Supporting Information

Three-Component Cross-Electrophile Coupling: Regioselective Electrochemical Dialkylation of Alkenes

Lingxiang Lu,[†] Yi Wang,[†] Wendy Zhang,[‡] Wen Zhang,[†] Kimberly A. See,[‡] Song Lin*[,†]

[†]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States
[‡]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

*Email: songlin@cornell.edu

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S1. General Information

All reactions were carried out in oven-dried glassware with magnetic stirring under nitrogen. 1,2-Dimethoxyethane (DME) and tetrahydrofuran (THF) were dried over molecular sieves before use. Mg anode and graphite cathode were polished before use. Since alkyl bromides decompose over time during storage, the use of freshly prepared/distilled substrates is recommended. All other chemicals were used as received. Flash column chromatography was performed using silica gel (230−400 mesh) from SiliCycle. Nuclear magnetic resonance (NMR) spectra were measured on Bruker NMR instruments (^{1}H at 500 MHz, ^{13}C{^{1}H} at 126 MHz, ^{19}F at 470 MHz, ^{19}F{^{1}H} at 376 MHz, ^{31}P at 202 MHz). Data for ^{1}H NMR spectra are reported as follows: chemical shift δ (ppm) referenced to $CHCl_3$ (7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constant J (Hz), and integration. Data for ^{13}C{^{1}H} NMR spectra are reported as follows: chemical shift δ (ppm) referenced to $CDCl_3$ (77.16 ppm), multiplicity (null = singlet, d = doublet, q = quartet), and coupling constant J (Hz). Data for ^{19}F and ^{31}P NMR spectra are reported in terms of chemical shift δ (ppm) and multiplicity (s = singlet, t = triplet, m = multiplet). Data for ^{19}F{^{1}H} NMR spectra are reported in terms of chemical shift δ (ppm). High-resolution mass spectra (HRMS) were recorded on Thermo Scientific Exactive Orbitrap mass spectrometers with direct analysis in real time (DART) or electron impact ionization (EI).

S2. General Procedure for Electrochemical Dialkylation of Alkenes

In a nitrogen-regulated glovebox, an oven-dried 5-mL ElectraSyn vial was charged with tetrabutylammonium perchlorate ($TBAClO_4$, 2.0 mmol, 2.0 equiv) and a stir bar. Then, a solution of alkene (1.0 mmol, 1.0 equiv), tertiary alkyl bromide (2.0 mmol, 2.0 equiv), and primary alkyl bromide (1.0 mmol, 1.0 equiv) in 4.0 mL of anhydrous DME was added and the reaction mixture was stirred to dissolve the electrolyte. After that, the ElectraSyn vial and cap equipped with anode (Mg plate) and cathode (graphite plate) were screwed tight, transferred out of the glovebox, and mounted onto the ElectraSyn 2.0 device. A nitrogen balloon was attached to the cap and the reaction mixture was electrolyzed with magnetic stirring (stirring rate: 1200 rpm) at a constant current of 2.5 mA until passing 3.0 F/mol of charge at room temperature (22 °C). Upon completion of electrolysis, the reaction mixture was passed through a plug of silica gel (ca. 8 cm thick) and eluted with 125 mL of 20% Et_2O in hexanes (the volume includes that of the solvent used to rinse the reaction vial and electrodes). The filtrate was concentrated under reduced pressure and the crude product was purified by flash column chromatography (silica gel) to afford the desired product.

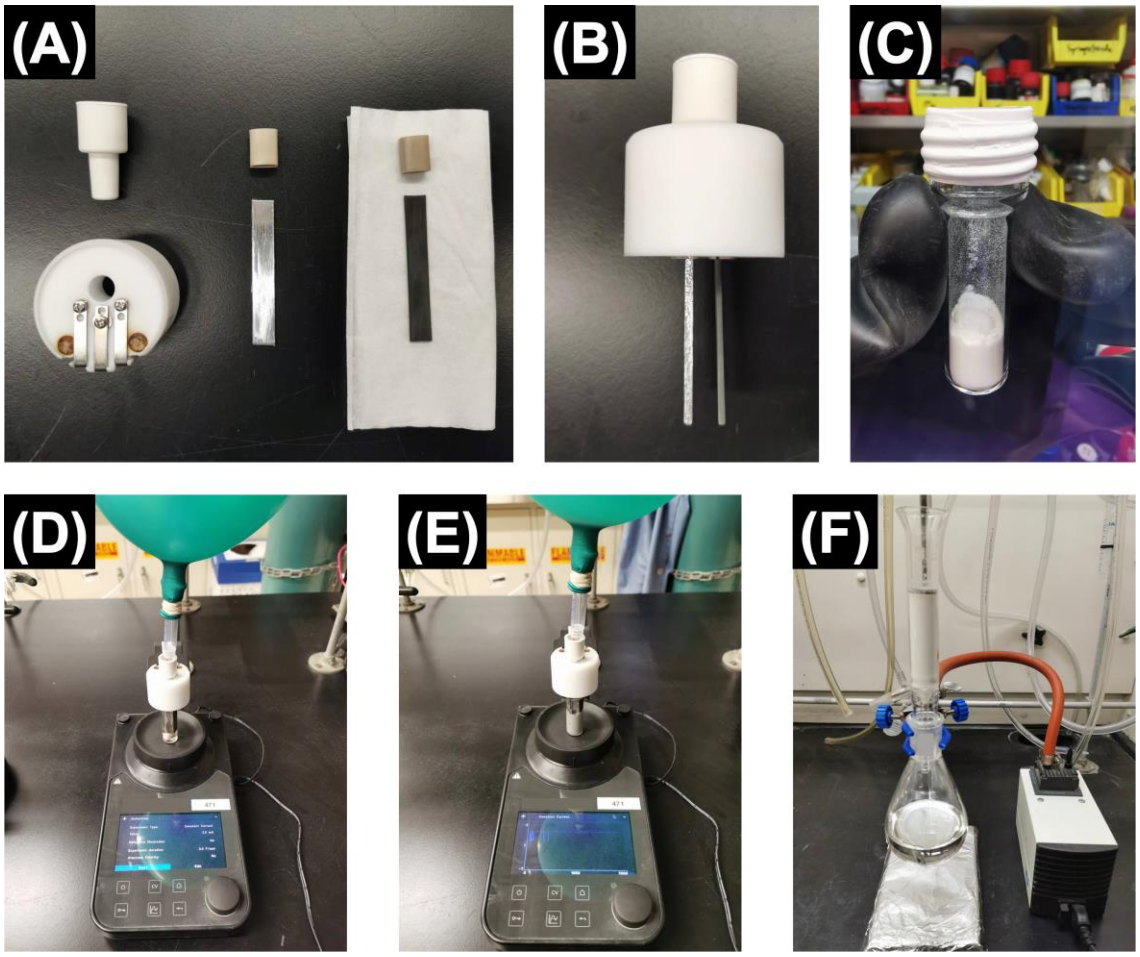
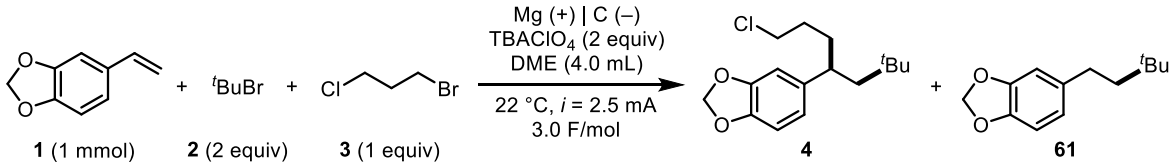


Figure S1. Electrochemical setup for alkene dialkylation. (A) Rubber septum, ElectraSyn cap, and electrodes. (B) ElectraSyn cap equipped with electrodes. (C) ElectraSyn vial with electrolyte and stir bar. The screw thread was covered with polytetrafluoroethylene (PTFE) tape. (D) Reaction mixture before electrolysis. (E) Reaction mixture after electrolysis. (F) Filtration to remove electrolyte and magnesium salts.

S3. Optimization of Reaction Conditions

The reaction optimization was shown in Table S1. The main identifiable side product **61** arose from hydroalkylation of **1** with tertiary alkyl bromide **2**, presumably from interception of carbanion intermediate **F** (see Scheme 2A in the main text for the structure) by the tetrabutylammonium electrolyte (via Hofmann elimination), **2** (via E2 elimination), or residual water (via protonation). For electron-rich alkenes, conditions in entry 5 were used for increasing the conversion of alkenes. For other alkenes, conditions in entry 1 were applied unless otherwise specified.

Table S1. Reaction Optimization[a]



1 (1 mmol) **2** (2 equiv) **3** (1 equiv) **4** **61**

entry	variation from above conditions	conversion of **1** (%)	yield of **4** (%)	yield of **61** (%)
1	none	>95	71	8
2	2.5 F/mol	>95	54	9
3	1 equiv of **2**	>95	49	7
4	2 equiv of **3**	>95	76	6
5	2 equiv of **3**, 3.5 F/mol	>95	80	6
6	entry 5, THF instead of DME	>95	8	<5
7	THF/^{t}BuCN instead of DME	>95/82	25/18	15/26
8	BDD/glassy carbon cathode	71/76	12/10	<5/<5
9	Ni foam/Pt cathode	94/>95	13/11	<5/<5
10	Zn/Al anode	>95/10	<5/<5	<5/<5
11	$TBABF_4$/TBAOTf	>95/>95	25/<5	9/<5
12	$LiClO_4$/LiOTf	80/>95	16/<5	6/<5
13	Mg powder without electrolysis	90	<5	<5
14	Mg electrode without electrolysis	46	<5	<5
15	divided cell, Zn anode	90	35	<5
16	0.5 mmol of **1**[b]	92	60	9

[a]Yields determined by ^{1}H NMR analysis using dibromomethane as the internal standard. [b]With **1** (0.5 mmol), **2** (2 equiv), **3** (1 equiv). BDD, boron-doped diamond. Tf, trifluoromethanesulfonyl.

S4. Cyclic Voltammetry Studies

All cyclic voltammetry studies were conducted in a nitrogen-regulated glovebox on EC Epsilon (BASi). Measurements were performed in 0.5 M $TBAClO_4$ in DME using a divided three-compartment cell. $Mg(OTf)_2$, which bears a redox-innocent anion, was used as the Mg^{2+} source instead of $MgCl_2$ due to its higher solubility in DME. Control experiments revealed no difference of $Mg(OTf)_2$ and $MgCl_2$ in the scan range of −3.0 to 0.5 V versus $Zn^{2+/0}$. Scan rate is 100 mV/s. Concentration of alkyl halides and alkenes is 0.5 mg/mL.

Supporting electrolyte: $TBAClO_4$ was recrystallized from EtOAc for three times and dried under vacuum at 65 °C overnight.

Solvent: DME was first dried overnight with KOH, and then refluxed with sodium and benzophenone under nitrogen for 5 h. The water content was determined by a Karl Fischer titrator to be <5 ppm.

Working electrode: The working electrode is a glassy carbon electrode (3 mm in diameter). It was polished with 1.0, 0.3, and 0.05 μm aluminum oxide, and then sonicated in distilled water and acetone before air drying and transferring into the glovebox.

Reference electrode: The reference electrode consisted of a zinc wire submerged in a saturated solution of $Zn(OTf)_2$ in THF. The Zn wire was polished with sandpaper and washed with acetone before transferring into the glovebox. After each set of scan, ferrocene was added to reference the final potential to ferrocenium/ferrocene redox couple ($Fc^{+/0}$).

Counter electrode: The counter electrode is a platinum wire that was burned for 30 s with a butane torch before transferring into the glovebox.

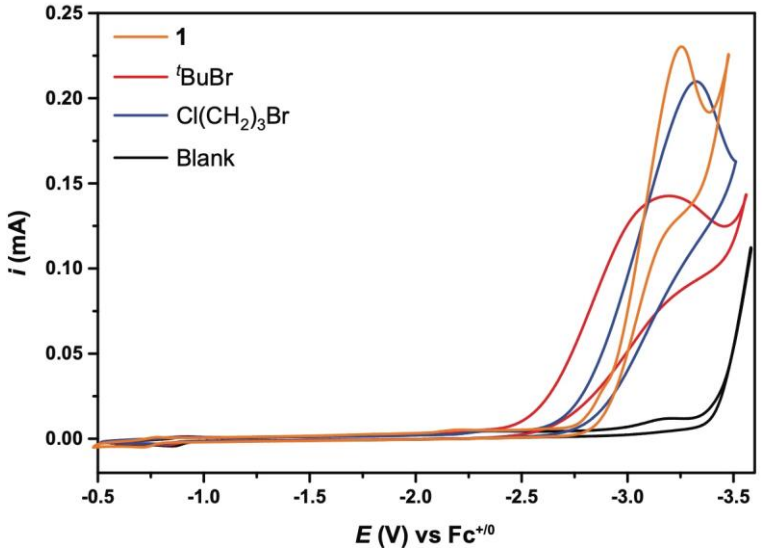


Figure S2. Cyclic voltammetry of alkene 1, *tert*-butyl bromide (2), and 1-bromo-3-chloropropane (3). The onset potential is −2.8, −2.4, and −2.6 V for **1**, **2**, and **3**, respectively, indicating *tert*-butyl bromide underwent reduction preferentially over the others.

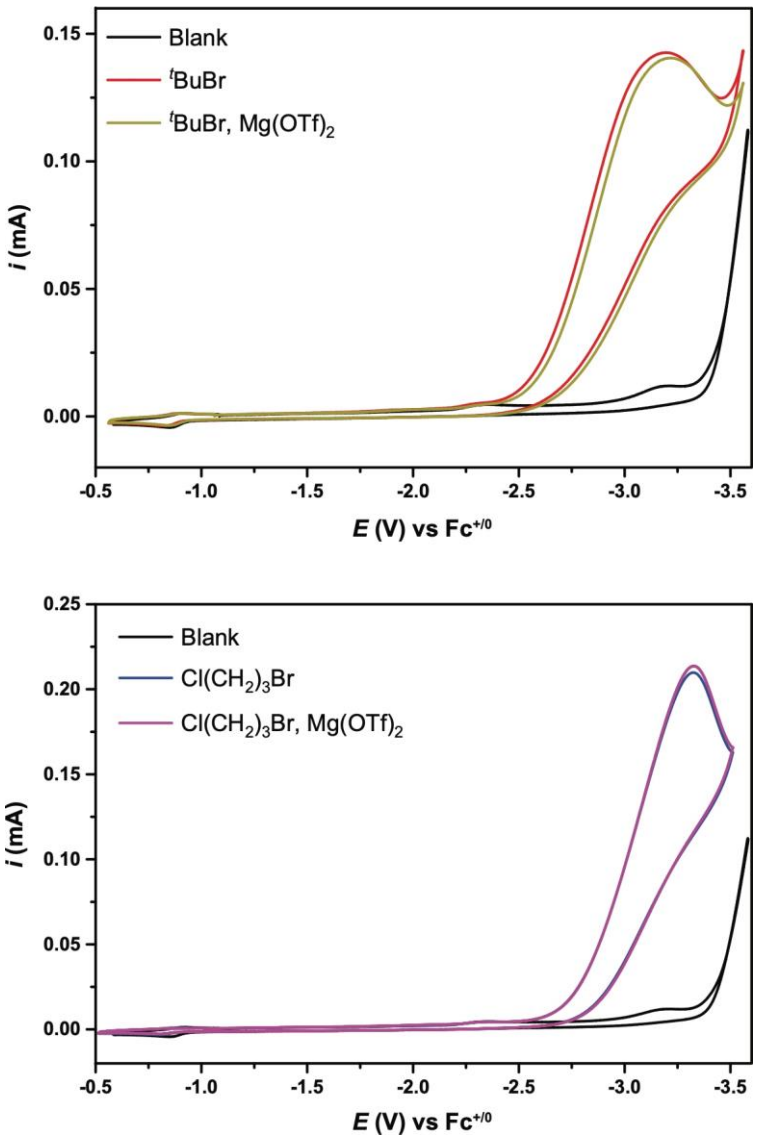


Figure S3. Cyclic voltammetry of tertiary and primary alkyl bromides with and without Mg^{2+}. Mg^{2+} does not affect the redox potential or peak current.

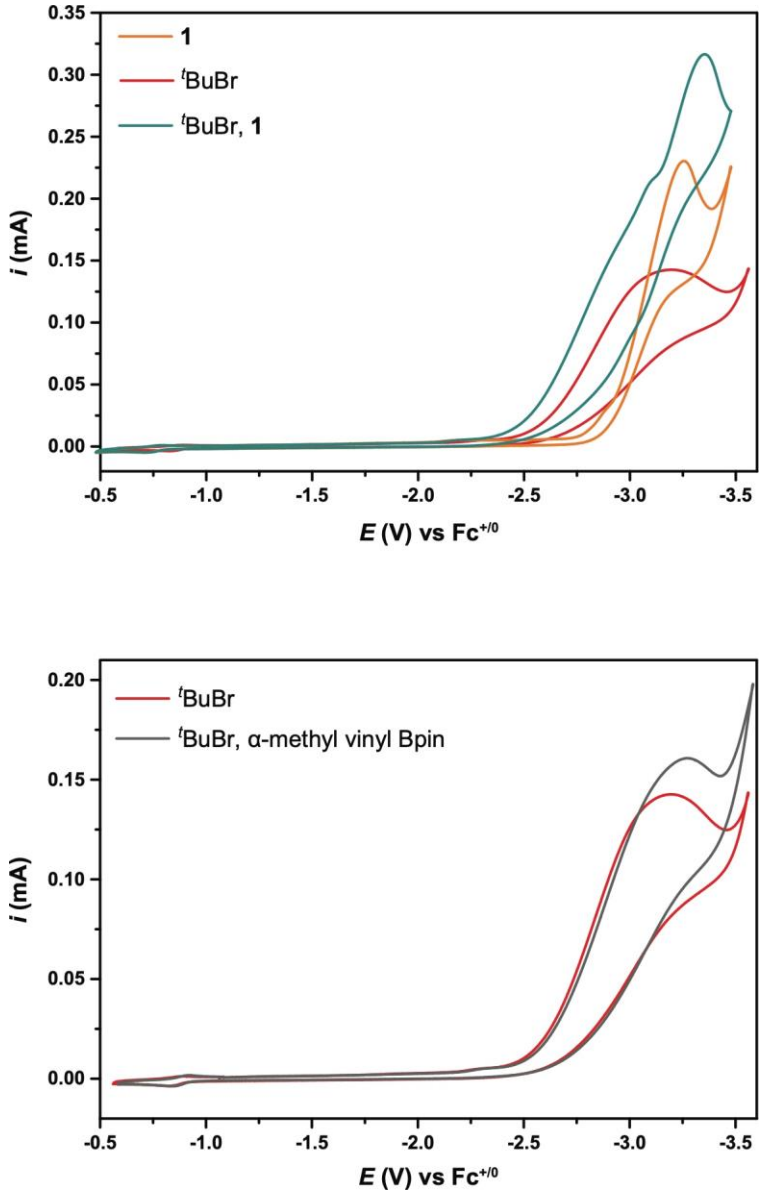


Figure S4. Cyclic voltammetry of *tert*-butyl bromide with and without alkenes. Current enhancement was observed in both cases, indicating that the intermediates from alkyl halide reduction can interact with alkenes.

S5. Voltage Profile Measurements

All experiments were conducted in a nitrogen-regulated glovebox on a VMP3 potentiostat (BioLogic). Electrochemical dialkylation of alkenes were conducted in a three-electrode configuration with Mg counter electrode (CE), graphite working electrode (WE), and Ag wire pseudo-reference electrode. The pseudo-reference electrode is used to isolate the CE potential changes from those at the WE. The Mg electrode was mechanically ablated within the glovebox, prior to use, to remove any oxide layer on the surface. The CE and WE were connected to the potentiostat via copper wire. The experiments were carried out in a 10-mL round-bottom vial equipped with a stir bar and a screw cap with pierceable PTFE septum. The reaction (1.5 mmol scale) was electrolyzed at a constant current of −2.5 mA (j = −0.5 mA/cm^2) until passing 3.5 F/mol of charge (57 h) at room temperature.

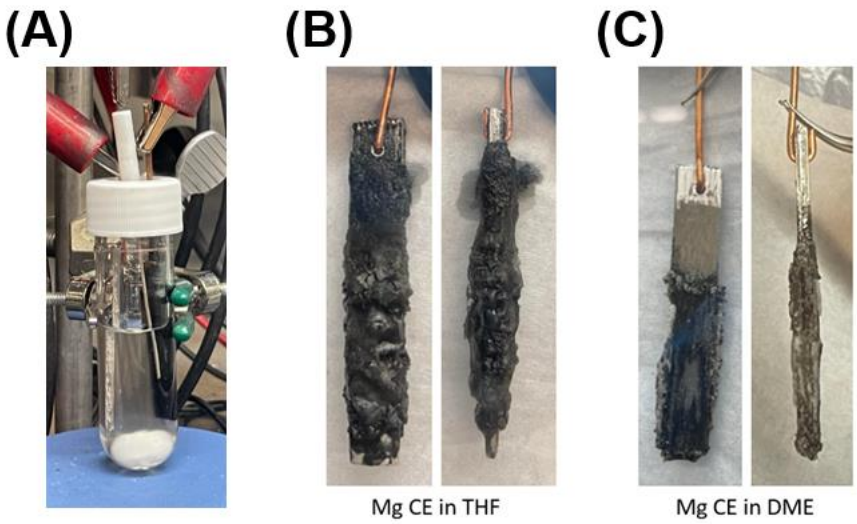


Figure S5. Electrochemical setup for voltage profile measurements. (A) Reaction mixture before electrolysis. (B) Mg counter electrode after electrolysis in THF. (C) Mg counter electrode after electrolysis in DME.

S6. Substrate Scope

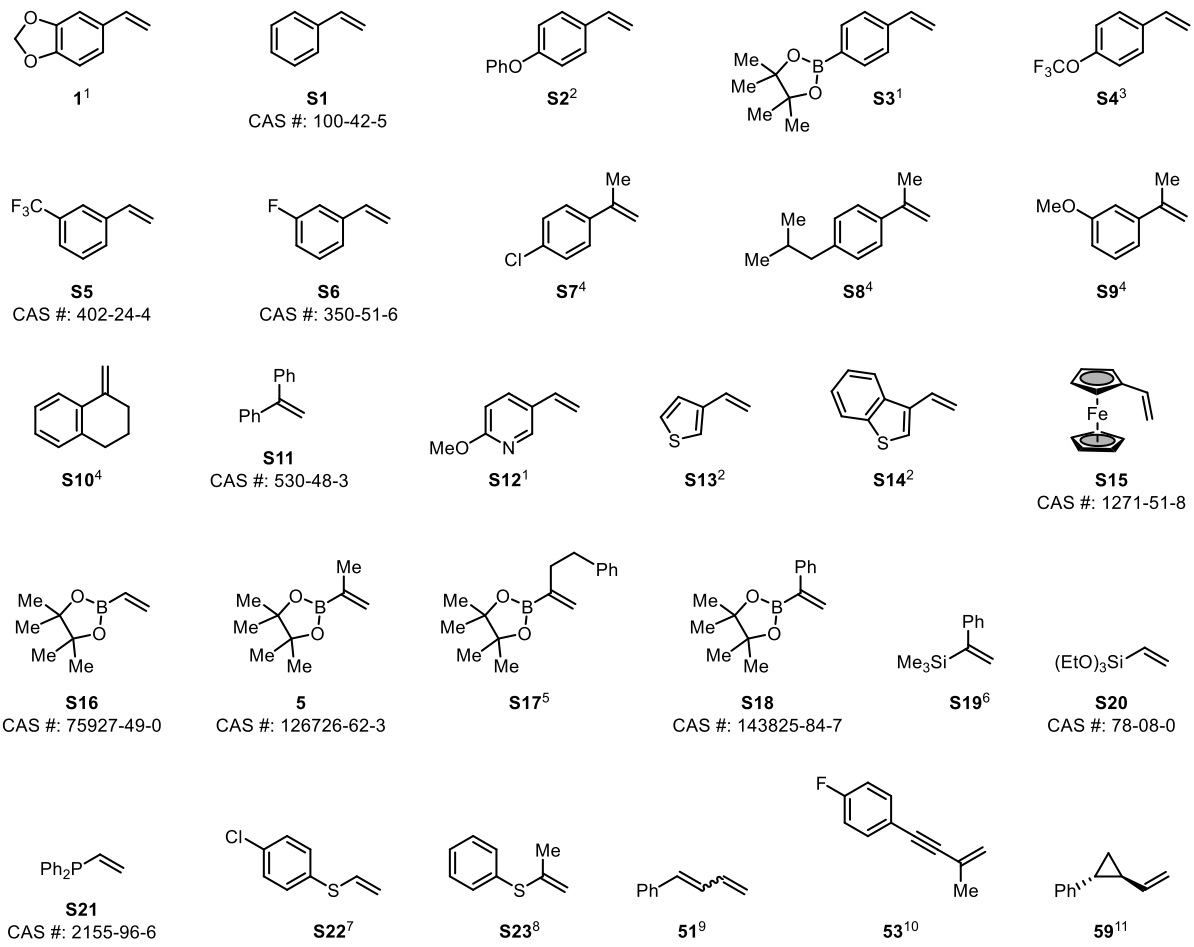


Figure S6. Scope of alkenes.

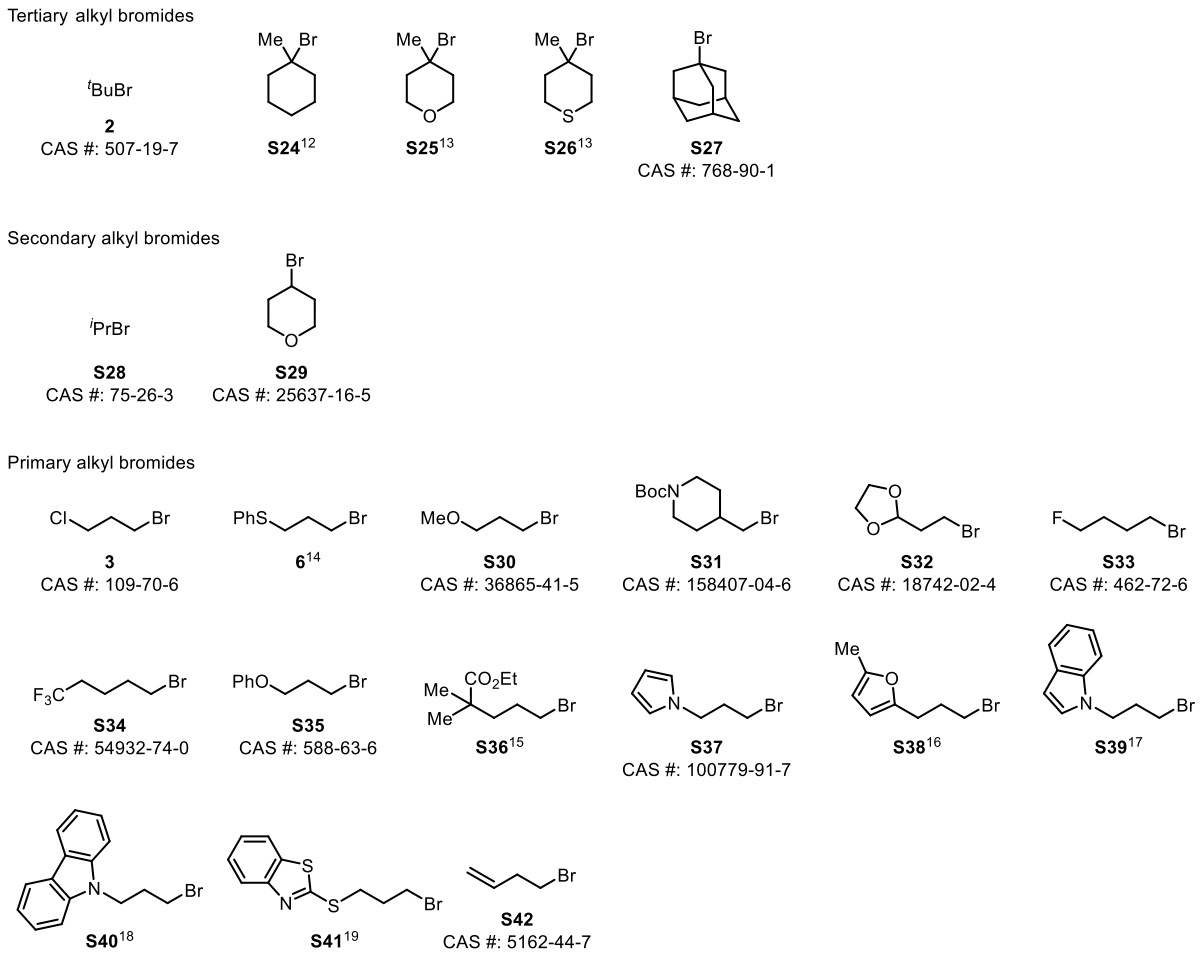


Figure S7. Scope of electrophiles. Boc, *tert*-butyloxycarbonyl. Ts, 4-toluenesulfonyl.

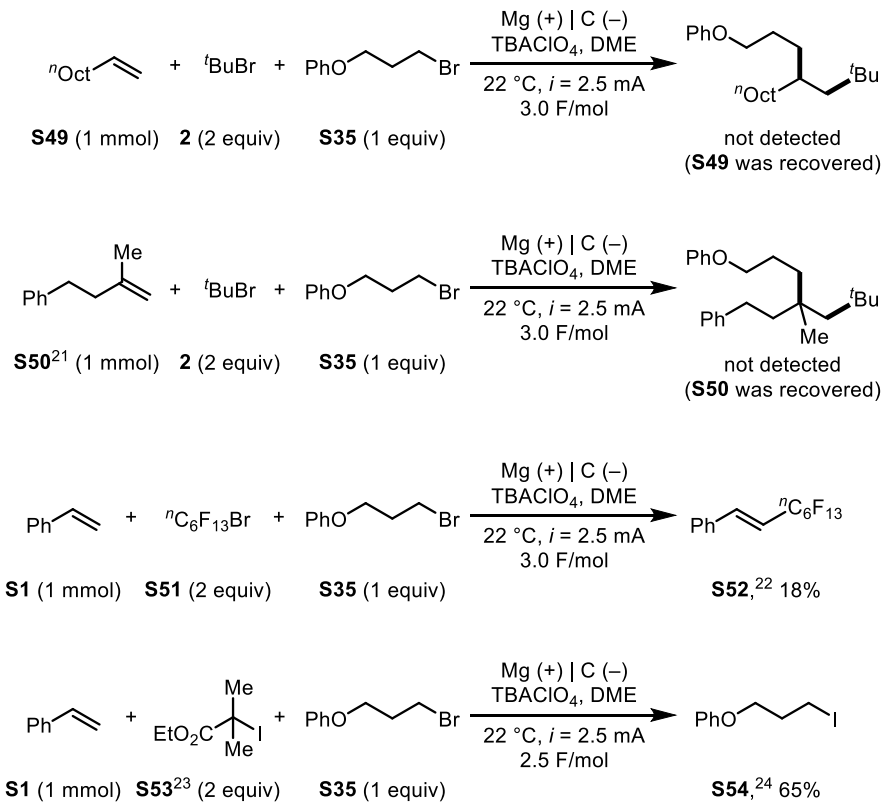
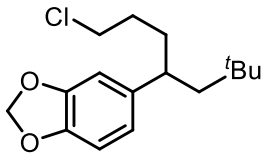


Figure S8. Unsuccessful substrates. The yields were determined by ^{1}H NMR analysis using dibromomethane as the internal standard.

S7. Characterization of Products



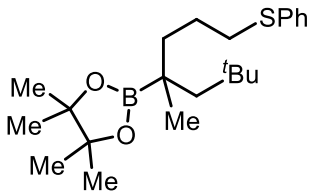
5-(1-Chloro-6,6-dimethylheptan-4-yl)benzo[*d*][1,3]dioxole (4)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (Q = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **4** (224 mg, 0.792 mg, 79%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.70 (d, J = 7.9 Hz, 1H), 6.65 (d, J = 1.6 Hz, 1H), 6.60 (dd, J = 7.9, 1.6 Hz, 1H), 5.92 (s, 2H), 3.48−3.40 (m, 2H), 2.59−2.51 (m, 1H), 1.75−1.46 (m, 6H), 0.78 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 147.8, 145.7, 141.0, 121.0, 108.2, 107.8, 100.9, 51.1, 45.3, 42.0, 37.1, 31.4, 30.9, 30.2.

HRMS (DART−Orbitrap, m/z): $[M - H]^+$ calculated for $C_{16}H_{22}ClO_2^+$: 281.1303; found: 281.1280.



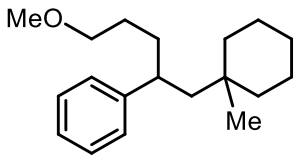
4,4,5,5-Tetramethyl-2-(4,6,6-trimethyl-1-(phenylthio)heptan-4-yl)-1,3,2-dioxaborolane (7)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **7** (278 mg, 0.739 mmol, 74%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.31 (d, J = 7.6 Hz, 2H), 7.28−7.23 (m, 2H), 7.14 (t, J = 7.3 Hz, 1H), 2.92−2.81 (m, 2H), 1.75−1.64 (m, 1H), 1.63−1.46 (m, 3H), 1.30 (apparent td, J = 12.7, 4.4 Hz, 1H), 1.22−1.15 (m, 13H), 0.95 (s, 3H), 0.93 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 137.2, 128.93, 128.90, 125.7, 83.2, 52.7, 41.1, 34.5, 31.8, 31.7, 25.3, 25.12, 25.08, 22.9. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{22}H_{38}BO_2S^+$: 377.2680; found: 377.2670.



(5-Methoxy-1-(1-methylcyclohexyl)pentan-2-yl)benzene (8)

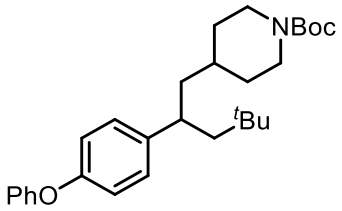
The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (Q = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **8** (184

mg, 0.671 mmol, 67%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.26−7.22 (m, 2H), 7.18−7.11 (m, 3H), 3.32−3.23 (m, 2H), 3.27 (s, 3H), 2.67−2.58 (m, 1H), 1.75 (dd, *J* = 14.1, 8.6 Hz, 1H), 1.69−1.60 (m, 1H), 1.57−1.48 (m, 2H), 1.48−1.33 (m, 4H), 1.33−1.17 (m, 6H), 1.06−1.00 (m, 2H), 0.73 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 148.0, 128.3, 128.0, 125.7, 73.0, 58.6, 49.4, 41.6, 38.7, 38.5, 36.6, 33.8, 28.0, 26.6, 25.4, 22.2, 22.1.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{19}H_{31}O^+$: 275.2369; found: 275.2356.



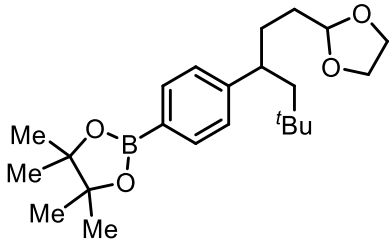
***tert*-Butyl 4-(4,4-dimethyl-2-(4-phenoxyphenyl)pentyl)piperidine-1-carboxylate (9)**

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **9** (315 mg, 0.697 mmol, 70%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.32 (apparent t, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 4.02 (brs, 2H), 2.79−2.70 (m, 1H), 2.66−2.45 (m, 2H), 1.76 (d, *J* = 12.0 Hz, 1H), 1.63 (dd, *J* = 13.9, 8.6 Hz, 1H), 1.55−1.38 (m, 4H), 1.44 (s, 9H), 1.17−0.98 (m, 3H), 0.78 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 157.8, 155.02, 155.01, 142.7, 129.8, 129.0, 123.0, 119.1, 118.6, 79.3, 51.4, 46.9, 38.6, 33.4, 33.0, 31.7, 31.5, 30.3, 28.6.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{29}H_{42}NO_3^+$: 452.3159; found: 452.3135.



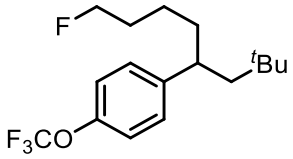
2-(4-(1-(1,3-Dioxolan-2-yl)-5,5-dimethylhexan-3-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **10** (198 mg, 0.510 mmol, 51%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.70 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.74 (apparent t, *J* = 4.7 Hz, 1H), 3.95−3.85 (m, 2H), 3.84−3.73 (m, 2H), 2.68−2.59 (m, 1H), 1.78−1.66 (m, 2H), 1.65−1.57 (m, 1H), 1.56−1.45 (m, 2H), 1.38−1.32 (m, 1H), 1.33 (s, 12H), 0.75 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 150.9, 135.0, 127.5, 104.7, 83.7, 65.0, 64.9, 50.6, 42.9, 33.9, 32.2, 31.5, 30.3, 25.04, 25.02. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M - H]^+$ calculated for $C_{23}H_{36}BO_4^+$: 387.2701; found: 387.2680.



1-(8-Fluoro-2,2-dimethyloctan-4-yl)-4-(trifluoromethoxy)benzene (11)

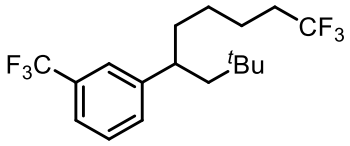
The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **11** (193 mg, 0.602 mmol, 60%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.17 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.45−4.37 (m, 1H), 4.35−4.27 (m, 1H), 2.67−2.59 (m, 1H), 1.73−1.46 (m, 6H), 1.30−1.20 (m, 1H), 1.18−1.05 (m, 1H), 0.77 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 147.4 (q, *J* = 2 Hz), 146.4, 129.0, 120.9, 120.7 (q, *J* = 256 Hz), 84.2 (d, *J* = 164 Hz), 50.8, 42.2, 39.6, 31.5, 30.5 (d, *J* = 19 Hz), 30.2, 23.4 (d, *J* = 5 Hz).

^{19}F NMR (470 MHz, $CDCl_3$, *δ*): −57.9 (s), −217.8 – −218.2 (m).

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{17}H_{25}F_4O^+$: 321.1836; found: 321.1817.



1-(9,9,9-Trifluoro-2,2-dimethylnonan-4-yl)-3-(trifluoromethyl)benzene (12)

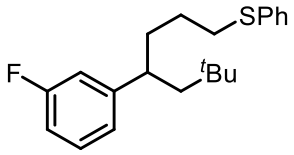
The reaction was performed on 1.00 mmol scale following the general procedure (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **12** (139 mg, 0.392 mmol, 39%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.43 (d, *J* = 7.7 Hz, 1H), 7.41−7.36 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 2.72−2.63 (m, 1H), 2.05−1.90 (m, 2H), 1.70 (dd, *J* = 14.1, 8.8 Hz, 1H), 1.66−1.37 (m, 5H), 1.28−1.16 (m, 1H), 1.12−0.99 (m, 1H), 0.77 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 148.6, 131.4, 130.8 (q, *J* = 32 Hz), 128.9, 127.3 (q, *J* = 276 Hz), 124.5 (q, *J* = 4 Hz), 124.4 (q, *J* = 272 Hz), 122.9 (q, *J* = 4 Hz), 50.7, 42.6, 39.4, 33.7 (q, *J* = 28 Hz), 31.5, 30.2, 26.8, 21.9 (q, *J* = 3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$, *δ*): −62.5 (s), −66.5 (apparent t, *J* = 10.9 Hz).

HRMS (EI−Orbitrap, *m*/*z*): $M^{+\bullet}$ calculated for $C_{18}H_{24}F_6^+$: 354.1777; found: 354.1779.



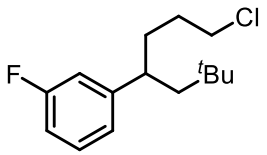
(4-(3-Fluorophenyl)-6,6-dimethylheptyl)(phenyl)sulfane (13)

The reaction was performed on 1.00 mmol scale following the general procedure (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **13** (248 mg, 0.750 mmol, 75%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.26−7.23 (m, 4H), 7.23−7.12 (m, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.88−6.81 (m, 2H), 2.89−2.76 (m, 2H), 2.65−2.56 (m, 1H), 1.77−1.56 (m, 3H), 1.53−1.43 (m, 2H), 1.43−1.32 (m, 1H), 0.77 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 163.1 (d, *J* = 245 Hz), 150.2 (d, *J* = 7 Hz), 136.8, 129.8 (d, *J* = 8 Hz), 129.2, 128.9, 125.9, 123.7 (d, *J* = 3 Hz), 114.5 (d, *J* = 21 Hz), 112.8 (d, *J* = 21 Hz), 50.8, 42.3 (d, *J* = 2 Hz), 38.7, 33.8, 31.4, 30.2, 27.1.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{21}H_{28}FS^+$: 331.1890; found: 331.1865.



1-(1-Chloro-6,6-dimethylheptan-4-yl)-3-fluorobenzene (14)

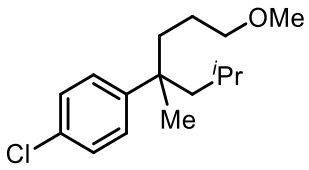
The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **14** (205 mg, 0.798 mmol, 80%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.25−7.19 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.90−6.83 (m, 2H), 3.50−3.38 (m, 2H), 2.67−2.60 (m, 1H), 1.80−1.66 (m, 2H), 1.65−1.56 (m, 2H), 1.56−1.46 (m, 2H), 0.78 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 163.2 (d, *J* = 245 Hz), 150.0 (d, *J* = 7 Hz), 129.9 (d, *J* = 8 Hz), 123.7 (d, *J* = 3 Hz), 114.5 (d, *J* = 21 Hz), 112.9 (d, *J* = 21 Hz), 50.8, 45.2, 42.1 (d, *J* = 2 Hz), 36.9, 31.4, 30.8, 30.2.

^{19}F NMR (470 MHz, $CDCl_3$, *δ*): −113.5 − −113.6 (m).

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{15}H_{23}ClF^+$: 257.1467; found: 257.1455.



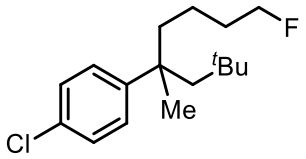
1-Chloro-4-(1-methoxy-4,6-dimethylheptan-4-yl)benzene (15)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **15** (171 mg, 0.636 mmol, 64%) as a light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.26−7.20 (m, 4H), 3.28−3.23 (m, 2H), 3.26 (s, 3H), 1.73−1.61 (m, 2H), 1.56−1.37 (m, 4H), 1.30 (s, 3H), 1.19−1.08 (m, 1H), 0.80 (d, *J* = 6.3 Hz, 3H), 0.56 (d, *J* = 6.4 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 146.6, 131.2, 128.2, 128.1, 73.4, 58.6, 52.7, 40.9, 40.8, 25.4, 24.8, 24.7, 24.5, 23.7.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{16}H_{26}ClO^+$: 269.1667; found: 269.1653.



1-Chloro-4-(8-fluoro-2,2,4-trimethyloctan-4-yl)benzene (16)

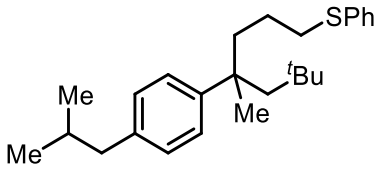
The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **16** (213 mg, 0.748 mmol, 75%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.23 (s, 4H), 4.43−4.35 (m, 1H), 4.33−4.25 (m, 1H), 1.86 (d, *J* = 14.6 Hz, 1H), 1.68−1.47 (m, 5H), 1.41 (s, 3H), 1.31−1.20 (m, 1H), 0.90−0.79 (m, 1H), 0.71 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 146.8, 131.1, 128.3, 128.0, 84.2 (d, *J* = 164 Hz), 56.6, 46.4, 41.6, 32.5, 32.2, 31.1 (d, *J* = 19 Hz), 24.0, 19.6 (d, *J* = 5 Hz).

^{19}F NMR (470 MHz, $CDCl_3$, *δ*): −217.7 − −218.1 (m).

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{17}H_{27}ClF^+$: 285.1780; found: 285.1765.



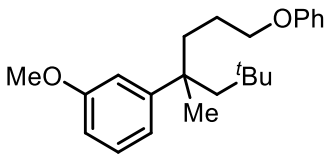
(4-(4-Isobutylphenyl)-4,6,6-trimethylheptyl)(phenyl)sulfane (17)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **17** (242 mg, 0.632 mmol, 63%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.23−7.20 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14−7.09 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 2.79 (apparent t, *J* = 7.2 Hz, 2H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.88−1.77 (m, 3H), 1.64 (apparent td, *J* = 12.7, 4.6 Hz, 1H), 1.55 (d, *J* = 14.7 Hz, 1H), 1.53−1.44 (m, 1H), 1.38 (s, 3H), 1.25−1.14 (m, 1H), 0.87 (apparent d, *J* = 6.5 Hz, 6H), 0.69 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 145.0, 138.6, 137.1, 128.9, 128.6, 126.5, 125.7, 56.9, 45.5, 45.1, 41.4, 34.5, 32.5, 32.1, 30.3, 24.3, 23.6, 22.52, 22.49.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{26}H_{39}S^+$: 383.2767; found: 383.2747.



1-Methoxy-3-(4,6,6-trimethyl-1-phenoxyheptan-4-yl)benzene (18)

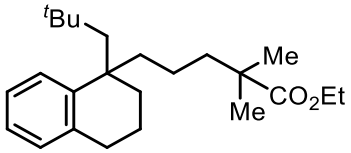
The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **18** (269 mg, 0.790 mmol, 79%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.26−7.22 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.96−6.87 (m, 3H), 6.85−6.80 (m, 2H), 6.70

(dd, *J* = 8.1, 2.3 Hz, 1H), 3.84−3.78 (m, 2H), 3.81 (s, 3H), 1.91 (d, *J* = 14.6 Hz, 1H), 1.84−1.75 (m, 1H), 1.70−1.62 (m, 2H), 1.60 (d, *J* = 14.6 Hz, 1H), 1.44 (s, 3H), 1.35−1.25 (m, 1H), 0.74 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, *δ*): 159.4, 159.2, 149.9, 129.5, 128.8, 120.6, 119.7, 114.5, 113.8, 109.8, 68.5, 56.8, 55.3, 42.7, 41.6, 32.5, 32.1, 24.2, 24.0.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{23}H_{33}O_2^+$: 341.2475; found: 341.2458.



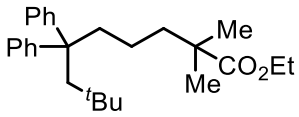
Ethyl 2,2-dimethyl-5-(1-neopentyl-1,2,3,4-tetrahydronaphthalen-1-yl)pentanoate (19)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **19** (245 mg, 0.683 mmol, 68%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.22 (d, *J* = 7.8 Hz, 1H), 7.09−7.04 (m, 1H), 7.04−6.97 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.81−2.66 (m, 2H), 2.07−1.98 (m, 1H), 1.88 (d, *J* = 14.9 Hz, 1H), 1.85−1.77 (m, 1H), 1.75−1.60 (m, 3H), 1.56−1.48 (m, 2H), 1.46−1.36 (m, 2H), 1.20−1.12 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 3H), 1.09 (s, 3H), 1.02−0.91 (m, 1H), 0.85 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, *δ*): 178.2, 145.0, 137.0, 129.2, 127.2, 125.4, 125.0, 60.3, 53.1, 45.3, 42.4, 41.8, 41.5, 32.5, 32.3, 31.8, 31.0, 25.5, 25.2, 20.1, 20.0, 14.4.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{24}H_{39}O_2^+$: 359.2945; found: 359.2925.



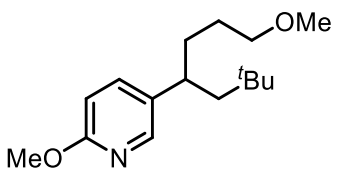
Ethyl 2,2,8,8-tetramethyl-6,6-diphenylnonanoate (20)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **20** (356 mg, 0.902 mmol, 90%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.23−7.14 (m, 8H), 7.13−7.08 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.23−2.16 (m, 2H), 2.22 (s, 2H), 1.47−1.40 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H), 1.04 (s, 6H), 0.95−0.86 (m, 2H), 0.68 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, *δ*): 178.0, 150.3, 128.3, 127.7, 125.5, 60.3, 49.6, 48.8, 42.3, 41.5, 39.1, 32.3, 31.9, 25.3, 20.1, 14.3.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{27}H_{39}O_2^+$: 395.2945; found: 395.2926.



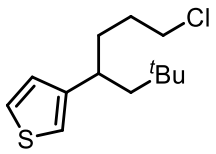
2-Methoxy-5-(1-methoxy-6,6-dimethylheptan-4-yl)pyridine (21)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (Q = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **21** (154 mg, 0.580 mmol, 58%) as a light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.93 (d, J = 2.4 Hz, 1H), 7.39 (dd, J = 8.5, 2.4 Hz, 1H), 6.68 (d, J = 8.5 Hz, 1H), 3.91 (s, 3H), 3.32−3.24 (m, 2H), 3.27 (s, 3H), 2.62−2.53 (m, 1H), 1.69−1.58 (m, 2H), 1.54 (dd, J = 14.1, 3.3 Hz, 1H), 1.51−1.36 (m, 2H), 1.36−1.23 (m, 1H), 0.77 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 162.8, 146.1, 137.8, 135.3, 110.8, 72.8, 58.7, 53.4, 50.5, 39.0, 36.2, 31.4, 30.3, 27.8.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{16}H_{28}NO_2^+$: 266.2115; found: 266.2093.



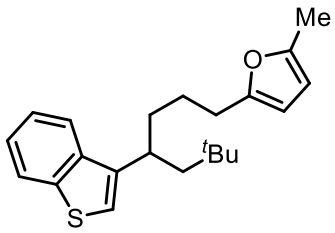
3-(1-Chloro-6,6-dimethylheptan-4-yl)thiophene (22)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide. Purification by flash column chromatography (silica gel) afforded the title compound **22** (127 mg, 0.519 mmol, 52%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25−7.22 (m, 1H), 6.92 (d, J = 4.9 Hz, 1H), 6.90−6.87 (m, 1H), 3.50−3.39 (m, 2H), 2.84−2.77 (m, 1H), 1.76−1.47 (m, 6H), 0.79 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 147.8, 126.8, 125.6, 119.9, 50.7, 45.3, 37.3, 36.5, 31.3, 30.8, 30.1.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{13}H_{22}ClS^+$: 245.1125; found: 245.1114.



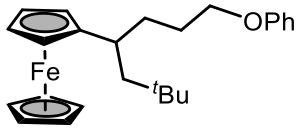
2-(4-(Benzo[*b*]thiophen-3-yl)-6,6-dimethylheptyl)-5-methylfuran (23)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (Q = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **23** (181 mg, 0.532 mmol, 53%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.88−7.81 (m, 2H), 7.39−7.30 (m, 2H), 7.07 (s, 1H), 5.81−5.77 (m, 1H), 5.74 (d, J = 2.3 Hz, 1H), 3.19−3.10 (m, 1H), 2.49 (apparent t, J = 7.5 Hz, 2H), 2.22 (s, 3H), 1.91 (dd, J = 14.0, 8.5 Hz, 1H), 1.81−1.68 (m, 2H), 1.66 (dd, J = 14.0, 3.4 Hz, 1H), 1.60−1.51 (m, 1H), 1.48−1.39 (m, 1H), 0.81 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 154.4, 150.2, 142.4, 141.0, 138.9, 124.1, 123.7, 123.1, 122.3, 120.8, 105.8, 105.4, 49.7, 38.3, 35.6, 31.4, 30.1, 28.2, 26.4, 13.6.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{22}H_{29}OS^+$: 341.1934; found: 341.1917.



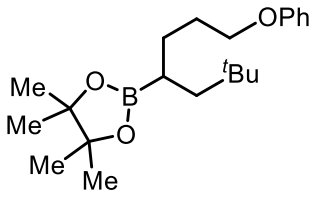
(6,6-Dimethyl-1-phenoxyheptan-4-yl)ferrocene (24)

The reaction was performed on 1.00 mmol scale following the general procedure (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **24** (187 mg, 0.462 mmol, 46%) as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.30−7.23 (m, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.16 (s, 5H), 4.12−4.02 (m, 4H), 3.94−3.86 (m, 2H), 2.38 (brs, 1H), 1.84−1.67 (m, 5H), 1.53−1.47 (m, 1H), 0.97 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 159.2, 129.5, 120.6, 114.6, 97.8, 68.6, 68.1, 67.5, 67.2, 66.8, 66.7, 49.2, 34.7, 34.0, 31.2, 30.6, 27.1.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{25}H_{33}FeO^+$: 405.1875; found: 405.1855.



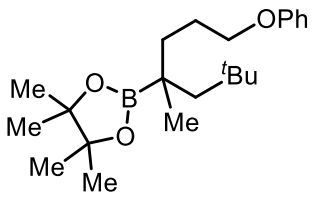
2-(6,6-Dimethyl-1-phenoxyheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **25** (197 mg, 0.569 mmol, 57%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.30−7.23 (m, 2H), 6.95−6.86 (m, 3H) 3.94 (apparent t, *J* = 6.6 Hz, 2H), 1.90−1.71 (m, 2H), 1.62−1.51 (m, 2H), 1.50−1.39 (m, 1H), 1.243 (s, 6H), 1.235 (s, 6H), 1.17 (dd, *J* = 13.4, 1.8 Hz, 1H), 1.04−0.96 (m, 1H), 0.88 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 159.2, 129.5, 120.5, 114.7, 83.1, 68.2, 45.9, 31.1, 29.9, 29.8, 28.8, 25.1, 25.0. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{21}H_{36}BO_3^+$: 347.2752; found: 347.2743.



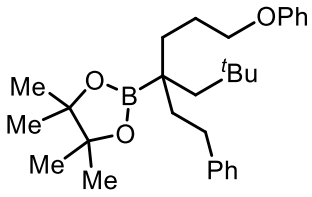
4,4,5,5-Tetramethyl-2-(4,6,6-trimethyl-1-phenoxyheptan-4-yl)-1,3,2-dioxaborolane (26)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **26** (247 mg, 0.686 mmol, 69%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.29−7.24 (m, 2H), 6.94−6.86 (m, 3H), 3.95−3.87 (m, 2H), 1.90−1.79 (m, 1H), 1.77−1.67 (m, 1H), 1.58 (d, *J* = 14.1 Hz, 1H), 1.53 (apparent td, *J* = 12.8, 4.4 Hz, 1H), 1.34 (apparent td, *J* = 12.8, 4.5 Hz, 1H), 1.26−1.20 (m, 13H), 1.01 (s, 3H), 0.96 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 159.3, 129.5, 120.5, 114.6, 83.2, 68.8, 52.5, 37.5, 31.8, 31.7, 25.3, 25.1, 24.9, 22.9. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{22}H_{38}BO_3^+$: 361.2909; found: 361.2899.



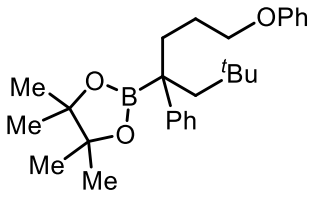
2-(6,6-Dimethyl-4-phenethyl-1-phenoxyheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27)

The reaction was performed on 1.00 mmol scale following the general procedure with 1.2 equiv of primary alkyl bromide (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **27** (304 mg, 0.675 mmol, 68%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.31−7.23 (m, 4H), 7.20−7.13 (m, 3H), 6.96−6.88 (m, 3H), 4.01−3.92 (m, 2H), 2.61 (apparent td, *J* = 13.0, 4.9 Hz, 1H), 2.50 (apparent td, *J* = 13.0, 4.5 Hz, 1H), 1.93−1.82 (m, 1H), 1.82−1.60 (m, 5H), 1.49 (ABq, *J* = 14.5 Hz, 2H), 1.28 (s, 6H), 1.27 (s, 6H), 1.01 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 159.2, 143.7, 129.5, 128.5, 128.4, 125.6, 120.5, 114.6, 83.3, 68.6, 49.0, 37.7, 32.0, 31.8, 30.6, 30.4, 25.6, 25.5, 23.6. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{29}H_{44}BO_3^+$: 451.3378; found: 451.3364.



2-(6,6-Dimethyl-1-phenoxy-4-phenylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)

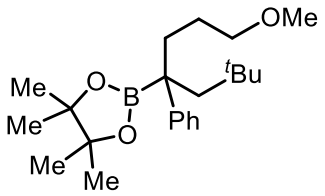
The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1% Et_2O in hexanes) afforded the title compound **28** (367 mg, 0.869 mmol, 87%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.51 (d, *J* = 8.0 Hz, 2H), 7.28−7.20 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 2H), 3.90−3.80 (m, 2H), 2.14−2.06 (m, 1H), 2.06−1.98 (m, 2H), 1.80 (d, *J* = 14.2 Hz, 1H), 1.64−1.50 (m, 2H), 1.25 (s, 6H), 1.21 (s, 6H), 0.77 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 159.2, 145.6, 129.5, 128.3, 128.0, 125.3, 120.4, 114.5, 83.4, 68.4, 49.8, 34.5, 32.2,

31.6, 25.3, 25.2, 24.9. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{27}H_{40}BO_3^+$: 423.3065; found: 423.3048.



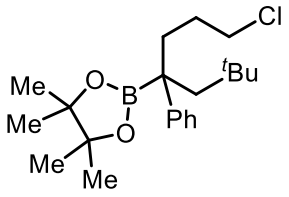
2-(1-Methoxy-6,6-dimethyl-4-phenylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−5% Et_2O in hexanes) afforded the title compound **29** (315 mg, 0.874 mmol, 87%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.49 (d, *J* = 8.0 Hz, 2H), 7.23 (apparent t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 3.28 (apparent t, *J* = 6.9 Hz, 2H), 3.25 (s, 3H), 2.01−1.86 (m, 3H), 1.78 (d, *J* = 14.3 Hz, 1H), 1.43−1.30 (m, 2H), 1.23 (s, 6H), 1.20 (s, 6H), 0.75 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 145.8, 128.3, 127.9, 125.2, 83.4, 73.6, 58.5, 49.6, 34.4, 32.2, 31.6, 25.5, 25.2, 24.9. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{22}H_{38}BO_3^+$: 361.2909; found: 361.2898.



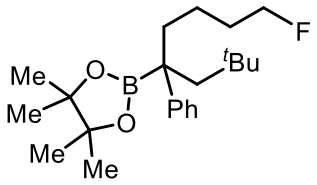
2-(1-Chloro-6,6-dimethyl-4-phenylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1% Et_2O in hexanes) afforded the title compound **30** (331 mg, 0.907 mmol, 91%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.49 (d, *J* = 7.8 Hz, 2H), 7.25 (apparent t, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 3.49−3.38 (m, 2H), 2.10−2.02 (m, 1H), 2.02−1.94 (m, 2H), 1.77 (d, *J* = 14.2 Hz, 1H), 1.60−1.51 (m, 2H), 1.25 (s, 6H), 1.21 (s, 6H), 0.75 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 145.3, 128.3, 128.1, 125.4, 83.5, 50.0, 46.0, 35.9, 32.2, 31.5, 28.8, 25.3, 24.9. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{21}H_{35}BClO_2^+$: 365.2413; found: 365.2402.



2-(8-Fluoro-2,2-dimethyl-4-phenyloctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31)

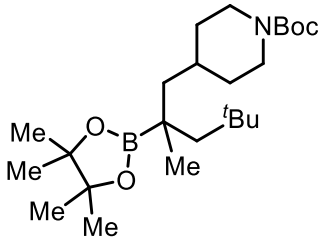
The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1% Et_2O in hexanes) afforded the title compound **31** (331 mg, 0.914 mmol, 91%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.49 (d, J = 8.0 Hz, 2H), 7.27−7.21 (m, 2H), 7.11 (t, J = 7.3 Hz, 1H), 4.40 (apparent td, J = 6.2, 2.3 Hz, 1H), 4.30 (apparent td, J = 6.2, 2.3 Hz, 1H), 2.02−1.86 (m, 3H), 1.76 (d, J = 14.2 Hz, 1H), 1.68−1.56 (m, 2H), 1.27−1.08 (m, 14H), 0.73 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 145.7, 128.3, 128.0, 125.2, 84.1 (d, J = 164 Hz), 83.4, 49.9, 38.1, 32.2, 31.5, 31.2 (d, J = 19 Hz), 25.2, 24.9, 21.1 (d, J = 6 Hz). The signal of the carbon atom attached to boron was not observed.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, δ): −217.4.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{22}H_{37}BFO_2^+$: 363.2865; found: 363.2855.



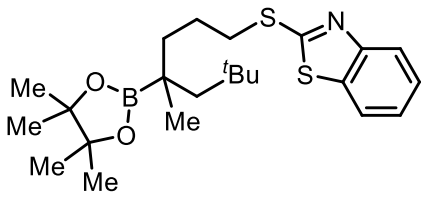
***tert*-Butyl 4-(2,4,4-trimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)piperidine-1-carboxylate (32)**

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 3−10% Et_2O in hexanes) afforded the title compound **32** (240 mg, 0.567 mmol, 57%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.97 (s, 2H), 2.78−2.59 (m, 2H), 1.66 (d, J = 12.4 Hz, 2H), 1.56 (d, J = 14.0 Hz, 1H), 1.48−1.40 (m, 10H), 1.36 (dd, J = 13.9, 4.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.17−1.05 (m, 4H), 1.01 (s, 3H), 0.94 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 155.1, 83.3, 79.2, 53.6, 48.8, 34.9, 34.5, 33.3, 31.9, 31.8, 28.6, 25.5, 25.4, 22.9. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{24}H_{47}BNO_4^+$: 424.3593; found: 424.3580.



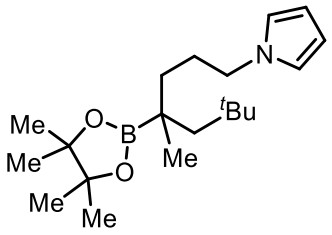
2-((4,6,6-Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)thio)benzo[*d*]thiazole (33)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 2−4% Et_2O in hexanes) afforded the title compound **33** (196 mg, 0.452 mmol, 45%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.85 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.43−7.36 (m, 1H), 7.30−7.26 (m, 1H), 3.35−3.23 (m, 2H), 1.94−1.83 (m, 1H), 1.82−1.71 (m, 1H), 1.63−1.52 (m, 2H), 1.37 (apparent td, *J* = 12.8, 4.5 Hz, 1H), 1.24−1.18 (m, 7H), 1.17 (s, 6H), 0.98 (s, 3H), 0.94 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 167.7, 153.5, 135.3, 126.1, 124.2, 121.6, 121.0, 83.2, 52.5, 40.8, 34.7, 31.8, 31.7, 25.3, 25.10, 25.07, 23.0. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{23}H_{37}BNO_2S_2^+$: 434.2353; found: 434.2341.



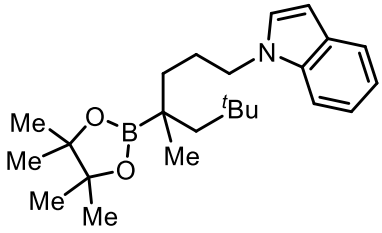
1-(4,6,6-Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)-1*H*-pyrrole (34)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−3% Et_2O in hexanes) afforded the title compound **34** (203 mg, 0.609 mmol, 61%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 6.66−6.61 (m, 2H), 6.14−6.10 (m, 2H), 3.88−3.74 (m, 2H), 1.88−1.76 (m, 1H), 1.76−1.65 (m, 1H), 1.52 (d, *J* = 14.1 Hz, 1H), 1.42 (apparent td, *J* = 12.8, 4.3 Hz, 1H), 1.25−1.14 (m, 14H), 0.95 (s, 3H), 0.93 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 120.6, 107.9, 83.2, 52.6, 50.7, 38.5, 31.8, 31.6, 27.4, 25.3, 25.1, 22.9. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{20}H_{37}BNO_2^+$: 334.2912; found: 334.2903.



1-(4,6,6-Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)-1*H*-indole (35)

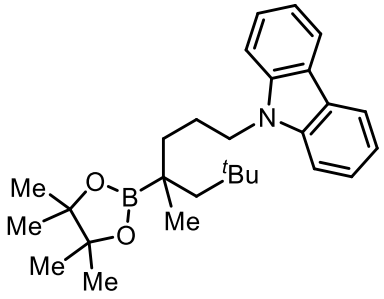
The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **35** (196 mg, 0.511 mmol, 51%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.63 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.19 (apparent t, *J* = 7.6 Hz, 1H), 7.12−7.06

(m, 2H), 6.48 (d, *J* = 2.3 Hz, 1H), 4.13−4.01 (m, 2H), 1.95−1.85 (m, 1H), 1.84−1.74 (m, 1H), 1.55−1.45 (m, 2H), 1.26 (apparent td, *J* = 12.8, 4.4 Hz, 1H), 1.22−1.15 (m, 13H), 0.95 (s, 3H), 0.94 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, *δ*): 136.1, 128.7, 127.9, 121.3, 121.0, 119.2, 109.5, 100.9, 83.2, 52.6, 47.5, 38.7, 31.8, 31.6, 26.1, 25.2, 25.1, 23.0. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{24}H_{39}BNO_2^+$: 384.3068; found: 384.3059.



