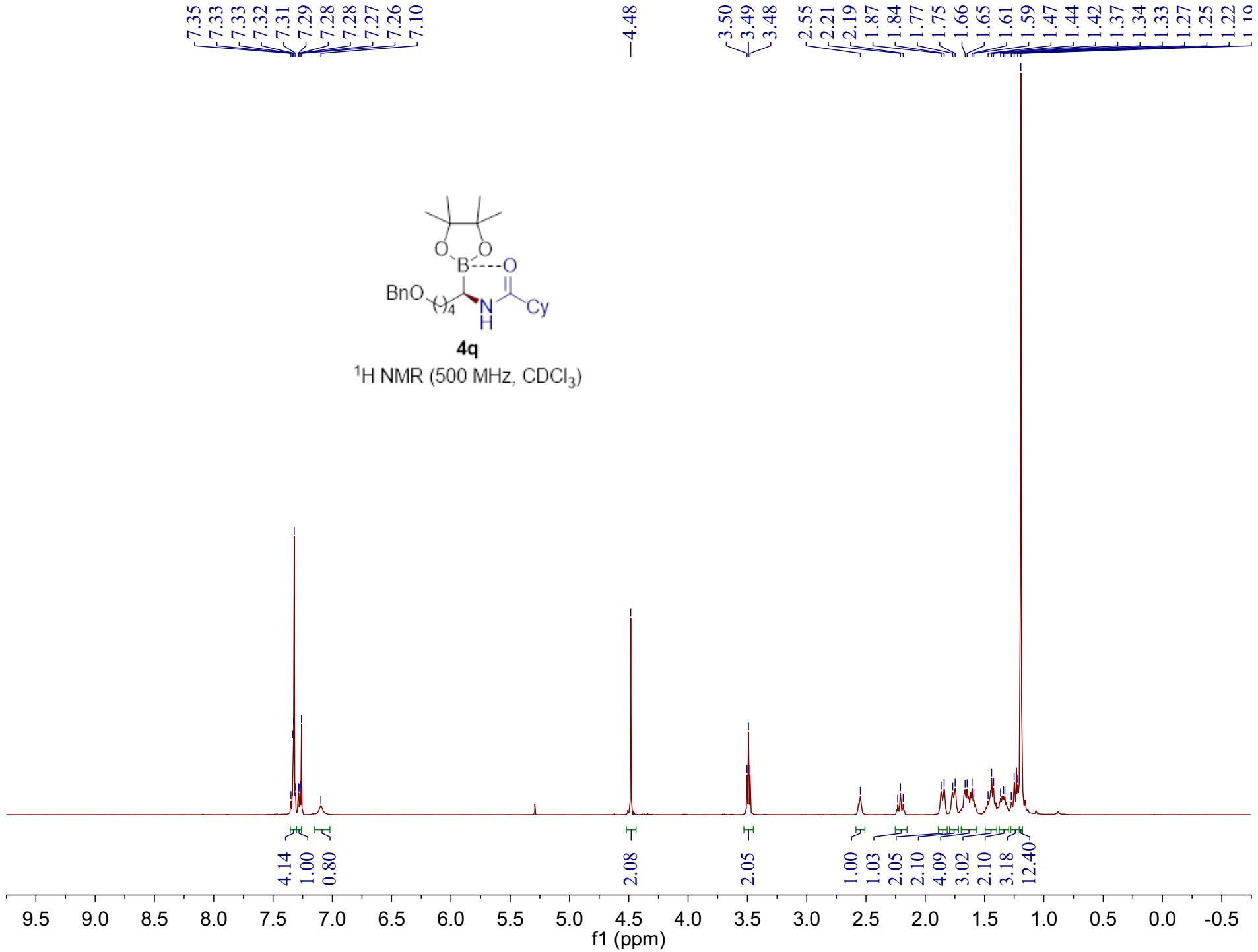
Supplementary Figure 101: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4p**.



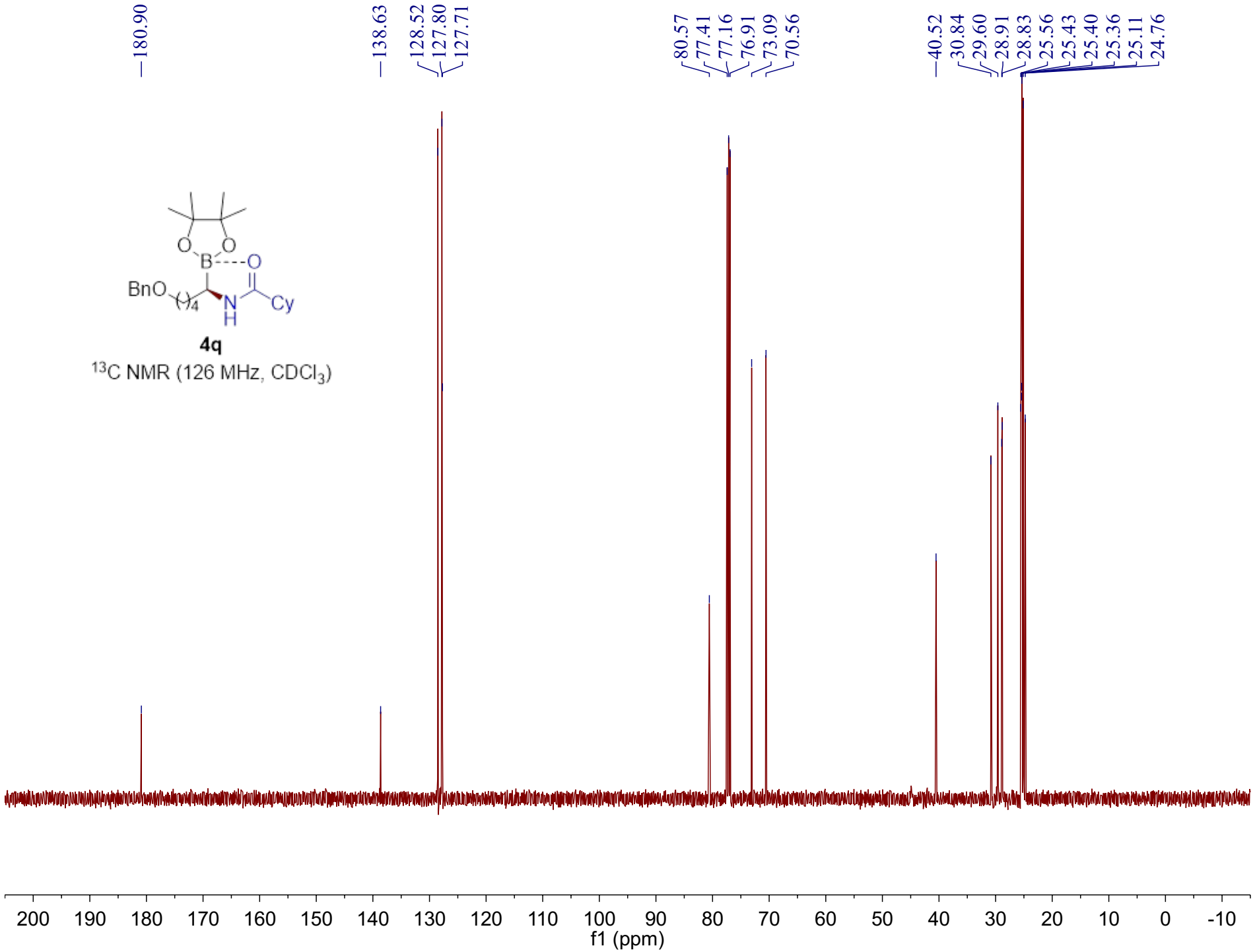
Supplementary Figure 102: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4p**.



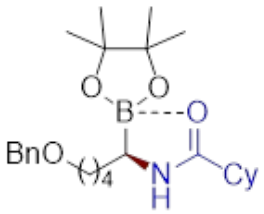
Supplementary Figure 103: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4p**.



Supplementary Figure 104: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4q**.

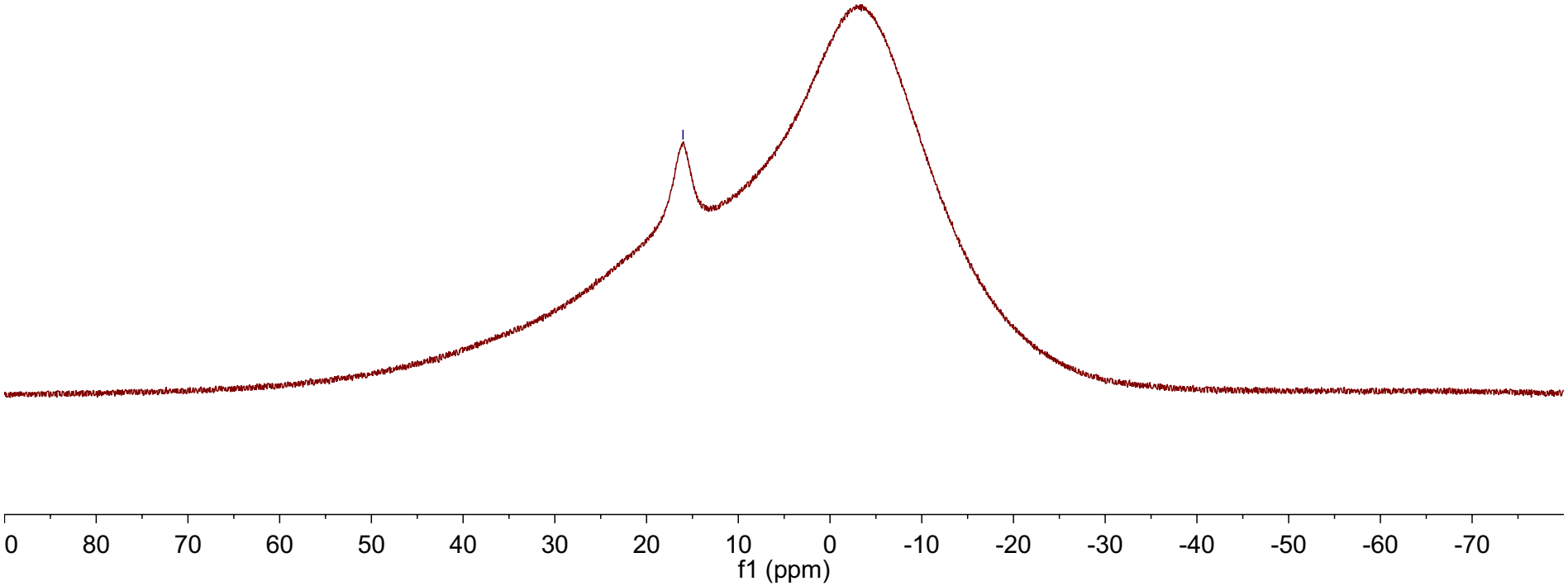


Supplementary Figure 105: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4q**.

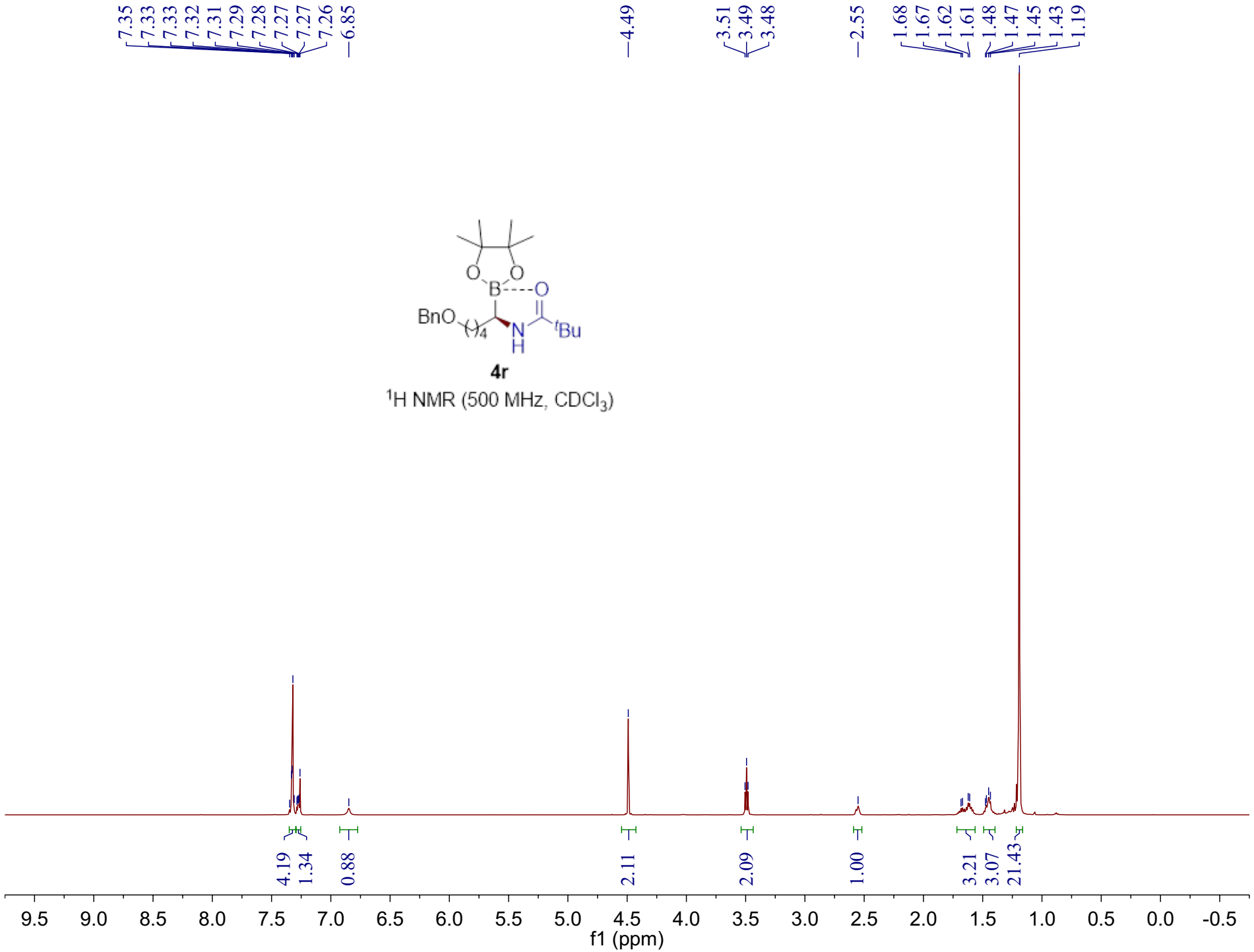


4q

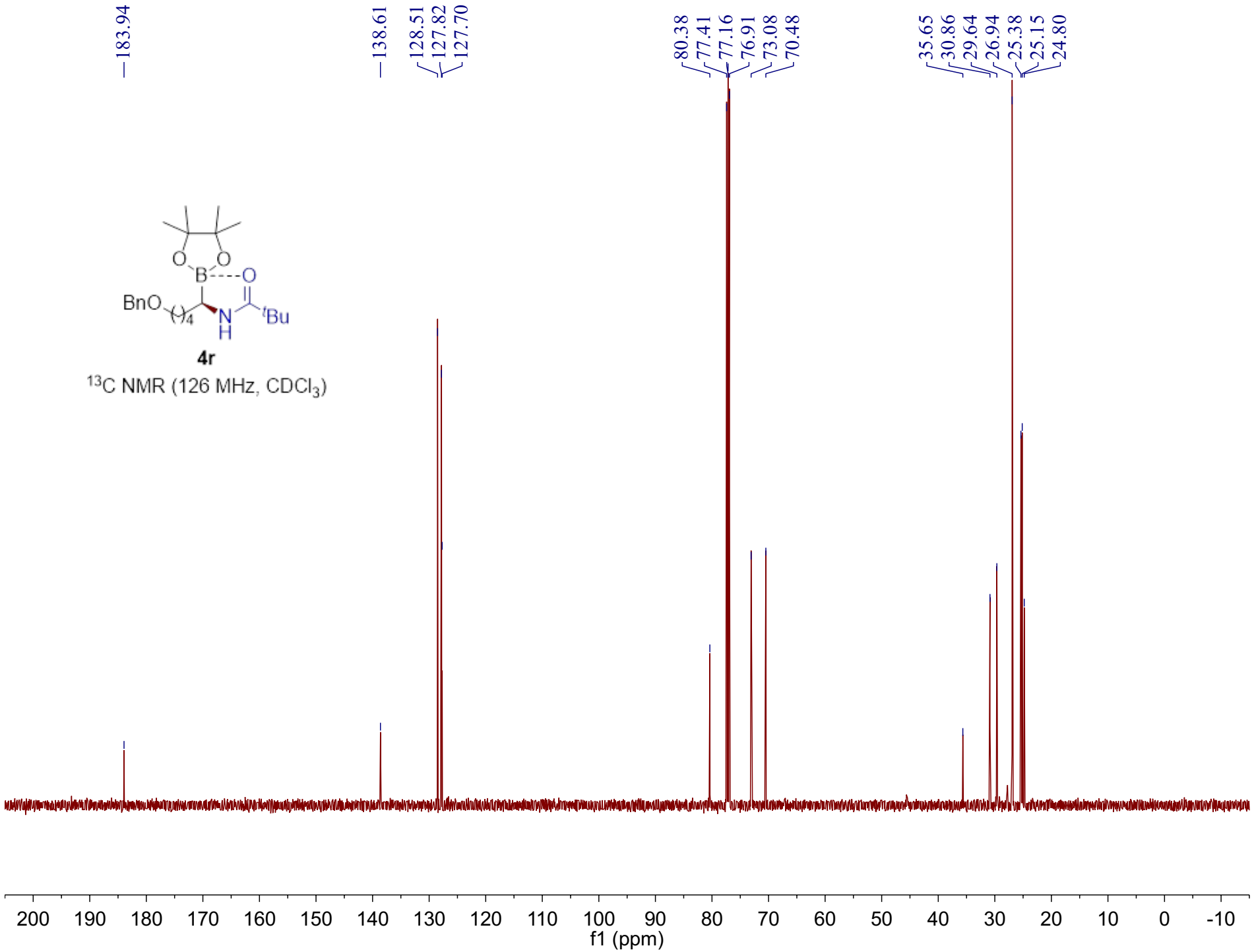
^{11}B NMR (160 MHz, $CDCl_3$)



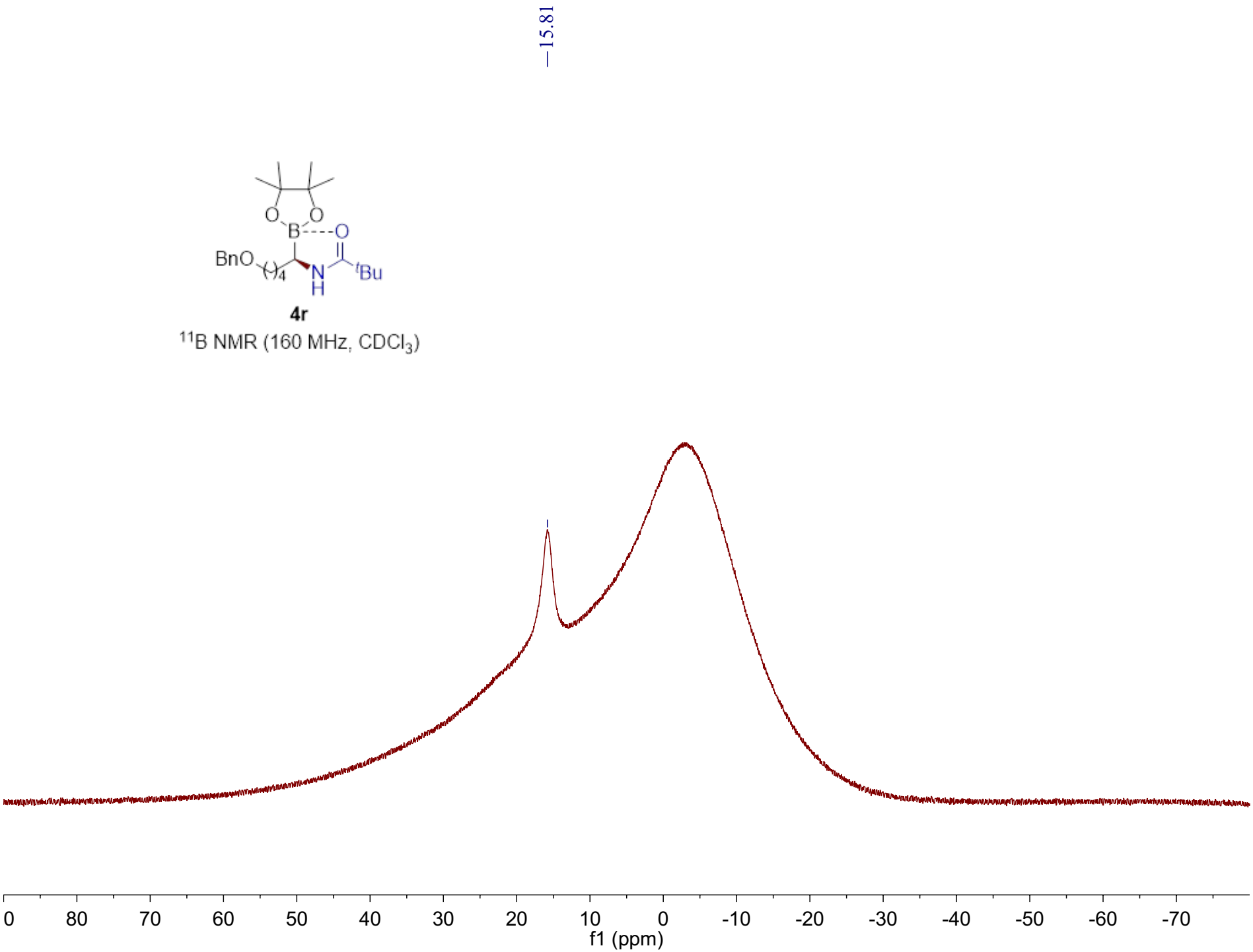
Supplementary Figure 106: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4q**.



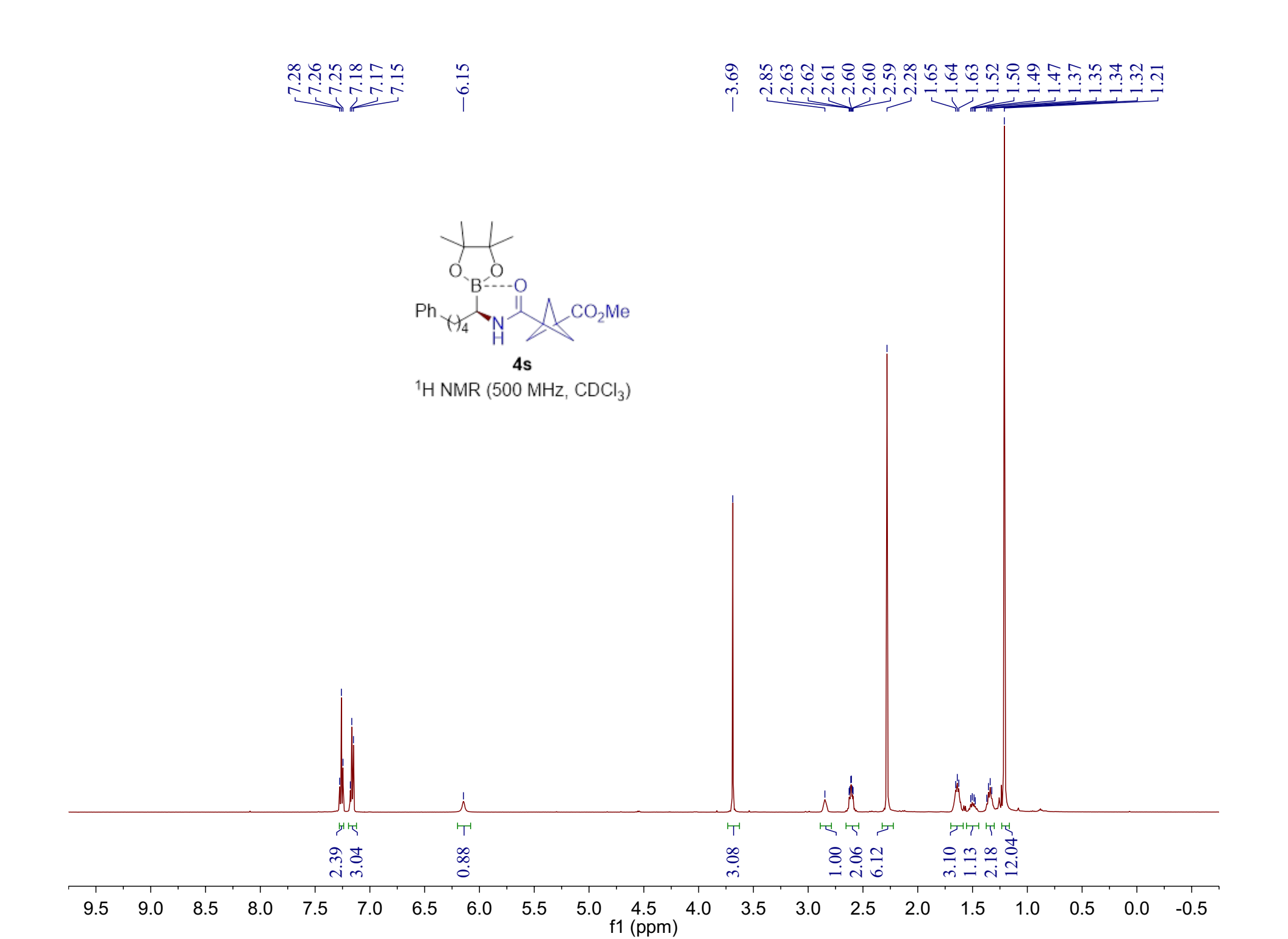
Supplementary Figure 107: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4r**.



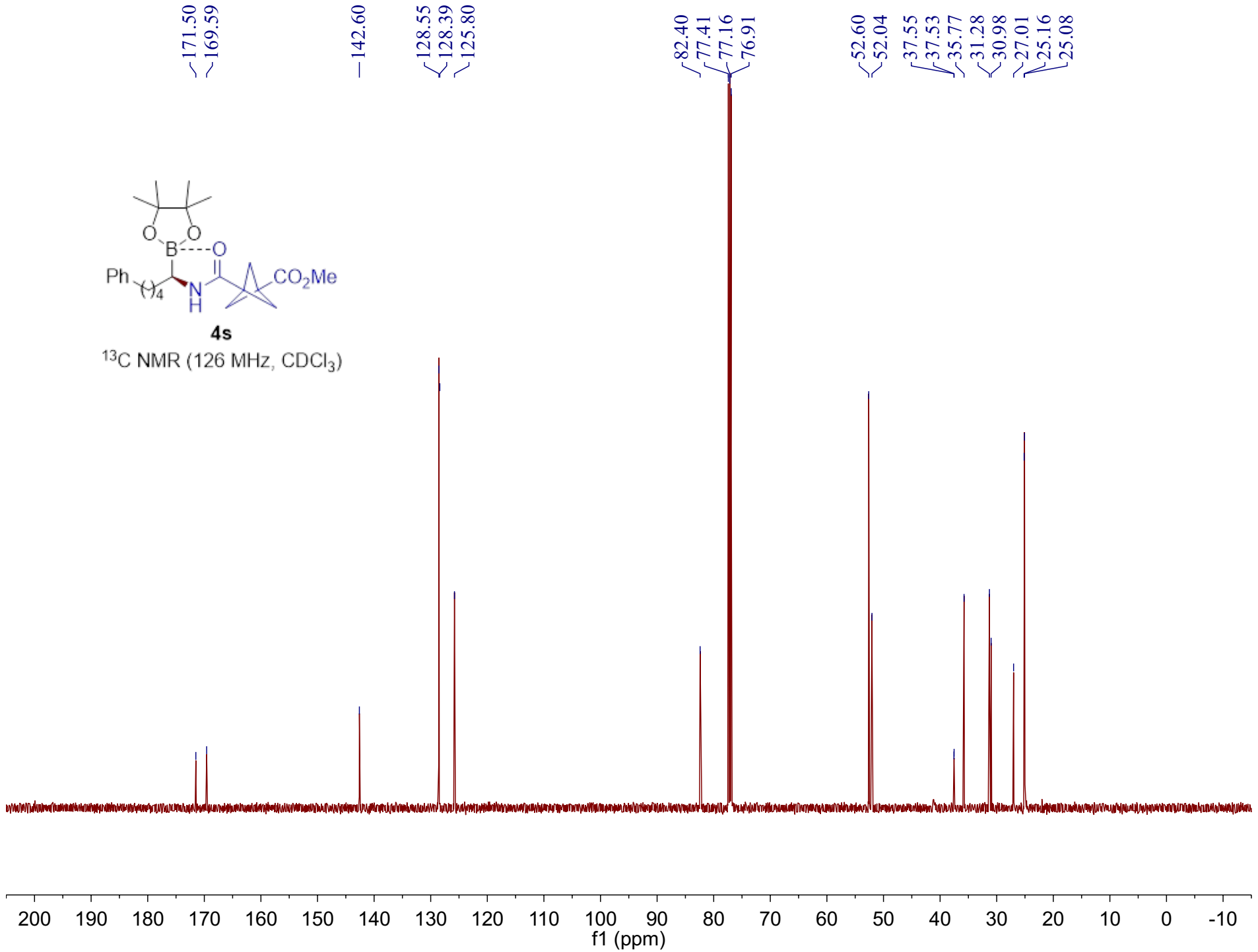
Supplementary Figure 108: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4r**.



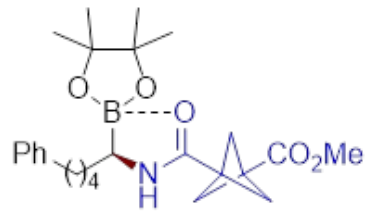
Supplementary Figure 109: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4r**.



Supplementary Figure 110: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4s**.



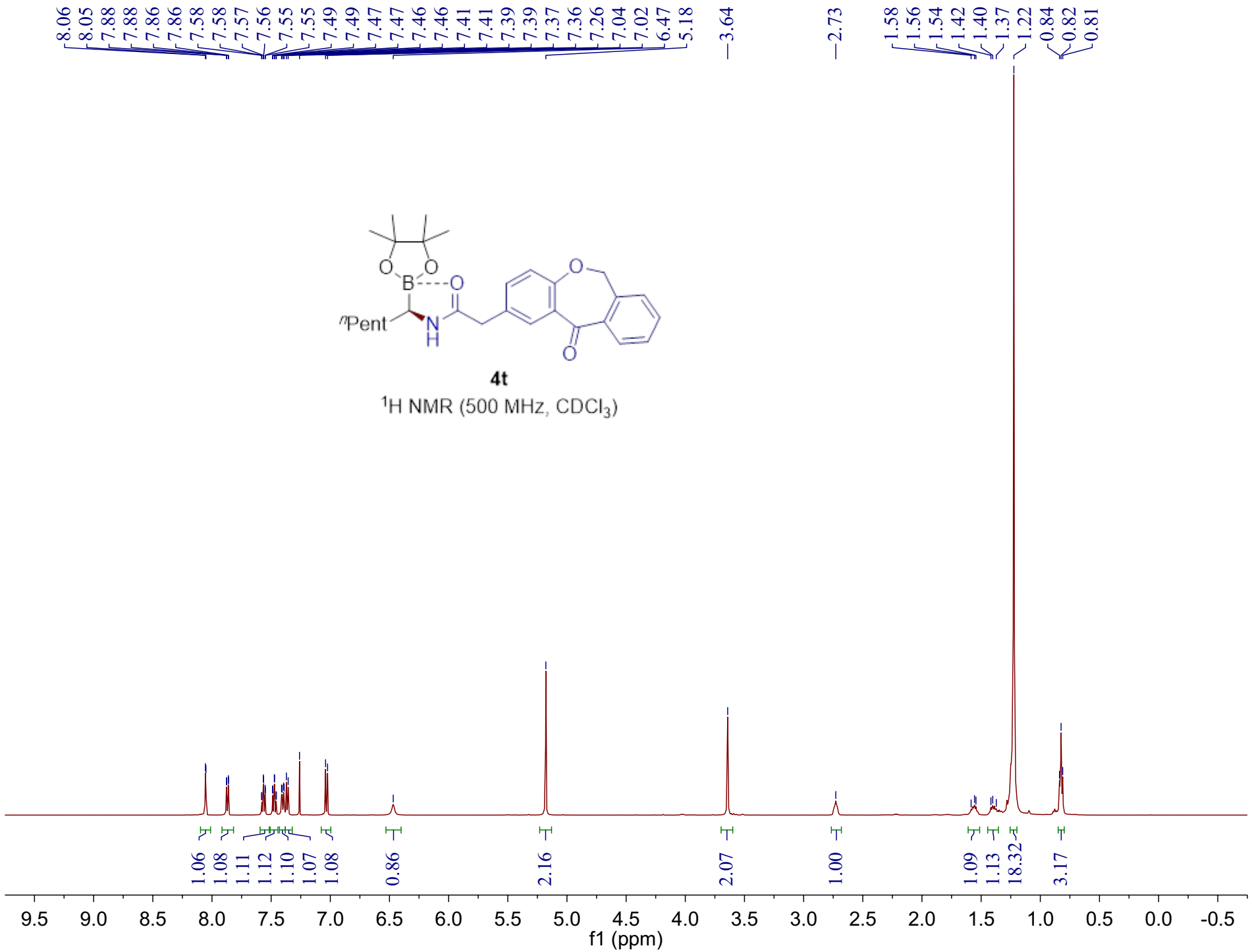
Supplementary Figure 111: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4s**.



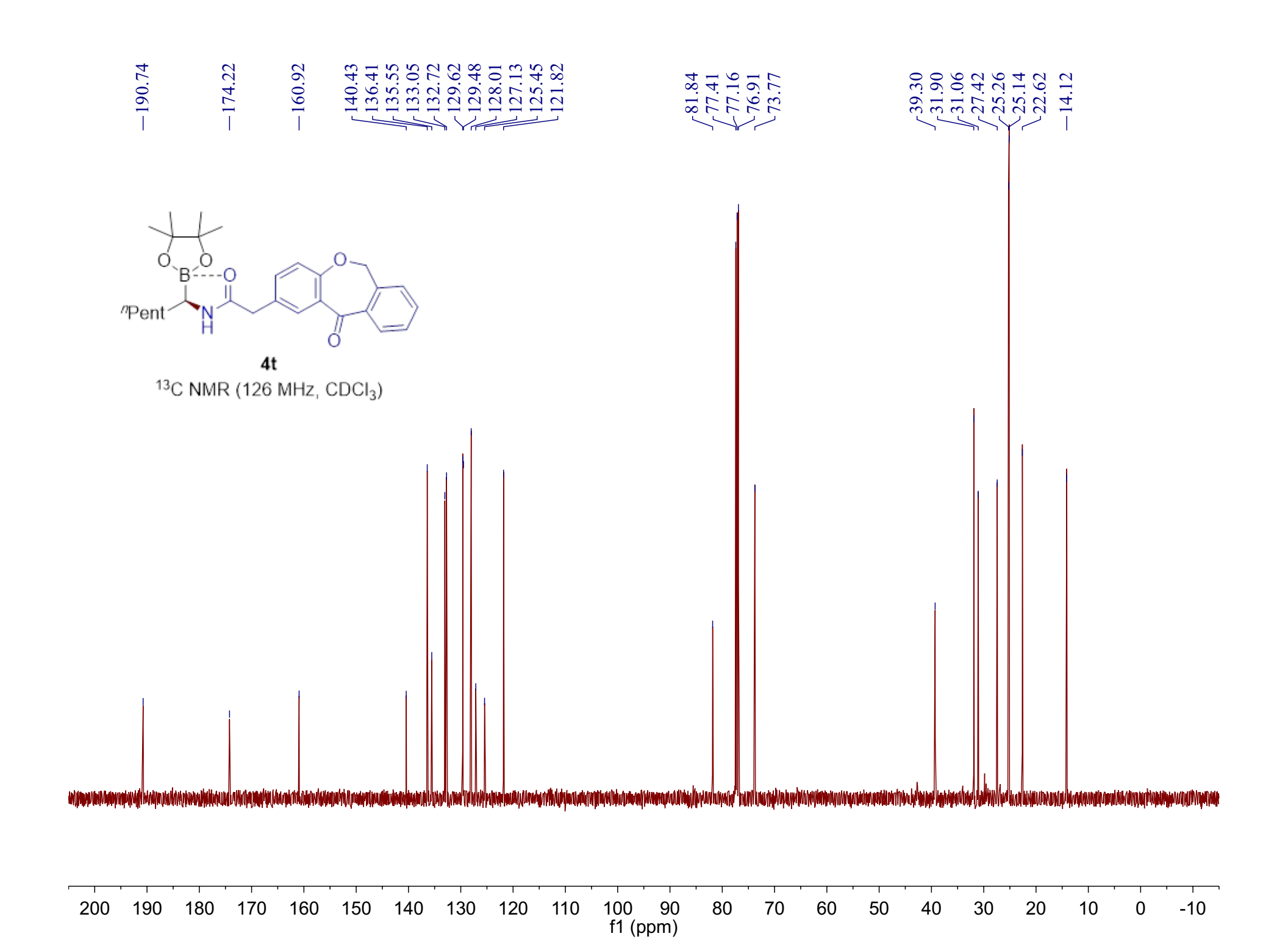
4s

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

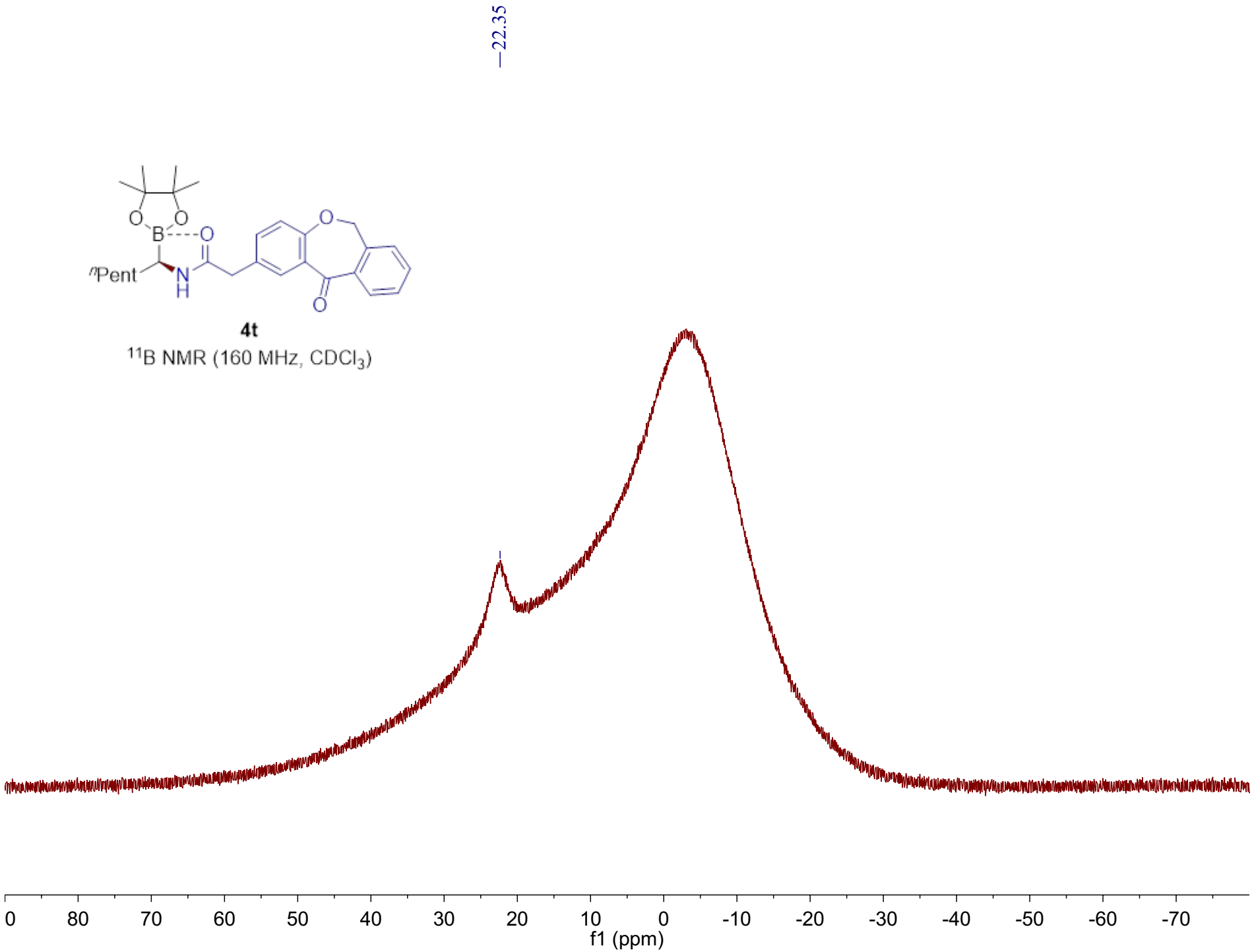
Supplementary Figure 112: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4s**.



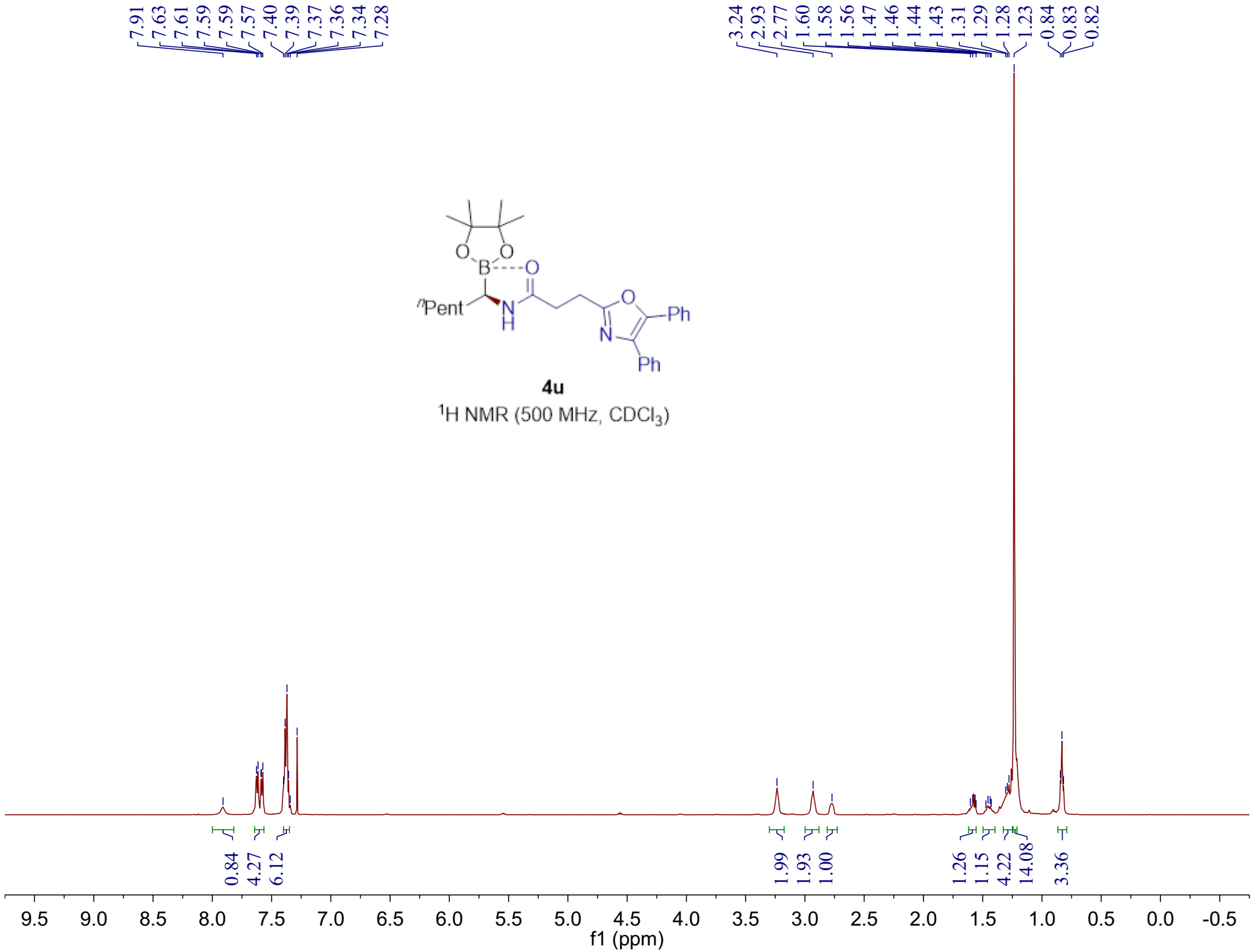
Supplementary Figure 113: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4t**.



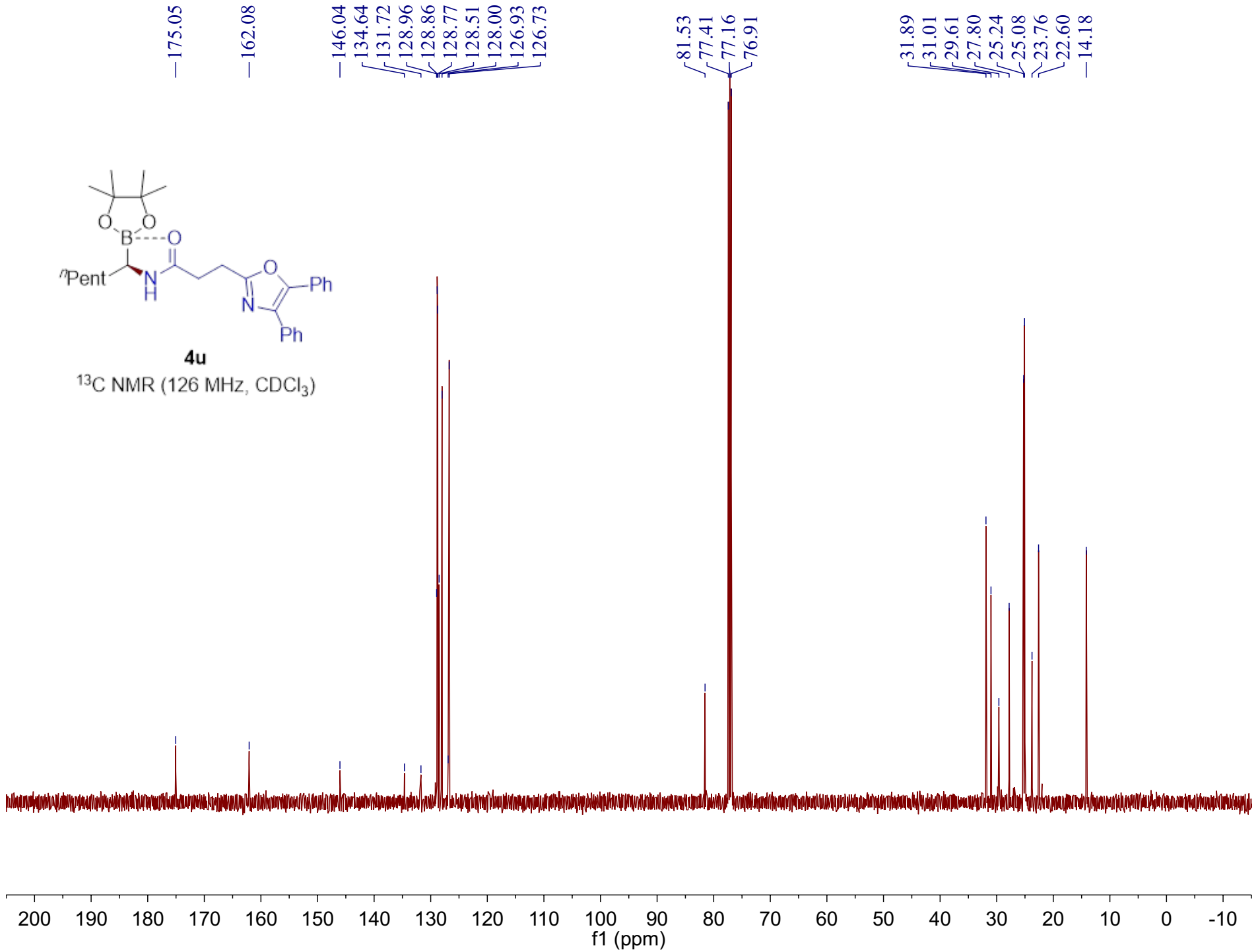
Supplementary Figure 114: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4t**.



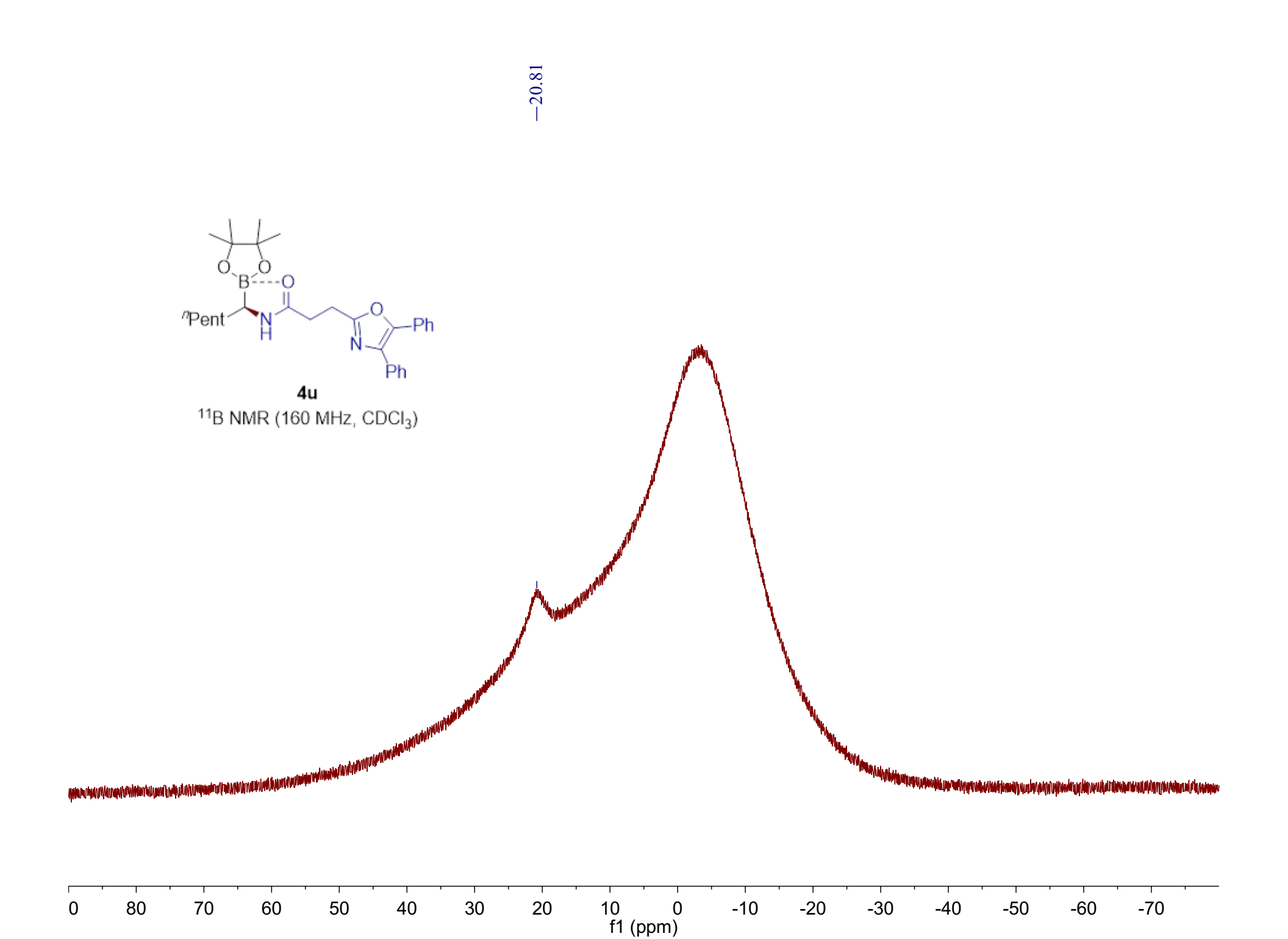
Supplementary Figure 115: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4t**.



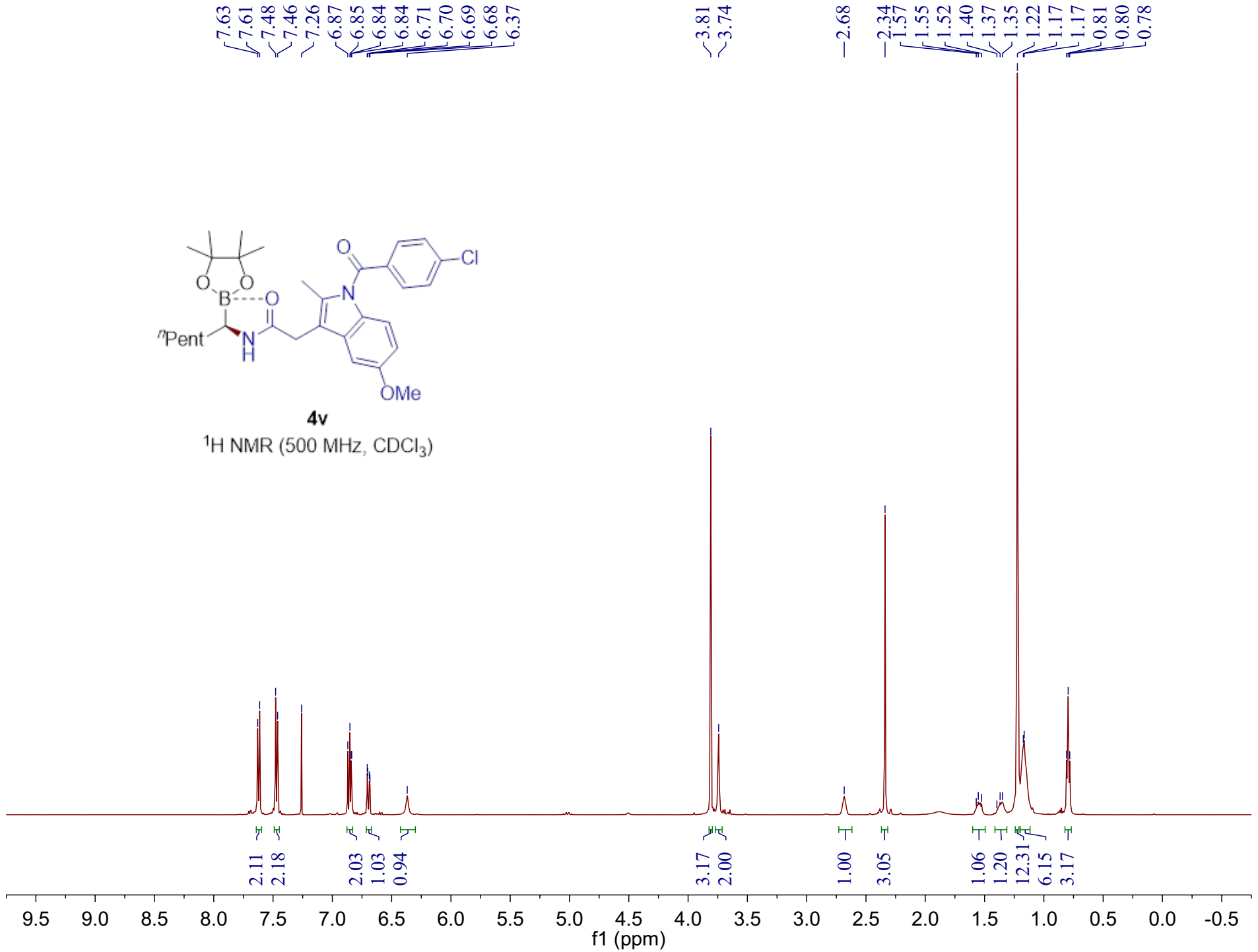
Supplementary Figure 116: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4u**.



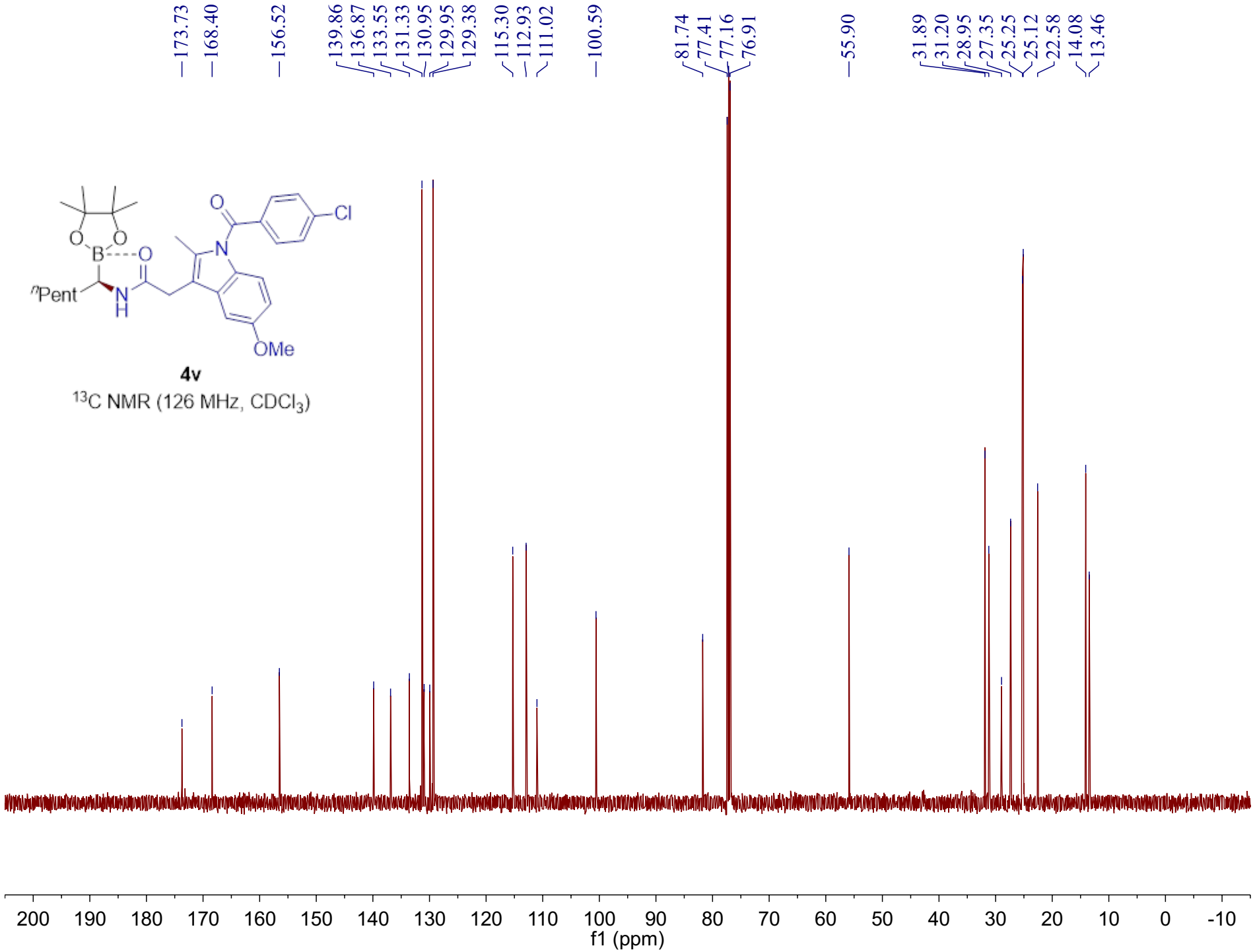
Supplementary Figure 117: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4u**.



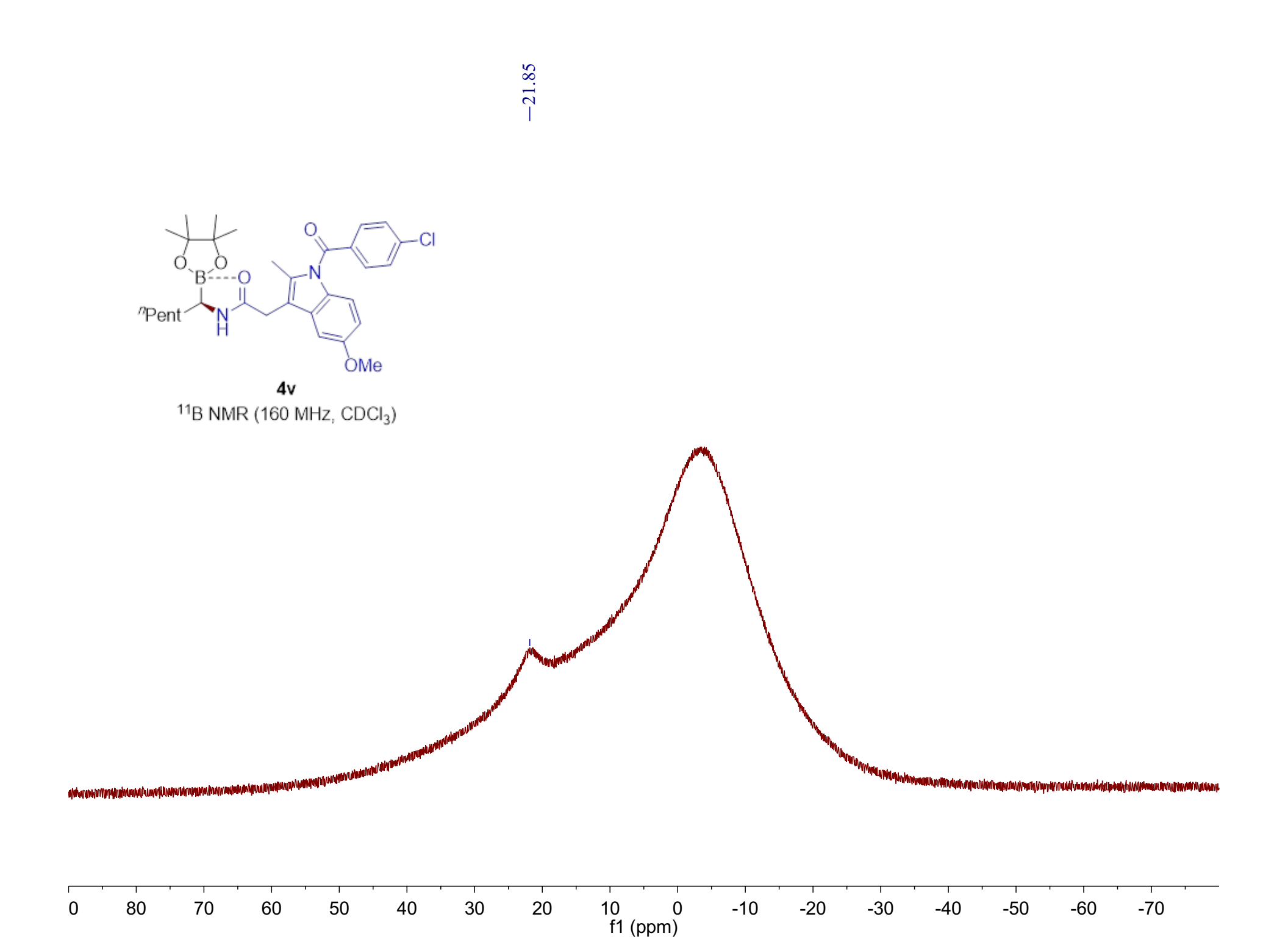
Supplementary Figure 118: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4u**.



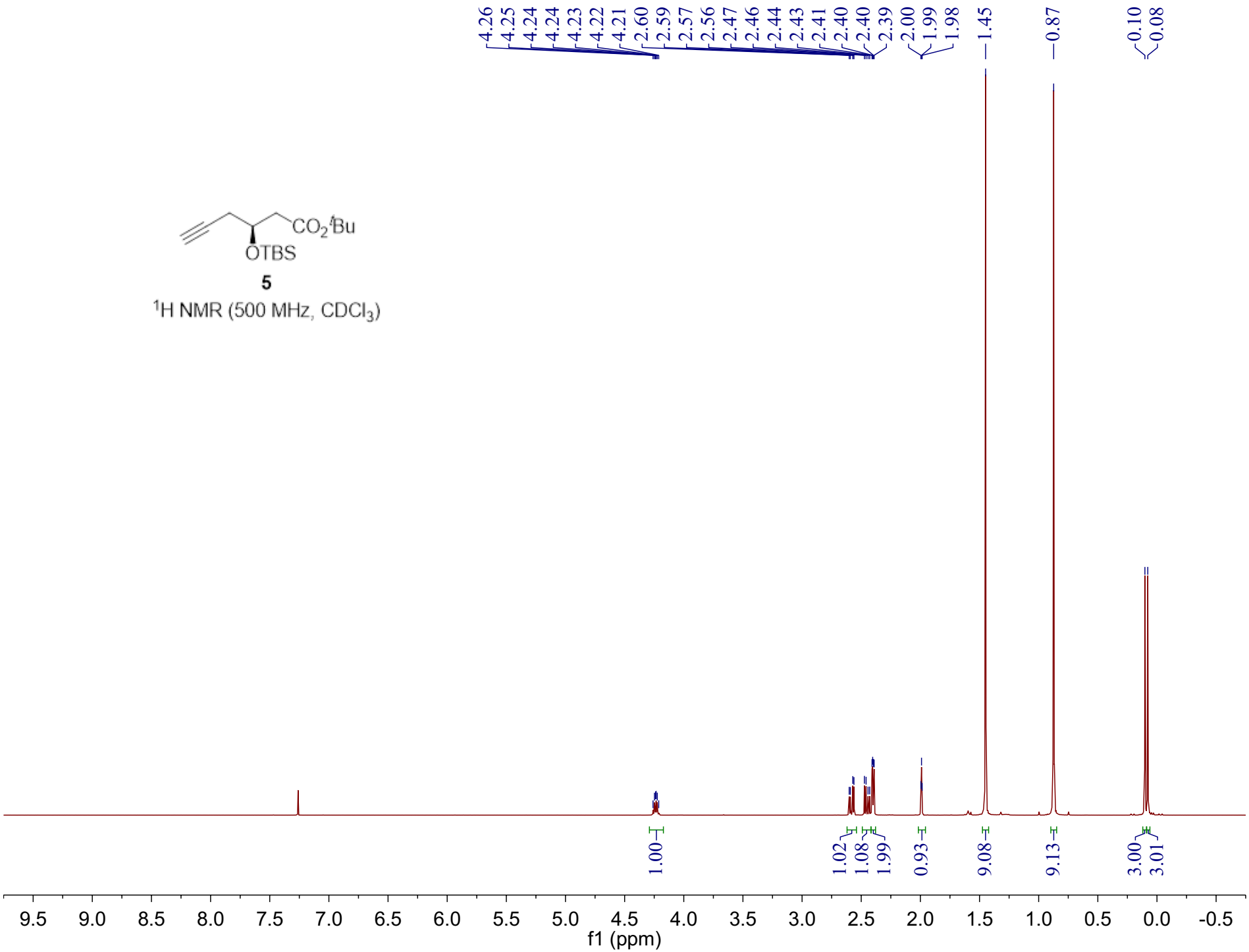
Supplementary Figure 119: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4v**.



