

Supporting Information For

Stereoselective Dynamic Cyclization of Allylic Azides: Synthesis of Tetralins, Chromanes, and Tetrahydroquinolines

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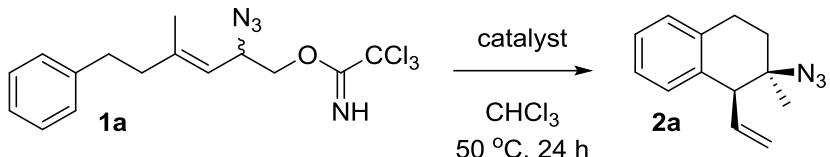
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Azide Precautions: Organic and inorganic azides are known to be high-energy materials and explosions have been reported with their use.¹ All of the azides reported herein were synthesized without incident; however, several precautions were taken. First, all azides synthesized herein have a C/N ratio of $\geq 3:1$. Second, reactions with more than 1 mmol of azide were placed behind safety shields both in the fume hood and during rotary evaporation. Third, all waste solutions (both organic and aqueous) that could be contaminated by azide were kept segregated in specially labeled containers and were kept STRICTLY free of acid to prevent incidental formation of HN₃.

General: All reactions sensitive to air or moisture were carried out in oven-dried glassware using standard Schlenk line techniques or were conducted using a glovebox (details are provided below). All reactions were mixed by magnetic stirring (100-600 rpm). All reactions conducted at elevated temperatures used aluminum block heating with an external thermocouple. Dry DCM and THF were obtained from a commercial solvent purification system using activated alumina columns and stored under a positive pressure of argon. Other reagents and solvents were purchased from commercial suppliers and were used as received. Reactions were monitored by gas chromatography or thin layer chromatography (TLC) using pre-coated plastic plates impregnated with a fluorescent indicator (254 nm). Visualization was carried out with UV light (254 nm), KMnO₄, or PMA stains. Column chromatography was performed using a Teledyne Isco CombiFlash R_f purification system utilizing normal phase pre-column load cartridges and gold high performance columns.

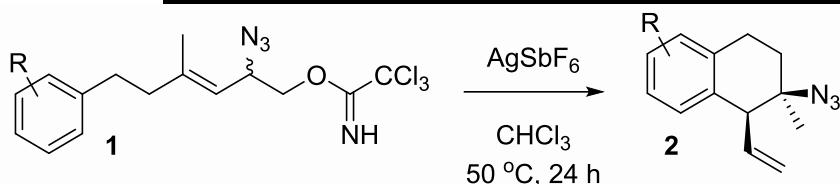
Instrumentation: All proton (¹H) NMR spectra were recorded at 400 or 500 MHz on a Bruker spectrometer. All carbon (¹³C) NMR spectra were recorded at either 101 or 126 MHz on a Bruker spectrometer. Chemical shifts are expressed in ppm and are referenced to residual solvent as an internal standard (¹H: CHCl₃, 7.27 ppm; ¹³C: CDCl₃, 77.2 ppm). Infrared (IR) spectra were performed as a film on NaCl plates on a Nexus 670 FT-IR and are reported in cm⁻¹. Gas chromatography (GC) was performed on a Shimadzu GC-2010 Plus using a SH-Rxi-5ms 15 m column and a flame ionization detector. The GC temperature ramp was as follows: Hold at 100 °C (1 min), 35 °C/min gradient (100-170 °C, 1.5 minutes), 3 °C/min gradient (170-180 °C, 3.3 min), 30 °C/min (180-250 °C, 2.3 min). Yields reported based on GC analysis were determined by linear regression of a 14-point calibration curve with naphthalene as the internal standard.

General Procedures for Reaction Optimization



Procedure for Catalyst Screen: A vial was charged with imidate **1a** (180 mg, 0.45 mmol) and naphthalene (19.0 mg, 0.15 mmol) before being transferred into a glovebox. Inside the glovebox, the vial containing imidate **1a** was charged with chloroform (3.6 mL). In the glovebox, separate vials were charged with varying catalysts (10 mol%) and a stir bar. To each vial containing catalyst, an aliquot of substrate solution (0.20 mL, 25 μmol) was added. The vials were sealed under nitrogen, removed from the glovebox, and heated to 50°C (external thermocouple) with a stir rate of 400 rpm. After 24 h, each reaction was cooled to rt and filtered through a plug of silica gel (100 % EtOAc). Yield and dr was determined through GC analysis with naphthalene as the internal standard.

General Procedure for Silver Catalyzed Resolution



General Procedure for Silver Catalyzed Resolution of Allylic Azides via Friedel-Crafts alkylation: Example given for $\text{R} = \text{H}$.

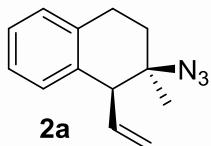
Compound 2a: In a glovebox, a 4 mL vial was sequentially charged with imidate **1a** (37.5 mg, 0.10 mmol) and silver hexafluoroantimonate (3.4 mg, 10 μmol , 10 mol %). To the mixture, CHCl_3 (1.0 mL, see note below) was added. The vial was sealed, removed from the glovebox, and placed in an aluminum block on a hot plate set to 50°C (external thermocouple) with a stir rate of 400 rpm. After 24 h, the resulting mixture was concentrated *in vacuo*, reconstituted in 1:1 DCM:hexanes and filtered through a short plug of silica gel, rinsing with 1:1 DCM:hexanes. This afforded tetralin **2a** (20.9 mg, 98 μmol , 98%) as a clear, colorless oil in a >25:1 dr. In a duplicate experiment, 38.5 mg of imidate **1a** afforded 16.3 mg of tetralin **2a** (75%) with a dr of > 25:1. The average yield of 87% is reported.

Procedure for Gram Scale Silver Catalyzed Resolution: In a glovebox an oven dried 100 mL round bottom flask was charged with silver hexafluoroantimonate (96.0 mg, 0.28 mmol, 10 mol %). Imidate **1a** (1.06 g, 2.81 mmol) was transferred into the flask using chloroform (3 x 10 mL). The flask was then sealed, removed from the glovebox, and heated to 50°C (external thermocouple) using an aluminum block with a stir rate of 400 rpm. After 24 h, the solution was cooled to rt and filtered to remove silver salts and rinsed with DCM:hexanes (1:2). The solution was then concentrated under reduced pressure to one third its original volume (~10 mL). Precipitated trichloroacetamide formed upon concentration and the solution was again filtered and rinsed with DCM:hexanes (1:2). The solution was then filtered through a short pass of silica gel and was rinsed with DCM:hexanes (1:2) to remove residual trichloroacetamide. The solution was concentrated under reduced pressure. This afforded compound **2a** (510 mg, 2.39 mmol, 85%) as a yellow oil. In a duplicate experiment, 1.1 g of imidate **1a** afforded 490 mg of tetralin **2a** (79%). The average yield of 82% is reported. The dr of the reaction was determined by crude ^1H NMR to be 33:1 and 20:1 in duplicate trials. The average dr of >25:1 is reported. Crude NMR of this reaction are provided in the spectral section.

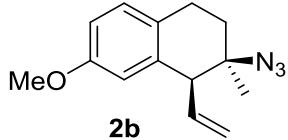
Note on solvent: This procedure used anhydrous chloroform stabilized with amylene (50-150 ppm). Chloroform stabilized with ethanol gave inferior results as did chloroform which was stored under ambient conditions. For best results, the salts, substrates, and solvent were transferred in a glovebox, after which the vials were sealed and removed from the glovebox. Procedures conducted under ambient conditions provided acceptable results, however these reactions occurred at a slower rate and were less reproducible. We speculate that adventitious water serves as a general base and inhibits ionization of the imidate under less rigorous condition.

Note: Several minor modifications were made based on the substrate. The most common of these are to 1) heat the reaction to different temperature (40°C – 60°C), 2) alter the catalyst loading (5% - 10% AgSbF_6), 3) change the reaction concentration (0.3 M – 0.05 M), or 4)

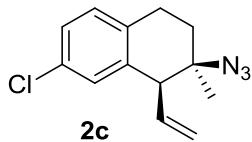
simplify final purification via a short pass of silica instead of a flash column. These variations are noted for each substrate below. The rate of the cyclization reaction was qualitatively dependent on the electron density of the arene. In general, a more electron rich arene required more mild conditions (lower temperature, more dilute, lower catalyst loading). An electron deficient arene required more vigorous conditions (higher temperature, more concentrated, higher catalyst loading). Substrates with a lower equilibrium concentration of the reactive isomer typically required higher temperatures but lower concentration and/or catalyst loading to reduce the rate of decomposition pathways relative to the Winstein rearrangement. These general trends were used as a first approximation for the optimal reaction conditions. Typically, a small screen of 4-9 reactions was conducted to find optimal conditions within these ranges for each substrate.



¹H NMR: (CDCl₃, 400 MHz) δ 7.20-7.10 (m, 4H), 5.87 (ddd, *J* = 17.1, 10.0, 9.1 Hz, 1H), 5.32 (dd, *J* = 10.1, 1.9 Hz, 1H), 5.17 (dd, *J* = 16.9, 1.4 Hz, 1H), 3.33 (d, *J* = 7.0 Hz, 1H), 3.07 (ddd, *J* = 17.1, 8.7, 6.5, 1H) 2.83 (dt, *J* = 17.4, 6.0, 1H), 2.17 (dt, *J* = 13.6, 6.0, 1H), 1.84 (ddd, *J* = 13.9, 8.5 6.4, 1H), 1.46 (s, 3H); **¹³C NMR:** (CDCl₃, 126 MHz), δ 137.7, 135.7, 134.5, 129.5, 128.7, 126.5, 126.1, 119.0, 62.1, 54.1, 32.0, 26.1, 24.3; **IR** (NaCl, thin film, cm⁻¹), 3076, 2927, 2855, 2100, 1637, 1491, 1452, 1259, 1127, 1110, 999, 921, 840, 468, 741; **HRMS** (EI-TOF) *m/z* calcd for C₁₃H₁₅(M-N₃)⁺, 171.1168, found 171.1169.

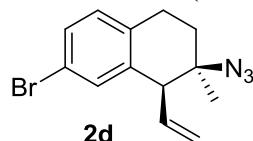


Compound 2b: A variation of the general procedure was used. The reaction was conducted at 0.30 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (2:1 DCM:hexanes). This afforded compound **2b** as a white solid in 87%, 73%, and 71% yield in triplicate trials. The average yield of 77% is reported. Compound **2b** was isolated in 11.3:1, 10.3:1, and 10.3:1 dr in triplicate trials. The average dr of 11:1 is reported. **¹H NMR** (500 MHz, CDCl₃) δ 7.05 (d, *J* = 8.4 Hz, 1H), 6.75 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.71 – 6.69 (m, 1H), 5.90 (dt, *J* = 17.1, 10.1, 9.0 Hz, 1H), 5.36 (dd, *J* = 10.1, 1.9 Hz, 1H), 5.19 (dd, *J* = 17.0, 1.1 Hz, 1H), 3.77 (s, 3H), 3.28 (d, *J* = 8.9 Hz, 1H), 2.99 (ddd, *J* = 16.8, 9.2, 6.2 Hz, 1H), 2.77 (dt, *J* = 16.9, 5.8 Hz, 1H), 2.15 (ddd, *J* = 13.6, 6.2, 5.3 Hz, 1H), 1.82 (ddd, *J* = 13.6, 9.2, 6.3 Hz, 1H), 1.45 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 158.0, 137.7, 137.1, 129.8, 126.8, 119.5, 114.5, 112.9, 62.2, 55.4, 54.5, 32.5, 25.4, 24.5; **IR** (NaCl, thin film, cm⁻¹) 2929, 2853, 2095, 1722, 1610, 1502, 1260, 1043, 925, 811; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₇N₃ONa⁺(M+Na)⁺ 266.1264, found 266.1269.



Compound 2c: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (1:1 DCM:hexanes). This afforded compound **2c** as a white

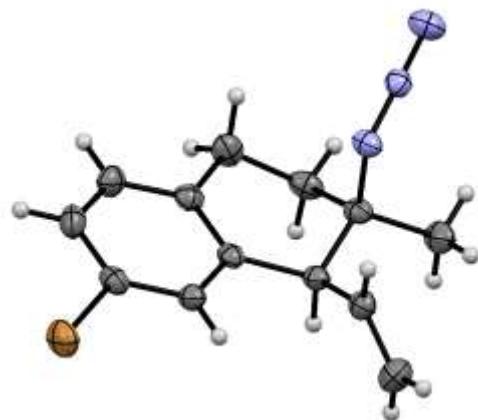
solid in 82% and 80% yield in duplicate trials. The average yield of 81% is reported. Compound **2c** was isolated in 21:1 and 16:1 dr in duplicate trials. The average dr of 19:1 is reported: **¹H NMR** (500 MHz, CDCl₃) δ 7.16 – 7.12 (m, 2H), 7.05 (d, J = 8.7 Hz, 1H), 5.85 (ddd, J = 17.1, 10.1, 8.9 Hz, 1H), 5.74 (dt, J = 17.1, 10.0, 9.1 Hz, 1H, minor diastereomer), 5.40 (dd, J = 10.1, 1.8 Hz, 1H), 5.20 (dd, J = 17.1, 1.7 Hz, 1H), 3.25 (d, J = 9.0 Hz, 1H), 3.01 (dt, J = 9.6, 6.3 Hz, 1H), 2.78 (dt, J = 17.3, 5.6 Hz, 1H), 2.15 (ddd, J = 13.6, 6.2, 4.8 Hz, 1H), 1.82 (ddd, J = 13.6, 9.6, 6.3 Hz, 1H), 1.45 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 137.9, 137.0, 133.3, 131.9, 130.2, 129.4, 126.9, 120.3, 61.8, 54.2, 32.5, 25.7, 24.5; **IR** (NaCl, thin film, cm⁻¹) 2927, 2854, 2096, 1484, 1457, 1379, 1248, 1095, 907, 925, 892, 814; **HRMS** (CI-TOF) *m/z* calcd for C₁₃H₁₈ClN₄⁺ (M+NH₄⁺) 265.1215, found 265.1203. Calcd for C₁₃H₁₅ClN⁺ (M+H-N₂⁺) 220.0888, found 220.0879. Calcd for C₁₃H₁₄Cl⁺ (M-N₃⁺) 205.0779, found 205.0775.

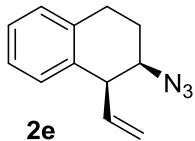


Compound 2d: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (1:1 DCM:hexanes). This afforded compound **2d** as a white solid in 85% and 80% yield in duplicate trials. The average yield of 83% is reported. Compound **2d** was isolated in 21:1 and 20:1 dr in duplicate trials. The average dr of 20:1 is reported: **¹H NMR** (500 MHz, CDCl₃) δ 7.31 – 7.25 (m, 2H), 7.00 (d, J = 8.4 Hz, 1H), 5.85 (ddd, J = 17.1, 10.1, 8.9 Hz, 1H), 5.41 (dd, J = 10.1, 1.8 Hz, 1H), 5.20 (dd, J = 17.0, 1.9 Hz, 1H), 3.26 (d, J = 9.0 Hz, 1H), 2.99 (dt, J = 9.6, 6.4 Hz, 1H), 2.76 (dt, J = 17.4, 5.6 Hz, 1H), 2.15 (ddd, J = 13.7, 6.3, 4.9 Hz, 1H), 1.82 (ddd, J = 13.7, 9.6, 6.3 Hz, 1H), 1.45 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 138.3, 137.0, 133.8, 132.3, 130.6, 129.8, 120.4, 119.9, 61.8, 54.2, 32.4, 25.8, 24.5; **IR** (NaCl, thin film, cm⁻¹) 2926, 2853, 2096, 1591, 1482, 1454, 1379, 1250, 1113, 1088, 996, 927, 855, 811; **HRMS** (CI-TOF) *m/z* calcd for C₁₃H₁₈BrN₄⁺ (M+NH₄⁺) 309.0709, found 309.0698.

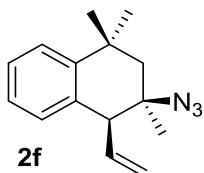
A sample of compound **2d** (10 mg) was recrystallized from CHCl₃ (0.1 mL) by slow evaporation at room temperature. These crystals were of sufficient quality for X-ray diffraction analysis. An ORTEP representation of compound **2d** is provided below. The full coordinates are provided at the end of this file.

X-ray Structure of Tetralin **2d**

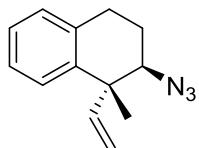
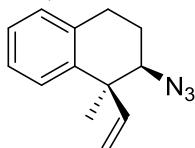




Compound 2e: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (4:1 DCM:hexanes). This afforded compound **2e** as a white solid in 96% and 80% yield in duplicate trials. The average yield of 88% is reported. Compound **2e** was isolated in 12:1 and 12:1 dr in duplicate trials. The average dr of 12:1 is reported: **1H NMR** (500 MHz, CDCl₃) δ 7.22 – 7.11 (m, 4H), 6.04 (ddd, *J* = 17.1, 10.1, 8.1 Hz, 1H), 5.29 (dd, *J* = 10.1, 1.7 Hz, 1H), 5.13 (dt, *J* = 17.0, 1.4 Hz, 1H), 4.00 (ddd, *J* = 9.7, 4.9, 3.2 Hz, 1H), 3.72 (dd, *J* = 8.1, 5.0 Hz, 1H), 3.04 (dt, *J* = 17.2, 5.9 Hz, 1H), 2.90 (ddd, *J* = 17.2, 8.0, 6.4 Hz, 1H), 2.16 – 2.01 (m, 2H); **13C NMR** (126 MHz, CDCl₃) δ 138.1, 135.8, 135.1, 130.1, 128.9, 126.9, 126.2, 118.6, 61.2, 47.9, 27.2, 24.8; **IR** (NaCl, thin film, cm⁻¹) 3077, 3019, 2913, 2095, 1489, 1455, 1337, 1259, 921, 771, 744; **HRMS** (EI-TOF) *m/z* calcd for C₁₂H₁₄N₃⁺ (M⁺) 200.1182, found 200.1181.

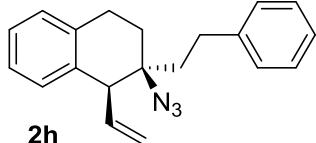


Compound 2f: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 60 °C for 48 h. Purification was conducted by filtering through a short plug of silica (1:1 DCM:hexanes). This afforded compound **2f** as a white solid in 74% and 69% yield in duplicate trials. The average yield of 72% is reported. In both replicates the observed dr was >25:1: **1H NMR** (400 MHz, CDCl₃) δ 7.39 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.18 – 7.13 (m, 2H), 5.96 (ddd, *J* = 16.9, 10.1, 8.7 Hz, 1H), 5.39 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.13 (dd, *J* = 16.4, 2.1 Hz, 1H), 3.31 (d, *J* = 8.6 Hz, 1H), 2.14 (d, *J* = 14.3 Hz, 1H), 1.81 (d, *J* = 14.3 Hz, 1H), 1.48 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H); **13C NMR** (101 MHz, CDCl₃) δ 143.8, 137.9, 134.8, 129.1, 127.3, 126.9, 126.1, 119.6, 62.2, 54.9, 47.6, 34.2 (2C), 33.7, 25.7; **IR** (NaCl, thin film, cm⁻¹) 2965, 2922, 2104, 1488, 1443, 1378, 1263, 1159, 919, 760, 655; **HRMS** (CI-TOF) *m/z* calcd for C₁₅H₂₃N₄⁺ (M+NH₄⁺) 259.1917, found 259.1906. Calcd for C₁₅H₁₉ (M-N₃⁺) 199.1481, found 199.1476.

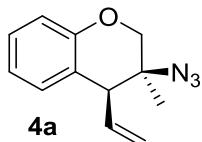


Compound 2g: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 10 mol% catalyst at 40 °C for 24 h. Purification was conducted by filtering through a short plug of silica (1:3 DCM:hexanes). This afforded compound **2g** as a clear oil in 59% and 57% yield in duplicate trials. The average yield of 58% is reported. Compound **2g** was isolated as a mixture of two diastereomers (**2g syn** and **2g anti**) in 1.8:1 and 1.6:1 dr in duplicate trials. The average dr of 1.7:1 is reported: **1H NMR** (500 MHz, CDCl₃) **2g syn** δ 7.21 – 7.08 (m, 4H), 6.08 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.21 (dd, *J* = 10.7, 1.4 Hz, 1H), 4.76 (dd, *J* = 17.4, 1.4 Hz, 1H), 3.60 (dd, *J* = 10.4, 3.1 Hz, 1H), 3.04 – 2.88 (m, 2H), 2.20 – 2.11 (m, 1H), 2.10

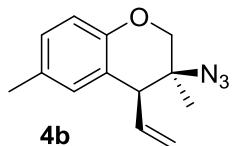
– 2.00 (m, 1H), 1.53 (s, 3H); **2g anti** δ 7.21 – 7.08 (m, 4H), 5.90 (dd, $J = 17.3, 10.6$ Hz, 1H), 5.28 (dd, $J = 10.5, 1.1$ Hz, 1H), 5.11 (dd, $J = 17.3, 1.1$ Hz, 1H), 3.73 (dd, $J = 10.1, 3.2$ Hz, 1H), 3.04 – 2.88 (m, 2H), 2.20 – 2.11 (m, 1H), 2.10 – 2.00 (m, 1H), 1.40 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 145.7, 143.5, 140.8, 140.4, 135.0, 134.5, 128.93, 128.89, 128.74, 128.61, 126.56, 126.52, 126.35, 126.31, 116.3, 115.6, 67.9, 66.3, 46.3, 45.7, 28.0, 27.7, 25.9, 24.2, 24.0, 22.5; **IR** (NaCl, thin film, cm⁻¹) 2976, 2936, 2097, 1489, 1446, 1264, 1002, 924, 760, 729; **HRMS** (CI-TOF) *m/z* calcd for C₁₃H₁₉N₄⁺ (M+NH₄)⁺ 231.1604, found 231.1605.



Compound 2h: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (1:1, DCM:hexanes). This afforded compound **2h** as a clear oil in 82% and 78% yield in duplicate trials. The average yield of 80% is reported. Compound **2h** was isolated in 23:1 and 19:1 dr in duplicate trials. The average dr of 21:1 is reported: **¹H NMR** (500 MHz, CDCl₃) δ 7.33 – 7.26 (m, 2H), 7.23 – 7.10 (m, 7H), 6.00 (ddd, $J = 17.1, 10.2, 8.6$ Hz, 1H), 5.32 (dd, $J = 10.1, 1.8$ Hz, 1H), 5.15 (ddd, $J = 17.1, 1.8, 1.2$ Hz, 1H), 3.51 (br d, $J = 8.6$ Hz, 1H), 3.06 (dt, $J = 17.5, 6.4$ Hz, 1H), 2.88 (dt, $J = 17.5, 7.2$ Hz, 1H), 2.78 (t, $J = 8.7$ Hz, 2H), 2.20 (ddd, $J = 14.1, 8.0, 6.3$ Hz, 1H), 2.07 – 1.94 (m, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 141.7, 138.1, 136.0, 134.5, 130.1, 128.9, 128.7, 128.5, 126.8, 126.3, 126.3, 118.9, 64.7, 53.0, 39.2, 30.3, 27.9, 26.2; **IR** (NaCl, thin film, cm⁻¹) 3061, 3025, 2934, 2862, 2097, 1603, 1492, 1453, 1263, 1000, 919, 740, 700; **HRMS** (CI-TOF) *m/z* calcd for C₂₀H₂₁⁺ (M-N₃)⁺ 261.1638, found 261.1637.

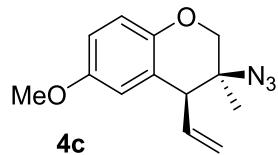


Compound 4a: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 40 °C for 24 h. Purification was conducted by filtering through a short plug of silica (1:1 DCM:hexanes). This afforded compound **4a** as a white solid in 95% and 86% yield in duplicate trials. The average yield of 91% is reported. In both replicates the observed dr was >25:1: **¹H NMR** (500 MHz, CDCl₃) δ 7.20 – 7.14 (m, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.96 – 6.83 (m, 2H), 5.84 (dt, $J = 16.9, 9.5$ Hz, 1H), 5.43 (dd, $J = 10.1, 1.7$ Hz, 1H), 5.27 (dd, $J = 17.1, 1.7$ Hz, 1H), 4.20 (d, $J = 11.4$ Hz, 1H), 3.92 (d, $J = 11.4$ Hz, 1H), 3.40 (d, $J = 8.9$ Hz, 1H), 1.41 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.0, 136.0, 129.8, 128.5, 121.7, 121.4, 120.8, 116.7, 70.7, 58.9, 50.9, 20.9; **IR** (NaCl, thin film, cm⁻¹), 3078, 2979, 2929, 2873, 2109, 1487, 1260, 1056, 757; **HRMS** (EI-TOF) *m/z* calcd for C₁₂H₁₃N₃O⁺ (M⁺) 215.1053, found 215.1047.

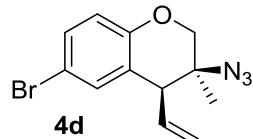


Compound 4b: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 40 °C for 24 h. Purification was conducted by filtering through a short plug of silica (9:1 DCM:hexanes). This afforded compound **4b** as a white

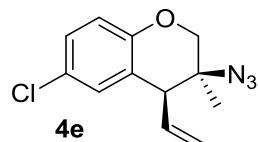
solid in 97% and 91% yield in duplicate trials. The average yield of 94% is reported. Compound **4b** was isolated in 22:1 and 20:1 dr in duplicate trials. The average dr of 21:1 is reported: **¹H NMR** (500 MHz, CDCl₃) δ 6.98 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.88 (d, *J* = 1.4 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.84 (ddd, *J* = 17.0, 10.1, 9.0 Hz, 1H), 5.43 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.28 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.17 (d, *J* = 11.3 Hz, 1H), 3.89 (d, *J* = 11.5 Hz, 1H), 3.36 (d, *J* = 9.0 Hz, 1H), 2.26 (s, 3H), 1.40 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 150.8, 136.2, 130.6, 130.0, 129.2, 121.3, 120.6, 116.4, 70.7, 59.0, 51.0, 20.9, 20.8; **IR** (NaCl, thin film, cm⁻¹) 2916, 2849, 2103, 1619, 1592, 1495, 1464, 1261, 1216, 1202, 1150, 1089, 1055, 918, 815; **HRMS** (ESI-TOF) *m/z* calcd for C₁₃H₁₅N₃ONa⁺ (M+Na)⁺ 252.1107, found 252.1110.



Compound 4c: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 40 °C for 24 h. Purification was conducted by filtering through a short plug of silica (100% DCM). This afforded compound **4c** as a white solid in 99% and 79% yield in duplicate trials. The average yield of 89% is reported. Compound **4c** was isolated in 23:1 and 21:1 dr in duplicate trials. The average dr of 22:1 is reported: **¹H NMR** (500 MHz, CDCl₃) δ 6.81 (d, *J* = 8.8 Hz, 1H), 6.75 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.63 (d, *J* = 2.9 Hz, 1H), 5.84 (ddd, *J* = 17.1, 10.0, 9.0 Hz, 1H), 5.44 (dd, *J* = 10.0, 1.8 Hz, 1H), 5.29 (dd, *J* = 17.0, 1.7 Hz, 1H), 4.17 (d, *J* = 11.4 Hz, 1H), 3.88 (d, *J* = 11.4 Hz, 1H), 3.75 (s, 3H), 3.36 (d, *J* = 9.0 Hz, 1H), 1.40 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 154.2, 147.0, 135.9, 122.4, 120.9, 117.3, 114.5, 114.4, 70.9, 59.0, 55.9, 51.2, 20.9; **IR** (NaCl, thin film, cm⁻¹) 2933, 2834, 2109, 1496, 1455, 1425, 1274, 1258, 1219, 1176, 1058, 928, 817; **HRMS** (ESI-TOF) *m/z* calcd for C₁₃H₁₅N₃O₂Na⁺ (M+Na)⁺ 268.1056, found 268.1062.

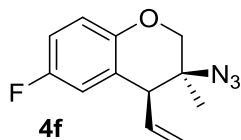


Compound 4d: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (3:2 DCM:hexanes). This afforded compound **4d** as a white solid in 94% and 92% yield in duplicate trials. The average yield of 93% is reported. In both replicates the observed dr was >25:1: **¹H NMR** (400 MHz, CDCl₃) δ 7.30 – 7.25 (m, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 5.84 (ddd, *J* = 17.1, 10.1, 8.9 Hz 1H), 5.50 (dd, *J* = 10.0, 1.6 Hz, 1H), 5.33 (dd, *J* = 17.0, 1.9 Hz, 1H), 4.22 (d, *J* = 11.3 Hz, 1H), 3.92 (d, *J* = 11.3 Hz, 1H), 3.35 (d, *J* = 8.8 Hz, 1H), 1.42 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 152.1, 134.9, 132.1, 131.2, 123.8, 121.5, 118.3, 113.3, 70.7, 58.3, 50.6, 20.5; **IR** (NaCl, thin film, cm⁻¹) 2954, 2923, 2874, 2110, 1479, 1256, 1234, 1048, 817; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₂BrN₃ONa⁺ (M+Na)⁺ 316.0056, found 316.0056.

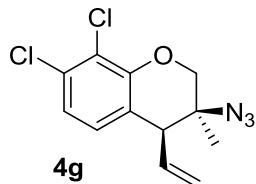


Compound 4e: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by

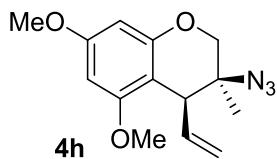
filtering through a short plug of silica (3:2 DCM:hexanes). This afforded compound **4e** as a white solid in 70% and 70% yield in duplicate trials. The average yield of 70% is reported. Compound **4e** was isolated in 25:1 and 16:1 dr in duplicate trials. The average dr of 20:1 is reported: **¹H NMR** (400 MHz, CDCl₃) δ 7.15 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 5.83 (ddd, *J* = 17.0, 10.1, 9.0, 1H), 5.51 (dd, *J* = 10.1, 1.6 Hz, 1H), 5.33 (dd, *J* = 17.0, 1.6 Hz, 1H), 4.23 (d, *J* = 11.6 Hz, 1H), 3.92 (d, *J* = 11.6 Hz, 1H), 3.36 (d, *J* = 9.0 Hz, 1H), 1.42 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 150.0, 134.8, 132.4, 127.9, 122.1, 121.6, 120.4, 117.8, 71.3, 58.1, 50.5, 20.4; **IR** (NaCl, thin film, cm⁻¹) 2925, 2879, 2010, 1481, 1282, 1254, 1232, 1048, 914; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₂ClN₃ONa⁺ (M+Na)⁺ 272.0561, found 272.0565.



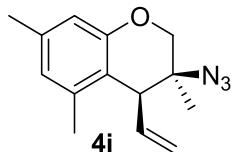
Compound 4f: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (3:2 DCM:hexanes). This afforded compound **4f** as a white solid in 85% and 81% yield in duplicate trials. The average yield of 83% is reported. In both replicates the observed dr was >25:1: **¹H NMR** (400 MHz, CDCl₃) δ 6.90 – 6.78 (m, 3H), 5.83 (ddd, *J* = 17.0, 10.1, 8.9 Hz, 1H), 5.48 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.32 (dd, *J* = 17.0, 1.6 Hz, 1H), 4.22 (d, *J* = 11.6 Hz, 1H), 3.91 (d, *J* = 11.4 Hz, 1H), 3.37 (d, *J* = 8.8 Hz, 1H), 1.42 (s, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -122.8; **¹³C NMR** (101 MHz, CDCl₃) δ 157.3 (d, *J*_{C-F} = 238.7 Hz), 148.9 (d, *J*_{C-F} = 2.1 Hz), 135.0, 122.8 (d, *J*_{C-F} = 7.1 Hz), 121.3, 117.5 (d, *J*_{C-F} = 8.2 Hz), 115.5 (d, *J*_{C-F} = 23.6 Hz), 115.1 (d, *J*_{C-F} = 23.4 Hz), 70.8, 58.4, 50.9, 20.6; **IR** (NaCl, thin film, cm⁻¹) 2933, 2910, 2112, 1430, 1265, 1240, 1090, 768; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₂FN₃ONa⁺ (M+Na)⁺ 256.0857, found 256.0852.



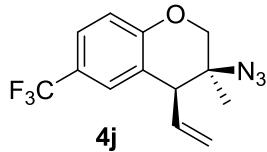
Compound 4g: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (3:2 DCM:hexanes). This afforded compound **4g** as a white solid in 74% and 72% yield in duplicate trials. The average yield of 73% is reported. Compound **4g** was isolated in 13:1 and 14:1 dr in duplicate trials. The average dr of 14:1 is reported: **¹H NMR** (400 MHz, CDCl₃) δ 7.05 (d, *J* = 8.4, Hz, 1H), 6.95 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.80 (ddd, *J* = 17.3, 10.1, 9.0 Hz 1H), 5.51 (dd, *J* = 10.0, 1.6 Hz, 1H), 5.33 (dd, *J* = 17.4, 1.5 Hz, 1H), 4.37 (d, *J* = 11.5 Hz, 1H), 4.02 (d, *J* = 11.6 Hz, 1H), 3.35 (d, *J* = 9.2 Hz, 1H), 1.44 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 151.5, 134.9, 129.2, 128.3, 126.0, 123.2, 121.5, 117.8, 70.8, 58.4, 50.7, 20.5; **IR** (NaCl, thin film, cm⁻¹) 2925, 2874, 2111, 1560, 1417, 1385, 1268, 1058, 932; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₁Cl₂N₃ONa⁺ (M+Na)⁺ 306.0171, found 306.0157.



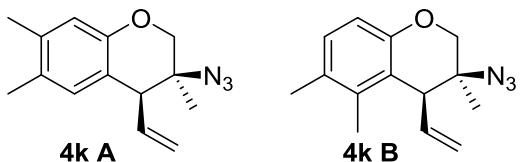
Compound 4h: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (9:1 DCM:hexanes). This afforded compound **4h** as a white solid in 78% and 74% yield in duplicate trials. The average yield of 76% is reported. In both replicates the observed dr was >25:1: **1H NMR** (500 MHz, CDCl₃) δ 6.09 (d, *J* = 2.3 Hz, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 5.94 (ddd, *J* = 17.0, 10.1, 7.0 Hz, 1H), 5.19 (dt, *J* = 10.2, 1.3 Hz, 1H), 4.94 (dt, *J* = 16.9, 1.5 Hz, 1H), 3.96 (d, *J* = 10.5 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.72 (dd, *J* = 10.5, 2.1 Hz, 1H), 3.59 (dt, *J* = 7.2, 1.3 Hz, 1H), 1.43 (s, 3H); **13C NMR** (126 MHz, CDCl₃) δ 160.5, 159.1, 153.8, 137.2, 117.8, 103.2, 93.1, 92.4, 67.6, 59.4, 55.7, 55.5, 43.8, 21.9; **IR** (NaCl, thin film, cm⁻¹) 2972, 2927, 2873, 2108, 1498, 1385, 1247, 1223, 1141, 1123, 1054, 995, 925, 817; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₇N₃O₃Na⁺ (M+Na)⁺ 298.1162, found 298.1157.



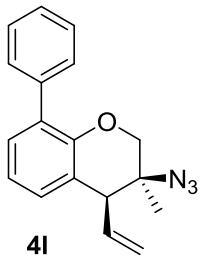
Compound 4i: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 10 mol% catalyst at 40 °C for 24 h. Purification was conducted by filtering through a short plug of silica (4:1 DCM:hexanes). This afforded compound **4i** as a white solid in 88% and 79% yield in duplicate trials. The average yield of 84% is reported. Compound **4i** was isolated in 25:1 and 25:1 dr in duplicate trials. The average dr of 25:1 is reported: **1H NMR** (400 MHz, CDCl₃) δ 6.62 (s, 1H), 6.55 (s, 1H), 5.98 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.29 (dt, *J* = 10.2, 1.3 Hz, 1H), 4.87 (dt, *J* = 17.1, 1.5 Hz, 1H), 3.96 (d, *J* = 10.4 Hz, 1H), 3.74 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.43 (d, *J* = 6.9 Hz, 1H), 2.27 (s, 3H), 2.18 (s, 3H), 1.44 (s, 3H); **13C NMR** (101 MHz, CDCl₃) δ 152.4, 138.3, 138.1, 136.7, 124.4, 119.1, 116.8, 114.9, 67.0, 59.8, 47.0, 22.1, 21.2, 18.9; **IR** (NaCl, thin film, cm⁻¹) 2923, 2102, 1619, 1577, 1452, 1292, 1259, 1147, 1079, 931, 841, 704; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₇N₃ONa⁺ (M+Na)⁺ 266.1264, found 266.1271.



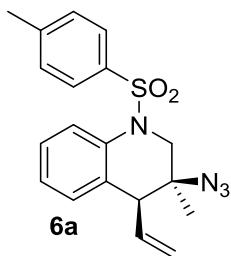
Compound 4j: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 10 mol% catalyst at 60 °C for 48 h. Purification was conducted by filtering through a short plug of silica (11:9, DCM:hexanes). This afforded compound **4j** as a clear oil in 39% and 35% yield in duplicate trials. The average yield of 37% is reported. Compound **4j** was isolated in 19:1 and 16:1 dr in duplicate trials. The average dr of 18:1 dr is reported: **1H NMR** (400 MHz, CDCl₃) δ 7.42 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.35 (d, *J* = 2.2 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 5.81 (ddd, *J* = 17.0, 10.1, 8.9 Hz, 1H), 5.52 (dd, *J* = 10.1, 1.6 Hz, 1H), 5.33 (dt, *J* = 16.8, 1.3 Hz, 1H), 4.26 (d, *J* = 11.6 Hz, 1H), 3.97 (d, *J* = 11.6 Hz, 1H), 3.39 (d, *J* = 8.9 Hz, 1H), 1.43 (s, 3H); **19F NMR** (376 MHz, CDCl₃) δ -61.58; **13C NMR** (126 MHz, CDCl₃) δ 155.7, 134.8, 127.2 (q, *J*_{C,F} = 3.8 Hz), 125.7 (q, *J*_{C,F} = 3.7 Hz), 124.5 (q, *J*_{C,F} = 272.2 Hz), 123.6 (q, *J*_{C,F} = 32.8 Hz), 122.2, 122.1, 117.1, 71.1, 58.5, 50.8, 20.6; **IR** (NaCl, thin film, cm⁻¹) 2918, 2111, 1621, 1592, 1505, 1330, 1269, 1159, 1120, 1045, 933, 832, 632; **HRMS** (ESI-TOF) *m/z* calcd for C₁₃H₁₂F₃N₃ONa⁺ (M+Na)⁺ 306.0825, found 306.0835.



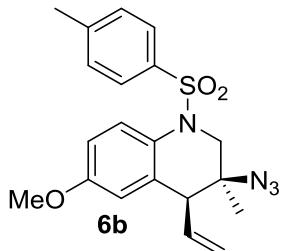
Compound 4k: A variation of the general procedure was used. The reaction was conducted at 0.30 M substrate and used 10 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (4:1, DCM:hexanes). This afforded compound **4k** as a clear oil in 84% and 80% yield in duplicate trials. The average yield of 82% is reported. Compound **4k** was isolated as a mixture of two regioisomers (**4k A** and **4k B**) in a 1.4:1 ratio. Compound **4k A** was isolated in 15:1 and 12:1 dr in duplicate trials, the average dr of 14:1 is reported. Compound **4k B** was isolated in 21:1 and 21:1 dr in duplicate trials, the average dr of 21:1 is reported: **¹H NMR** (500 MHz, CDCl₃) **4k A** δ 6.82 (s, 1H), 6.69 (s, 1H), 5.83 (ddd, *J* = 17.0, 10.1, 9.0 Hz, 1H), 5.42 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.30 – 5.25 (m, 1H), 4.16 (d, *J* = 11.3 Hz, 1H), 3.88 (d, *J* = 11.3 Hz, 1H), 3.33 (d, *J* = 9.0 Hz, 1H), 2.21 (s, 3H), 2.18 (s, 3H), 1.40 (s, 3H); **4k B** δ 6.99 (d, *J* = 8.3 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 6.03 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.32 – 5.28 (m, 1H), 4.84 (dt, *J* = 17.1, 1.5 Hz, 1H), 3.96 (d, *J* = 10.3 Hz, 1H), 3.74 (dd, *J* = 10.3, 2.0 Hz, 1H), 3.53 (dd, *J* = 6.8, 1.6 Hz, 1H), 2.23 (s, 3H), 2.10 (s, 3H), 1.46 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 150.8, 150.7, 137.1, 136.9, 136.5, 136.3, 130.4, 129.9, 129.44, 129.36, 120.3, 119.7, 119.4, 118.7, 117.5, 113.9, 70.7, 66.7, 59.9, 59.1, 50.7, 47.4, 22.2, 20.9, 20.2, 19.7, 19.0, 15.1; **IR** (NaCl, thin film, cm⁻¹) 2969, 2930, 2883, 2108, 1597, 1501, 1480, 1385, 1266, 1179, 1107, 999, 924, 813, 736; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₇N₃ONa⁺ (M+Na)⁺ 266.1264, found 266.1254.



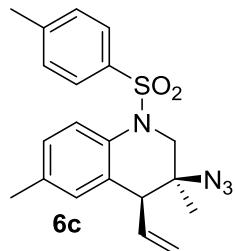
Compound 4l: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 60 °C for 24 h. Purification was conducted by filtering through a short plug of silica (3:2, DCM:hexanes). This afforded compound **4l** as a white solid in 83% and 77% yield in duplicate trials. The average yield of 80% is reported. In both replicates the observed dr was >25:1: **¹H NMR** (500 MHz, CDCl₃) δ 7.57 – 7.53 (m, 2H), 7.46 – 7.41 (m, 2H), 7.38 – 7.32 (m, 1H), 7.23 (ddd, *J* = 7.4, 1.7, 0.7 Hz, 1H), 7.11 (ddd, *J* = 7.7, 1.8, 1.1 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 5.91 (ddd, *J* = 17.0, 10.1, 9.0 Hz, 1H), 5.46 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.31 (ddd, *J* = 17.1, 1.8, 0.7 Hz, 1H), 4.22 (d, *J* = 11.4 Hz, 1H), 3.92 (dd, *J* = 11.5, 0.9 Hz, 1H), 3.46 (br d, *J* = 9.0 Hz, 1H), 1.43 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 150.0, 138.4, 136.2, 130.2, 130.0, 129.8, 129.3, 128.2, 127.2, 122.3, 121.2, 120.6, 70.8, 58.8, 51.3, 21.1; **IR** (NaCl, thin film, cm⁻¹) 3060, 3029, 2976, 2927, 2871, 2109, 1466, 1431, 1384, 1277, 1225, 1046, 927, 760, 699; **HRMS** (ESI-TOF) *m/z* calcd for C₁₈H₁₇N₃ONa⁺ (M+Na)⁺ 314.1264, found 314.1276.



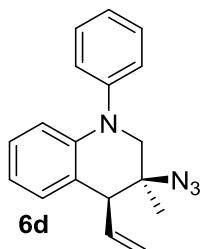
Compound 6a: A variation of the general procedure was used. The reaction was conducted at 0.05 M substrate and used 10 mol% catalyst at 50 °C for 48 h. Purification was conducted by filtering through a short plug of silica (4:1 DCM:hexanes). This afforded compound **6a** as a glassy oil in 76% and 74% yield in duplicate trials. The average yield of 75% is reported. In both replicates the observed dr was >25:1: **1H NMR** (400 MHz, CDCl₃) δ 7.75 – 7.66 (m, 3H), 7.33 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 7.11 – 7.02 (m, 2H), 5.75 (ddd, *J* = 17.1, 10.1, 8.7 Hz, 1H), 5.31 (dd, *J* = 10.1, 1.7 Hz, 1H), 5.00 (dd, *J* = 17.1, 1.9 Hz, 1H), 4.10 (d, *J* = 13.0 Hz, 1H), 3.72 (d, *J* = 13.0 Hz, 1H), 3.05 (d, *J* = 8.7 Hz, 1H), 2.42 (s, 3H), 1.45 (s, 3H); **13C NMR** (126 MHz, CDCl₃) δ 144.1, 136.8, 135.6, 135.5, 129.9, 129.6, 127.83, 127.77, 127.3, 124.3, 121.0, 120.8, 60.8, 53.5, 52.8, 22.7, 21.7; **IR** (NaCl, thin film, cm⁻¹) 2921, 2850, 2110, 1599, 1488, 1455, 1348, 1307, 1261, 1161, 1090, 920, 892, 814, 757, 660; **HRMS** (ESI-TOF) *m/z* calcd for C₁₉H₂₀N₄O₂SNa⁺ (M+Na)⁺ 391.1199, found 391.1200.



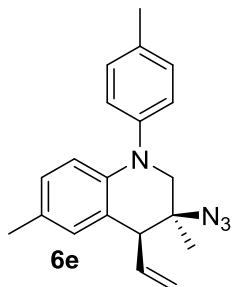
Compound 6b: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 40 °C for 48 h. Purification was conducted by filtering through a short plug of silica (100% DCM). This afforded compound **6b** as a clear oil in 86% and 74% yield in duplicate trials. The average yield of 80% is reported. Compound **6b** was isolated in 24:1 and 22:1 dr in duplicate trials. The average dr of 23:1 is reported: **1H NMR** (500 MHz, CDCl₃) δ 7.65 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.77 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 5.69 (ddd, *J* = 17.1, 10.1, 8.8 Hz, 1H), 5.28 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.91 (dd, *J* = 17.0, 1.7 Hz, 1H), 3.99 (d, *J* = 13.4 Hz, 1H), 3.76 (s, 3H), 3.70 (d, *J* = 13.4 Hz, 1H), 2.70 (d, *J* = 8.8 Hz, 1H), 2.41 (s, 3H), 1.38 (s, 3H); **13C NMR** (126 MHz, CDCl₃) δ 156.8, 144.0, 136.4, 134.6, 131.0, 129.8, 128.5, 127.3, 123.9, 121.0, 114.4, 112.8, 62.1, 55.5, 54.2, 52.5, 23.1, 21.7; **IR** (NaCl, thin film, cm⁻¹) 2917, 2107, 1612, 1496, 1349, 1260, 1227, 1161, 1090, 1039, 912, 812, 707, 648; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₂N₄O₂SNa⁺ (M+Na)⁺ 421.1305, found 421.1315.



Compound 6c: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 40 °C for 48 h. Purification was conducted by filtering through a short plug of silica (100% DCM). This afforded compound **6c** as a clear oil in 80% and 72% yield in duplicate trials. The average yield of 76% is reported. In both replicates the observed dr was >25:1: **1H NMR** (500 MHz, CDCl₃) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.00 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.87 – 6.83 (m, 1H), 5.71 (ddd, *J* = 17.1, 10.1, 8.7 Hz, 1H), 5.28 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.96 (ddd, *J* = 17.1, 1.8, 0.8 Hz, 1H), 4.03 (d, *J* = 13.1 Hz, 1H), 3.69 (dd, *J* = 13.1, 0.7 Hz, 1H), 2.93 (d, *J* = 8.7 Hz, 1H), 2.40 (s, 3H), 2.26 (s, 3H), 1.41 (s, 3H); **13C NMR** (126 MHz, CDCl₃) δ 144.0, 136.7, 135.4, 134.0, 133.0, 129.9, 129.8, 128.5, 128.0, 127.3, 121.3, 120.6, 61.2, 53.6, 52.6, 22.8, 21.7, 20.9; **IR** (NaCl, thin film, cm⁻¹) 2918, 2106, 1495, 1346, 1253, 1161, 1089, 921, 815, 704, 649; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₂N₄O₂SNa⁺ (M+Na)⁺ 405.1356, found 405.1364.

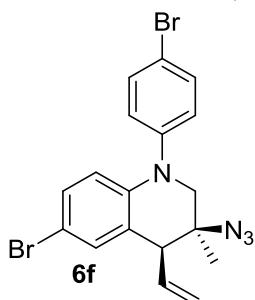


Compound 6d: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 40 °C for 24 h. Purification was conducted by filtering through a short plug of silica (3:2 DCM:hexanes). This afforded compound **6d** as a white solid in 76% and 68% yield in duplicate trials. The average yield of 72% is reported. In both replicates the observed dr was >25:1: **1H NMR** (500 MHz, CDCl₃) δ 7.43 – 7.36 (m, 2H), 7.32 – 7.28 (m, 2H), 7.19 (tt, *J* = 7.2, 1.3 Hz, 1H), 7.11 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.75 (td, *J* = 7.4, 1.2 Hz, 1H), 6.70 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.96 (ddd, *J* = 17.0, 10.1, 8.8 Hz, 1H), 5.41 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.24 (ddd, *J* = 17.0, 1.8, 0.9 Hz, 1H), 3.71 (d, *J* = 12.3 Hz, 1H), 3.57 (dd, *J* = 12.3, 1.1 Hz, 1H), 3.46 (d, *J* = 8.8 Hz, 1H), 1.44 (s, 3H); **13C NMR** (126 MHz, CDCl₃) δ 147.4, 142.9, 137.4, 130.1, 129.9, 127.5, 125.8, 125.1, 122.5, 119.8, 118.8, 114.9, 60.1, 57.9, 53.0, 22.9; **IR** (NaCl, thin film, cm⁻¹) 3062, 3031, 2977, 2917, 2849, 2105, 1592, 1573, 1494, 1461, 1318, 1259, 923, 750, 699; **HRMS** (ESI-TOF) *m/z* calcd for C₁₈H₁₈N₄Na⁺ (M+Na)⁺ 313.1424, found 313.1416.



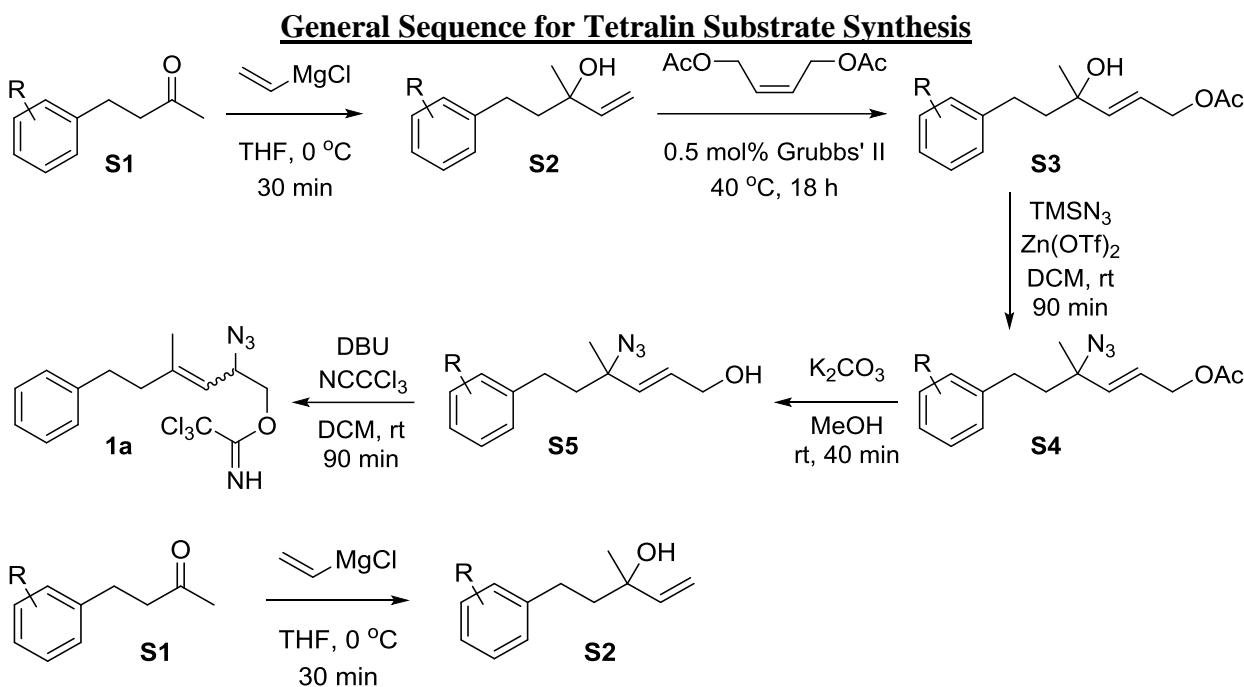
Compound 6e: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (2:3, DCM:hexanes). This afforded compound **6e** as a light yellow oil in 82% and 79% yield in duplicate trials. The average yield of 81% is reported. Compound **6e** was isolated in 16:1 and 15:1 dr in duplicate trials. The average dr of 16:1 is

reported: **¹H NMR** (400 MHz, CDCl₃) δ 7.22 – 7.15 (m, 4H), 6.91 (d, *J* = 2.3 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 5.95 (ddd, *J* = 17.0, 10.1, 8.9 Hz, 1H), 5.41 (dd, *J* = 10.1, 1.9 Hz, 1H), 5.24 (ddd, *J* = 17.1, 1.9, 0.8 Hz, 1H), 3.66 (d, *J* = 12.2 Hz, 1H), 3.52 (dd, *J* = 12.2, 1.2 Hz, 1H), 3.42 (d, *J* = 8.9 Hz, 1H), 2.38 (s, 3H), 2.23 (s, 3H), 1.42 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 145.0, 140.8, 137.5, 134.6, 130.43, 130.41, 128.2, 127.6, 125.7, 122.2, 119.6, 114.8, 60.2, 58.0, 53.0, 22.9, 21.1, 20.6; **IR** (NaCl, thin film, cm⁻¹) 3024, 2976, 2920, 2859, 2103, 1609, 1503, 1455, 1371, 1317, 1258, 1172, 1086, 1000, 921, 811; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₂N₄Na⁺ (M+Na)⁺ 341.1737, found 341.1729.

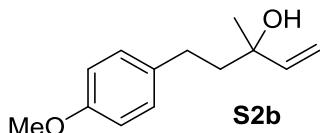


Compound 6f: A variation of the general procedure was used. The reaction was conducted at 0.10 M substrate and used 5 mol% catalyst at 50 °C for 24 h. Purification was conducted by filtering through a short plug of silica (2:3, DCM:hexanes). This afforded compound **6e** as a clear oil in 58% and 56% yield in duplicate trials. The average yield of 57% is reported. In both replicates the observed dr was >25:1: **¹H NMR** (400 MHz, CDCl₃) δ 7.54 – 7.47 (m, 2H), 7.21 (dd, *J* = 2.4, 1.1 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.08 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 5.88 (ddd, *J* = 17.1, 10.1, 8.8 Hz, 1H), 5.47 (dd, *J* = 10.1, 1.7 Hz, 1H), 5.27 (ddd, *J* = 17.1, 1.7, 0.8 Hz, 1H), 3.64 (d, *J* = 12.4 Hz, 1H), 3.53 (dd, *J* = 12.5, 1.0 Hz, 1H), 3.39 (d, *J* = 8.8 Hz, 1H), 1.41 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 146.2, 141.6, 136.1, 133.1, 132.6, 130.4, 127.2, 125.2, 121.1, 118.2, 116.8, 111.3, 59.6, 58.1, 52.8, 22.6; **IR** (NaCl, thin film, cm⁻¹) 2977, 2926, 2865, 2106, 1583, 1562, 1488, 1315, 1258, 1184, 1161, 1070, 1009, 927, 831, 808; **HRMS** (EI-TOF) *m/z* calcd C₁₈H₁₆Br₂N₂⁺ (M-N₂)⁺ 417.9675, found 417.9683.

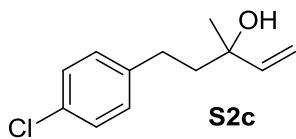
Tetralin Substrate Synthesis and Characterization Data



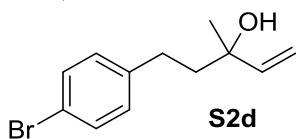
General Procedure 1: Addition of vinyl magnesium Grignard: Example given for R = H. An oven-dried round bottom flask was sequentially charged with THF (20 mL) and a solution of vinyl magnesium chloride (10.0 mL, 1.6 M in THF, 16.0 mmol), then cooled in an ice bath. To this solution neat 4-phenylbutane-2-one (**S1a**, R = H, 2.0 mL, 13 mmol) was added dropwise over 5 min. After 30 min, the reaction was quenched by the addition of saturated NH₄Cl (20 mL). The resulting solution was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried (MgSO₄), filtered through a plug of silica, and concentrated *in vacuo* to afford alcohol **S2a** (1.83 g, 10.3 mmol, 78%) as a slightly yellow oil. Characterization data for this compound has been reported.² The material obtained from this method provided an identical ¹H NMR spectrum.



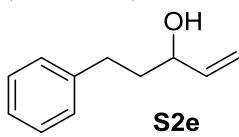
Compound S2b: General procedure 1 was used and the product was isolated in 95% yield as a yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.19 – 7.09 (m, 2H), 6.90 – 6.81 (m, 2H), 6.00 (dd, J = 17.3, 10.7 Hz, 1H), 5.29 (dd, J = 17.4, 1.3 Hz, 1H), 5.13 (dd, J = 10.8, 1.3 Hz, 1H), 3.79 (s, 3H), 2.73 – 2.55 (m, 2H), 2.10 (s, 1H), 1.96 – 1.75 (m, 2H), 1.36 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 157.7, 145.0, 134.5, 129.2, 113.9, 112.0, 73.2, 55.3, 44.4, 29.5, 27.9; **IR** (NaCl, thin film, cm⁻¹) 3436, 2934, 2835, 1612, 1513, 1250, 1036, 923, 822; **HRMS** (ESI-TOF) *m/z* calcd for C₁₃H₁₈O₂Na⁺ (M+Na)⁺ 229.1199, found 229.1203.



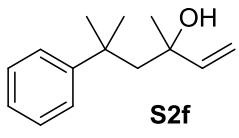
Compound S2c: General procedure 1 was used and the product was isolated in 97% yield as a yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.17 (m, 2H), 7.13 – 7.04 (m, 2H), 5.94 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.26 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.10 (dd, *J* = 10.8, 1.2 Hz, 1H), 2.71 – 2.52 (m, 2H), 2.09 (s, 1H), 1.89 – 1.70 (m, 2H), 1.33 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 144.7, 141.0, 131.4, 129.7, 128.5, 112.2, 73.1, 43.9, 29.8, 28.0; **IR** (NaCl, thin film, cm⁻¹) 3584, 3405, 3085, 2973, 2931, 2866, 1641, 1493, 1455, 1408, 1371, 1092, 1015, 924, 808, 748; **HRMS** (EI-TOF) *m/z* calcd for C₁₂H₁₅ClONa⁺ (M+Na)⁺ 233.0704, found 233.0713.



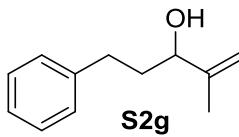
Compound S2d: General procedure 1 was used and the product was isolated in 95% yield as a yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.43 – 7.34 (m, 2H), 7.09 – 7.01 (m, 2H), 5.96 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.28 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.12 (dd, *J* = 10.7, 1.2 Hz, 1H), 2.71 – 2.52 (m, 2H), 2.03 (br s, 1H), 1.90 – 1.70 (m, 2H), 1.35 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 144.7, 141.5, 131.4, 130.2, 119.4, 112.3, 73.1, 43.9, 29.8, 28.0; **IR** (NaCl, thin film, cm⁻¹) 3565, 3397, 3085, 2972, 2934, 2866, 1895, 1641, 1591, 1488, 1455, 1371, 1011, 920, 840, 806, 752; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₅BrONa⁺ (M+Na)⁺ 277.0198, found 277.0205.



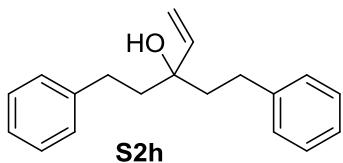
Compound S2e: General procedure 1 was used and the product was isolated in 89% yield as a yellow oil. Characterization data for this compound has been reported.³ The material obtained from this method provided an identical **¹H NMR** spectrum.



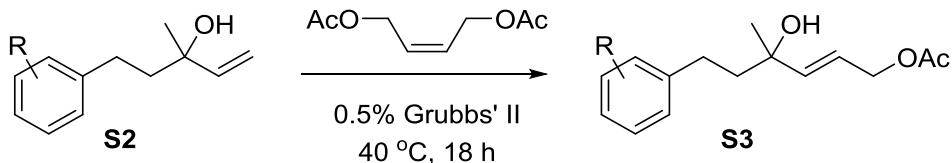
Compound S2f: General procedure 1 was used and the product was isolated in 80% yield as a yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.46 – 7.38 (m, 2H), 7.39 – 7.30 (m, 2H), 7.27 – 7.18 (m, 1H), 5.83 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.05 (dd, *J* = 17.2, 1.4 Hz, 1H), 4.88 (dd, *J* = 10.7, 1.4 Hz, 1H), 2.16 (d, *J* = 14.7 Hz, 1H), 2.03 (d, *J* = 14.7 Hz, 1H), 1.47 (s, 3H), 1.41 (s, 3H), 1.23 (br s, 1H), 1.10 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 148.8, 146.4, 128.3, 126.4, 126.0, 110.2, 74.3, 55.4, 37.8, 32.0, 30.8, 30.0; **IR** (NaCl, thin film, cm⁻¹) 3569, 3464, 3087, 3059, 3022, 2964, 2927, 1601, 1496, 1446, 1366, 1234, 998, 916, 766, 700; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₂₀ONa⁺ (M+Na)⁺ 227.1406, found 227.1412.



Compound S2g: General procedure 1 was used and the product was isolated in 92% yield as a yellow oil. Characterization data for this compound has been reported.⁴ The material obtained from this method provided an identical ¹H NMR spectrum.

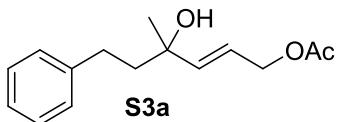


Compound S2h: General procedure 1 was used and the product was isolated in quantitative yield as a yellow oil: **¹H NMR** (500 MHz, CDCl₃) δ 7.32 – 7.26 (m, 4H), 7.22 – 7.17 (m, 6H), 5.97 (dd, J = 17.3, 10.9 Hz, 1H), 5.35 (dd, J = 17.3, 1.1 Hz, 1H), 5.27 (dd, J = 10.9, 1.1 Hz, 1H), 2.75 – 2.62 (m, 4H), 1.95 (ddd, J = 13.8, 11.2, 6.1 Hz, 2H), 1.86 (ddd, J = 13.8, 11.4, 5.6 Hz, 2H), 1.54 (br s, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 143.4, 142.5, 128.6, 128.5, 125.9, 113.5, 75.6, 43.0, 30.1; **IR** (NaCl, thin film, cm⁻¹) 3449, 3084, 3061, 3025, 2931, 2862, 1602, 1496, 1454, 1059, 1030, 1000, 922, 749, 698; **HRMS** (ESI-TOF) *m/z* calcd for C₁₉H₂₂ONa⁺ (M+Na)⁺ 289.1563, found 289.1570.

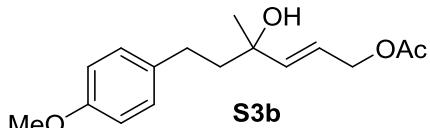


General Procedure 2: Formation of cross metathesis product: Example for R = H.

Compound S3a: In a glovebox, a 20 mL vial was charged with Grubbs' 2nd generation catalyst (32 mg, 38 µmol, 0.5 mol %). The vial was sealed and removed from the glovebox. The vial was uncapped and compound **S2a** (1.3 g, 7.6 mmol) and *cis*-1,4-diacetoxy-2-butene (3.5 mL, 23 mmol) were added as a neat mixture. The vial was attached to a vacuum adapter, placed under reduced pressure (< 1.0 torr), and heated to 40 °C. After 18 h, the vacuum was released and the resulting mixture was loaded directly onto a column load cartridge. Final purification by column chromatography (0 to 40% gradient, EtOAc in hexanes) afforded compound **3a** (1.6 g, 6.5 mmol, 85%) as a clear-yellow oil.

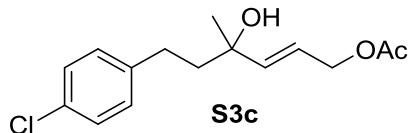


¹H NMR (CDCl_3 , 500 MHz): δ 7.30-7.25 (m, 2H), 7.20-7.16 (m, 3H), 5.89 (d, J = 15.6 Hz, 1H), 5.82 (dt, J = 15.6, 5.2 Hz, 1H), 4.60 (d, J = 5.2 Hz, 2H), 2.66 (m, 2H), 2.05 (s, 3H), 1.88 (m, 2H), 1.55 (br s, 1H), 1.36 (s, 3H); **¹³C NMR** (101 MHz, CDCl_3) δ 170.9, 142.3, 141.3, 128.5, 128.4, 125.9, 122.1, 72.7, 64.7, 44.3, 30.4, 28.2, 21.1; **IR** (NaCl, thin film, cm^{-1}) 3461, 3061, 2937, 1739, 1363, 1253; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 271.1305, found 271.1313.

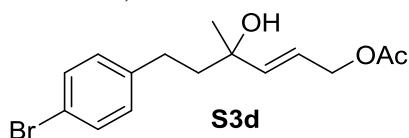


Compound S3b: General procedure 2 was used. Note, 1 mol % Grubbs' 2nd Generation Catalyst was used for this reaction. The product was isolated in 84% yield as a clear-yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.14 – 7.03 (m, 2H), 6.86 – 6.76 (m, 2H), 5.87 (d, *J* = 15.7 Hz, 1H), 5.79 (dt, *J* = 15.6, 5.5 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 2H), 3.76 (s, 3H), 2.68 – 2.51 (m, 2H), 2.07 (s, 3H),

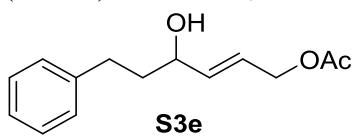
2.03 (br s, 1H), 1.90 – 1.73 (m, 2H), 1.34 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.9, 157.8, 141.4, 134.3, 129.2, 121.9, 113.9, 72.5, 64.7, 55.3, 44.4, 29.4, 28.1, 21.0. **IR** (NaCl, thin film, cm⁻¹) 3480, 2936, 1736, 1611, 1512, 1456, 1363, 1244, 1031, 974, 820; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₂₂O₄Na⁺ (M+Na)⁺ 301.1410, found 301.1416.



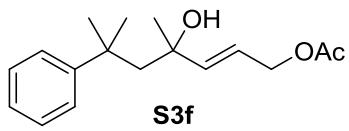
Compound S3c: General procedure 2 was used. Note, 1 mol % Grubbs' 2nd Generation Catalyst was used for this reaction. The product was isolated in 86% yield as a clear oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.24 – 7.16 (m, 2H), 7.13 – 7.03 (m, 2H), 5.84 (d, *J* = 15.7 Hz, 1H), 5.78 (dt, *J* = 15.6, 5.4 Hz, 1H), 4.57 (d, *J* = 5.0 Hz, 2H), 2.69 – 2.51 (m, 2H), 2.11 (br s, 1H), 2.05 (s, 3H), 1.88 – 1.70 (m, 2H), 1.33 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.9, 141.1, 140.8, 131.4, 129.7, 128.5, 122.0, 72.4, 64.6, 44.0, 29.7, 28.1, 21.0; **IR** (NaCl, thin film, cm⁻¹) 3468, 2937, 1738, 1492, 1363, 1236, 1093, 1024, 973, 808; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₁₉ClO₃Na⁺ (M+Na)⁺ 305.0915, found 305.0925.



Compound S3d: General procedure 2 was used. Note, 1 mol % Grubbs' 2nd Generation Catalyst was used for this reaction. The product was isolated in 88% yield as an off-clear oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.38 – 7.29 (m, 2H), 7.05 – 6.97 (m, 2H), 5.83 (d, *J* = 15.7 Hz, 1H), 5.77 (dt, *J* = 15.6, 5.4 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 2H), 2.67 – 2.48 (m, 2H), 2.26 (br s, 1H), 2.04 (s, 3H), 1.86 – 1.68 (m, 2H), 1.31 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.8, 141.3, 141.1, 131.3, 130.1, 121.9, 119.4, 72.3, 64.6, 43.9, 29.7, 28.0, 21.0; **IR** (NaCl, thin film, cm⁻¹) 3481, 2939, 1739, 1489, 1362, 1235, 1071, 1011, 973, 805; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₁₉BrO₃Na⁺ (M+Na)⁺ 349.0409, found 349.0415.

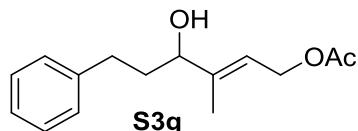


Compound S3e: General procedure 2 was used and the product was isolated in 70% yield as a brown oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 5.88 – 5.74 (m, 2H), 4.59 (dd, *J* = 4.9, 1.0 Hz, 2H), 4.17 (dt, *J* = 7.2, 5.3 Hz, 1H), 2.82 – 2.65 (m, 2H), 2.49 (br s, 1H), 2.08 (s, 3H), 1.95 – 1.80 (m, 2H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.9, 141.8, 137.3, 128.5, 128.4, 125.9, 124.5, 71.1, 64.4, 38.5, 31.6, 21.0; **IR** (NaCl, thin film, cm⁻¹) 3457, 3062, 3026, 2916, 2851, 1741, 1603, 1495, 1454, 1237, 1070, 1050, 971, 906, 749, 731; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₈O₃Na⁺ (M+Na)⁺ 257.1148, found 257.1152.

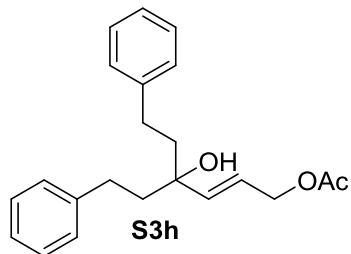


Compound S3f: General procedure 2 was used and the product was isolated as a mixture with (*E*)-but-2-ene-1,4-diyil diacetate in 79% yield as a clear oil. An analytically pure sample of **S3f** was obtained by heating an aliquot of the mixture at 80 °C under reduced pressure (0.5 torr) for 10 minutes. **¹H NMR** (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 4H), 7.21 – 7.15 (m, 1H), 5.53 (dd, *J* =

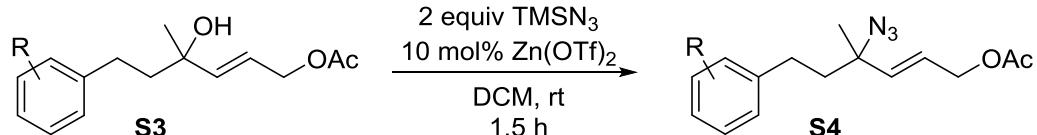
15.5, 0.8 Hz, 1H), 5.48 (dt, J = 15.7, 5.1 Hz, 1H), 4.42 – 4.31 (m, 2H), 2.08 (s, 6H), 2.05 (s, 3H), 1.10 (s, 3H); **^{13}C NMR** (126 MHz, CDCl_3) δ 171.0, 148.5, 142.5, 128.4, 126.4, 126.1, 119.9, 73.9, 64.7, 55.7, 37.8, 31.4, 31.3, 30.6, 21.1; **IR** (NaCl, thin film, cm^{-1}) 3496, 2964, 2928, 1739, 1496, 1446, 1364, 1236, 1029, 973, 765, 700; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 299.1618, found 299.1618.



Compound S3g: General procedure 2 was used. Note, 2 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used for this reaction. The product was isolated in 42% yield as a yellow oil: **^1H NMR** (500 MHz, CDCl_3) δ 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 3H), 5.60 (tp, J = 6.8, 1.3 Hz, 1H), 4.66 (d, J = 6.9 Hz, 2H), 4.07 (br t, J = 6.5 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.68 – 2.60 (m, 1H), 2.20, (br s, 1H), 2.07 (s, 3H), 1.91 – 1.86 (m, 2H), 1.72 (d, J = 1.4 Hz, 3H); **^{13}C NMR** (126 MHz, CDCl_3) δ 171.2, 143.2, 141.9, 128.5, 128.4, 125.9, 119.8, 76.1, 61.1, 36.5, 32.0, 21.0, 12.1; **IR** (NaCl, thin film, cm^{-1}) 3427, 3026, 2939, 2862, 1738, 1496, 1454, 1380, 1367, 1236, 1027, 963, 749, 700; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 271.1305, found 271.1310.



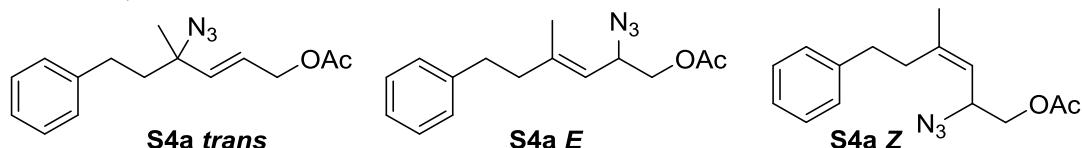
Compound S3h: General procedure 2 was used and the product was isolated as a mixture with (*E*)-but-2-ene-1,4-diyil diacetate in 87% yield as a tan oil. An analytically pure sample of **S3h** was obtained by heating an aliquot of the mixture at 80 °C under reduced pressure (0.5 torr) for 10 minutes. Note 1 mol % Grubbs' 2nd generation catalyst was used for this reaction: **^1H NMR** (400 MHz, CDCl_3) δ 7.33 – 7.28 (m, 4H), 7.24 – 7.18 (m, 6H), 5.94 – 5.84 (m, 2H), 4.67 (d, J = 4.7 Hz, 2H), 2.76 – 2.62 (m, 4H), 2.12 (s, 3H), 1.97 (ddd, J = 14.1, 11.0, 6.4 Hz, 2H), 1.88 (ddd, J = 13.7, 11.0, 6.0 Hz, 2H), 1.63 (br s, 1H); **^{13}C NMR** (101 MHz, CDCl_3) δ 171.0, 142.3, 139.9, 128.6, 128.5, 126.0, 123.5, 75.1, 64.7, 43.1, 30.1, 21.2; **IR** (NaCl, thin film, cm^{-1}) 3484, 3061, 3025, 2943, 2863, 1738, 1602, 1496, 1454, 1381, 1362, 1244, 1059, 1029, 973, 751, 700; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{26}\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 361.1774, found 361.1780.



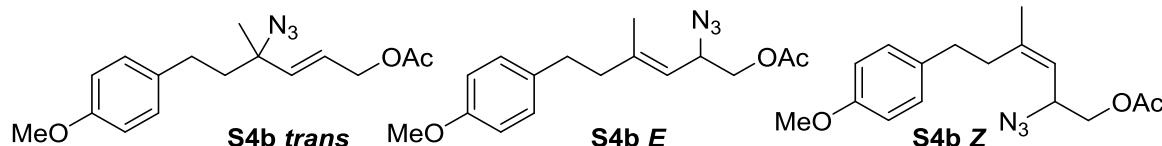
General Procedure 3: Azide Installation with TMSN_3 : Example given for $\text{R} = \text{H}$.

Compound S4a: To a solution of alcohol **S3a** (880 mg, 3.54 mmol) in DCM (1 mL) at room temperature, trimethylsilyl azide (0.94 mL, 7.1 mmol), and $\text{Zn}(\text{OTf})_2$ (130 mg, 0.35 mmol, 10 mol %) were sequentially added. The vial was sealed. After 1.5 h, the solution was quenched with trimethylamine (0.1 mL, 0.7 mmol) and methanol (1 mL), stirred for 5 min, and filtered through a plug of basic alumina before being concentrated *in vacuo*. Final purification by column

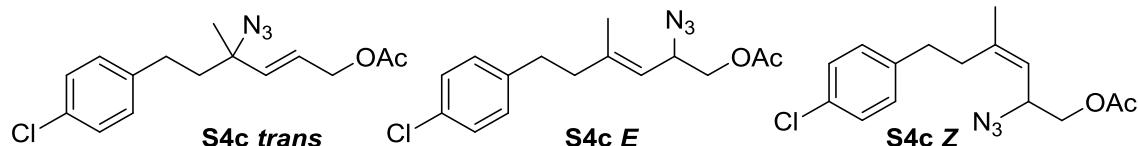
chromatography (0 to 40% gradient, EtOAc in hexanes) afforded azide **4a** (879 mg, 3.22 mmol, 91%) as a faintly yellow oil. Compound **S4a** was isolated as a mixture of three isomers (1.0:1.6:1.0 *trans:E:Z*).



¹H NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR**: (CDCl₃, 500 MHz) **S4a B**: δ 7.32 - 7.27 (m, 2H), 7.22-7.17 (m, 3H), 5.84 (dt, *J* = 15.5, 5.8 Hz, 1H) 5.76 (d, *J* = 15.5 Hz, 1H), 4.62 (d, *J* = 5.5 Hz, 2H), 2.66 (m, 2H), 2.09 (s, 3H), 1.89 (m, 2H), 1.45 (s, 3H); **S4a E**: δ 7.32-7.27 (m, 2H), 7.22-7.17 (m, 3H), 5.12 – 5.10 (m, 1H), 4.44 (ddd, *J* = 8.7, 8.2, 4.2 Hz, 1H), 4.05 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.93 (dd, *J* = 11.4, 8.0 Hz, 1H), 2.75 – 2.67 (m, 2H), 2.52 – 2.42 (m, 2H), 2.10 (s, 3H), 1.81 (s, 3H); **S4a Z**: δ 7.32-7.27 (m, 2H), 7.22-7.17 (m, 3H), 5.15 – 5.12 (m, 1H), 4.20 (ddd, *J* = 9.6, 7.0, 5.0 Hz, 1H), 3.81 – 3.77 (m, 2H), 2.74 (m, 2H), 2.44 (m, 2H), 2.10 (s, 3H), 1.81 (s, 3H); **¹³C NMR** (CDCl₃, 126 MHz): δ 170.8, 170.7, 170.6, 143.6, 143.4, 141.6, 141.5, 141.3, 136.3, 128.62, 128.61, 128.53, 128.51, 128.44, 128.40, 126.3, 126.15, 126.13, 124.9, 119.2, 118.5, 66.1, 66.0, 64.22, 64.17, 58.1, 57.3, 42.3, 41.4, 34.7, 34.5, 30.6, 23.8, 23.5, 21.0, 20.9, 17.2; **IR** (NaCl, thin film, cm⁻¹): 3062, 2938, 2860, 2100, 1743, 1224, 1031; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₁₉N₃O₂Na⁺ (M+Na)⁺ 296.1369, found 296.1380.

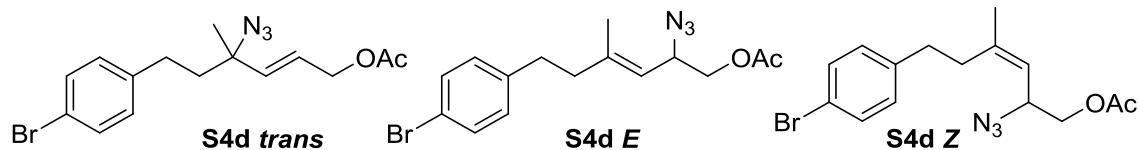


Compound S4b: A variation on general procedure 3 was used with the reaction run at 1 M concentration. The product was isolated in 70% yield as a clear oil. Compound **S4b** was isolated as a mixture of three isomers (1.0:1.8:1.2 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S4b trans**: δ 7.12 – 7.06 (m, 2H), 6.86 – 6.81 (m, 2H), 5.83 (dt, *J* = 15.6, 5.6 Hz, 1H), 5.75 (dt, *J* = 15.5, 1.1 Hz, 1H), 4.61 (dd, *J* = 5.7, 1.3 Hz, 2H), 3.78 (s, 3H), 2.61 – 2.55 (m, 2H), 2.09 (s, 3H), 1.88 – 1.81 (m, 2H), 1.43 (s, 3H); **S4b E**: δ 7.12 – 7.06 (m, 2H), 6.86 – 6.81 (m, 2H), 5.08 (dq, *J* = 9.1, 1.3 Hz, 1H), 4.43 (ddd, *J* = 9.1, 7.9, 4.3 Hz, 1H), 4.05 (dd, *J* = 11.4, 4.3 Hz, 1H), 3.93 (dd, *J* = 11.4, 7.9 Hz, 1H), 3.78 (s, 3H), 2.76 – 2.62 (m, 2H), 2.48 – 2.33 (m, 2H), 2.09 (s, 3H), 1.79 (d, *J* = 1.5 Hz, 3H); **S4b Z**: δ 7.12 – 7.06 (m, 2H), 6.86 – 6.81 (m, 2H), 5.11 (dd, *J* = 9.9, 1.6 Hz, 1H), 4.19 (ddd, *J* = 9.5, 7.5, 4.5 Hz, 1H), 3.83 – 3.75 (m, 2H), 3.78 (s, 3H), 2.76 – 2.62 (m, 2H), 2.48 – 2.33 (m, 2H), 2.08 (s, 3H), 1.85 (d, *J* = 1.5 Hz, 3H), 1.43 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.59, 170.56, 170.48, 158.1, 158.0, 157.9, 143.5, 143.3, 136.3, 133.5, 133.4, 133.2, 129.3, 129.22, 129.20, 124.7, 119.0, 118.4, 113.92, 113.88, 113.80, 66.0, 65.8, 64.09, 64.07, 58.0, 57.8, 55.22, 55.20, 55.18, 42.5, 41.5, 34.9, 33.49, 33.46, 29.6, 23.7, 23.4, 20.9, 20.72, 20.70, 17.1; **IR** (NaCl, thin film, cm⁻¹): 2935, 2836, 2104, 1744, 1612, 1513, 1456, 1380, 1246, 1178, 1036, 831; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₂₁N₃O₃Na⁺ (M+Na)⁺ 326.1475, found 326.1463.

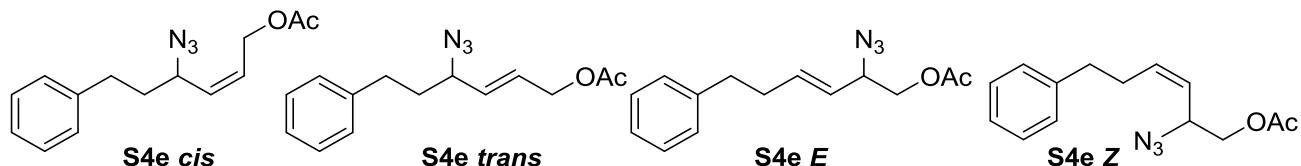


Compound S4c: A variation on general procedure 3 was used with the reaction run at 1 M concentration. The product was isolated in 75% yield as a clear oil. Compound **S4c** was isolated

as a mixture of three isomers (1.0:1.8:1.0 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: ¹H NMR (500 MHz, CDCl₃) **S4c trans**: δ 7.31 – 7.23 (m, 2H), 7.16 – 7.09 (m, 2H), 5.85 (dt, *J* = 15.7, 5.8 Hz, 1H), 5.76 (dt, *J* = 15.6, 1.3 Hz, 1H), 4.63 (dd, *J* = 5.7, 1.4 Hz, 2H), 2.66 – 2.58 (m, 2H), 2.11 (s, 3H), 1.89 – 1.82 (m, 2H), 1.46 (s, 3H); **S4c E**: δ 7.31 – 7.23 (m, 2H), 7.16 – 7.09 (m, 2H), 5.12 (dq, *J* = 9.2, 1.4 Hz, 1H), 4.44 (ddd, *J* = 9.1, 7.8, 4.3 Hz, 1H), 4.07 (dd, *J* = 11.4, 4.3 Hz, 1H), 3.96 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.78 – 2.68 (m, 2H), 2.42 – 2.36 (m, 2H), 2.11 (s, 3H), 1.81 (d, *J* = 1.5 Hz, 3H); **S4c Z**: δ 7.31 – 7.23 (m, 2H), 7.16 – 7.09 (m, 2H), 5.15 (dd, *J* = 9.6, 1.5 Hz, 1H), 4.24 (ddd, *J* = 9.5, 7.0, 5.2 Hz, 1H), 3.91 – 3.86 (m, 2H), 2.78 – 2.68 (m, 2H), 2.49 – 2.41 (m, 2H), 2.11 (s, 3H), 1.86 (d, *J* = 1.5 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.56, 170.53, 170.49, 143.1, 143.0, 140.0, 139.8, 139.7, 136.0, 132.0, 131.71, 131.69, 129.8, 129.7, 128.57, 128.55, 128.46, 125.0, 119.3, 118.8, 65.9, 65.8, 64.02, 63.96, 57.9, 57.7, 42.1, 41.1, 34.5, 33.8, 33.7, 29.9, 23.7, 23.4, 20.9, 20.7, 17.1; IR (NaCl, thin film, cm⁻¹) 2945, 2104, 1744, 1492, 1452, 1381, 1364, 1229, 1093, 1043, 816; HRMS: (ESI-TOF) *m/z* calcd for C₁₅H₁₈ClN₃O₂Na⁺ (M+Na)⁺ 330.0980, found 330.0980.

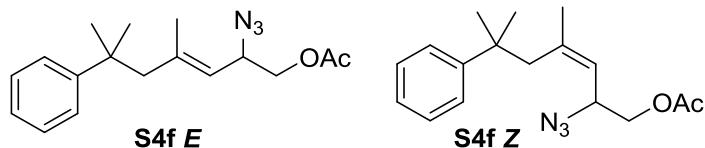


Compound S4d: A variation on general procedure 3 was used with the reaction run at 1 M concentration. The product was isolated in 80% yield as a clear oil. Compound **S4d** was isolated as a mixture of three isomers (1:1.8:1 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: ¹H NMR (400 MHz, CDCl₃) **S4d trans**: δ 7.42 – 7.35 (m, 2H), 7.07 – 7.00 (m, 2H), 5.82 (dt, *J* = 15.6, 5.6 Hz, 1H), 5.72 (dt, *J* = 15.7, 1.2 Hz, 1H), 4.60 (dd, *J* = 5.6, 1.1 Hz, 2H), 2.61 – 2.54 (m, 2H), 2.07 (s, 3H), 1.85 – 1.78 (m, 2H), 1.42 (s, 3H); **S4d E**: δ 7.42 – 7.35 (m, 2H), 7.07 – 7.00 (m, 2H), 5.08 (dq, *J* = 9.2, 1.4 Hz, 1H), 4.41 (ddd, *J* = 9.1, 7.8, 4.3 Hz, 1H), 4.04 (dd, *J* = 11.4, 4.3 Hz, 1H), 3.92 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.37 – 2.31 (m, 2H), 2.07 (s, 3H), 1.77 (d, *J* = 1.4 Hz, 3H); **S4d Z**: δ 7.42 – 7.35 (m, 2H), 7.07 – 7.00 (m, 2H), 5.12 (dd, *J* = 9.4, 1.5 Hz, 1H), 4.21 (dt, *J* = 9.5, 6.1 Hz, 1H), 3.85 (d, *J* = 6.0 Hz, 2H), 2.76 – 2.61 (m, 2H), 2.44 – 2.37 (m, 2H), 2.07 (s, 3H), 1.83 (d, *J* = 1.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.56, 170.53, 170.50, 143.0, 142.9, 140.5, 140.3, 140.2, 135.9, 131.52, 131.49, 131.40, 130.2, 130.1, 124.9, 120.0, 119.7, 119.3, 118.8, 65.9, 65.8, 64.02, 63.96, 57.9, 57.7, 42.0, 41.0, 34.4, 33.8, 33.7, 29.9, 23.7, 23.4, 20.9, 20.8, 17.1; IR (NaCl, thin film, cm⁻¹) 3024, 2945, 2863, 2105, 1744, 1665, 1488, 1451, 1380, 1364, 1227, 1072, 1043, 1011, 974, 836, 814; HRMS (ESI-TOF) *m/z* calcd for C₁₅H₁₈BrN₃O₂Na⁺ (M+Na)⁺ 374.0475, found 374.0486.

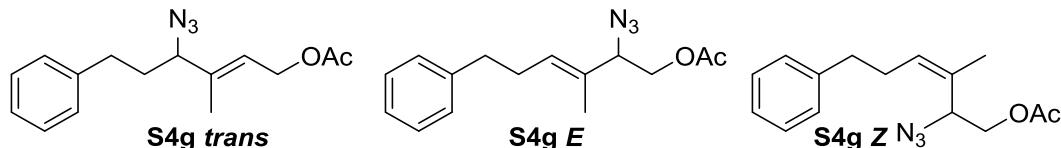


Compound S4e: A variation of general procedure 3 was used: The reaction was run at 1 M concentration for 3 d. The product was isolated in 31% yield as a clear oil. Compound **S4e** was isolated as a mixture of four isomers (trace:1:0.75:trace *cis:trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: ¹H NMR (500 MHz, CDCl₃) **S4e trans** δ 7.34 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 5.92 – 5.80 (m, 1H), 5.72 (ddt, *J* = 15.5, 7.6, 1.4 Hz, 1H), 4.61 (dd, *J* = 5.8, 1.3 Hz, 2H), 3.86 (q, *J* = 7.3 Hz, 1H), 2.78 – 2.64 (m, 2H), 2.10 (s, 3H), 1.94 – 1.80 (m, 2H); **S4e E** δ 7.34 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 5.92 – 5.80 (m, 1H), 5.40

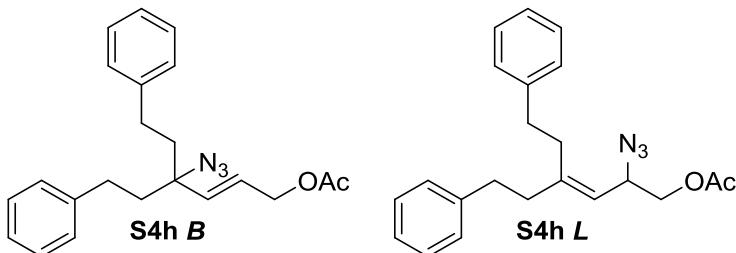
(ddt, $J = 15.5, 7.5, 1.5$ Hz, 1H), 4.14 – 4.08 (m, 2H), 3.98 (dd, $J = 12.4, 8.9$ Hz, 1H), 2.78 – 2.64 (m, 2H), 2.47 – 2.40 (m, 2H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.4, 141.1, 140.8, 140.5, 136.4, 134.1, 131.4, 128.5, 128.38, 128.36, 128.32, 128.1, 126.6, 126.12, 126.08, 125.96, 123.95, 65.6, 63.6, 63.5, 62.8, 62.1, 60.8, 39.7, 35.9, 35.3, 33.9, 32.4, 31.8, 20.8, 20.6; IR (NaCl, thin film, cm^{-1}) 3027, 2924, 2850, 2098, 1742, 1602, 1496, 1454, 1383, 1365, 1227, 1028, 970, 748, 700; HRMS (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 282.1213, found 282.1217.



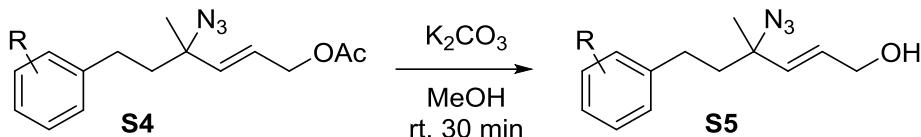
Compound S4f: General procedure 3 was used and the product was isolated in 98% as a clear oil. Compound **S4f** was isolated in a mixture of two isomers (1:0.25 *E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: ^1H NMR (500 MHz, CDCl_3) **S4f E** δ 7.41 – 7.28 (m, 4H), 7.23 – 7.16 (m, 1H), 4.92 (dq, $J = 9.1, 1.7$ Hz, 1H), 4.35 (ddd, $J = 9.2, 7.7, 4.5$ Hz, 1H), 3.98 (dd, $J = 11.4, 4.5$ Hz, 1H), 3.90 (dd, $J = 11.3, 7.6$ Hz, 1H), 2.43 (d, $J = 13.3$ Hz, 1H), 2.41 (d, $J = 13.3$ Hz, 1H), 2.09 (s, 3H), 1.46 – 1.33 (m, 9H); **S4f Z** δ 7.41 – 7.28 (m, 4H), 7.23 – 7.16 (m, 1H), 5.14 (dq, $J = 9.9, 1.6$ Hz, 1H), 4.20 (ddd, $J = 9.8, 7.8, 4.1$ Hz, 1H), 3.92 – 3.86 (m, 1H), 3.84 (dd, $J = 11.4, 7.8$ Hz, 1H), 2.57 (d, $J = 13.6$ Hz, 1H), 2.47 (d, $J = 13.4$ Hz, 1H), 2.10 (s, 3H), 1.46 – 1.33 (m, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.7, 148.9, 148.7, 142.4, 141.8, 128.3, 128.2, 126.05, 126.03, 125.98, 125.86, 121.8, 121.2, 66.0, 65.8, 58.0, 57.9, 54.5, 47.3, 38.3, 38.0, 29.54, 29.52, 29.2, 28.9, 25.8, 20.9, 20.8, 18.9; IR (NaCl, thin film, cm^{-1}) 3059, 3023, 2963, 2104, 1745, 1658, 1600, 1495, 1444, 1384, 1366, 1224, 1039, 872, 765, 700; HRMS (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 324.1682, found 324.1694.



Compound S4g: A variation of general procedure 3 was used. The reaction ran for 18 h instead of 90 min. The product was isolated in 44% yield as a clear pink oil. Compound **S4g** was isolated as a mixture of two isomers (1:0.6: *trans:E*). Trace amounts of **S4g Z** were observed. NMR data given below is based off of idealized integrations of the resulting mixture: ^1H NMR (500 MHz, CDCl_3) **S4g trans** δ 7.35 – 7.28 (m, 2H), 7.26 – 7.17 (m, 3H), 5.63 – 5.59 (m, 1H), 4.68 (d, $J = 6.8$ Hz, 2H), 3.85 (dd, $J = 8.1, 6.3$ Hz, 1H), 2.75 – 2.59 (m, 2H), 2.09 (s, 3H), 1.97 – 1.80 (m, 2H), 1.75 (d, $J = 1.4$ Hz, 3H), **S4g E** δ 7.35 – 7.28 (m, 2H), 7.26 – 7.17 (m, 3H), 5.60 – 5.56 (m, 1H), 4.15 – 4.10 (m, 2H), 4.06 (dd, $J = 12.2, 9.6$ Hz, 1H), 2.75 – 2.59 (m, 2H), 2.47 – 2.38 (m, 2H), 2.09 (s, 3H), 1.60 (d, $J = 1.3$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.7, 170.5, 141.4, 140.9, 138.9, 138.0, 131.2, 130.5, 130.3, 128.6, 128.5, 128.44, 128.40, 128.35, 128.34, 126.2, 126.14, 126.08, 125.97, 124.1, 123.6, 68.8, 67.7, 64.8, 64.7, 60.9, 60.5, 60.0, 59.3, 36.0, 35.5, 34.1, 34.0, 32.2, 29.6, 20.93, 20.87, 20.7, 18.6, 18.1, 12.4, 12.3; IR (NaCl, thin film, cm^{-1}) 3027, 2948, 2860, 2096, 1740, 1603, 1496, 1454, 1368, 1232, 1028, 751, 700; HRMS (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 296.1369, found 296.1375.

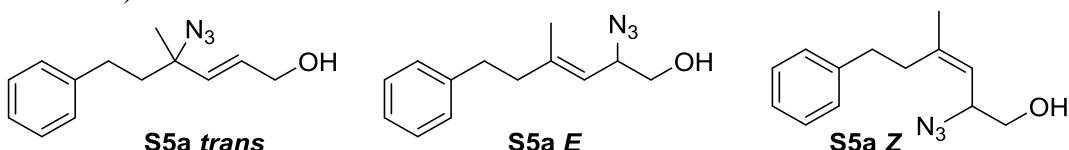


Compound S4h: General procedure 3 was used and the product was isolated in 70% yield as a yellow oil. Compound **S4h** was isolated as a mixture of two isomers (1:5 *B:L*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S4h B** δ 7.35 – 7.29 (m, 4H), 7.26 – 7.18 (m, 6H), 5.92 (dt, *J* = 15.6, 5.9 Hz, 1H), 5.73 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.67 (dd, *J* = 6.0, 1.4 Hz, 2H), 2.85 – 2.66 (m, 4H), 2.12 (s, 3H), 2.06 (ddd, *J* = 15.0, 7.3, 4.4 Hz, 2H), 1.97 (ddd, *J* = 14.2, 11.0, 6.3 Hz, 2H); **S4h L** δ 7.35 – 7.29 (m, 4H), 7.26 – 7.18 (m, 6H), 5.15 (d, *J* = 9.5 Hz, 1H), 4.26 (ddd, *J* = 9.5, 6.9, 5.0 Hz, 1H), 3.85 – 3.77 (m, 2H), 2.85 – 2.66 (m, 4H), 2.55 – 2.43 (m, 4H), 2.10 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.8, 170.7, 146.6, 141.6, 141.5, 141.2, 134.8, 128.69, 128.65, 128.57, 128.55, 128.50, 128.48, 126.41, 126.26, 126.21, 126.1, 119.3, 67.0, 66.0, 64.3, 57.8, 40.1, 38.4, 35.0, 34.8, 33.3, 30.5, 21.1, 20.9; **IR** (NaCl, thin film, cm⁻¹) 3026, 2934, 2860, 2104, 1744, 1602, 1496, 1454, 1364, 1226, 1041, 748, 699; **HRMS** (ESI-TOF) *m/z* calcd for C₂₂H₂₅N₃O₂Na⁺ (M+Na)⁺ 386.1839, found 386.1831.



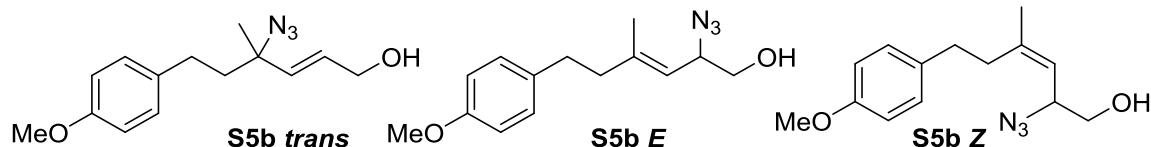
General Procedure 4: Acetate deprotection of allylic azides: Example given for R = H.

Compound S5a: To a solution of acetate **S4a** (840 mg, 3.0 mmol) in methanol (15 mL) at room temperature, potassium carbonate (1.25 g, 9.2 mmol) was added. After 40 min, the reaction was quenched by the addition of water (20 mL) and the resulting solution was extracted with DCM (3 x 10 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated *in vacuo* to afford alcohol **S5a** (690 mg, 2.9 mmol, 98%) as a light yellow oil of sufficient purity to advance without further purification. Compound **S5a** was isolated as a mixture of three isomers (1:5:3 *trans:E:Z*).



¹H NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR**: (CDCl₃, 500 MHz) **S5a trans**: δ 7.35–7.15 (m, 5H), 5.91 (dt, *J* = 15.6, 5.1 Hz, 1H), 5.74 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.23 (dd, *J* = 5.1, 1.6 Hz, 2H), 2.44 (m, 2H), 1.92 (br s, 1H), 1.88 (m, 2H), 1.47 (s, 3H); **S5a E**: δ 7.35–7.15 (m, 5H), 5.10 (dq, *J* = 9.3, 1.1 Hz, 1H), 4.35 (dt, *J* = 9.3, 6.0 Hz, 1H), 3.47 (d, *J* = 6.0 Hz, 2H), 2.81 (m, 2H), 2.44 (m, 2H), 1.92 (br s, 1H), 1.82 (d, *J* = 1.4 Hz, 3H); **S5a Z**: δ 7.35–7.15 (m, 5H), 5.17 (dq, *J* = 9.7, 1.6 Hz, 1H), 4.13 (ddd, *J* = 9.7, 7.5, 4.4 Hz, 1H), 3.32 (dd, *J* = 11.4, 7.5 Hz, 1H) 3.27 (dd, *J* = 11.4, 4.4, 1H), 2.81 (m, 2H), 2.44 (m, 2H), 1.91 (br s, 1H), 1.89 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (CDCl₃, 126 MHz) δ 143.6, 143.3, 141.7, 141.5, 141.4, 133.1, 129.9, 128.57, 128.56, 128.48, 128.45, 128.3, 126.3, 126.11, 126.08, 119.7, 119.1, 66.1, 65.0, 64.3, 62.9, 61.6, 61.5, 42.4, 41.5, 34.8, 34.61, 34.56, 34.5, 31.0, 30.7, 29.8, 23.9, 23.5, 17.2; **IR** (NaCl,

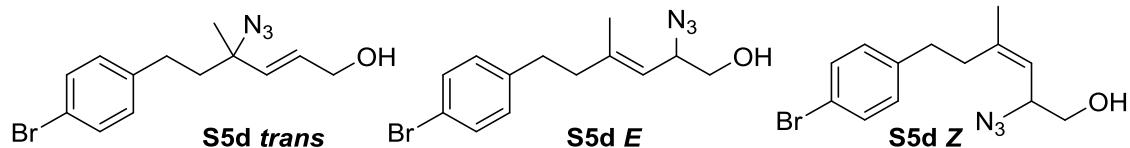
thin film, cm^{-1}): 3397, 3027, 2931, 2860, 2103, 1453, 1245; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{ONa}^+$ ($\text{M}+\text{Na}$)⁺ 254.1264, found 254.1256.



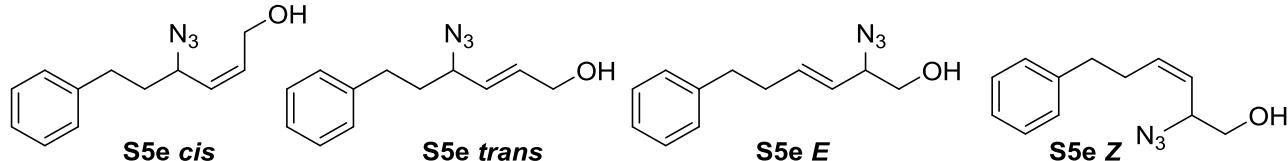
Compound S5b: General procedure 4 was used and the product was isolated in 94% yield as an off-clear oil. Compound **S5b** was isolated as a mixture of three isomers (1:5.7:3.3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl_3) **S5b trans**: δ 7.13 – 7.08 (m, 2H), 6.88 – 6.82 (m, 2H), 5.89 (dt, J = 15.6, 5.1 Hz, 1H), 5.74 (dt, J = 15.5, 1.6 Hz, 1H), 4.21 (dd, J = 5.1, 1.6 Hz, 2H), 3.79 (s, 3H), 2.77 – 2.58 (m, 2H), 2.18 (br s, 1H), 1.90 – 1.83 (m, 2H), 1.44 (s, 3H); **S5b E**: δ 7.13 – 7.08 (m, 2H), 6.88 – 6.82 (m, 2H), 5.11 (dq, J = 9.3, 1.4 Hz, 1H), 4.34 (dt, J = 9.3, 6.0 Hz, 1H), 3.79 (s, 3H), 3.48 (d, J = 6.1 Hz, 2H), 2.77 – 2.58 (m, 2H), 2.48 – 2.33 (m, 2H), 2.18 (br s, 1H), 1.80 (d, J = 1.5 Hz, 3H); **S5b Z**: δ 7.13 – 7.08 (m, 2H), 6.88 – 6.82 (m, 2H), 5.16 (dq, J = 9.7, 1.5 Hz, 1H), 4.15 (ddd, J = 9.5, 7.3, 4.4 Hz, 1H), 3.79 (s, 3H), 3.35 (dd, J = 11.4, 7.4 Hz, 1H), 3.30 (dd, J = 11.4, 4.4 Hz, 1H), 2.77 – 2.58 (m, 2H), 2.48 – 2.33 (m, 2H), 2.18 (br s, 1H), 1.87 (d, J = 1.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl_3) δ 158.1, 157.9, 143.6, 143.3, 133.7, 133.6, 133.4, 133.0, 129.9, 129.4, 129.30, 129.27, 119.6, 119.0, 114.0, 113.9, 65.1, 65.0, 64.3, 62.8, 61.6, 61.5, 55.4, 55.3, 42.6, 41.7, 34.9, 33.7, 33.5, 31.7, 29.7, 23.8, 23.5, 22.7, 17.2, 14.2; **IR** (NaCl, thin film, cm^{-1}) 3432, 2925, 2097, 1610, 1508, 1242, 1175, 825, 754; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 284.1369, found 284.1363.



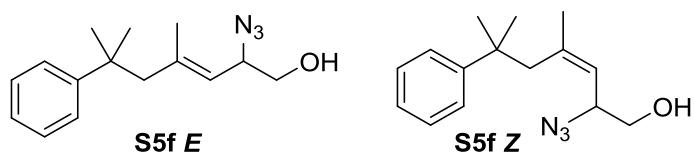
Compound S5c: General procedure 4 was used and the product was isolated in 84% yield as a clear oil. Compound **S5c** was isolated as a mixture of three isomers (1:6:3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl_3) **S5c trans**: δ 7.29 – 7.22 (m, 2H), 7.13 – 7.07 (m, 2H), 5.90 (dt, J = 15.6, 5.1 Hz, 1H), 5.73 (dt, J = 15.8, 1.6 Hz, 1H), 4.22 (dd, J = 5.2, 1.6 Hz, 2H), 2.65 – 2.59 (m, 2H), 2.23 (br s, 1H), 1.88 – 1.80 (m, 2H), 1.44 (s, 3H); **S5c E**: δ 7.29 – 7.22 (m, 2H), 7.13 – 7.07 (m, 2H), 5.11 (dq, J = 9.3, 1.4 Hz, 1H), 4.34 (ddd, J = 9.3, 7.0, 4.9 Hz, 1H), 3.50 (dd, J = 10.6, 4.1 Hz, 1H), 3.47 (dd, J = 10.6, 6.2 Hz, 1H), 2.78 – 2.66 (m, 2H), 2.47 – 2.32 (m, 2H), 2.23 (br s, 1H), 1.79 (d, J = 1.4 Hz, 3H); **S5c Z**: δ 7.29 – 7.22 (m, 2H), 7.13 – 7.07 (m, 2H), 5.18 (dq, J = 9.6, 1.5 Hz, 1H), 4.15 (ddd, J = 9.6, 7.2, 4.6 Hz, 1H), 3.39 (dd, J = 11.4, 7.2 Hz, 1H), 3.34 (dd, J = 11.3, 4.6 Hz, 1H), 2.78 – 2.66 (m, 2H), 2.47 – 2.32 (m, 2H), 2.23 (br s, 1H), 1.86 (d, J = 1.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl_3) δ 143.1, 143.0, 140.1, 139.9, 139.8, 132.8, 132.0, 131.8, 130.1, 129.79, 129.76, 129.75, 128.61, 128.59, 128.51, 119.9, 119.2, 65.1, 65.0, 64.2, 62.8, 61.6, 61.4, 42.3, 41.2, 34.5, 33.9, 33.8, 30.0, 23.9, 23.5, 17.2; **IR** (NaCl, thin film, cm^{-1}) 3393, 2932, 2865, 2103, 1664, 1492, 1453, 1407, 1381, 1245, 1092, 1070, 1043, 1015, 817; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{ClN}_3\text{ONa}^+$ ($\text{M}+\text{Na}$)⁺ 288.0874, found 288.0873.



Compound S5d: General procedure 4 was used and the product was isolated in 96% yield as a clear oil. Compound **S5d** was isolated as a mixture of three isomers (1:6:3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S5d trans:** δ 7.44 – 7.38 (m, 2H), 7.09 – 7.02 (m, 2H), 5.89 (dt, *J* = 15.8, 5.1 Hz, 1H), 5.73 (dt, *J* = 15.7, 1.7 Hz, 1H), 4.22 (dd, *J* = 5.2, 1.6 Hz, 2H), 2.63 – 2.58 (m, 2H), 2.08 (br s, 1H), 1.88 – 1.81 (m, 2H), 1.44 (s, 3H); **S5d E:** δ 7.44 – 7.38 (m, 2H), 7.09 – 7.02 (m, 2H), 5.11 (dq, *J* = 9.2, 1.5 Hz, 1H), 4.34 (ddd, *J* = 9.3, 7.0, 4.9 Hz, 1H), 3.50 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.46 (dd, *J* = 11.3, 7.0 Hz, 1H), 2.78 – 2.64 (m, 2H), 2.52 – 2.31 (m, 2H), 2.08 (br s, 1H), 1.79 (d, *J* = 1.4 Hz, 3H); **S5d Z:** δ 7.44 – 7.38 (m, 2H), 7.09 – 7.02 (m, 2H), 5.17 (dq, *J* = 9.7, 1.5 Hz, 1H), 4.15 (ddd, *J* = 9.6, 7.2, 4.6 Hz, 1H), 3.38 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.34 (dd, *J* = 11.4, 4.6 Hz, 1H), 2.78 – 2.64 (m, 2H), 2.52 – 2.31 (m, 2H), 2.08 (br s, 1H), 1.85 (d, *J* = 1.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 143.2, 143.0, 140.7, 140.4, 140.3, 132.8, 131.61, 131.59, 131.51, 131.45, 130.26, 130.22, 130.20, 130.18, 130.08, 120.0, 119.9, 119.81, 119.79, 119.3, 65.1, 65.0, 64.2, 62.8, 61.6, 61.4, 42.3, 41.2, 34.5, 34.0, 33.9, 30.1, 23.9, 23.5, 17.2; **IR** (NaCl, thin film, cm⁻¹) 3373, 2931, 2864, 2107, 1664, 1488, 1452, 1403, 1382, 1310, 1244, 1072, 1039, 1011, 921, 812; **HRMS** (ESI-TOF) *m/z* calcd for C₁₃H₁₆BrN₃ONa⁺ (M+Na)⁺ 332.0369, found 332.0355.

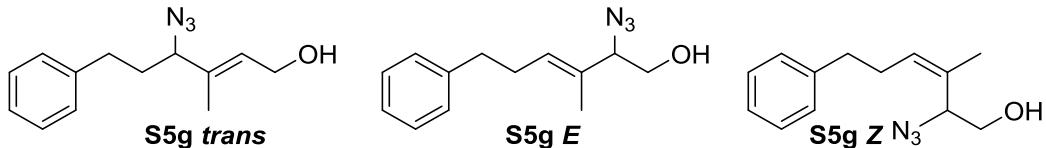


Compound S5e: General procedure 4 was used and the product was isolated in 97% yield as a clear oil. Compound **S5e** was isolated as a mixture of four isomers (trace:1:0.75:0.4 *cis:trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S5e trans** δ 7.40 – 7.31 (m, 2H), 7.29 – 7.20 (m, 3H), 5.96 – 5.87 (m, 1H), 5.73 (ddt, *J* = 15.3, 7.8, 1.8 Hz, 1H), 4.22 (dd, *J* = 5.0, 1.6 Hz, 2H), 3.91 (q, *J* = 7.4 Hz, 1H), 2.85 – 2.69 (m, 2H), 2.43 (br s, 1H), 1.99 – 1.85 (m, 2H); **S5e E** δ 7.40 – 7.31 (m, 2H), 7.29 – 7.20 (m, 3H), 5.96 – 5.87 (m, 1H), 5.44 (ddt, *J* = 15.4, 8.0, 1.6 Hz, 1H), 4.03 (ddd, *J* = 8.0, 7.3, 4.5 Hz, 1H), 3.60 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.53 (dd, *J* = 11.4, 7.3 Hz, 1H), 2.85 – 2.69 (m, 2H), 2.56 – 2.45 (m, 2H), 2.43 (br s, 1H); **S5e Z** δ 7.40 – 7.31 (m, 2H), 7.29 – 7.20 (m, 3H), 5.96 – 5.87 (m, 1H), 5.42 – 5.36 (m, 1H), 4.32 (ddd, *J* = 9.6, 6.8, 4.6 Hz, 1H), 3.48 – 3.36 (m, 2H), 2.85 – 2.69 (m, 2H), 2.56 – 2.45 (m, 2H), 2.43 (br s, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 141.2, 141.03, 140.97, 136.5, 135.9, 133.6, 131.8, 131.4, 128.7, 128.54, 128.53, 128.48, 128.40, 128.3, 126.8, 126.17, 126.13, 126.04, 124.6, 123.7, 66.0, 64.8, 64.7, 63.2, 62.4, 62.3, 61.6, 60.6, 40.0, 36.1, 35.7, 35.5, 34.1, 32.6, 32.0, 29.9; **IR** (NaCl, thin film, cm⁻¹) 3383, 3027, 2926, 2853, 2102, 1496, 1454, 1244, 1094, 1064, 1030, 971, 747, 700; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₅N₃ONa⁺ (M+Na)⁺ 240.1107, found 240.1108.

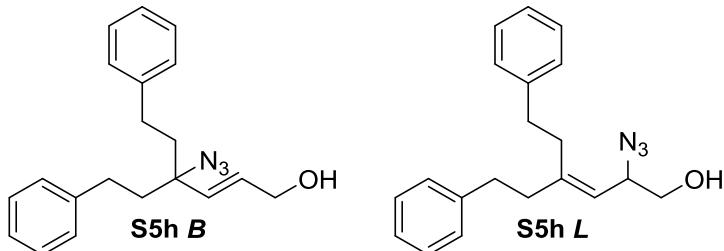


Compound S5f: General procedure 4 was used and the product was isolated in quantitative yield as a clear oil. Compound **S5f** was isolated in a mixture of two isomers (1:0.3 *E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S5f E** δ 7.45 – 7.29 (m, 4H), 7.26 – 7.19 (m, 1H), 4.93 (d, *J* = 9.3 Hz, 1H), 4.27 (dt, *J* = 9.3, 6.1 Hz, 1H), 3.42 (br s, 2H), 2.48 (d, *J* = 13.0 Hz, 1H), 2.43 (d, *J* = 13.1 Hz, 1H), 2.23 (br s,

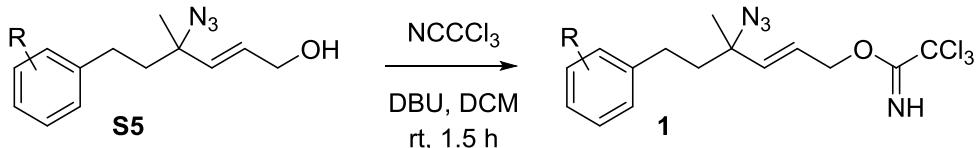
1H), 1.41 (s, 3H), 1.39 (s, 6H); **S5f Z** δ 7.45 – 7.29 (m, 4H), 7.26 – 7.19 (m, 1H), 5.19 (d, $J = 10.0$ Hz, 1H), 4.20 – 4.12 (m, 1H), 3.37 (br s, 2H), 2.61 (d, $J = 13.6$ Hz, 1H), 2.52 – 2.46 (m, 1H) 2.23 (br s, 1H), 1.44 (s, 3H), 1.41 (s, 6H); **¹³C NMR** (126 MHz, CDCl₃) δ 148.7, 142.1, 141.7, 128.2, 128.1, 126.1, 126.0, 125.9, 125.8, 122.3, 121.7, 65.0, 64.9, 61.7, 61.6, 54.6, 47.3, 38.3, 38.0, 29.6, 29.4, 28.6, 25.8, 18.9; **IR** (NaCl, thin film, cm⁻¹) 3386, 2965, 2928, 2873, 2112, 1495, 1446, 1386, 1243, 1076, 1033, 1013, 765, 703; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₂₁N₃ONa⁺ (M+Na)⁺ 282.1577, found 282.1576.



Compound S5g: General procedure 4 was used and the product was isolated in quantitative yield as a clear pink oil. Compound **S5g** was isolated as a mixture of two isomers (1:3.5 *trans:E*). Trace amounts of **S5g Z** were observed. NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S5g trans** δ 7.35 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 5.66 (tp, $J = 6.1, 1.1$ Hz, 1H), 4.28 (dd, $J = 13.2, 6.5$ Hz, 1H), 4.24 (dd, $J = 13.0, 6.4$ Hz, 1H), 3.85 (dd, $J = 8.1, 6.4$ Hz, 1H), 2.79 – 2.59 (m, 2H), 1.98 (br s, 1H), 2.04 – 1.77 (m, 2H), 1.71 (d, $J = 1.3$ Hz, H); **S5g E** δ 7.35 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 5.58 (tp, $J = 7.1, 1.0$ Hz, 1H), 4.01 (t, $J = 6.6$ Hz, 1H), 3.55 (d, $J = 6.7$ Hz, 2H), 2.79 – 2.59 (m, 2H), 2.51 – 2.38 (m, 2H), 1.98 (br s, 1H), 1.56 (d, $J = 1.4$ Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 141.6, 141.0, 135.5, 131.3, 130.8, 130.6, 128.9, 128.65, 128.62, 128.60, 128.57, 128.53, 128.50, 128.46, 126.22, 126.17, 126.08, 71.6, 69.2, 64.0, 63.6, 63.5, 59.0, 36.2, 35.6, 34.1, 32.4, 29.7, 18.9, 12.6, 12.2; **IR** (NaCl, thin film, cm⁻¹) 3376, 3062, 3027, 2925, 2859, 2098, 1603, 1496, 1453, 1386, 1317, 1244, 1047, 1010, 749, 699; **HRMS** (ESI-TOF) *m/z* calcd for C₁₃H₁₇N₃ONa⁺ (M+Na)⁺ 254.1264, found 254.1258.

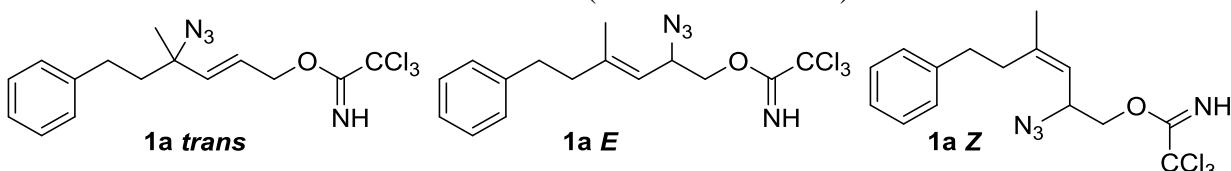


Compound S5h: General procedure 4 was used and the product was isolated in 89% as a yellow oil. Compound **xx** was isolated predominantly as a single isomer (**S5h L**). Trace amounts of **S5h B** were observed. NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) δ 7.43 (t, $J = 7.5$ Hz, 4H), 7.38 – 7.26 (m, 6H), 5.25 (d, $J = 9.7$ Hz, 1H), 4.26 (ddd, $J = 9.7, 7.3, 4.5$ Hz, 1H), 3.42 (dd, $J = 11.4, 7.3$ Hz, 1H), 3.34 (dd, $J = 11.4, 4.5$ Hz, 1H), 2.97 – 2.77 (m, 4H), 2.66 – 2.52 (m, 4H), 2.28 (br s, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 146.2, 141.4, 141.1, 128.46, 128.42, 128.39, 128.38, 126.2, 126.0, 119.8, 64.9, 61.2, 38.2, 34.9, 34.6, 32.9; **IR** (NaCl, thin film, cm⁻¹) 3424, 3026, 2926, 2881, 2101, 1495, 1453, 1243, 1196, 1077, 1030, 747, 699; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₃N₃ONa⁺ (M+Na)⁺ 344.1733, found 344.1721.

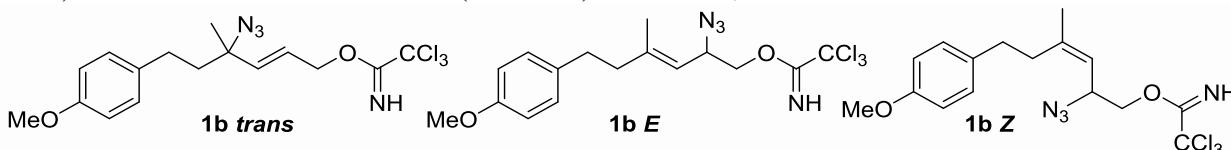


General Procedure 5: Activation as Trichloroacetimidate: Example given for R = H.

Compound 1a: To solution of alcohol **S5a** (264 mg, 1.14 mmol) in DCM (11 mL) at room temperature, trichloroacetonitrile (0.23 mL, 2.28 mmol), and DBU (43 μ L, 0.29 mmol, 25 mol%) were sequentially added. After 90 min, the solution was concentrated *in vacuo* and loaded onto a column cartridge. Final purification by column chromatography (0 to 40% gradient, EtOAc in hexanes) afforded trichloroacetimidate **1a** (417 mg, 1.08 mmol, 95%) as a yellow oil. Compound **1a** was isolated as a mixture of three isomers (1:1.3:0.7 *trans:E:Z*).

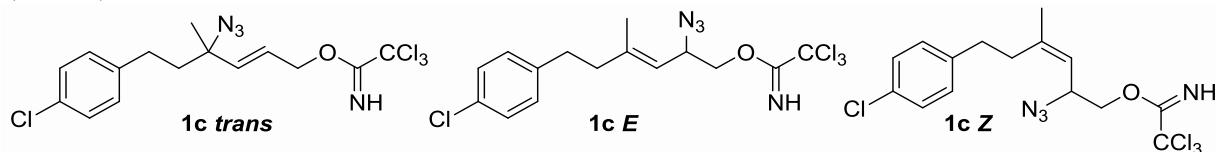


NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR**: (CDCl₃, 500 MHz) **1a trans**: δ 8.39 (s, 1H), 7.35–7.15 (m, 5H), 5.97 (dt, J = 15.7, 5.4 Hz, 1H), 5.90 (d, J = 15.9 Hz, 1H), 4.89 (d, J = 5.3 Hz, 2H), 2.70 – 2.61 (m, 2H), 1.90 (m, 2H), 1.48 (s, 3H); **1a E**: δ 8.39 (s, 1H), 7.35–7.15 (m, 5H), 5.21 (d, J = 9.3 Hz, 1H), 4.61 (ddd, J = 9.0, 7.5, 4.6 Hz 1H), 4.27 (dd, J = 11.2, 4.6 Hz, 1H), 4.21 (dd, J = 11.1, 7.4 Hz, 1H), 2.78 (t, J = 8.4 Hz, 2H), 2.42 (t, J = 8.1, 2H), 1.85 (s, 3H), **1a Z**: δ 8.39 (s, 1H), 7.35–7.15 (m, 5H), 5.21 (d, J = 9.3 Hz, 1H), 4.36 (ddd, J = 9.6, 7.8, 4.2 Hz, 1H), 4.04 (dd, J = 11.1, 7.6 Hz, 1H), 3.95 (dd, J = 11.2, 4.1 Hz, 1H), 2.79 (m, 2H), 2.50 (m, 2H), 1.89 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 162.6, 162.5, 162.4, 143.7, 143.4, 141.6, 141.5, 141.3, 136.8, 128.59, 128.51, 128.49, 128.41, 126.4, 126.12, 126.11, 124.0, 119.1, 118.4, 91.4, 91.2, 70.6, 70.5, 68.6, 64.2, 57.7, 57.5, 42.4, 41.4, 34.8, 34.5, 34.4, 30.6, 23.9, 23.5, 17.3; **IR** (NaCl, thin film, cm⁻¹) 3425, 2104, 1663, 1454, 1307, 832, 796; **HRMS** (CI-TOF) *m/z* calcd for C₁₅H₁₈Cl₃N₂O⁺ (M-N₂+H)⁺ 347.0479, found 347.0485.

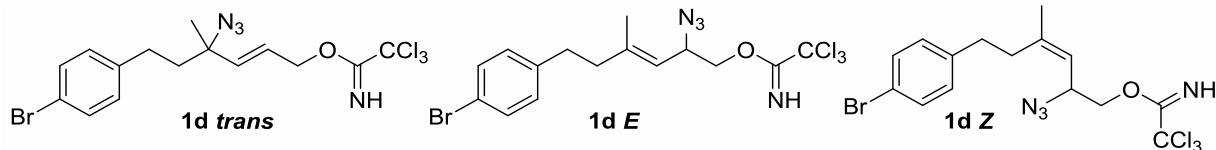


Compound 1b: General procedure 5 was used and the product was isolated in 71% yield as a clear oil. Compound **1b** was isolated as a mixture of three isomers (1:1.6:1 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **1b trans**: δ 8.40 (s, 1H), 7.12 – 7.09 (m, 2H), 6.87 – 6.83 (m, 2H), 5.96 (dt, J = 15.7, 5.3 Hz, 1H), 5.89 (dt, J = 15.7, 1.2 Hz, 1H), 4.88 (dd, J = 5.7, 1.0 Hz, 2H), 3.79 (s, 3H), 2.65 – 2.55 (m, 2H), 1.92 – 1.85 (m, 2H), 1.47 (s, 3H); **1b E**: δ 8.42 (s, 1H), 7.12 – 7.09 (m, 2H), 6.87 – 6.83 (m, 2H), 5.20 (dq, J = 9.2, 1.3 Hz, 1H), 4.60 (ddd, J = 9.1, 7.3, 4.6 Hz, 1H), 4.26 (dd, J = 11.2, 4.5 Hz, 1H), 4.21 (dd, J = 11.2, 7.3 Hz, 1H), 3.80 (s, 3H), 2.79 – 2.66 (m, 2H), 2.40 – 2.36 (m, 2H), 1.83 (d, J = 1.4 Hz, 3H); **1b Z**: δ 8.38 (s, 1H), 7.12 – 7.09 (m, 2H), 6.87 – 6.83 (m, 2H), 5.20 (dq, J = 9.2, 1.3 Hz, 1H), 4.37 (ddd, J = 9.5, 7.5, 4.1 Hz, 1H), 4.05 (dd, J = 11.2, 7.6 Hz, 1H), 3.97 (dd, J = 11.1, 4.2 Hz, 1H), 3.80 (s, 3H), 2.79 – 2.66 (m, 2H), 2.51 – 2.40 (m, 2H), 1.88 (d, J = 1.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 162.6, 162.5, 162.4, 158.2, 158.03, 158.00, 143.8, 143.4, 136.8, 133.64, 133.55, 133.3, 129.4, 129.3, 123.9, 119.1, 118.4, 114.1, 114.0, 113.9, 91.5, 91.2, 70.7, 70.5, 68.6, 64.2, 57.7, 57.6, 55.34, 55.33, 55.30, 42.6, 41.7, 35.0, 33.6, 33.5, 29.7, 23.9, 23.5, 17.3;

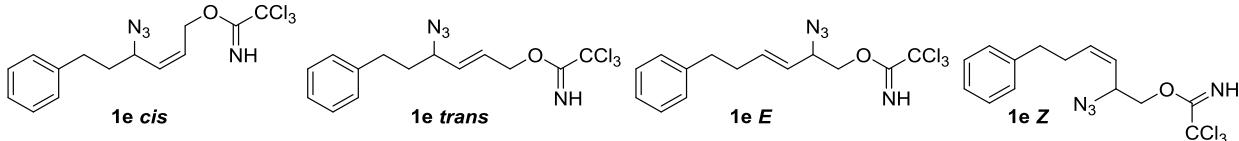
IR (NaCl, thin film, cm^{-1}) 3340, 2934, 2835, 2105, 1666, 1611, 1522, 1454, 1380, 1301, 1247, 1147, 1080, 1037, 1006, 827, 797; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{19}\text{N}_4\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 427.0466, found 427.0473.



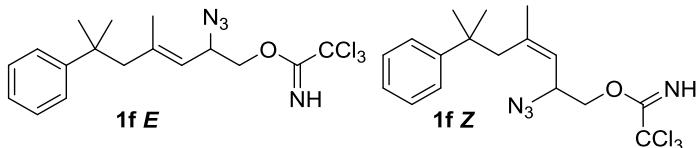
Compound 1c: General procedure 5 was used and the product was isolated in 84% yield as a clear oil. Compound **1c** was isolated as a mixture of three isomers (1:1.6:0.9 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl_3) **1c trans**: δ 8.39 (s, 1H), 7.29 – 7.23 (m, 2H), 7.14 – 7.07 (m, 2H), 5.95 (dt, $J = 15.7, 5.4$ Hz, 1H), 5.88 (dt, $J = 15.7, 1.1$ Hz, 1H), 4.87 (dd, $J = 5.4, 1.1$ Hz, 2H), 2.67 – 2.56 (m, 2H), 1.89 – 1.81 (m, 2H), 1.46 (s, 3H); **1c E**: δ 8.41 (s, 1H), 7.29 – 7.23 (m, 2H), 7.14 – 7.07 (m, 2H), 5.20 – 5.16 (m, 1H), 4.61 – 4.55 (m, 1H), 4.25 (dd, $J = 11.1, 4.6$ Hz, 1H), 4.20 (dd, $J = 11.1, 7.1$ Hz, 1H), 2.80 – 2.68 (m, 2H), 2.40 – 2.35 (m, 2H), 1.82 (d, $J = 1.5$ Hz, 2H); **1c Z**: δ 8.40 (s, 1H), 7.29 – 7.23 (m, 2H), 7.14 – 7.07 (m, 2H), 5.22 – 5.20 (m, 1H), 4.37 (ddd, $J = 9.5, 7.6, 4.2$ Hz, 1H), 4.07 (dd, $J = 11.2, 7.6$ Hz, 1H), 3.98 (dd, $J = 11.2, 4.3$ Hz, 1H), 2.80 – 2.68 (m, 2H), 2.52 – 2.40 (m, 2H), 1.86 (d, $J = 1.5$ Hz, 3H); **¹³C NMR** (126 MHz, CDCl_3) δ 162.6, 162.5, 162.4, 143.3, 143.1, 140.1, 139.9, 139.7, 136.6, 132.1, 131.9, 131.8, 129.9, 129.8, 128.71, 128.68, 128.59, 128.2, 124.2, 119.4, 118.8, 91.5, 91.18, 91.16, 70.6, 70.5, 68.5, 64.1, 64.0, 57.6, 57.5, 42.3, 41.2, 34.6, 33.79, 33.76, 30.0, 23.9, 23.5, 21.0, 17.3; **IR** (NaCl, thin film, cm^{-1}) 3341, 3026, 2944, 2863, 2104, 1741, 1667, 1492, 1453, 1407, 1379, 1305, 1250, 1093, 1015, 974, 831, 792, 722; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{Cl}_4\text{N}_4\text{O}\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 430.9970, found 430.9950.



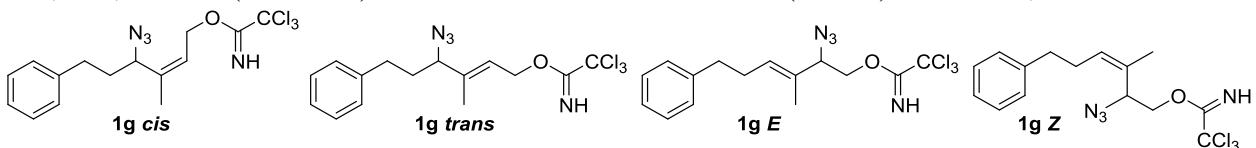
Compound 1d: General procedure 5 was used and the product was isolated in 81% yield as a clear oil. Compound **1d** was isolated as a mixture of three isomers (1:1.6:0.9 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl_3) **1d trans**: δ 8.39 (s, 1H), 7.44 – 7.38 (m, 2H), 7.09 – 7.03 (m, 2H), 5.95 (dt, $J = 15.7, 5.4$ Hz, 1H), 5.87 (dt, $J = 15.7, 1.3$ Hz, 1H), 4.87 (dd, $J = 5.4, 1.1$ Hz, 2H), 2.65 – 2.54 (m, 2H), 1.90 – 1.80 (m, 2H), 1.46 (s, 3H); **1d E**: δ 8.41 (s, 1H), 7.44 – 7.38 (m, 2H), 7.09 – 7.03 (m, 2H), 5.19 (dq, $J = 9.0, 1.4$ Hz, 1H), 4.58 (ddd, $J = 9.1, 7.2, 4.6$ Hz, 1H), 4.25 (dd, $J = 11.2, 4.6$ Hz, 1H), 4.20 (dd, $J = 11.2, 7.2$ Hz, 1H), 2.78 – 2.67 (m, 2H), 2.40 – 2.35 (m, 2H), 1.82 (d, $J = 1.5$ Hz, 3H); **1d Z**: δ 8.40 (s, 1H), 7.44 – 7.38 (m, 2H), 7.09 – 7.03 (m, 2H), 5.21 (dd, $J = 9.3, 1.6$ Hz, 1H), 4.37 (ddd, $J = 9.6, 7.6, 4.2$ Hz, 1H), 4.07 (dd, $J = 11.1, 7.6$ Hz, 1H), 3.98 (dd, $J = 11.2, 4.3$ Hz, 1H), 2.78 – 2.67 (m, 2H), 2.51 – 2.40 (m, 2H), 1.86 (d, $J = 1.5$ Hz, 3H); **¹³C NMR** (126 MHz, CDCl_3) δ 162.6, 162.5, 162.4, 143.3, 143.1, 140.6, 140.4, 140.2, 136.6, 131.68, 131.65, 131.59, 131.56, 130.3, 130.2, 124.2, 120.2, 119.9, 119.4, 118.8, 91.5, 91.18, 91.17, 70.6, 70.5, 68.5, 64.1, 57.7, 57.5, 42.2, 41.1, 34.5, 33.87, 33.84, 33.79, 30.1, 23.9, 23.5, 17.3; **IR** (NaCl, thin film, cm^{-1}) 3341, 2944, 2862, 2106, 1769, 1666, 1488, 1453, 1404, 1379, 1304, 1252, 1082, 1011, 973, 909, 834, 796, 730; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{BrCl}_3\text{N}_4\text{O}\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 474.9465, found 474.9462.



Compound 1e: General procedure 5 was used and the product was isolated in 89% yield as a clear oil. Compound **1e** was isolated as a mixture of four isomers (trace:1:1:0.1 *cis:trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **1H NMR** (500 MHz, CDCl₃) **1e trans** δ 8.43 (s, 1H), 7.37 – 7.30 (m, 2H), 7.29 – 7.19 (m, 3H), 6.01 – 5.90 (m, 1H), 5.87 (ddt, *J* = 15.5, 7.4, 1.4 Hz, 1H), 4.89 (d, *J* = 5.5 Hz, 2H), 3.92 (q, *J* = 7.2 Hz, 1H), 2.84 – 2.68 (m, 2H), 1.99 – 1.84 (m, 2H); **1e E** δ 8.45 (s, 1H), 7.37 – 7.30 (m, 2H), 7.29 – 7.19 (m, 3H), 6.01 – 5.90 (m, 1H), 5.51 (ddt, *J* = 15.5, 7.4, 1.6 Hz, 1H), 4.36 – 4.23 (m, 3H), 2.84 – 2.68 (m, 2H), 2.47 (q, *J* = 7.4 Hz, 2H); **1e Z** δ 8.45 (s, 1H), 7.37 – 7.30 (m, 2H), 7.29 – 7.19 (m, 3H), 6.01 – 5.90 (m, 1H), 5.49 – 5.41 (m, 1H), 4.59 – 4.51 (m, 1H), 4.17 (dd, *J* = 11.2, 6.8 Hz, 1H), 4.13 (dd, *J* = 11.2, 4.8 Hz, 1H), 2.84 – 2.68 (m, 2H), 2.57 – 2.50 (m, 2H); **13C NMR** (126 MHz, CDCl₃) δ 162.5, 162.3, 141.2, 141.0, 140.9, 136.7, 136.1, 132.1, 128.63, 128.59, 128.54, 128.50, 127.34, 126.29, 126.26, 126.1, 123.9, 123.3, 91.4, 91.1, 70.4, 70.3, 68.2, 62.9, 61.9, 56.8, 36.0, 35.7, 35.5, 34.1, 32.0, 30.0; **IR** (KBr, thin-film, cm⁻¹) 3340, 3086, 3063, 3027, 2920, 2857, 2102, 1667, 1603, 1496, 1454, 1382, 1289, 1074, 1051, 1008, 975, 911, 819, 799, 746, 702, 643; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₅Cl₃N₄ONa⁺ (M+Na)⁺ 383.0204, found 383.0198.

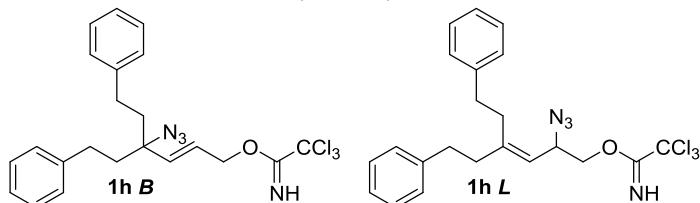


Compound 1f: General procedure 4 was used and the product was isolated in 93% yield as a clear oil. Compound **1f** was isolated in a mixture of two isomers (1:0.25 *E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **1H NMR** (500 MHz, CDCl₃) **1f E** δ 8.42 (s, 1H), 7.44 – 7.30 (m, 4H), 7.25 – 7.19 (m, 1H), 5.05 (dq, *J* = 9.1, 1.6 Hz, 1H), 4.51 (ddd, *J* = 9.1, 6.9, 4.8 Hz, 1H), 4.21 (dd, *J* = 10.3, 4.0 Hz, 1H), 4.18 (dd, *J* = 10.2, 6.0 Hz, 1H), 2.46 (s, 2H), 1.48 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H); **1f Z** δ 8.42 (s, 1H), 7.44 – 7.30 (m, 4H), 7.25 – 7.19 (m, 1H), 5.23 (dq, *J* = 9.8, 1.6 Hz, 1H), 4.34 (ddd, *J* = 9.8, 6.9, 4.7 Hz, 1H), 4.09 (dd, *J* = 10.4, 6.2 Hz, 1H), 4.06 (dd, *J* = 10.4, 4.0 Hz, 1H), 2.60 (d, *J* = 13.5 Hz, 1H), 2.53 (d, *J* = 13.6 Hz, 1H), 1.48 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H); **13C NMR** (126 MHz, CDCl₃) δ 162.62, 162.58, 148.9, 148.8, 142.4, 142.0, 128.3, 128.2, 126.09, 126.06, 125.99, 125.88, 121.8, 121.2, 91.2, 70.6, 70.5, 57.7, 57.58, 54.55, 47.4, 38.4, 38.0, 29.8, 29.4, 29.3, 29.0, 25.9, 19.0; **IR** (NaCl, thin film, cm⁻¹) 3342, 3058, 3024, 2963, 2925, 2105, 1667, 1495, 1445, 1385, 1312, 1250, 1075, 1010, 826, 799, 765, 699, 648; **HRMS** (ESI-TOF) *m/z* calcd for C₁₇H₂₁Cl₃N₄ONa⁺ (M+Na)⁺ 425.0673, found 425.0688.



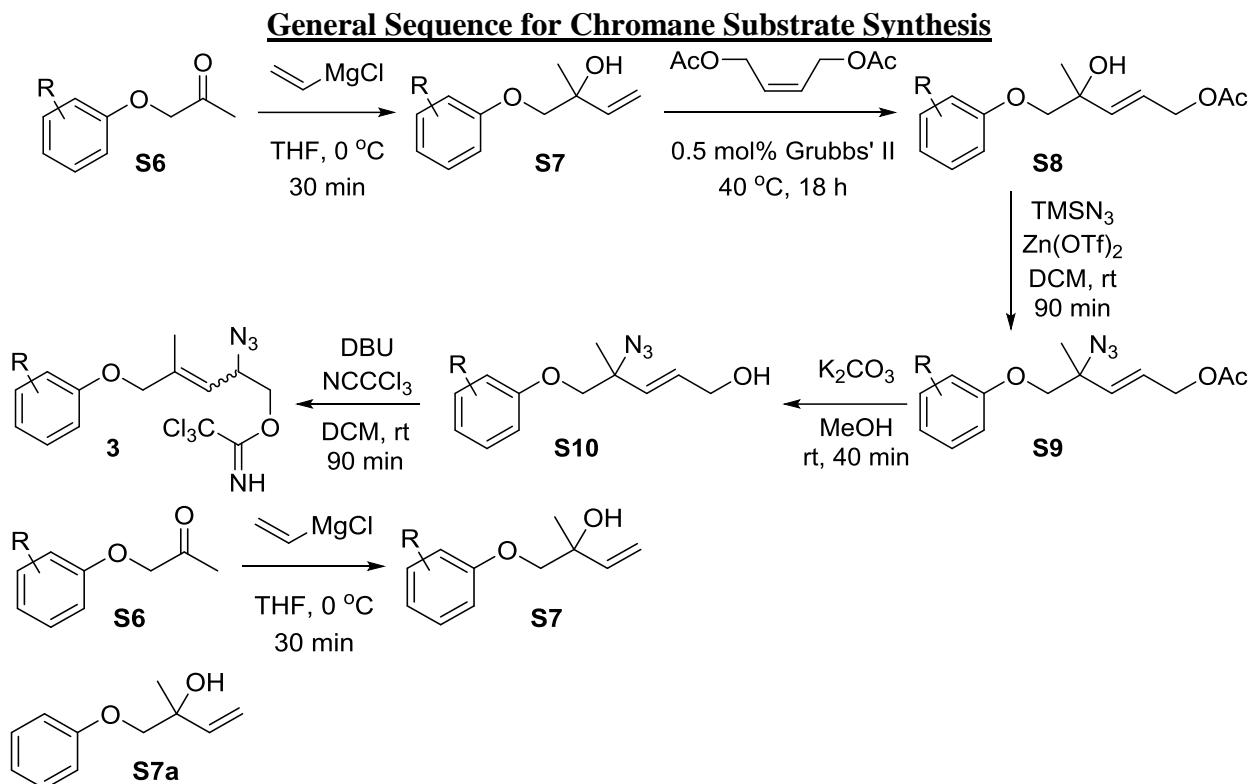
Compound 1g: General procedure 5 was used and the product was isolated in 75% yield as a clear oil. Compound **1g** was isolated as a mixture of four isomers (trace:1:0.7:trace *cis:trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **1H NMR** (500 MHz, CDCl₃) **1g trans** δ 8.39 (s, 1H), 7.36 – 7.29 (m, 2H), 7.26 – 7.18 (m, 3H), 5.77 – 5.73 (m, 1H), 4.93 (d, *J* = 6.6 Hz, 2H), 3.89 (t, *J* = 7.3 Hz, 1H), 2.77 – 2.61 (m, 2H), 1.99 – 1.85 (m, 2H), 1.81

(d, $J = 1.3$ Hz, 3H); **1g E** δ 8.43 (s, 1H), 7.36 – 7.29 (m, 2H), 7.26 – 7.18 (m, 3H), 5.66 – 5.61 (m, 1H), 4.36 – 4.29 (m, 3H), 2.77 – 2.61 (m, 2H), 2.52 – 2.38 (m, 2H), 1.66 (d, $J = 1.3$ Hz, 3H); ^{13}C **NMR** (126 MHz, CDCl_3) δ 162.6, 162.5, 141.5, 141.4, 140.9, 140.2, 139.1, 131.5, 130.8, 130.3, 129.7, 128.67, 128.62, 128.57, 128.54, 128.48, 128.45, 126.31, 126.26, 126.20, 126.09, 123.07, 122.97, 91.5, 91.2, 69.5, 69.3, 68.8, 67.3, 65.3, 64.3, 61.1, 59.7, 36.1, 35.6, 34.4, 34.0, 32.4, 32.3, 29.7, 18.8, 18.4, 12.63, 12.55; **IR** (NaCl, thin film, cm^{-1}) 3341, 3062, 3027, 2948, 2859, 2096, 1665, 1496, 1454, 1291, 1246, 1076, 999, 826, 797, 749, 699, 649; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{Cl}_3\text{N}_4\text{O}\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 397.0360, found 397.0352.

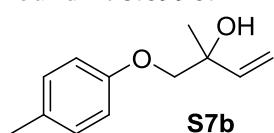


Compound 1h: General procedure 5 was used and the product was isolated in 90% as a yellow oil. Compound **1h** was isolated as a mixture of two isomers (1:4 *B:L*). NMR data given below is based off idealized integrations of the resulting mixture: **^1H NMR** (500 MHz, CDCl_3) **1h B** δ 8.53 (s, 1H), 7.47 – 7.39 (m, 4H), 7.37 – 7.26 (m, 6H), 6.13 (dt, $J = 15.6, 5.7$ Hz, 1H), 5.95 (dt, $J = 15.6, 1.4$ Hz, 1H), 5.02 (dd, $J = 5.7, 0.9$ Hz, 2H), 2.95 – 2.76 (m, 4H), 2.15 (ddd, $J = 14.0, 10.6, 6.3$ Hz, 2H), 2.07 (ddd, $J = 14.0, 10.9, 6.3$ Hz, 2H); **1h L** δ 8.51 (s, 1H), 7.47 – 7.39 (m, 4H), 7.37 – 7.26 (m, 6H), 5.33 (d, $J = 9.5$ Hz, 1H), 4.50 (ddd, $J = 9.5, 7.3, 4.3$ Hz, 1H), 4.15 (dd, $J = 11.1, 7.3$ Hz, 1H), 4.09 (dd, $J = 11.2, 4.3$ Hz, 1H), 2.95 – 2.76 (m, 4H), 2.66 – 2.52 (m, 4H); **^{13}C NMR** (126 MHz, CDCl_3) δ 162.5, 162.3, 146.51, 141.47, 141.40, 141.2, 135.4, 128.60, 128.57, 128.49, 128.47, 128.40, 128.39, 126.3, 126.2, 126.1, 125.0, 119.1, 118.4, 91.5, 91.2, 70.5, 68.5, 67.0, 57.3, 57.2, 40.1, 38.3, 38.2, 34.8, 34.7, 33.2, 30.4, 29.8; **IR** (NaCl, thin film, cm^{-1}) 3341, 3062, 3026, 2945, 2861, 2014, 1667, 1602, 1495, 1453, 1303, 1255, 1197, 1076, 1005, 828, 796, 749, 696, 646; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{23}\text{Cl}_3\text{N}_4\text{O}\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 487.0830, found 487.0847.

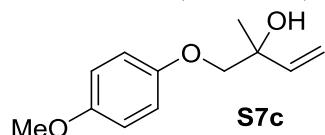
Chromane Substrate Synthesis and Characterization Data



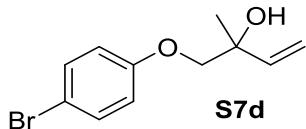
Compound S7a: General procedure 1 was used and the product was isolated in 95% yield as a light yellow oil: **1H NMR** (500 MHz, CDCl₃) δ 7.33 – 7.26 (m, 3H), 6.95 (m, 2H), 6.03 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.41 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.21 (dd, *J* = 10.8, 1.1 Hz, 1H), 3.90 (d, *J* = 8.9 Hz, 1H), 3.86 (d, *J* = 8.9 Hz, 1H), 2.42 (br s, 1H), 1.42 (s, 3H); **13C NMR** (101 MHz, CDCl₃) δ 158.8, 141.9, 129.7, 121.4, 114.9, 114.2, 75.0, 72.6, 24.6; **IR** (NaCl, thin film, cm⁻¹) 3420, 3062, 2979, 2930, 1599, 1497, 1245, 753; **HRMS** (EI-TOF) *m/z* calcd for C₁₁H₁₄O₂⁺ (M⁺) 178.0988, found 178.0990.



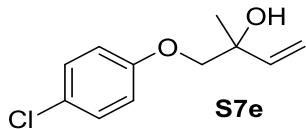
Compound S7b: General procedure 1 was used and the compound was isolated in a 92% yield as a yellow oil: **1H NMR** (400 MHz, CDCl₃) δ 7.13 – 7.06 (m, 2H), 6.85 – 6.80 (m, 2H), 6.03 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.41 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.20 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.87 (d, *J* = 8.9 Hz, 1H), 3.82 (d, *J* = 8.9 Hz, 1H), 2.45 (br s, 1H), 2.30 (s, 3H), 1.41 (s, 3H); **13C NMR** (101 MHz, CDCl₃) δ 156.7, 142.0, 130.6, 130.1, 114.7, 114.1, 75.2, 72.6, 24.6, 20.6; **IR** (NaCl, thin film, cm⁻¹) 3442, 3029, 2979, 2923, 2866, 1612, 1585, 1510, 1290, 1243, 1174, 1109, 1046, 924, 816; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₆O₂Na (M+Na)⁺ 215.1043, found 215.1042.



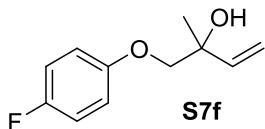
Compound S7c: General procedure 1 was used the product was isolated in 90% yield as a black oil: **¹H NMR** (400 MHz, CDCl₃) δ 6.90 – 6.81 (m, 4H), 6.04 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.42 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.21 (dd, *J* = 10.8, 1.1 Hz, 1H), 3.86 (d, *J* = 8.9 Hz, 1H), 3.82 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 2.45 (br s, 1H), 1.42 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 154.3, 153.0, 142.0, 115.9, 114.8, 114.1, 75.9, 72.7, 55.9, 24.6; **IR** (NaCl, thin film, cm⁻¹) 3444, 2932, 2834, 1509, 1462, 1232, 1046, 926, 824; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₆O₃Na⁺ (M+Na)⁺ 231.0992, found 231.0995.



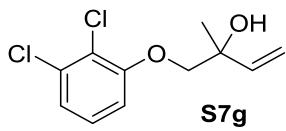
Compound S7d: General procedure 1 was used and the product was isolated in a 96% yield as a yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.02, (dd, *J* = 17.3, 10.8 Hz, 1H), 5.41, (dd, *J* = 17.4, 1.2 Hz, 1H), 5.22 (dd, *J* = 10.8, 1.1 Hz, 1H), 3.86 (d, *J* = 8.9 Hz, 1H), 3.82 (d, *J* = 8.9 Hz, 1H), 2.50 (br s, 1H), 1.41, (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 157.8, 141.2, 132.3, 116.5, 114.2, 113.4, 75.1, 72.4, 24.5; **IR** (NaCl, thin film, cm⁻¹) 3570, 3405, 2984, 2932, 2869, 1590, 1488, 1287, 1242, 1168, 820; **HRMS** (ESI-TOF) *m/z* calcd for C₁₀H₁₃BrO₂Na⁺ (M+Na)⁺ 278.9991, found 279.0004.



Compound S7e: General procedure 1 was used and the product was isolated in 95% yield as a yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.25 (dd, *J* = 9.2, 2.2 Hz, 2H), 6.86, (dd, *J* = 9.2, 2.2 Hz, 2H), 6.03 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.42 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.22 (dd, *J* = 10.8, 1.1 Hz, 1H), 3.87 (d, *J* = 8.9 Hz, 1H), 3.83 (d, *J* = 8.9 Hz, 1 H), 2.44 (br s, 1H), 1.42 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 157.3, 141.6, 129.4, 126.1, 117.0, 114.2, 75.2, 72.4, 24.5; **IR** (NaCl, thin film, cm⁻¹) 3413, 2976, 2933, 1492, 1243, 1093, 1043, 822; **HRMS** (ESI-TOF) *m/z* calcd for C₁₀H₁₃ClO₂Na⁺ (M+Na)⁺ 235.0496, found 235.0500.

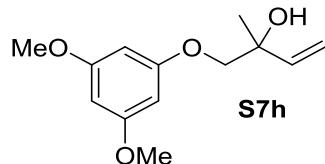


Compound S7f: General procedure 1 was used and the product was isolated in an 66% yield: **¹H NMR** (400 MHz, CDCl₃) δ 7.03 – 6.92 (m, 2H), 6.91 – 6.80 (m, 2H), 6.02 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.41 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.21 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.85 (d, *J* = 8.8 Hz, 1H), 3.80 (d, *J* = 8.8 Hz, 1H), 2.47 (br s, 1H), 1.41 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 157.5 (d, *J*_{C-F} = 238.8 Hz), 154.8 (d, *J*_{C-F} = 2.2 Hz), 141.7, 115.9 (d, *J*_{C-F} = 16.9 Hz), 115.7 (d, *J*_{C-F} = 1.7 Hz), 114.1, 75.7, 72.5, 24.5; **¹⁹F NMR** (376 MHz, CDCl₃) δ -123.3; **IR** (NaCl, thin film, cm⁻¹) 3415, 2086, 2980, 2931, 2871, 1601, 1507, 1460, 1248, 1210, 1044, 927, 829; **HRMS** *m/z* calcd for C₁₀H₁₃FO₂Na⁺ (M+Na)⁺ 219.0792, found 219.0800.

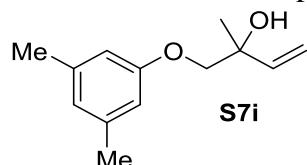


Compound S7g: General procedure 1 was used and the product was isolated in 88% yield as a yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.18 – 7.03 (m, 2H), 6.82 (dt, *J* = 8.1, 1.5 Hz, 1H), 6.05 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.44 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.23 (dd, *J* = 10.7, 1.1 Hz, 1H), 3.94

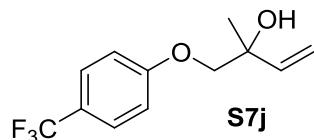
(d, $J = 8.8$ Hz, 1H), 3.88 (d, $J = 8.8$ Hz, 1H), 2.66 (br s, 1H), 1.46 (s, 3H); **^{13}C NMR** (101 MHz, CDCl_3) δ 155.5, 141.2, 133.8, 127.4, 122.8, 122.2, 114.4, 111.7, 76.4, 72.5, 24.4; **IR** (NaCl, thin film, cm^{-1}) 3428, 2982, 2934, 1580, 1450, 1294, 1268, 1059, 1040, 927, 768; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 269.0107, found 269.0107.



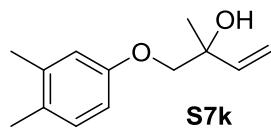
Compound S7h: General procedure 1 was used and the product was isolated in 96% yield as a light yellow oil. Characterization data for this compound has been reported.⁵ The compound gave an identical ^1H NMR spectra.



Compound S7i: General procedure 1 was used and the product was isolated in 86% yield as a light yellow oil: **^1H NMR** (400 MHz, CDCl_3) δ 6.67 (br s, 1H), 6.61 (br s, 2H), 6.05 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.44 (dd, $J = 17.4, 1.2$ Hz, 1H), 5.23 (dd, $J = 10.8, 1.2$ Hz, 1H), 3.90 (d, $J = 8.9$ Hz, 1H), 3.85 (d, $J = 8.9$ Hz, 1H), 2.60 (br s, 1H), 2.33 (s, 6H), 1.43 (s, 3H); **^{13}C NMR** (101 MHz, CDCl_3) δ 158.8, 142.0, 139.4, 123.1, 114.0, 112.6, 74.9, 72.6, 24.6, 21.5; **IR** (NaCl, thin film, cm^{-1}) 3423, 2975, 2921, 1612, 1596, 1458, 1324, 1295, 1155, 1073, 1038, 955, 827, 780; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 229.1199, found 229.1206.

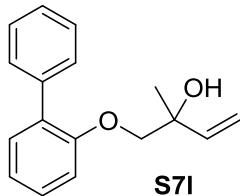


Compound S7j: General procedure 1 was used and the product was isolated in 98% yield as a light yellow oil: **^1H NMR** (400 MHz, CDCl_3) δ 7.56 – 7.50 (m, 2H), 7.00 – 6.93 (m, 2H), 6.02 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.42 (dd, $J = 17.4, 1.1$ Hz, 1H), 5.21 (dd, $J = 10.8, 1.1$ Hz, 1H), 3.91 (d, $J = 8.9$ Hz, 1H), 3.87 (d, $J = 8.9$ Hz, 1H), 2.88 (s, 1H), 1.42 (s, 3H); **^{13}C NMR** (101 MHz, CDCl_3) δ 161.2 (q, $J_{\text{C}-\text{F}} = 1.4$ Hz), 141.5, 127.0 (q, $J_{\text{C}-\text{F}} = 3.8$ Hz), 125.0 (q, $J_{\text{C}-\text{F}} = 272.1$ Hz), 123.4 (q, $J_{\text{C}-\text{F}} = 33.0$ Hz) 114.8, 114.4, 75.1, 72.5, 24.5; **^{19}F NMR** (376 MHz, CDCl_3) δ -61.5; **IR** (NaCl, thin film, cm^{-1}) 3401, 2924, 2853, 1616, 1591, 1519, 1331, 1258, 1162, 1111, 1069, 1037, 1010, 928, 835; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 269.0760, found 269.0773.

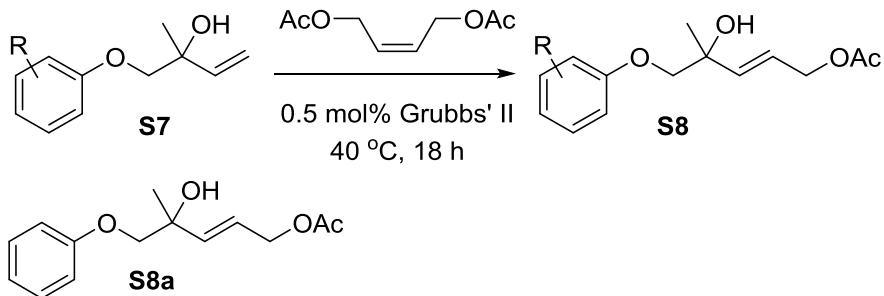


Compound S7k: General procedure 1 was used and the product was isolated in 61% yield as a light yellow oil: **^1H NMR** (400 MHz, CDCl_3) δ 7.07 (d, $J = 8.2$ Hz, 1H), 6.78 (d, $J = 2.7$ Hz, 1H), 6.70 (dd, $J = 8.2, 2.7$ Hz, 1H), 6.06 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.45 (dd, $J = 17.4, 1.2$ Hz, 1H), 5.23 (dd, $J = 10.8, 1.2$ Hz, 1H), 3.89 (d, $J = 8.9$ Hz, 1H), 3.85 (d, $J = 8.9$ Hz, 1H), 2.65 (s, 1H), 2.28 (s, 3H), 2.24 (s, 3H), 1.44 (s, 3H); **^{13}C NMR** (101 MHz, CDCl_3) δ 156.9, 142.0, 137.8, 130.4, 129.2, 116.5, 114.0, 111.7, 75.1, 72.6, 24.6, 20.1, 18.9; **IR** (NaCl, thin film, cm^{-1}) 3424, 2974,

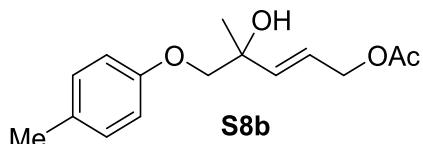
2923, 2865, 1610, 1580, 1503, 1455, 1414, 1303, 1254, 1203, 1164, 1120, 1053, 1023, 996, 924, 863, 811, 797; **HRMS** (ESI-TOF) m/z calcd for $C_{13}H_{18}O_2Na^+$ ($M+Na$)⁺ 229.1199, found 229.1201.



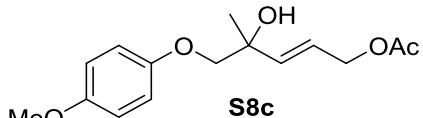
Compound S7l: General procedure 1 was used and the product was isolated in 89% yield as a yellow oil: **1H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.46 – 7.40 (m, 2H), 7.40 – 7.30 (m, 3H), 7.09 (td, J = 7.5, 1.1 Hz, 1H), 6.99 (dd, J = 8.2, 1.1 Hz, 1H), 5.93 (dd, J = 17.3, 10.8 Hz, 1H), 5.29 (dd, J = 17.3, 1.2 Hz, 1H), 5.15 (dd, J = 10.8, 1.2 Hz, 1H), 3.92 (d, J = 8.7 Hz, 1H), 3.84 (d, J = 8.7 Hz, 1H), 2.24 (br s, 1H), 1.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.6, 141.8, 138.4, 131.5, 130.9, 129.8, 128.8, 128.1, 127.2, 121.7, 114.0, 113.2, 76.0, 72.6, 24.5. **IR** (NaCl, thin film, cm^{-1}) 3556, 3434, 3061, 3025, 2978, 2930, 2869, 1597, 1583, 1482, 1434, 1263, 1232, 1122, 1056, 1037, 925, 835, 752, 732, 699; **HRMS** (ESI-TOF) m/z calcd for $C_{17}H_{18}O_2Na^+$ ($M+Na$)⁺ 277.1199, found 277.1205.



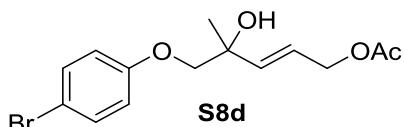
Compound S8a: General procedure 2 was used. Note, 4 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 70% yield as a clear-yellow oil: **1H NMR** (400 MHz, $CDCl_3$) δ 7.30 (m, 2H), 6.98–6.92 (m, 3H), 6.00 – 5.91 (m, 2H), 4.62 (d, J = 4.4 Hz, 2H), 3.89 (d, J = 8.9 Hz, 1H), 3.85 (d, 8.9 Hz, 1H), 2.05 (s, 3H), 1.96 (br s, 1H), 1.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 158.6, 137.6, 129.6, 124.0, 121.4, 114.8, 74.9, 72.0, 64.5, 24.8, 21.1; **IR** (NaCl, thin film, cm^{-1}) 3462, 2976, 2932, 1737, 1599, 1245, 1044; **HRMS** (ESI-TOF) m/z calcd for $C_{14}H_{18}O_4Na^+$ ($M+Na$)⁺ 273.1097, found 273.1103.



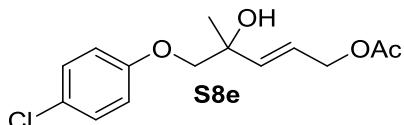
Compound S8b: General procedure 2 was used. Note, 2 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 78% yield as a clear oil: **1H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.2 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.00 – 5.88 (m, 2H), 4.61 (d, J = 4.3 Hz, 2H), 3.86 (d, J = 8.9 Hz, 1H), 3.82 (d, J = 8.9 Hz, 1H), 2.50 (br s, 1H), 2.30 (s, 3H), 2.09 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 156.6, 137.9, 130.7, 130.1, 124.0, 114.7, 75.2, 72.1, 64.5, 24.8, 21.1, 20.6; **IR** (NaCl, thin film, cm^{-1}) 3461, 2976, 2929, 2868, 1738, 1613, 1512, 1460, 1380, 1362, 1242, 1175, 1043, 971, 815; **HRMS** (ESI-TOF) m/z calcd for $C_{15}H_{20}O_4Na^+$ ($M+Na$)⁺ 287.1254, found 287.1261.



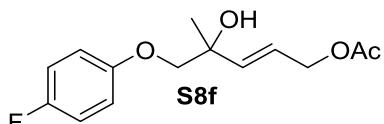
Compound S8c: General procedure 2 was used. Note, 2 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 82% yield as a clear oil: **¹H NMR** (400 MHz, CDCl₃) δ 6.88 – 6.81 (m, 4H), 5.99 – 5.88 (m, 2H), 4.61 (d, *J* = 4.4 Hz, 2H), 3.84 (d, *J* = 8.9 Hz, 1H), 3.80 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 3H), 2.48 (br s, 1H), 2.09 (s, 3H), 1.41 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.9, 154.4, 152.9, 137.9, 124.0, 115.9, 114.8, 75.8, 72.1, 64.6, 55.9, 24.8, 21.1; **IR** (NaCl, thin film, cm⁻¹) 3468, 2932, 2834, 1735, 1508, 1460, 1379, 1230, 1033, 965, 826, 748; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₂₀O₅Na⁺ (M+Na)⁺ 303.1203, found 303.1196



Compound S8d: General procedure 2 was used. Note, 2 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 80% yield as a clear oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.38 (dd, *J* = 9.0, 2.1 Hz, 2H), 6.80 (dd, *J* = 9.0, 2.1 Hz, 2H), 5.99 – 5.88 (m, 2H), 4.61 (d, *J* = 4.5 Hz, 2H), 3.85 (d, *J* = 8.9 Hz, 1H), 3.81, (d, *J* = 8.9 Hz, 1H), 2.52, (br s, 1H), 2.09 (s, 3H), 1.42 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.7, 157.7, 137.4, 132.3, 124.1, 116.5, 113.5, 75.1, 71.9, 64.3, 24.7, 21.0; **IR** (NaCl, thin film, cm⁻¹) 3447, 2934, 1735, 1489, 1284, 1243, 1032, 821; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₆BrO₄Na⁺ (M+Na)⁺ 351.0202, found 351.0204.

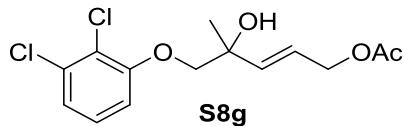


Compound S8e: General procedure 2 was used. Note, 2 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 71% yield as a clear oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.22 – 7.17 (m, 2H), 6.84 – 6.78 (m, 2H), 5.96 – 5.85 (m, 2H), 4.57 (d, *J* = 4.4 Hz, 2H), 3.81 (d, *J* = 8.9 Hz, 1H), 3.78 (d, *J* = 8.9 Hz, 1H), 2.79 (br s, 1H), 2.04 (s, 3H), 1.38 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.8, 157.2, 137.5, 129.3, 126.0, 123.9, 116.0, 75.2, 71.8, 64.3, 24.7, 20.9; **IR** (NaCl, thin film, cm⁻¹) 3442, 2976, 2931, 1737, 1492, 1452, 1242, 1059, 1039, 825; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₆ClO₄Na⁺ (M+Na)⁺ 307.0708, found 307.0709.

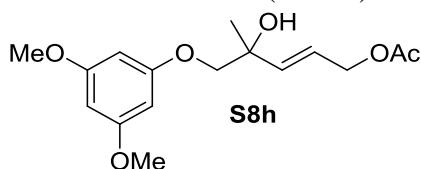


Compound S8f: General procedure 2 was used. Note, 1.5 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 77% yield as a clear oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.02 – 6.94 (m, 2H), 6.89 – 6.83 (m, 2H), 6.00 – 5.88 (m, 2H), 4.62 (d, *J* = 4.5 Hz, 2H), 3.85 (d, *J* = 8.9 Hz, 1H), 3.81 (d, *J* = 8.8 Hz, 1H), 2.41 (br s, 1H), 2.09 (s, 3H), 1.42 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.8, 157.5 (d, *J*_{C-F} = 238.8 Hz), 154.7 (d, *J*_{C-F} = 2.2 Hz), 137.6, 123.9, 115.9 (d, *J*_{C-F} = 15.6 Hz), 115.7, 75.6, 71.9, 64.4, 24.6, 20.9; **¹⁹F NMR** (376 MHz, CDCl₃) δ -123.3; **IR** (NaCl, thin film, cm⁻¹) 3469, 2934, 1738, 1507,

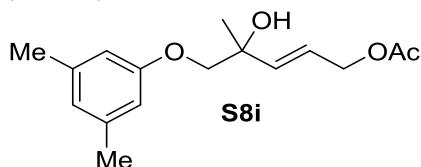
1458, 1245, 1029, 829, 761; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₆FO₄Na⁺ (M+Na)⁺ 291.1003, found 291.1009.



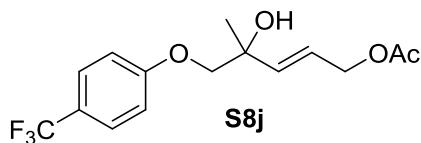
Compound S8g: General procedure 2 was used. Note, 1.5 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 71% yield as a clear oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.15 – 7.01 (m, 2H), 6.78 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.01 – 5.86 (m, 2H), 4.58 (d, *J* = 4.4 Hz, 2H), 3.89 (d, *J* = 8.8 Hz, 1H), 3.86 (d, *J* = 8.8 Hz, 1H), 2.83 (br s, 1H), 2.05 (s, 3H), 1.43 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.8, 155.4, 137.0, 133.8, 127.4, 124.2, 122.8, 122.2, 111.7, 78.3, 71.9, 64.3, 24.6, 21.0; **IR** (NaCl, thin film, cm⁻¹) 3444, 2975, 2935, 2878, 1737, 1581, 1462, 1379, 1265, 1040, 798; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₅Cl₂O₄Na⁺ (M+Na)⁺ 366.0383, found 366.0380.



Compound S8h: Note, 2 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used in this reaction. General procedure 2 was used and the product was isolated in 74% yield as a clear oil: **¹H NMR** (500 MHz, CDCl₃) δ 6.12 – 6.08 (m, 3H), 5.97 – 5.88 (m, 2H), 4.60 (d, *J* = 4.5 Hz, 2H), 3.83 (d, *J* = 8.9 Hz, 1H), 3.80 (d, *J* = 8.9 Hz, 1H), 3.76 (s, 6H), 2.52 (br s, 1H), 2.08 (s, 3H), 1.40 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.9, 161.7, 160.6, 137.7, 124.0, 93.8, 93.7, 75.0, 72.0, 64.5, 55.5, 24.8, 21.1; **IR** (NaCl, thin film, cm⁻¹) 3485, 2933, 2840, 1737, 1600, 1461, 1381, 1362, 1246, 1205, 1153, 1067, 1029, 974, 820, 684; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₂₂O₆Na⁺ (M+Na)⁺ 333.1309, found 333.1320.

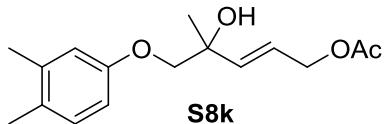


Compound S8i: General procedure 2 was used. Note, 2 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 82% yield as a light yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 6.63 (br s, 1H), 6.56 (br s, 2H), 5.97 – 5.87 (m, 2H), 4.61 (d, *J* = 4.4 Hz, 2H), 3.85 (d, *J* = 8.9 Hz, 1H), 3.82 (d, *J* = 8.9 Hz, 1H), 2.61 (br s, 1H), 2.30 (s, 6H), 2.09 (s, 3H), 1.41 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.9, 158.7, 139.4, 137.9, 123.9, 123.1, 112.6, 74.8, 72.0, 64.5, 24.8, 21.5, 21.1; **IR** (NaCl, thin film, cm⁻¹) 3425, 2937, 1741, 1595, 1457, 1371, 1324, 1242, 1156, 1072, 971, 829; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₂₂O₄Na⁺ (M+Na)⁺ 301.1410, found 301.1402.

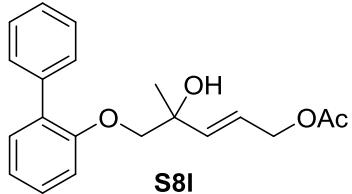


Compound S8j: General procedure 2 was used and the product was isolated in 60% yield as a clear oil: **¹H NMR** (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.94 – 5.85 (m, 2H), 4.54 (d, *J* = 4.2 Hz, 2H), 3.85 (d, *J* = 9.0 Hz, 1H), 3.82 (d, *J* = 9.0 Hz, 1H), 3.03 (s,

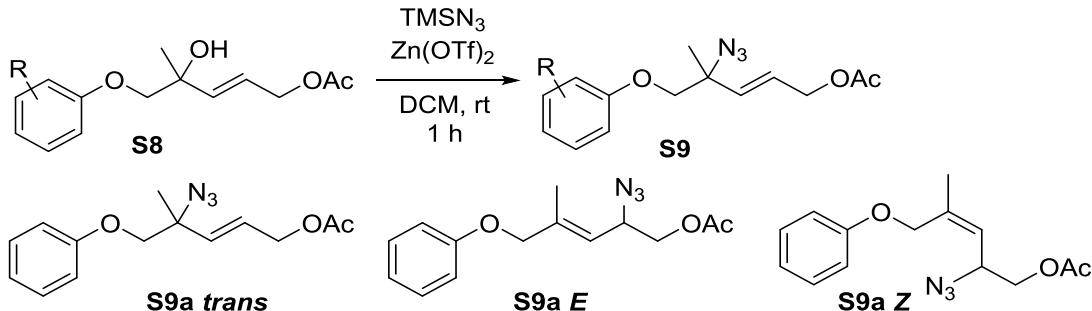
1H), 1.99 (s, 3H), 1.37 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.8, 161.1, 137.4, 126.8 (q, *J*_{C-F} = 3.8 Hz), 124.2 (q, *J*_{C-F} = 271.4 Hz) 124.0, 123.1 (q, *J* = 32.7 Hz) 114.7, 75.0, 71.7, 64.3, 24.6, 20.7; **¹⁹F NMR** (471 MHz, CDCl₃) δ -61.5; **IR** (NaCl, thin film, cm⁻¹) 3472, 2978, 2934, 2876, 1739, 1616, 1590, 1519, 1460, 1424, 1381, 1329, 1261, 1161, 1110, 1069, 1034, 1010, 972, 837, 637; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₁₇F₃O₄Na⁺ (M+Na)⁺ 341.0971, found 341.0978.



Compound S8k: General procedure 2 was used and the product was isolated in 71% yield as a light yellow oil: **¹H NMR** (500 MHz, CDCl₃) δ 7.01 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 2.7 Hz, 1H), 6.65 (dd, *J* = 8.2, 2.7 Hz, 1H), 5.98 – 5.93 (m, 2H), 4.63 – 4.58 (m, 2H), 3.84 (d, *J* = 9.0 Hz, 1H), 3.81 (d, *J* = 9.0 Hz, 1H), 3.17 (s, 1H), 2.23 (s, 3H), 2.19 (s, 3H), 2.06 (s, 3H), 1.42 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.5, 156.7, 137.9, 137.4, 130.1, 128.7, 123.3, 116.2, 111.5, 74.9, 71.6, 64.3, 24.5, 20.7, 19.7, 18.6; **IR** (NaCl, thin film, cm⁻¹) 3465, 2923, 2860, 1738, 1610, 1580, 1502, 1453, 1377, 1253, 1165, 1120, 1049, 1028, 972, 803; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₂₂O₄Na⁺ (M+Na)⁺ 301.1410, found 301.1412.

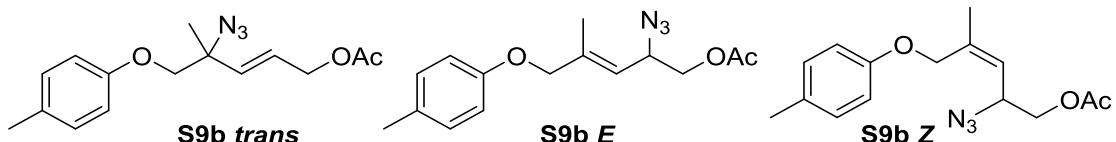


Compound S8l: General procedure 2 was used. Note, 2 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used for this reaction. The product was isolated in 67% yield as a clear oil: **¹H NMR** (500 MHz, CDCl₃) δ 7.53 – 7.47 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.08 (td, *J* = 7.5, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.85 – 5.74 (m, 2H), 4.60 – 4.50 (m, 2H), 3.90 (d, *J* = 8.8 Hz, 1H), 3.82 (d, *J* = 8.7 Hz, 1H), 2.24 (br s, 1H), 2.08 (s, 3H), 1.29 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.9, 155.5, 138.3, 137.9, 131.6, 131.0, 129.8, 128.9, 128.1, 127.3, 123.8, 121.8, 113.2, 76.0, 72.1, 64.5, 24.6, 21.1; **IR** (NaCl, thin film, cm⁻¹) 3465, 3027, 2975, 2931, 1737, 1597, 1583, 1482, 1434, 1380, 1230, 1122, 1030, 971, 753, 734, 700; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₂O₄Na⁺ (M+Na)⁺ 349.1410, found 349.1417.

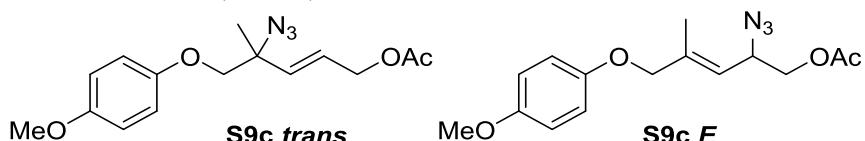


Compound S9a: General procedure 3 was used and the product was isolated in 86% yield as a clear oil. The molecule was isolated as a mixture of three isomers (1:1.5:0.3 *trans:E:Z*). **¹H NMR** data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S9a trans:** δ 7.40 – 7.24 (m, 2H), 7.07 – 6.85 (m, 3H), 6.01 (dt, *J* = 15.7, 5.6 Hz, 1H), 5.91 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.67 (dd, *J* = 5.7, 1.3 Hz, 2H), 3.97 (d, *J* = 9.3 Hz, 1H), 3.95 (d, *J* = 9.3 Hz, 1H), 2.14 (s, 3H), 1.57 (s, 3H); **S9a E:** δ 7.40 – 7.24 (m, 2H), 7.07 – 6.85 (m, 3H),

5.59 (dq, $J = 9.2, 1.5$ Hz, 1H), 4.56 (ddd, $J = 9.1, 7.8, 4.5$ Hz, 1H), 4.51 (s, 2H), 4.18 (dd, $J = 11.4, 4.4$ Hz, 1H), 4.08 (dd, $J = 11.4, 7.7$ Hz, 1H), 2.13 (s, 3H), 1.91 (d, $J = 1.6$ Hz, 3H); **S9a Z:** δ 7.40 – 7.24 (m, 2H), 7.07 – 6.85 (m, 3H), 5.43 (d, $J = 9.4$ Hz, 1H), 4.60 (d, $J = 2.5$ Hz, 2H), 4.58 – 4.54 (m, 1H), 4.20 – 4.14 (m, 1H), 4.10 – 4.05 (m, 1H) 2.13 (s, 3H), 2.00 (d, $J = 1.6$ Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.71, 170.69, 170.67, 158.51, 158.47, 158.46, 139.5, 139.2, 133.3, 129.65, 129.61, 129.57, 126.5, 122.5, 121.5, 121.4, 121.3, 120.5, 120.2, 115.4, 114.9, 114.79, 114.77, 74.1, 72.1, 67.0, 66.0, 65.7, 64.1, 63.3, 57.7, 57.6, 21.9, 21.3, 21.0, 20.8, 14.6; **IR** (NaCl, thin film, cm⁻¹) 3040, 2935, 2108, 1744, 1598, 1495, 1240, 1046, 755; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₇N₃ONa⁺ (M+Na)⁺ 298.1162, found 298.1168.



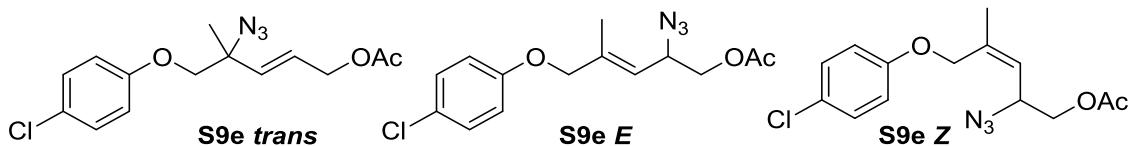
Compound S9b: General procedure 3 was used and the product was isolated in 67% yield as a clear oil. Compound **S9b** was isolated as a mixture of two isomers (1:1.3 *E*:*Z*). Trace amounts of **S9b Z** were observed. NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S9b trans** δ 7.13 – 7.06 (m, 2H), 6.87 – 6.80 (m, 2H), 5.97 (dt, $J = 15.7, 5.6$ Hz, 1H), 5.88 (dt, $J = 15.7, 1.3$ Hz, 1H), 4.64 (dd, $J = 5.7, 1.3$ Hz, 2H), 3.92 (d, $J = 9.3$ Hz, 1H), 3.89 (d, $J = 9.3$ Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H), 1.53 (s, 3H); **S9b E** δ 7.13 – 7.06 (m, 2H), 6.87 – 6.80 (m, 2H), 5.55 (dq, $J = 9.1, 1.5$ Hz, 1H), 4.53 (ddd, $J = 9.1, 7.8, 4.4$ Hz, 1H), 4.44 (s, 2H), 4.14 (dd, $J = 11.4, 4.4$ Hz, 1H), 4.04 (dd, $J = 11.4, 7.8$ Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H), 1.86 (d, $J = 1.7$ Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.5, 170.4, 156.34, 156.31, 139.5, 139.3, 133.2, 130.6, 130.5, 130.3, 129.99, 129.96, 129.92, 129.89, 126.4, 122.3, 119.9, 114.7, 114.60, 114.55, 76.9, 74.2, 72.1, 67.0, 65.8, 65.6, 63.9, 63.2, 57.5, 57.4, 21.8, 21.1, 20.8, 20.6, 20.43, 20.42, 14.4; **IR** (NaCl, thin film, cm⁻¹) 3030, 2922, 2865, 2108, 1743, 1612, 1585, 1510, 1452, 1381, 1363, 1243, 1175, 1049, 972, 820, 755, 669; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₁₉N₃O₃Na⁺ (M+Na)⁺ 312.1319, found 312.1314.



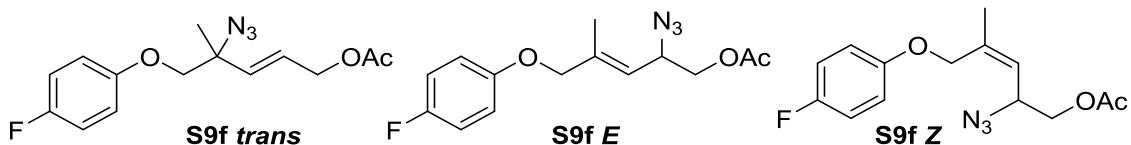
Compound S9c: General procedure 3 was used and the product was isolated in 68% yield as a clear oil. Compound **S9c** was isolated as a mixture of two isomers (1:1.3 *E*:*Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S9c trans** δ 6.89 – 6.80 (m, 4H), 5.95 (dt, $J = 15.7, 5.7$ Hz, 1H), 5.86 (dt, $J = 15.7, 1.3$ Hz, 1H), 4.62 (dd, $J = 5.7, 1.3$ Hz, 2H), 3.88 (d, $J = 9.3$ Hz, 1H), 3.85 (d, $J = 9.3$ Hz, 1H), 3.76 (s, 3H), 2.09 (s, 3H), 1.51 (s, 3H); **S9c E** δ 6.89 – 6.80 (m, 4H), 5.52 (dq, $J = 9.2, 1.5$ Hz, 1H), 4.51 (ddd, $J = 9.2, 7.8, 4.4$ Hz, 1H), 4.42 (s, 2H), 4.12 (dd, $J = 11.4, 4.4$ Hz, 1H), 4.02 (dd, $J = 11.4, 7.8$ Hz, 1H), 3.76 (s, 3H), 2.09 (s, 3H), 1.85 (d, $J = 1.4$ Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.7, 170.6, 154.4, 154.2, 152.7, 152.6, 139.5, 133.3, 126.5, 120.0, 115.94, 115.86, 114.82, 114.77, 114.75, 75.0, 72.9, 65.7, 64.1, 63.3, 57.7, 55.79, 55.77, 21.3, 21.0, 20.8, 14.6; **IR** (NaCl, thin film, cm⁻¹) 3045, 2935, 2835, 2108, 1743, 1509, 1462, 1381, 1364, 1228, 1107, 1038, 975, 827, 750; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₁₉N₃O₄Na⁺ (M+Na)⁺ 328.1268, found 328.1268.



Compound S9d: General procedure 3 was used and the product was isolated in an 80% yield. Compound **S9d** was isolated as a mixture of three isomers (1:1.6:0.3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S9d trans** δ 7.41 – 7.29 (m, 2H), 6.83 – 6.70 (m, 2H), 5.95 (dt, *J* = 15.7, 5.6 Hz, 1H), 5.84 (dt, *J* = 15.8, 1.3 Hz, 1H), 4.63 (dd, *J* = 5.6, 1.3 Hz, 2H), 3.89 (d, *J* = 9.2 Hz, 1H), 3.86 (d, *J* = 9.3 Hz, 1H), 2.09 (s, 3H), 1.52 (s, 3H); **S9d E** δ 7.41 – 7.29 (m, 2H), 6.83 – 6.70 (m, 2H), 5.51 (dq, *J* = 9.2, 1.5 Hz, 1H), 4.55 – 4.48 (m, 1H), 4.43 (s, 2H), 4.13 (dd, *J* = 11.4, 4.4 Hz, 1H), 4.02 (dd, *J* = 11.4, 7.7 Hz, 1H), 2.09 (s, 3H), 1.85 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.68, 170.64, 157.5, 139.0, 138.6, 132.8, 132.43, 132.40, 132.3, 132.2, 126.7, 122.7, 120.4, 117.2, 116.6, 116.51, 116.50, 113.6, 113.3, 74.3, 72.2, 67.1, 65.8, 65.6, 63.9, 63.1, 57.5, 57.4, 21.8, 21.1, 21.0, 20.9, 20.8, 20.7, 14.5; **IR** (NaCl, thin film, cm⁻¹) 2938, 2873, 2475, 2108, 1738, 1590, 1578, 1488, 1451, 1283, 1236, 1171, 1103, 1002, 823; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₆BrN₃O₃Na⁺ (M+Na)⁺ 376.0267, found 376.0269.

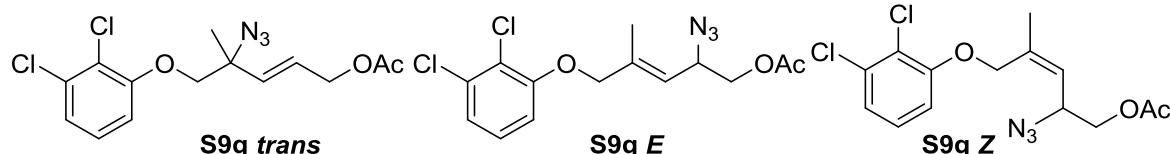


Compound S9e: General procedure 3 was used and the product was isolated in 85% yield as a clear oil. Compound **S9e** was isolated as a mixture of three isomers (1:1.6:0.3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S9e trans** δ 7.29 – 7.15 (m, 2H), 6.90 – 6.74 (m, 2H), 5.96 (dt, *J* = 15.7, 5.6 Hz, 1H), 5.85 (dt, *J* = 15.7, 1.3 Hz, 1H), 4.63 (dd, *J* = 5.6, 1.3 Hz, 2H), 3.90 (d, *J* = 9.2 Hz, 1H), 3.87 (d, *J* = 9.3 Hz, 1H), 2.10 (s, 3H), 1.53 (s, 3H); **S9e E** δ 7.29 – 7.15 (m, 2H), 6.90 – 6.74 (m, 2H), 5.52 (dq, *J* = 9.2, 1.5 Hz, 1H), 4.55 – 4.48 (m, 1H), 4.44 (s, 2H), 4.14 (dd, *J* = 11.4, 4.4 Hz, 1H), 4.03 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.10 (s, 3H), 1.86 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.65, 170.60, 157.05, 157.02, 157.00, 139.0, 138.6, 132.8, 129.47, 129.44, 129.42, 126.7, 126.3, 126.0, 122.7, 120.4, 116.7, 116.1, 116.0, 74.3, 72.3, 67.2, 65.8, 65.5, 63.9, 63.1, 57.5, 57.4, 21.8, 21.1, 20.9, 20.7, 14.5; **IR** (NaCl, thin film, cm⁻¹) 2954, 2923, 2105, 1738, 1492, 1223, 1167, 1031, 1013, 821; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₅ClN₃O₃Na⁺ (M+Na)⁺ 332.0772, found 332.0773.

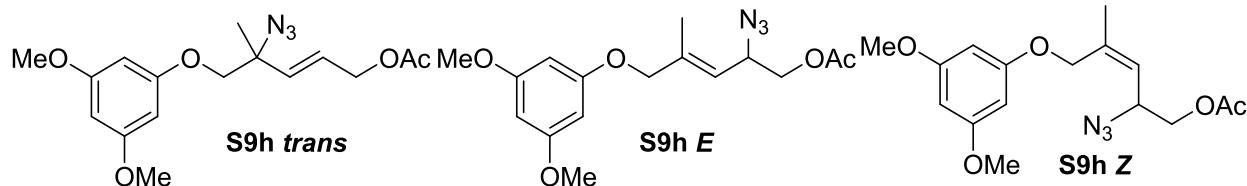


Compound S9f: General procedure 3 was used and the product was isolated in a 71% yield. Compound **S9f** was isolated as a mixture of three isomers (1:1.5:0.3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S9f trans** δ 7.04 – 6.92 (m, 2H), 6.91 – 6.81 (m, 2H), 5.96 (dt, *J* = 15.7, 5.6 Hz, 1H), 5.85 (dt, *J* = 15.7, 1.3 Hz, 1H), 4.63 (dd, *J* = 5.6, 1.2 Hz, 2H), 3.89 (d, *J* = 9.2 Hz, 1H), 3.86 (d, *J* = 9.2 Hz, 1H), 2.10 (s, 3H), 1.53 (s, 3H); **S9f E** δ 7.04 – 6.92 (m, 2H), 6.91 – 6.81 (m, 2H), 5.53 (dq, *J* = 9.2, 1.5 Hz, 1H), 4.55 – 4.48 (m, 1H), 4.43 (s, 2H), 4.14 (dd, *J* = 11.4, 4.5 Hz, 1H), 4.03 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.10 (s, 3H), 1.86 (d, *J* = 1.4 Hz, 3H). The carbon resonances corresponding to the arene

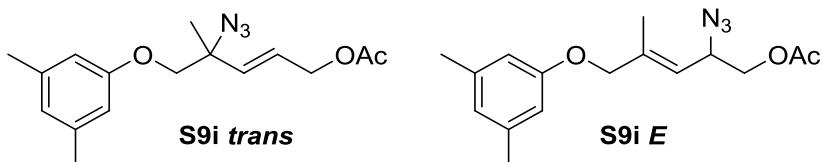
in this compound appear as a complex overlay between 170 and 115 ppm. Due to the complexities of this system the peaks are listed without attempting to group them into peak patterns; **¹³C NMR** (101 MHz, CDCl₃) δ 170.67, 170.65, 159.3, 158.1, 156.3, 155.5, 154.6, 154.4, 153.5, 139.2, 138.9, 133.0, 126.6, 122.5, 120.2, 116.0, 115.9, 115.84, 115.82, 74.8, 72.7, 67.6, 65.8, 65.6, 63.9, 63.1, 57.5, 57.4, 21.8, 14.5; **¹⁹F NMR** (376 MHz, CDCl₃) δ -123.0, -123.1, -123.4; **IR** (NaCl, thin film, cm⁻¹) 2936, 2106, 1744, 1506, 1461, 1381, 1223, 1042, 986, 829; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₅FN₃O₃Na⁺(M+Na)⁺ 316.1068, found 316.1069.



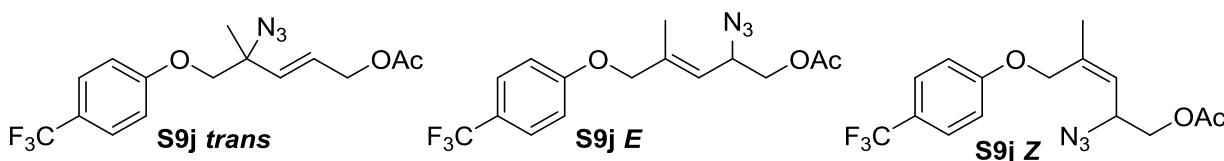
Compound S9g: General procedure 3 was used and the product was isolated in a 66% yield. Compound **S9g** was isolated as a mixture of three isomers (1:1.6:0.3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S9g *trans*** δ 7.19 – 7.05 (m, 2H), 6.89 – 6.75 (m, 1H), 6.00 (dt, *J* = 15.7, 5.6 Hz, 1H), 5.91 (dt, *J* = 15.7, 1.3 Hz, 1H), 4.64 (dd, *J* = 5.5, 1.2 Hz, 2H), 3.97 – 3.88 (m, 2H), 2.10 (s, 3H), 1.60 (s, 3H); **S9g *E*** δ 7.19 – 7.05 (m, 2H), 6.89 – 6.75 (m, 1H), 5.53 (dq, *J* = 9.1, 1.3 Hz, 1H), 4.56 – 4.47 (m, 3H), 4.15 (dd, *J* = 11.8, 4.0 Hz, 1H), 4.08 (dd, *J* = 11.8, 7.0 Hz, 1H), 2.10 (s, 3H), 1.89 (d, *J* = 1.3 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) 170.66, 170.64, 155.3, 155.28, 155.22, 138.1, 134.0, 133.9, 132.5, 127.4, 127.34, 127.32, 126.9, 123.0, 122.83, 122.80, 120.7, 111.6, 111.5, 111.4, 75.1, 73.1, 68.3, 65.9, 65.5, 63.9, 63.1, 57.4, 57.3, 21.1, 20.9, 20.7, 14.4; **IR** (NaCl, thin film, cm⁻¹) 2937, 2110, 1740, 1708, 1578, 1447, 1424, 1381, 1292, 1227, 867; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₅Cl₂N₃O₃Na⁺(M+Na)⁺ 366.0383, found 366.0379.



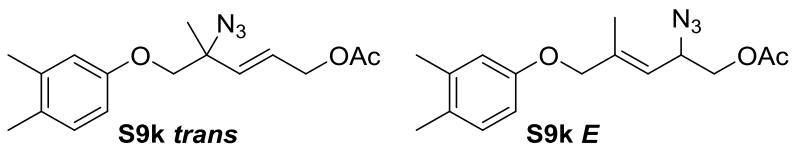
Compound S9h: A variation on general procedure 3 was used with the reaction run at 0.3 M concentration. The product was isolated in 30% yield as a light-brown oil. Compound **S9h** was isolated as a mixture of two isomers (1:1.3 *trans:E*). Trace amounts of **S9h *Z*** were observed. NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S9h *trans*** δ 6.14 – 6.01 (m, 3H), 5.95 (dt, *J* = 15.7, 5.7 Hz, 1H), 5.85 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.62 (dd, *J* = 5.6, 1.3 Hz, 2H), 3.88 (d, *J* = 9.3 Hz, 1H), 3.85 (d, *J* = 9.3 Hz, 1H), 3.76 (s, 6H), 2.09 (s, 3H), 1.51 (s, 3H); **S9h *E*** δ 6.14 – 6.01 (m, 3H), 5.52 (dq, *J* = 9.0, 1.5 Hz, 1H), 4.51 (ddd, *J* = 9.1, 7.8, 4.6 Hz, 1H), 4.42 (s, 2H), 4.13 (dd, *J* = 11.4, 4.4 Hz, 1H), 4.03 (dd, *J* = 11.4, 7.8 Hz, 1H), 3.76 (s, 6H), 2.09 (s, 3H), 1.85 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.74, 170.71, 161.73, 161.67, 161.64, 161.62, 161.4, 160.42, 160.39, 160.33, 158.0, 139.3, 139.1, 133.2, 126.6, 124.0, 122.6, 120.2, 96.3, 96.1, 94.3, 93.85, 93.80, 93.77, 93.70, 93.65, 93.58, 93.47, 92.9, 74.0, 72.1, 67.0, 65.9, 65.7, 64.9, 64.1, 63.2, 57.6, 57.5, 55.44, 55.42, 55.39, 55.32, 21.9, 21.2, 21.00, 20.97, 20.8, 14.6; **IR** (NaCl, thin film, cm⁻¹) 2928, 2843, 2109, 1743, 1600, 1459, 1382, 1226, 1205, 1151, 1068, 682; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₂₁N₃O₅Na(M+Na)⁺ 358.1373, found 358.1373.



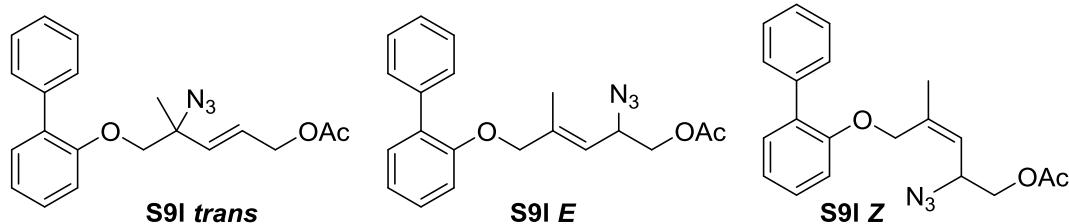
Compound S9i: General procedure 3 was used and the product was isolated in 47% yield as a clear oil. Compound **S9i** was isolated as a mixture of two isomers (1:1.4 *trans:E*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl_3) **S9i trans:** δ 6.67 – 6.62 (m, 1H), 6.59 – 6.55 (m, 2H), 5.97 (dt, J = 15.7, 5.6 Hz, 1H), 5.87 (dt, J = 15.7, 1.2 Hz, 1H), 4.64 (dd, J = 5.5, 1.2 Hz, 2H), 3.94 (d, J = 9.3 Hz, 1H), 3.90 (d, J = 9.3 Hz, 1H), 2.31 (s, 6H), 2.11 (s, 3H), 1.53 (s, 3H); **S9i E:** δ 6.67 – 6.62 (m, 1H), 6.59 – 6.55 (m, 2H), 5.55 (dq, J = 9.2, 1.5 Hz, 1H), 4.54 (ddd, J = 9.2, 7.8, 4.4 Hz, 1H), 4.45 (s, 2H), 4.15 (dd, J = 11.4, 4.4 Hz, 1H), 4.04 (dd, J = 11.4, 7.8 Hz, 1H), 2.31 (s, 6H), 2.11 (s, 3H), 1.87 (d, J = 1.4 Hz, 3H); **¹³C NMR** (101 MHz, CDCl_3) δ 170.69, 170.67, 158.6, 158.5, 139.5, 139.4, 139.3, 133.4, 126.4, 123.2, 123.0, 119.8, 112.6, 112.5, 74.0, 72.0, 65.7, 64.1, 63.2, 57.7, 31.0, 21.51, 21.49, 21.3, 21.0, 20.8, 14.6; **IR** (NaCl, thin film, cm^{-1}) 2921, 2107, 1612, 1595, 1452, 1381, 1322, 1295, 1228, 1155, 1041, 830; **HRMS(ESI-TOF)** m/z calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 326.1475, found 326.1475.



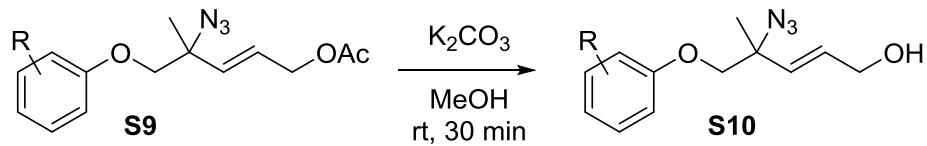
Compound S9j: General procedure 3 was used and the product was isolated in 58% yield as a clear oil. Compound **S9j** was isolated as a mixture of three isomers (1:1.5:0.2 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl_3) **S9j trans** δ 7.56 – 7.50 (m, 2H), 7.00 – 6.94 (m, 2H), 5.97 (dt, J = 15.7, 5.7 Hz, 1H), 5.85 (dt, J = 15.7, 1.5 Hz, 1H), 4.62 (dd, J = 5.7, 1.5 Hz, 2H), 3.95 (d, J = 9.2 Hz, 1H), 3.92 (d, J = 9.2 Hz, 1H), 2.06 (s, 3H), 1.52 (s, 3H); **S9j E** δ 7.56 – 7.50 (m, 2H), 7.00 – 6.94 (m, 2H), 5.53 (dq, J = 9.0, 1.5 Hz, 1H), 4.54 – 4.50 (m, 1H), 4.49 (s, 2H), 4.12 (dd, J = 11.4, 4.4 Hz, 1H), 4.02 (dd, J = 11.5, 7.6 Hz, 1H), 2.07 (s, 3H), 1.85 (d, J = 1.4 Hz, 3H); **S9j Z** δ 7.56 – 7.50 (m, 2H), 7.00 – 6.94 (m, 2H), 5.40 (dq, J = 9.3, 1.4 Hz, 1H), 4.59 (s, 2H), 4.58 – 4.55 (m, 1H), 4.16 – 4.09 (m, 1H), 4.06 – 3.99 (m, 1H), 2.06 (s, 3H), 1.94 (d, J = 1.4 Hz, 3H). The carbon resonances corresponding to the trifluoromethyl group in this compound appear as a complex overlay of quartet peaks between 140 and 110 ppm. Due to the complexities of this system, the peaks are listed without attempting to group them into peak patterns **¹³C NMR** (126 MHz, CDCl_3) δ 170.58, 170.55, 161.0, 160.9, 160.8, 138.7, 138.3, 132.7, 127.71, 127.66, 127.06, 127.03, 127.00, 126.98, 126.95, 126.92, 125.6, 125.5, 124.2, 124.1, 124.0, 123.73, 123.66, 123.57, 123.47, 123.40, 123.35, 123.31, 123.2, 123.14, 123.06, 122.9, 121.3, 121.2, 120.8, 114.8, 114.72, 114.71, 74.1, 72.1, 68.0, 67.0, 66.9, 65.8, 65.5, 64.8, 63.9, 63.1, 57.54, 57.49, 53.8, 21.7, 21.1, 20.8, 20.64, 20.62, 20.58, 14.4, 14.0; **¹⁹F NMR** (471 MHz, CDCl_3) δ -61.53, -61.55, -61.58; **IR** (NaCl, thin film, cm^{-1}) 2928, 2111, 1743, 1615, 1590, 1519, 1459, 1382, 1332, 1247, 1160, 1110, 1069, 1045, 1010, 973, 837; **HRMS (ESI-TOF)** m/z calcd for $\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_3\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 366.1036, found 366.1046.

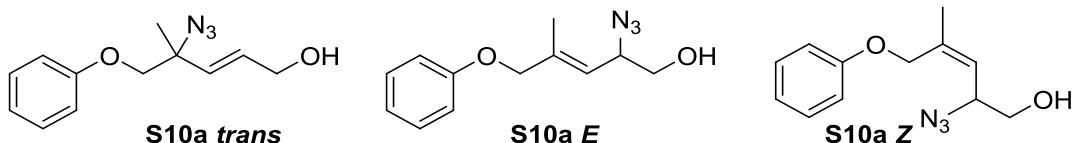


Compound S9k: A variation on general procedure 3 was used with the reaction run at 0.3 M concentration. The product was isolated in 74% yield as a clear oil. Compound **S9k** was isolated as a mixture of two isomers (1:2.6 *trans:E*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S9k** *trans* δ 7.06 – 7.02 (m, 1H), 6.77 – 6.73 (m, 1H), 6.69 – 6.64 (m, 1H), 5.97 (dt, *J* = 15.7, 5.6 Hz, 1H), 5.88 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.64 (dd, *J* = 5.6, 1.3 Hz, 2H), 3.91 (d, *J* = 9.2 Hz, 1H), 3.89 (d, *J* = 9.2 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H), 1.53 (s, 3H); **S9k E** δ 7.06 – 7.02 (m, 1H), 6.77 – 6.73 (m, 1H), 6.69 – 6.64 (m, 1H), 5.54 (dq, *J* = 9.1, 1.6 Hz, 1H), 4.53 (ddd, *J* = 9.2, 7.8, 4.3 Hz, 1H), 4.44 (s, 2H), 4.14 (dd, *J* = 11.4, 4.4 Hz, 1H), 4.04 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H), 1.87 (d, *J* = 1.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.73, 170.70, 156.7, 139.6, 138.0, 137.9, 134.9, 133.4, 130.5, 130.4, 129.5, 129.2, 127.8, 126.4, 119.9, 116.6, 116.5, 111.8, 111.7, 74.3, 72.3, 65.8, 64.1, 63.3, 57.7, 26.7, 21.4, 21.0, 20.8, 20.13, 20.10, 18.9, 14.6; **IR** (NaCl, thin film, cm⁻¹) 2923, 2108, 1746, 1609, 1580, 1502, 1452, 1381, 1227, 1164, 1121, 1044, 813; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₂₁N₃O₃Na⁺ (M+Na)⁺ 326.1475, found 326.1472.