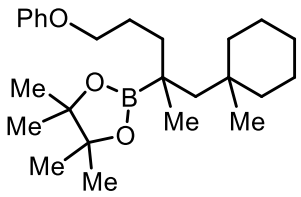
9-(4,6,6-Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)-9*H*-carbazole (36)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **36** (296 mg, 0.683 mmol, 68%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 8.10 (d, *J* = 7.7 Hz, 2H), 7.45 (apparent t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.22 (apparent t, *J* = 7.3 Hz, 2H), 4.25 (apparent t, *J* = 7.5 Hz, 2H), 1.98 – 1.87 (m, 1H), 1.87 – 1.76 (m, 1H), 1.58 (apparent td, *J* = 12.9, 4.2 Hz, 1H), 1.49 (d, *J* = 14.1 Hz, 1H), 1.35 (apparent td, *J* = 12.9, 4.5 Hz, 1H), 1.20 (d, *J* = 14.1 Hz, 1H), 1.154 (s, 6H), 1.150 (s, 6H), 0.93 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, *δ*): 140.5, 125.6, 122.9, 120.4, 118.8, 108.8, 83.2, 52.6, 44.0, 38.8, 31.8, 31.6, 25.2, 25.0, 24.8, 23.0. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{28}H_{41}BNO_2^+$: 434.3225; found: 434.3213.



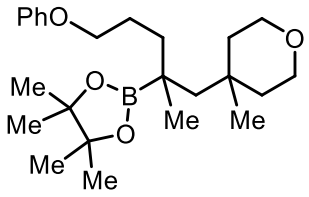
4,4,5,5-Tetramethyl-2-(2-methyl-1-(1-methylcyclohexyl)-5-phenoxypentan-2-yl)-1,3,2-dioxaborolane (37)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **37** (276 mg, 0.689 mmol, 69%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.30−7.23 (m, 2H), 6.95−6.86 (m, 3H), 3.96−3.86 (m, 2H), 1.90−1.79 (m, 1H), 1.76−1.67 (m, 1H), 1.56−1.18 (m, 26H), 1.01 (s, 3H), 0.96 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, *δ*): 159.3, 129.5, 120.5, 114.6, 83.2, 68.9, 53.1, 40.0, 39.7, 37.8, 34.1, 26.6, 25.3, 25.1, 24.9, 24.6, 23.3, 22.3, 22.2. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{25}H_{42}BO_3^+$: 401.3222; found: 401.3210.



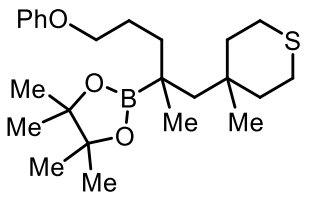
4,4,5,5-Tetramethyl-2-(2-methyl-1-(4-methyltetrahydro-2*H*-pyran-4-yl)-5-phenoxypentan-2-yl)-1,3,2-dioxaborolane (38)

The reaction was performed on 1.01 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 10−20% Et_2O in hexanes) afforded the title compound **38** (265 mg, 0.659 mmol, 65%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.30−7.23 (m, 2H), 6.94−6.90 (m, 1H), 6.90−6.86 (m, 2H), 3.97−3.86 (m, 2H), 3.75−3.67 (m, 2H), 3.62−3.53 (m, 2H), 1.90−1.79 (m, 1H), 1.77−1.66 (m, 1H), 1.62−1.51 (m, 4H), 1.43−1.25 (m, 4H), 1.24 (s, 6H), 1.23 (s, 6H), 1.08 (s, 3H), 1.02 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 159.2, 129.5 (2C), 120.5, 114.6 (2C), 83.3 (2C), 68.7, 64.1, 64.0, 53.3, 39.8 (2C), 37.8, 32.0, 25.3 (2C), 25.1 (2C), 24.9, 23.24, 23.20. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{24}H_{40}BO_4^+$: 403.3014; found: 403.3004.



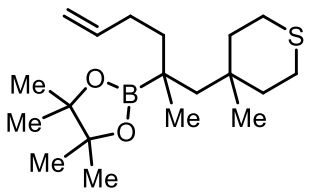
4,4,5,5-Tetramethyl-2-(2-methyl-1-(4-methyltetrahydro-2*H*-thiopyran-4-yl)-5-phenoxypentan-2-yl)-1,3,2-dioxaborolane (39)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 2−5% Et_2O in hexanes) afforded the title compound **39** (322 mg, 0.770 mmol, 77%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.29−7.24 (m, 2H), 6.94−6.90 (m, 1H), 6.90−6.86 (m, 2H), 3.96−3.87 (m, 2H), 2.69 (s, 2H), 2.56−2.43 (m, 2H), 1.89−1.79 (m, 1H), 1.77−1.64 (m, 4H), 1.64−1.59 (m, 1H), 1.55 (apparent td, *J* = 12.8, 4.4 Hz, 1H), 1.52 (d, *J* = 14.3 Hz, 1H), 1.35 (apparent td, *J* = 12.7, 4.6 Hz, 1H), 1.30 (d, *J* = 14.3 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.02 (s, 3H), 0.98 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 159.2, 129.5, 120.5, 114.6, 83.3, 68.7, 52.0, 40.3, 39.8, 37.9, 33.1, 25.3, 25.1, 24.9, 24.4, 24.0, 23.9, 23.3. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{24}H_{40}BO_3S^+$: 419.2786; found: 419.2773.



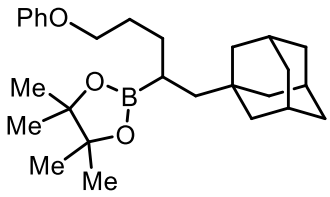
4,4,5,5-Tetramethyl-2-(2-methyl-1-(4-methyltetrahydro-2*H*-thiopyran-4-yl)hex-5-en-2-yl)-1,3,2-dioxaborolane (40)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography afforded the title compound **40** (212 mg, 0.626 mmol, 63%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.79 (apparent ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.01−4.94 (m, 1H), 4.93−4.87 (m, 1H), 2.74−2.64 (m, 2H), 2.53−2.46 (m, 2H), 2.13−2.04 (m, 1H), 2.01−1.92 (m, 1H), 1.75−1.62 (m, 3H), 1.62−1.55 (m, 1H), 1.54−1.45 (m, 2H), 1.30−1.25 (m, 2H), 1.24 (s, 6H), 1.23 (s, 6H), 0.99 (s, 3H), 0.96 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 139.8, 114.0, 83.3, 52.0, 41.4, 40.3, 39.8, 33.1, 29.5, 25.4, 25.1, 24.4, 24.0, 23.9, 23.1. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{19}H_{36}BO_2S^+$: 339.2524; found: 339.2507.



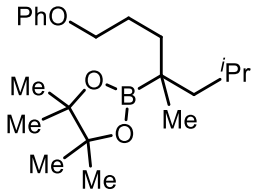
2-(1-Adamantan-1-yl-5-phenoxypentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (41)

The reaction was performed on 1.00 mmol scale following the general procedure (Q = 2.2 F/mol). Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **41** (56 mg, 0.13 mmol, 13%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.29−7.23 (m, 2H), 6.94−6.86 (m, 3H), 3.93 (apparent t, J = 6.6 Hz, 2H), 1.94−1.89 (m, 3H), 1.88−1.71 (m, 2H), 1.64 (ABq, J = 12.0 Hz, 6H), 1.55−1.47 (m, 4H), 1.46−1.38 (m, 5H), 1.25 (s, 6H), 1.24 (s, 6H), 1.07−1.00 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 159.3, 129.5, 120.5, 114.7, 83.1, 68.2, 46.6, 42.8, 37.3, 33.0, 29.9, 28.89, 28.86, 25.1, 25.0. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{27}H_{42}BO_3^+$: 425.3222; found: 425.3210.



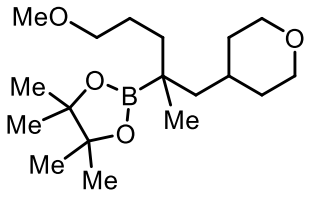
2-(4,6-Dimethyl-1-phenoxyheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **42** (186 mg, 0.537 mmol, 54%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.29−7.23 (m, 2H), 6.94−6.86 (m, 3H), 3.96−3.87 (m, 2H), 1.85−1.69 (m, 2H), 1.68−1.59 (m, 1H), 1.52 (apparent td, *J* = 12.8, 4.5 Hz, 1H), 1.39 (dd, *J* = 13.6, 6.9 Hz, 1H), 1.32 (apparent td, *J* = 12.8, 4.8 Hz, 1H), 1.23 (s, 12H), 1.18 (dd, *J* = 13.6, 6.2 Hz, 1H), 0.94 (s, 3H), 0.89 (apparent t, J = 6.4 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 159.2, 129.5, 120.5, 114.6, 83.2, 68.8, 48.1, 35.8, 25.8, 25.2, 25.1, 25.0, 24.6, 24.2, 21.7. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{21}H_{36}BO_3^+$: 347.2752; found: 347.2742.



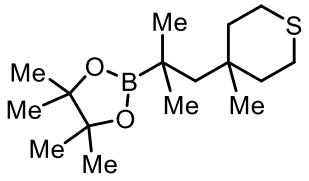
2-(5-Methoxy-2-methyl-1-(tetrahydro-2*H*-pyran-4-yl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (43)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography afforded the title compound **43** (195 mg, 0.598 mmol, 60%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.93−3.86 (m, 2H), 3.38−3.30 (m, 4H), 3.31 (s, 3H), 1.62−1.46 (m, 5H), 1.45−1.36 (m, 2H), 1.35−1.25 (m, 2H), 1.22 (s, 12H), 1.22−1.15 (m, 2H), 0.91 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 83.2, 73.9, 68.29, 68.25, 58.6, 46.2, 35.9, 34.8, 34.5, 32.8, 25.5, 25.1, 25.0, 21.8. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{18}H_{36}BO_4^+$: 327.2701; found: 327.2685.



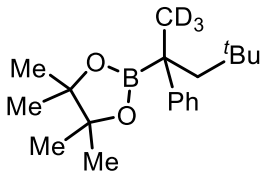
4,4,5,5-Tetramethyl-2-(2-methyl-1-(4-methyltetrahydro-2H-thiopyran-4-yl)propan-2-yl)-1,3,2-dioxaborolane (44)

The reaction was performed on 1.00 mmol scale following the general procedure with 3.0 equiv of MeOTs. Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the title compound **44** (148 mg, 0.496 mmol, 50%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.72−2.63 (m, 2H), 2.56−2.46 (m, 2H), 1.74−1.66 (m, 2H), 1.64−1.59 (m, 2H), 1.36 (s, 2H), 1.22 (s, 12H), 0.96 (s, 6H), 0.95 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 83.1, 53.6, 39.9, 33.0, 27.9, 24.9, 24.4, 24.0. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{16}H_{32}BO_2S^+$: 299.2211; found: 299.2187.



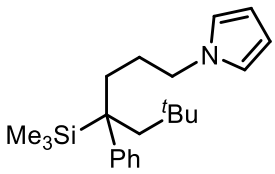
2-(4,4-Dimethyl-2-phenylpentan-2-yl-1,1,1-*d*$_3$)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (45)

The reaction was performed on 1.00 mmol scale following the general procedure with 1.0 equiv of CD_3OTs. Purification by flash column chromatography (silica gel, 1% Et_2O in hexanes) afforded the title compound **45** (229 mg, 0.750 mmol, 75%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.48−7.42 (m, 2H), 7.29−7.23 (m, 2H), 7.15−7.08 (m, 1H), 1.95 (d, *J* = 14.2 Hz, 1H), 1.70 (d, *J* = 14.2 Hz, 1H), 1.18 (s, 6H), 1.16 (s, 6H), 0.87 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 148.1, 127.9, 127.3, 125.1, 83.4, 52.5, 32.4, 31.7, 24.9, 24.6. The signals of the carbon atoms attached to boron or deuterium were not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{19}H_{29}D_3BO_2^+$: 306.2678; found: 306.2653.



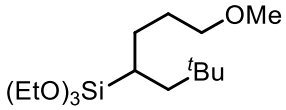
1-(6,6-Dimethyl-4-phenyl-4-(trimethylsilyl)heptyl)-1*H*-pyrrole (46)

The reaction was performed on 1.00 mmol scale following the general procedure. Purification by flash column chromatography (silica gel) afforded the title compound **46** (228 mg, 0.667 mmol, 67%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.23−7.18 (m, 2H), 7.18−7.13 (m, 2H), 7.06 (t, *J* = 6.9 Hz, 1H), 6.73−6.69 (m, 2H), 6.20−6.15 (m, 2H), 4.04−3.89 (m, 2H), 2.36−2.26 (m, 1H), 2.13 (d, *J* = 15.0 Hz, 1H), 2.07−1.92 (m, 2H), 1.84−1.74 (m, 1H), 1.69 (d, *J* = 15.0 Hz, 1H), 0.74 (s, 9H), −0.06 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 146.0, 127.6, 127.5, 124.2, 120.8, 108.2, 50.7, 46.7, 36.4, 34.2, 32.7, 32.2, 29.2, −1.1.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{22}H_{36}NSi^+$: 342.2612; found: 342.2595.



Triethoxy(1-methoxy-6,6-dimethylheptan-4-yl)silane (47)

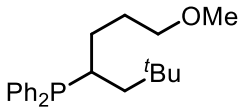
The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel, 3−5% Et_2O in hexanes) afforded the title compound **47** (65 mg, 0.20 mmol, 20%) as a light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 3.82 (q, *J* = 6.9 Hz, 6H), 3.34 (apparent t, *J* = 6.7 Hz, 2H), 3.32 (s, 3H), 1.78−1.68 (m, 1H), 1.68−1.57 (m, 2H), 1.56−1.48 (m, 1H), 1.47−1.38 (m, 1H), 1.22 (t, *J* = 6.9 Hz, 9H), 1.07 (dd, *J* = 14.2, 6.4 Hz, 1H), 0.88

(s, 9H), 0.81−0.74 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, δ): 73.5, 58.6, 58.5, 42.4, 32.1, 29.8, 29.0, 28.8, 18.5, 18.2.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{16}H_{37}O_4Si^+$: 321.2456; found: 321.2428.



(1-Methoxy-6,6-dimethylheptan-4-yl)diphenylphosphane (48)

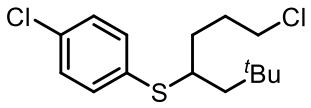
The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **48** (107 mg, 0.312 mmol, 31%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.55−7.46 (m, 4H), 7.35−7.29 (m, 6H), 3.27−3.22 (m, 2H), 3.25 (s, 3H), 2.32−2.22 (m, 1H), 1.80−1.58 (m, 3H), 1.48−1.29 (m, 3H), 0.82 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, δ): 137.4 (d, *J* = 16 Hz), 137.1 (d, *J* = 17 Hz), 134.3 (d, *J* = 19 Hz), 134.0 (d, *J* = 19 Hz), 128.8, 128.5, 128.33 (d, *J* = 2 Hz), 128.27 (d, *J* = 1 Hz), 73.0, 58.5, 43.7 (d, *J* = 15 Hz), 31.8 (d, *J* = 4 Hz), 31.7 (d, *J* = 4 Hz), 30.2, 29.1 (d, *J* = 9 Hz), 27.4 (d, *J* = 9 Hz).

^{31}P NMR (202 MHz, $CDCl_3$, δ): 0.3 (s).

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{22}H_{32}OP^+$: 343.2185; found: 343.2175.



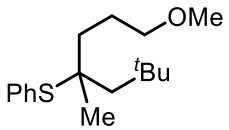
(1-Chloro-6,6-dimethylheptan-4-yl)(4-chlorophenyl)sulfane (49)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (*Q* = 3.5 F/mol). Flash column chromatography failed to afford the title compound **49** of sufficient purity. The yield (43%) was determined by ^{1}H NMR analysis using dibromomethane as the internal standard.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.35−7.31 (m, 2H), 7.28−7.25 (m, 2H), 3.51 (apparent t, *J* = 6.5 Hz, 2H), 3.09 (apparent pentet, *J* = 5.7 Hz, 1H), 2.02−1.85 (m, 2H), 1.79−1.70 (m, 1H), 1.70−1.61 (m, 1H), 1.55 (dd, *J* = 14.8, 5.8 Hz, 1H), 1.47 (dd, *J* = 14.8, 4.9 Hz, 1H), 0.94 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, δ): 134.2, 133.6, 133.2, 129.2, 48.3, 45.09, 45.05, 34.0, 31.3, 30.0, 29.6.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{15}H_{23}Cl_2S^+$: 305.0892; found: 305.0867.



(1-Methoxy-4,6,6-trimethylheptan-4-yl)(phenyl)sulfane (50)

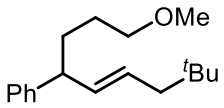
The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel, 1−2% Et_2O in hexanes) afforded the

title compound **50** (78 mg, 0.28 mmol, 28%) as a light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.53−7.47 (m, 2H), 7.37−7.28 (m, 3H), 3.39−3.30 (m, 2H), 3.33 (s, 3H), 1.96−1.87 (m, 1H), 1.86−1.76 (m, 1H), 1.65 (ABq, J = 15.0 Hz, 2H), 1.59−1.47 (m, 2H), 1.33 (s, 3H), 1.04 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 137.8, 132.6, 128.7, 128.5, 73.2, 58.7, 54.5, 51.8, 38.0, 32.8, 32.1, 28.2, 25.3.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{17}H_{29}OS^+$: 281.1934; found: 281.1906.



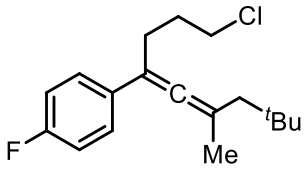
(*E*)-(1-Methoxy-8,8-dimethylnon-5-en-4-yl)benzene (52)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (Q = 3.5 F/mol). Purification by flash column chromatography (silica gel) afforded the title compound **52** (165 mg, 0.634 mmol, 63%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.32−7.26 (m, 2H), 7.21−7.15 (m, 3H), 5.57−5.45 (m, 2H), 3.36 (apparent t, J = 6.5 Hz, 2H), 3.31 (s, 3H), 3.22 (apparent q, J = 7.3 Hz, 1H), 1.93−1.82 (m, 2H), 1.79−1.69 (m, 2H), 1.66−1.56 (m, 1H), 1.52−1.43 (m, 1H), 0.86 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 145.4, 136.1, 128.5, 127.62, 127.56, 126.1, 72.9, 58.7, 49.0, 47.2, 32.7, 31.1, 29.5, 28.0.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{18}H_{29}O^+$: 261.2213; found: 261.2200.



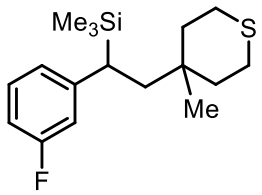
1-(1-Chloro-6,8,8-trimethylnona-4,5-dien-4-yl)-4-fluorobenzene (54)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (Q = 3.5 F/mol). Flash column chromatography failed to afford the title compound **54** of sufficient purity. The yield (71%) was determined by ^{1}H NMR analysis on the crude reaction mixture using dibromomethane as the internal standard.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34−7.29 (m, 2H), 7.02−6.96 (m, 2H), 3.62 (apparent t, J = 6.5 Hz, 2H), 2.59−2.50 (m, 2H), 2.04−1.94 (m, 4H), 1.85 (s, 3H), 0.94 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 203.2 (d, J = 2 Hz), 161.6 (d, J = 245 Hz), 133.8 (d, J = 3 Hz), 127.5 (d, J = 8 Hz), 115.3 (d, J = 21 Hz), 101.2, 101.1, 48.6, 44.9, 31.9, 31.1, 30.0, 27.9, 21.8.

HRMS (DART−Orbitrap, m/z): $[M + H]^+$ calculated for $C_{18}H_{25}ClF^+$: 295.1623; found: 295.1600.

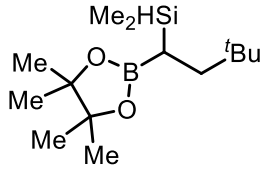


(1-(3-Fluorophenyl)-2-(4-methyltetrahydro-2*H*-thiopyran-4-yl)ethyl)trimethylsilane (55)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of $SiMe_3Cl$. Flash column chromatography failed to afford the title compound **55** of sufficient purity. The yield (90%) was determined by ^1H NMR analysis on the crude reaction mixture using dibromomethane as the internal standard.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.22−7.11 (m, 1H), 6.82 (d, J = 7.7 Hz, 1H), 6.78−6.71 (m, 2H), 2.68−2.60 (m, 1H), 2.55−2.43 (m, 2H), 2.35−2.28 (m, 1H), 2.15 (d, J = 10.7 Hz, 1H), 1.92−1.83 (m, 1H), 1.59−1.52 (m, 3H), 1.50−1.43 (m, 1H), 1.43−1.35 (m, 1H), 0.75 (s, 3H), −0.08 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 163.0 (d, J = 244 Hz), 148.7 (d, J = 7 Hz), 129.5 (d, J = 9 Hz), 123.4, 114.2 (d, J = 22 Hz), 111.1 (d, J = 21 Hz), 42.3, 38.8, 38.5, 34.3, 31.8 (d, J = 1 Hz), 24.4, 24.04, 23.98, −3.0.



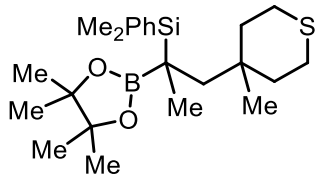
(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)dimethylsilane (56)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of $SiHMe_2Cl$ (i = 5 mA). Purification by flash column chromatography afforded the title compound **56** (158 mg, 0.585 mmol, 59%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.90−3.85 (m, 1H), 1.60 (dd, J = 13.1, 11.5 Hz, 1H), 1.25−1.23 (m, 1H), 1.23 (s, 12H), 0.84 (s, 9H), 0.43 (d, J = 11.1 Hz, 1H), 0.13−0.09 (m, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 82.9, 40.1, 32.1, 29.1, 25.10, 25.05, −4.3, −4.5. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, m/z): $[M - H]^+$ calculated for $C_{14}H_{30}BO_2Si^+$: 269.2103; found: 269.2082.



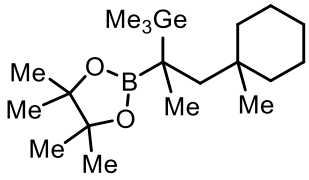
Dimethyl(1-(4-methyltetrahydro-2*H*-thiopyran-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)(phenyl)silane (57)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of $SiPhMe_2Cl$. Purification by flash column chromatography afforded the title compound **57** (297 mg, 0.710 mmol, 71%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.57−7.51 (m, 2H), 7.38−7.31 (m, 3H), 2.69−2.55 (m, 2H), 2.52−2.44 (m, 1H), 2.36−2.28 (m, 1H), 1.72−1.54 (m, 4H), 1.54−1.47 (m, 1H), 1.42 (d, *J* = 14.0 Hz, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 1.12 (s, 3H), 0.90 (s, 3H), 0.35 (s, 3H), 0.34 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 137.4, 135.2, 129.0, 127.5, 83.1, 44.2, 40.5, 39.7, 38.4, 34.6, 25.9, 25.2, 24.8, 24.2, 24.1, 23.8, 17.7. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{23}H_{40}BO_2SSi^+$: 419.2606; found: 419.2584.



Trimethyl(1-(1-methylcyclohexyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)germane (58)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of $GeMe_3Cl$. Purification by flash column chromatography afforded the title compound **58** (252 mg, 0.658 mmol, 66%) as a colorless oil.

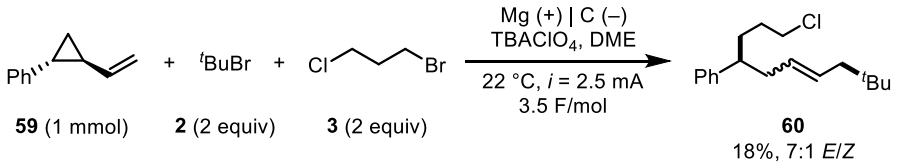
^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.64 (d, *J* = 13.9 Hz, 1H), 1.54−1.17 (m, 11H), 1.23 (s, 6H), 1.20 (s, 6H), 1.15 (s, 3H), 0.93 (s, 3H), 0.14 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 82.8, 46.0, 39.9, 39.5, 35.7, 26.7, 25.9, 25.1, 24.2, 22.6, 22.3, 18.0, −3.8. The signal of the carbon atom attached to boron was not observed.

HRMS (DART−Orbitrap, *m*/*z*): $[M - Me]^+$ calculated for $C_{18}H_{36}BGeO_2^+$: 369.2015; found: 369.1998.

S8. Mechanistic Studies

S8.1. Radical Probe Experiment



59 (1 mmol) **2** (2 equiv) **3** (2 equiv) **60** 18%, 7:1 *E*/*Z*

(1-Chloro-9,9-dimethyldec-6-en-4-yl)benzene (60)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (*Q* = 3.5 F/mol). Purification by flash column chromatography (silica gel, hexanes) afforded the title compound **60** (49 mg, 0.18 mmol, 18%) as a light yellow oil. The *E*/*Z* ratio (7:1) was determined by ^{1}H NMR analysis according to the signals of the *tert*-butyl group of the two isomers.

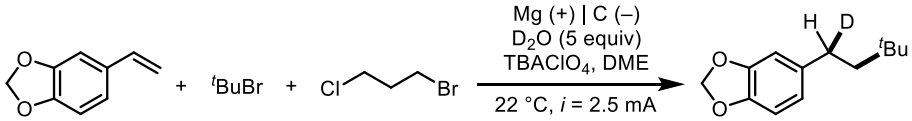
Data for NMR spectra of the *E* isomer are reported as follows:

^{1}H NMR (500 MHz, $CDCl_3$, *δ*): 7.31−7.26 (m, 2H), 7.21−7.16 (m, 1H), 7.16−7.12 (m, 2H), 5.39 (apparent dt, *J* = 15.0, 7.4 Hz, 1H), 5.24 (apparent dt, *J* = 15.0, 7.0 Hz, 1H), 3.49−3.43 (m, 2H), 2.63−2.54 (m, 1H), 2.33 (apparent t, *J* = 7.1 Hz, 2H), 1.93−1.83 (m, 1H), 1.83−1.77 (m, 2H), 1.71−1.56 (m, 3H), 0.79 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *δ*): 144.9, 130.2, 129.5, 128.5, 127.8, 126.3, 47.2, 45.9, 45.3, 40.5, 33.2, 30.9, 30.8, 29.3.

HRMS (DART−Orbitrap, *m*/*z*): $[M + H]^+$ calculated for $C_{18}H_{28}Cl^+$: 279.1874; found: 279.1866.

S8.2. Evidence for Carbanion Intermediates



1 (1 mmol) **2** (2 equiv) **3** (2 equiv) **61**, 8% (82% D incorporation)

The reaction was performed on 1.00 mmol scale following the general procedure with 2.0 equiv of primary alkyl bromide (*Q* = 3.5 F/mol). 5.0 equiv of D_2O was added prior to electrolysis. The yield (8%) was determined by ^{1}H NMR analysis using dibromomethane as the internal standard. The deuterium incorporation rate (82%) was determined by measuring the shift of isotope distribution between deuterated and non-deuterated samples using mass spectrometry (EI). ^{1}H NMR analysis failed to provide accurate deuterium incorporation rate due to the low reaction yield.

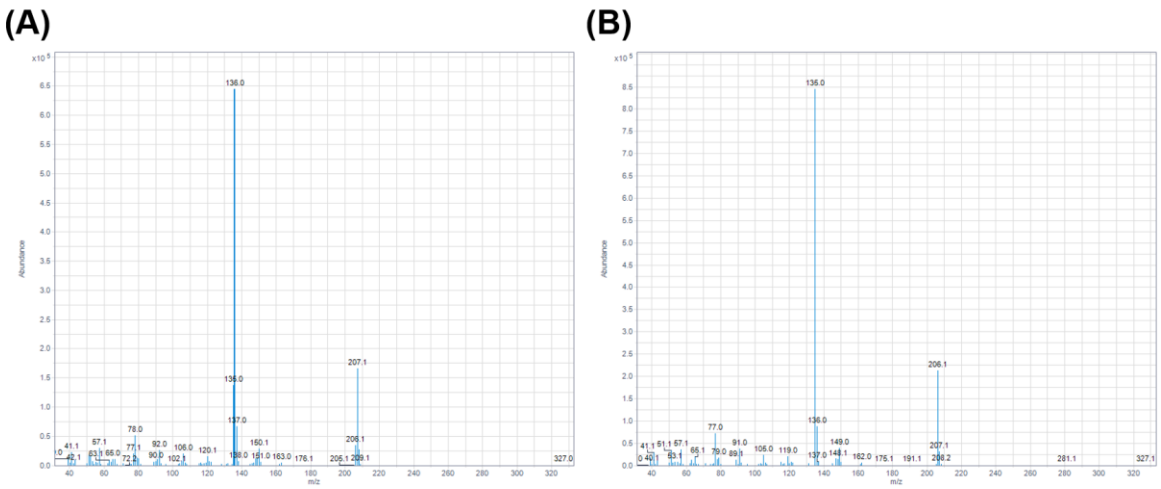


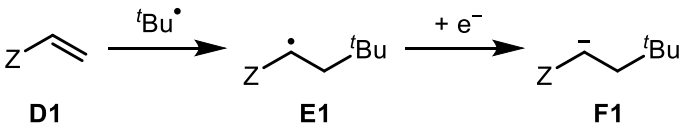
Figure S9. Isotope distribution of deuterated and non-deuterated samples. (A) Deuterated sample. 207.1/206.1 = 4.84:1. (B) Non-deuterated sample. 207.1/206.1 = 0.14:1.

S8.3. DFT Calculations

All DFT calculations were performed with Gaussian 16.[25] Geometry optimizations were carried out in the gas phase using the M06-2X functional[26] and the 6-311+G(d,p) basis set.[27] Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. Quasiharmonic corrections were applied during the entropy calculations by setting all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}.[28,29] On the basis of the gas-phase optimized structures, the Gibbs energies of solvation were computed at the SMD(DME)/M06-2X/6-311+G(d,p) level (Eps = 7.55; EpsInf = 1.90288; HbondAcidity = 0; HbondBasicity = 0.68; SurfaceTensionAtInterface = 35.42; CarbonAromaticity = 0; ElectronegativeHalogenicity = 0; standard state concentration = 1.0 M).[30,31] All discussed energy differences are based on Gibbs energies in DME at 298 K, except that bond dissociation energies are computed according to enthalpies in the gas phase at 298 K. The computed standard reduction potentials were all referenced to $Fc^{+/0}$ in DME. 3D structures were prepared with CYLview.[32]

We commenced our DFT calculations with the first C–C bond formation via radical addition (Table S2). To simplify the computations, we chose *tert*-butyl radical addition to monosubstituted alkenes as the model reaction. In all cases, the radical addition is predicted to be exergonic and mostly irreversible. For conjugated π-systems (e.g., styrene, diene, and enyne) and vinyl boronate, the radical addition is facile with Gibbs energy of activation of 10.4–12.6 kcal/mol; whereas other types of alkenes such as vinyl silane, phosphine, and sulfide are less reactive. A similar trend was observed for the reduction step, indicating that the nature of the radical/anion-stabilizing group Z is important for the success of the dialkylation. The mechanism for the second C–C bond formation is more straightforward—the substitution of primary alkyl bromides should follow an S_N2 mechanism (Scheme 6D).

Table S2. DFT Calculations on the Radical Addition and the Followed Reduction[a]



entry	Z	radical addition		reduction
		$\Delta G^{\ddagger}$ (kcal/mol)	ΔG (kcal/mol)	$E°$ versus $Fc^{+/0}$ (V)
1	Ph	12.6	−16.4	−2.80
2	vinyl	11.7	−19.1	−2.92
3	ethynyl	10.4	−18.3	−2.44
4	Bpin	12.1	−13.0	−2.63
5	$SiMe_3$	14.2	−10.5	−3.03
6	PMe_2	13.6	−11.7	−2.92
7	SMe	14.2	−12.5	−3.11

[a]Computed at the SMD(DME)/M06-2X/6-311+G(d,p)//M06-2X/6-311+G(d,p) level. The computed standard reduction potential of *tert*-butyl radical is −3.54 V versus $Fc^{+/0}$. Bpin, boronic acid pinacol ester.

Table S3. Computed Energies of Stationary Points

stationary point	SPE (a.u.)[a]	TCG (a.u.)[a,b]	SPE (a.u.)[c]
ferrocene	−1650.623799	0.137044	−1650.636870
ferrocenium	−1650.353632	0.136949	−1650.434209
$^{t}Bu^{\bullet}$	−157.744707	0.087914	−157.748078
$^{t}Bu^{-}$	−157.735676	0.087686	−157.820299
EtBr	−2653.372346	0.039226	−2653.379205
D1 (Z = Ph)	−309.581851	0.103417	−309.591202
radical addition TS (Z = Ph)	−467.327797	0.214790	−467.339696
E1 (Z = Ph)	−467.379842	0.220258	−467.391329
F1 (Z = Ph)	−467.414414	0.218002	−467.488738
S_N2 TS (Z = Ph)	−3120.800123	0.278958	−3120.863515
D1 (Z = vinyl)	−155.951019	0.059205	−155.955041
radical addition TS (Z = vinyl)	−313.696575	0.168956	−313.703352
E1 (Z = vinyl)	−313.751111	0.173981	−313.757365
F1 (Z = vinyl)	−313.773784	0.172924	−313.851698
D1 (Z = ethynyl)	−154.703598	0.035706	−154.708133
radical addition TS (Z = ethynyl)	−312.450600	0.145518	−312.458529
E1 (Z = ethynyl)	−312.502399	0.150586	−312.509392
F1 (Z = ethynyl)	−312.536997	0.149430	−312.620989
D1 (Z = Bpin)	−489.201815	0.190073	−489.210574
radical addition TS (Z = Bpin)	−646.948619	0.302102	−646.960447

E1 (Z = Bpin)	−646.994734	0.307485	−647.005827
F1 (Z = Bpin)	−647.035083	0.304936	−647.109178
S_N2 TS (Z = Bpin)	−3300.422370	0.366283	−3300.484905
D1 (Z = $SiMe_3$)	−487.197970	0.120434	−487.200277
radical addition TS (Z = $SiMe_3$)	−644.941426	0.232120	−644.946556
E1 (Z = $SiMe_3$)	−644.986211	0.237040	−644.990689
F1 (Z = $SiMe_3$)	−645.013134	0.234077	−645.079036
D1 (Z = PMe_2)	−499.119157	0.088505	−499.122896
radical addition TS (Z = PMe_2)	−656.863101	0.199748	−656.869553
E1 (Z = PMe_2)	−656.908687	0.204483	−656.914626
F1 (Z = PMe_2)	−656.937285	0.202278	−657.007683
D1 (Z = SMe)	−516.055860	0.053873	−516.061342
radical addition TS (Z = SMe)	−673.798599	0.164387	−673.806346
E1 (Z = SMe)	−673.845015	0.168006	−673.852570
F1 (Z = SMe)	−673.866070	0.166257	−673.939206

[a]Computed at the M06-2X/6-311+G(d,p) level. [b]Computed at 1 atm and 298 K with quasiharmonic corrections. [c]Computed at the SMD(DME)/M06-2X/6-311+G(d,p)//M06-2X/6-311+G(d,p) level. Cartesian coordinates of the stationary points are available upon request from the corresponding author (Song Lin: songlin@cornell.edu). SPE, single-point energy. TCG, thermal correction to Gibbs energy. TS, transition state.

Table S4. Energetic Data for Bond Dissociation Energy Calculations[a]

stationary point	SPE (a.u.)	TCH (a.u.)
$D^{\bullet}$	−0.498134	0.002360
D_2O	−76.420833	0.019534
$DO^{\bullet}$	−75.726528	0.009591
1-deuterio-1-phenylethane	−310.808706	0.162650
α-methylbenzyl radical	−310.159889	0.151839

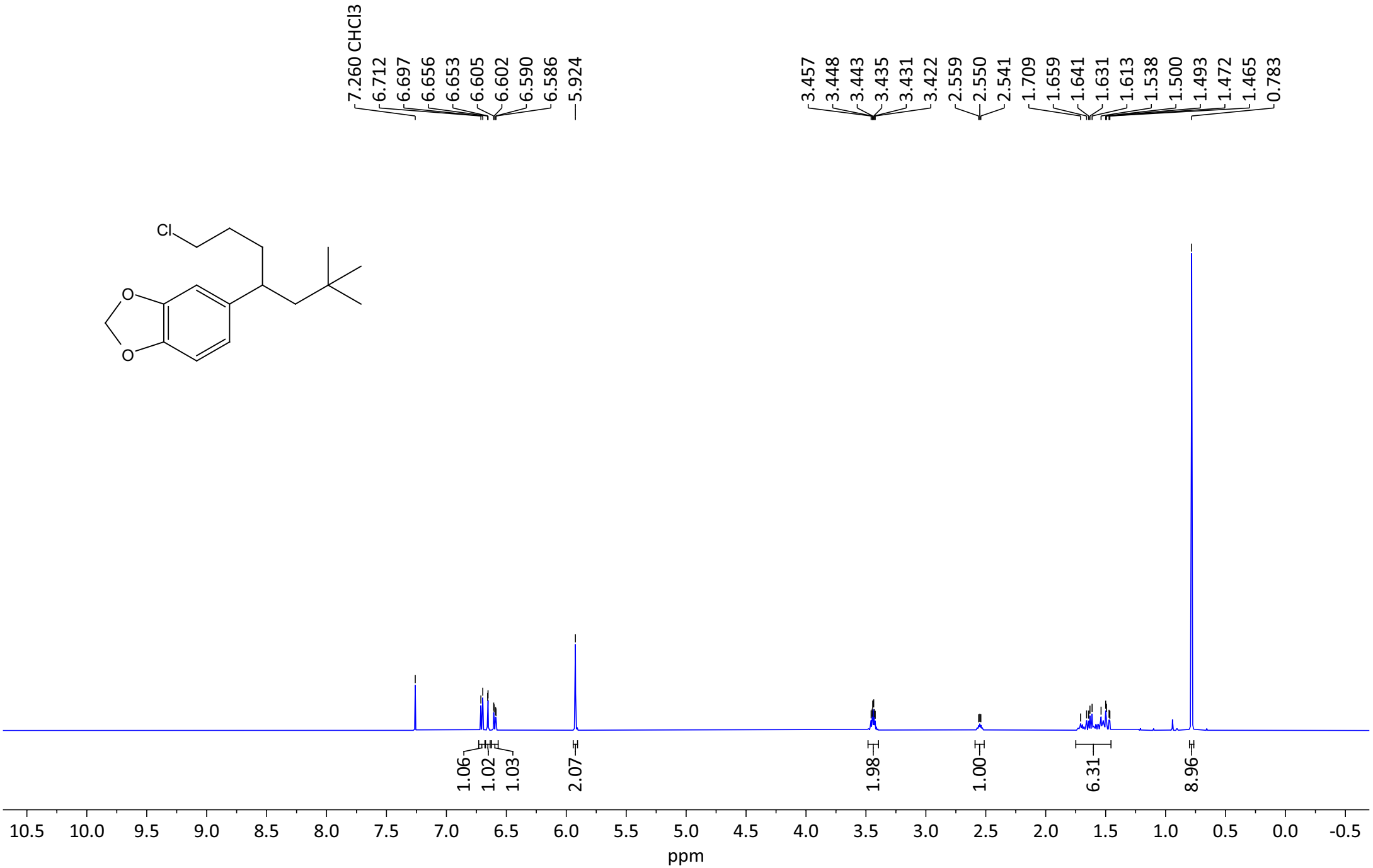
[a]Computed at the M06-2X/6-311+G(d,p) level. Cartesian coordinates of the stationary points are available upon request from the corresponding author (Song Lin: songlin@cornell.edu). TCH, thermal correction to enthalpy.

S9. Copies of NMR Spectra

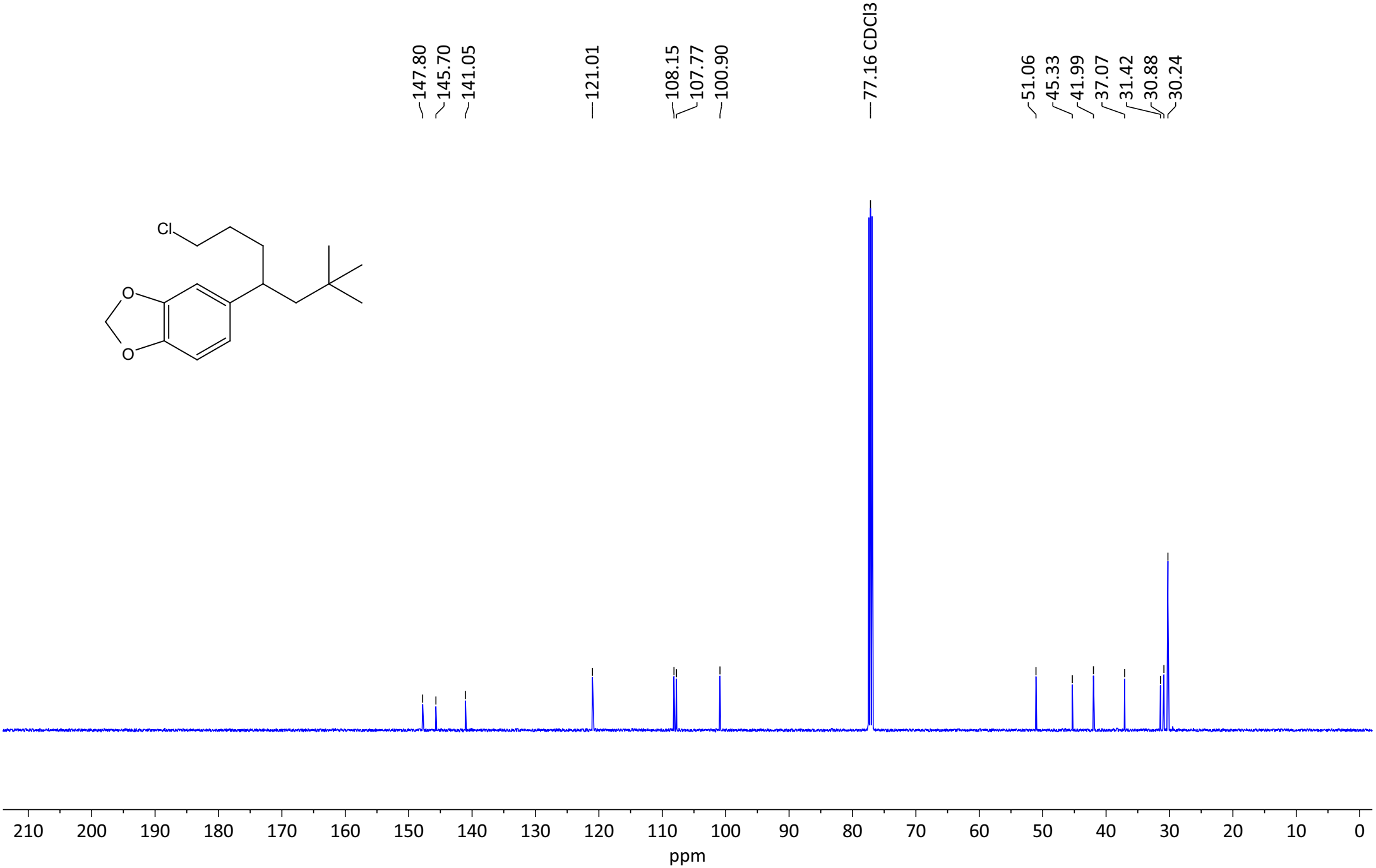
Table S5. Summary of NMR Spectra

compound	NMR	page
4	^{1}H NMR, 500 MHz, $CDCl_3$	S40
4	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S41
7	^{1}H NMR, 500 MHz, $CDCl_3$	S42
7	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S43
8	^{1}H NMR, 500 MHz, $CDCl_3$	S44
8	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S45
9	^{1}H NMR, 500 MHz, $CDCl_3$	S46
9	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S47
10	^{1}H NMR, 500 MHz, $CDCl_3$	S48
10	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S49
11	^{1}H NMR, 500 MHz, $CDCl_3$	S50
11	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S51
11	^{19}F NMR, 470 MHz, $CDCl_3$	S52
12	^{1}H NMR, 500 MHz, $CDCl_3$	S53
12	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S54
12	^{19}F NMR, 470 MHz, $CDCl_3$	S55
13	^{1}H NMR, 500 MHz, $CDCl_3$	S56
13	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S57
14	^{1}H NMR, 500 MHz, $CDCl_3$	S58
14	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S59
14	^{19}F NMR, 470 MHz, $CDCl_3$	S60
15	^{1}H NMR, 500 MHz, $CDCl_3$	S61
15	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S62
16	^{1}H NMR, 500 MHz, $CDCl_3$	S63
16	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S64
16	^{19}F NMR, 470 MHz, $CDCl_3$	S65
17	^{1}H NMR, 500 MHz, $CDCl_3$	S66
17	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S67
18	^{1}H NMR, 500 MHz, $CDCl_3$	S68
18	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S69
19	^{1}H NMR, 500 MHz, $CDCl_3$	S70
19	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S71
20	^{1}H NMR, 500 MHz, $CDCl_3$	S72
20	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S73
21	^{1}H NMR, 500 MHz, $CDCl_3$	S74
21	$^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$	S75

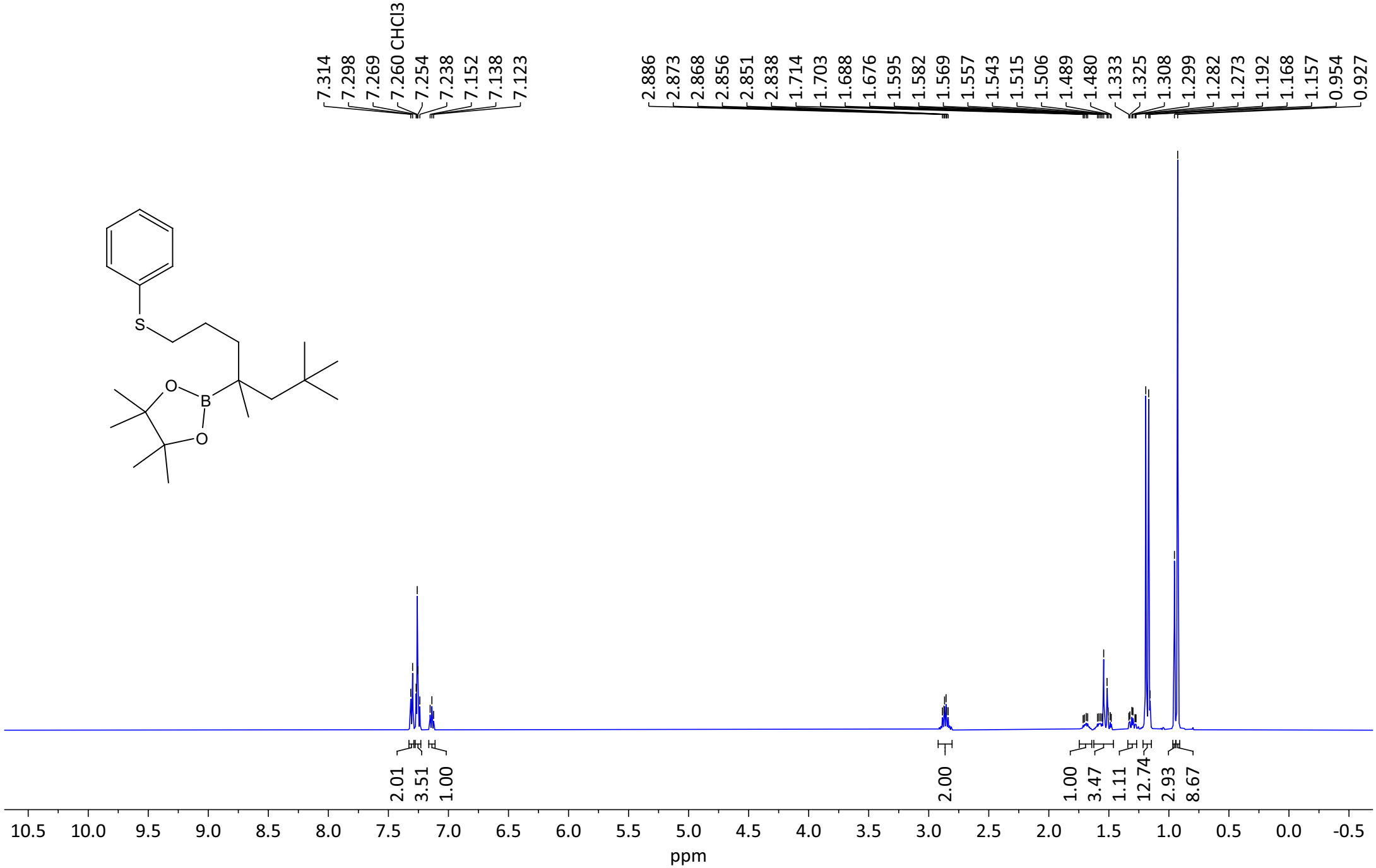
Compound **4**: ^{1}H NMR (500 MHz, $CDCl_3$)



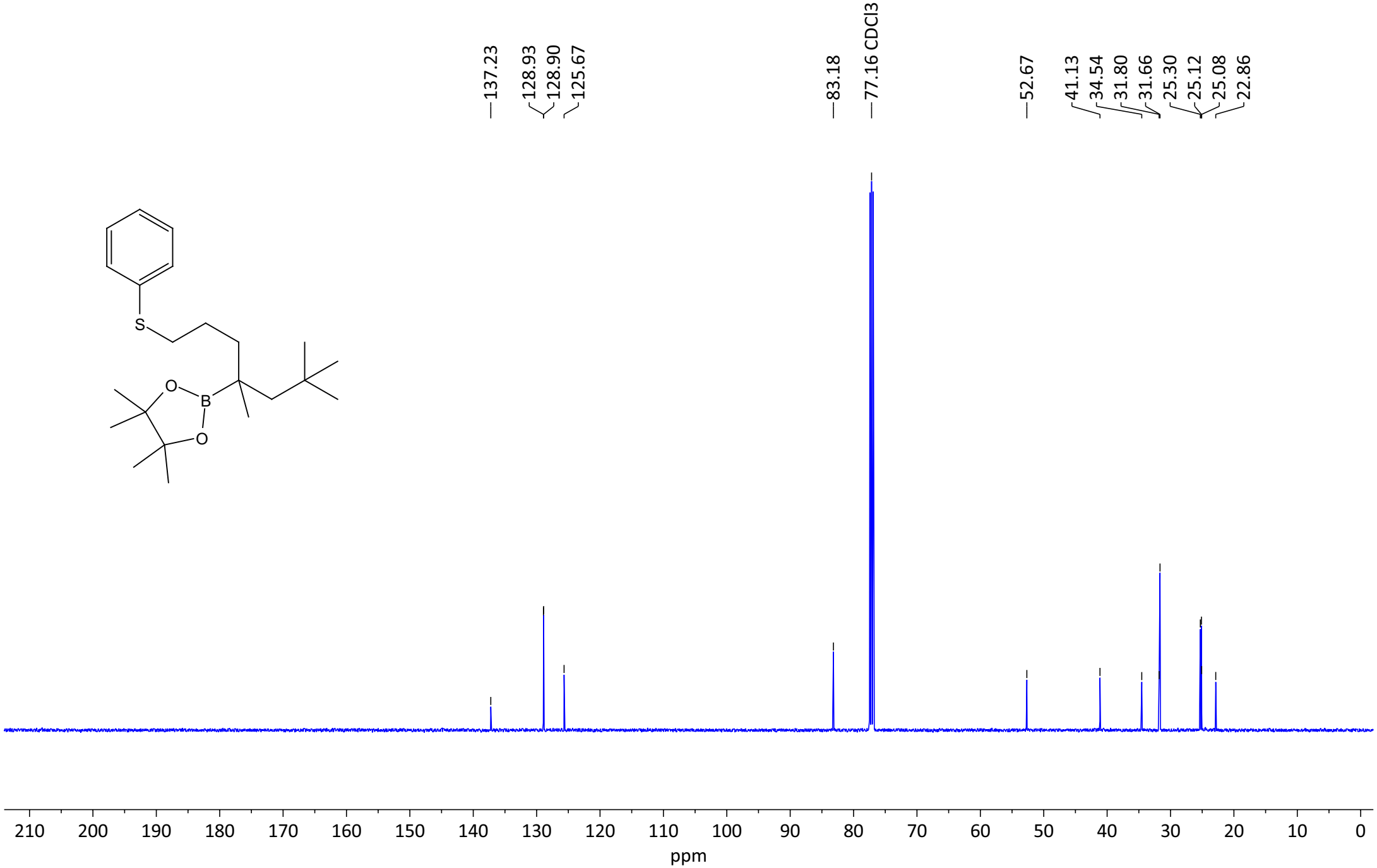
Compound **4**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



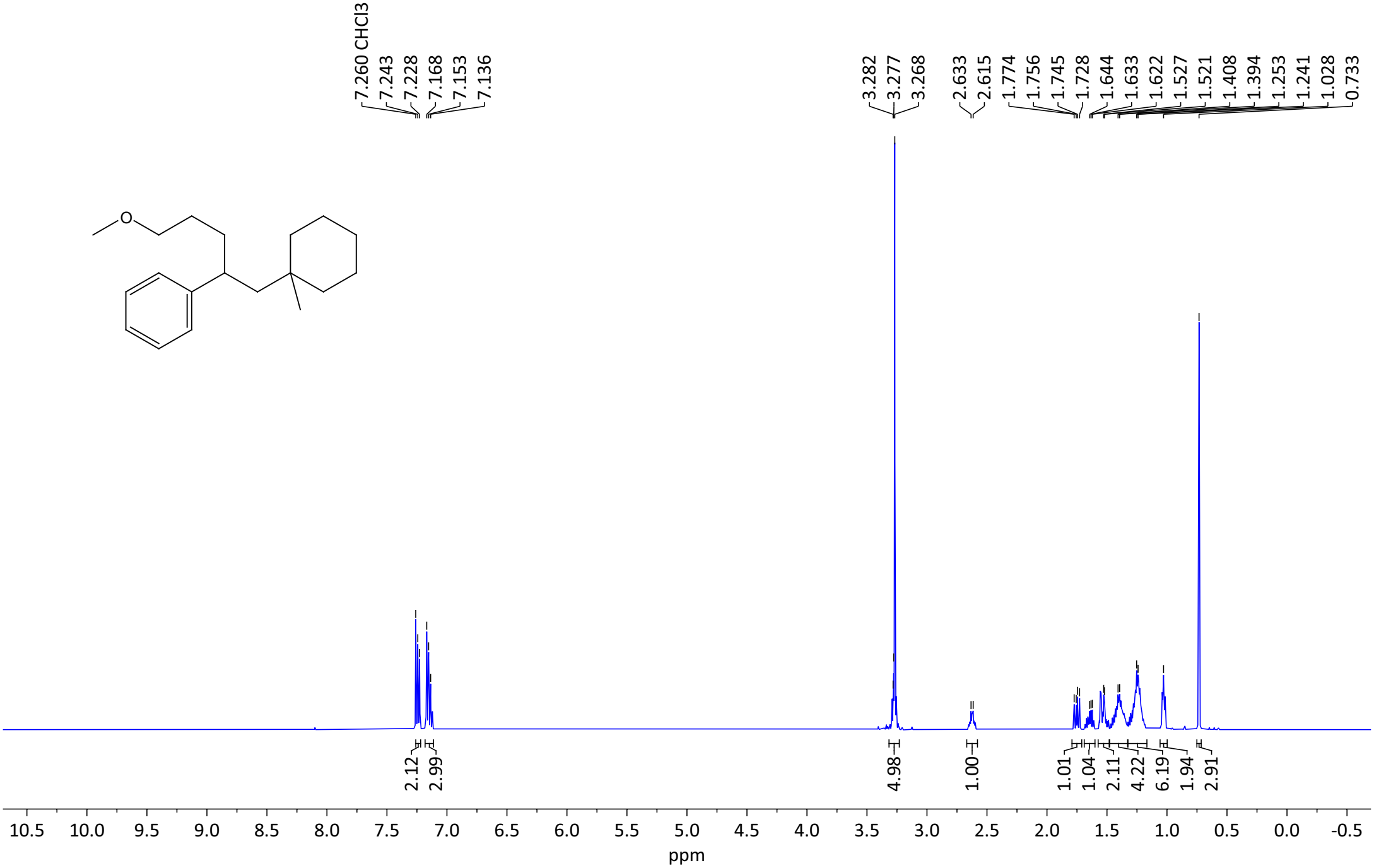
Compound **7**: ^{1}H NMR (500 MHz, $CDCl_3$)



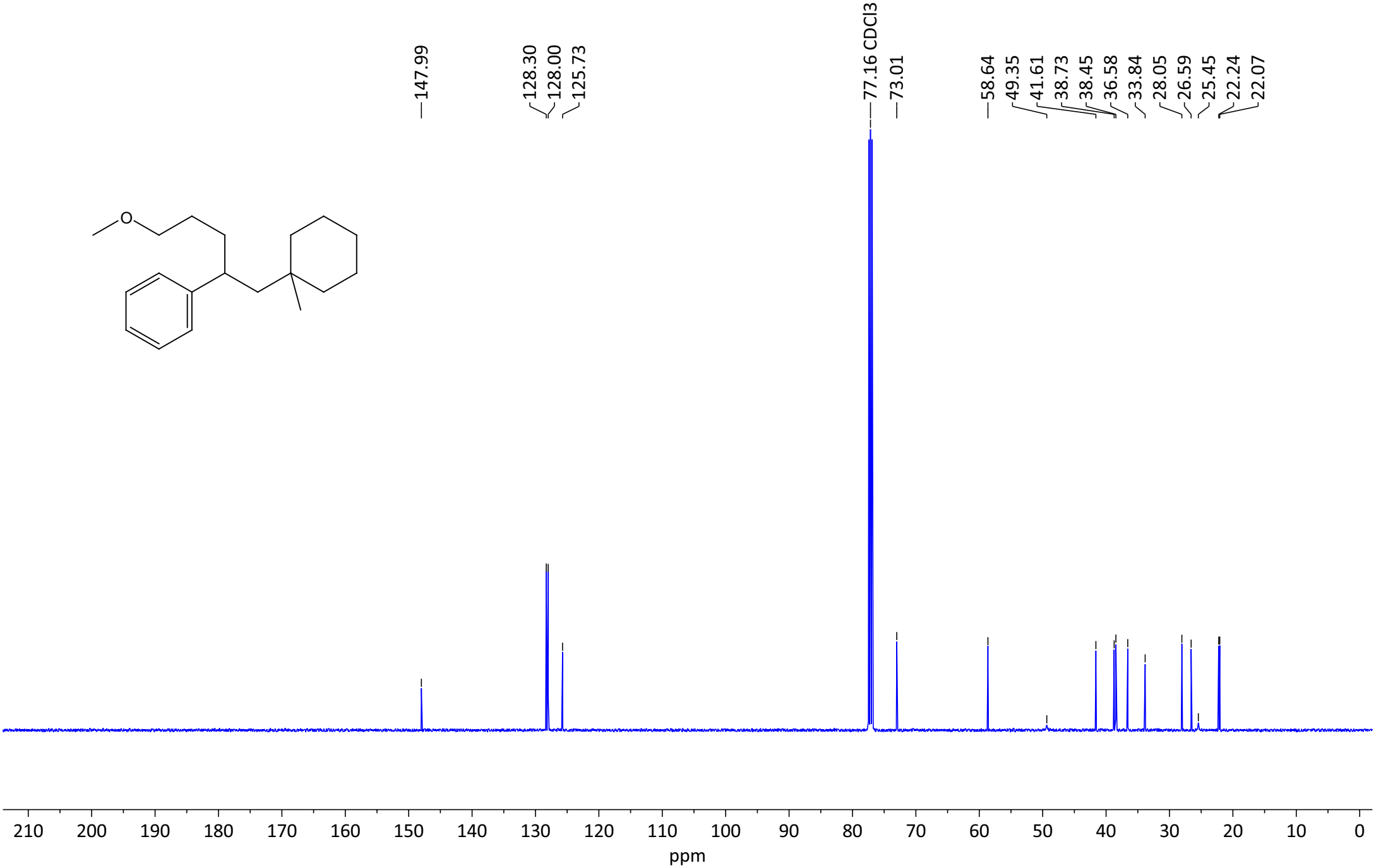
Compound **7**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



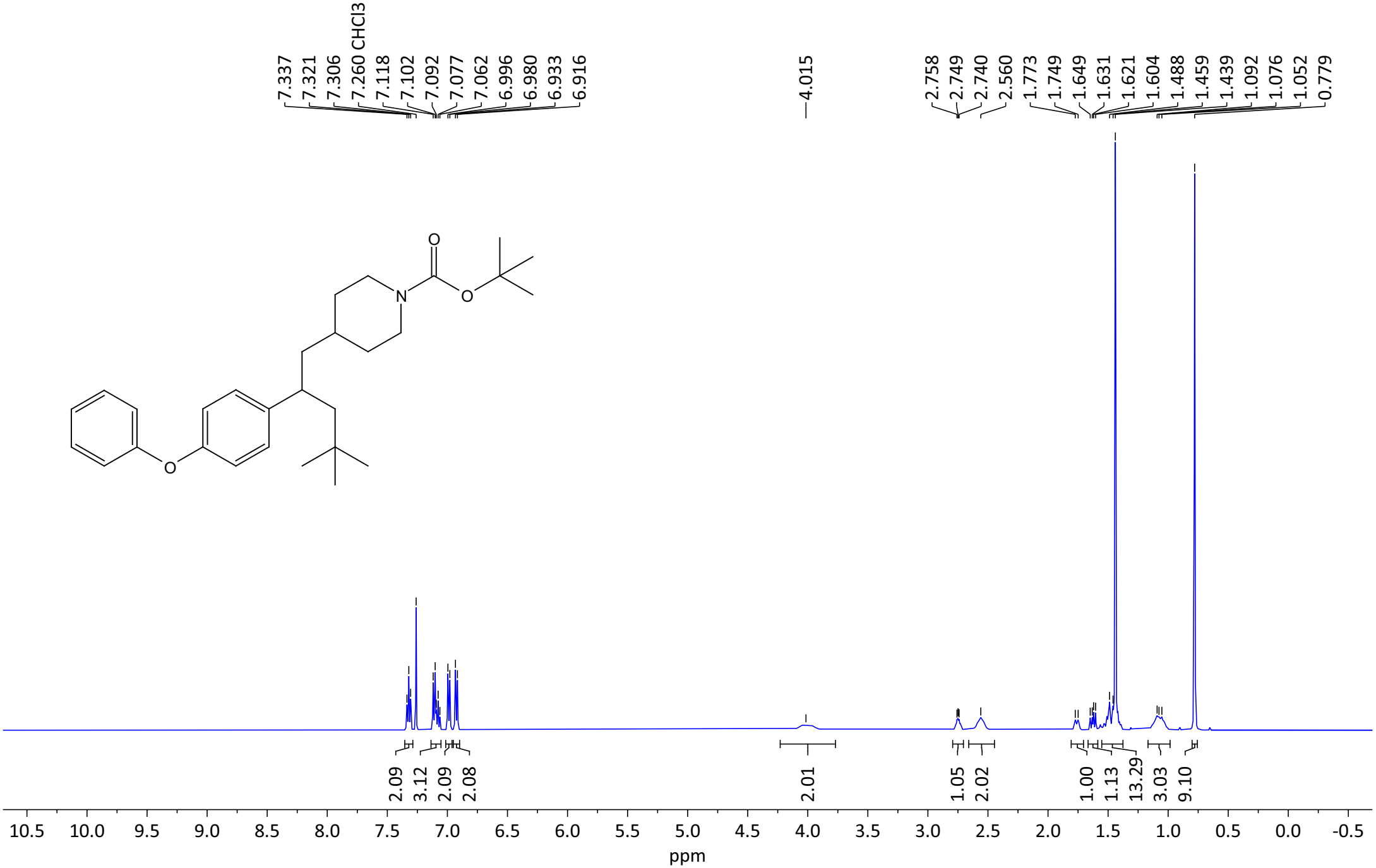
Compound **8**: ^{1}H NMR (500 MHz, $CDCl_3$)