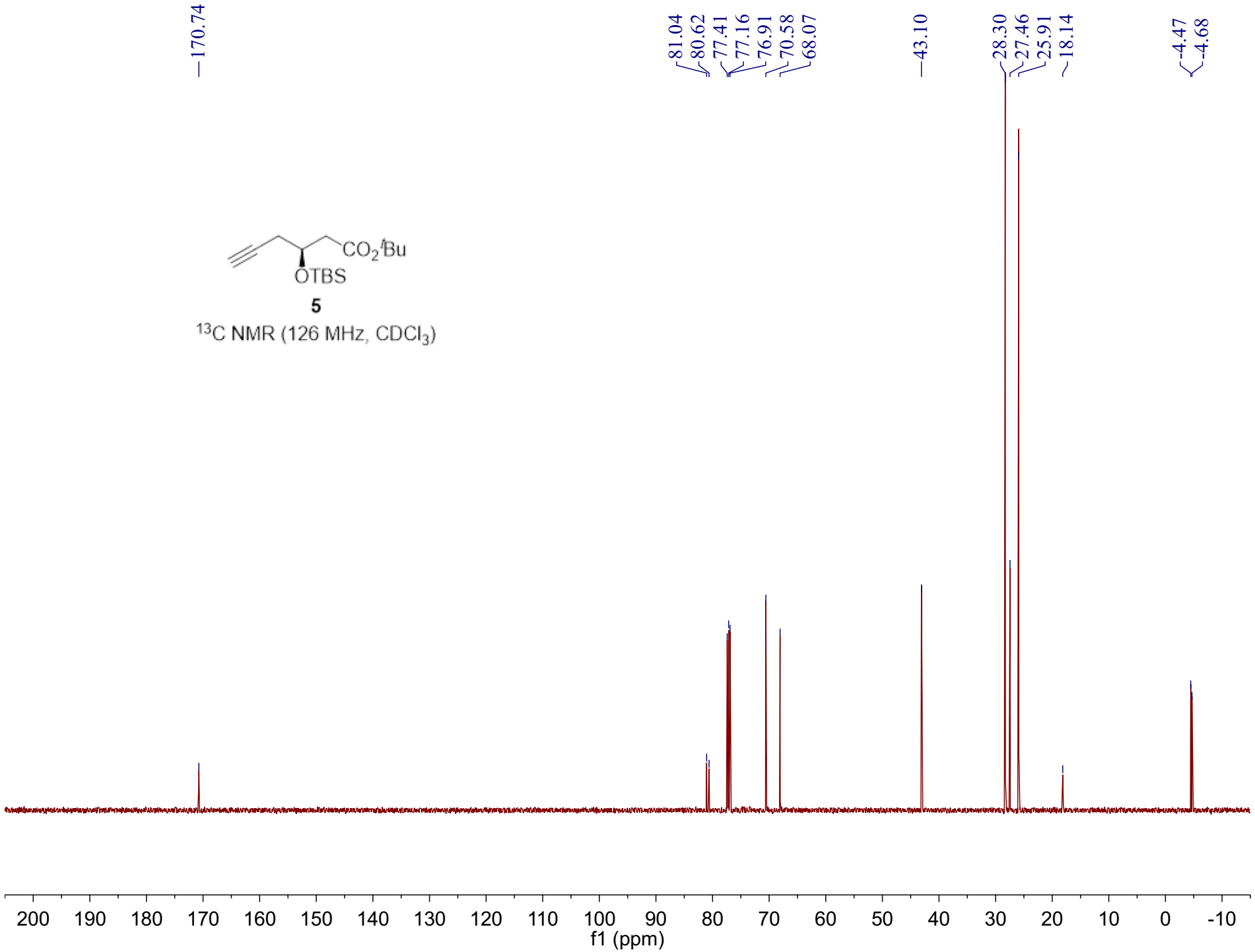
Supplementary Figure 120: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4v**.



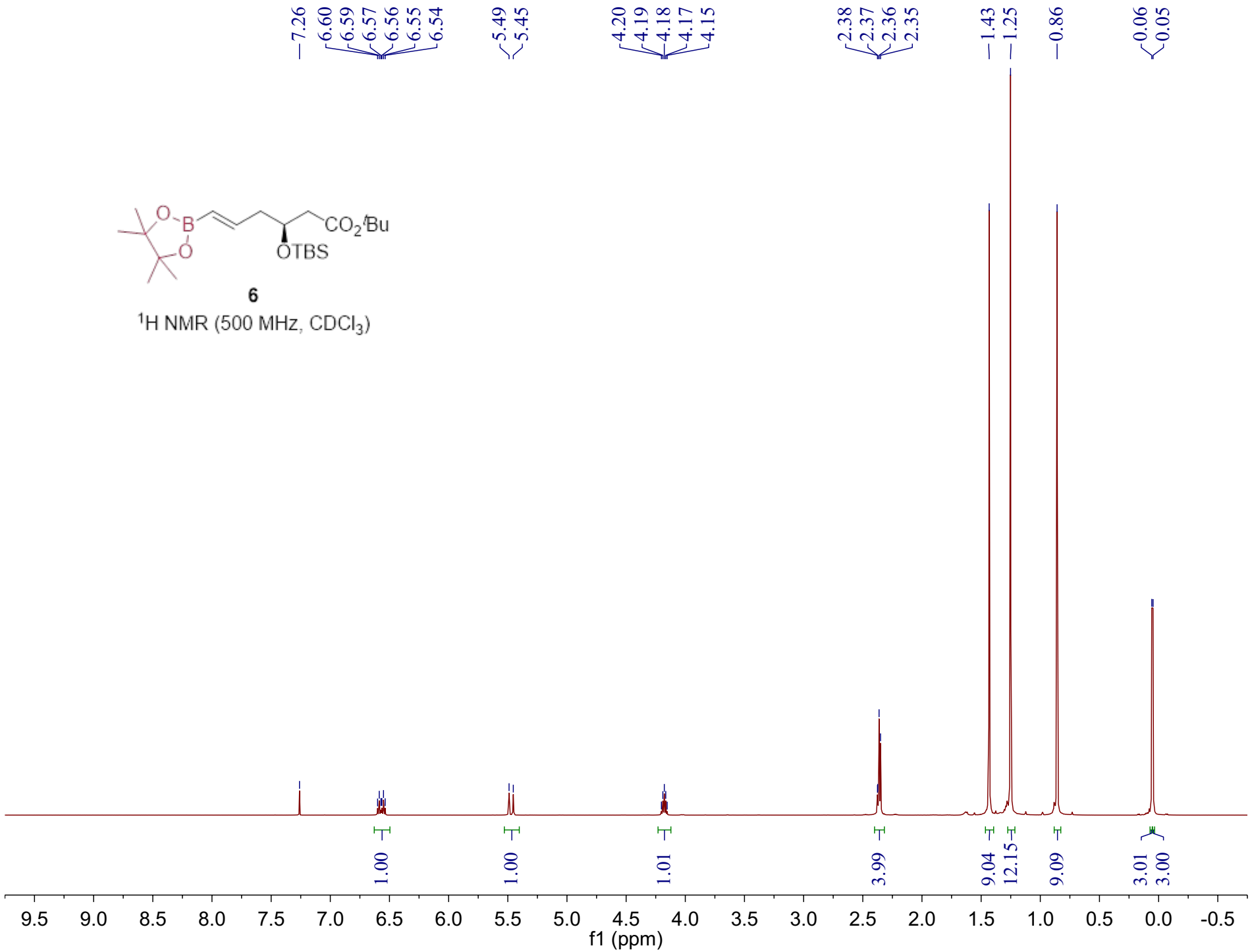
Supplementary Figure 121: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **4v**.



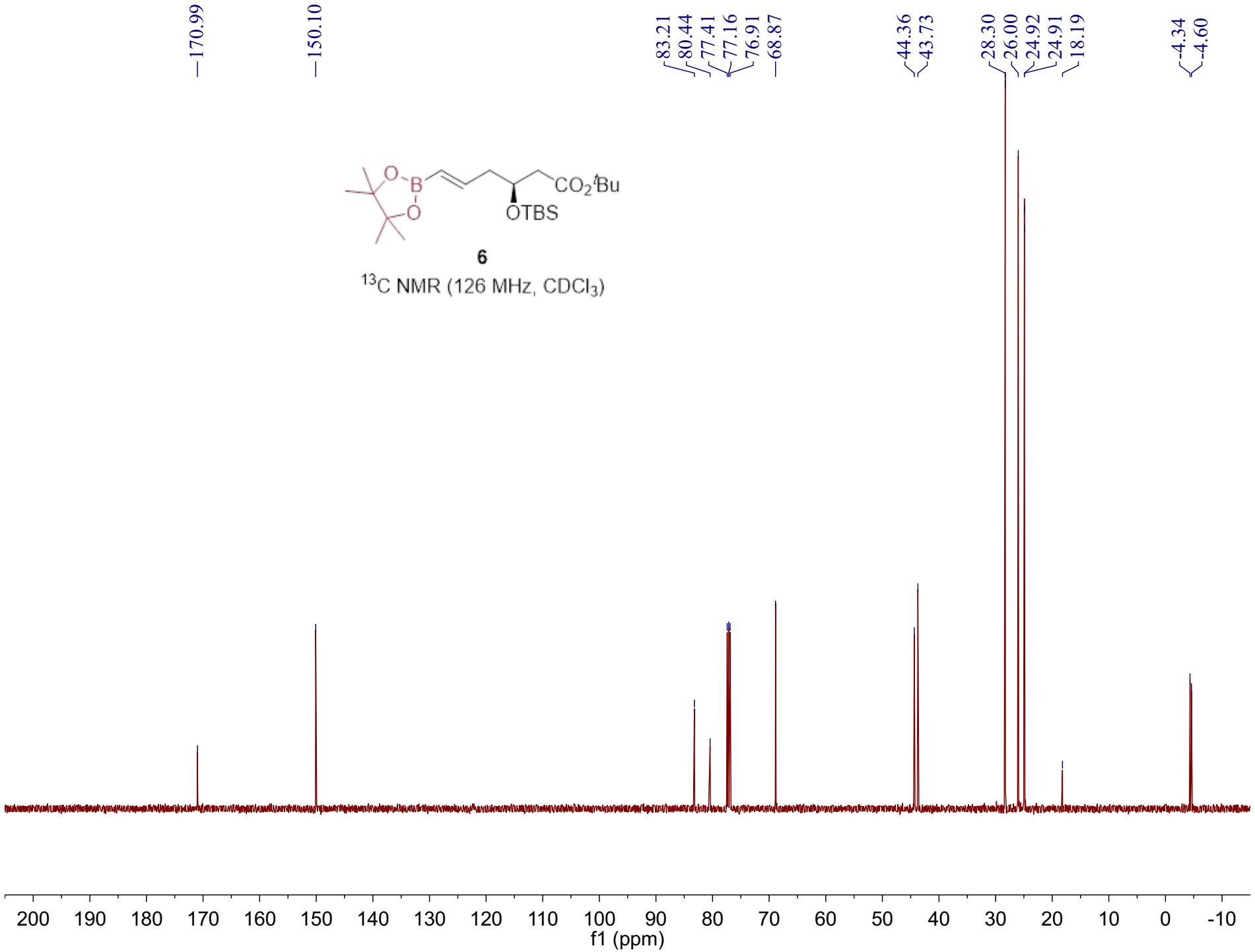
Supplementary Figure 122: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5**.



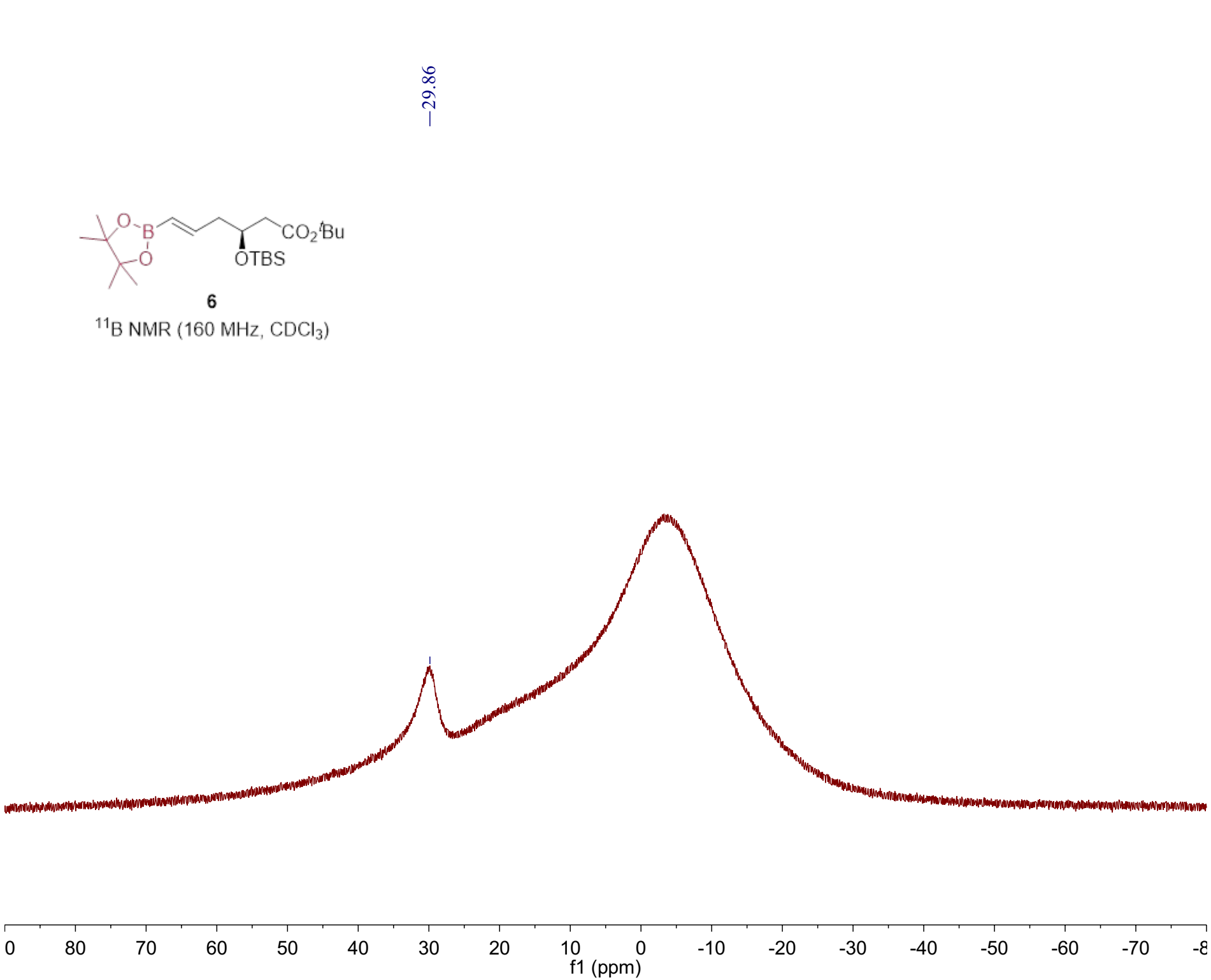
Supplementary Figure 123: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5**.



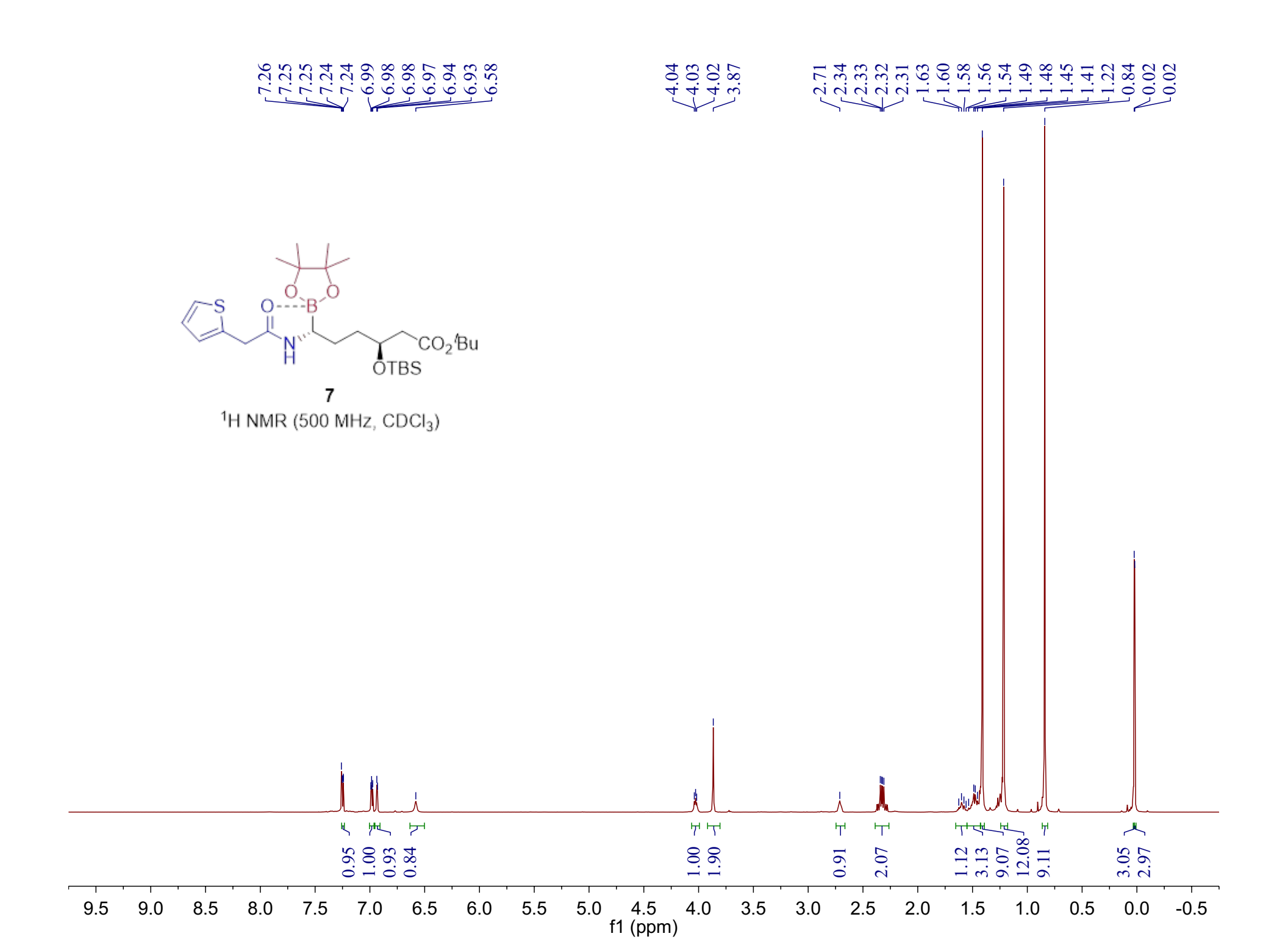
Supplementary Figure 124: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **6**.



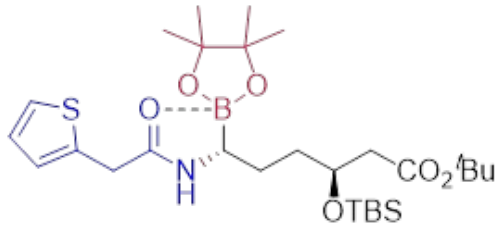
Supplementary Figure 125: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **6**.



Supplementary Figure 126: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **6**.



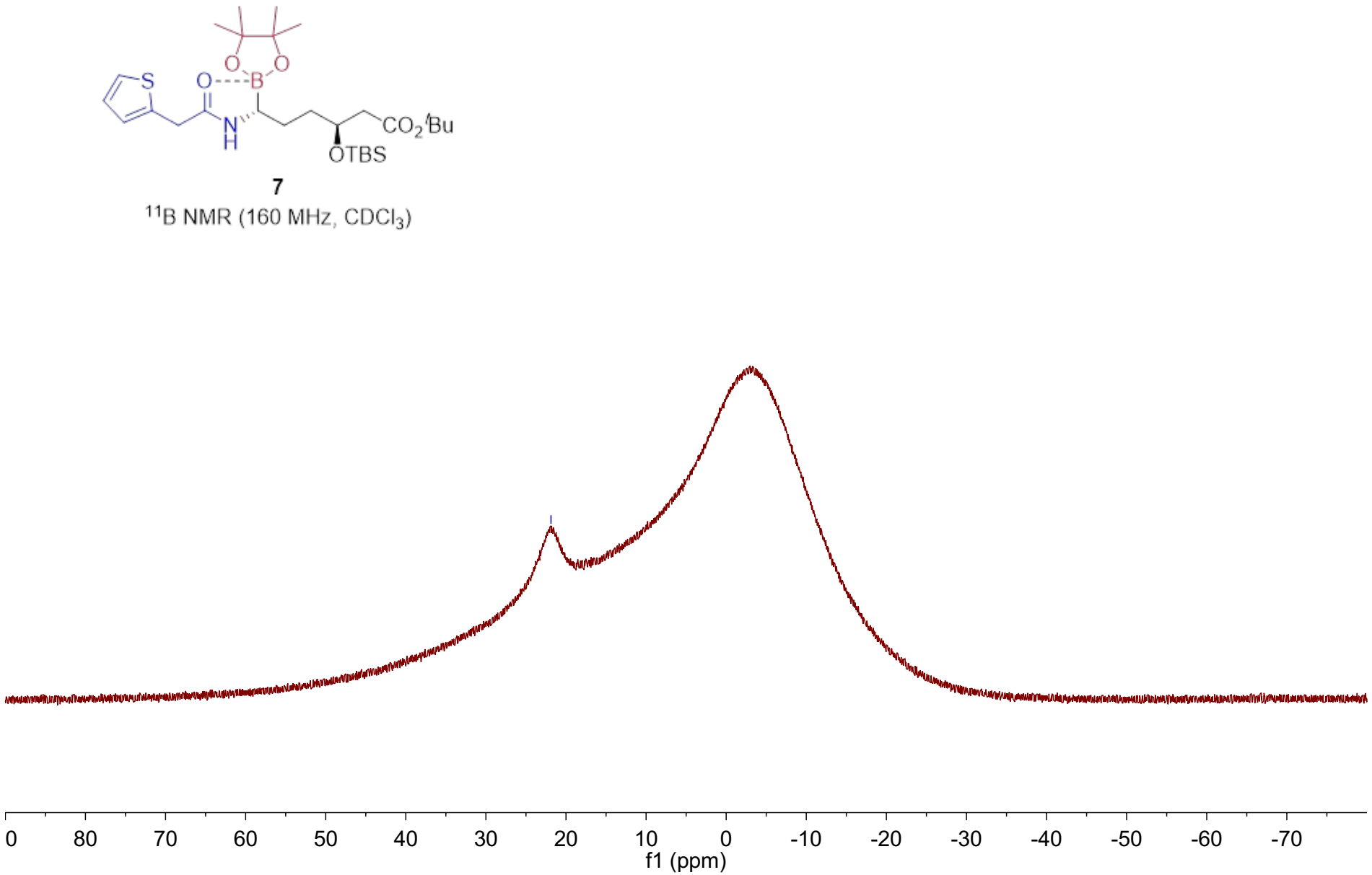
Supplementary Figure 127: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7**.



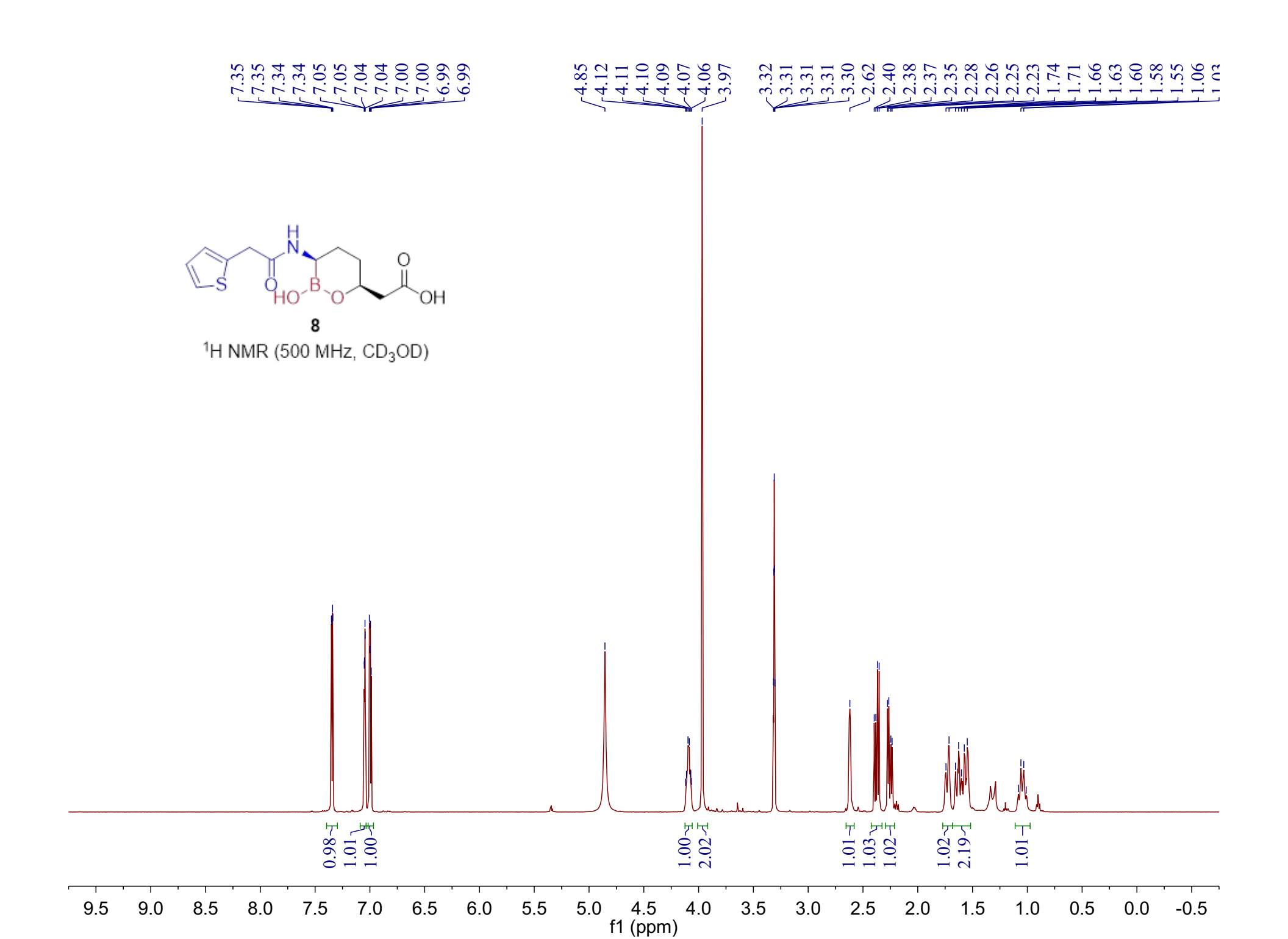
7

^{13}C NMR (126 MHz, $CDCl_3$)

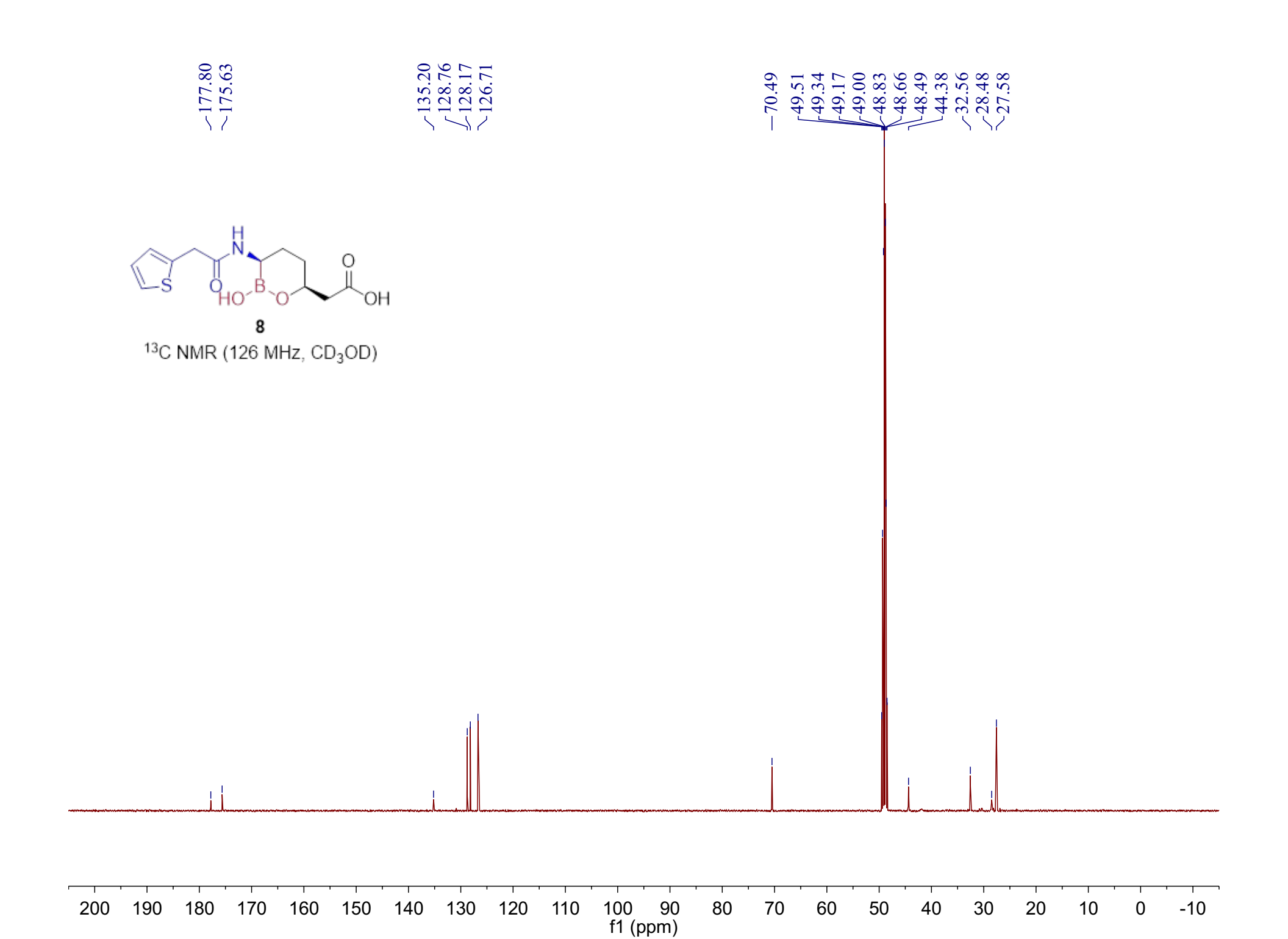
Supplementary Figure 128: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **7**.



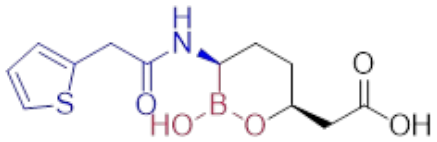
Supplementary Figure 129: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **7**.



Supplementary Figure 130: ^{1}H NMR (500 MHz, CD_3OD) spectrum of **8**.

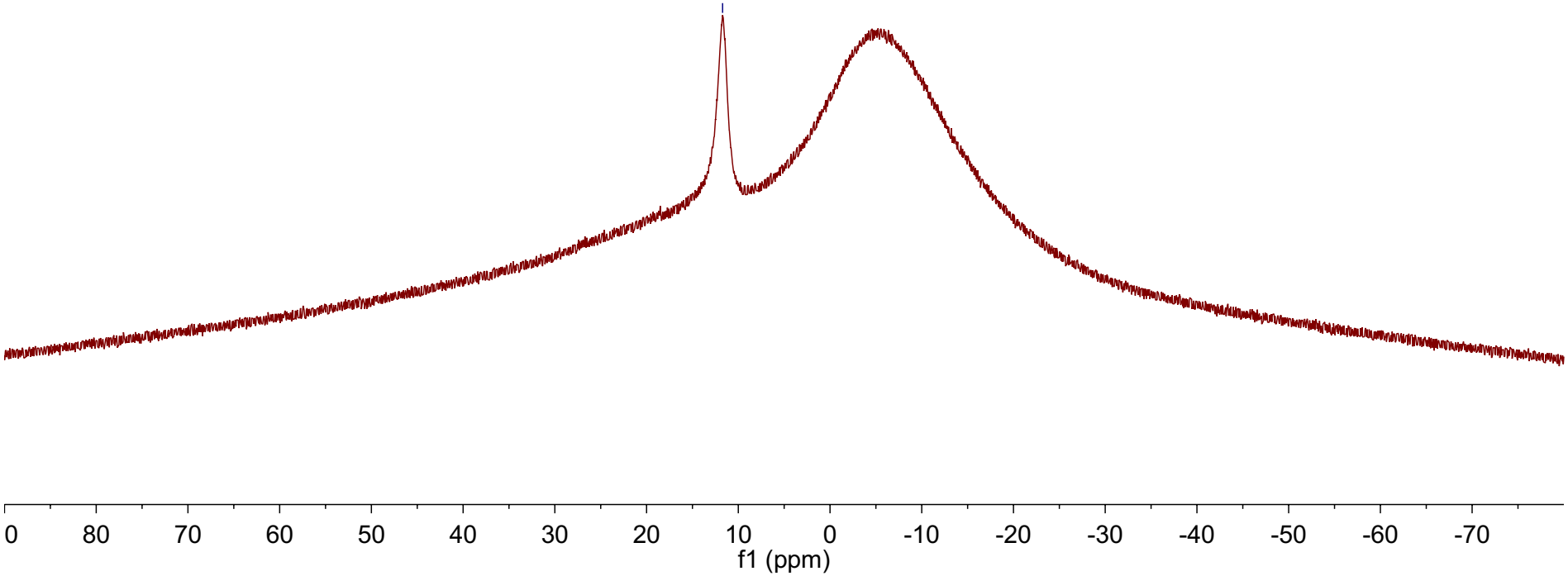


Supplementary Figure 131: ^{13}C NMR (126 MHz, CD_3OD) spectrum of **8**.

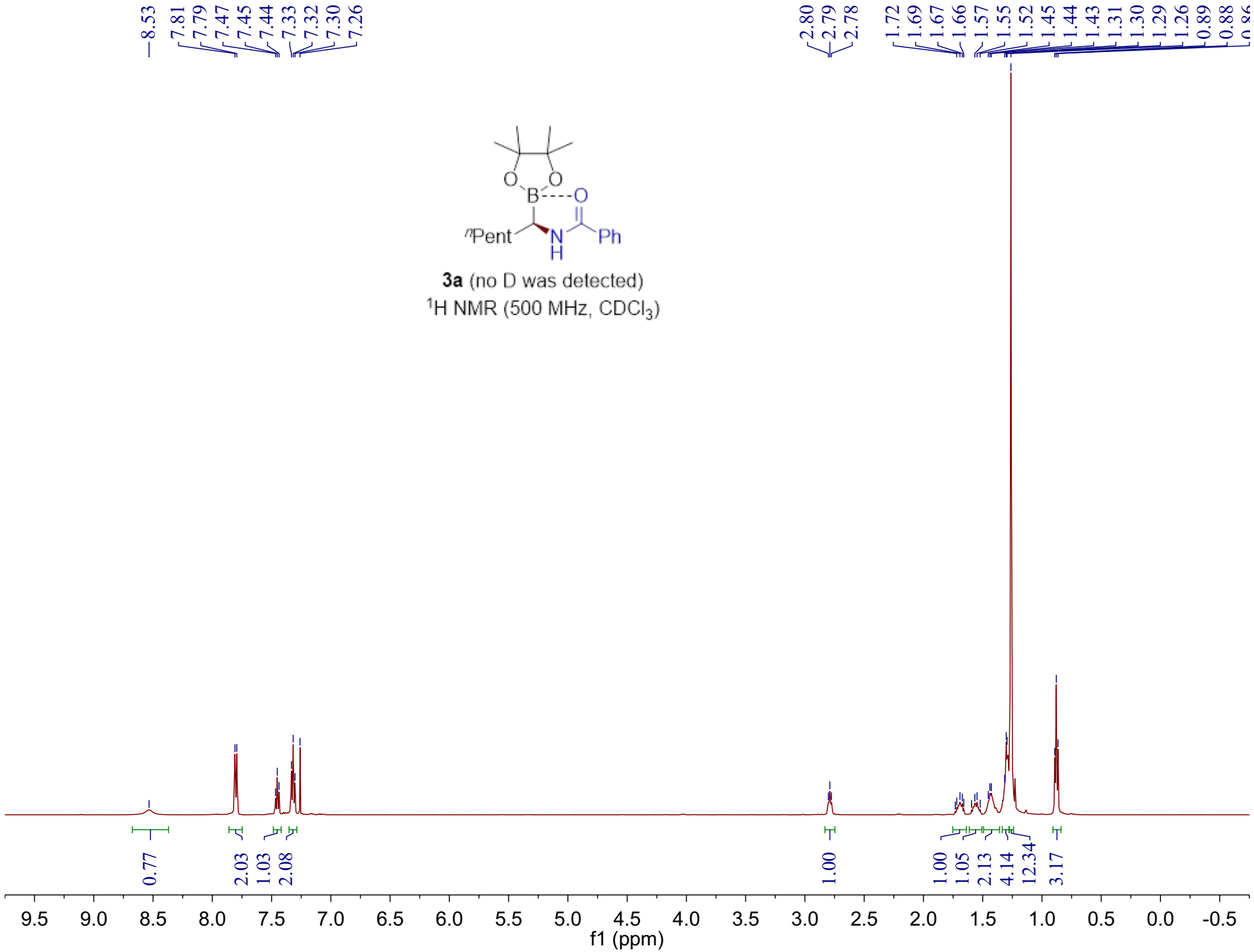


8

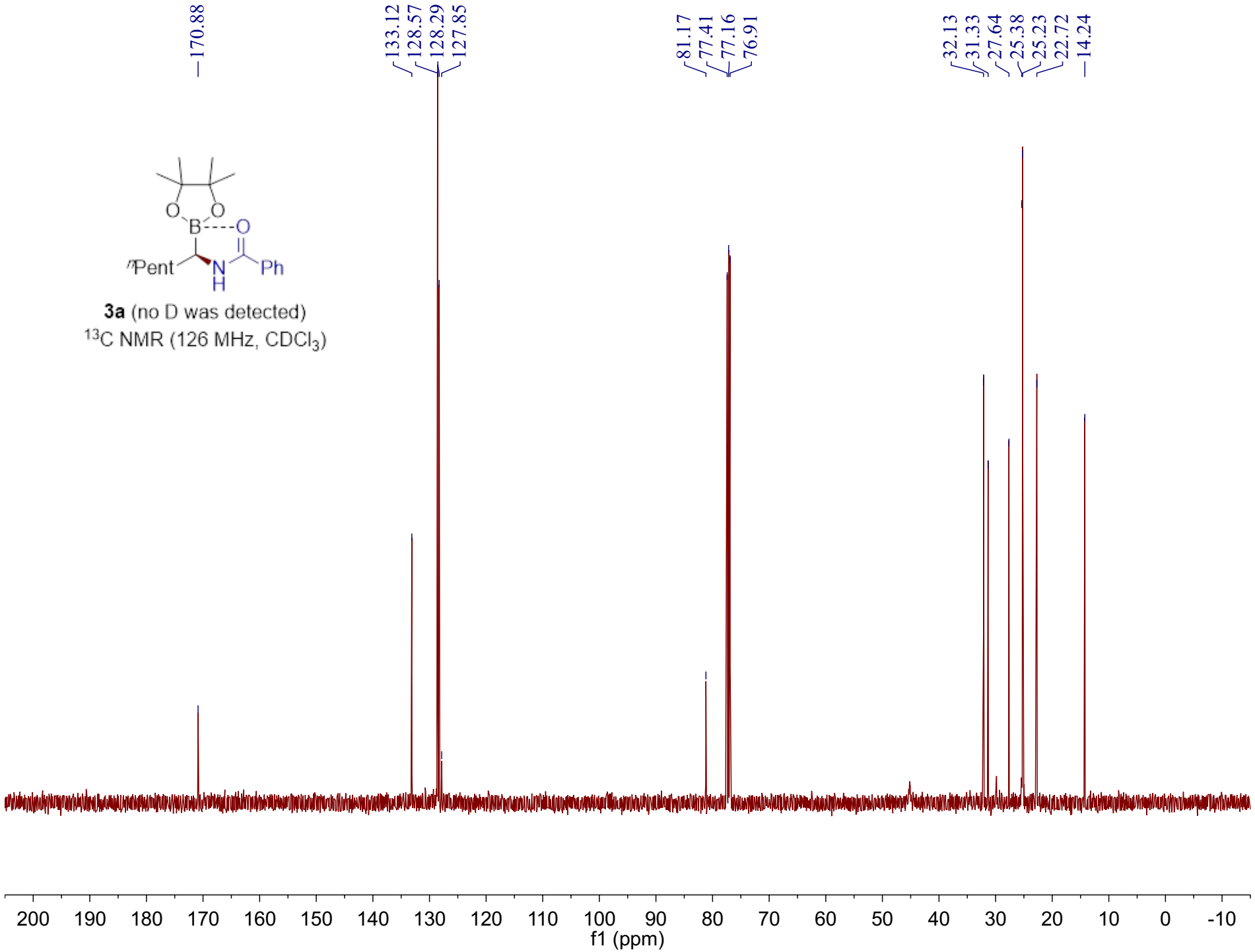
^{11}B NMR (160 MHz, CD_3OD)



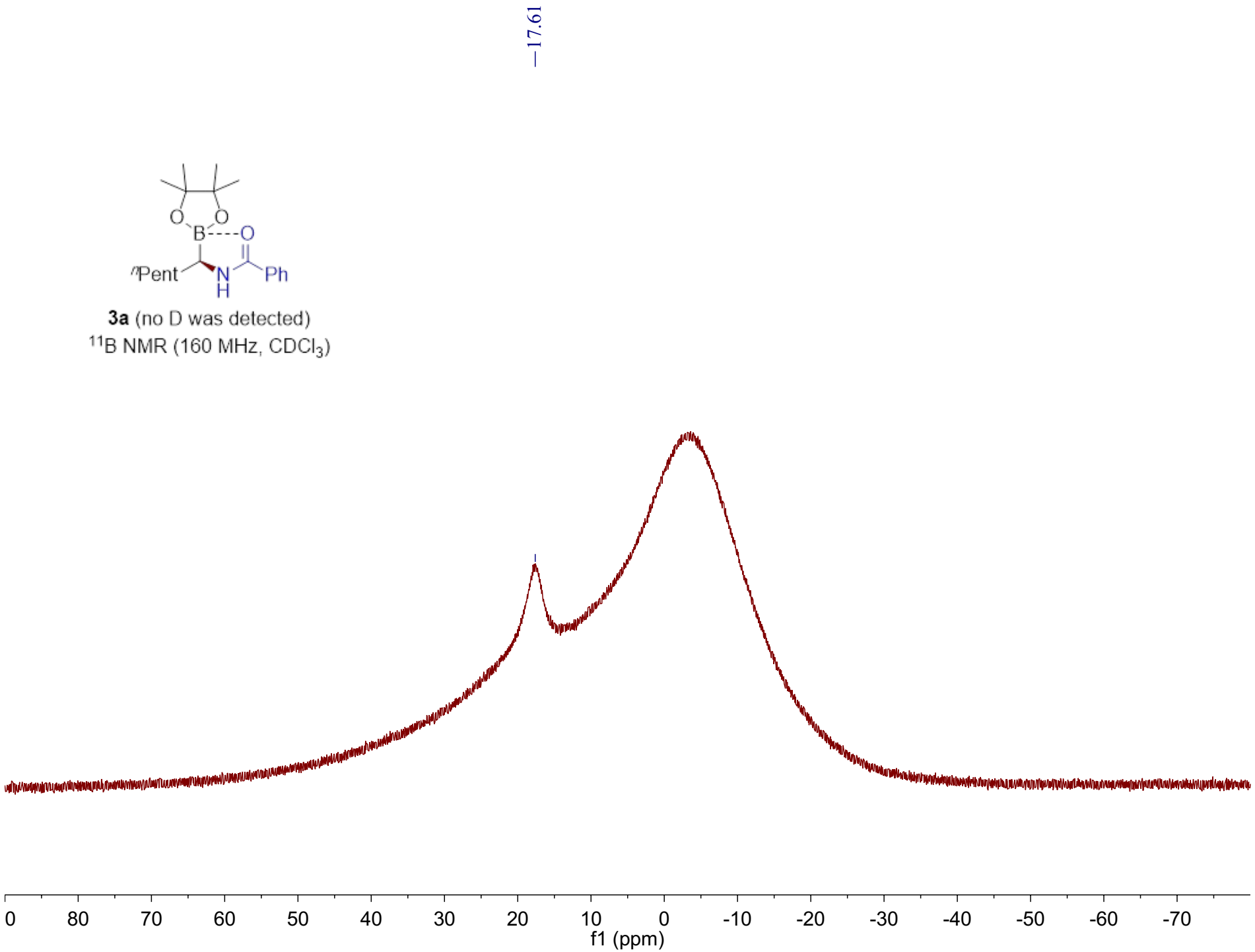
Supplementary Figure 132: ^{11}B NMR (160 MHz, CD_3OD) spectrum of **8**.



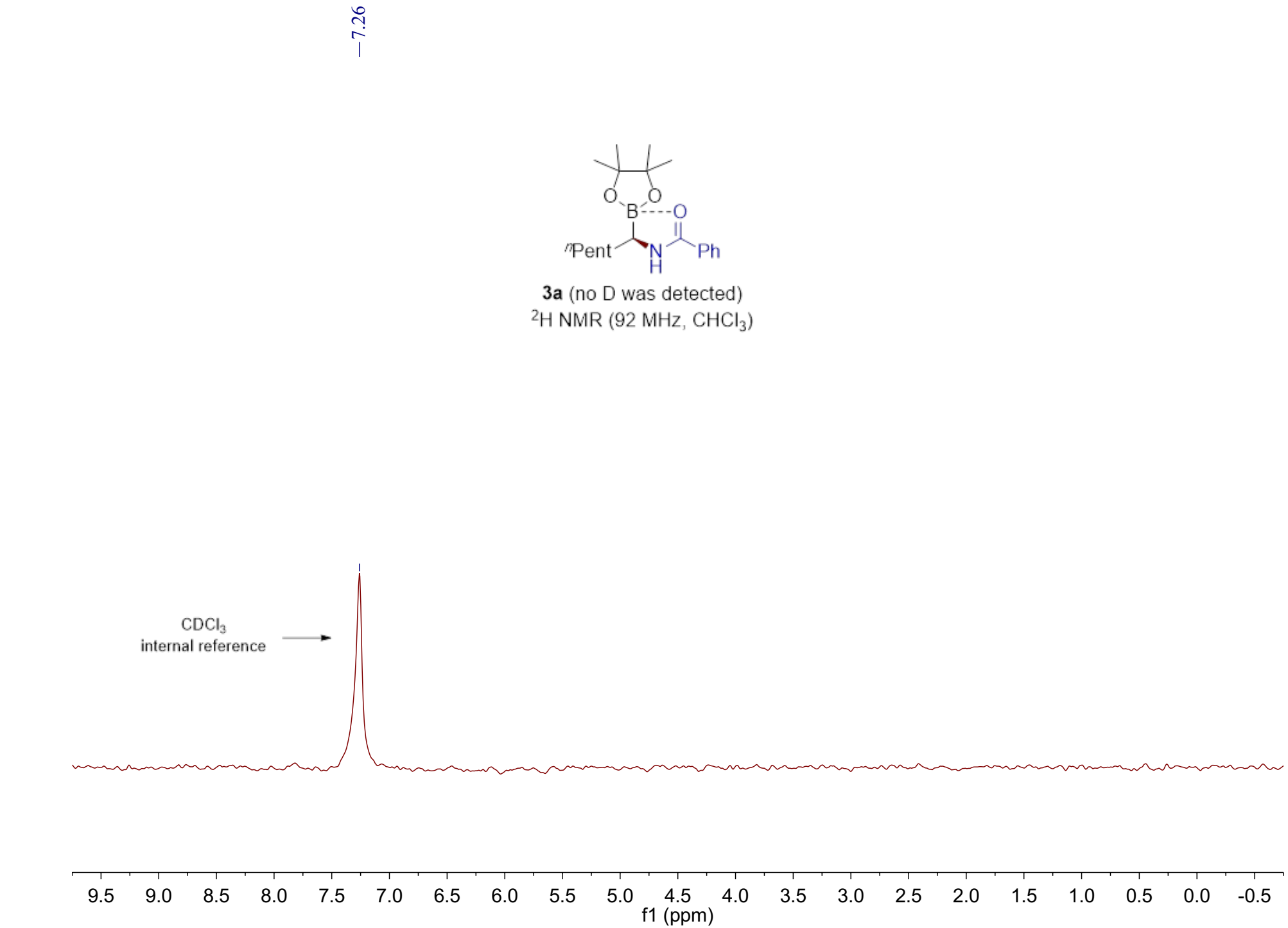
Supplementary Figure 133: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3a** (no D was detected).



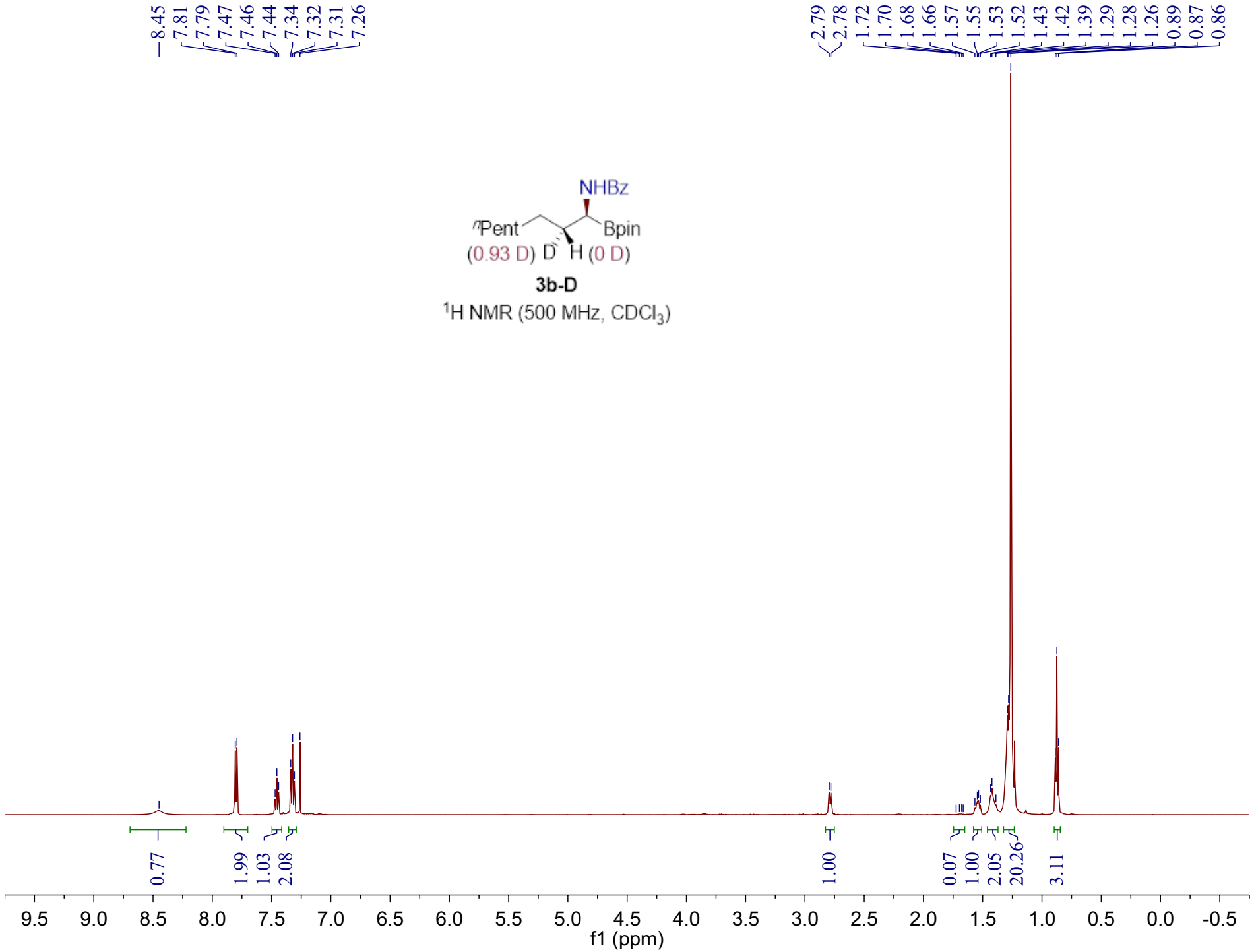
Supplementary Figure 134: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3a** (no D was detected).



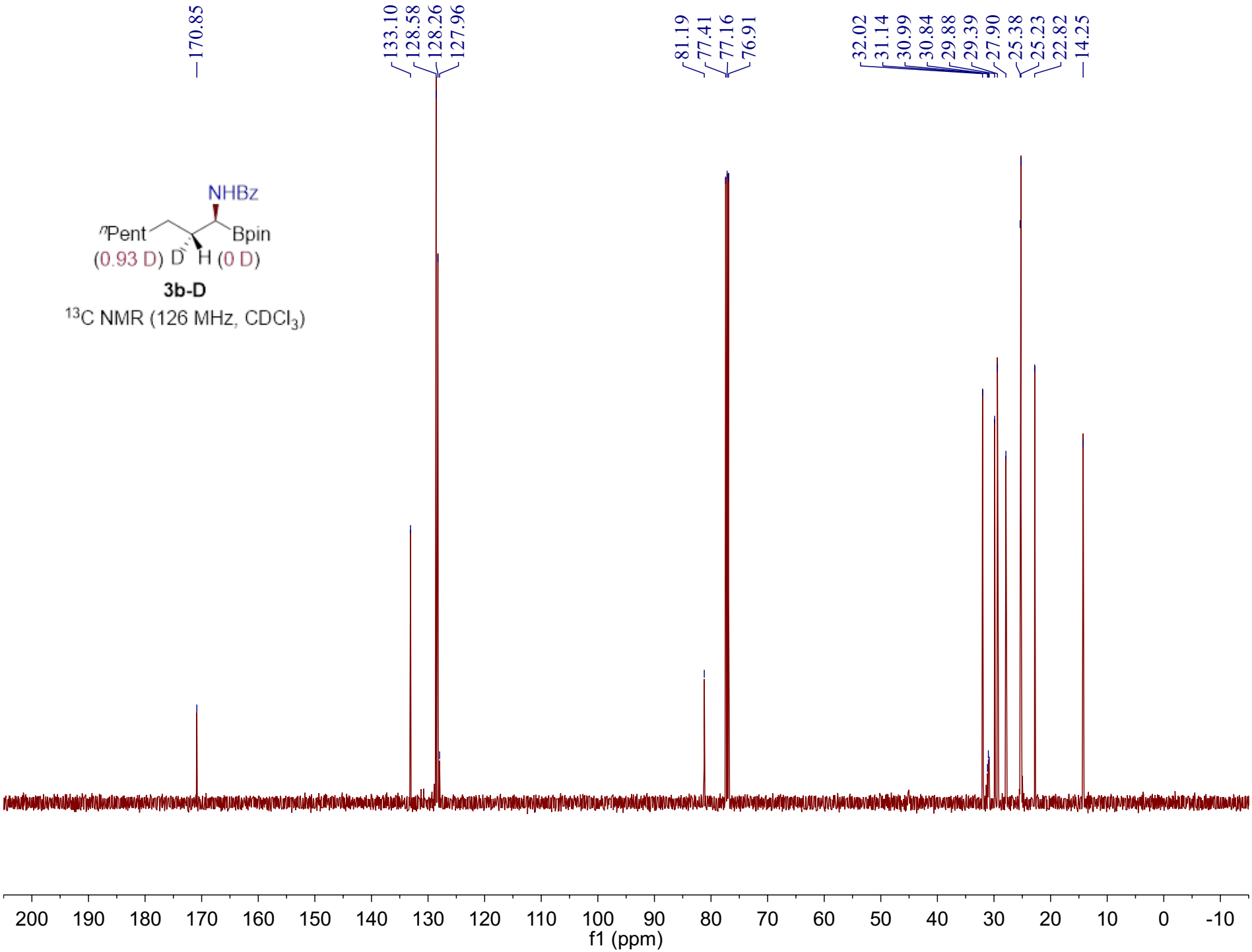
Supplementary Figure 135: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3a** (no D was detected).



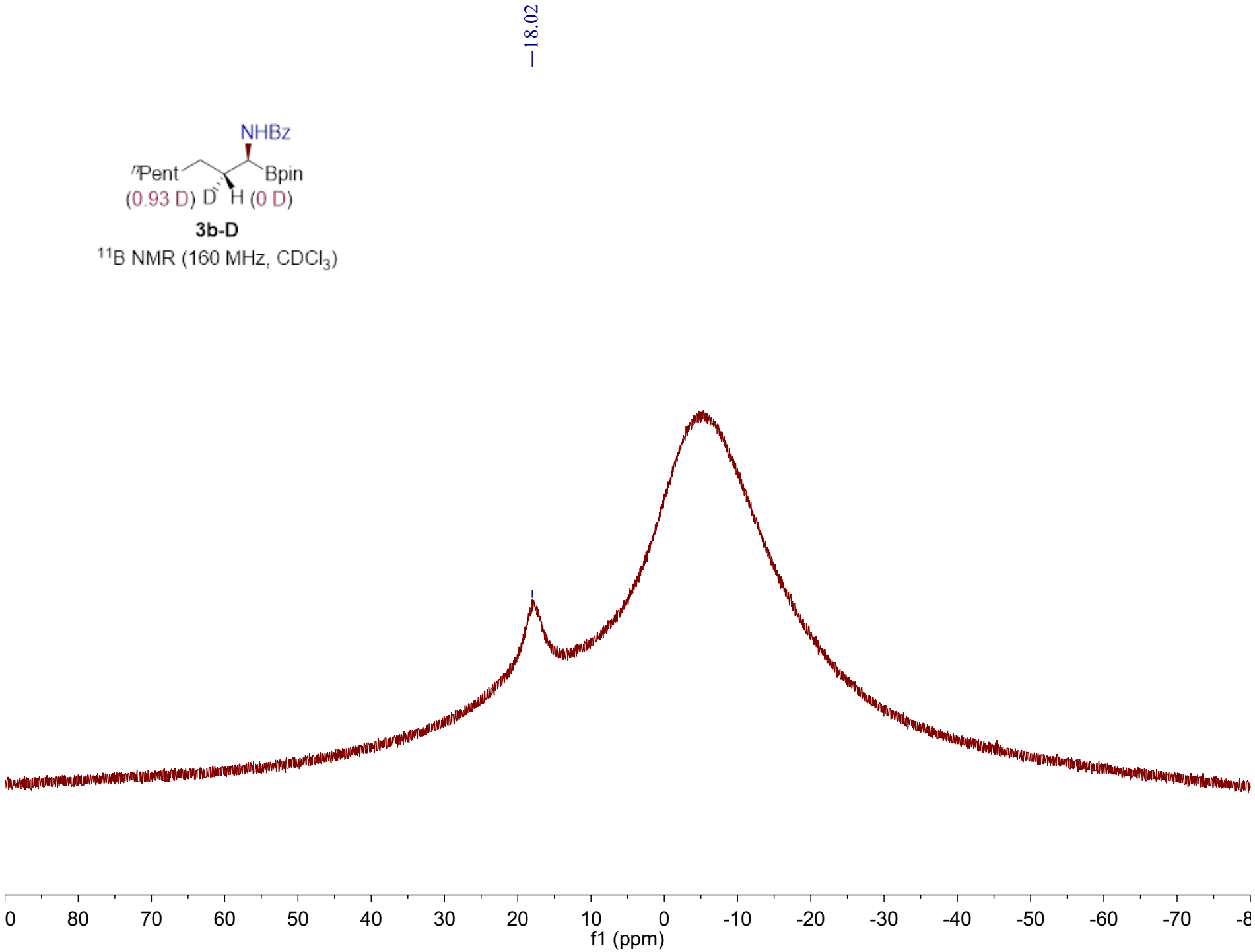
Supplementary Figure 136: ^{2}H NMR (92 MHz, $CHCl_3$) spectrum of **3a** (no D was detected).



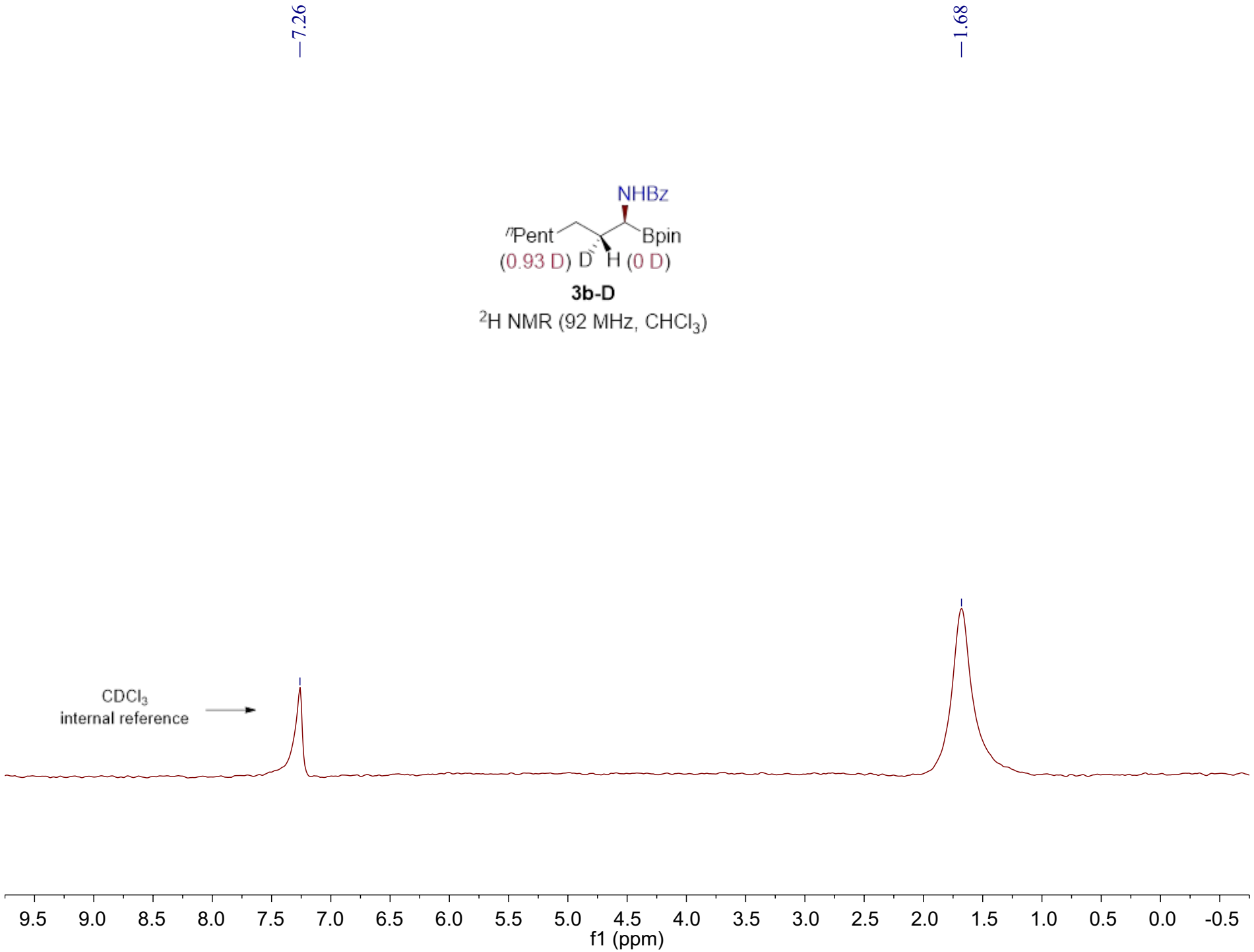
Supplementary Figure 137: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3b-D**.



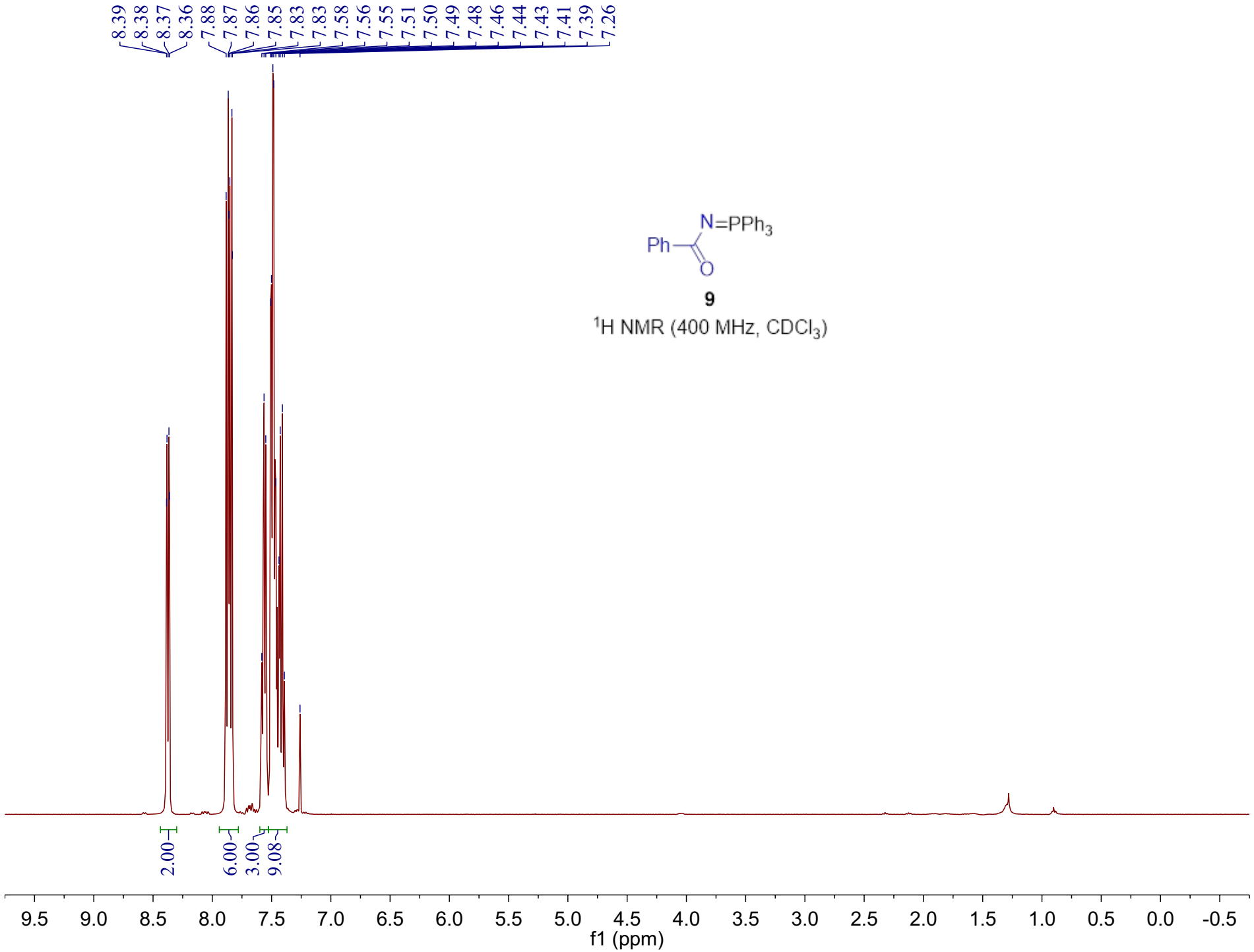
Supplementary Figure 138: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3b-D**.