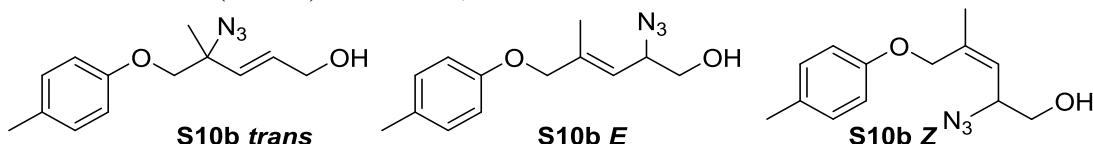


Compound S9l: General procedure 3 was used and the product was isolated in 44% yield as a clear oil. Compound **S9l** was isolated as a mixture of three isomers (1:1:3:0.2 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S9l** *trans* δ 7.57 – 7.48 (m, 2H), 7.45 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 7.12 – 7.03 (m, 1H), 6.99 – 6.93 (m, 1H), 5.82 (dt, *J* = 15.7, 5.7 Hz, 1H), 5.71 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.53 (dd, *J* = 5.7, 1.4 Hz, 2H), 3.86 (s, 2H), 2.08 (s, 3H), 1.37 (s, 3H); **S9l E** δ 7.57 – 7.48 (m, 2H), 7.45 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 7.12 – 7.03 (m, 1H), 6.99 – 6.93 (m, 1H), 5.44 (dq, *J* = 9.3, 1.5 Hz, 1H), 4.49 – 4.42 (m, 3H), 4.07 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.96 (dd, *J* = 11.4, 7.7 Hz, 1H), 2.07 (s, 3H), 1.77 (d, *J* = 1.5 Hz, 3H); **S9l Z** δ 7.57 – 7.48 (m, 2H), 7.45 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 7.12 – 7.03 (m, 1H), 6.99 – 6.93 (m, 1H), 5.29 (dq, *J* = 9.7, 1.2 Hz, 1H), 4.49 – 4.42 (m, 3H), 4.10 – 4.05 (m, 1H), 3.98 – 3.91 (m, 1H), 2.06 (s, 3H), 1.83 (d, *J* = 1.6 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.72, 170.68, 155.5, 155.4, 139.6, 139.2, 138.5, 138.3, 133.3, 131.7, 131.5, 131.2, 131.10, 131.08, 129.78, 129.72, 129.64, 128.80, 128.74, 128.72, 128.07, 128.03, 127.95, 127.13, 127.11, 127.09, 126.5, 122.0, 121.9, 121.6, 119.7, 113.5, 113.2, 113.0, 74.6, 72.6, 67.9, 65.9, 65.7, 64.1, 63.4, 57.5, 57.3, 21.8, 21.2, 21.0, 20.83, 20.82, 14.6, 14.3; **IR** (NaCl, thin film, cm⁻¹) 3026, 2918, 2107, 1742, 1482, 1434, 1381, 1363, 1229, 1123, 1043, 754, 700; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₁N₃O₃Na⁺ (M+Na)⁺ 374.1475, found 374.1479.

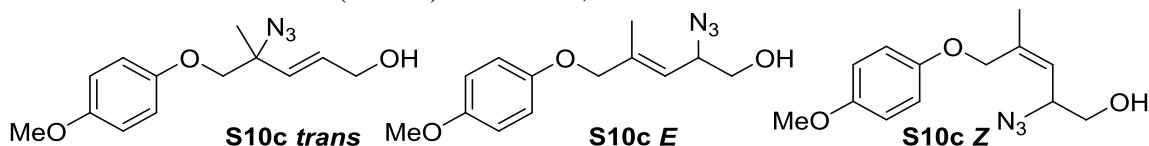




Compound S10a: General procedure 4 was used and the product was isolated in quantitative yield as an off-clear oil. Compound **S10a** was isolated as a mixture of three isomers (1:4.5:0.8 *trans:E:Z*). ¹H NMR data given below is based off of idealized integrations of the resulting mixture: ¹H NMR (500 MHz, CDCl₃) **S10a trans**: δ 7.34 – 7.26 (m, 2H), 7.01–6.91 (m, 3H), 6.04 (dt, *J* = 15.7, 5.0 Hz, 1H), 5.86 (dq, *J* = 15.7, 1.6 Hz, 1H), 4.25 (dd, *J* = 5.0, 1.6 Hz, 2H), 3.94 (d *J* = 9.2 Hz, 1H), 3.91 (d, *J* = 9.2 Hz, 1H), 1.89 (br s, 1H), 1.54 (s, 3H); **S10 E**: δ 7.34 – 7.26 (m, 2H), 7.01–6.91 (m, 3H), 5.59 (d, *J* = 9.3 Hz, 1H), 4.49 (s, 2H), 4.44 (ddd, *J* = 9.3, 7.1, 4.8 Hz, 1H), 3.62–3.55 (m, 2H), 1.89 (br s, 1H), 1.88 (s, 3H); **S10 Z**: δ 7.34 – 7.26 (m, 2H), 7.01–6.91 (m, 3H), 5.45 (d, *J* = 9.6 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.51 (m, 1 H), 3.62–3.58 (m, 2H), 1.98 (s, 3H), 1.89 (br s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 158.6, 158.5, 139.4, 139.2, 131.7, 130.2, 129.73, 129.68, 129.65, 123.3, 121.51, 121.49, 121.3, 120.7, 115.0, 114.9, 114.8, 74.2, 72.3, 67.1, 65.2, 65.0, 63.4, 62.9, 61.3, 61.1, 22.2, 21.5, 14.7; IR (NaCl, thin film, cm⁻¹) 3402, 2922, 2875, 2104, 1598, 1495, 1241, 755; HRMS (ESI-TOF) *m/z* calcd for C₁₂H₁₅N₃O₂Na⁺ (M+Na)⁺ 256.1056, found 256.1055.

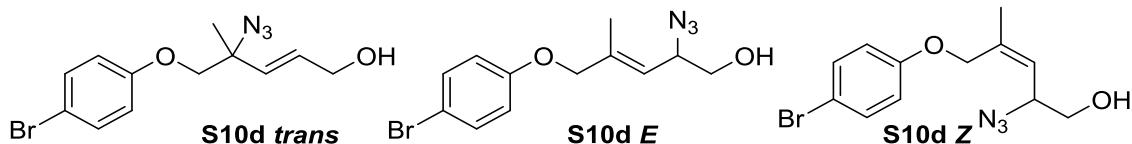


Compound S10b: General procedure 4 was used and the product was isolated in quantitative yield as a clear oil. Compound **S10b** was isolated as a mixture of three isomers (1:4:0.6 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: ¹H NMR (500 MHz, CDCl₃) **S10b trans** δ 7.15 – 7.08 (m, 2H), 6.88 – 6.81 (m, 2H), 6.03 (dt, *J* = 15.7, 5.0 Hz, 1H), 5.86 (dt, *J* = 15.7, 1.7 Hz, 1H), 4.23 (dd, *J* = 5.0, 1.6 Hz, 2H), 3.92 (d, *J* = 9.3 Hz, 1H), 3.89 (d, *J* = 9.3 Hz, 1H), 2.36 (br s, 1H), 2.32 (s, 3H), 1.53 (s, 3H); **S10b E** δ 7.15 – 7.08 (m, 2H), 6.88 – 6.81 (m, 2H), 5.58 (dq, *J* = 9.3, 1.6 Hz, 1H), 4.46 (s, 2H), 4.45 – 4.40 (m, 1H), 3.63 – 3.53 (m, 2H), 2.36 (br s, 1H), 2.32 (s, 3H), 1.87 (d, *J* = 1.5 Hz, 3H); **S10b Z** δ 7.15 – 7.08 (m, 2H), 6.88 – 6.81 (m, 2H), 5.43 (dq, *J* = 9.5, 1.2 Hz, 1H), 4.56 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.52 – 4.47 (m, 1H), 3.63 – 3.53 (m, 2H), 2.36 (br s, 1H), 2.32 (s, 3H), 1.97 (d, *J* = 1.5 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 156.47, 156.42, 156.40, 139.5, 139.2, 131.6, 130.7, 130.5, 130.2, 130.1, 130.03, 130.01, 123.1, 120.6, 114.8, 114.73, 114.65, 74.4, 72.5, 67.2, 65.1, 64.9, 63.4, 62.8, 61.2, 61.1, 22.0, 21.39, 20.6, 14.6; IR (NaCl, thin film, cm⁻¹) 3409, 3031, 2923, 2869, 2100, 1613, 1585, 1513, 1454, 1386, 1290, 1230, 1174, 1110, 1054, 1014, 817, 756; HRMS (ESI-TOF) *m/z* calcd for C₁₃H₁₇N₃O₂Na⁺ (M+Na)⁺ 270.1213, found 270.1208.

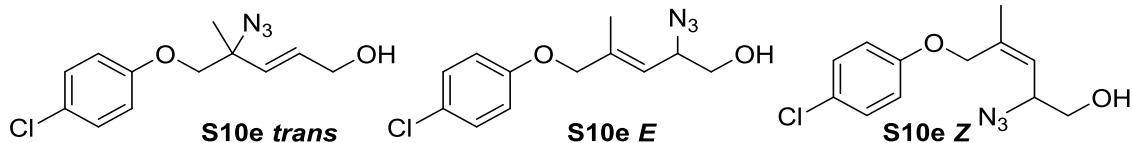


Compound S10c: General procedure 4 was used and the product was isolated in quantitative yield as a clear oil. Compound **5m** was isolated as a mixture of three isomers (1:3:0.5 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: ¹H NMR (500 MHz, CDCl₃) **S10c trans** δ 6.89 – 6.81 (m, 4H), 6.02 (dt, *J* = 15.7, 5.1 Hz, 1H), 5.84 (dt, *J* = 15.7, 1.7 Hz, 1H), 4.23 (dd, *J* = 5.0, 1.7 Hz, 2H), 3.88 (d, *J* = 9.2 Hz, 1H), 3.85 (d, *J* = 9.3 Hz, 1H), 3.77 (s,

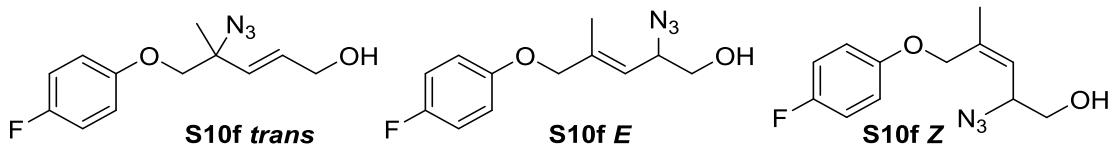
3H), 2.15 (br s, 1H), 1.51 (s, 3H); **S10c E** δ 6.89 – 6.81 (m, 4H), 5.56 (dq, $J = 9.4, 1.5$ Hz, 1H), 4.43 (s, 2H), 4.46 – 4.40 (m, 1H), 3.77 (s, 3H), 3.63 – 3.53 (m, 2H), 2.15 (br s, 1H), 1.86 (d, $J = 1.4$ Hz, 3H); **S10c Z** δ 6.89 – 6.81 (m, 4H), 5.41 (dq, $J = 9.5, 1.3$ Hz, 1H), 4.53 (d, $J = 11.6$ Hz, 1H), 4.48 (d, $J = 11.4$ Hz, 1H), 4.46 – 4.40 (m, 1H), 3.77 (s, 3H), 3.63 – 3.53 (m, 2H), 2.15 (br s, 1H), 1.96 (d, $J = 1.5$ Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 154.4, 154.2, 152.8, 152.7, 139.6, 139.4, 131.6, 130.2, 123.2, 120.7, 116.03, 116.02, 115.9, 114.88, 114.82, 114.80, 75.1, 73.2, 68.0, 65.2, 64.9, 63.5, 62.9, 61.2, 61.1, 55.87, 55.85, 29.8, 22.1, 21.4, 14.7; **IR** (NaCl, thin film, cm⁻¹) 3432, 2918, 2850, 2106, 1505, 1463, 1379, 1233, 1214, 1070, 1030, 827, 667; **HRMS** (ESI-TOF) *m/z* calcd for ₁₃H₁₇N₃O₃Na⁺ (M+Na)⁺ 286.1162, found 286.1159.



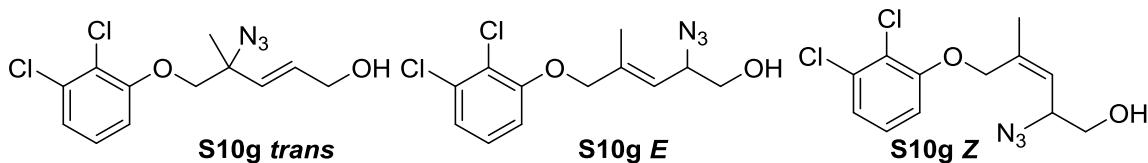
Compound S10d: General procedure 4 was used and the product was isolated in 65% yield as a yellow oil. Compound **5z** was isolated as a mixture of three isomers (1:5:0.7 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S10d trans** δ 7.41 – 7.34 (m, 2H), 6.83 – 6.76 (m, 2H), 6.01 (dt, $J = 15.7, 5.0$ Hz, 1H), 5.83 (dt, $J = 15.7, 1.6$ Hz, 1H), 4.23 (dd, $J = 5.0, 1.7$ Hz, 2H), 3.88 (d, $J = 9.3$ Hz, 1H), 3.85 (d, $J = 9.3$ Hz, 1H), 2.30 (br s, 1H), 1.51 (s, 3H); **S10 E** δ 7.41 – 7.34 (m, 2H), 6.83 – 6.76 (m, 2H), 5.55 (dq, $J = 9.4, 1.5$ Hz, 1H), 4.43 (s, 2H), 4.45 – 4.38 (m, 1H), 3.62 – 3.52 (m, 2H), 2.30 (br s, 1H), 1.85 (d, $J = 1.5$ Hz, 3H); **S10 Z** δ 7.41 – 7.34 (m, 2H), 6.83 – 6.76 (m, 2H), 5.44 (dq, $J = 9.6, 1.4$ Hz, 1H), 4.51 (s, 2H), 4.48 – 4.45 (m, 1H), 3.62 – 3.52 (m, 2H), 2.30 (br s, 1H), 1.94 (d, $J = 1.5$ Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 157.55, 157.53, 157.50, 138.8, 138.5, 132.4, 132.38, 132.35, 129.7, 123.4, 120.9, 116.6, 116.54, 116.53, 113.6, 113.3, 21.9, 21.2, 14.5; **IR** (NaCl, thin film, cm⁻¹) 3392, 2924, 2105, 1497, 1457, 1241, 1171, 1002, 820; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₄BrN₃O₂Na⁺ (M+Na)⁺ 334.0162 found 334.0154.



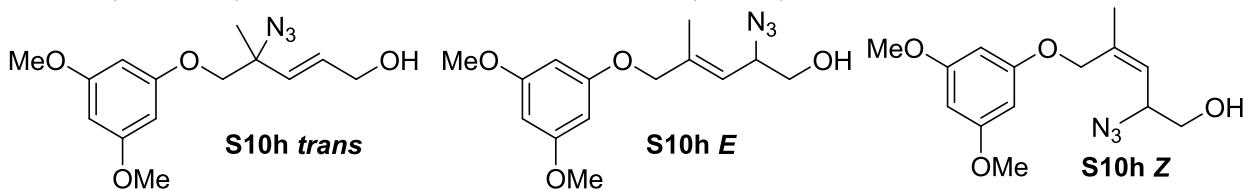
Compound S10e: General procedure 4 was used and the product was isolated in 95% yield as a yellow oil. Compound **S10e** was isolated as a mixture of three isomers (1:5:0.8 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S10e trans** δ 7.25 (m, 2H), 6.85 (m, 2H), 6.04 (dt, $J = 15.7, 4.9$ Hz, 1H), 5.85 (dt, $J = 15.7, 1.7$ Hz, 1H), 4.26 (dd, $J = 4.9, 1.7$ Hz, 2H), 3.92 (d, $J = 9.0$ Hz, 1H), 3.90 (d, $J = 9.0$ Hz, 1H), 2.07 (br s, 1H), 1.53 (s, 3H); **S10e E** δ 7.25 (m, 2H), 6.85 (m, 2H), 5.58 (dq, $J = 9.4, 1.5$ Hz, 1H), 4.50 – 4.39 (m, 3H), 3.60 (m, 2H), 2.07 (br s, 1H), 1.87 (d, $J = 1.4$ Hz, 3H); **S10e Z** δ 7.25 (m, 2H), 6.85 (m, 2H), 5.46 (dq, $J = 9.8, 1.4$ Hz, 1H), 4.31 – 4.20 (m, 3H), 3.60 (m, 2H), 2.07 (br s, 1H), 1.97 (d, $J = 1.5$ Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 157.05, 157.02, 138.9, 138.6, 131.7, 129.8, 129.5, 129.44, 129.40, 126.3, 126.0, 123.4, 120.8, 116.1, 116.0, 119.0, 74.5, 72.4, 67.2, 65.0, 64.8, 63.2, 62.7, 61.0, 60.9, 21.9, 21.3, 14.5; **IR** (NaCl, thin film, cm⁻¹) 3358, 2919, 2104, 1490, 1456, 1240, 1168, 1000, 825, 812, 771; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₄ClN₃O₂Na⁺ (M+Na)⁺ 290.0667, found 290.0658.



Compound S10f: General procedure 4 was used and the product was isolated in 82% yield as a yellow oil. Compound **S10f** was isolated as a mixture of three isomers (1:4:0.6 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S10f trans** δ 7.03 – 6.92 (m, 2H), 6.91 – 6.81 (m, 2H), 6.02 (dt, *J* = 15.7, 5.0 Hz, 1H), 5.84 (dt, *J* = 15.7, 1.7 Hz, 1H), 4.25 – 4.21 (m, 2H), 3.88 (d, *J* = 9.2 Hz, 1H), 3.85 (d, *J* = 9.2 Hz, 1H), 2.31 (br s, 1H), 1.85 (d, *J* = 1.4 Hz, 3H); **S10f E** δ 7.03 – 6.92 (m, 2H), 6.91 – 6.81 (m, 2H), 5.56 (dq, *J* = 9.4, 1.5 Hz, 1H), 4.45 – 4.38 (m, 1H), 4.43 (s, 2H), 3.63 – 3.51 (m, 2H), 2.31 (br s, 1H), 1.51 (d, *J* = 1.4 Hz, 3H); **S10f Z** δ 7.03 – 6.92 (m, 2H), 6.91 – 6.81 (m, 2H), 5.43 (dq, *J* = 9.5, 1.2 Hz, H), 4.51 (d, 11.6 Hz, 1H), 4.50 (d, 11.6 Hz, 1H), 4.49 – 4.45 (m, 1H), 3.63 – 3.51 (m, 2H), 2.31 (br s, 1H), 1.95 (d, *J* = 1.5 Hz, 3H). The carbon resonances corresponding to the arene in this compound appear as a complex overlay between 170 and 115 ppm. Due to the complexities of this system the peaks are listed without attempting to group them into peak patterns; **¹³C NMR** (101 MHz, CDCl₃) δ 158.8, 158.6, 156.4, 156.3, 154.6, 154.5, 139.1, 138.8, 131.6, 129.8, 123.3, 120.8, 116.0, 115.8, 74.9, 72.9, 67.7, 65.0, 64.8, 63.3, 62.6, 61.0, 60.9, 21.9, 21.2, 14.5; **¹⁹F NMR** (376 MHz, CDCl₃) δ -123.05, -123.10, -123.4; **IR** (NaCl, thin film, cm⁻¹) 3378, 2927, 2871, 2105, 1507, 1458, 1387, 1247, 1209, 1052, 828; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₄FN₃O₂Na⁺ (M+Na)⁺ 290.0667, found 290.0658.



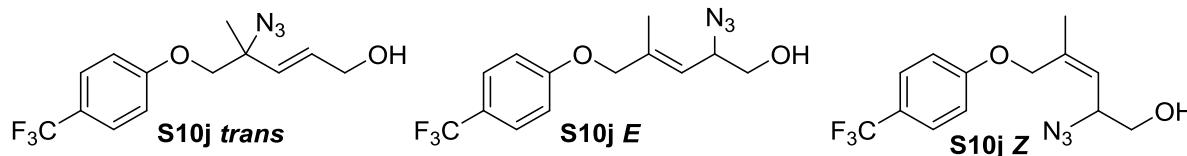
Compound S10g: General procedure 4 was used and the product was isolated in 80% yield as a yellow oil. Compound **S10g** was isolated as a mixture of three isomers (1:5:0.8 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S10g trans** δ 7.16 – 7.06 (m, 2H), 6.87 – 6.77 (m, 1H), 6.05 (dt, *J* = 15.7, 5.0 Hz, 1H), 5.86 (dt, *J* = 15.6, 1.7 Hz, 1H), 4.24 (dd, *J* = 4.9, 1.7 Hz, 2H), 3.94 (d, *J* = 9.1 Hz, 1H), 3.91 (d, *J* = 9.2 Hz, 1H), 2.19 (br s, 1H), 1.58 (s, 3H); **S10g E** δ 7.16 – 7.06 (m, 2H), 6.87 – 6.77 (m, 1H), 5.61 (dq, *J* = 9.4, 1.5 Hz, 1H), 4.54 (s, 2H), 4.43 (ddd, *J* = 9.3, 7.0, 4.7 Hz, 1H), 3.65 – 3.54 (m, 2H), 2.19 (br s, 1H), 1.89 (d, *J* = 1.4 Hz, 3H); **S10g Z** δ 7.16 – 7.06 (m, 2H), 6.87 – 6.77 (m, 1H), 5.47 (dq, *J* = 9.7, 1.7 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.54 – 4.48 (m, 1H), 3.65 – 3.54 (m, 2H), 2.19 (br s, 1H), 1.99 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 155.2, 138.0, 133.9, 131.9, 129.5, 127.4, 127.3, 123.6, 123.0, 122.8, 122.2, 121.2, 111.7, 111.5, 111.4, 75.2, 73.4, 68.4, 65.0, 64.8, 63.2, 62.7, 61.0, 60.9, 21.8, 21.2, 14.5; **IR** (NaCl, thin film, cm⁻¹) 3350, 2929, 2872, 2106, 1580, 1452, 1292, 1267, 1020, 798; **HRMS** (ESI-TOF) *m/z* calcd for C₁₂H₁₃Cl₂N₃O₂Na⁺ (M+Na)⁺ 324.0277, found 324.0282.



Compound S10h: General procedure 4 was used and the product was isolated in 89% yield as a clear oil. Compound **S10h** was isolated as a mixture of three isomers (1:4:0.7 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S10h trans** δ 6.14 – 6.06 (m, 3H), 6.01 (dt, *J* = 15.7, 4.9 Hz, 1H), 5.83 (dt, *J* = 15.7, 1.7 Hz, 1H), 4.23 (dd, *J* = 4.9, 1.7 Hz, 2H), 3.88 (d, *J* = 9.3 Hz, 1H), 3.85 (d, *J* = 9.3 Hz, 1H), 3.76 (s, 6H), 2.27 (br s, 1H), 1.50 (s, 3H); **S10h E** δ 6.14 – 6.06 (m, 3H), 5.56 (dq, *J* = 9.4, 1.5 Hz, 1H), 4.45 – 4.39 (m, 1H), 4.42 (s, 2H), 3.76 (s, 6H), 3.63 – 3.53 (m, 2H), 2.27 (br s, 1H), 1.85 (d, *J* = 1.5 Hz, 3H); **S10h Z** δ 6.14 – 6.06 (m, 3H), 5.42 (dq, *J* = 9.6, 1.3 Hz, 1H), 4.52 (d, *J* = 9.5 Hz, 1H), 4.49 (d, *J* = 9.5 Hz, 1H), 4.48 – 4.44 (m, 1H), 3.76 (s, 6H), 3.63 – 3.53 (m, 2H), 2.27 (br s, 1H), 1.95 (d, *J* = 1.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 161.69, 161.65, 161.64, 160.48, 160.45, 139.1, 138.9, 131.8, 130.0, 123.4, 120.8, 93.84, 93.79, 93.75, 93.67, 93.61, 93.5, 74.2, 72.4, 67.1, 65.2, 64.9, 63.3, 62.8, 61.2, 61.1, 55.50, 55.46, 31.0, 29.8, 24.9, 22.1, 21.4, 14.7; **IR** (NaCl, thin film, cm⁻¹) 3445, 2926, 2844, 2103, 1596, 1477, 1461, 1389, 1246, 1204, 1151, 1067, 819, 681; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₉N₃O₄Na⁺ (M+Na)⁺ 316.1268, found 316.1269.

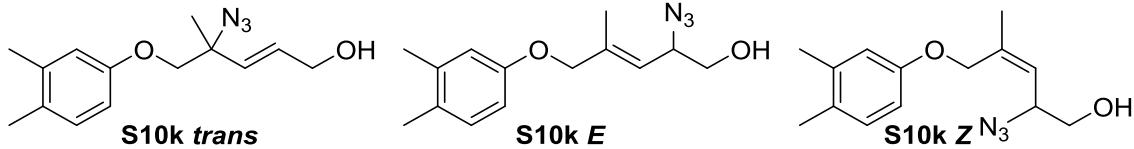


Compound S10i: General procedure 4 was used and the product was isolated in 82% yield as a clear oil. Compound **S10i** was isolated as a mixture of three isomers (1:3:0.8 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S10i trans** δ 6.62 (s, 1H), 6.56 (s, 2H), 6.03 (dt, *J* = 15.7, 5.0 Hz, 1H), 5.85 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.49 – 4.41 (m, 2H), 3.91 (d, *J* = 9.3 Hz, 1H), 3.88 (d, *J* = 9.3 Hz, 1H), 2.29 (s, 7H), 1.56 (s, 3H); **S10i E** δ 6.62 (s, 1H), 6.56 (s, 2H), 5.57 (dq, *J* = 9.5, 1.5 Hz, 1H), 4.46 (s, 2H), 4.49 – 4.41 (m, 1H), 3.64 – 3.53 (m, 2H), 2.29 (s, 7H), 1.87 (d, *J* = 1.4 Hz, 3H); **S10i Z** δ 6.62 (s, 1H), 6.56 (s, 2H), 5.43 (dq, *J* = 9.4, 1.3 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.25 (td, *J* = 5.6, 1.6 Hz, 1H), 3.64 – 3.53 (m, 2H), 2.29 (s, 7H), 1.96 (d, *J* = 1.5 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 158.56, 158.53, 158.51, 139.47, 139.40, 139.36, 139.31, 139.26, 131.5, 130.2, 123.2, 123.01, 122.99, 120.4, 112.7, 112.51, 112.46, 74.1, 72.2, 66.9, 65.1, 64.8, 63.4, 62.8, 61.1, 61.0, 22.0, 21.48, 21.46, 21.37, 14.6; **IR** (NaCl, thin film, cm⁻¹) 3376, 2917, 2864, 2103, 1614, 1594, 1506, 1418, 1321, 1295, 1248, 1154, 1069, 1002, 878, 832; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₉N₃O₂Na⁺ (M+Na)⁺ 284.1370, found 284.1375.

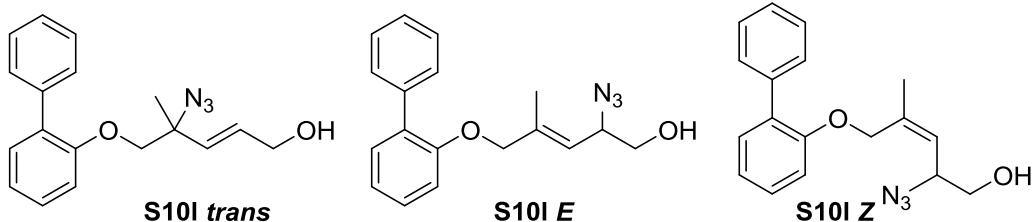


Compound S10j: General procedure 4 was used and the product was isolated in 82% yield as a light-yellow oil. Compound **S10j** was isolated as a mixture of three isomers (1:4.5:0.7 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **S10j trans** δ 7.59 – 7.51 (m, 2H), 7.02 – 6.94 (m, 2H), 6.04 (dt, *J* = 15.7, 5.0 Hz, 1H), 5.85 (dt, *J* = 15.7, 1.7 Hz, 1H), 4.24 (dd, *J* = 4.9, 1.7 Hz, 2H), 3.96 (d, *J* = 9.3 Hz, 1H), 3.92 (d, *J* = 9.3 Hz, 1H), 2.53 (br s, 1H), 1.53 (s, 3H); **S10j E** δ 7.59 – 7.51 (m, 2H), 7.02 – 6.94 (m, 2H), 5.59 (dq, *J* = 9.3, 1.5 Hz, 1H), 4.51 (s, 2H), 4.43 (ddd, *J* = 9.3, 7.1, 4.5 Hz, 1H), 3.62 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.57 (dd, *J* = 11.5, 7.2 Hz, 1H), 2.53 (br s, 1H), 1.87 (d, *J* = 1.4 Hz, 3H); **S10j Z** δ 7.59 – 7.51 (m, 2H), 7.02 – 6.94 (m, 2H), 5.47 (dq, *J* = 9.7, 1.3 Hz, 1H), 4.60 (s, 2H), 4.49 –

4.46 (m, 1H), 3.64 – 3.54 (m, 2H), 2.53 (s, 1H), 1.96 (d, J = 1.4 Hz, 3H). The carbon resonances corresponding to the trifluoromethyl group in this compound appear as a complex overlay of quartet peaks between 140 and 110 ppm. Due to the complexities of this system, the peaks are listed without attempting to group them into peak patterns. **^{13}C NMR** (101 MHz, CDCl_3) δ 160.99, 160.98, 160.92, 160.91, 160.87, 138.6, 138.2, 132.0, 129.6, 128.6, 127.10, 127.07, 127.03, 126.99, 126.95, 125.85, 123.79, 123.72, 123.6, 123.5, 123.4, 123.3, 123.2, 123.14, 123.10, 122.8, 121.2, 120.5, 118.2, 114.9, 114.7, 74.3, 72.3, 67.1, 65.0, 64.89, 63.2, 62.7, 61.1, 61.0, 21.9, 21.2, 14.5; **^{19}F NMR** (376 MHz, CDCl_3) δ -61.49, -61.51, -61.53; **IR** (NaCl, thin film, cm^{-1}) 3386, 2924, 2854, 2104, 1614, 1589, 1518, 1329, 1252, 1160, 1109, 1069, 1008, 836, 643; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{N}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 325.1003, found 325.0990.

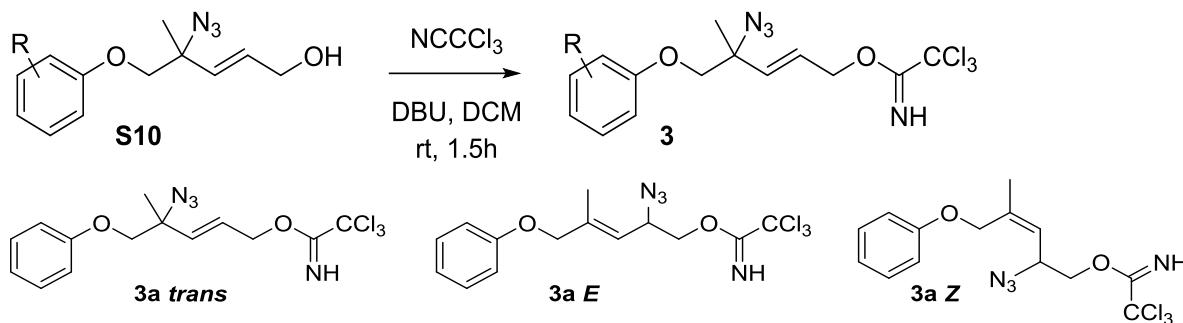


Compound S10k: General procedure 4 was used and the product was isolated in 84% yield as a clear oil. Compound **S10k** was isolated as a mixture of three isomers (1:4:0.7 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **^1H NMR** (400 MHz, CDCl_3) **S10k trans** δ 7.13 – 7.06 (m, 1H), 6.83 – 6.79 (m, 1H), 6.76 – 6.69 (m, 1H), 6.06 (dt, J = 15.7, 5.0 Hz, 1H), 5.89 (dt, J = 15.7, 1.6 Hz, 1H), 4.25 (dd, J = 5.0, 1.7 Hz, 2H), 3.96 (d, J = 9.3 Hz, 1H), 3.92 (d, J = 9.3 Hz, 1H), 2.95 (br s, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 1.56 (s, 3H); **S10k E** δ 7.13 – 7.06 (m, 1H), 6.83 – 6.79 (m, 1H), 6.76 – 6.69 (m, 1H), 5.61 (dq, J = 9.3, 1.6 Hz, 1H), 4.48 (s, 2H), 4.45 (ddd, J = 9.4, 7.0, 5.0 Hz, 1H), 3.68 – 3.57 (m, 2H), 2.95 (br s, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 1.91 (d, J = 1.5 Hz, 3H); **S10k Z** δ 7.13 – 7.06 (m, 1H), 6.83 – 6.79 (m, 1H), 6.76 – 6.69 (m, 1H), 5.46 (dq, J = 9.6, 1.4 Hz, 1H), 4.57 (s, 2H), 4.53 (ddd, J = 9.6, 6.8, 4.8 Hz, 1H), 3.68 – 3.57 (m, 2H), 2.95 (br s, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 2.00 (d, J = 1.4 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl_3) δ 156.6, 156.5, 139.3, 139.1, 137.78, 137.74, 137.69, 131.4, 130.33, 130.27, 130.0, 129.24, 129.20, 129.0, 122.9, 120.5, 116.4, 116.3, 111.7, 111.6, 111.5, 74.2, 72.3, 67.0, 64.9, 64.7, 63.3, 62.5, 61.0, 60.9, 21.8, 21.2, 19.93, 19.90, 18.7, 14.4; **IR** (NaCl, thin film, cm^{-1}) 3384, 2922, 2859, 2105, 1609, 1580, 1502, 1385, 1304, 1252, 1206, 1163, 1120, 1022, 865, 814; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 284.1369, found 284.1372.

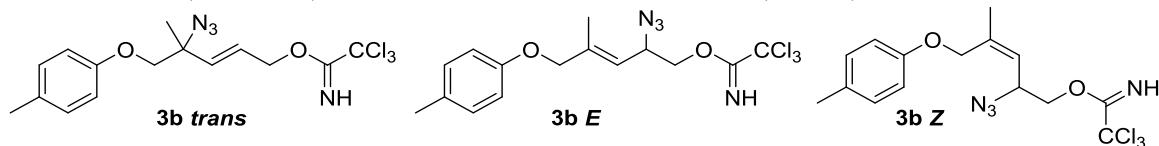


Compound S10l: General procedure 4 was used and the product was isolated in 98% yield as a clear oil. Compound **S10l** was isolated as a mixture of three isomers (1:2.7:0.4 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **^1H NMR** (500 MHz, CDCl_3) **S10l trans** δ 7.63 – 7.56 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43 – 7.31 (m, 3H), 7.15 – 7.08 (m, 1H), 7.07 – 6.97 (m, 1H), 5.89 (dt, J = 15.7, 5.0 Hz, 1H), 5.70 (dt, J = 15.7, 1.7 Hz, 1H), 4.11 (br d, J = 5.3 Hz, 2H), 3.90 (s, 2H), 1.76 (br s, 1H), 1.41 (s, 3H); **S10l E** δ 7.63 – 7.56 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43 – 7.31 (m, 3H), 7.15 – 7.08 (m, 1H), 7.07 – 6.97 (m, 1H), 5.50 (dq, J = 9.4, 1.6 Hz, 1H), 4.50 – 4.47 (m, 2H), 4.39 (ddd, J = 9.4, 7.1, 4.8 Hz, 1H), 3.57 – 3.48 (m, 2H), 2.27 (br s, 1H), 1.80 (d, J = 1.5 Hz, 3H); **S10l Z** δ 7.63 – 7.56 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43

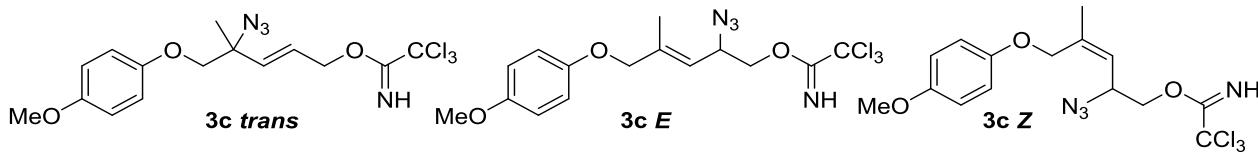
– 7.31 (m, 3H), 7.15 – 7.08 (m, 1H), 7.07 – 6.97 (m, 1H), 5.36 (dq, J = 9.6, 1.4 Hz, 1H), 4.58 (d, J = 11.7 Hz, 1H), 4.53 (d, J = 11.8 Hz, 1H), 4.33 (dt, J = 9.6, 5.8 Hz, 1H), 3.46 – 3.42 (m, 2H), 2.11 (br s, 1H), 1.87 (d, J = 1.5 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.5, 155.4, 155.3, 139.2, 139.0, 138.50, 138.46, 138.3, 131.7, 131.53, 131.51, 131.4, 131.2, 131.01, 130.99, 130.1, 129.8, 129.7, 129.6, 129.1, 128.75, 128.71, 128.68, 128.04, 127.98, 127.89, 127.07, 127.04, 126.99, 122.7, 121.9, 121.8, 121.6, 120.1, 113.5, 113.2, 113.0, 74.7, 72.7, 68.0, 65.0, 64.8, 63.5, 62.7, 60.9, 60.8, 21.9, 21.3, 14.6; IR (NaCl, thin film, cm^{-1}) 3376, 3061, 2923, 2871, 2106, 1596, 1583, 1481, 1434, 1262, 1229, 1123, 1053, 1009, 754, 729, 700; HRMS (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 332.1369, found 332.1365.



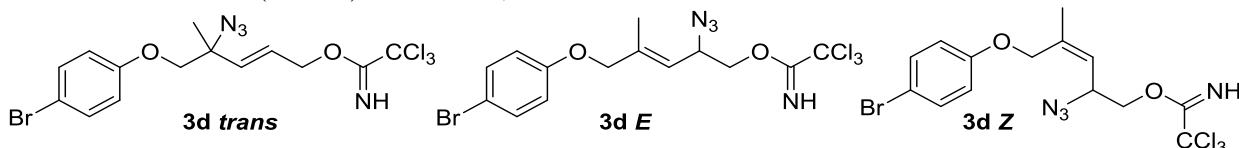
Compound 3a: General procedure 5 was used and the product was isolated in 70% yield as a clear oil. Compound **3a** was isolated as a mixture of three isomers (1:2:0.2 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: ^1H NMR (500 MHz, CDCl_3) **3a trans**: δ 8.41 (s, 1H), 7.36 – 7.21 (m, 2H), 7.02 – 6.86 (m, 3H), 6.07 (dt, J = 15.7, 5.2 Hz, 1H), 6.00 (d, J = 15.8 Hz, 1H), 4.88 (d, J = 5.2 Hz, 2H), 3.95 (d, J = 9.4 Hz, 1H), 3.92 (d, J = 9.4 Hz, 1H), 1.55 (s, 3H); **3a E**: δ 8.41 (s, 1H), 7.36 – 7.21 (m, 2H), 7.02 – 6.86 (m, 3H), 5.63 (d, J = 9.1 Hz, 1H), 4.67 (ddd, J = 9.0, 7.1, 4.7 Hz, 1H), 4.48 (s, 2H), 4.36 – 4.23 (m, 2H), 1.89 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.7, 162.5, 158.61, 158.58, 158.55, 139.4, 133.7, 129.75, 129.70, 129.67, 125.7, 121.6, 121.3, 120.1, 114.94, 114.88, 114.86, 91.2, 74.2, 72.1, 70.3, 68.6, 63.4, 57.4, 22.0, 21.4, 14.7; IR (NaCl, thin film, cm^{-1}) 3341, 3040, 2930, 2108, 1666, 1495, 1303, 1243, 1078, 797; HRMS (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{Cl}_3\text{N}_4\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 399.0153, found 399.0152.



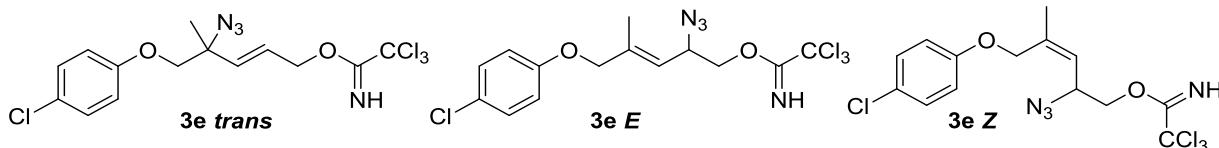
Compound 3b: General procedure 5 was used and the product was isolated in 89% yield as a clear oil. Compound **3b** was isolated as a mixture of three isomers (1:1.3:0.2 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: ^1H NMR (500 MHz, CDCl_3) **3b trans**: δ 8.41 (s, 1H), 7.15 – 7.07 (m, 2H), 6.89 – 6.80 (m, 2H), 6.09 (dt, J = 15.8, 5.2 Hz, 1H), 6.01 (dt, J = 15.7, 1.3 Hz, 1H), 4.90 (dd, J = 5.3, 1.0 Hz, 2H), 3.94 (d, J = 9.3 Hz, 1H), 3.92 (d, J = 9.2 Hz, 1H), 2.32 (s, 3H), 1.56 (s, 3H); **3b E**: δ 8.44 (s, 1H), 7.15 – 7.07 (m, 2H), 6.89 – 6.80 (m, 2H), 5.64 (dq, J = 9.1, 1.5 Hz, 1H), 4.68 (ddd, J = 9.2, 7.1, 4.7 Hz, 1H), 4.47 (s, 2H), 4.38 – 4.24 (m, 2H), 2.32 (s, 3H), 1.90 (d, J = 1.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.6, 162.3, 156.5, 156.4, 139.7, 139.5, 133.7, 130.74, 130.66, 130.4, 130.10, 130.05, 130.02, 125.6, 122.2, 119.9, 114.74, 114.68, 91.4, 91.1, 74.3, 72.2, 70.6, 70.3, 68.5, 67.3, 63.4, 57.30, 57.28, 21.9, 21.3, 20.60, 20.58, 14.6; IR (NaCl, thin film, cm^{-1}) 3338, 3030, 2917, 2861, 2103, 1665, 1613, 1585, 1510, 1461, 1379, 1293, 1225, 1175, 1087, 1054, 1005, 975, 830, 810, 794, 757, 720, 672, 646; HRMS (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{Cl}_3\text{N}_4\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 413.0309, found 413.0291.



Compound 3c: General procedure 5 was used and the product was isolated in 75% yield as a clear oil. Compound **3c** was isolated as a mixture of three isomers (1:1.3:0.2 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **3c** *trans* δ 8.41 (s, 1H), 6.91 – 6.80 (m, 4H), 6.06 (dt, *J* = 15.8, 5.2 Hz, 1H), 5.99 (dt, *J* = 15.8, 1.2 Hz, 1H), 4.88 (dd, *J* = 5.3, 1.2 Hz, 2H), 3.90 (d, *J* = 9.3 Hz, 1H), 3.88 (d, *J* = 9.3 Hz, 1H), 3.78 (s, 3H), 1.54 (s, 3H); **3c** *E* δ 8.41 (s, 1H), 6.91 – 6.80 (m, 4H), 5.61 (dq, *J* = 9.1, 1.5 Hz, 1H), 4.66 (ddd, *J* = 9.1, 7.1, 4.7 Hz, 1H), 4.43 (s, 2H), 4.32 (dd, *J* = 11.1, 4.7 Hz, 1H), 4.28 (dd, *J* = 11.2, 7.1 Hz, 1H), 3.78 (s, 3H), 1.88 (d, *J* = 1.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 162.7, 162.6, 162.4, 154.49, 154.45, 154.3, 152.8, 152.7, 139.8, 139.7, 133.7, 125.6, 122.3, 120.0, 116.01, 115.95, 114.9, 114.8, 91.5, 91.2, 75.1, 73.0, 70.6, 70.3, 68.6, 68.0, 63.5, 57.4, 57.3, 55.9, 22.0, 21.4, 14.7 **IR** (NaCl, thin film, cm⁻¹) 3339, 2934, 2834, 2108, 1667, 1506, 1456, 1381, 1302, 1228, 1181, 1038, 1009, 983, 828, 795, 750, 719, 651; **HRMS** (ESI-TOF) *m/z* calcd for C₁₅H₁₇Cl₃N₄O₃Na⁺ (M+Na)⁺ 429.0258, found 429.0261.

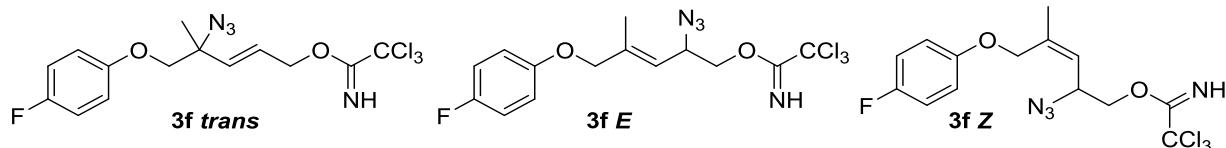


Compound 3d: General procedure 5 was used and the product was isolated in 65% yield as a thick yellow oil. Compound **3d** was isolated as a mixture of three isomers (1:1.6:0.2 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **3d** *trans* δ 8.38 (s, 1H), 7.42 – 7.34 (m, 2H), 6.84 – 6.76 (m, 2H), 6.07 (dt, *J* = 15.7, 5.2 Hz, 1H), 5.97 (dt, *J* = 15.7, 1.3 Hz, 1H), 4.88 (dd, *J* = 5.2, 1.2 Hz, 2H), 3.91 (d, *J* = 9.3 Hz, 1H), 3.88 (d, *J* = 9.5 Hz, 1H), 1.54 (s, 3H); **3d** *E* δ 8.42 (s, 1H), 7.42 – 7.34 (m, 2H), 6.84 – 6.76 (m, 2H), 5.60 (dq, *J* = 9.2, 1.5 Hz, 1H), 4.66 (ddd, *J* = 9.1, 6.8, 4.8 Hz, 1H), 4.44 (s, 2H), 4.35 – 4.23 (m, 2H), 1.88 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 162.5, 162.2, 157.55, 157.51, 139.0, 138.7, 133.1, 132.4, 132.3, 125.8, 122.6, 120.3, 116.6, 116.5, 114.7, 113.3, 91.3, 91.0, 74.3, 72.2, 70.4, 70.1, 68.3, 67.2, 63.1, 57.14, 57.13, 21.7, 21.2, 14.5; **IR** (NaCl, thin film, cm⁻¹) 3341, 2923, 2106, 1666, 1498, 1287, 1241, 1072, 822, 798; **HRMS** (ESI-TOF) *m/z* calcd for C₁₄H₁₅BrCl₃N₄O₂Na⁺ (M+Na)⁺ 476.9258, found 476.9246.

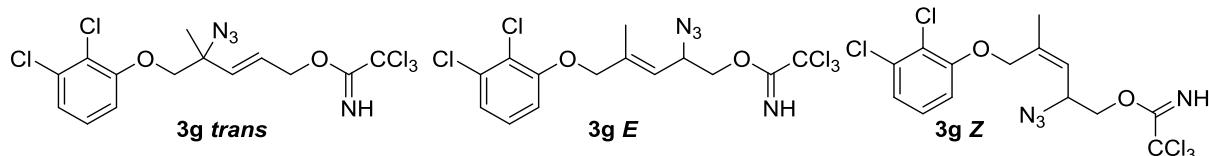


Compound 3e: General procedure 5 was used and the product was isolated in 80% yield as a thick yellow oil. Compound **3e** was isolated as a mixture of three isomers (1:1.6:0.2 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **3e** *trans* δ 8.39 (s, 1H), 7.26 – 7.20 (m, 2H), 6.88 – 6.80 (m, 2H), 6.07 (dt, *J* = 15.7, 5.2 Hz, 1H), 5.97 (dt, *J* = 15.7, 1.3 Hz, 1H), 4.88 (dd, *J* = 5.2, 1.2 Hz, 2H), 3.90 (d, *J* = 9.1 Hz, 1H), 3.88 (d, *J* = 9.3 Hz, 1H), 1.53 (s, 3H); **3e** *E* δ 8.43 (s, 1H), 7.26 – 7.20 (m, 2H), 6.88 – 6.80 (m, 2H), 5.61 (dq, *J* = 9.1, 1.5 Hz, 1H), 4.66 (ddd, *J* = 9.1, 6.9, 4.8 Hz, 1H), 4.44 (s, 2H), 4.34 – 4.24 (m, 2H), 1.87 (d, *J* = 1.6 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 162.43, 162.41, 162.2, 167.0,

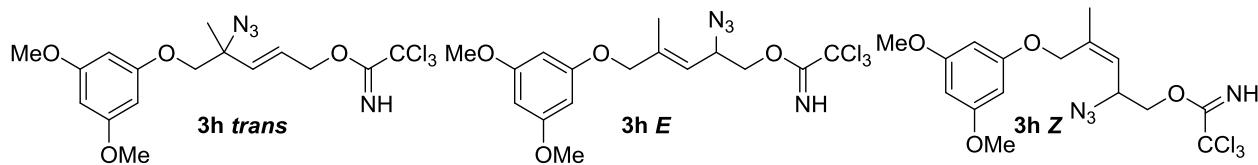
157.0, 139.1, 138.7, 133.1, 132.3, 129.5, 129.44, 129.41, 126.3, 126.0, 125.8, 125.6, 122.6, 120.3, 116.5, 116.0, 91.2, 91.0, 74.3, 72.2, 70.4, 70.1, 68.3, 67.2, 63.1, 57.12, 57.11, 21.7, 21.2, 14.5; **IR** (NaCl, thin film, cm^{-1}) 3342, 2933, 2108, 1667, 1491, 1290, 1241, 1091, 1006, 823, 765; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{Cl}_4\text{N}_4\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 432.9763, found 432.9756.



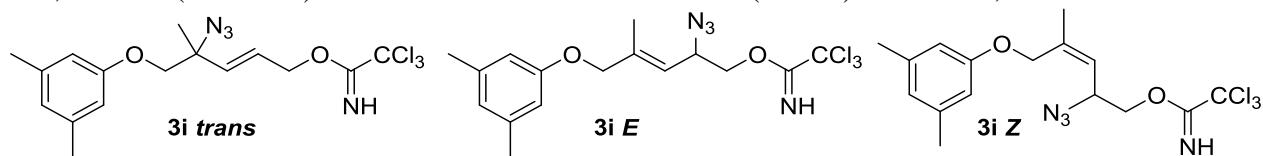
Compound 3f: General procedure 5 was used and the product was isolated in 70% yield as a thick yellow oil. Compound **3f** was isolated as a mixture of three isomers (1:1.6:0.1 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl_3) **3f trans** δ 8.38 (s, 1H), 7.03 – 6.93 (m, 2H), 6.90 – 6.81 (m, 2H), 6.07 (dt, $J = 15.7, 5.2$ Hz, 1H), 5.98 (dt, $J = 15.7, 1.2$ Hz, 1H), 4.88 (dd, $J = 5.2, 1.2$ Hz, 2H), 3.91 (d, $J = 9.2$ Hz, 1H), 3.88 (d, $J = 9.2$ Hz, 1H), 1.54 (s, 3H); **3f E** δ 8.42 (s, 1H), 7.03 – 6.93 (m, 2H), 6.90 – 6.81 (m, 2H), 5.61 (dq, $J = 9.2, 1.5$ Hz, 1H), 4.66 (ddd, $J = 9.1, 6.9, 4.8$ Hz, 1H), 4.44 (s, 2H), 4.35 – 4.25 (m, 2H), 1.88 (d, $J = 1.4$ Hz, 3H). The carbon resonances corresponding to the arene in this compound appear as a complex overlay between 170 and 115 ppm. Due to the complexities of this system the peaks are listed without attempting to group them into peak patterns; **¹³C NMR** (101 MHz, CDCl_3) δ 162.5, 162.3, 158.7, 156.3, 154.54, 154.52, 139.0, 133.3, 125.7, 122.4, 120.1, 115.9, 115.8, 115.7, 91.3, 91.0, 74.8, 72.7, 70.1, 68.3, 63.22, 57.1, 21.2, 14.5; **¹⁹F NMR** (376 MHz, CDCl_3) δ -123.0, -123.1, -123.4; **IR** (NaCl, thin film, cm^{-1}) 3342, 2940, 2108, 1667, 1506, 1445, 1381, 1301, 1246, 1208, 828; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{Cl}_3\text{FN}_4\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 417.0059, found 417.0054.



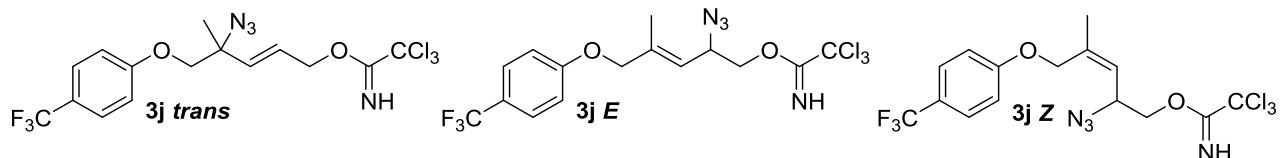
Compound 3g: General procedure 5 was used and the product was isolated in 70% yield as a thick yellow oil. Compound **3g** was isolated as a mixture of three isomers (1:1.8:0.3 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl_3) **3g trans** δ 8.38 (s, 1H), 7.19 – 7.06 (m, 2H), 6.89 – 6.78 (m, 1H), 6.10 (dt, $J = 15.7, 5.1$ Hz, 1H), 6.02 (dt, $J = 15.8, 1.2$ Hz, 1H), 4.88 (dd, $J = 5.1$ Hz, 2H), 3.98 – 3.92 (m, 2H), 1.61 (s, 3H); **3g E** δ 8.42 (s, 1H), 7.19 – 7.06 (m, 2H), 6.89 – 6.78 (m, 1H), 5.68 (dq, $J = 8.9, 1.6$ Hz, 1H), 4.67 (ddd, $J = 9.4, 6.7, 4.9$ Hz, 1H), 4.55 (s, 2H), 4.37 – 4.24 (m, 2H), 1.92 (d, $J = 1.4$ Hz, 3H); **¹³C NMR** (101 MHz, CDCl_3) δ 162.7, 162.5, 155.4, 155.3, 138.9, 134.23, 134.15, 133.0, 127.5, 126.2, 123.2, 122.9, 122.8, 122.3, 120.8, 111.7, 111.62, 111.58, 91.1, 75.3, 73.3, 70.6, 70.2, 68.6, 68.5, 63.3, 57.2, 21.8, 21.3, 14.7; **IR** (NaCl, thin film, cm^{-1}) 3342, 2941, 2110, 1667, 1580, 1452, 1294, 1297, 1065, 798; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{Cl}_5\text{N}_4\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 466.9373, found 466.9377.



Compound 3h: General procedure 5 was used and the product was isolated in 78% yield as a clear oil. Compound **3h** was isolated as a mixture of three isomers (1:1.4:0.3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **3g** *trans* δ 8.38 (s, 1H), 6.16 – 6.06 (m, 3H), 6.10 – 6.01 (m, 1H), 5.98 (dt, *J* = 15.8, 1.2 Hz, 1H), 4.88 (dd, *J* = 5.2, 1.1 Hz, 2H), 3.90 (d, *J* = 9.3 Hz, 1H), 3.87 (d, *J* = 9.3 Hz, 1H), 3.77 (s, 6H), 1.53 (s, 3H); **3g E** δ 8.42 (s, 1H), 6.16 – 6.06 (m, 3H), 5.62 (dq, *J* = 9.0, 1.5 Hz, 1H), 4.67 (ddd, *J* = 9.1, 7.1, 4.7 Hz, 1H), 4.43 (s, 2H), 4.33 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.29 (dd, *J* = 11.2, 7.0 Hz, 1H), 3.77 (s, 6H), 1.89 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 162.7, 162.4, 161.73, 161.69, 161.68, 160.5, 160.4, 139.2, 133.5, 125.8, 120.1, 93.8, 93.72, 93.68, 93.5, 74.1, 72.2, 70.3, 68.5, 63.3, 57.4, 57.3, 55.55, 55.53, 55.50, 21.7, 14.8; **IR** (NaCl, thin film, cm⁻¹) 3339, 2936, 2109, 1666, 1589, 1574, 1475, 1381, 1305, 1285, 1243, 1226, 1067, 1009, 830, 796, 774, 648; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₁₉Cl₃N₄O₄Na⁺ (M+Na)⁺ 459.0364, found 459.0364.

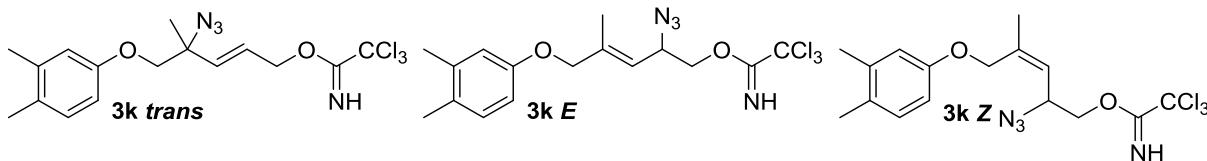


Compound 3i: General procedure 5 was used and the product was isolated in 60% yield as a clear oil. Compound **3i** was isolated as a mixture of three isomers (1:1.2:0.3 *trans:E:Z*). NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl₃) **3i** *trans* δ 8.41 (s, 1H), 6.65 (s, 1H), 6.58 (s, 2H), 6.09 (dt, *J* = 15.8, 5.1 Hz, 1H), 6.01 (dt, *J* = 15.8, 1.3 Hz, 1H), 4.90 (dd, *J* = 5.1, 1.0 Hz, 2H), 3.95 (d, *J* = 9.2 Hz, 1H), 3.92 (d, *J* = 9.2 Hz, 1H), 2.32 (s, 6H), 1.56 (s, 3H); **3i E** δ 8.44 (s, 1H), 6.65 (s, 1H), 6.57 (s, 2H), 5.65 (dq, *J* = 9.2, 1.5 Hz, 1H), 4.69 (ddd, *J* = 9.2, 7.0, 4.7 Hz, 1H), 4.47 (s, 2H), 4.38 – 4.26 (m, 2H), 2.32 (s, 6H), 1.91 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 162.6, 162.5, 162.3, 158.6, 158.5, 139.7, 139.6, 139.40, 139.37, 139.31, 133.7, 125.6, 123.23, 123.16, 123.0, 122.1, 119.7, 112.6, 112.53, 112.50, 91.4, 91.1, 74.0, 71.9, 70.6, 70.3, 68.5, 67.0, 63.3, 57.31, 57.27, 21.9, 21.54, 21.51, 21.4, 14.6; **IR** (NaCl, thin film, cm⁻¹) 3343, 2945, 2107, 1666, 1613, 1593, 1453, 1379, 1318, 1294, 1253, 1154, 1074, 1057, 1037, 824, 797, 652; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₁₉Cl₃N₄O₂Na⁺ (M+Na)⁺ 427.0466, found 427.0480.

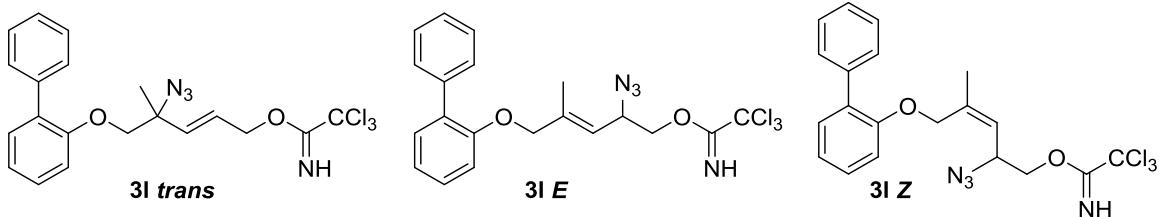


Compound 3j: General procedure 5 was used and the product was isolated in 93% yield as a light-yellow oil. Compound **3j** was isolated as a mixture of two isomers (1:2 *trans:E*). Trace amounts of **3j Z** were observed. NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **3j** *trans* δ 8.39 (s, 1H), 7.60 – 7.52 (m, 2H), 7.03 – 6.94 (m, 2H), 6.09 (dt, *J* = 15.8, 5.3 Hz, 1H), 5.99 (d, *J* = 15.8 Hz, 1H), 4.89 (d, *J* = 5.1 Hz, 2H), 3.98 (d, *J* = 9.3 Hz, 1H), 3.96 (d, *J* = 9.3 Hz, 1H), 1.56 (s, 3H); **3j E** δ 8.43 (s, 1H), 7.60 – 7.52 (m, 2H), 7.03 – 6.94 (m, 2H), 5.63 (dq, *J* = 9.1, 1.8 Hz, 1H), 4.67 (ddd, *J* = 9.3, 6.8, 4.8 Hz, 1H), 4.52 (s, 2H), 4.33 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.30 (dd, *J* = 11.1, 6.9 Hz, 1H), 1.90 (d, *J* = 1.8 Hz, 3H). The carbon resonances corresponding to the trifluoromethyl group in this compound appear as a complex overlay of quartet peaks between 140 and 110 ppm. Due to the complexities of this system, the peaks are listed without attempting to group them into peak patterns; **¹³C NMR** (126

MHz, CDCl₃) δ 162.6, 162.4, 161.0, 160.9, 138.5, 133.1, 127.8, 127.2, 127.14, 127.10, 127.07, 127.04, 126.2, 125.6, 123.9, 123.8, 123.63, 123.55, 123.45, 123.3, 123.0, 120.7, 114.9, 114.8, 91.4, 91.1, 74.2, 72.2, 70.2, 68.4, 63.2, 57.2, 21.2, 14.6; ¹⁹F NMR (471 MHz, CDCl₃) δ -61.49, -61.54; IR (NaCl, thin film, cm⁻¹) 3343, 2925, 2110, 1667, 1615, 1591, 1518, 1459, 1381, 1330, 1255, 1162, 1112, 1070, 1049, 835, 797, 648; HRMS (ESI-TOF) *m/z* calcd for C₁₅H₁₄Cl₃F₃N₄O₂Na⁺ (M+Na)⁺ 467.0027, found 467.0046.



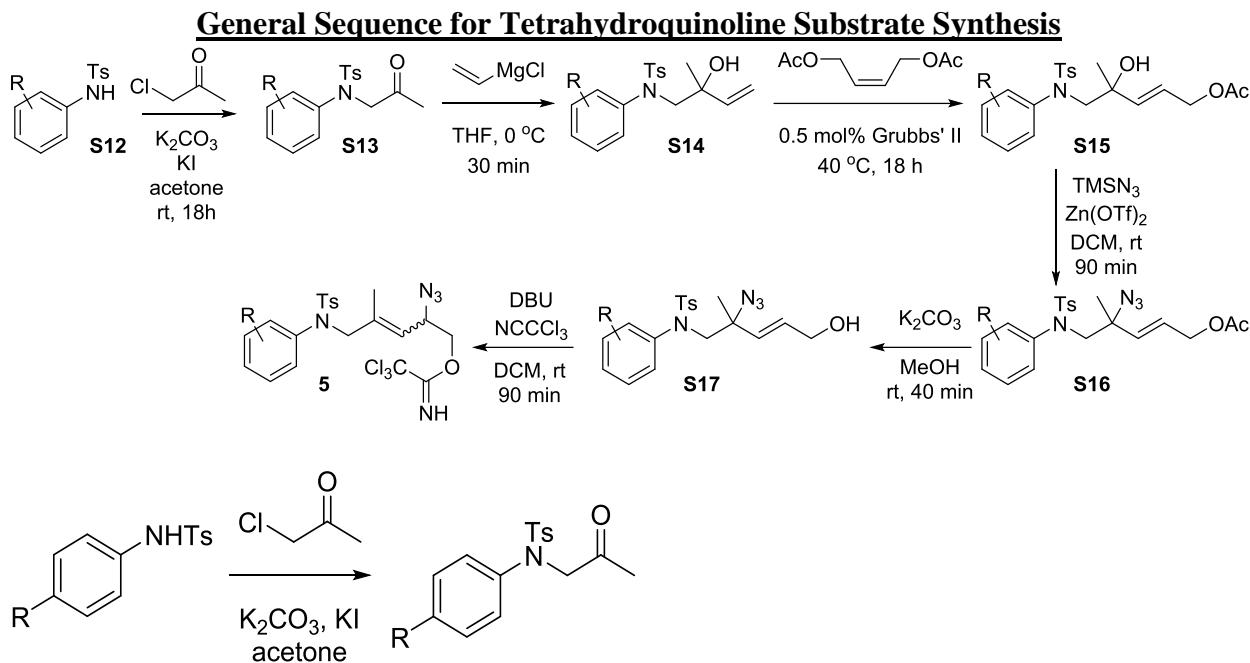
Compound 3k: General procedure 5 was used and the product was isolated in 86% yield as a clear oil. Compound **3k** was isolated as a mixture of three isomers (1:0.8:0.3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: ¹H NMR (500 MHz, CDCl₃) **3k *trans*** 8.44 (s, 1H), 7.09 – 7.02 (m, 1H), 6.78 – 6.74 (m, 1H), 6.72 – 6.65 (m, 1H), 6.08 (dt, *J* = 15.7, 5.2 Hz, 1H), 6.01 (dt, *J* = 15.7, 1.4 Hz, 1H), 4.90 (dd, *J* = 5.2, 1.1 Hz, 2H), 3.94 (d, *J* = 9.3 Hz, 1H), 3.91 (d, *J* = 9.3 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 1.55 (s, 3H); **3k *E*** δ 8.40 (s, 1H), 7.09 – 7.02 (m, 1H), 6.78 – 6.74 (m, 1H), 6.72 – 6.65 (m, 1H), 5.64 (dq, *J* = 9.2, 1.5 Hz, 1H), 4.68 (ddd, *J* = 9.1, 7.1, 4.6 Hz, 1H), 4.46 (s, 2H), 4.34 (dd, *J* = 11.1, 4.7 Hz, 1H), 4.30 (dd, *J* = 11.1, 7.1 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 3H), 1.90 (d, *J* = 1.4 Hz, 3H); **3k *Z*** δ 8.44 (s, 1H), 7.09 – 7.02 (m, 1H), 6.78 – 6.74 (m, 1H), 6.72 – 6.65 (m, 1H), 5.45 (dq, *J* = 9.6, 1.6 Hz, 1H), 4.80 (ddd, *J* = 9.4, 7.4, 4.6 Hz, 1H), 4.58 (s, 2H), 4.37–4.27 (m, 2H), 2.26 (s, 3H), 2.22 (s, 3H), 1.97 (d, *J* = 1.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.53, 162.49, 162.3, 156.67, 156.66, 139.8, 139.6, 137.89, 137.86, 137.79, 133.70, 133.6, 130.5, 130.4, 129.4, 129.3, 129.1, 125.5, 123.1, 122.1, 119.7, 116.5, 116.4, 111.8, 111.7, 111.6, 91.4, 91.1, 74.2, 72.1, 70.6, 70.3, 69.6, 68.5, 67.2, 63.3, 57.3, 21.9, 21.3, 20.1, 20.09, 20.06, 18.89, 18.88, 14.6; IR (NaCl, thin film, cm⁻¹) 3342, 2923, 2857, 2109, 1666, 1608, 1580, 1502, 1454, 1383, 1305, 1252, 1206, 1077, 1009, 828, 797, 647; HRMS (ESI-TOF) *m/z* calcd for C₁₆H₁₉Cl₃N₄O₂Na⁺ (M+Na)⁺ 427.0466, found 427.0463.



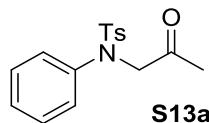
Compound 3l: General procedure 5 was used and the product was isolated in 82% yield as a clear oil. Compound **3l** was isolated as a mixture of three isomers (1:2:0.3 *trans:E:Z*). NMR data given below is based off of idealized integrations of the resulting mixture: ¹H NMR (500 MHz, CDCl₃) **3l *trans*** δ 8.40 (s, 1H), 7.60 – 7.53 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.30 (m, 3H), 7.14 – 7.07 (m, 1H), 7.06 – 6.96 (m, 1H), 5.96 (dt, *J* = 15.7, 5.4 Hz, 1H), 5.86 (dt, *J* = 15.7, 1.5 Hz, 1H), 4.81 (br d, *J* = 5.4 Hz, 2H), 3.90 (s, 2H), 1.41 (s, 3H); **3l *E*** δ 8.43 (s, 1H), 7.60 – 7.53 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.30 (m, 3H), 7.14 – 7.07 (m, 1H), 7.06 – 6.96 (m, 1H), 5.55 (dq, *J* = 9.2, 1.5 Hz, 1H), 4.64 (ddd, *J* = 9.2, 7.1, 4.9 Hz, 1H), 4.48 (s, 2H), 4.29 (dd, *J* = 11.2, 4.9 Hz, 1H), 4.25 (dd, *J* = 11.2, 7.1 Hz, 1H), 1.82 (d, *J* = 1.4 Hz, 3H); **3l *Z*** δ 8.42 (s, 1H), 7.60 – 7.53 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.30 (m, 3H), 7.14 – 7.07 (m, 1H), 7.06 – 6.96 (m, 1H), 5.39 (dq, *J* = 9.4, 1.4 Hz, 1H), 4.62 – 4.59 (m, 1H), 4.58 – 4.56 (m, 2H), 4.18 (d, *J* = 5.8 Hz, 2H), 1.86 (d, *J* = 1.5 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.61, 162.55, 162.4, 155.6, 155.4, 139.7, 139.3, 138.5, 138.3, 133.7, 131.9, 131.7, 131.5, 131.2, 131.11, 131.09, 129.80, 129.73, 129.65, 128.79, 128.74,

128.72, 128.10, 128.06, 128.00, 127.15, 127.13, 127.11, 125.7, 121.98, 121.92, 121.84, 121.6, 119.7, 113.7, 113.2, 113.1, 91.4, 91.1, 74.7, 72.7, 70.5, 70.2, 68.6, 68.0, 63.5, 57.2, 57.0, 21.8, 21.3, 14.6; **IR** (NaCl, thin film, cm^{-1}) 3340, 3061, 2920, 2107, 1666, 1481, 1434, 1301, 1264, 1231, 1074, 1009, 829, 797, 752, 699, 646; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{Cl}_3\text{N}_4\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 475.0466, found 475.0460.

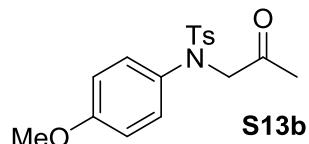
Tetrahydroquinoline Substrate Synthesis and Characterization Data



General Procedure 7: Alkylation of tosyl-protected anilines

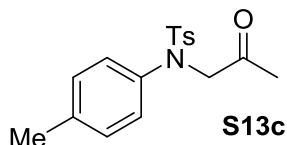


Compound S13a: To a solution of *N*-phenyl-*p*-toluenesulfonamide (1.00 g, 4.0 mmol), K₂CO₃ (1.7 g, 12.0 mmol), and KI (860 mg, 5.2 mmol) in acetone (8 mL) was added chloroacetone (0.40 mL, 4.8 mmol) at room temperature. After 18 h, the solution was diluted with water (20 mL) and extracted with DCM (3 x 15 mL). The combined organic layers were washed with brine, dried (MgSO₄) and concentrated *in vacuo* to afford compound S13a (1.05 g, 3.36 mmol, 84 %) as a brown solid: **¹H NMR** (400 MHz, CDCl₃) δ 7.50 – 7.44 (m, 2H), 7.36 – 7.23 (m, 5H), 7.18 – 7.13 (m, 2H), 4.31 (s, 2H), 2.44 (s, 3H), 2.27 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 204.2, 144.1, 140.1, 134.8, 129.6, 129.4, 128.39, 128.27, 128.0, 60.9, 27.4, 21.8; **IR** (NaCl, thin film, cm⁻¹) 3064, 2921, 2850, 1737, 1596, 1493, 1350, 1162, 1118, 1092, 933, 814, 734, 696, 659; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₁₇NSO₃Na⁺ (M+Na)⁺ 326.0821, found 326.0831.

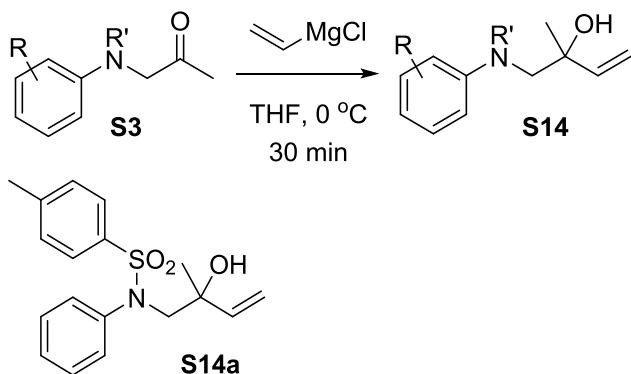


Compound S13b: General procedure 7 was used and the compound was isolated in 89% yield as a brown oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.52 – 7.45 (m, 2H), 7.31 – 7.23 (m, 2H), 7.10 – 7.02 (m, 2H), 6.85 – 6.78 (m, 2H), 4.27 (s, 2H), 3.81 (s, 3H), 2.44 (s, 3H), 2.26 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 204.2, 159.4, 144.0, 135.0, 132.5, 129.9, 129.6, 128.3, 114.5, 61.2, 55.6, 27.3, 21.7; **IR** (NaCl, thin film, cm⁻¹) 3003, 2957, 2923, 2839, 1737, 1604, 1508, 1463, 1443, 1350,

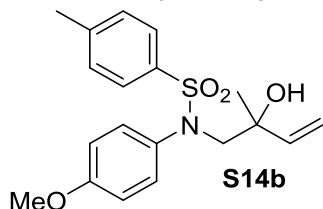
1303, 1251, 1160, 1118, 1091, 1060, 1030, 975, 918, 838, 785, 732, 658; **HRMS** (ESI-TOF) *m/z* calcd for C₁₇H₁₉NO₄SNa⁺ (M+Na)⁺ 356.0927, found 356.0943.



Compound S13c: General procedure 7 was used and the compound was isolated in 95% yield as a tan solid: **¹H NMR** (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 4.26 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 204.3, 144.0, 138.4, 137.4, 134.9, 130.0, 129.6, 128.1, 128.0, 61.0, 27.4, 21.6, 21.2; **IR** (NaCl, thin film, cm⁻¹) 2921, 1738, 1720, 1597, 1509, 1350, 1162, 1119, 1091, 1060, 1019, 923, 816, 784, 709, 665; **HRMS** (ESI-TOF) *m/z* calcd for C₁₇H₁₉NO₃SNa⁺ (M+Na)⁺ 340.0978, found 340.0988.

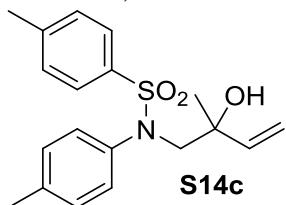


Compound S14a: General procedure 1 was used the product was isolated in 80% yield as a viscous brown oil: **¹H NMR** (500 MHz, CDCl₃) δ 7.45 – 7.41 (m, 2H), 7.33 – 7.22 (m, 5H), 7.08 – 7.03 (m, 2H), 5.77 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.33 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.06 (dd, *J* = 10.7, 1.3 Hz, 1H), 3.67 (d, *J* = 14.5 Hz, 1H), 3.61 (d, *J* = 14.6 Hz, 1H), 2.69 (br s, 1H), 2.43 (s, 3H), 1.27 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 143.9, 142.7, 141.6, 135.0, 129.6, 129.4, 129.2, 128.1, 128.0, 113.9, 73.9, 61.1, 26.2, 21.7; **IR** (NaCl, thin film, cm⁻¹) 3514, 2980, 2926, 1596, 1491, 1453, 1344, 1162, 1090, 1068, 1024, 927, 839, 815, 774, 697, 656; **HRMS** (ESI-TOF) *m/z* calcd for C₁₈H₂₁NO₃SNa⁺ (M+Na)⁺ 354.1134, found 354.1138.

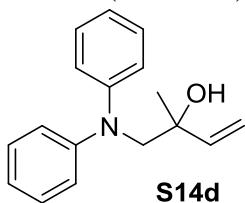


Compound S14b: General procedure 1 was used the product was isolated in 85% yield as a light-yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.49 – 7.41 (m, 2H), 7.29 – 7.21 (m, 2H), 6.98 – 6.91 (m, 2H), 6.84 – 6.76 (m, 2H), 5.78 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.33 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.07 (dd, *J* = 10.7, 1.4 Hz, 1H), 3.81 (s, 3H), 3.62 (d, *J* = 14.5 Hz, 1H), 3.55 (d, *J* = 14.5 Hz, 1H), 2.70 (br s, 1H), 2.43 (s, 3H), 1.27 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 159.1, 143.8, 142.7, 135.0, 134.0, 130.5, 129.6, 128.0, 114.3, 113.8, 73.9, 61.3, 55.6, 26.1, 21.7; **IR** (NaCl, thin film, cm⁻¹) 3508, 2976, 2932, 2838, 1604, 1508, 1457, 1343, 1298, 1250, 1161, 1089, 1073, 1031, 913,

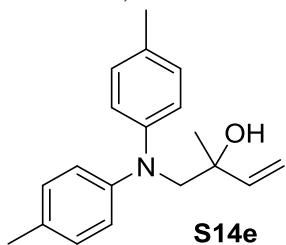
845, 816, 789, 733, 711, 671, 654; **HRMS** (ESI-TOF) m/z calcd for $C_{19}H_{23}NO_4SNa^+$ ($M+Na$)⁺ 384.1240, found 384.1254.



Compound (S14c): General procedure 1 was used the product was isolated in 95% yield as a light yellow oil: **1H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.28 – 7.21 (m, 2H), 7.13 – 7.06 (m, 2H), 6.97 – 6.88 (m, 2H), 5.78 (dd, J = 17.2, 10.7 Hz, 1H), 5.33 (dd, J = 17.2, 1.4 Hz, 1H), 5.07 (dd, J = 10.6, 1.4 Hz, 1H), 3.63 (d, J = 14.5 Hz, 1H), 3.57 (d, J = 14.5 Hz, 1H), 2.70 (br s, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 142.7, 138.8, 138.1, 134.9, 129.8, 129.6, 129.1, 128.0, 113.8, 73.9, 61.1, 26.1, 21.7, 21.2; **IR** (NaCl, thin film, cm^{-1}) 3511, 3029, 2982, 2924, 1598, 1508, 1343, 1162, 1090, 1072, 1019, 920, 846, 815, 709; **HRMS** (ESI-TOF) m/z calcd for $C_{19}H_{23}NO_3SNa^+$ ($M+Na$)⁺ 368.1291, found 368.1291.

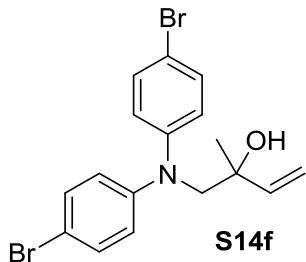


Compound S14d: Using a known procedure:⁶ To a solution of diphenylamine (2.8 mL, 30.3 mmol) in THF (10 mL) cooled in an ice bath was added *n*-butyl lithium (4.7 mL, 2.5 M in hexanes, 11.7 mmol). After 10 min, 2-methyl-2-vinyloxirane (1 mL, 10.1 mmol) was added dropwise as a neat oil. The solution was allowed to warm to room temperature. After 18 h, the solution was quenched by the addition of saturated aqueous NH₄Cl (15 mL). The resulting solution was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. Final purification by column chromatography (0 to 90% gradient, EtOAc in hexanes) afforded compound **S14d** (1.2 g, 6.8 mmol, 67%) as a clear oil: **1H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.11 – 7.04 (m, 4H), 7.04 – 6.98 (m, 2H), 5.92 (dd, J = 17.2, 10.7 Hz, 1H), 5.30 (dd, J = 17.2, 0.9 Hz, 1H), 5.05 (dd, J = 10.9, 0.9 Hz, 1H), 3.94 (s, 2H), 2.10 (br s, 1H), 1.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7, 143.8, 129.5, 122.1, 122.0, 112.9, 75.2, 63.3, 26.4; **IR** (NaCl, thin film, cm^{-1}) 3455, 3061, 2974, 2918, 1588, 1496, 1360, 1247, 1184, 922, 748, 694; **HRMS** (ESI-TOF) m/z calcd for $C_{17}H_{19}NONa^+$ ($M+Na$)⁺ 276.1359, found 276.1350.

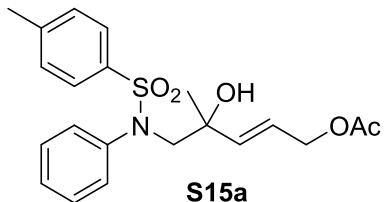
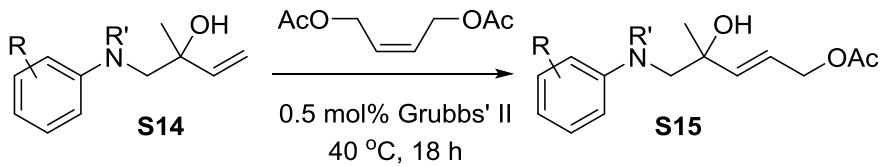


Compound S14e: To a solution of di-*p*-tolylamine (1.3 g, 6.1 mmol) in THF (6.0 mL) cooled in an ice bath was added *n*-butyl lithium (2.3 mL, 2.5 M in hexanes, 5.8 mmol). After 10 min, 2-methyl-2-vinyloxirane (0.50 mL, 5.1 mmol) was added dropwise as a neat oil. After the addition, the solution was allowed to warm to room temperature. After 18 h, the solution was quenched by

the addition of saturated aqueous NH₄Cl (10 mL). The resulting solution was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried (MgSO₄), and concentrated *in vacuo*. Final purification by column chromatography (0 to 80% gradient, EtOAc in hexanes) afforded compound **S14e** (790 mg, 3.3 mmol, 57%) as an orange oil: **¹H NMR** (500 MHz, CDCl₃) δ 7.10 (d, *J* = 8.6 Hz, 4H), 6.96 (d, *J* = 8.6 Hz, 4H), 5.94 (dd, *J* = 17.1, 10.9 Hz, 1H), 5.31 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.05 (dd, *J* = 10.8, 1.4 Hz, 1H), 3.89 (s, 2H), 2.34 (s, 6H), 2.20 (br s, 1H), 1.32 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 147.6, 143.9, 131.3, 130.0, 121.9, 112.8, 75.0, 63.5, 26.3, 20.7 (2C); **IR** (NaCl, thin film, cm⁻¹) 3458, 3087, 3025, 2976, 2921, 2863, 1609, 1570, 1510, 1455, 1411, 1361, 1248, 1184, 1112, 1073, 1018, 996, 921, 850, 811, 733, 707; **HRMS** (ESI-TOF) *m/z* calcd for C₁₉H₂₃NONa⁺ (M+Na)⁺ 304.1672, found 304.1660.

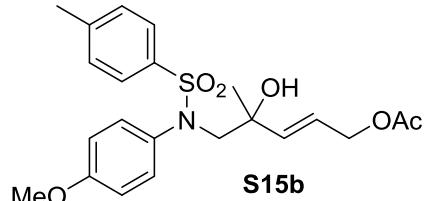


Compound S14f: To a solution of bis-(4-bromophenyl)amine (2.0 g, 6.1 mmol) in THF (6.0 mL) cooled in an ice bath was added *n*-butyl lithium (2.3 mL, 2.5 M in hexanes, 5.8 mmol). After 10 min, 2-methyl-2-vinyloxirane (0.50 mL, 5.1 mmol) was added dropwise as a neat oil. After the addition, the solution was allowed to warm to room temperature. After 18 h, the solution was quenched by the addition of saturated aqueous NH₄Cl (10 mL). The resulting solution was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried (MgSO₄), and concentrated *in vacuo*. Final purification by column chromatography (0 to 40% gradient, EtOAc in hexanes) afforded compound **S14f** (1.56 g, 4.55 mmol, 75%) as a tan oil: **¹H NMR** (500 MHz, CDCl₃) δ 7.38 – 7.33 (m, 4H), 6.94 – 6.90 (m, 4H), 5.86 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.27 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.04 (dd, *J* = 10.7, 1.1 Hz, 1H), 3.82 (s, 2H), 1.84 (br s, 1H), 1.28 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 148.4, 143.4, 132.4, 123.7, 114.9, 113.4, 75.2, 63.0, 26.5; **IR** (NaCl, thin film, cm⁻¹) 3457, 2974, 2928, 1579, 1488, 1454, 1363, 1247, 1184, 1136, 1068, 1009, 924, 814, 757; **HRMS** (ESI-TOF) *m/z* calcd for C₁₇H₁₇Br₂NONa⁺ (M+Na)⁺ 431.9569, found 431.9567.

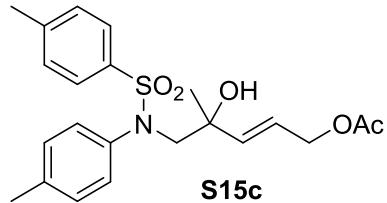


Compound S15a: General procedure 2 was used. Note, 4 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 73% yield as a viscous brown oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.47 – 7.39 (m, 2H), 7.35 – 7.22 (m, 5H), 7.09 – 6.99 (m, 2H), 5.86 (dt, *J* = 15.5, 5.9 Hz, 1H), 5.57 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.46 (dd,

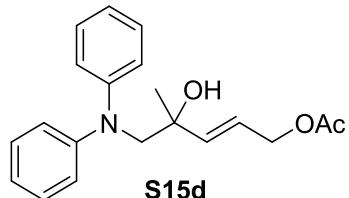
$J = 5.9, 1.4$ Hz, 2H), 3.69 (d, $J = 14.6$ Hz, 1H), 3.58 (d, $J = 14.6$ Hz, 1H), 2.99 (br s, 1H), 2.43 (s, 3H), 2.05 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.8, 144.0, 141.4, 138.5, 134.8, 129.6, 129.4, 129.1, 128.1, 128.0, 123.6, 73.2, 64.3, 61.2, 26.2, 21.7, 21.1; IR (NaCl, thin film, cm^{-1}) 3503, 2979, 2933, 1737, 1596, 1492, 1453, 1379, 1345, 1234, 1163, 1090, 1066, 1026, 971, 841, 815, 771, 729, 698, 657; HRMS (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_5\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 426.1346, found 426.1347.



Compound S15b: General procedure 2 was used. Note, 4 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 58% yield as a dark green oil: ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.36 (m, 2H), 7.23 – 7.18 (m, 2H), 6.92 – 6.85 (m, 2H), 6.78 – 6.72 (m, 2H), 5.81 (dt, $J = 15.5, 5.9$ Hz, 1H), 5.55 (dt, $J = 15.6, 1.5$ Hz, 1H), 4.43 (dd, $J = 5.9, 1.6$ Hz, 2H), 3.75 (s, 3H), 3.61 (d, $J = 14.5$ Hz, 1H), 3.50 (d, $J = 14.5$ Hz, 1H), 3.05 (br s, 1H), 2.38 (s, 3H), 2.00 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.6, 158.9, 143.8, 138.5, 134.7, 133.7, 130.3, 129.5, 127.8, 123.4, 114.1, 72.9, 64.1, 61.2, 55.4, 26.0, 21.5, 20.9; IR (NaCl, thin film, cm^{-1}) 3511, 2977, 2933, 2839, 1736, 1605, 1508, 1457, 1343, 1294, 1251, 1162, 1089, 1070, 1030, 972, 916, 846, 815, 789, 731, 709, 655. HRMS (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{27}\text{NSO}_6\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 456.1451, found 456.1472.

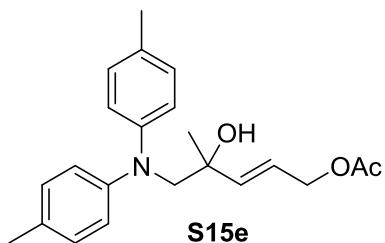


Compound S15c: General procedure 2 was used. Note, 4 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. The product was isolated in 30% yield as a brown oil: ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 8.1$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.85 (d, $J = 8.1$ Hz, 2H), 5.79 (dt, $J = 15.5, 5.9$ Hz, 1H), 5.54 (d, $J = 15.5$ Hz, 1H), 4.40 (d, $J = 5.9$ Hz, 2H), 3.62 (d, $J = 14.6$ Hz, 1H), 3.51 (d, $J = 14.4$ Hz, 1H), 3.13 (br s, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.98 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.5, 143.6, 138.5, 138.4, 137.7, 134.6, 129.4, 129.3, 128.8, 127.7, 123.1, 72.8, 64.0, 60.9, 25.9, 21.4, 20.9, 20.8; IR (NaCl, thin film, cm^{-1}) 3508, 2979, 2927, 1736, 1598, 1508, 1345, 1232, 1163, 1089, 1068, 1020, 973, 850, 816, 709, 655; HRMS (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_5\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 440.1502, found 440.1521.

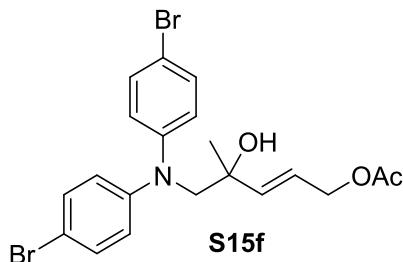


Compound S15d: General procedure 2 was used. Note, 4 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. Compound S15d was isolated after column chromatography as a mixture with (*E*)-but-2-ene-1,4-diyil diacetate. The mixture was

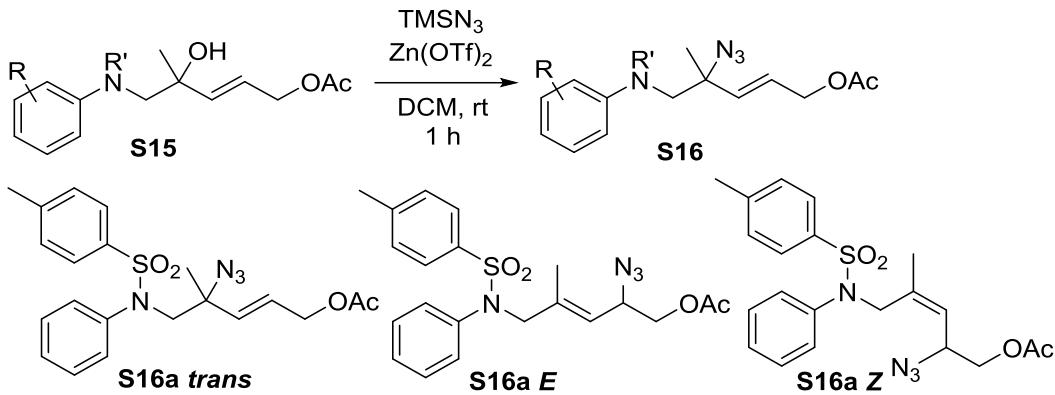
further purified by heating at 80 °C under reduced pressure (<0.5 torr) for 10 minutes. This afforded compound **S15d** (360 mg, 70 %) as a clear oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.31 – 7.23 (m, 4H), 7.08 – 7.02 (m, 4H), 7.01 – 6.95 (m, 2H), 5.79 (dt, *J* = 15.6, 5.3 Hz, 1H), 5.73 (d, *J* = 15.7 Hz, 1H), 4.42 (d, *J* = 5.0 Hz, 2H), 3.95 (d, *J* = 15.2 Hz, 1H), 3.90 (d, *J* = 15.2 Hz, 1H), 2.34 (br s, 1H), 2.10 (s, 3H), 1.32 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.9, 149.6, 140.0, 129.5, 122.6, 122.2, 122.0, 74.5, 64.4, 63.4, 26.4, 21.1; **IR** (NaCl, thin film, cm⁻¹) 3472, 2926, 1736, 1588, 1496, 1361, 1241, 1026, 971, 750, 694; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₃NO₃Na⁺ (M+Na)⁺ 348.1570, found 348.1570.



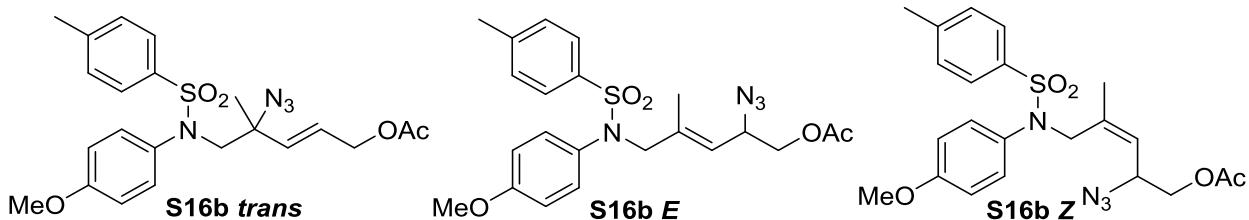
Compound S15e: General procedure 2 was used. Note, 4 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used as the catalyst for this reaction. Compound **S15e** was isolated after column chromatography as a mixture with (*E*)-but-2-ene-1,4-diyil diacetate. The mixture was further purified by heating at 80 °C under reduced pressure (<0.5 torr) for 10 minutes. This afforded compound **S15e** (560 mg, 63 %): **¹H NMR** (500 MHz, CDCl₃) δ 7.08 – 7.04 (m, 4H), 6.91 – 6.88 (m, 4H), 5.77 (dt, *J* = 15.6, 5.1 Hz, 1H), 5.72 (d, *J* = 15.7 Hz, 1H), 4.43 (dd, *J* = 5.0, 1.1 Hz, 2H), 3.86 (d, *J* = 15.1 Hz, 1H), 3.82 (d, *J* = 15.1 Hz, 1H), 2.29 (s, 6H), 2.22 (br s, 1H), 2.04 (s, 3H), 1.29 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.9, 147.5, 140.2, 131.5, 130.0, 122.5, 121.9, 74.5, 64.5, 63.7, 26.3, 21.1, 20.8; **IR** (NaCl, thin film, cm⁻¹) 3468, 3025, 2920, 2863, 1743, 1680, 1610, 1510, 1364, 1231, 1034, 810; **HRMS** (ESI-TOF) *m/z* calcd for C₂₂H₂₇NO₃Na⁺ (M+Na)⁺ 376.1883, found 376.1875.



Compound S15f: General procedure 2 was used. Note, 4 mol % Hoveyda-Grubbs' 2nd Generation Catalyst was used for this reaction. Compound **S15f** was isolated after column chromatography as a mixture with (*E*)-but-2-ene-1,4-diyil acetate. The product was isolated as an inseparable mixture with (*E*)-but-2-ene-1,4-diyil diacetate. The mixture was further purified by heating at 80 °C under reduced pressure (<0.5 torr) for 10 minutes. This afforded **S15f** (840 mg, 74 %) as a brown oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.40 – 7.34 (m, 4H), 6.95 – 6.90 (m, 4H), 5.79 (dt, *J* = 15.7, 5.4 Hz, 1H), 5.72 (dt, *J* = 15.6, 0.9 Hz, 1H), 4.50 – 4.41 (m, 2H), 3.86 (d, *J* = 15.4 Hz, 1H), 3.82 (d, *J* = 15.4 Hz, 1H), 2.06 (s, 3H), 1.93 (br s, 1H), 1.31 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.8, 148.3, 139.4, 132.5, 123.7, 123.2, 115.0, 74.6, 64.2, 63.1, 26.6, 21.1; **IR** (NaCl, thin film, cm⁻¹) 3477, 2927, 1736, 1579, 1488, 1362, 1244, 1180, 1068, 1025, 1009, 968, 817; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₁Br₂NO₃Na⁺ (M+Na)⁺ 503.9780, found 503.9790.

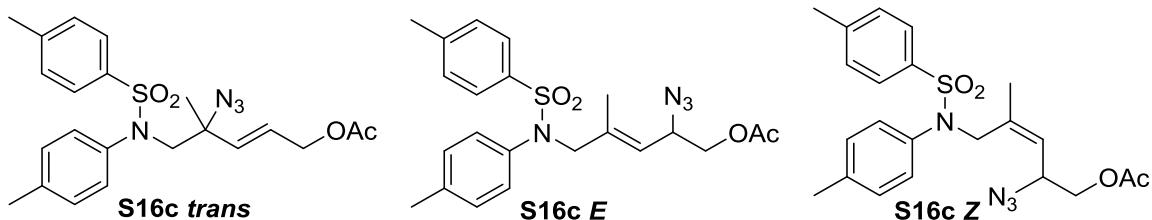


Compound S16a: General procedure 3 was used and the product was isolated in 72% as a brown oil. Compound **S16a** was isolated in a mixture of two isomers (**S16a E** and **S16a Z**) in a 1:0.25 ratio. Trace amounts of **S16a trans** were observed. NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S16a E** δ 7.51 – 7.36 (m, 2H), 7.32 – 7.20 (m, 5H), 7.05 – 6.97 (m, 2H), 5.08 (dq, *J* = 9.1, 1.3 Hz, 1H), 4.28 (ddd, *J* = 9.0, 7.5, 4.6 Hz, 1H), 4.17 (d, *J* = 13.7 Hz, 1H), 4.10 (d, *J* = 14.0 Hz, 1H), 3.81 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.76 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.43 (s, 3H), 2.00 (s, 3H), 1.81 (d, *J* = 1.3 Hz, 3H); **S16a Z** δ 7.51 – 7.36 (m, 2H), 7.32 – 7.20 (m, 5H), 7.05 – 6.97 (m, 2H), 5.16 (dq, *J* = 9.6, 1.3 Hz, 1H), 4.27 – 4.19 (m, 2H), 4.09 – 4.04 (m, 1H), 3.67 (dd, *J* = 11.4, 7.6 Hz, 1H), 3.61 (dd, *J* = 11.4, 4.3 Hz, 1H), 2.44 (s, 3H), 2.03 (s, 3H), 1.91 (d, *J* = 1.4 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.52, 170.46, 143.8, 143.7, 140.5, 138.8, 138.52, 138.44, 138.0, 135.4, 135.1, 133.8, 129.7, 129.6, 129.5, 129.3, 129.1, 128.99, 128.97, 128.91, 128.86, 128.80, 128.6, 128.5, 128.04, 128.00, 127.9, 127.8, 126.3, 123.4, 123.1, 65.7, 65.3, 64.7, 63.8, 58.6, 57.9, 57.5, 57.1, 51.0, 22.0, 21.66, 21.64, 21.57, 21.0, 20.78, 20.75, 15.1; **IR** (NaCl, thin film, cm⁻¹) 3063, 2923, 2107, 1744, 1596, 1492, 1453, 1382, 1349, 1228, 1164, 1092, 1043, 1025, 870, 815, 771, 725, 697, 659; **HRMS** (ESI-TOF) *m/z* calcd for C₂₁H₂₄N₄O₄SnA⁺ (M+Na)⁺ 451.1410, found 451.1428.

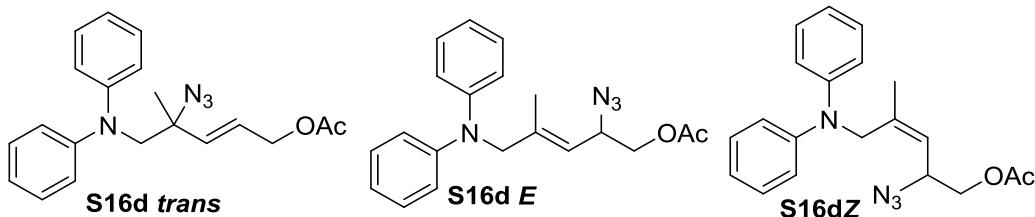


Compound S16b: General procedure 3 was used and the product was isolated in 70% as a brown oil. Compound **S16b** was isolated in a mixture of two isomers (**S16b E** and **S16b Z**) in a 1:0.25 ratio. Trace amounts of **S16b trans** were observed. NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (500 MHz, CDCl₃) **S16b E** δ 7.49 – 7.32 (m, 2H), 7.29 – 7.15 (m, 2H), 6.91 – 6.80 (m, 2H), 6.78 – 6.69 (m, 2H), 5.03 (dq, *J* = 9.0, 1.3 Hz, 1H), 4.26 (ddd, *J* = 9.1, 7.4, 4.7 Hz, 1H), 4.08 (d, *J* = 13.6 Hz, 1H), 4.01 (d, *J* = 13.7 Hz, 1H), 3.79 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.76 – 3.72 (m, 1H), 3.71 (s, 3H), 2.38 (s, 3H), 1.96 (s, 3H), 1.77 (d, *J* = 1.4 Hz, 3H); **S16b Z** δ 7.49 – 7.32 (m, 2H), 7.29 – 7.15 (m, 2H), 6.91 – 6.80 (m, 2H), 6.78 – 6.69 (m, 2H), 5.12 (dq, *J* = 9.6, 1.4 Hz, 1H), 4.18 (d, *J* = 13.9 Hz, 1H), 4.13 (d, *J* = 13.9 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.71 (s, 3H), 3.65 – 3.59 (m, 1H), 3.58 – 3.52 (m, 1H), 2.39 (s, 3H), 1.98 (s, 3H), 1.86 (d, *J* = 1.5 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.41, 170.35, 170.27, 159.3, 159.0, 158.9, 143.6, 143.5, 138.3, 138.0, 135.3, 135.1, 133.7, 132.8, 131.0, 130.8, 130.18, 130.12, 129.93, 129.76, 129.73, 129.54, 129.44, 129.37, 127.7, 127.6, 126.0, 123.2, 123.1, 114.3, 114.1, 114.0, 65.6, 65.2,

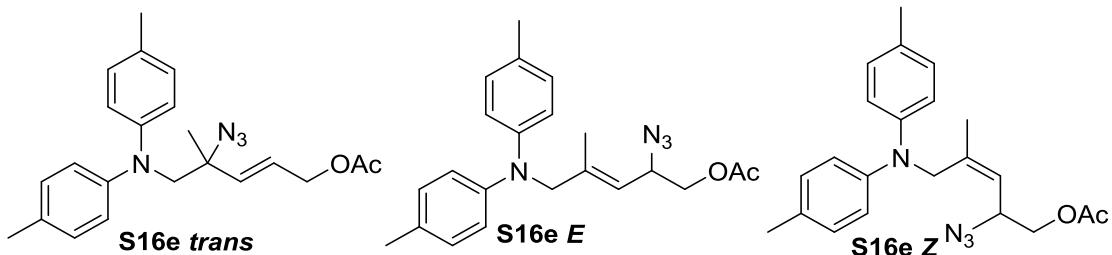
64.5, 63.6, 58.7, 58.1, 57.3, 57.0, 55.33, 55.31, 51.1, 21.8, 21.50, 21.47, 20.8, 20.57, 20.55, 14.9; **IR** (NaCl, thin film, cm^{-1}) 2953, 2819, 2107, 1742, 1606, 1584, 1509, 1443, 1382, 1348, 1302, 1228, 1160, 1092, 1068, 1037, 913, 875, 835, 815, 730, 708, 656; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_5\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 481.1516, found 481.1533.



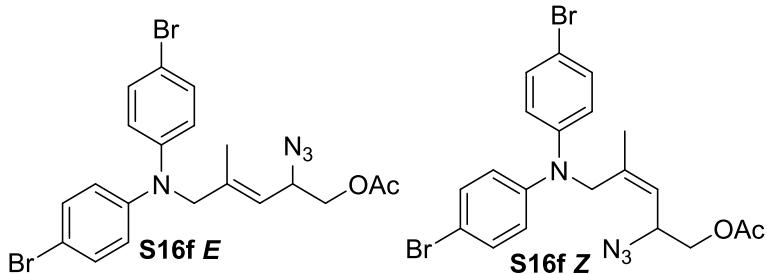
Compound S16c: General procedure 3 was used and the product was isolated in 65% as a brown oil. Compound **S16d** was isolated in a mixture of two isomers (**S16c E**, and **S16c Z**) in a 1:0.2 ratio. Trace amounts of **S16c trans** were observed. NMR data given below is based off idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl_3) **S16c E** δ 7.53 – 7.34 (m, 2H), 7.31 – 7.17 (m, 2H), 7.12 – 7.00 (m, 2H), 6.92 – 6.82 (m, 2H), 5.07 (dq, $J = 9.3, 1.6$ Hz, 1H), 4.28 (ddd, $J = 9.1, 7.5, 4.7$ Hz, 1H), 4.14 (d, $J = 13.9$ Hz, 1H), 4.06 (d, $J = 13.8$ Hz, 1H), 3.81 (dd, $J = 11.4, 4.7$ Hz, 1H), 3.75 (dd, $J = 11.4, 7.4$ Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H), 1.99 (s, 3H), 1.80 (d, $J = 1.3$ Hz, 3H); **S16c Z** δ 7.53 – 7.34 (m, 2H), 7.31 – 7.17 (m, 2H), 7.12 – 7.00 (m, 2H), 6.92 – 6.82 (m, 2H), 5.15 (d, $J = 9.2$ Hz, 1H), 4.33 – 4.24 (m, 1H), 4.22 (d, $J = 13.8$ Hz, 1H), 4.16 (d, $J = 13.9$ Hz, 1H), 3.65 (dd, $J = 11.4, 8.0$ Hz, 1H), 3.55 (dd, $J = 11.4, 4.2$ Hz, 1H), 2.43 (s, 3H), 2.29 (s, 3H), 2.02 (s, 3H), 1.89 (d, $J = 1.3$ Hz, 3H); **¹³C NMR** (101 MHz, CDCl_3) δ 170.44, 170.35, 143.7, 143.6, 138.5, 138.3, 138.0, 137.9, 137.7, 135.9, 135.7, 135.4, 135.1, 133.8, 129.8, 129.68, 129.59, 129.56, 129.53, 129.48, 129.41, 129.32, 128.8, 128.6, 128.3, 127.72, 127.70, 126.1, 123.2, 123.0, 65.7, 65.3, 64.6, 63.7, 58.6, 57.9, 57.4, 57.1, 51.0, 21.9, 21.58, 21.56, 21.12, 21.09, 21.07, 20.9, 20.67, 20.64, 15.00; **IR** (NaCl, thin film, cm^{-1}) 2922, 2106, 1744, 1598, 1508, 1452, 1348, 1228, 1164, 1092, 1042, 875, 816, 708, 691, 654; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 465.1567, found 465.1572.



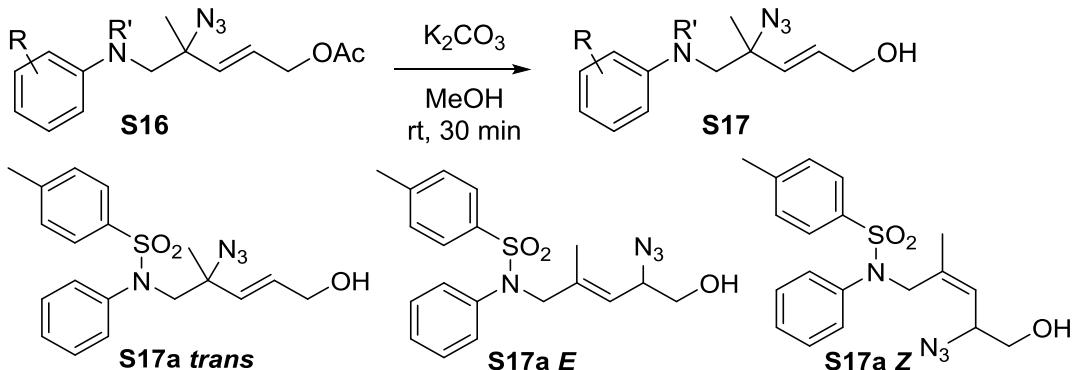
Compound S16d: General procedure 3 was used and the product was isolated in 50% yield as a clear oil. Compound **S16d** was isolated as a mixture of two isomers (**S16d E** and **S16d Z**) in a 1:0.1 ratio. Trace amounts of **S16d trans** were observed. NMR data given below is based off of idealized integrations of the resulting mixture: **¹H NMR** (400 MHz, CDCl_3) **S16d E** δ 7.32 (t, $J = 7.8$ Hz, 4H), 7.08 (d, $J = 8.2$ Hz, 4H), 7.02 (t, $J = 7.4$ Hz, 2H), 5.54 (d, $J = 9.2$ Hz, 1H), 4.55 (ddd, $J = 9.2, 7.5, 4.5$ Hz, 1H), 4.38 (s, 2H), 4.07 (dd, $J = 11.4, 4.6$ Hz, 1H), 4.02 (dd, $J = 11.3, 7.3$ Hz, 1H), 2.08 (s, 3H), 1.86 (s, 3H); **S16d Z** δ 7.37 – 7.27 (m, 4H), 7.13 – 7.05 (m, 4H), 7.05 – 6.98 (m, 2H), 5.34 (d, $J = 9.6$ Hz, 1H), 4.60 – 4.50 (m, 1H), 4.38 (s, 2H), 4.12 – 3.96 (m, 2H), 2.16 (s, 3H), 1.95 (s, 3H); **¹³C NMR** (101 MHz, CDCl_3) δ 170.6, 147.8, 139.8, 129.4, 129.3, 121.9, 121.62, 121.57, 121.0, 120.6, 118.5, 65.6, 59.1, 57.7, 20.7, 15.2; **IR** (NaCl, thin film, cm^{-1}) 3060, 3037, 2917, 2102, 1747, 1590, 1496, 1448, 1362, 1240, 1046, 868, 753, 696; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 373.1635, found 373.1641.



Compound S16e: General procedure 3 was used and the product was isolated in 68% yield as a clear oil. Compound **S16e** was isolated predominantly as isomer **S16e E**. Trace amounts of **S16e trans** and **S16e Z** were observed: **1H NMR** (500 MHz, CDCl₃) δ 7.13 (d, *J* = 8.3 Hz, 4H), 6.96 (d, *J* = 8.4 Hz, 4H), 5.54 (dq, *J* = 9.2, 1.6 Hz, 1H), 4.55 (ddd, *J* = 9.2, 7.5, 4.6 Hz, 1H), 4.33 (s, 2H), 4.08 (dd, *J* = 11.4, 4.6 Hz, 1H), 4.03 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.37 (s, 6H), 2.09 (s, 3H), 1.86 (d, *J* = 1.5 Hz, 3H); **13C NMR** (126 MHz, CDCl₃) δ 170.5, 145.7, 140.1, 130.7, 129.8, 120.5, 118.5, 65.7, 59.3, 57.7, 20.62, 20.60 (2C), 15.2; **IR** (NaCl, thin film, cm⁻¹) 3027, 2920, 2861, 2106, 1746, 1608, 1515, 1445, 1362, 1319, 1226, 1042, 876, 809, 728; **HRMS** (ESI-TOF) *m/z* calcd for C₂₂H₂₆N₄O₂Na⁺ (M+Na)⁺ 401.1948, found 401.1948.

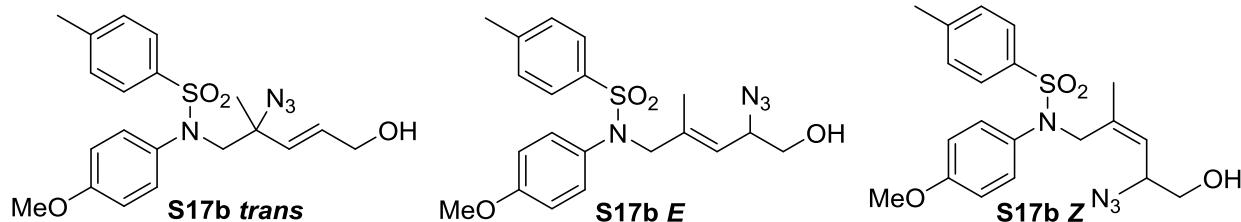


Compound S16f: General procedure 3 was used and the product was isolated in 68% yield as a clear oil. Compound **S16f** was isolated predominantly as isomer **S16f E**. Trace amounts of **S16e Z** were observed: **1H NMR** (500 MHz, CDCl₃) δ 7.32 (d, *J* = 8.9 Hz, 4H), 6.86 (d, *J* = 9.0 Hz, 4H), 5.37 (dq, *J* = 9.2, 1.6 Hz, 1H), 4.46 (ddd, *J* = 9.2, 7.2, 4.7 Hz, 1H), 4.25 (s, 2H), 4.00 (dd, *J* = 11.3, 4.7 Hz, 1H), 3.94 (dd, *J* = 11.4, 7.2 Hz, 1H), 2.00 (s, 3H), 1.77 (d, *J* = 1.5 Hz, 3H); **13C NMR** (126 MHz, CDCl₃) δ 170.8, 146.5, 139.2, 132.5, 122.4, 119.2, 114.6, 65.7, 59.2, 57.7, 20.9, 15.4; **IR** (NaCl, thin film, cm⁻¹) 2918, 2105, 1744, 1580, 1489, 1363, 1226, 1072, 1044, 1009, 814; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₀Br₂N₄O₂Na⁺ (M+Na)⁺ 528.9845, found 528.9859.

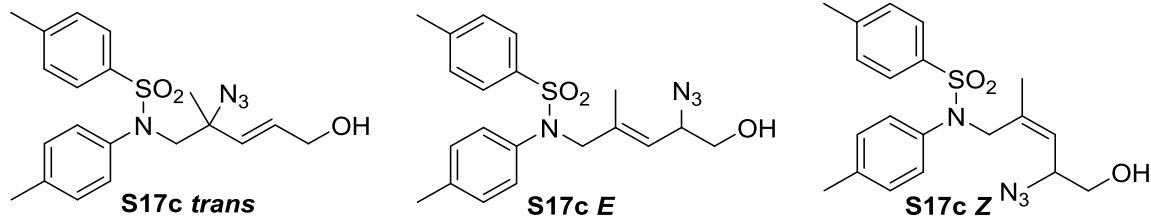


Compound S17a: General procedure 4 was used and the product was isolated in 96% yield as a thick, clear oil. Compound **S17a** was isolated as a mixture of two isomers (**S17a E** and **S17a Z**) in a 1:0.25 ratio. Trace amounts of **S17a trans** were observed. NMR data given below is based

off idealized integrations of the resulting mixture: **1H NMR** (500 MHz, CDCl₃) **S17a E** δ 7.56 – 7.42 (m, 2H), 7.40 – 7.20 (m, 5H), 7.08 – 6.94 (m, 2H), 5.11 (dq, *J* = 9.4, 1.3 Hz, 1H), 4.25 – 4.14 (m, 2H), 4.08 (d, *J* = 13.9 Hz, 1H), 3.34 – 3.24 (m, 2H), 2.44 (s, 3H), 1.82 (br s, 1H), 1.81 (d, *J* = 1.4 Hz, 3H); **S17a Z** δ 7.56 – 7.42 (m, 2H), 7.40 – 7.20 (m, 5H), 7.08 – 6.94 (m, 2H), 5.18 (dq, *J* = 9.8, 1.4 Hz, 1H), 4.25 – 4.14 (m, 2H), 3.97 (ddd, *J* = 9.8, 7.4, 4.4 Hz, 1H), 3.20 (dd, *J* = 11.4, 7.4 Hz, 1H), 3.06 (dd, *J* = 11.4, 4.4 Hz, 1H), 2.45 (s, 3H), 1.90 (d, *J* = 1.5 Hz, 3H), 1.82 (br s, 1H); **13C NMR** (126 MHz, CDCl₃) δ 143.9, 143.80, 138.79, 138.6, 138.1, 137.8, 135.0, 129.7, 129.6, 129.3, 129.02, 128.98, 128.91, 128.7, 128.5, 128.1, 127.81, 127.79, 124.2, 123.9, 64.9, 64.6, 60.9, 60.8, 58.2, 51.1, 22.0, 21.7, 15.2; **IR** (NaCl, thin film, cm⁻¹) 3525, 2923, 2872, 2103, 1596, 1491, 1453, 1345, 1306, 1290, 1248, 1163, 1092, 1072, 1043, 1019, 914, 871, 815, 770, 728, 697, 659; **HRMS** (ESI-TOF) *m/z* calcd for C₁₉H₂₂N₄O₃SnNa⁺ (M+Na)⁺ 409.1305, found 409.1323.

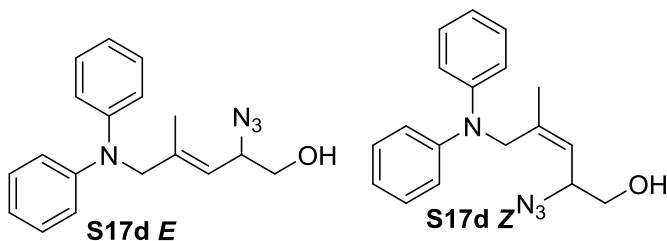


Compound S17b: General procedure 4 was used and the product was isolated in 87% yield as a thick, brown oil. Compound **S17b** was isolated as a mixture of two isomers (**S17b E** and **S17b Z**) in a 1:0.25 ratio. Trace amounts of **S17b trans** were observed. NMR data given below is based off idealized integrations of the resulting mixture: **1H NMR** (500 MHz, CDCl₃) **S17b E** δ 7.49 – 7.32 (m, 2H), 7.27 – 7.18 (m, 2H), 6.91 – 6.80 (m, 2H), 6.79 – 6.69 (m, 2H), 5.07 (dq, *J* = 9.3, 1.3 Hz, 1H), 4.18 – 4.10 (m, 1H), 4.06 (d, *J* = 13.8 Hz, 1H), 4.02 (d, *J* = 13.7 Hz, 1H), 3.72 (s, 3H), 3.27 (d, *J* = 6.0 Hz, 2H), 2.39 (s, 3H), 2.30 (br s, 1H), 1.76 (d, *J* = 1.5 Hz, 3H); **S17b Z** δ 7.49 – 7.32 (m, 2H), 7.27 – 7.18 (m, 2H), 6.91 – 6.80 (m, 2H), 6.79 – 6.69 (m, 2H), 5.15 (dq, *J* = 9.8, 1.3 Hz, 1H), 4.18 – 4.10 (m, 2H), 3.92 (ddd, *J* = 9.9, 7.4, 4.4 Hz, 1H), 3.72 (s, 3H), 3.18 (dd, *J* = 11.4, 7.4 Hz, 1H), 3.09 (dd, *J* = 11.3, 4.4 Hz, 1H), 2.39 (s, 3H), 2.30 (br s, 1H), 1.84 (d, *J* = 1.4 Hz, 3H); **13C NMR** (126 MHz, CDCl₃) δ 159.3, 159.0, 143.7, 143.6, 137.7, 137.6, 135.1, 134.9, 131.0, 130.9, 129.9, 129.8, 129.6, 129.5, 129.4, 127.66, 127.64, 124.0, 114.3, 114.1, 114.0, 64.7, 64.4, 60.9, 60.7, 58.4, 55.41, 55.37, 51.1, 21.9, 21.52, 21.50, 15.0; **IR** (NaCl, thin film, cm⁻¹) 3521, 2923, 2872, 2839, 2102, 1606, 1584, 1506, 1455, 1341, 1303, 1251, 1160, 1091, 1031, 911, 880, 840, 814, 731, 708, 654; **HRMS** (ESI-TOF) *m/z* calcd for C₂₀H₂₄N₄O₄SnNa⁺ (M+Na)⁺ 439.1410, found 439.1431.

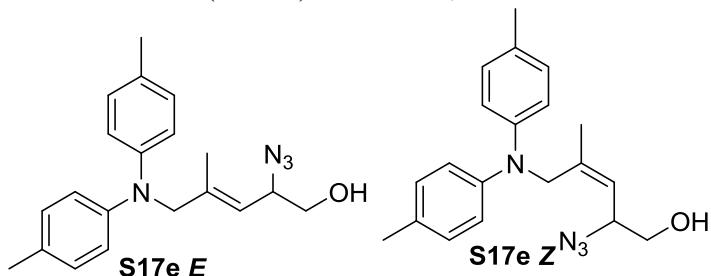


Compound S17c: General procedure 4 was used and the product was isolated in 86% yield as a thick, brown oil. Compound **S17c** was isolated as a mixture of two isomers (**S17c E** and **S17c Z**) in a 1:0.3 ratio. Trace amounts of **S17c trans** were observed. NMR data given below is based off idealized integrations of the resulting mixture: **1H NMR** (500 MHz, CDCl₃) **S17c E** δ 7.54 – 7.44 (m, 2H), 7.31 – 7.23 (m, 2H), 7.12 – 7.04 (m, 2H), 6.92 – 6.82 (m, 2H), 5.10 (dq, *J* = 9.0, 1.4 Hz, 1H), 4.21 – 4.12 (m, 2H), 4.05 (d, *J* = 13.4 Hz, 1H), 3.33 – 3.26 (m, 2H), 2.43 (s, 3H), 2.30 (s, 3H), 2.02 (br s, 1H), 1.79 (d, *J* = 1.4 Hz, 3H); **S17c Z** δ 7.54 – 7.44 (m, 2H), 7.31 – 7.23 (m, 2H),

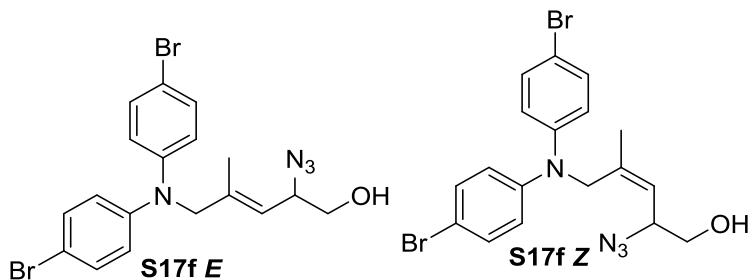
7.12 – 7.04 (m, 2H), 6.92 – 6.82 (m, 2H), 5.17 (dq, $J = 9.7, 1.7$ Hz, 1H), 4.21 – 4.12 (m, 2H), 3.96 (ddd, $J = 9.7, 7.4, 4.5$ Hz, 1H), 3.21 (dd, $J = 11.4, 7.4$ Hz, 1H), 3.10 (dd, $J = 11.4, 4.5$ Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H), 2.02 (br s, 1H), 1.88 (d, $J = 1.5$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.7, 138.04, 137.96, 137.8, 136.0, 135.9, 135.1, 129.8, 129.64, 129.60, 129.56, 129.53, 128.6, 128.5, 127.78, 127.75, 124.1, 123.9, 64.9, 64.5, 60.9, 60.8, 58.3, 51.1, 22.0, 21.6, 21.14, 21.11, 15.13; IR (NaCl, thin film, cm^{-1}) 3525, 2992, 2871, 2103, 1598, 1509, 1451, 1345, 1163, 1092, 1041, 1018, 877, 816, 707, 690, 655; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_3\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 423.1461, found 423.1479.



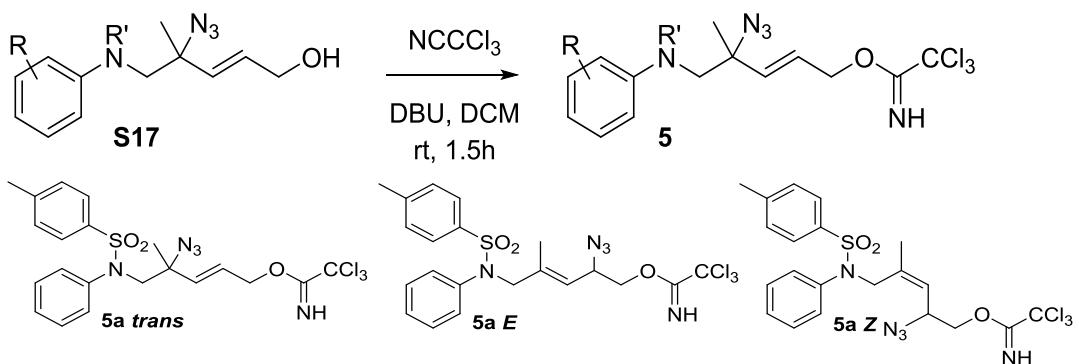
Compound S17d: General procedure 4 was used and the product was isolated in 94% yield as a clear oil. Compound **S17d** was isolated in a mixture of two isomers (**S17d E** and **S17d Z**) in a 1:0.2 ratio. NMR data given below is based off idealized integrations of the resulting mixture: ^1H NMR (500 MHz, CDCl_3) **S17d E** δ 7.31 – 7.22 (m, 4H), 7.07 – 6.93 (m, 6H), 5.46 (dq, $J = 9.4, 1.6$ Hz, 1H), 4.43 – 4.38 (m, 1H), 4.36 (d, $J = 17.8$ Hz, 1H), 4.32 (d, $J = 17.8$ Hz, 1H), 3.46 (dd, $J = 10.6, 6.3$ Hz, 1H), 3.43 (dd, $J = 10.6, 4.5$ Hz, 1H), 1.81 (d, $J = 1.3$ Hz, 3H), 1.59 (br s, 1H); **S17d Z** δ 7.31 – 7.22 (m, 4H), 7.07 – 6.93 (m, 6H), 5.30 (dq, $J = 9.7, 1.6$ Hz, 1H), 4.51 – 4.42 (m, 2H), 4.43 – 4.38 (m, 3H), 3.42 – 3.39 (m, 1H), 3.36 (dd, $J = 11.3, 4.6$ Hz, 1H), 1.90 (d, $J = 1.4$ Hz, 3H), 1.59 (br s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 139.8, 129.43, 129.35, 121.9, 121.6, 121.1, 120.7, 119.2, 64.9, 61.3, 60.8, 59.2, 22.2, 15.4; IR (NaCl, thin film, cm^{-1}) 3394, 3059, 3036, 2920, 2870, 2104, 1589, 1496, 1363, 1230, 1072, 1032, 871, 750, 693; HRMS (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{N}_4\text{ONa}^+$ ($\text{M}+\text{Na}$) $^+$ 331.1529, found 331.1533.



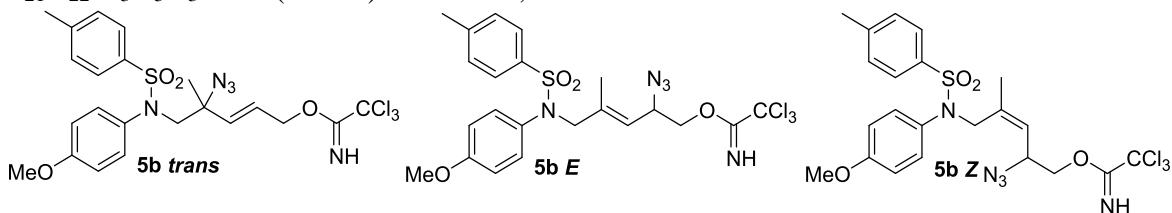
Compound S17e: General procedure 4 was used and the product was isolated in 97% as a yellow oil: Compound **S17e** was isolated predominantly as isomer **S17e E**. Trace amounts of **S17e Z** were observed: ^1H NMR (500 MHz, CDCl_3) δ 7.17 – 7.08 (m, 4H), 7.01 – 6.94 (m, 4H), 5.53 (dq, $J = 9.4, 1.6$ Hz, 1H), 4.45 (ddd, $J = 9.5, 6.9, 5.4$ Hz, 1H), 4.37 (d, $J = 17.6$ Hz, 1H), 4.33 (d, $J = 17.7$ Hz, 1H), 3.54 – 3.48 (m, 2H), 2.37 (s, 6H), 2.20 (br s, 1H), 1.87 (d, $J = 1.4$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 145.8, 140.2, 130.7, 129.8, 120.6, 119.1, 64.9, 61.3, 59.5, 20.66, 20.65 15.3; IR (NaCl, thin film, cm^{-1}) 3404, 3026, 2920, 2862, 2103, 1608, 1511, 1444, 1361, 1232, 1071, 1039, 809, 728; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{N}_4\text{ONa}^+$ ($\text{M}+\text{Na}$) $^+$ 359.1842, found 359.1856.



Compound S17f: General procedure 4 was used and the product was isolated in quantitative yield as a yellow oil: Compound **S17f** was isolated predominantly as isomer **S17f E**. Trace amounts of **S17f Z** were observed: **1H NMR** (400 MHz, CDCl₃) δ 7.40 – 7.34 (m, 4H), 6.93 – 6.87 (m, 4H), 5.43 (dq, *J* = 9.3, 1.5 Hz, 1H), 4.41 (ddd, *J* = 9.4, 6.9, 5.0 Hz, 1H), 4.29 (s, 2H), 3.52 – 3.44 (m, 2H), 2.14 (br s, 1H), 1.80 (d, *J* = 1.4 Hz, 3H); **13C NMR** (101 MHz, CDCl₃) δ 146.4, 139.0, 132.4, 122.3, 119.5, 114.5, 64.8, 61.2, 59.2, 15.4; **IR** (NaCl, thin film, cm⁻¹) 3381, 2917, 2105, 1580, 1488, 1361, 1309, 1231, 1187, 1074, 1008, 814; **HRMS** (ESI-TOF) *m/z* calcd for C₁₈H₁₈Br₂N₄ONa⁺ (M+Na)⁺ 486.9740, found 486.9733.

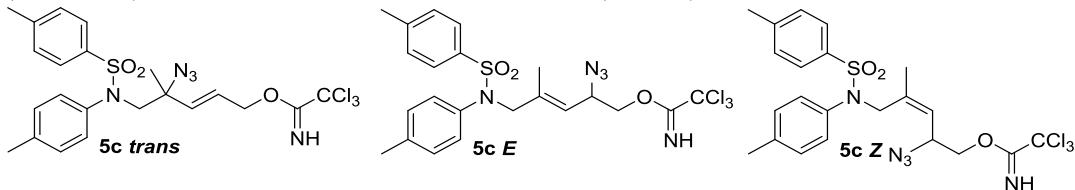


Compound 5a: General procedure 5 was used and the product was isolated in 85% yield as a clear oil. Compound **5a** was isolated predominantly as isomer **5a E**. Trace amounts of **5a trans** and **5a Z** were observed: **1H NMR** (500 MHz, CDCl₃) δ 8.36 (s, 1H), 7.55 – 7.37 (m, 2H), 7.34 – 7.20 (m, 5H), 7.08 – 6.98 (m, 2H), 5.18 (dq, *J* = 9.1, 1.4 Hz, 1H), 4.44 (ddd, *J* = 9.0, 7.0, 4.5 Hz, 1H), 4.18 (d, *J* = 14.1 Hz, 1H), 4.14 (d, *J* = 14.1 Hz, 1H), 4.06 (dd, *J* = 11.2, 4.6 Hz, 1H), 4.02 (dd, *J* = 11.2, 7.0 Hz, 1H), 2.45 (s, 3H), 1.85 (d, *J* = 1.4 Hz, 3H); **13C NMR** (126 MHz, CDCl₃) δ 162.5, 143.8, 138.6, 138.3, 135.3, 129.6, 129.1, 128.7, 128.1, 127.9, 123.1, 91.1, 70.0, 58.0, 57.3, 21.7, 15.2; **IR** (NaCl, thin film, cm⁻¹) 3340, 3063, 2922, 2106, 1668, 1596, 1492, 1453, 1348, 1305, 1164, 1092, 1020, 912, 871, 816, 798, 770, 728, 696, 658; **HRMS** (ESI-TOF) *m/z* calcd for C₂₁H₂₂Cl₃N₅O₃Sn⁺ (M+Na)⁺ 552.0410, found 552.0414.

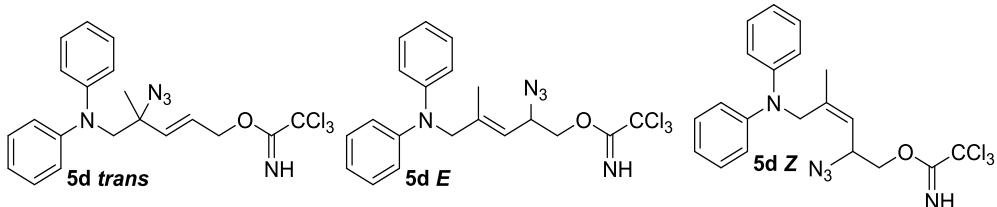


Compound 5b: General procedure 5 was used and the product was isolated in 83% yield as a thick yellow oil. Compound **5b** was isolated predominantly as isomer **5b E**. Trace amounts of **5b trans** and **5b Z** were observed: **1H NMR** (500 MHz, CDCl₃) δ 8.36 (s, 1H), 7.53 – 7.37 (m, 2H), 7.30 –

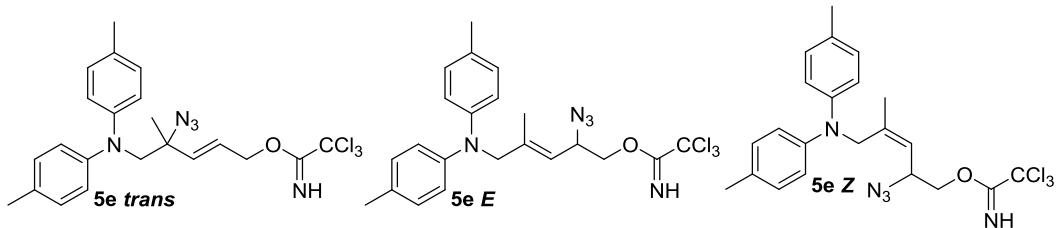
7.20 (m, 2H), 6.95 – 6.85 (m, 2H), 6.82 – 6.72 (m, 2H), 5.16 (dq, $J = 9.1, 1.3$ Hz, 1H), 4.44 (ddd, $J = 9.0, 6.9, 4.5$ Hz, 1H), 4.14 – 4.08 (m, 2H), 4.06 (dd, $J = 11.2, 4.6$ Hz, 1H), 4.02 (dd, $J = 11.2, 7.0$ Hz, 1H), 3.76 (s, 3H), 2.42 (s, 3H), 1.84 (d, $J = 1.6$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.3, 159.1, 143.6, 138.3, 135.2, 131.0, 129.8, 129.5, 127.8, 123.0, 114.2, 91.0, 70.0, 58.2, 57.2, 55.4, 21.6, 15.1; IR (NaCl, thin film, cm^{-1}) 3340, 2953, 2838, 2107, 1667, 1606, 1584, 1508, 1455, 1381, 1344, 1303, 1251, 1163, 1091, 1033, 1009, 910, 874, 832, 798, 732, 708, 691, 647; HRMS (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{24}\text{Cl}_3\text{N}_5\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 582.0507, found 582.0528.



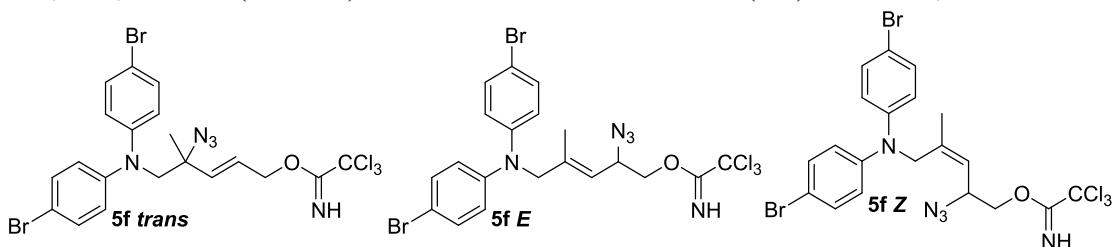
Compound 5c: General procedure 5 was used and the product was isolated in 85% yield as a thick yellow oil. Compound **5c** was isolated as a mixture of two isomers (**5c E** and **5c Z**) in a 1:0.2 ratio. Trace amounts of **5c trans** were observed. NMR data given below is based off idealized integrations of the resulting mixture: ^1H NMR (500 MHz, CDCl_3) **5c E** δ 8.36 (s, 1H), 7.56 – 7.38 (m, 2H), 7.32 – 7.20 (m, 2H), 7.13 – 7.02 (m, 2H), 6.94 – 6.83 (m, 2H), 5.17 (dq, $J = 9.1, 1.3$ Hz, 1H), 4.44 (ddd, $J = 9.0, 7.0, 4.5$ Hz, 1H), 4.15 (d, $J = 13.7$ Hz, 1H), 4.09 (d, $J = 14.1$ Hz, 1H), 4.08 – 4.04 (m, 1H), 4.02 (dd, $J = 11.2, 6.9$ Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H), 1.84 (d, $J = 1.3$ Hz, 3H); **5c Z** δ 8.36 (s, 1H), 7.56 – 7.38 (m, 2H), 7.32 – 7.20 (m, 2H), 7.13 – 7.02 (m, 2H), 6.94 – 6.83 (m, 2H), 5.21 (d, $J = 9.4$ Hz, 1H), 4.27 (d, $J = 13.9$ Hz, 1H), 4.21 – 4.15 (m, 2H), 3.88 (dd, $J = 11.1, 7.6$ Hz, 1H), 3.65 – 3.60 (m, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 1.93 (d, $J = 1.4$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.4, 162.3, 143.7, 143.6, 138.6, 138.3, 138.0, 136.0, 135.9, 135.6, 135.4, 134.2, 130.0, 129.70, 129.64, 129.55, 129.48, 128.9, 128.7, 128.4, 127.9, 127.8, 125.4, 123.1, 123.0, 91.0, 70.4, 70.0, 68.4, 64.8, 58.1, 57.2, 57.1, 51.3, 22.0, 21.68, 21.66, 21.22, 21.20, 21.18, 15.2; IR (NaCl, thin film, cm^{-1}) 3341, 2922, 2107, 1667, 1598, 1508, 1451, 1348, 1305, 1164, 1092, 1043, 873, 815, 798, 707, 689, 651; HRMS (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{24}\text{Cl}_3\text{N}_5\text{O}_3\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 566.0558, found 566.0572.



Compound 5d: General procedure 5 was used and the product was isolated in 81% yield as a clear oil. Compound **5d** was isolated predominantly as isomer **5d E**. Trace amounts of **5d trans** and **5d Z** were observed: ^1H NMR (500 MHz, CDCl_3) δ 8.41 (s, 1H), 7.37 – 7.26 (m, 4H), 7.12 – 6.97 (m, 6H), 5.66 (dq, $J = 9.1, 1.7$ Hz, 1H), 4.66 (dt, $J = 9.3, 5.7$ Hz, 1H), 4.38 (s, 2H), 4.31 – 4.23 (m, 2H), 1.88 (d, $J = 1.5$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.6, 147.9, 140.0, 129.4, 121.6, 120.6, 118.4, 91.1, 70.3, 59.2, 57.3, 15.4; IR (NaCl, thin film, cm^{-1}) 3339, 3036, 2916, 2849, 2105, 1667, 1589, 1496, 1362, 1303, 1251, 1231, 1080, 1018, 793, 749, 699, 643; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{20}\text{Cl}_3\text{N}_5\text{ONa}^+$ ($\text{M}+\text{Na}$)⁺ 474.0626, found 474.0631.

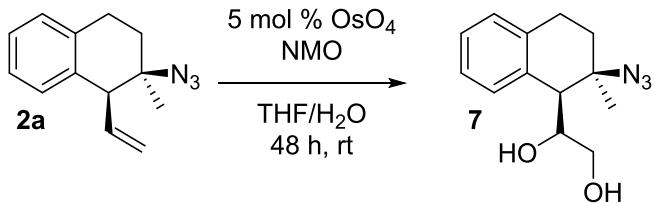


Compound 5e: General procedure 5 was used and the product was isolated in 82% yield as a clear oil. Compound **5e** was isolated predominantly as isomer **5e E**. Trace amounts of **5e trans** and **5e Z** were observed: **1H NMR** (400 MHz, CDCl₃) δ 8.42 (s, 1H), 7.17 – 7.09 (m, 4H), 7.01 – 6.92 (m, 4H), 5.65 (dq, *J* = 9.2, 1.6 Hz, 1H), 4.68 (dt, *J* = 9.2, 5.7 Hz, 1H), 4.34 (s, 2H), 4.32 – 4.26 (m, 2H), 2.36 (s, 6H), 1.88 (d, *J* = 1.4 Hz, 3H); **13C NMR** (101 MHz, CDCl₃) δ 162.5, 145.7, 140.3, 130.7, 129.9, 120.5, 118.2, 91.1, 70.3, 59.4, 57.3, 20.7, 15.3; **IR** (NaCl, thin film, cm⁻¹) 3341, 3027, 2920, 2861, 2105, 1667, 1608, 1510, 1447, 1361, 1308, 1251, 1085, 1012, 876, 797, 727, 648; **HRMS** (EI-TOF) *m/z* calcd for C₂₂H₂₄Cl₃N₅O⁺ (M⁺) 479.1041, found 479.1031.

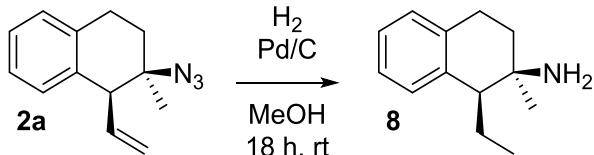


Compound 5f: General procedure 5 was used and the product was isolated in 82% yield as a clear oil. Compound **5f** was isolated predominantly as isomer **5f E**. Trace amounts of **5f trans** and **5f Z** were observed: **1H NMR** (500 MHz, CDCl₃) δ 8.39 (s, 1H), 7.39 – 7.33 (m, 4H), 6.92 – 6.87 (m, 4H), 5.54 (dq, *J* = 9.2, 1.6 Hz, 1H), 4.61 (dt, *J* = 9.2, 5.6 Hz, 1H), 4.29 (s, 2H), 4.27 – 4.24 (m, 2H), 1.83 (d, *J* = 1.3 Hz, 3H); **13C NMR** (126 MHz, CDCl₃) δ 162.4, 146.4, 139.2, 132.4, 122.2, 118.8, 114.5, 91.0, 70.1, 59.0, 57.1, 15.4; **IR** (NaCl, thin film, cm⁻¹) 3339, 3036, 2917, 2105, 1667, 1580, 1489, 1444, 1362, 1309, 1251, 1074, 1009, 815, 795, 734, 647; **HRMS** (ESI-TOF) *m/z* calcd for C₁₇H₁₆Br₂N⁺ (M-N₃-CH₂OCNCl₃)⁺ 391.9644, found 391.9640. (EI-TOF) *m/z* calcd for C₁₂H₉Br₂N (M-C₇H₉OCl₃N₄)⁺ 324.9096, found 324.9090.

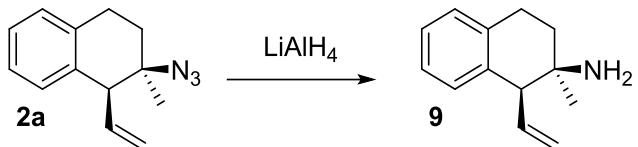
Elaboration of Cyclized Product



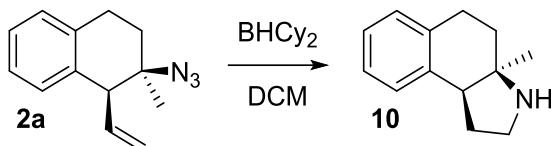
Diol 7: To a solution of azide **2a** (24.1 mg, 0.11 mmol) in THF (0.3 mL) at room temperature was added NMO (50 μ L, 50% in H₂O, 0.21 mmol) and OsO₄ (200 μ L, 11 mM in H₂O, 2.2 μ mol). After 24 h, additional NMO (100 μ L, 50% in H₂O, 0.42 mmol) and OsO₄ (200 μ L, 11 mM in H₂O, 2.2 μ mol) were added. After an additional 24 h, the reaction was diluted with EtOAc, basified with 3M NaOH, and extracted with EtOAc. The combined organic phases were washed with water, brine, dried (MgSO_4), filtered, and concentrated under reduced pressure. This afforded diol **7** (24.3 mg, 0.096 mmol, 87%) as a faint yellow oil. Crude ¹H NMR analysis showed trace amounts (>25:1) of a minor diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 7.21 (dd, J = 7.5, 1.5 Hz, 1H), 7.18 (td, J = 7.3, 1.6 Hz, 1H), 7.13 (td, J = 7.5, 1.5 Hz, 1H), 7.09 (dd, J = 7.5, 1.4 Hz, 1H), 4.22 (br s, 1H), 3.91 (ddd, J = 7.9, 6.2, 3.2 Hz, 1H), 3.39 (dd, J = 11.4, 6.2 Hz, 1H), 3.26 (dd, J = 11.4, 3.3 Hz, 1H), 3.05 (ddd, J = 17.7, 8.2, 2.0 Hz, 1H), 2.89 (dd, J = 7.9, 1.8 Hz, 1H), 2.83 (ddd, J = 18.0, 10.5, 8.0 Hz, 1H), 2.34 (ddd, J = 13.5, 10.4, 8.2 Hz, 1H), 2.26 (br s, 1H), 1.98 (ddt, J = 13.5, 8.2, 2.0 Hz, 1H), 1.34 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 134.1, 134.0, 131.2, 128.9, 127.5, 126.0, 73.8, 65.0, 63.7, 51.8, 28.9, 26.2, 23.9; IR (NaCl, thin film, cm⁻¹) 3418, 2931, 2096, 1492, 1452, 1379, 1257, 1126, 1089, 1034, 875, 772, 745; HRMS (ESI-TOF) *m/z* calcd for C₁₃H₁₇N₃O₂Na⁺ (M+Na)⁺ 270.1213, found 270.1219.



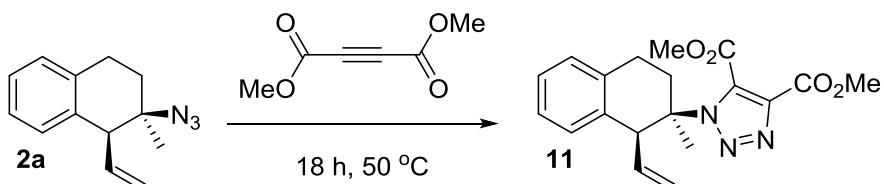
Amine 8: To a solution of azide **2a** (24 mg, 0.11 mmol) in MeOH (2 mL) at room temperature was added palladium on carbon (17.2 mg, 10 w% Pd). The vial was sealed and the head space was flushed with hydrogen gas (approx. 2L). The vial was fitted with 2 balloons of hydrogen gas and stirred vigorously. After 18h, the reaction was diluted EtOAc and filtered through a short plug of silica gel. The filtrate was concentrated under reduced pressure which afforded compound **8** (16.1 mg, 0.086 mmol, 76%) as a tan oil: ¹H NMR (500 MHz, CDCl₃) δ 7.18 – 7.03 (m, 4H), 2.94 (ddd, J = 17.2, 8.2, 2.8 Hz, 1H), 2.84 (ddd, J = 17.9, 10.5, 7.8 Hz, 1H), 2.34 (ddd, J = 9.7, 3.6, 1.5 Hz, 1H), 2.30 (br s, 2H), 2.02 – 1.92 (m, 2H), 1.64 (ddt, J = 13.2, 7.8, 2.1 Hz, 1H), 1.35 – 1.24 (m, 1H), 1.11 (s, 3H), 0.97 (t, J = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 140.3, 134.4, 130.4, 129.0, 126.1, 125.0, 52.5, 52.0, 32.9, 28.0, 27.0, 25.1, 13.6; IR (NaCl, thin film, cm⁻¹) 3352, 3059, 3016, 2957, 2928, 2872, 1683, 1578, 1489, 1455, 1374, 1339, 1240, 1157, 1138, 877, 764, 751; HRMS (ESI-TOF) *m/z* calcd for C₁₃H₁₉NNa⁺ (M+Na)⁺ 212.1410, found 212.1417.



Amine 9: To a solution of azide **2a** (22.2 mg, 0.10 mmol) in THF (1.0 mL) cooled in an ice bath was added powdered lithium aluminum hydride (4.6 mg, 0.12 mmol). After the addition the solution was allowed to warm to rt. After 24 h, the solution was sequentially quenched with acetone (0.5 mL) and water (0.5 mL). The resulting solution was extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine, dried (MgSO_4), and concentrated under reduced pressure. This afforded amine **9** (16.0 mg, 0.86 mmol, 83%) as a clear oil: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.14 (s, 4H), 5.84 (dt, $J = 17.0, 9.8$ Hz, 1H), 5.28 (dd, $J = 10.1, 2.0$ Hz, 1H), 5.17 (dd, $J = 17.0, 1.8$ Hz, 1H), 3.20 (d, $J = 9.3$ Hz, 1H), 2.98 (dt, $J = 17.6, 6.9$ Hz, 1H), 2.85 (dt, $J = 17.5, 6.8$ Hz, 1H), 1.84 (dt, $J = 13.4, 6.7$ Hz, 1H), 1.70 (dt, $J = 13.5, 6.8$ Hz, 1H), 1.53 (br s, 2H), 1.18 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.9, 137.7, 135.0, 130.3, 129.0, 126.3, 126.0, 118.5, 56.1, 50.0, 35.4, 28.7, 26.7; IR (NaCl, thin film, cm^{-1}) 3357, 3072, 3016, 2961, 2924, 2854, 1635, 1577, 1489, 1450, 1374, 1263, 997, 916, 842, 773, 740, 666; HRMS (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 188.1434, found 188.1430.



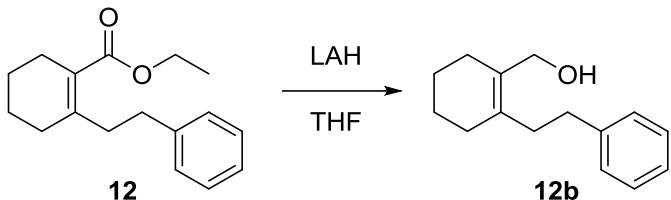
Pyrrolidine 10: In a glovebox a 4 mL vial was charged with HBCy₂ (72 mg, 0.4 mmol). The vial was sealed with a septa cap and removed from the glovebox. The vial was then placed in an ice bath and charged with DCM (1 mL). A solution of azide **2a** in DCM (50 mg, 0.23 mmol, 0.2 M) was added and rinsed with additional DCM (0.2 mL). After the addition, the ice bath was removed and the solution was allowed to gradually warm to room temperature. After 18 h, the reaction was quenched by the addition of solid sodium fluoride (320 mg, 7.7 mmol). After 1 h, the solution was loaded onto a short plug of silica gel. The silica gel was washed with EtOAc (~1 mL x 2) to remove residual cyclohexanol. The product was then eluted from the silica gel (MeOH:EtOAc:NEt₃ 25:75:1, 1 mL x 4) and the resulting eluent was concentrated under reduced pressure to afford Pyrrolidine **10** (32 mg, 0.18 mmol, 76%) as a yellow oil: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22 – 7.06 (m, 4H), 5.72 (s, 1H), 3.34 – 3.21 (m, 2H), 3.09 (t, $J = 9.1$ Hz, 1H), 2.90 (dt, $J = 17.0, 5.4$ Hz, 1H), 2.79 (ddd, $J = 16.6, 10.1, 5.2$ Hz, 1H), 2.49 (dddd, $J = 12.8, 8.6, 7.4, 4.2$ Hz, 1H), 2.00 (ddd, $J = 13.2, 10.0, 5.4$ Hz, 1H), 1.92 – 1.81 (m, 2H), 1.48 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 135.4, 133.8, 129.6, 129.1, 127.0, 126.8, 64.7, 47.9, 42.7, 33.9, 29.7, 26.3, 23.3; IR (NaCl, thin film, cm^{-1}) 3392, 2931, 2801, 1595, 1491, 1450, 1385, 1131; HRMS (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 188.1434, found 188.1431.



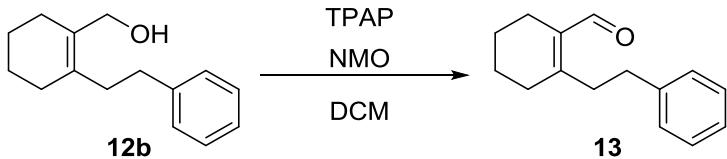
Triazole 11: A vial was sequentially charged with azide **2a** (24.0 mg, 0.11 mmol) and dimethyl acetylenedicarboxylate (140 mg, 1.0 mmol). The vial was sealed under air and heated to 50 °C.

After 18 hours the resulting mixture was cooled to room temperature. Final purification by column chromatography (0 to 80% gradient, EtOAc in hexanes) yielded triazole **11** (30 mg, 75%) as a clear oil: **¹H NMR** (500 MHz, CDCl₃) δ 7.22 – 7.13 (m, 3H), 7.09 (dd, *J* = 7.6, 1.8 Hz, 1H), 5.52 (ddd, *J* = 16.9, 10.1, 8.4 Hz, 1H), 4.88 – 4.80 (m, 2H), 4.09 (dd, *J* = 8.6, 1.7 Hz, 1H), 4.04 (s, 3H), 3.96 (s, 3H), 3.12 (ddd, *J* = 17.6, 7.1, 2.0 Hz, 1H), 3.03 (ddd, *J* = 17.8, 11.8, 6.5 Hz, 1H), 2.89 (td, *J* = 12.3, 7.0 Hz, 1H), 2.36 (ddt, *J* = 12.8, 6.4, 1.9 Hz, 1H), 1.70 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 162.2, 160.8, 138.5, 137.3, 135.7, 133.2, 133.1, 130.9, 128.9, 127.2, 126.6, 118.5, 68.0, 54.4, 54.2, 52.6, 27.9, 26.3, 24.4; **IR** (NaCl, thin film, cm⁻¹) 2953, 2850, 1742, 1562, 1450, 1344, 1269, 1228, 1145, 1043, 828, 774; **HRMS** (ESI-TOF) *m/z* calcd for C₁₉H₂₁N₃O₄Na⁺ (M+Na)⁺ 378.1424, found 378.1440.

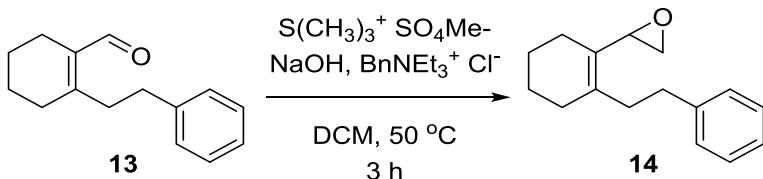
Synthesis of Hasubanan



Alcohol 12b: To a solution of alcohol **12** (1.22 g, 4.7 mmol) in THF (20 mL) cooled in an ice bath, a slurry of lithium aluminum hydride (210 mg, 5.6 mmol) in THF (5 mL) was added dropwise. After the addition was complete, the solution was stirred for 5 min before the ice bath was removed and the solution allowed to warm to rt. After 30 min, the ice bath was replaced and the reaction quenched by the addition of water (20 mL). The resulting solution was extracted with DCM (3 x 15 mL). The combined organic phases were washed with brine, dried (MgSO_4), and concentrated under reduced pressure. This afforded alcohol **12b** (960 mg, 4.4 mmol, 96%) as a clear oil in sufficient purity to advance without further purification: **$^1\text{H NMR}$** (CDCl_3 , 400 MHz) δ 7.34-7.29 (m, 2H), 7.24-7.21 (m, 1H), 7.20-7.16 (m, 2H), 3.85 (s, 2H), 2.72 (t, J = 7.4 Hz, 2H), 2.39 (t, J = 7.4 Hz, 2H), 2.09 (m, 4H), 1.65 (apparent pentet, J = 3.1 Hz, 4H), 0.93, (br s, 1H); **$^{13}\text{C NMR}$** (CDCl_3 , 101 MHz) δ 142.0, 133.3, 131.4, 128.7, 128.3, 126.0, 62.7, 35.0, 34.8, 29.5, 27.5, 23.1, 23.0; **IR** (NaCl, thin film, cm^{-1}) 3316, 2926, 2857, 2831, 1496, 1454, 1436, 995, 754; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{ONa}^+ (\text{M}+\text{Na})^+$ 239.1406, found 239.1405.

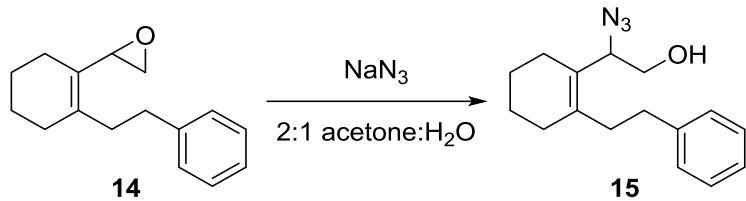


Aldehyde 13: To a solution of alcohol **12b** (301 mg, 1.39 mmol) in DCM (3.5 mL), was added 4 Å molecular sieve beads (~1 g), anhydrous NMO (321 mg, 2.74 mmol), and TPAP (18 mg, 50 μmol , 4 mol%). After 2 h, the reaction was diluted with DCM, filtered through a plug of celite and silica gel, and concentrated under reduced pressure. This afforded aldehyde **13** (259 mg, 1.21 mmol, 87% yield) in sufficient purity to advance without further purification: **$^1\text{H NMR}$** (CDCl_3 , 400 MHz) δ 9.95 (s, 1H), 7.34-7.28 (m, 2H), 7.23 (tt, J = 7.4, 1.5 Hz, 1H), 7.18-7.14 (m, 2H), 2.84 (s, 4H), 2.31-2.25 (m, 2H), 2.22-2.17 (m, 2H), 1.69-1.58 (m, 4H); **$^{13}\text{C NMR}$** (CDCl_3 , 101 MHz) δ 190.6, 158.6, 140.6, 134.3, 128.6, 128.4, 126.4, 36.2, 34.2, 32.2, 22.21, 22.16, 21.7; **IR** (NaCl, thin film, cm^{-1}) 3061, 3026, 2932, 2862, 1666, 1629, 1603, 1495, 1453, 1434, 1368, 1275, 1235, 1168; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{ONa}^+ (\text{M}+\text{Na})^+$ 237.1250, found 237.1251.

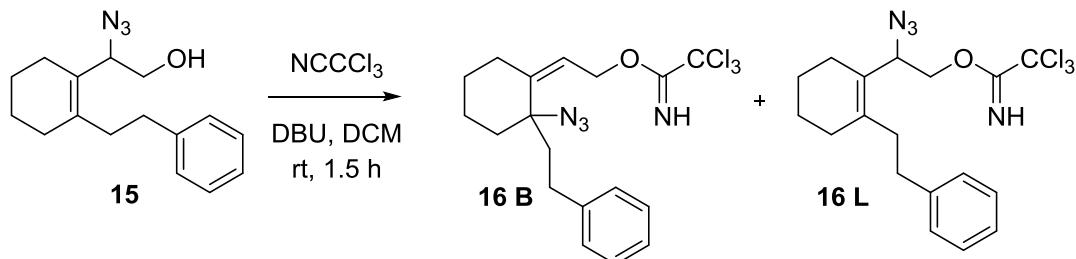


Epoxide 14: To a solution of aldehyde **13** (710 mg, 3.33 mmol) in DCM (6 mL) in a 20 mL vial was sequentially added trimethylsulfonium methyl sulfate (750 mg, 4.0 mmol), solid benzyltriethylammonium chloride (47 mg, 0.17 mmol), and 50% w/v aqueous NaOH (1.5 mL). The vial was sealed and heated to 50 °C. After 3 h, the vial was cooled to room temperature and diluted with water (5 mL). The resulting solution was extracted with DCM (3 x 15 mL). The

combined organic extracts were washed with water, washed with brine, dried (MgSO_4), filtered, and concentrated under reduced pressure. This afforded epoxide **14** (710 mg, 3.1 mmol, 93%) in sufficient purity to advance without further purification. **Note:** Epoxide **14** is unstable to column chromatography. Epoxide **14** should be stored at low temperature (-15 °C) because decomposition occurs at room temperature: **¹H NMR** (400 MHz, CD_3CN) δ 7.33 – 7.17 (m, 5H), 3.57 (t, J = 3.6 Hz, 1H), 2.81 – 2.70 (m, 2H), 2.67 (dd, J = 5.2, 4.3 Hz, 1H), 2.62 (dd, J = 5.2, 2.8 Hz, 1H), 2.58 – 2.49 (m, 1H), 2.44 – 2.35 (m, 1H), 2.11 – 2.06 (m, 2H), 1.85 – 1.73 (m, 1H), 1.71 – 1.45 (m, 5H); **¹³C NMR** (126 MHz, CD_3CN) δ 142.2, 137.1, 128.6, 128.2, 126.9, 125.8, 50.1, 45.0, 34.9, 34.7, 30.0, 22.6, 22.2, 22.1; **IR** (NaCl, thin film, cm^{-1}) 3025, 2924, 2856, 1495, 1452, 883, 748, 699, 640; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{ONa}^+$ ($\text{M}+\text{Na}$)⁺ 251.1406, found 251.1411.

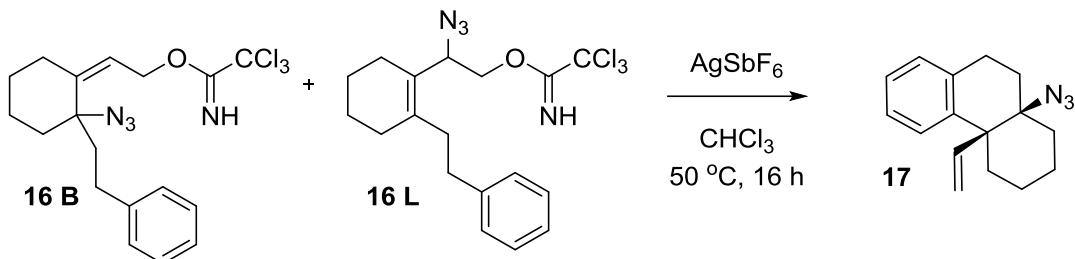


To a vial containing a solution of epoxide **14** (98.5 mg, 0.43 mmol) in acetone (600 μL) and water (300 μL), solid sodium azide (36.4 mg, 0.56 mmol) was added. The vial was sealed and heated to 60 °C. After 24 h, the solution was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to afford alcohol **15** as a brown oil (88.3 mg, 0.33 mmol, 76%) in sufficient purity to advance without further purification; **¹H NMR** (CDCl_3 , 400 MHz) δ 7.36-7.18 (m, 5H), 4.49 (dd, J = 9.0, 4.7 Hz, 1H), 3.53 (dd, J = 11.3, 9.0 Hz, 1H), 3.21 (dd, J = 11.3, 4.7 Hz, 1H), 2.74 (m, 2H), 2.49 (dt, J = 13.6, 8.1 Hz, 1H), 2.38 (dt, J = 14.0, 7.5 Hz, 1H), 2.17-2.05 (m, 3H), 1.90-1.50 (m, 6H); **¹³C NMR** (CDCl_3 , 101 MHz) δ 141.6, 137.5, 128.5, 128.4, 126.2, 126.1, 64.9, 64.0, 35.20, 35.16, 29.9, 24.3, 22.8, 22.6; **IR** (NaCl, thin film, cm^{-1}) 3384, 2930, 2859, 2102, 1496, 1453, 1249, 1059, 1029, 793; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{N}_3\text{ONa}^+$ ($\text{M}+\text{Na}$)⁺ 294.1577, found 294.1576.

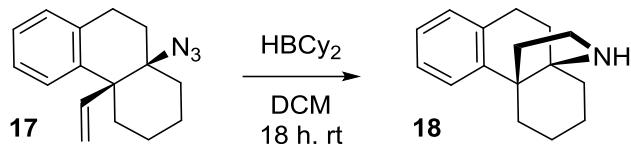


Imidate 16: General procedure 5 was used to afford imidate **16** in 86% yield. Compound **16** was isolated as an equilibrating mixture of two isomers (**16 B** and **16 L**) in a 5:1 ratio. **¹H NMR** (CDCl_3 , 400 MHz) **16 L** δ 8.38 (s, 1H), 7.35-7.28 (m, 2H), 7.25-7.18 (m, 3H), 4.82 (dd, J = 8.9, 5.0 Hz, 1H), 4.24 (dd, J = 11.1, 8.9 Hz, 1H), 3.96 (dd, J = 11.1, 5.0 Hz, 1H), 2.75 (t, J = 7.9 Hz, 2H), 2.49 (dt, J = 13.6, 8.0 Hz, 1H) 2.38 (dt, J = 13.9, 7.6 Hz, 1H), 2.18-2.10 (m, 2H), 1.95-1.45 (m, 6H); **16 B** δ 8.32 (s, 1H), 7.33 – 7.26 (m, 2H), 7.24 – 7.15 (m, 3H), 5.85 (t, J = 6.7 Hz, 1H), 4.92 (dd, J = 6.7, 1.8 Hz, 2H), 2.77 – 2.71 (m, 2H), 2.70 – 2.55 (m, 2H), 2.53 – 2.43 (m, 1H), 2.41 – 2.33 (m, 1H), 2.21 – 2.05 (m, 2H), 1.95-1.45 (m, 6H); **¹³C NMR** (101 MHz, CDCl_3) δ 162.7, 141.7, 137.9, 128.67, 128.63, 128.57, 126.3, 126.2, 125.8, 117.7, 91.3, 69.7, 68.0, 65.3, 60.8, 37.9, 37.1, 35.5, 35.3, 30.23, 30.19, 26.9, 26.7, 24.4, 22.9, 22.8, 22.7; **IR** (NaCl, thin film, cm^{-1}) 3340, 3026, 2930,

2862, 2101, 1667, 1559, 1304, 1269, 1086, 1020, 829, 797; **HRMS** (ESI-TOF) *m/z* calcd for C₁₈H₂₁Cl₃N₄ONa⁺ (M+Na)⁺ 437.0673, found 437.0679.



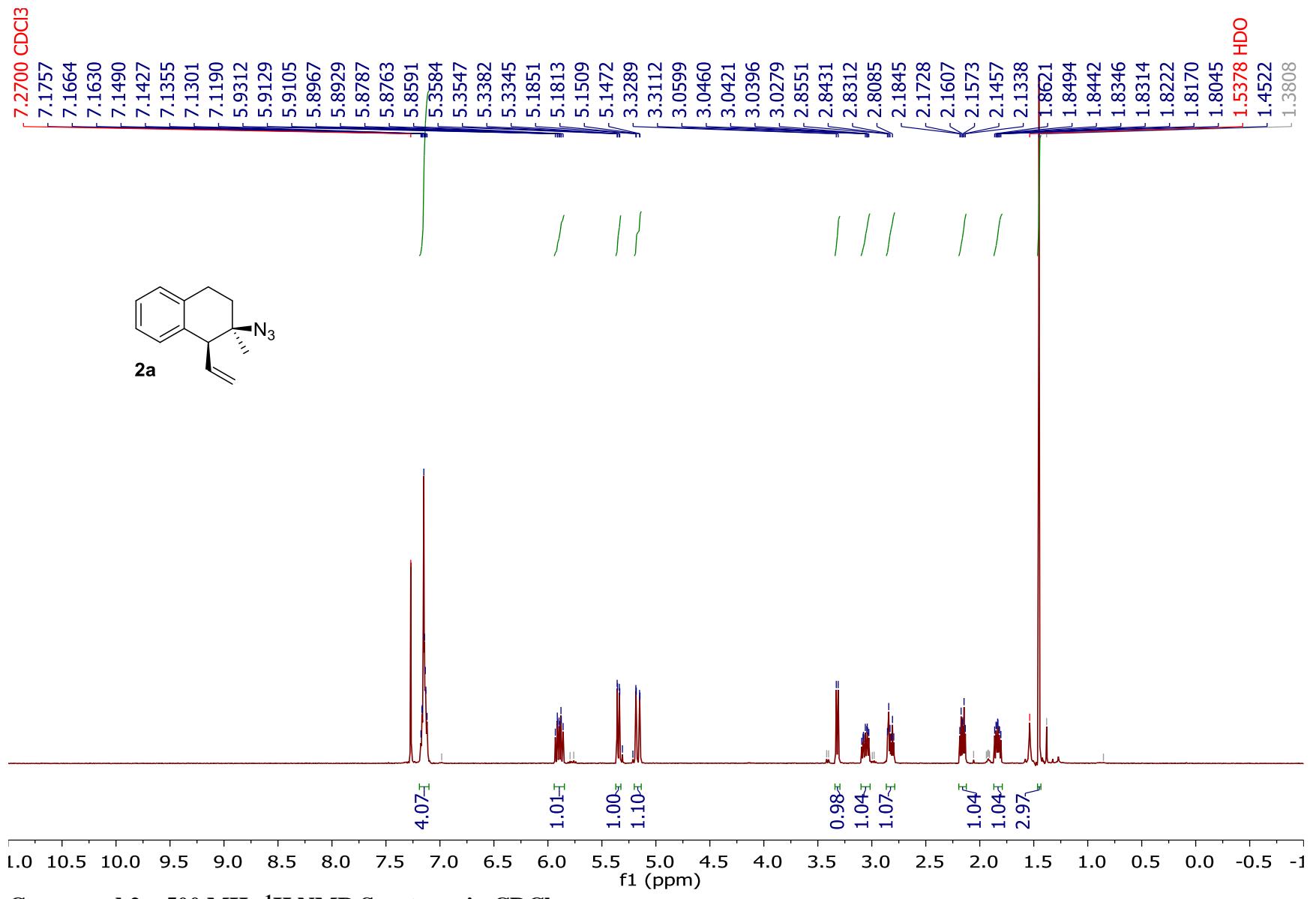
Azide 17: A variation of general procedure 1 was used. The reaction was conducted at 0.10 M substrate and used 5 mol % AgSbF₆ at 50 °C for 16 h. Purification was conducted by filtering through a short plug of silica (2:1 DCM:hexanes). This afforded tetralin **17** as an opaque oil in 78% and 82% yield in duplicate trials. The average yield of 80% is reported. Tetralin **17** was isolated as a single observable diastereomer; **¹H NMR** (CDCl₃, 400 MHz) δ 7.25-7.14 (m, 4H), 6.10 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.11, (d, *J* = 10.6 Hz, 1H), 4.37 (br d, *J* = 17.1 Hz, 1H), 3.05-2.88 (m, 2H), 2.35-2.23 (m, 1H), 2.17-2.01 (m, 2H), 1.93-1.83 (m, 1H), 1.79-1.67 (m, 3H), 1.65-1.49 (m, 2H), 1.35-1.21 (m, 1H); **¹³C NMR** (CDCl₃, 101 MHz) δ 145.4, 138.3, 135.2, 129.2, 127.7, 126.1, 126.0, 116.5, 65.6, 48.8, 31.3, 29.9, 28.5, 26.6, 21.7, 21.2; **IR** (NaCl, thin film, cm⁻¹) 2936, 2862, 2095, 1490, 1449, 1404, 1264, 1155, 999, 921, 763; **HRMS** (ESI) *m/z* calcd for C₁₆H₂₀N⁺ (M-N₂+H)⁺ 226.1590, found 226.1594.



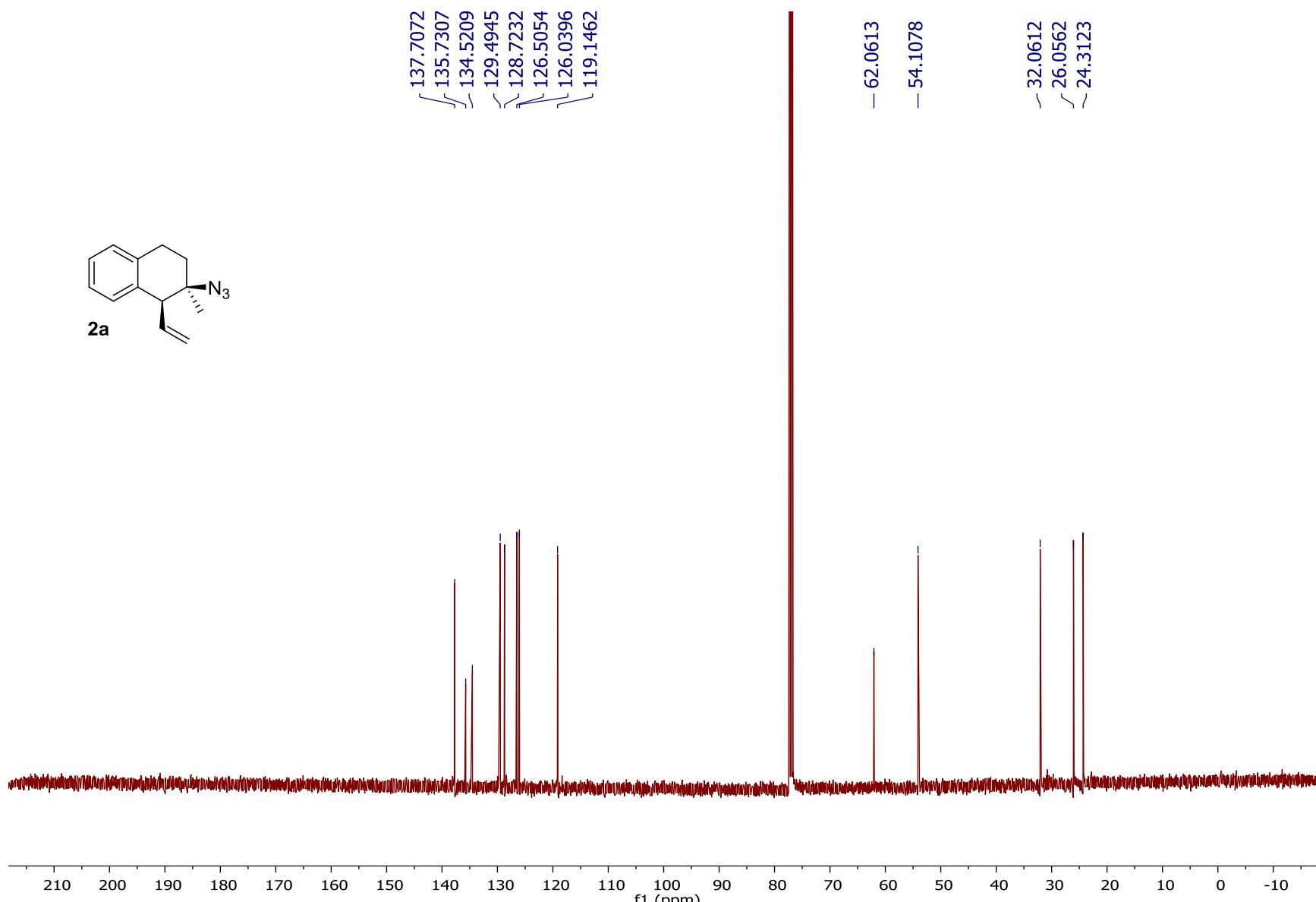
Hasubanan (18): In a glovebox, a 4 mL vial was charged with dicyclohexylborane (73 mg, 0.41 mmol). The vial was sealed, removed from the glovebox, and placed in an ice bath. To the vial, DCM (1 mL) and a solution of azide **17** in DCM (57 mg, 0.22 mmol, 0.22 M) were sequentially added. After 5 min, the ice bath was removed and the solution was allowed to gradually warm to room temperature. After 18 h, the reaction was quenched by the addition of NaF (423 mg, 10 mmol) and water (100 μL, 5.6 mmol). After 2h, the solution was filtered through a pre-equilibrated plug of silica gel (1.5 g of gel, equilibrated with EtOAc:Hexanes 75:25), the plug was washed (2x1 mL, 75:25 EtOAc:Hexanes), then washed further (3x1 mL, 5:95 MeOH:EtOAc). Finally, the product was eluted from the silica gel (14 mL, 25:75:1 MeOH:EtOAc:TEA). The final fractions were combined and concentrated under reduced pressure to yield hasubanan (**18**, 34 mg, 0.15 mmol, 71 %) as a yellow oil: **¹H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.30 (m, 1H), 7.20 – 7.15 (m, 1H), 7.14 – 7.06 (m, 2H), 3.21 (ddd, *J* = 11.4, 9.4, 5.7 Hz, 1H), 3.01 (ddd, *J* = 11.1, 9.3, 5.7 Hz, 1H), 2.92 (q, *J* = 6.9 Hz, 2H), 2.60 (br s, 1H), 2.24 – 2.15 (m, 1H), 2.09 (ddd, *J* = 12.9, 9.5, 5.7 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.89 – 1.80 (m, 3H), 1.78 – 1.60 (m, 3H), 1.58 – 1.42 (m, 2H), 1.30 – 1.21 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 143.0, 134.5, 129.3, 127.4, 126.5, 125.8, 61.8, 47.7, 41.8, 39.1, 34.7, 32.4, 28.8, 26.3, 22.6, 22.2; **IR** (NaCl, thin film, cm⁻¹) 3332, 3015, 2930, 2857, 1593, 1488, 1447, 1413, 756; **HRMS** (ESI-TOF) *m/z* calcd for C₁₆H₂₀N⁺ (M-N₂+H)⁺ 226.1590, found 226.1594.

References:

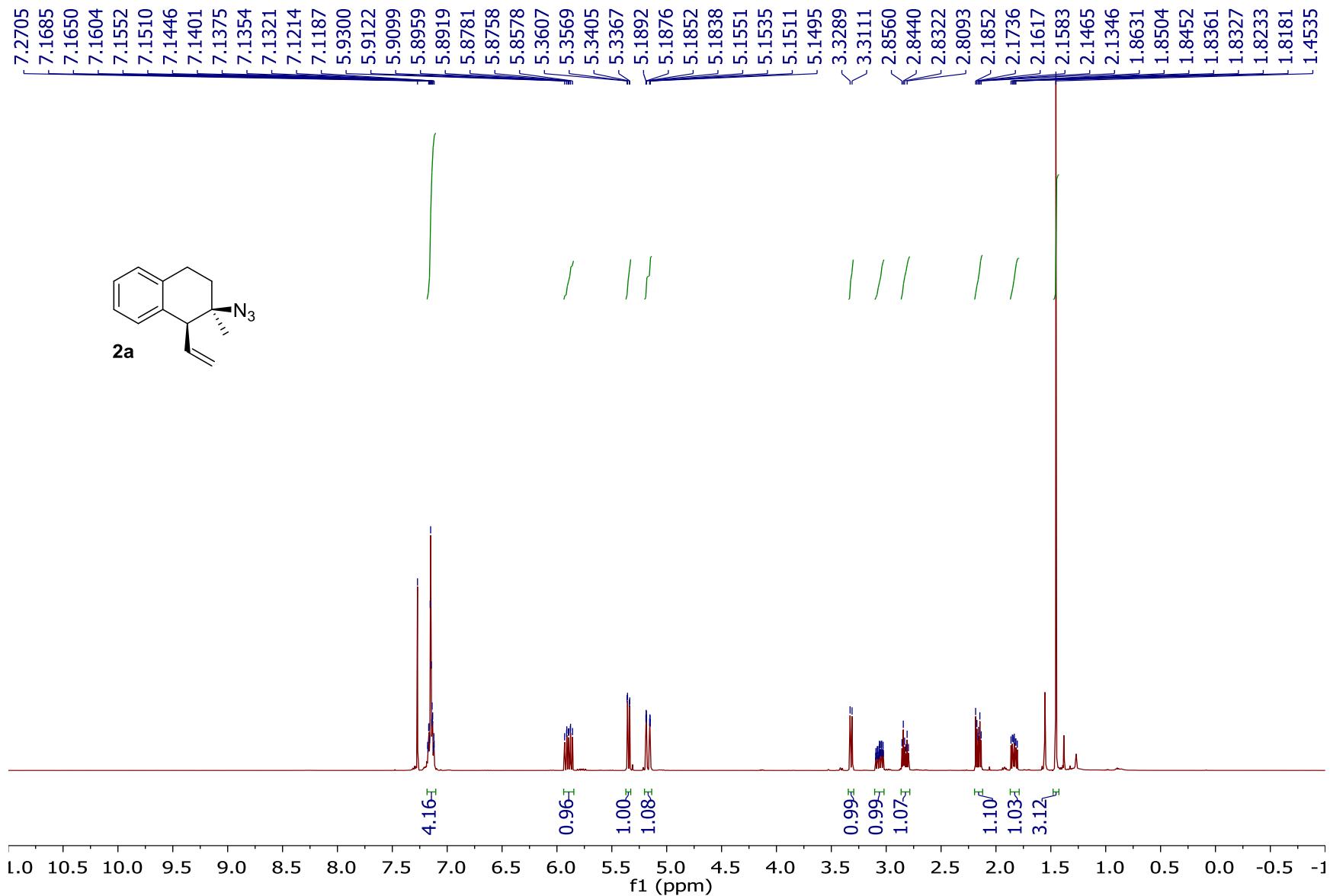
1. Kemsley, J. More Details on the University of Minnesota Explosion and Response. <http://cenblog.org/the-safety-zone/2014/07/more-details-on-the-university-of-minnesota-explosion-and-response/> (accessed 9/24/2016).
2. Hadfield, M. S.; Lee, A.-L., *Org. Lett.*, **2010**, 12, 484-487.
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5. Li, S.; Li, F.; Gong, J.; Yang, Z., *Org. Lett.*, **2015**, 17, 1240-1243.
6. Overman, L. E.; Kakimoto, M.; Okazaki, M. E.; Meier, G. P., *J. Am. Chem. Soc.*, **1983**, 105, 6622-6629.



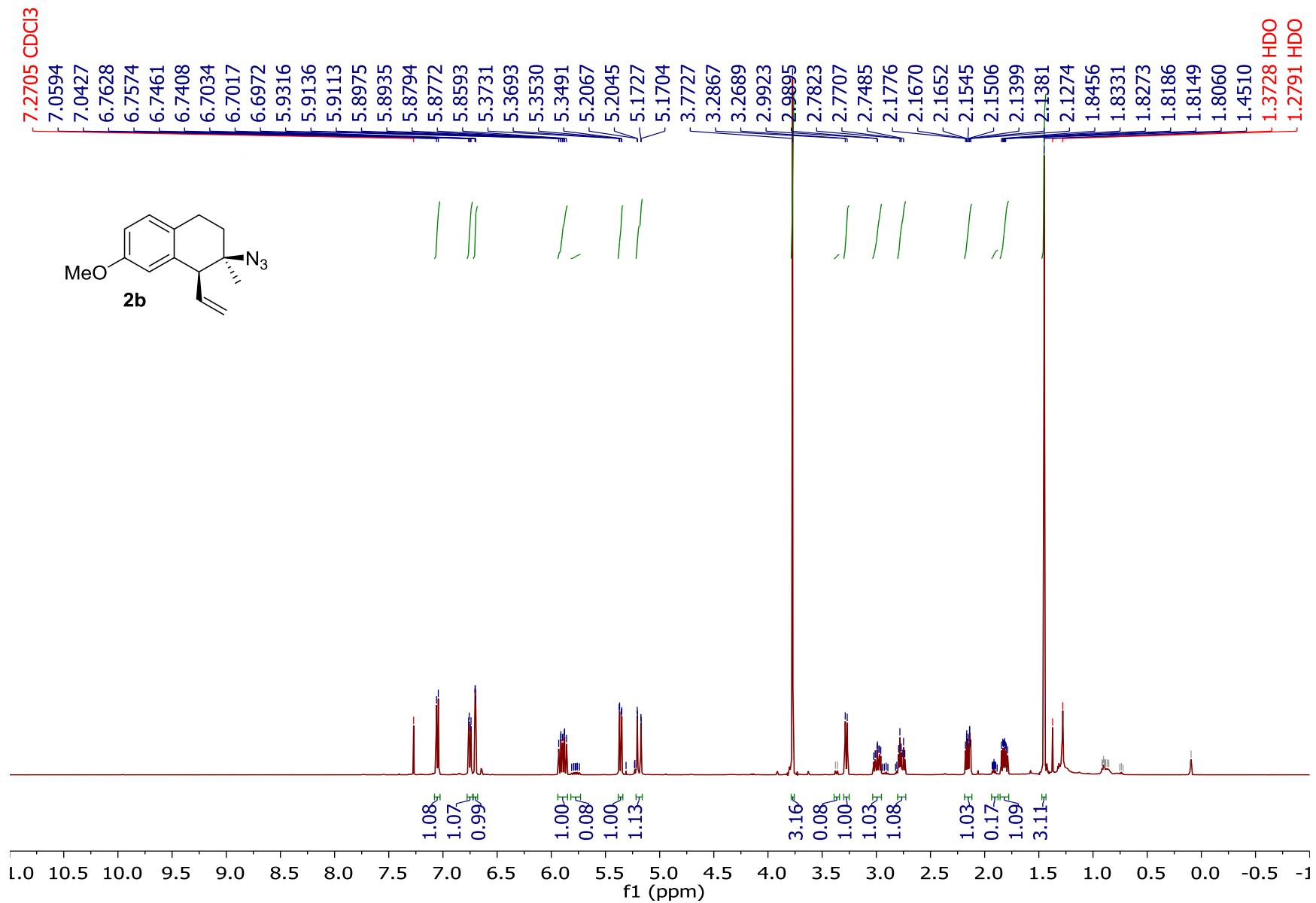
Compound 2a, 500 MHz ¹H NMR Spectrum in CDCl₃



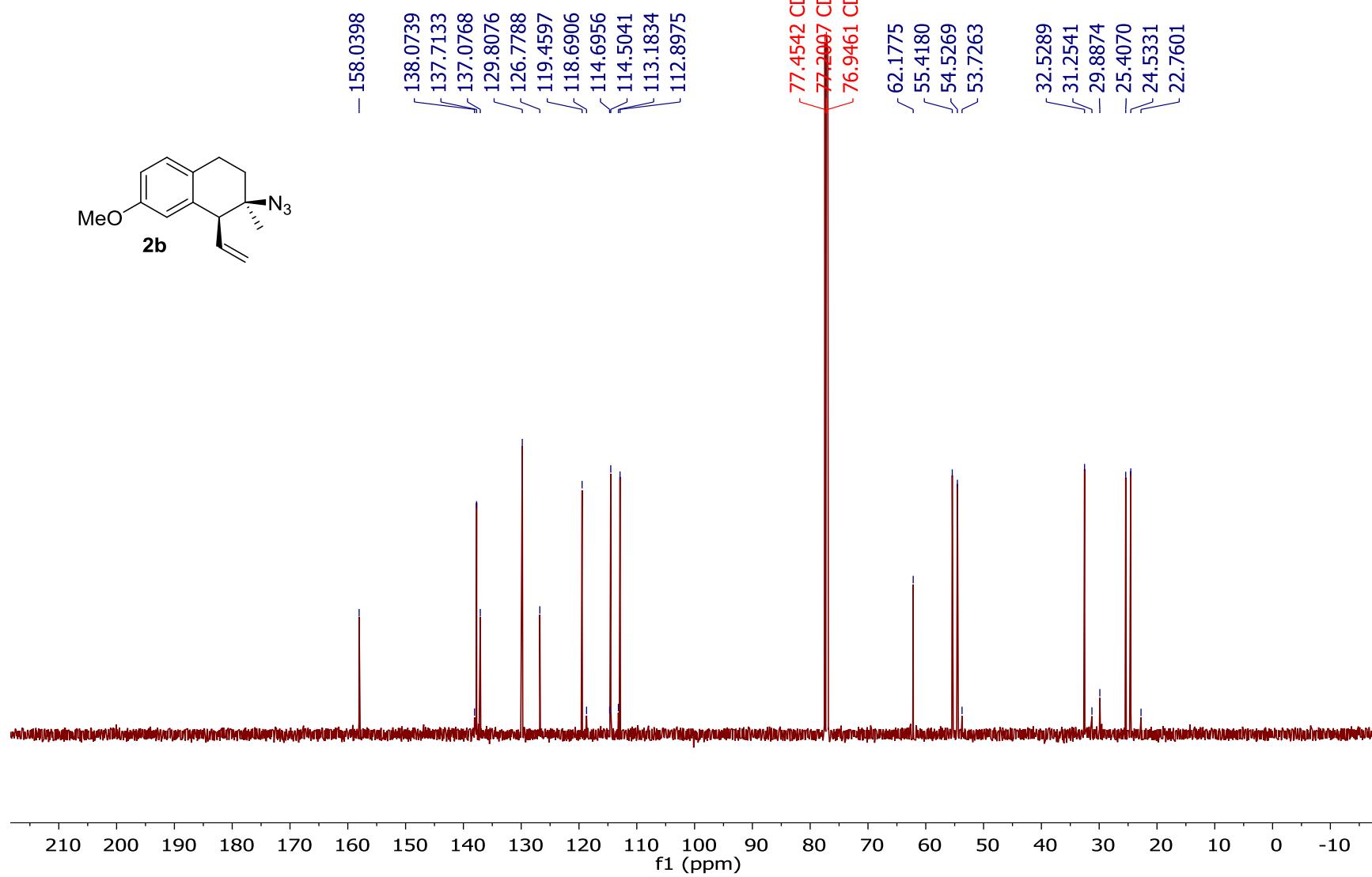
Compound 2a, 126 MHz ^{13}C NMR Spectrum in CDCl_3



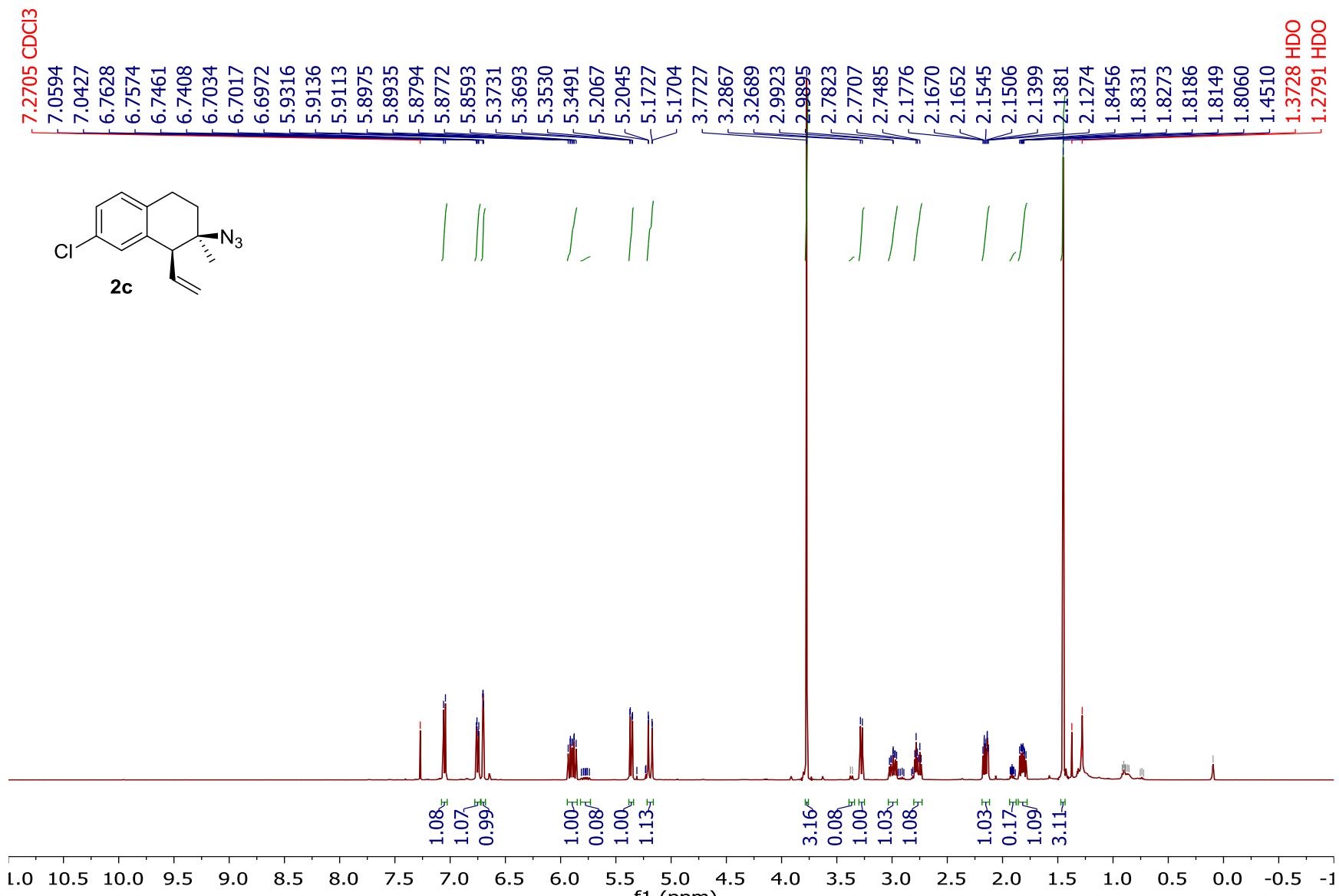
Compound 2a, 500 MHz ^1H NMR Spectrum in CDCl_3 . Crude material as isolated from gram scale reaction.



