Supporting Information

Decarboxylative ring-opening of 2-oxazolidinones: a facile and modular synthesis of β-chalcogen amines

Fábio Z. Galetto,[*a] Cleiton da Silva,[a] Ricardo I. M. Beche,[a] Renata A. Balaguez,[a] Marcelo S. Franco,[a] Francisco F. de Assis,[a] Tiago E. A. Frizon[b] and Xiao Su[c]

[a]Departament of Chemistry, Federal University of Santa Catarina, Florianópolis-SC, 88040-900, Brazil.
[b]Department of Energy and Sustainability, Federal University of Santa Catarina, Araranguá-SC, Brazil.
[c]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, 61801, USA.

**e-mail: galetto.f.z@ufsc.br ; Phone:+554837213649;*

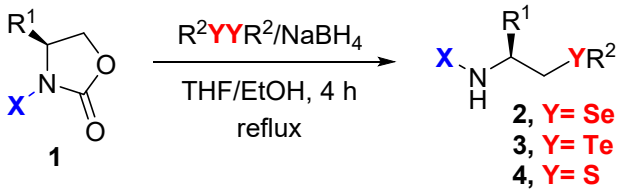
List of contents

Materials and methods

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 400 MHz on a Bruker AC-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Abbreviations to denote the multiplicity of a particular signal are: s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), ddd (doble doble doublet), ddt (doble doble triplet), t (triplet), tt (triplet of triplet) and m (multiplet). Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz on a Bruker AC-400 NMR spectrometer. Spectra were recorded in $CDCl_3$. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. High resolution mass spectra were recorded on a Bruker microTOF-Q II APPI/APCI mass spectrometer equipped with an automatic syringe pump for sample injection. HPLC analyzes were carried out on an Agilent Technologies 1200 Series (Waldbronn, Germany) cromatograph equipped with an online degasser, quaternary pump, independent temperature-controlled column system, autosampler and diode array detector. The analyzes were conducted under the following conditions: column: CHIRALPAK IG-3 (150 X 4.6 mm d.i., 3 um); eluent: 90:10 hexane:ethanol; flow rate: 1.0 $mL.min^{-1}$; detection: 258 nm. Optical rotation analyzes were performed on a Schimidt-Haensch Polartronic E polarimeter equipped with a sodium lamp (589 nm) using a 0.95 dm long cell. Melting points of synthesized compounds were determined in a Microquimica MQRPF-301 digital model equipment with heating plate and are uncorrected. Column chromatography was performed using 230-400 mesh silica gel. Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained

with iodine vapor and acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. Unless otherwise stated, all reagents and solvents were obtained from commercial sources and used without any further purification. The following starting materials were prepared according to procedures described in the literature: β-aminoalcohols,[1] 2-oxazolidinones,[2] *N*-alkyl-2-oxazolidinones,[3] *N*-phenyl-2-oxazolidinones,[4] diorganoyl disulfides,[5] diorganoyl diselenides[6,7] and diorganoyl ditellurides.[8] Air sensitive reactions were conducted in glassware equipped with tightly fitted rubber septa and under a positive atmosphere of nitrogen. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a Variac controller. The yields are based on isolated compounds after purification.

General procedure for the synthesis of β-chalcogenoamines.



Milligram-scale reactions: In a two-necked flask equipped with reflux condenser, the appropriate 2-oxazolidinone (1.0 mmol) was diluted in THF (5 mL) under nitrogen atmosphere. In a second flask, the appropriate dichalcogenide (0.60 mmol) and sodium borohydride (3.0 mmol, 0.114 g) were mixture in THF (2 mL), and then ethanol (95%, 0.6 mL) was added slowly. The content of this second flask was rapidly transferred to the flask containing the 2-oxazolidinone, and the mixture was stirred for 4 h under reflux. After the system returns to room temperature, the reaction was quenched with aqueous saturated solution of potassium carbonate (20 mL) and extracted with dichloromethane (4 x 10 mL). The organic layers were combined,

treated with anhydrous sodium sulfate and the solvent was removed in the rotary evaporator. The crude products were purified by silica-gel chromatography using a mixtures of hexane/ethyl acetate as eluent.

Gram-scale reactions: In a two-necked flask equipped with reflux condenser, 2-oxazolidinone **1b** (30 mmol, 2.612 g) was diluted in THF (40 mL) under nitrogen atmosphere. In a second flask, the appropriate dichalcogenide (18 mmol) and sodium borohydride (90 mmol, 3.420 g) were mixture in THF (16 mL), and then ethanol (95%, 4.8 mL) was added dropwise. The content of this second flask was rapidly transferred to the flask containing the 2-oxazolidinone, and the mixture was stirred under reflux for 4 h. The volume of the reaction mixture was reduced by half, then transferred to a separatory funnel and aqueous 1.0 M HCl solution (50 mL) was added. The resulting mixture was washed with hexane (4 x 40 mL) and then the aqueous phase was basified to pH 12-13 with aqueous 2.0M NaOH solution and extracted with dichloromethane (4 x 40 mL). The organic layers were combined, treated with anhydrous sodium sulfate and the solvent was removed in the rotary evaporator.

Characterization data of the synthesized compounds

(S)-1-phenyl-3-(phenylselanyl)propan-2-amine (2a): Yield: 0.253 g (87%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.32 – 7.19 (m, 6H), 7.18 – 7.11 (m, 2H), 3.22 – 3.08 (m, 2H), 2.88 – 2.78 (m, 2H), 2.63 (dd, *J* = 13.3, 7.9 Hz, 1H), 1.52 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 132.7, 130.1 129.3, 129.2, 128.6, 127.0, 126.5, 52.5, 44.0, 36.6. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NSe$, 292.0599; found, 292.0599. $[\alpha]_D^{20}$= +35.6 (c= 0.013, CH_2Cl_2).

2-(phenylselanyl)ethanamine (2b): Yield: 0.143 g (71%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.28 – 7.22 (m, 3H), 3.00 – 2.96 (m, 2H), 2.93 – 2.90 (m, 2H), 1.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 129.5, 129.1, 127.1, 41.7, 32.6. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_8H_{12}NSe$, 202.0130; found, 202.0128.

(S)-3-methyl-1-(phenylselanyl)butan-2-amine (2c): Yield: 0.107 g (44%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 2H), 7.29 – 7.21 (m, 3H), 3.15 (dd, *J* = 11.9, 3.2 Hz, 1H), 2.78 (dd, *J* = 11.9, 9.4 Hz, 1H), 2.73 – 2.66 (m, 1H), 1.76 – 1.64 (m, 1H), 1.46 (s, 2H), 0.91 (dd, *J* = 6.8, 5.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 130.3, 129.2, 127.0, 56.3, 35.3, 33.6, 19.4, 17.8. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{11}H_{18}NSe$, 244.0599; found, 244.0602. $[\alpha]_D^{20}$= +64.6 (c= 0.002, CH_2Cl_2).

(S)-4-methyl-1-(phenylselanyl)pentan-2-amine (2d): Yield: 0.177 g (69%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.29 – 7.20 (m, 3H), 3.09 (dd, *J* = 12.2, 3.9 Hz, 1H), 3.00 – 2.92 (m, 1H), 2.77 (dd, *J* = 12.2, 8.3 Hz, 1H), 1.74 – 1.62 (m, 1H), 1.51 (s, 2H), 1.32 – 1.26 (m, 2H), 0.86 (dd, *J* = 8.4, 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 130.3, 129.2, 127.0, 48.8, 47.1, 38.4, 25.2, 23.3, 22.2. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}NSe$, 258.0756; found, 258.0758. $[\alpha]_D^{20}$= +51.2 (c= 0.011, CH_2Cl_2).

(2S,3S)-3-methyl-1-(phenylselanyl)pentan-2-amine (2e): Yield: 0.116 g (45%); Colorless solid; mp 70.6 – 72.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H), 7.31 – 7.19 (m, 3H), 3.19 – 3.12 (m, 1H), 2.83 – 2.70 (m, 2H), 1.61 – 1.37 (m, 4H), 1.23 – 1.09 (m, 1H), 0.95 – 0.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 130.3, 129.2, 127.0, 55.1, 40.5, 34.9, 25.3, 15.1, 11.8. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}NSe$, 258.0755; found, 258.0757. $[\alpha]_D^{20}$= +23.9 (c= 0.005, CH_2Cl_2).

(S)-1-(1*H*-indol-3-yl)-3-(phenylselanyl)propan-2-amine (2f): Yield: 0.152 g (46%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.57 – 7.42 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.14 (m, 4H), 7.12 – 7.04 (m, 1H), 6.96 (d, *J* = 2.1 Hz, 1H), 3.38 – 3.27 (m, 1H), 3.17 (dd, *J* = 12.4, 4.4 Hz, 1H), 3.02 (dd, *J* = 14.1, 5.0 Hz, 1H), 2.83 (ddd, *J* = 28.5, 13.3, 7.9 Hz, 2H), 1.77 (s, 2H). Note: Ethyl acetate is still present in the ^{1}H NMR spectrum even after the sample has been under high vacuum for extended periods. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 132.7, 130.3, 129.2, 127.6, 127.0, 122.8, 122.1, 119.5, 119.0, 112.6, 111.3, 51.3, 36.7, 33.4. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2Se$, 331.0709; found, 331.0707. $[\alpha]_D^{20}$= +13.5 (c= 0.003, CH_2Cl_2).

(S)-1-phenyl-3-(*p*-tolylselanyl)propan-2-amine (2g): Yield: 0.232 g (76%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dt, *J* = 8.2, 1.8 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 – 7.12 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 3.21 – 3.13 (m, 1H), 3.08 (dd, *J* = 12.4, 4.2 Hz, 1H), 2.88 – 2.75 (m, 2H), 2.62 (dd, *J* = 13.4, 8.0 Hz, 1H), 2.32 (s, 3H), 1.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.2, 133.3, 130.1, 129.4, 128.6, 126.5, 126.2, 52.5, 44.0, 37.1, 21.2. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NSe$, 306.0756; found, 306.0756. $[\alpha]_D^{20}$= +40.9 (c= 0.013, CH_2Cl_2).

(S)-1-((4-methoxyphenyl)selanyl)-3-phenylpropan-2-amine (2h): Yield: 0.209 g (65%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 2H), 7.31 – 7.12 (m, 5H), 6.83 – 6.78 (m, 2H), 3.79 (s, 3H), 3.19 – 3.08 (m, 1H), 3.02 (dd, *J* = 12.3, 4.3 Hz, 1H), 2.84 (dd, *J* = 13.4, 5.2 Hz, 1H), 2.75 (dd, *J* = 12.3, 8.2 Hz, 1H), 2.60 (dd, *J* = 13.3, 8.1 Hz, 1H), 1.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 139.0, 135.7, 129.4, 128.6, 126.5, 119.8, 115.0, 55.4, 52.4, 44.0, 37.9. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NOSe$, 322.0705; found, 322.0704. $[\alpha]_D^{20}$= +25.8 (c= 0.007, CH_2Cl_2).

(S)-1-((4-chlorophenyl)selanyl)-3-phenylpropan-2-amine (2i): Yield: 0.250 g (77%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.10 (m, 9H), 3.22 – 3.04 (m, 2H), 2.88 – 2.75 (m, 2H), 2.64 (dd, *J* = 13.4, 7.8 Hz, 1H), 1.49 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 134.1, 133.3, 129.4, 129.3, 128.7, 128.4, 126.7, 52.6, 44.1, 37.0. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{17}ClNSe$, 326.0207; found, 326.0203. $[\alpha]_D^{20}$= +39.7 (c= 0.015, CH_2Cl_2).

(S)-1-((4-fluorophenyl)selanyl)-3-phenylpropan-2-amine (2j): Yield: 0.207 g (67%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 2H), 7.33 – 7.18 (m, 3H), 7.18 – 7.08 (m, 2H), 7.00 – 6.88 (m, 2H), 3.20 – 3.09 (m, 1H), 3.07 (dd, *J* = 12.3, 4.2 Hz, 1H), 2.88 – 2.74 (m, 2H), 2.63 (dd, *J* = 13.4, 7.9 Hz, 1H), 1.53 (s, 2H). ^{13}C NMR (100 MHz, CDCl3) δ 162.5 (d, *J* = 249.7 Hz), 138.8, 135.3 (d, *J* = 8.0 Hz), 129.3, 128.7, 126.6, 124.5 (d, *J* = 3.4 Hz), 116.4 (d, *J* = 22.0 Hz), 52.5, 44.0, 37.6. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{17}FNSe$, 310.0505; found, 310.0502. $[\alpha]_D^{20}$= +39.9 (c= 0.010, CH_2Cl_2).

(S)-*N*-(1-phenyl-3-(phenylselanyl)propan-2-yl)prop-2-en-1-amine (2k): Yield: 0.301 g (91%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.33 – 7.18 (m, 6H), 7.17 – 7.11 (m, 2H), 5.78 (ddt, *J* = 16.3, 10.2, 6.0 Hz, 1H), 5.13 – 4.99 (m, 2H), 3.22 (d, *J* = 5.3 Hz, 2H), 3.10 – 2.98 (m, 2H), 2.96 – 2.75 (m, 3H), 1.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 136.8, 132.7, 130.5, 129.4, 129.1, 128.6, 126.9, 126.5, 116.1, 58.1, 49.8, 40.7, 33.1. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{18}H_{21}NSe$, 332.0912; found, 332.0910. $[\alpha]_D^{20}$= +14.3 (c= 0.015, CH_2Cl_2).

(S)-*N*-benzyl-1-phenyl-3-(phenylselanyl)propan-2-amine (2l): Yield: 0.289 g (76%); Colorless solid; mp 40.3 – 42.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.30 – 7.14 (m, 11H), 7.13 – 7.08 (m, 2H), 3.81 – 3.70 (m, 2H), 3.10 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.06 – 2.80 (m, 4H), 1.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.8, 132.7, 130.6, 129.5,

129.2, 128.6, 128.5, 128.2, 127.0, 126.9, 126.5, 58.0, 51.3, 40.8, 33.3. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NSe$, 382.1069; found, 382.1071. $[\alpha]_D^{20}$= +11.8 (c= 0.016, CH_2Cl_2).

(S)-*N*-(1-phenyl-3-(phenylselanyl)propan-2-yl)aniline (2m): Yield: 0.327 g (89%); Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.32 – 7.08 (m, 10H), 6.72 – 6.64 (m, 1H), 6.53 – 6.41 (m, 2H), 3.86 (s, 1H), 3.78 (s, 1H), 3.13 – 2.93 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 138.0, 133.4, 130.0, 129.5, 129.5, 129.3, 128.6, 127.3, 126.6, 117.8, 113.7, 54.0, 40.0, 32.7. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}NSe$, 368.0913; found, 368.0918. $[\alpha]_D^{20}$= +65.6 (c= 0.007, CH_2Cl_2).

***N*-(2-(phenylselanyl)ethyl)prop-2-en-1-amine (2n):** Yield: 0.207 g (86%); Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.46 (m, 2H), 7.32 – 7.20 (m, 3H), 5.94 – 5.80 (m, 1H), 5.21 – 5.03 (m, 2H), 3.23 (dt, *J* = 6.0, 1.4 Hz, 2H), 3.05 (t, *J* = 6.6 Hz, 2H), 2.88 (t, *J* = 6.7 Hz, 2H), 1.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 132.9, 129.7, 129.1, 127.1, 116.1, 51.9, 48.4, 28.5. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{11}H_{16}NSe$, 242.0442; found, 242.0440.

***N*-benzyl-2-(phenylselanyl)ethan-1-amine (2o):** Yield: 0.265 g (91%); Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.35 – 7.20 (m, 8H), 3.78 (s, 2H), 3.06 (t, *J* = 6.5 Hz, 2H), 2.89 (t, *J* = 6.6 Hz, 2H), 1.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 133.0, 129.7, 129.2, 128.5, 128.2, 127.1, 127.1, 53.5, 48.3, 28.7. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NSe$, 292.0599; found, 292.0598.

***N*-(2-(phenylselanyl)ethyl)aniline (2p):** Yield: 0.263 g (95%); Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.46 (m, 2H), 7.33 – 7.22 (m, 3H), 7.20 – 7.07 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 3.99 (s, 1H), 3.37 (t, *J* = 6.7 Hz, 2H), 3.08 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 133.4, 129.4, 129.3, 129.1, 127.4, 117.8, 113.2, 43.5, 27.7. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{14}H_{16}NSe$, 278.0442; found, 278.0455.

(S)-*N*-benzyl-3-methyl-1-(phenylselanyl)butan-2-amine (2q): Yield: 0.117 g (35%); Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 2H), 7.30 (d, *J* = 4.4 Hz, 4H), 7.26 – 7.20 (m, 4H), 3.74 (s, 2H), 3.14 (dd, *J* = 12.1, 4.6 Hz, 1H), 2.96 (dd, *J* = 12.1, 7.7 Hz, 1H), 2.57 (dt, *J* = 7.6, 4.9 Hz, 1H), 2.03 – 1.90 (m, 1H), 1.63 (s, 1H), 0.91 (dd, *J* = 6.8, 1.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 132.9, 130.8, 129.1, 128.4, 128.3, 127.0, 126.9, 61.9, 51.7, 31.3, 30.3, 18.8, 18.2. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}NSe$, 334.1069; found, 334.1065. $[\alpha]_D^{20}$= +48.8 (c= 0.002, CH_2Cl_2).

(S)-1-phenyl-3-(phenyltellanyl)propan-2-amine (3a): Yield: 0.290 g (85%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.63 (m, 2H), 7.32 – 7.11 (m, 8H), 3.26 – 3.08 (m, 2H), 2.96 – 2.79 (m, 2H), 2.64 (dd, *J* = 13.3, 7.7 Hz, 1H), 1.38 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.4, 129.4, 129.3, 128.6, 127.7, 126.5, 112.0, 53.5, 45.4, 20.0. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NTe$, 342.0497; found, 342.0493. $[\alpha]_D^{20}$= +44.3 (c= 0.013, CH_2Cl_2).

(S)-3-methyl-1-(phenyltellanyl)butan-2-amine (3b): Yield: 0.044 g (15%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 2H), 7.29 – 7.23 (m, 1H), 7.19 (tt, *J* = 6.6, 1.4 Hz, 2H), 3.10 (dd, *J* = 11.6, 4.0 Hz, 1H), 2.96 (dd, *J* = 11.6, 9.3 Hz, 1H), 2.77 – 2.69 (m, 1H), 1.73 – 1.60 (m, 1H), 1.33 (s, 2H), 0.91 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 129.2, 127.6, 112.4, 57.8, 34.8, 19.5, 18.3, 18.0. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{11}H_{18}NTe$, 294.0496; found, 294.0491. $[\alpha]_D^{20}$= +23.9 (c= 0.001, CH_2Cl_2).

(S)-4-methyl-1-(phenyltellanyl)pentan-2-amine (3c): Yield: 0.230 g (75%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.65 (m, 2H), 7.27 (tt, *J* = 6.5, 1.3 Hz, 1H), 7.23 – 7.14 (m, 2H), 3.11 (dd, *J* = 11.3, 3.8 Hz, 1H), 3.02 – 2.84 (m, 2H), 1.72 – 1.58 (m, 1H), 1.44 – 1.19 (m,

4H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 129.3, 127.6, 112.0, 49.7, 48.5, 25.5, 23.2, 22.4, 21.9. $[\alpha]_D^{20}$= +35.4 (c= 0.010, CH_2Cl_2).

(S)-1-phenyl-3-(*p*-tolyltellanyl)propan-2-amine (3d): Yield: 0.316 g (89%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.31 – 7.12 (m, 5H), 7.01 (d, J = 7.7 Hz, 2H), 3.23 – 3.15 (m, 1H), 3.11 (dd, J = 11.9, 4.5 Hz, 1H), 2.93 – 2.80 (m, 2H), 2.62 (dd, J = 13.3, 7.9 Hz, 1H), 2.33 (s, 3H), 1.37 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.8, 137.8, 130.3, 129.4, 128.6, 126.5, 107.7, 53.5, 45.4, 21.3, 20.0. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NTe$, 356.0653; found, 356.0657. $[\alpha]_D^{20}$= +29.1 (c= 0.012, CH_2Cl_2).

(S)-1-((4-chlorophenyl)tellanyl)-3-phenylpropan-2-amine (3e): Yield: 0.316 g (52%); Colorless solid; mp 41.9 – 43.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.32 – 7.12 (m, 7H), 3.25 – 3.12 (m, 2H), 2.91 (dd, J = 11.7, 7.6 Hz, 1H), 2.84 (dd, J = 13.3, 5.4 Hz, 1H), 2.64 (dd, J = 13.3, 7.7 Hz, 1H), 1.37 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 138.9, 134.2, 129.5, 129.3, 128.7, 126.6, 109.7, 53.5, 45.5, 20.4. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{17}ClNTe$, 376.0106; found, 376.0092. $[\alpha]_D^{20}$= +36.1 (c= 0.007, CH_2Cl_2).

(S)-1-phenyl-3-(phenylthio)propan-2-amine (4a): Yield: 0.124 g (51%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.14 (m, 10H), 3.22 – 3.09 (m, 2H), 2.86 (dd, J = 13.4, 5.3 Hz, 1H), 2.79 (dd, J = 13.1, 8.0 Hz, 1H), 2.65 (dd, J = 13.4, 7.8 Hz, 1H), 1.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.1, 129.5, 129.4, 129.1, 128.6, 126.6, 126.2, 51.9, 43.5, 41.6. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NS$, 244.1156; found, 244.1154. $[\alpha]_D^{20}$= +30.7 (c= 0.008, CH_2Cl_2).

2-(phenylthio)ethan-1-amine (4b): Yield: 0.129 g (84%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.32 – 7.24 (m, 2H), 7.22 – 7.14 (m, 1H), 3.05 – 2.97 (m, 2H),

2.94 – 2.86 (m, 2H), 1.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 129.7, 129.0, 126.2, 40.9, 38.1. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_8H_{12}NS$, 154.0685; found, 154.0682.

(S)-3-methyl-1-(phenylthio)butan-2-amine (4c): Yield: 0.041 g (21%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.32 – 7.25 (m, 2H), 7.21 – 7.15 (m, 1H), 3.23 – 3.13 (m, 1H), 2.77 – 2.67 (m, 2H), 1.78 – 1.68 (m, 1H), 1.48 (s, 2H), 0.93 (dd, *J* = 7.8, 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 129.6, 129.0, 126.2, 55.5, 40.2, 33.1, 19.4, 17.7. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{11}H_{18}NS$, 196.1154; found, 196.1154. $[\alpha]_D^{20}$= +69.7 (c= 0.009, CH_2Cl_2).

(S)-4-methyl-1-(phenylthio)pentan-2-amine (4d): Yield: 0.075 g (36%); Colorless solid; mp 46.4 – 48.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.25 (m, 2H), 7.21 – 7.16 (m, 1H), 3.10 (dd, *J* = 13.0, 3.8 Hz, 1H), 3.01 – 2.93 (m, 1H), 2.72 (dd, *J* = 13.0, 8.5 Hz, 1H), 1.79 – 1.67 (m, 1H), 1.60 (s, 2H), 1.34 – 1.28 (m, 2H), 0.88 (dd, *J* = 11.7, 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 129.7, 129.1, 126.2, 48.3, 46.6, 43.3, 25.1, 23.4, 22.2. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}NS$, 210.1311; found, 210.1310. $[\alpha]_D^{20}$= +21.3 (c= 0.007, CH_2Cl_2).

(2S,3S)-3-methyl-1-(phenylthio)pentan-2-amine (4e): Yield: 0.038 g (18%); Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 1H), 3.18 (dd, *J* = 12.8, 2.8 Hz, 1H), 2.82 – 2.76 (m, 1H), 2.69 (dd, *J* = 12.8, 9.8 Hz, 1H), 1.61 (s, 2H), 1.53 – 1.41 (m, 2H), 1.22 – 1.12 (m, 1H), 0.94 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 129.7, 129.0, 126.2, 54.4, 40.1, 39.7, 25.2, 15.1, 11.8. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}NS$, 210.1311; found, 210.1307. $[\alpha]_D^{20}$= +9.1 (c= 0.001, CH_2Cl_2).

(S)-1-phenyl-3-(*p*-tolylthio)propan-2-amine (4f): Yield: 0.177 g (69%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 7H), 7.12 – 7.04 (m, 2H), 3.19 – 3.12 (m, 1H), 3.08 (dd, *J* = 13.2, 4.2 Hz, 1H), 2.85 (dd, *J* = 13.4, 5.2 Hz, 1H), 2.76 (dd, *J* = 13.2, 8.2 Hz, 1H), 2.62 (dd, *J* = 13.3, 8.0 Hz, 1H), 2.32 (s, 3H), 1.49 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 136.5, 132.3, 130.3, 129.8, 129.4, 128.6, 126.5, 51.9, 43.4, 42.4, 21.1. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NS$, 258.1311; found, 258.1309. $[\alpha]_D^{20}$= +33.0 (c= 0.005, CH_2Cl_2).

(S)-1-((4-chlorophenyl)thio)-3-phenylpropan-2-amine (4g): Yield: 0.186 g (67%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.14 (m, 9H), 3.20 – 3.04 (m, 2H), 2.84 (dd, *J* = 13.3, 5.5 Hz, 1H), 2.77 (dd, *J* = 13.2, 8.2 Hz, 1H), 2.65 (dd, *J* = 13.4, 7.8 Hz, 1H), 1.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.7, 132.2, 130.7, 129.3, 129.2, 128.7, 126.7, 51.9, 43.5, 41.8. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{17}ClNS$, 278.0765; found, 278.0764. $[\alpha]_D^{20}$= +37.8 (c= 0.011, CH_2Cl_2).

2-(*p*-tolylthio)ethan-1-amine (4h): Yield: 0.137 g (82%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.01 – 2.94 (m, 2H), 2.91 – 2.84 (m, 2H), 2.32 (s, 3H), 1.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 131.9, 130.8, 129.9, 41.1, 39.0, 21.1. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_9H_{14}NS$, 168.0841; found, 168.0840.

(S)-3-methyl-1-(*p*-tolylthio)butan-2-amine (4i): Yield: 0.040 g (19%); Colorless solid; mp 55.4 – 57.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.16 – 3.10 (m, 1H), 2.70 – 2.64 (m, 2H), 2.32 (s, 3H), 1.74 – 1.66 (m, 1H), 1.48 (s, 2H), 0.92 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 132.6, 130.4, 129.8, 55.5, 41.0, 33.1, 21.1, 19.4, 17.7. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}NS$, 210.1311; found, 210.1312. $[\alpha]_D^{20}$= +12.0 (c= 0.003, CH_2Cl_2).

(S)-1-((4-chlorophenyl)thio)-3-methylbutan-2-amine (4j): Yield: 0.082 g (36%); Colorless solid; mp 65.7 – 67.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 4H), 3.17 – 3.10 (m, 1H), 2.75 – 2.65 (m, 2H), 1.76 – 1.67 (m, 1H), 1.55 (s, 2H), 0.93 (dd, *J* = 7.7, 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 132.2, 130.9, 129.2, 55.5, 40.5, 33.1, 19.3, 17.7. HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}ClNS$, 230.0765; found, 230.0763. $[\alpha]_D^{20}$= +64.0 (c= 0.012, CH_2Cl_2).

(S)-4-methyl-1-(*p*-tolylthio)pentan-2-amine (4k): Yield: 0.071 g (32%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.05 (dd, *J* = 13.0, 3.8 Hz, 1H), 2.97 – 2.90 (m, 1H), 2.67 (dd, *J* = 13.0, 8.5 Hz, 1H), 2.32 (s, 3H), 1.77 – 1.65 (m, 1H), 1.51 (s, 2H), 1.32 – 1.25 (m, 2H), 0.87 (dd, *J* = 10.5, 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 132.6, 130.4, 129.8, 48.3, 46.6, 44.0, 25.1, 23.4, 22.2, 21.1. HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{13}H_{22}NS$, 224.1467; found, 224.1469. $[\alpha]_D^{20}$= +31.5 (c= 0.011, CH_2Cl_2).

(S)-1-((4-chlorophenyl)thio)-4-methylpentan-2-amine (4l): Yield: 0.088 g (36%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 4H), 3.06 (dd, *J* = 13.0, 3.9 Hz, 1H), 3.00 – 2.91 (m, 1H), 2.71 (dd, *J* = 13.0, 8.4 Hz, 1H), 1.78 – 1.64 (m, 3H), 1.34 – 1.27 (m, 2H), 0.88 (dd, *J* = 12.3, 6.6 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 135.0, 132.2, 130.9, 129.2, 48.2, 46.5, 43.5, 25.1, 23.4, 22.2. HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{12}H_{19}ClNS$, 244.0921; found, 244.0918. $[\alpha]_D^{20}$= +24.6 (c= 0.006, CH_2Cl_2).

(S)-*N*-(1-phenyl-3-(phenylthio)propan-2-yl)prop-2-en-1-amine (4m): Yield: 0.238 g (84%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 7H), 7.18 – 7.12 (m, 3H), 5.84 – 5.72 (m, 1H), 5.12 – 5.00 (m, 2H), 3.27 – 3.21 (m, 2H), 3.05 – 2.97 (m, 2H), 2.95 – 2.77 (m, 3H), 1.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.8, 136.5, 129.5, 129.4, 129.0,

128.6, 126.5, 126.1, 116.1, 57.6, 49.9, 40.1, 37.89. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{13}H_{22}NS$, 284.1467; found, 284.1468. $[\alpha]_D^{20}$= +10.2 (c= 0.012, CH_2Cl_2).

(S)-*N*-benzyl-1-phenyl-3-(phenylthio)propan-2-amine (4n): Yield: 0.210 g (63%); Colorless solid; mp 45.9 – 47.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.11 (m, 15H), 3.78 (s, 2H), 3.08 – 2.91 (m, 3H), 2.87 (d, *J* = 6.4 Hz, 2H), 1.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.7, 136.5, 129.5, 129.5, 129.0, 128.6, 128.5, 128.2, 127.0, 126.5, 126.1, 57.5, 51.3, 40.2, 38.1. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NS$, 334.1624; found, 334.1625. $[\alpha]_D^{20}$= +14.7 (c= 0.010, CH_2Cl_2).

(S)-*N*-benzyl-1-phenyl-3-(*p*-tolylthio)propan-2-amine (4o): Yield: 0.181 g (52%); Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 12H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.75 (s, 2H), 3.03 – 2.83 (m, 5H), 2.31 (s, 3H), 1.77 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 138.8, 136.3, 132.7, 130.3, 129.8, 129.5, 128.6, 128.5, 128.2, 127.0, 126.5, 57.5, 51.3, 40.1, 38.8, 21.1. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{23}H_{26}NS$, 348.1780; found, 348.1777. $[\alpha]_D^{20}$= +13.9 (c= 0.007, CH_2Cl_2).

(S)-*N*-benzyl-1-((4-chlorophenyl)thio)-3-phenylpropan-2-amine (4p): Yield: 0.256 g (68%); Colorless solid; mp 42.6 – 44.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.05 (m, 14H), 3.77 (s, 2H), 3.04 – 2.78 (m, 5H), 1.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 138.5, 135.0, 132.0, 130.7, 129.4, 129.1, 128.6, 128.5, 128.1, 127.1, 126.6, 57.2, 51.3, 40.1, 38.3. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}ClNS$, 368.1234; found, 368.1232. $[\alpha]_D^{20}$= +12.6 (c= 0.010, CH_2Cl_2).

(S)-*N*-(1-phenyl-3-(phenylthio)propan-2-yl)aniline (4q): Yield: 0.265 g (83%); Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.11 (m, 12H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 7.9 Hz,

2H), 3.83 – 3.78 (m, 2H), 3.09 – 2.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 137.9, 136.1, 130.3, 129.6, 129.5, 129.1, 128.7, 126.7, 126.6, 117.9, 113.7, 53.5, 39.0, 37.8. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}NS$, 320.1467; found, 320.1471. $[\alpha]_D^{20}$= +50.6 (c= 0.016, CH_2Cl_2).

(S)-*N*-benzyl-3-methyl-1-(phenylthio)butan-2-amine (4r): Yield: 0.037 g (13%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.14 (m, 10H), 3.75 (s, 2H), 3.13 (dd, *J* = 13.0, 4.5 Hz, 1H), 2.91 (dd, *J* = 13.0, 7.8 Hz, 1H), 2.57 (dt, *J* = 7.8, 4.7 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.67 (s, 1H), 0.93 (dd, *J* = 6.9, 2.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.8, 129.6, 129.0, 128.4, 128.3, 127.0, 126.1, 61.2, 51.9, 36.0, 29.9, 18.6, 18.2. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}NS$, 286.1624; found, 286.1621. $[\alpha]_D^{20}$= +15.3 (c= 0.001, CH_2Cl_2).

***N*-(2-(phenylthio)ethyl)prop-2-en-1-amine (4s):** Yield: 0.178 g (91%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.25 (m, 2H), 7.22 – 7.16 (m, 1H), 5.93 – 5.82 (m, 1H), 5.21 – 5.05 (m, 2H), 3.31 – 3.20 (m, 2H), 3.08 (t, *J* = 6.5 Hz, 2H), 2.85 (t, *J* = 6.5 Hz, 2H), 1.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 135.9, 129.7, 129.0, 126.3, 116.1, 52.0, 47.7, 34.3. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{11}H_{16}NS$, 194.0998; found, 194.0999.

***N*-(2-(*p*-tolylthio)ethyl)prop-2-en-1-amine (4t):** Yield: 0.191 g (92%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.93 – 5.81 (m, 1H), 5.19 – 5.05 (m, 2H), 3.24 (dt, *J* = 6.0, 1.4 Hz, 2H), 3.03 (t, *J* = 6.5 Hz, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 2.32 (s, 3H), 1.63 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 136.5, 132.0, 130.6, 129.8, 116.1, 52.0, 47.7, 35.0, 21.1. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{12}H_{18}NS$, 208.1154; found, 208.1152.

***N*-(2-((4-chlorophenyl)thio)ethyl)prop-2-en-1-amine (4u):** Yield: 0.200 g (88%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 4H), 5.95 – 5.79 (m, 1H), 5.21 – 5.06 (m, 2H), 3.31 – 3.21 (m, 2H), 3.06 (t, *J* = 6.5 Hz, 2H), 2.84 (t, *J* = 6.5 Hz, 2H), 1.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.6, 132.3, 131.0, 129.2, 116.2, 52.1, 47.6, 34.6. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{11}H_{15}ClNS$, 228.0608; found, 228.0606.

***N*-benzyl-2-(phenylthio)ethan-1-amine (4v):** Yield: 0.209 g (86%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.15 (m, 10H), 3.78 (s, 2H), 3.08 (t, *J* = 6.5 Hz, 2H), 2.85 (t, *J* = 6.5 Hz, 2H), 1.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 135.9, 129.8, 129.0, 128.5, 128.2, 127.1, 126.3, 53.6, 47.6, 34.4. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NS$, 244.1154; found, 244.1153.

***N*-benzyl-2-(*p*-tolylthio)ethan-1-amine (4w):** Yield: 0.242 g (94%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 7H), 7.07 (d, *J* = 7.9 Hz, 2H), 3.76 (s, 2H), 3.03 (t, *J* = 6.4 Hz, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.30 (s, 3H), 1.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 136.5, 131.9, 130.7, 129.8, 128.5, 128.2, 127.0, 53.5, 47.6, 35.0, 21.1. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NS$, 258.1311; found, 258.1311.

***N*-benzyl-2-((4-chlorophenyl)thio)ethan-1-amine (4x):** Yield: 0.252 g (91%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.15 (m, 9H), 3.78 (s, 2H), 3.04 (t, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 6.5 Hz, 2H), 1.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 134.4, 132.3, 131.1, 129.1, 128.5, 128.2, 128.5, 127.1, 53.5, 47.4, 34.6. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{15}H_{17}ClNS$, 278.0765; found, 278.0766.

***N*-(2-(phenylthio)ethyl)aniline (4y):** Yield: 0.208 g (91%); Colorless solid; mp 31.7 – 33.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.34 – 7.13 (m, 5H), 6.72 (tt, *J* = 7.4, 1.0 Hz,

1H), 6.64 – 6.56 (m, 2H), 4.03 (s, 1H), 3.35 (t, J = 6.5 Hz, 2H), 3.14 (t, J = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 135.2, 130.4, 129.4, 129.2, 126.8, 117.9, 113.2, 42.7, 33.8. HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{14}H_{16}NS$, 230.0998; found, 230.0996.

NMR Spectra

Figure S-01. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.

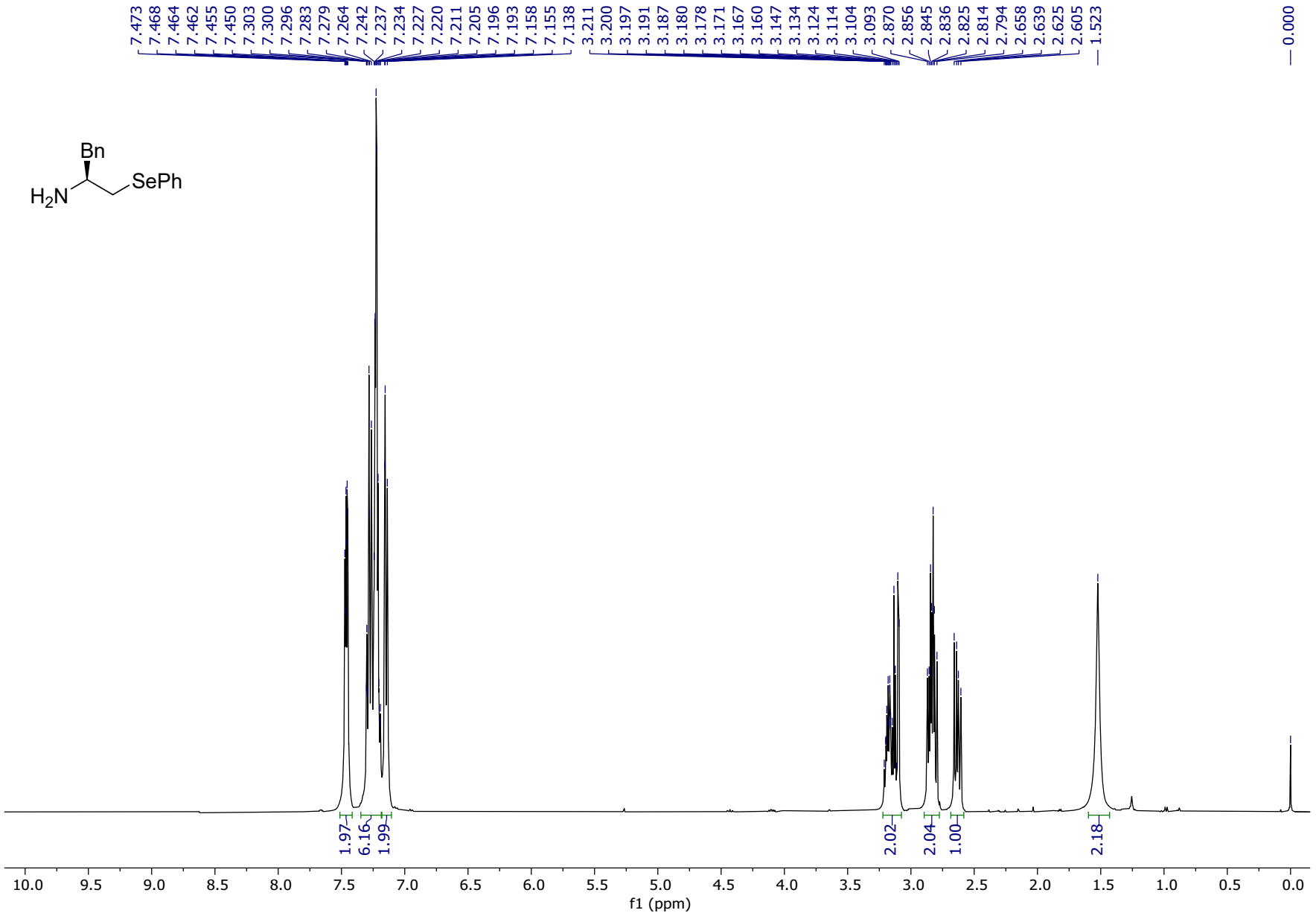


Figure S-02. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.

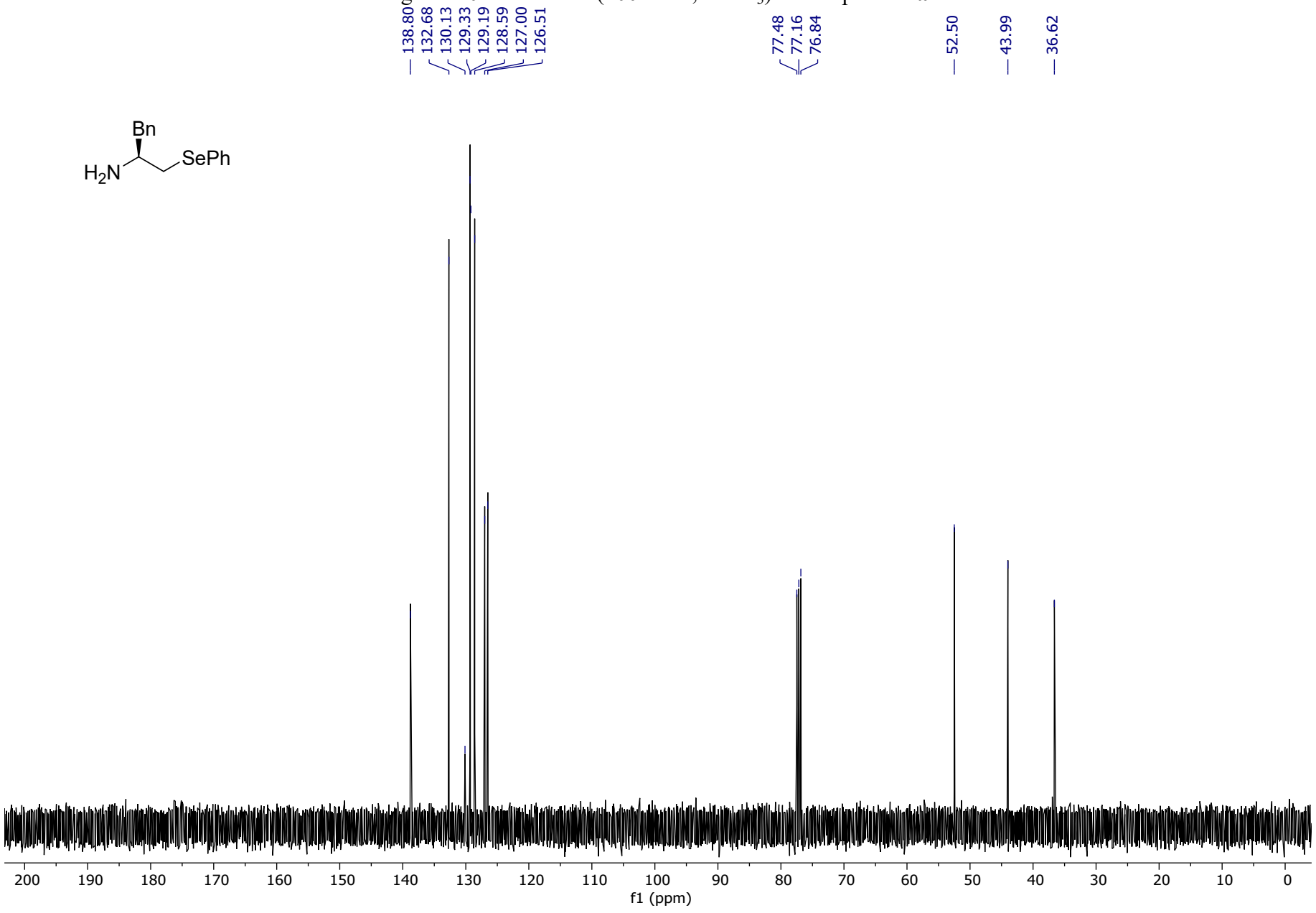


Figure S-03. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**.

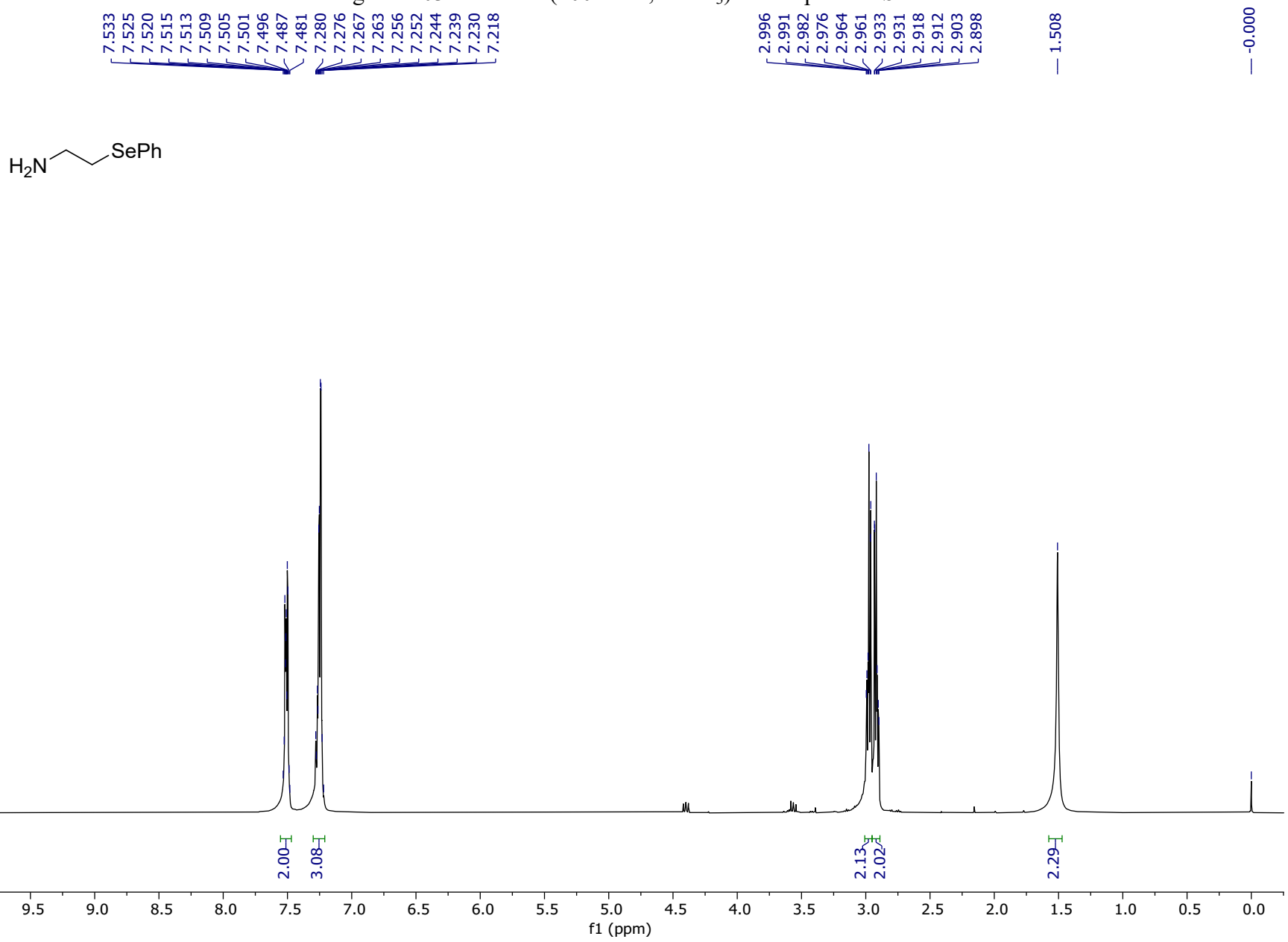


Figure S-04. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**.

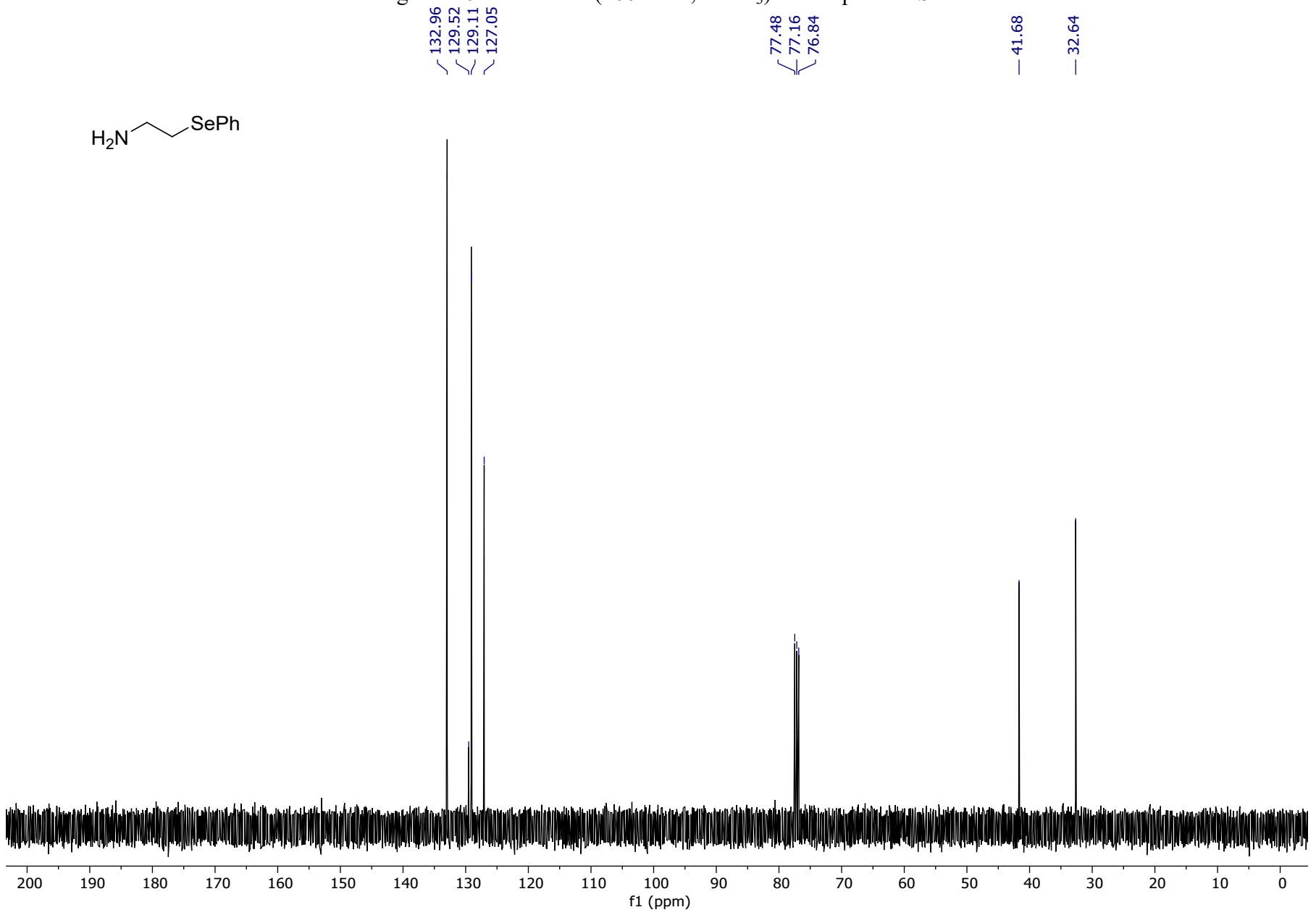


Figure S-05. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c**.