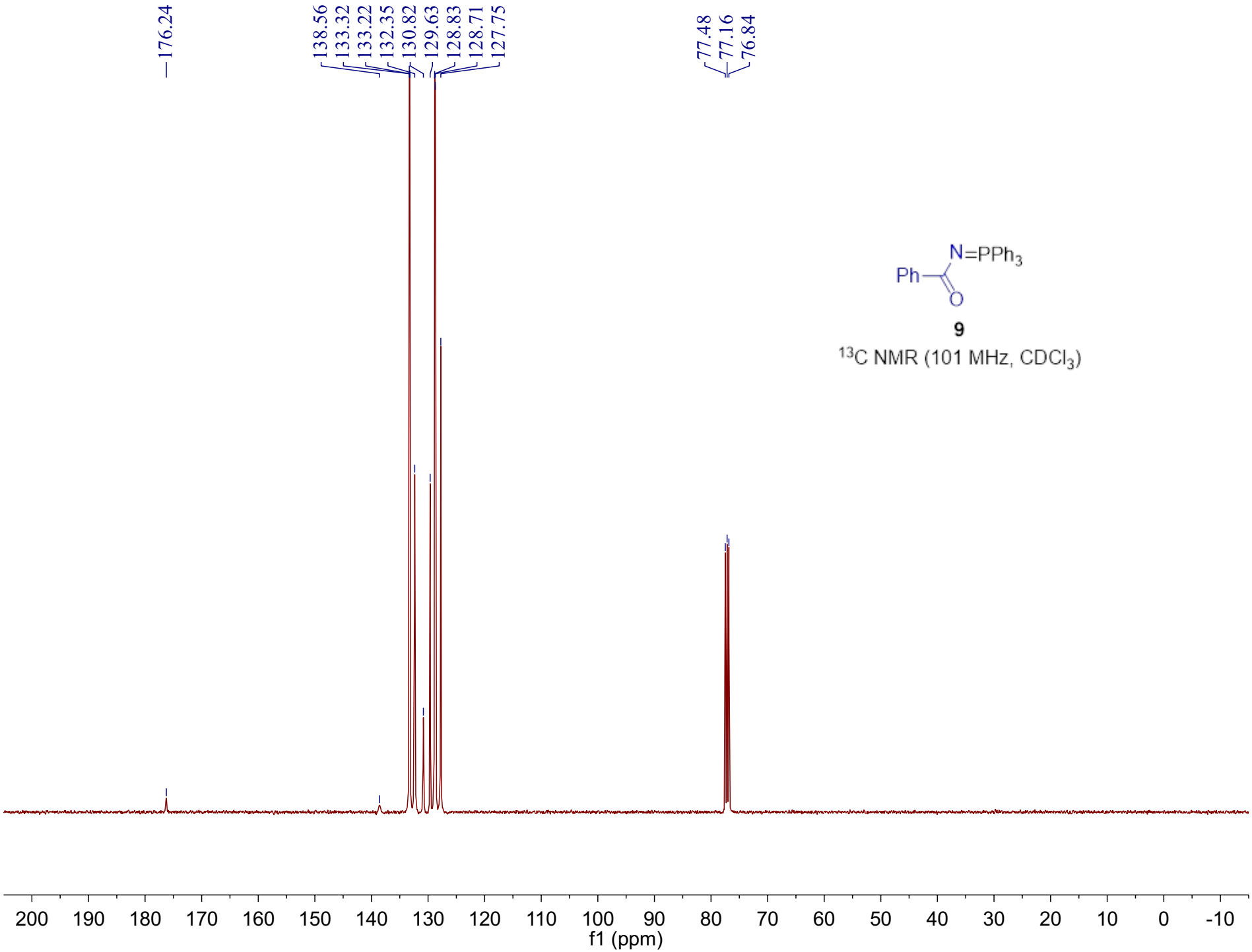
Supplementary Figure 139: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **3b-D**.



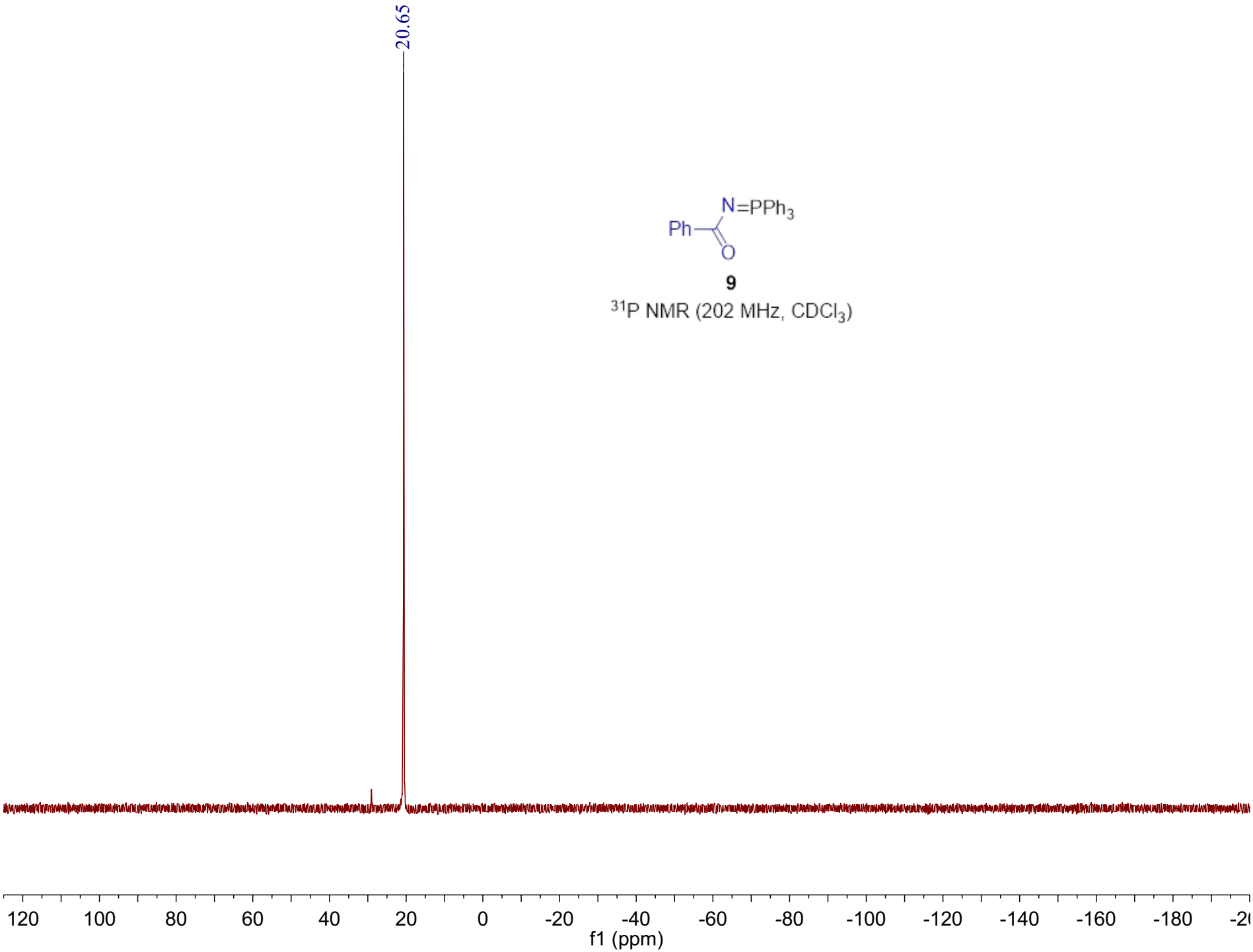
Supplementary Figure 140: ^{2}H NMR (92 MHz, $CHCl_3$) spectrum of **3b-D**.



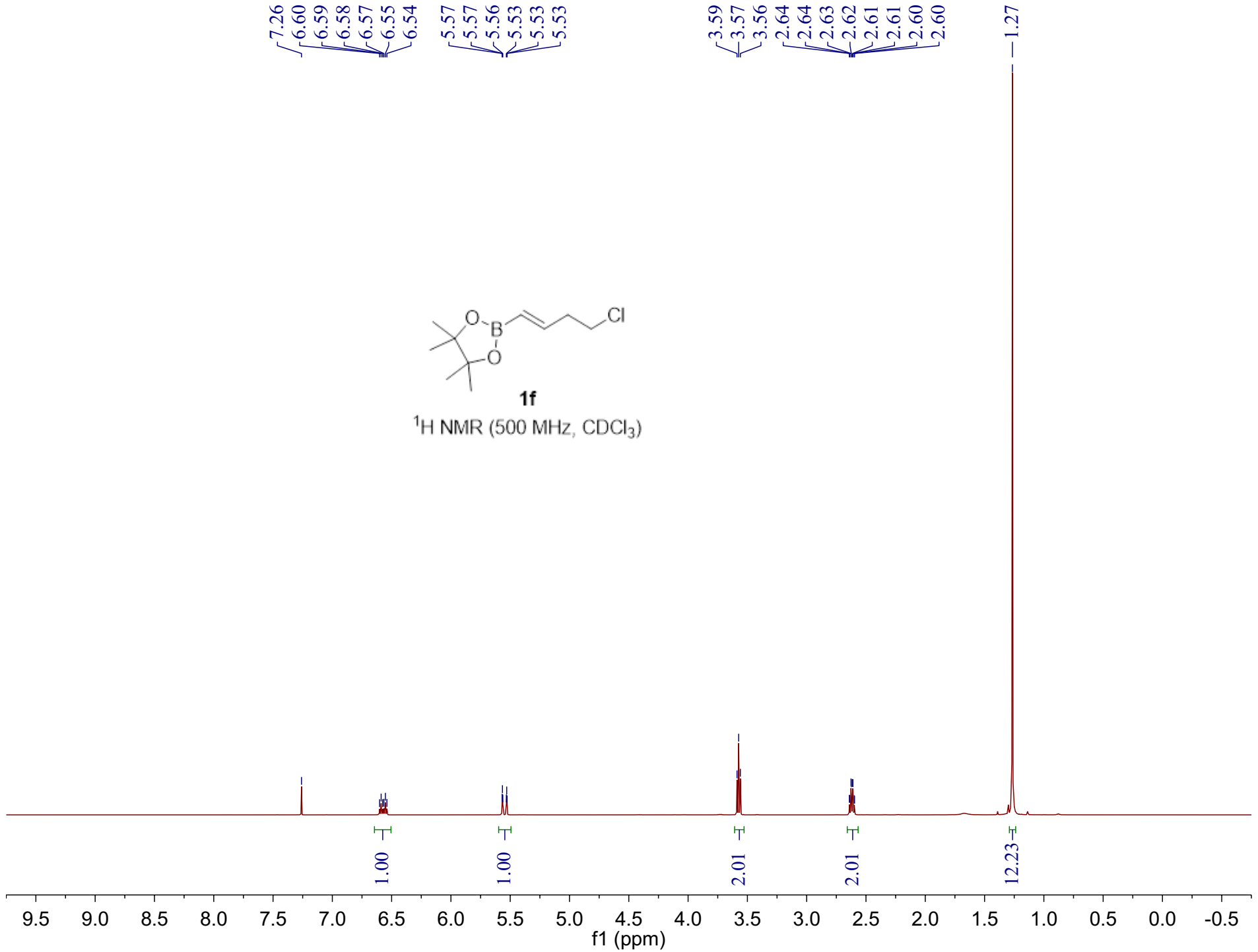
Supplementary Figure 141: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**.



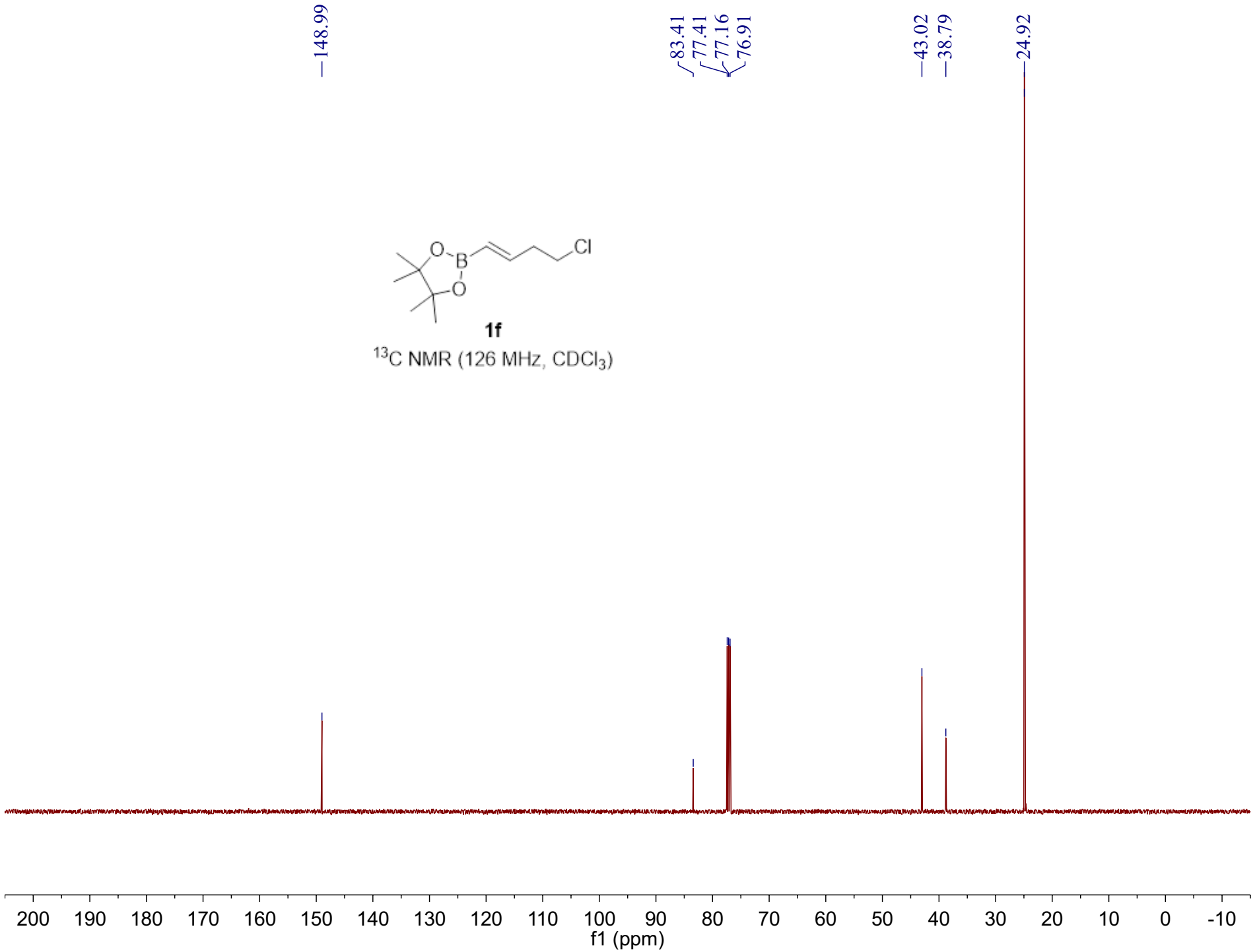
Supplementary Figure 142: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **9**.



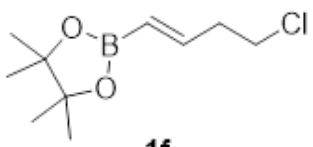
Supplementary Figure 143: ^{31}P NMR (202 MHz, $CDCl_3$) spectrum of **9**.



Supplementary Figure 144: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1f**.



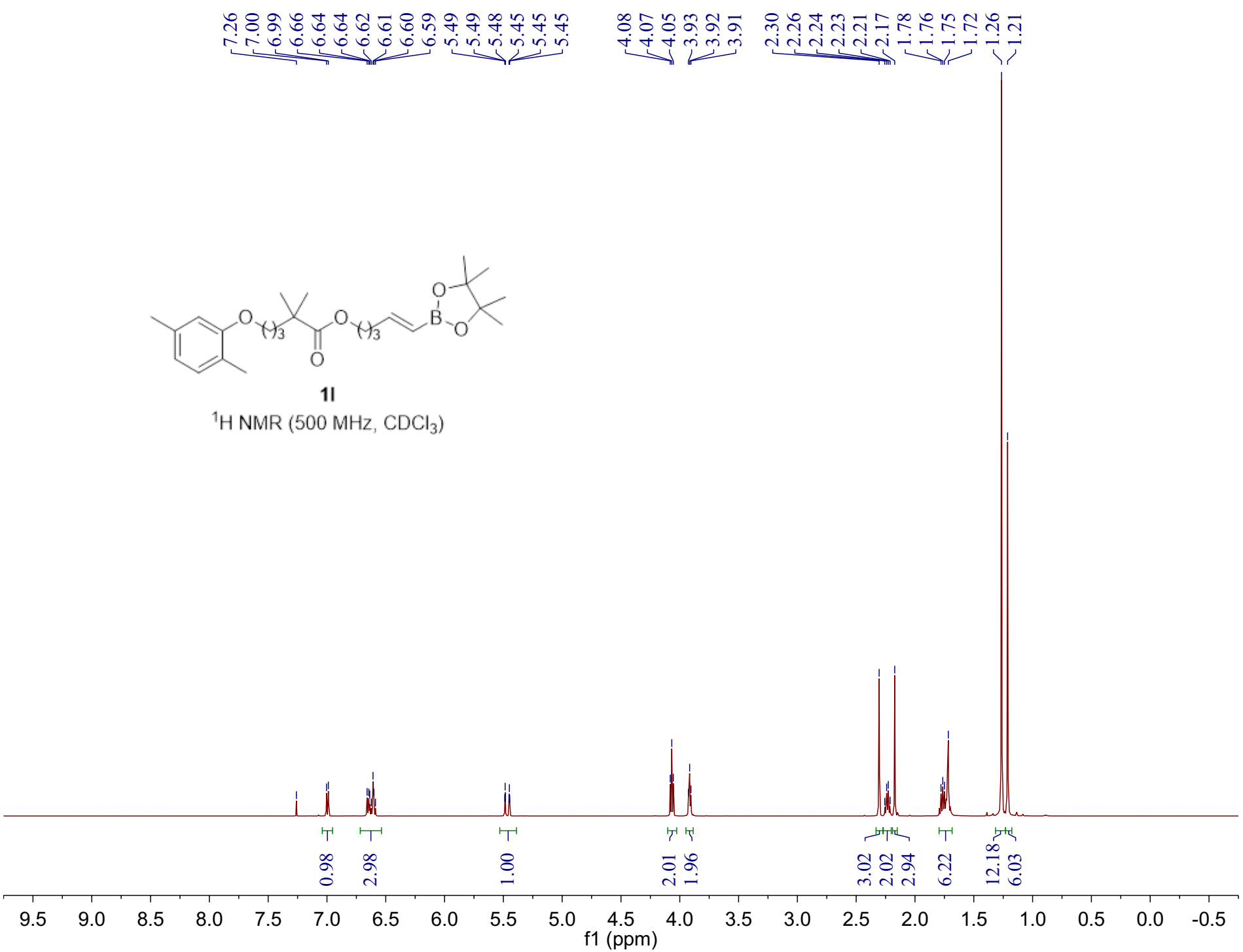
Supplementary Figure 145: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1f**.



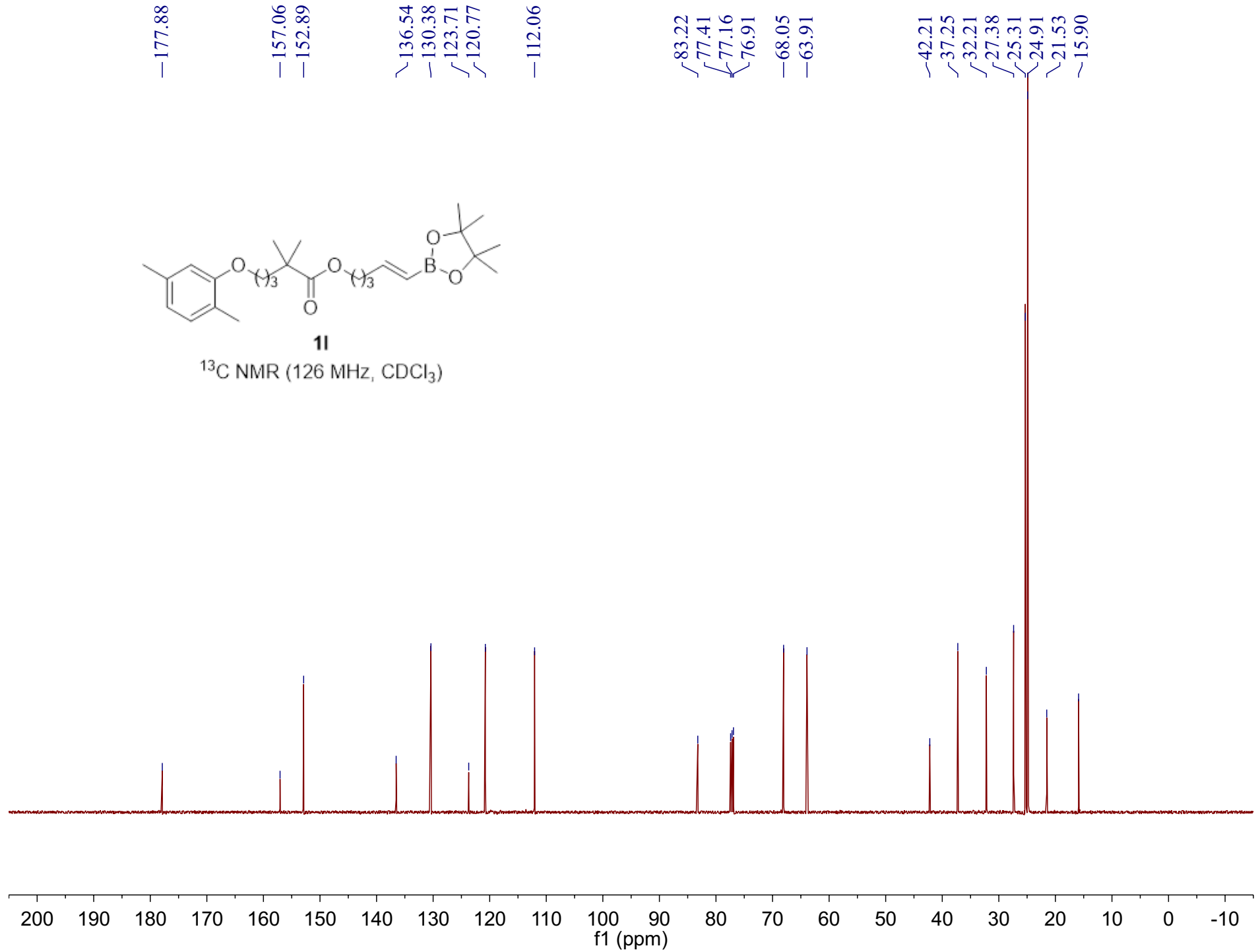
1f

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

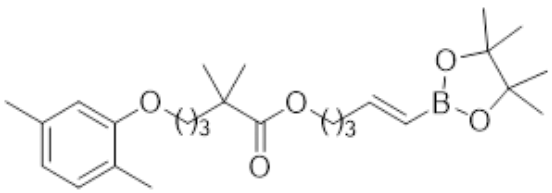
Supplementary Figure 146: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **1f**.



Supplementary Figure 147: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1l**.



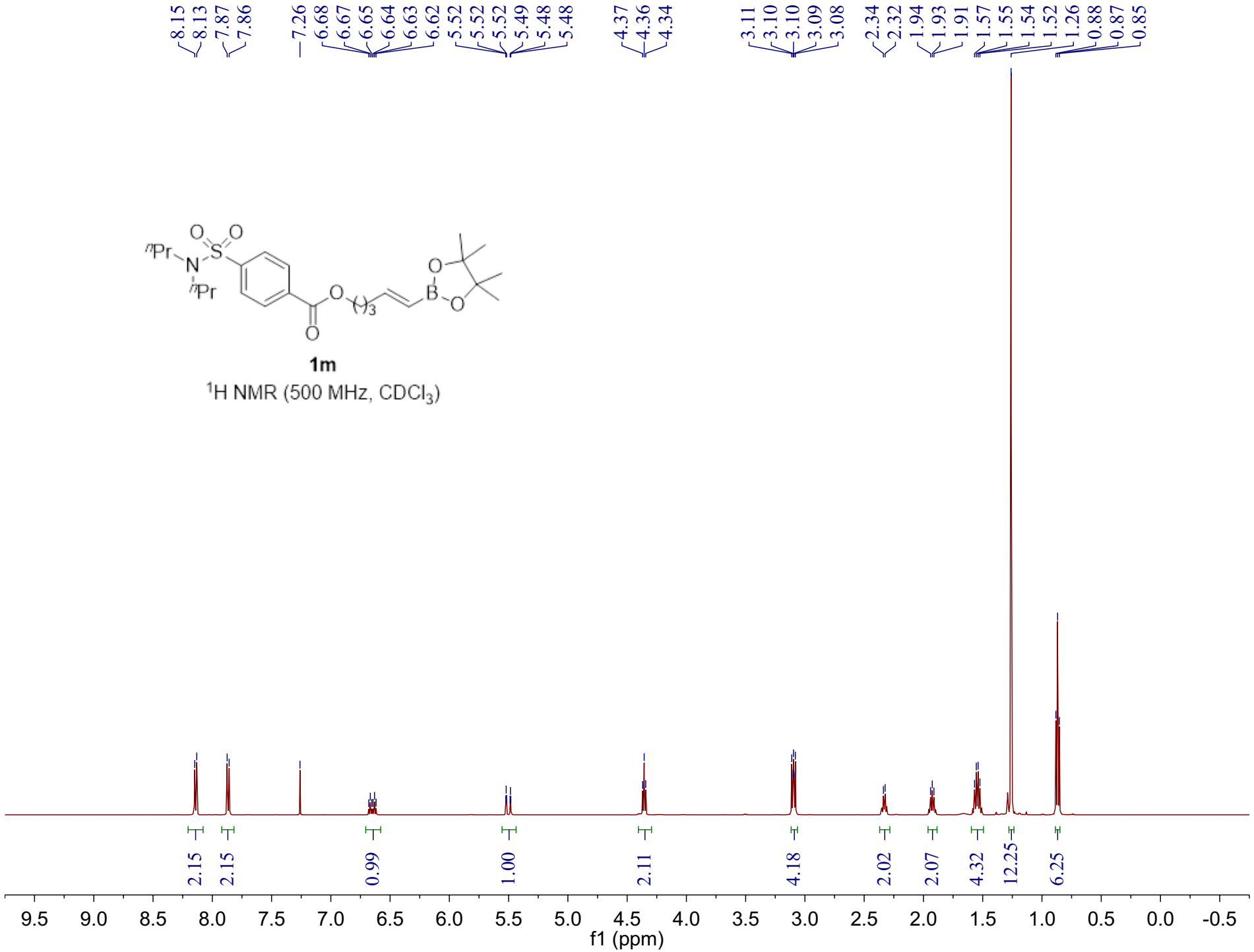
Supplementary Figure 148: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1l**.



1l

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

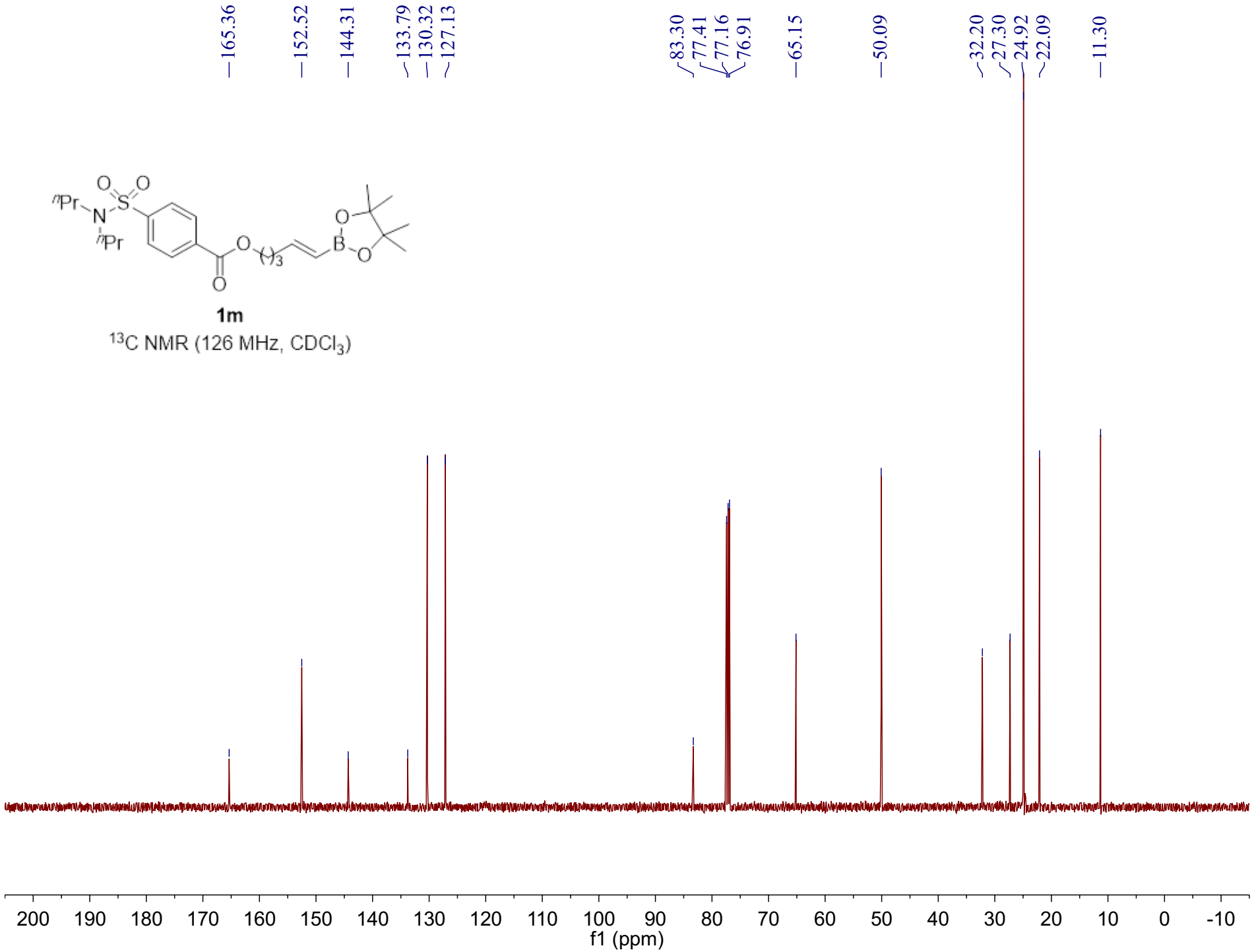
Supplementary Figure 149: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **1l**.



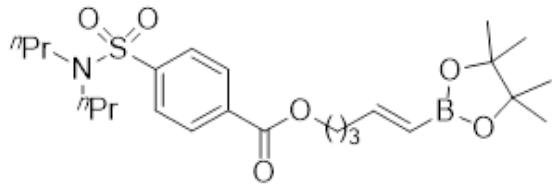
1m

^{1}H NMR (500 MHz, $CDCl_3$)

Supplementary Figure 150: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1m**.



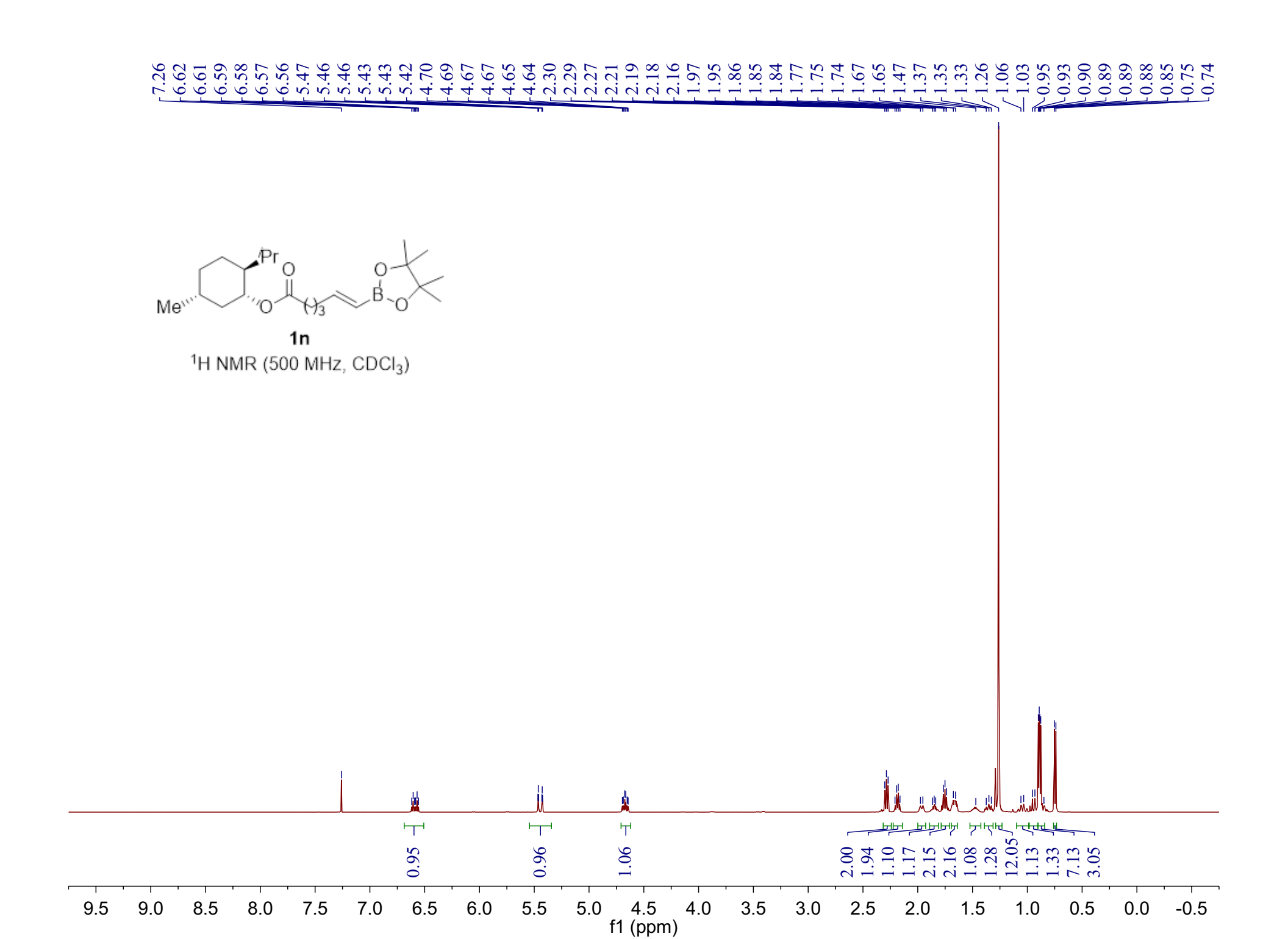
Supplementary Figure 151: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1m**.



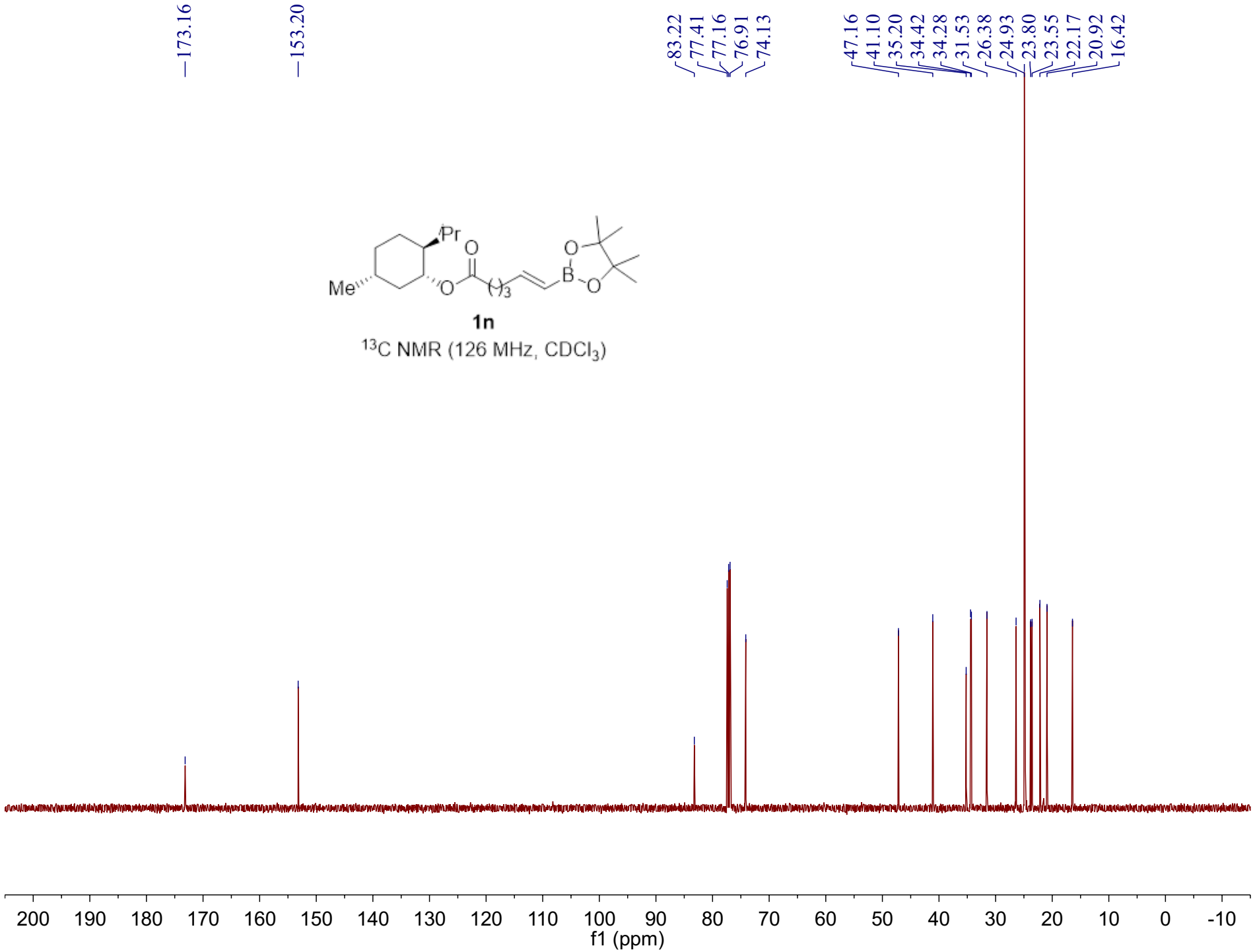
1m

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

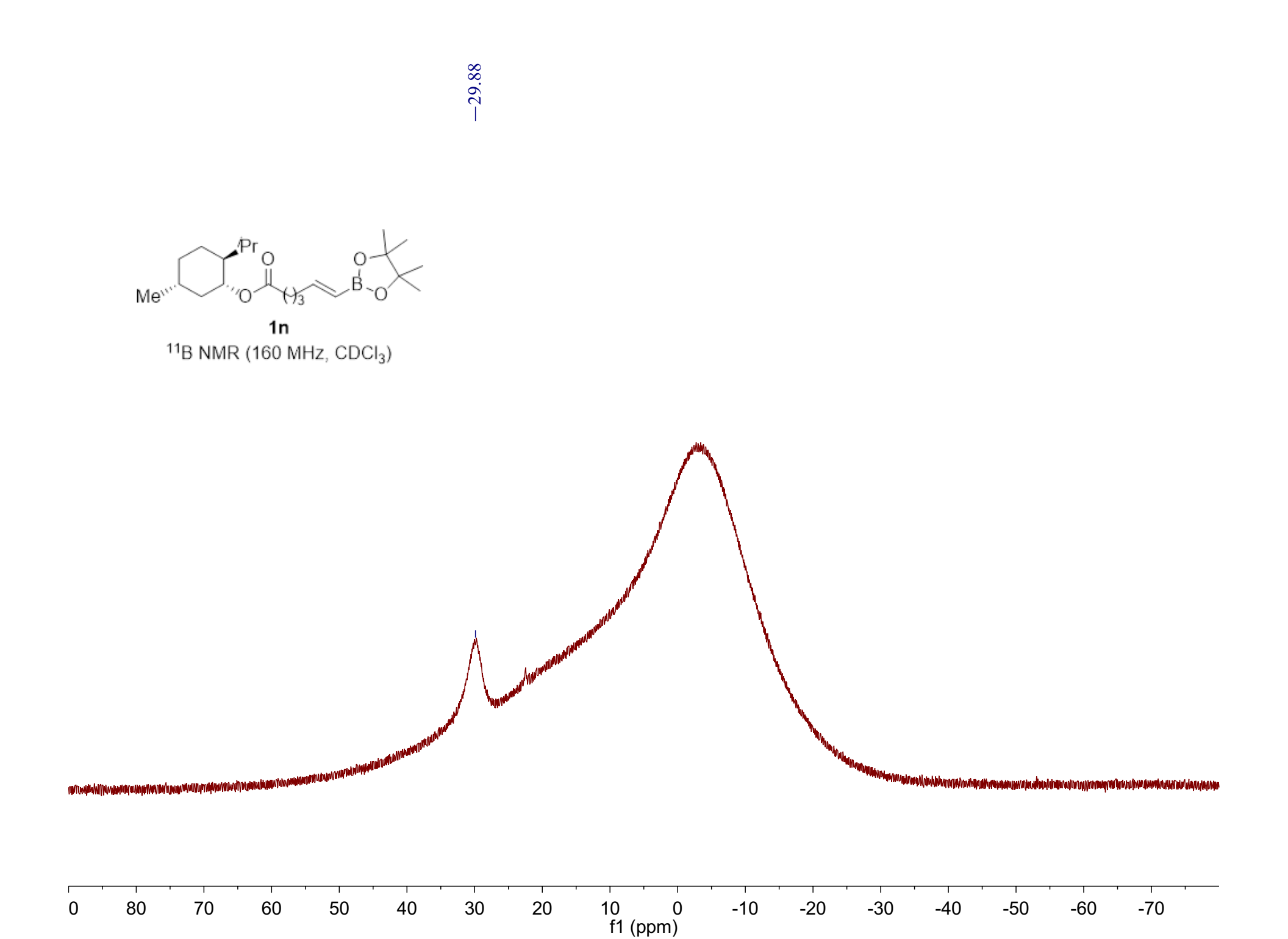
Supplementary Figure 152: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **1m**.



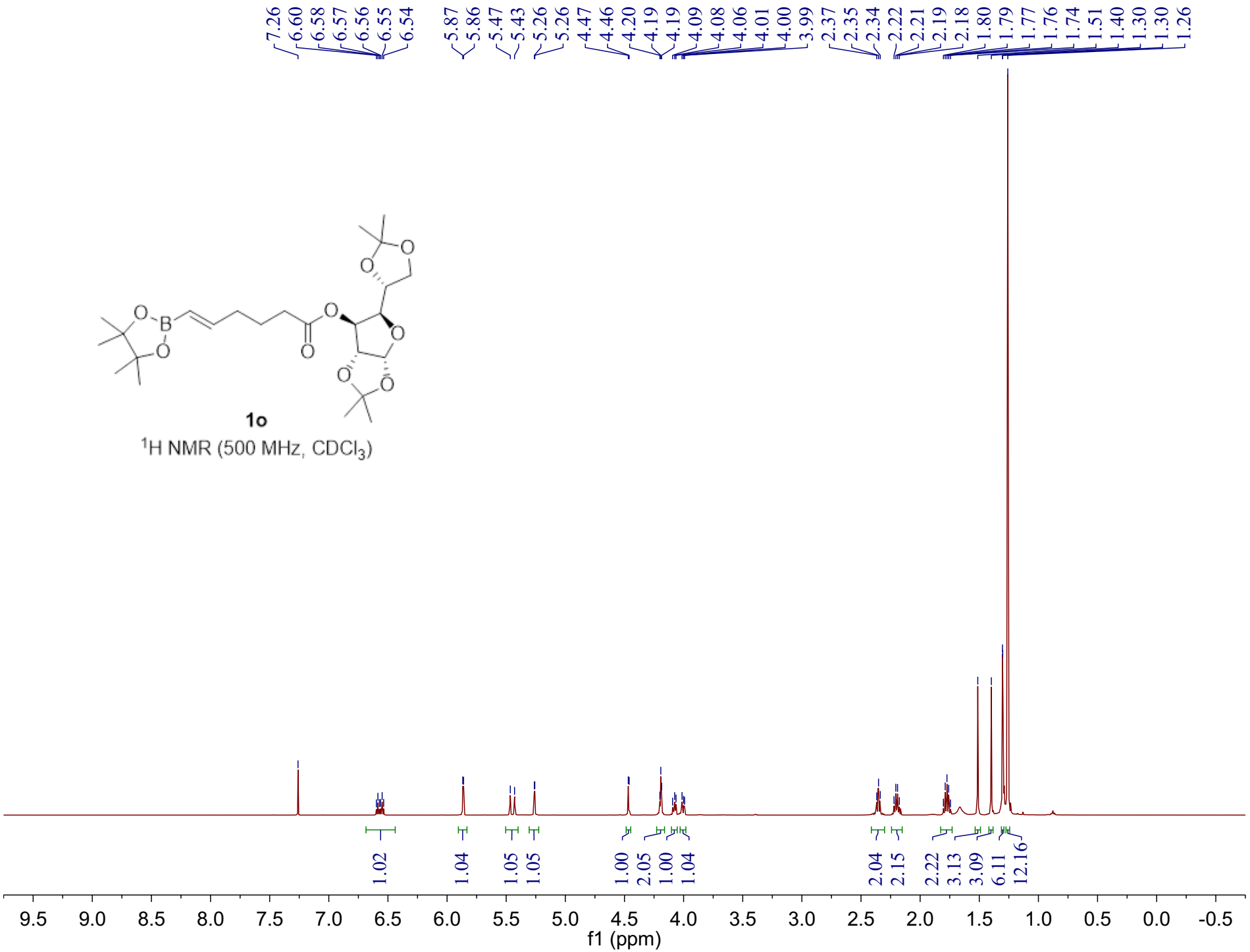
Supplementary Figure 153: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1n**.



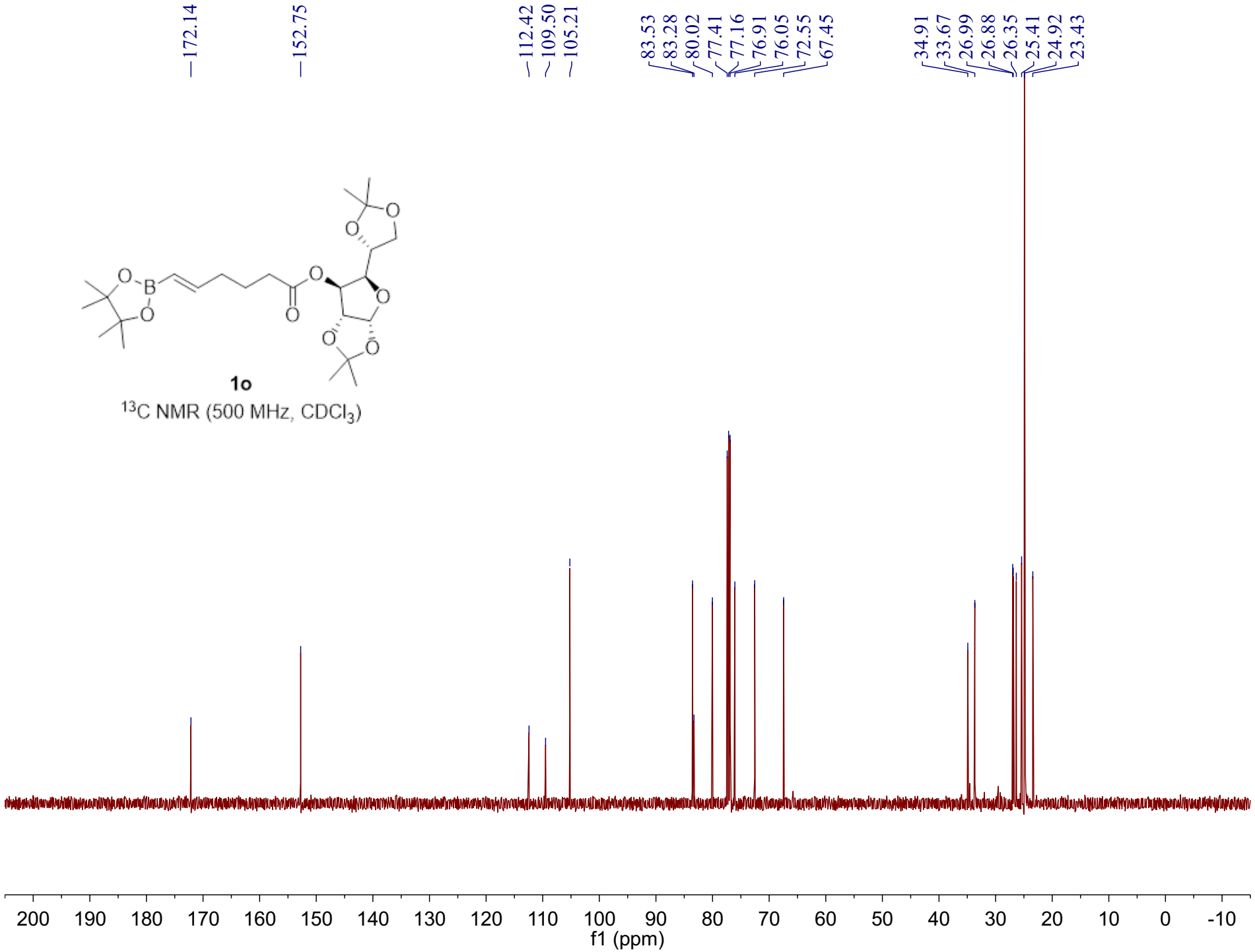
Supplementary Figure 154: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1n**.



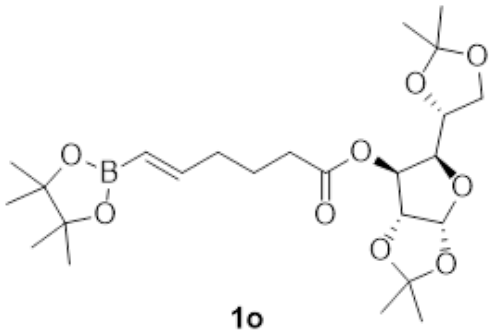
Supplementary Figure 155: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **1n**.



Supplementary Figure 156: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1o**.



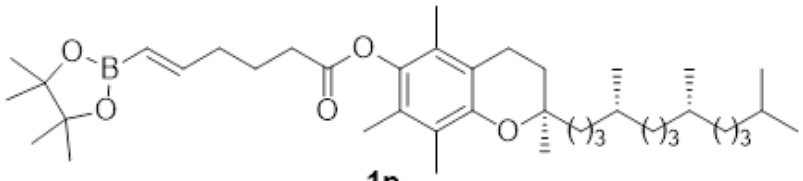
Supplementary Figure 157: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1o**.



1o

^{11}B NMR (500 MHz, $CDCl_3$)

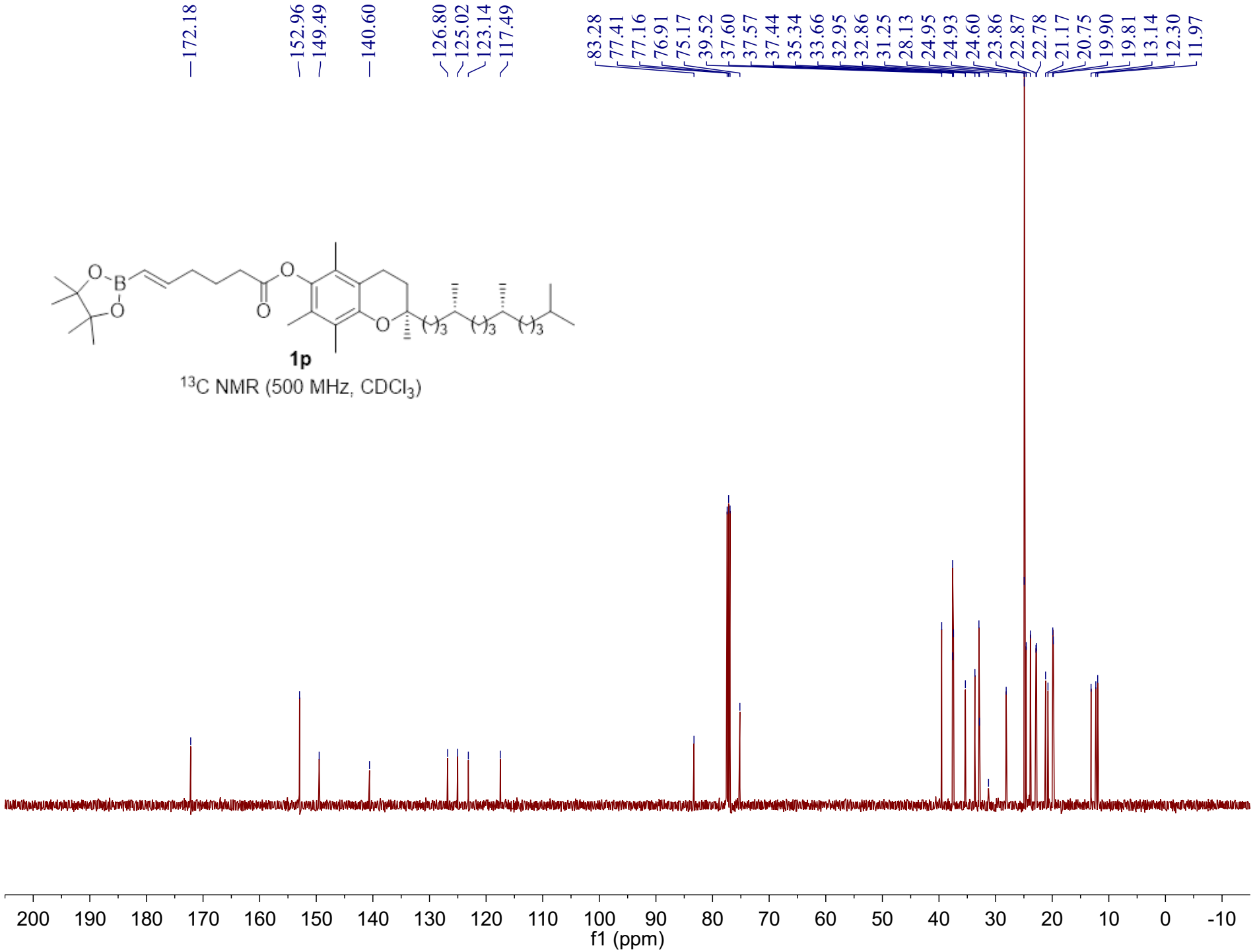
Supplementary Figure 158: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **1o**.



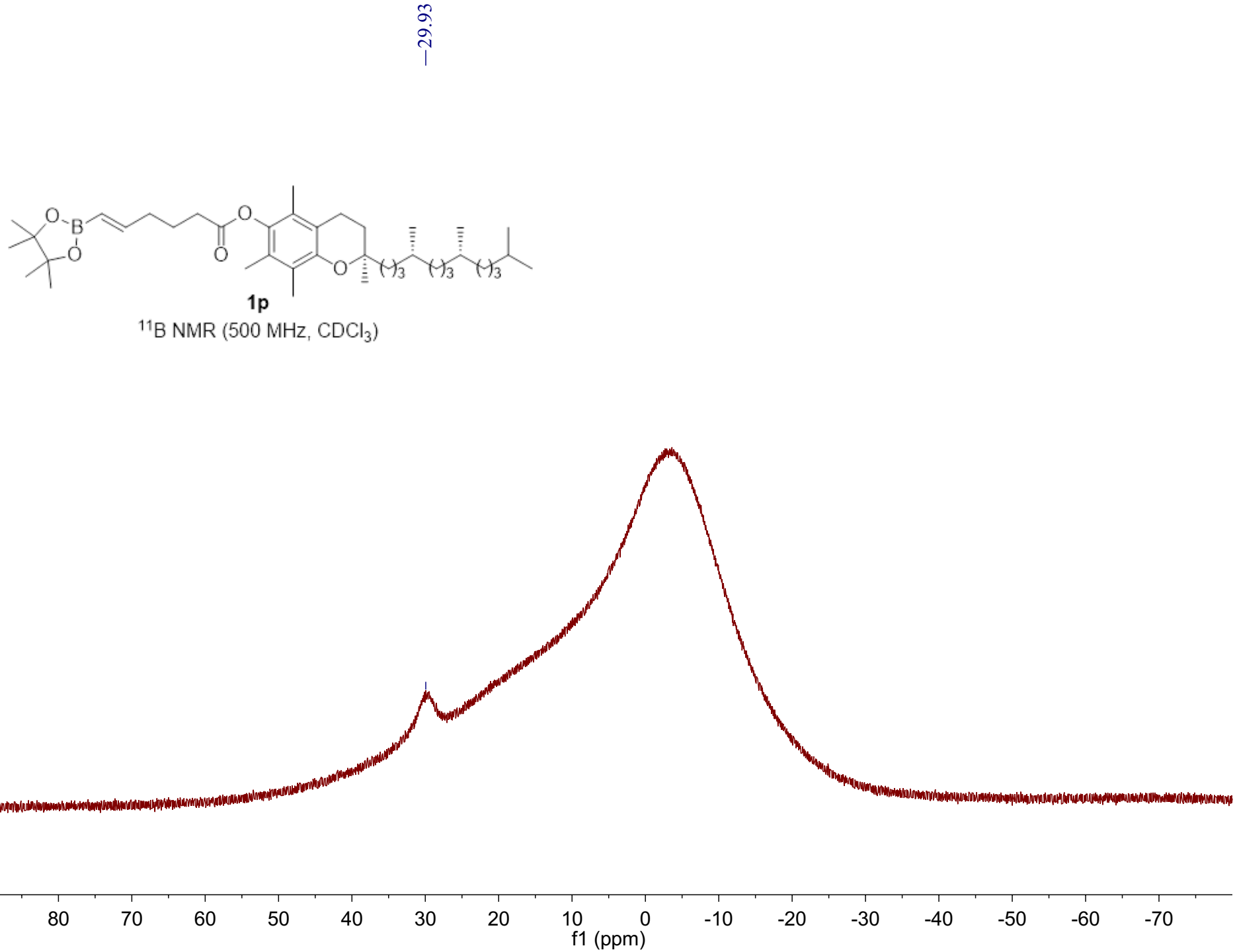
1p

^{1}H NMR (500 MHz, $CDCl_3$)

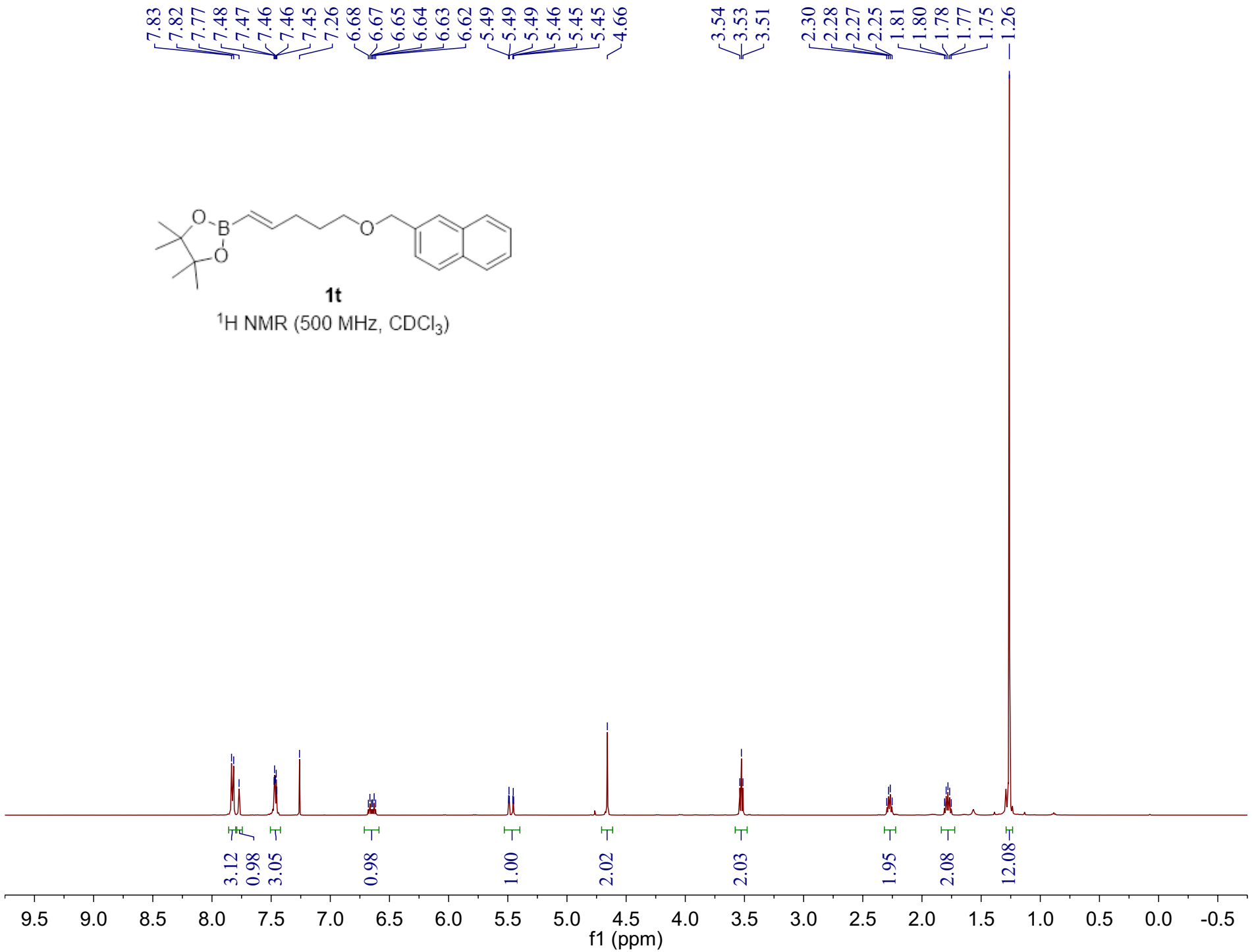
Supplementary Figure 159: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1p**.



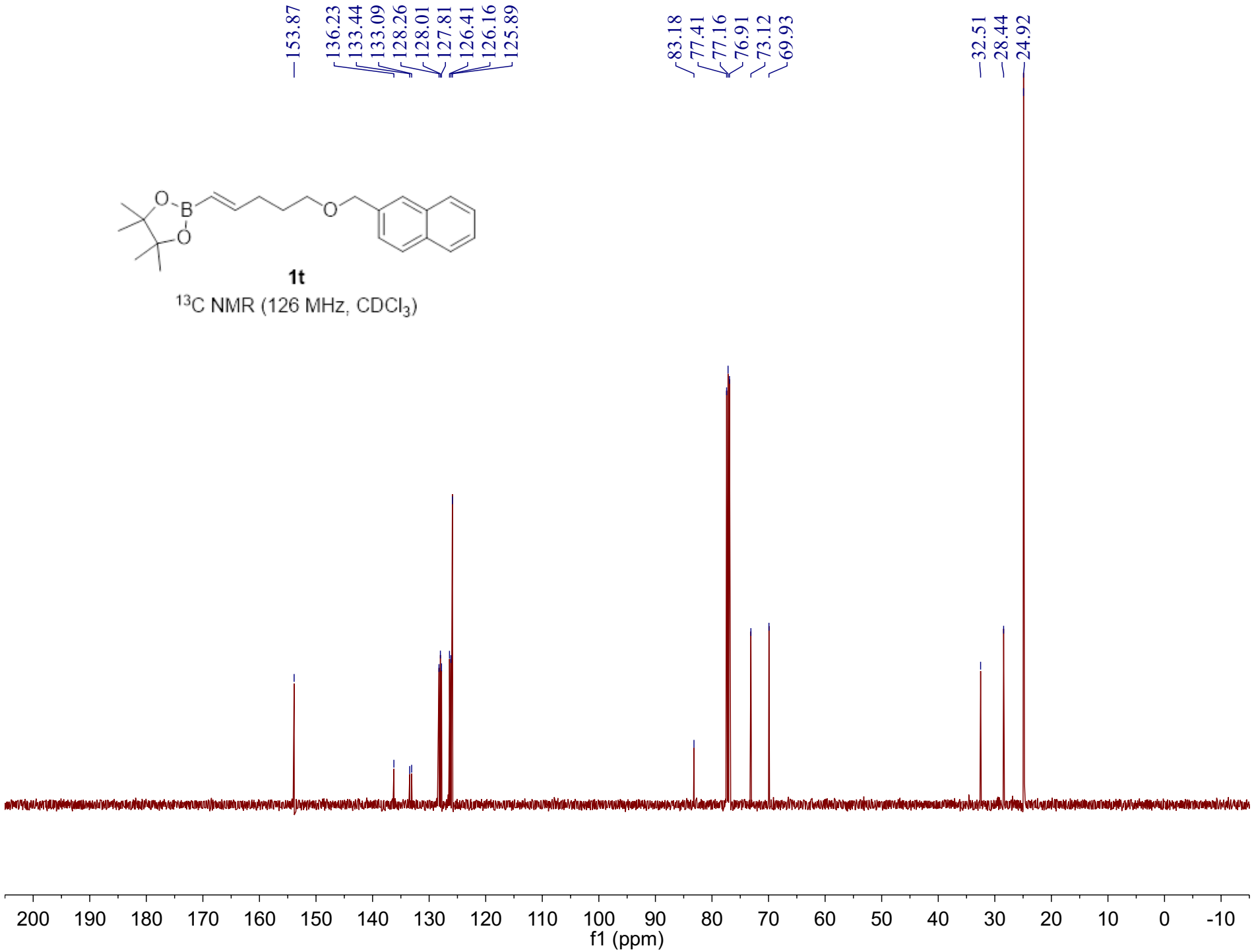
Supplementary Figure 160: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1p**.