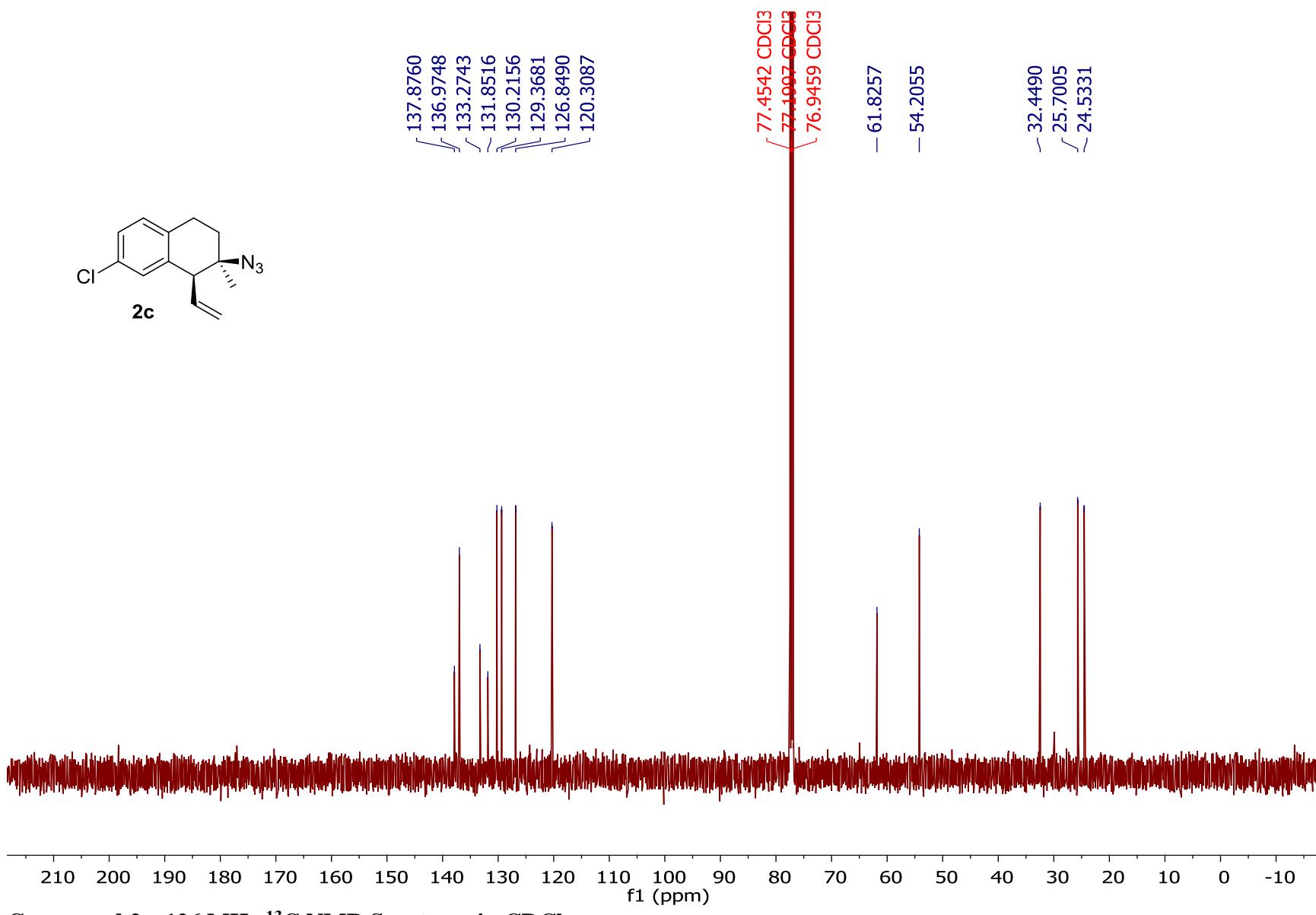
Compound 2b, 500 MHz ^1H NMR Spectrum in CDCl_3



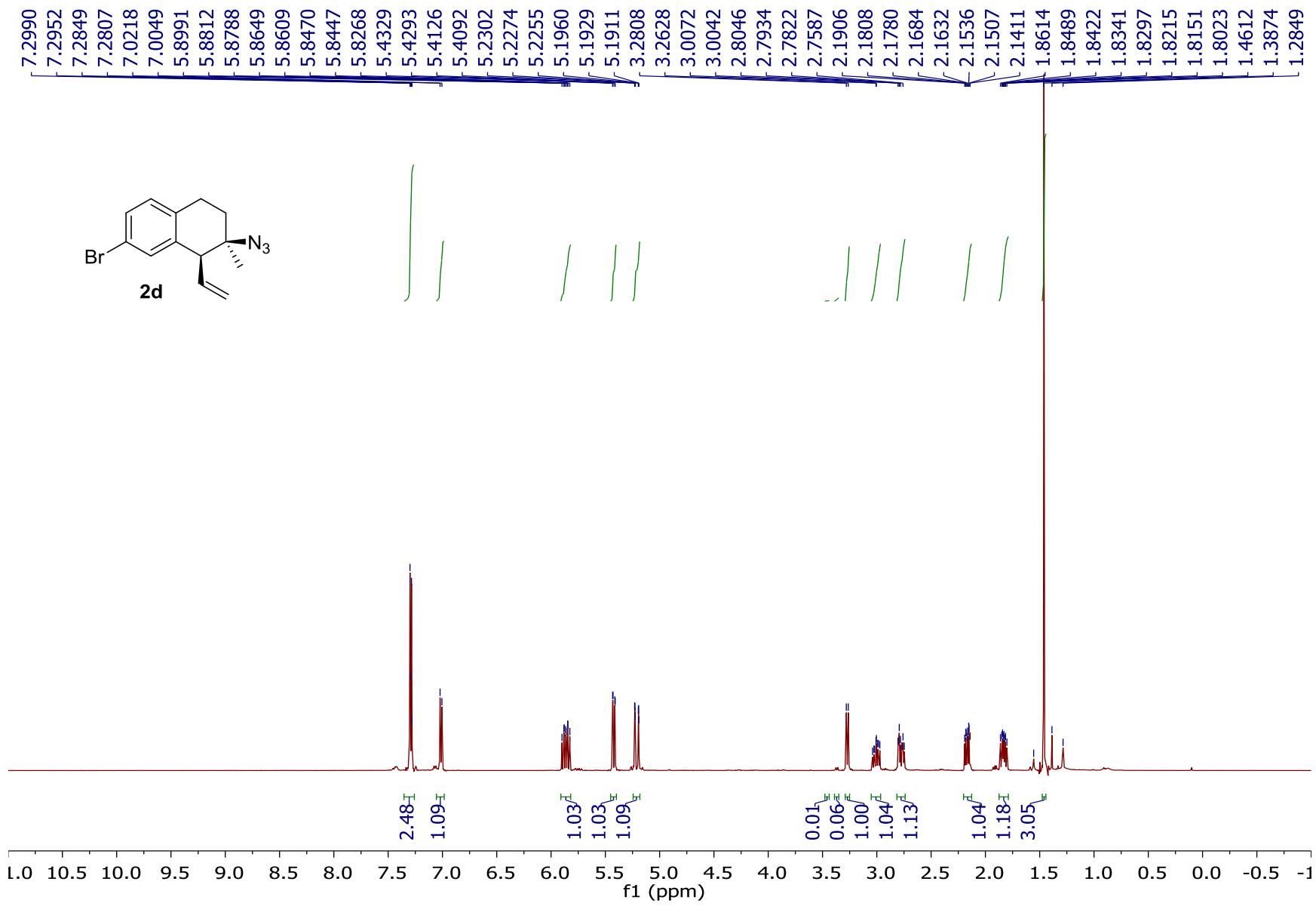
Compound 2b, 126 MHz ^{13}C NMR Spectrum in CDCl₃



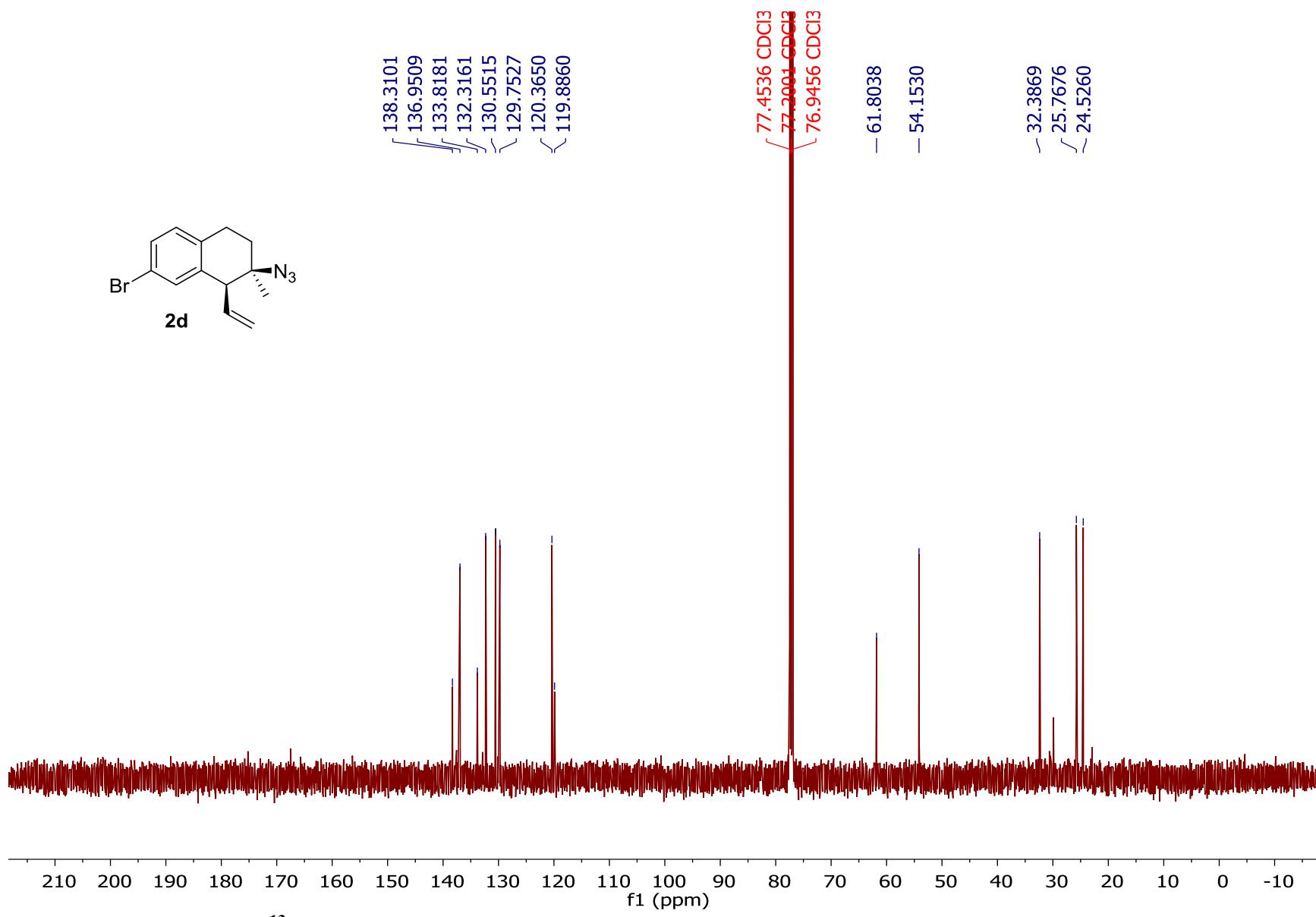
Compound 2c, 500 MHz ¹H NMR Spectrum in CDCl₃



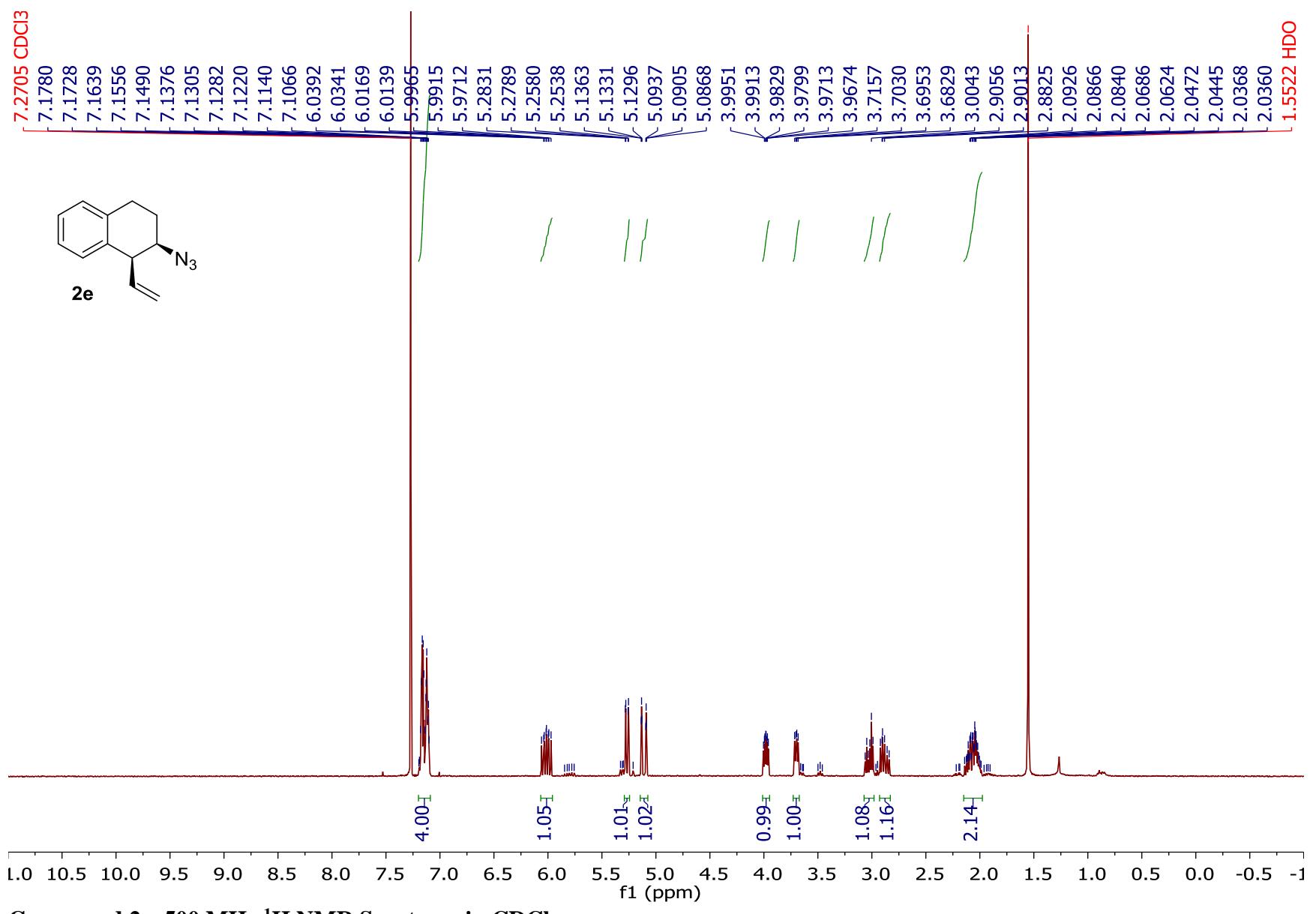
Compound 2c, 126 MHz ^{13}C NMR Spectrum in CDCl_3

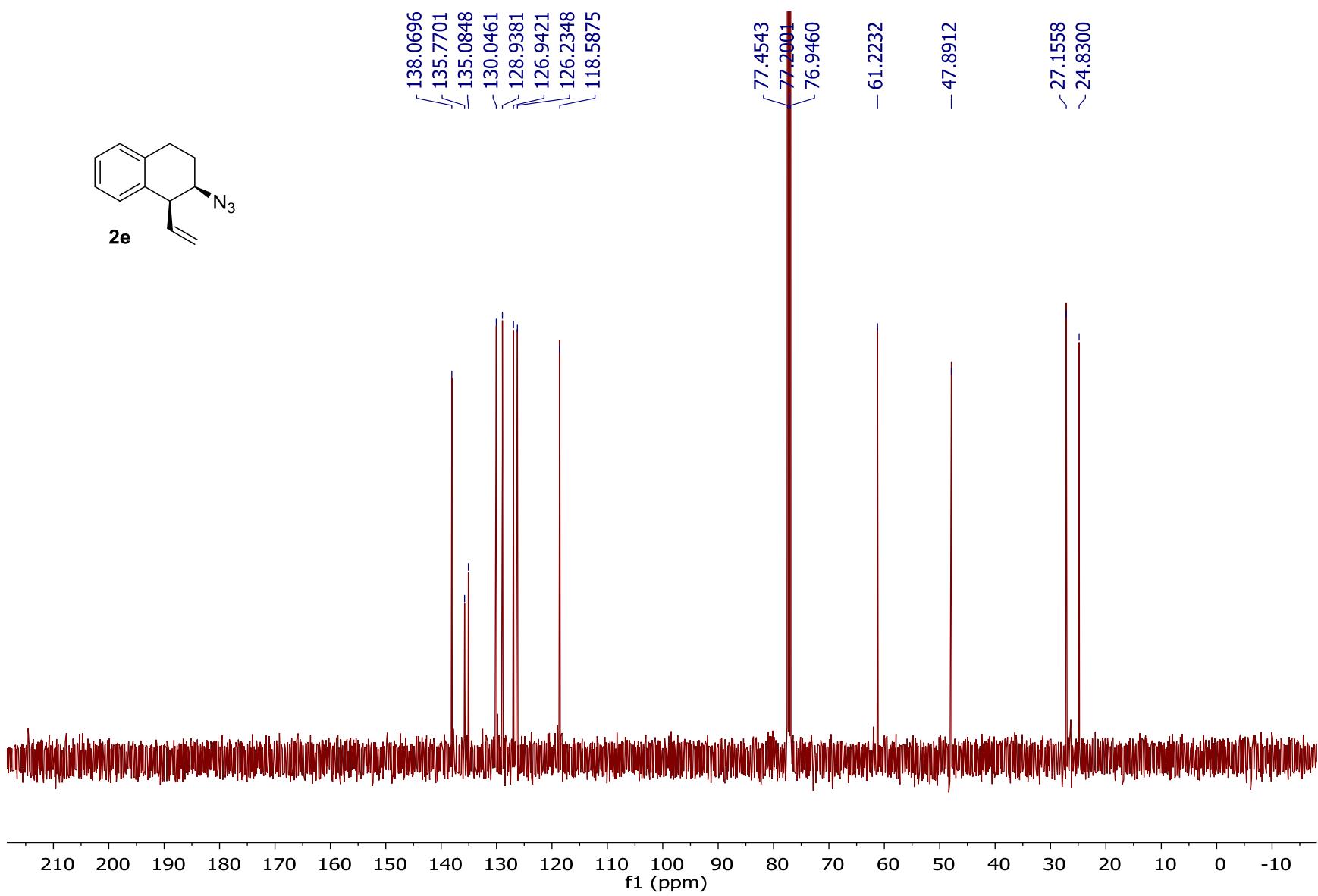
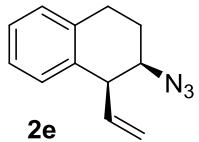


Compound 2d, 500 MHz ^1H NMR Spectrum in CDCl_3

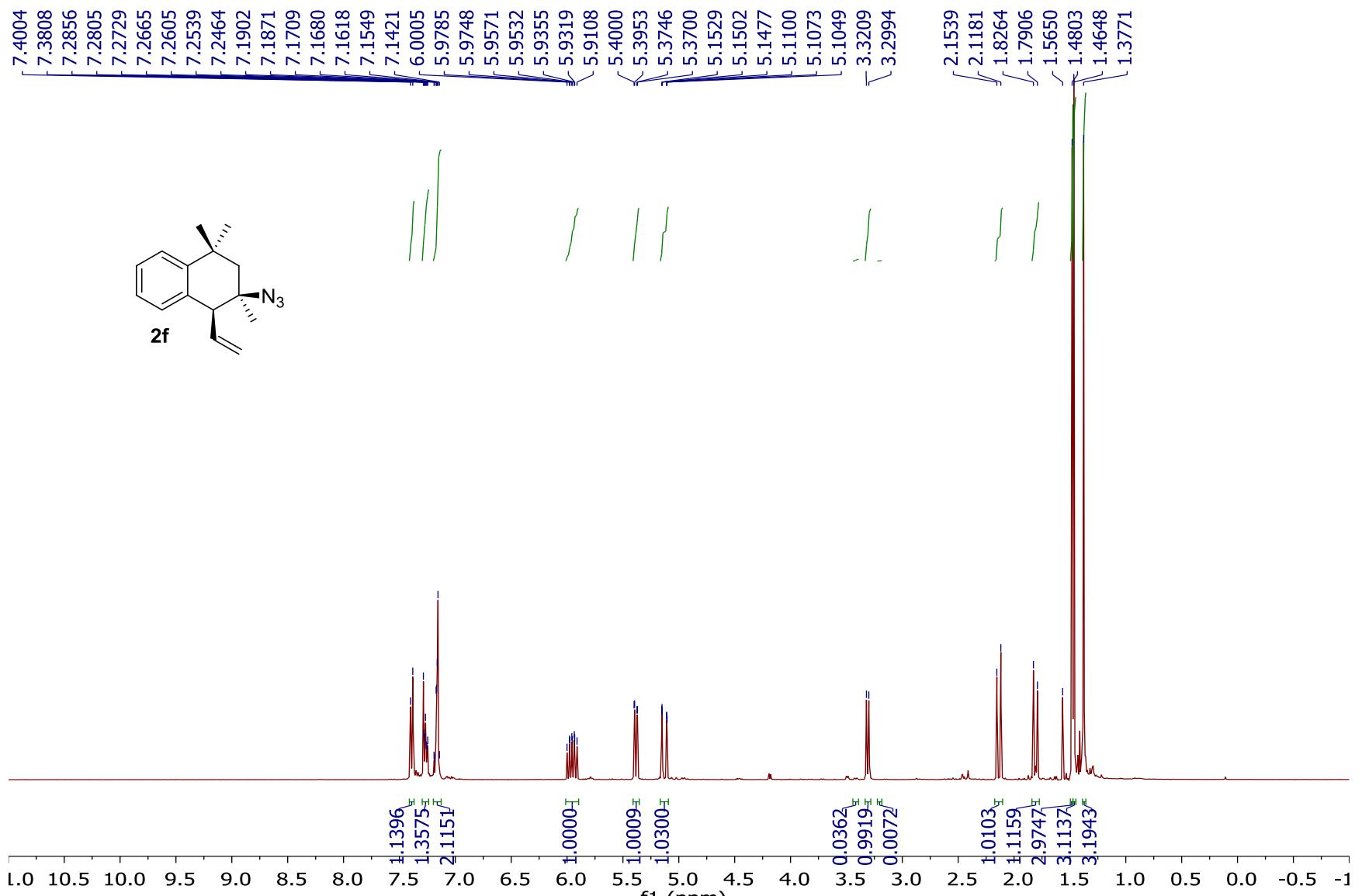


Compound 2d, 126 MHz ¹³C NMR Spectrum in CDCl₃

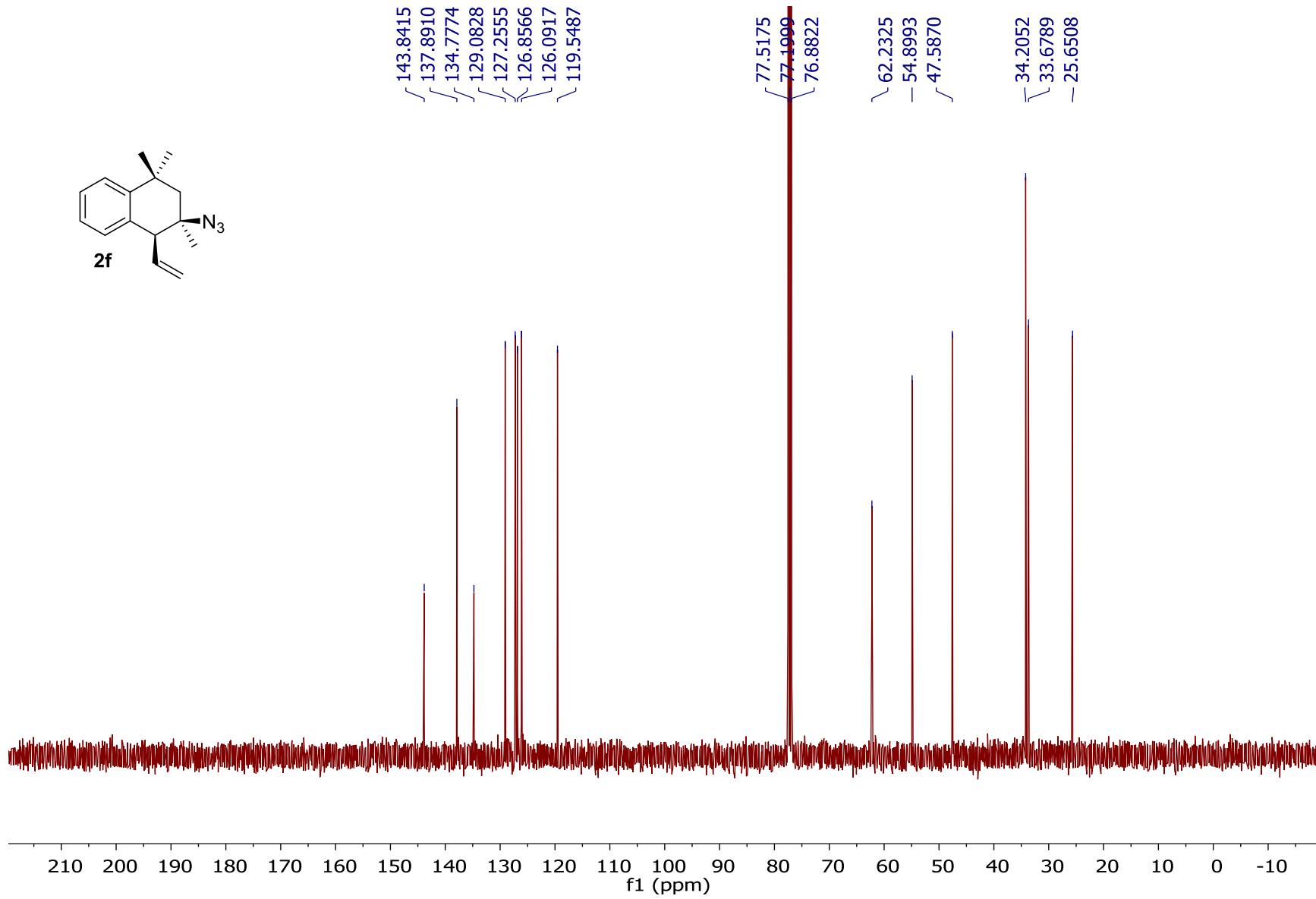


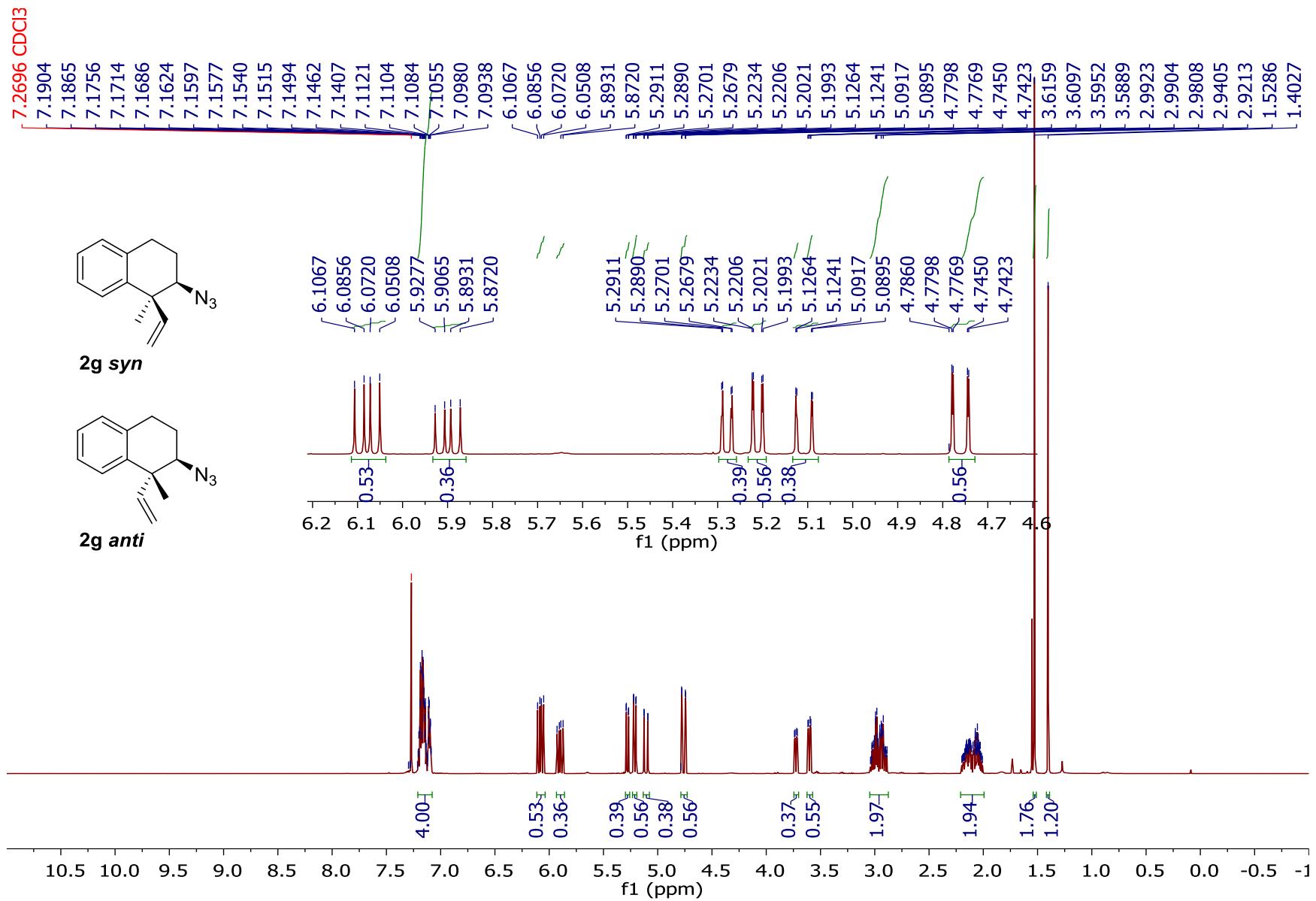


Compound 2e, 126 MHz ^{13}C NMR Spectrum in CDCl_3

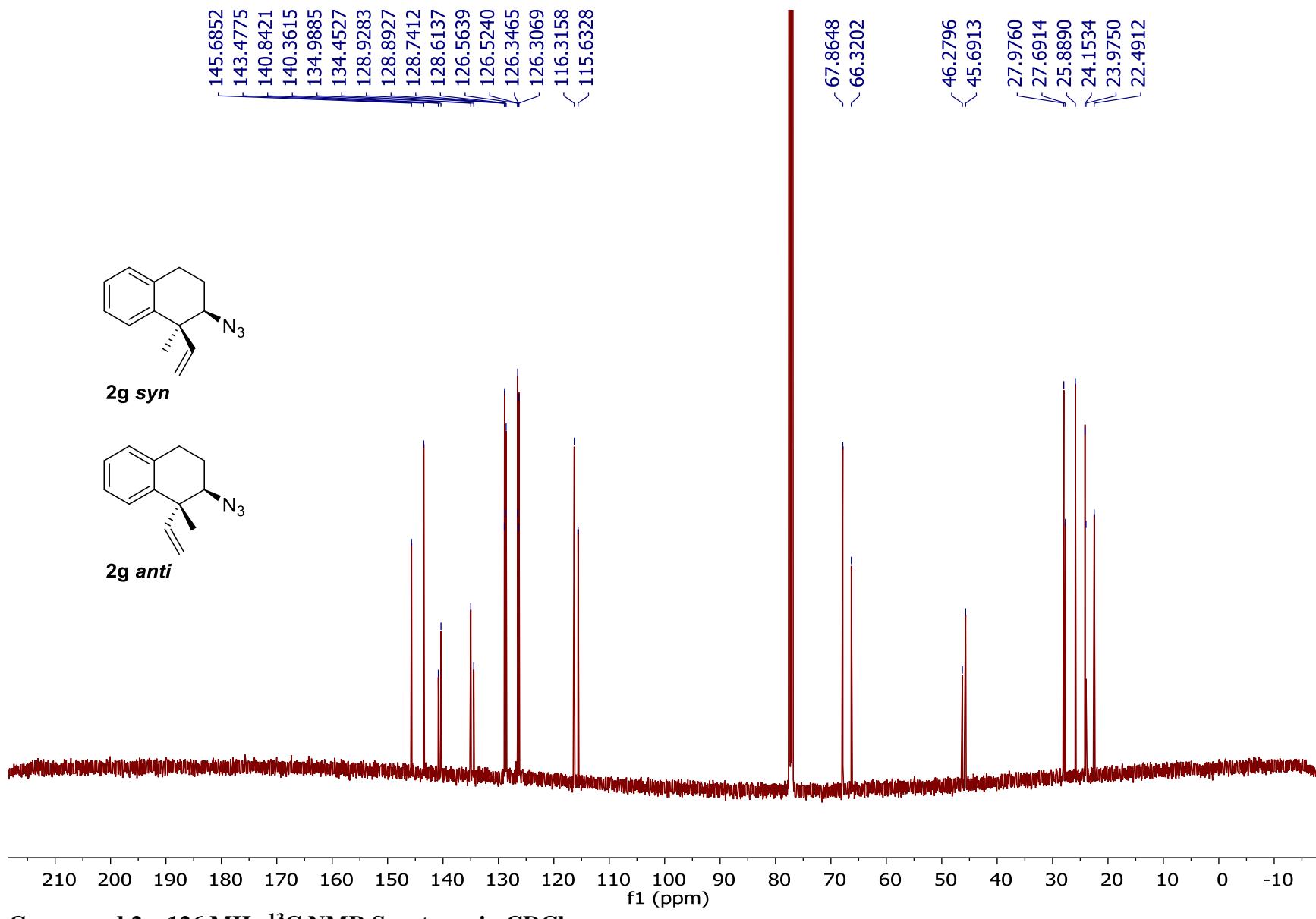


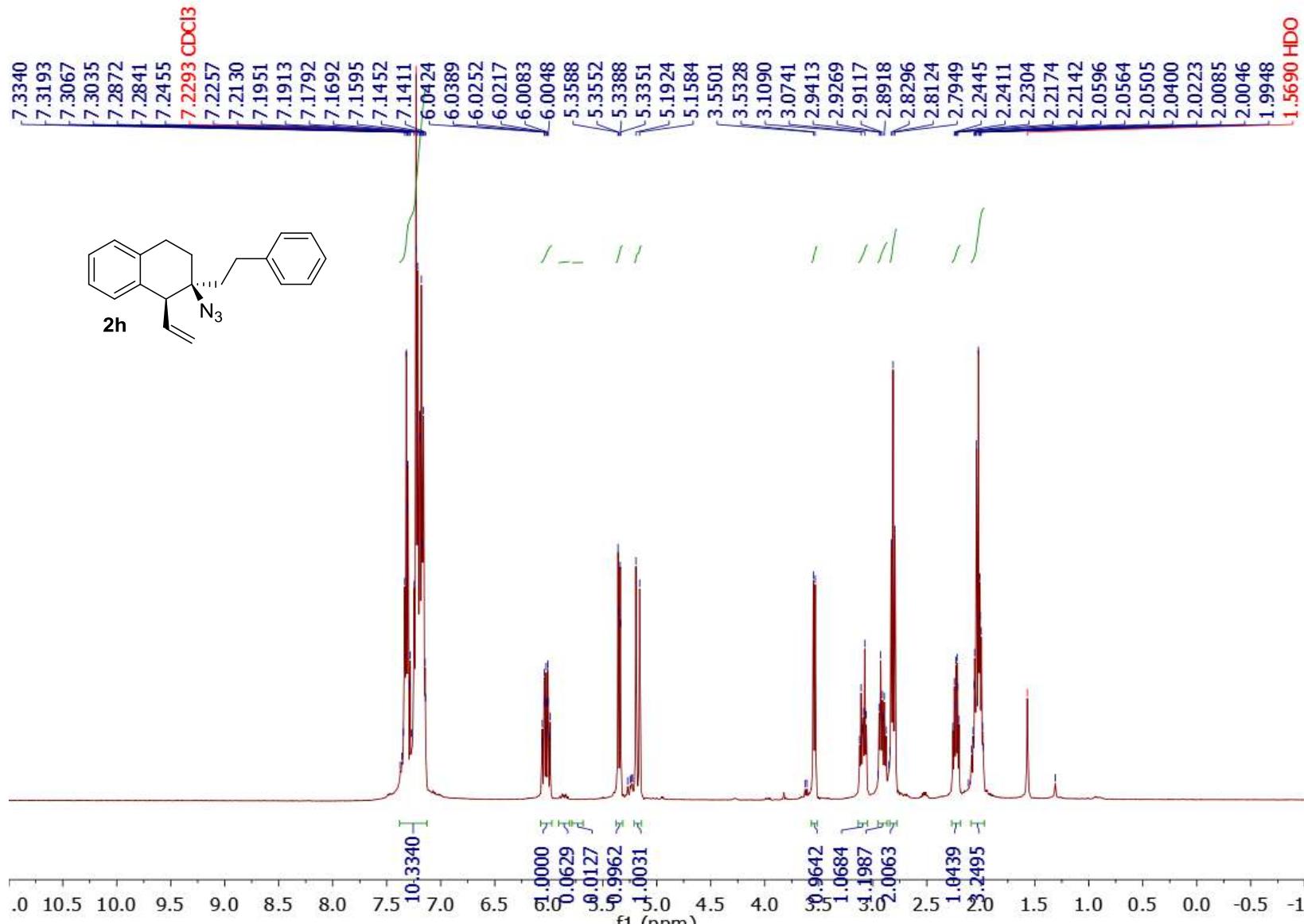
Compound 2f, 400 MHz ^1H NMR Spectrum in CDCl_3



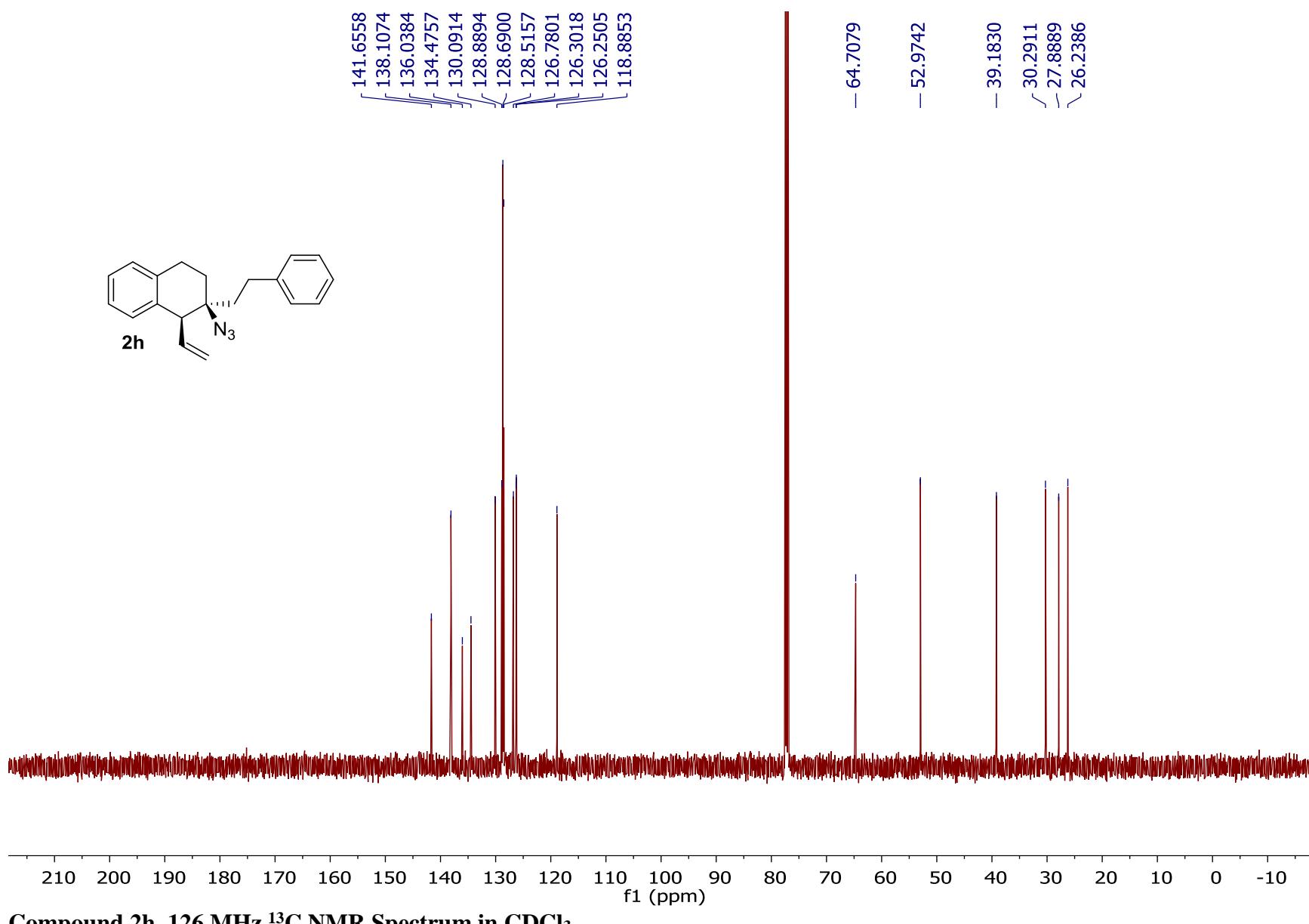


Compound 2g, 500 MHz ¹H NMR Spectrum in CDCl₃



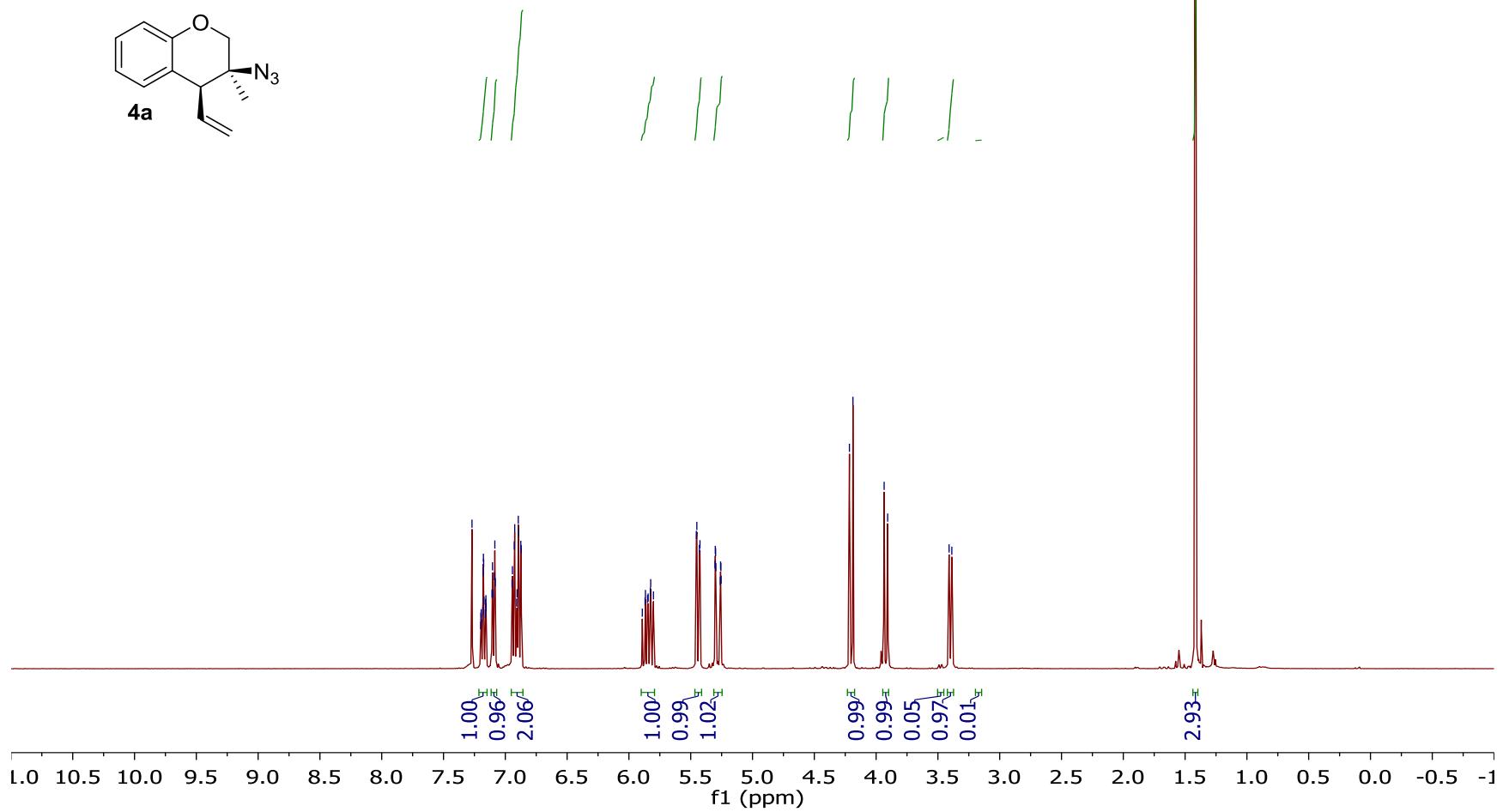
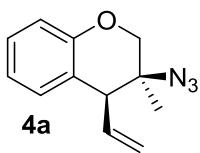


Compound 2h, 500 MHz ¹H NMR Spectrum in CDCl₃

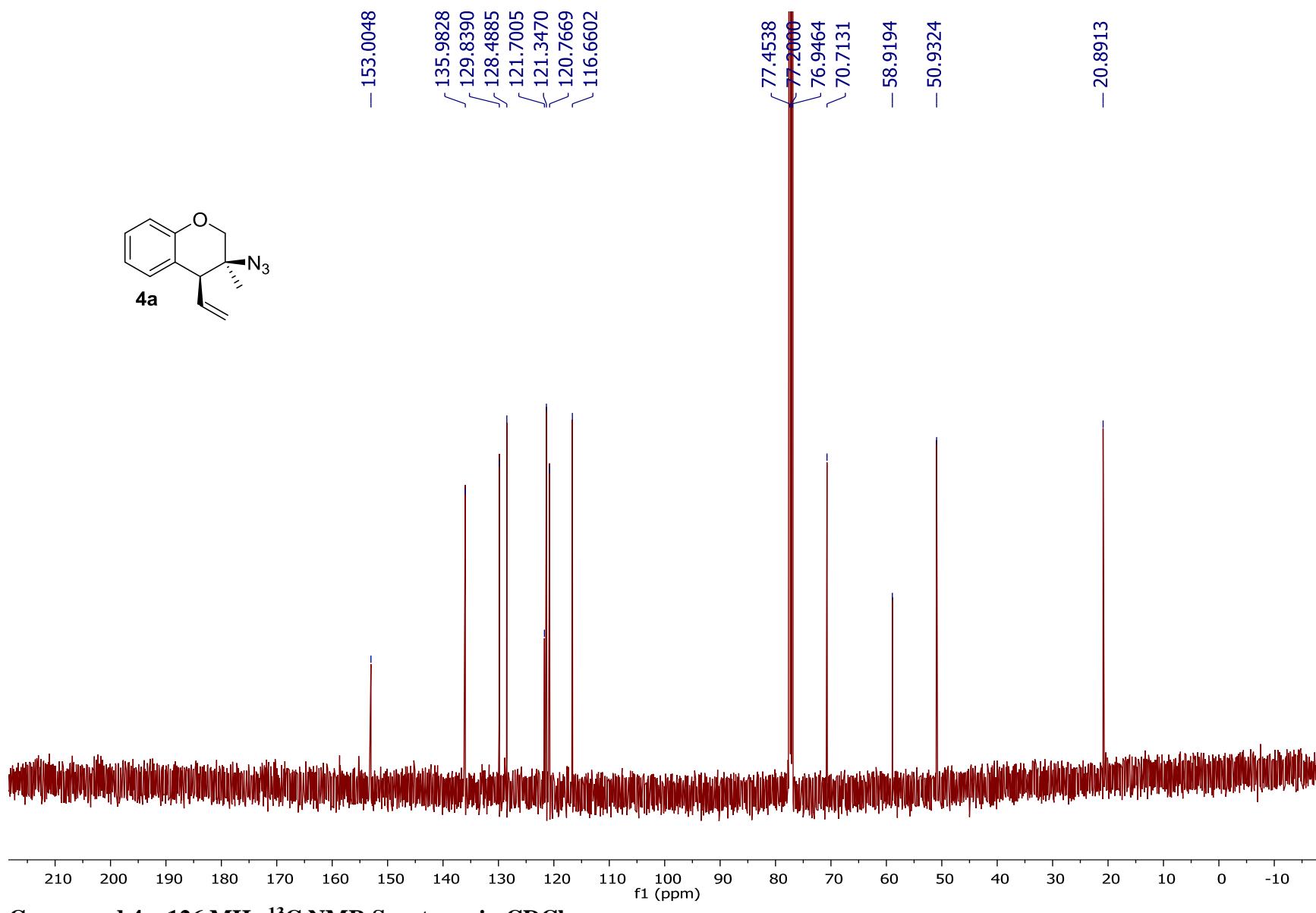


Compound 2h, 126 MHz ^{13}C NMR Spectrum in CDCl_3

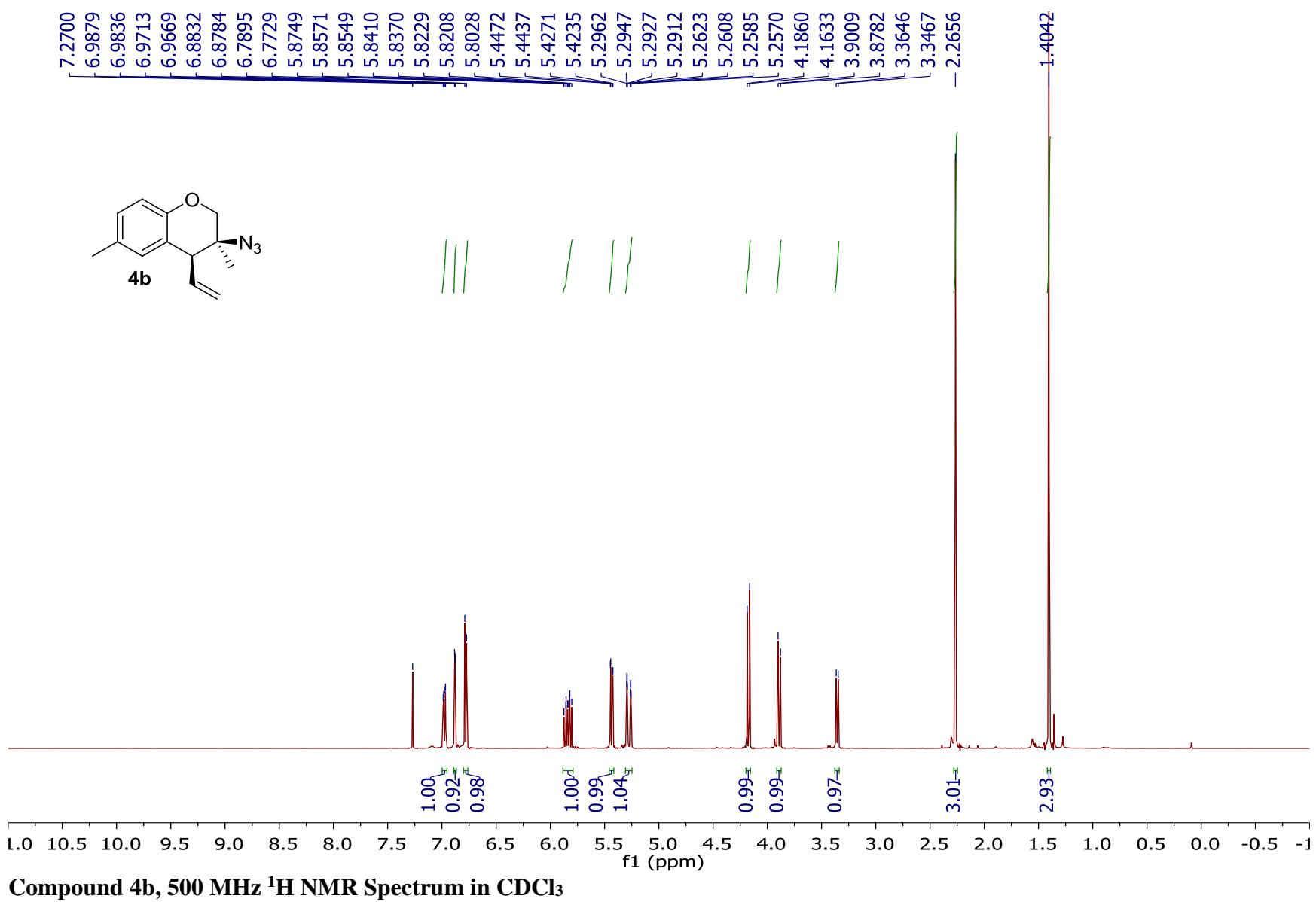
7.2695	7.1818	7.1794	7.1772	7.1751	7.1730	7.1592	7.1568	7.1549	7.1073	7.1039	7.1005	7.0881	7.0847	7.0812	6.9457	6.9425	6.9271	6.9238	6.9082	6.9051	6.8949	6.8918	6.8747	6.8715	5.8692	5.8663	5.8490	5.8441	5.8267	5.8237	5.8014	5.4546	5.4503	5.4294	5.4250	5.3029	5.3010	5.2986	5.2966	5.2604	5.2583	5.2558	5.2539	4.2157	4.1873	3.9349	3.9064	3.4096	3.3873	1.4170
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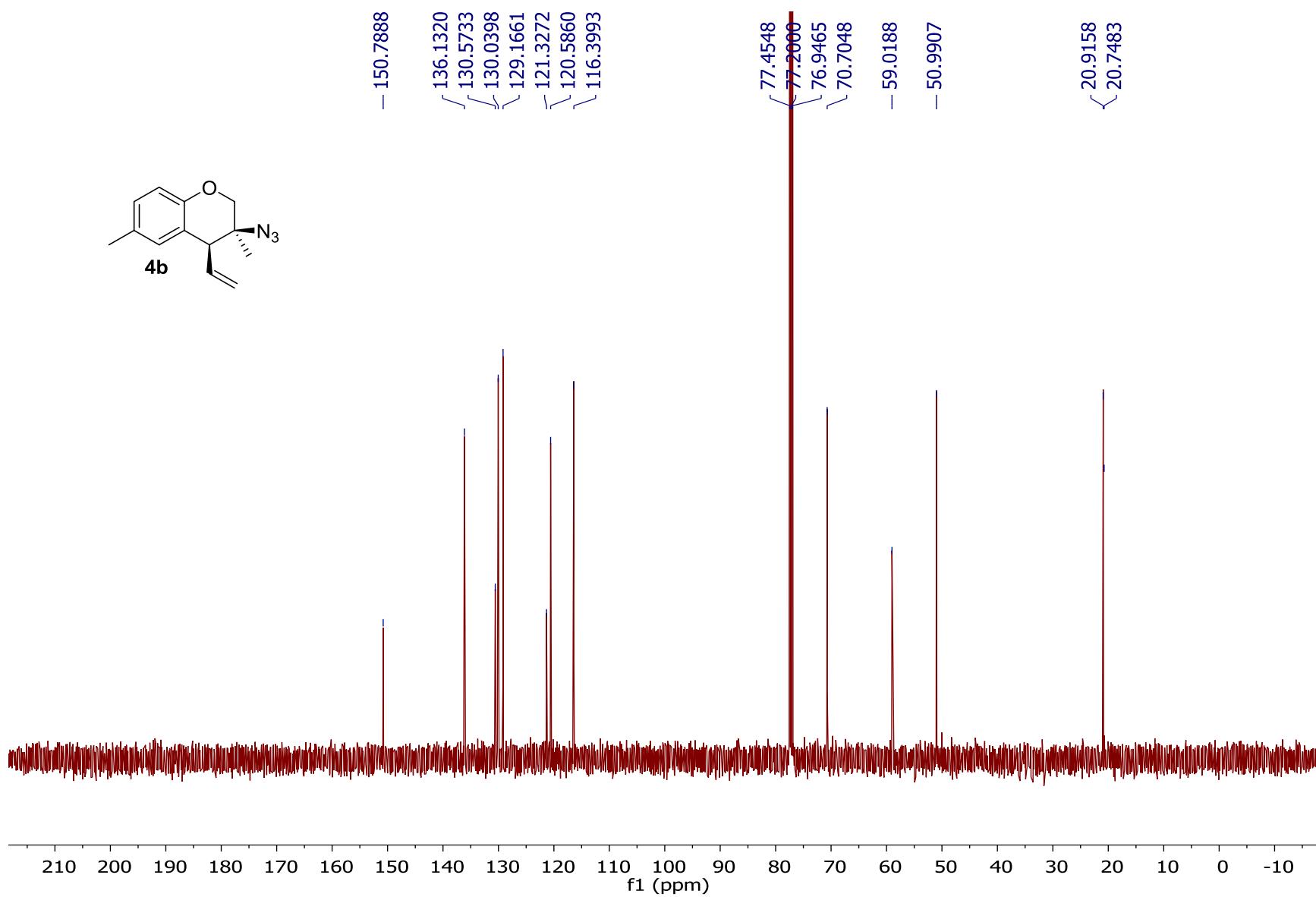


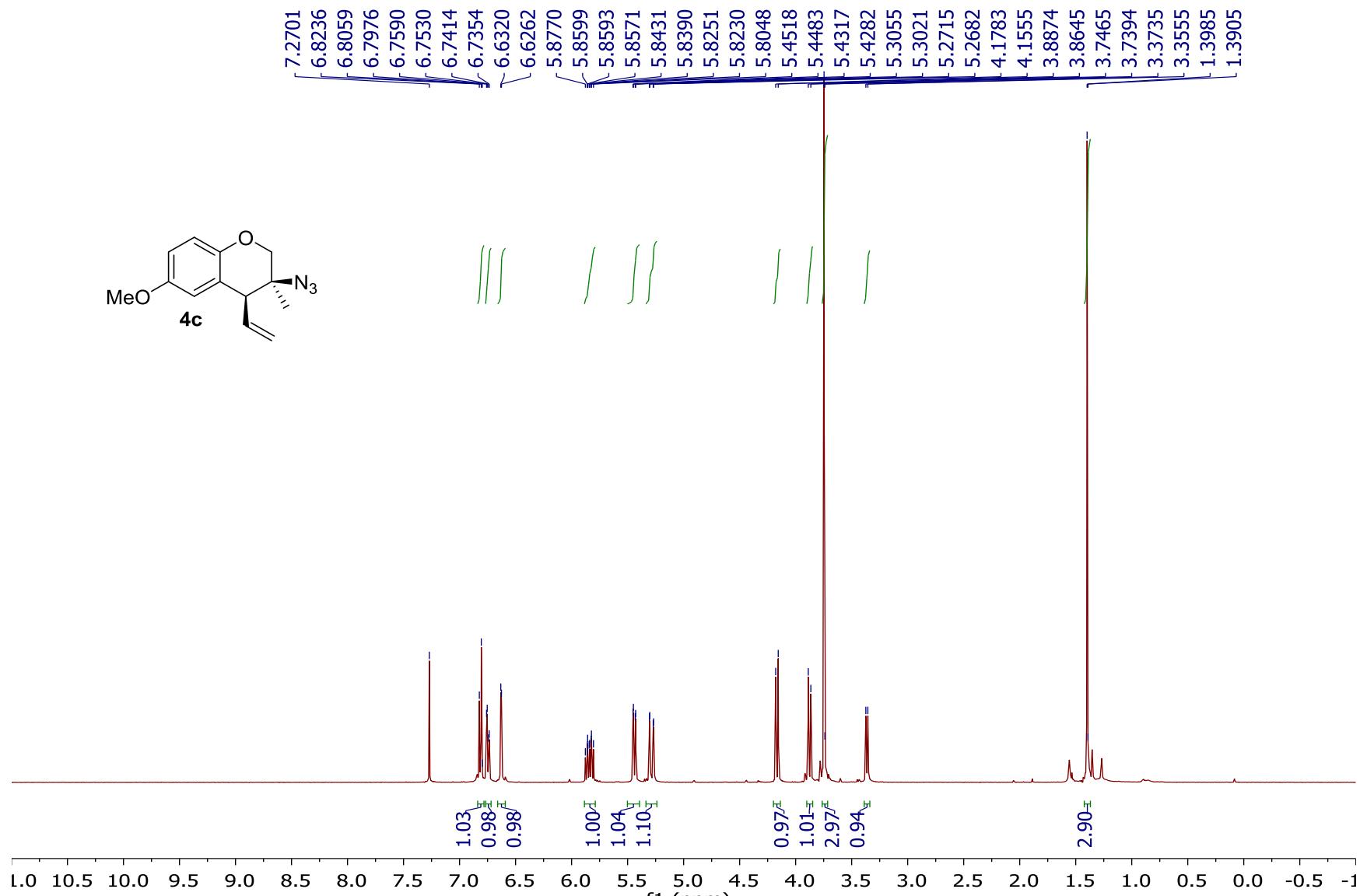
Compound 4a, 500 MHz ^1H NMR Spectrum in CDCl_3



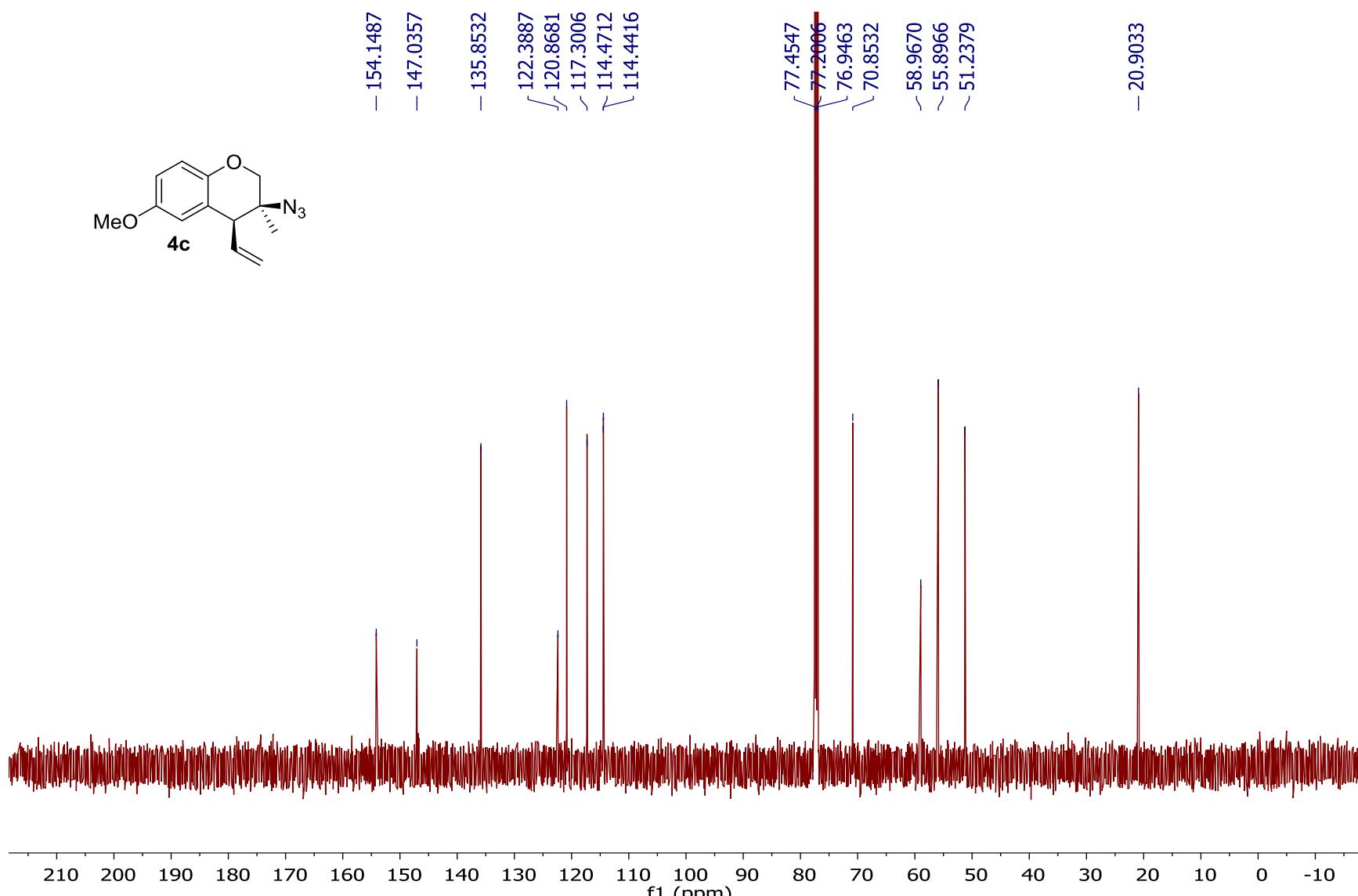
Compound 4a, 126 MHz ^{13}C NMR Spectrum in CDCl_3



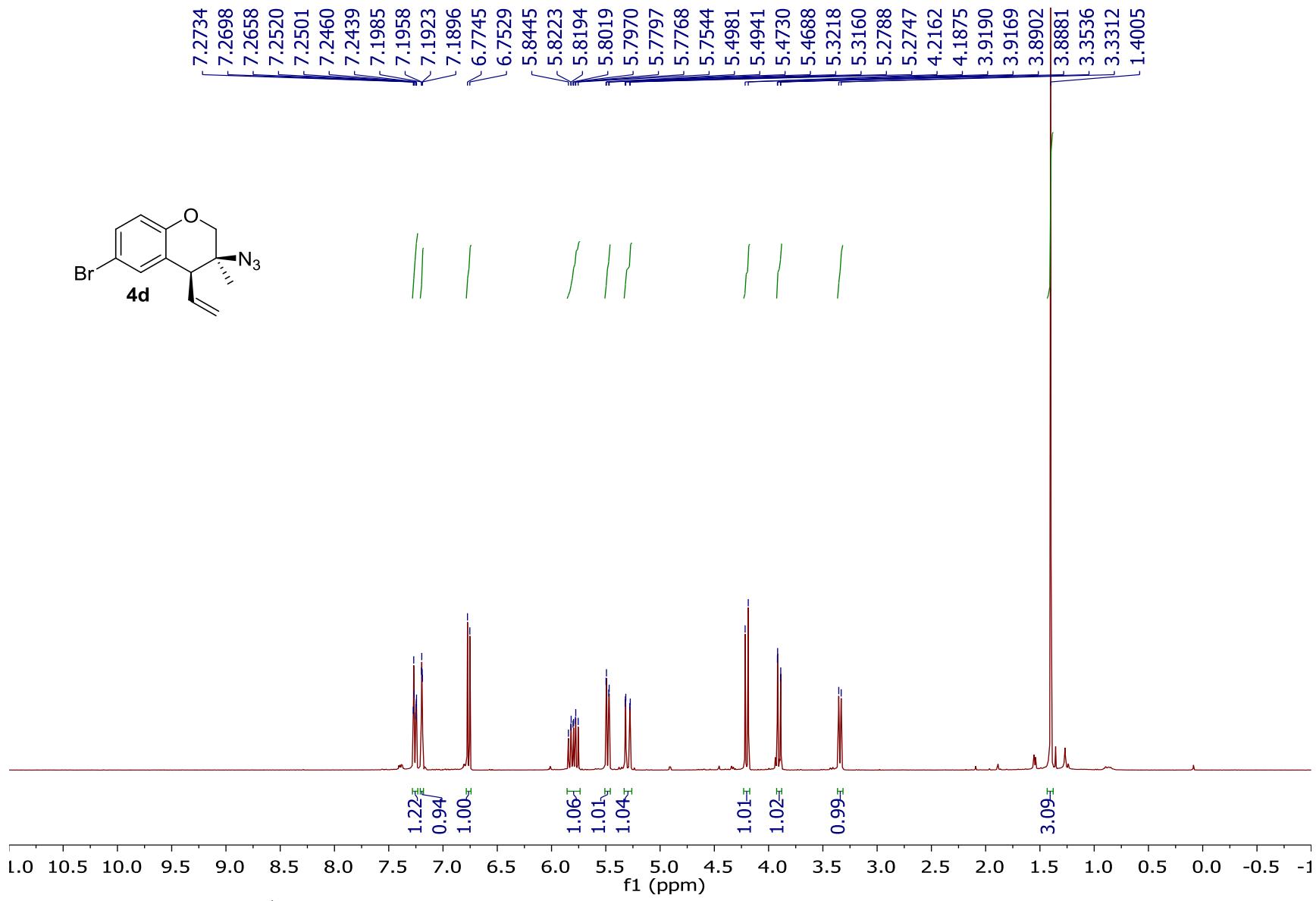
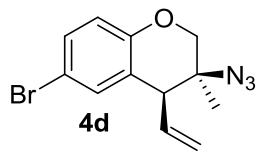




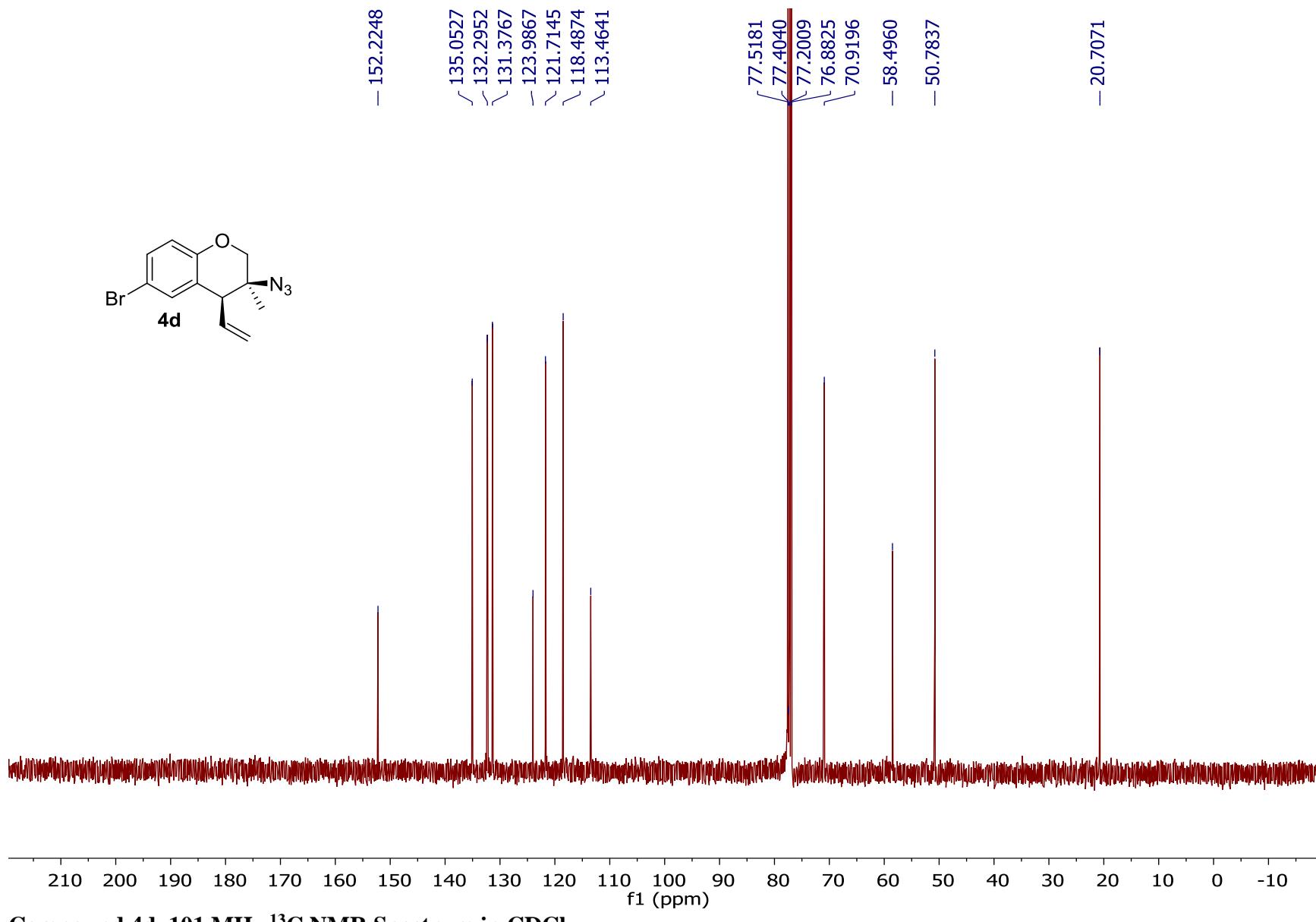
Compound 4c, 500 MHz ^1H NMR Spectrum in CDCl_3



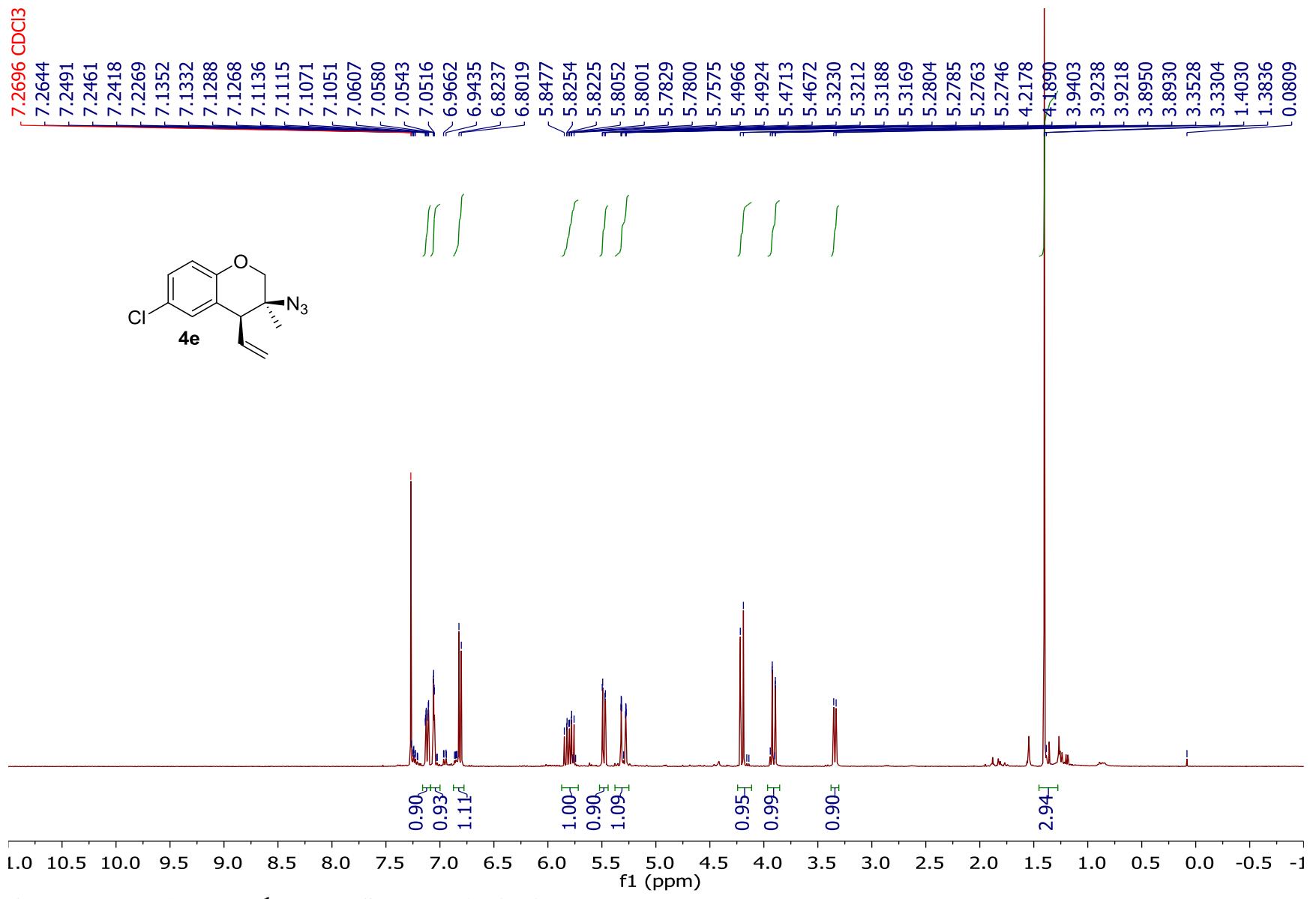
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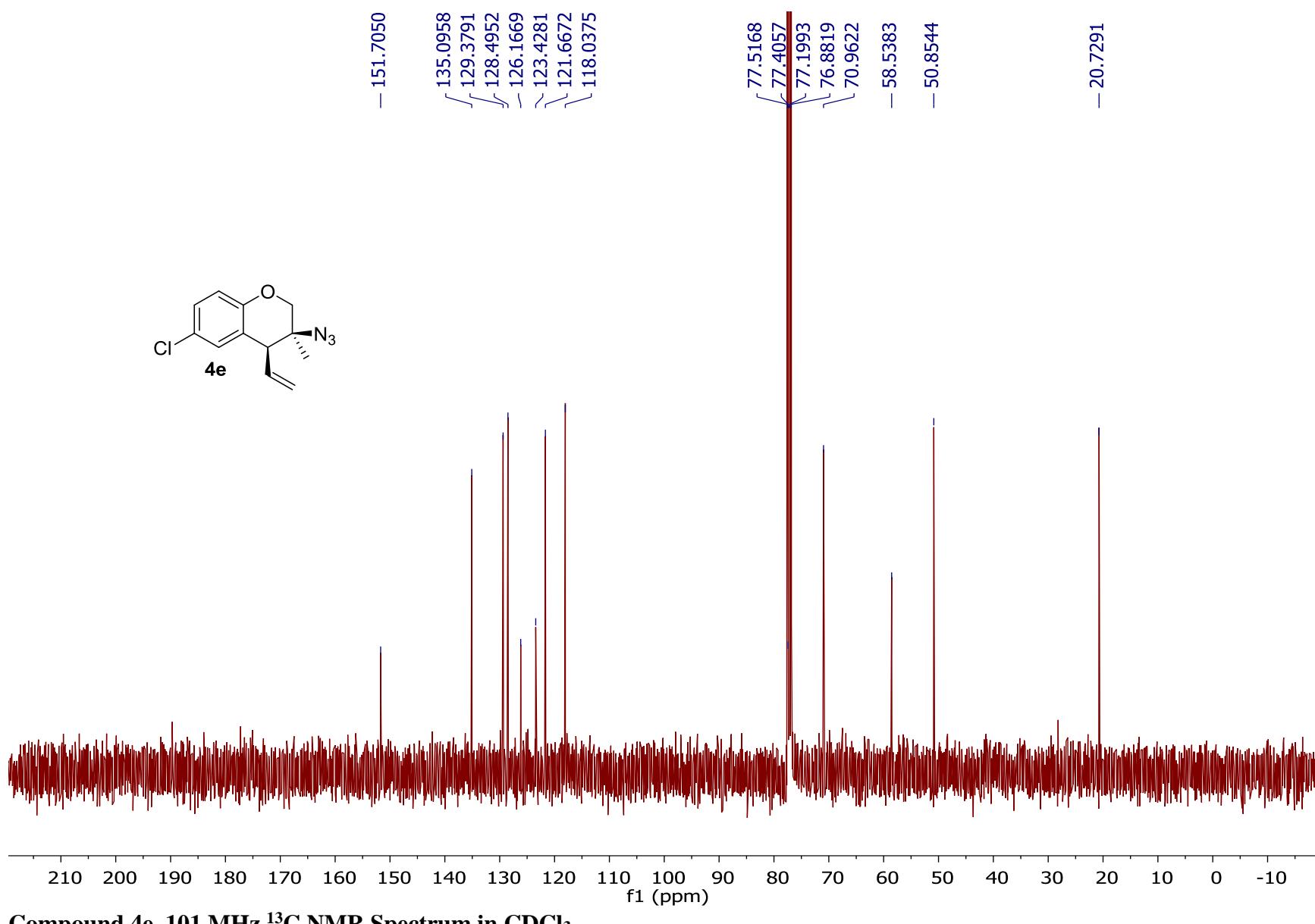
Compound 4d, 400 MHz ^1H NMR Spectrum in CDCl_3



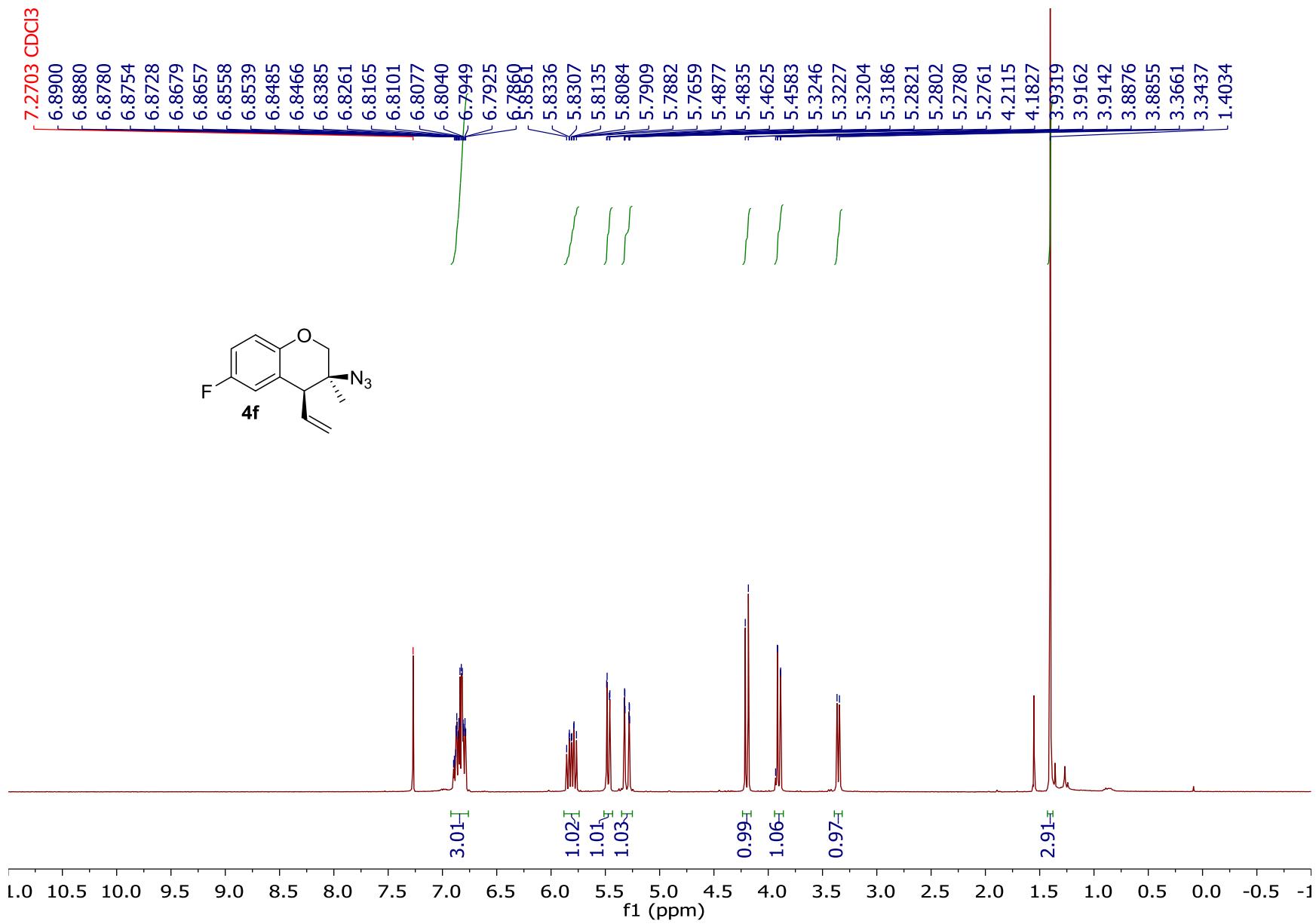
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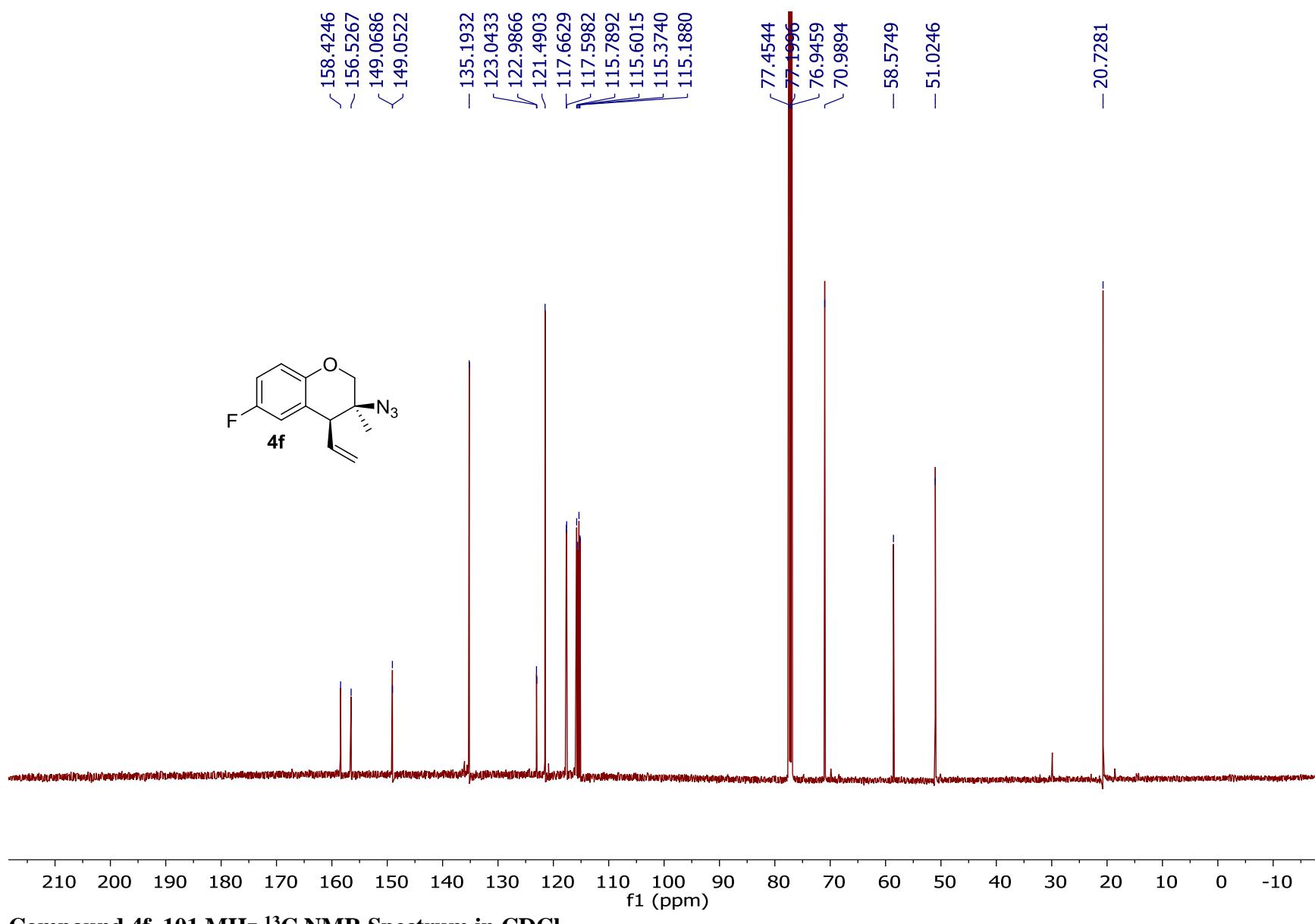
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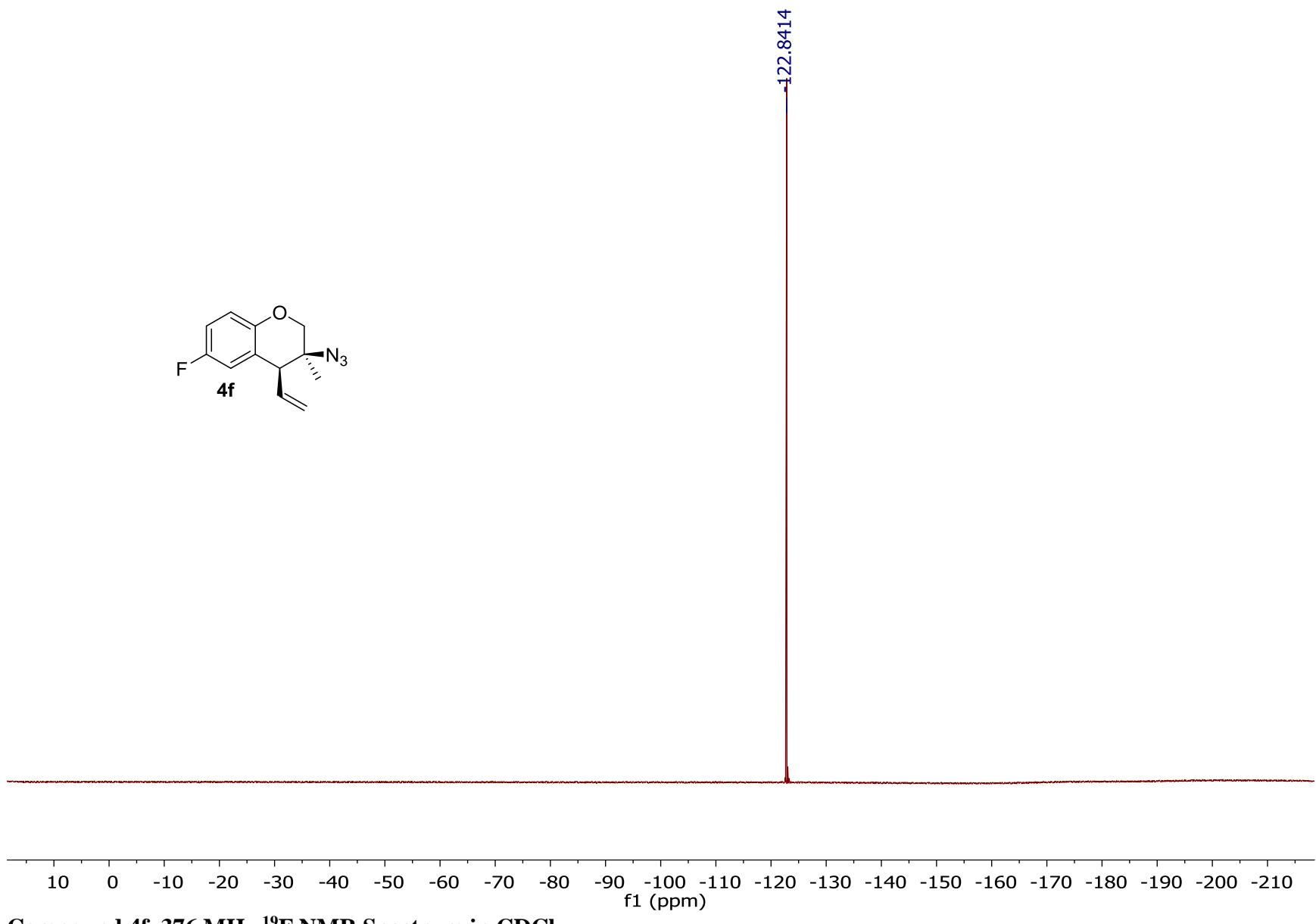
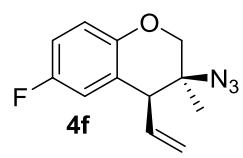
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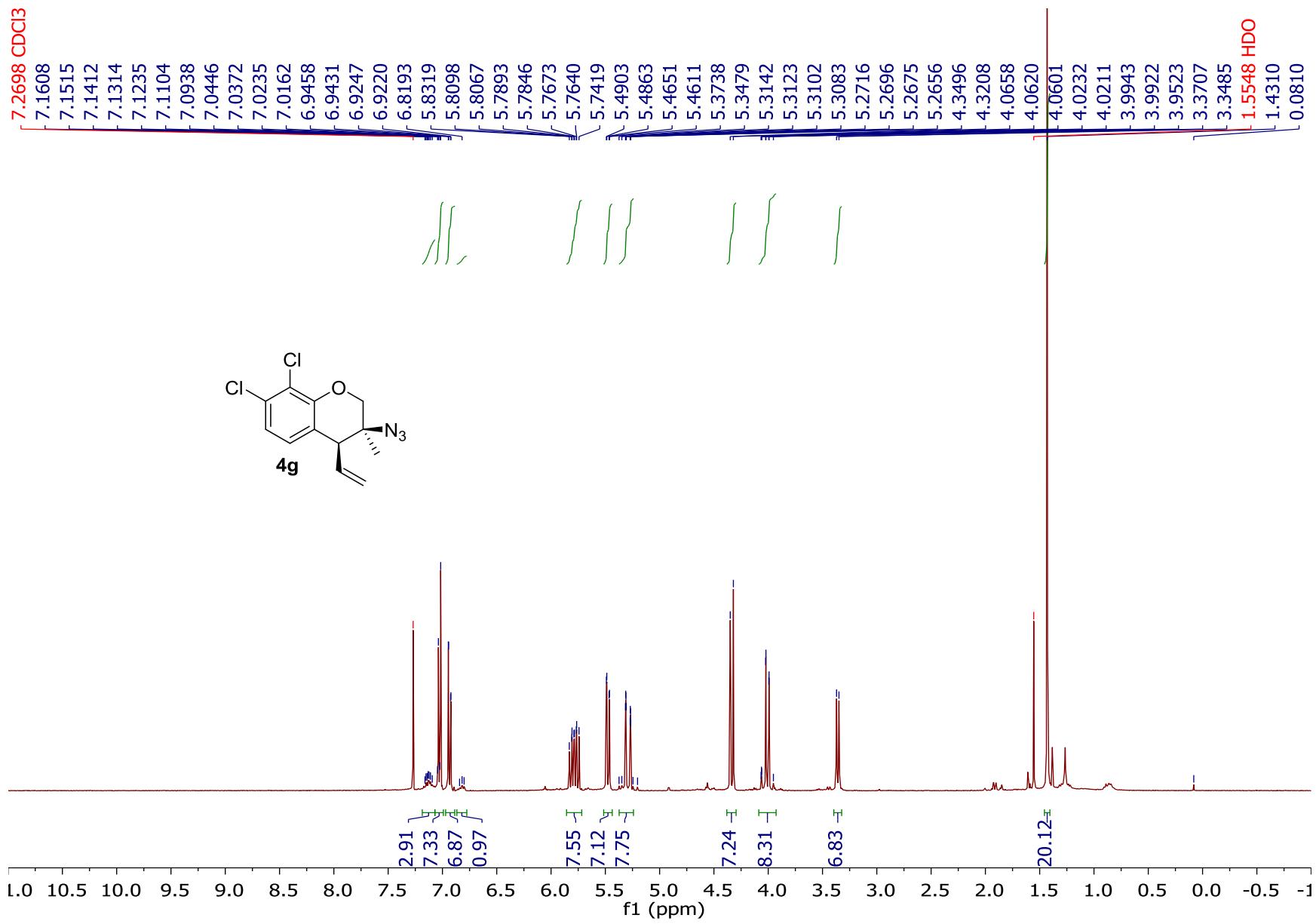
Compound 4f, 400 MHz ¹H NMR Spectrum in CDCl₃



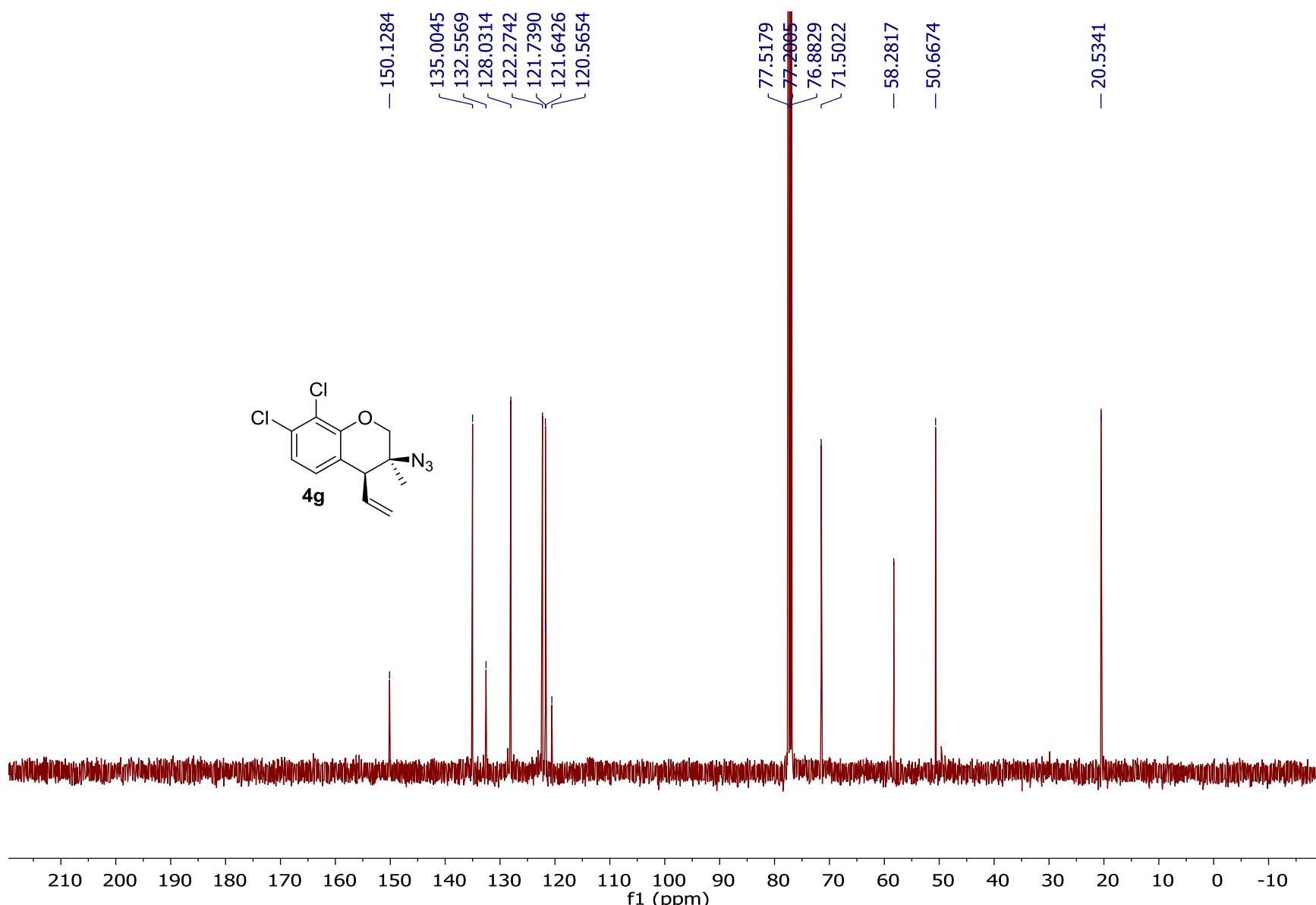
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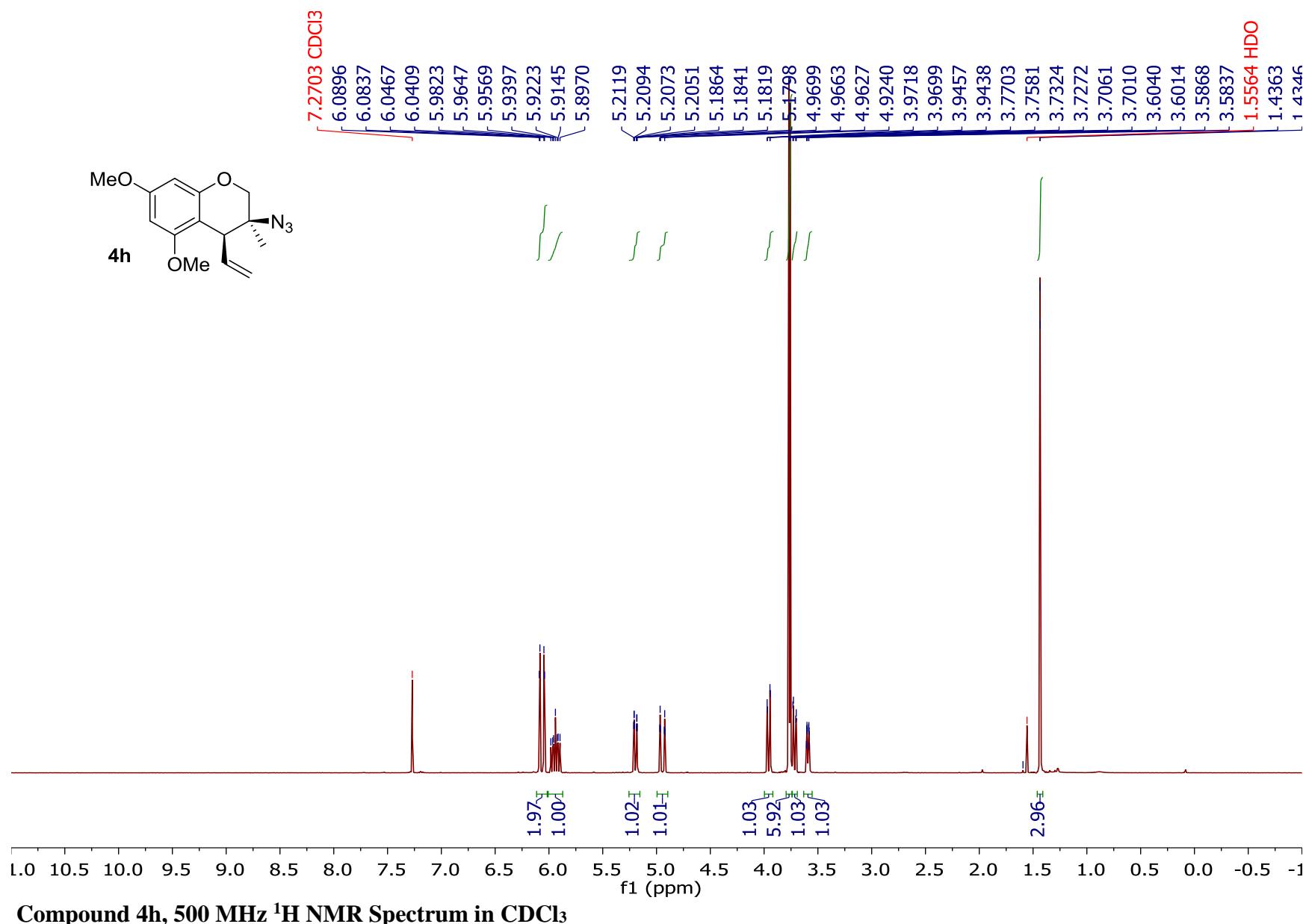
Compound 4f, 376 MHz ^{19}F NMR Spectrum in CDCl_3

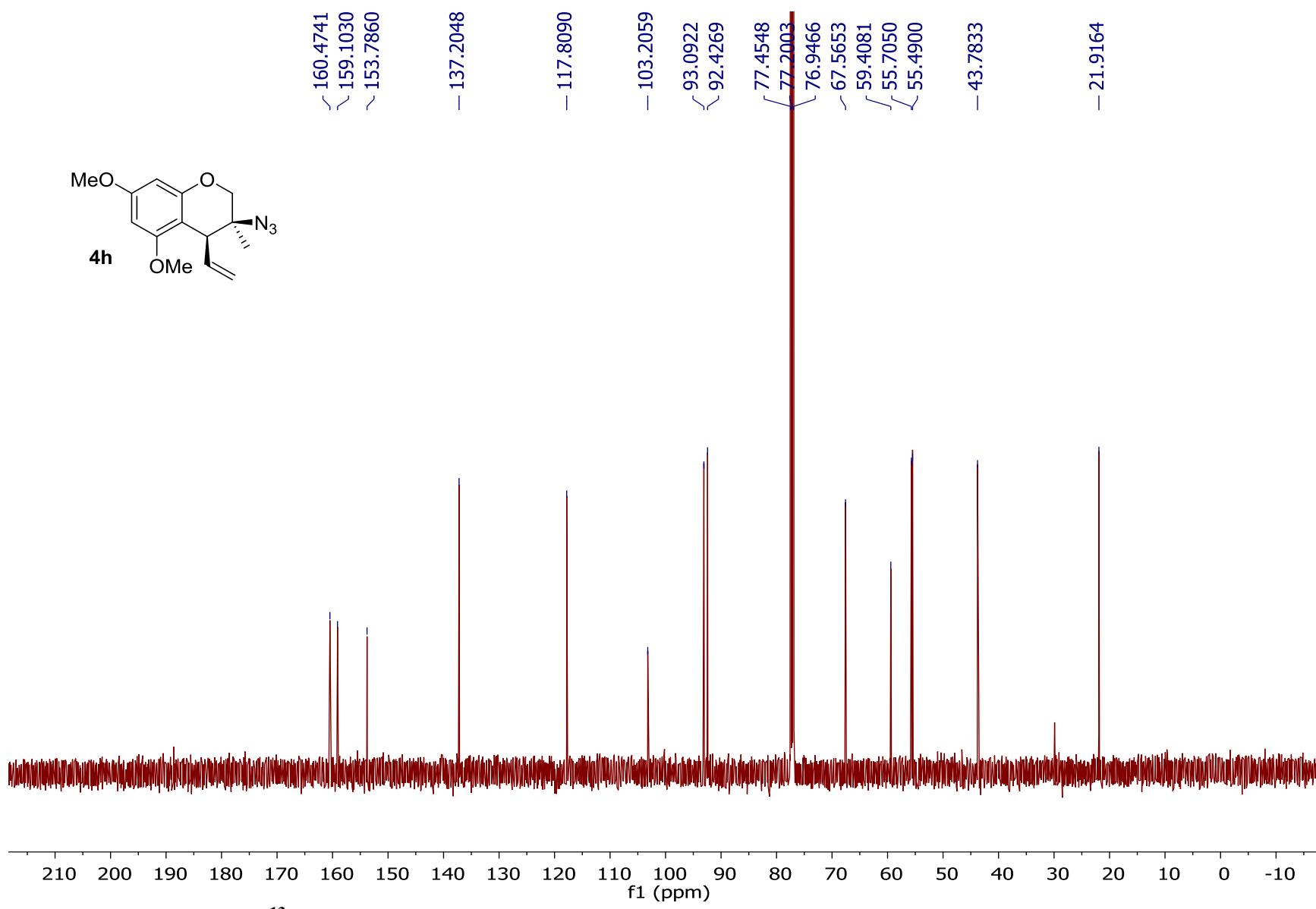


Compound 4g, 400 MHz ¹H NMR Spectrum in CDCl₃

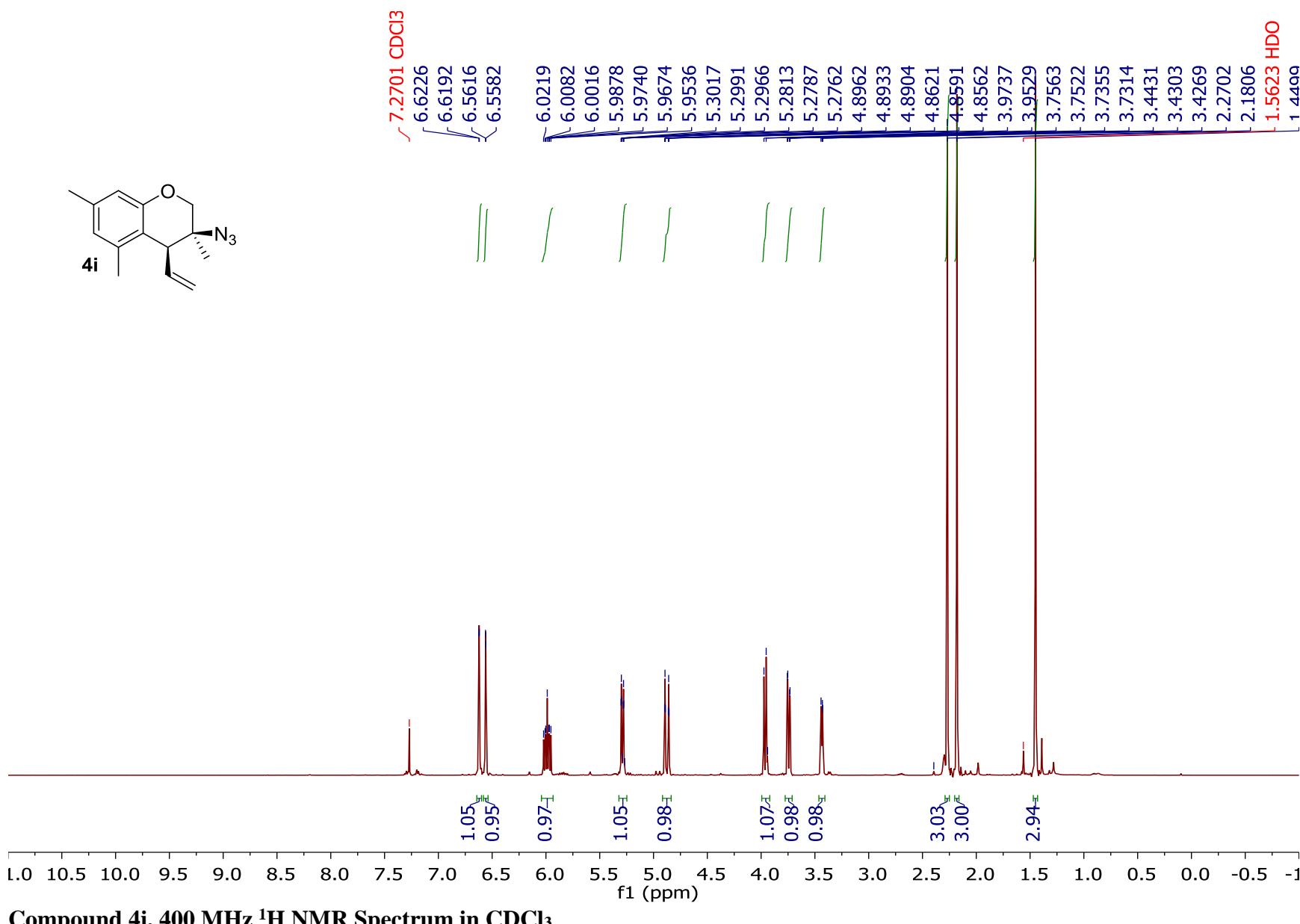


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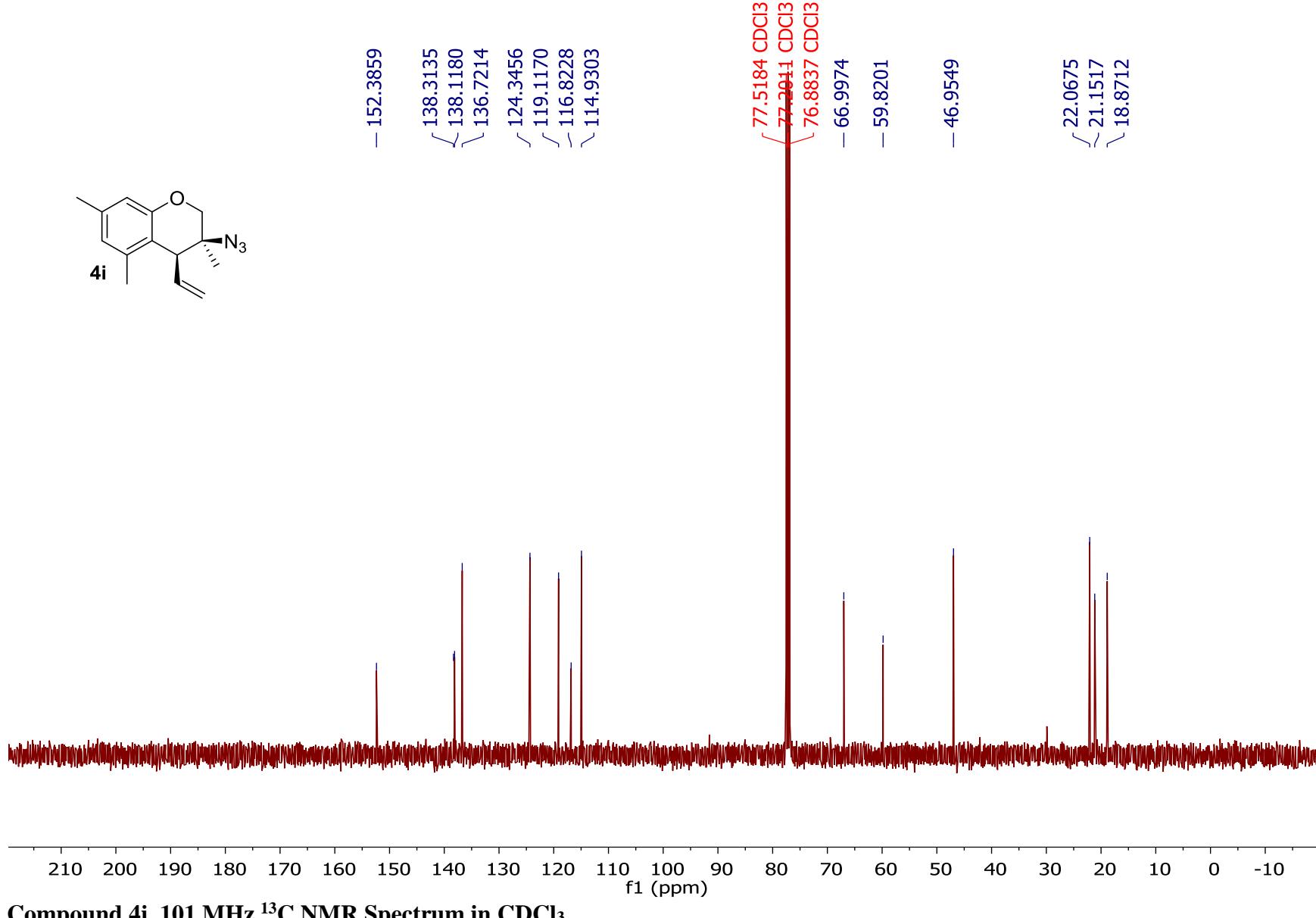




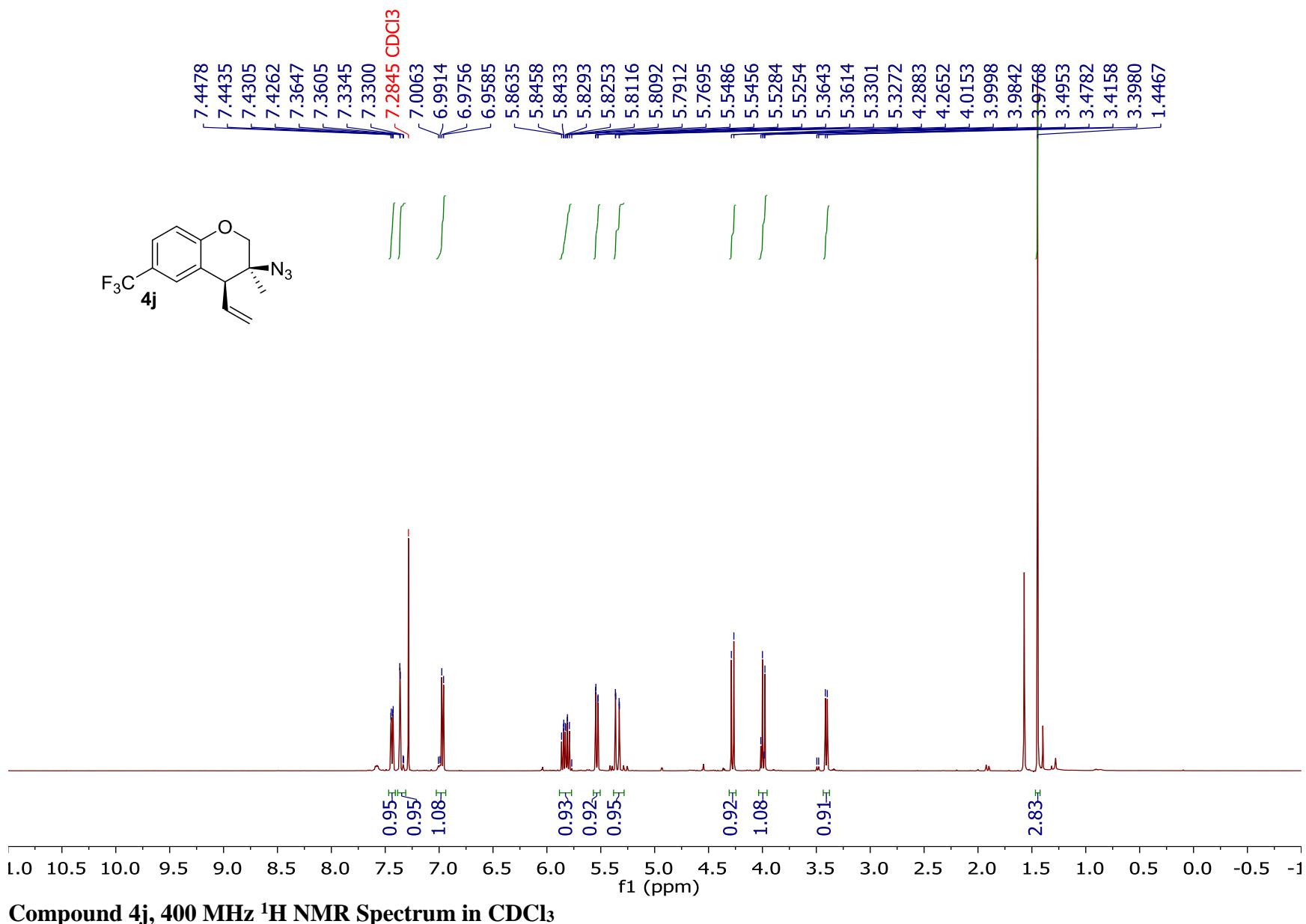
Compound 4h, 126 MHz ^{13}C NMR Spectrum in CDCl_3

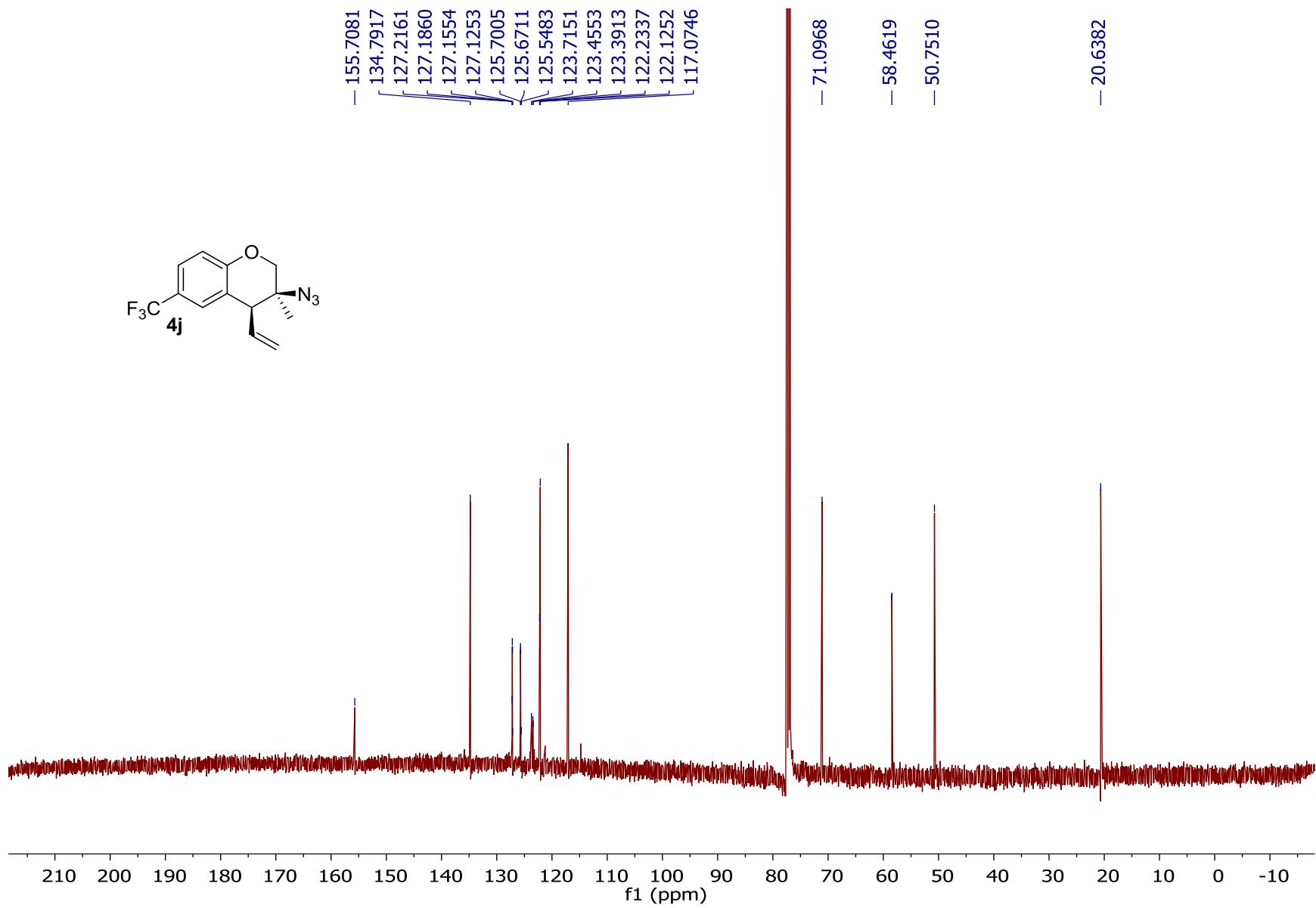


Compound 4i, 400 MHz ^1H NMR Spectrum in CDCl₃

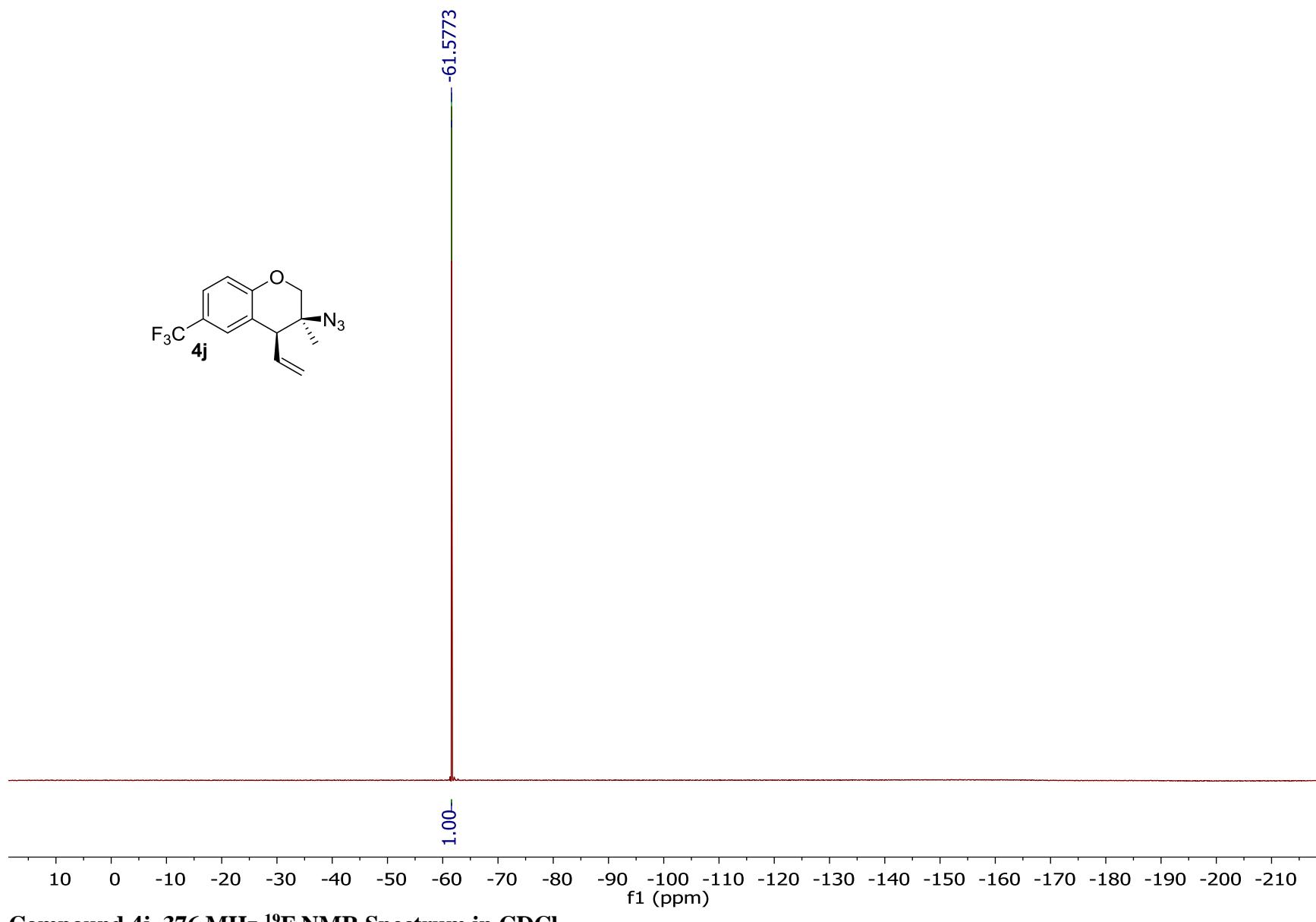


Compound 4i, 101 MHz ^{13}C NMR Spectrum in CDCl_3



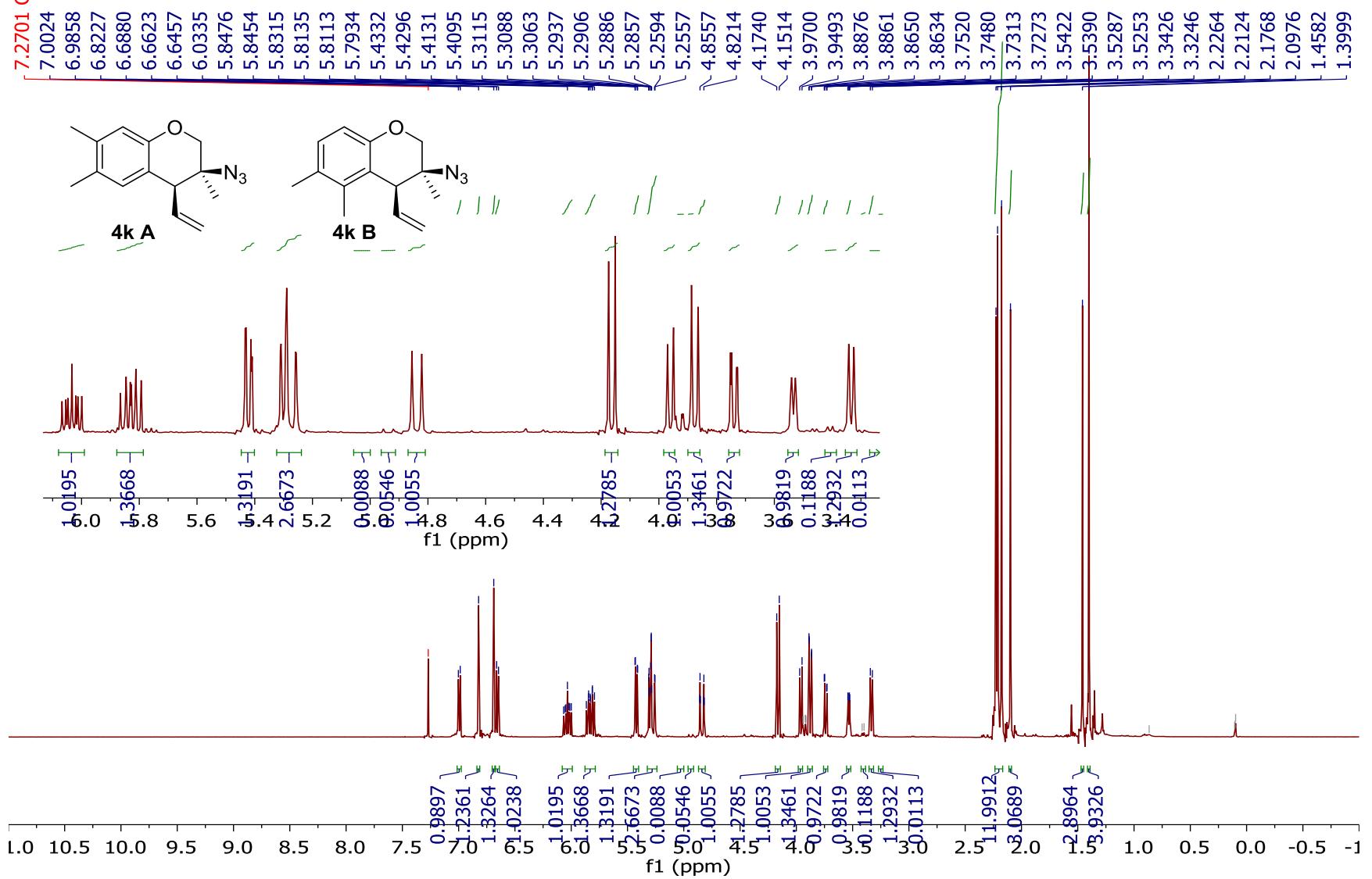


Compound 4j, 101 MHz ^{13}C NMR Spectrum in CDCl_3

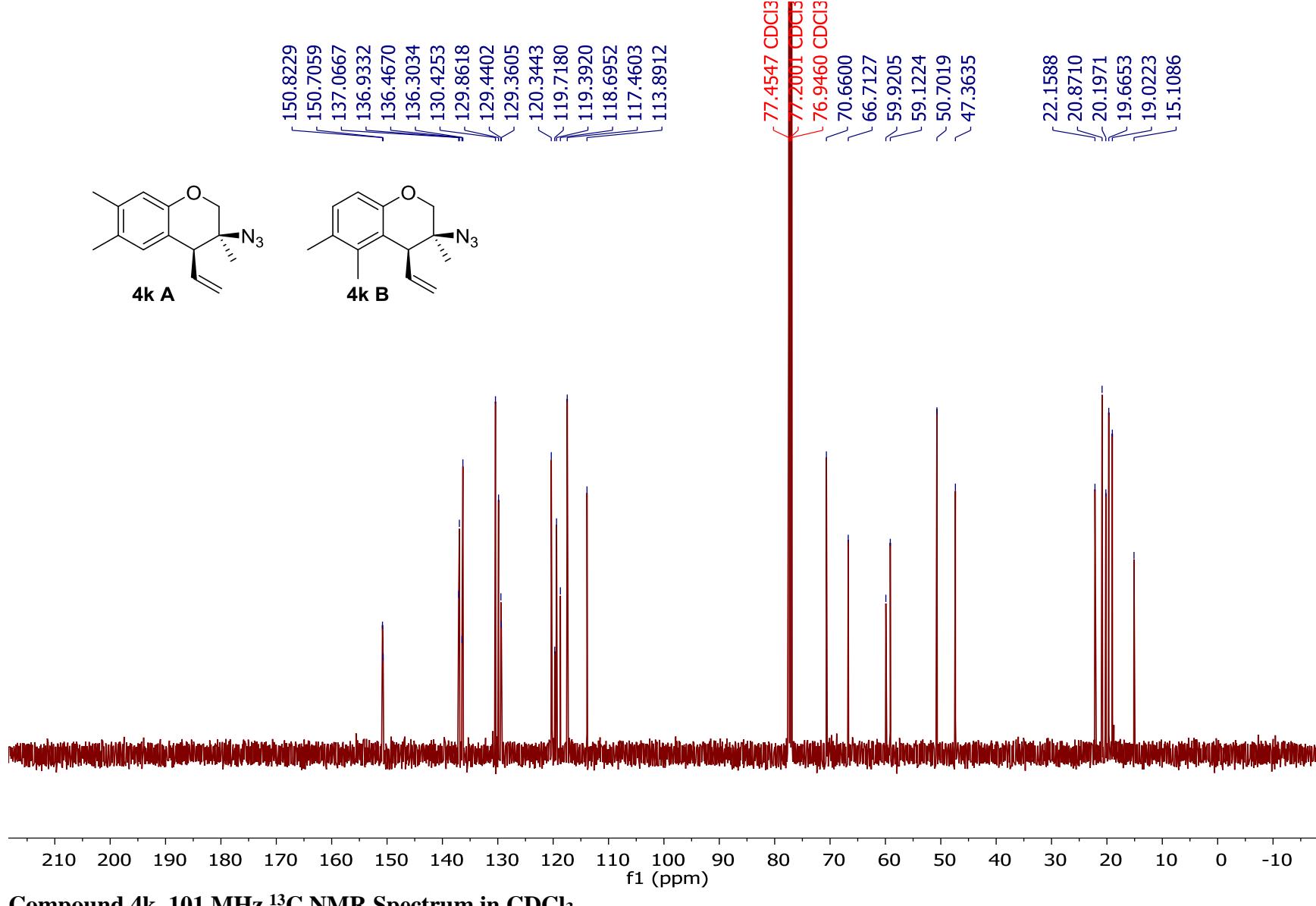


Compound 4j, 376 MHz ^{19}F NMR Spectrum in CDCl_3

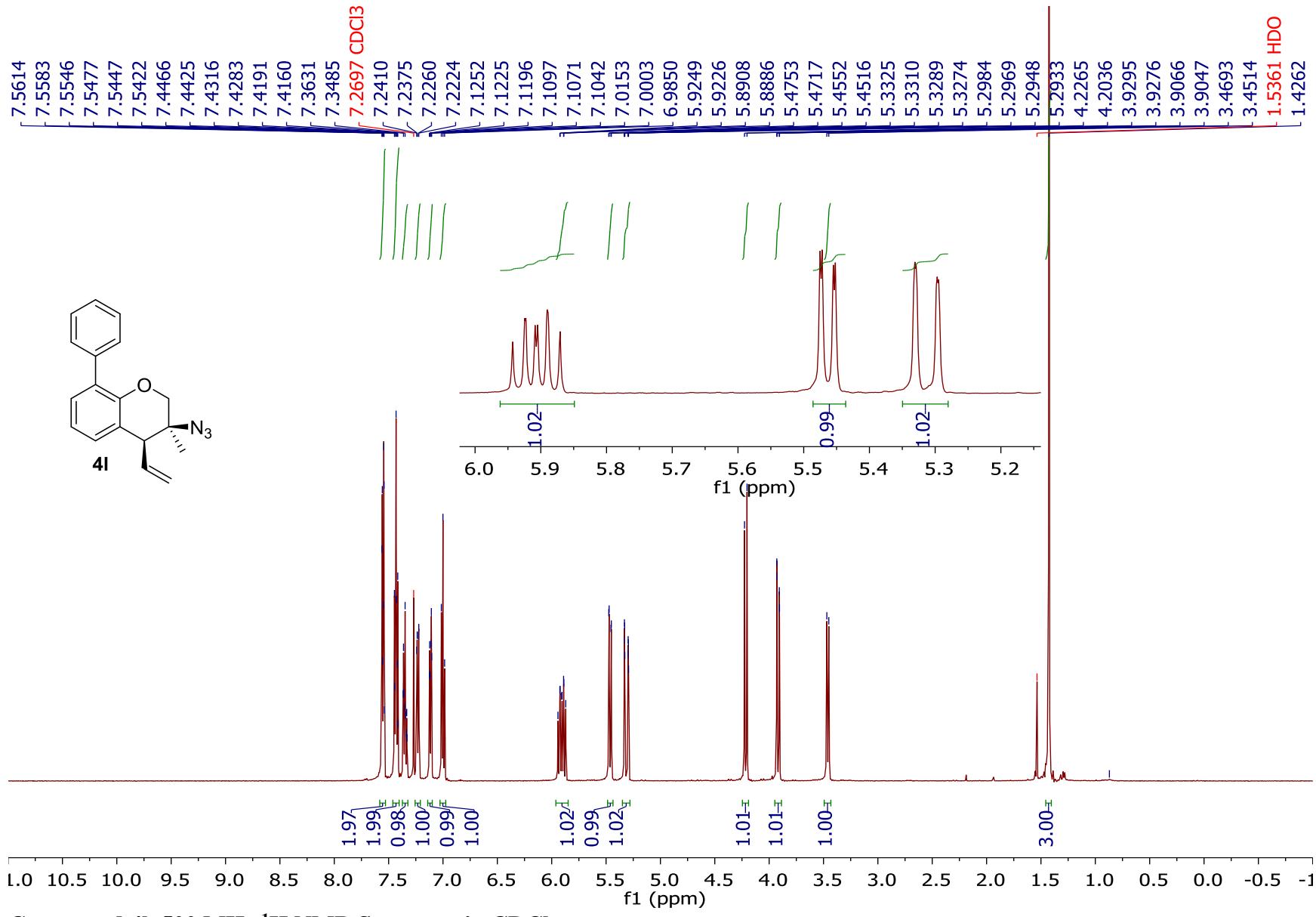
- 7.2701 CDCl₃

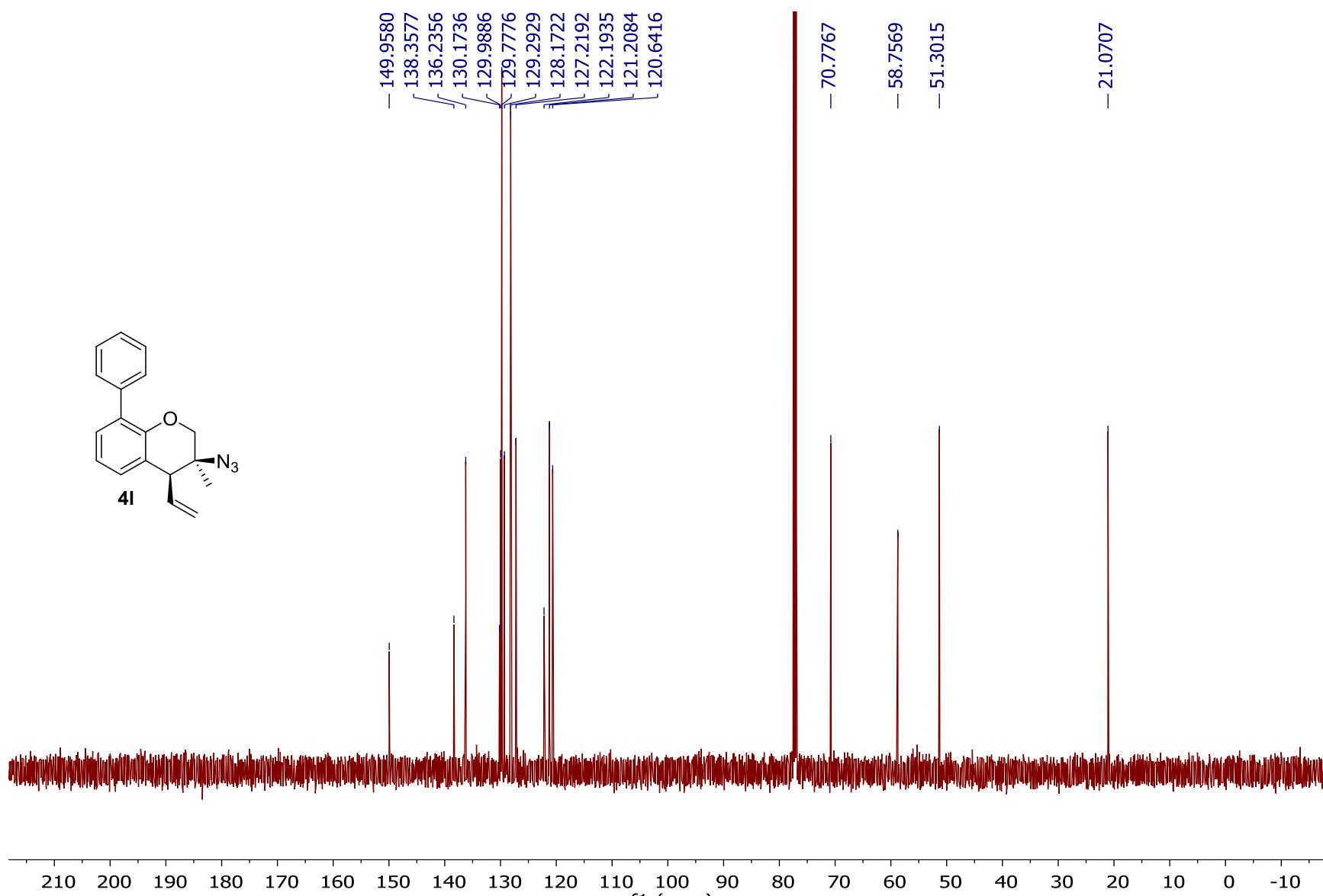


Compound 4k, 400 MHz ^1H NMR Spectrum in CDCl_3

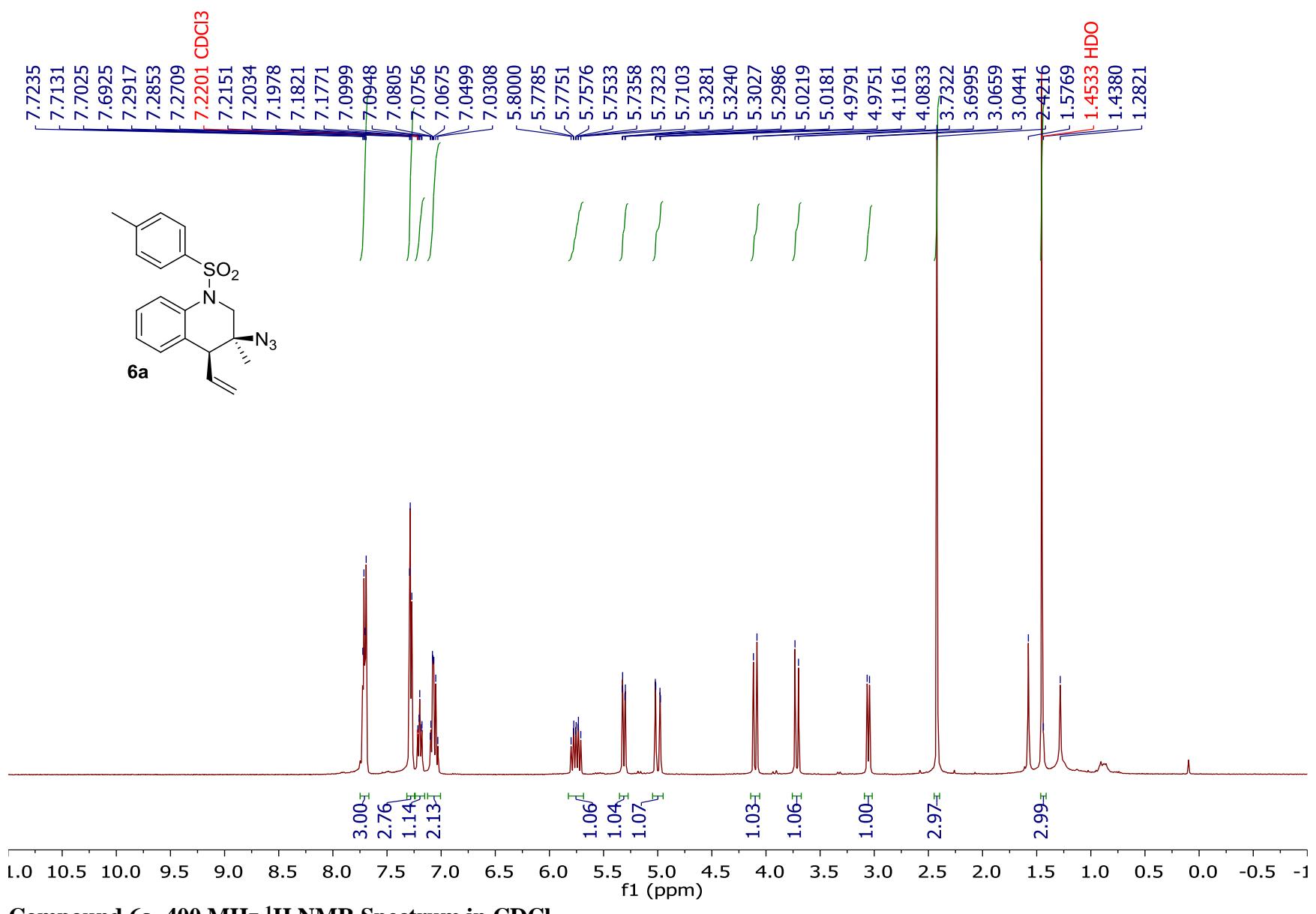


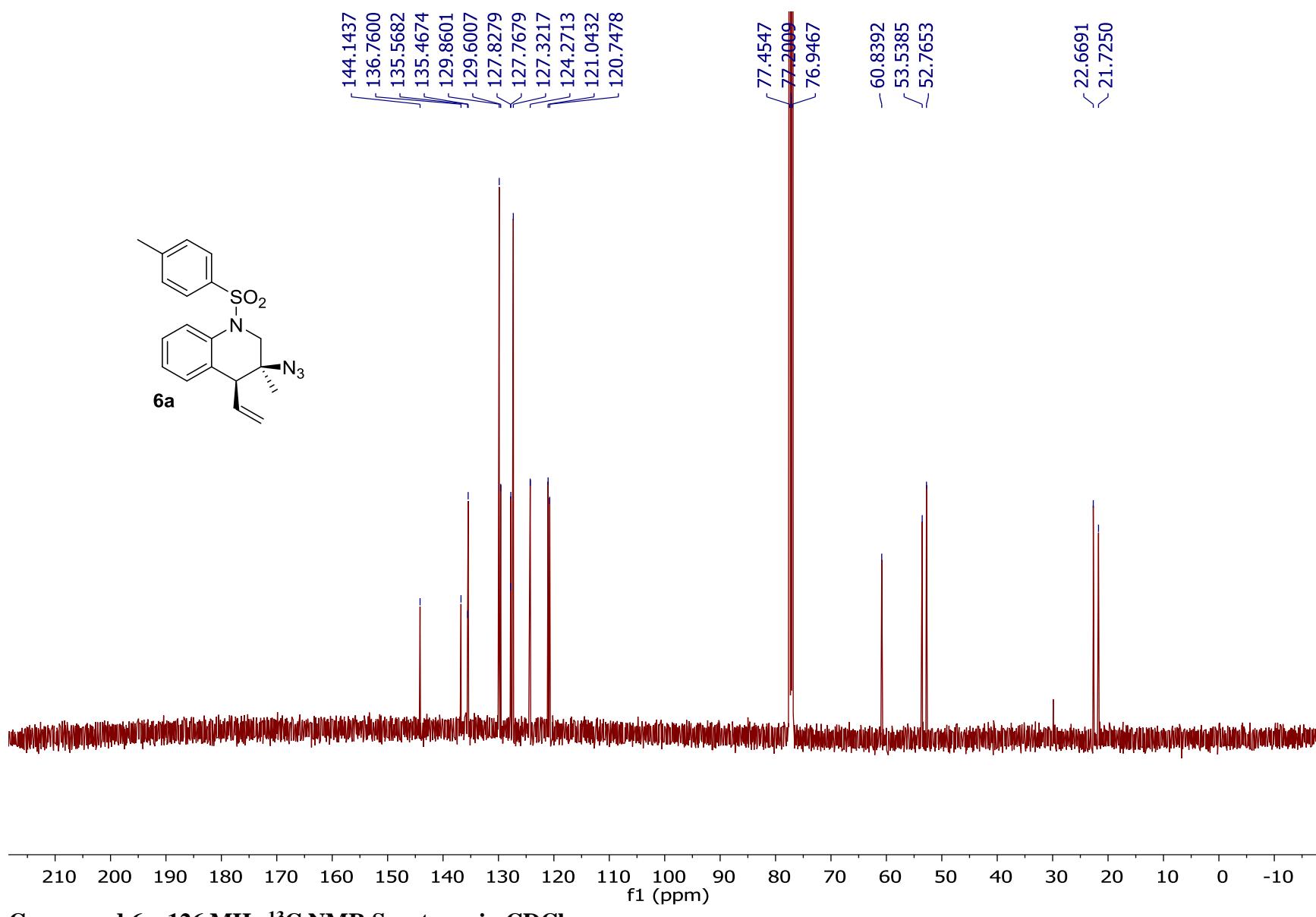
Compound 4k, 101 MHz ¹³C NMR Spectrum in CDCl₃



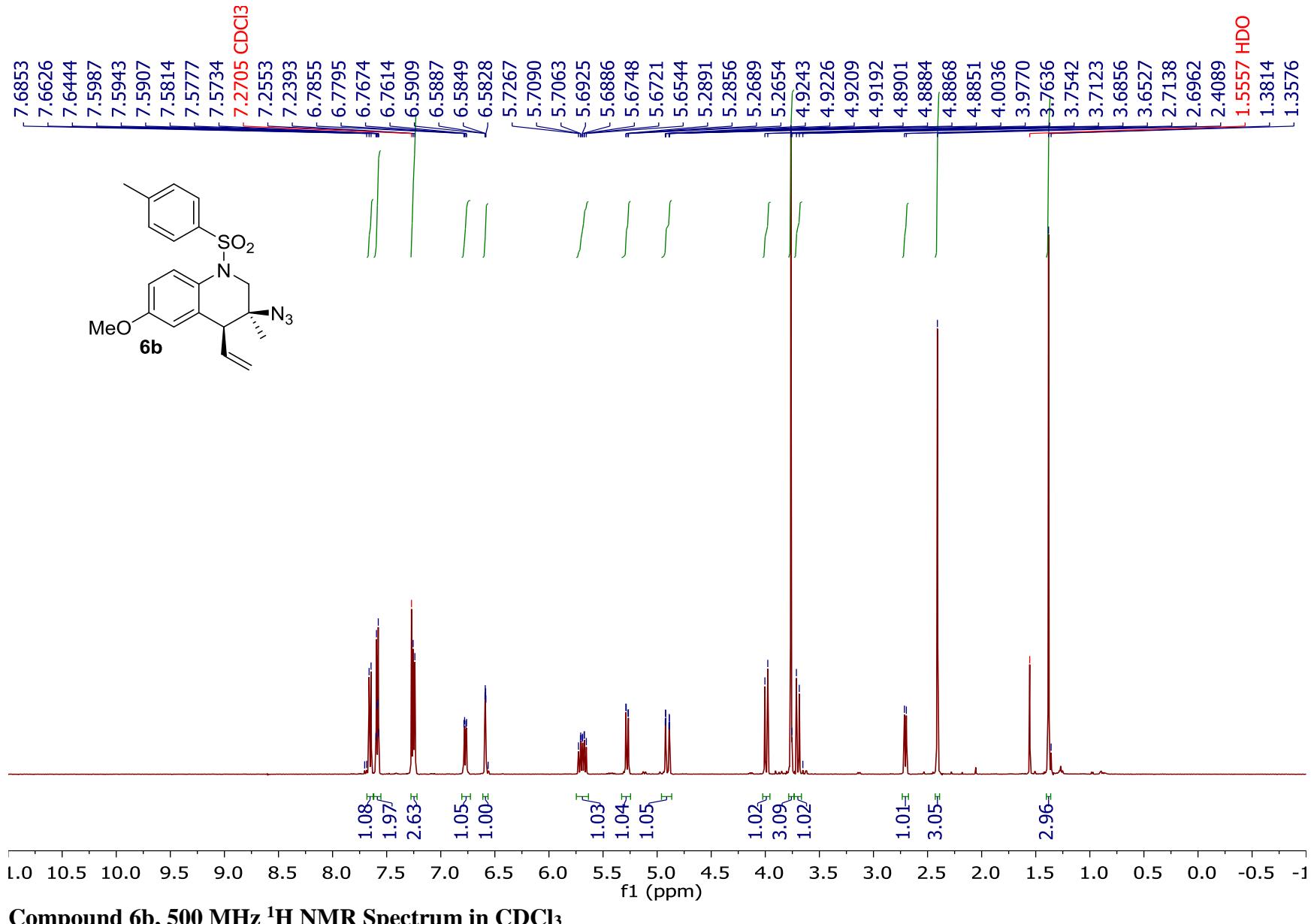


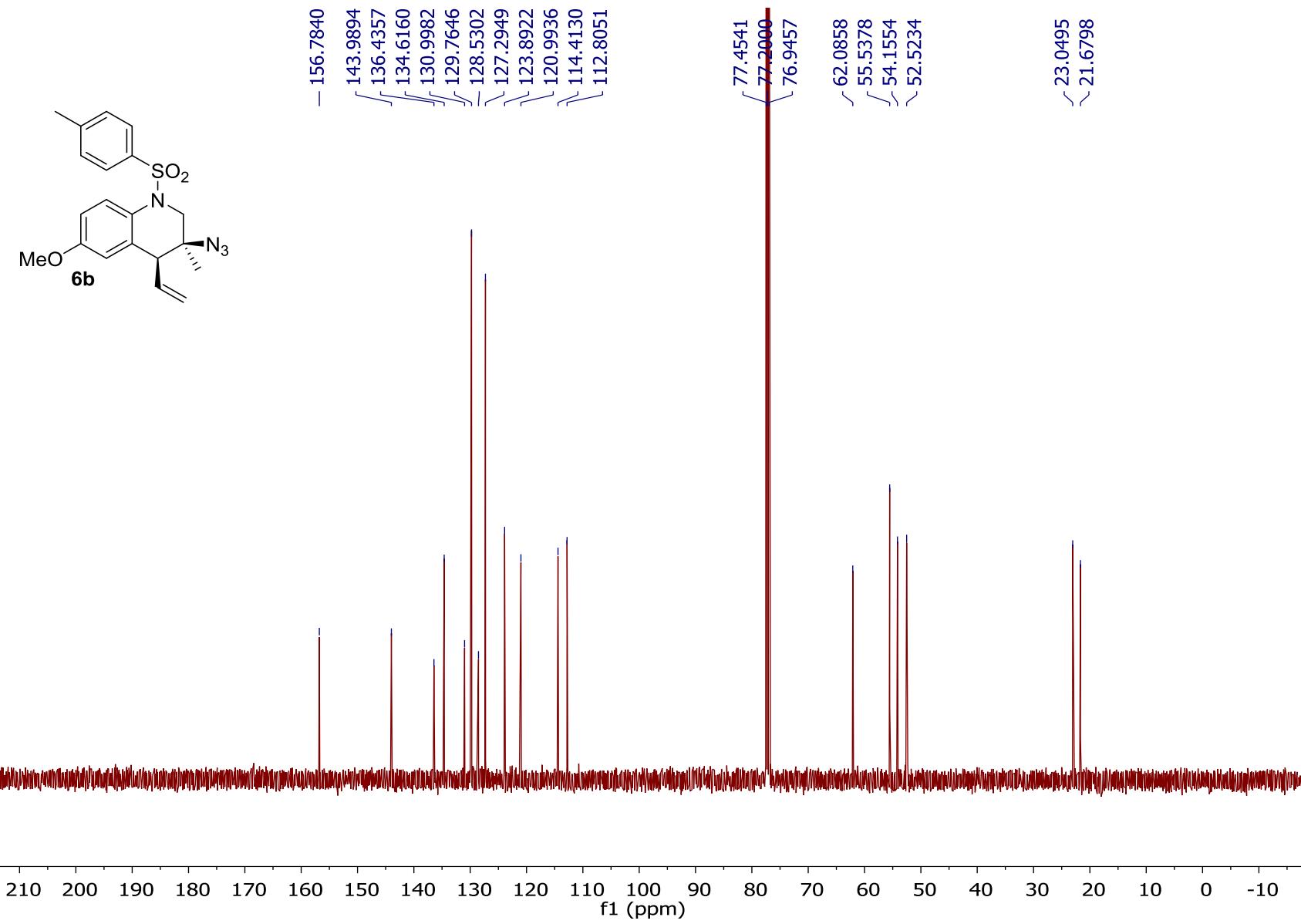
Compound 4l, 126 MHz ^{13}C NMR Spectrum in CDCl_3



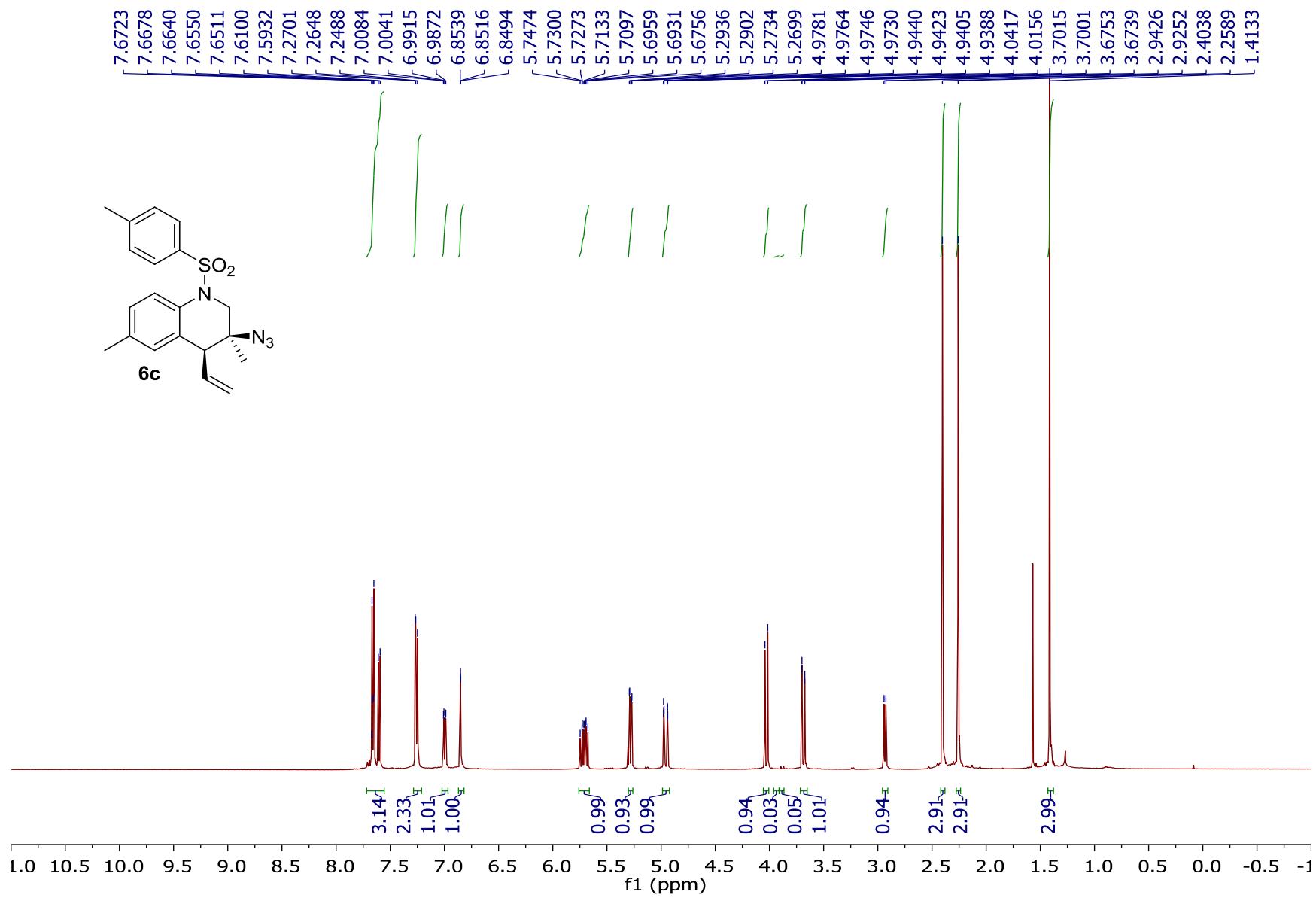
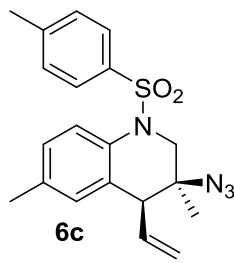


Compound 6a, 126 MHz ^{13}C NMR Spectrum in CDCl_3

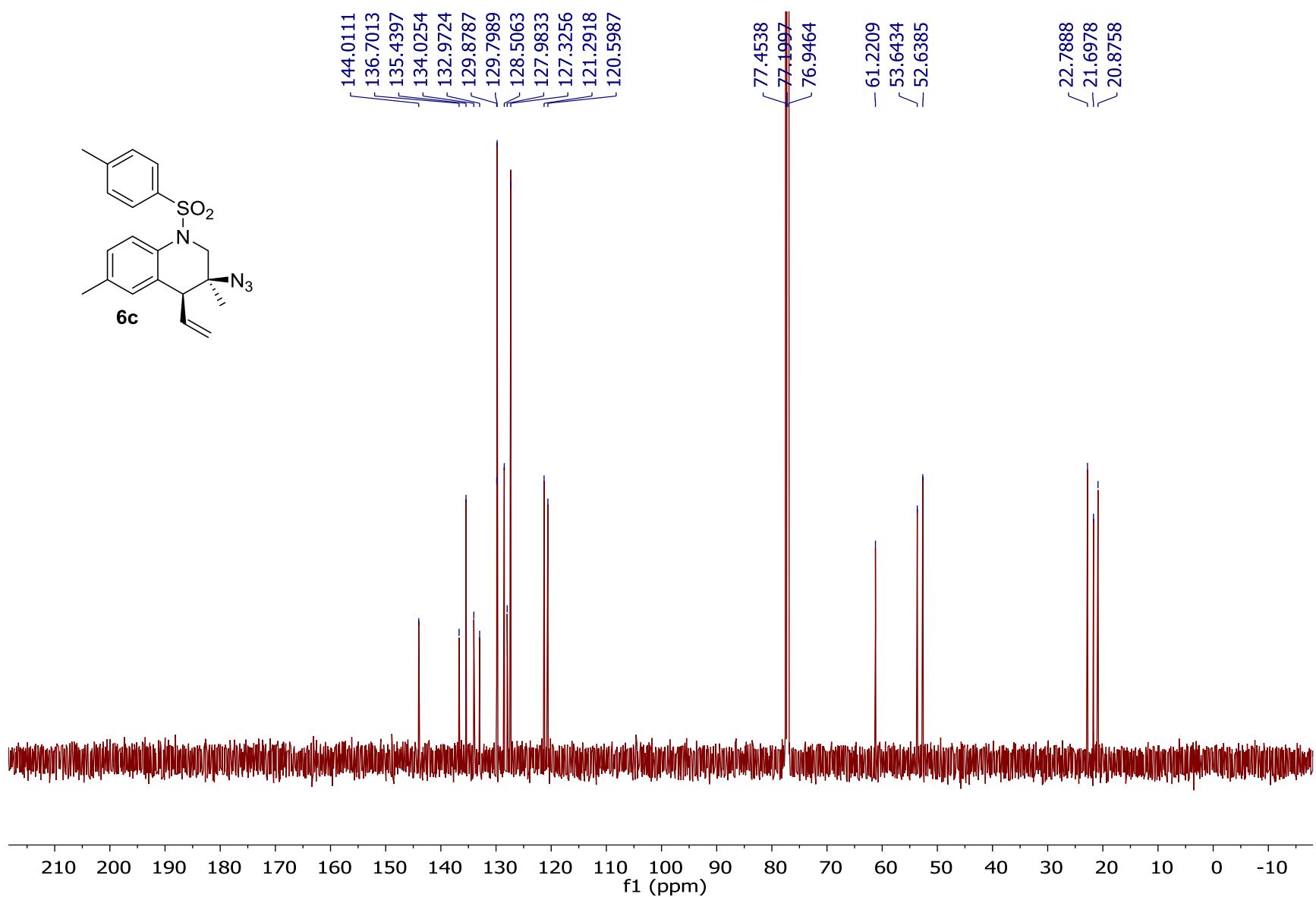




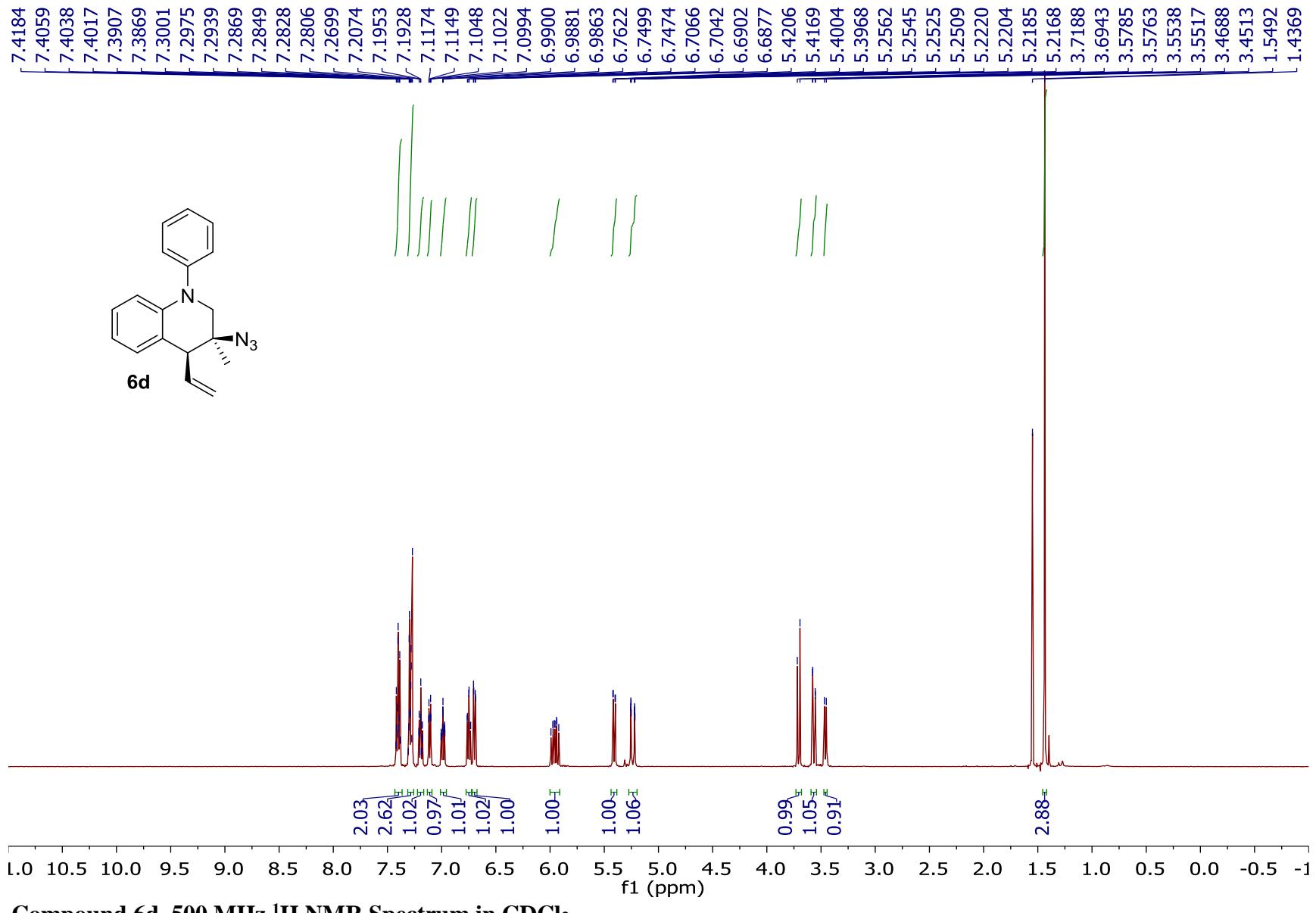
Compound 6b, 126 MHz ^{13}C NMR Spectrum in CDCl_3



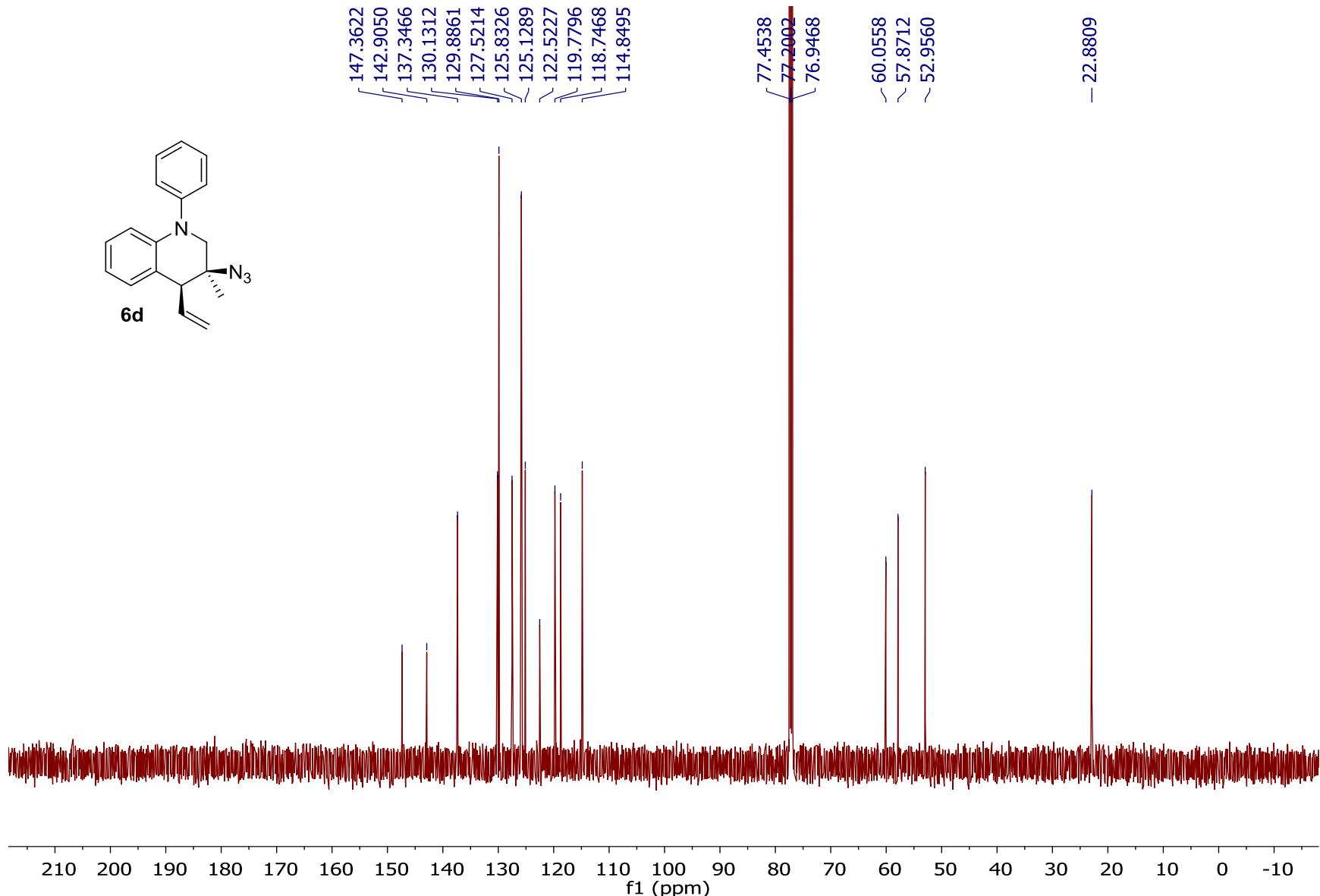
Compound 6c, 500 MHz ^1H NMR Spectrum in CDCl_3



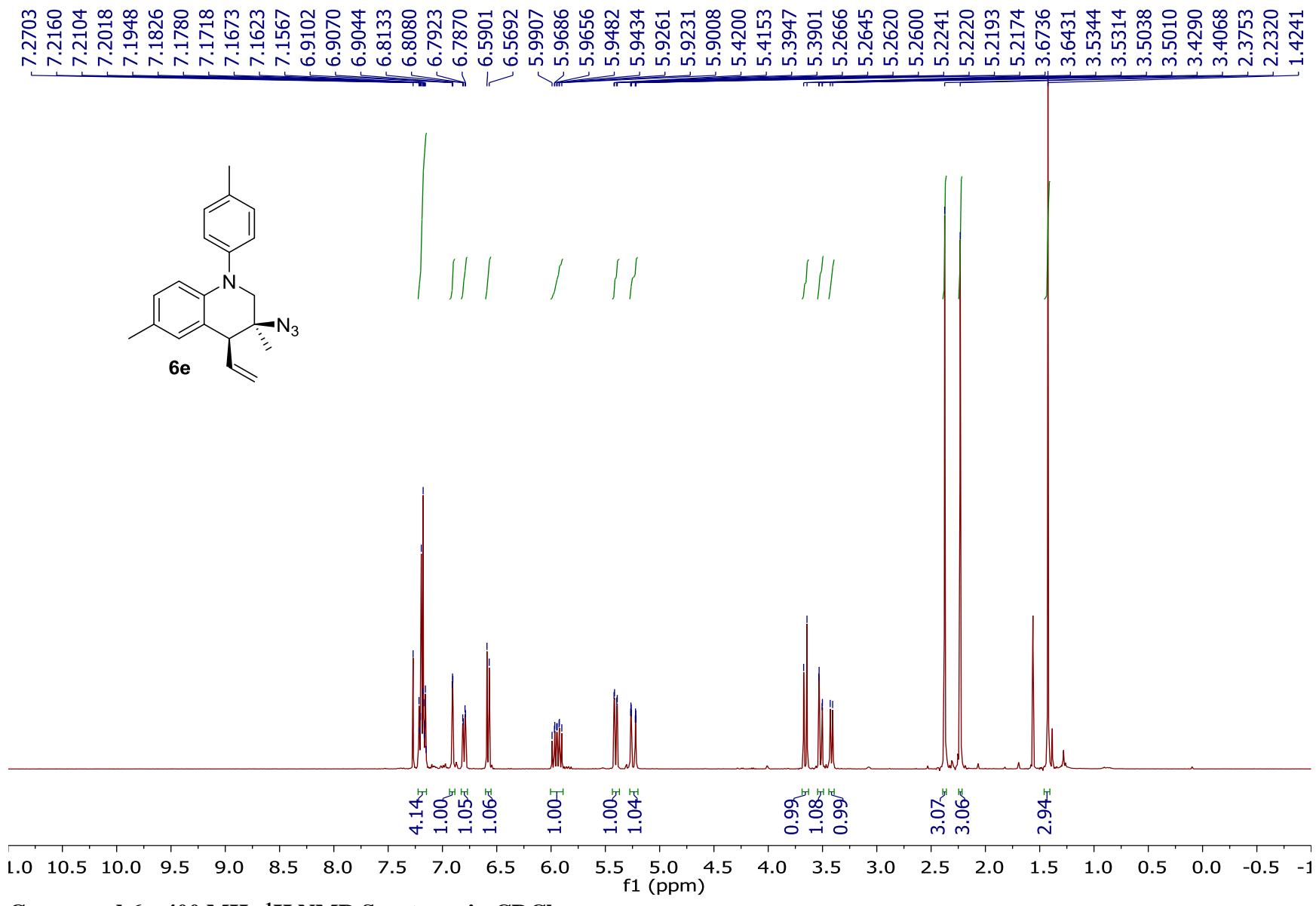
Compound 6c, 126 MHz ^{13}C NMR Spectrum in CDCl_3



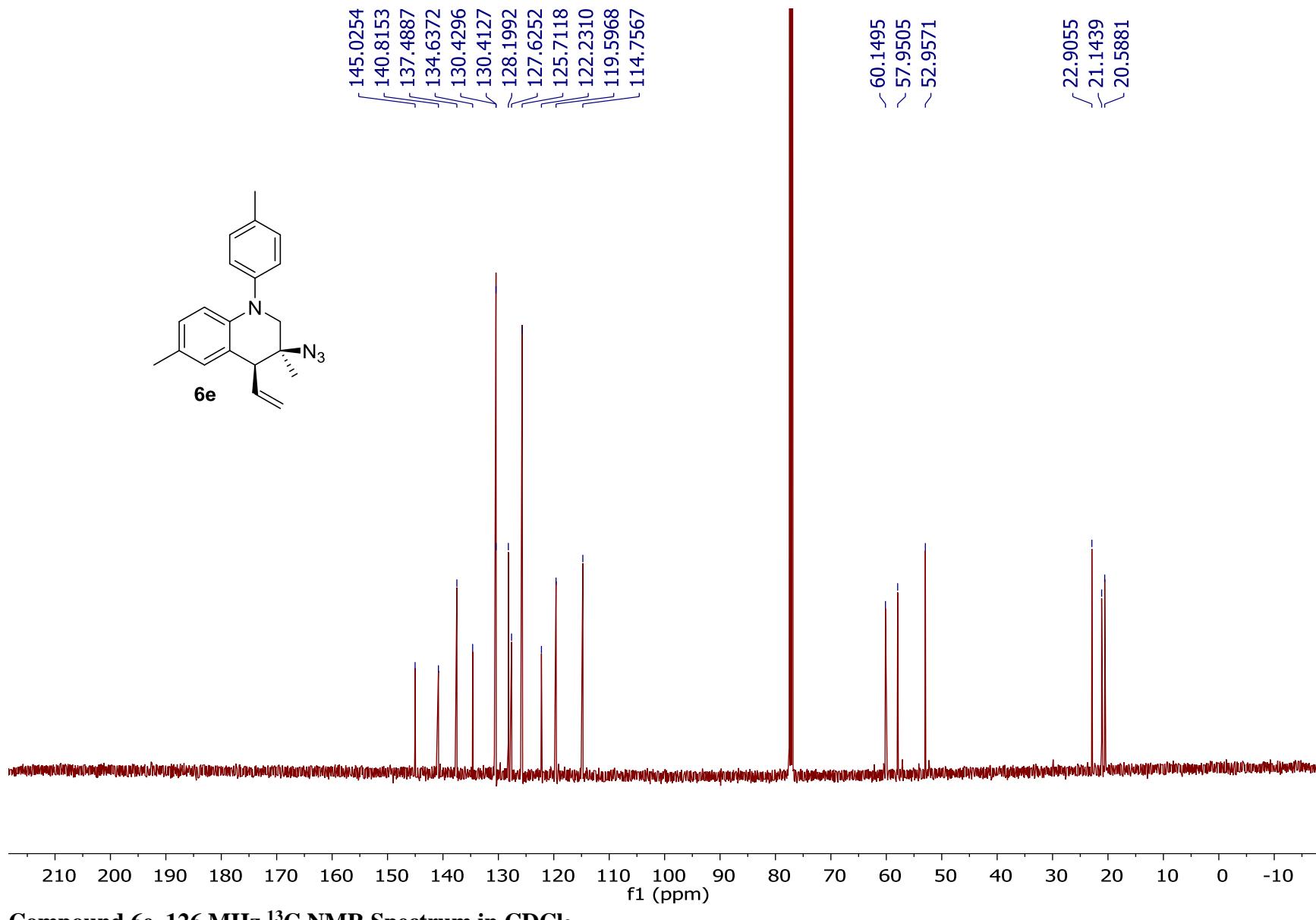
Compound 6d, 500 MHz ^1H NMR Spectrum in CDCl_3

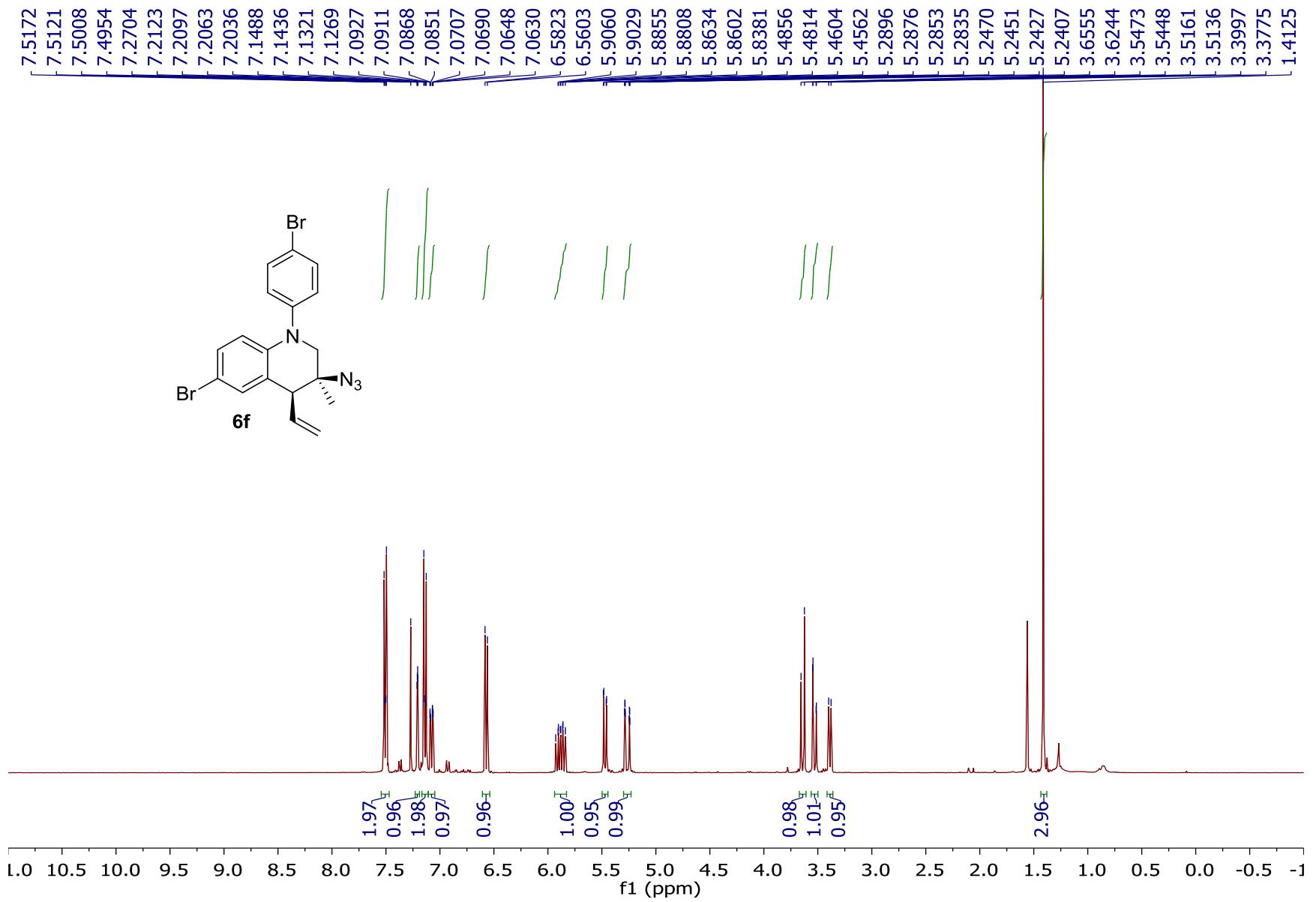


Compound 6d, 126 MHz ^{13}C NMR Spectrum in CDCl_3

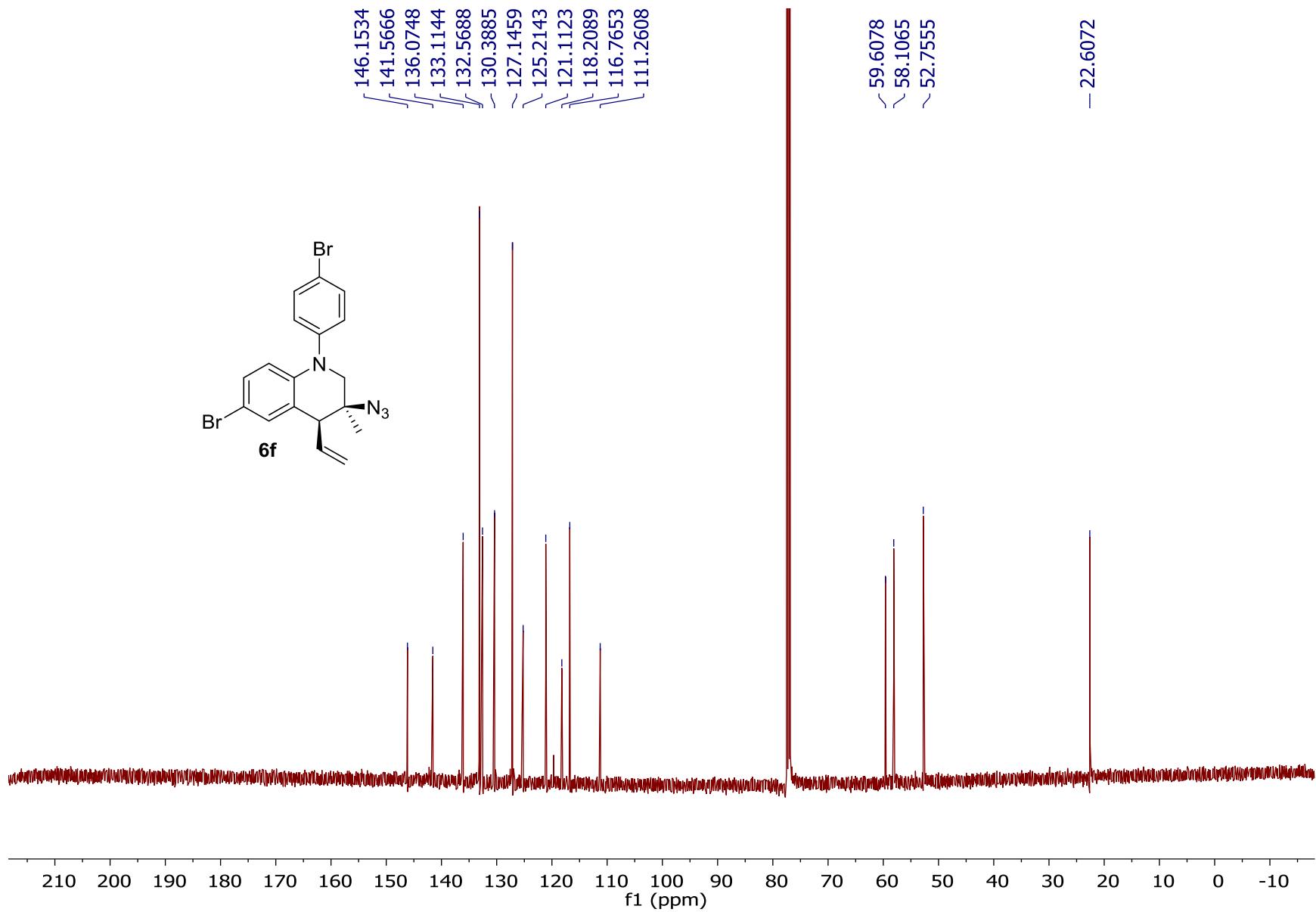


Compound 6e, 400 MHz ^1H NMR Spectrum in CDCl_3

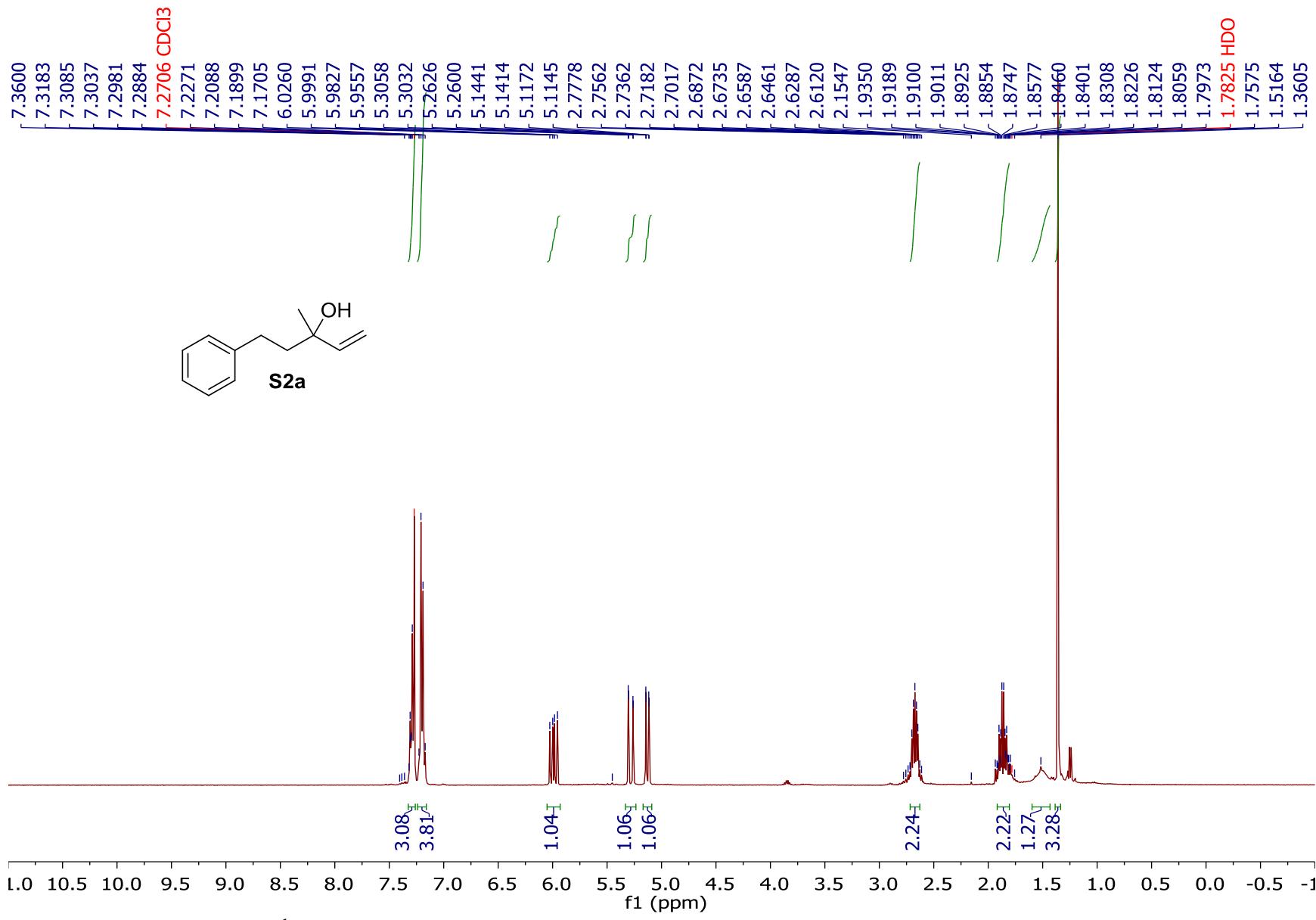




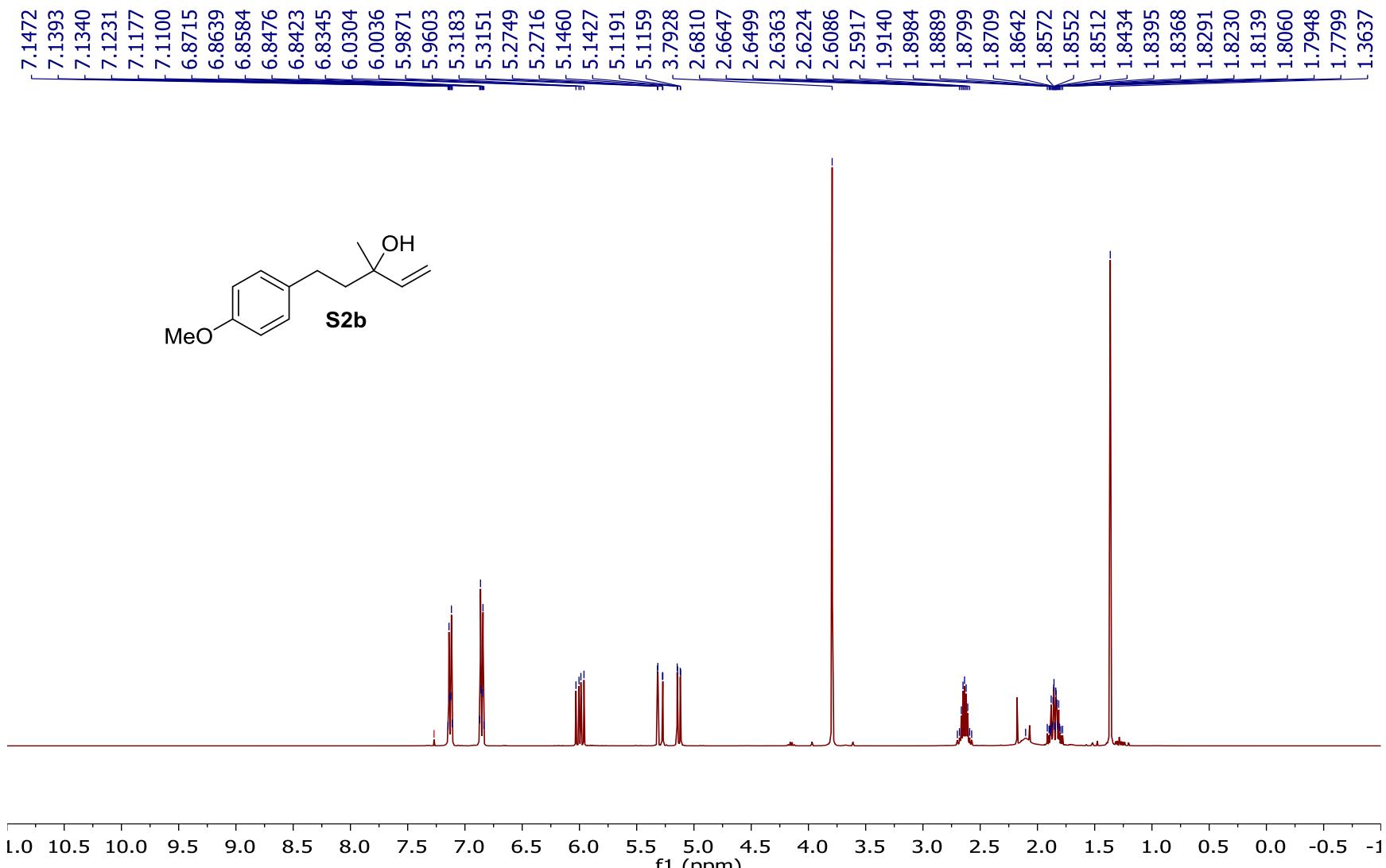
Compound 6f, 400 MHz ^1H NMR Spectrum in CDCl_3



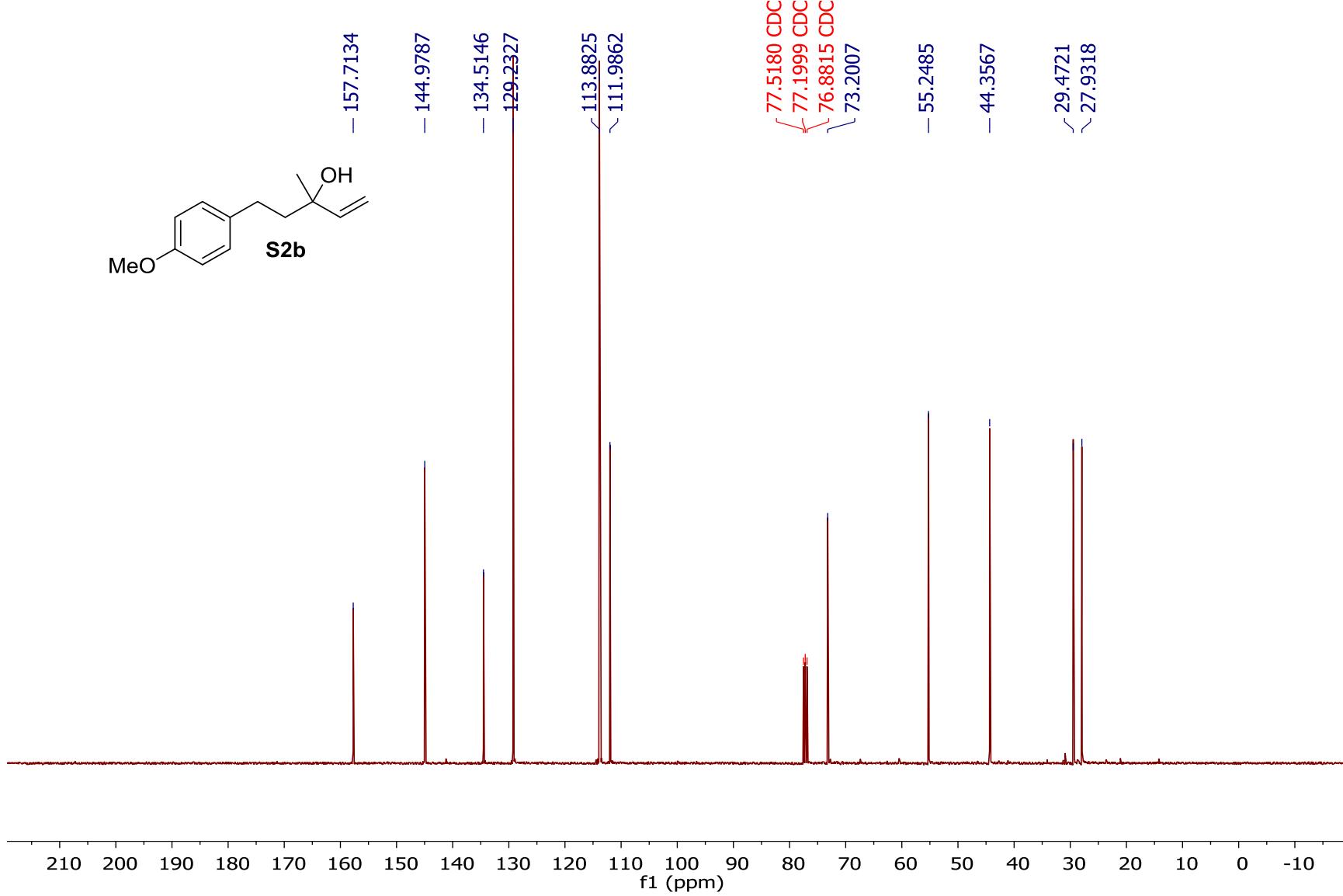
Compound 6f, 126 MHz ^{13}C NMR Spectrum in CDCl_3



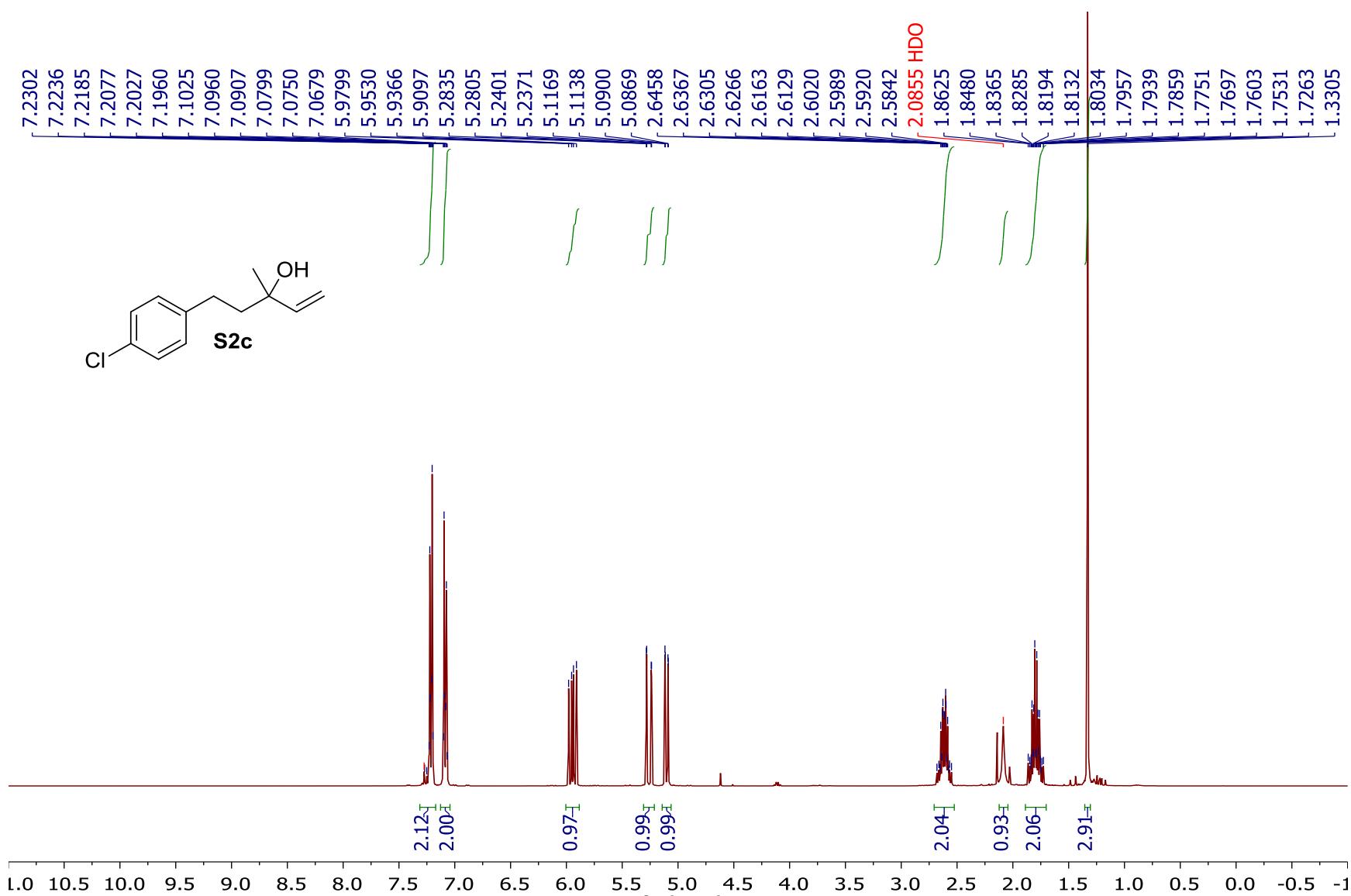
Compound S2a, 400 MHz ¹H NMR Spectrum in CDCl₃



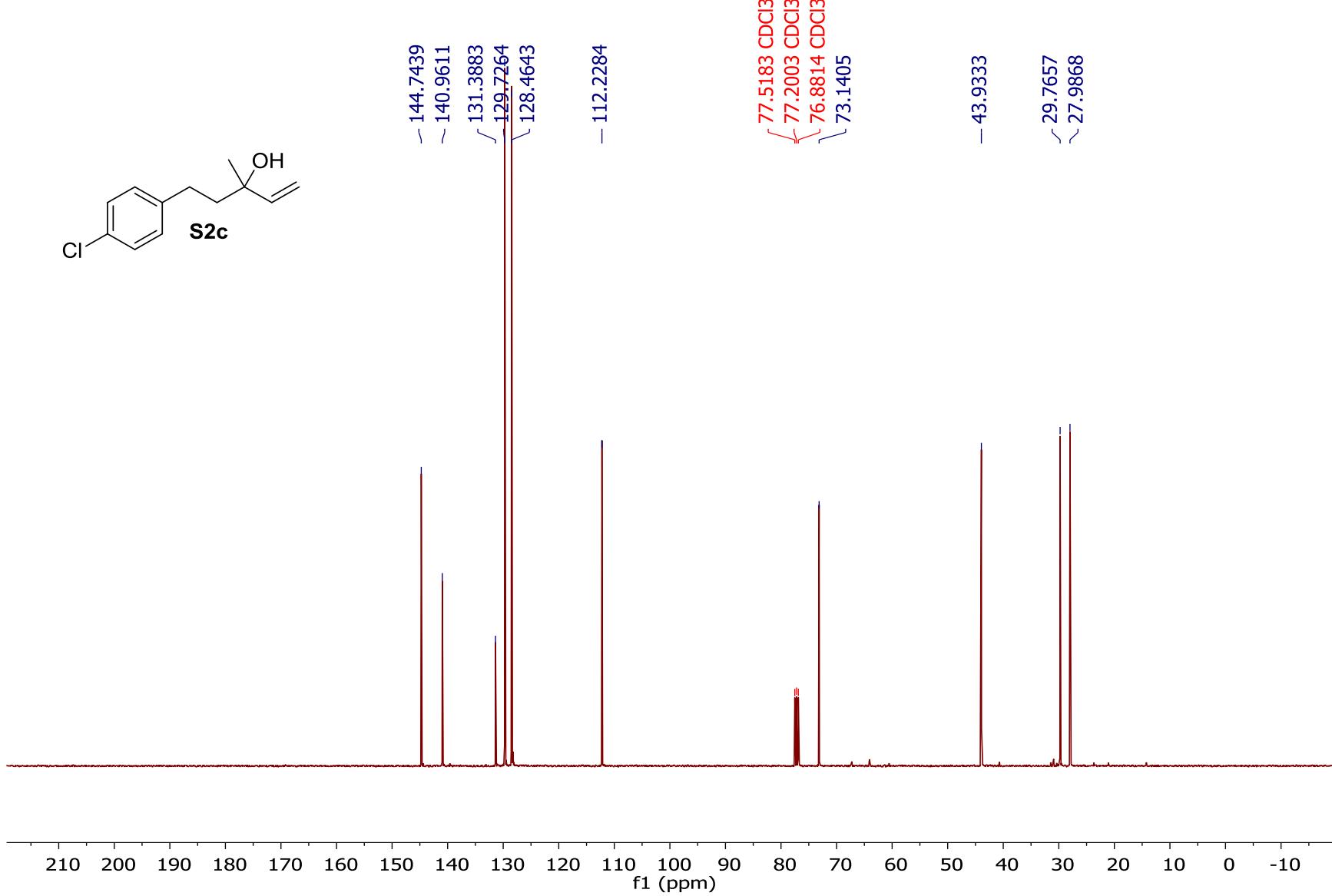
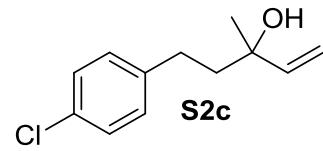
Compound S2b, 400 MHz ^1H NMR Spectrum in CDCl_3