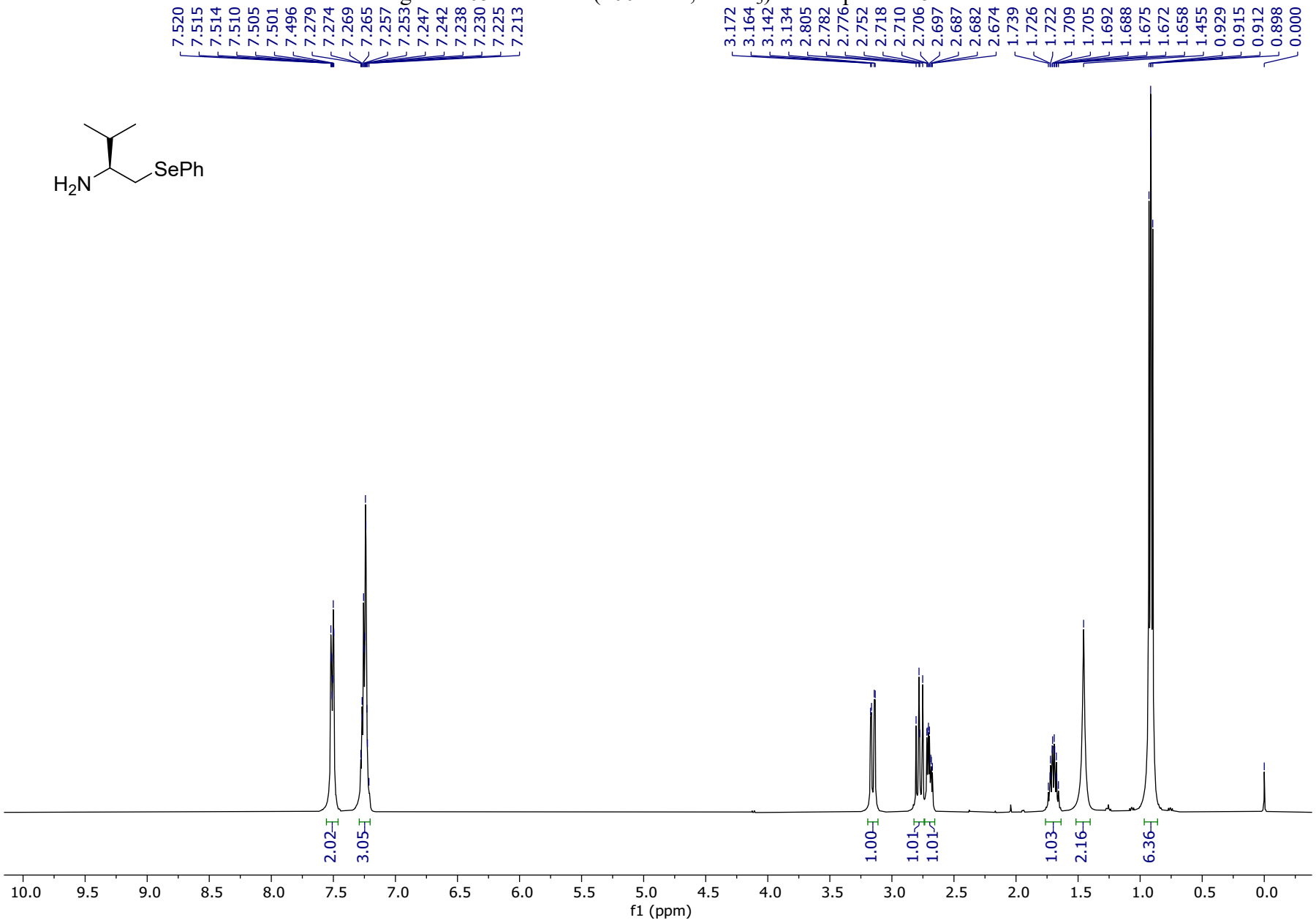


Figure S-06. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2c**.

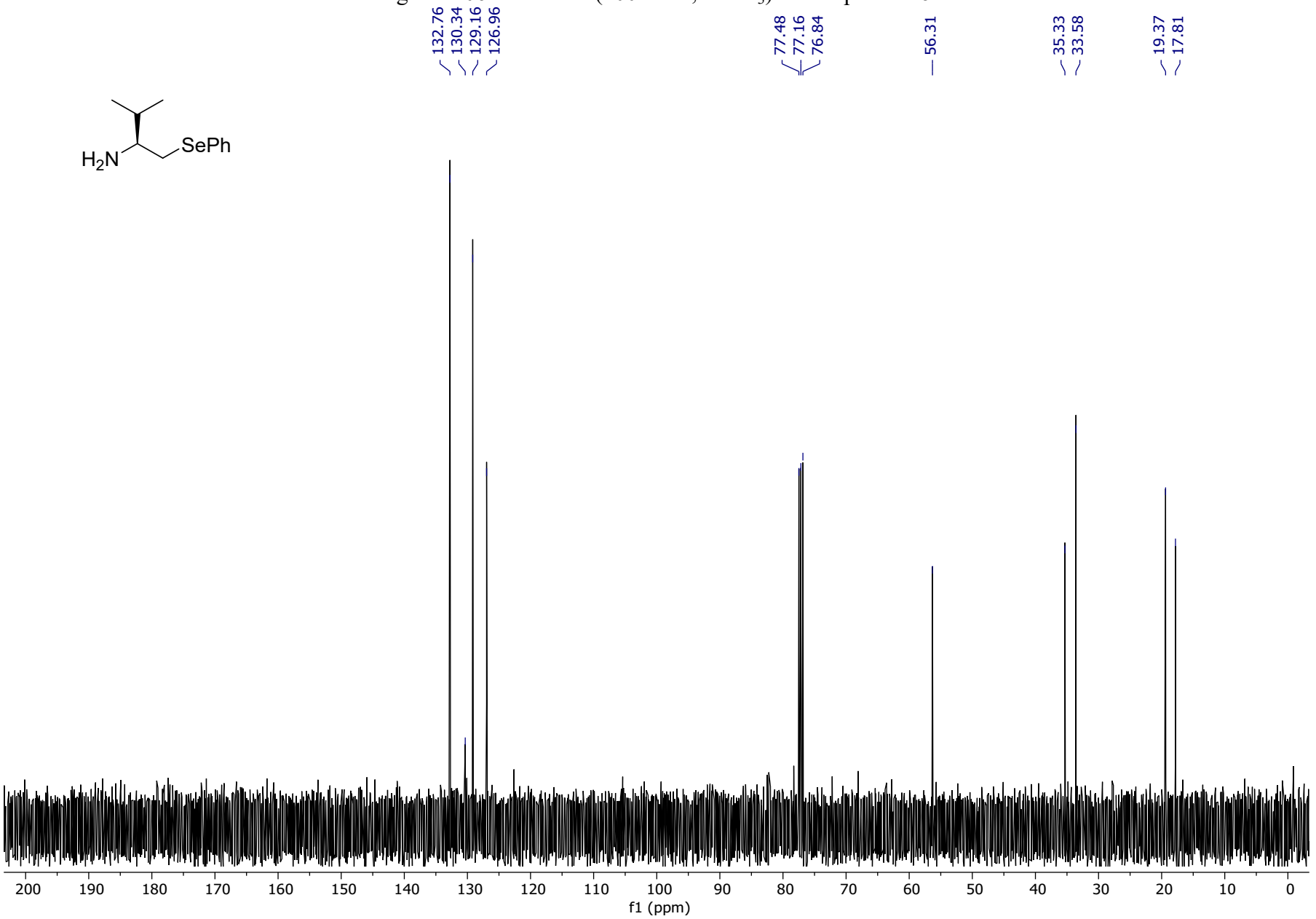


Figure S-07. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2d**.

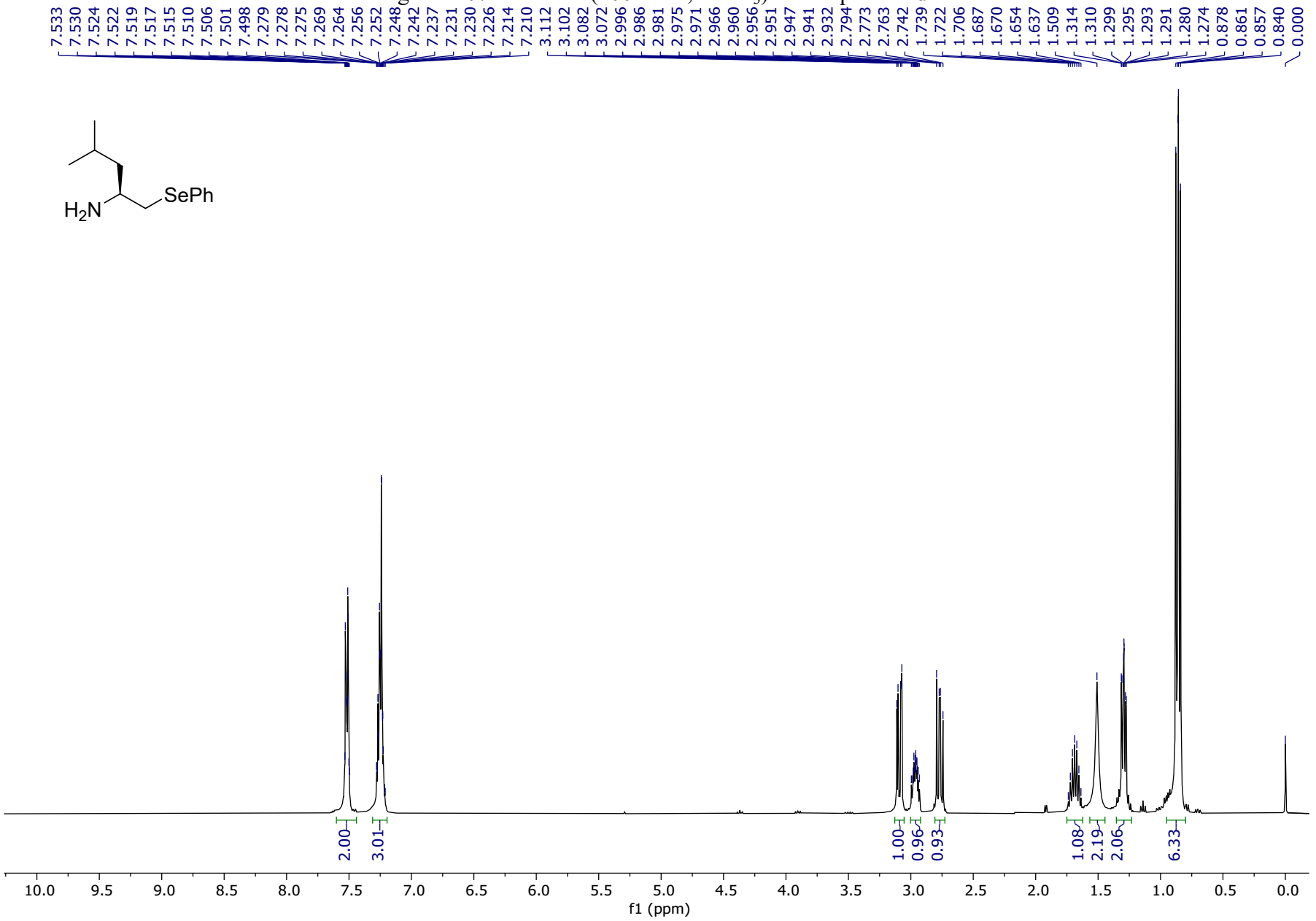


Figure S-08. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2d**.

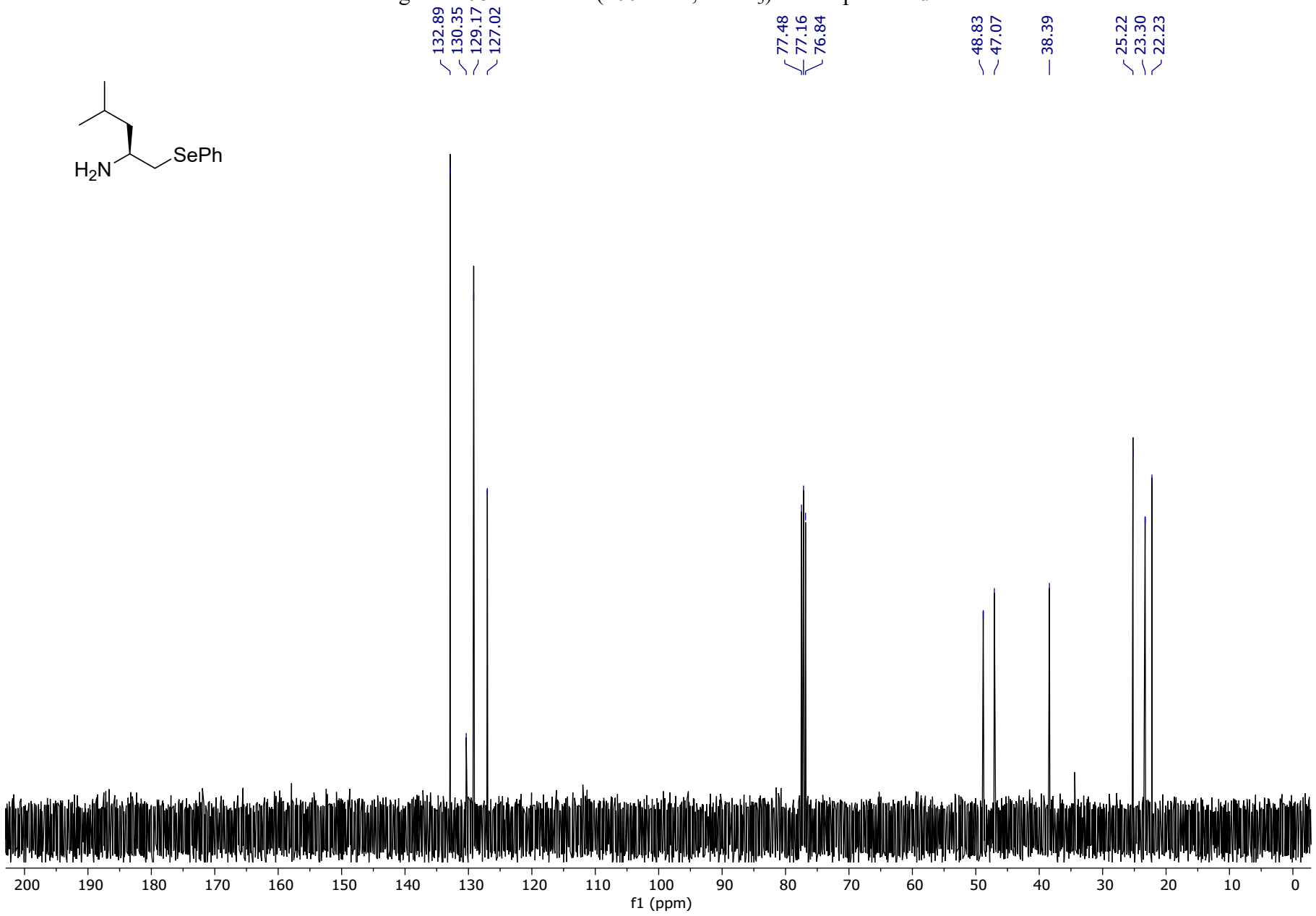


Figure S-09. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e**.

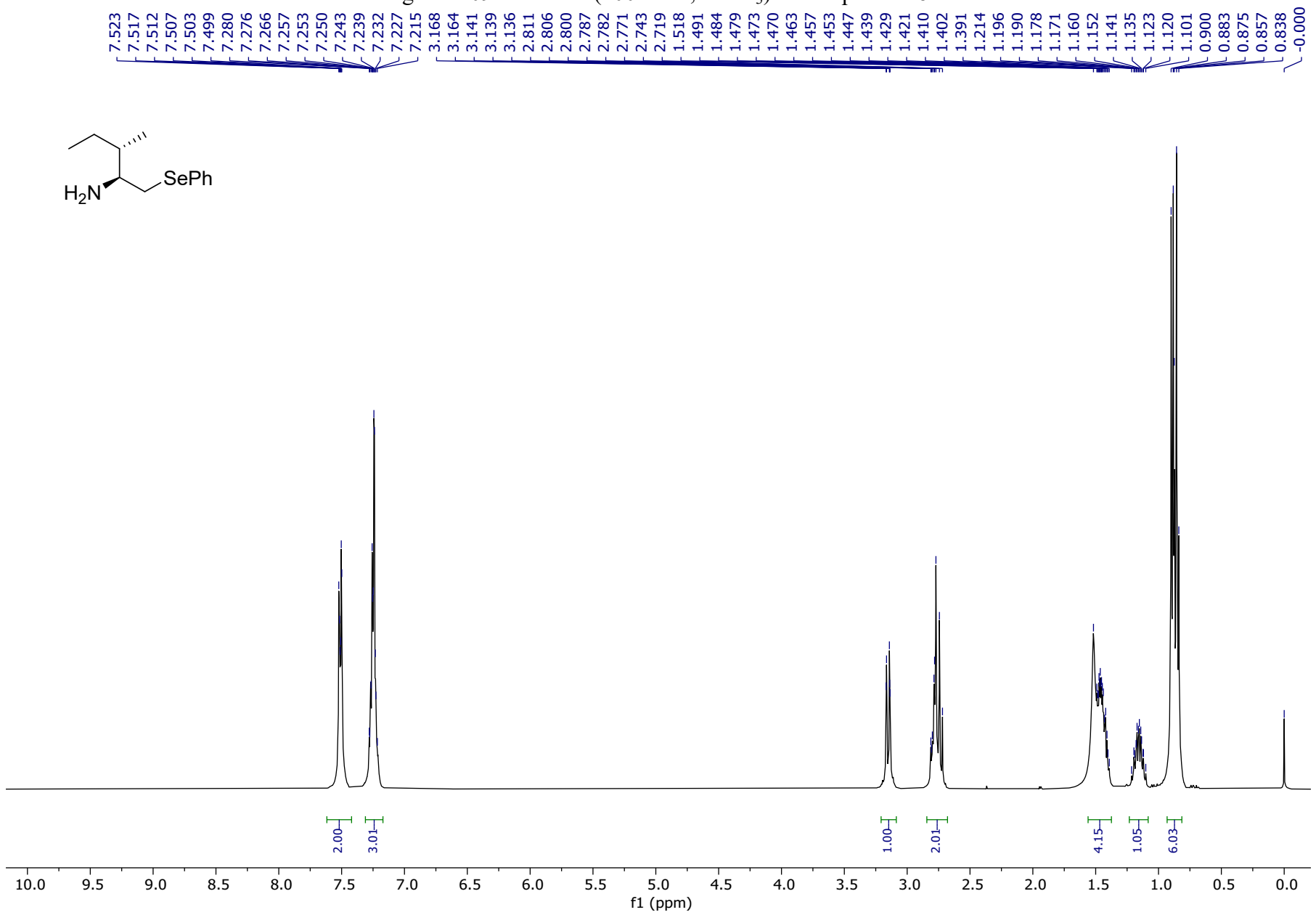


Figure S-10. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2e**.

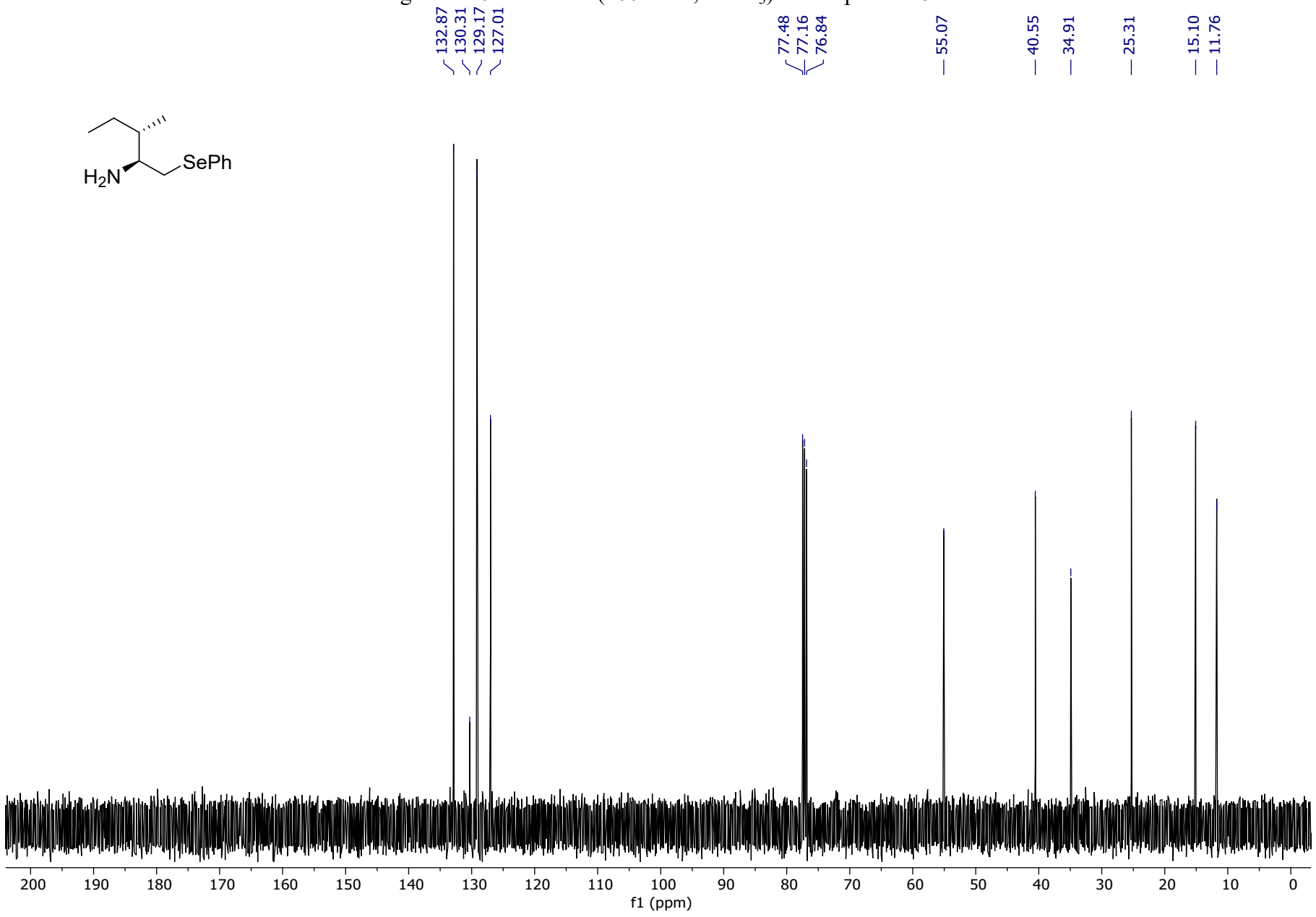


Figure S-11. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2f**.

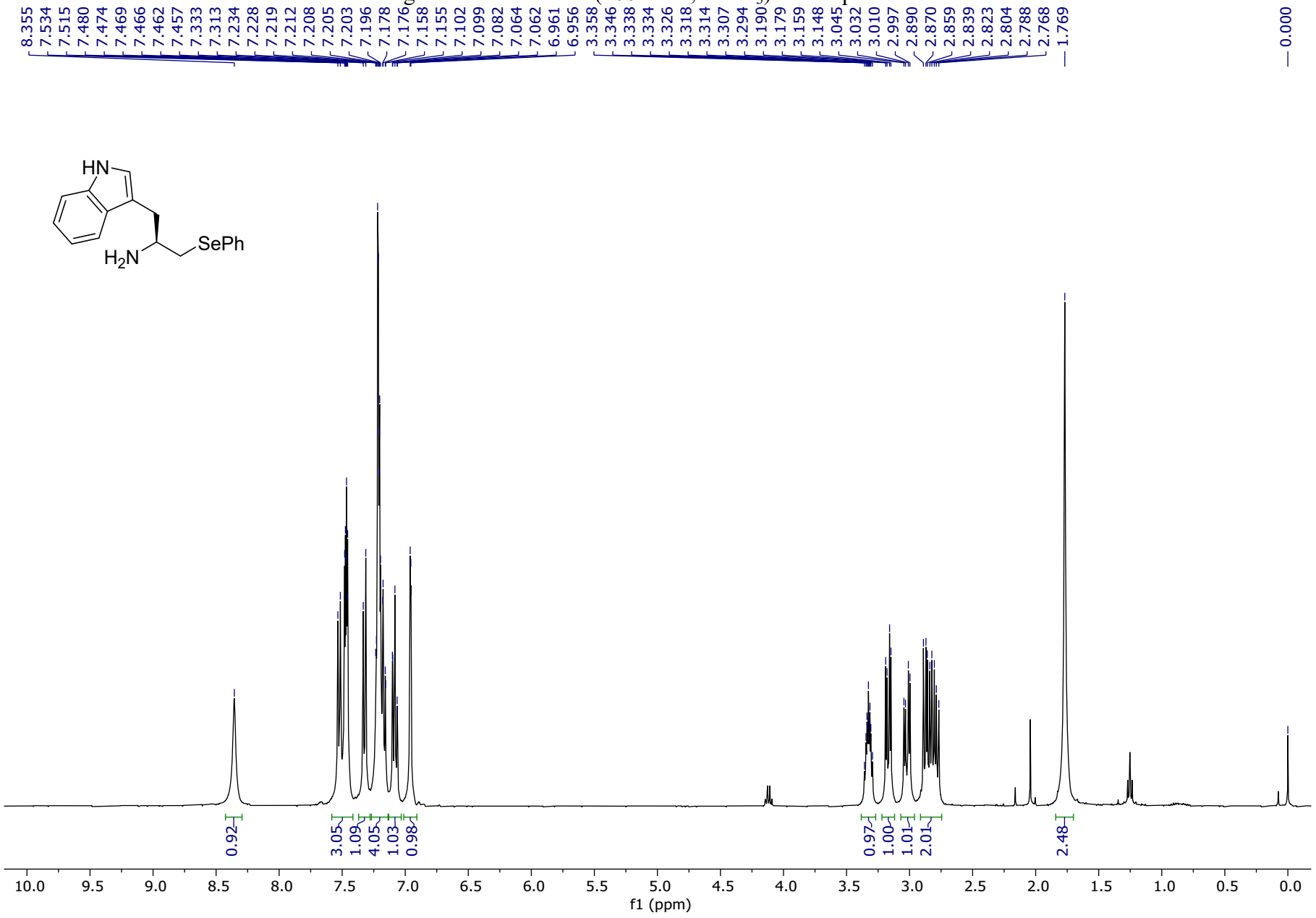


Figure S-12. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2f**.

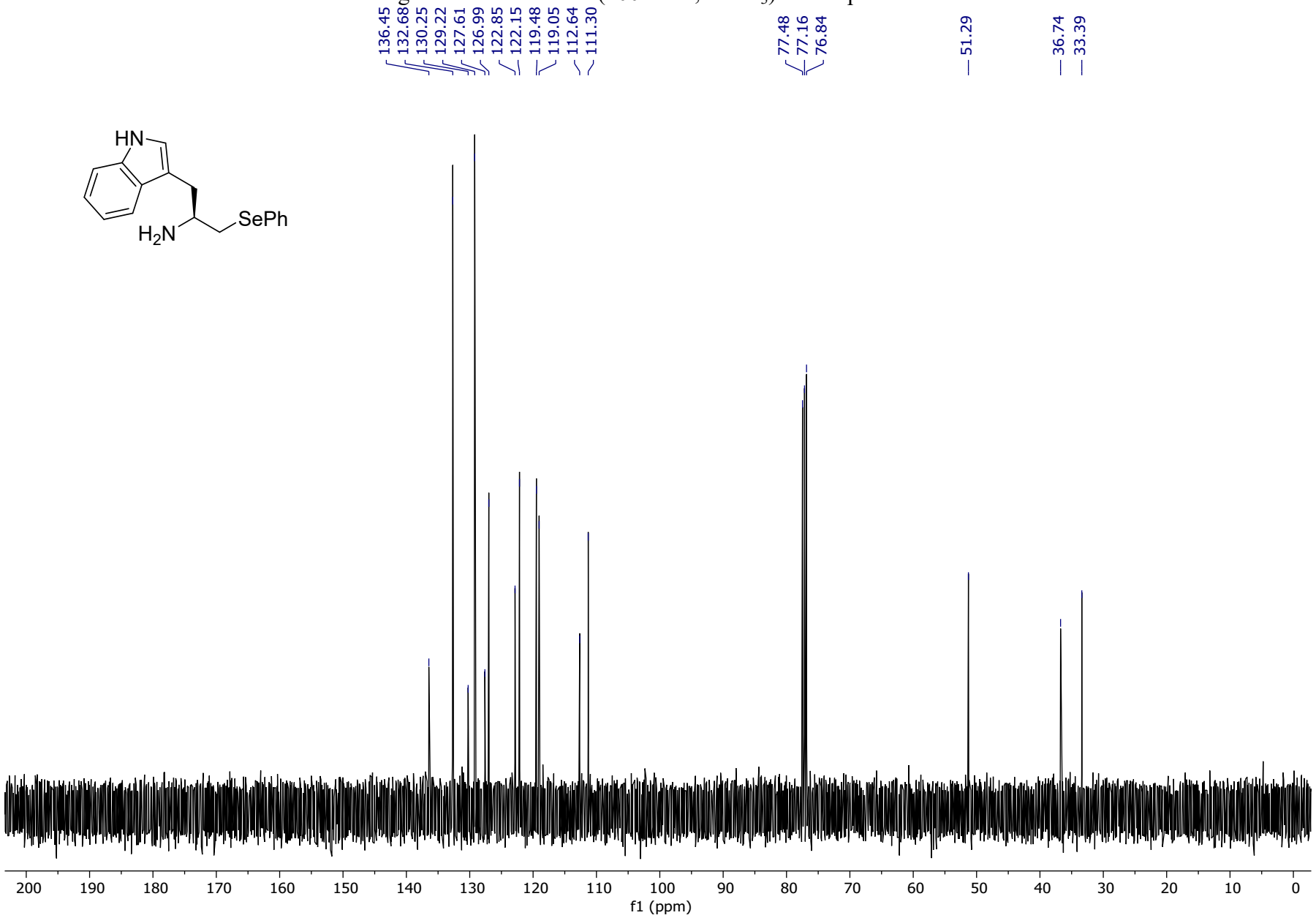


Figure S-13. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2g**.

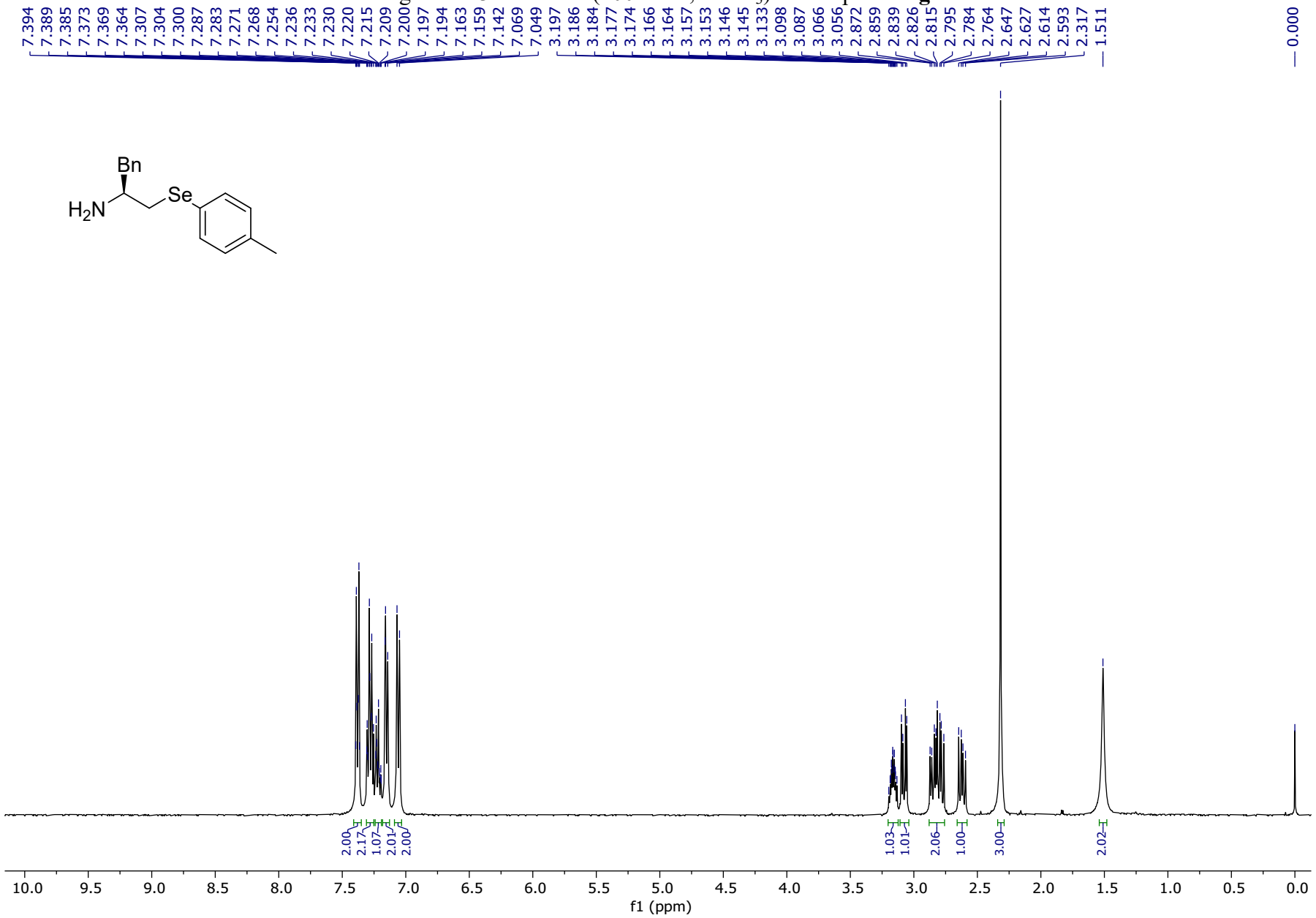


Figure S-14. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2g**.

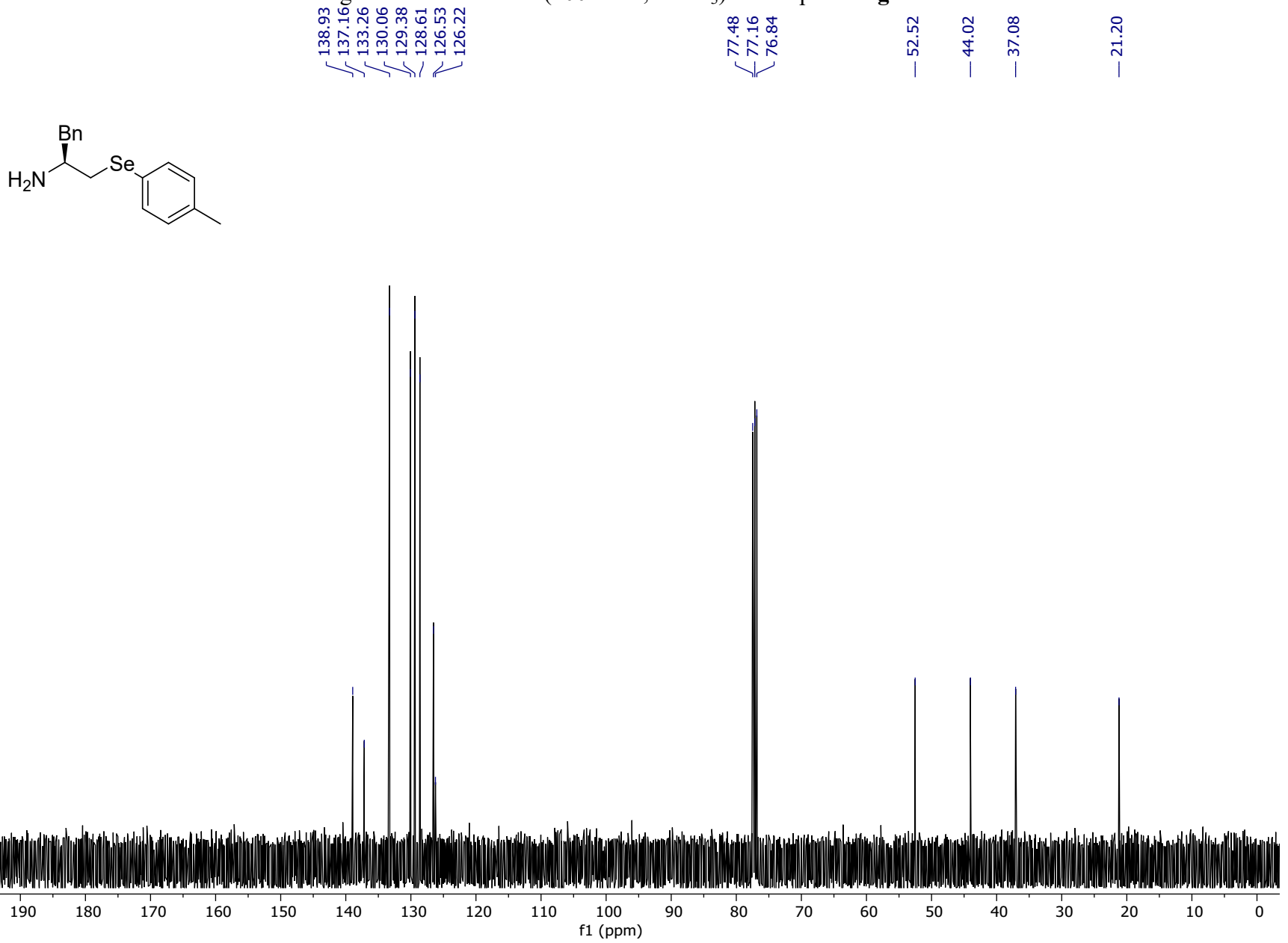


Figure S-15. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2h**.

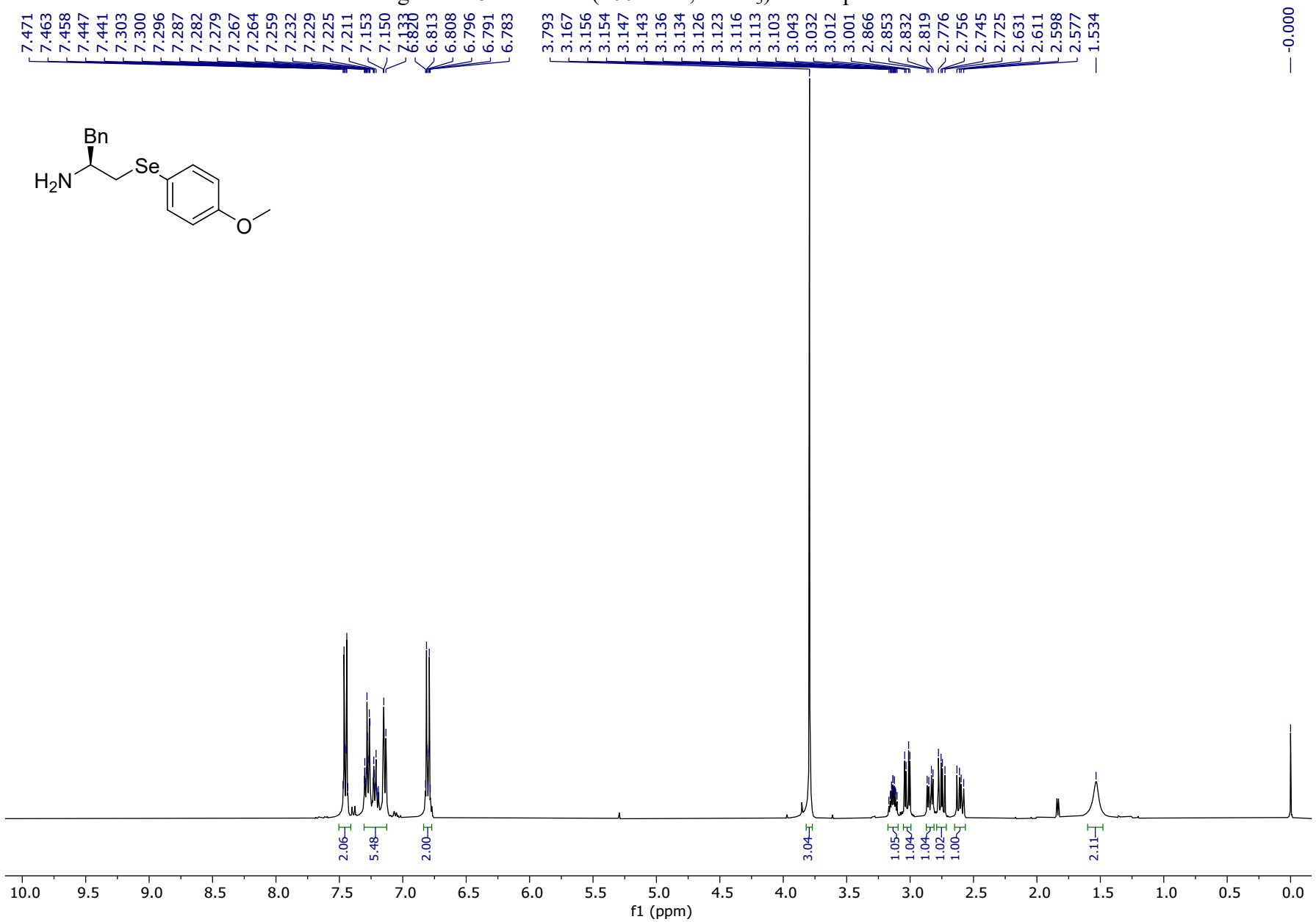


Figure S-16. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2h**.

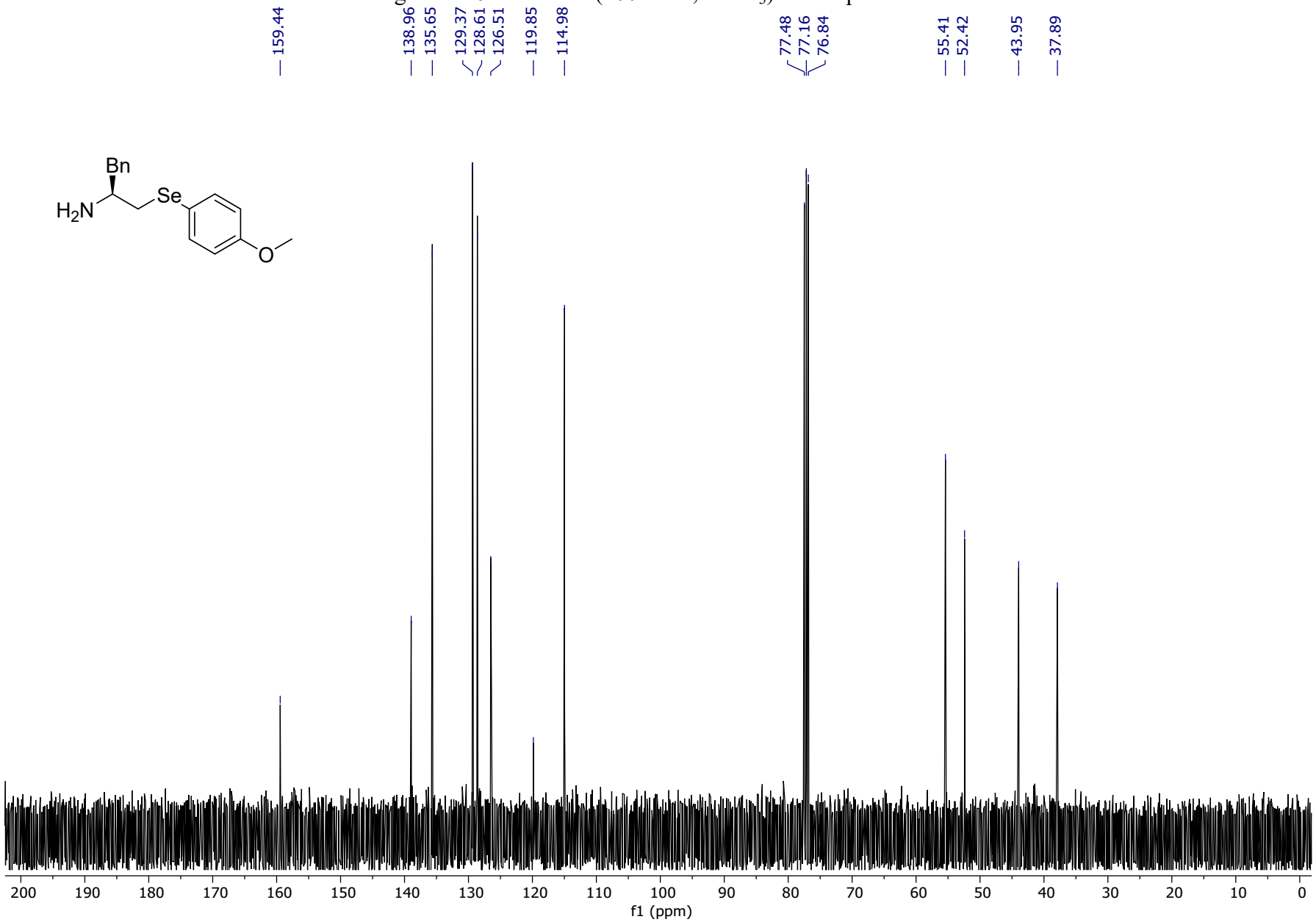


Figure S-17. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2i**.

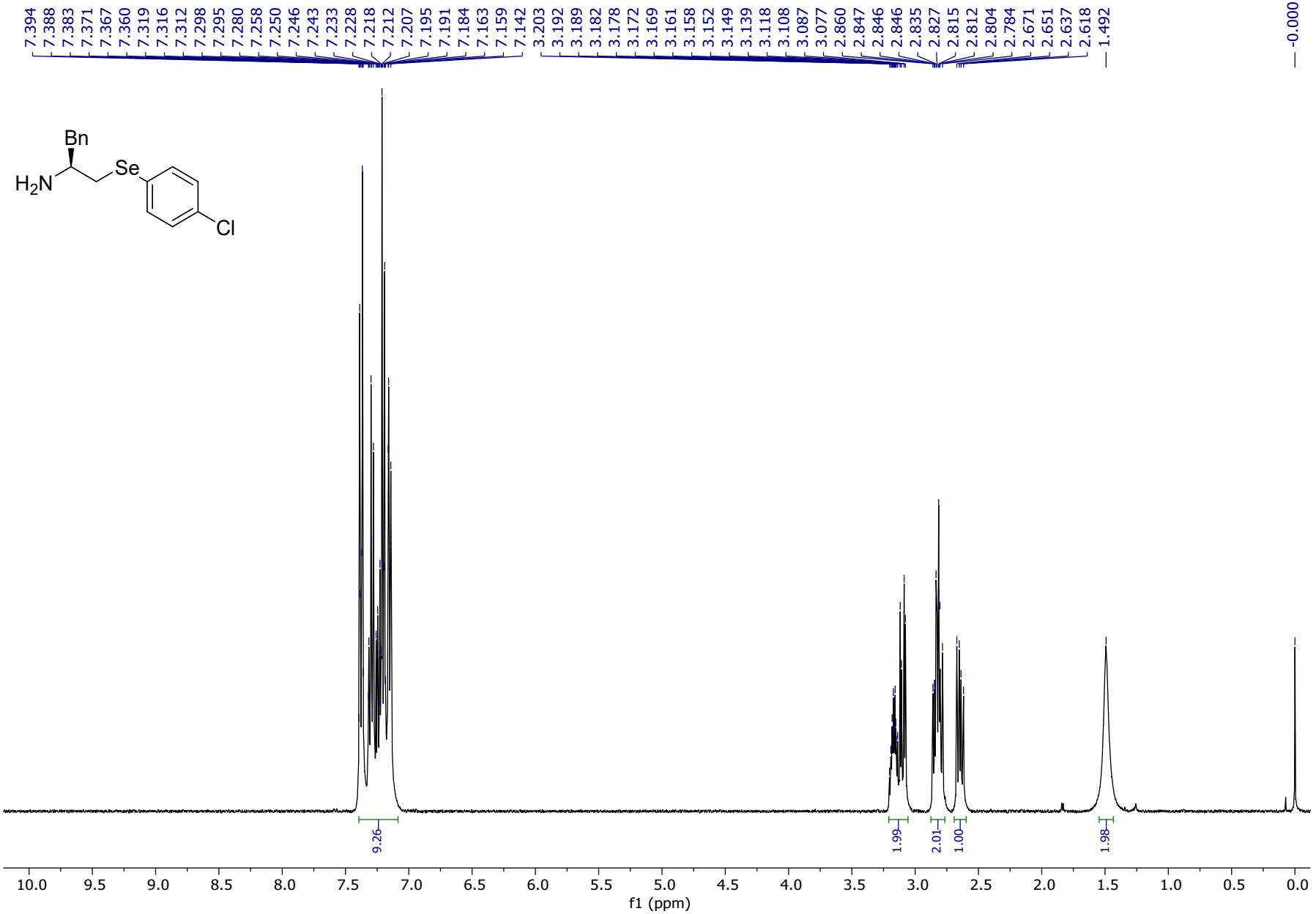


Figure S-18. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2i**.