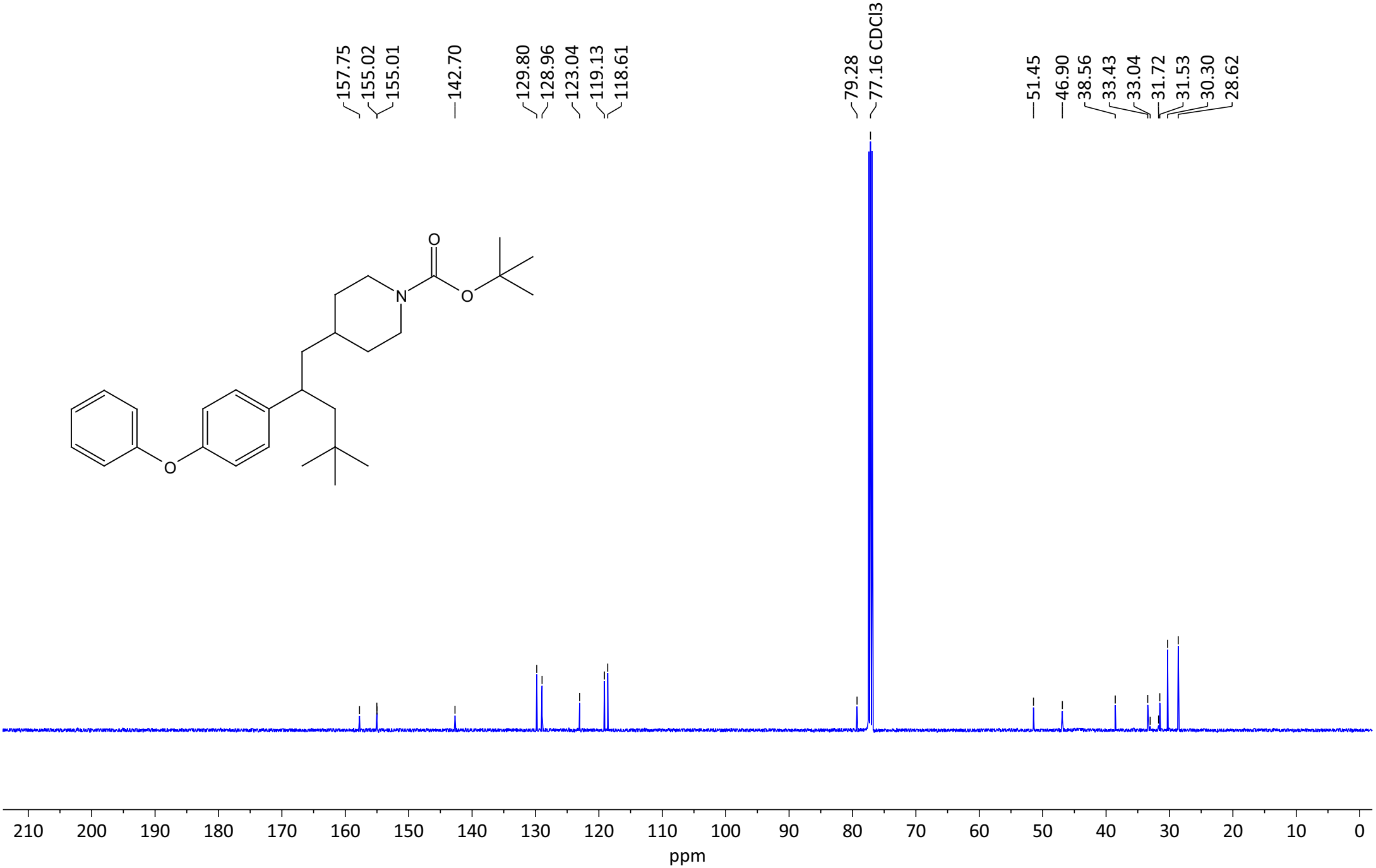
Compound **8**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



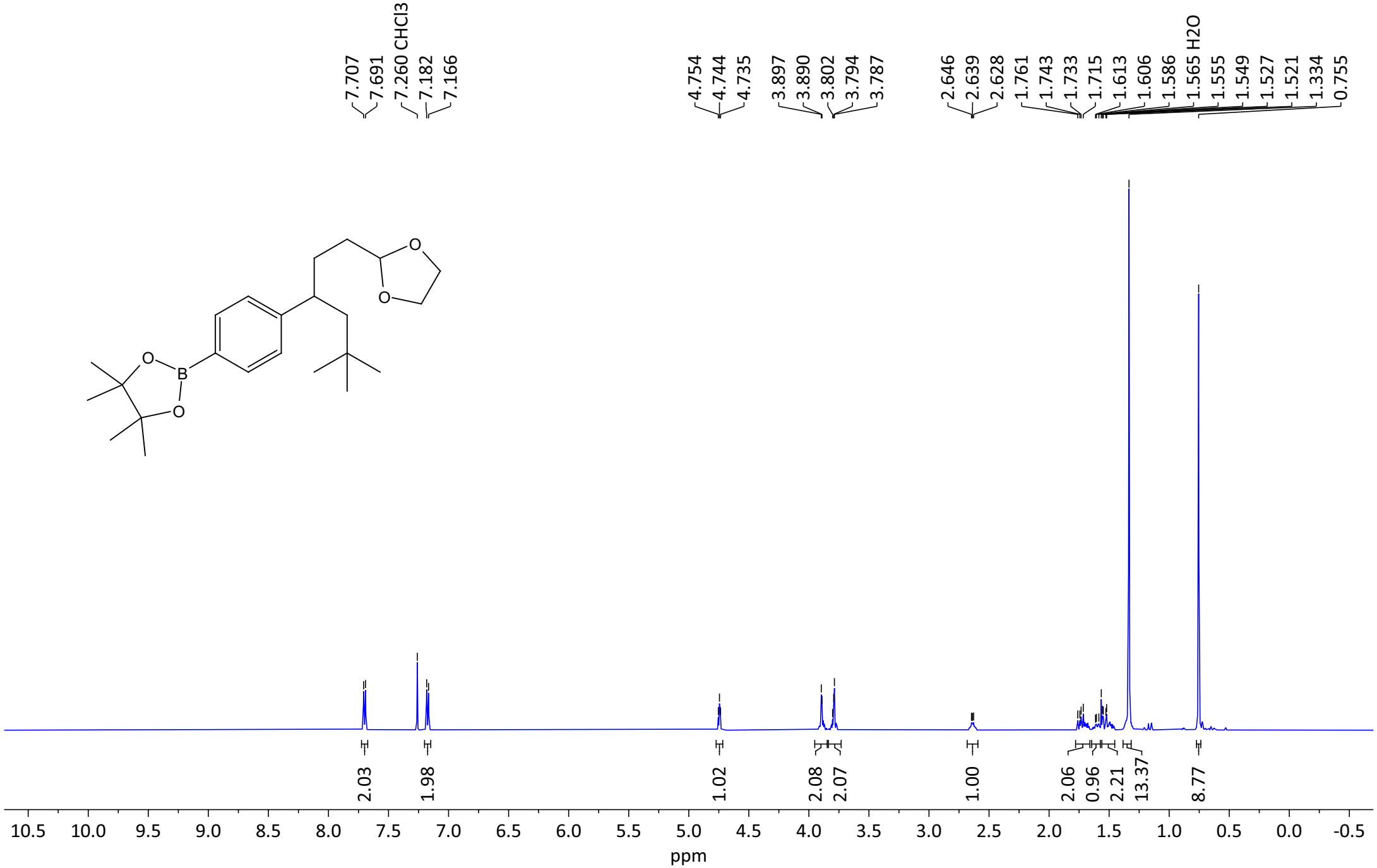
Compound **9**: ^{1}H NMR (500 MHz, $CDCl_3$)



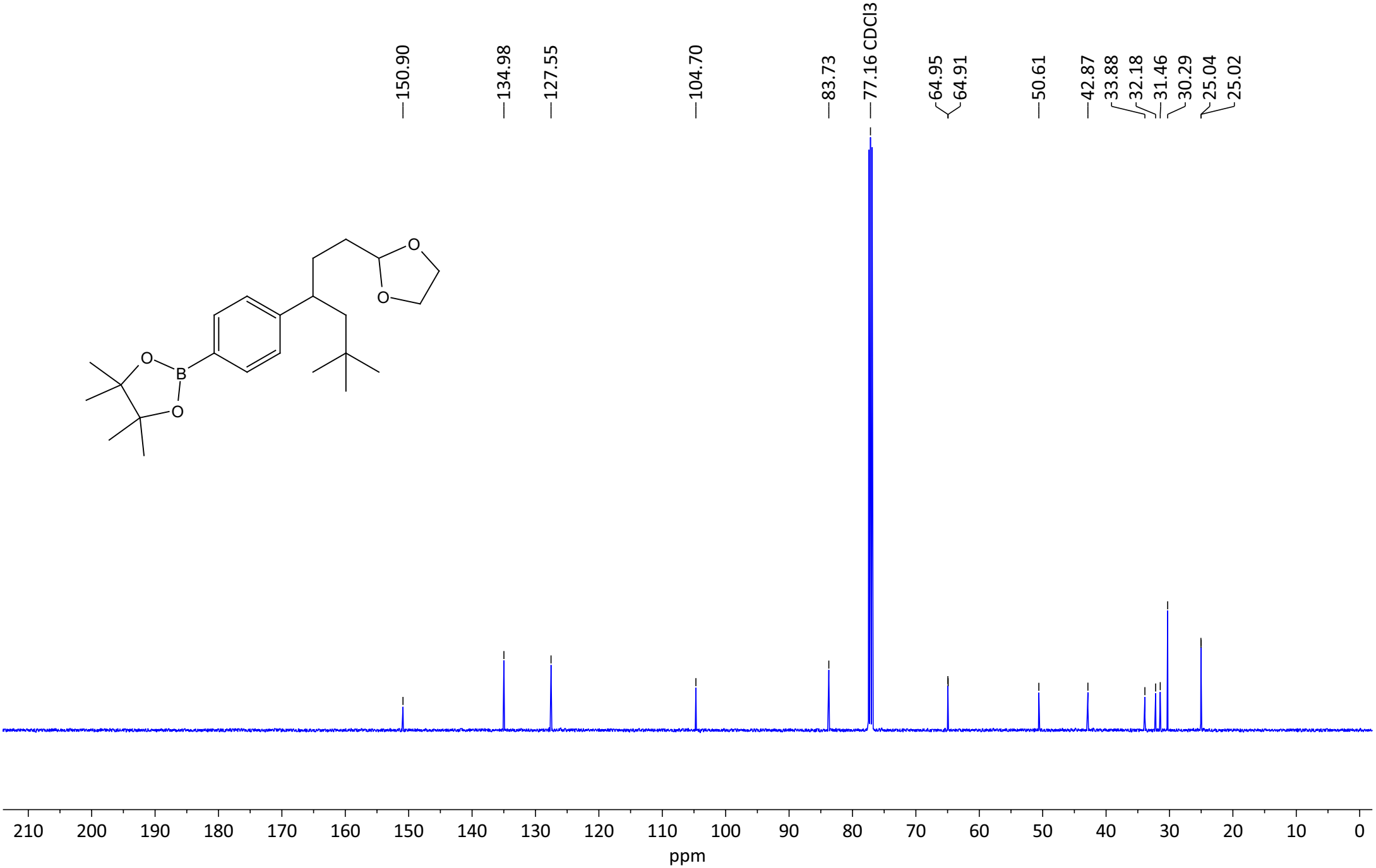
Compound **9**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



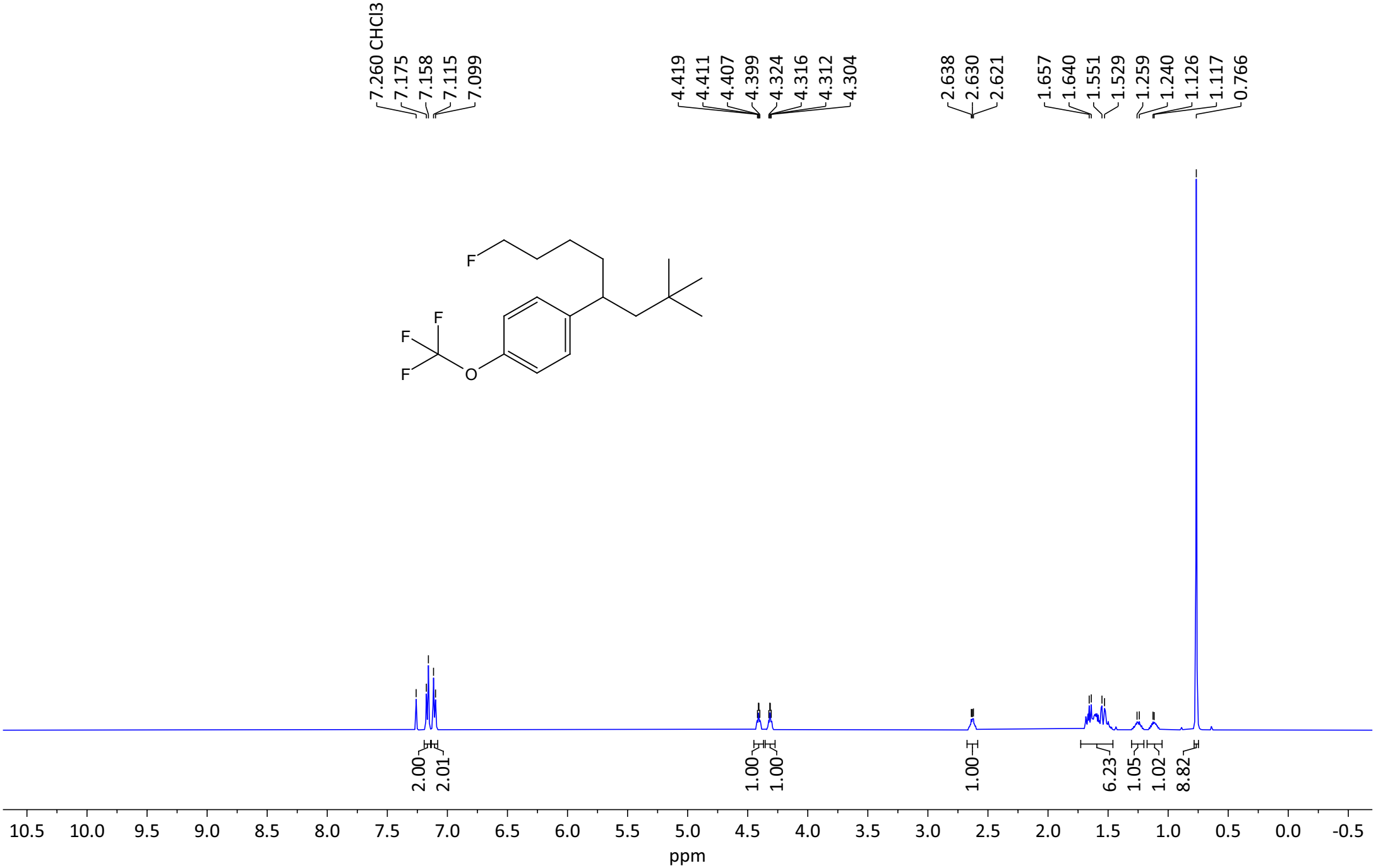
Compound **10**: ^{1}H NMR (500 MHz, $CDCl_3$)



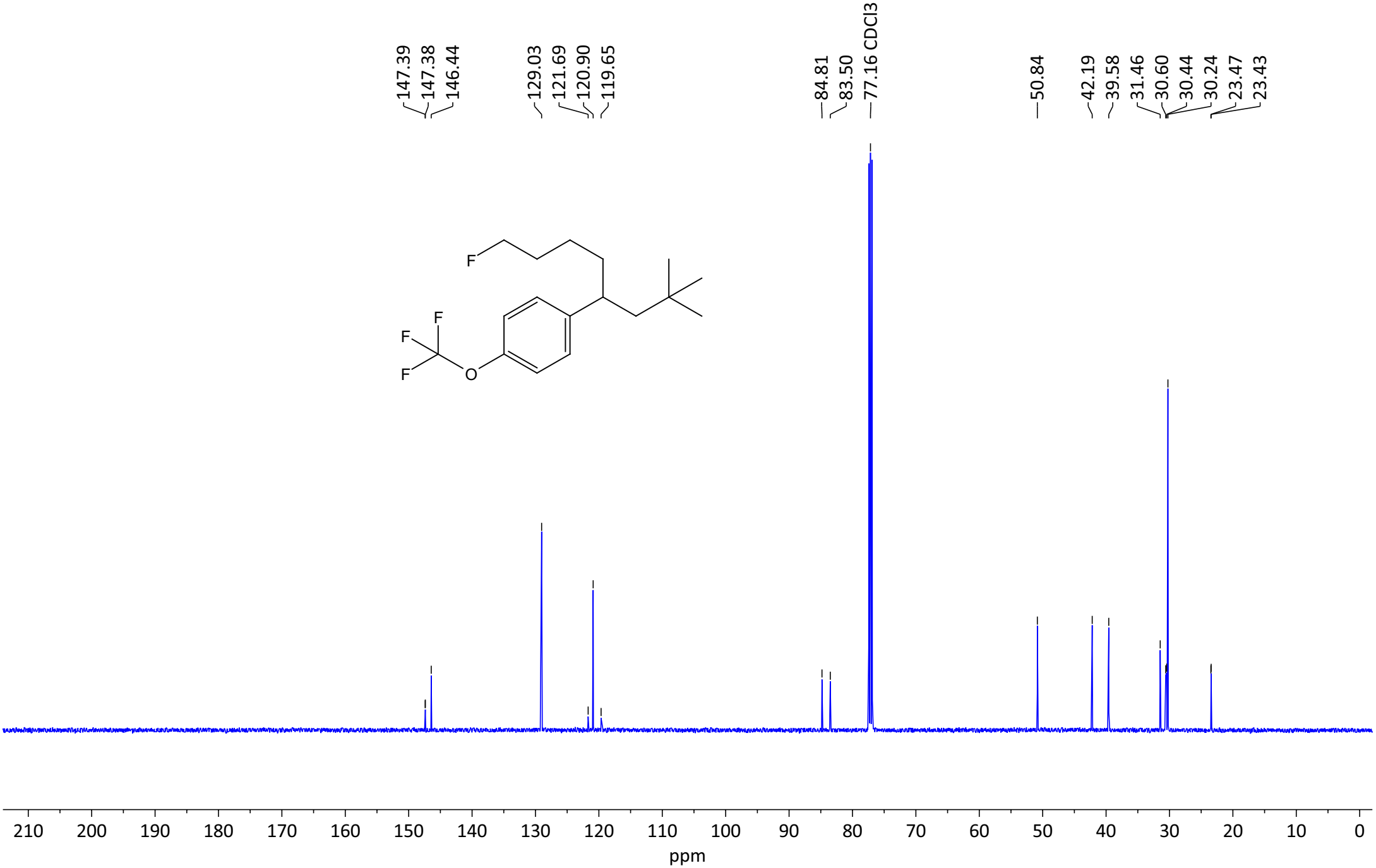
Compound **10**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



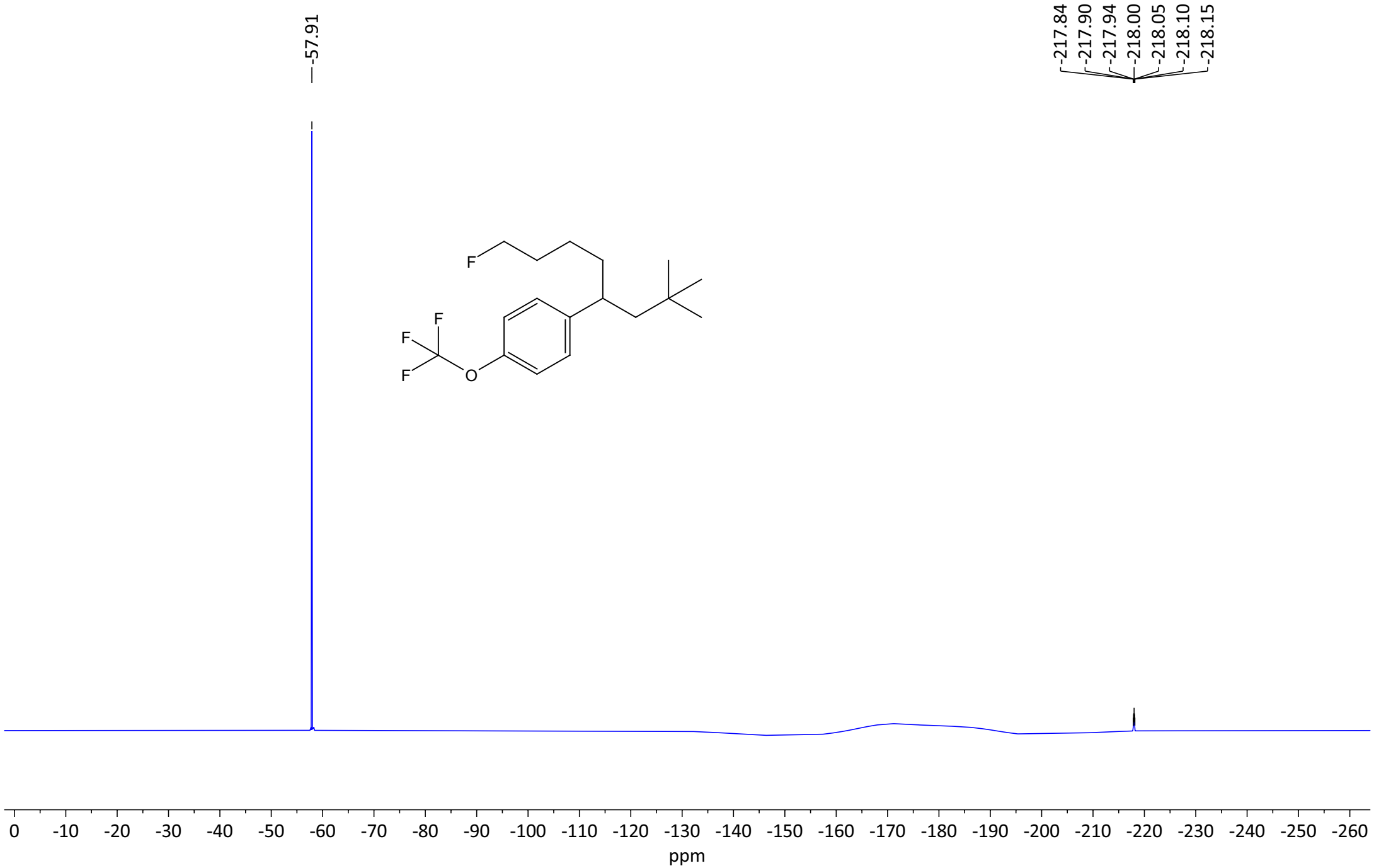
Compound **11**: ^{1}H NMR (500 MHz, $CDCl_3$)



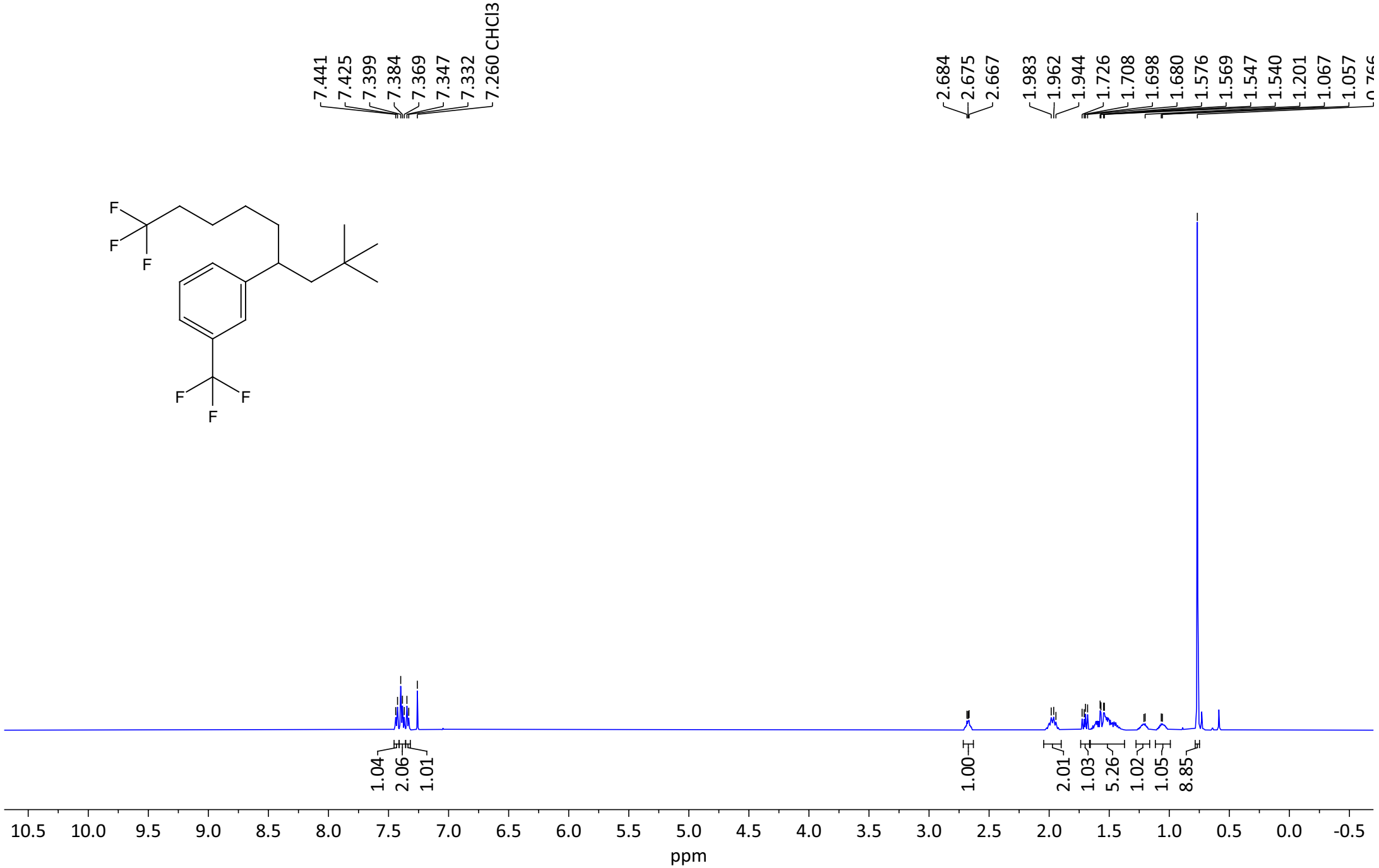
Compound **11**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



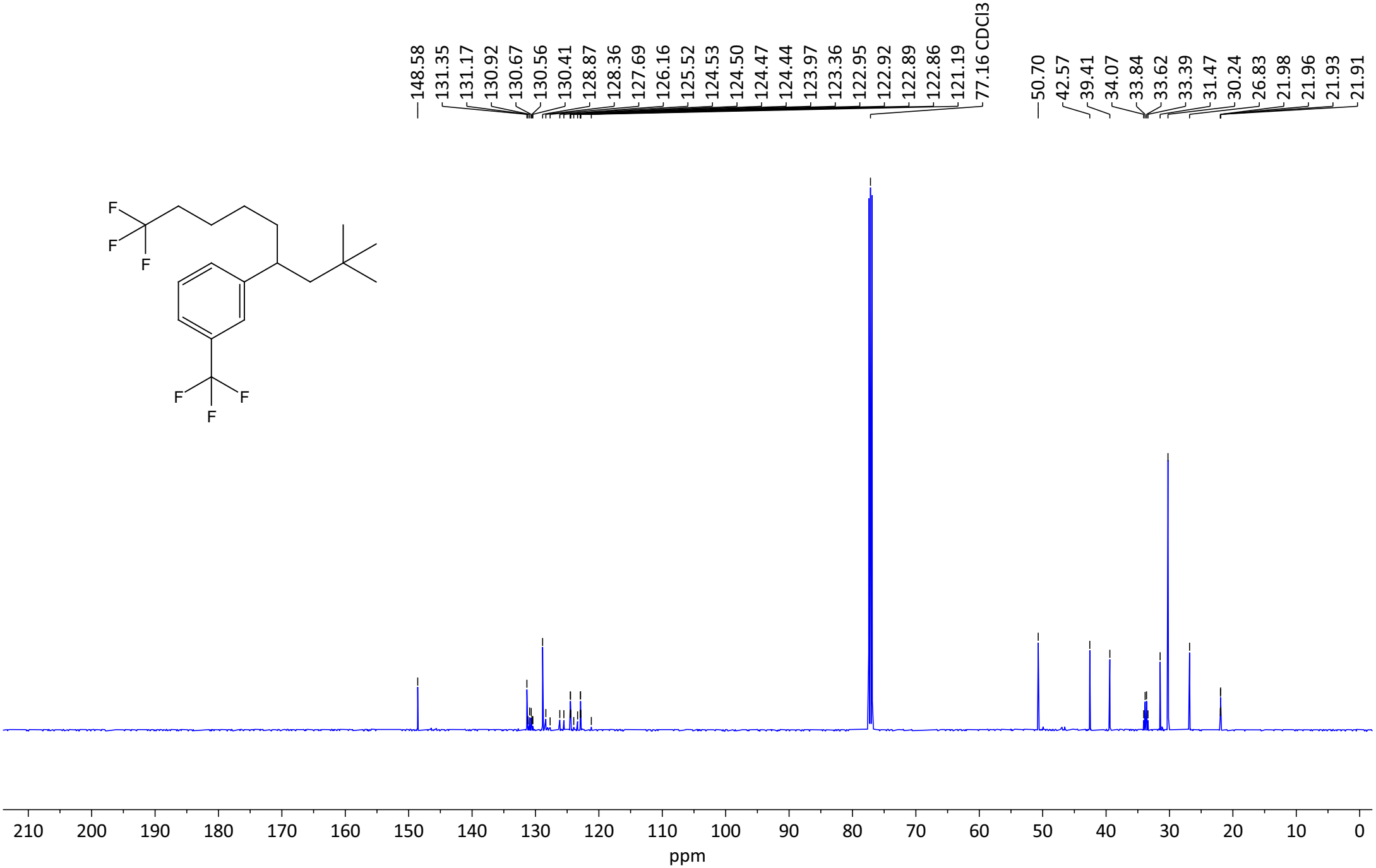
Compound **11**: ^{19}F NMR (470 MHz, $CDCl_3$)



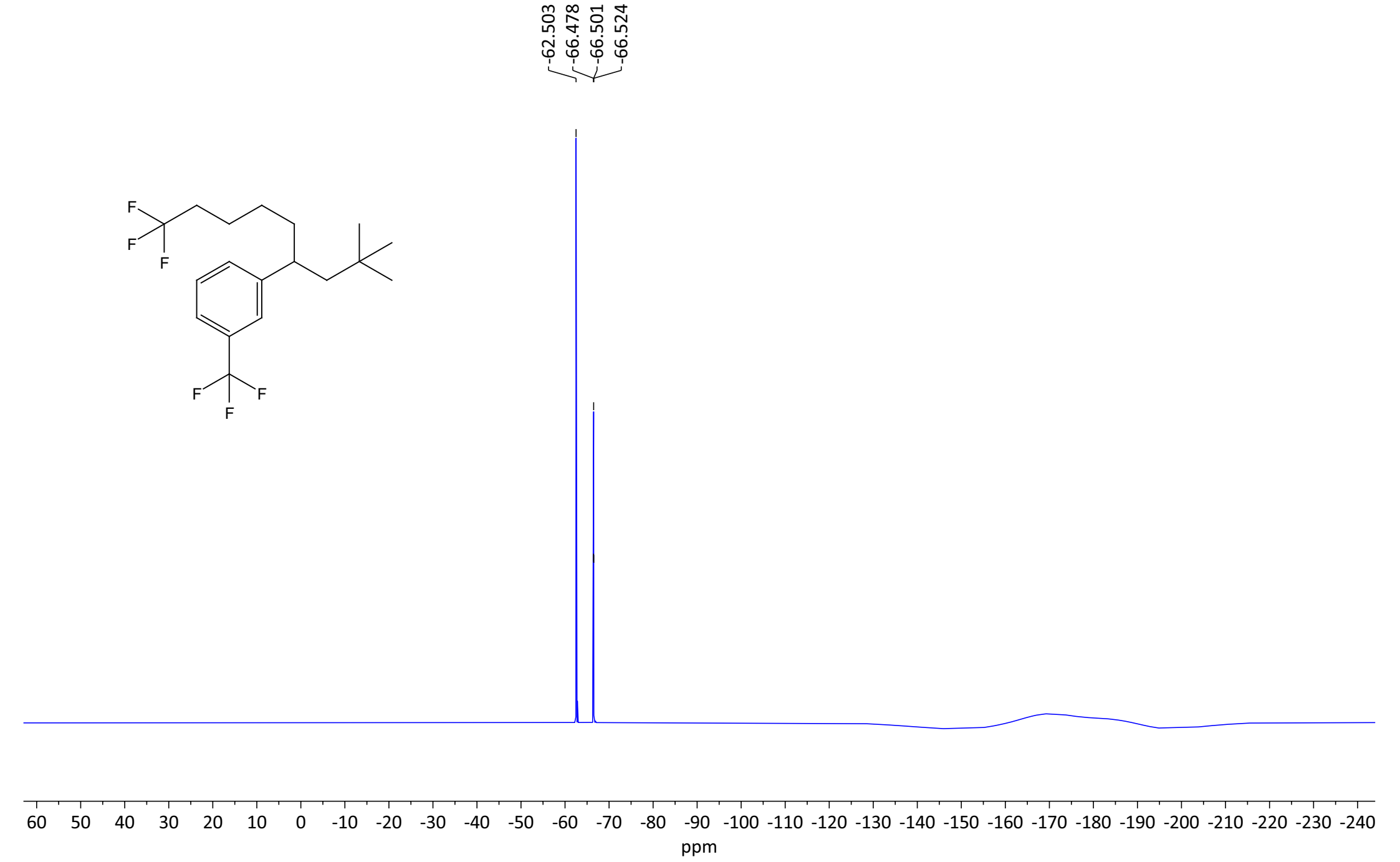
Compound **12**: ^{1}H NMR (500 MHz, $CDCl_3$)



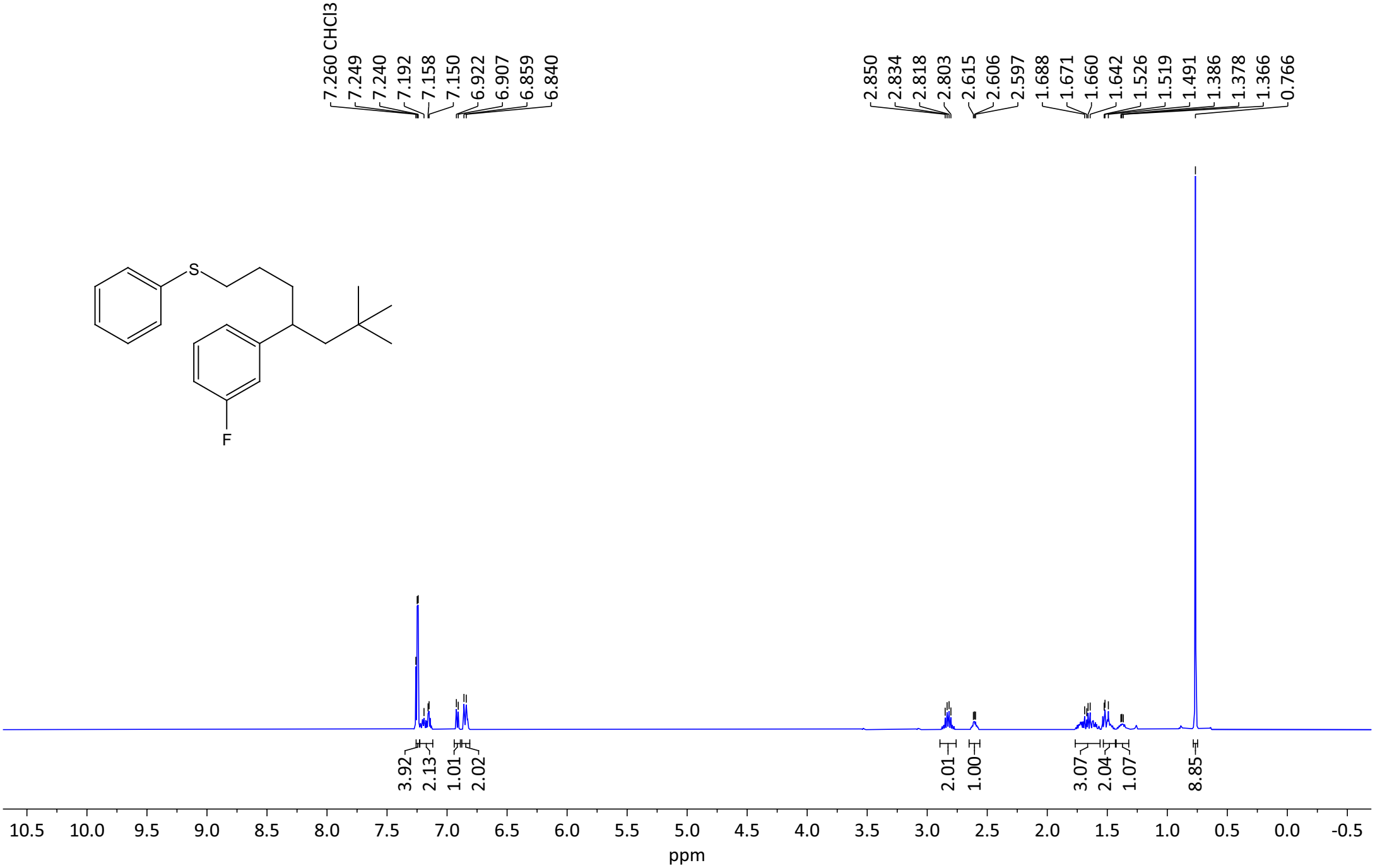
Compound **12**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



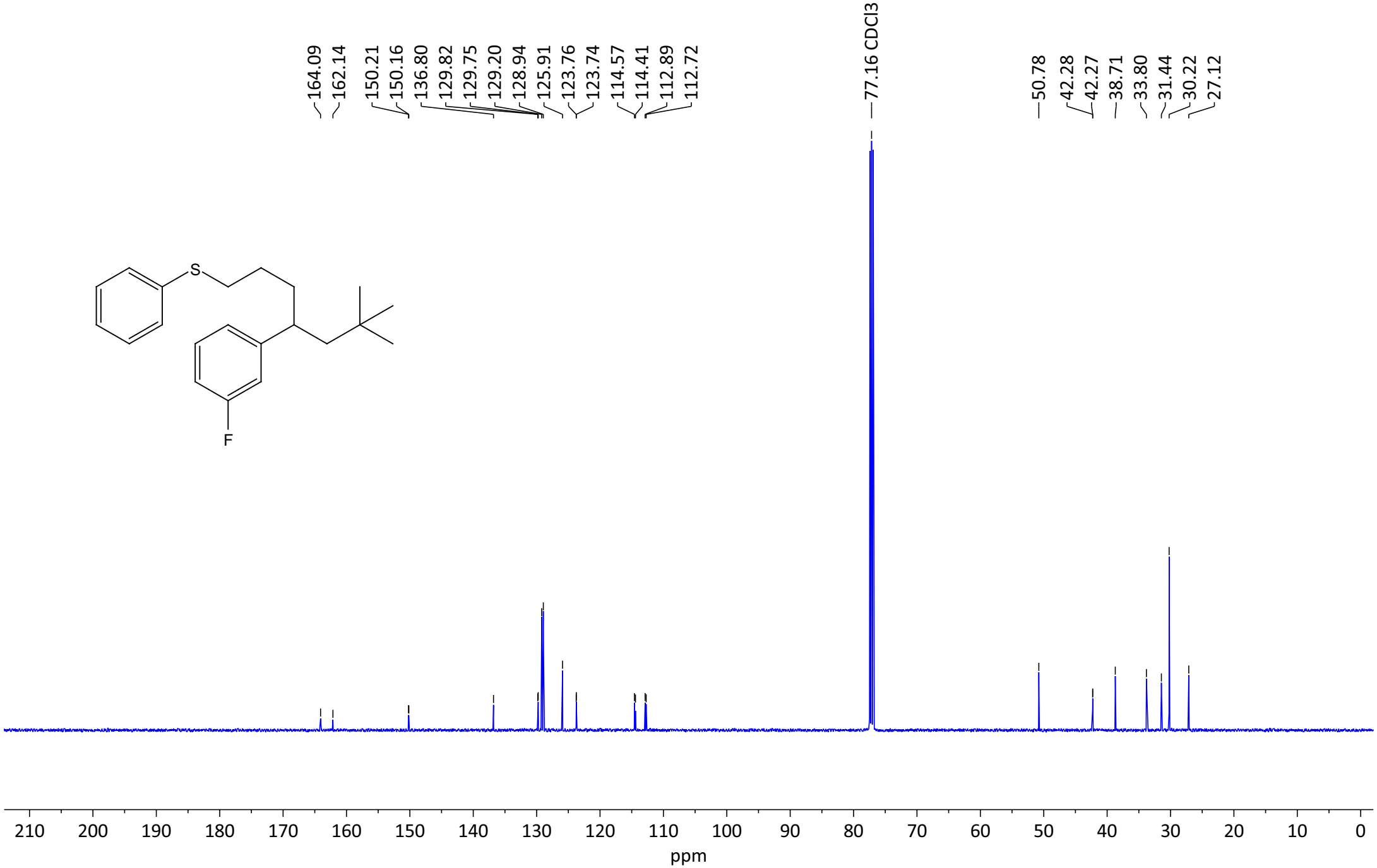
Compound **12**: ^{19}F NMR (470 MHz, $CDCl_3$)



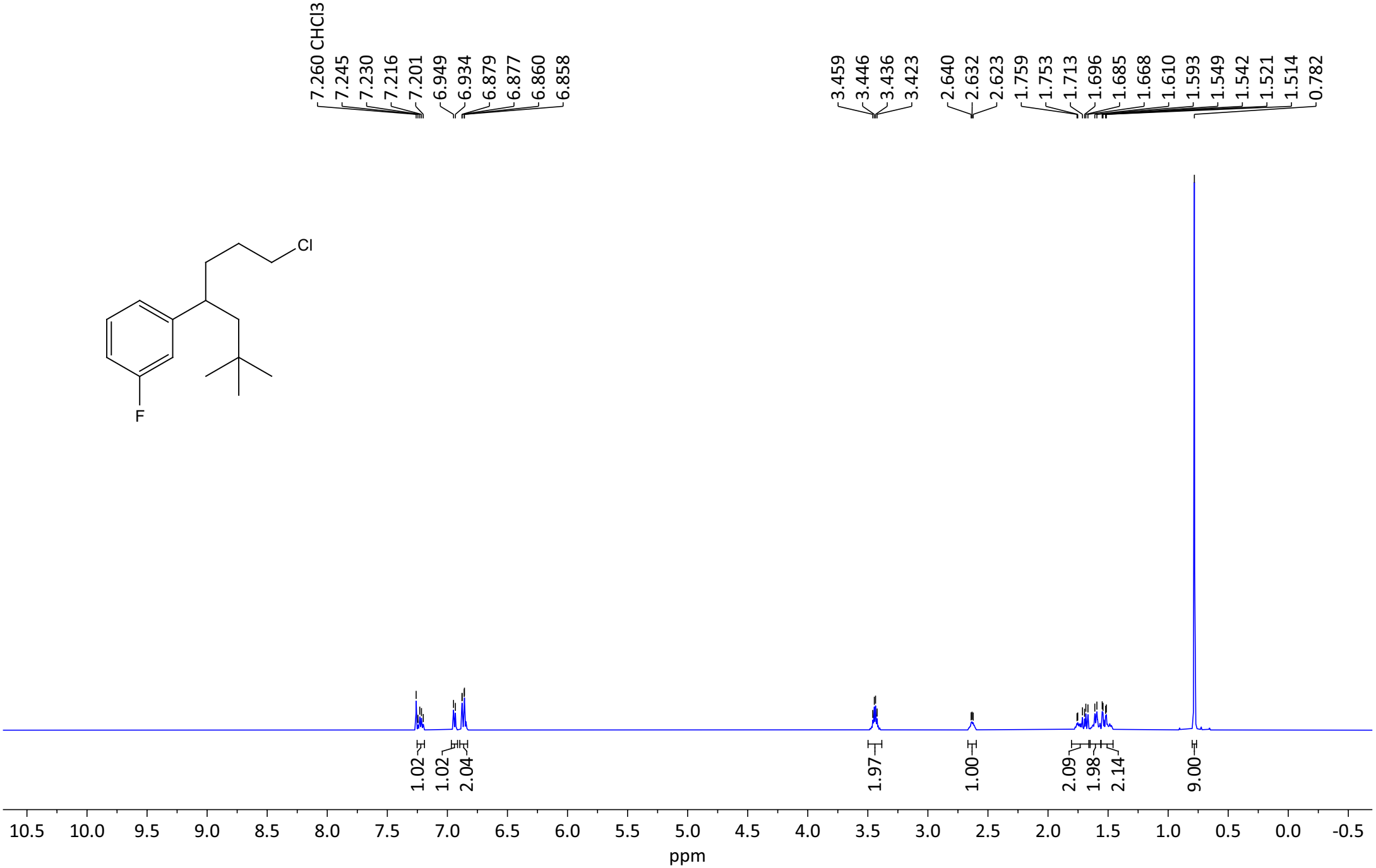
Compound **13**: ^{1}H NMR (500 MHz, $CDCl_3$)



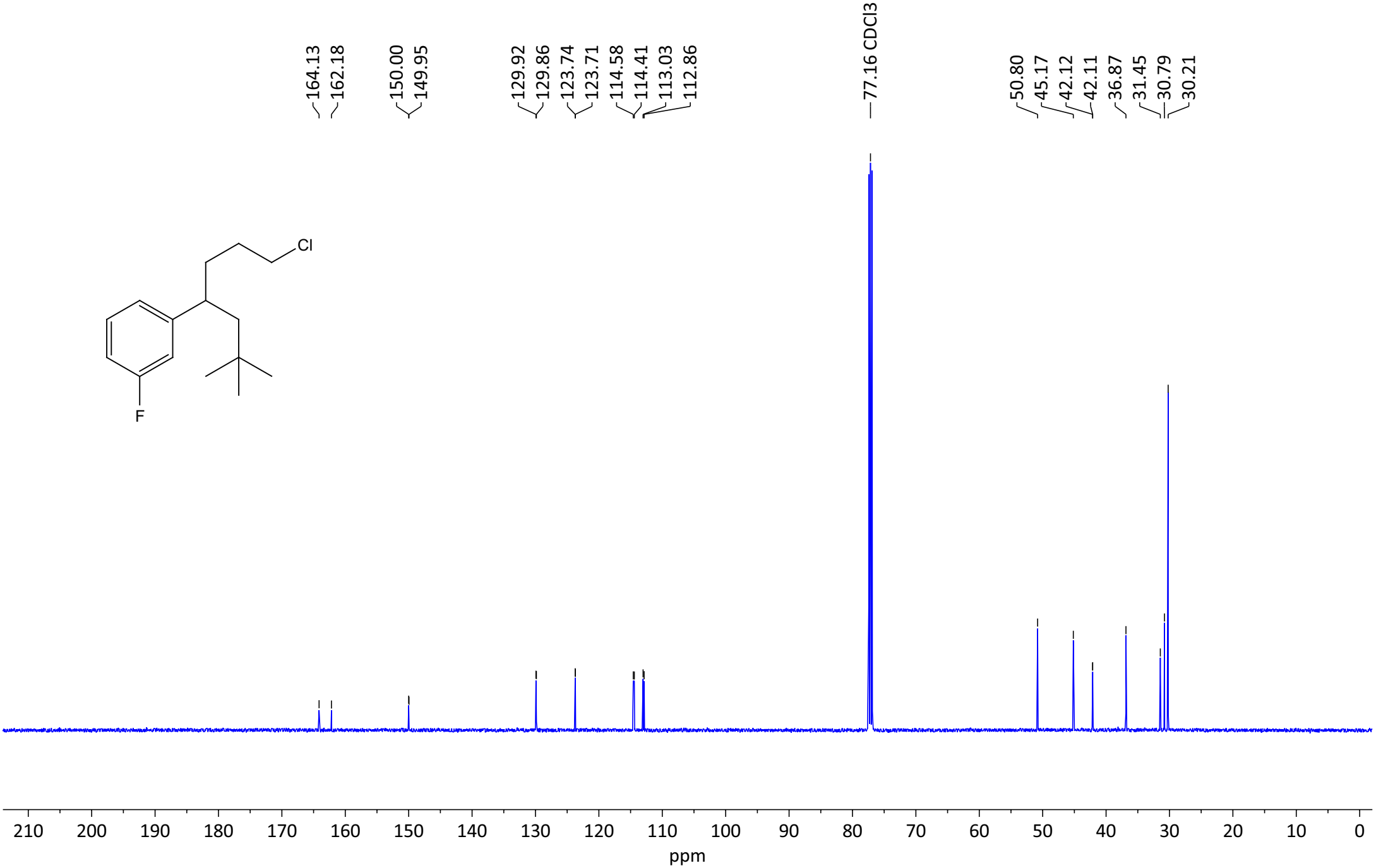
Compound **13**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



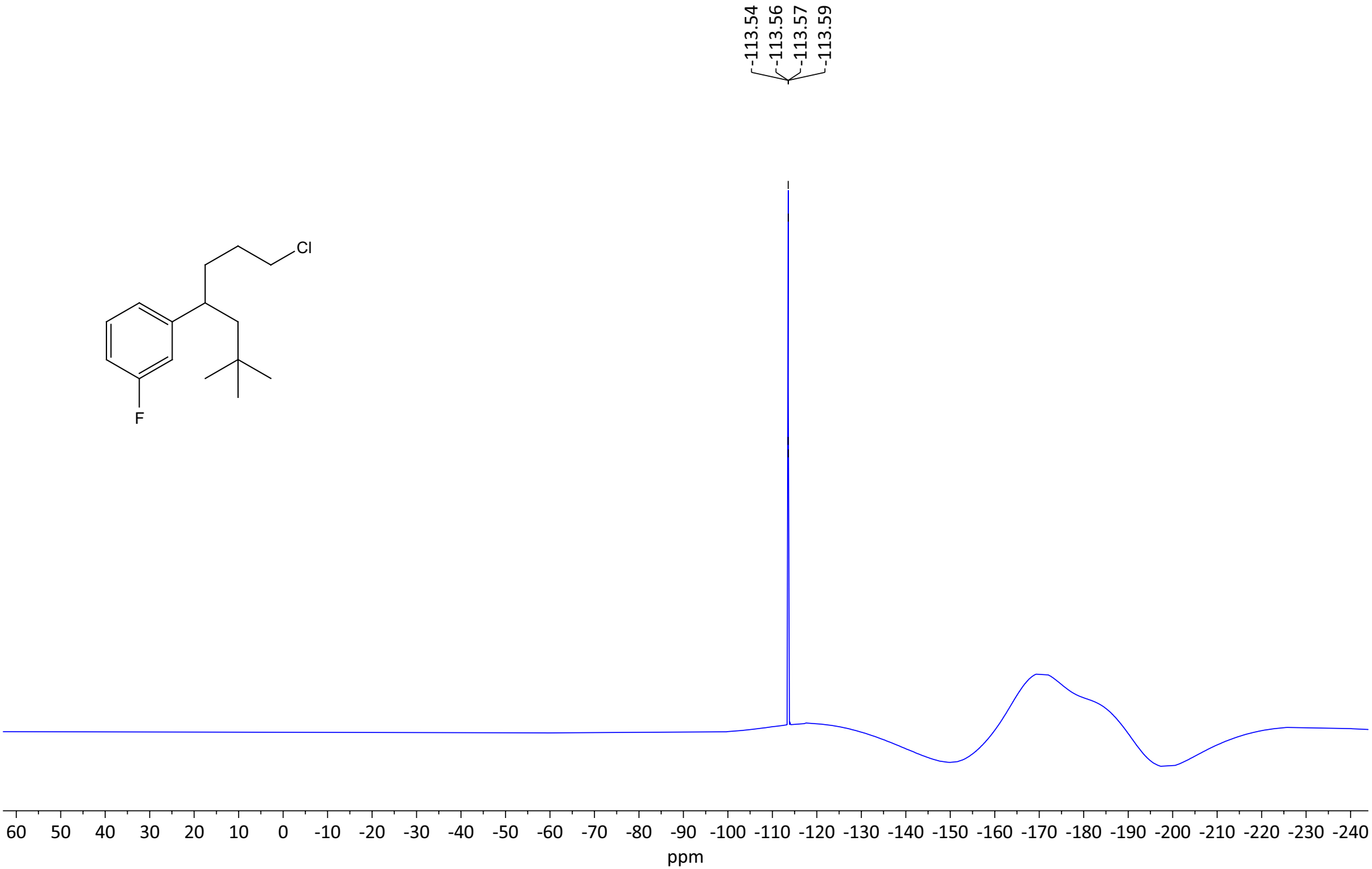
Compound **14**: ^{1}H NMR (500 MHz, $CDCl_3$)



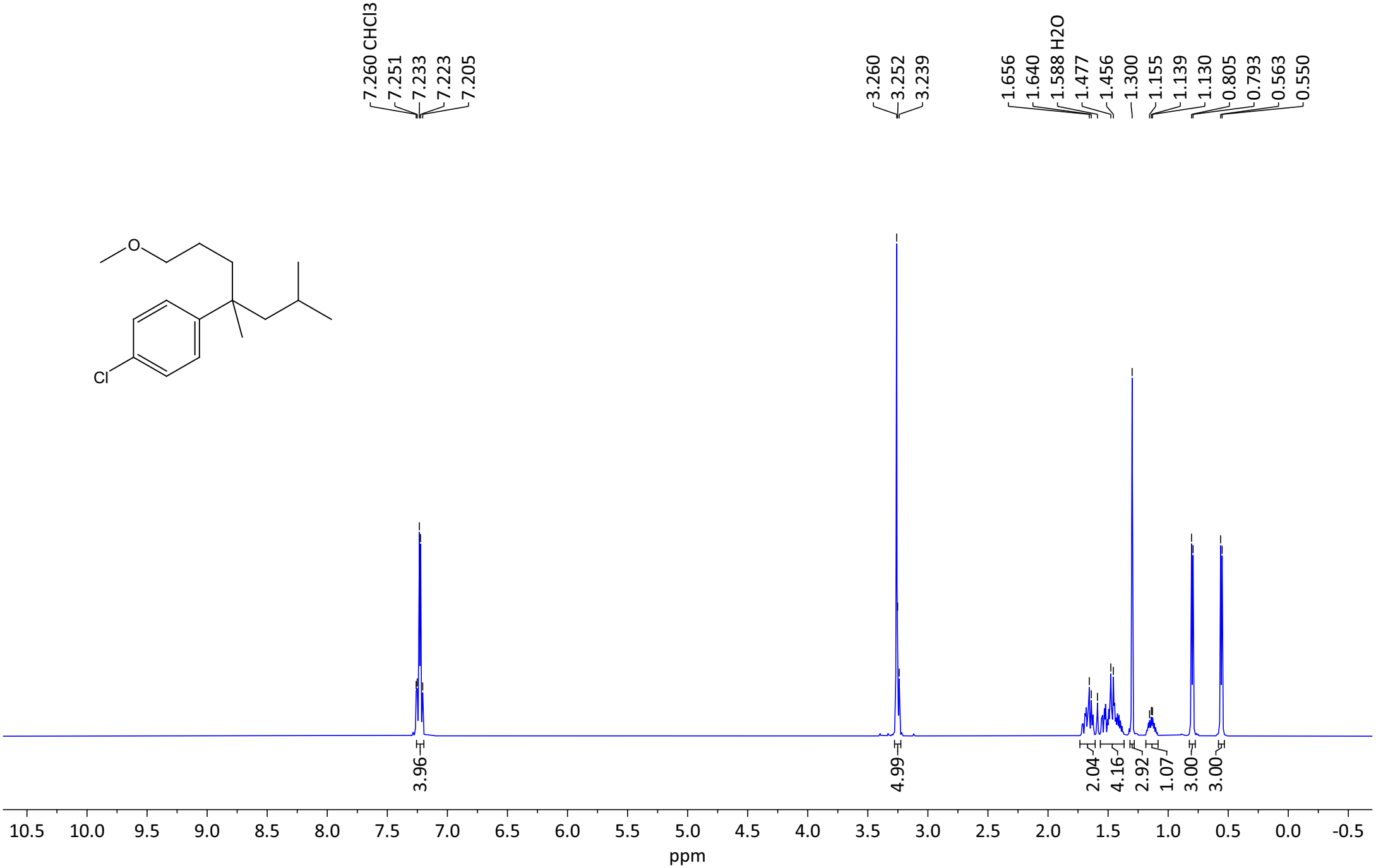
Compound **14**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



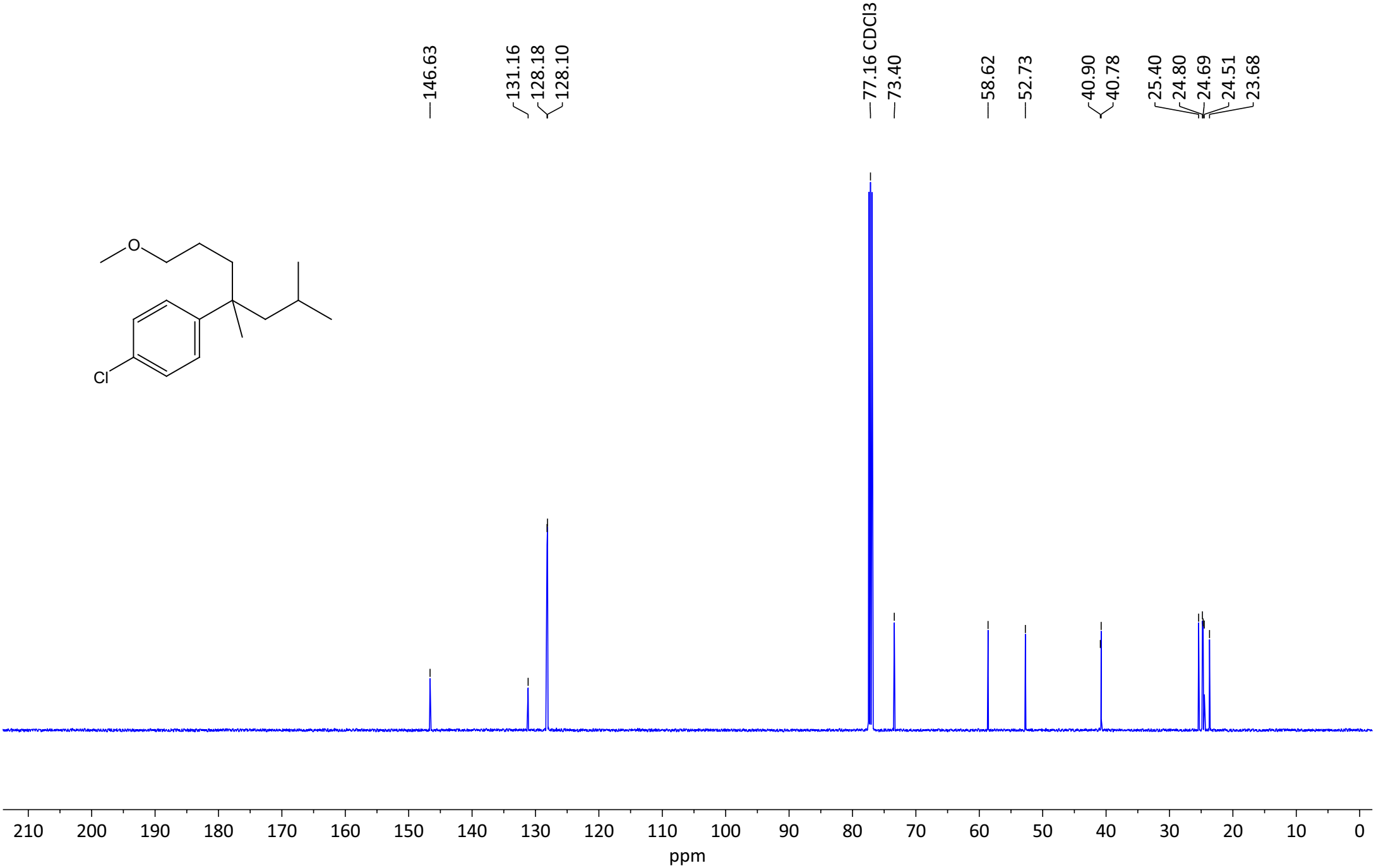
Compound **14**: ^{19}F NMR (470 MHz, $CDCl_3$)



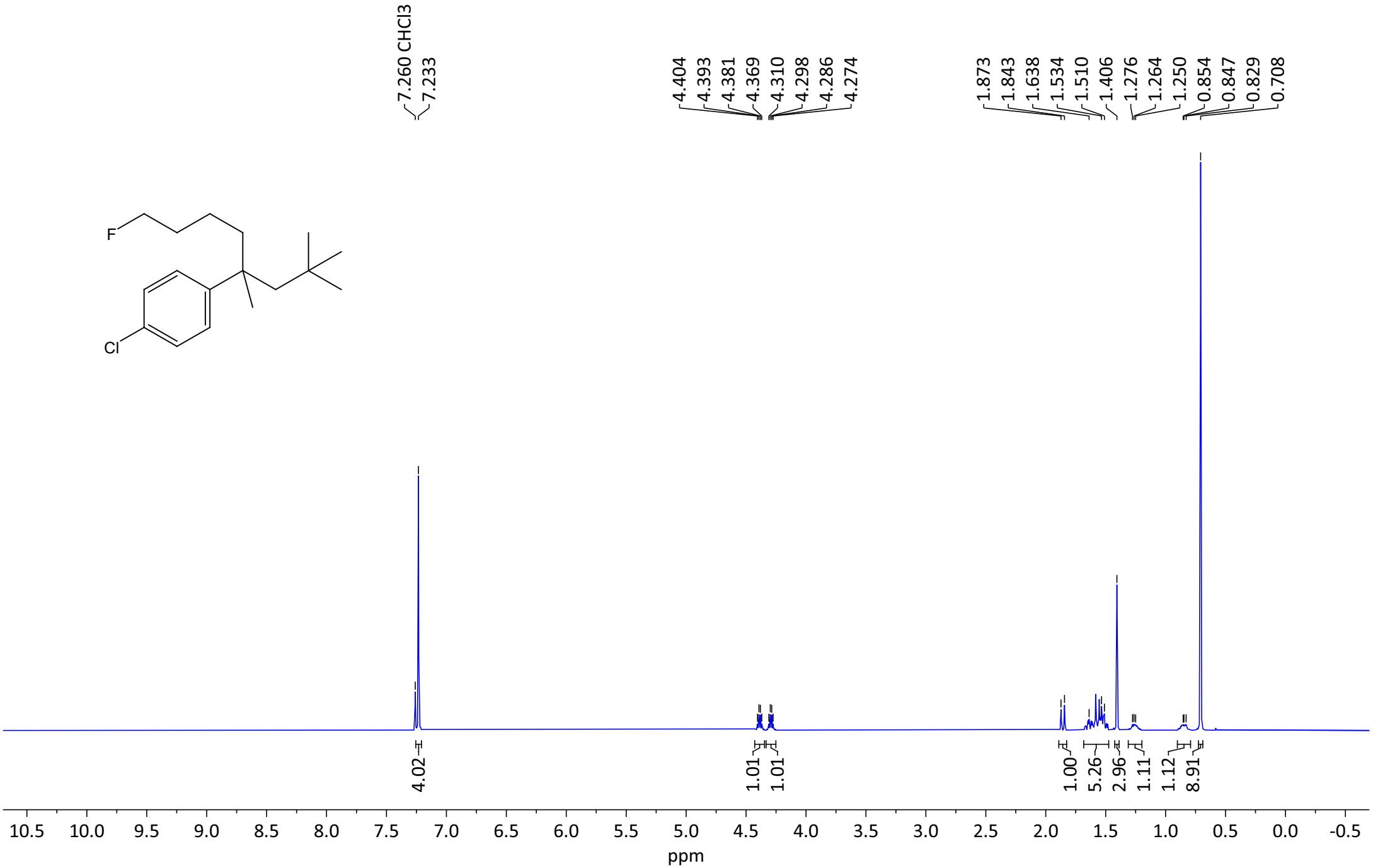
Compound **15**: ^{1}H NMR (500 MHz, $CDCl_3$)