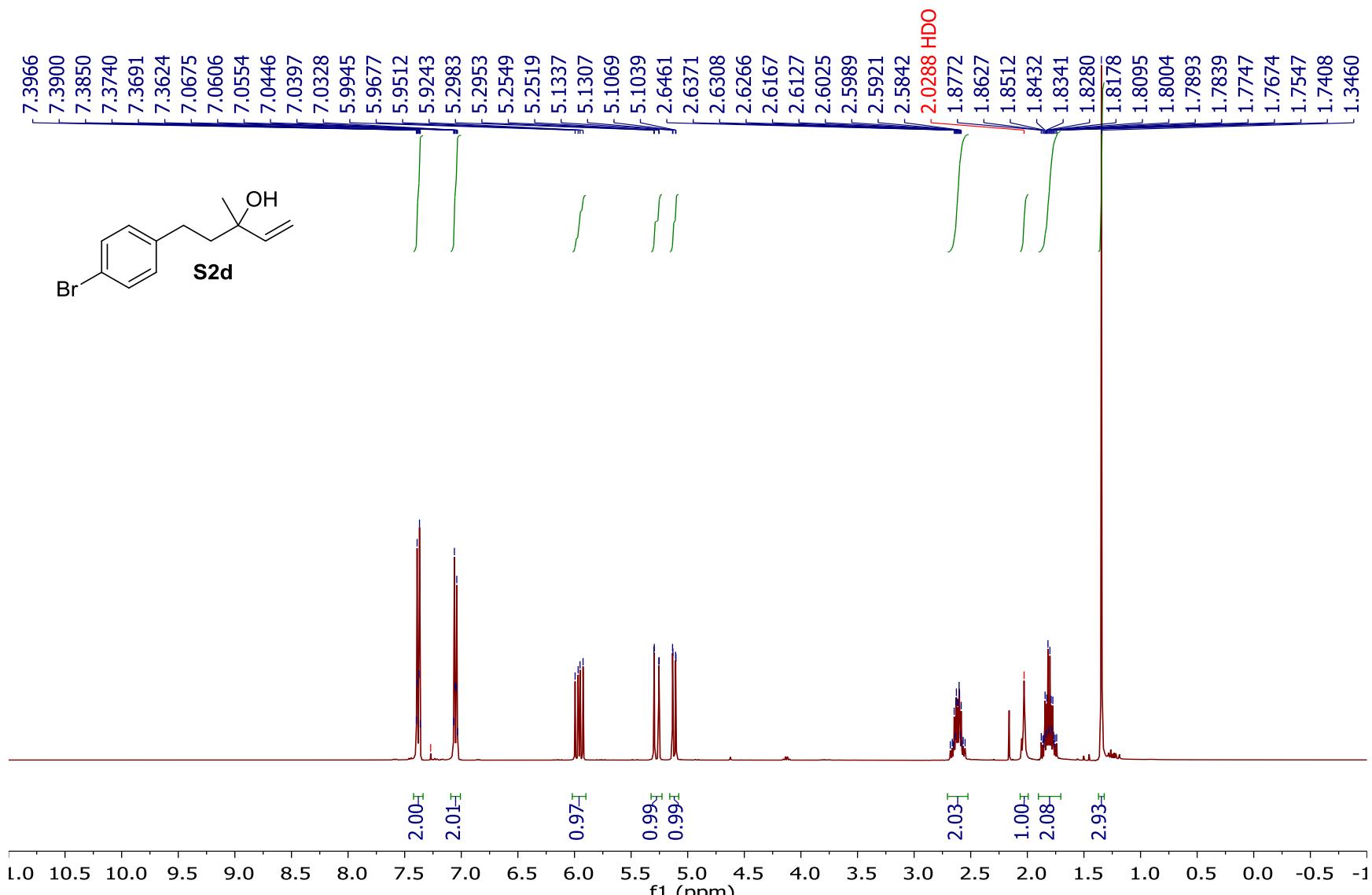
Compound S2b 101 MHz ¹³C NMR in CDCl₃



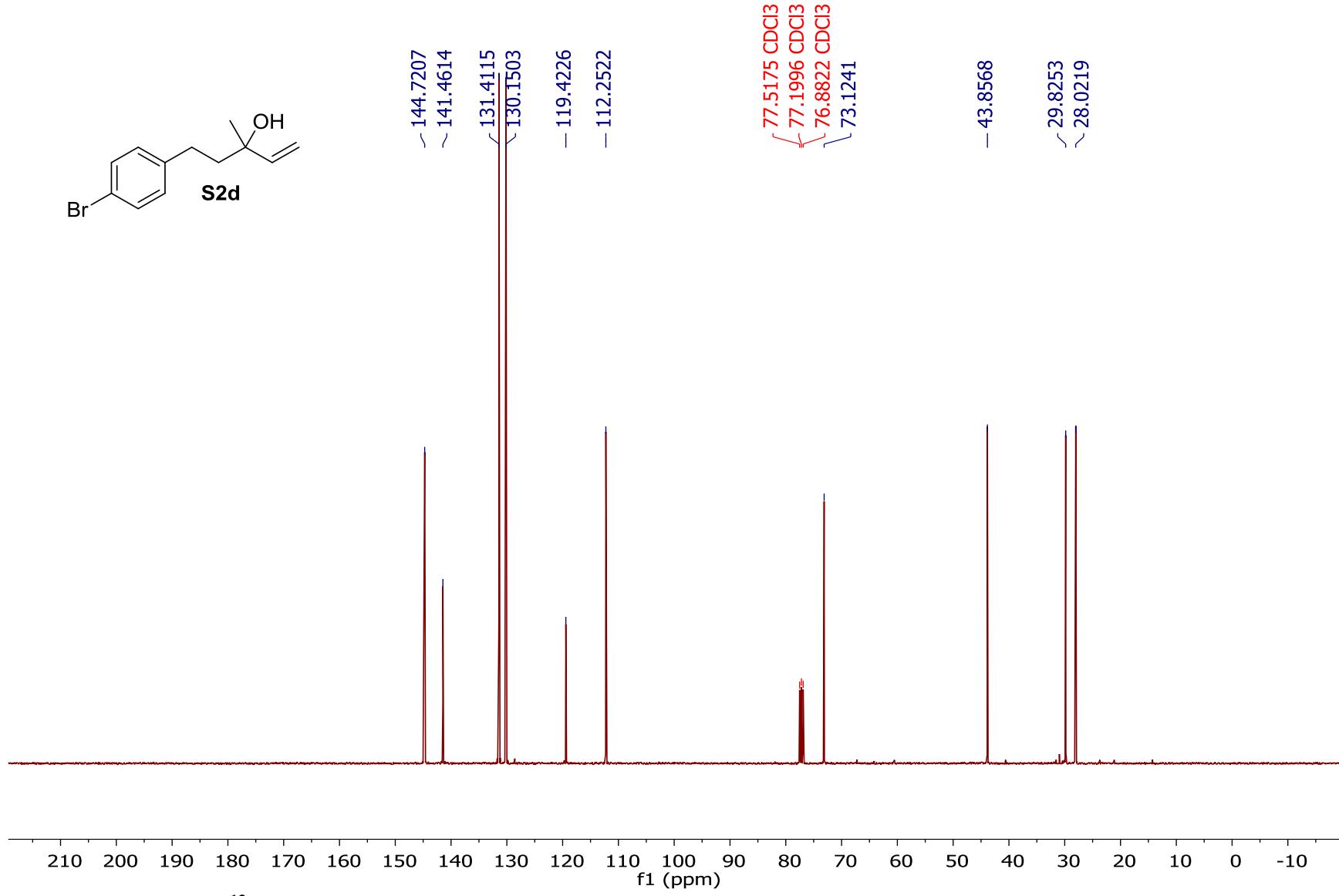
Compound S2c, 400 MHz ^1H NMR in CDCl_3



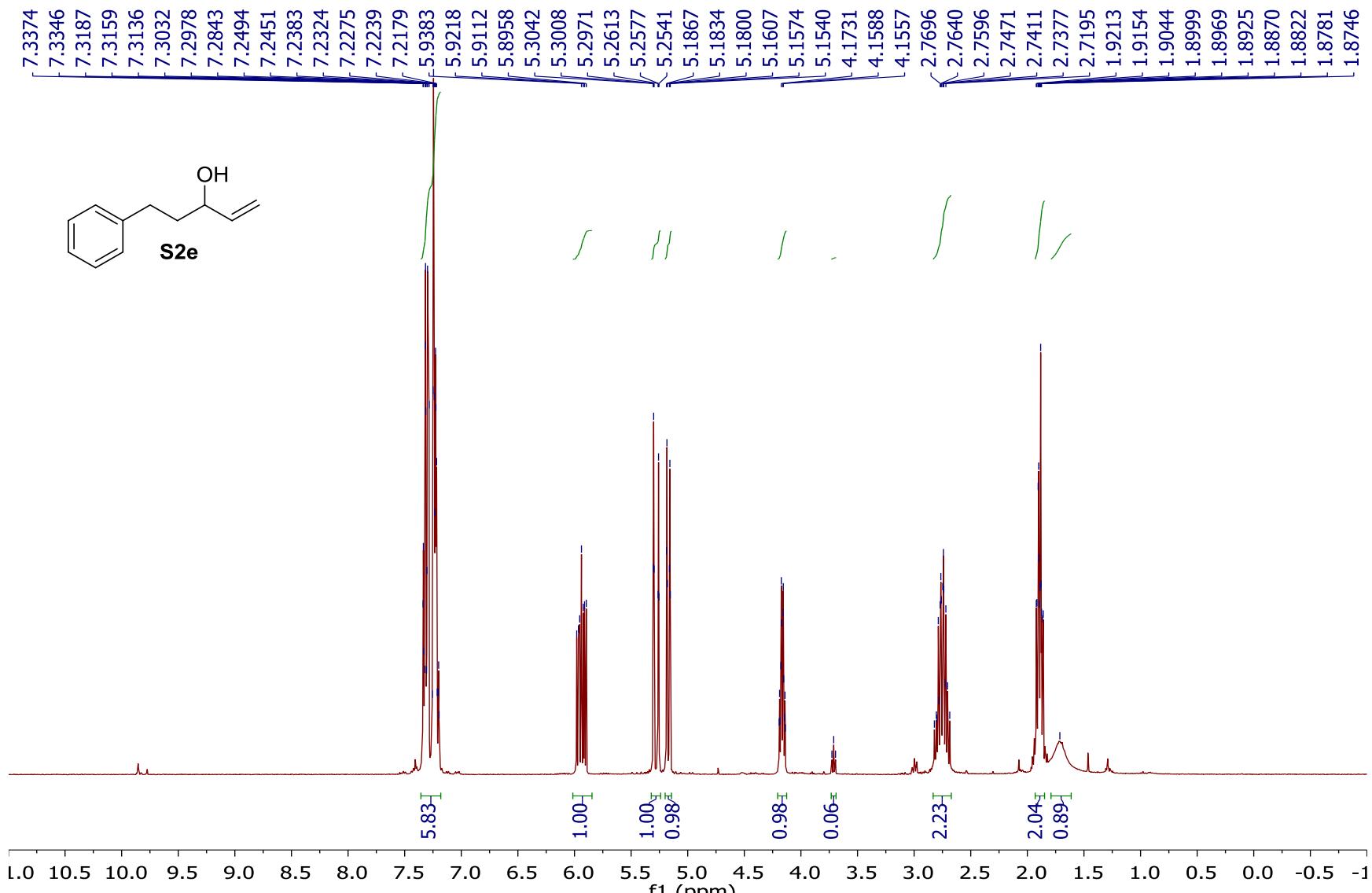
Compound S2c, 101 MHz ^{13}C NMR in CDCl_3



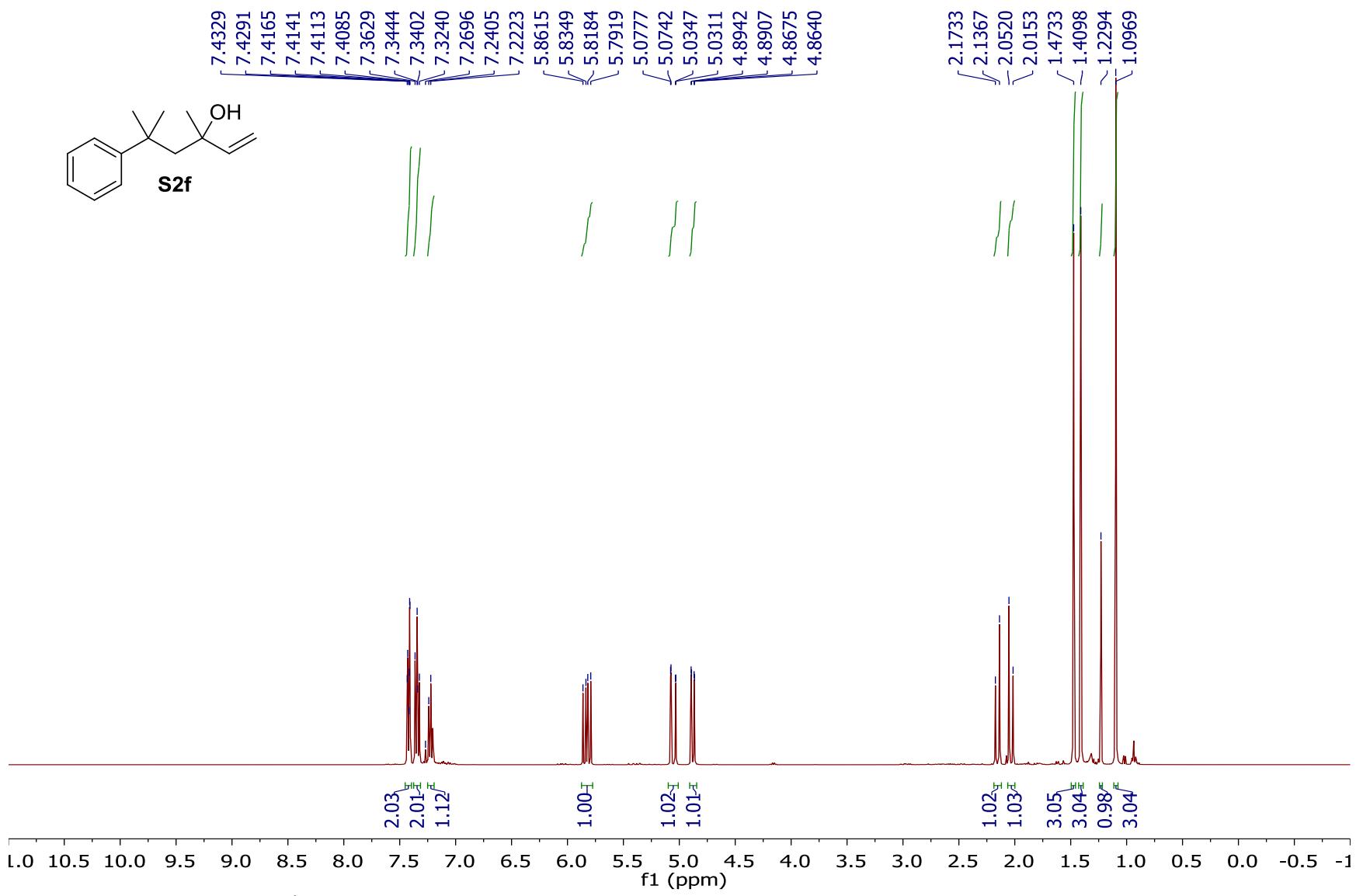
Compound S2d, 400 MHz ^1H NMR in CDCl_3

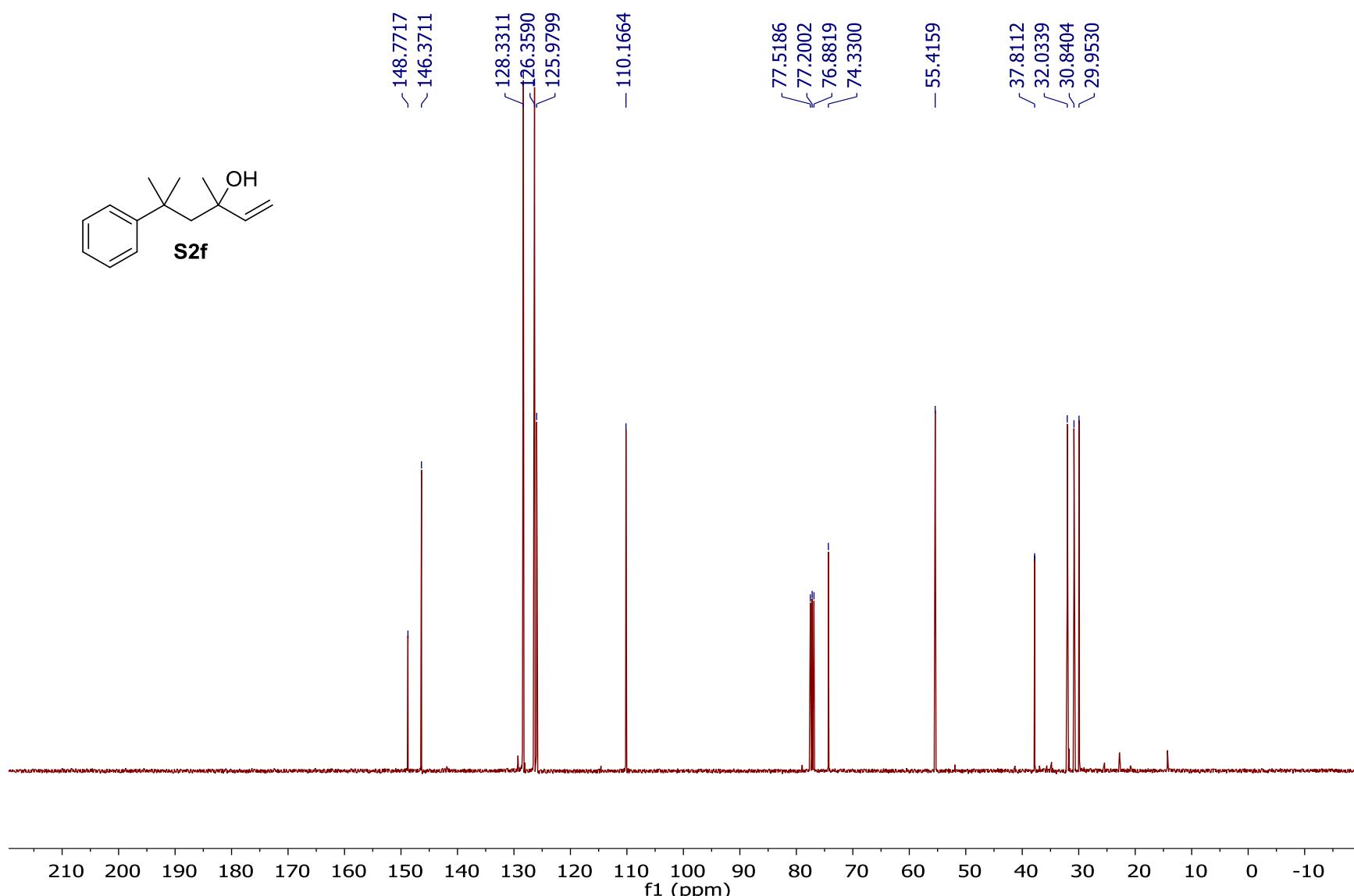
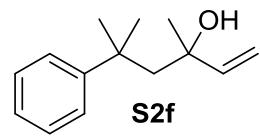


Compound S2d, ¹³C NMR in CDCl_3

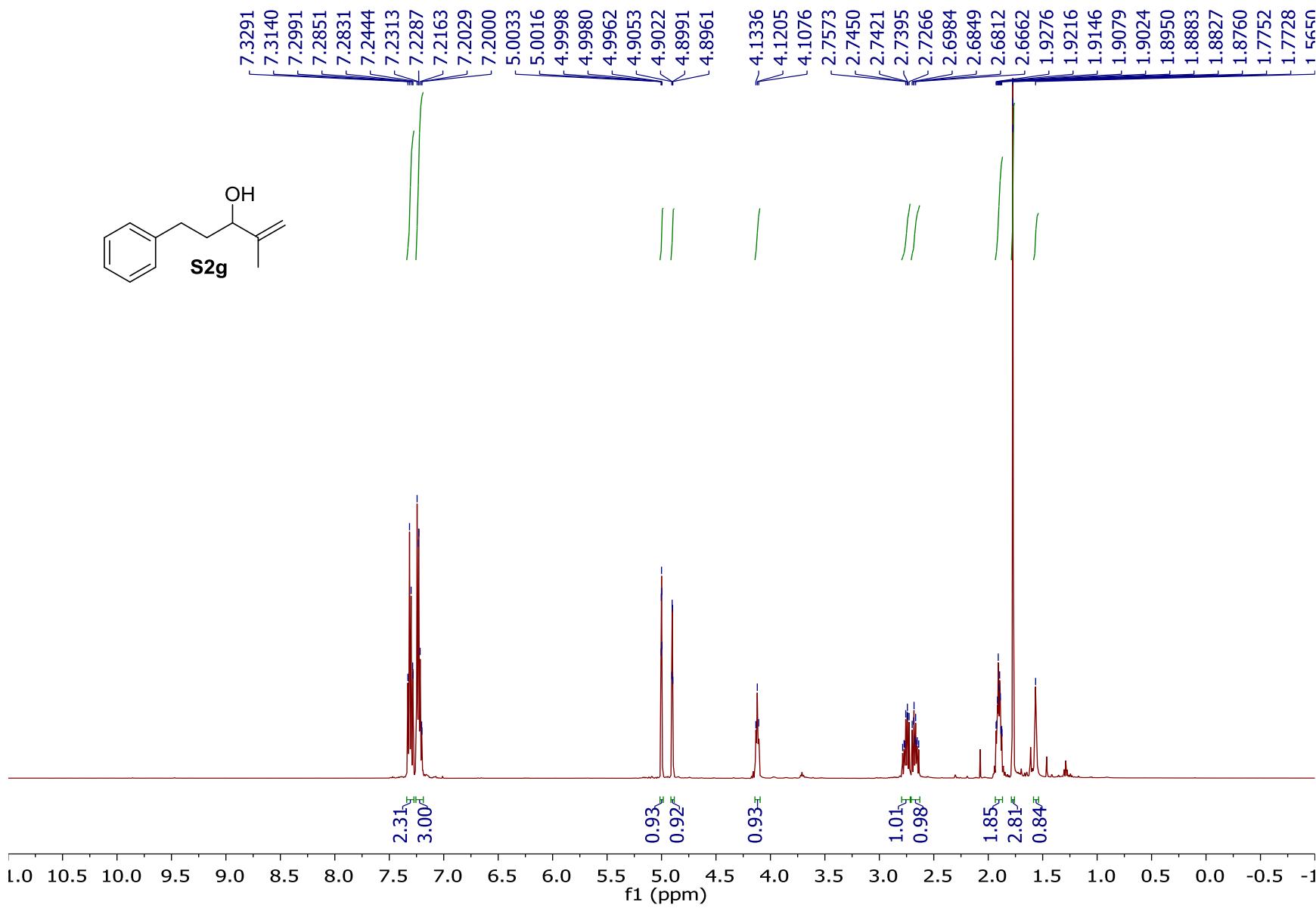


Compound S2e, 400 MHz ^1H NMR in CDCl_3

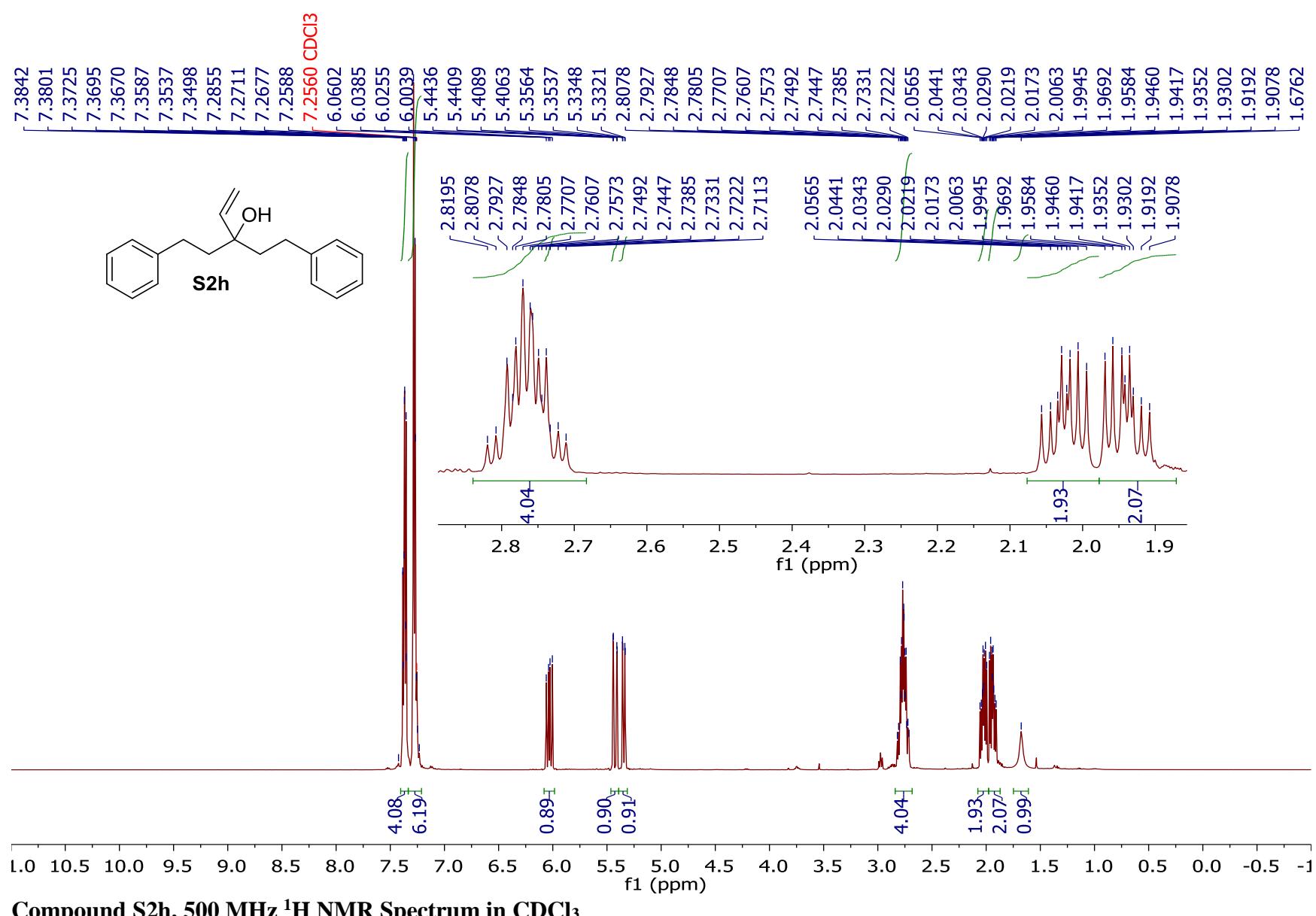




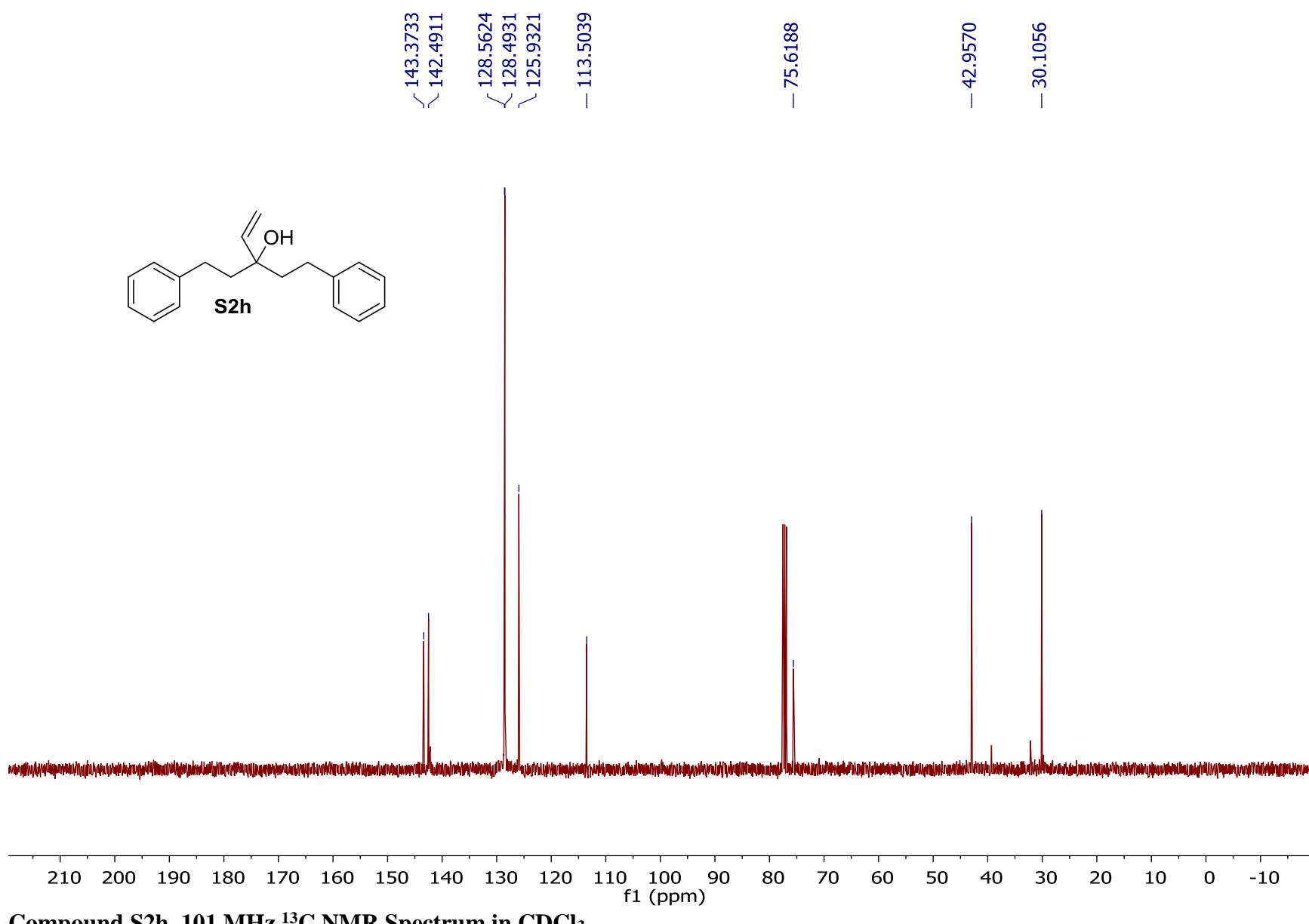
Compound S2f, 101 MHz ^{13}C NMR in CDCl_3

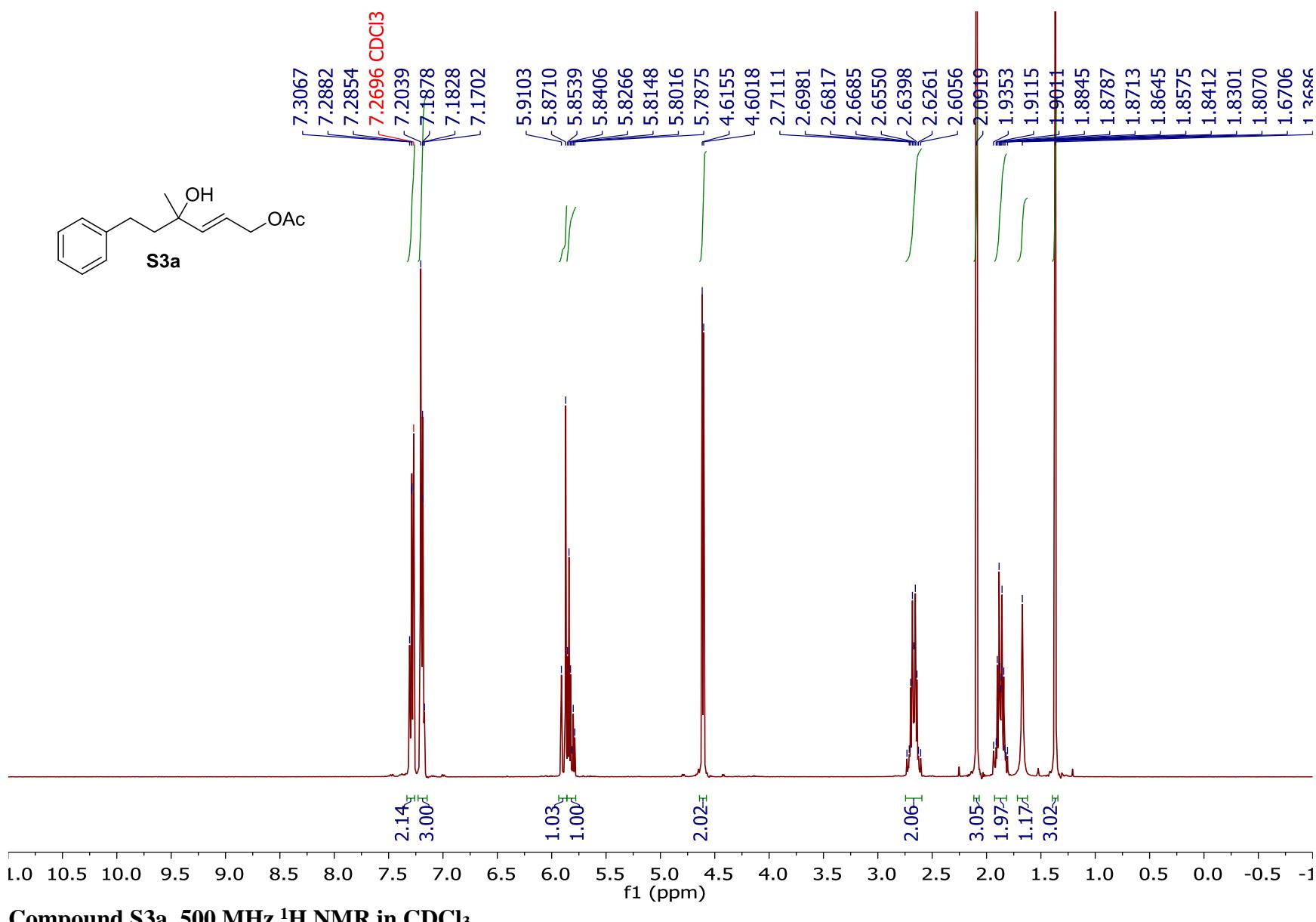


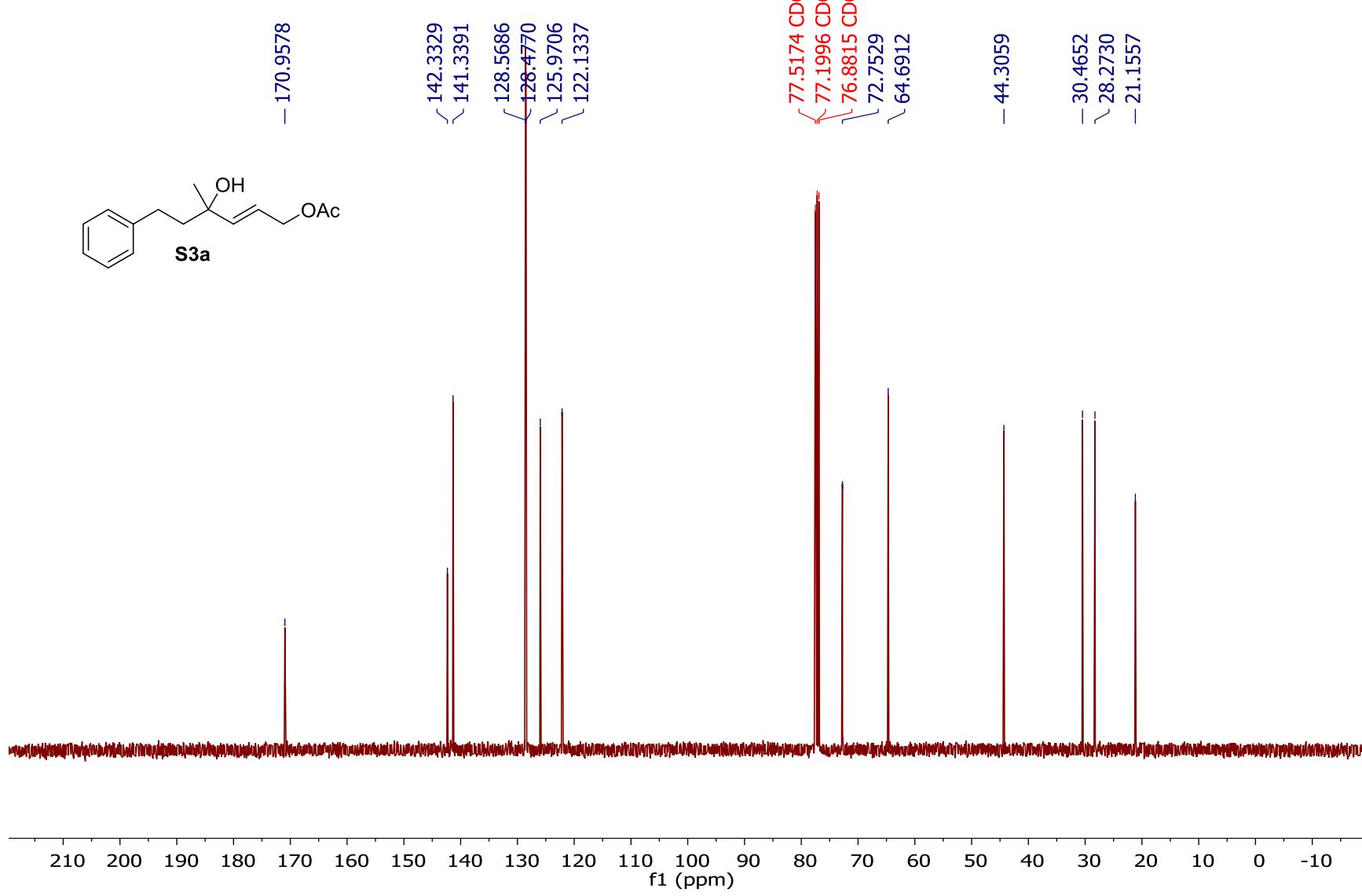
Compound S2g, 500 MHz ¹H NMR Spectrum in CDCl₃



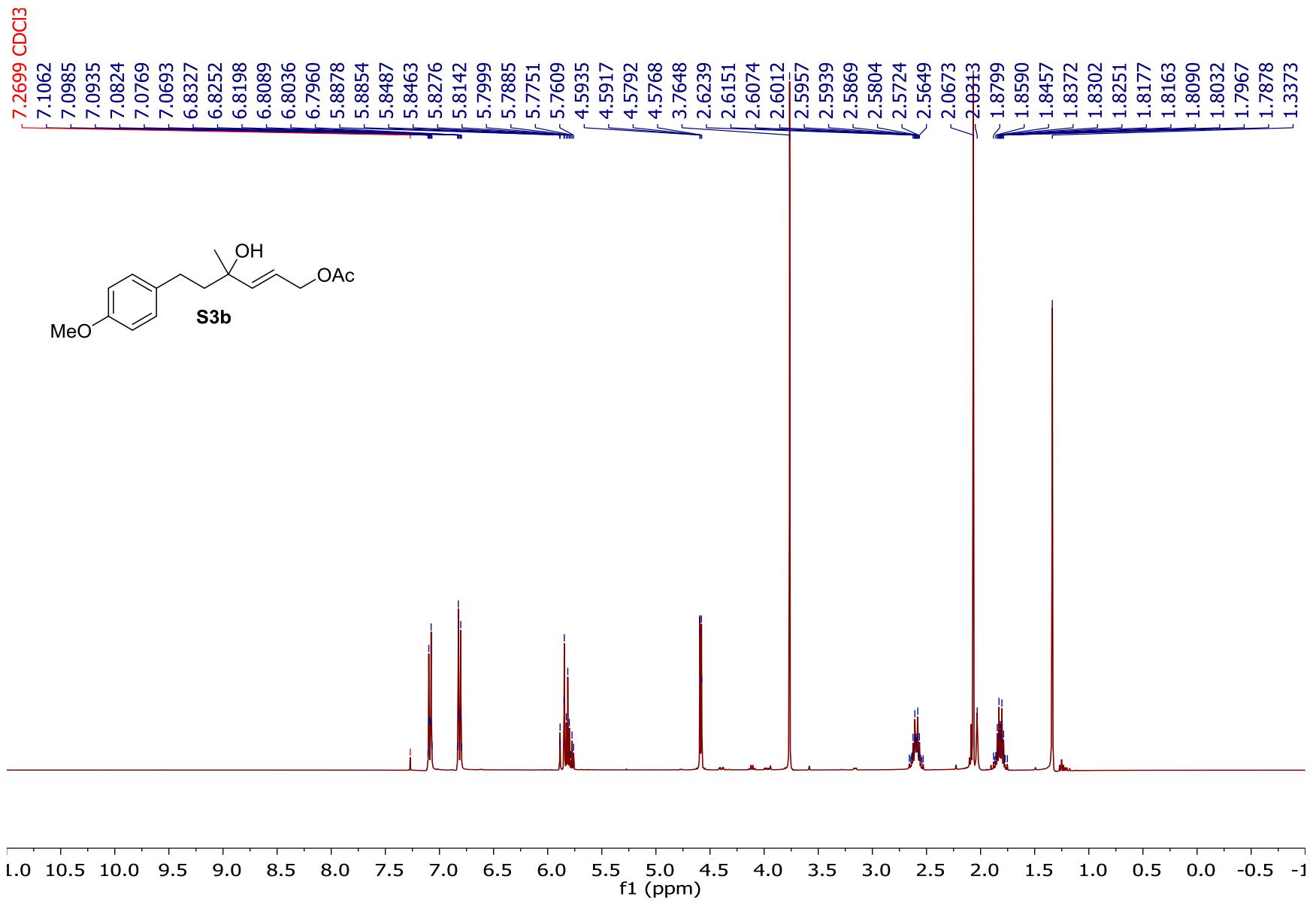
Compound S2h, 500 MHz ^1H NMR Spectrum in CDCl_3

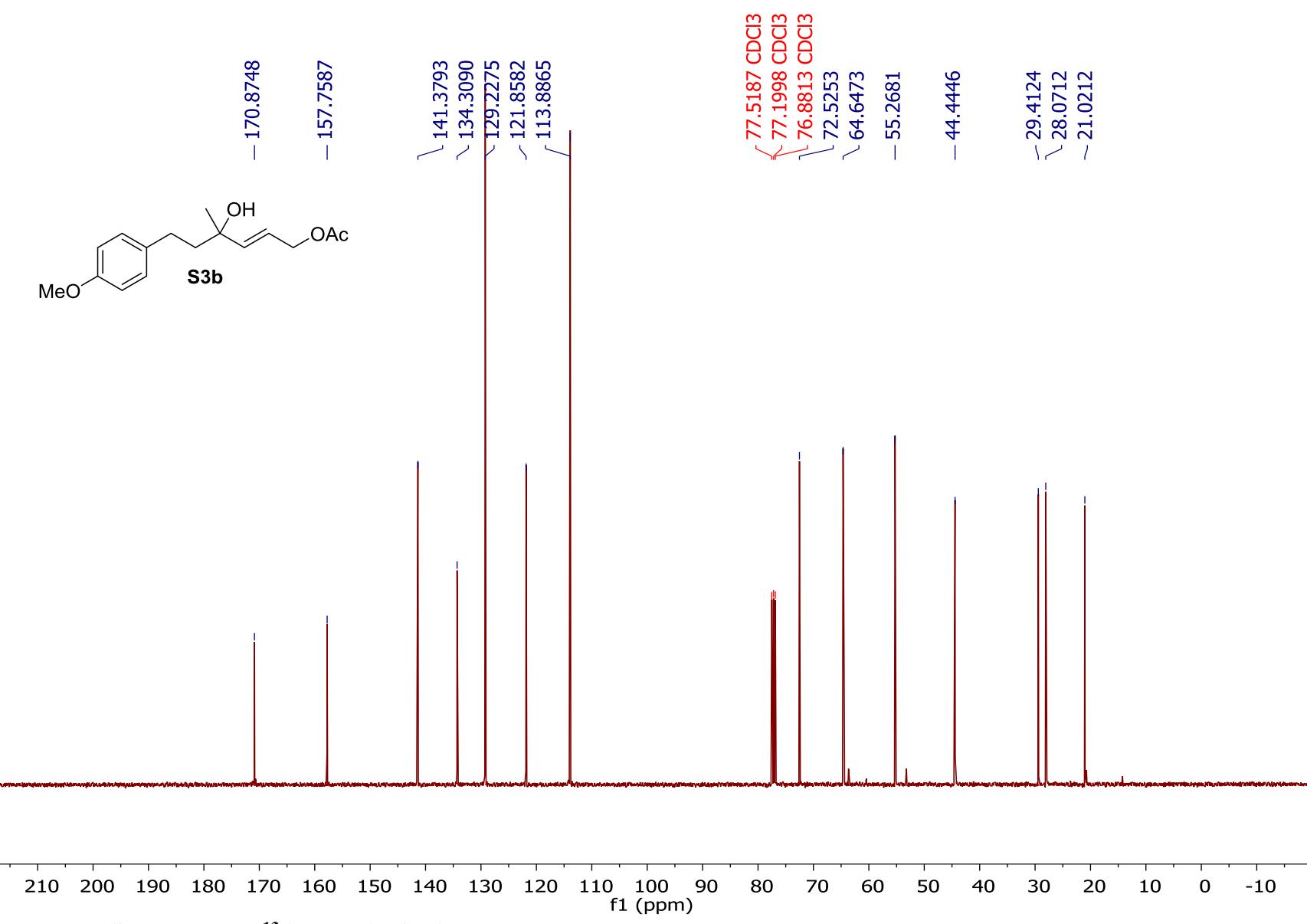




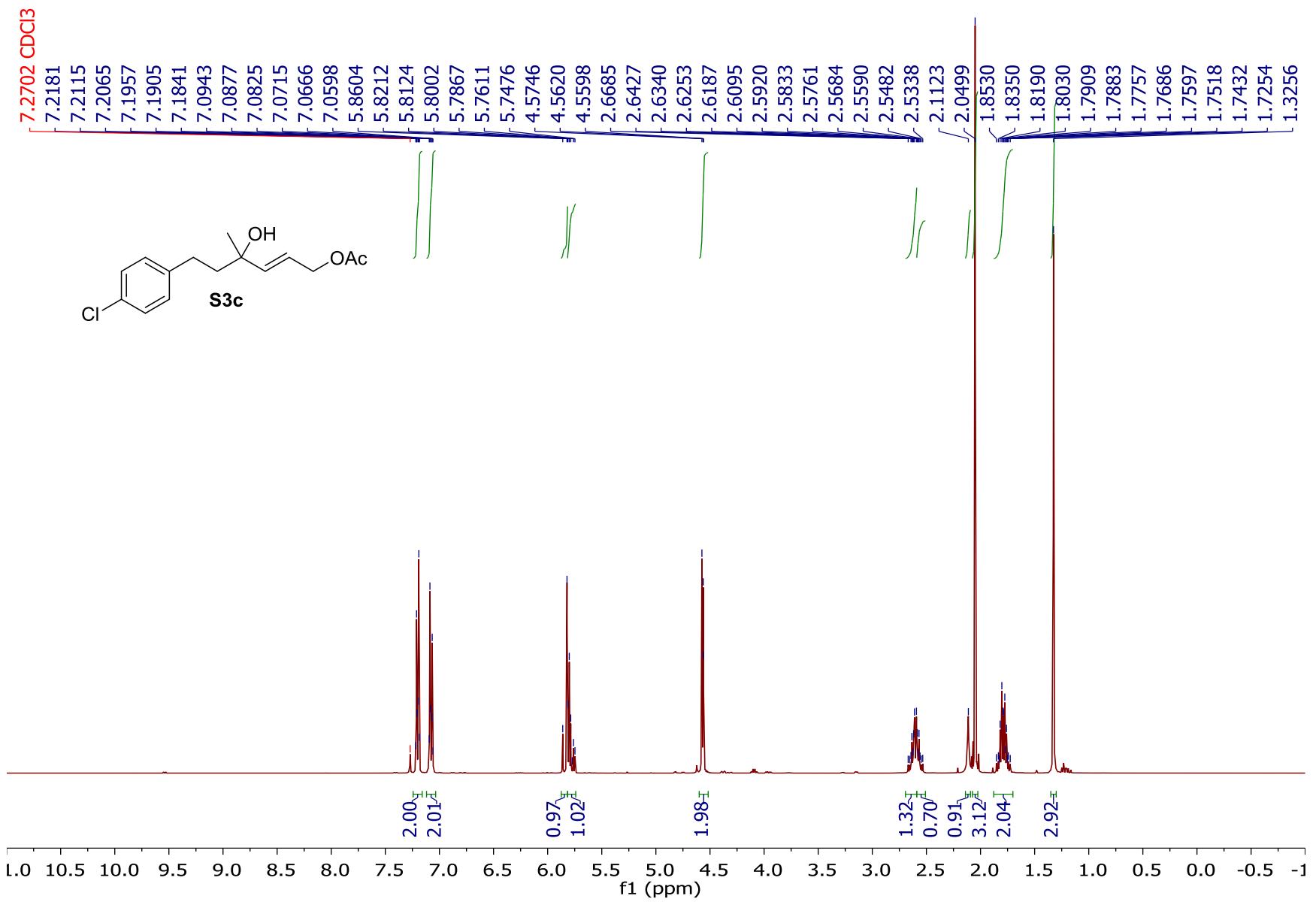


Compound S3a, 101 MHz ¹³C NMR in CDCl₃

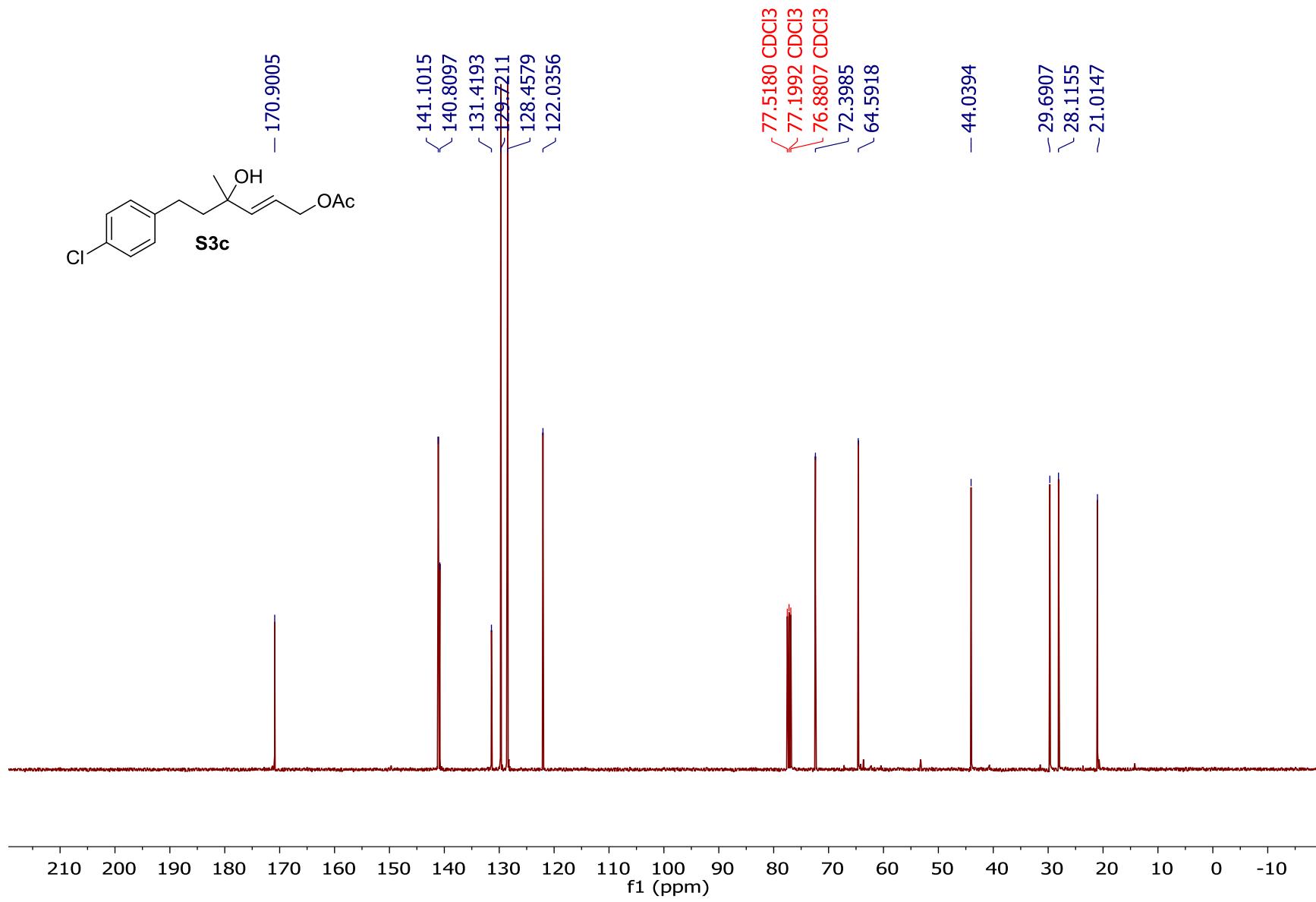
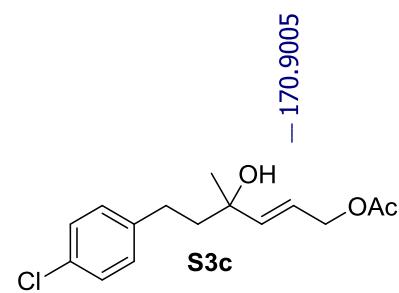




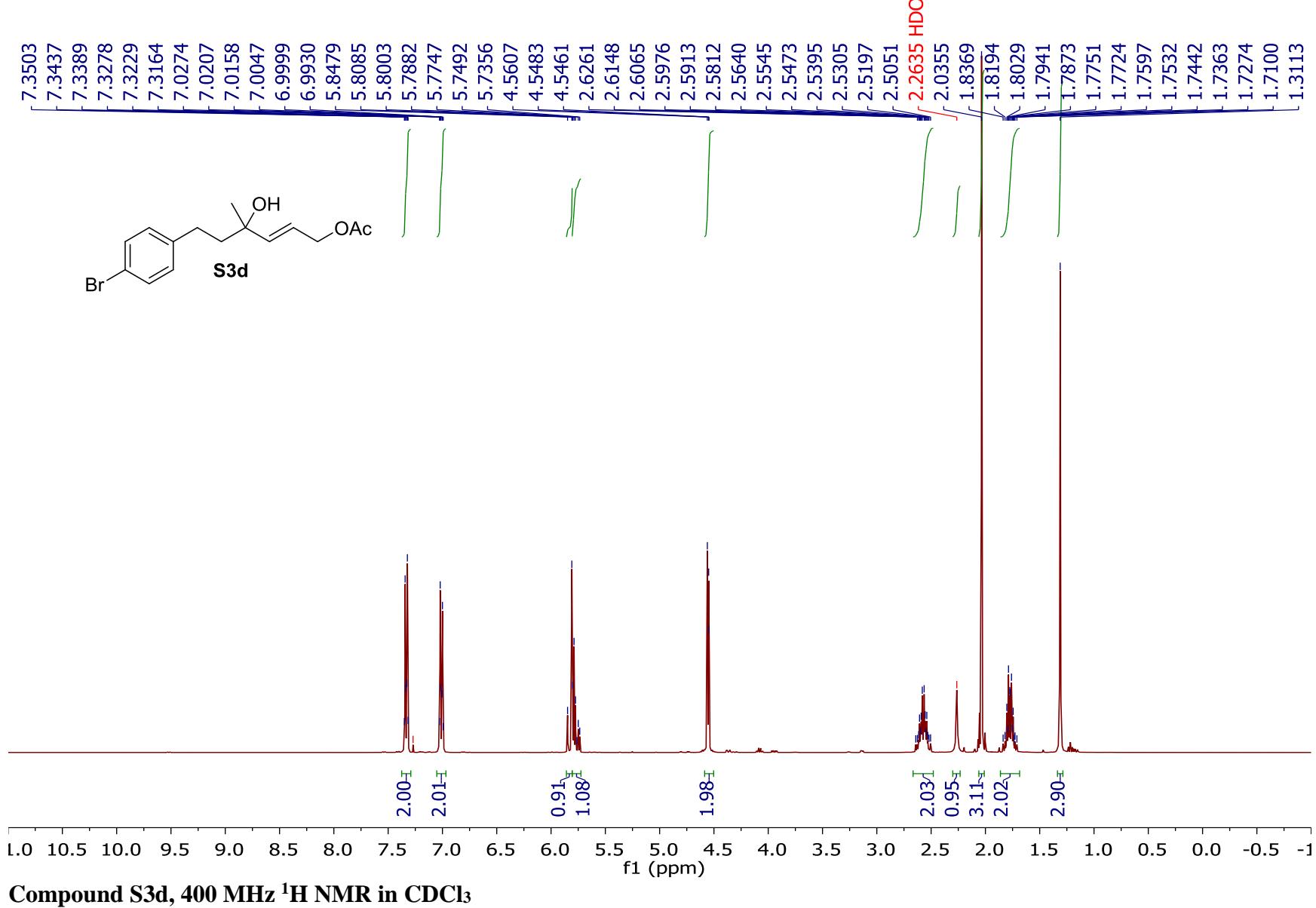
Compound S3b, 101 MHz ¹³C NMR in CDCl₃

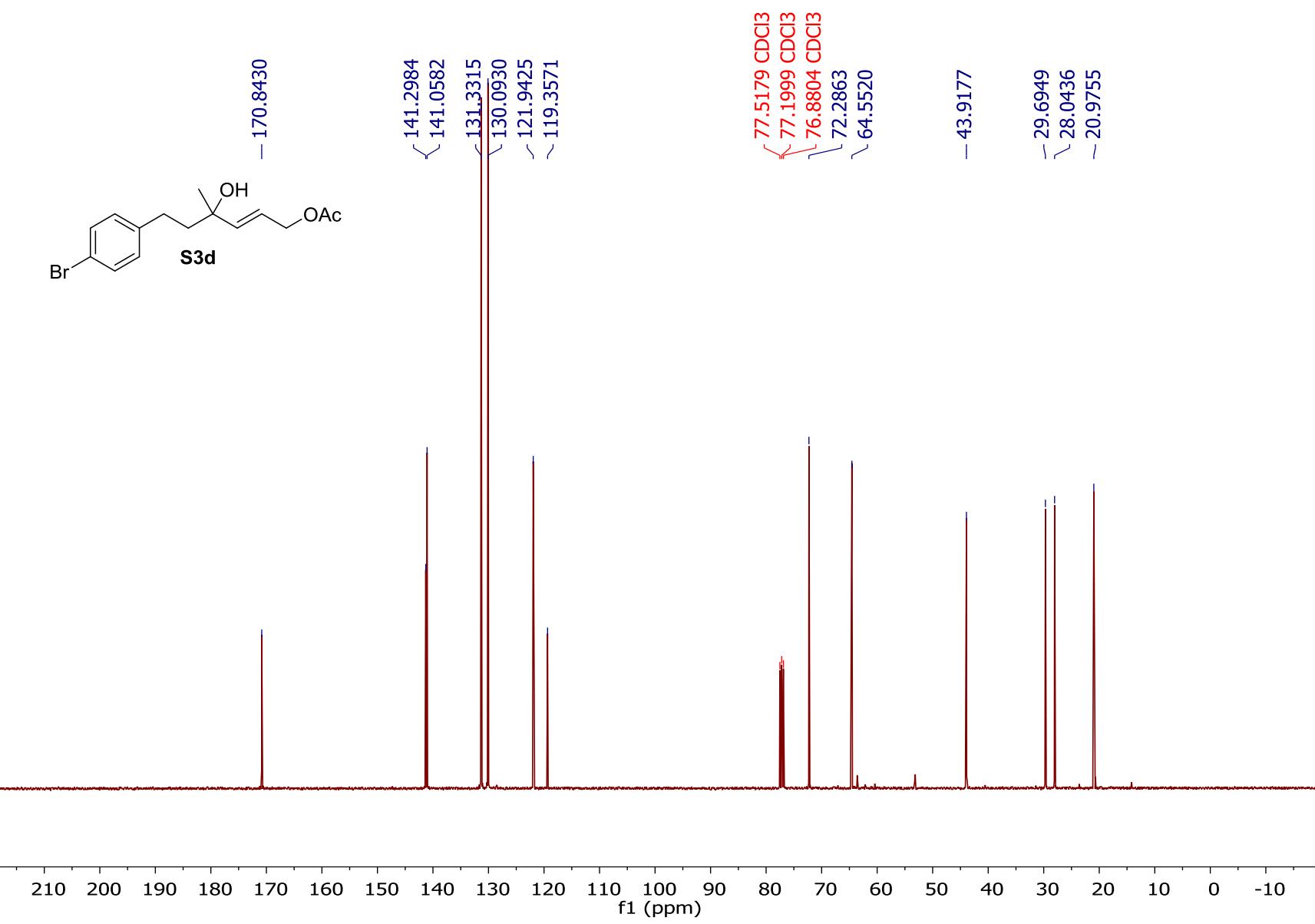


Compound S3c, 400 MHz ¹H NMR in CDCl₃

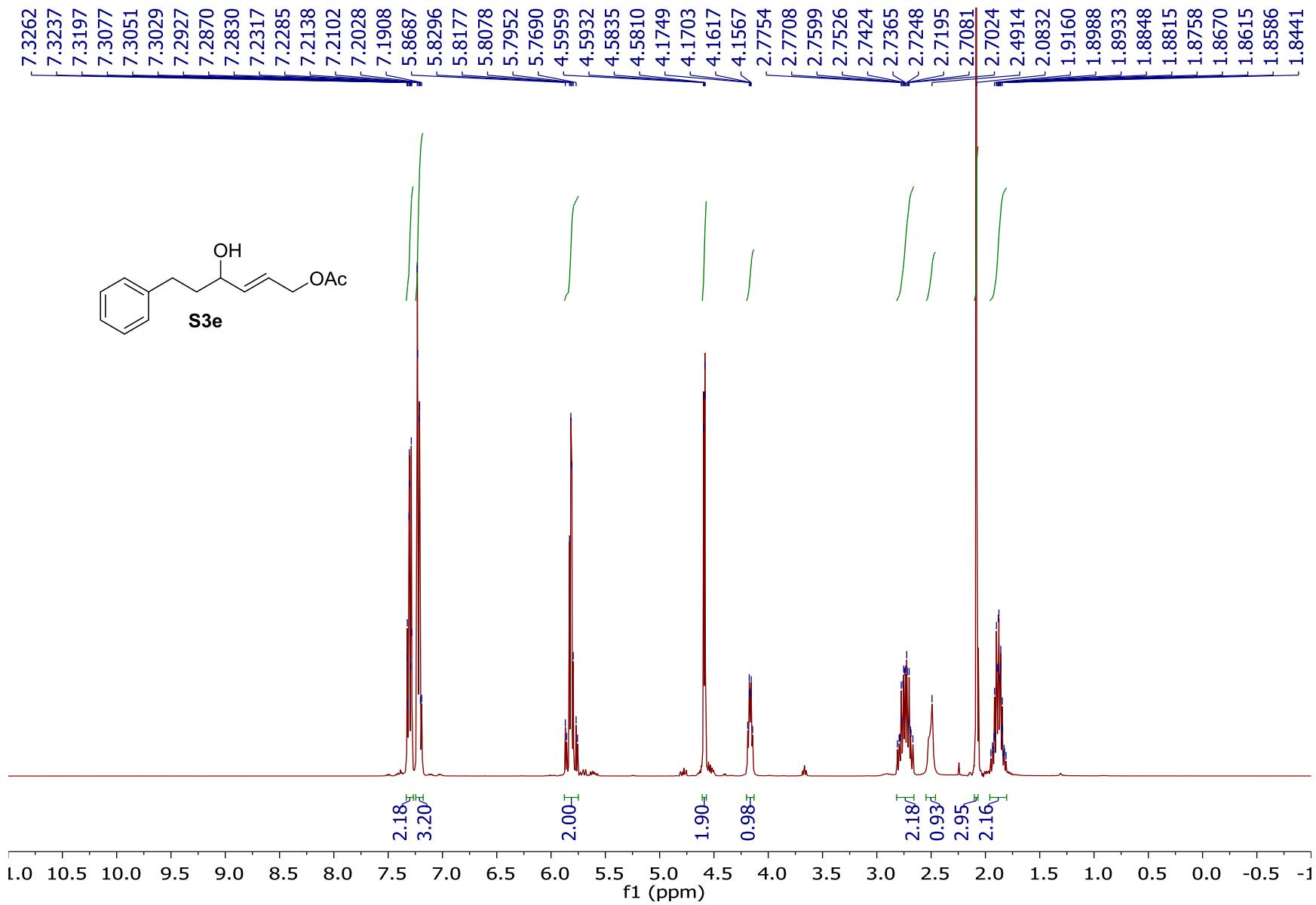


Compound S3c, 101 MHz ^{13}C NMR in CDCl_3

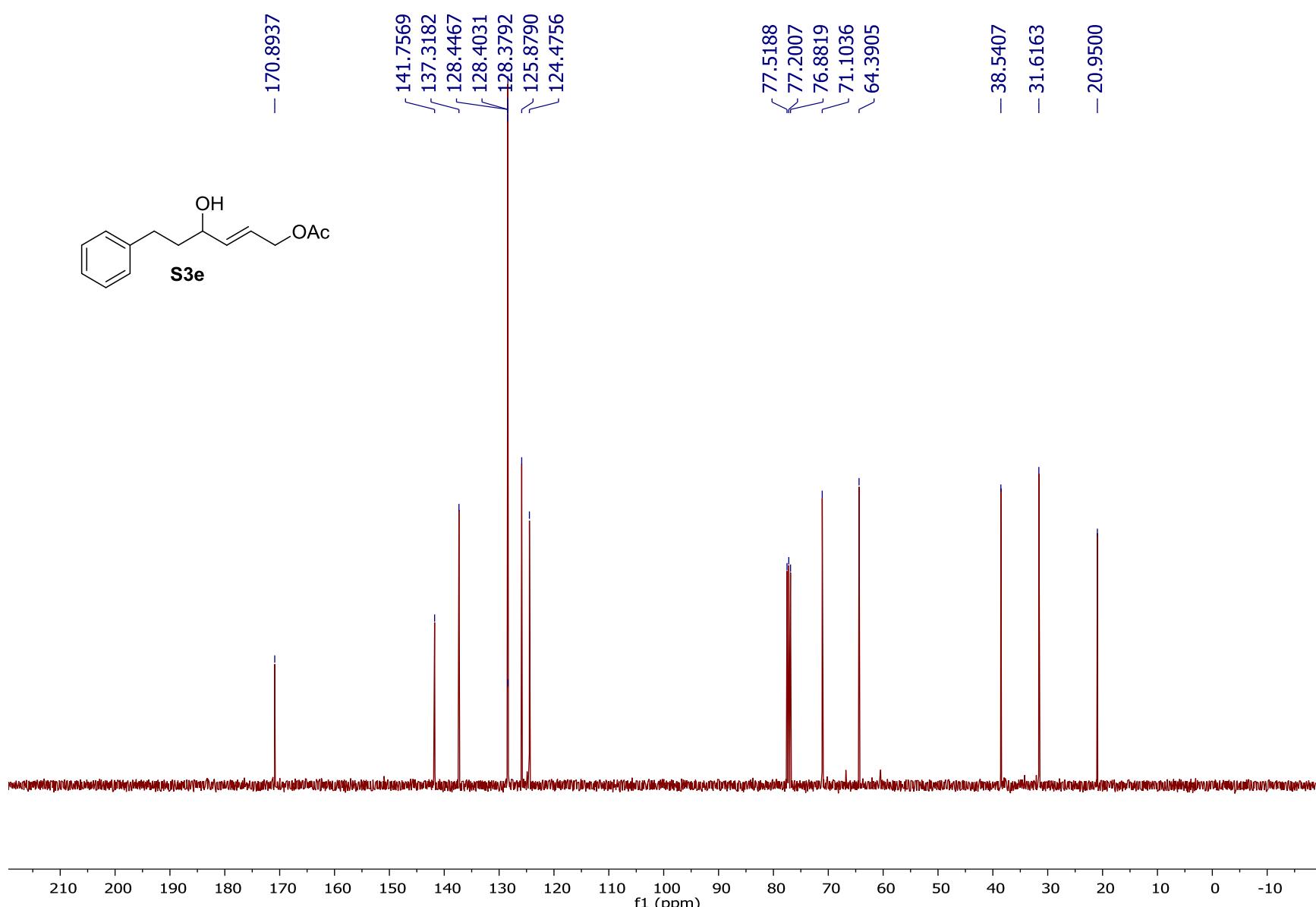


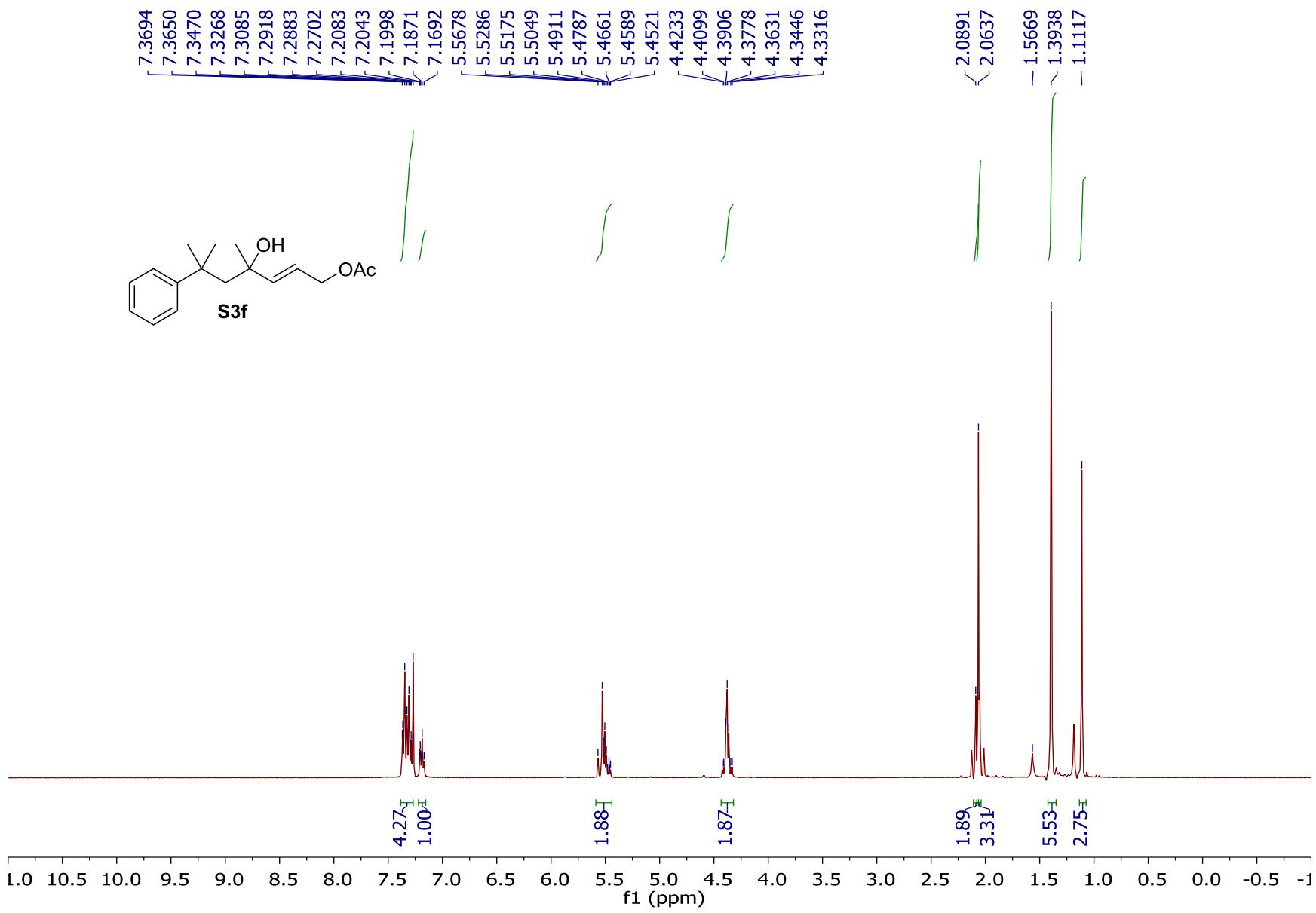


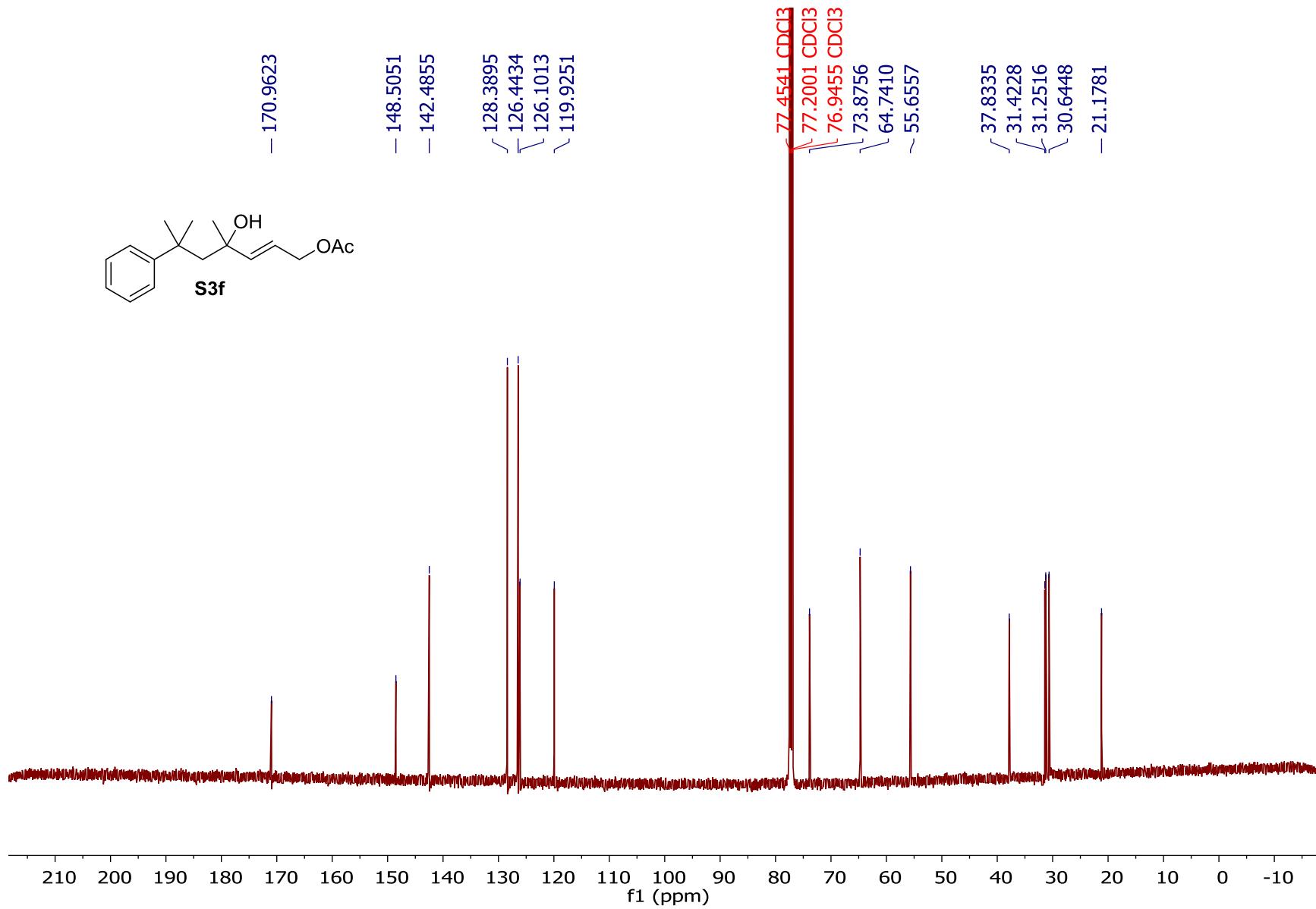
Compound S3d, 101 MHz ¹³C NMR in CDCl₃



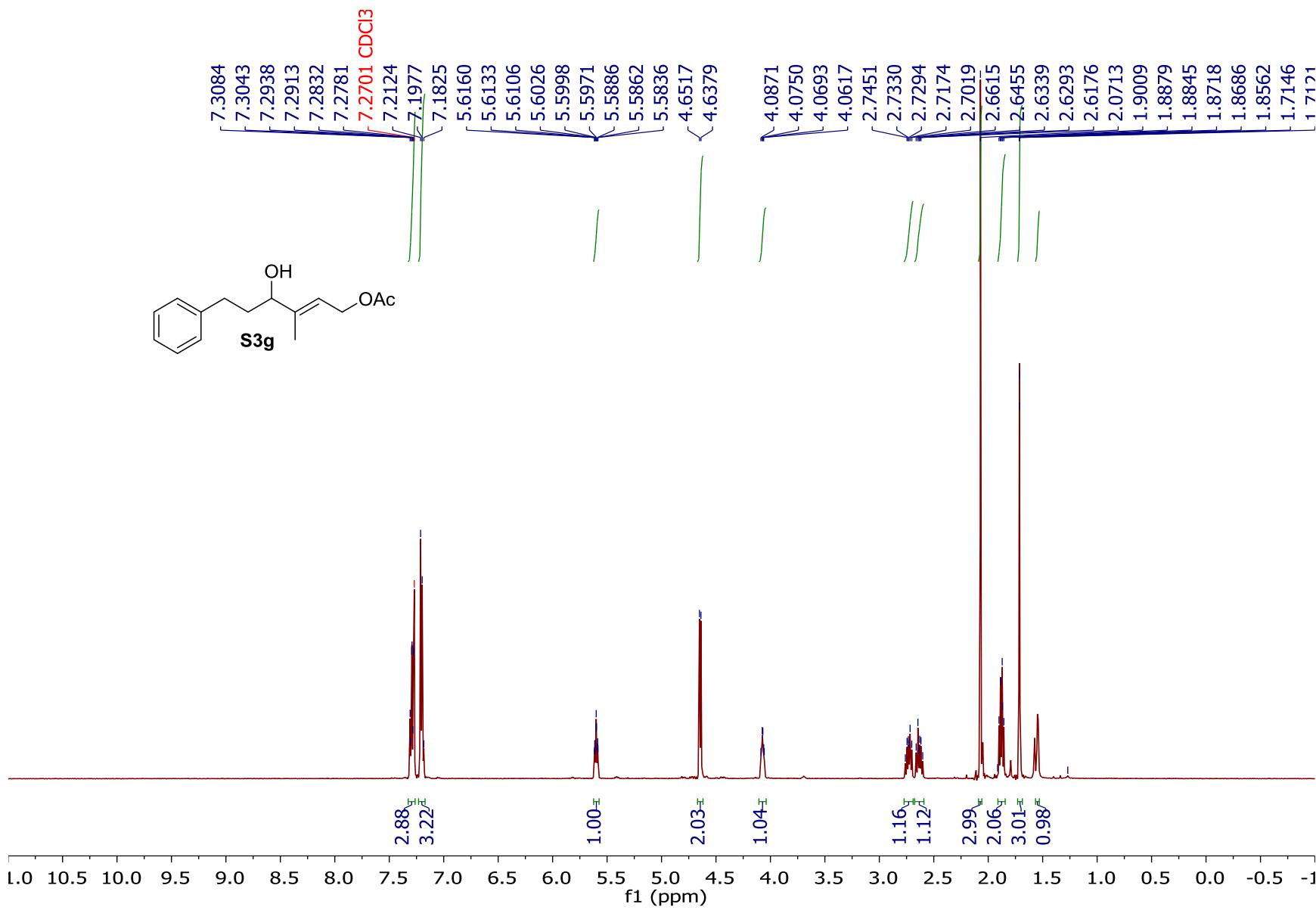
Compound S3e, 400 MHz ^1H NMR in CDCl_3

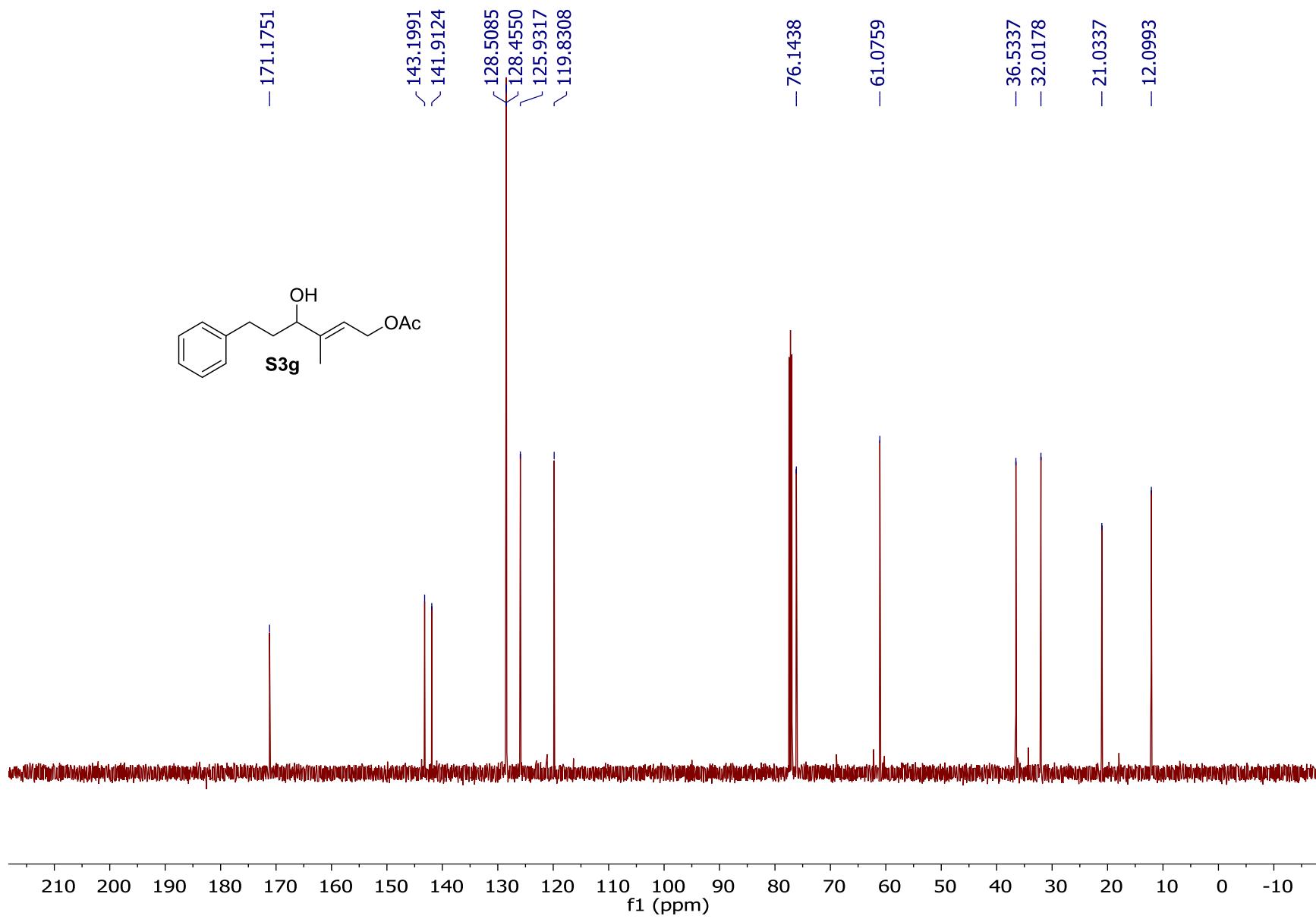




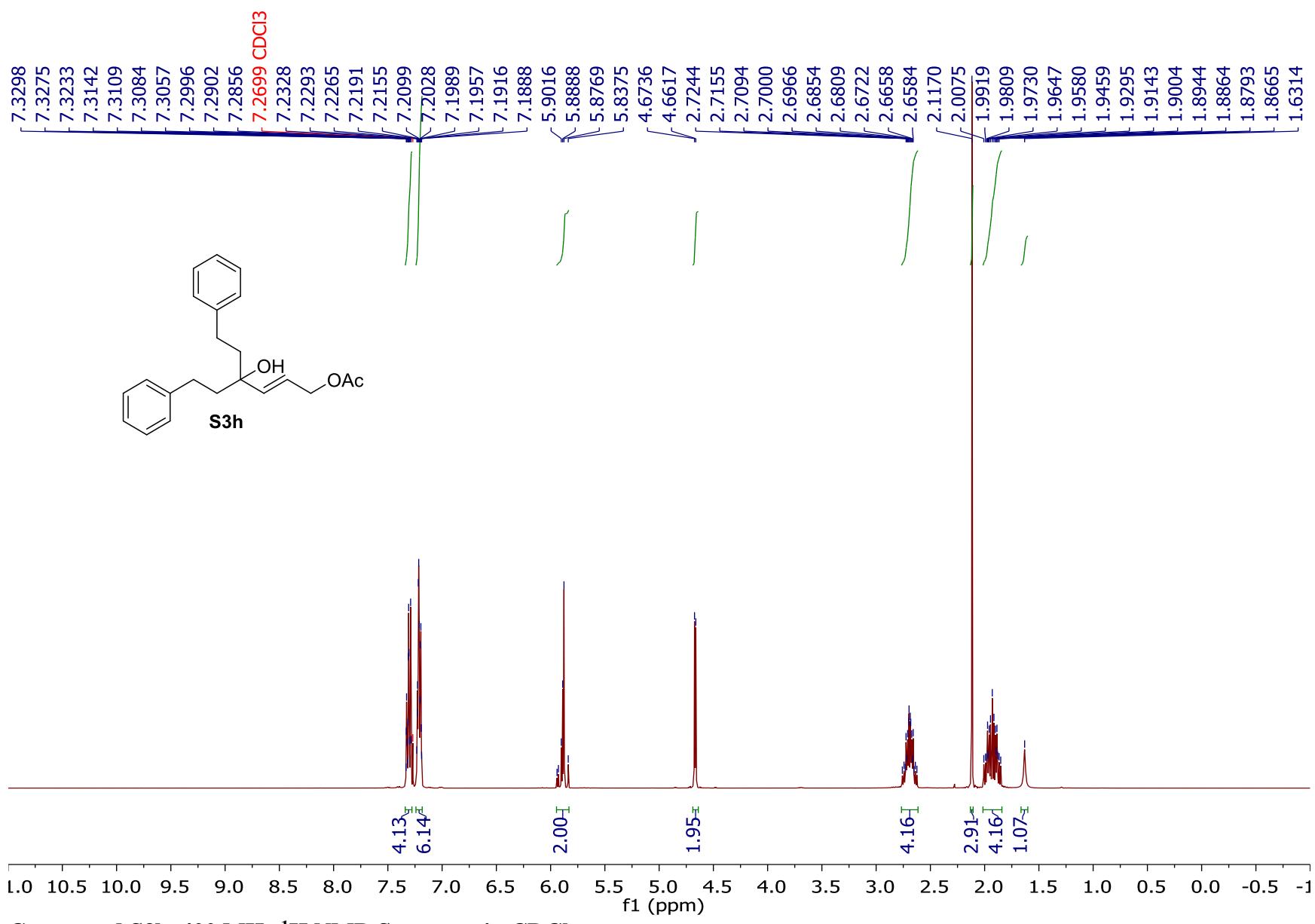


Compound S3f, 126 MHz ¹³C NMR in CDCl₃

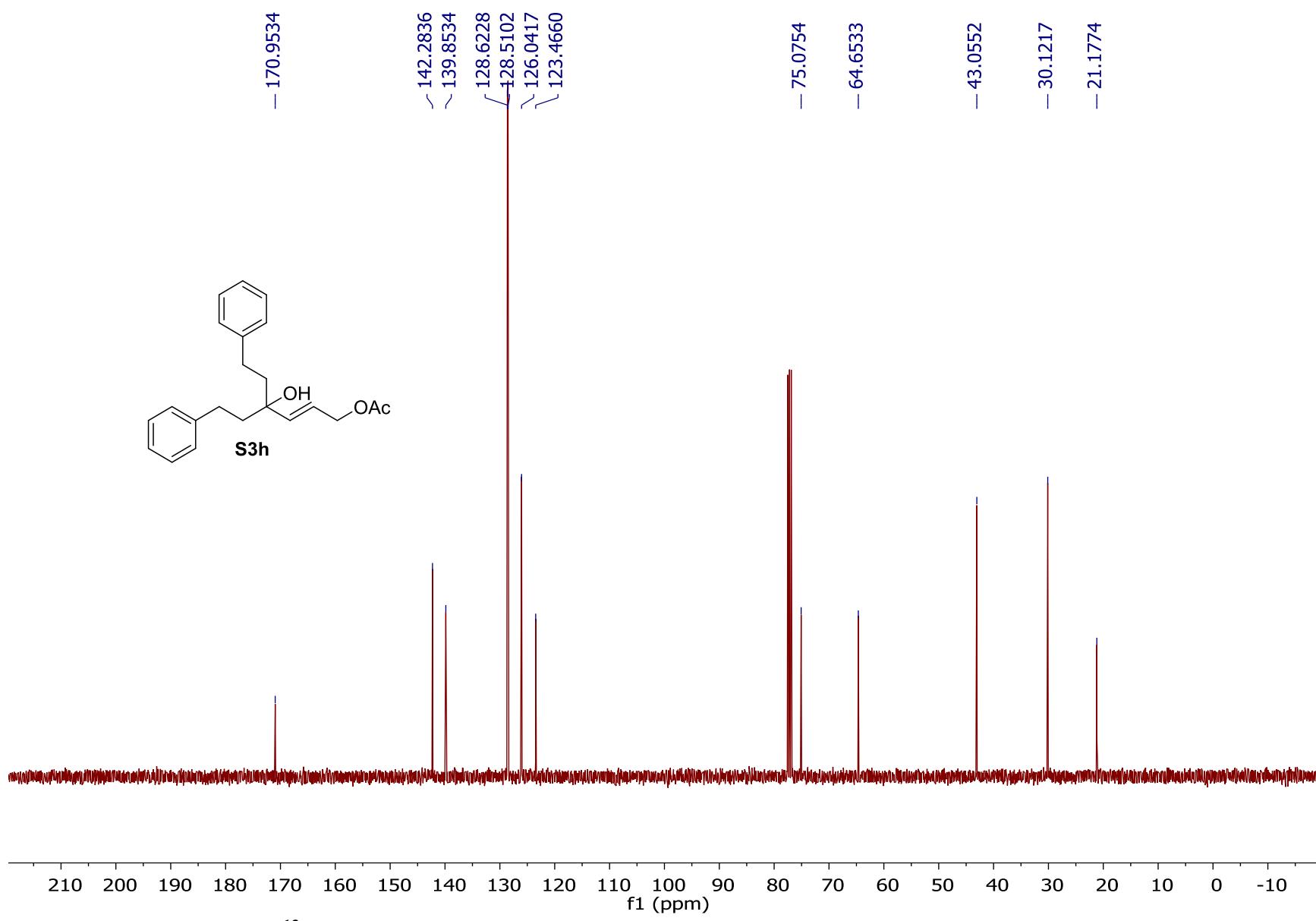




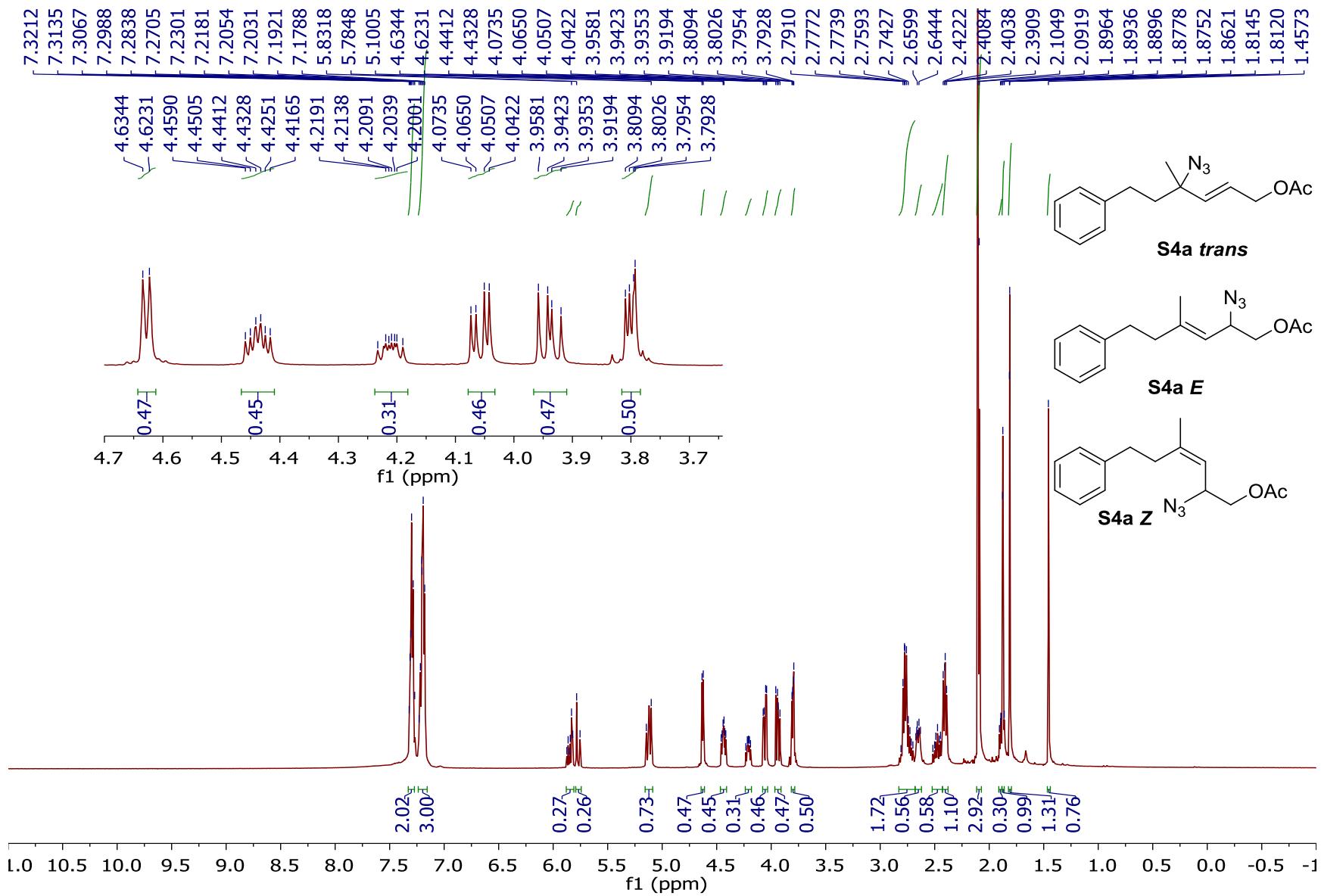
Compound S3g, 126 MHz ^{13}C NMR Spectrum in CDCl_3

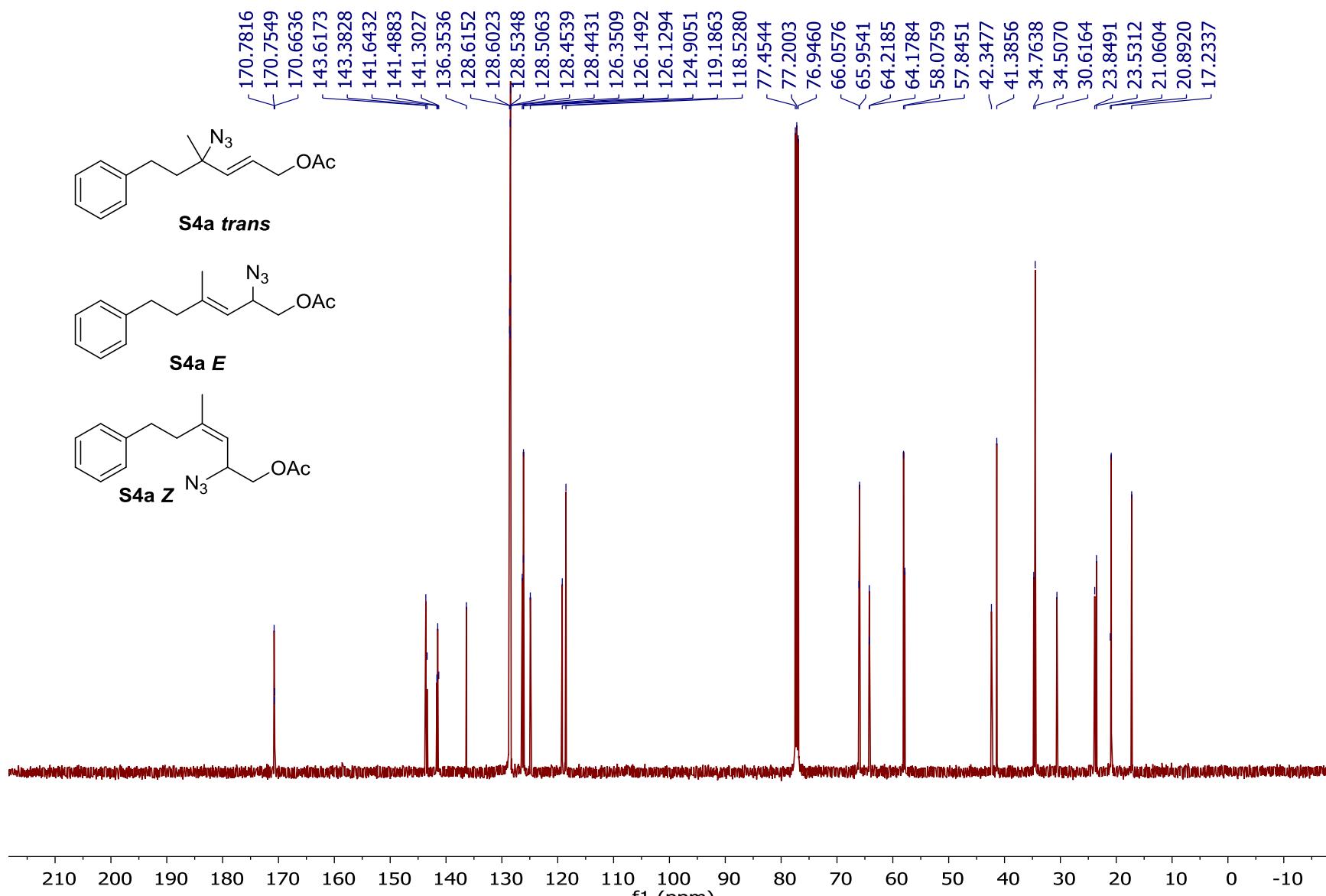


Compound S3h, 400 MHz ¹H NMR Spectrum in CDCl₃

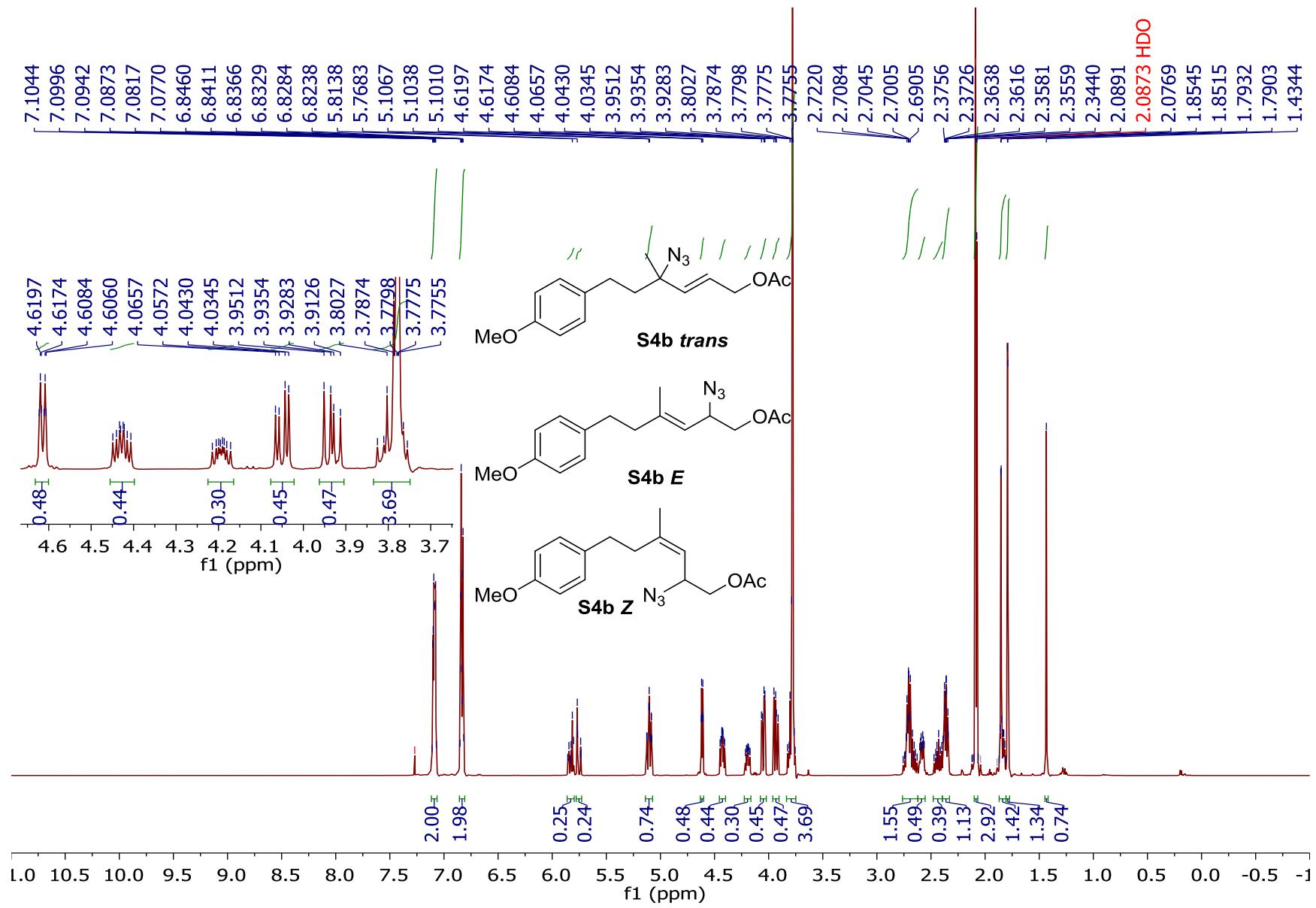


Compound S3h, 101 MHz ^{13}C NMR Spectrum in CDCl_3

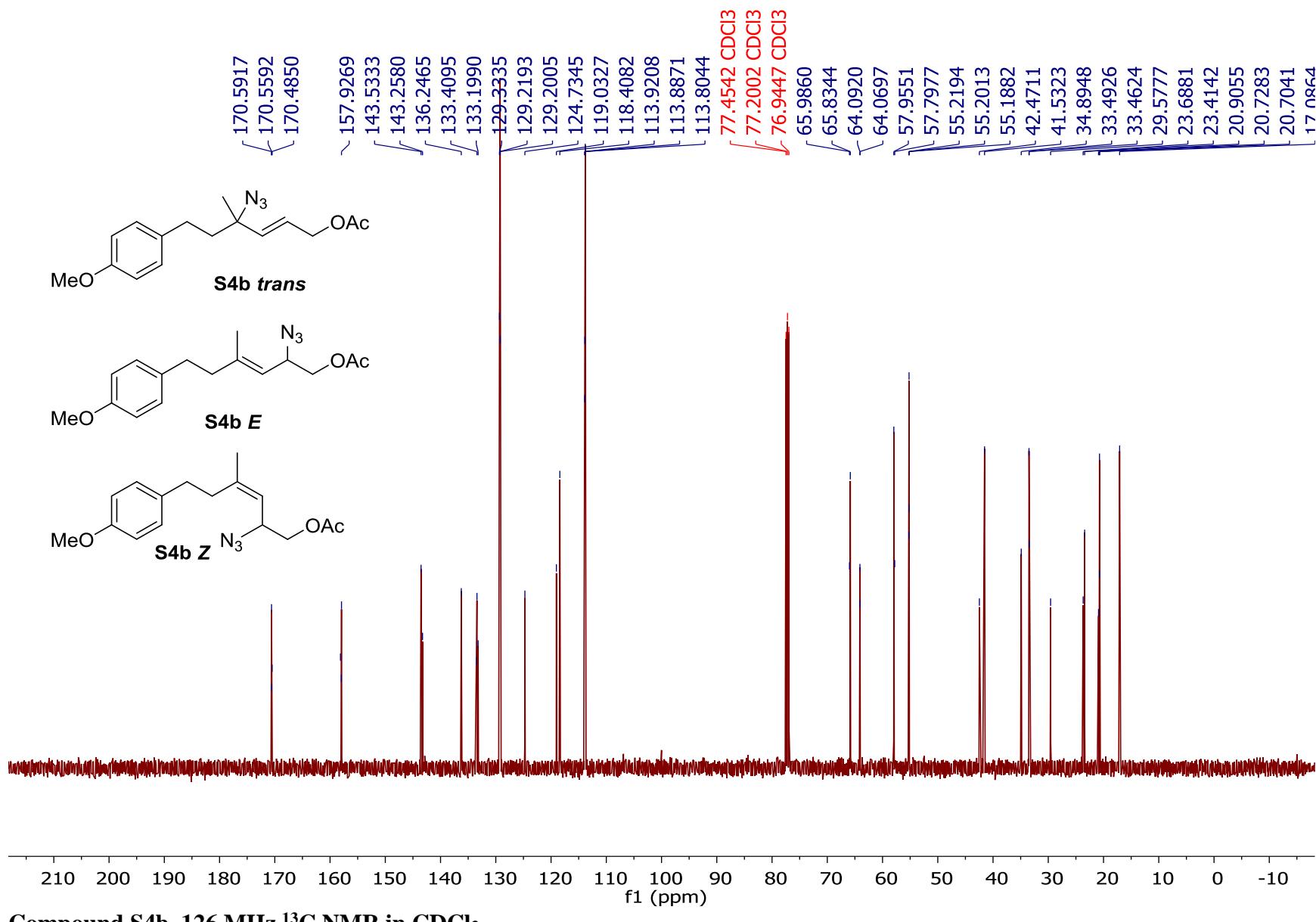


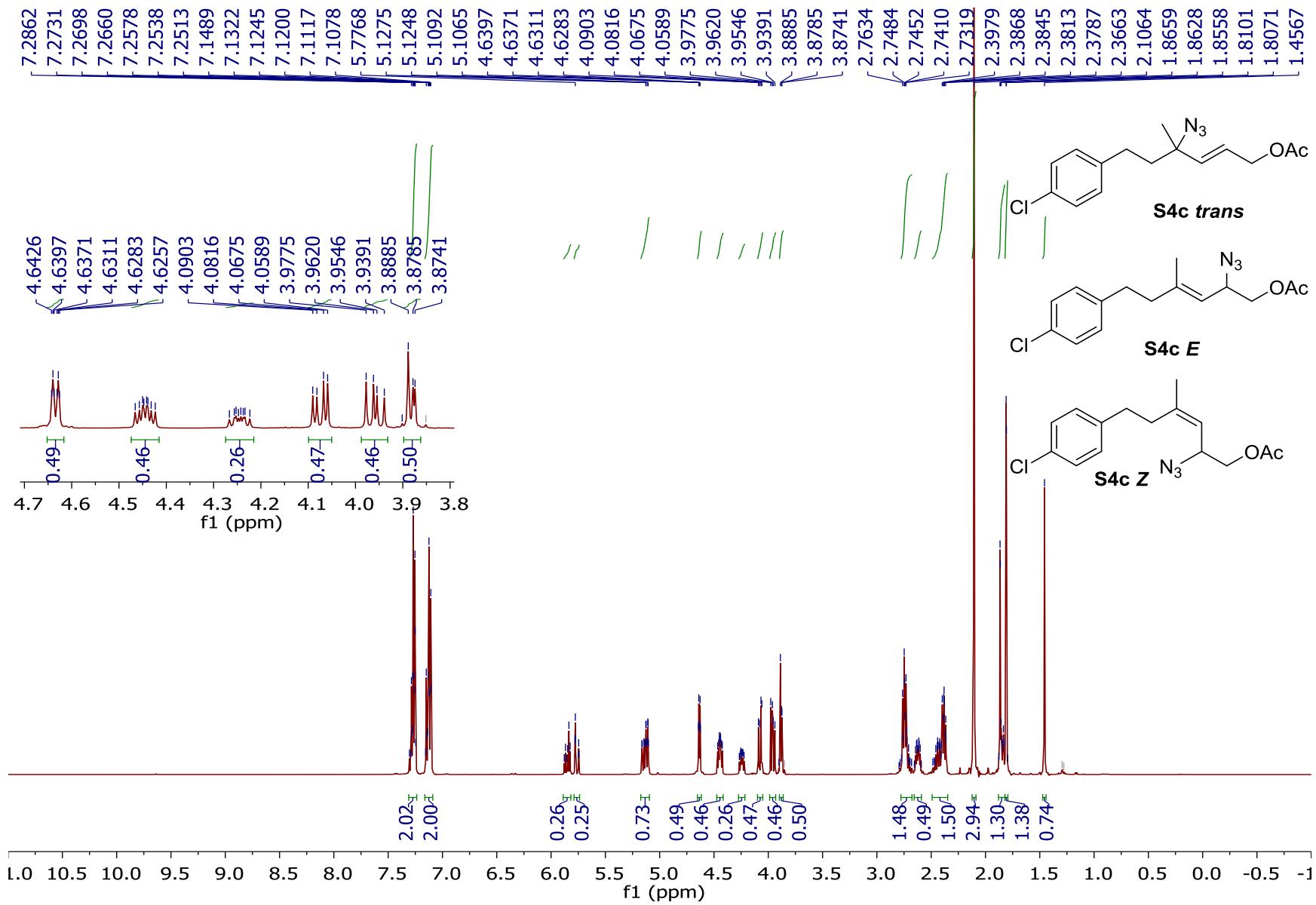


Compound S4a, 126 MHz ^{13}C NMR in CDCl_3

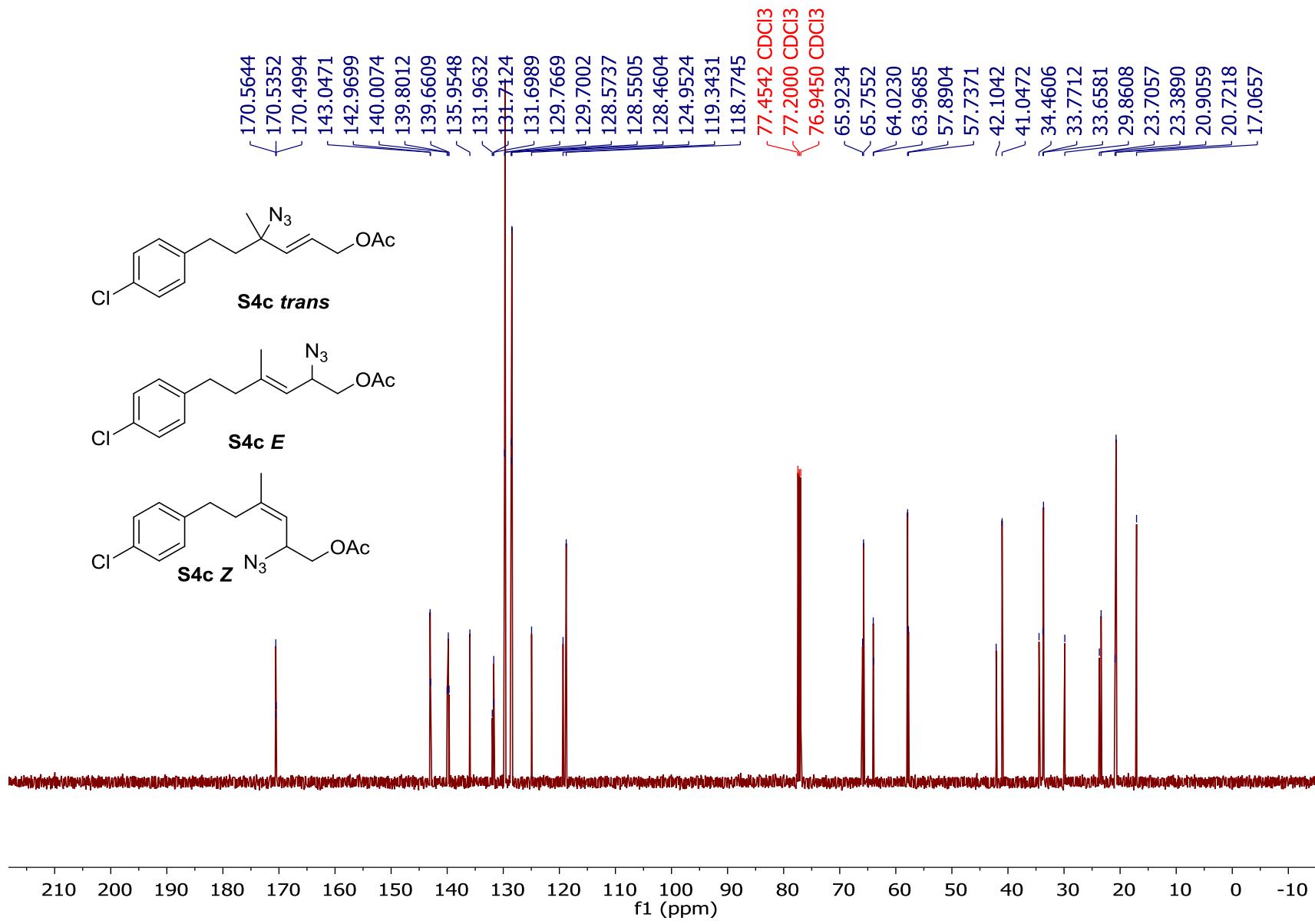


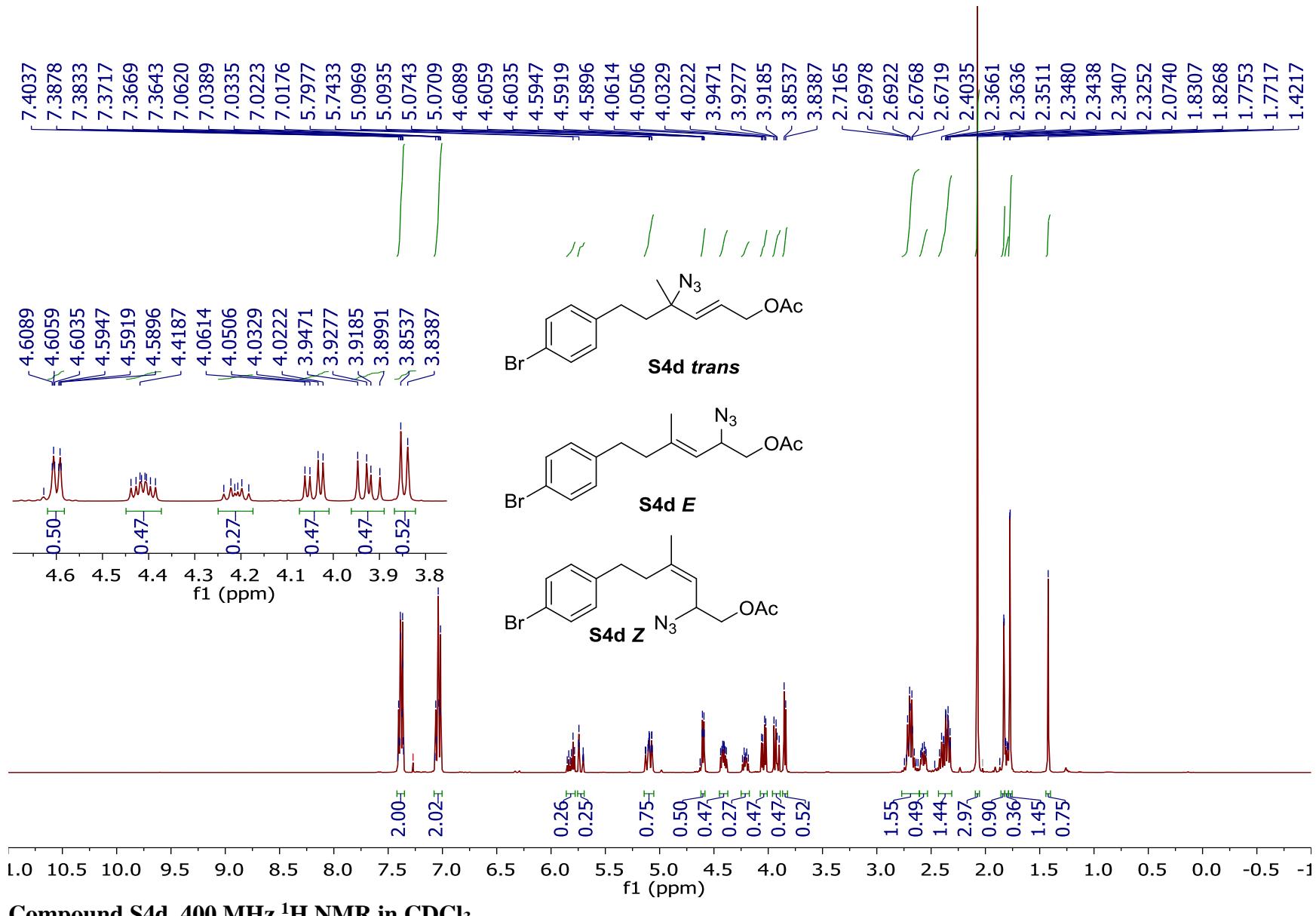
Compound S4b, 500 MHz ^1H NMR in CDCl_3

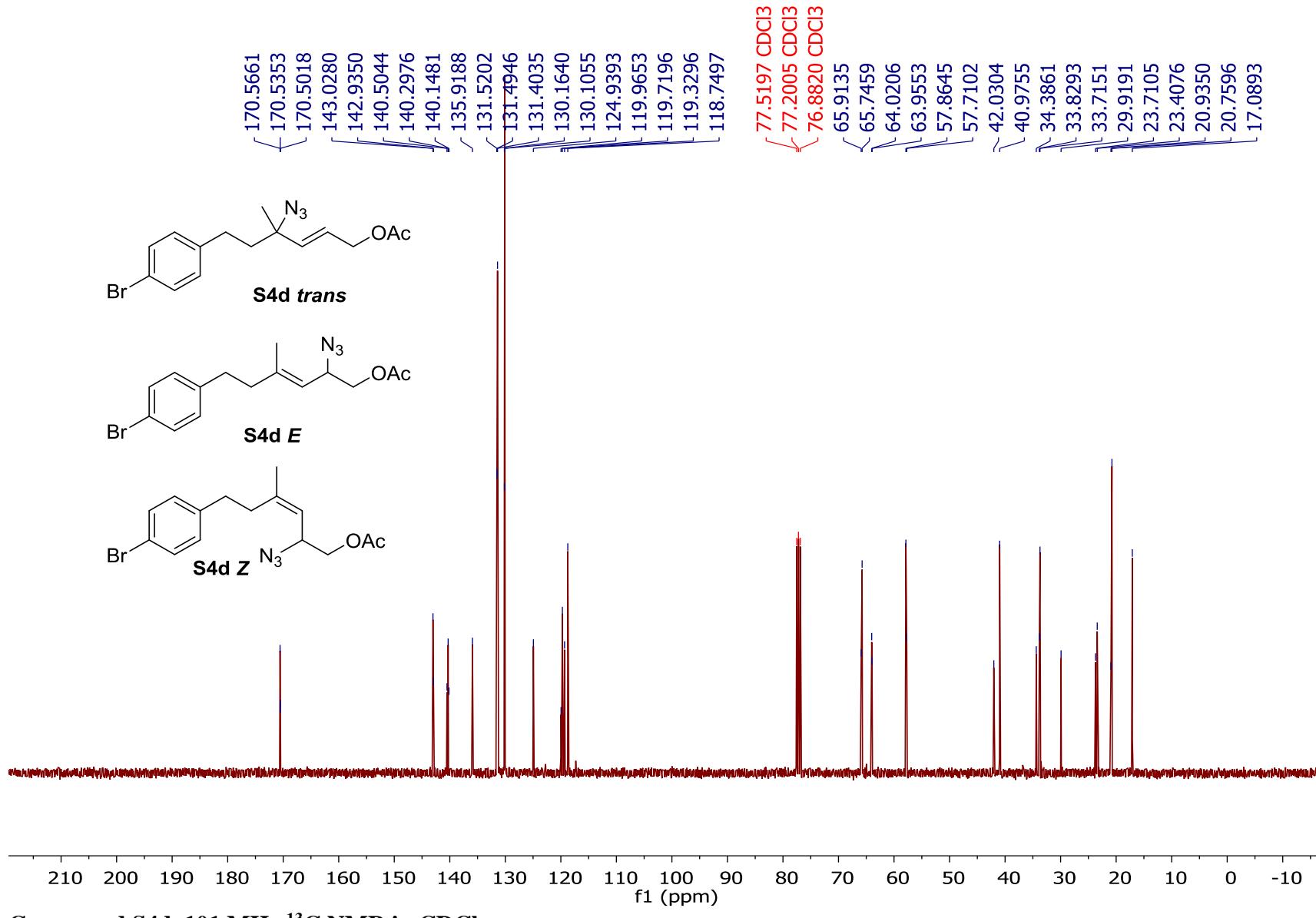


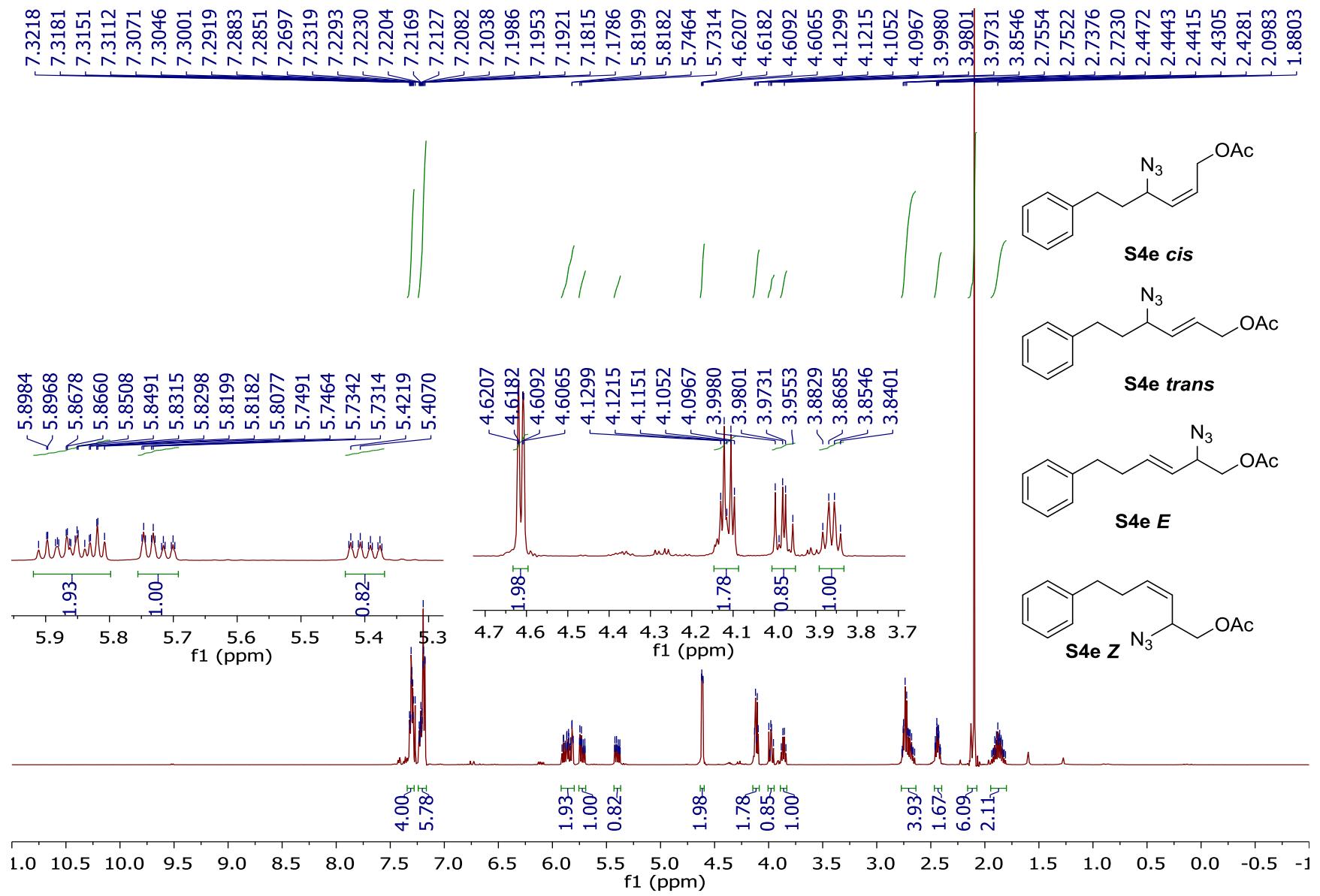


Compound S4c, 500 MHz ^1H NMR in CDCl_3

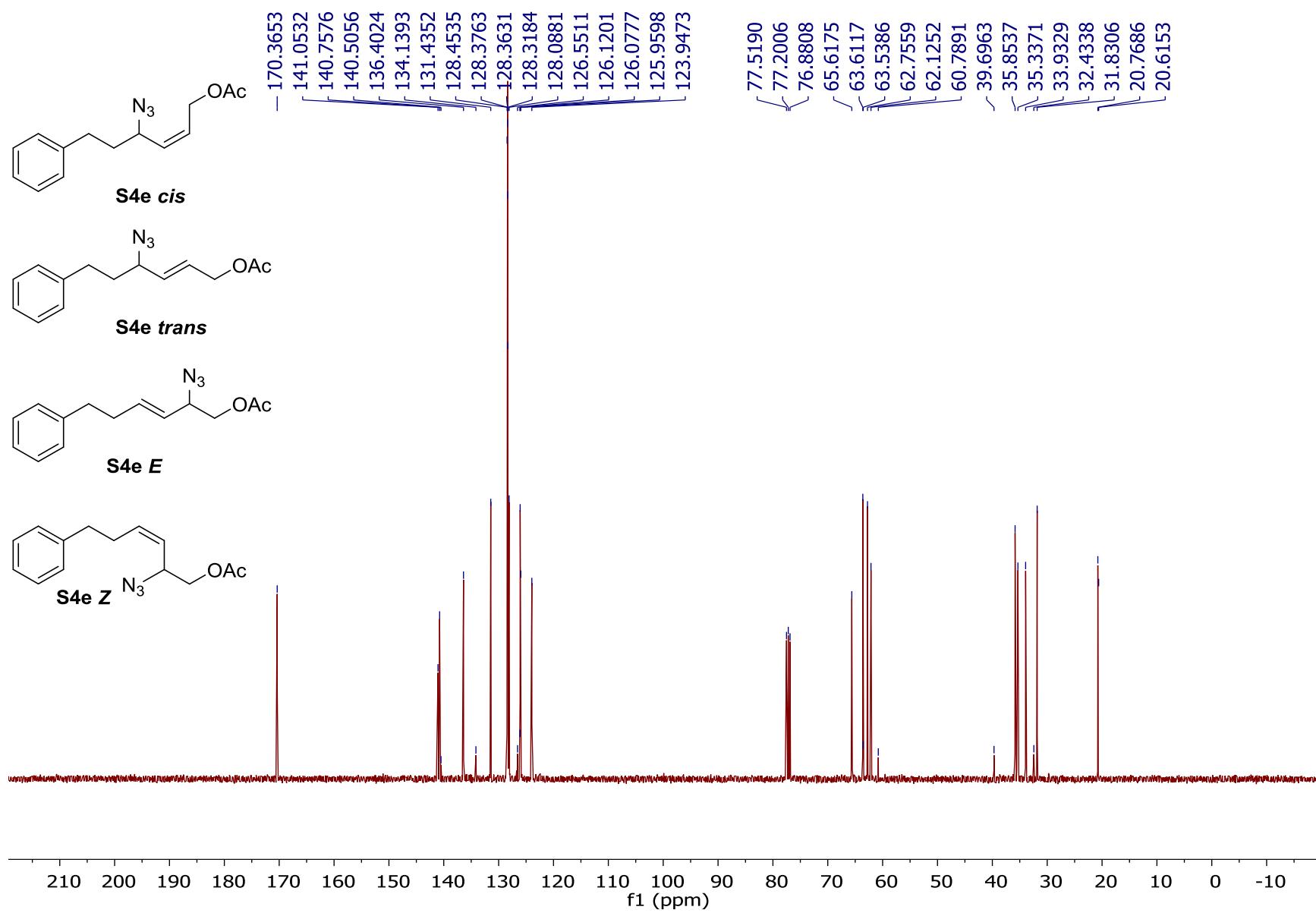


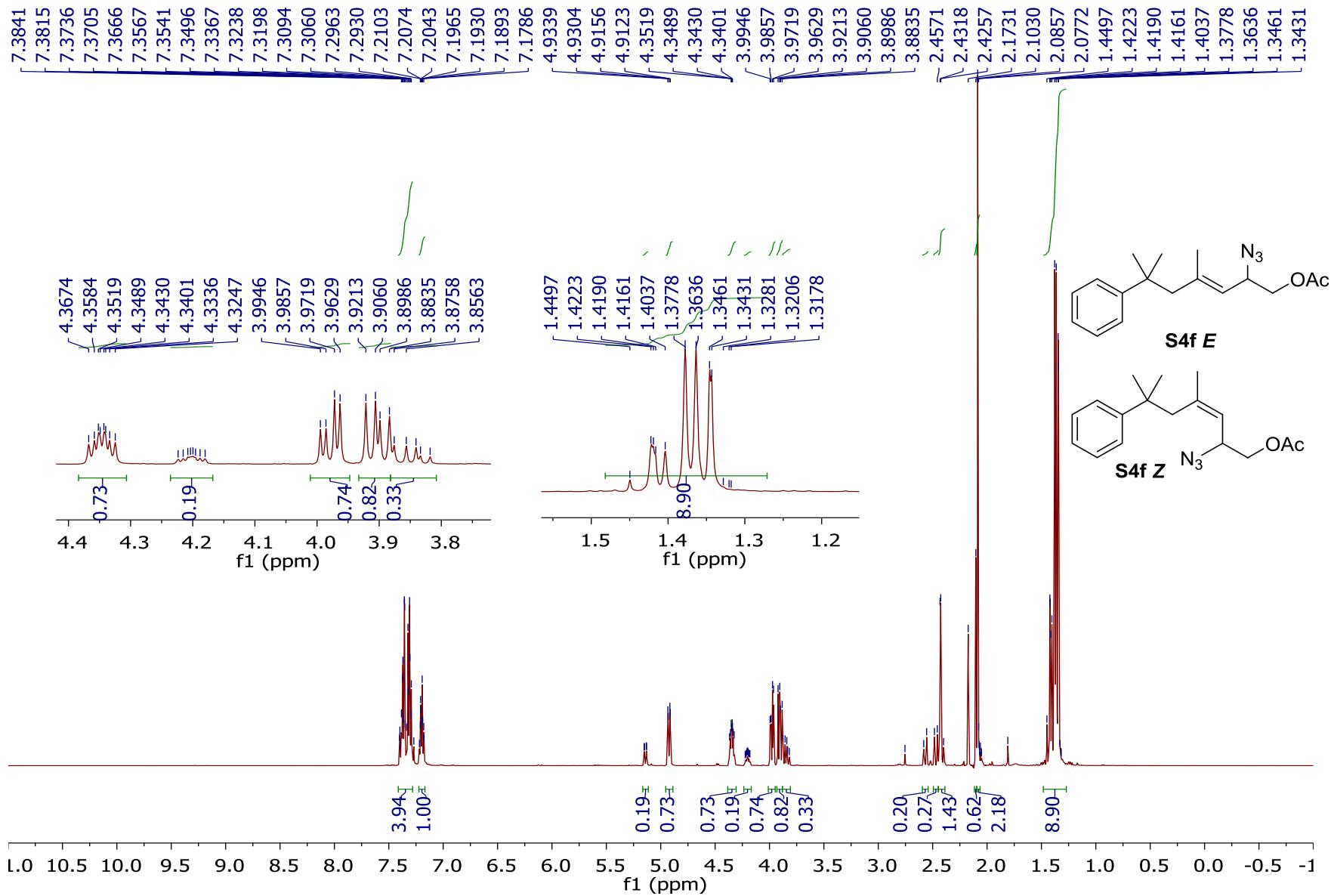


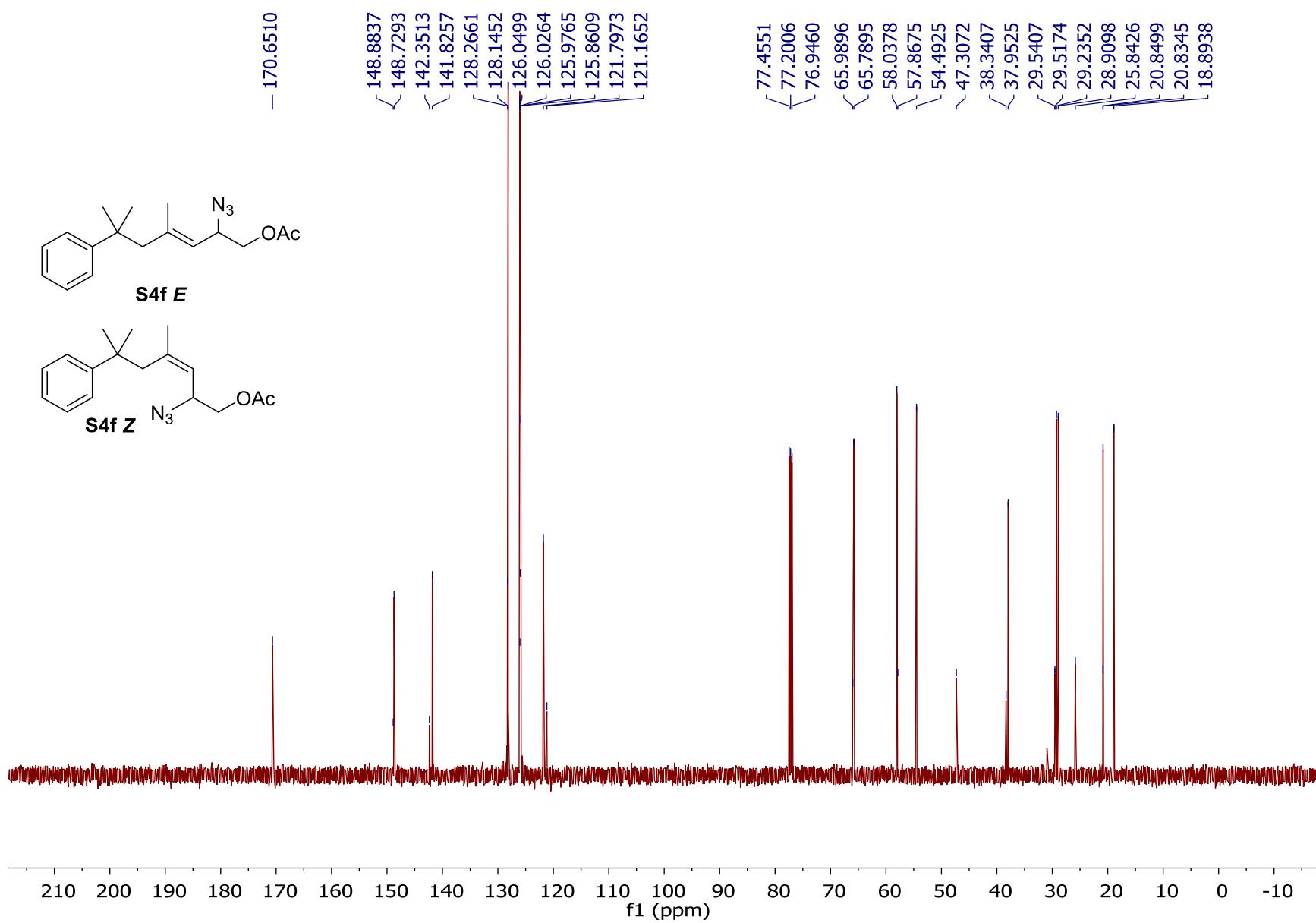




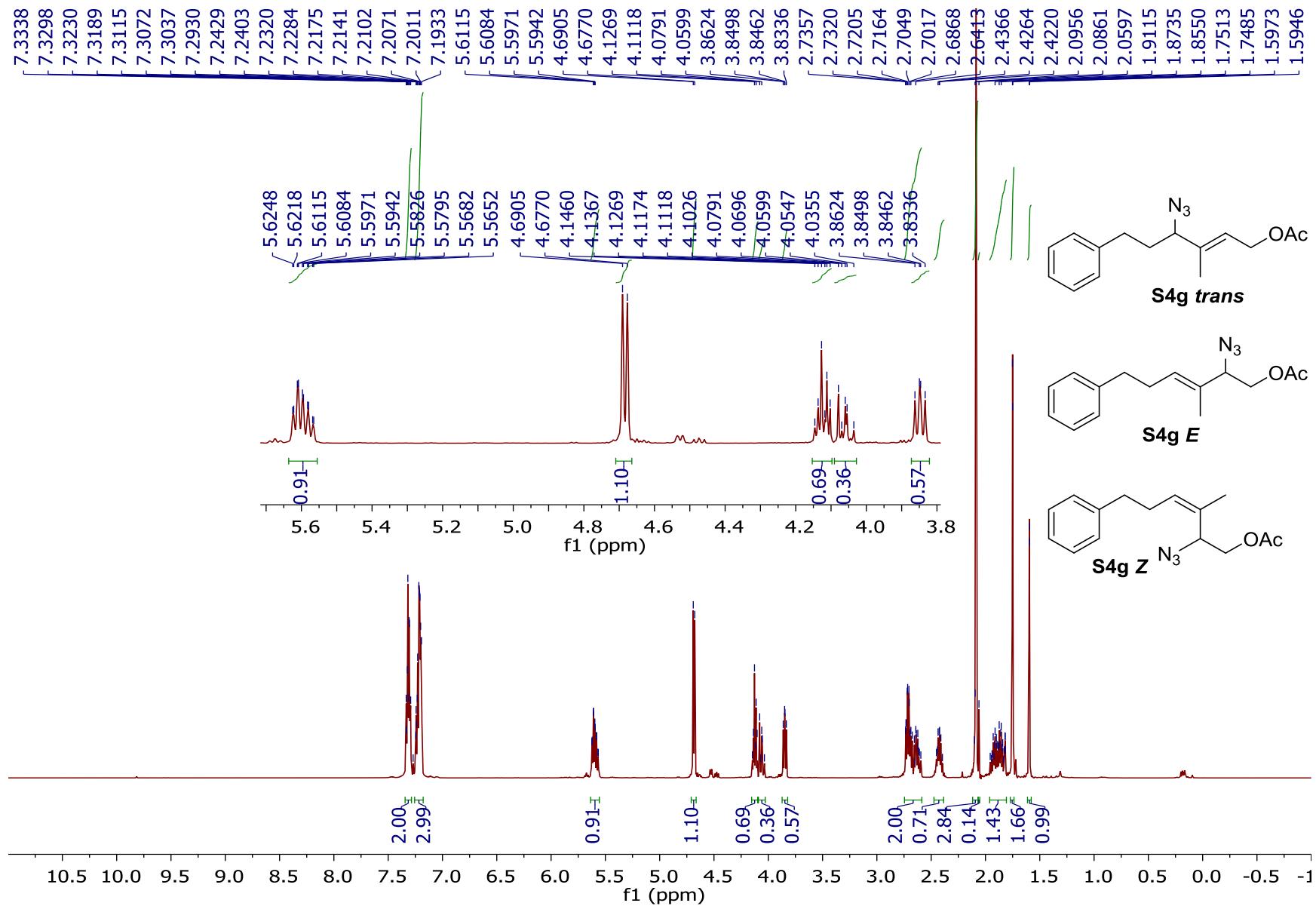
Compound **S4e**, 500 MHz ^1H NMR in CDCl_3



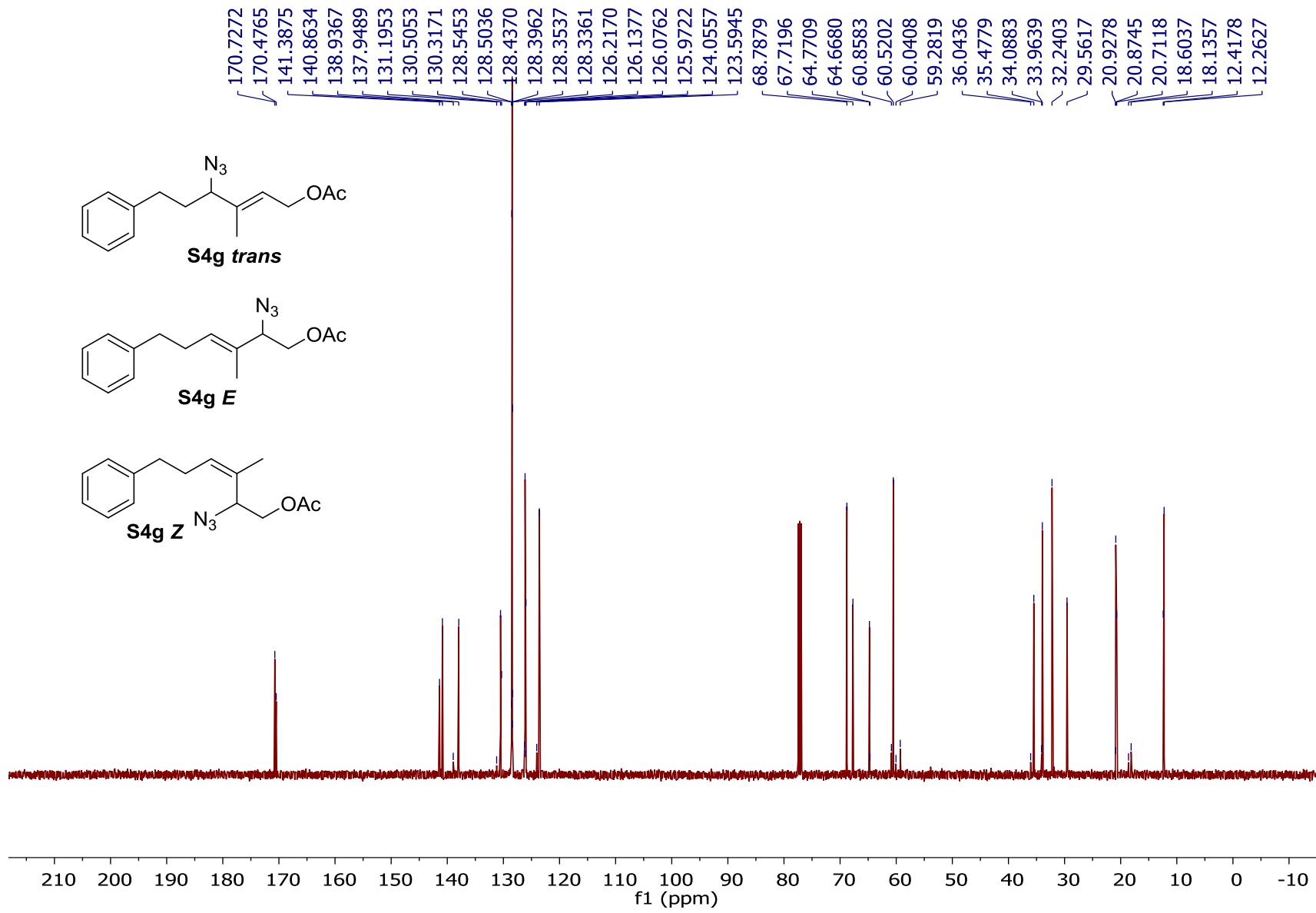




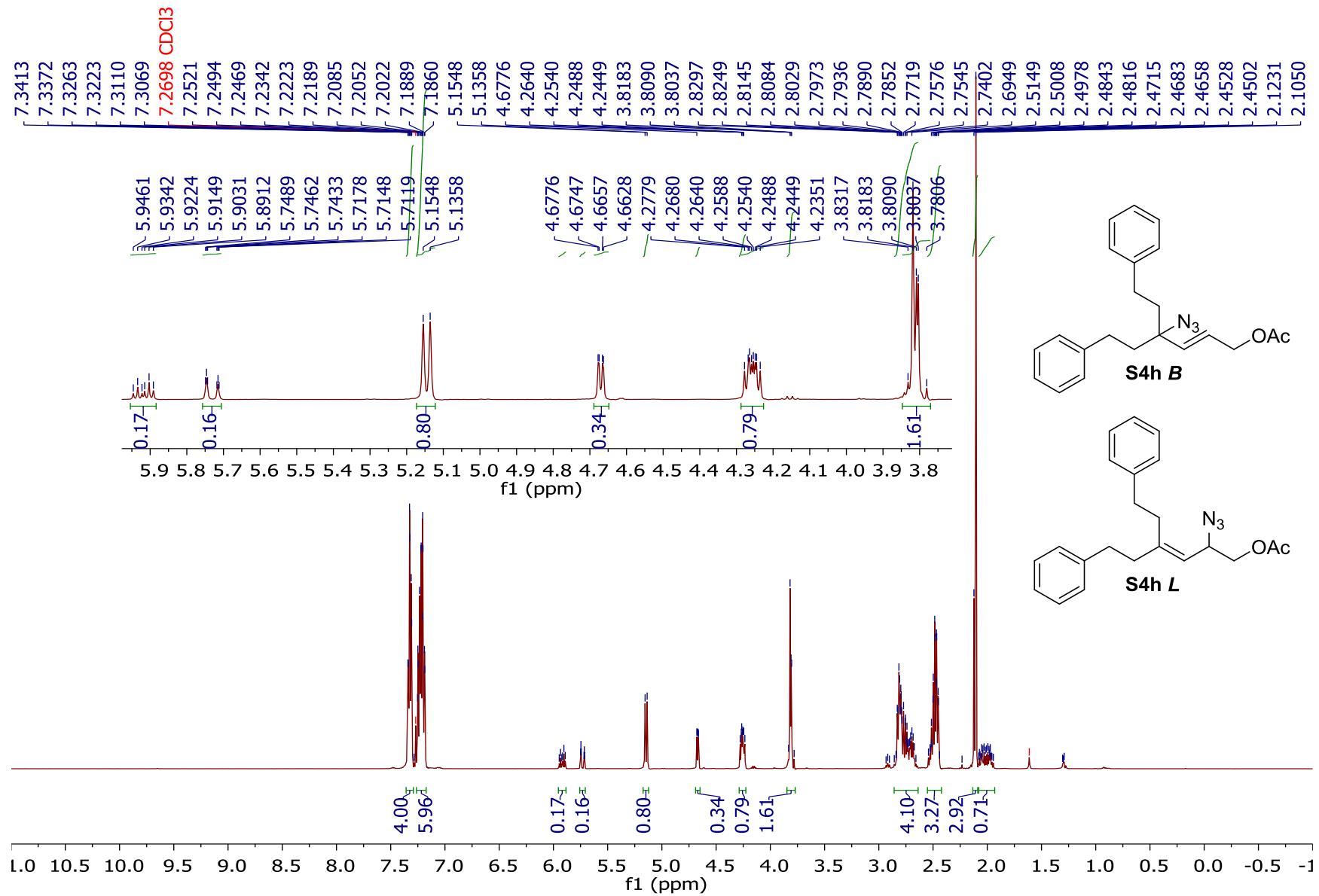
Compound S4f, 126 MHz ^{13}C NMR in CDCl_3



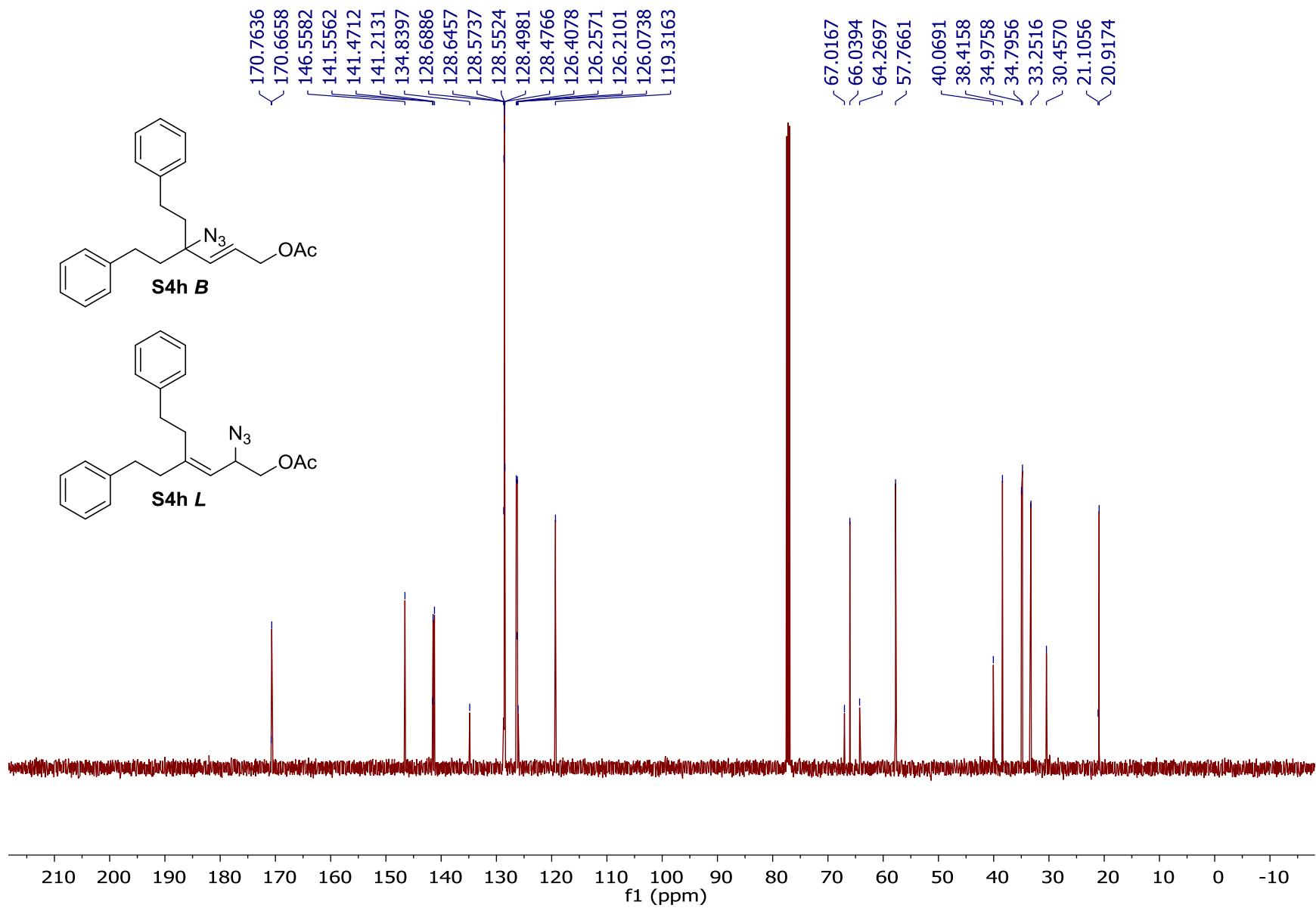
Compound S4g, 500 MHz ^1H NMR Spectrum in CDCl_3



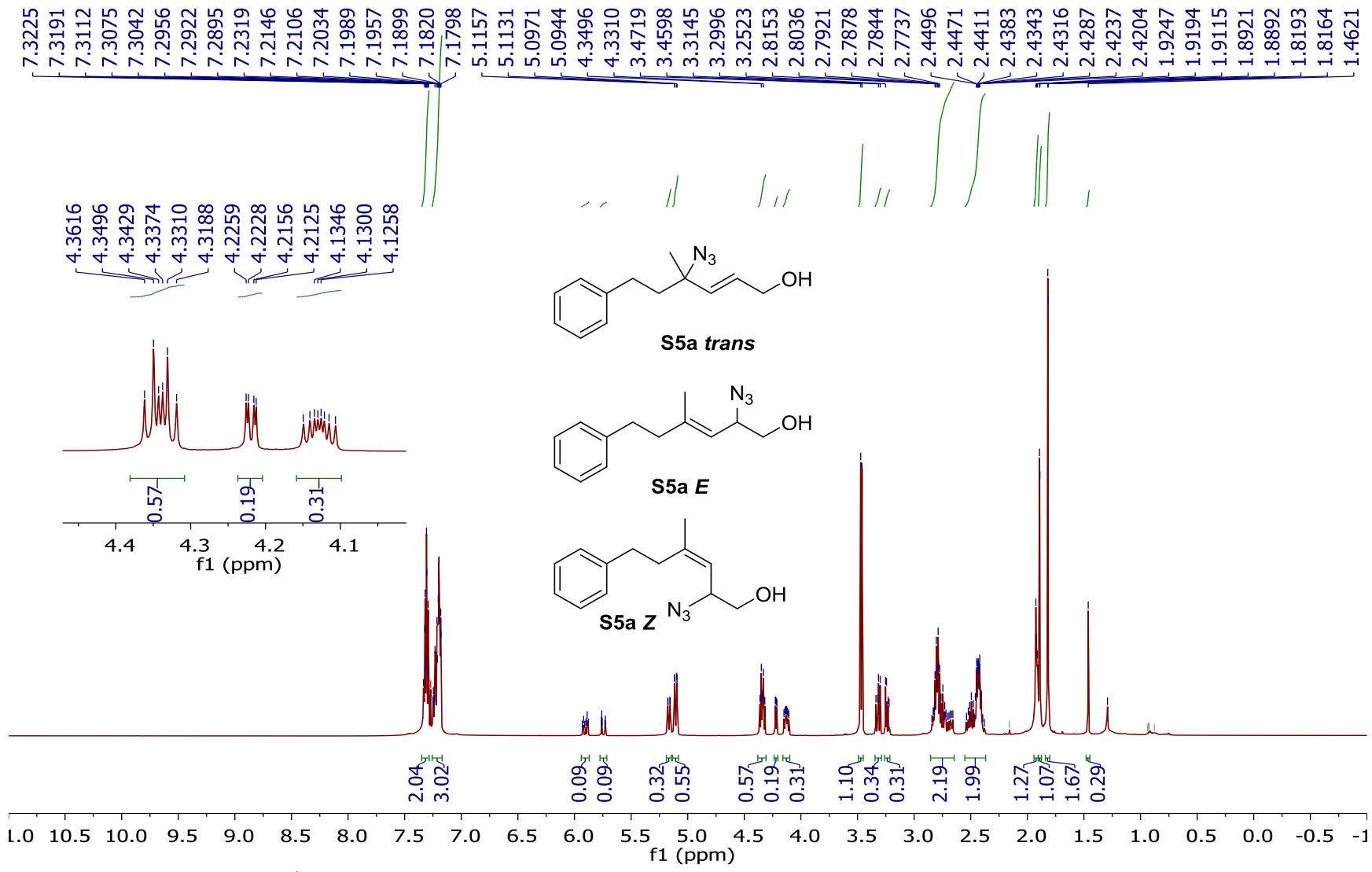
Compound S4g, 126 MHz ^{13}C NMR Spectrum in CDCl_3

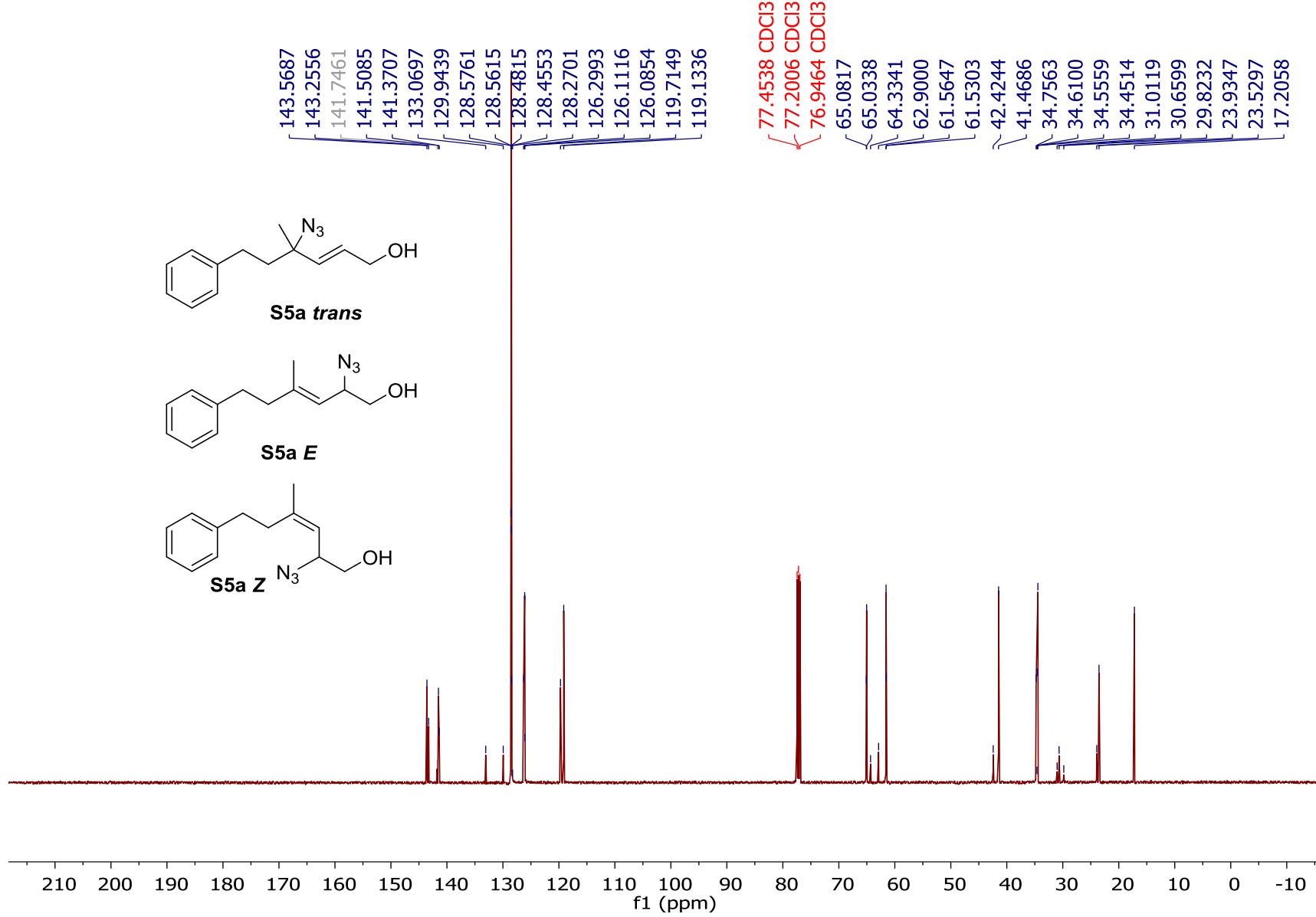


Compound S4h, 500 MHz ^1H NMR Spectrum in CDCl_3

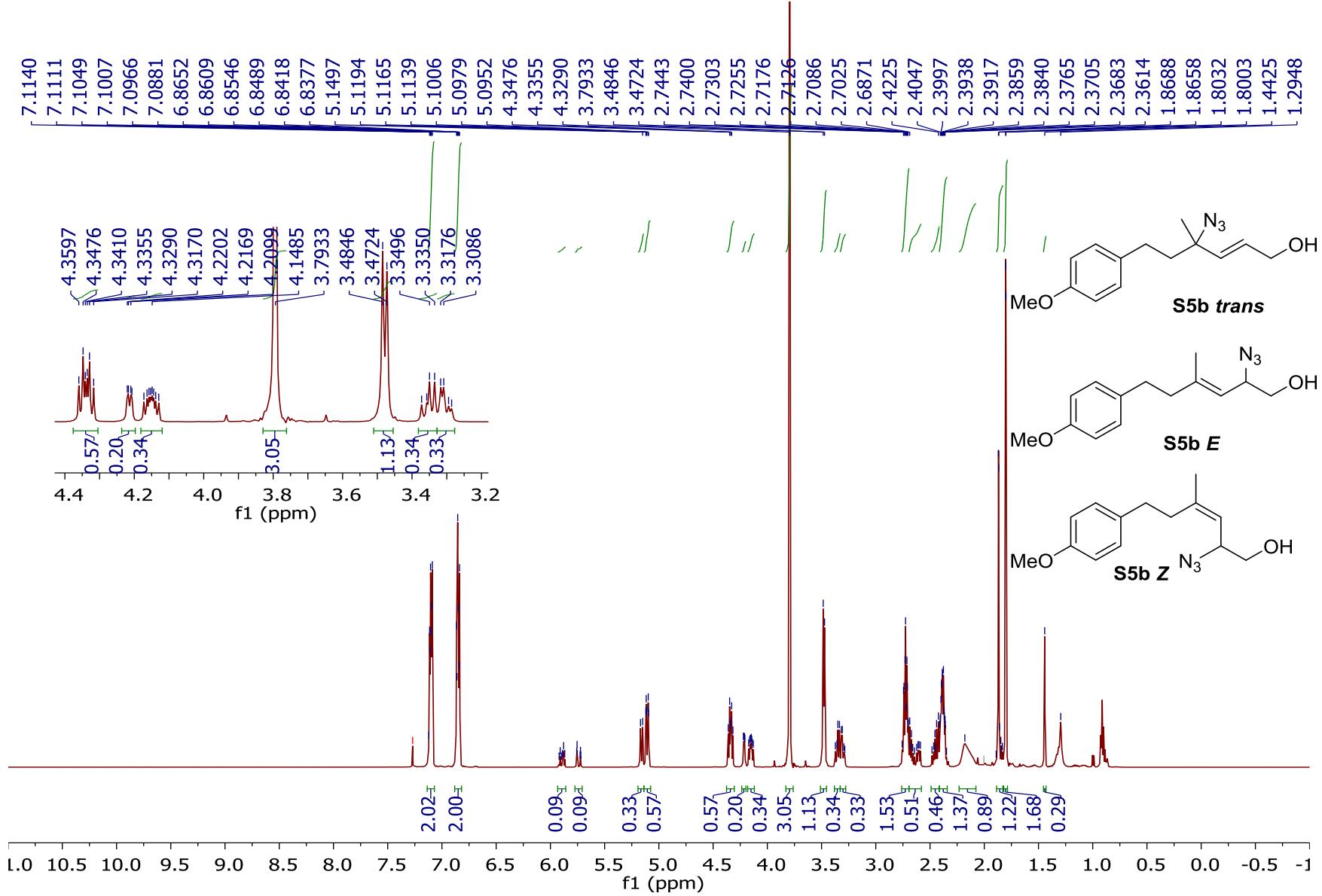


Compound S4h, 126 MHz ^{13}C NMR Spectrum in CDCl_3

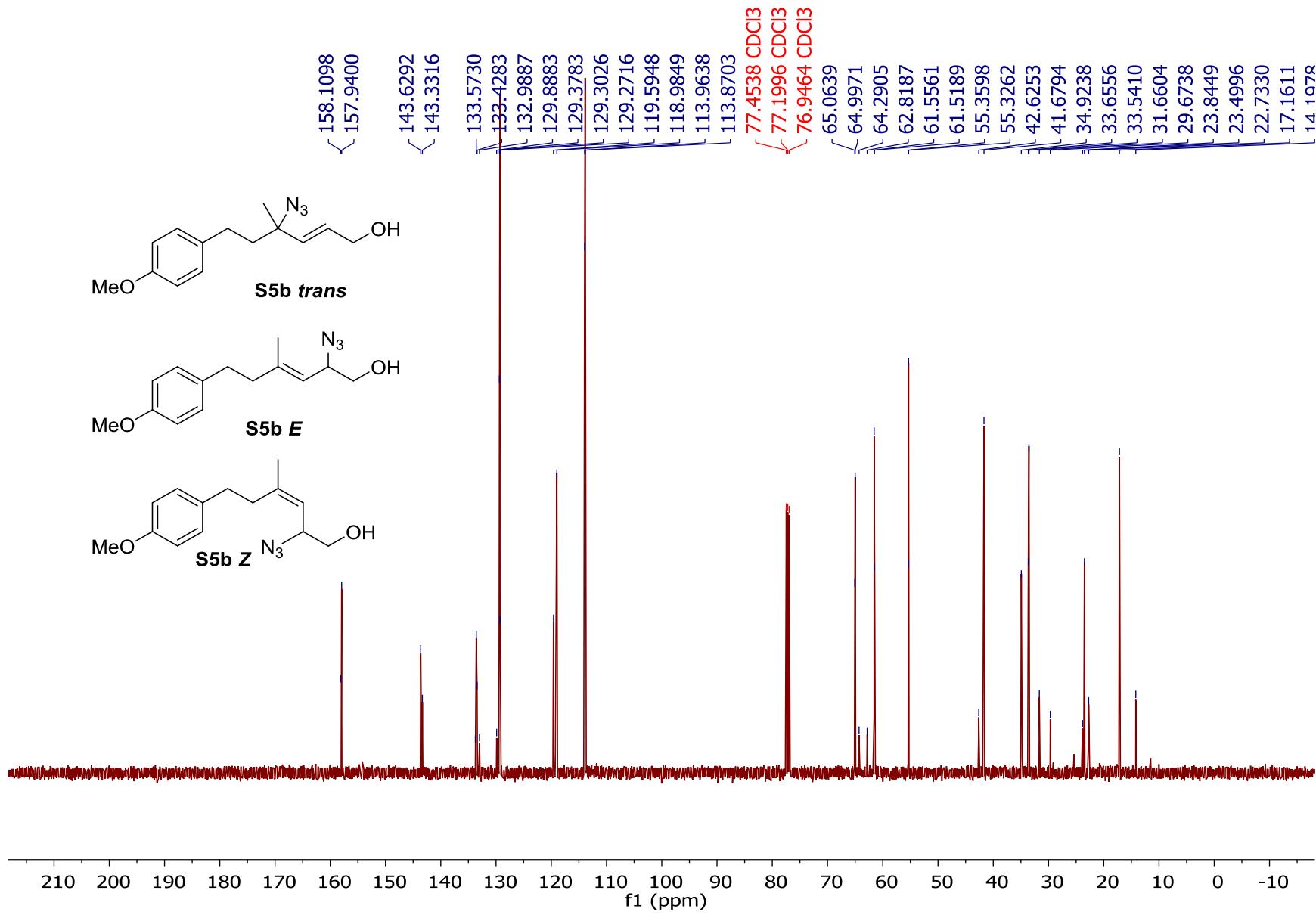


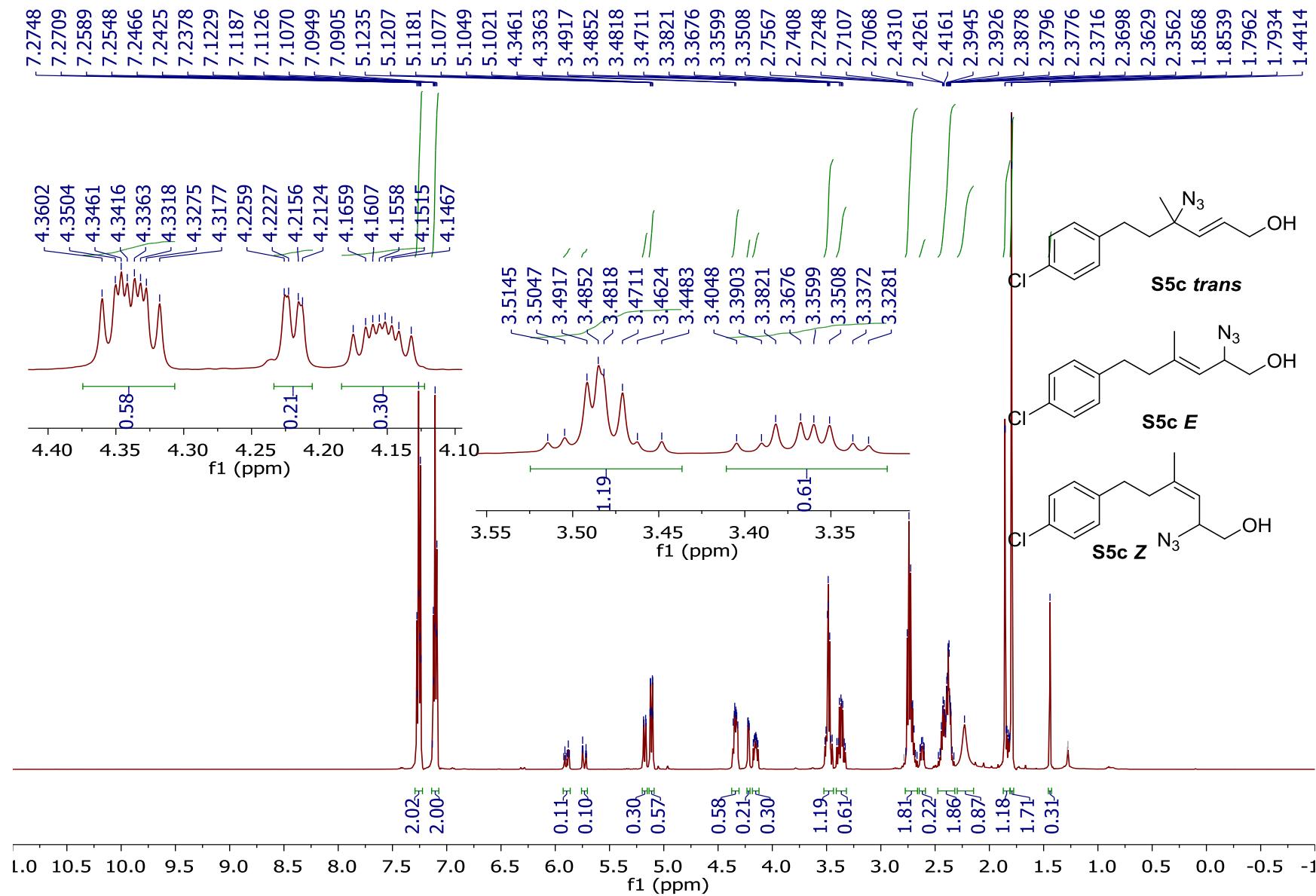


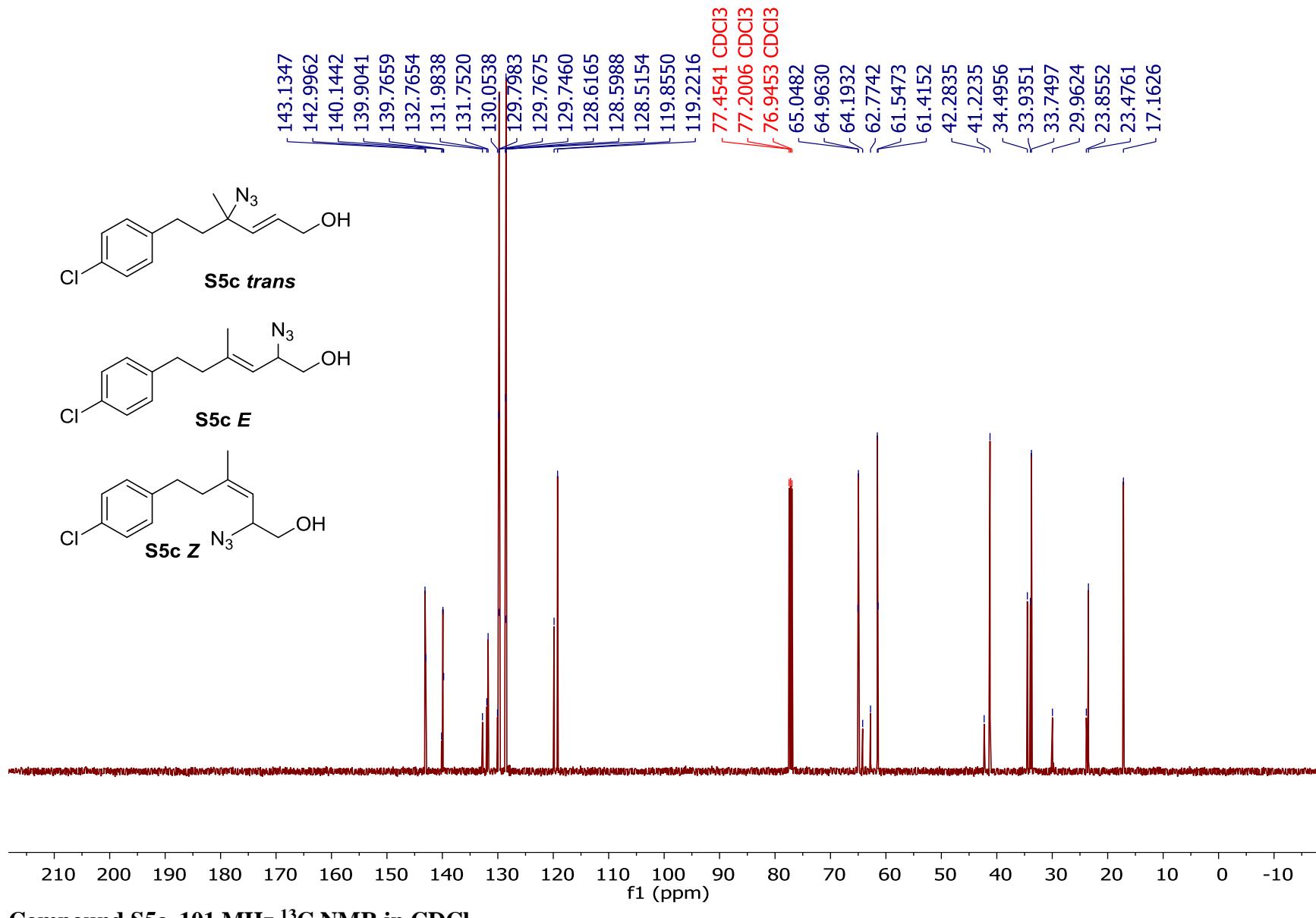
Compound S5a, 101 MHz ¹³C NMR in CDCl₃



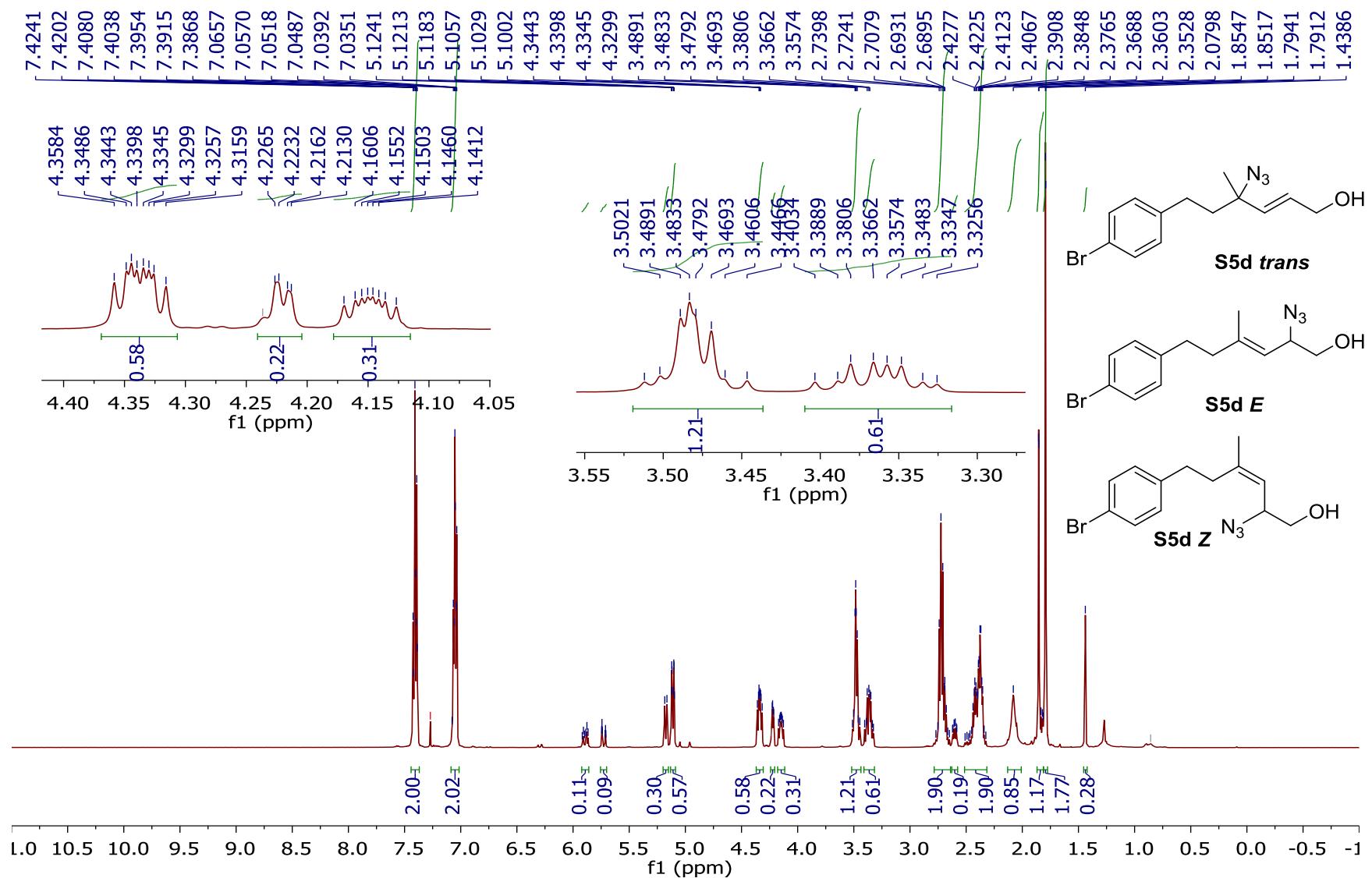
Compound S5b, 400 MHz ^1H NMR in CDCl_3



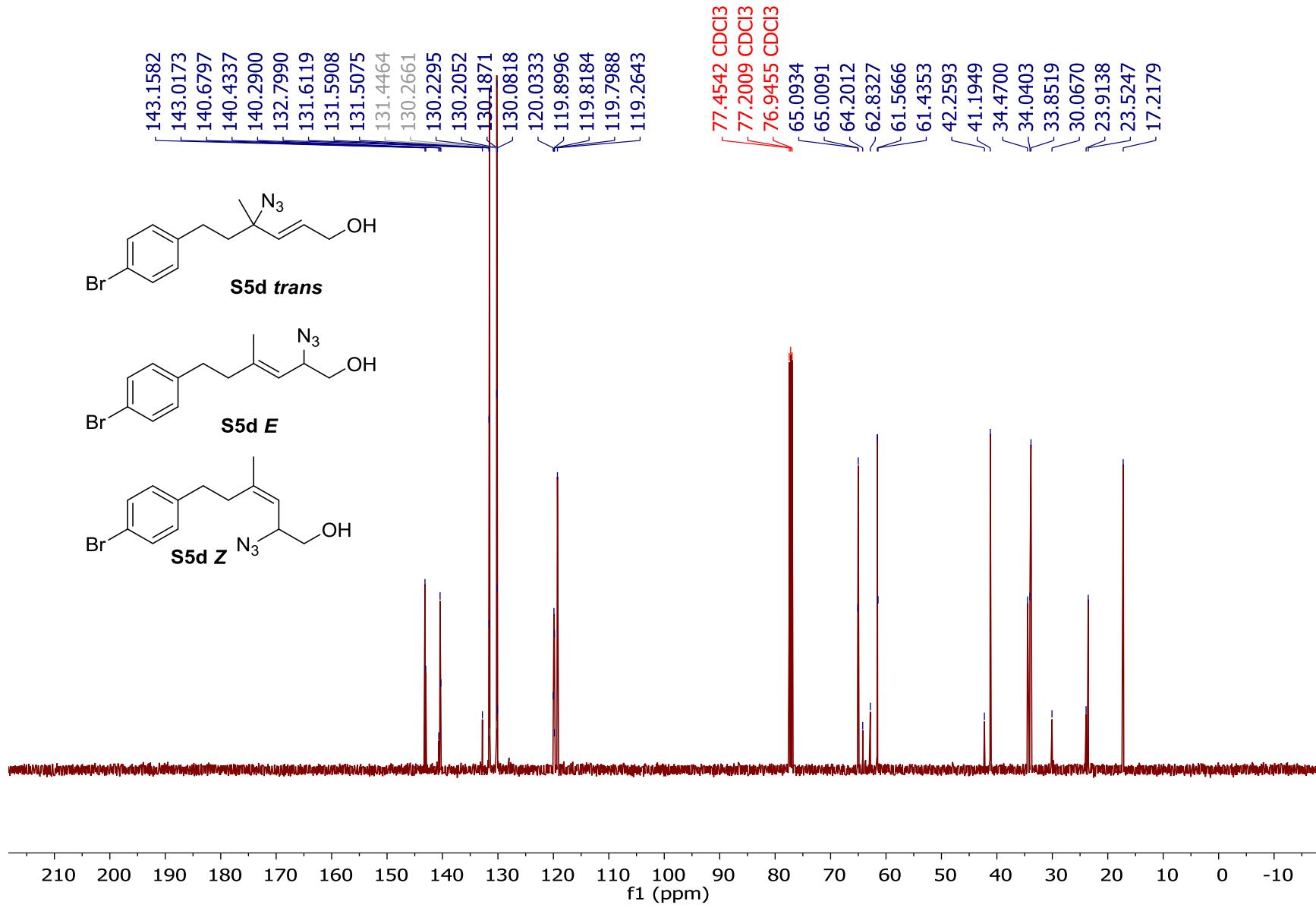


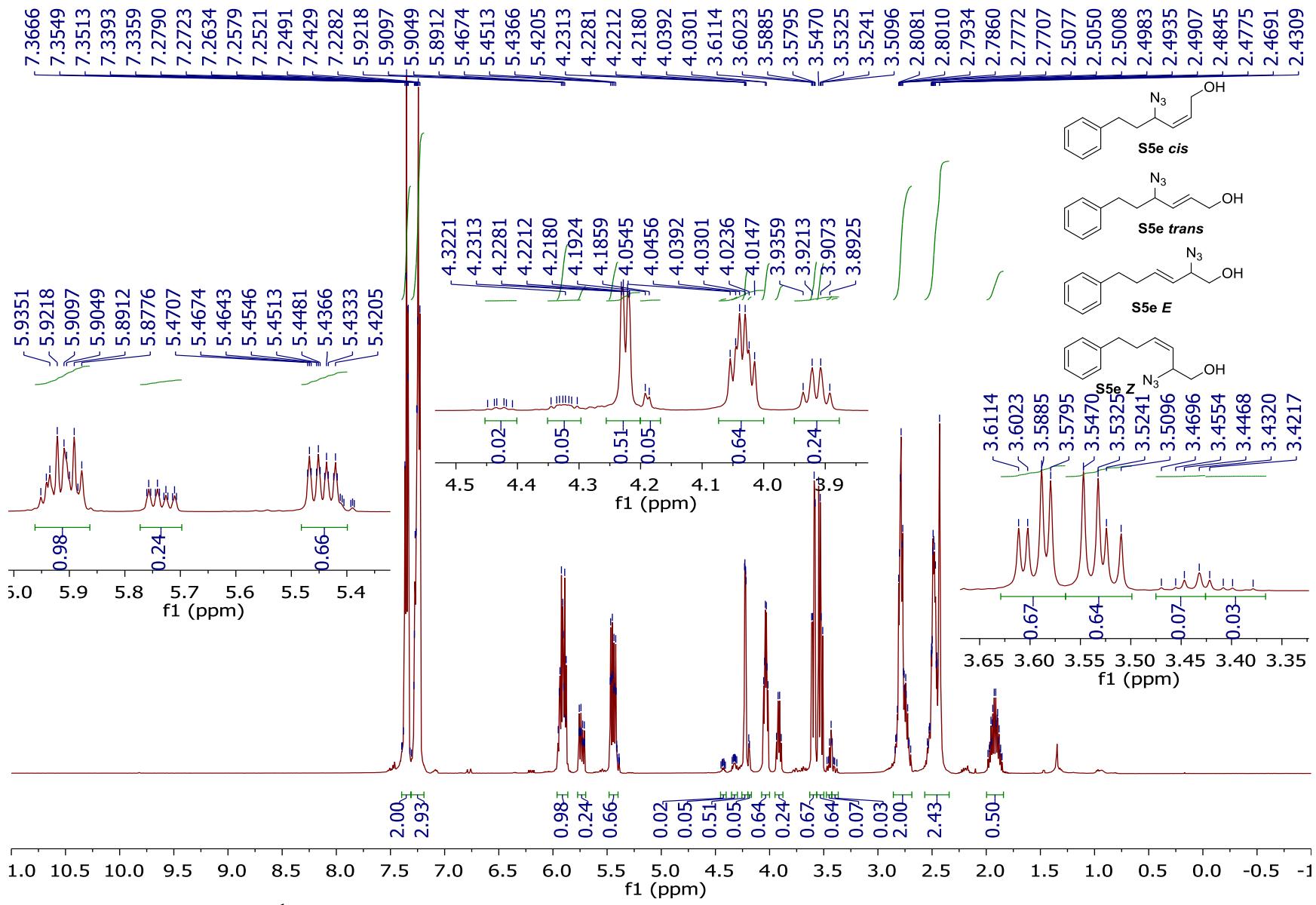


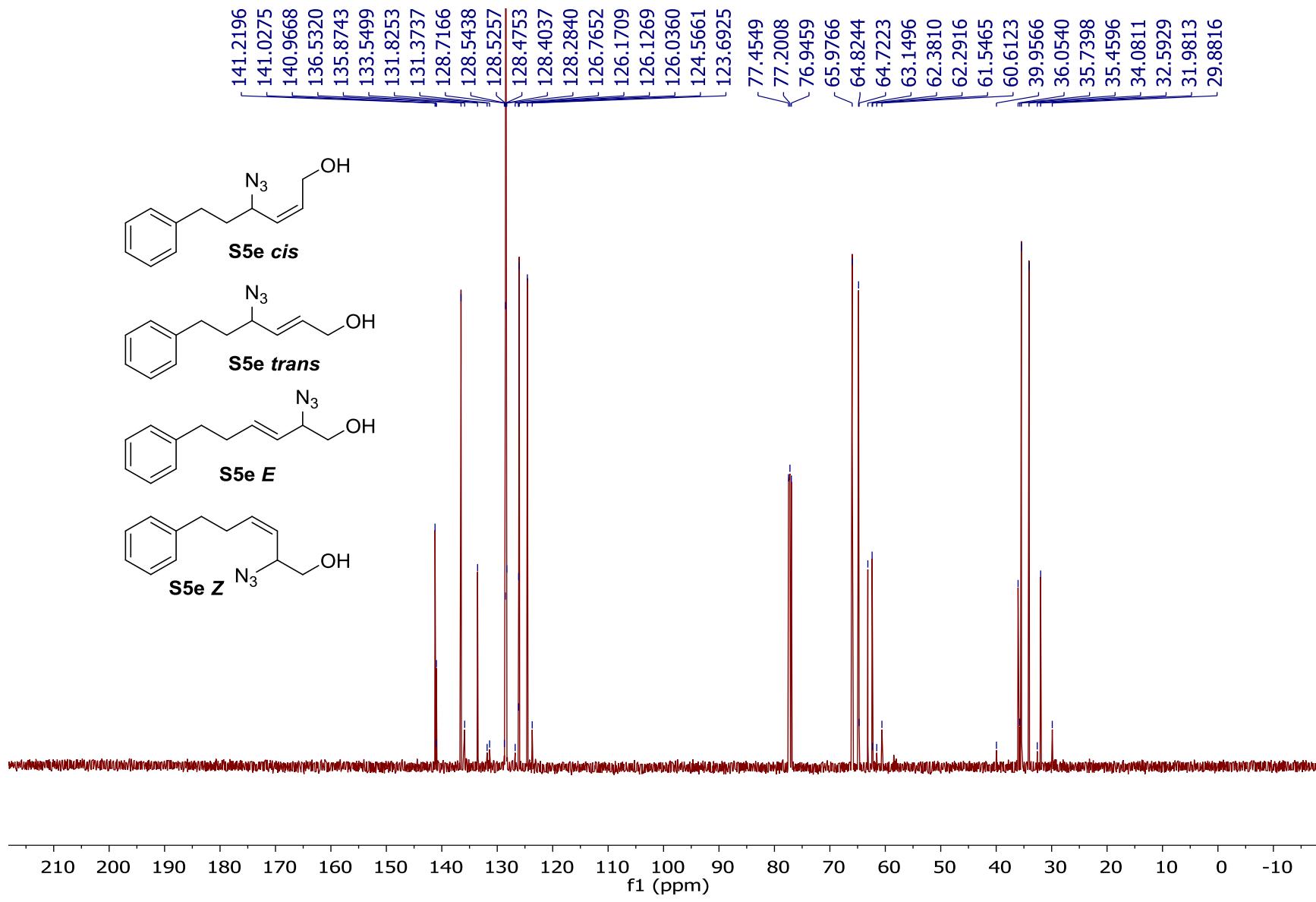
Compound S5c, 101 MHz ¹³C NMR in CDCl₃



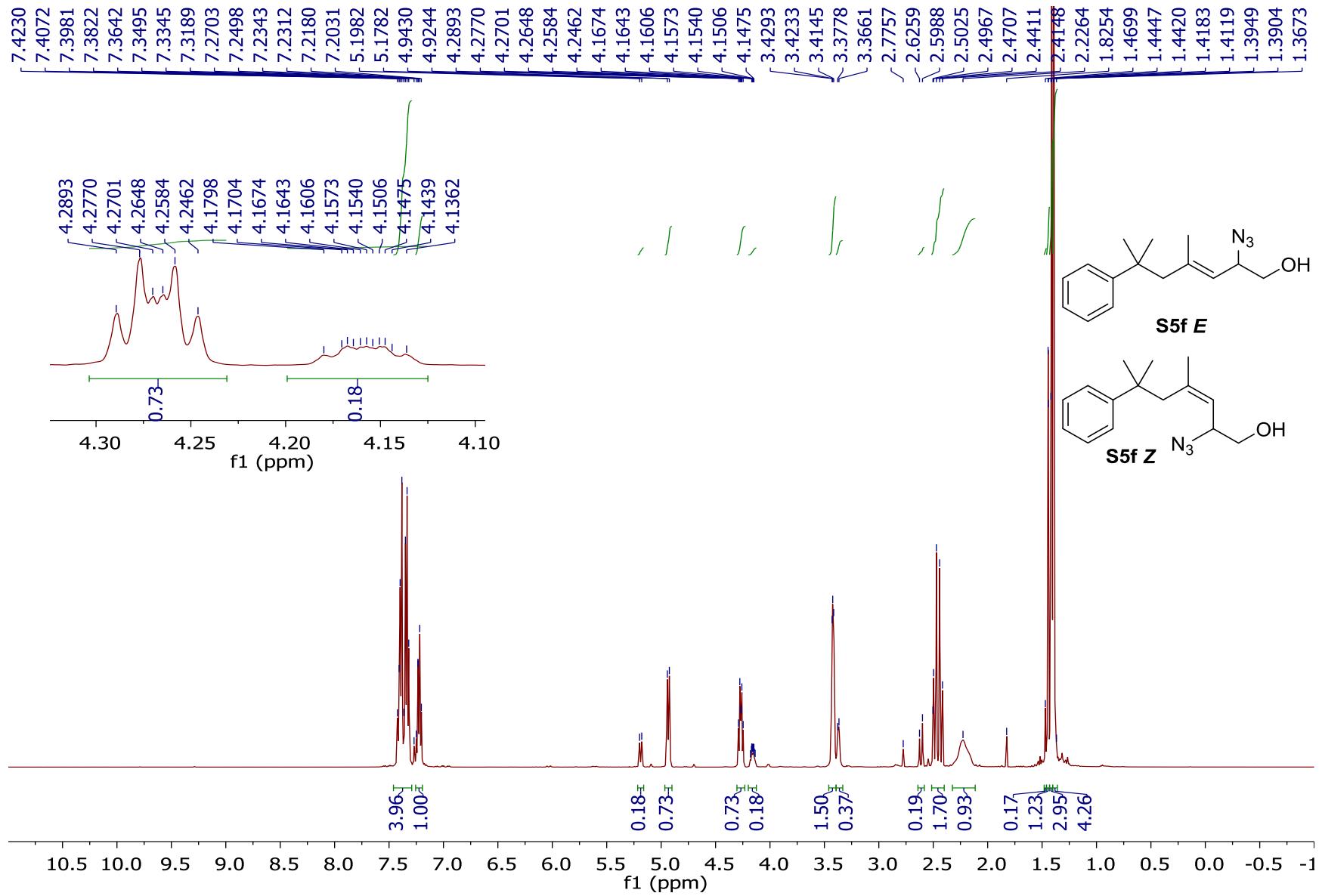
Compound S5d, 400 MHz ^1H NMR in CDCl_3



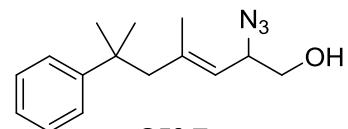




Compound S5e, 101 MHz ^{13}C NMR in CDCl_3



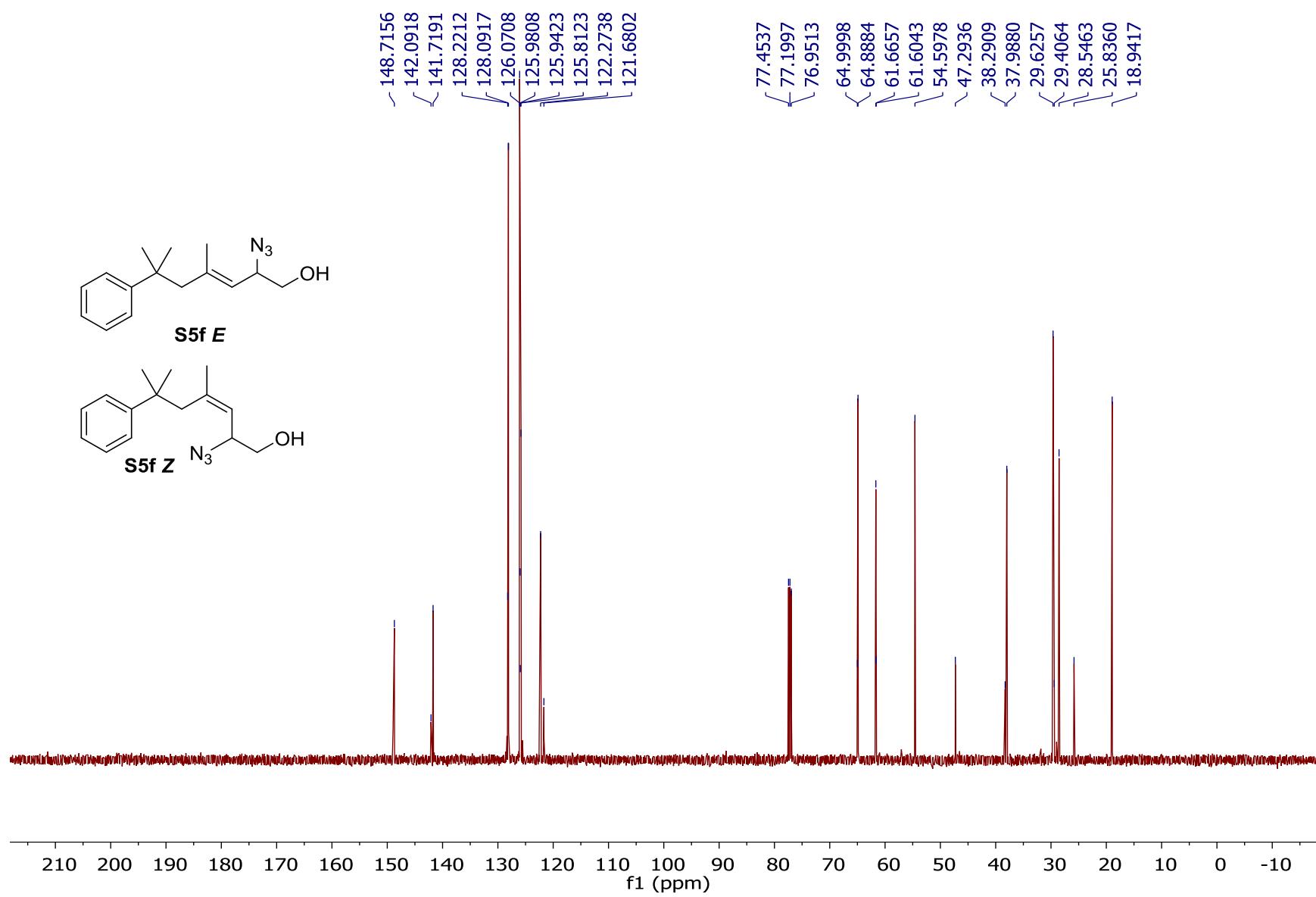
Compound S5f, 400 MHz ^1H NMR in CDCl_3



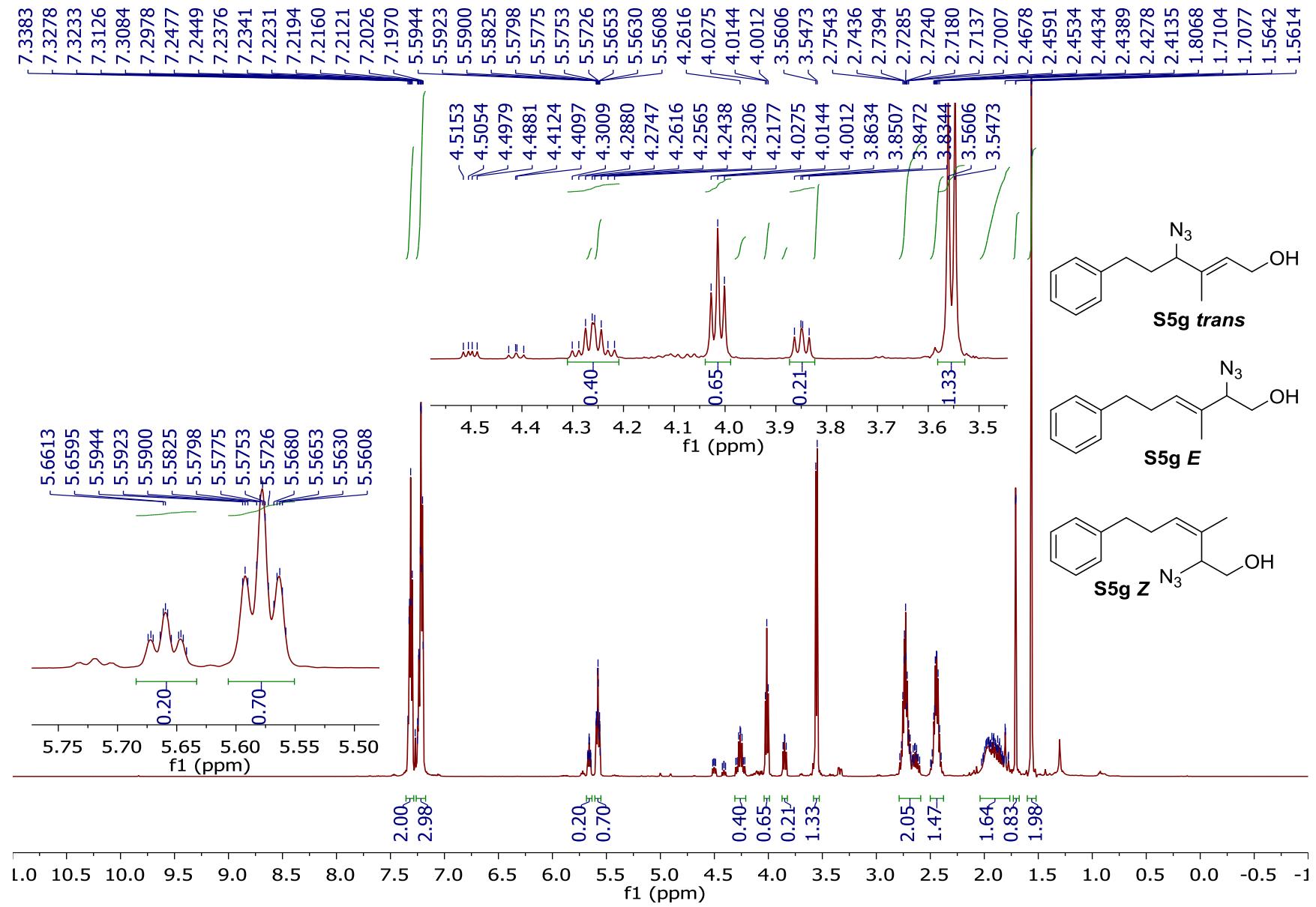
S5f E



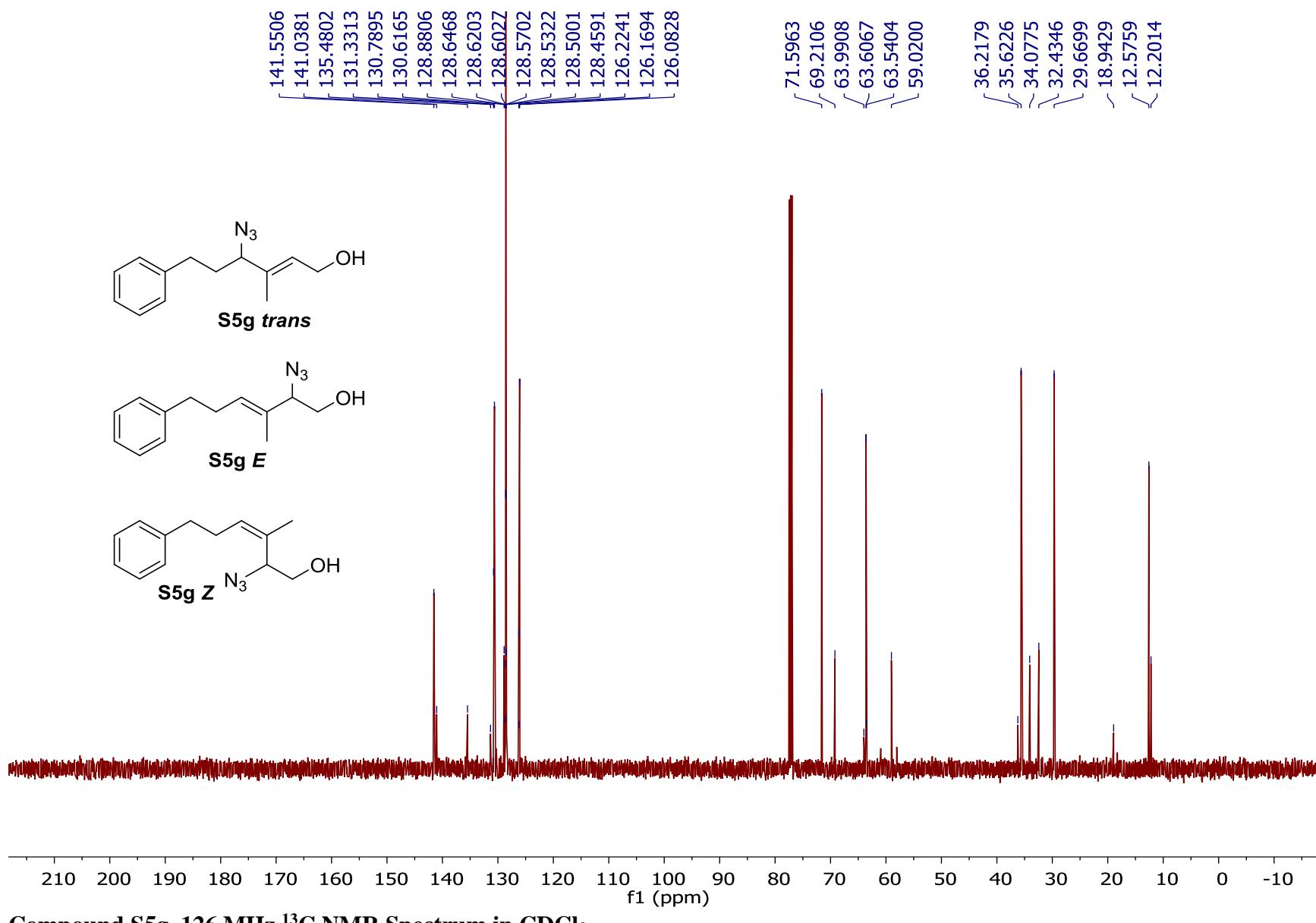
S5f Z



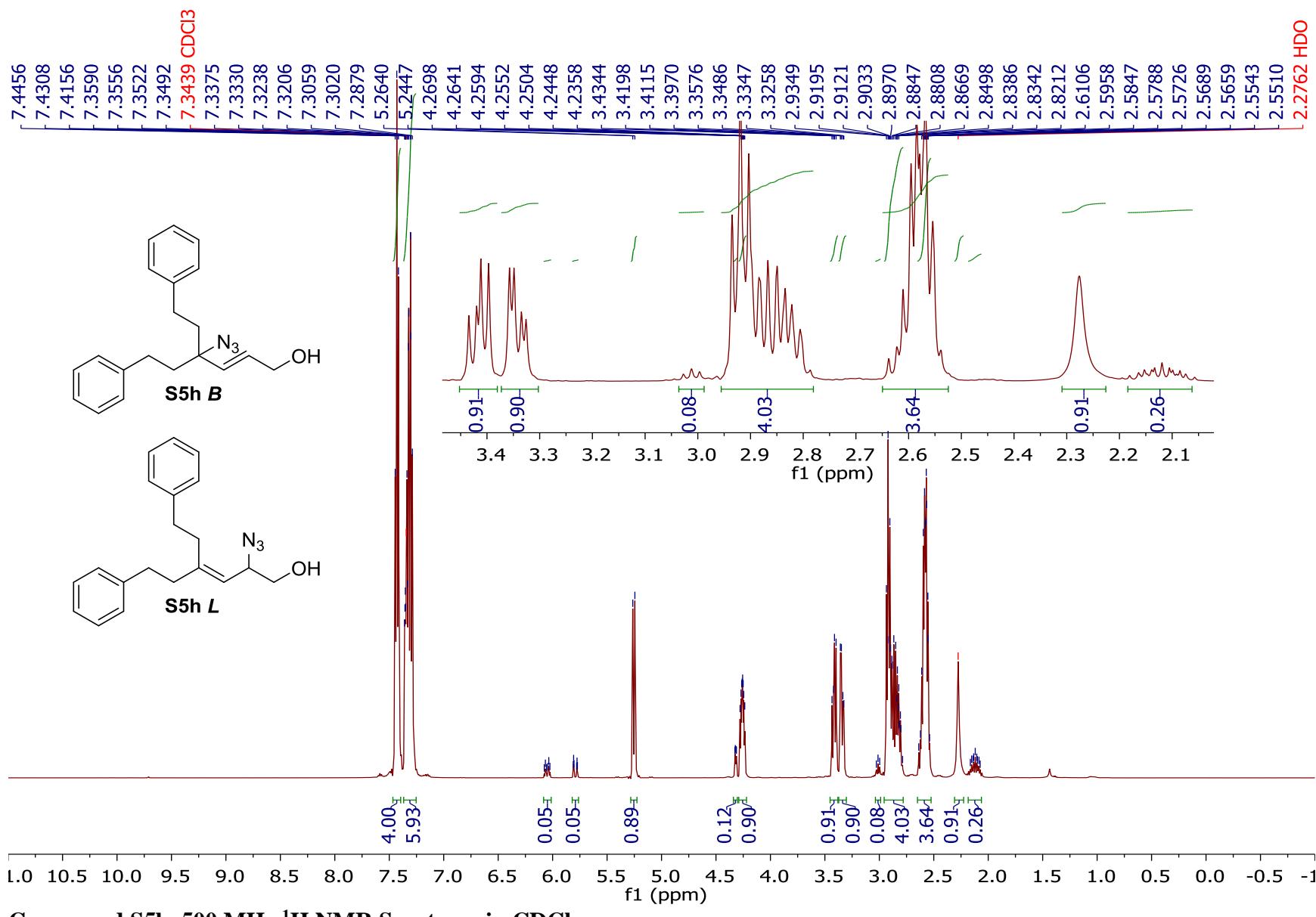
Compound S5f, 101 MHz ^{13}C NMR in CDCl_3