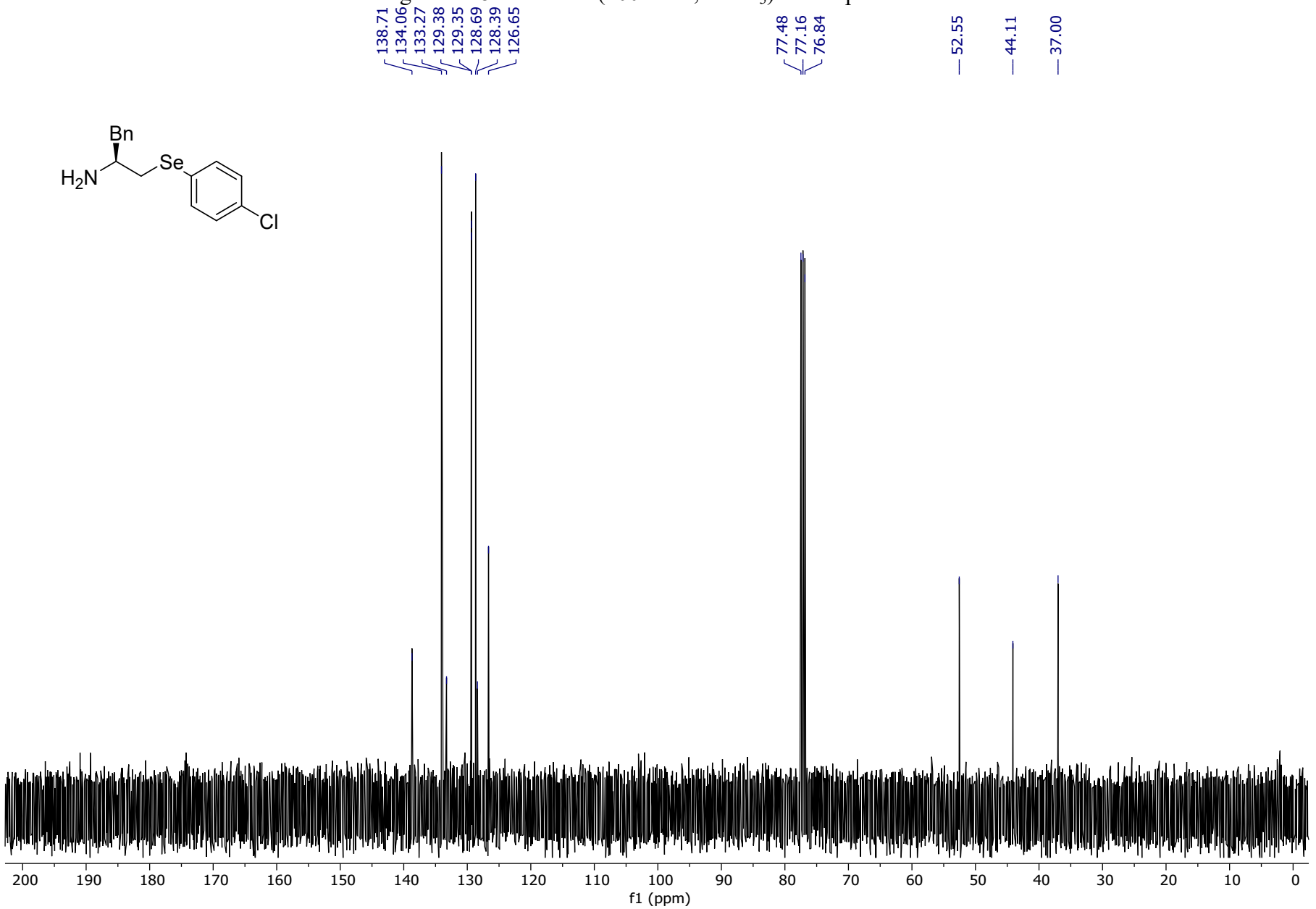


Figure S-19. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2j**.

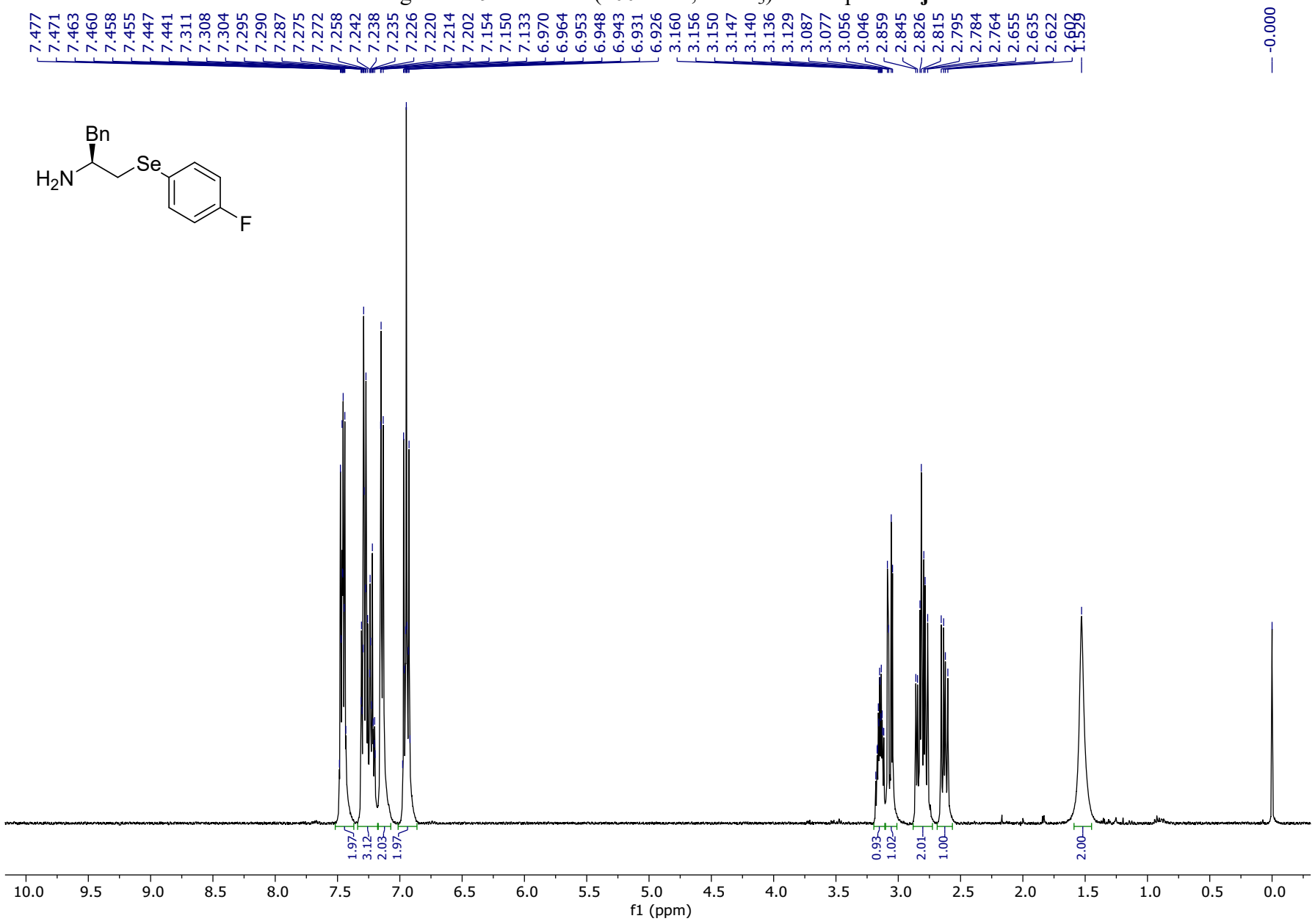


Figure S-20. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2j**.

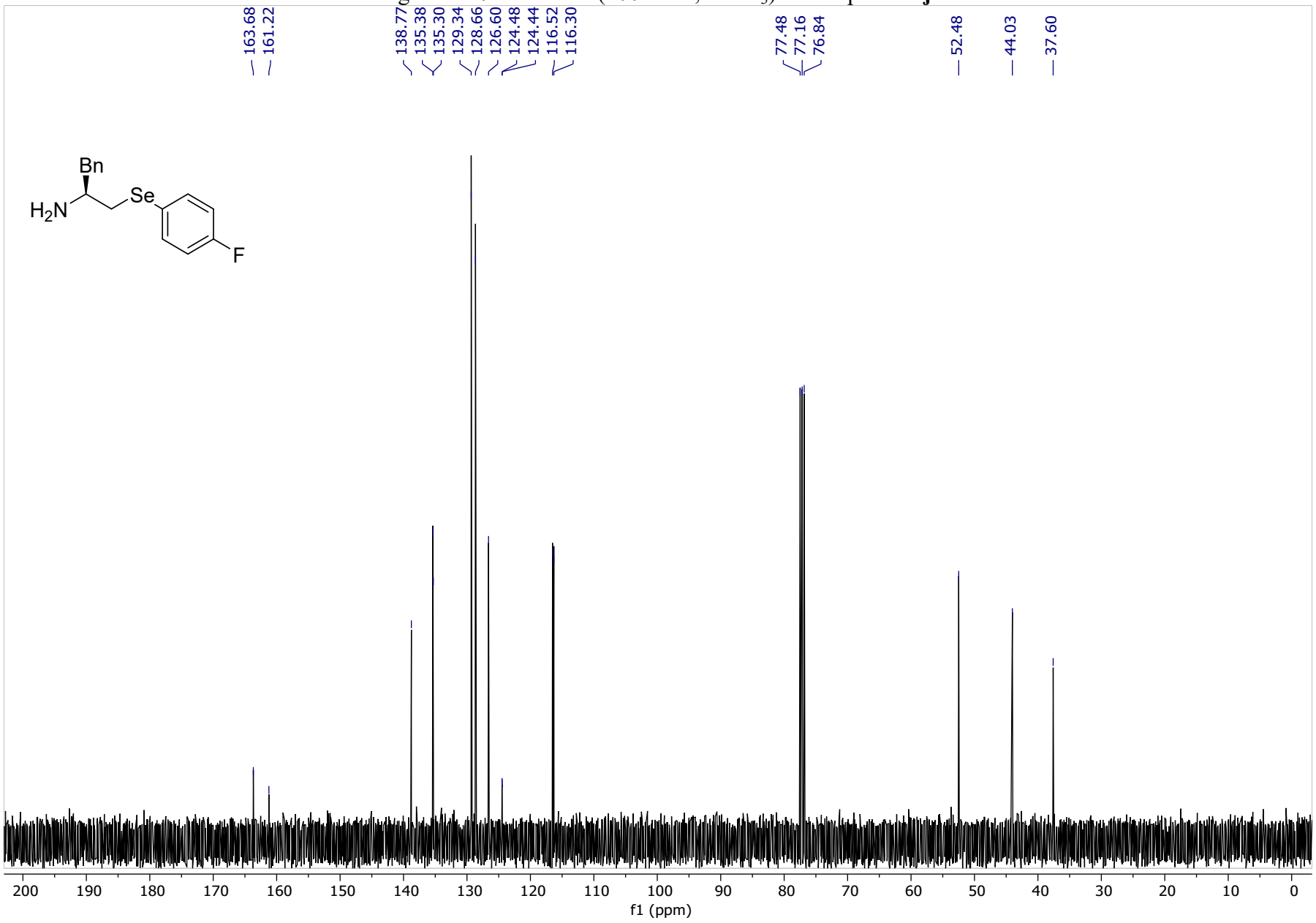


Figure S-21. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2k**.

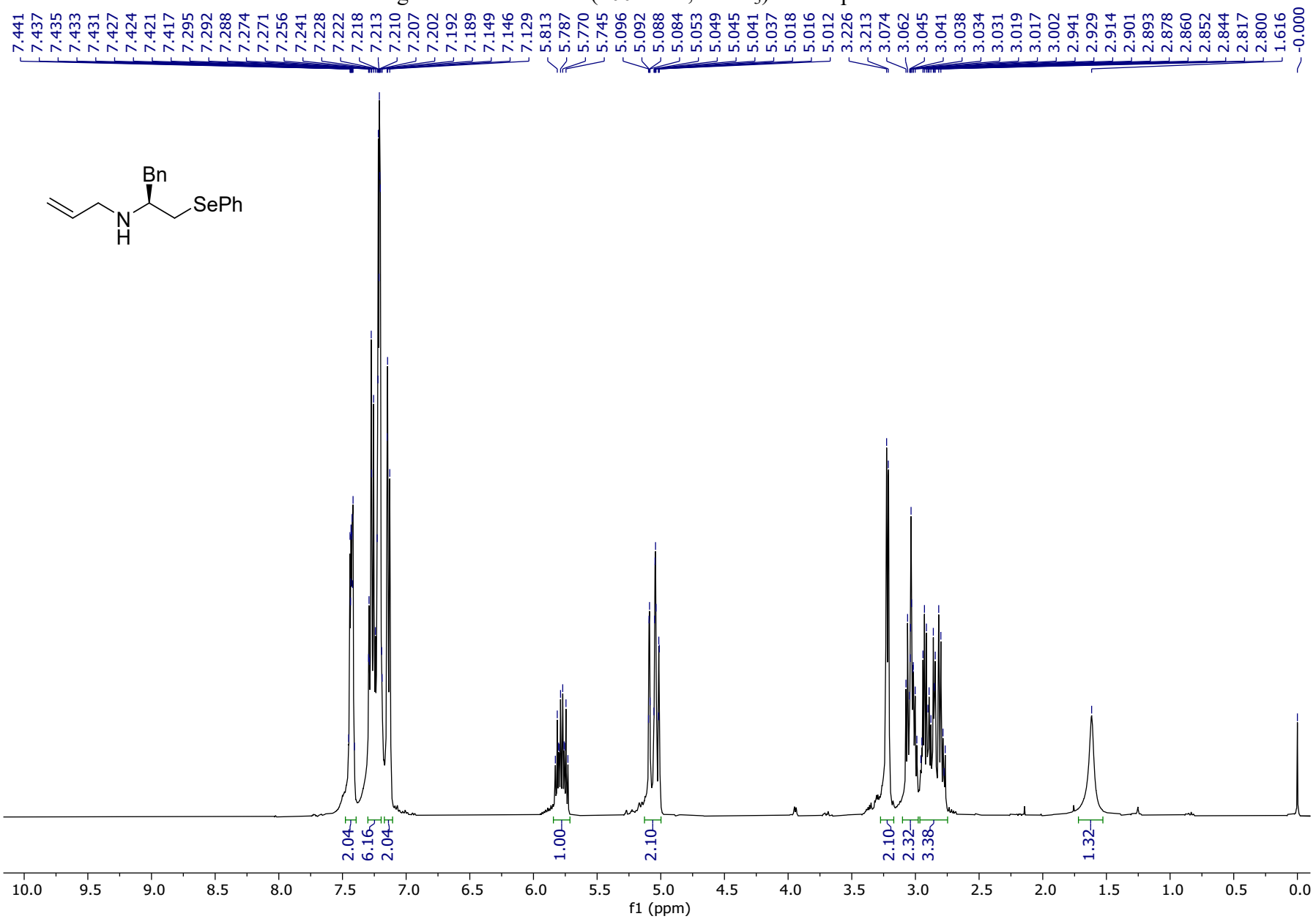


Figure S-22. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2k**.

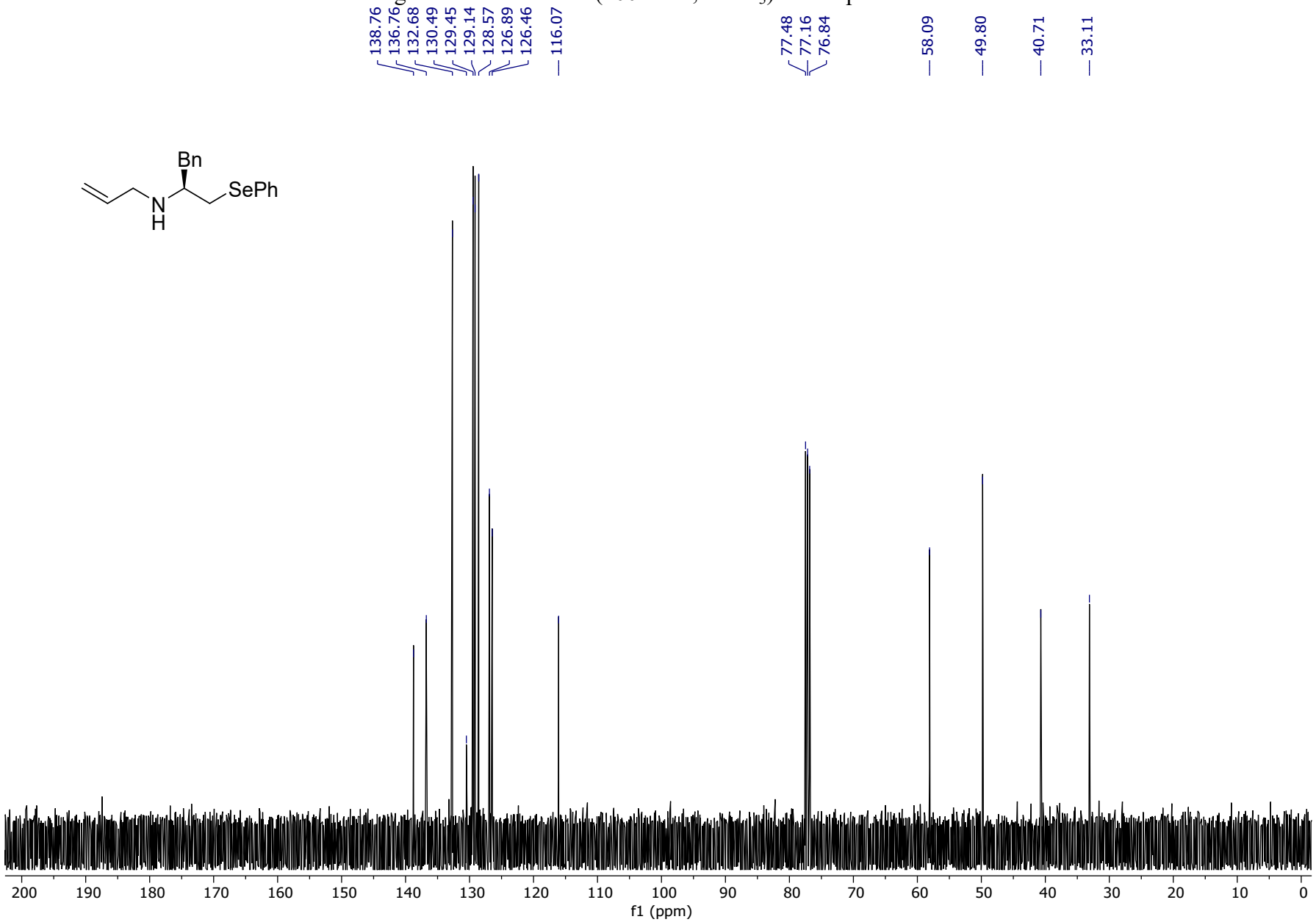


Figure S-23. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2l**.

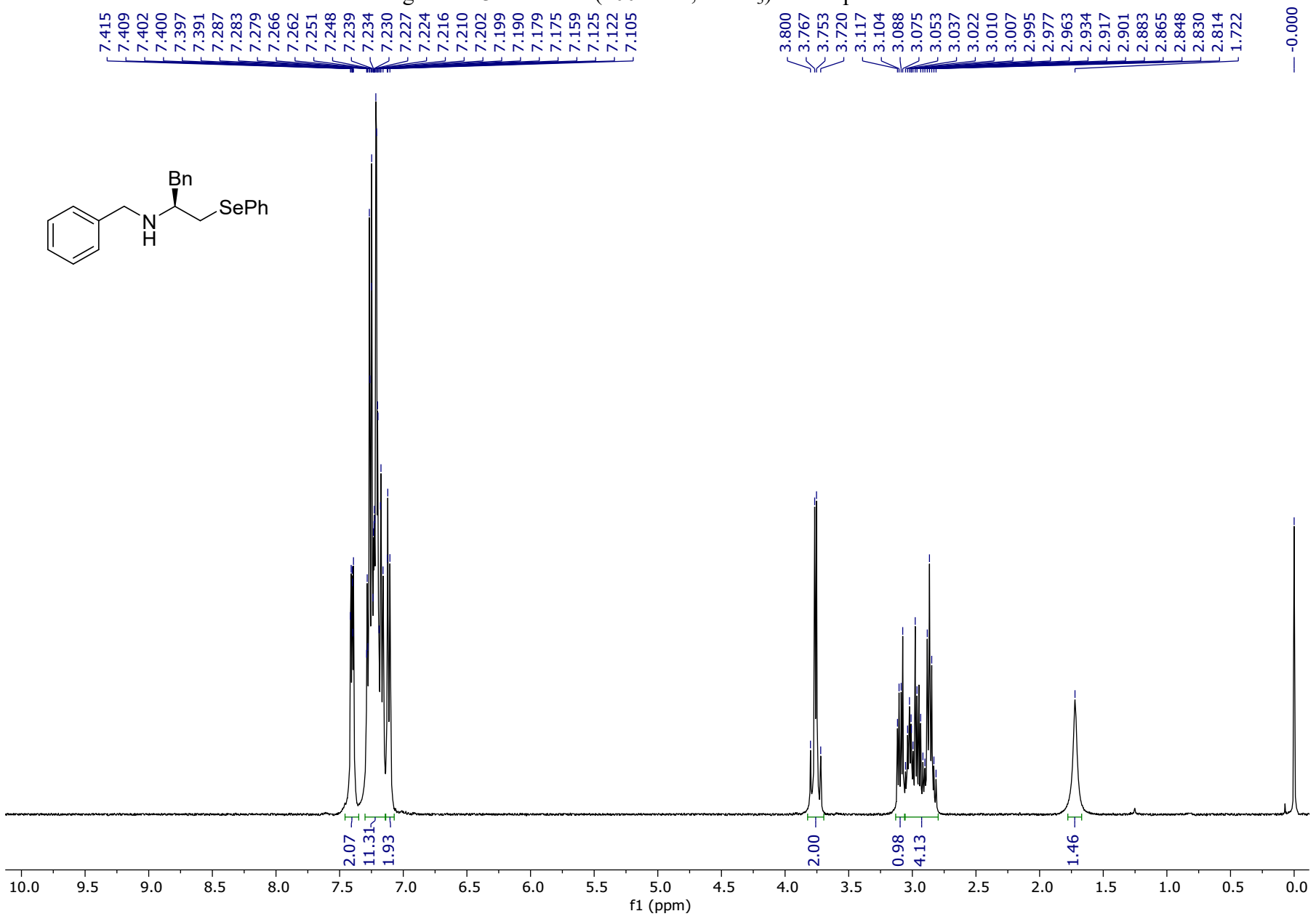


Figure S-24. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2l**.

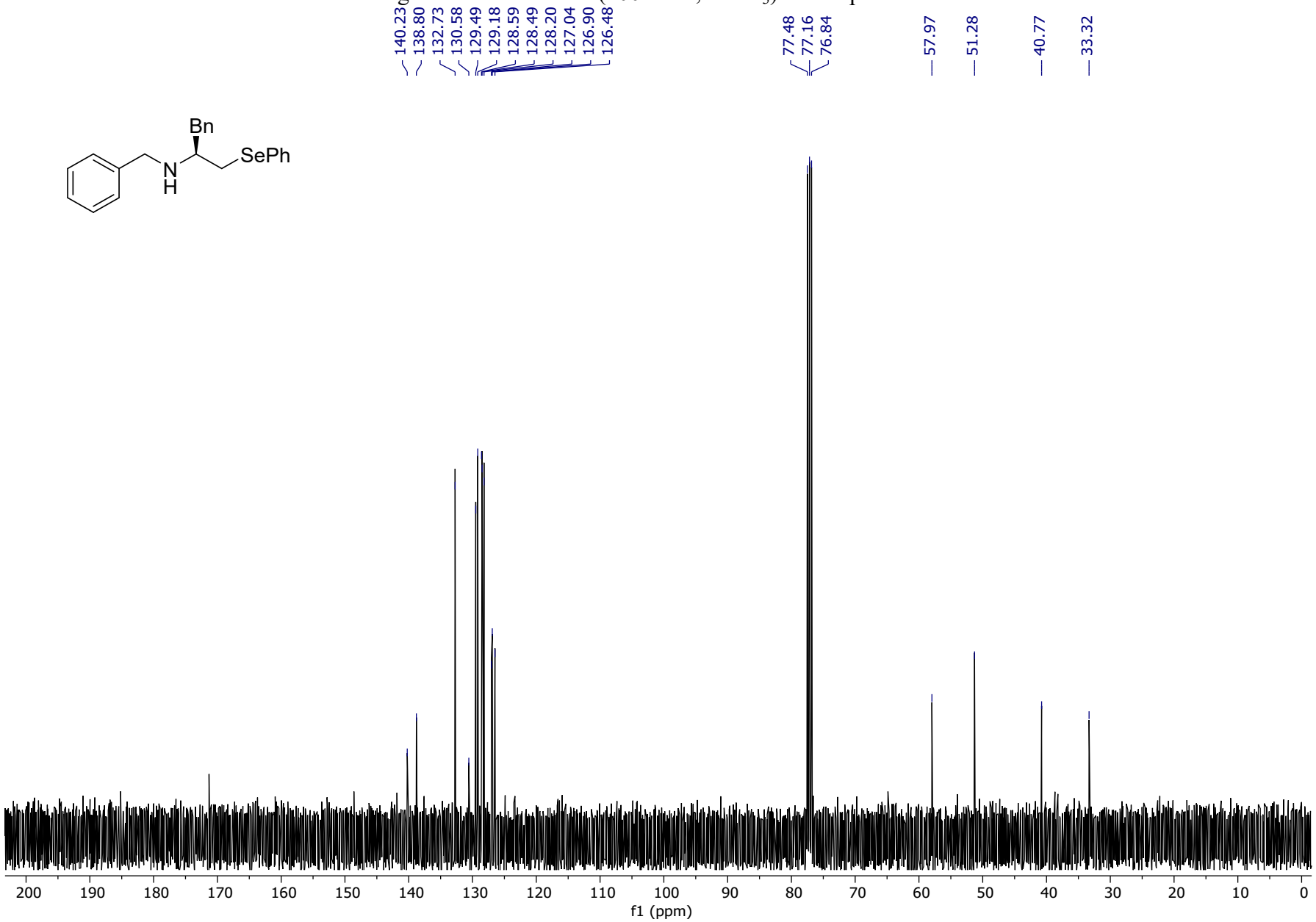


Figure S-25. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2m**.

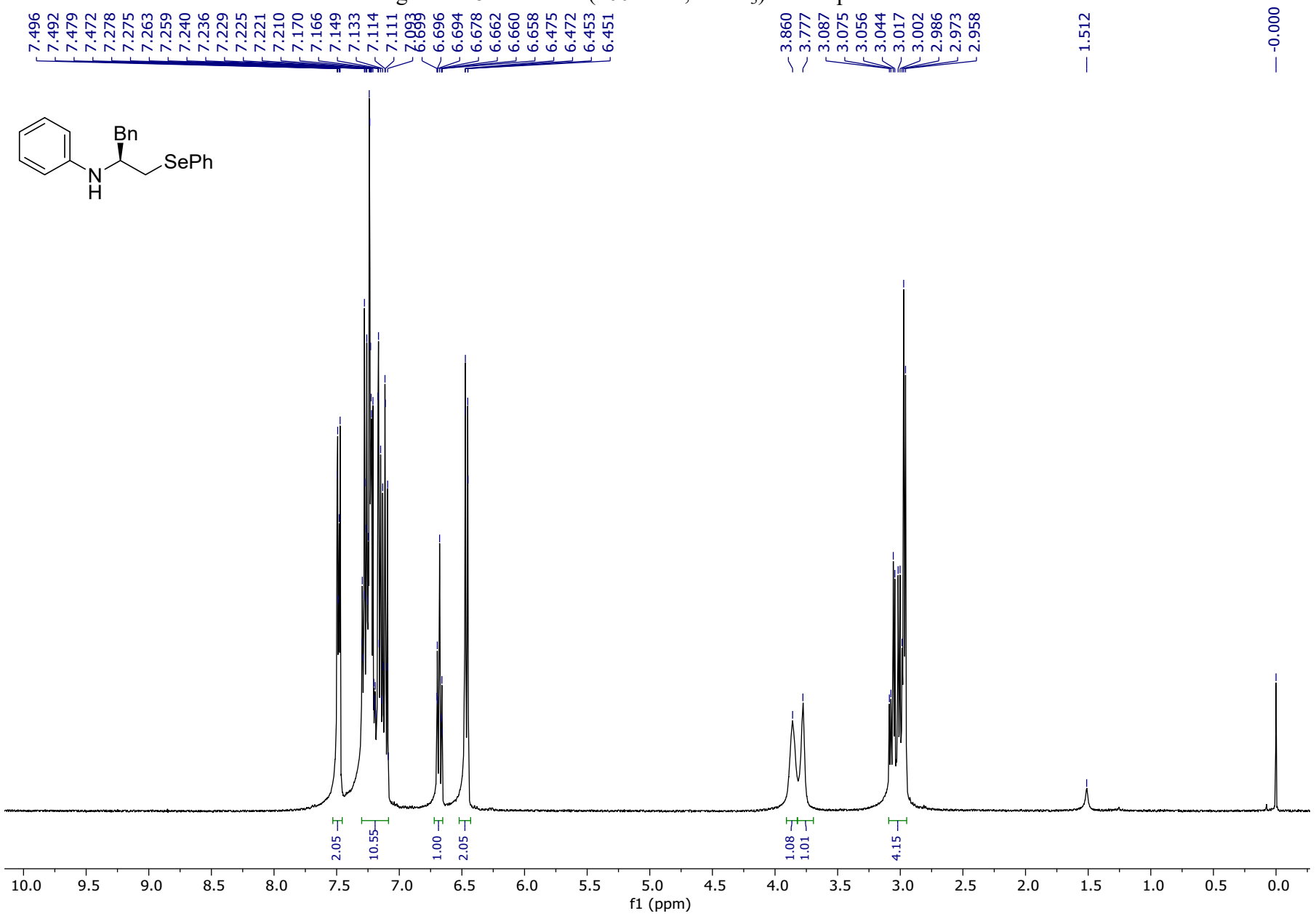


Figure S-26. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2m**.

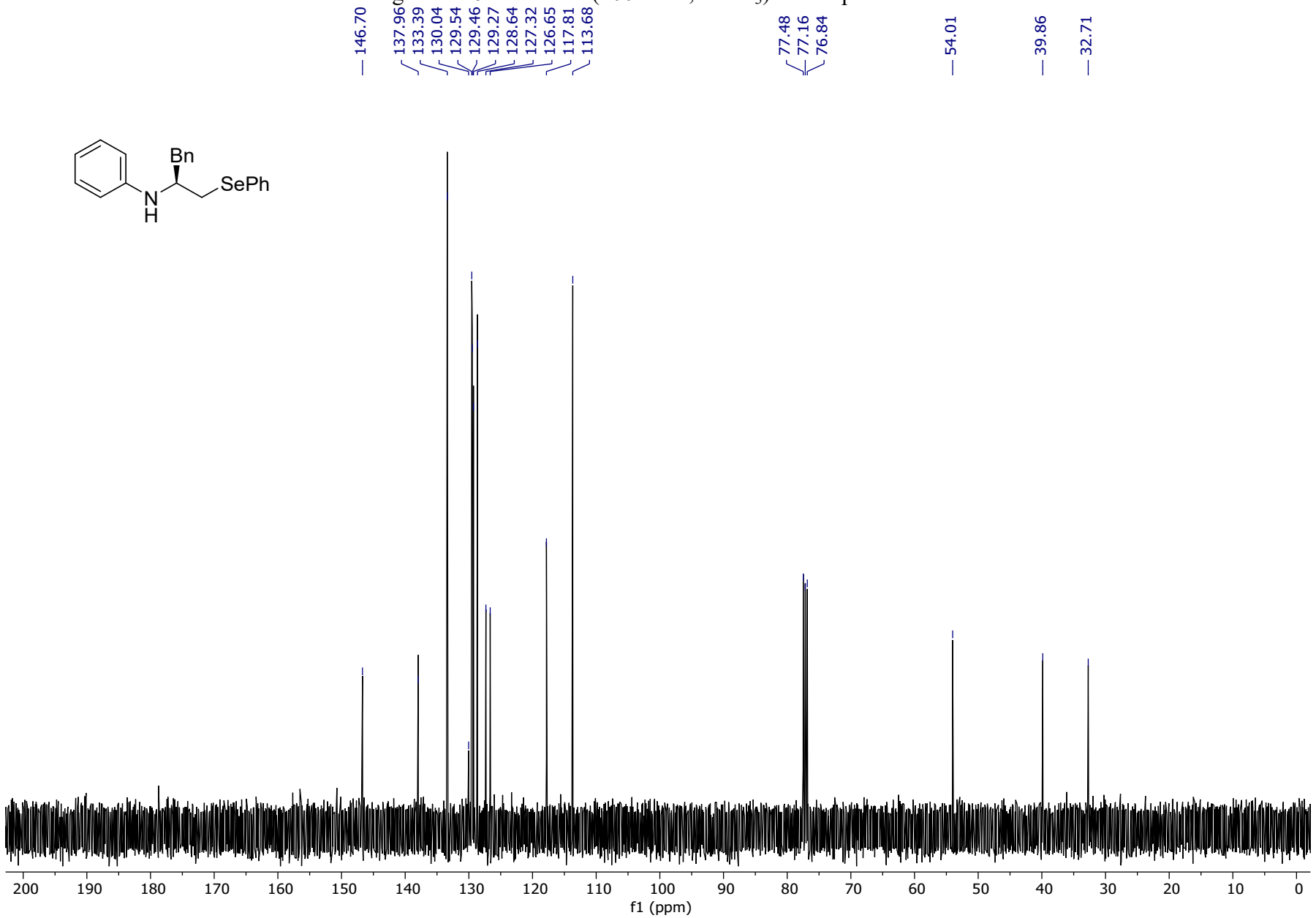


Figure S-27. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2n**.

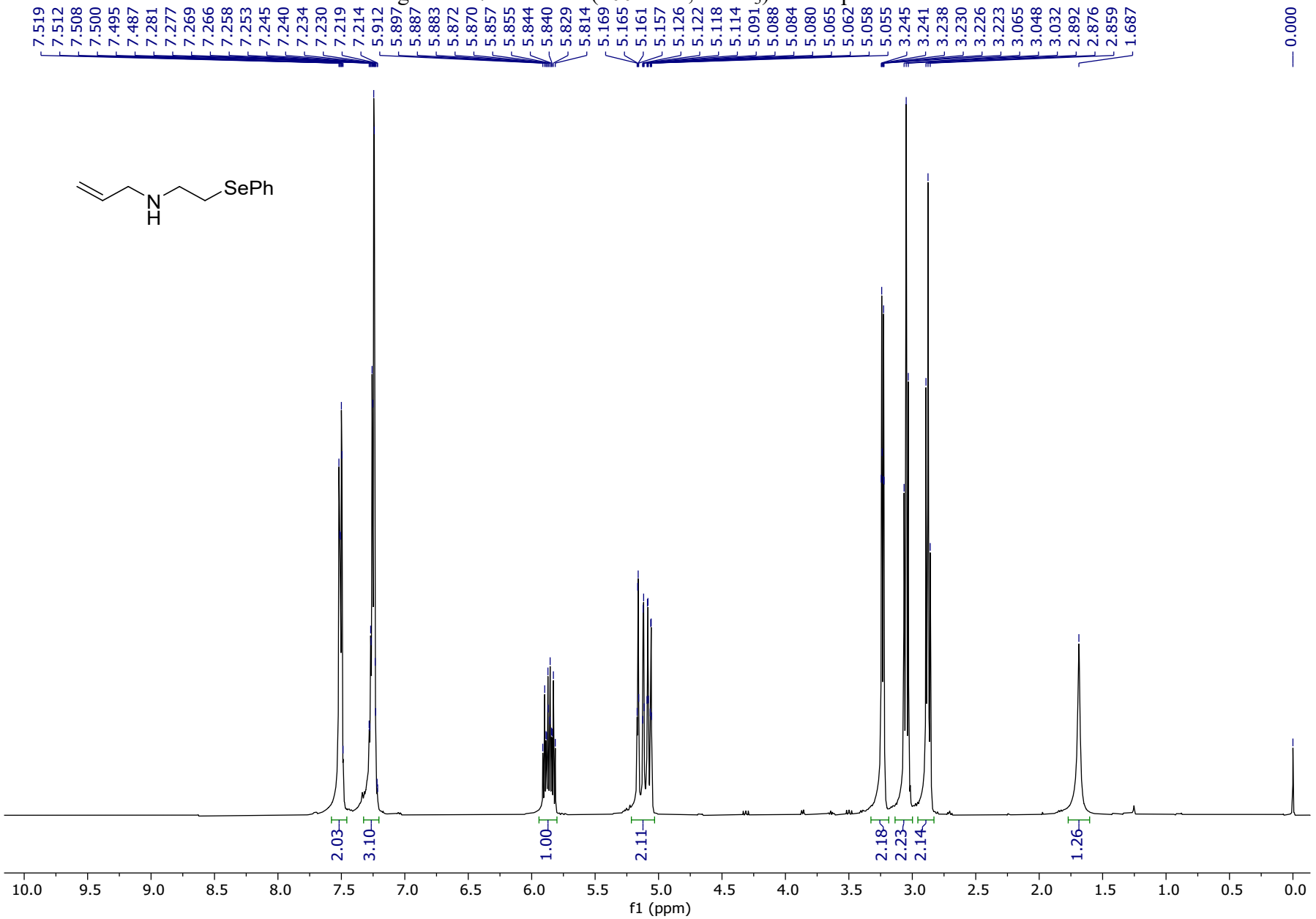


Figure S-28. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2n**.

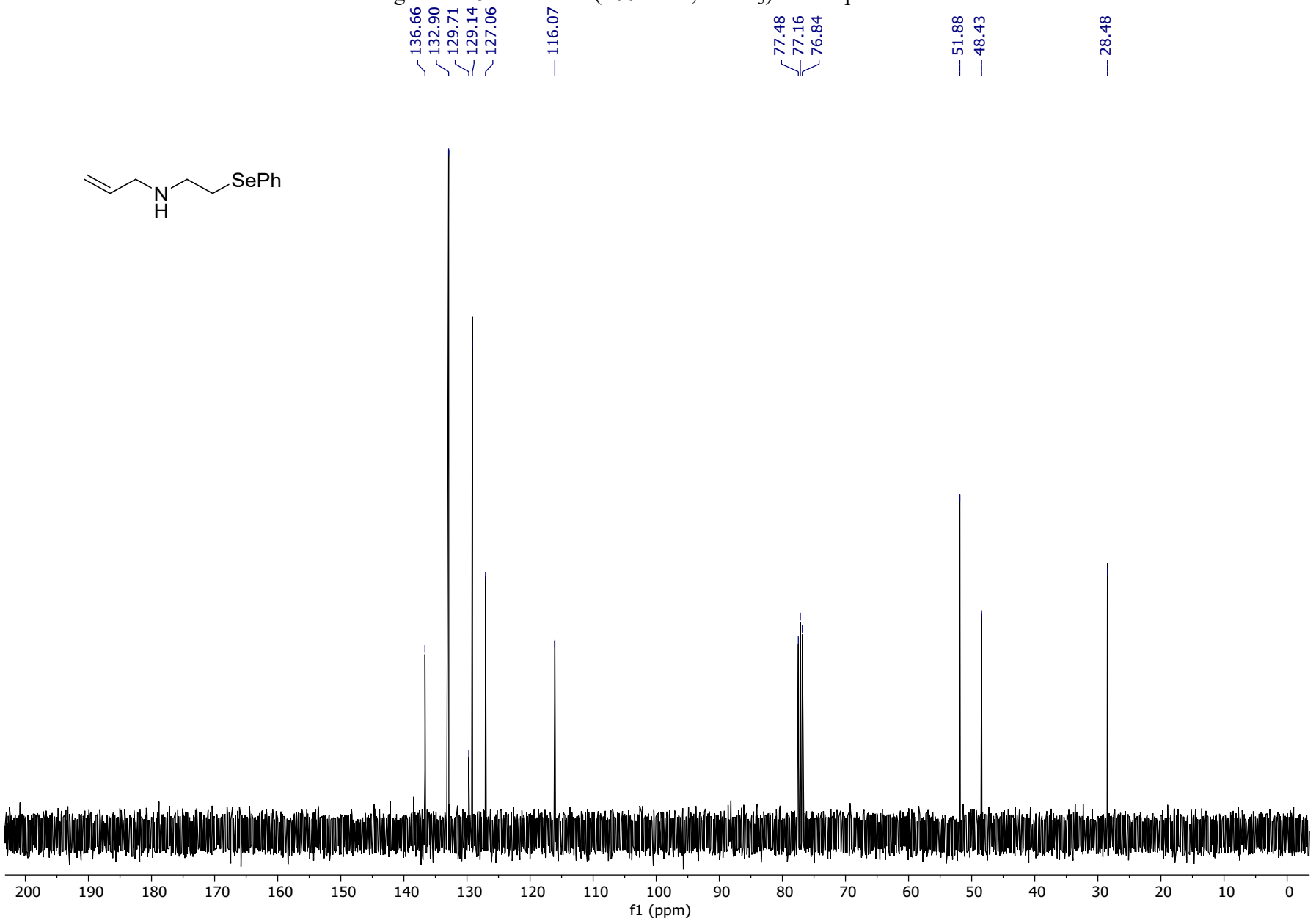


Figure S-29. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2o**.

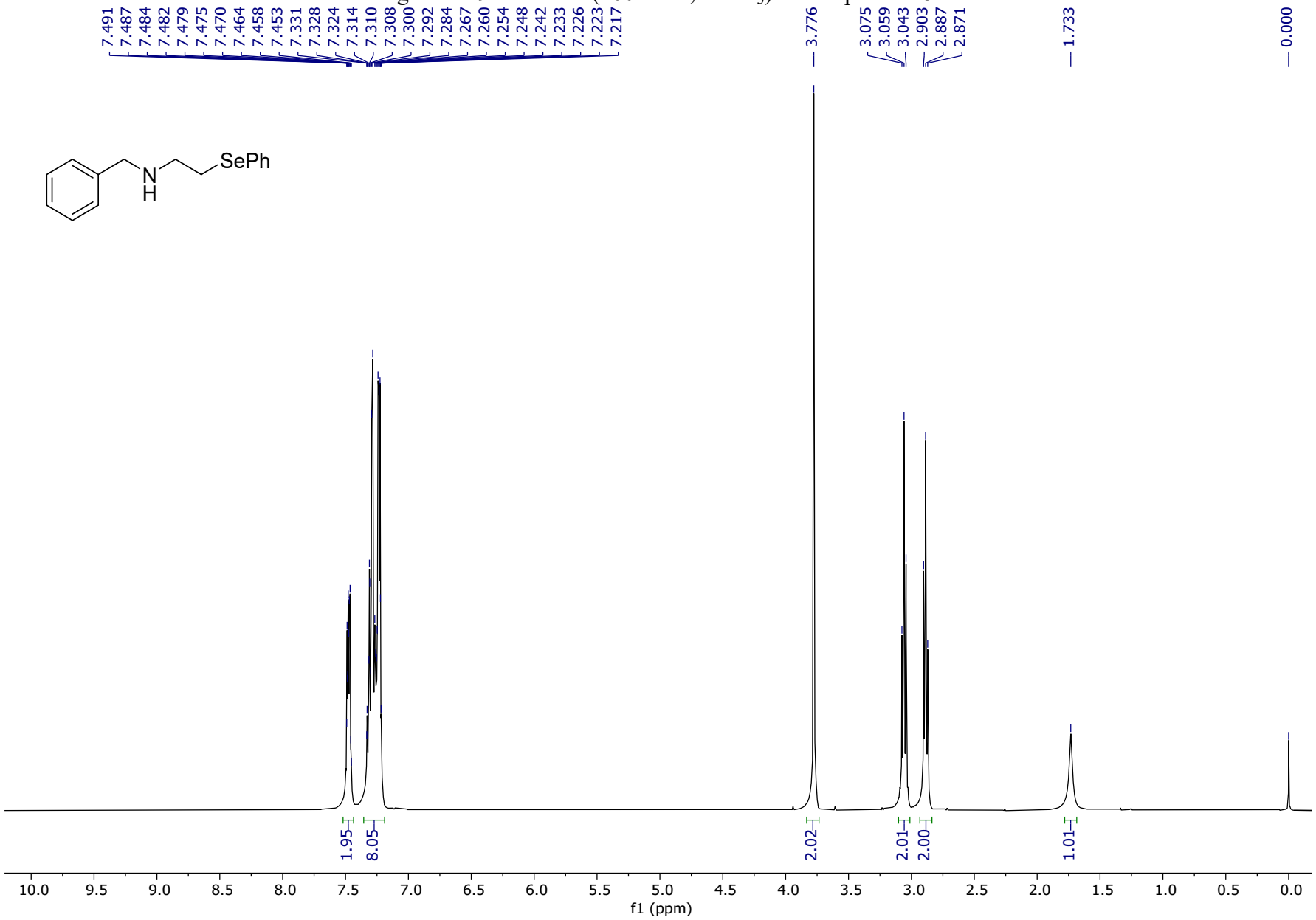


Figure S-30. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2o**.

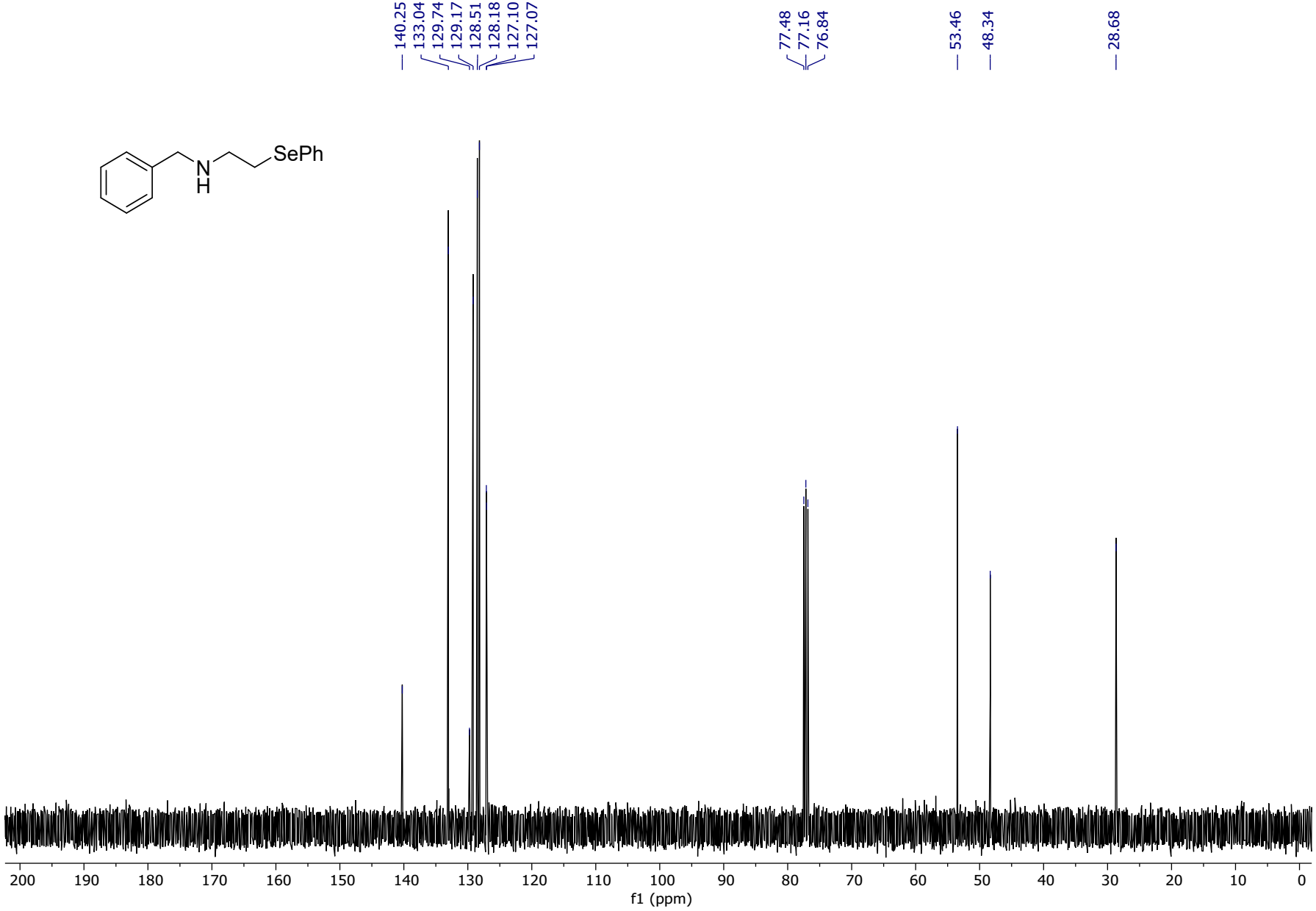


Figure S-31. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2p**.