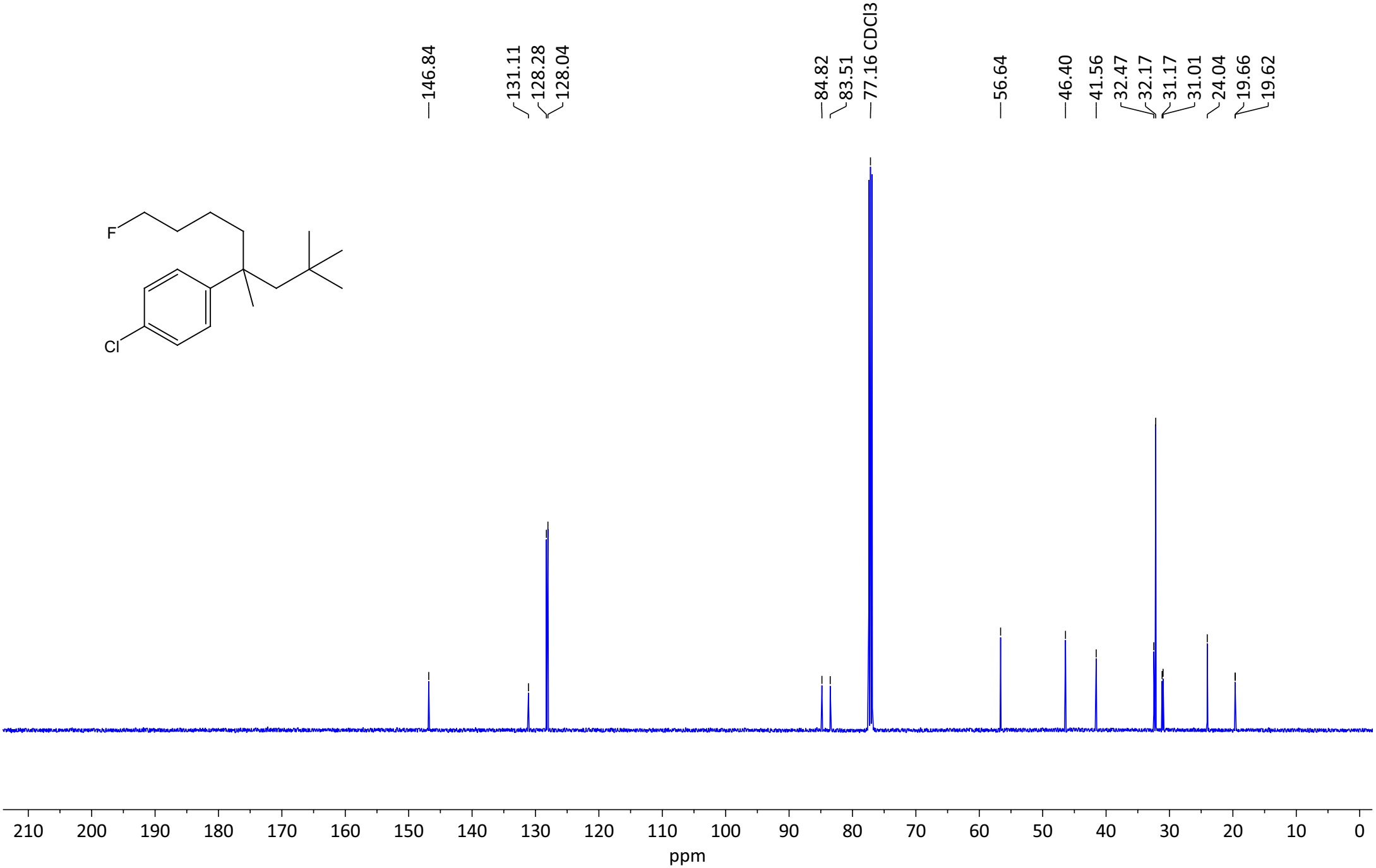
Compound **15**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



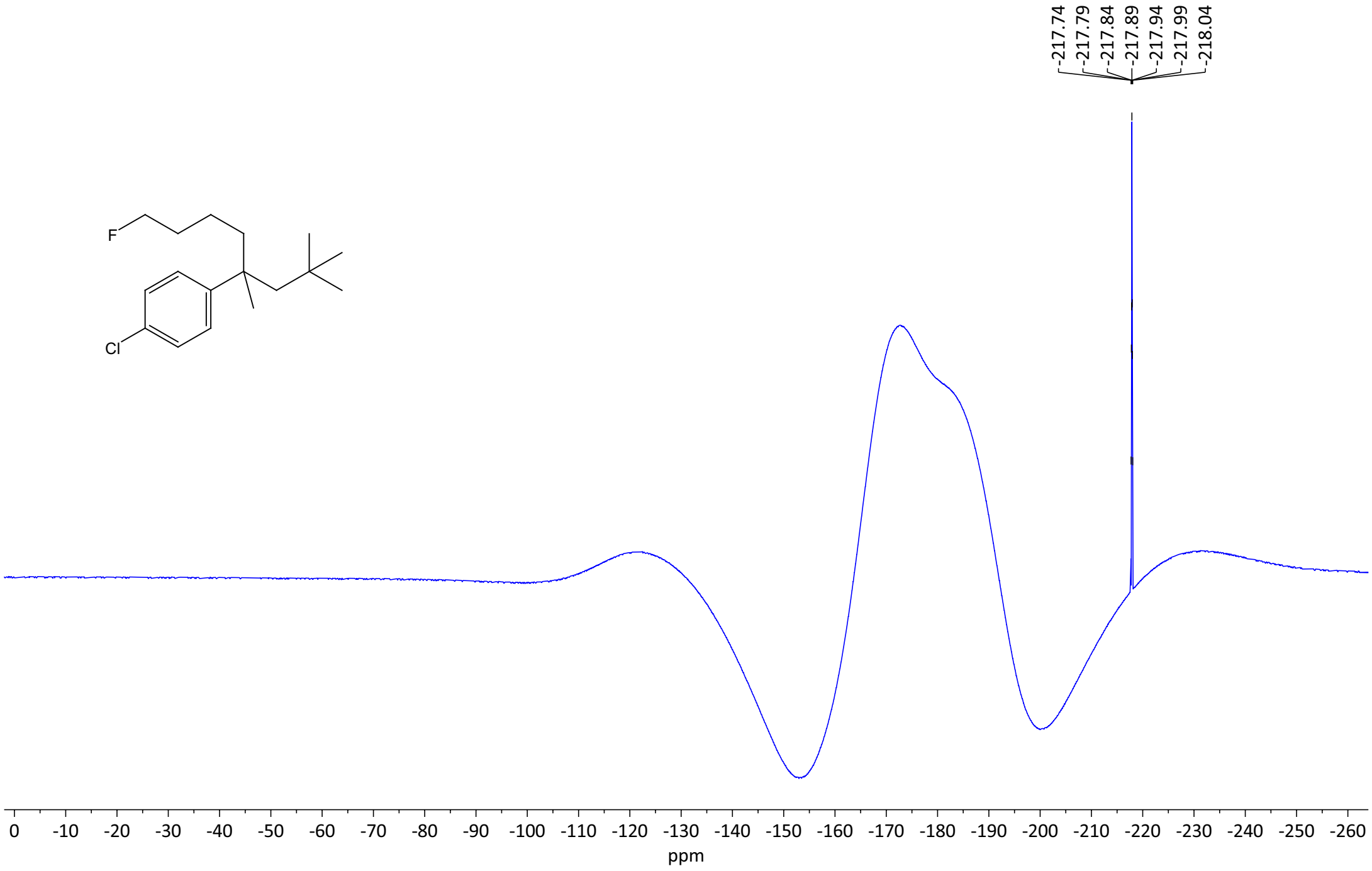
Compound **16**: ^{1}H NMR (500 MHz, $CDCl_3$)



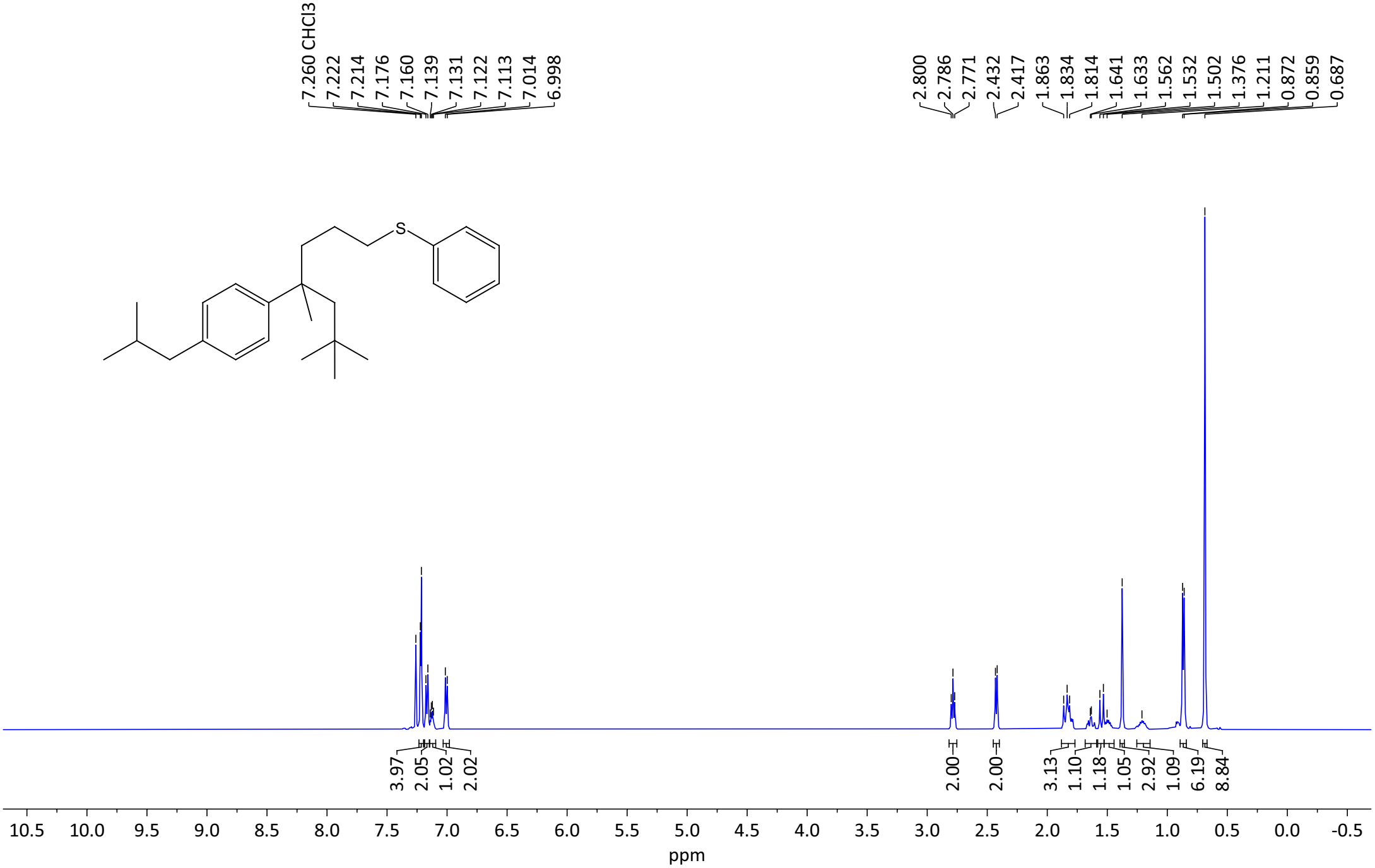
Compound **16**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



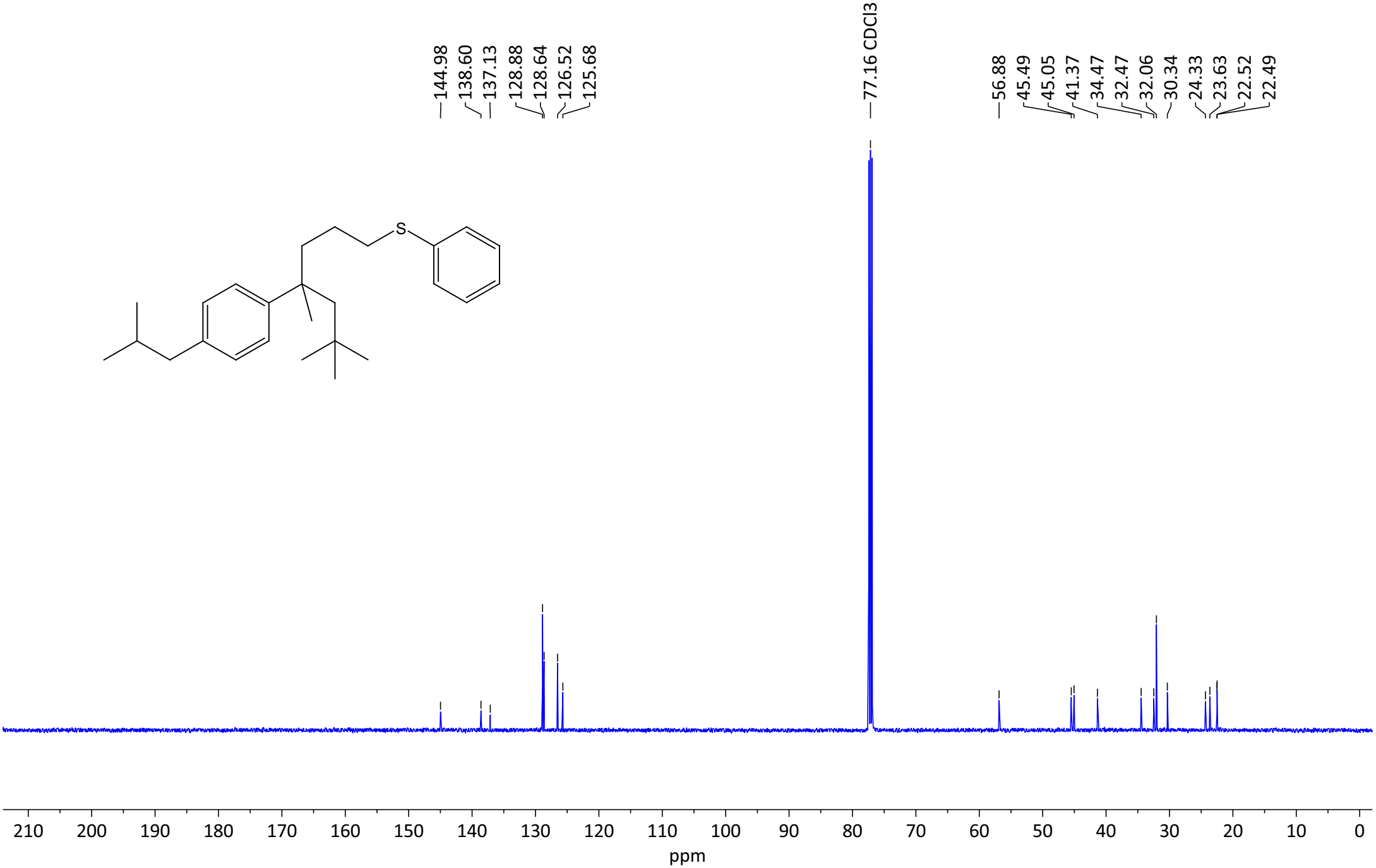
Compound **16**: ^{19}F NMR (470 MHz, $CDCl_3$)



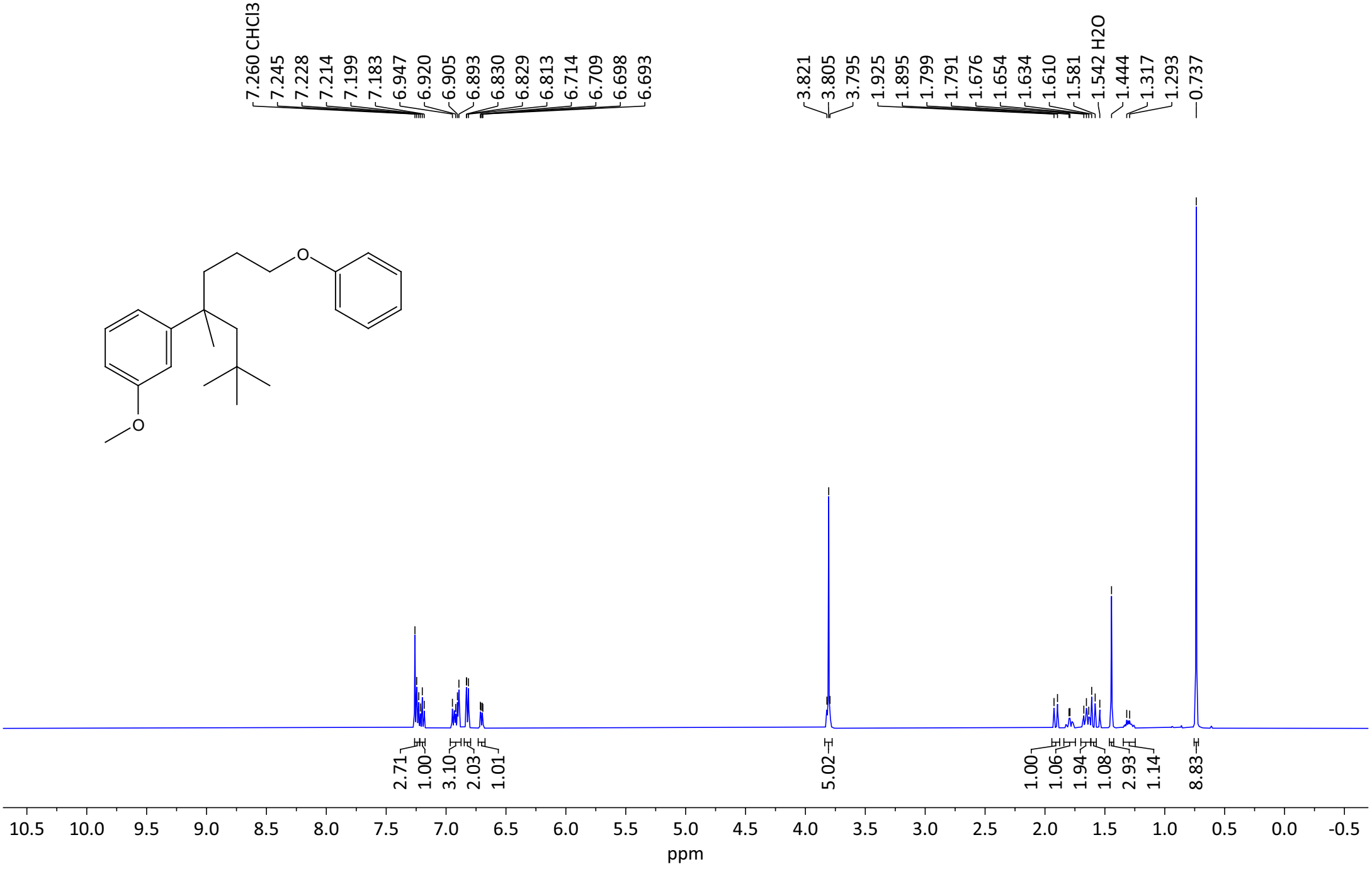
Compound **17**: ^{1}H NMR (500 MHz, $CDCl_3$)



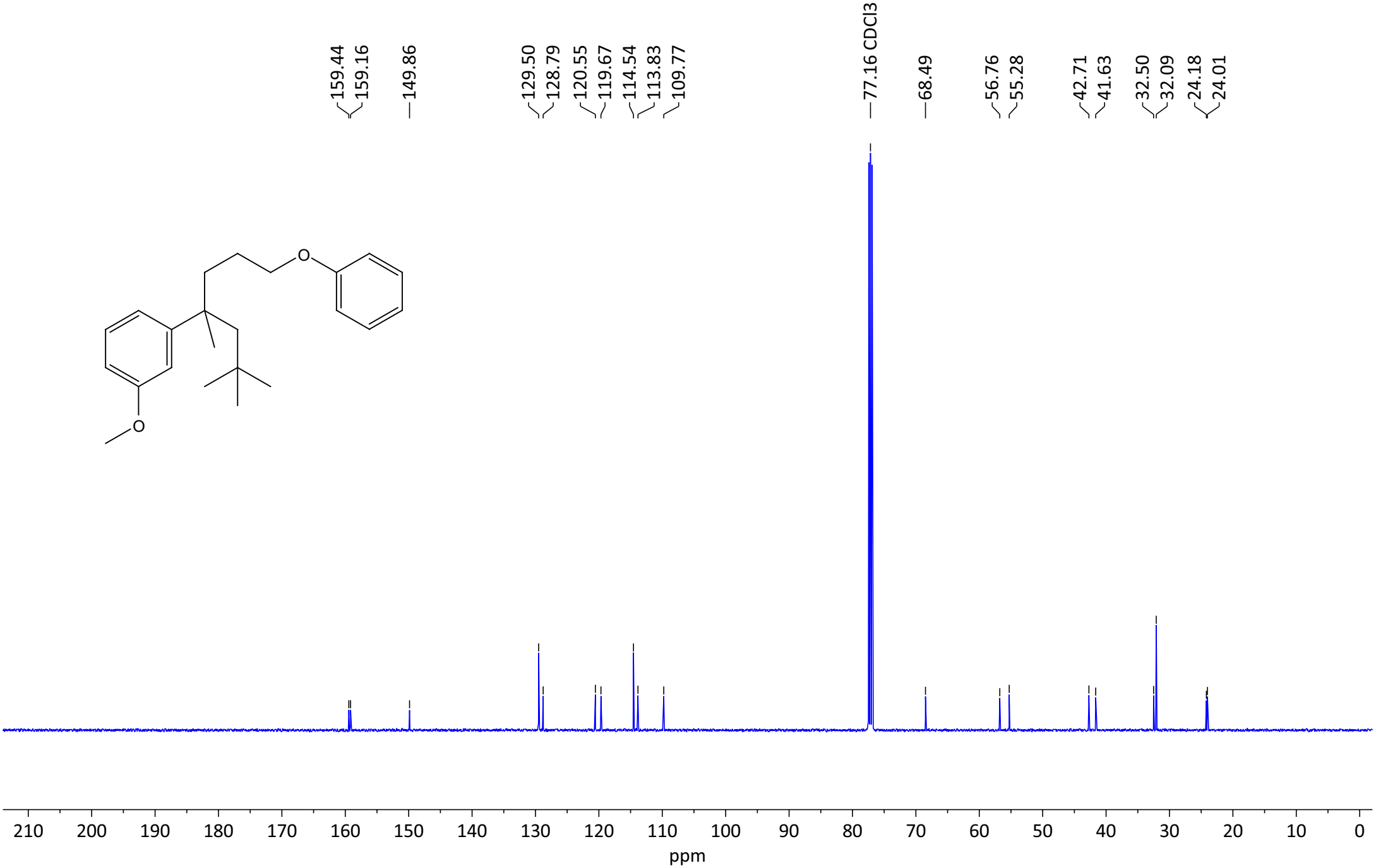
Compound **17**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



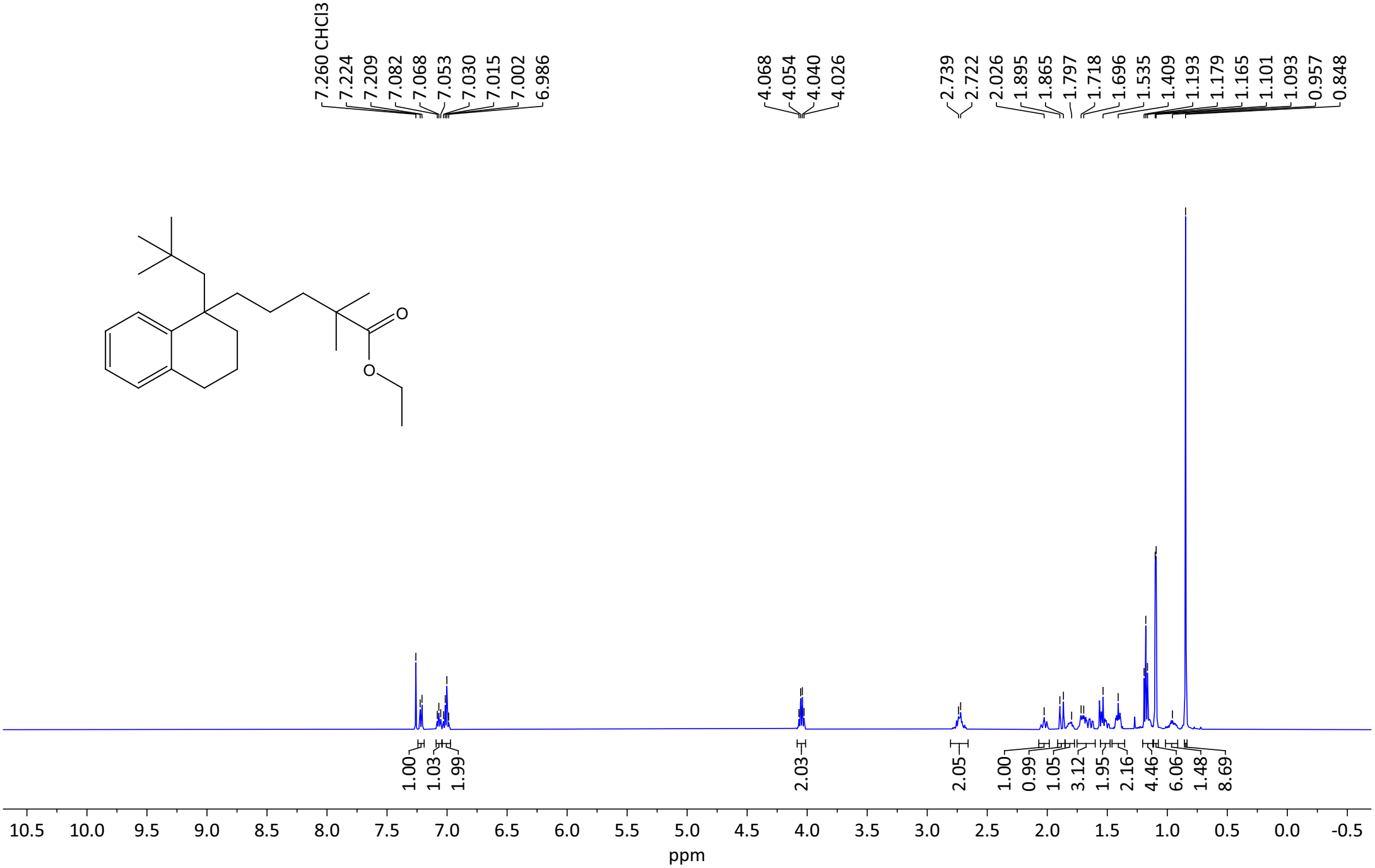
Compound **18**: ^{1}H NMR (500 MHz, $CDCl_3$)



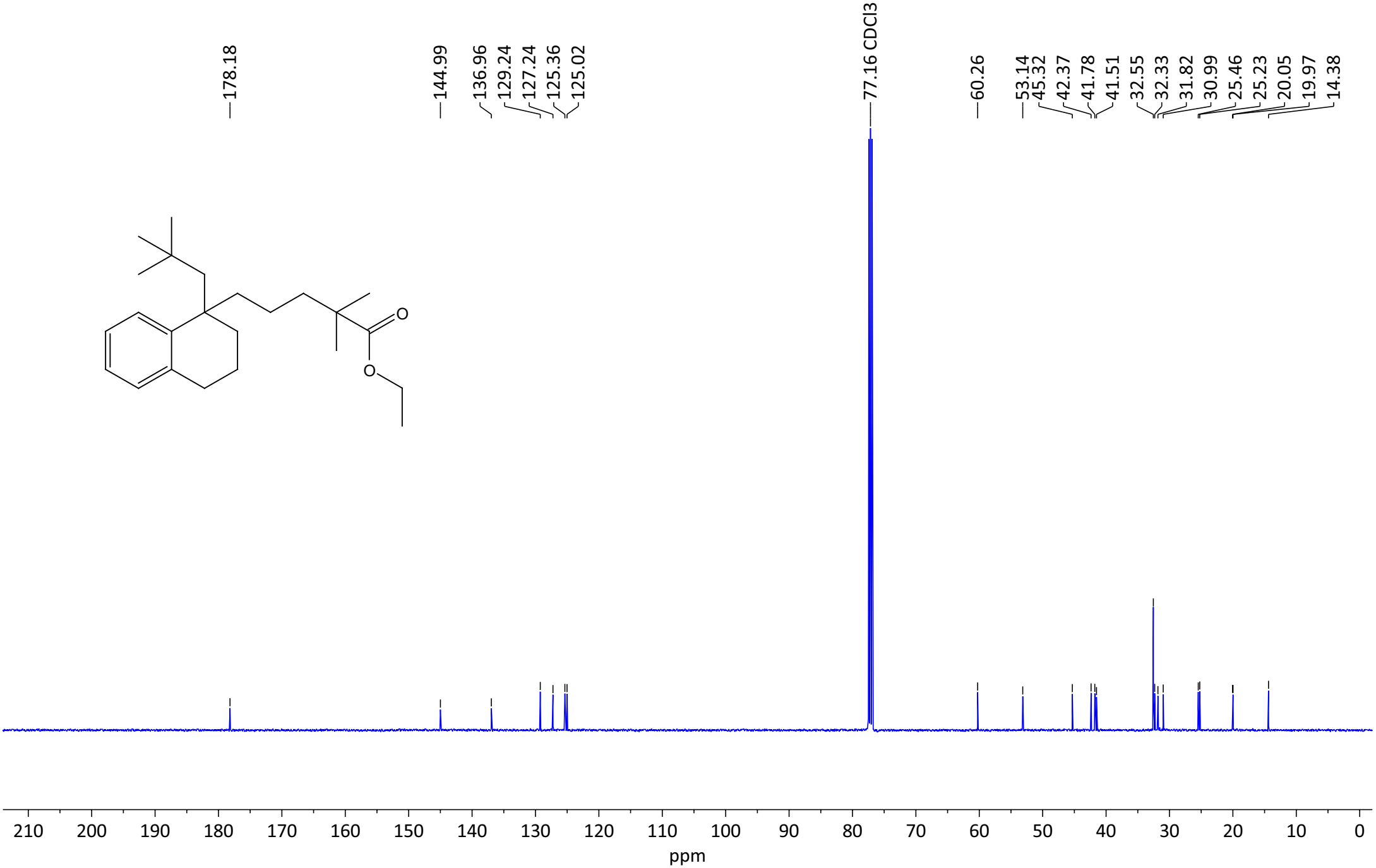
Compound **18**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



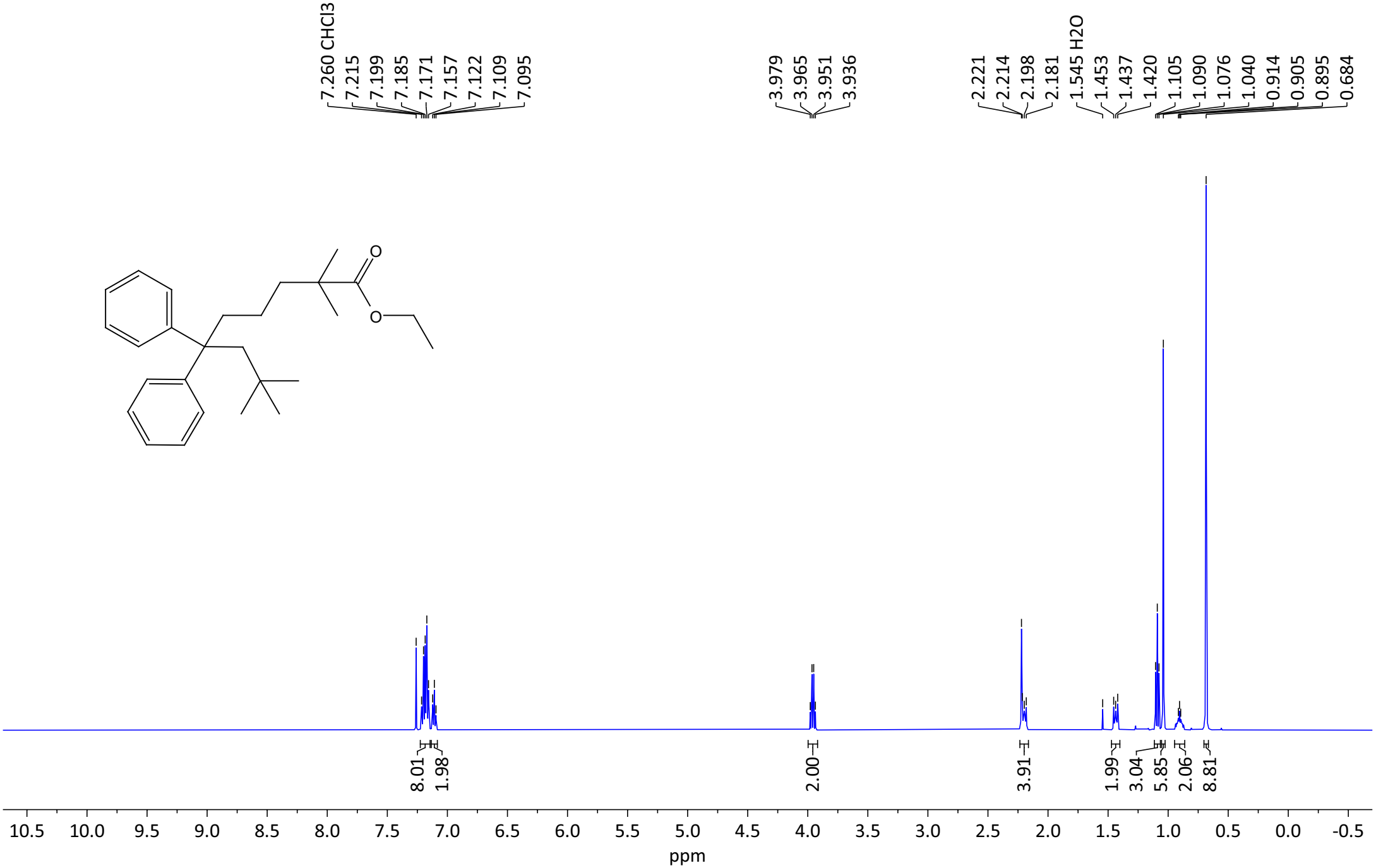
Compound **19**: ^{1}H NMR (500 MHz, $CDCl_3$)



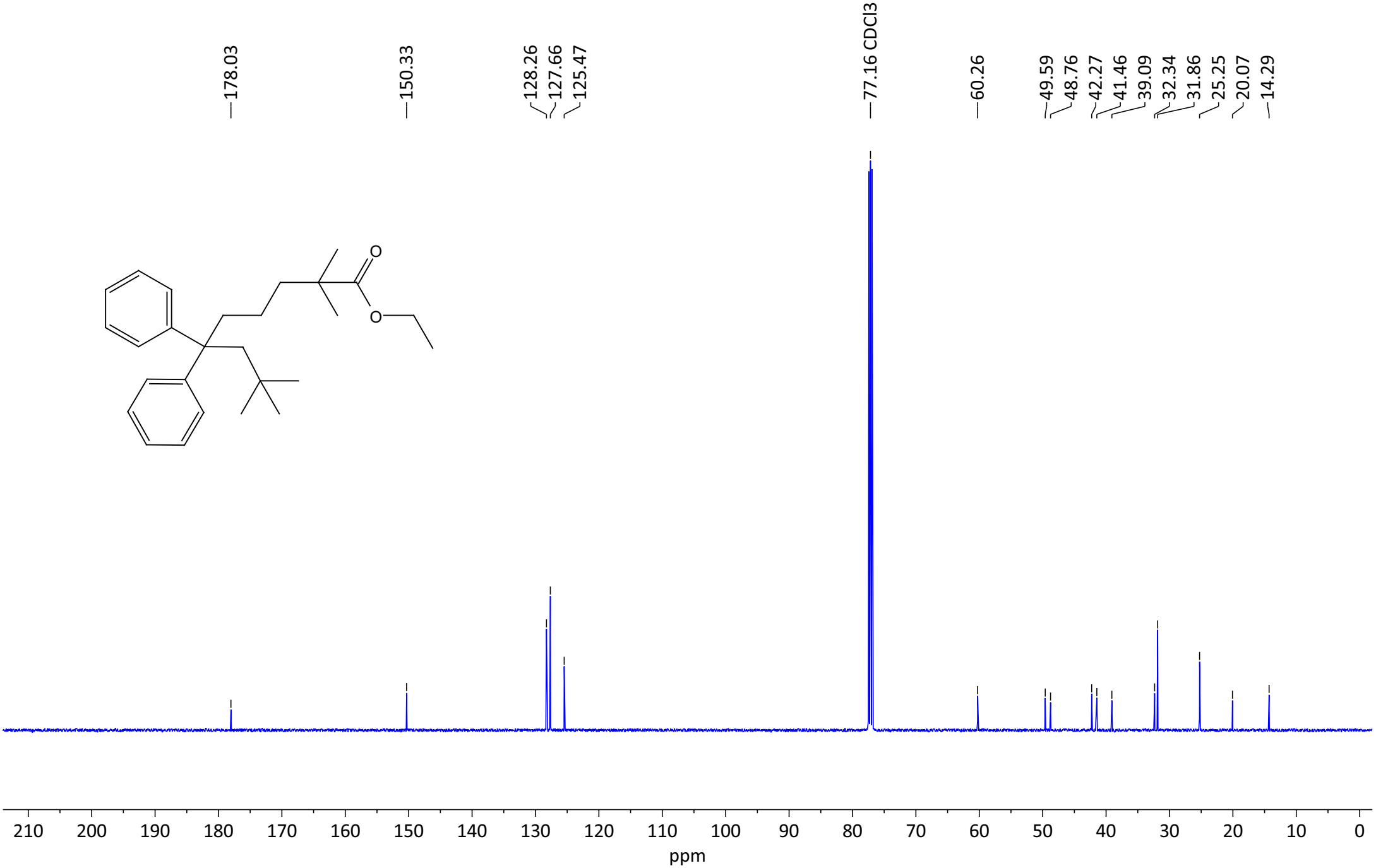
Compound **19**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



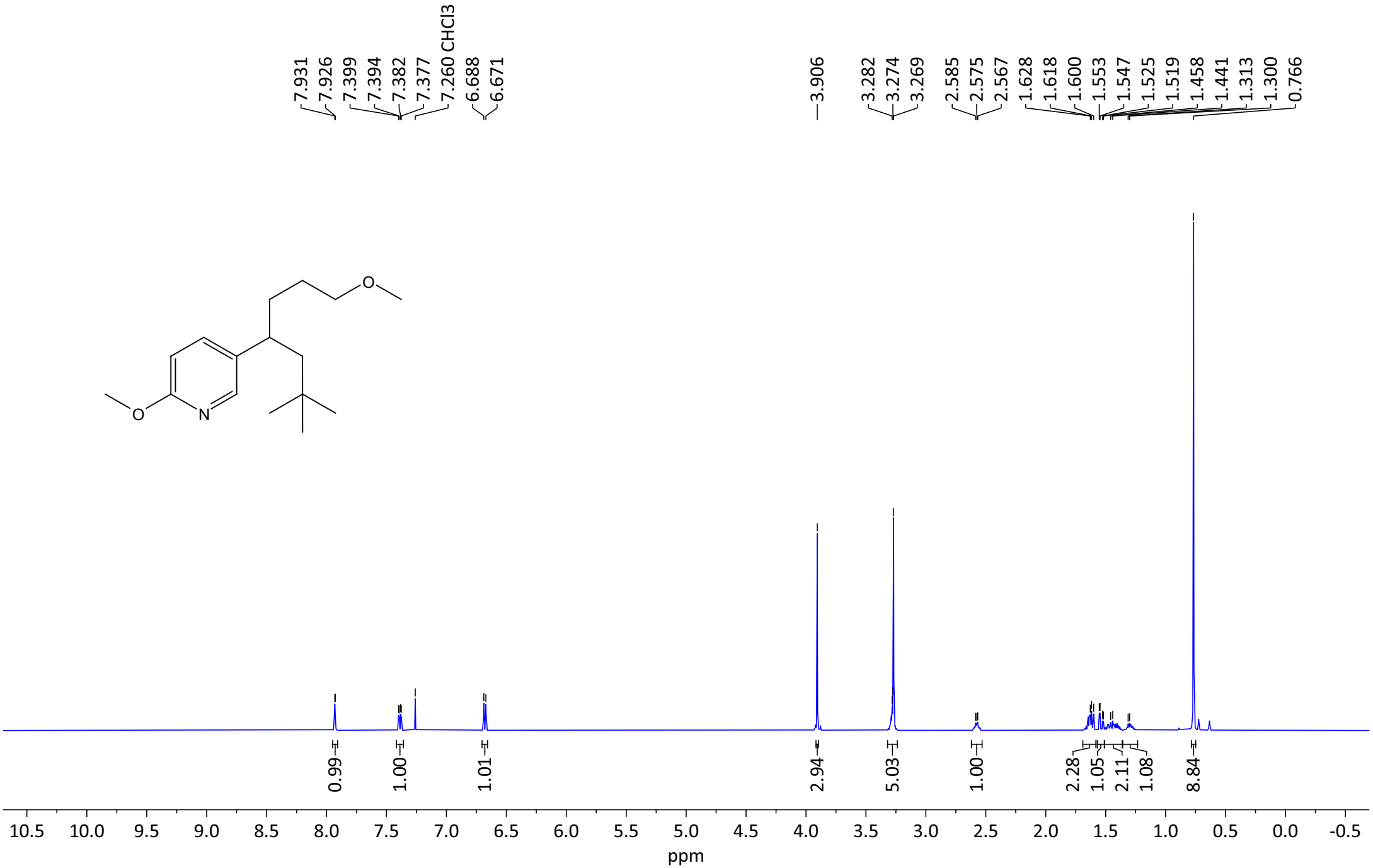
Compound **20**: ^{1}H NMR (500 MHz, $CDCl_3$)



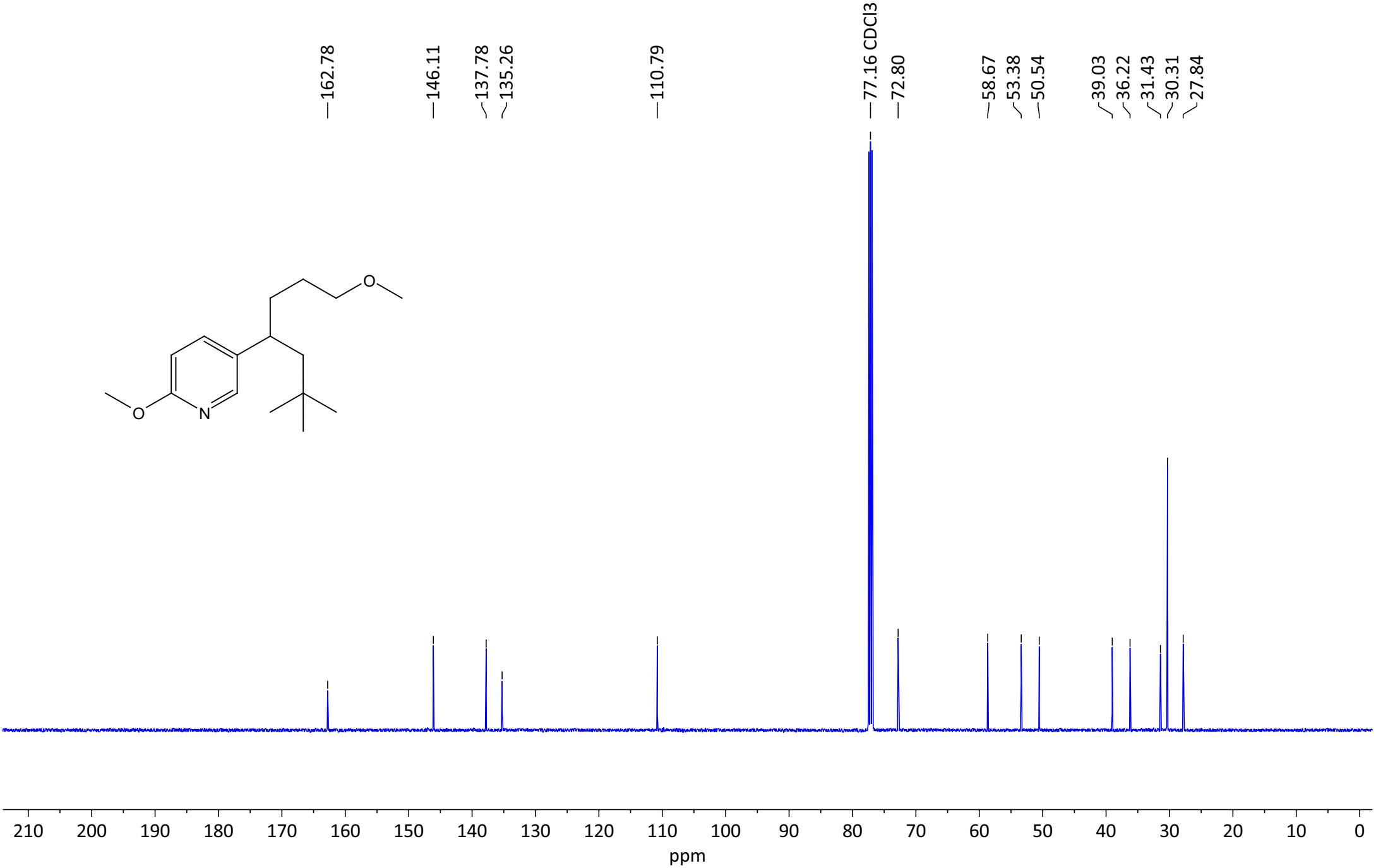
Compound **20**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



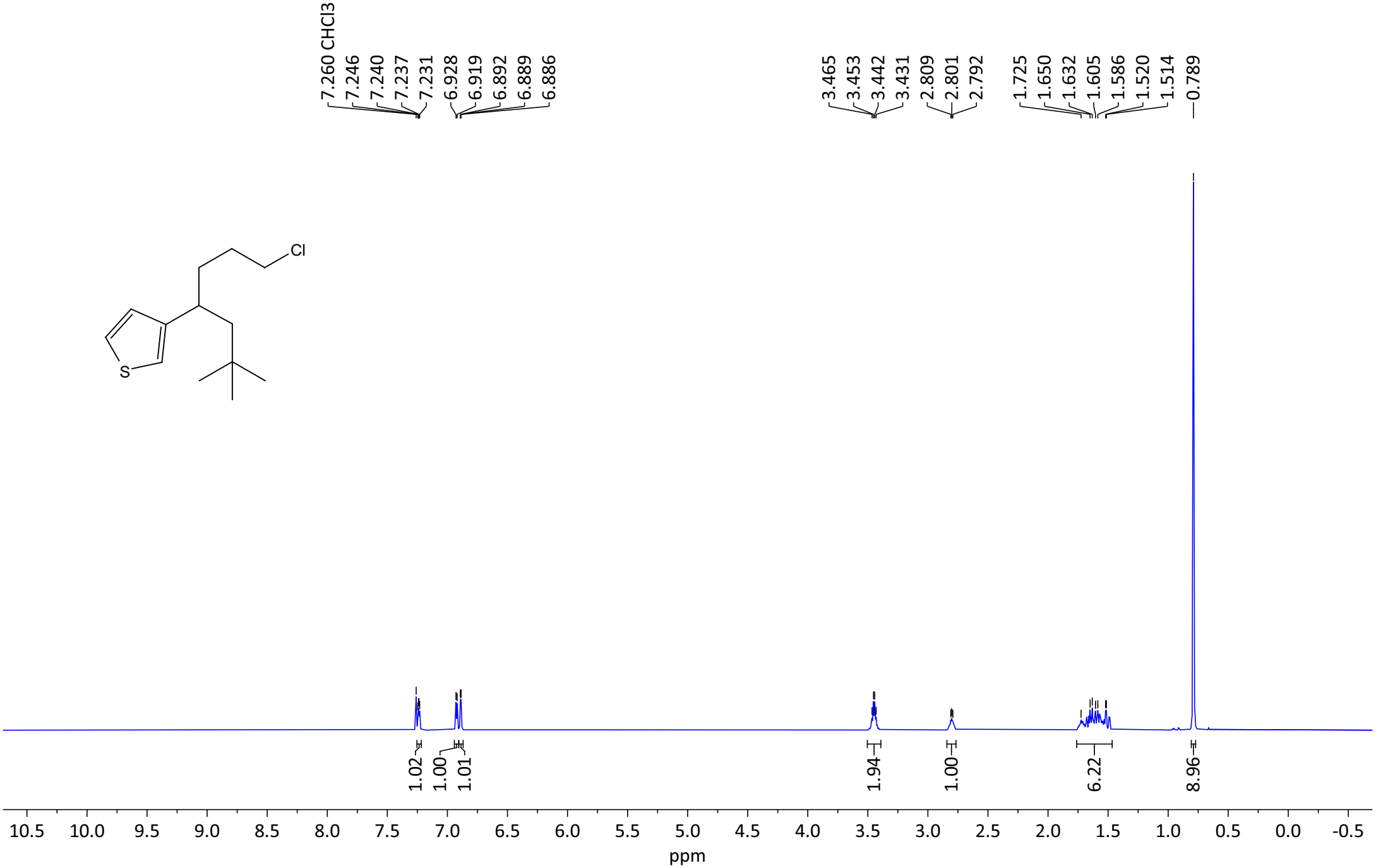
Compound **21**: ^{1}H NMR (500 MHz, $CDCl_3$)



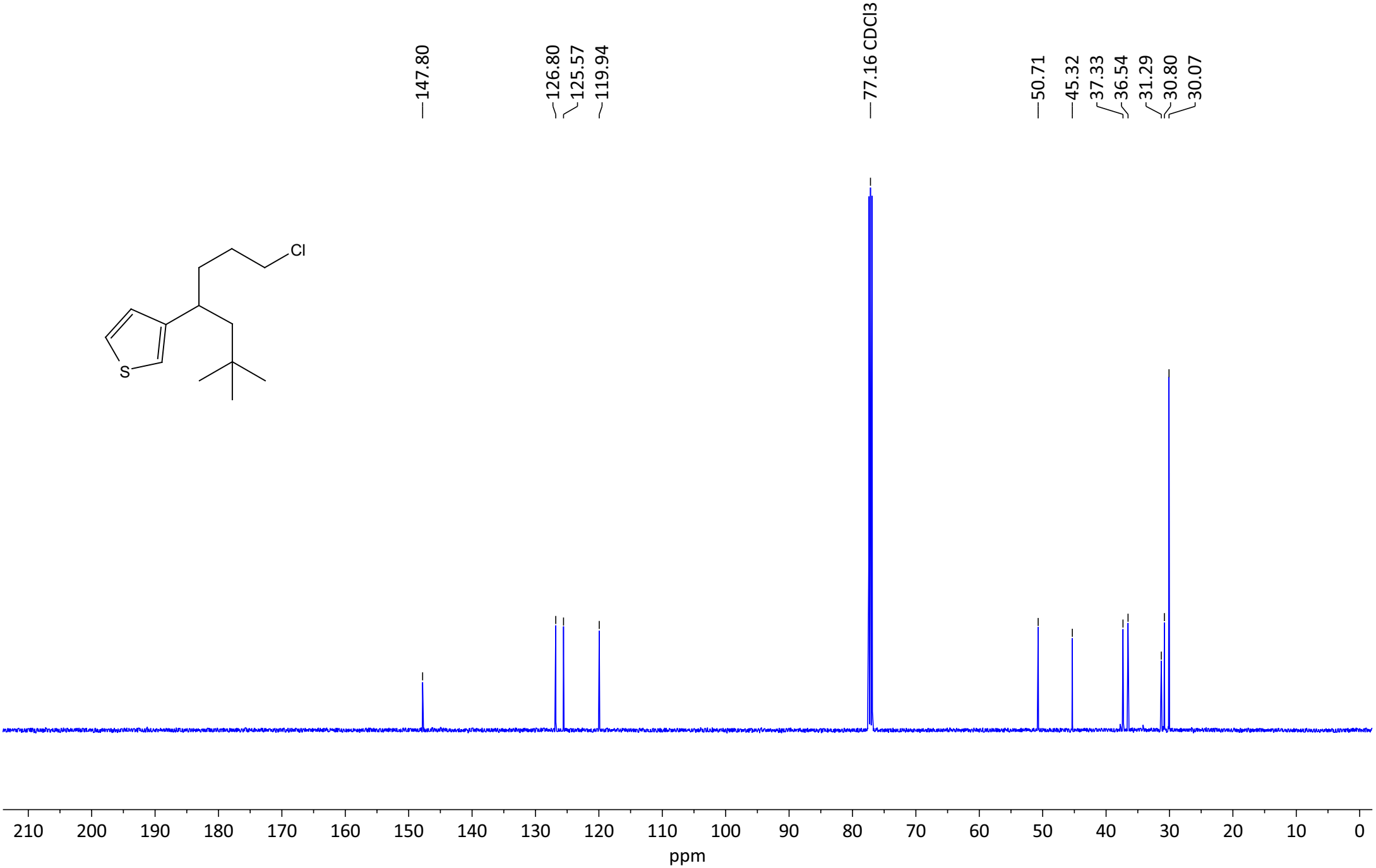
Compound **21**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



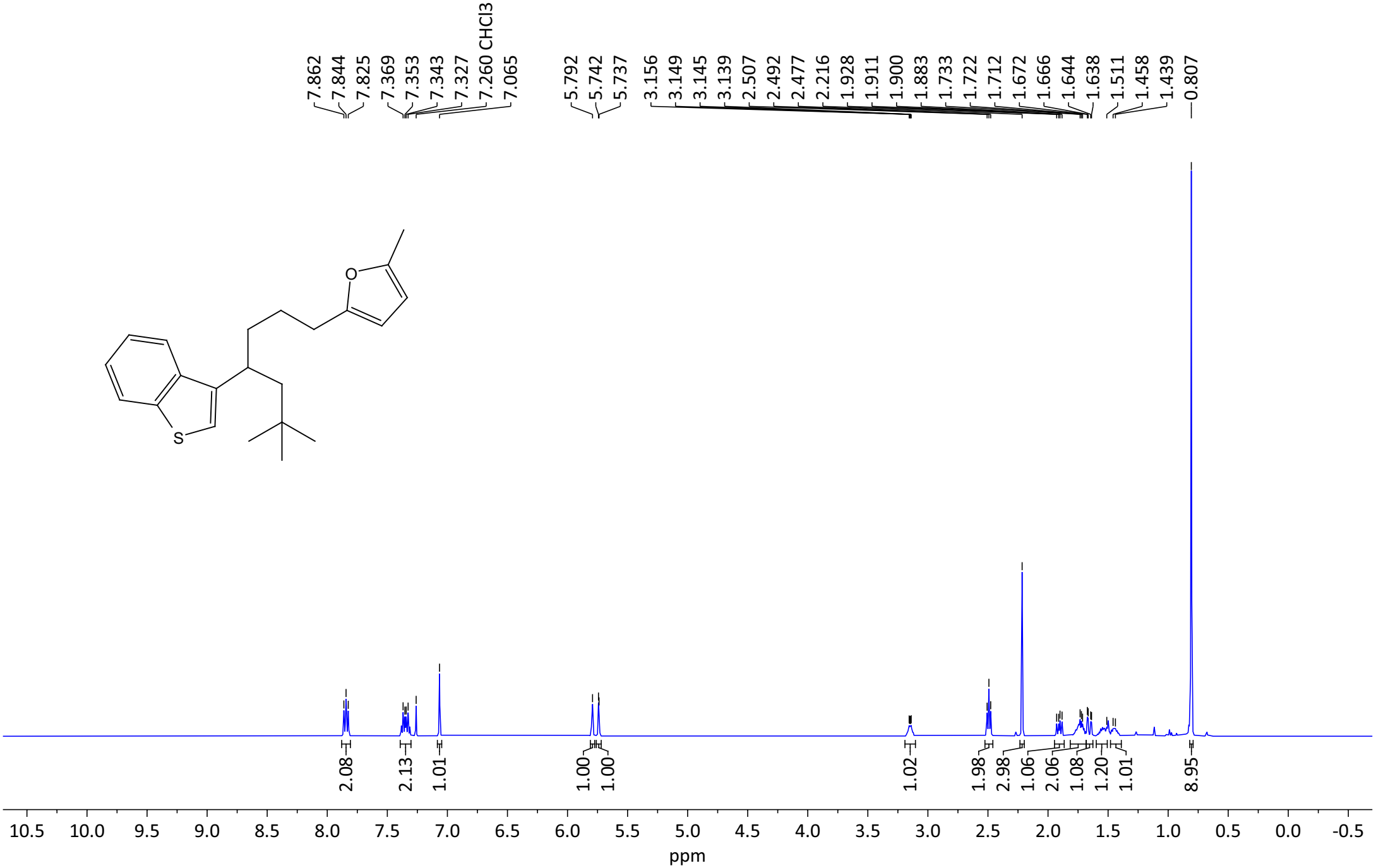
Compound **22**: ^{1}H NMR (500 MHz, $CDCl_3$)



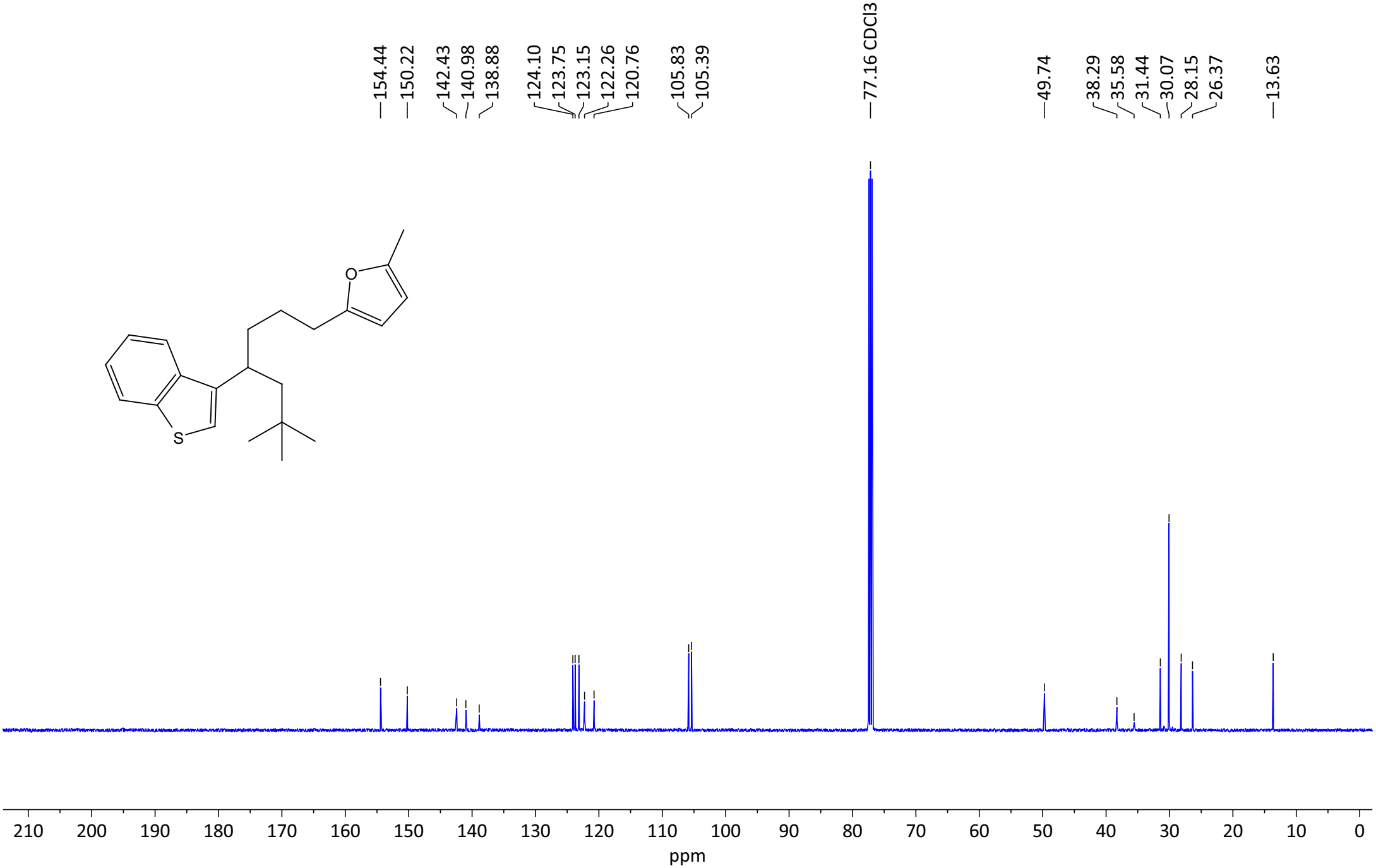
Compound **22**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



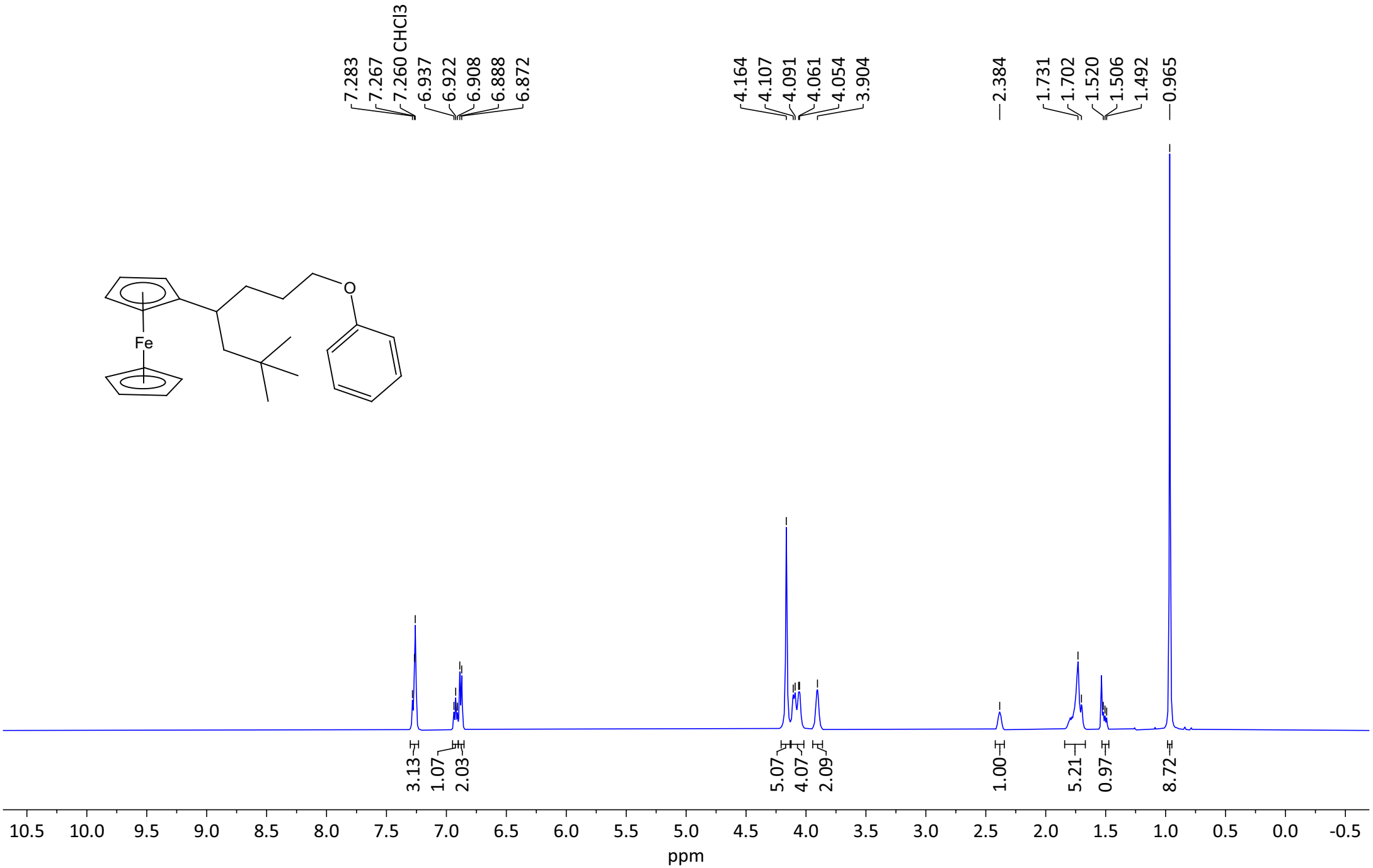
Compound **23**: ^{1}H NMR (500 MHz, $CDCl_3$)