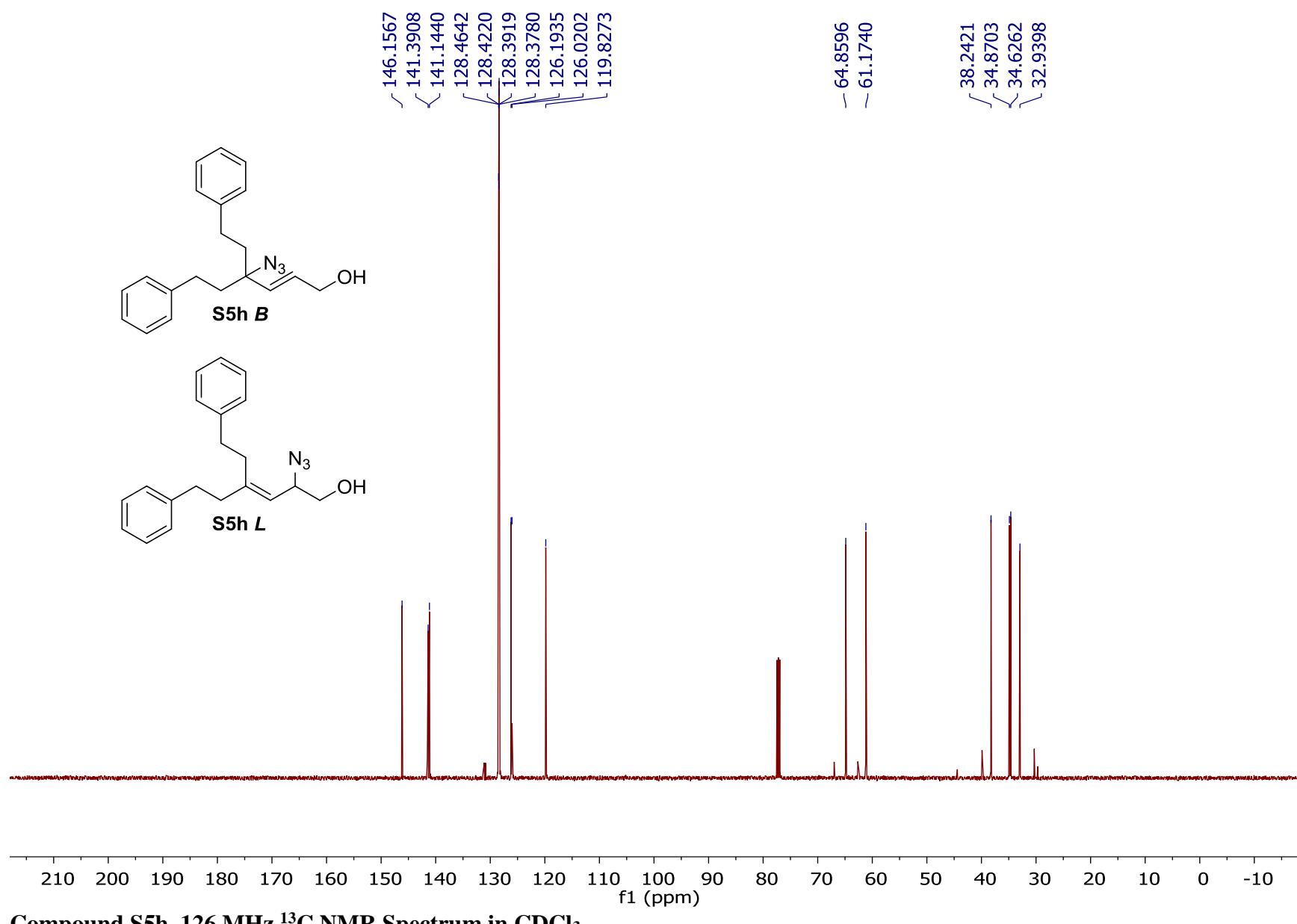


Compound S5g, 500 MHz ^1H NMR Spectrum in CDCl_3

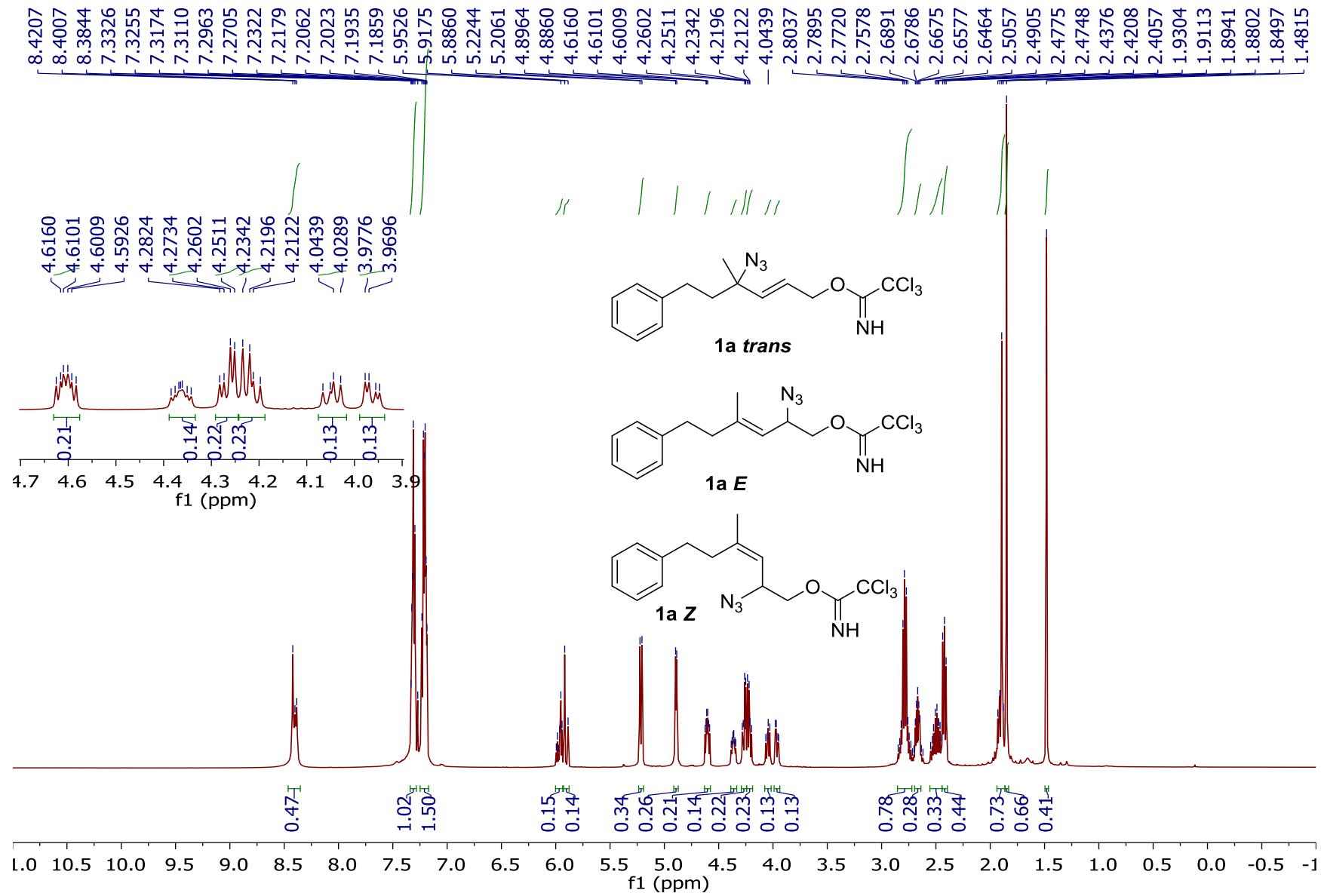


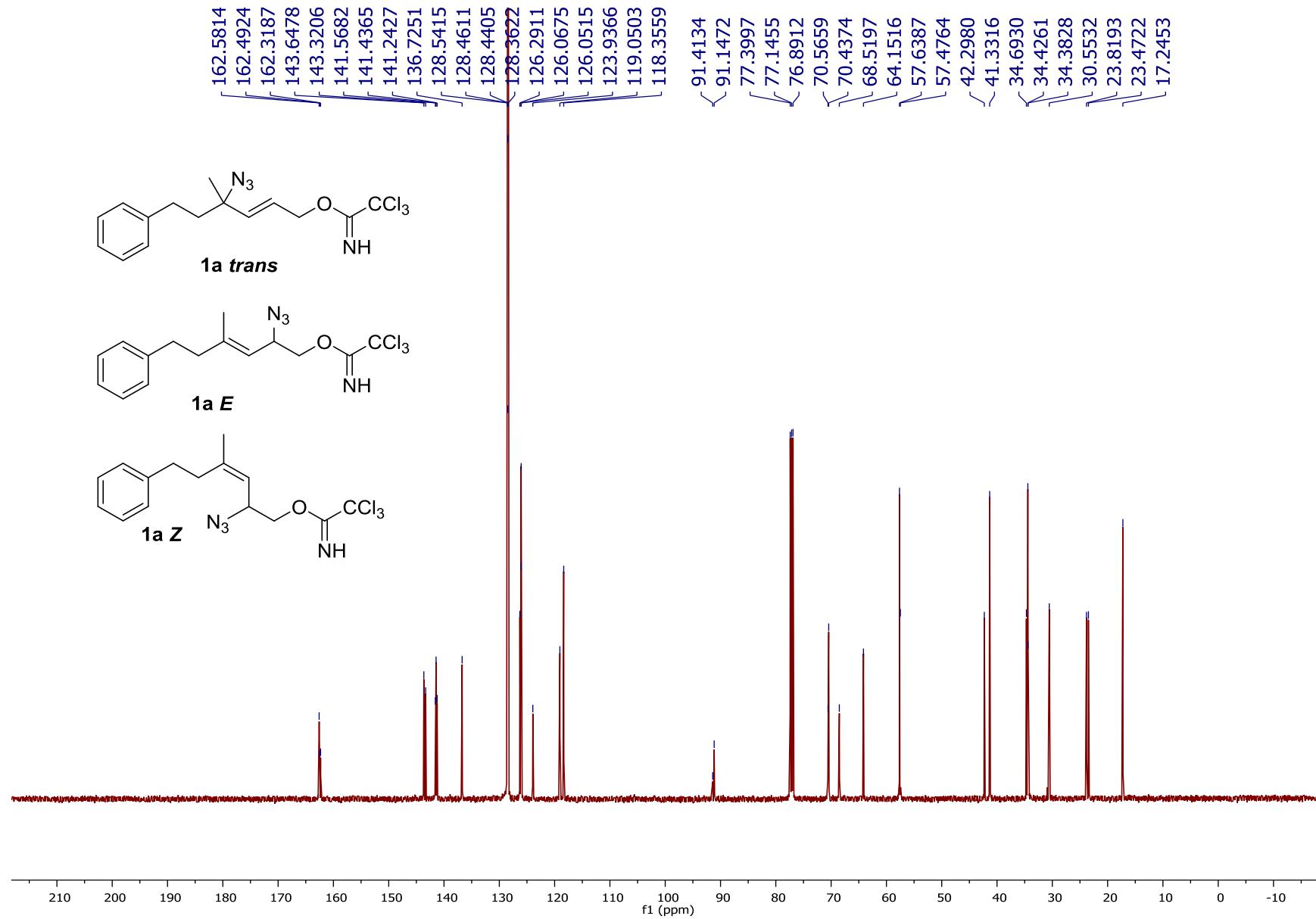
Compound S5g, 126 MHz ^{13}C NMR Spectrum in CDCl_3



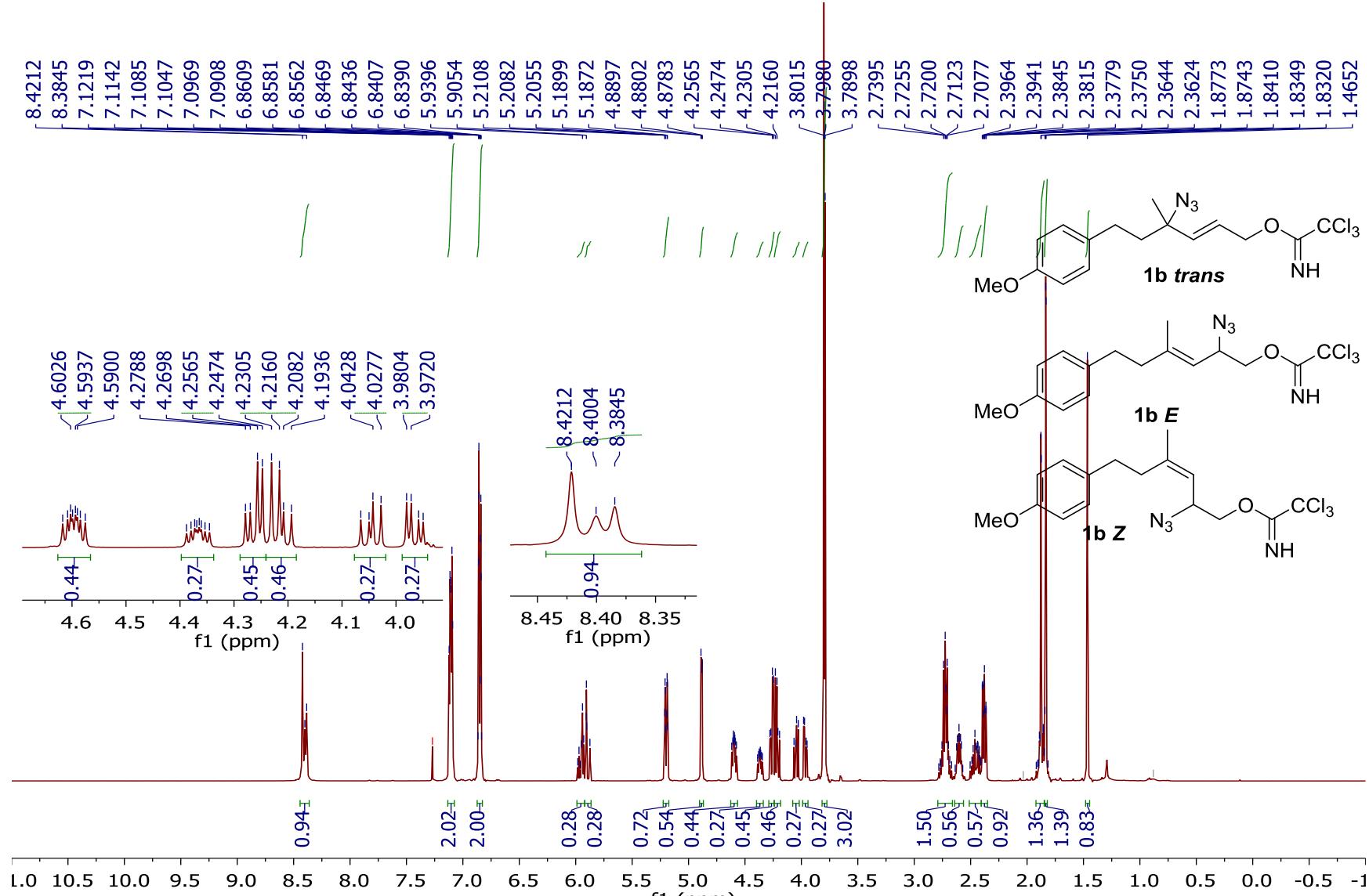


Compound S5h, 126 MHz ^{13}C NMR Spectrum in CDCl_3

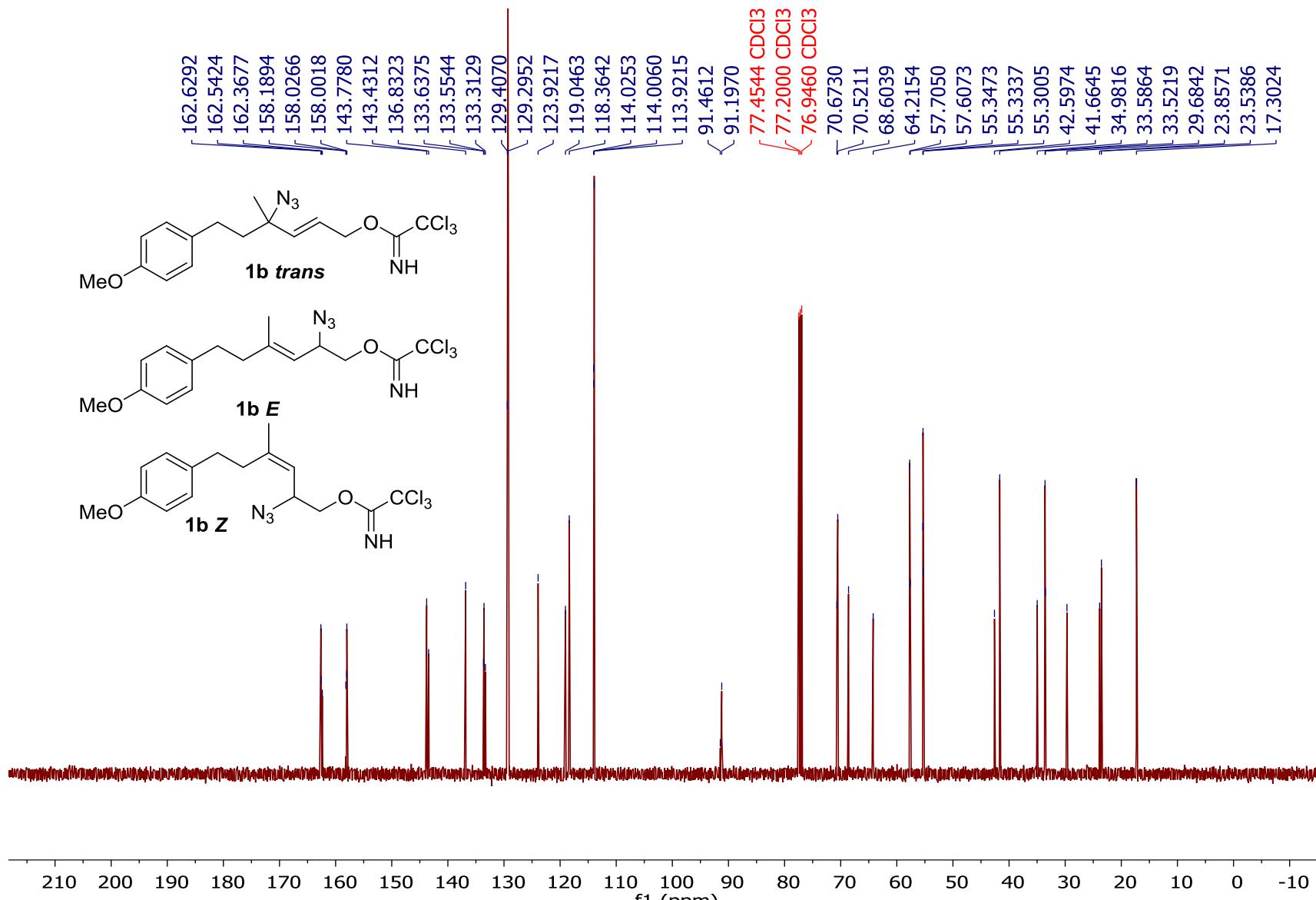




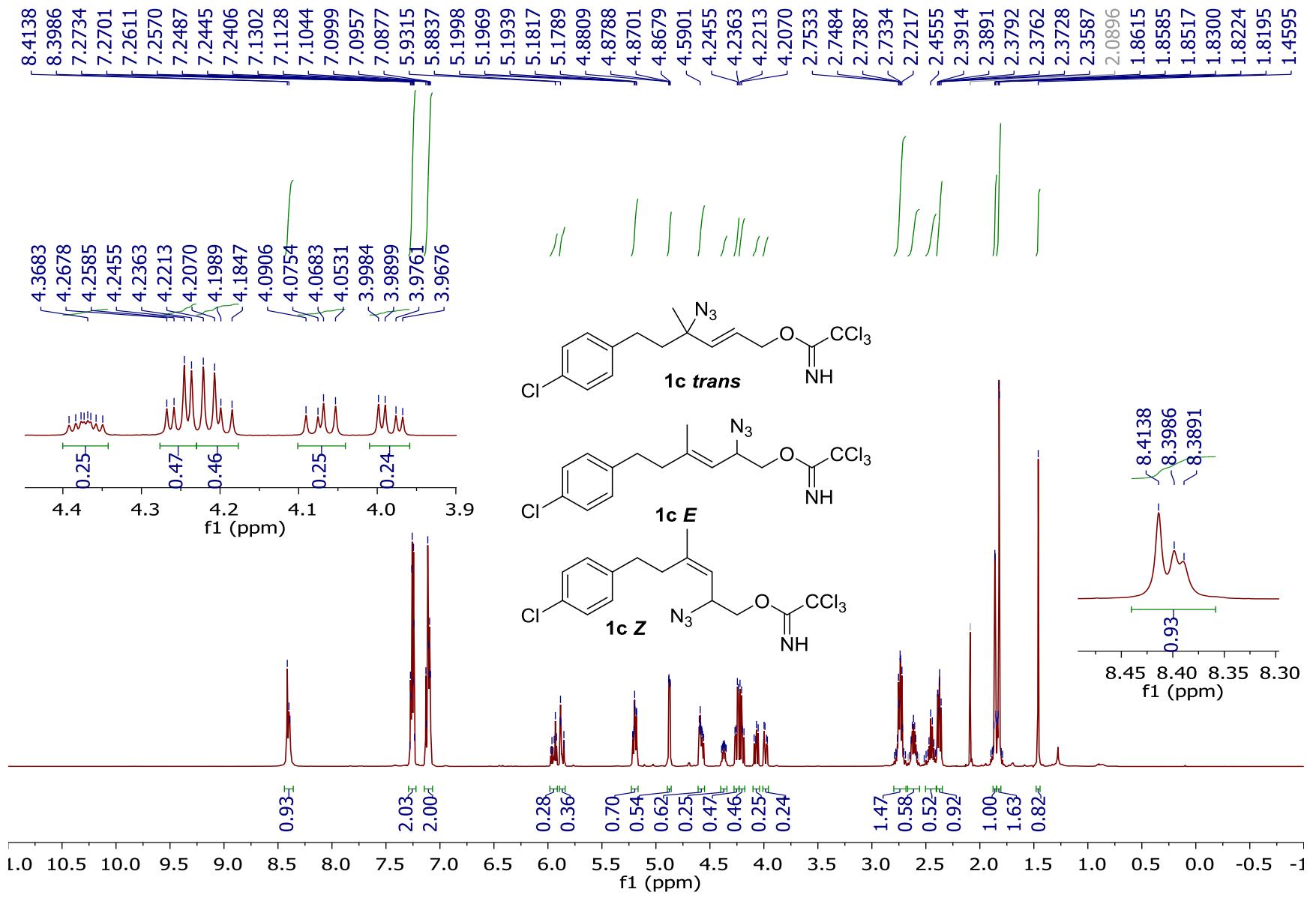
Compound 1a, 126 MHz ^{13}C NMR in CDCl_3

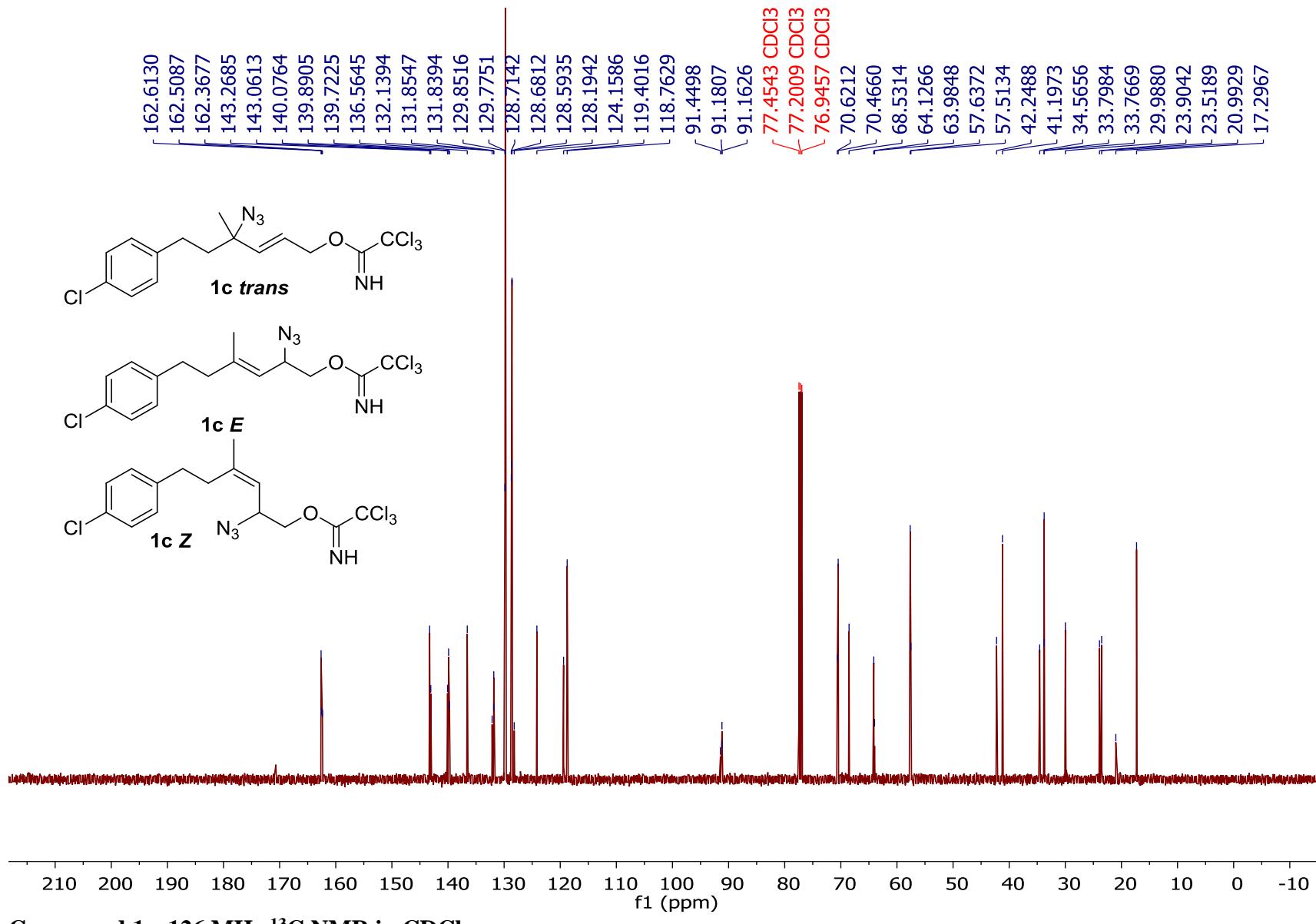


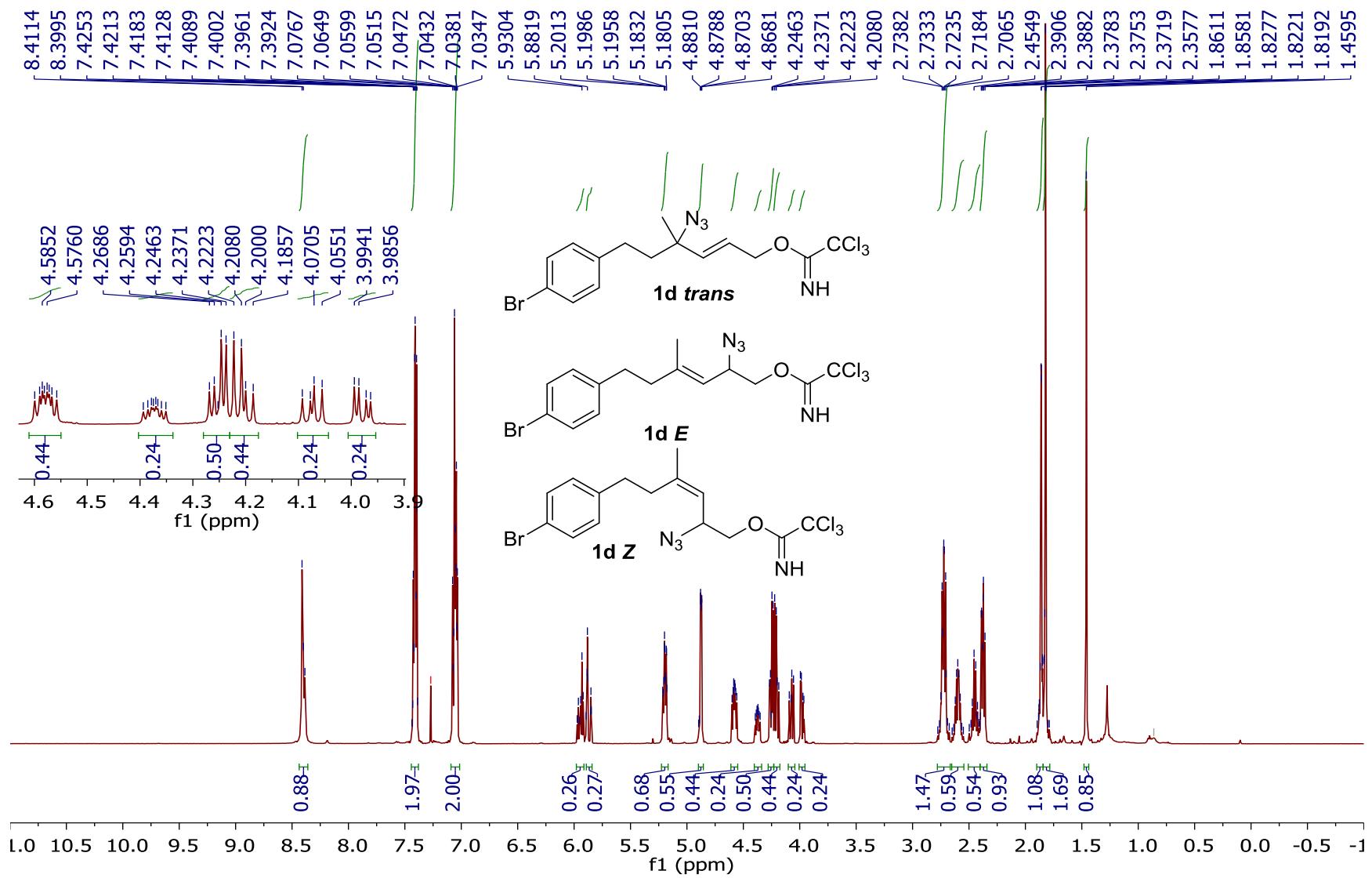
Compound 1b, 500 MHz ^1H NMR in CDCl_3



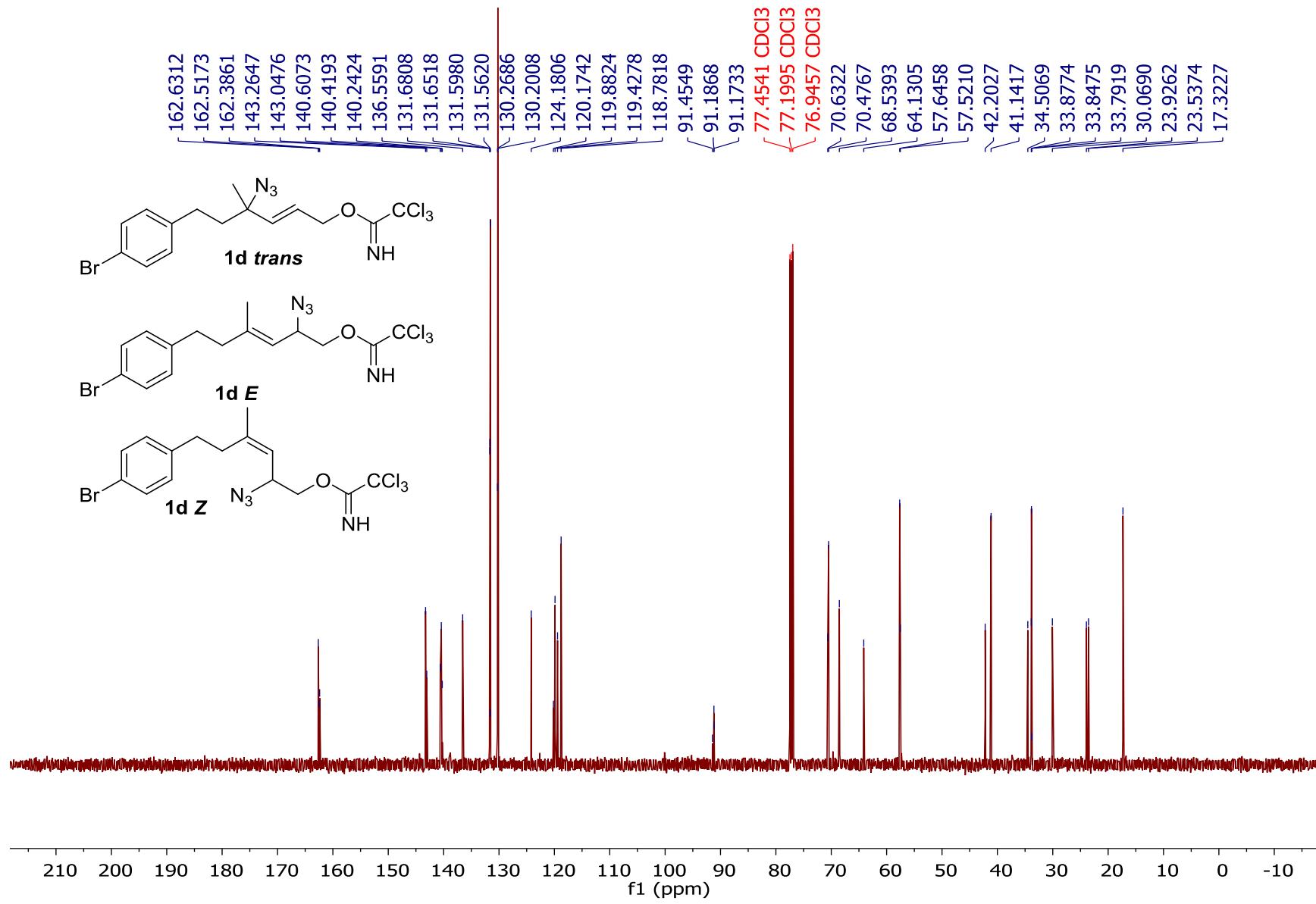
Compound 1b, 126 MHz ¹³C NMR in CDCl₃



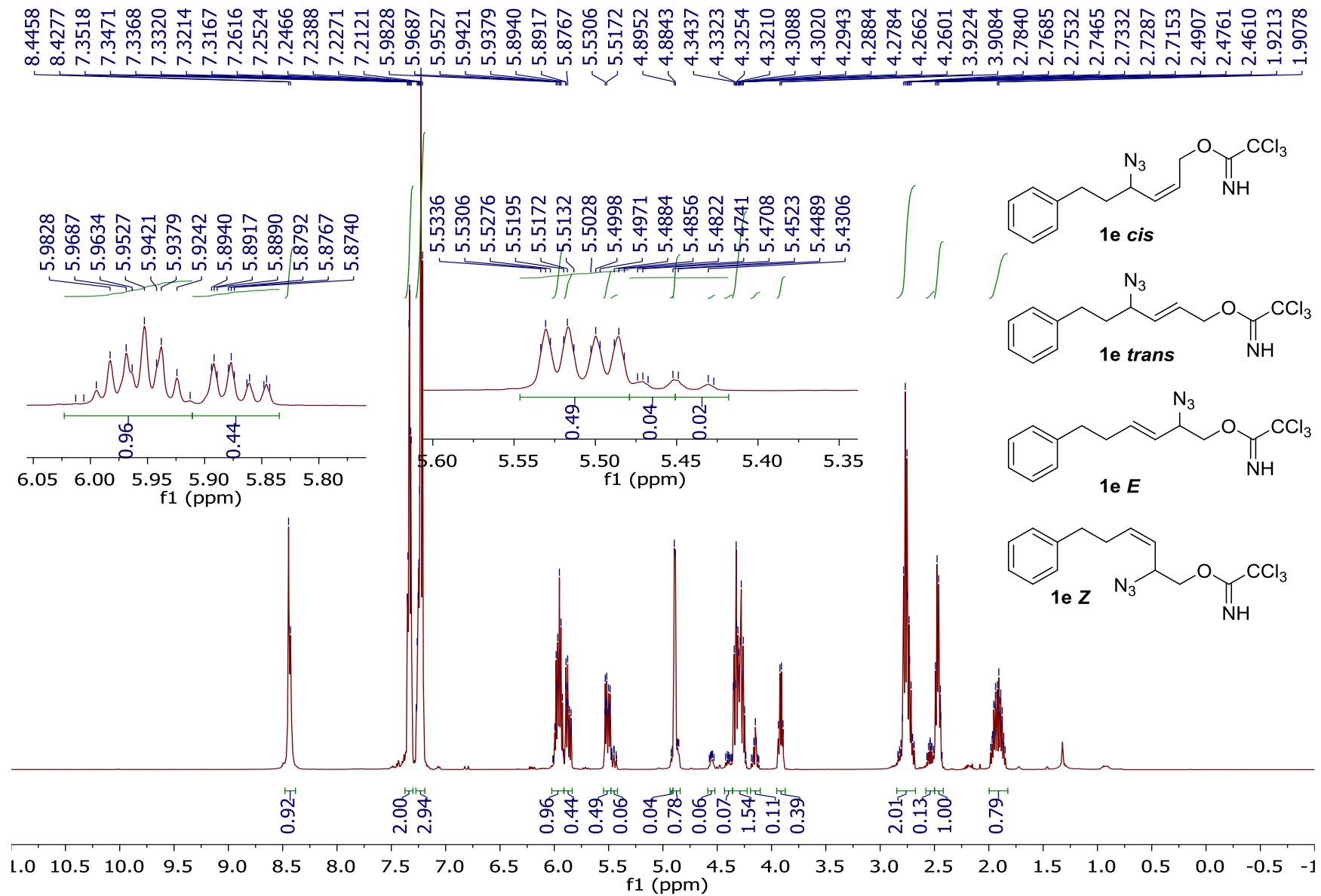




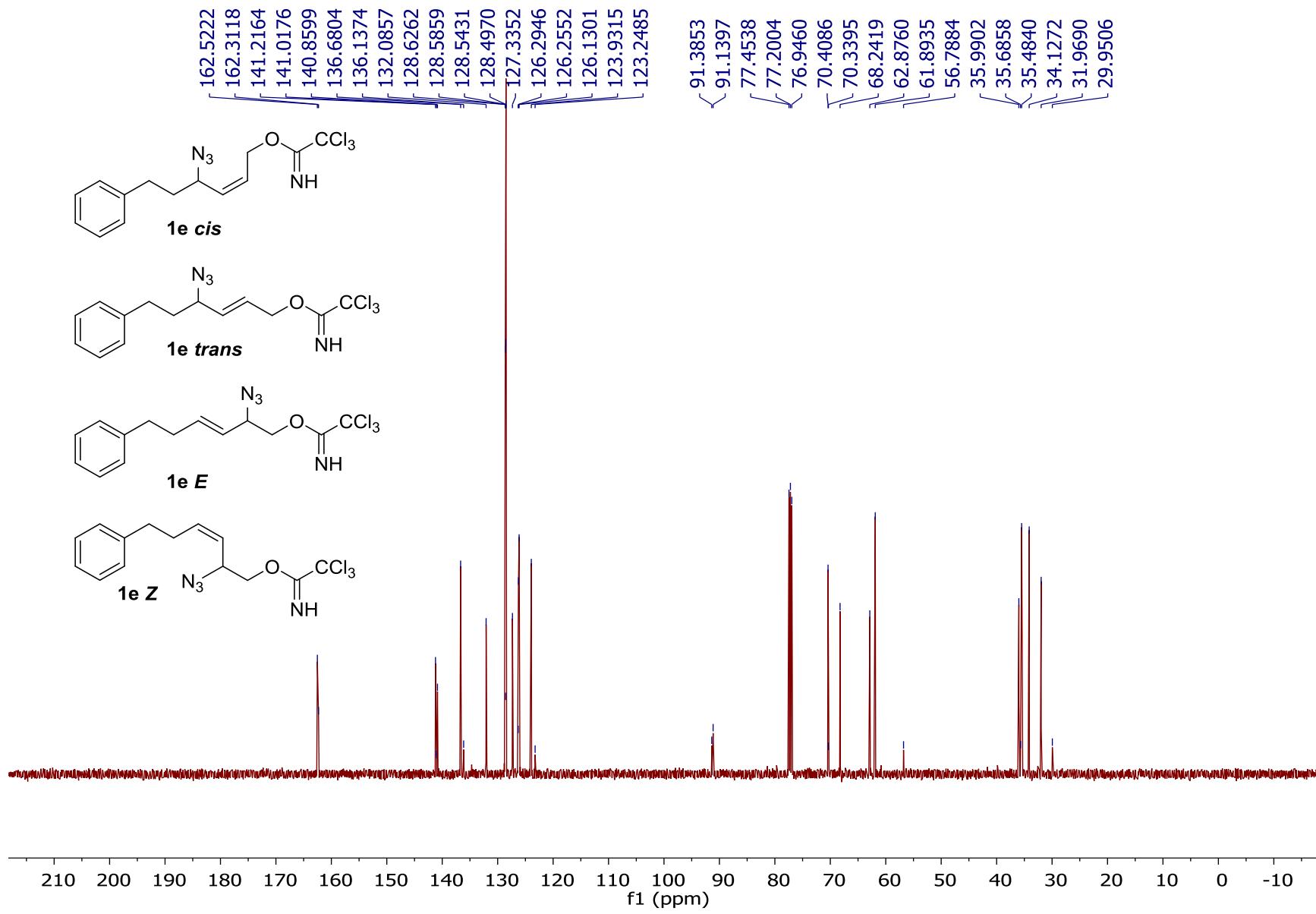
Compound 1d, 500 MHz ^1H NMR in CDCl_3



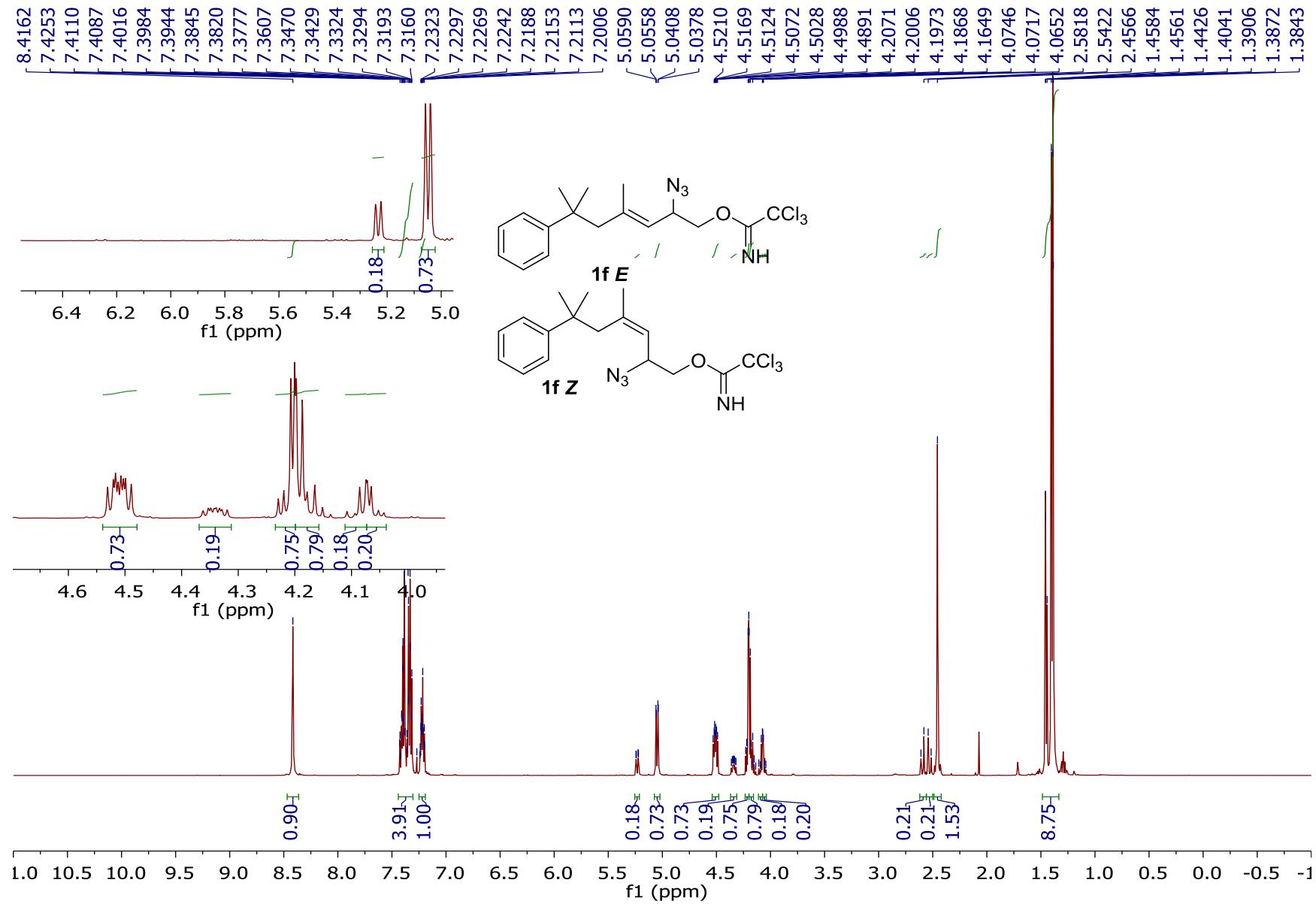
Compound 1d, 126 MHz ^{13}C NMR in CDCl_3

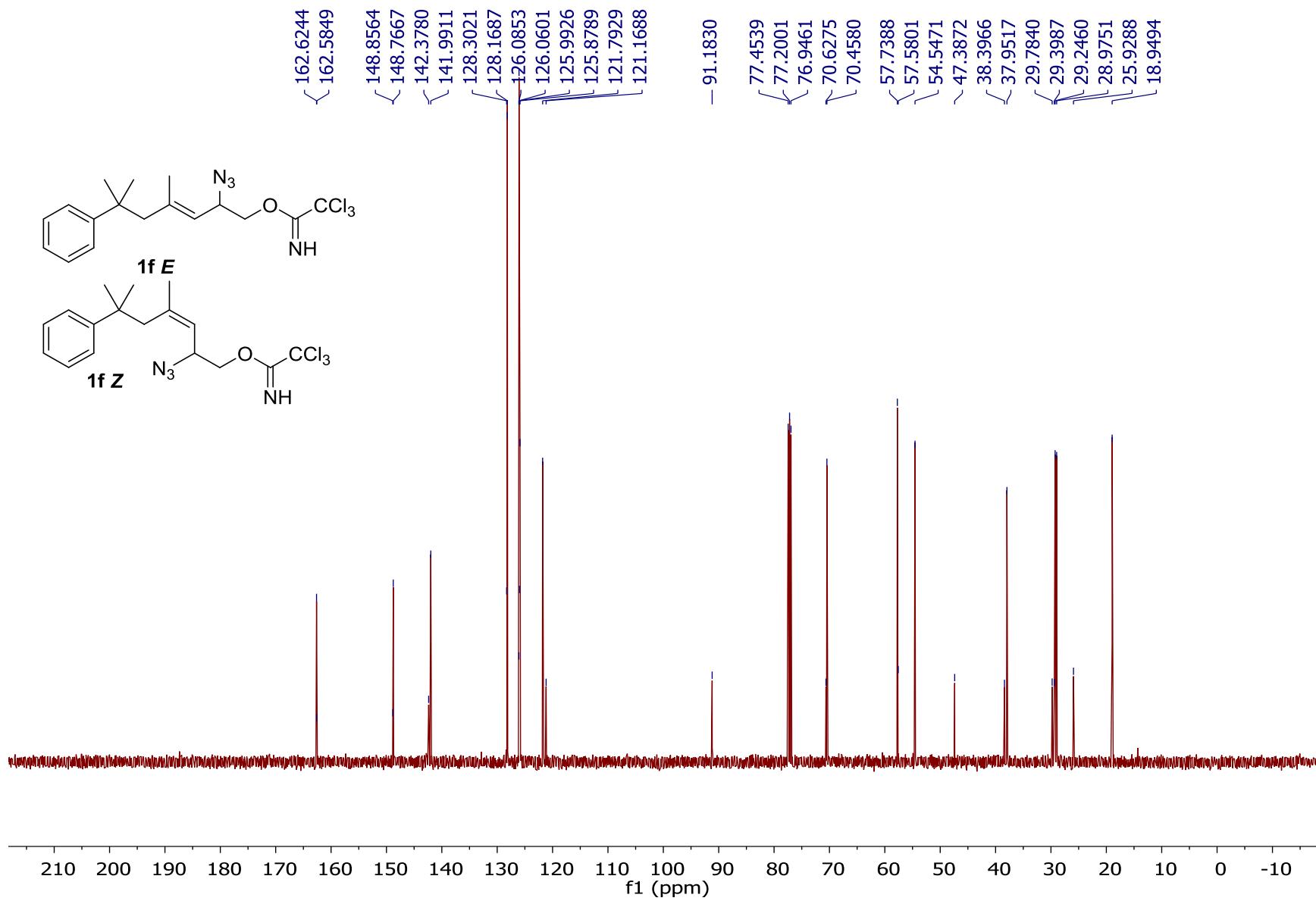
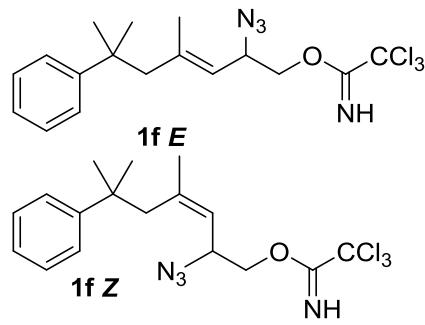


Compound 1e, 500 MHz ^1H NMR in CDCl_3

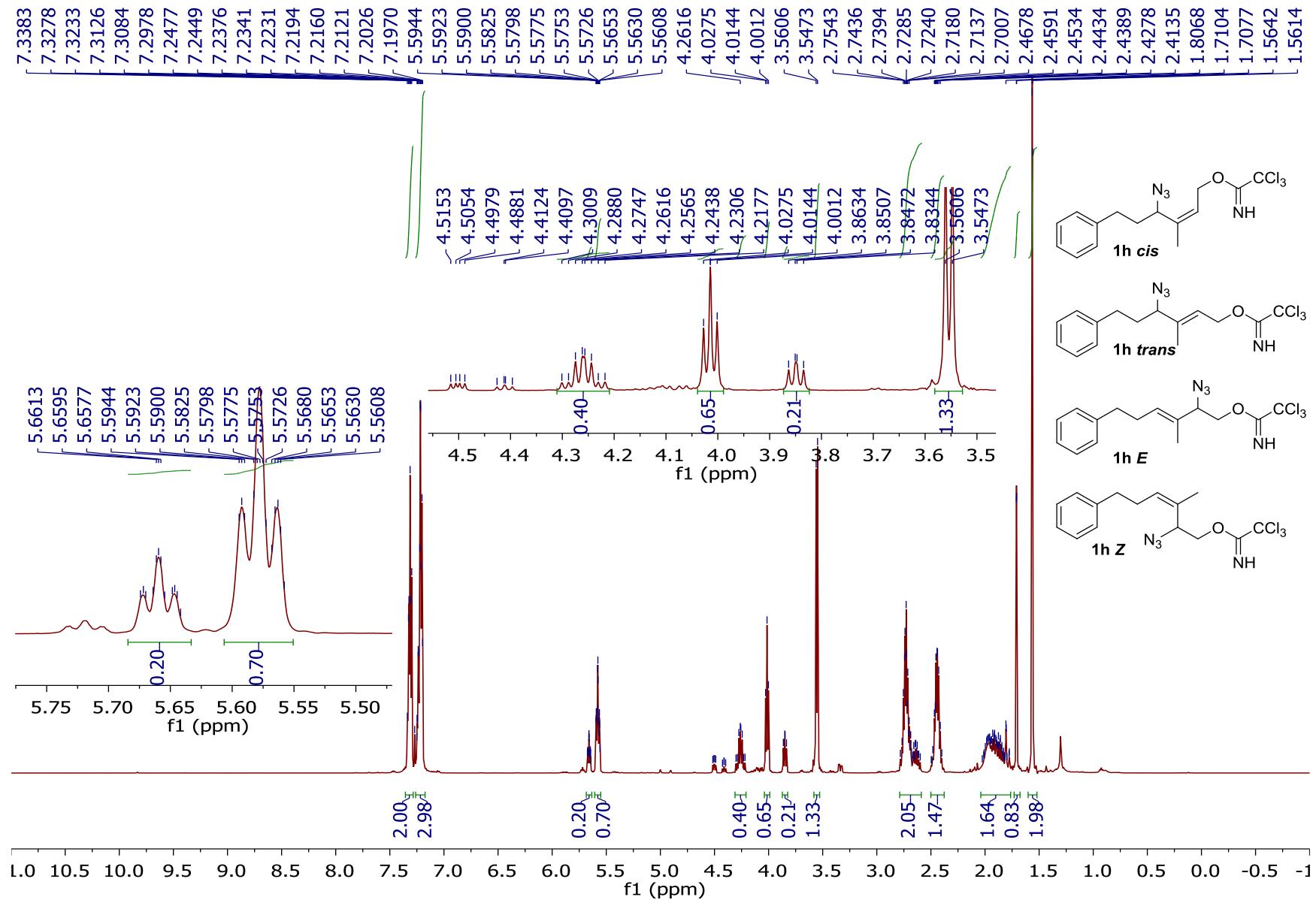


Compound 1e, 126 MHz ^{13}C NMR in CDCl_3

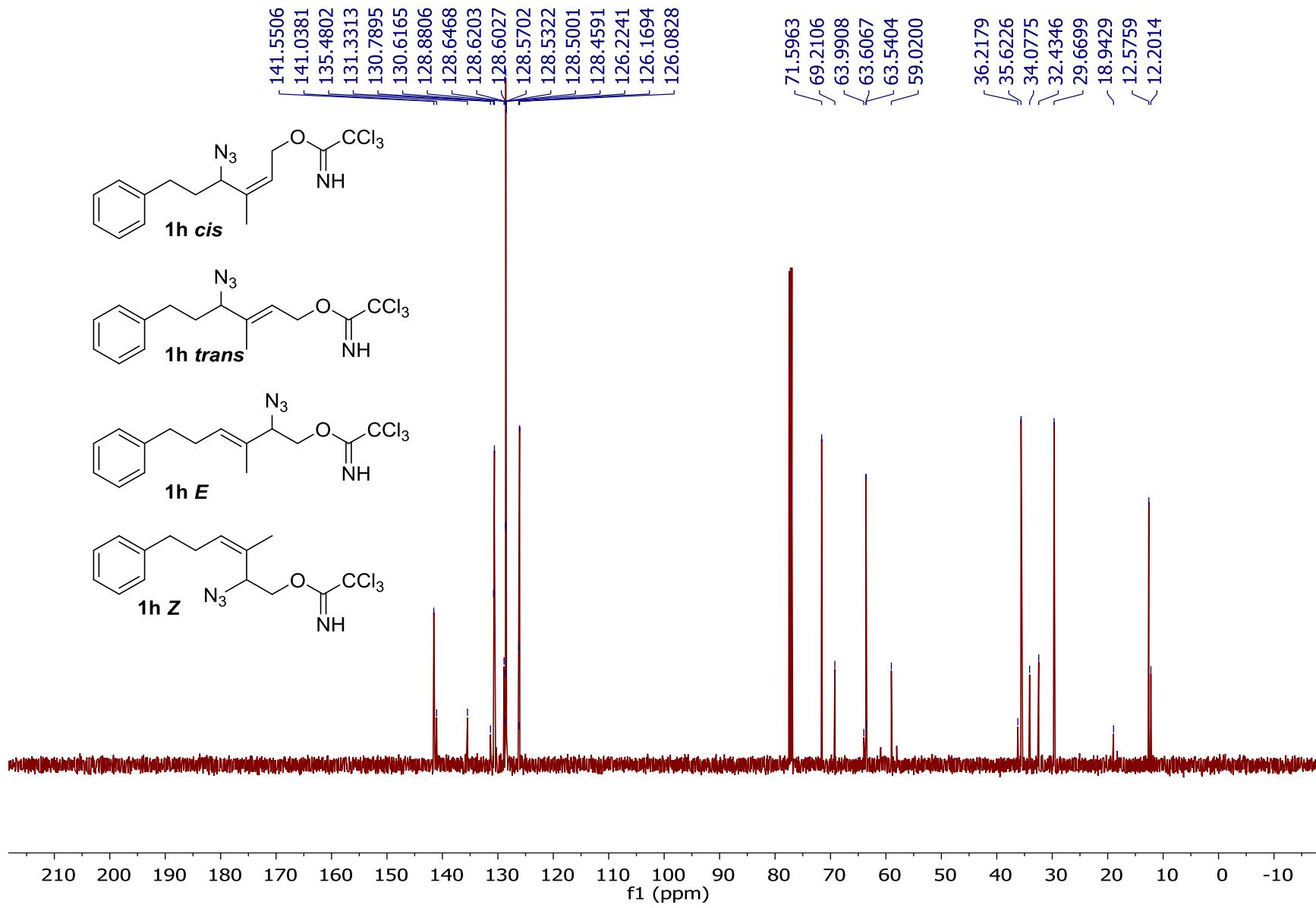




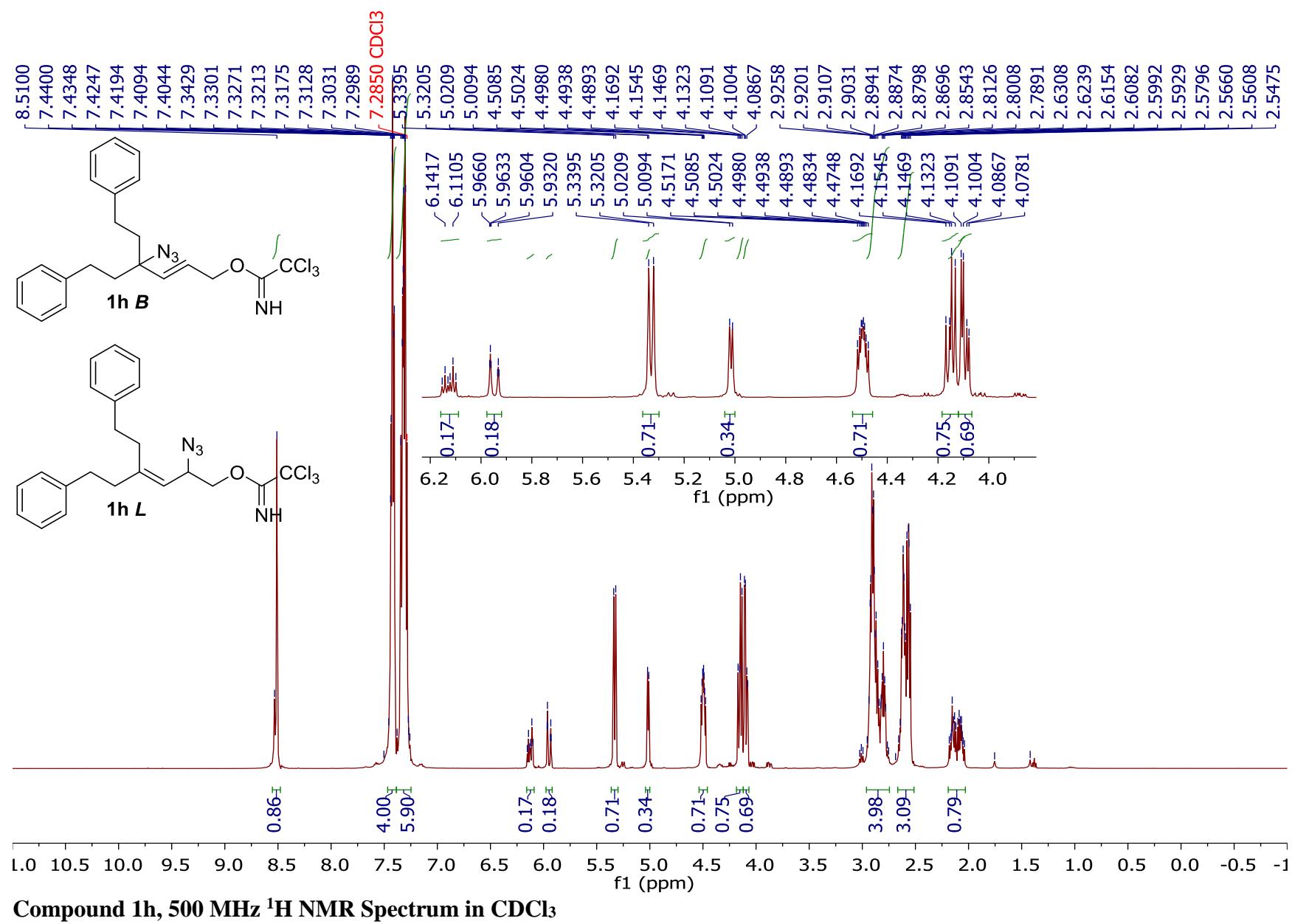
Compound 1f, 126 MHz ^{13}C NMR in CDCl_3



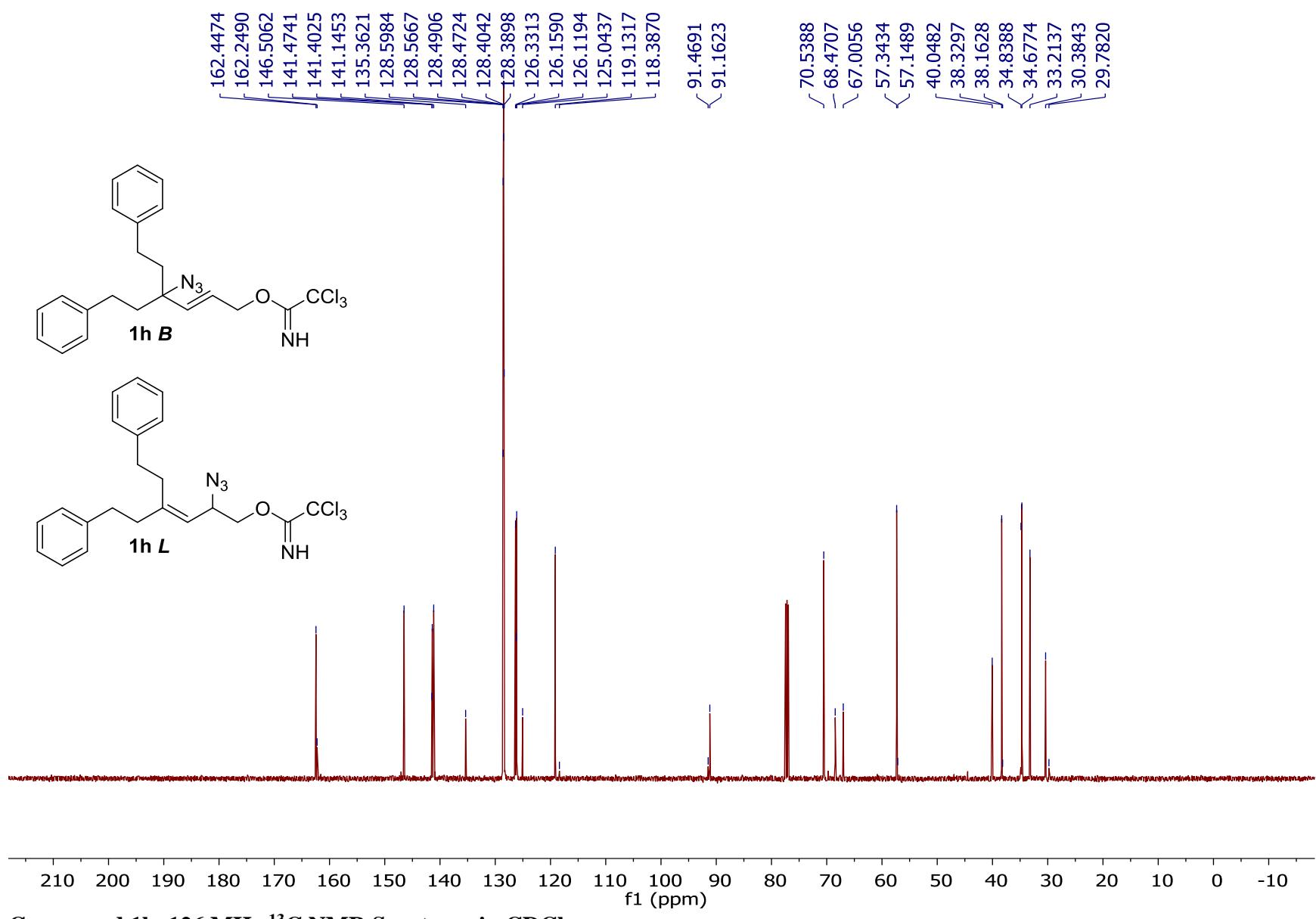
Compound 1g, 500 MHz ^1H NMR Spectrum in CDCl_3



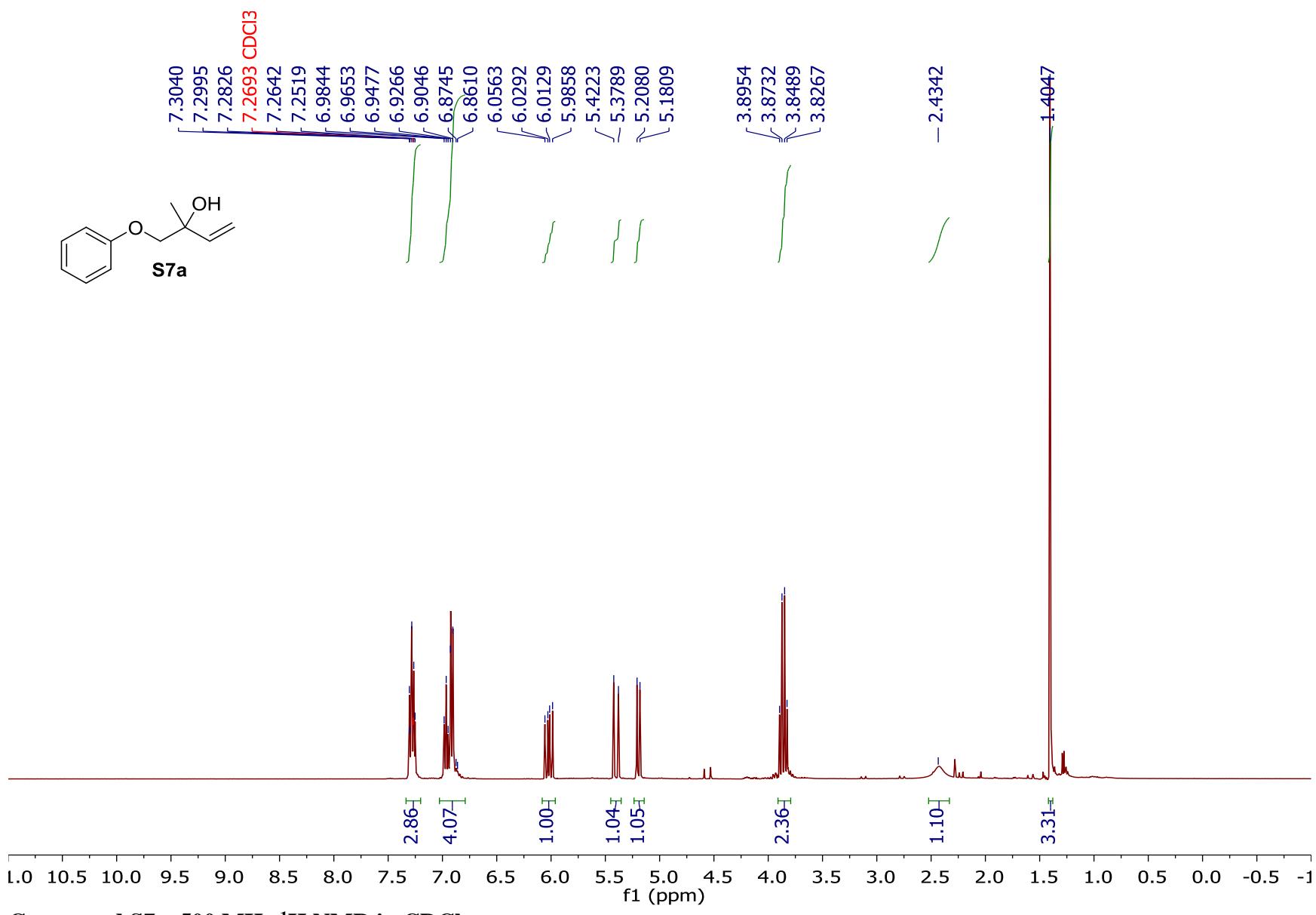
Compound 1g, 126 MHz ^{13}C NMR Spectrum in CDCl_3

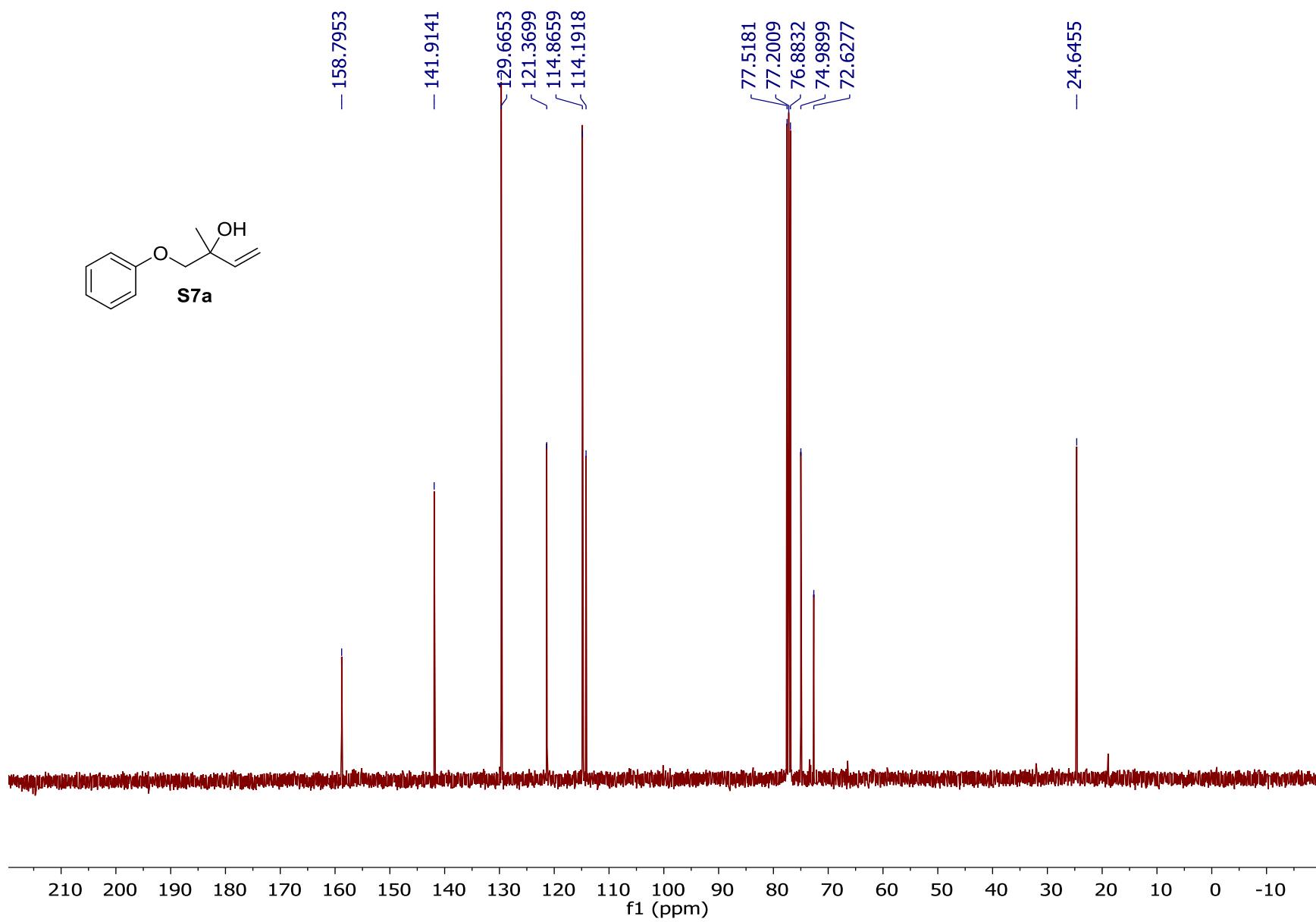
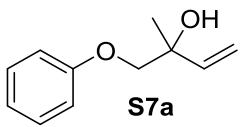


Compound **1h**, 500 MHz ^1H NMR Spectrum in CDCl_3

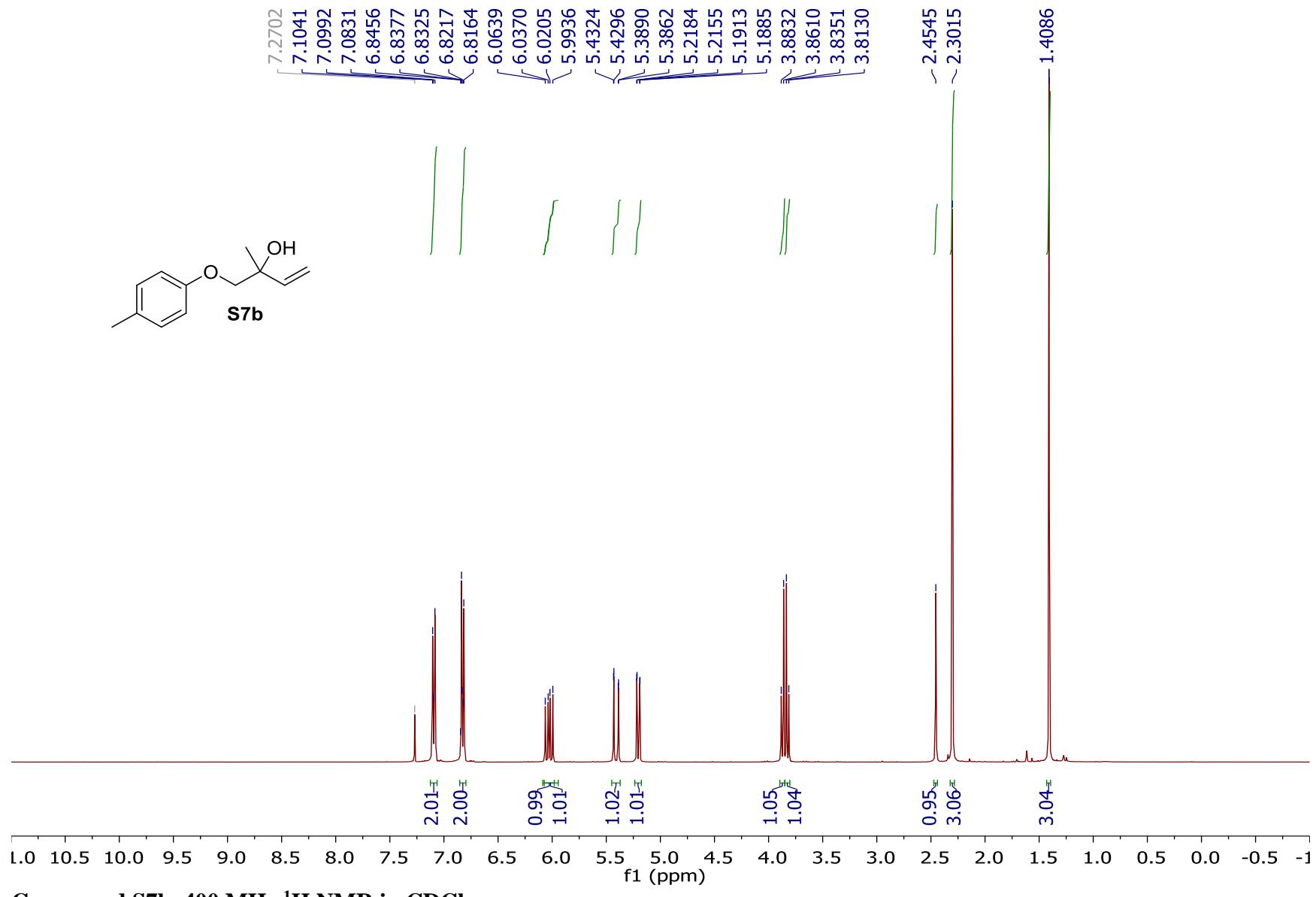
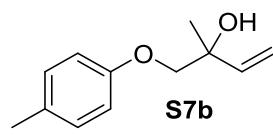


Compound **1h**, 126 MHz ^{13}C NMR Spectrum in CDCl_3

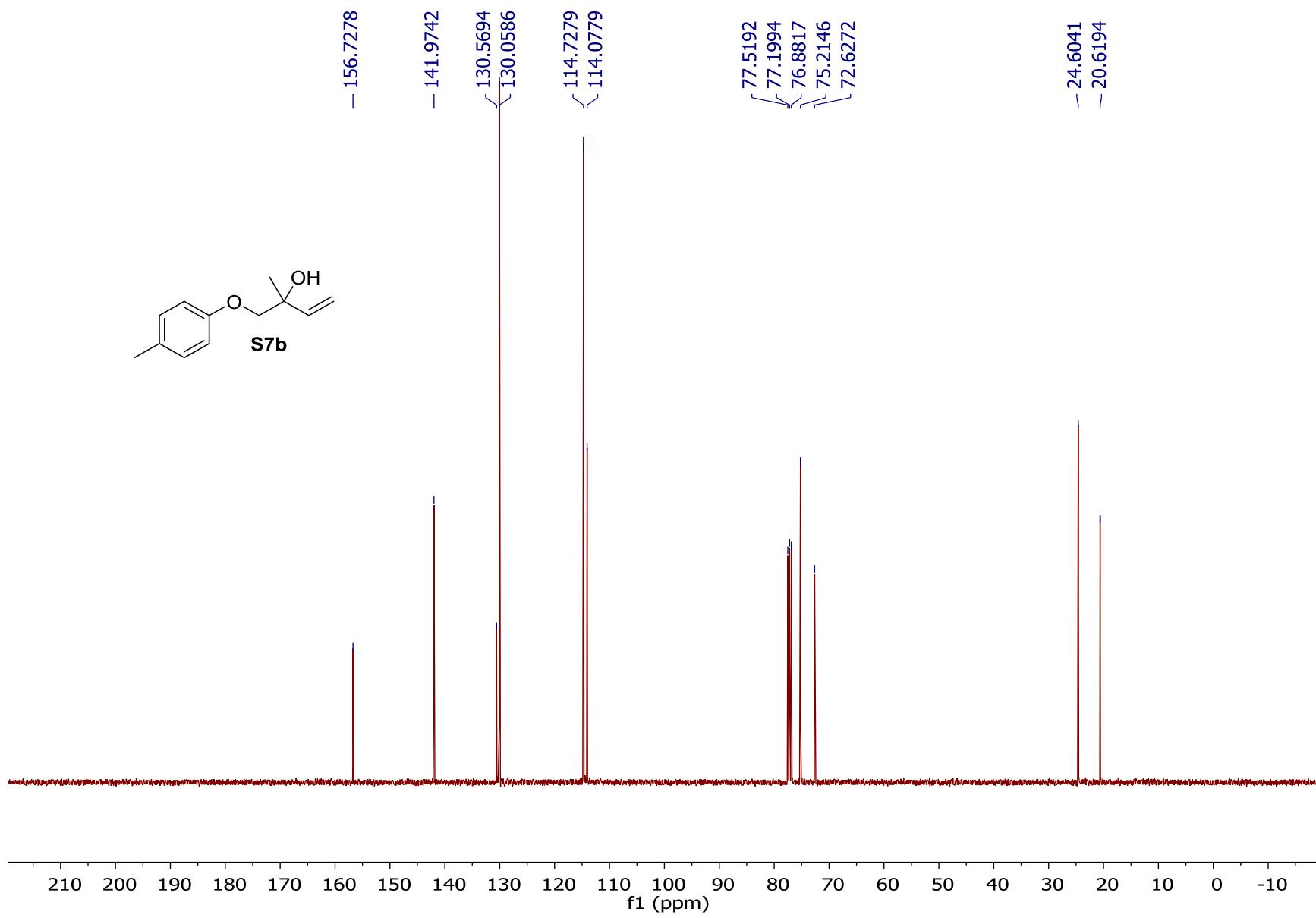




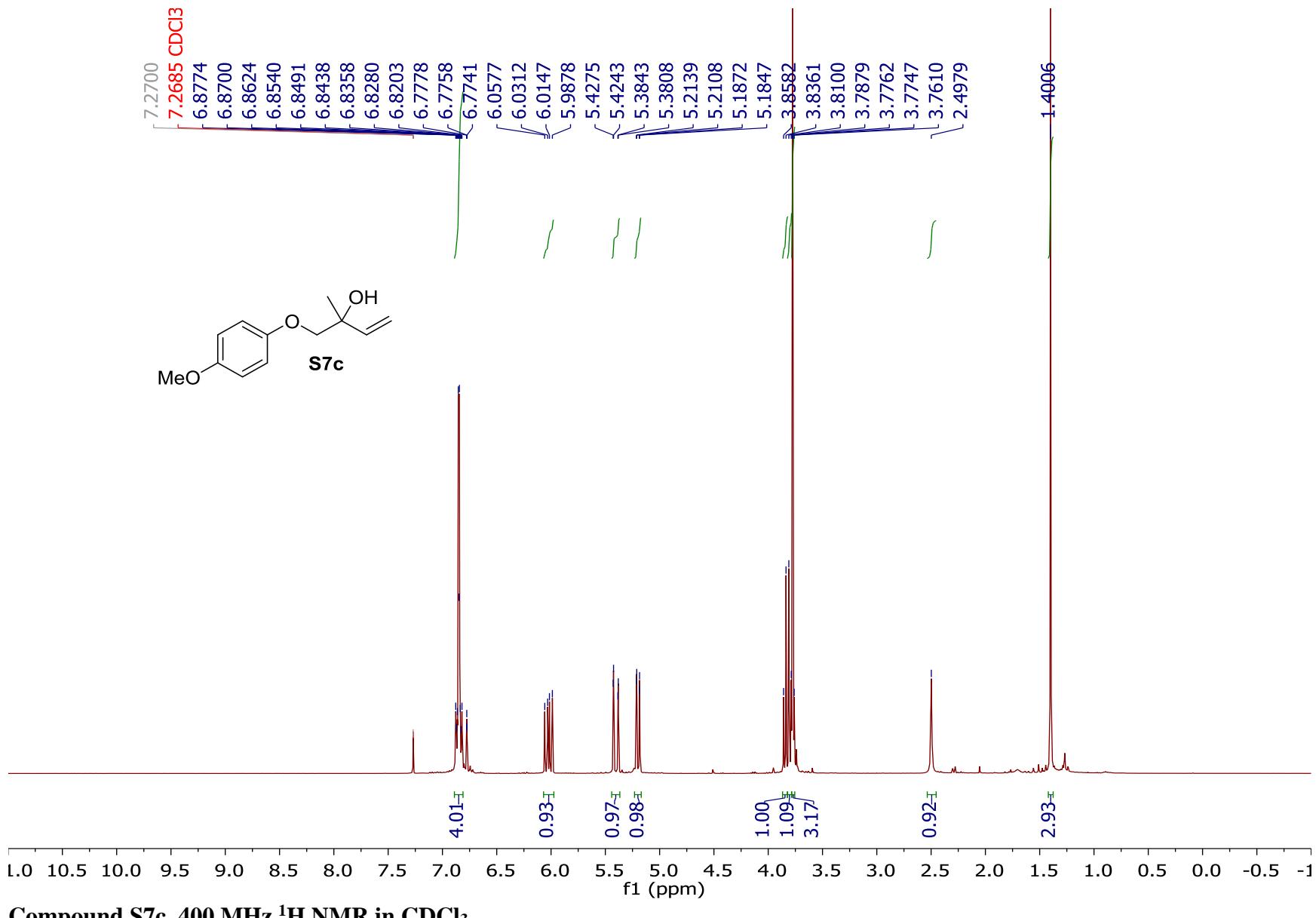
Compound S7a, 101 MHz ¹³C NMR in CDCl₃



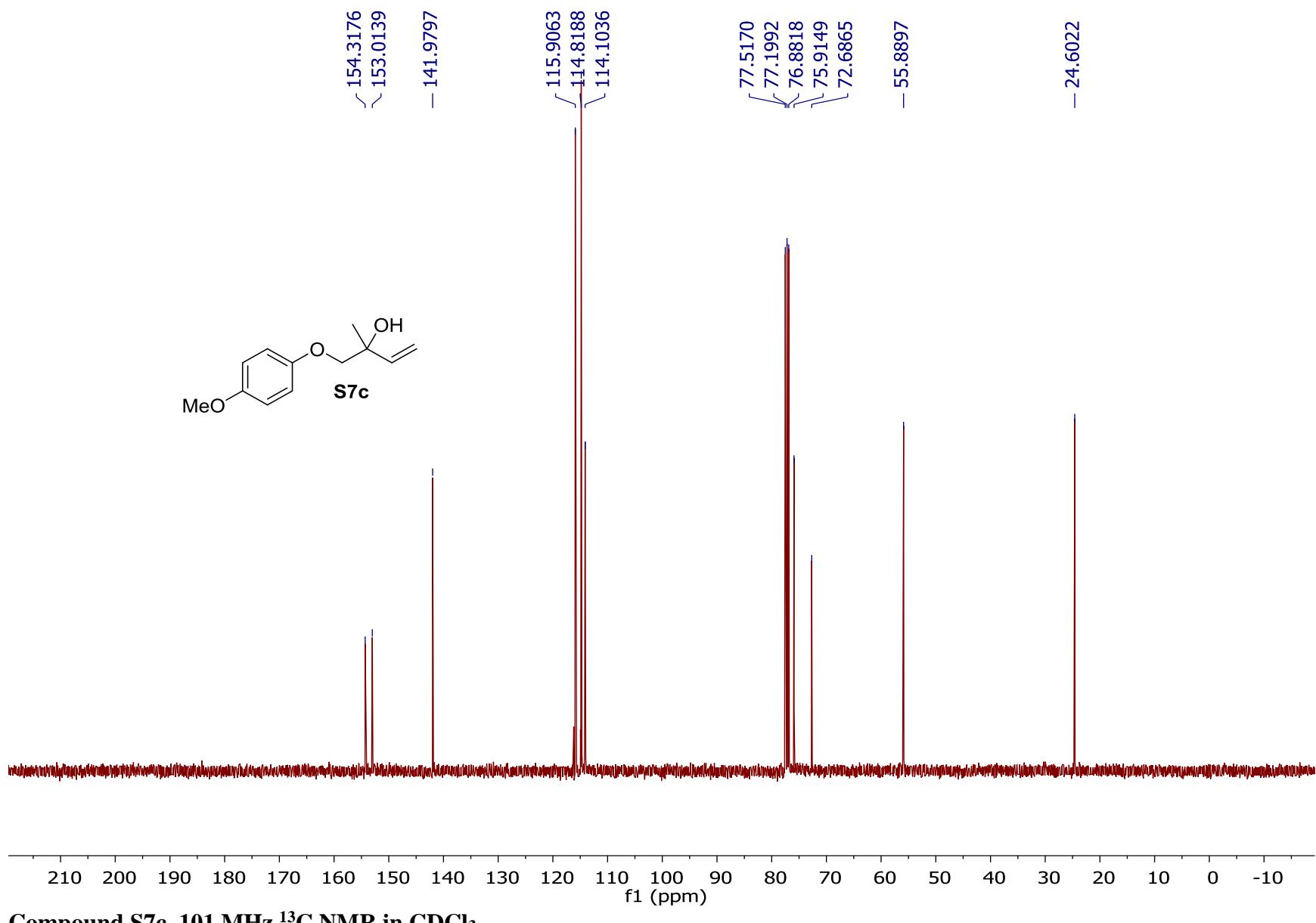
Compound S7b, 400 MHz ^1H NMR in CDCl_3



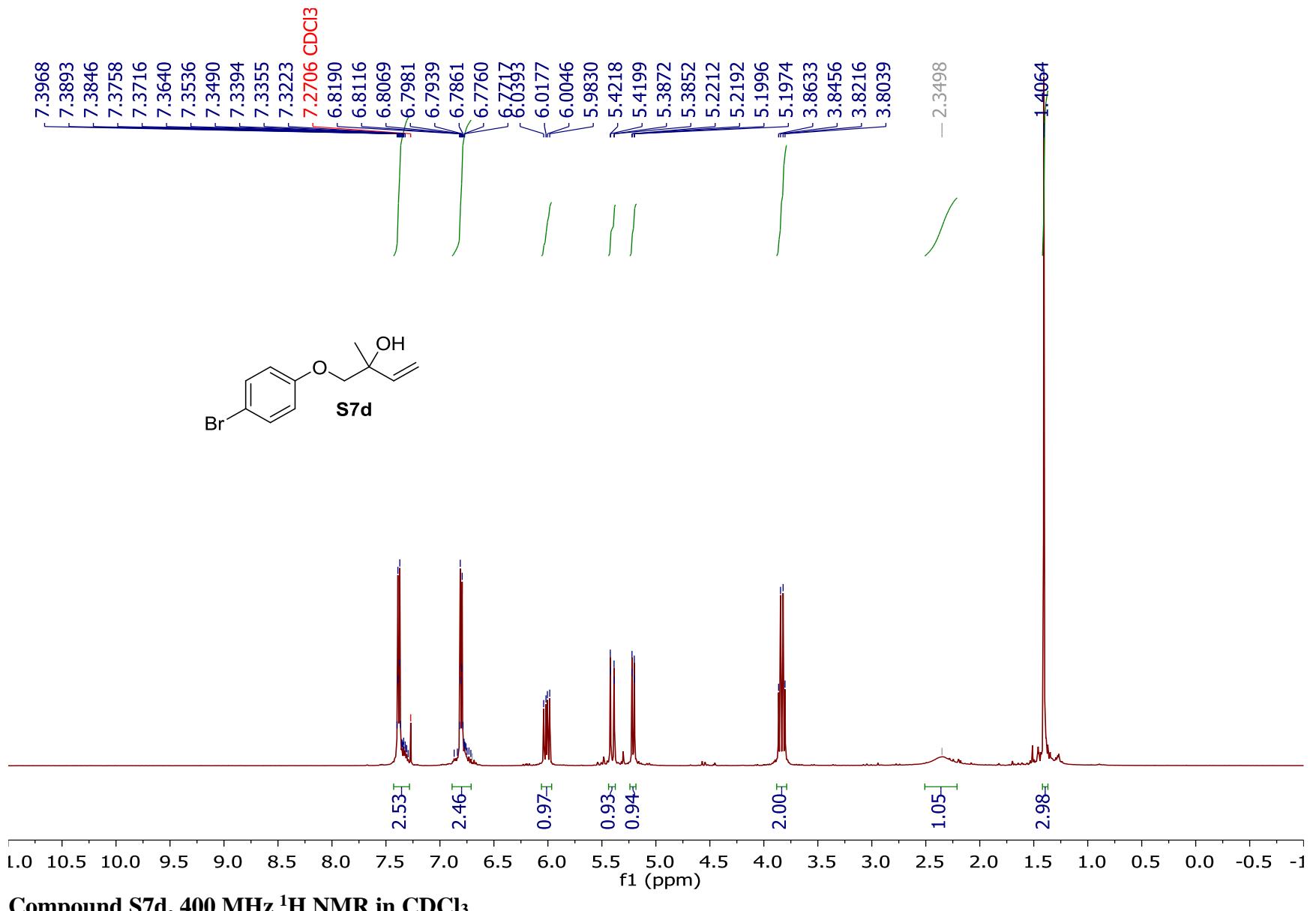
Compound S7b, 101 MHz ^{13}C NMR in CDCl_3

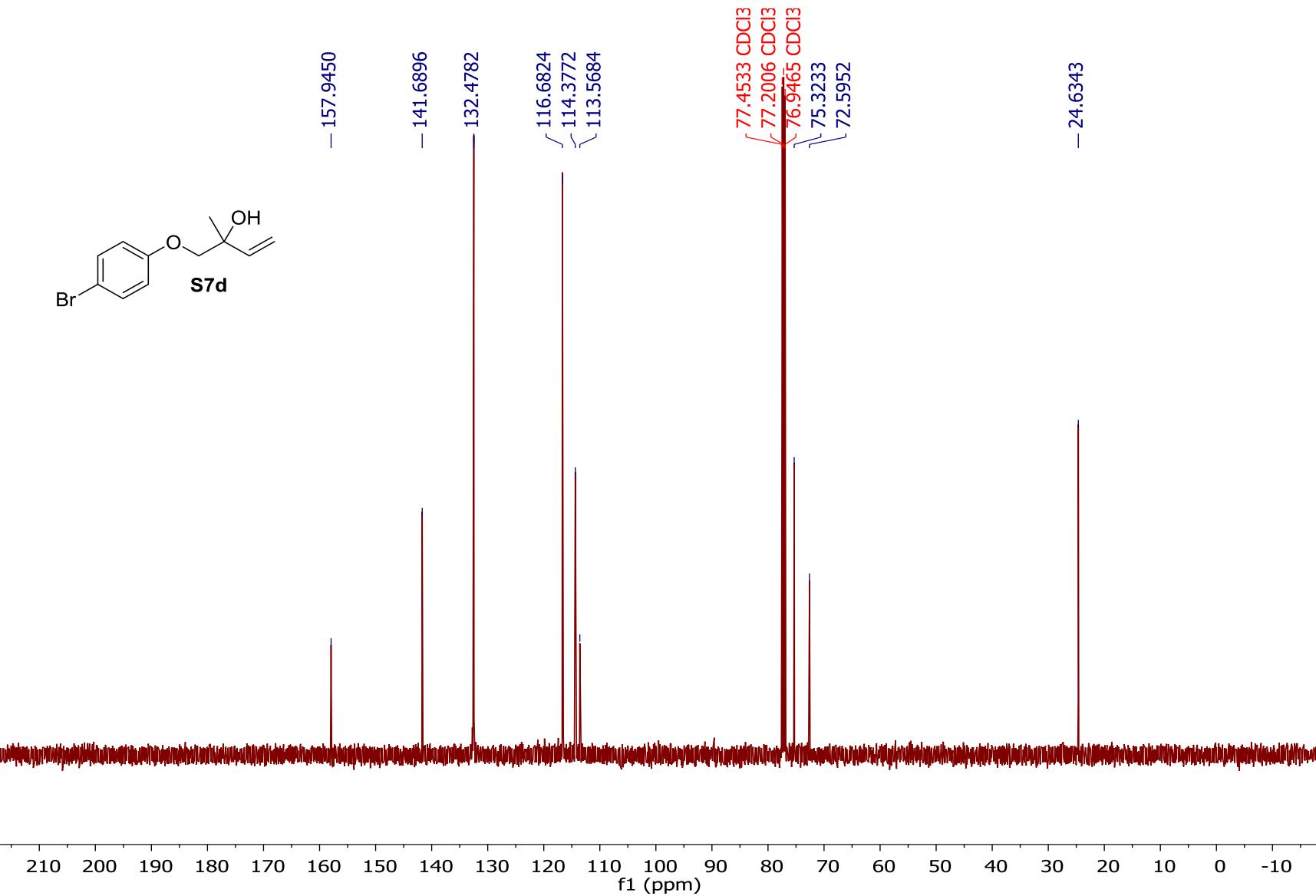


Compound S7c, 400 MHz ¹H NMR in CDCl₃

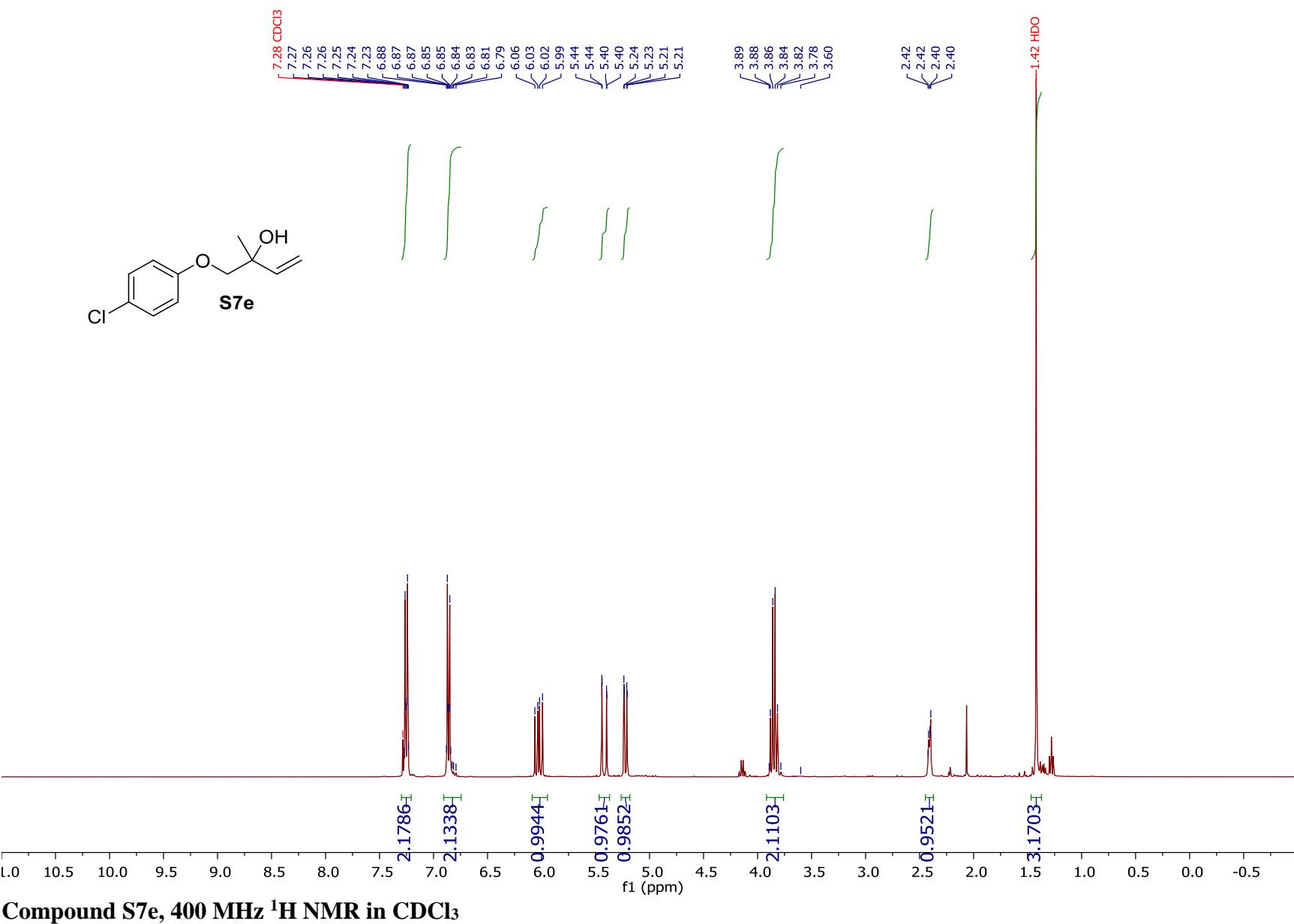


Compound S7c, 101 MHz ^{13}C NMR in CDCl_3

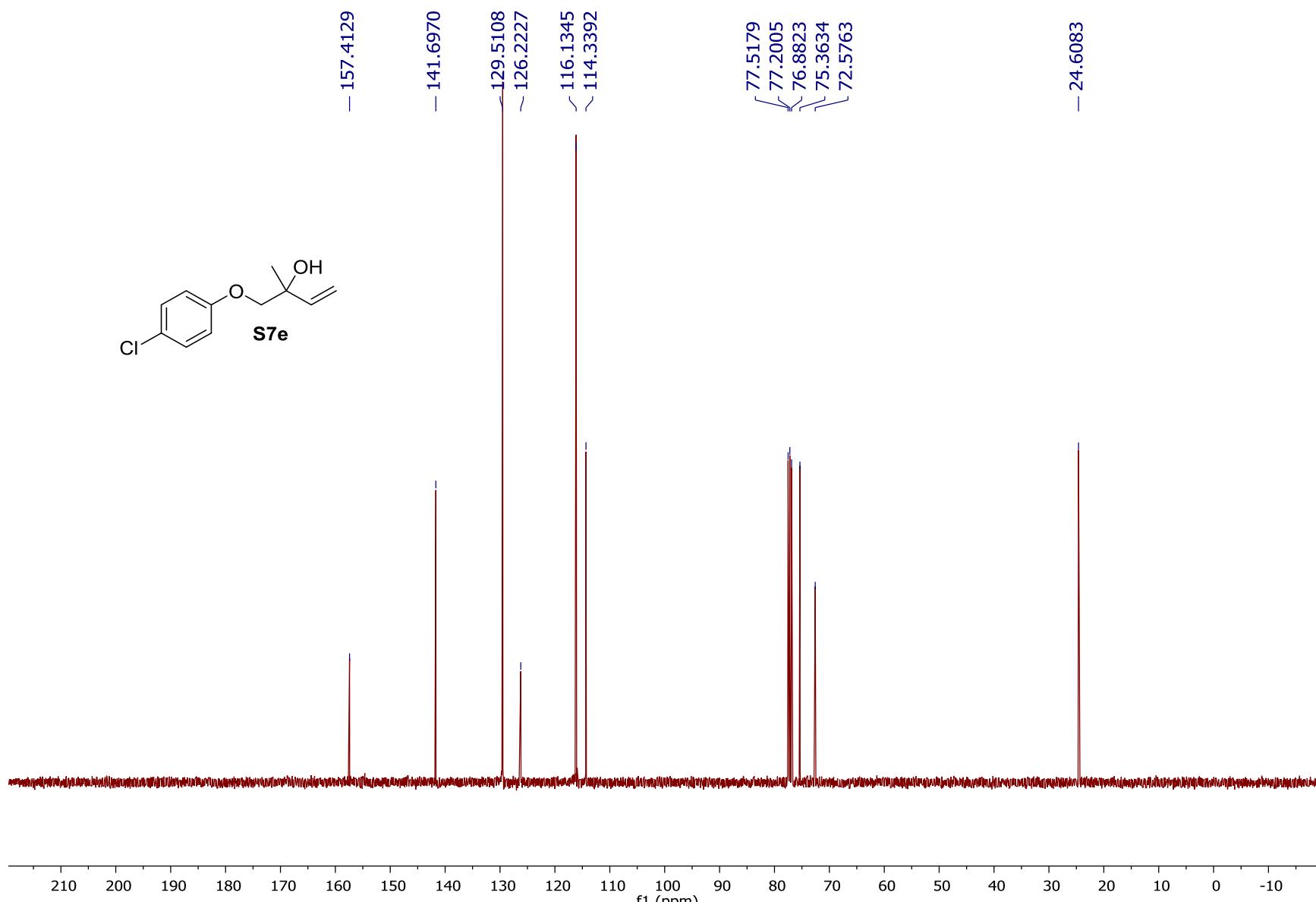




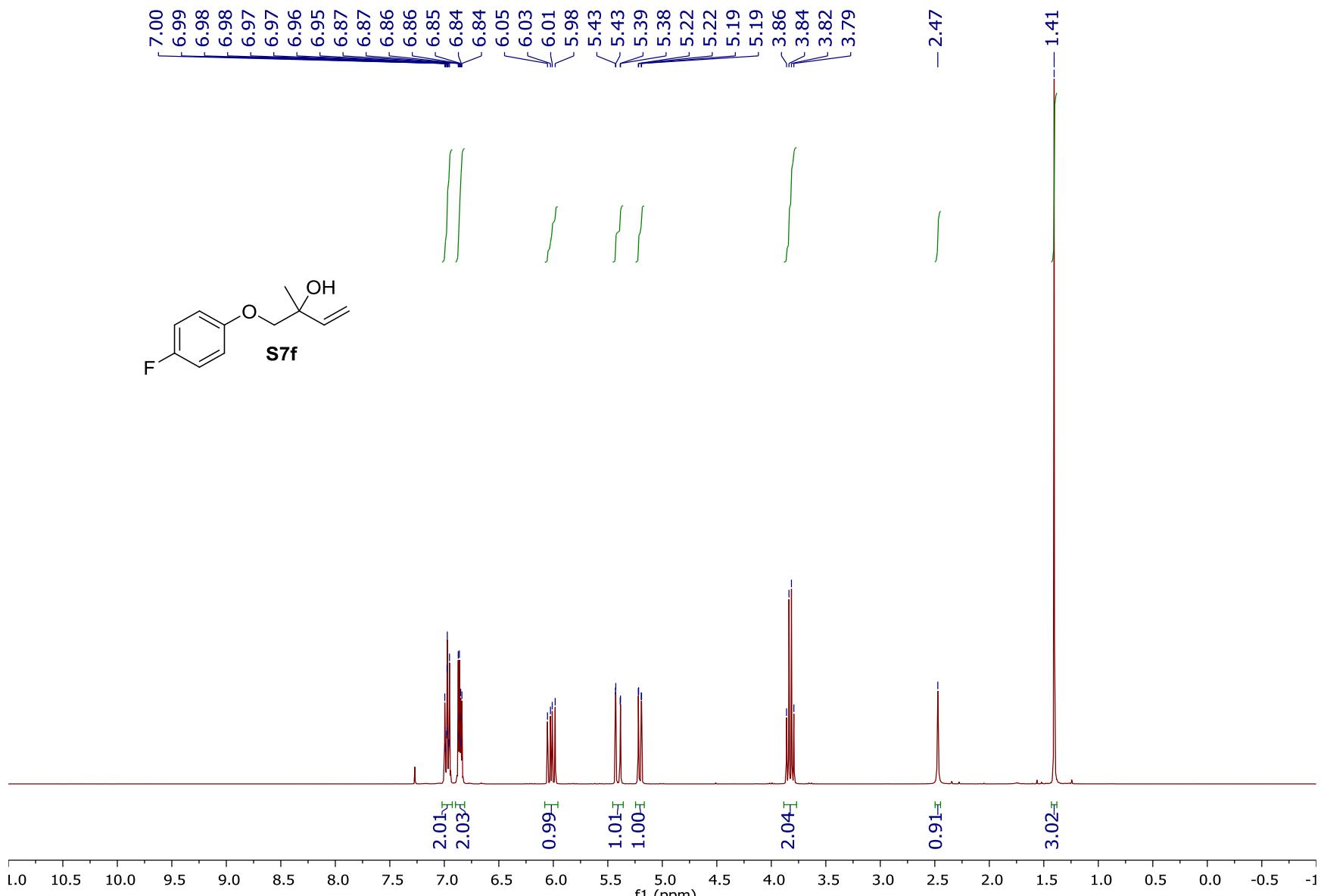
Compound S7d, 101 MHz ¹³C NMR in CDCl₃



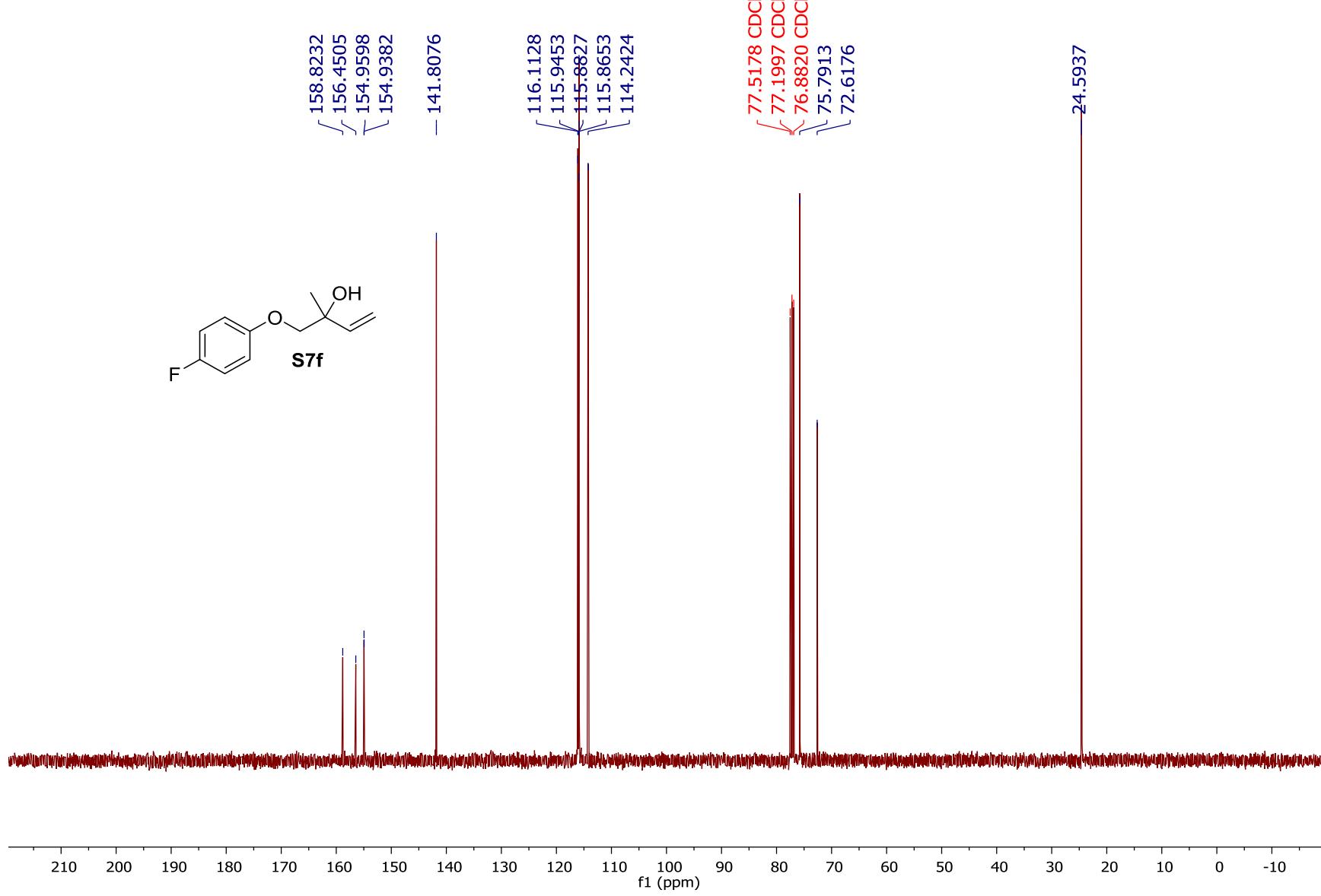
Compound S7e, 400 MHz ¹H NMR in CDCl₃



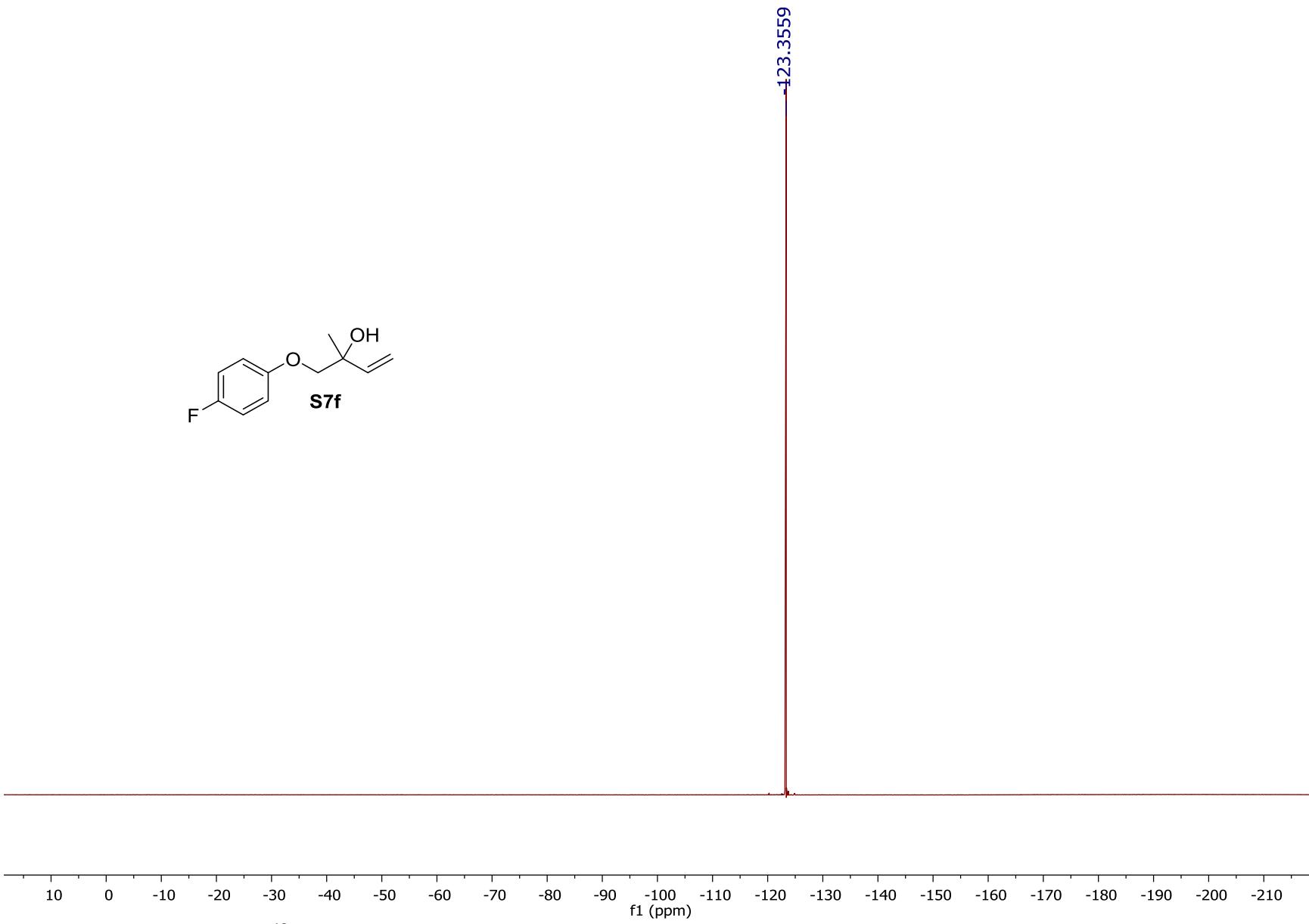
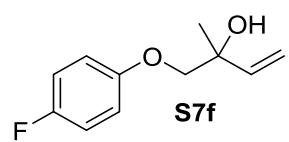
Compound S7e, 101 MHz ^{13}C NMR in CDCl_3



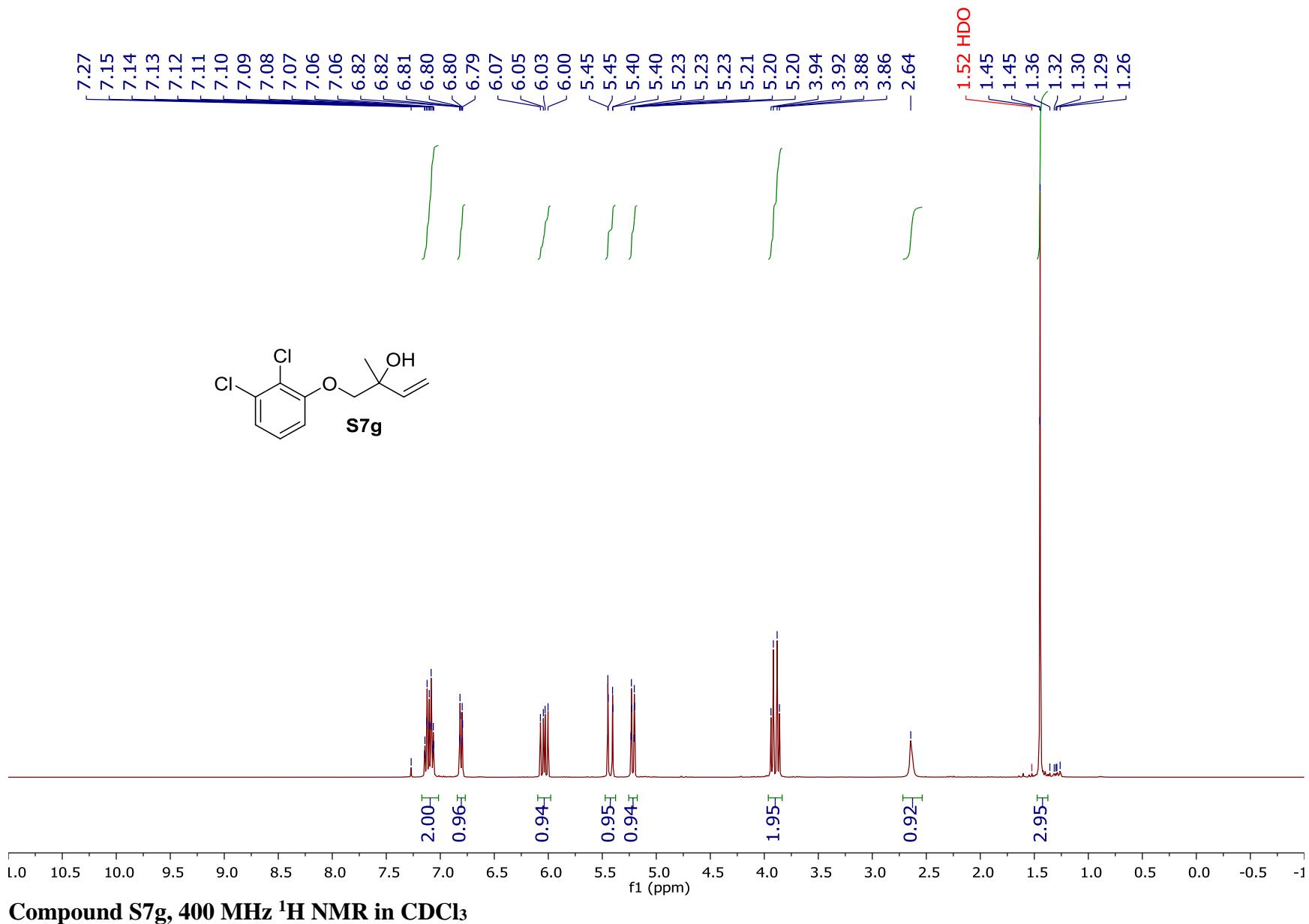
Compound S7f, 400 MHz ¹H NMR in CDCl₃

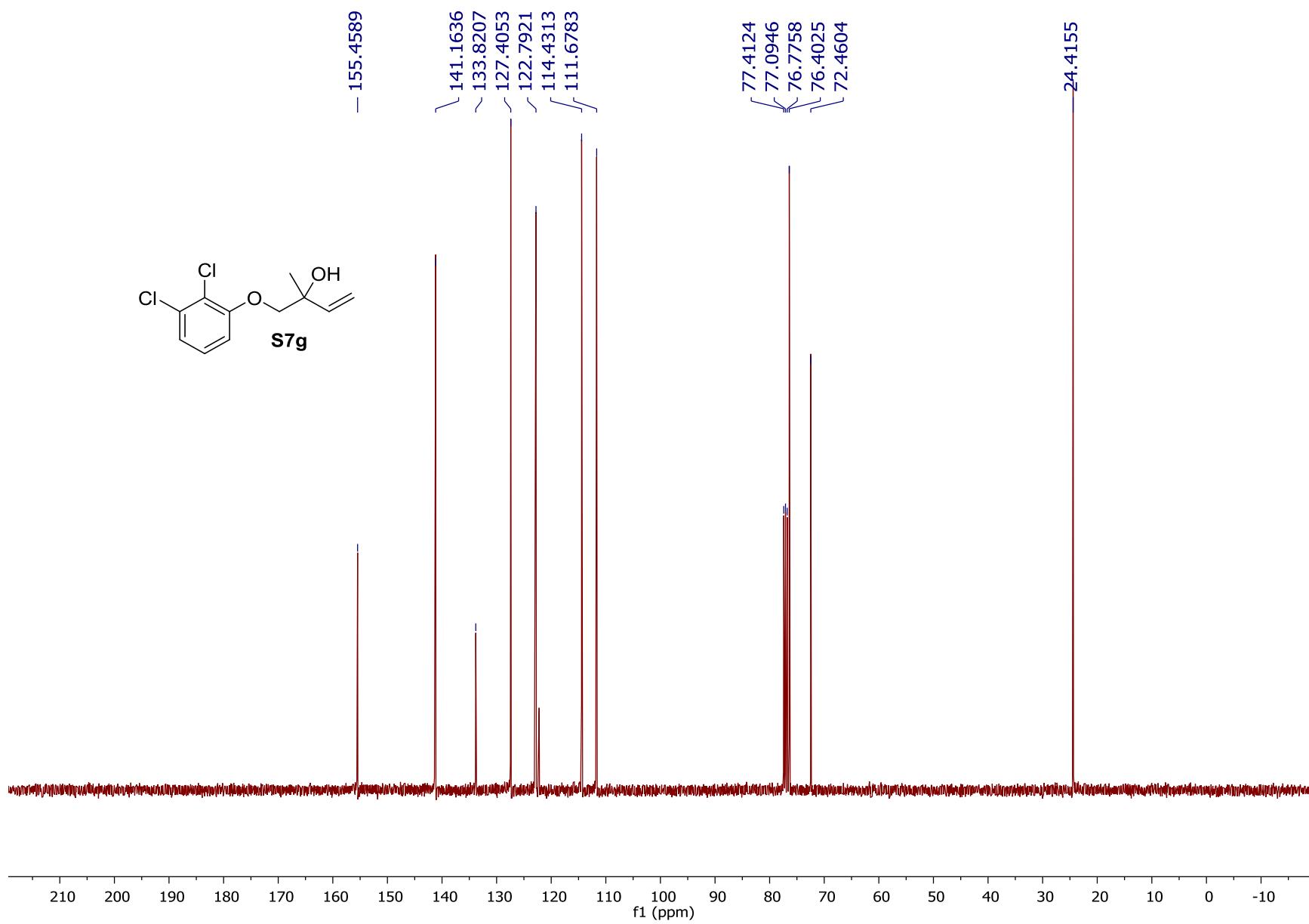


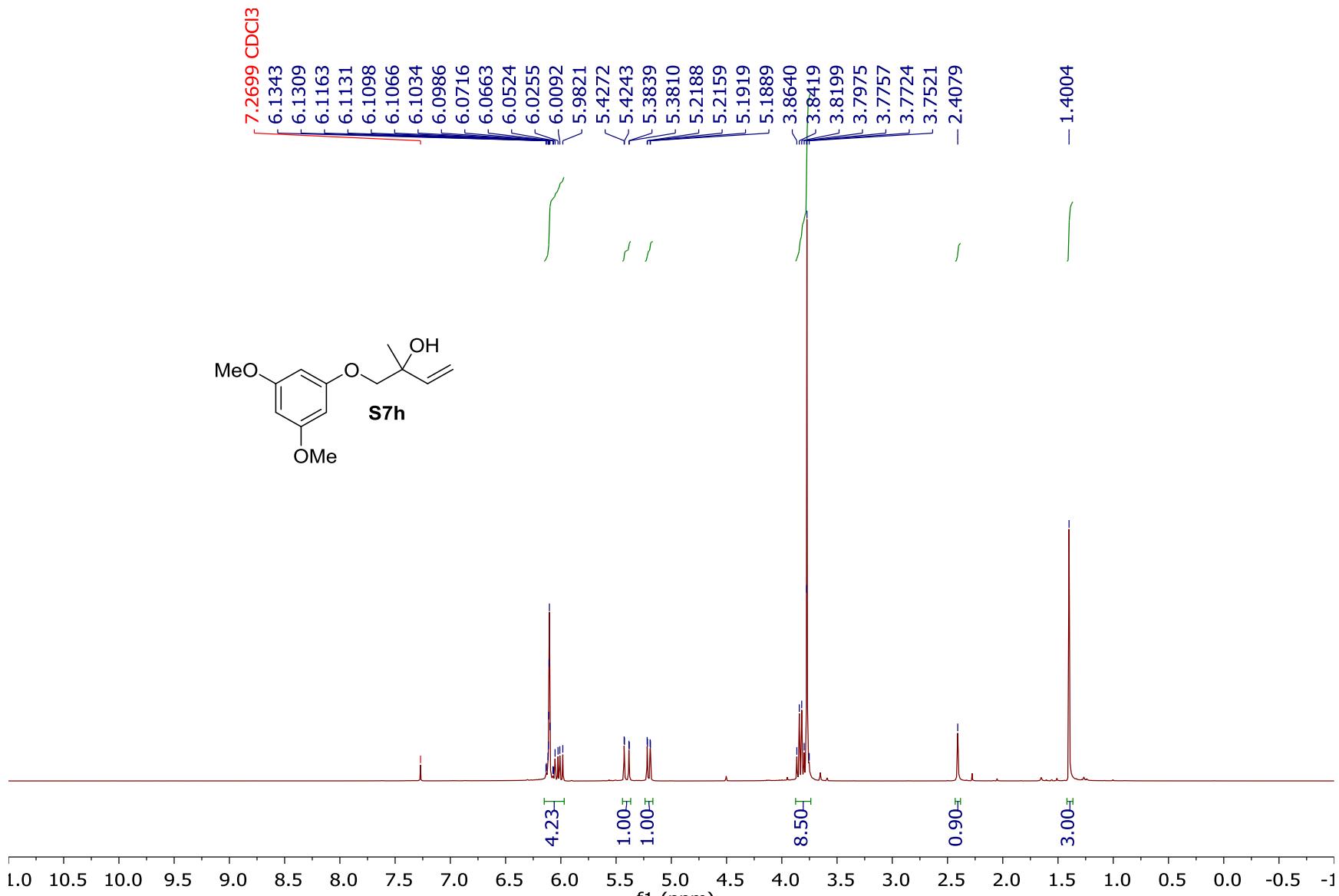
Compound S7f, 101 MHz ¹³C NMR in CDCl₃



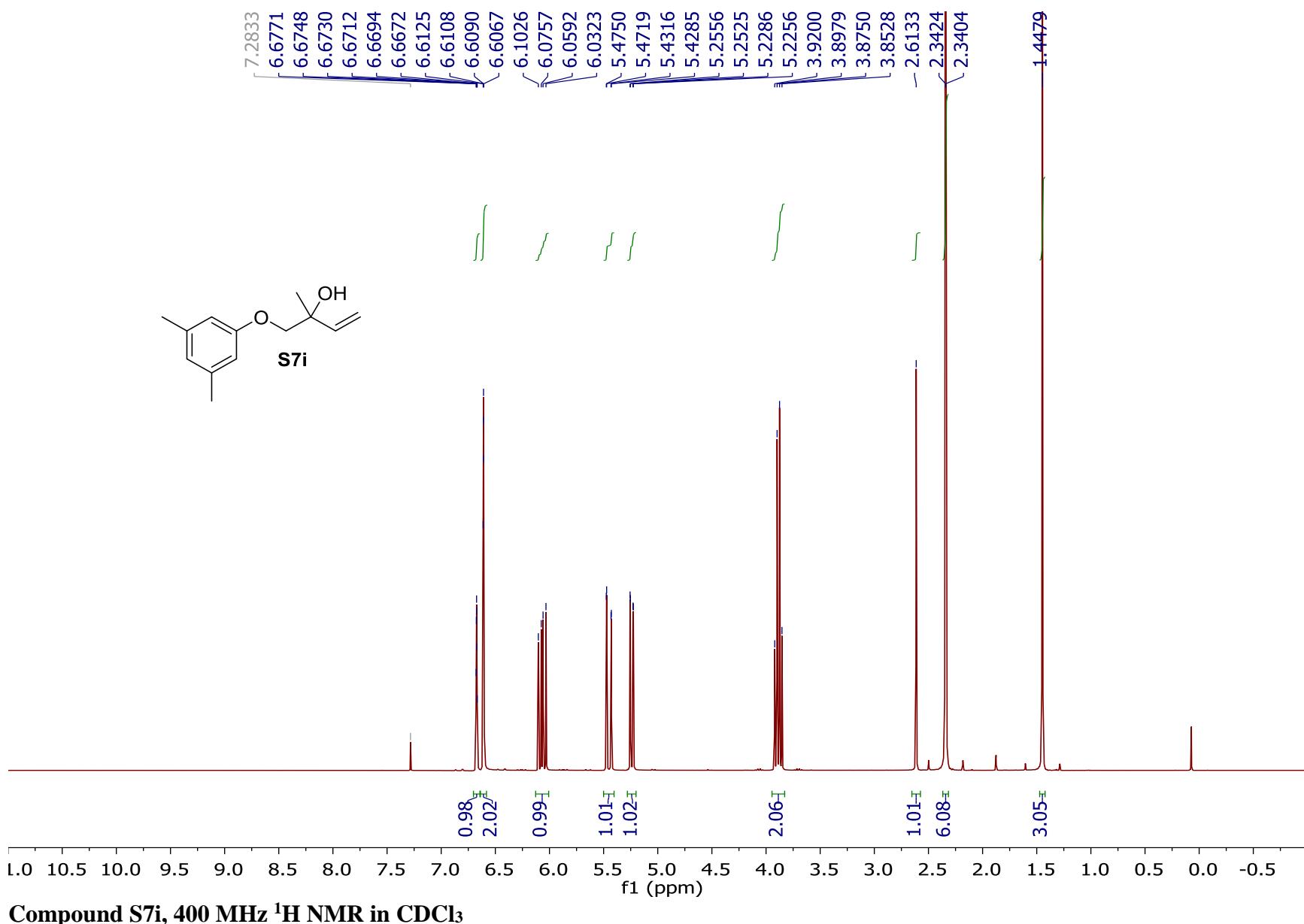
Compound S7f, 376 MHz ¹⁹F NMR in CDCl₃



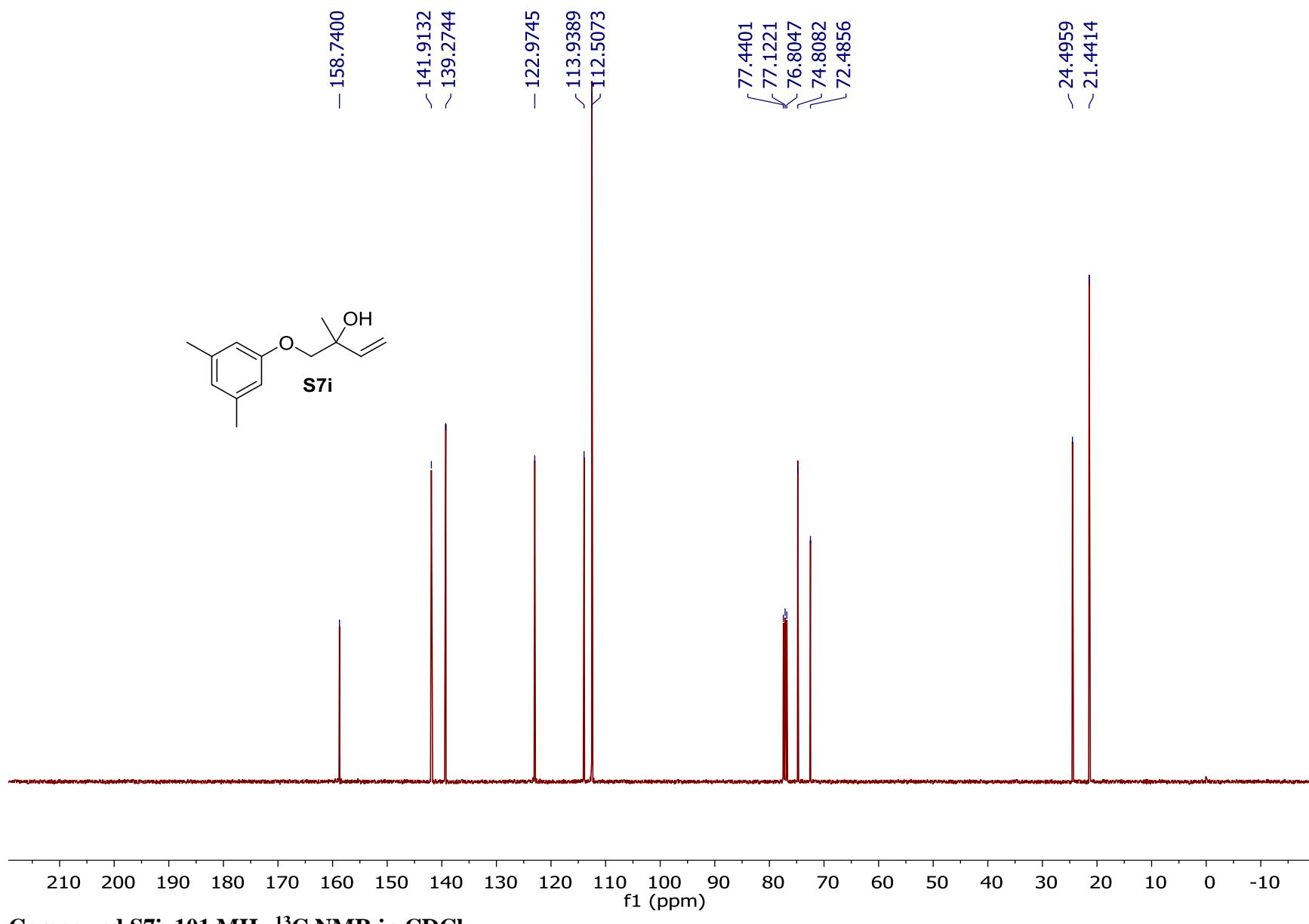




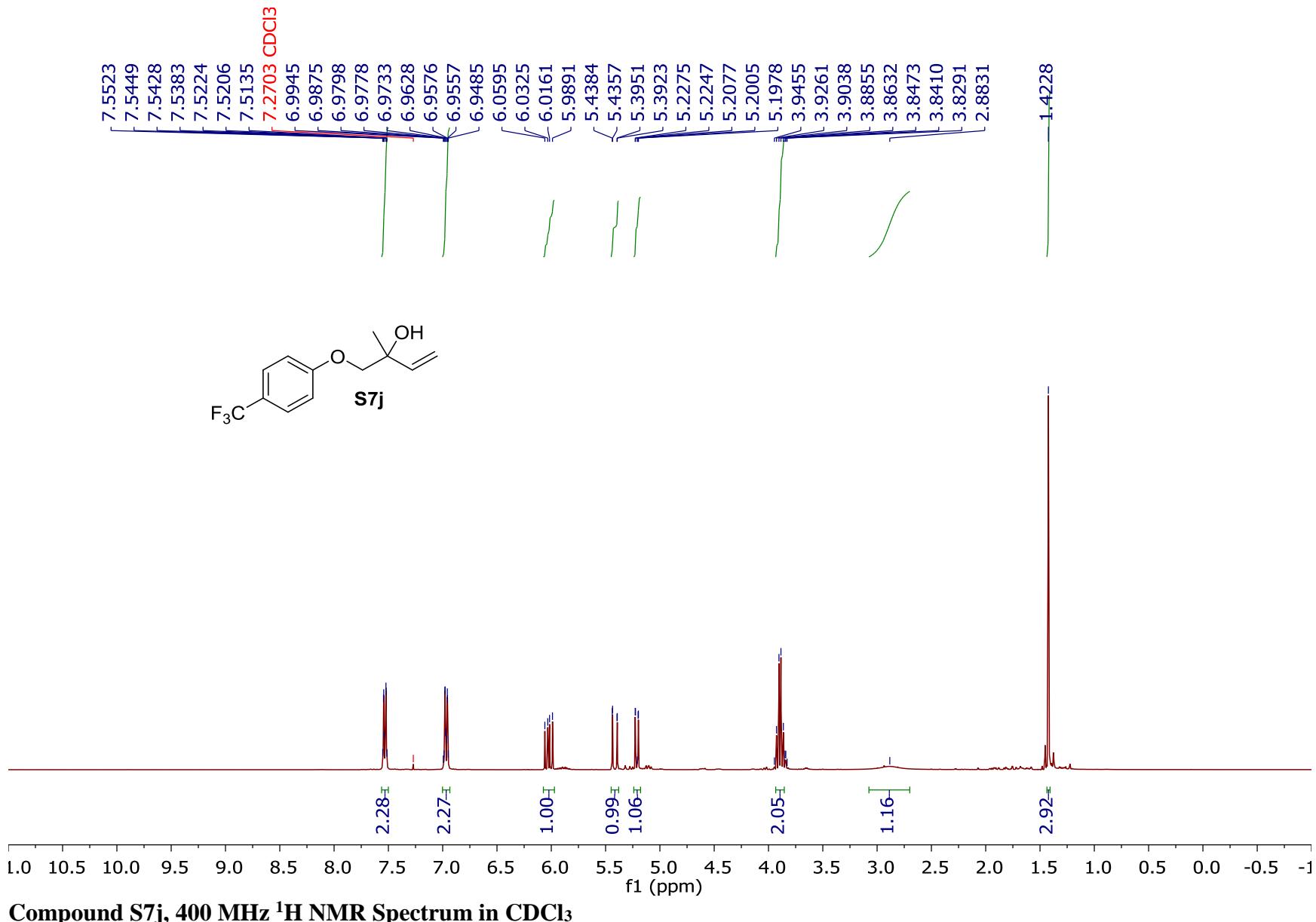
Compound S7h, 400 MHz ¹H NMR in CDCl₃

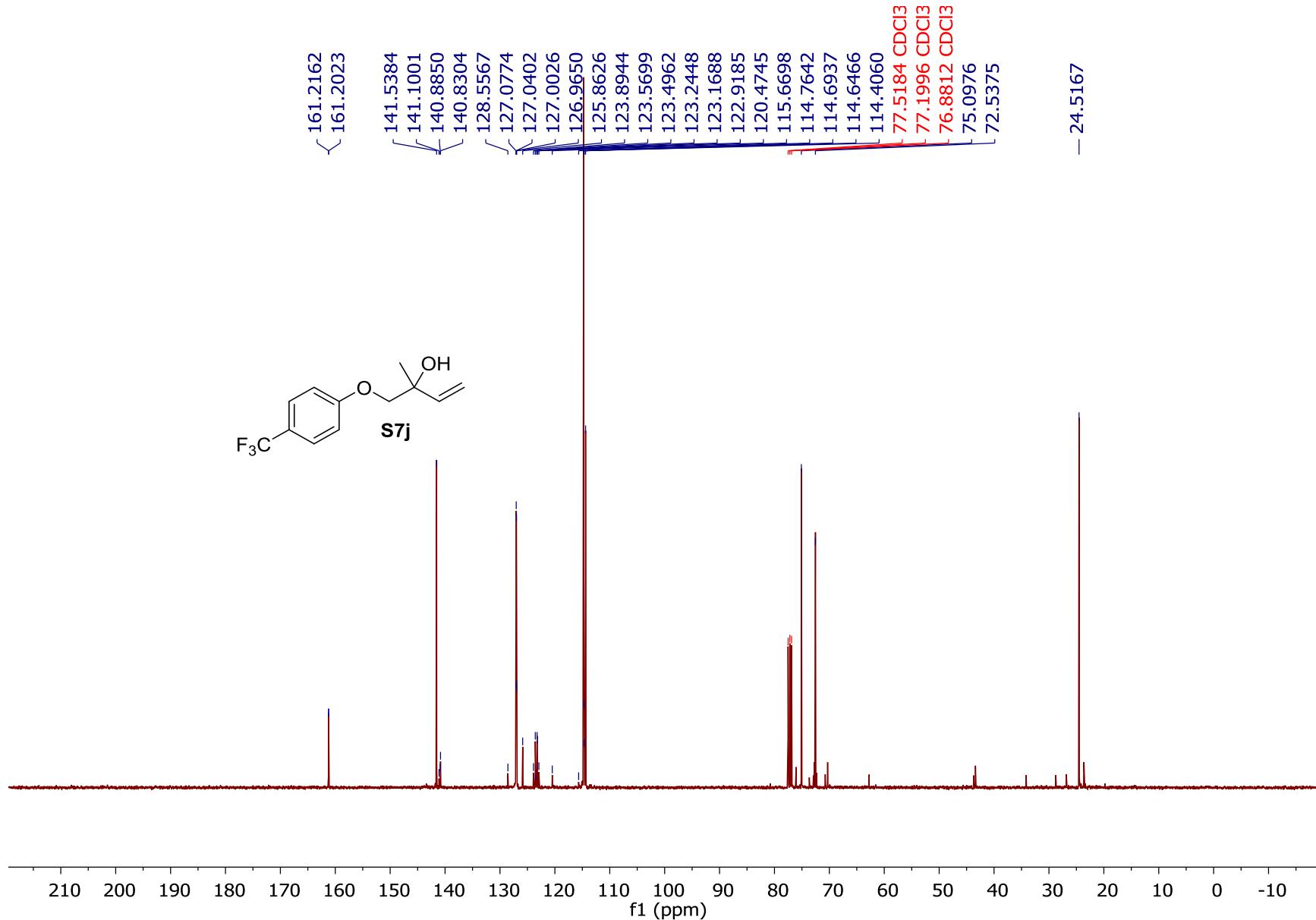


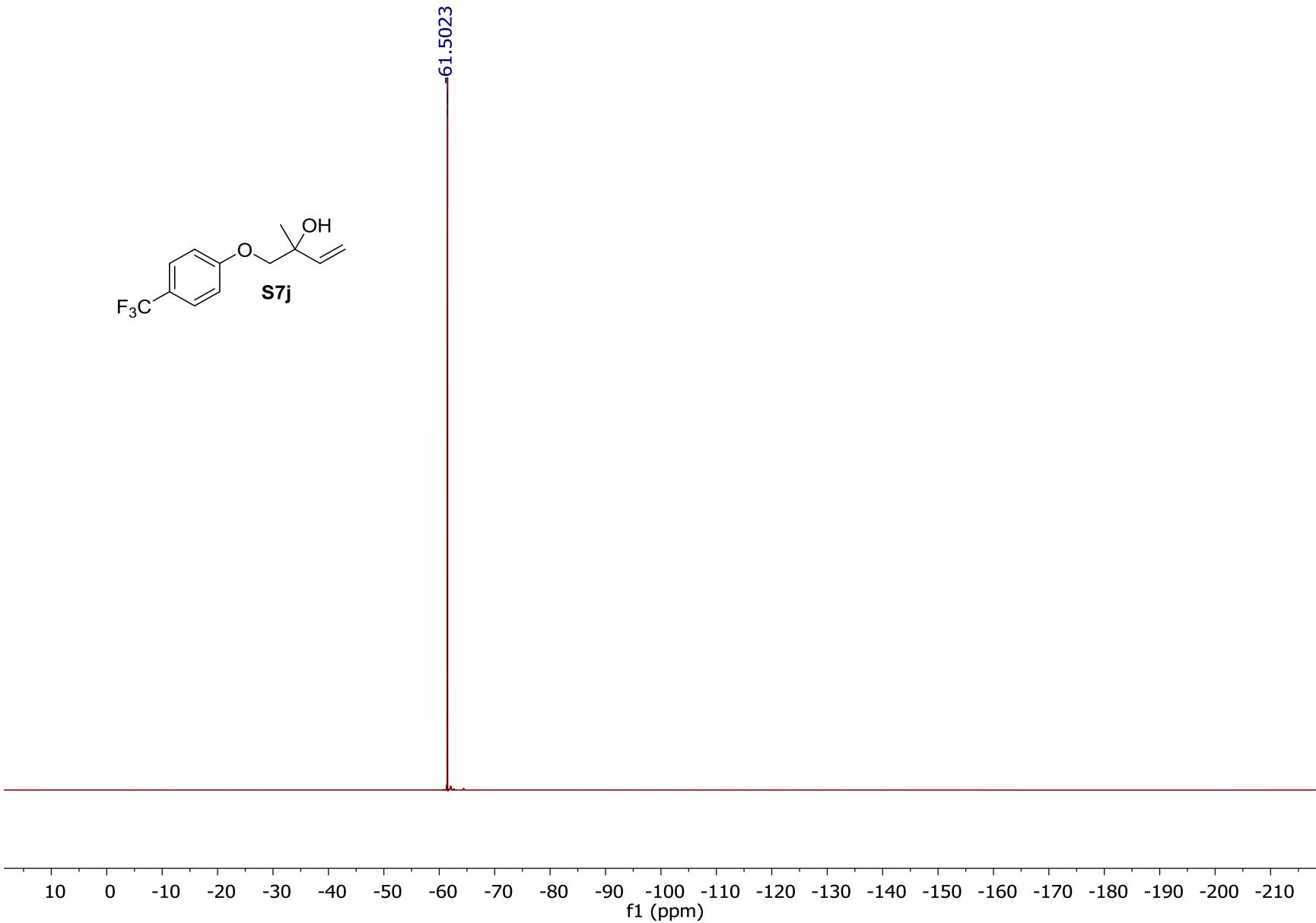
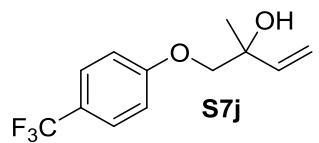
Compound S7i, 400 MHz ^1H NMR in CDCl_3



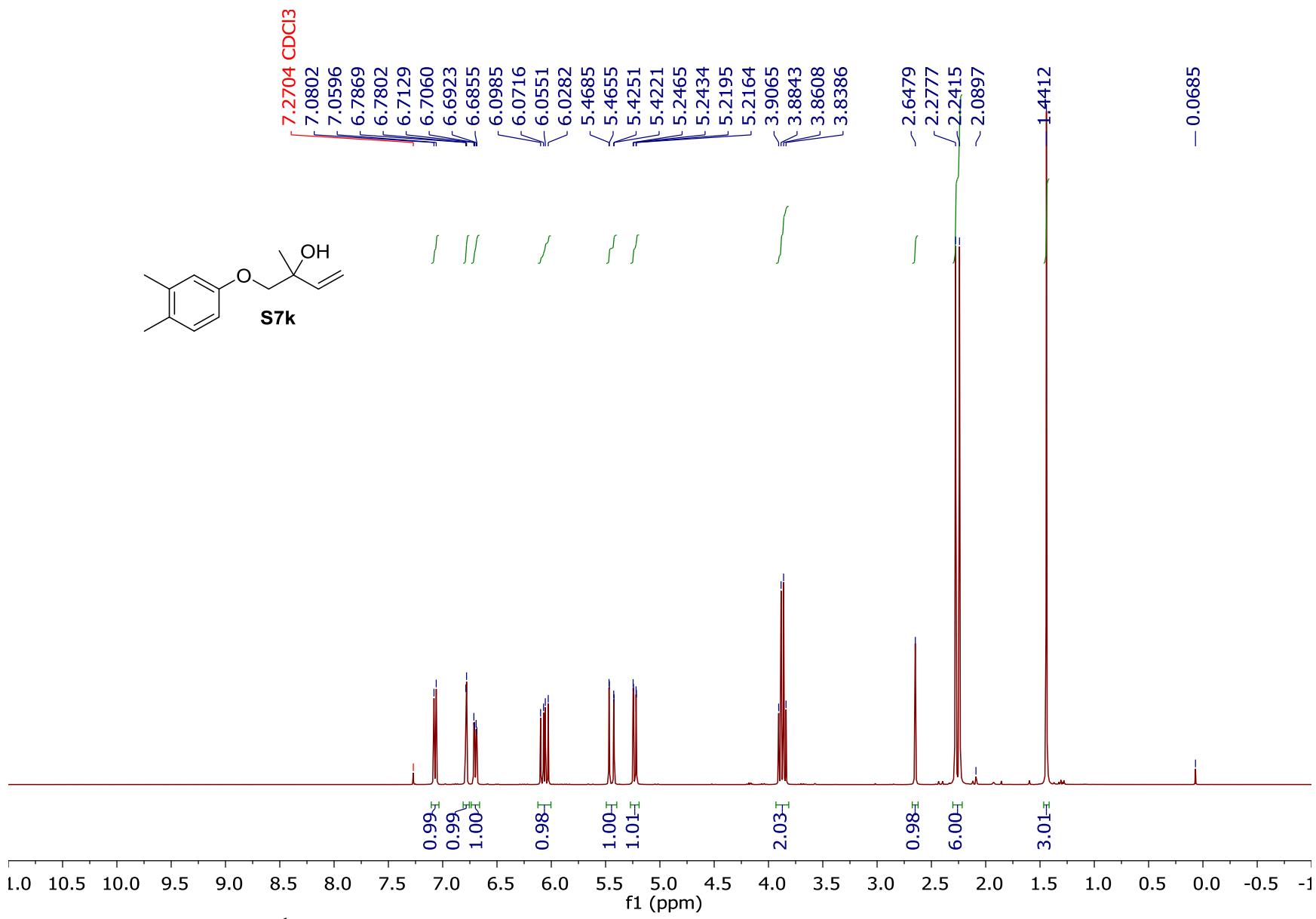
Compound S7i, 101 MHz ^{13}C NMR in CDCl_3

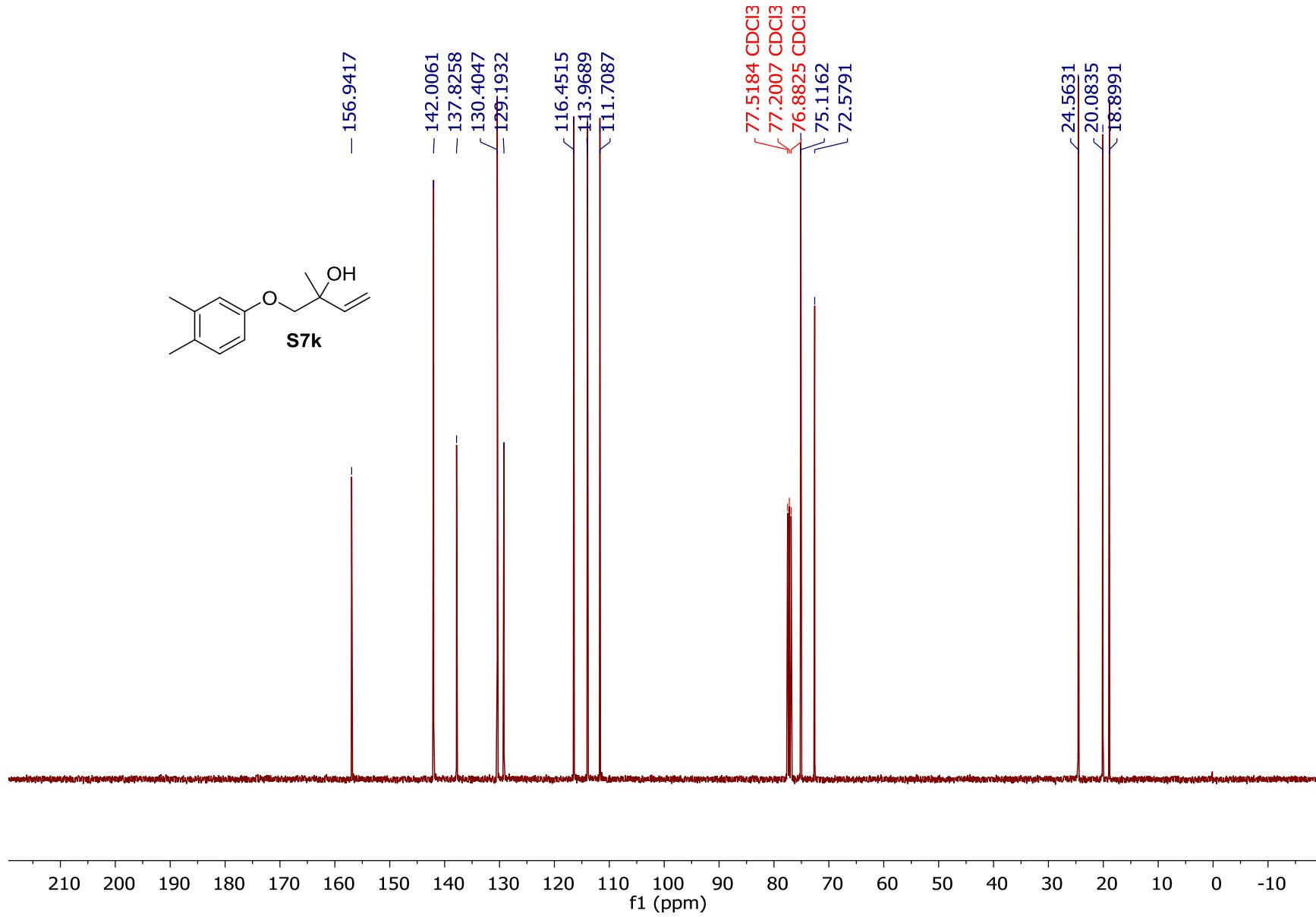




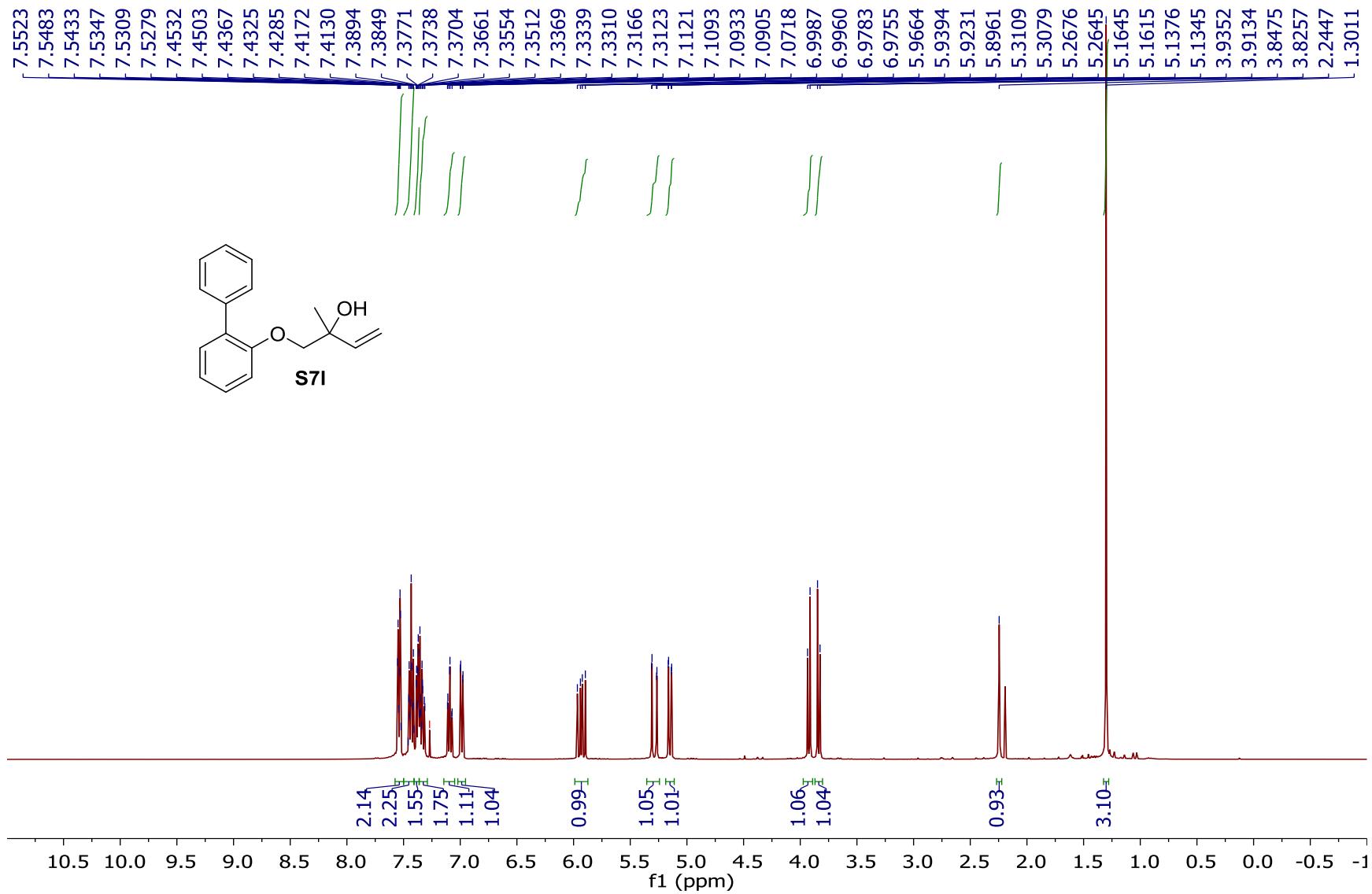


Compound S7j, 376 MHz ${}^{19}\text{F}$ NMR Spectrum in CDCl_3

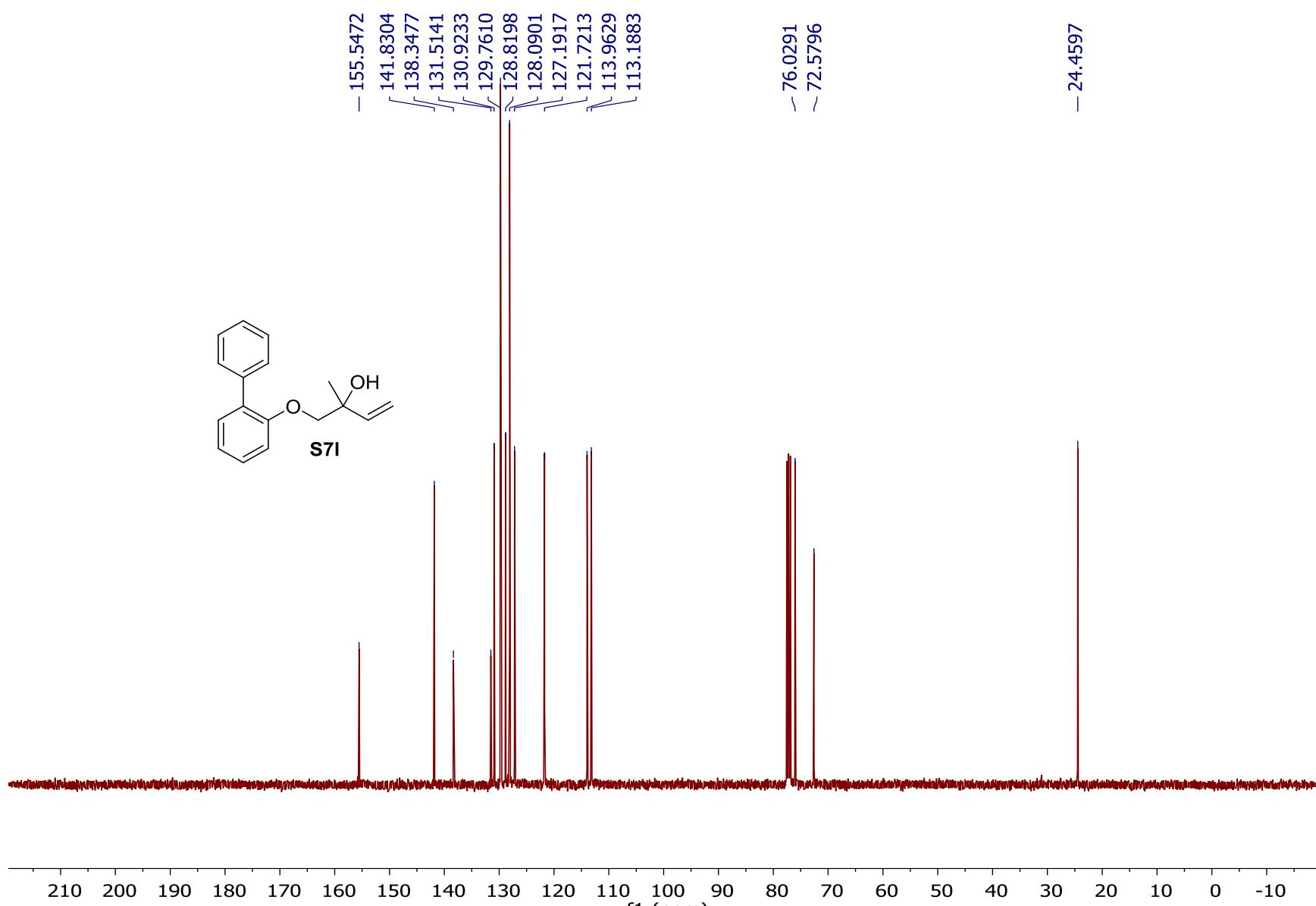




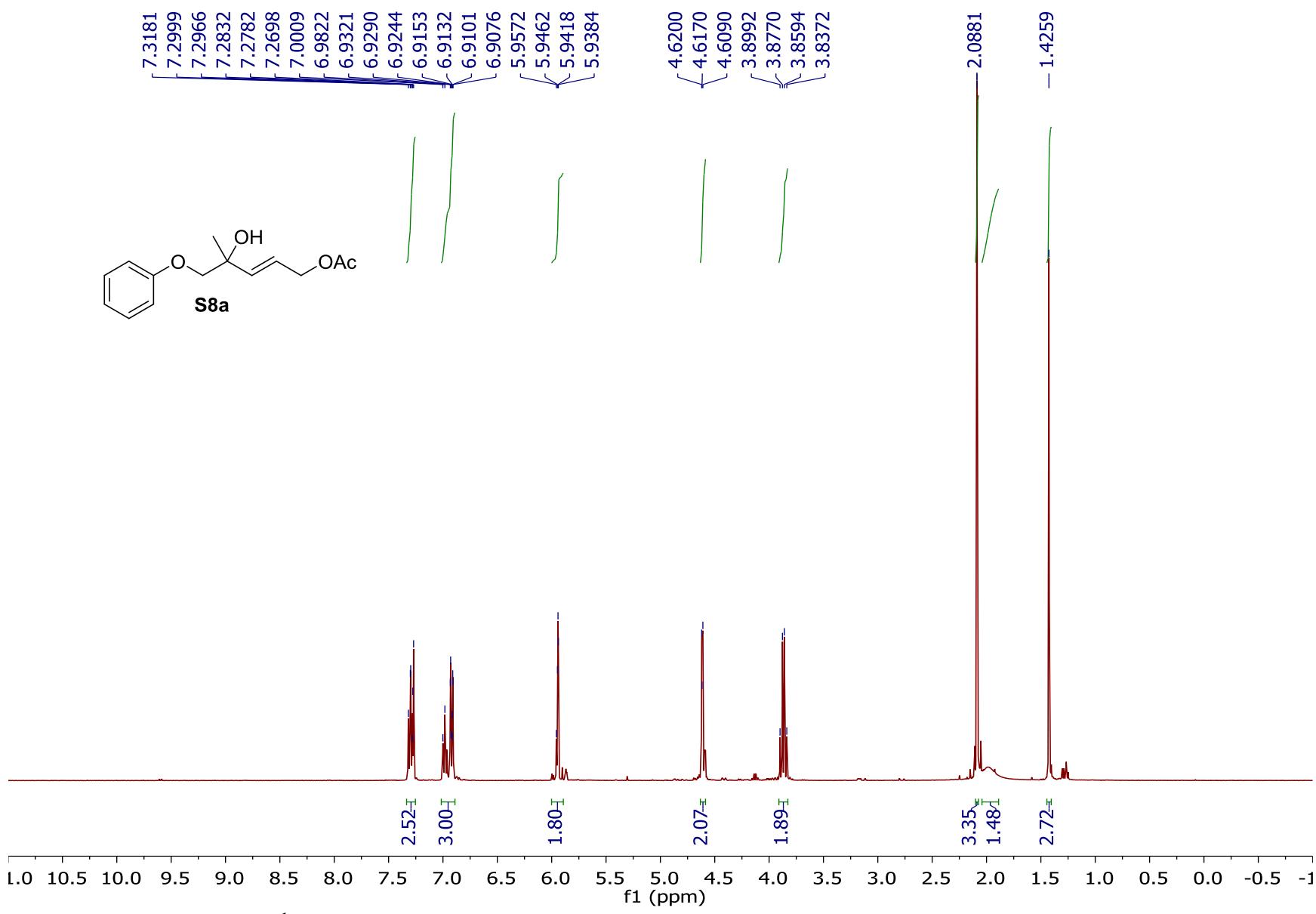
Compound S7k, 101 MHz ¹³C NMR Spectrum in CDCl₃



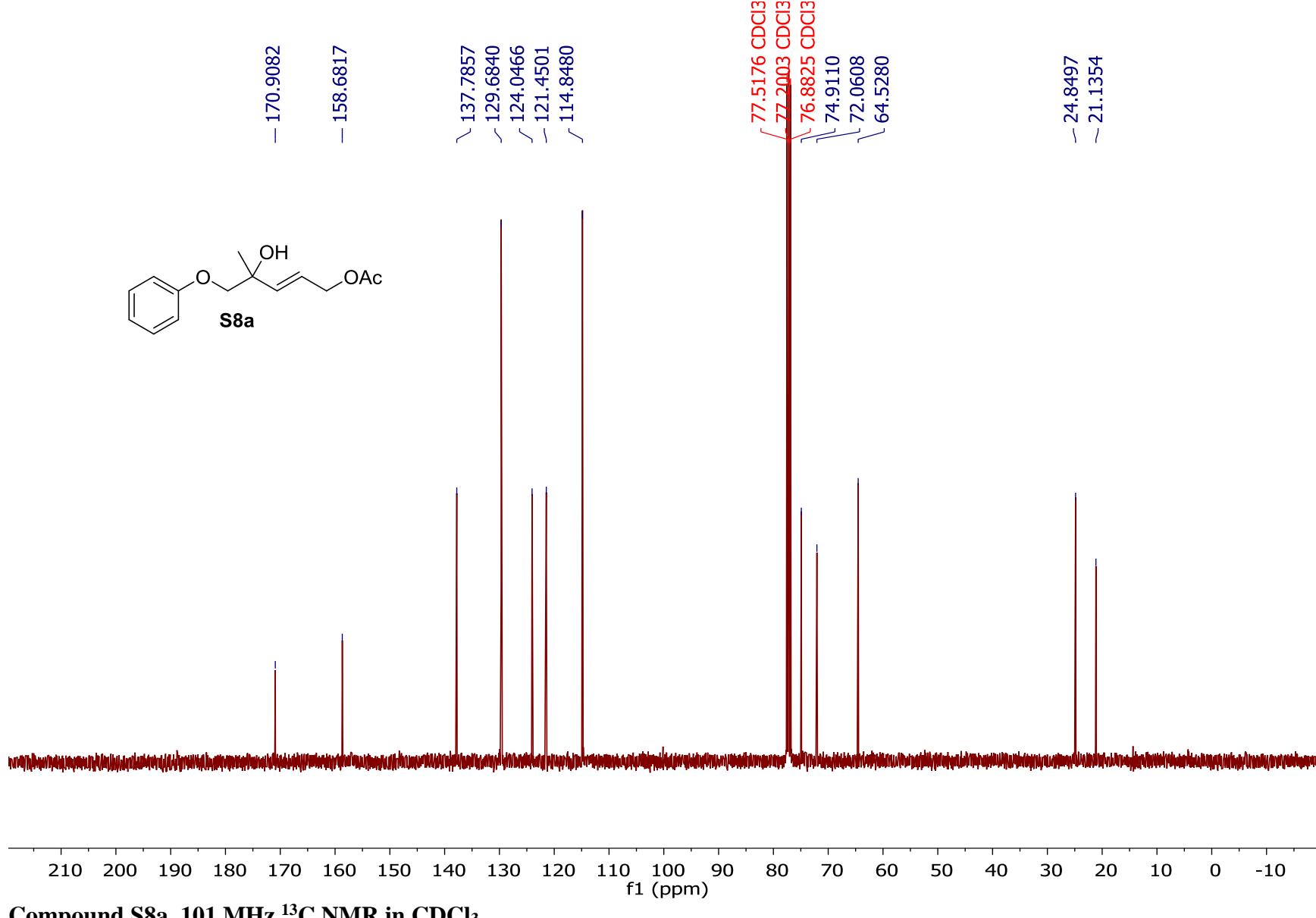
Compound S7l, 400 MHz ^1H NMR Spectrum in CDCl_3

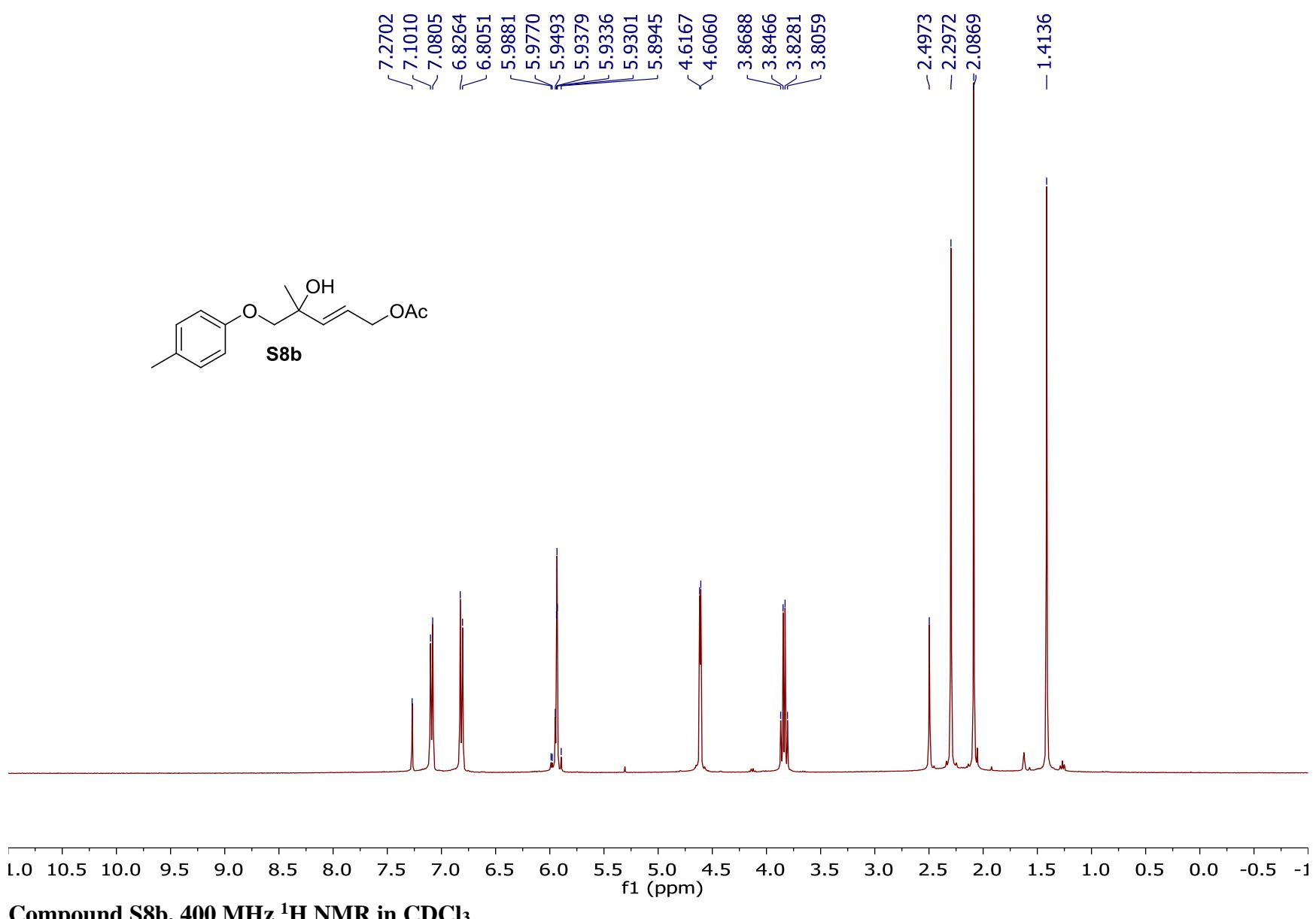


Compound S7l, 101 MHz ^{13}C NMR Spectrum in CDCl_3

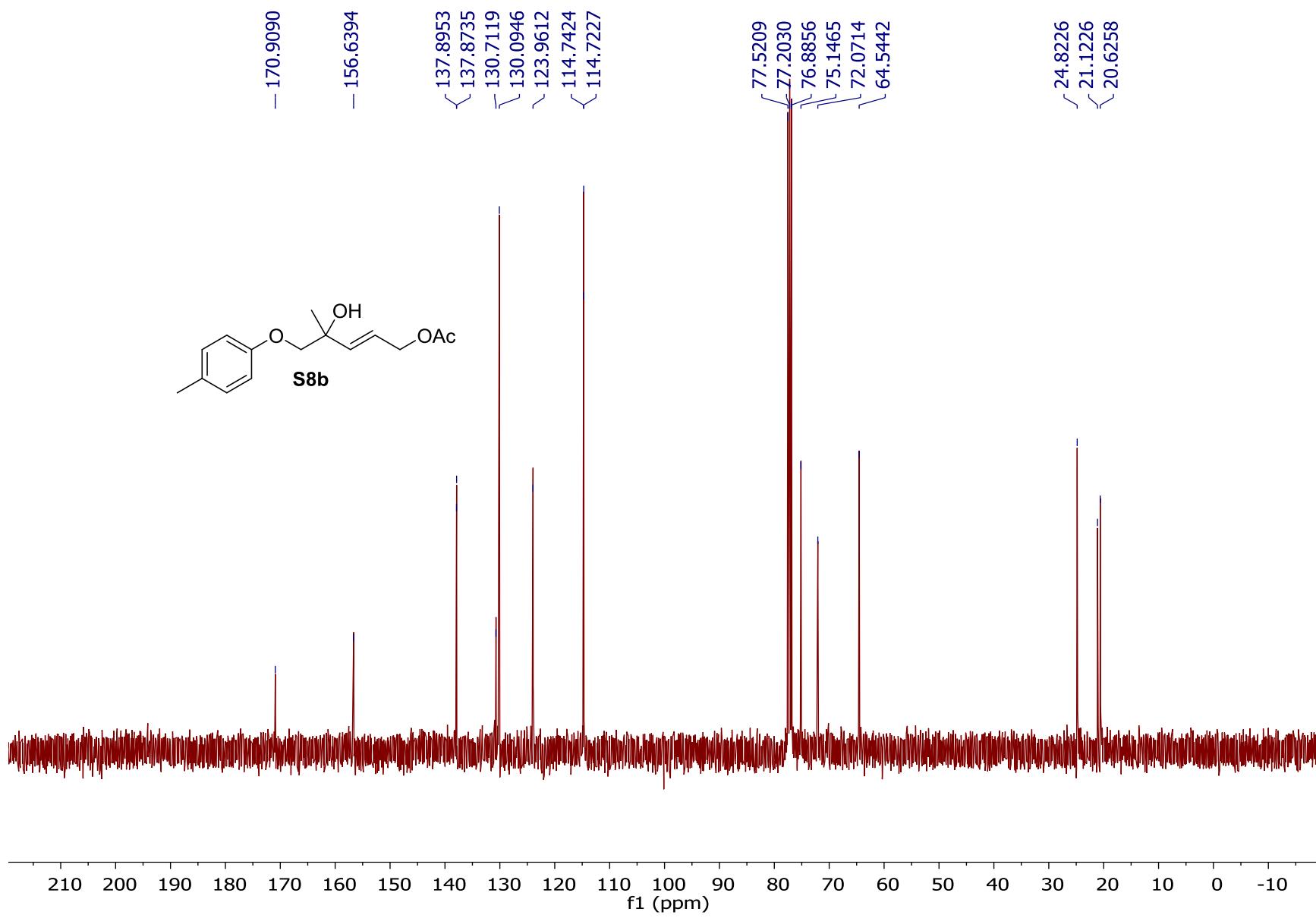


Compound S8a, 500 MHz ^1H NMR in CDCl_3

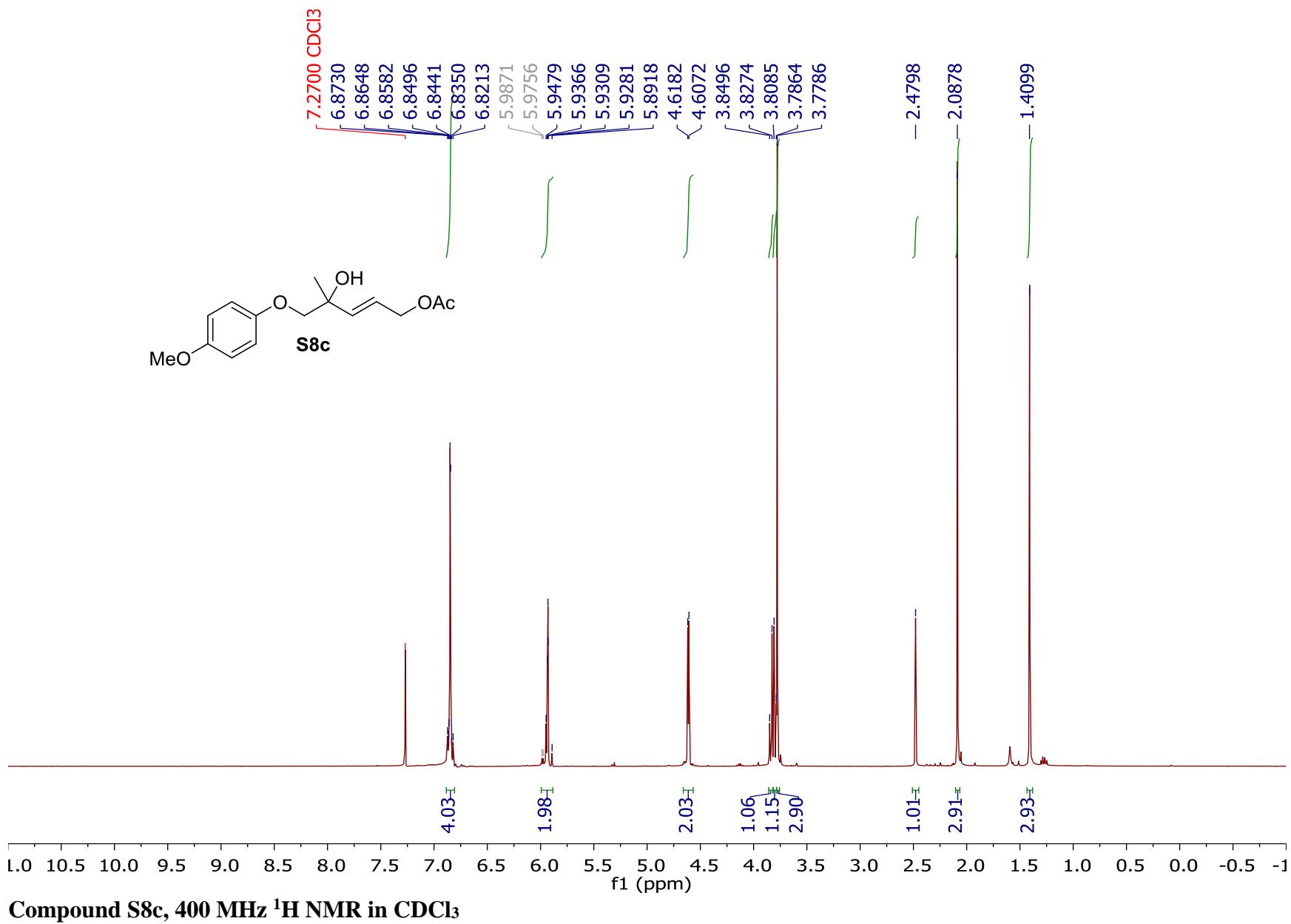


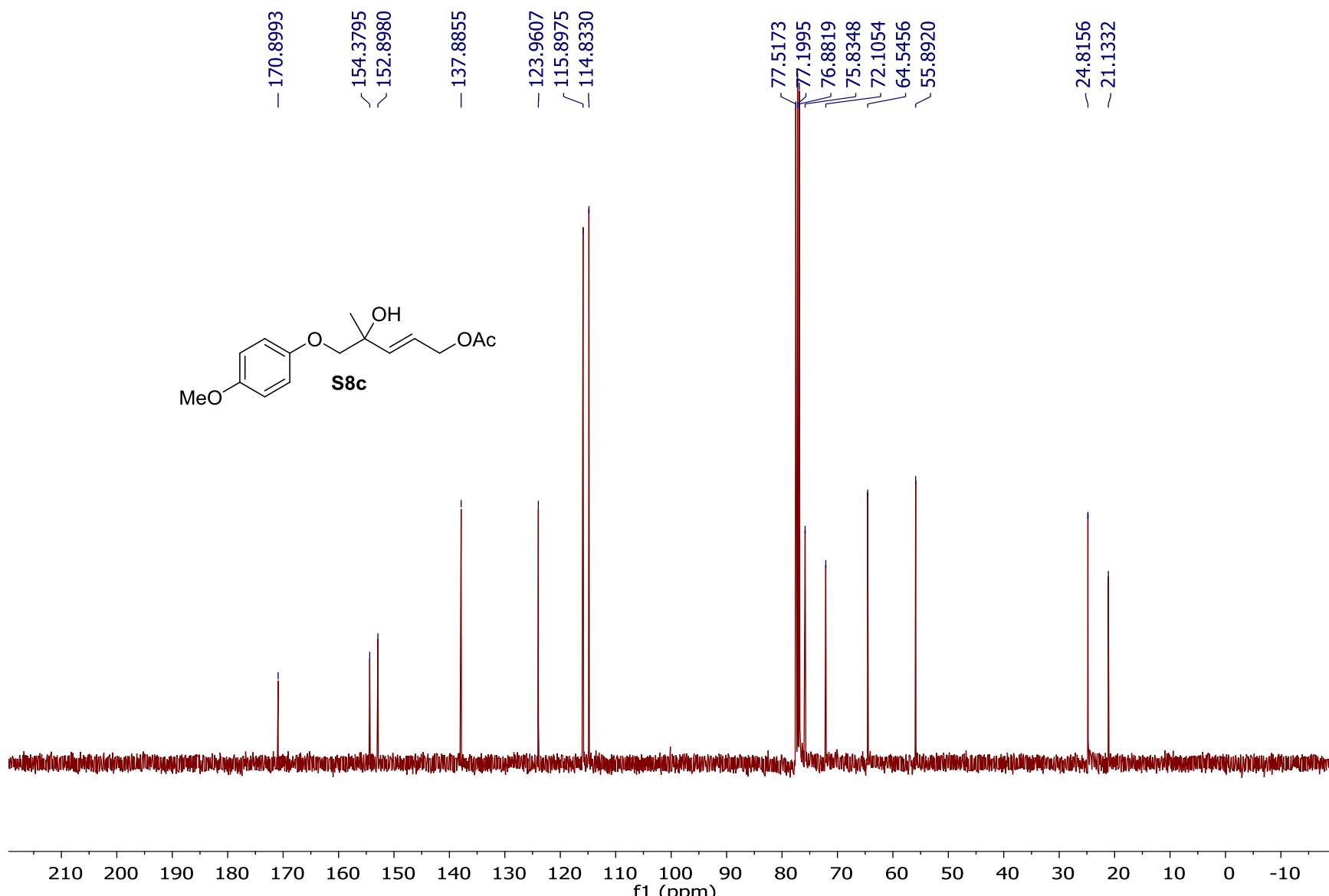


Compound S8b, 400 MHz ¹H NMR in CDCl₃

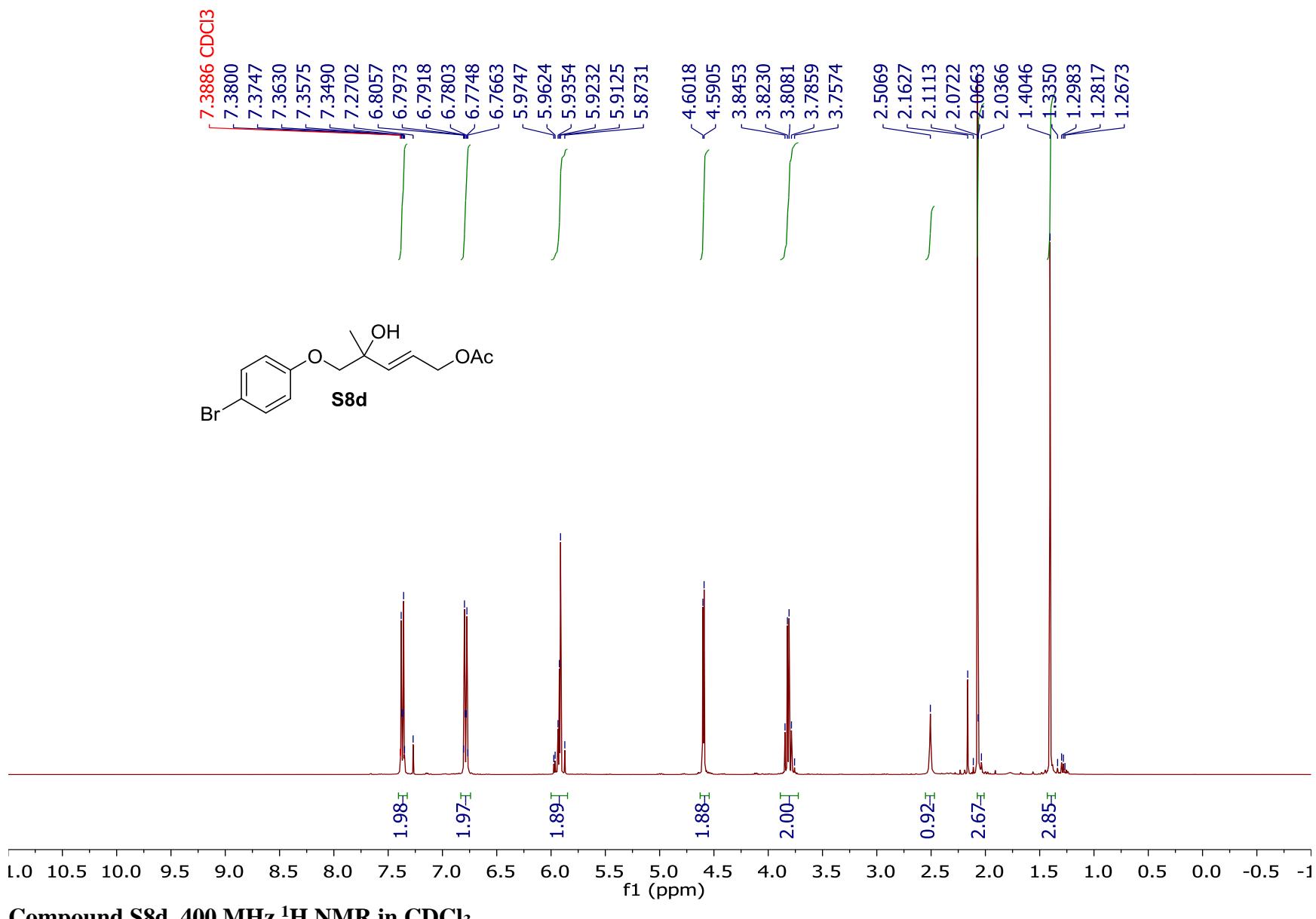


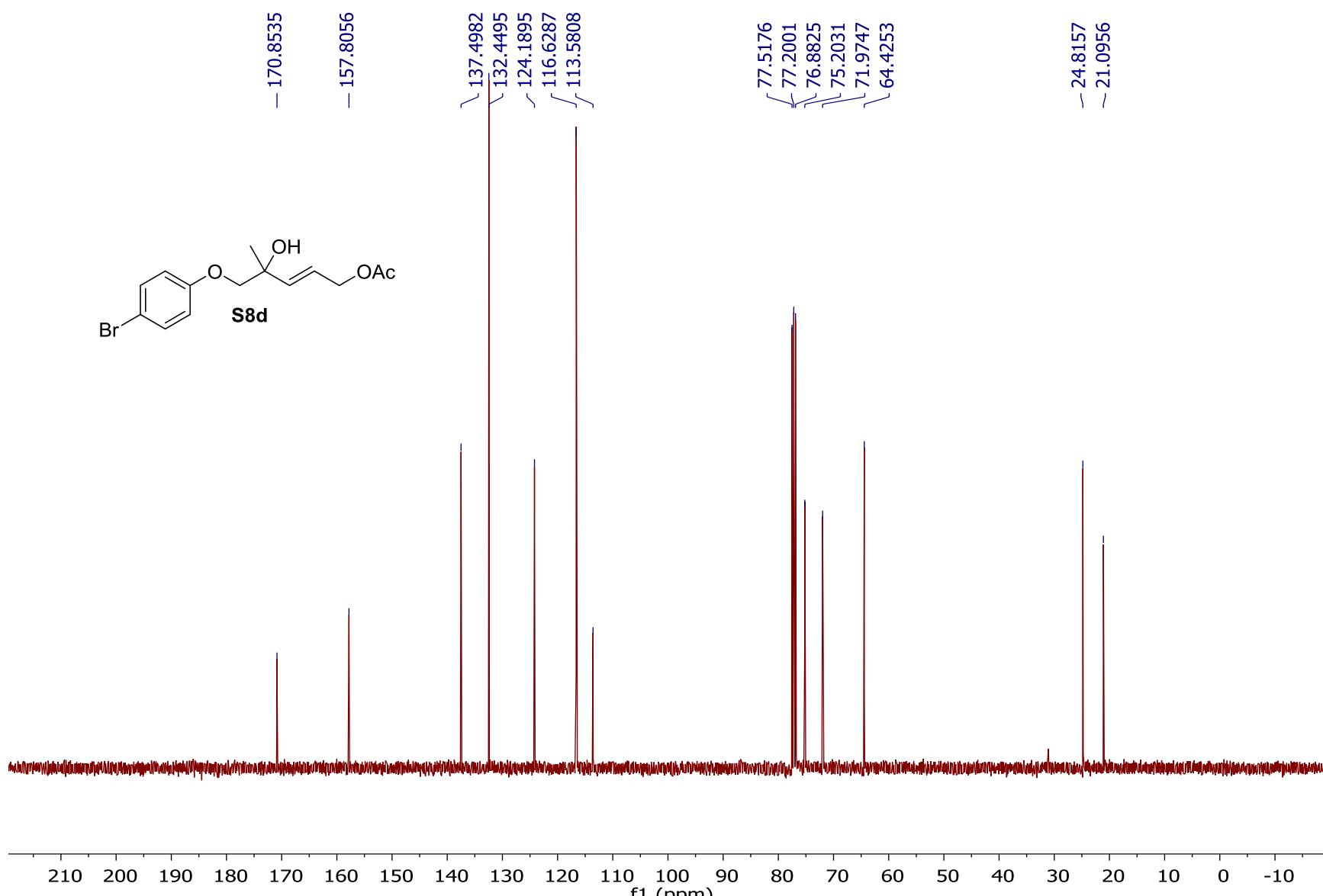
Compound S8b, 101 MHz ^{13}C NMR in CDCl_3



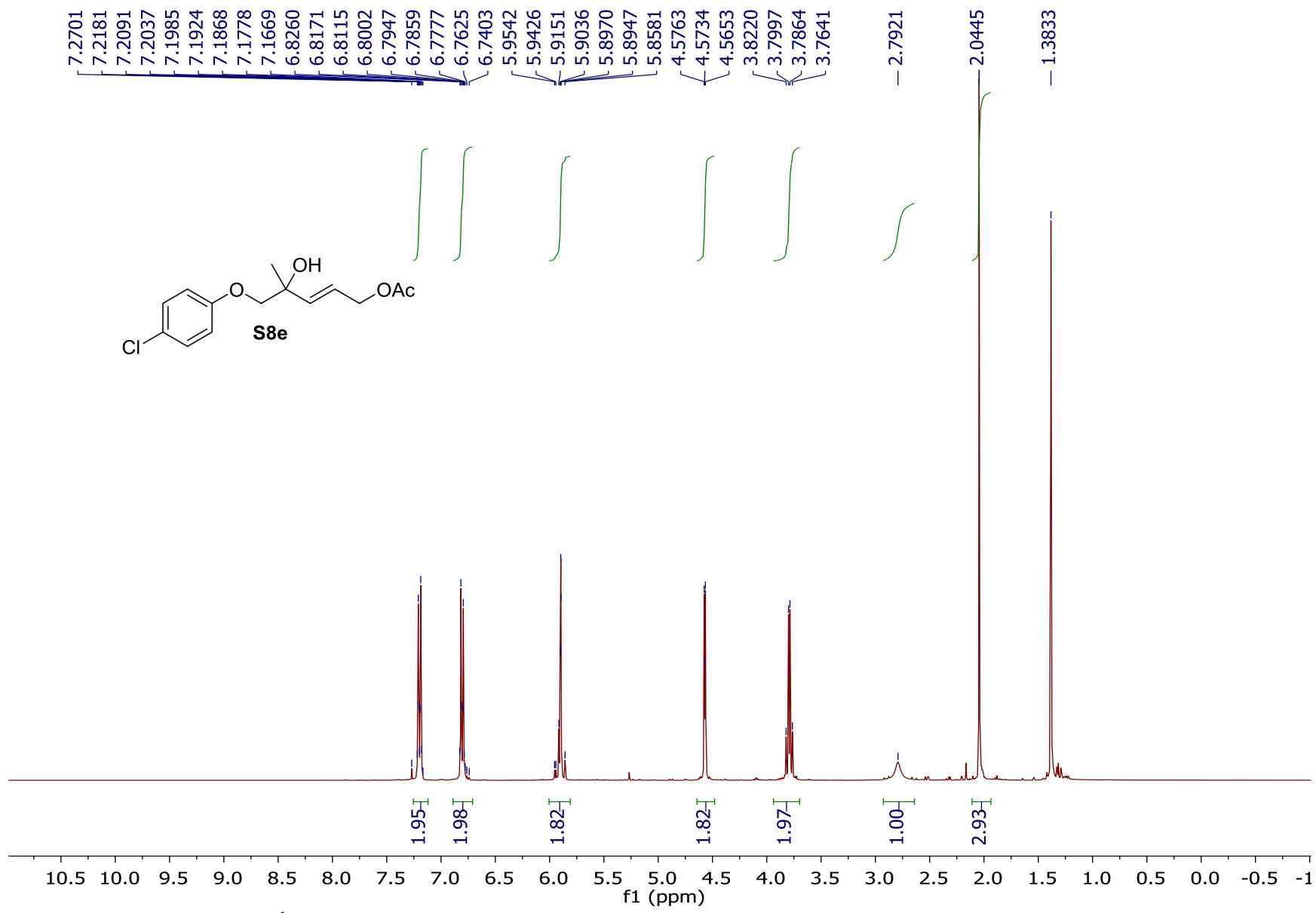


Compound S8c, 101 MHz ^{13}C NMR in CDCl_3

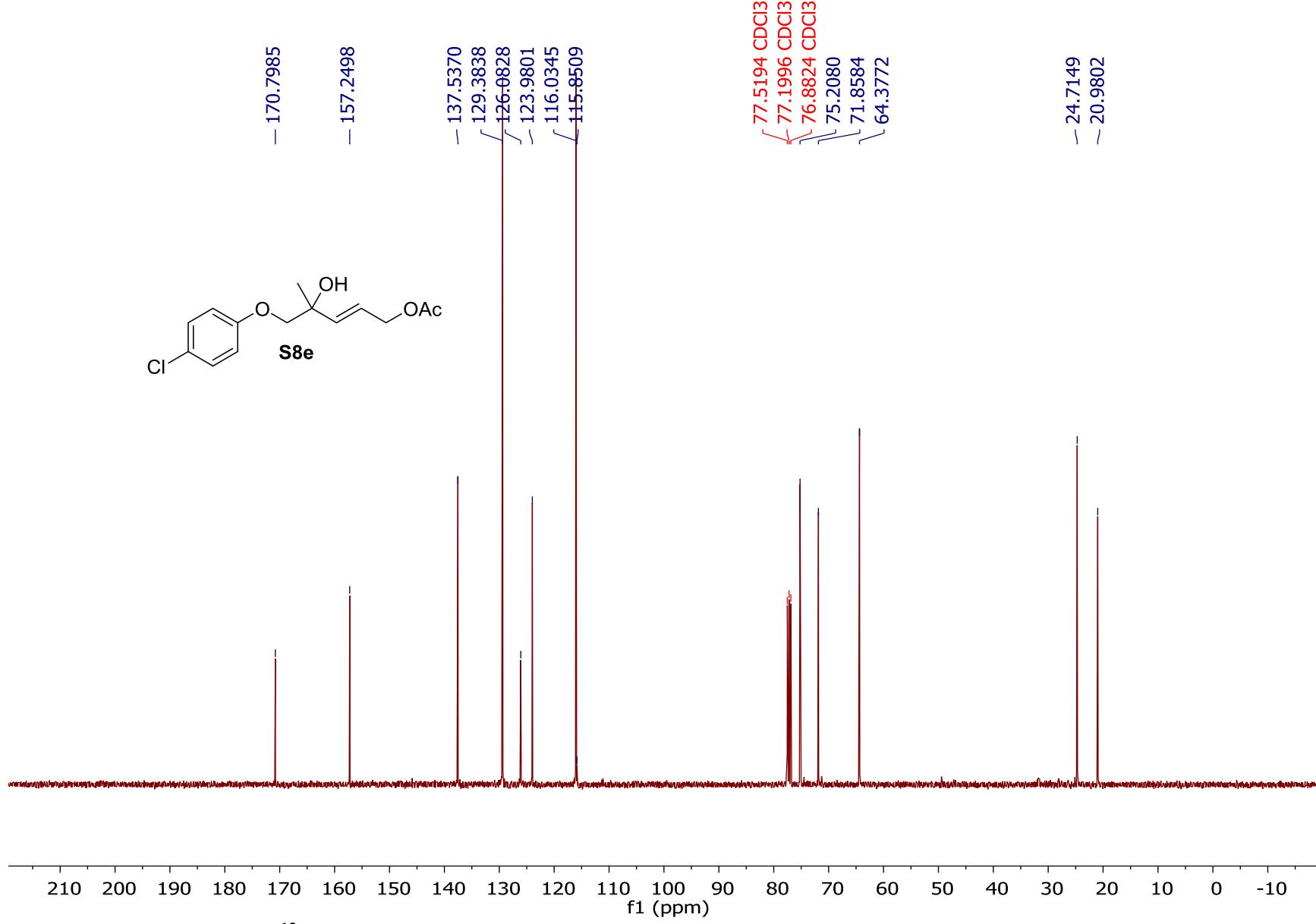


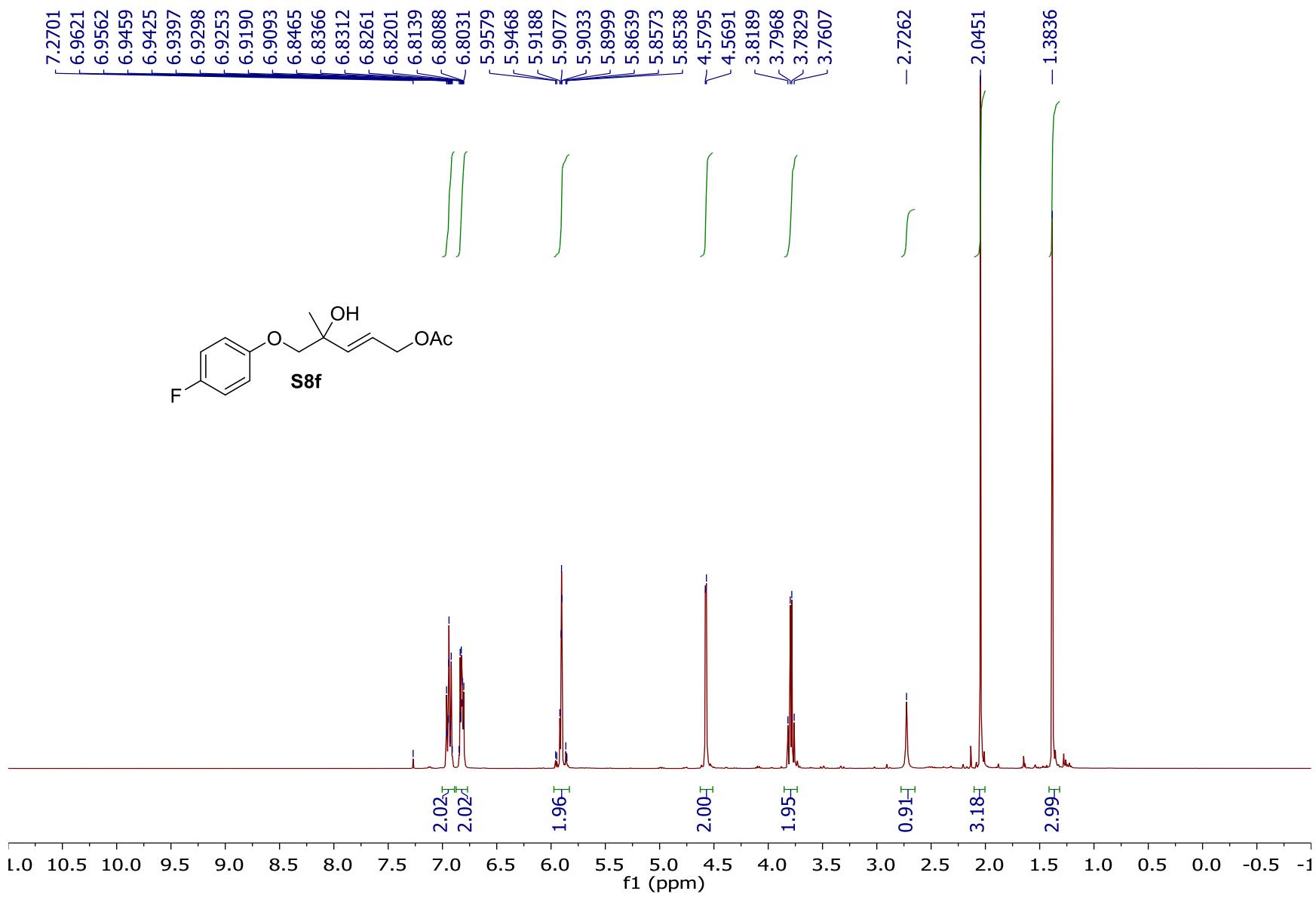


Compound S8d, 101 MHz ^{13}C NMR in CDCl_3

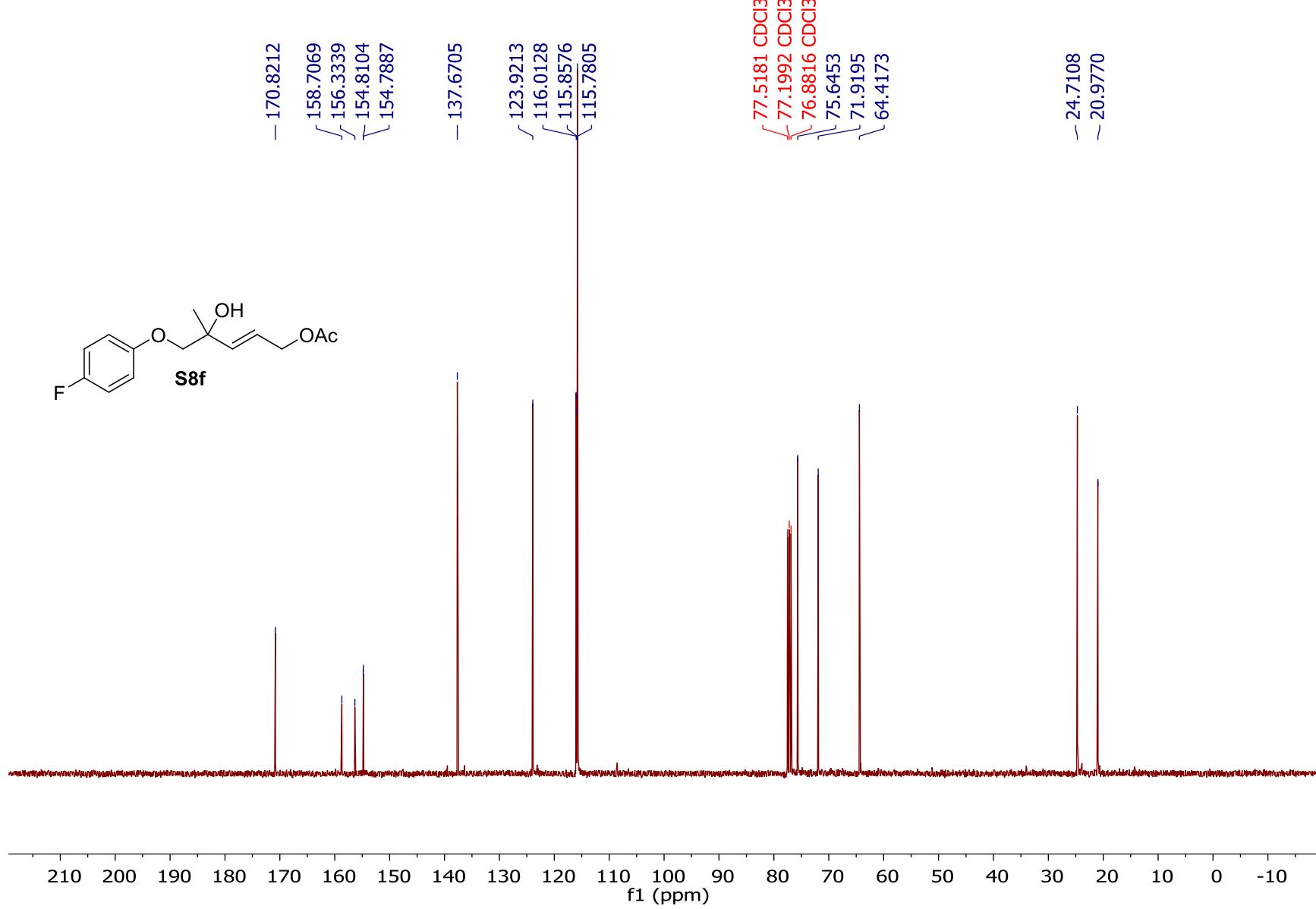


Compound S8e, 400 MHz ^1H NMR in CDCl_3

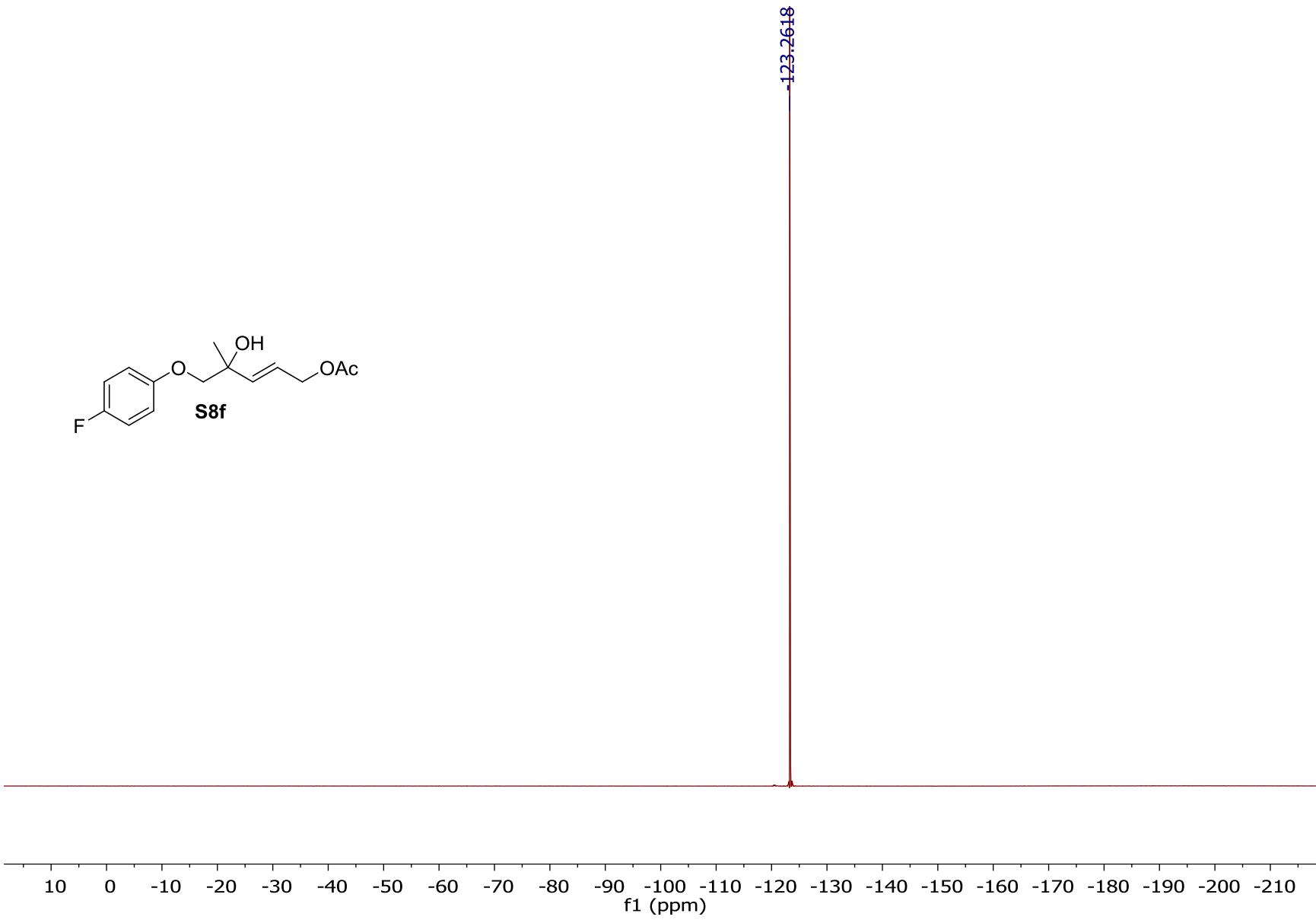
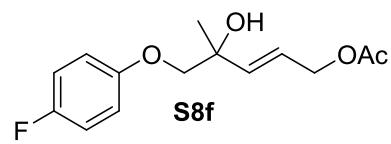