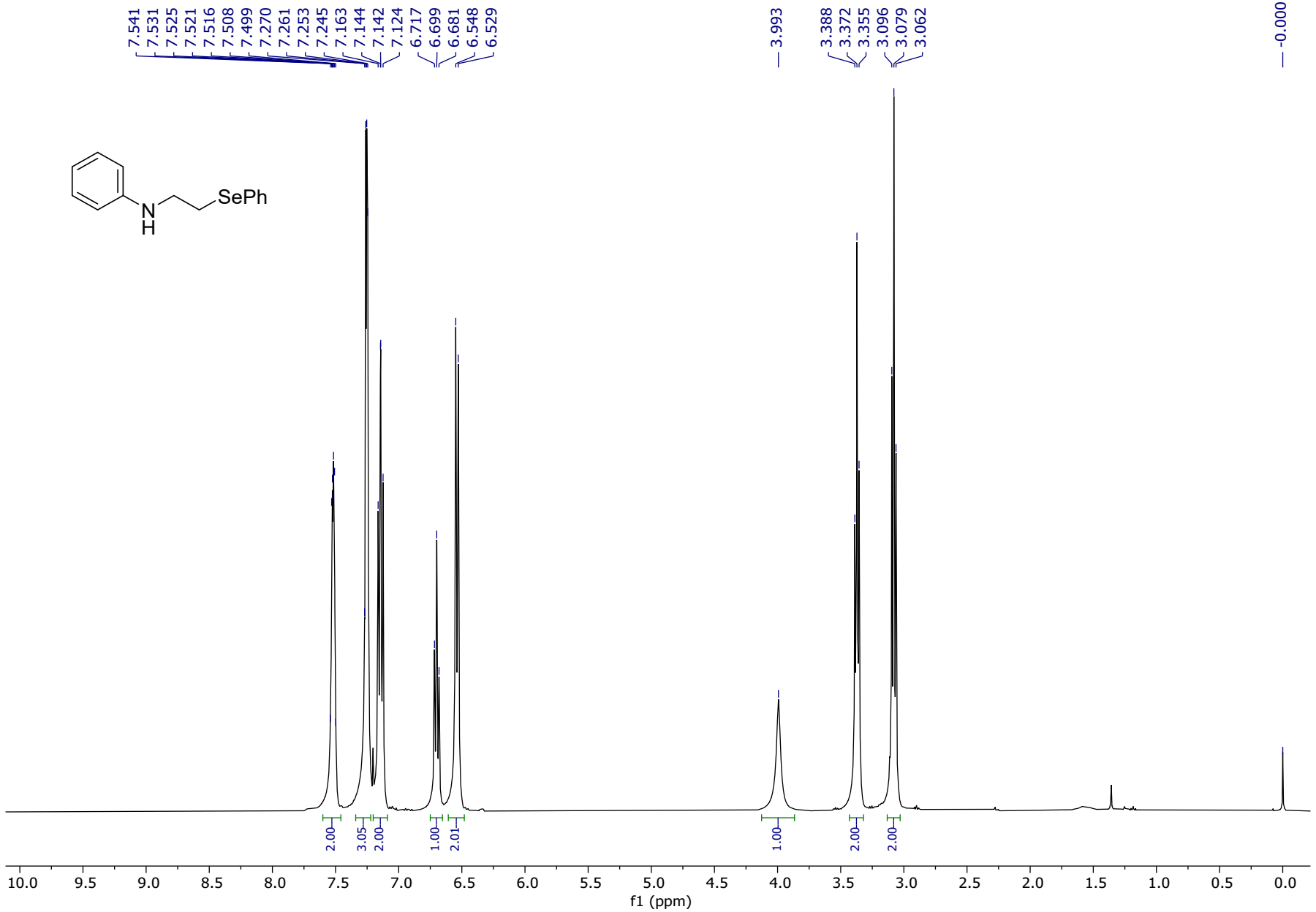


Figure S-32. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2p**.

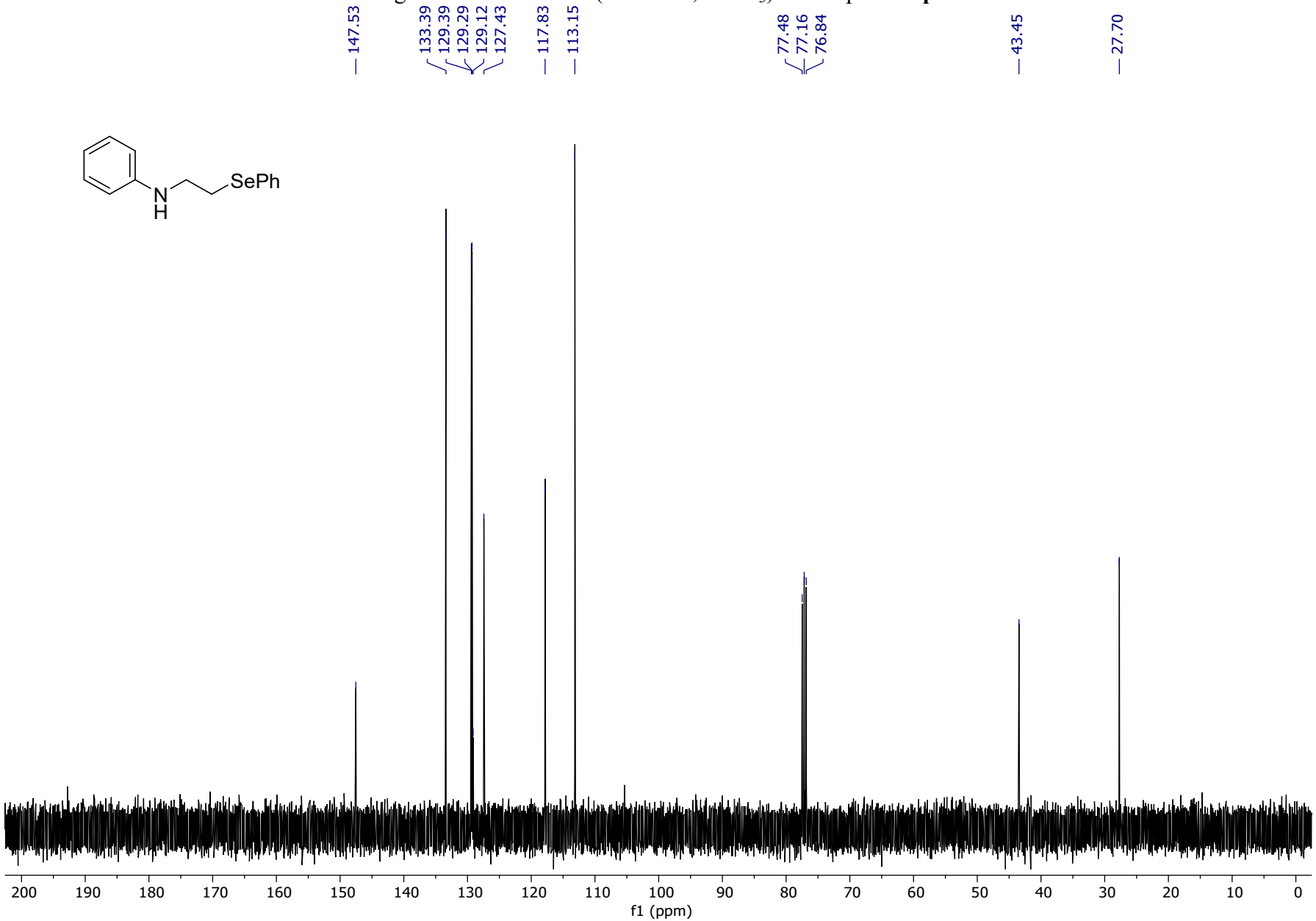


Figure S-33. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2q**.

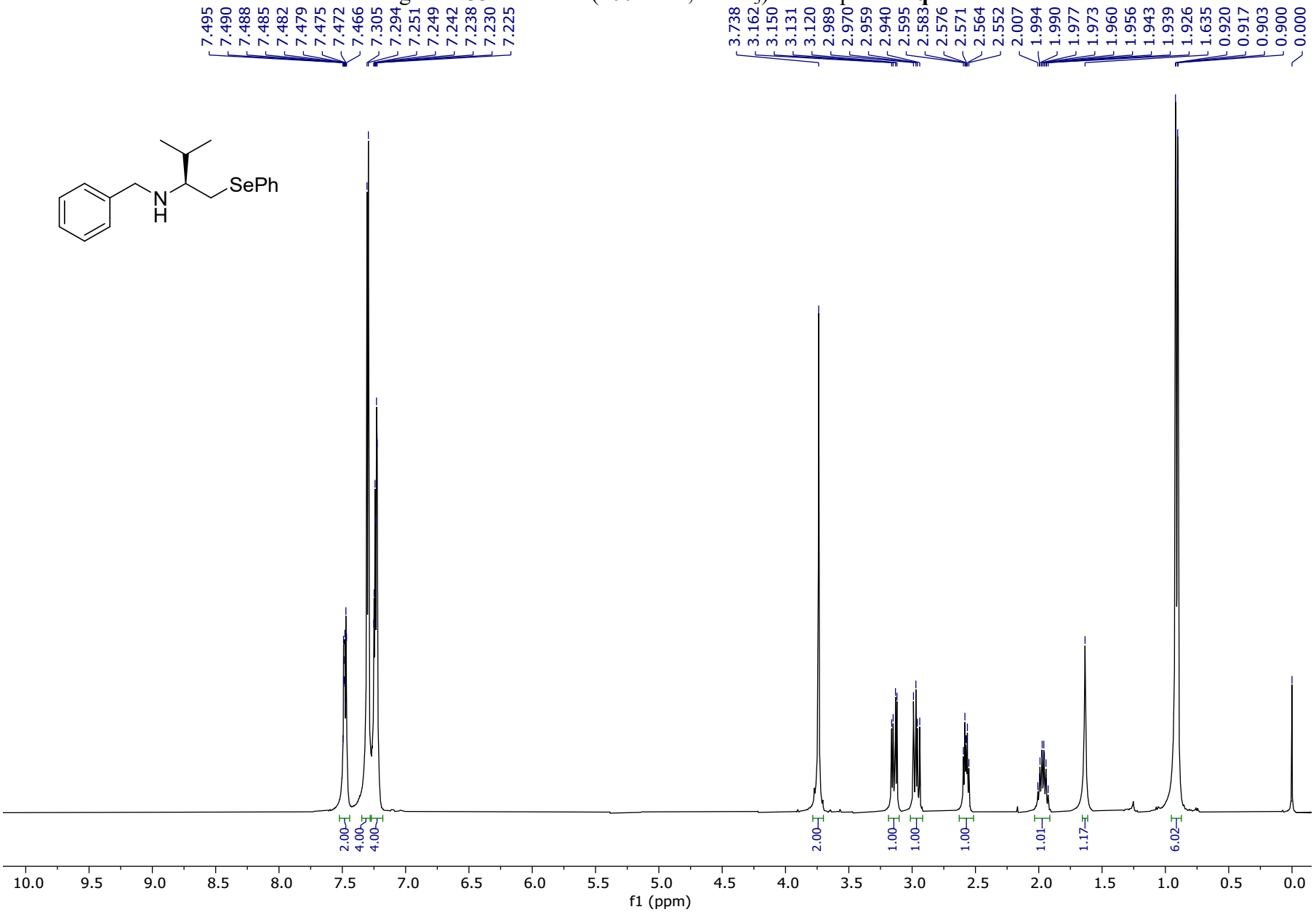


Figure S-34. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2q**.

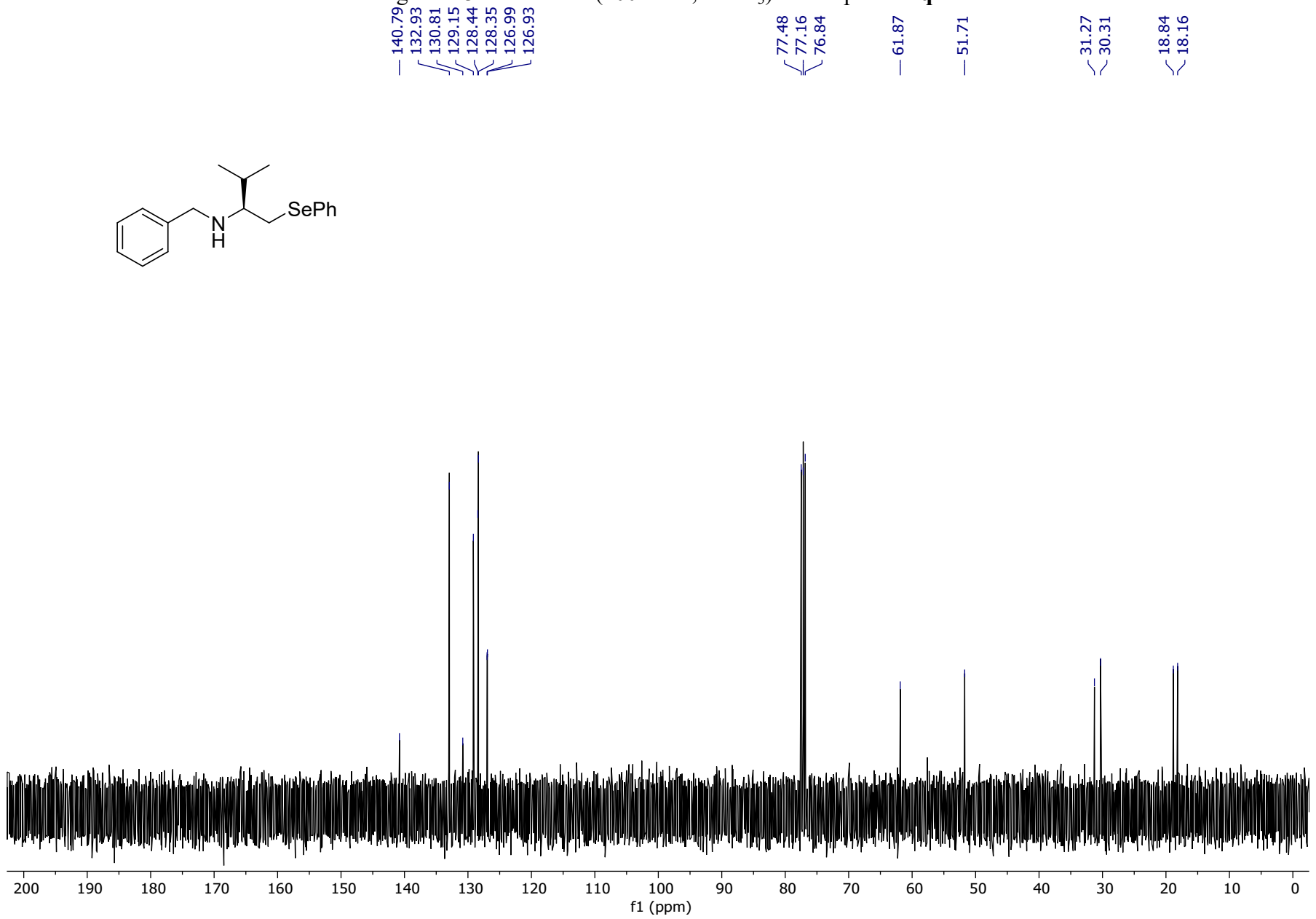


Figure S-35. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**.

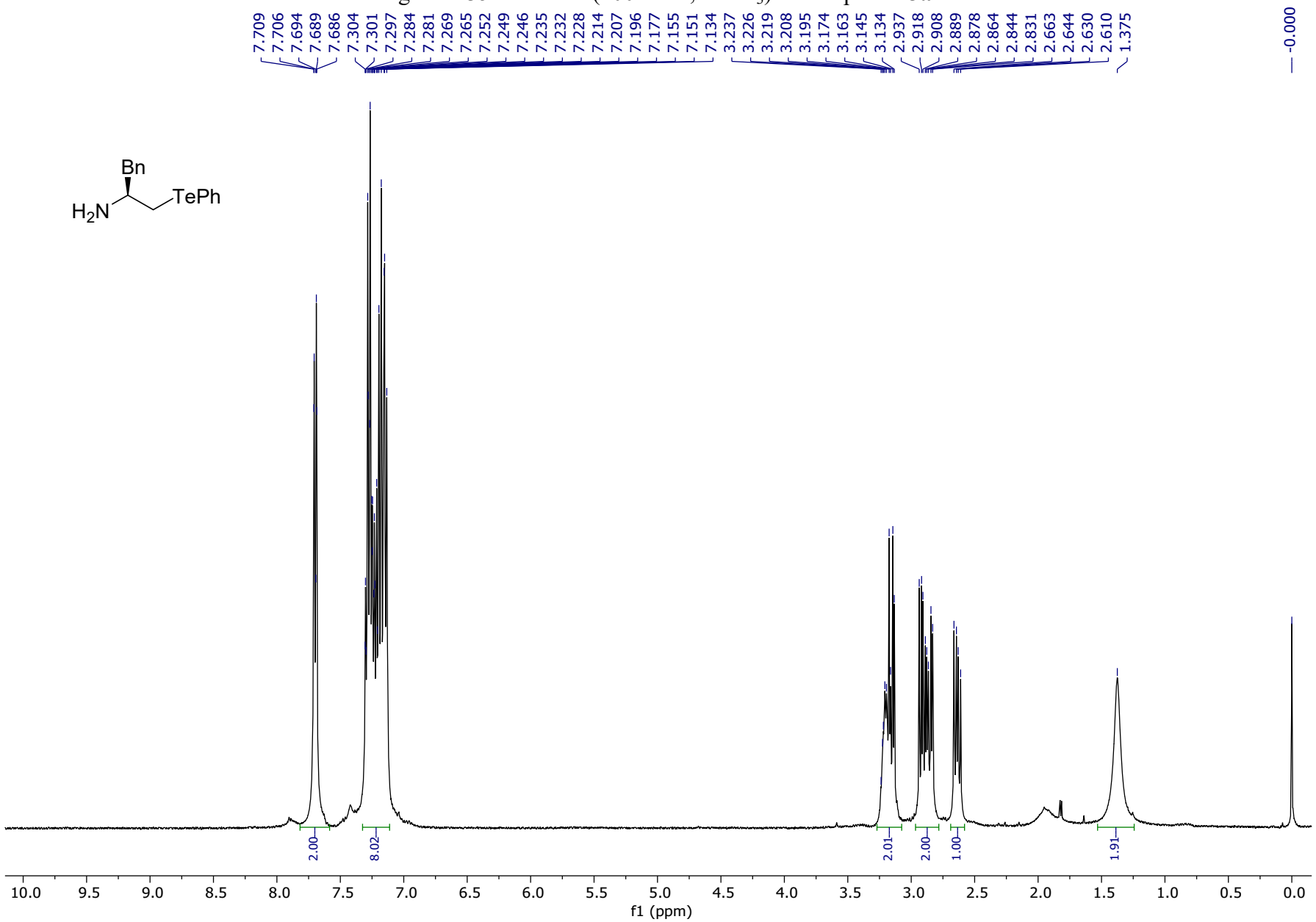


Figure S-36. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**.

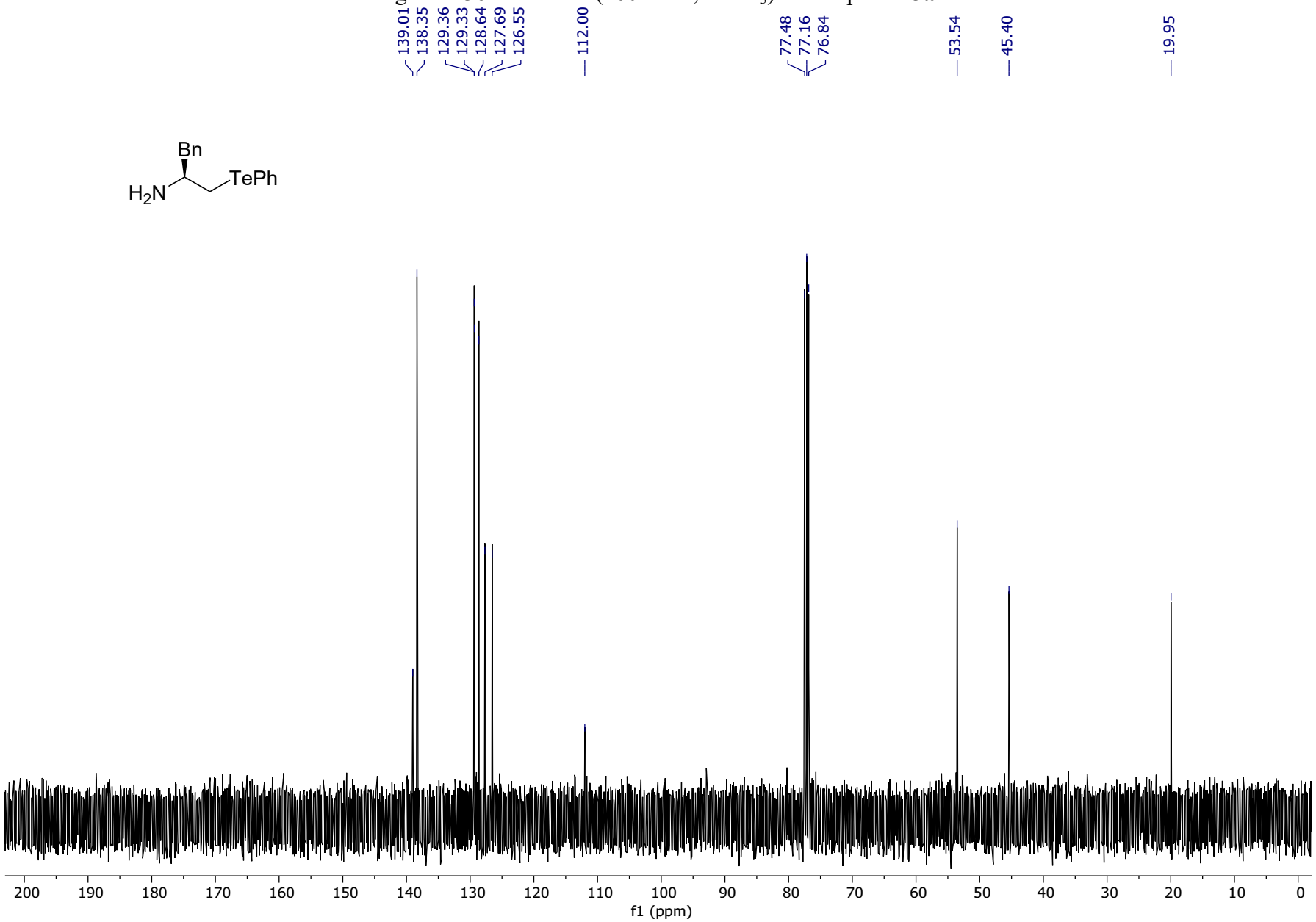


Figure S-37. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**.

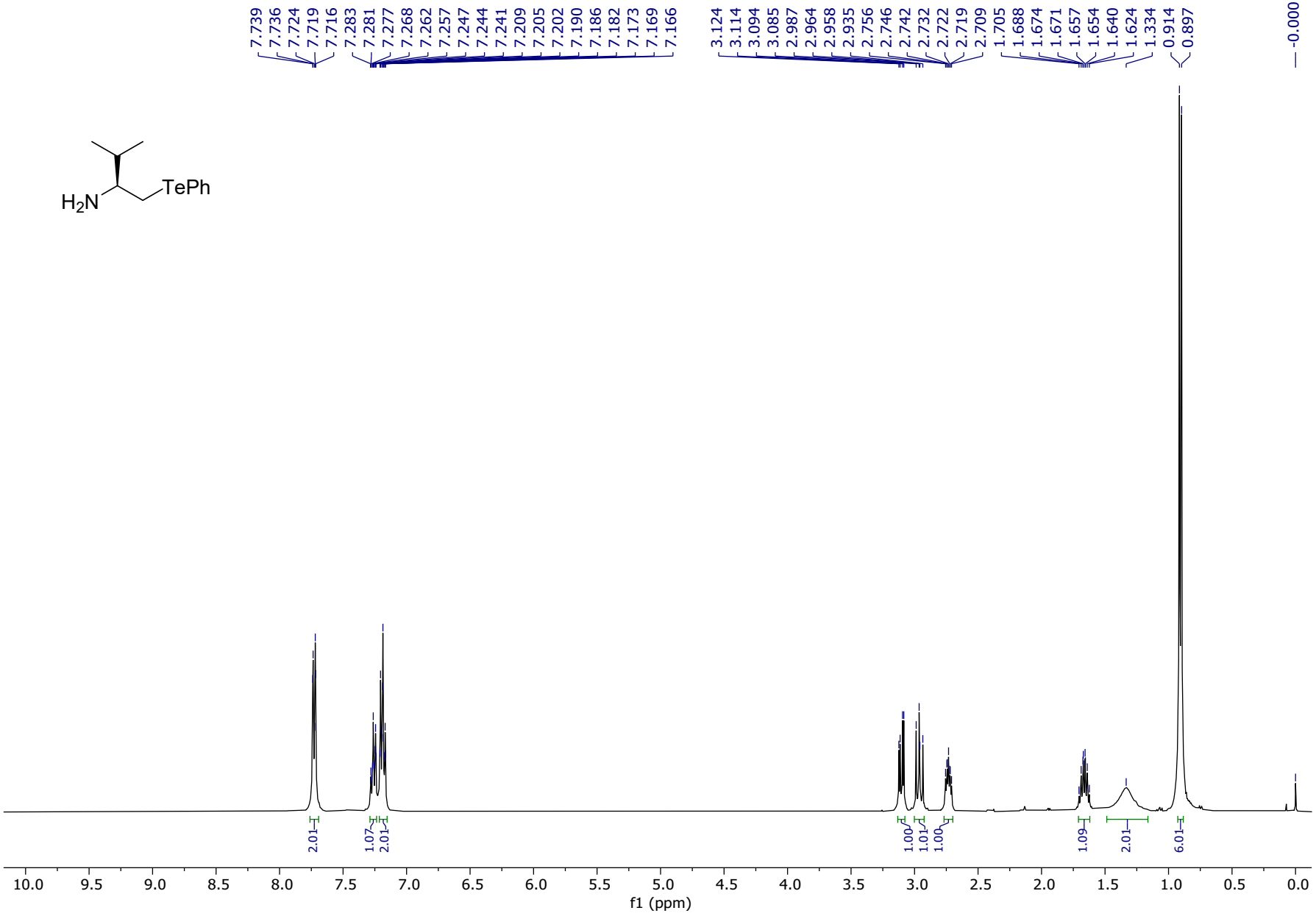


Figure S-38. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3b**.

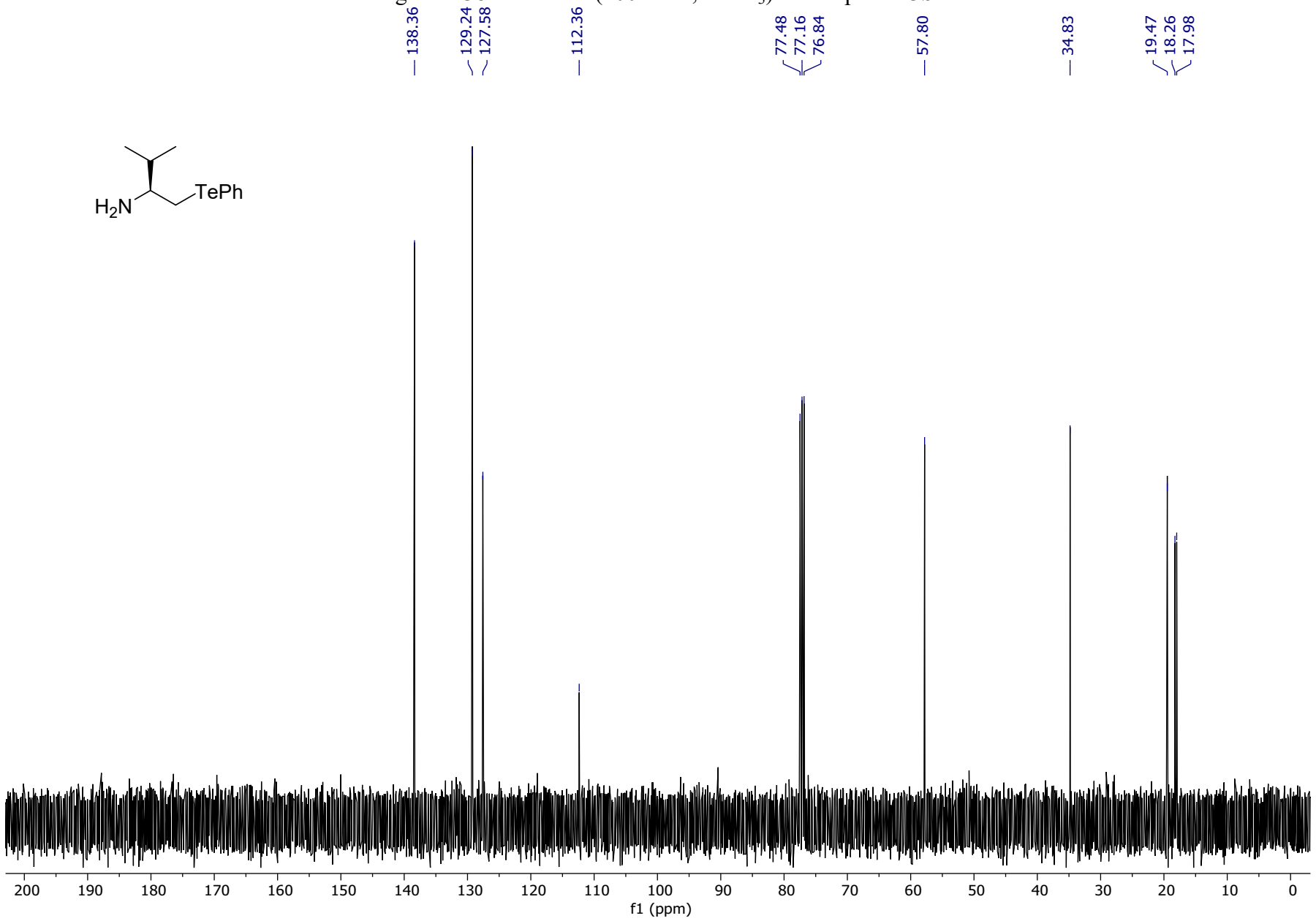


Figure S-39. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**.

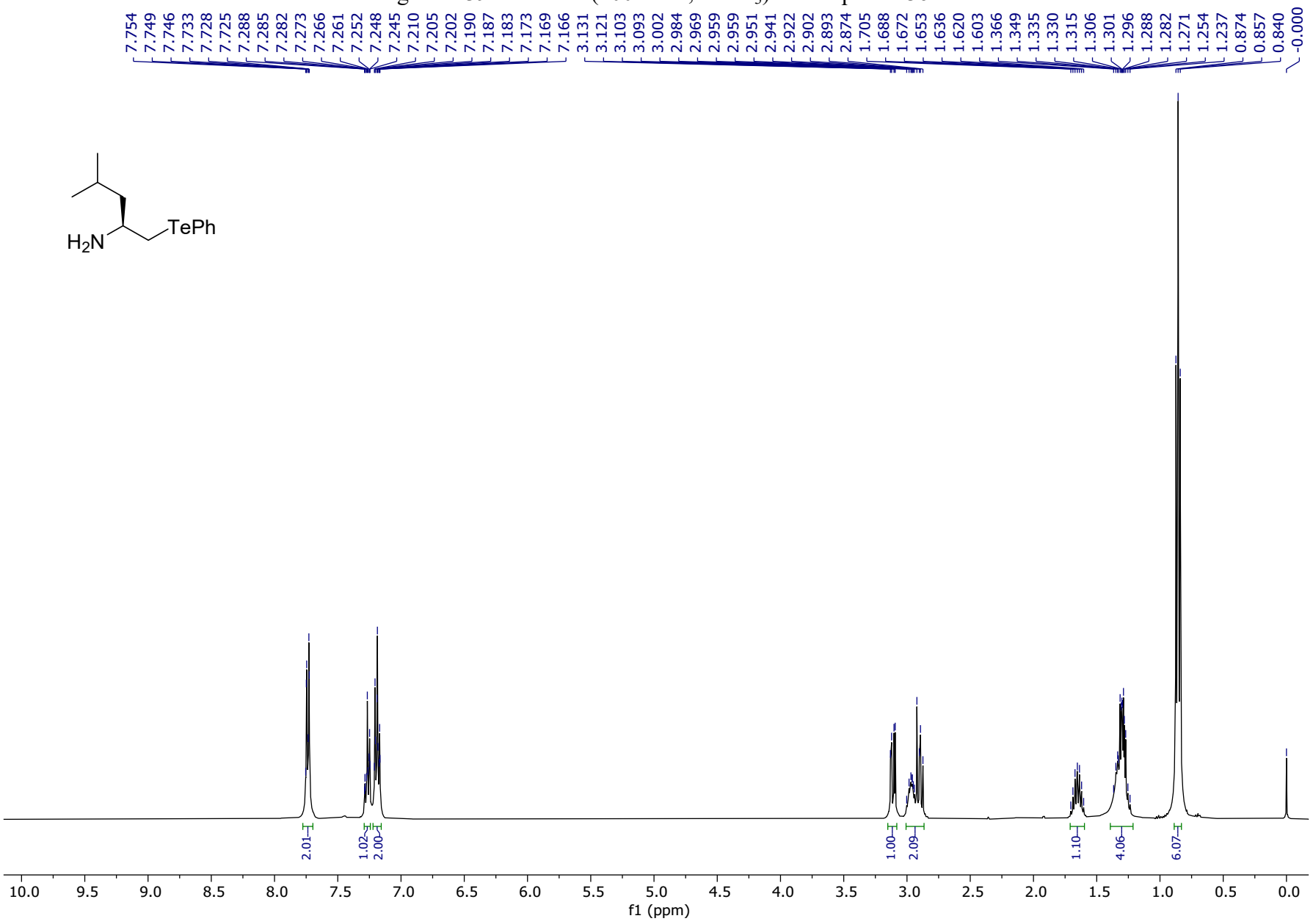


Figure S-40. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3c**.

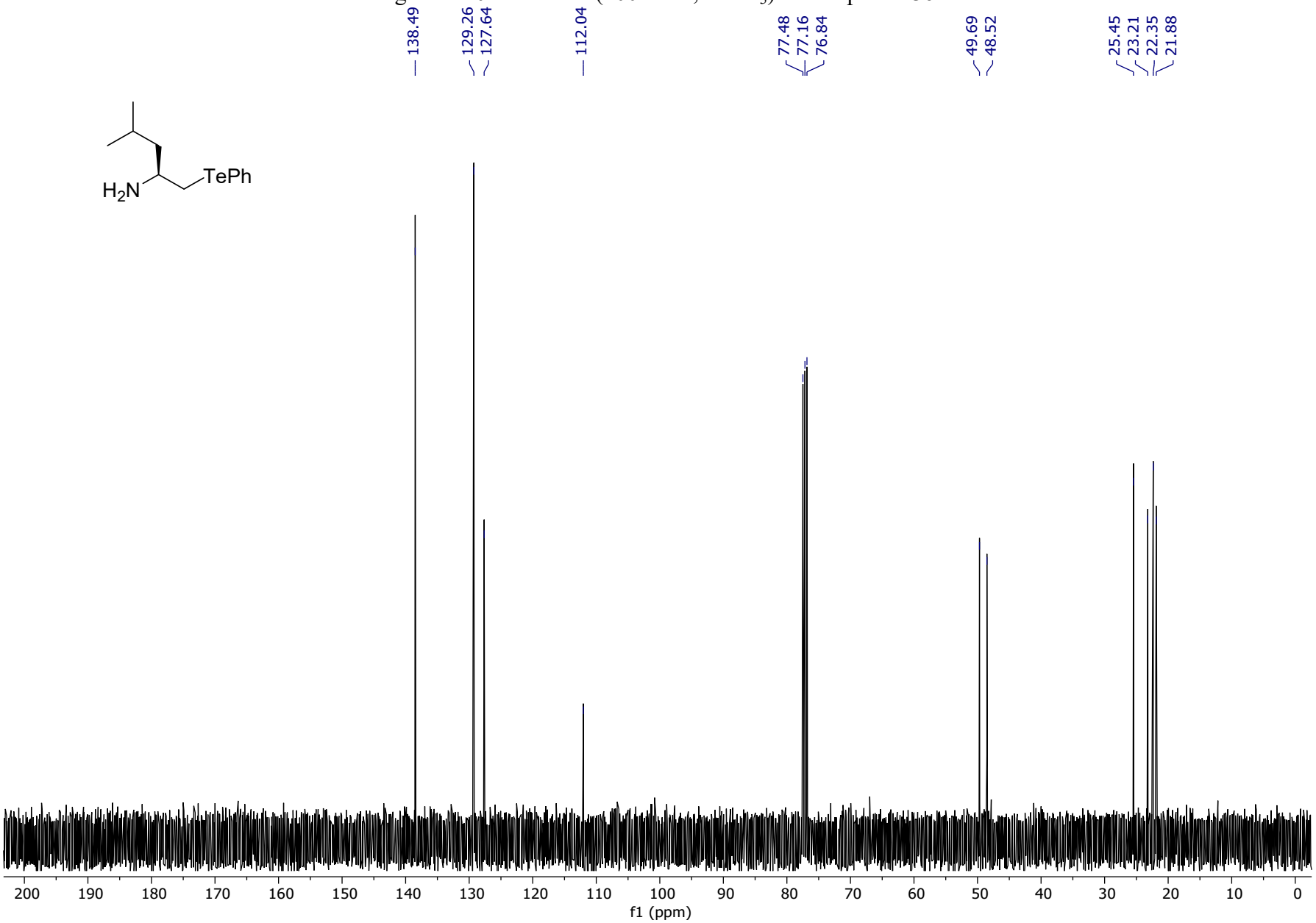


Figure S-41. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**.

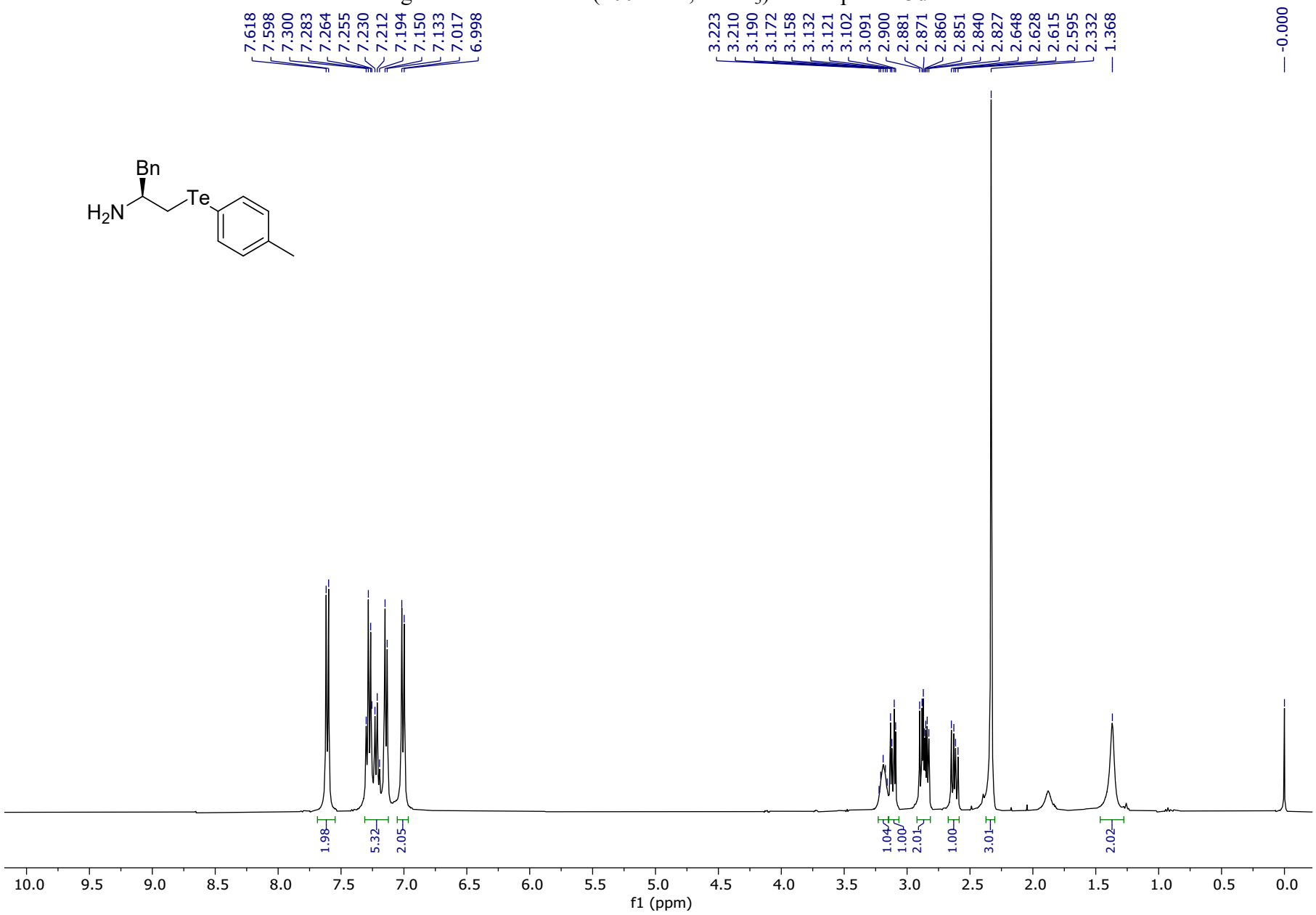


Figure S-42. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**.

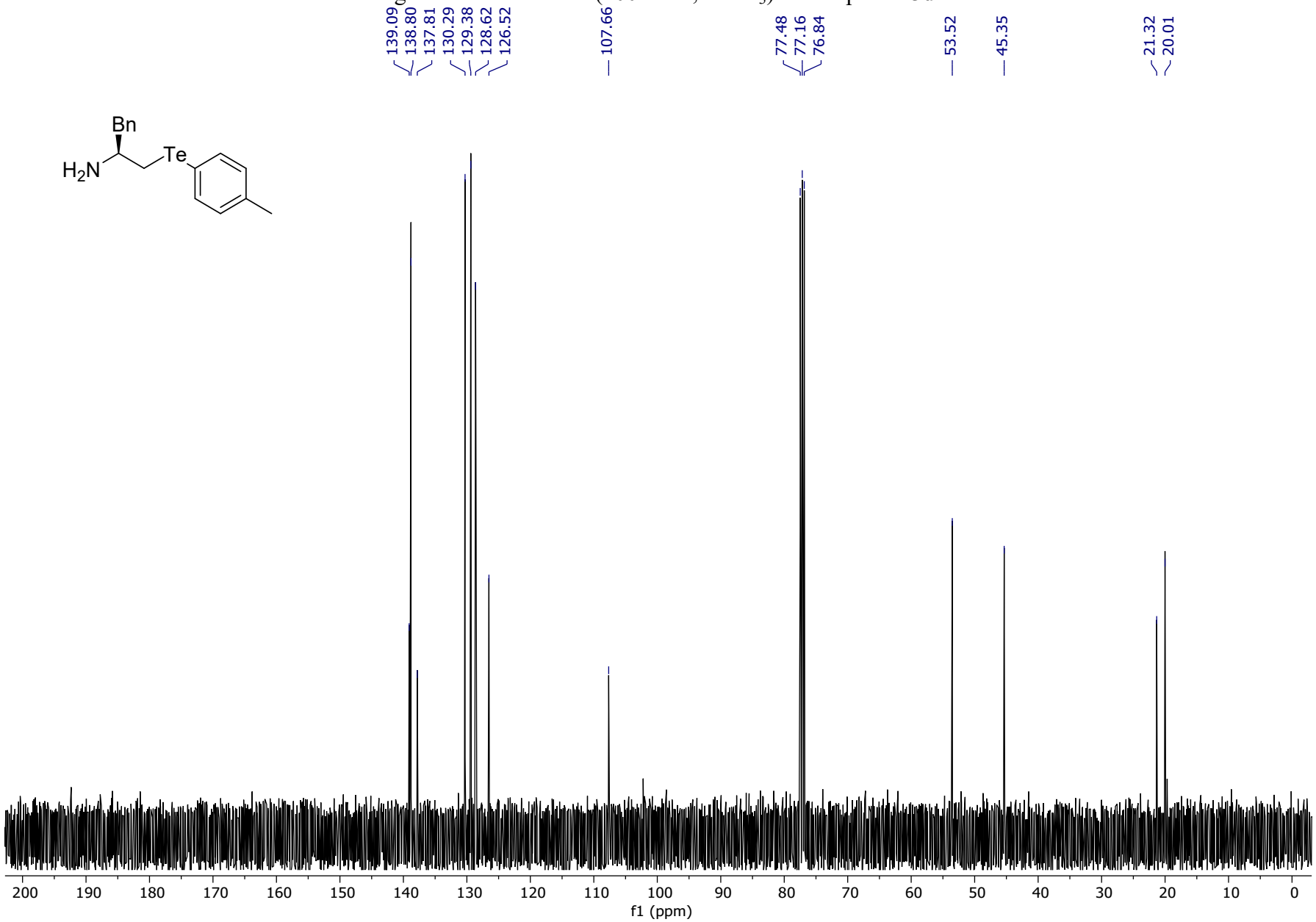


Figure S-43. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**.

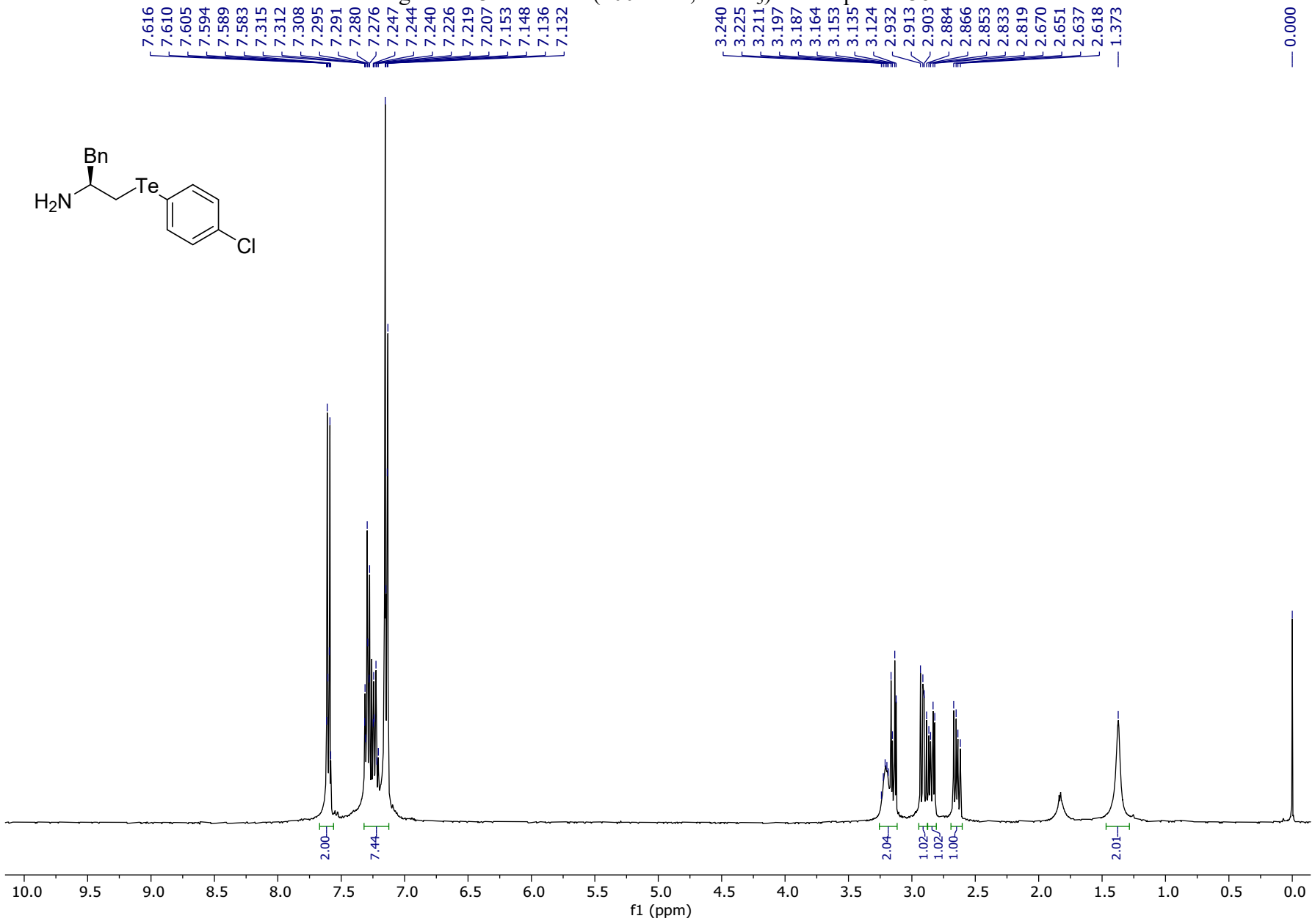


Figure S-44. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3e**.