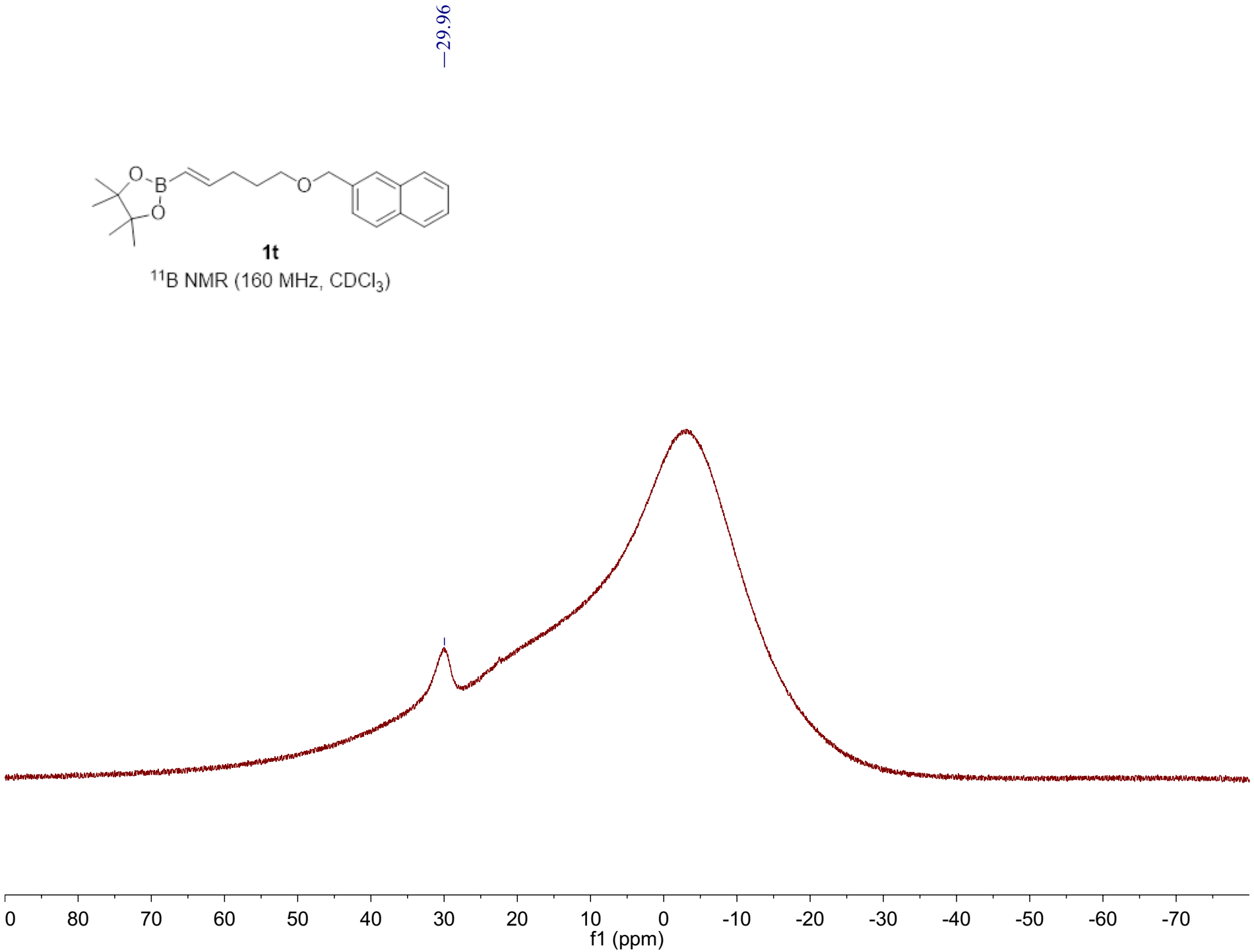
Supplementary Figure 161: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **1p**.



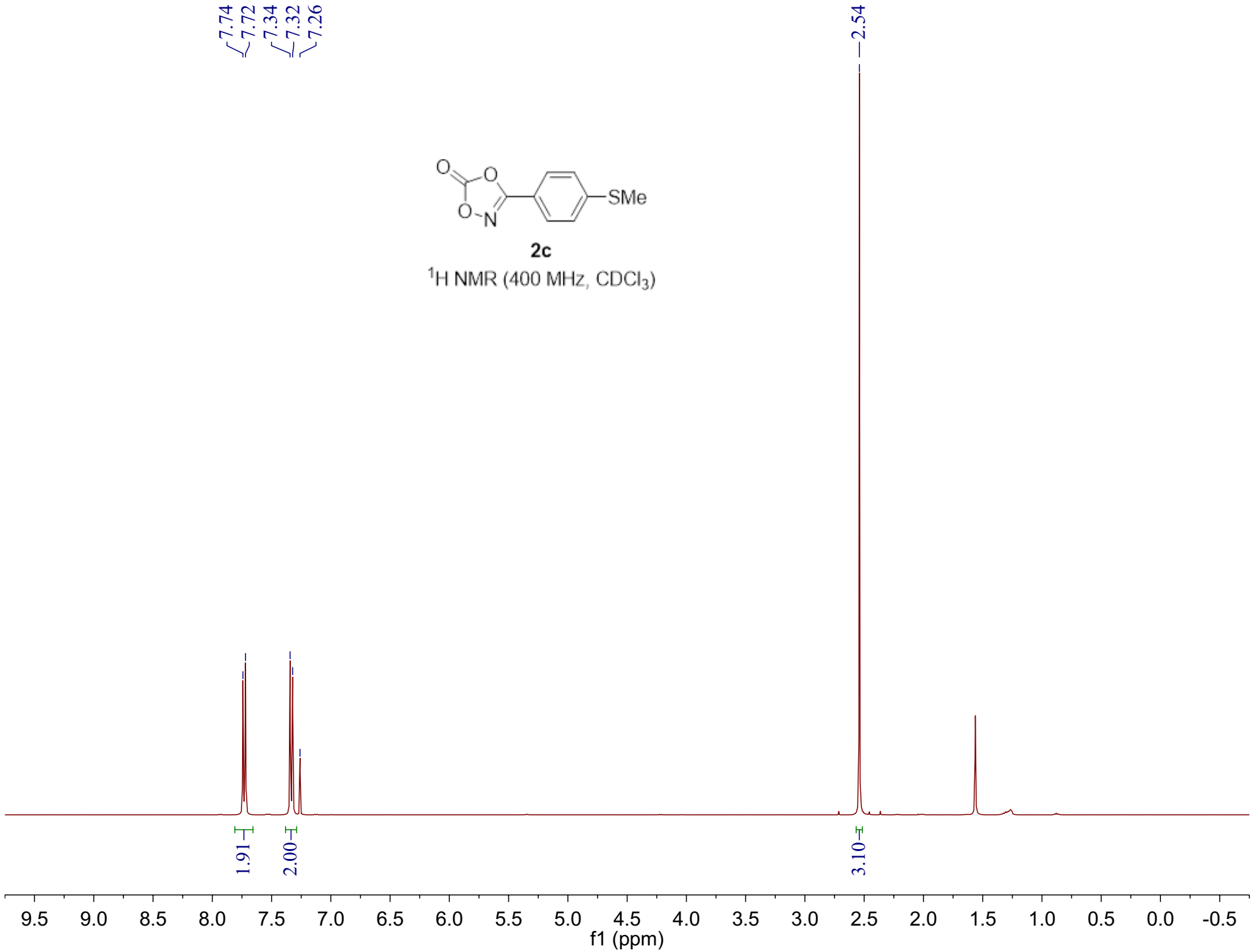
Supplementary Figure 162: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1t**.



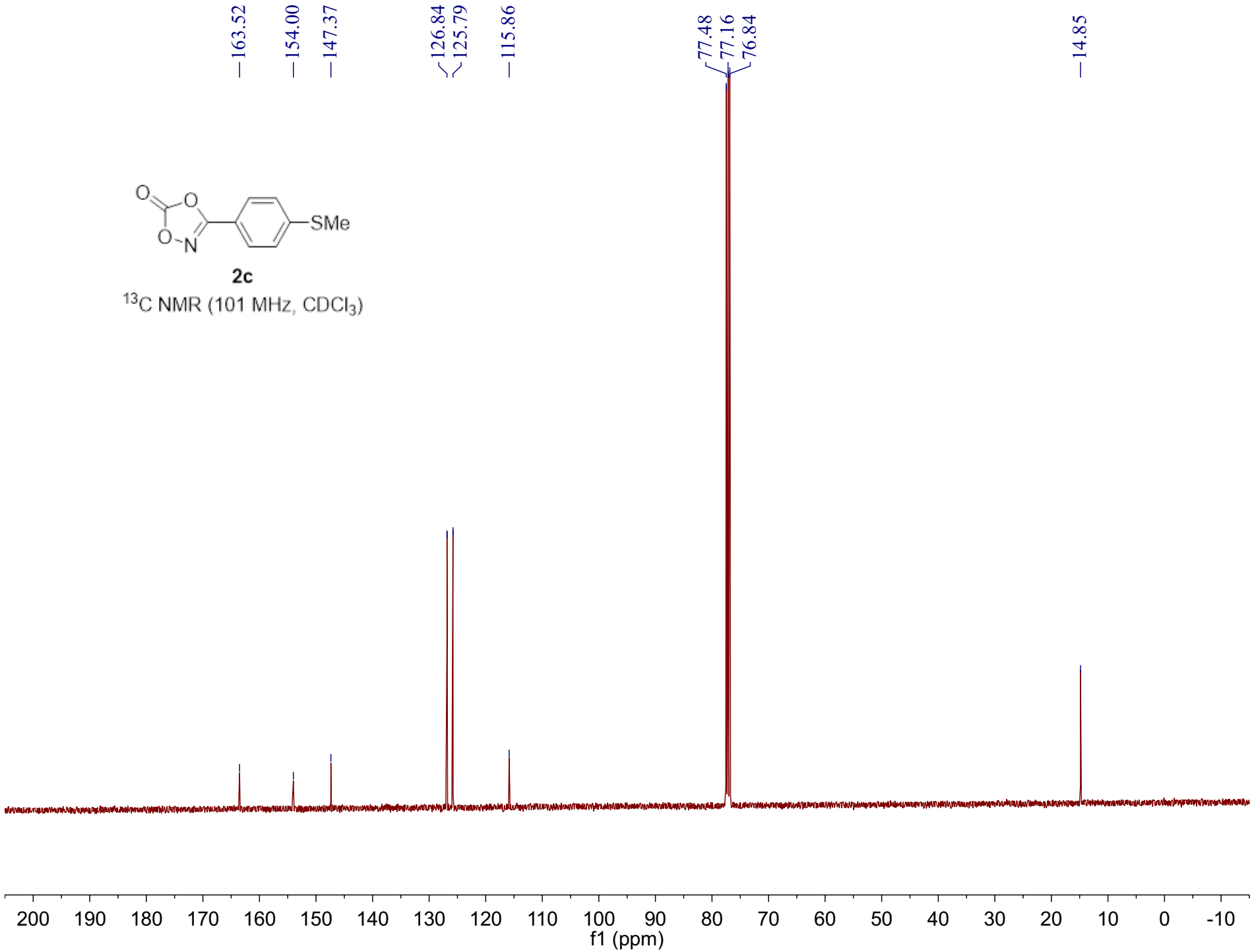
Supplementary Figure 163: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1t**.



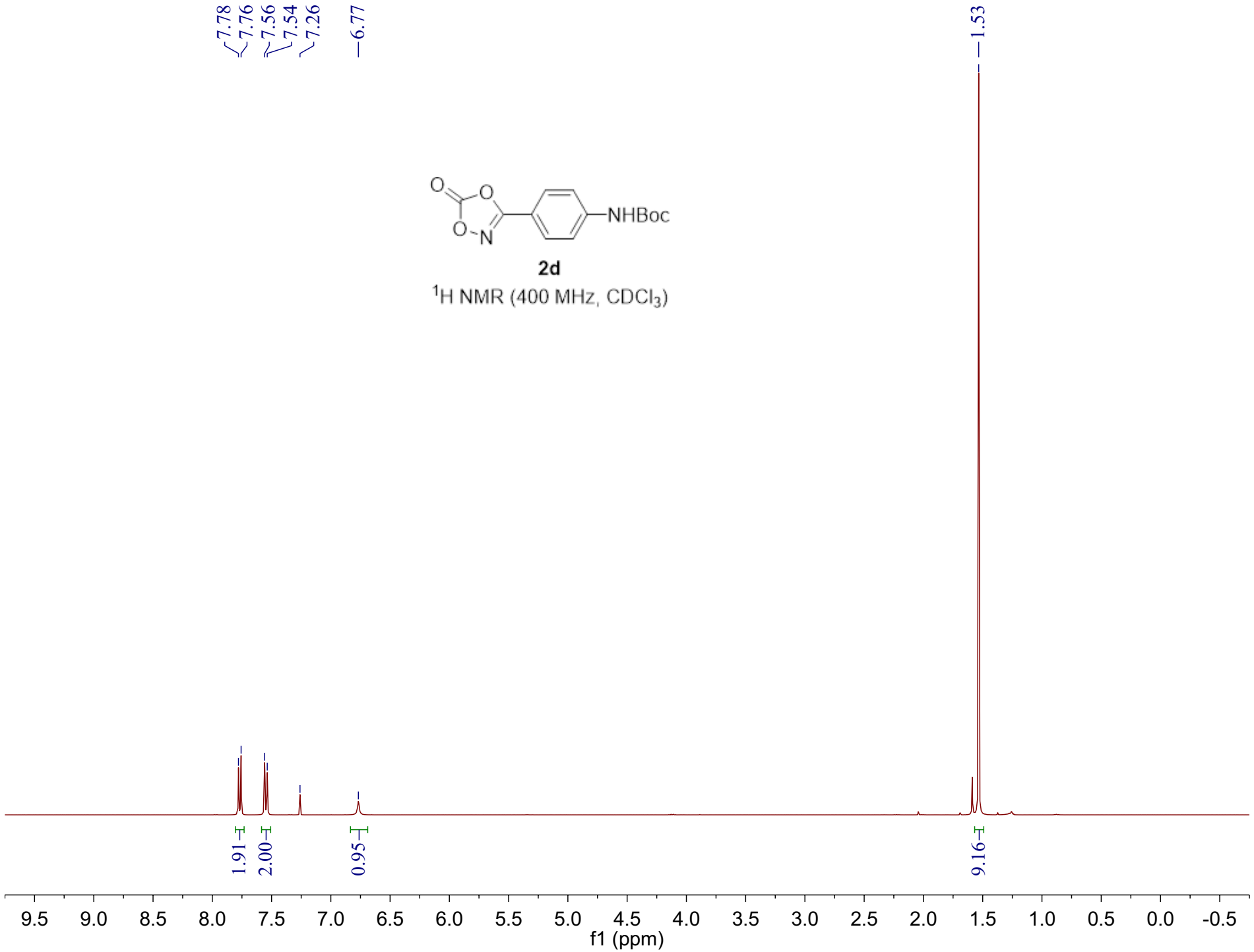
Supplementary Figure 164: ^{11}B NMR (160 MHz, $CDCl_3$) spectrum of **1t**.



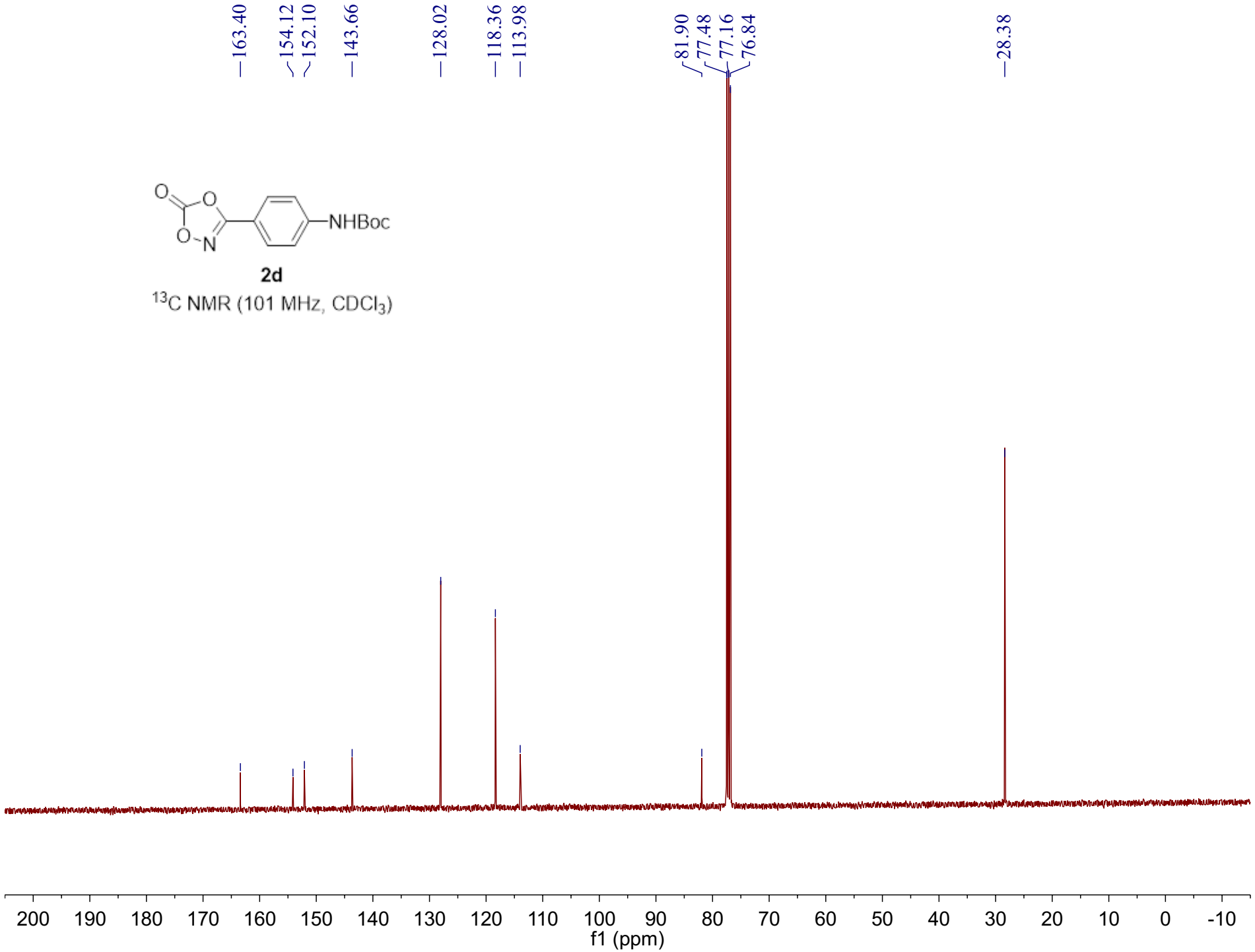
Supplementary Figure 165: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**.



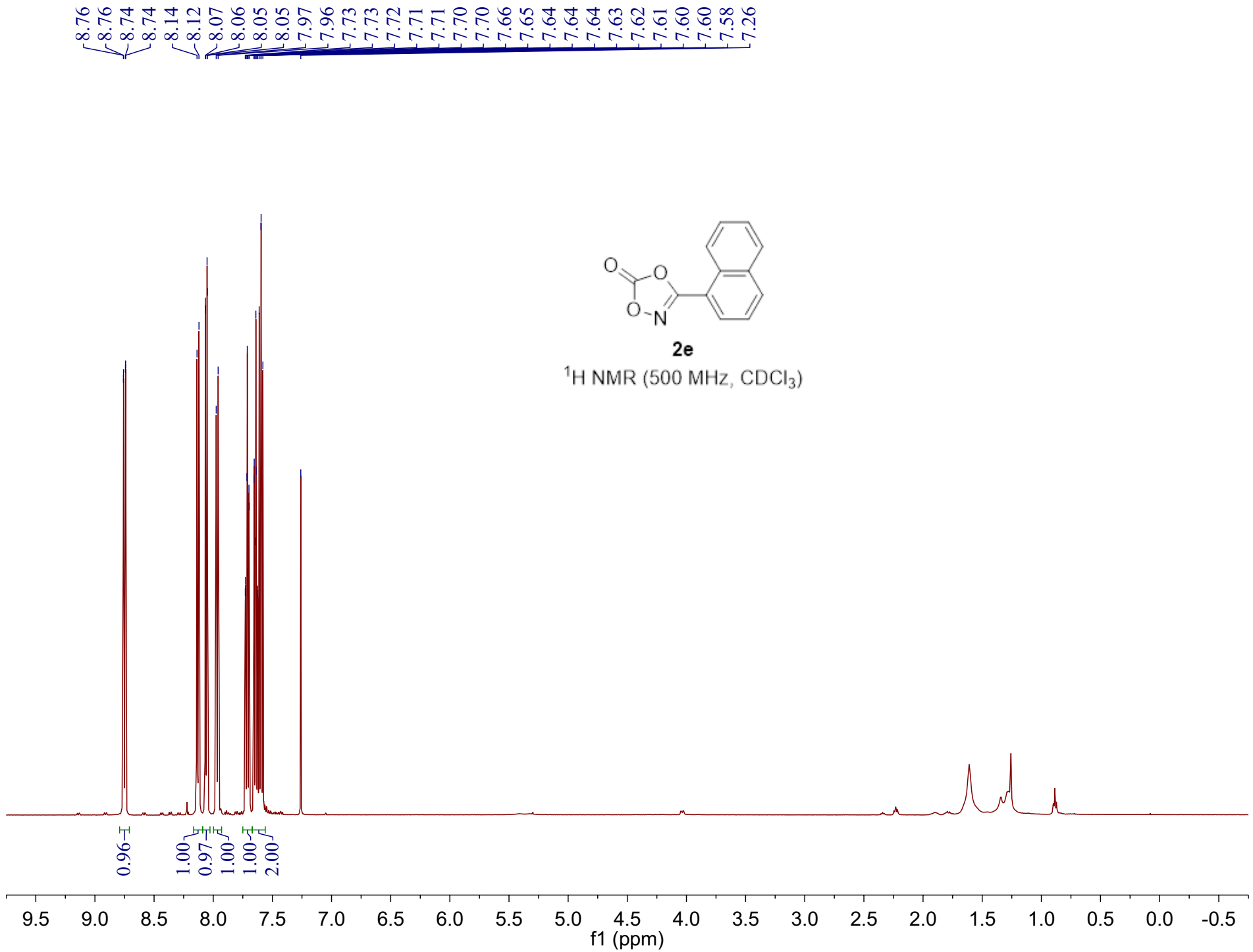
Supplementary Figure 166: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2c**.



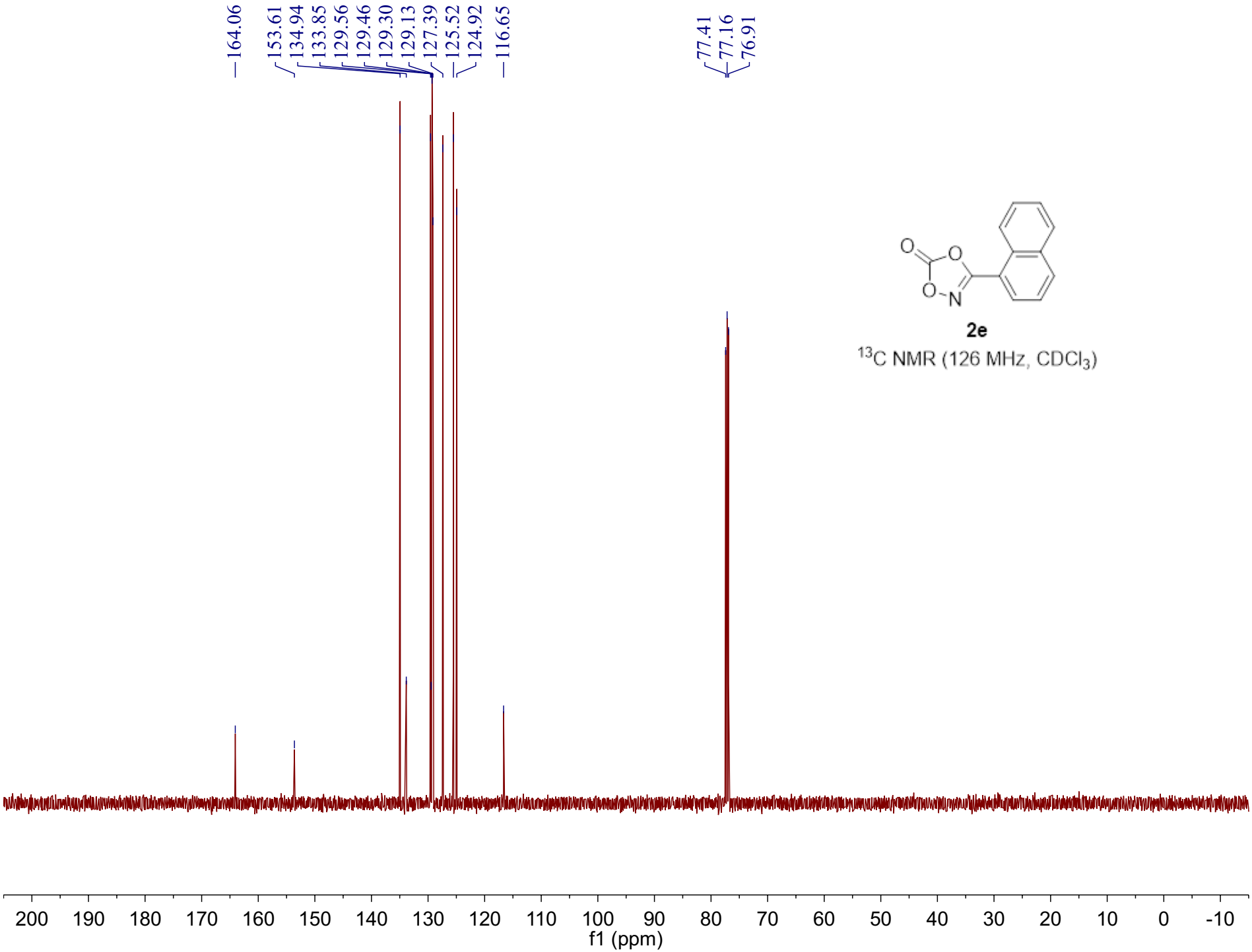
Supplementary Figure 167: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2d**.



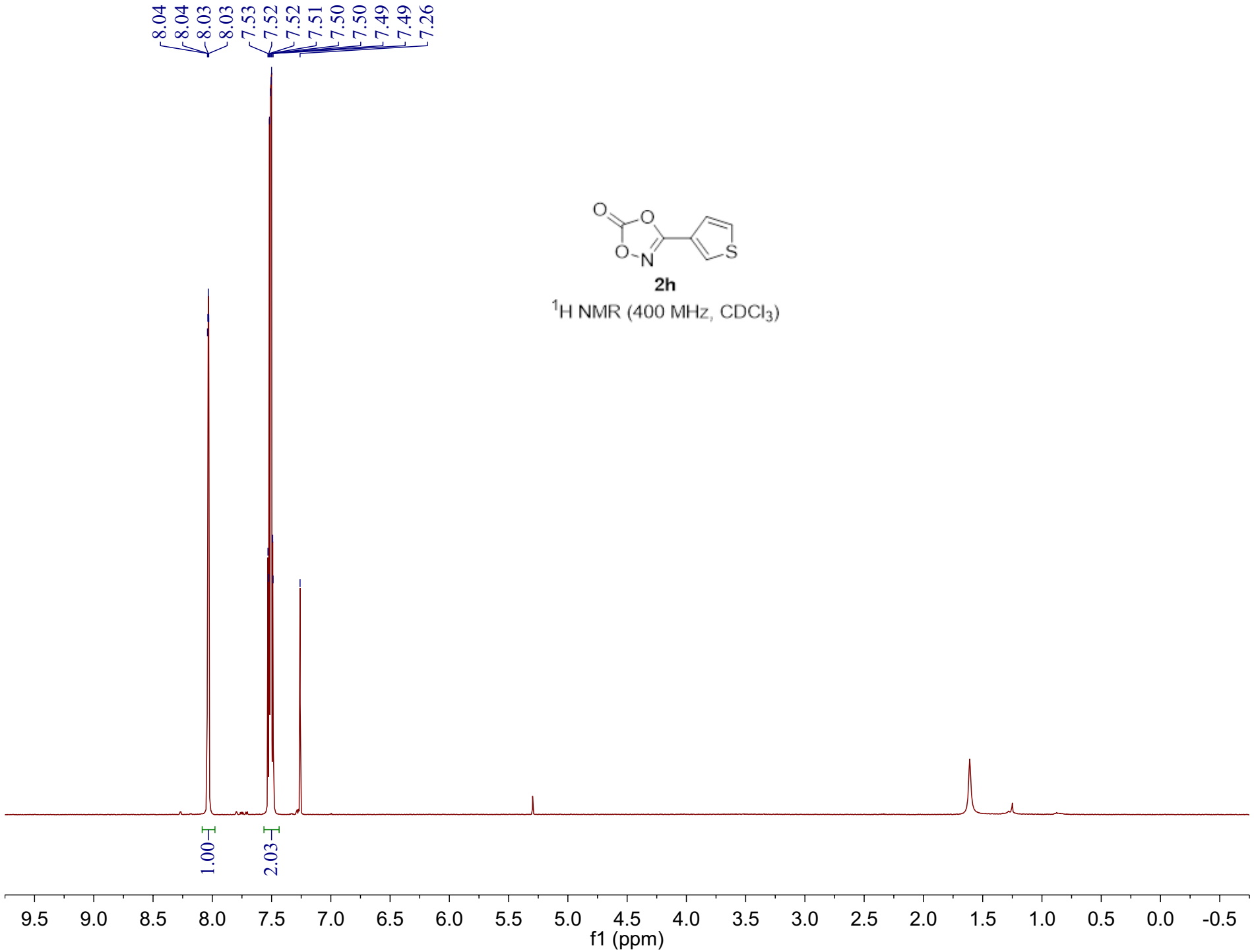
Supplementary Figure 168: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2d**.



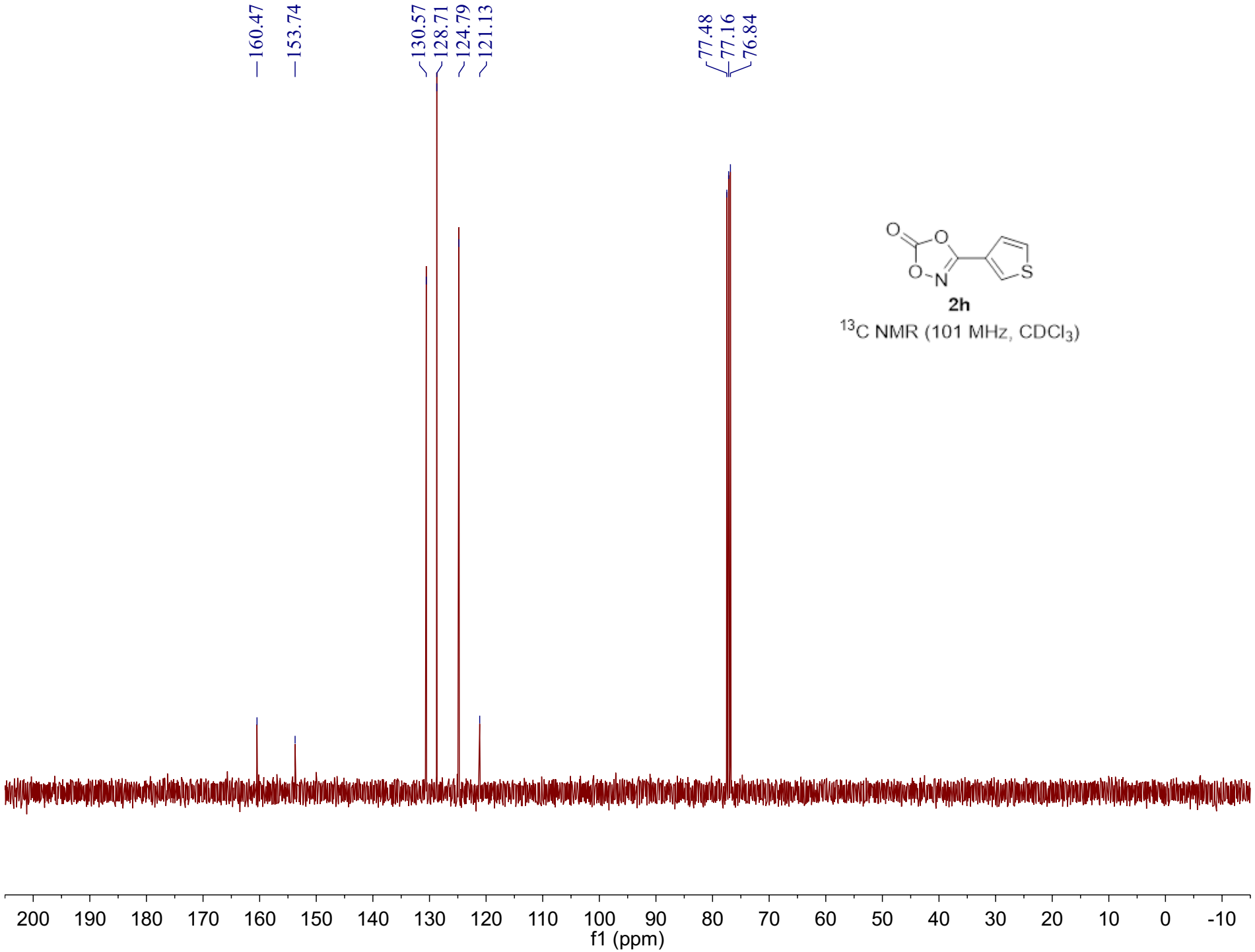
Supplementary Figure 169: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2e**.



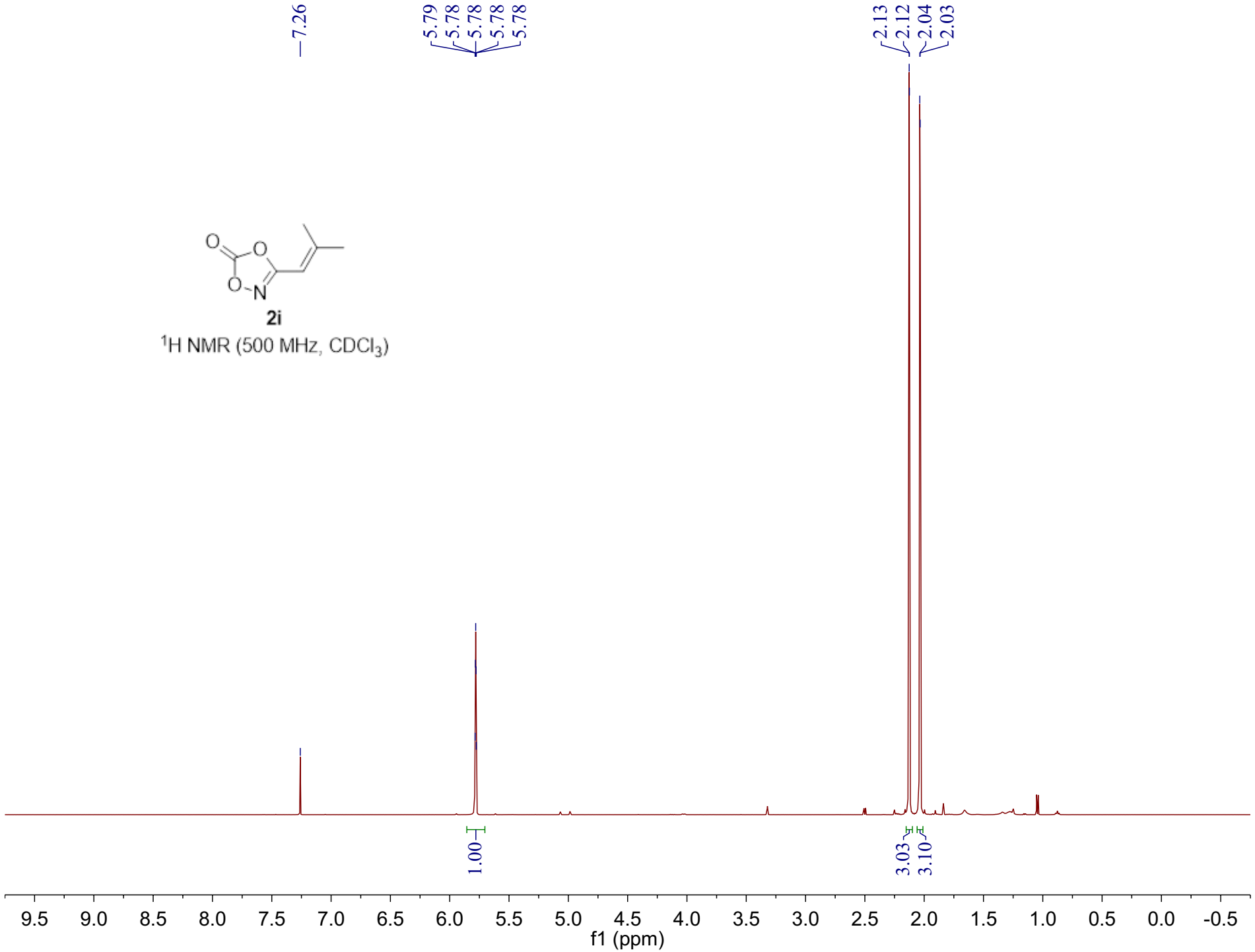
Supplementary Figure 170: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2e**.



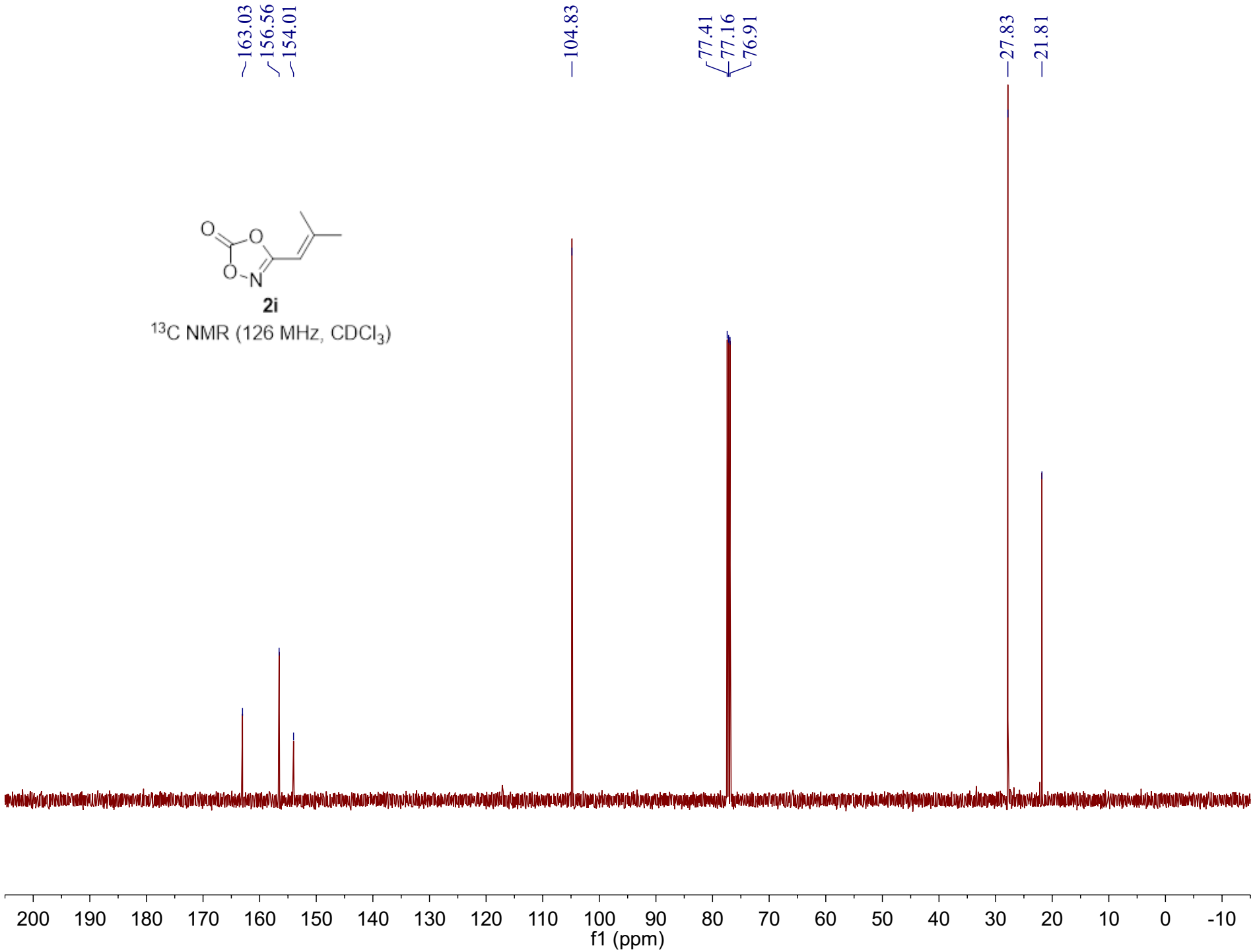
Supplementary Figure 171: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2h**.



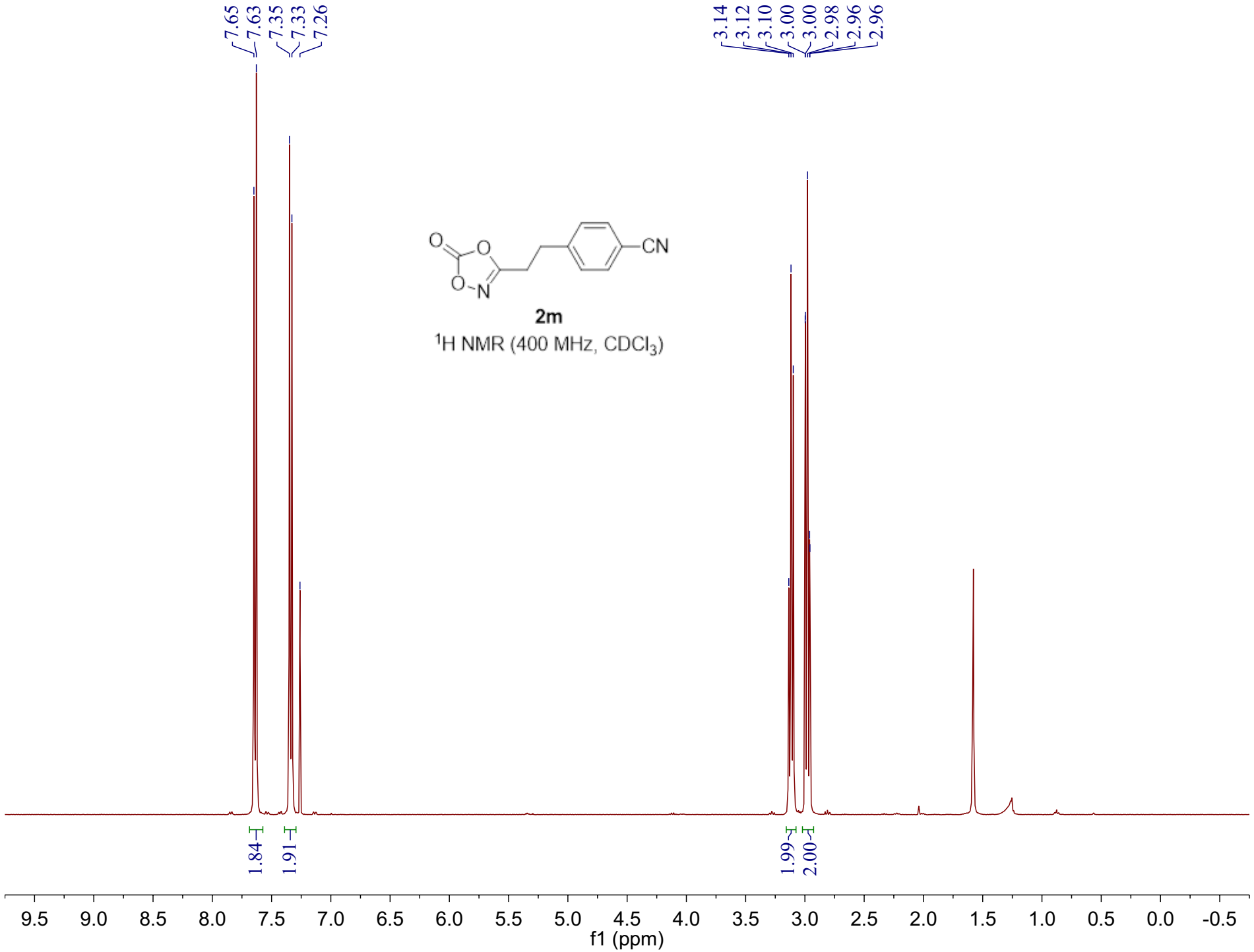
Supplementary Figure 172: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2h**.



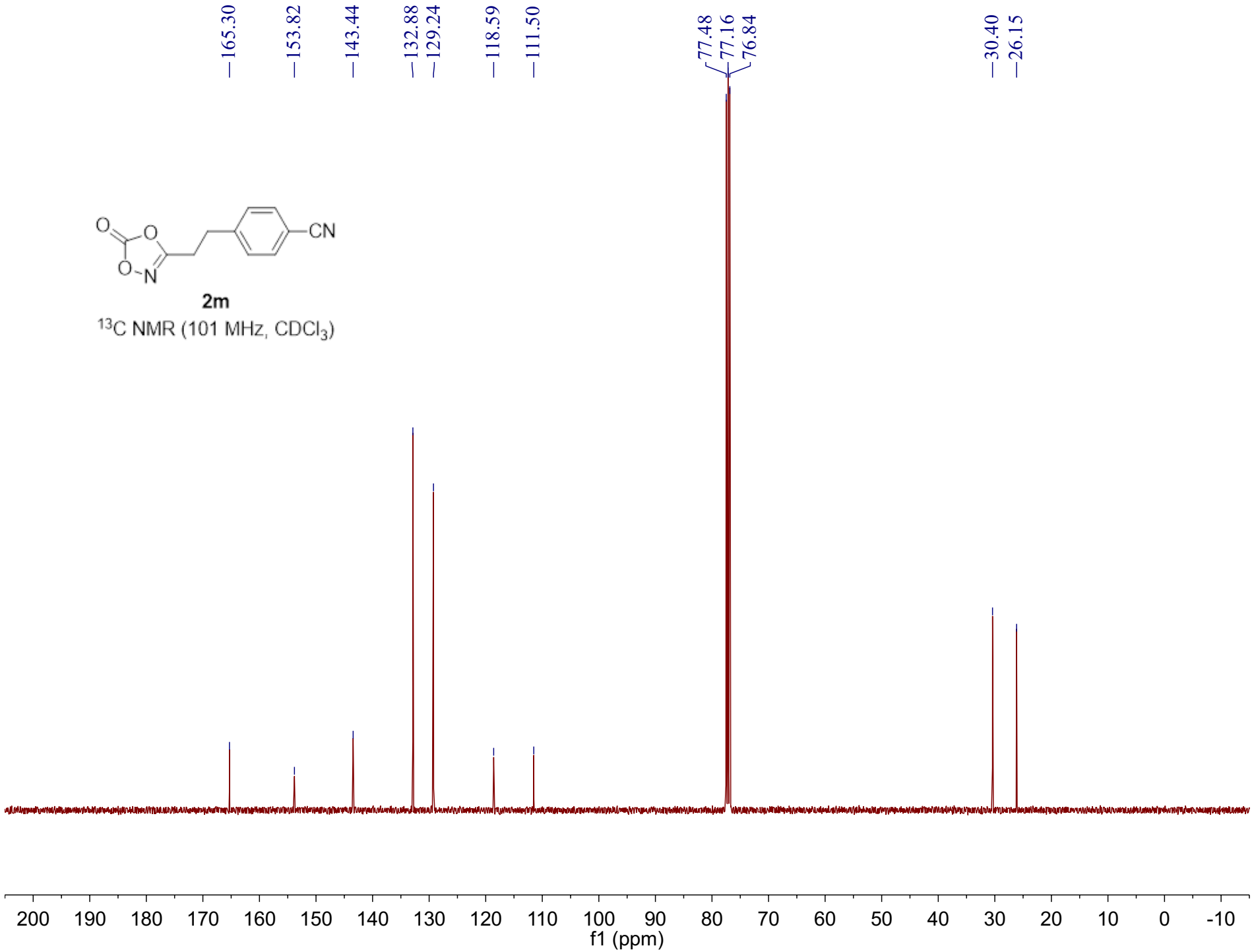
Supplementary Figure 173: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2i**.



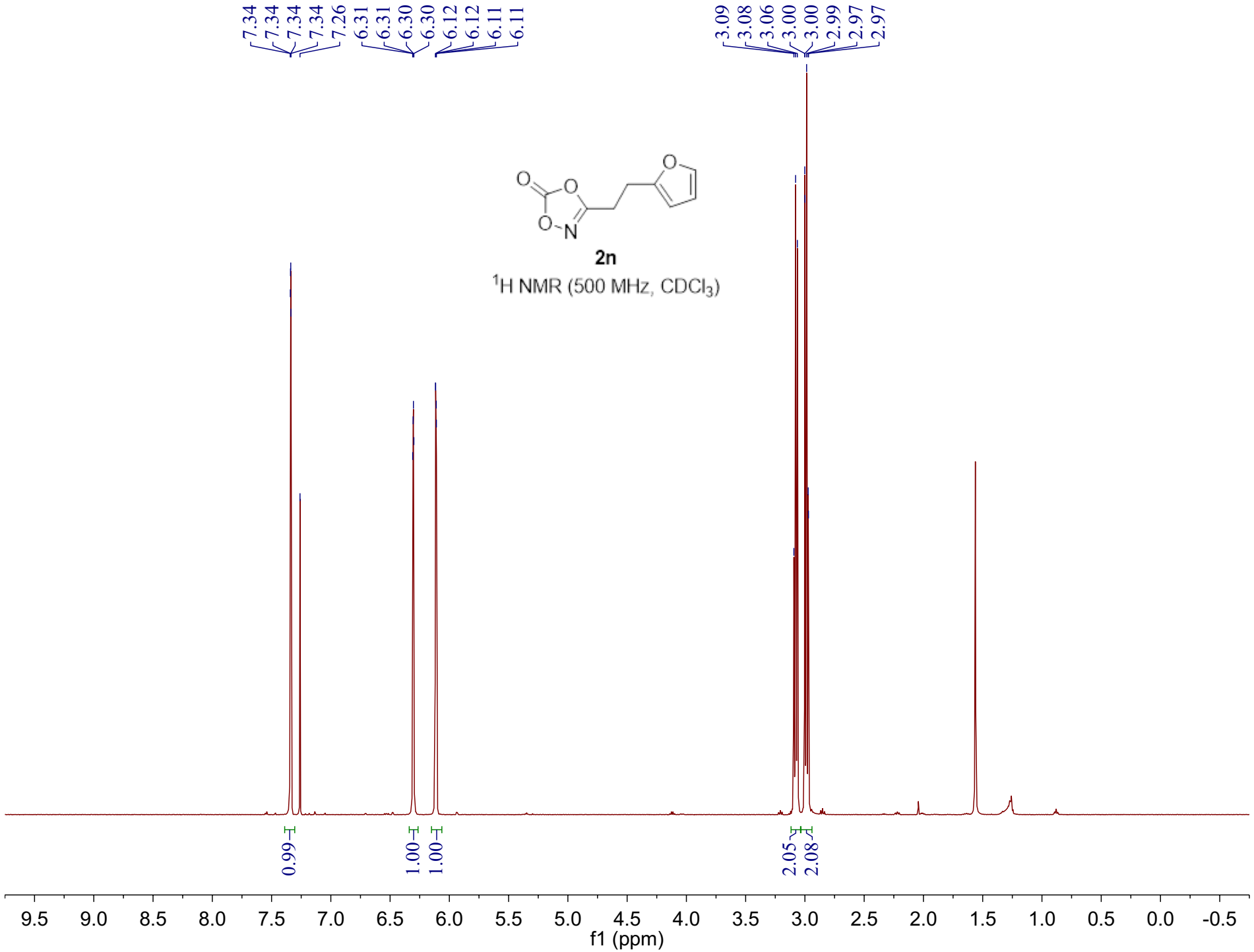
Supplementary Figure 174: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2i**.



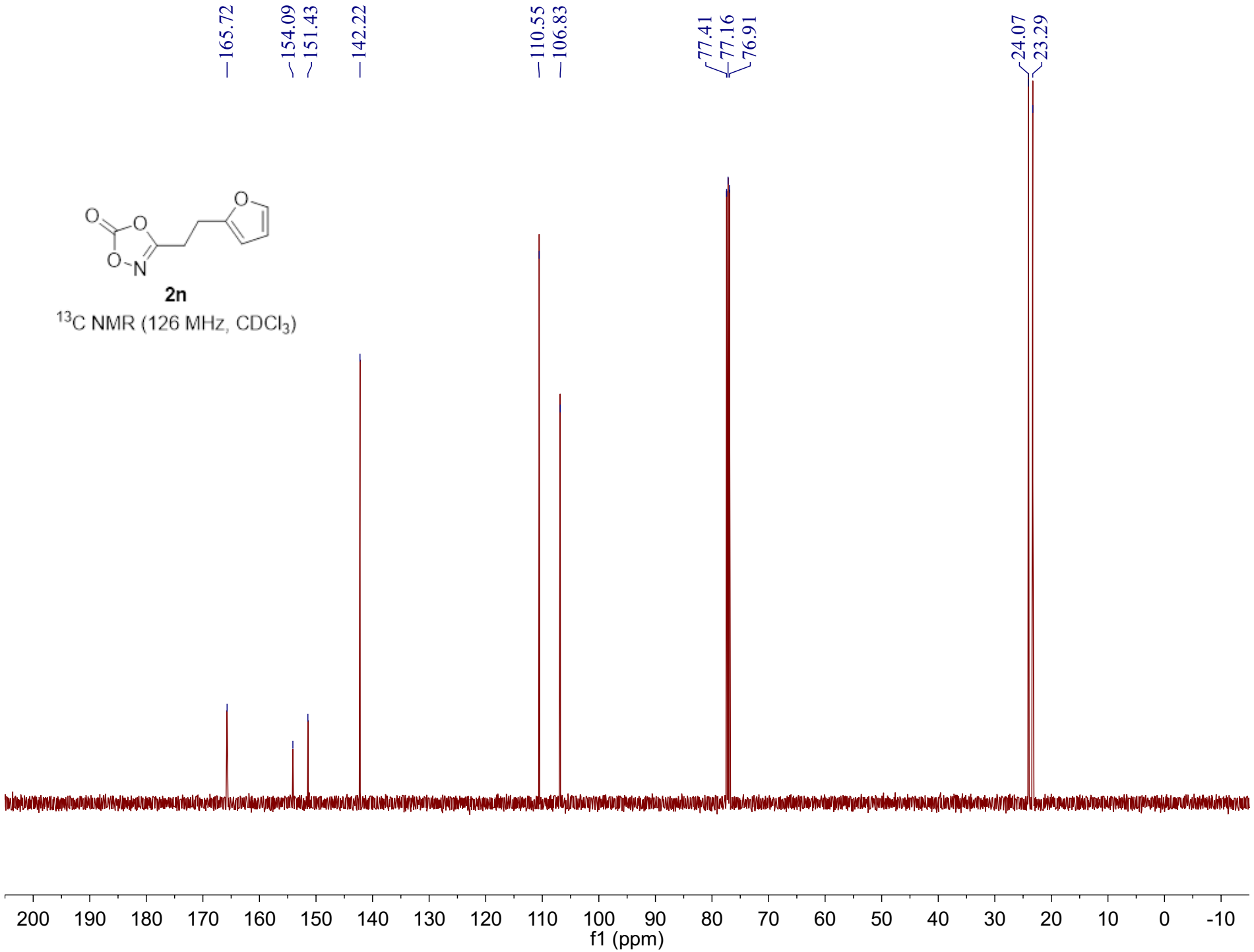
Supplementary Figure 175: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2m**.



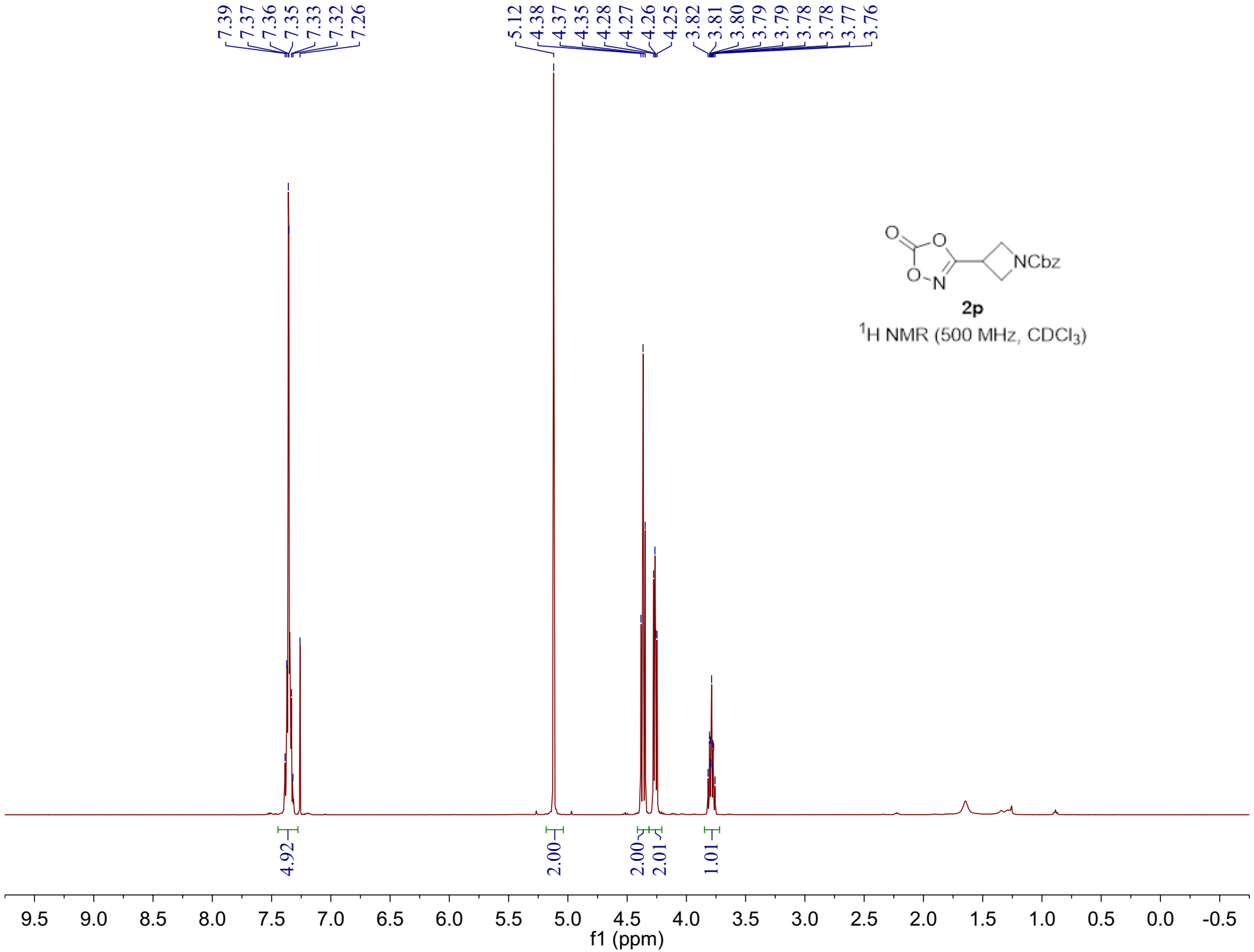
Supplementary Figure 176: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **2m**.



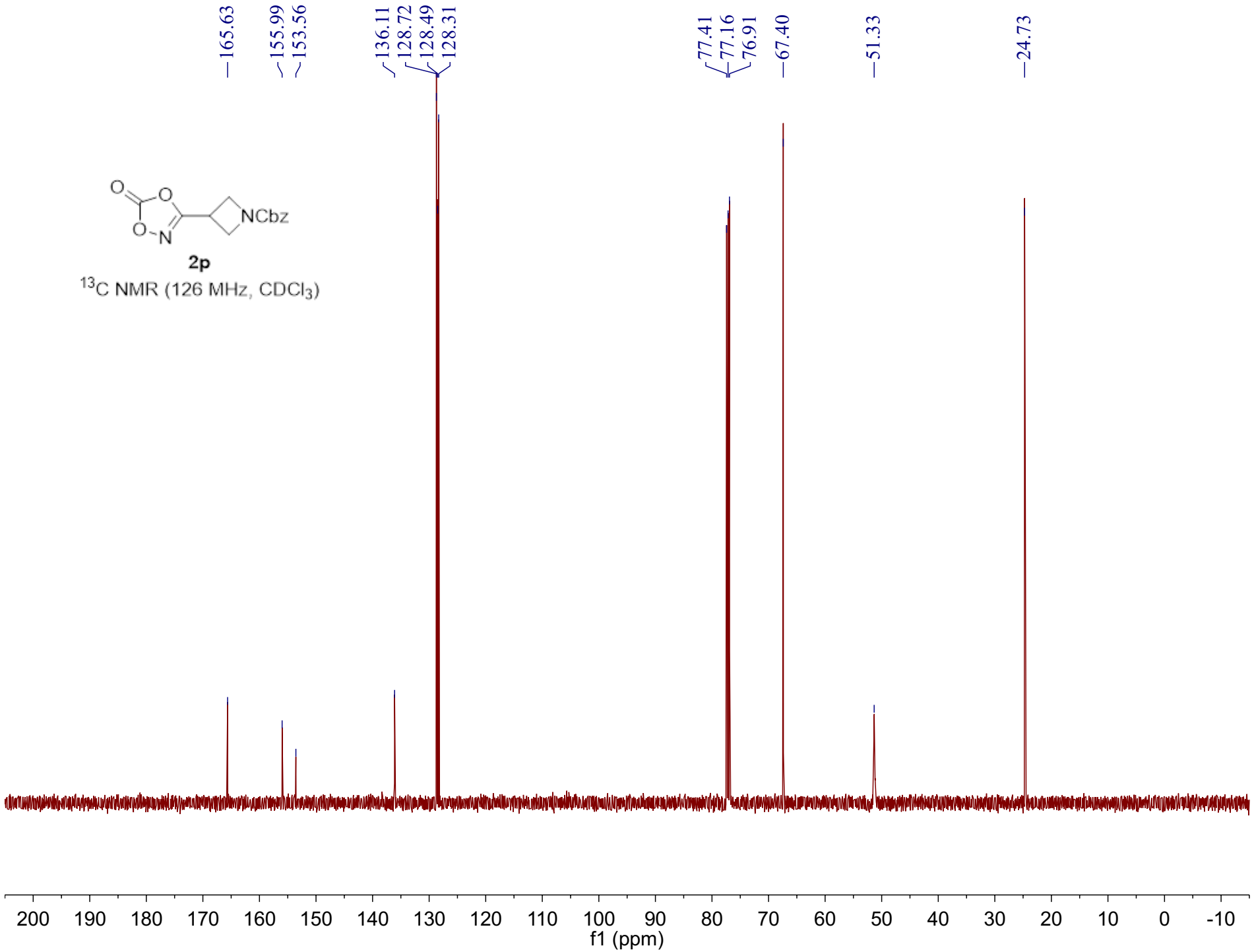
Supplementary Figure 177: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2n**.



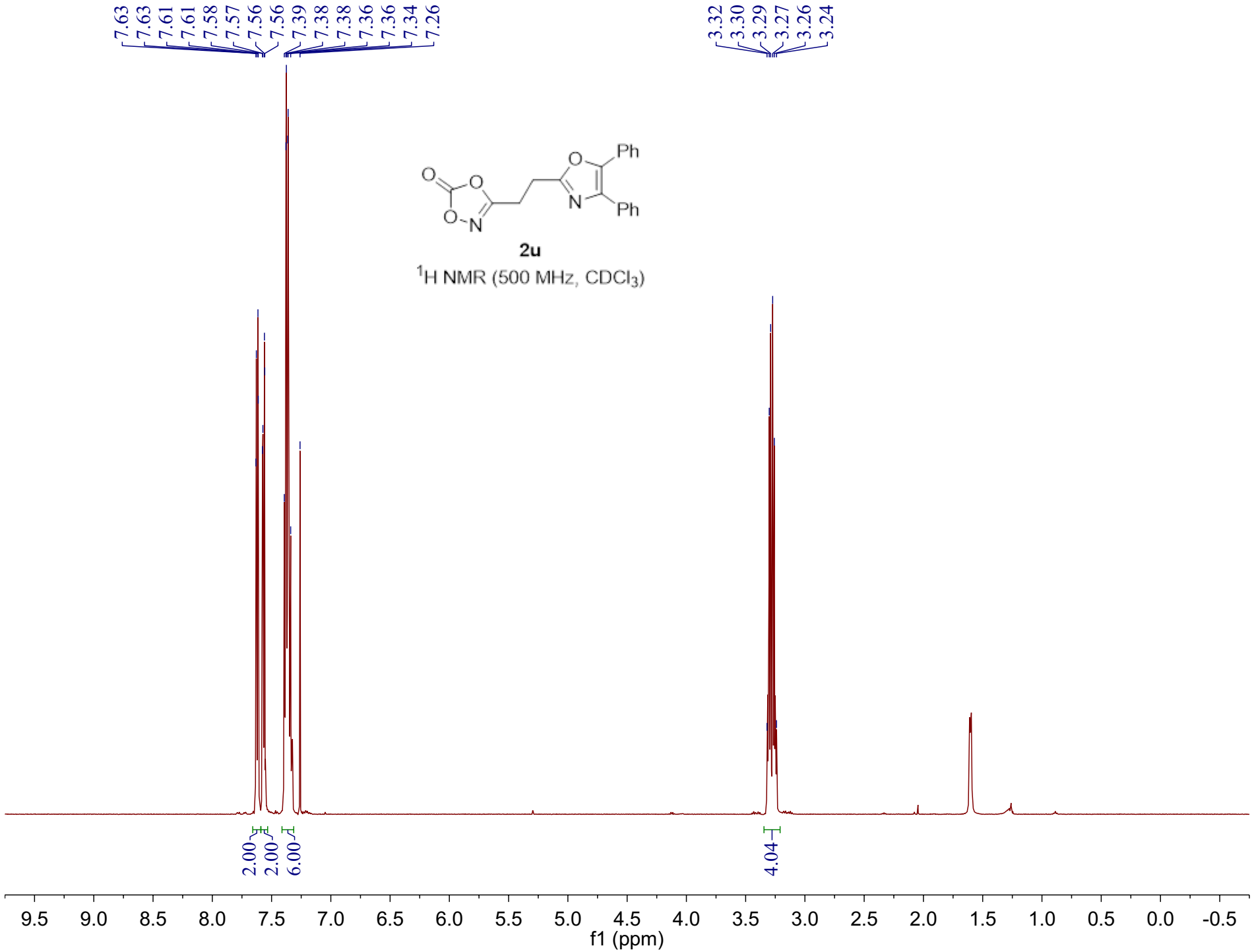
Supplementary Figure 178: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2n**.