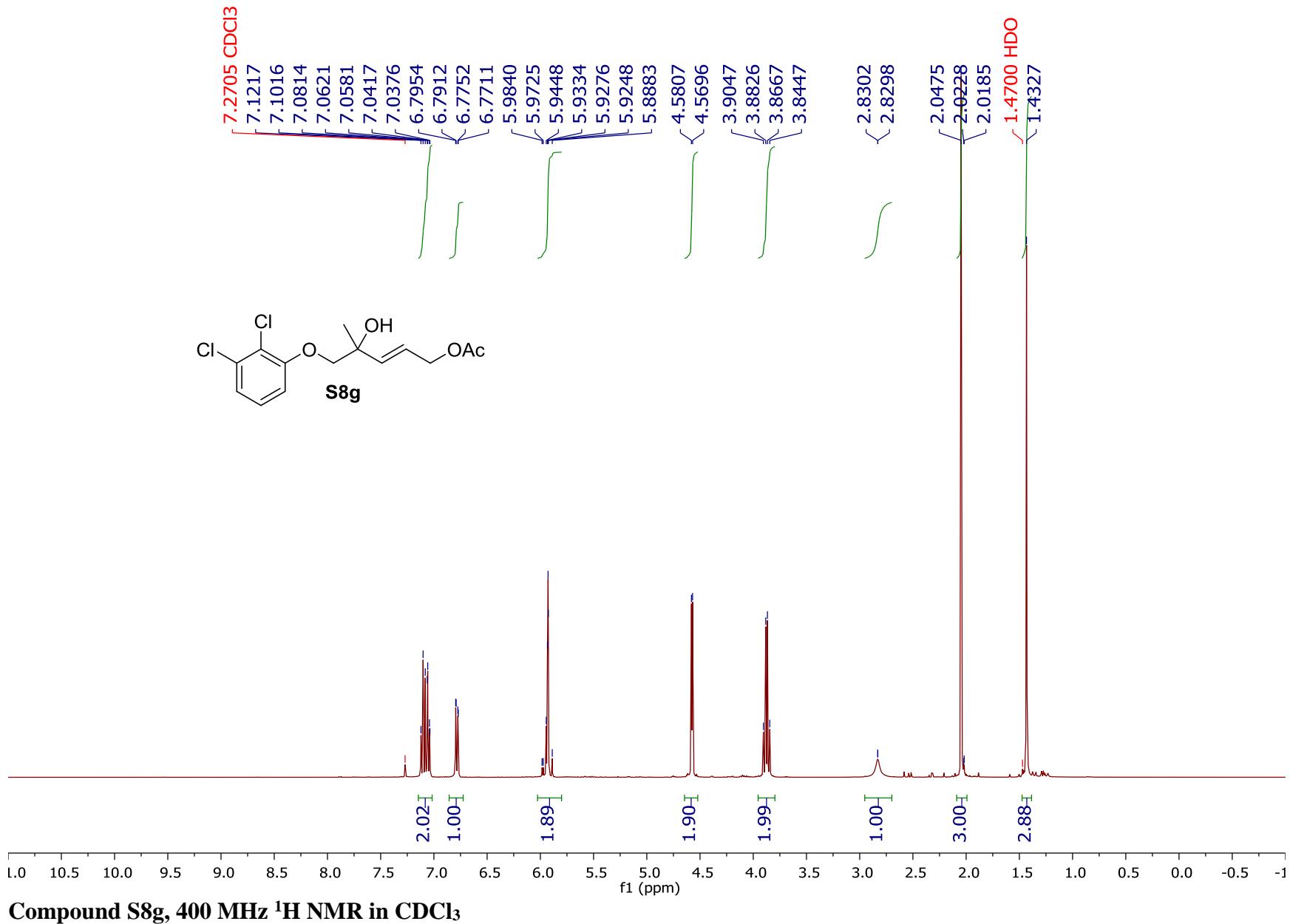
Compound S8f, 400 MHz ^1H NMR in CDCl_3

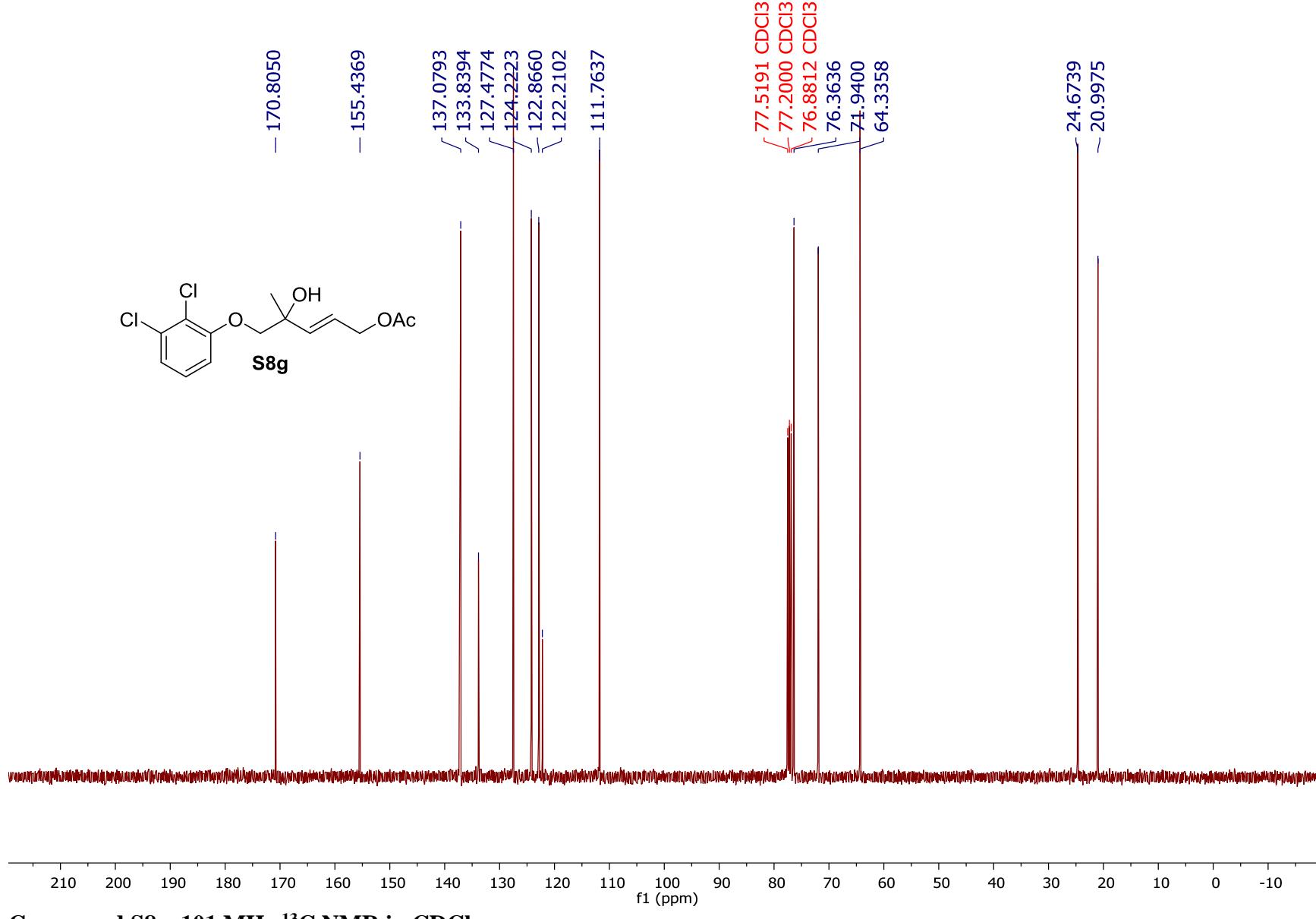


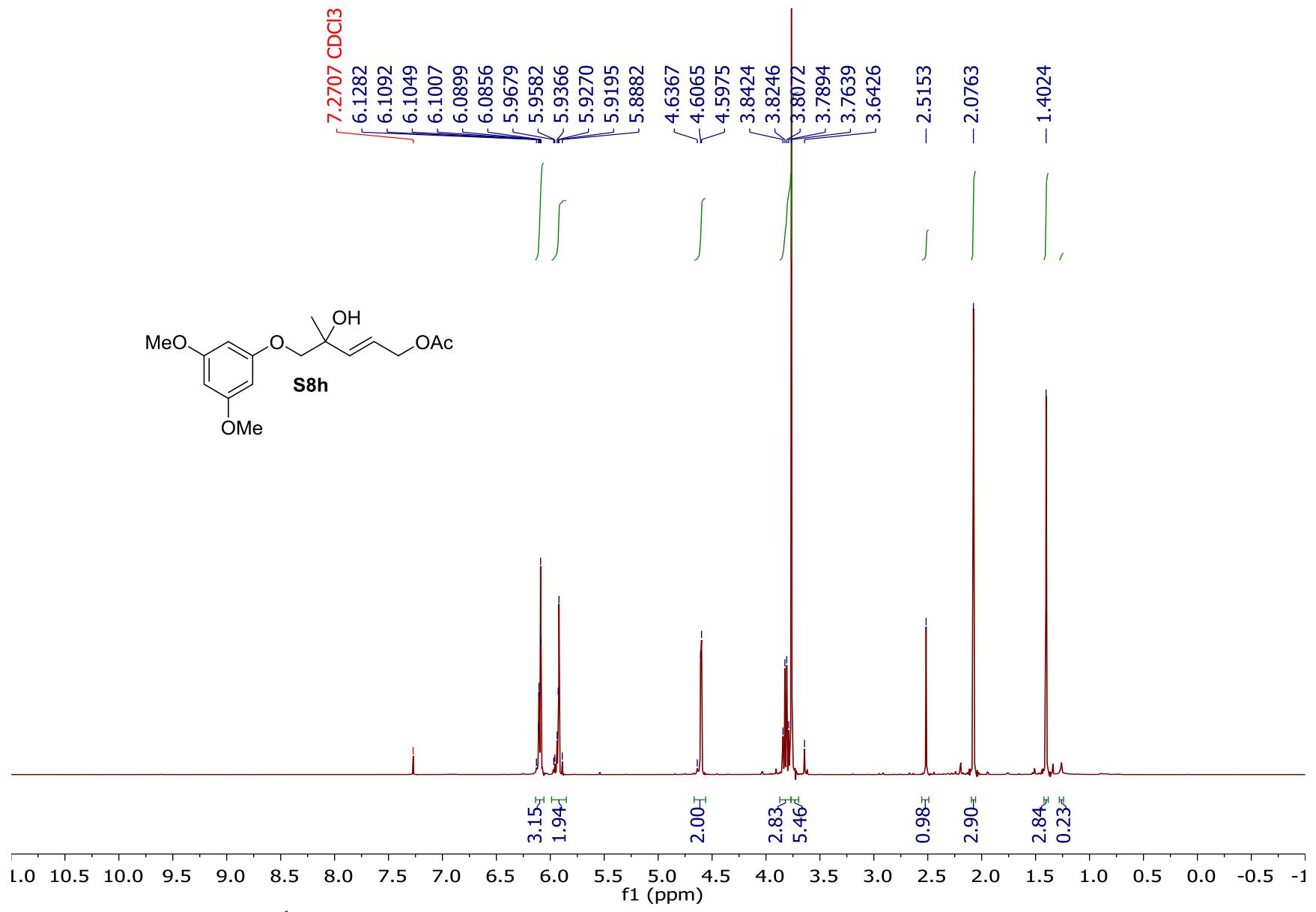
Compound S8f, 101 MHz ^{13}C NMR in CDCl₃



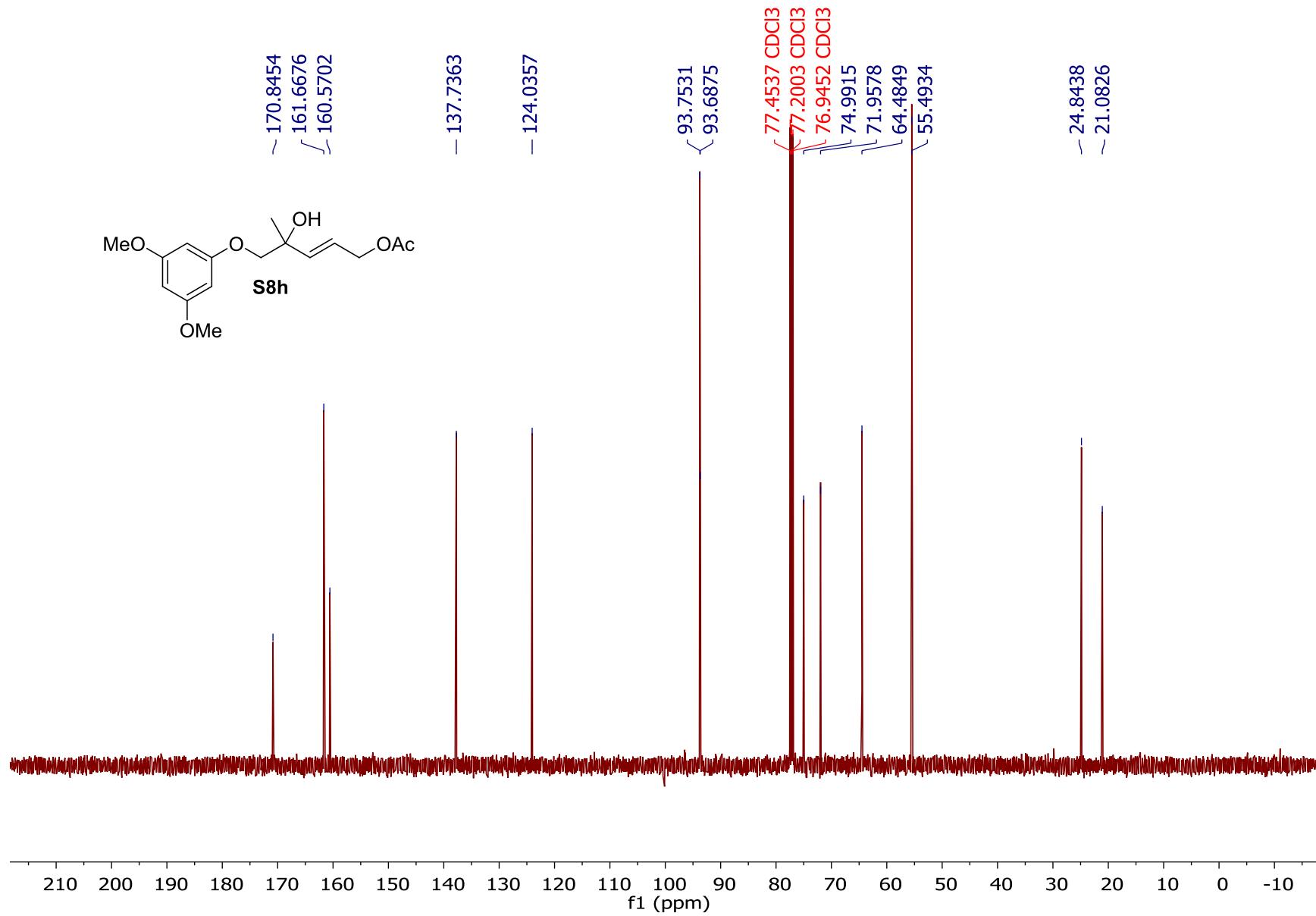
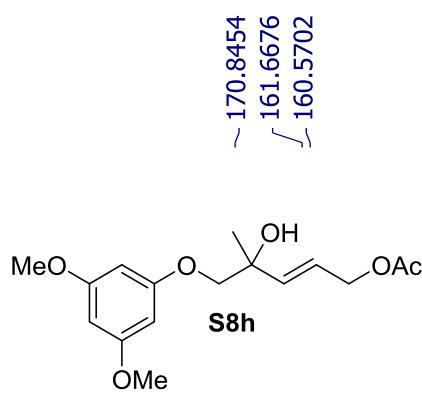
Compound S8f, 376 MHz ¹⁹F NMR in CDCl₃



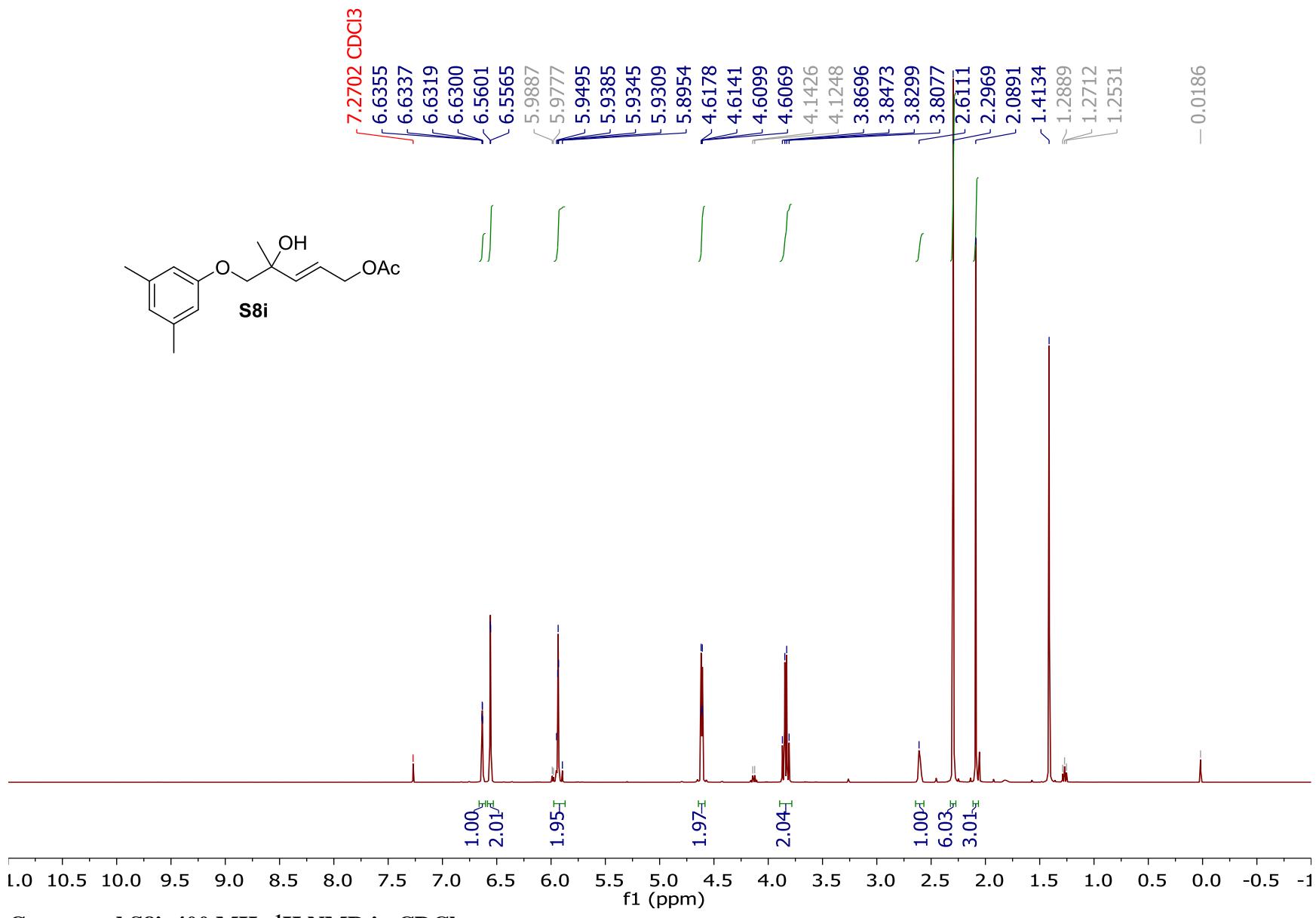




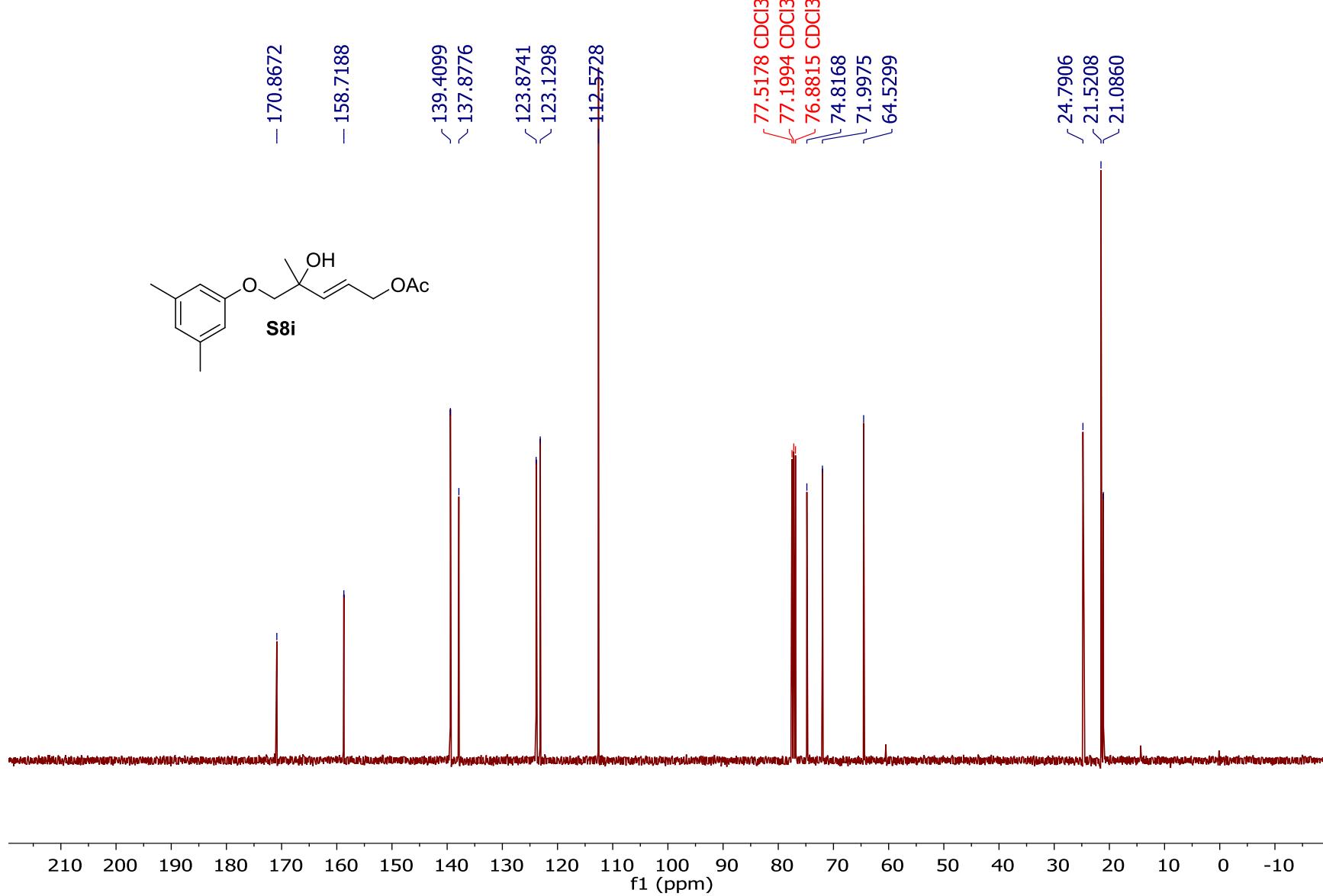
Compound S8h, 400 MHz ^1H NMR in CDCl_3



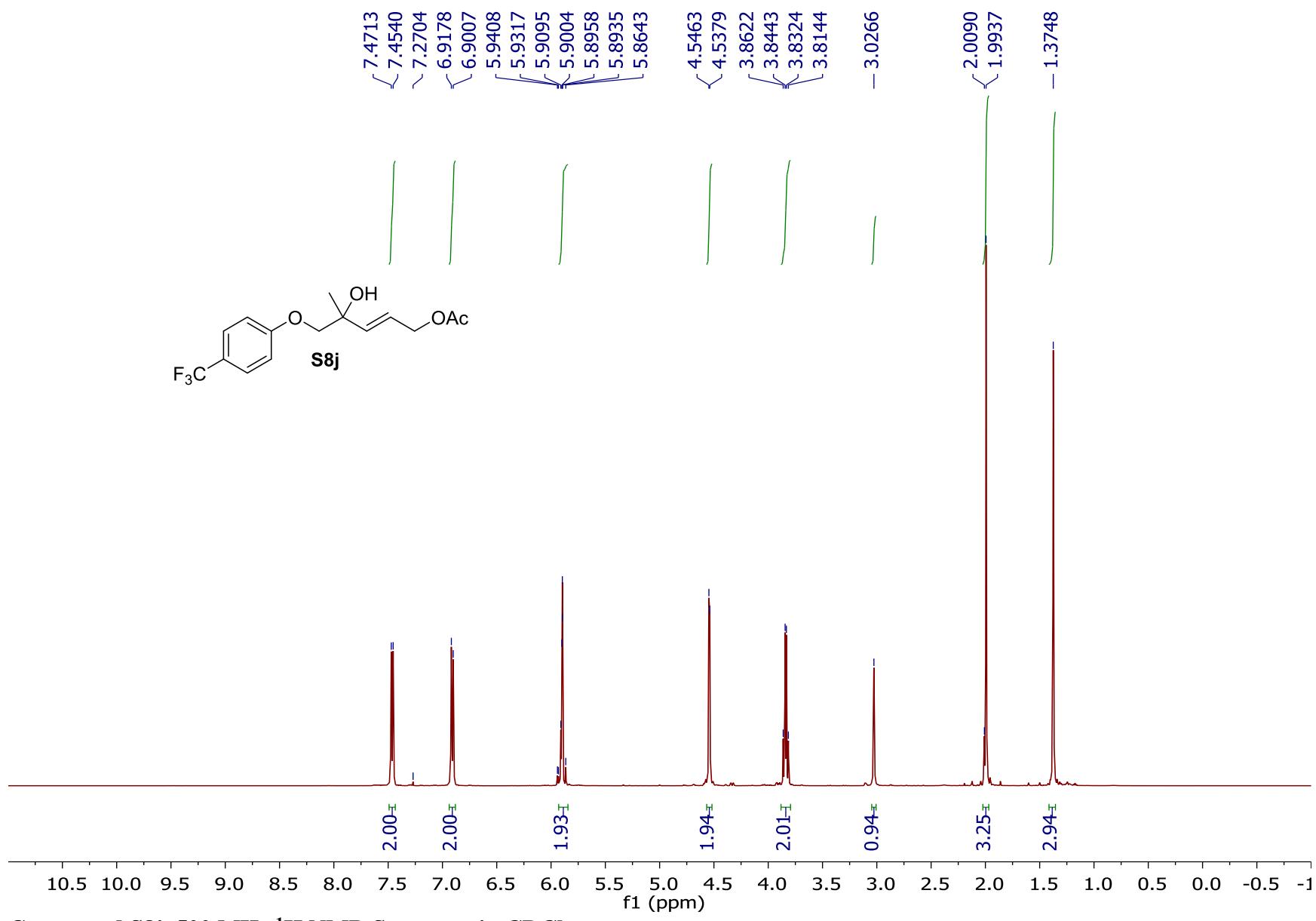
Compound S8h, 101 MHz ^{13}C NMR in CDCl_3



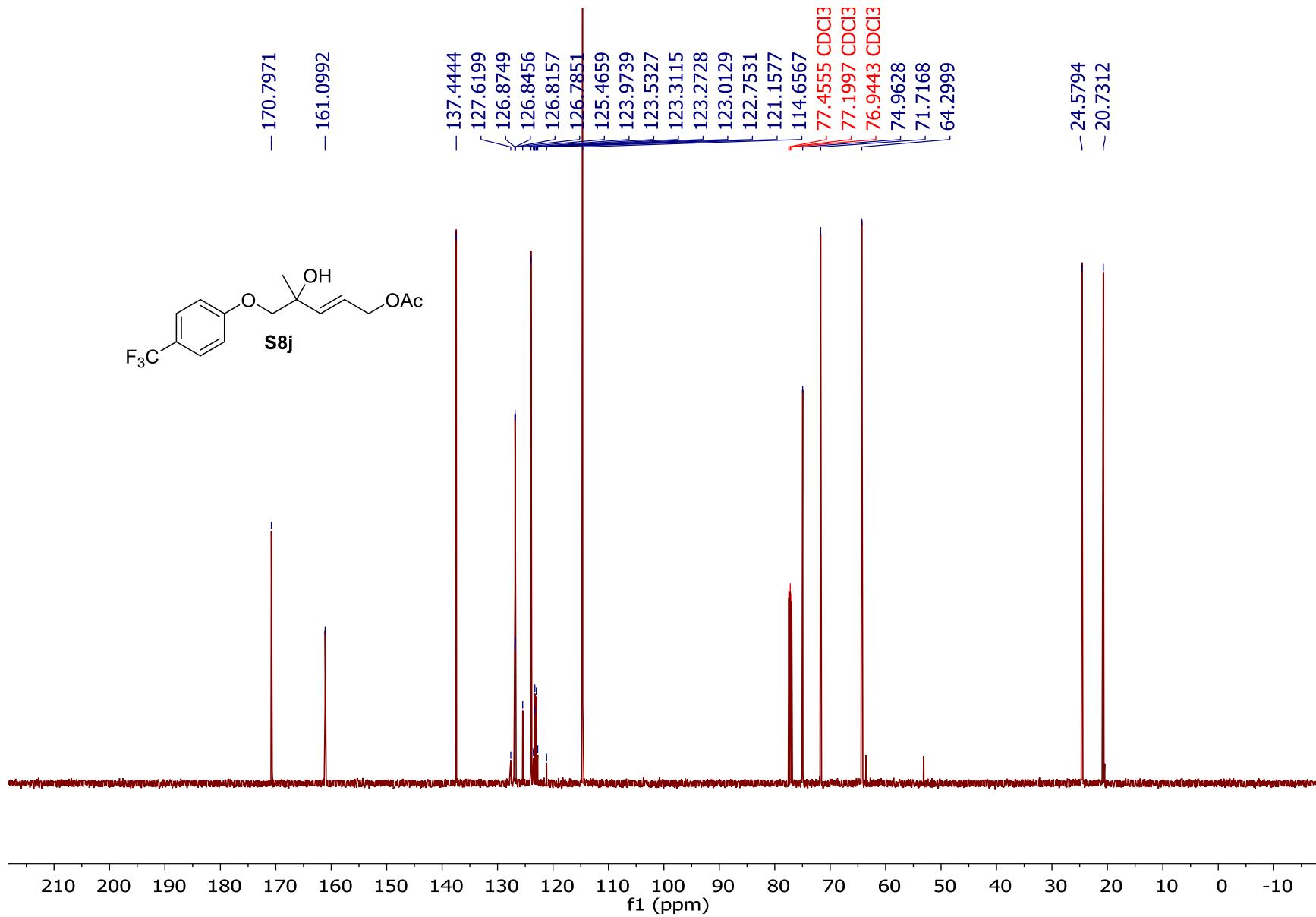
Compound S8i, 400 MHz ^1H NMR in CDCl_3



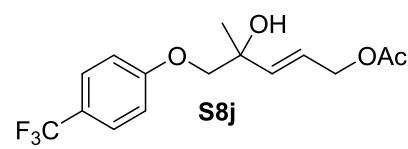
Compound S8i, 101 MHz ¹³C NMR in CDCl₃



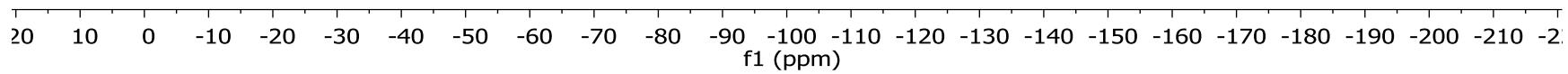
Compound S8j, 500 MHz ^1H NMR Spectrum in CDCl_3



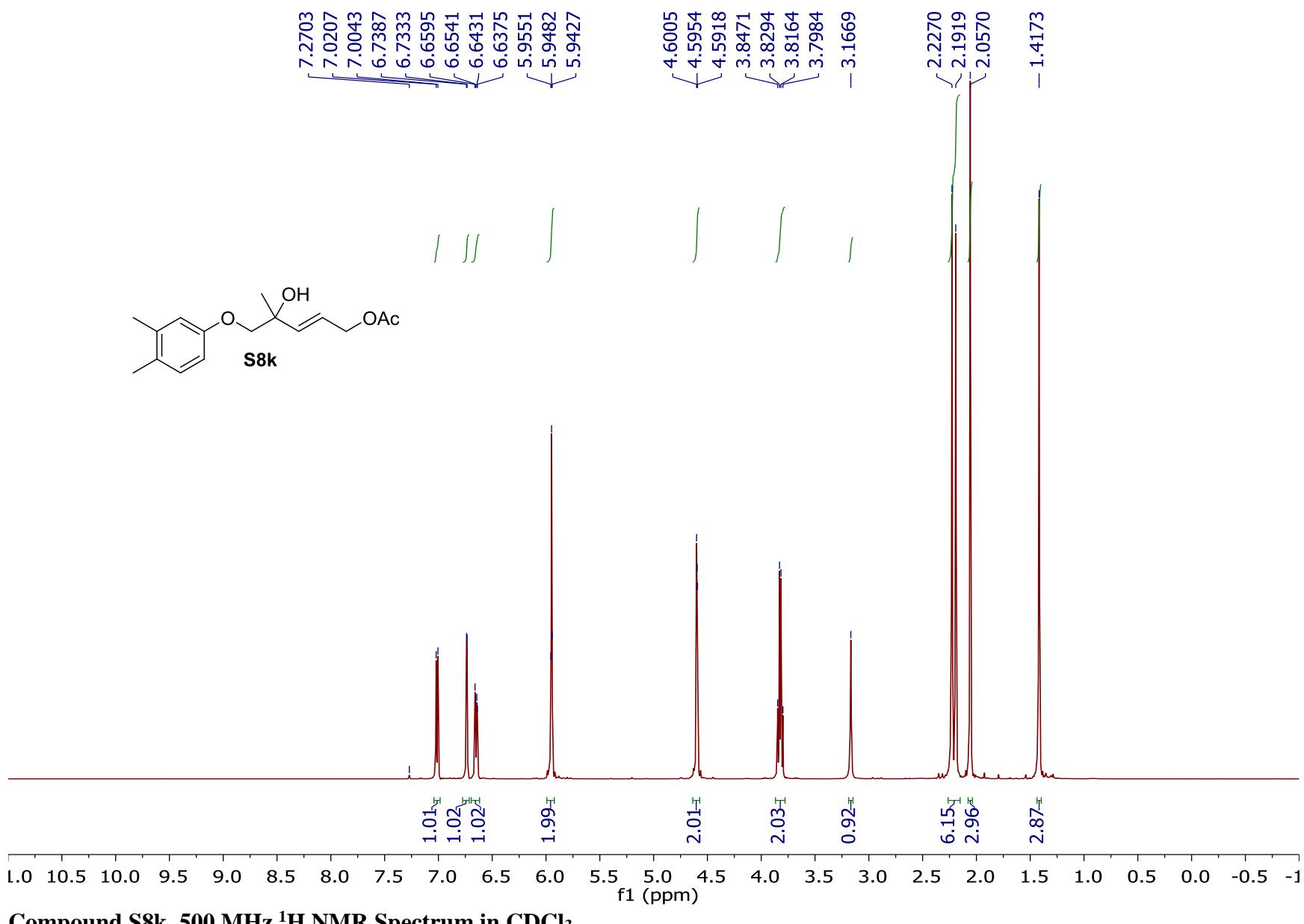
Compound S8j, 126 MHz ¹³C NMR Spectrum in CDCl₃

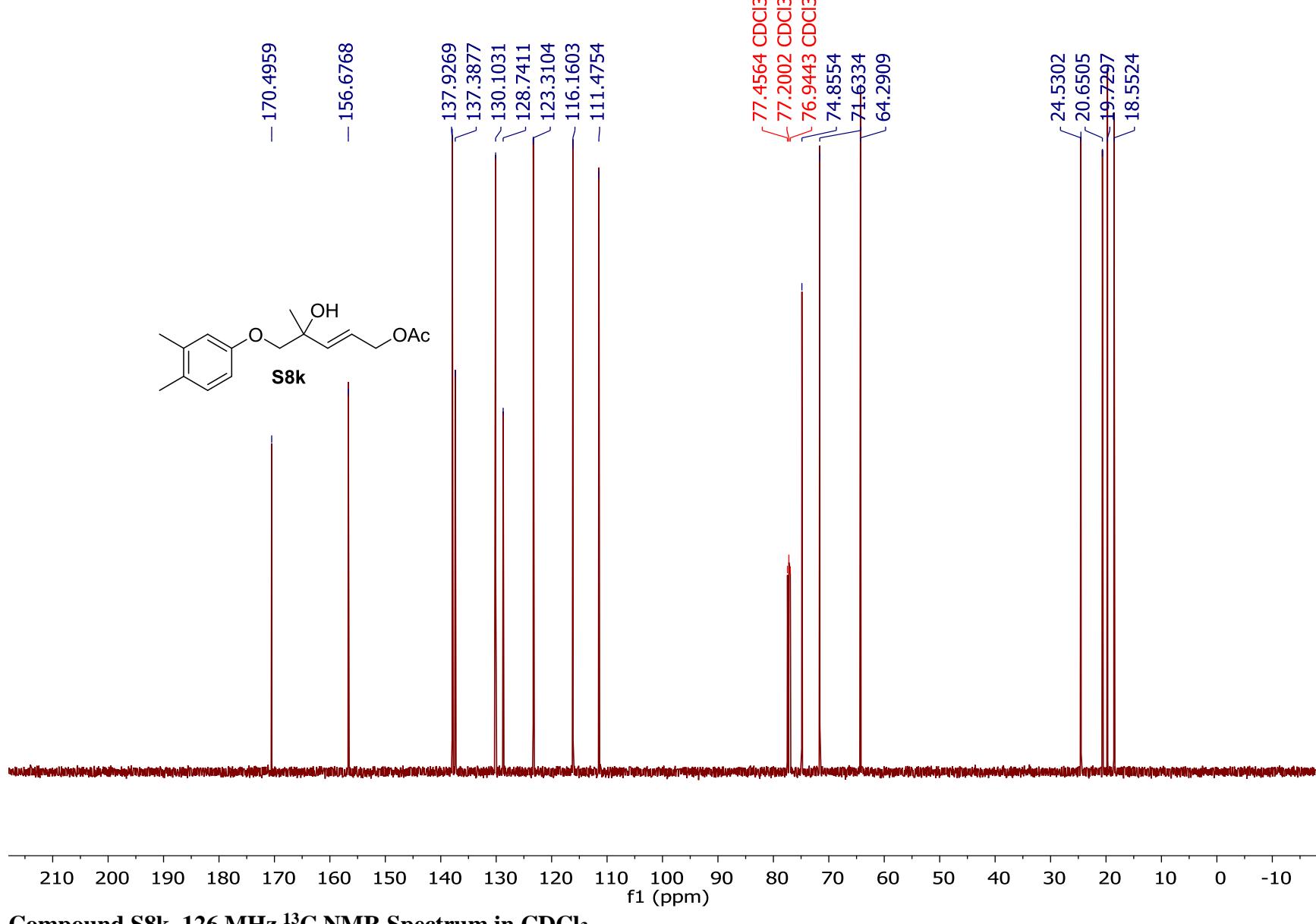


61.4966

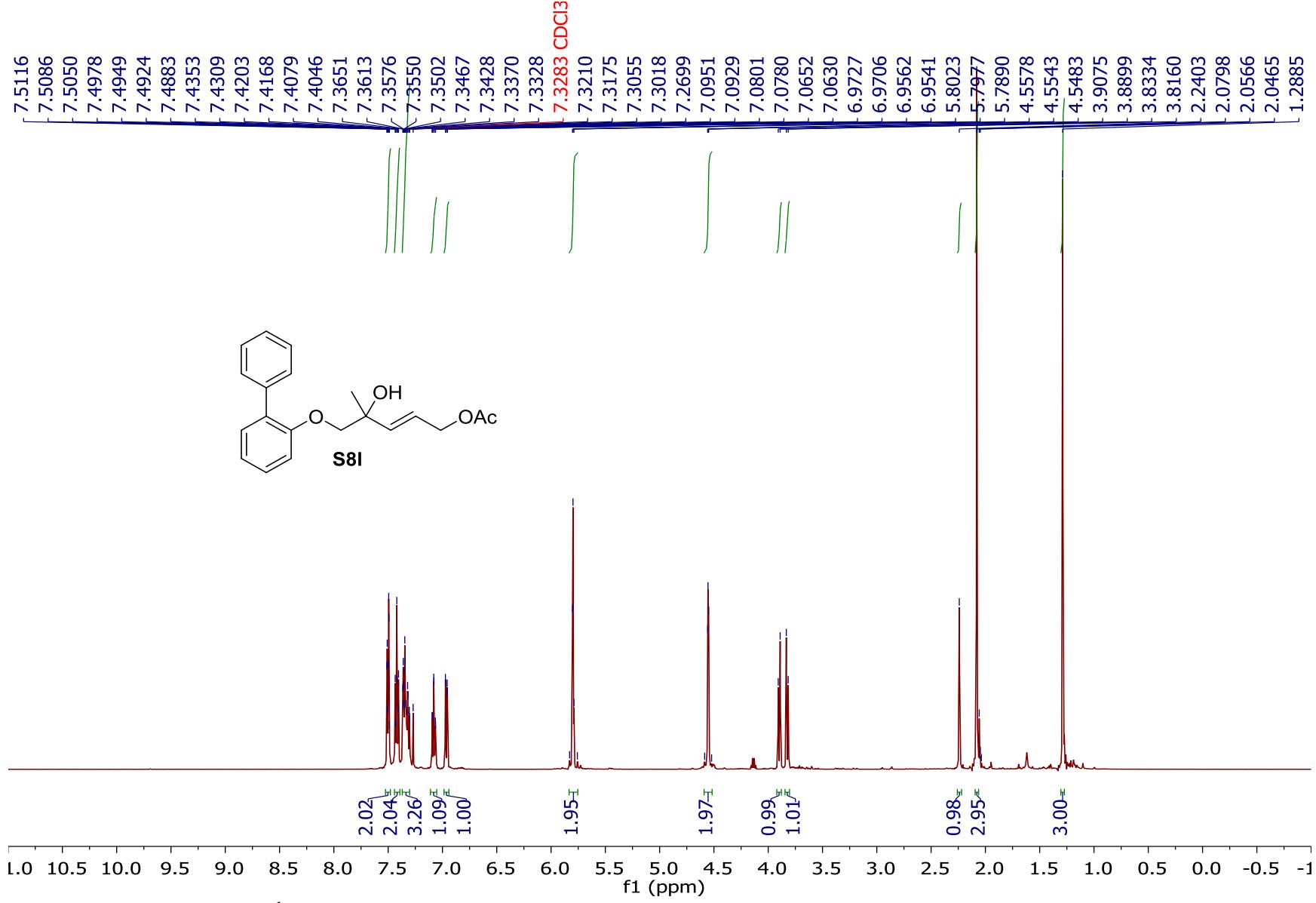


Compound S8j, 471 MHz ^{19}F NMR Spectrum in CDCl_3

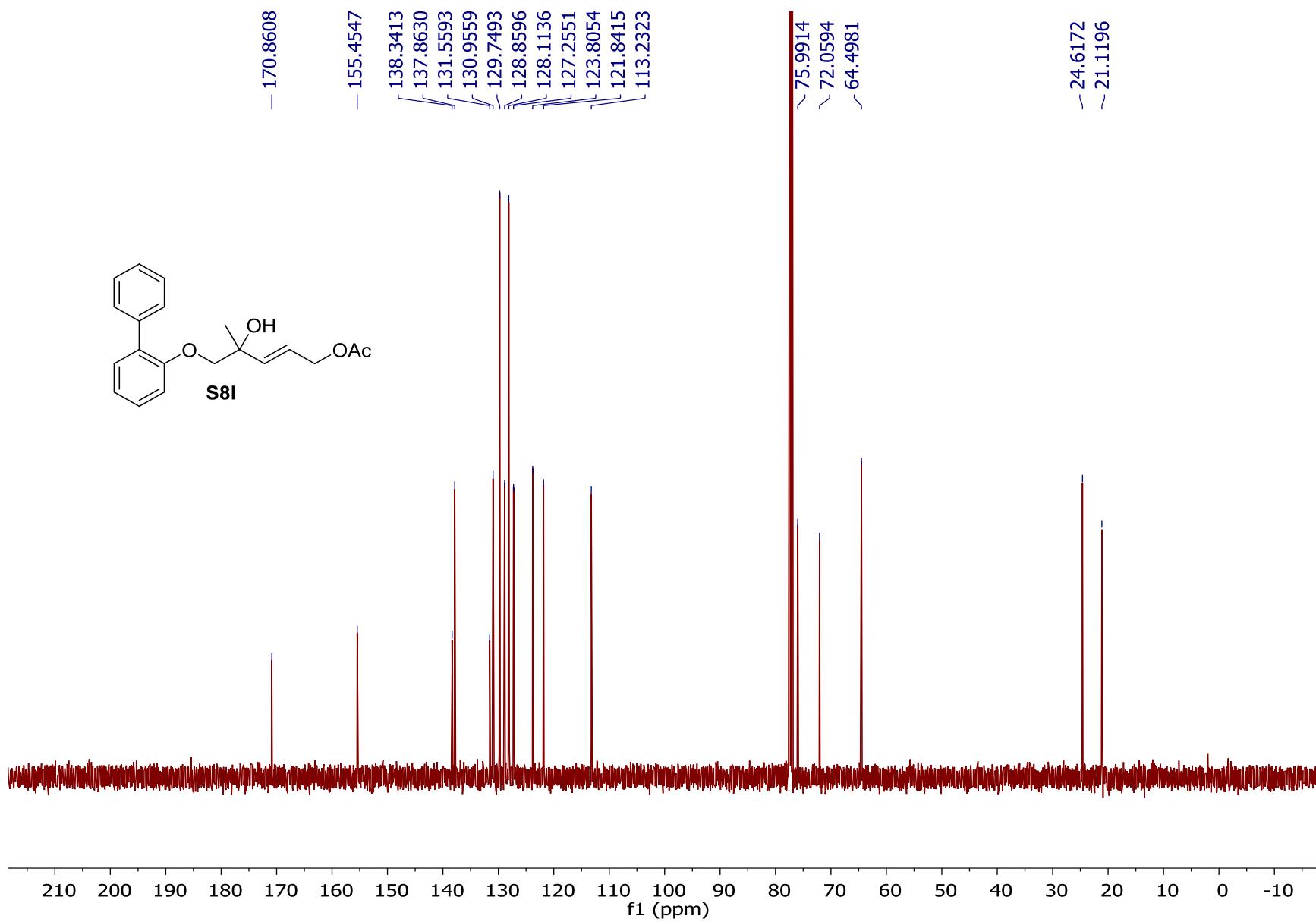




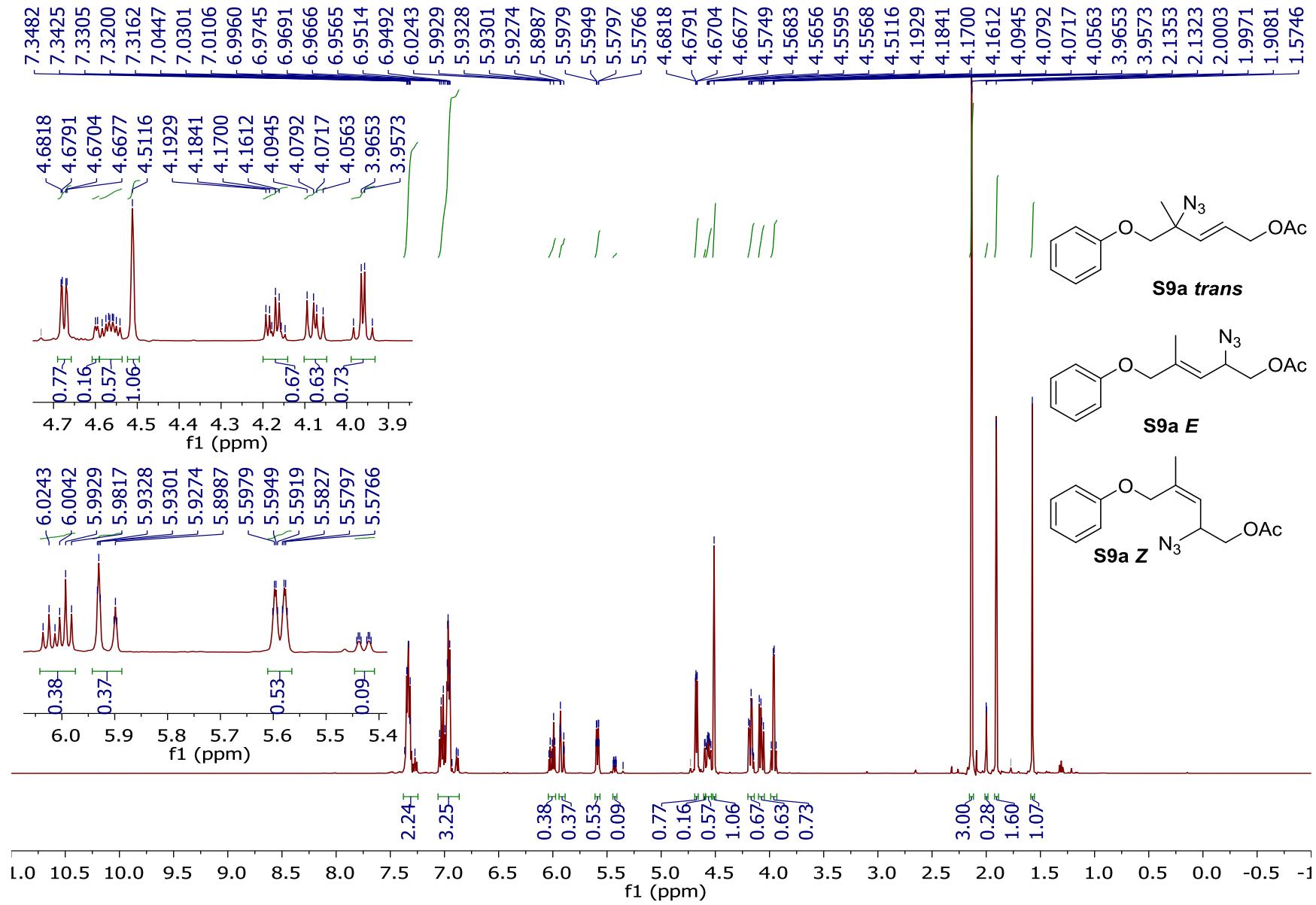
Compound S8k, 126 MHz ¹³C NMR Spectrum in CDCl₃



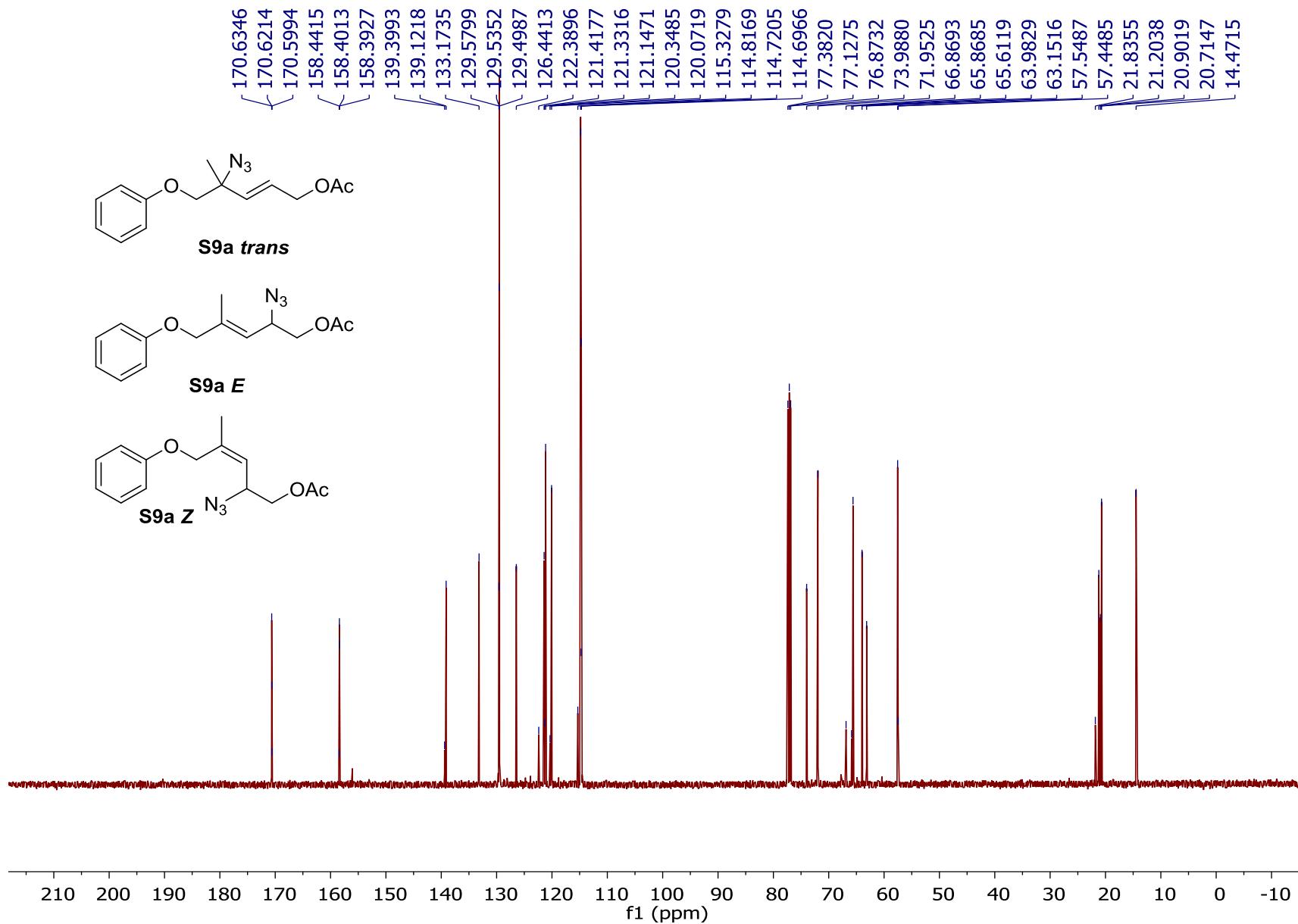
Compound S8l, 500 MHz ^1H NMR Spectrum in CDCl_3



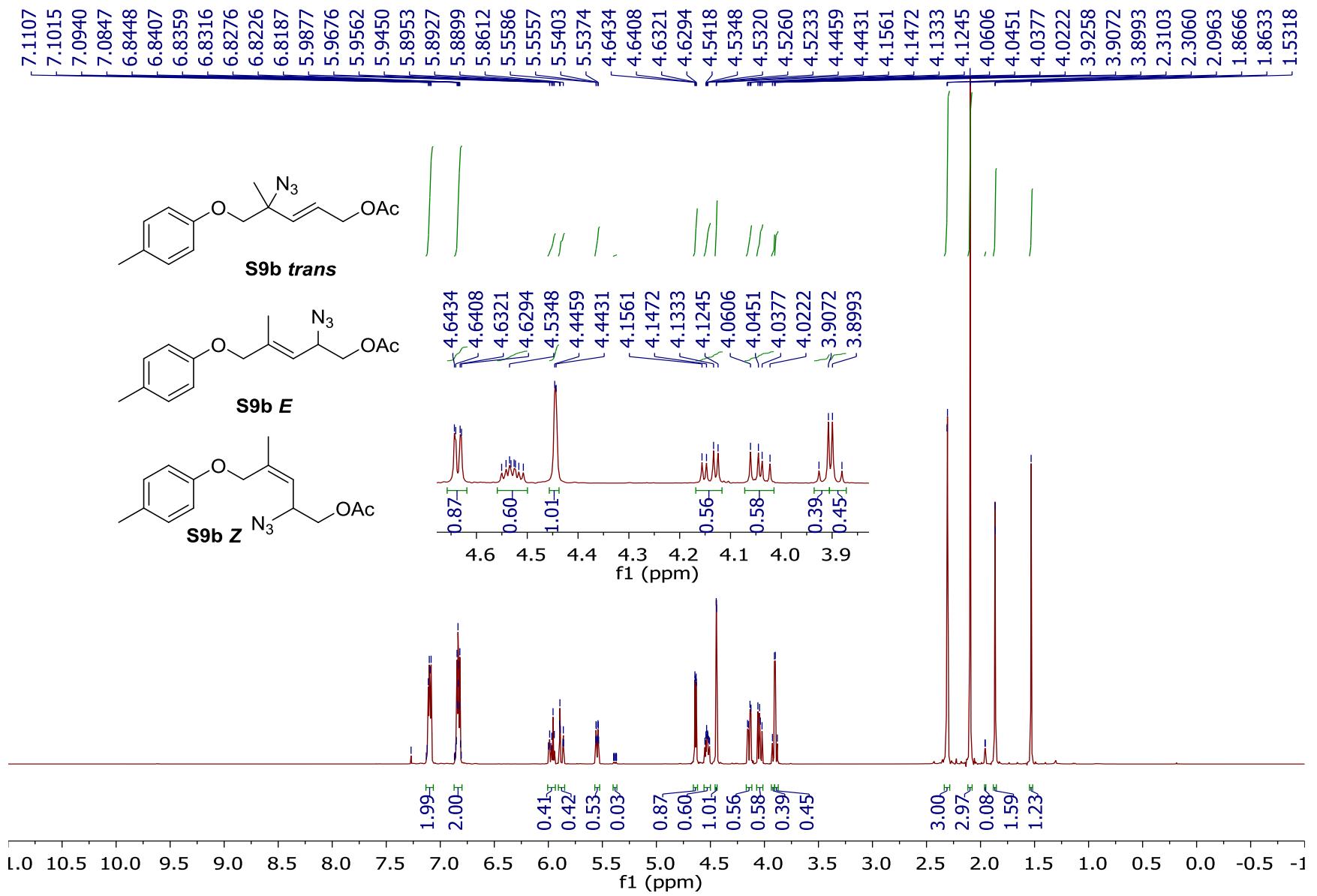
Compound S8l, 126 MHz ^{13}C NMR Spectrum in CDCl_3



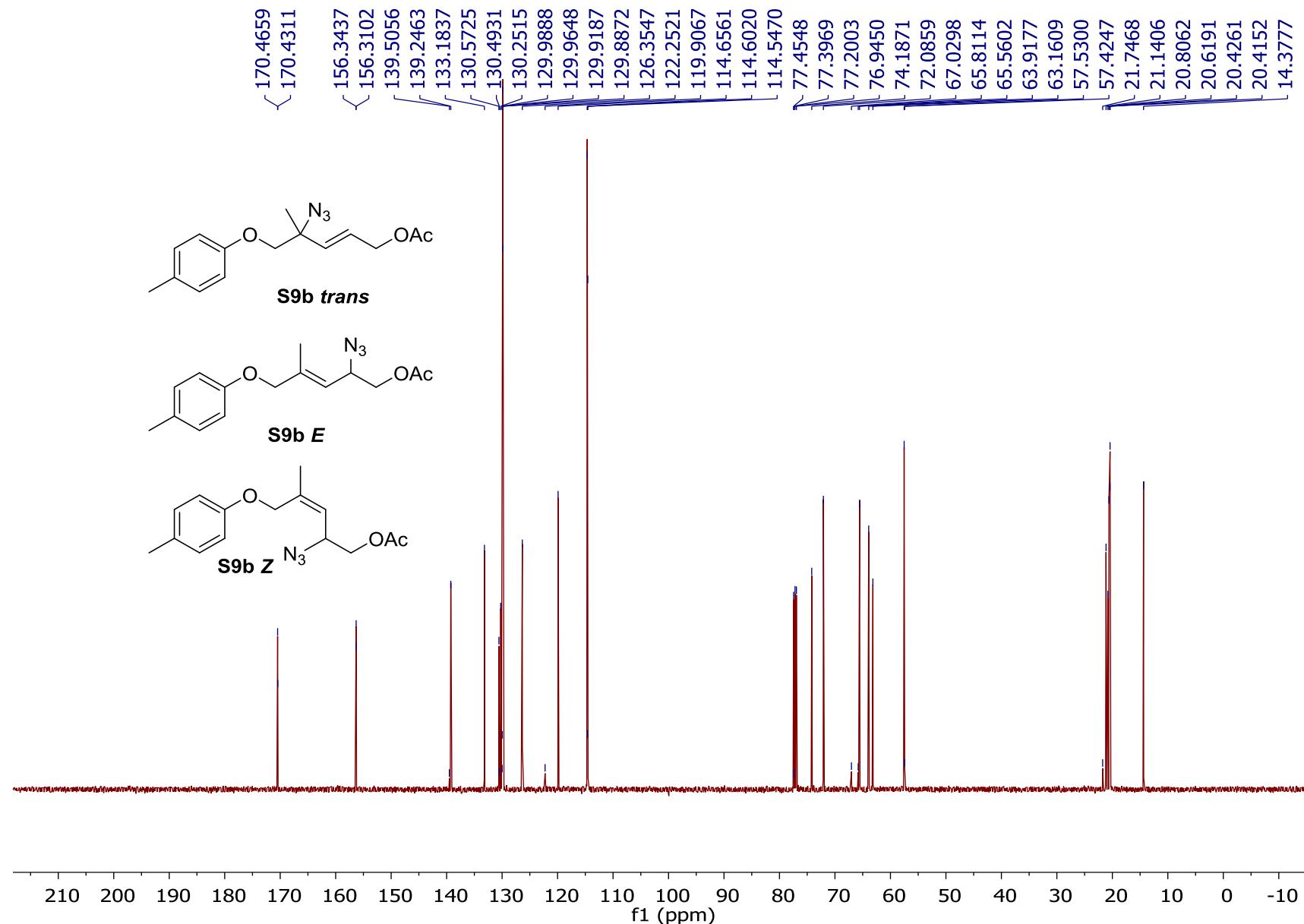
Compound S9a, 500 MHz ^1H NMR in CDCl_3



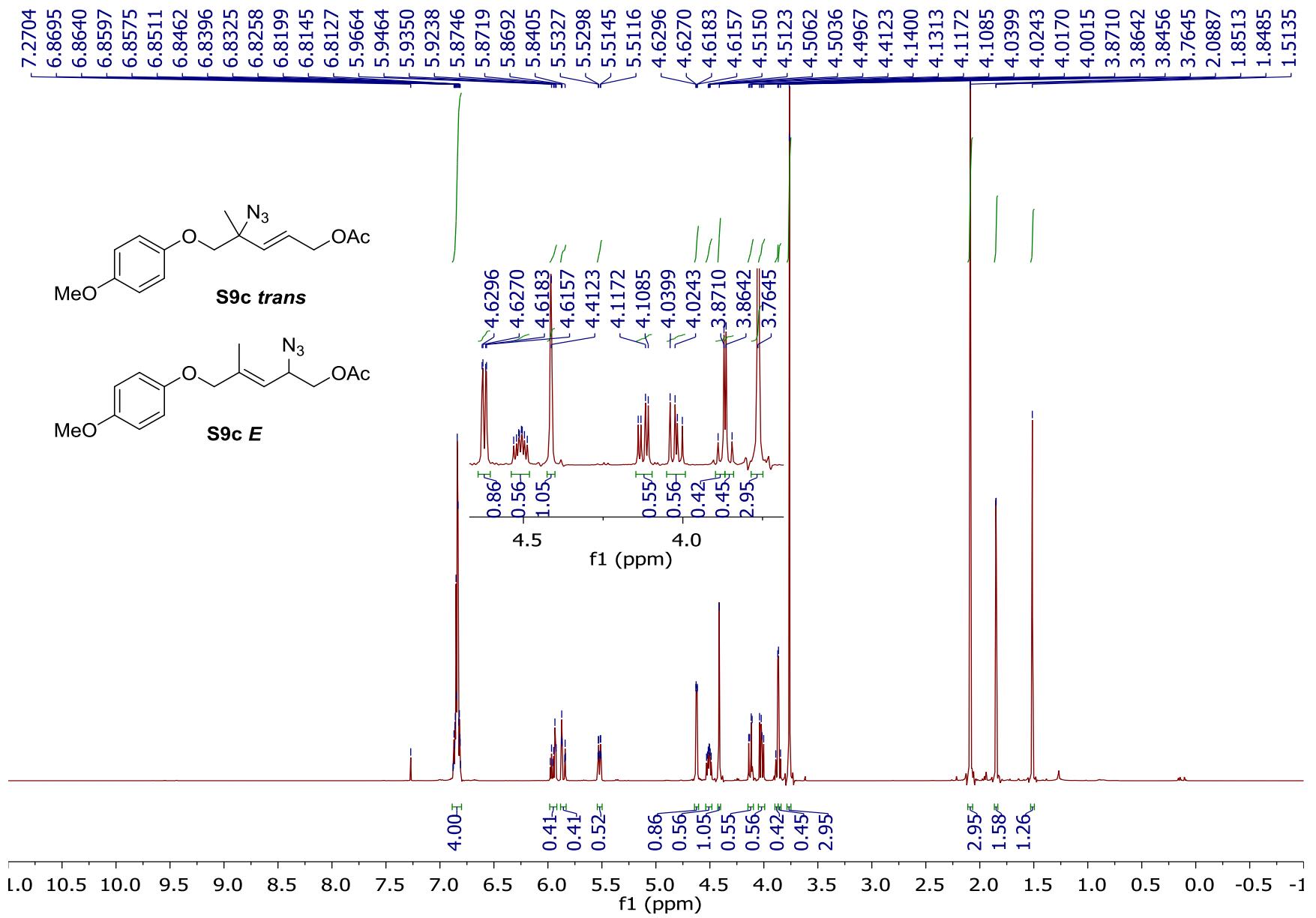
Compound S9a, 101 MHz ^{13}C NMR in CDCl_3



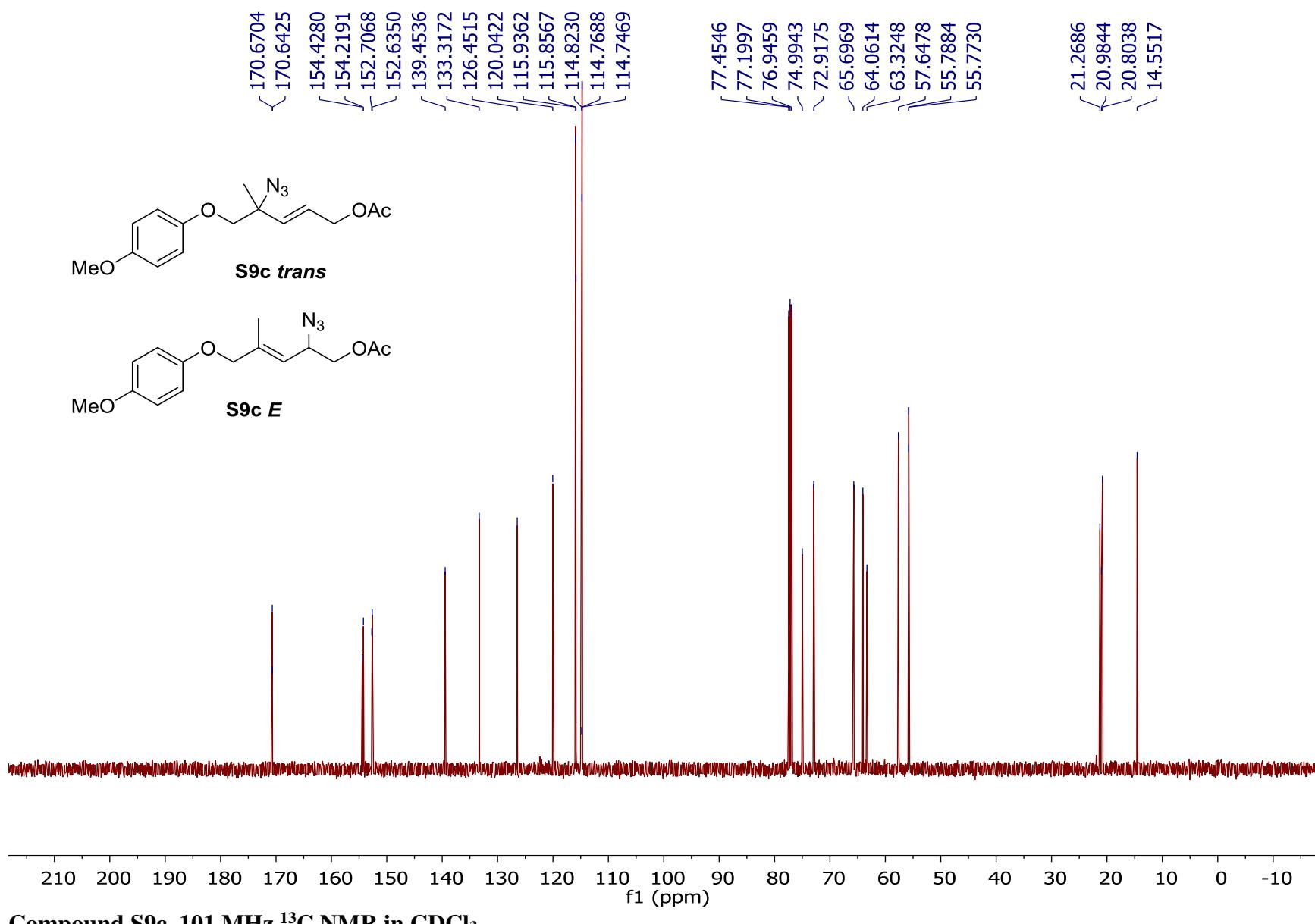
Compound S9b, 400 MHz ^1H NMR in CDCl_3



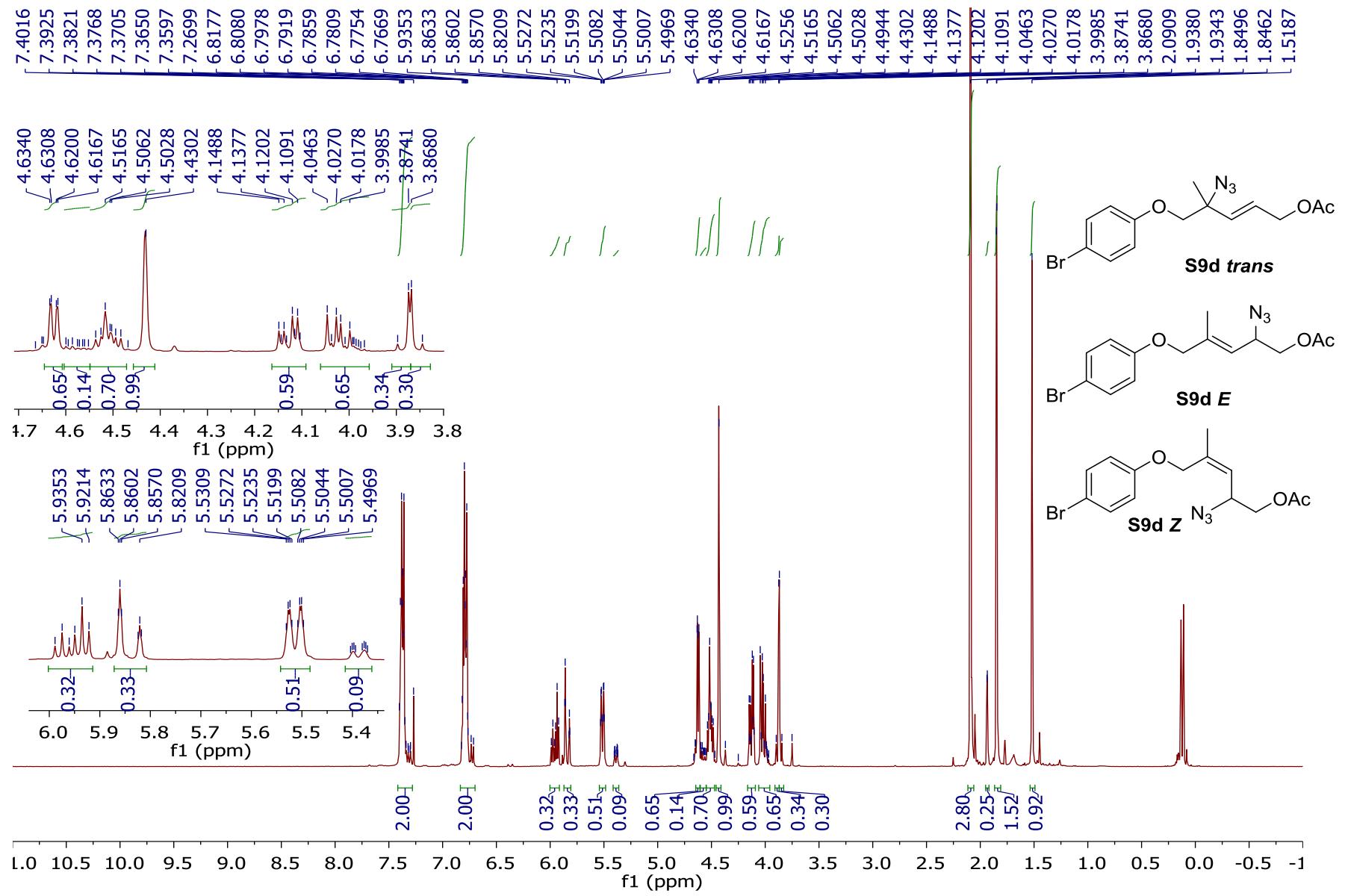
Compound S9b, 101 MHz ^{13}C NMR in CDCl_3

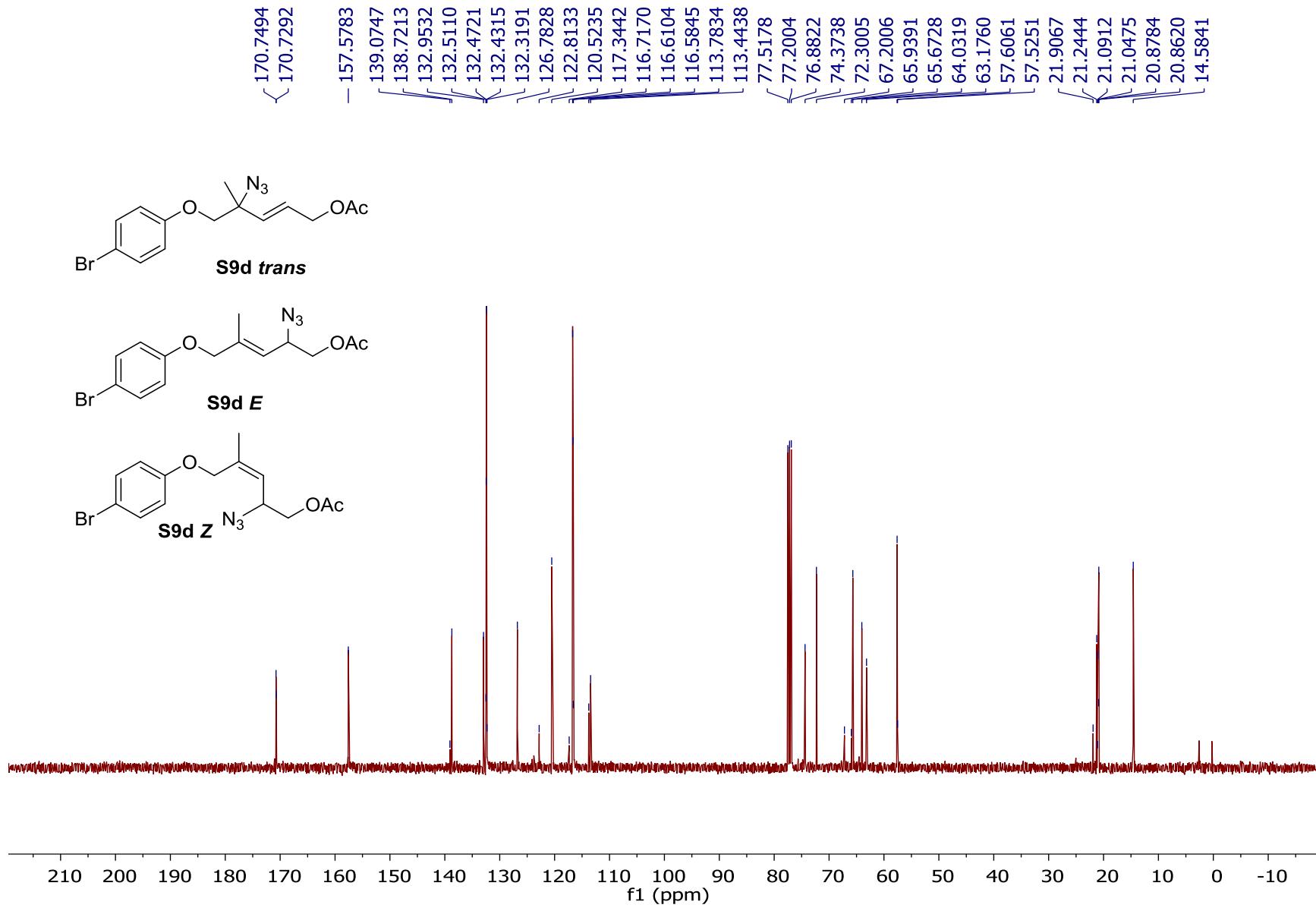


Compound S9c, 400 MHz ^1H NMR in CDCl_3

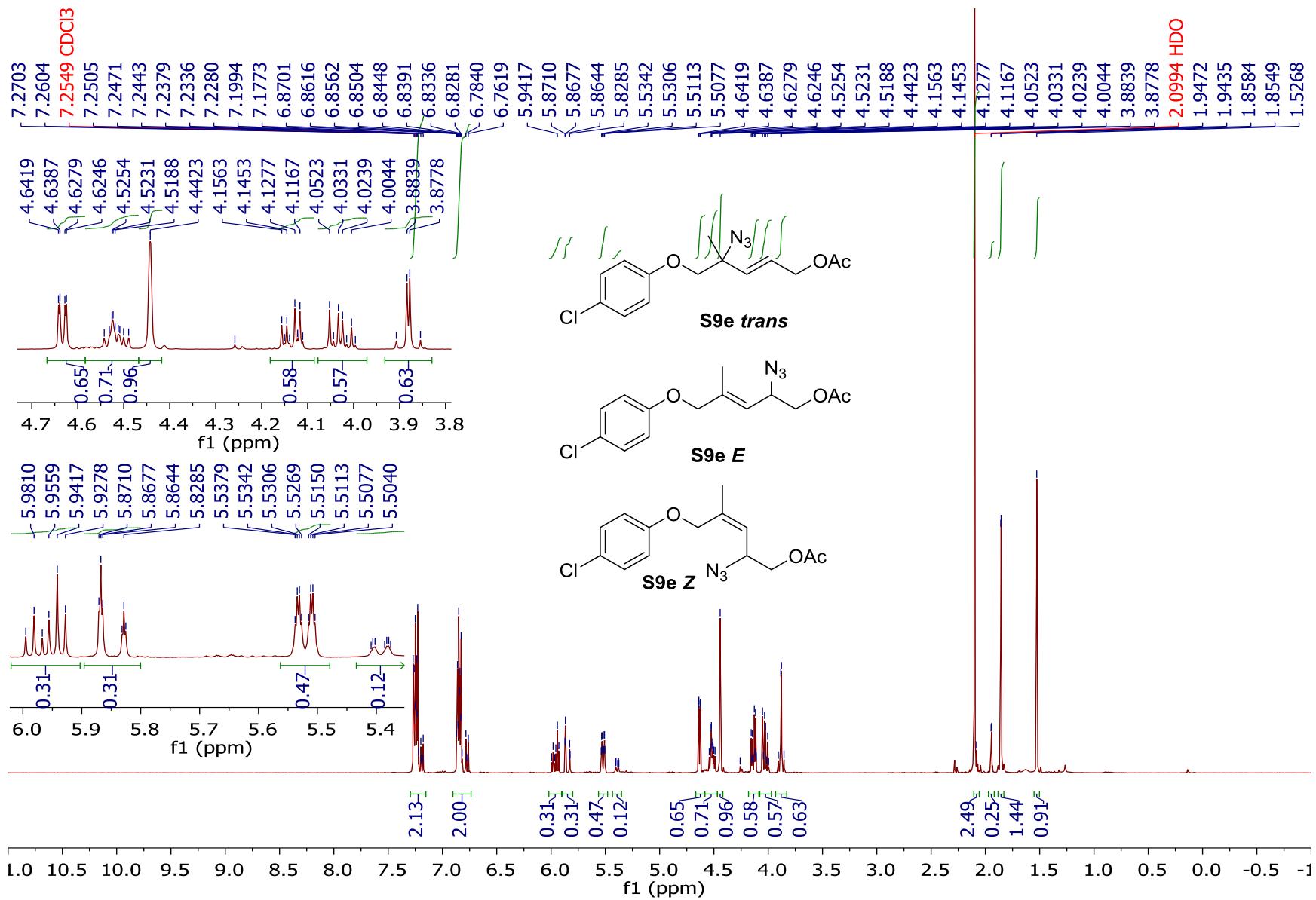


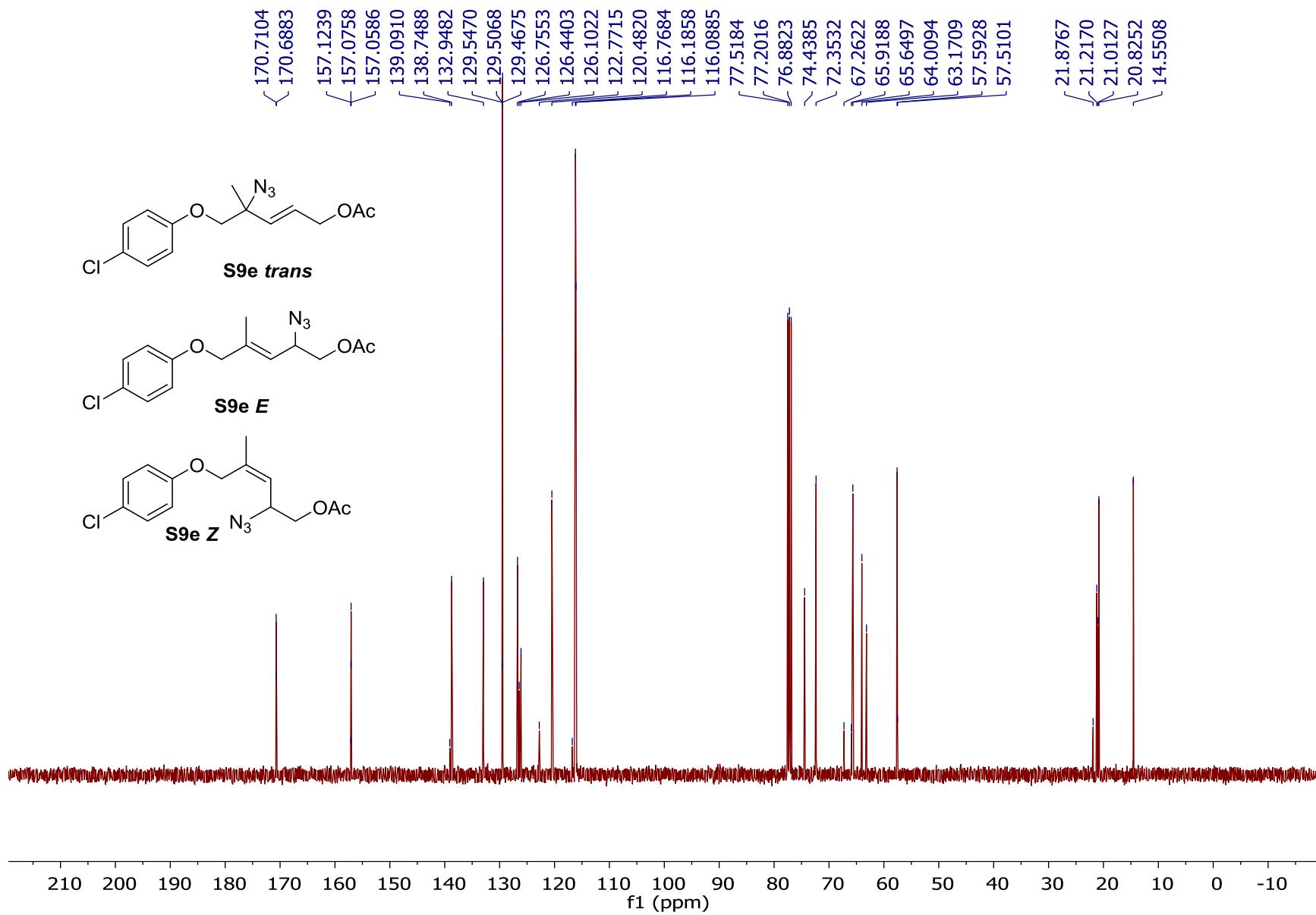
Compound **S9c**, 101 MHz ^{13}C NMR in CDCl_3



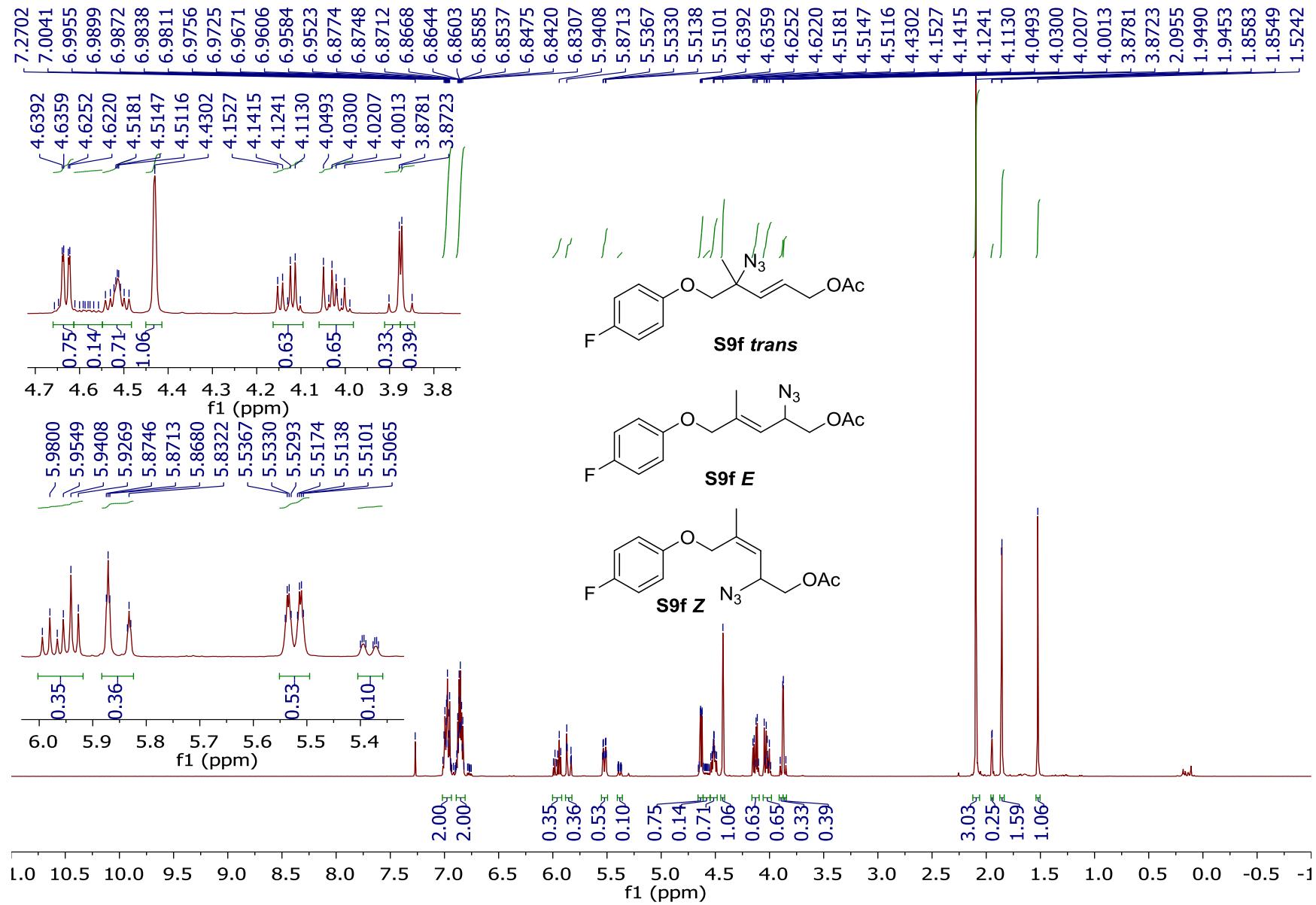


Compound S9d, 101 MHz ^{13}C NMR in CDCl_3

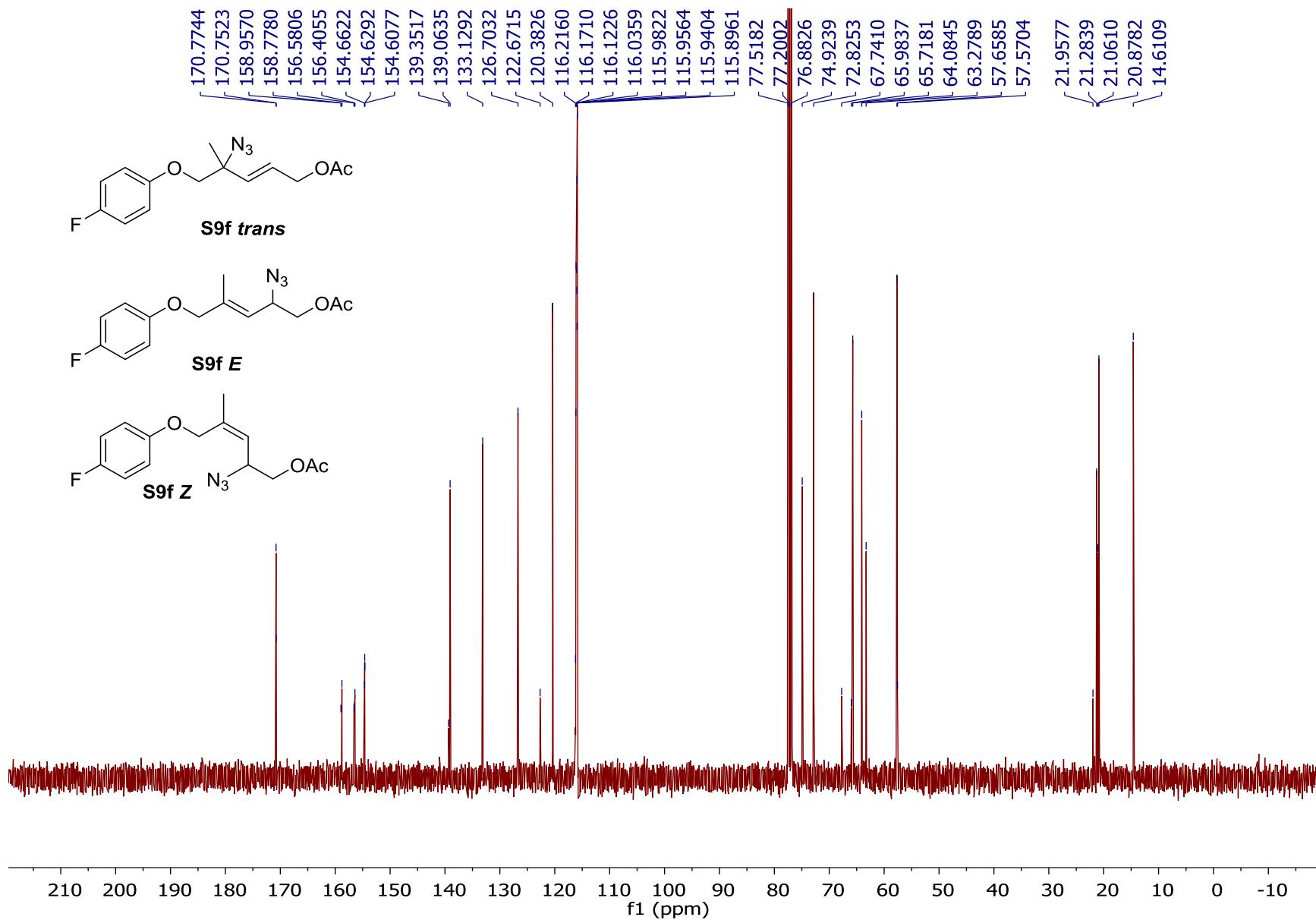




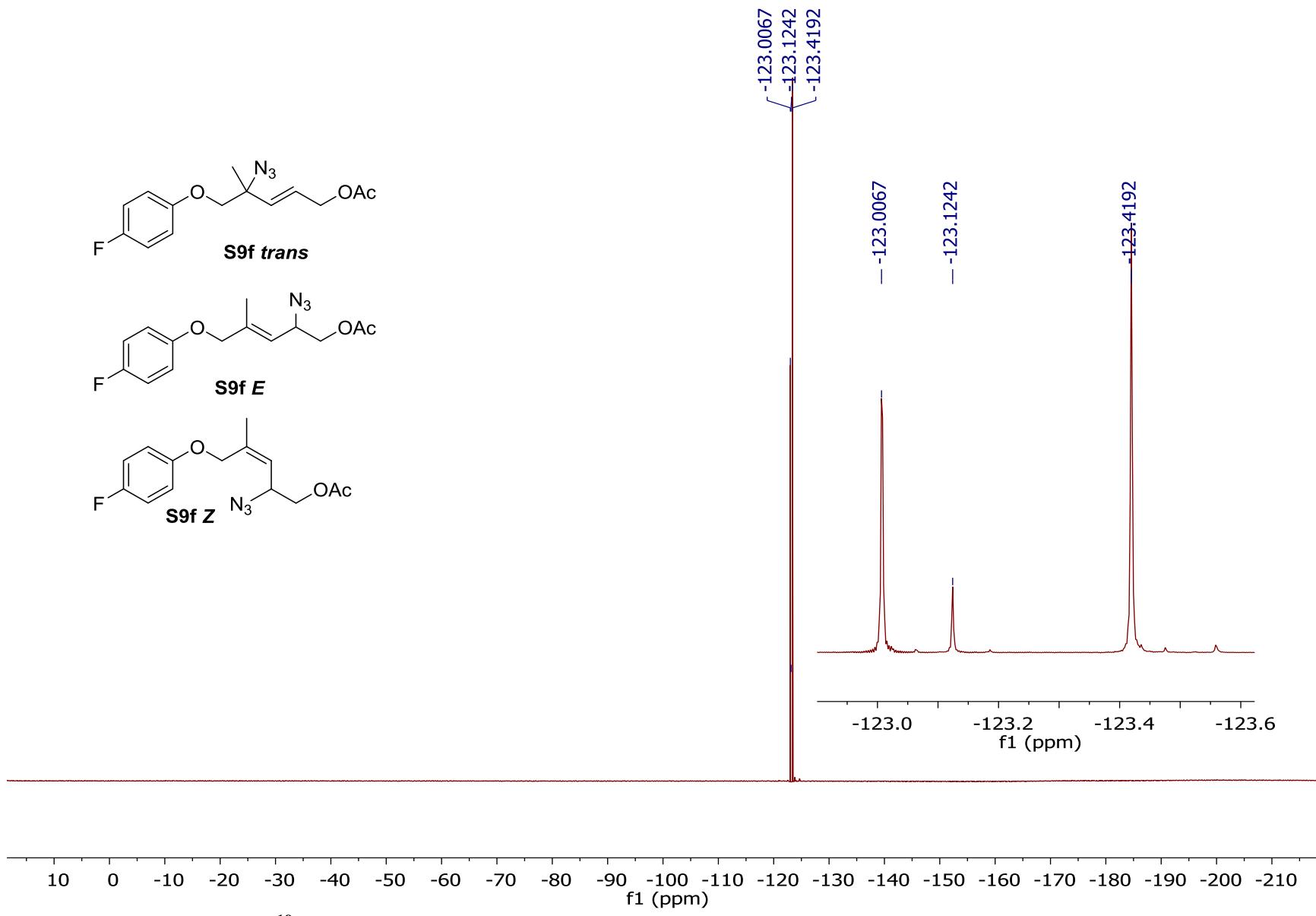
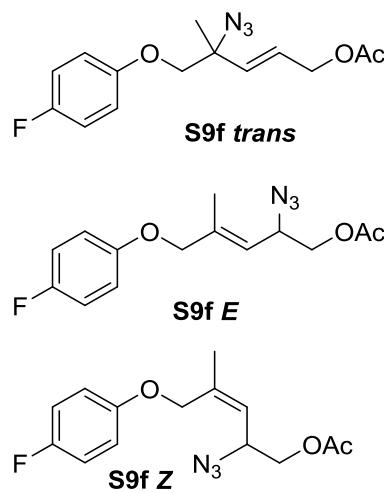
Compound S9e, 101 MHz ¹³C NMR in CDCl₃



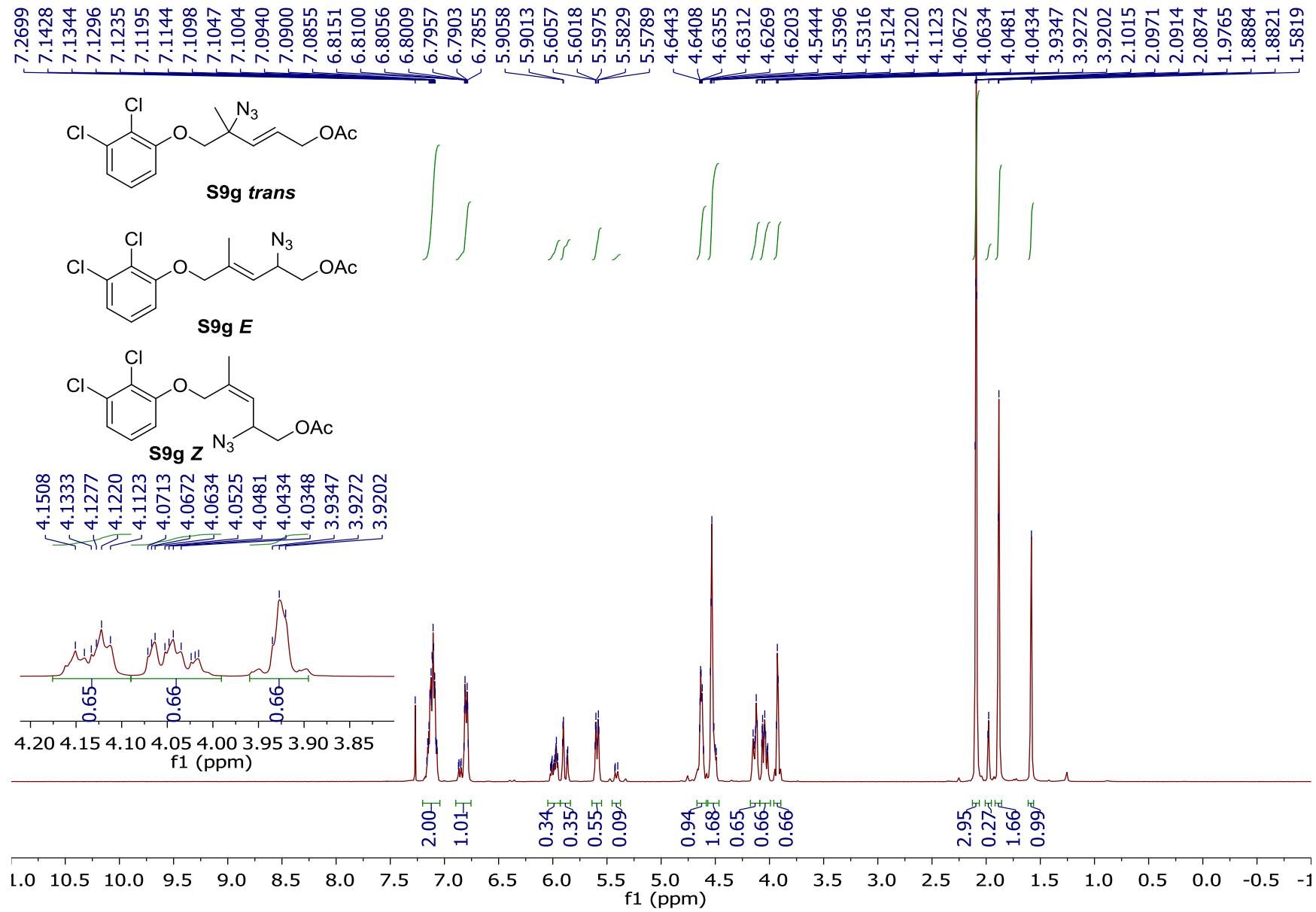
Compound S9f, 400 MHz ^1H NMR in CDCl_3



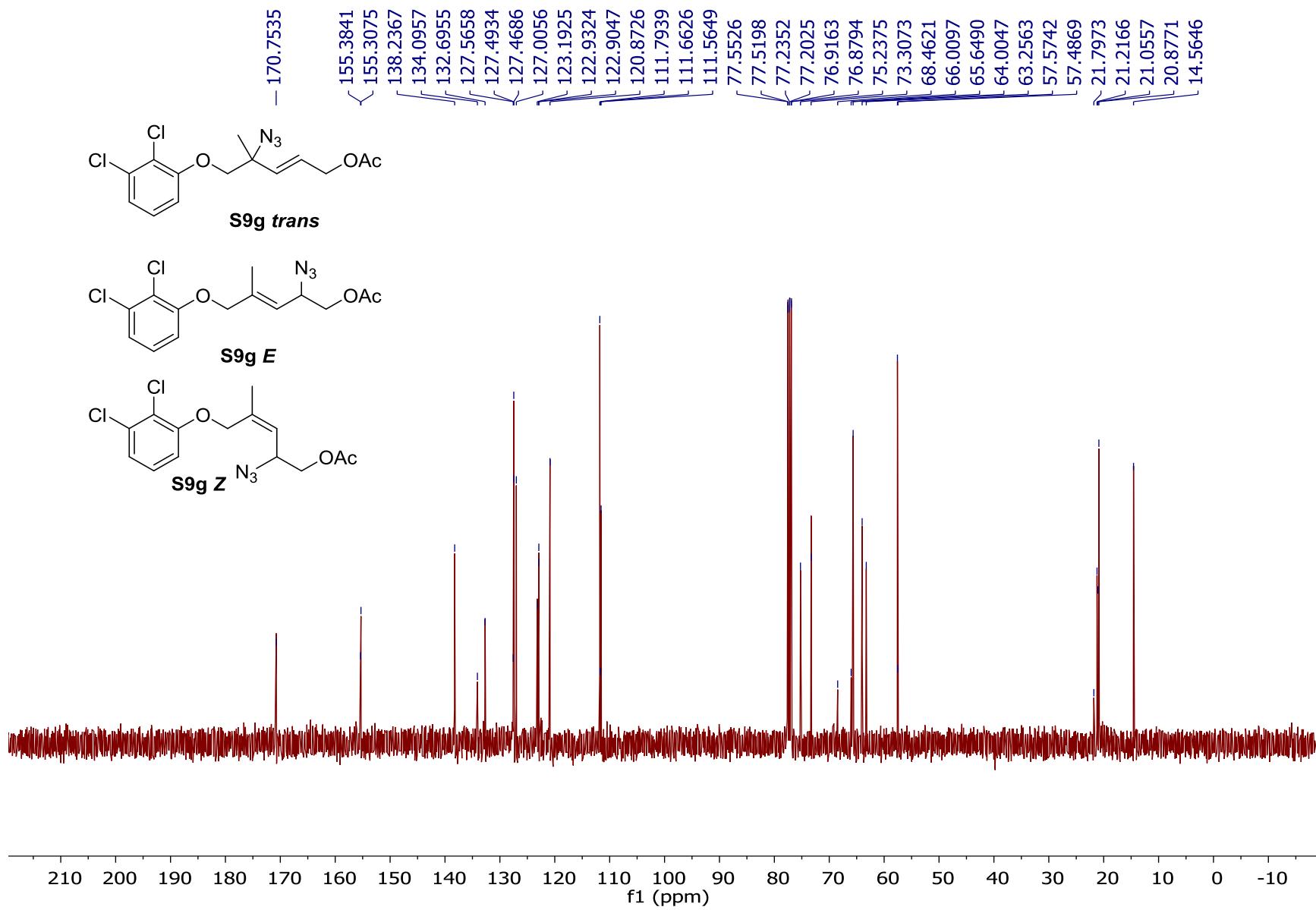
Compound S9f, 101 MHz ^{13}C NMR in CDCl_3



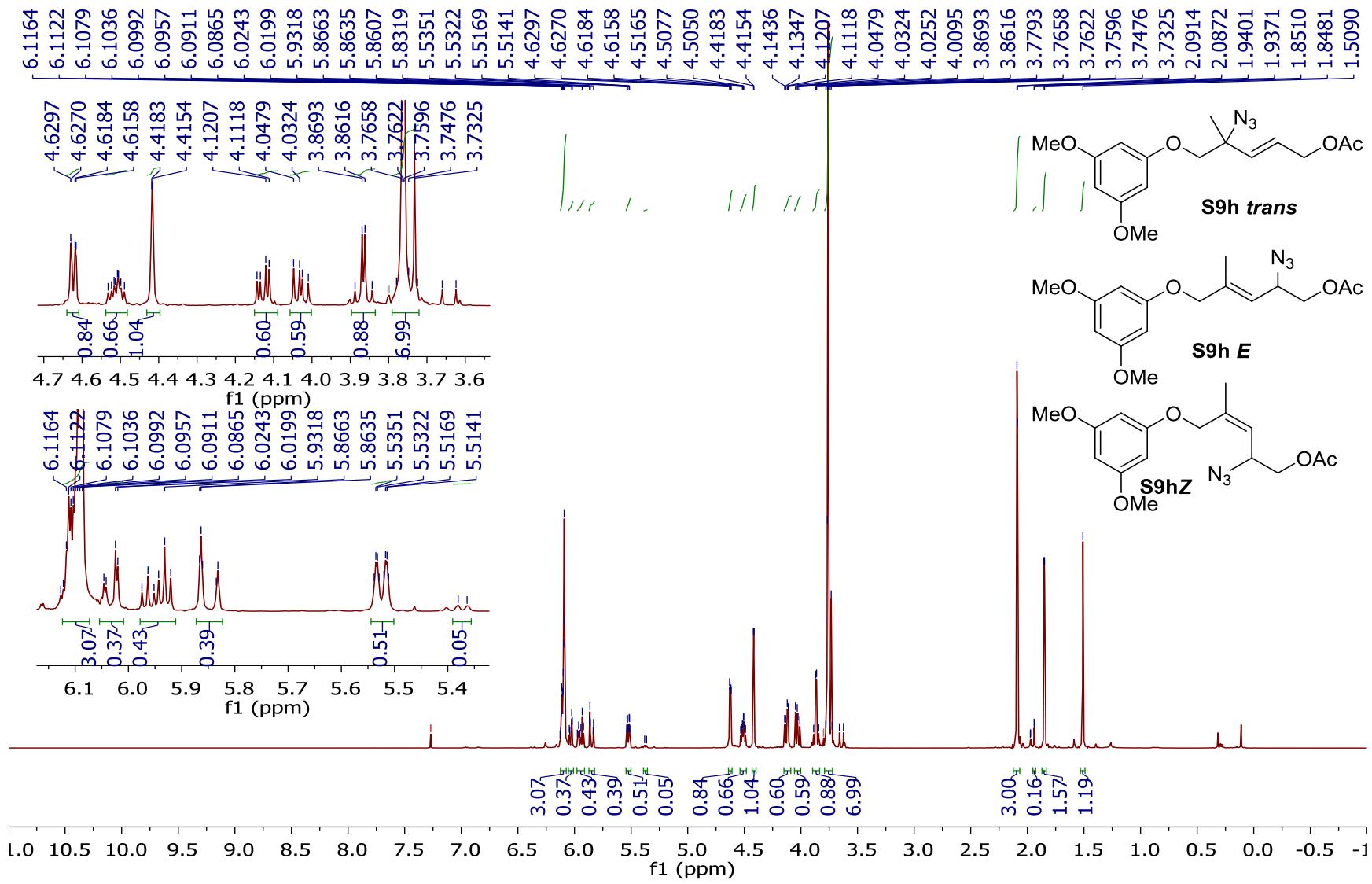
Compound S9f, 376 MHz ^{19}F NMR in CDCl_3

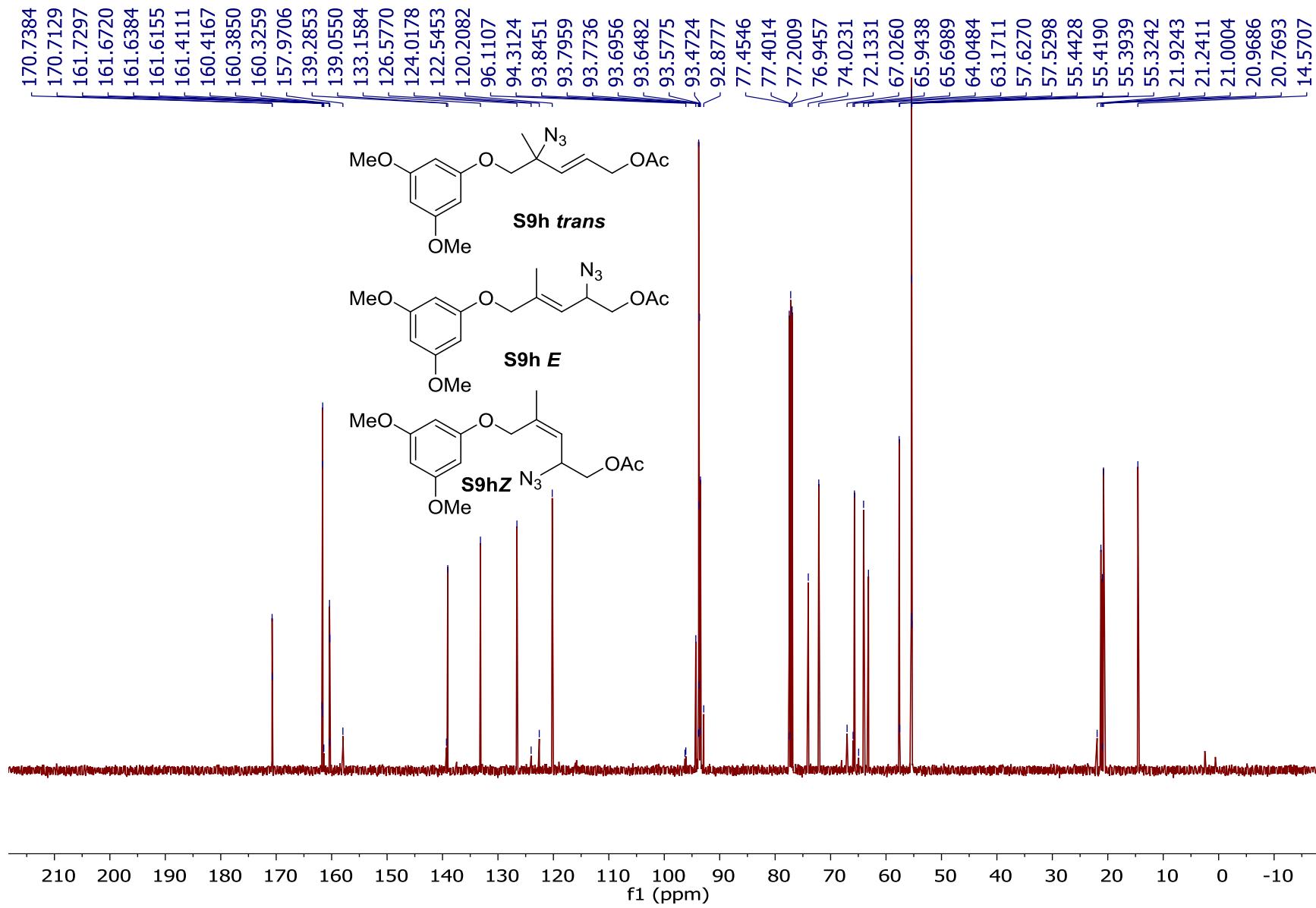


Compound S9g, 400 MHz ^1H NMR in CDCl_3

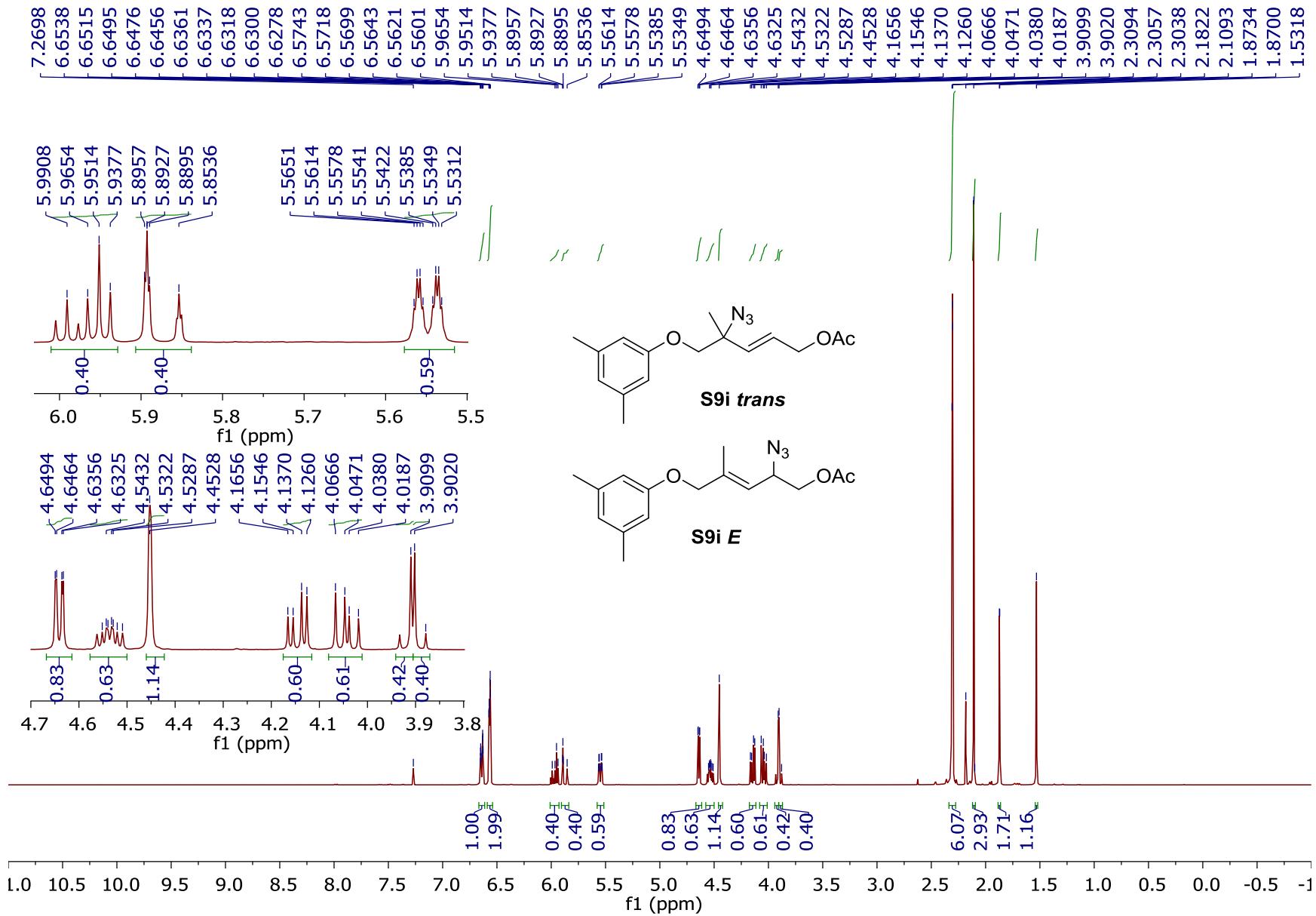


Compound S9g, 101 MHz ^{13}C NMR in CDCl_3

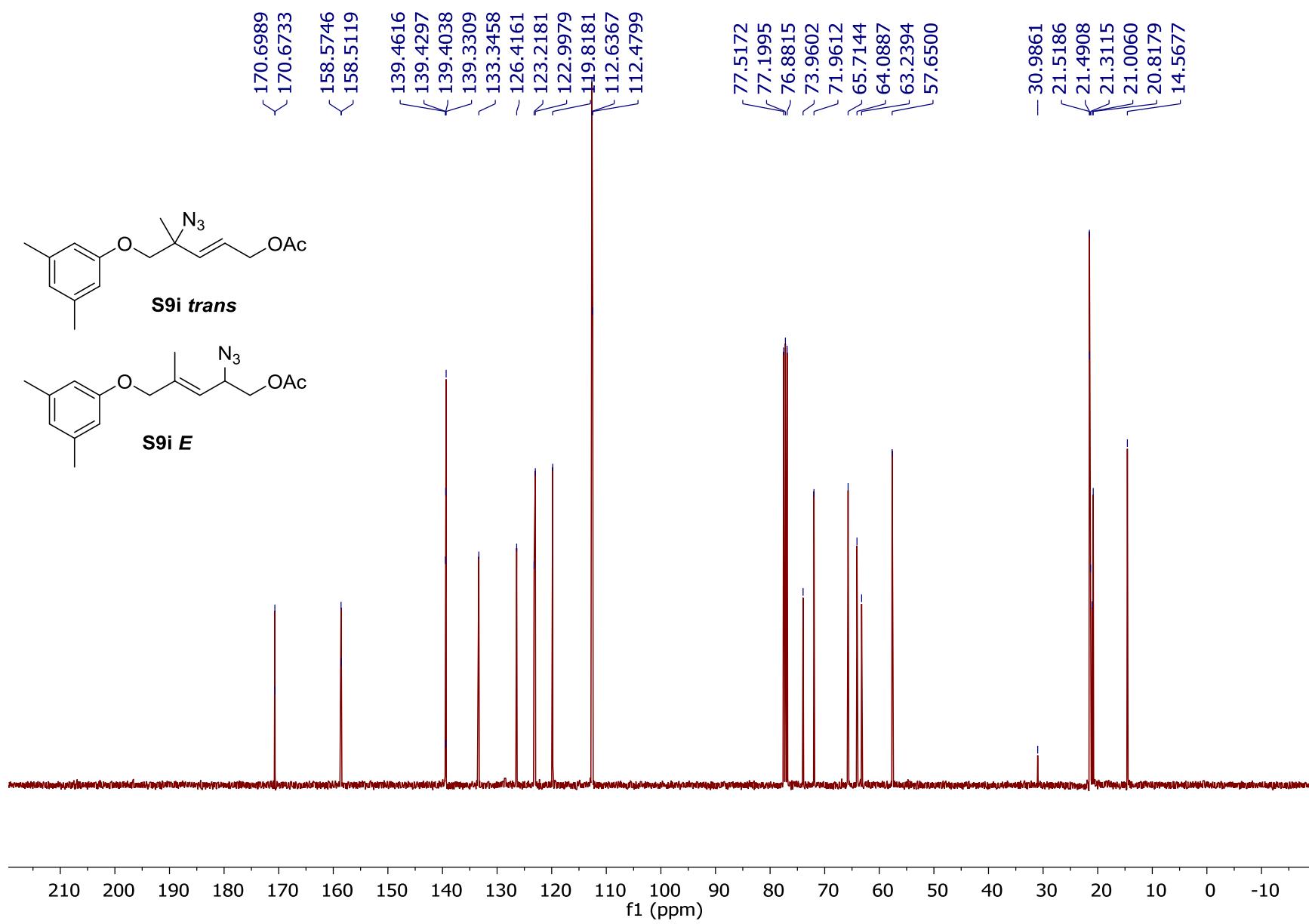




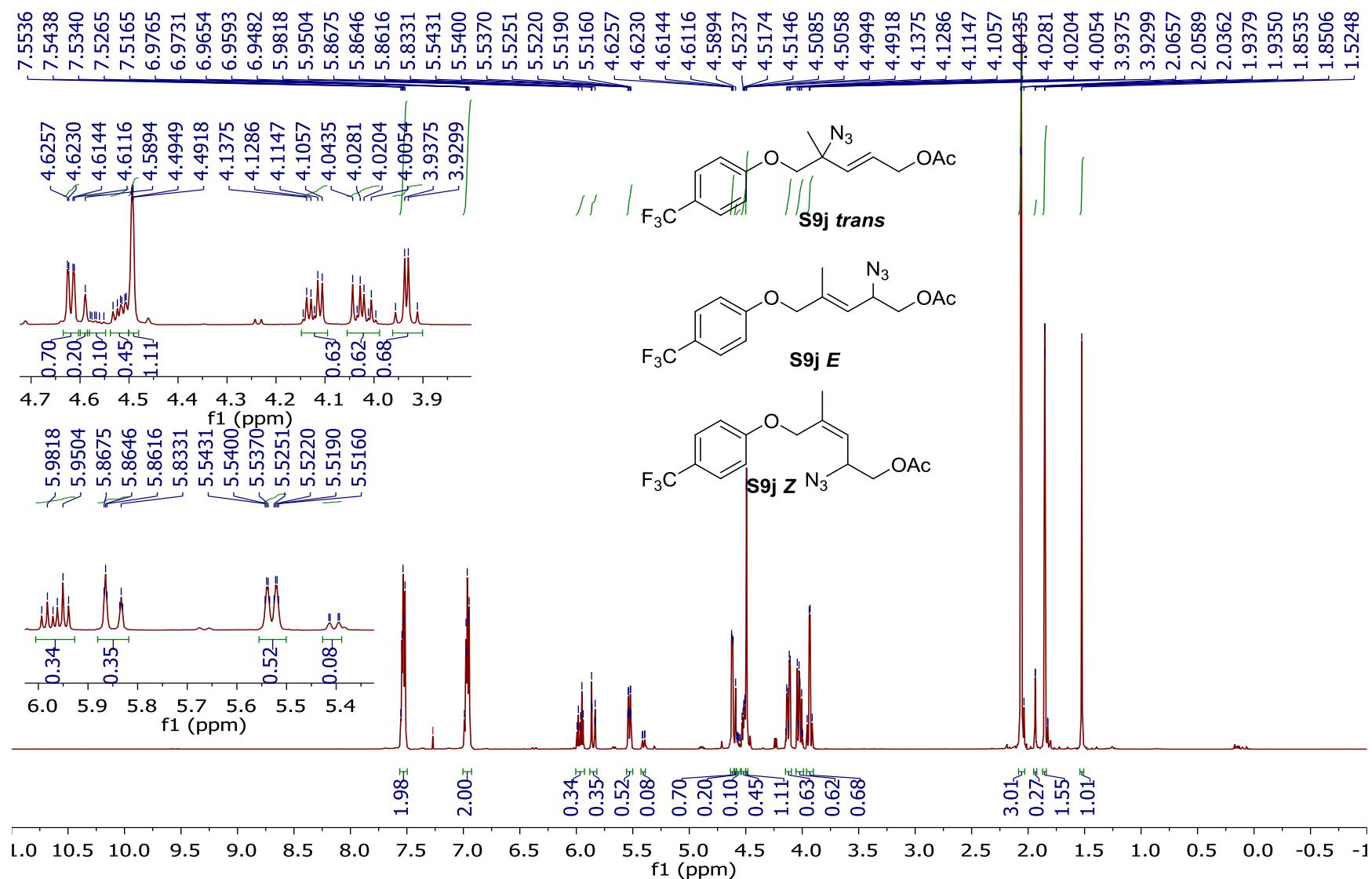
Compound S9h, 101 MHz ^{13}C NMR in CDCl_3



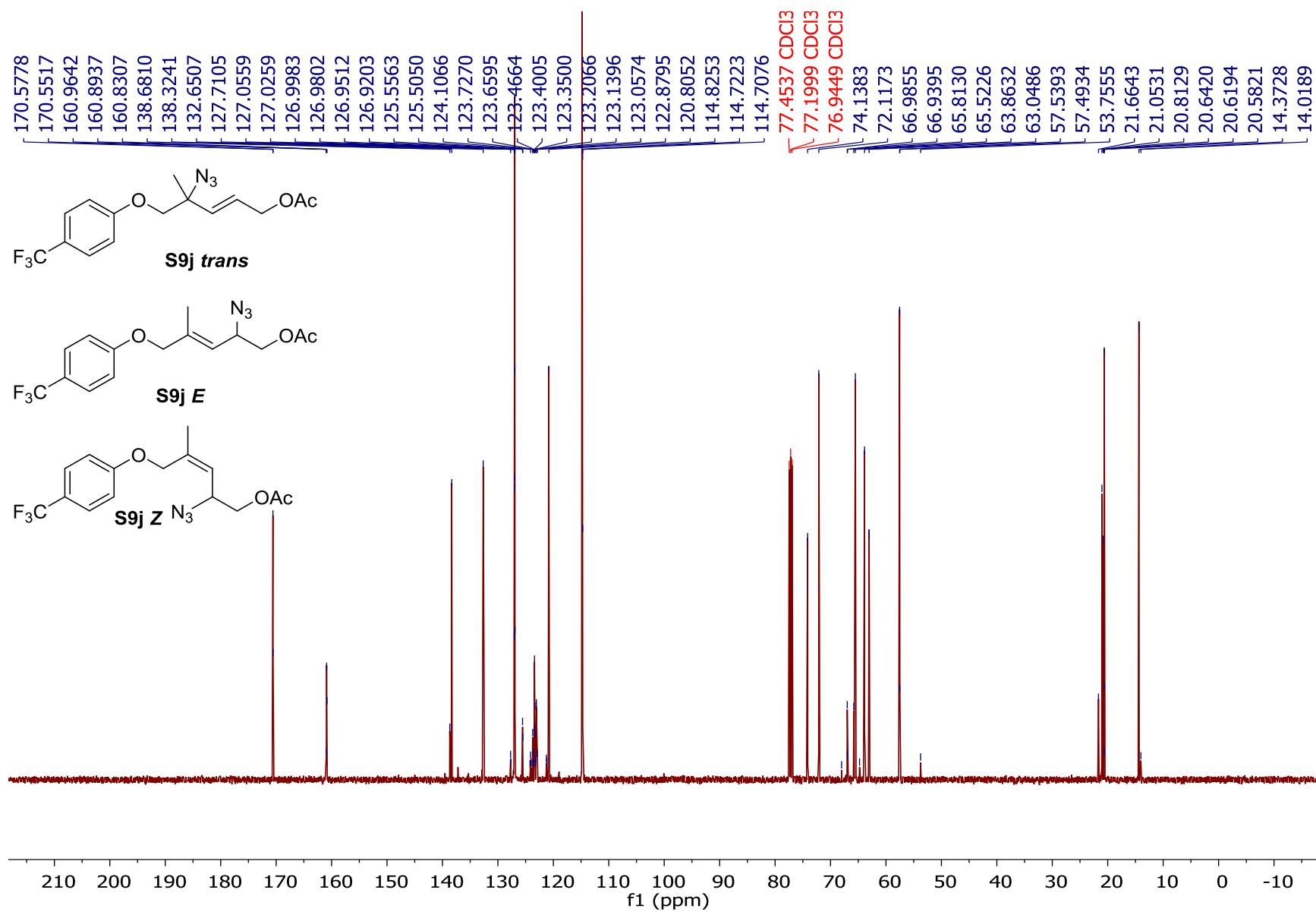
'Compound S9i, 400 MHz ^1H NMR in CDCl_3

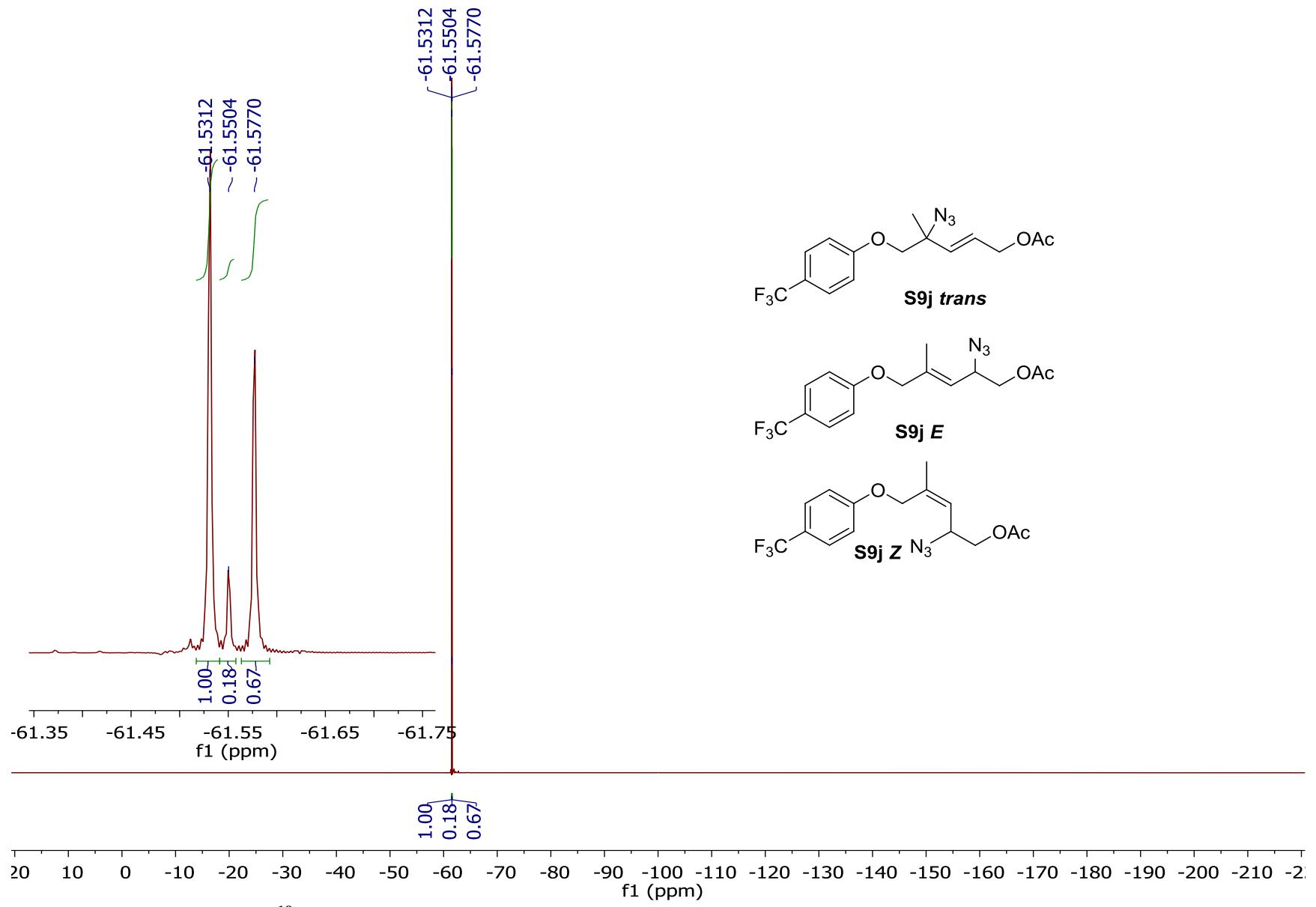


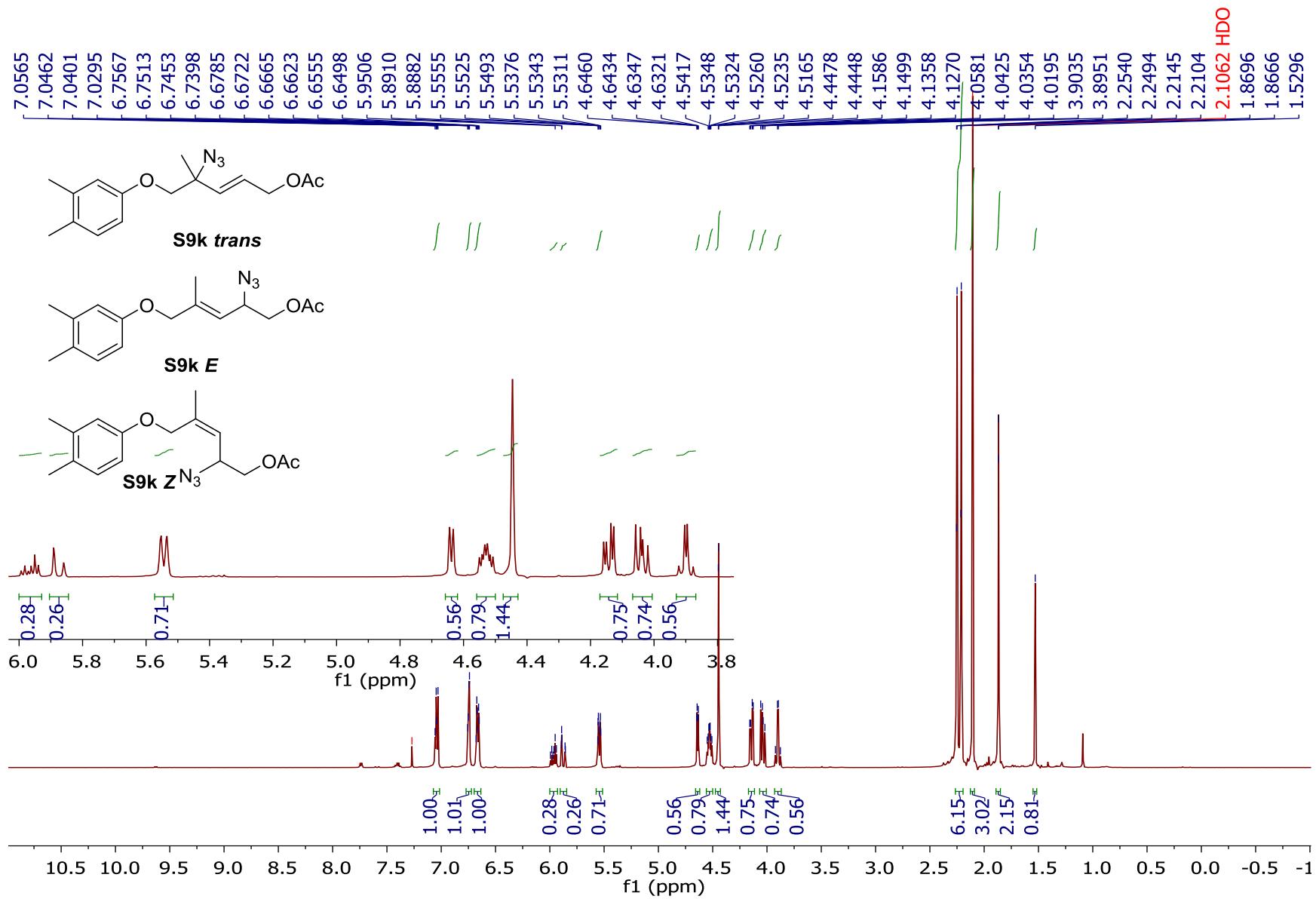
Compound **S9i**, 101 MHz ^{13}C NMR in CDCl_3



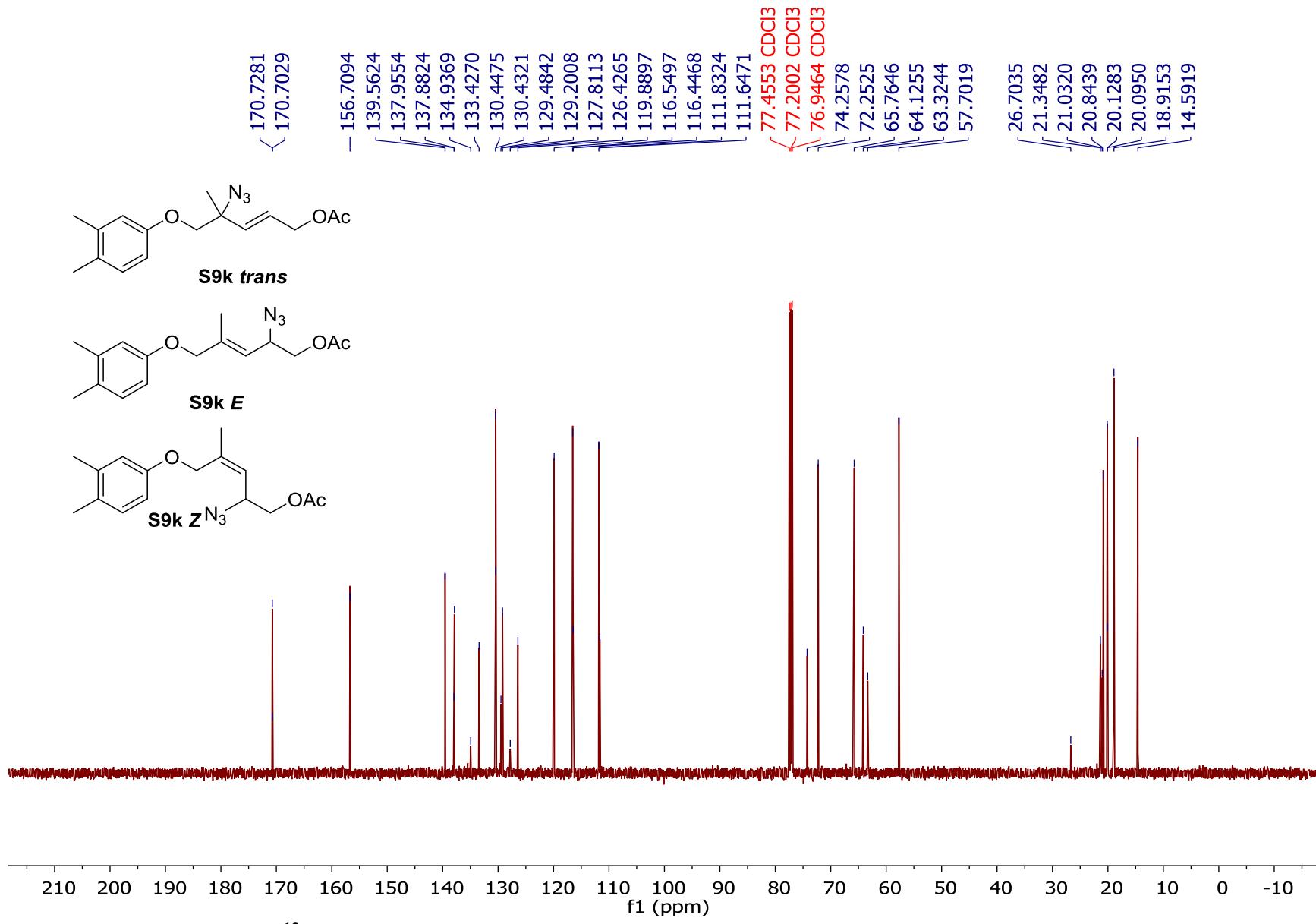
Compound S9j, 500 MHz ^1H NMR Spectrum in CDCl_3



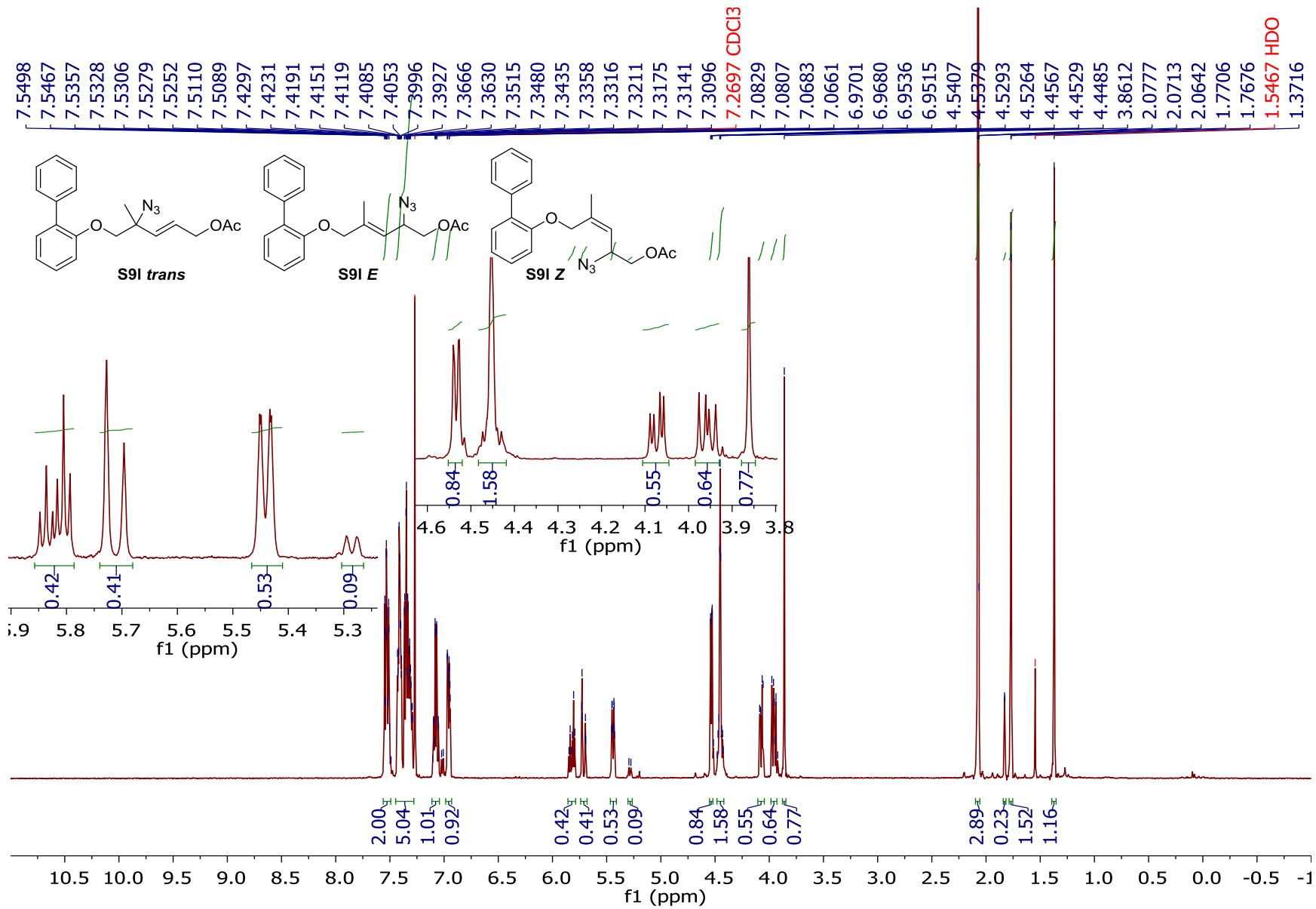




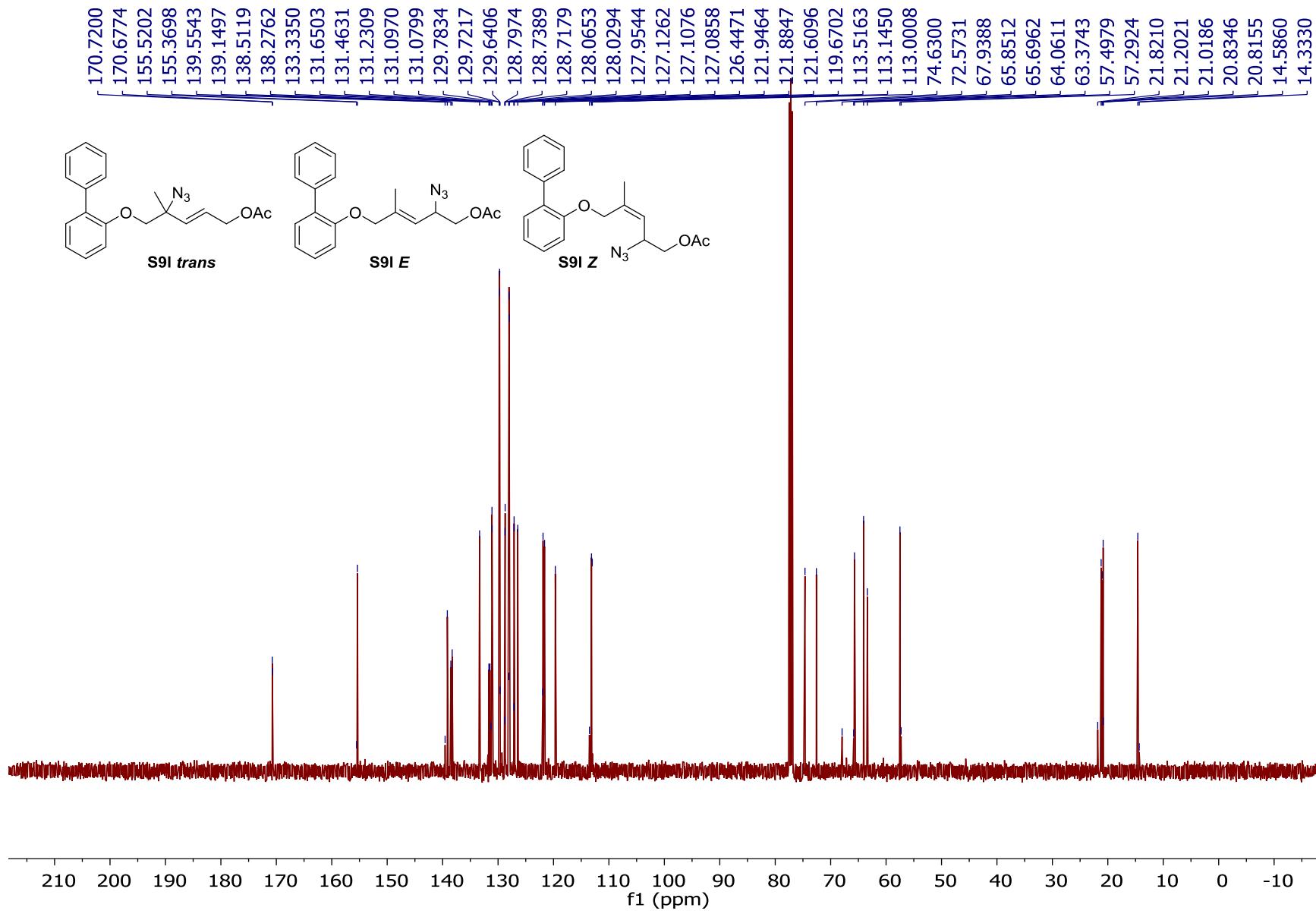
Compound S9k, 500 MHz ^1H NMR Spectrum in CDCl_3

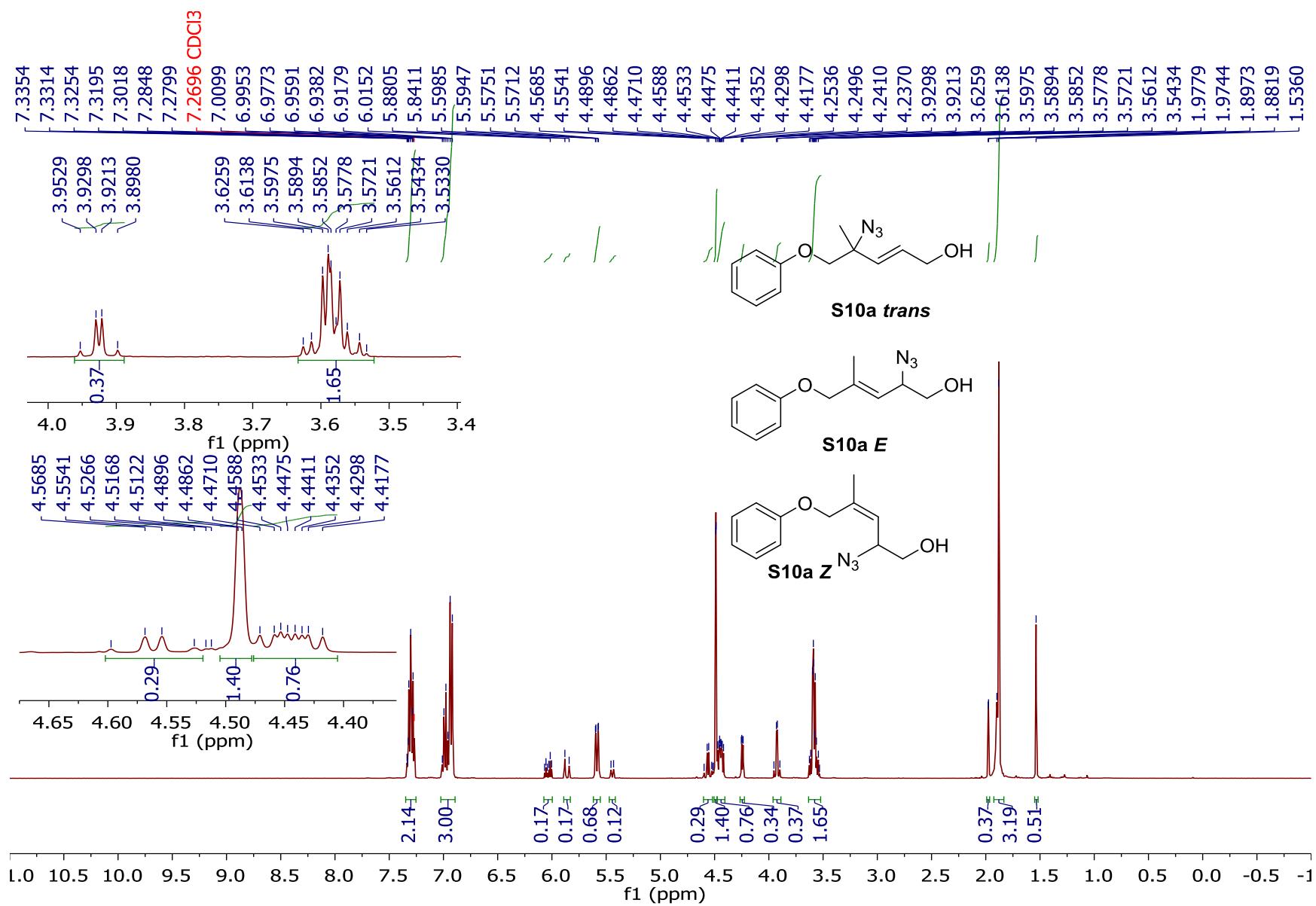


Compound S9k, 126 MHz ^{13}C NMR Spectrum in CDCl_3

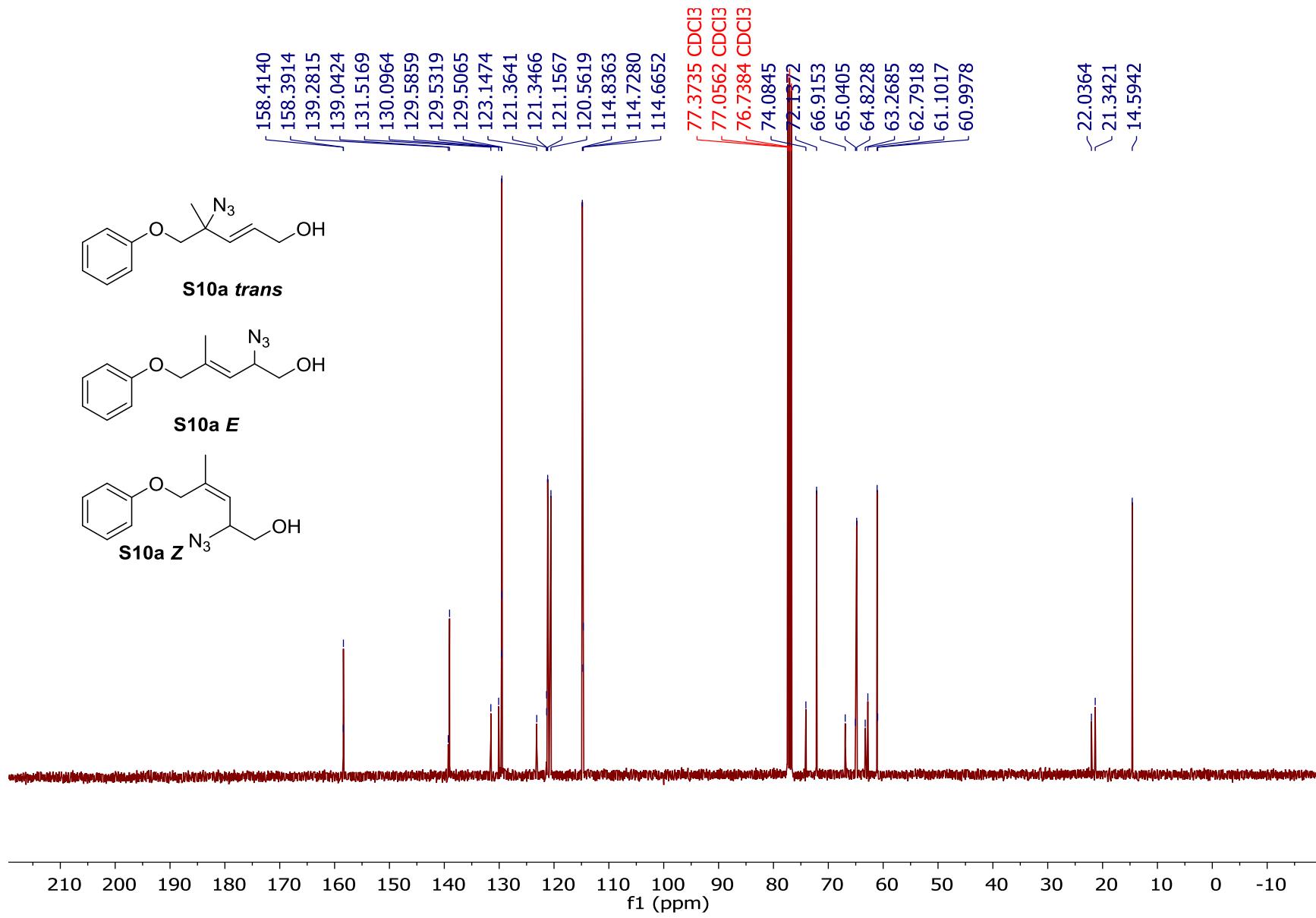


Compound S9l, 500 MHz ^1H NMR Spectrum in CDCl_3

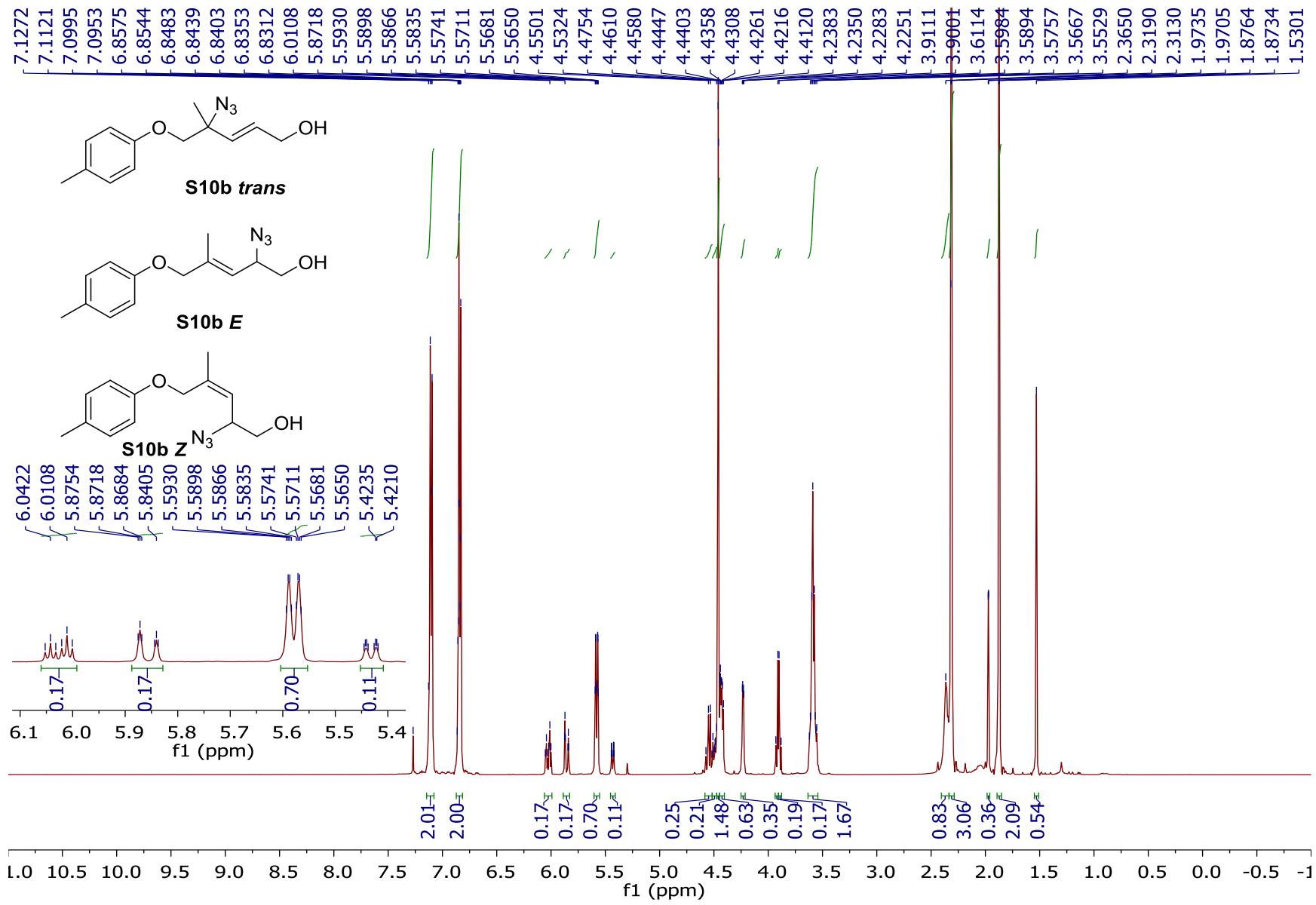




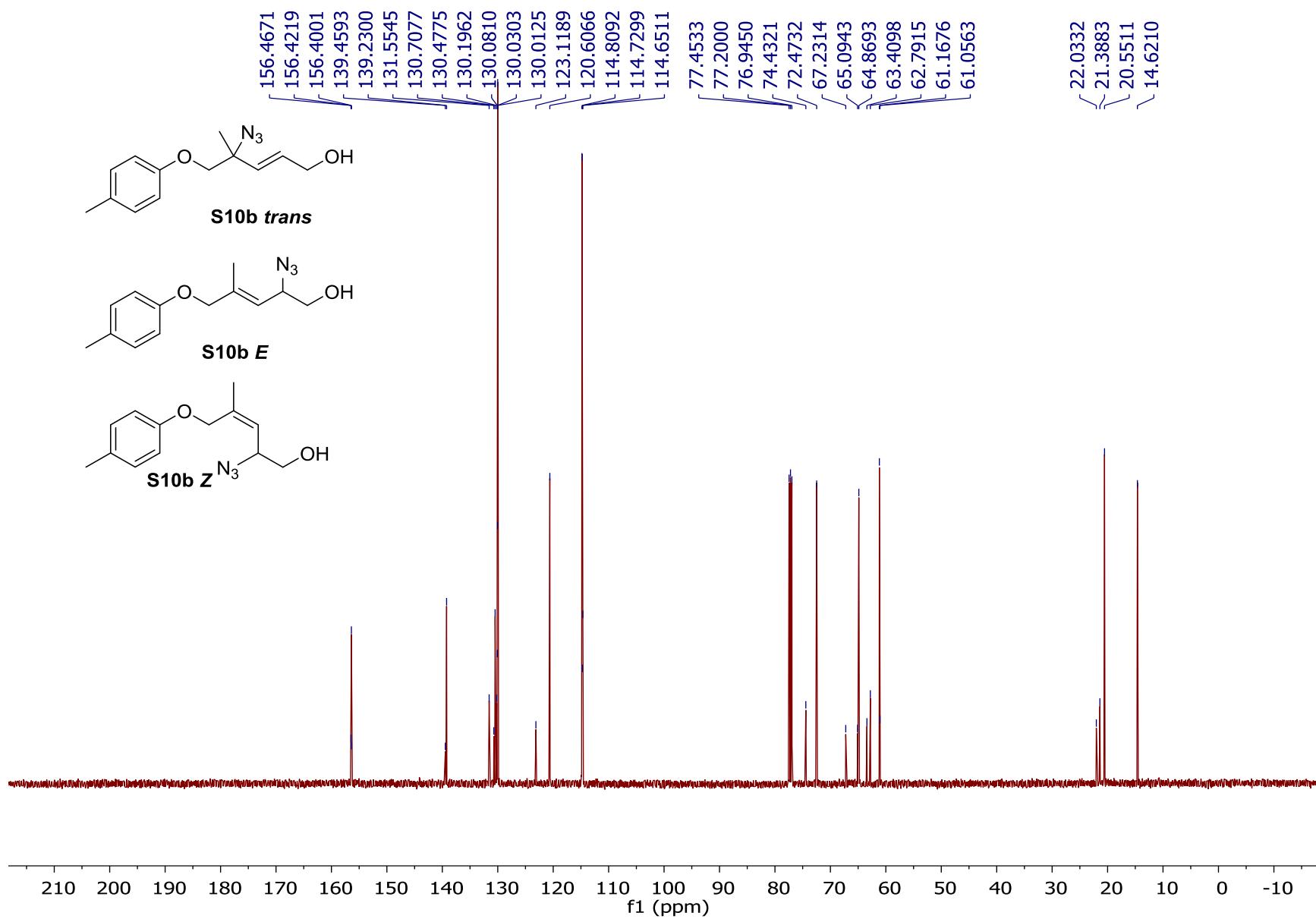
Compound S10a, 500 MHz ^1H NMR in CDCl_3



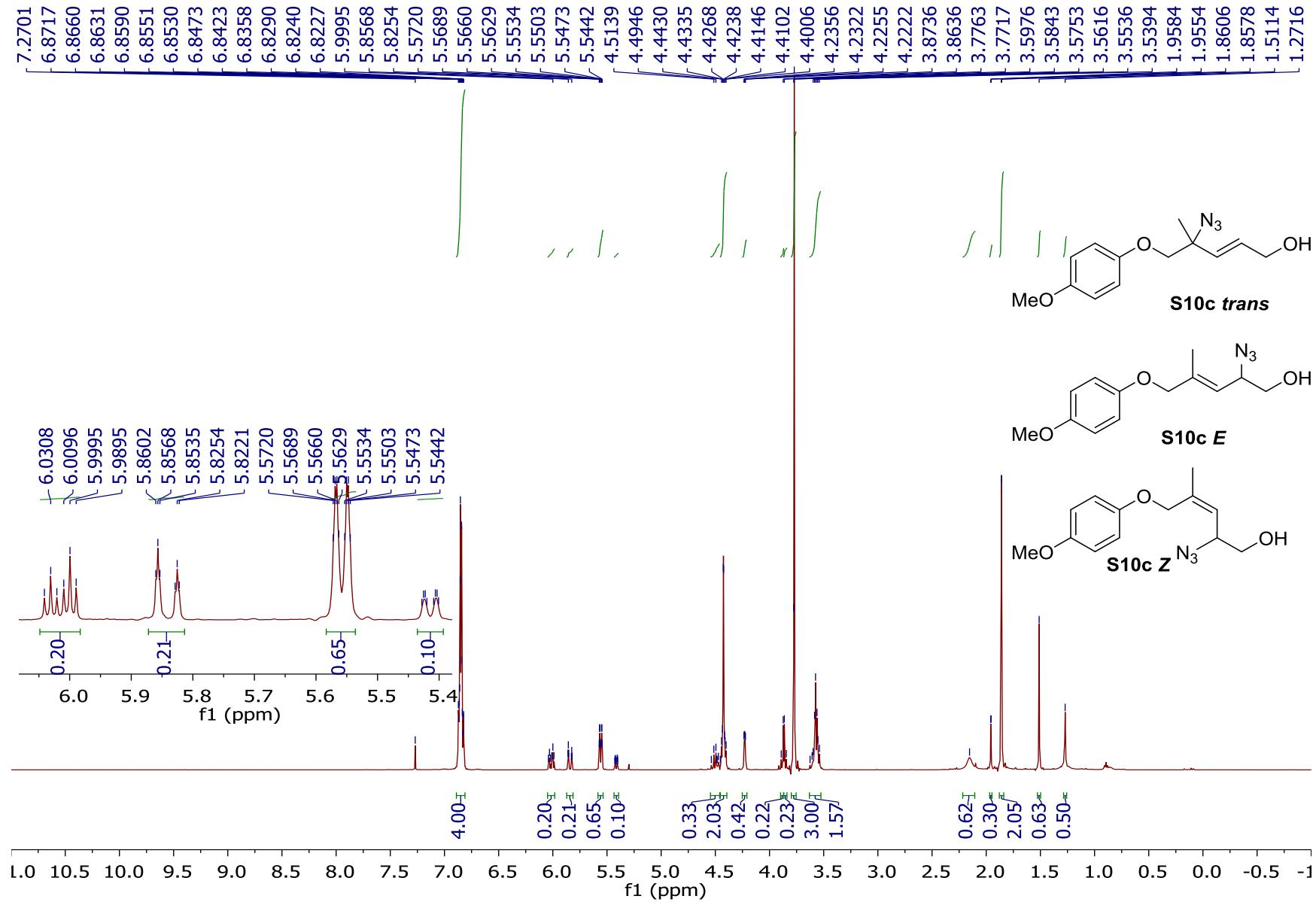
Compound S10a, 101 MHz ¹³C NMR in CDCl₃



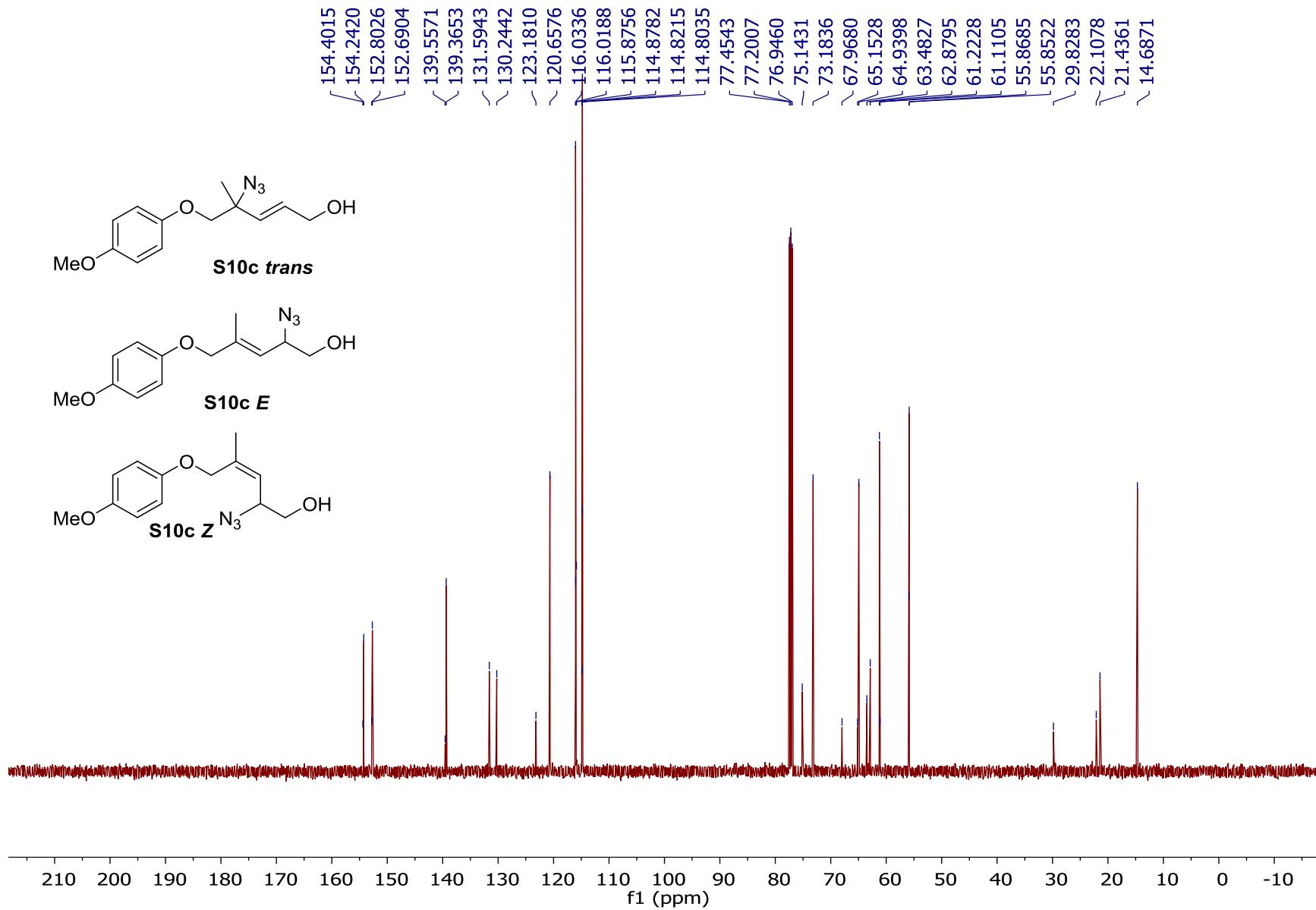
Compound S10b, 400 MHz ^1H NMR in CDCl_3



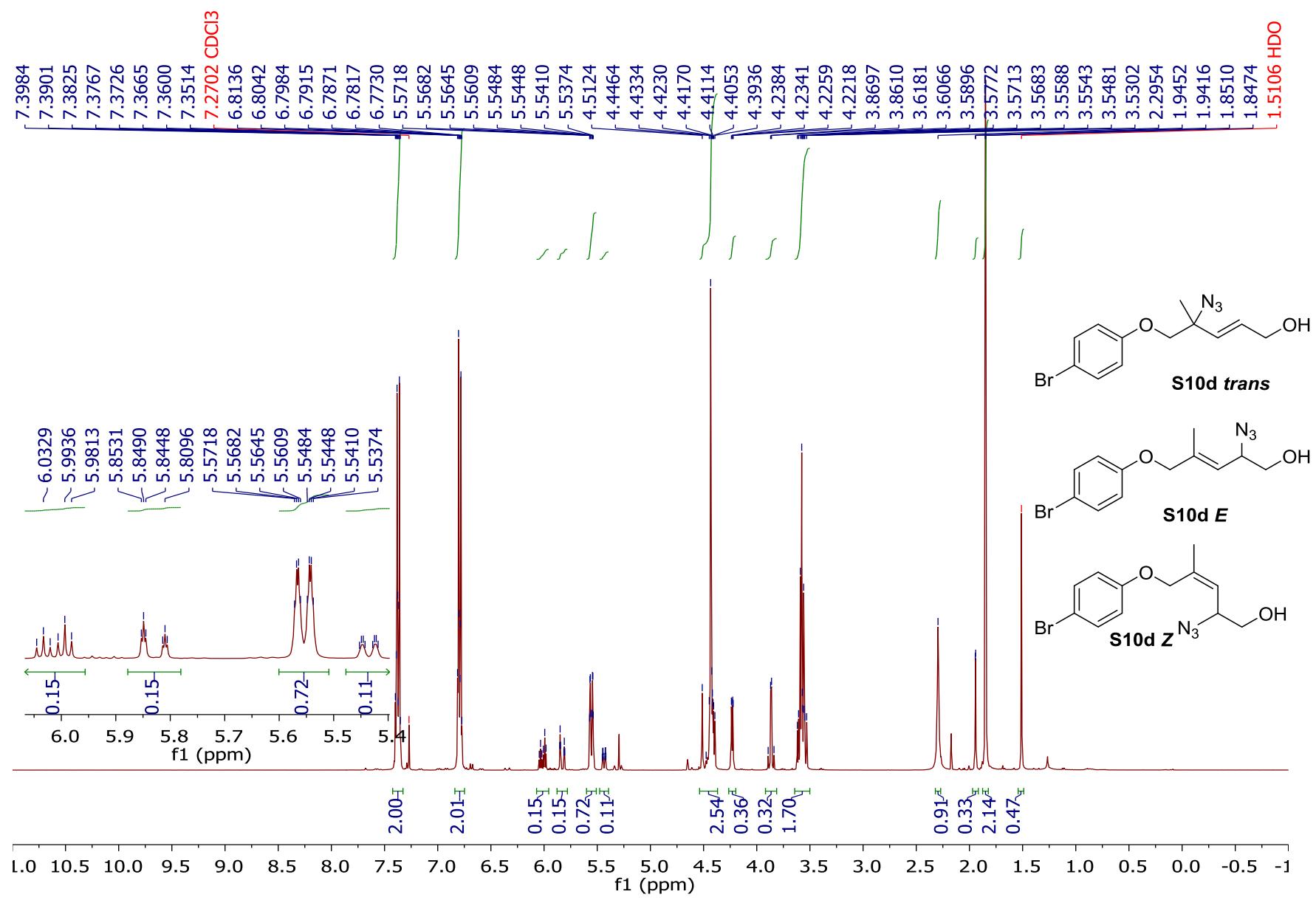
Compound S10b, 101 MHz ^{13}C NMR in CDCl_3

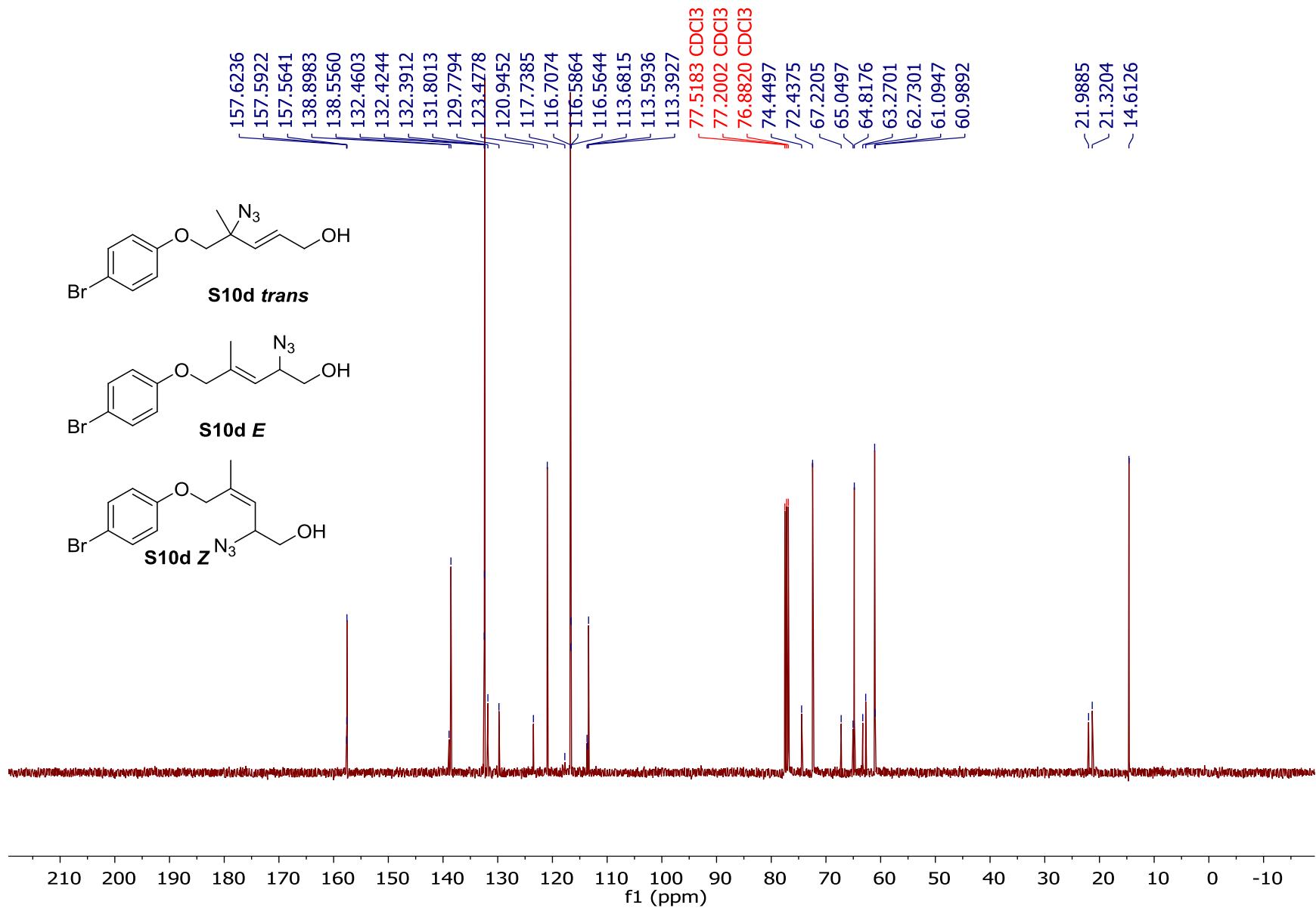


Compound S10c, 400 MHz ^1H NMR in CDCl_3

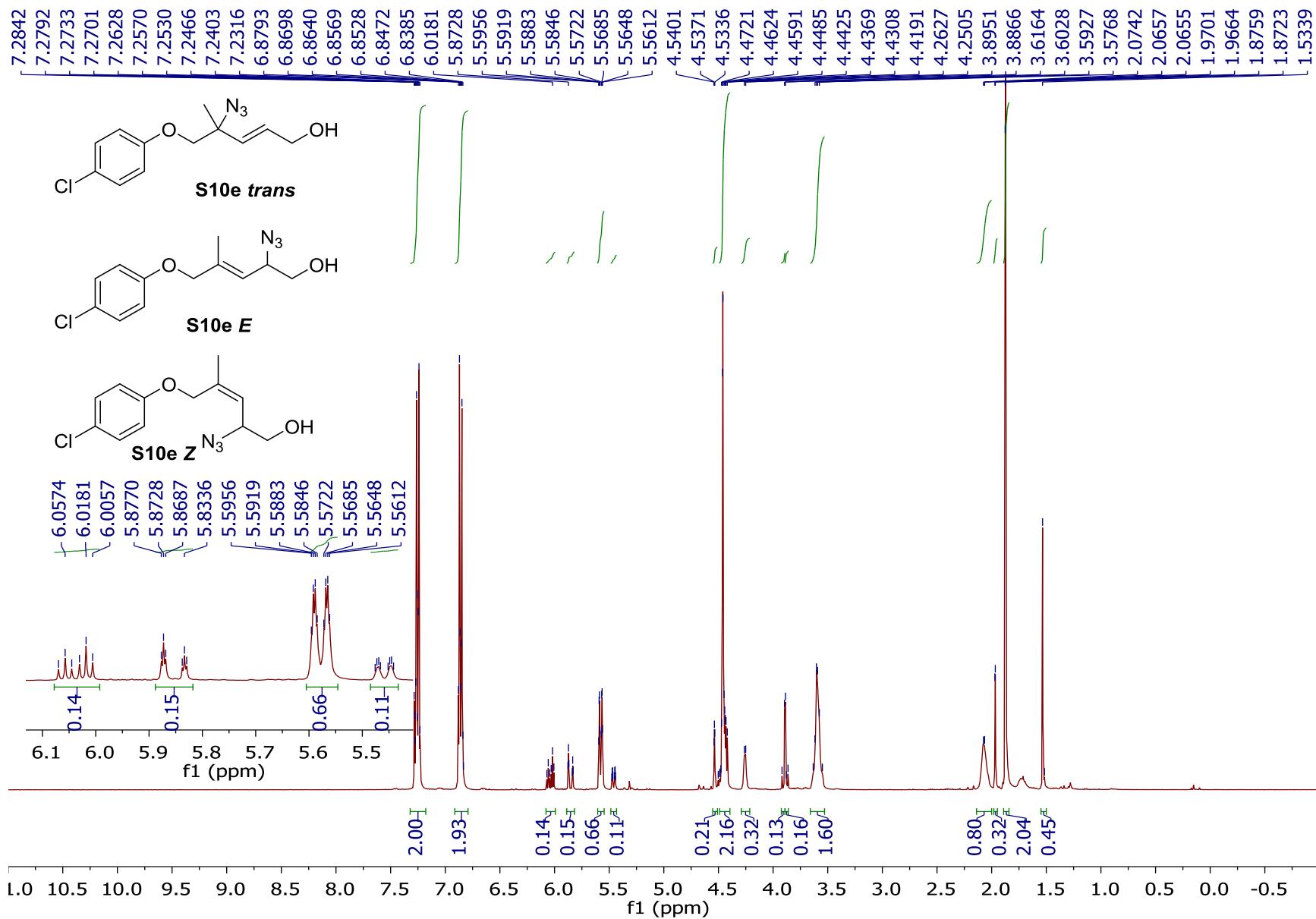


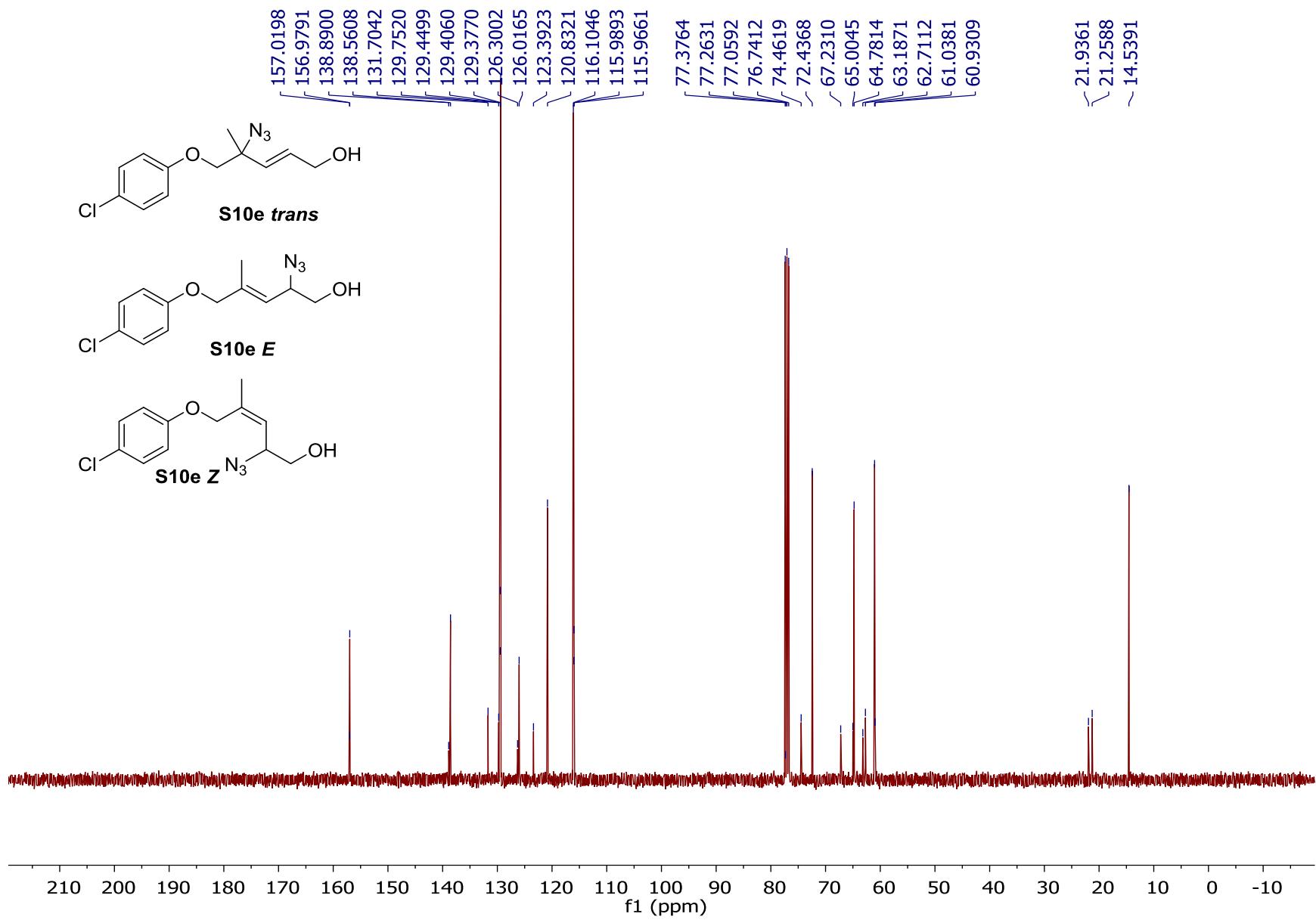
Compound S10c, 101 MHz ¹³C NMR in CDCl₃



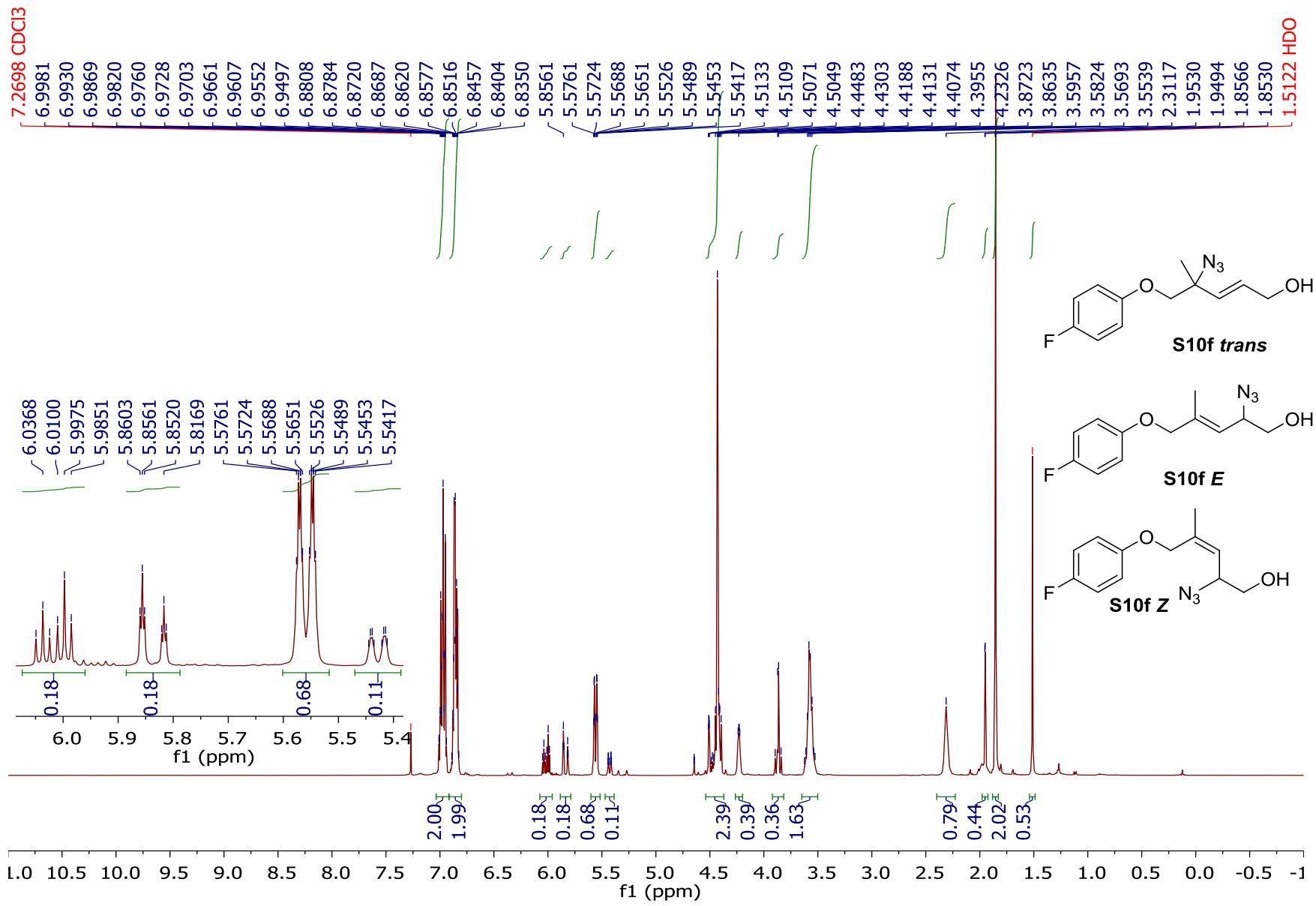


Compound S10d, 101 MHz ¹³C NMR in CDCl₃

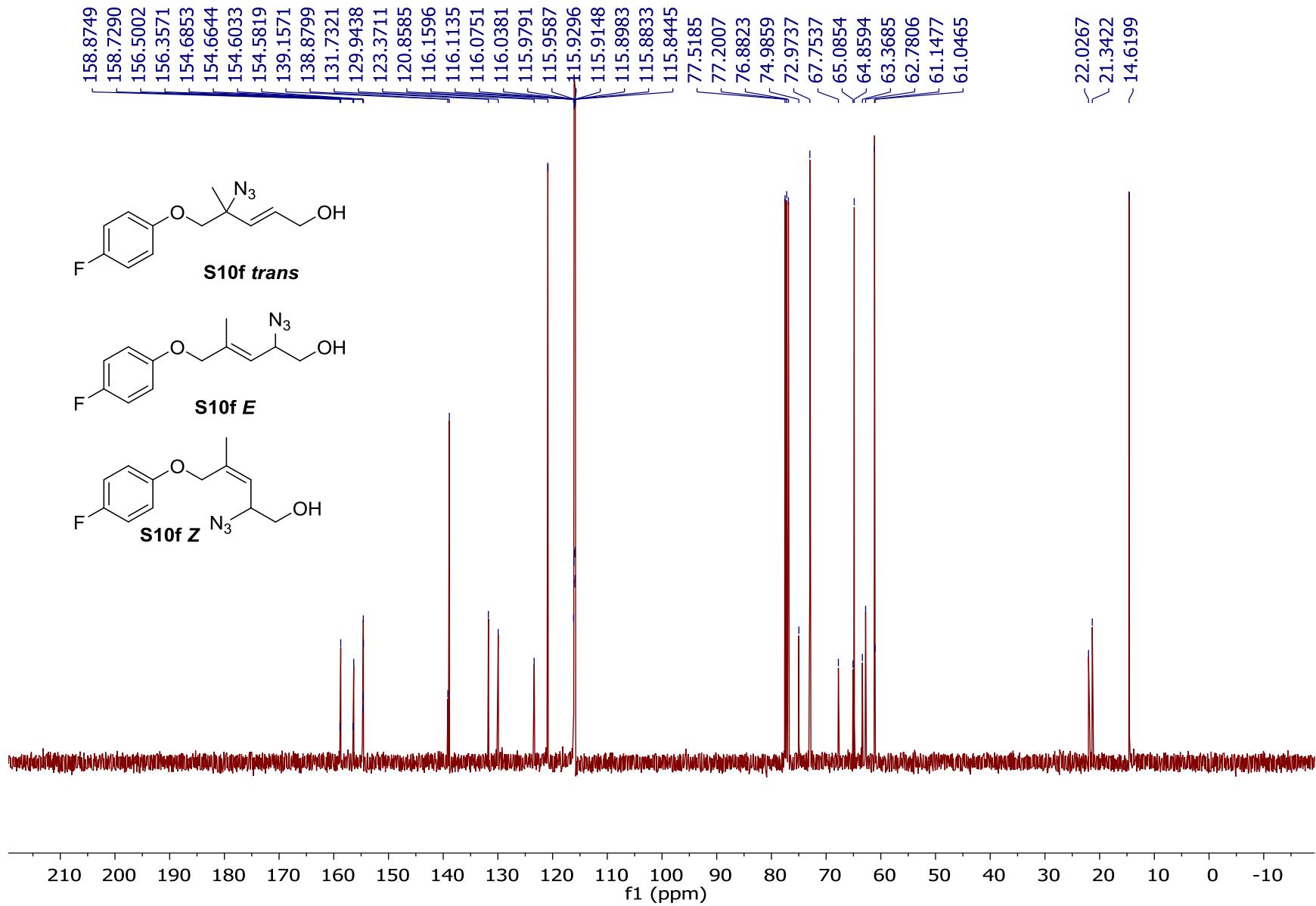




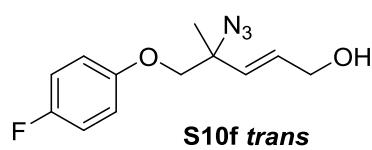
Compound S10e, 101 MHz ^{13}C NMR in CDCl_3



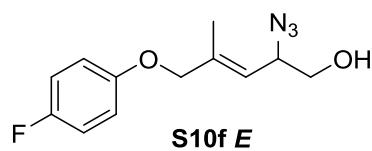
Compound S10f, 400 MHz ¹H NMR in CDCl₃



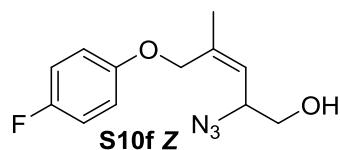
Compound S10f, 101 MHz ^{13}C NMR in CDCl_3



