Simplifying Nickel(0) Catalysis: An Air-Stable Nickel Precatalyst for the Internally Selective Benzylation of Terminal Alkenes

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Section I. Materials, Methods, and General Considerations

For couplings catalyzed by *trans*-$(PCy_2Ph)_2Ni$(*o*-tolyl)Cl (**1**), no precaution to exclude air or water was taken, non-dried glassware was employed, and all reagents and solvents were used as received. For reactions requiring dry and/or oxygen-free conditions, tetrahydrofuran, toluene, dichloromethane, triethylamine, diethyl ether, benzene, and acetonitrile were degassed by sparging with nitrogen and dried by passage through a column of activated alumna on an SG Water solvent purification system. Manipulation of all air-sensitive reagents was carried out in a glovebox (MBraun Unilab) filled with dry nitrogen. Couplings using $(PCy_2Ph)_2Ni(\eta^2\text{-}C_2H_4)$ (**2**) required the exclusion of oxygen, so all liquid reagents were degassed by three freeze-pump-thaw cycles. Liquid alkenes were distilled from sodium metal, CaH_2 or 4Å molecular sieves as appropriate. Thin-layer chromatography was carried out on EMD Millipore 60 F_{254} glass-backed plates (silica gel, 250 µm coating thickness) and spots were visualized using UV light, basic potassium permanganate, ethanolic phosphomolybdic acid (PMA), or ceric ammonium nitrate (CAN) stains. Column chromatography was carried out on a Biotage Isolera chromatography system using SNAP KP-Sil columns (silica gel, 50 µm average particle size). Bis(1,5-cyclooctadiene)nickel(0)[1] was purchased from Strem Chemicals (Newburyport, MA) and stored at –30°C in a glovebox. Ethylene and 1-butene were purchased from Sigma-Aldrich (Milwaukee, WI). Benzene-d_6 (99.6% atom D, Sigma-Aldrich) for NMR spectroscopy of oxygen-sensitive species was degassed by three freeze-pump-thaw cycles prior to usage and stored over activated 4Å molecular sieves. All other chemicals were purchased from Sigma-Aldrich (Milwaukee, WI), Alfa Aesar (Ward Hill, MA), TCI America (Portland, OR), Oakwood Products, Inc. (West Columbia, SC), or GFS Chemicals (Columbus, OH).

^1H NMR Spectra were obtained on either a Varian Mercury 300 (at 300 MHz) or Varian Inova 500 (at 500 MHz); ^{13}C spectra were recorded on a Varian Mercury 300 (at 75 MHz) or a Varian Inova 500 (at 126 MHz); ^{31}P spectra were recorded on either a Varian Mercury 300 (at 121 MHz) or a Varian Inova 500 (at 202 MHz). Chemical shifts (^1H and ^{13}C) are reported in parts per million relative to TMS (δ = 0.00 ppm) and were referenced to the residual solvent peak; ^{31}P NMR spectra were referenced to an external standard of 85% phosphoric acid (δ = 0.00 ppm). The following designations are used to describe multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), br (broad), v (very), app (apparent). IR spectra were obtained on an Agilent Cary 630 FT-IR spectrometer equipped with an ATR accessory. Intensities are reported relative to the most intense peak of the spectrum and are defined as follows: w (weak, intensity between 0 and 33.3%), m (medium, between 33.3% and 66.6%), and s (strong, between

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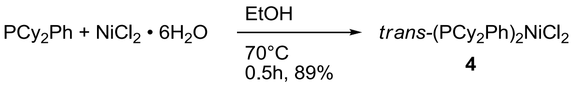
[1] The physical appearance of the bis(1,5-cyclooctadiene)nickel(0) used for all experiments was bright yellow-orange and crystalline, with block-shaped crystals ca. 0.4–0.8 mm on each side. Samples appearing as dull yellow powder, yellow-gray powder, or any sample with visible black spots (nickel) may give poor results, as these conditions all indicate at least some level of decomposition.

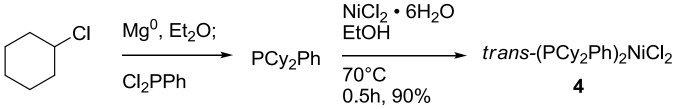
66.6% and 100%). Gas chromatography (GC) was performed on an Agilent 5870 GC (HP-5 column) with a flame ionization detector. GC/MS was performed on an Agilent 5870 GC (HP-5ms column) with an Agilent 5975C MSD. Dodecane (99+%, Alfa Aesar) was used as an internal standard for quantitation. Exact masses (high resolution mass spectra) were obtained on a Bruker Daltonics APEX IV 4.7T FT-ICR spectrometer operating with electrospray ionization (ESI) in positive ion mode. Samples not suitable for ESI were ionized using an IonSense DART ion source operating in positive ion mode.

Section II. Synthesis and Characterization of Complexes 1, 2, and 4



$$PCy_2Ph + NiCl_2 \cdot 6H_2O \xrightarrow[\text{70°C, 0.5h, 89\%}]{\text{EtOH}} \textit{trans}\text{-}(PCy_2Ph)_2NiCl_2\ \mathbf{4}$$

***trans*-bis(dicyclohexylphenylphosphine)nickel(II) chloride (4, Method A).** To a 25 mL round-bottom flask equipped with a magnetic stir bar was added $NiCl_2 \cdot 6H_2O$ (0.50 mmol, 119 mg) and PCy_2Ph (1.05 mmol, 288 mg). Ethanol (10 mL) was added, the flask fitted with a reflux condenser, placed under an atmosphere of argon, and the mixture was heated to 70°C. After 30 minutes, the mixture was cooled to 0°C with a water-ice bath and the solid collected by vacuum filtration. The solid was washed twice with cold ethanol (5 mL) and twice with cold ether (5 mL). Drying under vacuum[2] yielded **4** (302 mg, 89%) as a fine, purple powder.



***trans*-bis(dicyclohexylphenylphosphine)nickel(II) chloride (4, Method B).** An oven dried, 500 mL, two-neck, round-bottom flask was charged with a magnetic stir bar and magnesium turnings (251 mmol, 6.10 g), fitted with a reflux condenser and rubber septum, and the apparatus thoroughly flushed with argon. Diethyl ether (50 mL) was transferred to the flask along with a single crystal of iodine. The septum was removed and replaced with a dropping funnel containing chlorocyclohexane (254 mmol, 30.10 mL) in 250 mL of anhydrous diethyl ether. Approximately 15 mL of this chlorocyclohexane solution was added to the flask, which was then gently warmed with a heating mantle to initiate the reaction, as indicated by disappearance of the iodine color and mild bubbling of the ether. Following initiation, the chlorocyclohexane solution was added at such a rate so as to keep the solution at a moderate reflux without external heating (ca. 1–2 drops per second). After complete addition of the chlorocyclohexane solution, the mixture was heated to reflux for 1 hour, after which the flask was cooled to –30°C and a solution of phenyldichlorophosphine (100 mmol, 13.57 mL) in 100 mL of diethyl ether was added dropwise with vigorous stirring. After addition of the phenyldichlorophosphine, the solution was allowed to warm to room temperature and stirred for 1 hour. The reaction was quenched with saturated aqueous ammonium chloride and the ether layer washed twice with water. The ether was evaporated under reduced pressure and 200 mL of ethanol were added, followed by $NiCl_2 \cdot 6H_2O$ (45 mmol, 10.70 g), after which the solution was heated to 70°C for 30 minutes. The mixture was cooled to

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[2] It is suggested to place a piece of cotton or glass wool inside the inlet adapter connected to the flask to prevent fine particles of **4** from traveling into the vacuum manifold.

0°C with a water-ice bath and the solid collected by vacuum filtration. The solid was washed with two 15 mL portions of cold ethanol and two 15 mL portions of diethyl ether. The solid was collected and dried under vacuum for several hours to yield **4** (27.46 g, 90%) as a fine, purple powder.

*Characterization of **4**.*

mp 225–226°C dec (lit.[3] 226–228 °C dec). ^{1}H NMR (500 MHz, C_6D_6) δ 7.80 (d, *J* = 7.6 Hz, 4H), 7.27 (t, *J* = 7.5 Hz, 4H), 7.00 (t, *J* = 7.5 Hz, 2H), 3.59 (br s, 4H), 2.52 (d, *J* = 10.7 Hz, 4H), 2.05 (q, *J* = 11.5, 11.0 Hz, 4H), 1.96 – 1.72 (m, 16H), 1.61 (d, *J* = 10.0 Hz, 4H), 1.32 (q, *J* = 12.5 Hz, 4H), 1.25 – 1.10 (m, 8H). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.82 (app s, 4H), 7.43 (app s, 4H), 7.09 (app s, 2H), 2.57 – 2.12 (m, 8H), 1.89 (d, *J* = 12.6 Hz, 4H), 1.80 – 1.61 (m, 12H), 1.56 (q, *J* = 11.8, 4H), 1.42 – 1.28 (m, 12H), 1.22 (q, *J* = 12.8 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 131.80 (br s), 127.46, 31.70 (br s), 30.09 (br s), 28.00, 27.12. ^{31}P{^{1}H} (121 MHz, CD_2Cl_2) ca. 25 (v br s). See discussion below for details. IR (ATR, cm^{-1}): 3075 (w), 3051 (w), 2928 (s), 2850 (m), 1445 (m), 1434 (s), 1294 (w), 1266 (w), 1199 (w), 1186 (w), 1171 (m), 1111 (m), 1098 (w), 999 (m), 914 (w), 895 (w), 887 (w), 846 (m), 818 (w), 740 (s), 697 (s), 688 (s). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation (at room temperature) of a THF/ethanol solution of the complex. Slow evaporation of THF/isopropanol, benzene/ethanol, and benzene/isopropanol solutions also yielded satisfactory crystals.

Initial attempts to characterize **4** by ^{31}P NMR spectroscopy showed no signals, even after several hundred transients on a CD_2Cl_2 solution nearly saturated with **4**. Further attempts to obtain a spectrum, including collecting an even larger number of transients, yielded a spectrum with an extremely broad signal centered at approximately 25 ppm spanning from ca. 120 to –70 ppm and two small singlets, one at 3.13 ppm (PCy_2Ph) and one at 45.59 ($OPCy_2Ph$). The presence of these two signals suggests some decomposition of the complex (caused by oxygen—a J-Young tube was not used) in the time required to obtain the spectrum, which was several hours. The location of the peak's maximum is very sensitive to the phasing of the spectrum, so determination of a precise chemical shift is not possible. Given the appearance of the ^{1}H and ^{13}C spectra, which have multiple broadened signals, it is apparent that the proximity to the nickel atom is allowing very rapid relaxation for some atoms of the complex, causing severe broadening. Since the phosphorus atoms are directly bonded to nickel, it is not surprising that they experience this effect to a greater extent. These results were verified on several different spectrometers to rule out hardware or acquisition problems.

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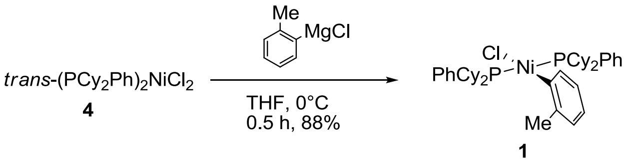
[3] Stone, P. J. and Zvi, D. *Inorg. Chim. Acta* **1970**, *5*, 434–438. Samples prepared by Methods A and B, neither of which had been recrystallized, both melted at 225–226°C dec.



***trans*-bis(dicyclohexylphenylphosphine) nickel(*o*-tolyl) chloride (1)**: *trans*-$(PCy_2Ph)_2NiCl_2$ (**4**, 15.46 mmol, 10.49 g) was added to an oven-dried, round-bottom flask with a magnetic stir bar. Tetrahydrofuran (250 mL) was added and the mixture stirred for 10 minutes. This homogeneous solution was cooled to 0°C with an ice bath and *o*-tolylmagnesium chloride (15.46 mmol, 0.865 M in THF, 17.87 mL) was added dropwise at a rate of ca. 2 drops per second with vigorous stirring. Near the end of the addition, the solution began to lighten in color from dark purple to red-orange. The solution was allowed to stir for 30 minutes at 0°C, after which anhydrous methanol (15 mL) was added to quench any unreacted Grignard reagent. The stir bar was removed and the solution was evaporated to dryness under reduced pressure. Anhydrous methanol (100 mL) was added and the mixture was sonicated until a uniform, yellow suspension with no large aggregates was obtained (approx. 15 minutes). After cooling to 0°C, the yellow precipitate was collected by vacuum filtration, washed with two portions of cold methanol, and dried under high vacuum[4] to yield **1** (9.97 g, 88%) as a fine, yellow powder.

*Characterization of **1**.*

mp 149–150°C dec. ^{1}H NMR (500 MHz, C_6D_6) δ 7.49 (s, 4H), 7.10 (app s, 7H), 6.76 – 6.58 (m, 3H), 3.51 (s, 3H), 2.52 (s, 4H), 2.42 – 2.21 (m, 4H), 1.95 – 0.83 (m, 36H). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6) δ 149.86 (t, J = 32.3 Hz), 142.76, 138.45, 132.91, 130.70 (t, J = 15.5 Hz), 127.09, 124.17, 122.27, 33.90 (t, J = 9.8 Hz), 33.32 (t, J = 9.7 Hz), 30.25 (d, J = 21.6 Hz), 29.47 (d, J = 7.5 Hz), 28.28 (t, J = 5.3 Hz), 28.09 (t, J = 6.2 Hz), 27.88 (t, J = 5.2 Hz), 27.66, 26.79 (d, J = 7.3 Hz). $^{31}P\{^{1}H\}$ (202 MHz, C_6D_6): 16.09 (s). $^{31}P\{^{1}H\}$ (202 MHz, CD_2Cl_2): 15.00 (s), 44.89 (s), 3.13 (s). 3049 (w), 2922 (m), 2852 (m), 1570 (w), 1561 (w), 1447 (m), 1432 (m), 1326 (w), 1296 (w), 1264 (m), 1203 (w), 1178 (w), 1115 (w), 1027 (w), 1003 (m), 917 (w), 889 (w), 848 (m), 731 (s), 695 (s). HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{43}H_{61}ClNiP_2$, 733.3363; found, 733.3354. $[M - Cl]^+$ calcd for $C_{43}H_{61}ClNiP_2$, 697.3596; found, 697.3592. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by the slow evaporation (at room temperature) of a THF solution of the complex. An ether solution also yielded high-quality crystals.

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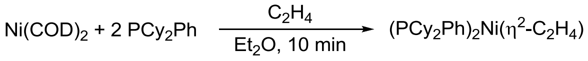
[4] As with complex **4**, complex **1** forms a very fine powder. It is therefore suggested to place a piece of cotton or glass wool inside the inlet adapter connected to the flask to prevent fine particles of **1** from traveling into the vacuum manifold.



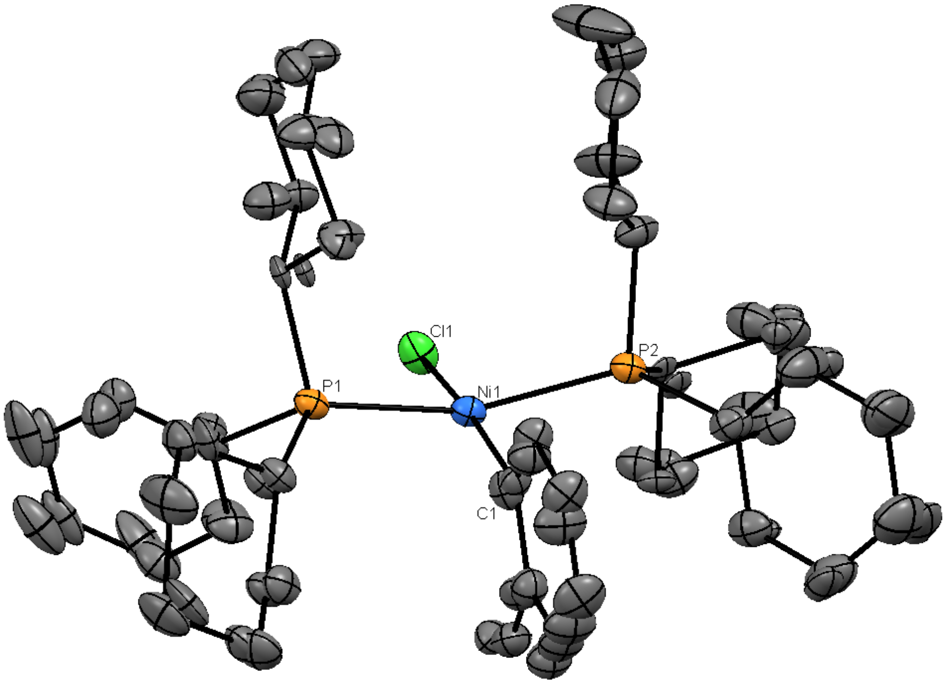
$$Ni(COD)_2 + 2\ PCy_2Ph \xrightarrow[Et_2O,\ 10\ min]{C_2H_4} (PCy_2Ph)_2Ni(\eta^2\text{-}C_2H_4)$$

2

ethylenebis(dicyclohexylphenylphosphine)nickel(0) (**2**): In a glovebox, $Ni(COD)_2$ (2.00 mmol, 0.550 g) and PCy_2Ph (4.00 mmol, 1.098 g) were combined in a 20 mL vial with a magnetic stir bar and diethyl ether (12 mL) was added, yielding an intensely colored, dark red solution. After stirring for 10 minutes, ethylene was bubbled through the solution, causing a rapid change in the color to orange and subsequently to bright yellow. Ethylene was bubbled through the solution for an additional 10 minutes, after which the vial was sealed and allowed to stand at –20°C to complete the precipitation. The precipitate was collected by vacuum filtration and washed with two small portions of cold diethyl ether. Drying under vacuum yielded the complex as a fine, yellow powder (1.048 g, 86%). ^1H NMR (300 MHz, C_6D_6) δ 7.65 – 7.56 (m, 4H), 7.09 – 7.00 (m, 6H), 2.43 (s, 4H), 2.33 – 2.19 (m, 4H), 2.19 – 2.06 (m, 4H), 2.00 – 1.84 (m, 4H), 1.77 – 1.61 (m, 8H), 1.61 – 1.50 (m, 4H), 1.50 – 1.37 (m, 4H), 1.37 – 1.10 (m, 12H), 1.09 – 0.91 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 134.85 (dd, *J* = 10.9, 8.2 Hz), 133.99 (t, *J* = 6.0 Hz), 127.18 (t, *J* = 3.9 Hz), 39.69 (t, *J* = 6.3 Hz), 35.18 (dd, *J* = 10.8, 9.7 Hz), 30.20 (t, *J* = 3.2 Hz), 29.54, 27.92 (t, *J* = 6.0 Hz), 27.62 (t, *J* = 4.3 Hz), 26.87. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): 37.6 ppm. IR (ATR, cm^{-1}): 3074 (w), 3047 (w), 2922 (s), 2848 (m), 1481 (w), 1445 (m), 1434 (m), 1335 (w), 1270 (w), 1203 (w), 1180 (m), 1111 (w), 1001 (m), 882 (s), 848 (m), 742 (s), 697 (s).

Section III. X-Ray Diffraction Characterization of Ni Complexes 1 and 4

Figure SI 1. Thermal ellipsoid depiction of complex 1

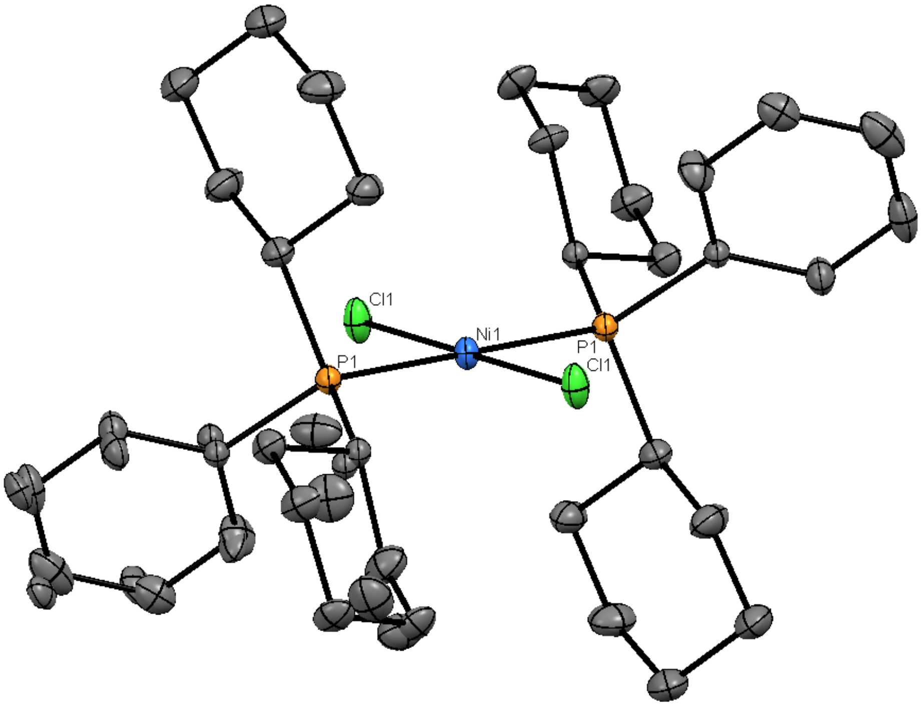


Ellipsoid probability set at 50%.

Table SI 1. Selected bond angles and distances from the X-ray structure of 1

Atoms	*Distance (Å)*	*Atoms*	*Angle (Deg.)*
Ni(1)–P(1)	2.2318(5)	P(1)–Ni(1)–P(2)	160.740(17)
Ni(1)–P(2)	2.2402(5)	C(1A)–Ni(1)–Cl(1)	166.5(4)
Cl(1)–Ni(1)	2.2203(4)	C(1)–Ni(1)–Cl(1)	170.4(4)
C(1A)–Ni(1)	1.877(13)	C(1A)–Ni(1)–P(1)	89.5(6)
C(1)–Ni(1)	1.911(11)	C(1)–Ni(1)–P(1)	91.8(5)
		Cl(1)–Ni(1)–P(1)	91.464(16)
		C(1A)–Ni(1)–P(2)	92.9(6)
		C(1)–Ni(1)–P(2)	89.2(5)
		Cl(1)–Ni(1)–P(2)	90.628(16)

Figure SI 2. Thermal ellipsoid depiction of complex 4



Ellipsoid probability set at 50%.

Table SI 2. Selected bond angles and distances from the X-ray structure of complex 4

Atoms	***Distance (Å)***	***Atoms***	***Angle (Deg.)***
Cl(1)–Ni(1)	2.1628(4)	Cl(1)#1–Ni(1)–Cl(1)	179.999(12)
Ni(1)–Cl(1)#1	2.1628(4)	P(1)#1–Ni(1)–P(1)	180
Ni(1)–P(1)#1	2.2511(4)	Cl(1)#1–Ni(1)–P(1)#1	90.762(14)
Ni(1)–P(1)	2.2511(4)	Cl(1)–Ni(1)–P(1)#1	89.238(14)
		Cl(1)#1–Ni(1)–P(1)	89.238(14)
		Cl(1)–Ni(1)–P(1)	90.762(14)

Table SI 3. Parameters of X-ray crystallographic characterization of complexes 1 and 4

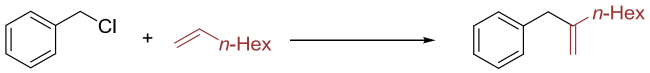
	Complex 1	**Complex 4**
Crystal Data		
Chemical formula	$C_{43}H_{61}ClNiP_2$	$C_{36}H_{54}Cl_2NiP_2$
Formula weight	734.02	678.34
Crystal system, Space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a, *b*, *c* (Å)	10.5776(7), 12.2542(8), 17.3312(11)	9.4047(5), 10.1216(6), 10.5171(6)
α, β, γ (deg.)	103.8850(10), 94.5290(10), 113.7470(10)	112.7030(10), 107.6740(10), 91.3780(10)
Volume (Å^3)	1956.8(2)	868.53(9)
Z	2	1
Temperature (K)	100(2) K	100(2) K
Crystal dimensions (mm)	0.27 x 0.19 x 0.15	0.58 x 0.47 x 0.19
Crystal habit	block	plate
Crystal color	orange	purple
Radiation Type, wavelength (Å)	Mo *K*α, 0.71073	Mo *K*α, 0.71073
F(000)	788	362
Data Collection		
Diffractometer	Bruker X8 Kappa DUO four-circle	Bruker X8 Kappa DUO four-circle
Detector type	Bruker APEX2 CCD	Bruker APEX2 CCD
Absorption correction	multi-scan, SADABS (Sheldrick, 2009)	multi-scan, SADABS (Sheldrick, 2009)
T_{min}, T_{max}	0.8367, 0.9056	0.6456, 0.8598
Reflections, total	96996	31072
Reflections, independent	12389 [R(int) = 0.0299]	5529 [R(int) = 0.0274]
Reflections with $I > 2\sigma(I)$	10970	5165
Theta range for data collection	1.23 to 31.00°	2.21 to 31.00°
Completeness to theta = 31.00°	99.3%	99.9%
Refinement		
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0372, wR^2 = 0.0958	R1 = 0.0281, wR^2 = 0.0726
R indices (all data) [$R_w(F^2)$]	R1 = 0.0436, wR^2 = 0.1000	R1 = 0.0302, wR^2 = 0.0738
Goodness-of-fit on F_2 [S]	1.046	1.055
Reflections / restraints / parameters	12389 / 2152 / 717	5529 / 595 / 248
Hydrogen atom treatment	constrained	mixed
Crystallographer's comments	The position of the Ph ring on both $PPhCy_2$ ligands is disordered; on P1 over three and on P2 over two positions. EADP was required. One SUMP used for the three-fold disorder.	The position of the Ph ring is disordered over two positions. EADP was required.

Section IV. Procedures for Nickel-catalyzed Benzylation Reactions

General Procedure A: To an 8 mL screw-top vial containing a magnetic stir-bar was added precatalyst **1** (0.050 mmol, 36.7 mg), alkene (5.00 mmol), triethylamine (6.00 mmol, 836 µL), the benzyl chloride (1.00 mmol), and CH_2Cl_2 (500 µL). After stirring the mixture for a few seconds, silyl triflate (1.5 mmol) was added, the vial capped, and left to stir for 4 to 8 hours as indicated. After the necessary time had elapsed, the reaction mixture was allowed to stir open to the air for 5 minutes, after which it was passed through a 4 cm plug of silica gel (pre-wetted with dichloromethane). The silica gel plug was washed with 25 mL of dichloromethane followed by 25 mL of a 1:1 mixture of hexanes/ethyl acetate. After concentration under reduced pressure, the crude material was purified by column chromatography on silica gel with the indicated eluent.

General Procedure B (modification for substrates with free –OH, –NH_2, –CO_2H groups): To an 8 mL screw-top vial containing a magnetic stir-bar was added alkene (3.00–5.00 mmol), triethylamine (6.00–12.00 mmol), the benzyl chloride (1.00 mmol), and CH_2Cl_2 (500 µL). The mixture was cooled to 0°C, after which the appropriate silyl triflate (4.50–10.00 mmol) was added dropwise. After the addition was complete, the mixture was warmed to room temperature, precatalyst **1** (0.050 mmol, 36.7 mg) was added, the vial was closed with a screw-cap, and the mixture was stirred at room temperature for 4 to 8 hours as indicated. Work-up and purification were carried out as indicated for each substrate.

General Procedure C (modification for reactions run with precatalyst 2): In a glovebox, precatalyst **2** (0.05 mmol, 31.8 mg) was added to an 8 mL screw-top vial containing a magnetic stir-bar. To the catalyst was added alkene (5.00 mmol), triethylamine (6.00 mmol, 836 µL), the benzyl chloride (1.00 mmol), and toluene (500 µL). After briefly stirring the mixture, silyl triflate (1.5 mmol) was added, the vial capped, and left to stir for the indicated length of time (12–24 hours). After this length of time, the reaction was worked up and purified as in General Procedure A.



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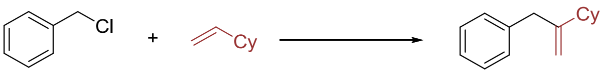
(2-methyleneoctyl)benzene (7): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), benzyl chloride (1.00 mmol, 115 µL), 1-octene (5 mmol, 785 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.46) yielded **7** (186 mg, 92%, 98:2 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 4.82 (dtt, J = 2.0, 1.2, 0.6 Hz, 1H), 4.72 (dtt, J = 2.0, 1.3, 0.7 Hz, 1H), 3.33 (s, 2H), 1.99 – 1.94 (m, 2H), 1.47 – 1.39 (m, 2H), 1.33 – 1.22 (m, 5H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.39, 140.05, 129.14, 128.36, 126.11, 111.05, 43.18, 35.58, 31.91, 29.16, 27.75, 22.79, 14.25. The ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[5]



8

(2-cyclohexylallyl)benzene (8): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), benzyl chloride (1.00 mmol, 115 µL), vinylcyclohexane (5 mmol, 684 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.53) yielded **8** (140 mg, 70%, 93:7 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 4.84 (dq, J = 1.7, 0.8 Hz, 1H), 4.64 – 4.62 (m, 1H), 3.37 (s, 2H), 1.89 – 1.59 (m, 4H), 1.33 – 1.03 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.66, 140.37, 129.27, 128.33, 126.01, 109.63, 43.55, 41.98, 32.64, 26.88, 26.55. The ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[5]

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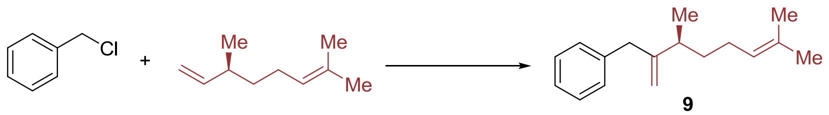
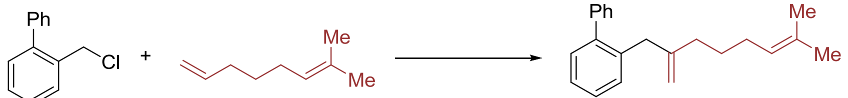
[5] Matsubara, R.; Gutierrez, A. C.; Jamison, T. F. *J. Am. Chem. Soc.* **2011**, *133*, 19020–19023.



9

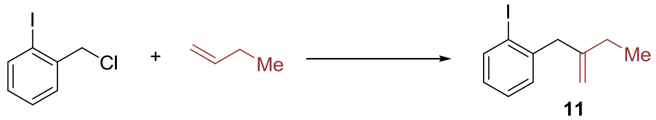
(S)-(3,7-dimethyl-2-methyleneoct-6-enyl)benzene (9): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), benzyl chloride (1.00 mmol, 115 µL), (S)-(+)-β-citronellene (5 mmol, 910 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.58) yielded **9** (108 mg, 47%, 93:7 ratio) as a clear, colorless liquid. $[\alpha]_D^{20} = +0.13$ (c 24.90, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (tq, *J* = 7.8, 1.1 Hz, 2H), 7.28 – 7.22 (m, 3H), 5.13 (tdd, *J* = 5.9, 2.2, 0.8 Hz, 1H), 4.91 (dq, *J* = 1.7, 0.8 Hz, 1H), 4.68 (q, *J* = 1.5 Hz, 1H), 3.43 – 3.34 (m, 2H), 2.19 (h, *J* = 6.9 Hz, 1H), 2.04 – 1.93 (m, 2H), 1.74 (q, *J* = 1.3 Hz, 3H), 1.68 – 1.63 (m, 3H), 1.57 (ddt, *J* = 13.4, 8.7, 7.0 Hz, 1H), 1.40 (ddt, *J* = 13.6, 8.6, 6.8 Hz, 1H), 1.09 (dd, *J* = 6.9, 0.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.03, 140.14, 131.38, 129.47, 128.31, 126.04, 124.81, 110.39, 41.16, 38.86, 35.86, 25.97, 25.86, 20.18, 17.81. IR (ATR, cm^{-1}): 3083 (w), 3066 (w), 3029 (w), 2964 (w), 2917 (m), 2857 (w), 1641 (w), 1604 (w), 1496 (w), 1453 (m), 1376 (w), 1108 (w), 1074 (w), 1031 (w), 893 (m), 832 (w), 729 (m), 697 (s). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{17}H_{24}$, 229.1951; found, 229.1975.



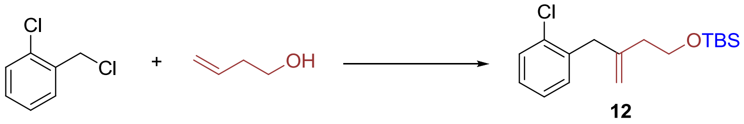
S1

10

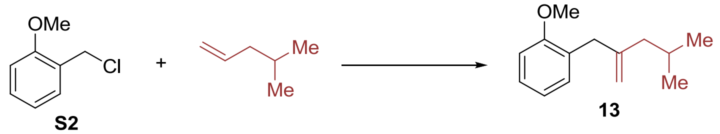
2-(7-methyl-2-methyleneoct-6-enyl)biphenyl (10): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 2-(chloromethyl)biphenyl **S1** (1.00 mmol, 203 mg), 7-methyl-1,6-octadiene (5 mmol, 825 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 7 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.40) yielded **10** (253 mg, 87%, 96:4 ratio) as a clear, colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.34 (m, 9H), 5.26 – 5.17 (m, 1H), 5.00 – 4.95 (m, 1H), 4.70 – 4.65 (m, 1H), 3.46 – 3.42 (m, 2H), 2.11 – 2.00 (m, 4H), 1.84 (d, *J* = 4.6 Hz, 3H), 1.72 (d, *J* = 4.4 Hz, 3H), 1.54 – 1.44 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 149.79, 142.46, 141.88, 137.06, 131.44, 130.50, 130.12, 129.26, 128.03, 127.29, 126.92, 126.17, 124.67, 111.43, 39.88, 36.05, 27.99, 27.78, 25.85, 17.82. IR (ATR, cm^{-1}): 3061 (w), 3023 (w), 2967 (w), 2926 (w), 2857 (w), 1645 (w), 1598 (w), 1479 (m), 1438 (m), 1376 (w), 1106 (w), 1072 (w), 1052 (w), 1011 (w), 891 (m), 830 (w), 772 (m), 746 (s), 723 (w), 701 (s). HRMS (DART, *m/z*): [M + H]$^+$ calcd for $C_{22}H_{26}$, 291.2107; found, 291.2103.



1-iodo-2-(2-methylenebutyl)benzene (11): A magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 2-iodobenzyl chloride (1.00 mmol, 252 mg), Et$_3$N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial, which was fitted with a rubber septum. A stream of 1-butene gas was bubbled through the solution for 10 minutes to saturate the solution, after which the reaction was kept under a static atmosphere of 1-butene with a balloon. Trimethylsilyl triflate (1.50 mmol, 271 µL) was added via syringe and the reaction mixture was allowed to stir for 6 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.64) yielded **10** (229 mg, 84%, 95:5 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.86 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.31 (td, *J* = 7.5, 1.3 Hz, 1H), 7.24 (ddd, *J* = 7.6, 1.7, 0.4 Hz, 1H), 6.93 (td, *J* = 7.8, 1.8 Hz, 1H), 4.93 (qd, *J* = 1.5, 0.7 Hz, 1H), 4.57 (qt, *J* = 1.5, 0.9 Hz, 1H), 3.50 (s, 1H), 2.12 (qdd, *J* = 7.4, 1.6, 0.8 Hz, 2H), 1.13 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 149.23, 142.73, 139.55, 130.23, 128.24, 127.96, 110.58, 101.75, 47.49, 29.12, 12.47. IR (ATR, cm^{-1}): 3061 (w), 2965 (w), 2934 (w), 2878 (w), 1647 (w), 1585 (w), 1561 (w), 1464 (m), 1434 (m), 1374 (w), 1046 (w), 1011 (s), 891 (s), 742 (s), 714 (m). HRMS (DART, *m/z*): [M + H]$^+$ calcd for $C_{11}H_{13}I$, 273.0135; found, 273.0132.



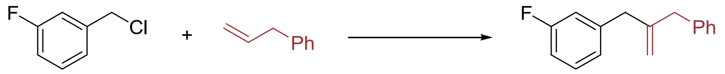
***tert*-butyl(3-(2-chlorobenzyl)but-3-enyloxy)dimethylsilane (12):** Following General Procedure B, a magnetic stir bar, 2-chlorobenzyl chloride (1.00 mmol, 126 µL), 3-buten-1-ol (3 mmol, 258 µL), Et$_3$N (9.00 mmol, 1254 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was cooled to 0°C, after which TBSOTf (4.5 mmol, 1033 µL) was added dropwise. After the addition was complete, the mixture was warmed to room temperature, precatalyst **1** (0.050 mmol, 36.7 mg) was added, the vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. After this time, the reaction mixture was allowed to stir open to the air for 5 minutes, then passed through a 4 cm plug of silica gel (pre-wetted with dichloromethane). The silica gel plug was washed with 25 mL of dichloromethane followed by 25 mL of a 1:1 mixture of hexanes:ethyl acetate. After concentration under reduced pressure, the crude material was purified by column chromatography on silica gel (5% EtOAc/Hex, R_f = 0.45) to yield **12** (280 mg, 90%, 96:4 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.25 – 7.14 (m, 3H), 4.91 – 4.89 (m, 1H), 4.67 – 4.65 (m, 1H), 3.76 (t, *J* = 7.0 Hz, 2H), 3.50 (s, 2H), 2.29 (dd, *J* = 7.0, 0.7 Hz, 2H), 0.91 (s, 9H), 0.07 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.64, 137.44, 134.60, 131.20, 129.59, 127.72, 126.78, 113.21, 62.40, 40.33, 39.45, 26.10, 18.47, -5.15. IR (ATR, cm^{-1}): 3075 (w), 2954 (w), 2930 (m), 2896 (w), 2859 (w), 1647 (w), 1473 (m), 1443 (w), 1387 (w), 1361 (w), 1253 (m), 1095 (s), 1052 (m), 1039 (m), 1005 (w), 938 (w), 895 (m), 832 (s), 811 (m), 774 (s), 746 (s), 682 (m), 662 (m). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{17}H_{29}OClSi$, 311.1592; found, 311.1594.



1-methoxy-2-(4-methyl-2-methylenepentyl)benzene (13): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 2-methoxybenzyl chloride (1.00 mmol, 157 mg), 4-methyl-1-pentene (5 mmol, 633 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 5 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.27) yielded **13** (141 mg, 69%, 95:5 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 1H), 7.17 – 7.13 (m, 1H), 6.92 (td, *J* = 7.4, 1.1 Hz, 1H), 6.88 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.77 (dt, *J* = 2.1, 1.0 Hz, 1H), 4.62 (dt, *J* = 2.5, 1.5 Hz, 1H), 3.82 (s, 2H), 3.33 (s, 2H), 1.96 – 1.83 (m, 4H), 0.91 (dd, *J* = 6.4, 0.7 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.67, 147.91, 130.68, 128.54, 127.35, 120.47, 111.77, 110.52, 55.46, 46.09, 35.92, 26.22, 22.63. IR (ATR, cm^{-1}): 3072 (w), 2954 (m), 2924 (w), 2911 (w), 2870 (w), 2837 (w), 1645 (w), 1600 (w), 1589 (w), 1492 (m), 1464 (m), 1384 (w), 1367 (w), 1322 (w), 1289 (w), 1242 (s), 1182 (w), 1162 (w), 1109 (m), 1052 (m), 1033 (m), 889 (m), 749 (s), 725 (m). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{14}H_{20}O$, 205.1587; found, 205.1589.

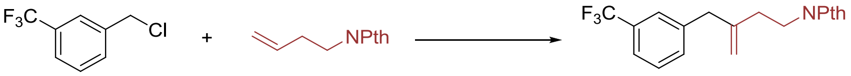
14

1-fluoro-3-(3-methyl-2-methylenepentyl)benzene (14): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 3-fluorobenzyl chloride (1.00 mmol, 145 mg), 3-methyl-1-pentene (5 mmol, 628 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.63) yielded **14** (144 mg, 75%, 96:4 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 7.02 – 6.99 (m, 1H), 6.97 – 6.91 (m, 2H), 4.92 (dq, *J* = 1.6, 0.8 Hz, 1H), 4.70 (q, *J* = 1.5 Hz, 1H), 3.47 – 3.26 (m, 2H), 2.11 – 2.02 (m, 1H), 1.58 – 1.34 (m, 2H), 1.07 (d, *J* = 6.9 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.05 (d, *J* = 245.2 Hz), 153.15, 142.88 (d, *J* = 7.1 Hz), 129.65 (d, *J* = 8.3 Hz), 125.08 (d, *J* = 2.8 Hz), 116.20 (d, *J* = 20.9 Hz), 112.96 (d, *J* = 21.1 Hz), 110.90, 40.95 (d, *J* = 1.7 Hz), 40.83, 28.30, 19.66, 11.82. IR (ATR, cm^{-1}): 3079 (w), 2964 (m), 2928 (w), 2878 (w), 1643 (w), 1615 (m), 1589 (s), 1488 (s), 1447 (s), 1378 (w), 1249 (s), 1136 (m), 1074 (w), 1005 (w), 960 (m), 895 (s), 878 (m), 858 (w), 785 (s), 761 (s), 740 (w), 688 (s). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{13}H_{17}F$, 193.1387; found, 193.1378.



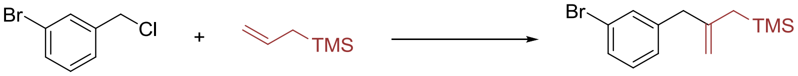
15

1-(2-benzylallyl)-3-fluorobenzene (15): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 3-fluorobenzyl chloride (1.00 mmol, 145 mg), allylbenzene (5 mmol, 662 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, *Rf* = 0.36) yielded **15** (208 mg, 92%, 97:3 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.28 – 7.21 (m, 2H), 7.18 – 7.14 (m, 2H), 6.95 – 6.85 (m, 3H), 4.90 – 4.88 (m, 1H), 4.87 – 4.85 (m, 1H), 3.28 (s, 2H), 3.27 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.05 (d, *J* = 245.3 Hz), 147.73, 142.21 (d, *J* = 7.2 Hz), 139.34, 129.79 (d, *J* = 8.3 Hz), 129.18, 128.50, 126.36, 124.90 (d, *J* = 2.7 Hz), 115.98 (d, *J* = 21.0 Hz), 114.02, 113.18 (d, *J* = 21.0 Hz), 42.29, 41.92 (d, *J* = 1.7 Hz). IR (ATR, cm^{-1}): 3083 (w), 3068 (w), 3031 (w), 2906 (w), 2831 (w), 1647 (w), 1615 (m), 1589 (m), 1486 (s), 1449 (m), 1438 (m), 1249 (m), 1134 (m), 1074 (w), 1029 (w), 964 (w), 897 (m), 874 (m), 785 (s), 761 (m), 757 (m), 738 (s), 697 (s), 688 (s). HRMS (DART, *m/z*): M^+ calcd for $C_{16}H_{15}F$, 226.1152; found, 226.1144.



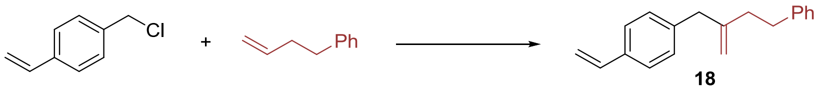
16

2-(3-(3-(trifluoromethyl)benzyl)but-3-enyl)isoindoline-1,3-dione (16): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 3-(trifluoromethyl)benzyl chloride (1.00 mmol, 155 µL), *N*-(3-buten-1-yl)phthalimide (3 mmol, 604 mg), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TESOTf (1.50 mmol, 339 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. Following work-up according to the general procedure, silica gel chromatography (70% CH_2Cl_2/Hex, R_f = 0.54) yielded **16** (298 mg, 83%, 99:1 ratio) as a clear, colorless liquid that solidified on standing at 5°C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.73 – 7.69 (m, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.38 (m, 2H), 4.87 – 4.85 (m, 1H), 4.72 – 4.70 (m, 1H), 3.84 (t, *J* = 7.1 Hz, 2H), 3.49 (s, 2H), 2.37 (t, *J* = 7.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.15, 144.57, 140.10, 133.87, 132.60 (q, *J* = 1.4 Hz), 132.00, 130.62 (q, *J* = 31.9 Hz), 128.78, 125.80 (q, *J* = 3.8 Hz), 124.22 (q, *J* = 272.6 Hz), 123.13, 123.12 (q, *J* = 3.0 Hz), 114.70, 41.84, 36.19, 34.18. The ^1H and ^{13}C NMR spectra are in agreement with those reported in the literature.[5]

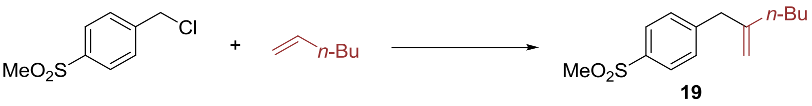


17

(2-(3-bromobenzyl)allyl)trimethylsilane (17): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 3-bromobenzyl chloride (1.00 mmol, 128 µL), allyltrimethylsilane (5 mmol, 795 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TESOTf (1.50 mmol, 339 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, *Rf* = 0.60) yielded **17** (142 mg, 50%, 97:3 ratio) as a clear, colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.17 (dd, *J* = 8.3, 7.7 Hz, 1H), 7.15 – 7.11 (m, 1H), 4.67 (dt, *J* = 1.8, 0.9 Hz, 1H), 4.61 – 4.59 (m, 1H), 3.28 – 3.22 (m, 2H), 1.49 (d, *J* = 1.0 Hz, 2H), 0.07 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 146.05, 142.37, 132.18, 129.90, 129.32, 127.91, 122.50, 110.26, 44.77, 26.25, –1.10. IR (ATR, cm^{-1}): 3074 (w), 2956 (w), 2900 (w), 1634 (w), 1594 (w), 1568 (w), 1473 (w), 1423 (w), 1247 (m), 1154 (w), 1070 (w), 998 (w), 835 (s), 770 (s), 694 (m). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{13}H_{19}BrSi$, 283.0512; found, 283.0521.



1-(2-methylene-4-phenylbutyl)-4-vinylbenzene (18): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 4-vinylbenzyl chloride (1.00 mmol, 141 µL), 4-phenyl-1-butene (5 mmol, 751 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.34) yielded **18** (211 mg, 85%, 97:3 ratio) as a clear, colorless liquid.[6] ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.31 – 7.22 (m, 2H), 7.21 – 7.08 (m, 5H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (dt, *J* = 17.6, 0.8 Hz, 1H), 5.21 (dt, *J* = 10.9, 0.8 Hz, 1H), 4.95 – 4.85 (m, 1H), 4.85 – 4.77 (m, 1H), 3.36 (s, 2H), 2.84 – 2.70 (m, 2H), 2.37 – 2.21 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 148.42, 142.11, 139.46, 136.78, 135.67, 129.29, 128.44, 128.40, 126.33, 125.91, 113.23, 111.71, 43.17, 37.23, 34.38. IR (ATR, cm^{-1}): 3085 (w), 3066 (w), 3027 (w), 2924 (w), 2859 (w), 1645 (w), 1630 (w), 1604 (w), 1509 (m), 1496 (w), 1455 (w), 1438 (w), 1406 (w), 1287 (w), 1111 (w), 1076 (w), 1031 (w), 1018 (w), 988 (m), 895 (s), 850 (m), 826 (m), 744 (m), 731 (m), 697 (s). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{19}H_{20}$, 249.1638; found, 249.1652.



1-(2-methylenehexyl)-4-(methylsulfonyl)benzene (19): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 4-(methylsulfonyl)benzyl chloride (1.00 mmol, 205 mg), 1-hexene (5 mmol, 621 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TESOTf (1.50 mmol, 339 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica

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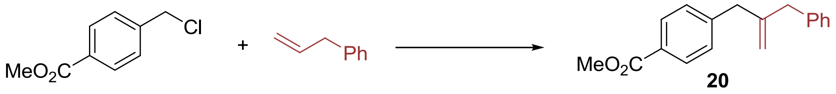
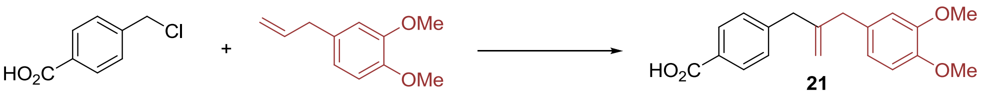
[6] In the absence of an inhibitor (such as 4-*t*-butylcatechol) compound **18** undergoes slow polymerization if stored neat at room temperature. However, compound **18** was stored for several weeks in the absence of inhibitor frozen in benzene at –30°C with no polymerization observed.

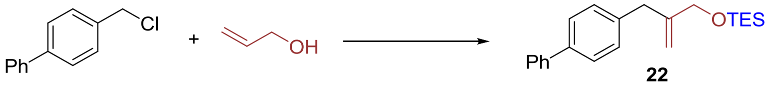
gel chromatography (20% EtOAc/Hex, R_f = 0.27) yielded **19** (202 mg, 80%, 98:2 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.35 – 7.31 (m, 2H), 4.84 – 4.81 (m, 1H), 4.69 – 4.66 (m, *J* = 0.6 Hz, 1H), 3.36 (s, 2H), 3.00 (s, 3H), 1.93 – 1.87 (m, 2H), 1.41 – 1.32 (m, 2H), 1.27 – 1.18 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.70, 146.49, 129.84, 127.29, 112.06, 44.46, 42.71, 35.07, 29.61, 22.24, 13.89. IR (ATR, cm^{-1}): 3075 (w), 2958 (w), 2930 (w), 2861 (w), 1647 (w), 1596 (w), 1458 (w), 1438 (w), 1408 (w), 1303 (s), 1147 (s), 1089 (m), 1018 (w), 957 (m), 908 (m), 895 (m), 770 (m), 759 (s), 729 (s). HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{14}H_{20}O_2S$, 253.1257; found, 253.1250.