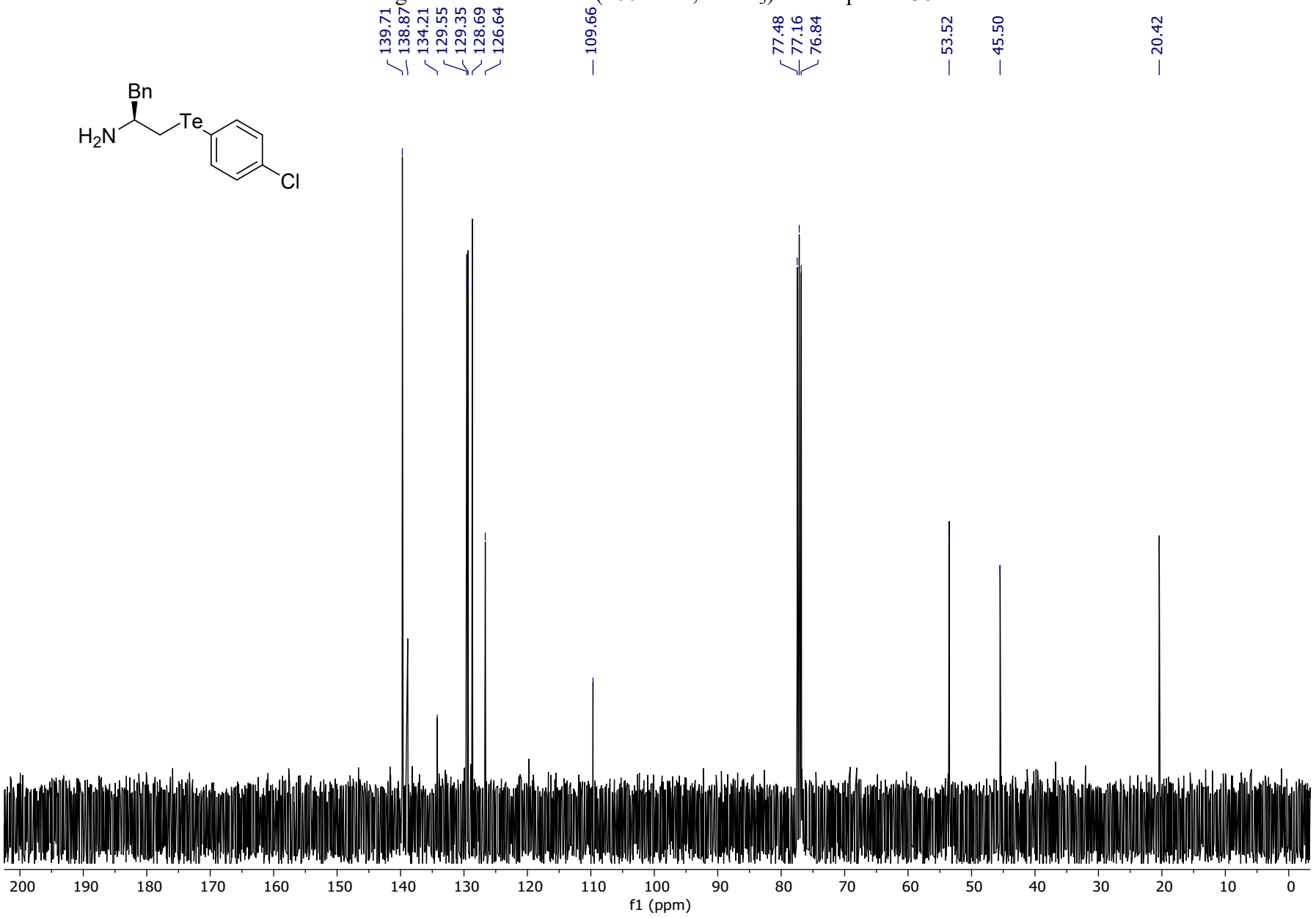


Figure S-45. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**.

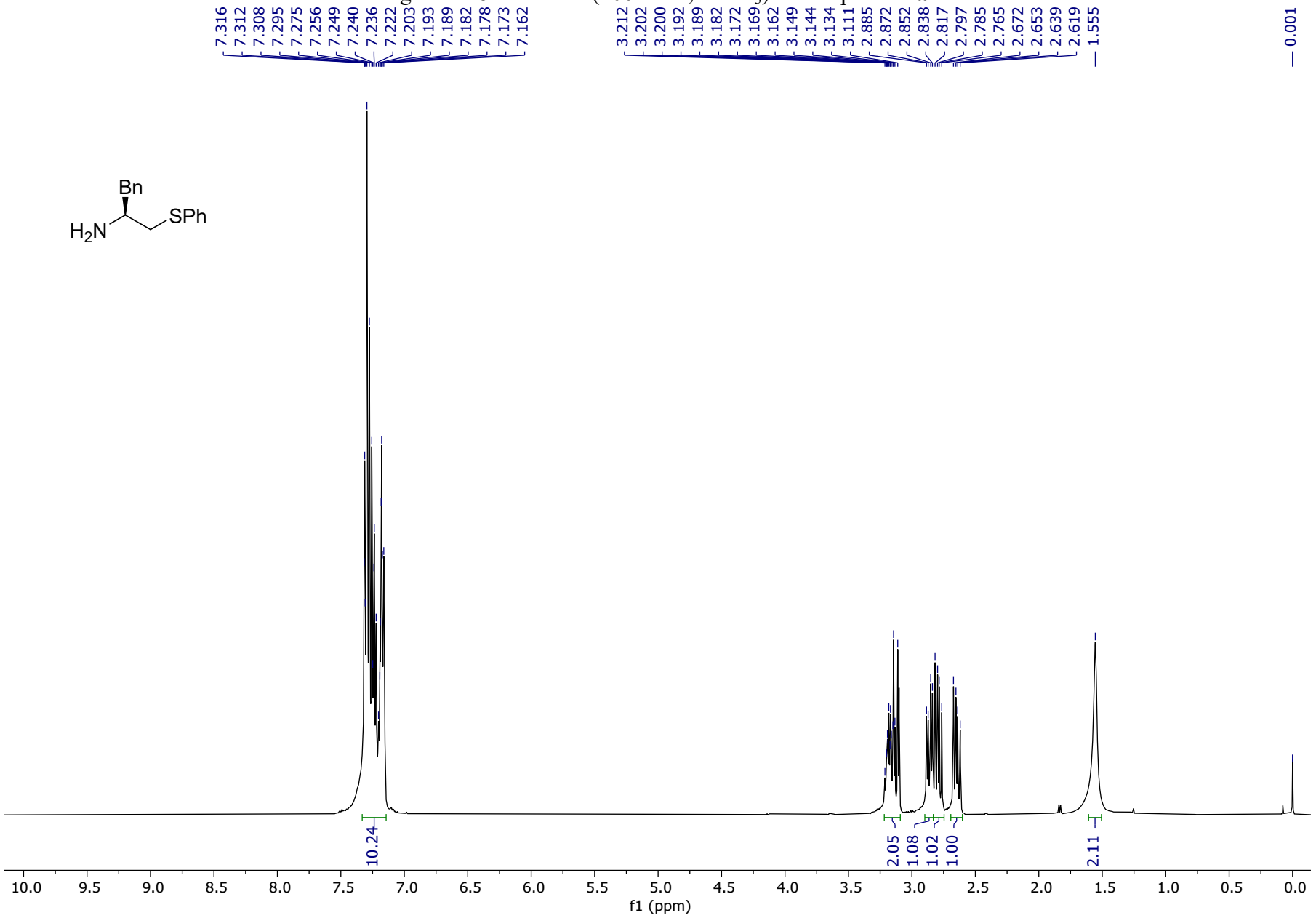


Figure S-46. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4a**.

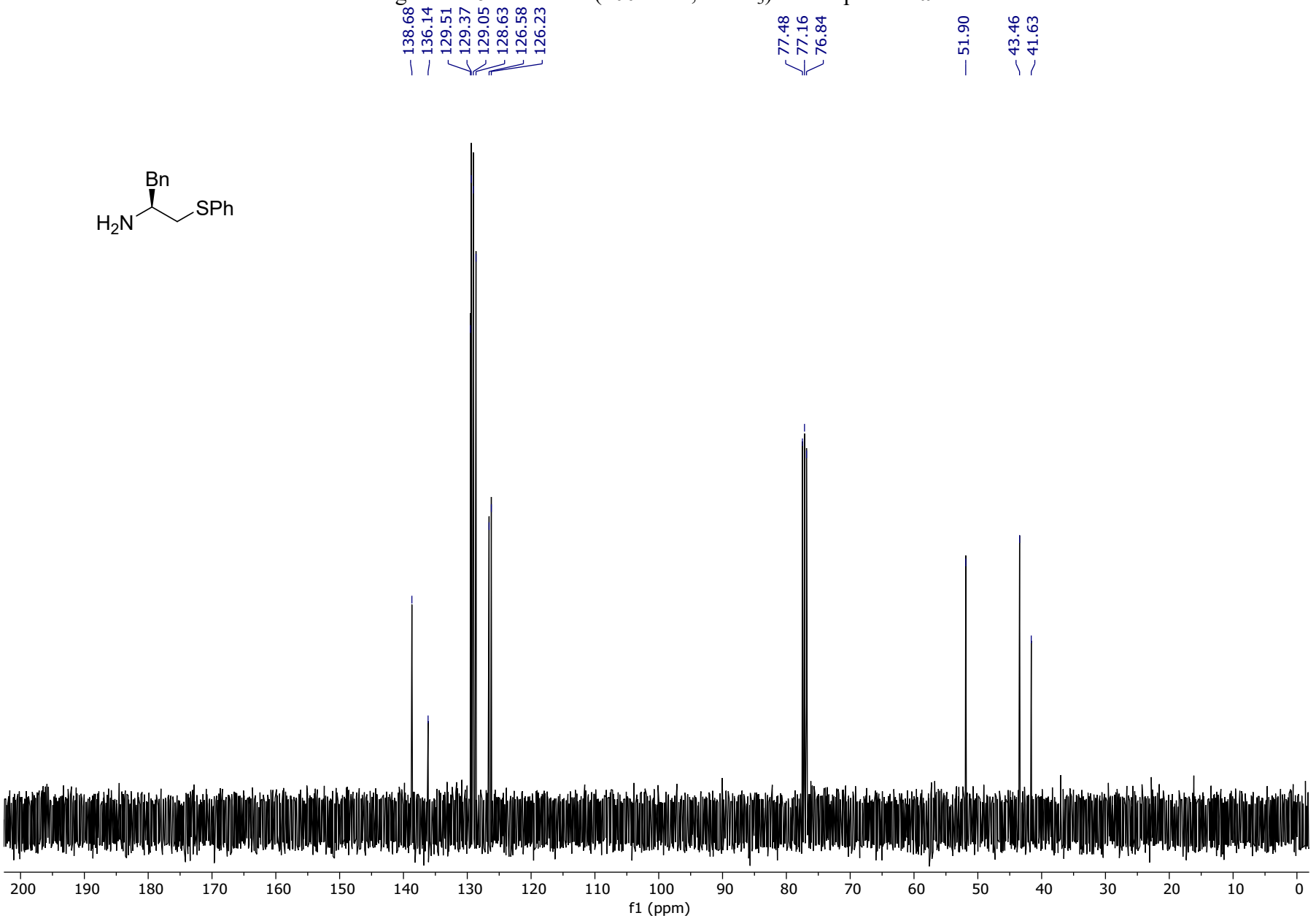


Figure S-47. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**.

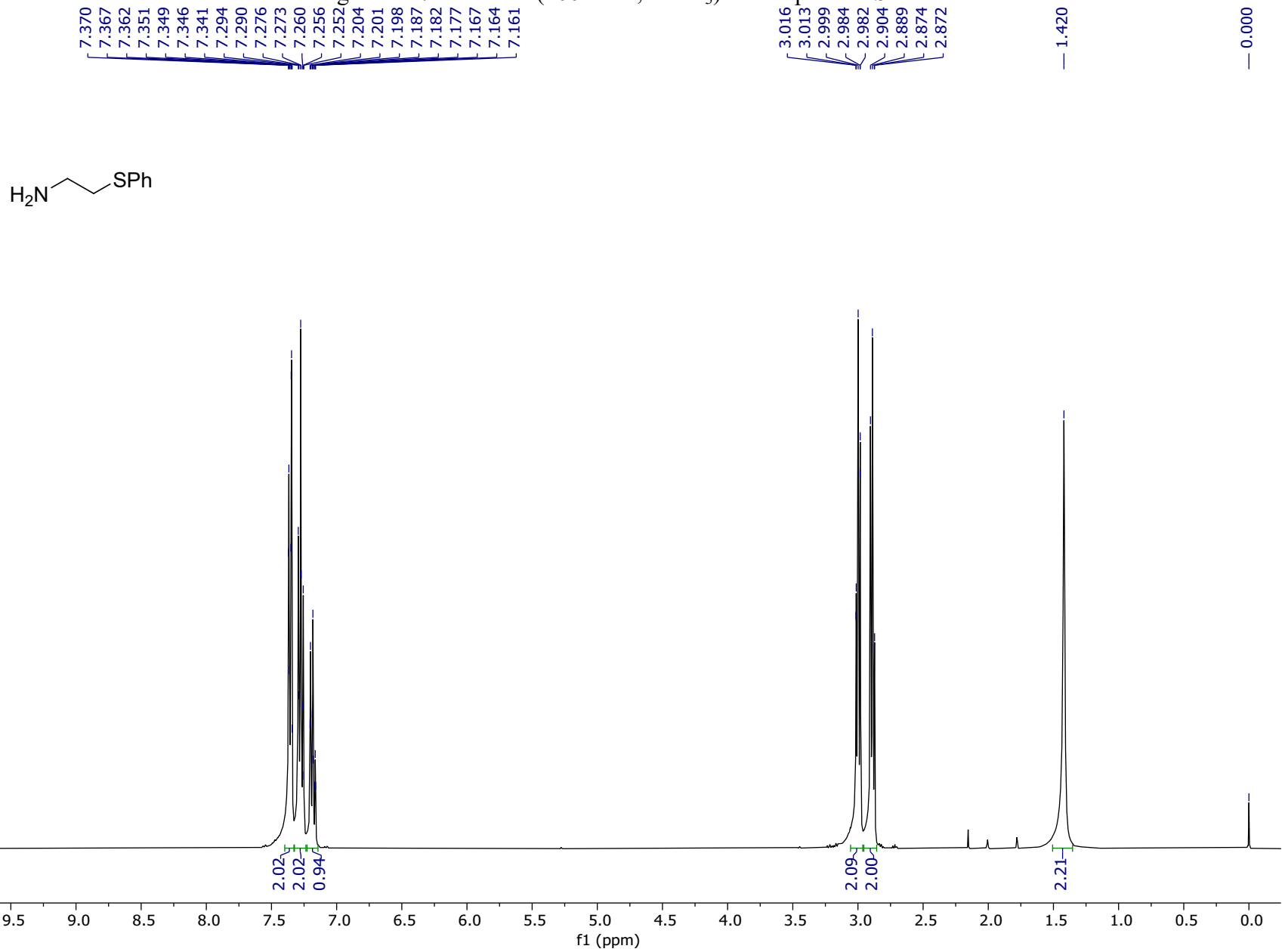


Figure S-48. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4b**.

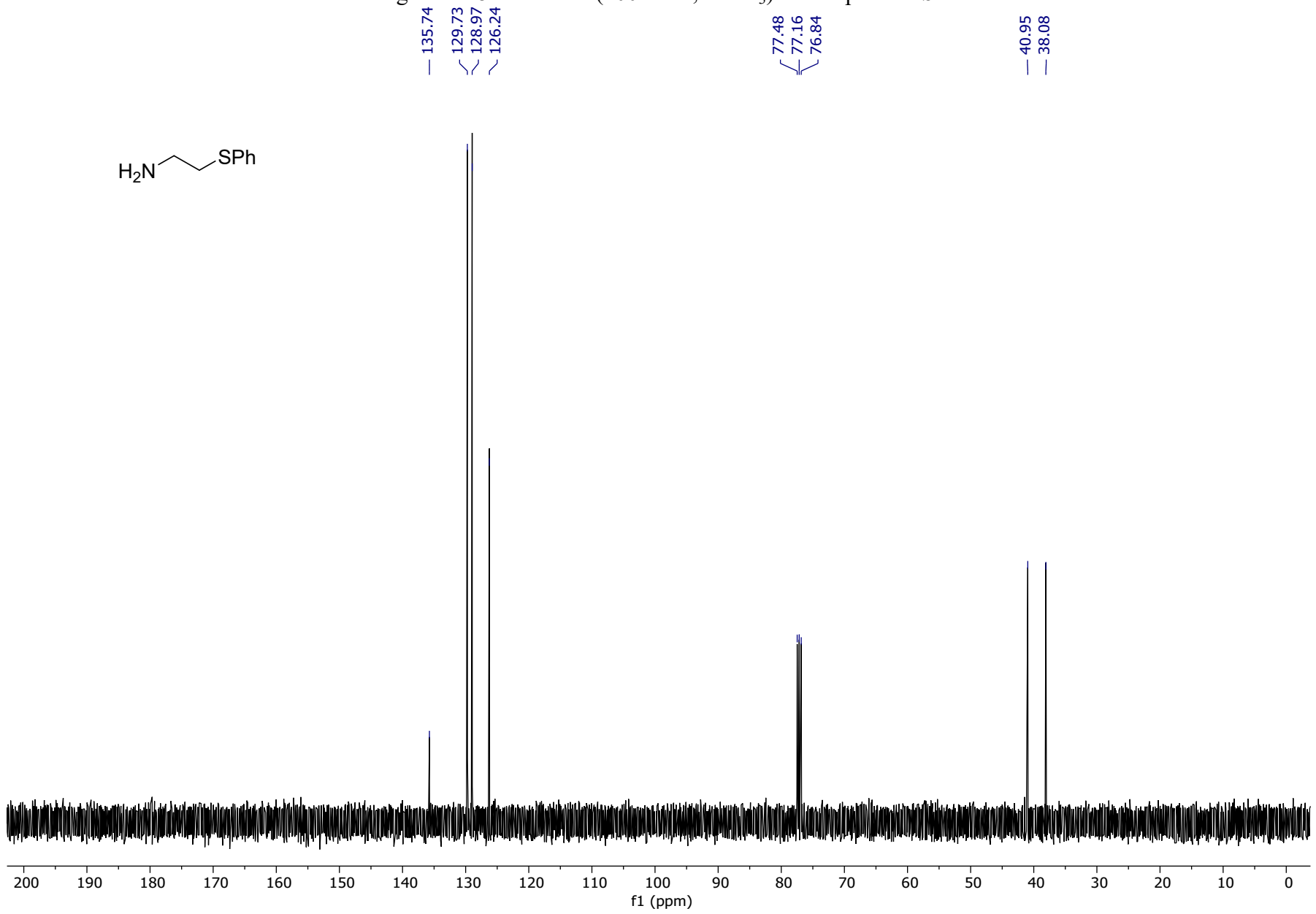


Figure S-49. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**.

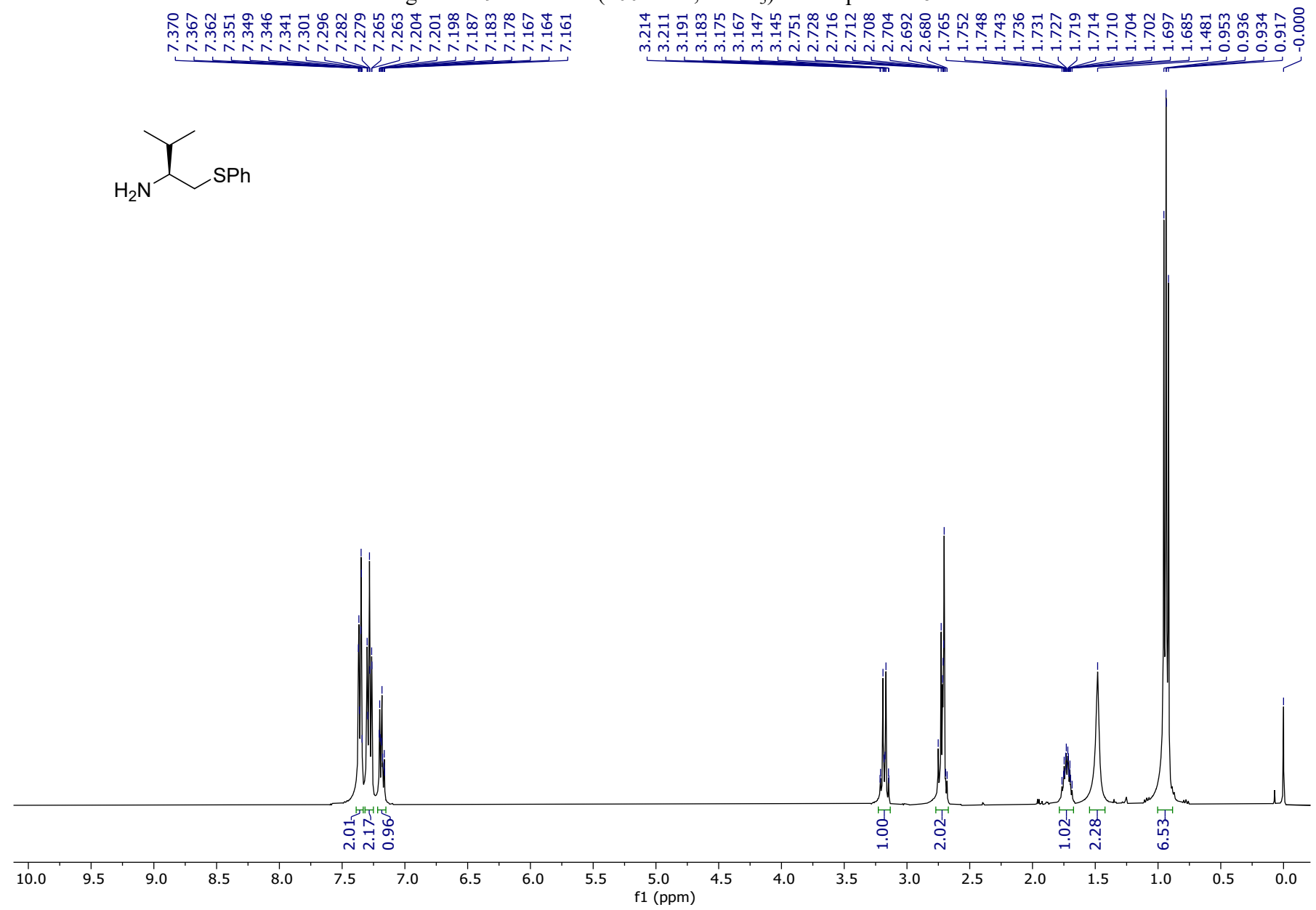


Figure S-50. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4c**.

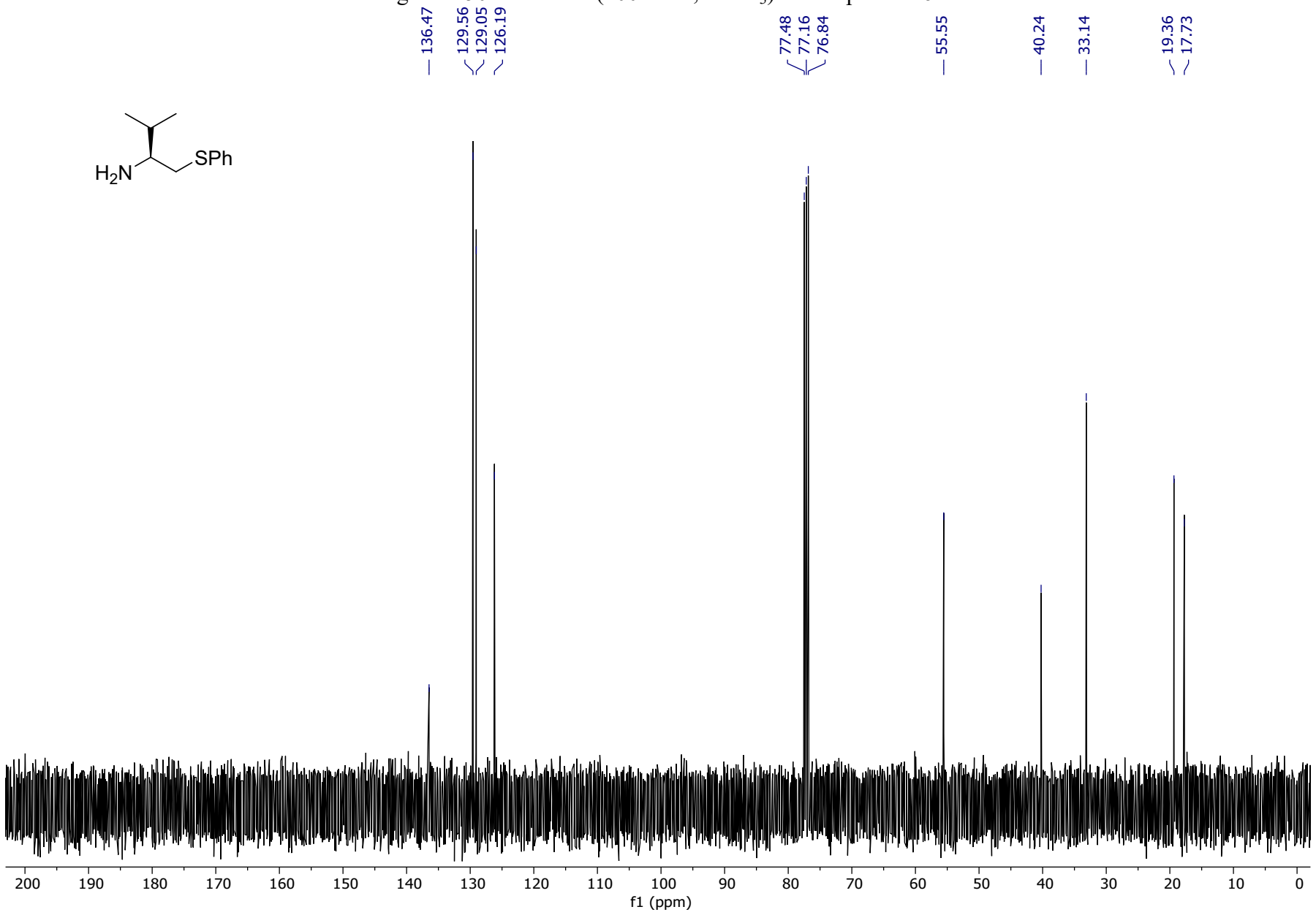


Figure S-51. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**.

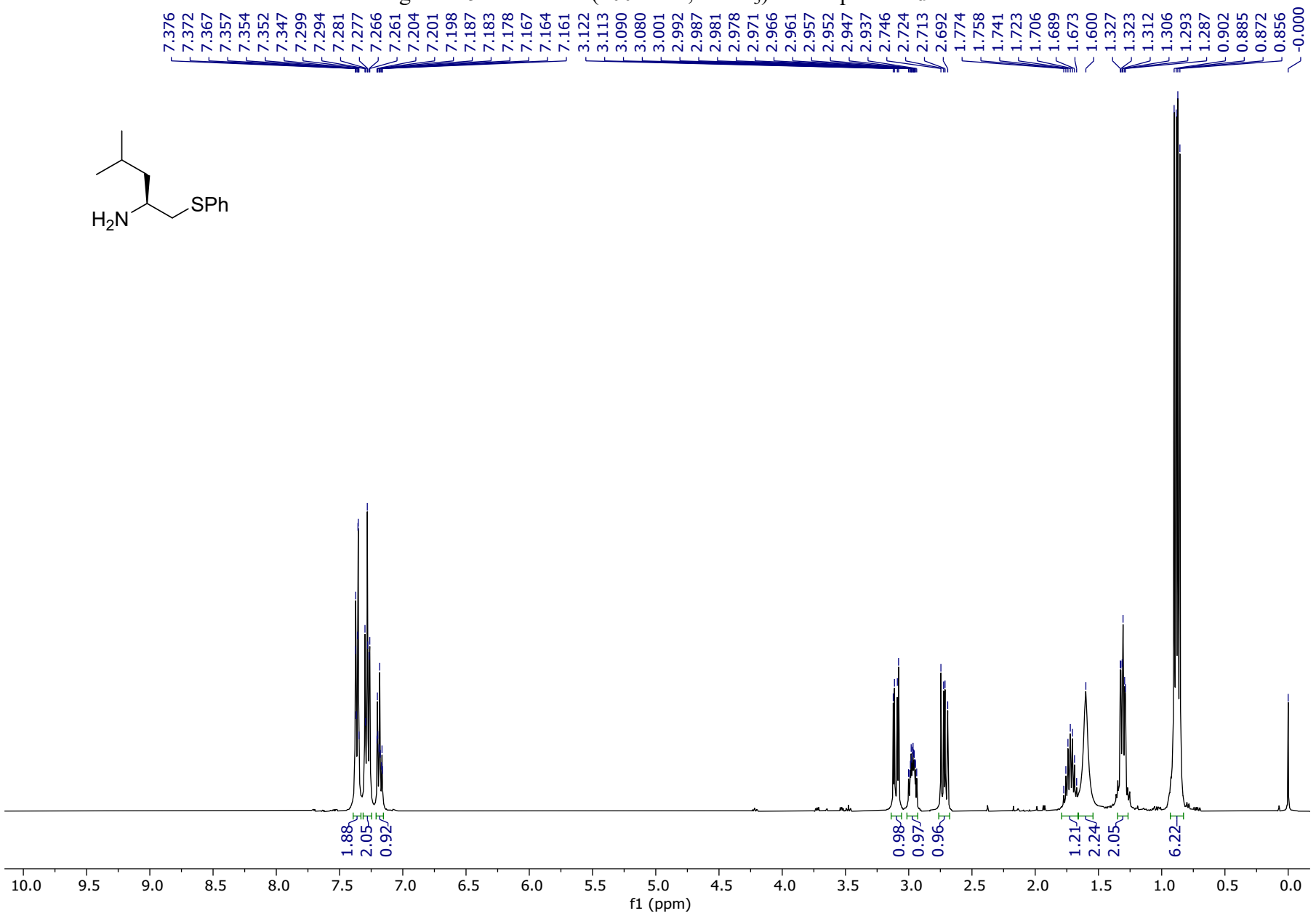


Figure S-52. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4d**.

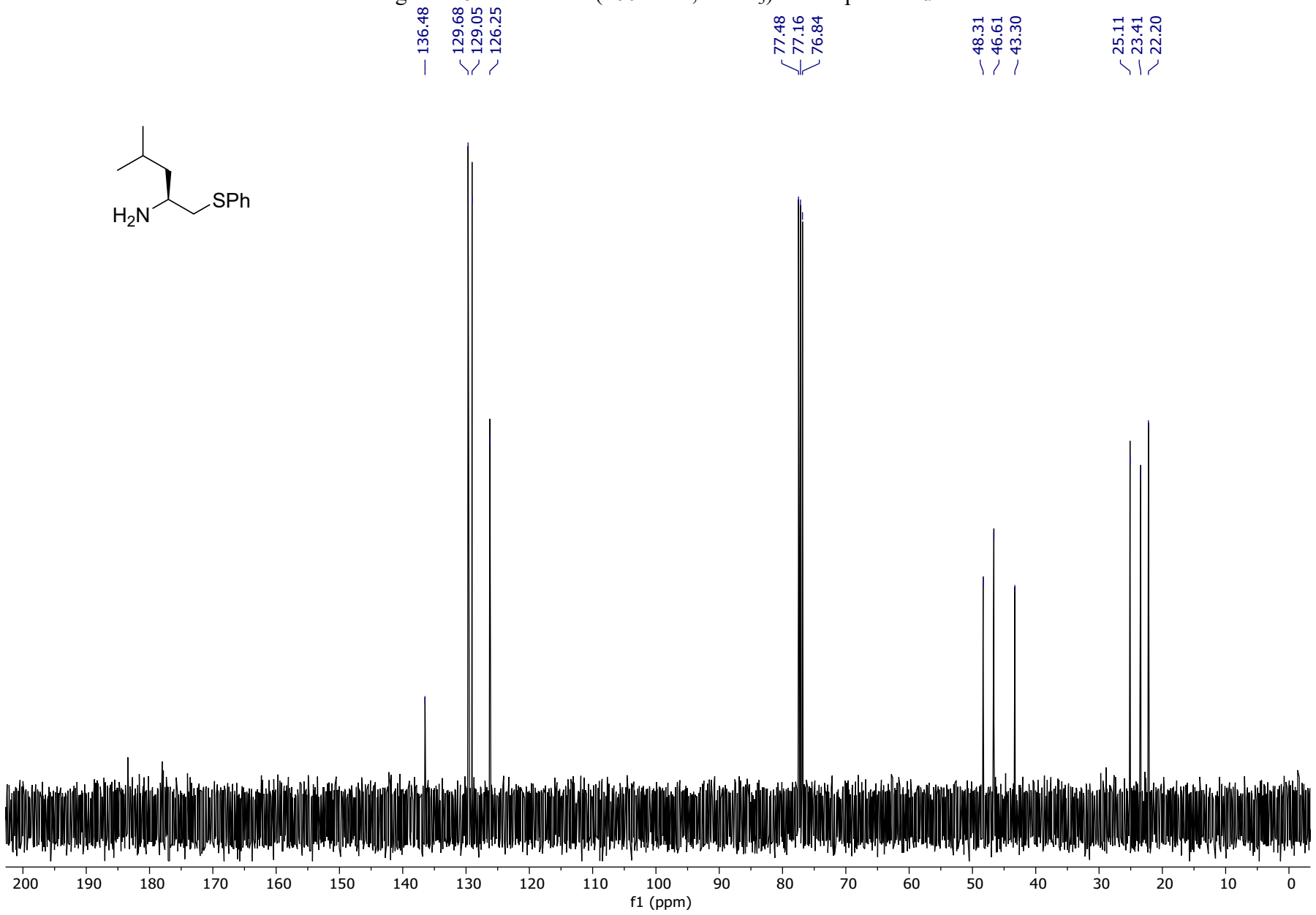


Figure S-53. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4e**.

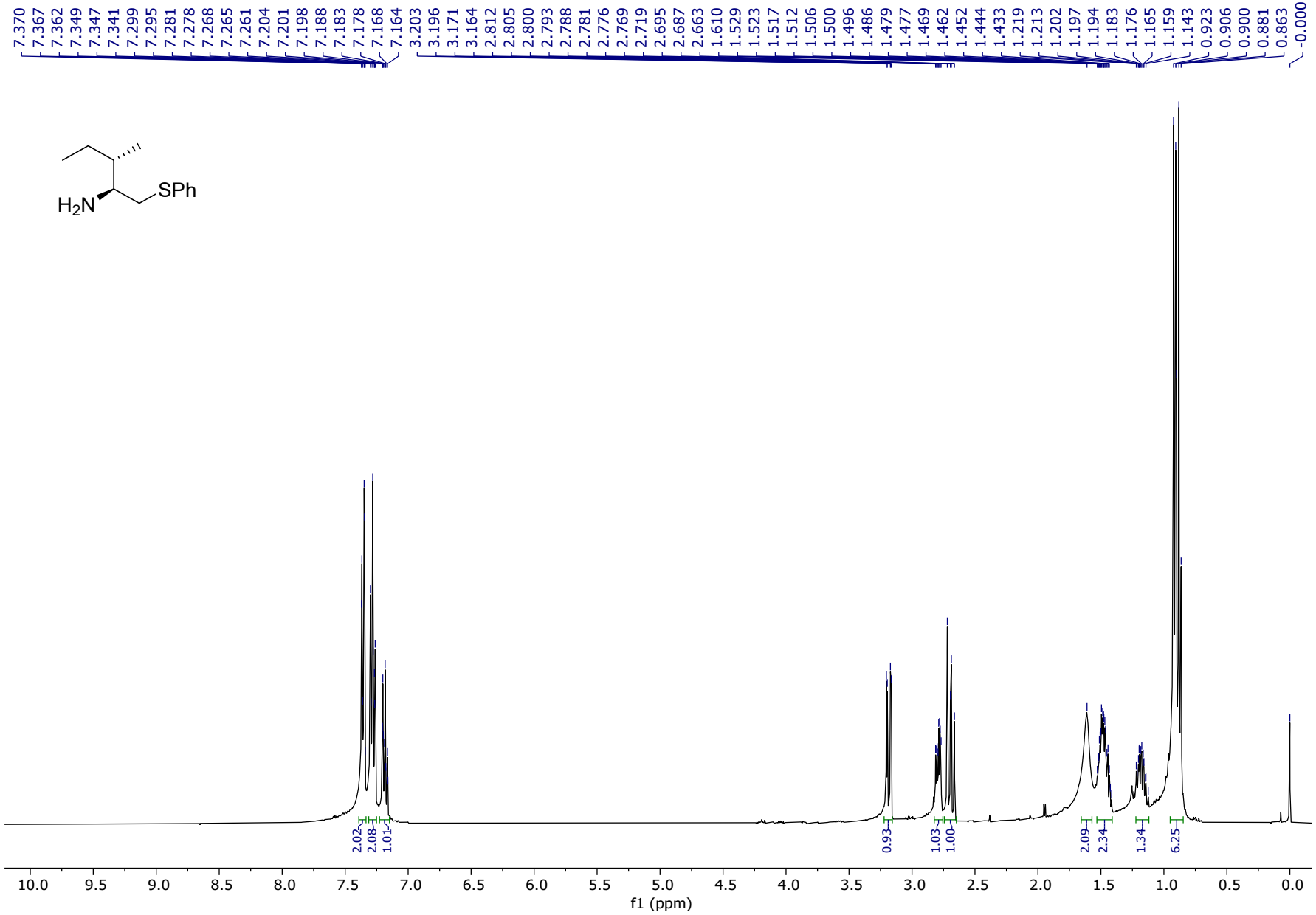


Figure S-54. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4e**.

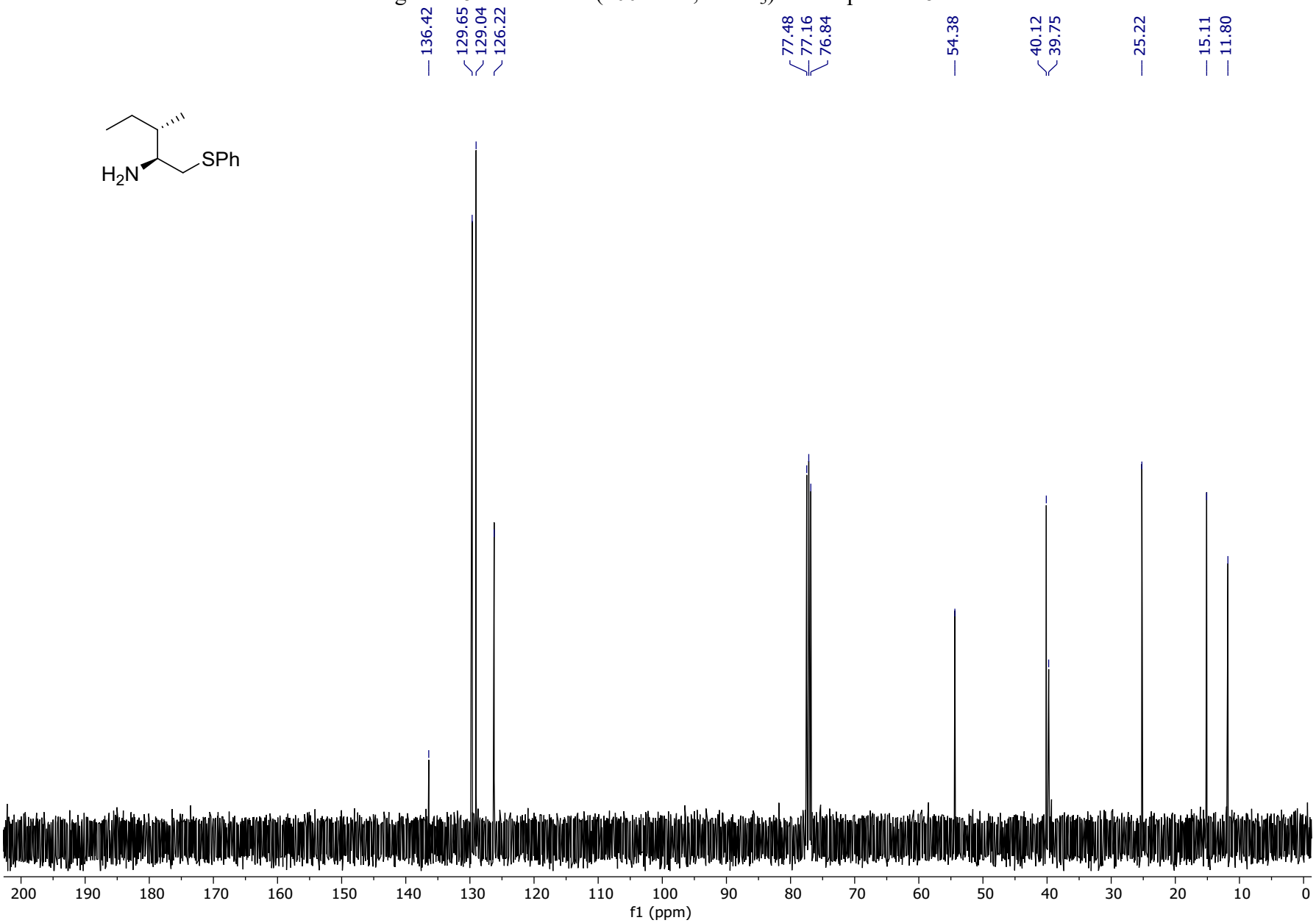


Figure S-55. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4f**.

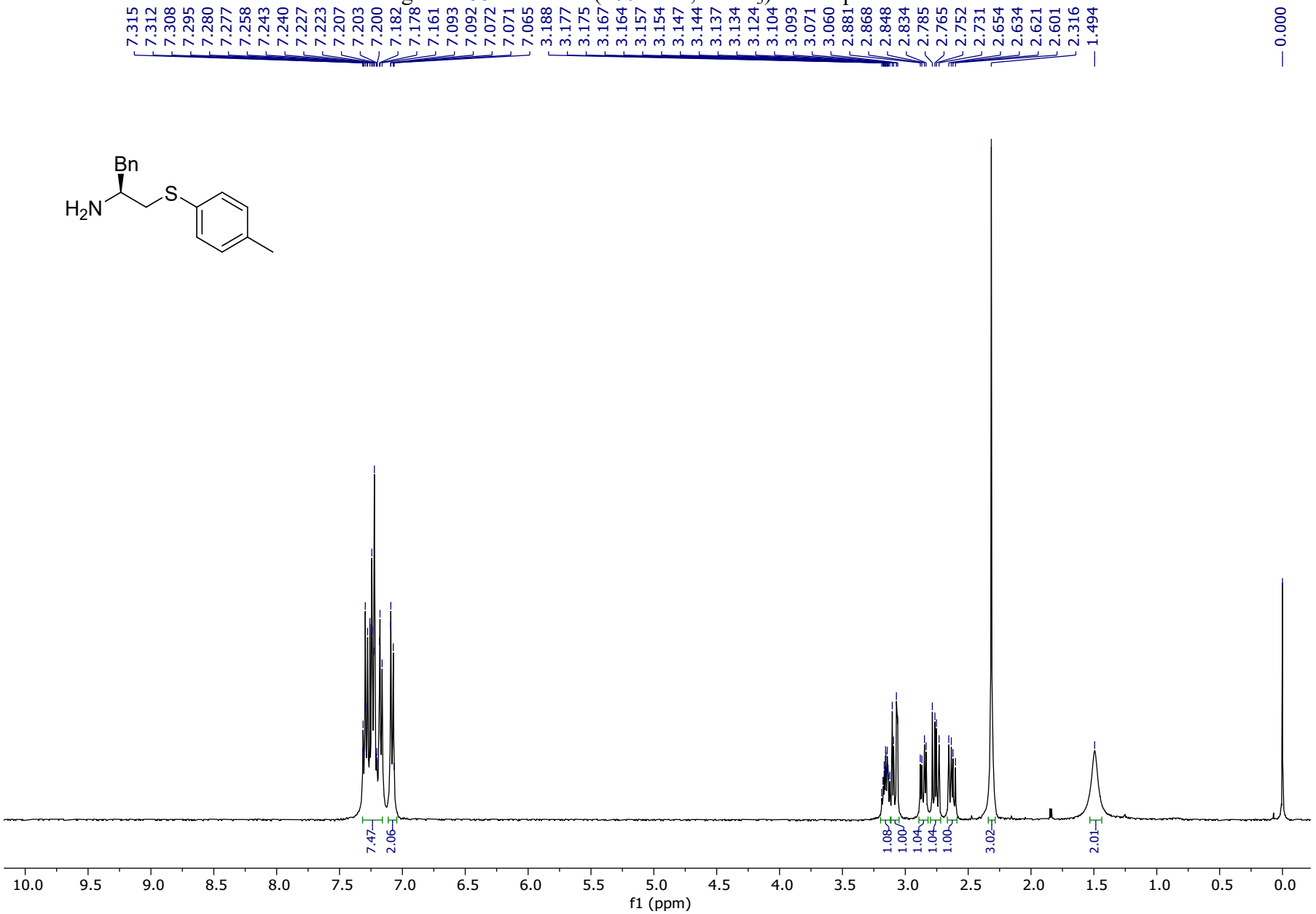


Figure S-56. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4f**.

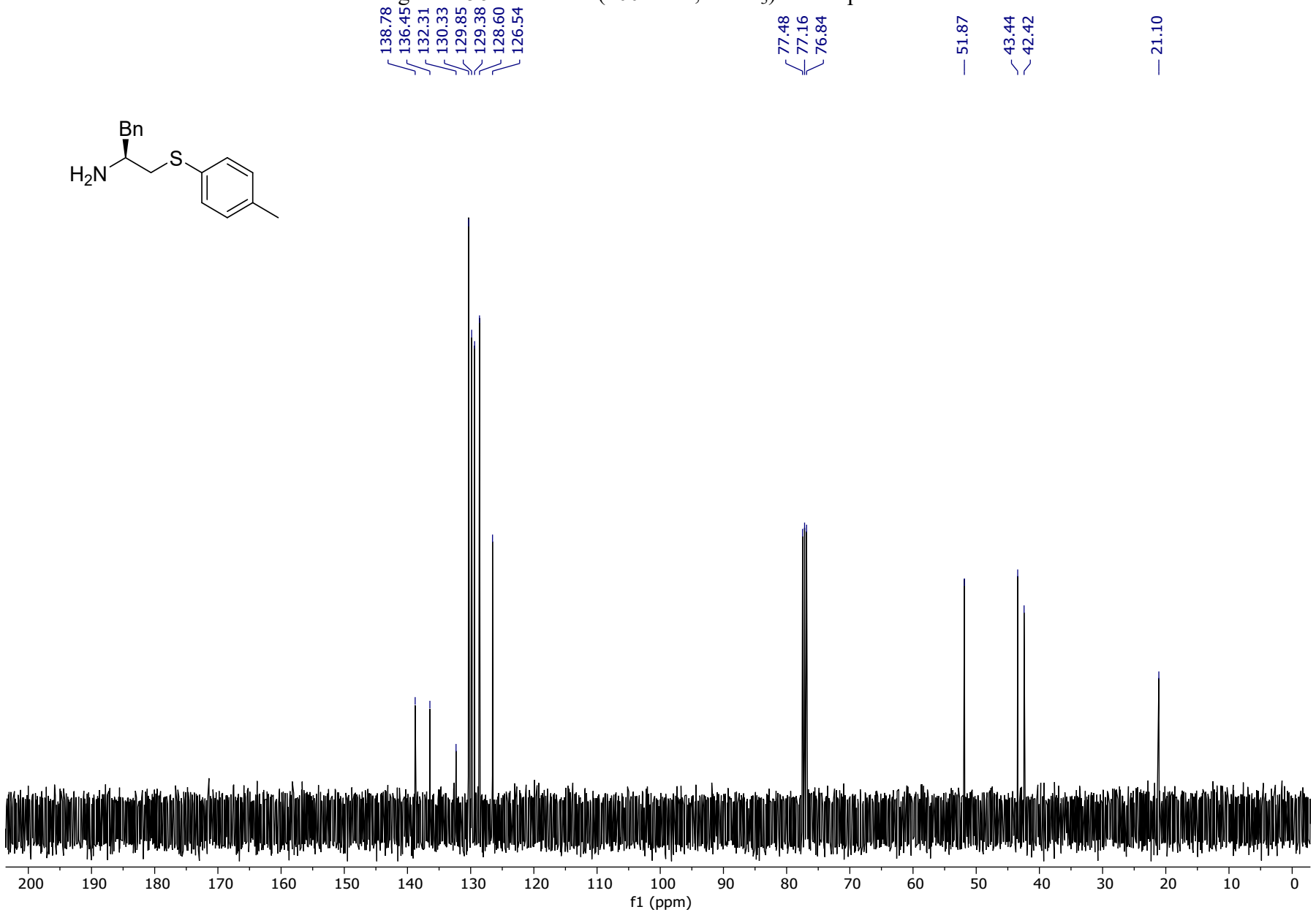


Figure S-57. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4g**.