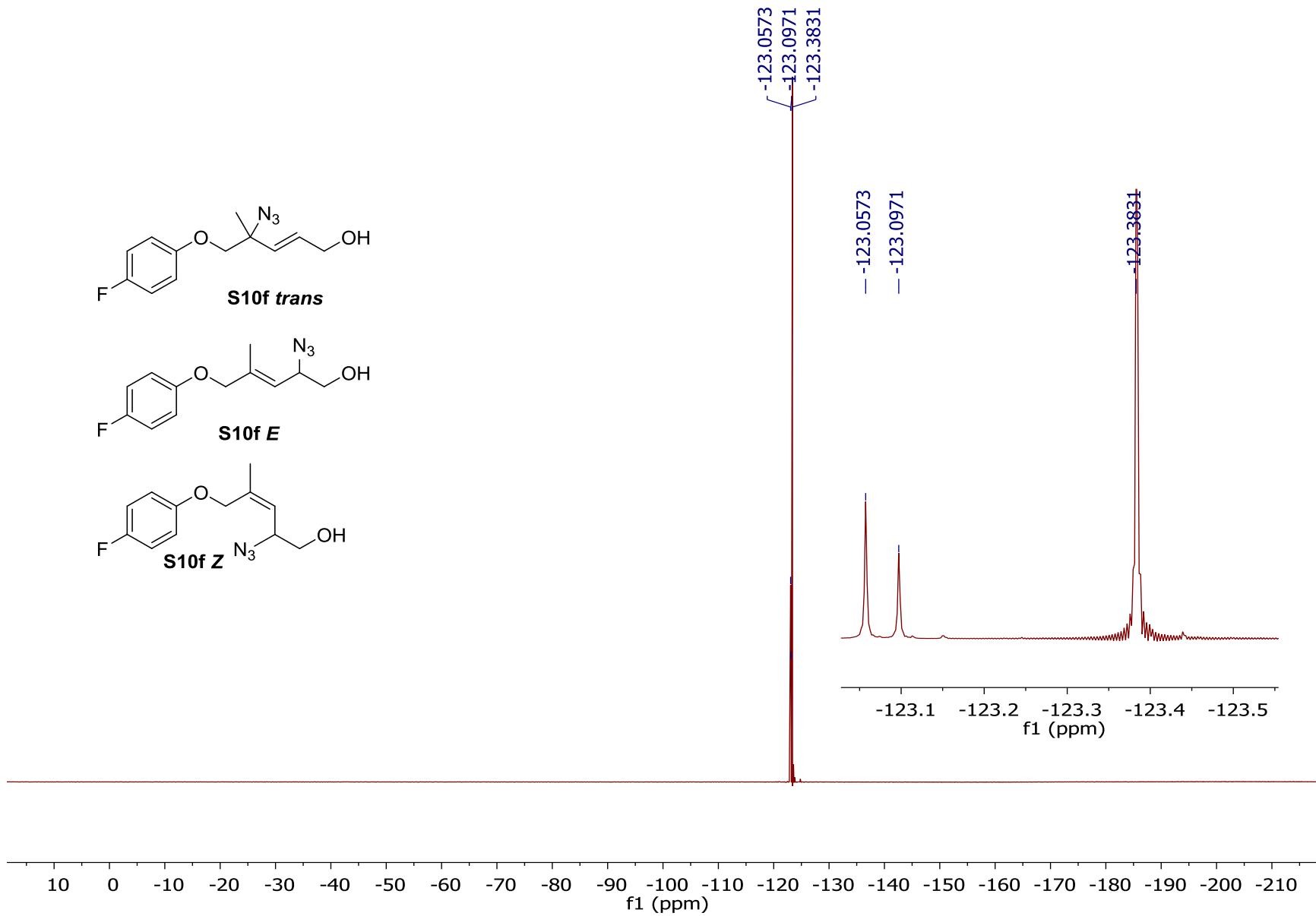
S10f trans



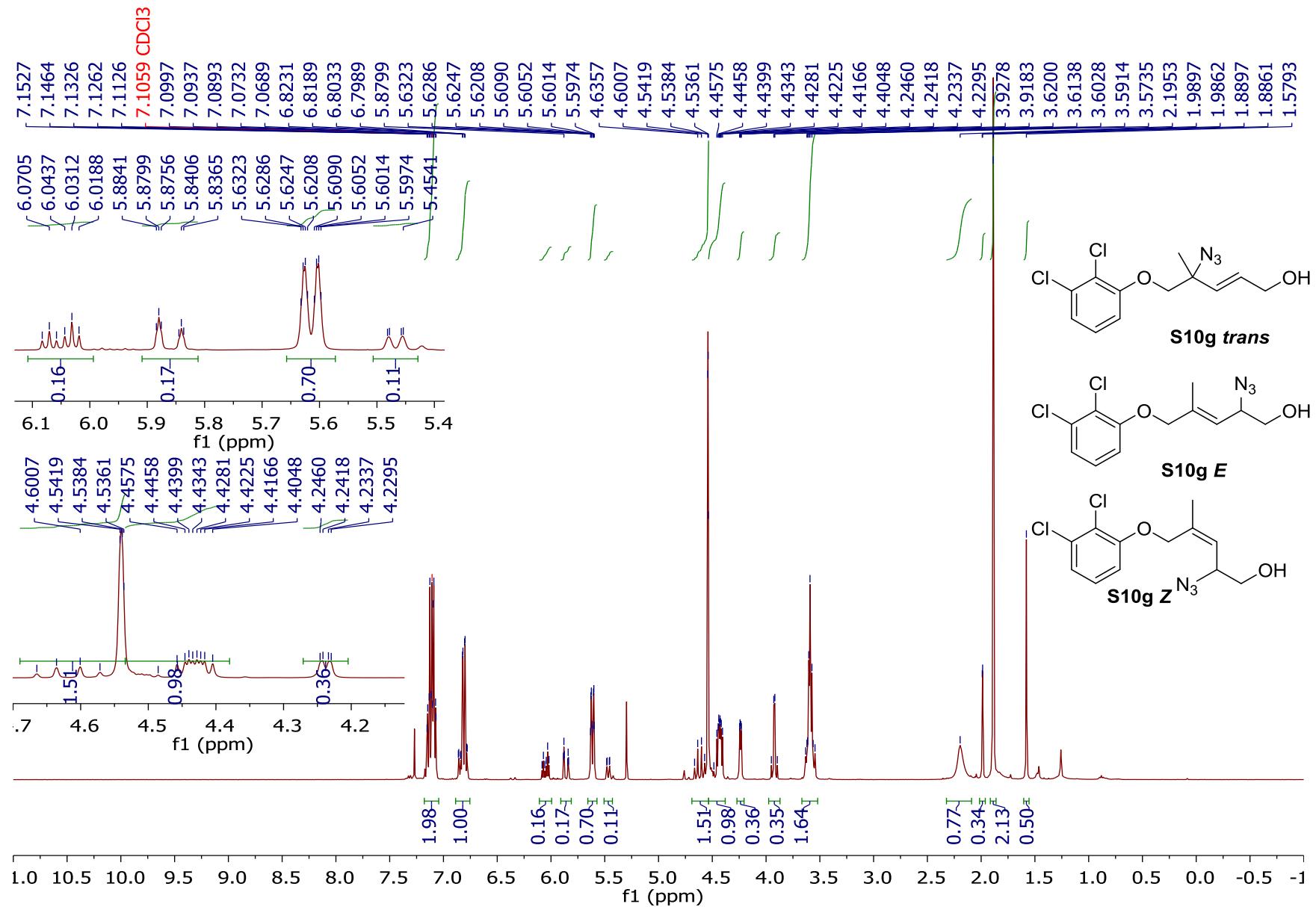
S10f E



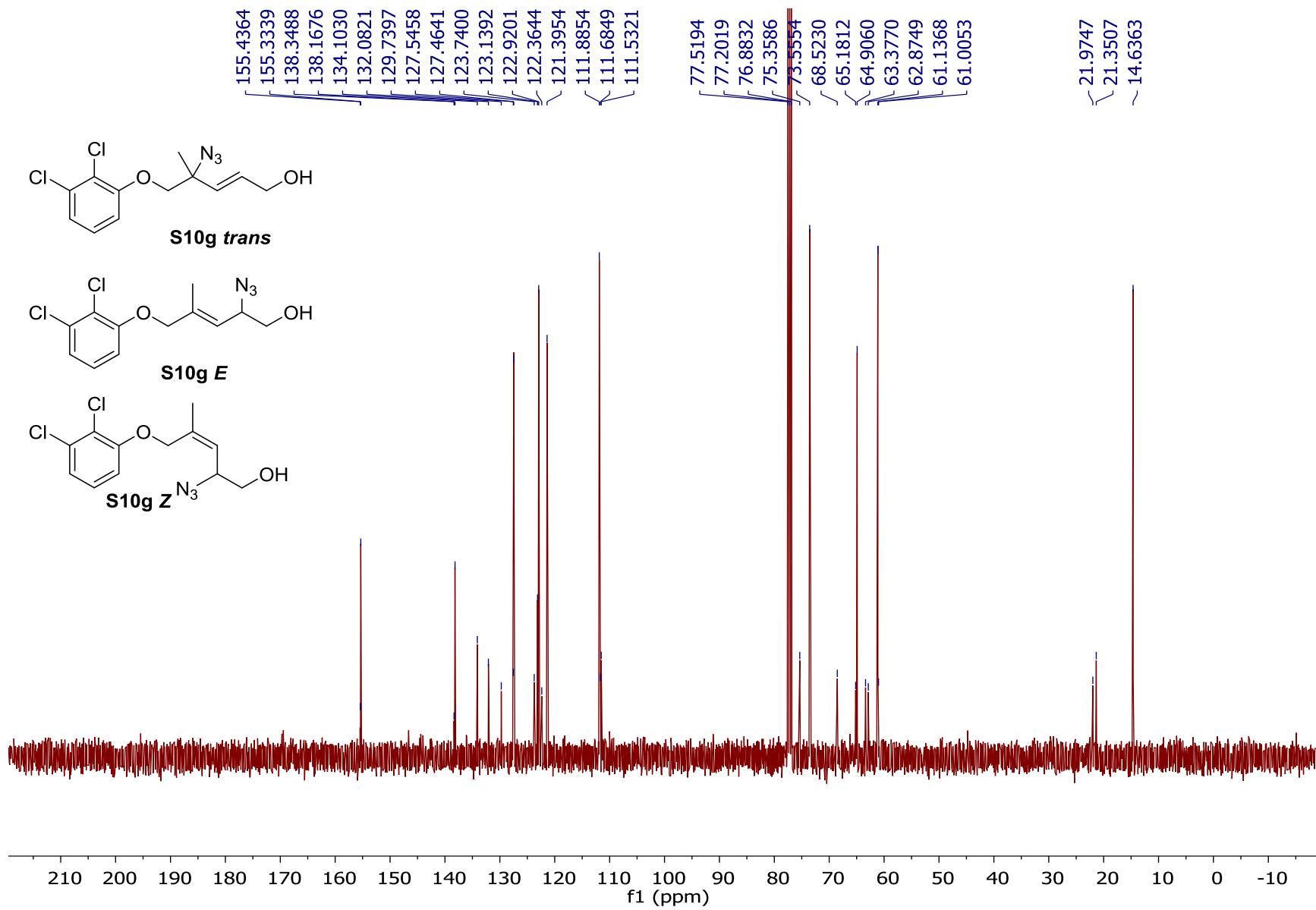
S10f Z



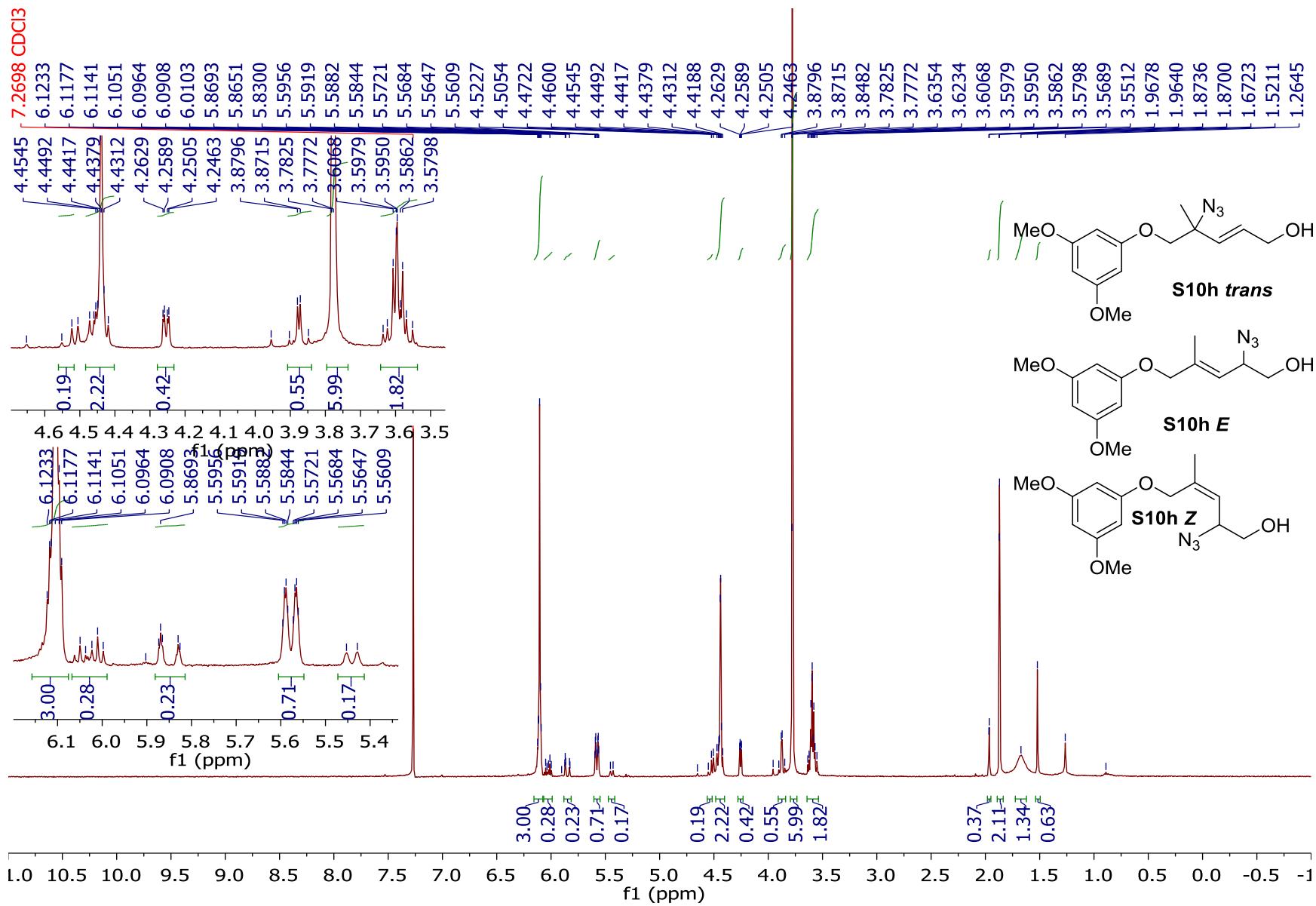
Compound **S10f**, 376 MHz ¹⁹F NMR in CDCl₃

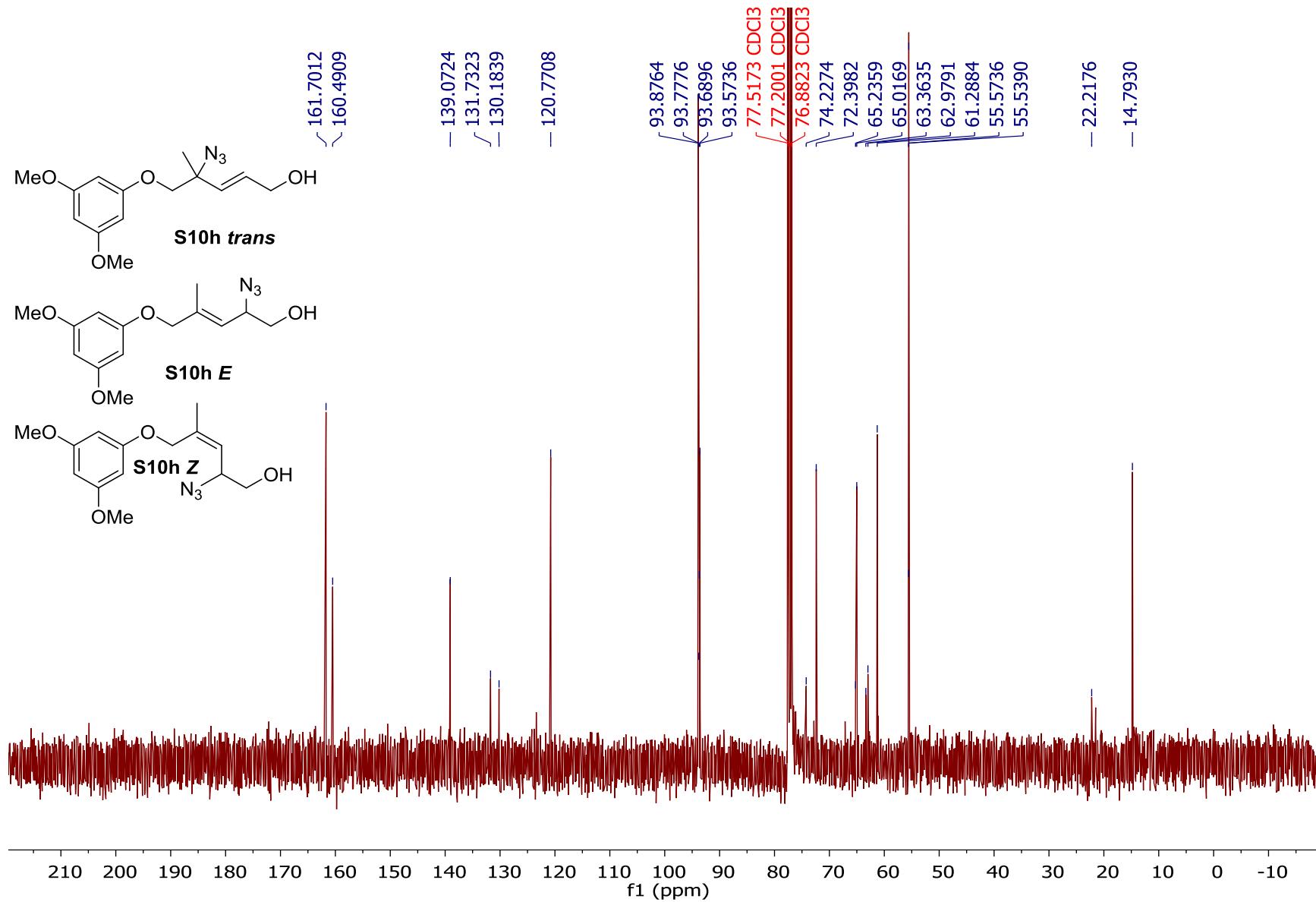


Compound S10g, 400 MHz ^1H NMR in CDCl_3

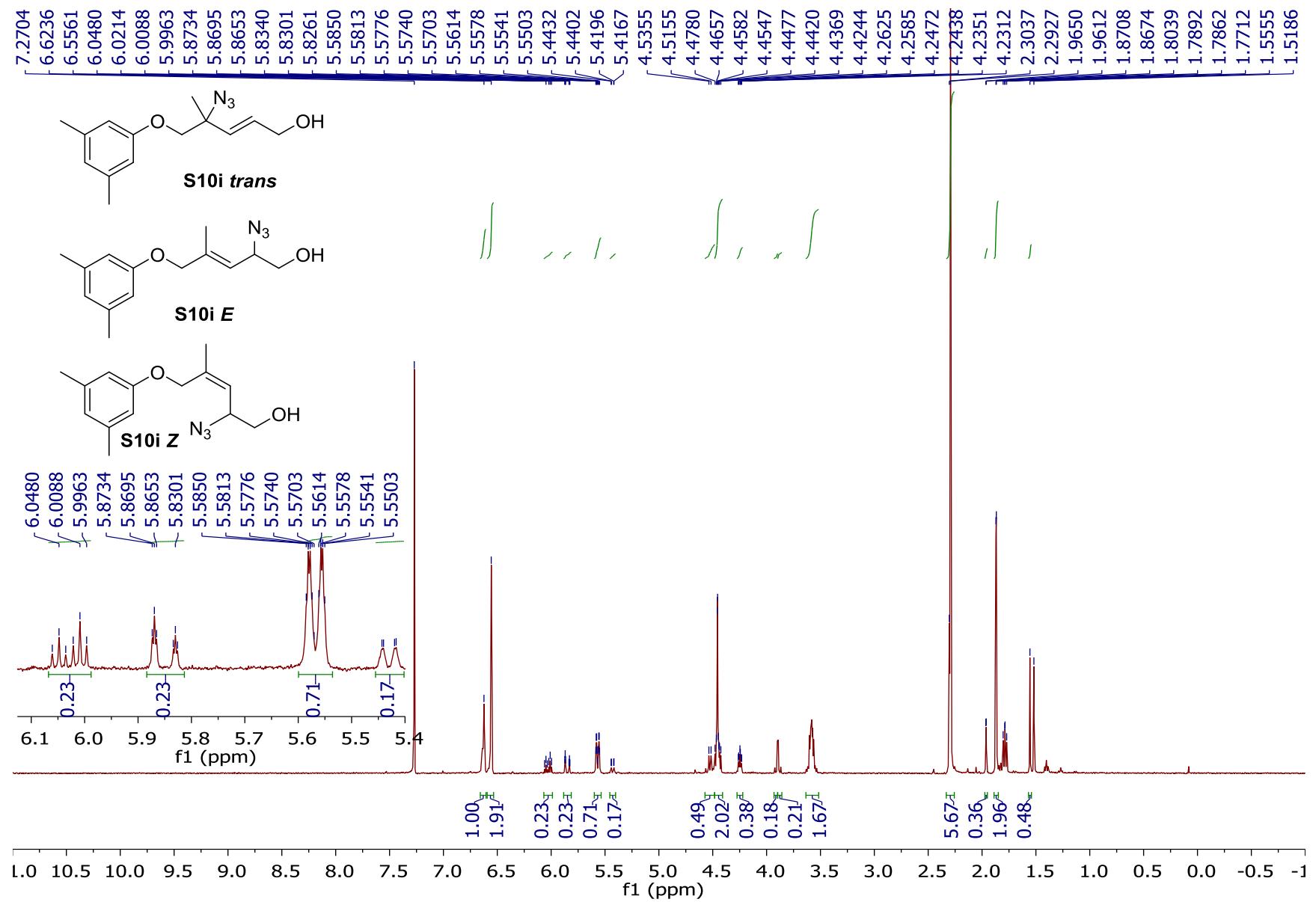


Compound S10g, 101 MHz ^{13}C NMR in CDCl_3

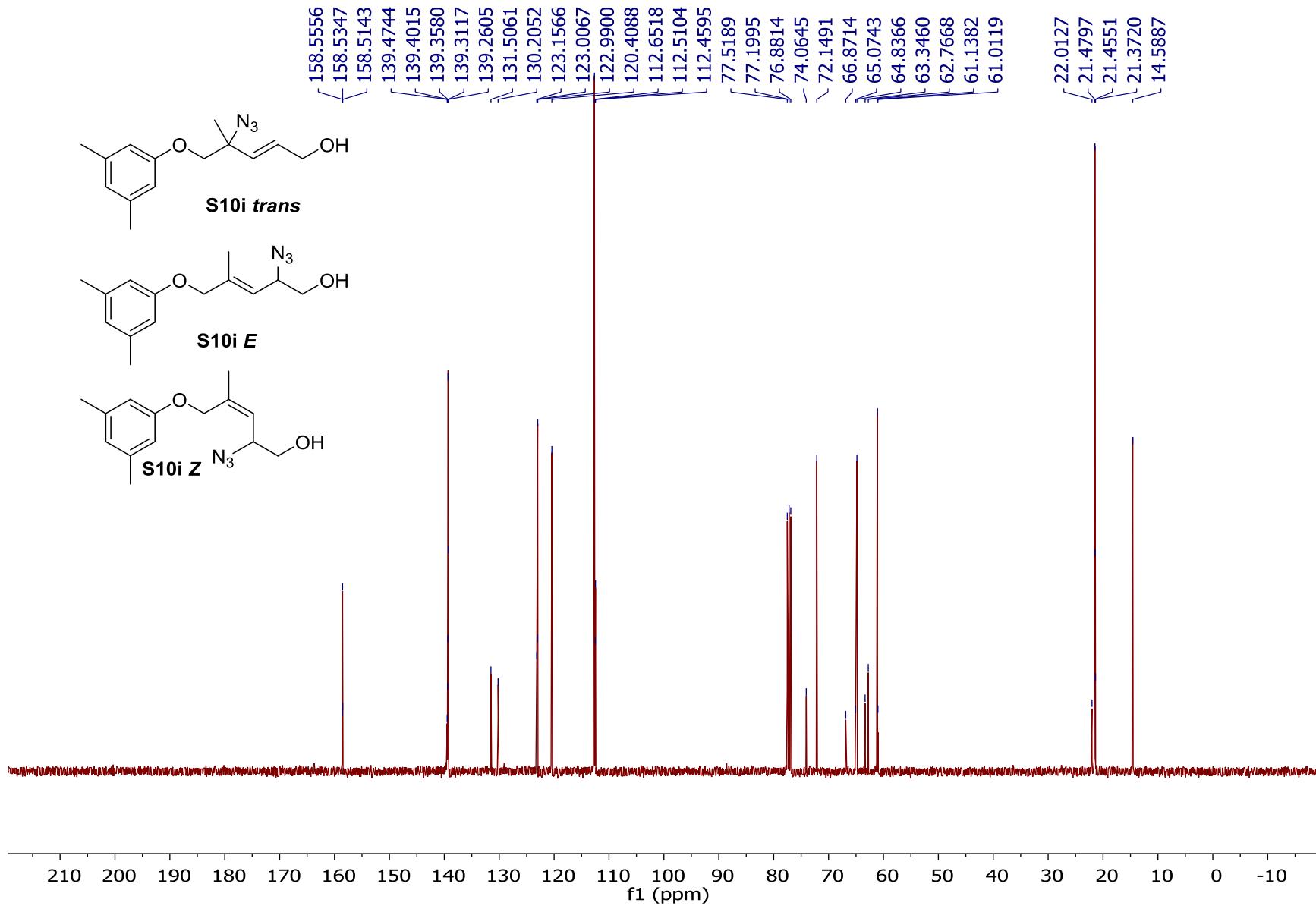




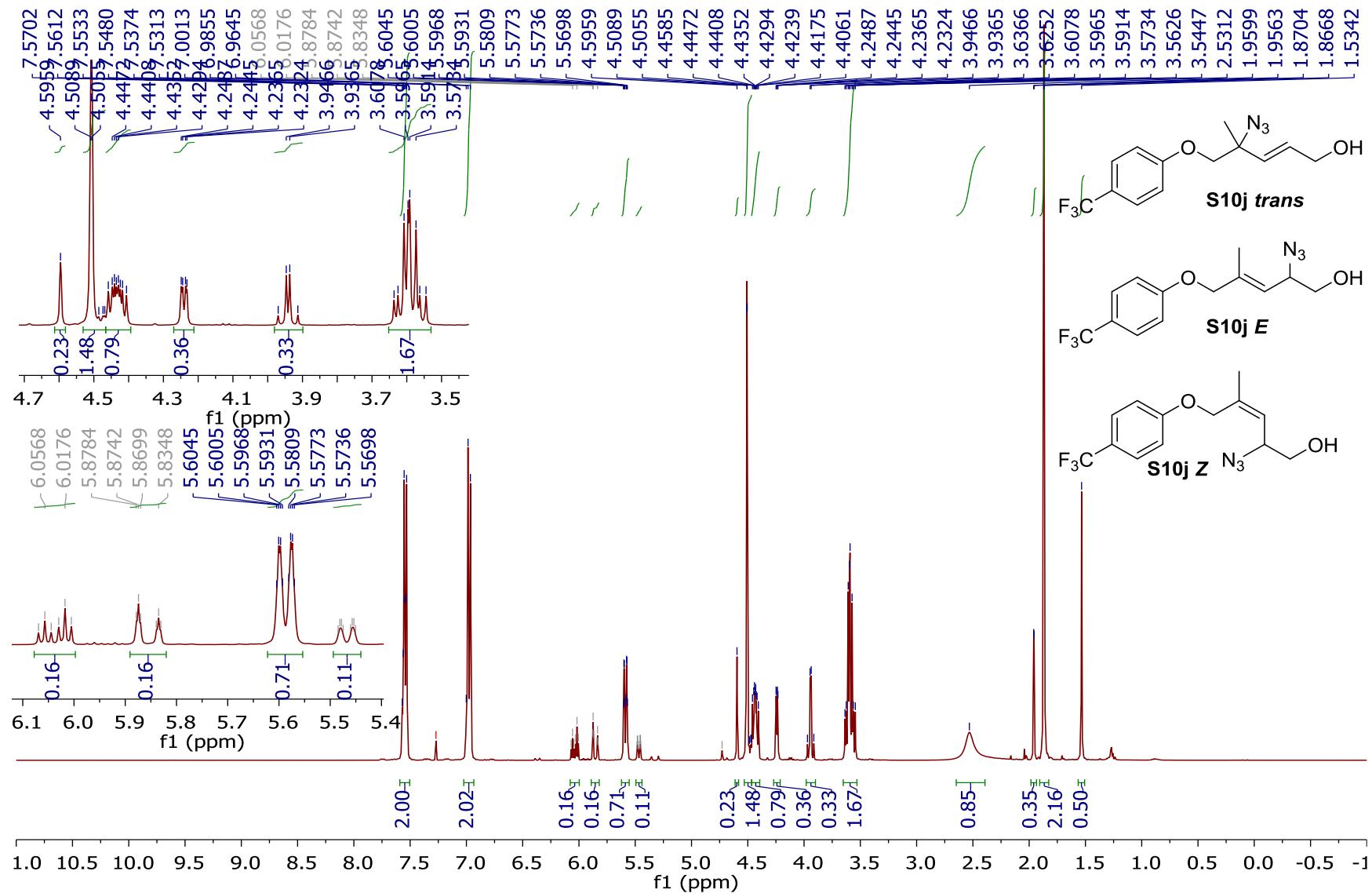
Compound S10h, 101 MHz ¹³C NMR in CDCl₃



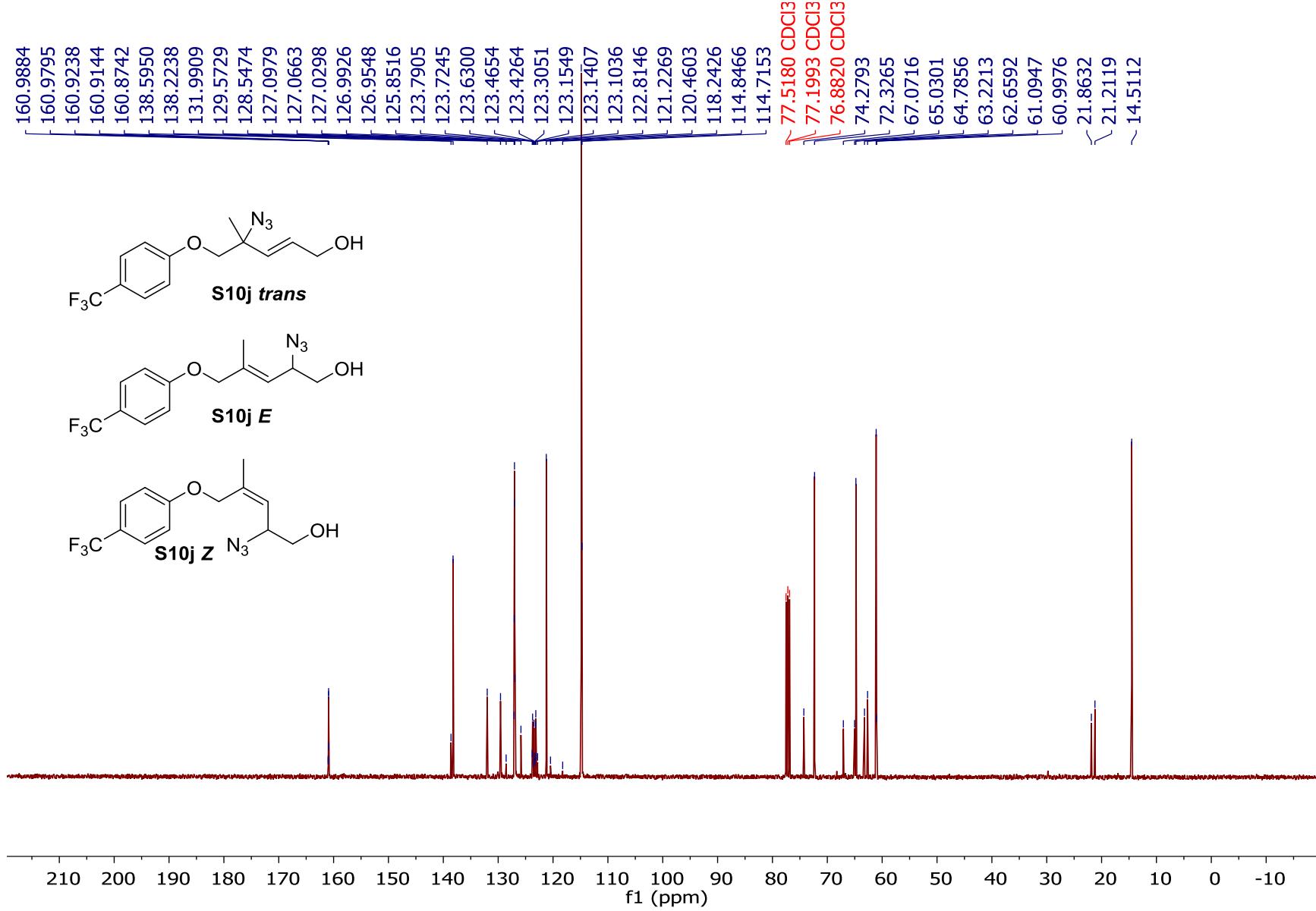
Compound S10i, 400 MHz ^1H NMR in CDCl_3



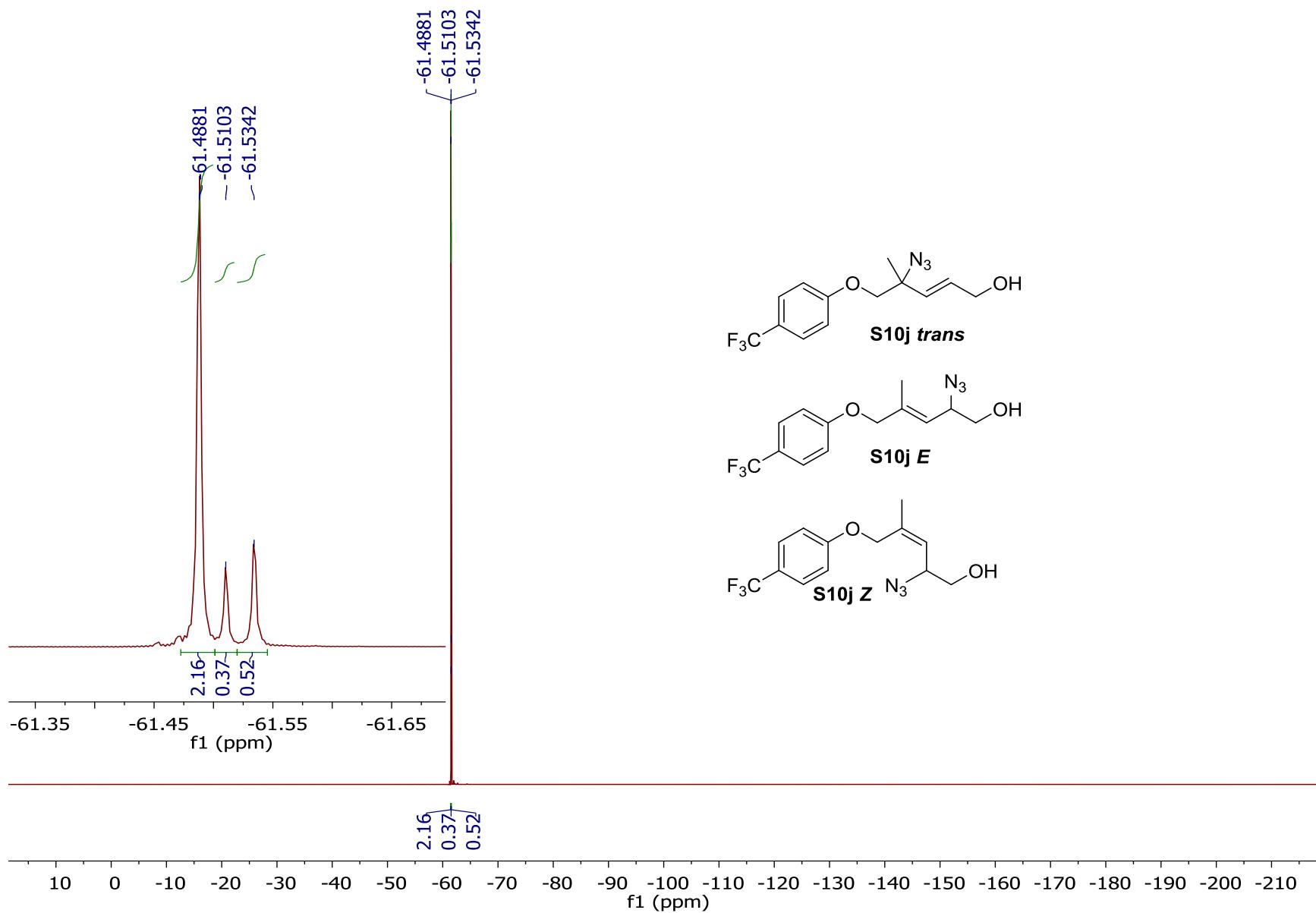
Compound S10i, 101 MHz ^{13}C NMR in CDCl_3

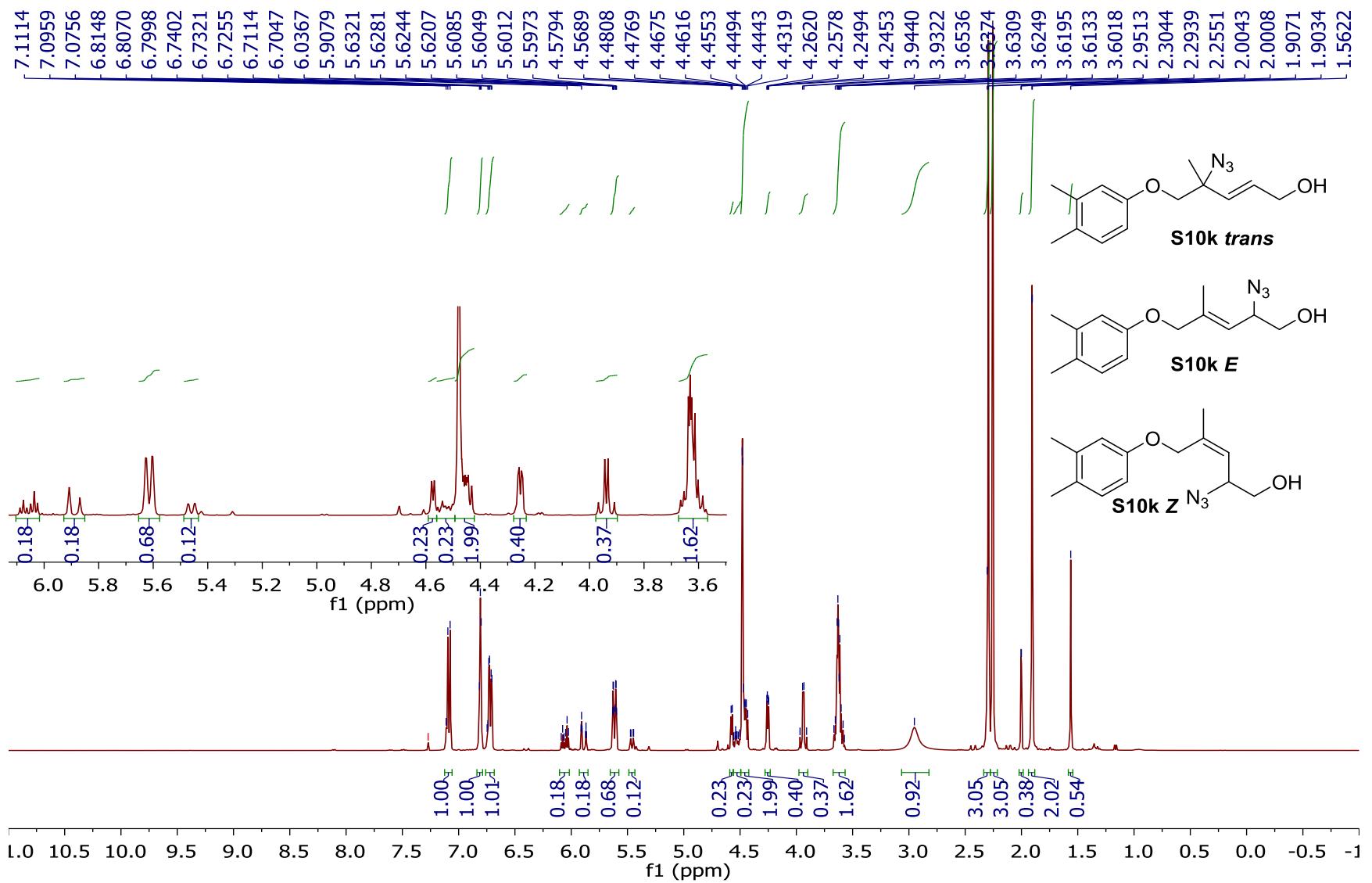


Compound S10j, 400 MHz ^1H NMR Spectrum in CDCl_3

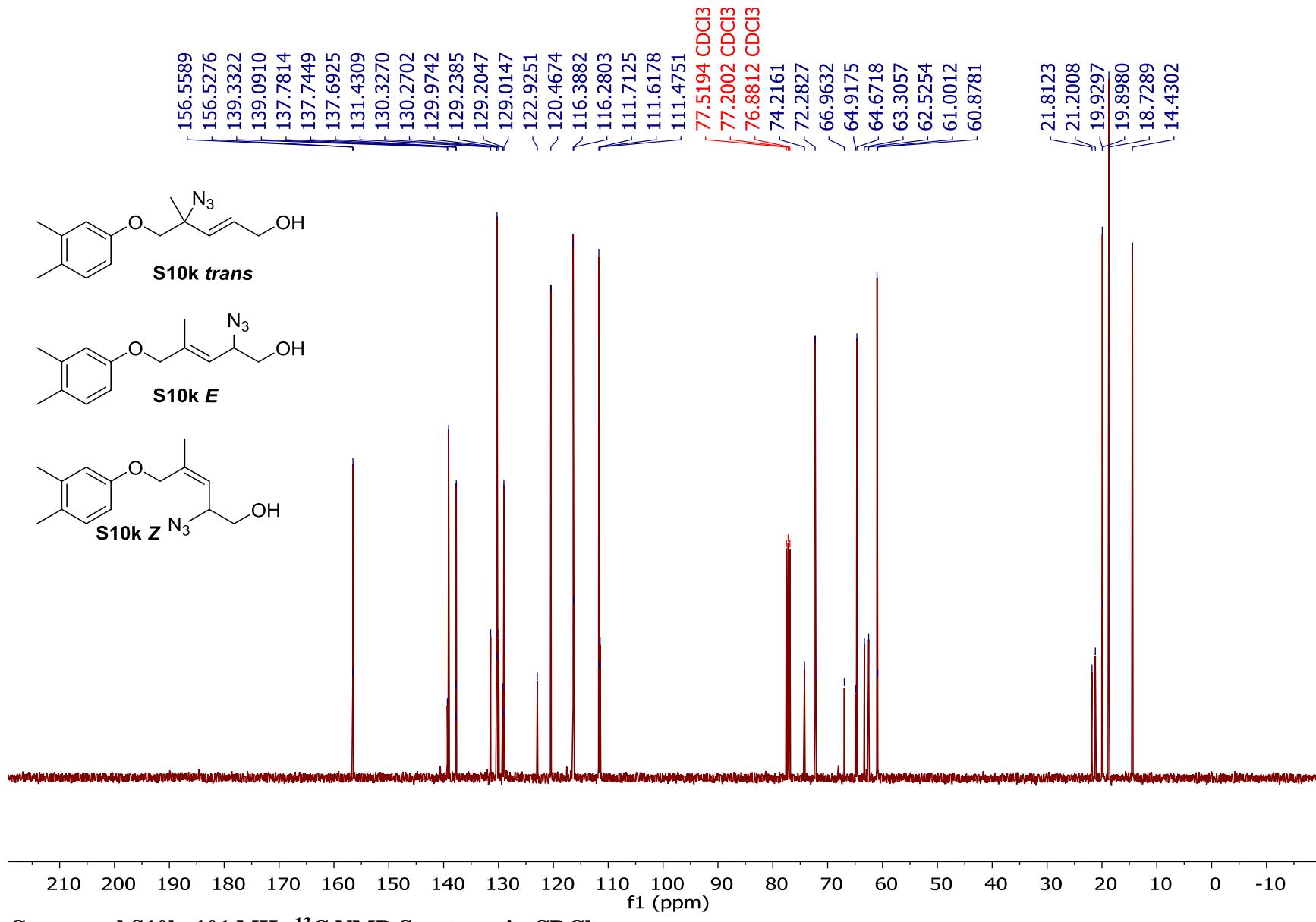


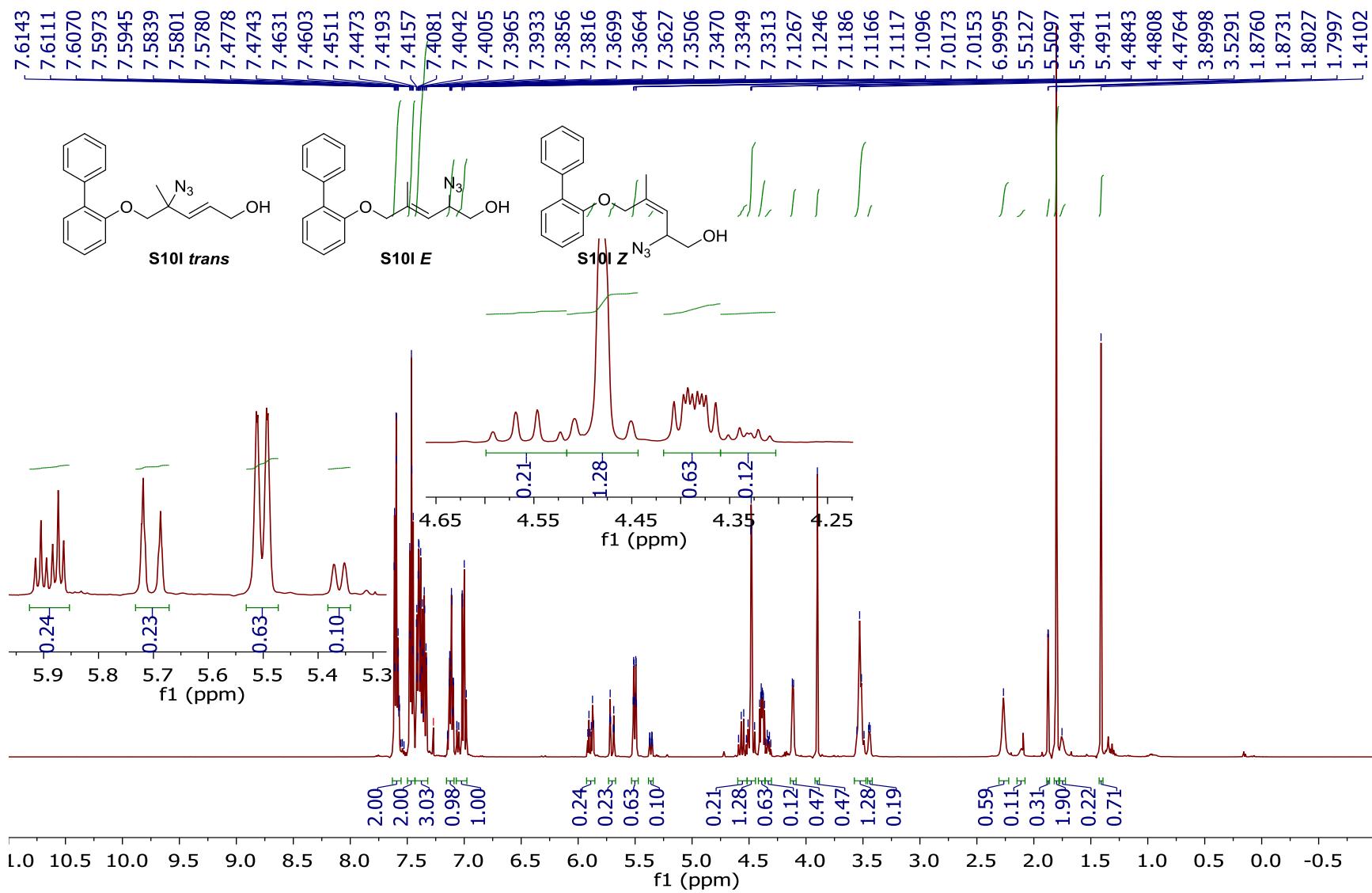
Compound S10j, 101 MHz ¹³C NMR Spectrum in CDCl₃



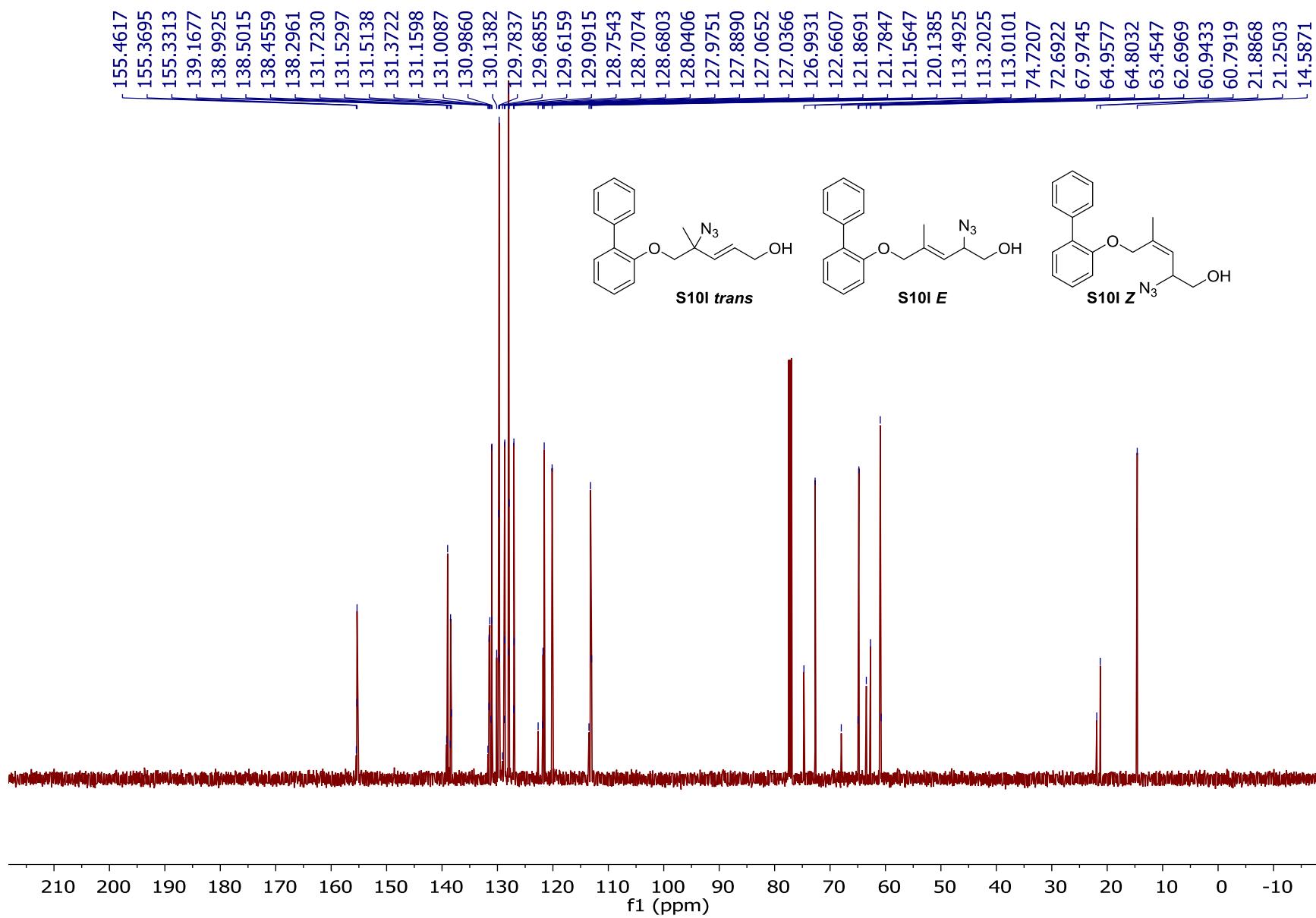


Compound S10k, 400 MHz ^1H NMR Spectrum in CDCl_3

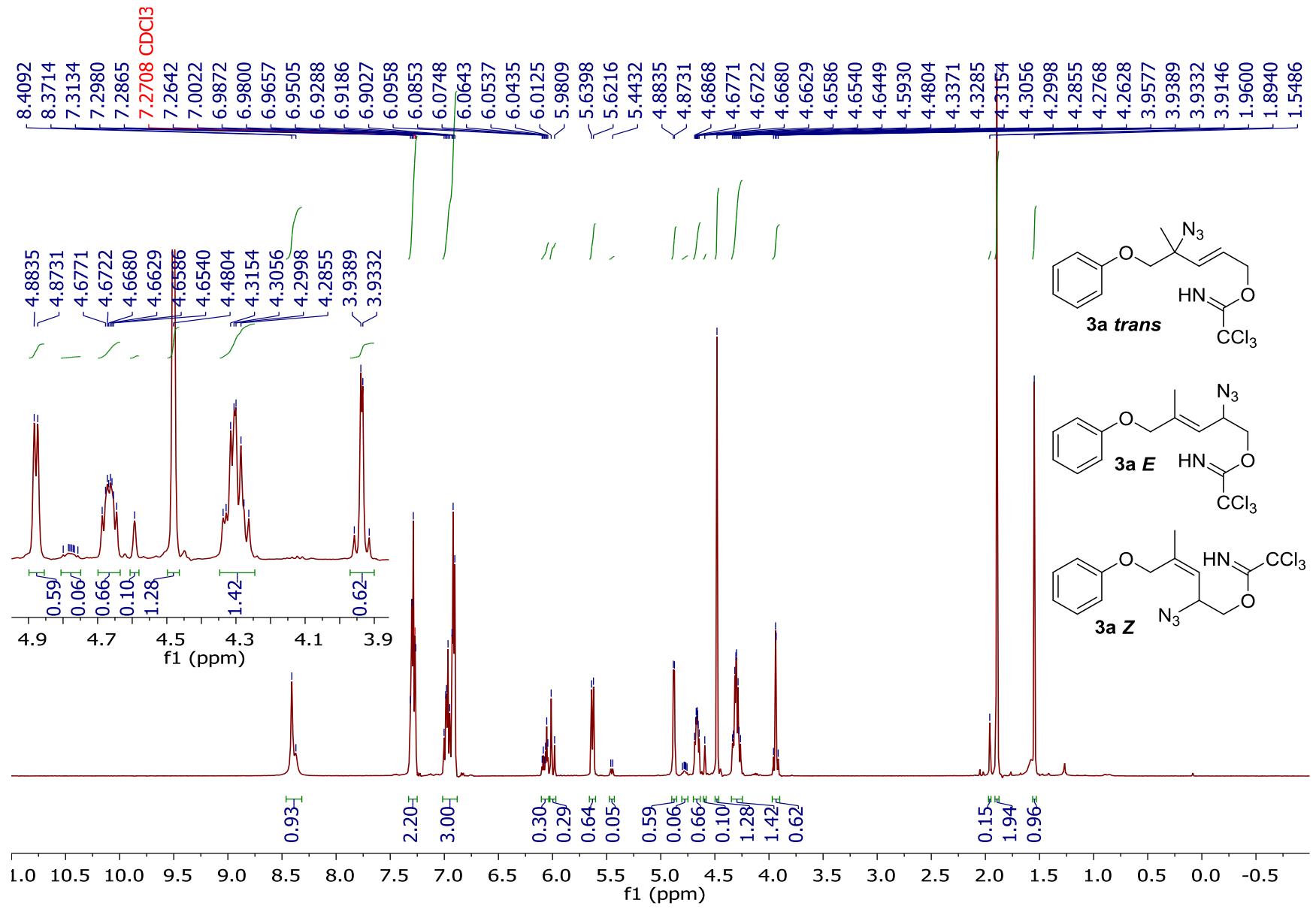




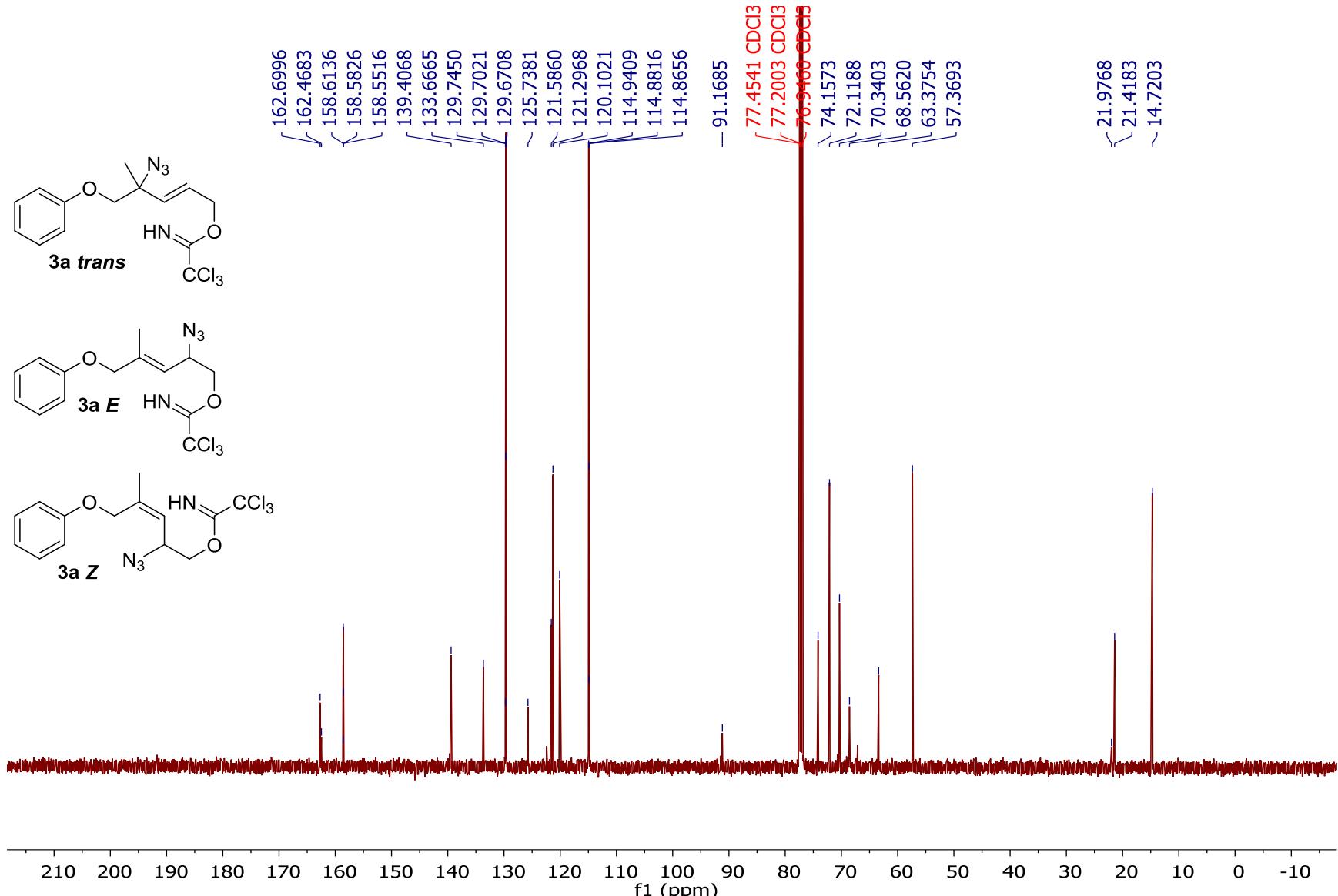
Compound S10l, 500 MHz ^1H NMR Spectrum in CDCl_3



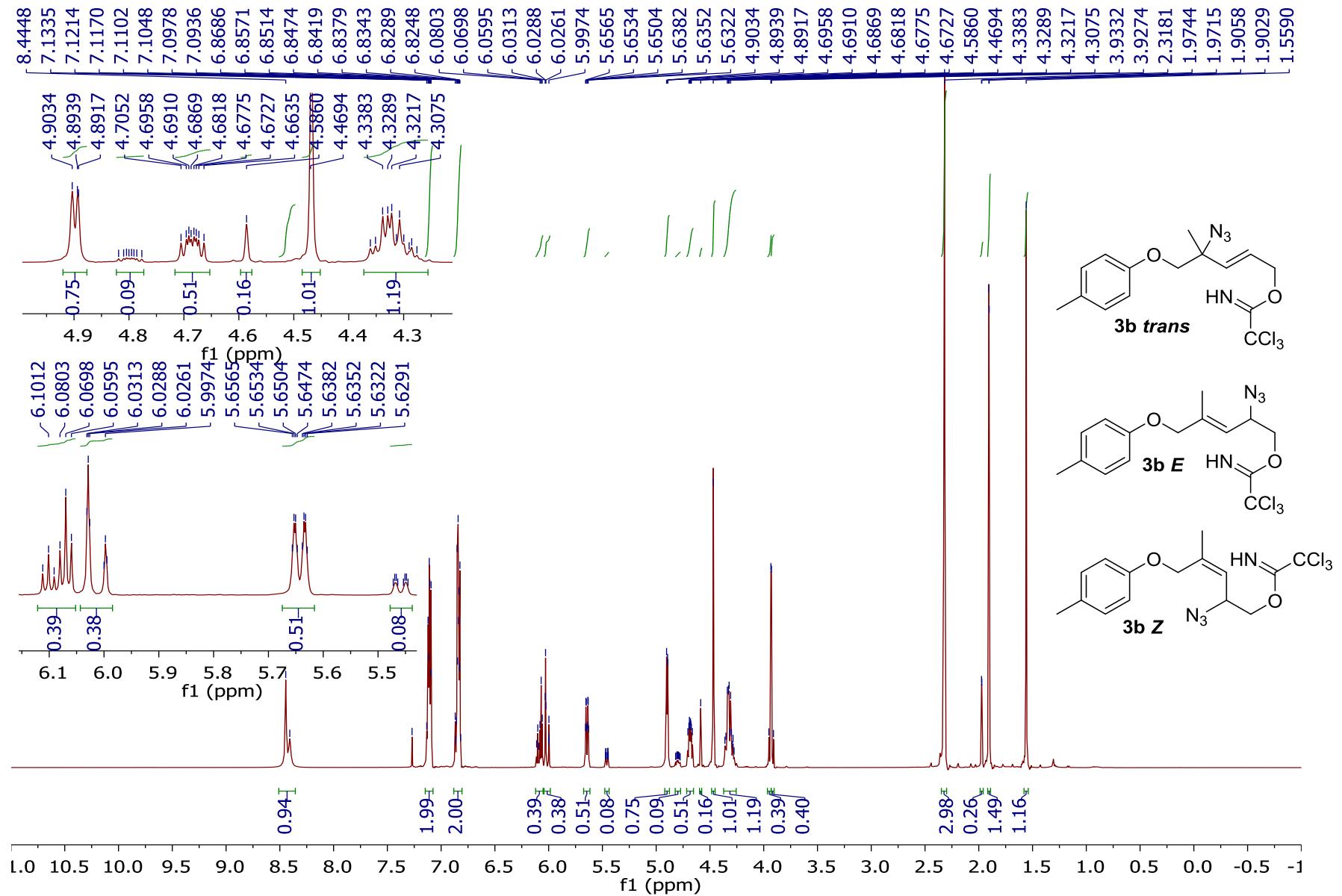
Compound S10l, 126 MHz ^{13}C NMR Spectrum in CDCl_3



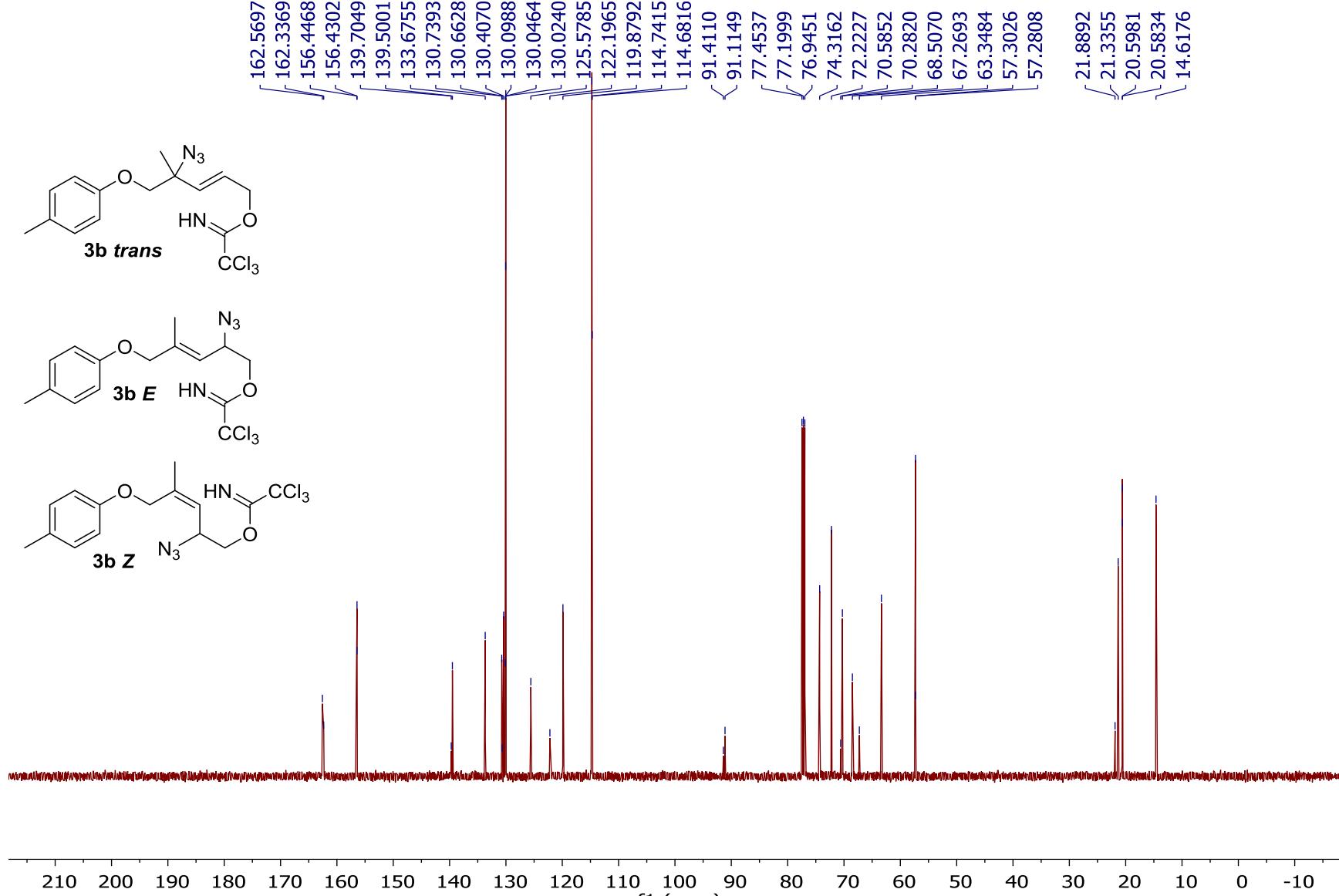
Compound 3a, 500 MHz ^1H NMR in CDCl_3



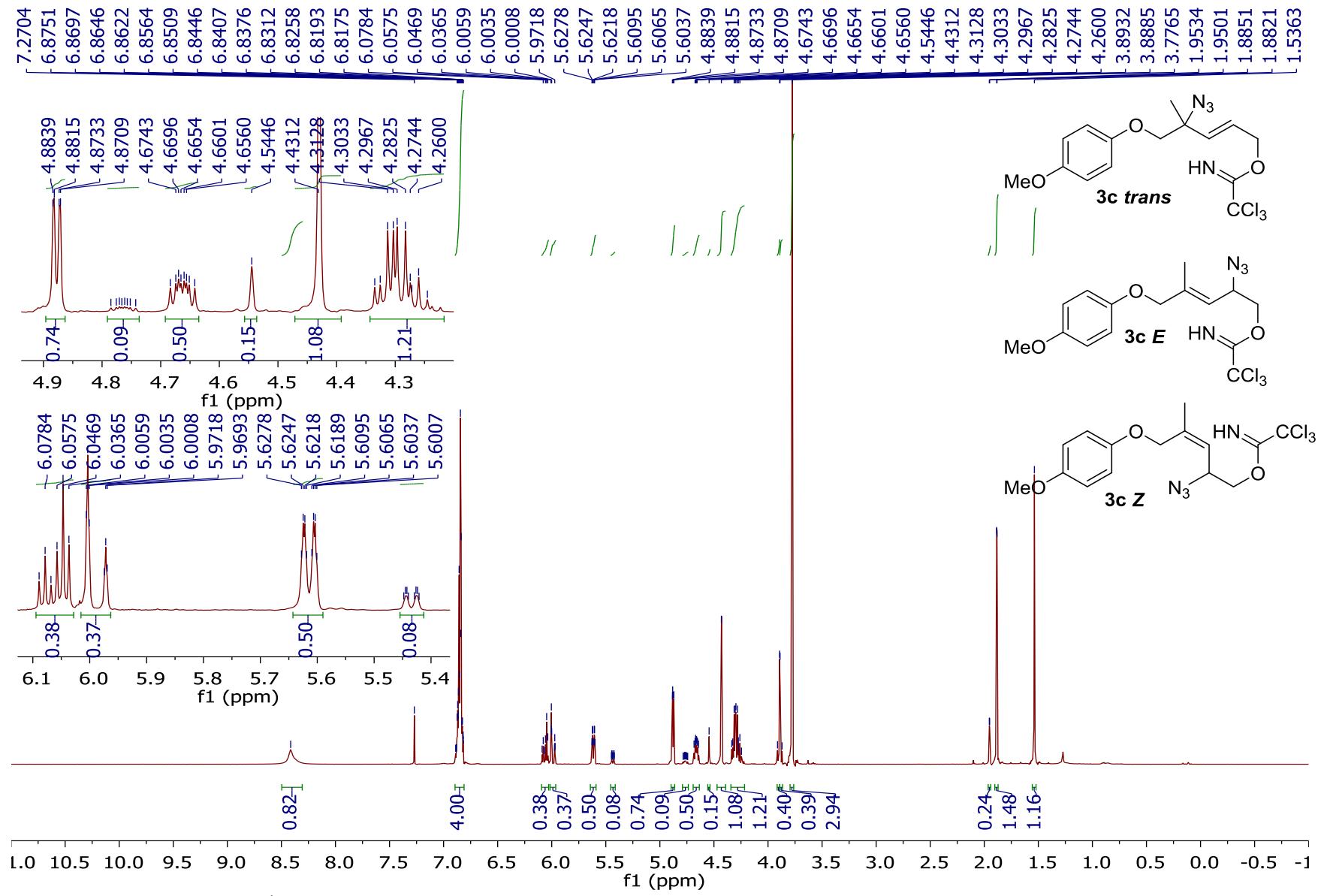
Compound 3a, 101 MHz ¹³C NMR in CDCl₃



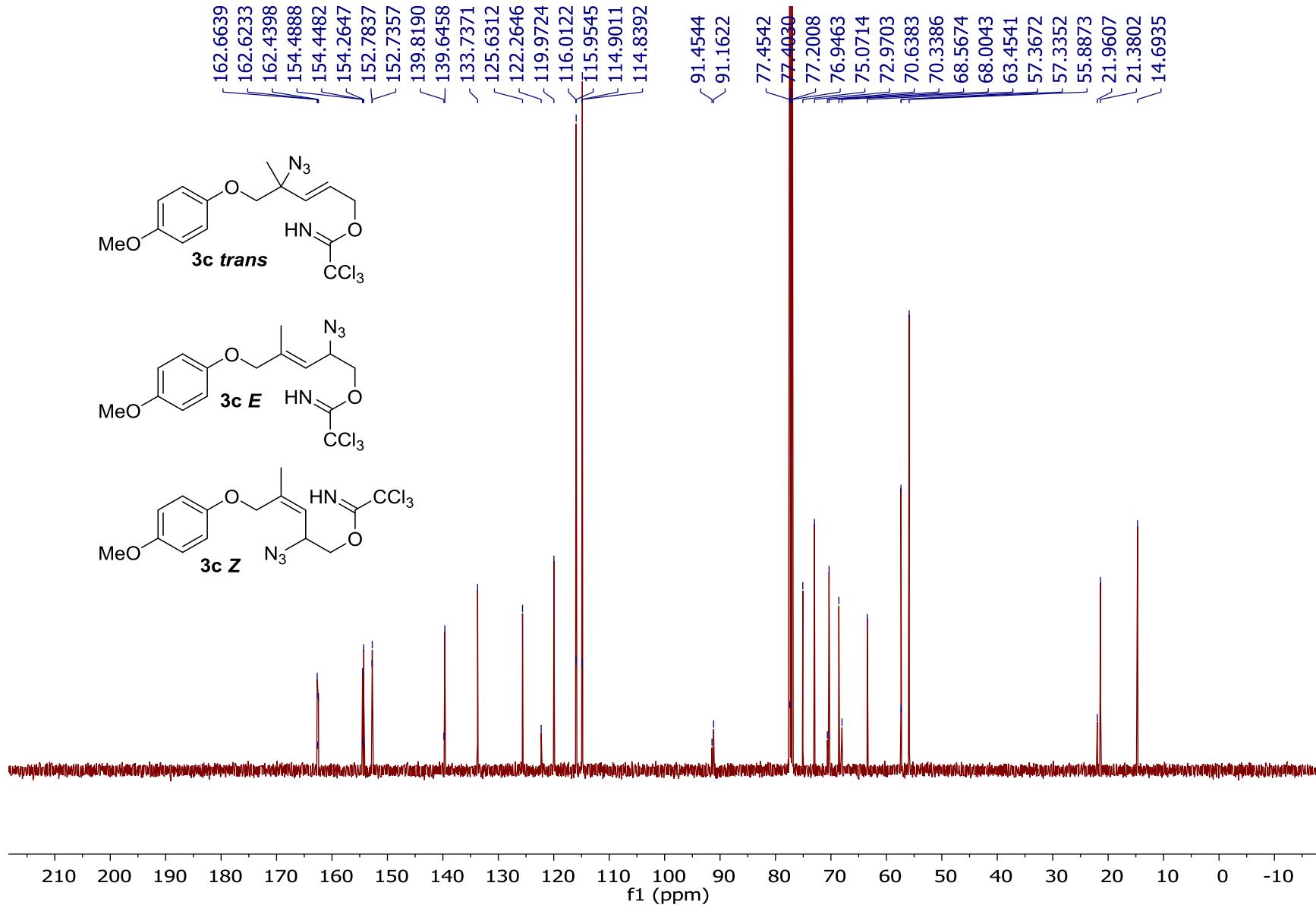
Compound 3b, 400 MHz ^1H NMR in CDCl_3

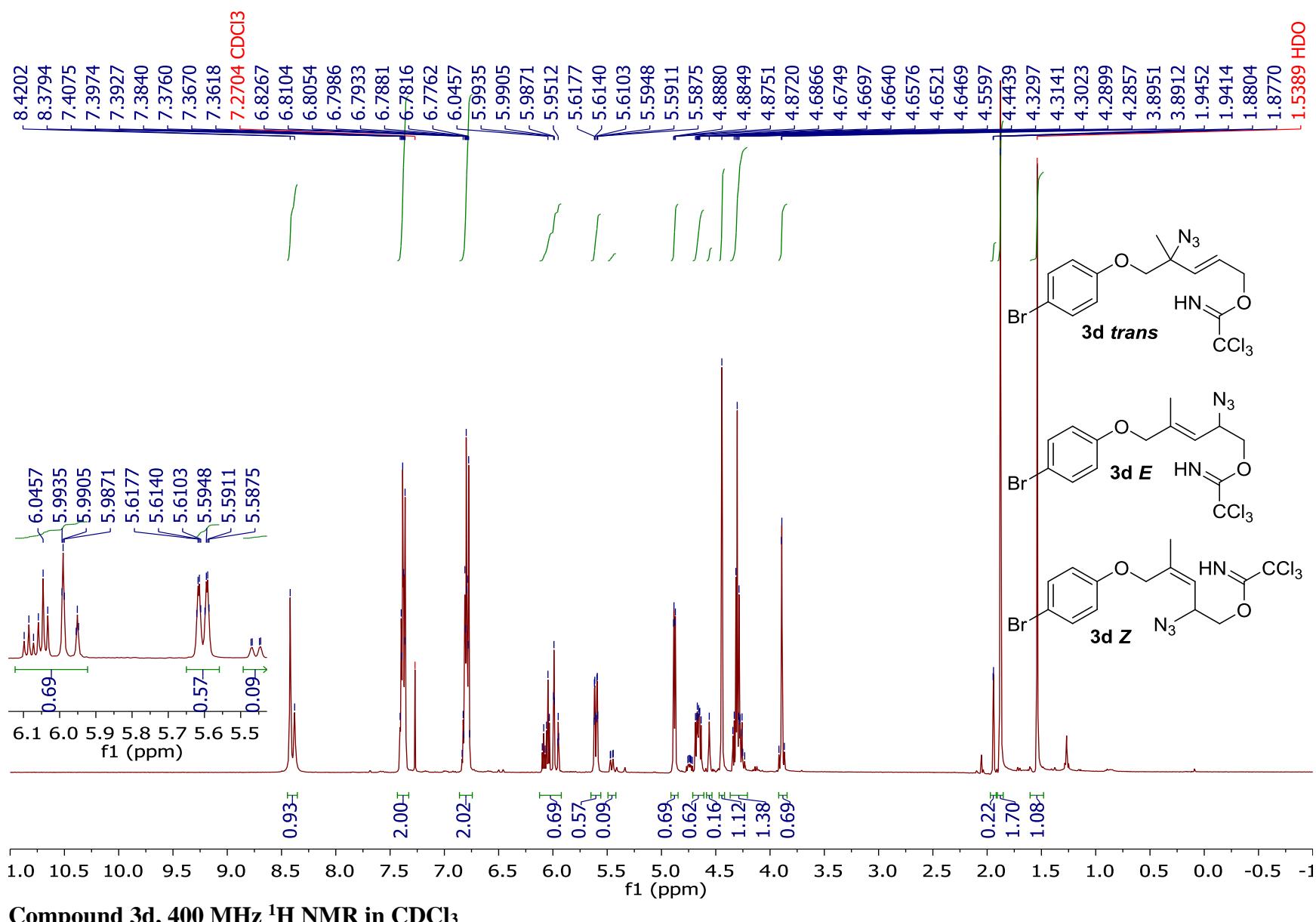


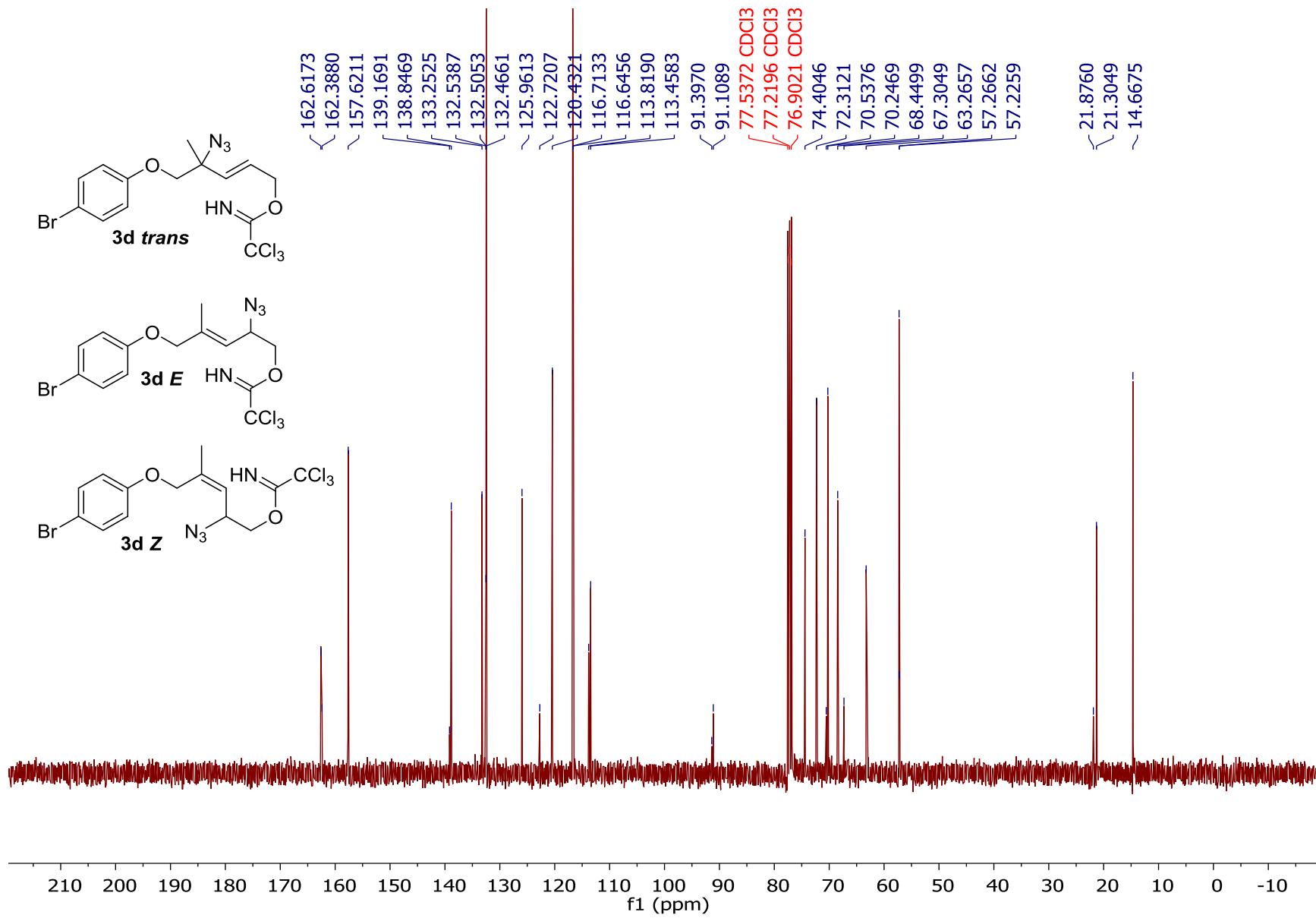
Compound 3b, 101 MHz ^{13}C NMR in CDCl_3



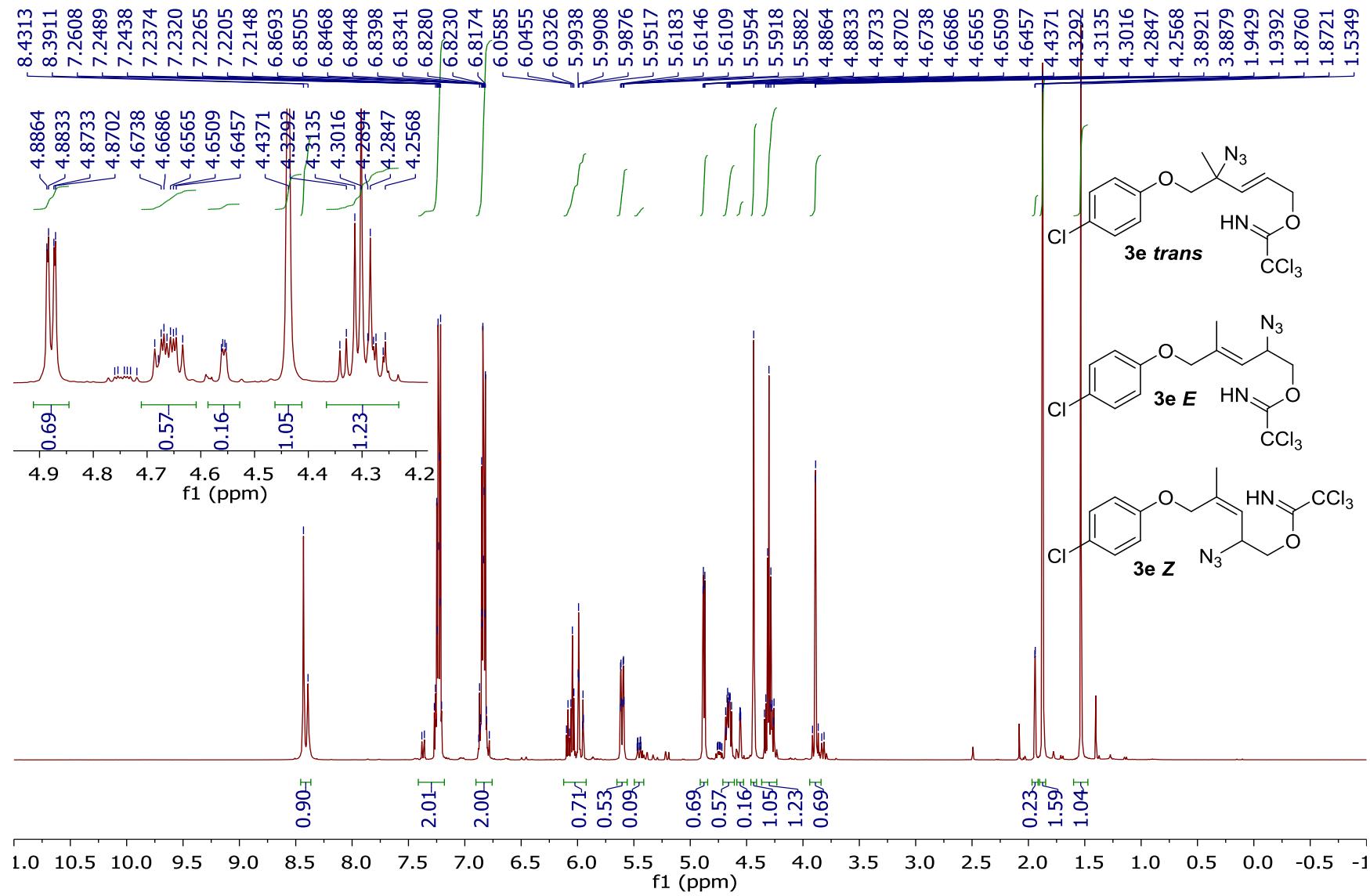
Compound 3c, 400 MHz ^1H NMR in CDCl_3

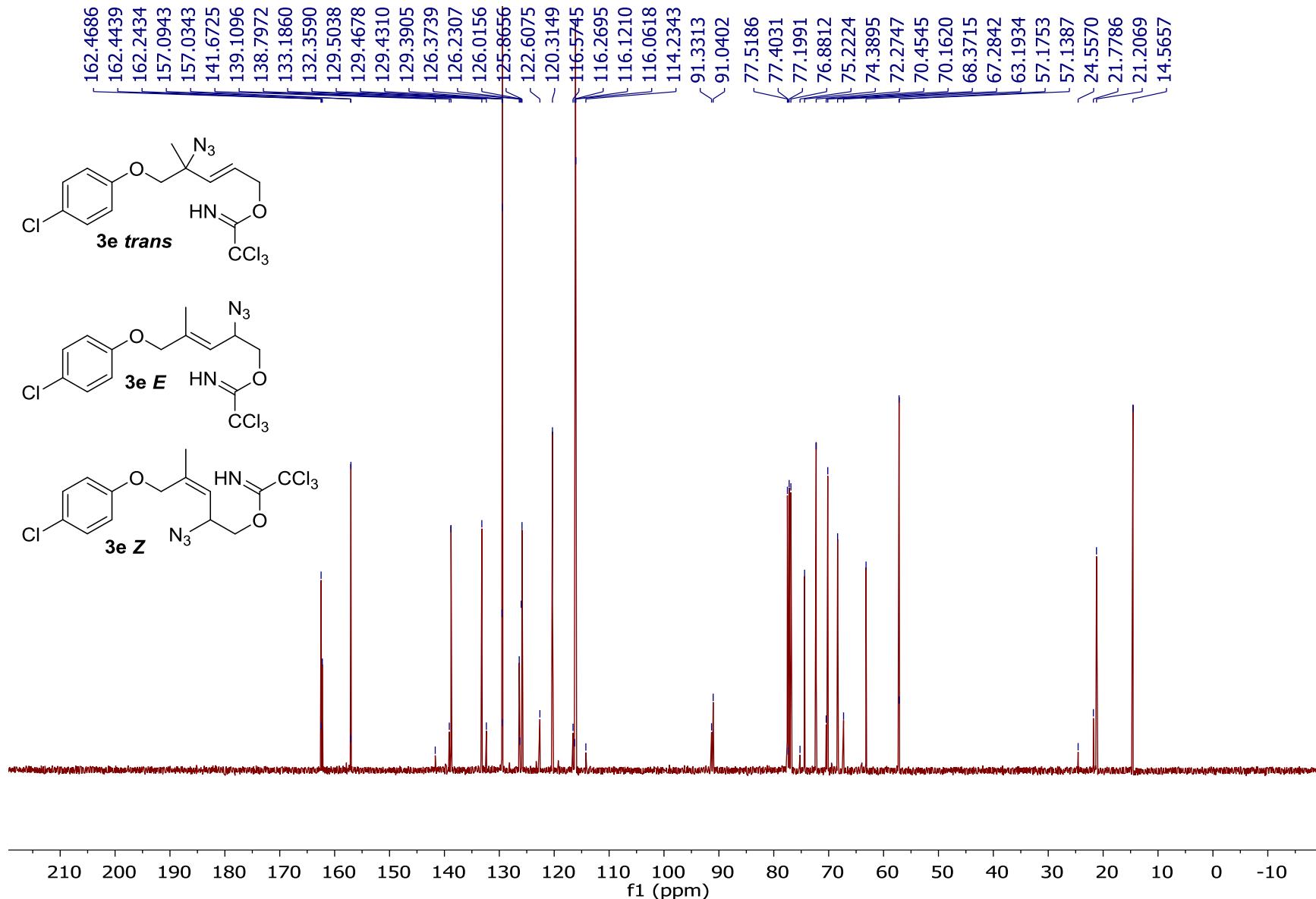


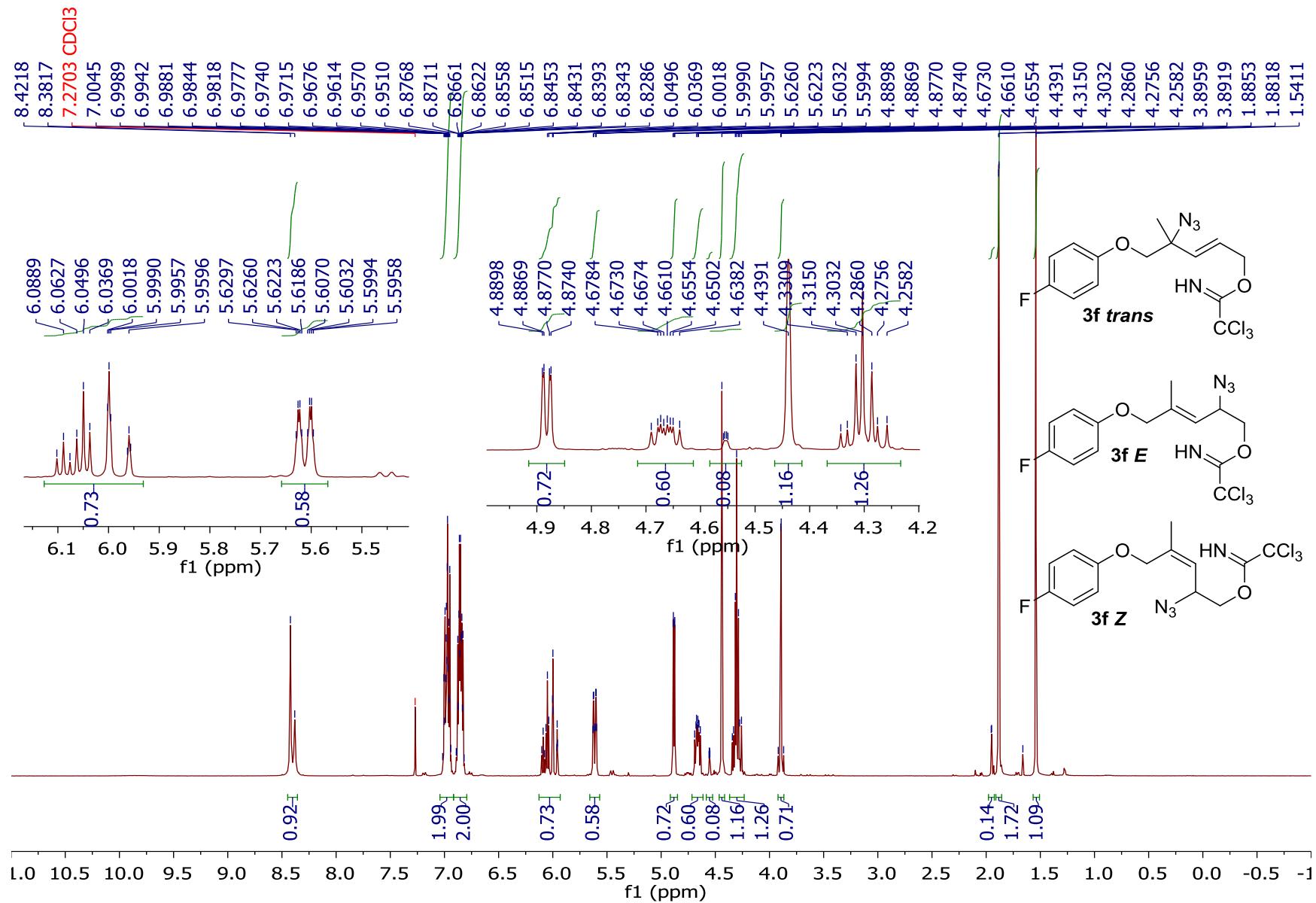


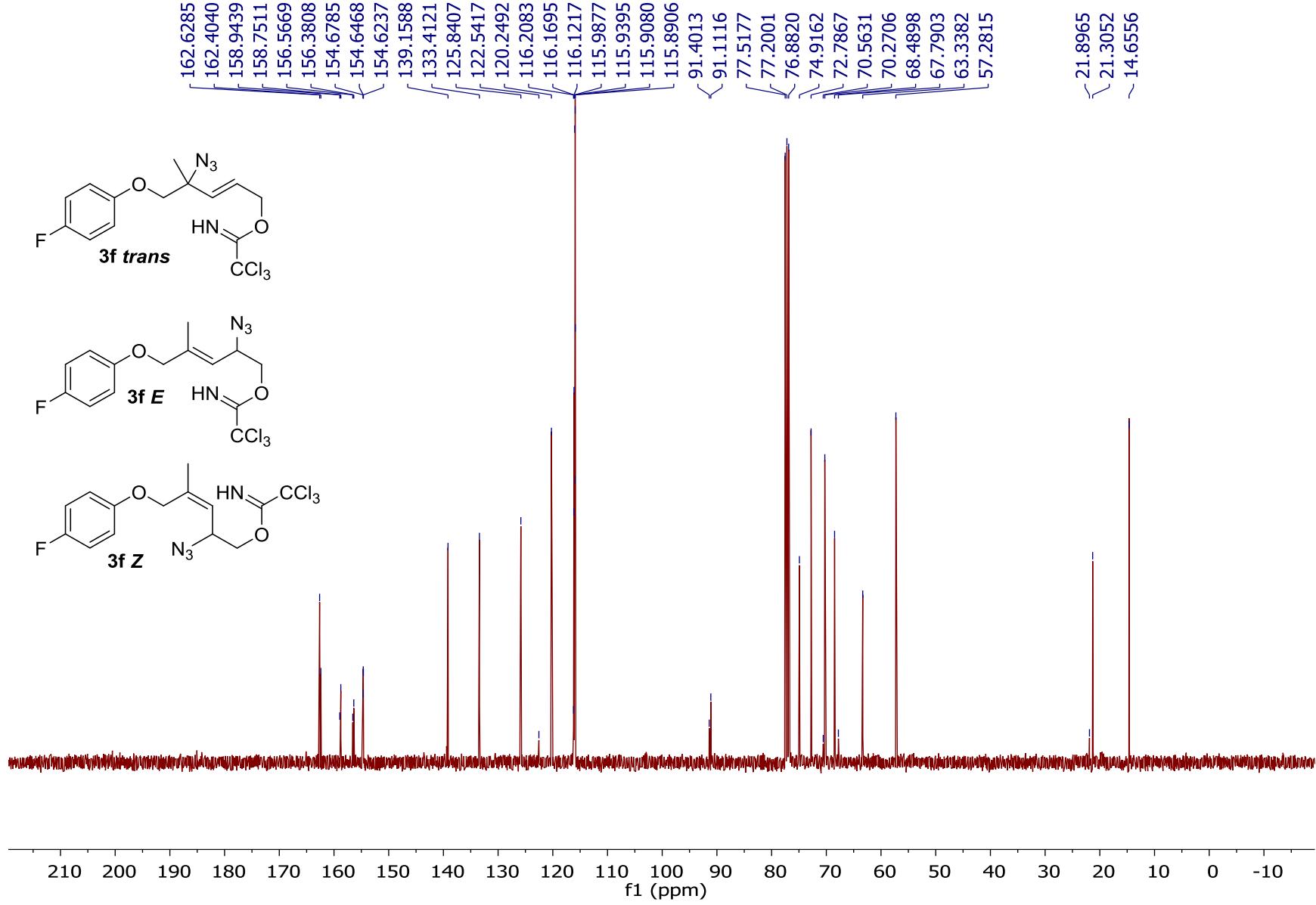


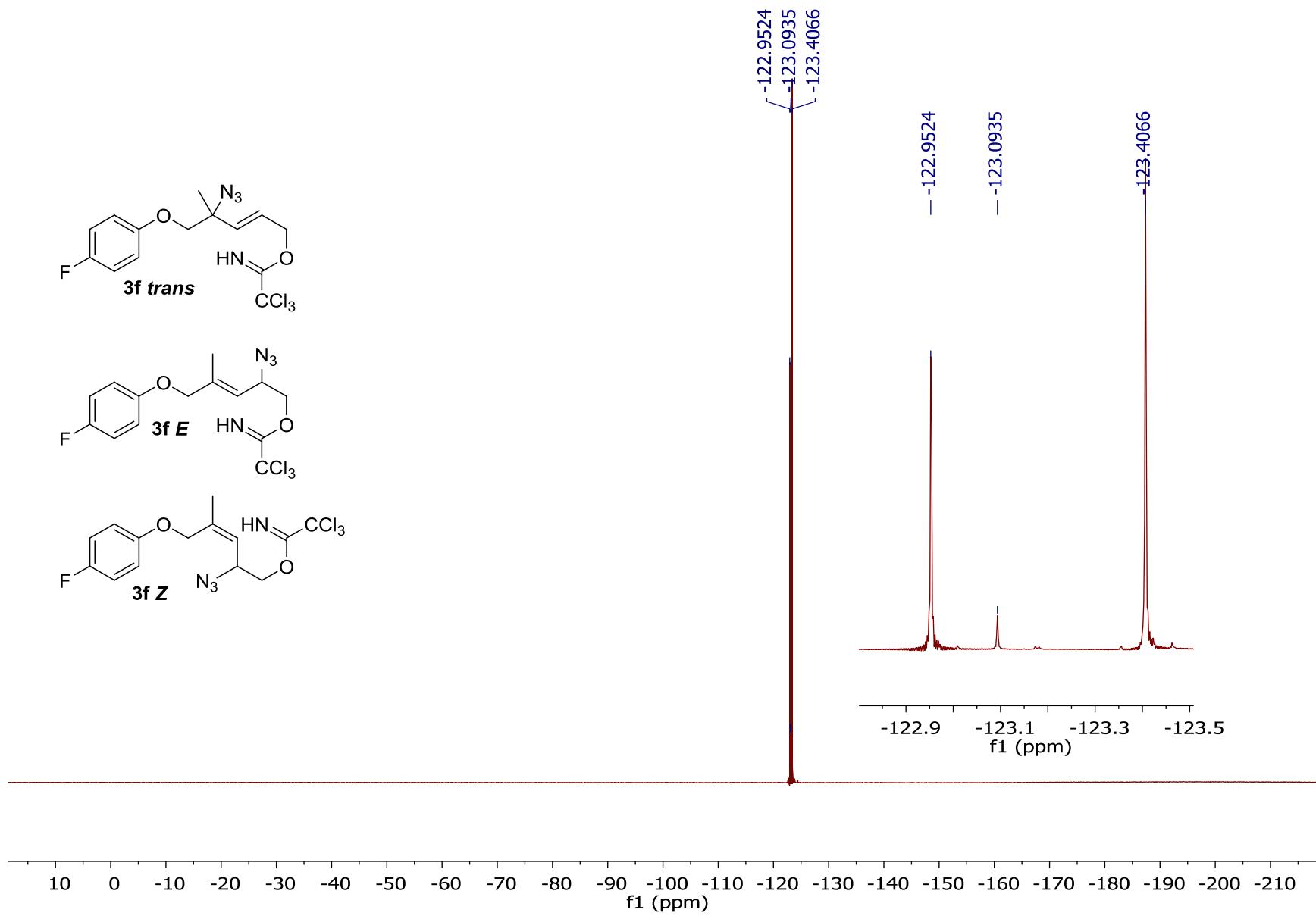
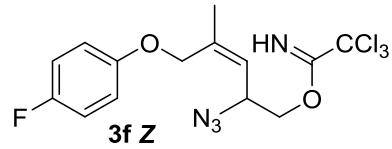
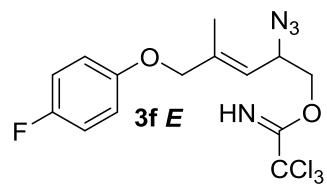
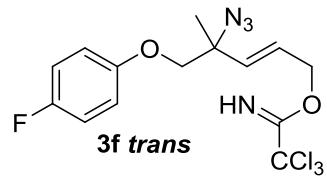
Compound **3d**, 101 MHz ¹³C NMR in CDCl_3



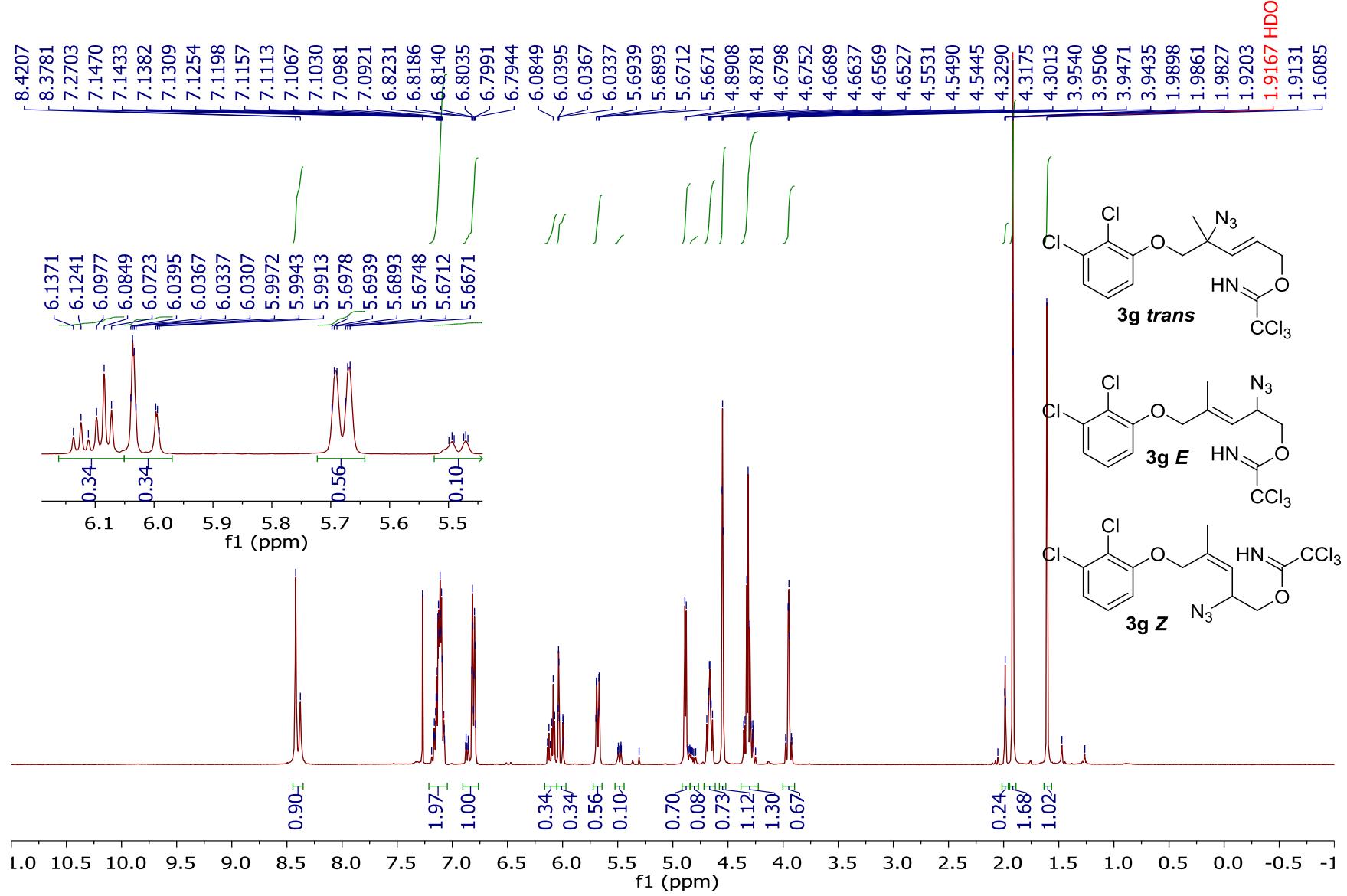


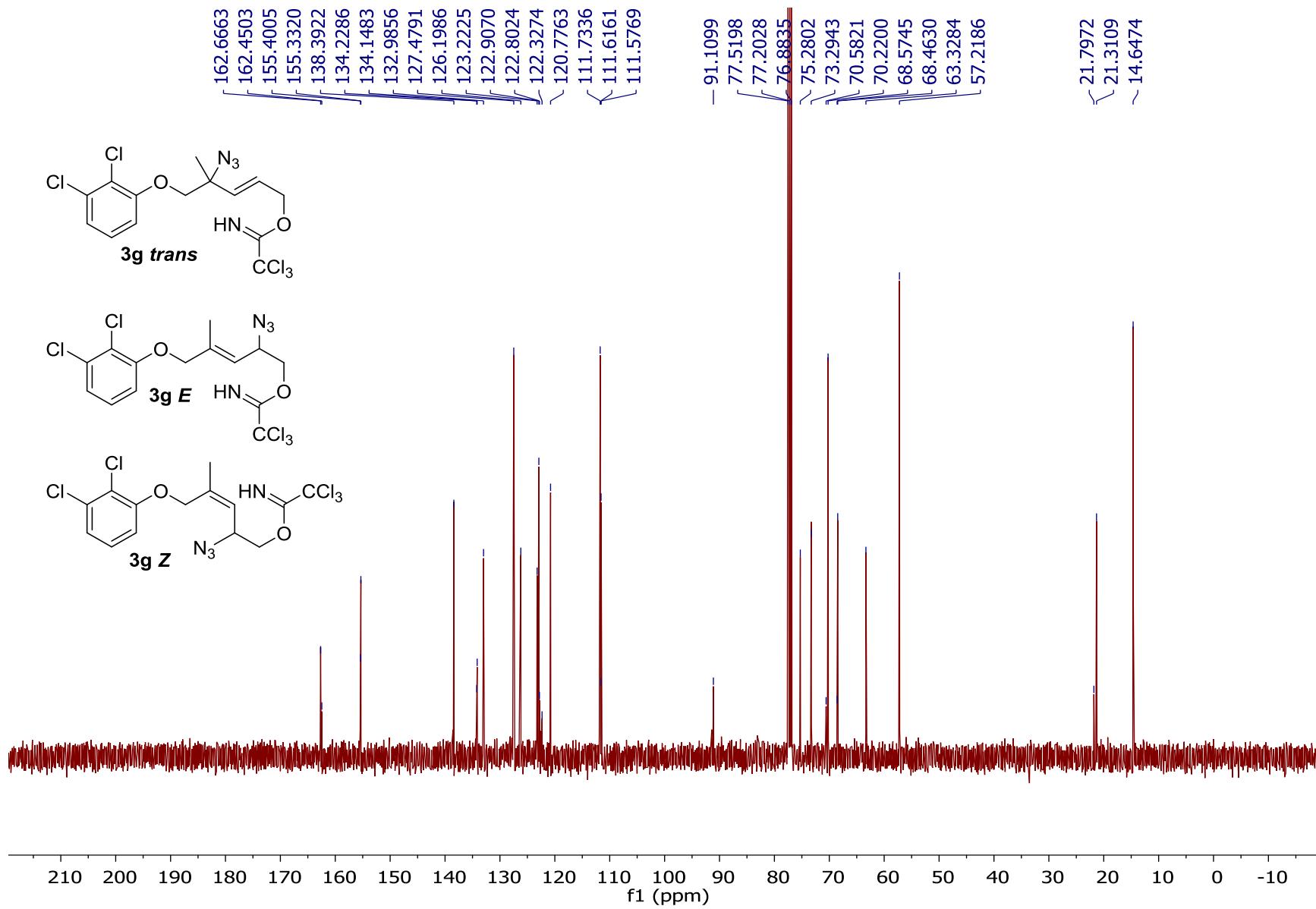


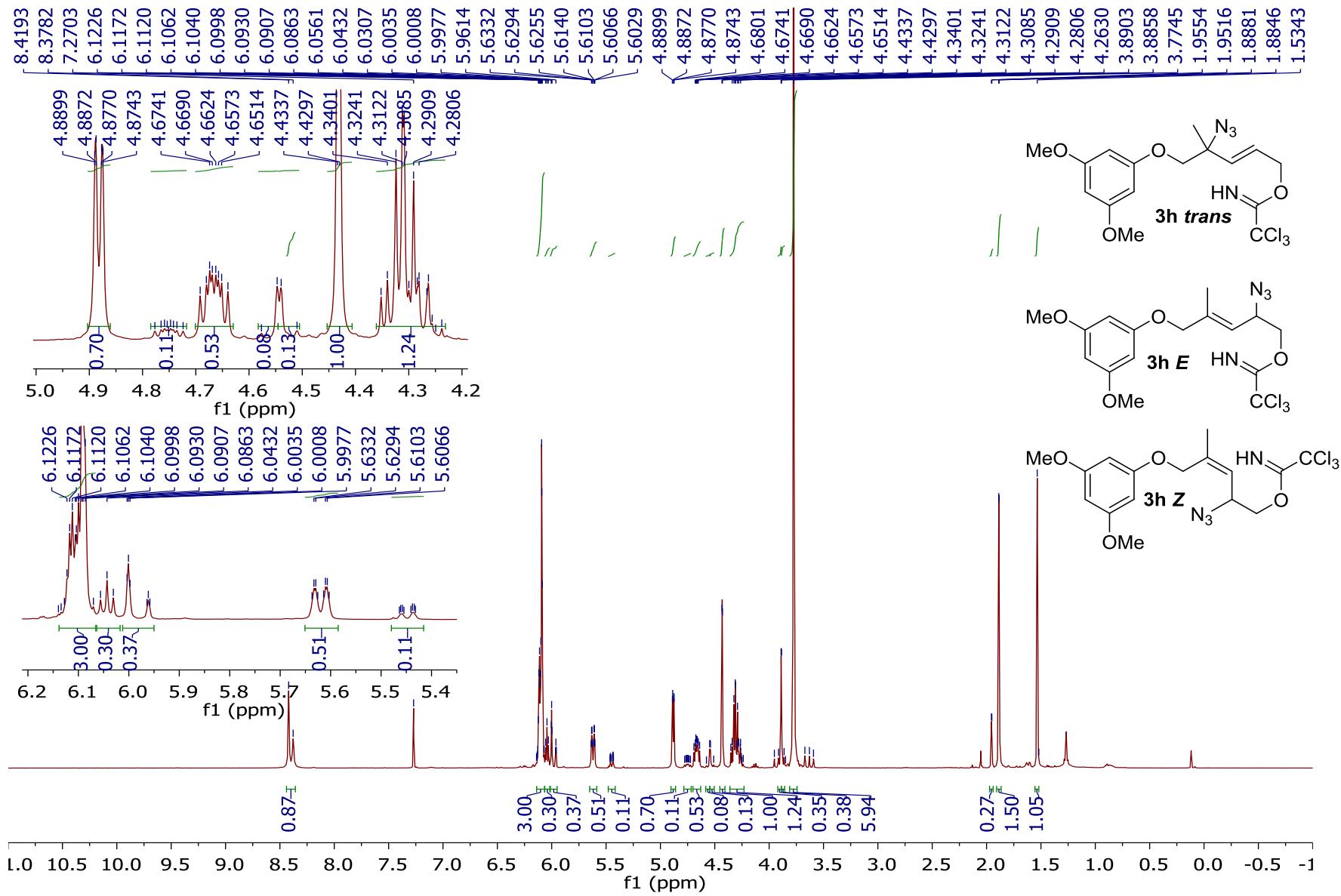


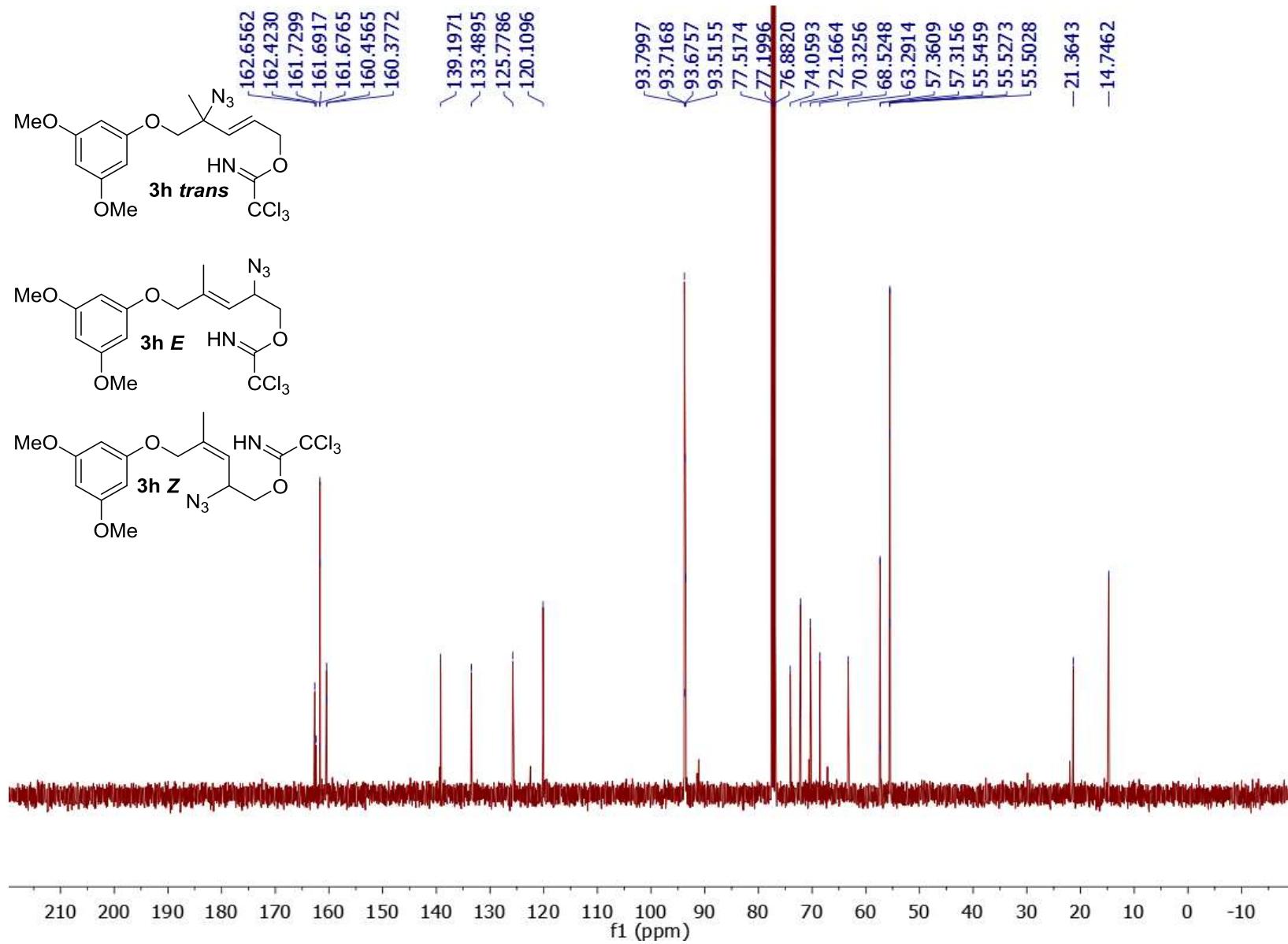


Compound 3f, 376 MHz ¹⁹F NMR in CDCl₃

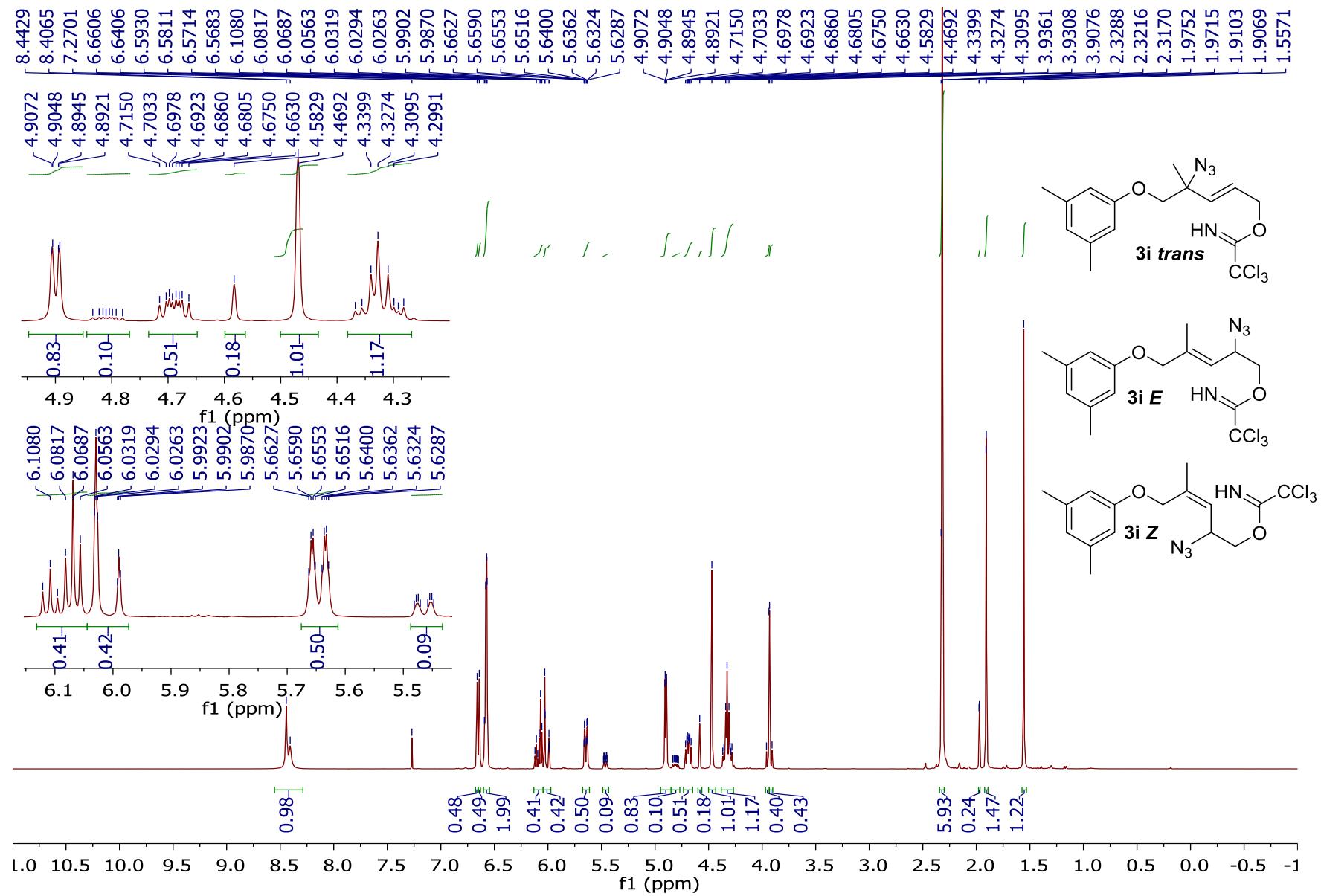




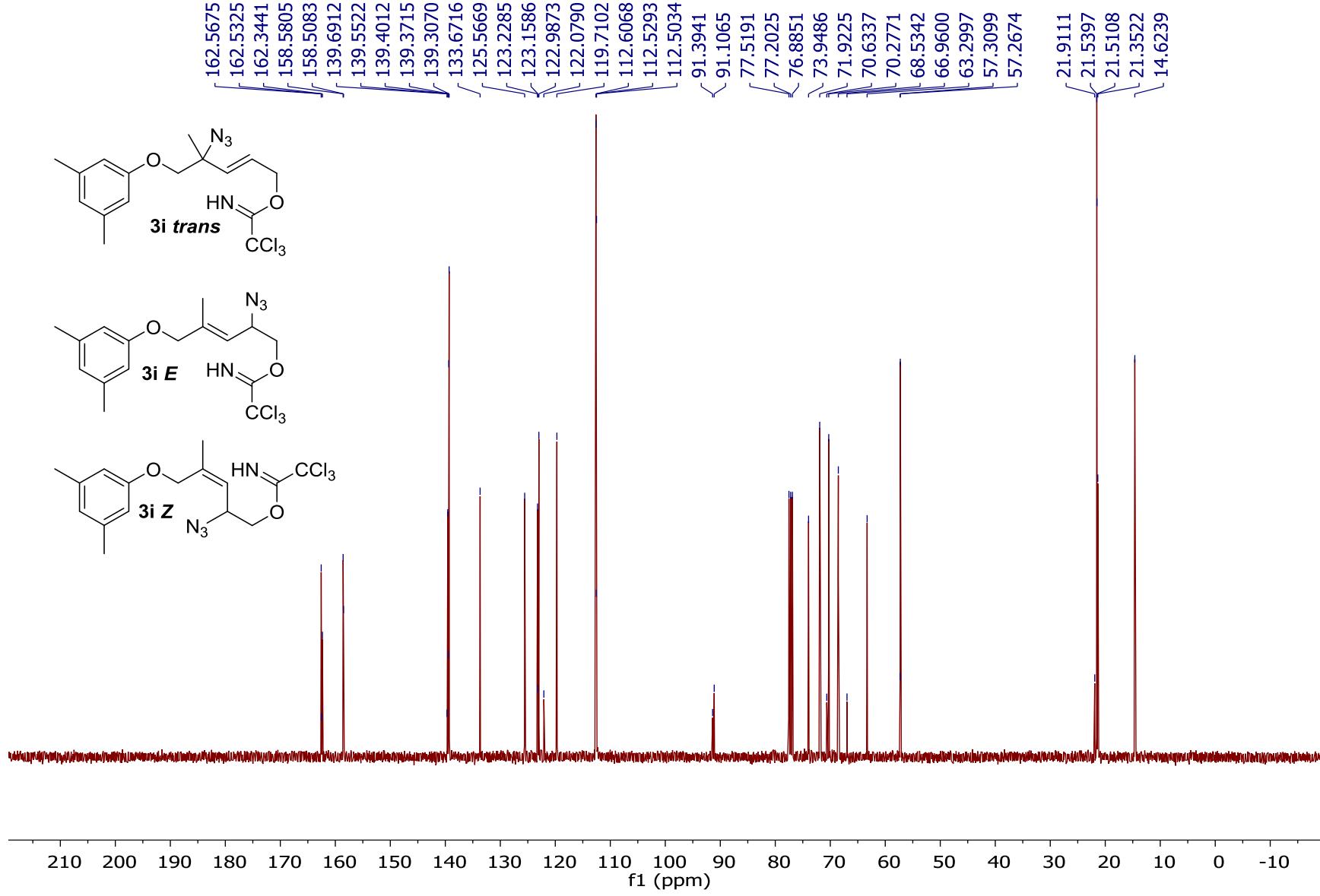


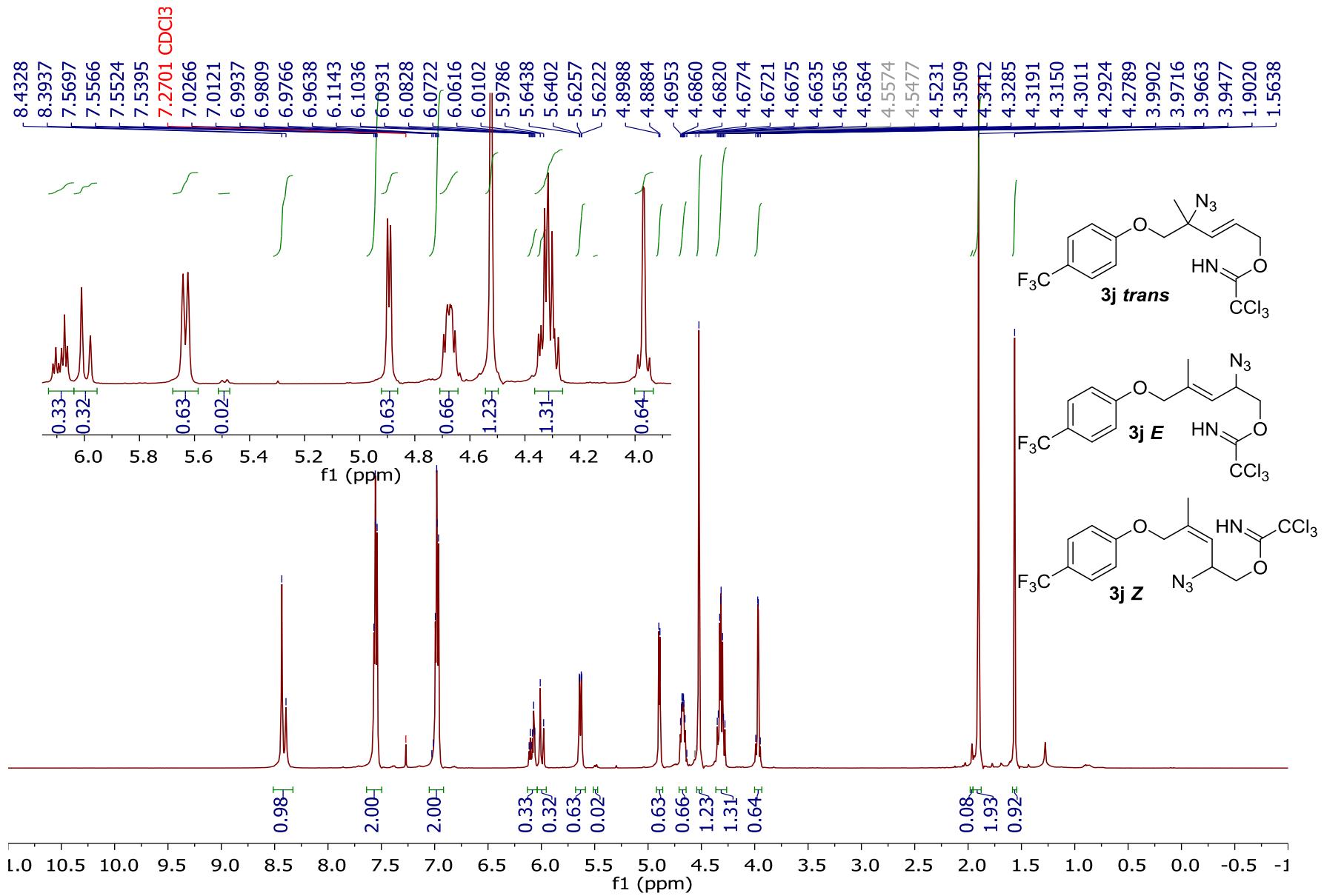


Compound 3h, 101 MHz ^{13}C NMR in CDCl_3

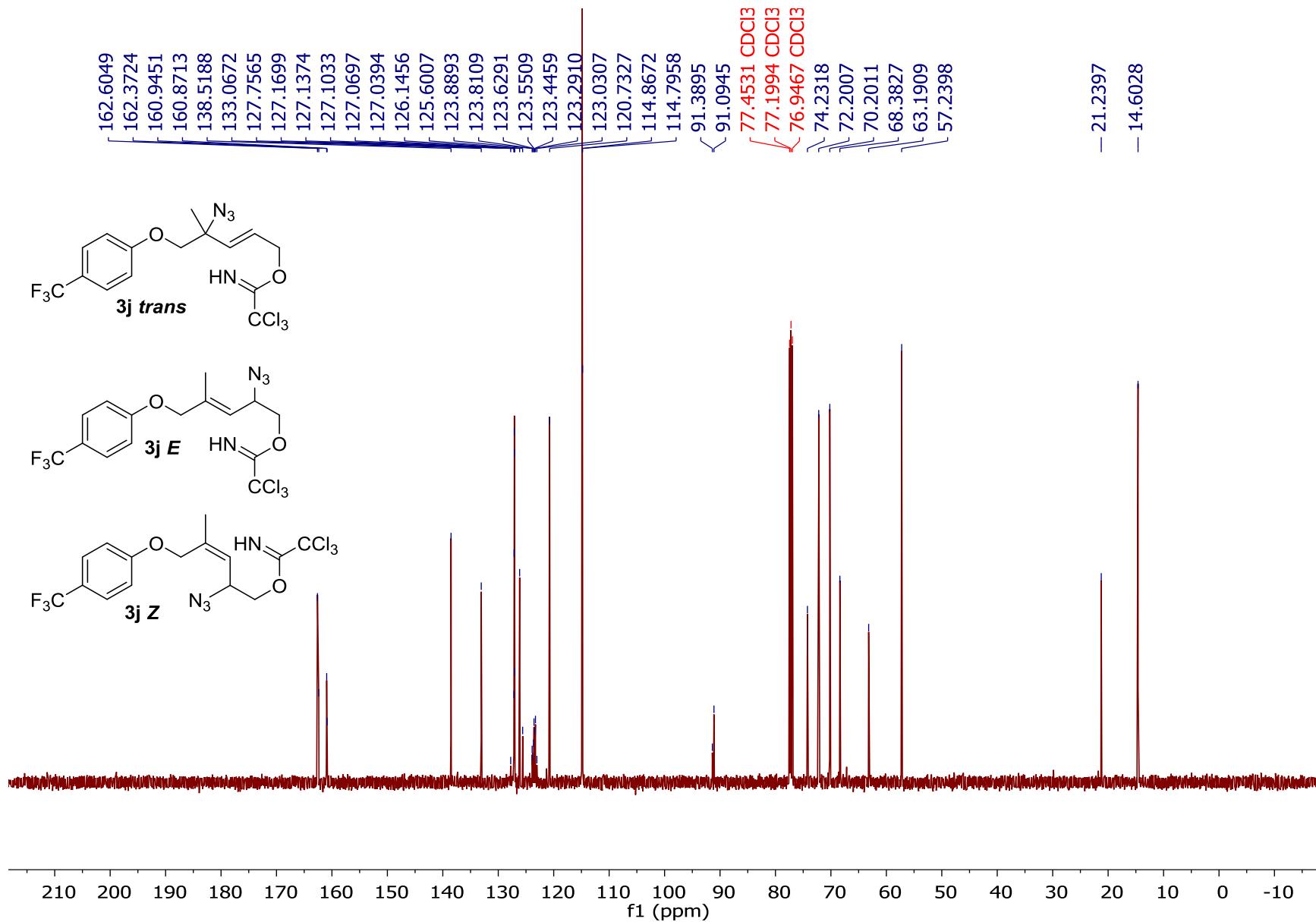


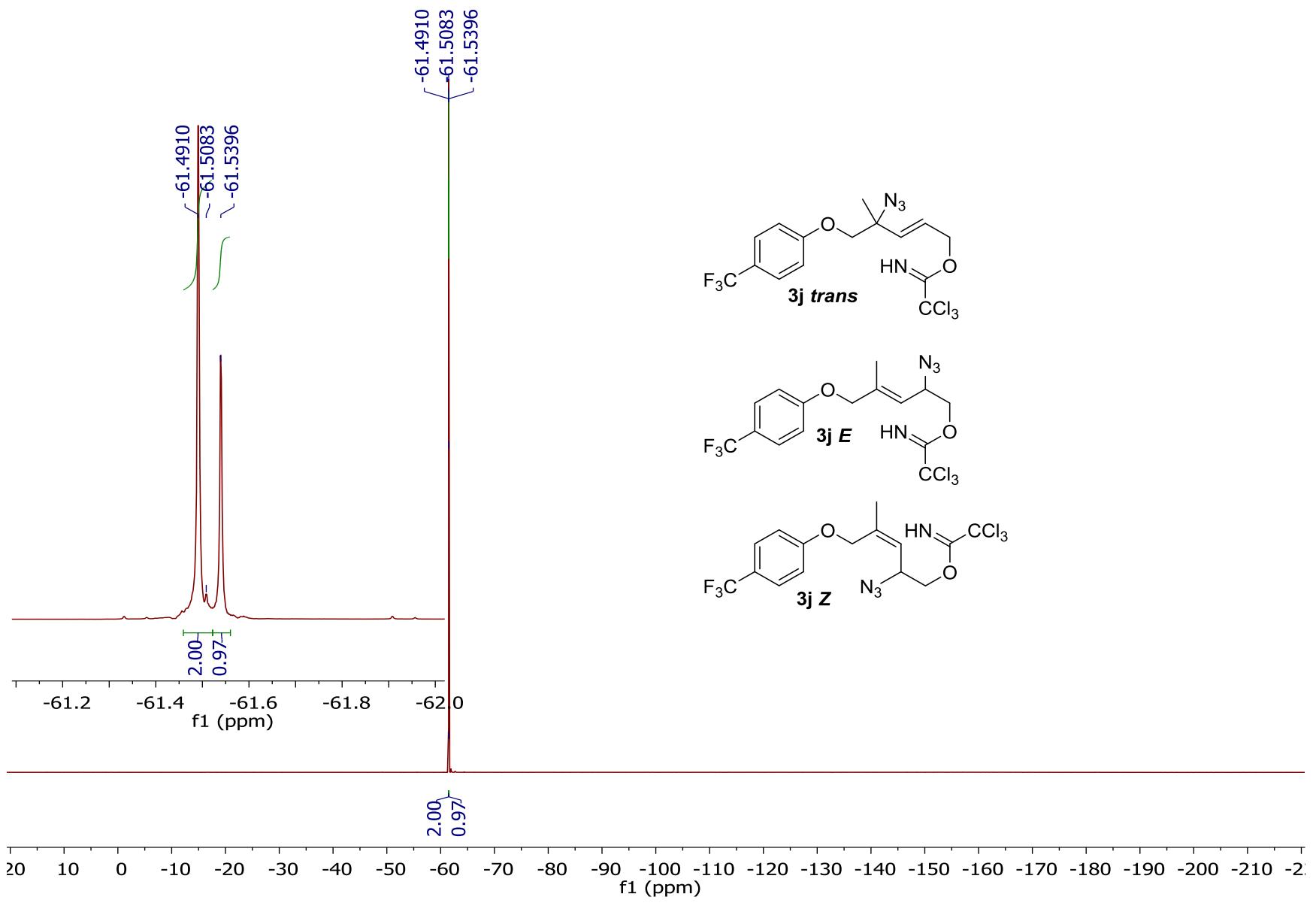
Compound 3i, 400 MHz ^1H NMR in CDCl_3

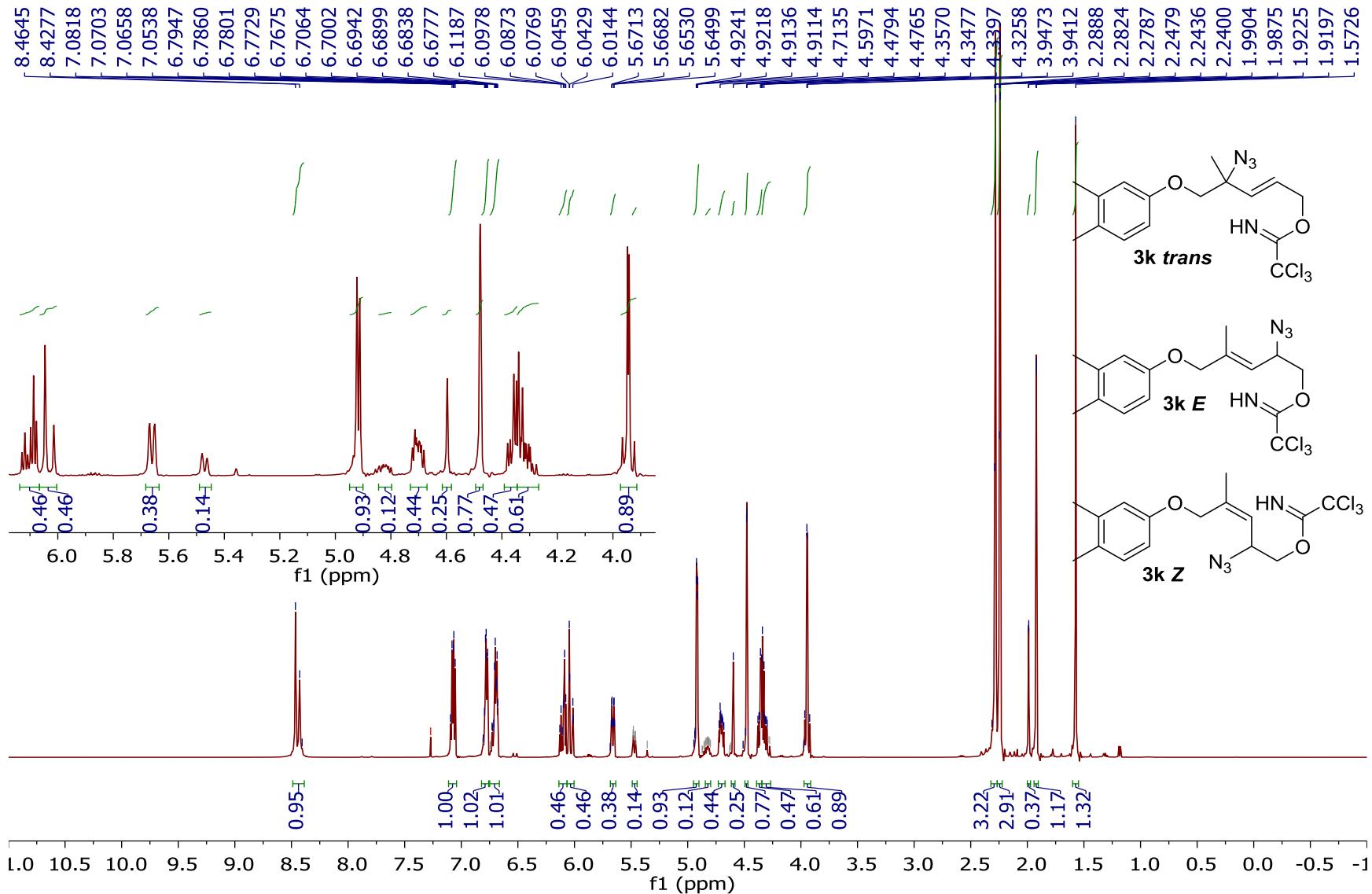


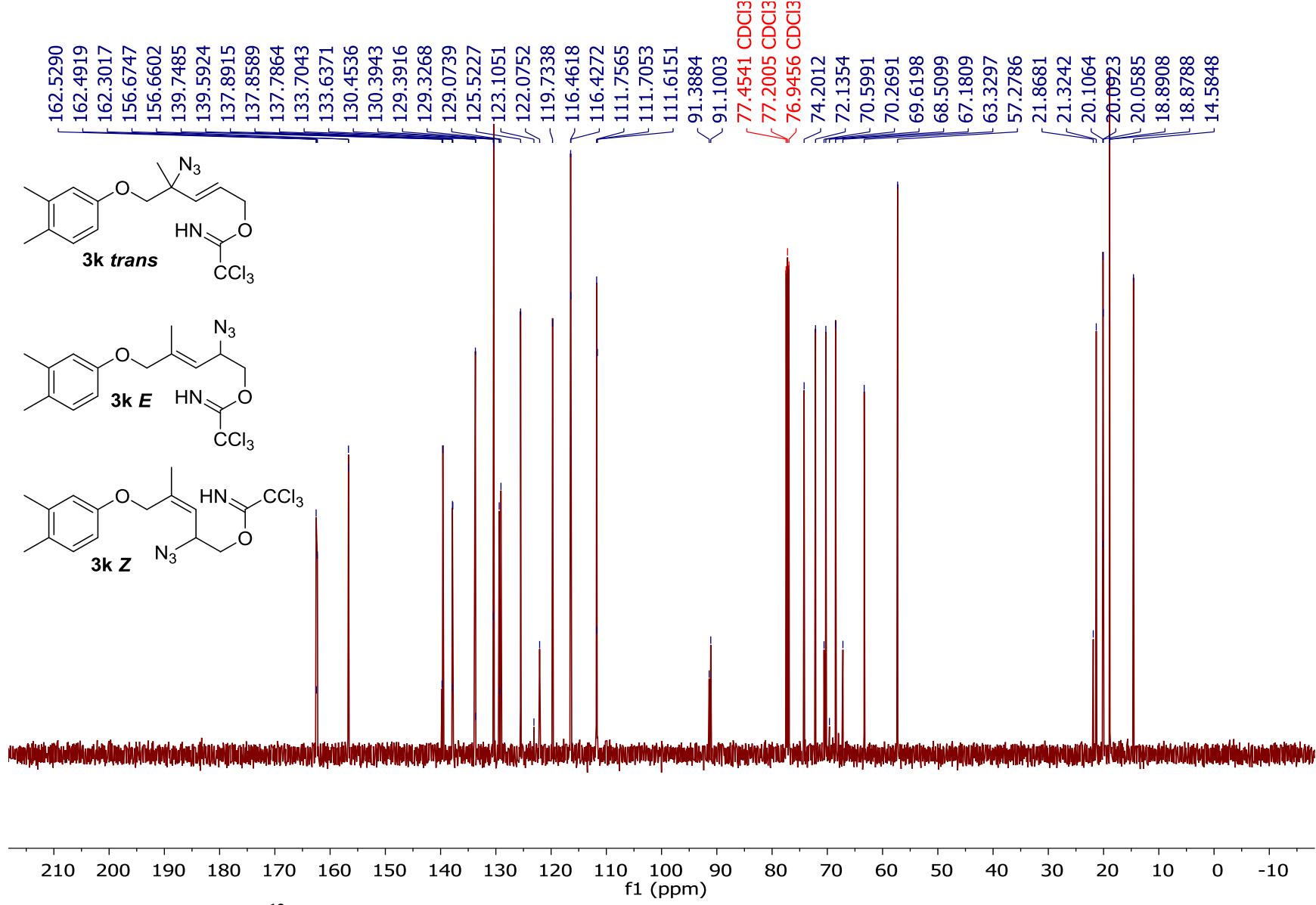


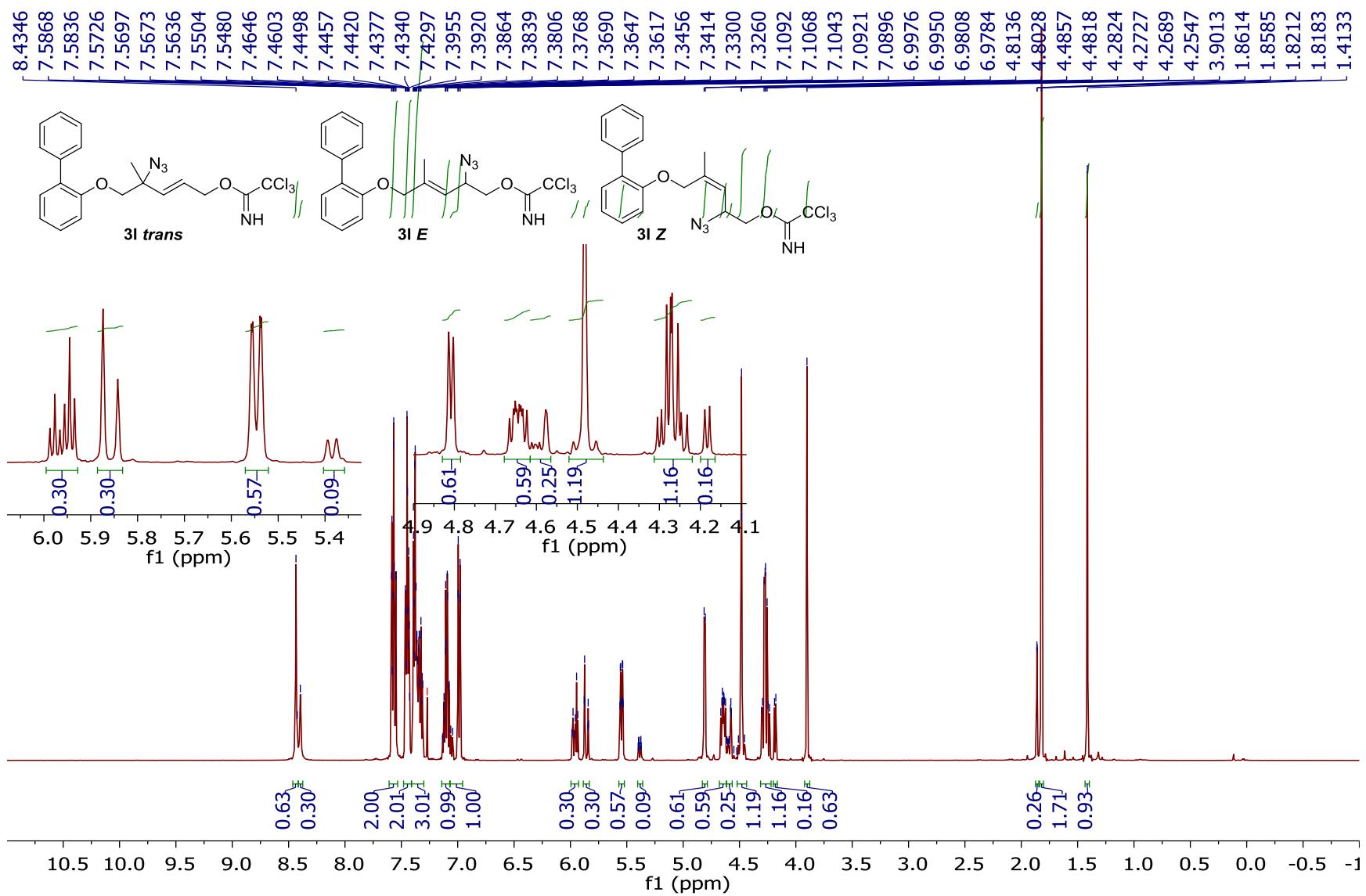
Compound 3j, 500 MHz ^1H NMR Spectrum in CDCl_3



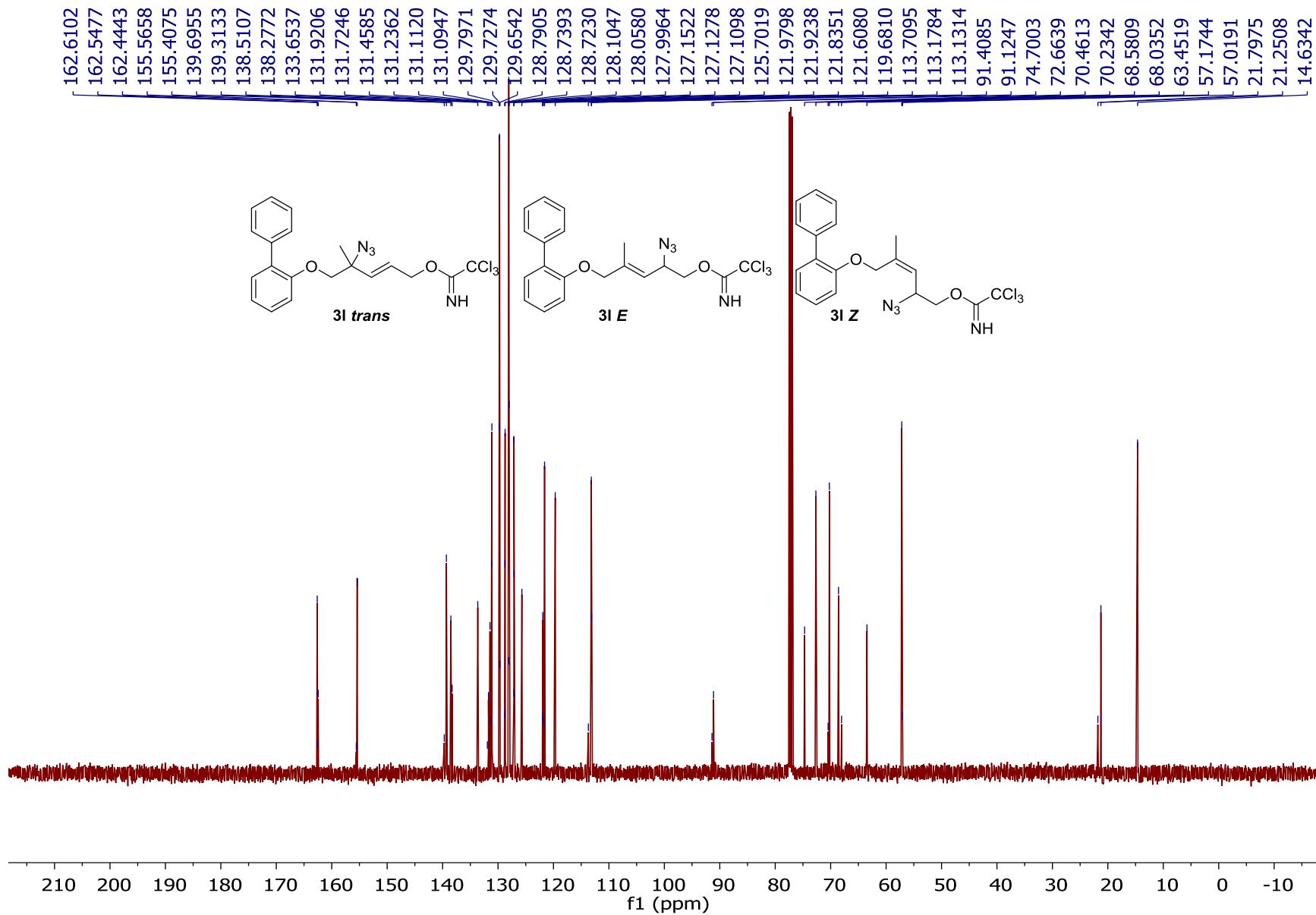




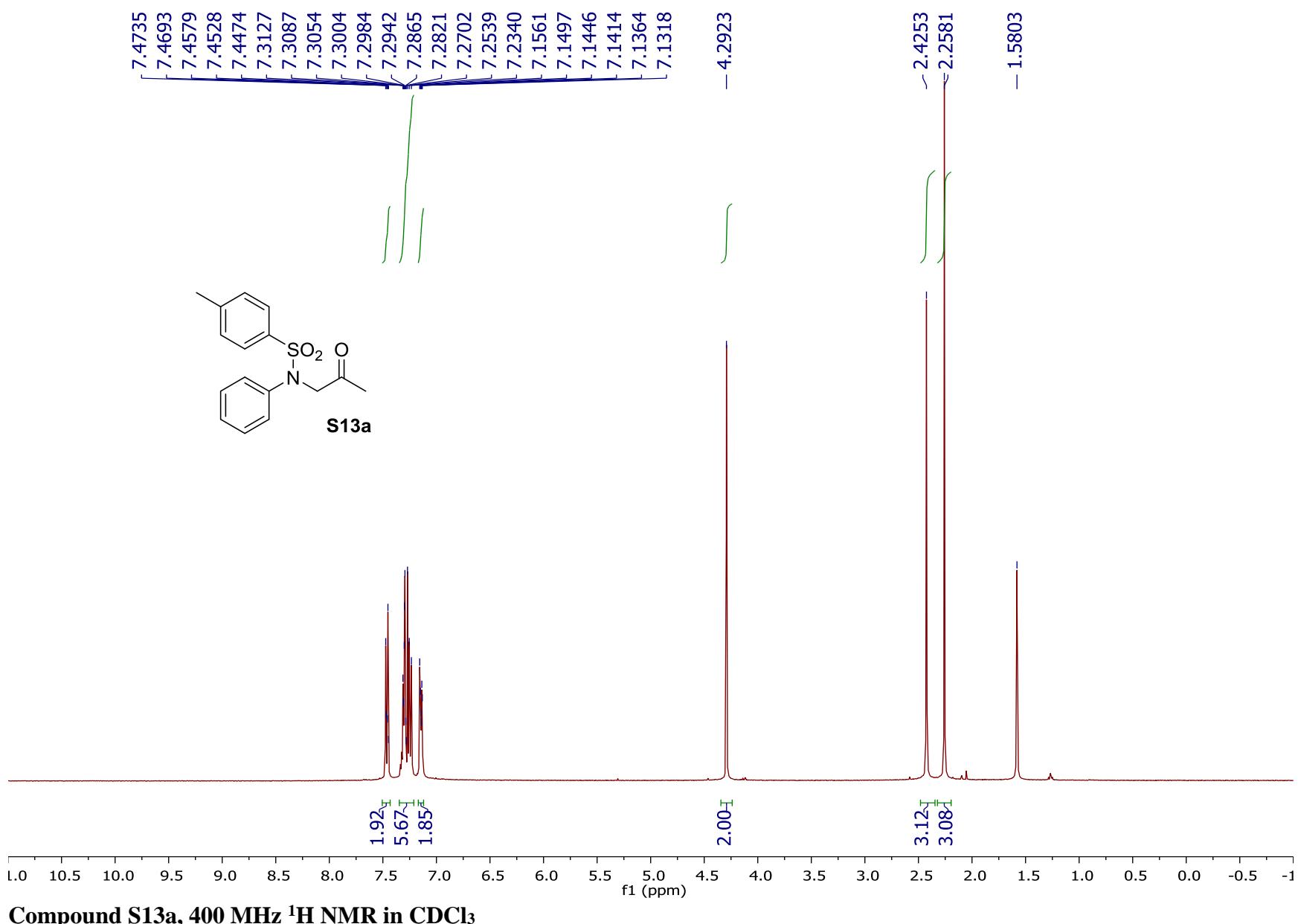


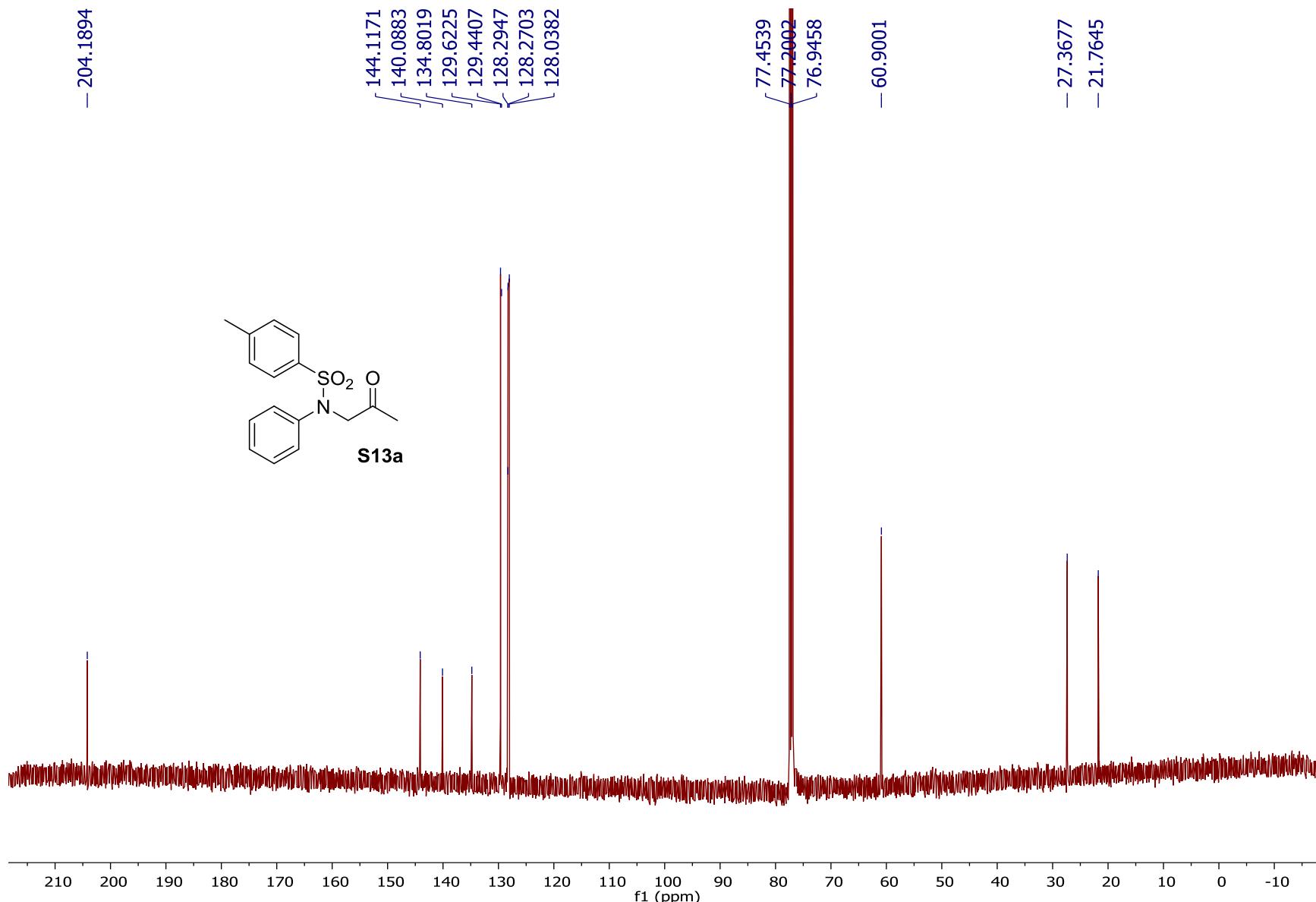


Compound 3l, 500 MHz ^1H NMR Spectrum in CDCl_3

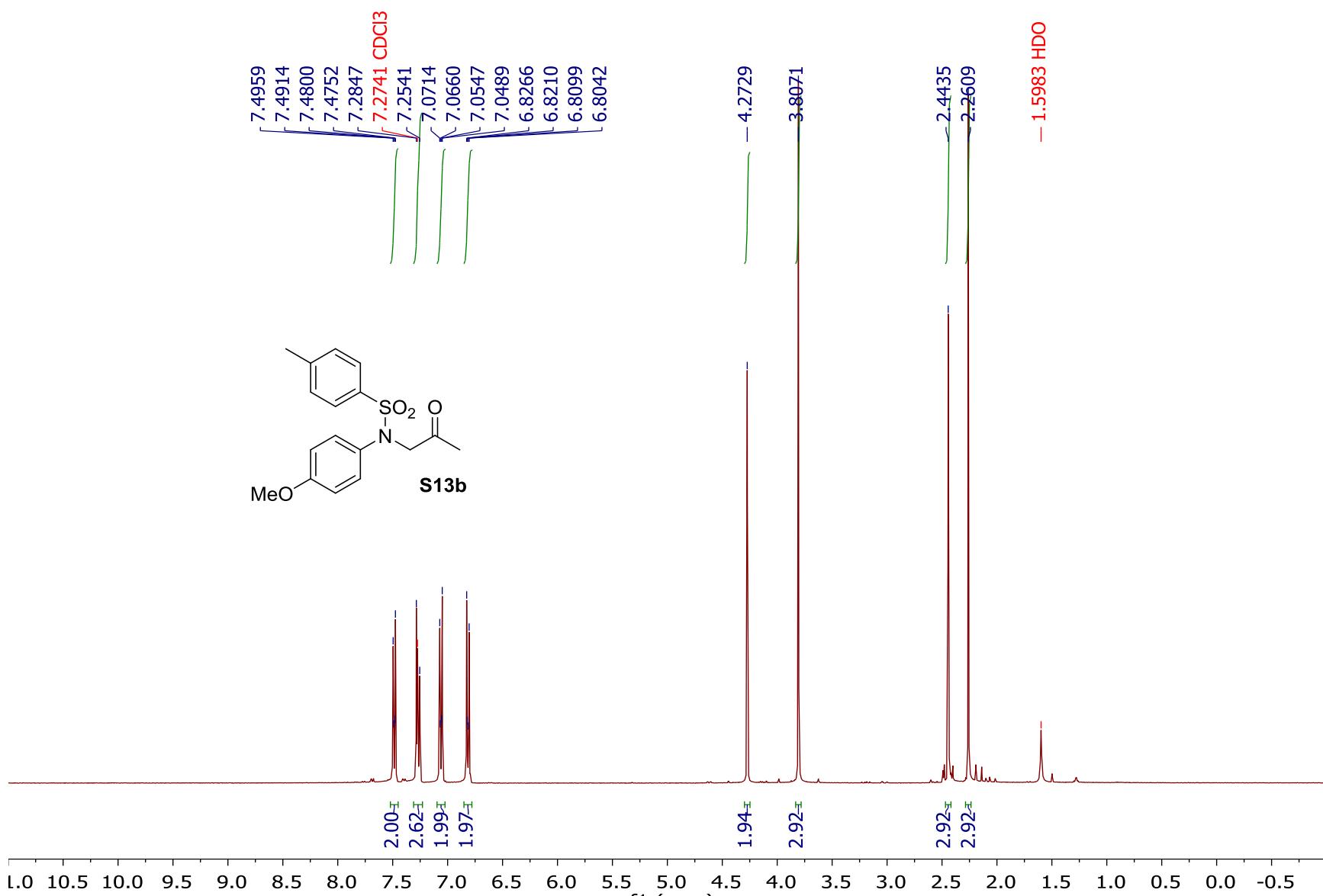


Compound 3l, 126 MHz ^{13}C NMR Spectrum in CDCl_3

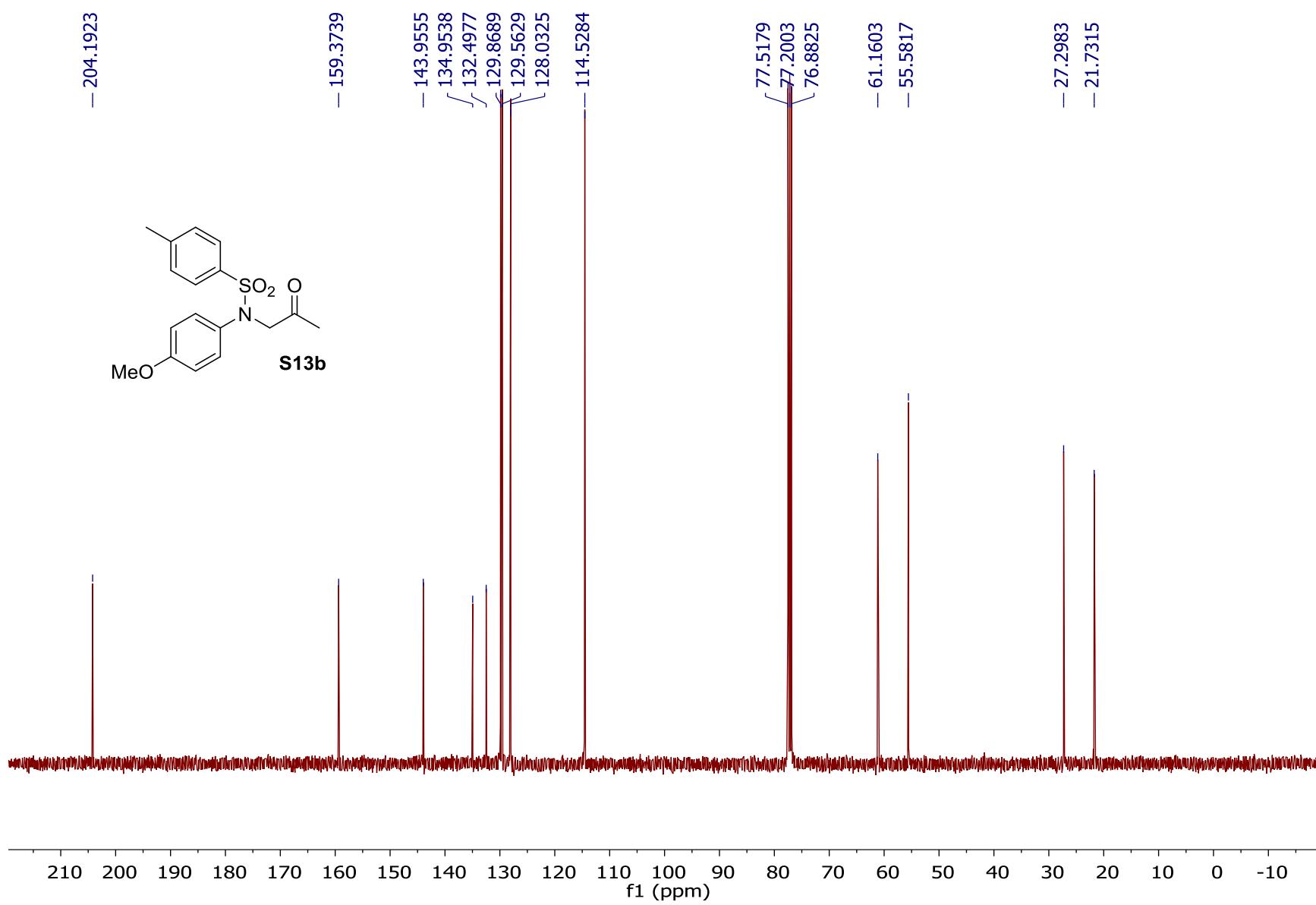




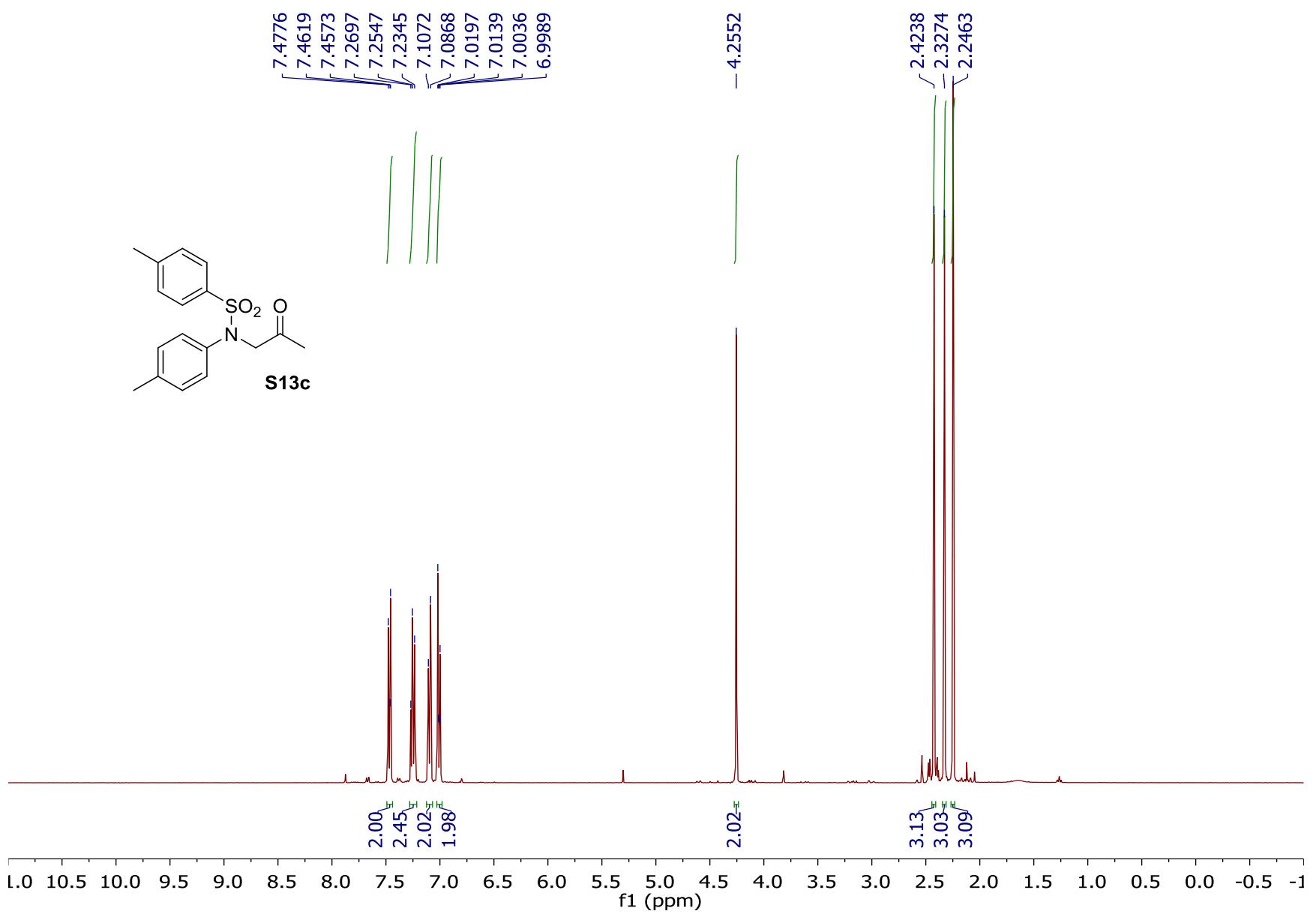
Compound S13a, 126 MHz ^{13}C NMR in CDCl_3



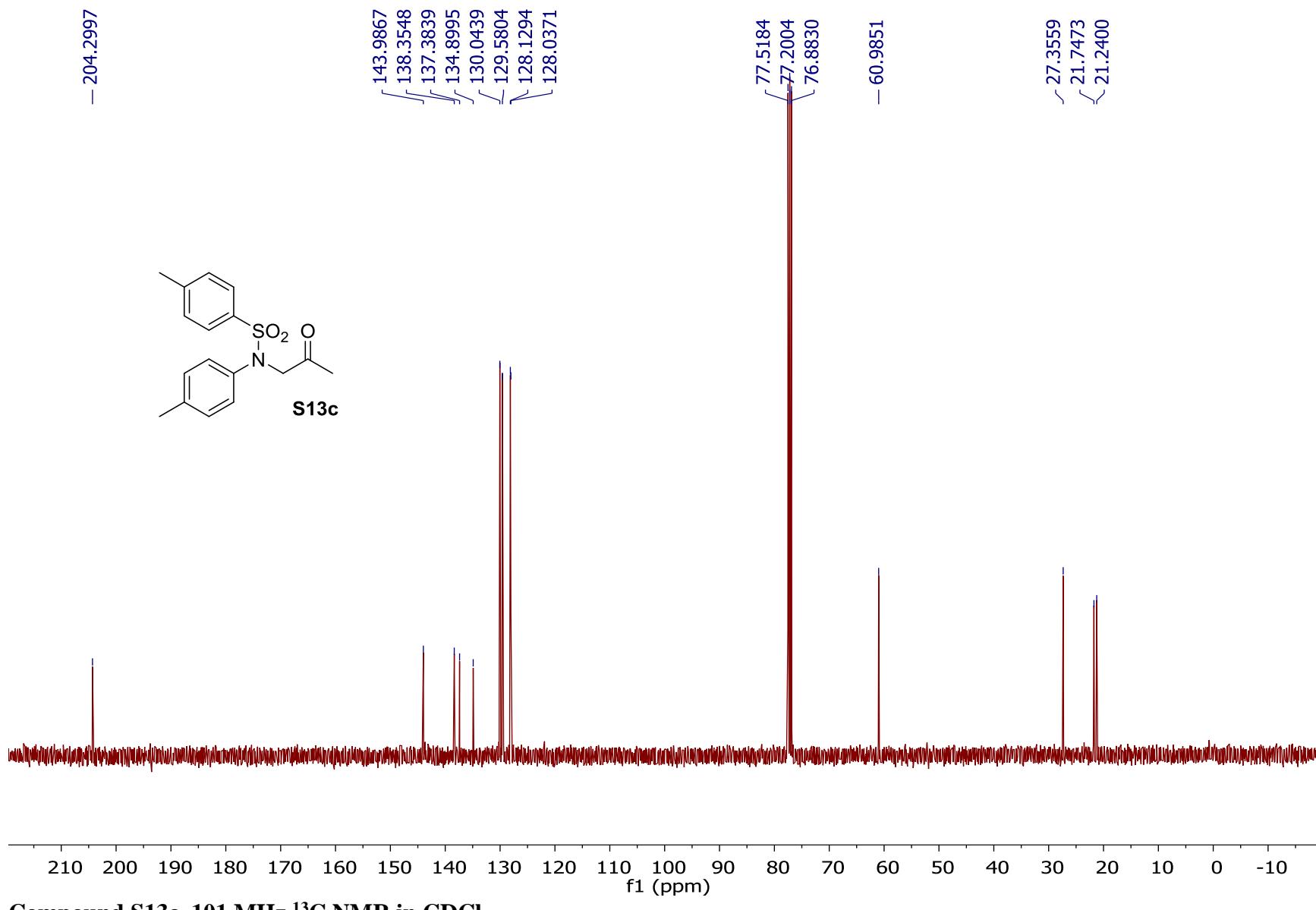
Compound S13b, 400 MHz ^1H NMR in CDCl_3

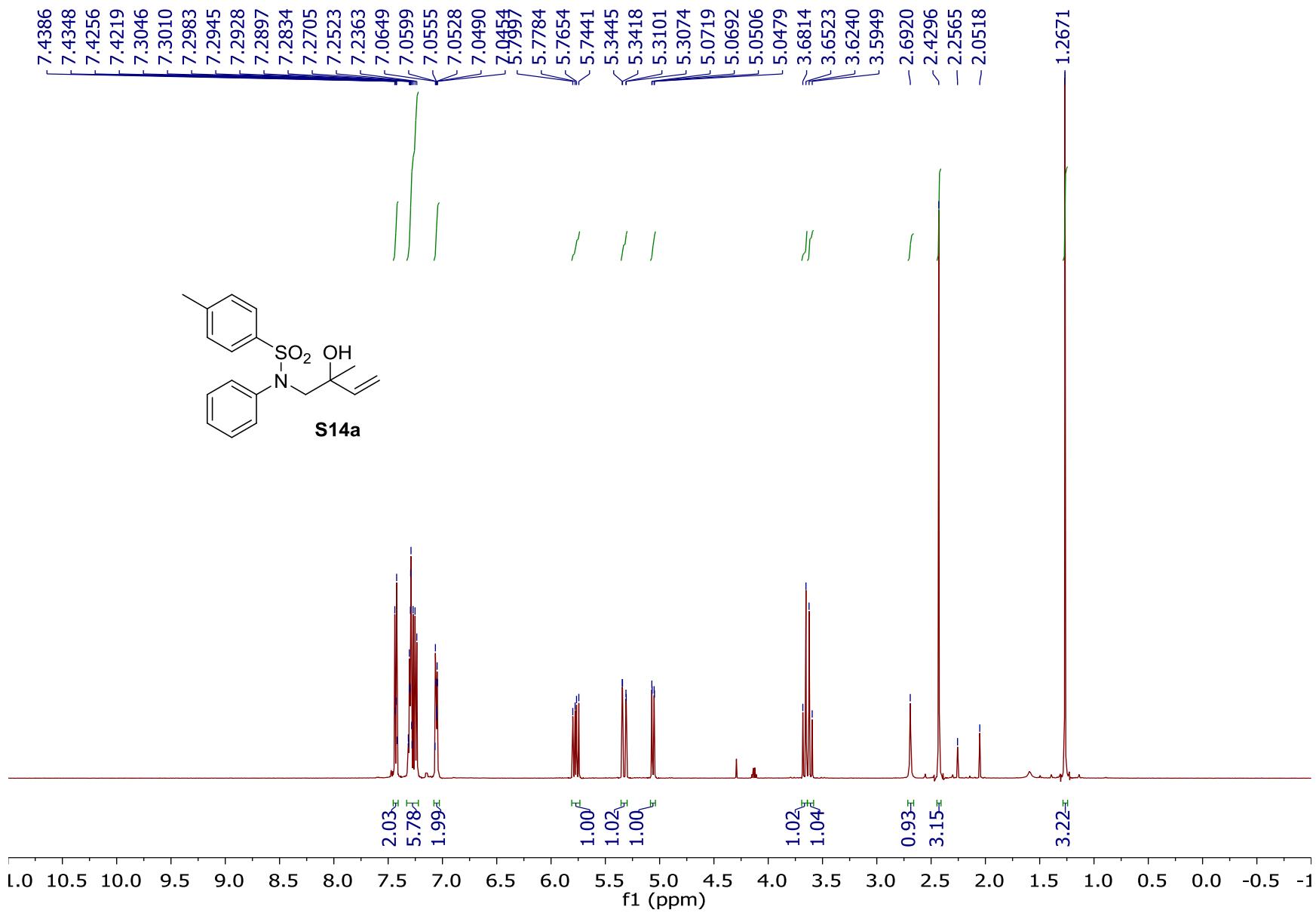


Compound S13b, 101 MHz ^{13}C NMR in CDCl_3

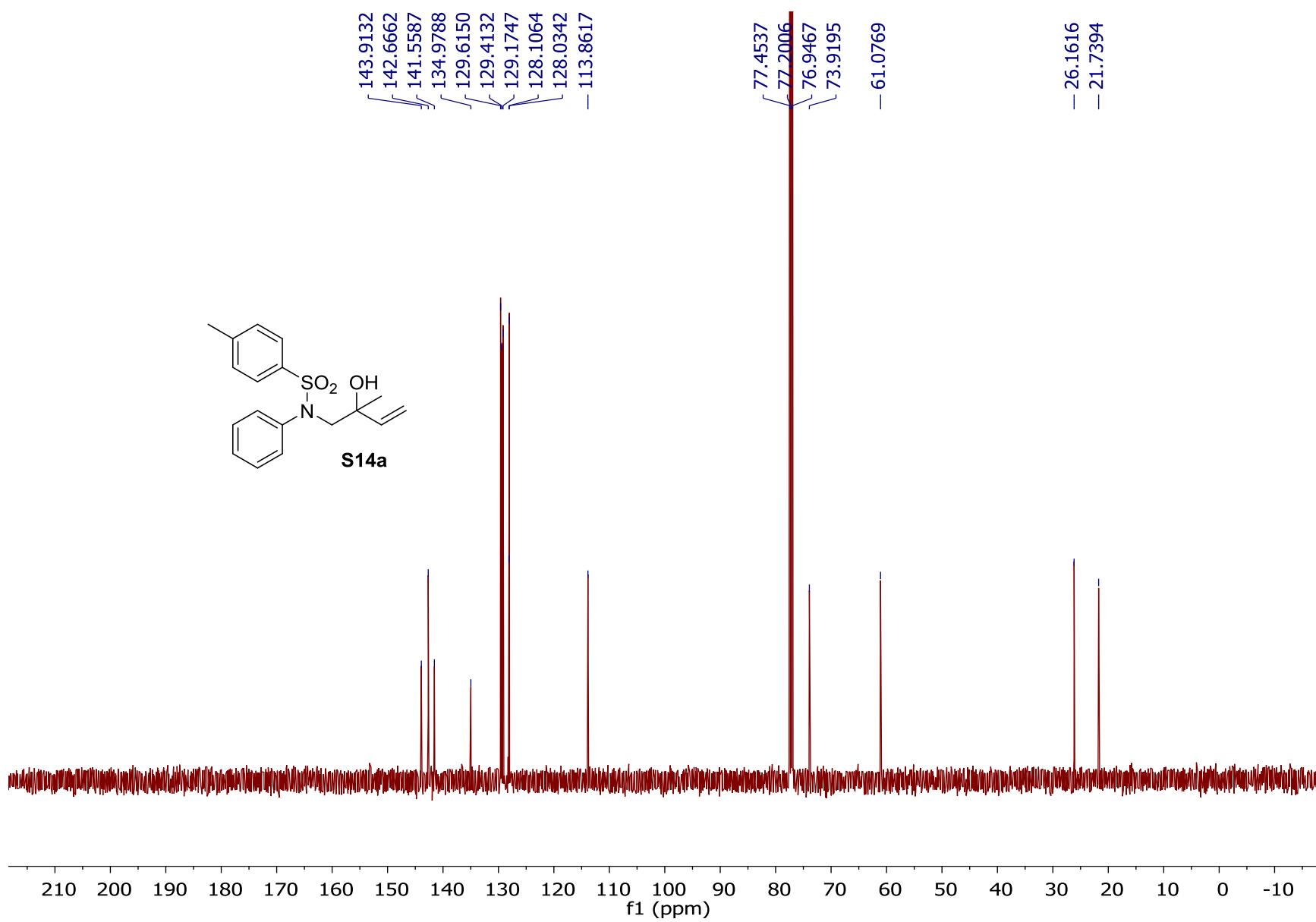


Compound S13c, 400 MHz ¹H NMR in CDCl₃

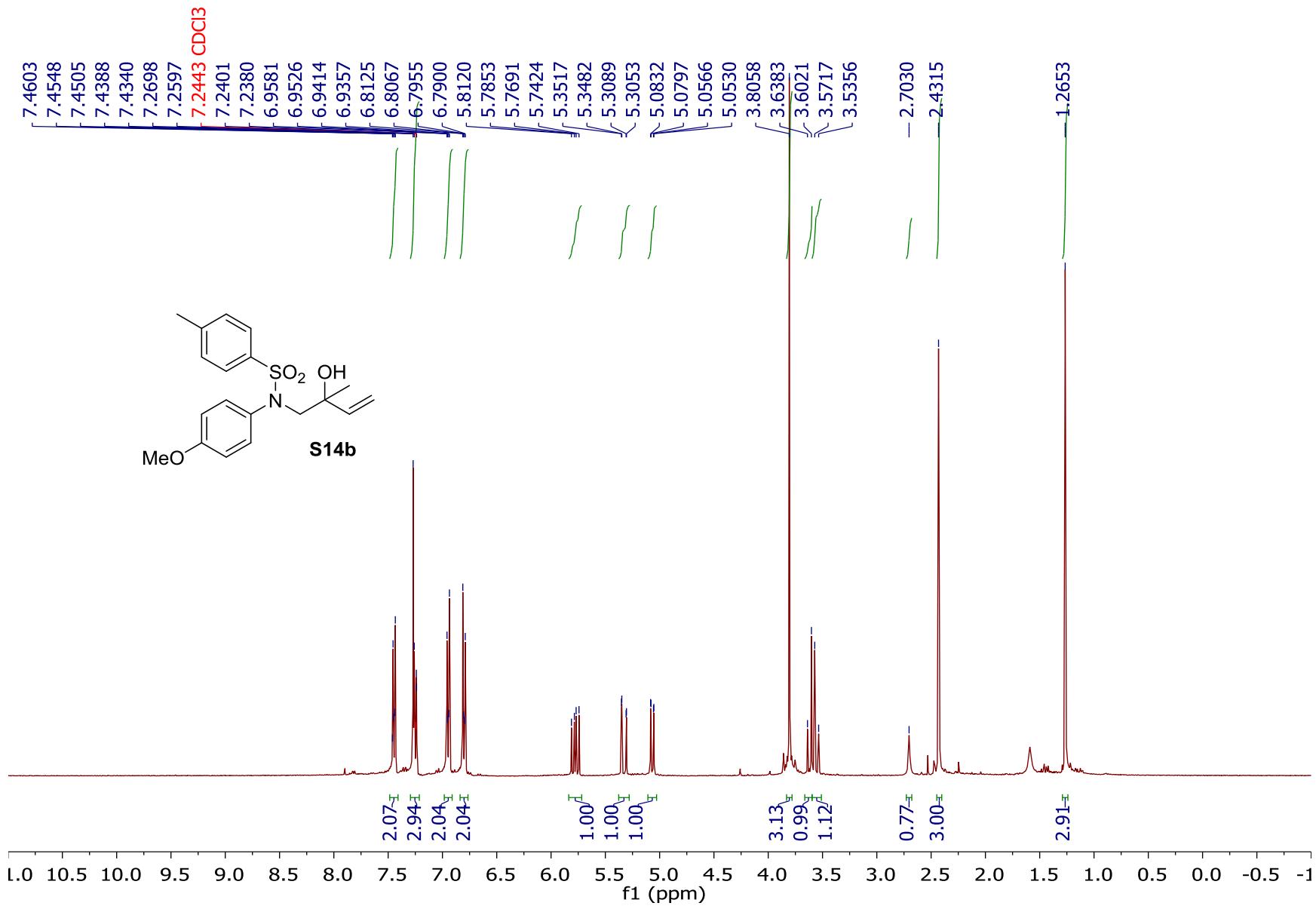




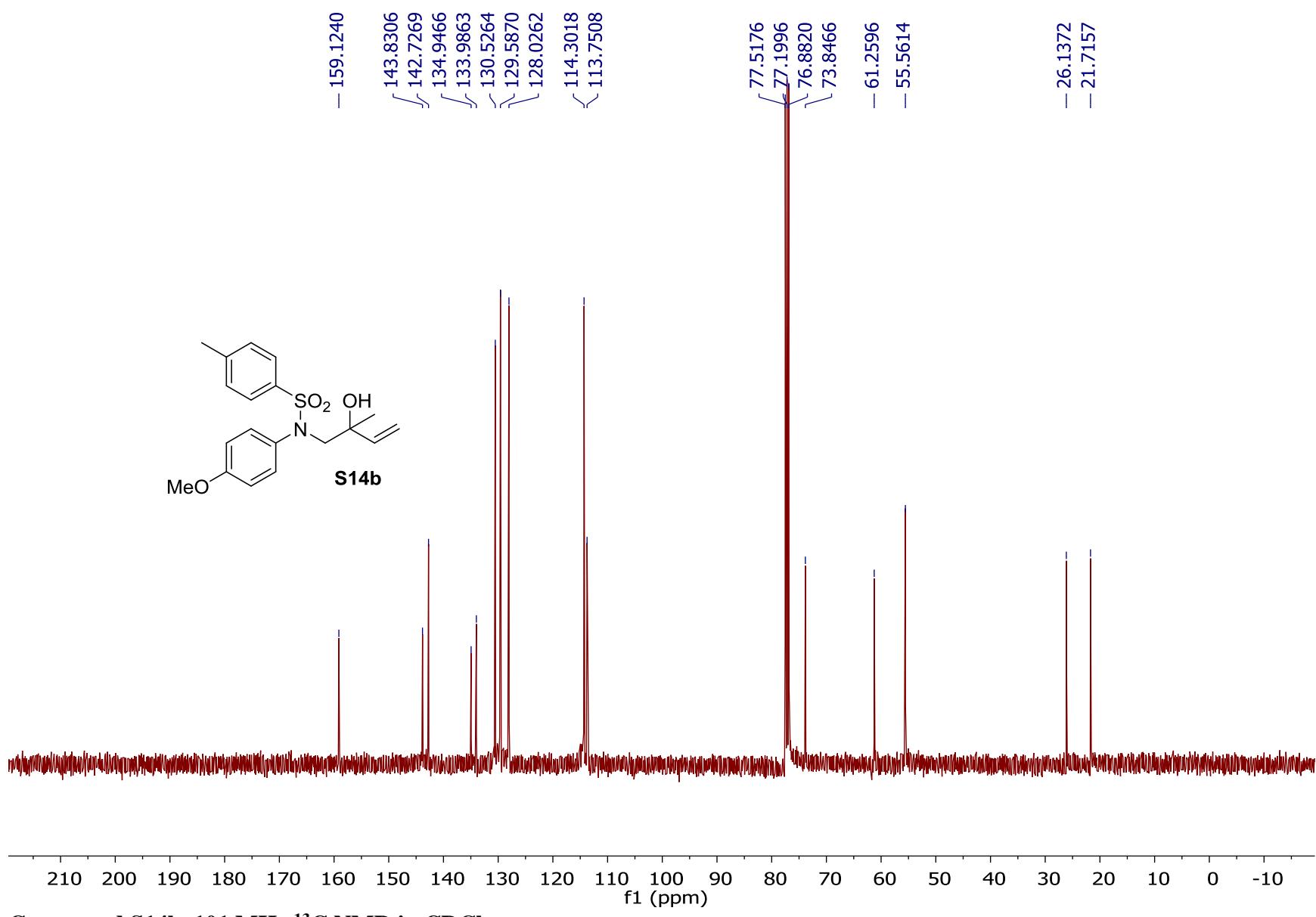
Compound S14a, 500 MHz ^1H NMR in CDCl_3

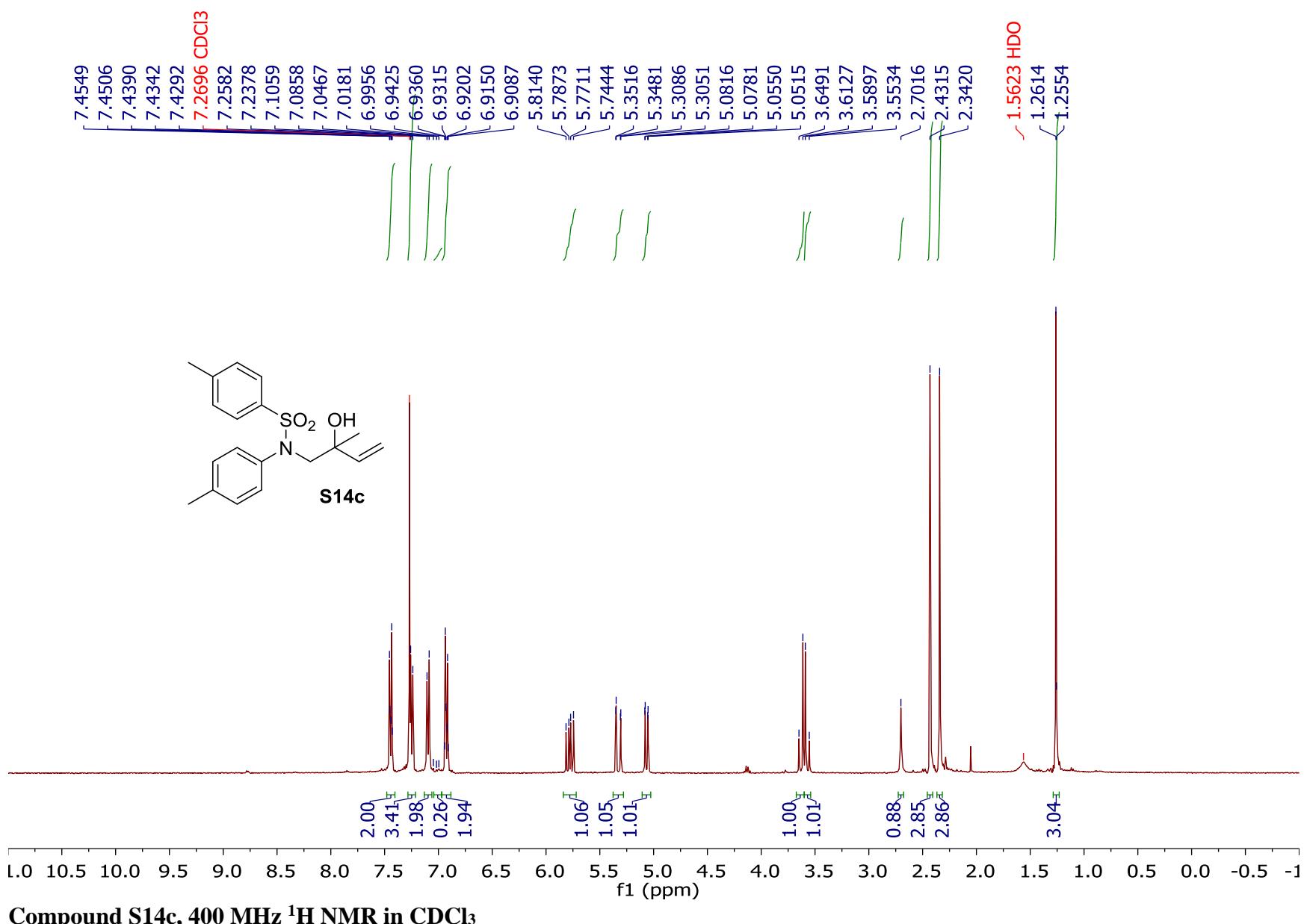


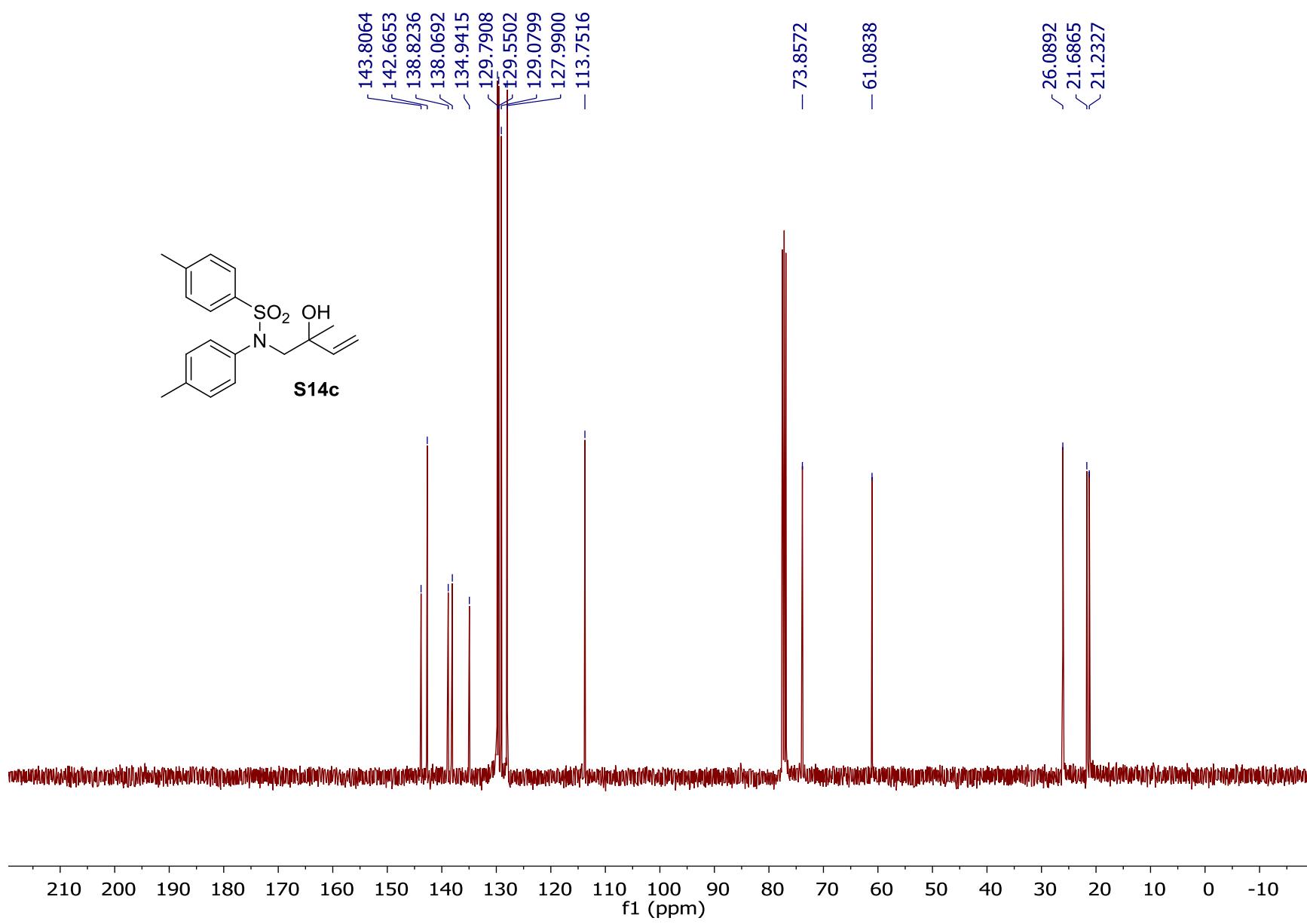
Compound S14a, 126 MHz ^{13}C NMR in CDCl₃



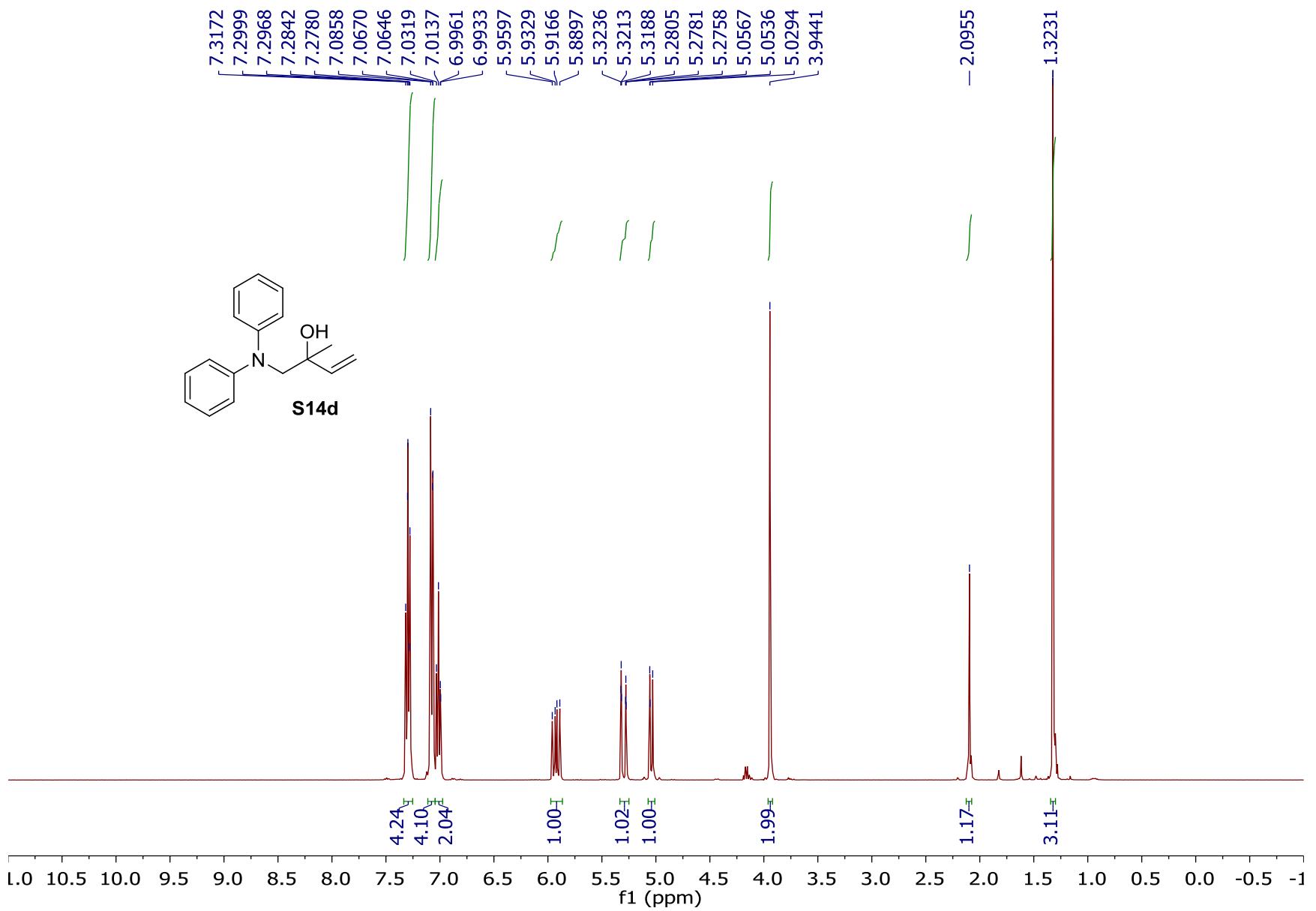
Compound **S14b**, 400 MHz ¹H NMR in CDCl₃