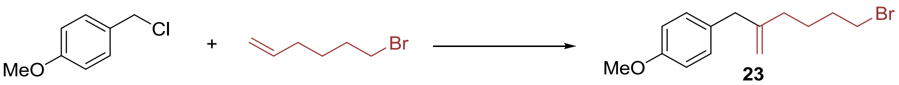
methyl 4-(2-benzylallyl)benzoate (20): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), methyl 4-(chloromethyl)benzoate (1.00 mmol, 185 mg), allylbenzene (5 mmol, 662 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (5% EtOAc/Hex, R_f = 0.33) yielded **20** (221 mg, 83%, 98:2 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 – 7.20 (m, 2H), 7.16 – 7.12 (m, 2H), 4.90 – 4.88 (m, 1H), 4.85 – 4.83 (m, 1H), 3.91 (s, 3H), 3.32 (s, 2H), 3.27 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.19, 147.56, 145.11, 139.21, 129.76, 129.24, 129.14, 128.47, 128.25, 126.35, 114.12, 52.11, 42.37, 42.15. IR (ATR, cm^{-1}): 3064 (w), 3029 (w), 2952 (w), 2904 (w), 2842 (w), 1719 (s), 1647 (w), 1609 (m), 1576 (w), 1496 (w), 1453 (w), 1434 (m), 1415 (w), 1311 (w), 1274 (s), 1192 (m), 1177 (m), 1106 (s), 1076 (w), 1027 (w), 968 (w), 899 (m), 867 (w), 757 (s), 731 (s), 697 (s). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{18}H_{18}O_2$, 267.1380; found, 267.1366.



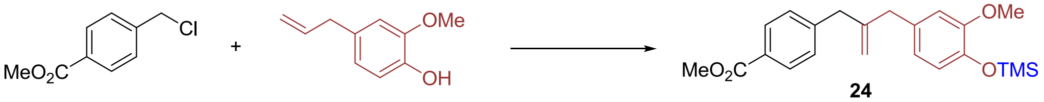
4-(2-(3,4-dimethoxybenzyl)allyl)benzoic acid (21): Following General Procedure B, a magnetic stir bar, 4-(chloromethyl)benzoic acid (1.00 mmol, 171 mg), methyl eugenol (5.00 mmol, 860 µL), Et_3N (8.00 mmol, 1115 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was cooled to 0°C, after which TMSOTf (3.00 mmol, 543 µL) was added dropwise. After the addition was complete, the mixture was warmed to room temperature, precatalyst **1** (0.050 mmol, 36.7 mg) was added, the vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. After this time, water (1.5 mL) was added to the reaction mixture, which was then allowed to stir open to the air for 10 minutes. To this mixture was added 20 mL CH_2Cl_2 and 10 mL of 1 M HCl, the phases were separated, and the organic phase was collected. The aqueous layer was extracted twice more with CH_2Cl_2 and the combined organic extracts dried over Na_2SO_4. After concentration under reduced pressure, the crude material was purified by column chromatography on silica gel (gradient of 20% EtOAc/CH_2Cl_2 to 100% EtOAc, R_f = 0.48 in 100% EtOAc). The material obtained from the column was further purified by mixed solvent recrystallization from $CHCl_3$/Hexanes to yield **21** (256 mg, 82%, >95:5 ratio) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.35 (br s, 1H), 8.08 – 8.02 (m, 2H), 7.28 – 7.24 (m, 3H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.71 – 6.66 (m, 1H), 6.66 – 6.64 (m, 1H), 4.94 – 4.91 (m, 1H), 4.86 – 4.84 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.34 (s, 2H), 3.23 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.06, 149.05, 147.73, 146.32, 131.76, 130.45, 129.44, 127.44, 121.23, 114.11, 112.35, 111.33, 56.08, 55.99, 42.21, 42.11. IR (ATR, cm^{-1}): 3066 (w), 3005 (w), 2971 (m), 2936 (m), 2906 (m), 2840 m br, 2673 (w), 2549 (w), 1684 (s), 1639 (m), 1607 (m), 1589 (m), 1576 (m), 1514 (s), 1462 (m), 1417 (s), 1343 (m), 1318 (s), 1283 (s), 1257 (s), 1231 (s), 1182 (s), 1149 (s), 1137 (s), 1126 (s), 1029 (s), 1020 (s), 934 (s), 895 (s), 858 (s), 804 (s), 749 (s), 703 (s). HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{19}H_{20}O_4$, 313.1434; found, 313.1430.



(2-(biphenyl-4-ylmethyl)allyloxy)triethylsilane (22): Following General Procedure B, a magnetic stir bar, 4-(chloromethyl)biphenyl (1.00 mmol, 203 mg), allyl alcohol (3 mmol, 204 µL), Et_3N (9.00 mmol, 1254 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was cooled to 0°C, after which TESOTf (4.5 mmol, 1018 µL) was added dropwise. After the addition was complete, the mixture was warmed to room temperature, precatalyst **1** (0.050 mmol, 36.7 mg) was added, the vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. After this time, the reaction mixture was allowed to stir open to the air for 5 minutes, then passed through a 4 cm plug of silica gel (pre-wetted with dichloromethane). The silica gel plug was washed with 25 mL of dichloromethane followed by 25 mL of a 1:1 mixture of hexanes:ethyl acetate. After concentration under reduced pressure, the crude material was purified by column chromatography on silica gel (20% CH_2Cl_2/Hex, R_f = 0.26) to yield **22** (298 mg, 88%, >99:1 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.55 – 7.52 (m, 2H), 7.47 – 7.42 (m, 2H), 7.36 – 7.32 (m, 1H), 7.30 – 7.26 (m, 2H), 5.19 (t, *J* = 1.6 Hz, 1H), 4.89 (dq, *J* = 2.9, 1.3 Hz, 1H), 4.09 (s, 2H), 3.43 (s, 2H), 0.97 (td, *J* = 8.0, 1.1 Hz, 8H), 0.62 (qd, *J* = 8.0, 1.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.94, 141.19, 139.17, 138.60, 129.50, 128.85, 127.18, 127.16, 127.13, 111.08, 65.20, 39.36, 6.94, 4.60. IR (ATR, cm^{-1}): 3061 (w), 3031 (w), 2954 (m), 2911 (w), 2878 (m), 1654 (w), 1600 (w), 1488 (m), 1458 (w), 1412 (w), 1238 (w), 1102 (m), 1076 (m), 1007 (m), 973 (w), 901 (m), 807 (m), 759 (s), 738 (s), 725 (s), 695 (s). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{22}H_{30}OSi$, 339.2139; found, 339.2140.

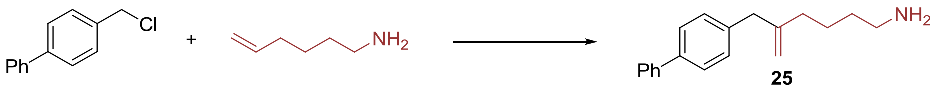


1-(6-bromo-2-methylenehexyl)-4-methoxybenzene (23): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 4-methoxybenzyl chloride (1.00 mmol, 136 µL), 6-bromo-1-hexene (5 mmol, 668 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TESOTf (1.50 mmol, 339 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 6 hours. Following work-up according to the general procedure, silica gel chromatography (5% EtOAc/Hex, R_f = 0.42) yielded **23** (218 mg, 77%, 96:4 ratio) as a clear, colorless liquid. ^1H NMR (500 MHz,) δ 7.12 – 7.08 (m, 2H), 6.86 – 6.82 (m, 2H), 4.83 – 4.80 (m, 1H), 4.78 – 4.75 (m, 1H), 3.80 (s, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 3.28 (s, 2H), 2.01 – 1.96 (m, 2H), 1.87 – 1.79 (m, 2H), 1.62 – 1.54 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.10, 148.72, 131.75, 129.98, 113.82, 111.41, 55.37, 42.15, 34.38, 33.96, 32.40, 26.10. IR (ATR, cm^{-1}): 3074 (w), 3005 (w), 2937 (w), 2909 (w), 2837 (w), 1645 (w), 1611 (w), 1583 (w), 1509 (s), 1464 (w), 1438 (m), 1300 (m), 1244 (s), 1175 (m), 1106 (w), 1037 (m), 895 (m), 846 (m), 807 (m), 755 (s), 733 (s), 679 (m). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{14}H_{19}OBr$, 283.0692; found, 283.0702.



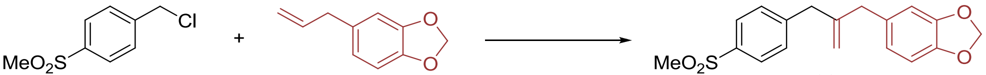
methyl 4-(2-(3-methoxy-4-(trimethylsilyloxy)benzyl)allyl)benzoate (24): Following General Procedure B, a magnetic stir bar, methyl (4-chloromethyl)benzoate (1.00 mmol, 185 mg), eugenol (3 mmol, 462 µL), Et_3N (9.00 mmol, 1254 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was cooled to 0°C, after which TMSOTf (4.5 mmol, 814 µL) was added dropwise. After the addition was complete, the mixture was warmed to room temperature, precatalyst **1** (0.050 mmol, 36.7 mg) was added, the vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. After this time, the reaction mixture was allowed to stir open to the air for

5 minutes, then passed through a 4 cm plug of silica gel (pre-wetted with dichloromethane). The silica gel plug was washed with 25 mL of dichloromethane followed by 25 mL of a 1:1 mixture of hexanes:ethyl acetate. After concentration under reduced pressure, the crude material was purified by column chromatography on silica gel (10% EtOAc/Hex, R_f = 0.37) to yield **24** (369 mg, 96%, >99:1 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.22 – 7.20 (m, 2H), 6.79 – 6.76 (m, 1H), 6.62 – 6.57 (m, 2H), 4.92 – 4.89 (m, 1H), 4.84 – 4.82 (m, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 3.32 (s, 2H), 3.20 (s, 2H), 0.25 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.14, 150.71, 147.78, 145.21, 142.92, 132.71, 129.68, 129.21, 128.18, 121.29, 120.67, 113.85, 112.86, 55.51, 52.06, 42.12, 42.05, 0.39. IR (ATR, cm^{-1}): 2954 (w), 2906 (w), 2840 (w), 1721 (s), 1609 (w), 1510 (s), 1464 (w), 1449 (w), 1436 (m), 1415 (m), 1274 (s), 1249 (s), 1231 (s), 1190 (m), 1178 (m), 1154 (m), 1102 (s), 1039 (m), 1020 (m), 897 (s), 839 (s), 811 (s), 753 (s), 733 (m), 705 (m). HRMS (ESI, *m/z*): [M + H]$^+$ calcd for $C_{22}H_{28}O_4$, 385.1830; found, 385.1835.



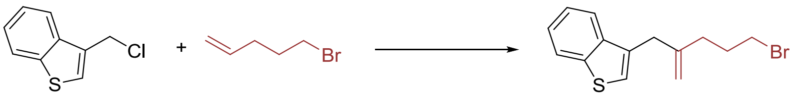
5-(biphenyl-4-ylmethyl)hex-5-en-1-amine (25): To an 8 mL screw-cap vial equipped with a magnetic stir bar was added 1-amino-5-hexene (3.00 mmol, 379 µL), Et_3N (12.00 mmol, 1673 µL), and CH_2Cl_2 (500 µL). The mixture was cooled to 0°C, after which TMSOTf (6.00 mmol, 1086 µL) was added dropwise. After the addition was complete, the mixture was warmed to room temperature and a syringe and needle were used to withdraw the bottom layer of $Et_3N{\cdot}HOTf$. Next, 4-(chloromethyl)-biphenyl (1.00 mmol, 203 mg) and precatalyst **1** (0.050 mmol, 36.7 mg) were added to the mixture. A second portion of TMSOTf (2.00 mmol, 362 µL) was added, the vial was closed with a screw-cap, and the mixture was stirred at room temperature for 8 hours. After this time, water (1.5 mL) was added to the reaction mixture, which was then allowed to stir open to the air for 10 minutes. To this mixture was added 20 mL CH_2Cl_2 and 10 mL water, and the aqueous phase was basified with 3 M NaOH to adjust the pH >12. The phases were separated and the organic phase was collected. The aqueous layer was extracted twice more with CH_2Cl_2 and the combined organic extracts dried over Na_2SO_4. After concentration under reduced pressure, the crude material was purified by column chromatography on silica gel that had been pretreated with several column volumes of 1% Et_3N in CH_2Cl_2 (gradient of 100% CH_2Cl_2 to 10% MeOH/CH_2Cl_2, R_f = 0.13 in 2% MeOH/CH_2Cl_2) to yield **25** (183 mg, 69%, >95:5 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dq, *J* = 7.1, 1.0 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.46 – 7.42 (m, 2H), 7.34 (ddt, *J* = 8.5, 6.7, 1.2 Hz, 1H), 7.29 – 7.25 (m, 2H), 4.89 – 4.87 (m, 1H), 4.82 – 4.80 (m, 1H), 3.39 (s, 2H), 2.69 (td, *J* = 6.9, 0.7 Hz, 2H), 2.06 – 2.00 (m, 2H), 1.56 –

1.40 (m, 4H), 1.24 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 148.81, 141.08, 139.04, 138.99, 129.46, 128.78, 127.12, 127.07, 127.05, 111.40, 42.71, 42.18, 35.28, 33.50, 24.94. IR (ATR, cm^{-1}): 3379 w br, 3079 (w), 3029 (w), 2928 (m), 2857 (w), 1645 (w), 1600 (w), 1561 (w), 1518 (w), 1486 (m), 1438 (w), 1408 (w), 1109 (w), 1076 (w), 1009 (m), 891 (m), 846 (m), 809 (m), 759 (s), 729 (s), 695 (s). HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{19}H_{23}N$, 266.1903; found, 266.1898.



26

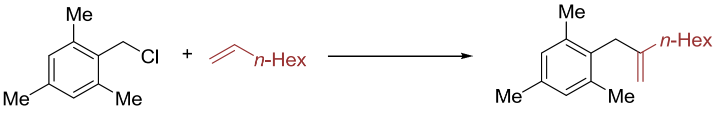
5-(2-(4-(methylsulfonyl)benzyl)allyl)benzo[*d*][1,3]dioxole (26): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 4-(methylsulfonyl)benzyl chloride (1.00 mmol, 205 mg), safrole (5 mmol, 741 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TESOTf (1.50 mmol, 339 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (30% EtOAc/Hex, R_f = 0.33) yielded **26** (221 mg, 67%, 99:1 ratio) as a clear, colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.31 – 7.27 (m, 2H), 6.67 (d, J = 7.9 Hz, 1H), 6.58 (d, J = 1.7 Hz, 1H), 6.53 (dt, J = 7.9, 1.1 Hz, 1H), 5.87 (s, 2H), 4.91 – 4.87 (m, 1H), 4.81 – 4.77 (m, 1H), 3.30 (s, 2H), 3.14 (s, 2H), 3.02 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 147.54, 146.95, 145.96, 145.91, 138.29, 132.45, 129.87, 127.24, 121.78, 114.32, 109.11, 107.96, 100.76, 44.35, 41.93, 41.59. IR (ATR, cm^{-1}): 3075 (w), 2902 (w), 1647 (w), 1596 (w), 1503 (m), 1488 (s), 1441 (m), 1408 (w), 1361 (w), 1303 (s), 1244 (s), 1186 (m), 1147 (s), 1089 (m), 1037 (s), 957 (m), 906 (s), 858 (m), 809 (m), 770 (m), 759 (s), 725 (s). HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{18}H_{18}O_4$, 331.0999; found, 331.1000.



S4

27

3-(5-bromo-2-methylenepentyl)benzo[*b*]thiophene (27): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 3-(chloromethyl)benzo[*b*]thiophene (1.00 mmol, 183 mg), 5-bromo-1-pentene (5 mmol, 592 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TESOTf (1.50 mmol, 339 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (20% CH_2Cl_2/Hex, R_f = 0.48) yielded **27** (231 mg, 78%, 94:6 ratio) as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 1H), 7.77 – 7.75 (m, 1H), 7.43 – 7.34 (m, 2H), 7.16 (td, *J* = 1.0, 0.4 Hz, 1H), 4.96 (tt, *J* = 1.3, 0.6 Hz, 1H), 4.91 (tq, *J* = 1.4, 0.7 Hz, 1H), 3.62 – 3.59 (m, 2H), 3.42 (t, *J* = 6.7 Hz, 2H), 2.26 – 2.21 (m, 2H), 2.08 – 2.01 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.38, 140.62, 139.03, 133.77, 124.29, 123.96, 123.15, 122.94, 122.12, 112.67, 35.93, 34.04, 33.33, 30.85. IR (ATR, cm^{-1}): 3072 (w), 2932 (w), 2904 (w), 2844 (w), 1647 (w), 1458 (w), 1427 (m), 1359 (w), 1249 (m), 1205 (w), 1156 (w), 1076 (w), 1020 (w), 968 (w), 897 (m), 835 (m), 755 (s), 727 (s). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{14}H_{15}BrS$, 295.0151; found, 295.0164.



28

1,3,5-trimethyl-2-(2-methyleneoctyl)benzene (28): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 2,4,6-trimethylbenzyl chloride (1.00 mmol, 169 mg), 1-octene (5 mmol, 785 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 8 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.65) yielded **28** (100 mg, 41%, 96:4 ratio[7]) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (s, 2H), 4.72 – 4.69 (m, 1H), 4.21 – 4.19 (m, 1H), 3.28 – 3.26 (m, 2H), 2.30 (s, 3H), 2.23 (s, 6H), 2.21 – 2.13 (m, 2H), 1.63 – 1.52 (m, 2H), 1.44 – 1.30 (m, 6H), 0.98 – 0.91 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.21, 137.01, 135.30, 133.69, 128.69, 108.65, 37.64, 35.64, 31.98, 29.30, 28.16, 22.83, 21.02, 19.83, 14.28. IR (ATR, cm^{-1}): 2958 (m), 2926 (s), 2857 (m), 1645 (w), 1615 (w), 1484 (w), 1458 (m), 1445 (m), 1376 (w), 1031 (w), 1012 (w), 908 (m), 897 (m), 850 (m), 733 (s), 714 (w). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{18}H_{28}$, 245.2264; found, 245.2278.

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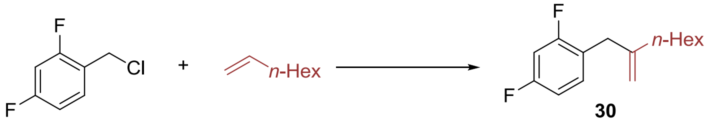
[7] The ratio of isomers was 78:22 prior to column chromatography. In this particular instance, the linear and branched products were separable by column chromatography.

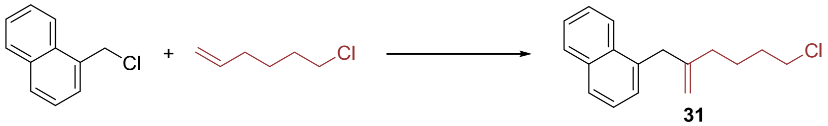

29

4-((6-chlorobenzo[*d*][1,3]dioxol-5-yl)methyl)pent-4-enyl 4-methylbenzenesulfonate (29): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 6-chloropiperonyl chloride (1.00 mmol, 205 mg), 4-pentenyl tosylate (3 mmol, 721 mg), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TESOTf (1.50 mmol, 339 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (20% EtOAc/Hex, R_f = 0.37) yielded **29** (213 mg, 52%, >95:5 ratio) as a clear, colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.35 – 7.31 (m, 2H), 6.79 (s, 1H), 6.60 (s, 1H), 5.94 (s, 2H), 4.74 – 4.72 (m, 1H), 4.60 – 4.57 (m, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 3.26 (s, 2H), 2.43 (s, 3H), 2.06 – 1.98 (m, 2H), 1.86 – 1.75 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 146.80, 146.74, 145.63, 144.80, 133.10, 129.90, 129.87, 127.93, 125.70, 112.26, 110.22, 109.72, 101.70, 70.05, 39.56, 31.39, 26.86, 21.69. IR (ATR, cm^{-1}): 2958 (w), 2902 (w), 1598 (w), 1505 (m), 1477 (s), 1358 (m), 1231 (m), 1190 (m), 1175 (s), 1117 (m), 1098 (m), 1037 (m), 973 (m), 929 (s), 910 (s), 835 (m), 813 (m), 751 (s), 731 (s), 690 (m), 662 (s). HRMS (ESI, *m/z*): $[M + NH_4]^+$ calcd for $C_{20}H_{21}O_5ClS$, 426.1136; found, 426.1123.


30

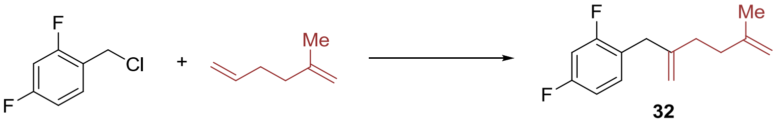
2,4-difluoro-1-(2-methyleneoctyl)benzene (30): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.50 mmol, 367 mg), 2,4-difluorobenzyl chloride (10.0 mmol, 1.63 g), 1-octene (50 mmol, 7.85 mL), Et_3N (60 mmol, 8.36 mL), and dichloromethane (5 mL) were added to a 25 mL round-bottom flask. The flask was fitted with a rubber septum and an argon inlet and the mixture was stirred for 5 minutes, after which TMSOTf (15.0 mmol, 2.71 mL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 4 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.67) yielded **30** (2.12 g, 89%, 97:3 ratio) as a clear, colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 1H), 6.84 – 6.76 (m, 2H), 4.85 – 4.82 (m, 1H), 4.67 – 4.64 (m, 1H), 3.32 (s, 2H), 2.03 – 1.98 (m, 2H), 1.50 – 1.42 (m, 2H), 1.35 – 1.25 (m, 6H), 0.92 – 0.87 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 161.74 (dd, *J* = 246.5, 11.8 Hz), 161.17 (dd, *J* = 247.8, 11.7 Hz), 147.85, 131.79 (dd, *J* = 9.4, 6.3 Hz), 122.74 (dd, *J* = 16.2, 3.8 Hz), 111.16, 111.03 (dd, *J* = 20.9, 3.8 Hz), 103.68 (dd, *J* = 26.4, 25.1 Hz), 35.88, 34.91 (d, *J*

= 2.4 Hz), 31.94, 29.19, 27.79, 22.82, 14.21. IR (ATR, cm^{-1}): 2958 (w), 2930 (m), 2859 (w), 1647 (w), 1619 (m), 1604 (m), 1505 (s), 1460 (w), 1438 (w), 1428 (m), 1277 (m), 1262 (m), 1137 (s), 1089 (m), 970 (s), 895 (m), 848 (s), 826 (w), 791 (m), 733 (m). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{15}H_{20}F_2$, 239.1606; found, 239.1606.



31

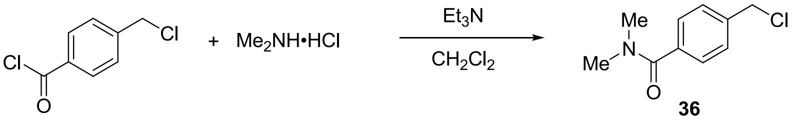
1-(6-chloro-2-methylenehexyl)naphthalene (31): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 1-(chloromethyl)naphthalene (1.00 mmol, 177 mg), 6-chloro-1-hexene (5 mmol, 662 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 6 hours. Following work-up according to the general procedure, silica gel chromatography (gradient of 100% hexanes to 20% CH_2Cl_2/Hex, R_f = 0.59 in 20% CH_2Cl_2/hex) yielded **31** (233 mg, 90%, 83:17 ratio) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 1H), 7.91 – 7.86 (m, 1H), 7.81 – 7.76 (m, 1H), 7.56 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.37 (ddt, *J* = 7.0, 1.3, 0.7 Hz, 1H), 4.93 – 4.90 (m, 1H), 4.68 – 4.66 (m, 1H), 3.83 (s, 2H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.17 – 2.10 (m, 2H), 1.86 – 1.78 (m, 2H), 1.75 – 1.67 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.84, 135.66, 133.95, 132.51, 128.73, 127.43, 127.15, 125.85, 125.59, 125.59, 124.41, 112.02, 45.11, 40.04, 35.49, 32.29, 25.03. IR (ATR, cm^{-1}): 3068 (w), 3046 (w), 2939 (w), 2865 (w), 1647 (w), 1596 (w), 1509 (w), 1443 (w), 1397 (w), 1300 (w), 1262 (w), 1218 (w), 1165 (w), 1078 (w), 1016 (w), 893 (m), 791 (s), 776 (s), 731 (m). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{17}H_{19}Cl$, 259.1248; found, 259.1254.



32

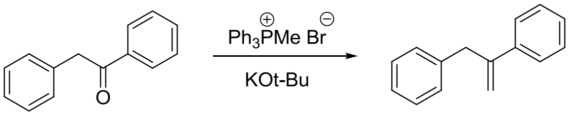
2,4-difluoro-1-(5-methyl-2-methylenehex-5-enyl)benzene (32): Following General Procedure A, a magnetic stir bar, precatalyst **1** (0.050 mmol, 36.7 mg), 2,4-difluorobenzyl chloride (1.00 mmol, 163 mg), 2-methyl-1,5-hexadiene (5 mmol, 675 µL), Et_3N (6.00 mmol, 836 µL), and dichloromethane (500 µL) were added to an 8 mL screw-cap vial. The mixture was stirred for ca. 10 seconds, after which TMSOTf (1.50 mmol, 271 µL) was added in one portion. The vial was closed with a screw-cap and the mixture was stirred at room temperature for 6 hours. Following work-up according to the general procedure, silica gel chromatography (pentane, R_f = 0.51) yielded **32** (136 mg, 61%, 96:4 ratio) as a clear, colorless liquid. This product contained an impurity of oligomerized 2-methyl-1,5-hexadiene (ca. 10% by mass) that could not be separated by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 1H), 6.85 – 6.72 (m, 2H), 4.87 – 4.84 (m, 1H), 4.74 – 4.71 (m, 1H), 4.70 – 4.67 (m, 2H), 3.34 (s, 2H), 2.16 (qd, *J* = 7.4, 3.9 Hz, 4H), 1.72 (dd, *J* = 1.5, 0.8 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.71 (dd, *J* = 246.5, 11.8 Hz), 161.10 (dd, *J* = 247.8, 11.7 Hz), 147.34 (app t, *J* = 0.9 Hz), 145.52, 131.80 (dd, *J* = 9.4, 6.2 Hz), 122.53 (dd, *J* = 16.2, 3.8 Hz), 111.43, 111.10 (dd, *J* = 21.0, 3.8 Hz), 110.24, 103.74 (dd, *J* = 26.4, 25.1 Hz), 36.07, 34.97 (d, *J* = 2.4 Hz), 33.94, 22.55. IR (ATR, cm^{-1}): 3079 (w), 2934 (w), 2859 (w), 1649 (w), 1619 (m), 1604 (m), 1503 (s), 1440 (m), 1427 (m), 1374 (w), 1277 (m), 1262 (m), 1136 (s), 1091 (m), 966 (s), 889 (s), 848 (s), 792 (m), 731 (w). HRMS (DART, *m/z*): $[M + H]^+$ calcd for $C_{14}H_{16}F_2$, 223.1293; found, 223.1311.

Section V. Synthesis of Substrates and Authentic Samples



36

4-(chloromethyl)-N,N-dimethylbenzamide (36):[8] To an oven-dried, 100 mL round-bottom flask equipped with a magnetic stir bar was added 4-(chloromethyl)benzoyl chloride (20 mmol, 3.78 g) and $Me_2NH·HCl$ (25 mmol, 2.04 g). Dichloromethane (50 mL) was added, the flask was fitted with a rubber septum and attached to an argon line. The mixture was cooled to 0° C with an ice bath and Et_3N (60 mmol, 8.36 mL) was added dropwise over the course of 20 minutes. The reaction mixture was allowed to warm to room temperature and stirred for another 1 hour, after which the organic phase was washed twice with water and once with brine. The organic phase was dried over Na_2SO_4, concentrated in vacuo, and purified by column chromatography on silica gel (80:15:5 EtOAc:Hex:MeOH, R_f in 80% EtOAc/Hex = 0.36) to yield **36** (3.57g, 90%) as a colorless solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (app s, 4H), 4.60 (s, 2H), 3.11 (br s, 3H), 2.98 (br s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.01, 138.80, 136.42, 128.59, 127.54, 45.68, 39.60, 35.38. HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{10}H_{13}ClNO$, 198.0680; found, 198.0672.



40

prop-2-ene-1,2-diyldibenzene (40): In an oven-dried, 100 mL, 2-necked round-bottom flask equipped with a magnetic stir bar was added KO*t*-Bu (10 mmol, 1.12 g). A reflux condenser was fitted to one neck of the flask and a rubber septum to the other. The apparatus was purged with dry argon for several minutes, after which 25 mL of THF were added. The septum was removed and methyltriphenylphosphonium bromide (12 mmol, 4.29 g) was added portion-wise through the second neck of the flask (against a flow of argon) causing immediate formation of an intensely colored, yellow slurry. After complete addition of the methyltriphenylphosphonium bromide, the rubber septum was replaced and the reaction heated to 60°C. A solution of 2-phenylacetophenone (11 mmol, 2.16 g) in 10 mL of THF was added dropwise via syringe. The reaction mixture was held at 60°C until the yellow color faded, indicating complete consumption of the phosphorane. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure, after which the reaction mixture was

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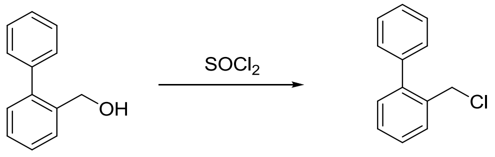
[8] **36** was prepared according to a modified procedure based on that reported in Ray, N. C.; Bull, R. J.; Finch, H.; Van den Heuvel, M.; Bravo, J. A. Oxazole and Thiazole Derivatives and their Uses. Int. Pat. Appl. WO 2008/096093, 2008.

triturated with pentane (25 mL) for 10 minutes. The slurry was filtered through a pad of diatomaceous earth and the residue washed with a few milliliters of pentane. Concentration of the filtrate followed by column chromatography on silica gel (pentane, R_f = 0.30) yielded the product **40** as a clear, colorless liquid (1.73 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dq, *J* = 7.3, 1.2 Hz, 2H), 7.41 – 7.29 (m, 7H), 7.29 – 7.24 (m, 1H), 5.59 (ddd, *J* = 2.0, 1.2, 0.6 Hz, 1H), 5.11 (dt, *J* = 2.4, 1.2 Hz, 1H), 3.92 (t, *J* = 1.4 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.93, 140.79, 139.54, 129.00, 128.42, 128.32, 127.52, 126.17, 114.62, 41.66. The ^{1}H and ^{13}C NMR spectra are in agreement with those previously reported in the literature.[9]



S1

2-(chloromethyl)biphenyl (S1): To an oven-dried, 50 mL round-bottom flask equipped with a magnetic stir bar was added 2-biphenylmethanol (5.23 mmol, 1.00 g). The flask was fitted with a rubber septum, an argon inlet, and 20 mL of CH_2Cl_2 were added, which yielded a slightly heterogeneous mixture. After cooling this mixture to 0° C, the argon inlet was replaced with a connection to a mineral oil bubbler, and $SOCl_2$ (10 mmol, 0.73 mL) was added dropwise over the course of 20 minutes, causing the solution to become homogeneous. The solution was allowed to warm to room temperature and stirred for an additional 3 hours, after which the mixture was quenched by the cautious addition of 1 M aqueous $NaHCO_3$, washed once with saturated aqueous $NaHCO_3$, once with water, and once with brine. After drying the organic phase over Na_2SO_4 and evaporation under reduced pressure, the crude product mixture was purified by column chromatography on silica gel (5% EtOAc/Hex, R_f = 0.30) to yield the product **S1** (0.871g, 82%) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 1H), 7.56 – 7.50 (m, 4H), 7.50 – 7.43 (m, 3H), 7.40 – 7.36 (m, 1H), 4.62 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.13, 140.23, 134.98, 130.61, 130.41, 129.22, 128.61, 128.39, 128.02, 127.54, 44.56. The ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[10]

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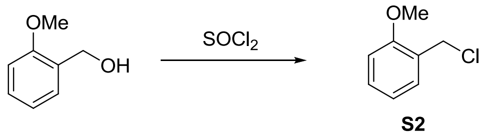
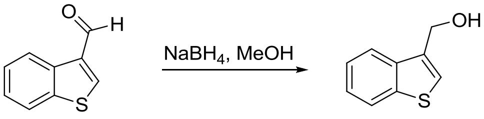
[9] Alacid, E. and Nájera, C. *Org. Lett.* **2008**, *10*, 5011–5014.

[10] Savarin, C. and Liebeskind, L. S. *Org. Lett.* **2001**, *3*, 2149–2152.



S2

1-(chloromethyl)-2-methoxybenzene (S2): Following the same procedure used for **S1**, 2-methoxybenzyl alcohol (7.24 mmol, 0.962 mL) was added to an oven-dried, 50 mL round-bottom flask equipped with a magnetic stir bar and rubber septum. Dichloromethane (25 mL) was added, the mixture was cooled to 0° C, the argon inlet replaced with a connection to a mineral oil bubbler, and $SOCl_2$ (15 mmol, 1.09 mL) was added dropwise over the course of 20 minutes. The mixture was allowed to warm to room temperature and stirred for an additional 3 hours, after which the mixture was quenched by the cautious addition of 1 M aqueous $NaHCO_3$, washed once with saturated aqueous $NaHCO_3$, once with water, and once with brine. After drying the organic phase over Na_2SO_4 and evaporation under reduced pressure, the crude product mixture was purified by column chromatography on silica gel (5% EtOAc/Hex, R_f = 0.19) to yield the product **S3** (0.779g, 69%) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (ddt, *J* = 7.5, 1.7, 0.4 Hz, 1H), 7.34 – 7.30 (m, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.92 – 6.89 (m, 1H), 4.67 (s, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.38, 130.59, 130.13, 125.78, 120.65, 110.81, 55.55, 41.70. The ^{1}H and ^{13}C NMR spectra are consistent with those previously reported in the literature.[11]



S3

benzo[b]thiophen-3-ylmethanol (S3): Thiophene-3-carboxaldehdye (6.17 mmol, 1.00 g) was added to a 50 mL round-bottom flask equipped with a magnetic stir bar. Methanol (15 mL) was added, the mixture stirred for several minutes to dissolve the aldehyde, and then $NaBH_4$ (6.17 mmol, 0.228 g) was added in several portions over the course of 20 minutes. Stirring was continued until the reaction was determined to be complete by TLC (CH_2Cl_2, R_f of starting aldehyde = 0.72, R_f of **S3** = 0.29), which was ca. 30 minutes after beginning the addition of $NaBH_4$. The reaction mixture was quenched by careful addition of water (10 mL), after which the mixture was extracted 3x with CH_2Cl_2, and the combined organic extracts dried over Na_2SO_4. After concentration in vacuo, the crude product was purified by column chromatography on silica gel (100% CH_2Cl_2) to afford **S4** (0.86 g, 85%) as a pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.43 – 7.35 (m, 3H), 4.93 – 4.91 (m, 2H), 1.91 (br s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.89, 137.77, 136.07, 124.70, 124.33,

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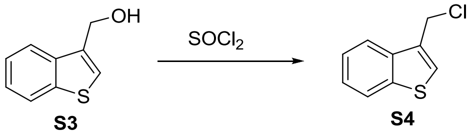
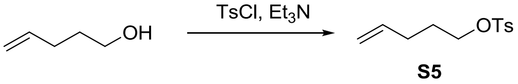
[11] Amin, S.; Hecht, S. S.; Hoffman, D. *J. Org. Chem.* **1981**, *46*, 2394–2398.

123.94, 123.00, 122.05, 59.90. The ^{1}H and ^{13}C NMR spectra are in agreement with those previously reported in the literature.[12]



3-(chloromethyl)benzo[*b*]thiophene (S4): Following the same procedure as **S2**, benzo[*b*]thiophen-3-ylmethanol **(S3)** (5.23 mmol, 0.86 g) was dissolved into 15 mL of CH_2Cl_2 in 50 a mL, oven-dried, round-bottom flask. The flask was fitted with a rubber septum, a connection to a mineral oil bubbler, and cooled to 0°C, after which $SOCl_2$ (8.4 mmol, 0.613 mL) was added dropwise over 20 minutes. The mixture was allowed to warm to room temperature and stirred for an additional 3 hours, after which the mixture was quenched by the cautious addition of 1 M aqueous $NaHCO_3$, washed once with saturated aqueous $NaHCO_3$, once with water, and once with brine. After drying of the organic phase over Na_2SO_4 and evaporation under reduced pressure, the crude product mixture was purified by column chromatography on silica gel (50% Hex/CH_2Cl_2, R_f = 0.70) to yield the product **S4** (0.634g, 66%) as a pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.51 – 7.40 (m, 3H), 4.87 (d, J = 0.7 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.62, 137.32, 131.97, 126.39, 124.91, 124.53, 123.05, 122.01, 39.68. The ^{1}H and ^{13}C NMR spectra are in agreement with those previously reported in the literature.[12]



pent-4-enyl 4-methylbenzenesulfonate (S5): To a dry, 100 mL round-bottom flask equipped with a magnetic stir bar was added TsCl (15 mmol, 2.85 g) and 4-DMAP (1 mmol, 0.122 g). The flask was sealed with a rubber septum and connected to an argon inlet. Dichloromethane (35 mL) and triethylamine (20 mmol, 2.79 mL) were added via syringe and the flask was cooled to 0°C with an ice bath, after which 4-penten-1-ol (12.48 mmol, 1.29 mL) was added dropwise via syringe. The mixture was allowed to warm to room temperature and stirring was continued for an additional 1 hour. The reaction mixture was quenched by the slow addition of water (25 mL), the phases were separated and the organic phase was washed once with saturated aqueous ammonium chloride, once with water, and once with brine. After drying of the organic phase over Na_2SO_4 and concentration under reduced pressure, the crude reaction product was purified by column chromatography on silica gel (80% CH_2Cl_2/Hex, R_f in

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[12] Paul, N. M.; Taylor, M.; Kumar, R.; Deschamps, J. R.; Luedtke, R. R.; Newman, A. H. *J. Med. Chem.* **2008**, *51*, 6095–6109.

CH_2Cl_2 = 0.81) to yield **S5** as a clear, colorless liquid (2.85 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.30 (ddt, *J* = 8.0, 1.3, 0.9 Hz, 2H), 5.69 – 5.59 (m, 1H), 4.93 – 4.86 (m, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 2.39 (s, 3H), 2.03 (dtt, *J* = 7.8, 6.6, 1.4 Hz, 2H), 1.68 (dtd, *J* = 8.4, 6.7, 5.4 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.71, 136.54, 132.96, 129.79, 127.75, 115.72, 69.78, 29.27, 27.86, 21.51. The ^{1}H and ^{13}C NMR spectra are in agreement with those previously reported in the literature.[13]

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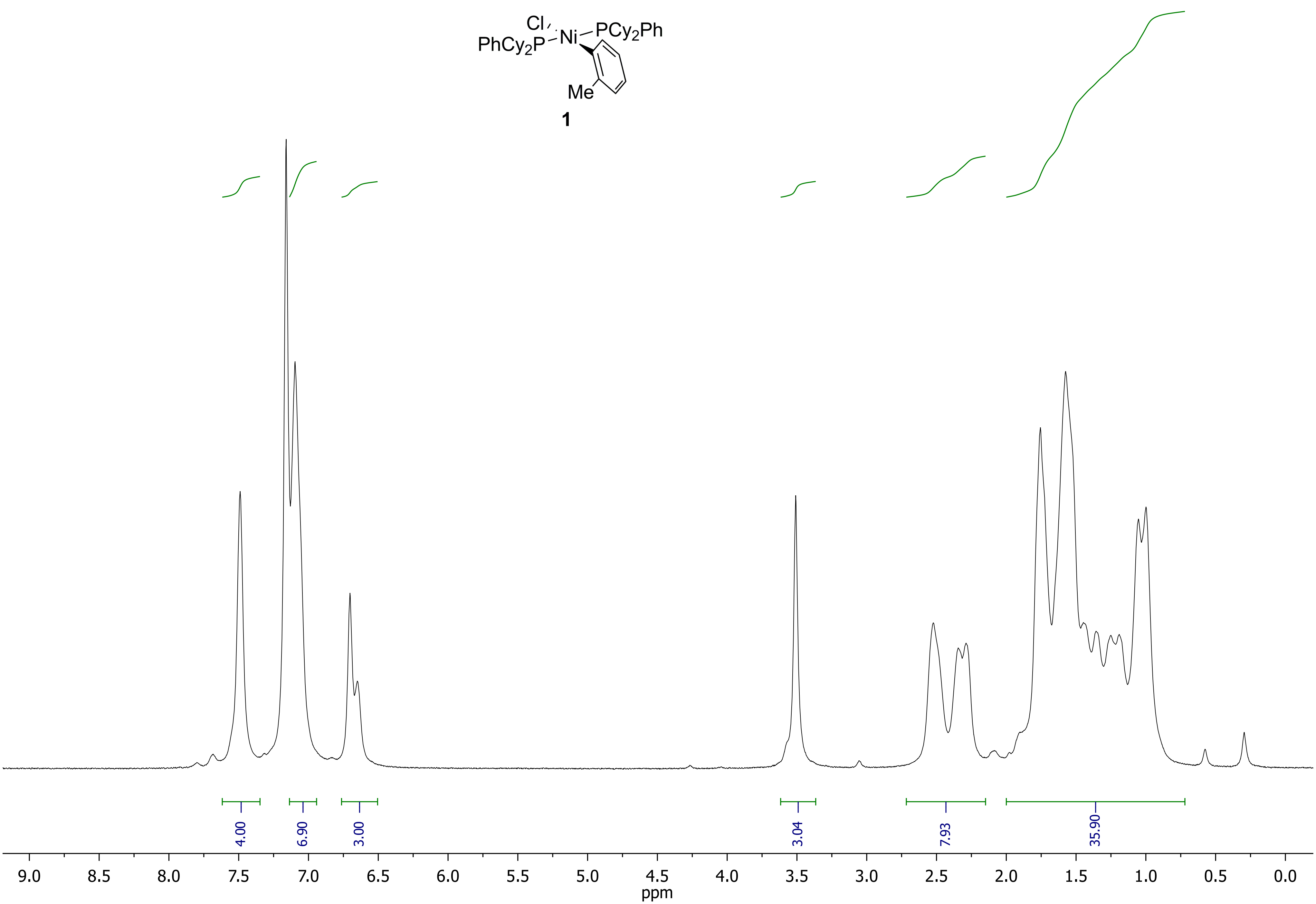
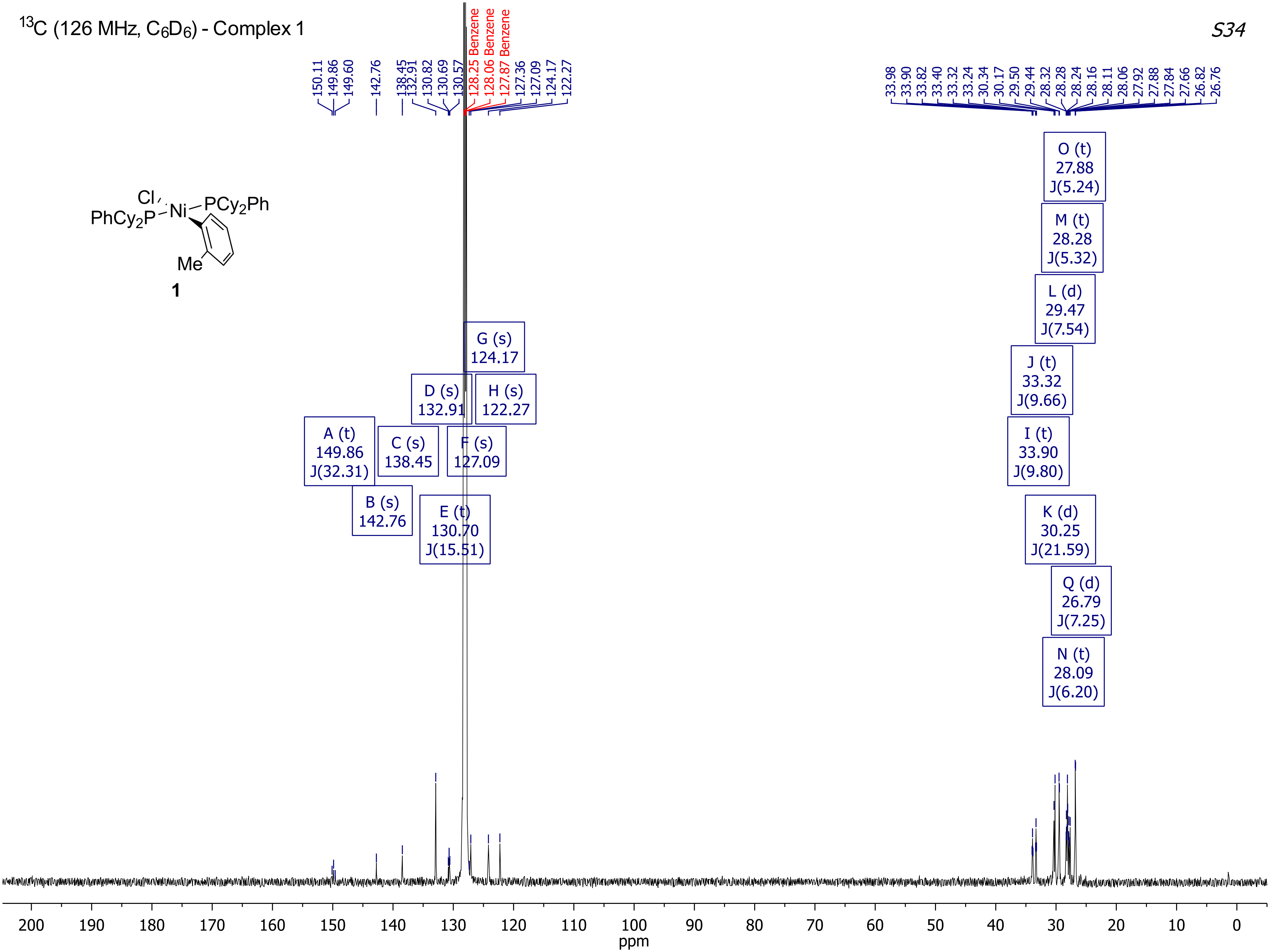
[13] Stokes, B. J.; Opra, S. M.; Sigman, M. S. *J. Am. Chem. Soc.* **2012**, *134*, 11408–11411.