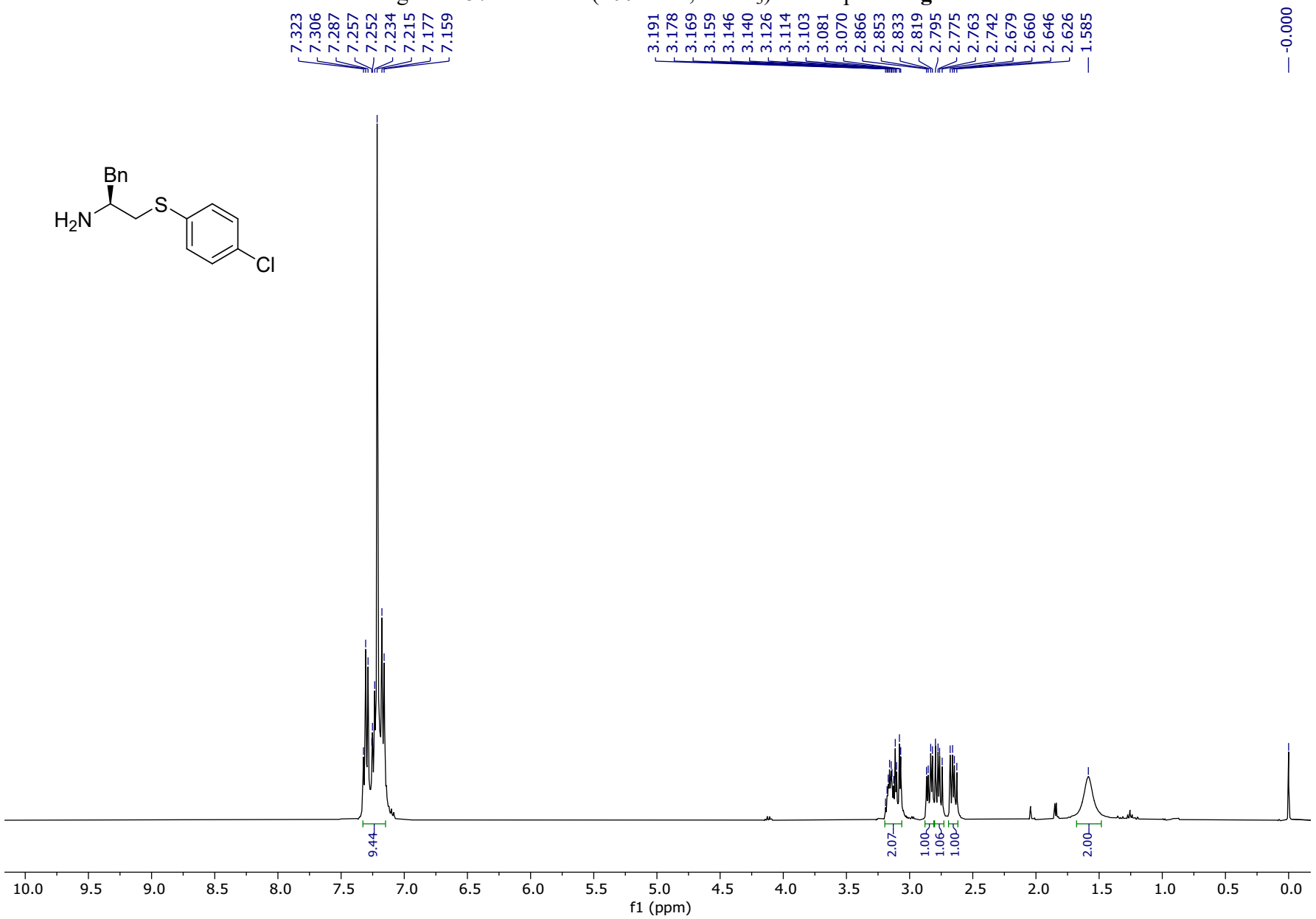


Figure S-58. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4g**.

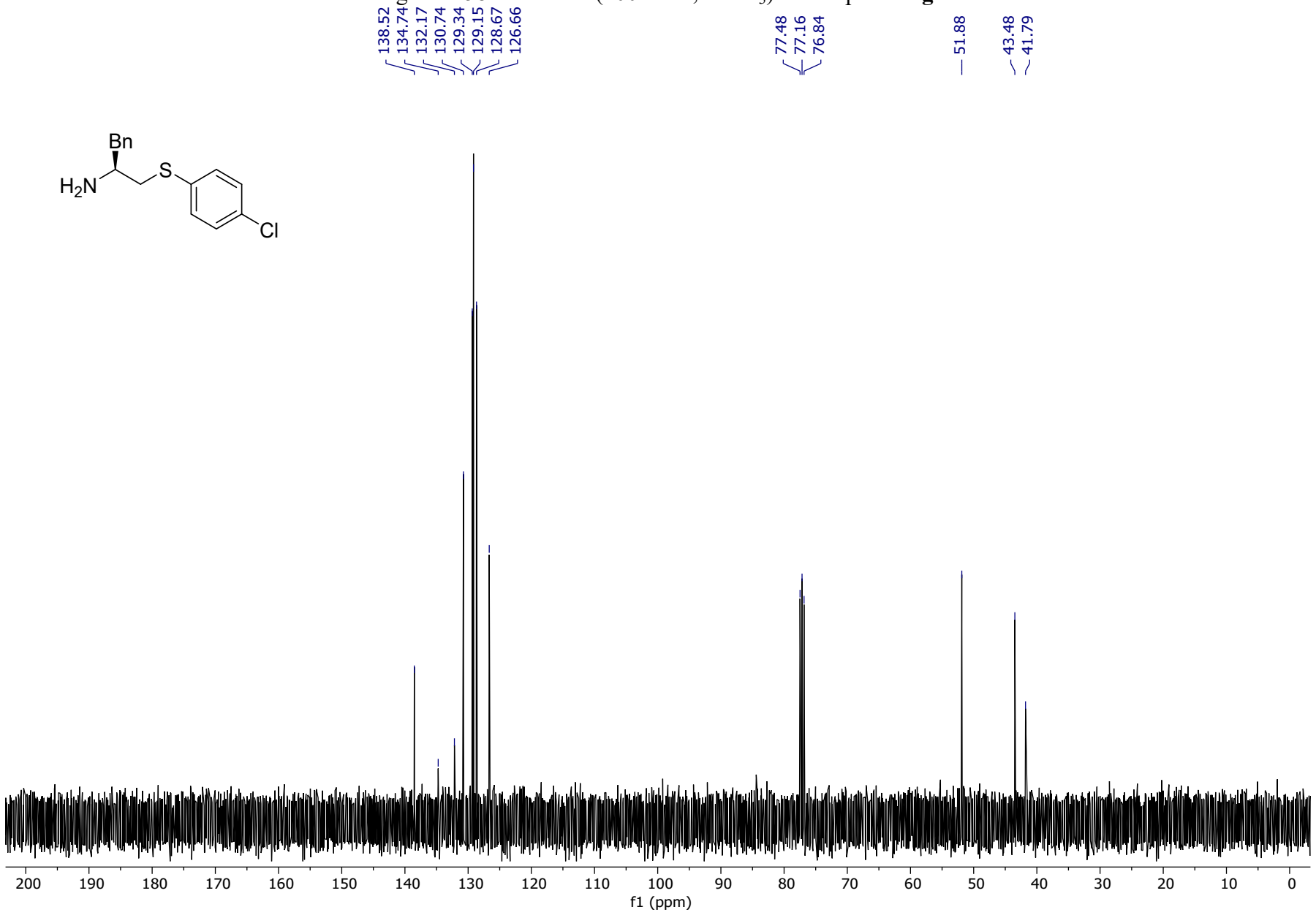


Figure S-59. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4h**.

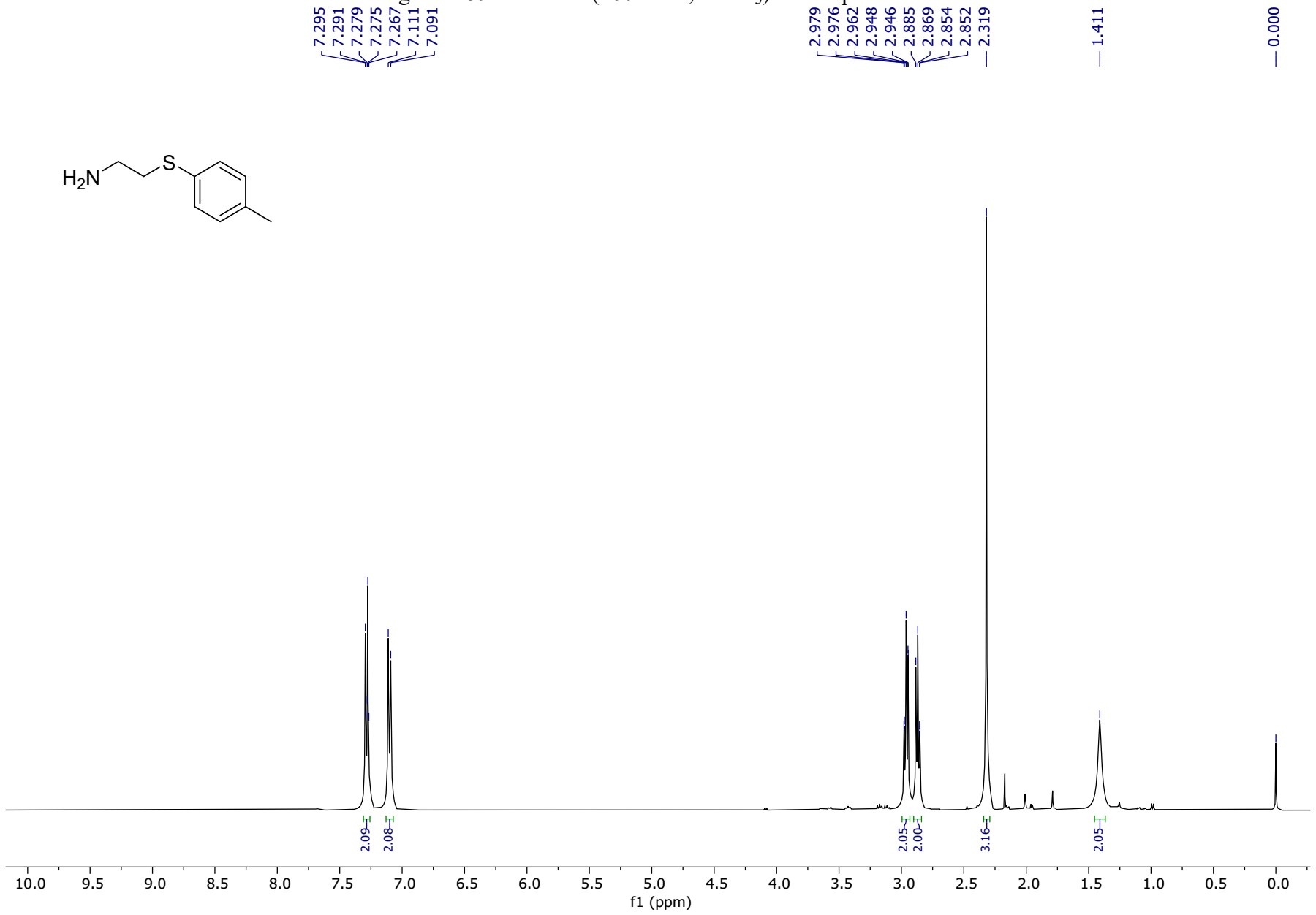


Figure S-60. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4h**.

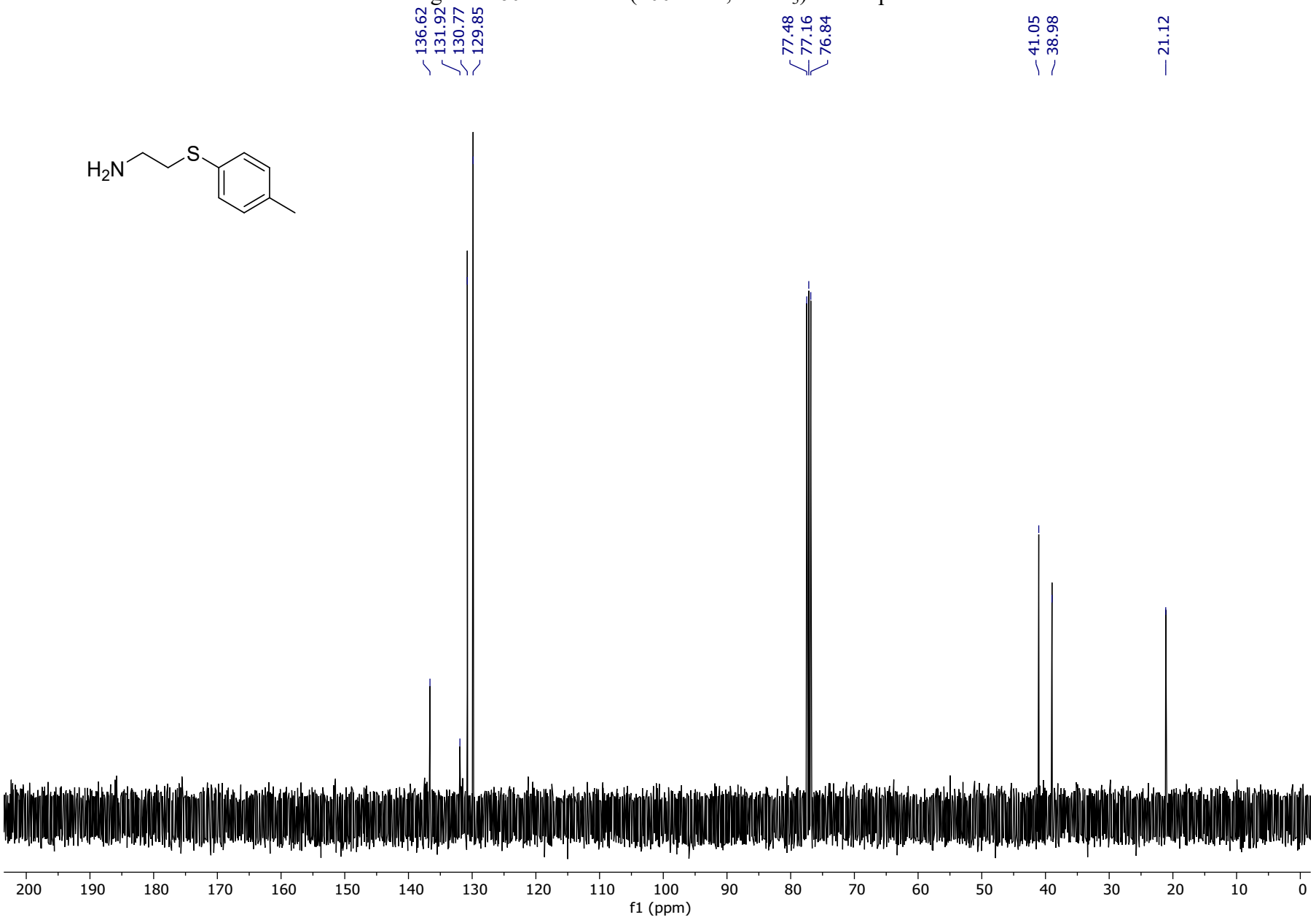


Figure S-61. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4i**.

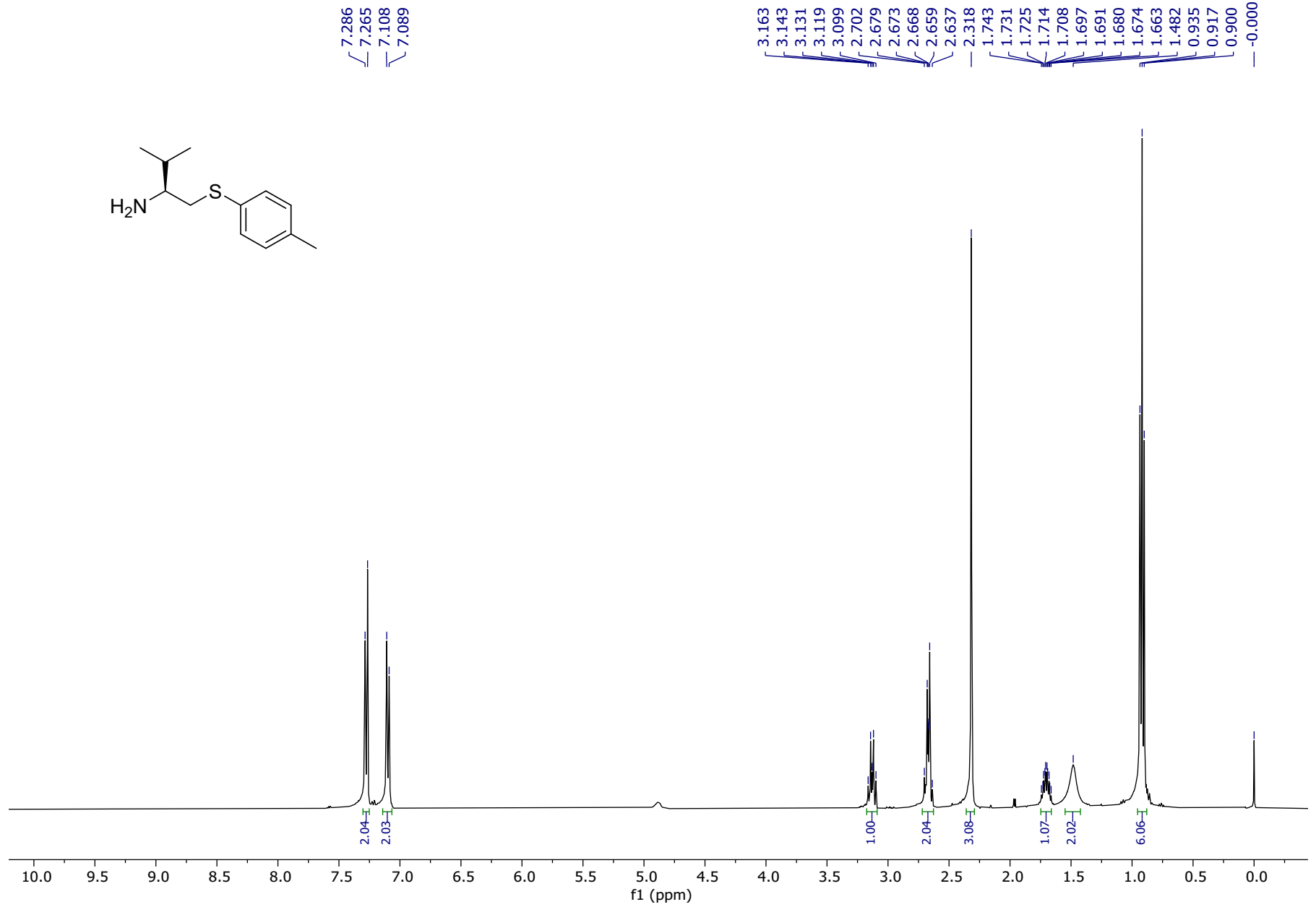


Figure S-62. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4i**.

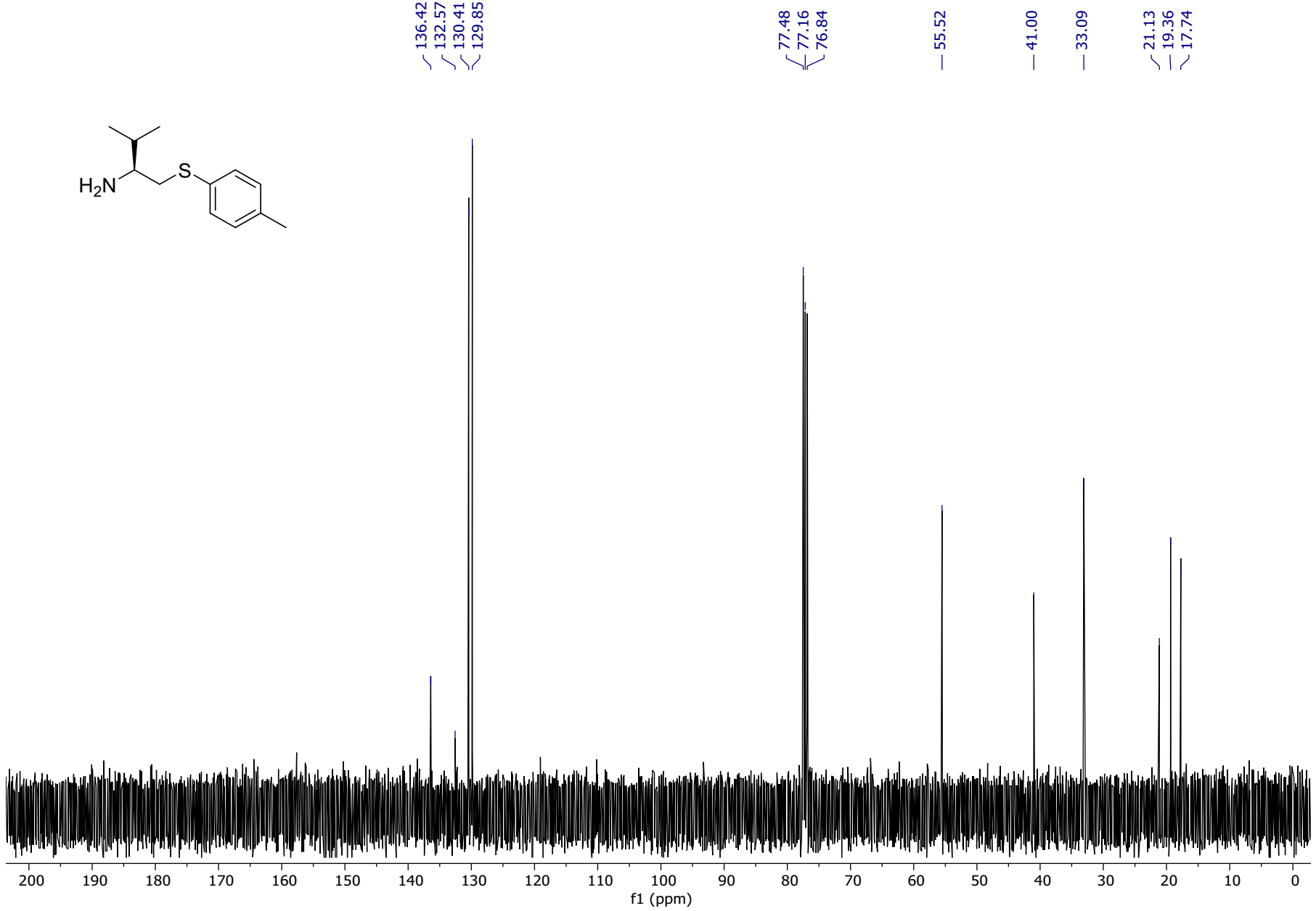


Figure S-63. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4j**.

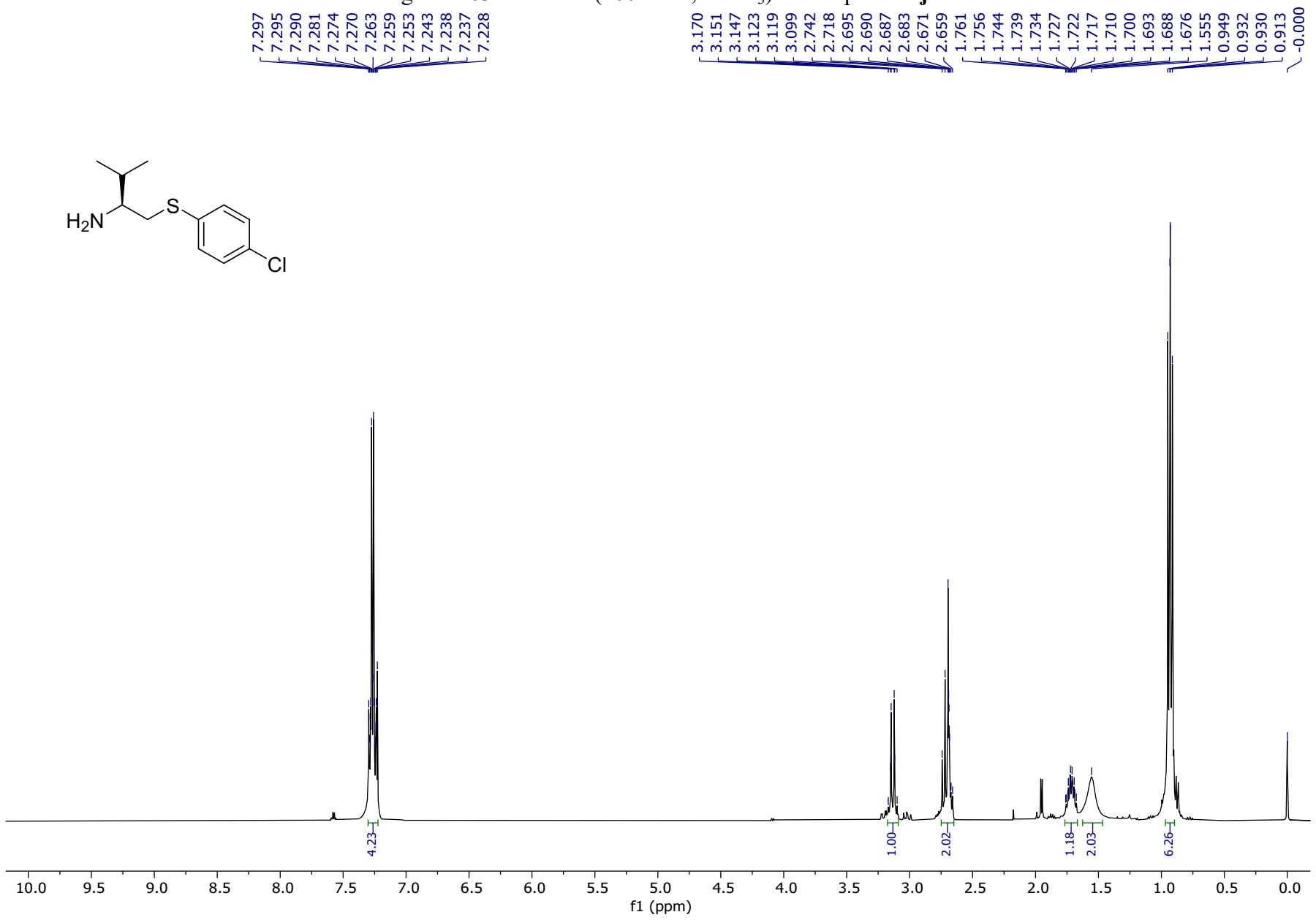


Figure S-64. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4j**.

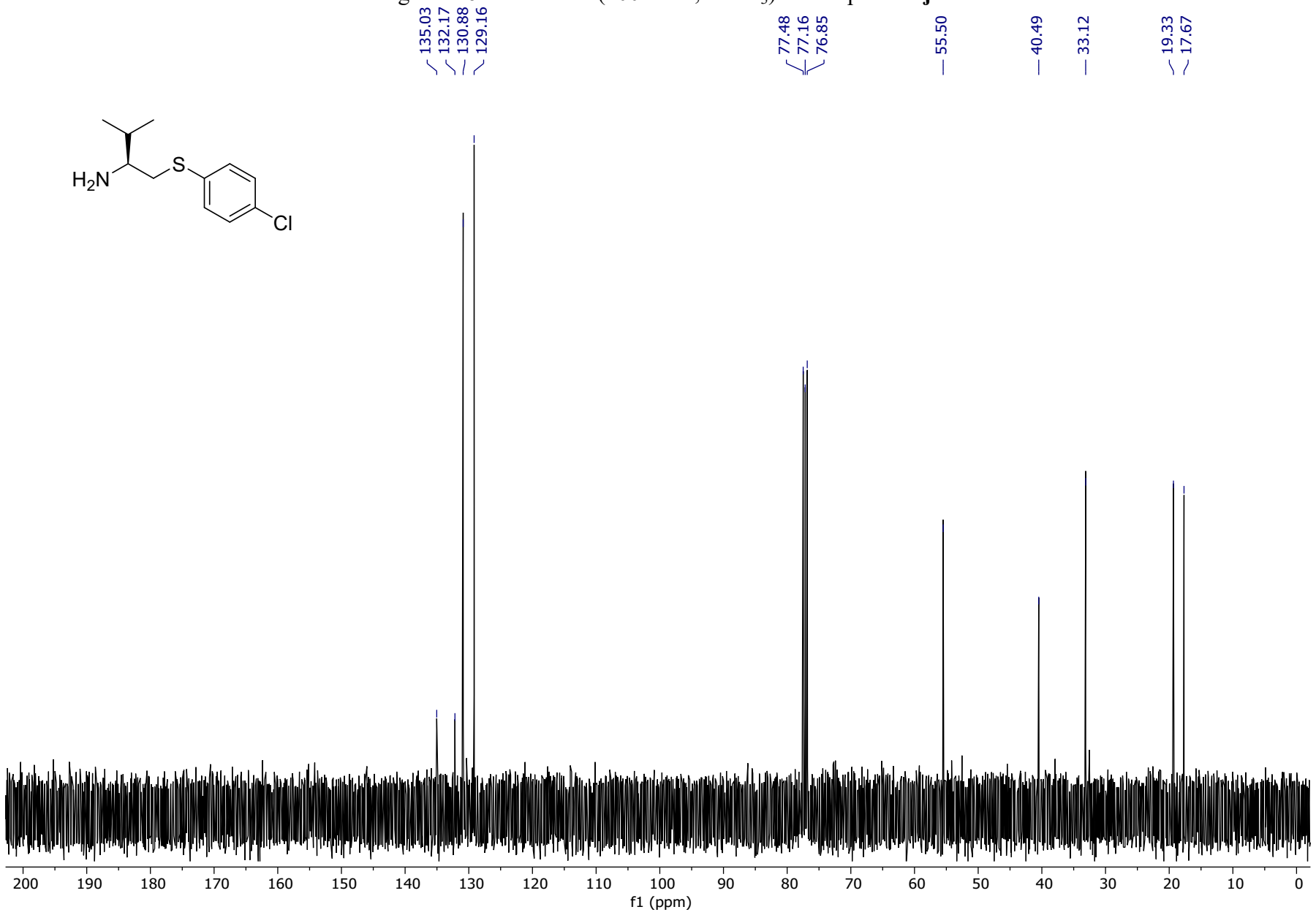


Figure S-65. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4k**.

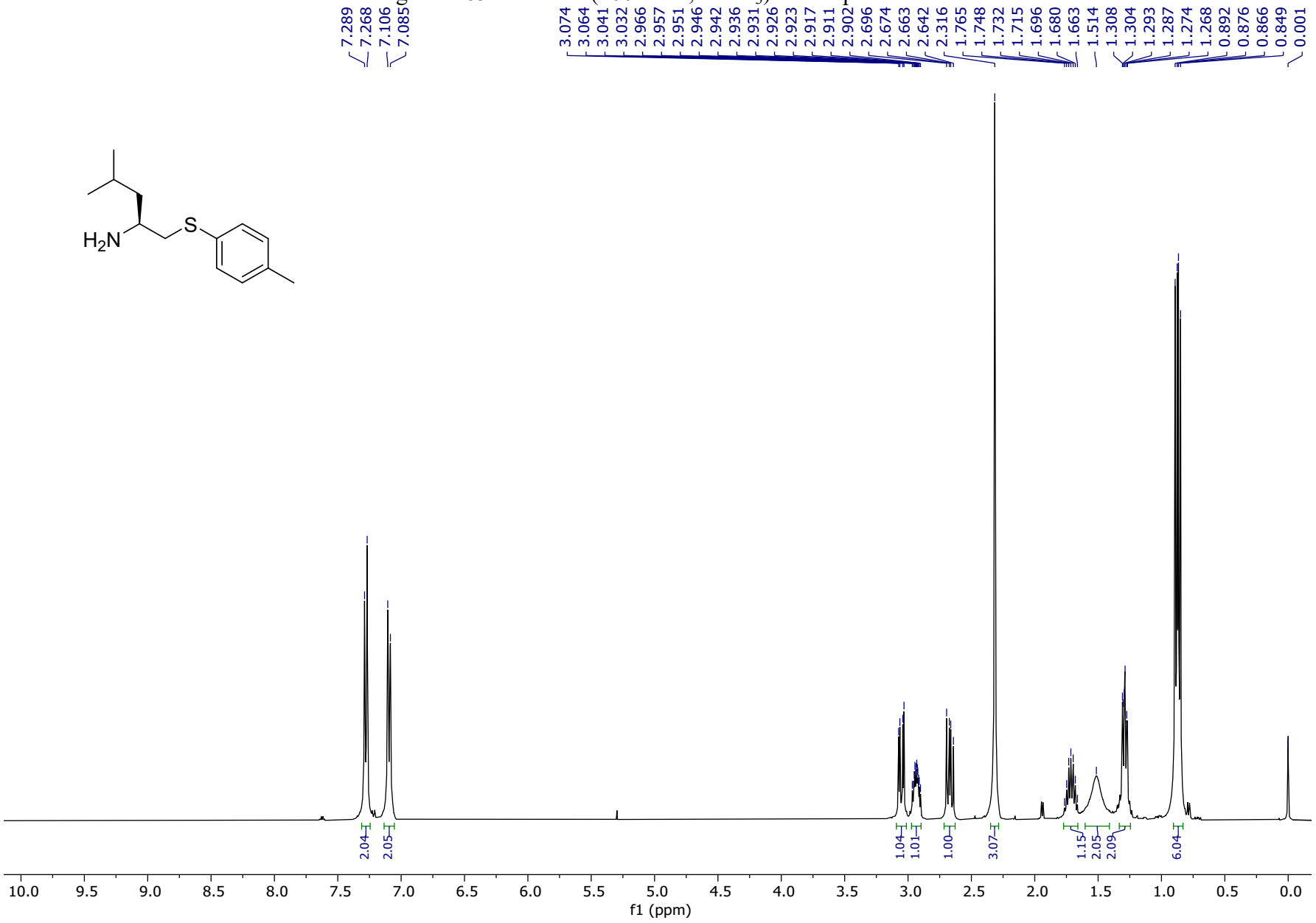


Figure S-66. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4j**.

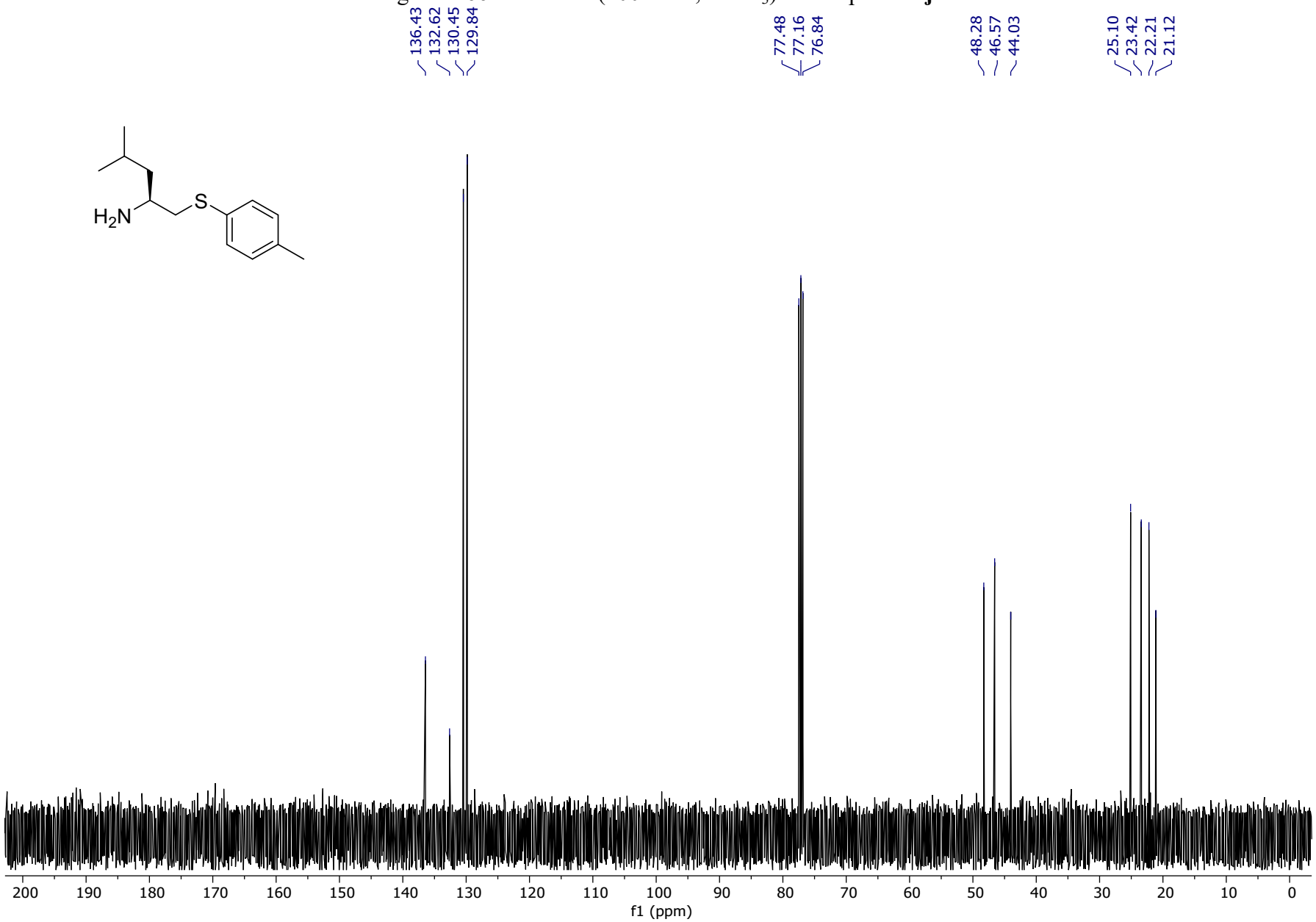


Figure S-67. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4l**.

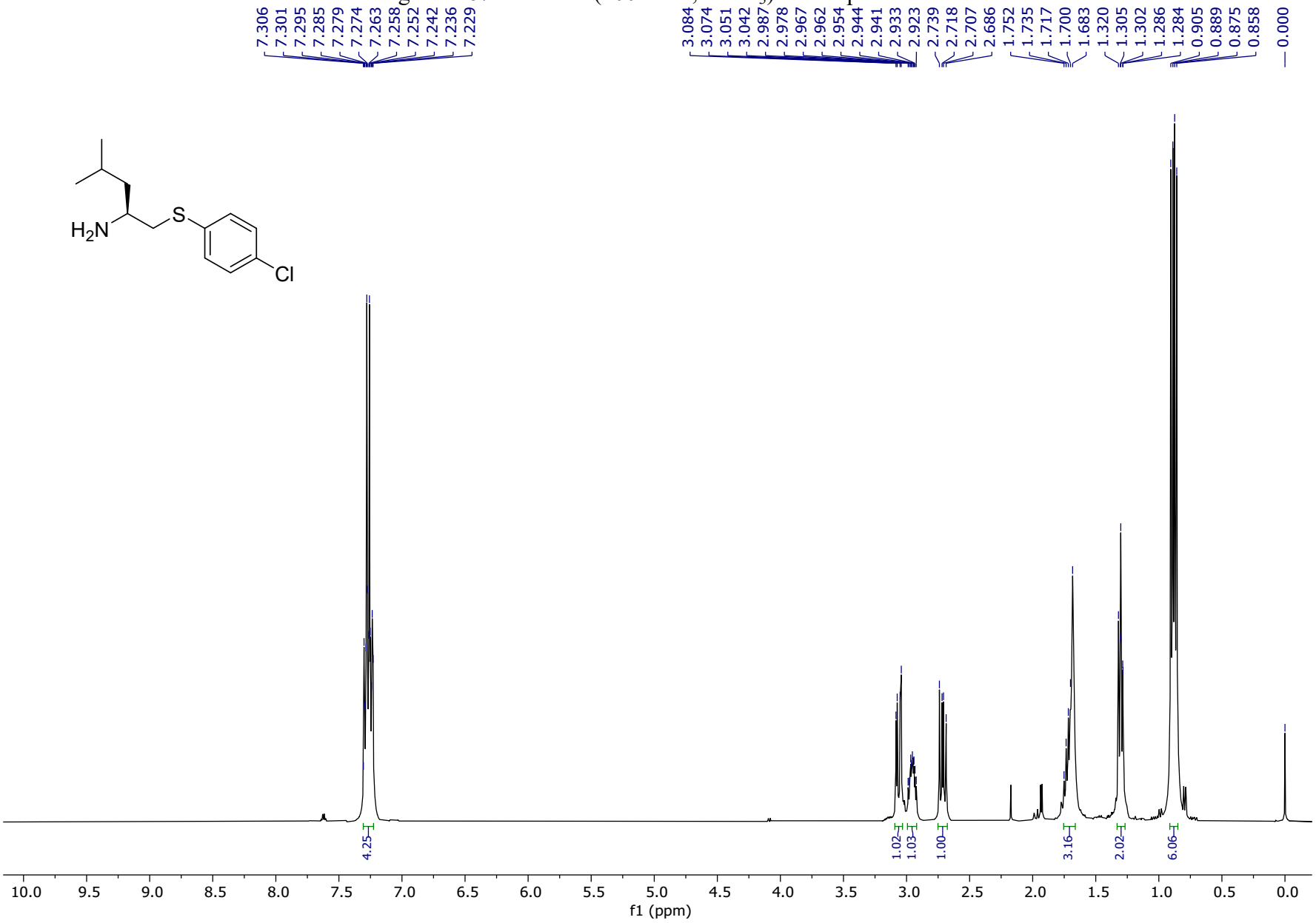


Figure S-68. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4l**.

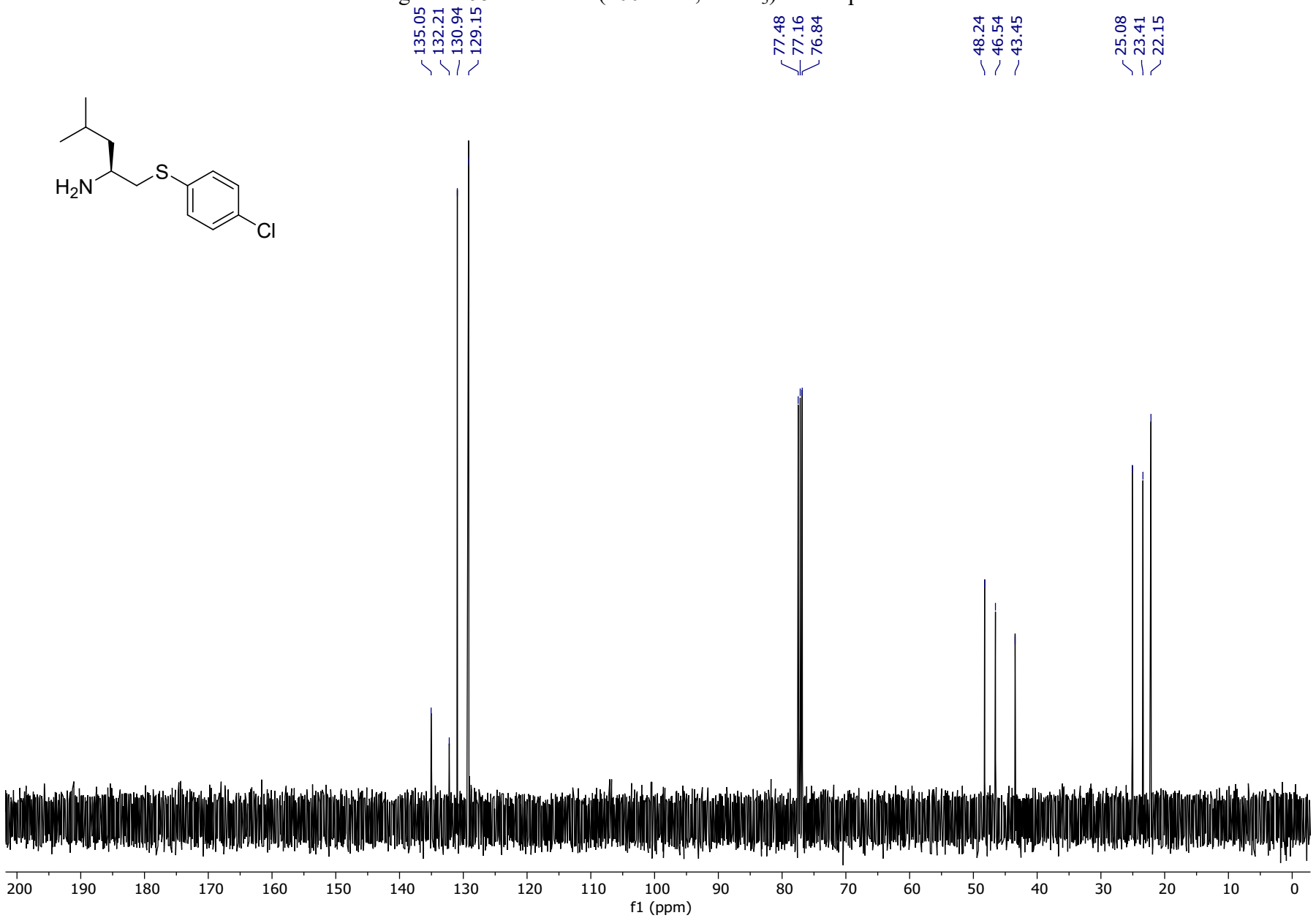


Figure S-69. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4m**.

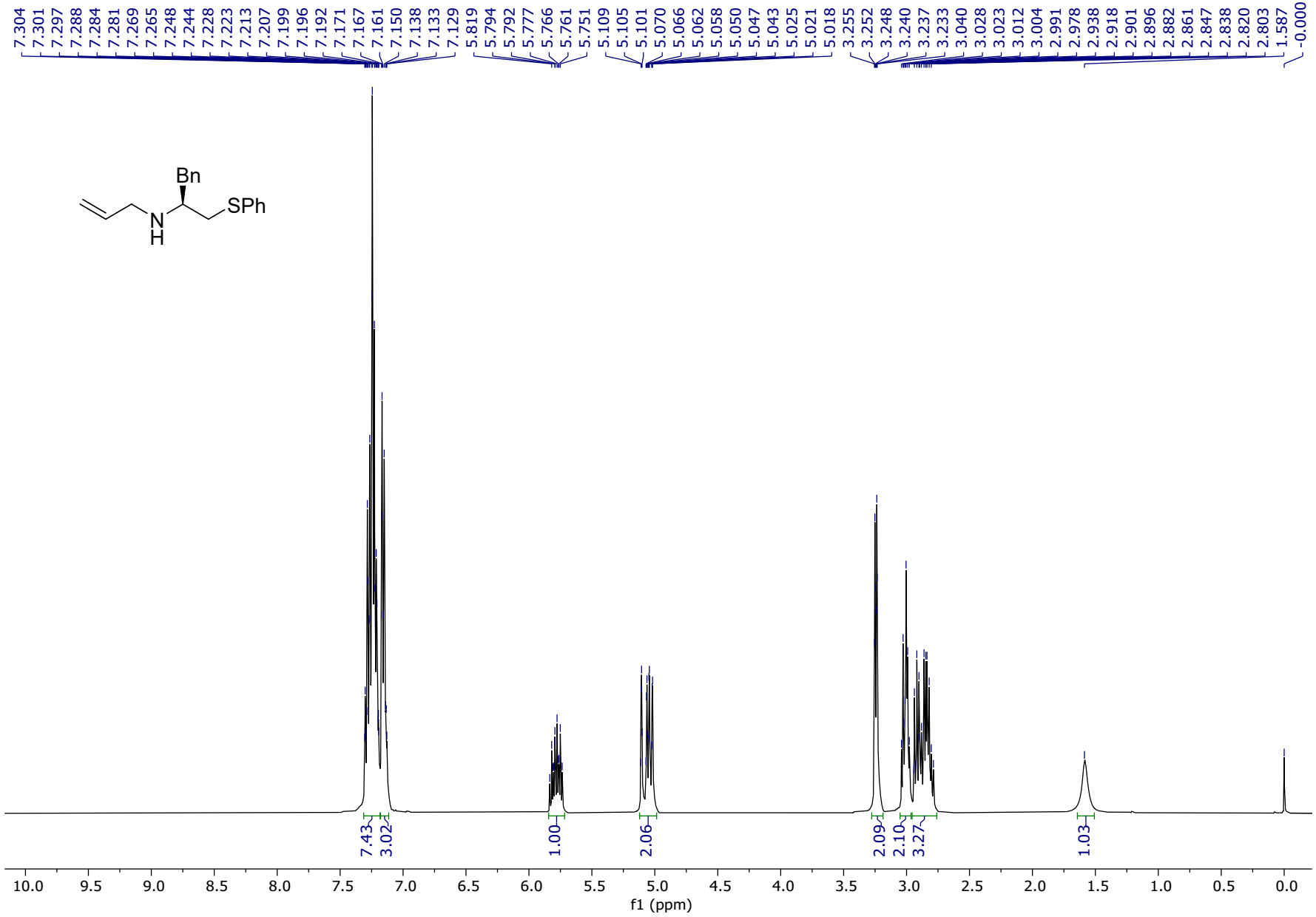


Figure S-70. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4m**.

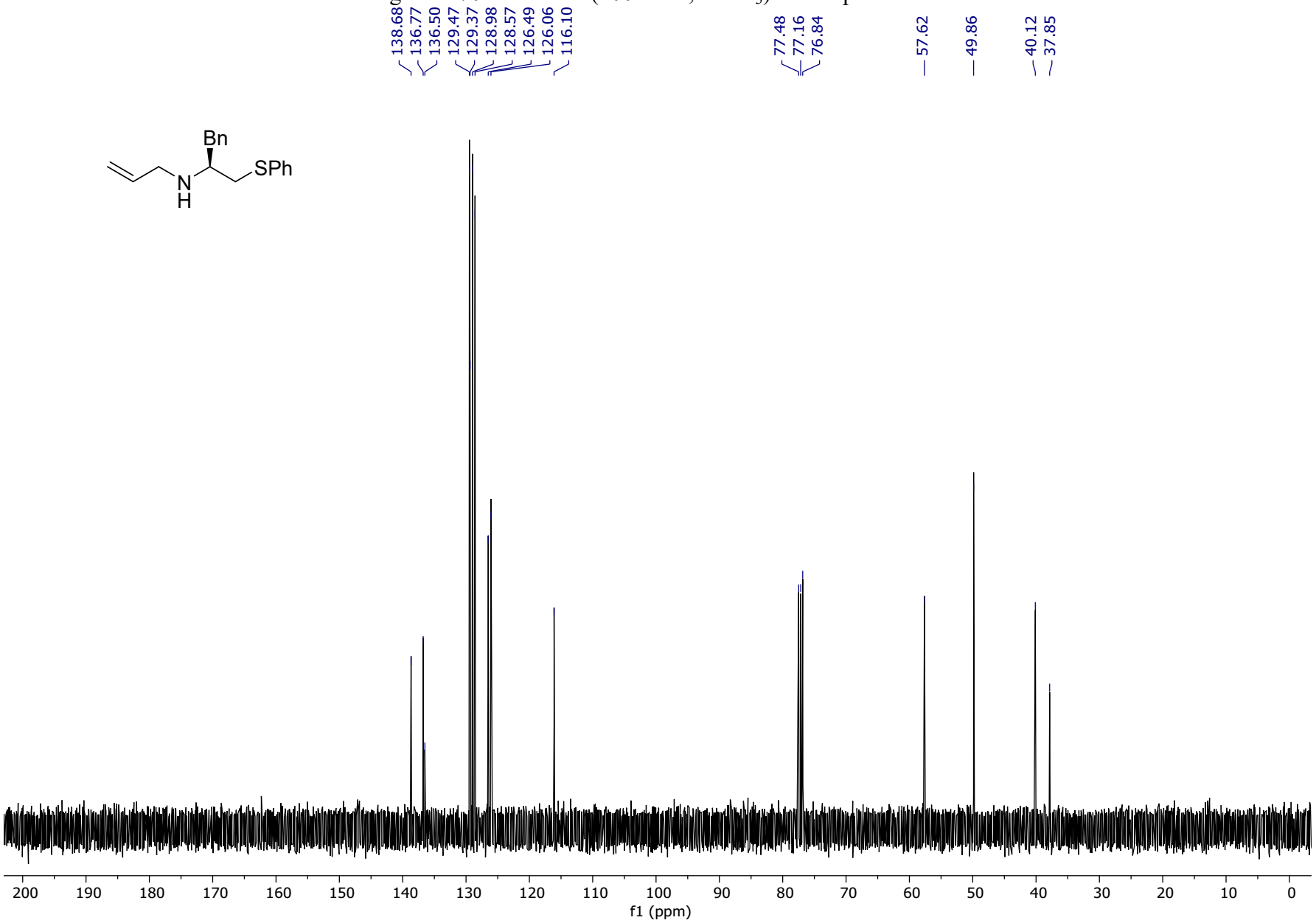


Figure S-71. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4n**.