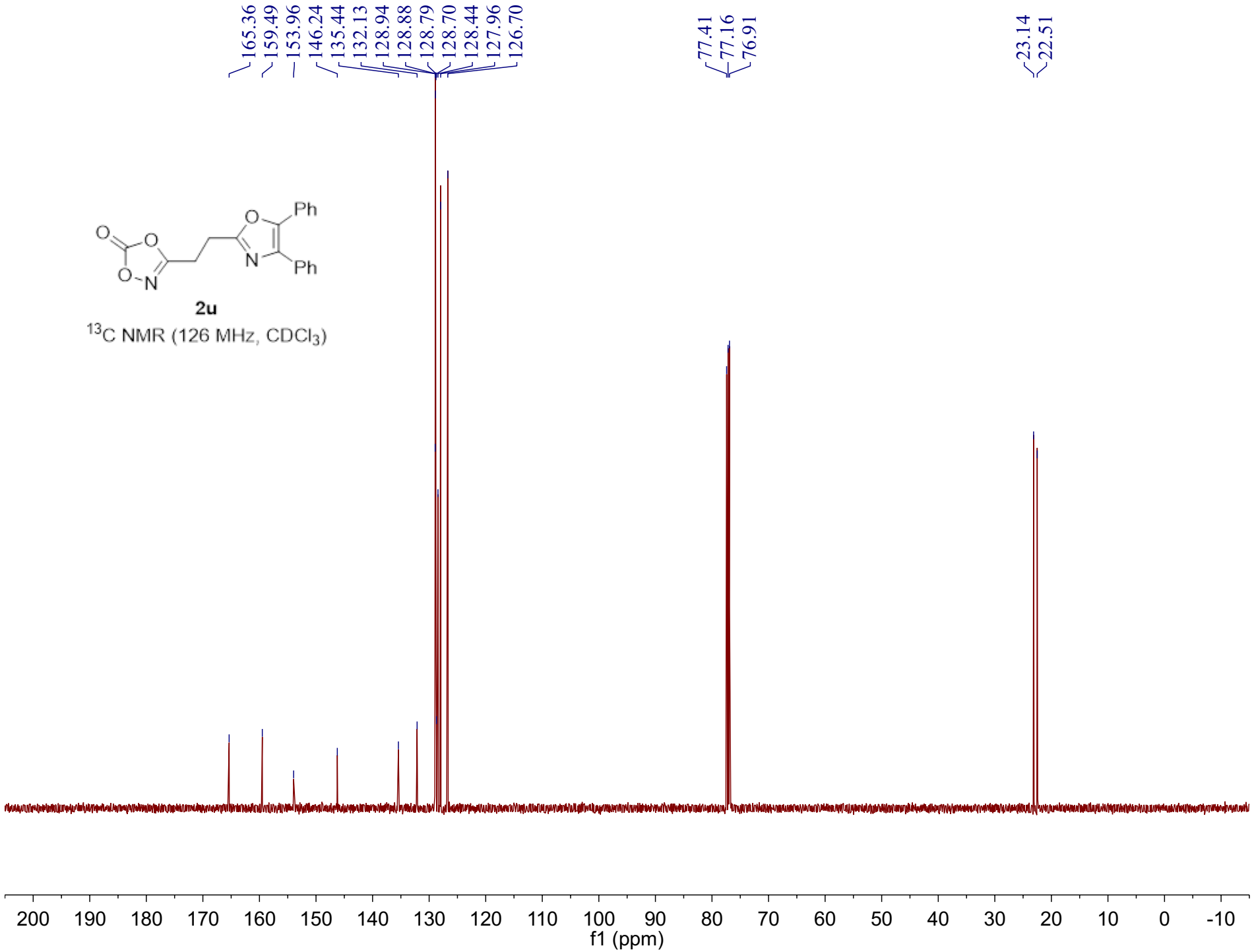
Supplementary Figure 179: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2p**.



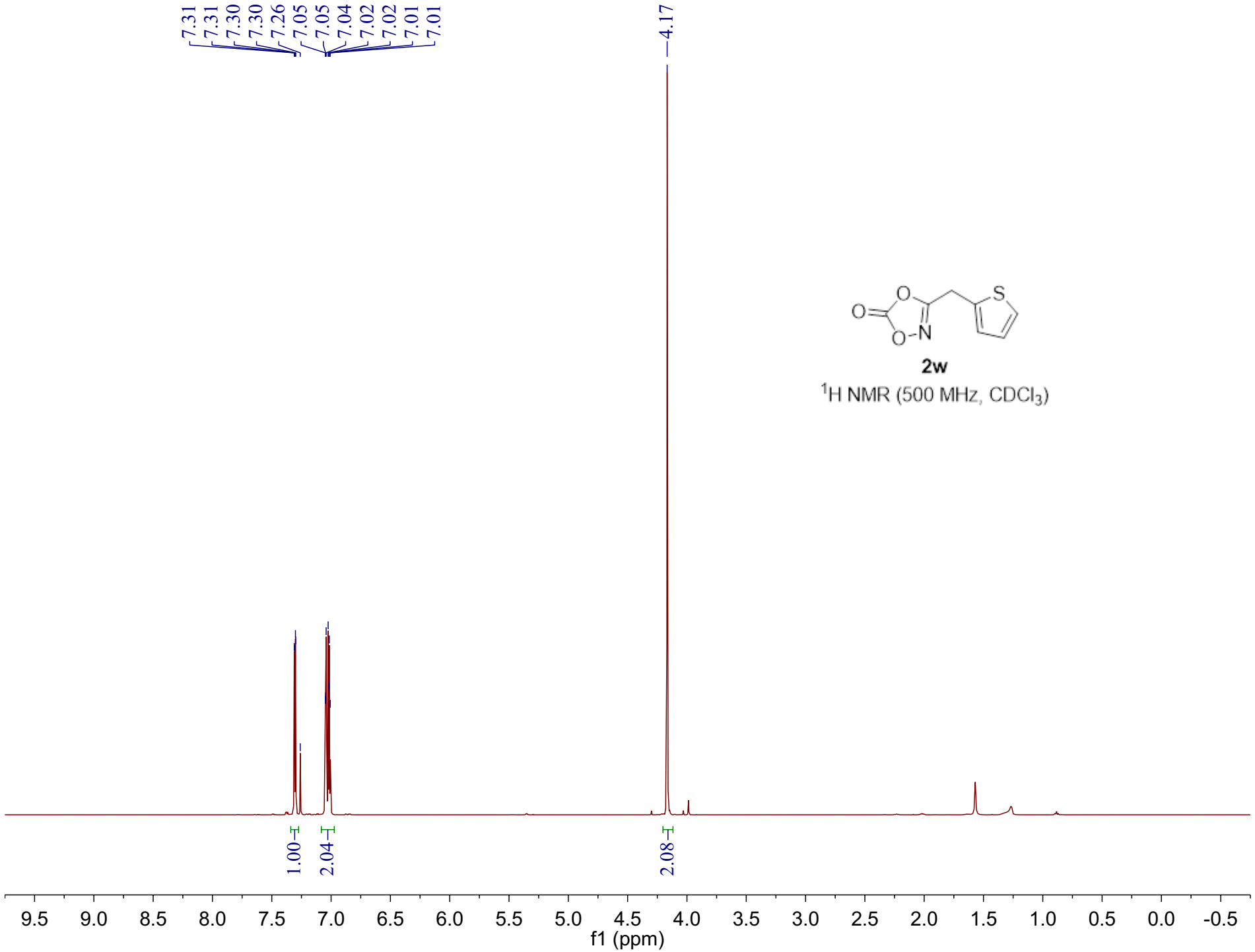
Supplementary Figure 180: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2p**.



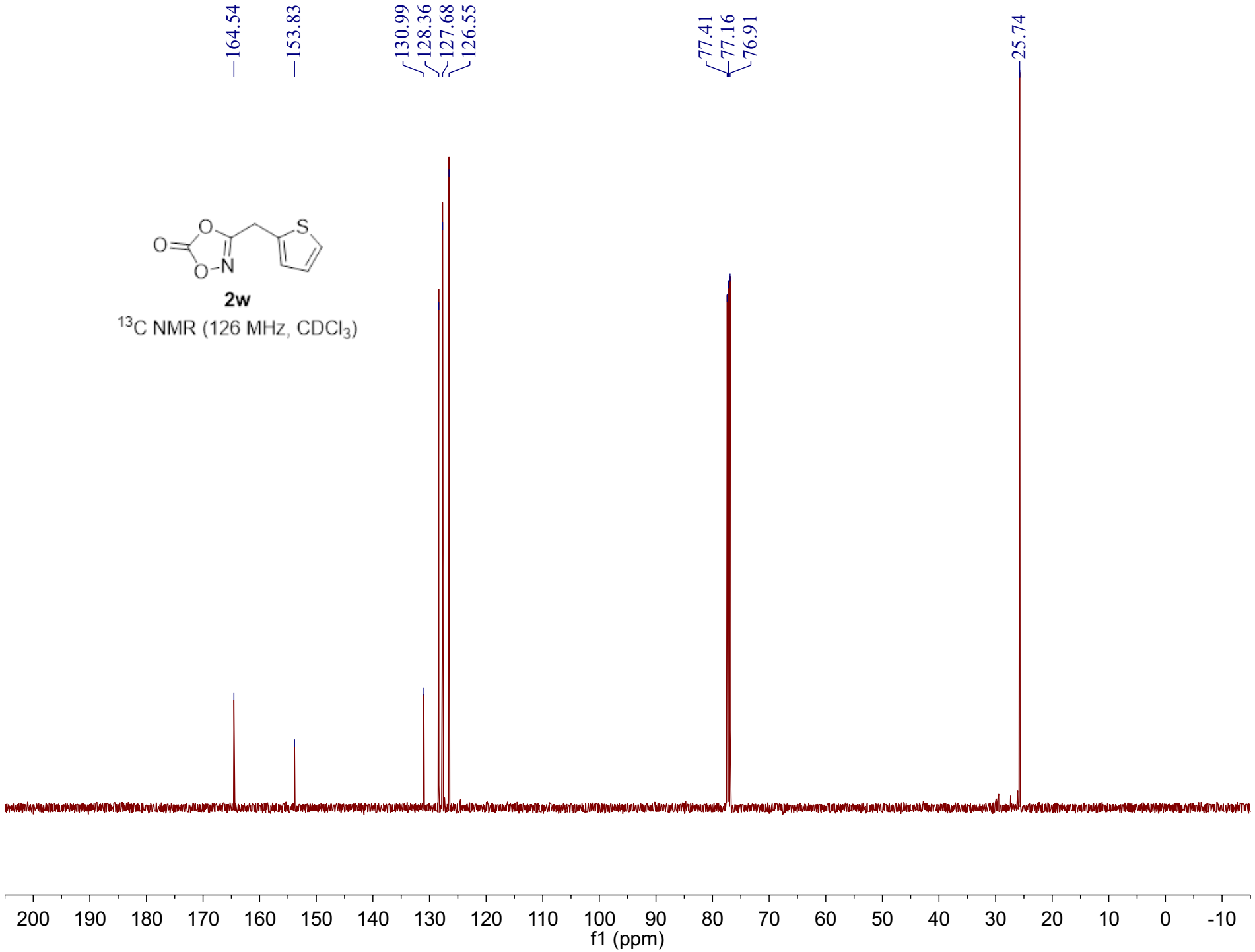
Supplementary Figure 181: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2u**.



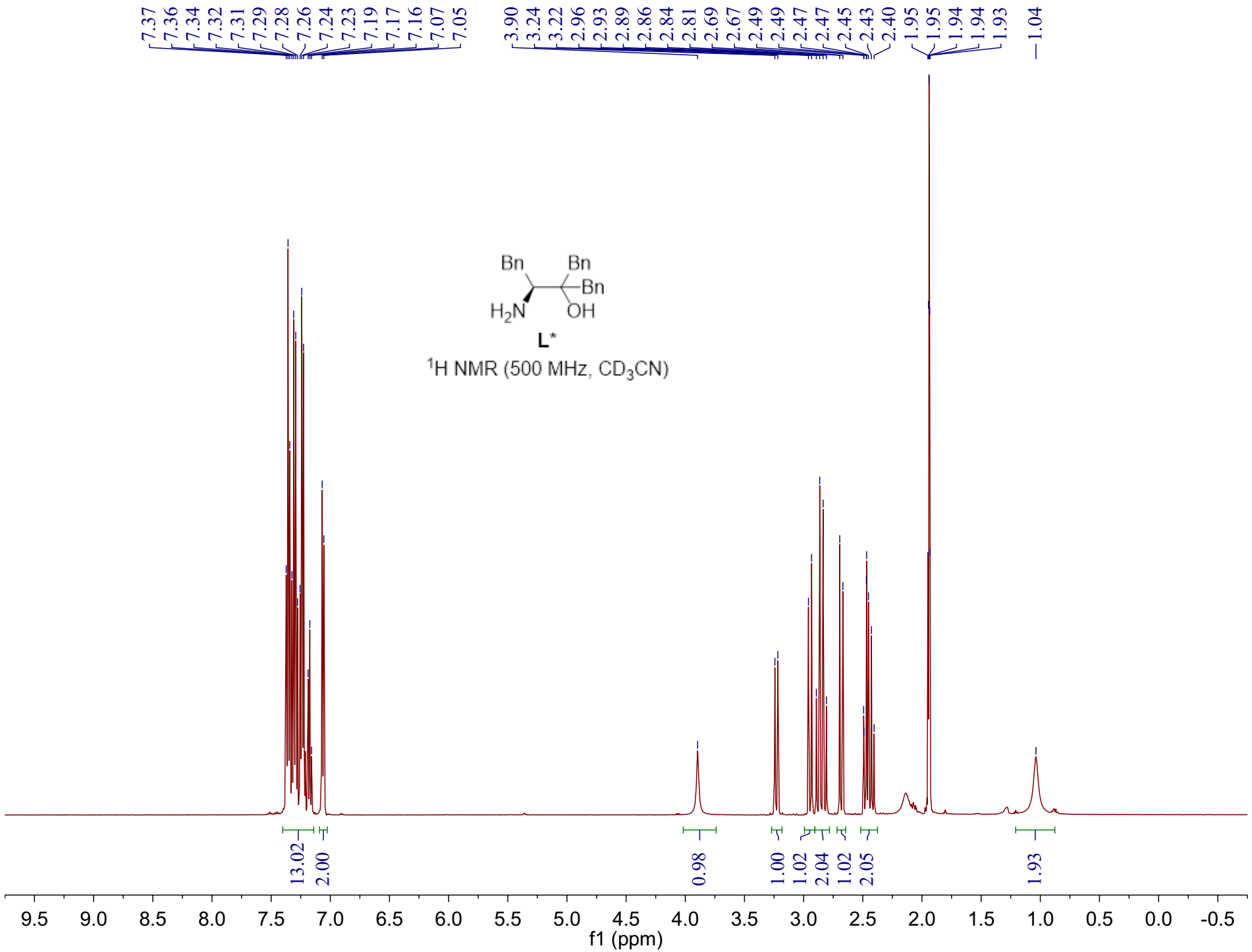
Supplementary Figure 182: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2u**.



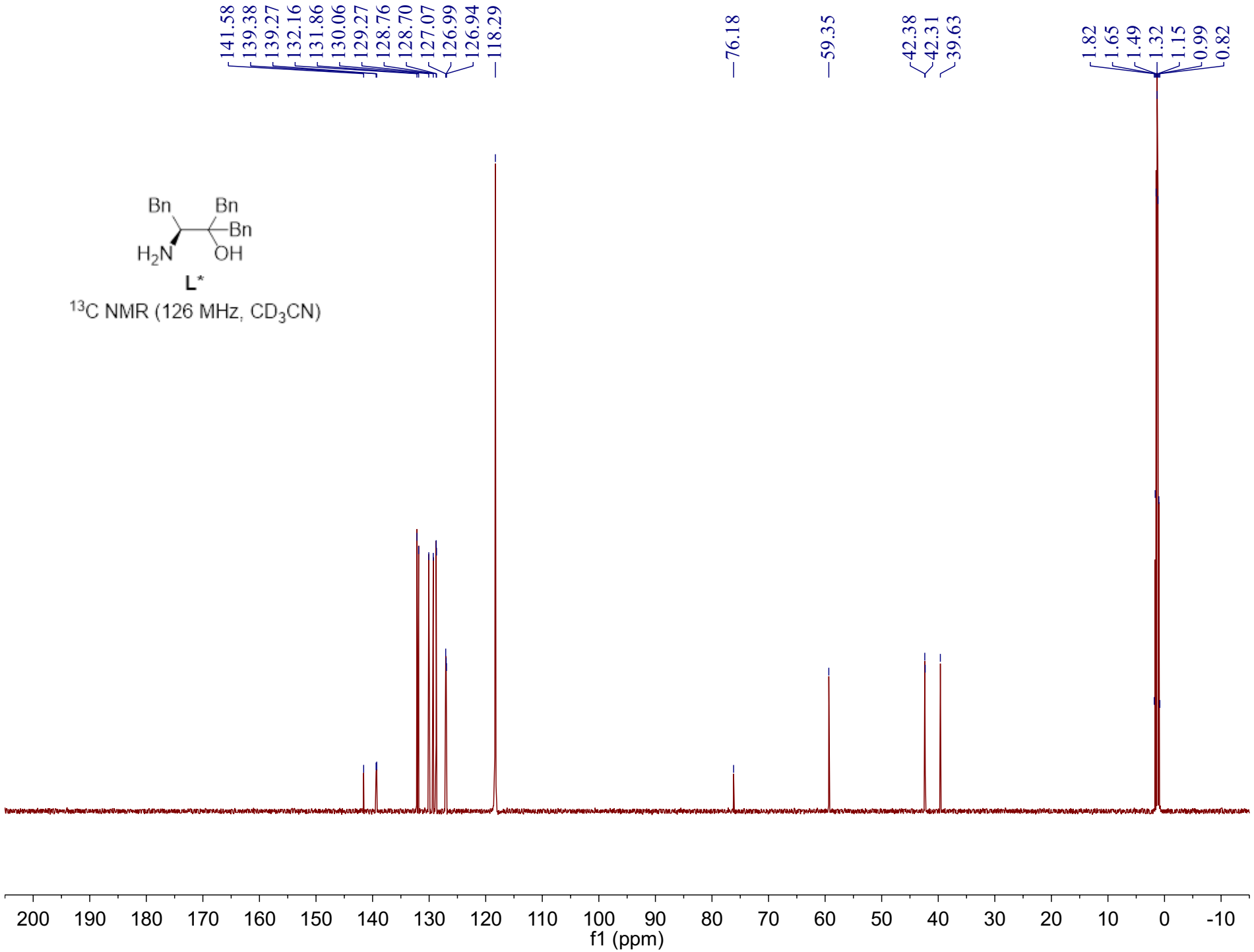
Supplementary Figure 183: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2w**.



Supplementary Figure 184: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2w**.



Supplementary Figure 185: ^{1}H NMR (500 MHz, CD_3CN) spectrum of **L***.



Supplementary Figure 186: ^{13}C NMR (126 MHz, CD_3CN) spectrum of **L***.

2. HPLC Trace

```
Data File H:\ORIGINAL DATA\ZY-09-146-10-RAC.D
Sample Name: ZY-09-146-10-IE

    ======================================================================
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    Acq. Instrument : HPLC-1260                      Location :   61
    Injection Date  : 1/29/2022 5:06:07 PM              Inj :   1
                                                   Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
    Acq. Method     : D:\zy\20220124\YH 2022-01-29 16-32-07\5EtOH10_10-1-6-240.M
    Last changed    : 1/29/2022 4:32:31 PM by 系统
    Analysis Method : E:\DATA\20220317\LC 2022-03-28 16-47-04\3IPA_30_8_2.-SFT.M (Sequence Method
                      )
    Last changed    : 3/28/2022 10:48:30 PM by SYSTEM
                      (modified after loading)
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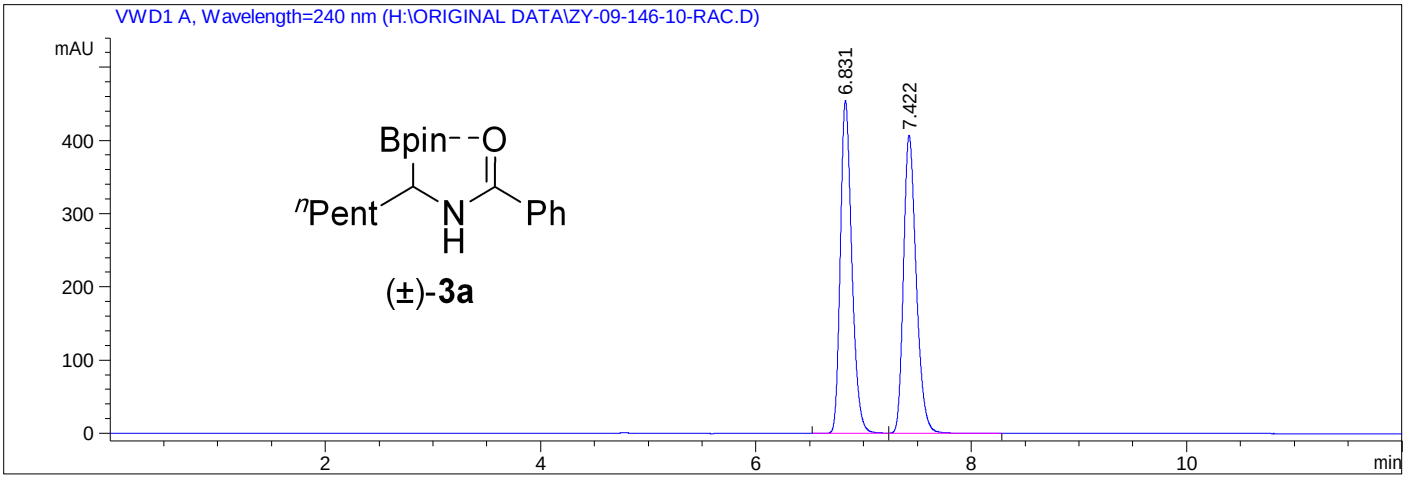


```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=240 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.831 VB R  0.1130 3366.24365  454.14883  50.1751
       2   7.422 BB    0.1259 3342.75000  406.73416  49.8249

    Totals :                   6708.99365  860.88300


    ======================================================================
                              *** End of Report ***
```

Supplementary Figure 187: HPLC spectrum of (±)-**3a**.

Data File H:\ORIGINAL DATA\ZY-09-146-10-EE.D
Sample Name: ZY-09-146-10-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   2
Acq. Instrument : HPLC-1260                      Location :   63
Injection Date  : 1/29/2022 9:49:47 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\zy\20220124\YH 2022-01-29 21-31-36\5EtOH10_10-1-6-240.M
Last changed    : 1/29/2022 9:31:43 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-03-28 16-47-04\3IPA_30_8_2.-SFT.M (Sequence Method
                  )
Last changed    : 3/28/2022 10:47:29 PM by SYSTEM
                  (modified after loading)
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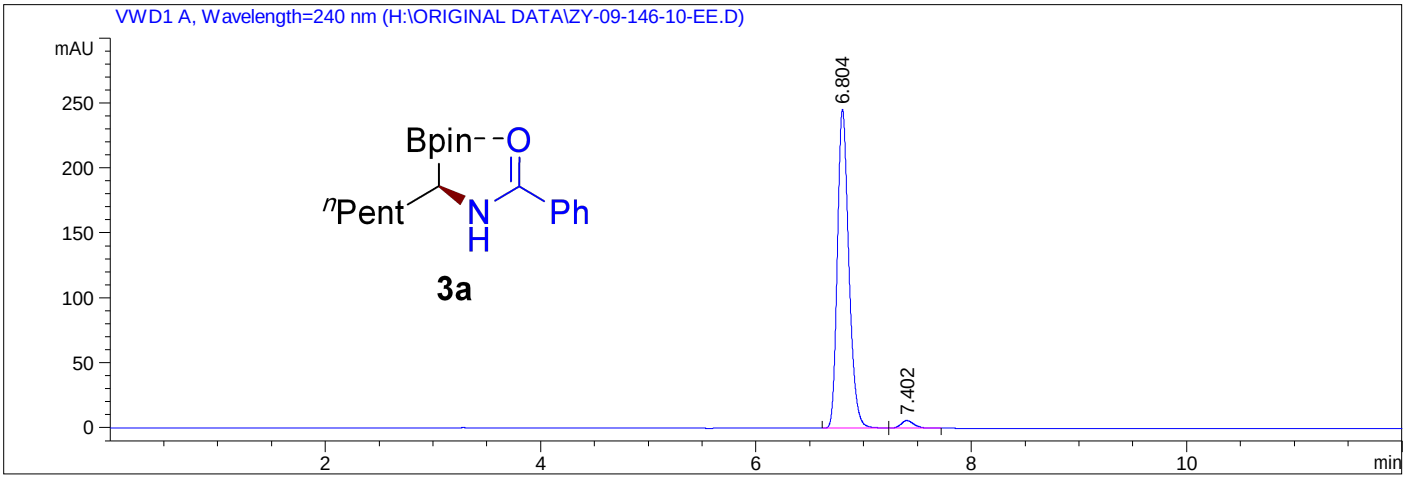


```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.804 BB    0.1133 1815.76379  245.36716  97.4591
   2   7.402 BB    0.1244   47.33982    5.81724   2.5409

Totals :                  1863.10361  251.18439


==========================================================================
                          *** End of Report ***
```

Supplementary Figure 188: HPLC spectrum of **3a**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-195-2-EE.D
Sample Name: ZY-09-195-2-EE

```
==================================================================
Acq. Operator   : 系统                          Seq. Line :   7
Acq. Instrument : HPLC-1260                      Location :   84
Injection Date  : 2/15/2022 10:02:32 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\zy\20220201\YH 2022-02-15 08-43-37\5EtOH15_10-1-2-240.M
Last changed    : 2/15/2022 9:33:50 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:51:28 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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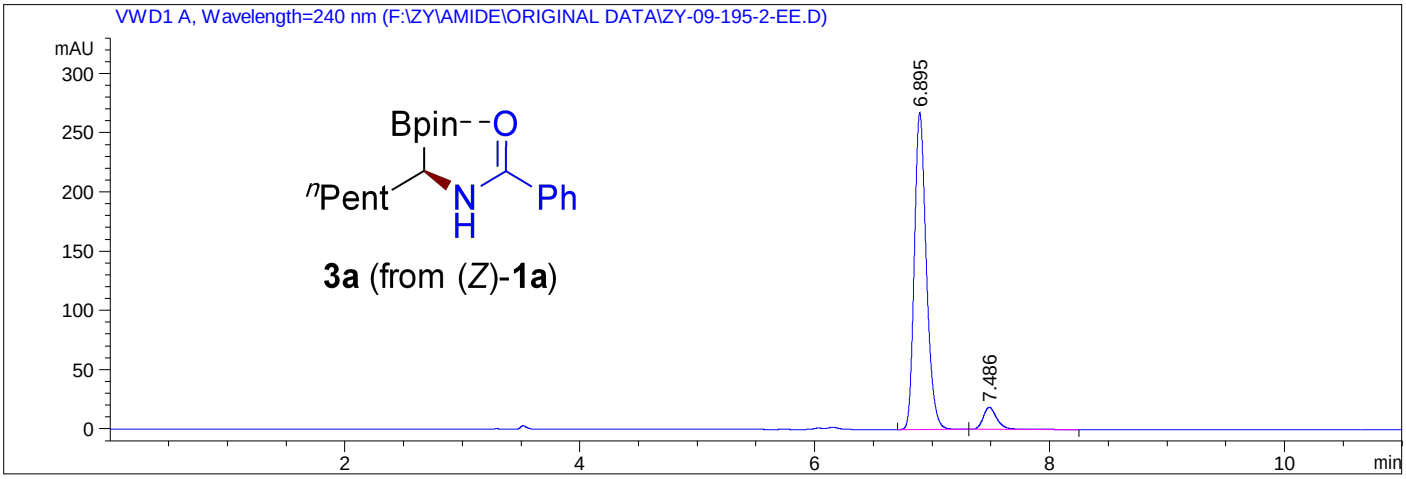


```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.895 BB    0.1081 1892.65186  267.47192  92.4615
   2   7.486 BB    0.1246  154.30952   18.72402   7.5385

Totals :                  2046.96138  286.19595


==================================================================
                        *** End of Report ***
```

Supplementary Figure 189: HPLC spectrum of **3a** (from (*Z*)-**1a**).

Data File E:\DATA\20220317\LC 2022-03-21 09-08-37\1FB-0401--006.D
Sample Name: ZY-10-57-1-RAC

```
=====================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   6
Acq. Instrument : HPLC1260                         Location :   P1-F2
Injection Date  : 3/21/2022 10:24:39 AM                 Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : E:\DATA\20220317\LC 2022-03-21 09-08-37\8IPA_15_0.5_1-254.M
Last changed    : 3/21/2022 9:08:37 AM by SYSTEM
Analysis Method : E:\DATA\20220317\LC 2022-03-21 09-08-37\8IPA_15_0.5_1-254.M (Sequence
                  Method)
Last changed    : 3/21/2022 12:17:47 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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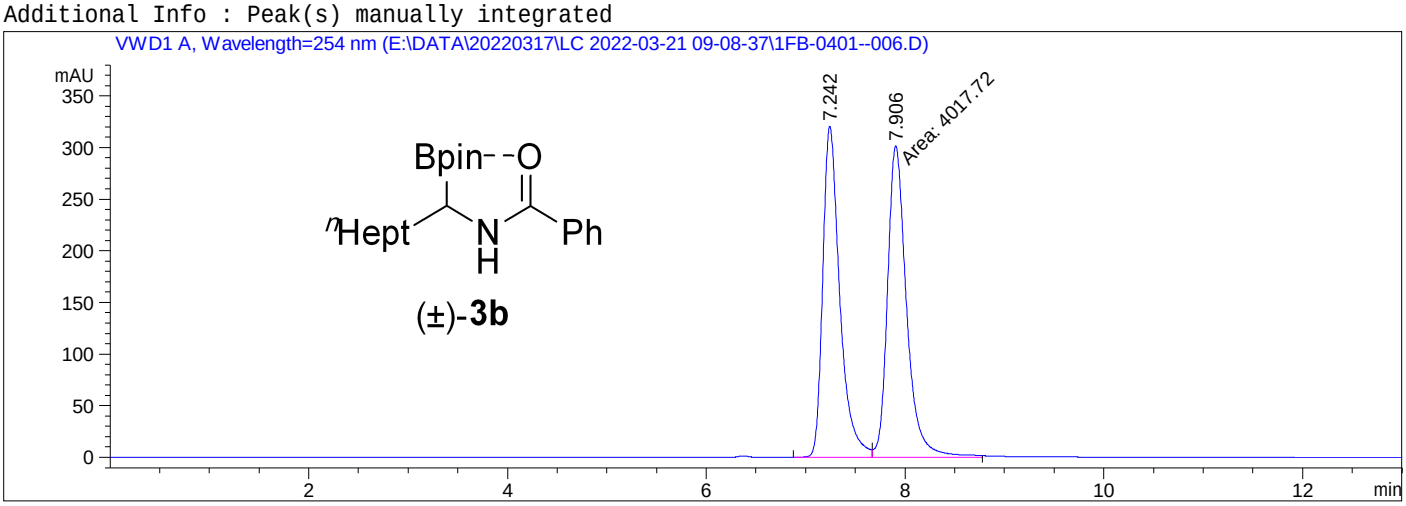


```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.242 BV    0.1790 3818.48267  320.39621  48.7287
   2   7.906 MF    0.2222 4017.72388  301.33694  51.2713

Totals :                  7836.20654  621.73315


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 190: HPLC spectrum of (±)-**3b**.

Data File E:\DATA\20220317\LC 2022-03-21 09-08-37\OnlineEdited--003.D
Sample Name: ZY-09-168-1-EE

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : HPLC1260                         Location :   P1-F3
Injection Date  : 3/21/2022 9:37:16 AM                Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : E:\DATA\20220317\LC 2022-03-21 09-08-37\8IPA_15_0.5_1-254.M
Last changed    : 3/21/2022 9:08:37 AM by SYSTEM
Analysis Method : E:\DATA\20220317\LC 2022-03-21 09-08-37\8IPA_15_0.5_1-254.M (Sequence
                  Method)
Last changed    : 3/21/2022 12:17:47 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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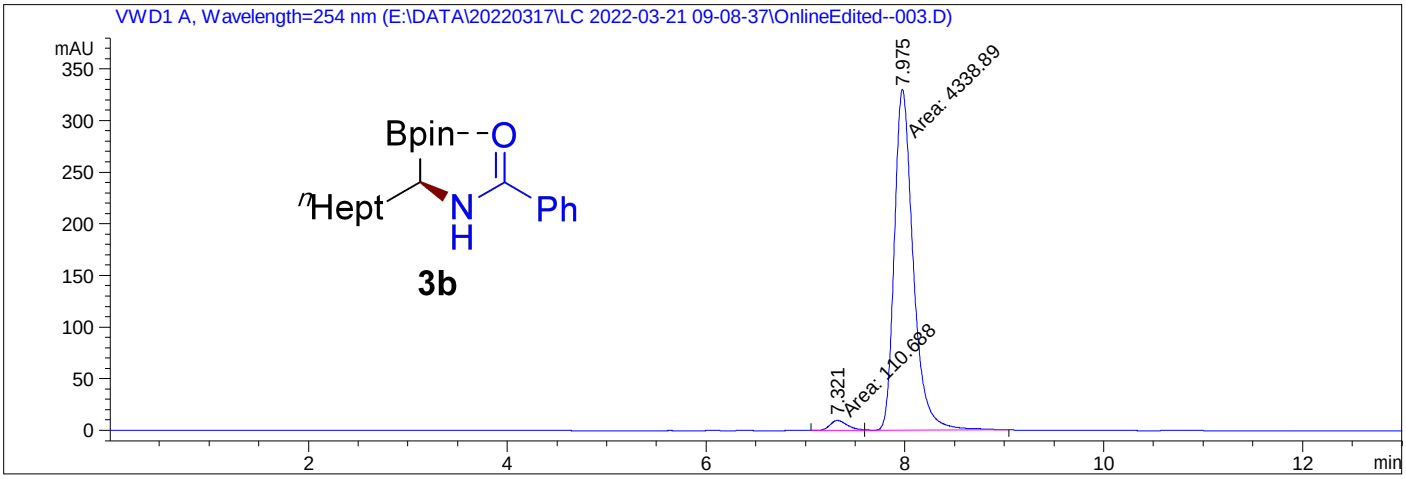


```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.321 MF    0.1973  110.68835    9.35163   2.4876
   2   7.975 FM    0.2193 4338.88623  329.76462  97.5124

Totals :                   4449.57458  339.11625


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 191: HPLC spectrum of **3b**.

Data File E:\DATA\20220317\LC 2022-03-21 09-08-37\1FA-0301--004.D
Sample Name: ZY-10-57-1-EE

```
=====================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   4
Acq. Instrument : HPLC1260                         Location :   P1-F1
Injection Date  : 3/21/2022 9:53:03 AM                  Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\20220317\LC 2022-03-21 09-08-37\8IPA_15_0.5_1-254.M
Last changed    : 3/21/2022 9:08:37 AM by SYSTEM
Analysis Method : E:\DATA\20220317\LC 2022-03-21 09-08-37\8IPA_15_0.5_1-254.M (Sequence
                  Method)
Last changed    : 3/21/2022 12:17:47 PM by SYSTEM
                  (modified after loading)
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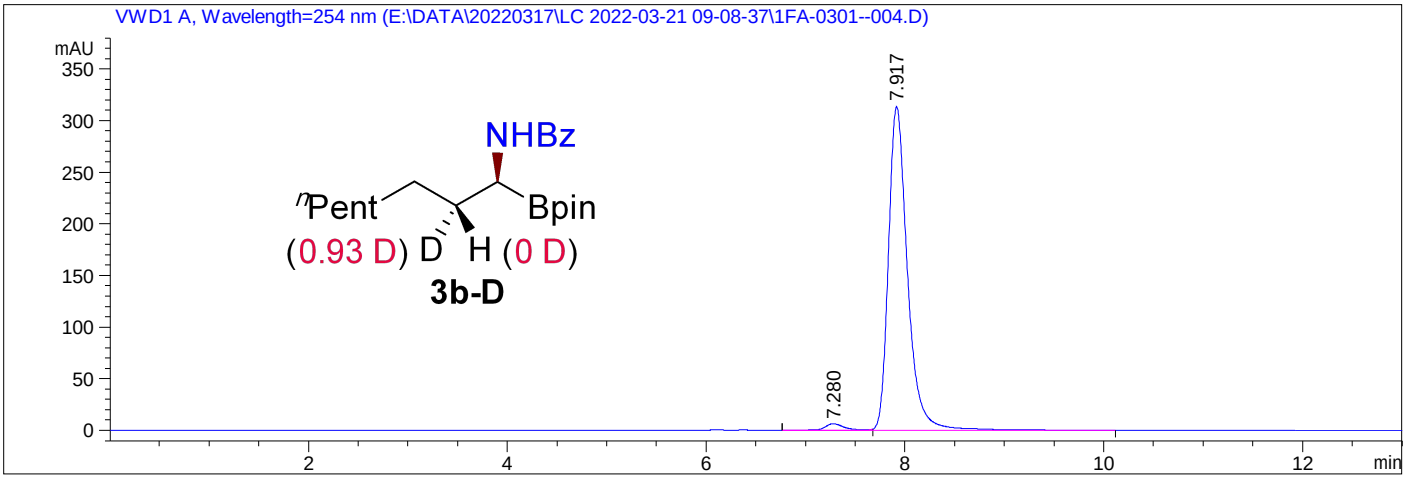


```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.280 BV E  0.1991   85.09237    6.39980   1.9985
   2   7.917 VB R  0.2023 4172.81006  313.51718  98.0015

Totals :                  4257.90243  319.91699


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 192: HPLC spectrum of **3b-D**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-187-2-RAC.D
Sample Name: ZY-09-187-2-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   5
Acq. Instrument : HPLC-1260                      Location :   44
Injection Date  : 12/23/2021 10:10:24 AM             Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\zy\20211219\YH 2021-12-23 09-03-54\10EtOH-15-0.8-1-6-240.M
Last changed    : 12/23/2021 9:03:56 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:27:30 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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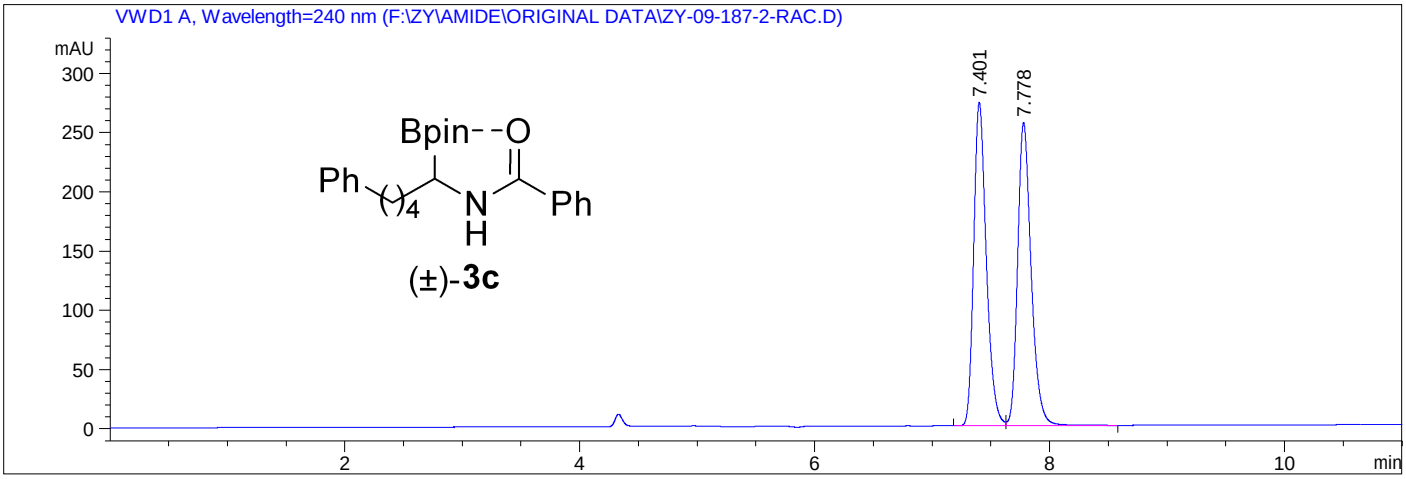



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.401 BV    0.1128 2031.66479  273.12259  49.7983
   2   7.778 VB    0.1209 2048.12427  255.81441  50.2017

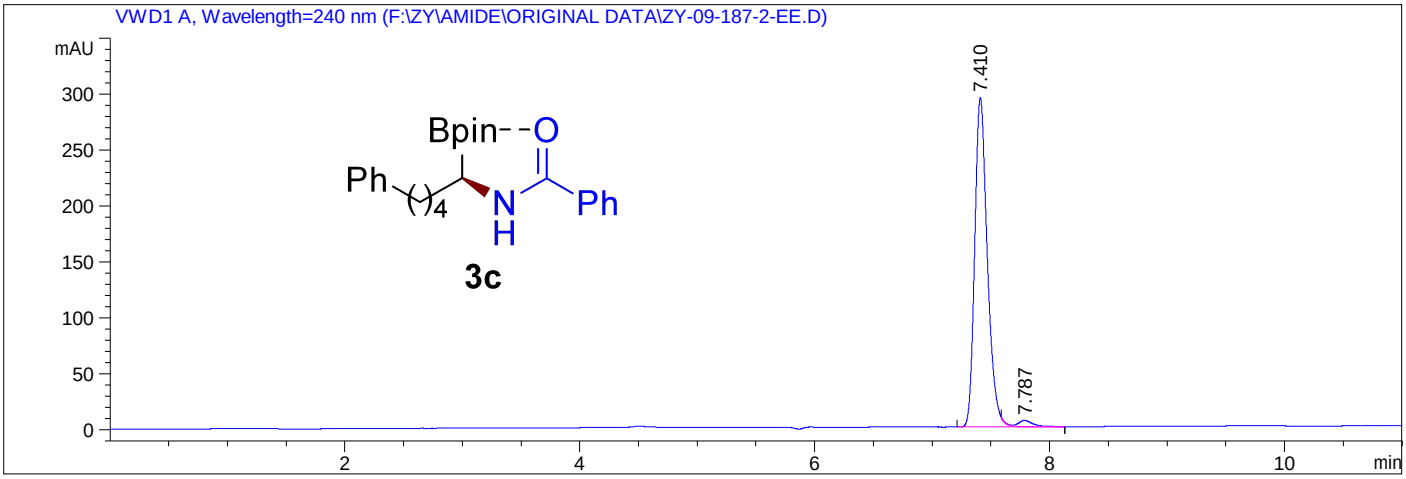
Totals :                  4079.78906  528.93700


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 193: HPLC spectrum of (±)-**3c**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-187-2-EE.D
Sample Name: ZY-09-187-2-EE

```
    ======================================================================
    Acq. Operator    : 系统                          Seq. Line :   4
    Acq. Instrument : HPLC-1260                       Location :   43
    Injection Date  : 12/23/2021 9:54:02 AM              Inj :   1
                                                    Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
    Acq. Method     : D:\zy\20211219\YH 2021-12-23 09-03-54\10EtOH-15-0.8-1-6-240.M
    Last changed    : 12/23/2021 9:03:56 AM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                      Method)
    Last changed    : 3/29/2022 9:27:03 AM by SYSTEM
                      (modified after loading)
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=240 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   7.410 BV R  0.1140 2207.72168  294.35645  97.8049
       2   7.787 VB E  0.1295   49.54852    5.61053   2.1951

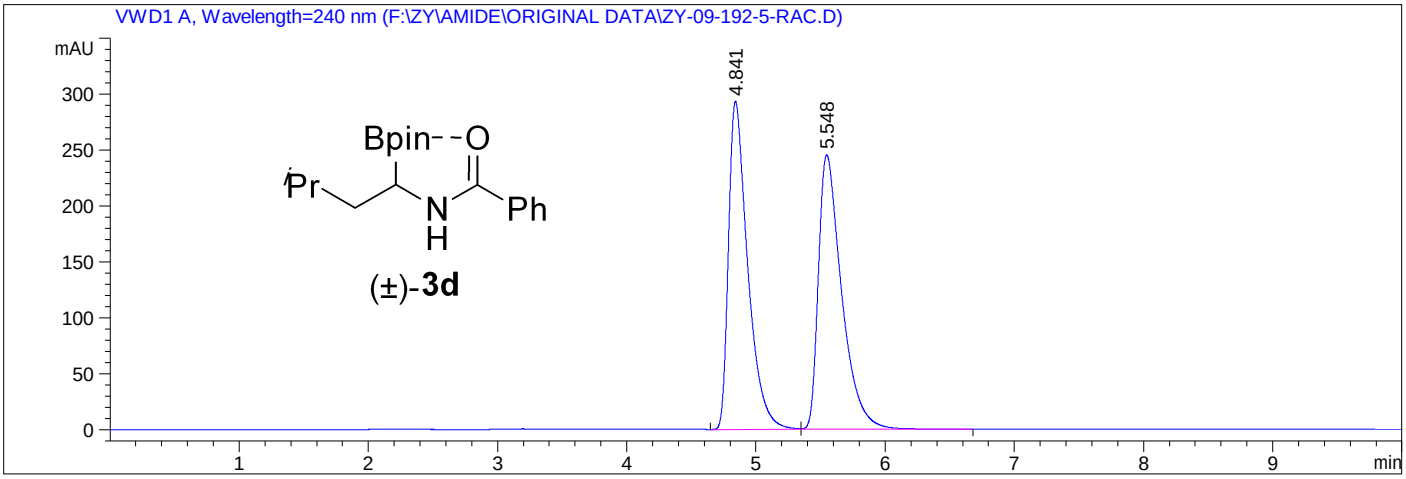
    Totals :                  2257.27020  299.96697


    ======================================================================
                               *** End of Report ***
```

Supplementary Figure 194: HPLC spectrum of **3c**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-192-5-RAC.D
Sample Name: ZY-09-192-7-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                      Location :   82
Injection Date  : 3/1/2022 2:24:02 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220224\YH 2022-03-01 13-37-55\5IPA15_10-1-6-240.M
Last changed    : 3/1/2022 1:37:55 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:42:28 AM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.841 BV    0.1531 3033.27930  293.32916  49.7162
   2   5.548 VB    0.1874 3067.90430  245.37120  50.2838

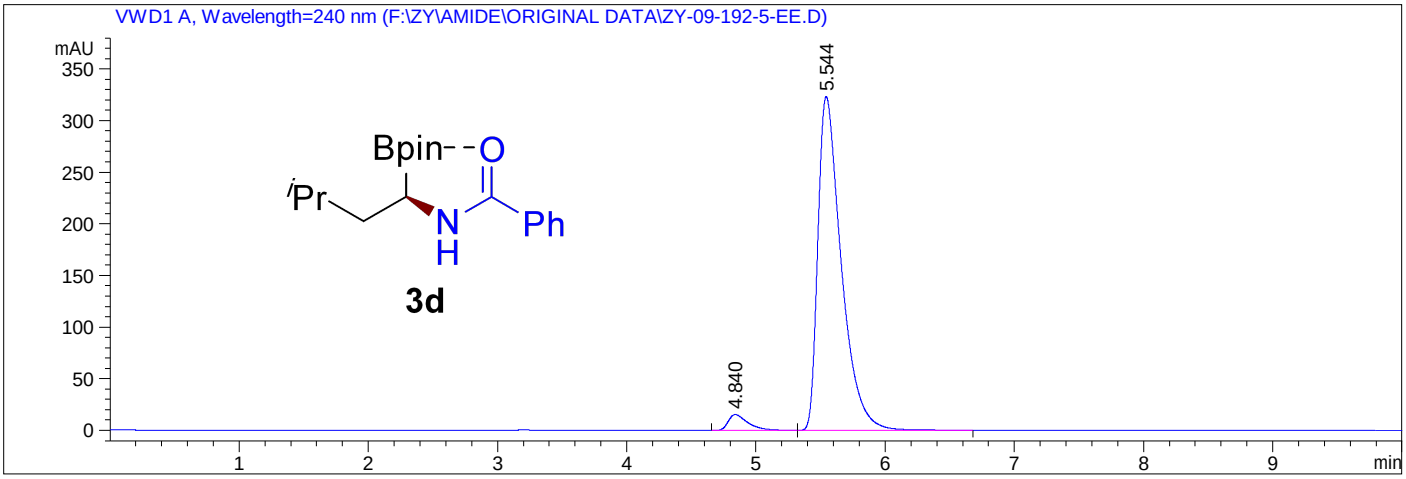
Totals :                  6101.18359  538.70036


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 195: HPLC spectrum of (±)-**3d**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-192-5-EE.D
Sample Name: ZY-09-192-5-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 3/1/2022 5:01:13 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.200 µl
Acq. Method     : D:\zy\20220224\YH 2022-03-01 16-20-30\5IPA15_10-1-6-240.M
Last changed    : 3/1/2022 4:20:31 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:41:21 AM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.840 BB    0.1574  163.37755   15.37929   3.8617
   2   5.544 BB    0.1893 4067.31079  323.30203  96.1383

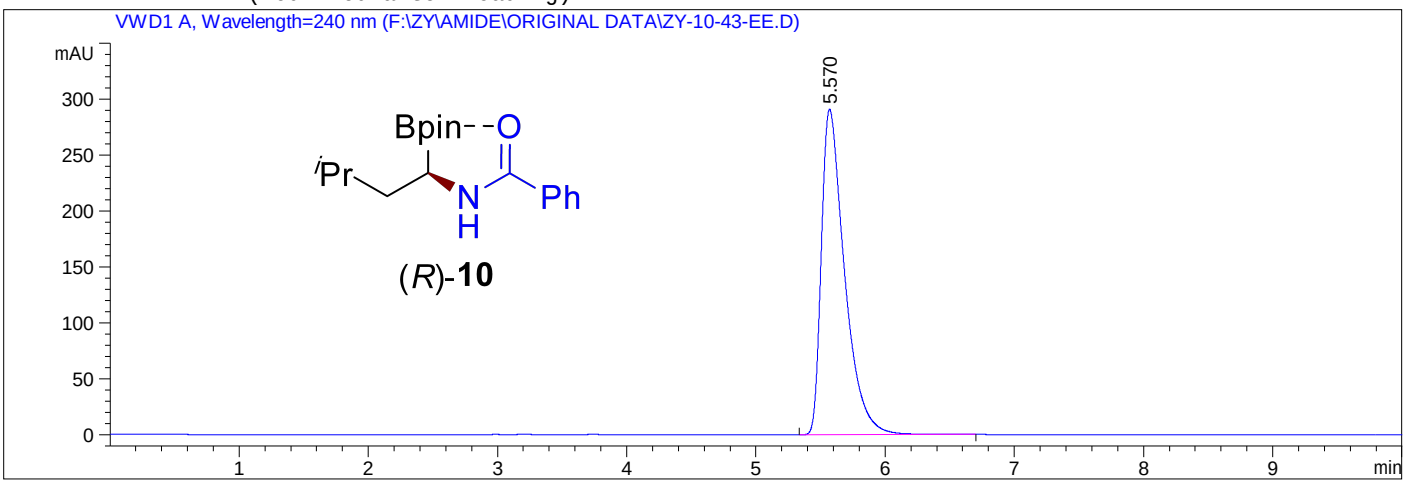
Totals :                   4230.68834  338.68133


==========================================================================
                          *** End of Report ***
```

Supplementary Figure 196: HPLC spectrum of **3d**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-43-EE.D
Sample Name: ZY-10-43-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   3
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 3/1/2022 2:07:38 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220224\YH 2022-03-01 13-37-55\5IPA15_10-1-6-240.M
Last changed    : 3/1/2022 1:37:55 PM by 系统
Analysis Method : C:\CHEM32\1\METHODS\0.2IPA-10-0.5-1-XYH-EQ.M
Last changed    : 3/29/2022 10:09:24 AM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.570 BB    0.1852 3632.72119  290.84302 100.0000

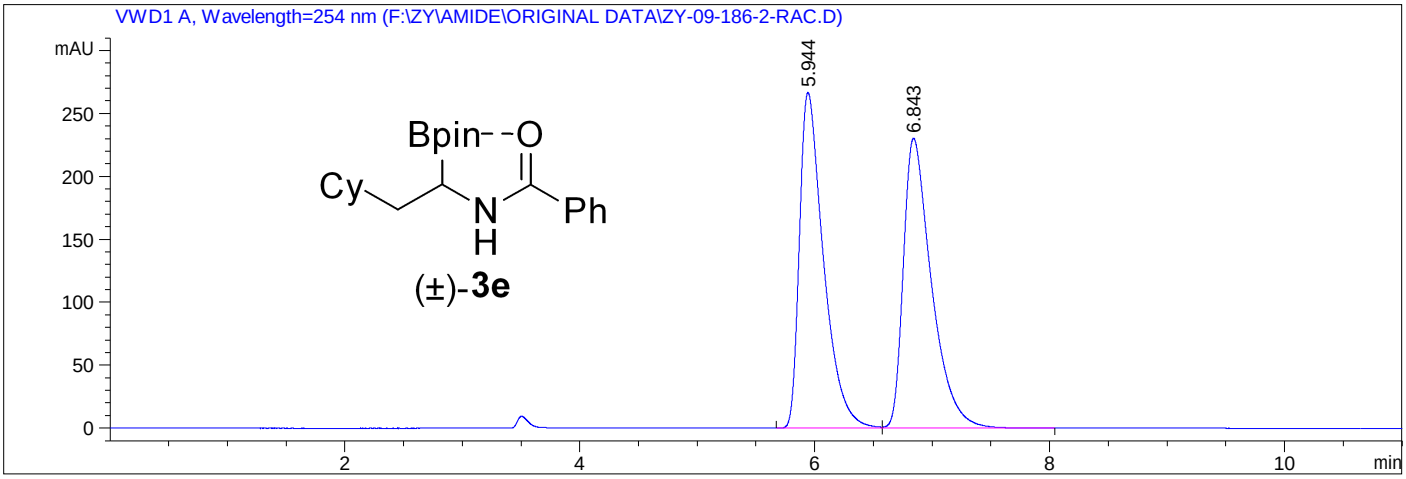
Totals :                  3632.72119  290.84302


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 197: HPLC spectrum of (*R*)-**10**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-186-2-RAC.D
Sample Name: ZY-09-186-2-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  10
Acq. Instrument : HPLC-1260                      Location :  11
Injection Date  : 12/15/2021 11:47:34 AM             Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\zy\20211129\YH 2021-12-15 09-26-25\5IPA-15-1.0-1-6-254-ZH.M
Last changed    : 12/15/2021 11:14:11 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:25:16 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.944 BV    0.2142 3801.18140  266.80502  49.7416
   2   6.843 VB    0.2460 3840.67212  230.42453  50.2584

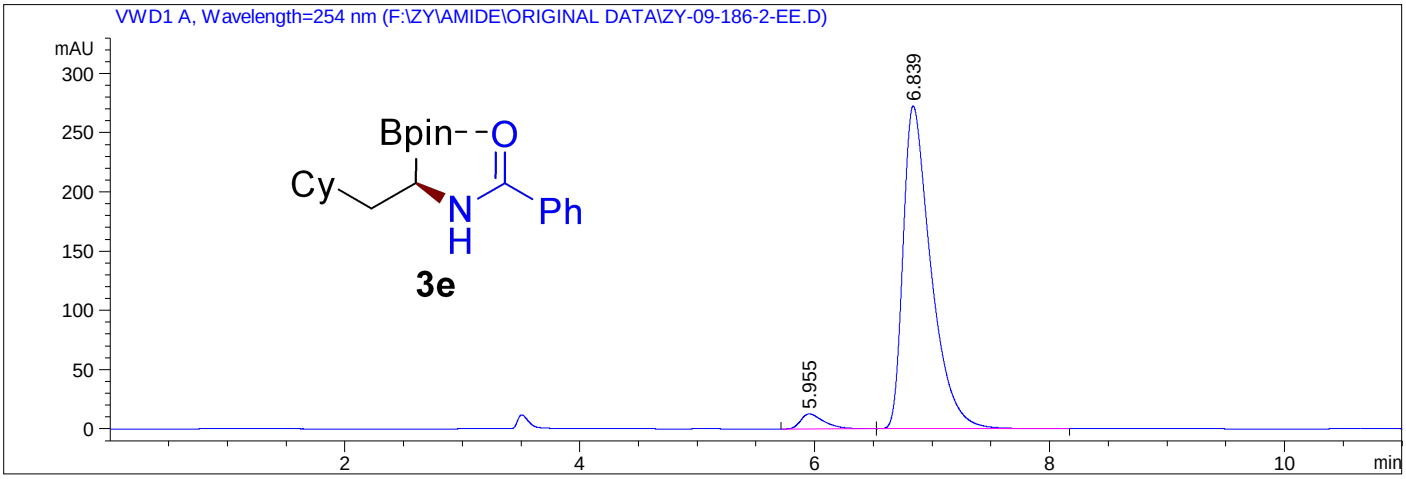
Totals :                  7641.85352  497.22955


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 198: HPLC spectrum of (±)-**3e**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-186-2-EE.D
Sample Name: ZY-09-186-2-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   9
Acq. Instrument : HPLC-1260                     Location :   13
Injection Date  : 12/15/2021 11:31:08 AM            Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.200 µl
Acq. Method     : D:\zy\20211129\YH 2021-12-15 09-26-25\5IPA-15-1.0-1-6-254-ZH.M
Last changed    : 12/15/2021 11:14:11 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:24:40 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.955 BB    0.2016  174.05440   12.64594   3.7263
   2   6.839 BB    0.2464 4496.94629  272.66776  96.2737

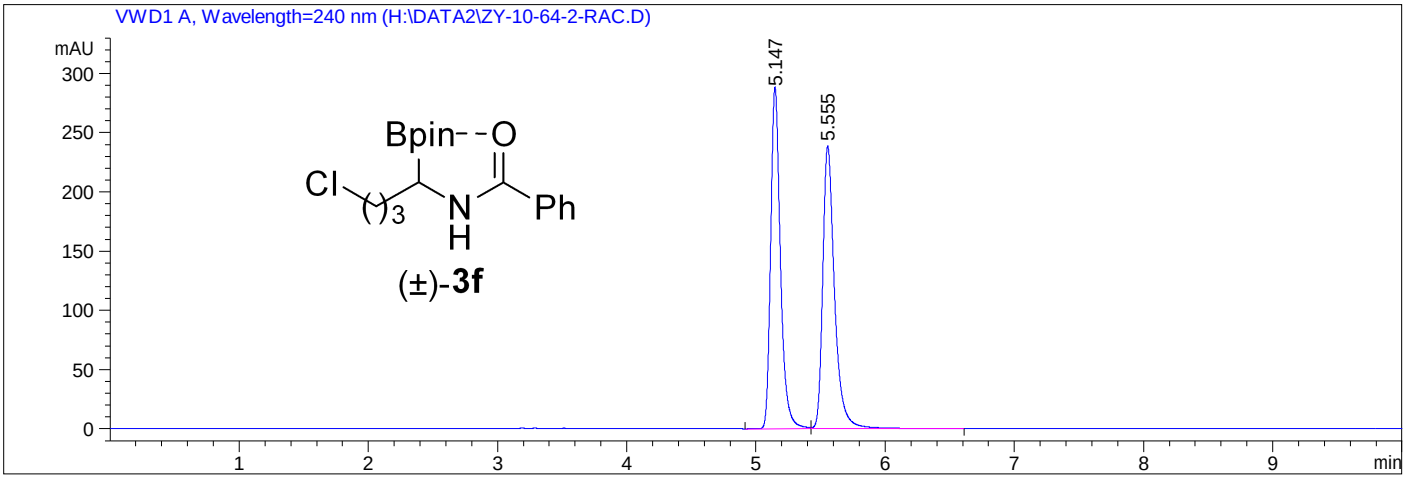
Totals :                   4671.00069  285.31369


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 199: HPLC spectrum of **3e**.

Data File H:\DATA2\ZY-10-64-2-RAC.D
Sample Name: ZY-10-64-3-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   7
Acq. Instrument : HPLC-1260                      Location :   41
Injection Date  : 5/24/2022 7:49:56 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\zy\20220524\YH 2022-05-24 18-17-05\5EtOH15_10-1-2-240.M
Last changed    : 5/24/2022 7:13:28 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-06-04 08-49-06\0.3IPA-0.3-60-220-1-CCP.M (Sequence
                  Method)
Last changed    : 6/7/2022 10:11:57 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.147 VV R  0.0792 1514.91614  288.64532  49.8930
   2   5.555 VB    0.0954 1521.41443  238.66467  50.1070

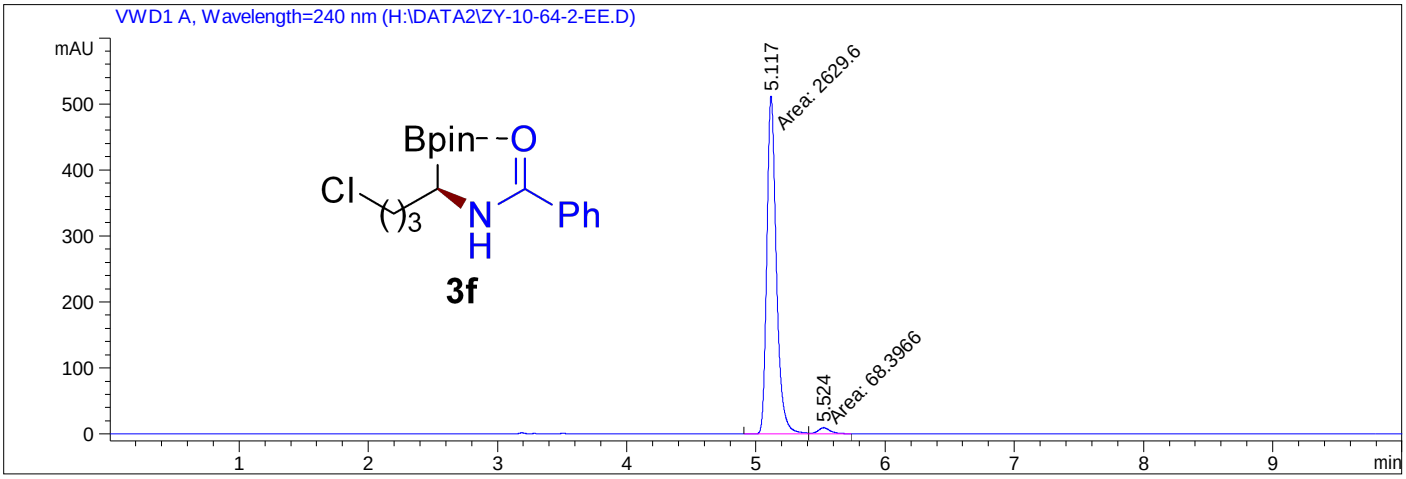
Totals :                  3036.33057  527.31000


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 200: HPLC spectrum of (±)-**3f**.

Data File H:\DATA2\ZY-10-64-2-EE.D
Sample Name: ZY-10-64-2-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   5
Acq. Instrument : HPLC-1260                      Location :   42
Injection Date  : 5/24/2022 7:15:09 PM               Inj :   2
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\zy\20220524\YH 2022-05-24 18-17-05\5EtOH15_10-1-2-240.M
Last changed    : 5/24/2022 7:13:28 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-06-04 08-49-06\0.3IPA-0.3-60-220-1-CCP.M (Sequence
                  Method)
Last changed    : 6/7/2022 10:10:23 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.117 MF    0.0856 2629.60010  512.06506  97.4649
   2   5.524 MF    0.1180   68.39656    9.66246   2.5351

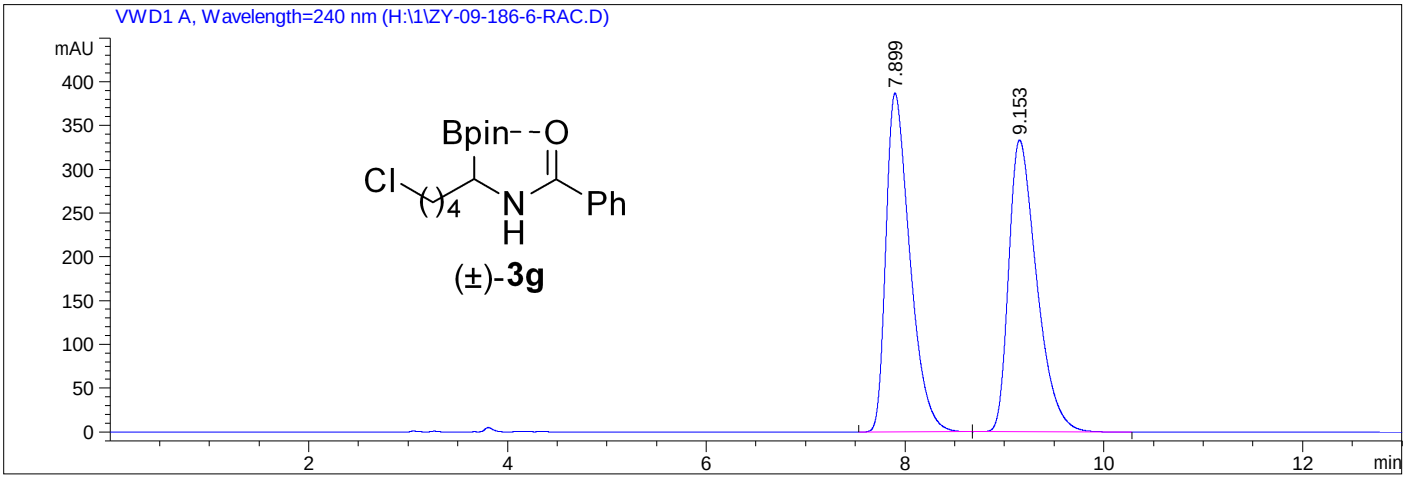
Totals :                  2697.99666  521.72753


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 201: HPLC spectrum of **3f.**

Data File H:\1\ZY-09-186-6-RAC.D
Sample Name: ZY-09-186-6-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  32
Acq. Instrument : HPLC-1260                      Location :  78
Injection Date  : 8/20/2022 5:00:51 PM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.600 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-20 08-41-06\5IPA20_10-1-2-240.M
Last changed    : 8/20/2022 1:41:14 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence
                  Method)
Last changed    : 8/22/2022 7:02:33 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.899 BB    0.2586 6487.87744  387.00372  49.8193
   2   9.153 BB    0.2952 6534.93945  333.38983  50.1807

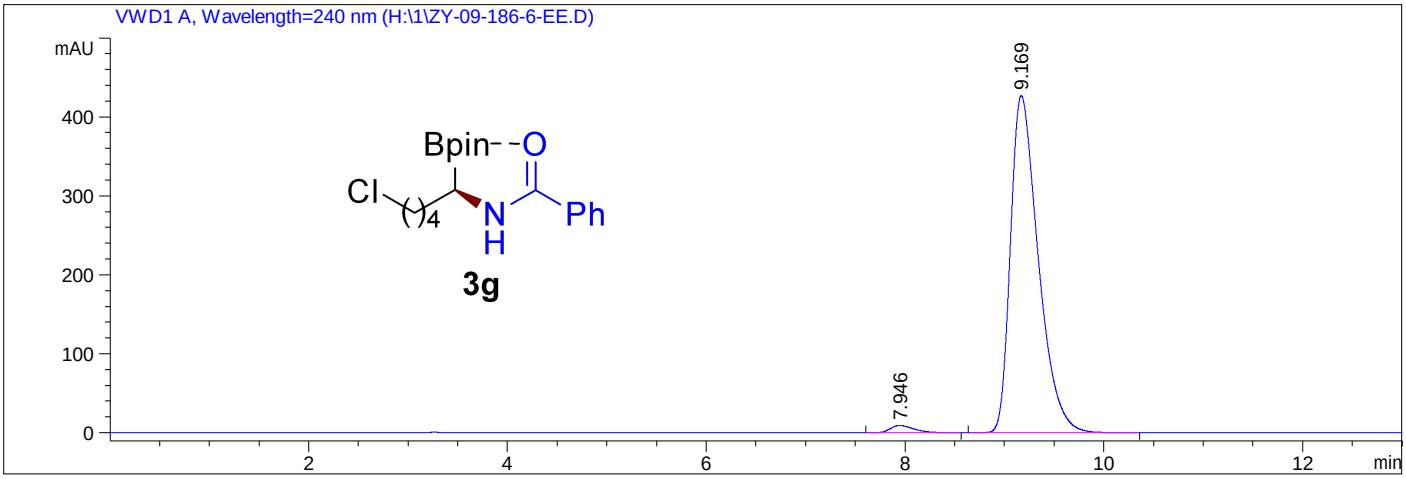
Totals :                  1.30228e4   720.39355


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 202: HPLC spectrum of (±)-**3g**.