^{1}H (500 MHz, C_6D_6) - Complex 1

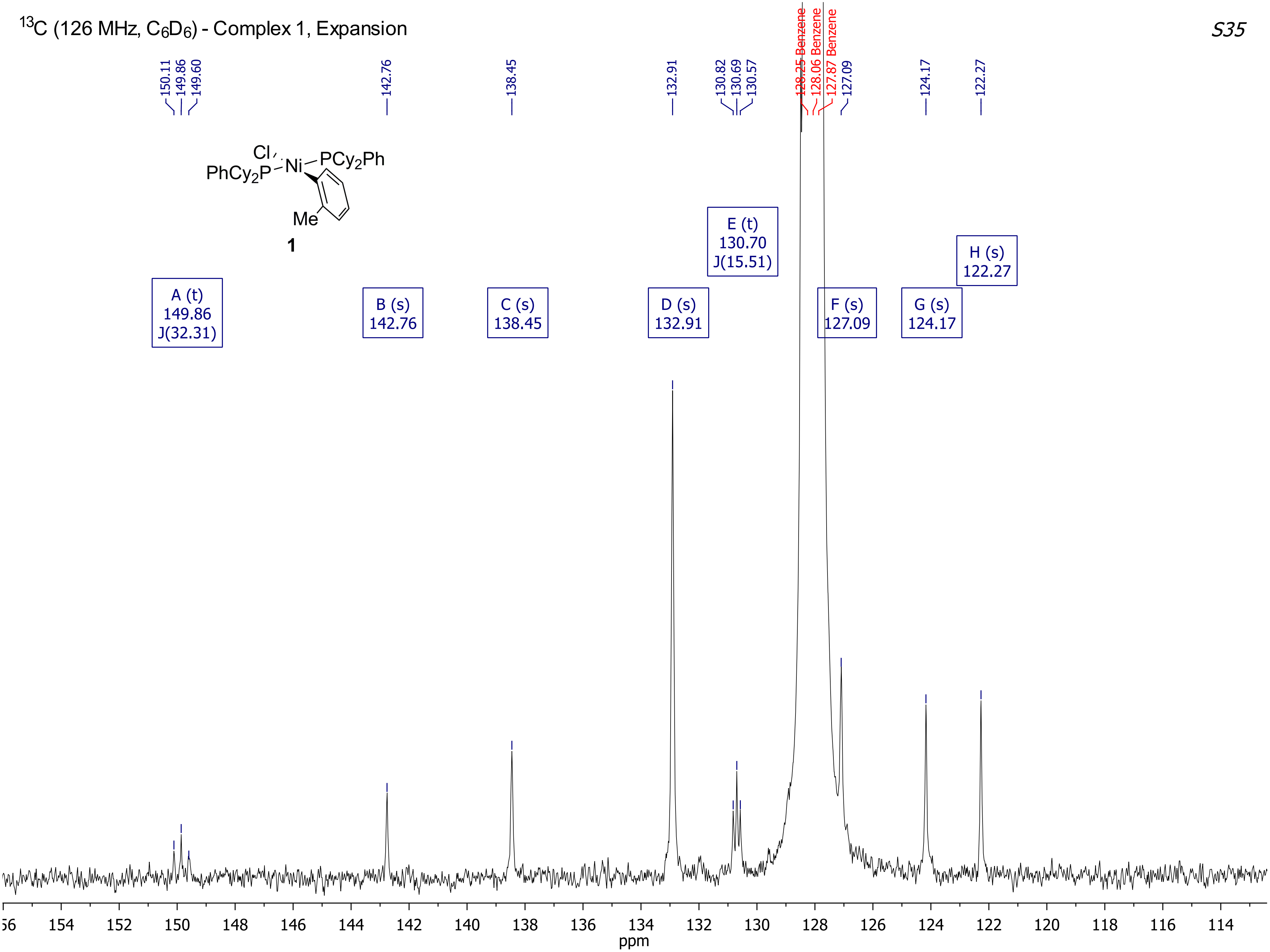


^{13}C (126 MHz, C_6D_6) - Complex 1

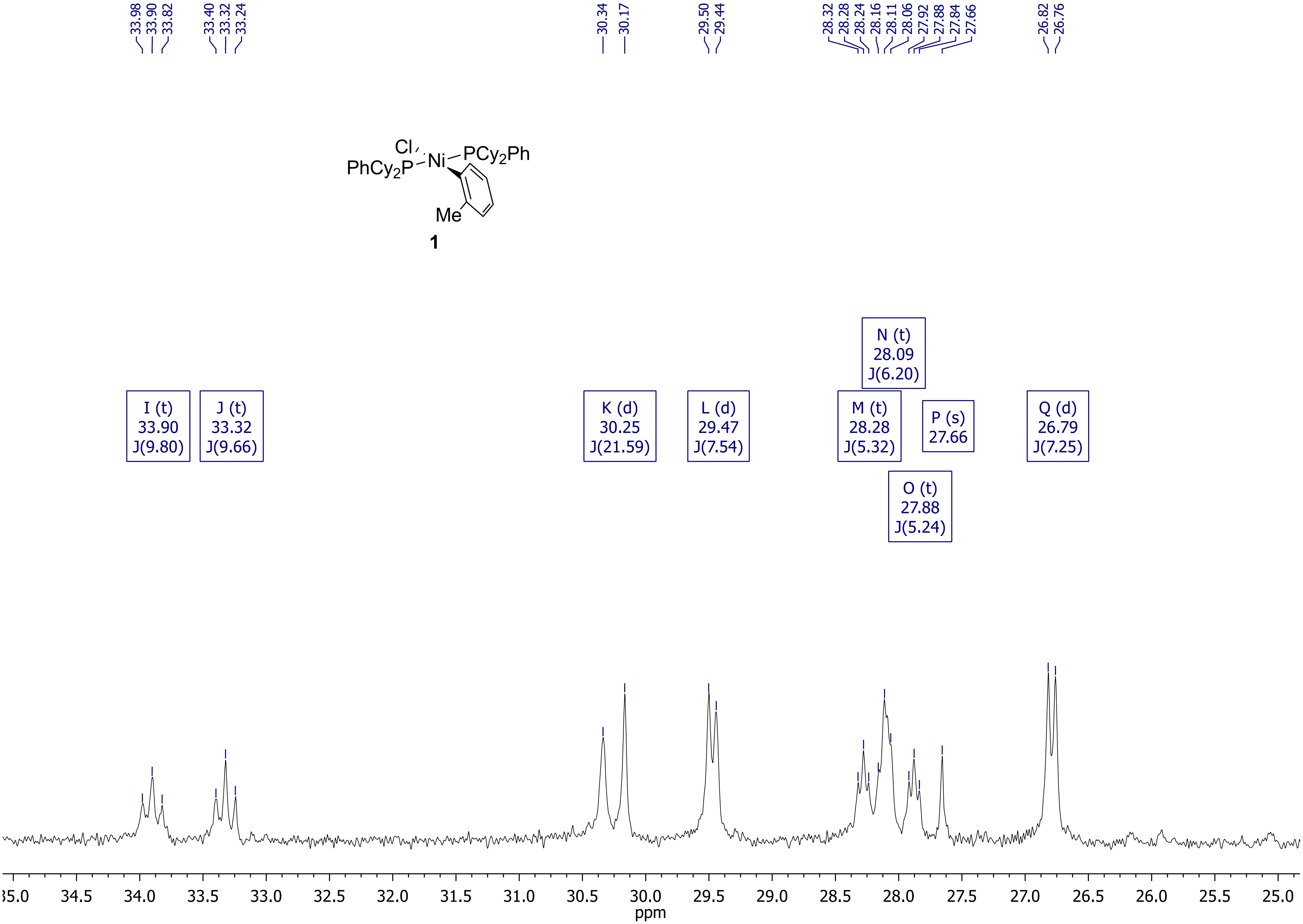
1



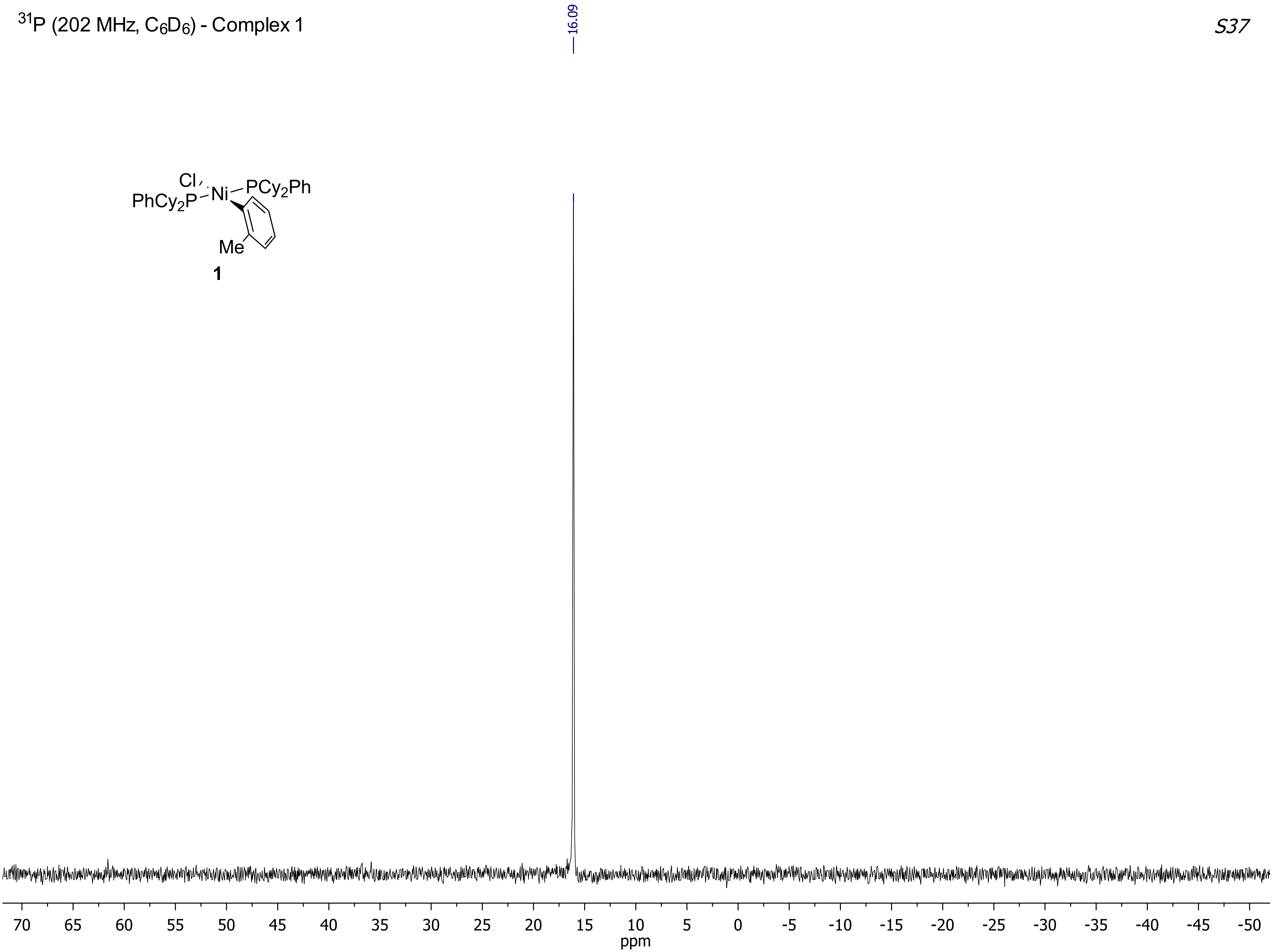
^{13}C (126 MHz, C_6D_6) - Complex 1, Expansion



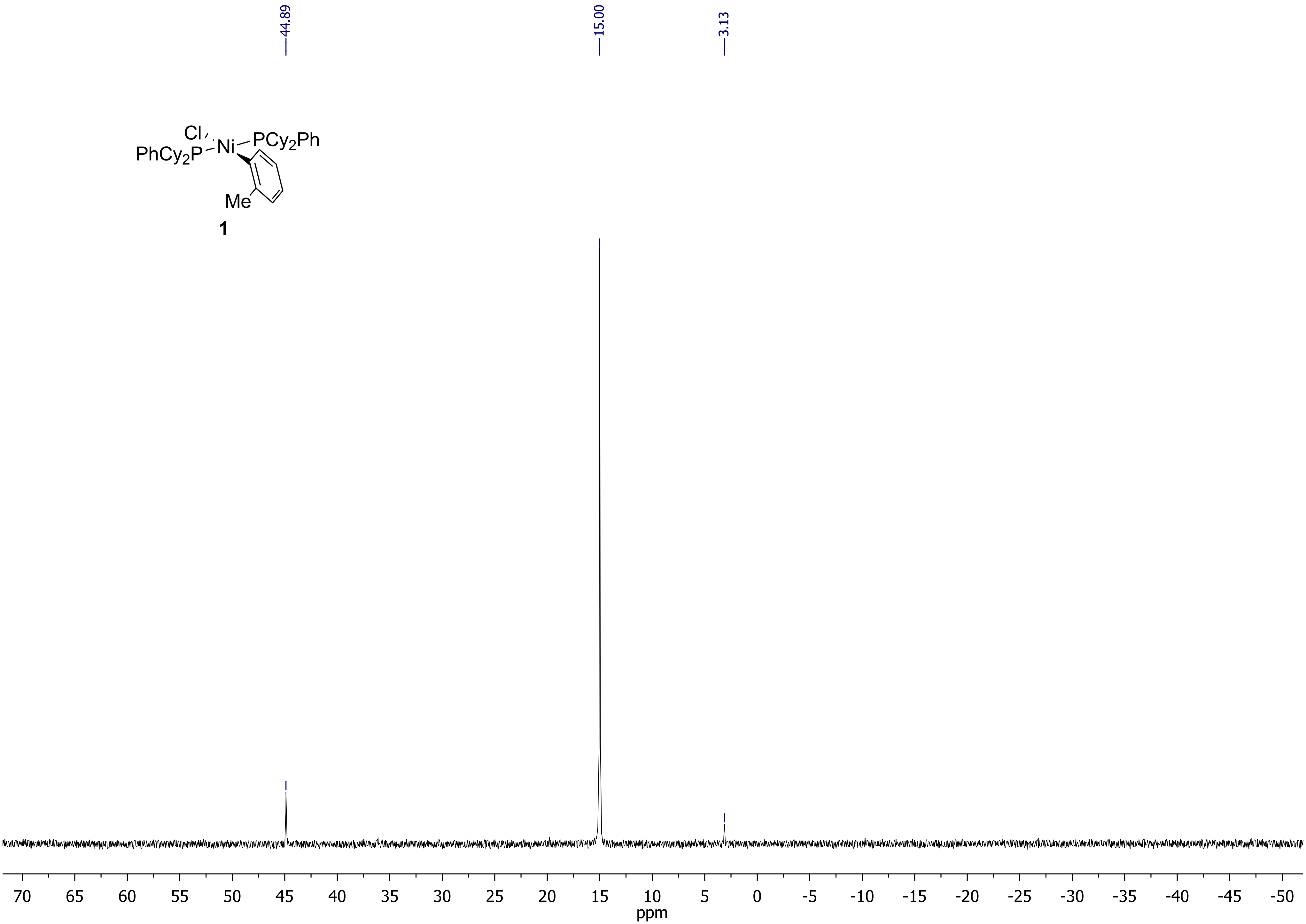
^{13}C (126 MHz, C_6D_6) - Complex 1, Expansion



^{31}P (202 MHz, C_6D_6) - Complex 1



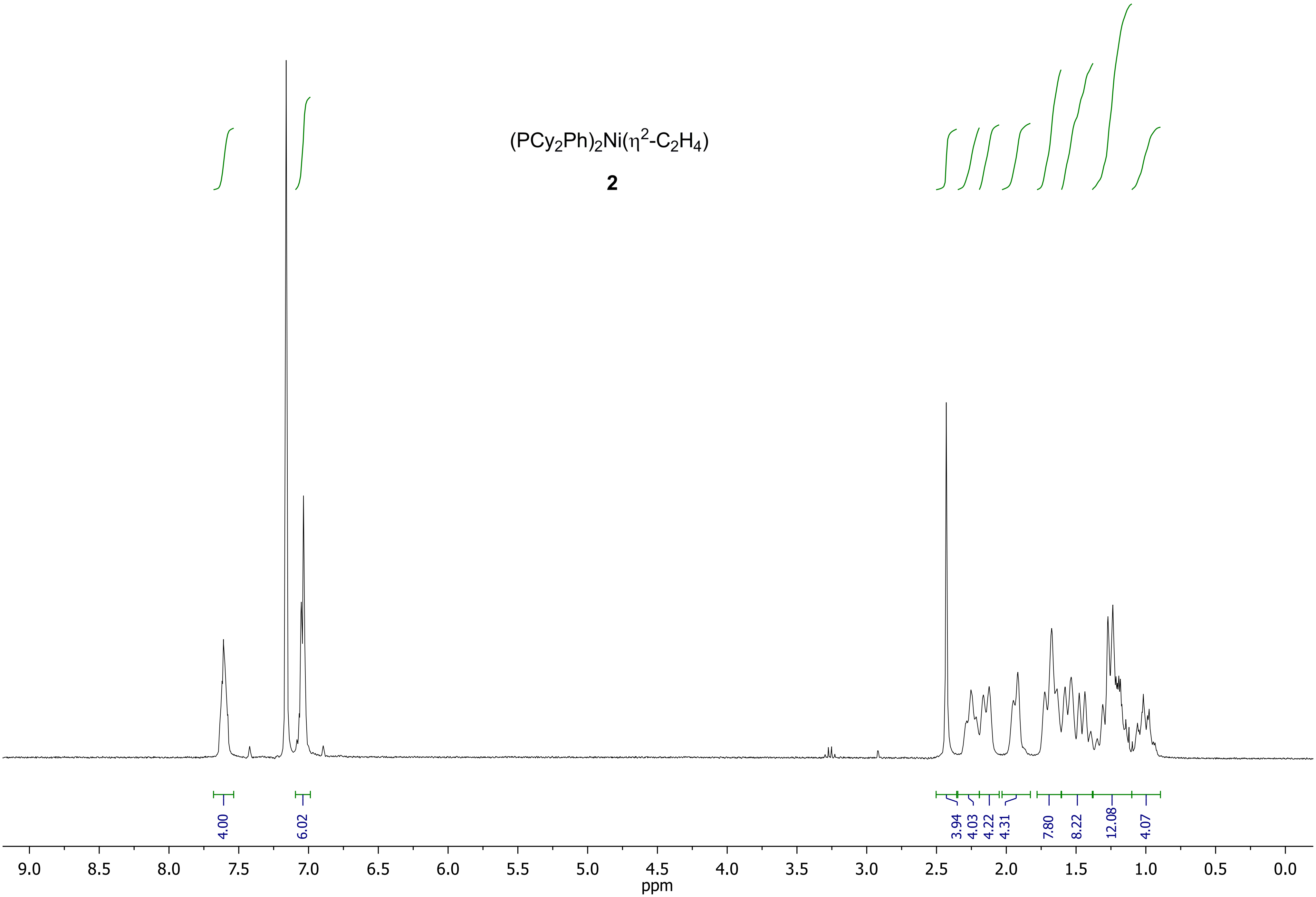
^{31}P (202 MHz, CD_2Cl_2) - Complex 1



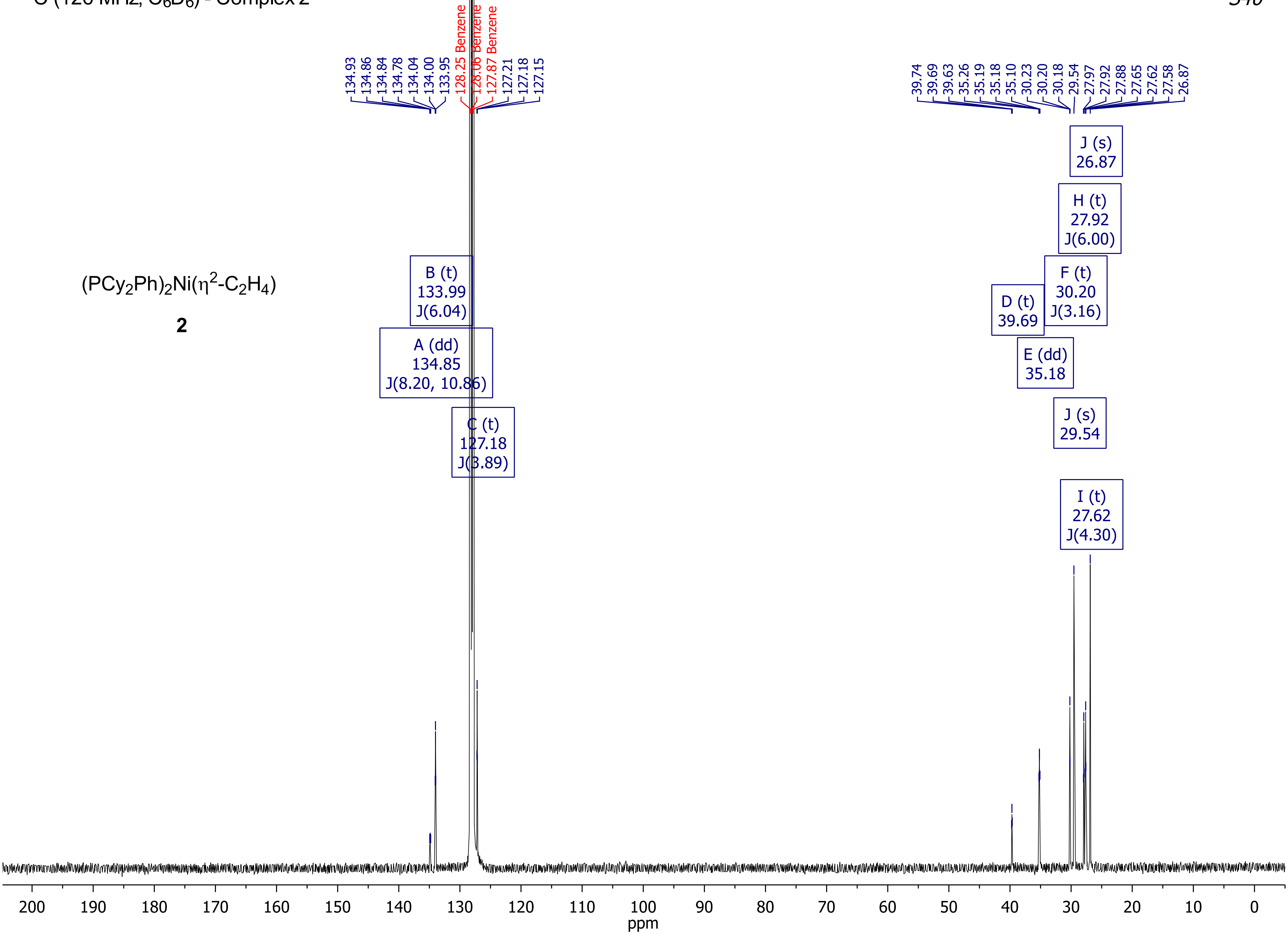
^{1}H (300 MHz, C_6D_6) - Complex 2

$(PCy_2Ph)_2Ni(\eta^2\text{-}C_2H_4)$

2



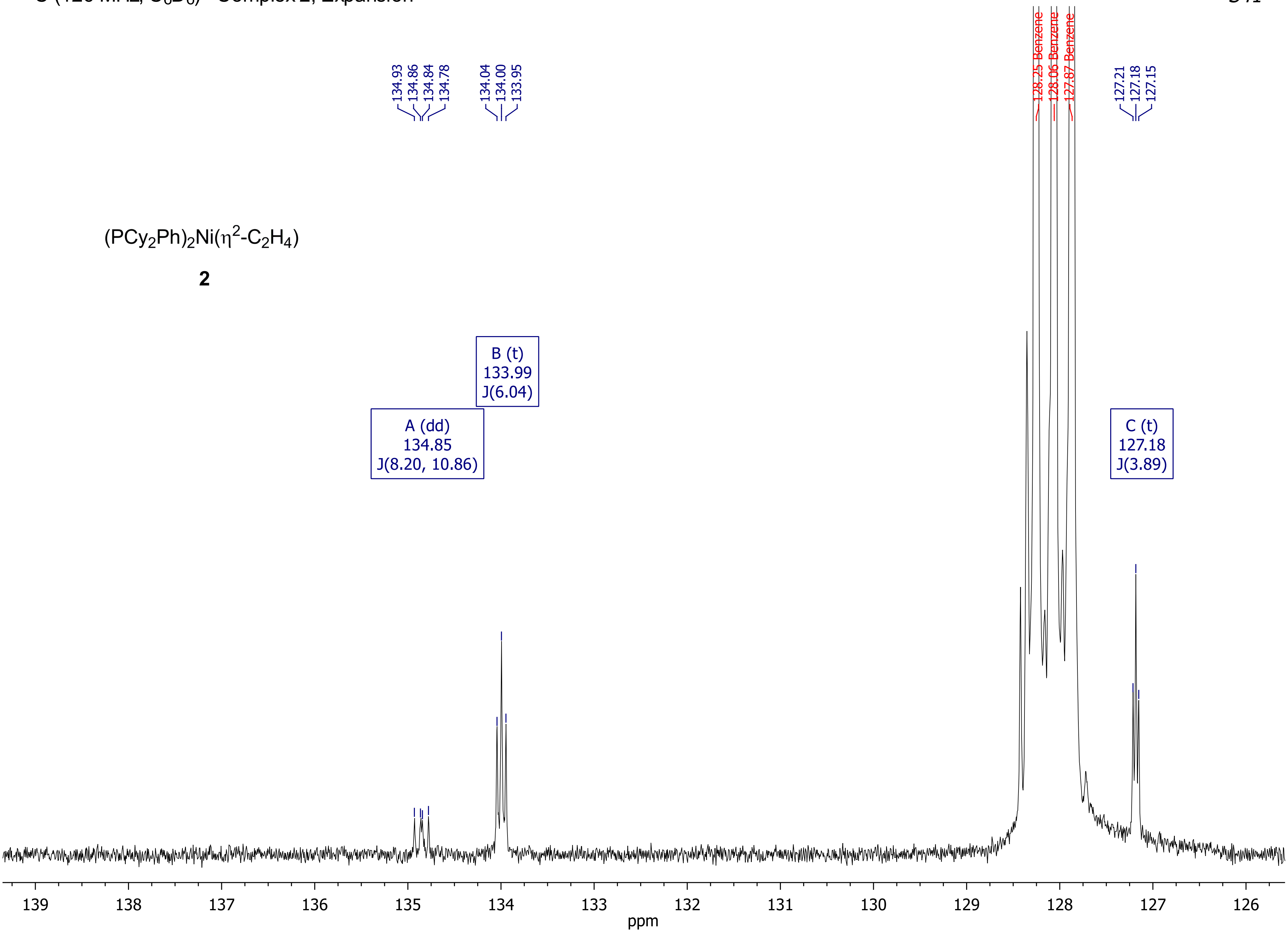
^{13}C (126 MHz, C_6D_6) - Complex 2



$(PCy_2Ph)_2Ni(\eta^2\text{-}C_2H_4)$

2

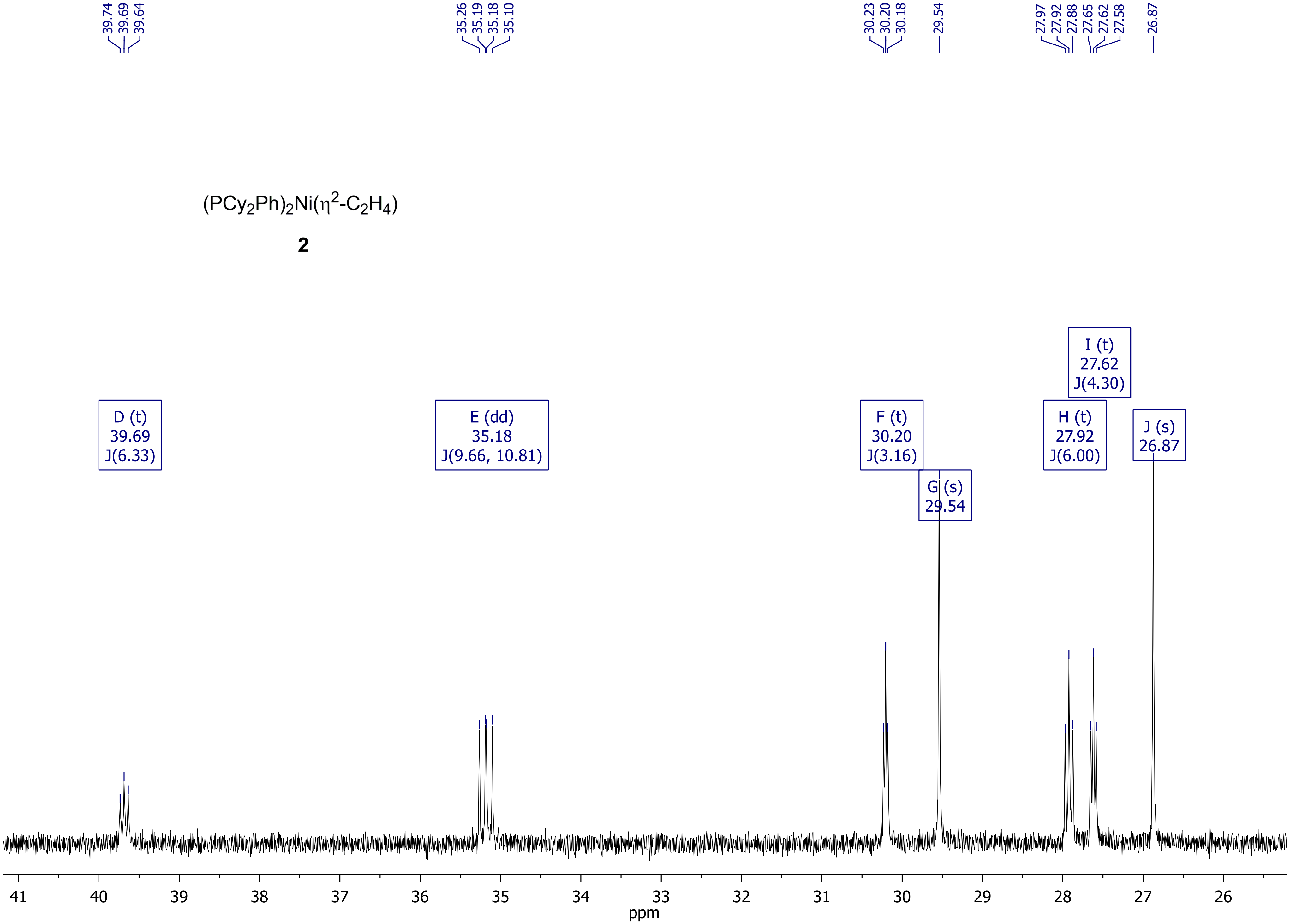
^{13}C (126 MHz, C_6D_6) - Complex 2, Expansion