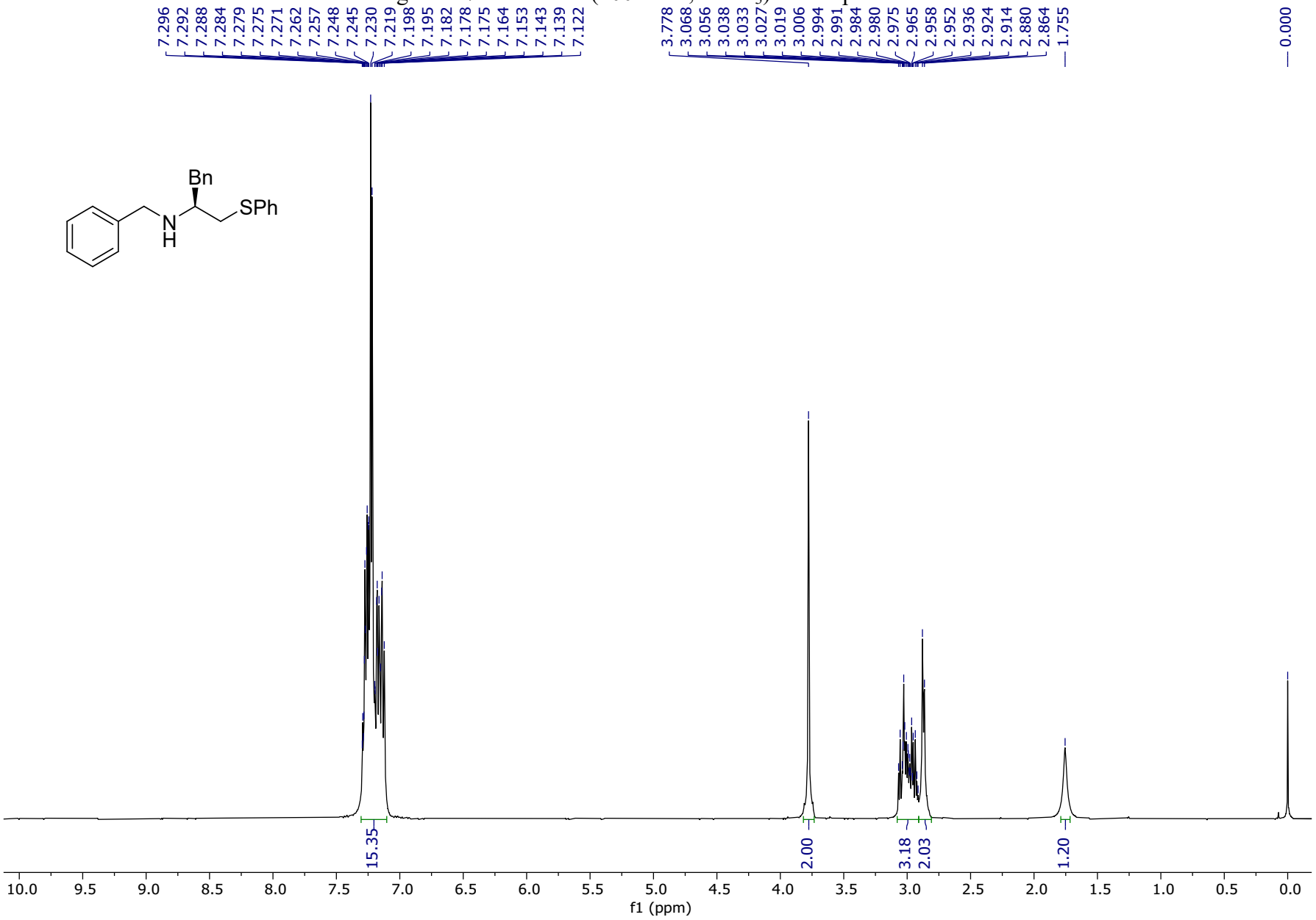


Figure S-72. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4n**.

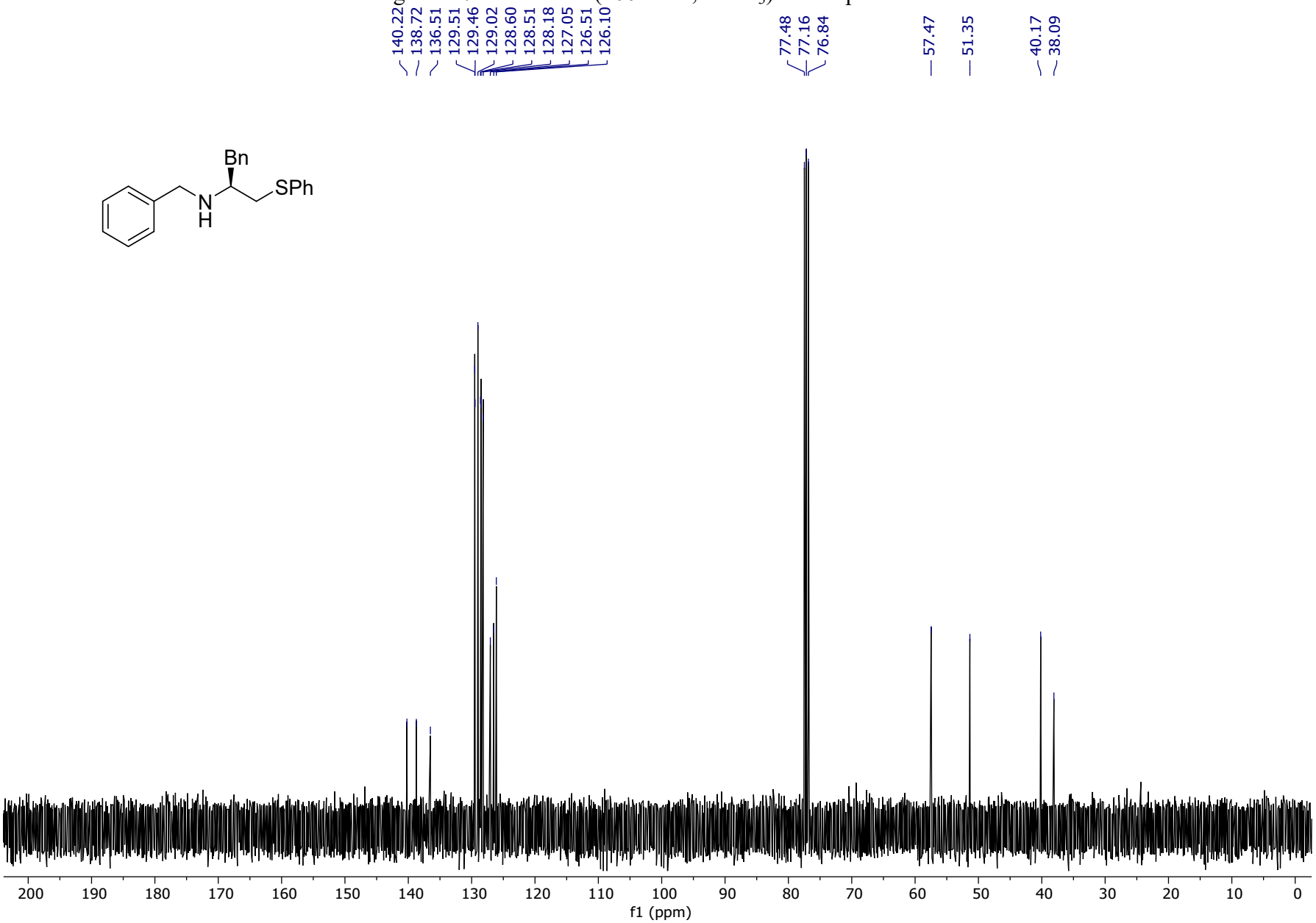


Figure S-73. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4o**.

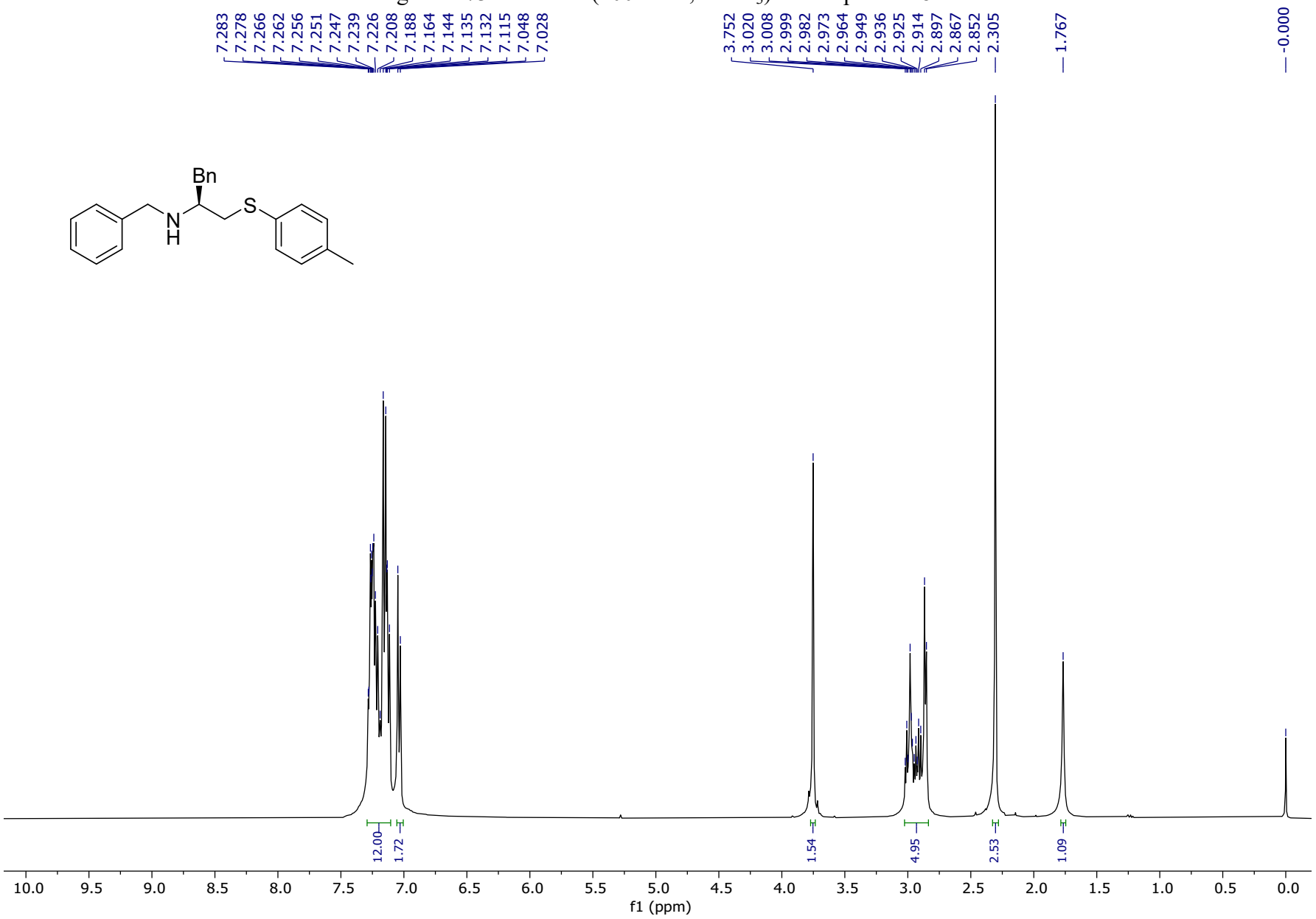


Figure S-74. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4o**.

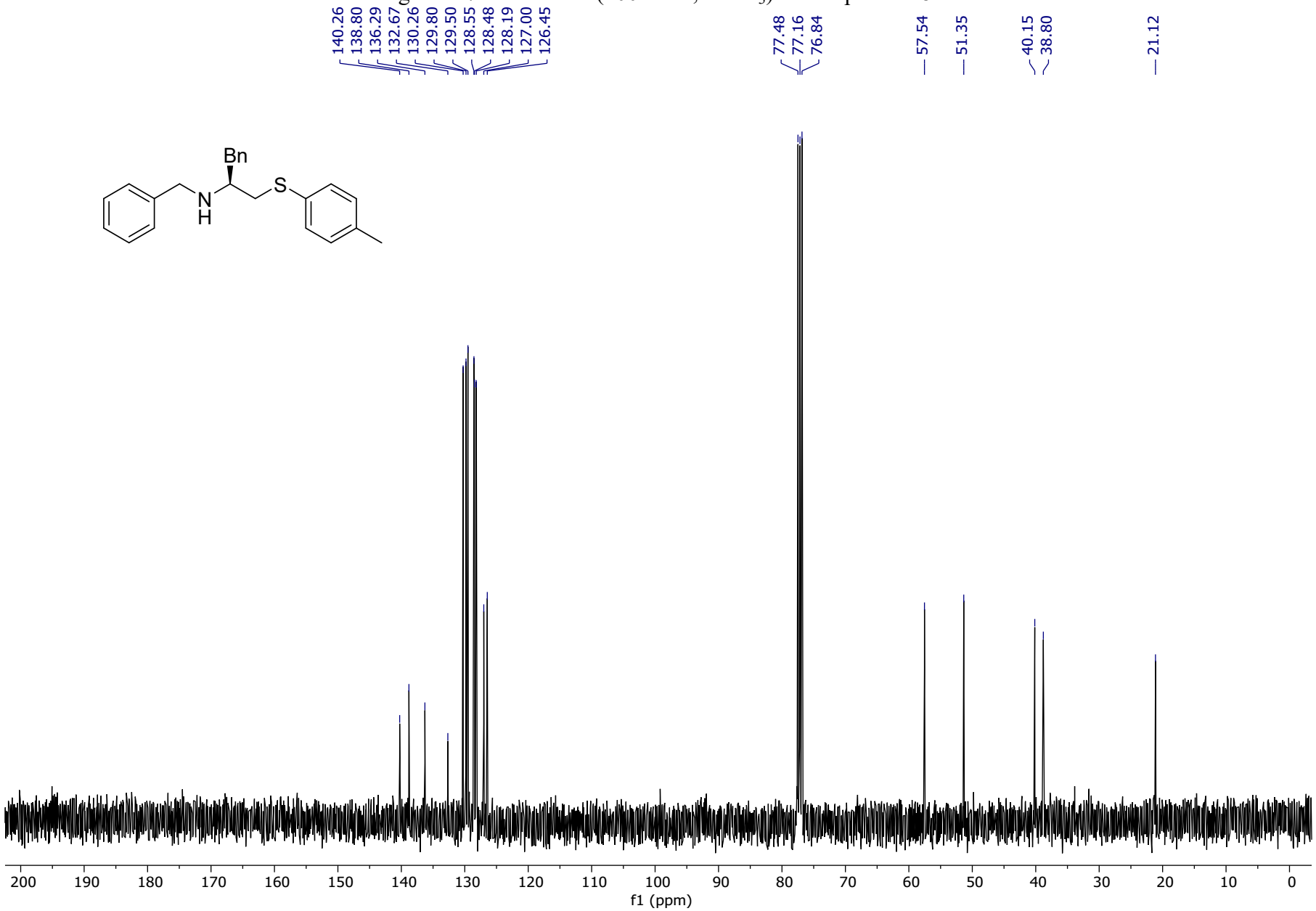


Figure S-75. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4p**.

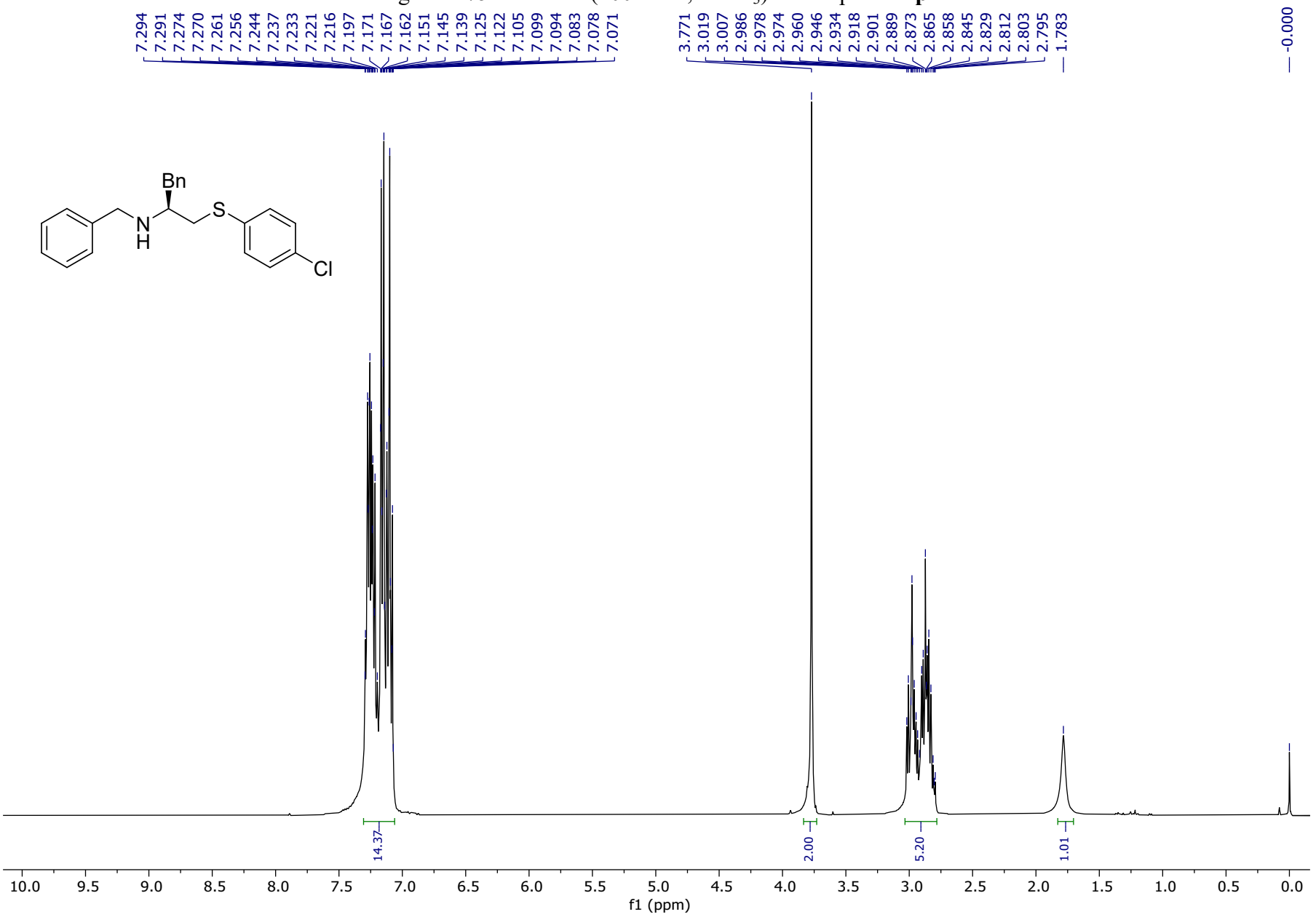


Figure S-76. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4p**.

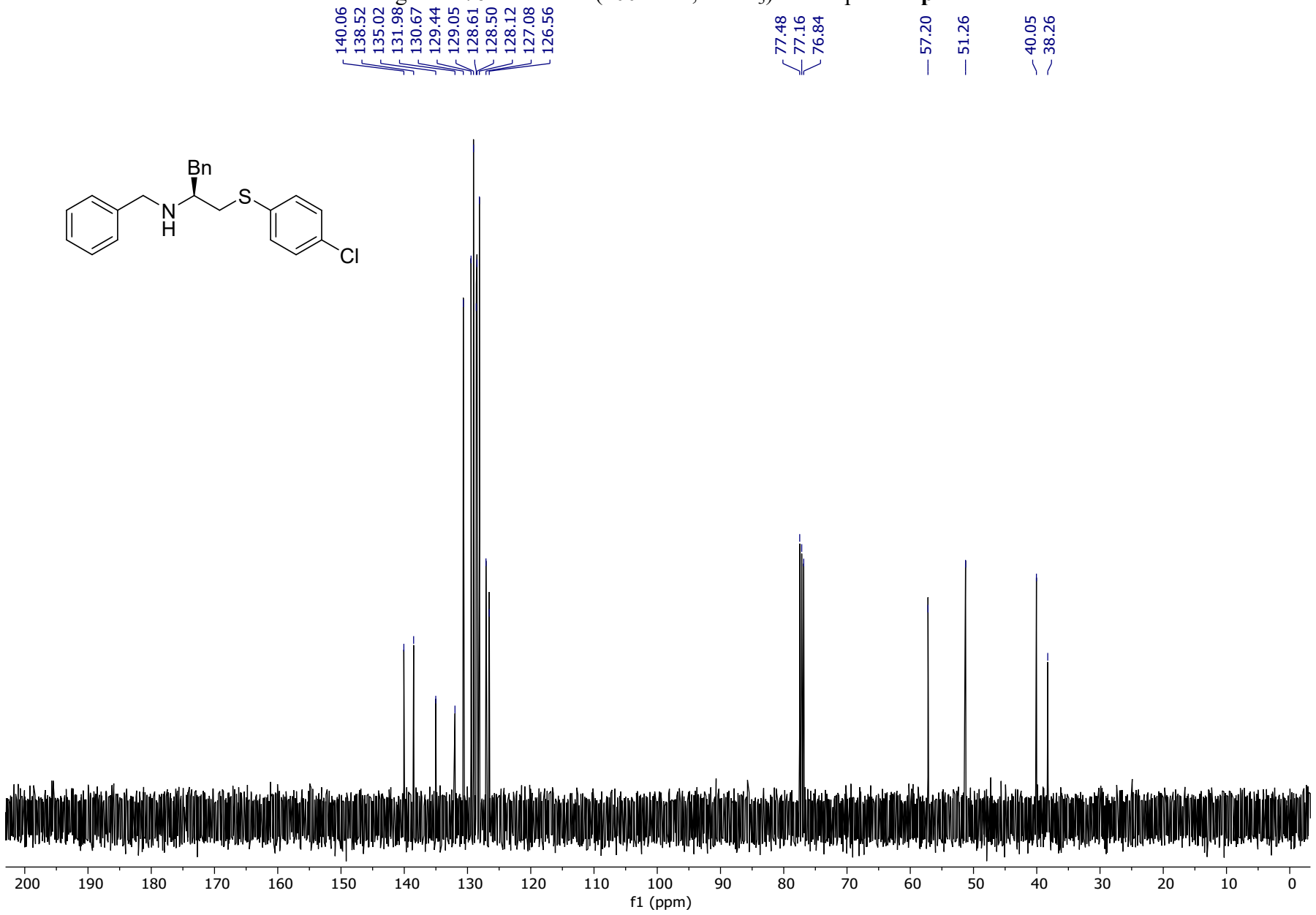


Figure S-77. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4q**.

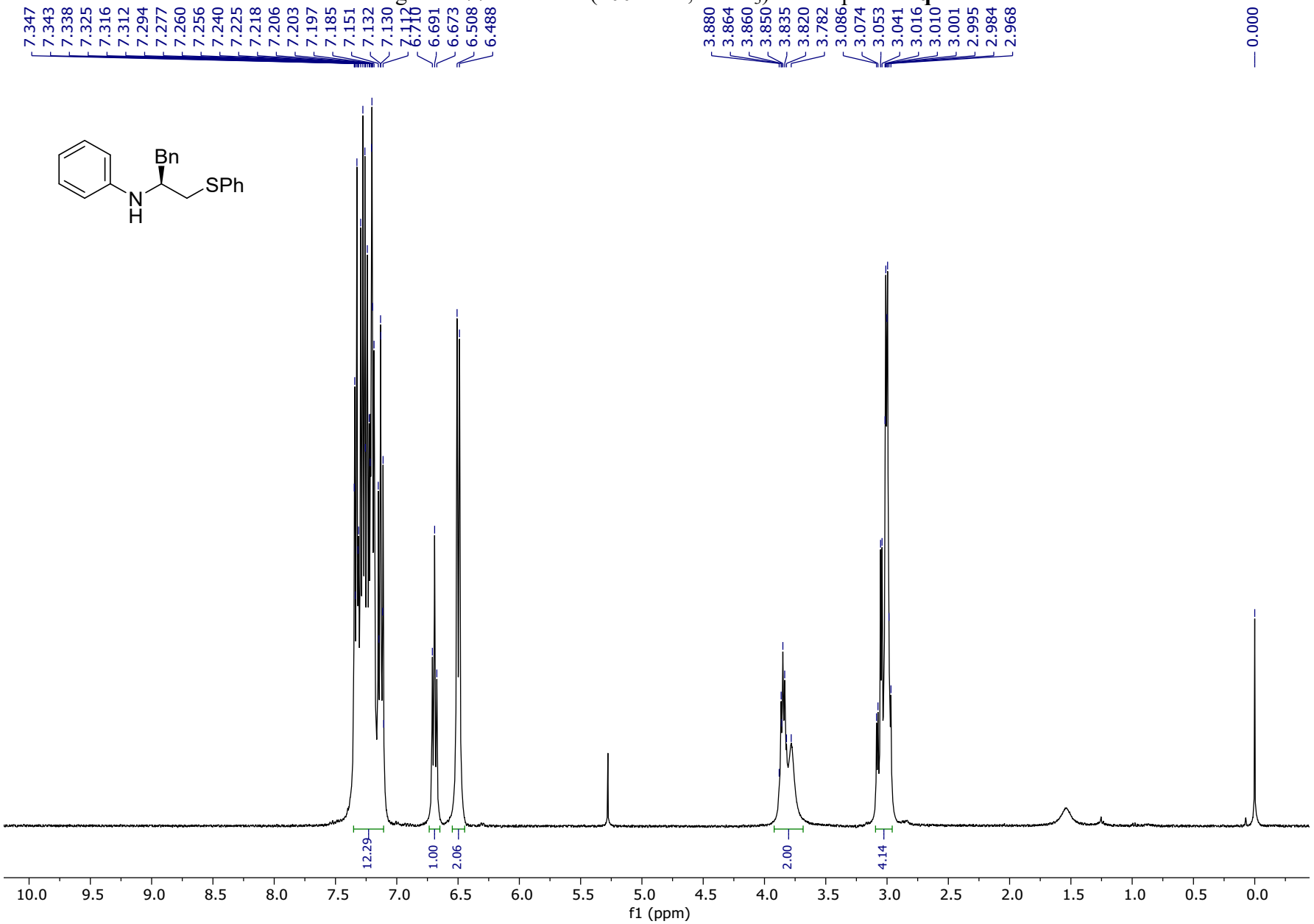


Figure S-78. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4q**.

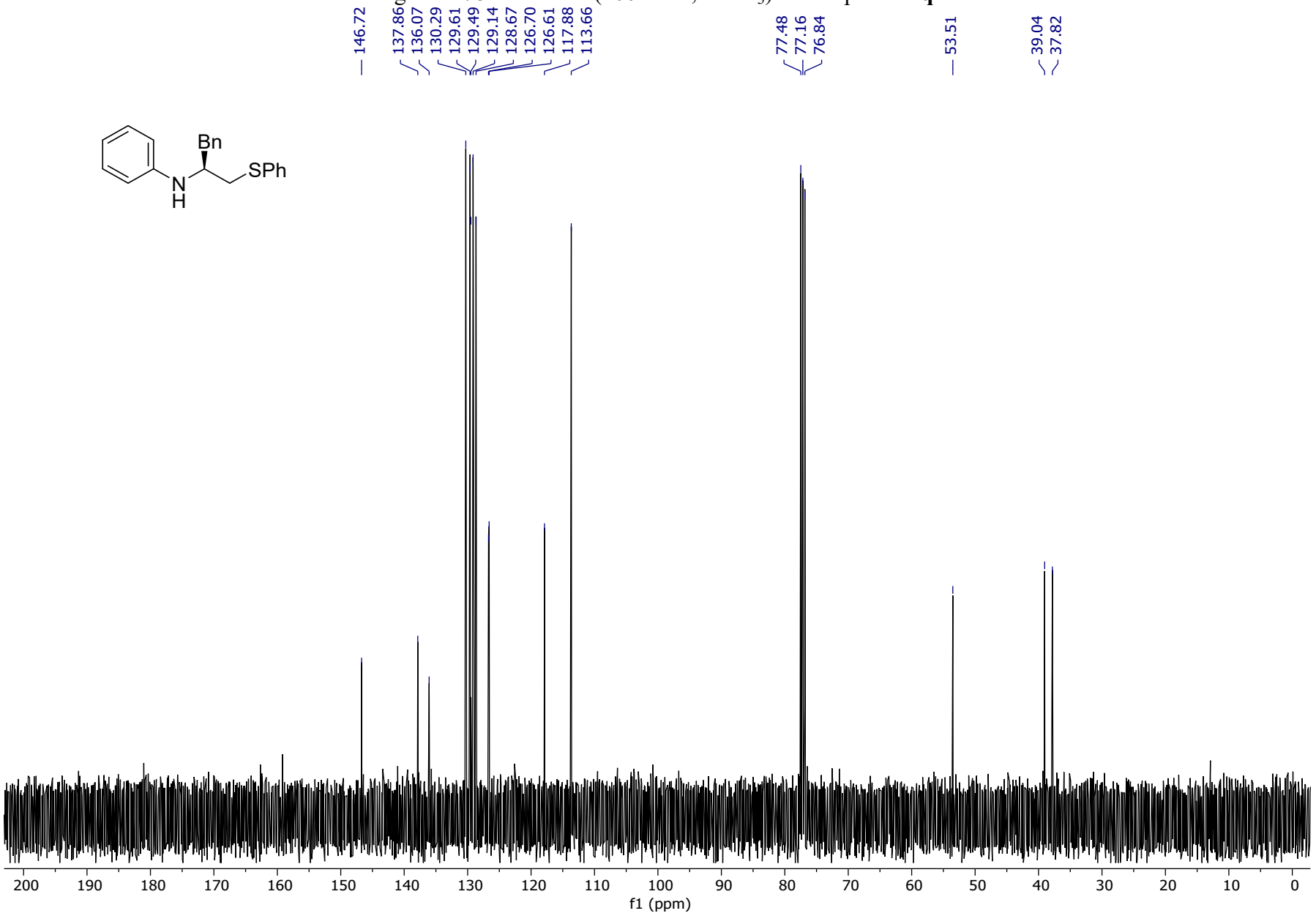


Figure S-79. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4r**.

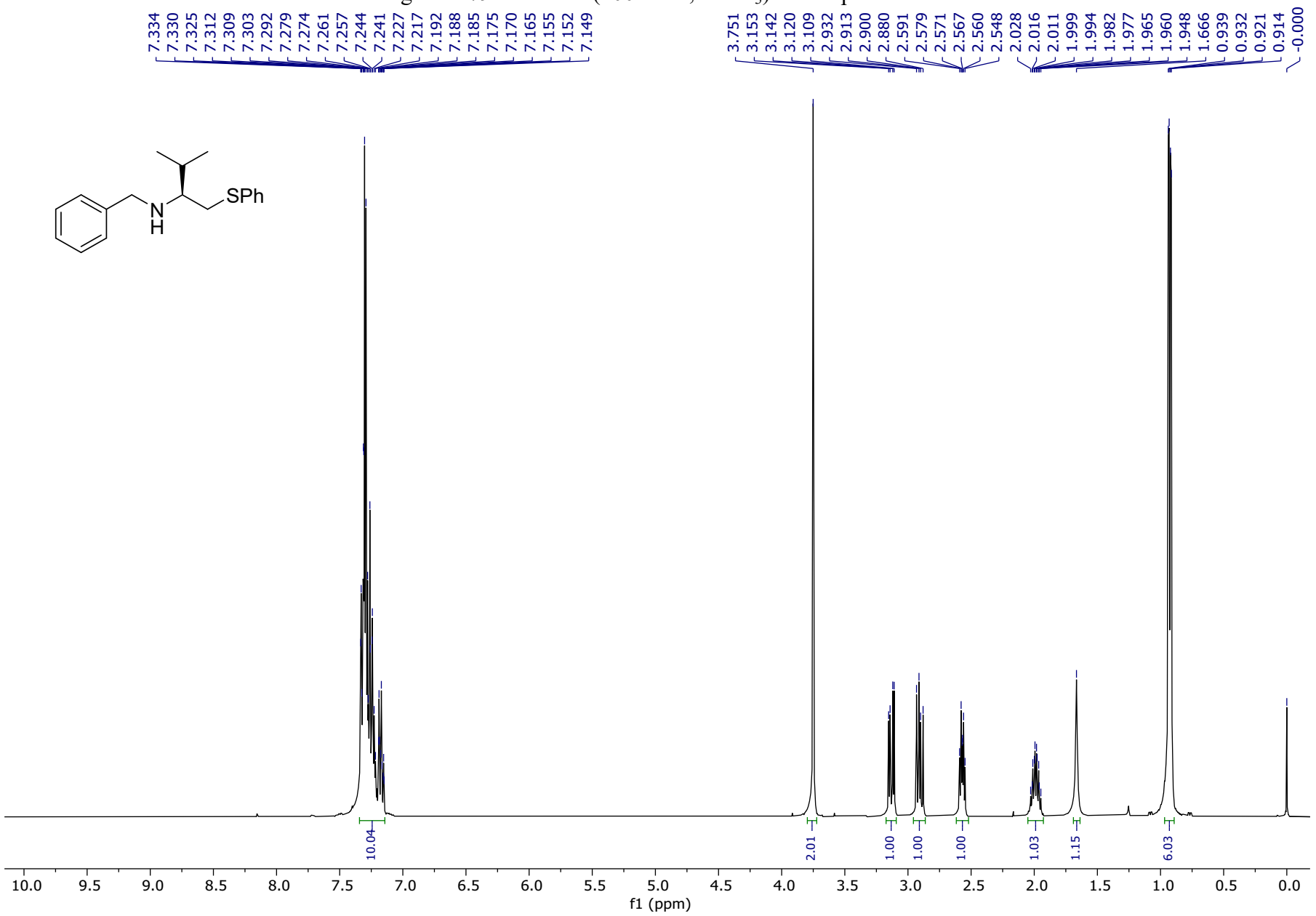


Figure S-80. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4r**.

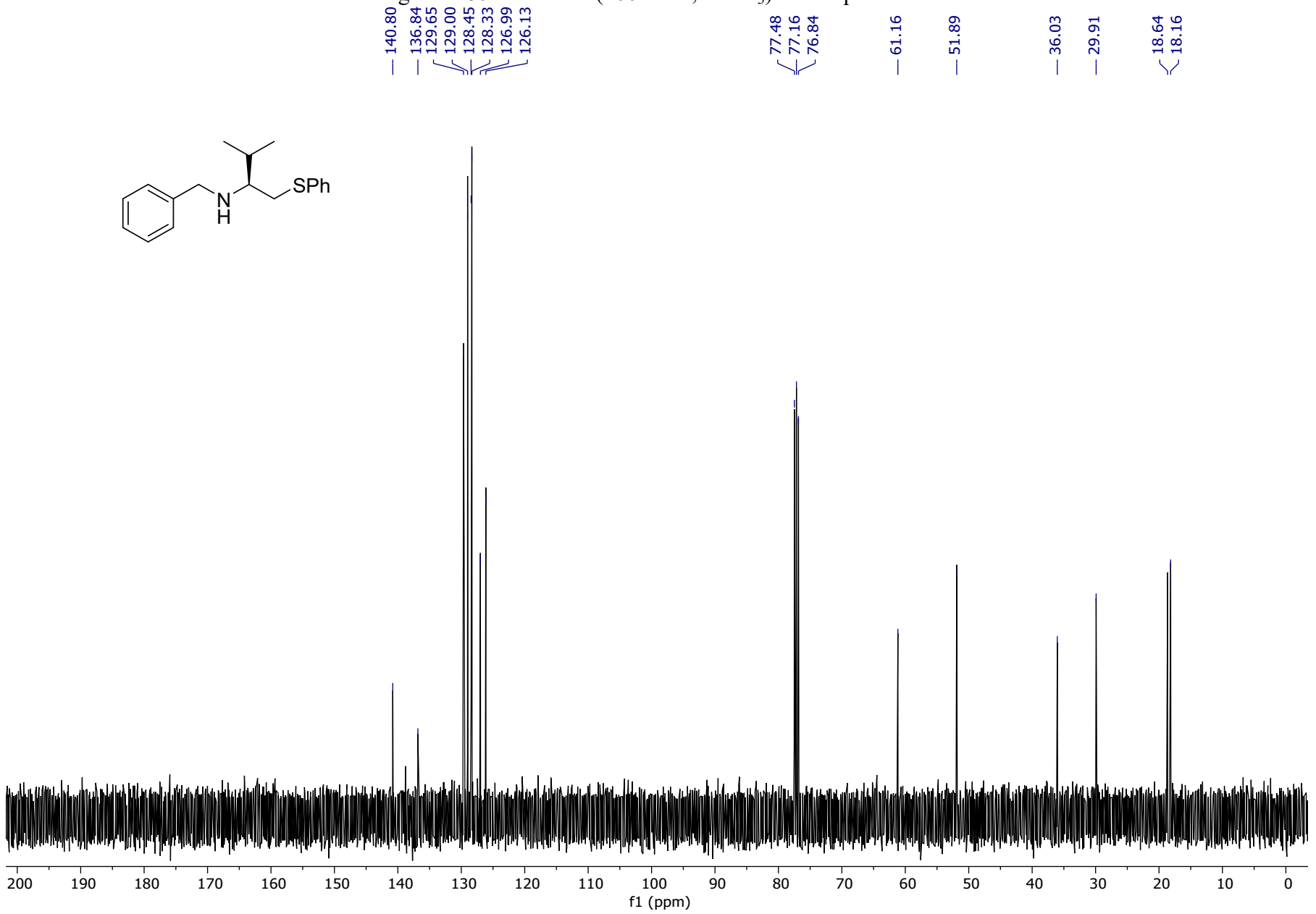


Figure S-81. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4s**.

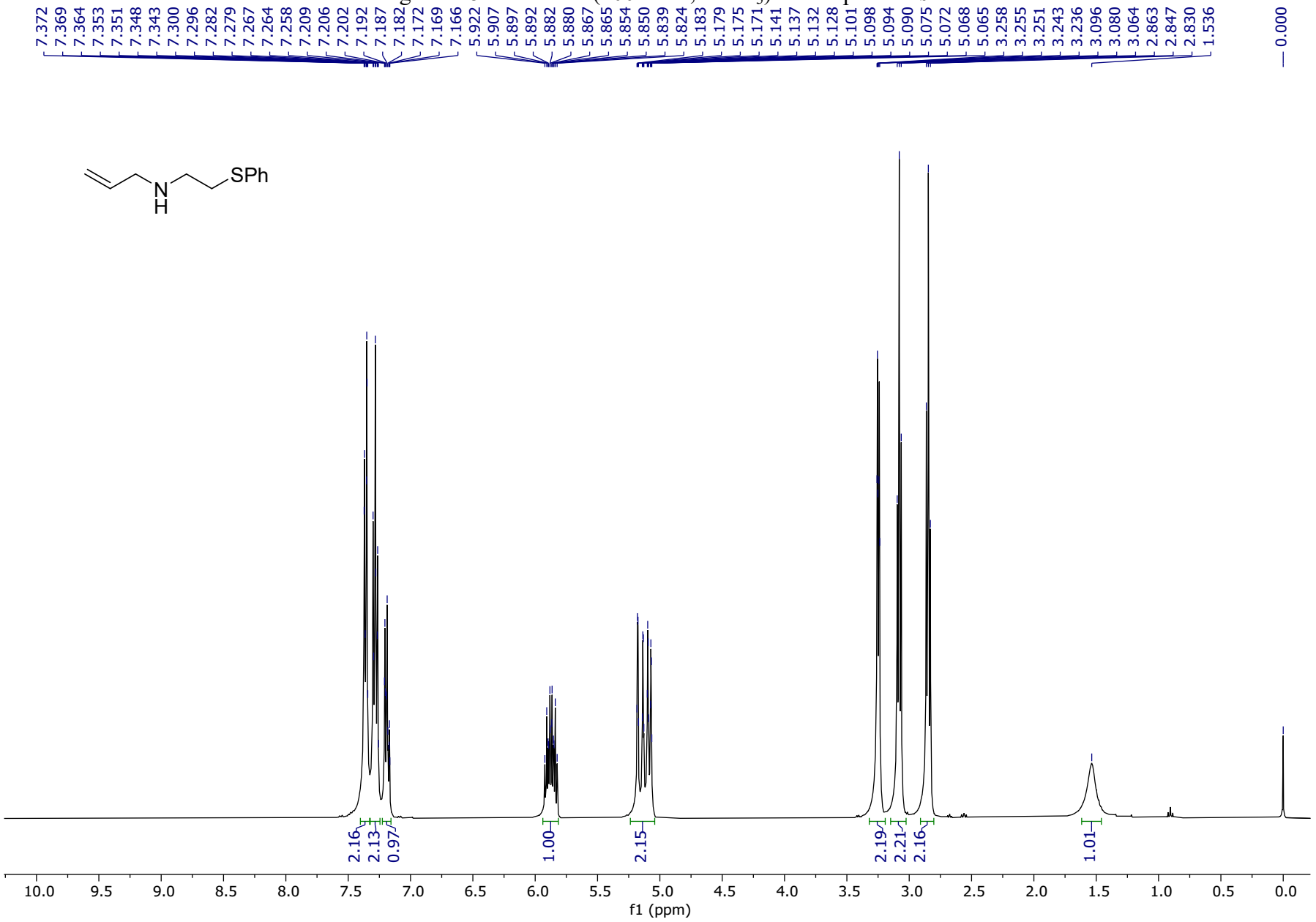


Figure S-82. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4s**.

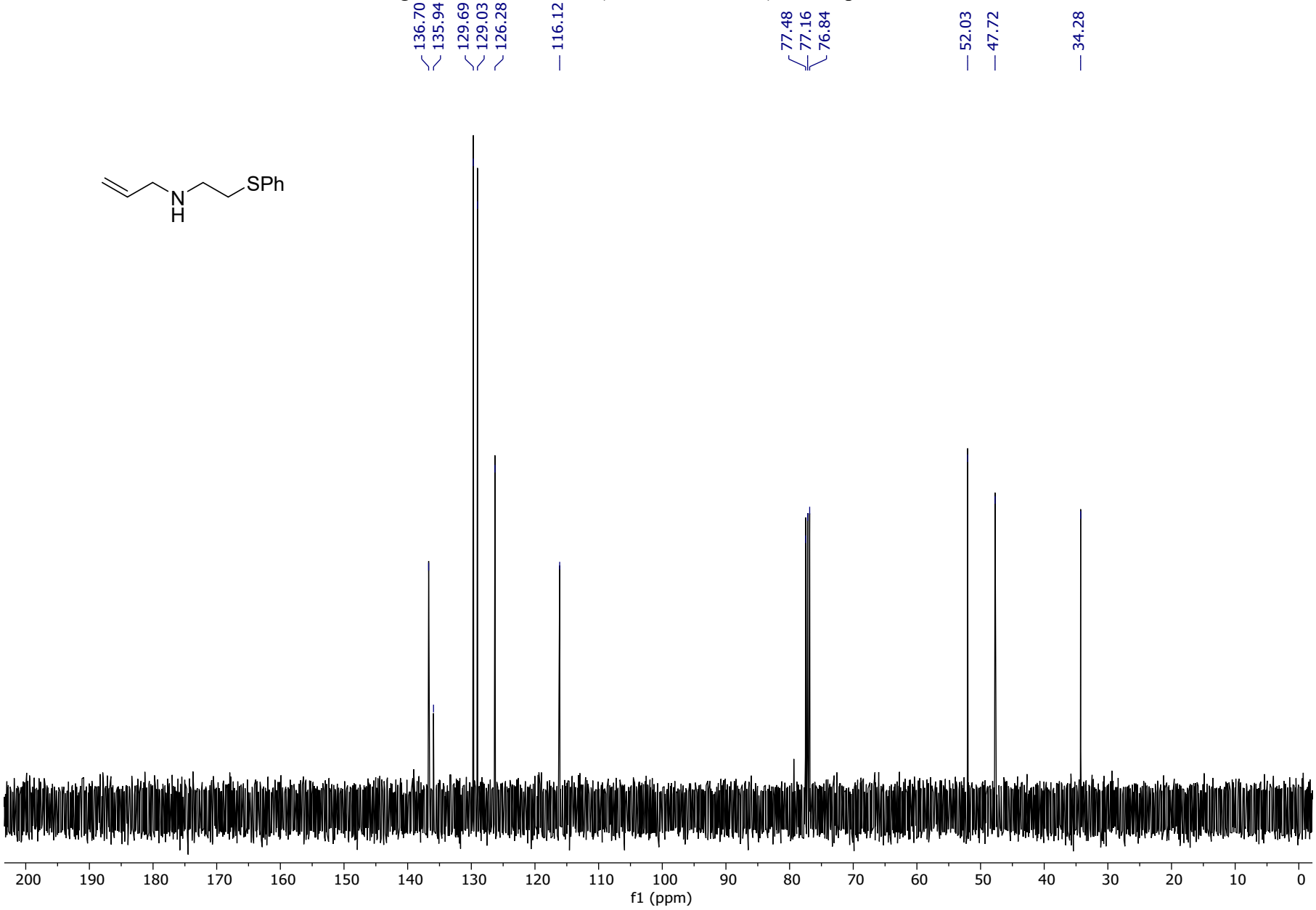


Figure S-83. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4t**.

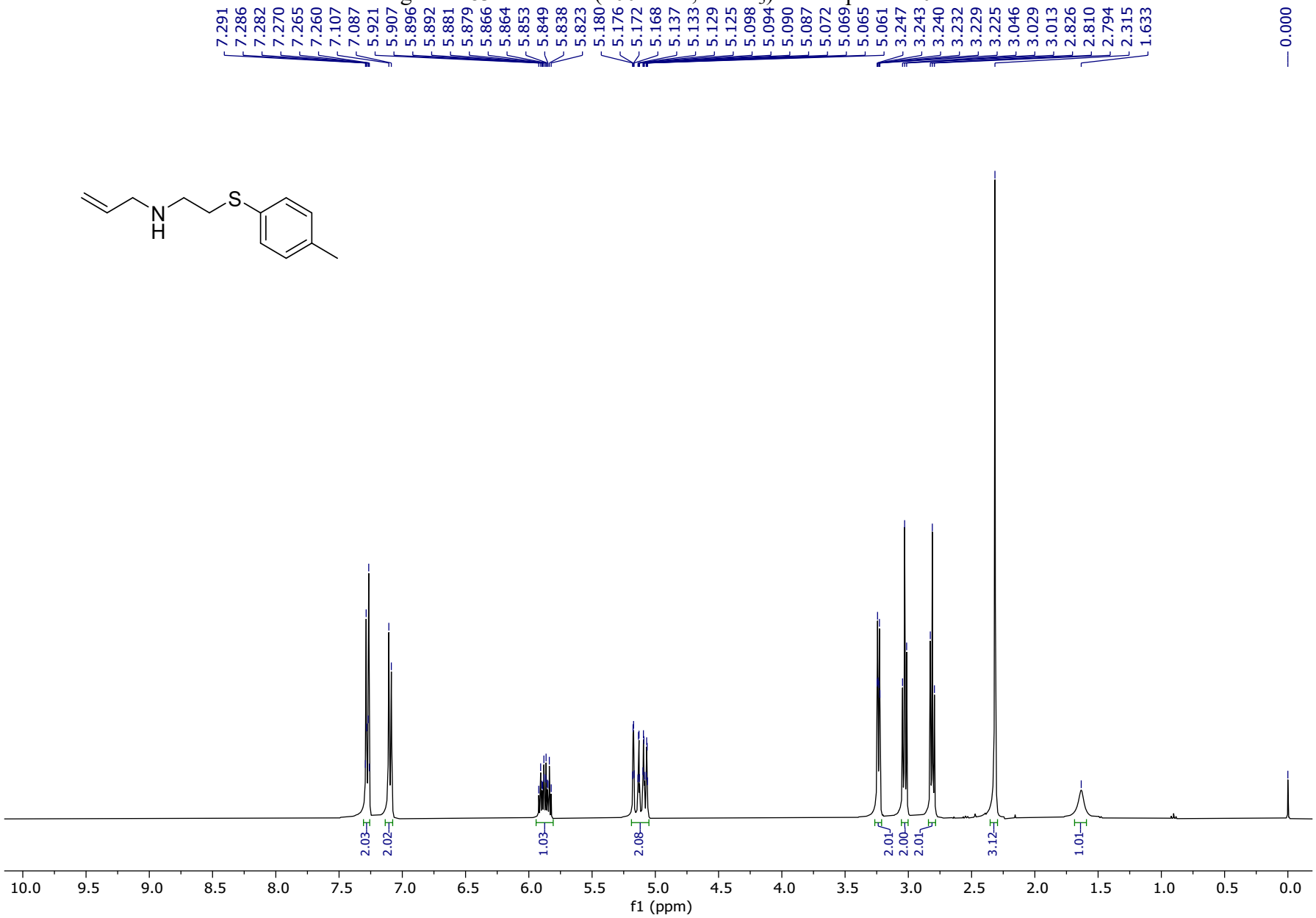


Figure S-84. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4t**.