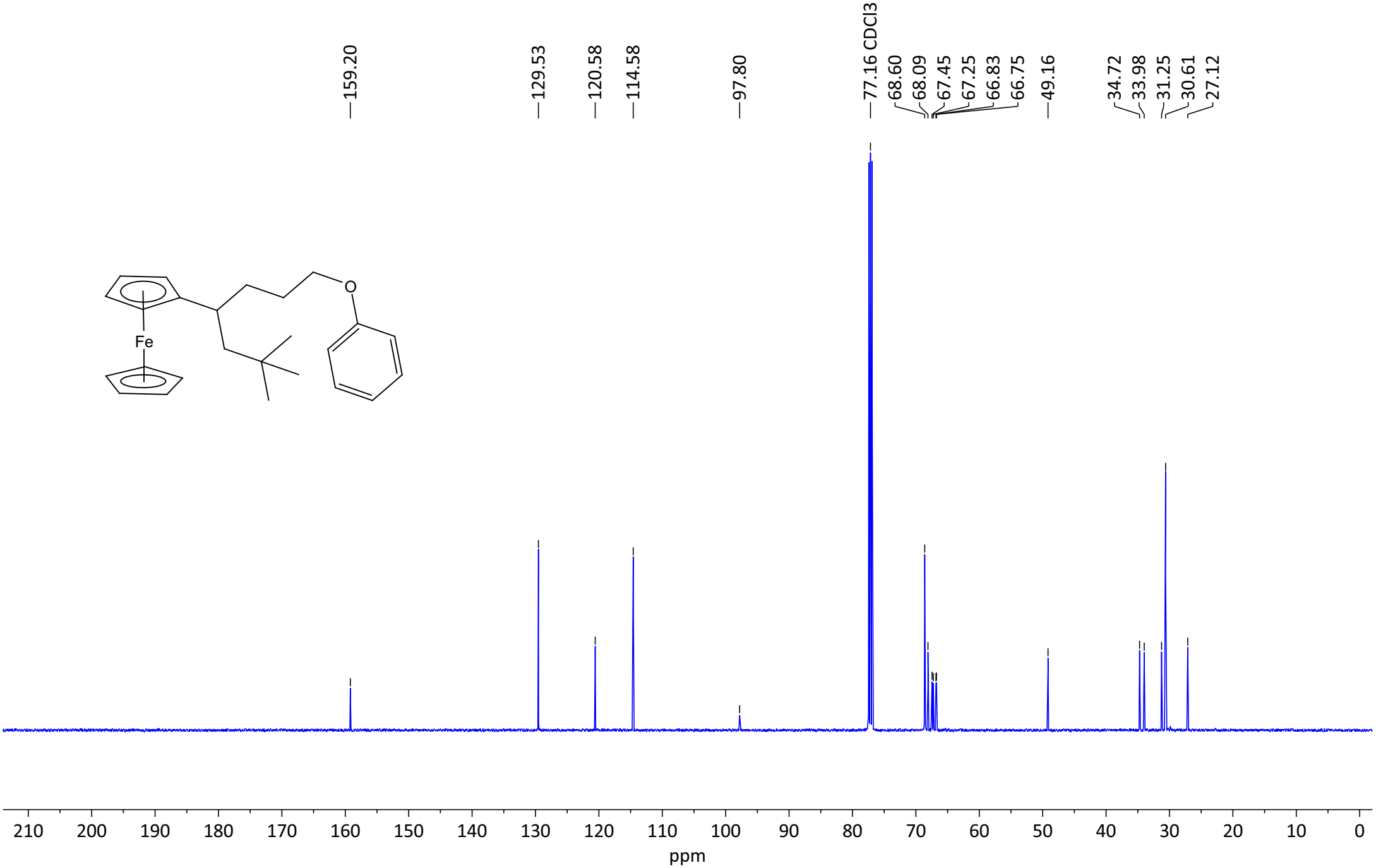
Compound **23**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



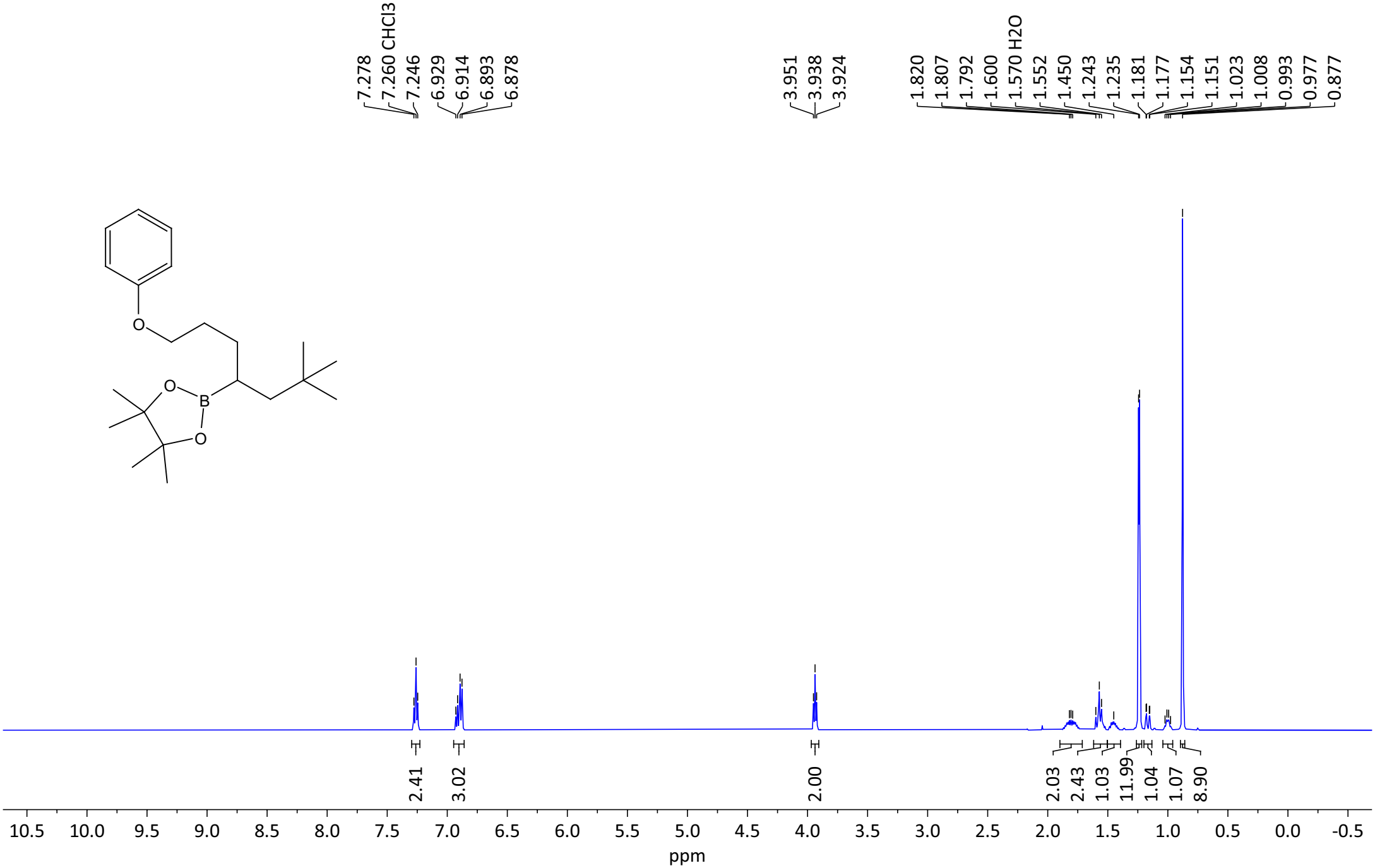
Compound **24**: ^{1}H NMR (500 MHz, $CDCl_3$)



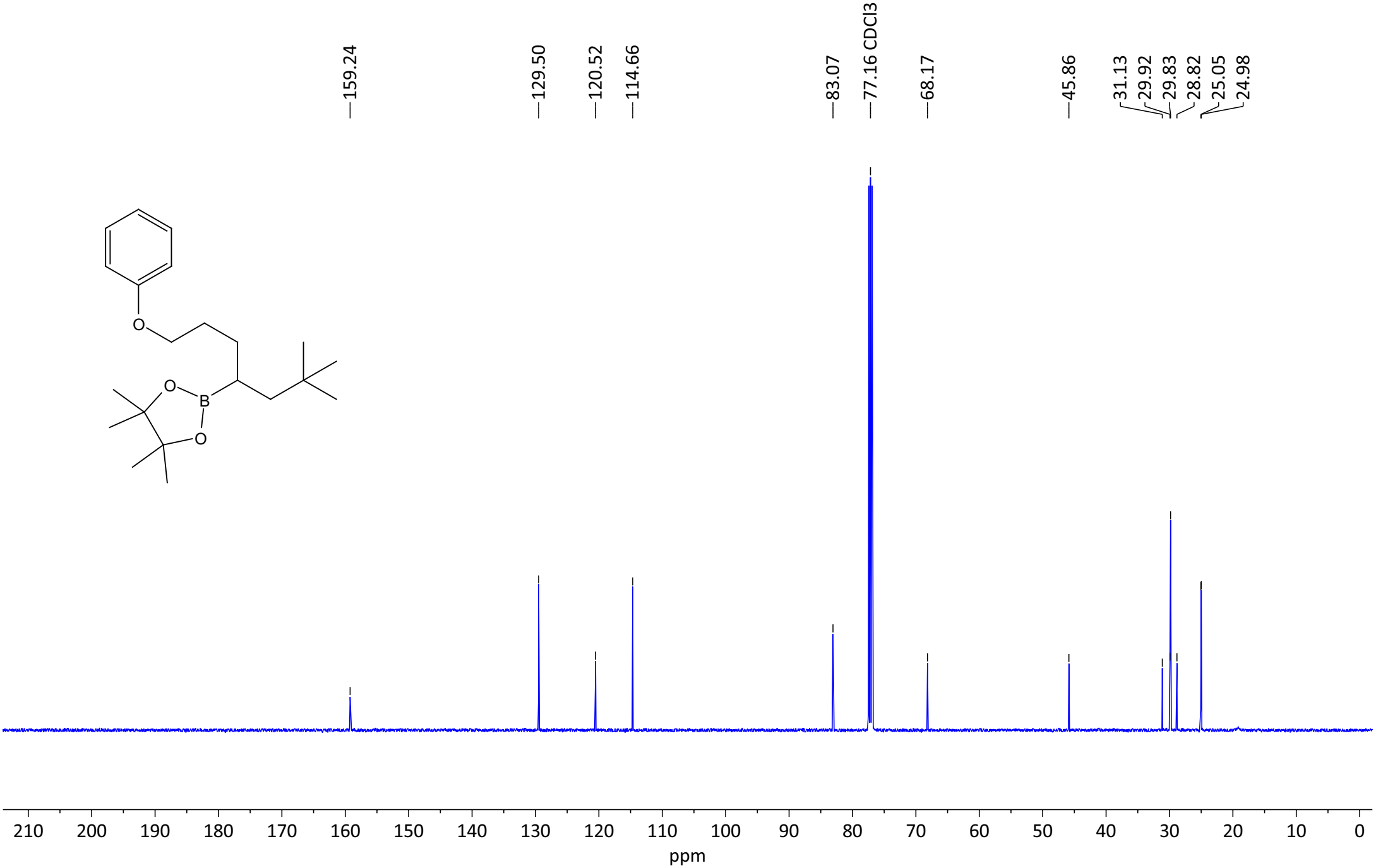
Compound **24**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



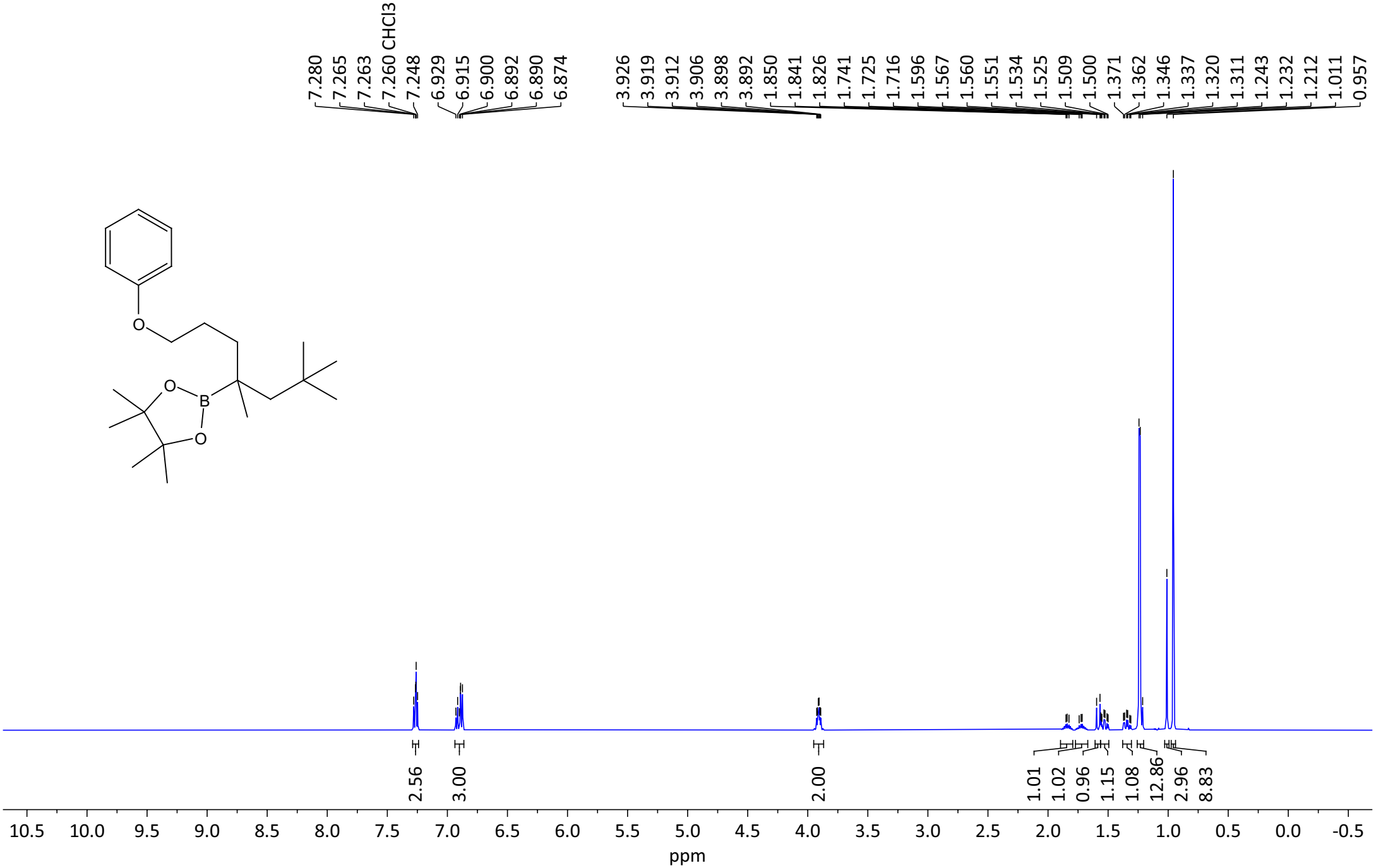
Compound **25**: ^{1}H NMR (500 MHz, $CDCl_3$)



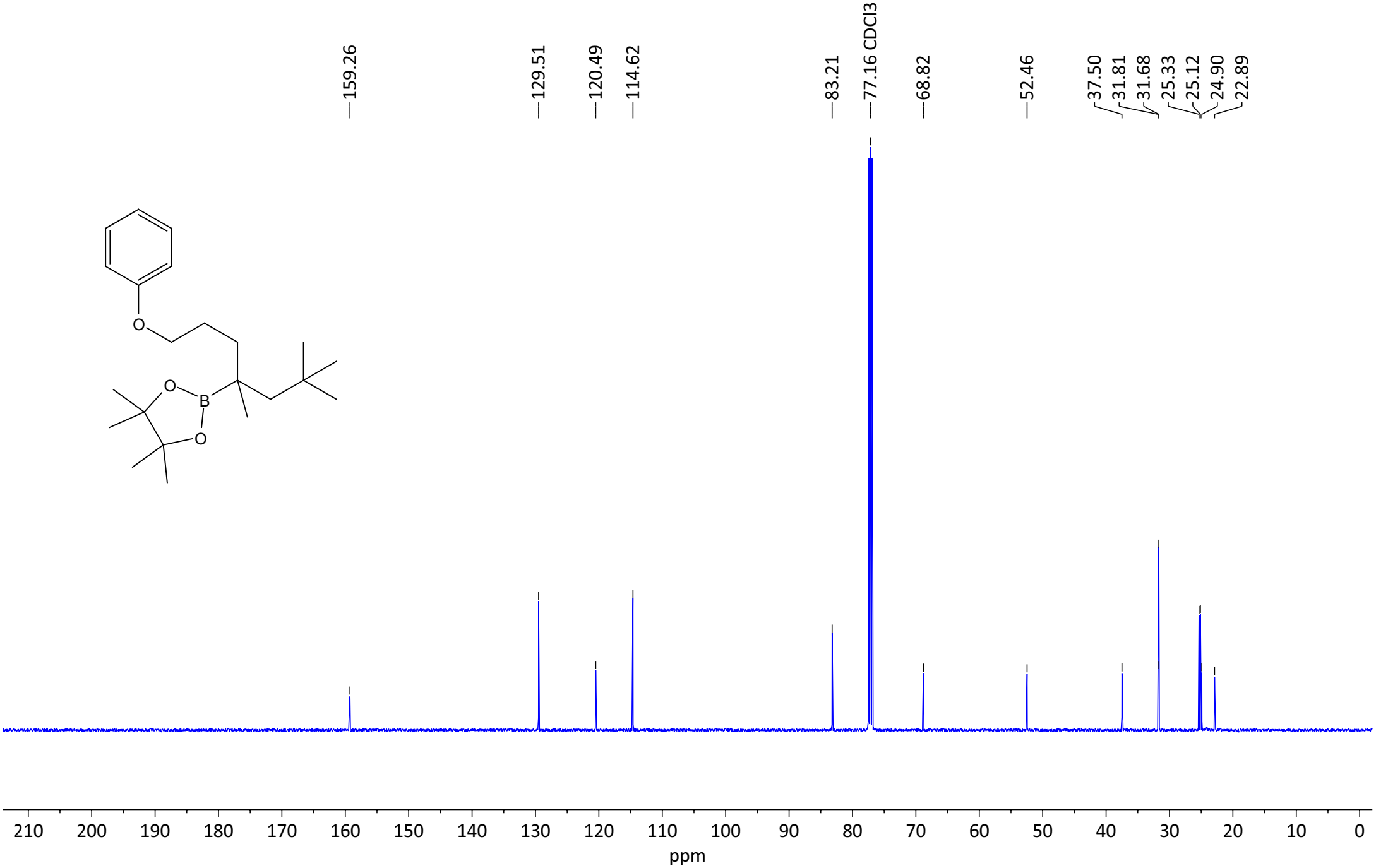
Compound **25**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



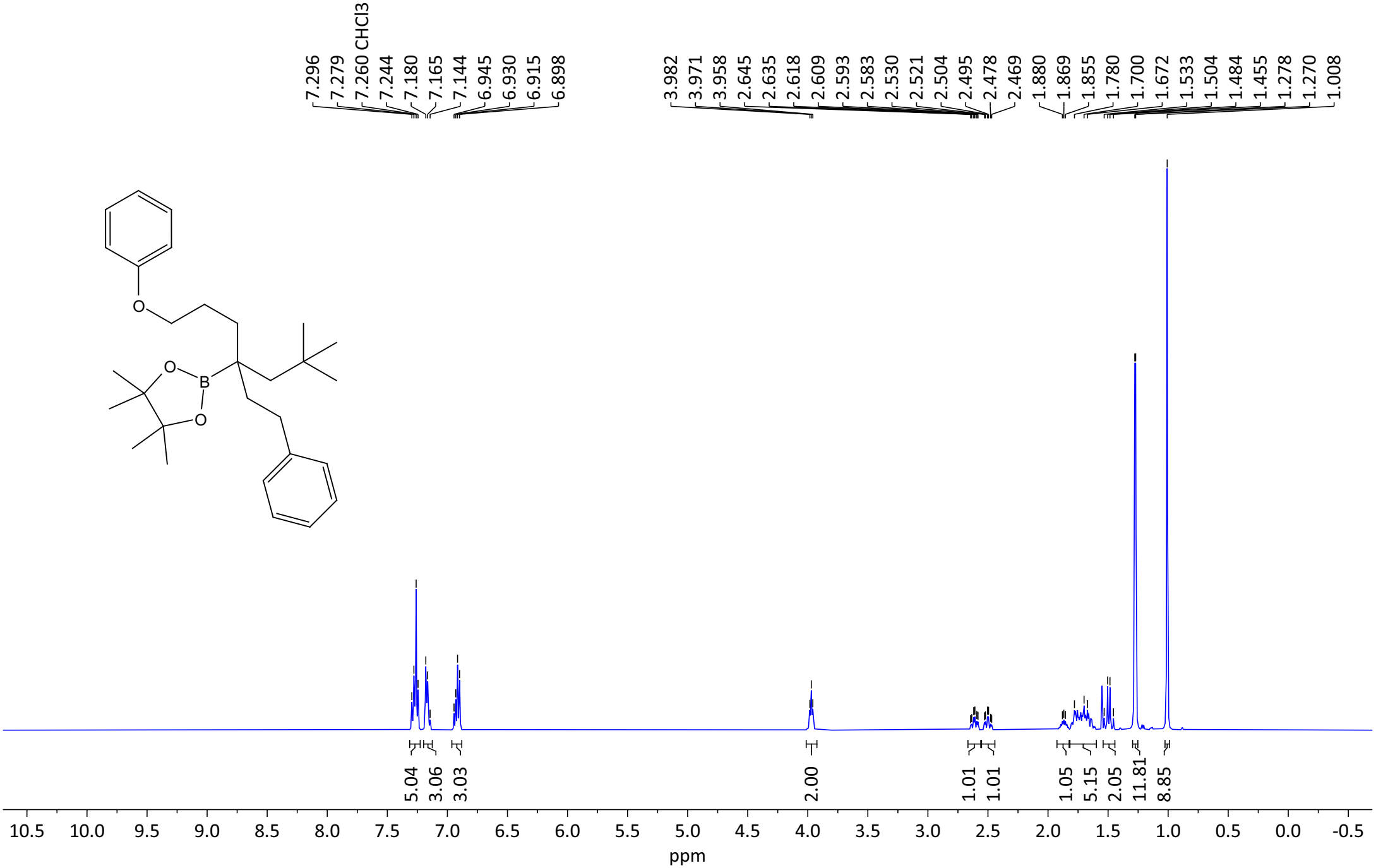
Compound **26**: ^{1}H NMR (500 MHz, $CDCl_3$)



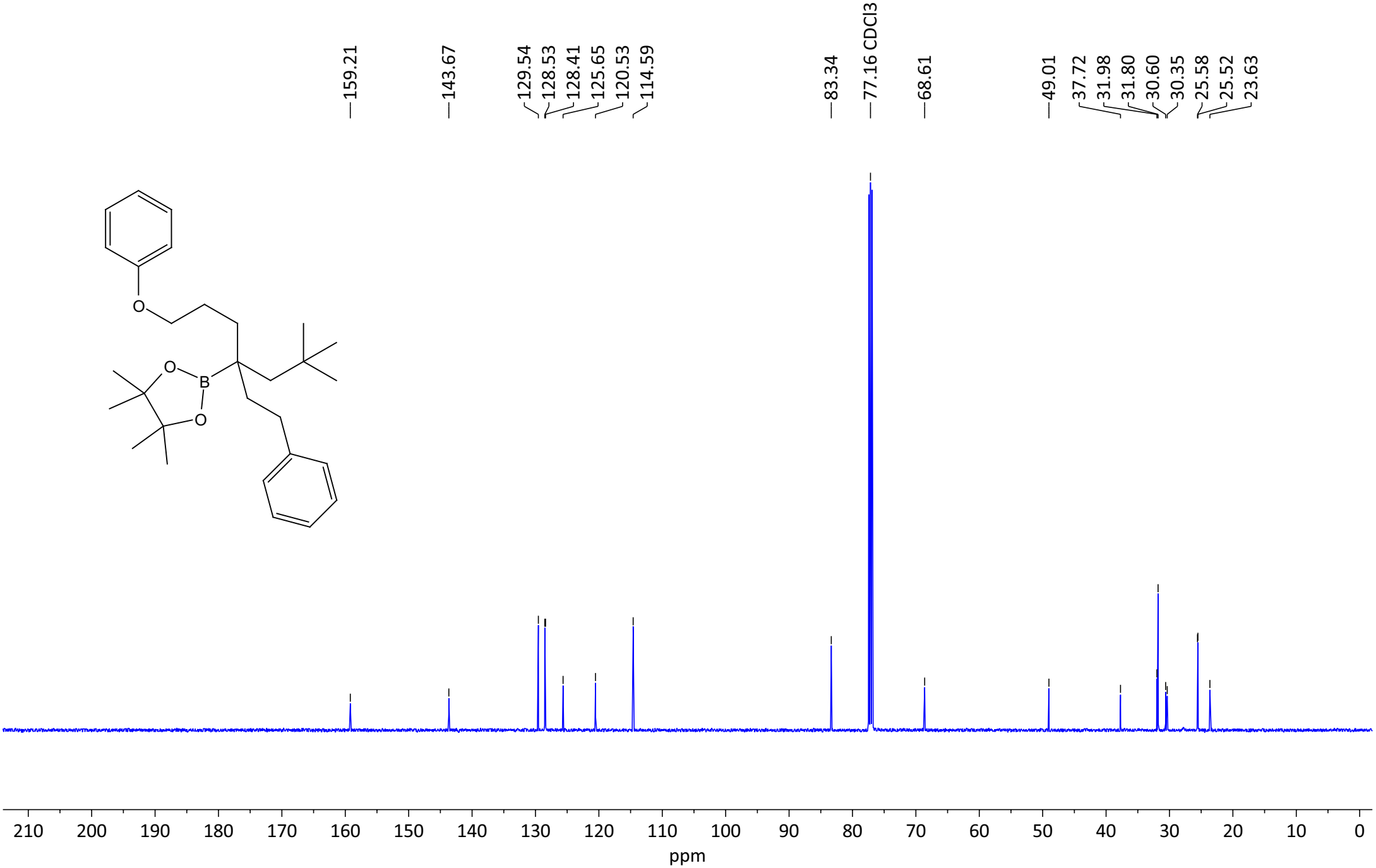
Compound **26**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



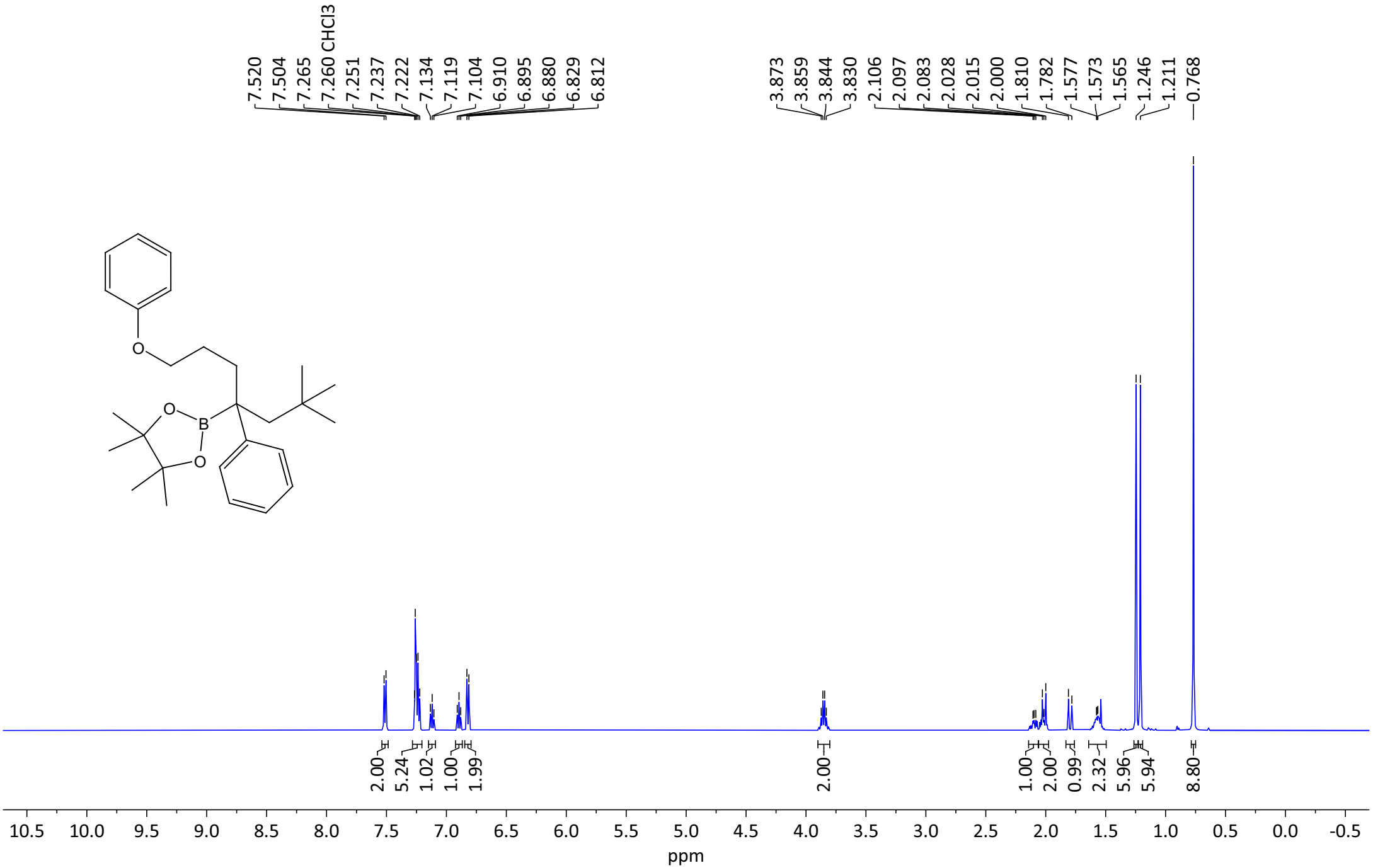
Compound **27**: ^{1}H NMR (500 MHz, $CDCl_3$)



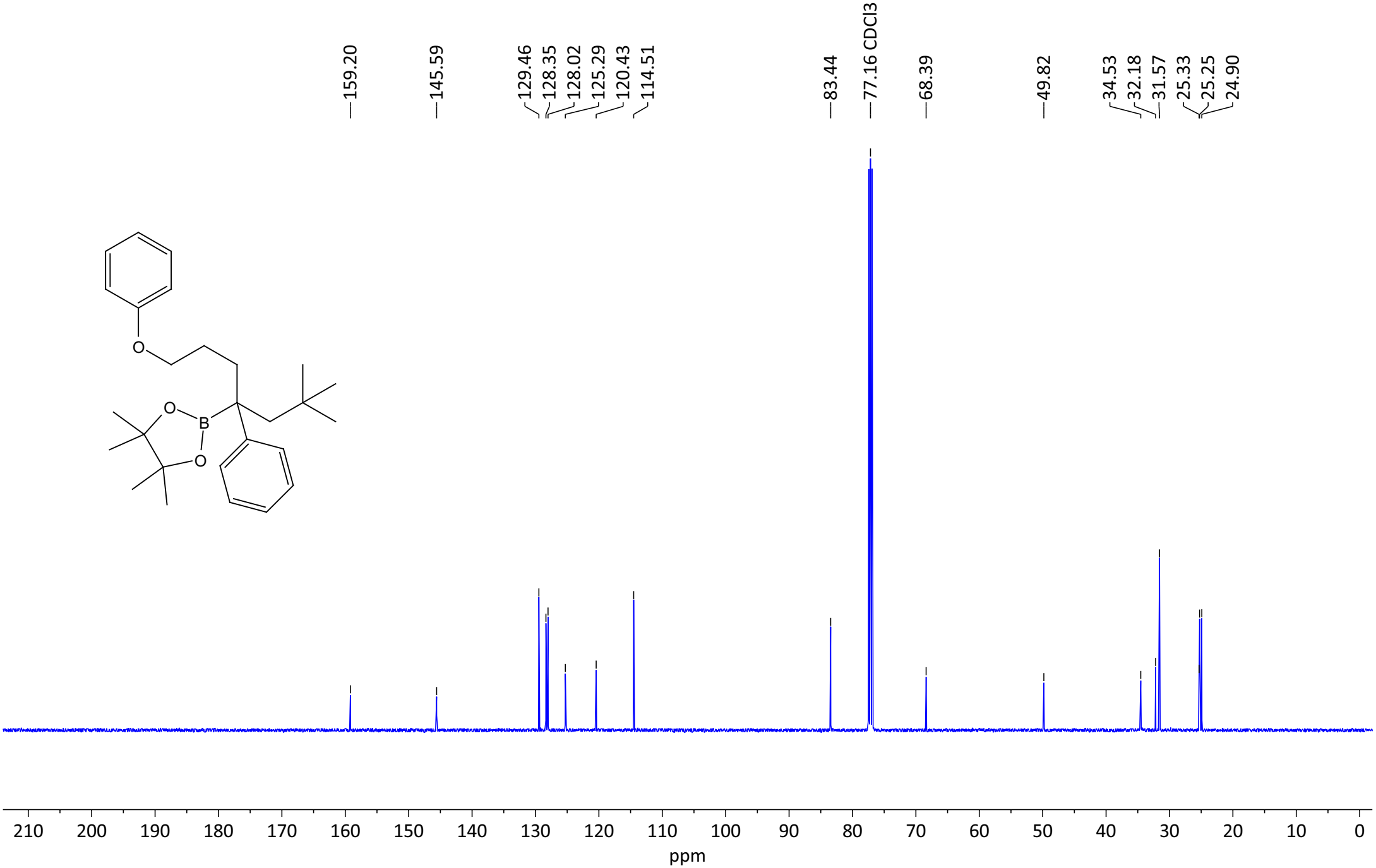
Compound **27**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



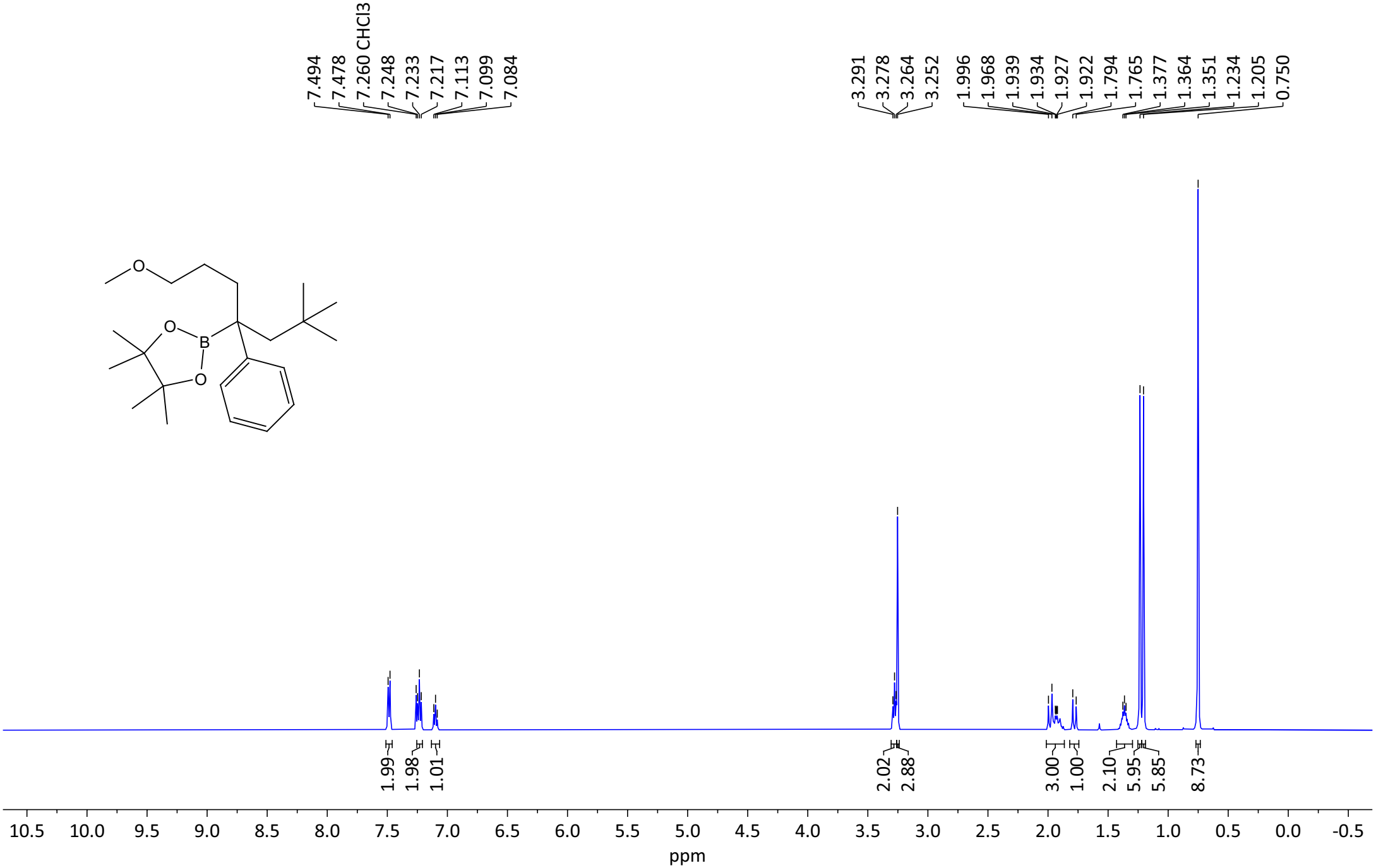
Compound **28**: ^{1}H NMR (500 MHz, $CDCl_3$)



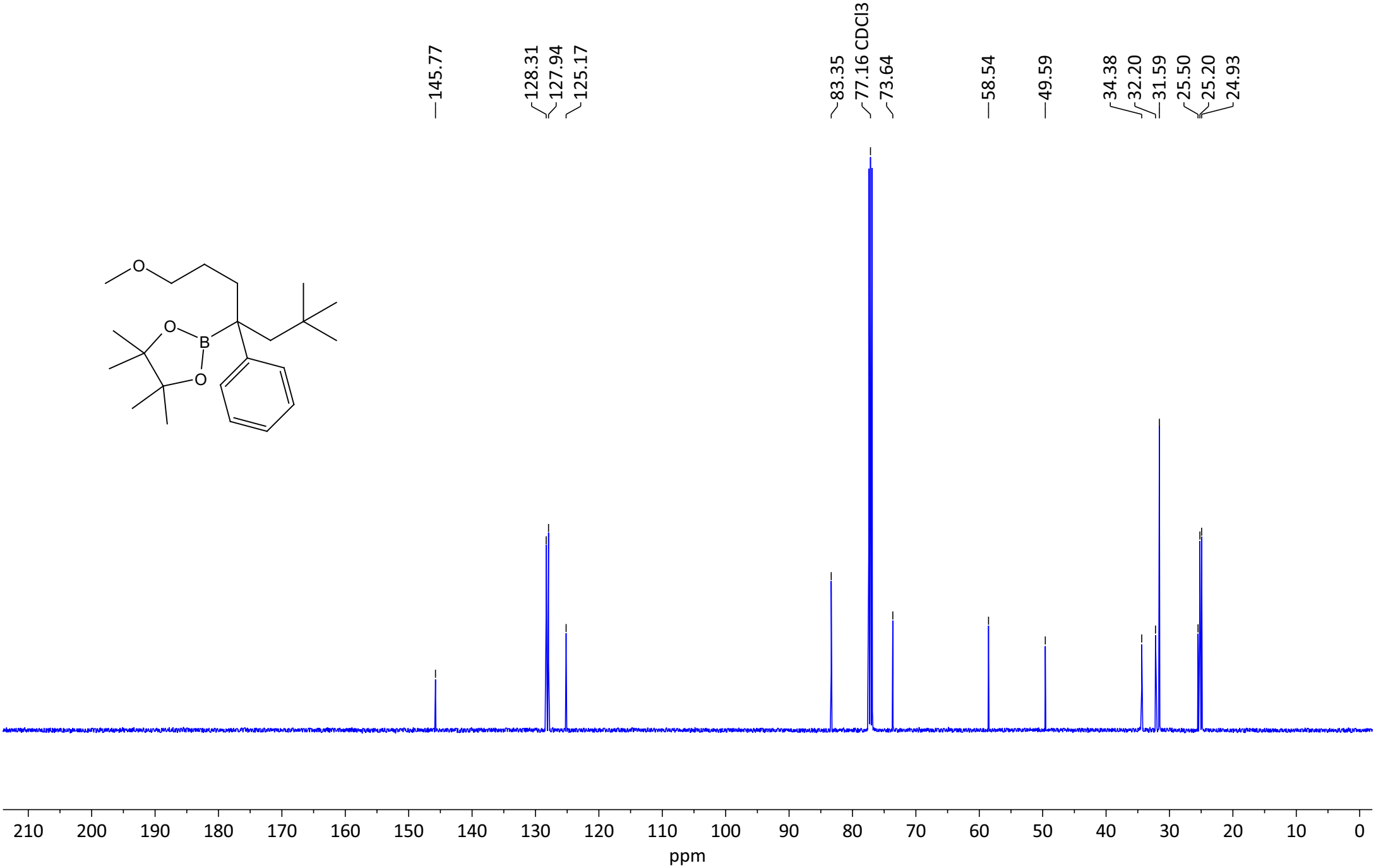
Compound **28**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



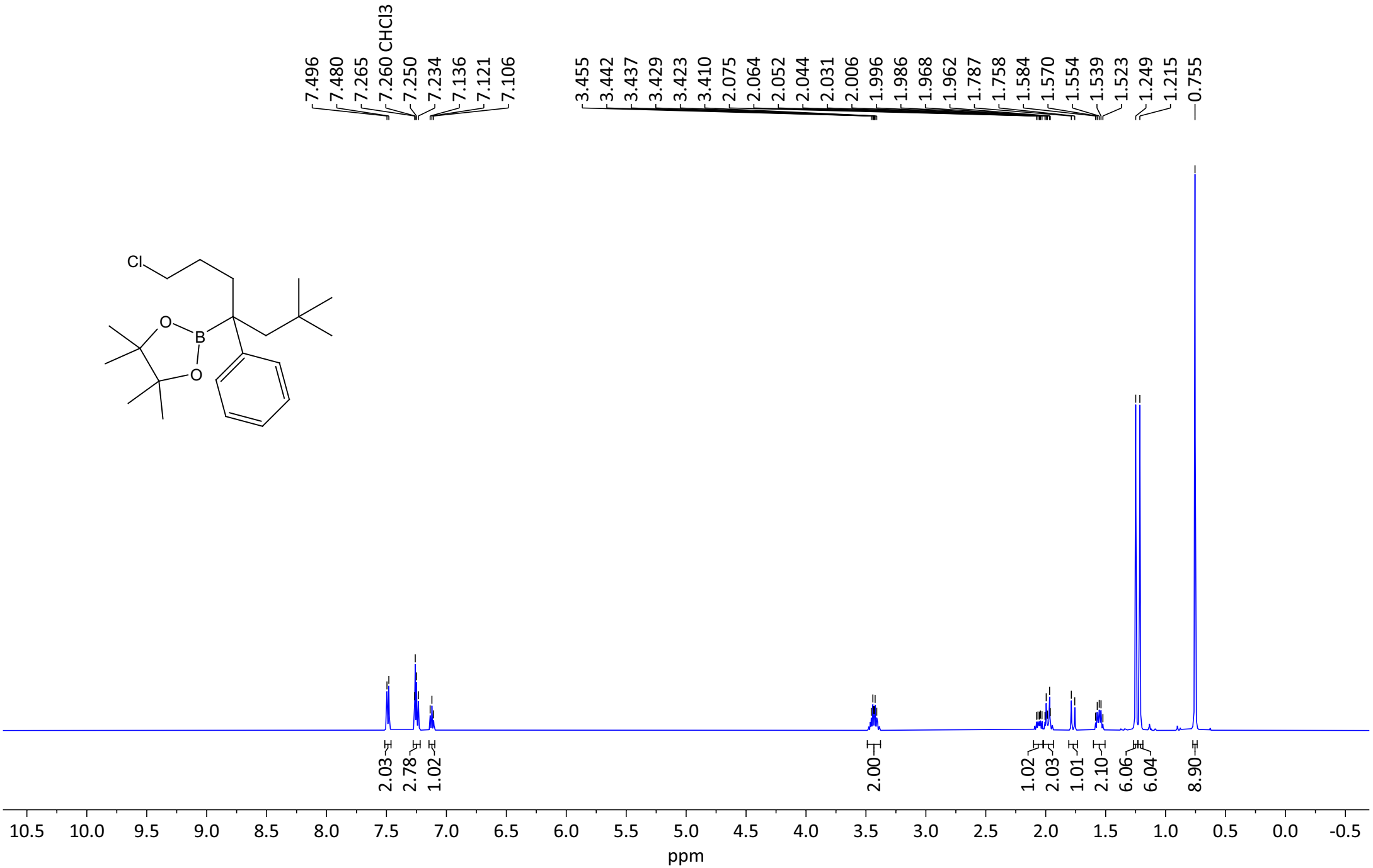
Compound **29**: ^{1}H NMR (500 MHz, $CDCl_3$)



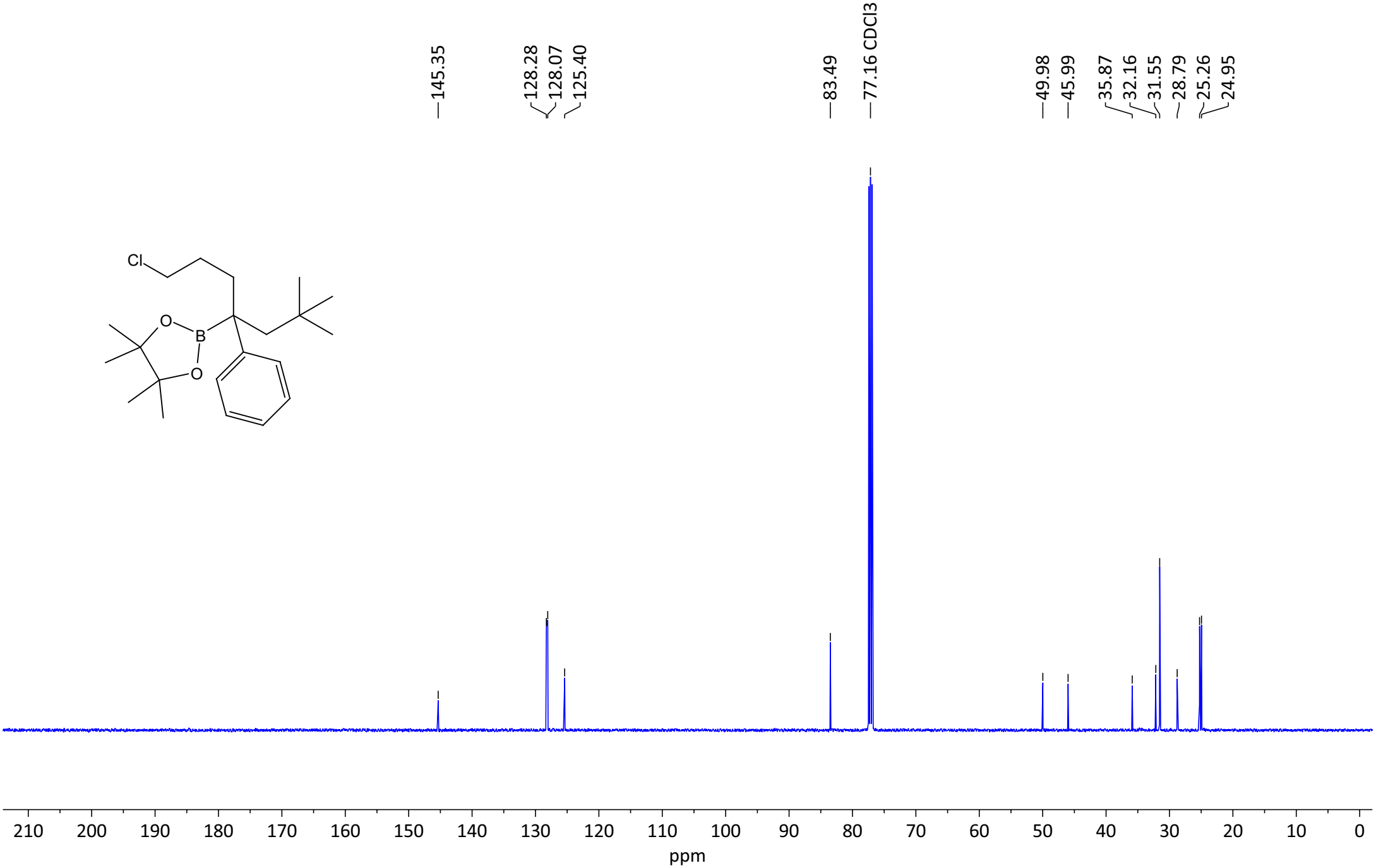
Compound **29**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



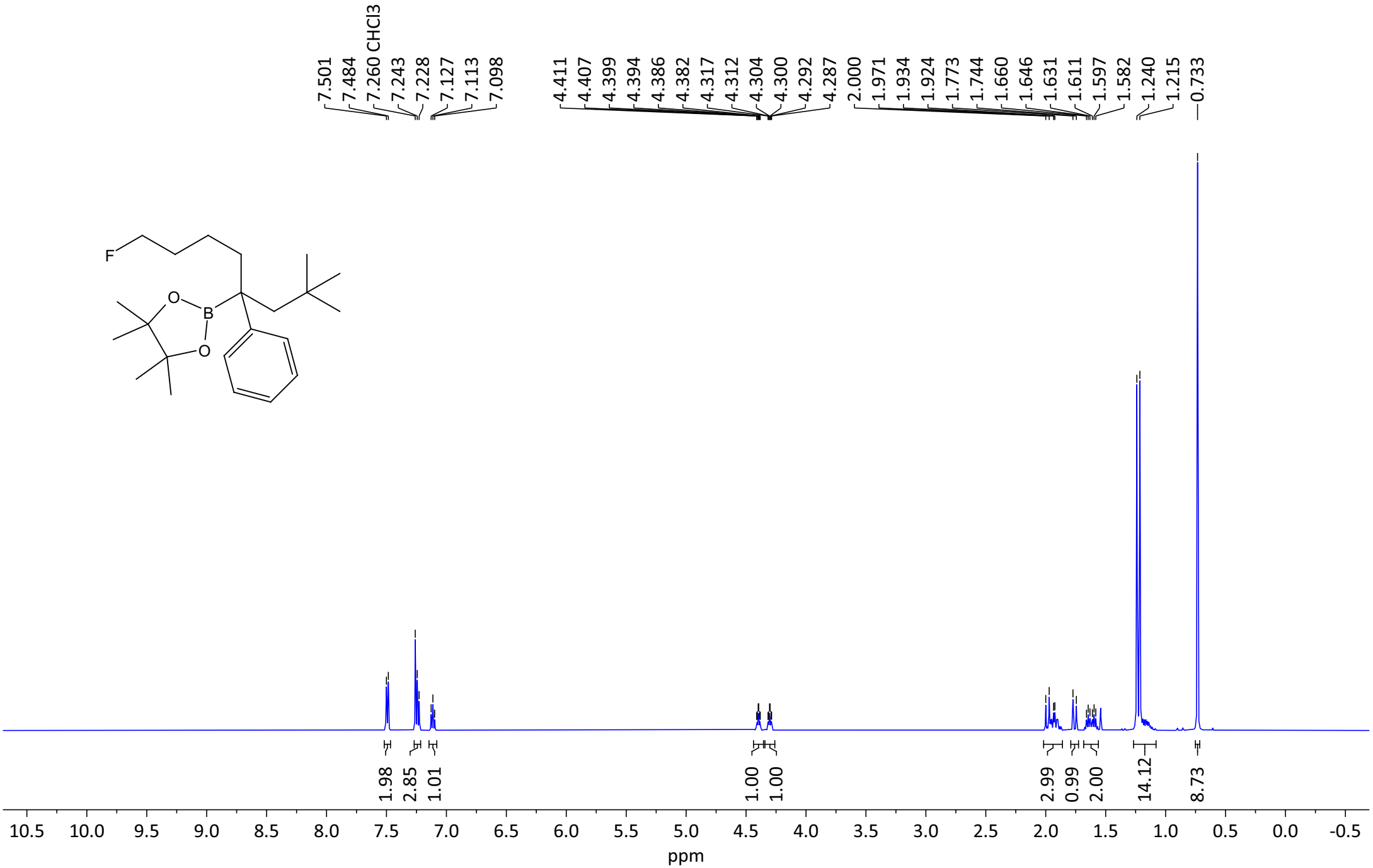
Compound **30**: ^{1}H NMR (500 MHz, $CDCl_3$)



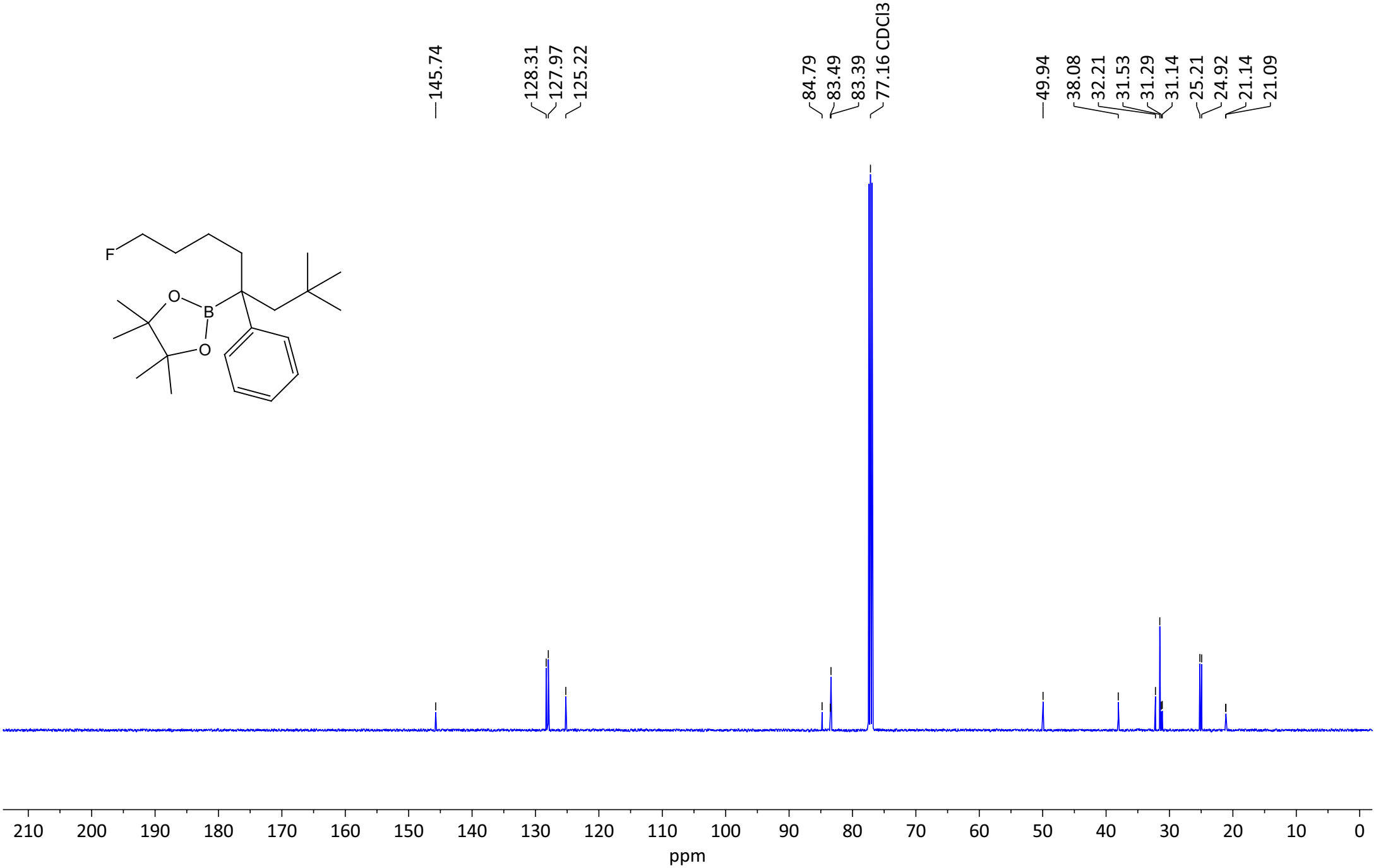
Compound **30**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



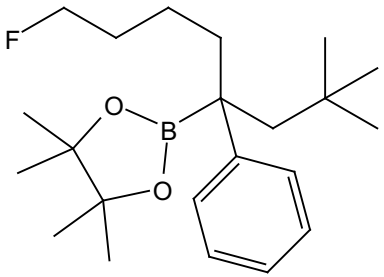
Compound **31**: ^{1}H NMR (500 MHz, $CDCl_3$)



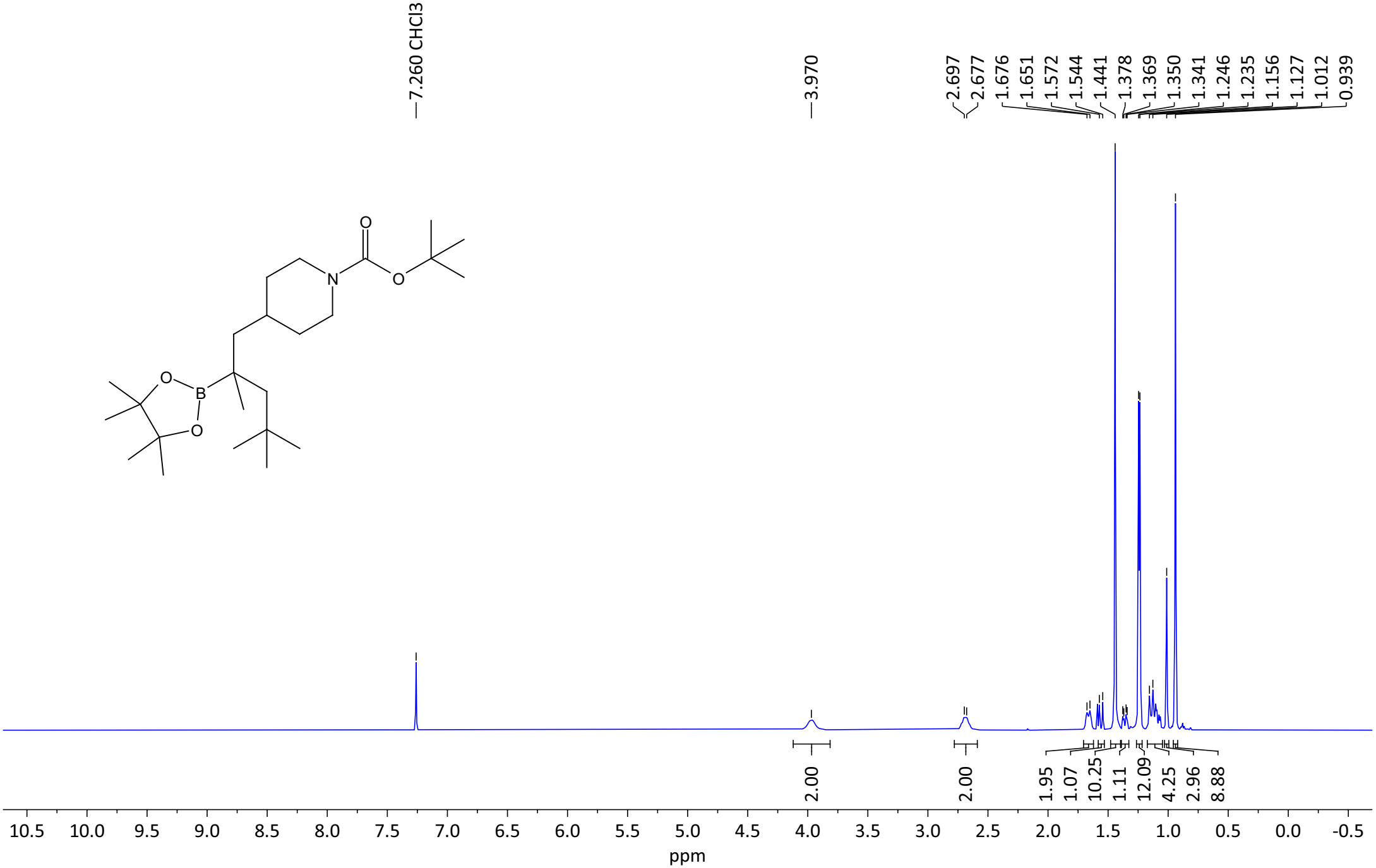
Compound **31**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



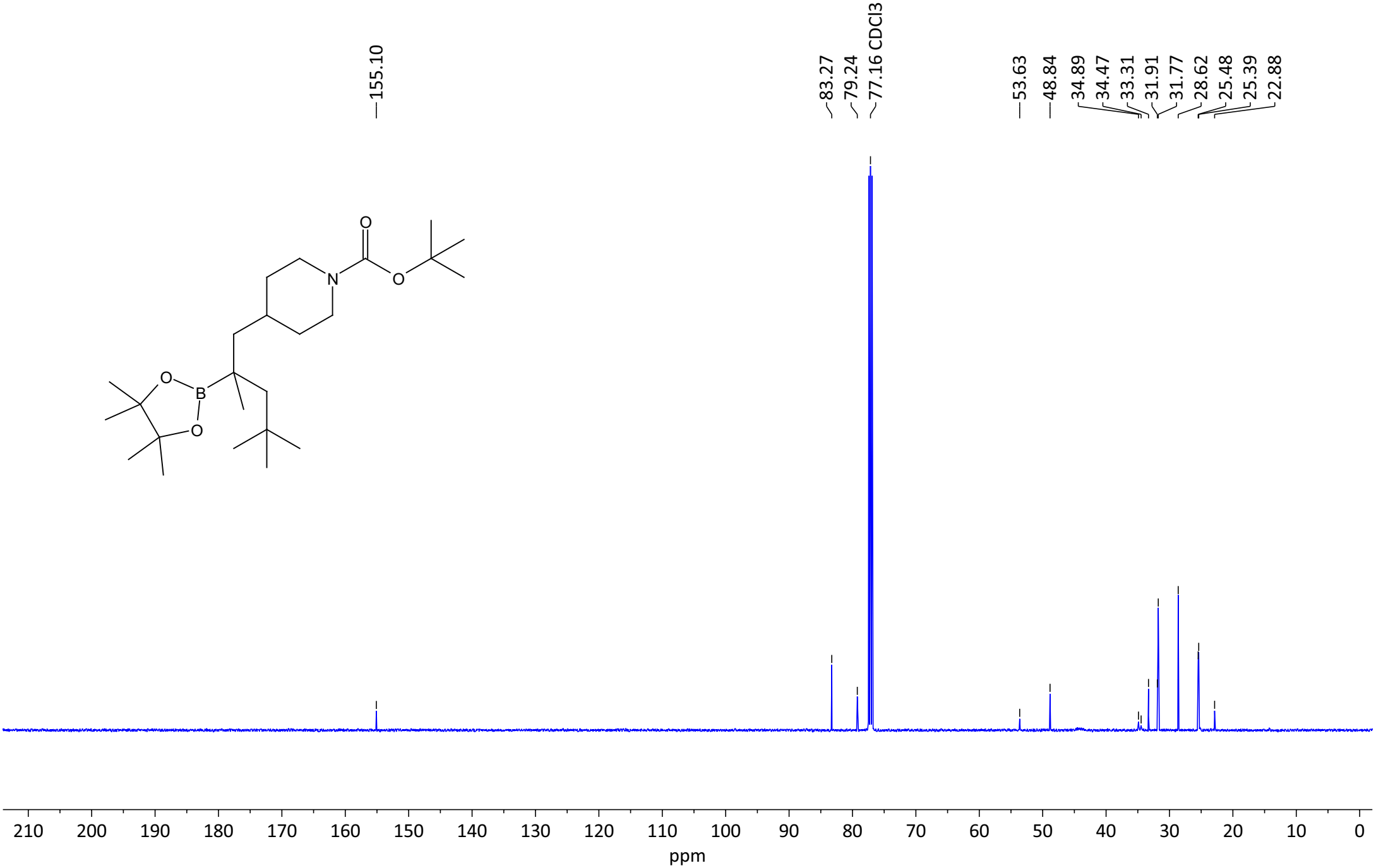
Compound **31**: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