$(PCy_2Ph)_2Ni(\eta^2\text{-}C_2H_4)$

2

^{13}C (126 MHz, C_6D_6) - Complex 2, Expansion



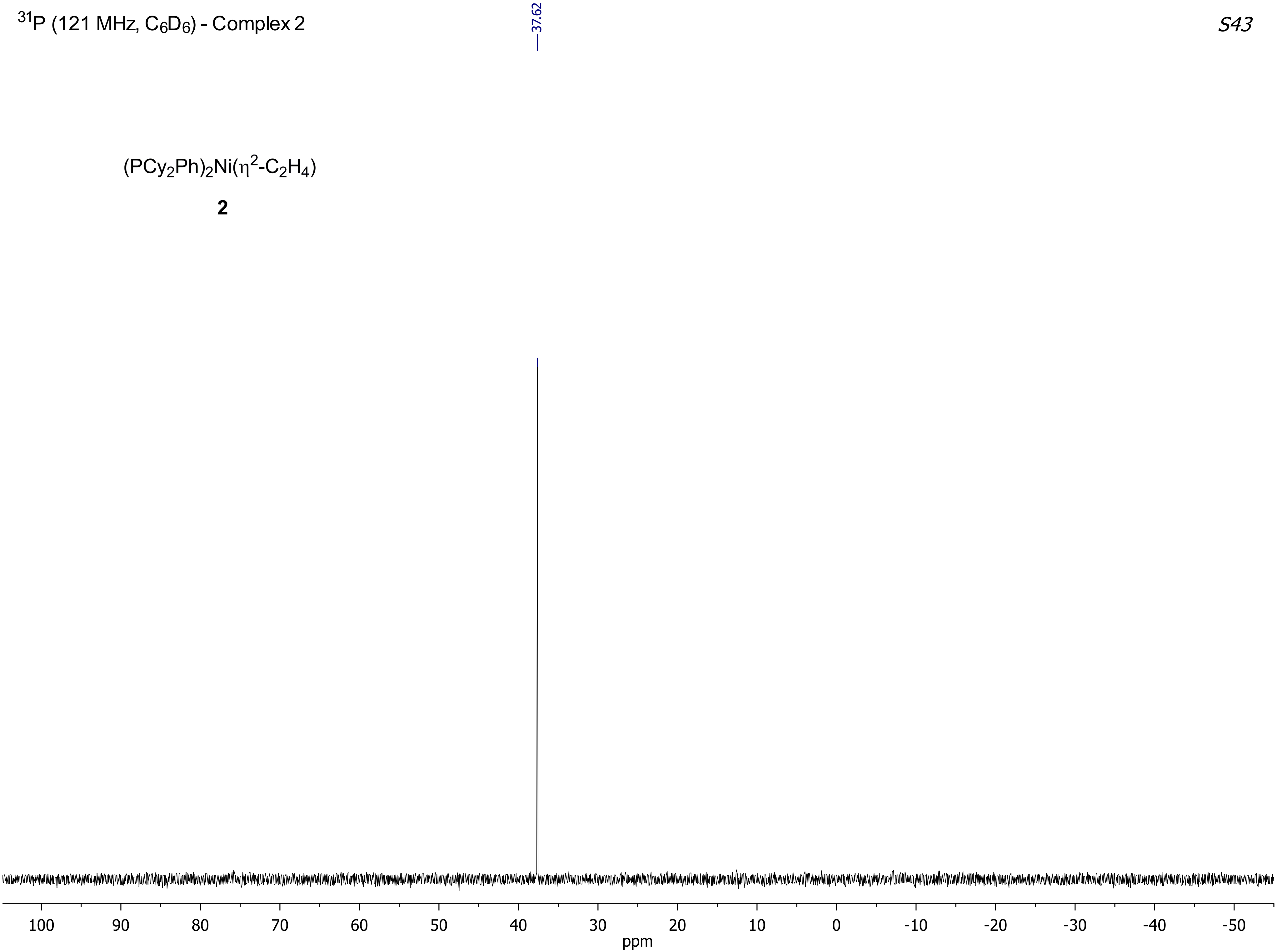
$(PCy_2Ph)_2Ni(\eta^2\text{-}C_2H_4)$

2

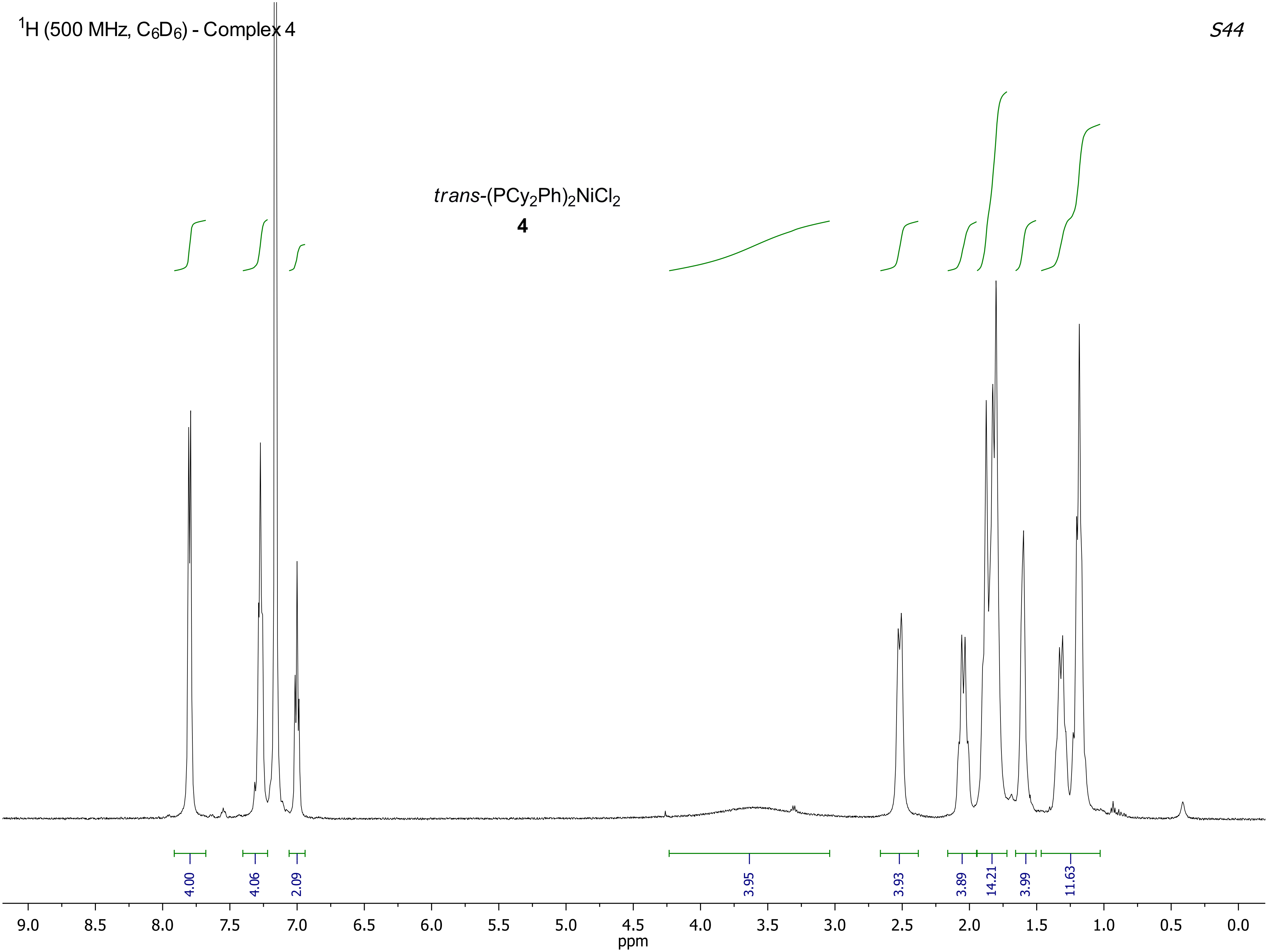
^{31}P (121 MHz, C_6D_6) - Complex 2

$(PCy_2Ph)_2Ni(\eta^2-C_2H_4)$

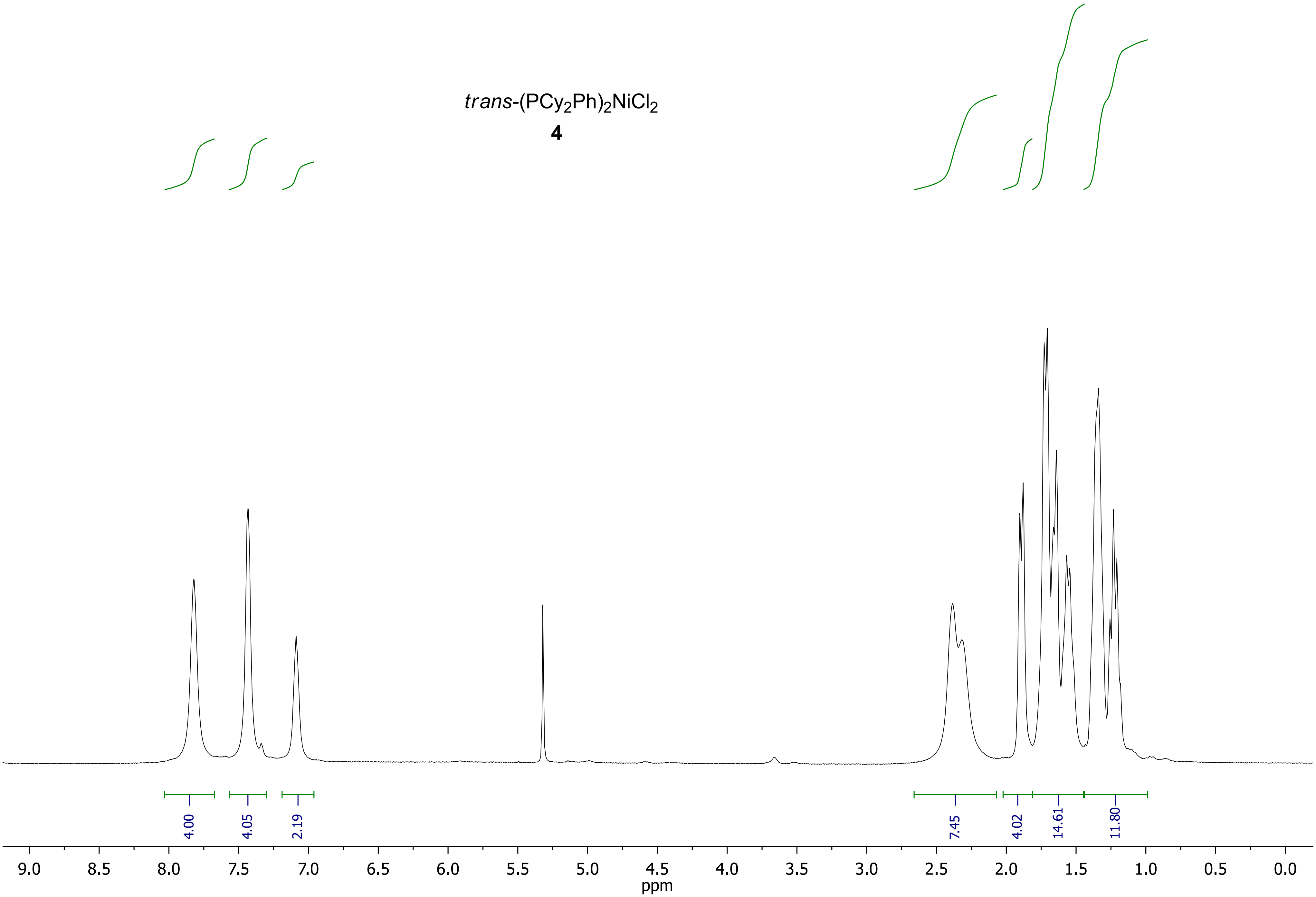
2



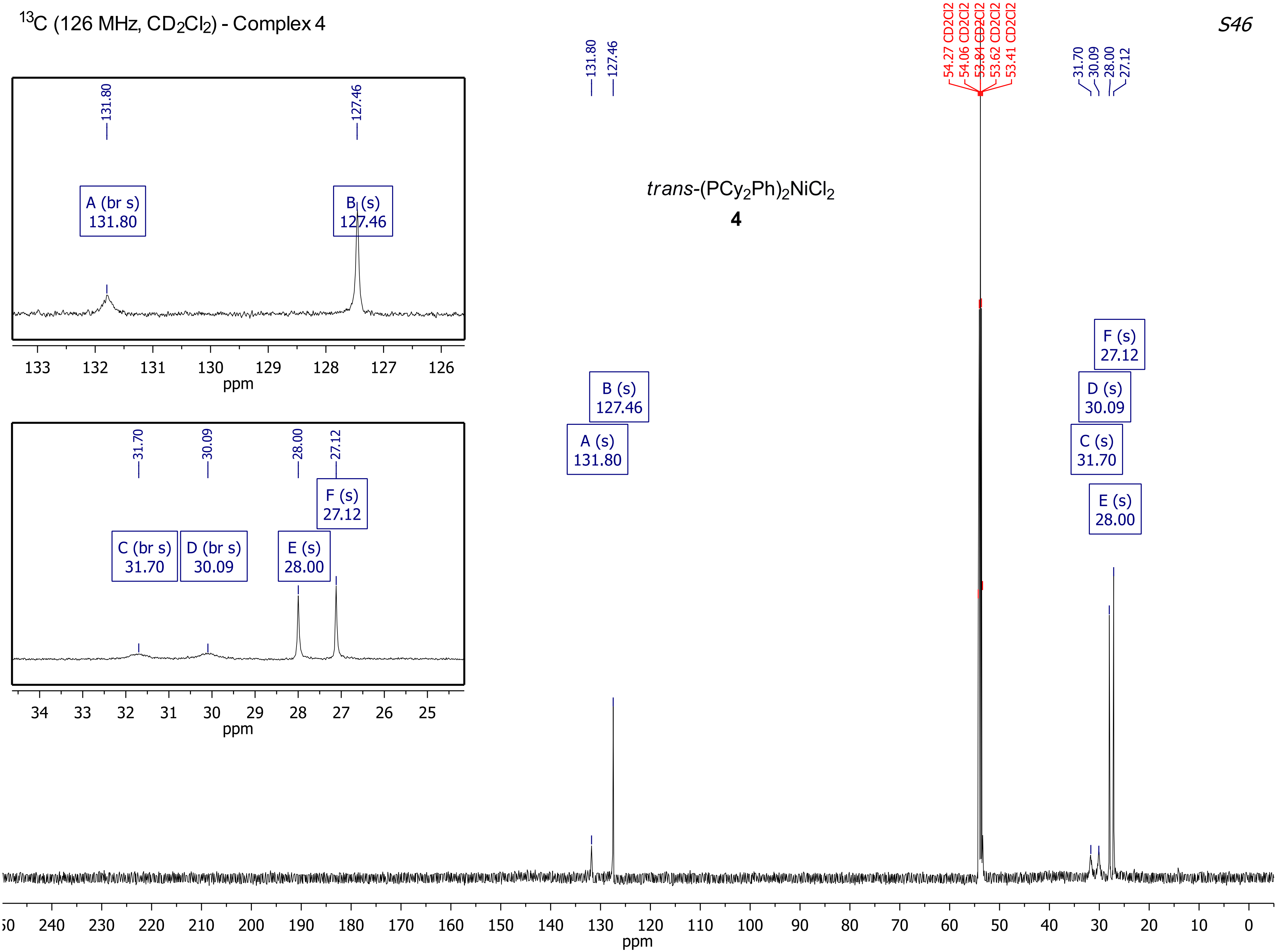
^{1}H (500 MHz, C_6D_6) - Complex 4



^1H (500 MHz, CD_2Cl_2) - Complex 4



^{13}C (126 MHz, CD$_2$Cl$_2$) - Complex 4



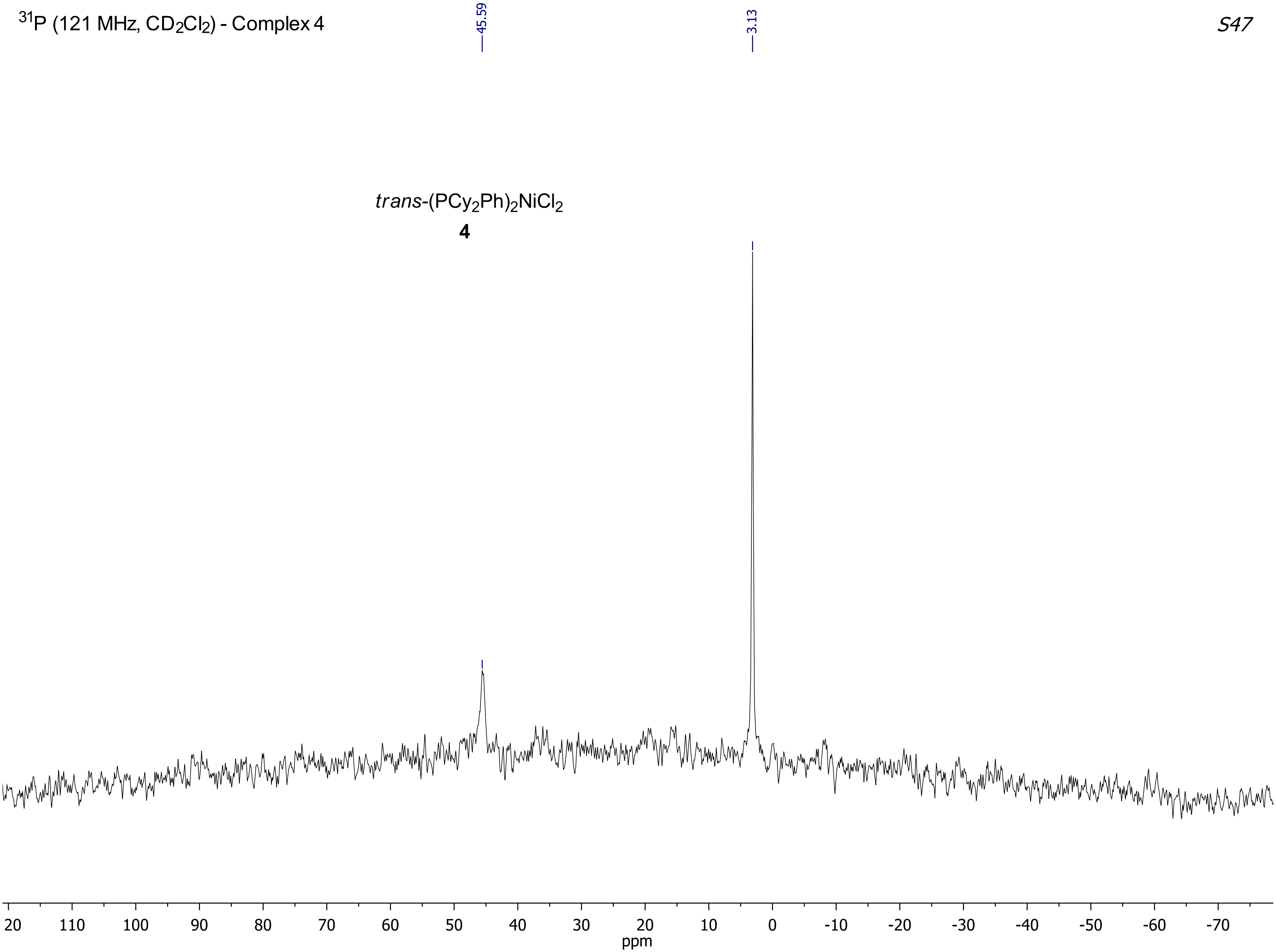
trans-(PCy$_2$Ph)$_2$NiCl$_2$

4

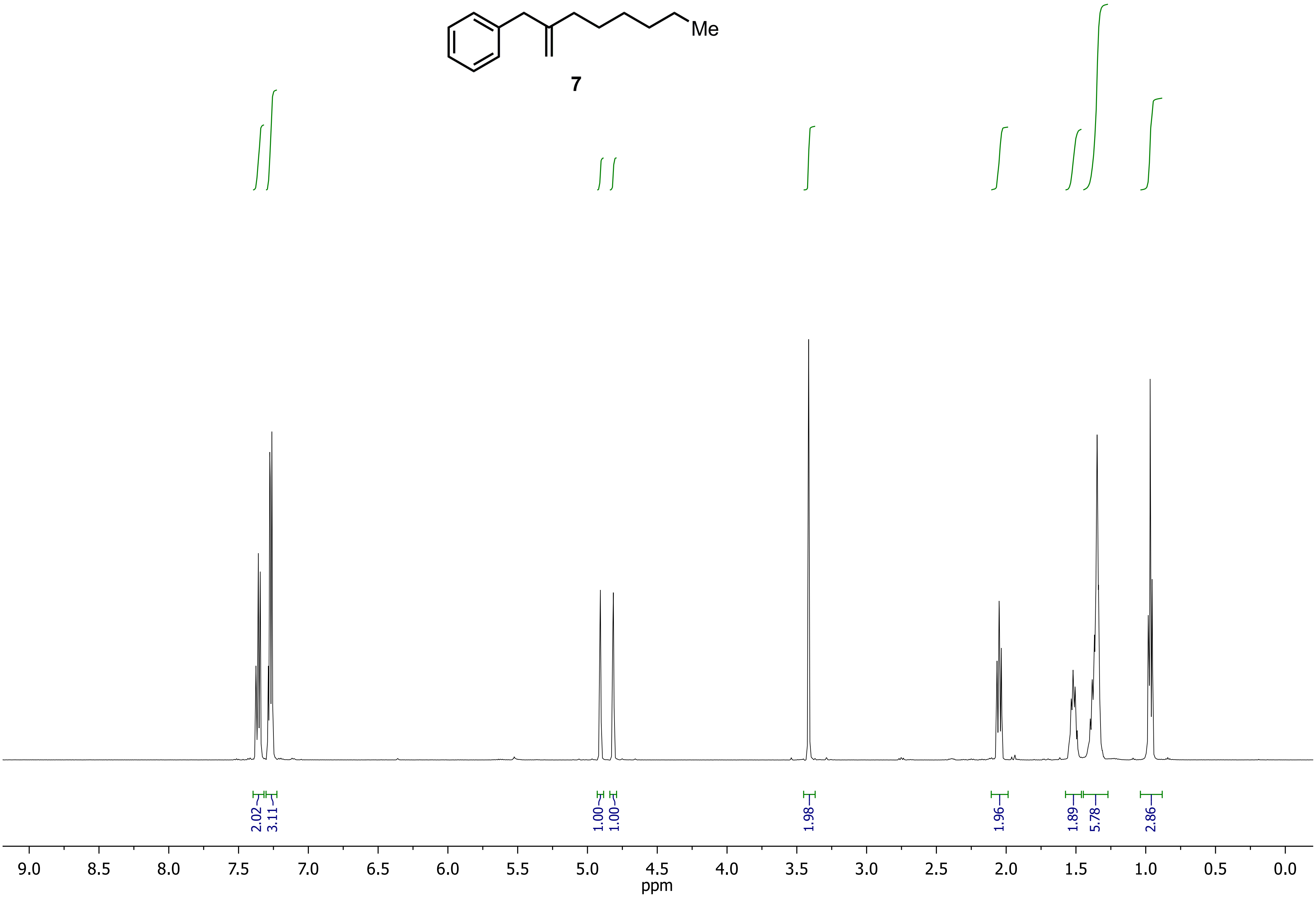
^{31}P (121 MHz, CD_2Cl_2) - Complex 4

trans-$(PCy_2Ph)_2NiCl_2$

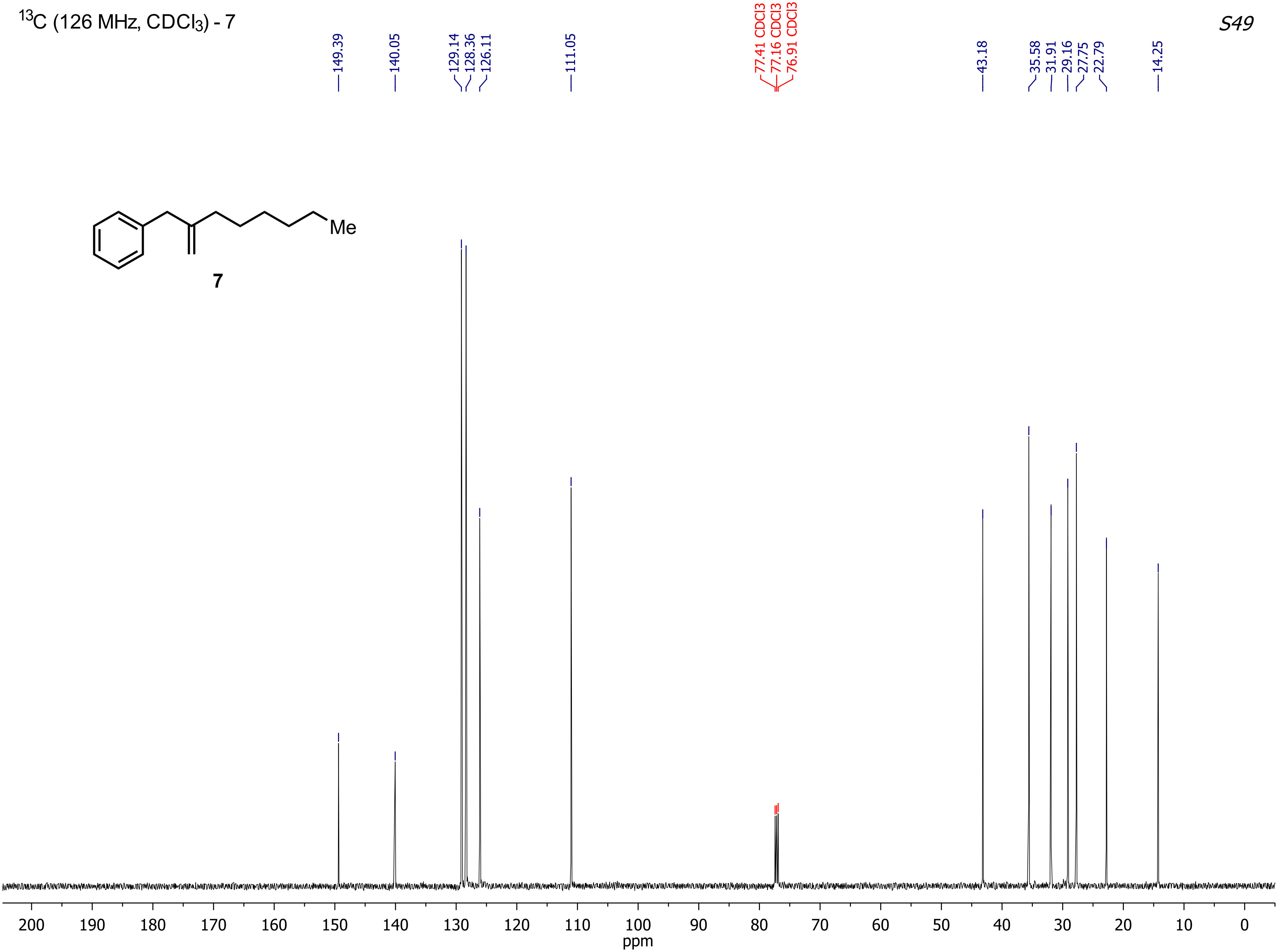
4



^{1}H (500 MHz, CDCl$_3$) - 7



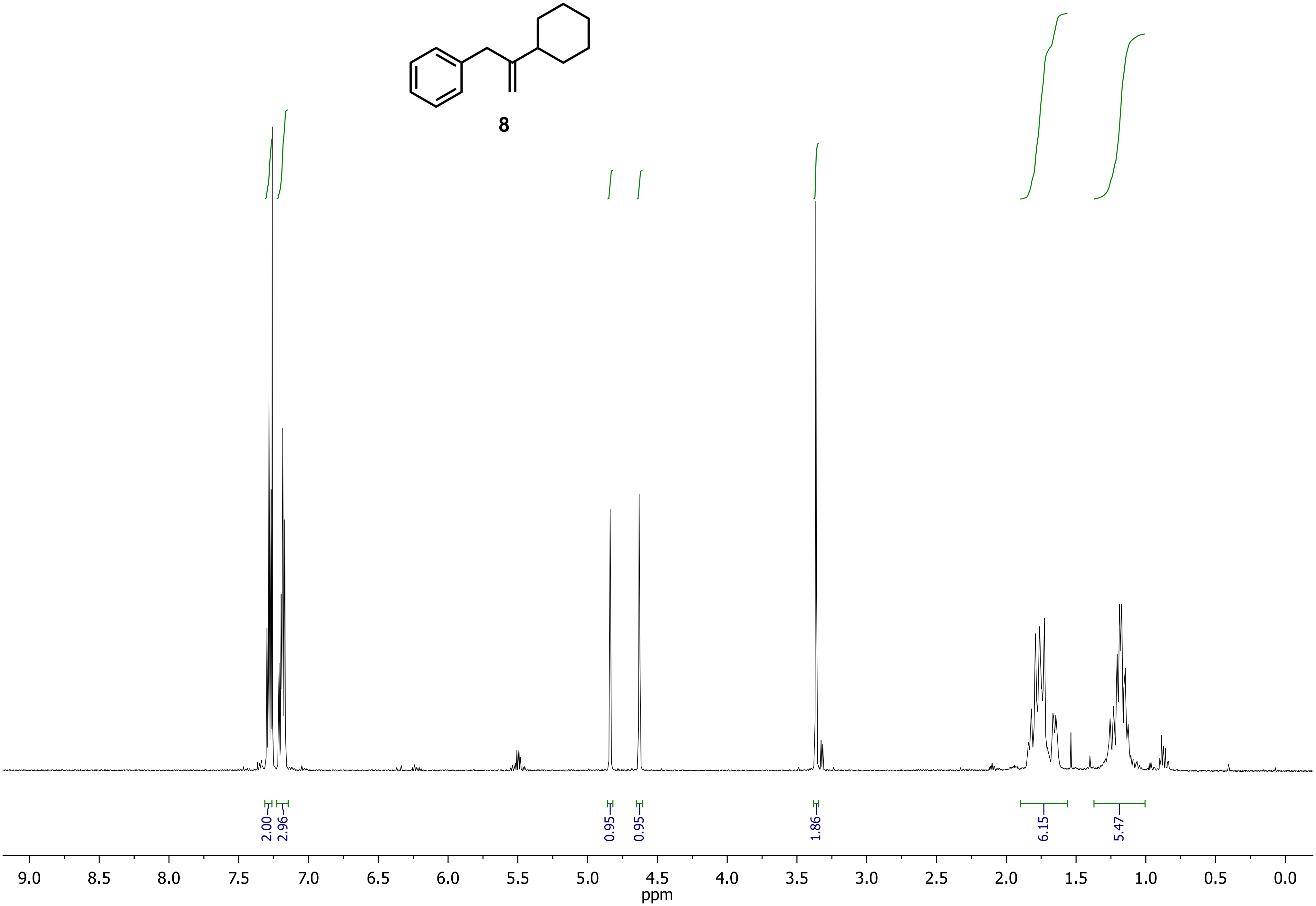
^{13}C (126 MHz, $CDCl_3$) - 7



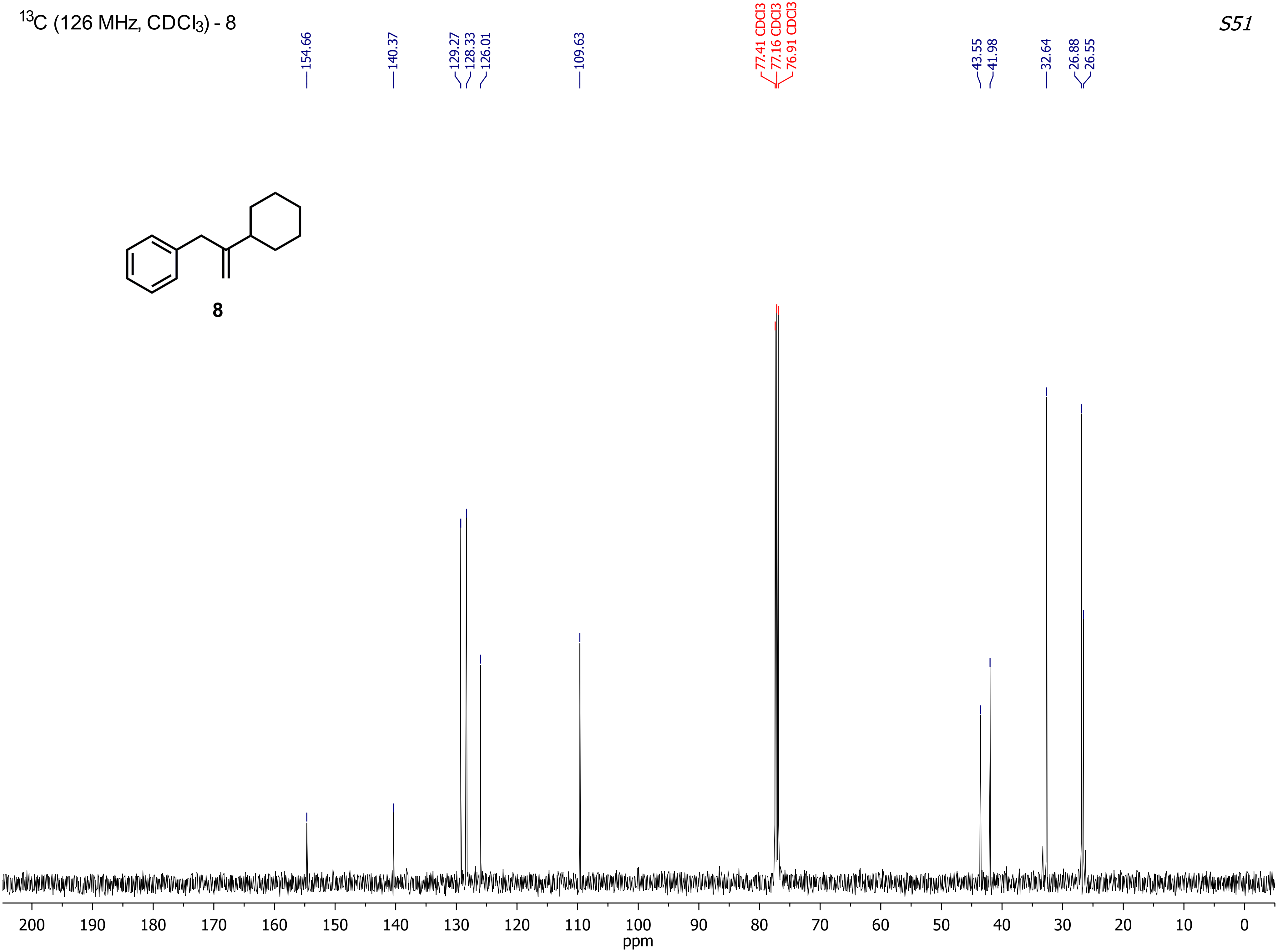
7

^{1}H (500 MHz, $CDCl_3$) - 8

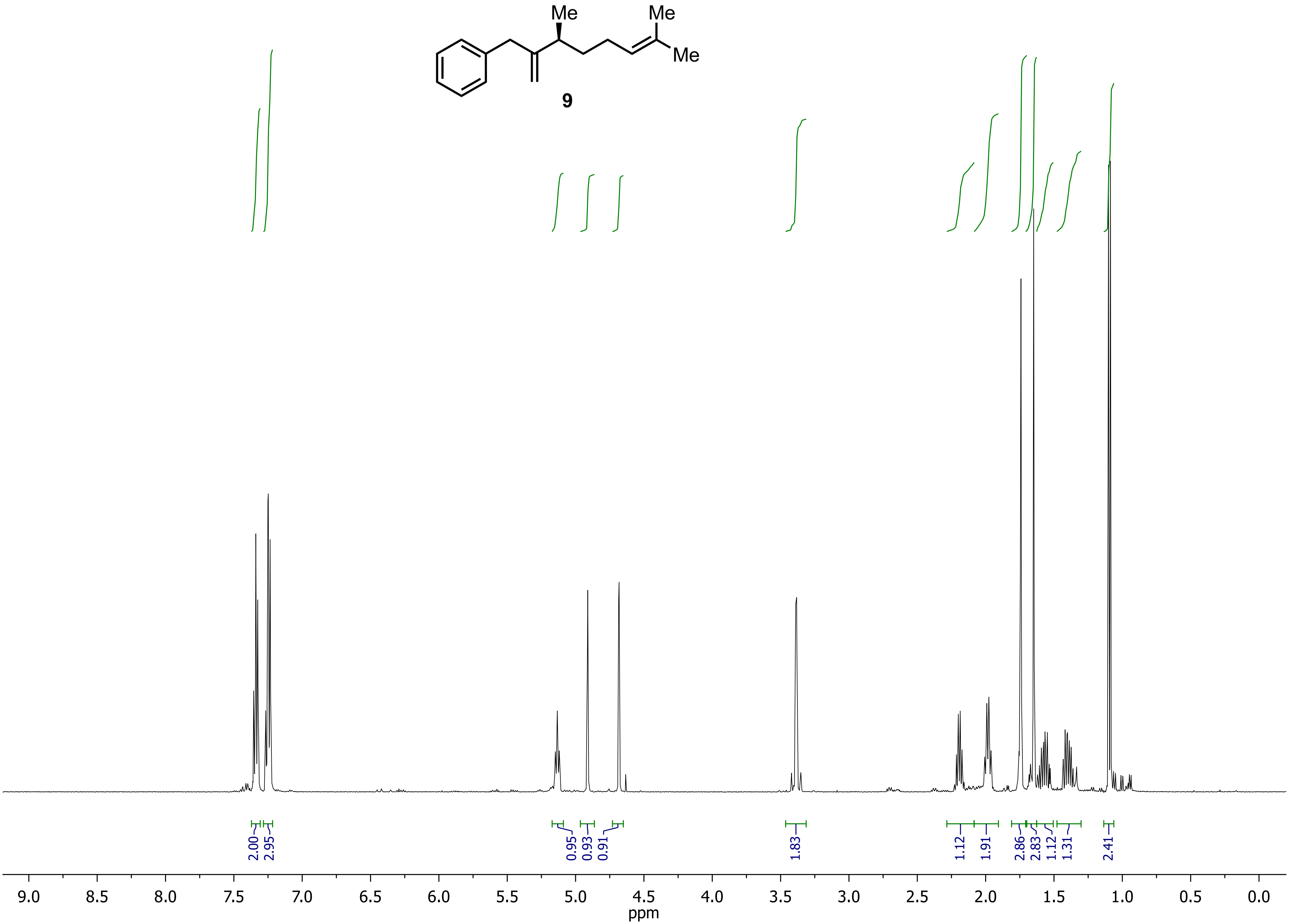
8



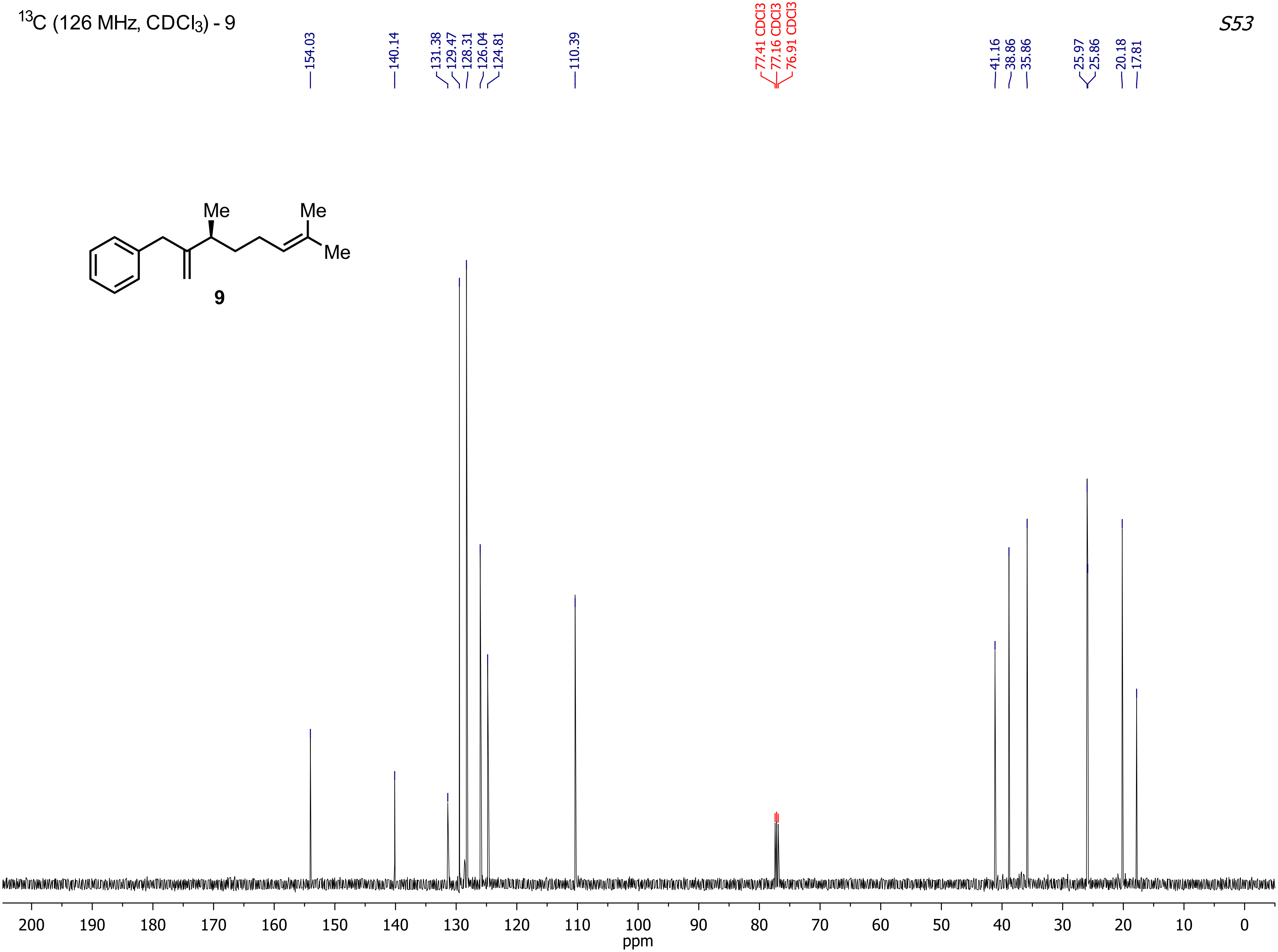
^{13}C (126 MHz, $CDCl_3$) - 8



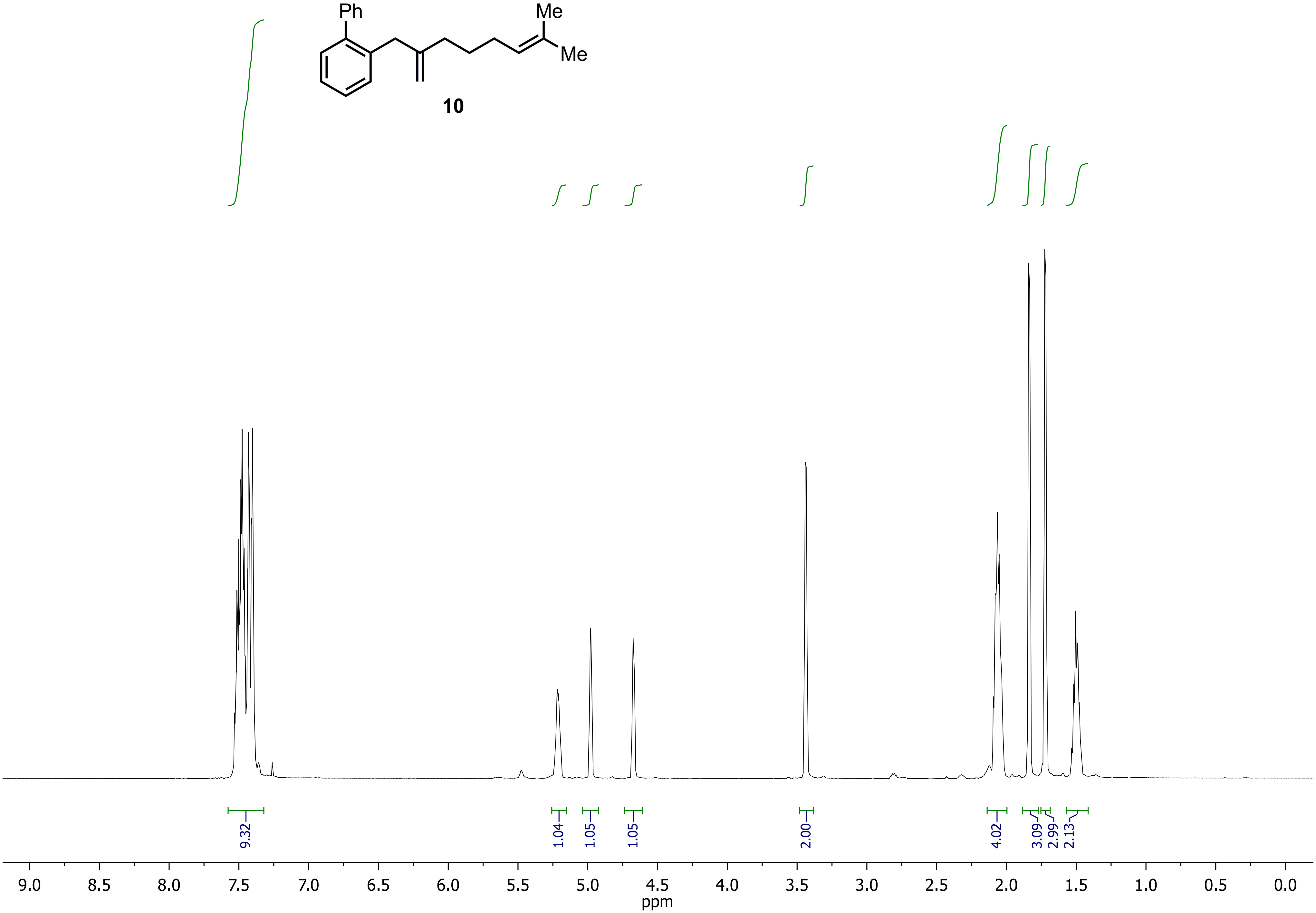
^{1}H (500 MHz, CDCl$_3$) - 9



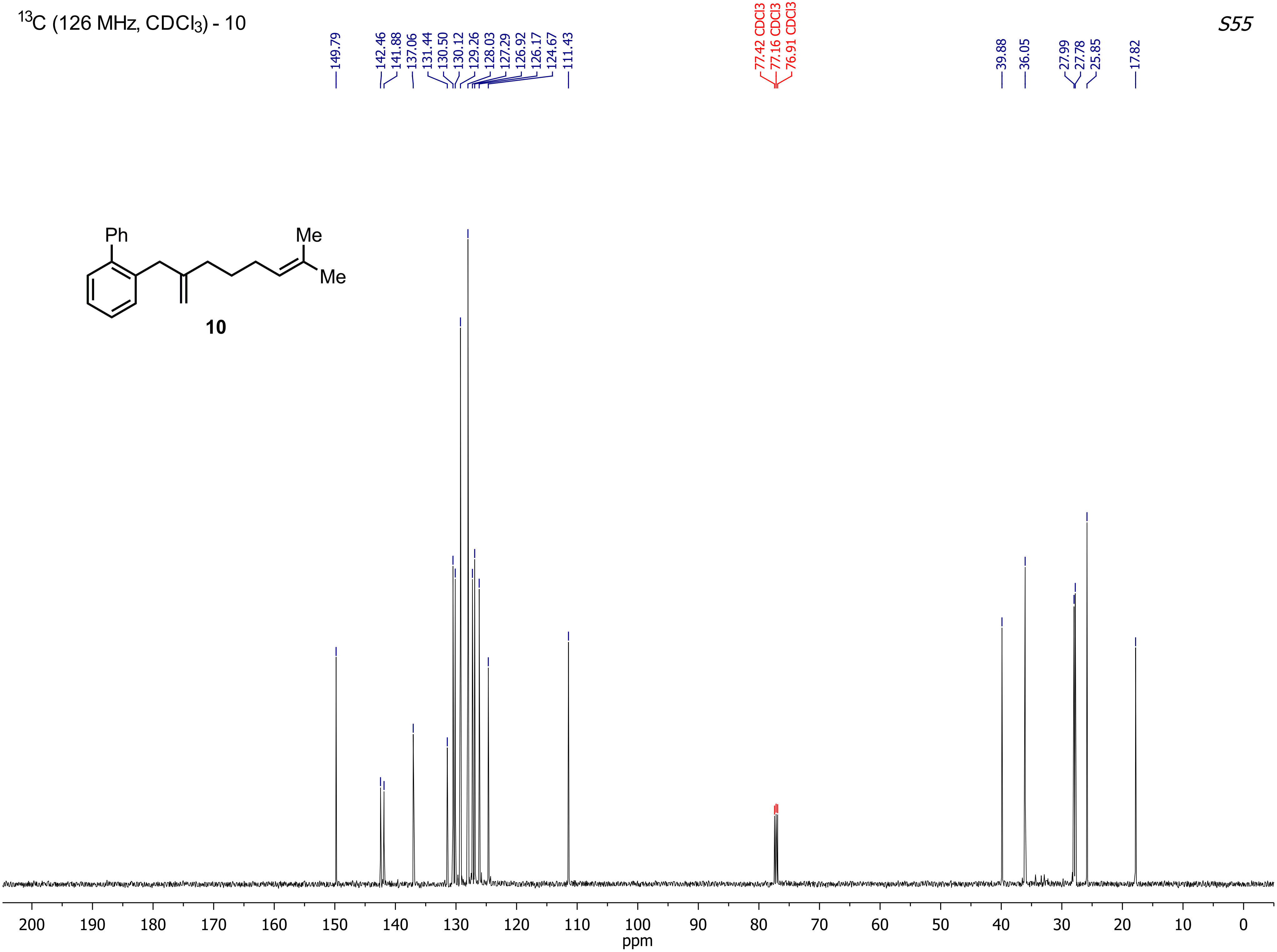
^{13}C (126 MHz, $CDCl_3$) - 9



^{1}H (500 MHz, $CDCl_3$) - 10



^{13}C (126 MHz, CDCl$_3$) - 10



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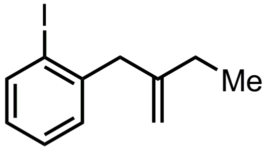
^{1}H (500 MHz, CDCl$_3$) - 11



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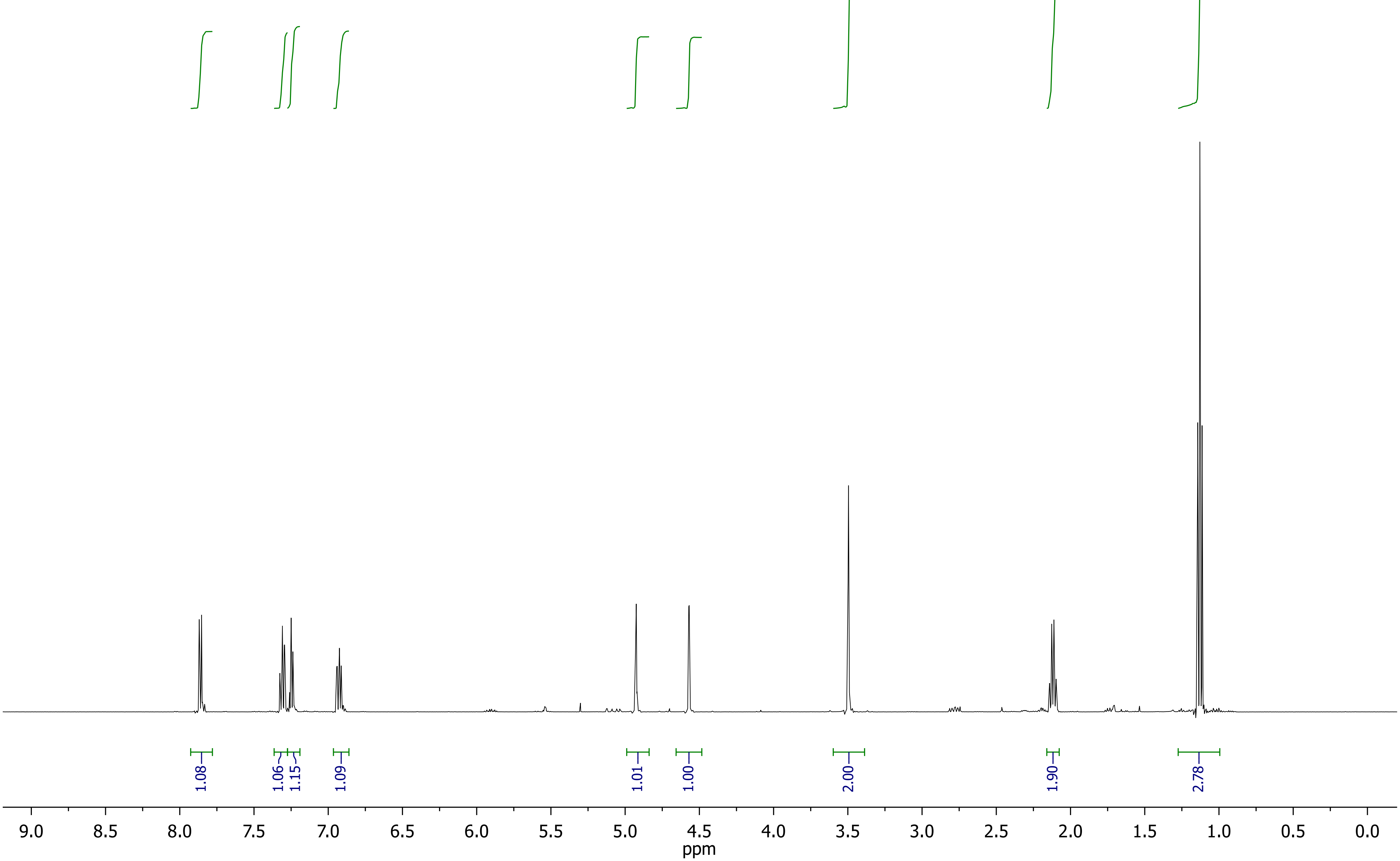
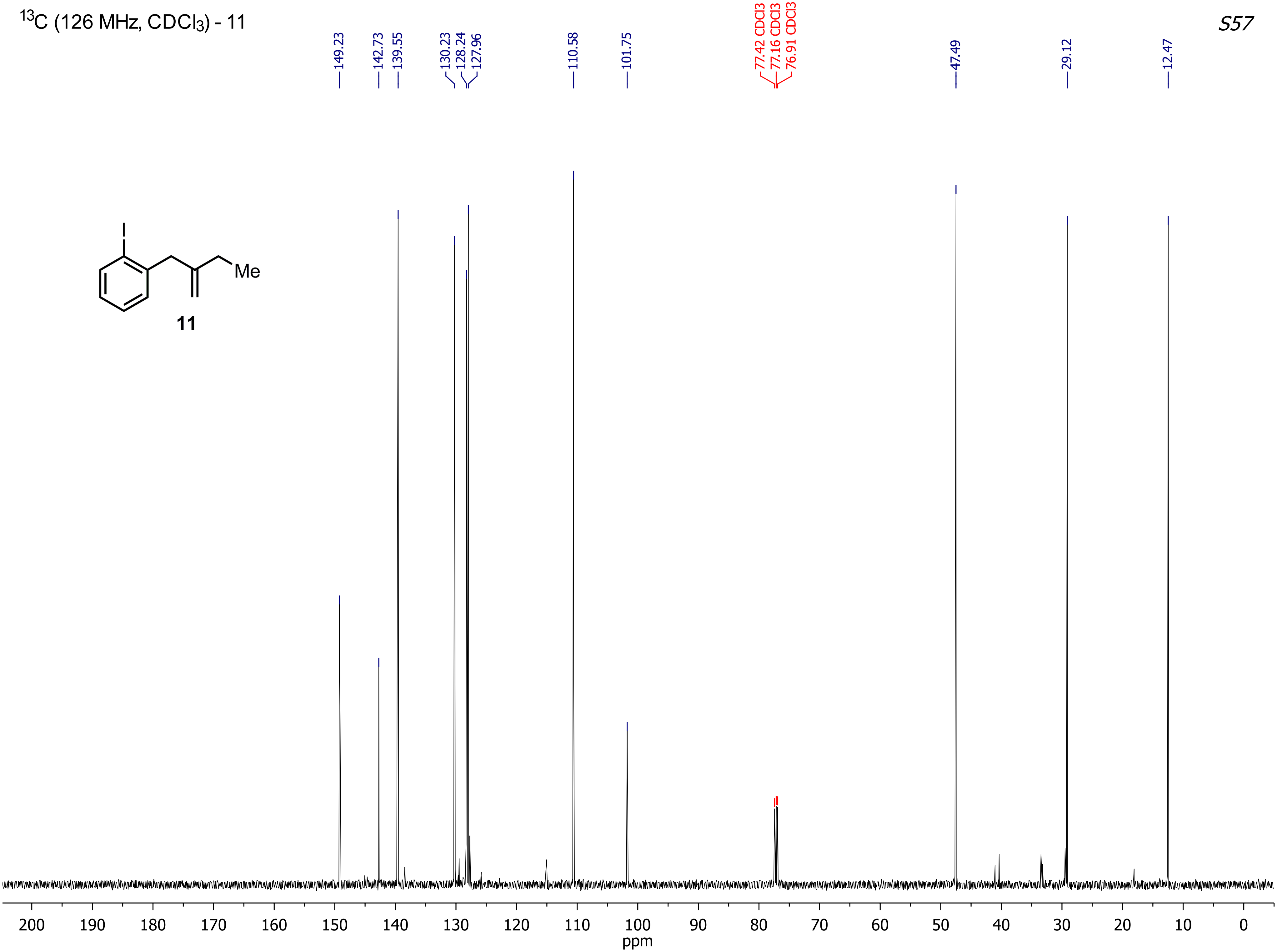
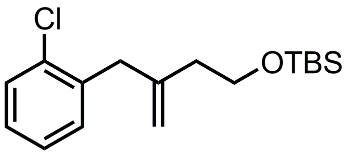


^{13}C (126 MHz, CDCl$_3$) - 11



^{1}H (500 MHz, $CDCl_3$) - 12



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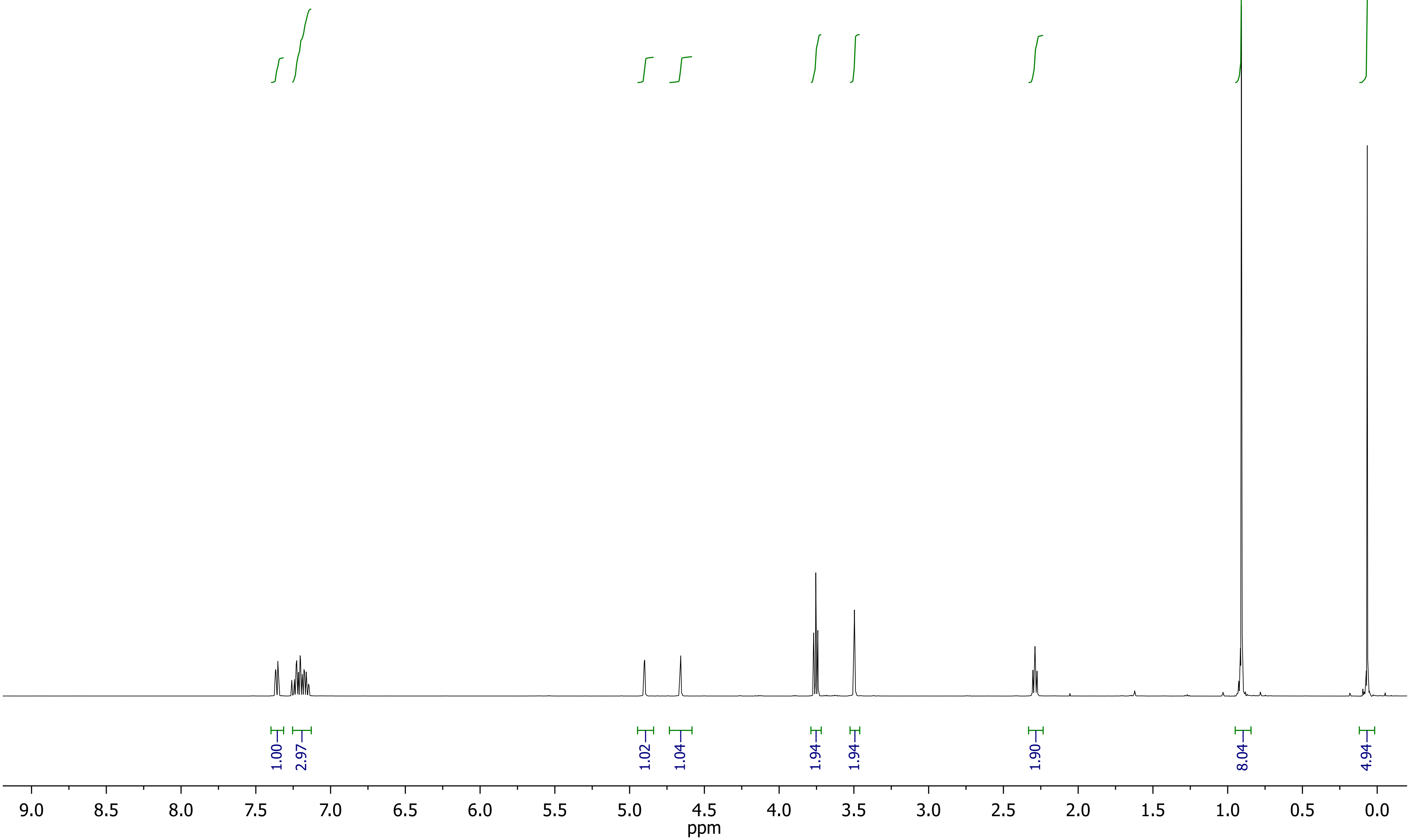
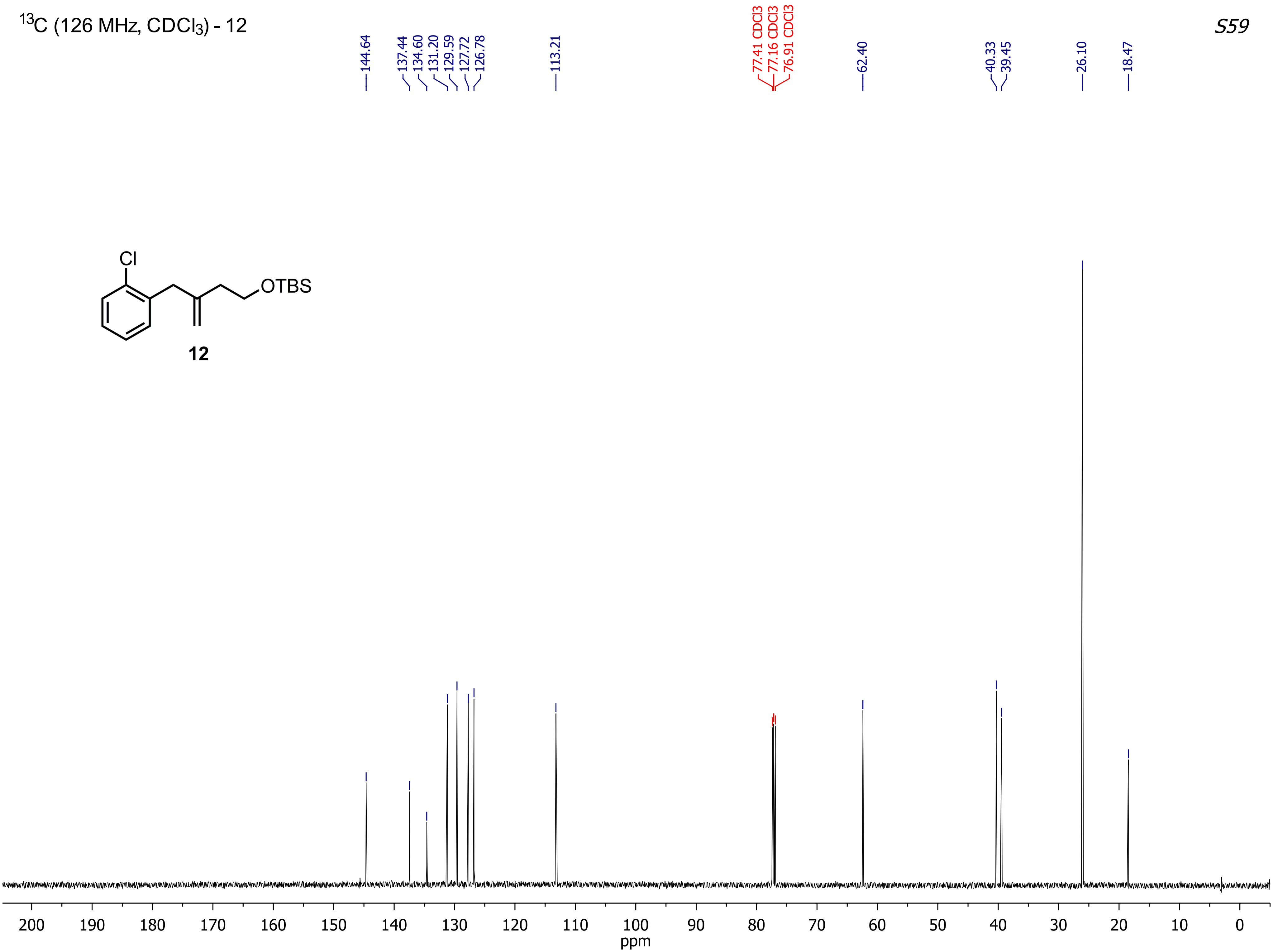
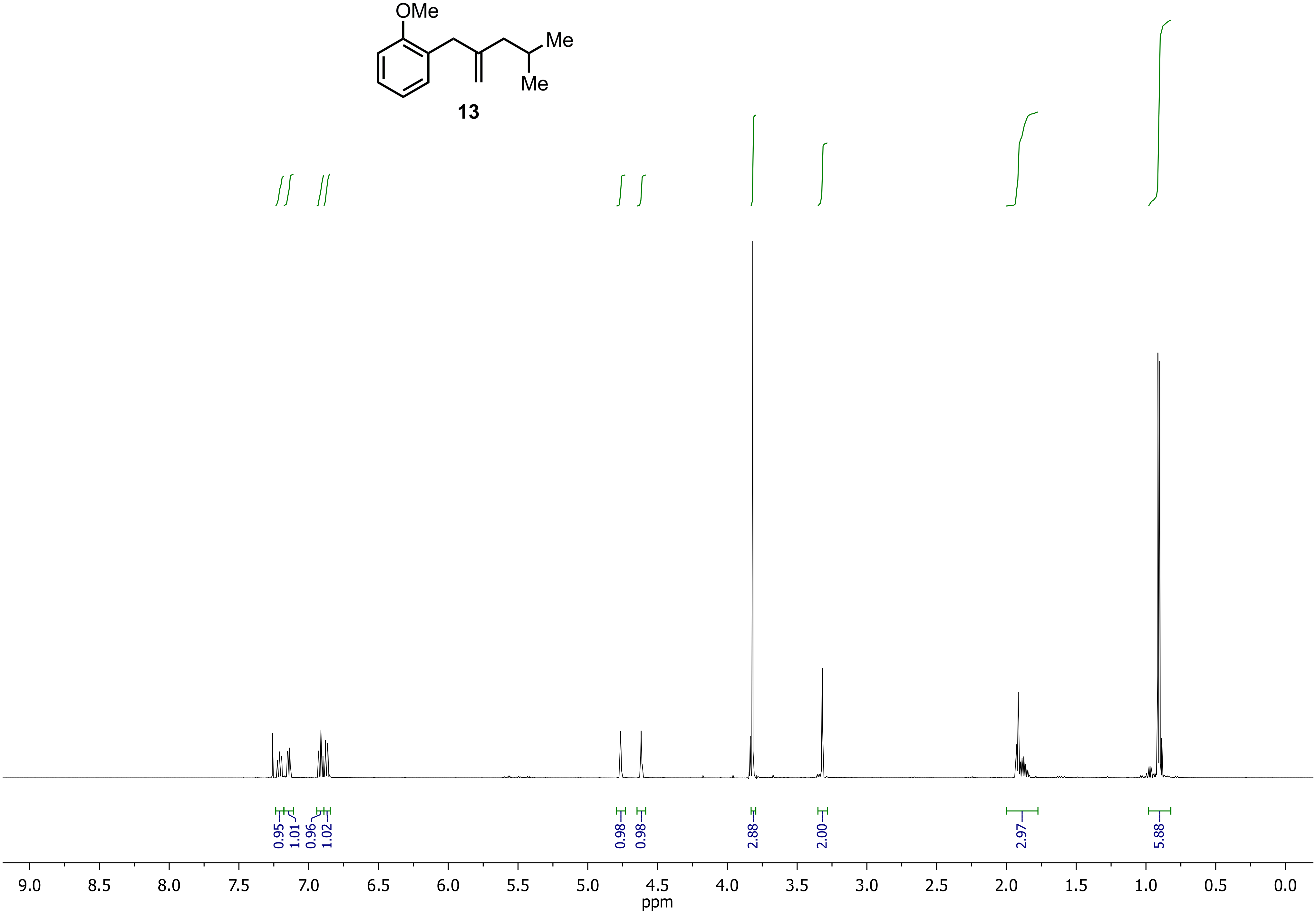