Data File H:\1\ZY-09-186-6-EE.D
Sample Name: ZY-09-186-6-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  30
Acq. Instrument : HPLC-1260                      Location :   80
Injection Date  : 8/20/2022 4:28:28 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.500 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-20 08-41-06\5IPA20_10-1-2-240.M
Last changed    : 8/20/2022 1:41:14 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence
                  Method)
Last changed    : 8/22/2022 7:01:09 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.946 BB    0.2433  155.65434    9.34727   1.8400
   2   9.169 BB    0.2853 8304.04688  427.10986  98.1600

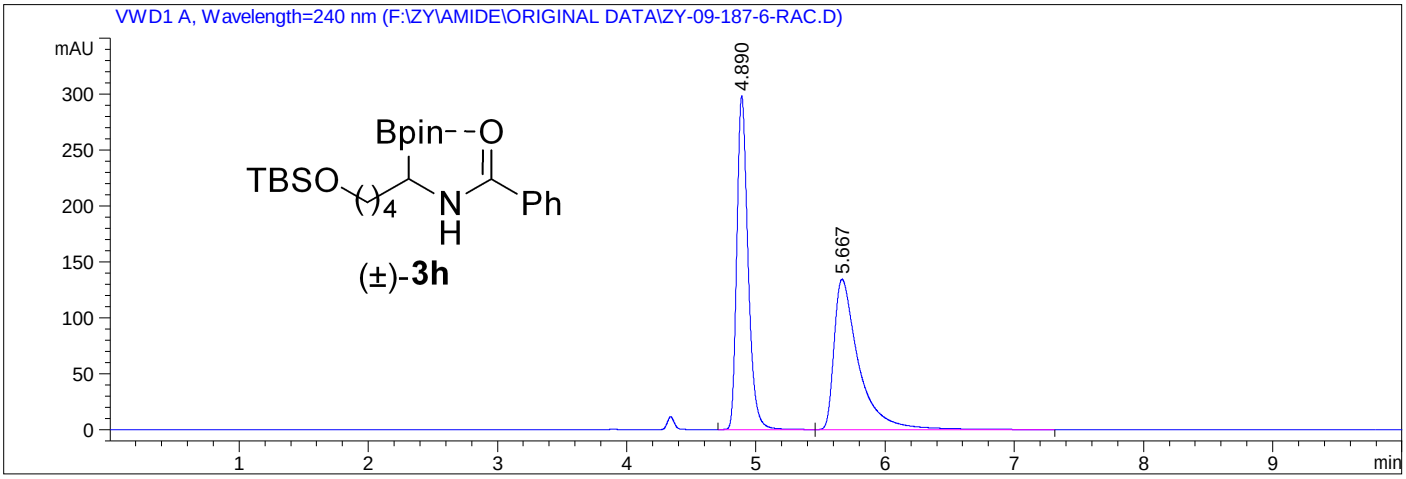
Totals :                   8459.70122  436.45713


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 203: HPLC spectrum of **3g**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-187-6-RAC.D
Sample Name: ZY-09-187-6-RAC

```
=====================================================================
Acq. Operator    : 系统                          Seq. Line :  19
Acq. Instrument : HPLC-1260                       Location :   62
Injection Date  : 12/24/2021 3:31:27 PM               Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\zy\20211219\YH 2021-12-24 08-46-39\5EtOH15_8-1-2-240-.M
Last changed    : 12/24/2021 12:39:49 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:29:19 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.890 BB    0.0919 1800.99927  298.45135  50.3802
   2   5.667 BB    0.1930 1773.81934  134.34425  49.6198

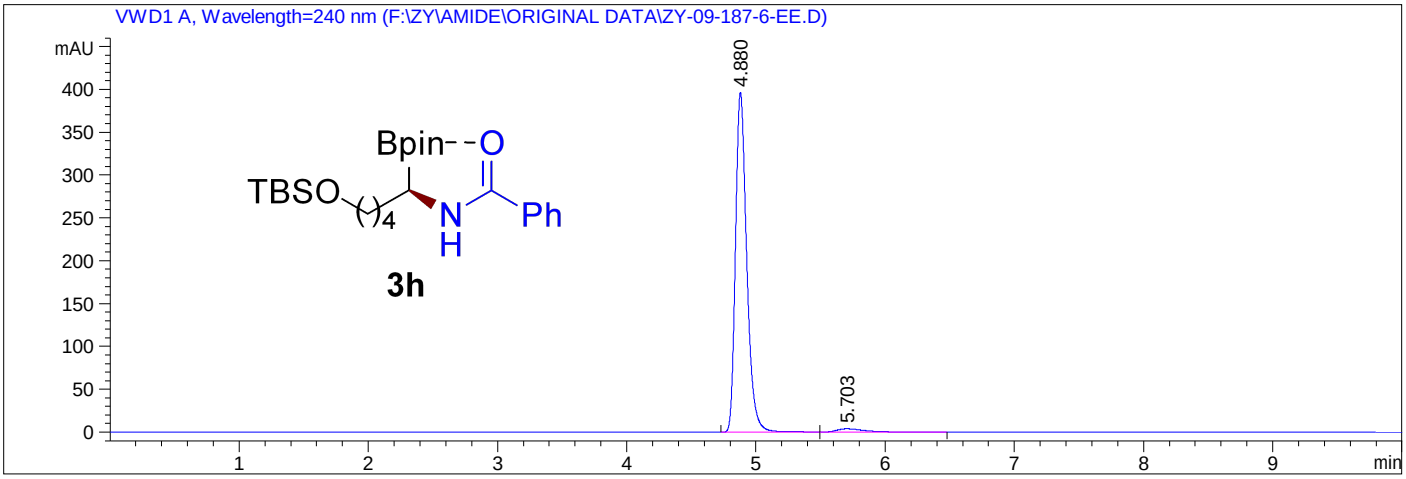
Totals :                  3574.81860  432.79561


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 204: HPLC spectrum of (±)-**3h**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-187-6-EE.D
Sample Name: ZY-09-187-6-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  18
Acq. Instrument : HPLC-1260                      Location :   61
Injection Date  : 12/24/2021 3:15:06 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
Acq. Method     : D:\zy\20211219\YH 2021-12-24 08-46-39\5EtOH15_8-1-2-240-.M
Last changed    : 12/24/2021 12:39:49 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:28:52 AM by SYSTEM
                  (modified after loading)
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.880 BV R  0.0919 2393.51636  396.38632  97.5608
   2   5.703 BB    0.2241   59.84169    3.93127   2.4392

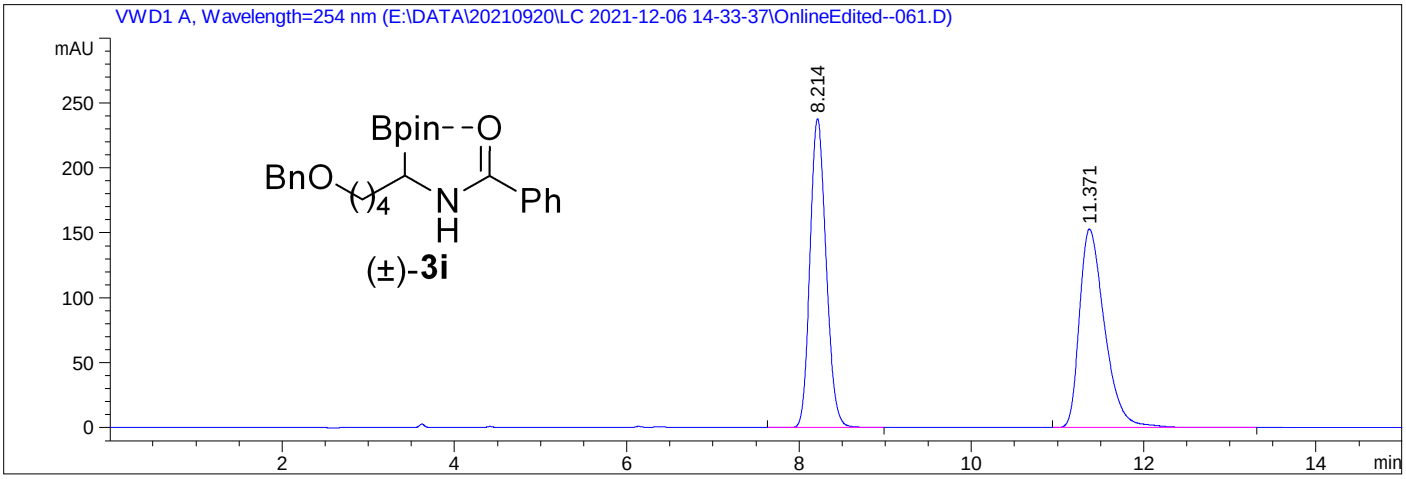
Totals :                  2453.35805  400.31759


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 205: HPLC spectrum of **3h**.

Data File E:\DATA\20210920\LC 2021-12-06 14-33-37\OnlineEdited--061.D
Sample Name: ZY-09-168-5-RAC

```
=====================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  61
Acq. Instrument : HPLC1260                         Location :   P1-E2
Injection Date  : 12/7/2021 6:44:55 PM                  Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : E:\DATA\20210920\LC 2021-12-06 14-33-37\5EtOH_15_10_4.M
Last changed    : 12/7/2021 5:06:46 PM by SYSTEM
Analysis Method : E:\DATA\20210920\LC 2021-12-06 14-33-37\5EtOH_15_10_4.M (Sequence Method)
Last changed    : 12/7/2021 9:56:54 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.214 BB    0.2025 3088.16382  237.84897  49.9227
   2  11.371 BB    0.3116 3097.72485  152.74744  50.0773

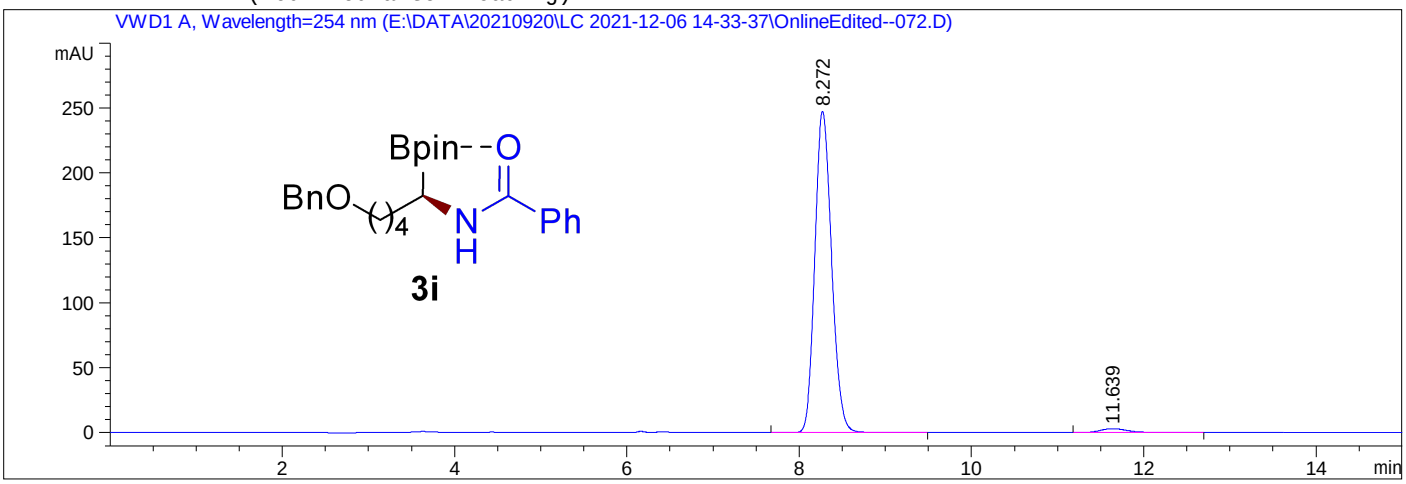
Totals :                  6185.88867  390.59641


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 206: HPLC spectrum of (±)-**3i**.

Data File E:\DATA\20210920\LC 2021-12-06 14-33-37\OnlineEdited--072.D
Sample Name: ZY-09-168-5-EE

```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  72
Acq. Instrument : HPLC1260                       Location :   P1-E1
Injection Date  : 12/7/2021 9:40:07 PM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : E:\DATA\20210920\LC 2021-12-06 14-33-37\5EtOH_15_10_4.M
Last changed    : 12/7/2021 9:19:59 PM by SYSTEM
Analysis Method : E:\DATA\20210920\LC 2021-12-06 14-33-37\5EtOH_15_10_4.M (Sequence Method)
Last changed    : 12/7/2021 9:56:16 PM by SYSTEM
                  (modified after loading)
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.272 BB    0.2106 3343.16821  247.41263  97.8705
   2  11.639 BB    0.3530   72.74094    3.13104   2.1295

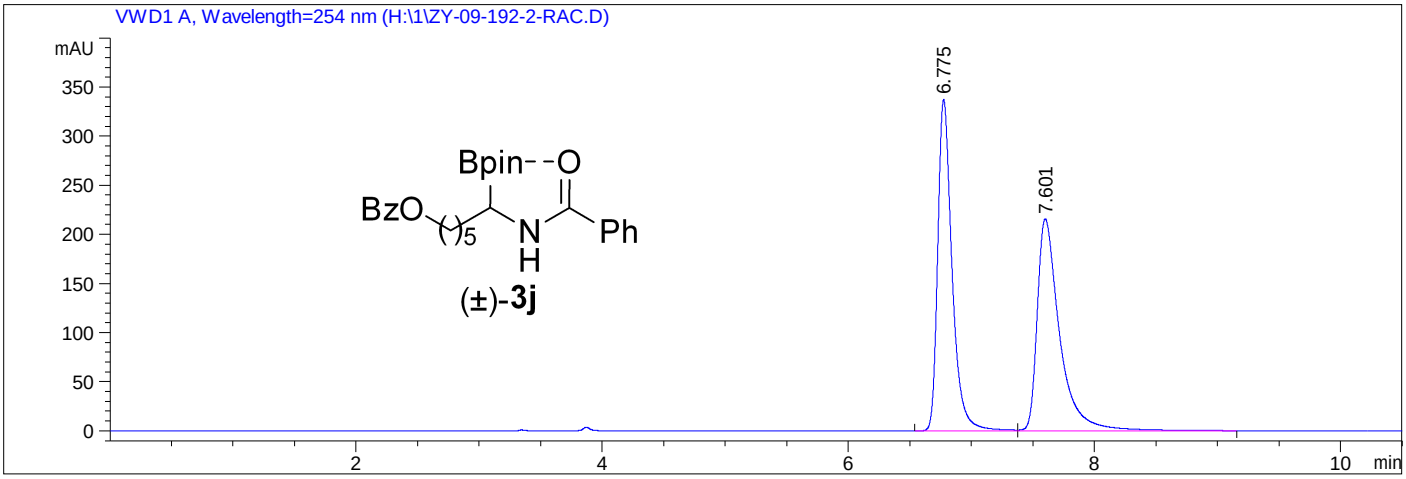
Totals :                  3415.90915  250.54367


==================================================================
                        *** End of Report ***
```

Supplementary Figure 207: HPLC spectrum of **3i**.

Data File H:\1\ZY-09-192-2-RAC.D
Sample Name: ZY-09-192-2-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  39
Acq. Instrument : HPLC-1260                      Location :   72
Injection Date  : 8/20/2022 6:59:26 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-20 08-41-06\10EtOH20_10-1-6-254.M
Last changed    : 8/20/2022 1:58:22 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence
                  Method)
Last changed    : 8/22/2022 7:14:35 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.775 BV    0.1214 2731.93823  337.47751  49.9922
   2   7.601 VB    0.1882 2732.78638  215.87651  50.0078

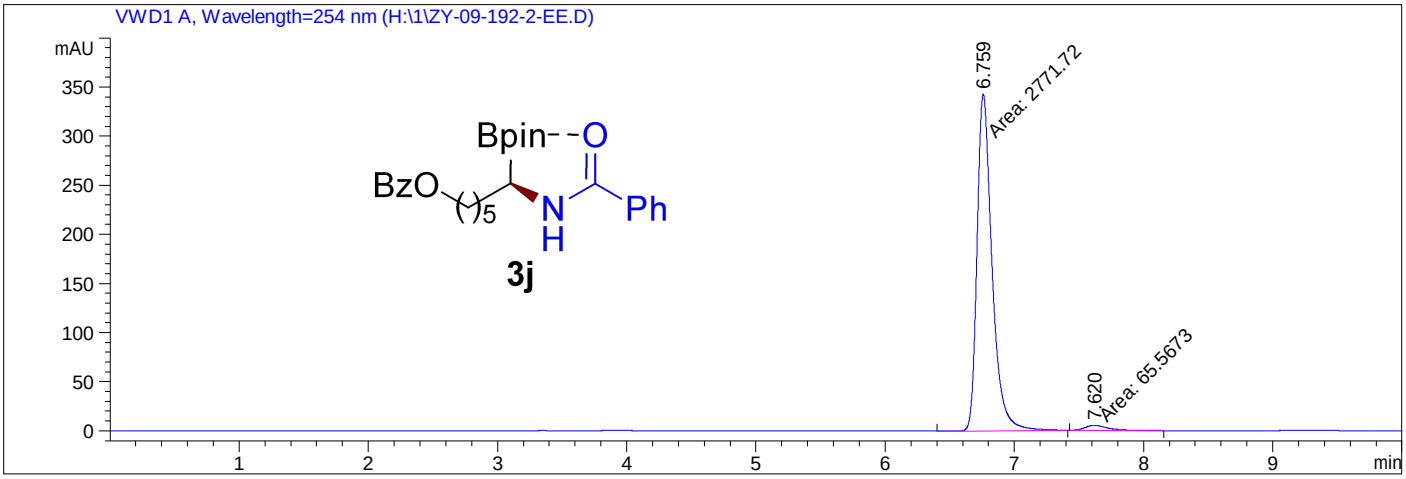
Totals :                  5464.72461  553.35402


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 208: HPLC spectrum of (±)-**3j**.

Data File H:\1\ZY-09-192-2-EE.D
Sample Name: ZY-09-192-2-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  38
Acq. Instrument : HPLC-1260                      Location :  71
Injection Date  : 8/20/2022 6:37:59 PM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-20 08-41-06\10EtOH20_10-1-6-254.M
Last changed    : 8/20/2022 1:58:22 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence
                  Method)
Last changed    : 8/22/2022 7:12:33 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.759 MM    0.1347 2771.72437  342.95248  97.6891
   2   7.620 MM    0.2110   65.56731    5.17876   2.3109

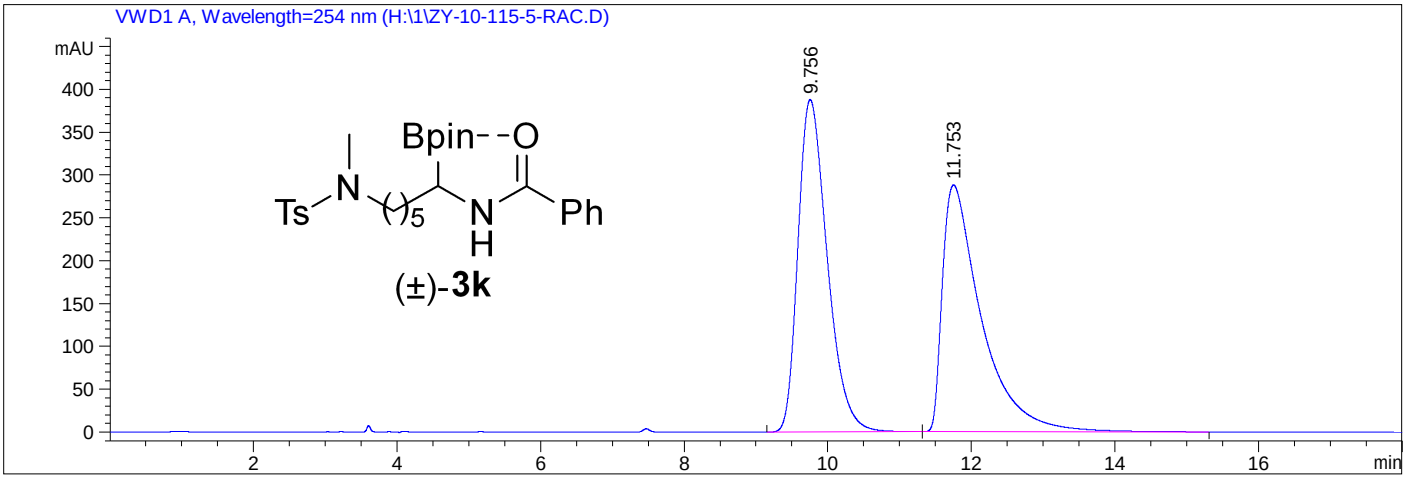
Totals :                  2837.29167  348.13124


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 209: HPLC spectrum of **3j**.

Data File H:\1\ZY-10-115-5-RAC.D
Sample Name: ZY-10-115-6-12

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  27
Acq. Instrument : HPLC-1260                      Location :   54
Injection Date  : 8/19/2022 10:13:31 PM              Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 4.000 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-19 14-14-07\20EtOH20_10-1-2-254.M
Last changed    : 8/19/2022 2:14:07 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence
                  Method)
Last changed    : 8/22/2022 7:33:29 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.756 BB    0.4317 1.09960e4   387.94690  50.3217
   2  11.753 BB    0.5502 1.08554e4   288.05551  49.6783

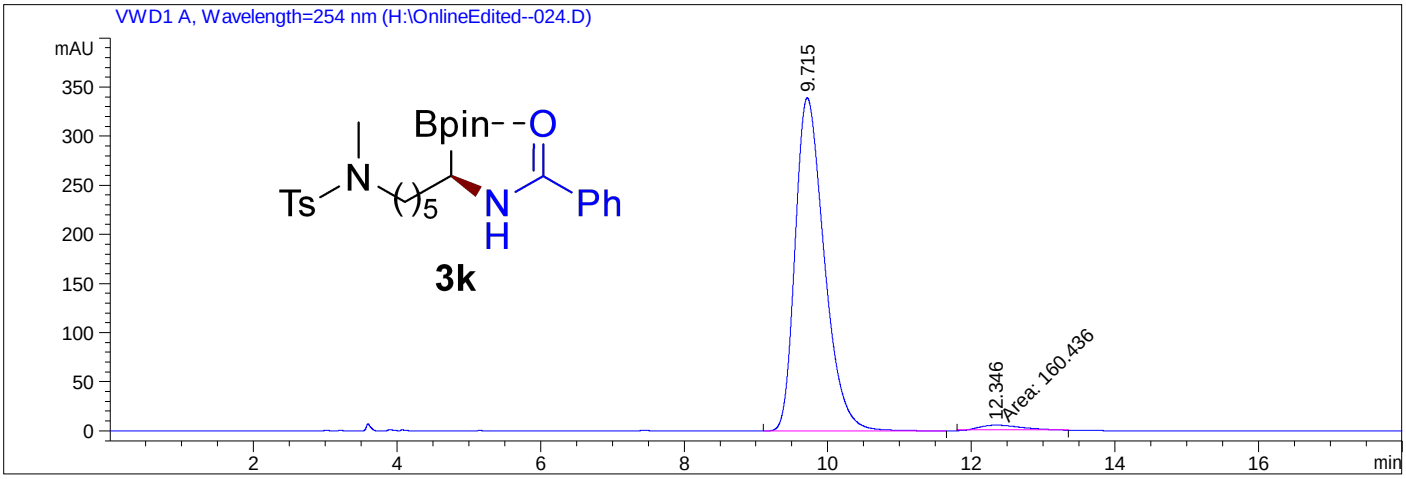
Totals :                  2.18514e4   676.00241


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 210: HPLC spectrum of (±)-**3k**.

Data File H:\OnlineEdited--024.D
Sample Name: ZY-10-115-5-13

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  24
Acq. Instrument : HPLC-1260                     Location :   75
Injection Date  : 8/19/2022 9:19:43 PM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 3.200 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-19 14-14-07\20EtOH20_10-1-2-254.M
Last changed    : 8/19/2022 2:14:07 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-19 14-05-28\10IPA_10_8_3.M (Sequence Method)
Last changed    : 8/19/2022 10:26:56 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.715 BB    0.4357 9538.70508  339.05954  98.3459
   2  12.346 MM    0.5951  160.43559    4.49287   1.6541

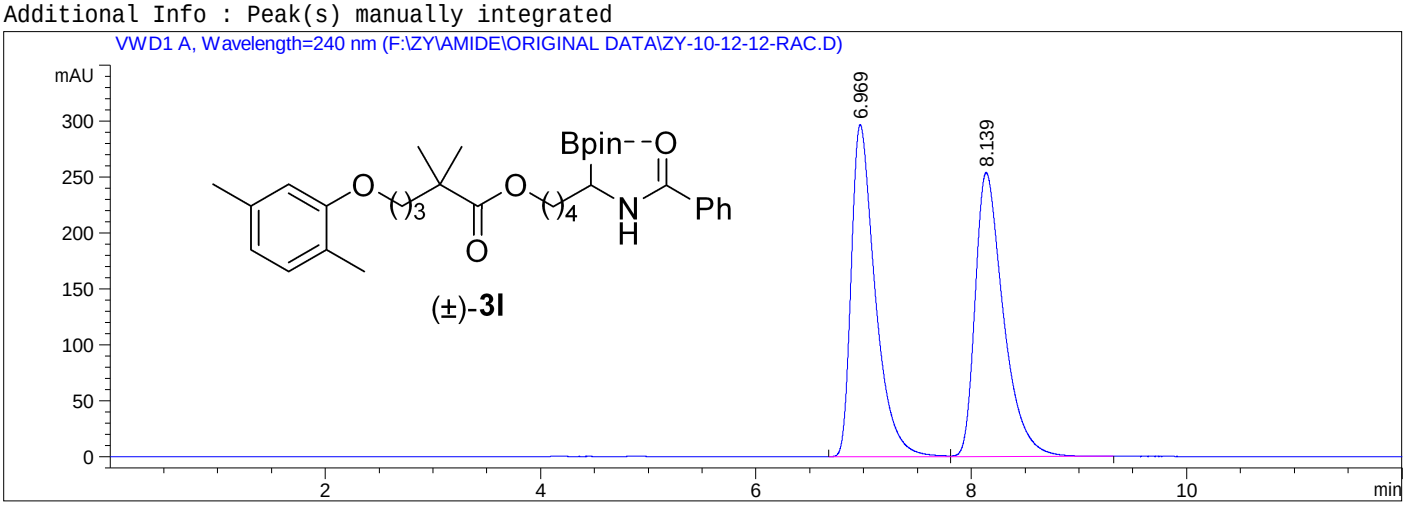
Totals :                  9699.14067  343.55241


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 211: HPLC spectrum of **3k**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-12-12-RAC.D
Sample Name: ZY-10-12-12-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   9
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 3/14/2022 8:10:38 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.200 µl
Acq. Method     : D:\zy\20220302\YH 2022-03-14 18-14-35\8IPA20_8-1-2-240.M
Last changed    : 3/14/2022 7:50:44 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:59:19 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.969 BV    0.2315 4579.07910  296.74182  49.7372
   2   8.139 VB    0.2682 4627.47461  253.77185  50.2628

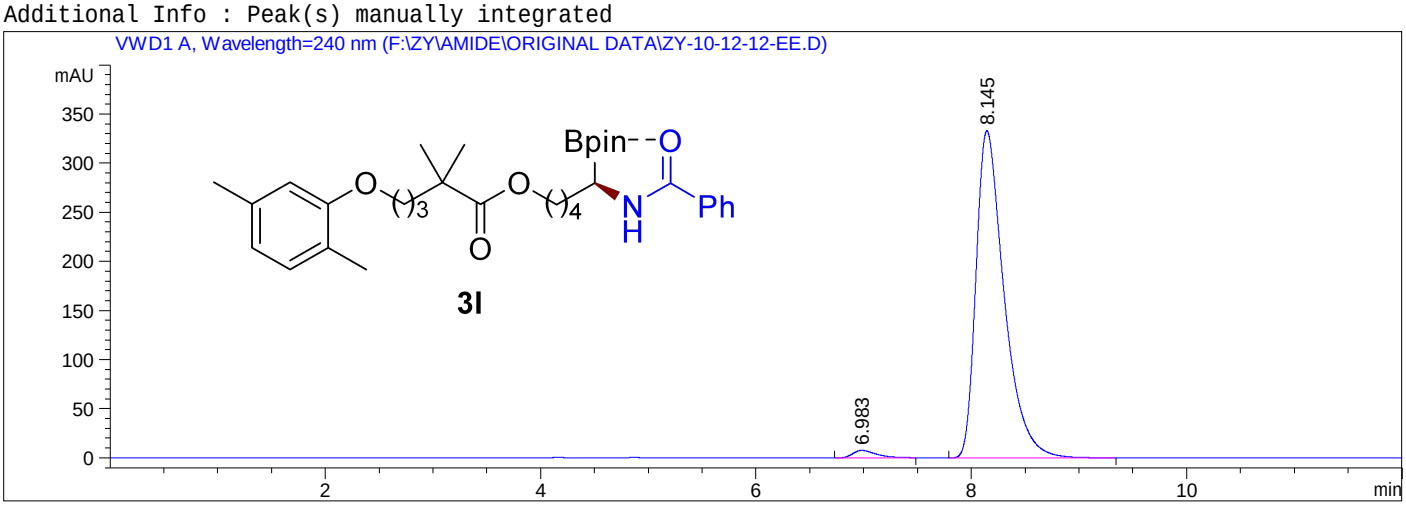
Totals :                  9206.55371  550.51367


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 212: HPLC spectrum of (±)-**3l**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-12-12-EE.D
Sample Name: ZY-10-12-12-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   8
Acq. Instrument : HPLC-1260                      Location :   82
Injection Date  : 3/14/2022 7:52:12 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220302\YH 2022-03-14 18-14-35\8IPA20_8-1-2-240.M
Last changed    : 3/14/2022 7:50:44 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:59:57 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.983 BB    0.2180  115.32585    7.70988   1.8705
   2   8.145 BB    0.2674 6050.16260  333.05563  98.1295

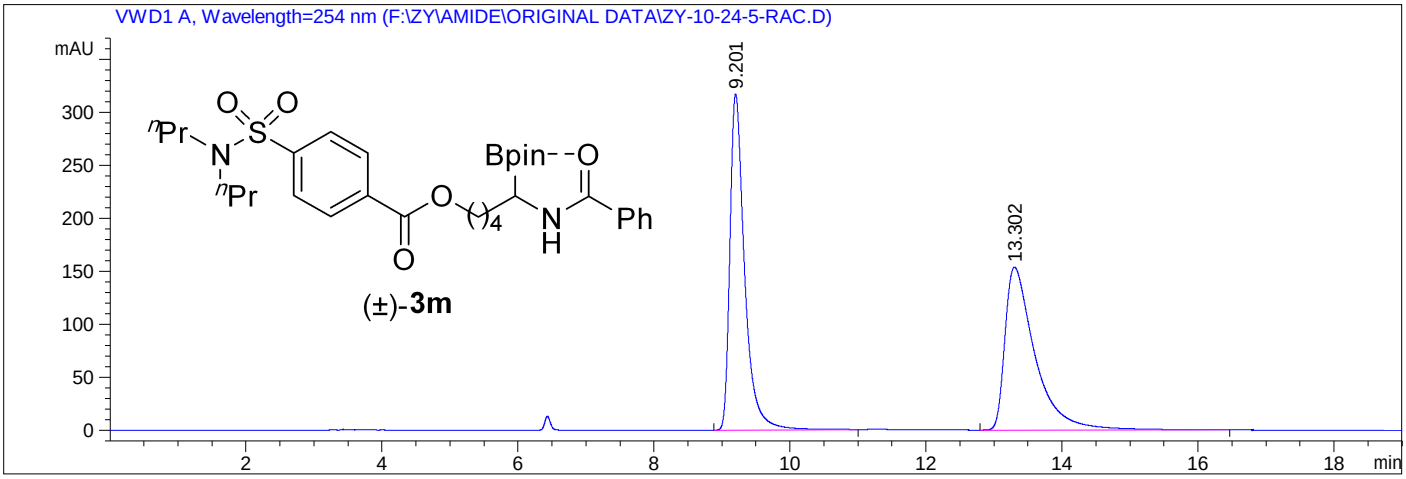
Totals :                   6165.48845  340.76552


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 213: HPLC spectrum of **3l**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-24-5-RAC.D
Sample Name: ZY-10-24-5-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  27
Acq. Instrument : HPLC-1260                      Location :   71
Injection Date  : 2/14/2022 10:13:51 PM              Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220201\YH 2022-02-14 12-55-19\15EtOH30_10-1-2-254.M
Last changed    : 2/14/2022 9:50:04 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 10:02:54 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.201 BB    0.2237 4765.29834  317.25735  50.2247
   2  13.302 BB    0.4520 4722.66553  153.67970  49.7753

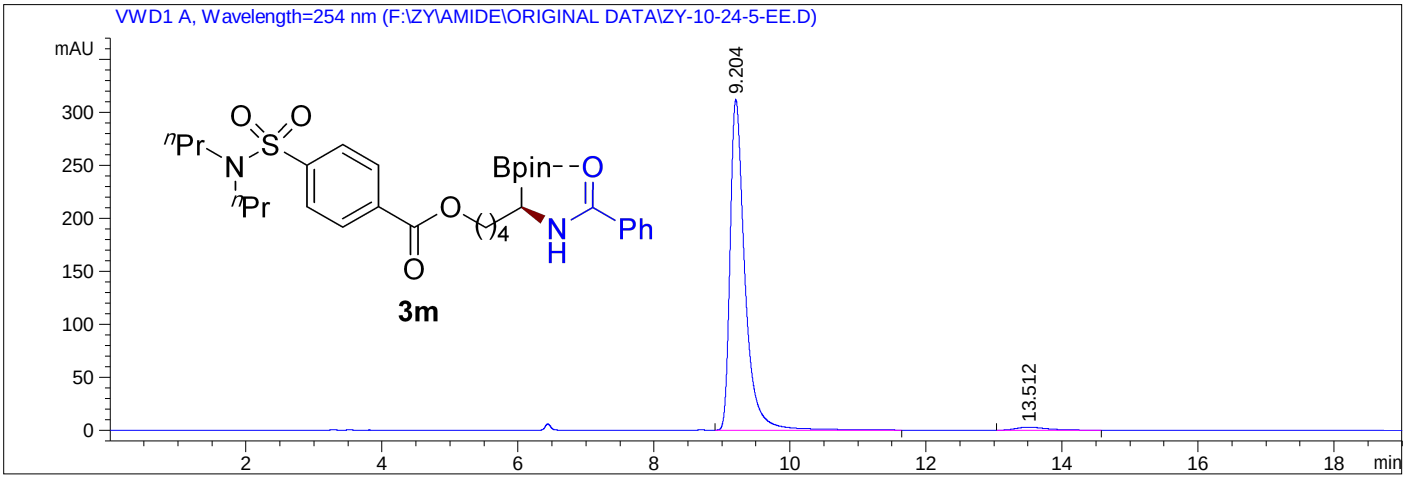
Totals :                  9487.96387  470.93706


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 214: HPLC spectrum of (±)-**3m**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-24-5-EE.D
Sample Name: ZY-10-24-5-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  26
Acq. Instrument : HPLC-1260                      Location :   72
Injection Date  : 2/14/2022 9:51:27 PM              Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220201\YH 2022-02-14 12-55-19\15EtOH30_10-1-2-254.M
Last changed    : 2/14/2022 9:50:04 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 10:02:54 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.204 BB    0.2267 4723.18945  311.85480  98.1437
   2  13.512 BB    0.3615   89.33582    2.91907   1.8563

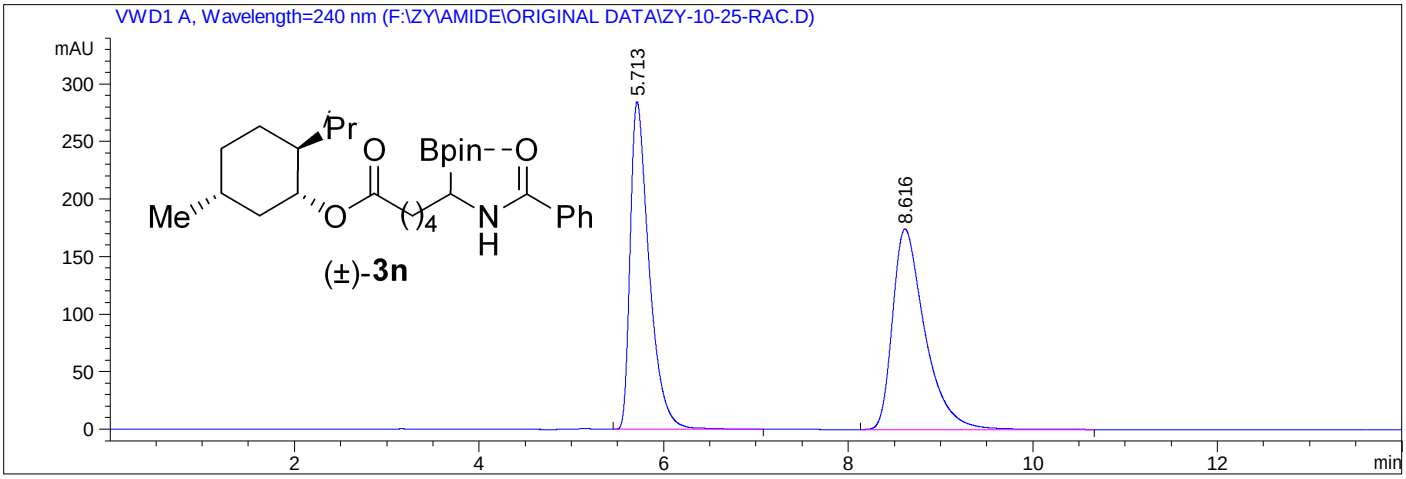
Totals :                  4812.52527  314.77387


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 215: HPLC spectrum of **3m**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-25-RAC.D
Sample Name: ZY-10-25-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  35
Acq. Instrument : HPLC-1260                      Location :  81
Injection Date  : 2/15/2022 12:45:00 AM             Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\zy\20220201\YH 2022-02-14 12-55-19\5IPA15_10-1-6-240.M
Last changed    : 2/14/2022 9:25:27 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 10:04:39 AM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.713 BB    0.2128 4071.67749  284.85623  49.0033
   2   8.616 BB    0.3652 4237.30811  174.26460  50.9967

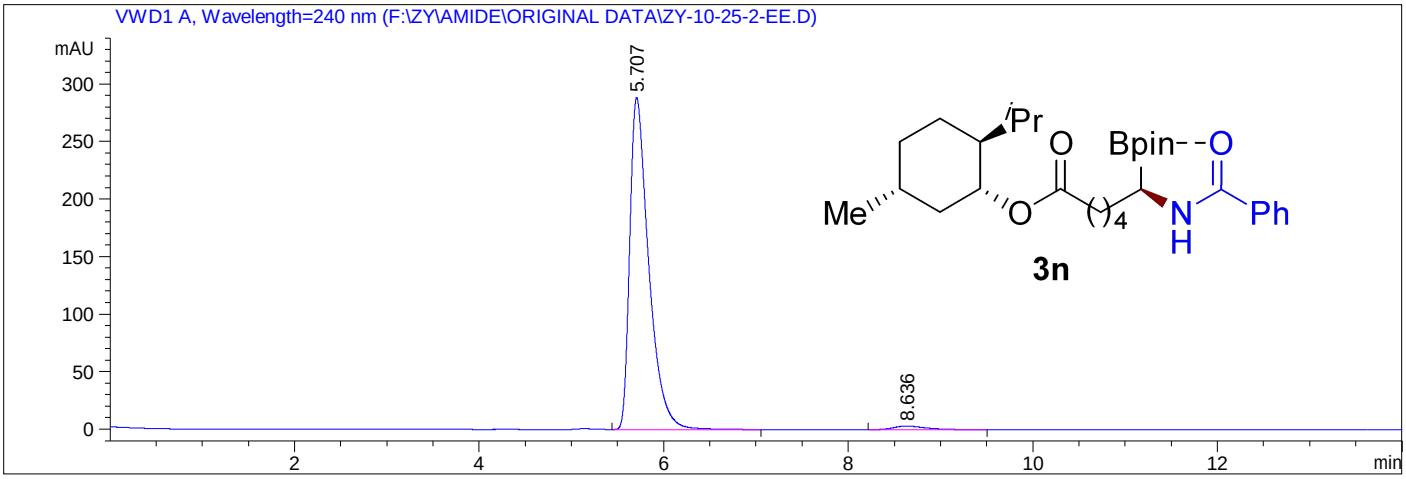
Totals :                  8308.98560  459.12083


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 216: HPLC spectrum of (±)-**3n**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-25-2-EE.D
Sample Name: ZY-10-25-2-EE

```
    ======================================================================
    Acq. Operator    : 系统                          Seq. Line :  32
    Acq. Instrument : HPLC-1260                       Location :   83
    Injection Date  : 2/14/2022 11:55:42 PM              Inj :   1
                                                    Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
    Acq. Method     : D:\zy\20220201\YH 2022-02-14 12-55-19\5IPA15_10-1-6-240.M
    Last changed    : 2/14/2022 9:25:27 PM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/29/2022 10:04:39 AM by SYSTEM
                      (modified after loading)
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=240 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.707 BB    0.2122 4119.90674  288.39926  98.2076
       2   8.636 BB    0.2825   75.19337    3.14431   1.7924

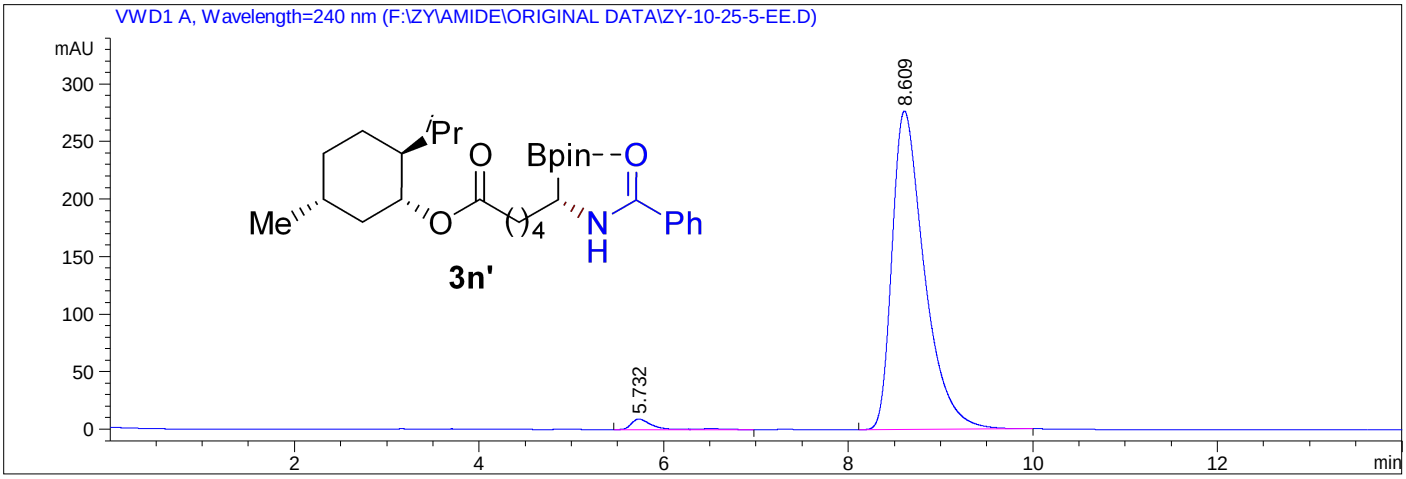
    Totals :                  4195.10011  291.54357


    ======================================================================
                              *** End of Report ***
```

Supplementary Figure 217: HPLC spectrum of **3n**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-25-5-EE.D
Sample Name: ZY-10-25-5-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  33
Acq. Instrument : HPLC-1260                      Location :  82
Injection Date  : 2/15/2022 12:12:05 AM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.400 µl
Acq. Method     : D:\zy\20220201\YH 2022-02-14 12-55-19\5IPA15_10-1-6-240.M
Last changed    : 2/14/2022 9:25:27 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 10:04:39 AM by SYSTEM
                  (modified after loading)
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.732 BV R  0.2280  143.65533    9.10710   2.0901
   2   8.609 BB    0.3617 6729.62012  276.75131  97.9099

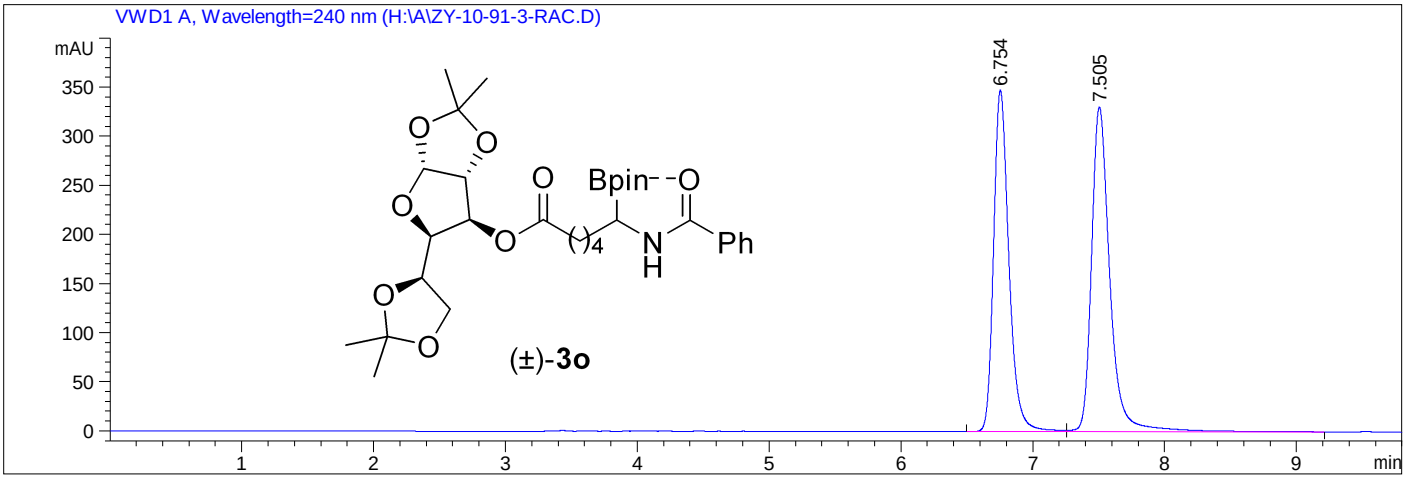
Totals :                   6873.27545  285.85841


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 218: HPLC spectrum of **3n'**.

Data File H:\A\ZY-10-91-3-RAC.D
Sample Name: ZY-10-91-3-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   5
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 6/26/2022 3:12:35 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220624\YH 2022-06-26 14-05-25\12EtOH20_10-1-2-240.M
Last changed    : 6/26/2022 2:05:25 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M (Sequence
                  Method)
Last changed    : 8/9/2022 9:05:21 AM by SYSTEM
                  (modified after loading)
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.754 BV    0.1230 2800.11133  347.39279  46.7353
   2   7.505 VB    0.1456 3191.31055  330.62488  53.2647

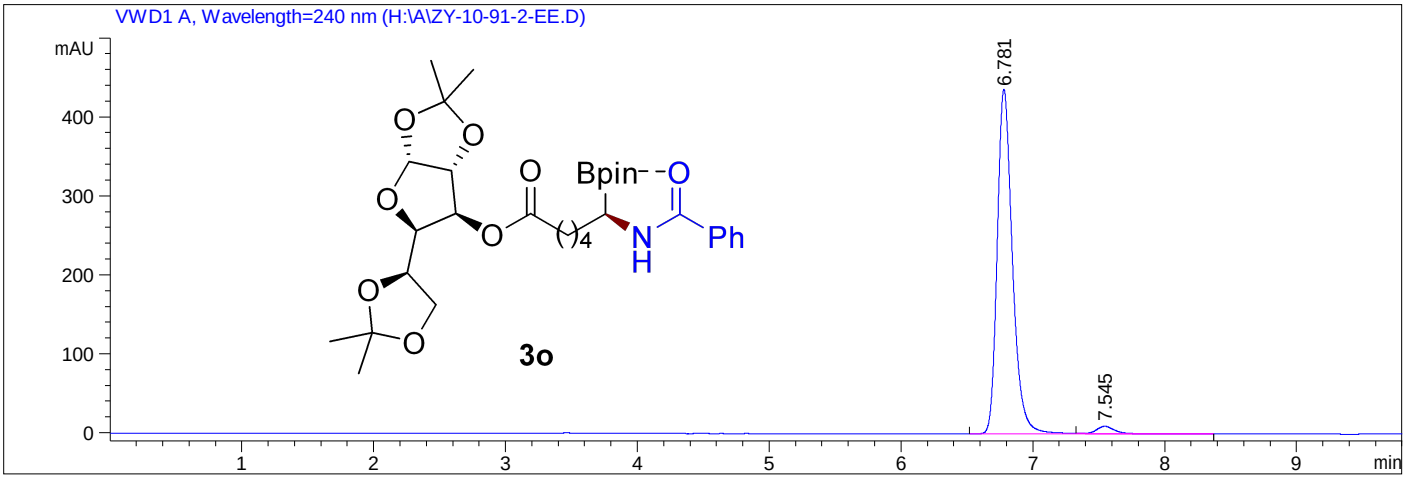
Totals :                  5991.42188  678.01767


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 219: HPLC spectrum of (±)-**3o**.

Data File H:\A\ZY-10-91-2-EE.D
Sample Name: ZY-10-91-2-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   3
Acq. Instrument : HPLC-1260                      Location :   82
Injection Date  : 6/26/2022 2:29:40 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220624\YH 2022-06-26 14-05-25\12EtOH20_10-1-2-240.M
Last changed    : 6/26/2022 2:05:25 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M (Sequence
                  Method)
Last changed    : 8/9/2022 9:03:39 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.781 BV R  0.1229 3513.69751  436.44815  97.4507
   2   7.545 VB E  0.1465   91.91974    9.48676   2.5493

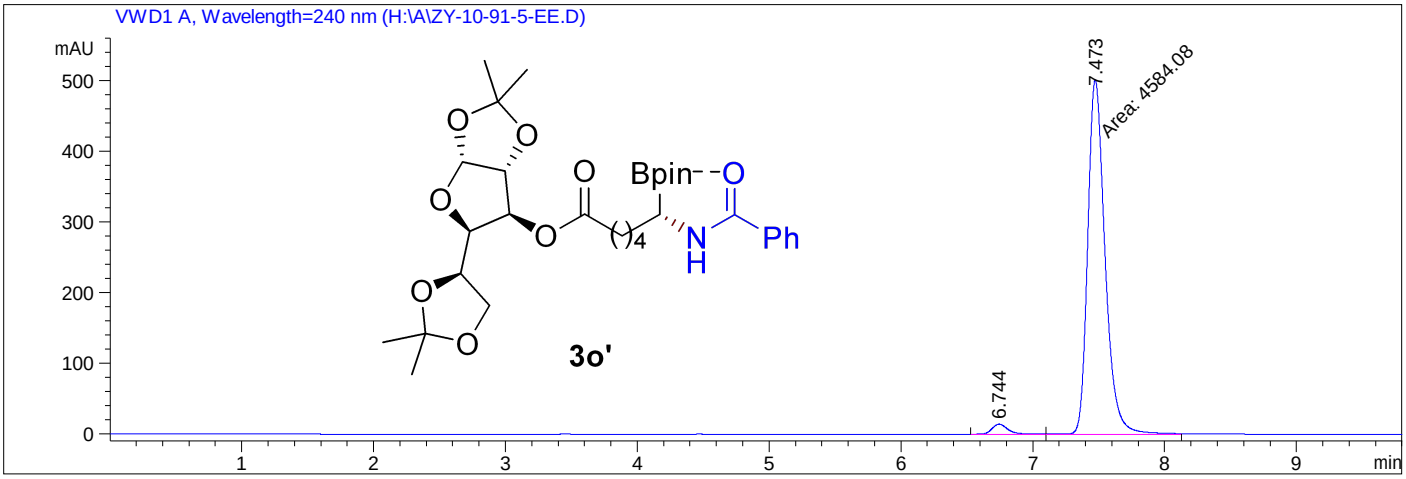
Totals :                  3605.61725  445.93491


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 220: HPLC spectrum of **3o**.

Data File H:\A\ZY-10-91-5-EE.D
Sample Name: ZY-10-91-5-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                      Location :   83
Injection Date  : 6/26/2022 2:51:11 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220624\YH 2022-06-26 14-05-25\12EtOH20_10-1-2-240.M
Last changed    : 6/26/2022 2:05:25 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M (Sequence
                  Method)
Last changed    : 8/9/2022 9:04:32 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.744 BV    0.1267  118.68422   14.24024   2.5237
   2   7.473 MF    0.1523 4584.07568  501.71143  97.4763

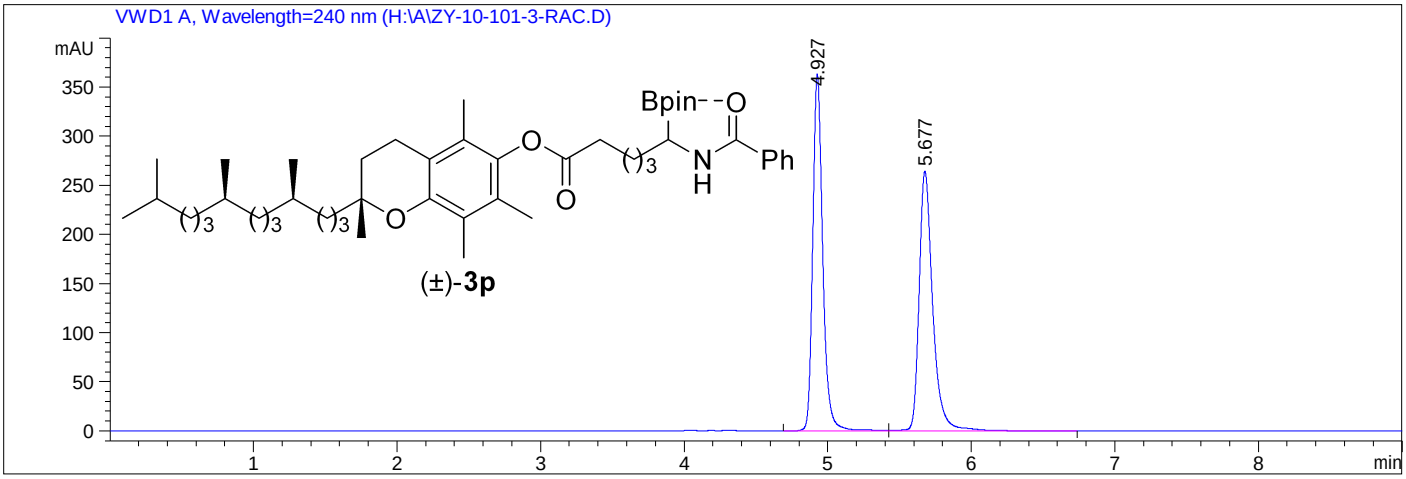
Totals :                   4702.75990  515.95166


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 221: HPLC spectrum of **3o'**.

Data File H:\A\ZY-10-101-3-RAC.D
Sample Name: ZY-10-101-3-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  33
Acq. Instrument : HPLC-1260                      Location :  61
Injection Date  : 7/5/2022 1:25:35 AM                 Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220624\YH 2022-07-04 14-04-41\10EtOH15_10-1-6-240.M
Last changed    : 7/4/2022 7:42:02 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M (Sequence
                  Method)
Last changed    : 8/9/2022 9:10:28 AM by SYSTEM
                  (modified after loading)
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.927 BV R  0.0736 1760.48340  363.18640  50.2205
   2   5.677 VB    0.0991 1745.02710  264.16177  49.7795

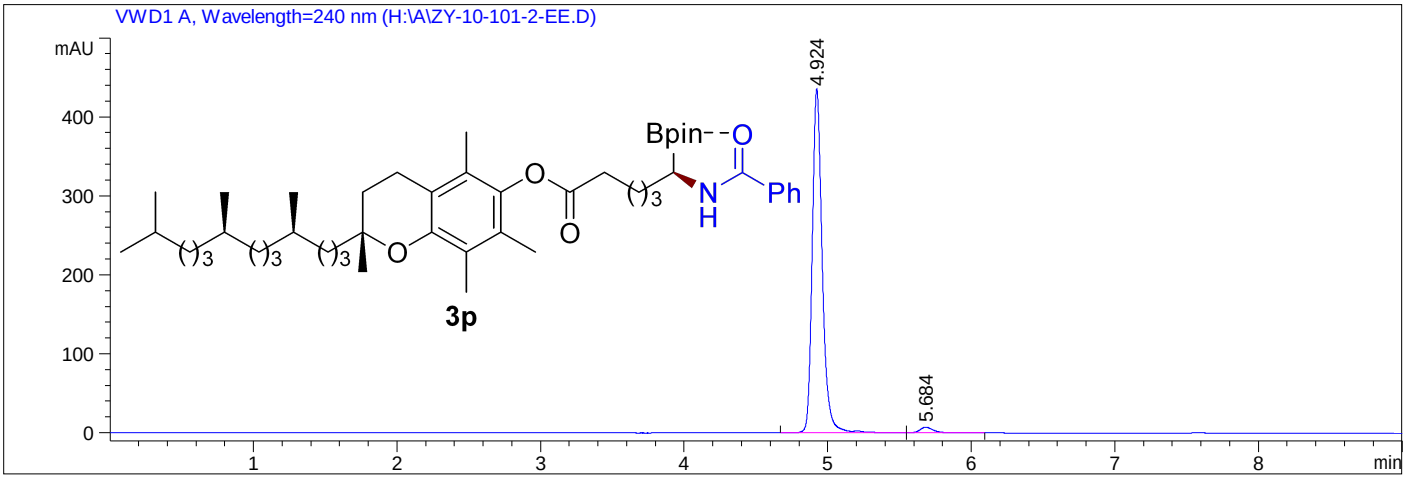
Totals :                  3505.51050  627.34818


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 222: HPLC spectrum of (±)-**3p**.

Data File H:\A\ZY-10-101-2-EE.D
Sample Name: ZY-10-101-2-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  31
Acq. Instrument : HPLC-1260                      Location :  62
Injection Date  : 7/5/2022 12:52:46 AM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\zy\20220624\YH 2022-07-04 14-04-41\10EtOH15_10-1-6-240.M
Last changed    : 7/4/2022 7:42:02 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M (Sequence
                  Method)
Last changed    : 8/9/2022 9:09:56 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.924 BV R  0.0737 2114.95093  435.55344  97.8851
   2   5.684 BB    0.0982   45.69511    7.04339   2.1149

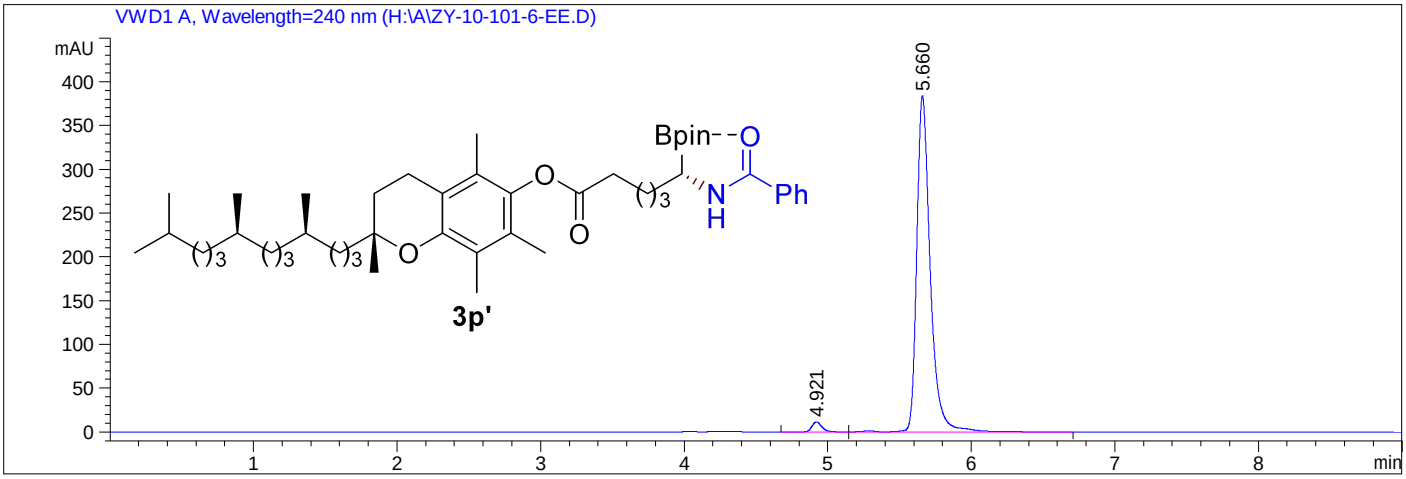
Totals :                  2160.64604  442.59682


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 223: HPLC spectrum of **3p**.

Data File H:\A\ZY-10-101-6-EE.D
Sample Name: ZY-10-101-6-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  32
Acq. Instrument : HPLC-1260                      Location :   63
Injection Date  : 7/5/2022 1:09:09 AM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\zy\20220624\YH 2022-07-04 14-04-41\10EtOH15_10-1-6-240.M
Last changed    : 7/4/2022 7:42:02 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-08 20-30-16\2IPA-50-0.8-3-210-JXL.M (Sequence
                  Method)
Last changed    : 8/9/2022 9:09:12 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.921 BB    0.0754   58.30293   11.65547   2.2584
   2   5.660 VB R  0.0991 2523.31274  384.16348  97.7416

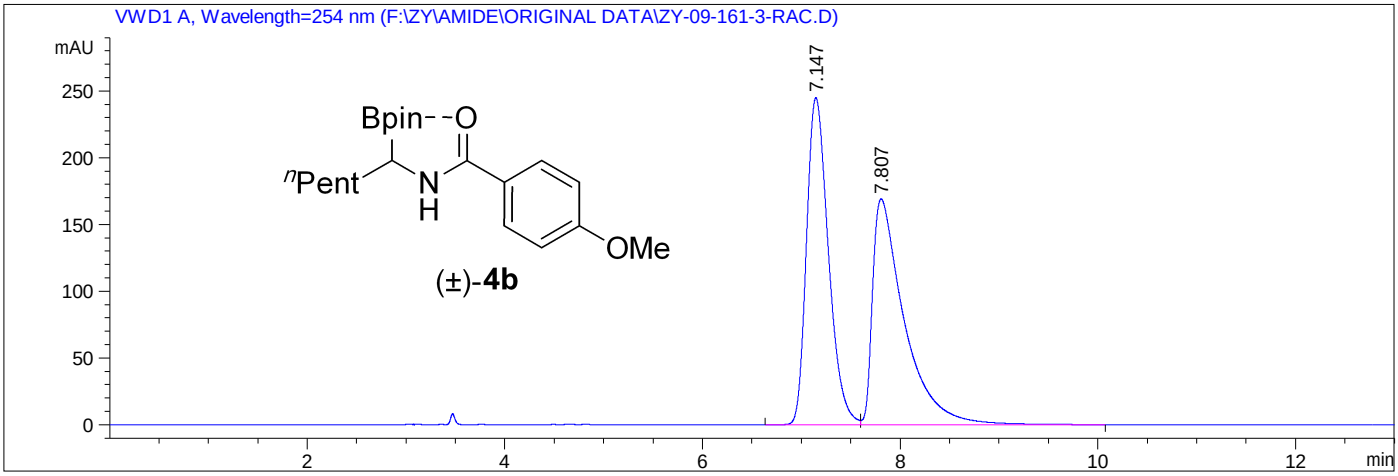
Totals :                  2581.61567  395.81895


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 224: HPLC spectrum of **3p'**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-161-3-RAC.D
Sample Name: ZY-09-161-3-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                      Location :   71
Injection Date  : 11/23/2021 9:59:34 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
Acq. Method     : D:\zy\20211119\YH 2021-11-23 09-08-50\5EtOH15_10-1-2-254.M
Last changed    : 11/23/2021 10:14:40 AM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/28/2022 11:08:25 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.147 BV    0.2367 3775.47705  245.07373  50.0009
   2   7.807 VB    0.3262 3775.33398  169.27411  49.9991

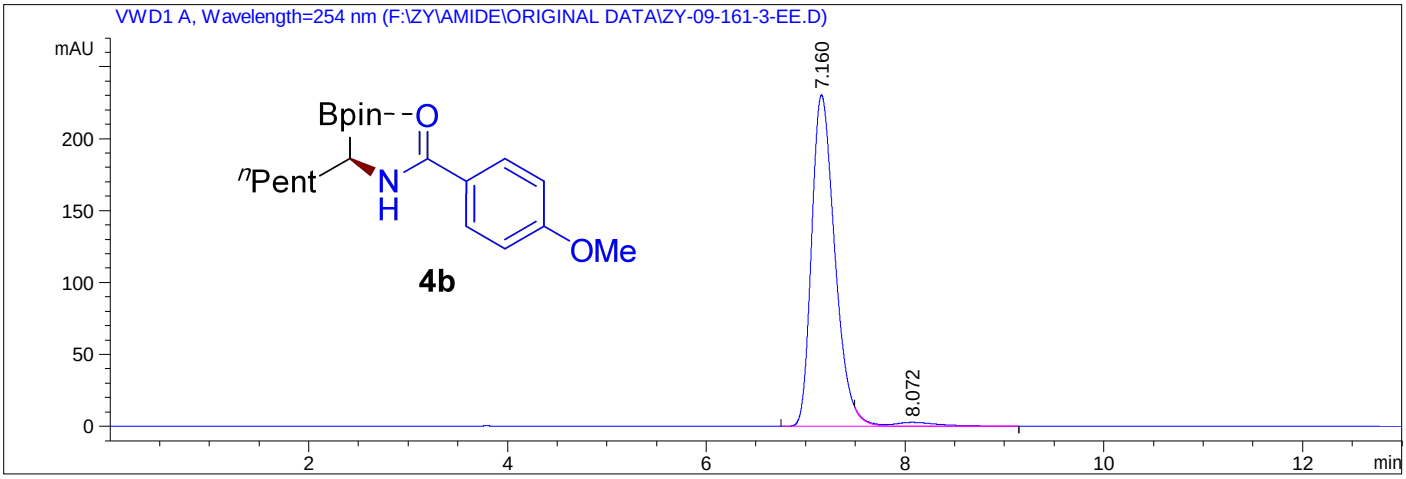
Totals :                  7550.81104  414.34784


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 225: HPLC spectrum of (±)-**4b**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-161-3-EE.D
Sample Name: ZY-09-161-3-EE

```
    ======================================================================
    Acq. Operator    : 系统                          Seq. Line :   5
    Acq. Instrument : HPLC-1260                       Location :   72
    Injection Date  : 11/23/2021 10:16:12 AM             Inj :   1
                                                   Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
    Acq. Method     : D:\zy\20211119\YH 2021-11-23 09-08-50\5EtOH15_10-1-2-254.M
    Last changed    : 11/23/2021 10:14:40 AM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/28/2022 11:07:48 PM by SYSTEM
                      (modified after loading)
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   7.160 BV R  0.2495 3752.35693  230.38501  97.6166
       2   8.072 VB E  0.4021   91.61741    2.72957   2.3834

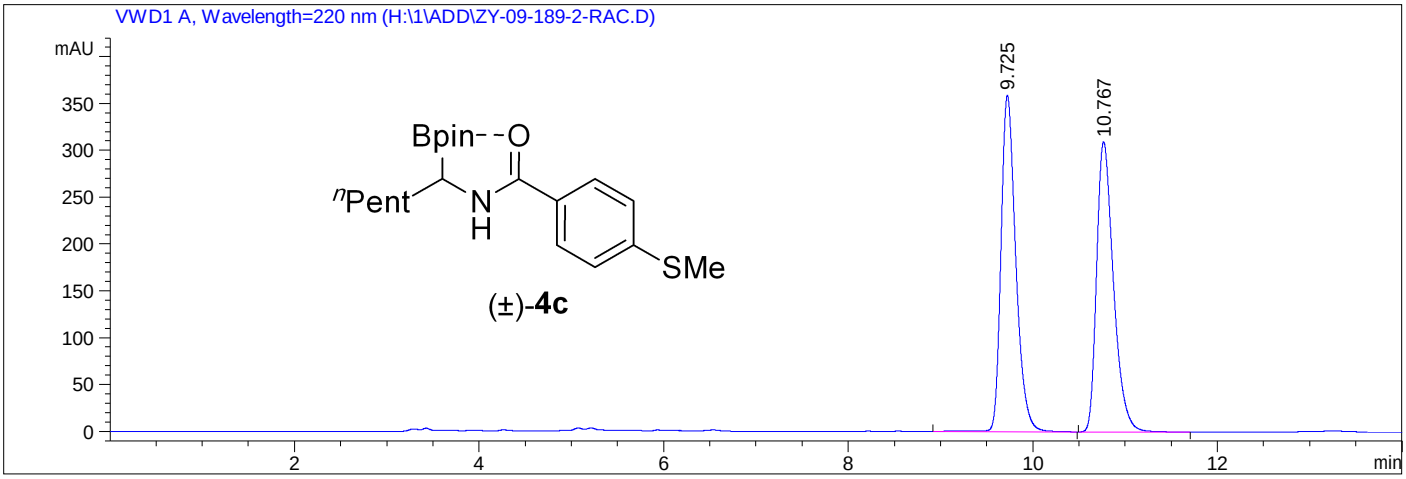
    Totals :                  3843.97434  233.11458


    ======================================================================
                              *** End of Report ***
```

Supplementary Figure 226: HPLC spectrum of **4b**.