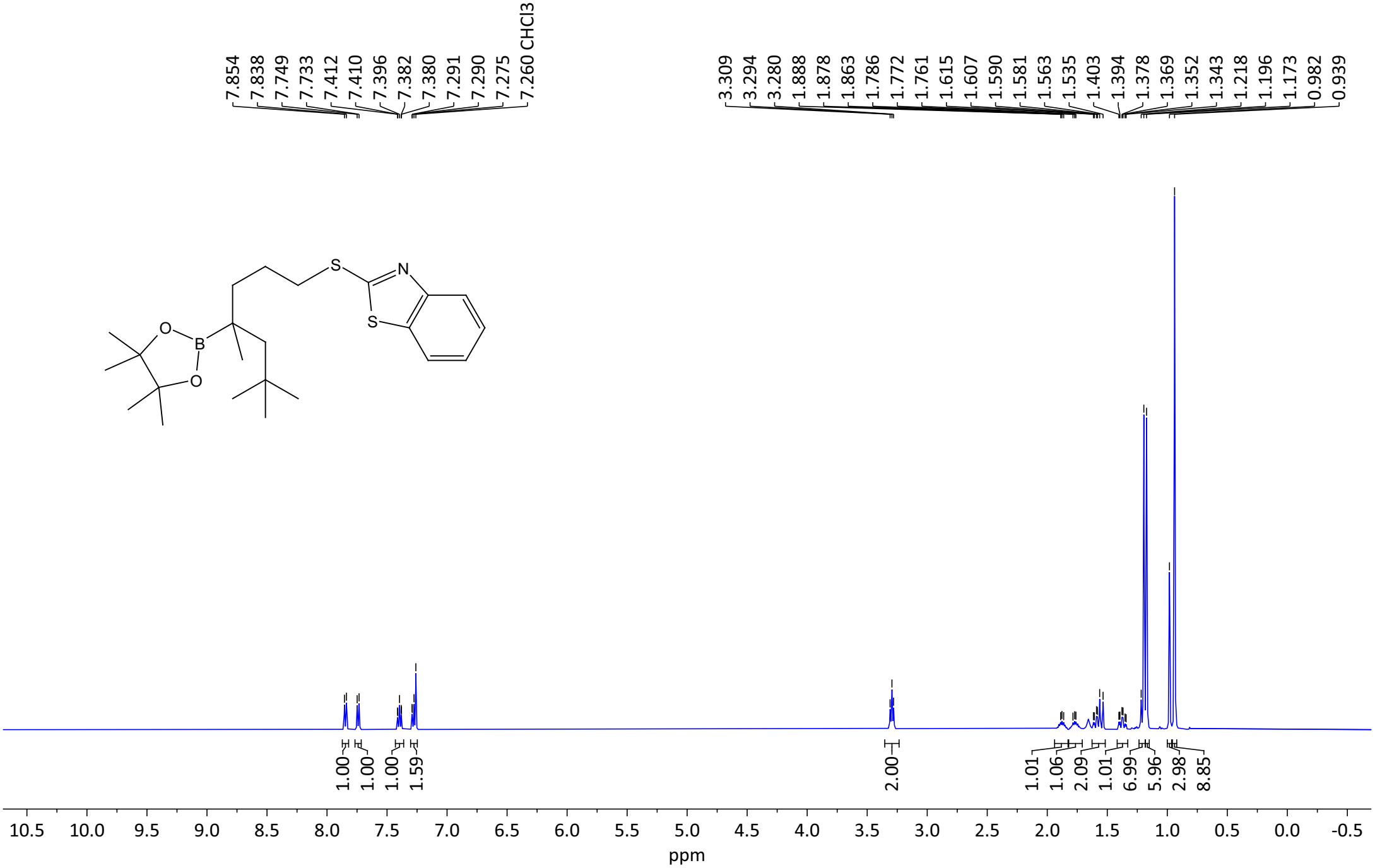
Compound **32**: ^{1}H NMR (500 MHz, $CDCl_3$)



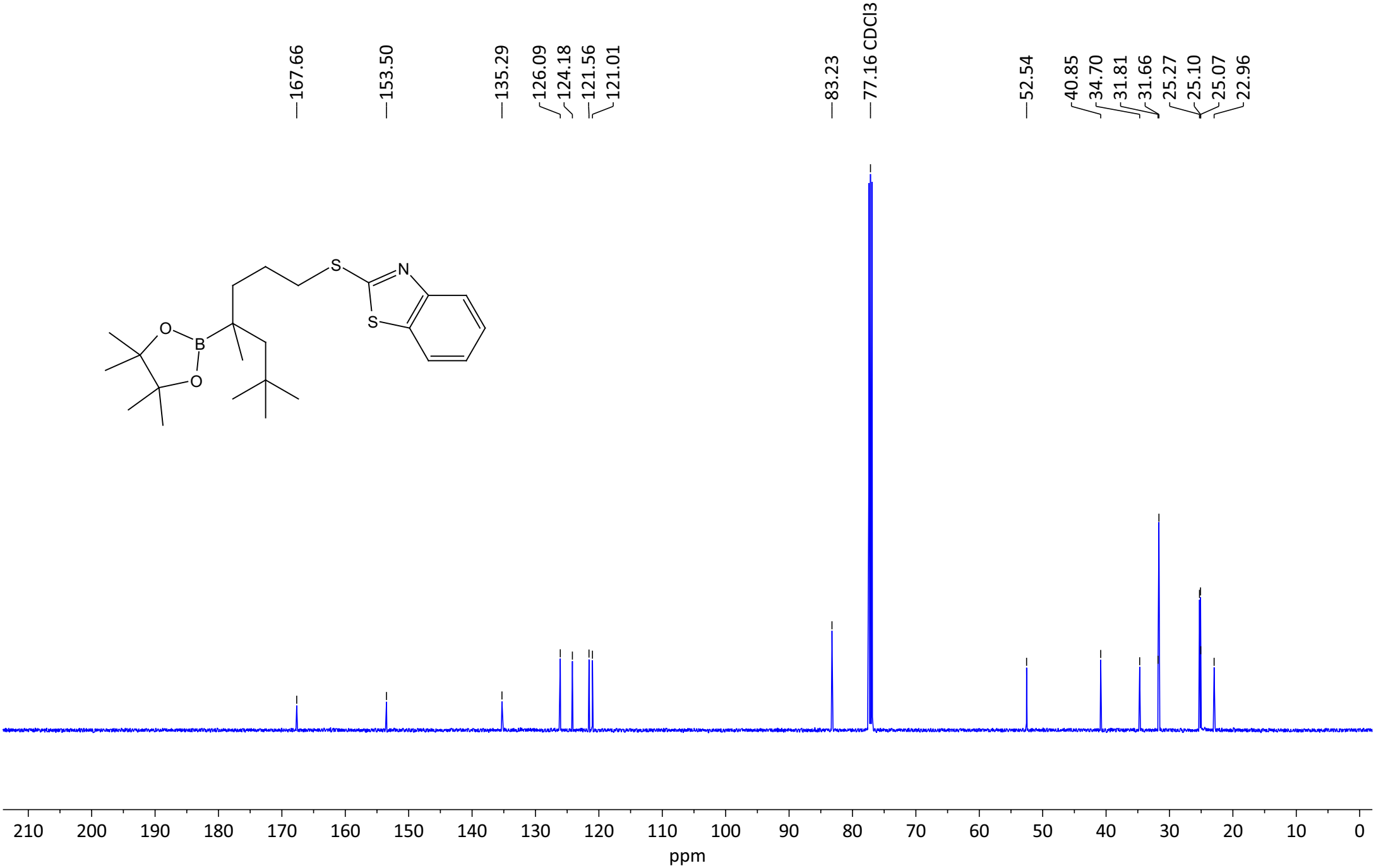
Compound **32**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



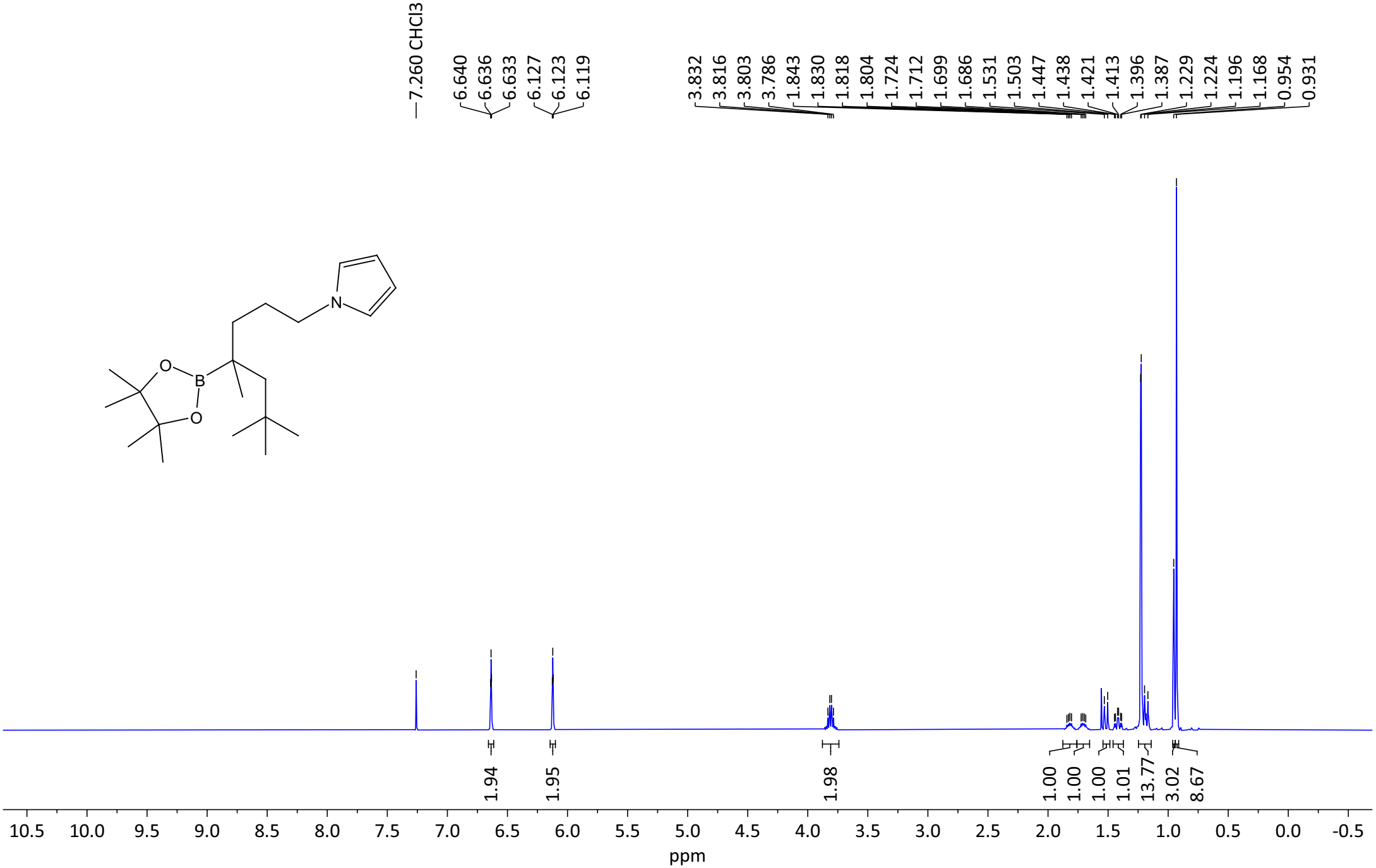
Compound **33**: ^{1}H NMR (500 MHz, $CDCl_3$)



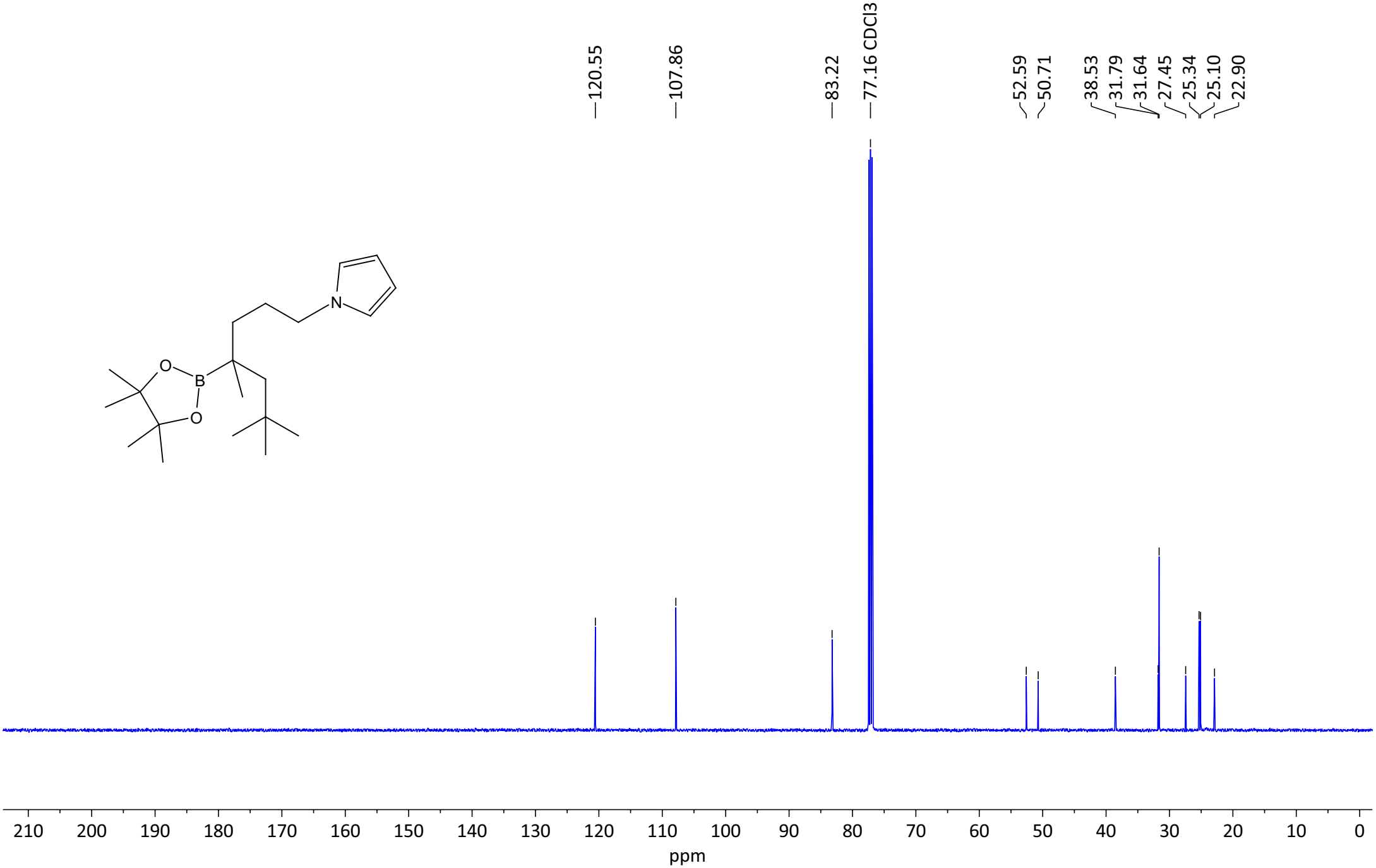
Compound **33**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



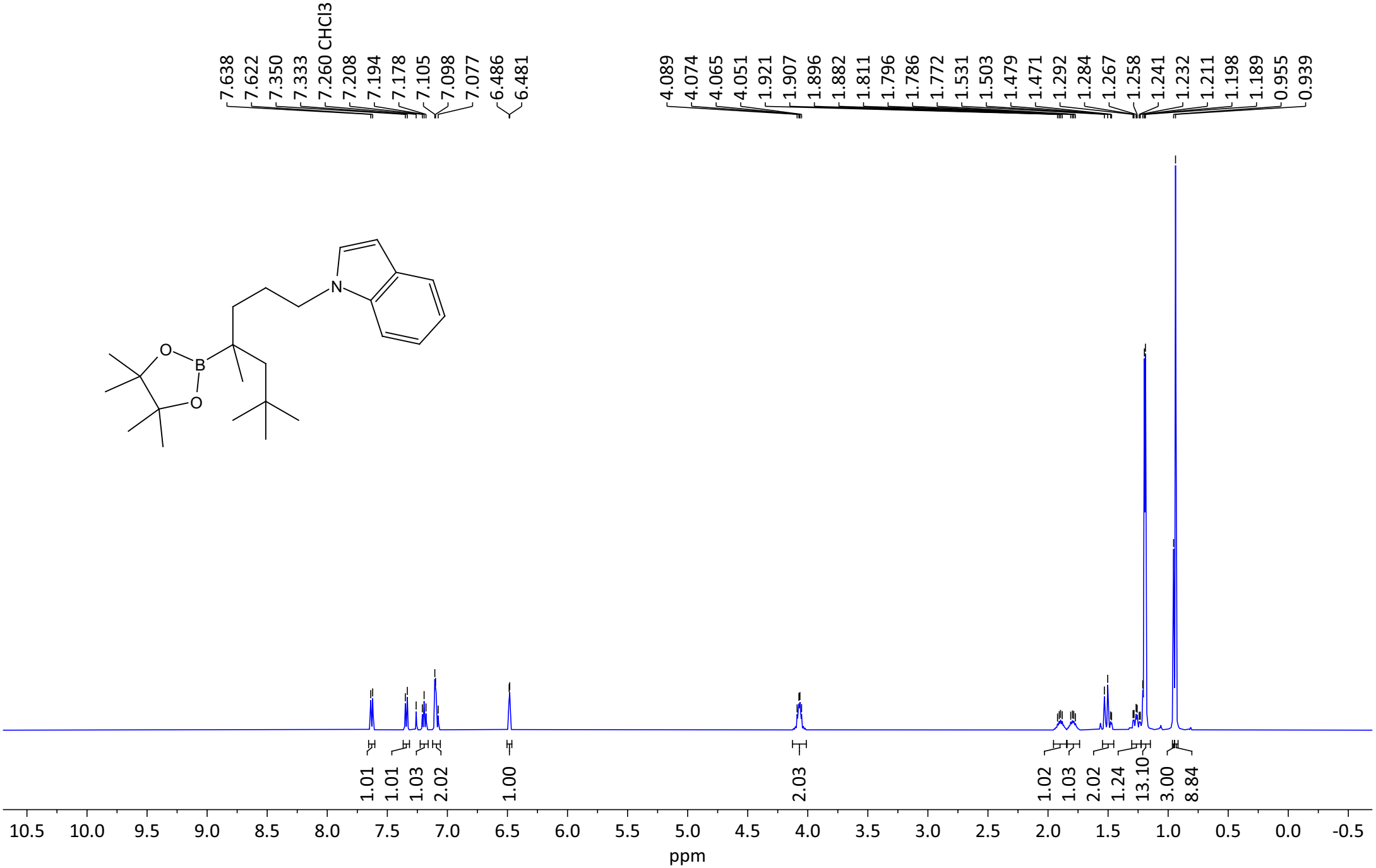
Compound **34**: ^{1}H NMR (500 MHz, $CDCl_3$)



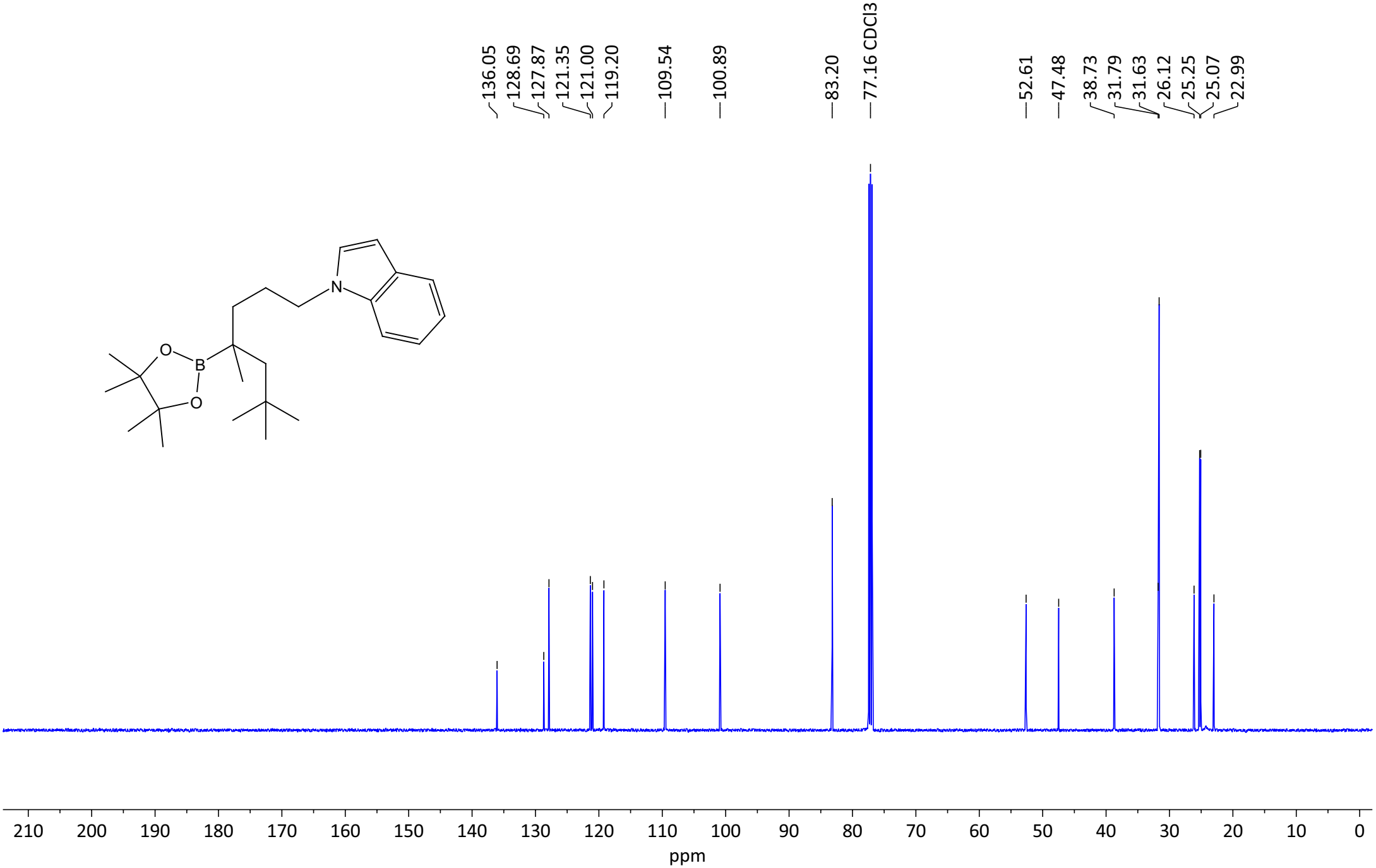
Compound **34**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



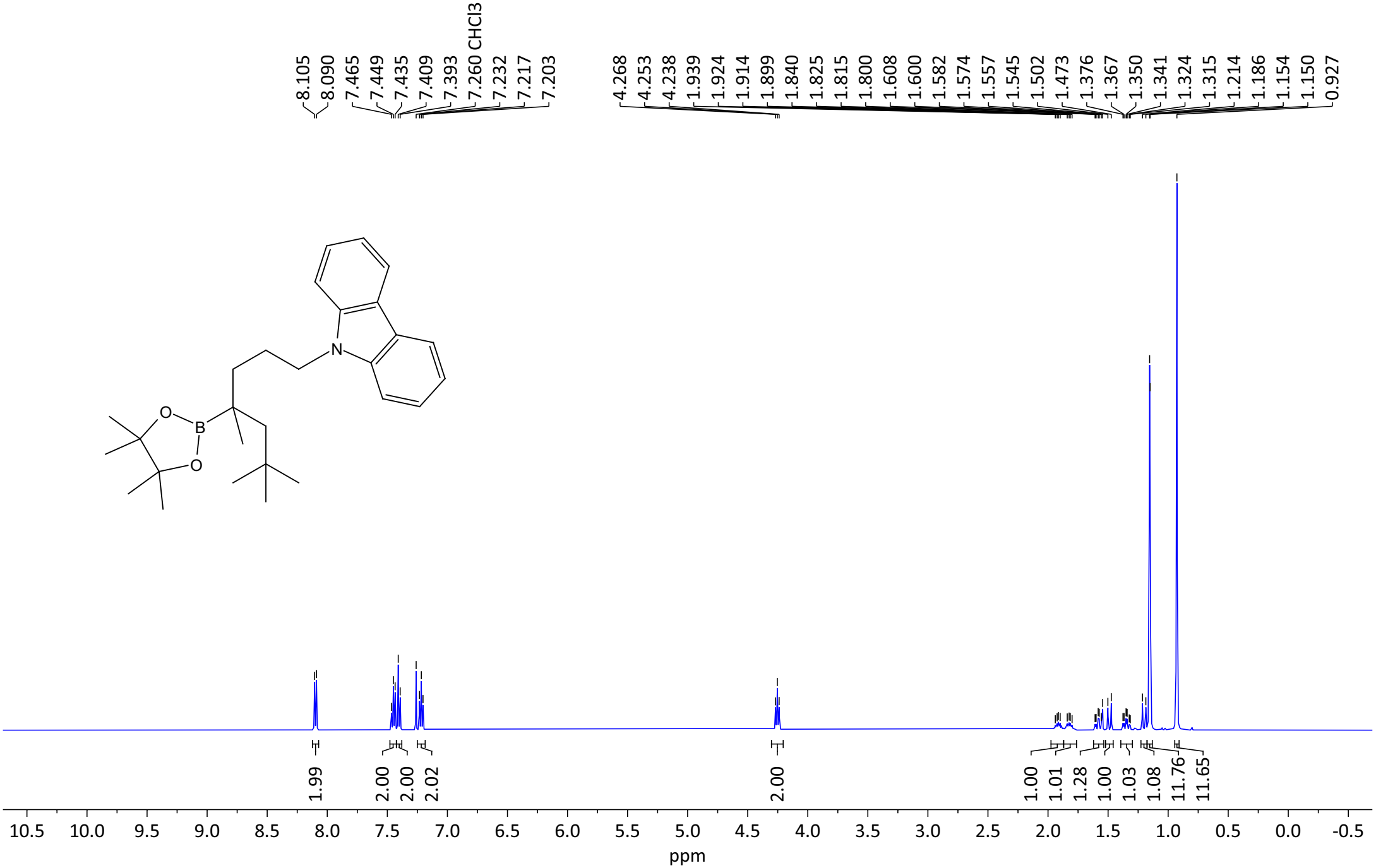
Compound **35**: ^{1}H NMR (500 MHz, $CDCl_3$)



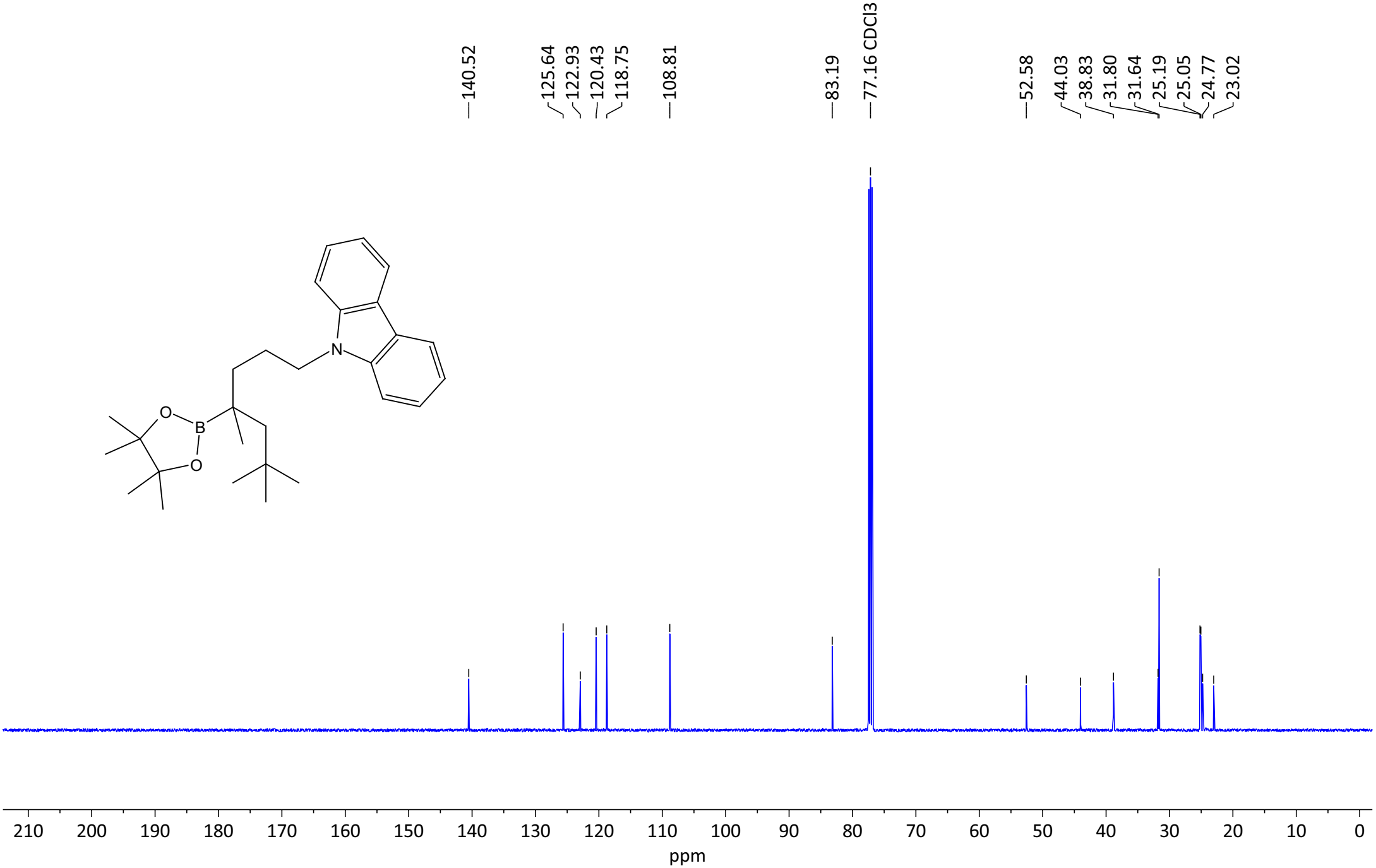
Compound **35**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



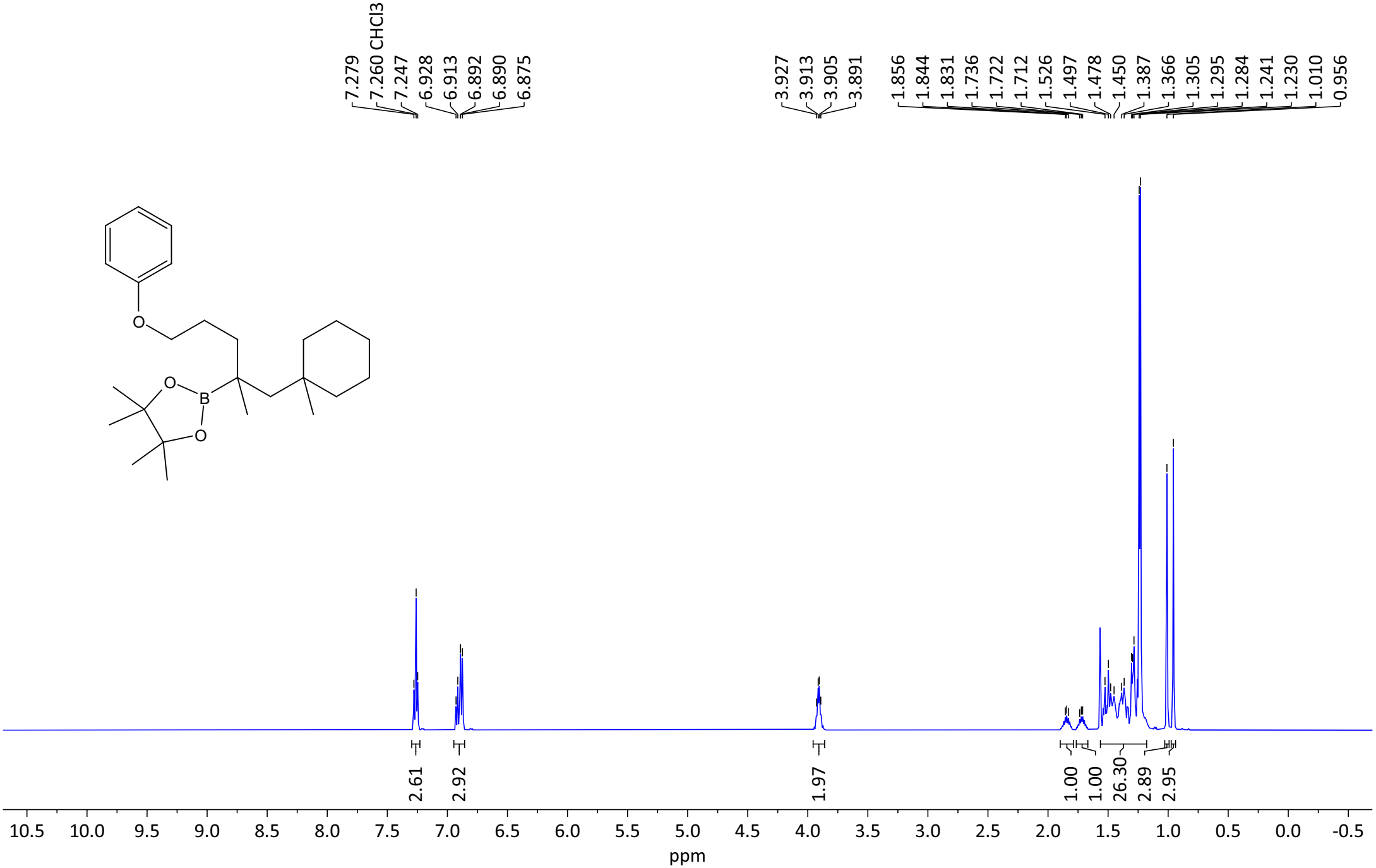
Compound **36**: ^{1}H NMR (500 MHz, $CDCl_3$)



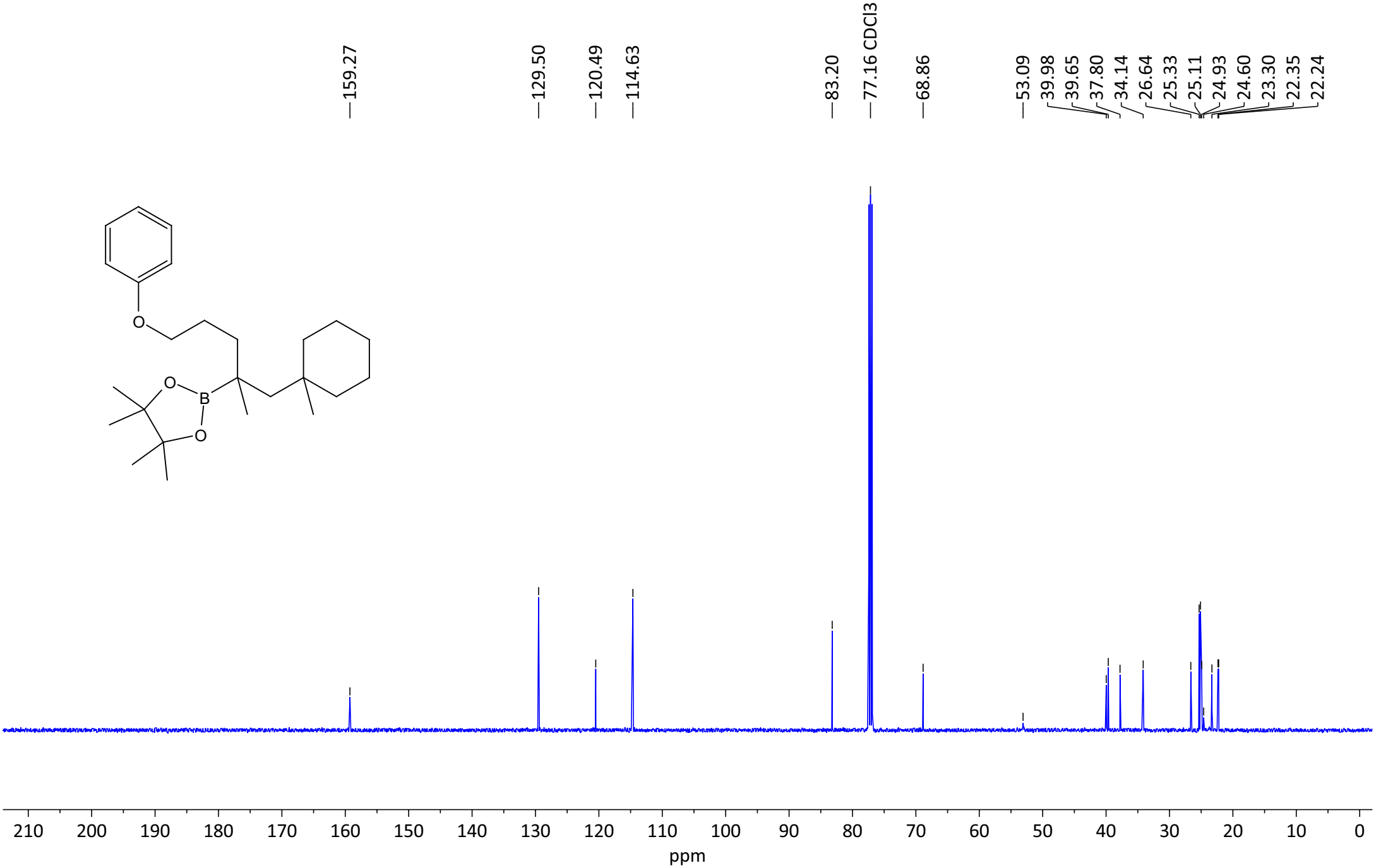
Compound **36**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



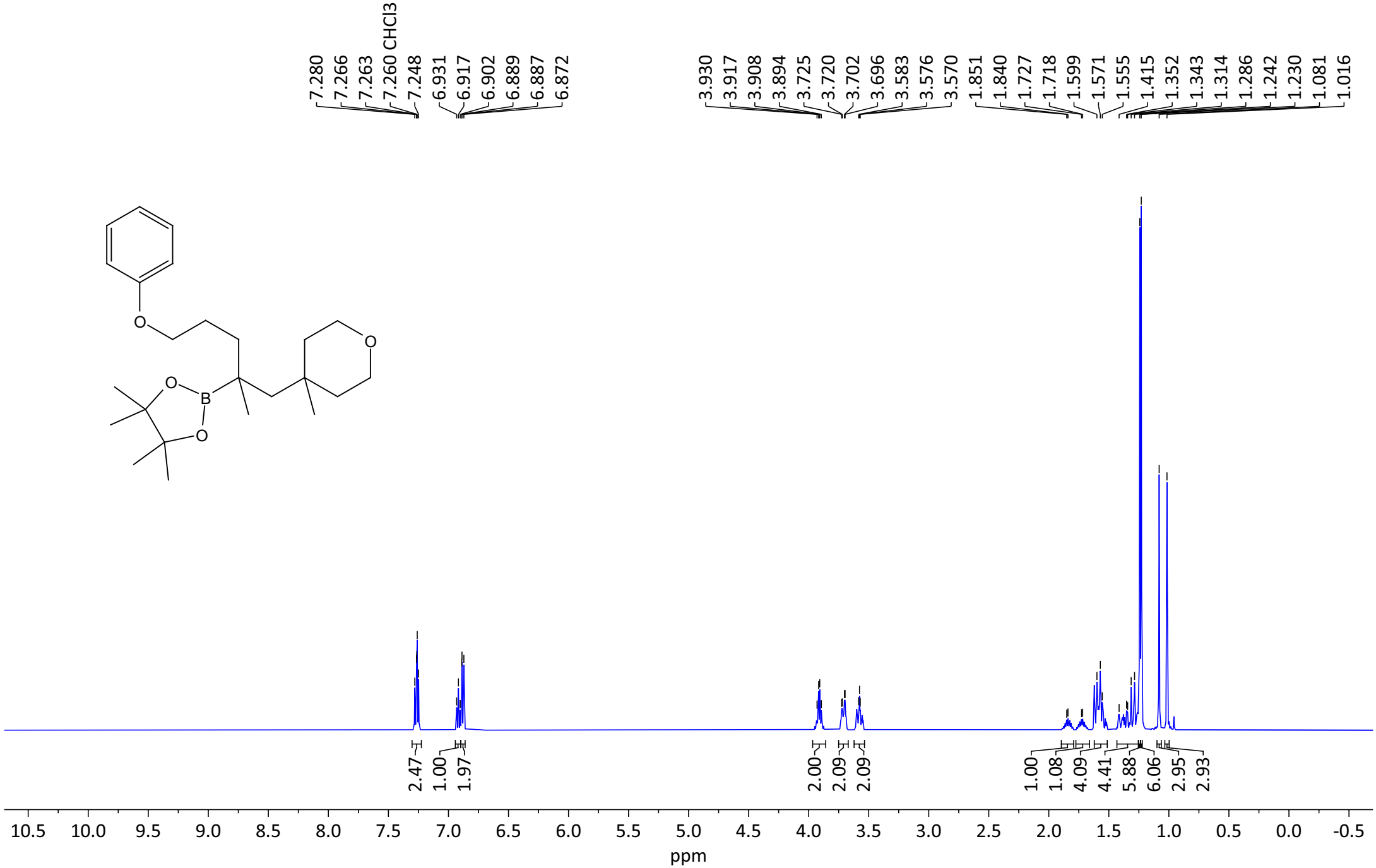
Compound **37**: ^{1}H NMR (500 MHz, $CDCl_3$)



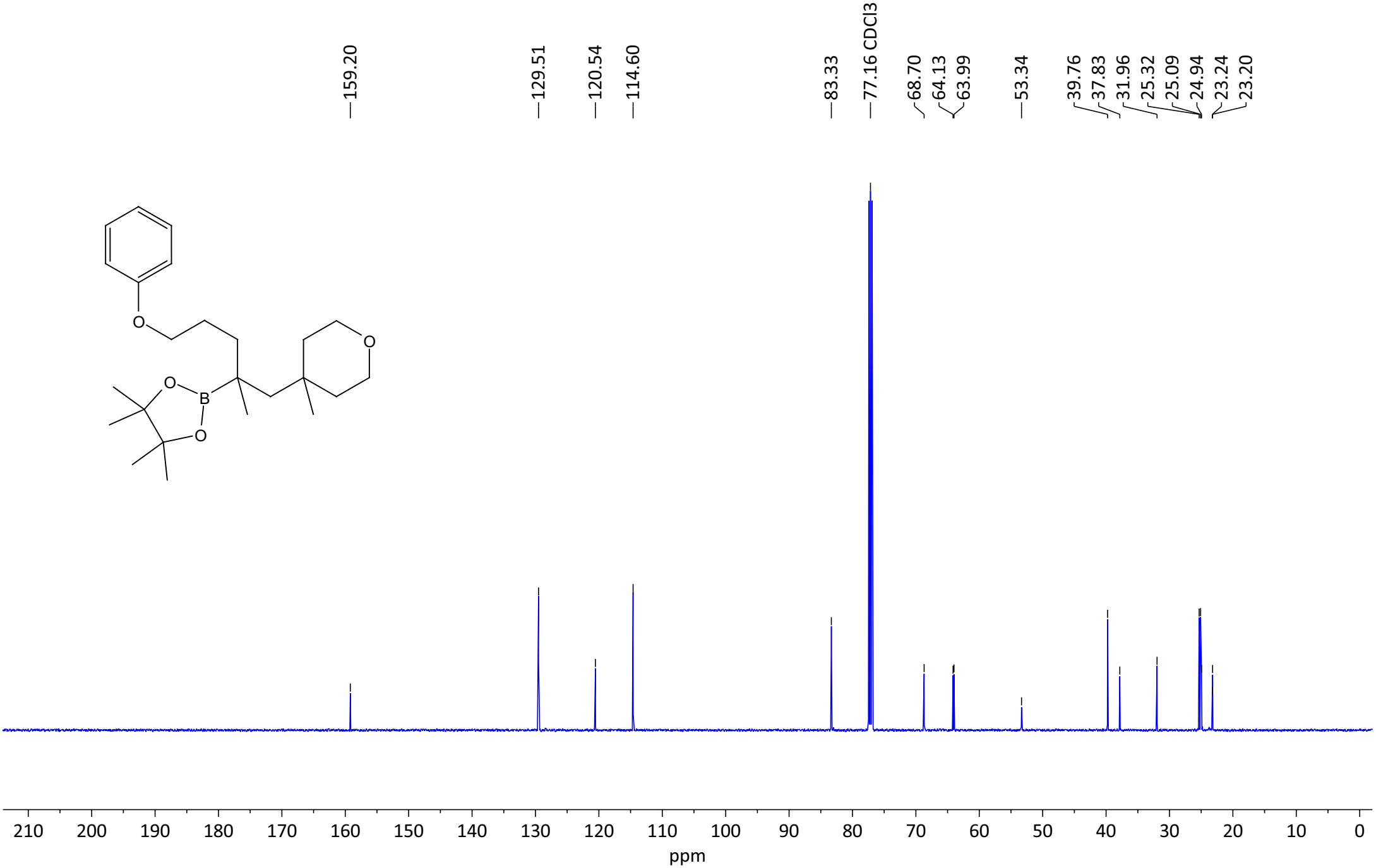
Compound **37**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



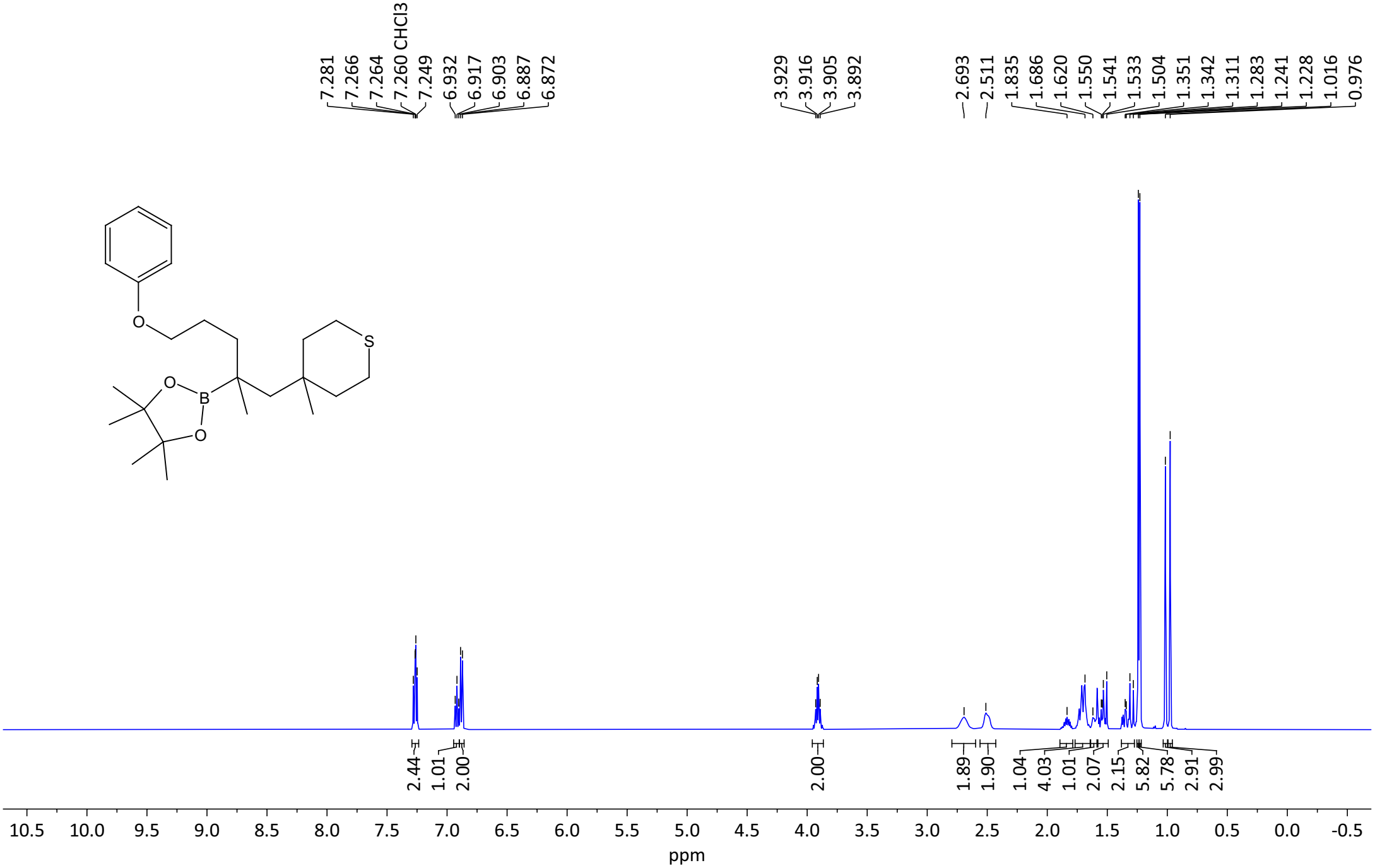
Compound **38**: ^{1}H NMR (500 MHz, $CDCl_3$)



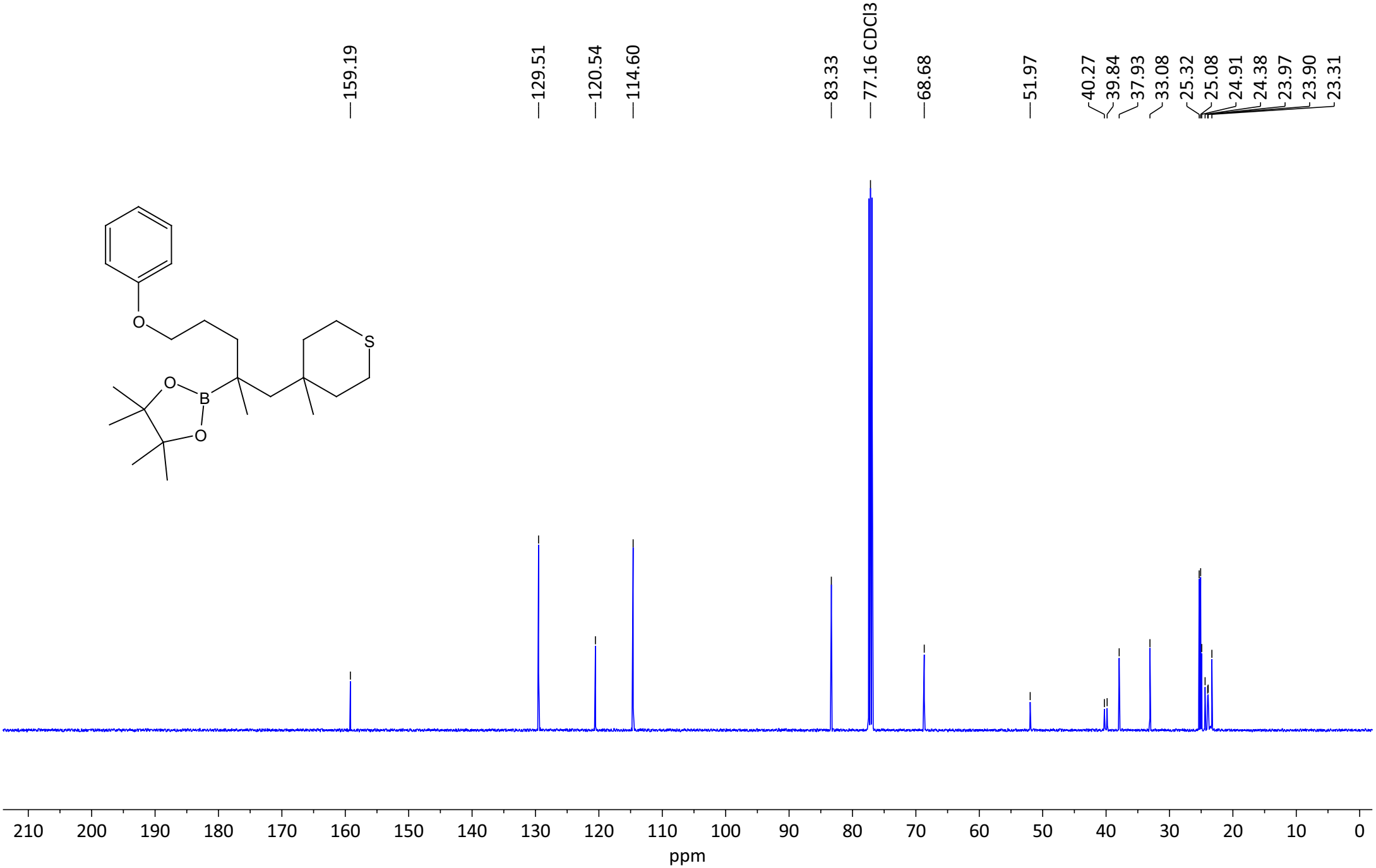
Compound **38**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



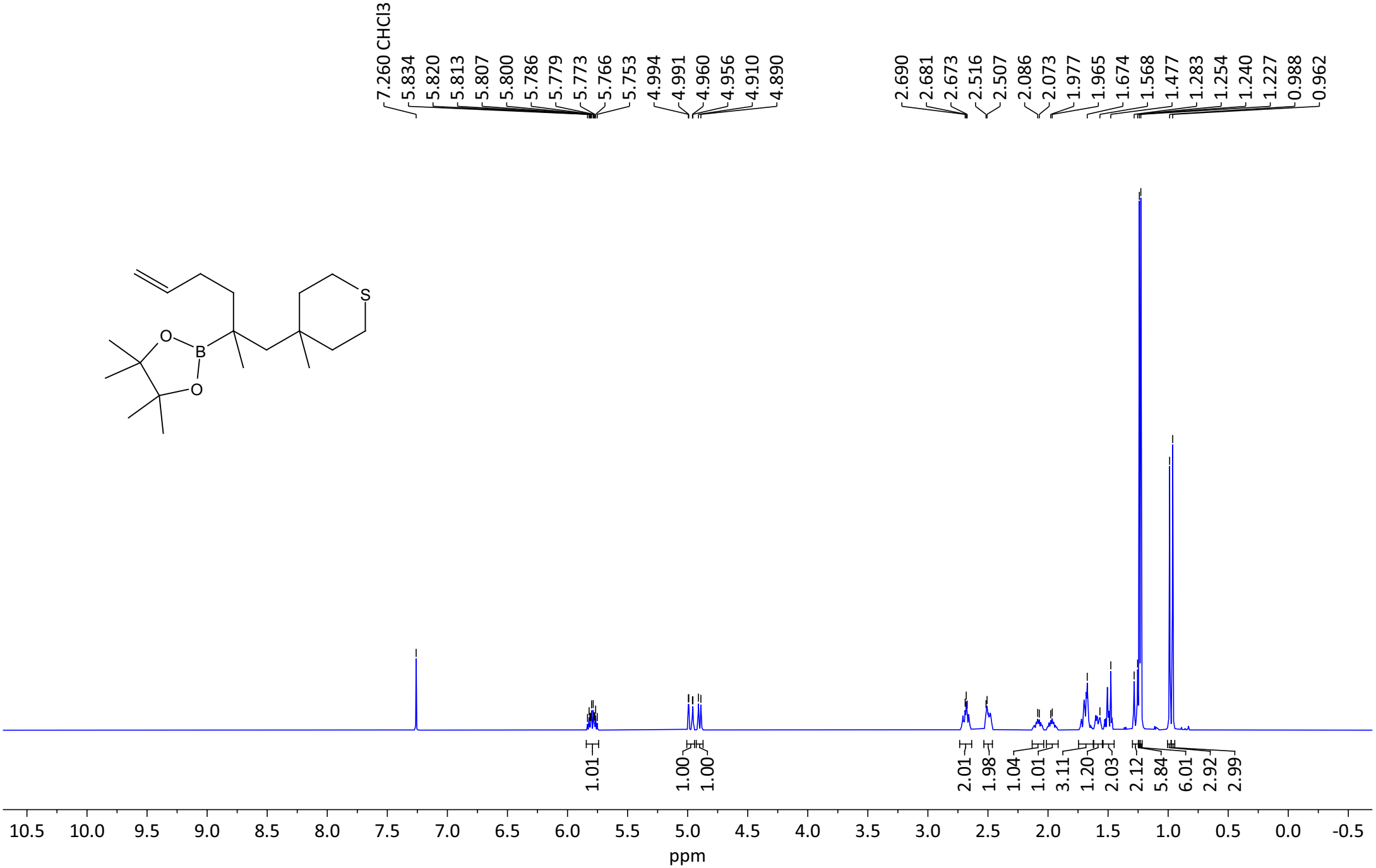
Compound **39**: ^{1}H NMR (500 MHz, $CDCl_3$)



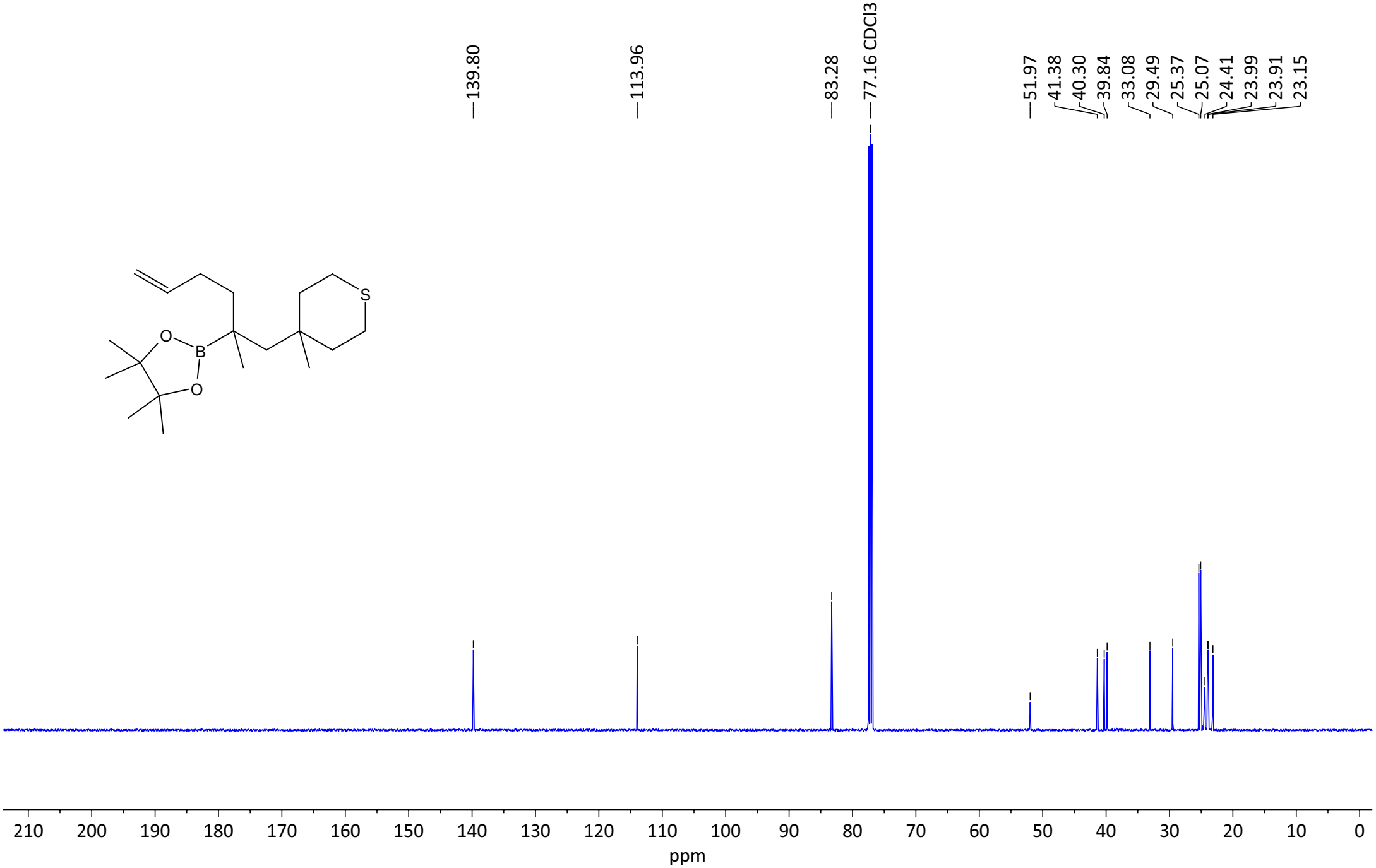
Compound **39**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



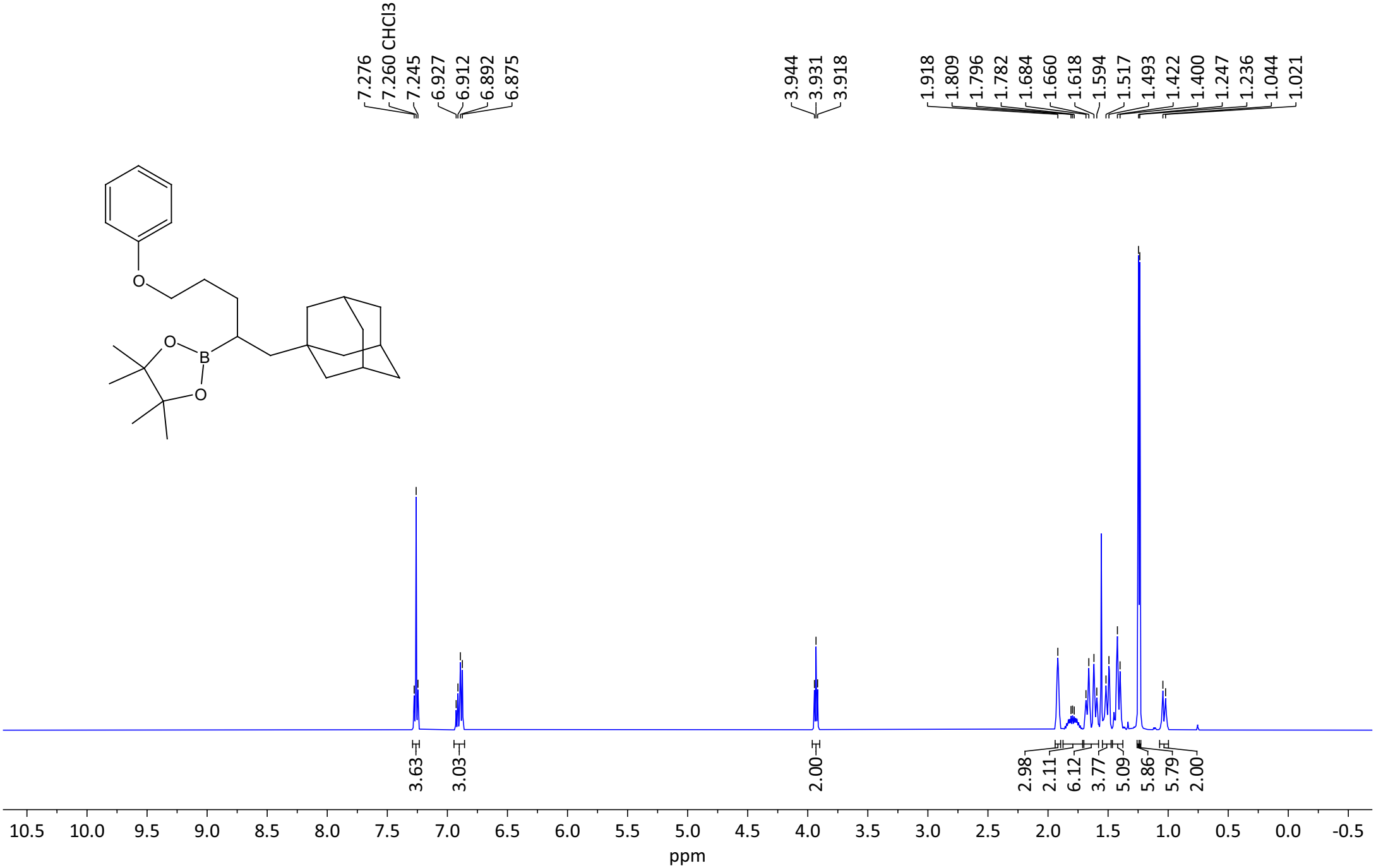
Compound **40**: ^{1}H NMR (500 MHz, $CDCl_3$)