^{13}C (126 MHz, $CDCl_3$) - 12



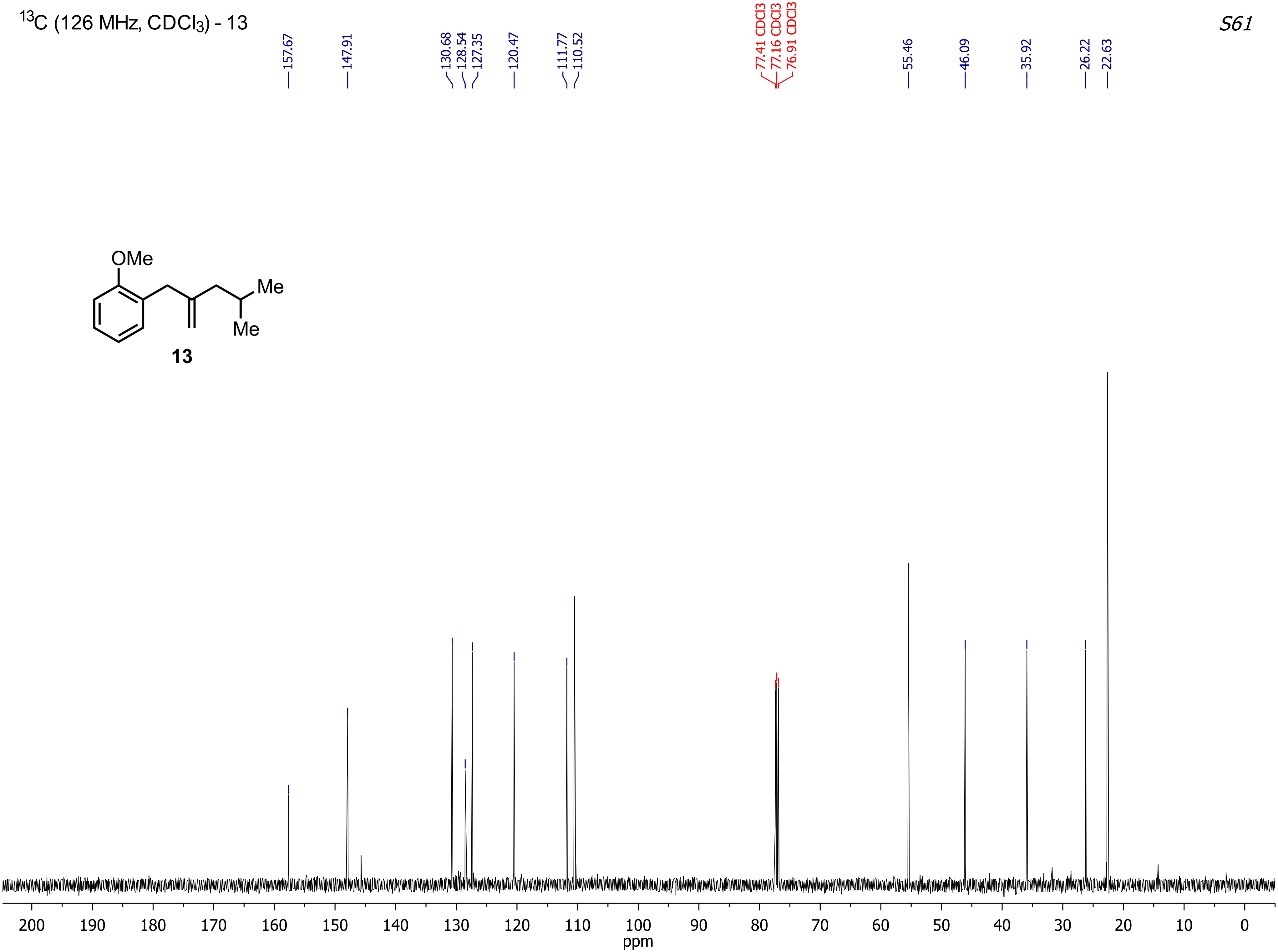
^{1}H (500 MHz, $CDCl_3$) - 13



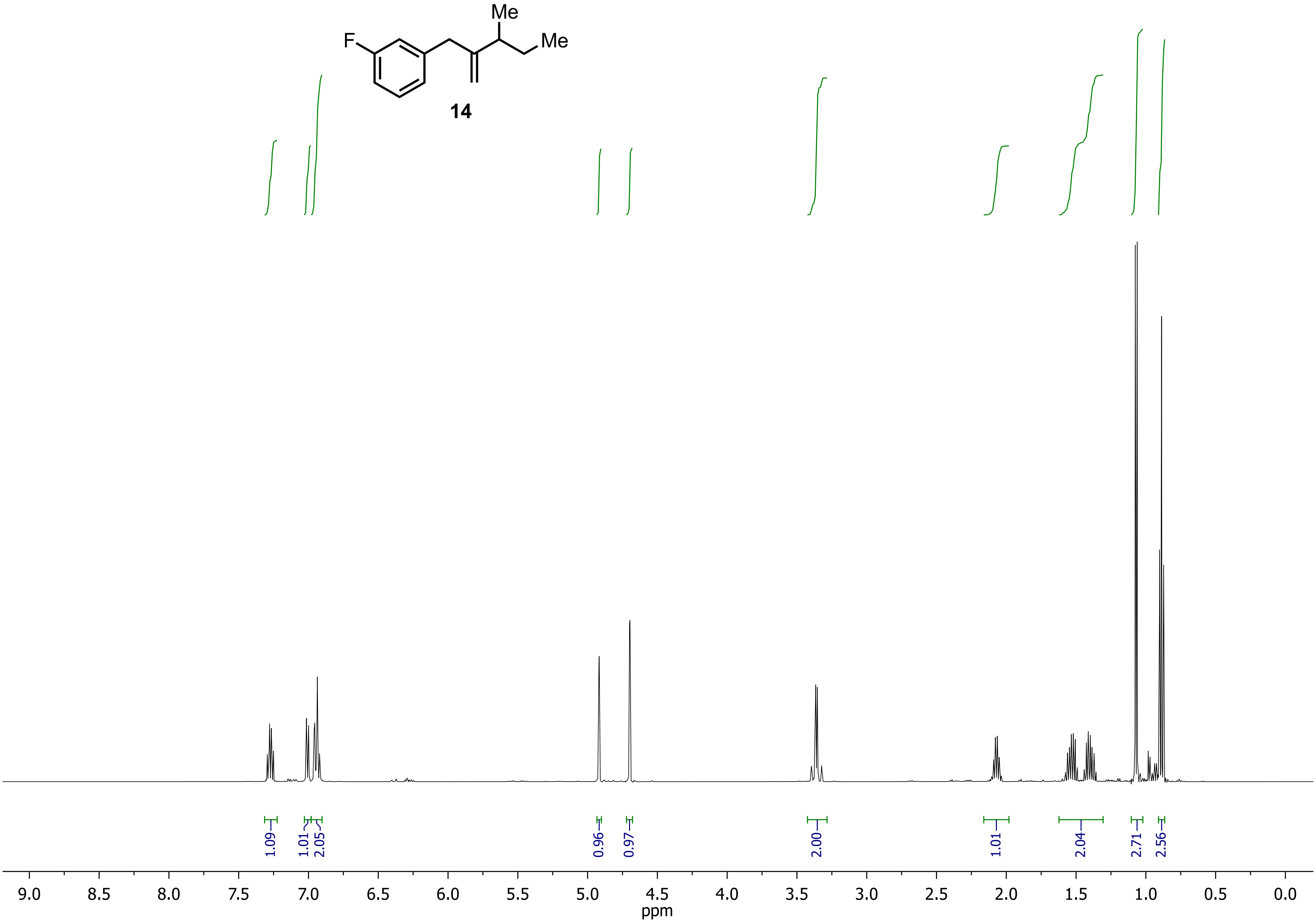
13

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

13



^{1}H (500 MHz, CDCl$_3$) - 14



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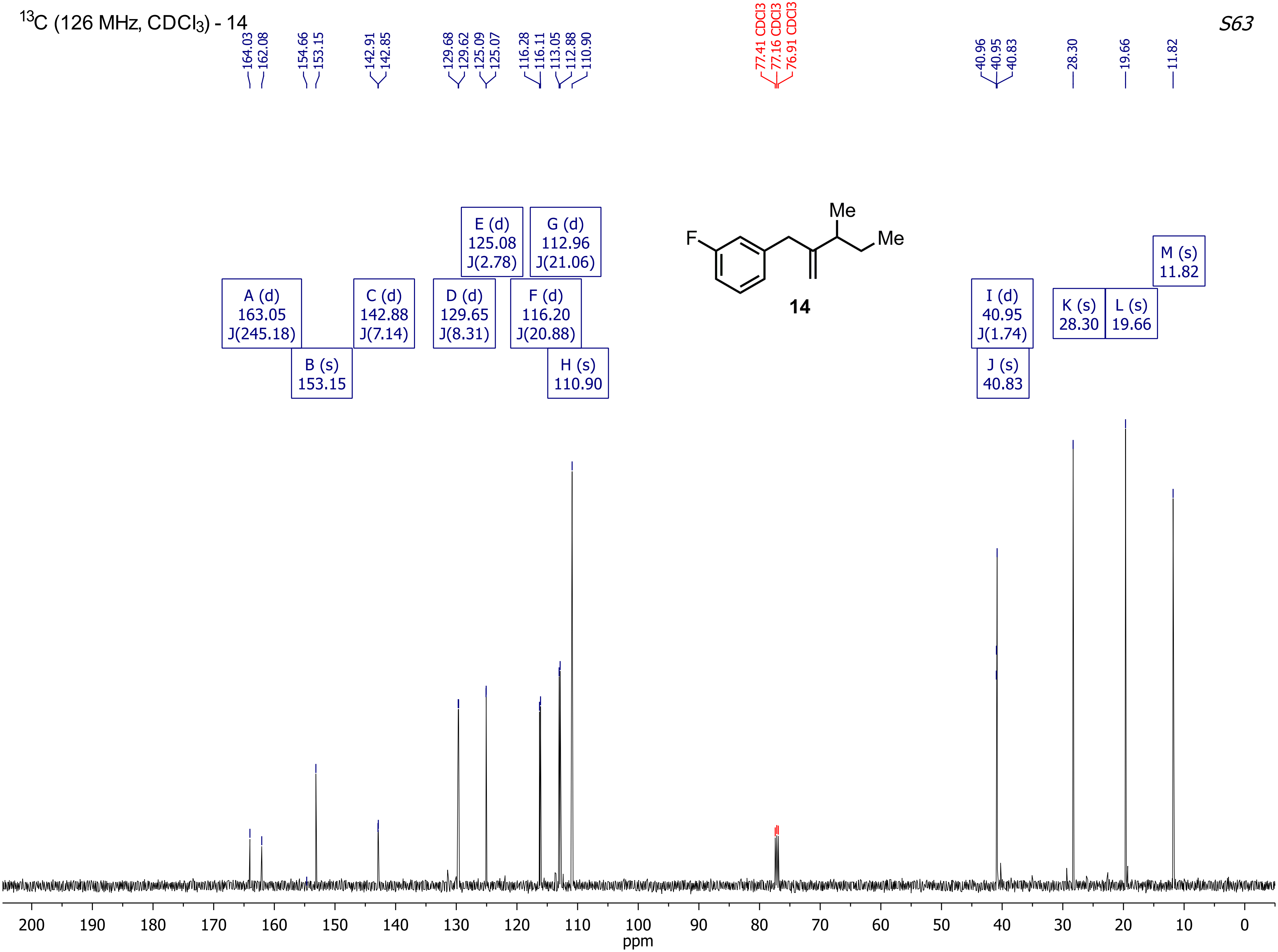
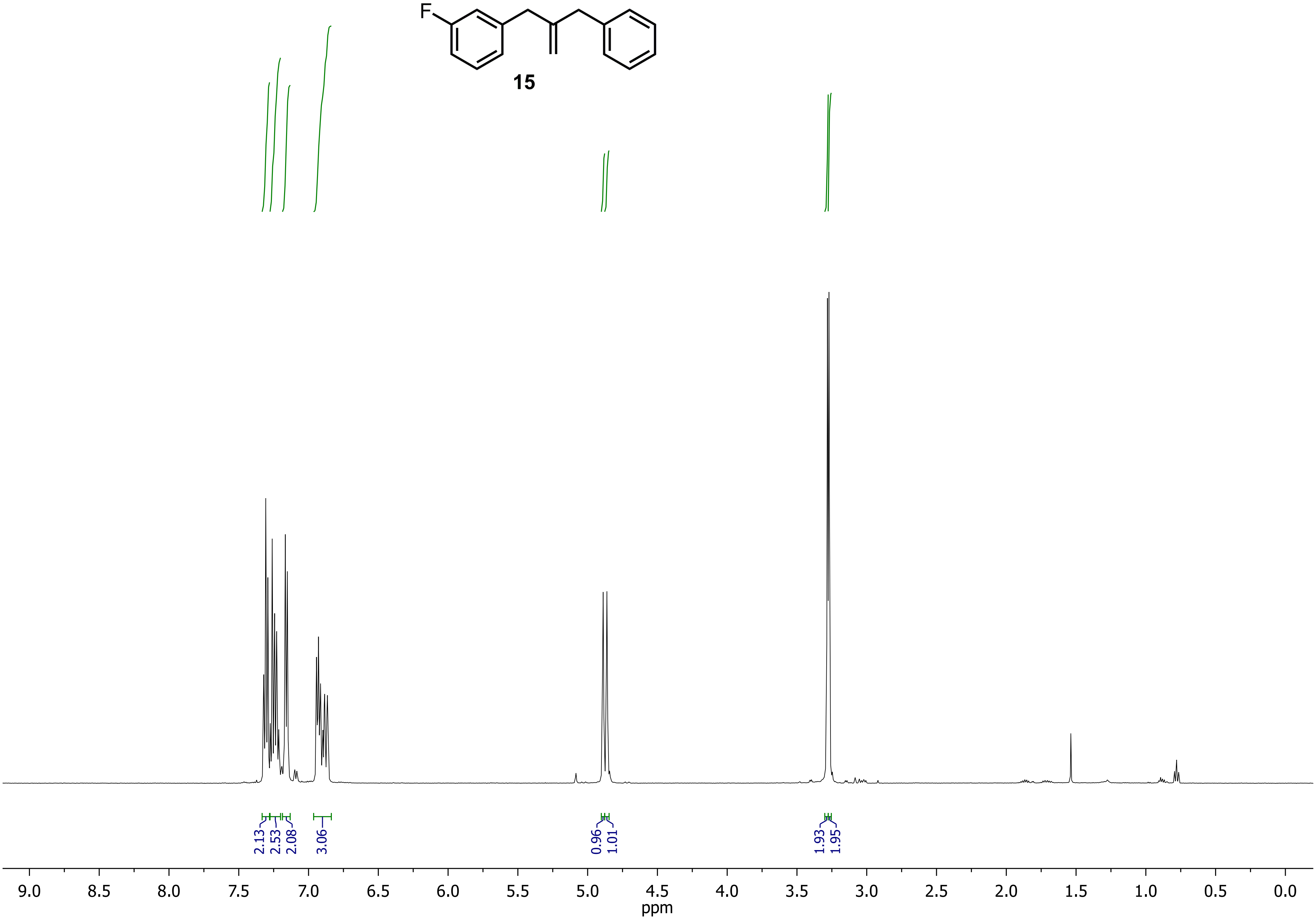
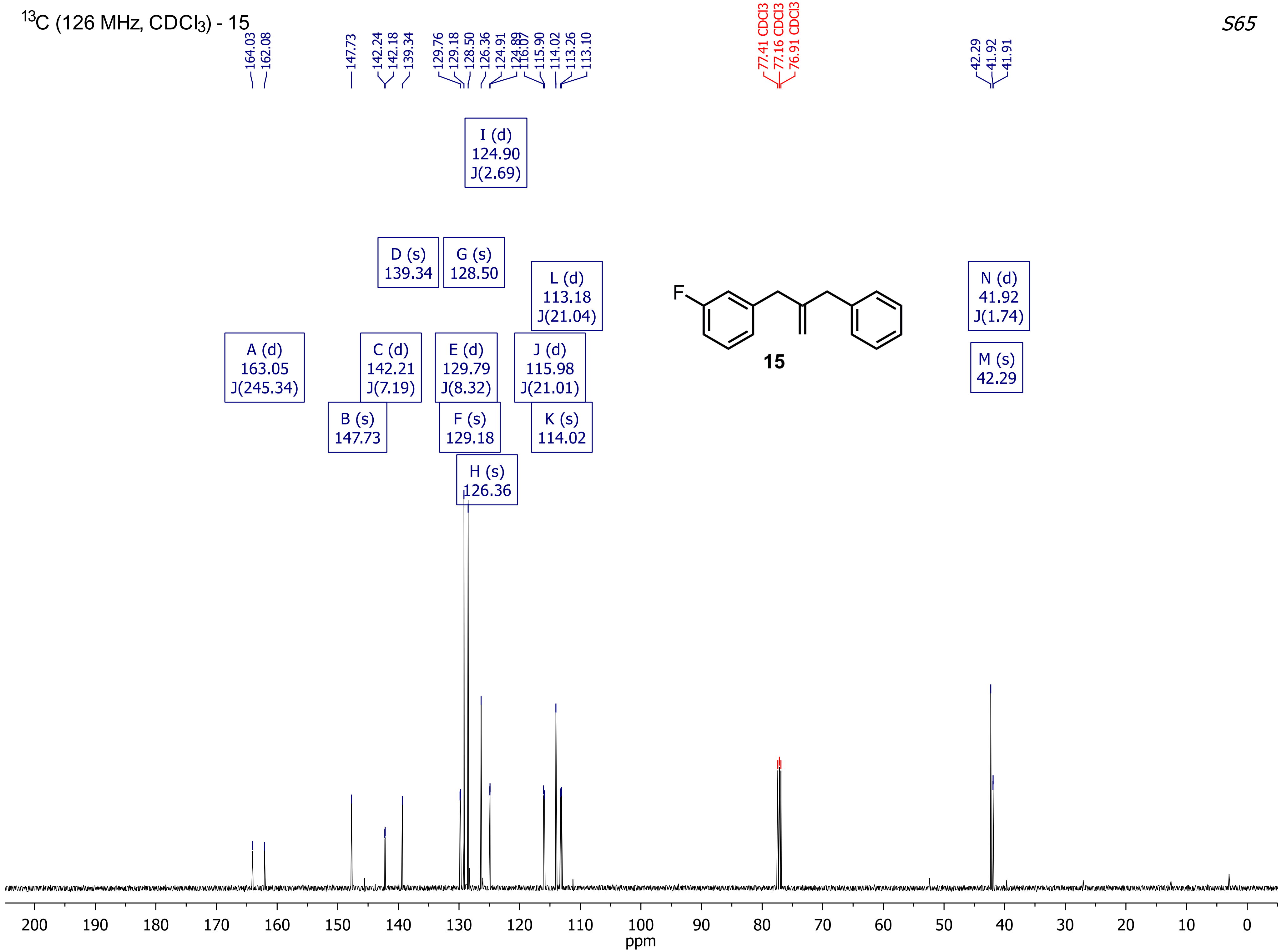
^{13}C (126 MHz, CDCl$_3$) - 14



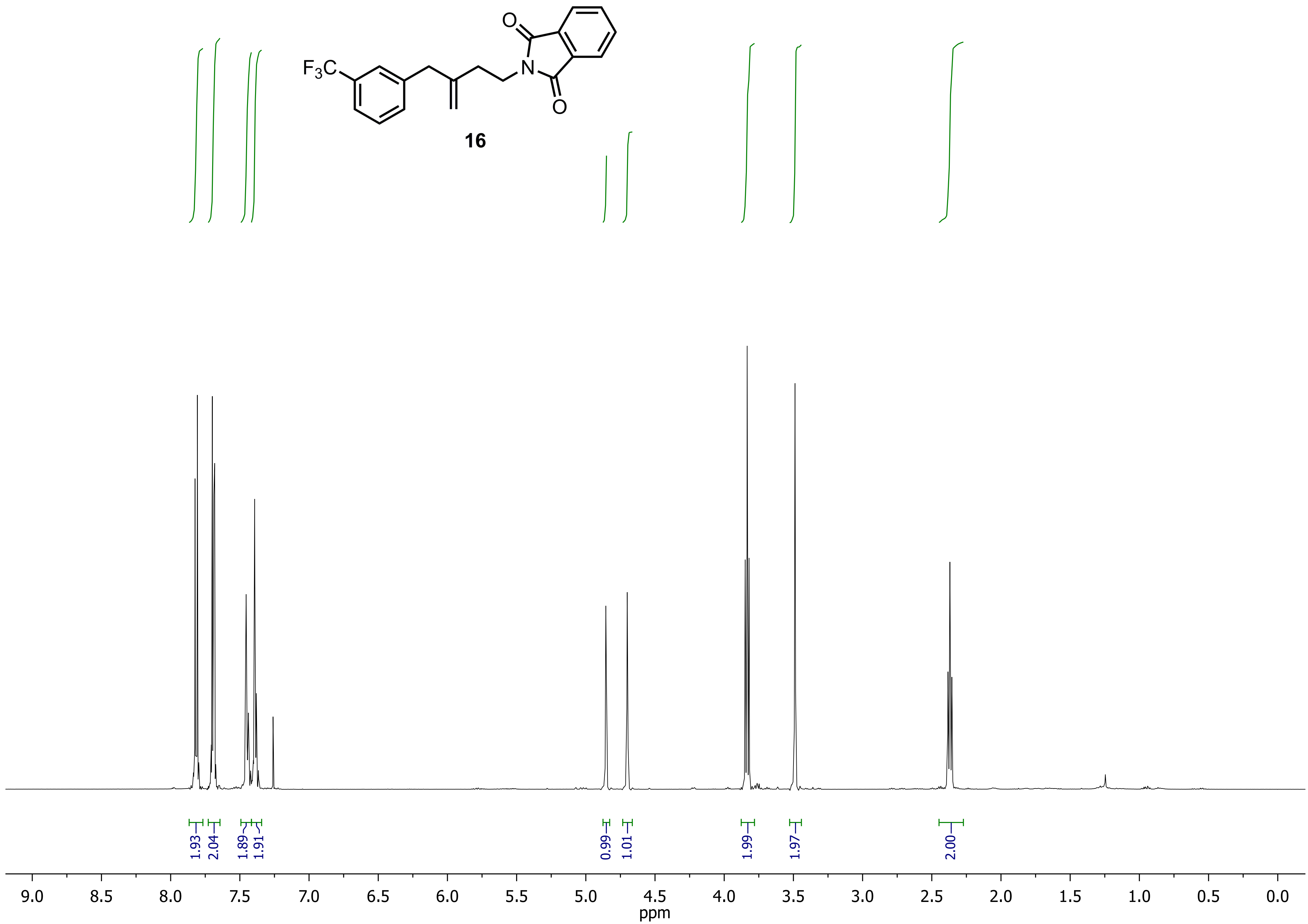
^{1}H (500 MHz, CDCl$_3$) - 15



^{13}C (126 MHz, $CDCl_3$) - 15

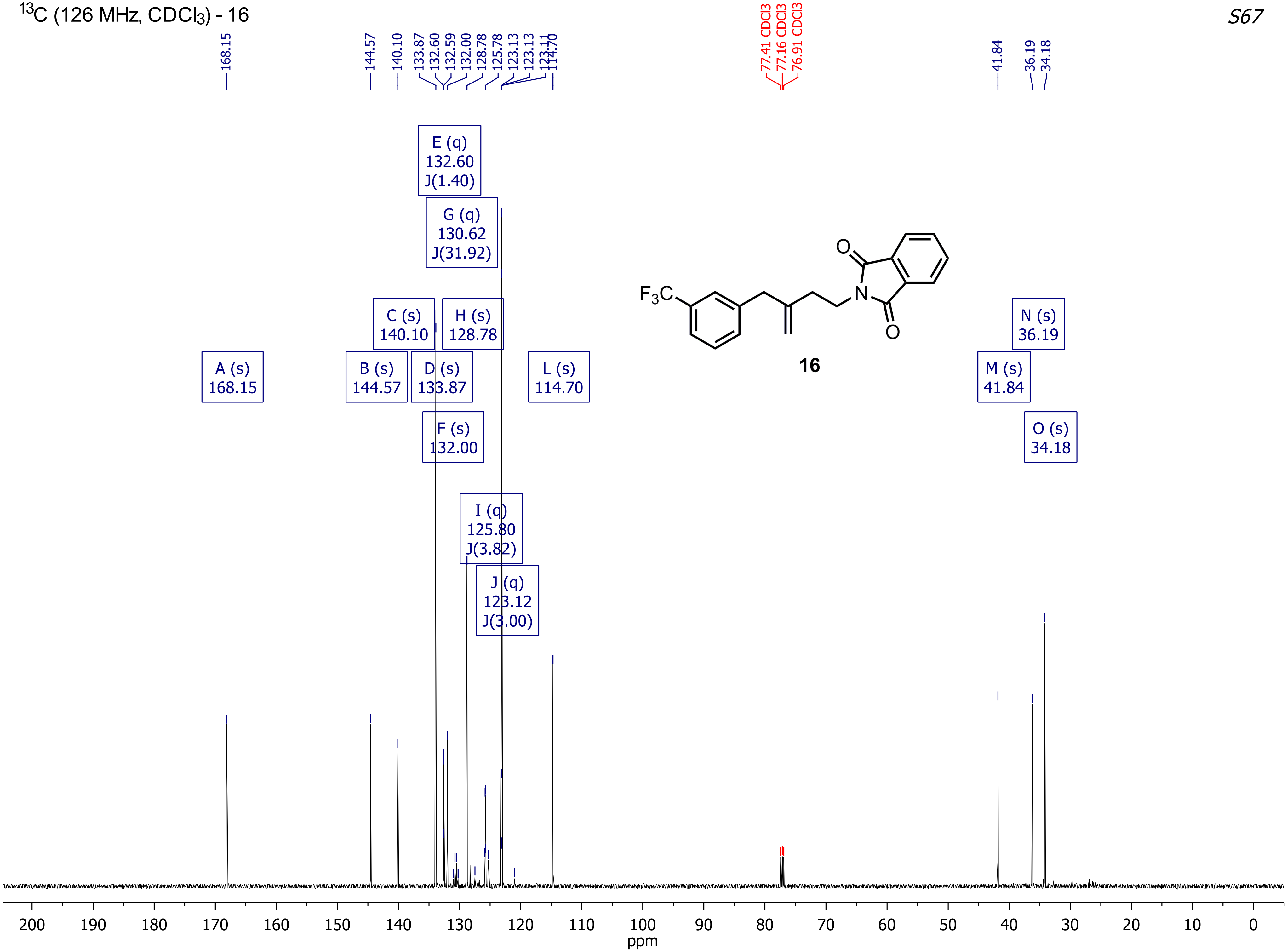


^{1}H (500 MHz, CDCl$_3$) - 16

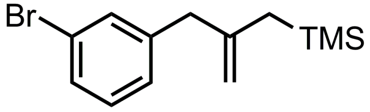


16

^{13}C (126 MHz, CDCl$_3$) - 16



^{1}H (500 MHz, $CDCl_3$) - 17



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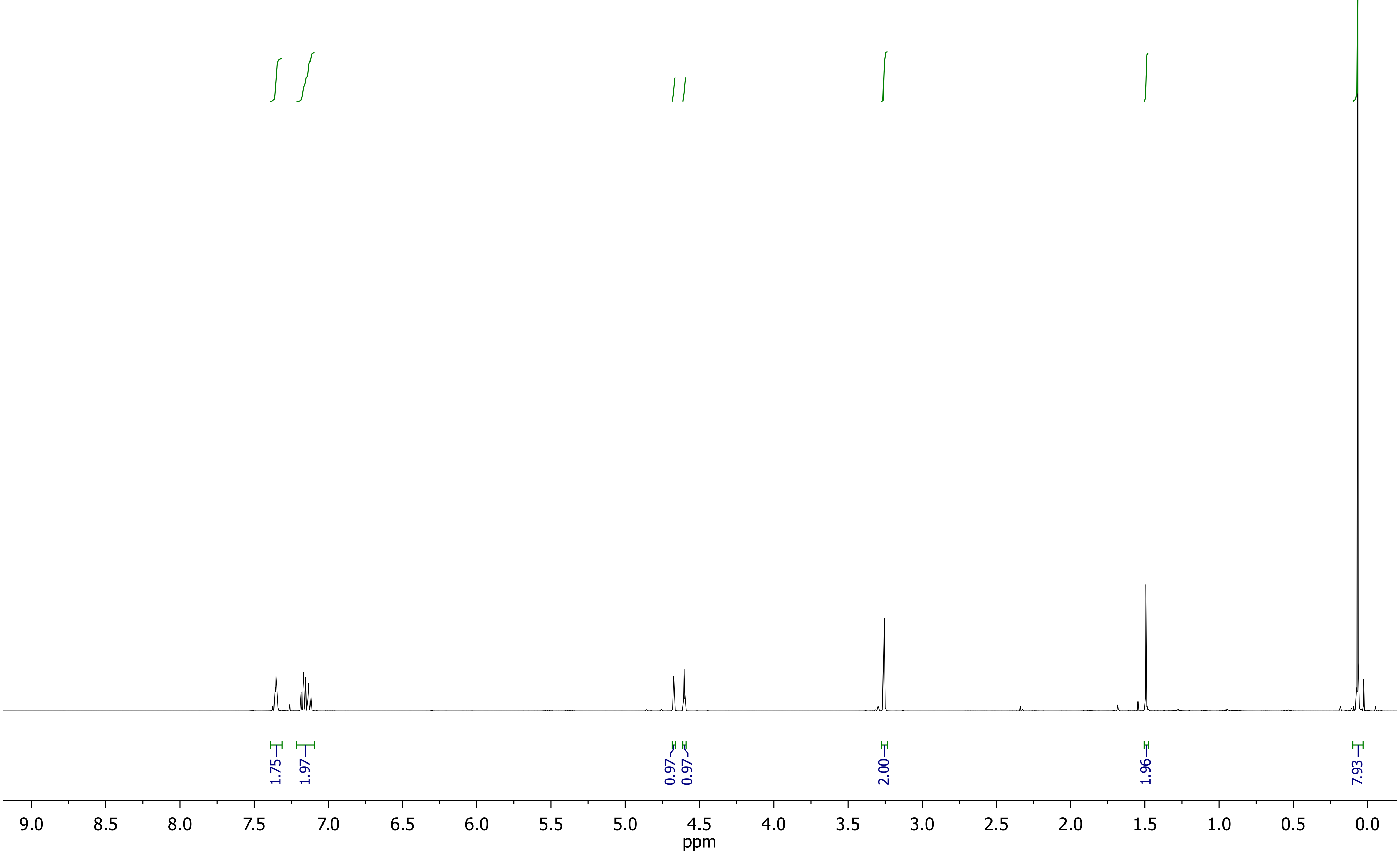
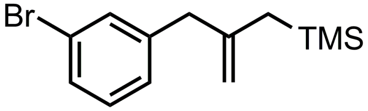


^{13}C (126 MHz, CDCl$_3$) - 17



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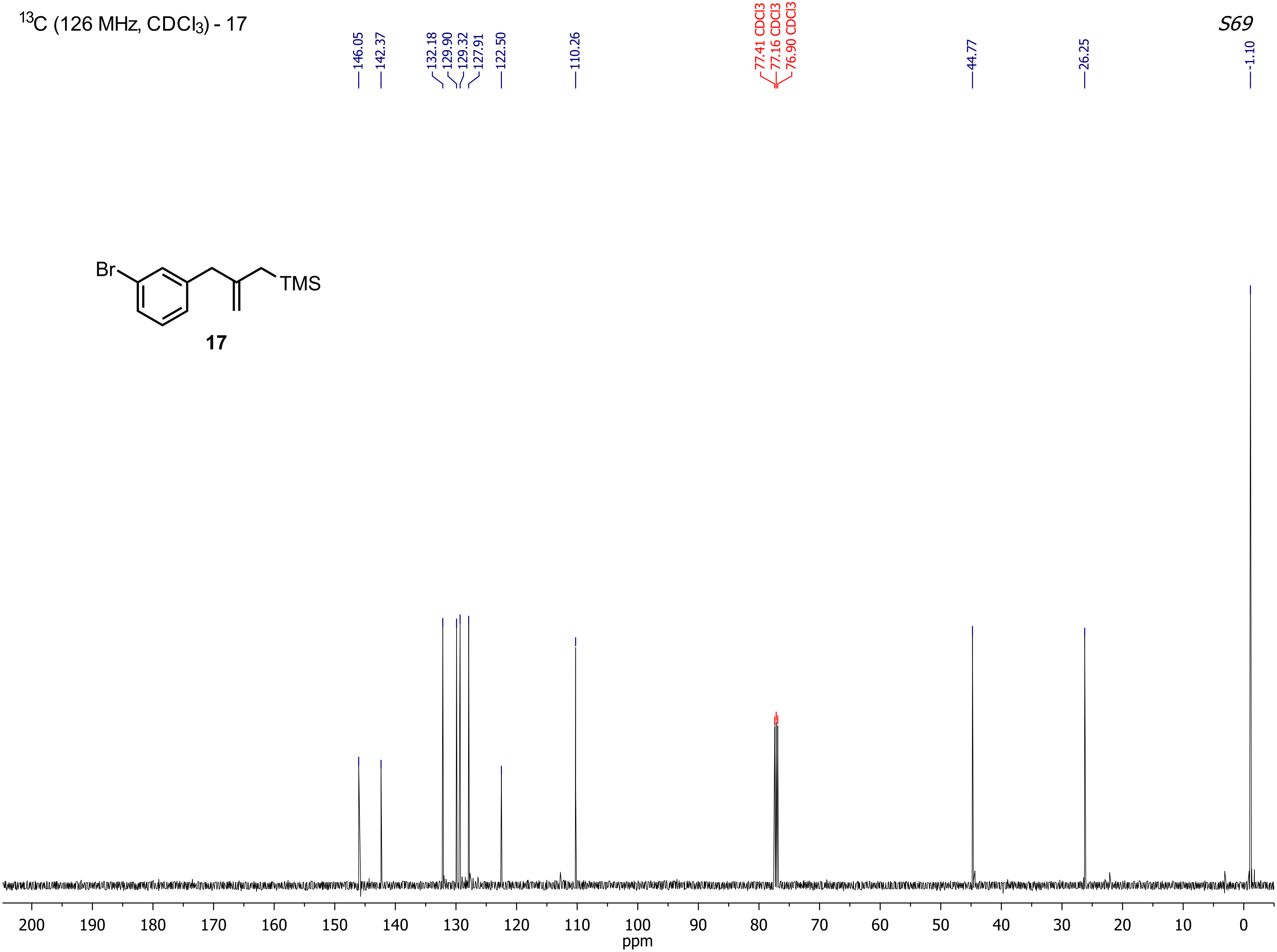
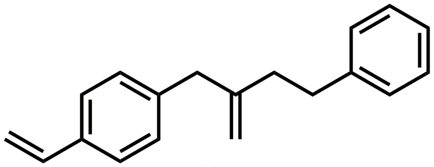


^{1}H (500 MHz, CDCl$_3$) - 18



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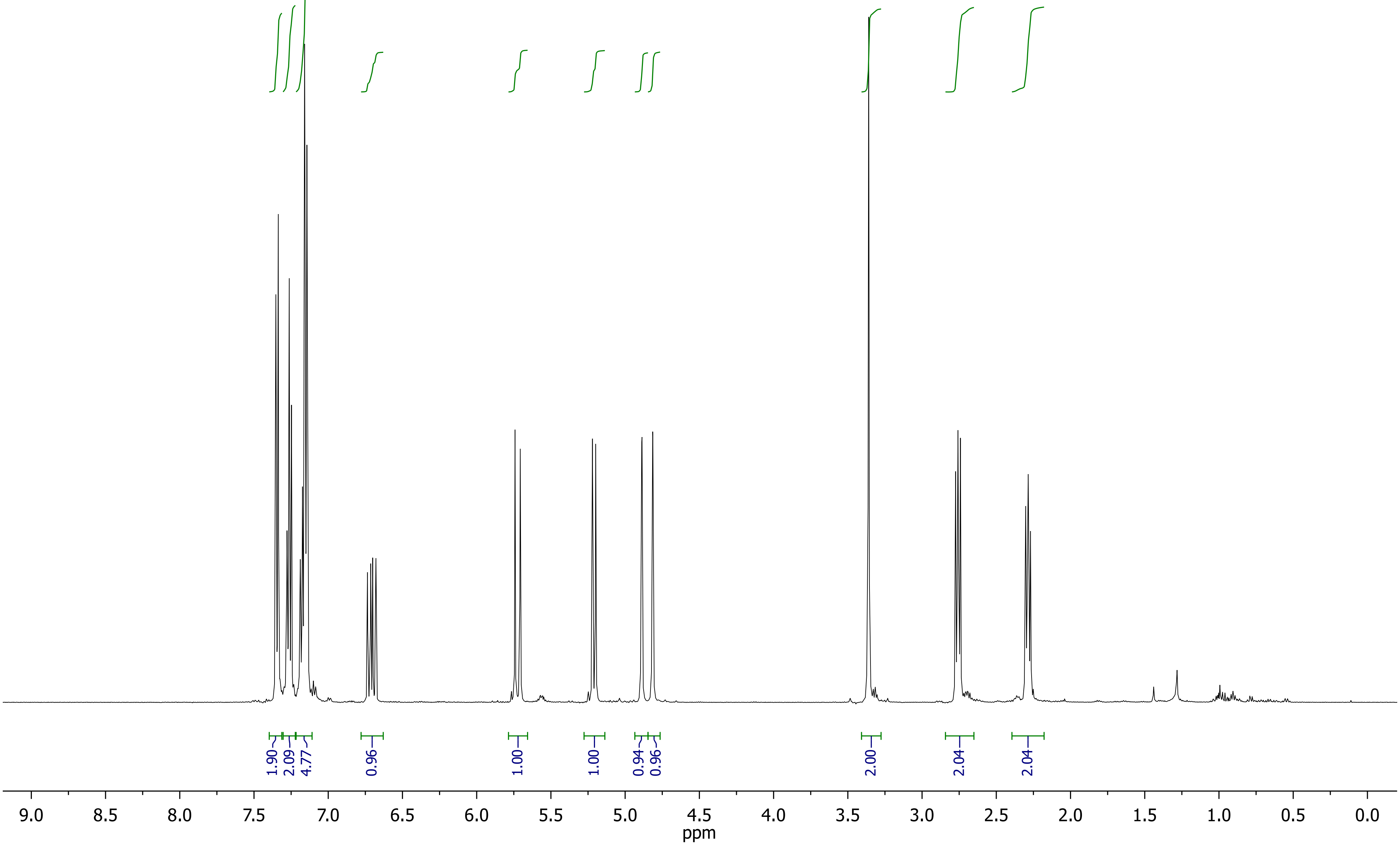
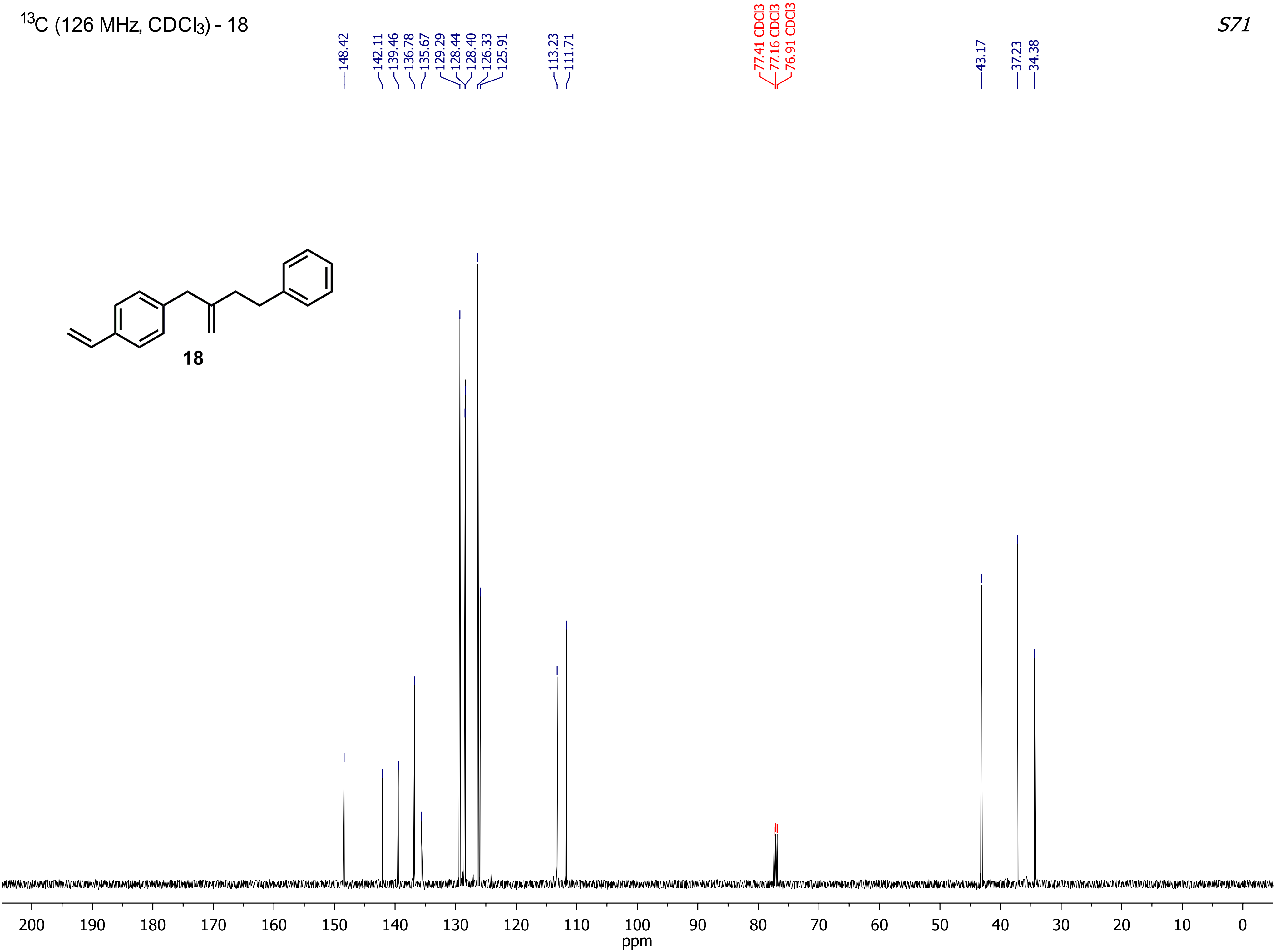
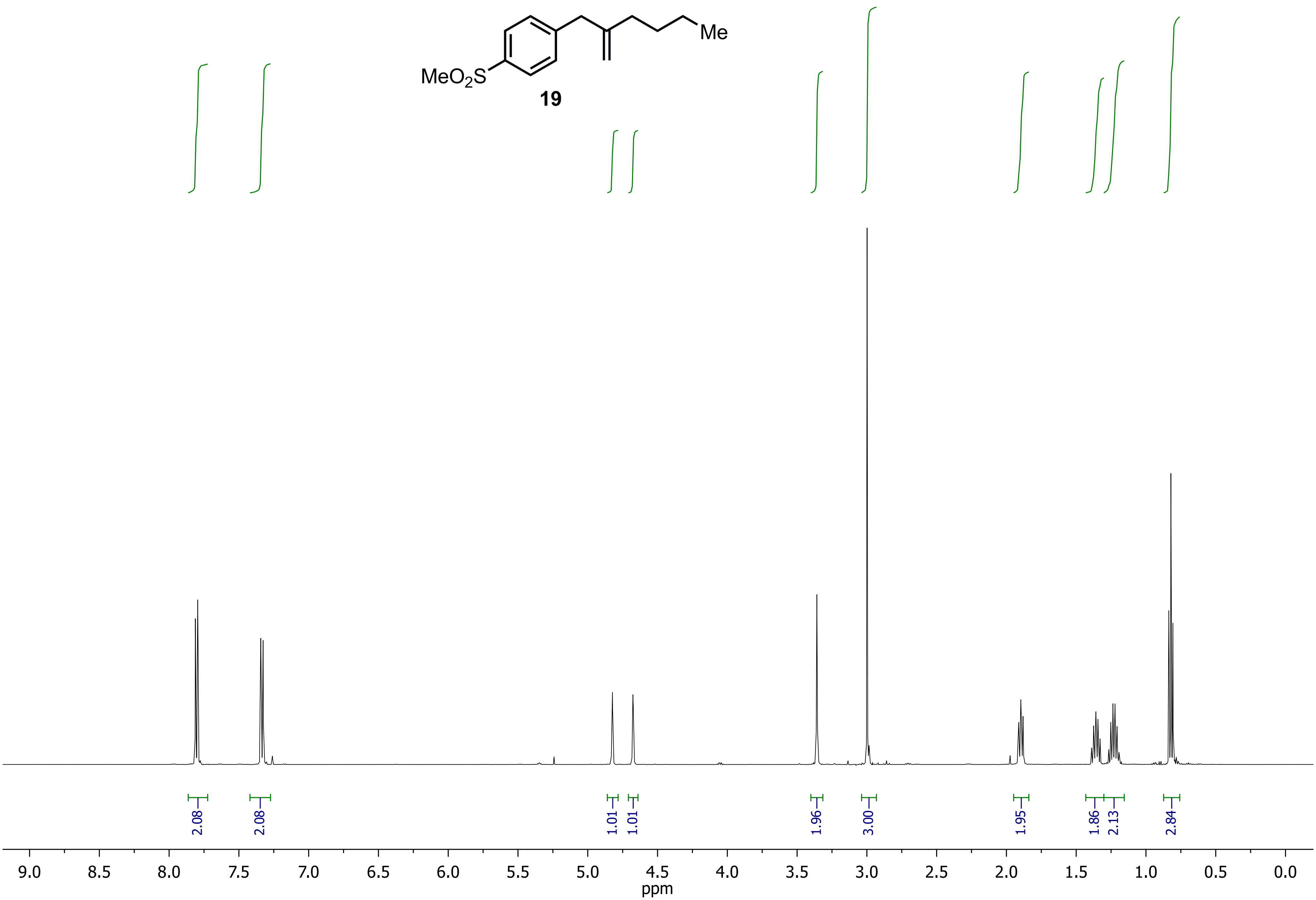