Data File H:\1\ADD\ZY-09-189-2-RAC.D
Sample Name: ZY-09-189-2-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  22
Acq. Instrument : HPLC-1260                      Location :   77
Injection Date  : 8/20/2022 2:05:52 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-20 08-41-06\5EtOH15_10-1-6-220.M
Last changed    : 8/20/2022 2:00:54 PM by 系统
Analysis Method : C:\Chem32\1\Data\LC 2020-08-14 14-31-12\test2.M (Sequence Method)
Last changed    : 8/23/2022 3:25:25 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.725 VB R  0.1710 4004.30542  359.31268  50.4995
   2  10.767 BB    0.1953 3925.08423  309.83737  49.5005

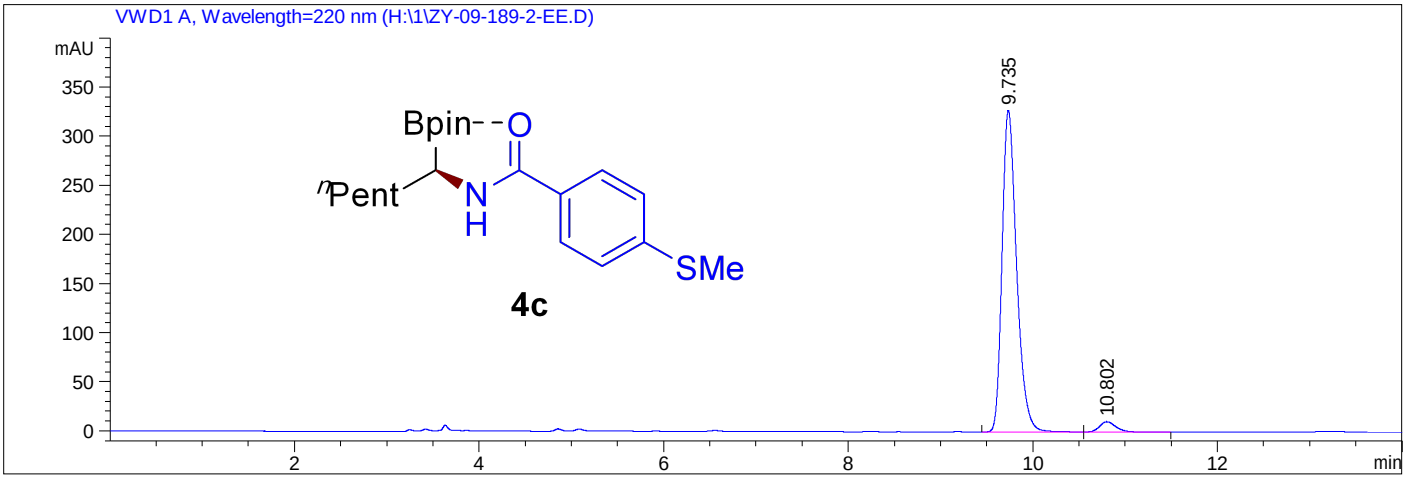
Totals :                  7929.38965  669.15005


==========================================================================
                          *** End of Report ***
```

Supplementary Figure 227: HPLC spectrum of **(±)-4c**.

Data File H:\1\ZY-09-189-2-EE.D
Sample Name: ZY-09-189-2-EE

```
=====================================================================
Acq. Operator    : 系统                          Seq. Line :  19
Acq. Instrument : HPLC-1260                       Location :   79
Injection Date  : 8/20/2022 1:19:09 PM                 Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-20 08-41-06\5EtOH15_10-1-6-220.M
Last changed    : 8/20/2022 9:59:08 AM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence
                  Method)
Last changed    : 8/22/2022 7:04:29 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.735 BV    0.1678 3588.63062  327.61975  96.4551
   2  10.802 VB    0.1891  131.88794   10.52918   3.5449

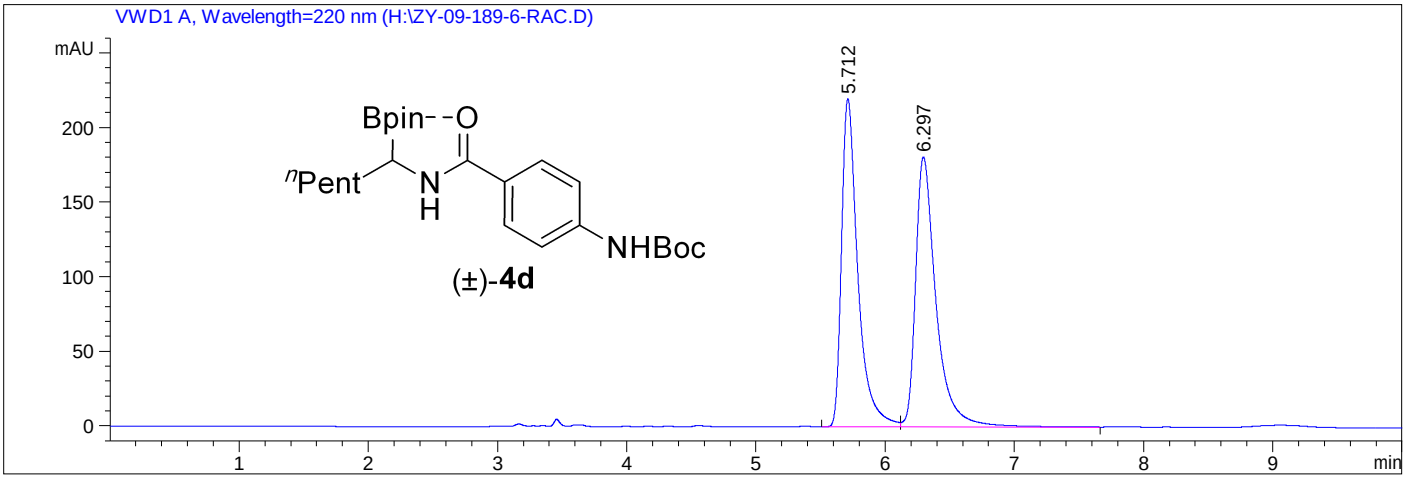
Totals :                  3720.51855  338.14893


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 228: HPLC spectrum of **4c**.

Data File H:\ZY-09-189-6-RAC.D
Sample Name: ZY-09-189-6-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  31
Acq. Instrument : HPLC-1260                      Location :  44
Injection Date  : 12/21/2021 10:14:13 PM             Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\zy\20211219\YH 2021-12-21 13-59-57\5EtOH20_10-1-2-220.M
Last changed    : 12/21/2021 9:45:37 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-03-29 18-02-36\1.0IPA_15_0.8_1-254-SFT.M (Sequence
                  Method)
Last changed    : 3/29/2022 8:47:13 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.712 BV    0.1316 1935.34534  220.14615  49.1952
   2   6.297 VB    0.1642 1998.66370  181.10876  50.8048

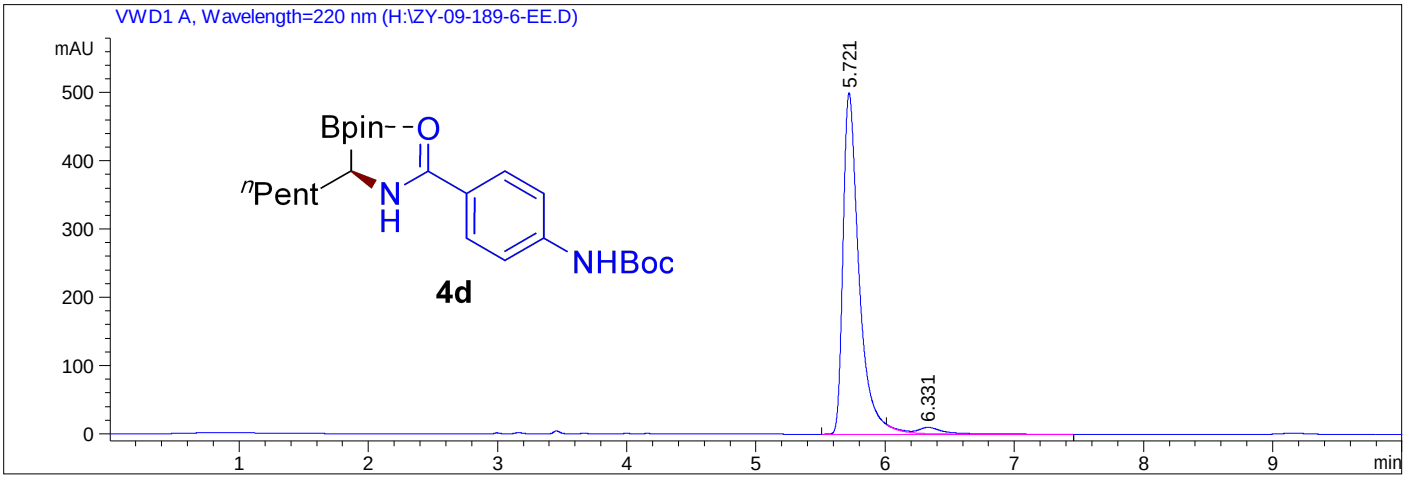
Totals :                  3934.00903  401.25491


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 229: HPLC spectrum of (±)-**4d**.

Data File H:\ZY-09-189-6-EE.D
Sample Name: ZY-09-189-6-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  30
Acq. Instrument : HPLC-1260                      Location :   43
Injection Date  : 12/21/2021 9:57:49 PM             Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\zy\20211219\YH 2021-12-21 13-59-57\5EtOH20_10-1-2-220.M
Last changed    : 12/21/2021 9:45:37 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-03-29 18-02-36\1.0IPA_15_0.8_1-254-SFT.M (Sequence
                  Method)
Last changed    : 3/29/2022 8:46:33 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.721 BV R  0.1284 4325.95020  499.95084  96.8165
   2   6.331 VB E  0.2160  142.24498    9.32273   3.1835

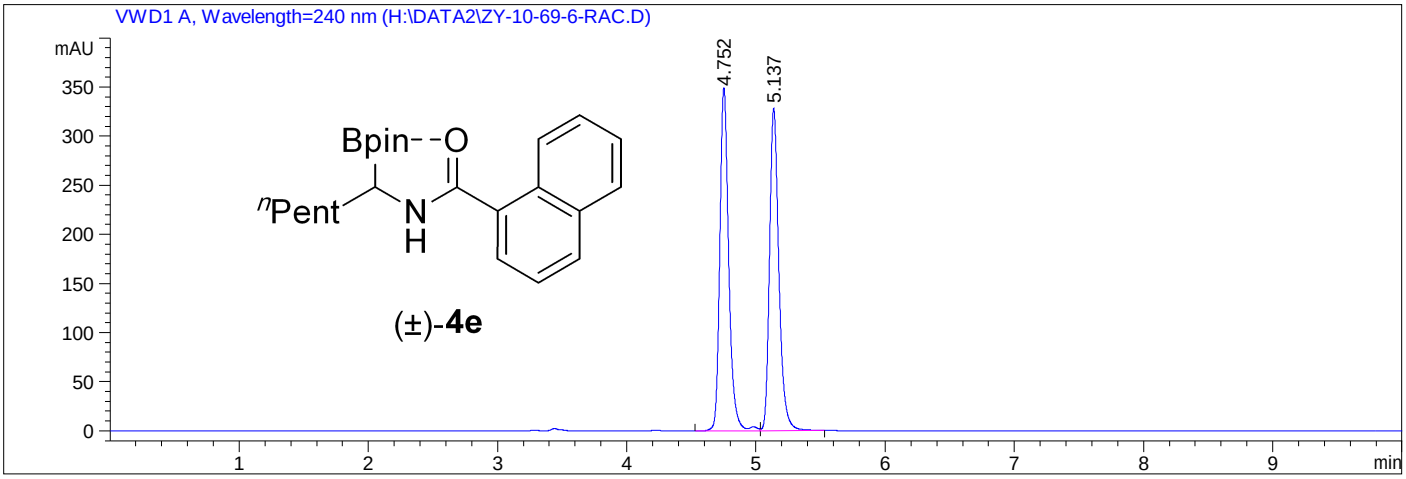
Totals :                  4468.19518  509.27357


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 230: HPLC spectrum of **4d**.

Data File H:\DATA2\ZY-10-69-6-RAC.D
Sample Name: ZY-10-69-6-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   3
Acq. Instrument : HPLC-1260                      Location :   41
Injection Date  : 5/29/2022 8:39:19 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\zy\20220328\YH 2022-05-29 20-09-39\5EtOH15_10-1-2-240.M
Last changed    : 5/29/2022 8:09:40 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-06-04 08-49-06\0.3IPA-0.3-60-220-1-CCP.M (Sequence
                  Method)
Last changed    : 6/7/2022 10:14:44 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.752 BV R  0.0720 1679.71350  349.52957  50.4898
   2   5.137 VB    0.0766 1647.12341  328.13077  49.5102

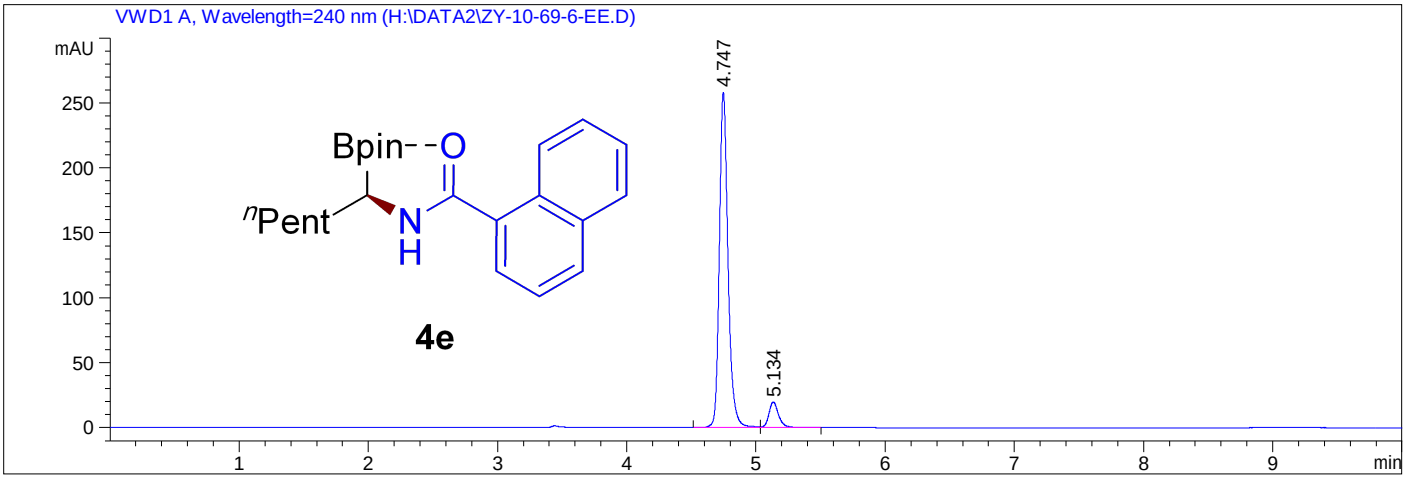
Totals :                  3326.83691  677.66034


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 231: HPLC spectrum of (±)-**4e**.

Data File H:\DATA2\ZY-10-69-6-EE.D
Sample Name: ZY-10-69-6-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                      Location :   42
Injection Date  : 5/29/2022 8:55:45 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.100 µl
Acq. Method     : D:\zy\20220328\YH 2022-05-29 20-09-39\5EtOH15_10-1-2-240.M
Last changed    : 5/29/2022 8:09:40 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-06-04 08-49-06\0.3IPA-0.3-60-220-1-CCP.M (Sequence
                  Method)
Last changed    : 6/7/2022 10:13:51 AM by SYSTEM
                  (modified after loading)
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.747 BV    0.0710 1203.43774  257.80865  92.1441
   2   5.134 VB    0.0789  102.60114   19.82286   7.8559

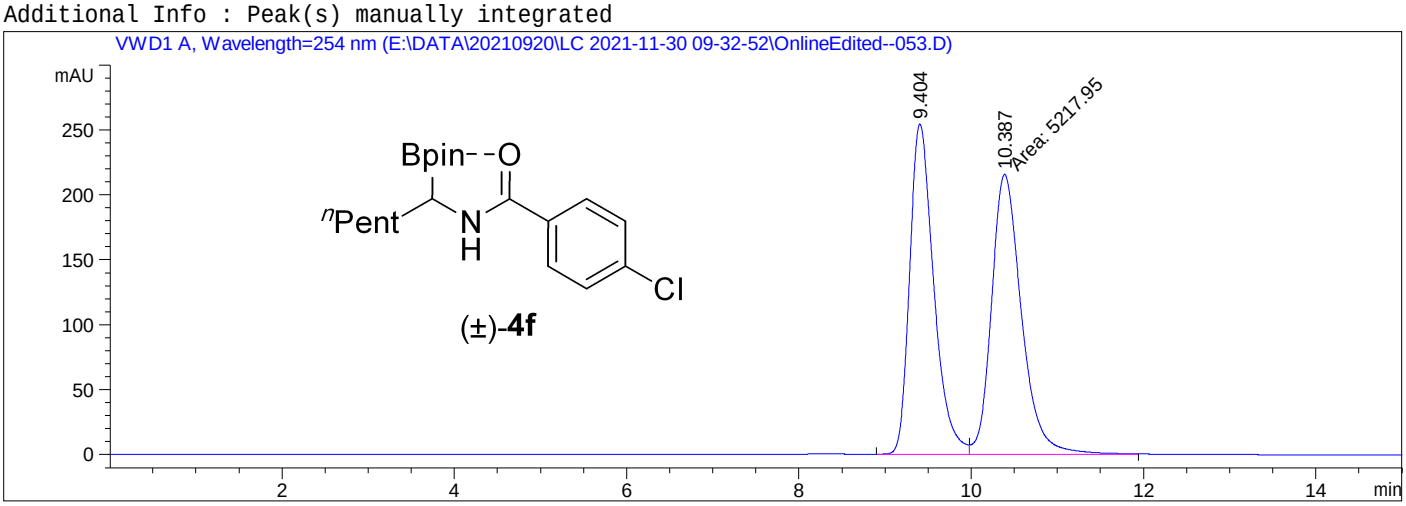
Totals :                  1306.03889  277.63151


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 232: HPLC spectrum of **4e**.

Data File E:\DATA\20210920\LC 2021-11-30 09-32-52\OnlineEdited--053.D
Sample Name: ZY-09-164-5-RAC

```
=====================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  53
Acq. Instrument : HPLC1260                         Location :   P1-E4
Injection Date  : 12/1/2021 9:28:54 AM                  Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : E:\DATA\20210920\LC 2021-11-30 09-32-52\3IPA_20_0.4_3-254.M
Last changed    : 12/1/2021 9:25:40 AM by SYSTEM
Analysis Method : E:\DATA\20210920\LC 2021-11-30 09-32-52\3IPA_20_0.4_3-254.M (Sequence
                  Method)
Last changed    : 12/1/2021 12:28:00 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.404 BV    0.2968 4941.78369  254.15439  48.6409
   2  10.387 MF    0.4034 5217.95313  215.57483  51.3591

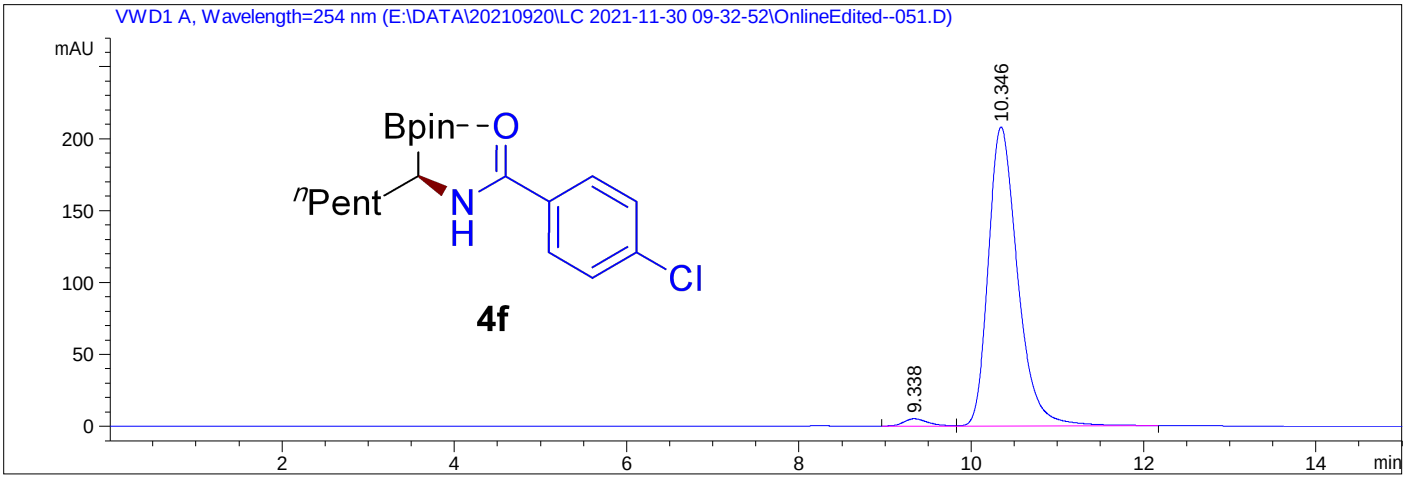
Totals :                  1.01597e4   469.72922


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 233: HPLC spectrum of (±)-**4f**.

Data File E:\DATA\20210920\LC 2021-11-30 09-32-52\OnlineEdited--051.D
Sample Name: ZY-09-164-5-EE

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  51
Acq. Instrument : HPLC1260                         Location :   P1-E3
Injection Date  : 12/1/2021 8:47:09 AM                Inj :   1
                                                  Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : E:\DATA\20210920\LC 2021-11-30 09-32-52\3IPA_20_0.4_3-254.M
Last changed    : 11/30/2021 11:50:22 PM by SYSTEM
Analysis Method : E:\DATA\20210920\LC 2021-11-30 09-32-52\3IPA_20_0.4_3-254.M (Sequence
                  Method)
Last changed    : 12/1/2021 12:28:54 PM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.338 BV    0.2937   96.96291    5.03491   1.9338
   2  10.346 VB    0.3610 4917.21289  207.83859  98.0662

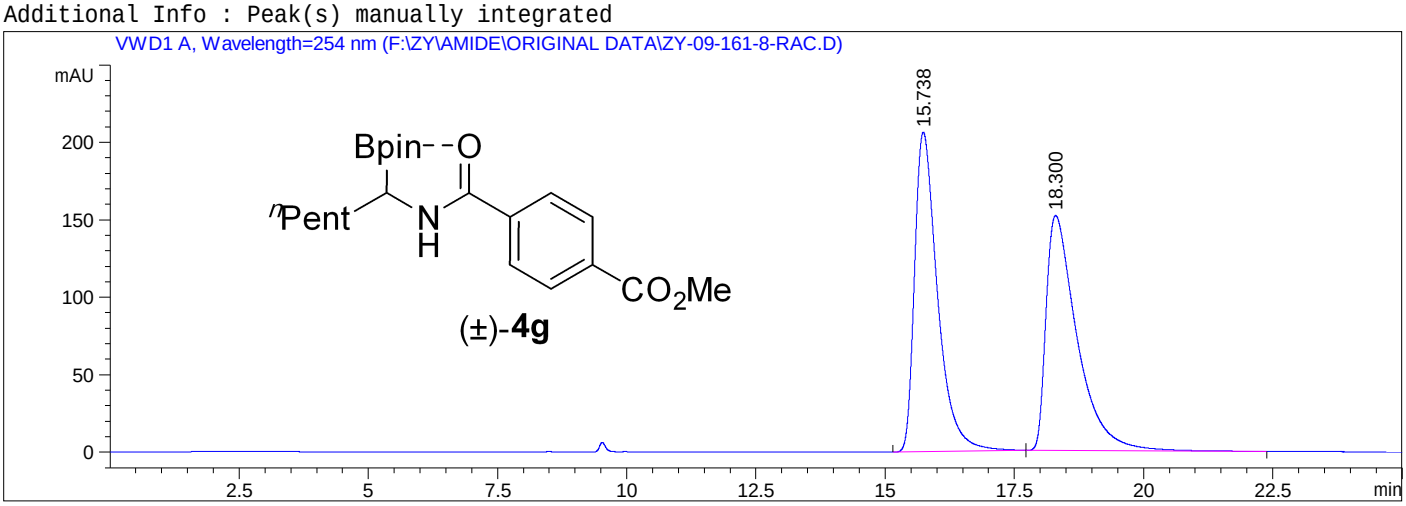
Totals :                  5014.17580  212.87350


==========================================================================
                          *** End of Report ***
```

Supplementary Figure 234: HPLC spectrum of **4f**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-161-8-RAC.D
Sample Name: ZY-09-161-8-RAC

```
    ======================================================================
    Acq. Operator    : 系统                              Seq. Line :   7
    Acq. Instrument : HPLC-1260                          Location :   21
    Injection Date  : 11/24/2021 12:11:30 AM                 Inj :   1
                                                      Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.500 µl
    Acq. Method     : D:\zy\20211119\YH 2021-11-23 21-47-26\3IPA-30-0.8-1-2-254.M
    Last changed    : 11/23/2021 9:47:27 PM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/28/2022 11:10:10 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  15.738 BB    0.4680 6377.62256  206.38446  50.1471
       2  18.300 BB    0.6098 6340.20410  151.79956  49.8529

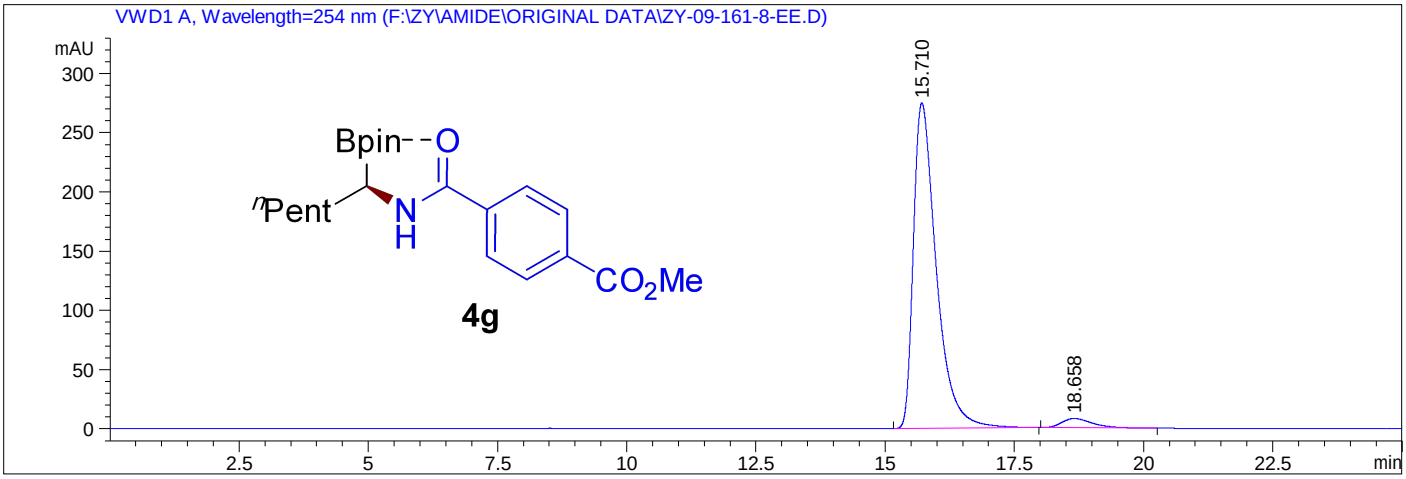
    Totals :                  1.27178e4   358.18402


    ======================================================================
                            *** End of Report ***
```

Supplementary Figure 235: HPLC spectrum of (±)-**4g**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-161-8-EE.D
Sample Name: ZY-09-161-8-EE

```
======================================================================
Acq. Operator    : 系统                          Seq. Line :   6
Acq. Instrument : HPLC-1260                       Location :   22
Injection Date  : 11/23/2021 11:40:07 PM             Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.700 µl
Acq. Method     : D:\zy\20211119\YH 2021-11-23 21-47-26\3IPA-30-0.8-1-2-254.M
Last changed    : 11/23/2021 9:47:27 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/28/2022 11:09:37 PM by SYSTEM
                  (modified after loading)
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.710 BB    0.4667 8486.95020  274.90009  96.3010
   2  18.658 BB    0.5090  325.99210    7.82603   3.6990

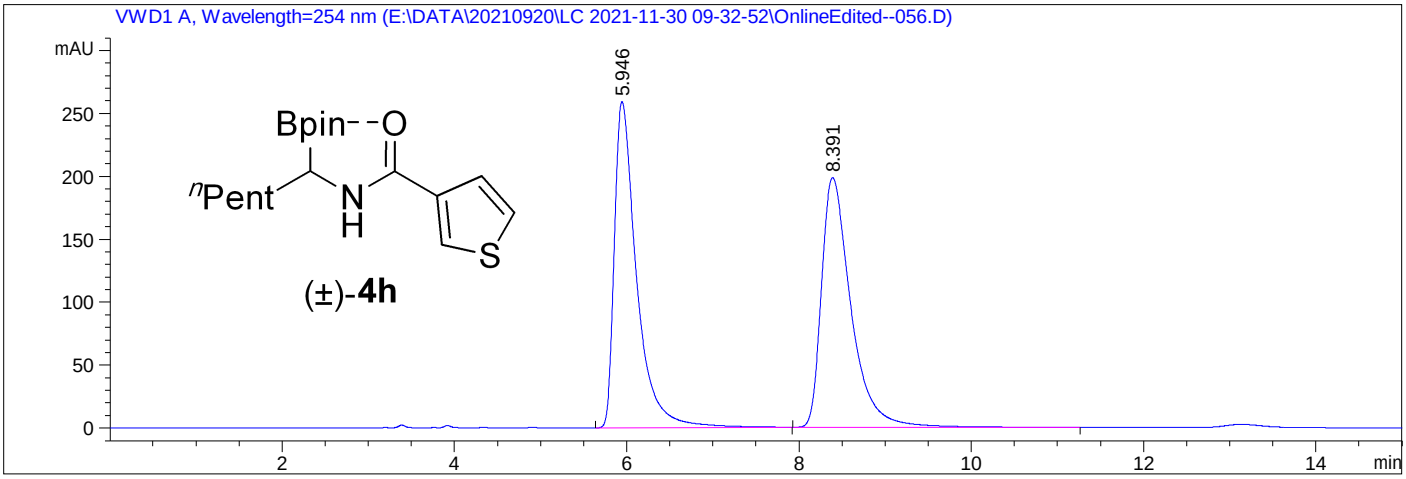
Totals :                  8812.94229  282.72612


======================================================================
                        *** End of Report ***
```

Supplementary Figure 236: HPLC spectrum of **4g**.

Data File E:\DATA\20210920\LC 2021-11-30 09-32-52\OnlineEdited--056.D
Sample Name: ZY-09-165-2-RAC

```
======================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  56
Acq. Instrument : HPLC1260                         Location :   P1-E2
Injection Date  : 12/1/2021 10:26:45 AM                Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.600 µl
Acq. Method     : E:\DATA\20210920\LC 2021-11-30 09-32-52\2IPA_20_1.0_2-254.M
Last changed    : 12/1/2021 9:31:40 AM by SYSTEM
Analysis Method : E:\DATA\20210920\LC 2021-11-30 09-32-52\2IPA_20_1.0_2-254.M (Sequence
                  Method)
Last changed    : 12/1/2021 12:30:19 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.946 BB    0.2665 4652.44141  259.13269  49.6479
   2   8.391 BB    0.3575 4718.43799  198.40140  50.3521

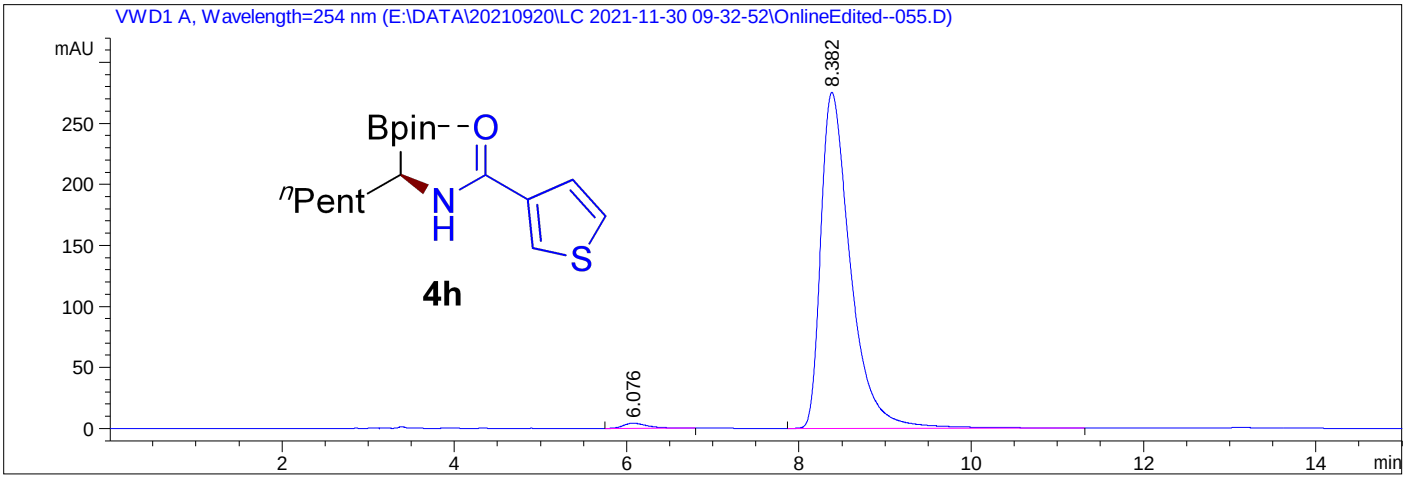
Totals :                  9370.87939  457.53409


======================================================================
                        *** End of Report ***
```

Supplementary Figure 237: HPLC spectrum of (±)-**4h**.

Data File E:\DATA\20210920\LC 2021-11-30 09-32-52\OnlineEdited--055.D
Sample Name: ZY-09-165-2-EE

```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  55
Acq. Instrument : HPLC1260                       Location :   P1-E1
Injection Date  : 12/1/2021 10:05:47 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.500 µl
Acq. Method     : E:\DATA\20210920\LC 2021-11-30 09-32-52\2IPA_20_1.0_2-254.M
Last changed    : 12/1/2021 9:31:40 AM by SYSTEM
Analysis Method : E:\DATA\20210920\LC 2021-11-30 09-32-52\2IPA_20_1.0_2-254.M (Sequence
                  Method)
Last changed    : 12/1/2021 12:30:52 PM by SYSTEM
                  (modified after loading)
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.076 BB    0.2913   81.13868    4.18332   1.2148
   2   8.382 BB    0.3615 6597.98486  275.45410  98.7852

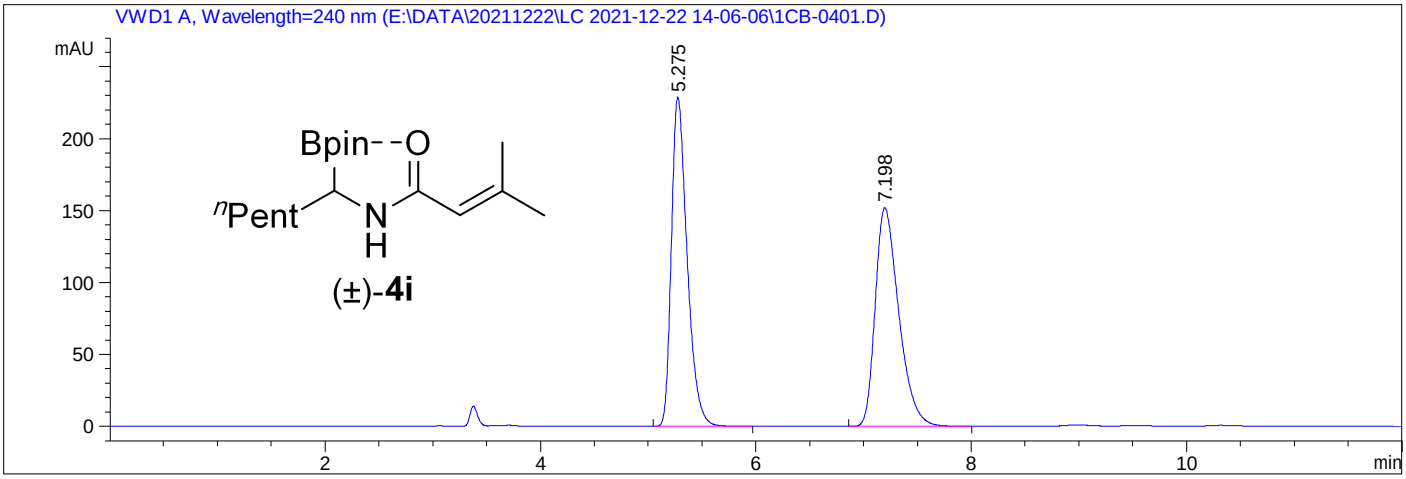
Totals :                   6679.12354  279.63742


==================================================================
                        *** End of Report ***
```

Supplementary Figure 238: HPLC spectrum of **4h**.

Data File E:\DATA\20211222\LC 2021-12-22 14-06-06\1CB-0401.D
Sample Name: ZY-09-167-6-RAC

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   4
Acq. Instrument : HPLC1260                         Location :   P1-C2
Injection Date  : 12/22/2021 2:55:43 PM                Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : E:\DATA\20211222\LC 2021-12-22 14-06-06\5IPA15_10_3-240.M
Last changed    : 12/22/2021 2:06:06 PM by SYSTEM
Analysis Method : E:\DATA\20211222\LC 2021-12-22 14-06-06\5IPA15_10_3-240.M (Sequence Method)
Last changed    : 12/22/2021 3:19:21 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.275 BB    0.1542 2320.10425  228.95290  50.1665
   2   7.198 BB    0.2309 2304.70605  152.02585  49.8335

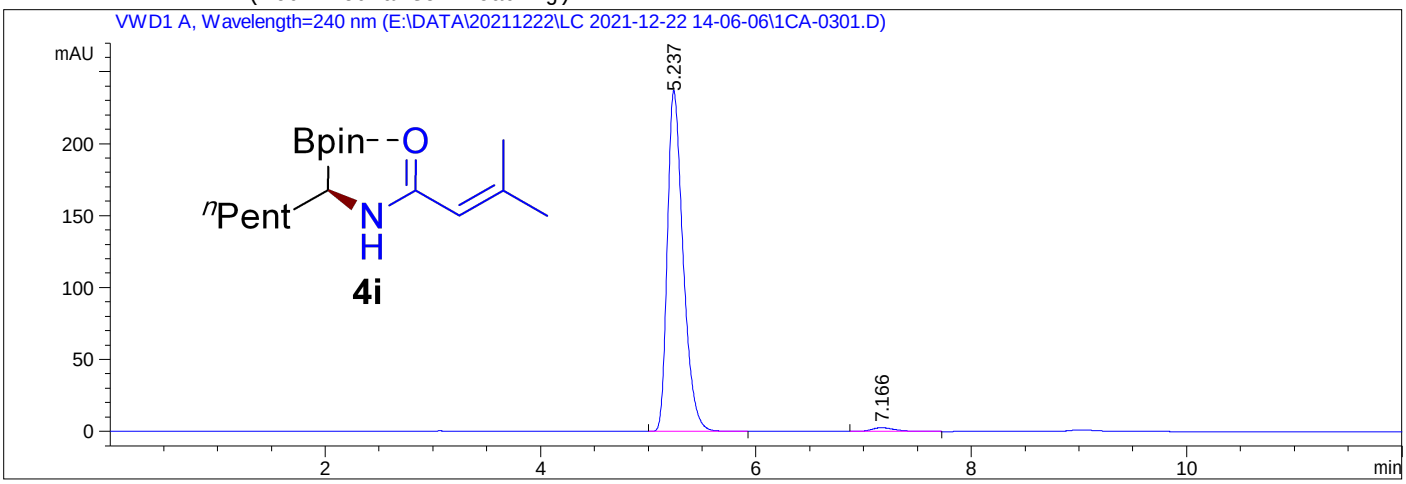
Totals :                  4624.81030  380.97874


==========================================================================
                          *** End of Report ***
```

Supplementary Figure 239: HPLC spectrum of (±)-**4i**.

Data File E:\DATA\20211222\LC 2021-12-22 14-06-06\1CA-0301.D
Sample Name: ZY-09-167-6-EE

```
=====================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : HPLC1260                         Location :   P1-C1
Injection Date  : 12/22/2021 2:39:59 PM                 Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : E:\DATA\20211222\LC 2021-12-22 14-06-06\5IPA15_10_3-240.M
Last changed    : 12/22/2021 2:06:06 PM by SYSTEM
Analysis Method : E:\DATA\20211222\LC 2021-12-22 14-06-06\5IPA15_10_3-240.M (Sequence Method)
Last changed    : 12/22/2021 3:19:21 PM by SYSTEM
                  (modified after loading)
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.237 BB    0.1545 2407.39844  236.98210  98.3816
   2   7.166 BB    0.2291   39.60282    2.63921   1.6184

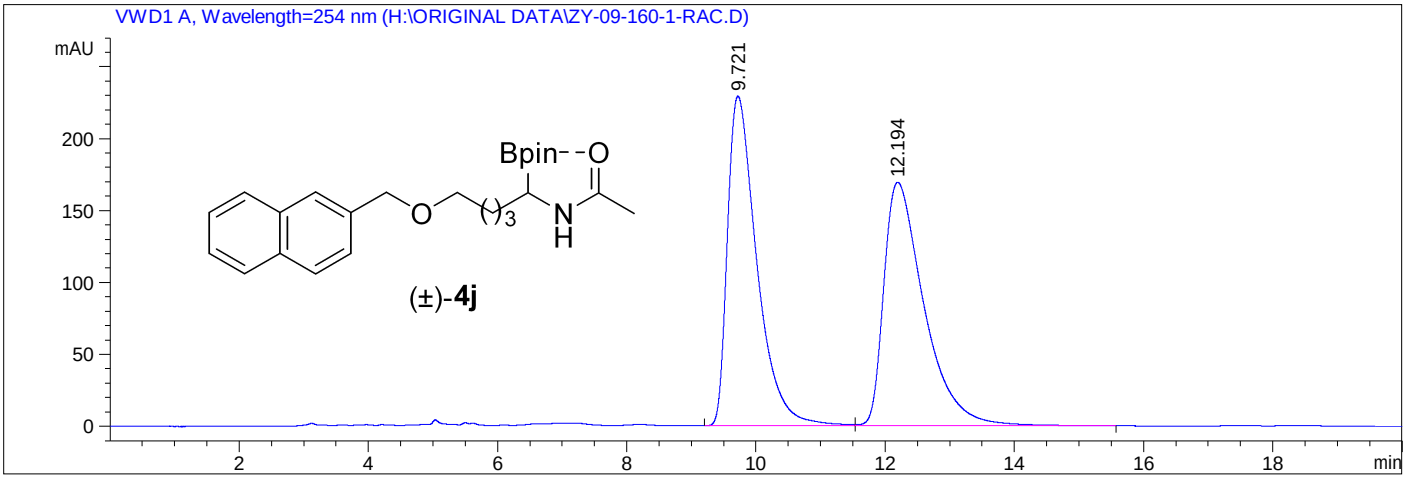
Totals :                  2447.00126  239.62132


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 240: HPLC spectrum of **4i**.

Data File H:\ORIGINAL DATA\ZY-09-160-1-RAC.D
Sample Name: ZY-09-160-1-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   8
Acq. Instrument : HPLC-1260                      Location :   31
Injection Date  : 11/20/2021 11:50:54 AM             Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 5.000 µl
Acq. Method     : D:\zy\20211023\YH 2021-11-20 09-04-54\5IPA20_10-1-6-254.M
Last changed    : 11/20/2021 9:33:00 AM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-03-28 16-47-04\0.2IPA-40-0.5-1-XYH.M (Sequence
                  Method)
Last changed    : 3/28/2022 11:00:12 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.721 BV    0.4782 7264.92676  229.26585  49.8054
   2  12.194 VB    0.6462 7321.70605  169.41502  50.1946

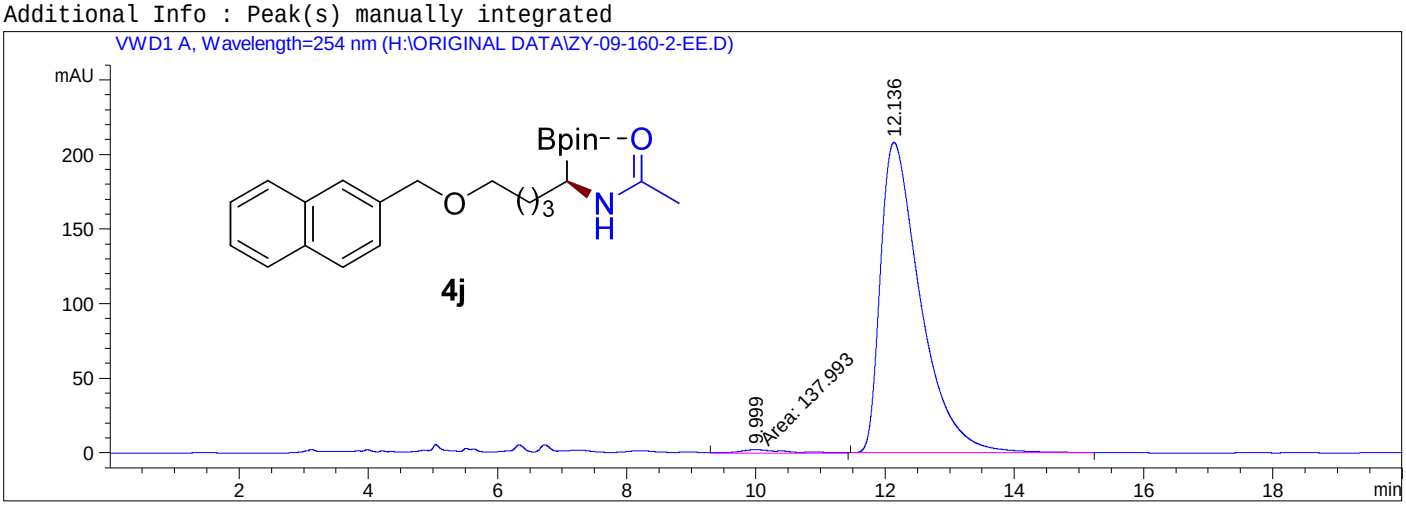
Totals :                  1.45866e4   398.68088


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 241: HPLC spectrum of (±)-**4j**.

Data File H:\ORIGINAL DATA\ZY-09-160-2-EE.D
Sample Name: ZY-09-160-2-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   7
Acq. Instrument : HPLC-1260                     Location :   32
Injection Date  : 11/20/2021 11:29:33 AM            Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 5.000 µl
Acq. Method     : D:\zy\20211023\YH 2021-11-20 09-04-54\5IPA20_10-1-6-254.M
Last changed    : 11/20/2021 9:33:00 AM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-03-28 16-47-04\0.2IPA-40-0.5-1-XYH.M (Sequence
                  Method)
Last changed    : 3/28/2022 10:59:28 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.999 MM    0.9422  137.99254    2.44099   1.5152
   2  12.136 BB    0.6388 8969.10059  208.12076  98.4848

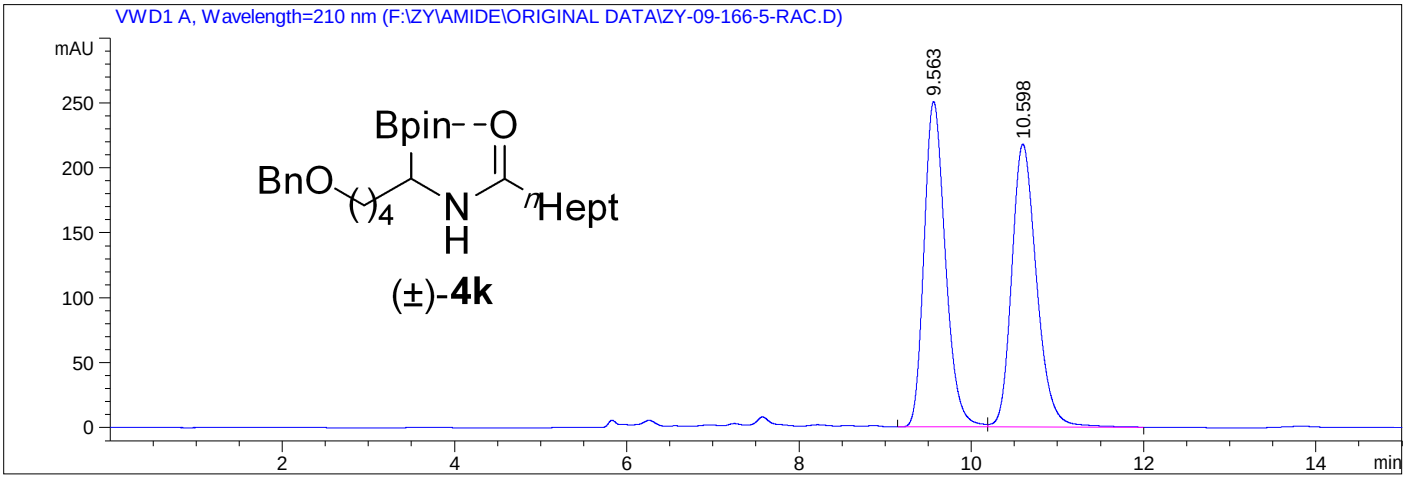
Totals :                  9107.09312  210.56175


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 242: HPLC spectrum of **4j**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-166-5-RAC.D
Sample Name: ZY-09-166-7-OD

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  13
Acq. Instrument : HPLC-1260                      Location :  31
Injection Date  : 12/4/2021 12:57:37 PM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\zy\20211129\YH 2021-12-04 09-05-16\8IPA20_5-1-2-210.M
Last changed    : 12/4/2021 9:13:44 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/28/2022 11:23:29 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.563 BV    0.2638 4313.62402  250.64847  49.6492
   2  10.598 VB    0.3083 4374.57373  217.81007  50.3508

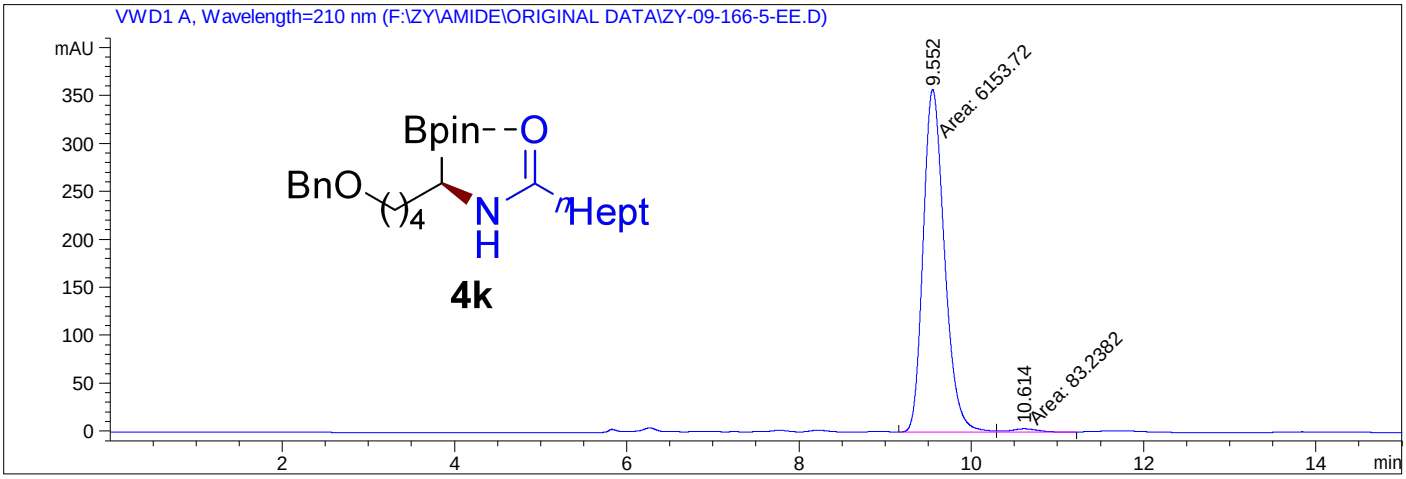
Totals :                  8688.19775  468.45854


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 243: HPLC spectrum of (±)-**4k**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-166-5-EE.D
Sample Name: ZY-09-166-5-EE

```
    ======================================================================
    Acq. Operator    : 系统                          Seq. Line :  14
    Acq. Instrument : HPLC-1260                       Location :   35
    Injection Date  : 12/4/2021 1:18:58 PM                 Inj :   1
                                                    Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
    Acq. Method     : D:\zy\20211129\YH 2021-12-04 09-05-16\8IPA20_5-1-2-210.M
    Last changed    : 12/4/2021 9:13:44 AM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/28/2022 11:22:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.552 MF    0.2872 6153.71680  357.14899  98.6654
       2  10.614 FM    0.3918   83.23817    3.54073   1.3346

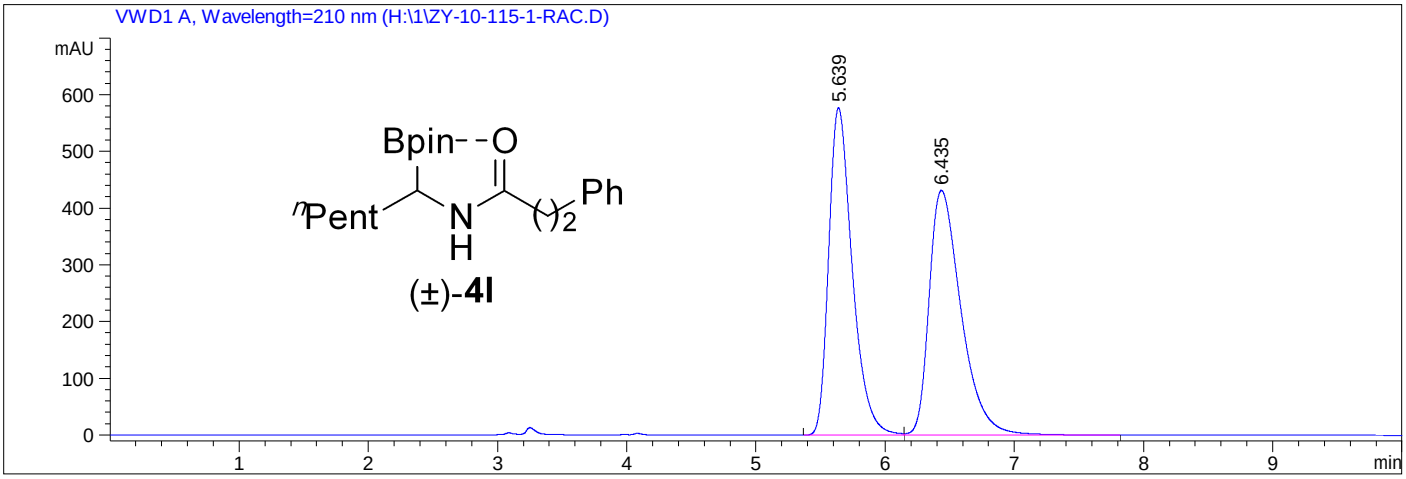
    Totals :                  6236.95496  360.68971


    ======================================================================
                            *** End of Report ***
```

Supplementary Figure 244: HPLC spectrum of **4k**.

Data File H:\1\ZY-10-115-1-RAC.D
Sample Name: ZY-10-115-2-9

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  45
Acq. Instrument : HPLC-1260                      Location :   52
Injection Date  : 8/20/2022 8:27:49 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-20 08-41-06\5IPA16_10-1-2-210.M
Last changed    : 8/20/2022 3:56:20 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence
                  Method)
Last changed    : 8/22/2022 7:20:24 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.639 BV    0.1913 7313.53271  577.17682  49.6464
   2   6.435 VV R  0.2596 7417.70801  431.49738  50.3536

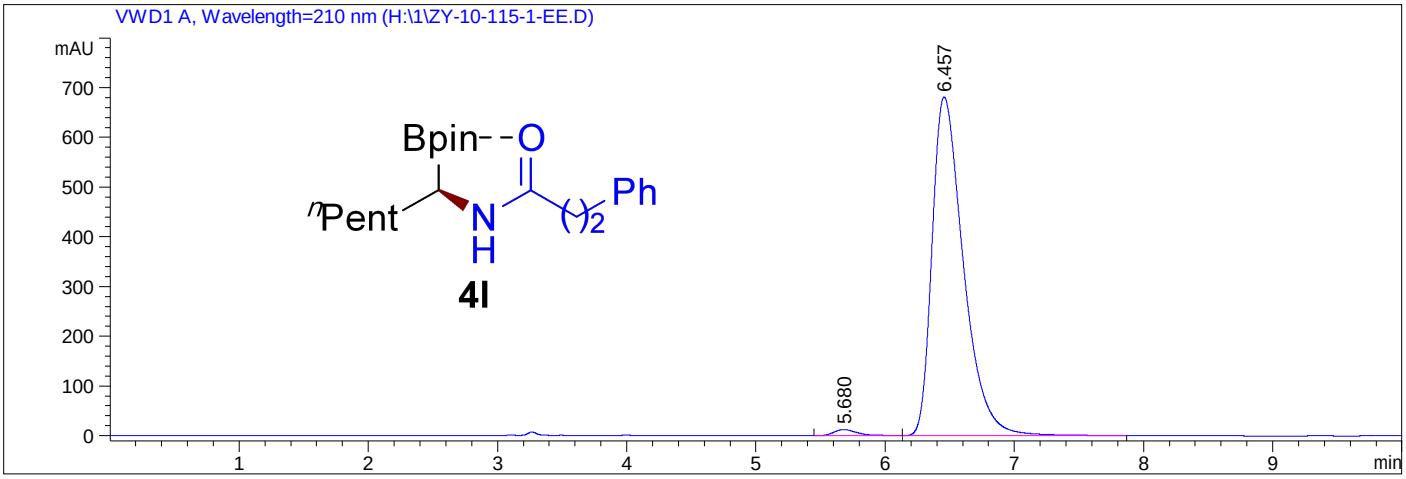
Totals :                  1.47312e4  1008.67419


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 245: HPLCspectrum of (±)-**4l**.