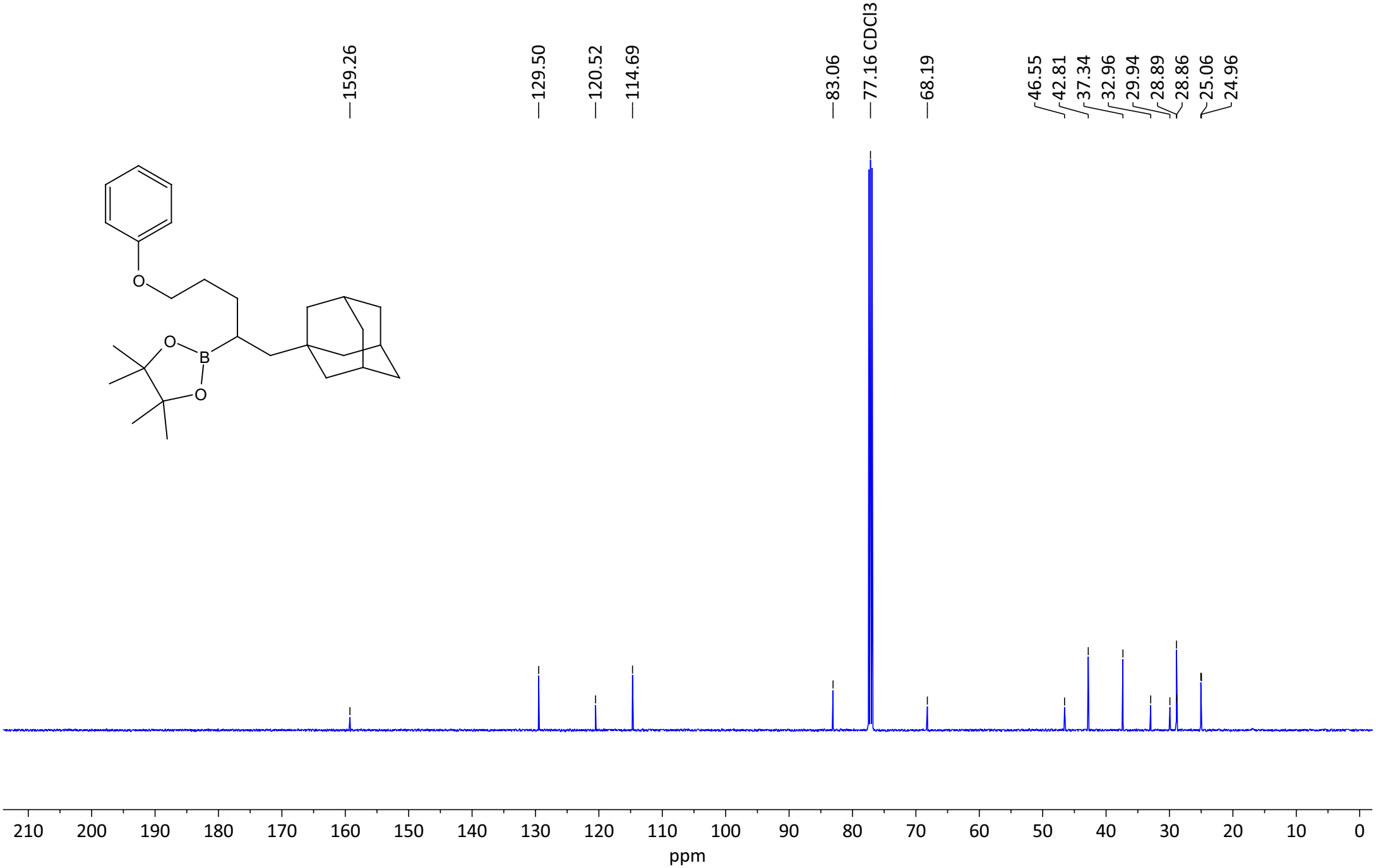
Compound **40**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



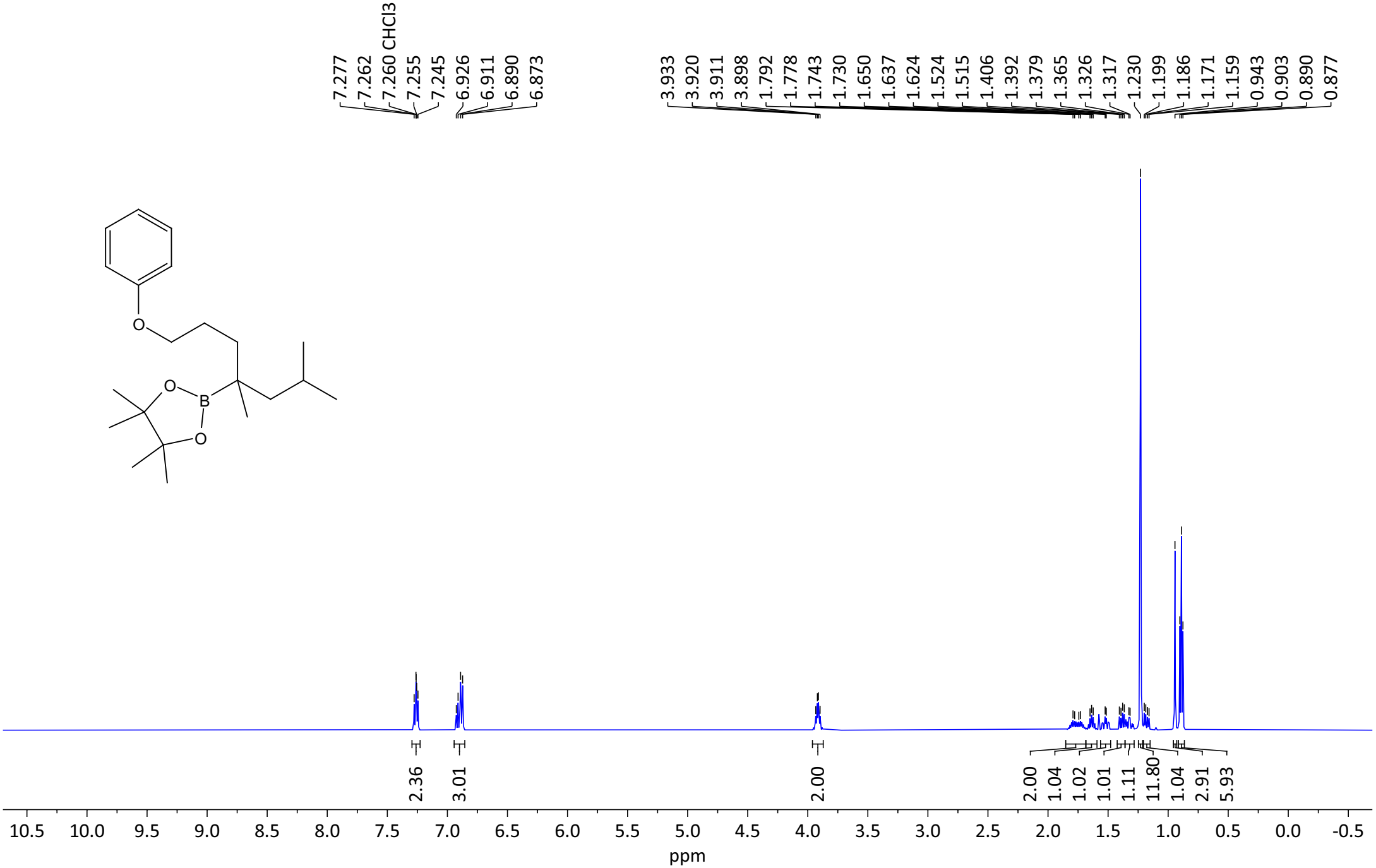
Compound **41**: ^{1}H NMR (500 MHz, $CDCl_3$)



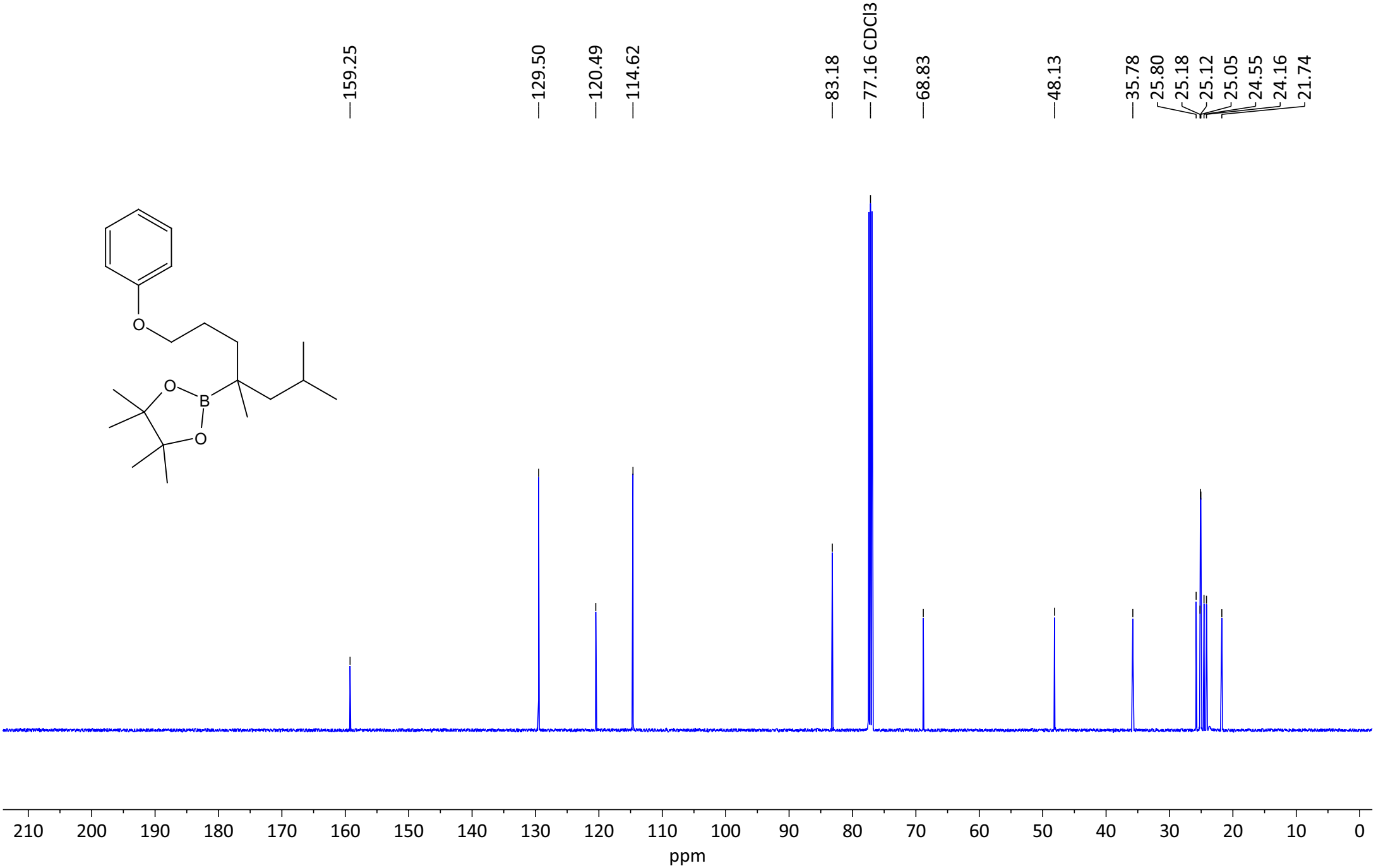
Compound **41**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



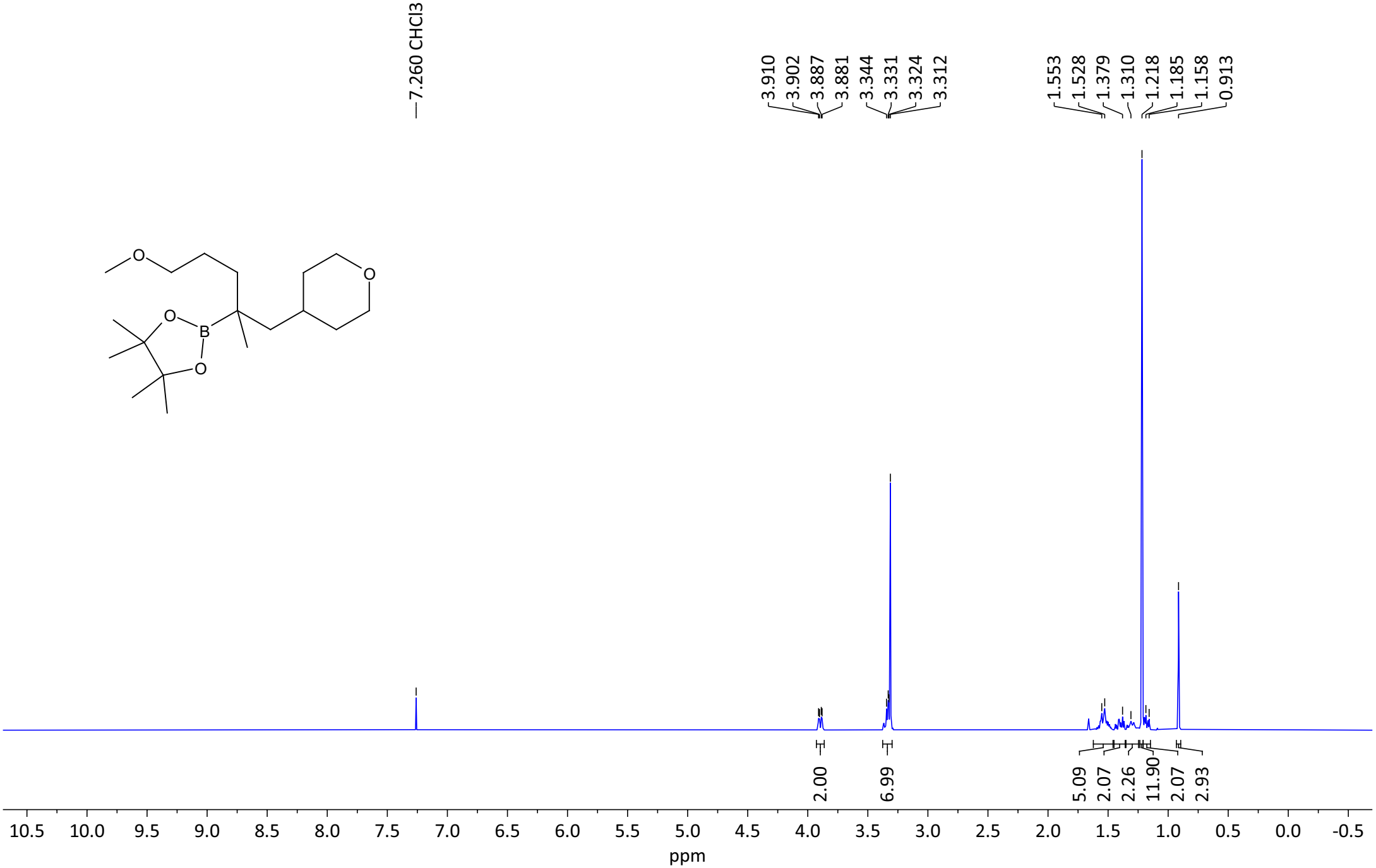
Compound **42**: ^{1}H NMR (500 MHz, $CDCl_3$)



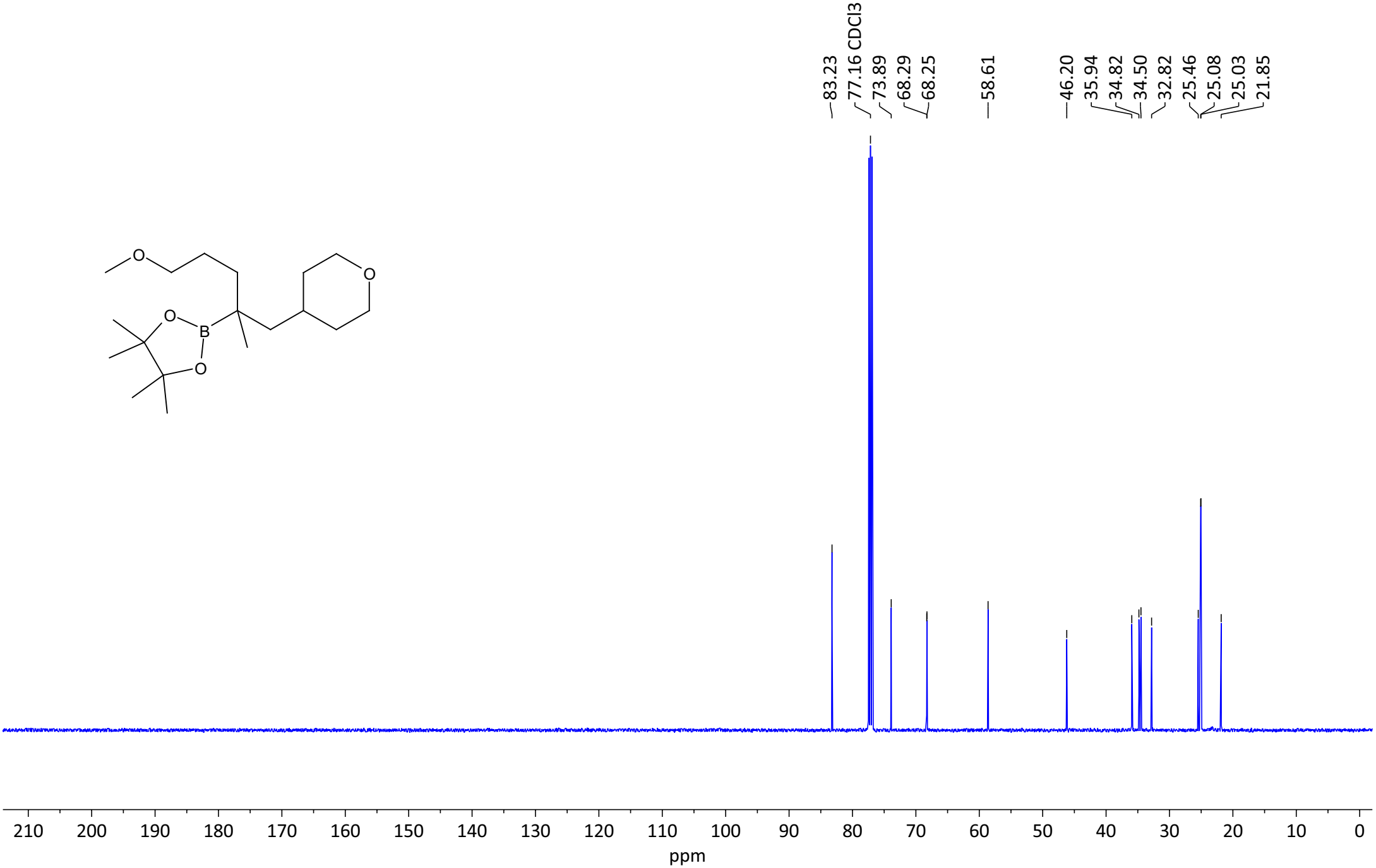
Compound **42**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



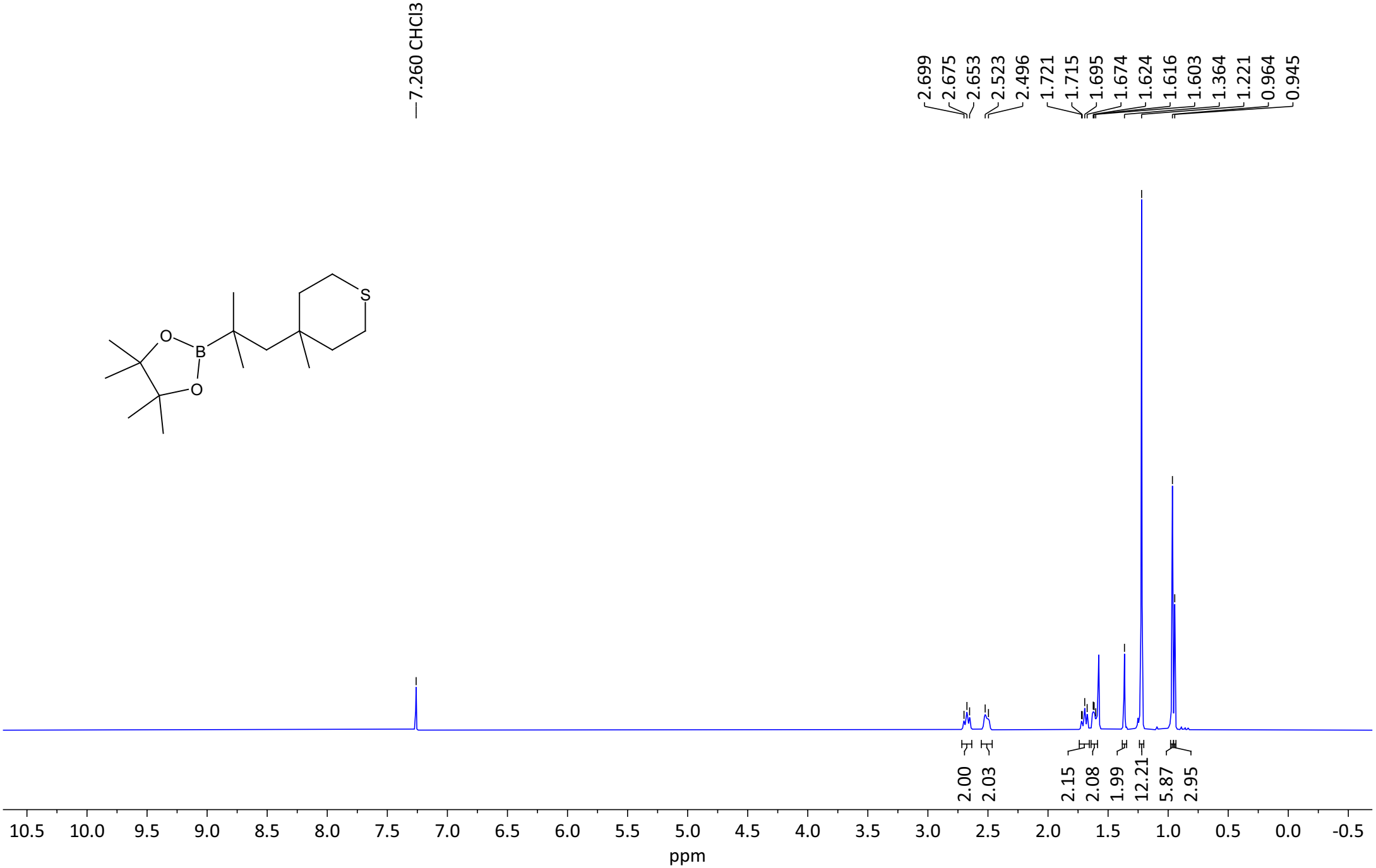
Compound **43**: ^{1}H NMR (500 MHz, $CDCl_3$)



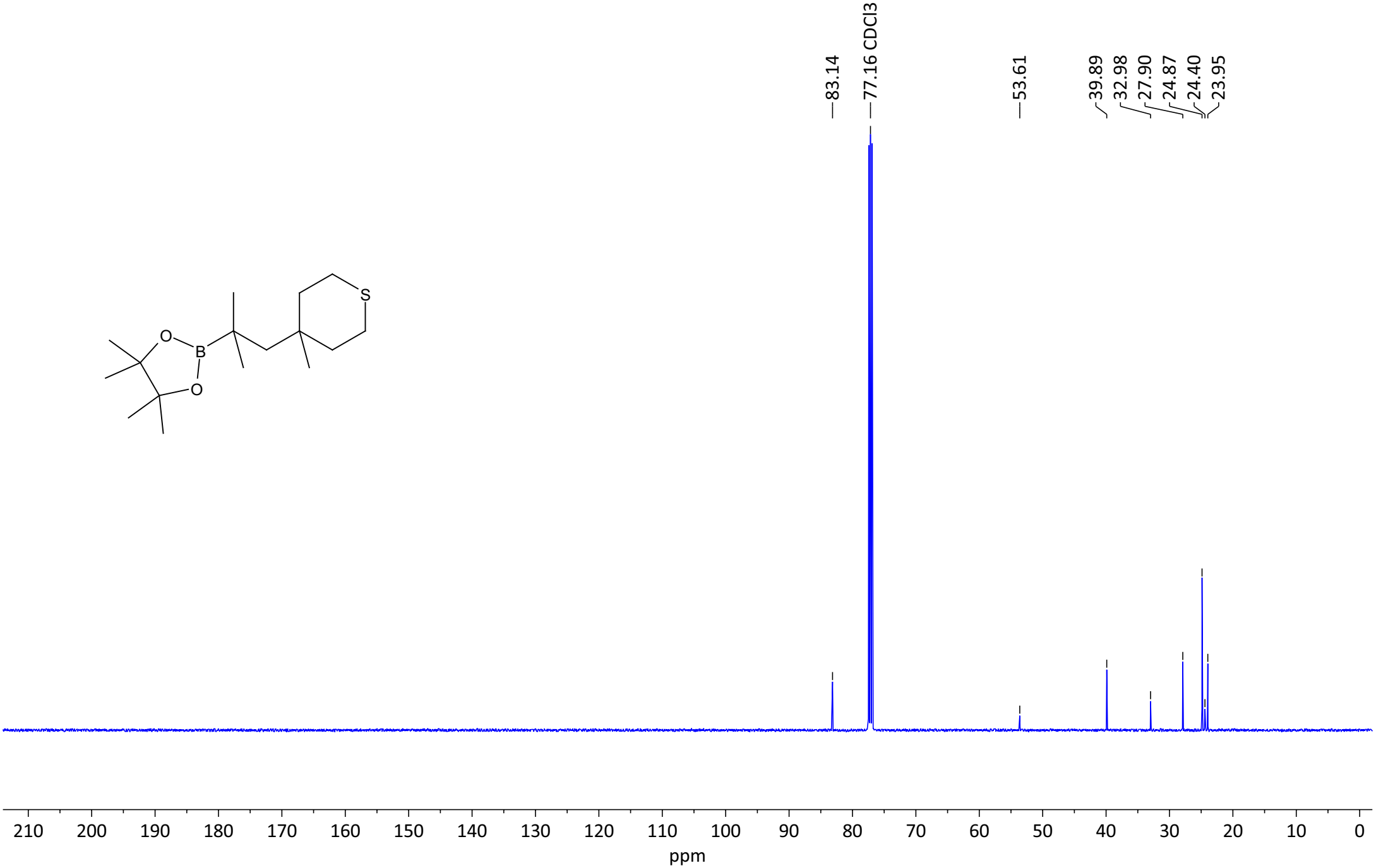
Compound **43**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



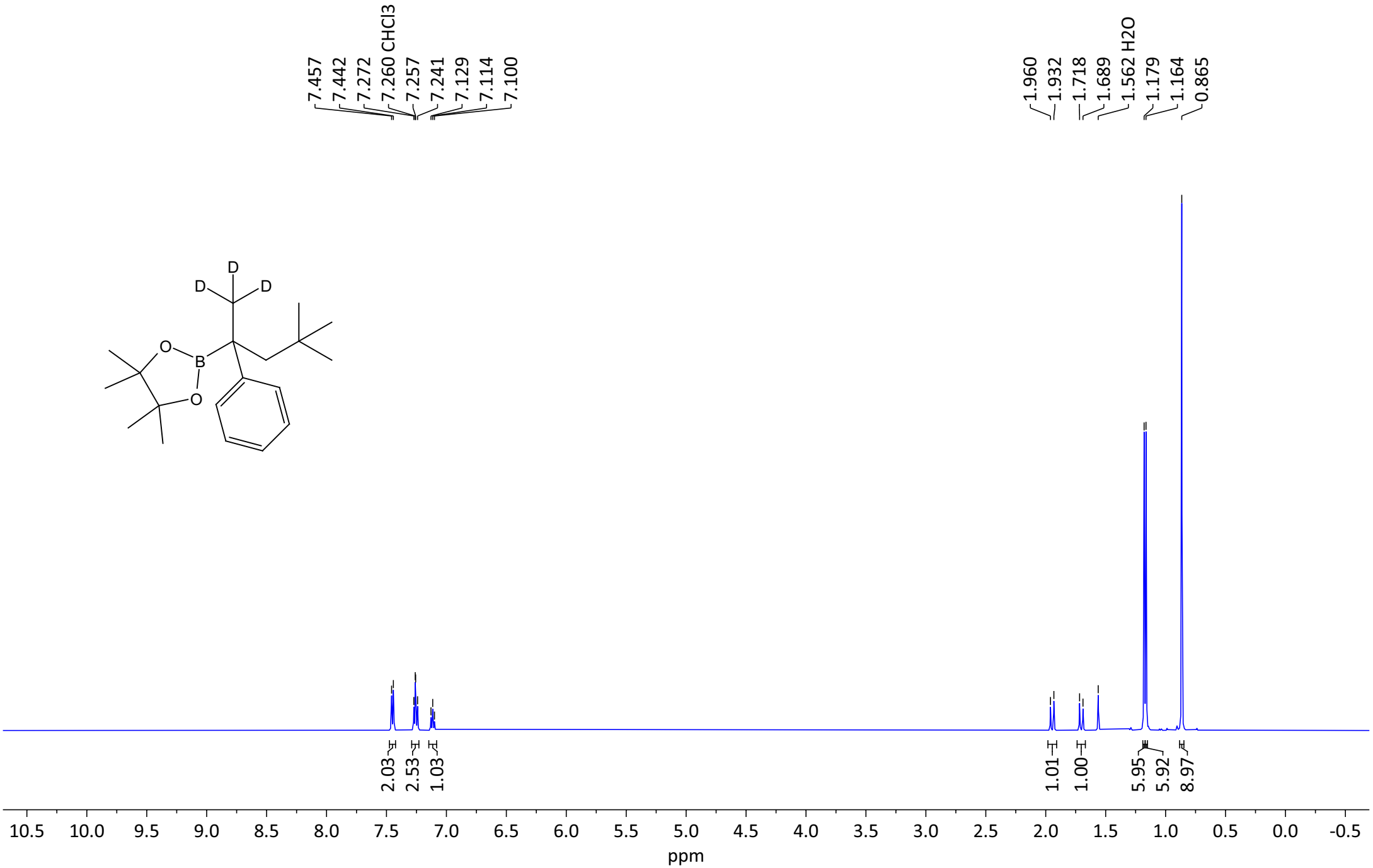
Compound **44**: ^{1}H NMR (500 MHz, $CDCl_3$)



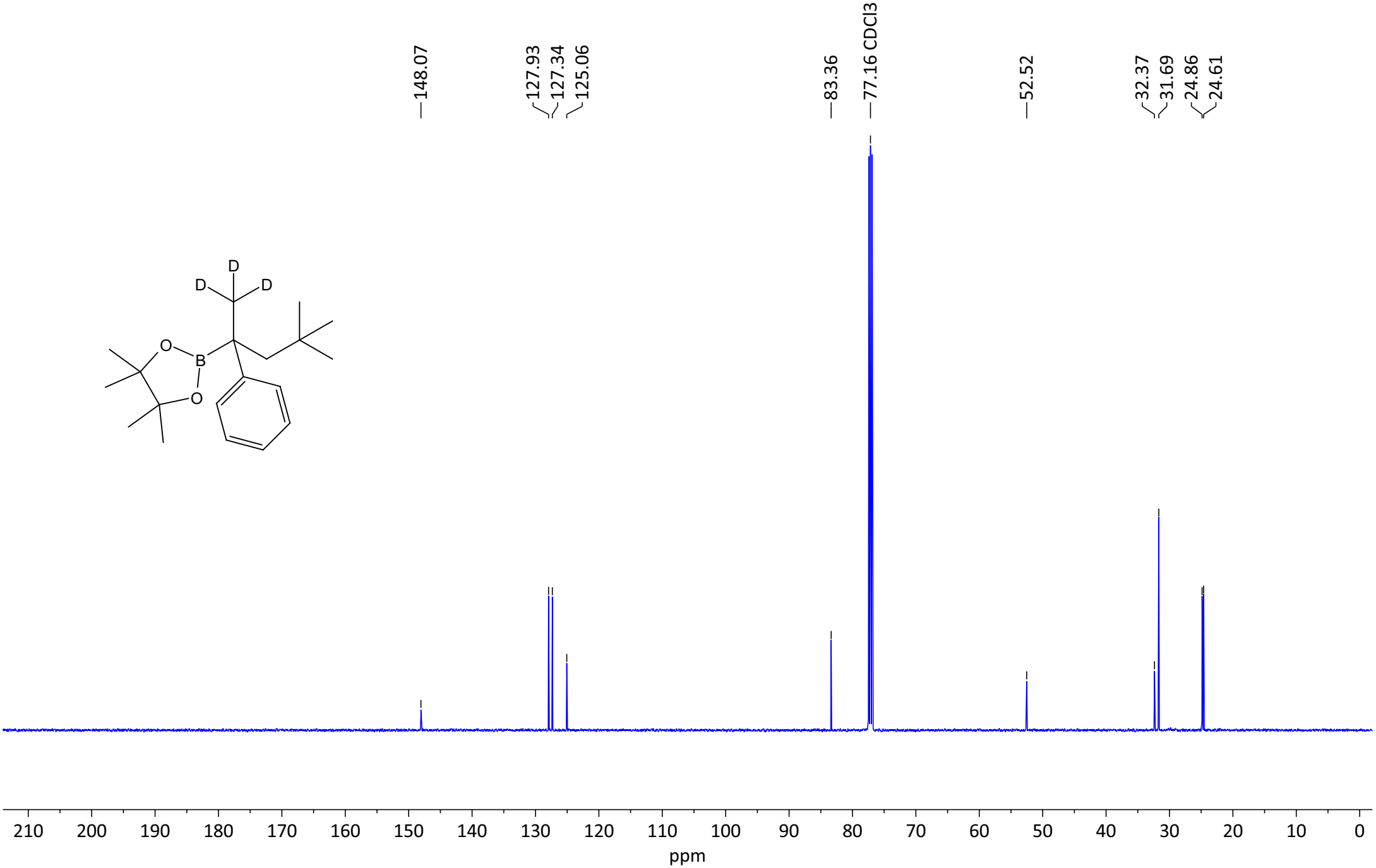
Compound **44**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



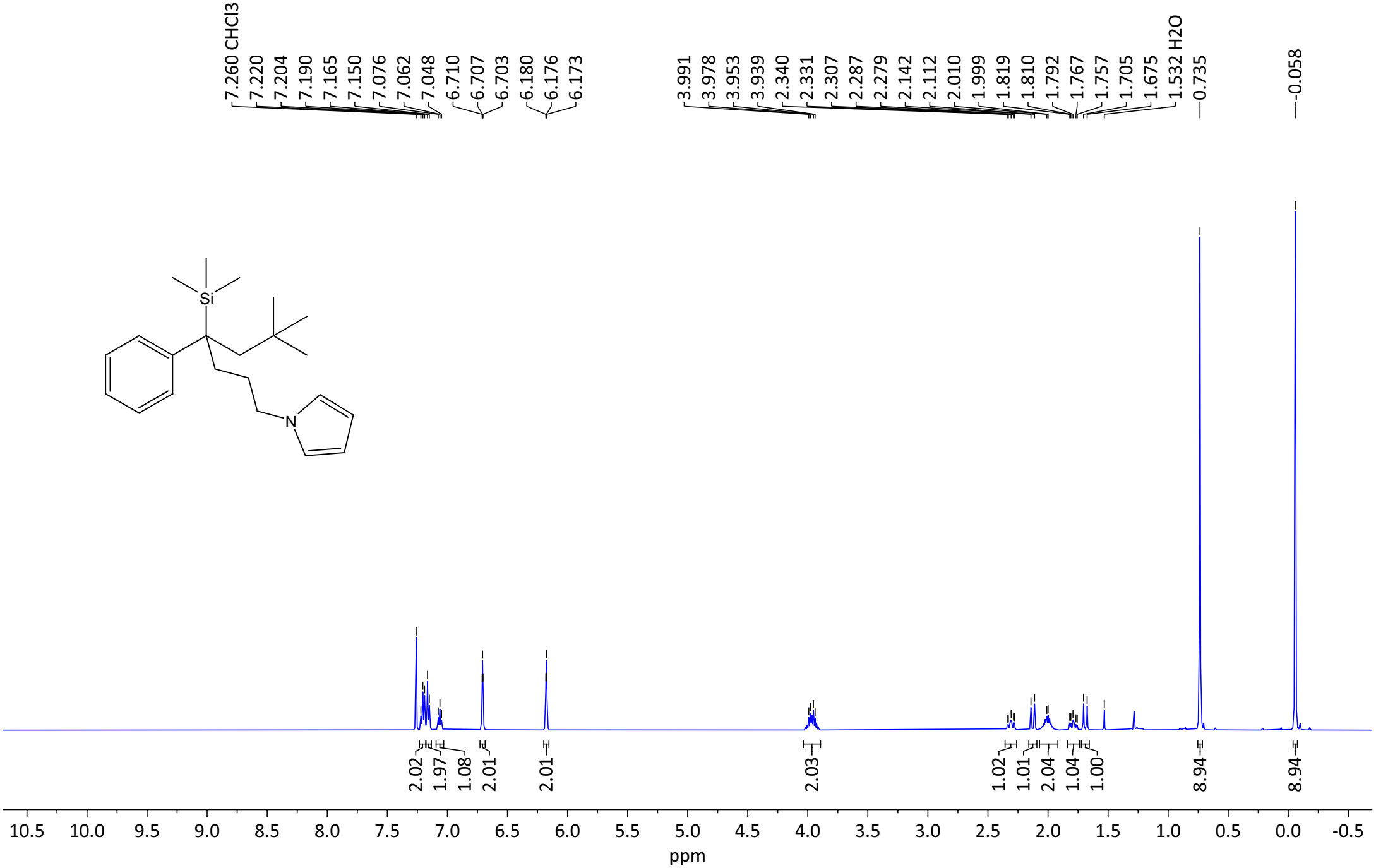
Compound **45**: ^{1}H NMR (500 MHz, $CDCl_3$)



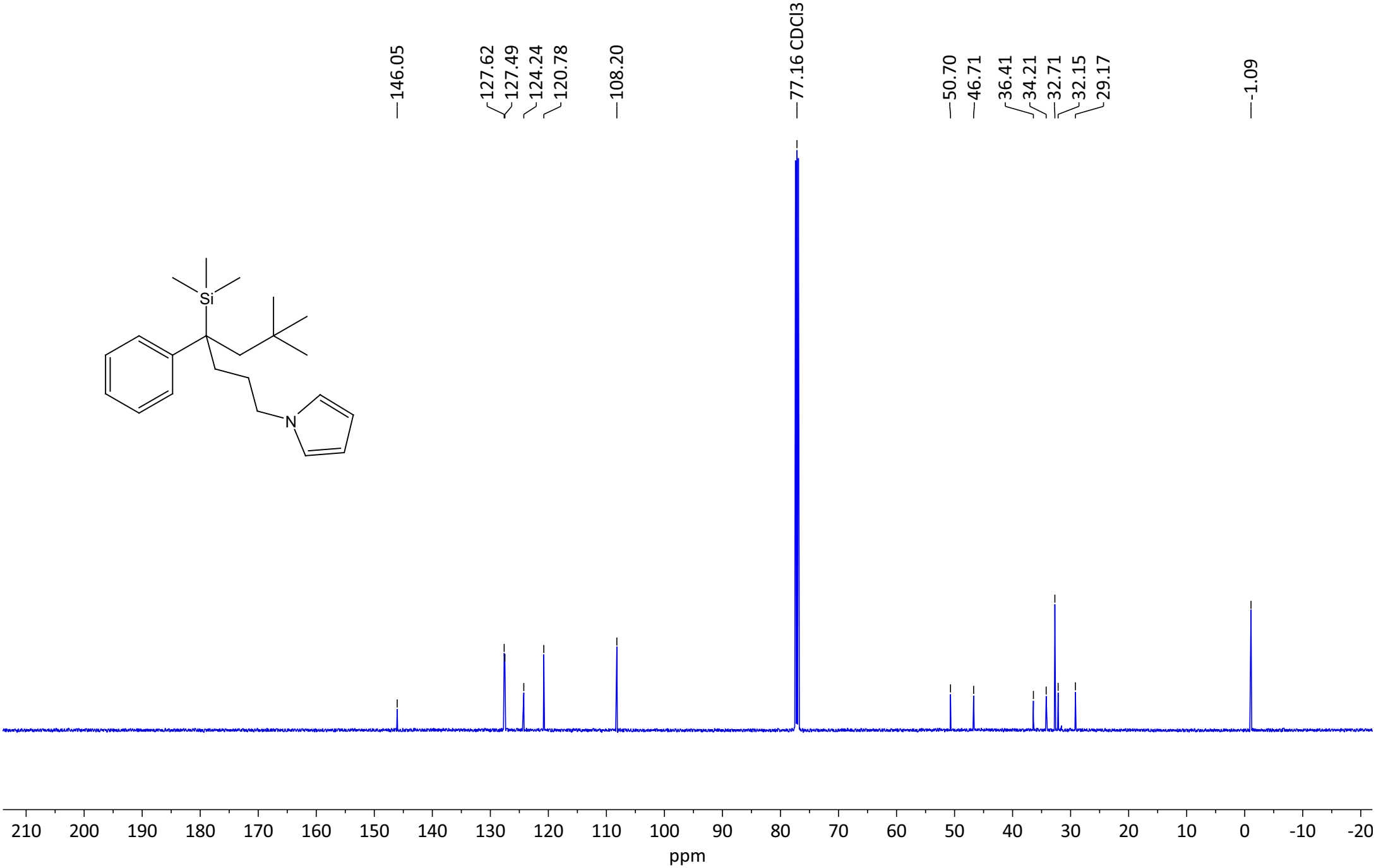
Compound **45**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



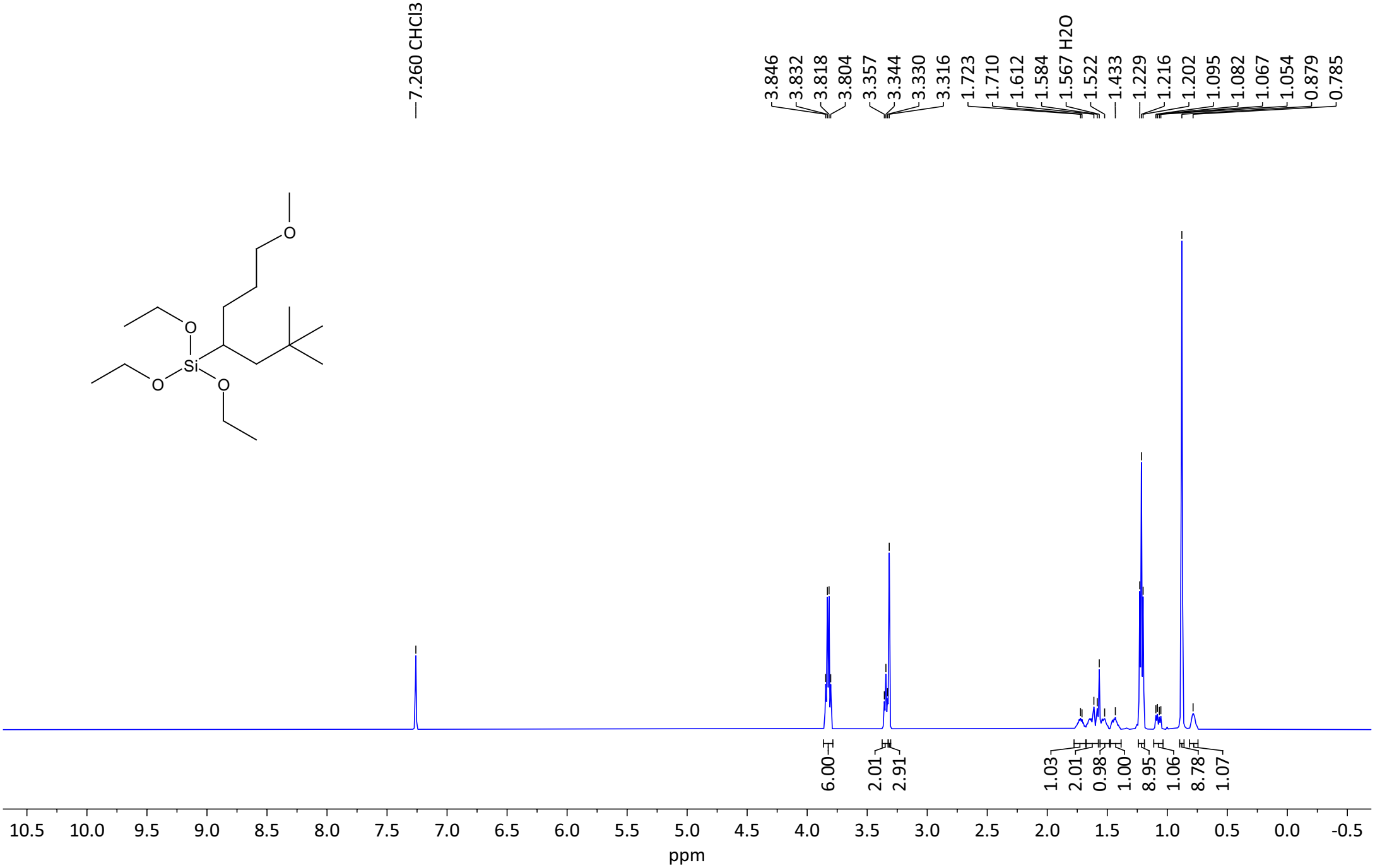
Compound **46**: ^{1}H NMR (500 MHz, $CDCl_3$)



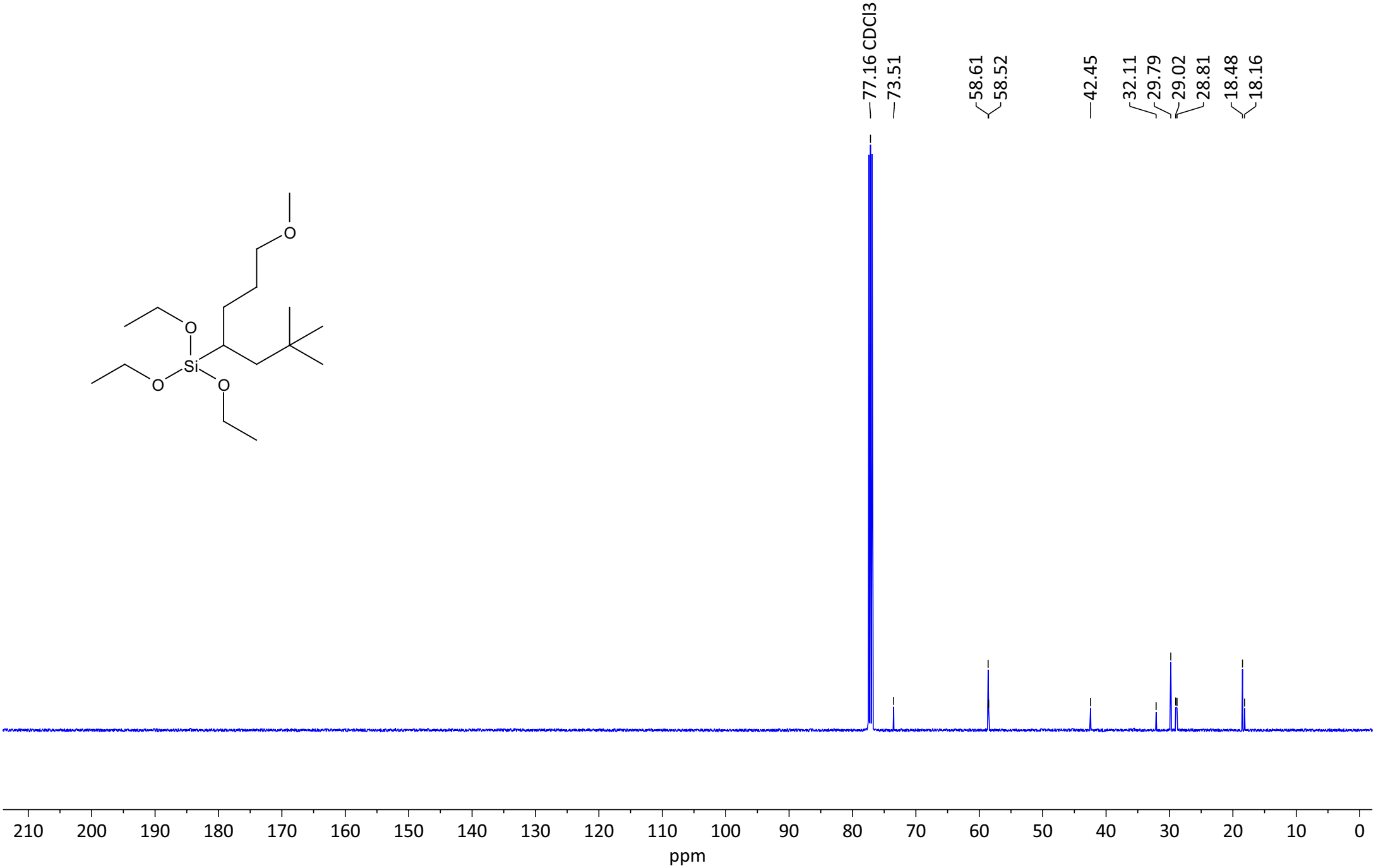
Compound **46**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



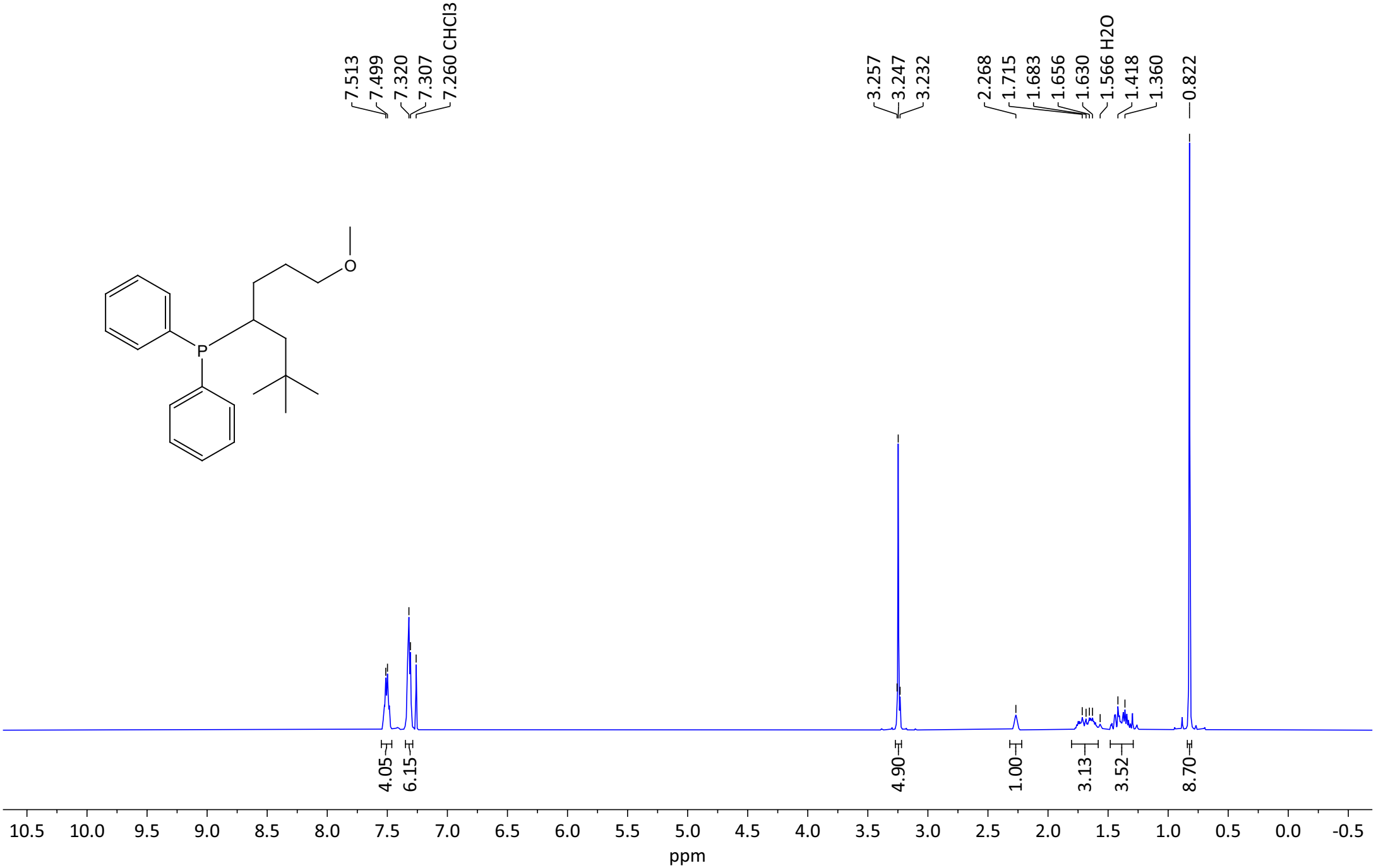
Compound **47**: ^{1}H NMR (500 MHz, $CDCl_3$)



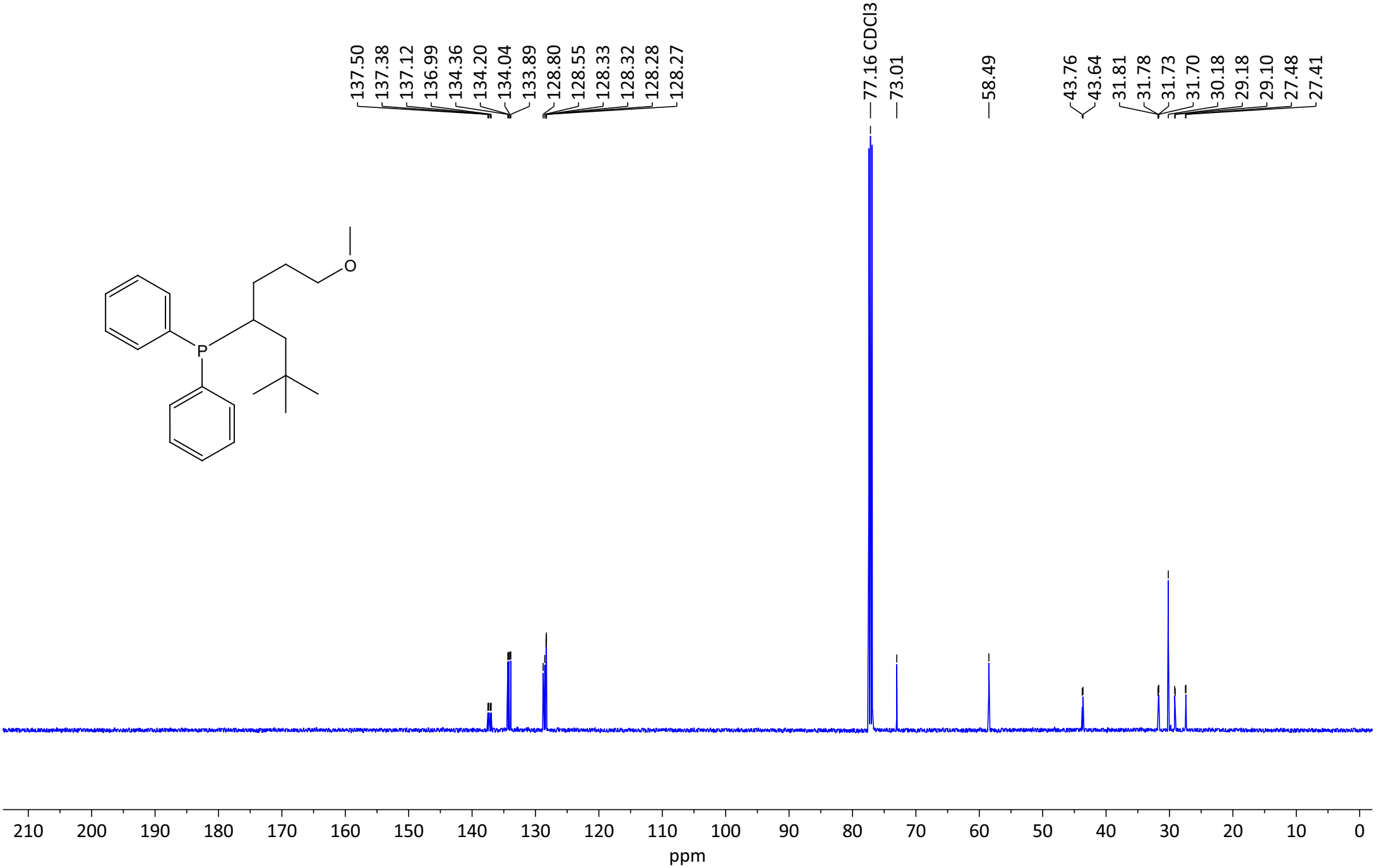
Compound **47**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



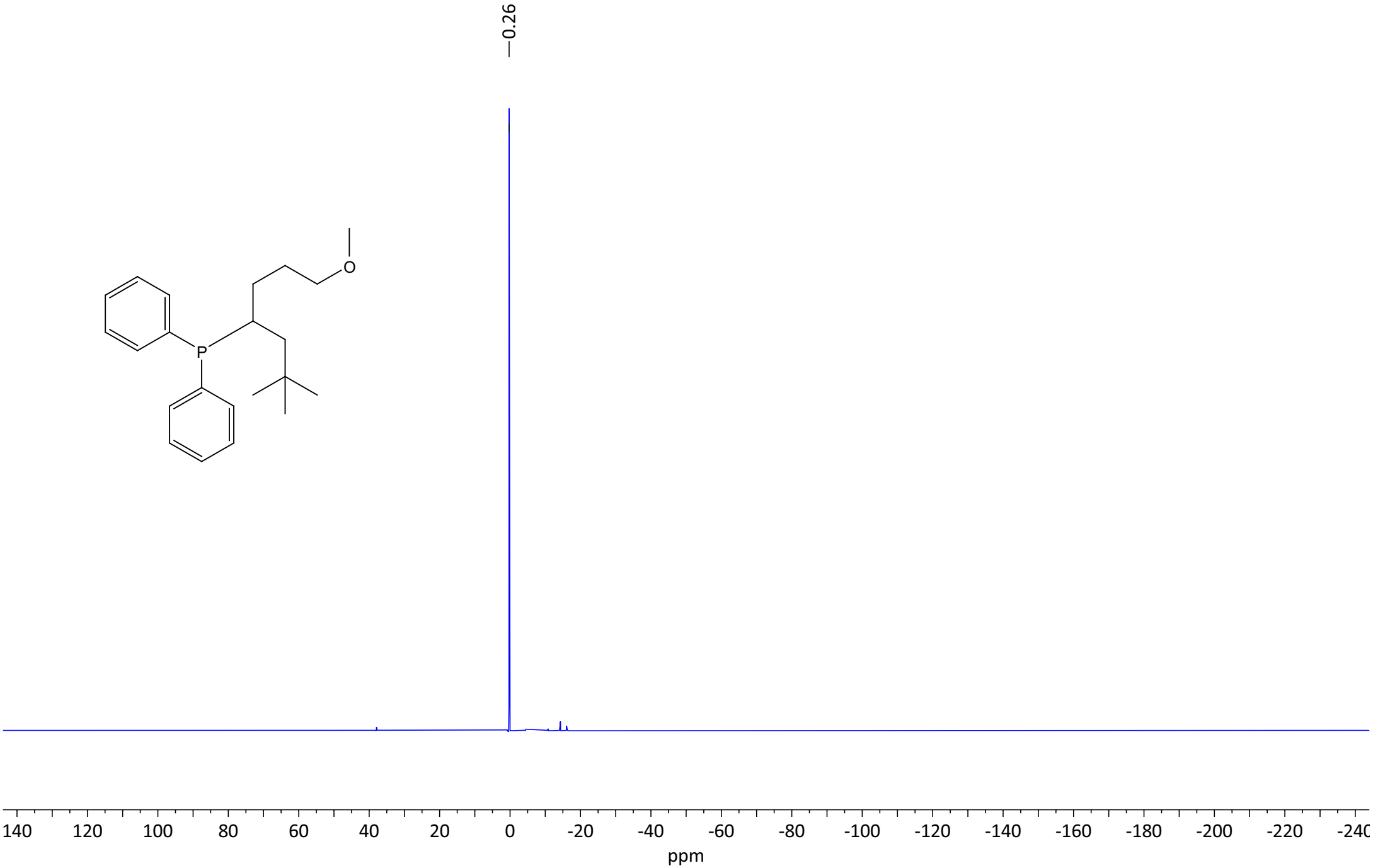
Compound **48**: ^{1}H NMR (500 MHz, $CDCl_3$)



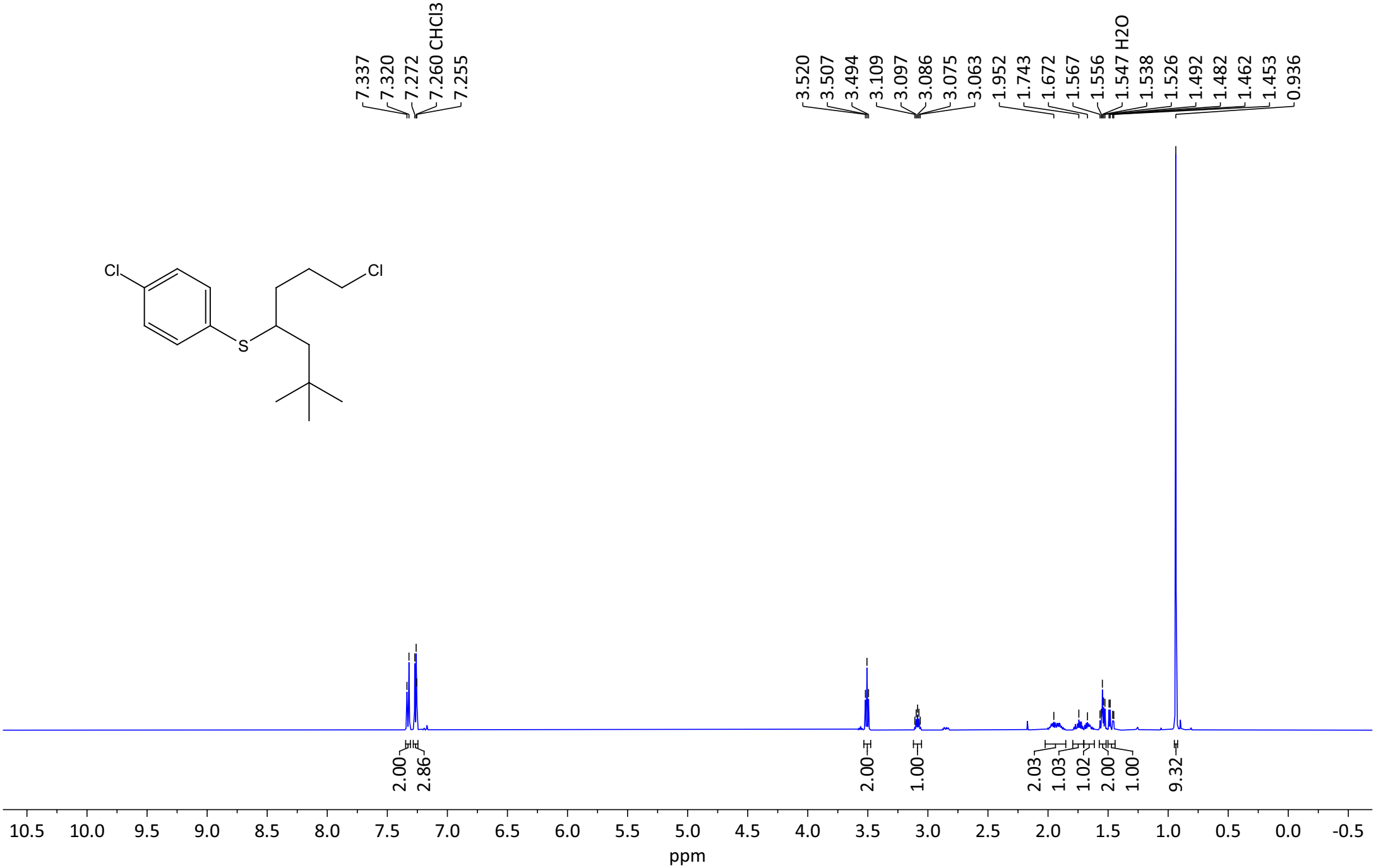
Compound **48**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