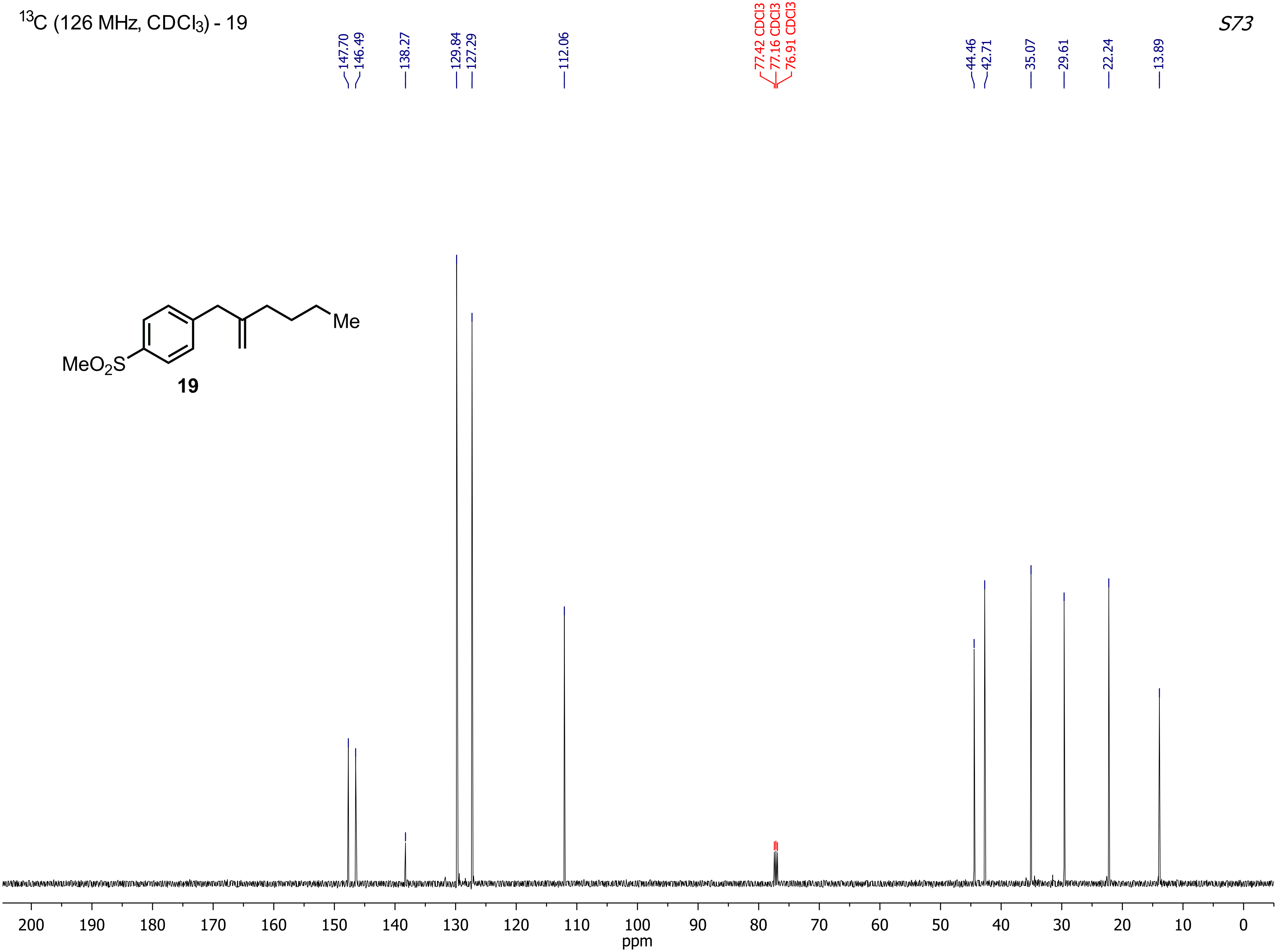
^{13}C (126 MHz, CDCl$_3$) - 18



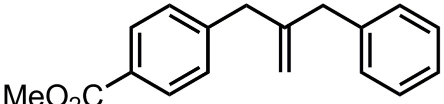
^{1}H (500 MHz, CDCl$_3$) - 19



^{13}C (126 MHz, CDCl$_3$) - 19



^{1}H (500 MHz, CDCl$_3$) - 20



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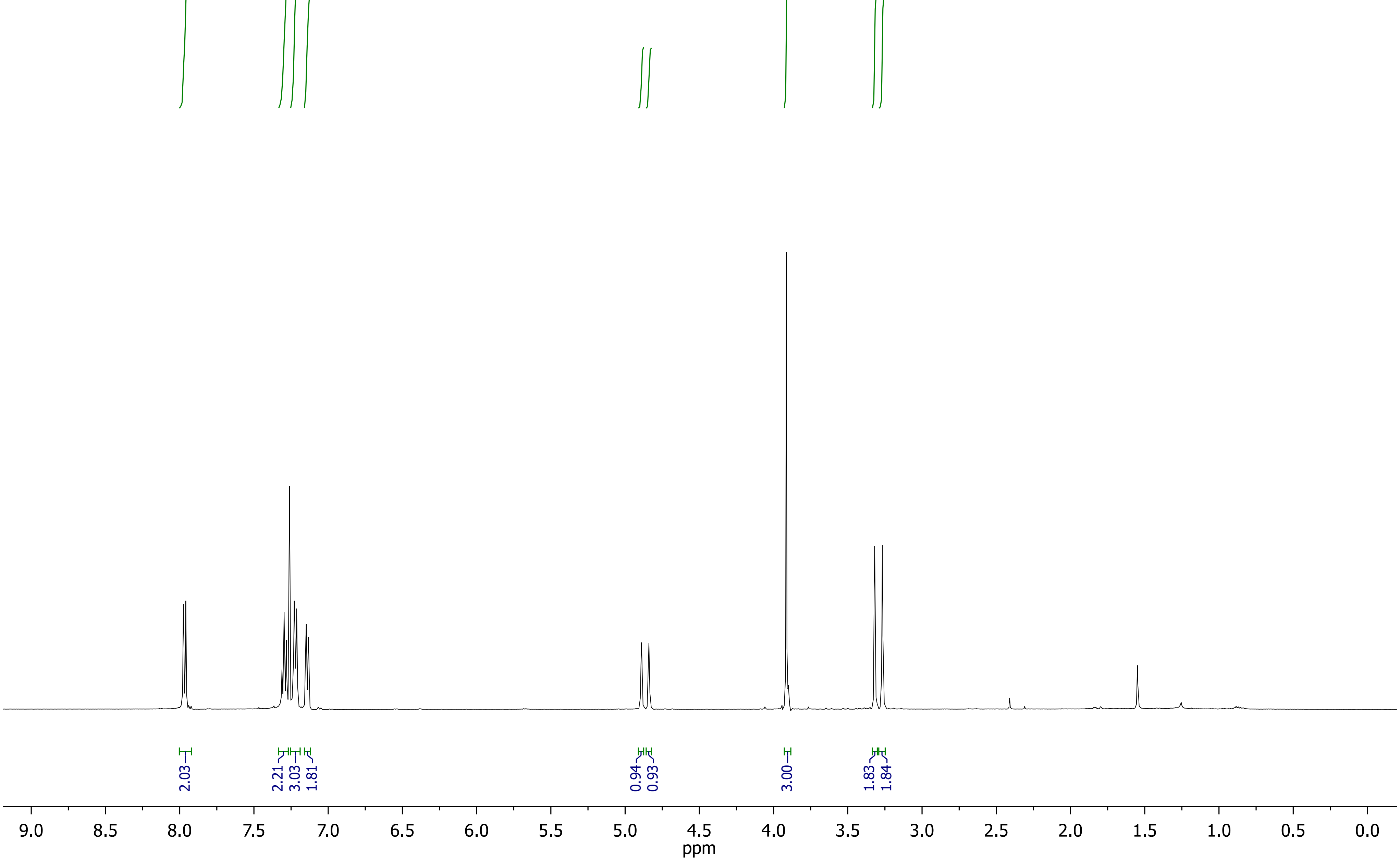
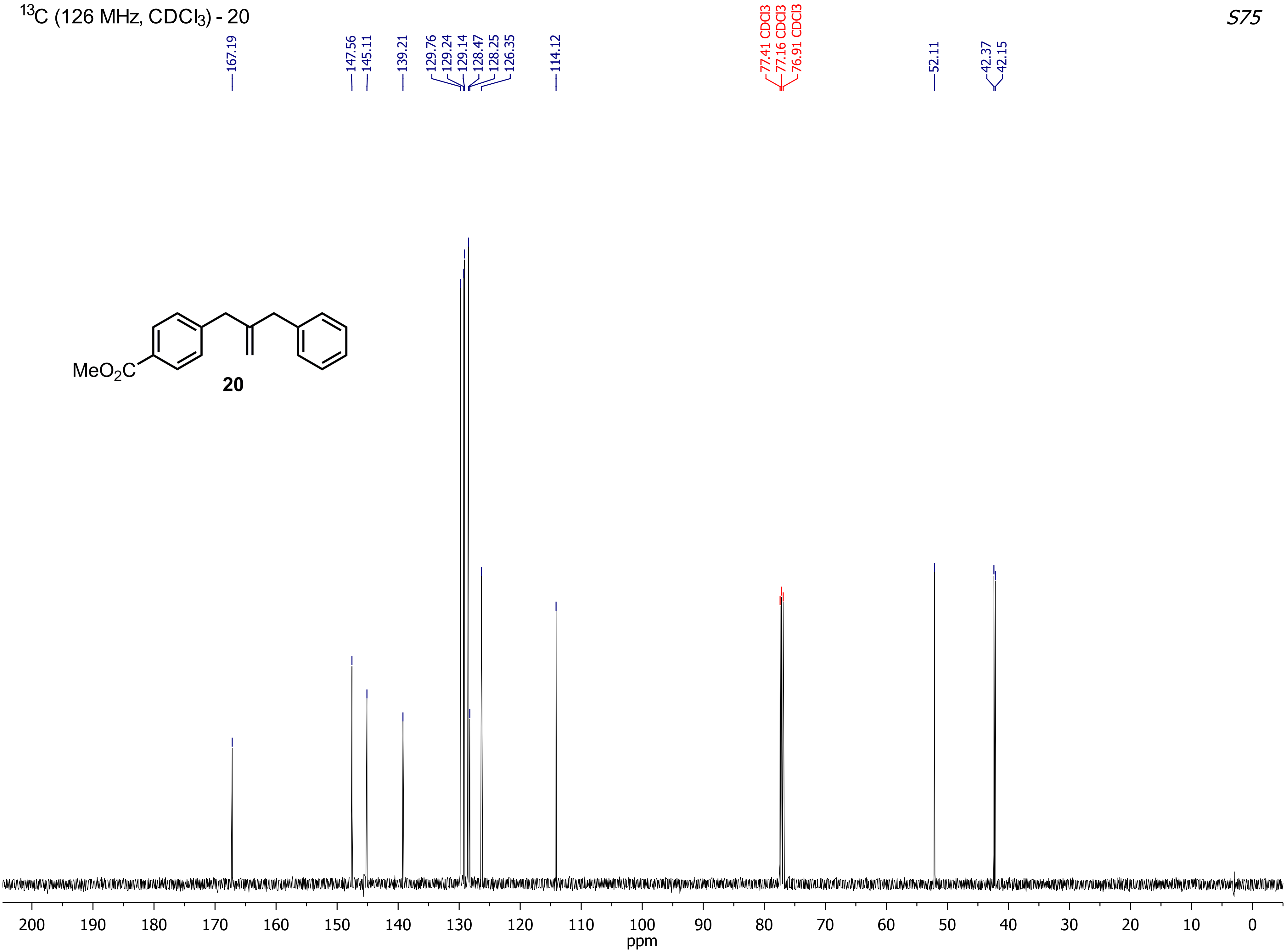
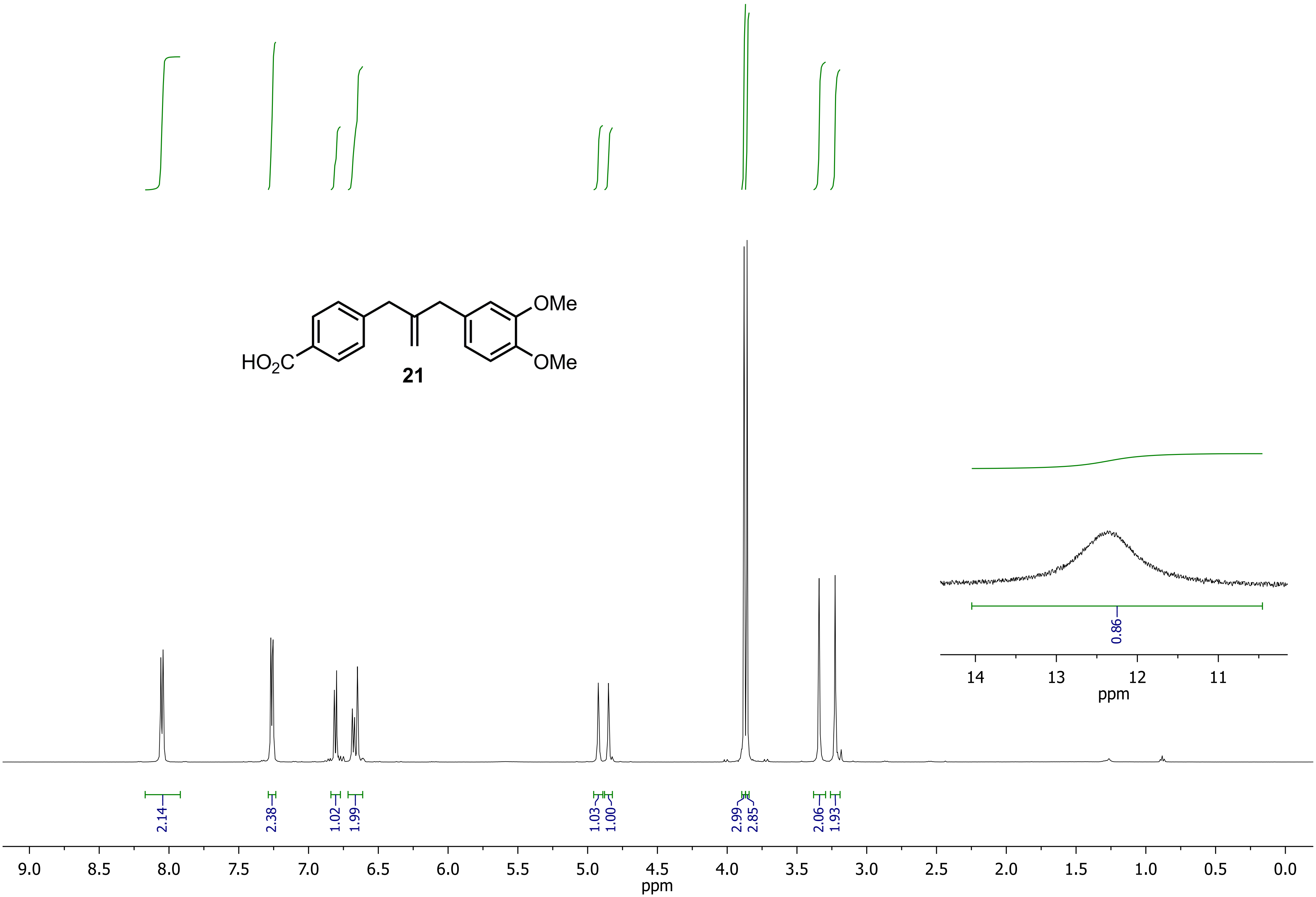


^{13}C (126 MHz, CDCl$_3$) - 20

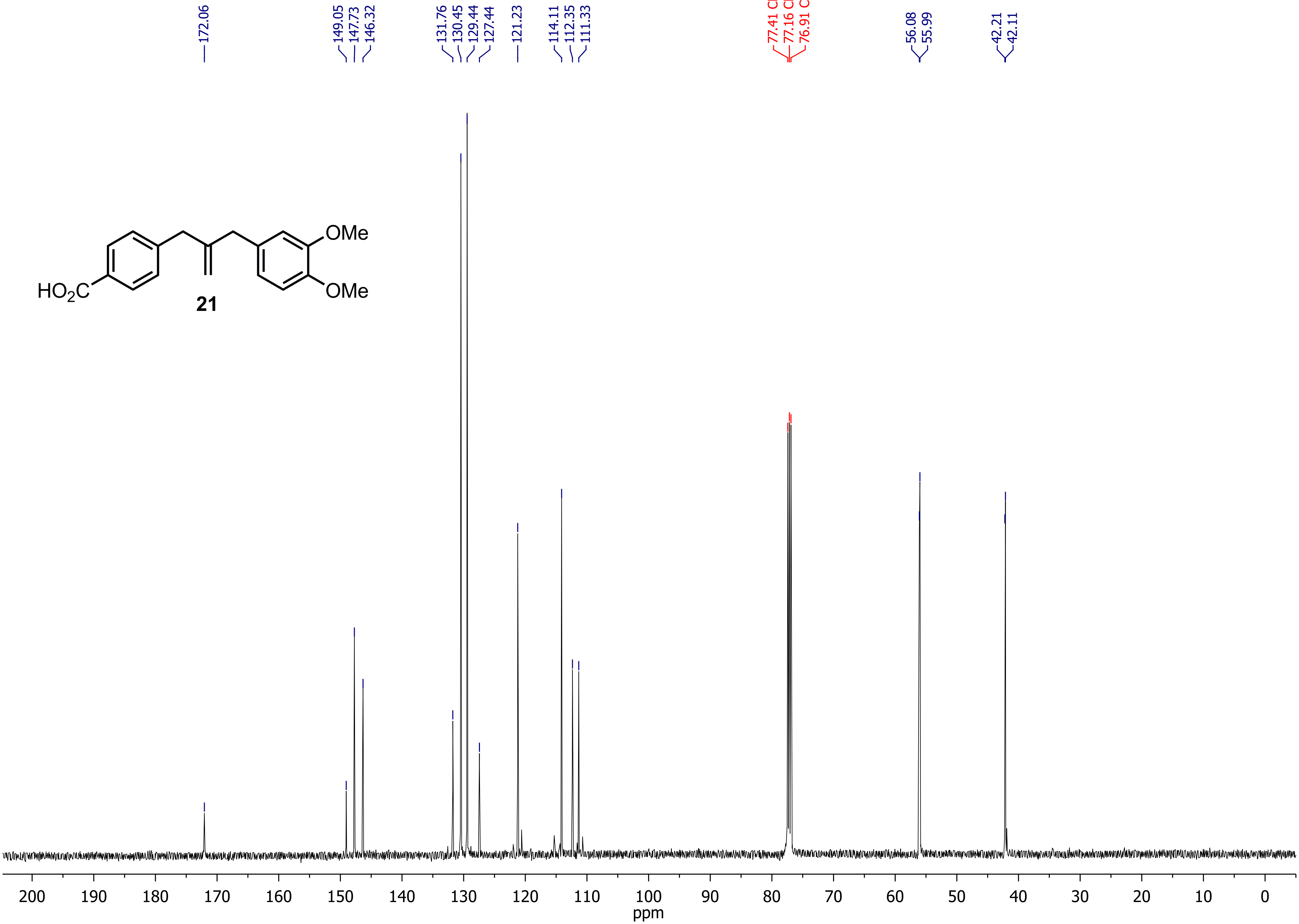


20

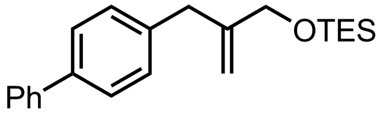
^{1}H (500 MHz, CDCl$_3$) - 21



^{13}C (126 MHz, CDCl$_3$) - 21



^{1}H (500 MHz, CDCl$_3$) - 22



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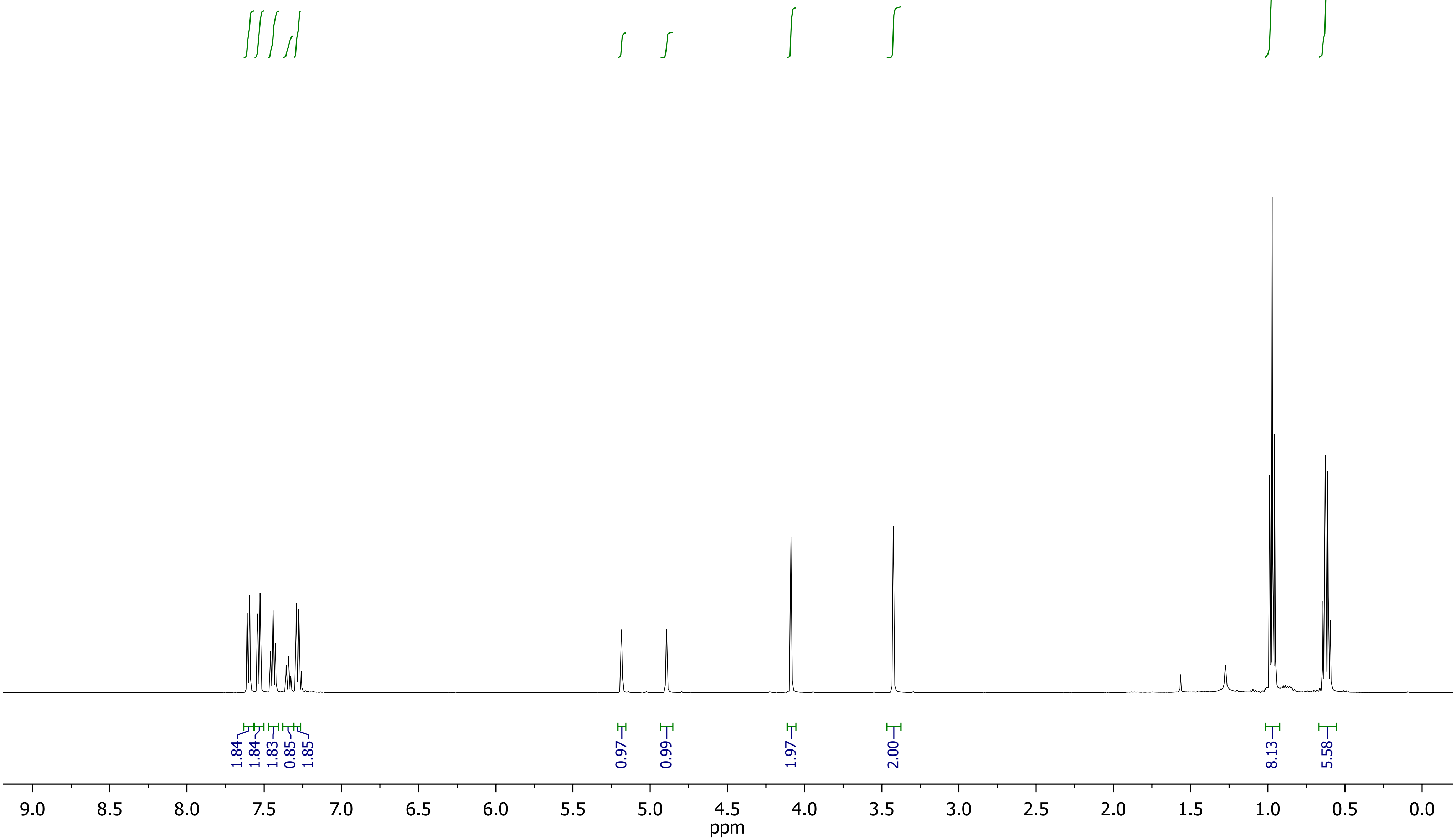
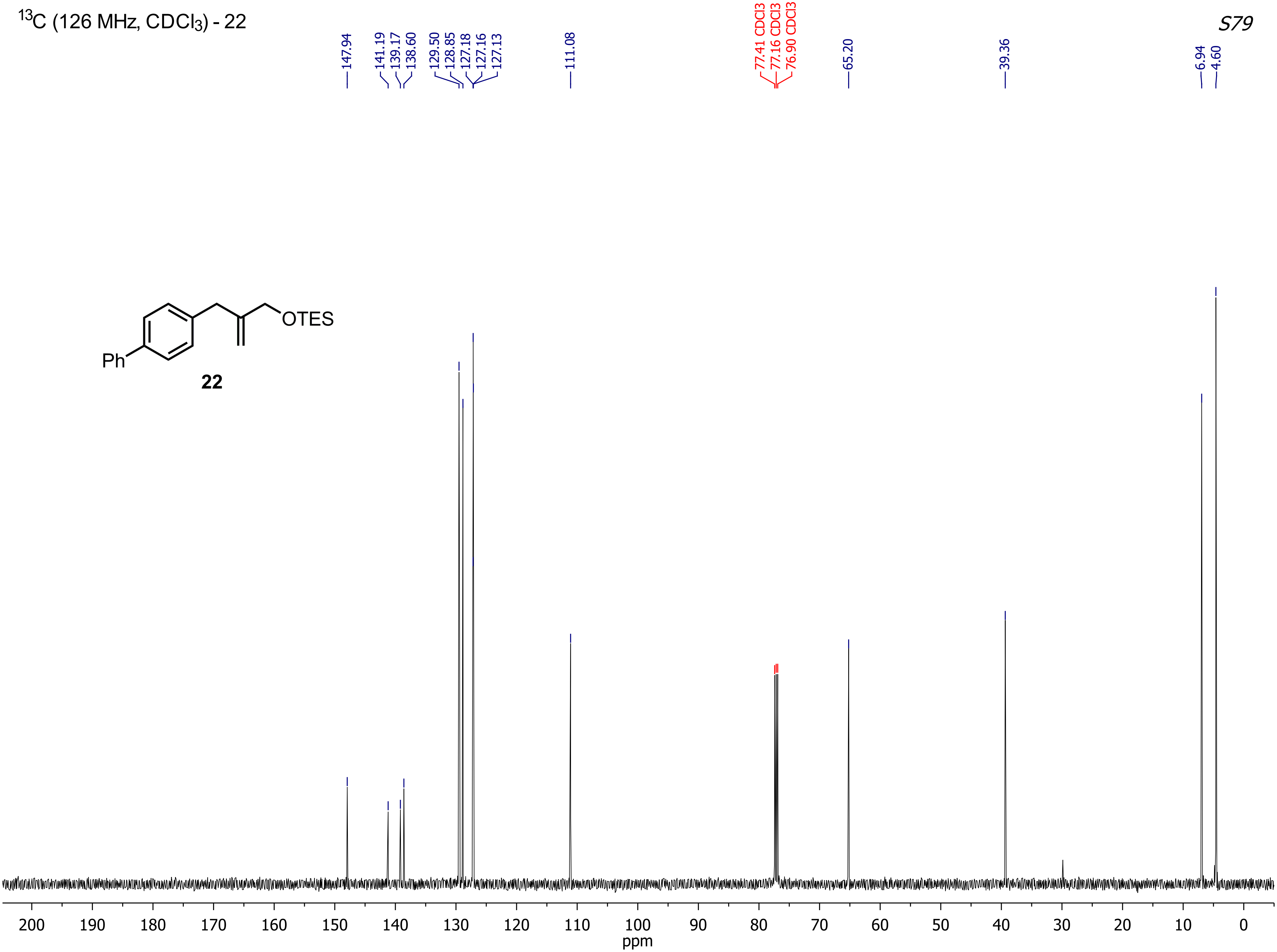
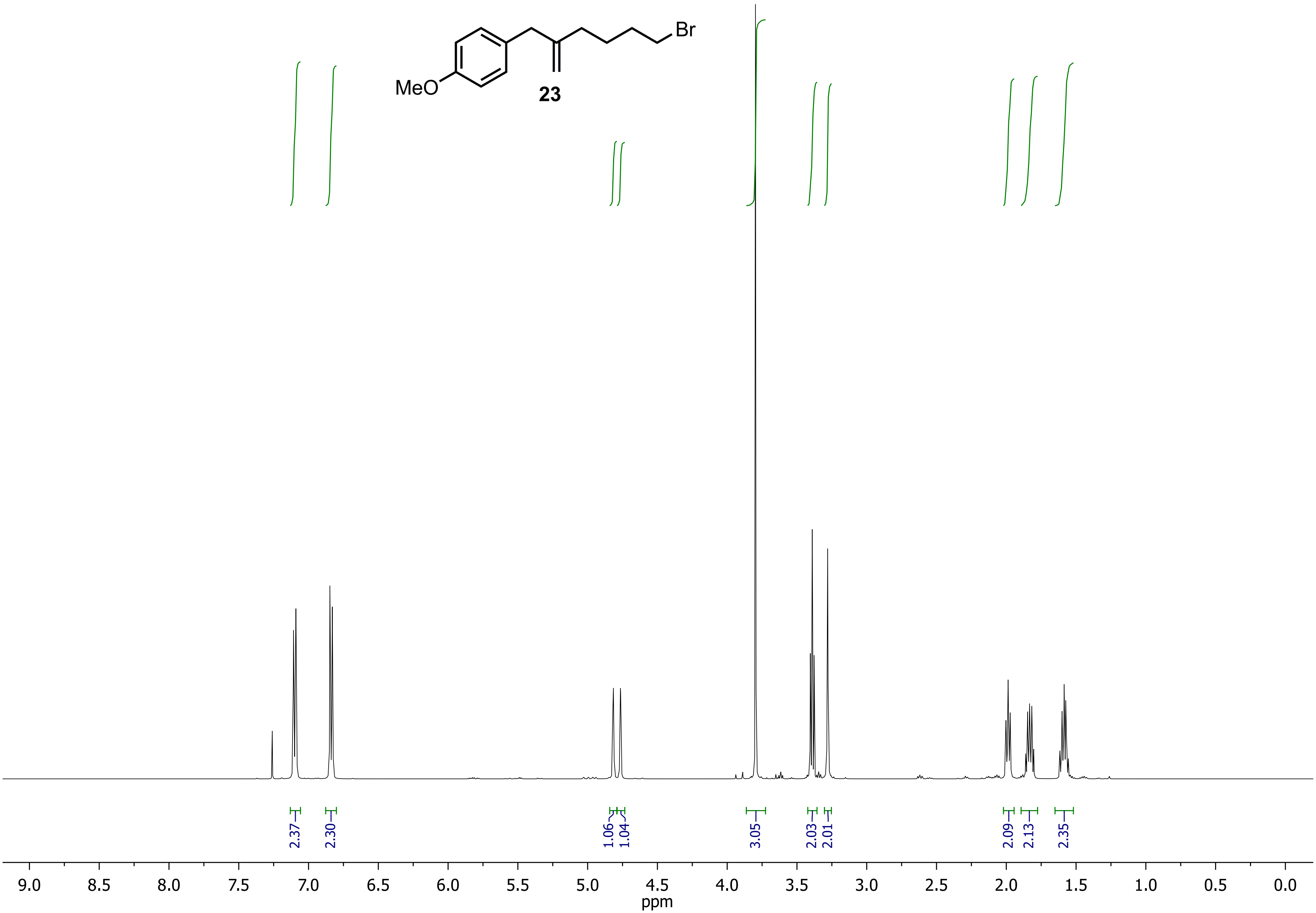


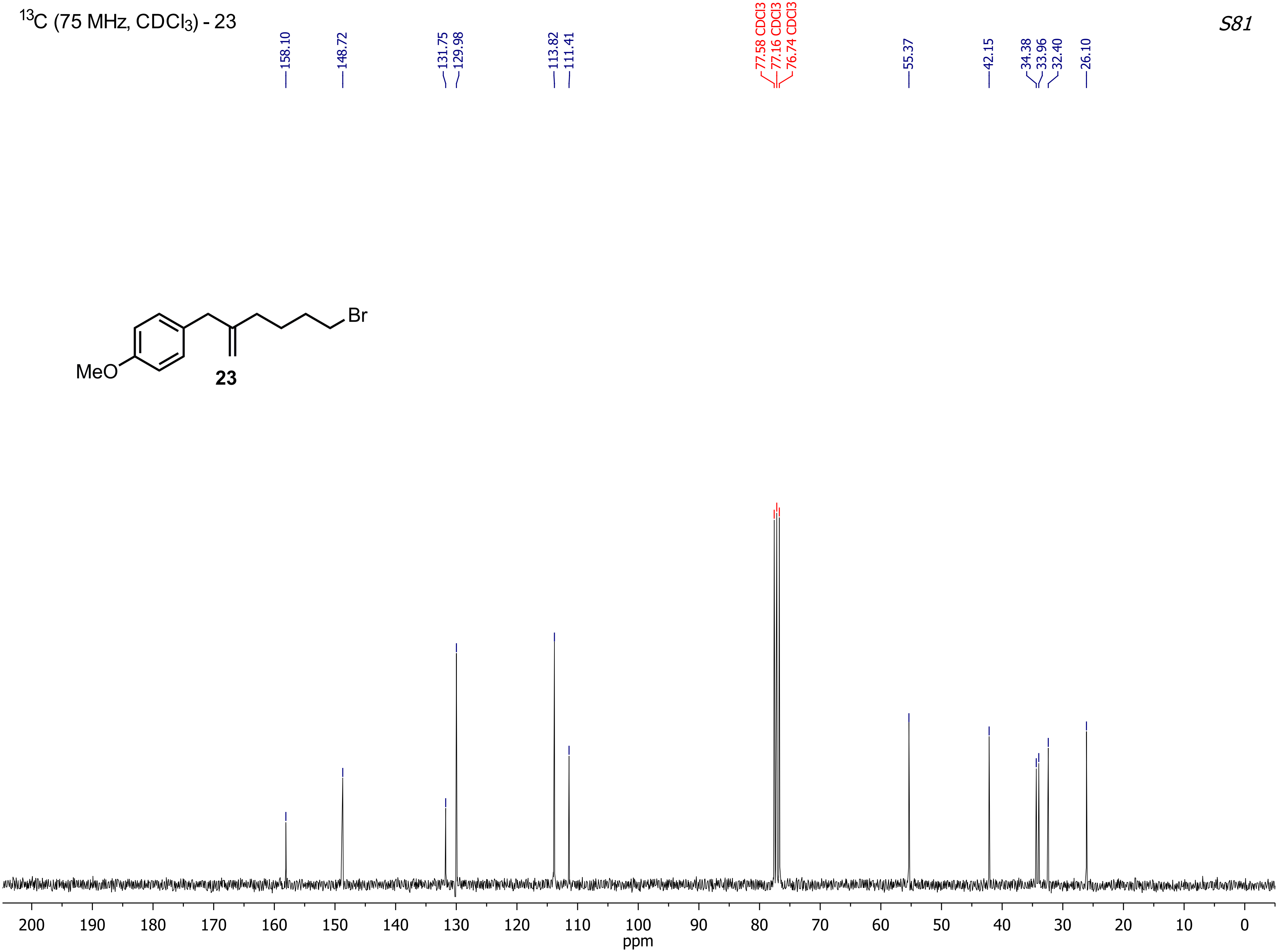
^{13}C (126 MHz, CDCl$_3$) - 22



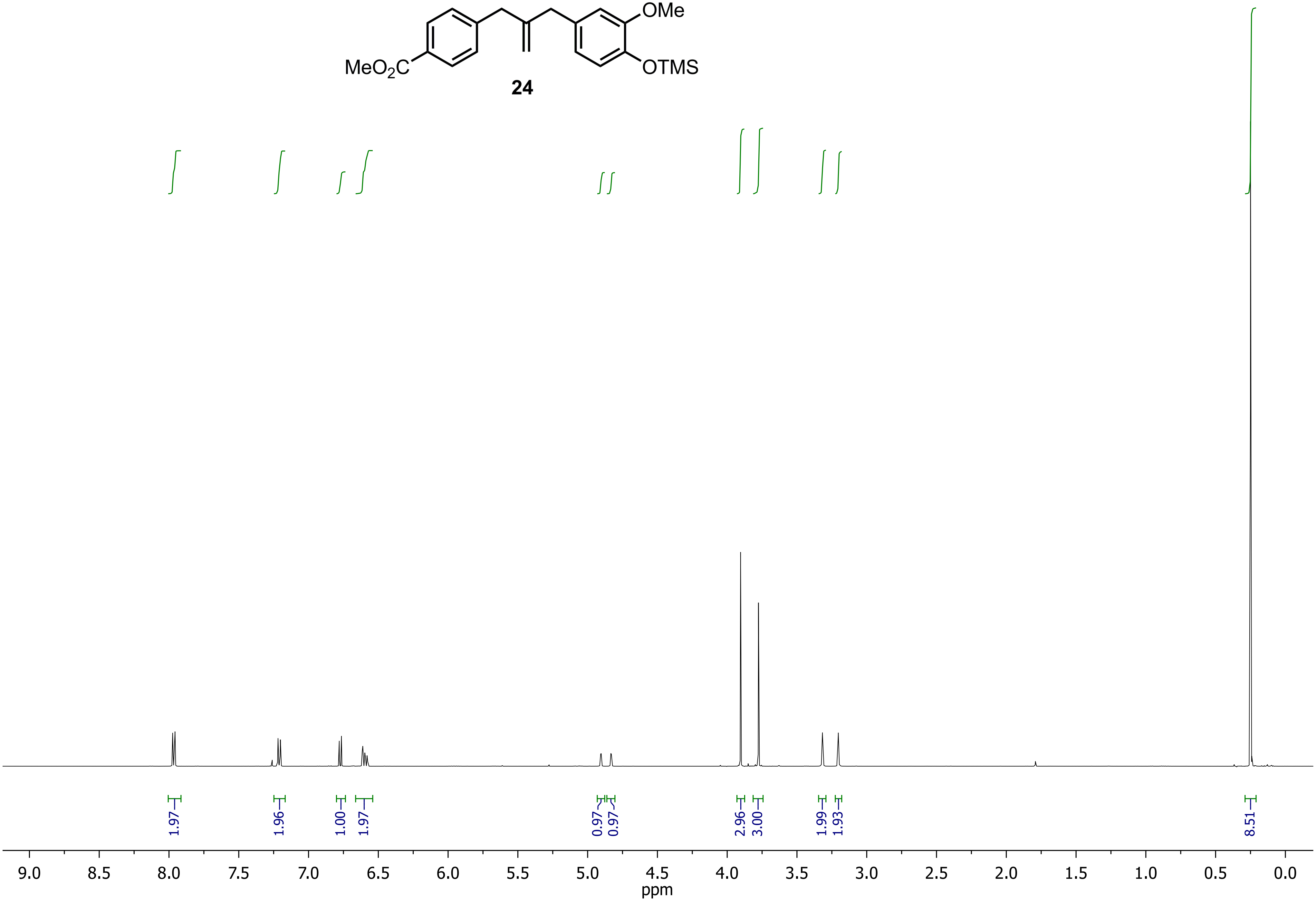
^{1}H (500 MHz, CDCl$_3$) - 23



^{13}C (75 MHz, CDCl$_3$) - 23

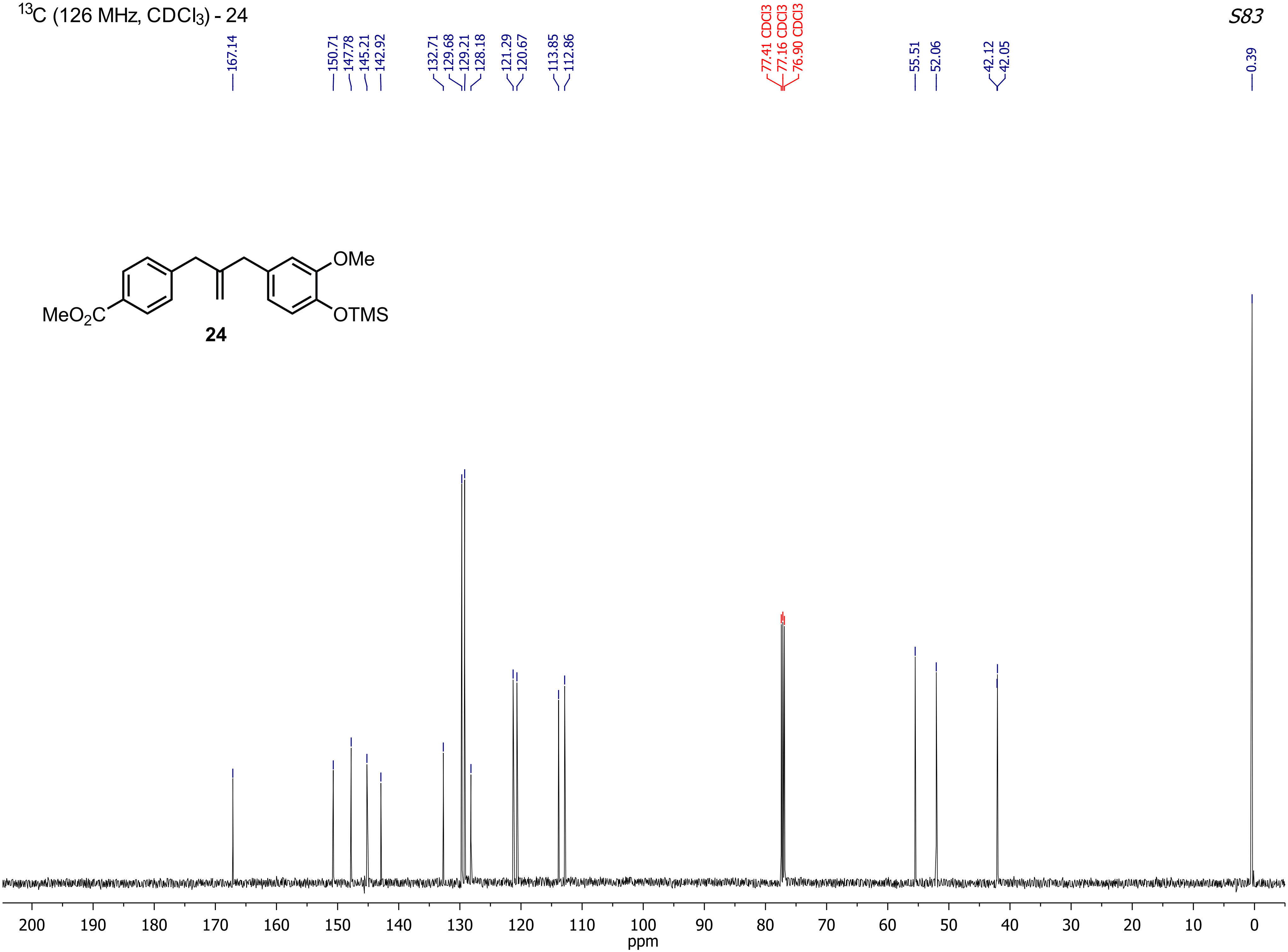


^{1}H (500 MHz, $CDCl_3$) - 24

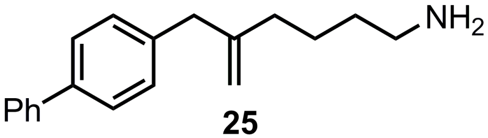


24

^{13}C (126 MHz, CDCl$_3$) - 24



^{1}H (500 MHz, CDCl$_3$) - 25



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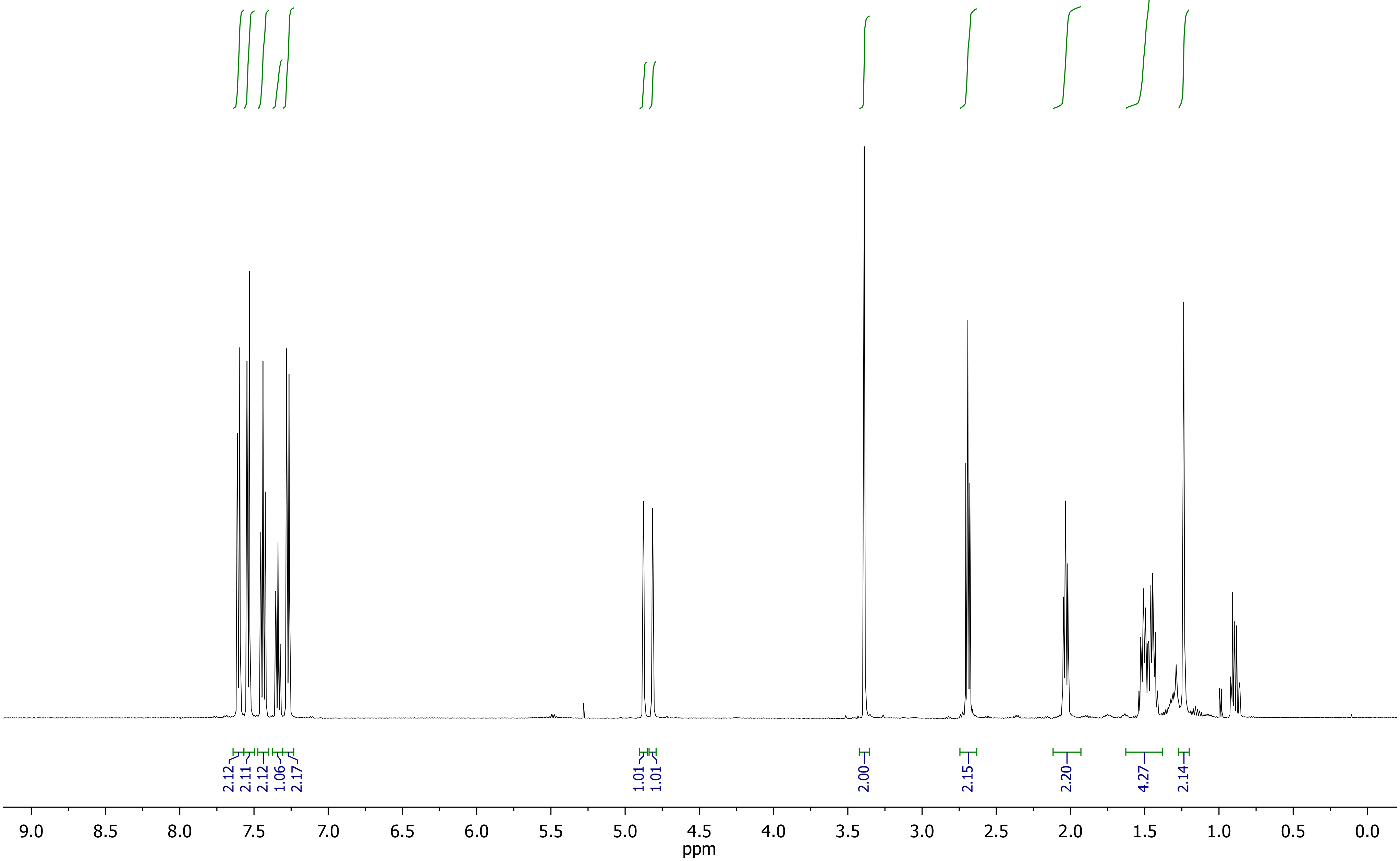
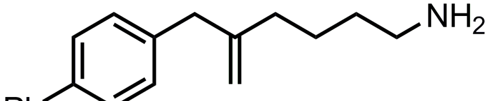


^{13}C (126 MHz, CDCl$_3$) - 25



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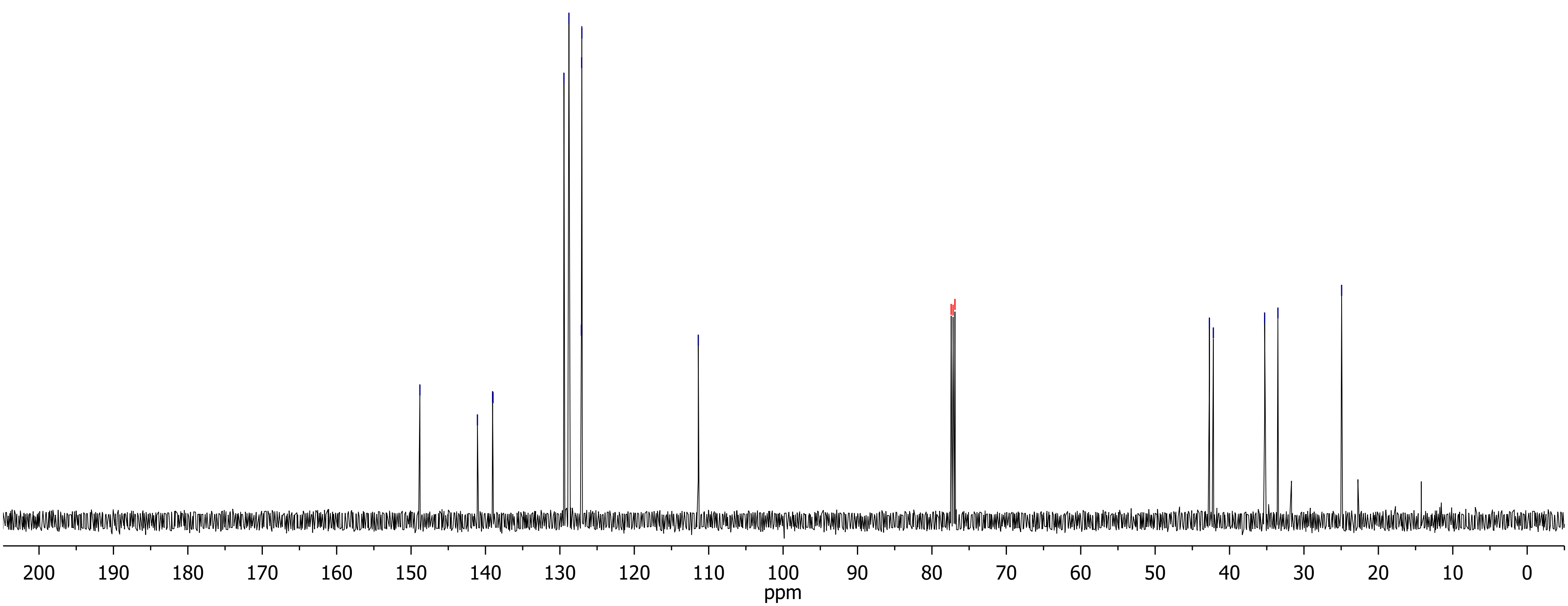
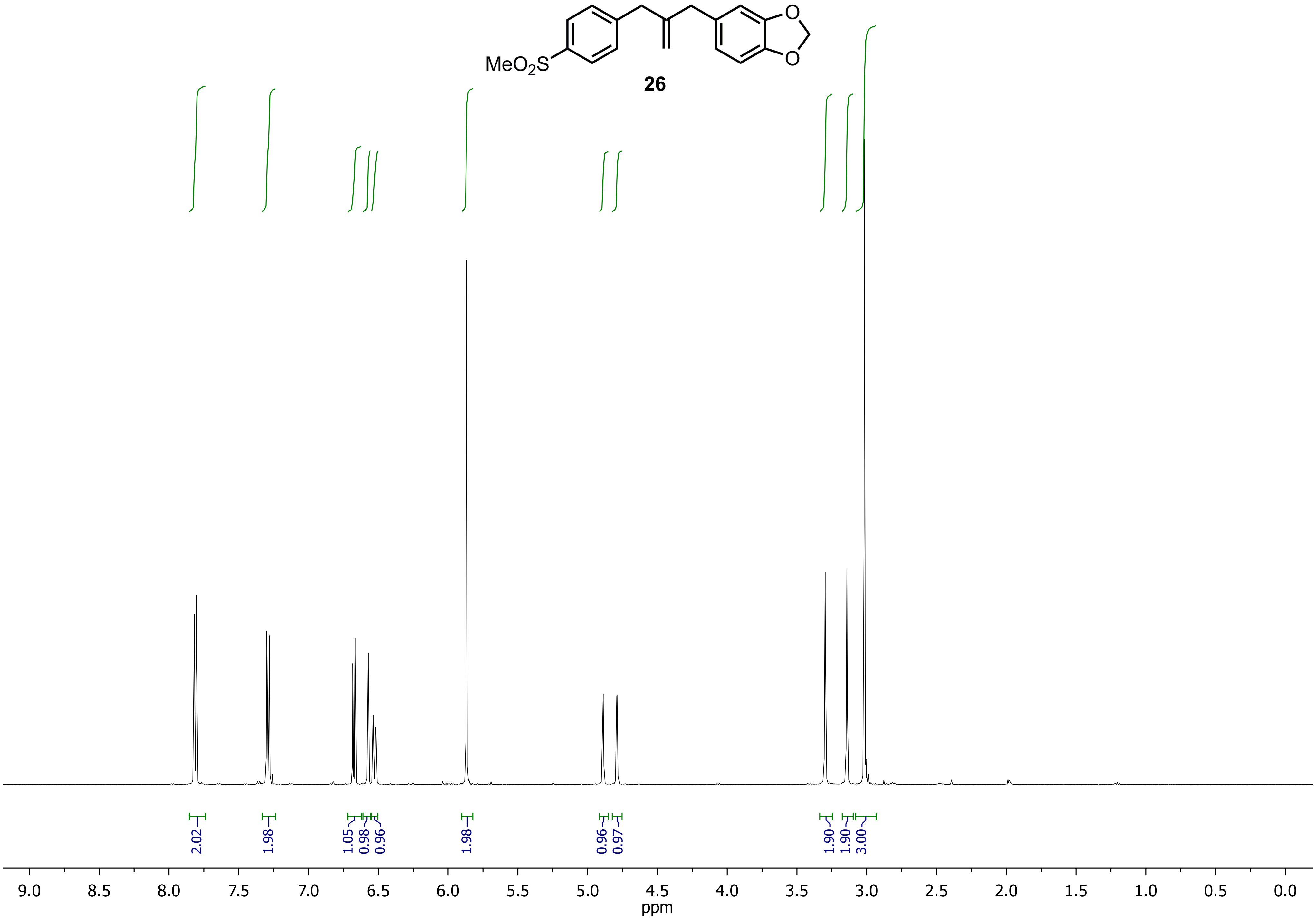
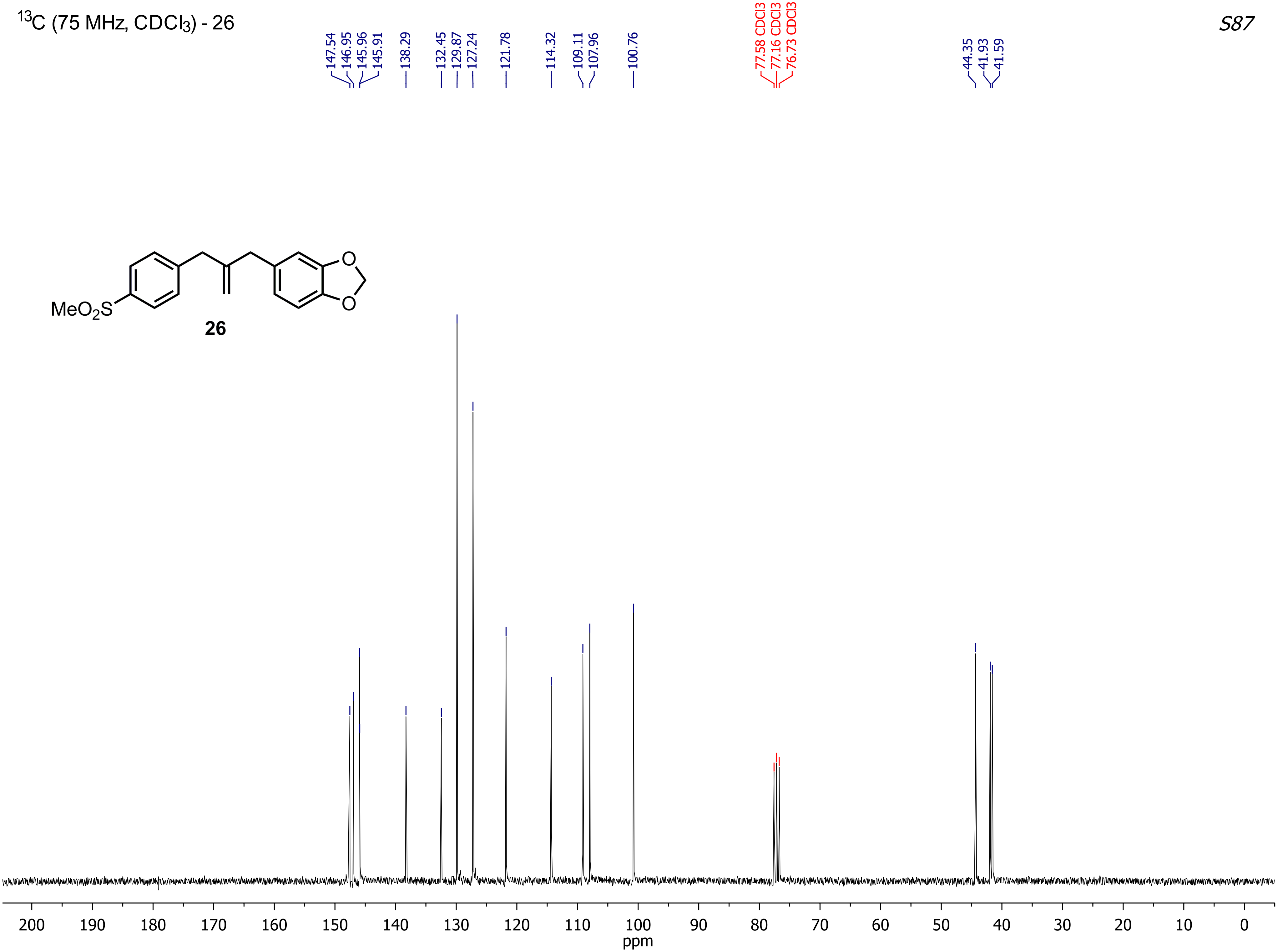