Data File H:\1\ZY-10-115-1-EE.D
Sample Name: ZY-10-115-1-EE1

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  50
Acq. Instrument : HPLC-1260                      Location :   58
Injection Date  : 8/20/2022 9:53:47 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\zy\20220803\YH 2022-08-20 08-41-06\5IPA16_10-1-2-210.M
Last changed    : 8/20/2022 9:47:09 PM by 系统
Analysis Method : E:\DATA\20220317\LC 2022-08-22 08-37-45\5IPA-40-1.0-1-220-QDY.M (Sequence
                  Method)
Last changed    : 8/22/2022 7:19:25 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.680 BV    0.1935  161.75188   12.53654   1.3883
   2   6.457 VB    0.2532 1.14890e4   681.26971  98.6117

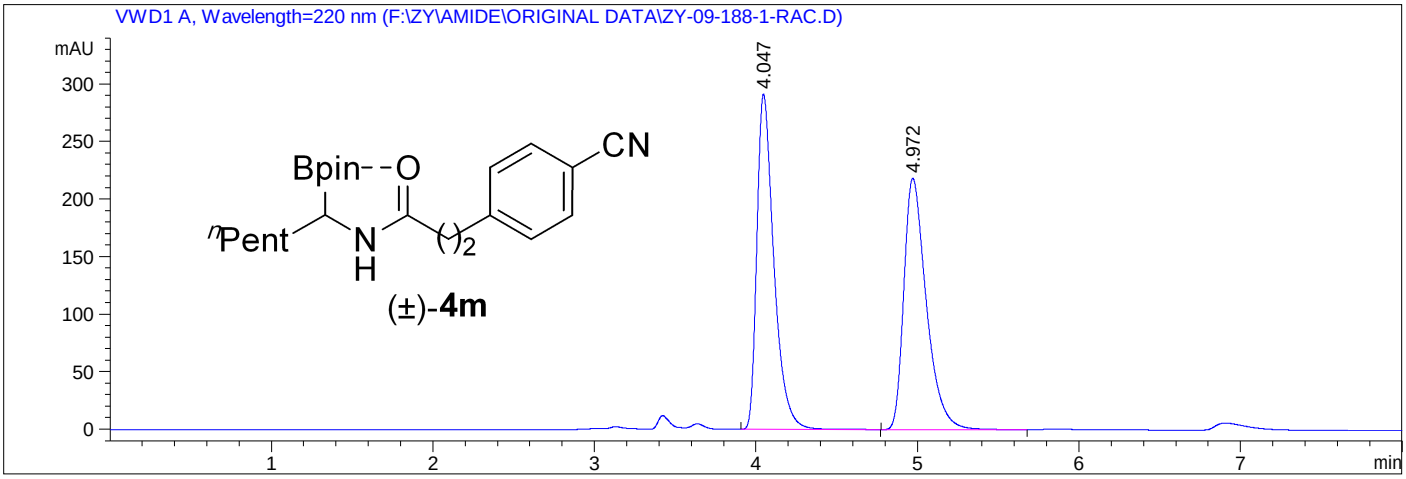
Totals :                  1.16508e4   693.80625


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 246: HPLC spectrum of **4l**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-188-1-RAC.D
Sample Name: ZY-09-188-1-RAC

```
    ======================================================================
    Acq. Operator   : 系统                          Seq. Line :   8
    Acq. Instrument : HPLC-1260                      Location :   52
    Injection Date  : 12/19/2021 5:05:45 PM              Inj :   1
                                                   Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
    Acq. Method     : D:\zy\20211219\YH 2021-12-19 15-11-05\10IPA15_10-1-6-220-FZ.M
    Last changed    : 12/19/2021 3:11:05 PM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                      Method)
    Last changed    : 3/29/2022 9:32:27 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.047 BV R  0.1112 2139.70337  291.44876  50.2747
       2   4.972 BB    0.1464 2116.31763  218.64890  49.7253

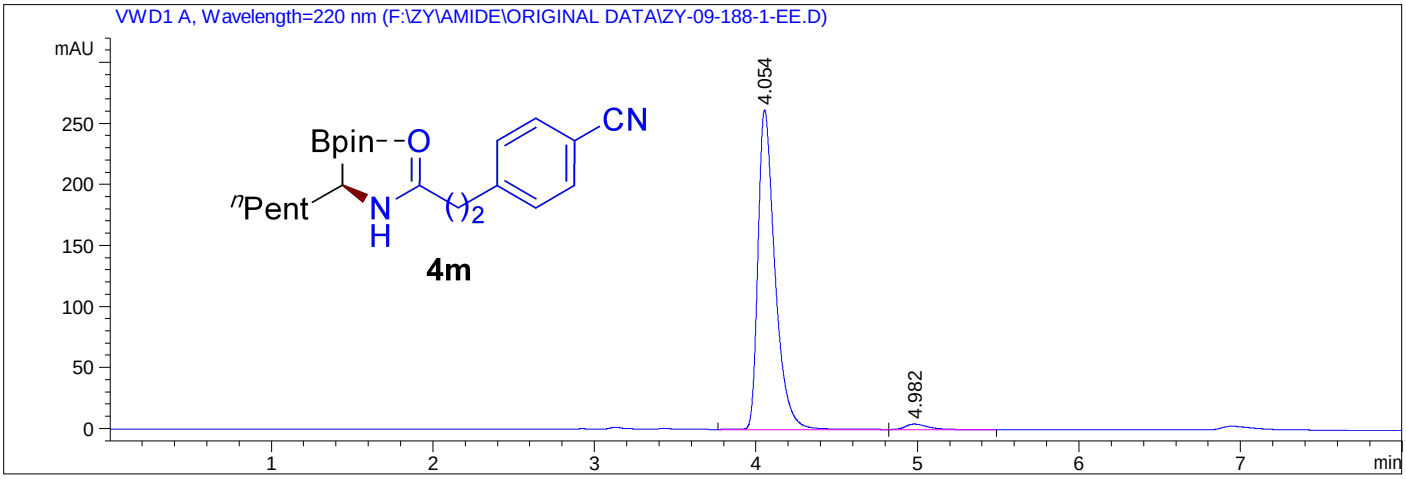
    Totals :                   4256.02100  510.09766


    ======================================================================
                            *** End of Report ***
```

Supplementary Figure 247: HPLC spectrum of (±)-**4m**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-188-1-EE.D
Sample Name: ZY-09-188-1-EE

```
    ======================================================================
    Acq. Operator   : 系统                          Seq. Line :   6
    Acq. Instrument : HPLC-1260                      Location :   51
    Injection Date  : 12/19/2021 4:33:36 PM               Inj :   1
                                                  Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
    Acq. Method     : D:\zy\20211219\YH 2021-12-19 15-11-05\10IPA15_10-1-6-220-FZ.M
    Last changed    : 12/19/2021 3:11:05 PM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                      Method)
    Last changed    : 3/29/2022 9:31:28 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.054 VV R  0.1098 1915.36646  261.94006  97.7296
       2   4.982 VB    0.1468   44.49722    4.54354   2.2704

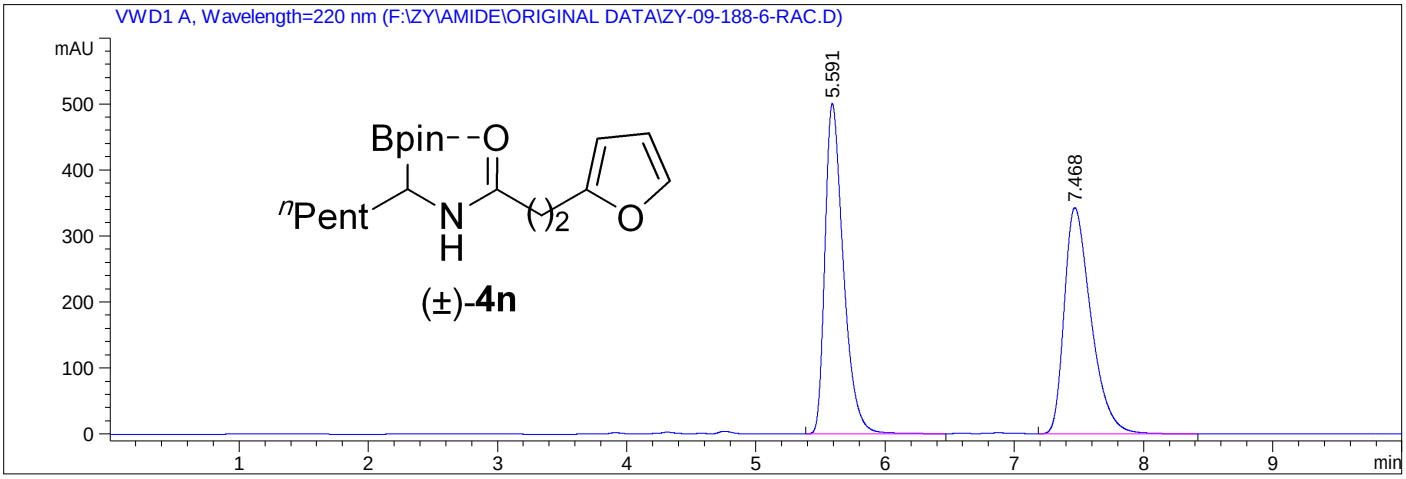
    Totals :                  1959.86367  266.48360


    ======================================================================
                            *** End of Report ***
```

Supplementary Figure 248: HPLC spectrum of **4m**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-188-6-RAC.D
Sample Name: ZY-09-188-6-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  43
Acq. Instrument : HPLC-1260                      Location :  52
Injection Date  : 12/19/2021 3:00:44 AM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
Acq. Method     : D:\zy\20211129\YH 2021-12-18 15-56-07\5IPA15_8-1-6-220.M
Last changed    : 12/18/2021 7:59:12 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:35:09 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.591 BV R  0.1505 4951.50684  499.95935  50.0940
   2   7.468 BB    0.2189 4932.93262  342.67126  49.9060

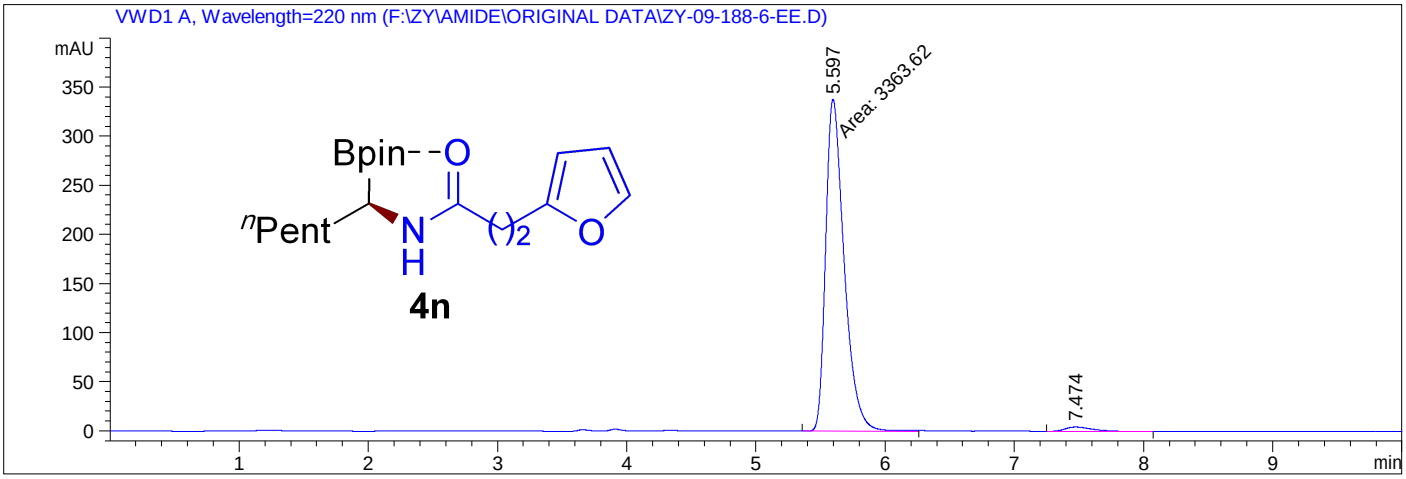
Totals :                  9884.43945  842.63062


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 249: HPLC spectrum of (±)-**4n**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-188-6-EE.D
Sample Name: ZY-09-188-6-EE

```
==================================================================
Acq. Operator   : 系统                          Seq. Line :  40
Acq. Instrument : HPLC-1260                      Location :  51
Injection Date  : 12/19/2021 2:12:39 AM             Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
Acq. Method     : D:\zy\20211129\YH 2021-12-18 15-56-07\5IPA15_8-1-6-220.M
Last changed    : 12/18/2021 7:59:12 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\0.6IPA-15-0.8-1-210-JXL.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:34:29 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.597 MF    0.1660 3363.61768  337.73022  98.0657
   2   7.474 BB    0.2115   66.34515    4.51200   1.9343

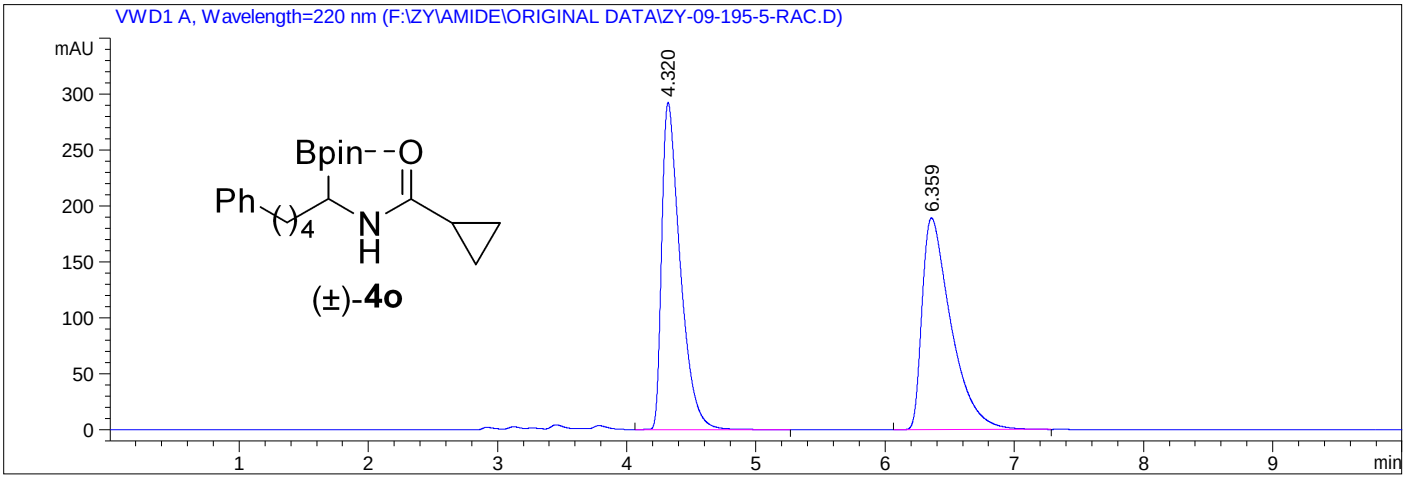
Totals :                  3429.96283  342.24223


==================================================================
                        *** End of Report ***
```

Supplementary Figure 250: HPLC spectrum of **4n**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-195-5-RAC.D
Sample Name: ZY-09-195-5-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   8
Acq. Instrument : HPLC-1260                      Location :   62
Injection Date  : 12/31/2021 6:45:20 PM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\zy\20211226\YH 2021-12-31 16-20-46\5IPA-15-1.0-1-2-220.M
Last changed    : 12/31/2021 5:46:49 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:53:44 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.320 BB    0.1479 2904.71558  292.34595  49.6171
   2   6.359 BB    0.2328 2949.54614  189.23438  50.3829

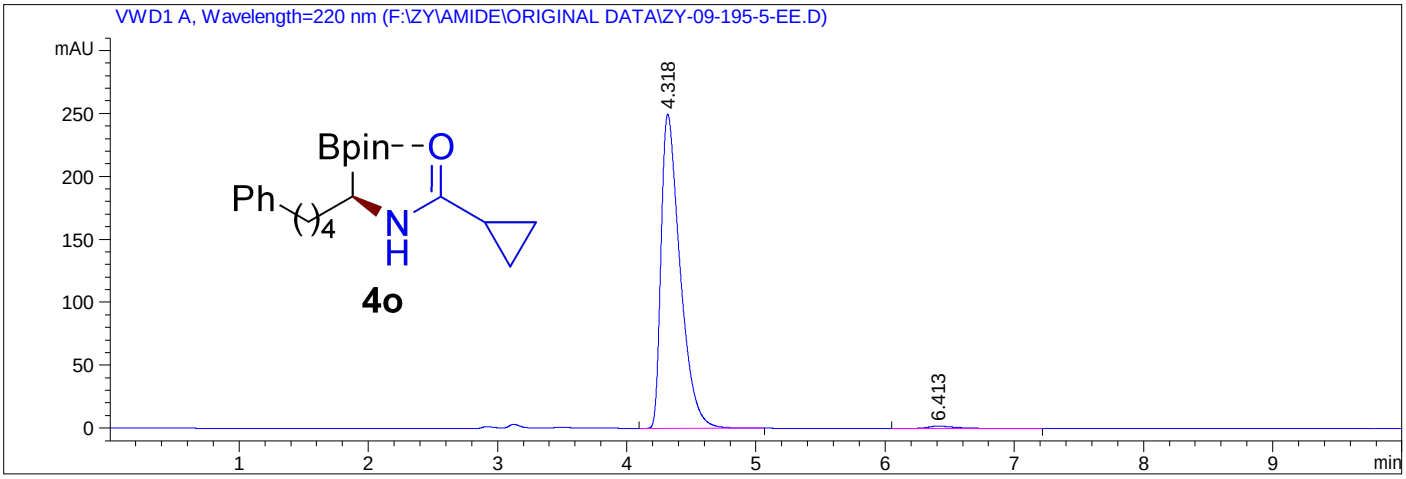
Totals :                  5854.26172  481.58032


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 251: HPLC spectrum of (±)-**4o**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-195-5-EE.D
Sample Name: ZY-09-195-5-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   9
Acq. Instrument : HPLC-1260                      Location :   61
Injection Date  : 12/31/2021 7:01:41 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.800 µl
Acq. Method     : D:\zy\20211226\YH 2021-12-31 16-20-46\5IPA-15-1.0-1-2-220.M
Last changed    : 12/31/2021 5:46:49 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:54:16 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.318 BB    0.1538 2553.71533  249.79950  98.7791
   2   6.413 BB    0.2204   31.56495    1.86559   1.2209

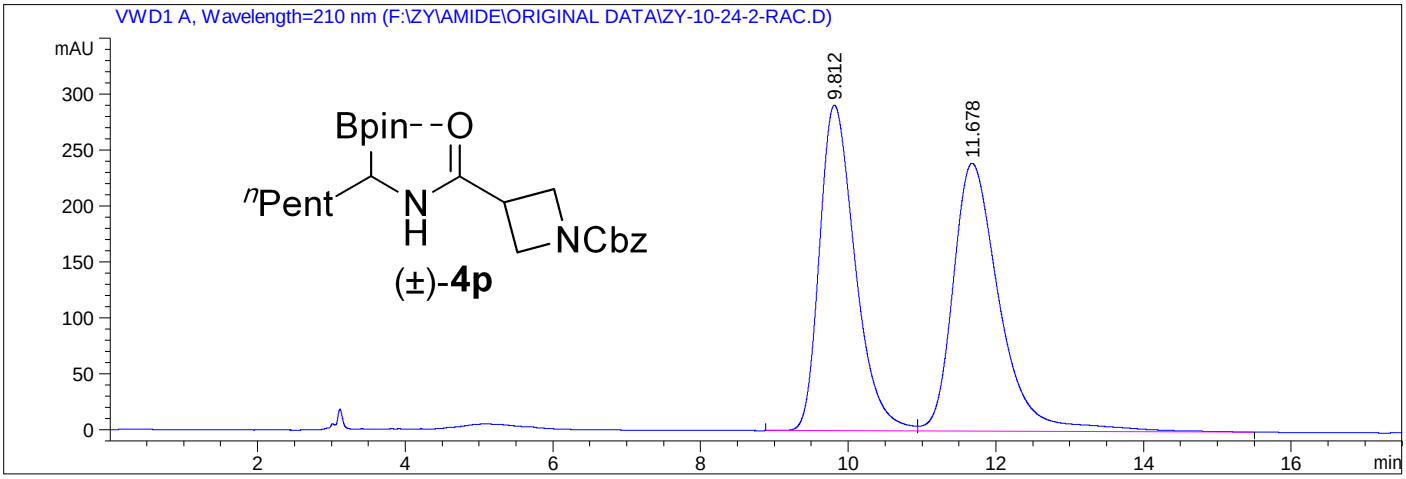
Totals :                  2585.28028  251.66509


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 252: HPLC spectrum of **4o**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-24-2-RAC.D
Sample Name: ZY-10-24-2-RAC

```
    ======================================================================
    Acq. Operator   : 系统                          Seq. Line :  19
    Acq. Instrument : HPLC-1260                      Location :   82
    Injection Date  : 2/15/2022 8:34:49 PM               Inj :   1
                                                   Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.600 µl
    Acq. Method     : D:\zy\20220201\YH 2022-02-15 14-53-54\5IPA20_10-1-2-210.M
    Last changed    : 2/15/2022 7:02:39 PM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/29/2022 10:00:58 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.812 BV    0.5117 9773.50684  291.12683  48.2130
       2  11.678 VB    0.6469 1.04980e4   239.47452  51.7870

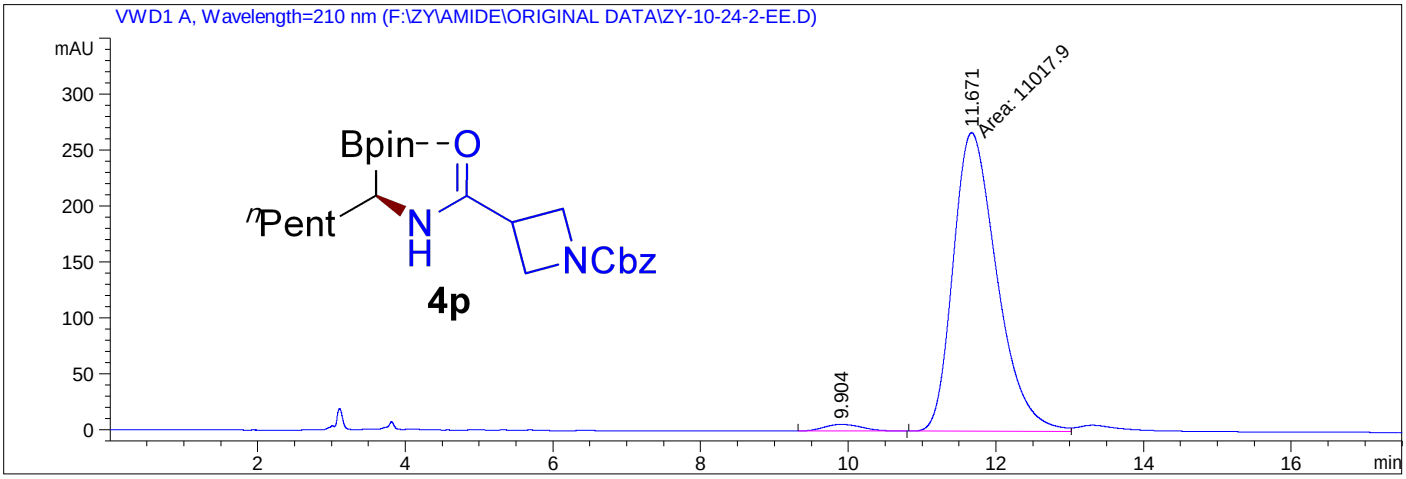
    Totals :                  2.02715e4   530.60135


    ======================================================================
                            *** End of Report ***
```

Supplementary Figure 253: HPLC spectrum of (±)-**4p**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-24-2-EE.D
Sample Name: ZY-10-24-2-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  18
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 2/15/2022 8:13:24 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.800 µl
Acq. Method     : D:\zy\20220201\YH 2022-02-15 14-53-54\5IPA20_10-1-2-210.M
Last changed    : 2/15/2022 7:02:39 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 10:00:58 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.904 BV R  0.4181  211.22409    5.92163   1.8810
   2  11.671 MF    0.6879 1.10179e4   266.93561  98.1190

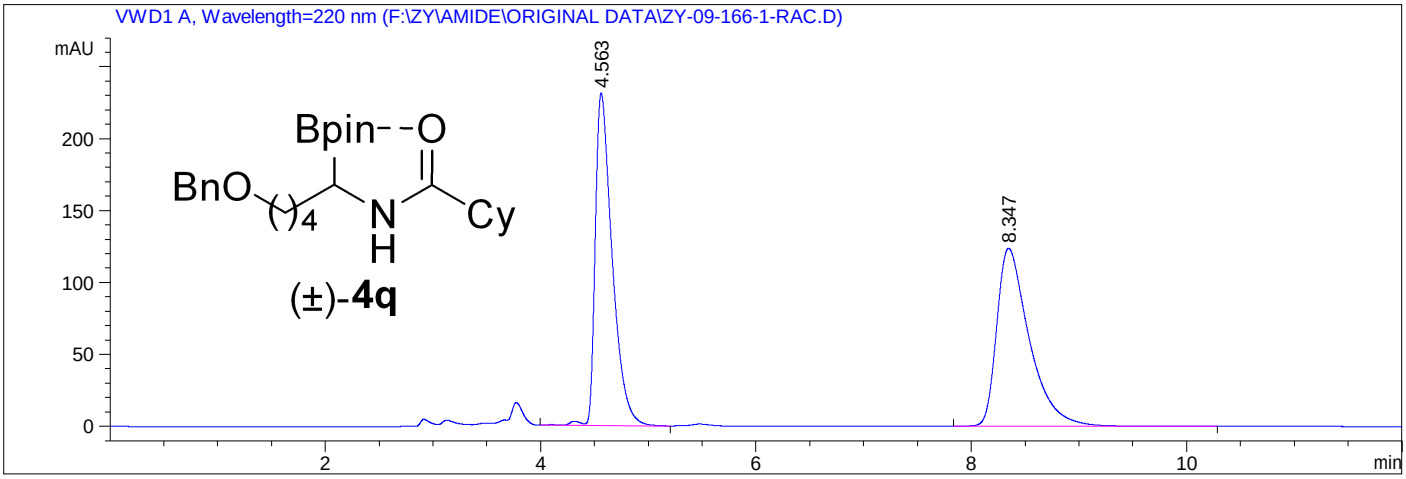
Totals :                  1.12291e4   272.85724


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 254: HPLC spectrum of **4p**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-166-1-RAC.D
Sample Name: ZY-09-166-1-RAC

```
    ======================================================================
    Acq. Operator   : 系统                          Seq. Line :  10
    Acq. Instrument : HPLC-1260                      Location :   1
    Injection Date  : 12/3/2021 12:10:23 PM               Inj :   1
                                                  Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.800 µl
    Acq. Method     : D:\zy\20211203\YH 2021-12-03 09-47-06\5IPA-20-1.0-1-6-220-JXL.M
    Last changed    : 12/3/2021 11:14:35 AM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/28/2022 11:19:50 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.563 VB R  0.1617 2529.77661  231.13509  49.2039
       2   8.347 BB    0.3129 2611.63428  123.91994  50.7961

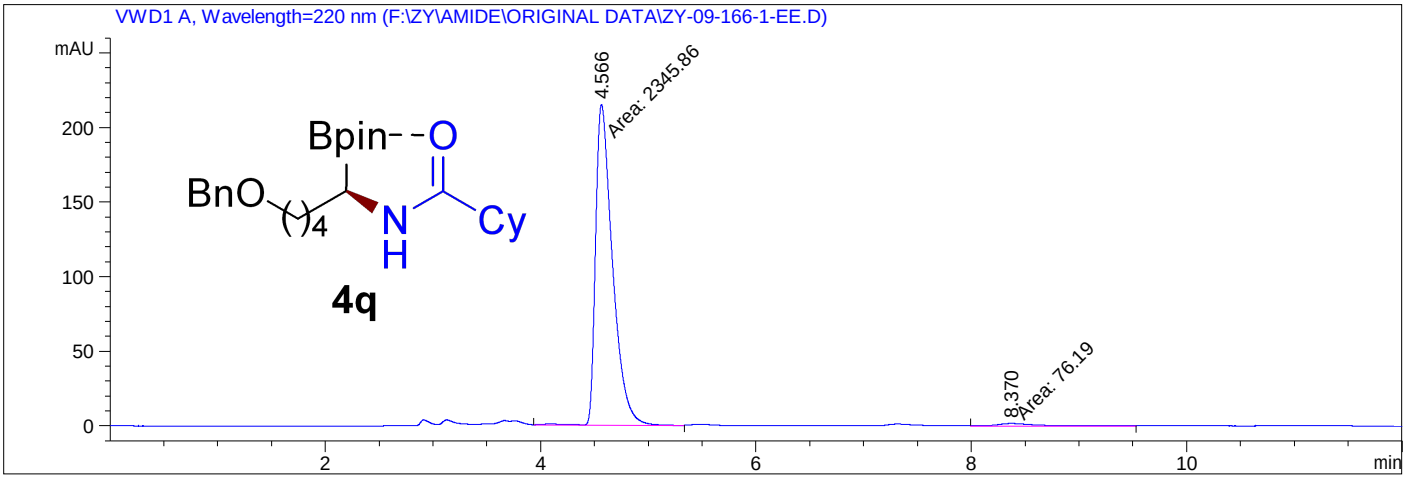
    Totals :                   5141.41089  355.05503


    ======================================================================
                            *** End of Report ***
```

Supplementary Figure 255: HPLC spectrum of (±)-**4q**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-166-1-EE.D
Sample Name: ZY-09-166-1-EE

```
    ======================================================================
    Acq. Operator    : 系统                              Seq. Line :   9
    Acq. Instrument : HPLC-1260                          Location :   2
    Injection Date  : 12/3/2021 11:53:59 AM                  Inj :   1
                                                      Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.800 µl
    Acq. Method     : D:\zy\20211203\YH 2021-12-03 09-47-06\5IPA-20-1.0-1-6-220-JXL.M
    Last changed    : 12/3/2021 11:14:35 AM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/28/2022 11:19:09 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.566 MF    0.1819 2345.85986  214.88185  96.8543
       2   8.370 MM    0.6441   76.19001    1.97147   3.1457

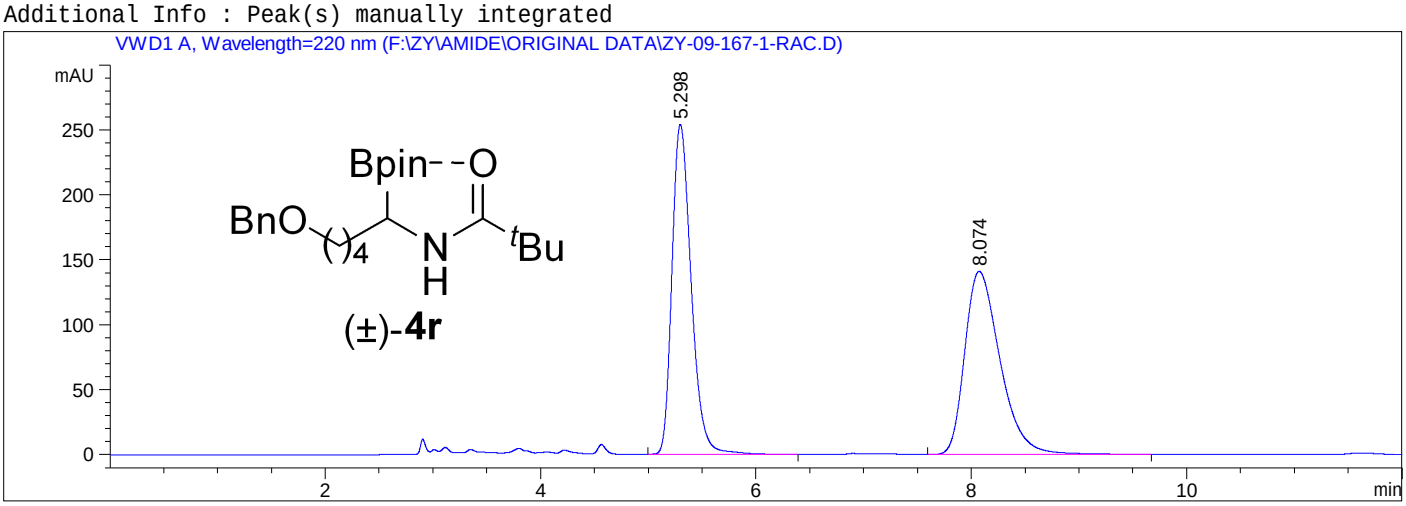
    Totals :                  2422.04987  216.85332


    ======================================================================
                            *** End of Report ***
```

Supplementary Figure 256: HPLC spectrum of **4q**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-167-1-RAC.D
Sample Name: ZY-09-167-1-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                      Location :   31
Injection Date  : 12/5/2021 10:10:44 PM              Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.800 µl
Acq. Method     : D:\zy\20211129\YH 2021-12-05 21-28-00\5IPA-15-1-1-2-220-JXL.M
Last changed    : 12/5/2021 9:53:06 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/28/2022 11:26:24 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.298 BB    0.1920 3145.98950  253.95166  49.5685
   2   8.074 BB    0.3471 3200.76025  140.88438  50.4315

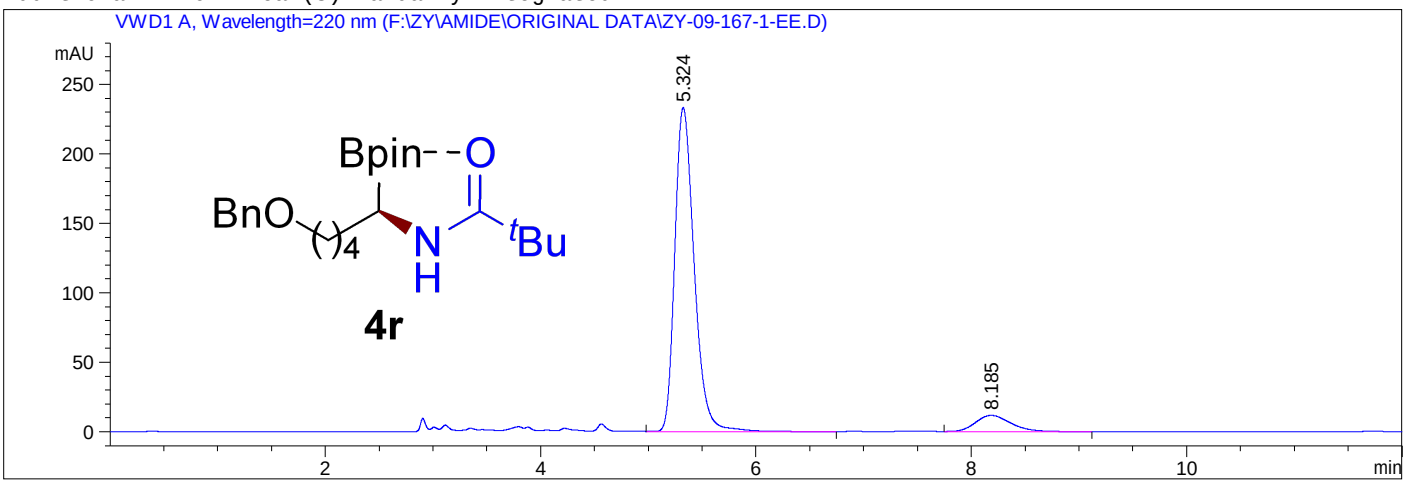
Totals :                  6346.74976  394.83604


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 257: HPLC spectrum of (±)-**4r**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-167-1-EE.D
Sample Name: ZY-09-167-1-EE

```
    ======================================================================
    Acq. Operator    : 系统                          Seq. Line :   3
    Acq. Instrument : HPLC-1260                       Location :   32
    Injection Date  : 12/5/2021 9:53:10 PM                 Inj :   1
                                                   Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.600 µl
    Acq. Method     : D:\zy\20211129\YH 2021-12-05 21-28-00\5IPA-15-1-1-2-220-JXL.M
    Last changed    : 12/5/2021 9:53:06 PM by 系统
                      (modified after loading)
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/28/2022 11:25:31 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.324 BB    0.1931 2913.18408  233.36481  91.6417
       2   8.185 BB    0.3437  265.69937   11.66675   8.3583

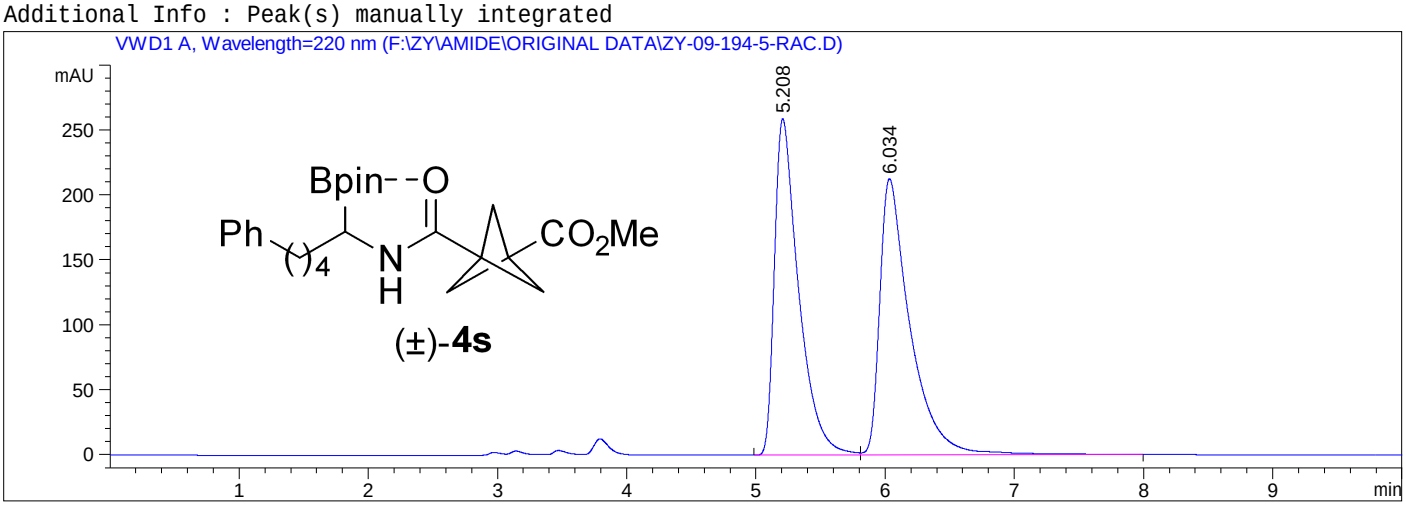
    Totals :                   3178.88345  245.03156


    ======================================================================
                              *** End of Report ***
```

Supplementary Figure 258: HPLC spectrum of **4r**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-194-5-RAC.D
Sample Name: ZY-09-194-5-RAC

```
    ======================================================================
    Acq. Operator    : 系统                              Seq. Line :   7
    Acq. Instrument : HPLC-1260                          Location :   22
    Injection Date  : 1/3/2022 10:53:04 AM                    Inj :   1
                                                      Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.600 µl
    Acq. Method     : D:\zy\20211226\YH 2022-01-03 09-22-34\5IPA-15-1.0-1-2-220.M
    Last changed    : 1/3/2022 10:03:22 AM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/29/2022 9:49:15 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.208 BV    0.1897 3366.52661  258.92990  49.2252
       2   6.034 VV R  0.2345 3472.50415  212.65123  50.7748

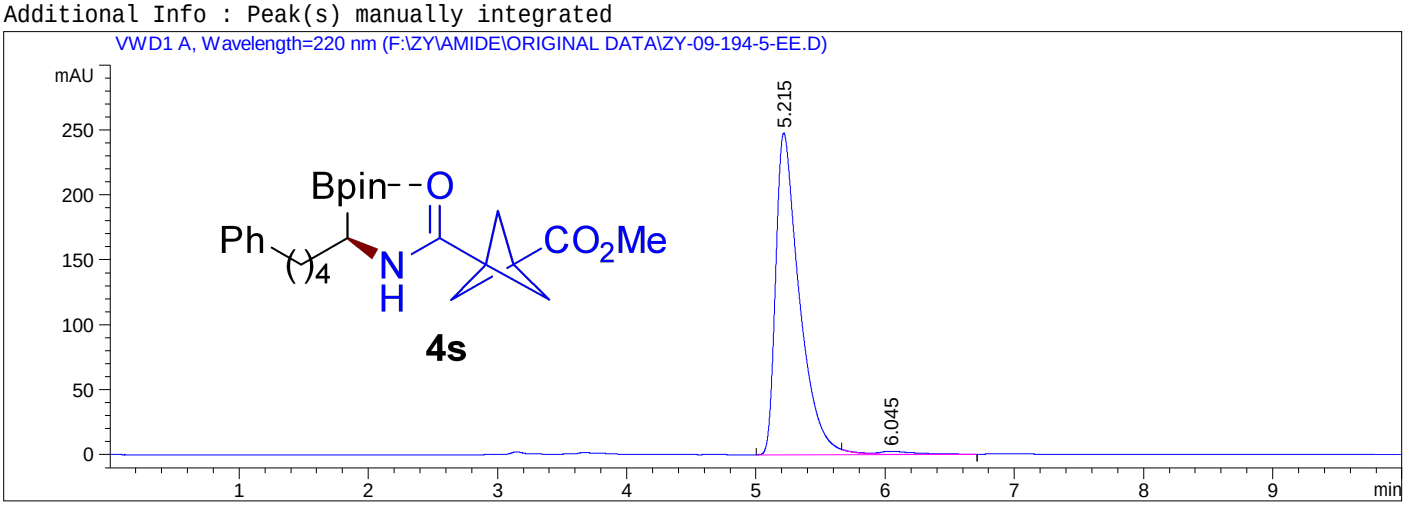
    Totals :                   6839.03076  471.58113


    ======================================================================
                            *** End of Report ***
```

Supplementary Figure 259: HPLC spectrum of (±)-**4s**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-194-5-EE.D
Sample Name: ZY-09-194-5-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   6
Acq. Instrument : HPLC-1260                      Location :   21
Injection Date  : 1/3/2022 10:36:44 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\zy\20211226\YH 2022-01-03 09-22-34\5IPA-15-1.0-1-2-220.M
Last changed    : 1/3/2022 10:03:22 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:49:15 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.215 BV R  0.1852 3155.59595  247.50763  98.5435
   2   6.045 VB E  0.2622   46.64185    2.39526   1.4565

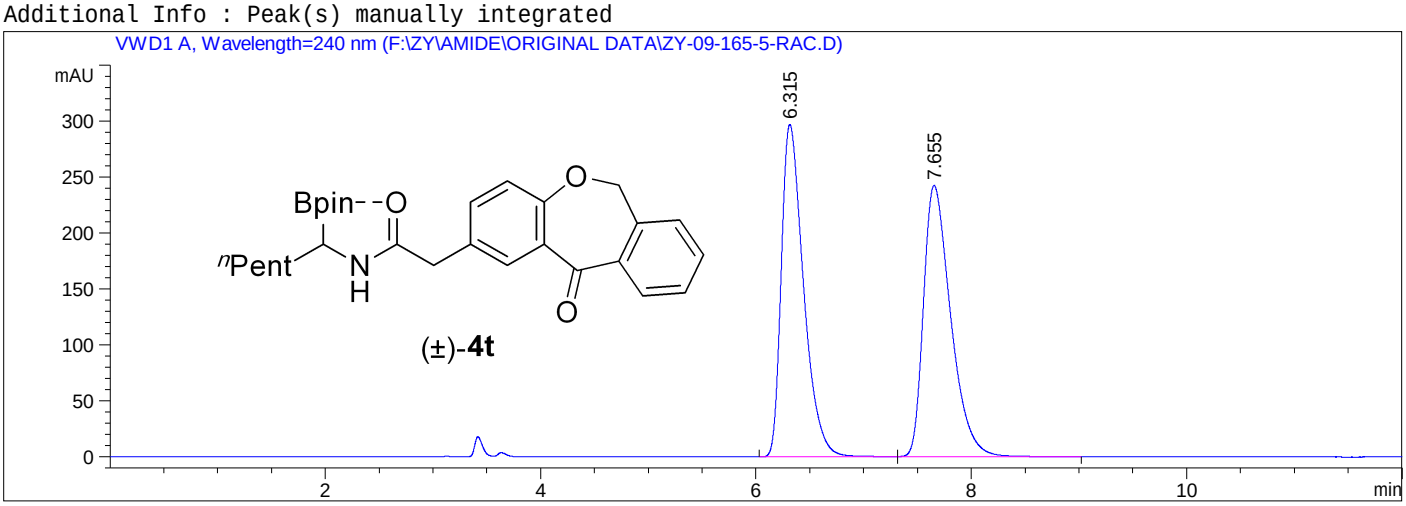
Totals :                  3202.23780  249.90289


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 260: HPLC spectrum of **4s**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-165-5-RAC.D
Sample Name: ZY-09-165-5-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   3
Acq. Instrument : HPLC-1260                      Location :   52
Injection Date  : 12/27/2021 9:31:34 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\zy\20211226\YH 2021-12-27 08-56-44\10IPA15_1-1-2-240.M
Last changed    : 12/27/2021 8:56:44 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/28/2022 11:11:46 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.315 BB    0.2177 4259.83740  297.23294  50.0306
   2   7.655 BB    0.2678 4254.63379  242.33784  49.9694

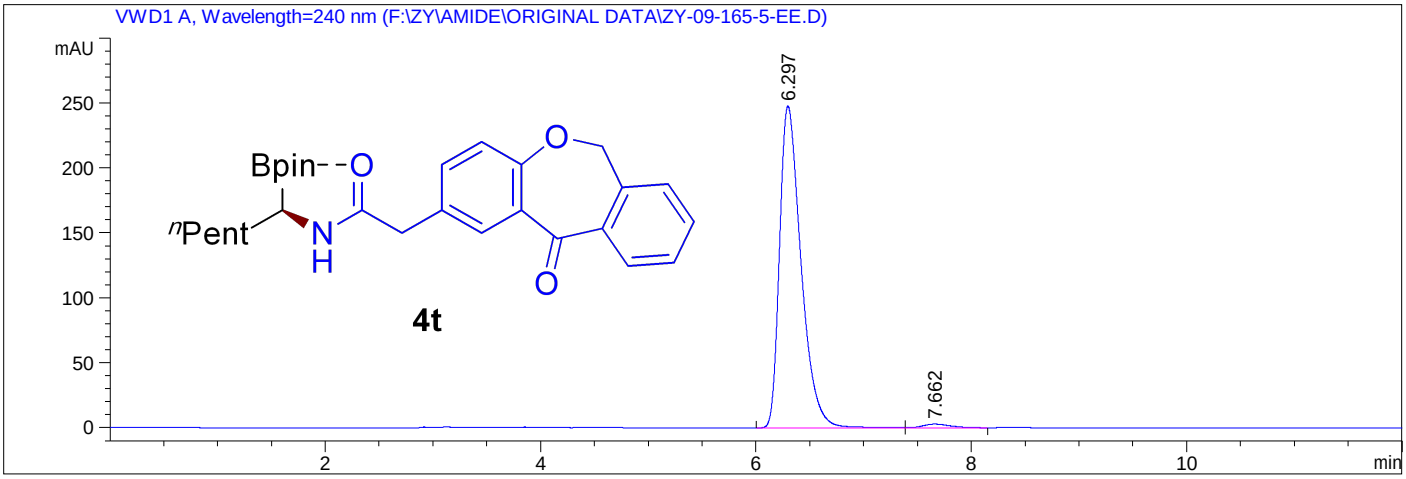
Totals :                  8514.47119  539.57079


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 261: HPLC spectrum of (±)-**4t**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-165-5-EE.D
Sample Name: ZY-09-165-5-EE

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   9
Acq. Instrument : HPLC-1260                      Location :   51
Injection Date  : 12/27/2021 10:58:49 AM             Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.300 µl
Acq. Method     : D:\zy\20211226\YH 2021-12-27 08-56-44\10IPA15_1-1-2-240.M
Last changed    : 12/27/2021 8:56:44 AM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/28/2022 11:11:10 PM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.297 BV    0.2116 3430.65576  247.72098  98.5969
   2   7.662 VB    0.2450   48.82105    2.81994   1.4031

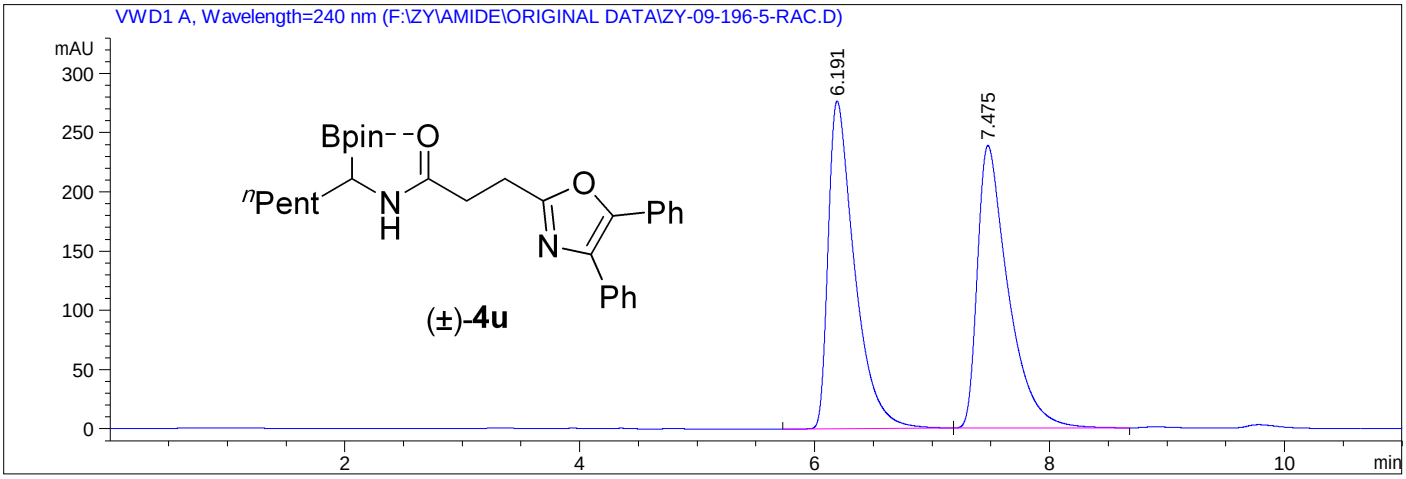
Totals :                  3479.47681  250.54092


==========================================================================
                          *** End of Report ***
```

Supplementary Figure 262: HPLC spectrum of **4t**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-196-5-RAC.D
Sample Name: ZY-09-196-5-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   7
Acq. Instrument : HPLC-1260                      Location :   22
Injection Date  : 1/2/2022 7:10:31 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\zy\20211226\YH 2022-01-02 17-33-48\5IPA20_8-1-2-240.M
Last changed    : 1/2/2022 6:35:59 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:57:32 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.191 BB    0.2315 4319.26270  276.83588  49.8534
   2   7.475 BB    0.2675 4344.66309  238.48940  50.1466

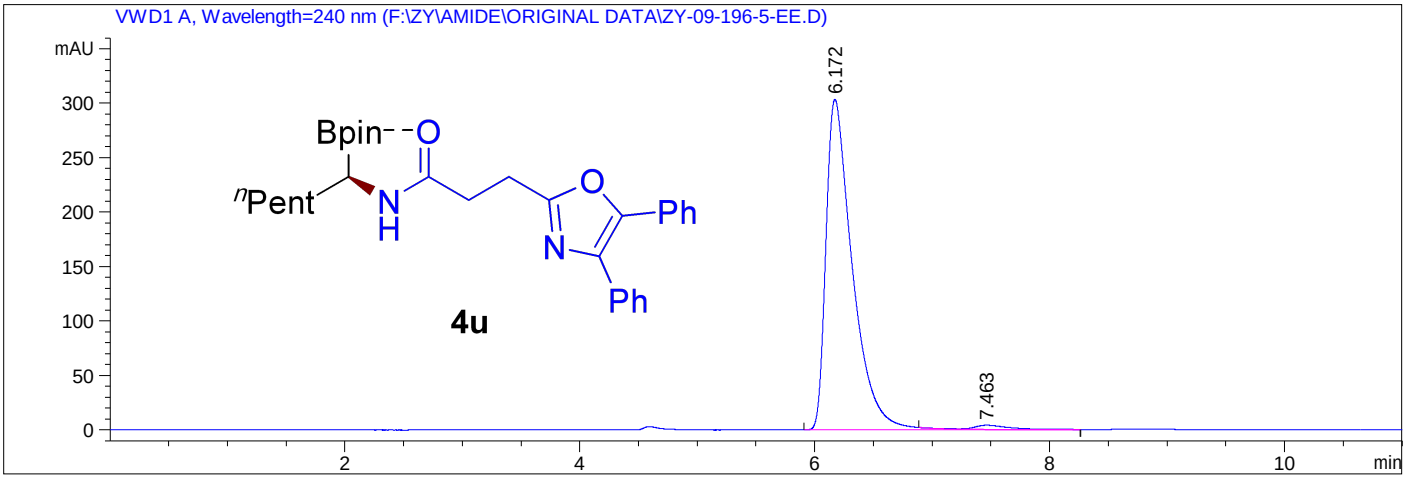
Totals :                  8663.92578  515.32527


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 263: HPLC spectrum of (±)-**4u**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-196-5-EE.D
Sample Name: ZY-09-196-5-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   6
Acq. Instrument : HPLC-1260                      Location :   21
Injection Date  : 1/2/2022 6:49:09 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\zy\20211226\YH 2022-01-02 17-33-48\5IPA20_8-1-2-240.M
Last changed    : 1/2/2022 6:35:59 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:58:14 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.172 BV R  0.2321 4751.24121  303.63879  98.3375
   2   7.463 VB E  0.2815   80.32556    3.88019   1.6625

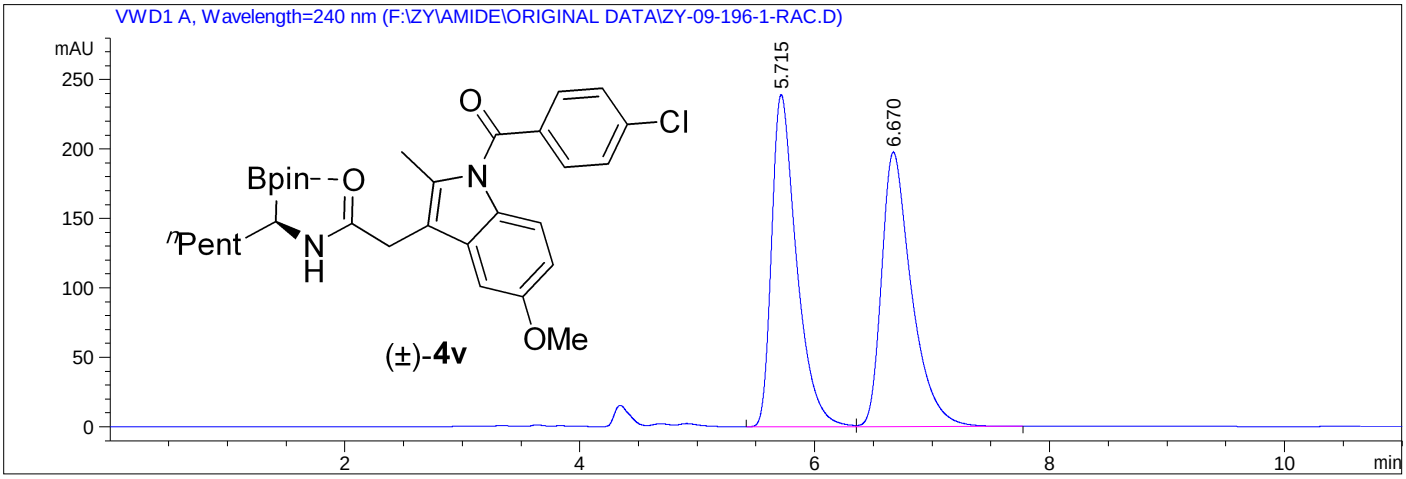
Totals :                  4831.56677  307.51899


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 264: HPLC spectrum of **4u**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-196-1-RAC.D
Sample Name: ZY-09-196-1-RAC

```
    ======================================================================
    Acq. Operator   : 系统                          Seq. Line :   4
    Acq. Instrument : HPLC-1260                      Location :   62
    Injection Date  : 12/31/2021 2:05:31 PM              Inj :   1
                                                   Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
    Acq. Method     : D:\zy\20211226\YH 2021-12-31 13-15-03\10IPA15_1-1-2-240.M
    Last changed    : 12/31/2021 1:15:03 PM by 系统
    Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                      Method)
    Last changed    : 3/29/2022 9:56:17 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                           Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=240 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.715 BV    0.2207 3531.01099  239.23489  50.1104
       2   6.670 VB    0.2635 3515.44824  197.65958  49.8896

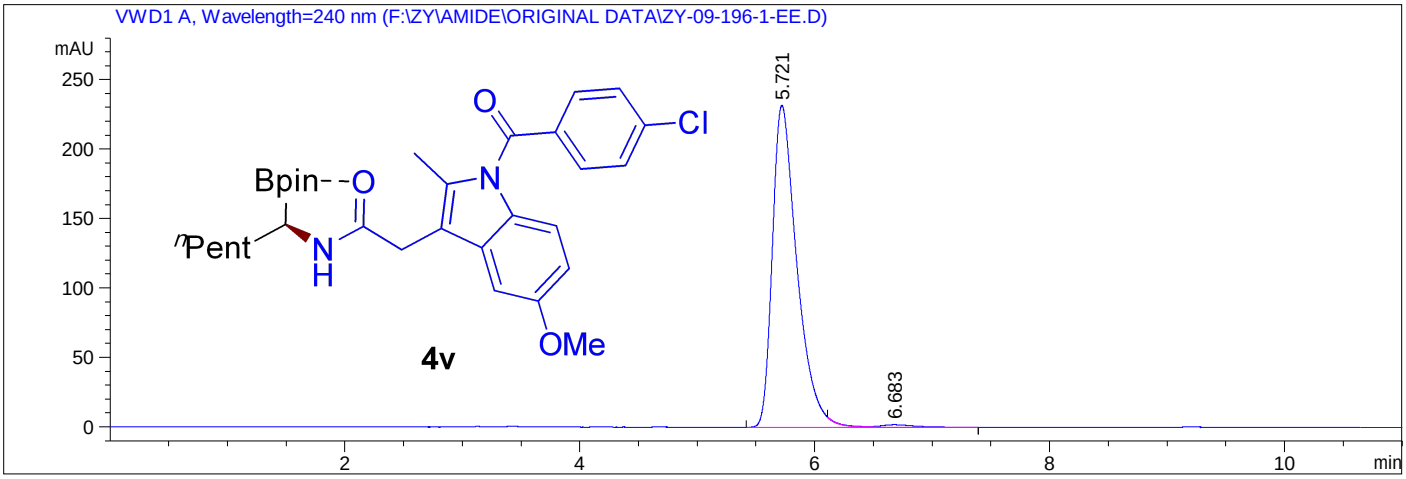
    Totals :                   7046.45923  436.89447


    ======================================================================
                           *** End of Report ***
```

Supplementary Figure 265: HPLC spectrum of (±)-**4v**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-09-196-1-EE.D
Sample Name: ZY-09-196-1-EE

```
==========================================================================
Acq. Operator    : 系统                          Seq. Line :   3
Acq. Instrument : HPLC-1260                       Location :   61
Injection Date  : 12/31/2021 1:49:06 PM              Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\zy\20211226\YH 2021-12-31 13-15-03\10IPA15_1-1-2-240.M
Last changed    : 12/31/2021 1:15:03 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 9:56:17 AM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.721 BV R  0.2181 3378.15308  231.75551  98.8486
   2   6.683 VB E  0.2638   39.34804    1.82285   1.1514

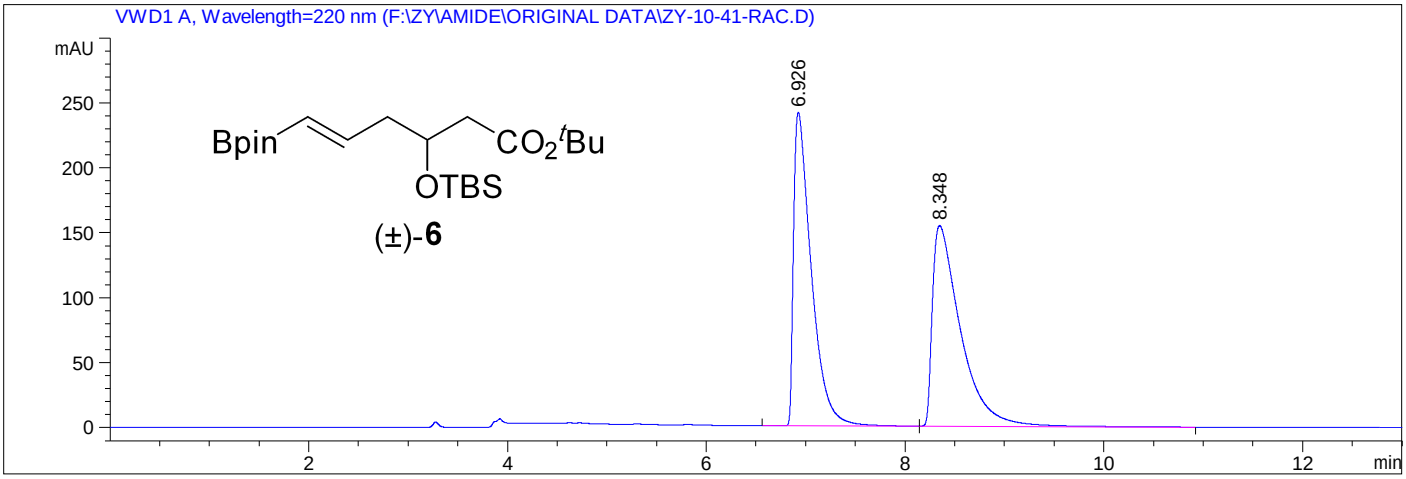
Totals :                  3417.50111  233.57836


==========================================================================
                          *** End of Report ***
```

Supplementary Figure 266: HPLC spectrum of **4v**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-41-RAC.D
Sample Name: ZY-10-41-RAC

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   6
Acq. Instrument : HPLC-1260                      Location :   83
Injection Date  : 3/2/2022 9:59:13 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.800 µl
Acq. Method     : D:\zy\20220302\YH 2022-03-02 20-49-54\0.5IPA-15-1.0-1-2-220-SFT.M
Last changed    : 3/2/2022 9:25:44 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 10:06:28 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.926 VB R  0.1845 2990.16821  241.46602  49.5881
   2   8.348 BB    0.2910 3039.84058  154.54143  50.4119

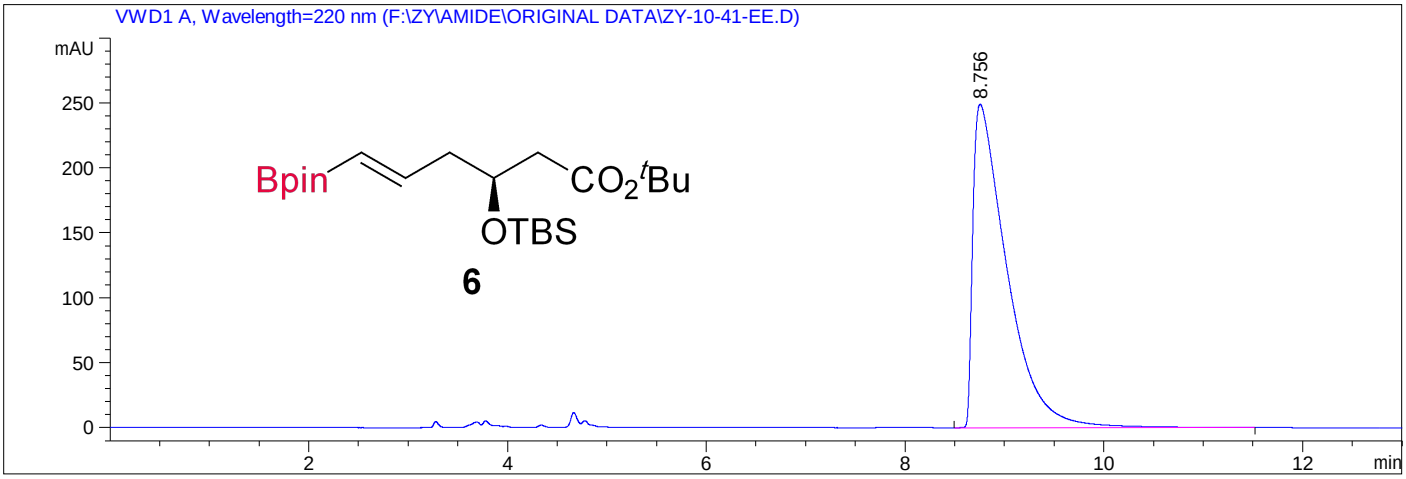
Totals :                  6030.00879  396.00745


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 267: HPLC spectrum of (±)-**6**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-41-EE.D
Sample Name: ZY-10-41-EE

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   5
Acq. Instrument : HPLC-1260                      Location :   82
Injection Date  : 3/2/2022 9:44:50 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.500 µl
Acq. Method     : D:\zy\20220302\YH 2022-03-02 20-49-54\0.5IPA-15-1.0-1-2-220-SFT.M
Last changed    : 3/2/2022 9:25:44 PM by 系统
Analysis Method : E:\DATA\20220316\LC 2022-03-16 22-19-08\10IPA-10-1.0-1.MZWJ.M (Sequence
                  Method)
Last changed    : 3/29/2022 10:06:28 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.756 BB    0.3500 5931.49121  248.95393 100.0000

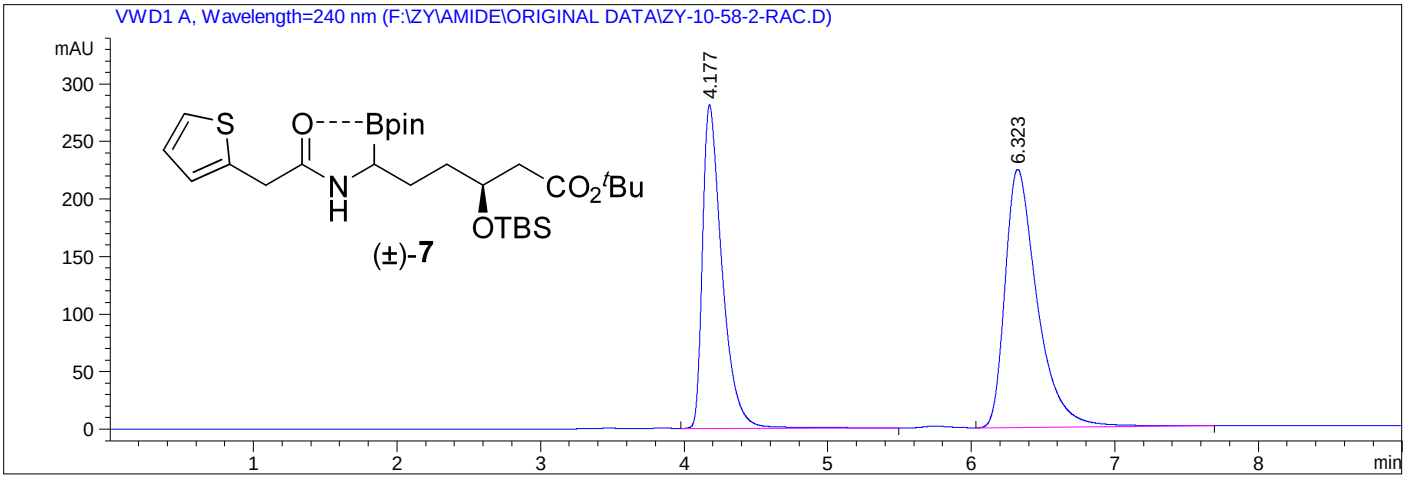
Totals :                  5931.49121  248.95393


=====================================================================
                        *** End of Report ***
```

Supplementary Figure 268: HPLC spectrum of **6**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-58-2-RAC.D
Sample Name: ZY-10-58-2-RAC

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  18
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 3/23/2022 7:12:12 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.500 µl
Acq. Method     : D:\zy\20220302\YH 2022-03-23 15-01-36\5IPA-15-1.0-1-6-240.M
Last changed    : 3/23/2022 6:43:30 PM by 系统
Analysis Method : C:\CHEM32\1\METHODS\0.2IPA-10-0.5-1-XYH-EQ.M
Last changed    : 3/29/2022 10:11:05 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.177 BV R  0.1429 2674.33887  281.27936  43.2703
   2   6.323 BB    0.2293 3506.19946  224.38475  56.7297

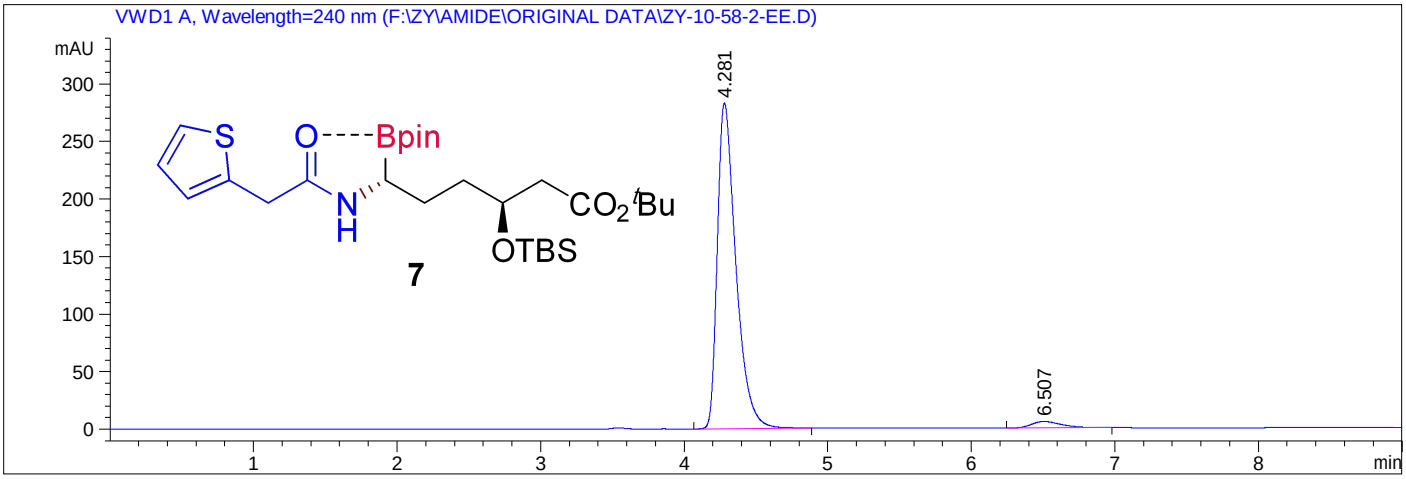
Totals :                  6180.53833  505.66411


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 269: HPLC spectrum of (±)-**7**.

Data File F:\ZY\AMIDE\ORIGINAL DATA\ZY-10-58-2-EE.D
Sample Name: ZY-10-58-2

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   7
Acq. Instrument : HPLC-1260                      Location :   87
Injection Date  : 3/28/2022 11:27:04 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 4.500 µl
Acq. Method     : D:\zy\20220328\YH 2022-03-28 10-02-43\5IPA15_10-1-2-240.M
Last changed    : 3/28/2022 10:02:43 AM by 系统
Analysis Method : C:\CHEM32\1\METHODS\0.2IPA-10-0.5-1-XYH-EQ.M
Last changed    : 3/29/2022 10:10:25 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=240 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.281 BB    0.1348 2543.26392  283.05804  96.8887
   2   6.507 BB    0.2216   81.67083    5.60107   3.1113

Totals :                  2624.93475  288.65911


==========================================================================
                        *** End of Report ***
```

Supplementary Figure 270: HPLC spectrum of **7**.

III. Supplementary References

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