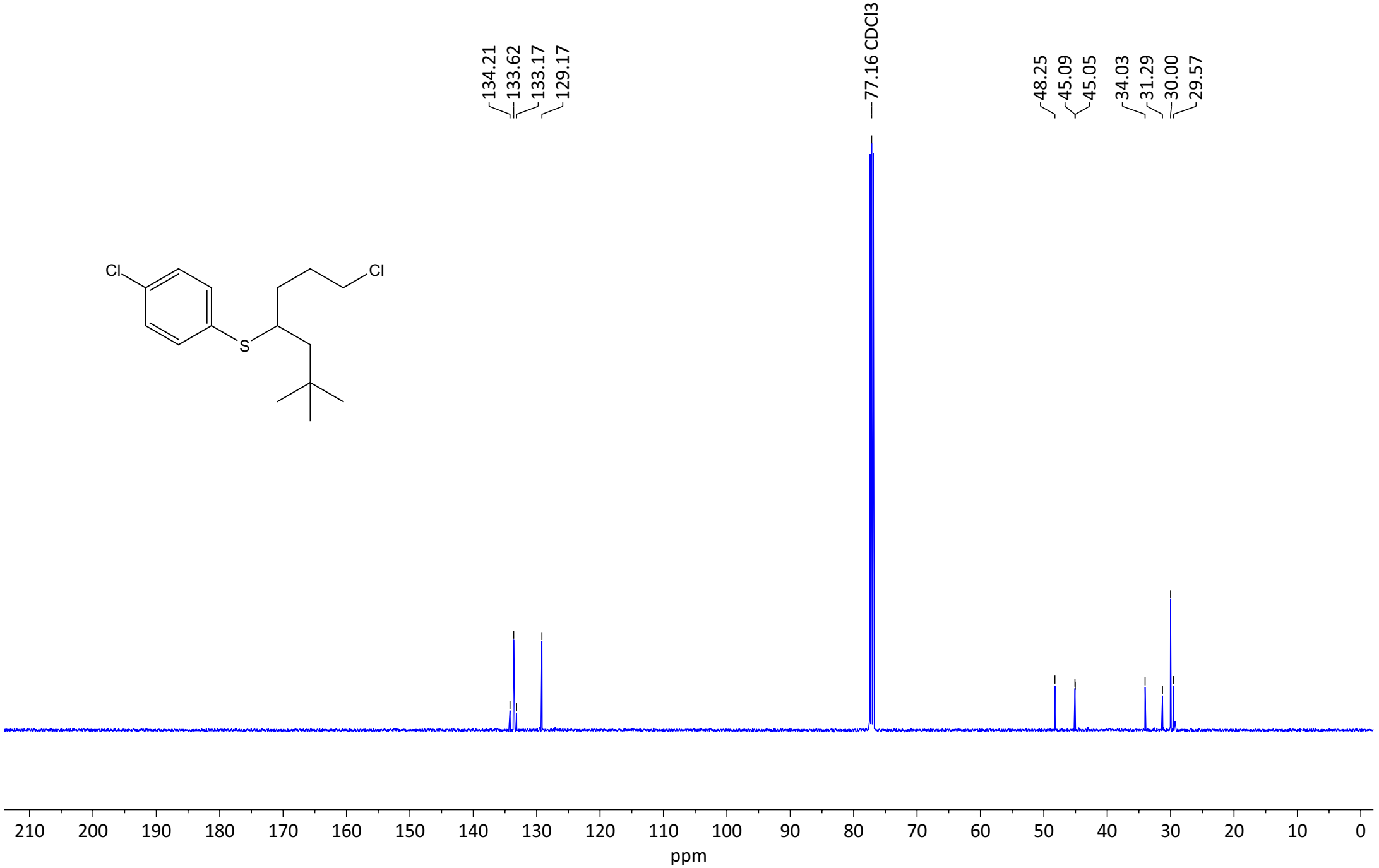
Compound **48**: ^{31}P NMR (202 MHz, $CDCl_3$)



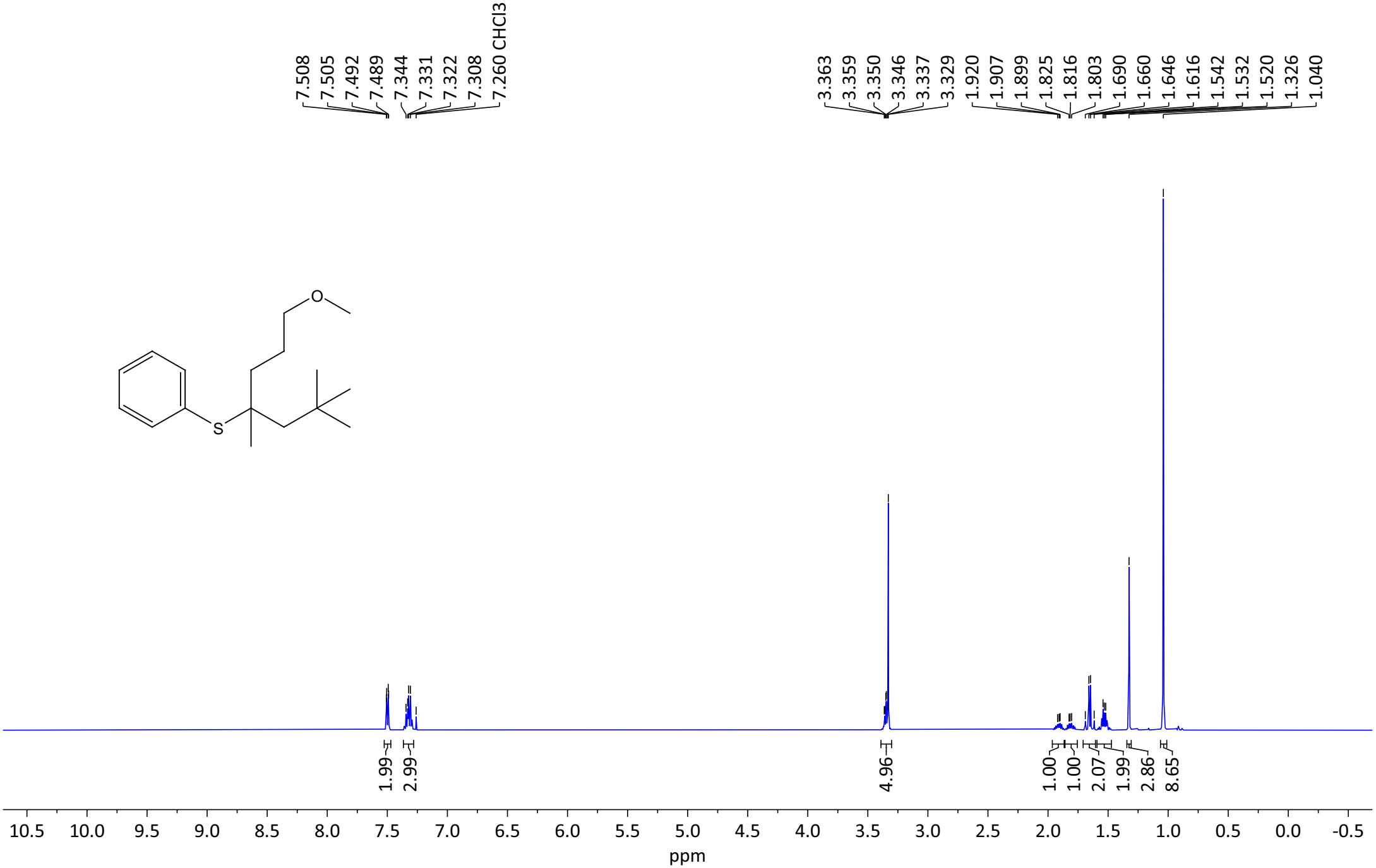
Compound **49** (impure): ^{1}H NMR (500 MHz, $CDCl_3$)



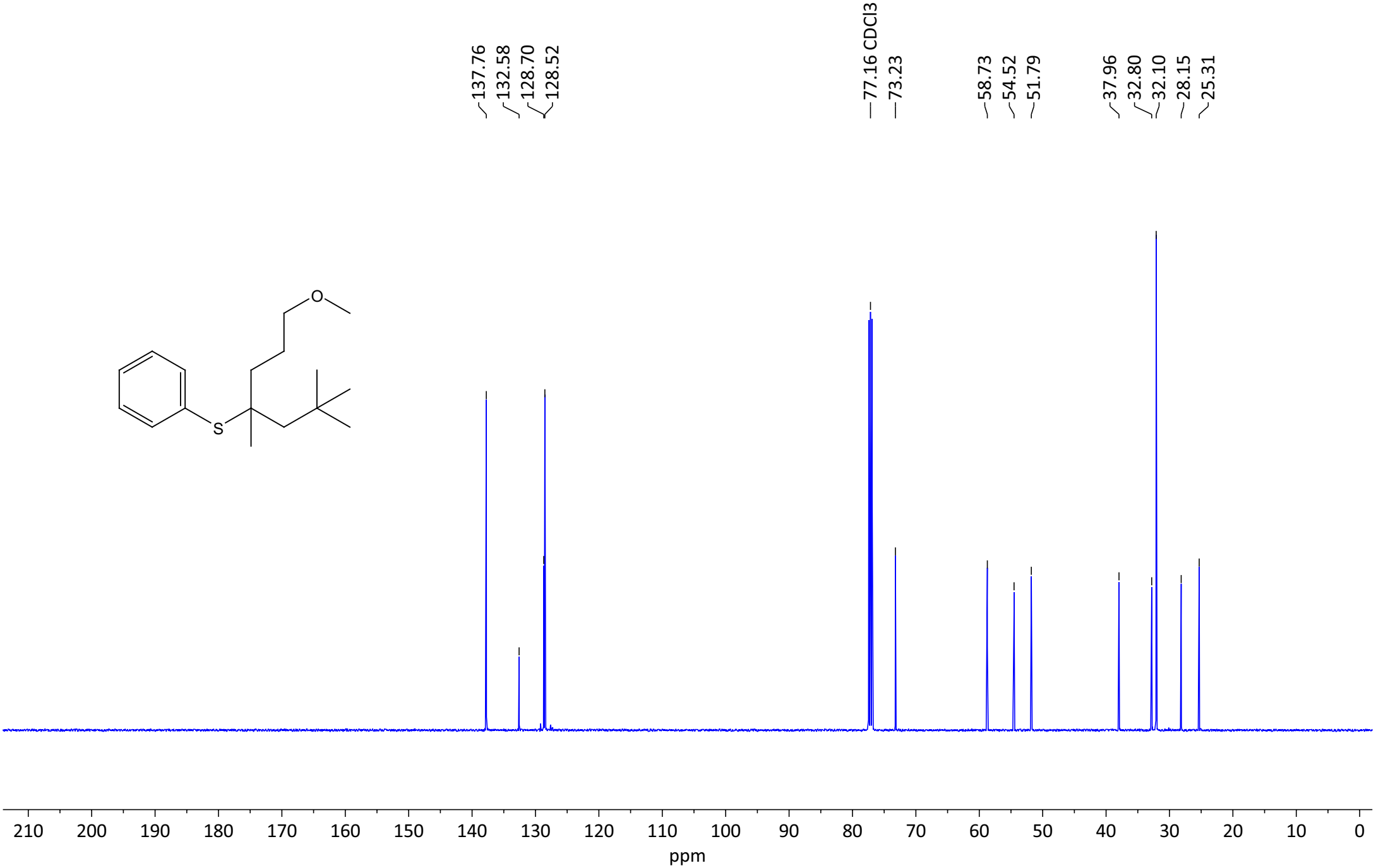
Compound **49** (impure): $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



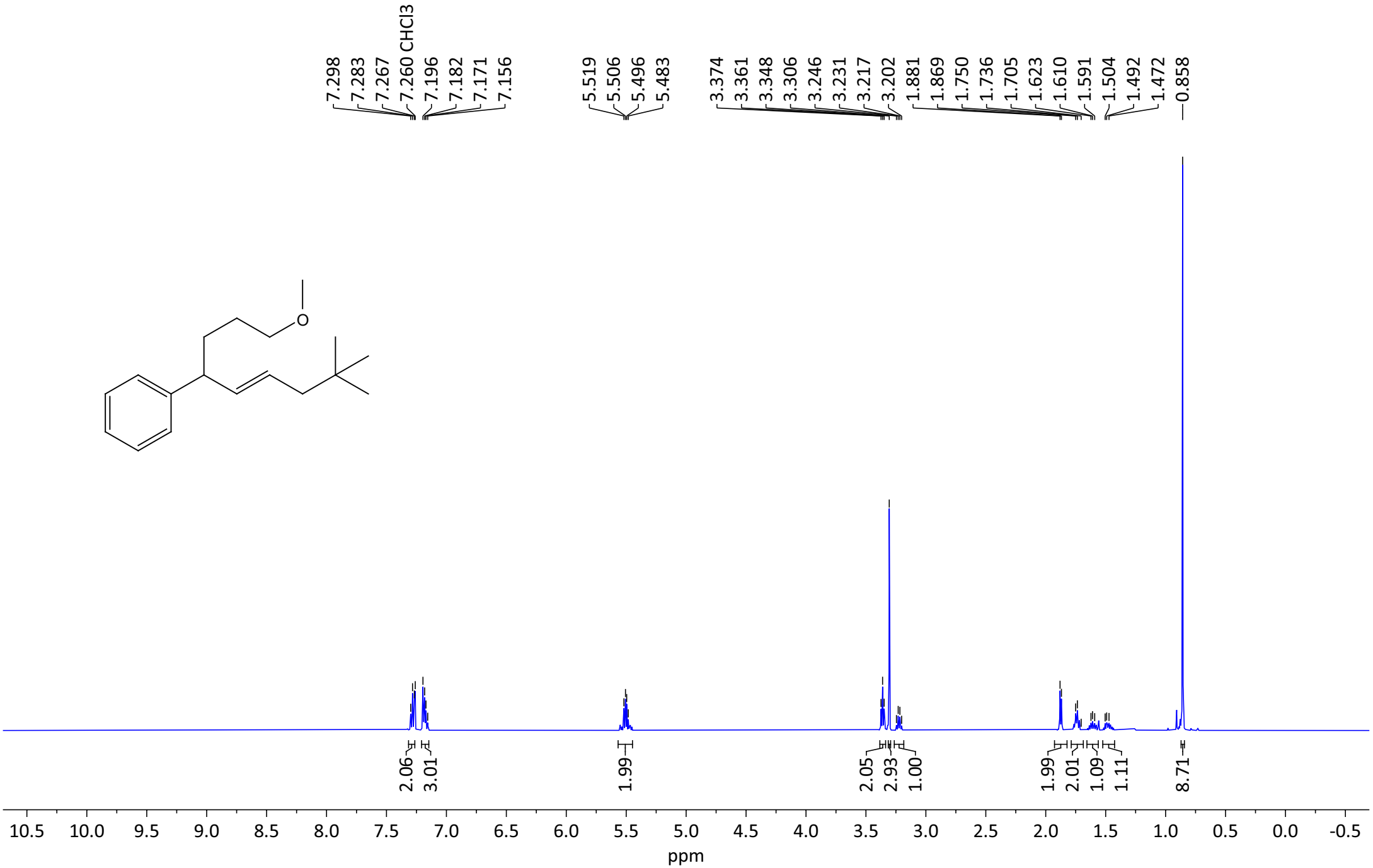
Compound **50**: ^{1}H NMR (500 MHz, $CDCl_3$)



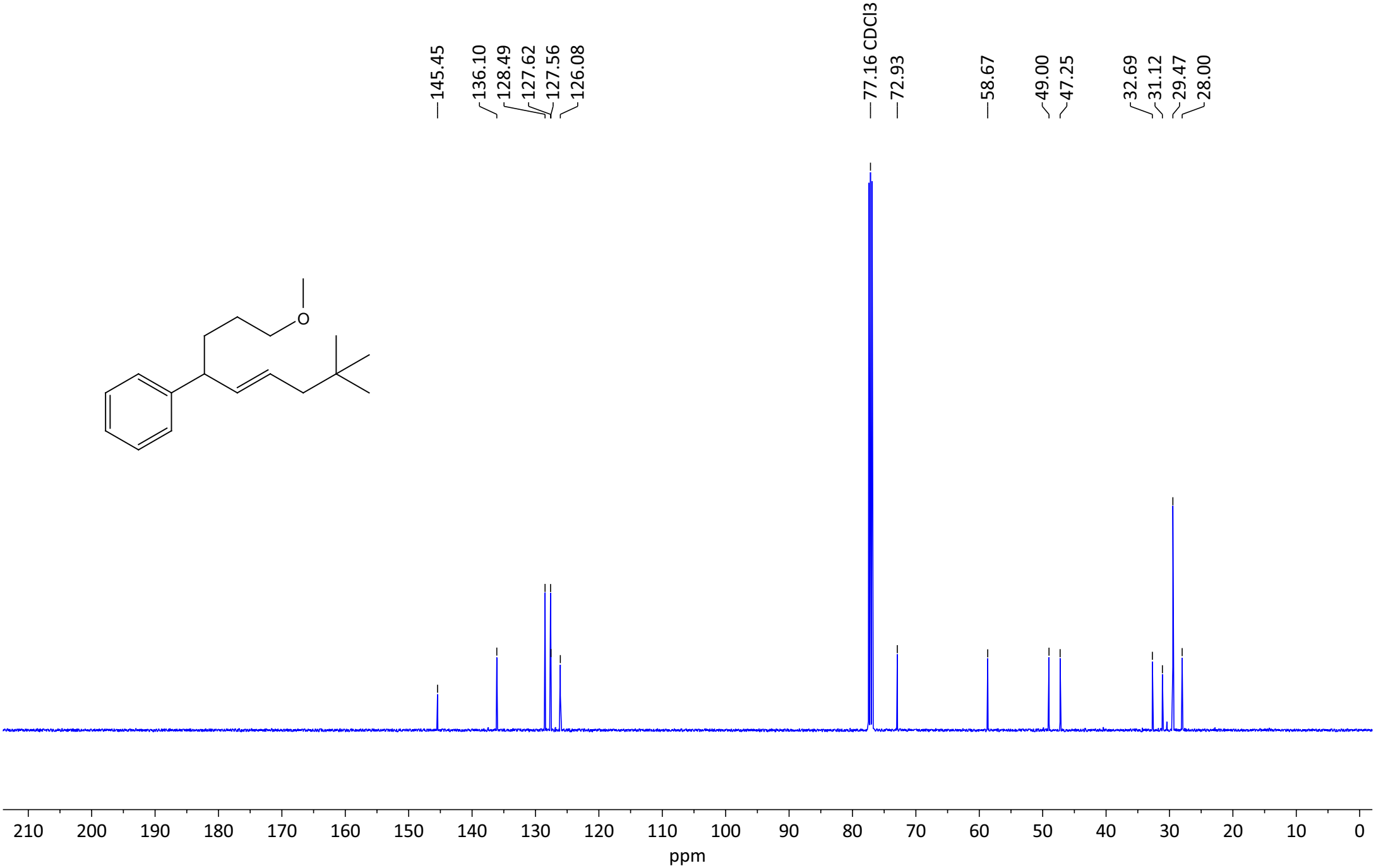
Compound **50**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



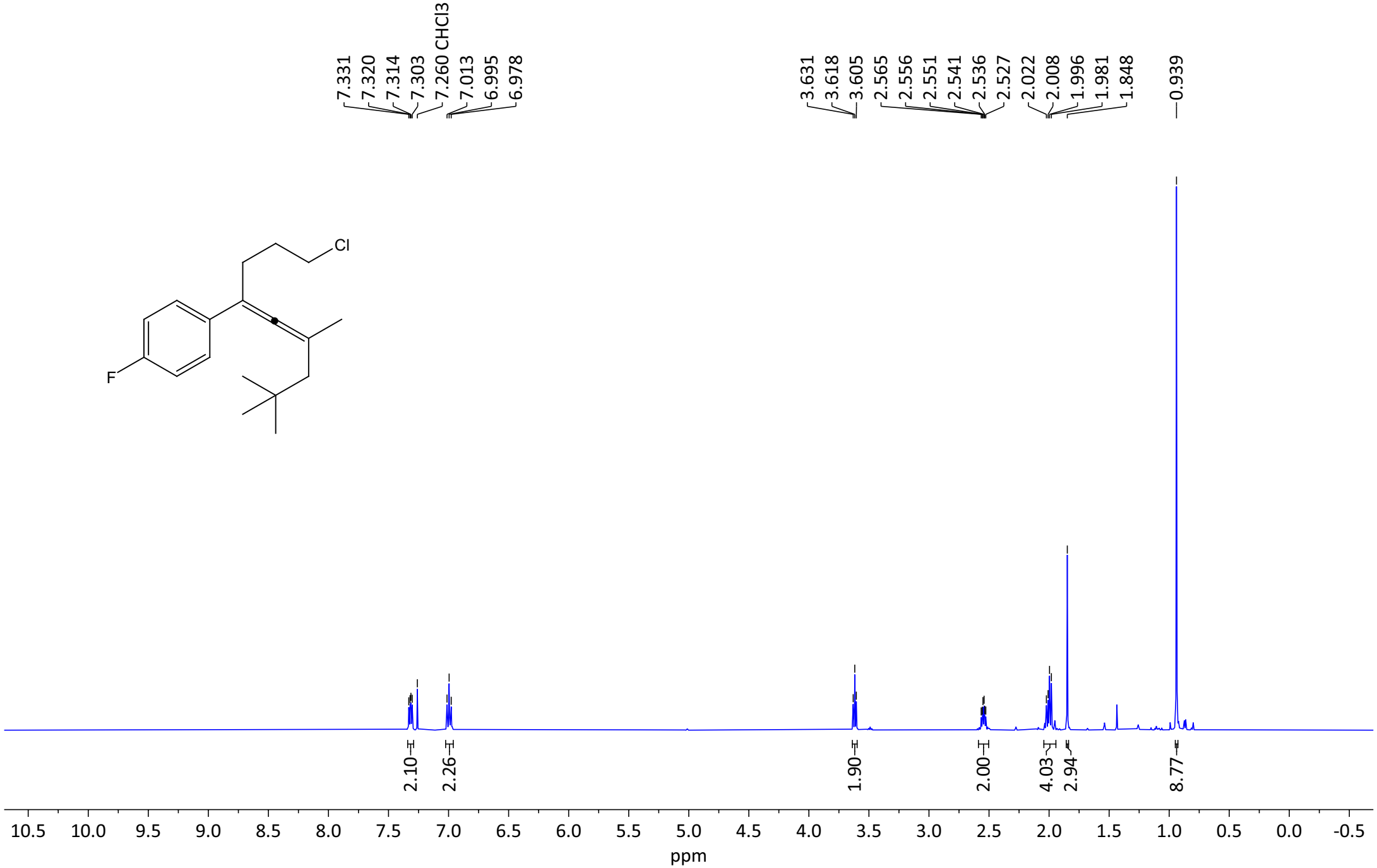
Compound **52**: ^{1}H NMR (500 MHz, $CDCl_3$)



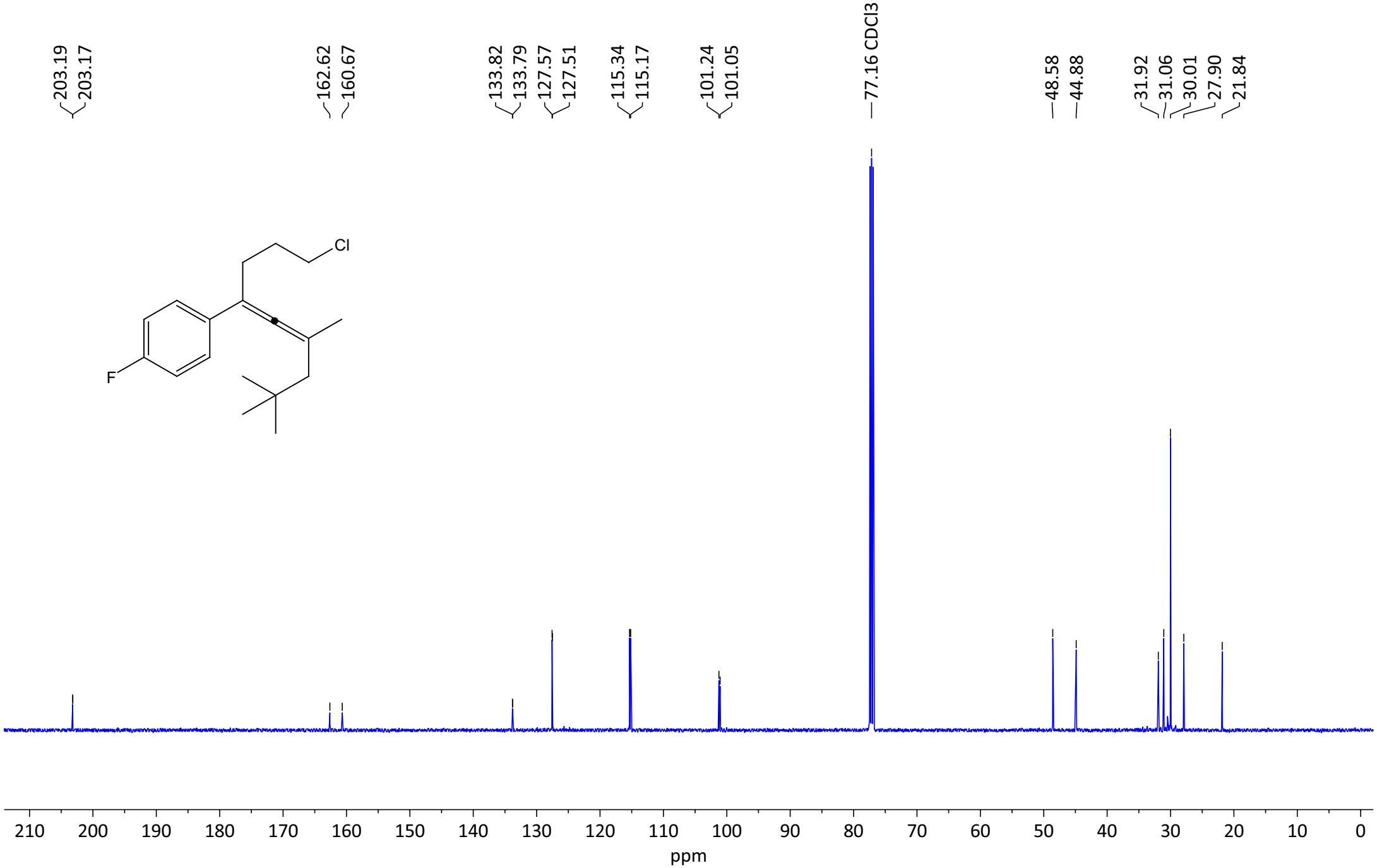
Compound **52**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



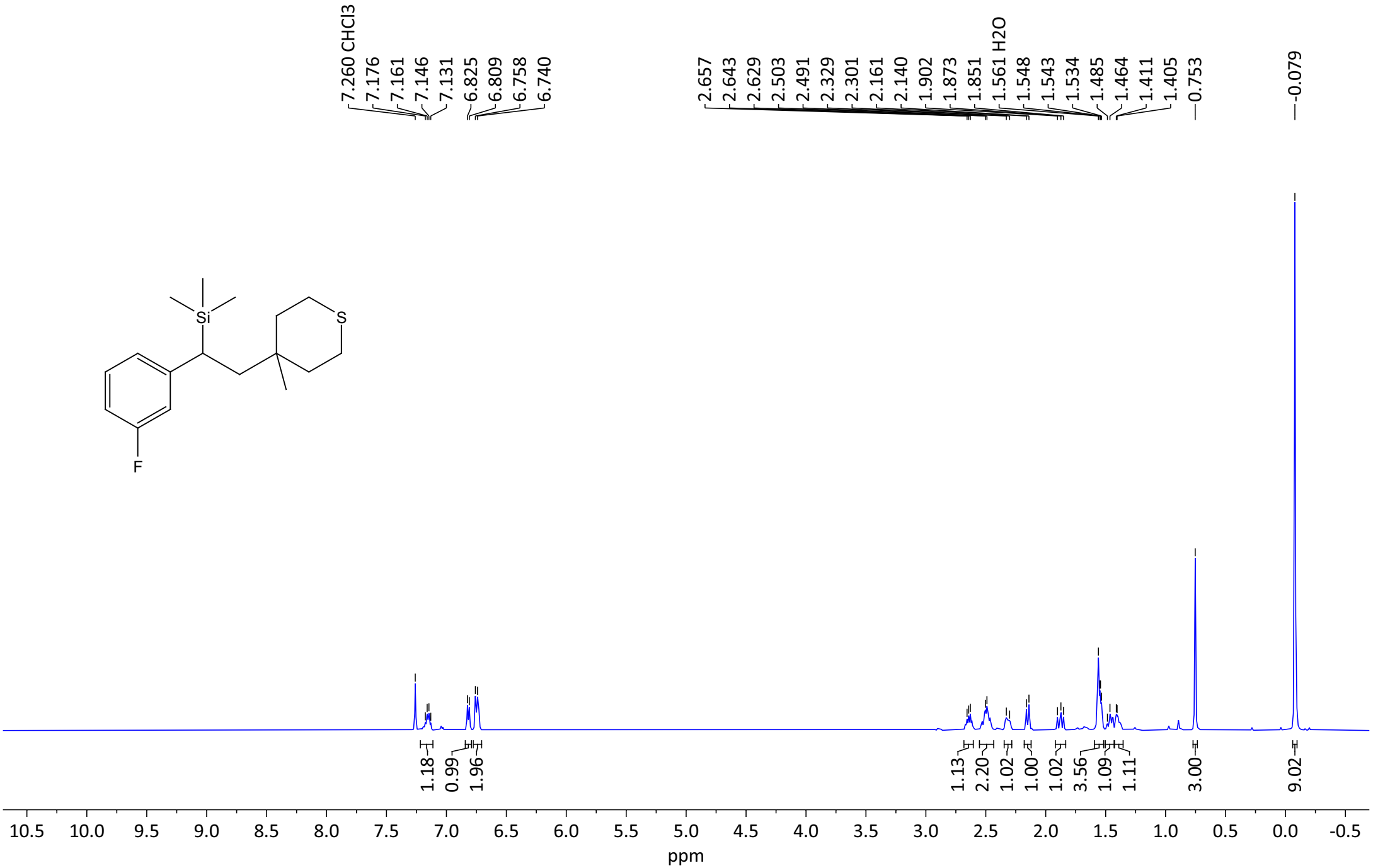
Compound **54** (impure): ^{1}H NMR (500 MHz, $CDCl_3$)



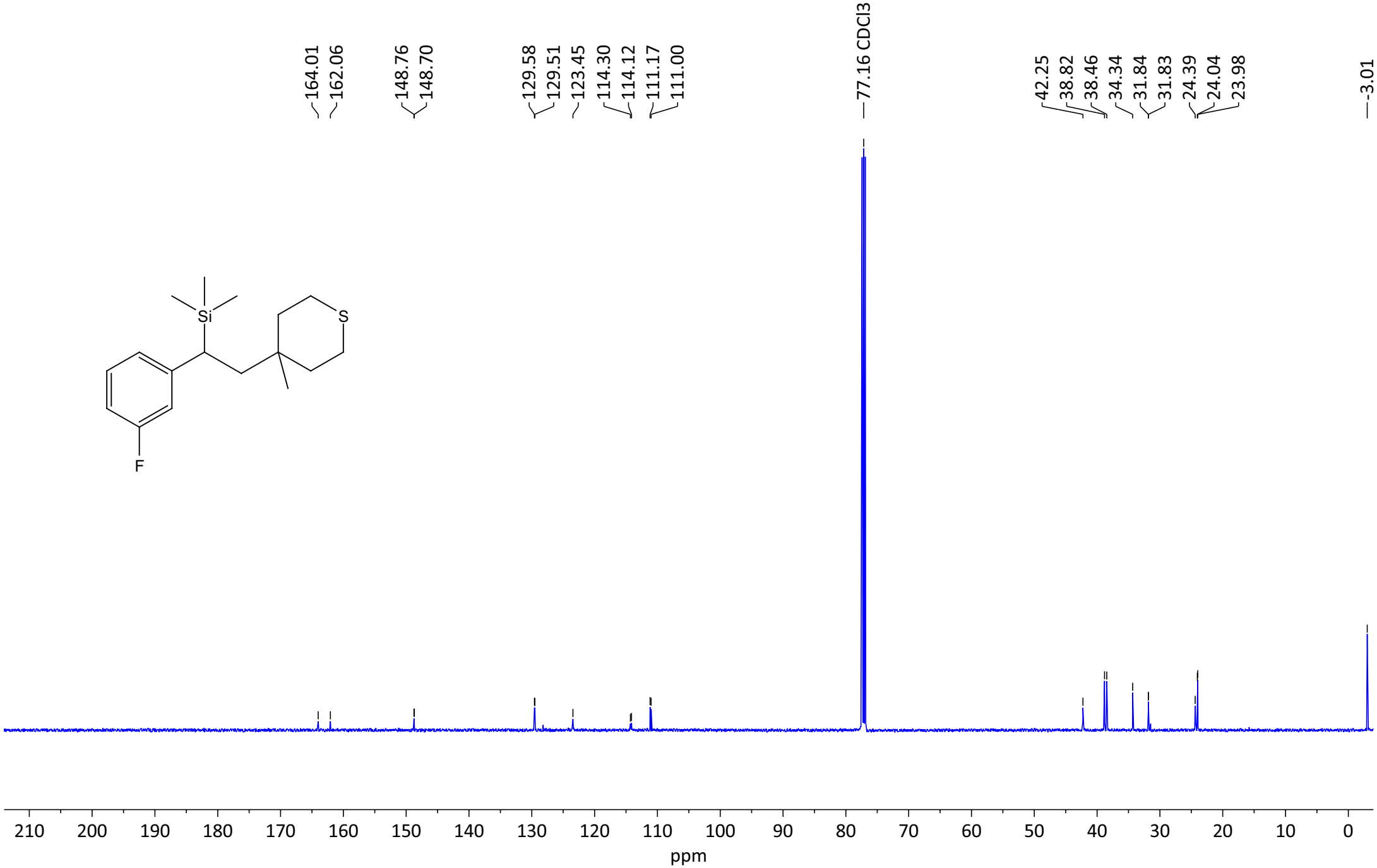
Compound **54** (impure): $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



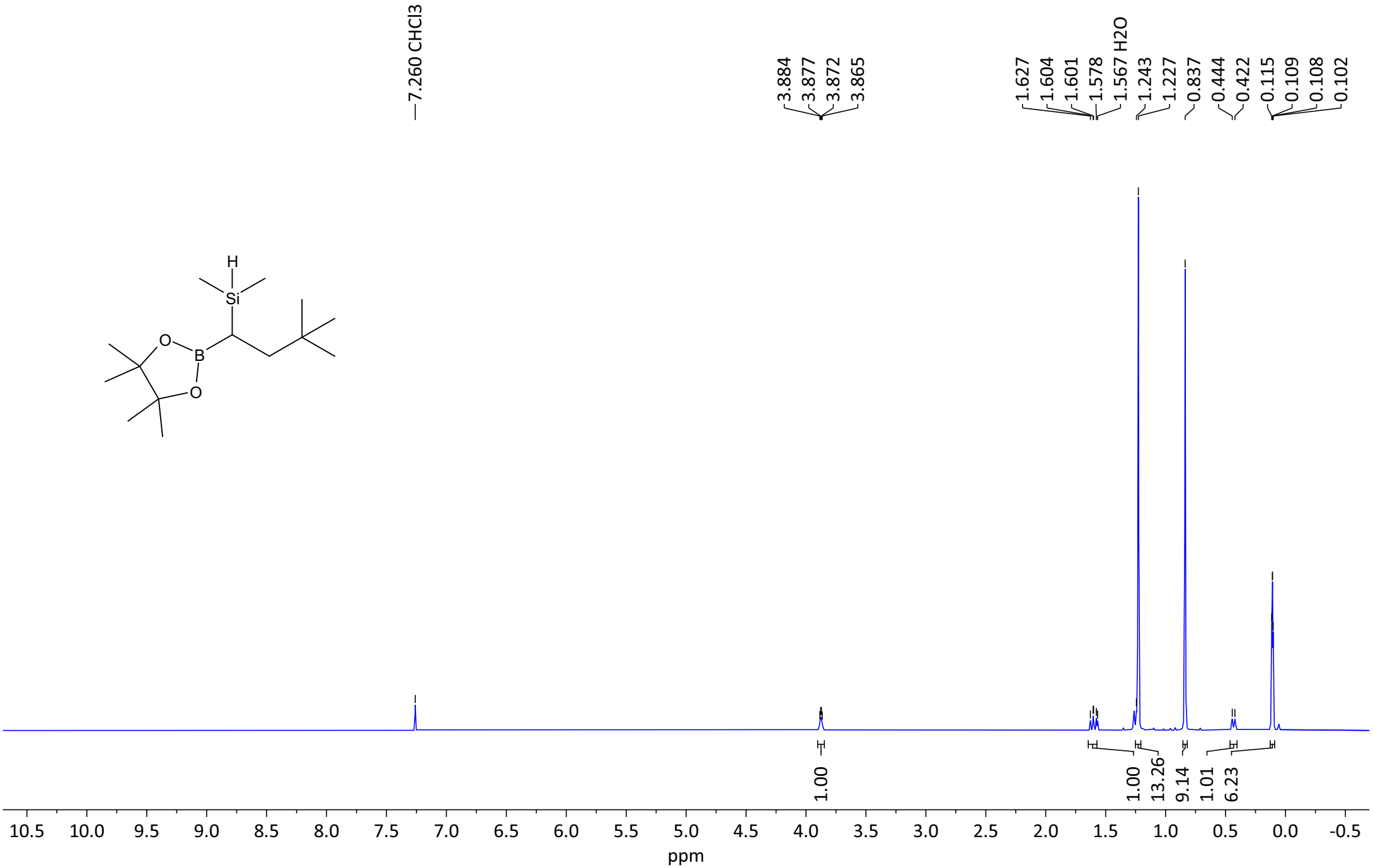
Compound **55** (impure): ^{1}H NMR (500 MHz, $CDCl_3$)



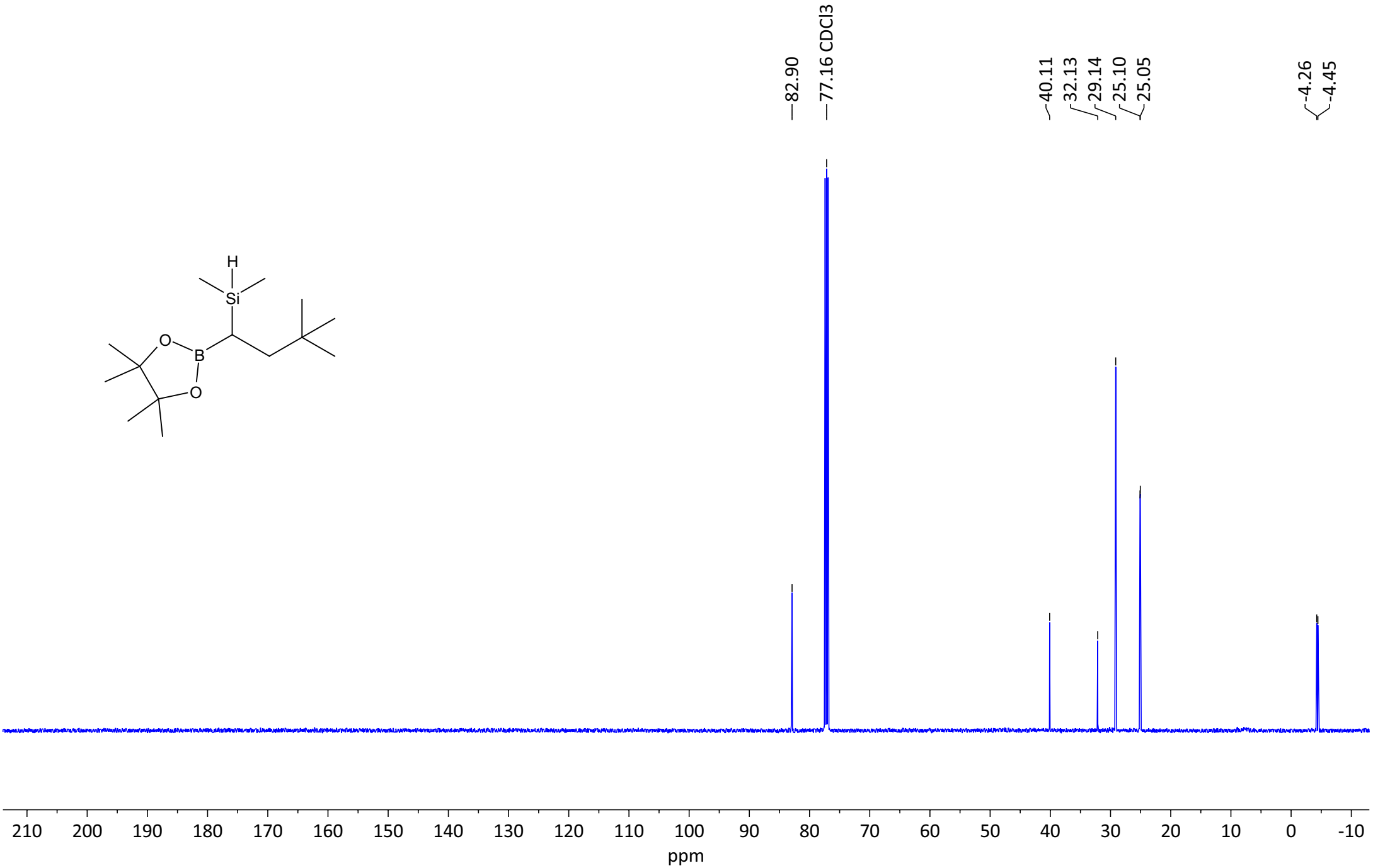
Compound **55** (impure): $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



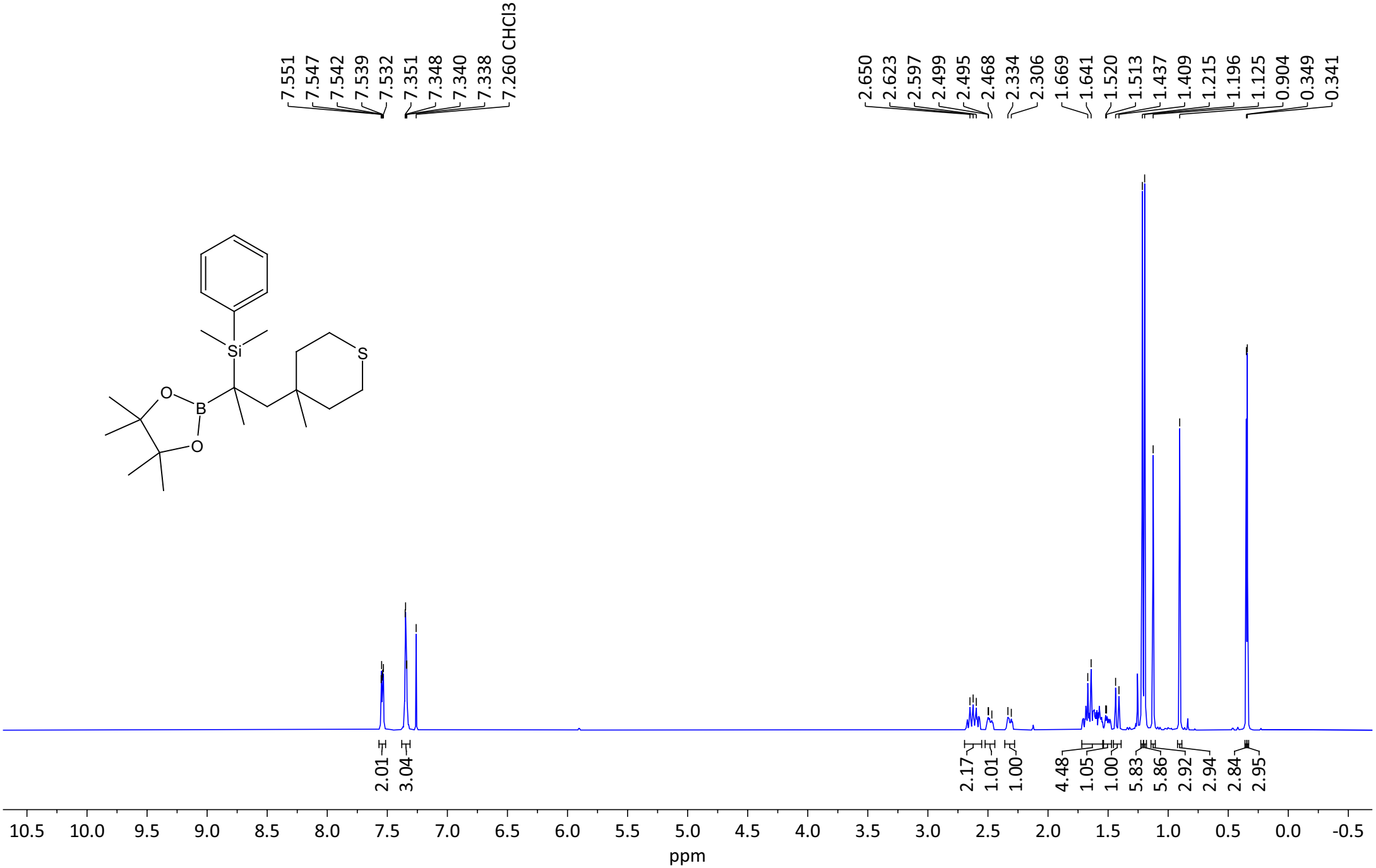
Compound **56**: ^{1}H NMR (500 MHz, $CDCl_3$)



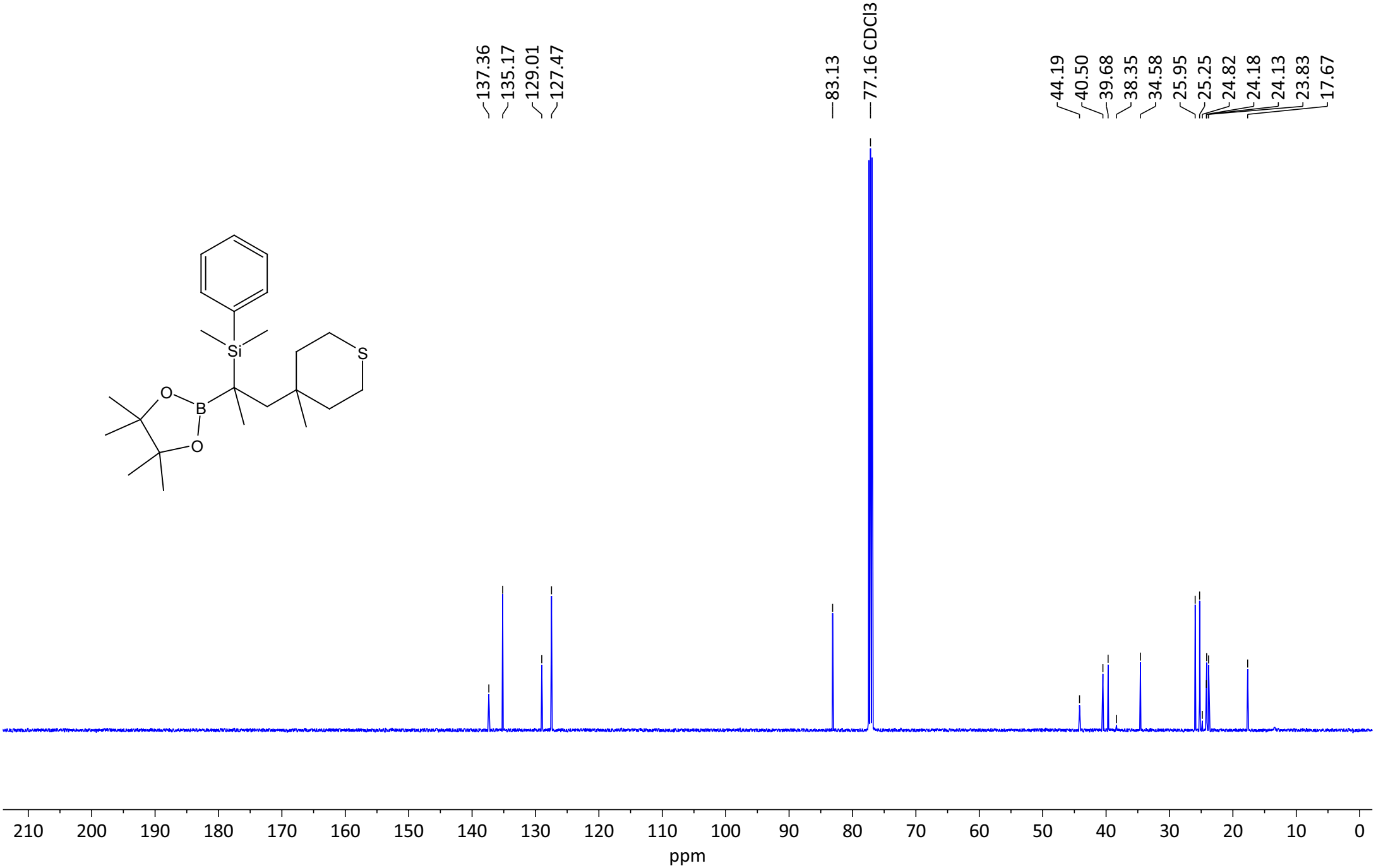
Compound **56**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



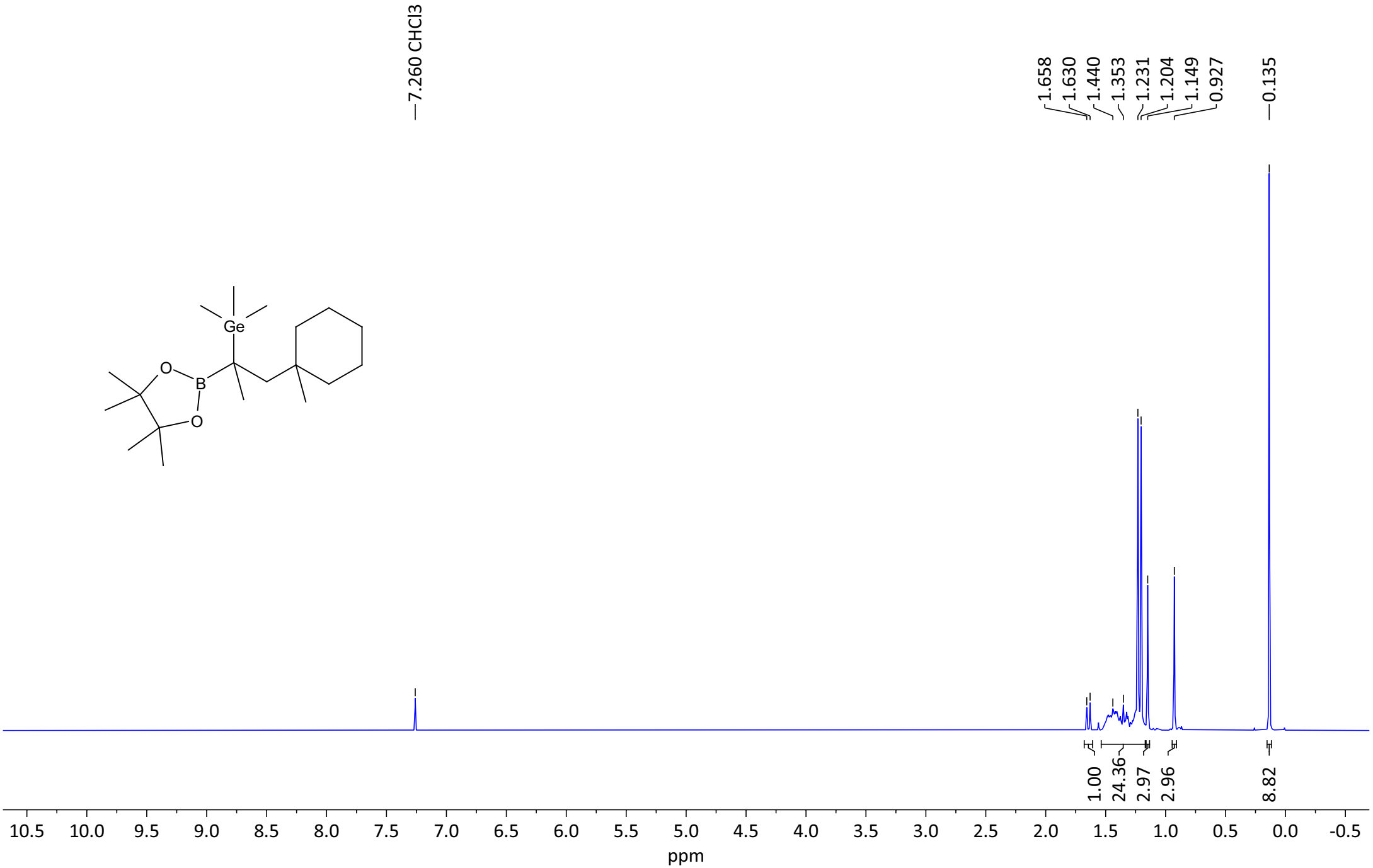
Compound **57**: ^{1}H NMR (500 MHz, $CDCl_3$)



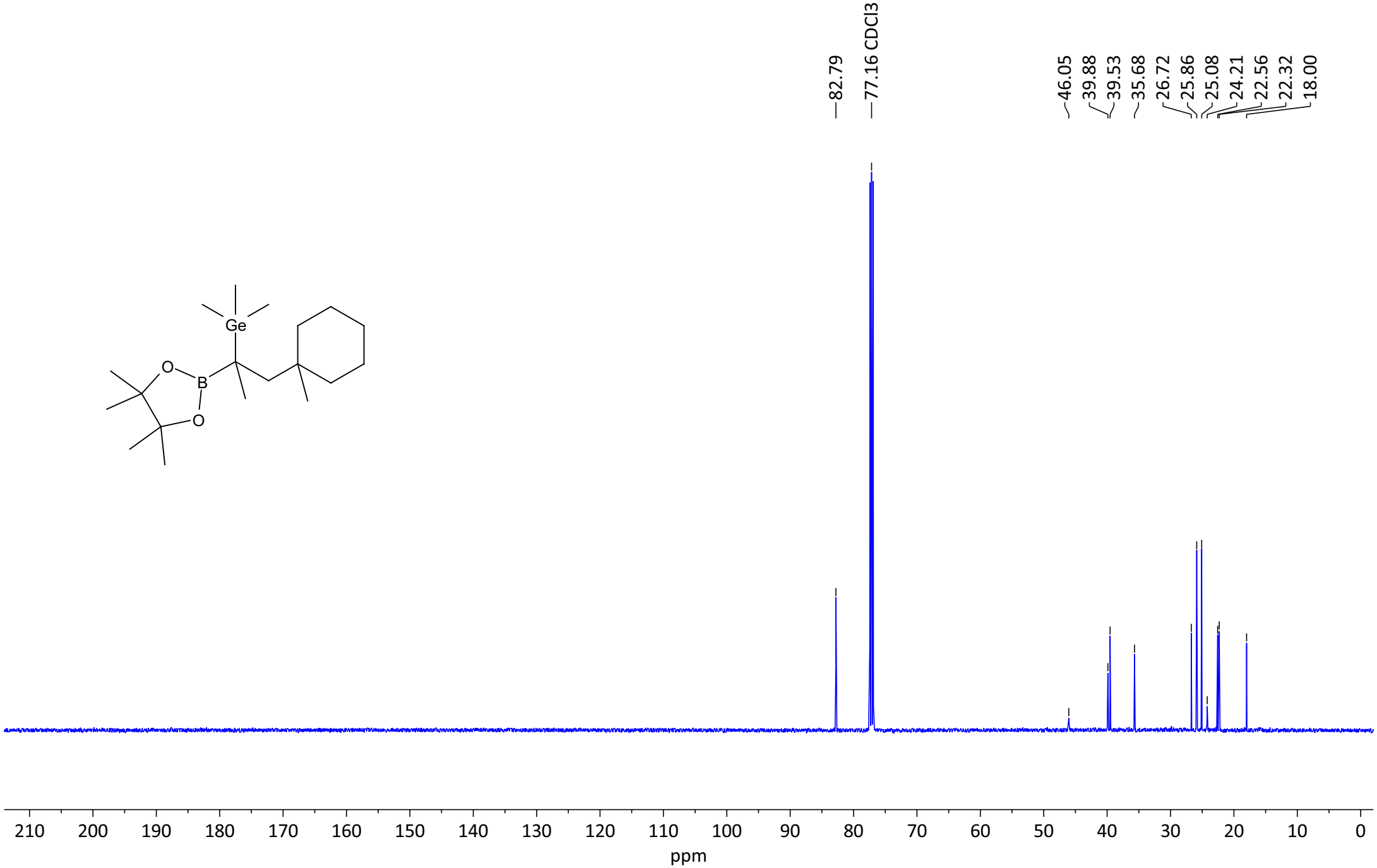
Compound **57**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



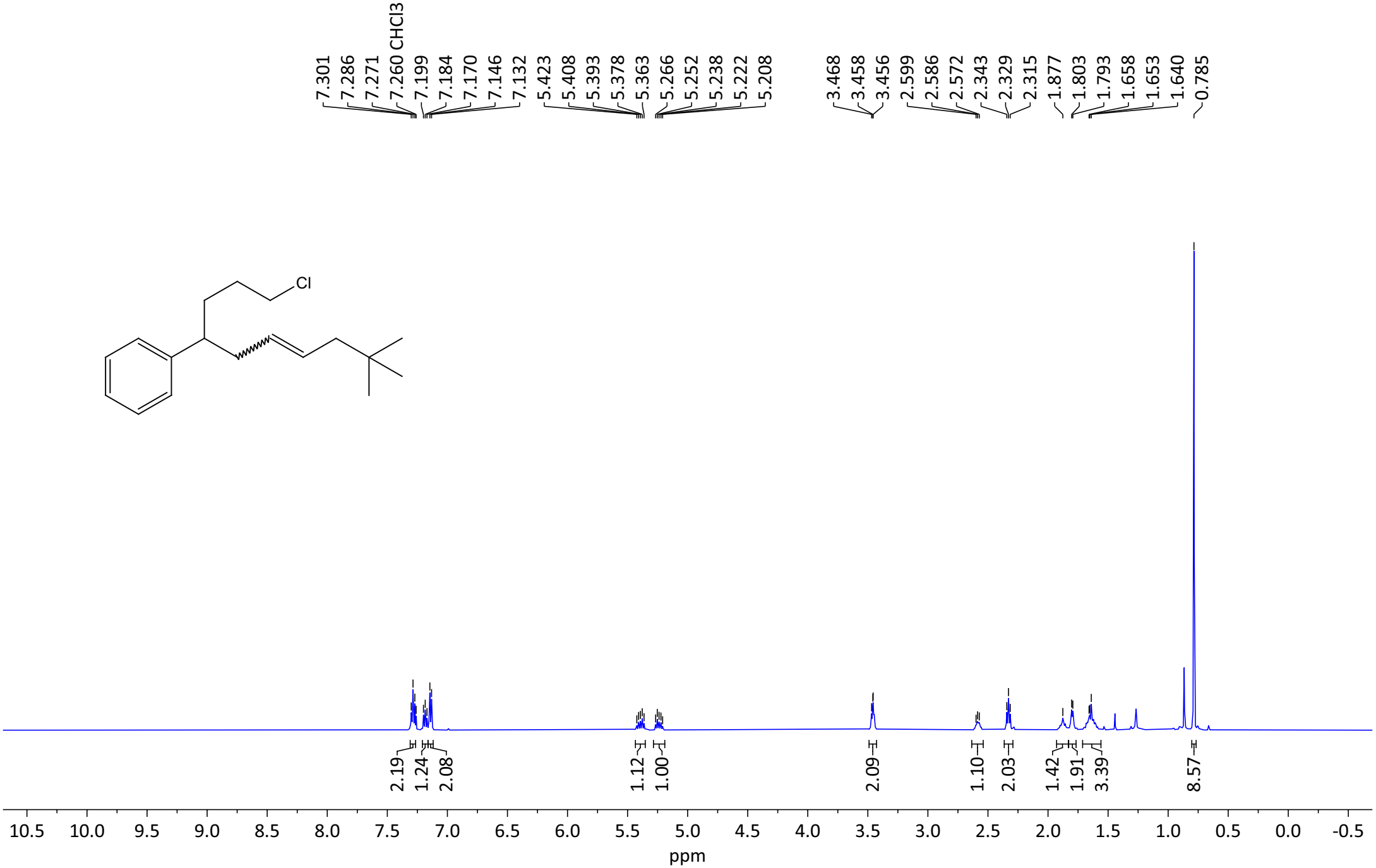
Compound **58**: ^{1}H NMR (500 MHz, $CDCl_3$)



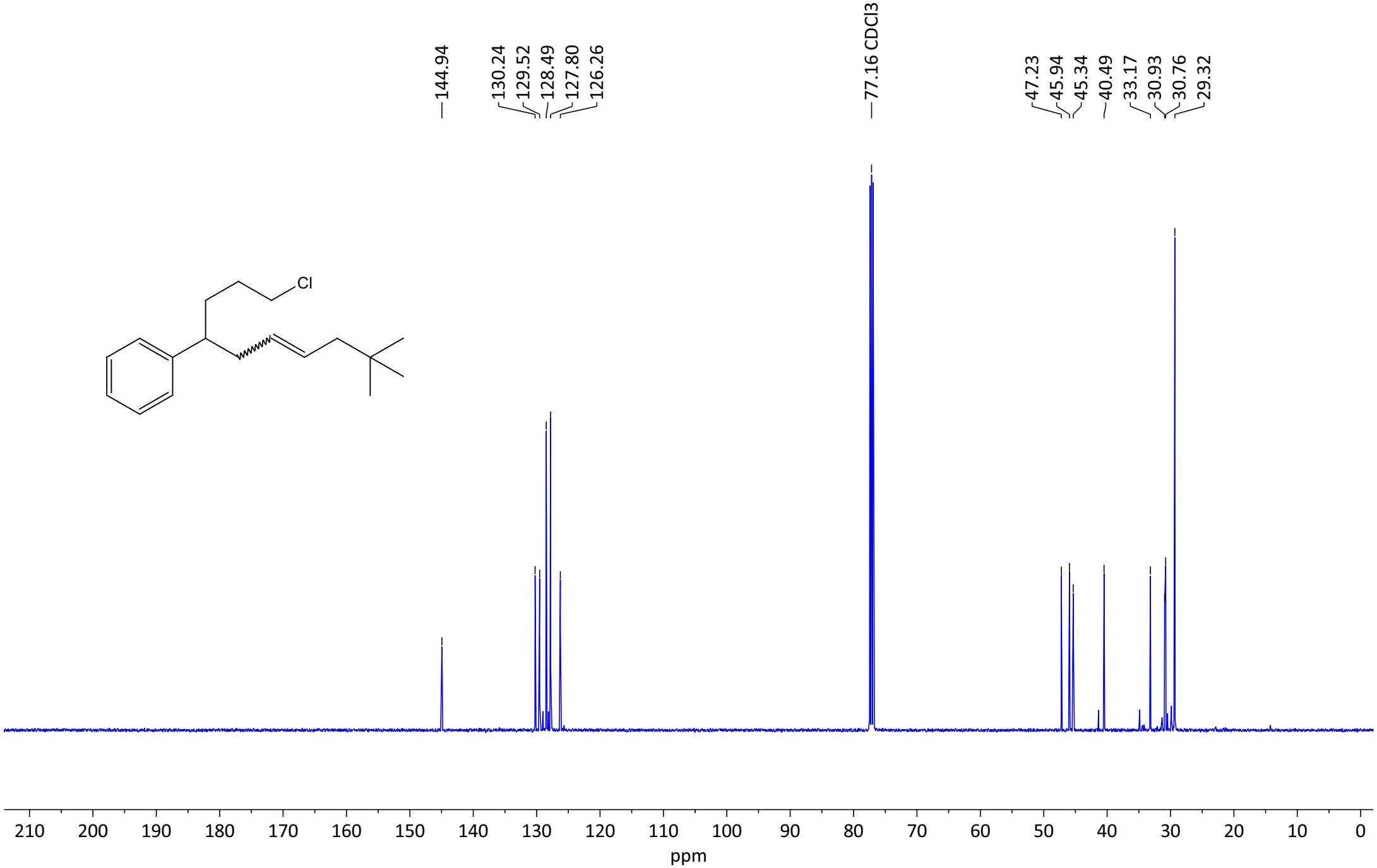
Compound **58**: $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



Compound **60** (7:1 *E*/*Z* mixture): ^{1}H NMR (500 MHz, $CDCl_3$)



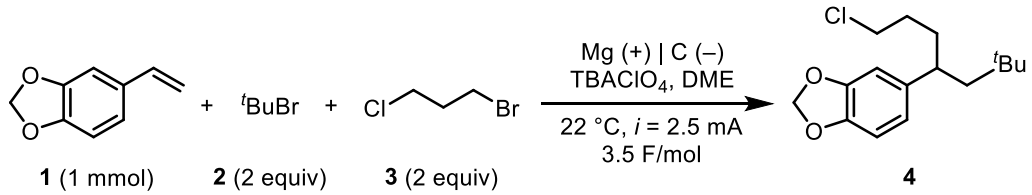
Compound **60** (7:1 *E*/*Z* mixture): $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



S10. Reaction Reproduction Report

Reproduced by Jinjian Liu

Reaction 1:

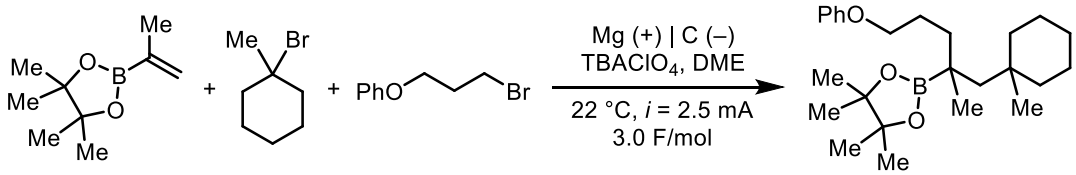


1 (1 mmol) **2** (2 equiv) **3** (2 equiv) **4**

Result: 75% ^{1}H NMR yield.

Reported result: 80% ^{1}H NMR yield, 79% isolated yield.

Reaction 2:



5 (1 mmol) **S24** (2 equiv) **S35** (1 equiv) **37**

Result: 65% isolated yield.

Reported result: 69% isolated yield.

S11. References

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