^{1}H (500 MHz, CDCl$_3$) - 26

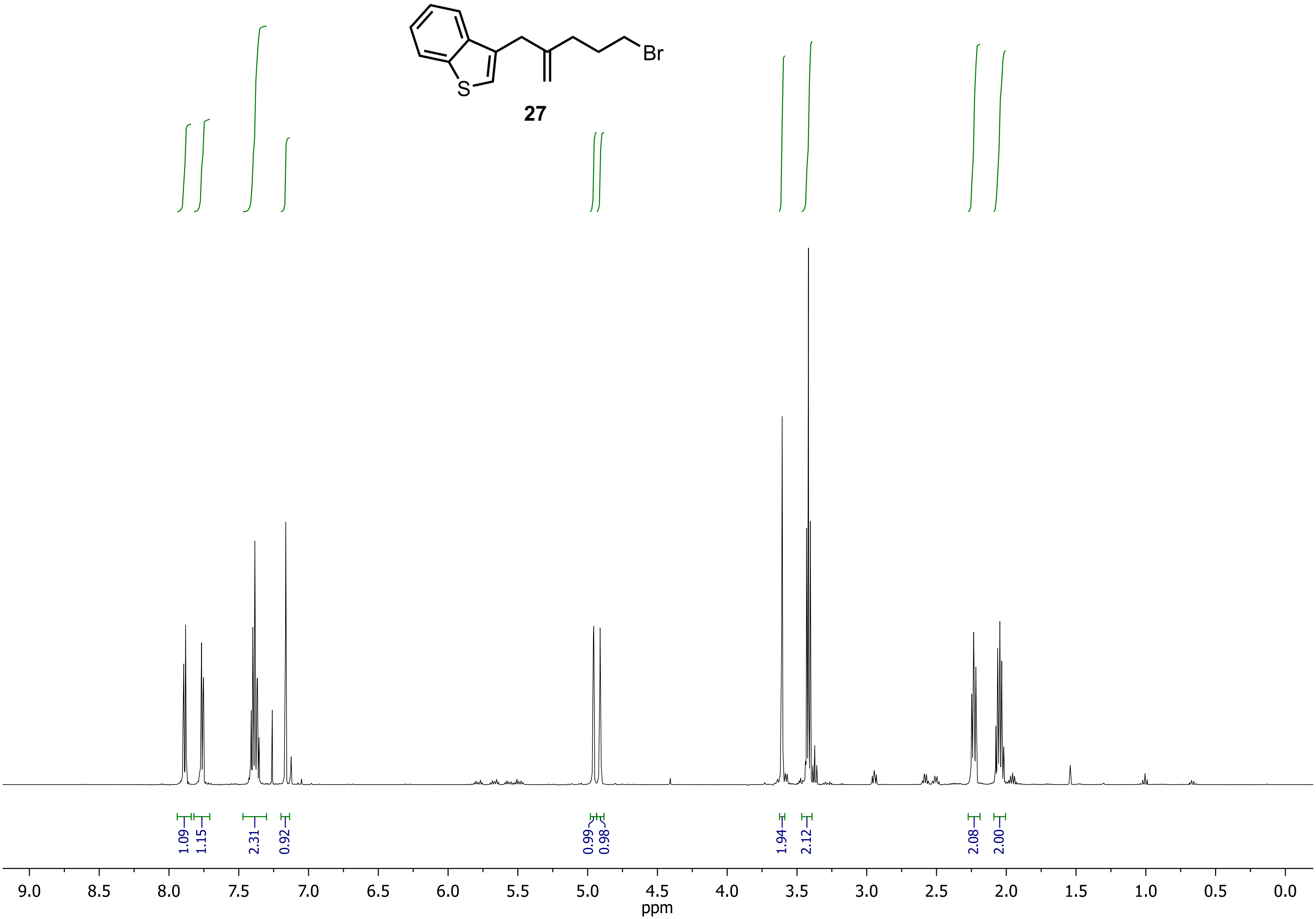


^{13}C (75 MHz, $CDCl_3$) - 26



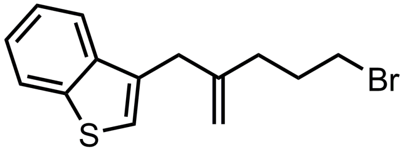
26

^{1}H (500 MHz, $CDCl_3$) - 27

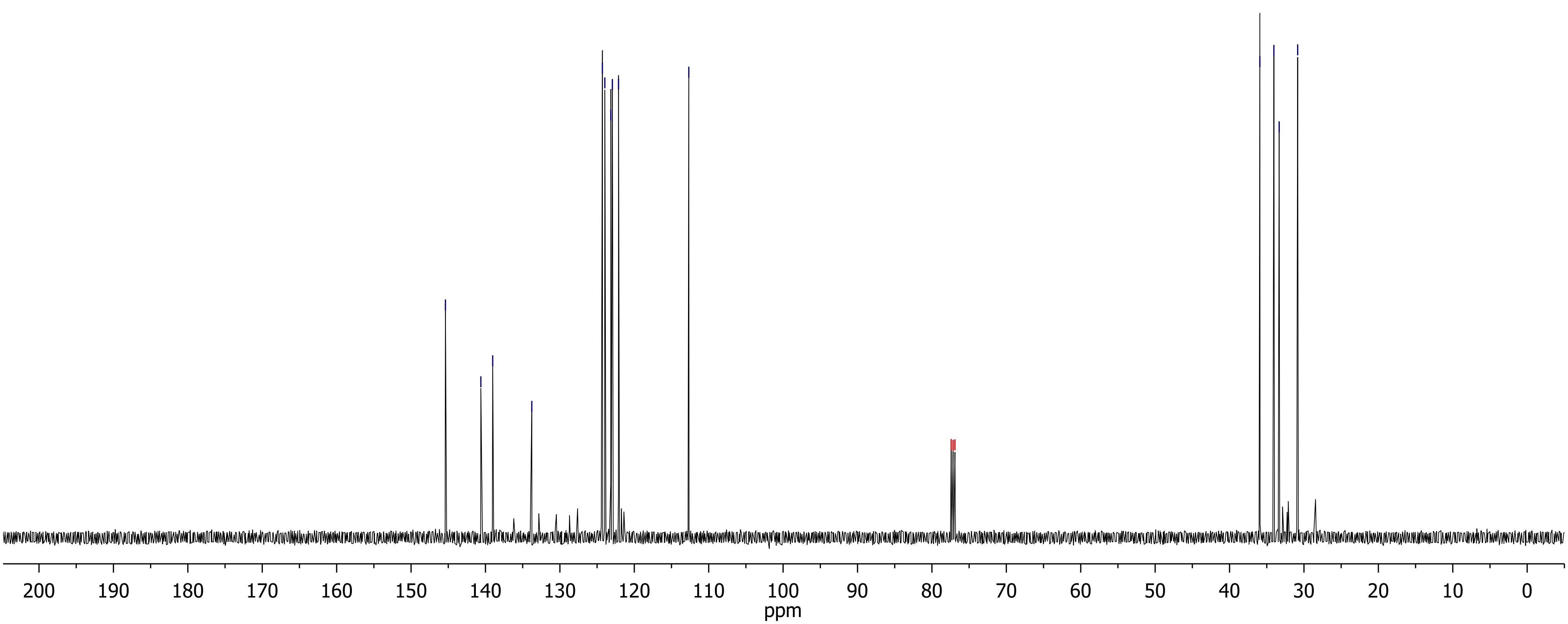


27

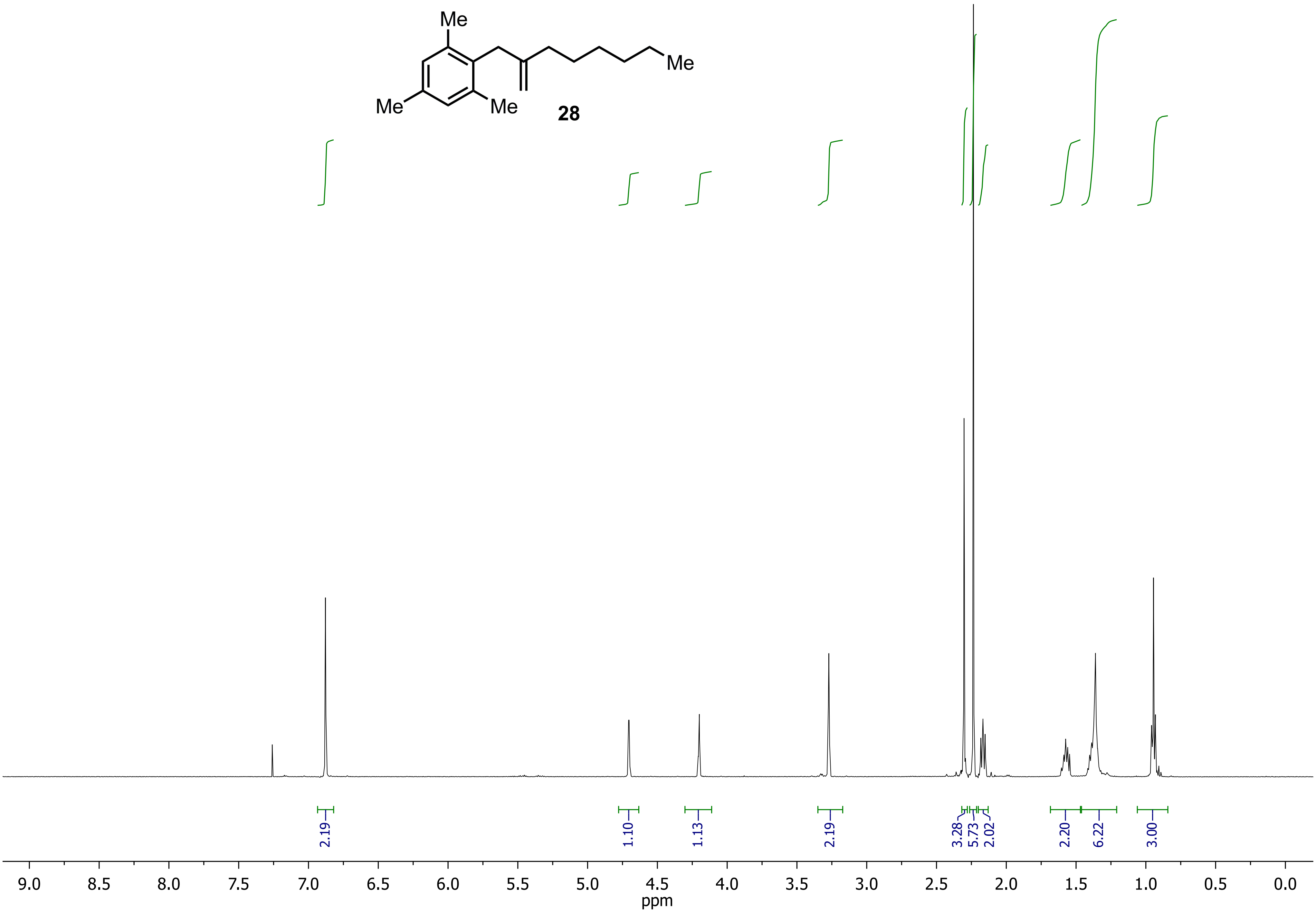
^{13}C (126 MHz, $CDCl_3$) - 27



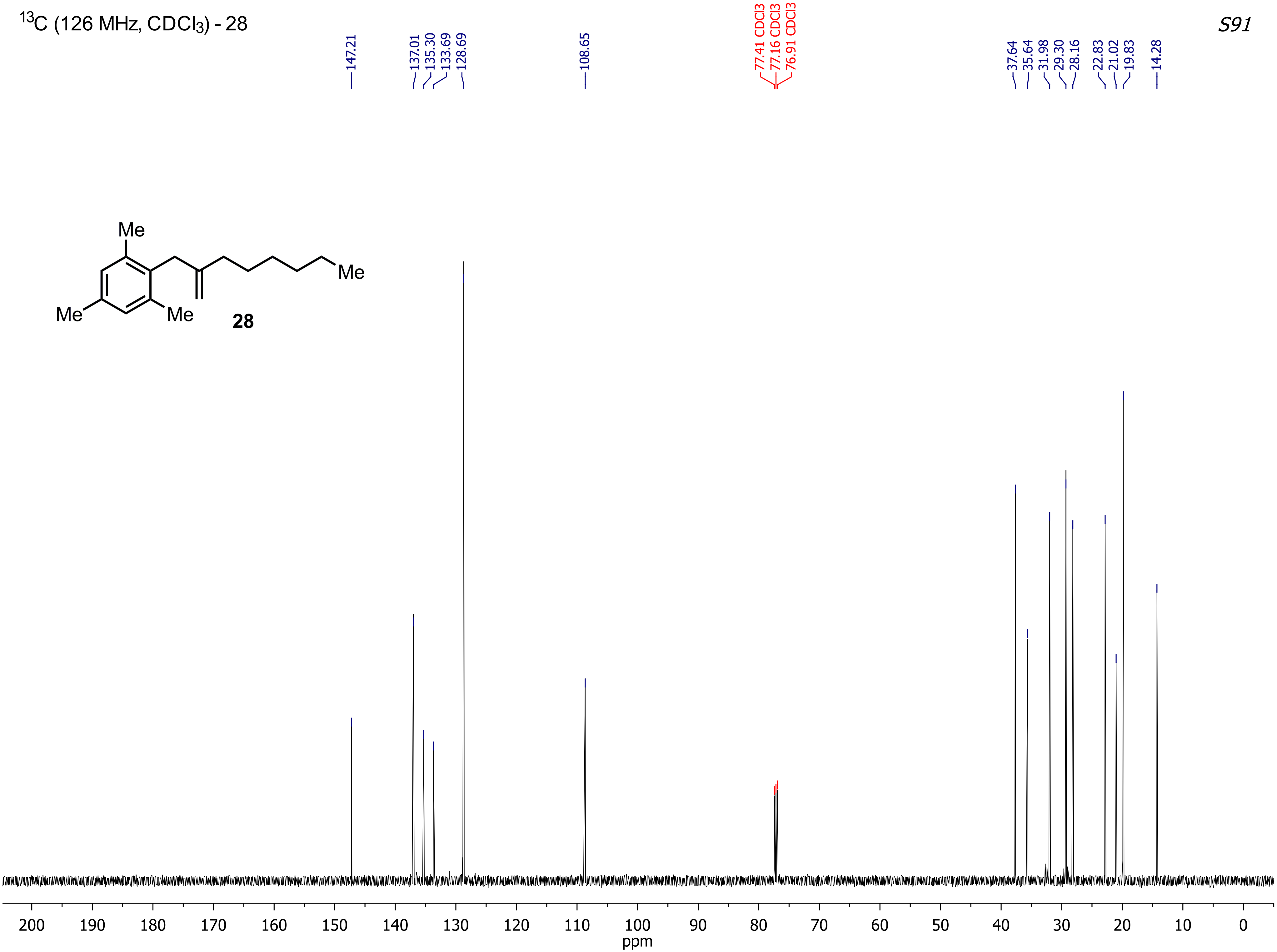
27



^{1}H (500 MHz, $CDCl_3$) - 28

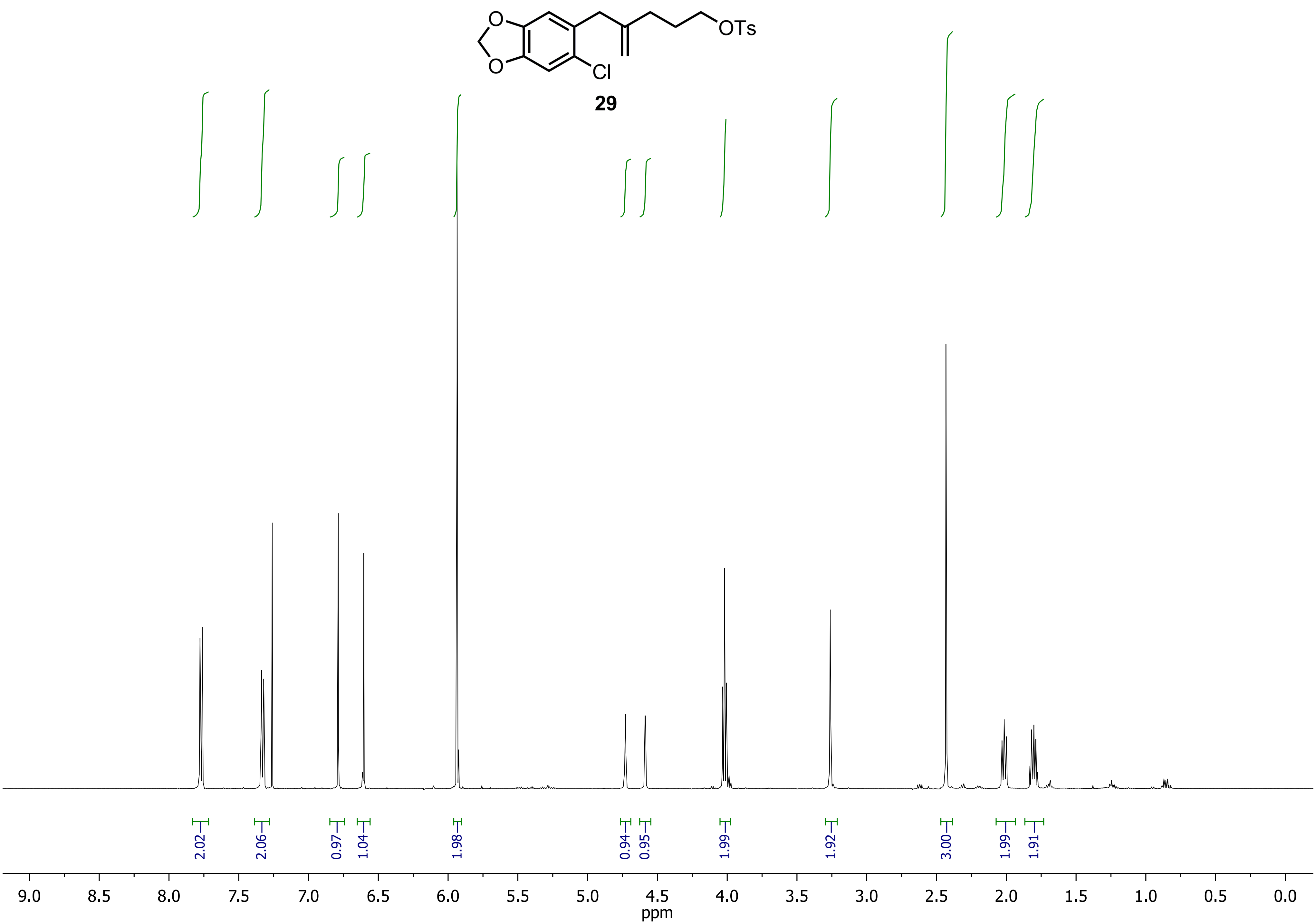


^{13}C (126 MHz, CDCl$_3$) - 28

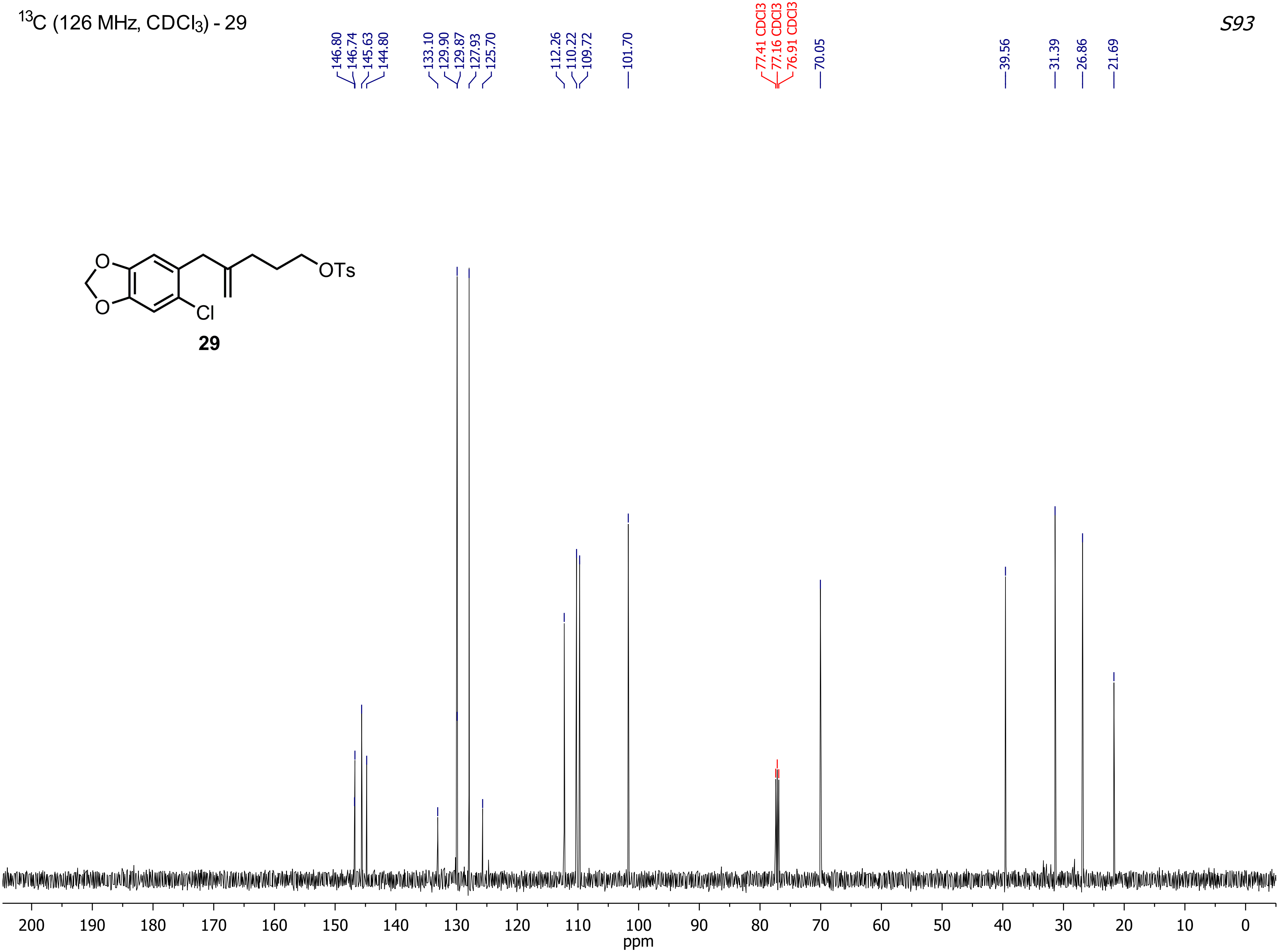


28

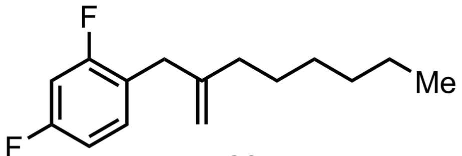
^{1}H (500 MHz, $CDCl_3$) - 29



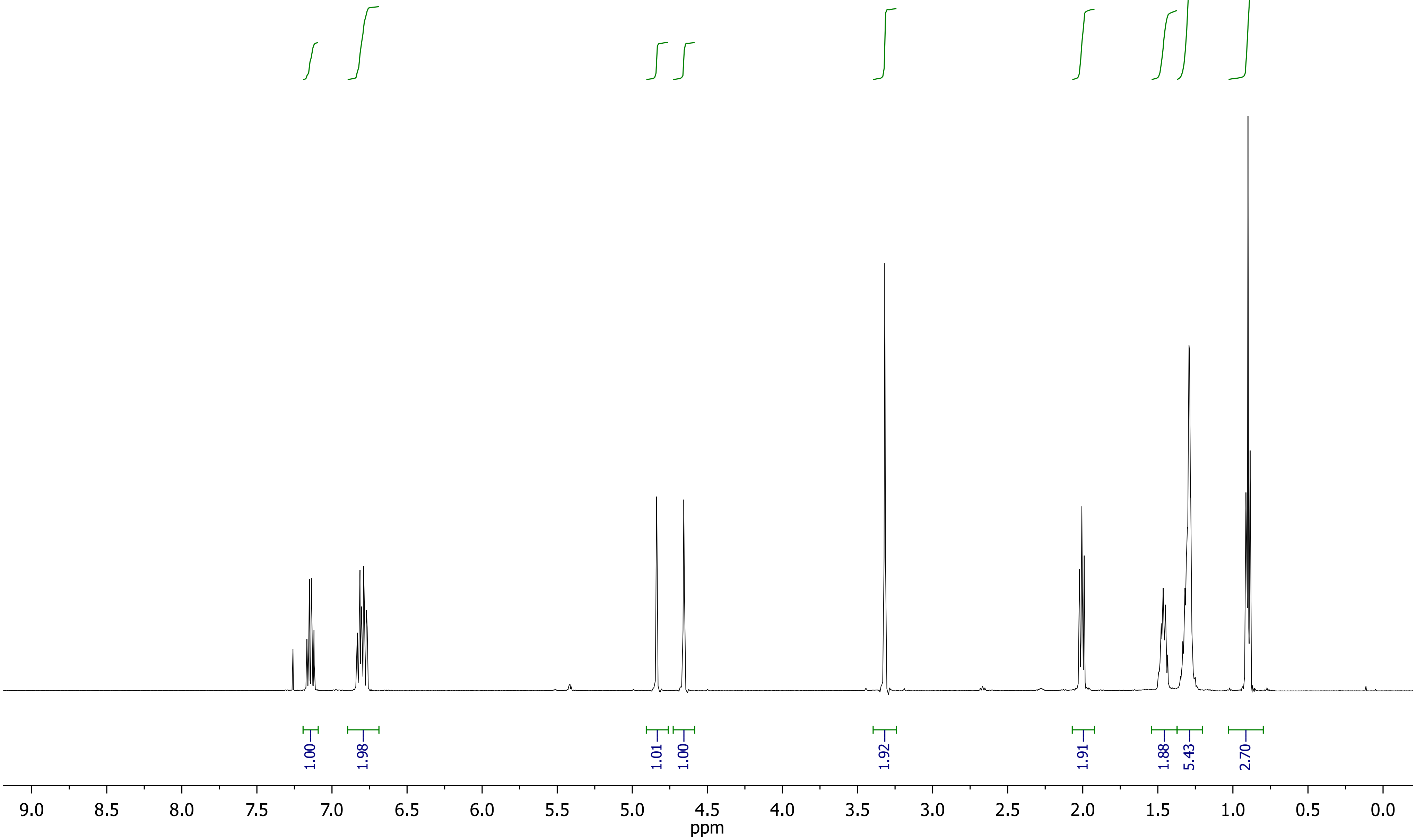
^{13}C (126 MHz, CDCl$_3$) - 29



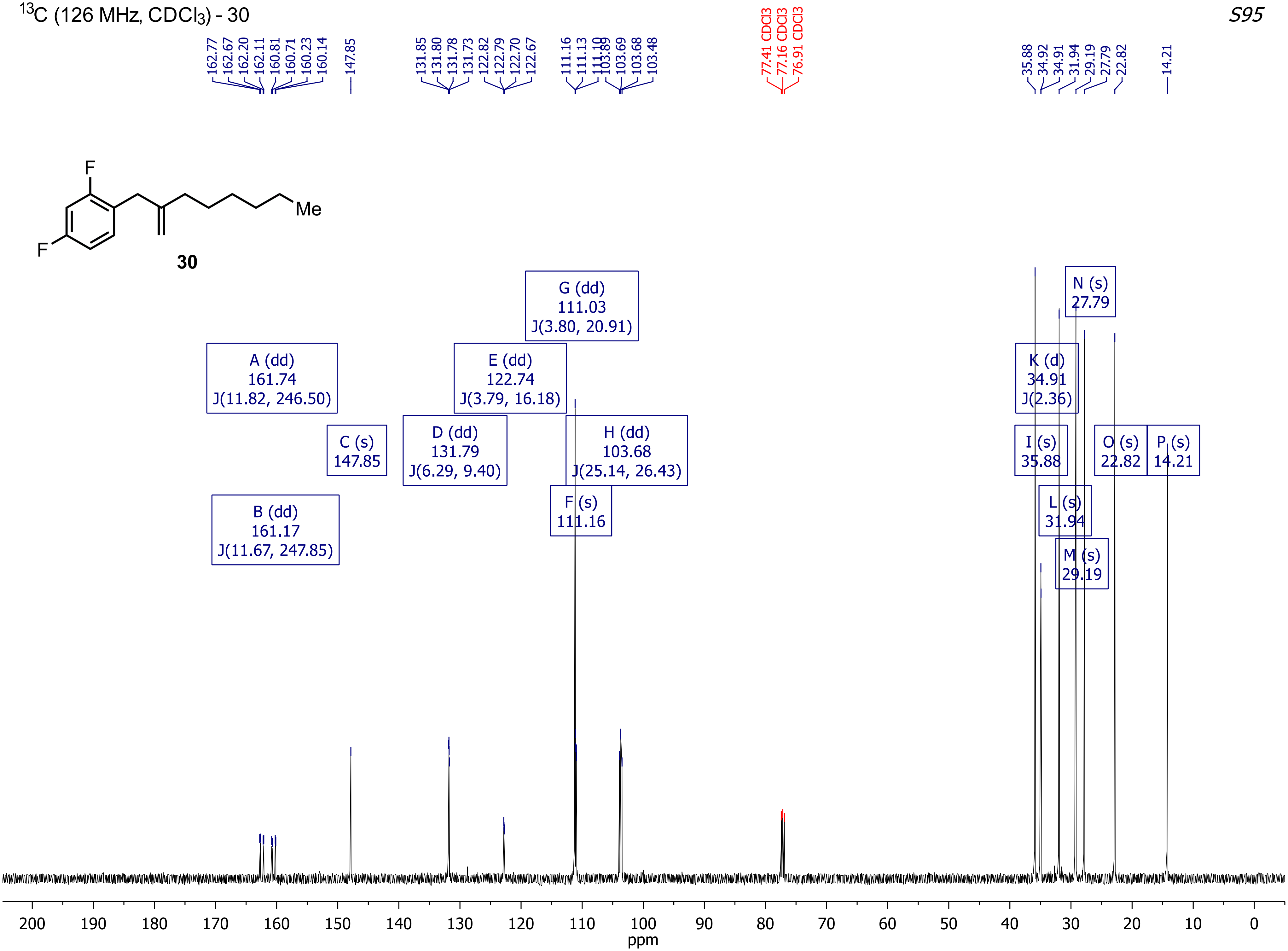
^{1}H (500 MHz, CDCl$_3$) - 30



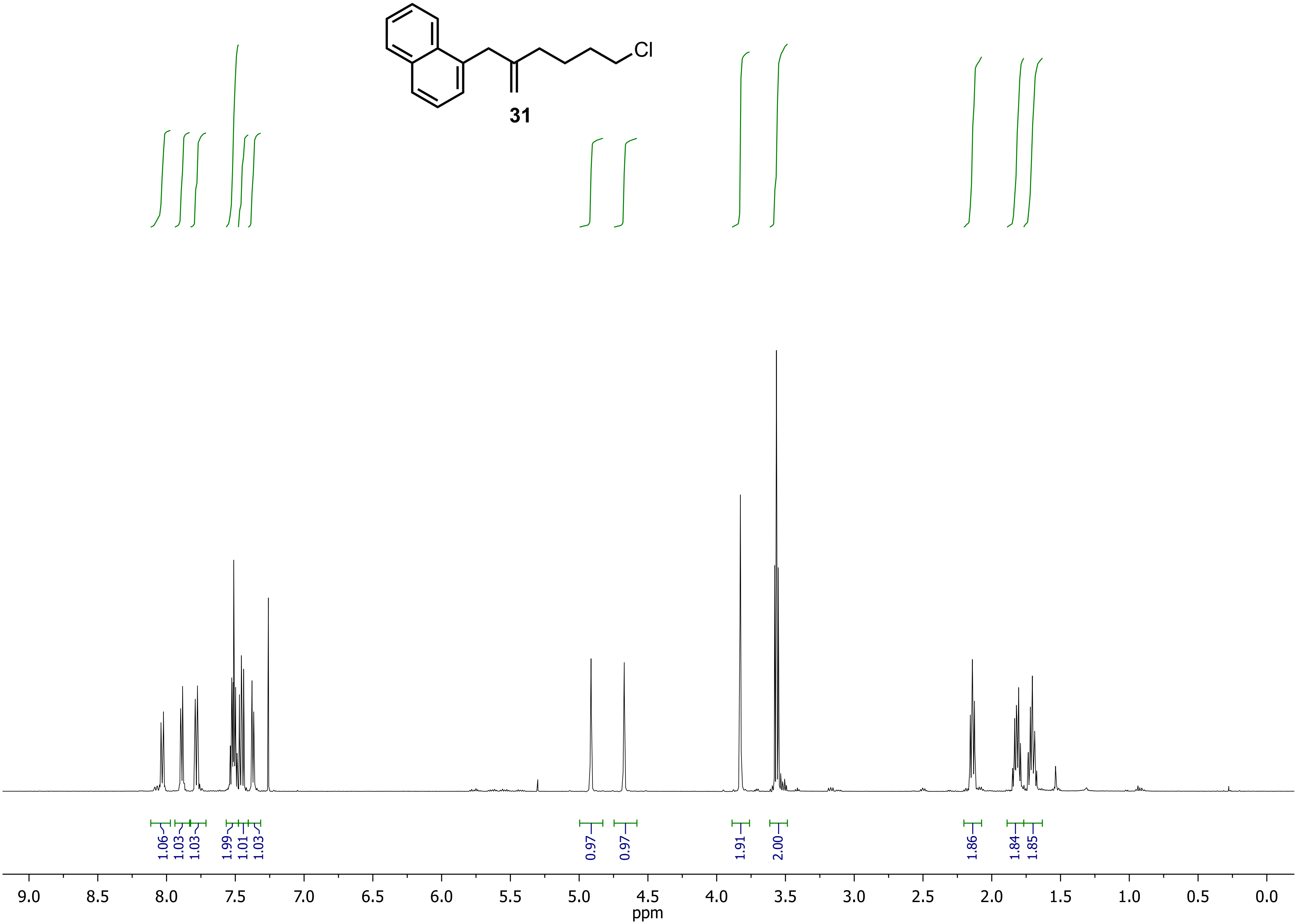
30



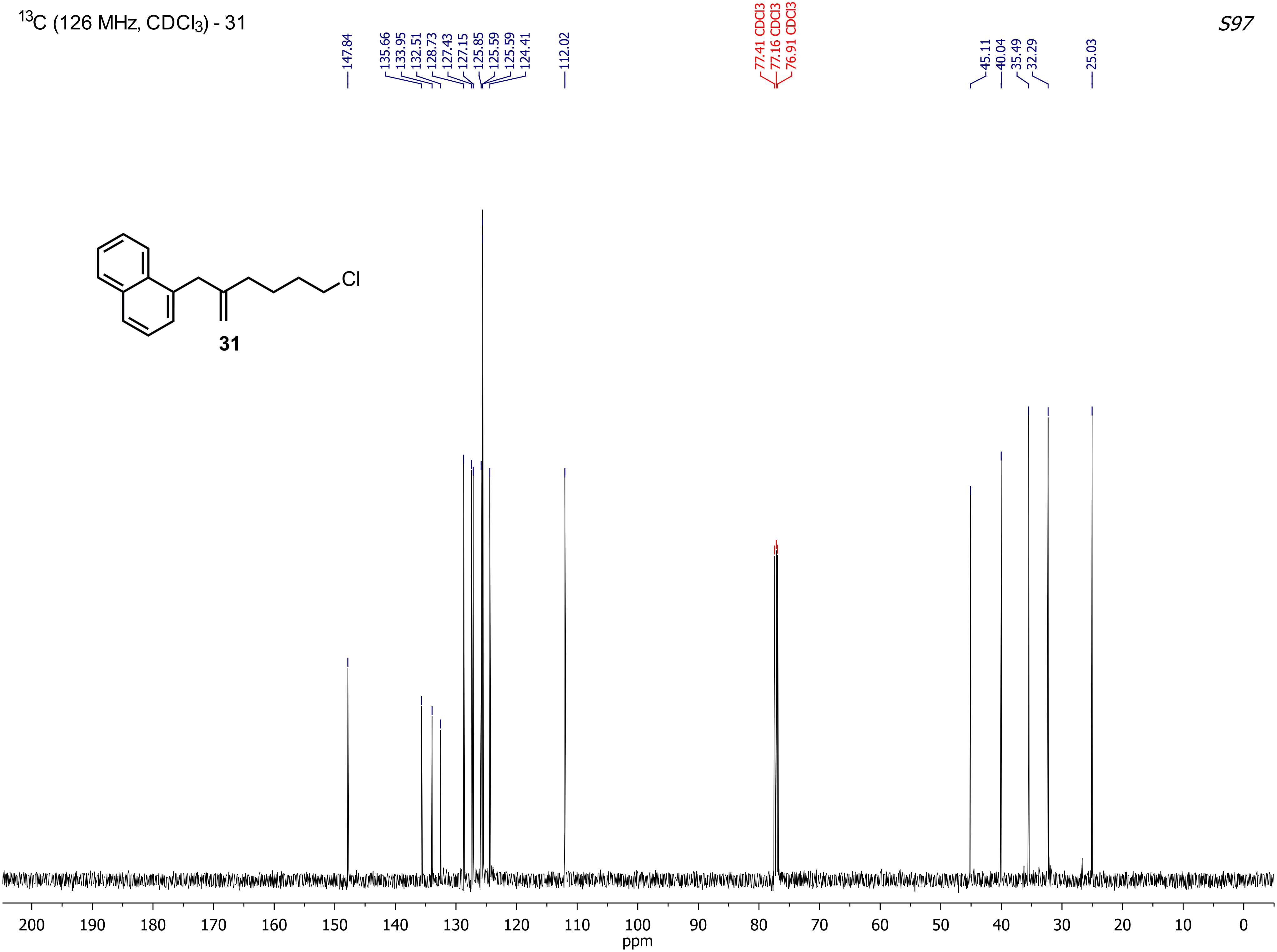
^{13}C (126 MHz, $CDCl_3$) - 30



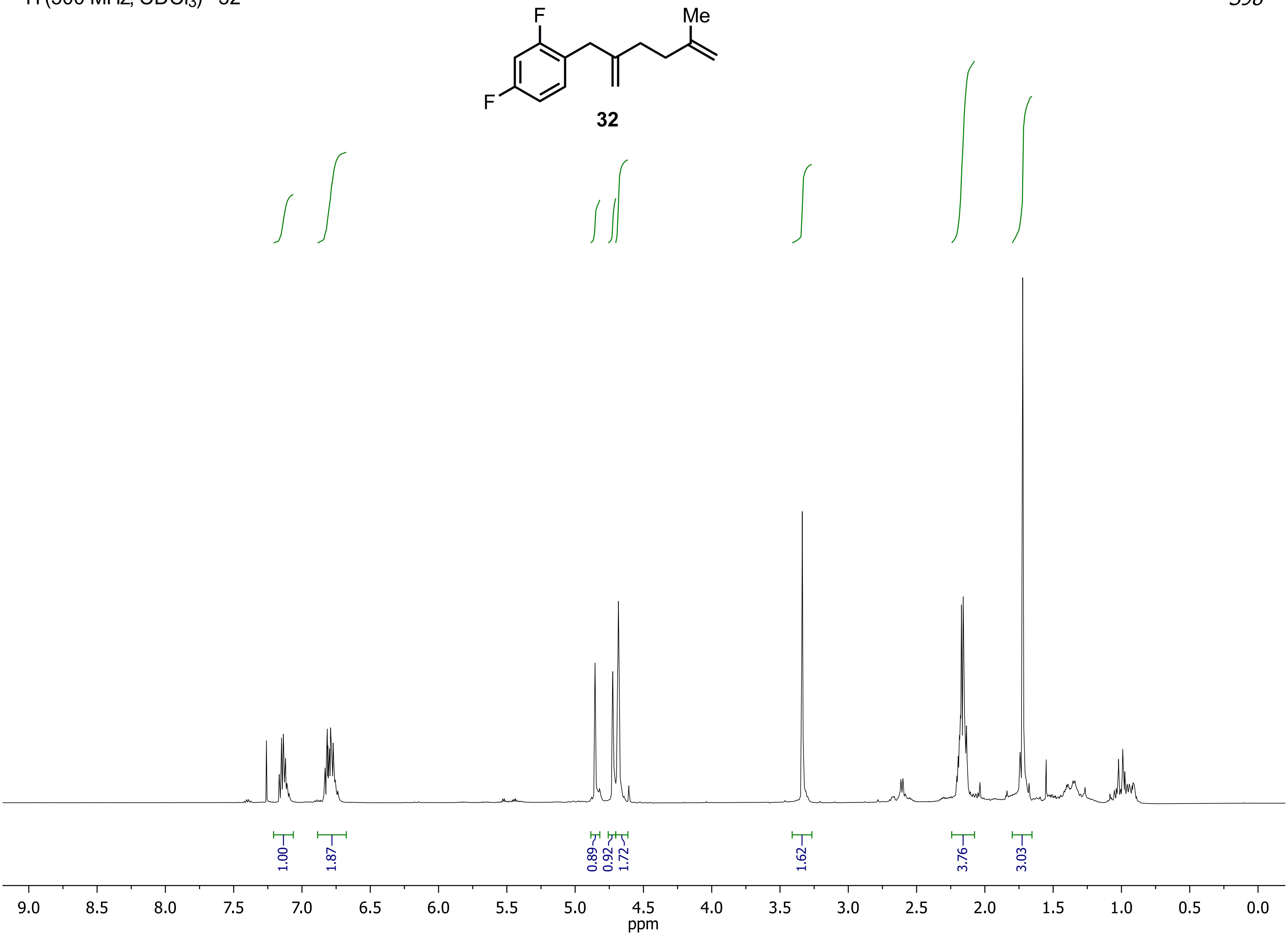
^{1}H (500 MHz, CDCl$_3$) - 31



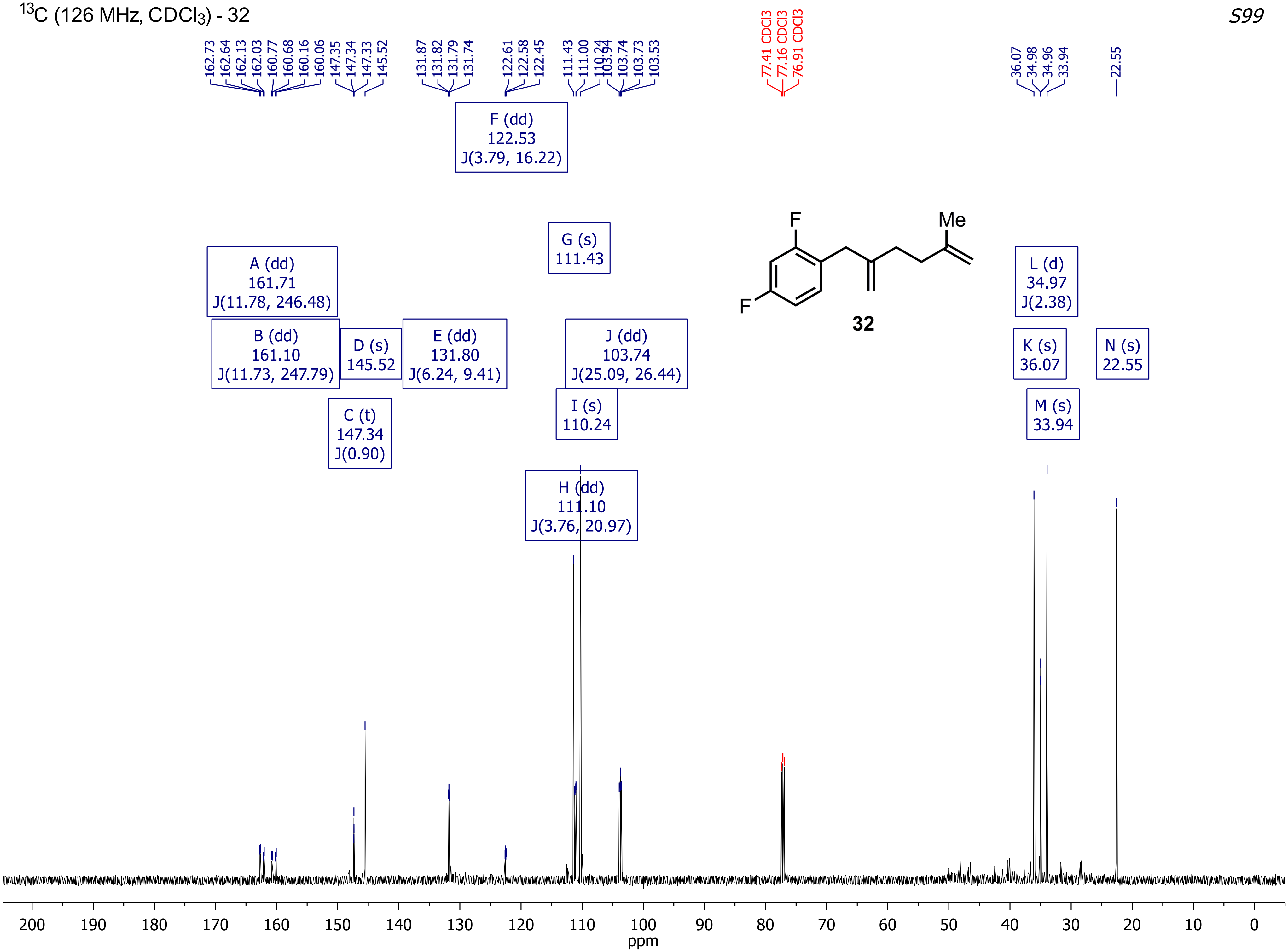
^{13}C (126 MHz, $CDCl_3$) - 31



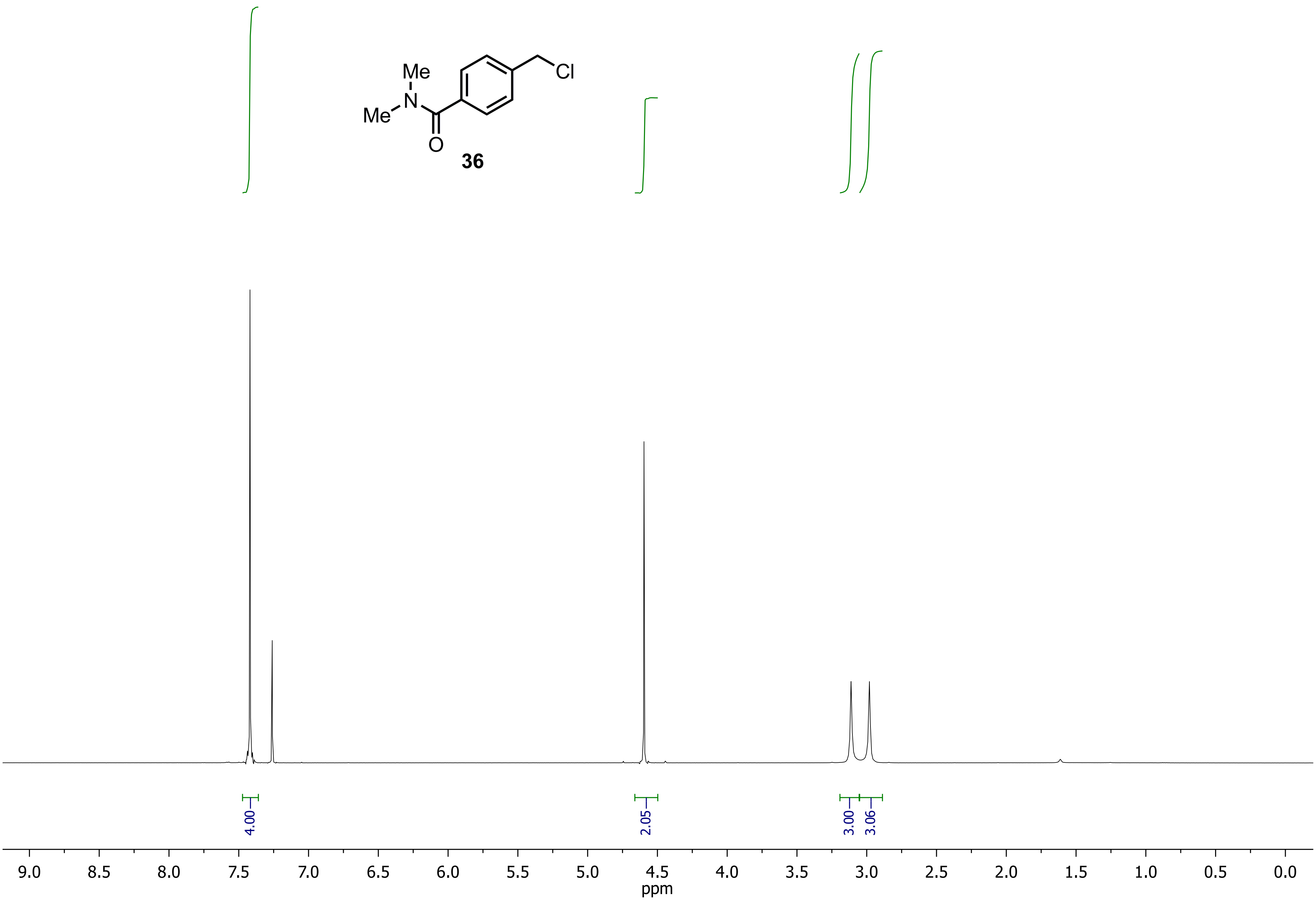
^{1}H (500 MHz, CDCl$_3$) - 32



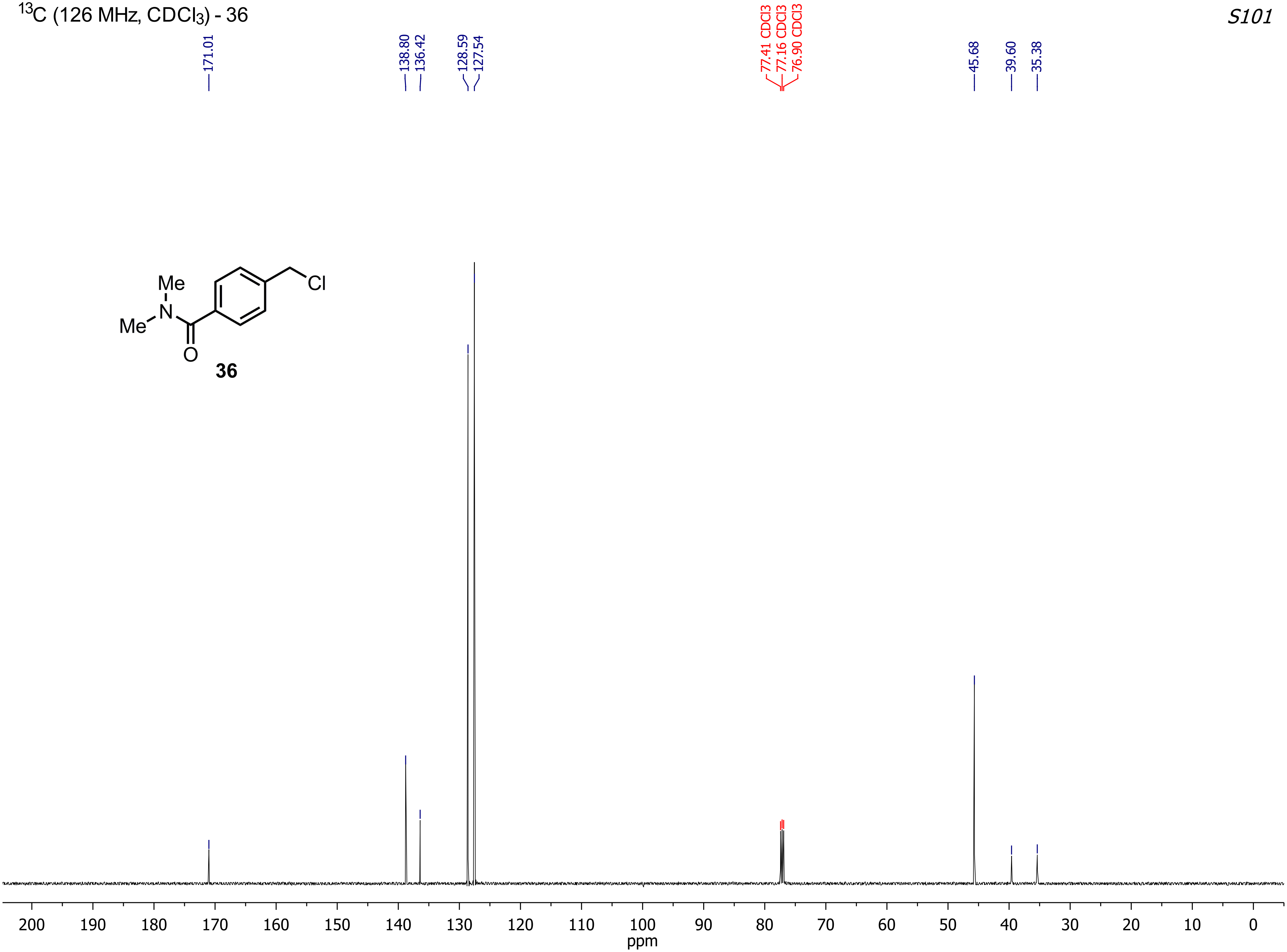