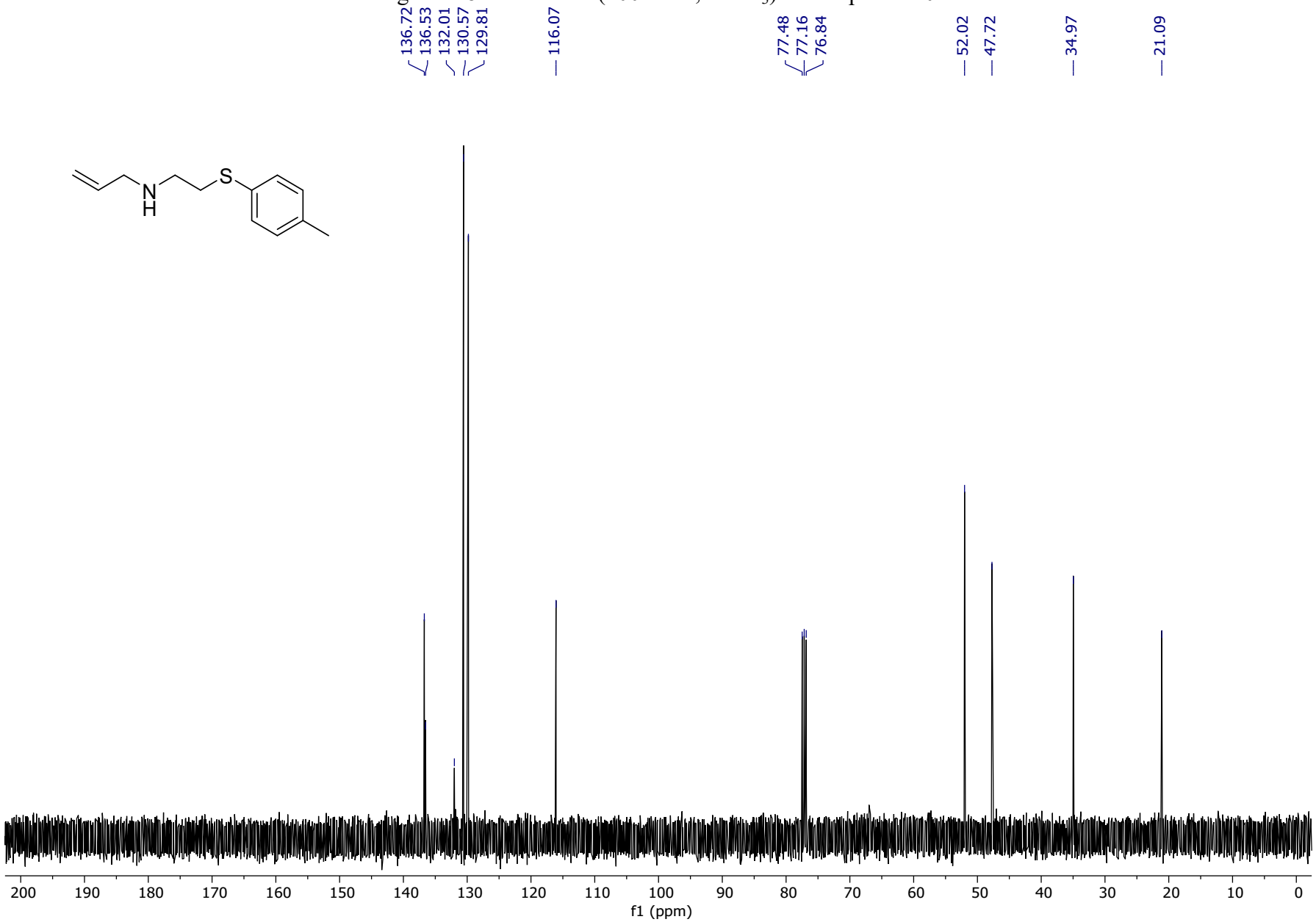


Figure S-85. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4u**.

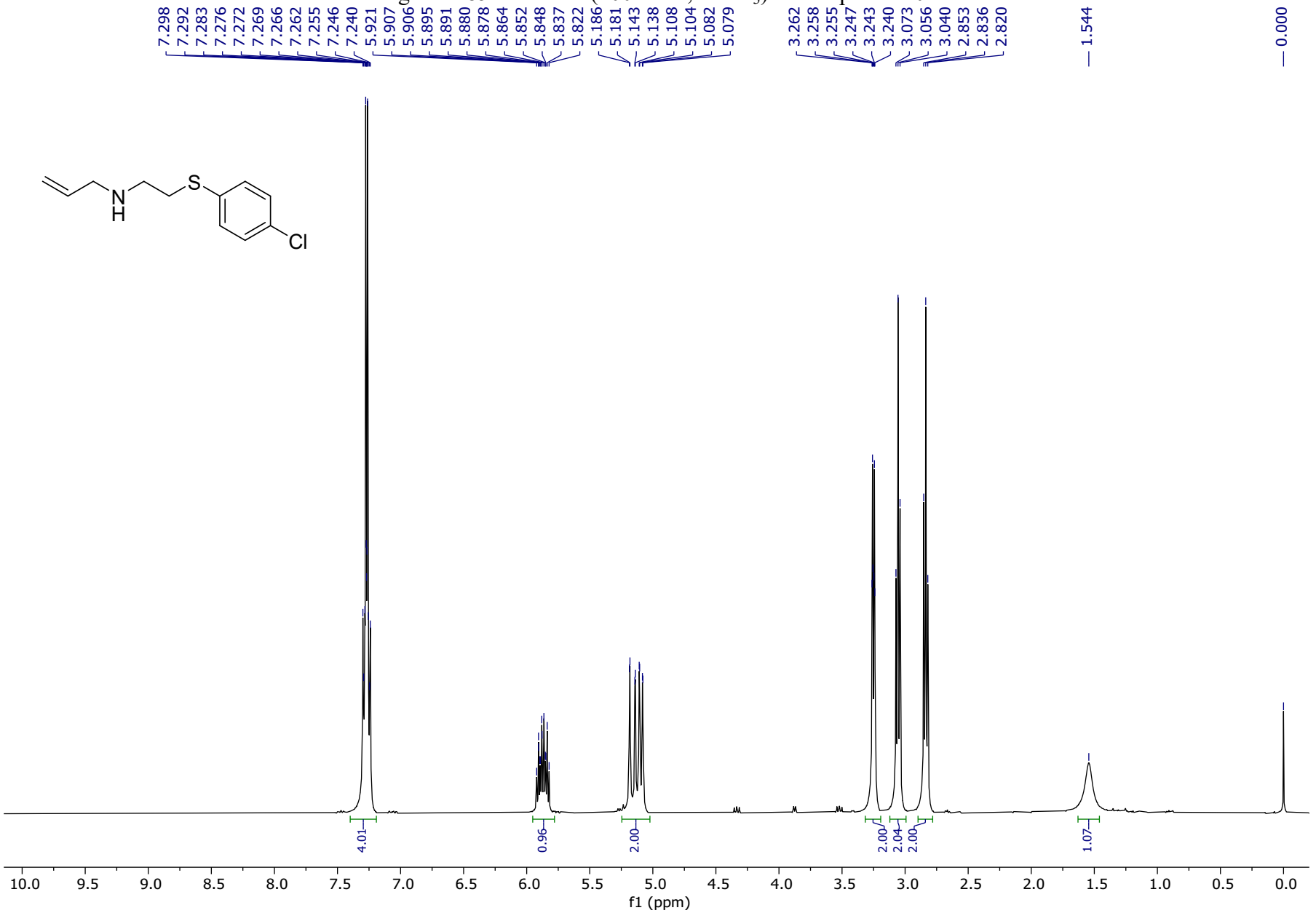


Figure S-86. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4u**.

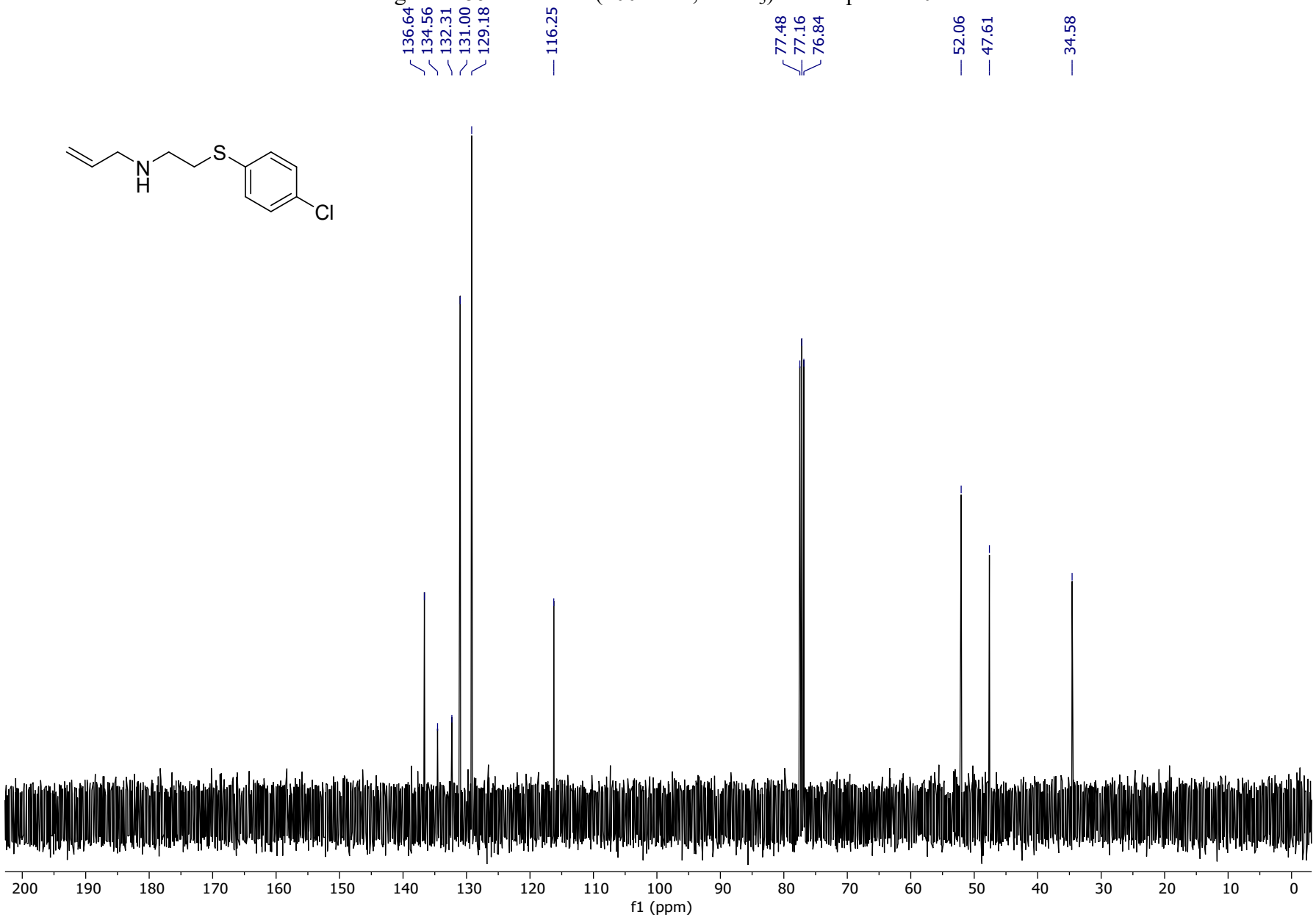


Figure S-87. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4v**.

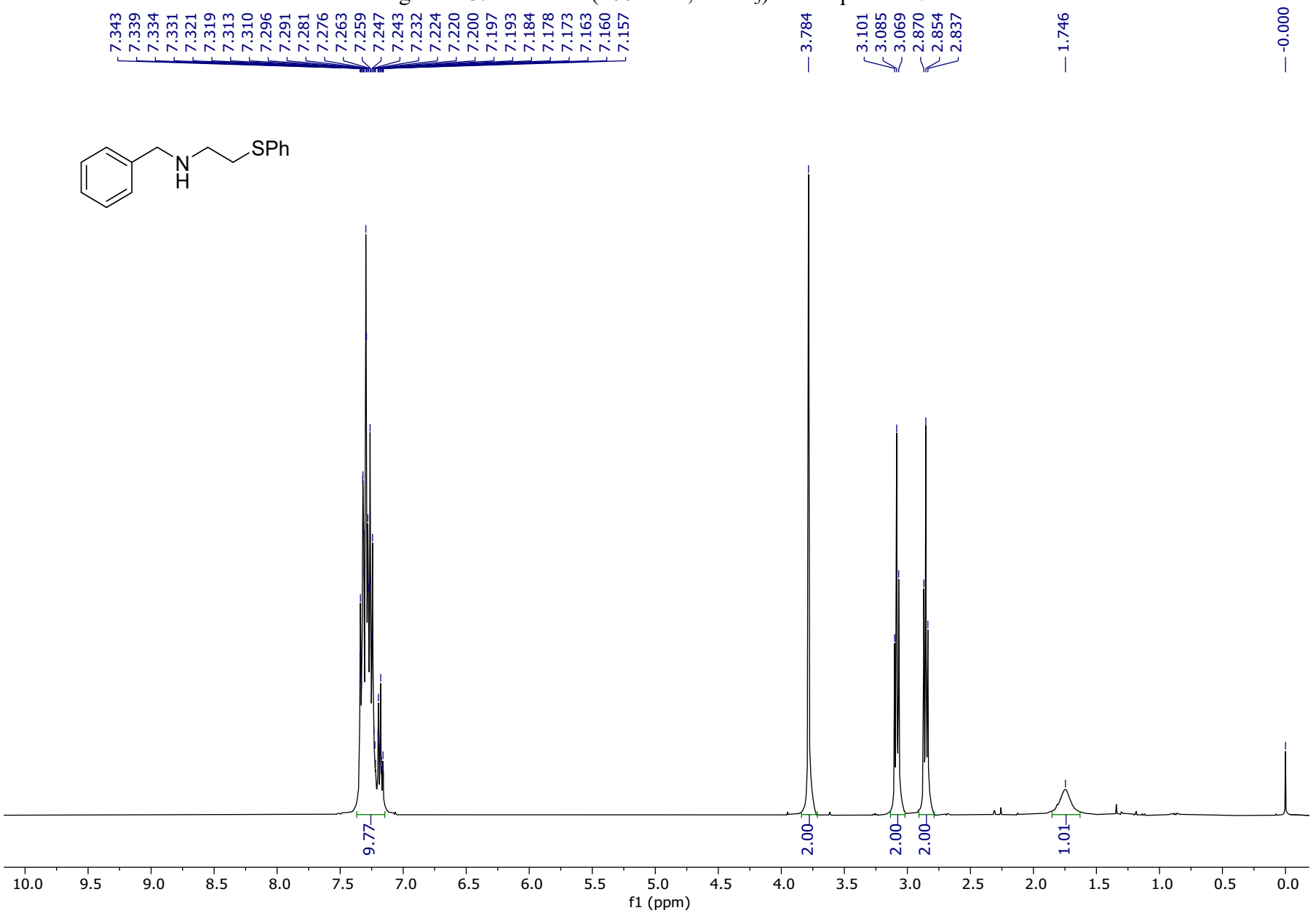


Figure S-88. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4v**.

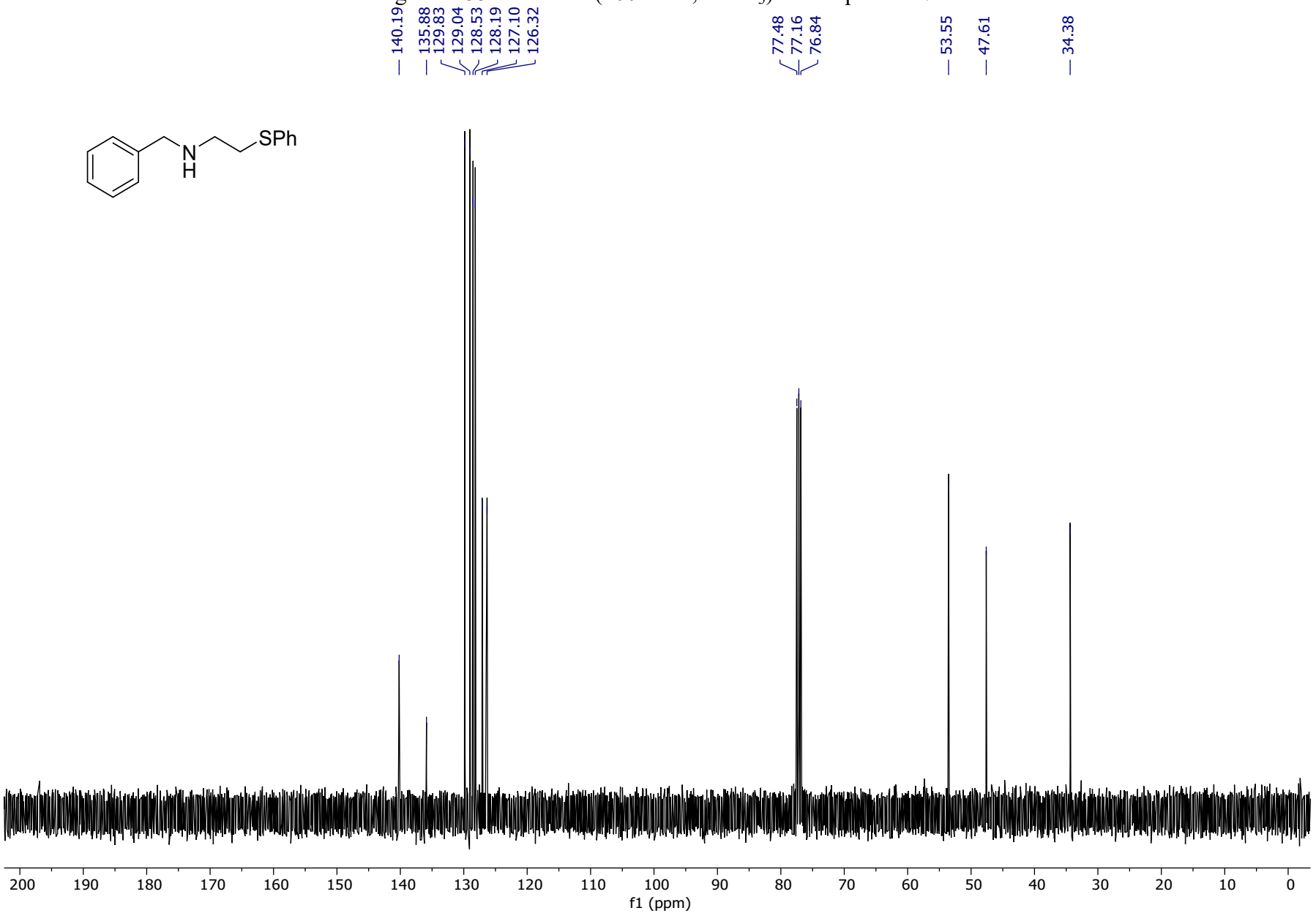


Figure S-89. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4w**.

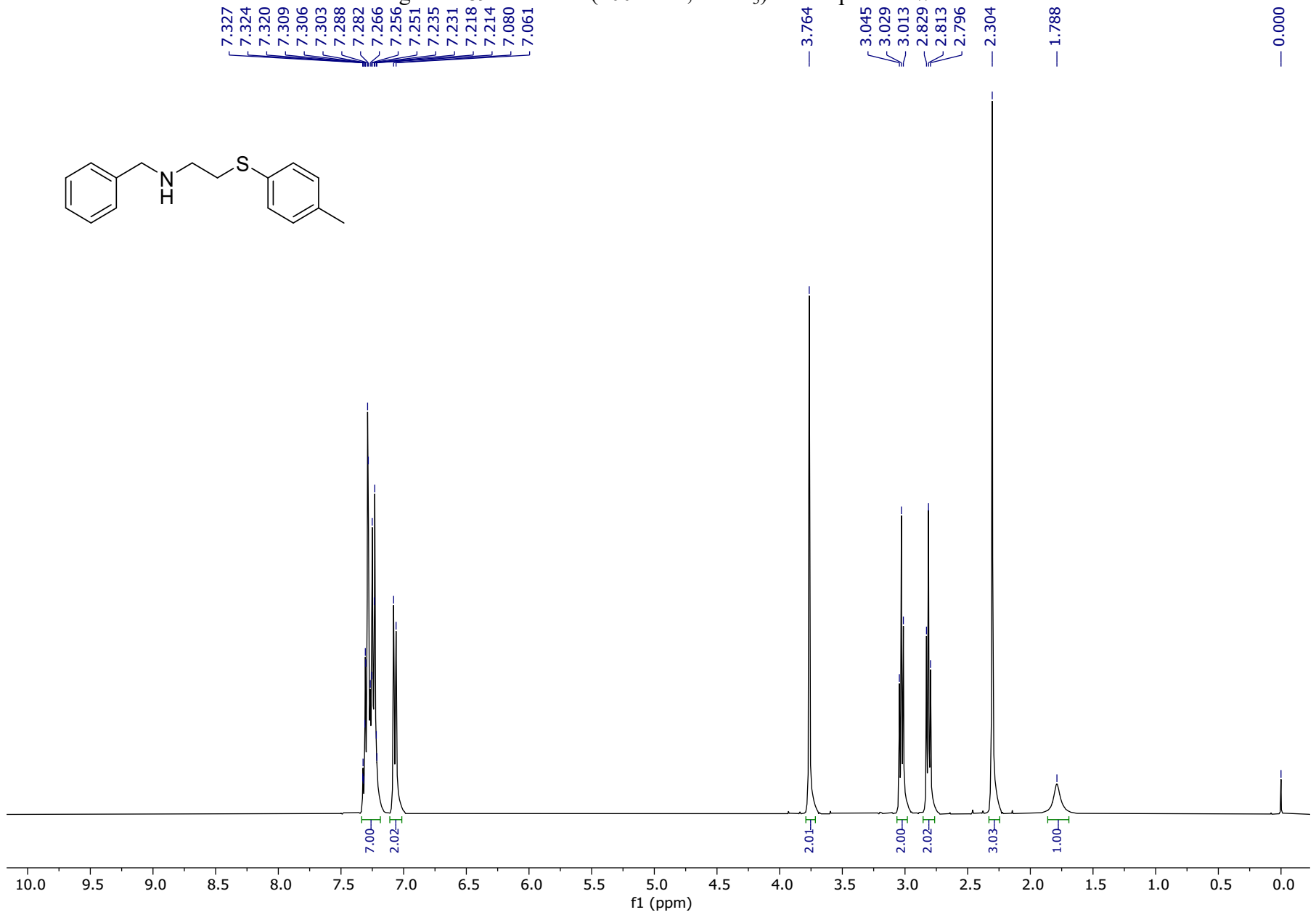


Figure S-90. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4w**.

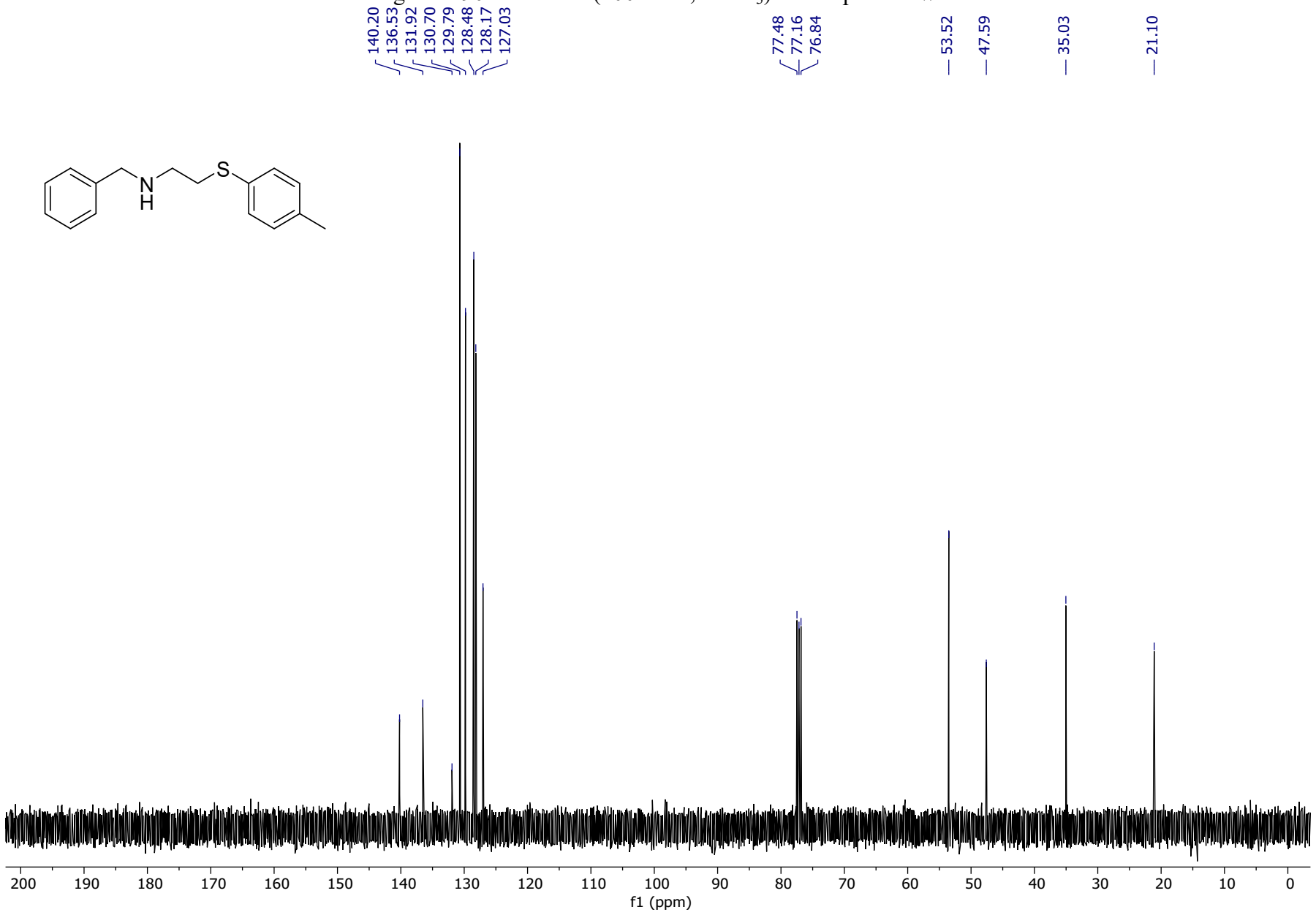


Figure S-91. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4x**.

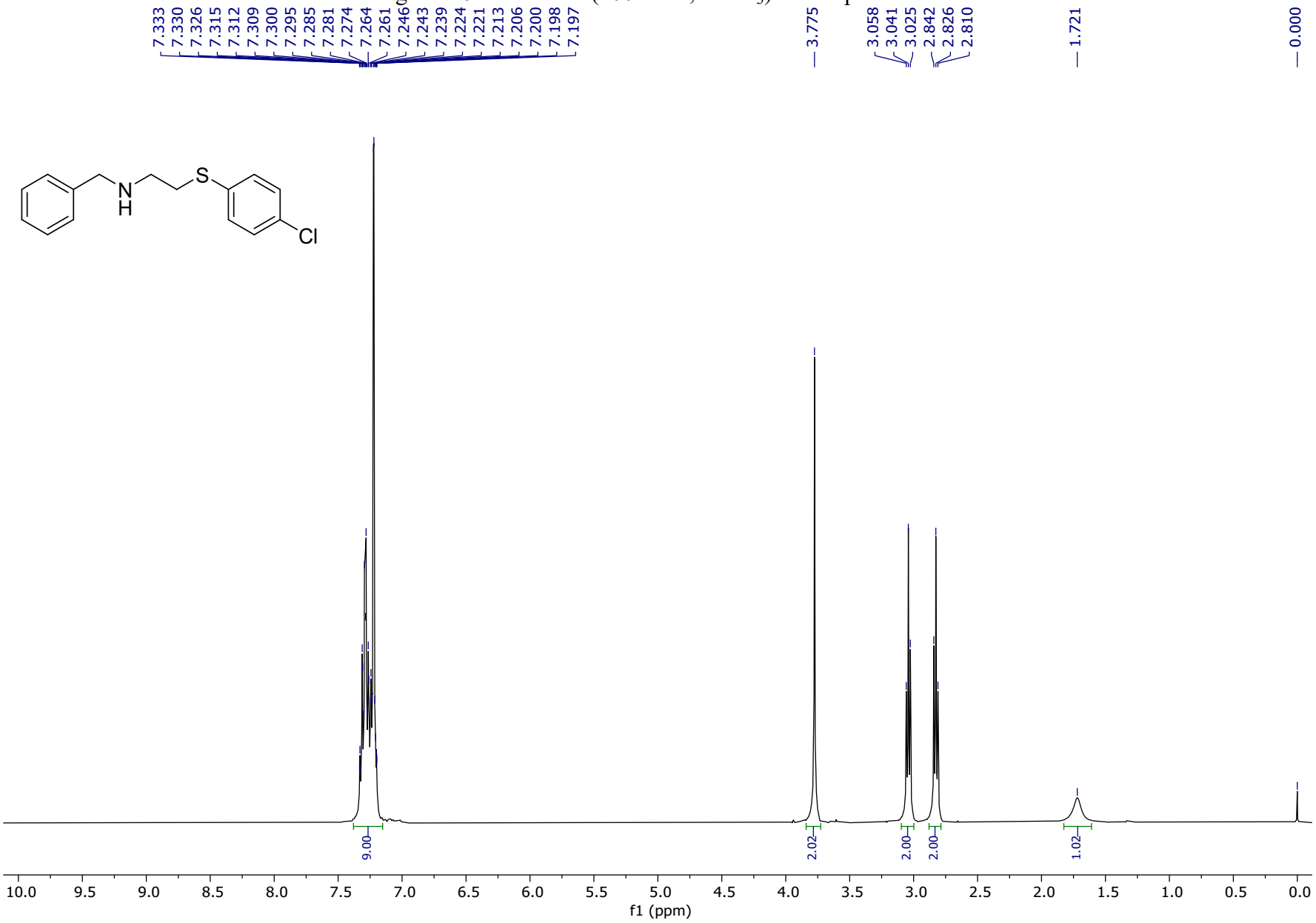


Figure S-92. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4x**.

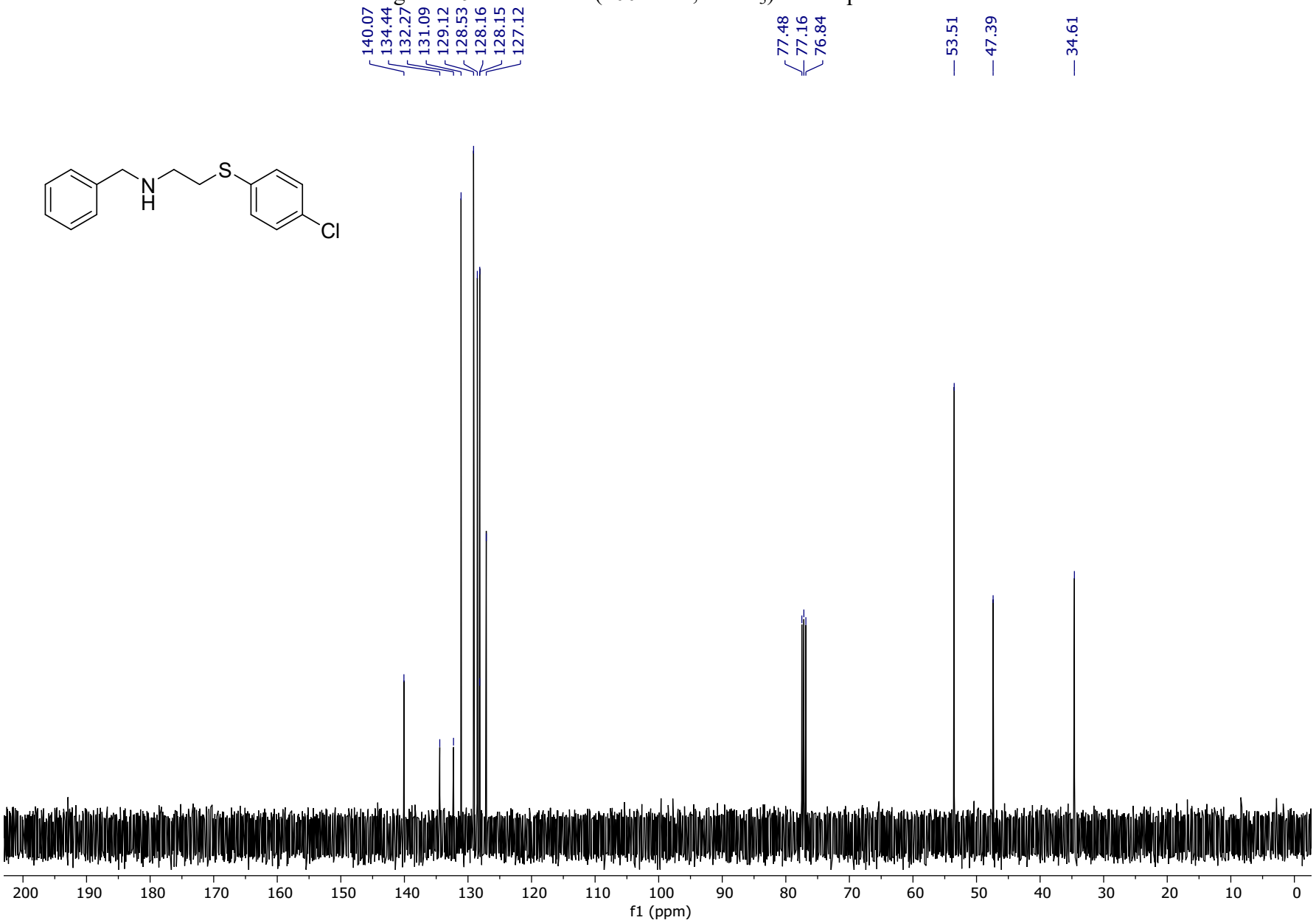


Figure S-93. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4y**.

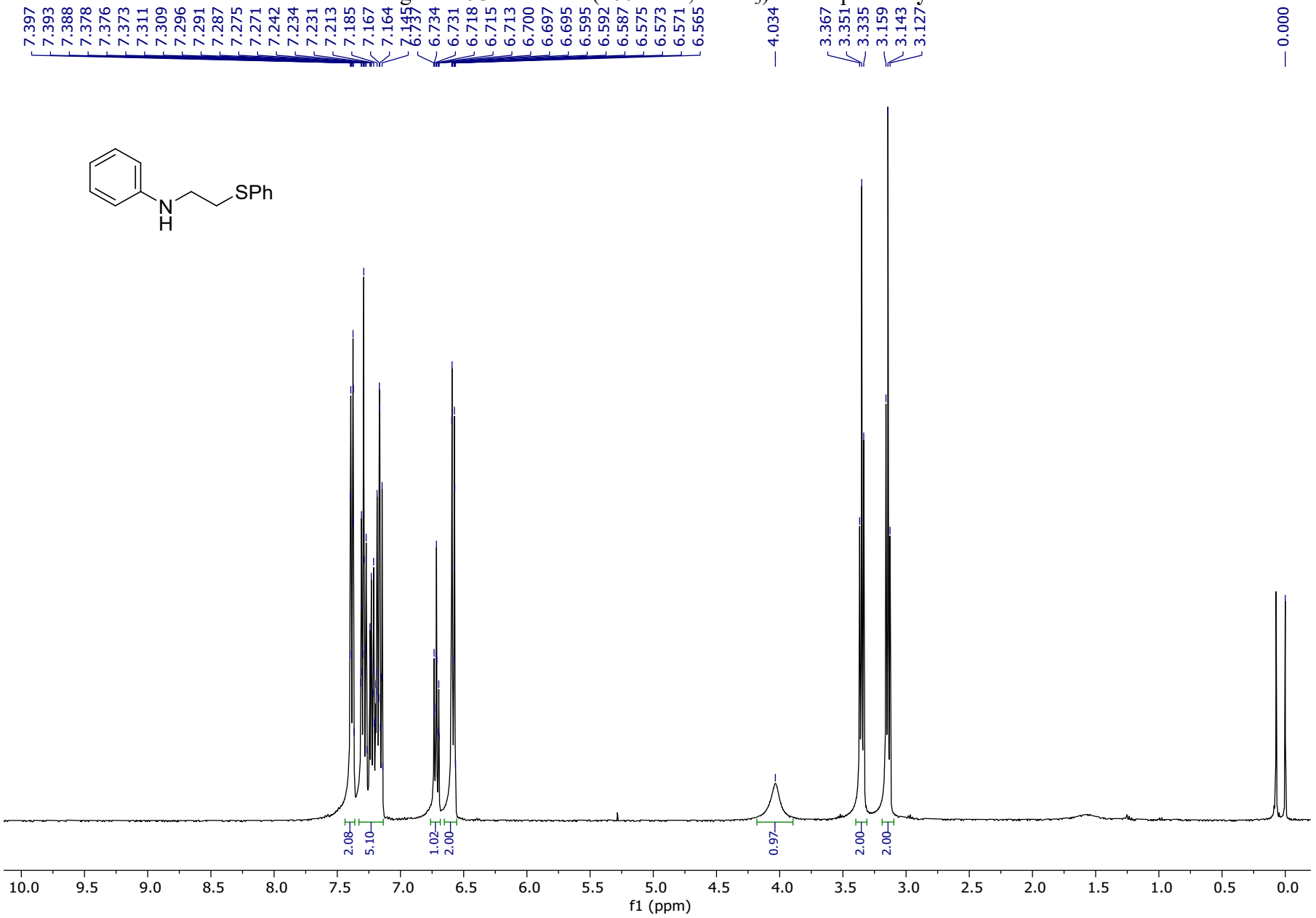
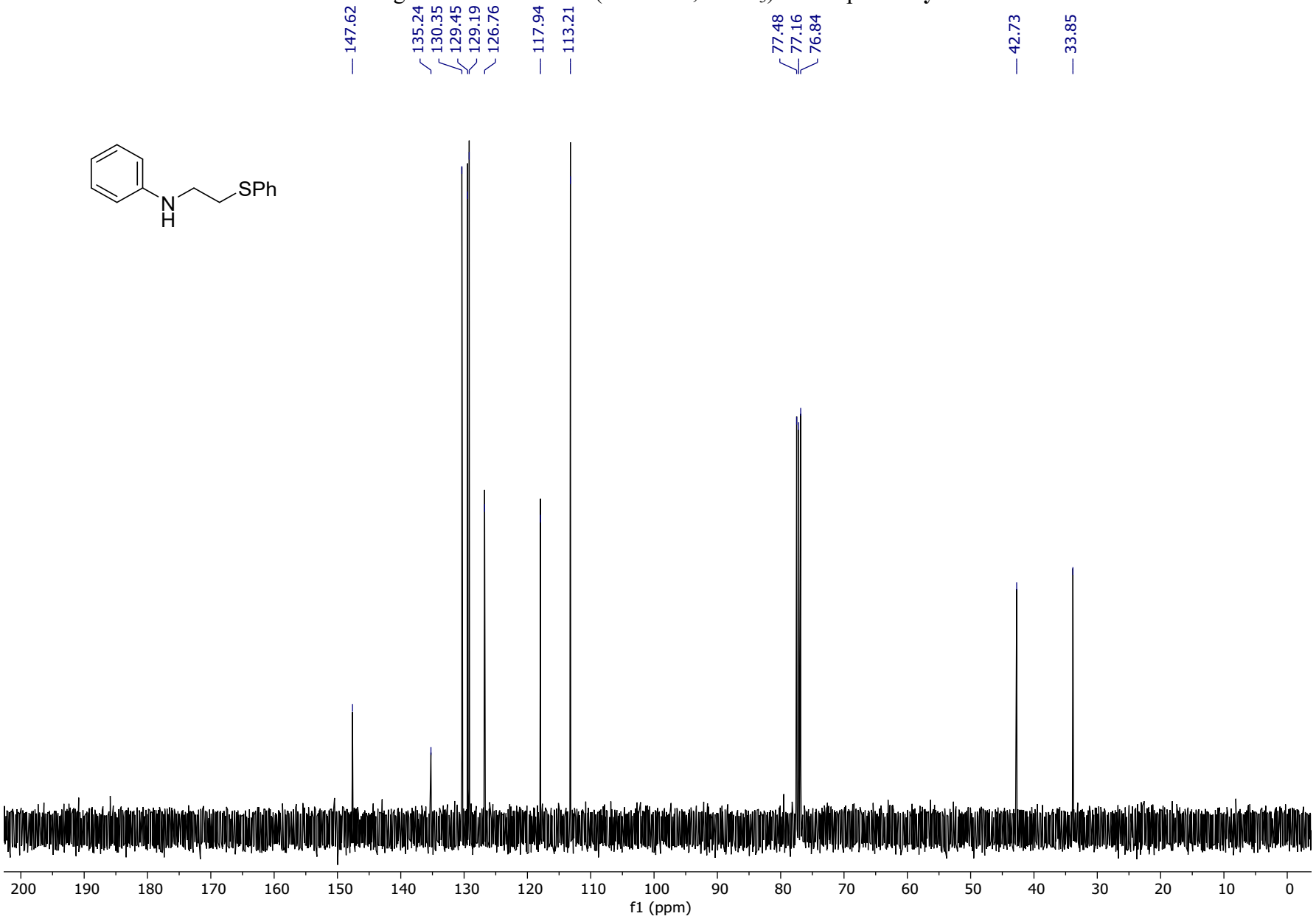


Figure S-94. ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4y**.



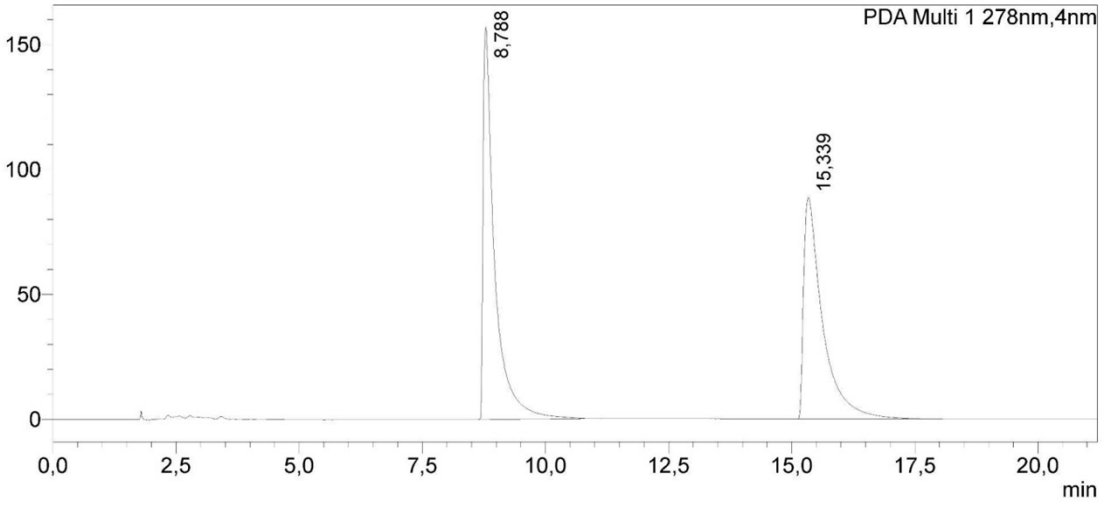
HPLC data

The (*R*)-**2a** enantiomer was prepared from (*R*)-4-benzyl-2-oxazolidinone following the same procedure described on pages S3-S4 (milligram scale reactions). The racemic mixture (*R,S*)-**2a** was prepared by mixing equimolar amounts of the enantiomers (*R*)-**2a** and (*S*)-**2a**.

Experimental conditions:

LC-MS: Agilent Technologies 1200 Series; **Detector**: Diode Array Detector (278 nm); **Oven Temperature**: 25 ºC; **Column**:CHIRALPAK IG-3 (150 X 4.6 mm d.i., 3 um); **Eluent**: hexane:ethanol (90:10); **Flow rate**: 1.0 mL/min.

Figure S-95. Chromatogram for (*R*,*S*)-**2a**.

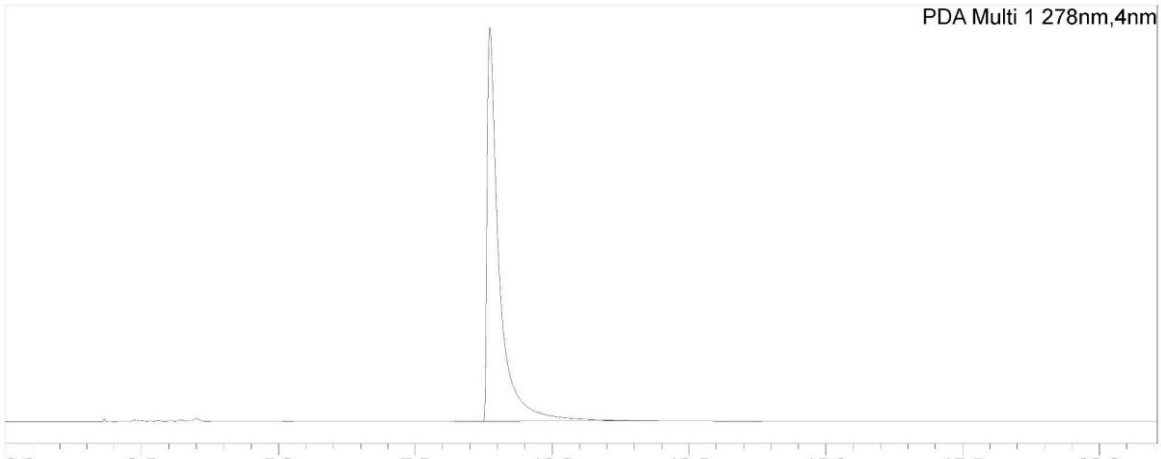


Peak Table

PDA Ch1 278nm

Peak#	Ret. Time	Resolution(USP)	Area	Area%
1	8,788	--	2546585	51,910
2	15,339	13,570	2359138	48,090
Total			4905722	100,000

Figure S-96. Chromatogram for (*S*)-**2a**.

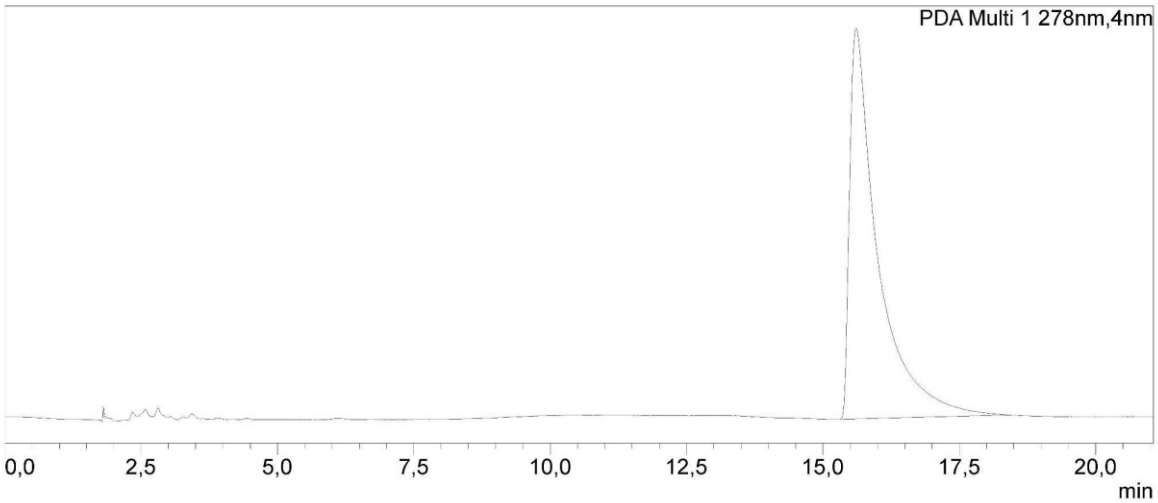


Peak Table

PDA Ch1 278nm

Peak#	Ret. Time	Resolution(USP)	Area	Area%
1	8,861	--	4822885	100,000
Total			4822885	100,000

Figure S-97. Chromatogram for (*R*)-**2a**.



Peak Table

PDA Ch1 278nm

Peak#	Ret. Time	Resolution(USP)	Area	Area%
1	15,607	--	1425354	100,000
Total			1425354	100,000

References

1. A. Abiko, S. Masamune, *Tetrahedron Lett.*, 1992, **33**, 5517-5518.

2. D. A. Evans, A. E. Weber, *J. Am. Chem. Soc.*, 1986, **108**, 6757-6761.

3. S. Jeschke, A. C. Gentschev, H. D. Wiemhöfer, *Chem. Commun.*, 2013, **49**, 1190-1192.

4. S. M. Kelly, C. Han, L. Tung, F. Gosselin, *Org. Lett.*, 2017, **19**, 3021–3024.

5. L. Bettanin, S. Saba, F. Z. Galetto, G. A. Mike, J. Rafique, A. L. Braga, *Tetrahedron Lett.*, 2017, **58**, 4713-4716.

6. C. Paulmier, Selenium Reagents and Intermediates in Organic Synthesis , 1st Edition - September 29, 1986.

7. K. B. Sharpless, M. W. Young, *J. Org. Chem.*, 1975, **40**, 947–949.

8. B. Kohne, W. Lohner, K. Praefcke, H. J. Jakobsen, B. Villadsen, *J. Organomet. Chem.*, 1979, **166**, 373-377.