^{13}C (126 MHz, CDCl$_3$) - 32



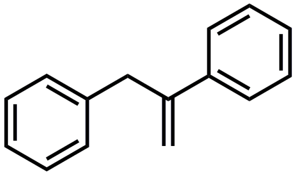
^{1}H (500 MHz, $CDCl_3$) - 36



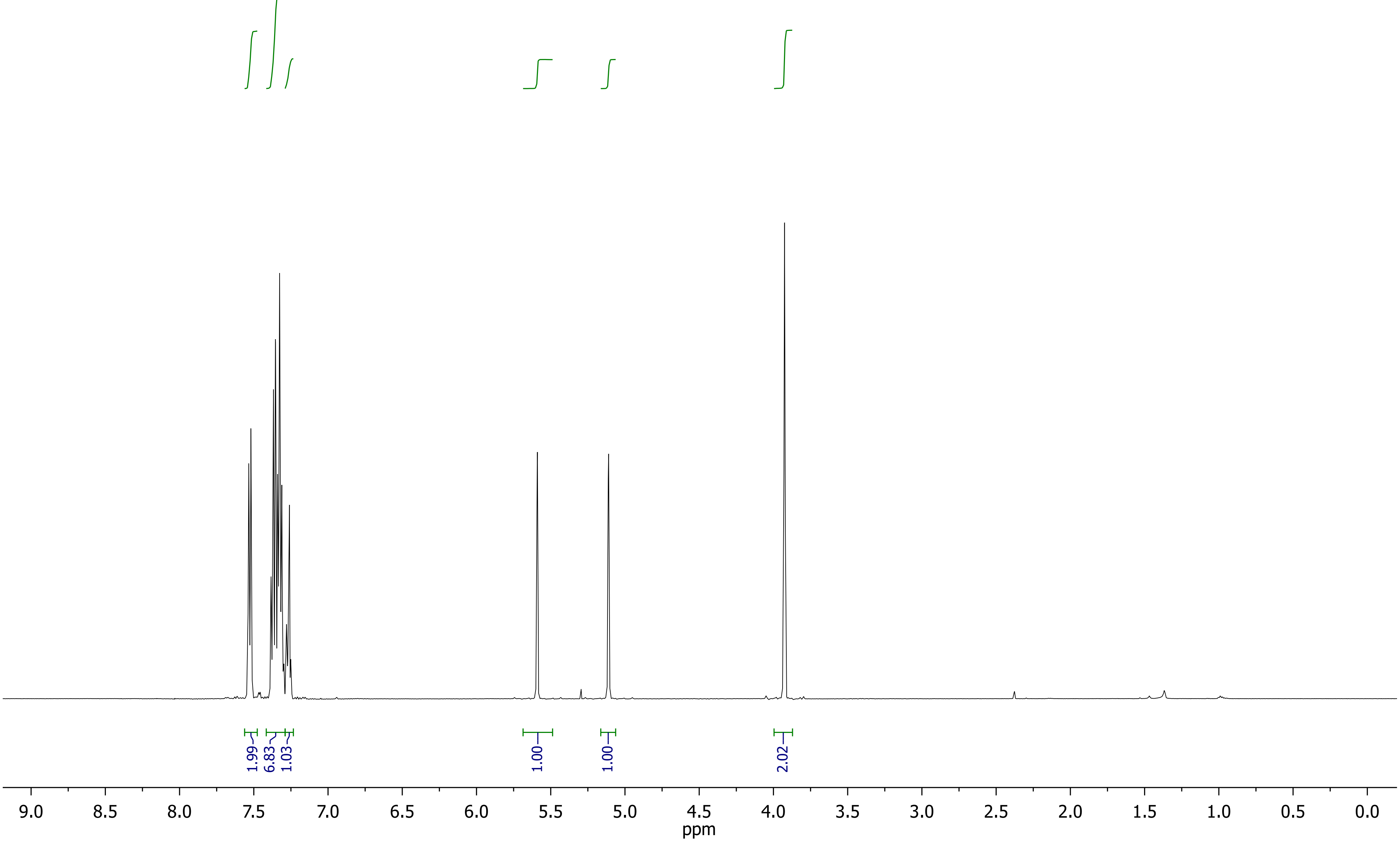
^{13}C (126 MHz, CDCl$_3$) - 36



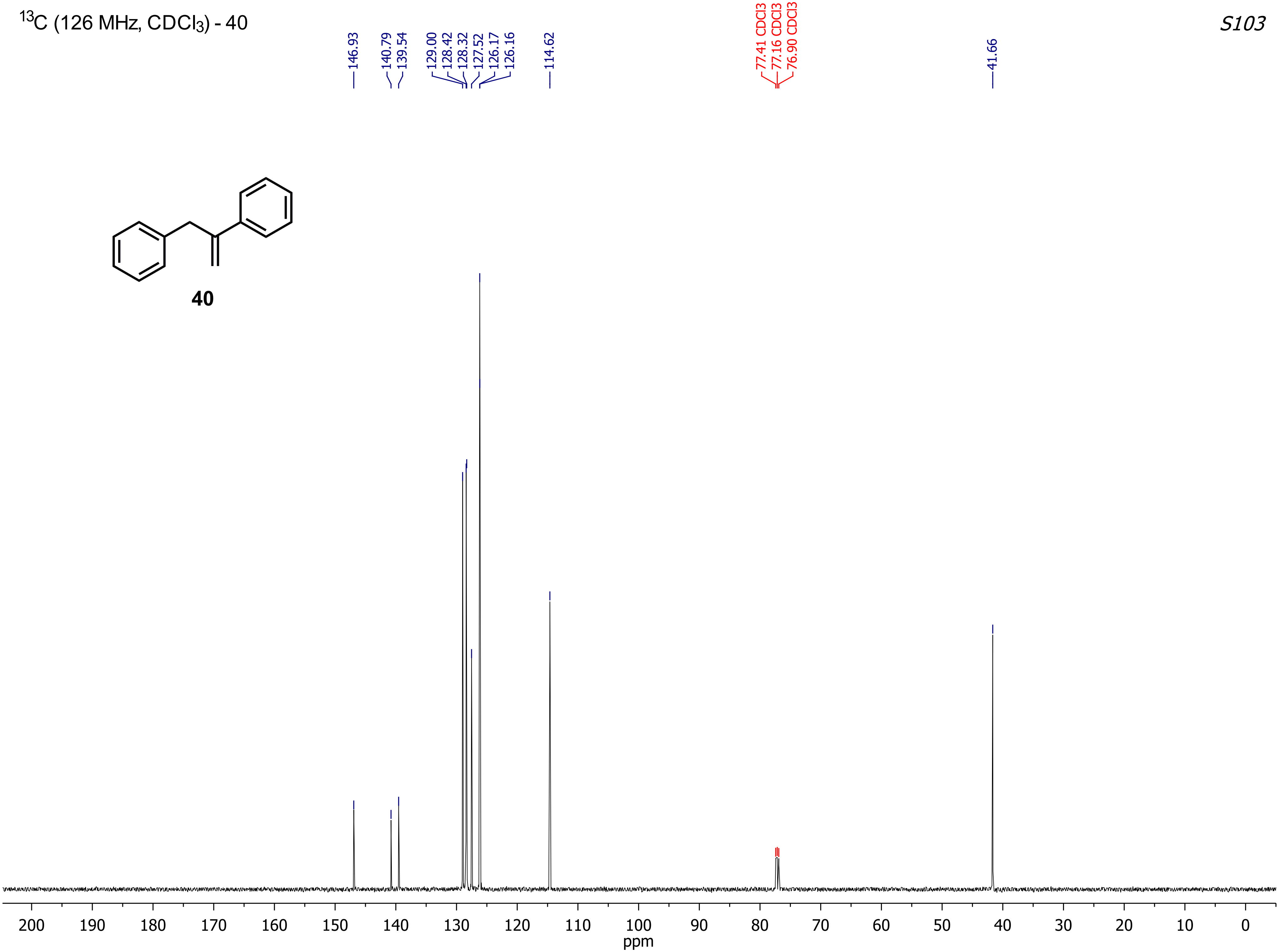
^{1}H (500 MHz, $CDCl_3$) - 40



40

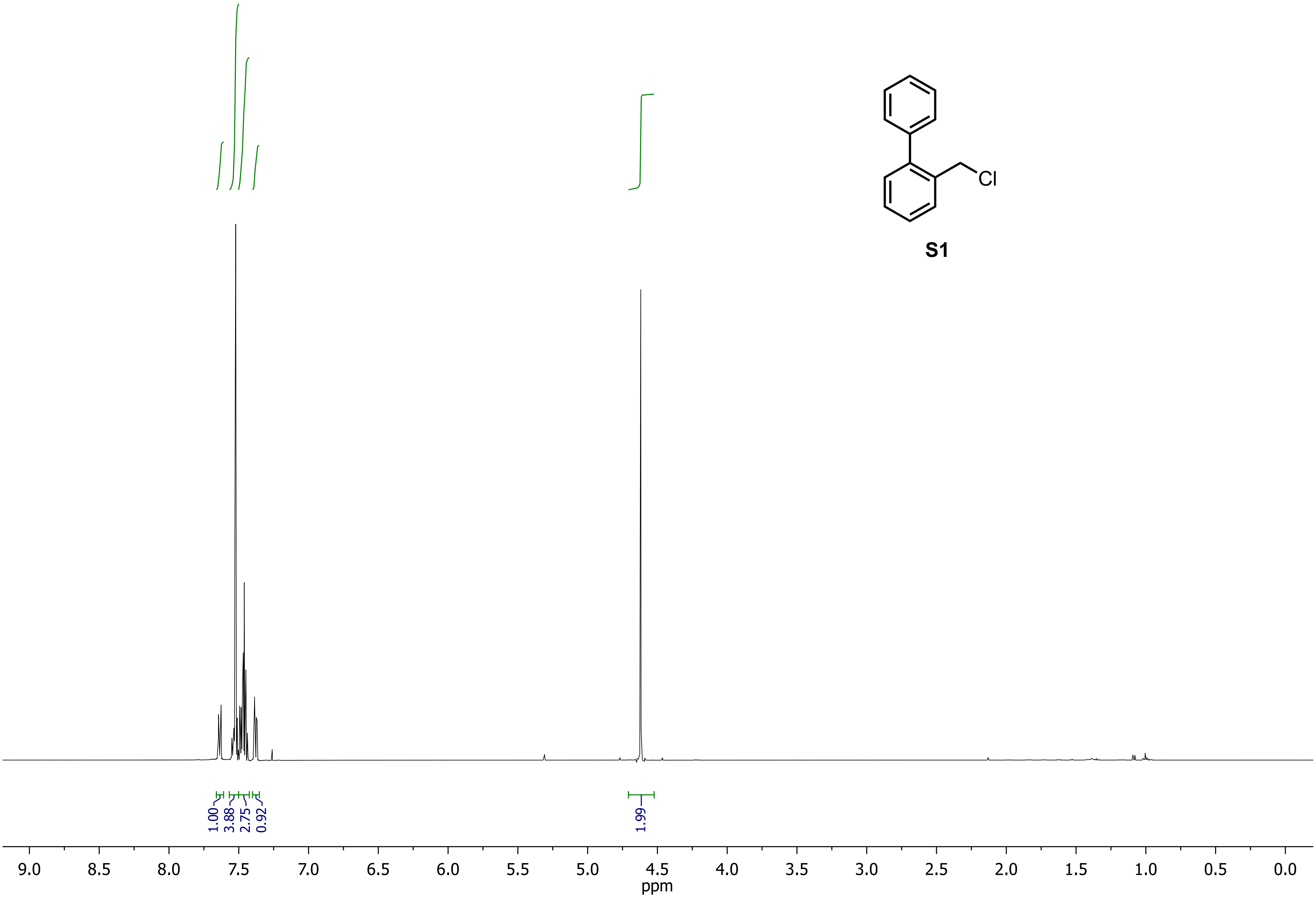


^{13}C (126 MHz, CDCl$_3$) - 40

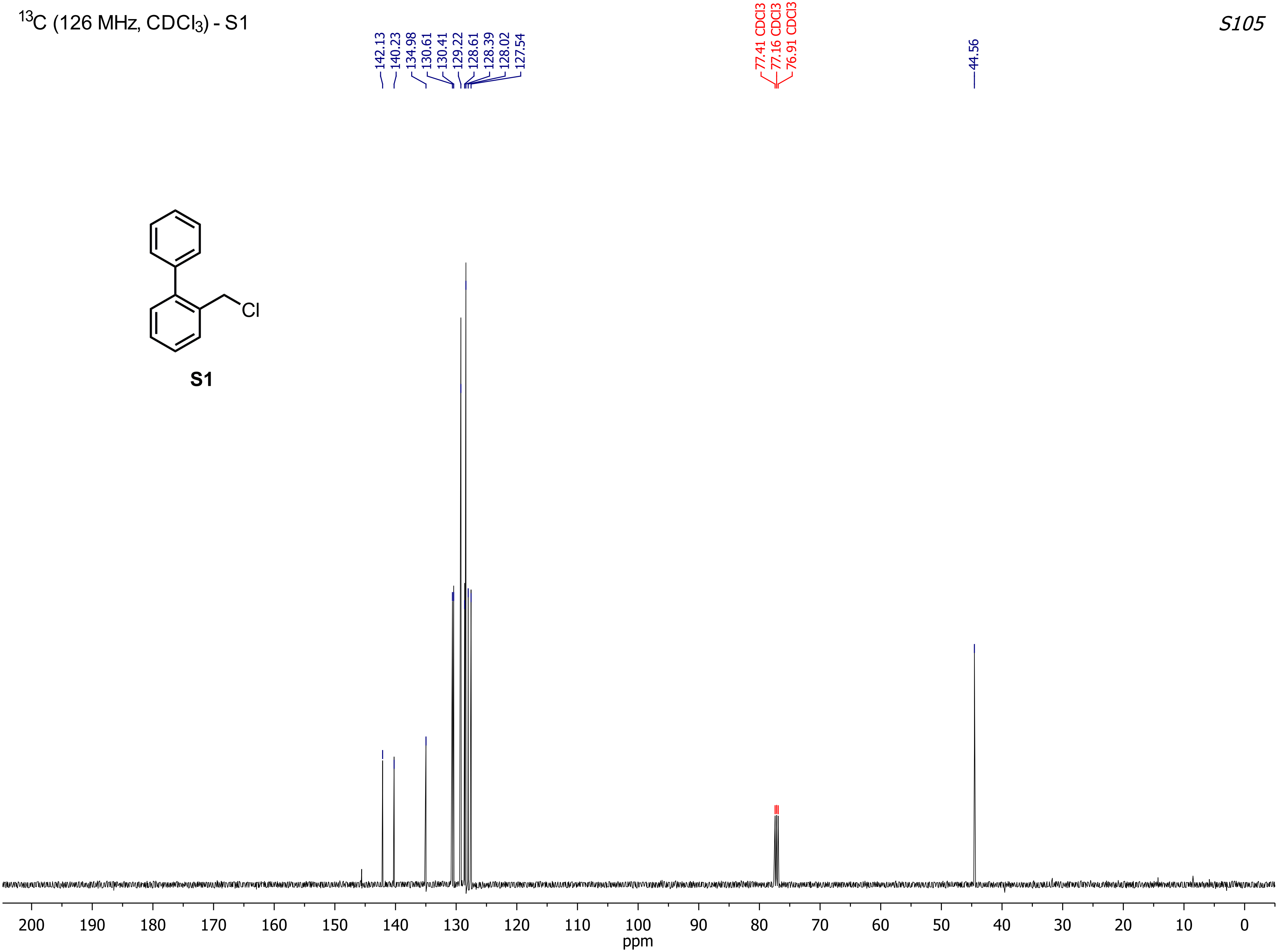


40

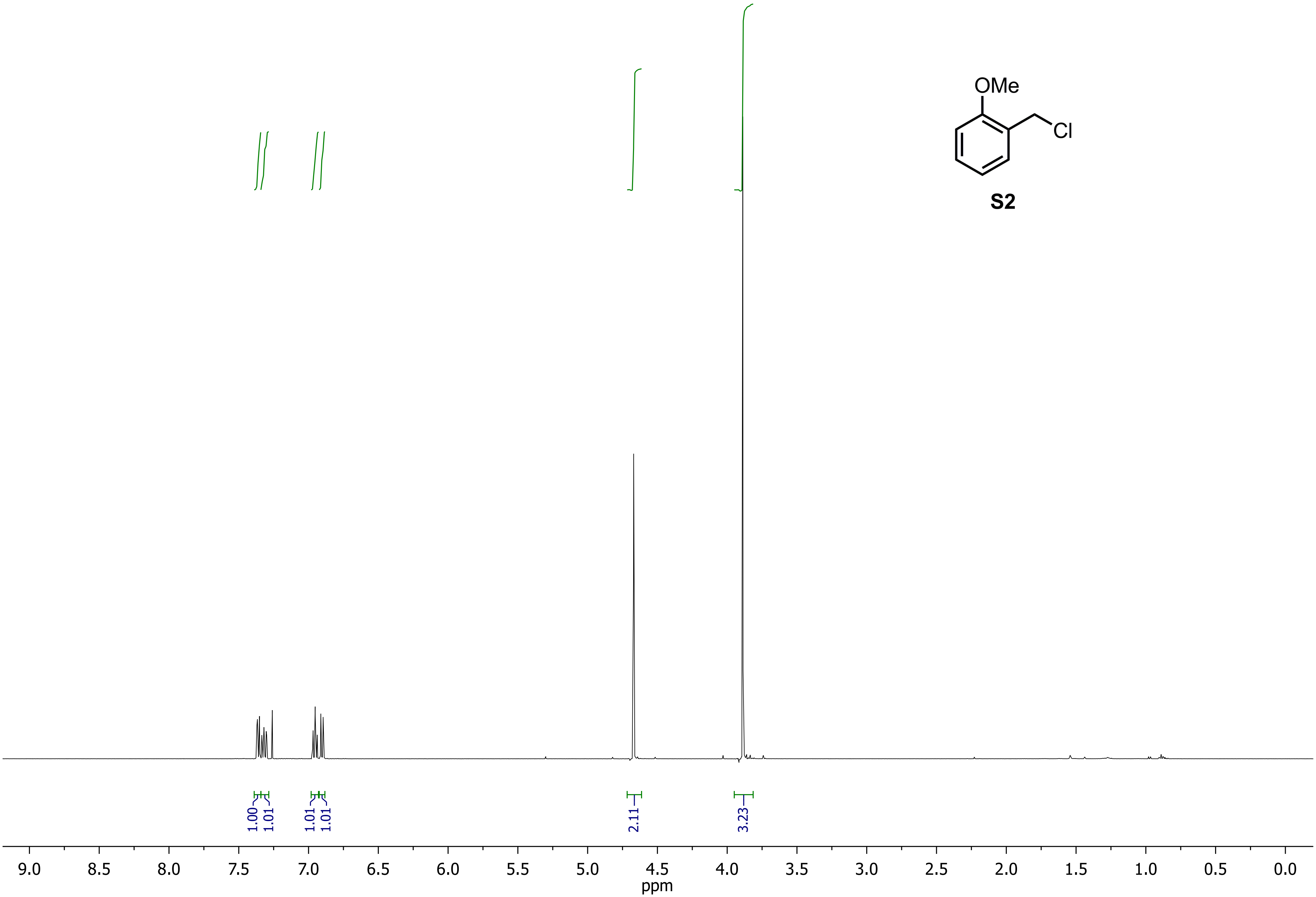
^{1}H (500 MHz, $CDCl_3$) - S1



^{13}C (126 MHz, $CDCl_3$) - S1

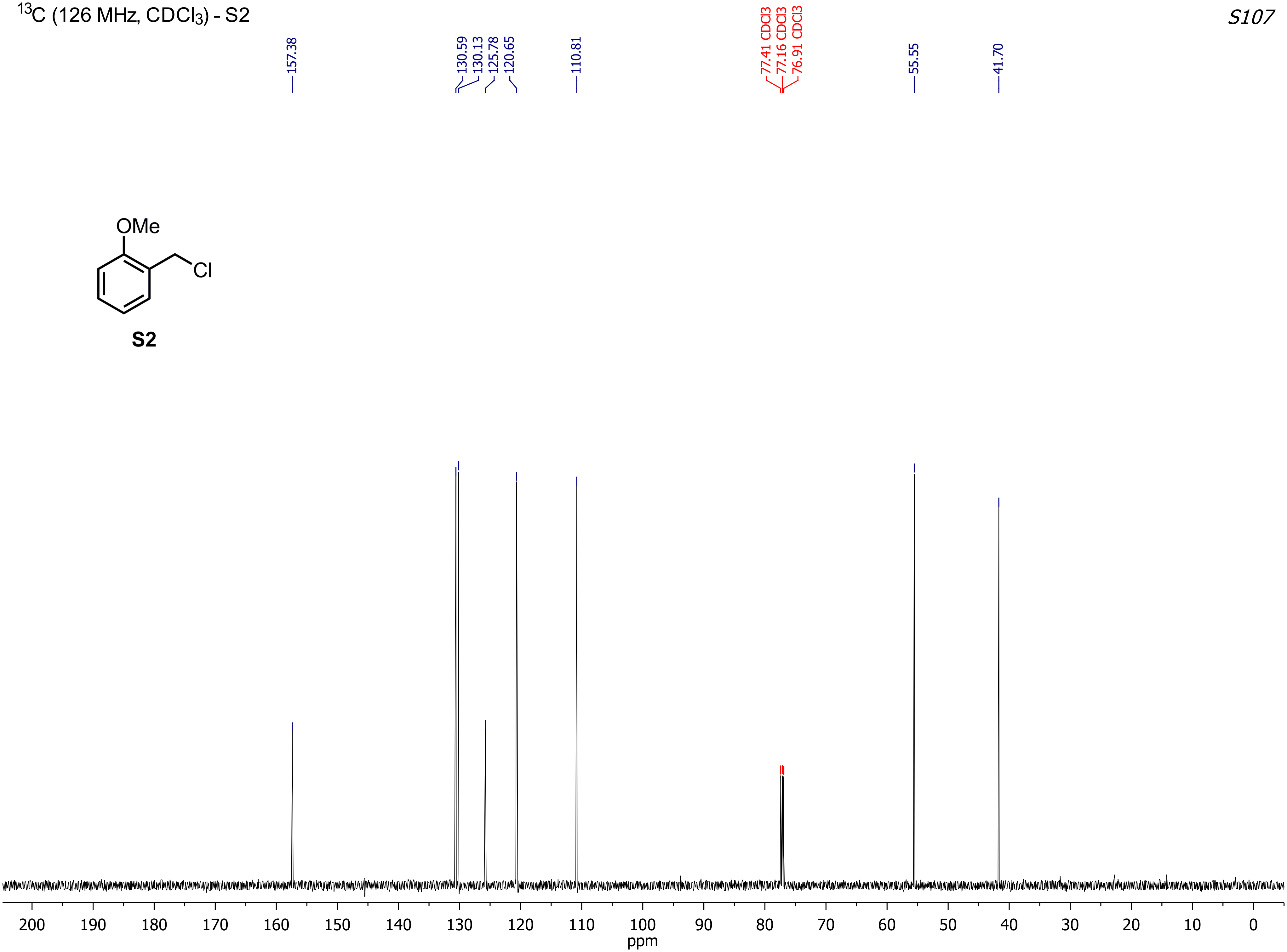


^{1}H (500 MHz, CDCl$_3$) - S2



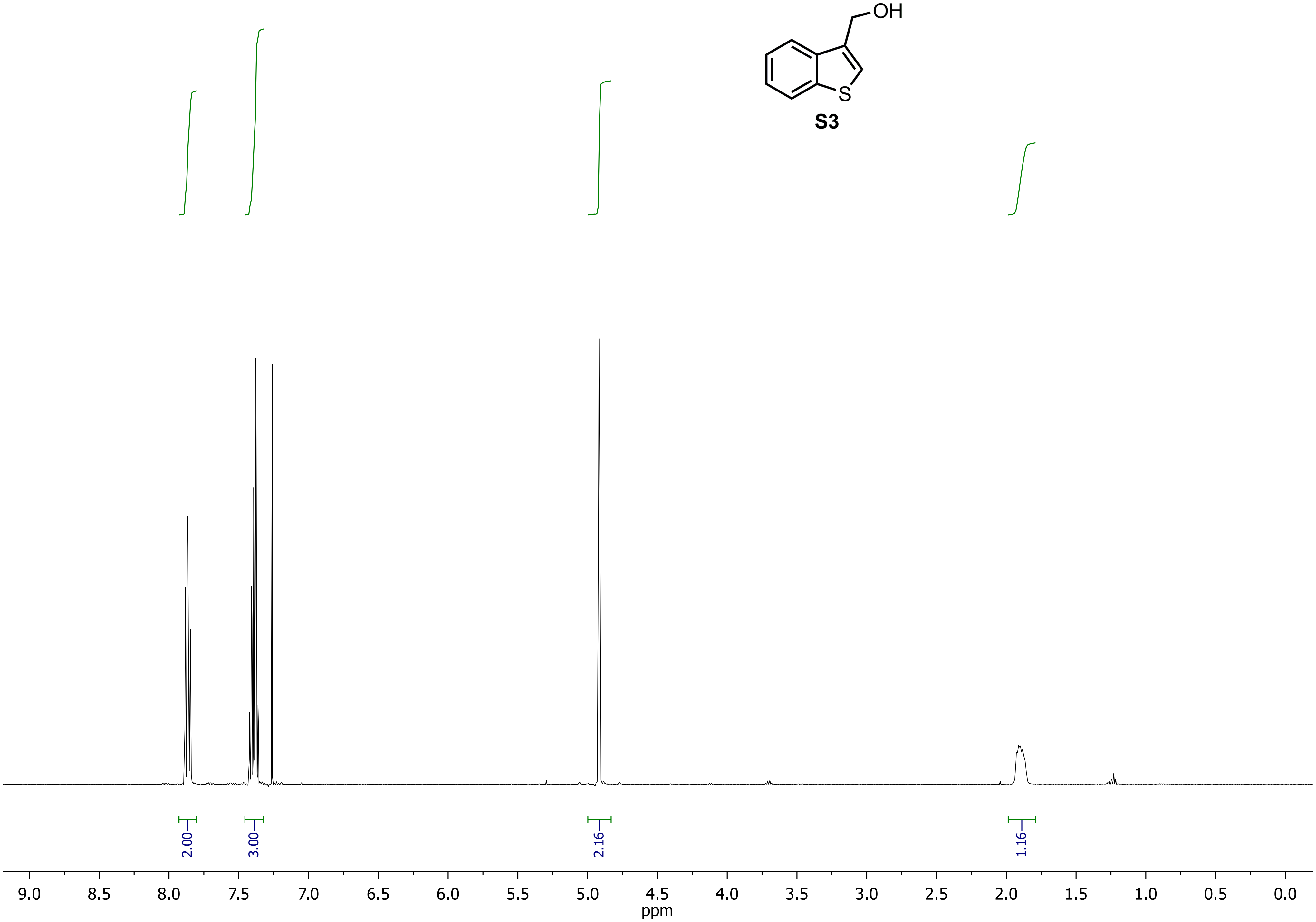
S2

^{13}C (126 MHz, CDCl$_3$) - S2

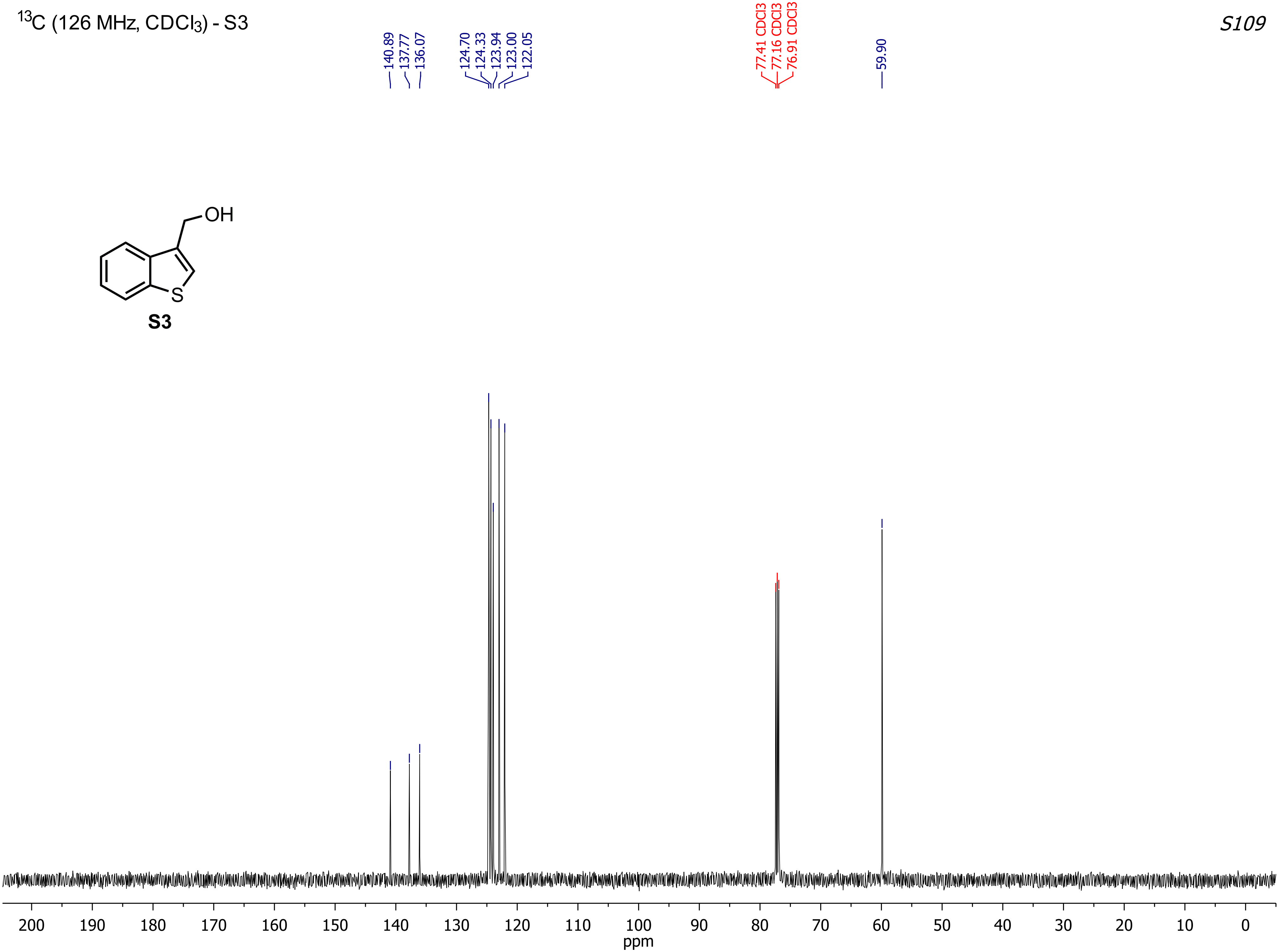


S2

^{1}H (500 MHz, CDCl$_3$) - S3

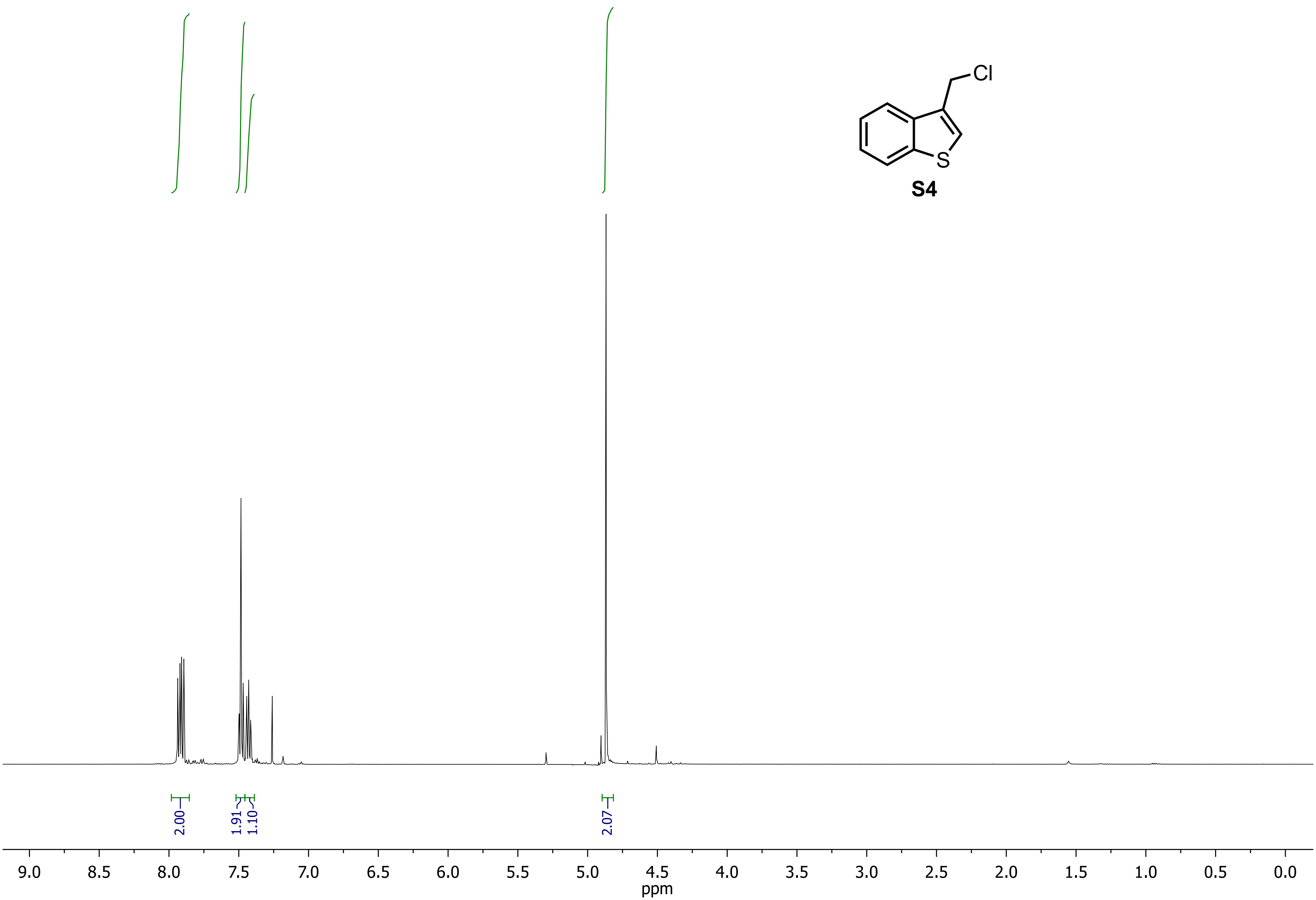


^{13}C (126 MHz, CDCl$_3$) - S3



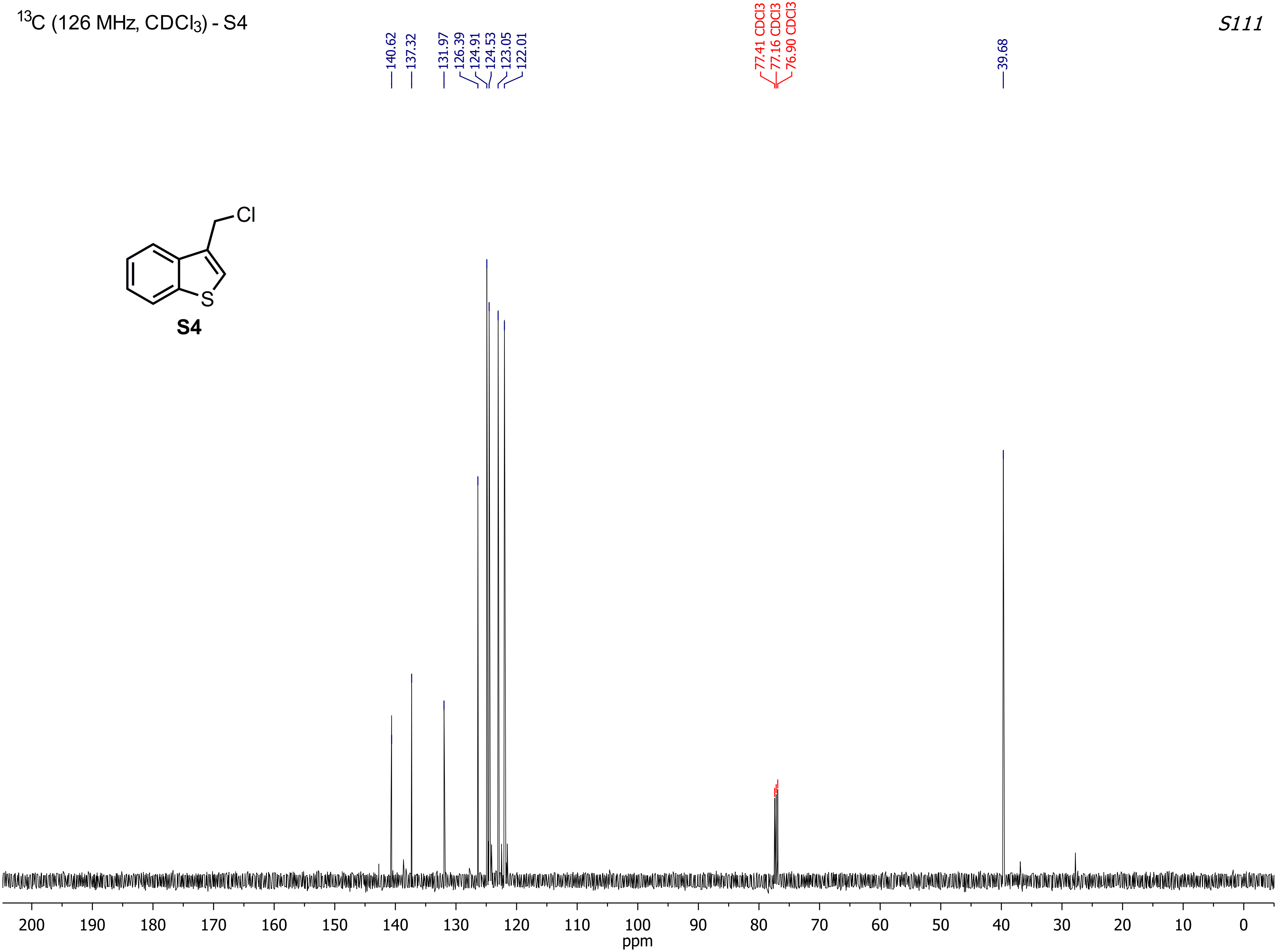
S3

^{1}H (500 MHz, CDCl$_3$) - S4

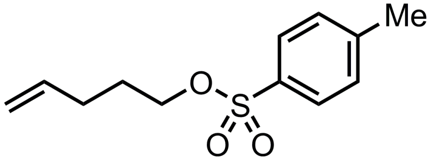


^{13}C (126 MHz, $CDCl_3$) - S4

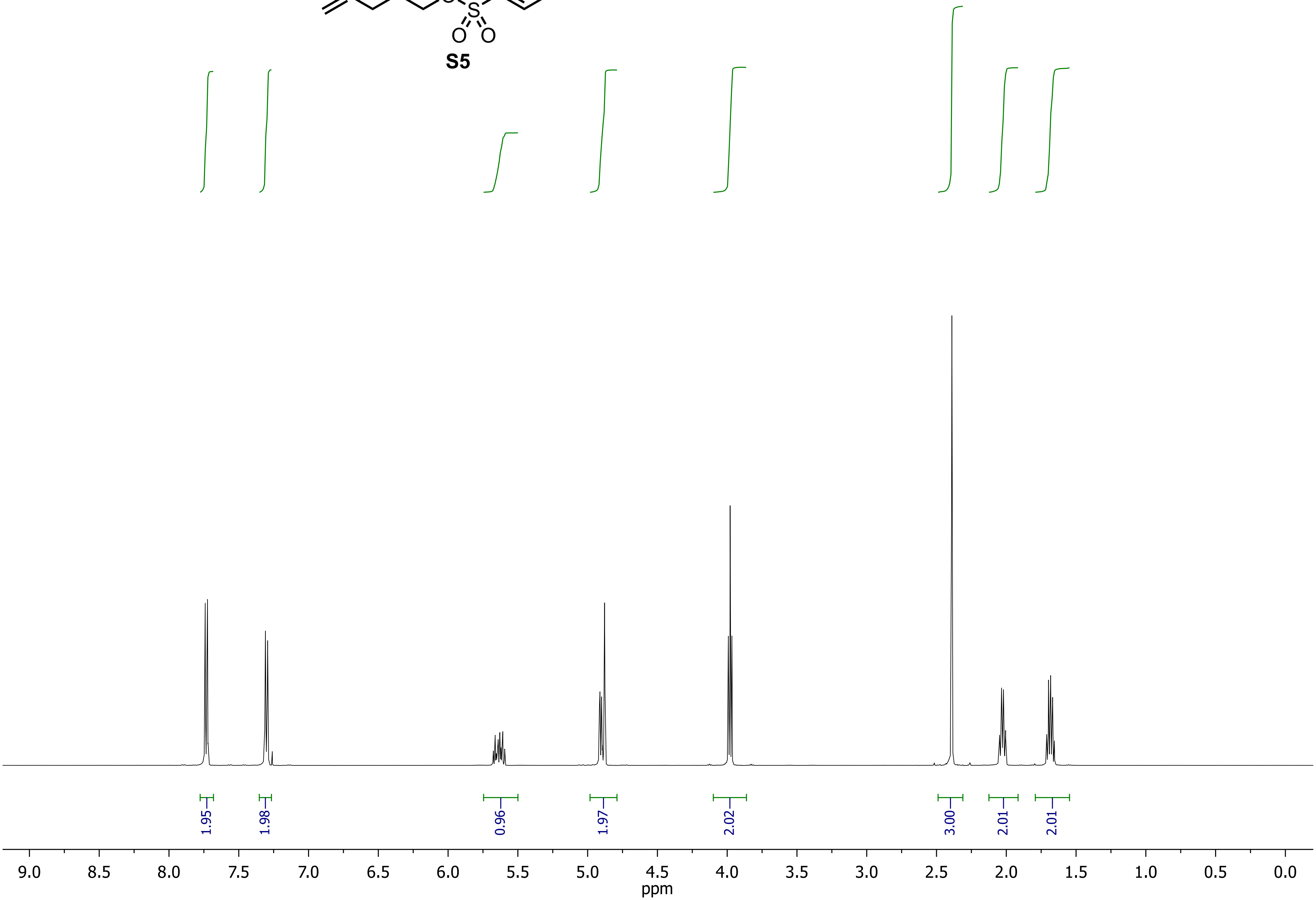
S4



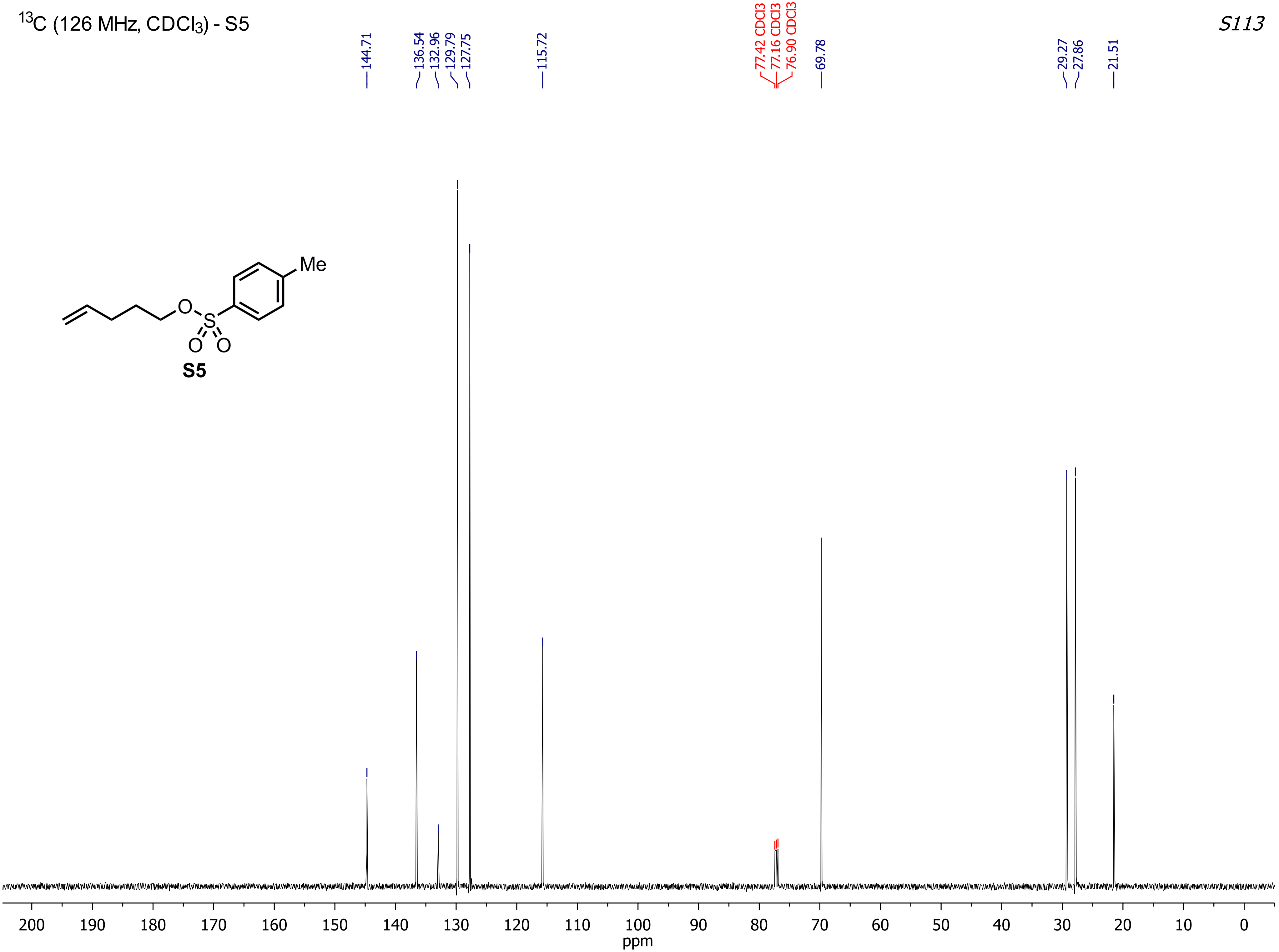
^{1}H (500 MHz, CDCl$_3$) - S5



S5



^{13}C (126 MHz, CDCl$_3$) - S5



S5