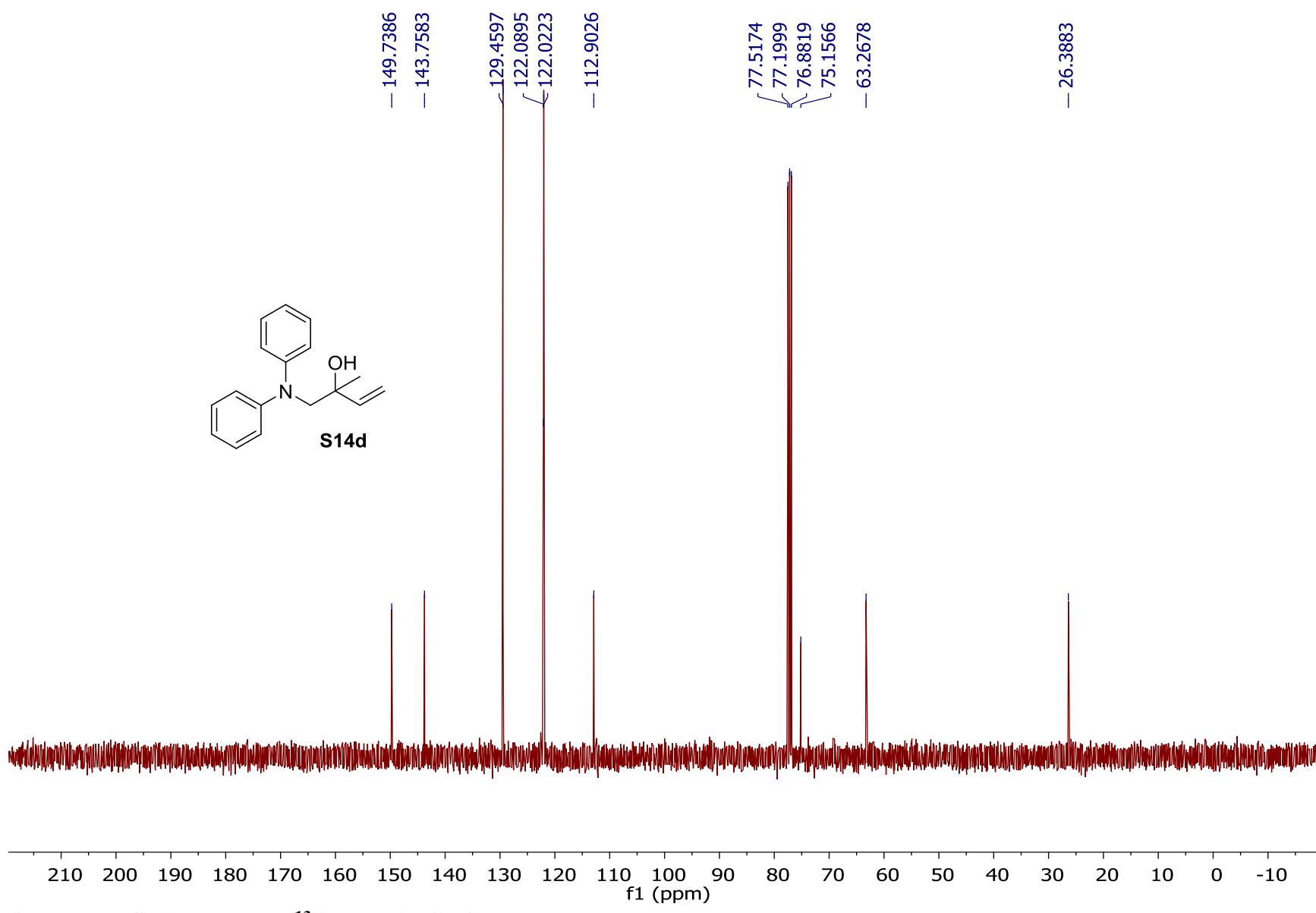




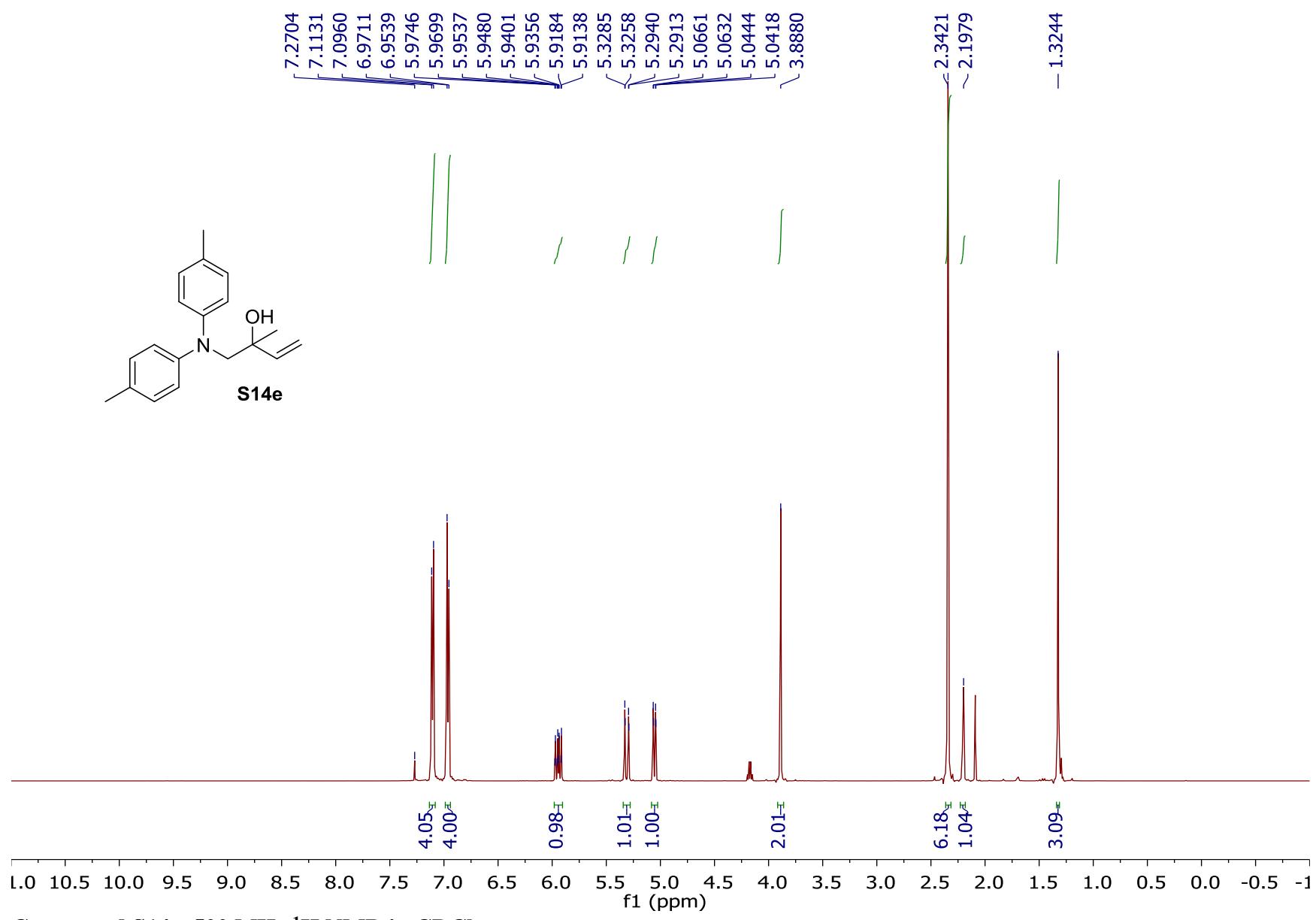
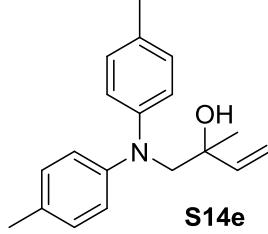
Compound S14c, 101 MHz ^{13}C NMR in CDCl_3



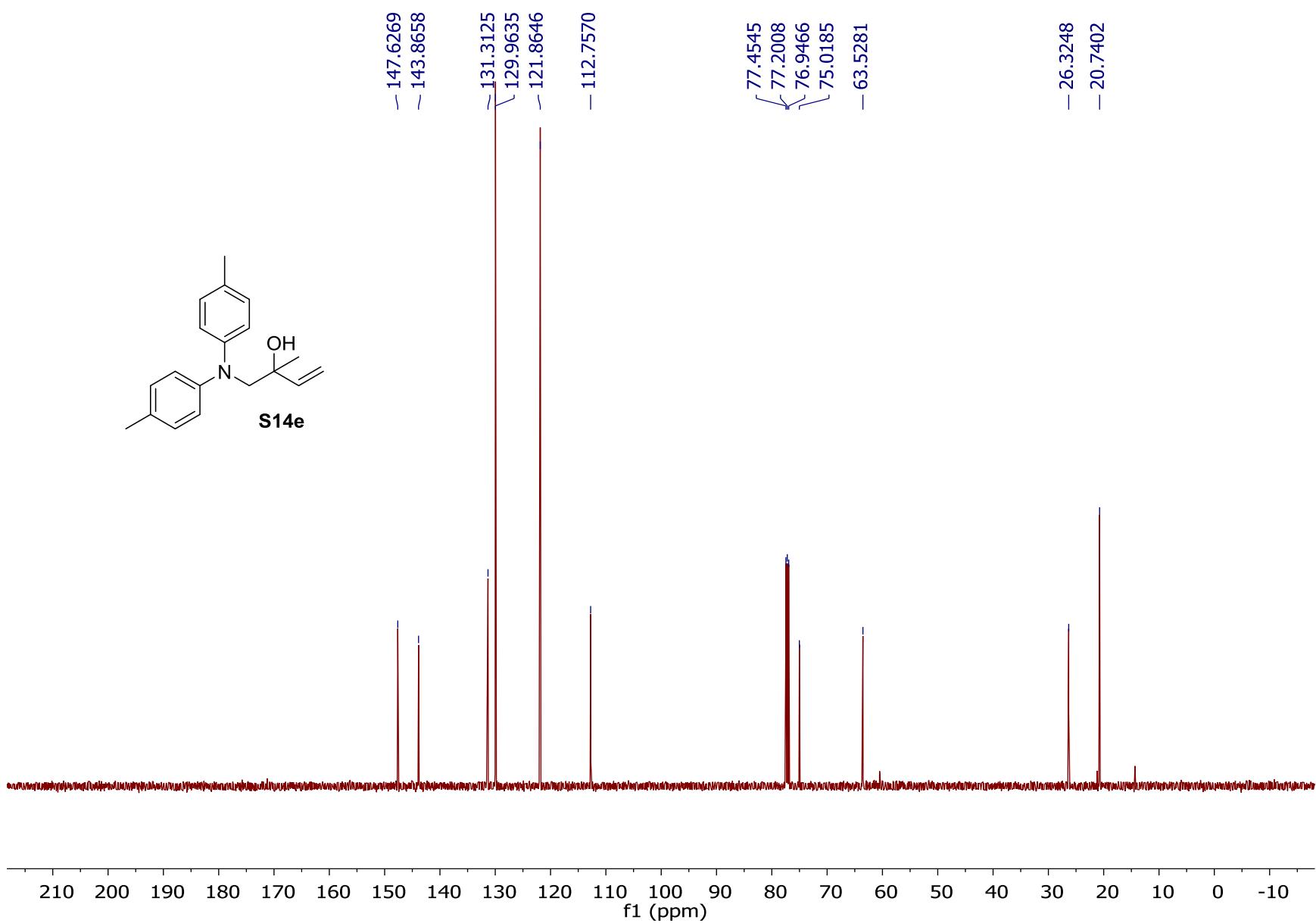
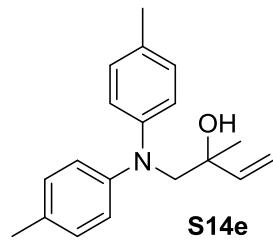
Compound S14d, 400 MHz ^1H NMR in CDCl_3



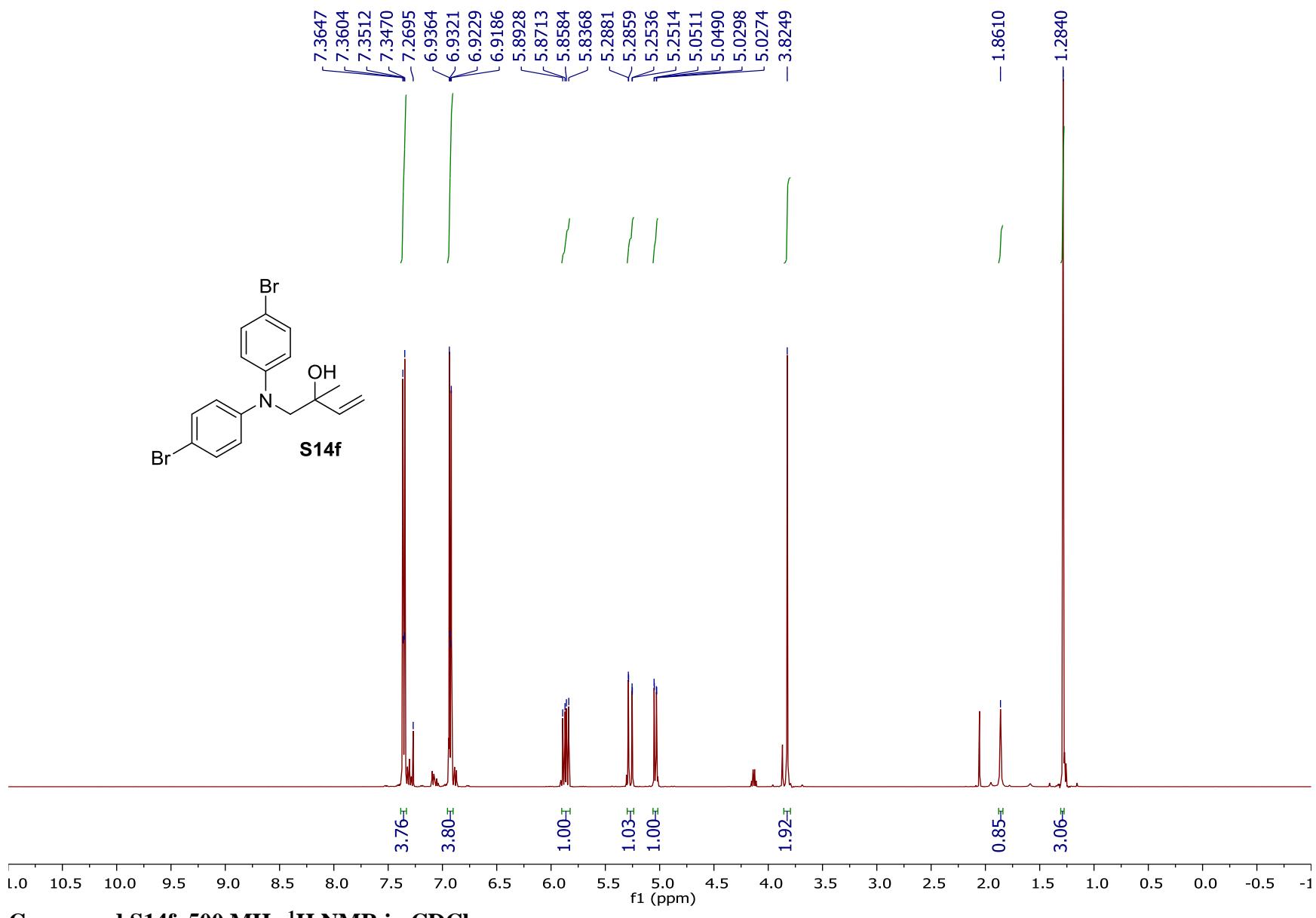
Compound S14d, 101 MHz ^{13}C NMR in CDCl_3

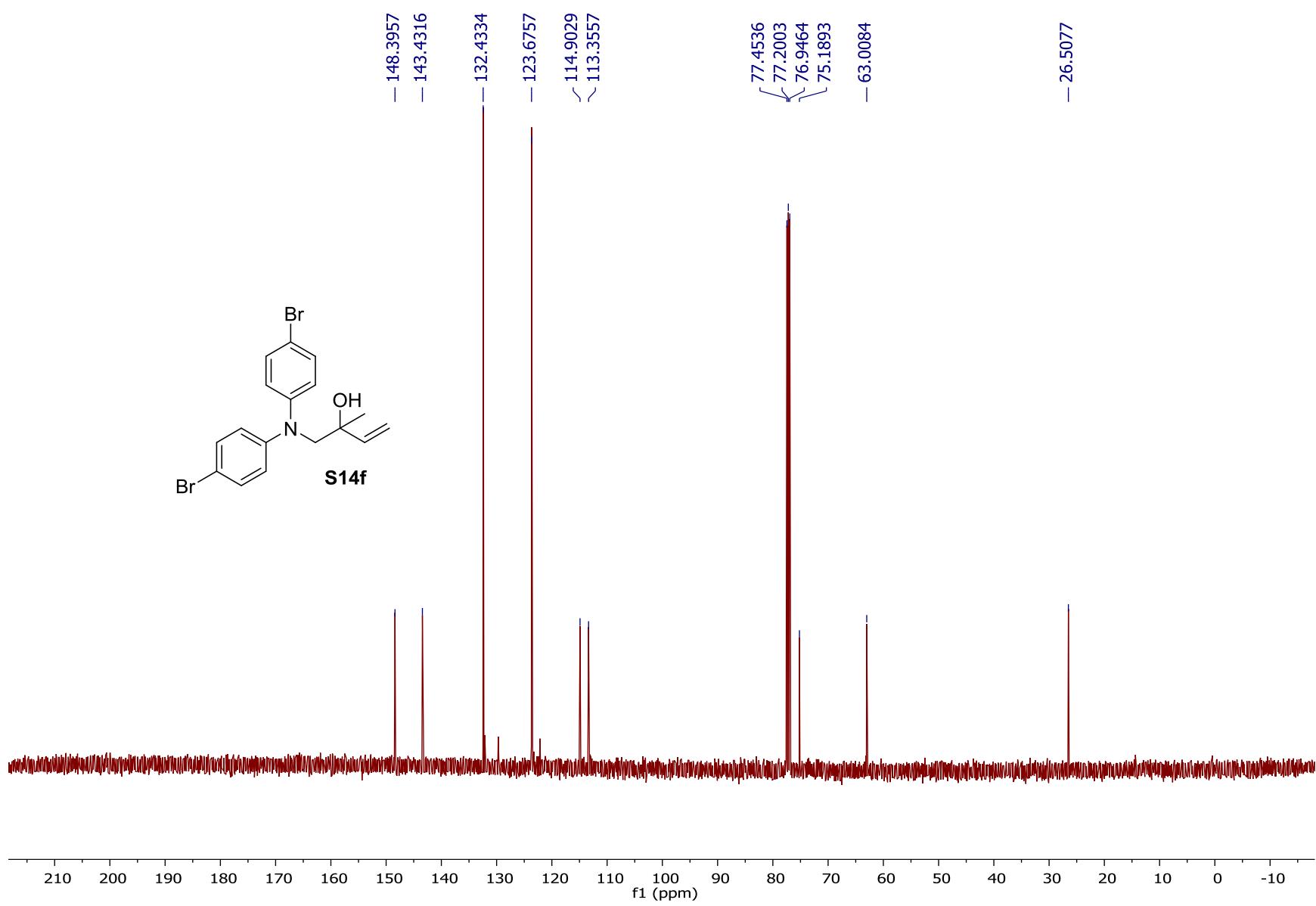


Compound S14e, 500 MHz ^1H NMR in CDCl_3

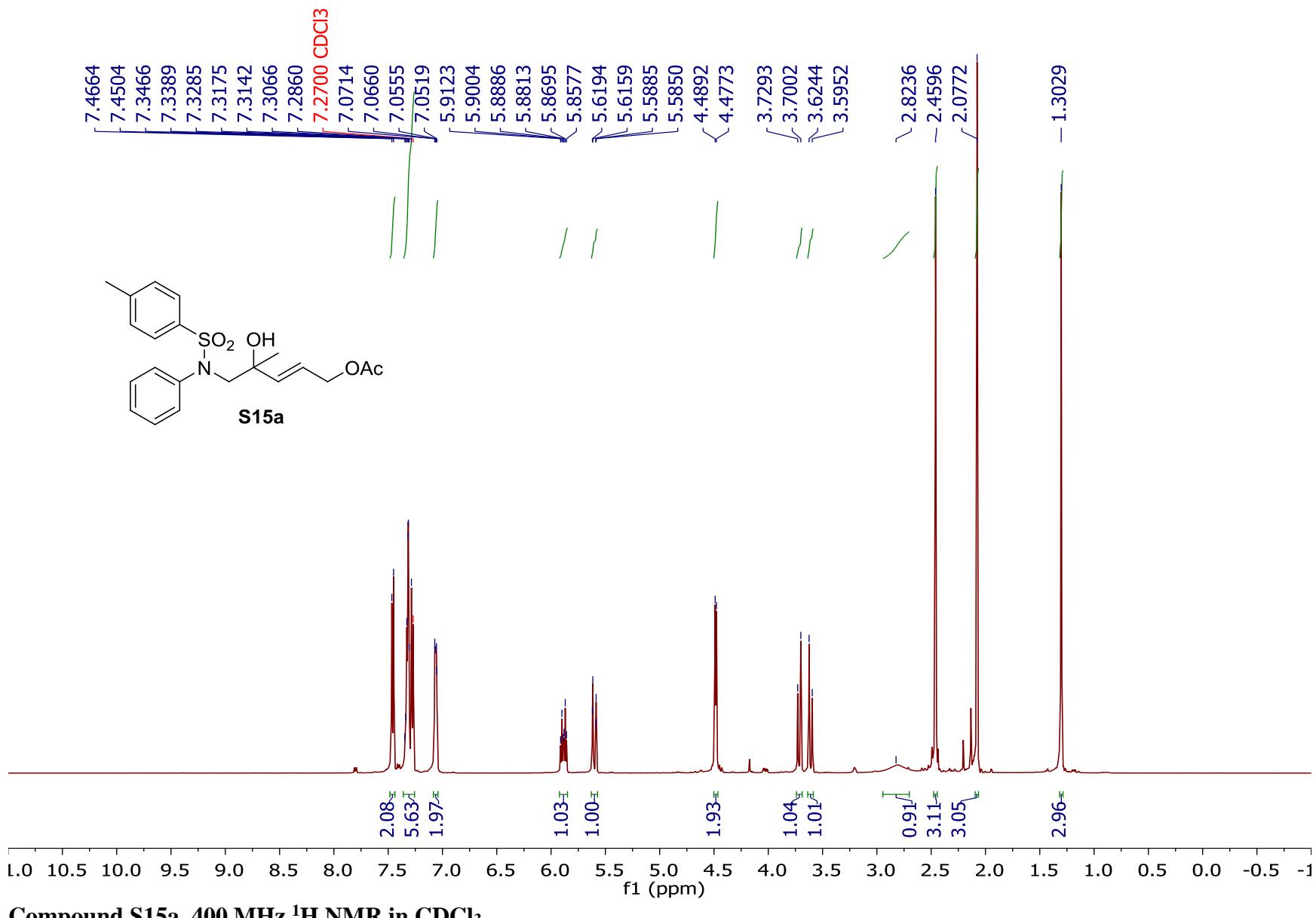


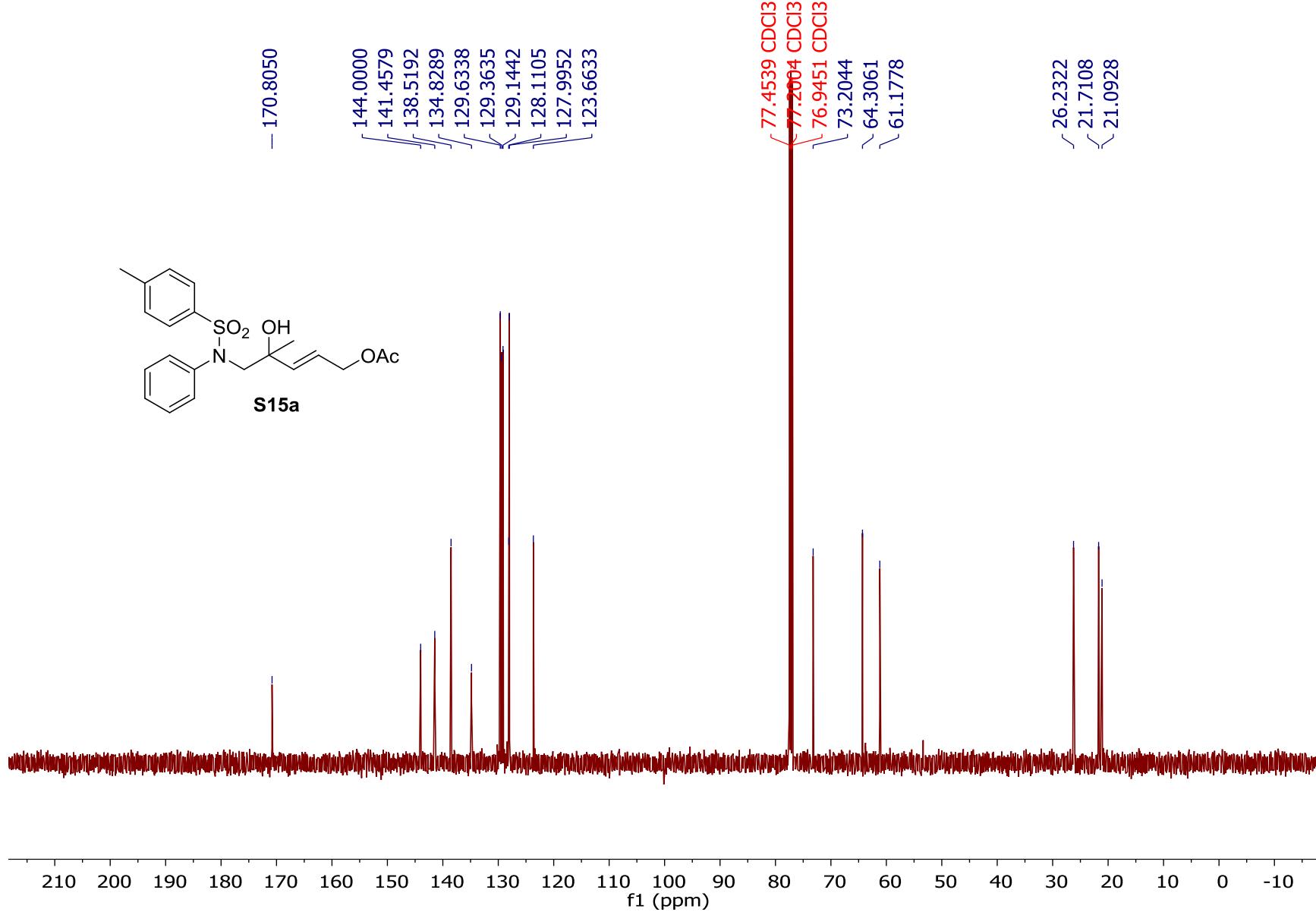
Compound S14e, 126 MHz ¹³C NMR in CDCl₃



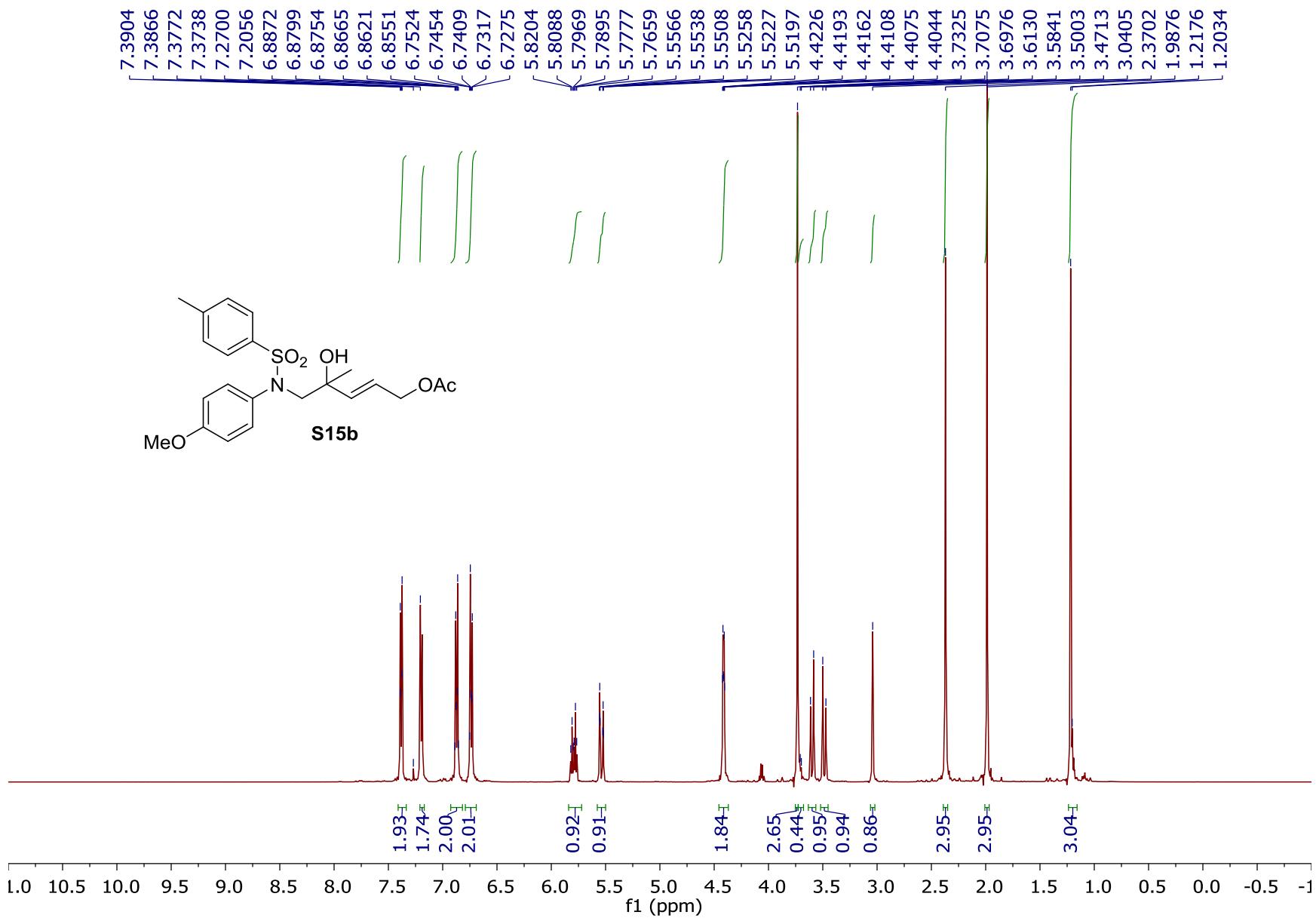


Compound S14f, 126 MHz ^{13}C NMR in CDCl_3

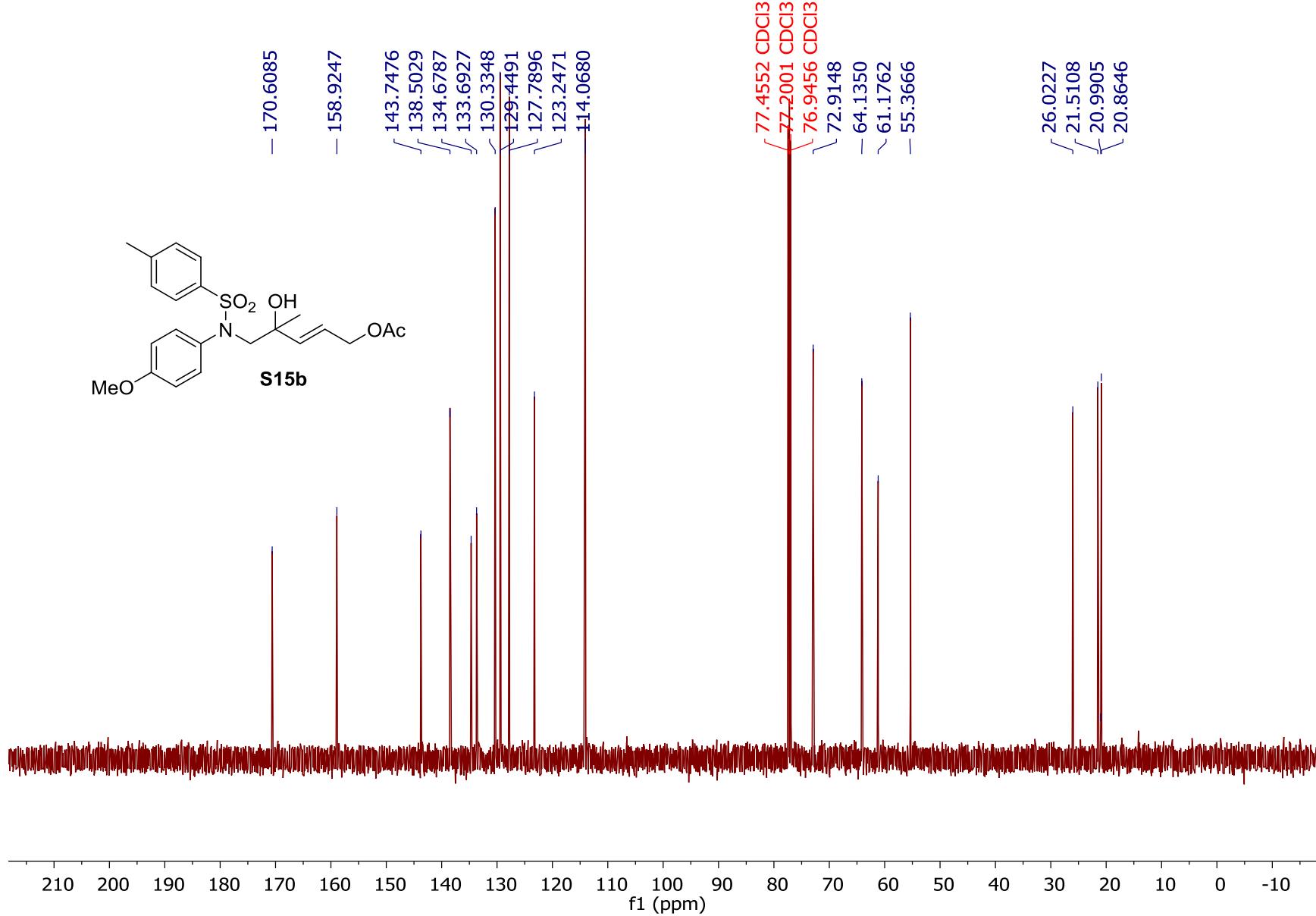




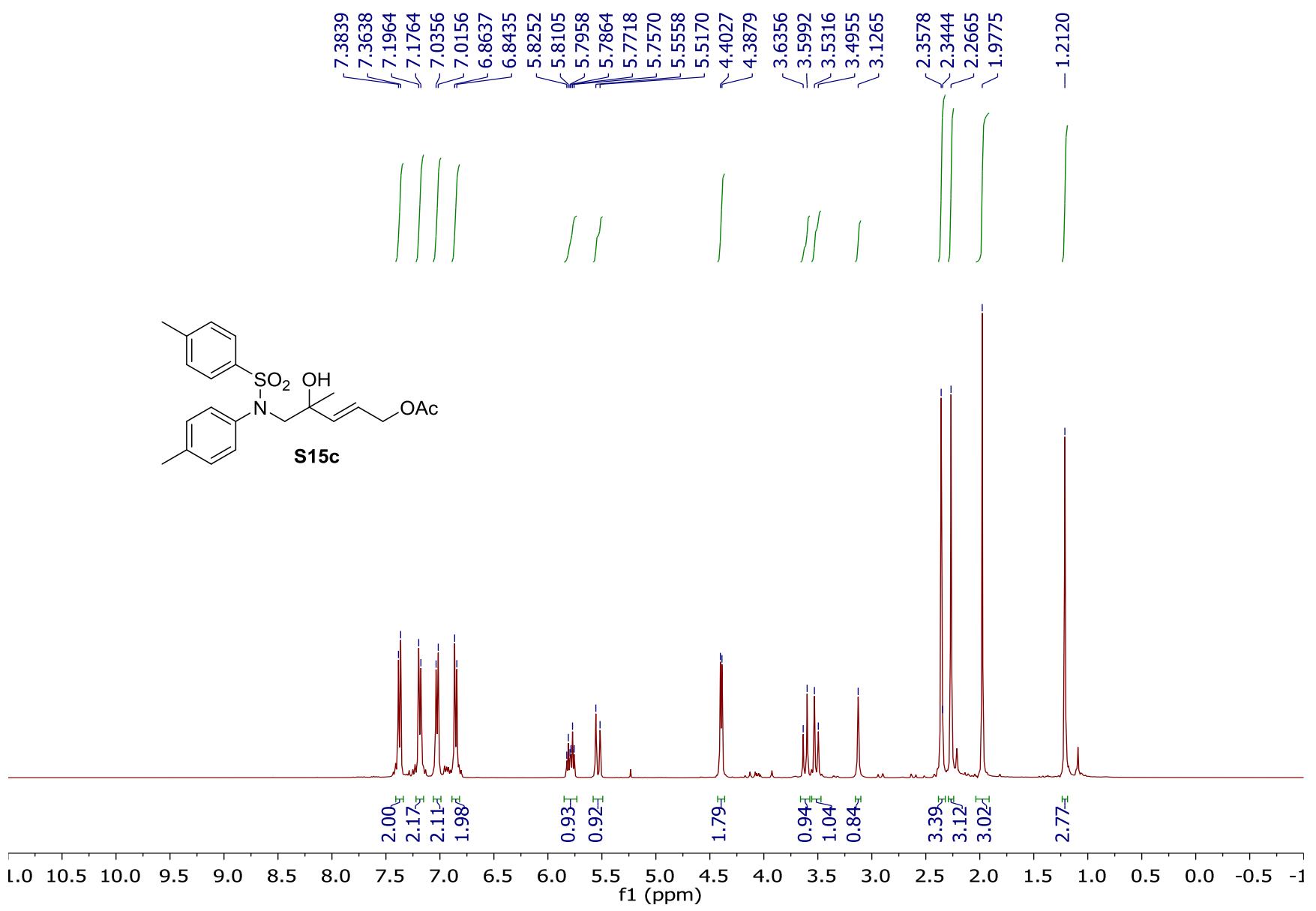
Compound S15a, 101 MHz ^{13}C NMR in CDCl₃



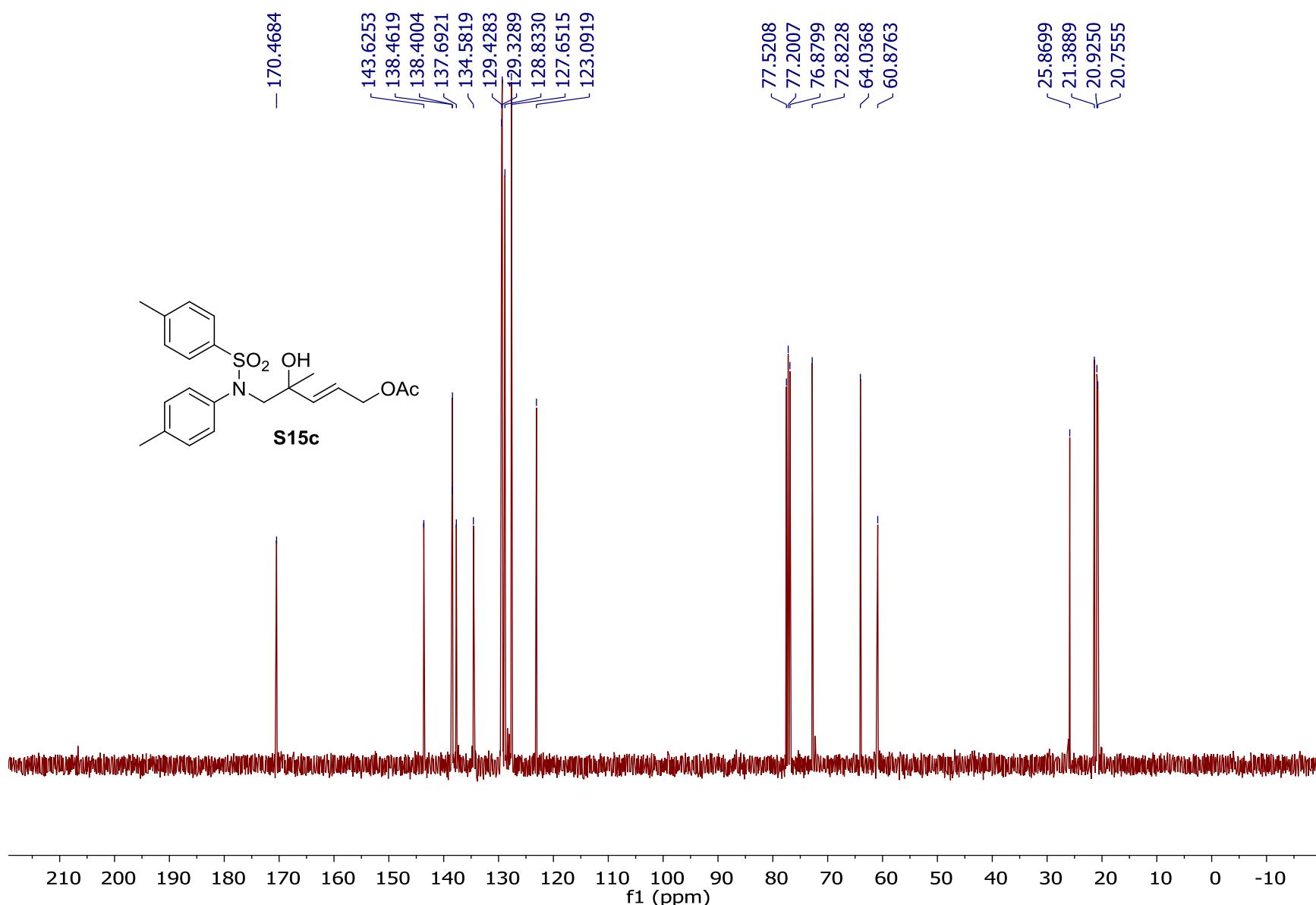
Compound S15b, 500 MHz ^1H NMR in CDCl_3



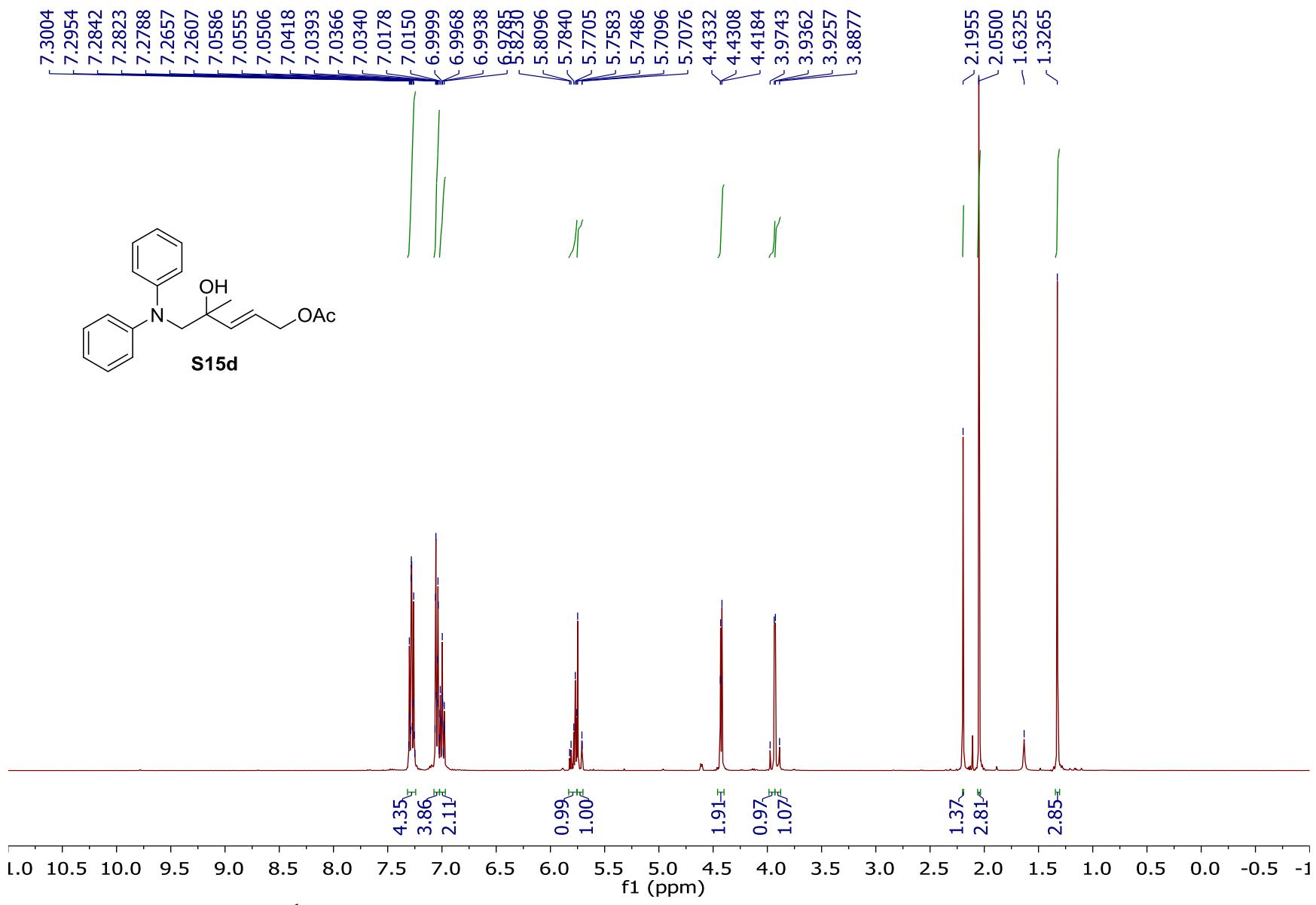
Compound S15b, 126 MHz ^{13}C NMR in CDCl_3



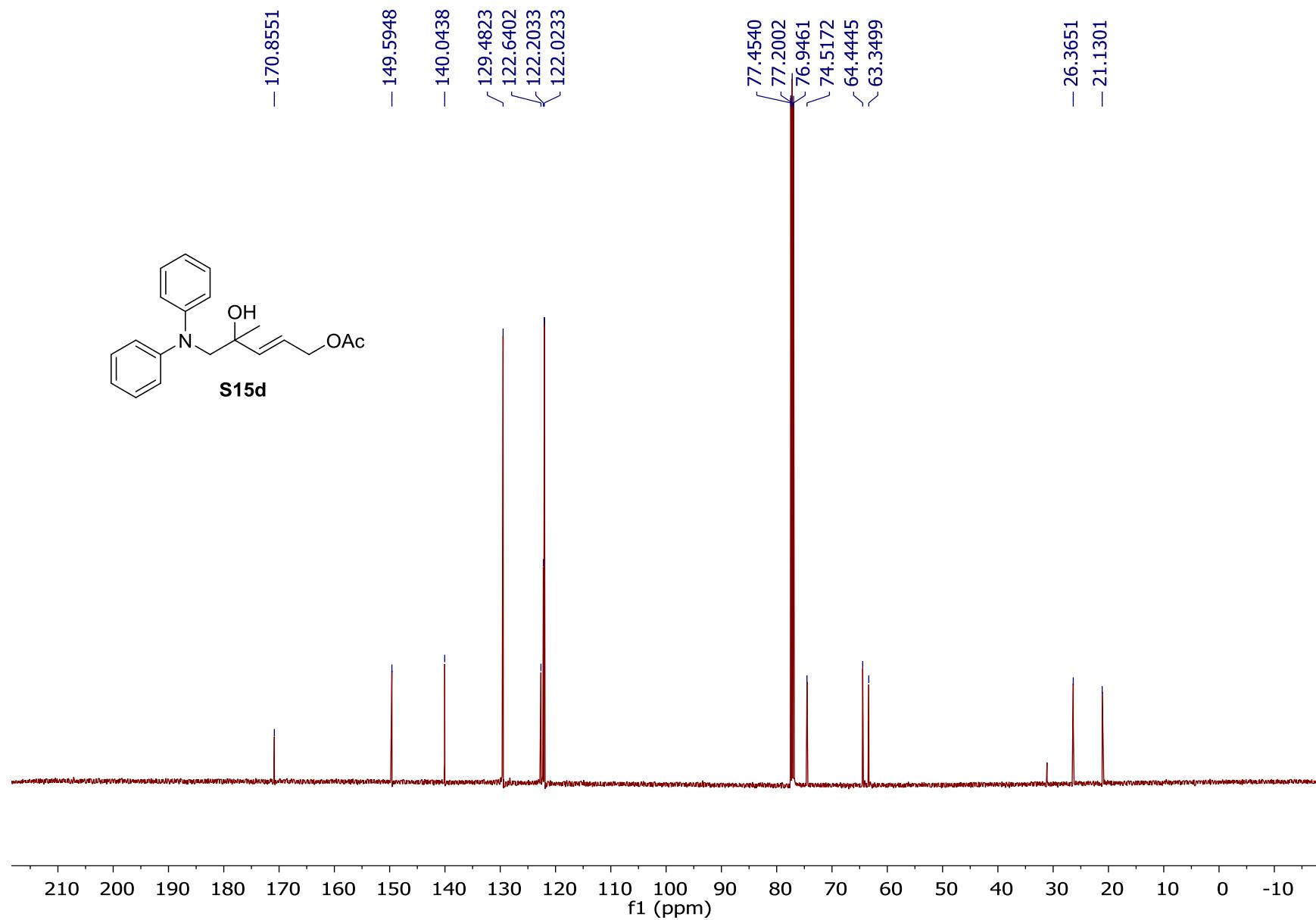
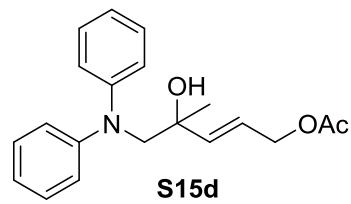
Compound S15c, 400 MHz ^1H NMR in CDCl_3



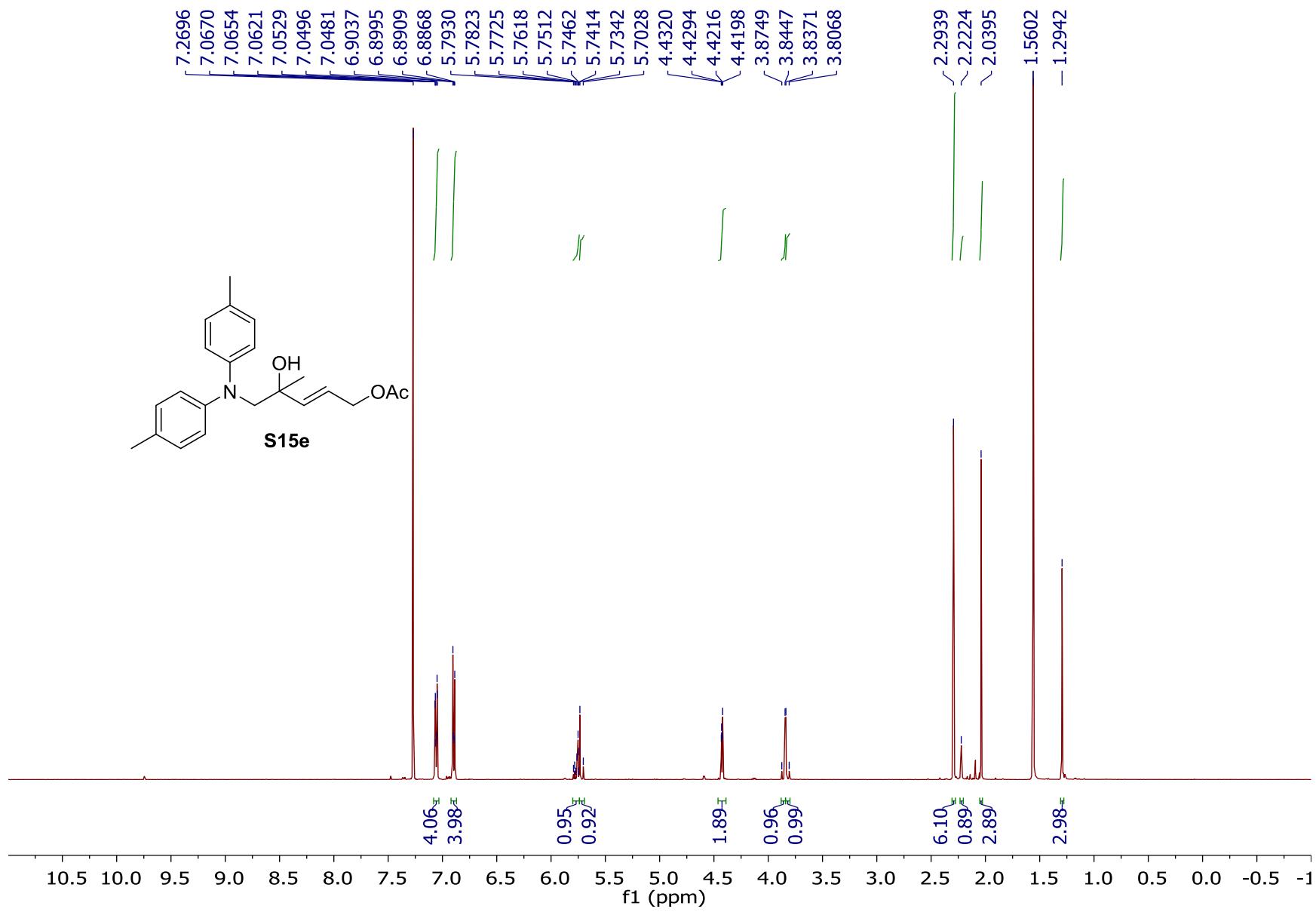
Compound S15c, 101 MHz ^{13}C NMR in CDCl_3

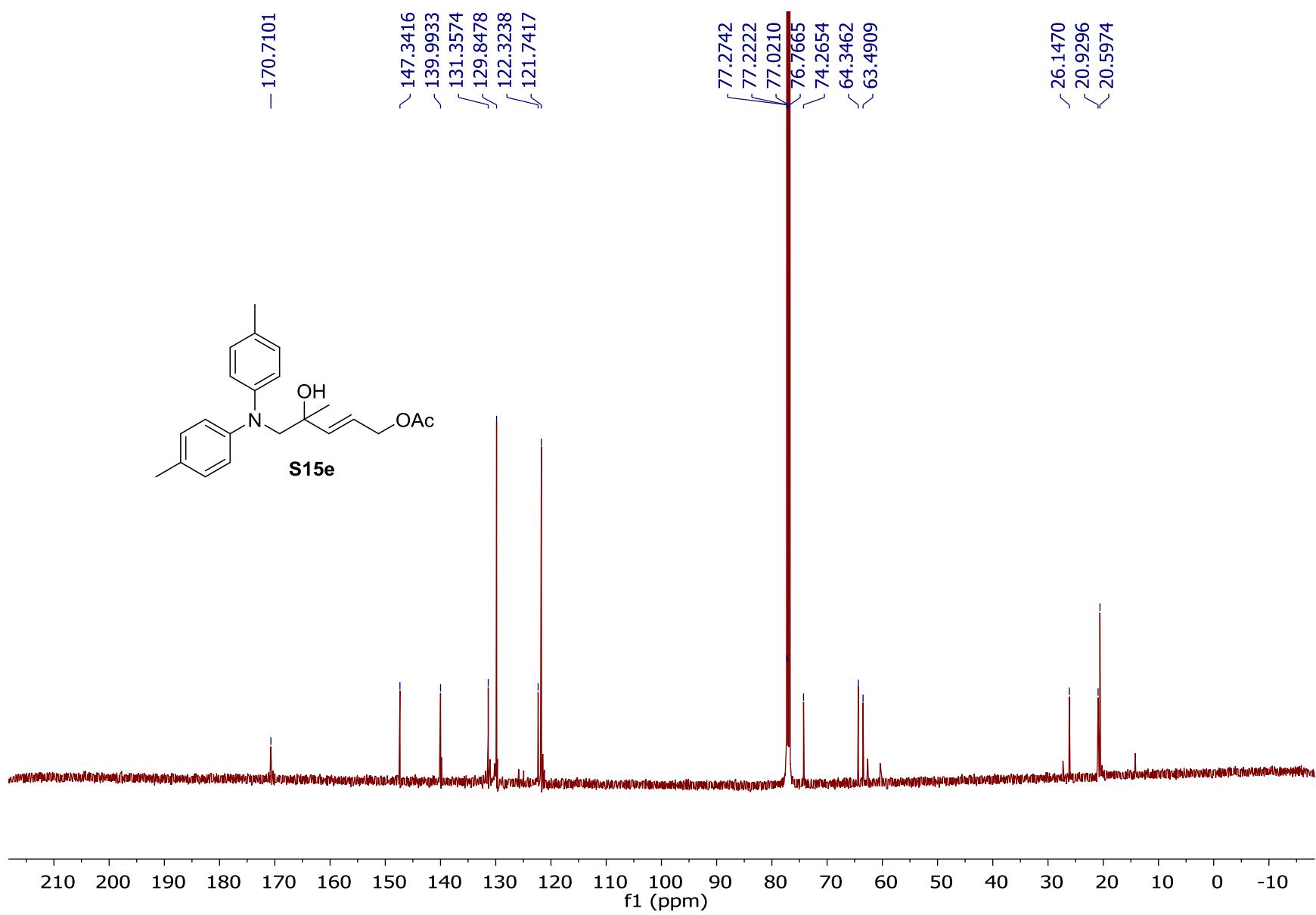


Compound S15d, 400 MHz ^1H NMR in CDCl_3

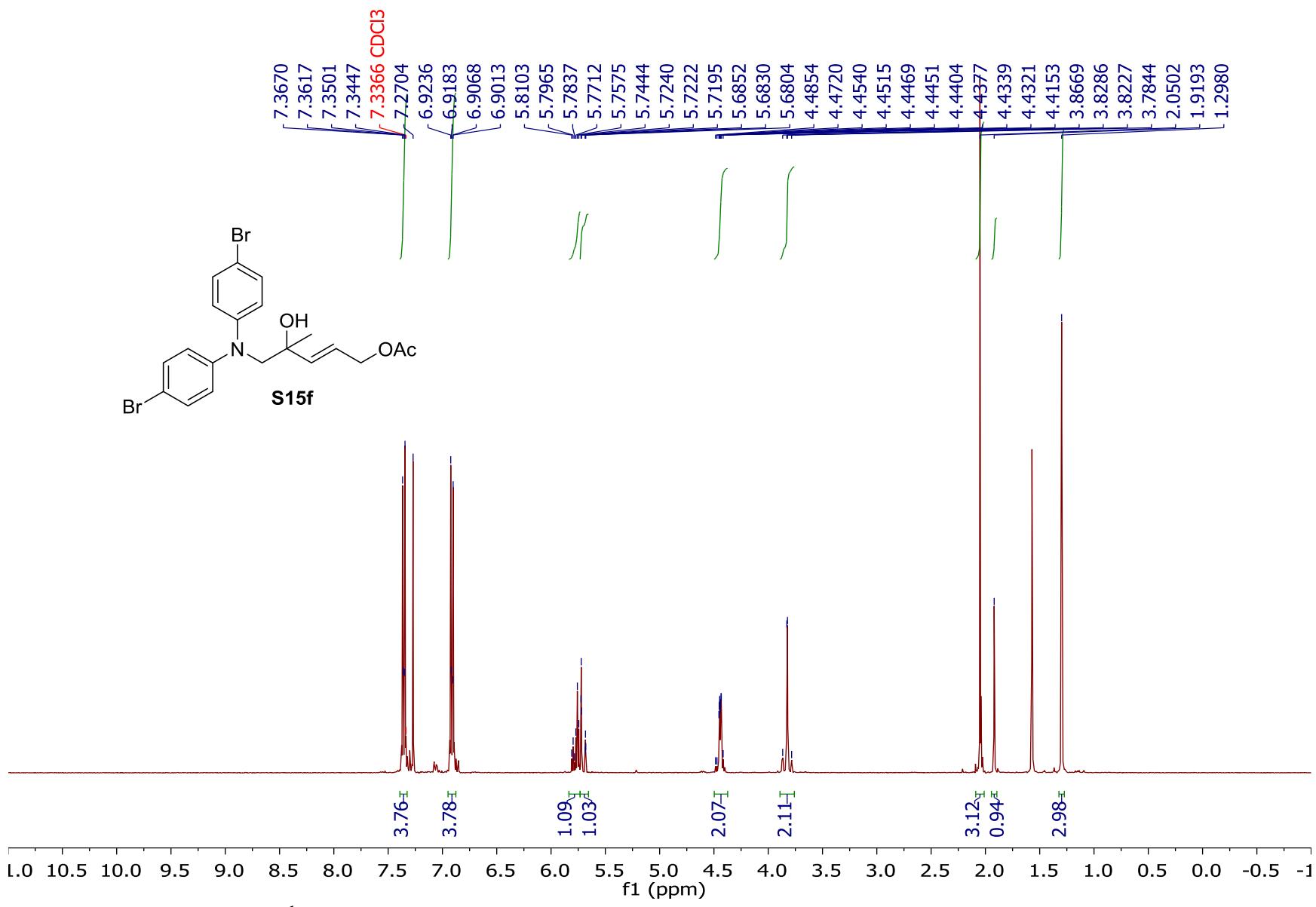


Compound S15d, 126 MHz ¹³C NMR in CDCl₃

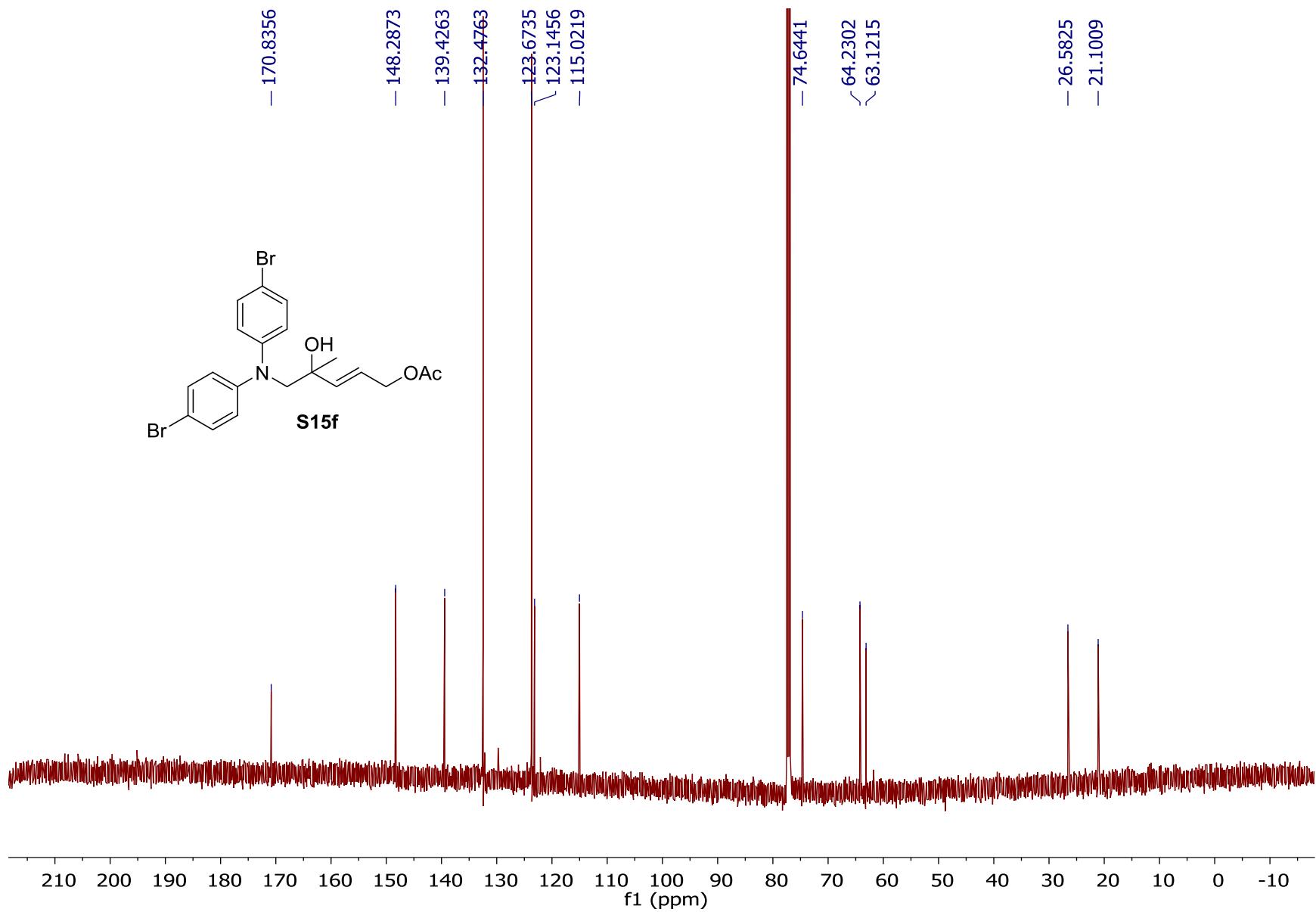




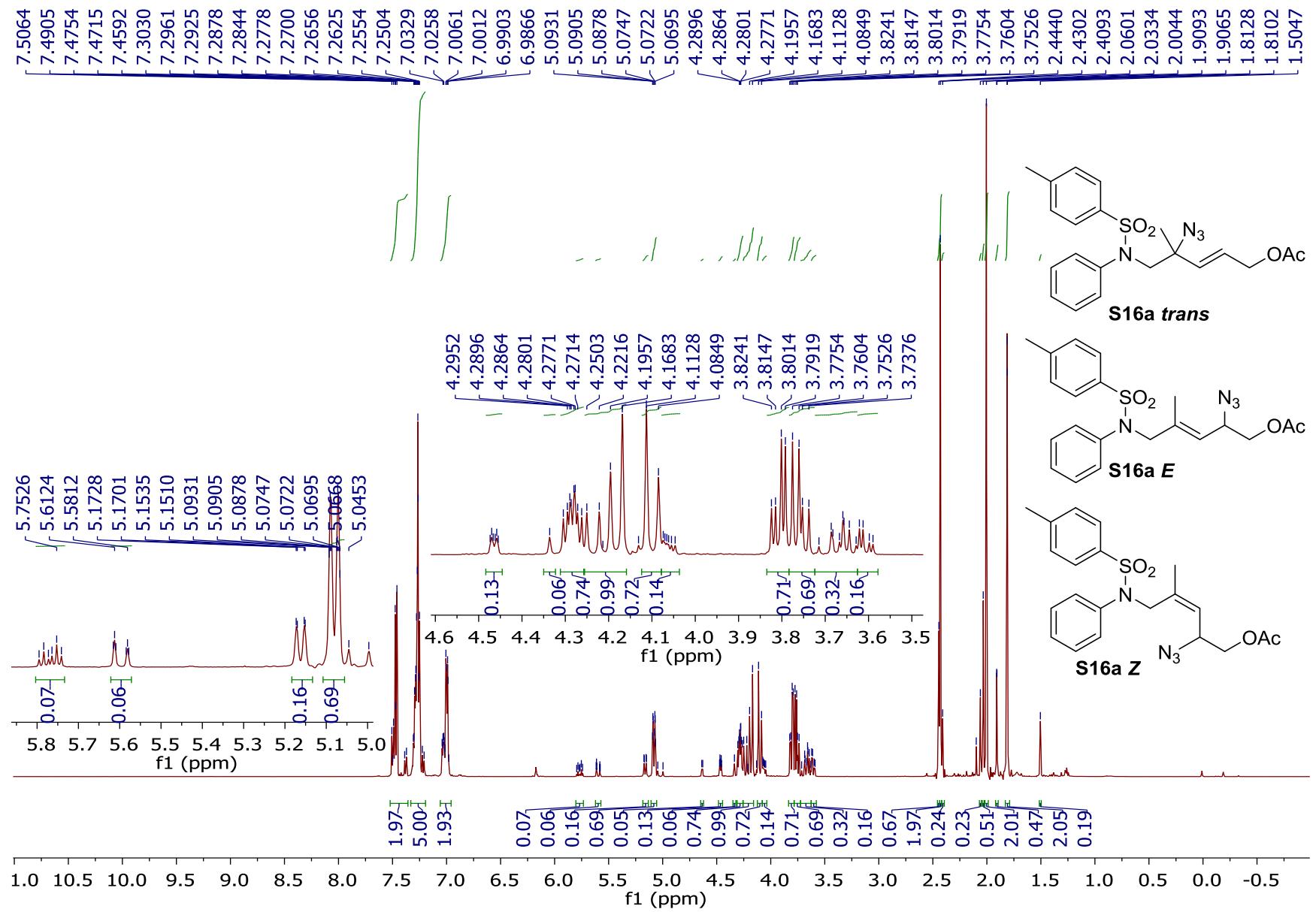
Compound S15e, 126 MHz ^{13}C NMR in CDCl_3



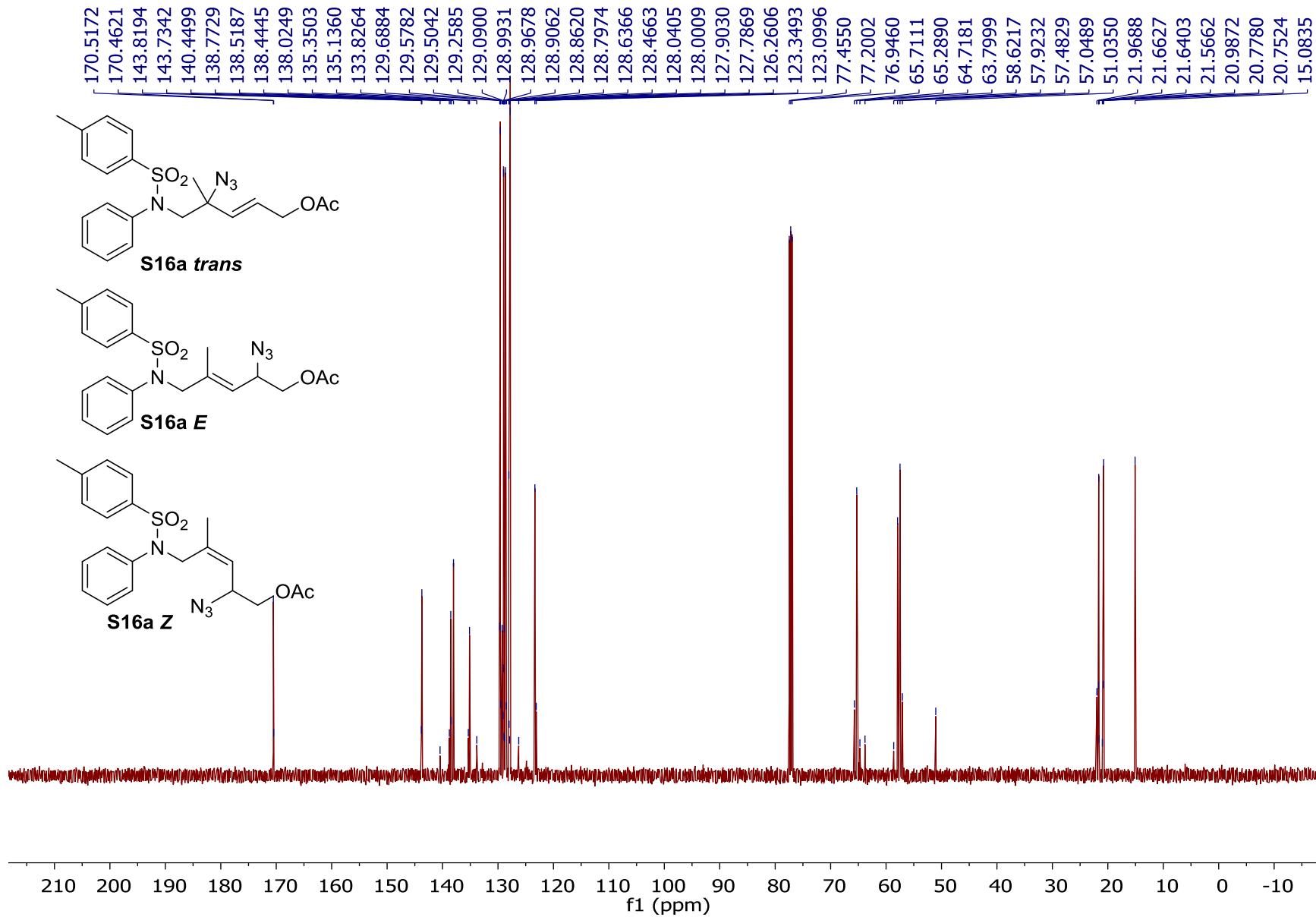
Compound S15f, 400 MHz ¹H NMR in CDCl₃



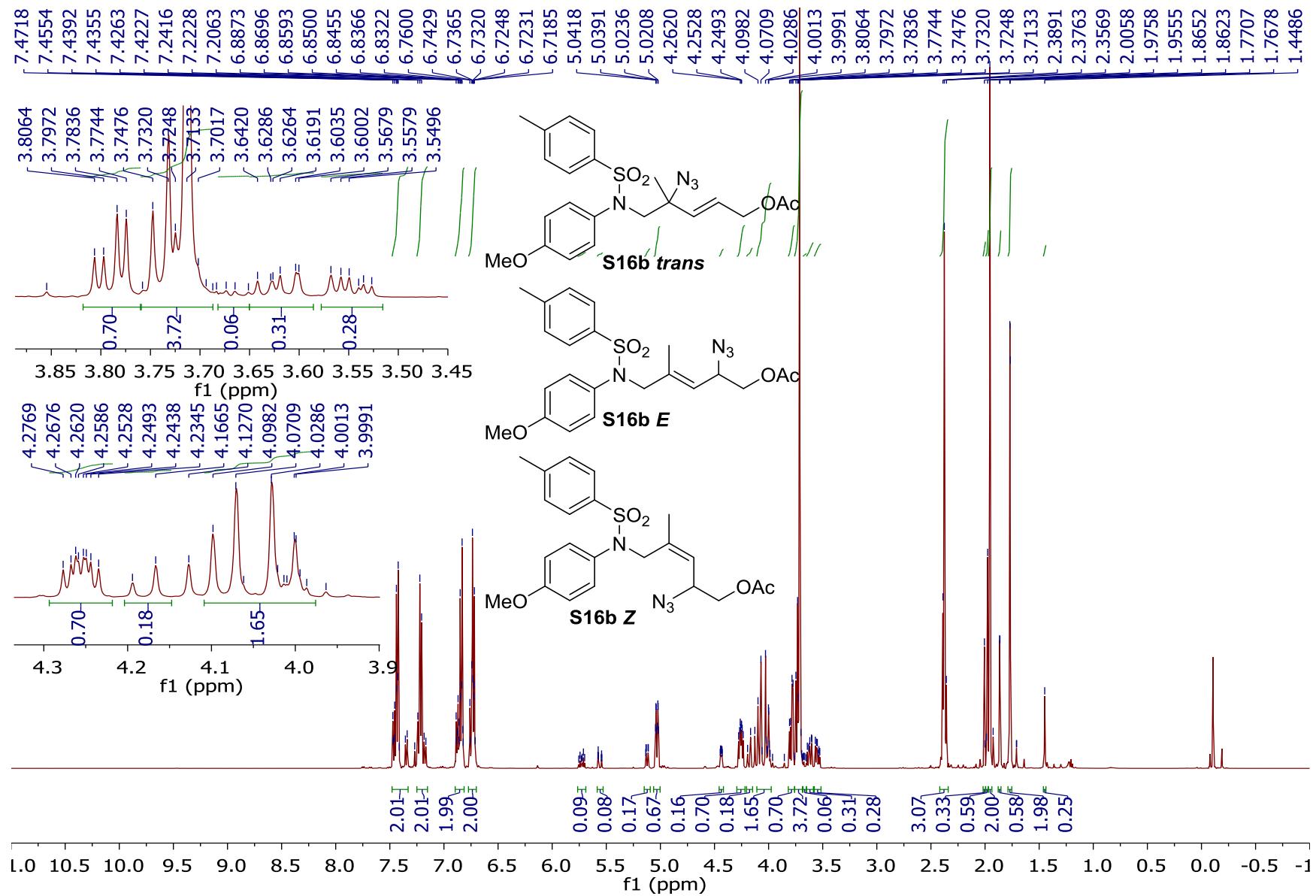
Compound S15f, 126 MHz ^{13}C NMR in CDCl_3



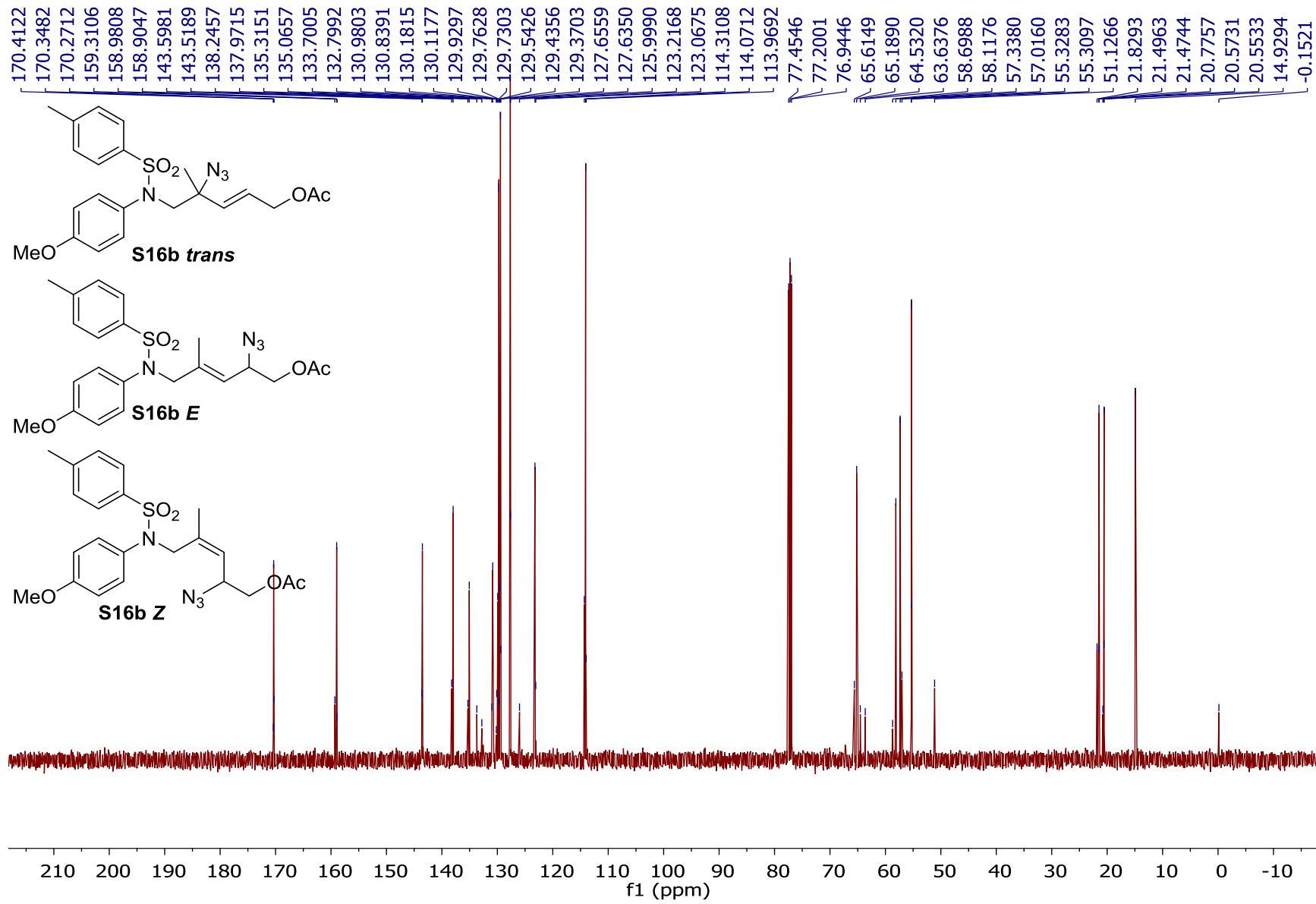
Compound S16a, 500 MHz ^1H NMR in CDCl_3



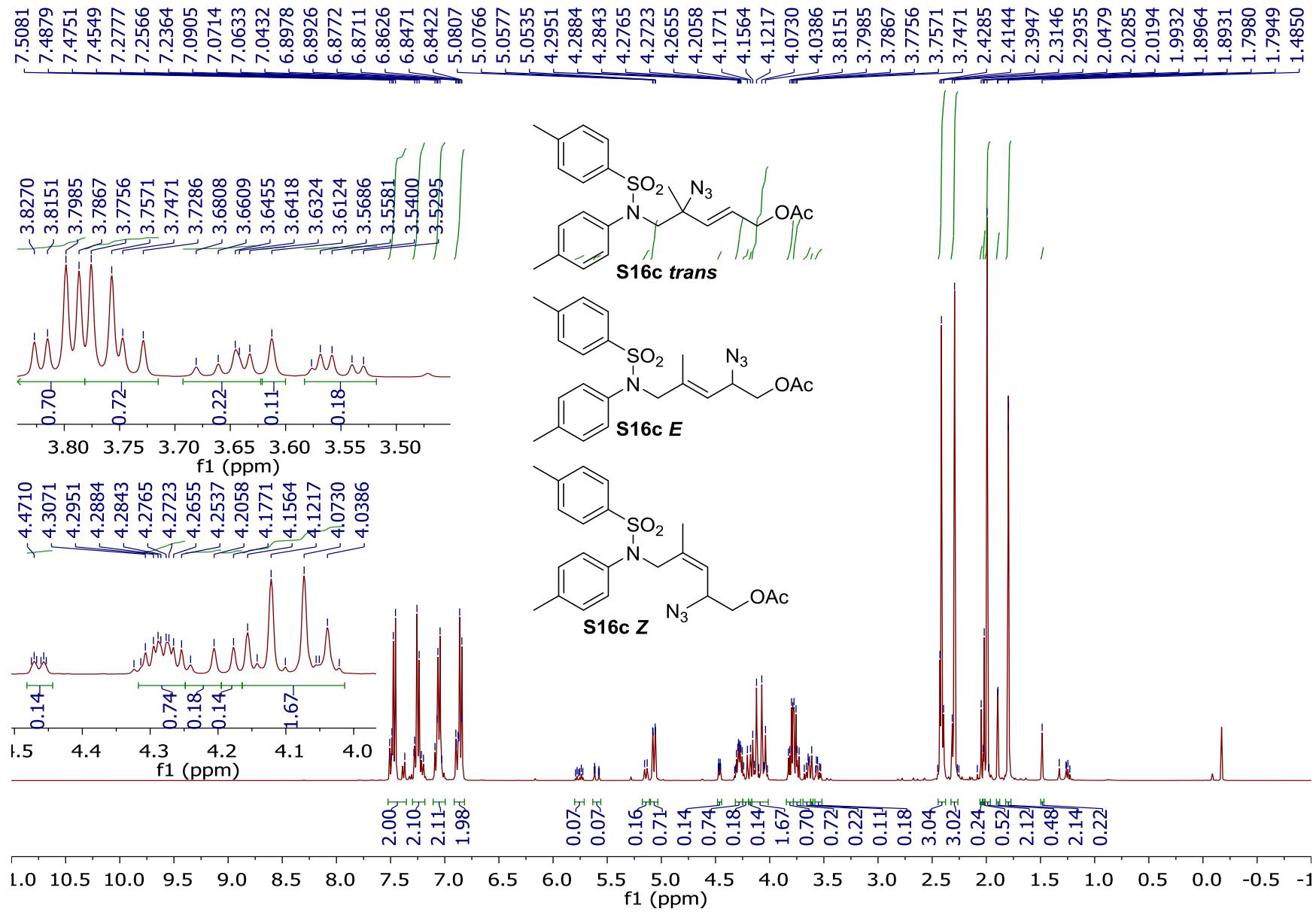
Compound S16a, 126 MHz ^{13}C NMR in CDCl_3



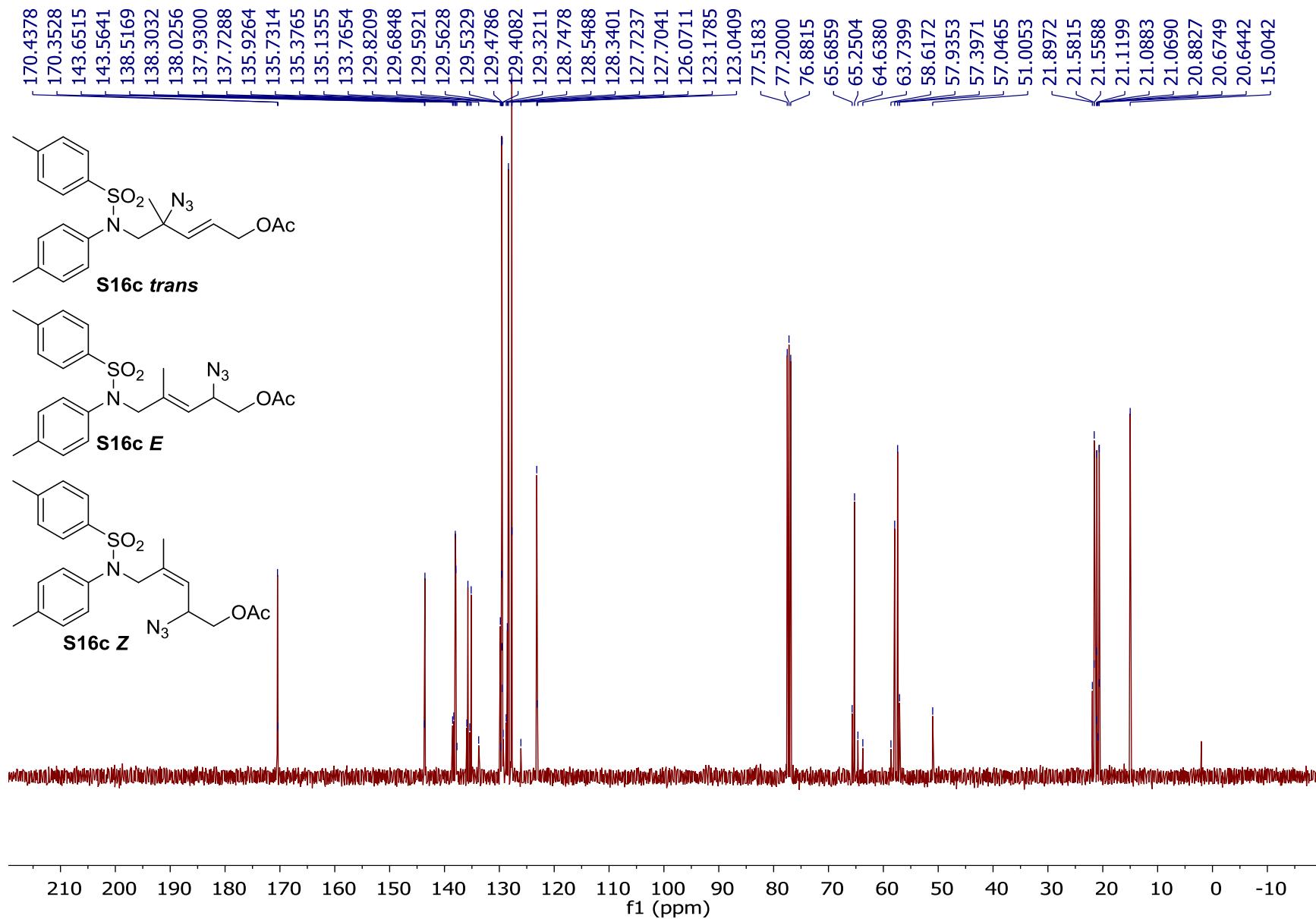
Compound S16b, 500 MHz ^1H NMR in CDCl_3



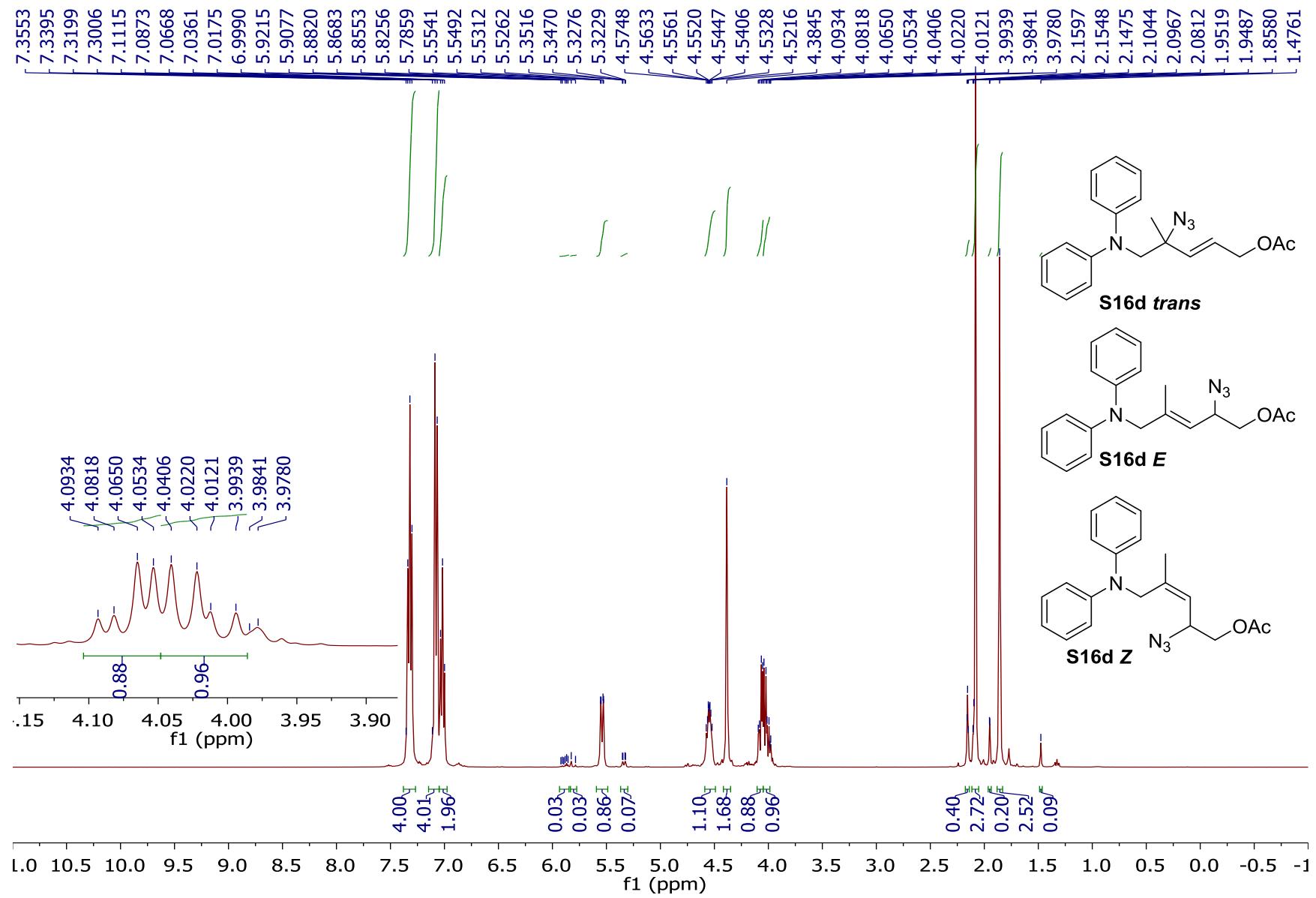
Compound S16b, 126 MHz ^{13}C NMR in CDCl_3



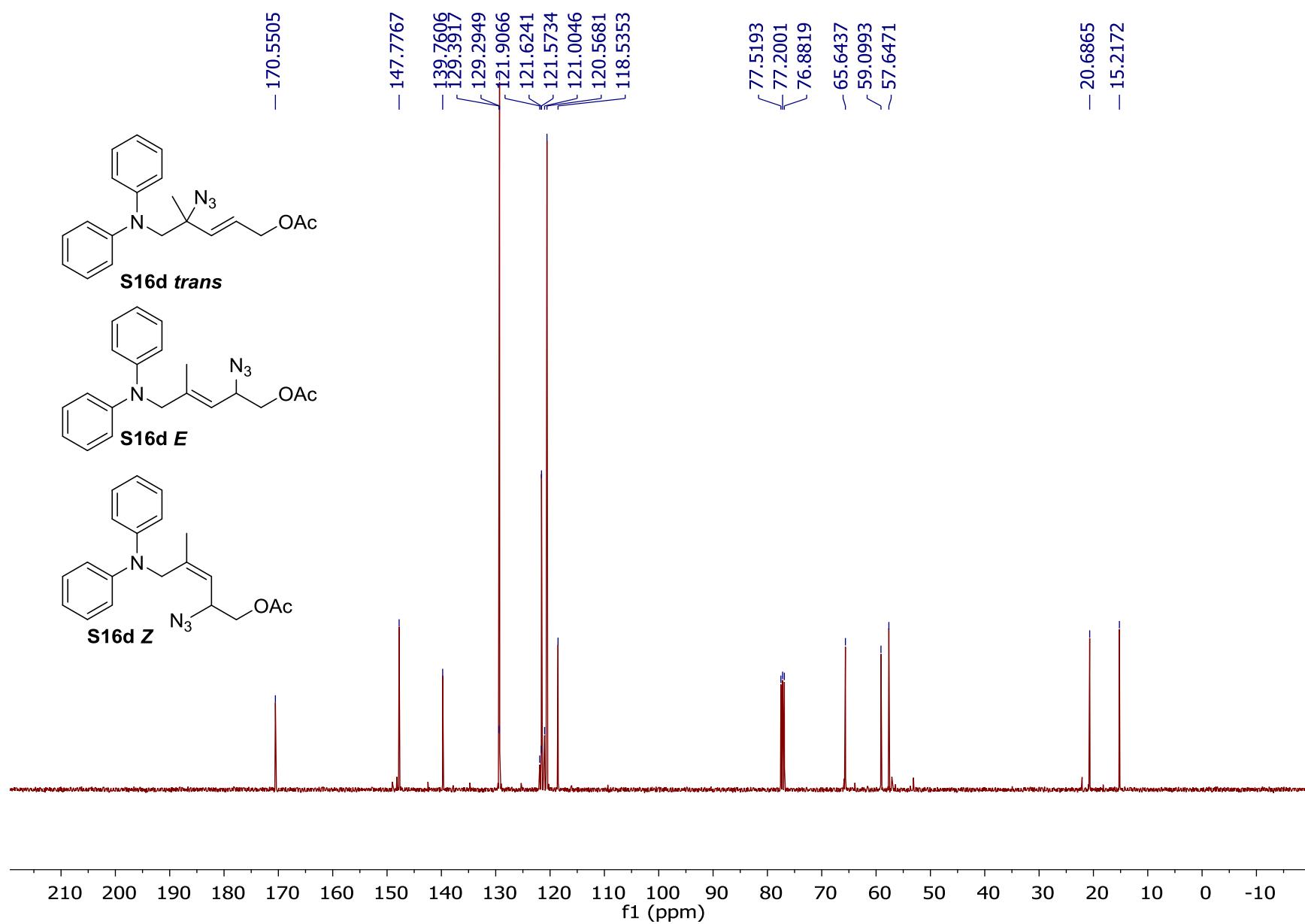
Compound S16c, 400 MHz ^1H NMR in CDCl_3



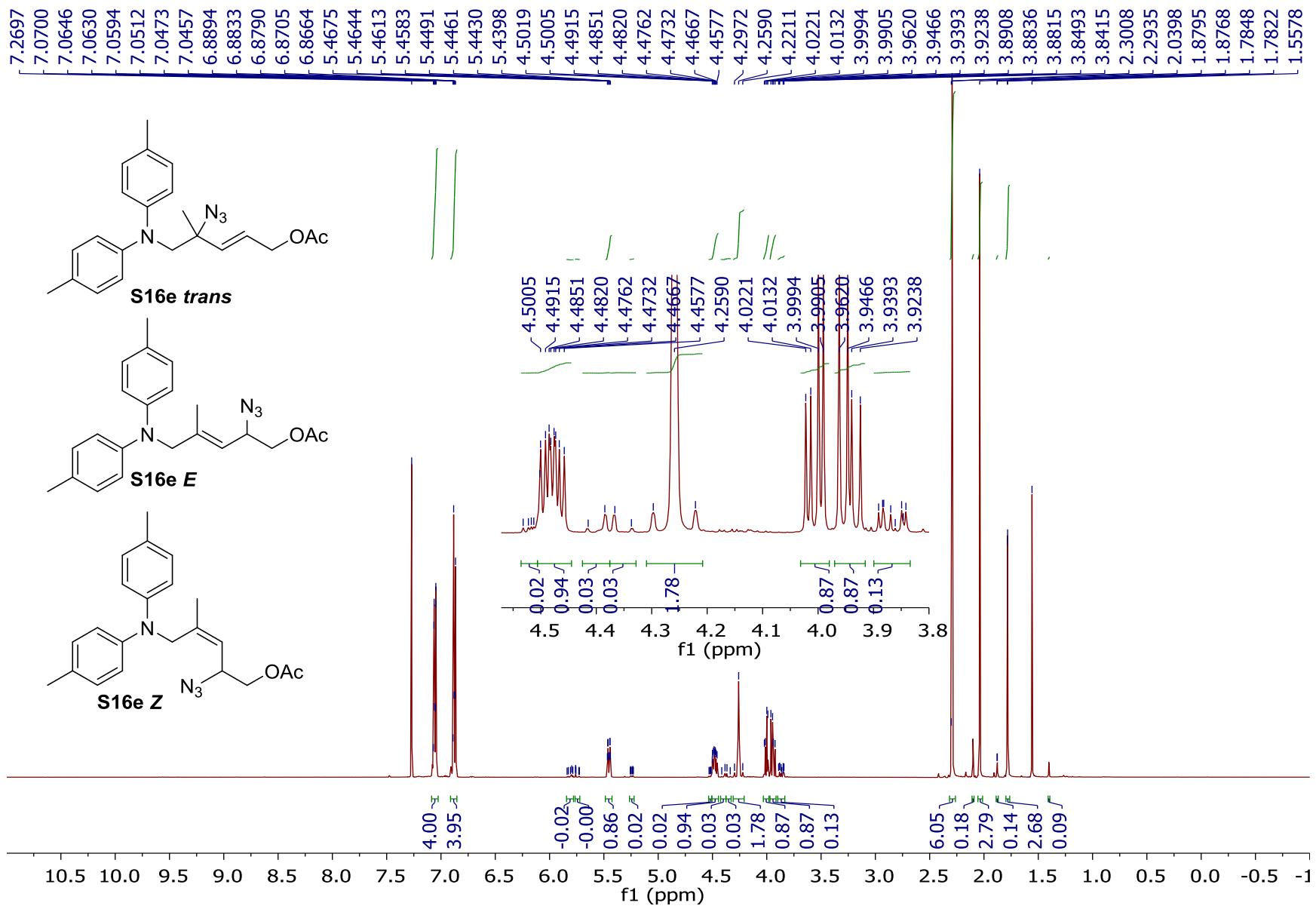
Compound S16c, 101 MHz ^{13}C NMR in CDCl_3



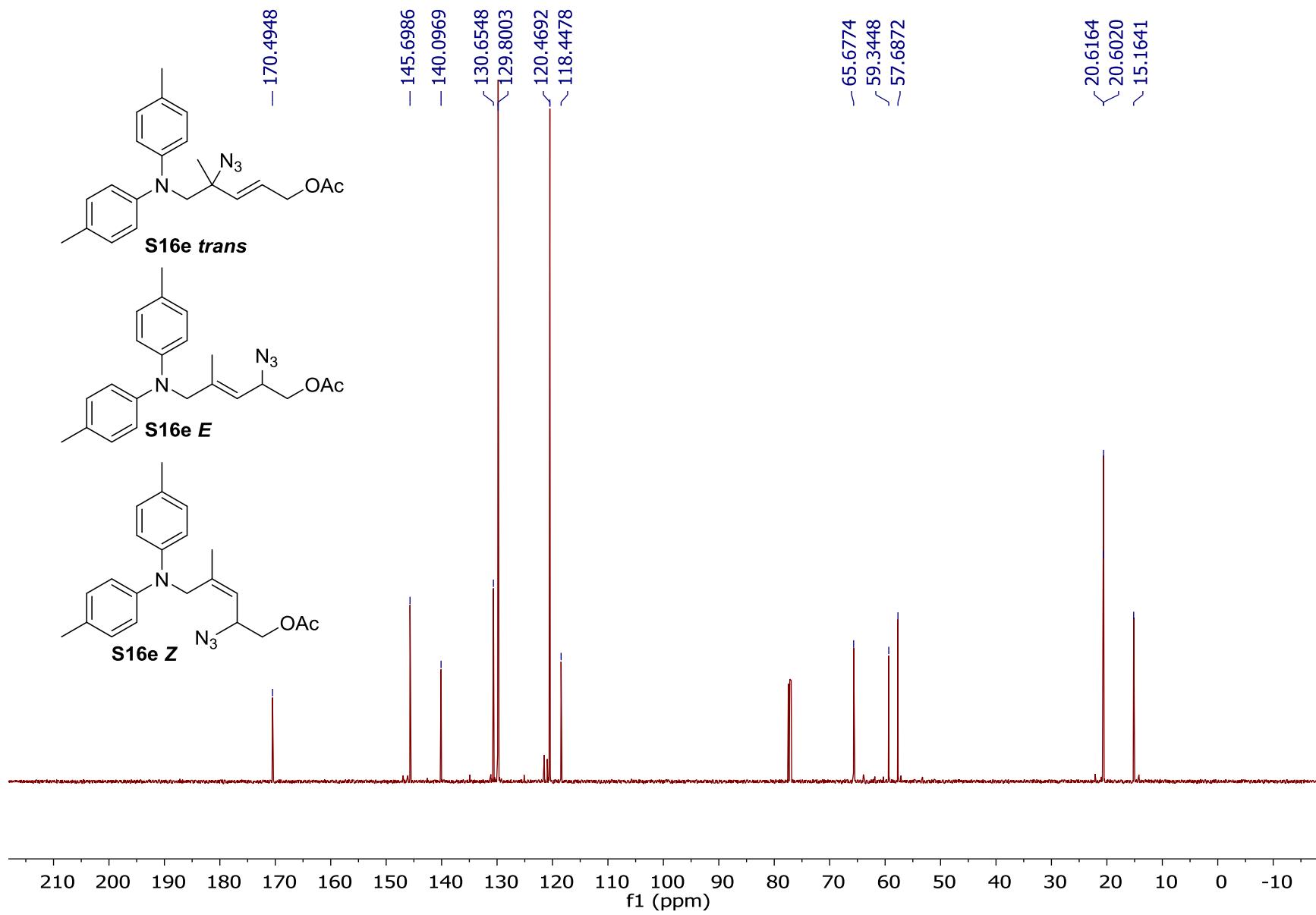
Compound S16d, 400 MHz ^1H NMR in CDCl_3



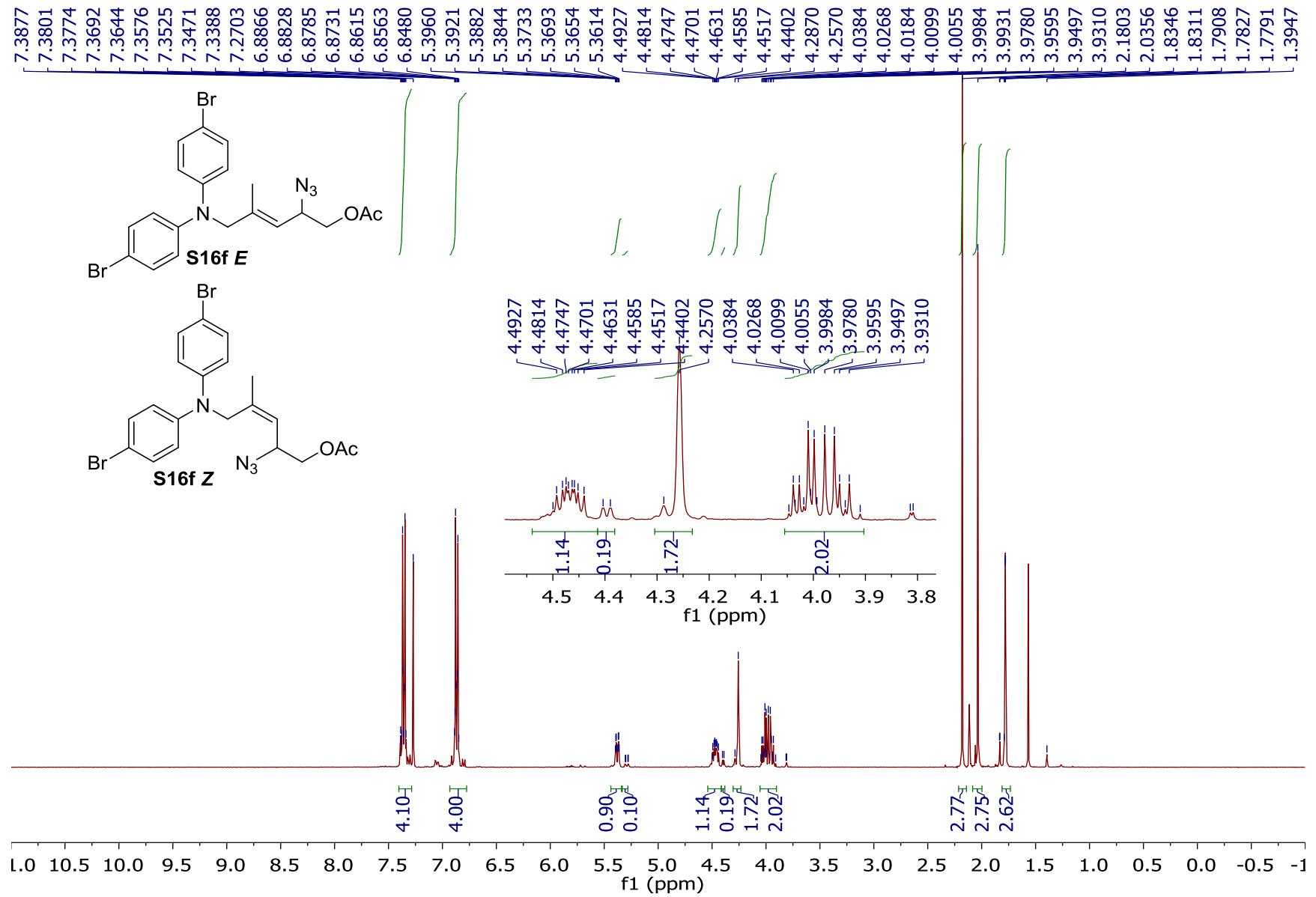
Compound S16d, 101 MHz ^{13}C NMR in CDCl_3



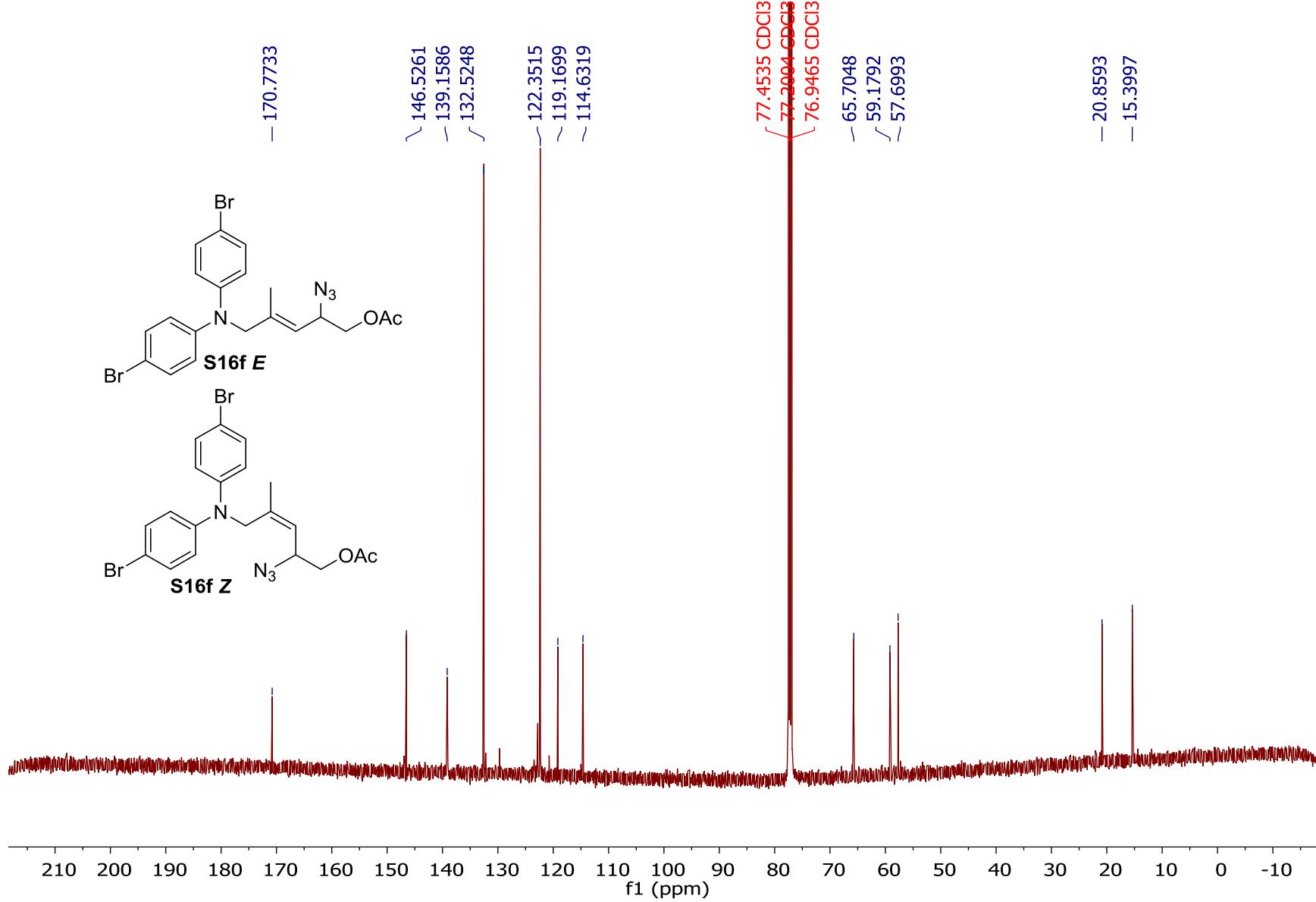
Compound S16e, 500 MHz ^1H NMR in CDCl_3



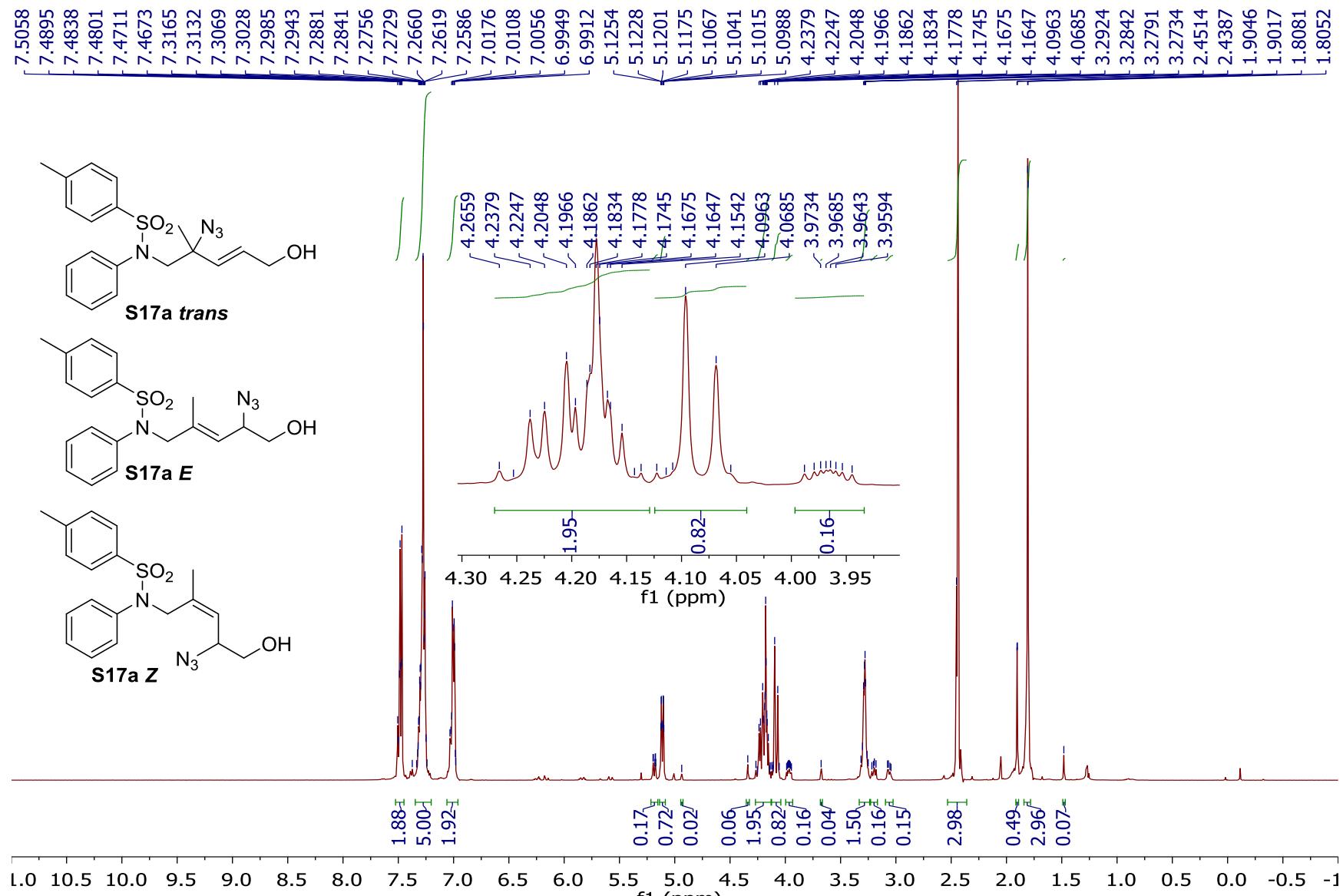
Compound S16e, 126 MHz ^{13}C NMR in CDCl_3

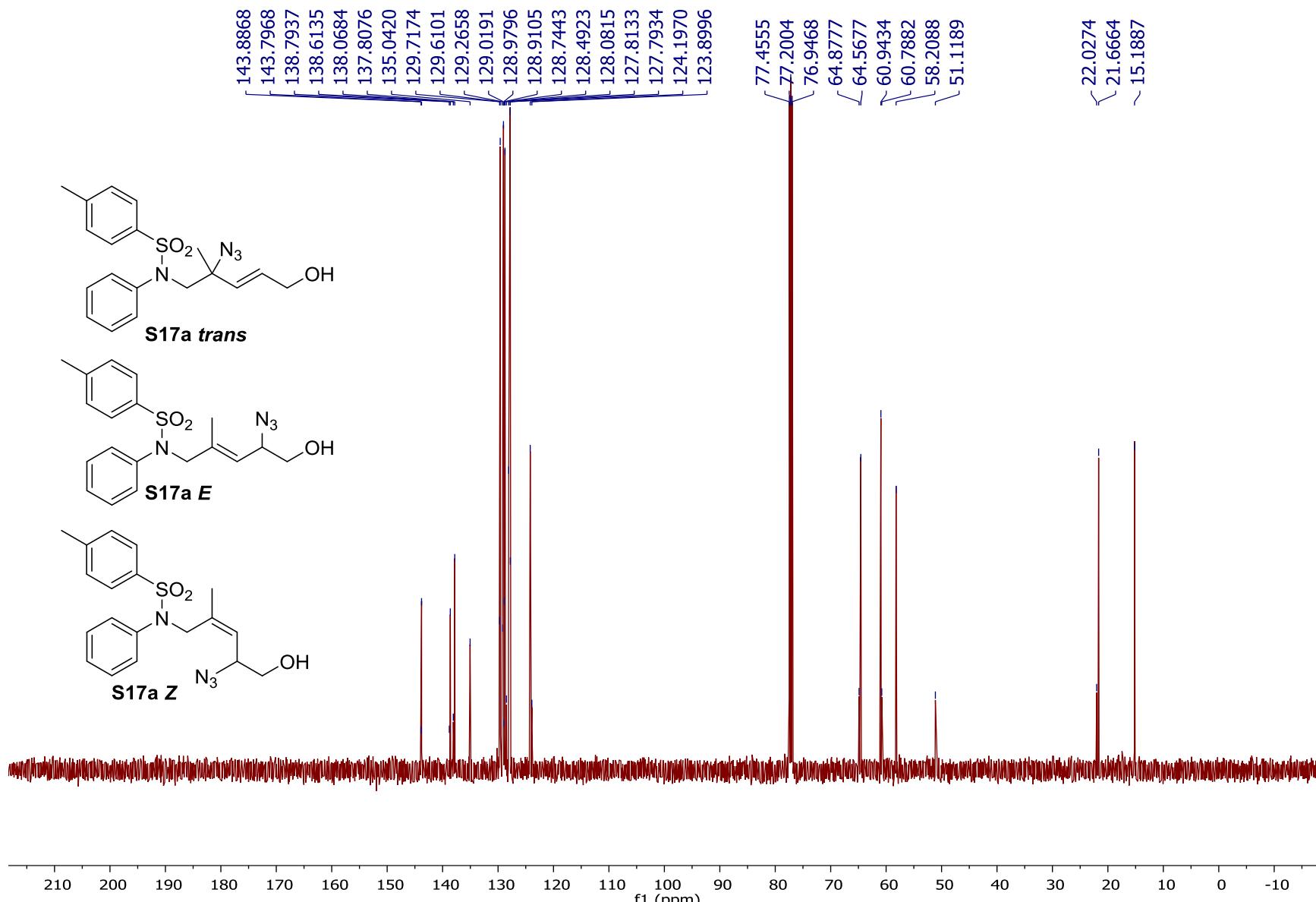


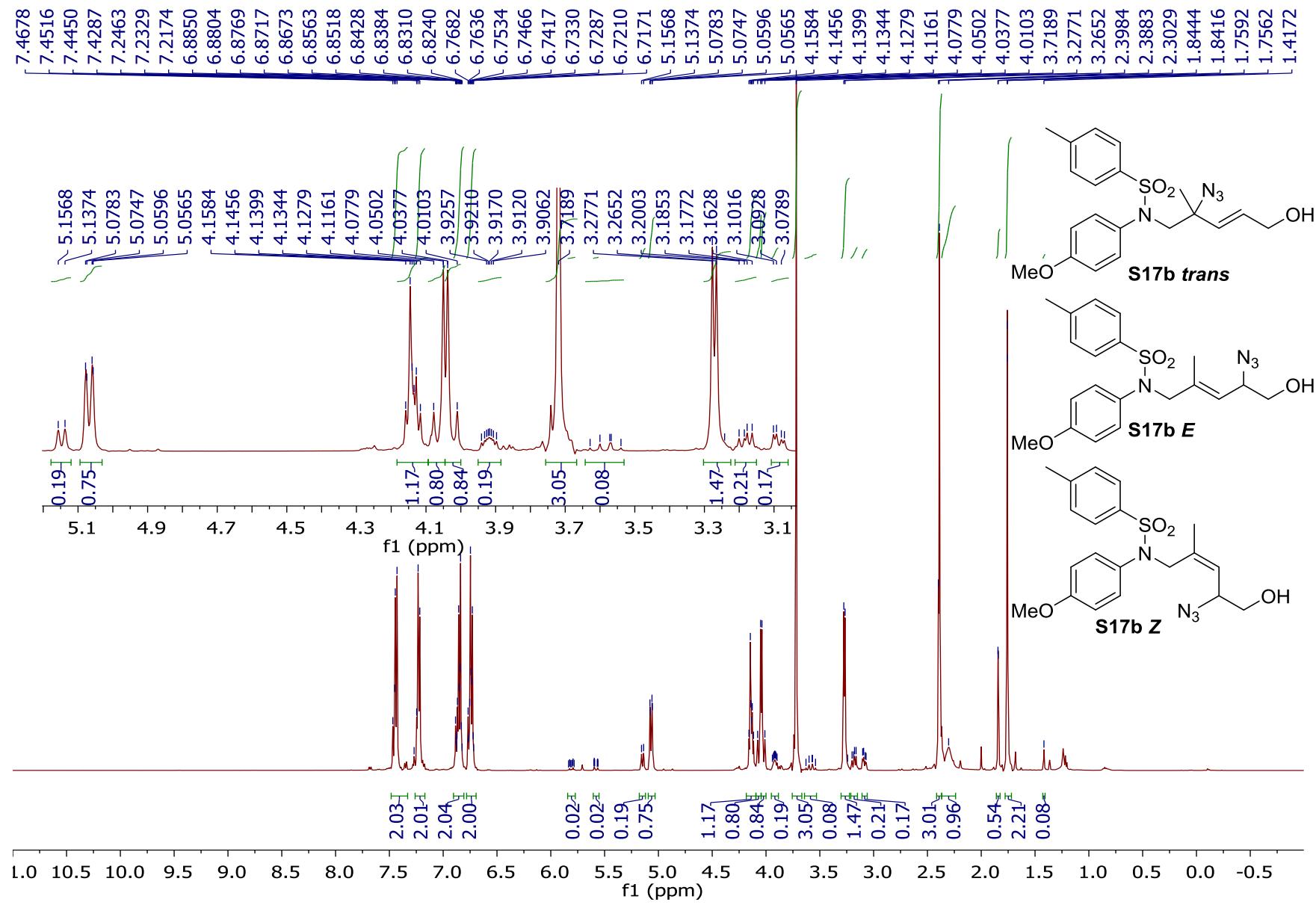
Compound S16f, 500 MHz ^1H NMR in CDCl_3



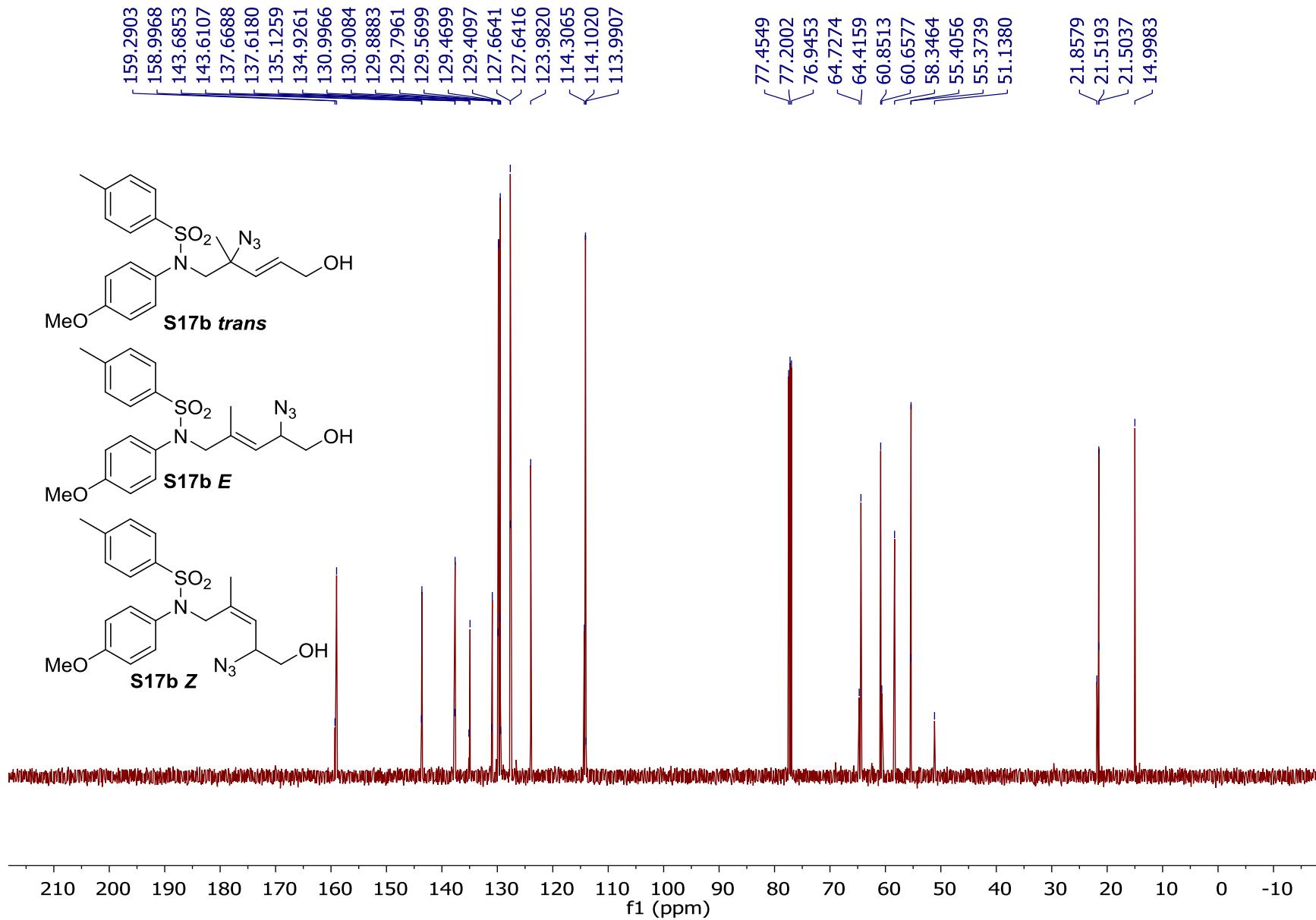
Compound S16f, 101 MHz ¹³C NMR in CDCl₃

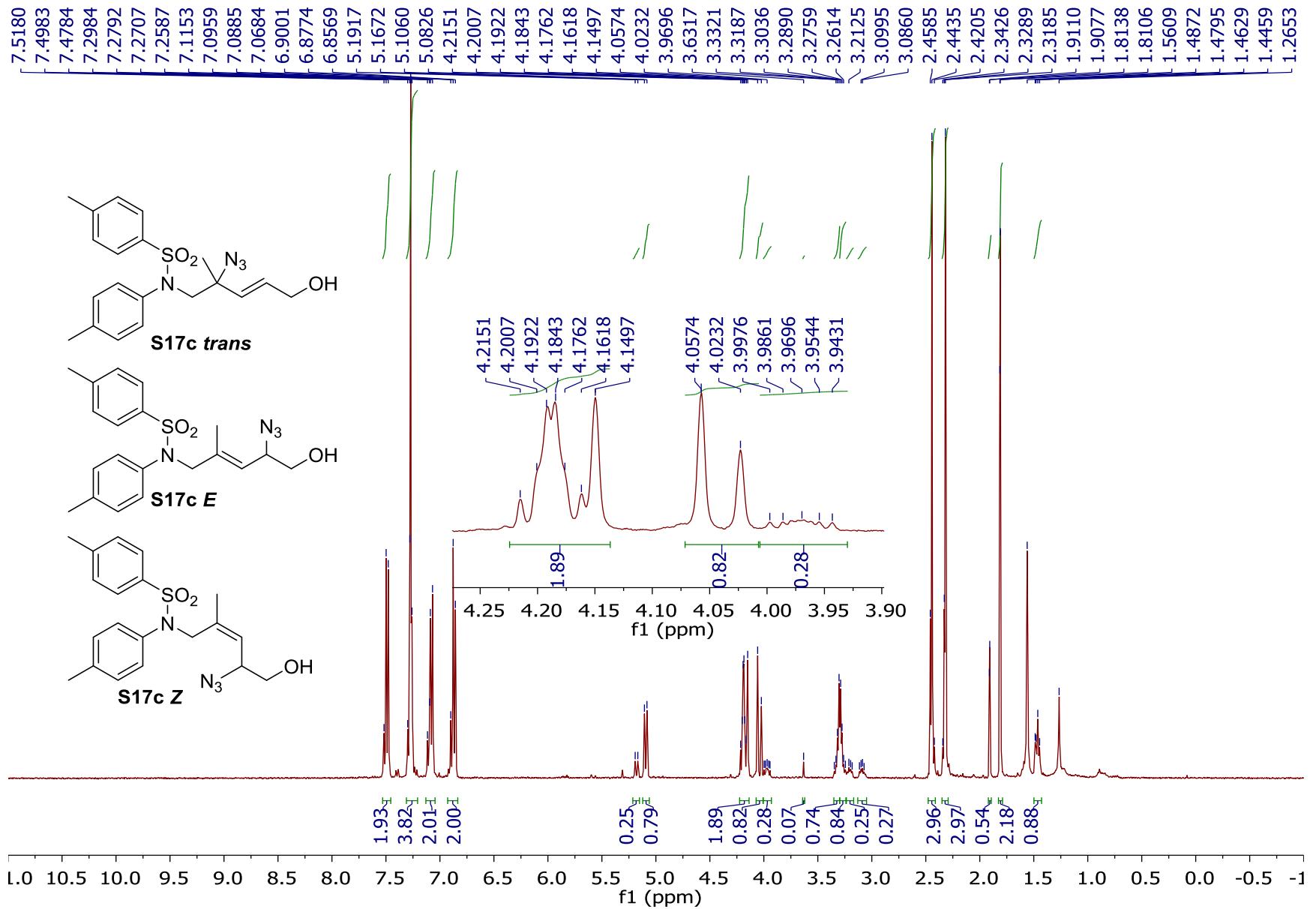




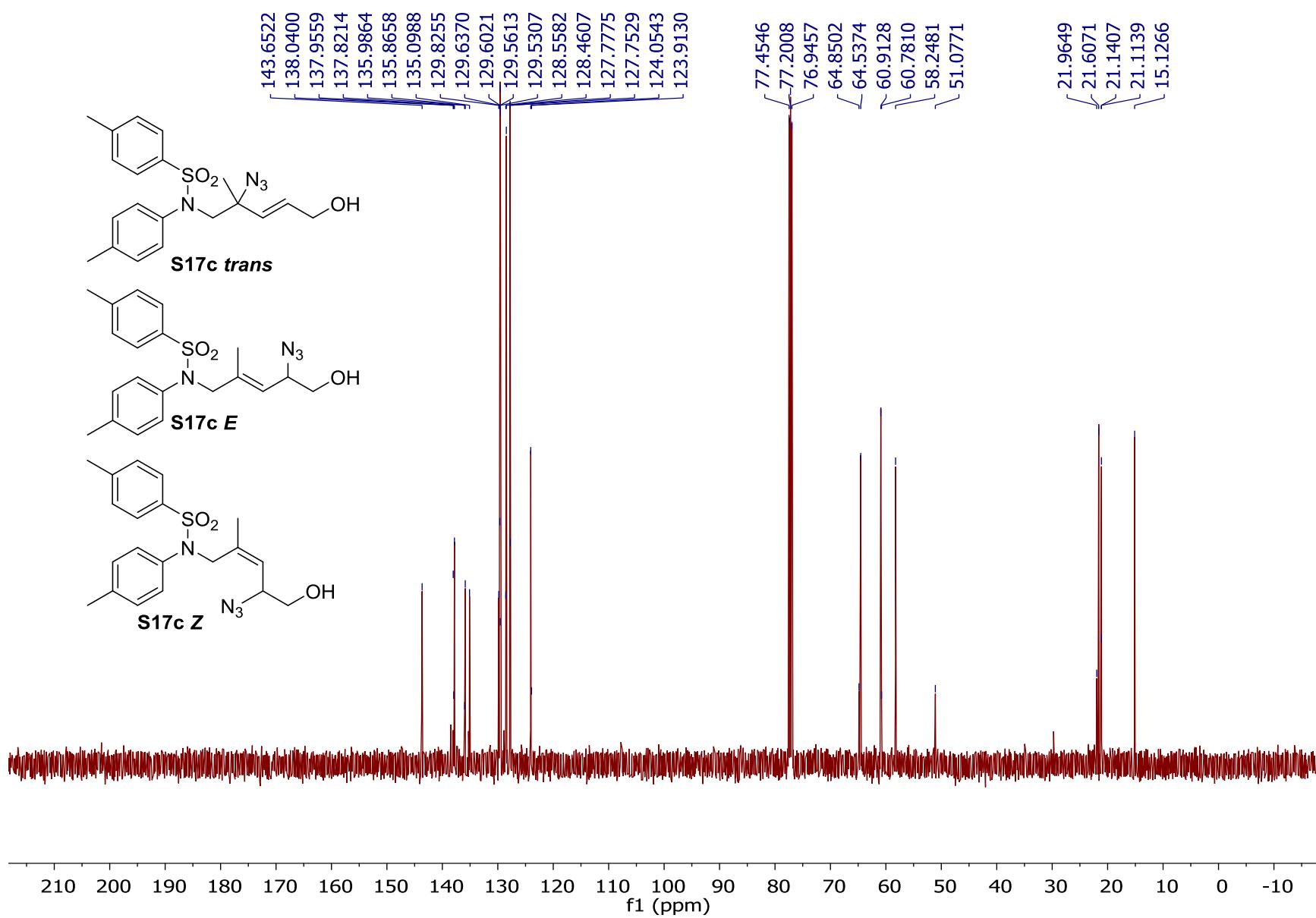


Compound S17b, 500 MHz ^1H NMR in CDCl_3

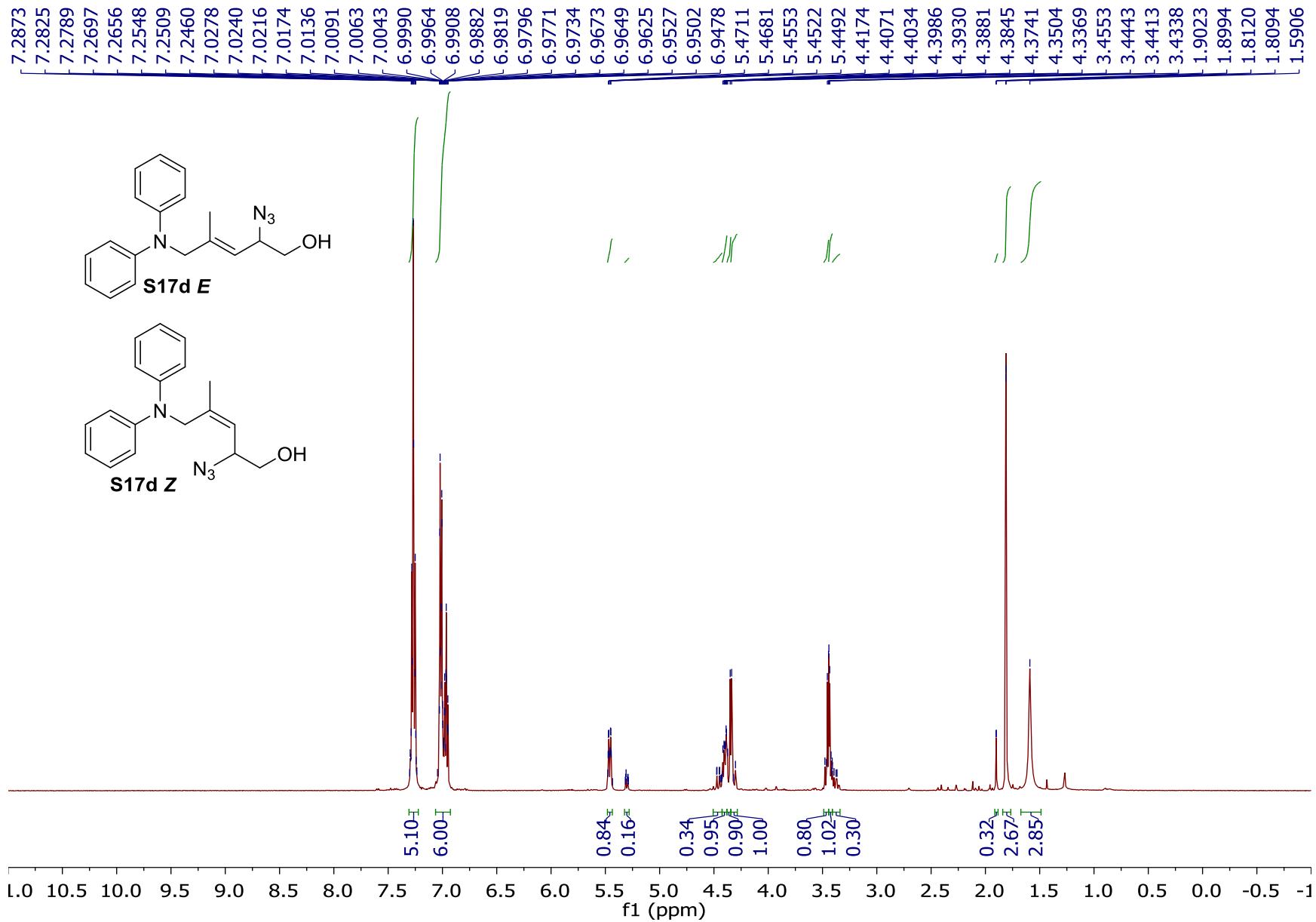




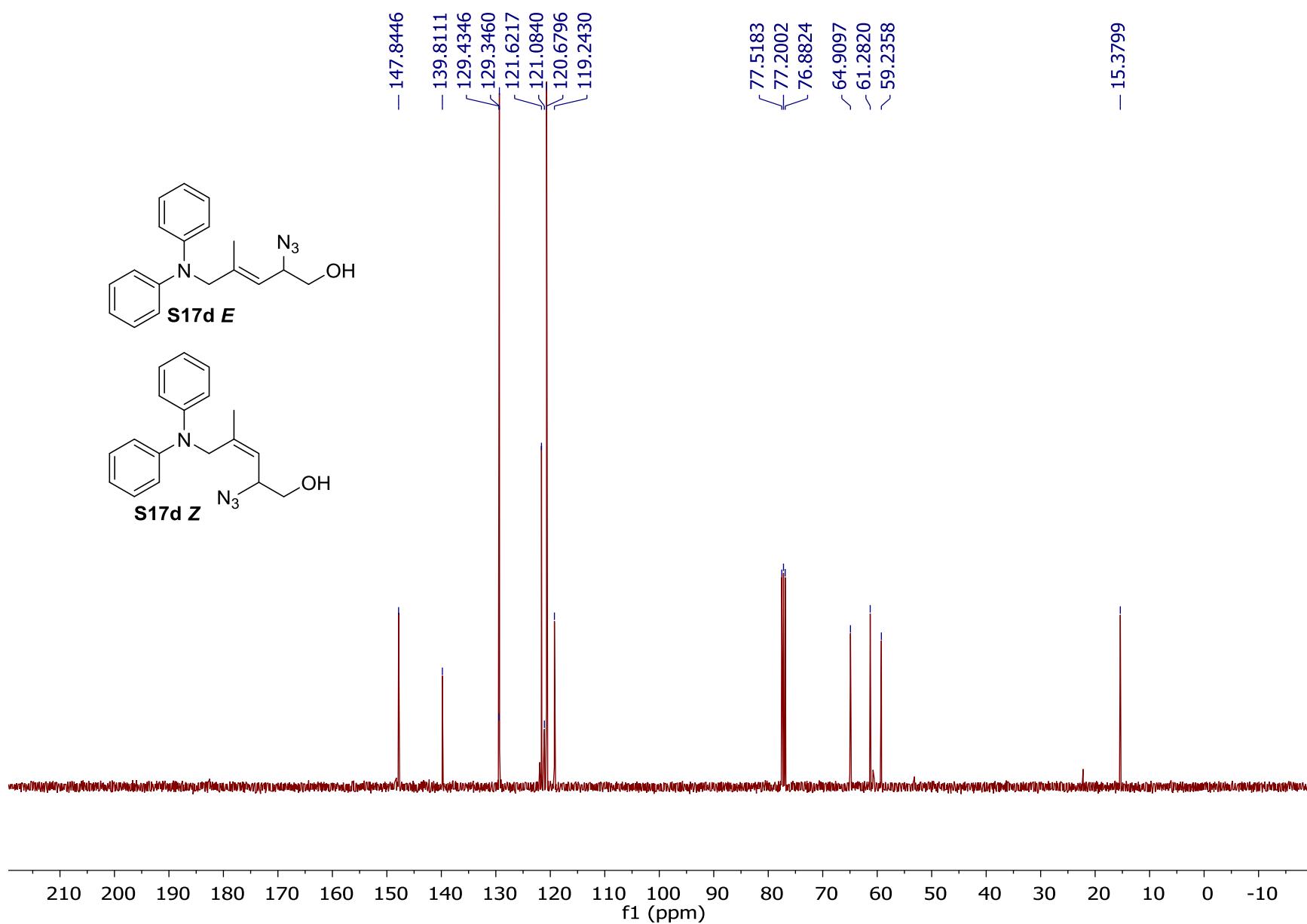
Compound S17c, 500 MHz ^1H NMR in CDCl_3



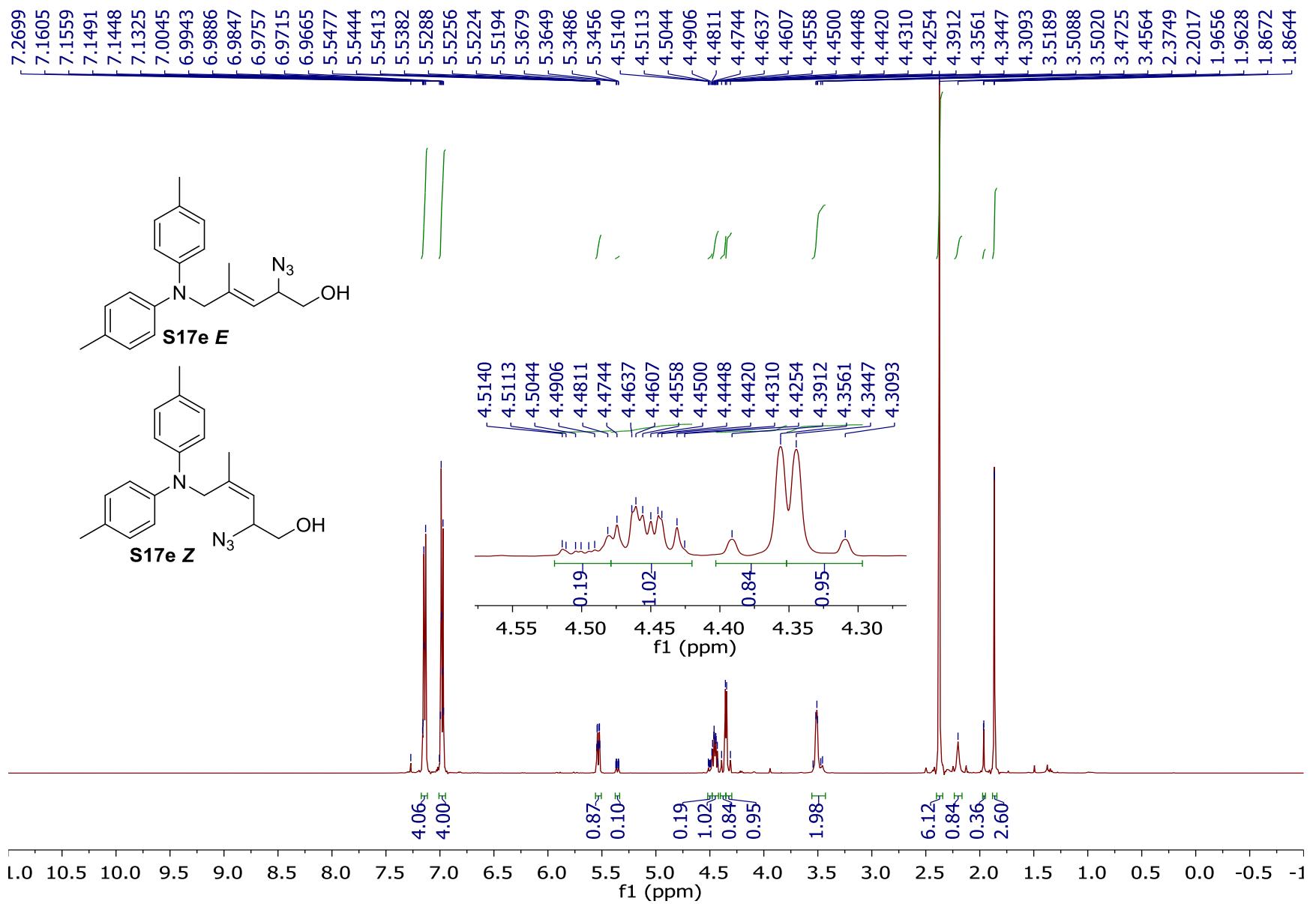
Compound S17c, 126 MHz ^{13}C NMR in CDCl_3



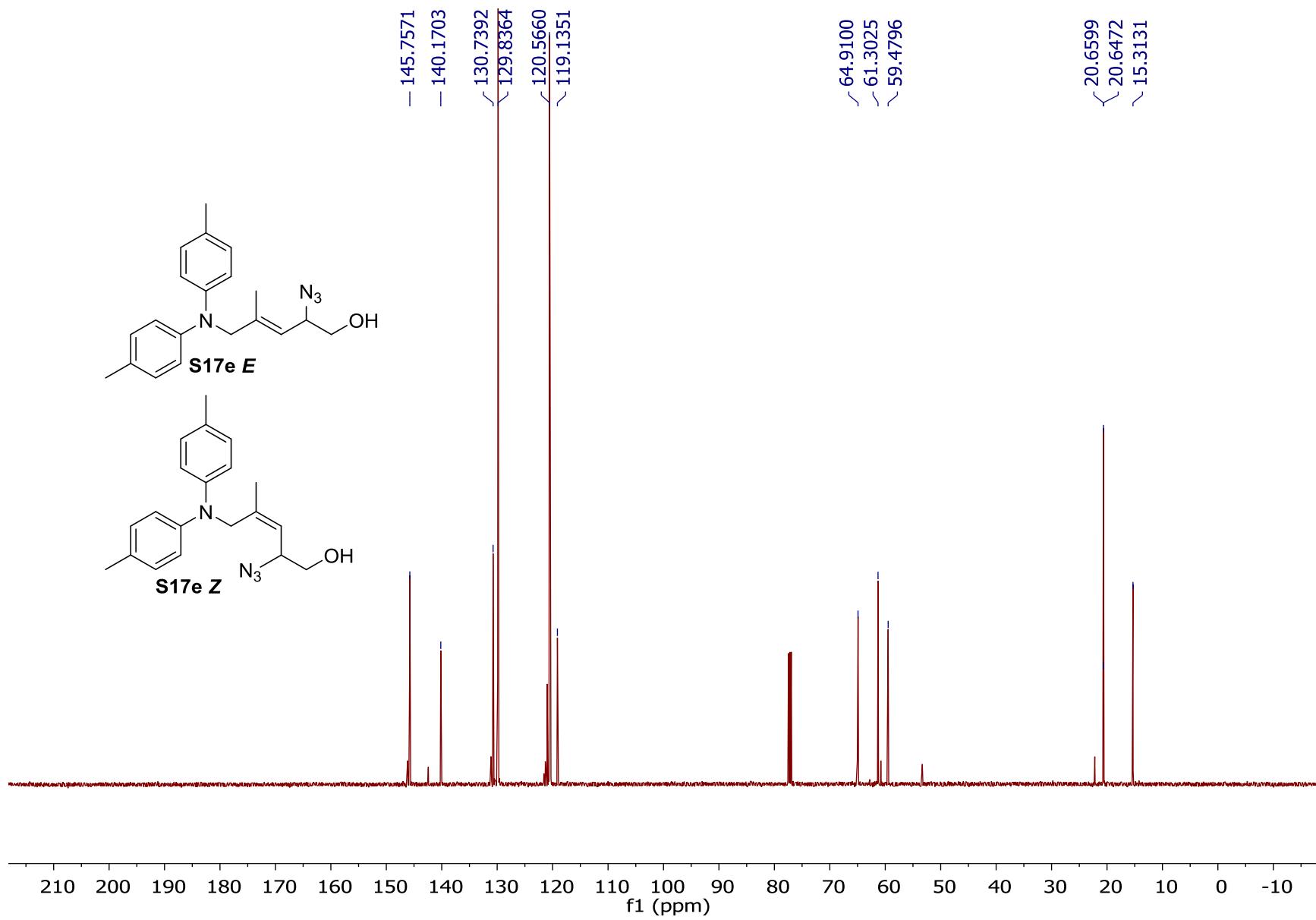
Compound S17d, 500 MHz ^1H NMR in CDCl_3



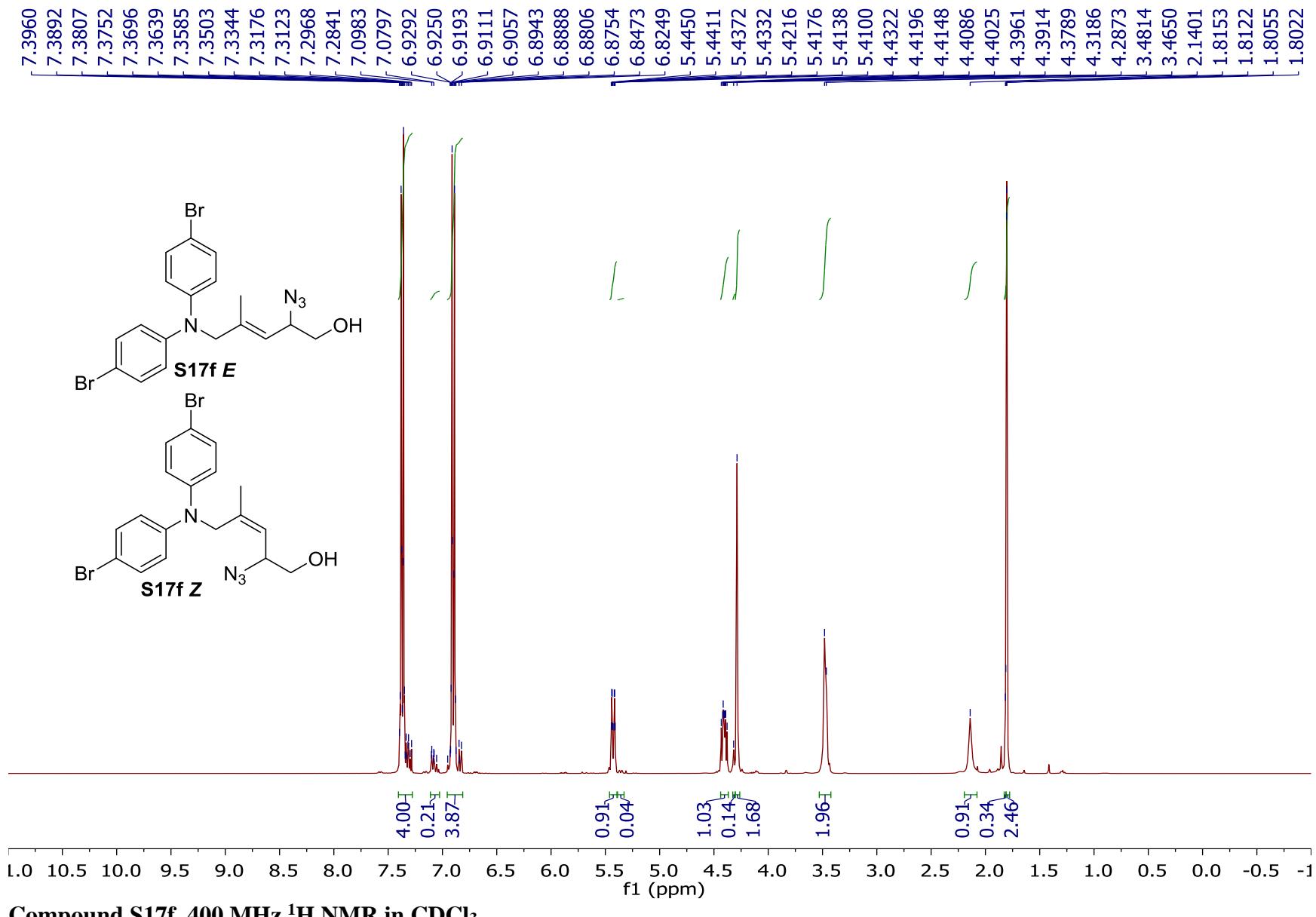
Compound S17d, 101 MHz ^{13}C NMR in CDCl_3



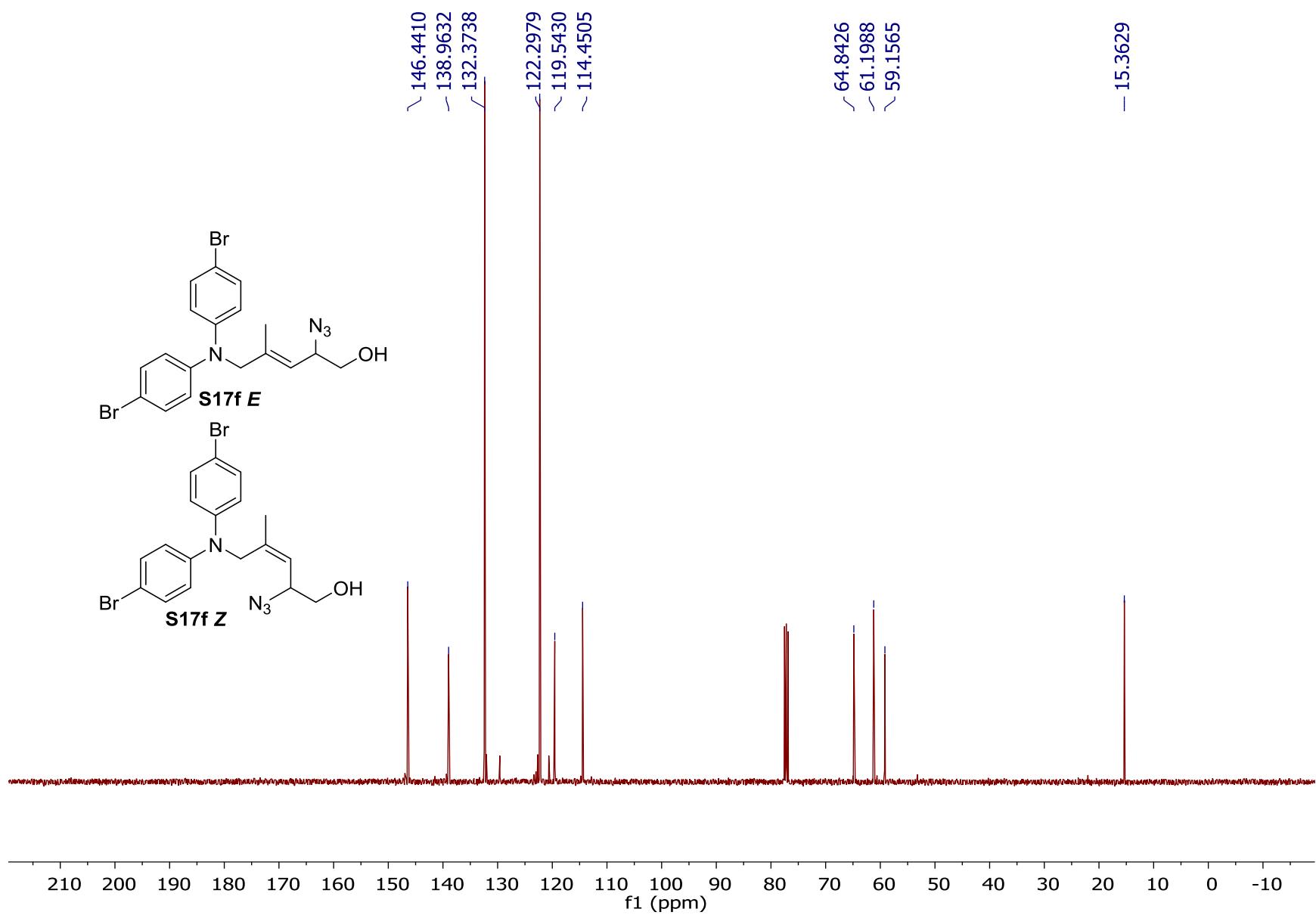
Compound S17e, 500 MHz ^1H NMR in CDCl_3



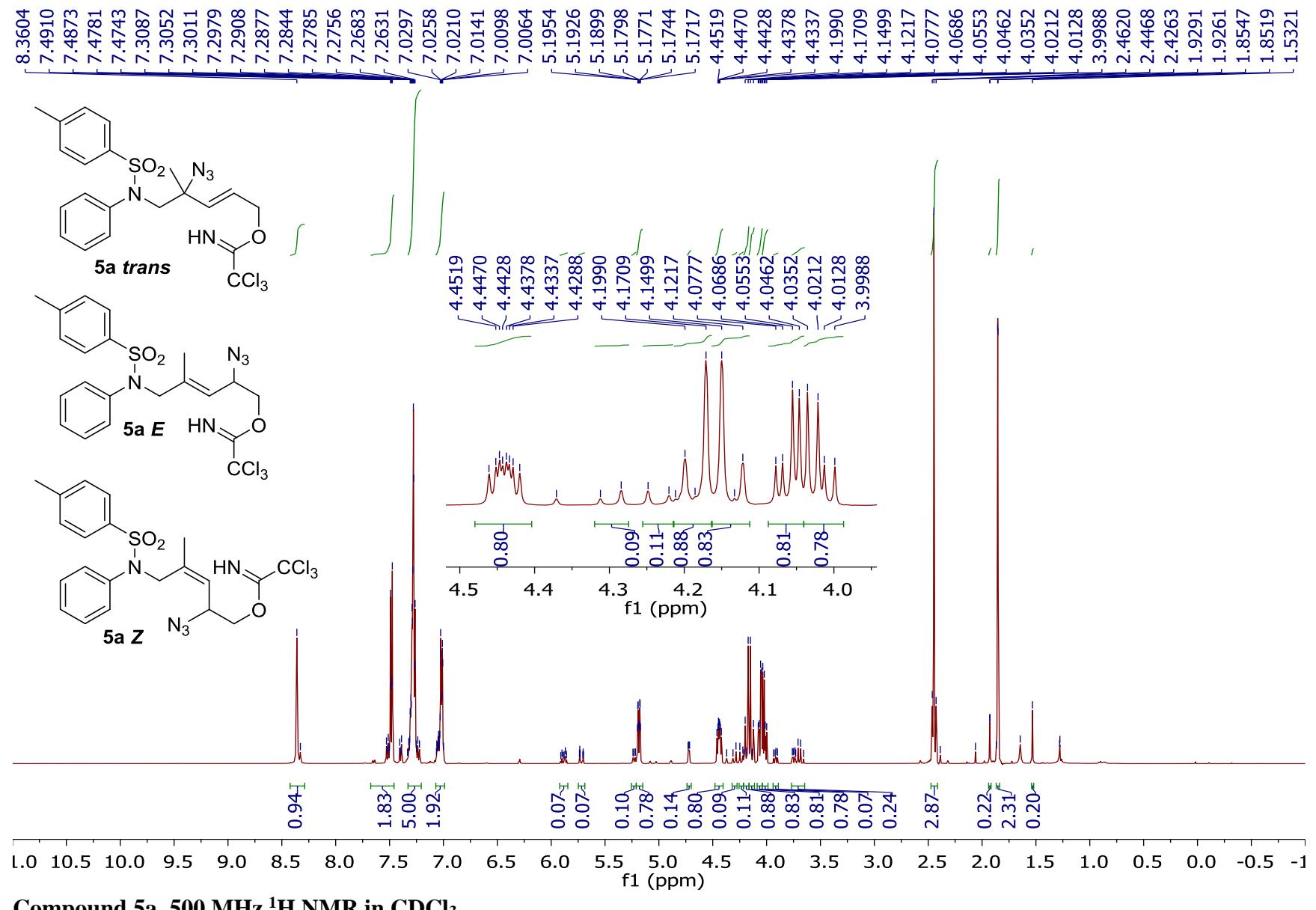
Compound S17e, 126 MHz ^{13}C NMR in CDCl_3

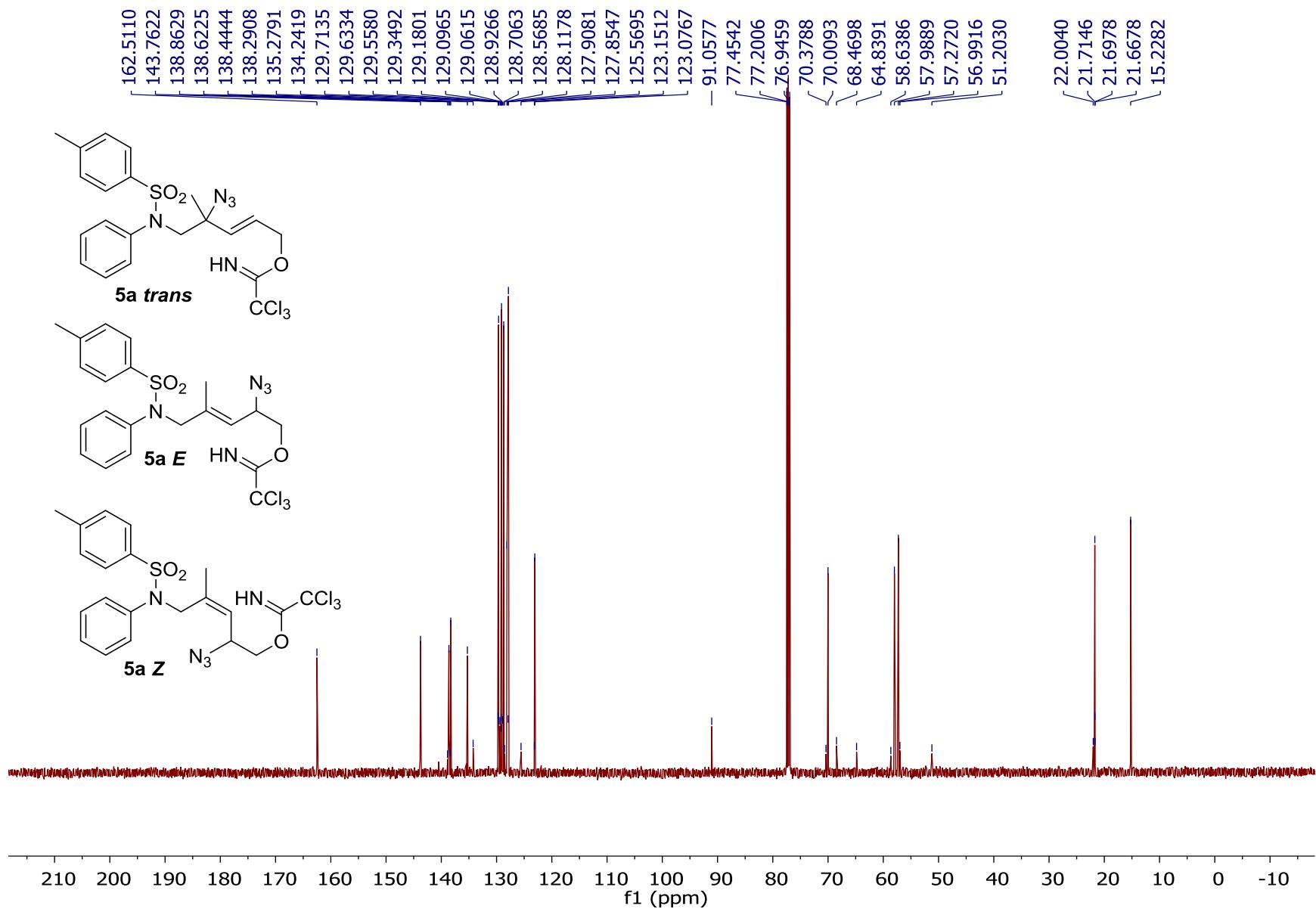


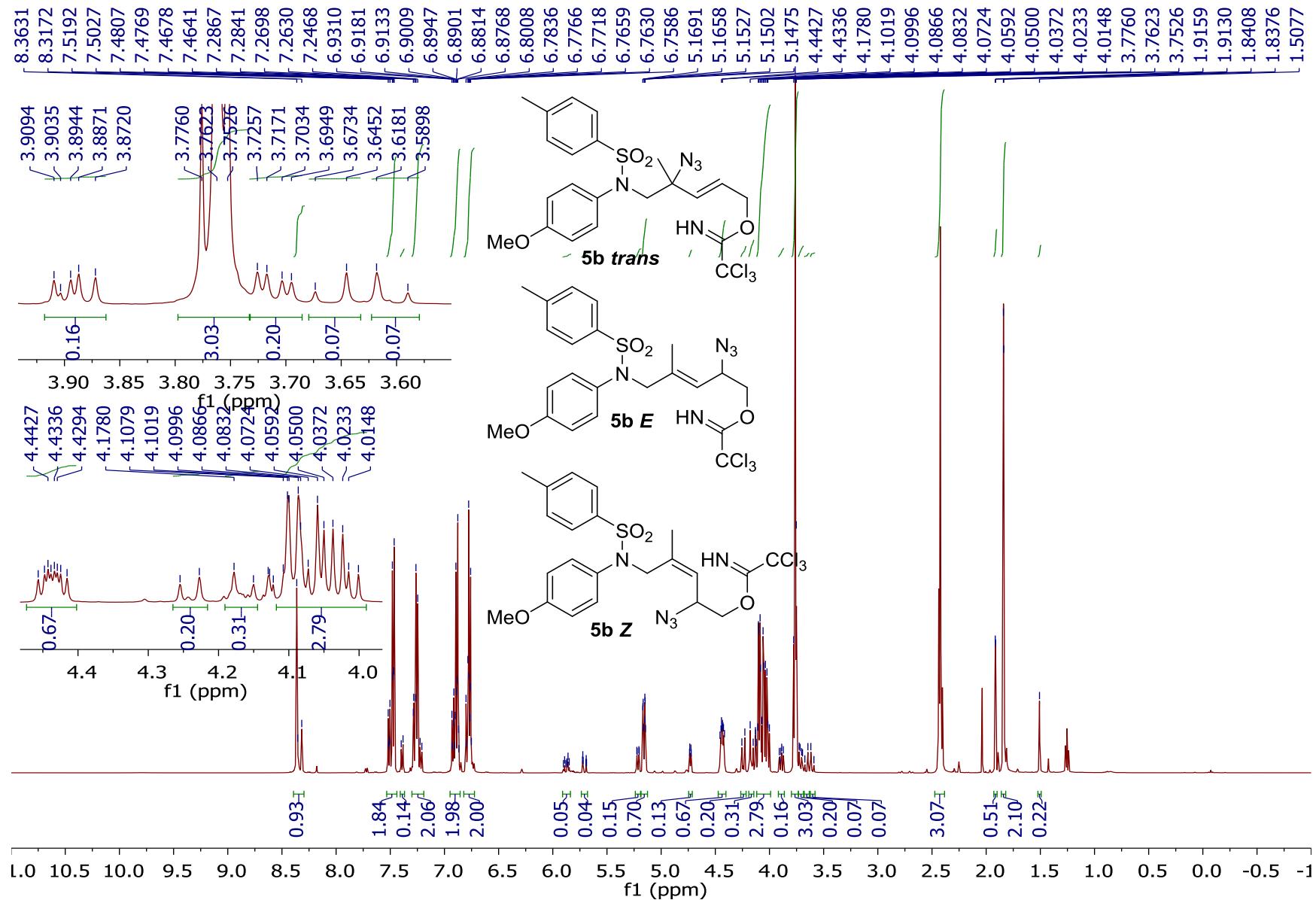
Compound S17f, 400 MHz ^1H NMR in CDCl_3



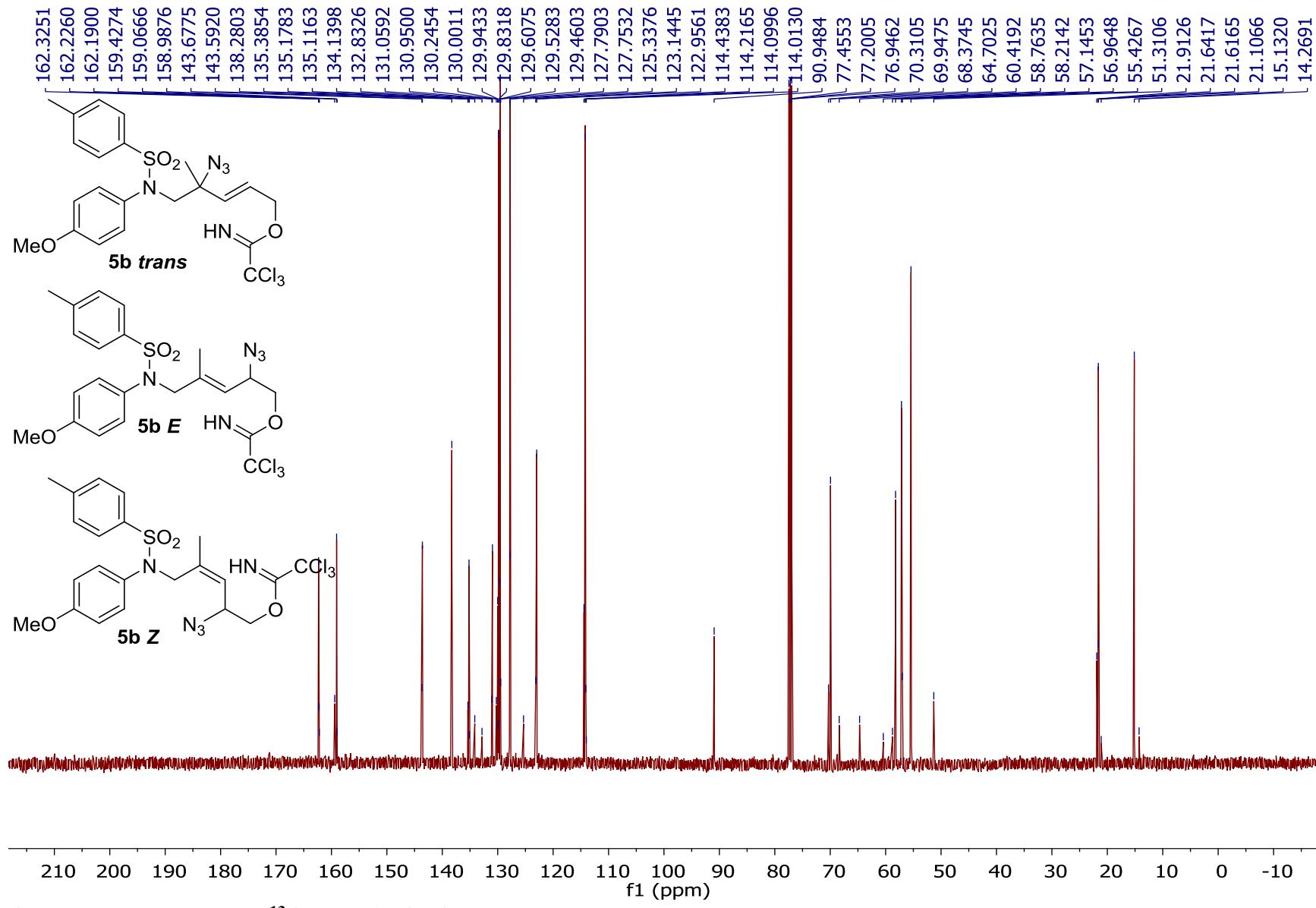
Compound S17f, 101 MHz ^{13}C NMR in CDCl_3

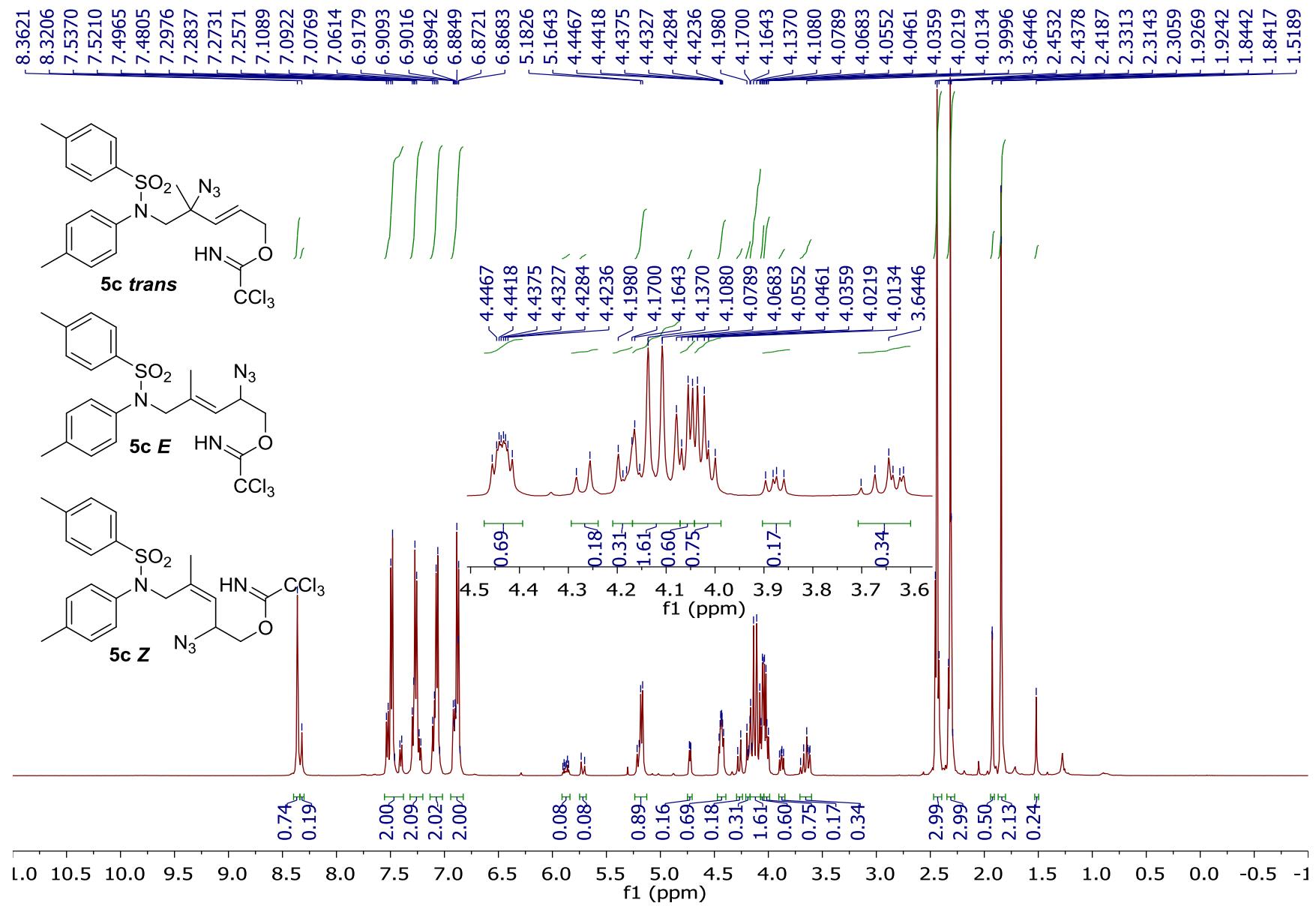




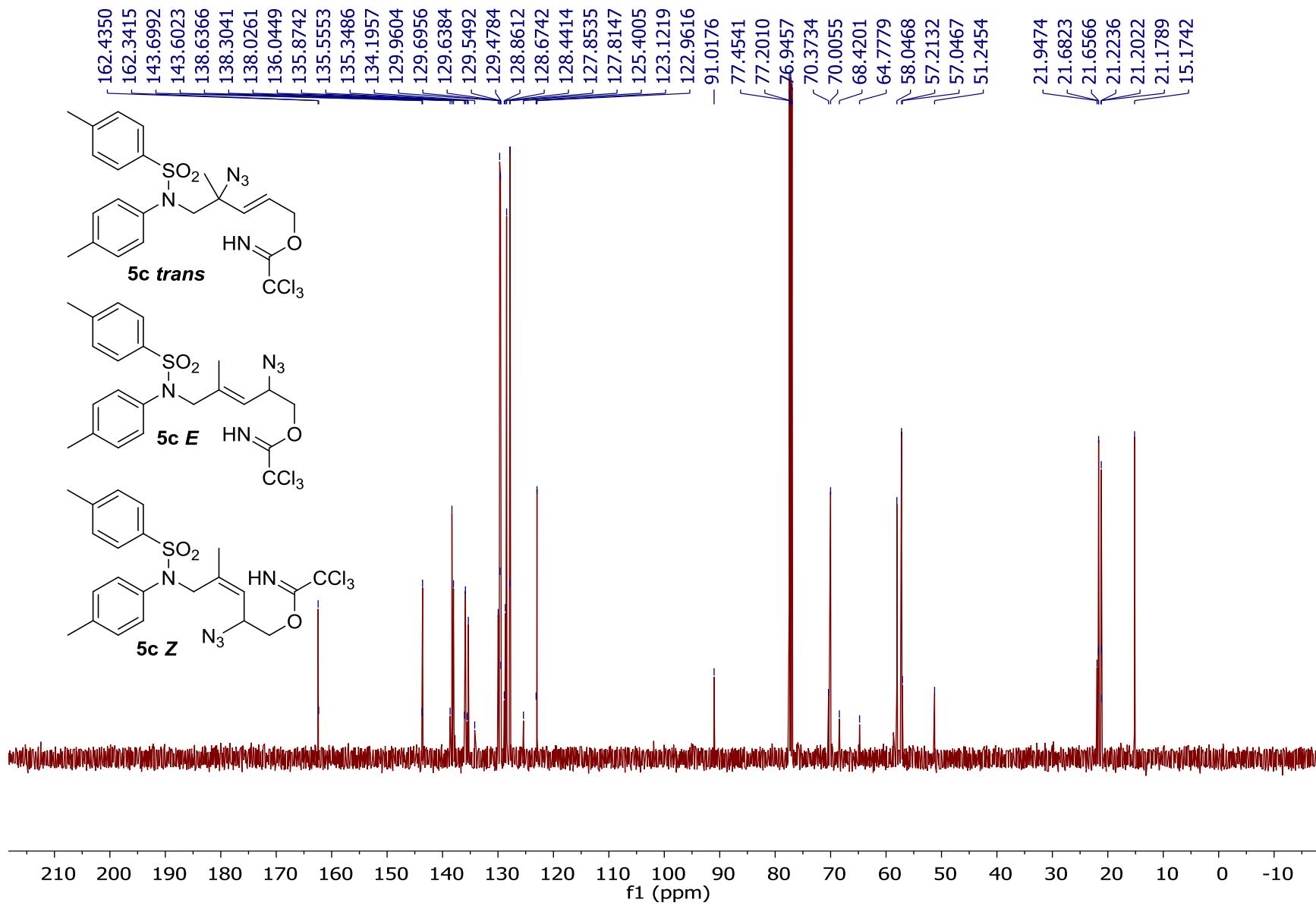


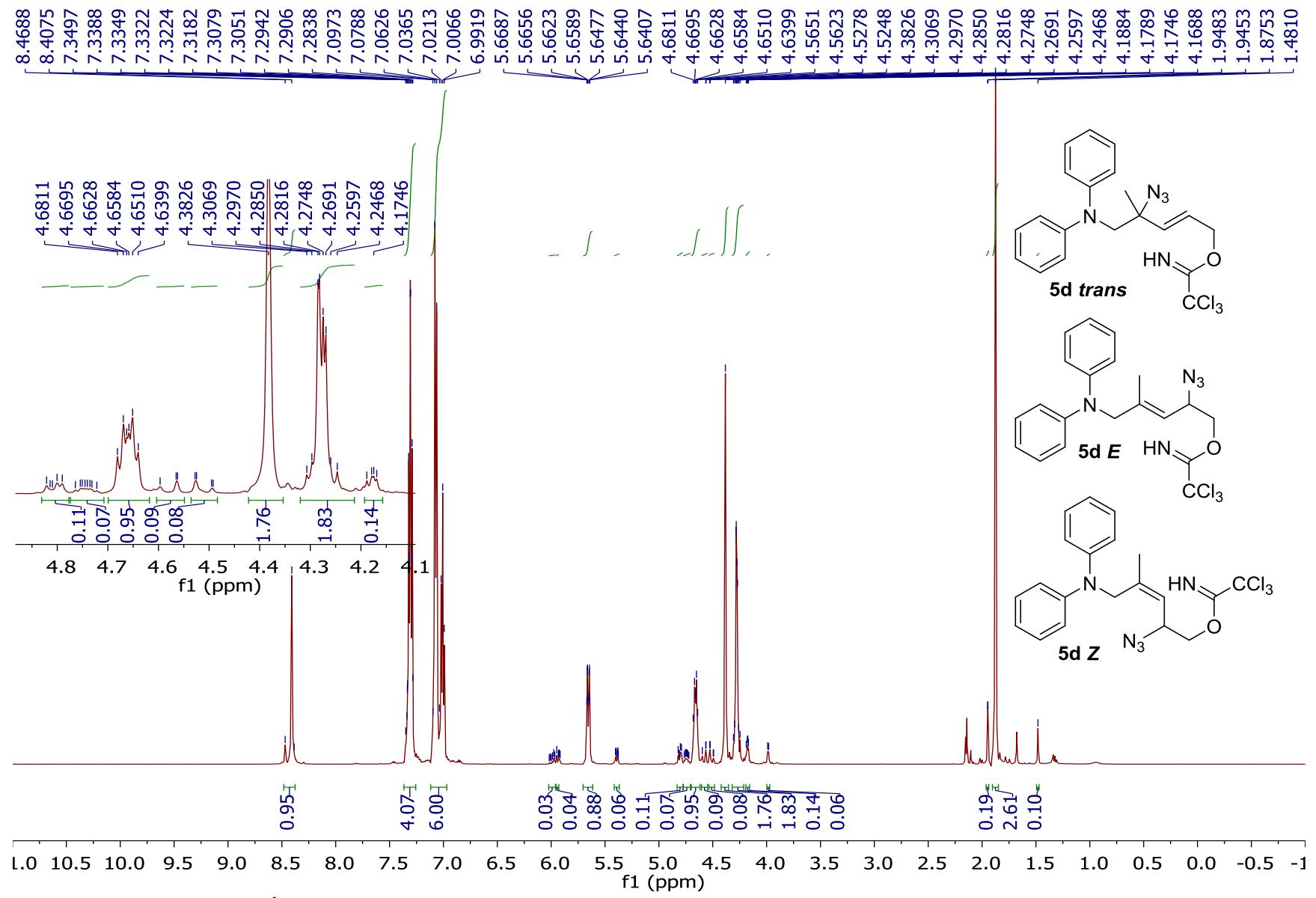
Compound 5b, 500 MHz ^1H NMR in CDCl_3

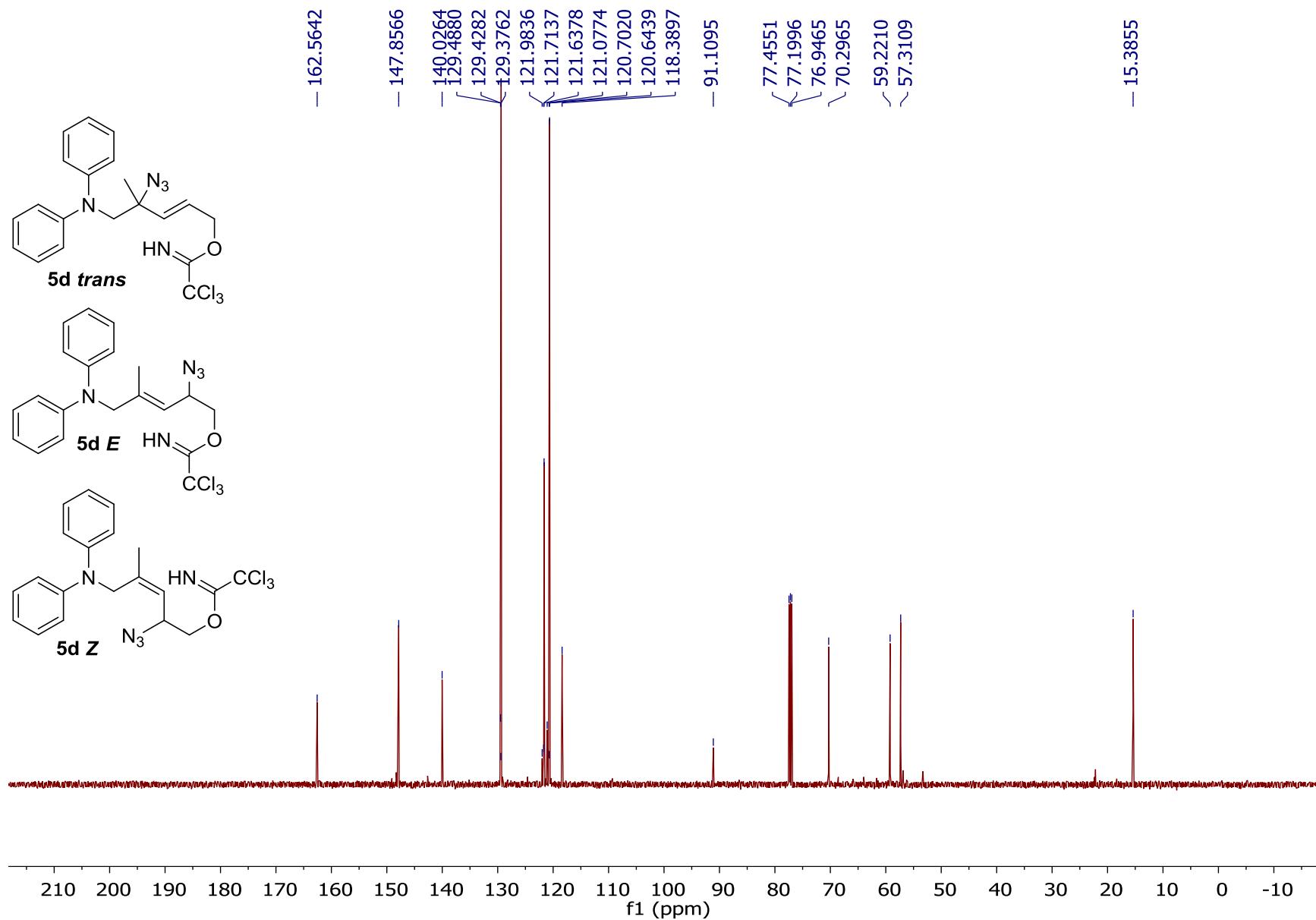




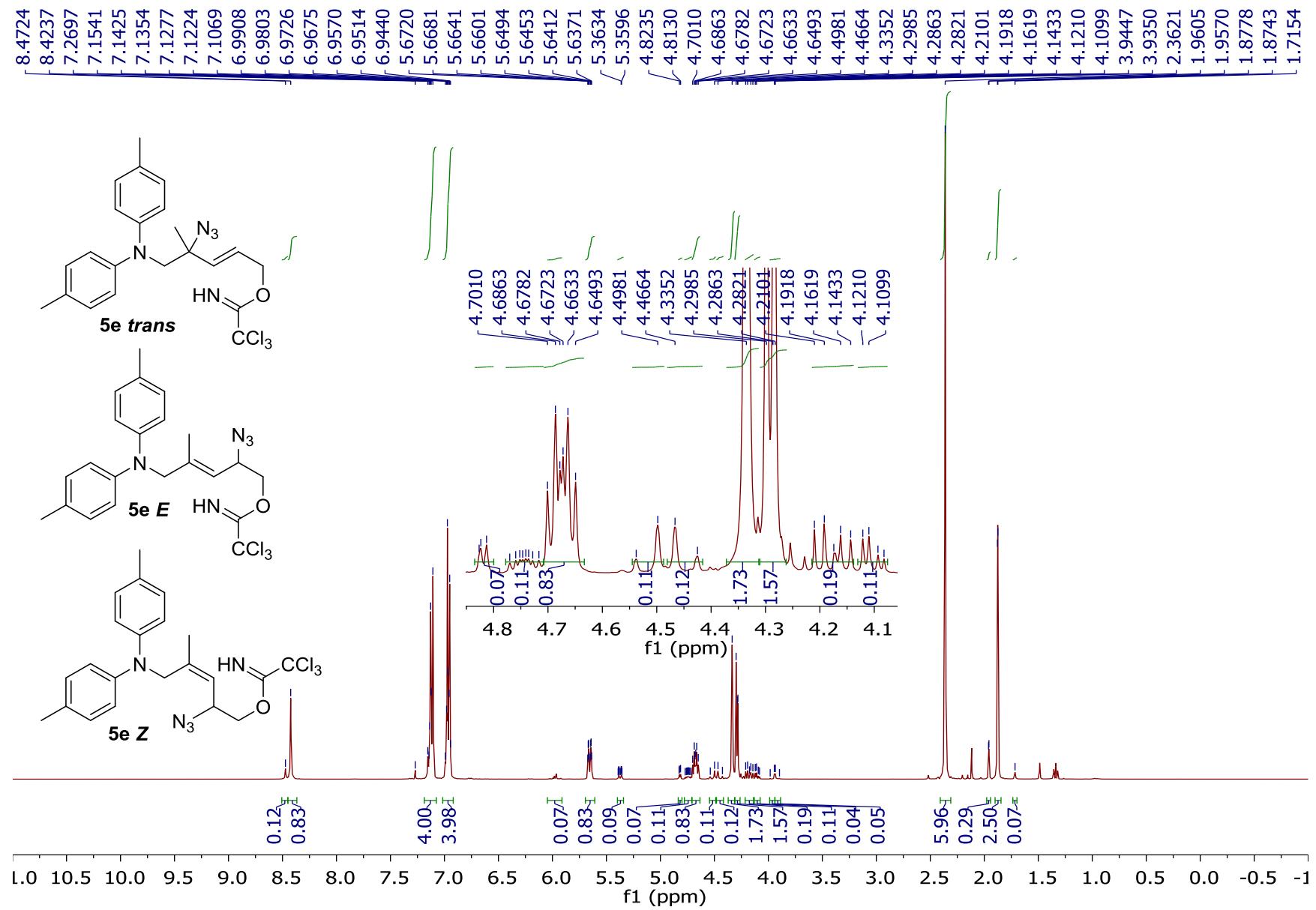
Compound 5c, 500 MHz ^1H NMR in CDCl_3



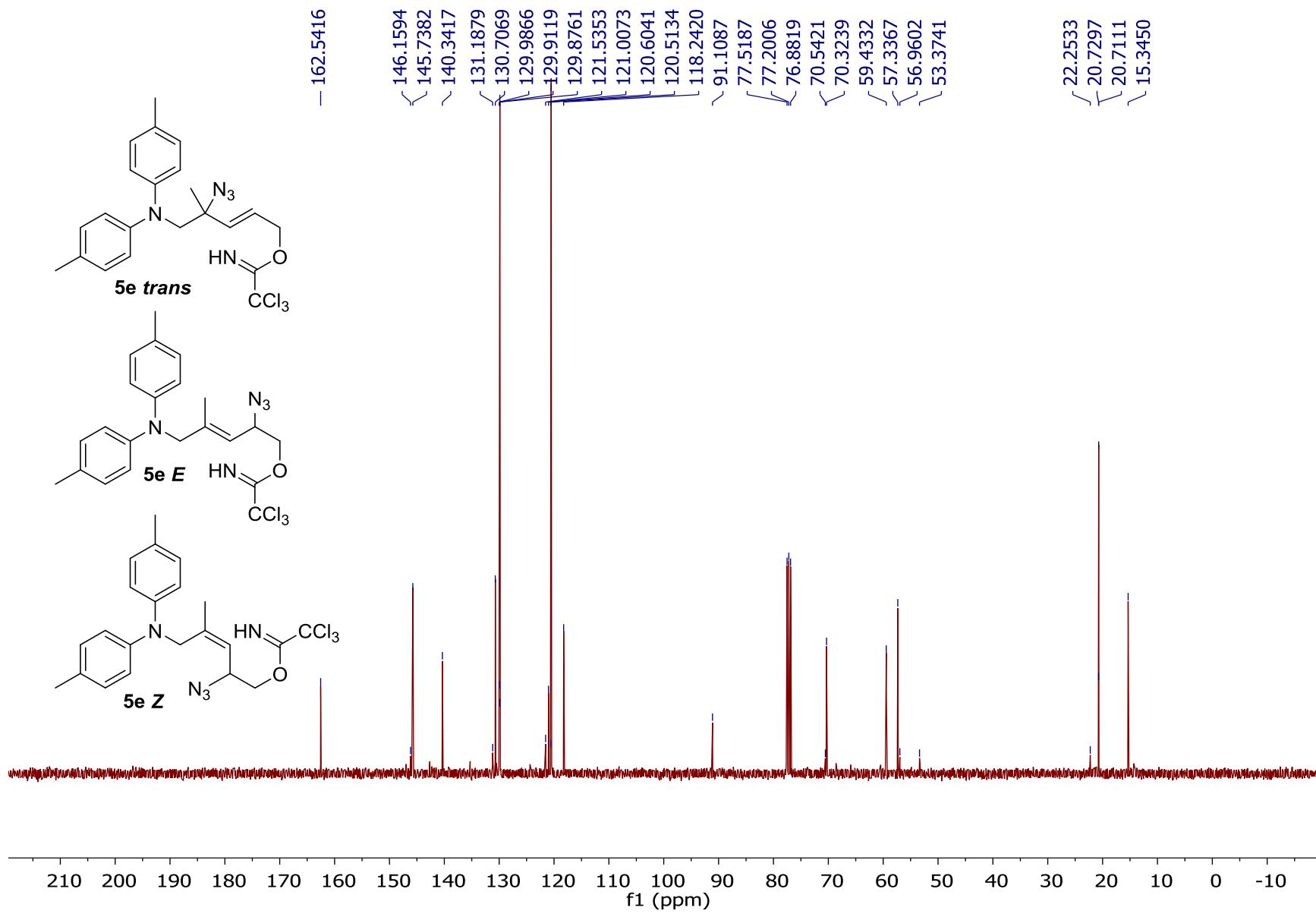




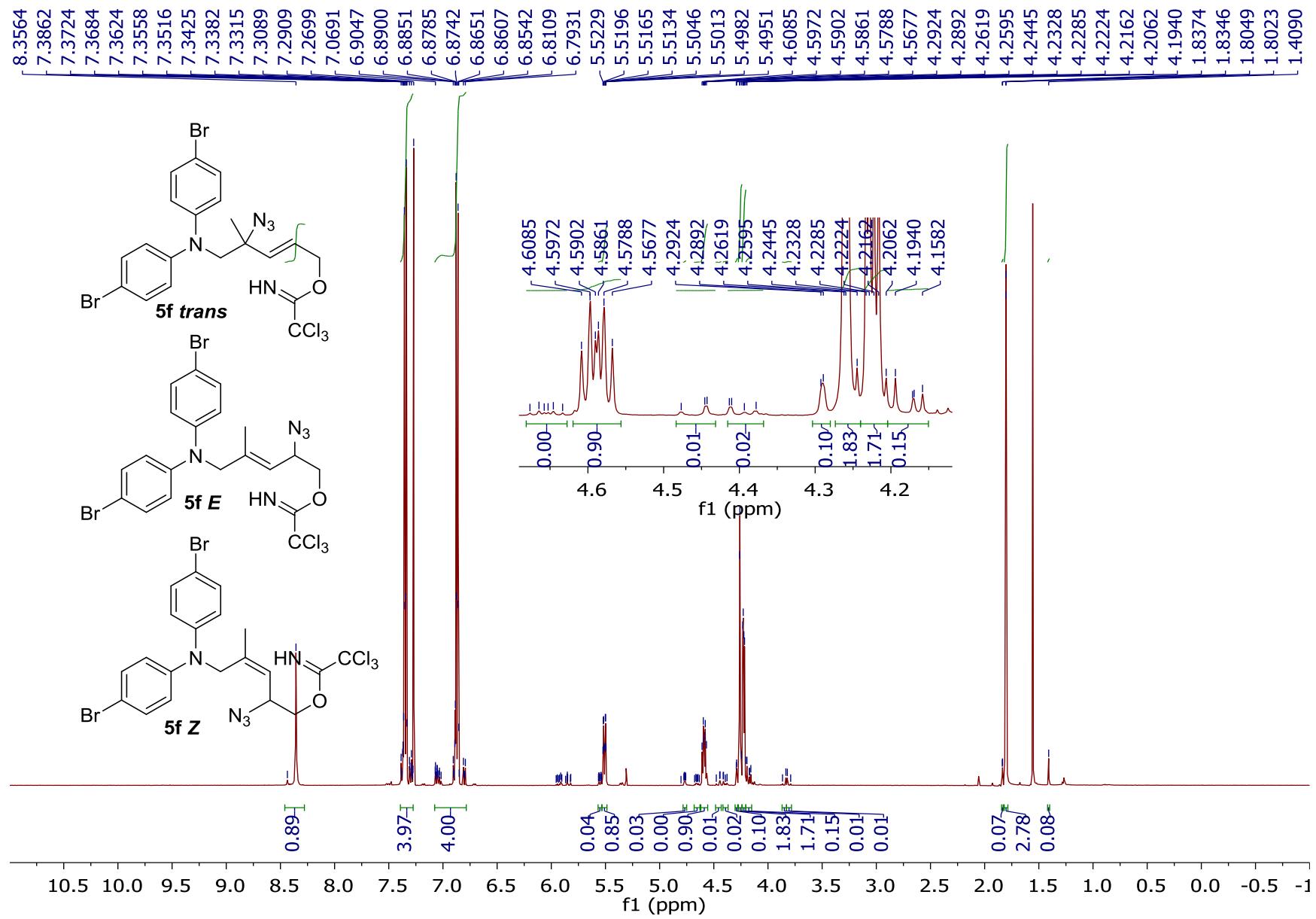
Compound 5d, 126 MHz ^{13}C NMR in CDCl_3



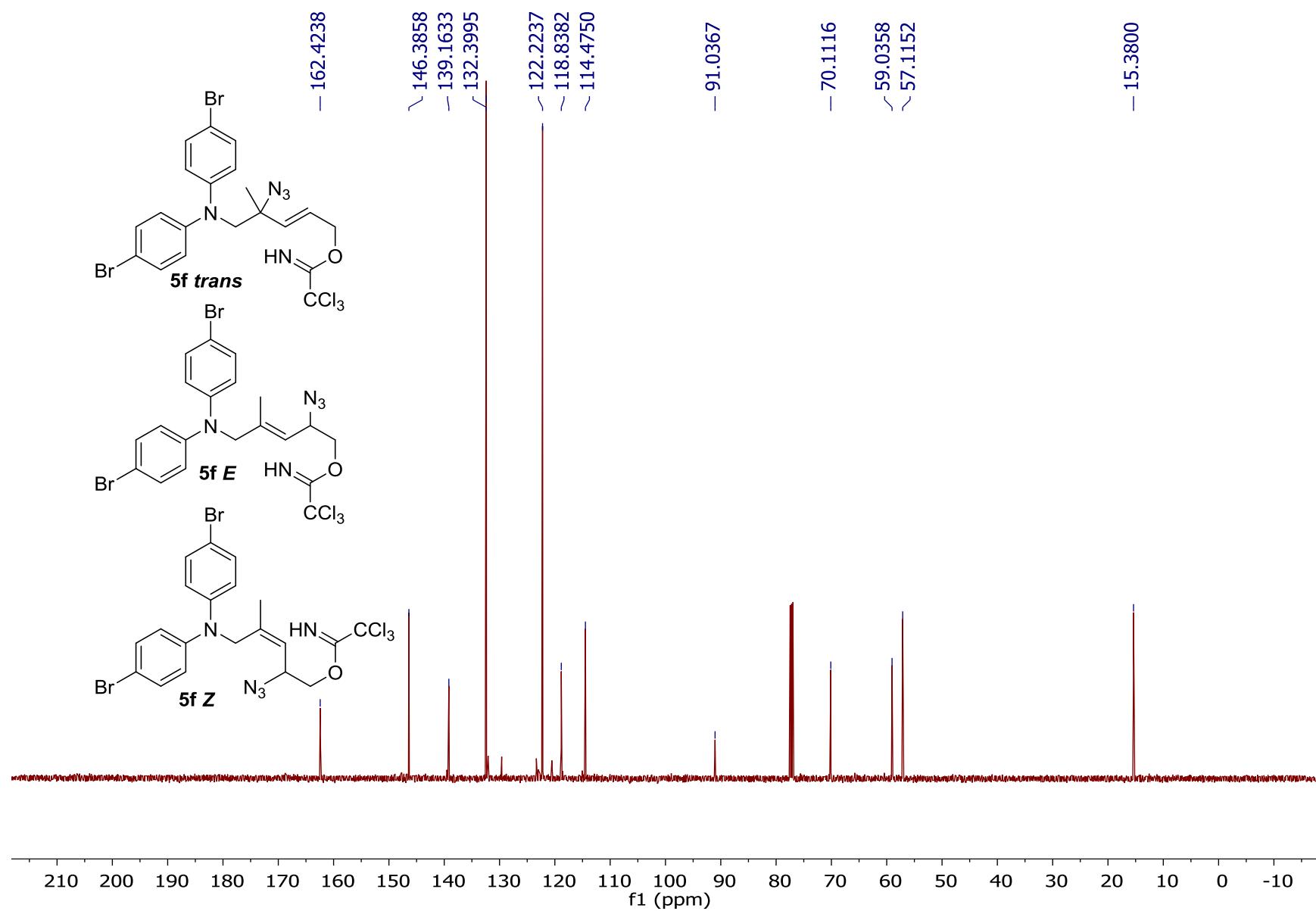
Compound 5e, 400 MHz ^1H NMR in CDCl_3

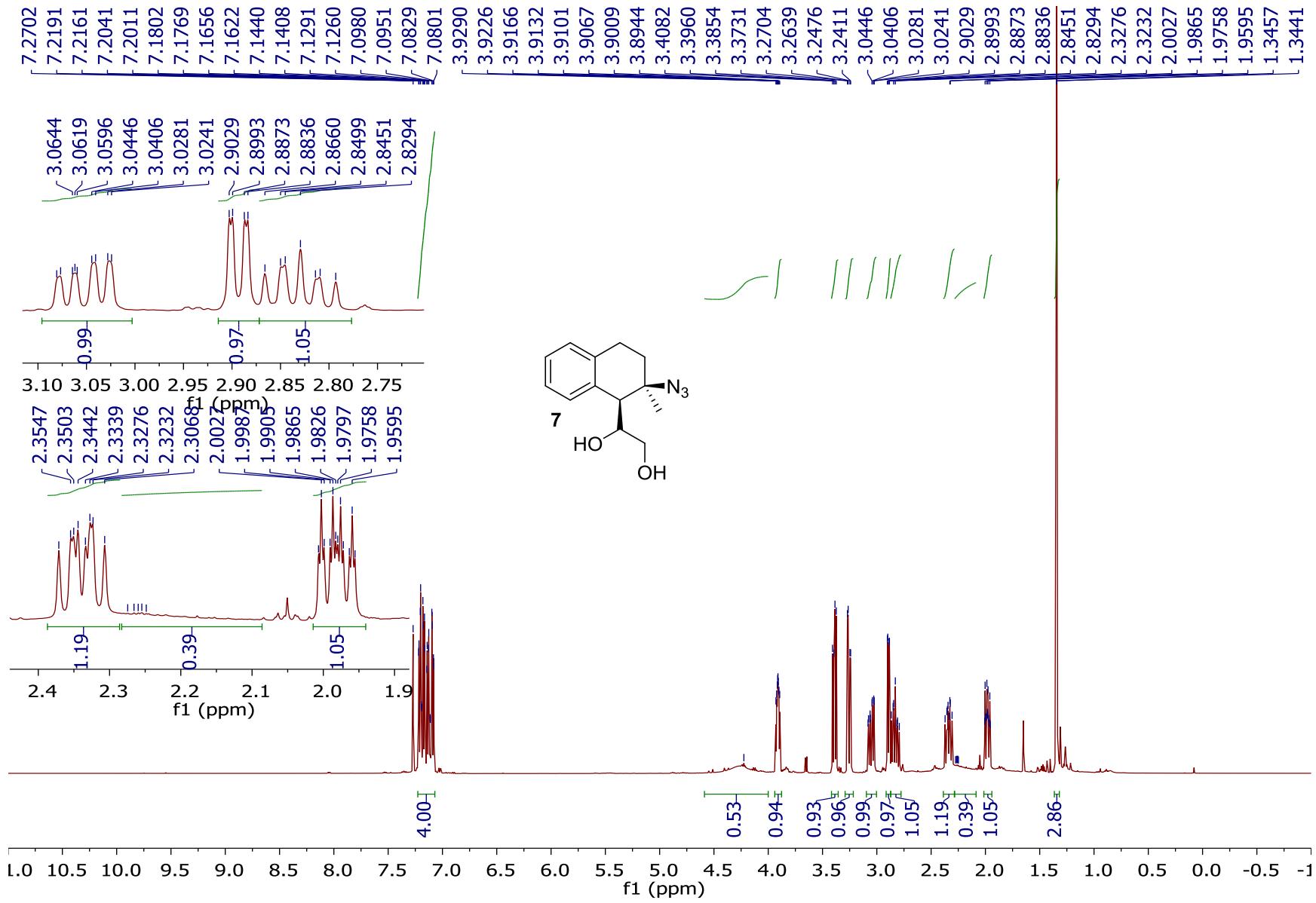


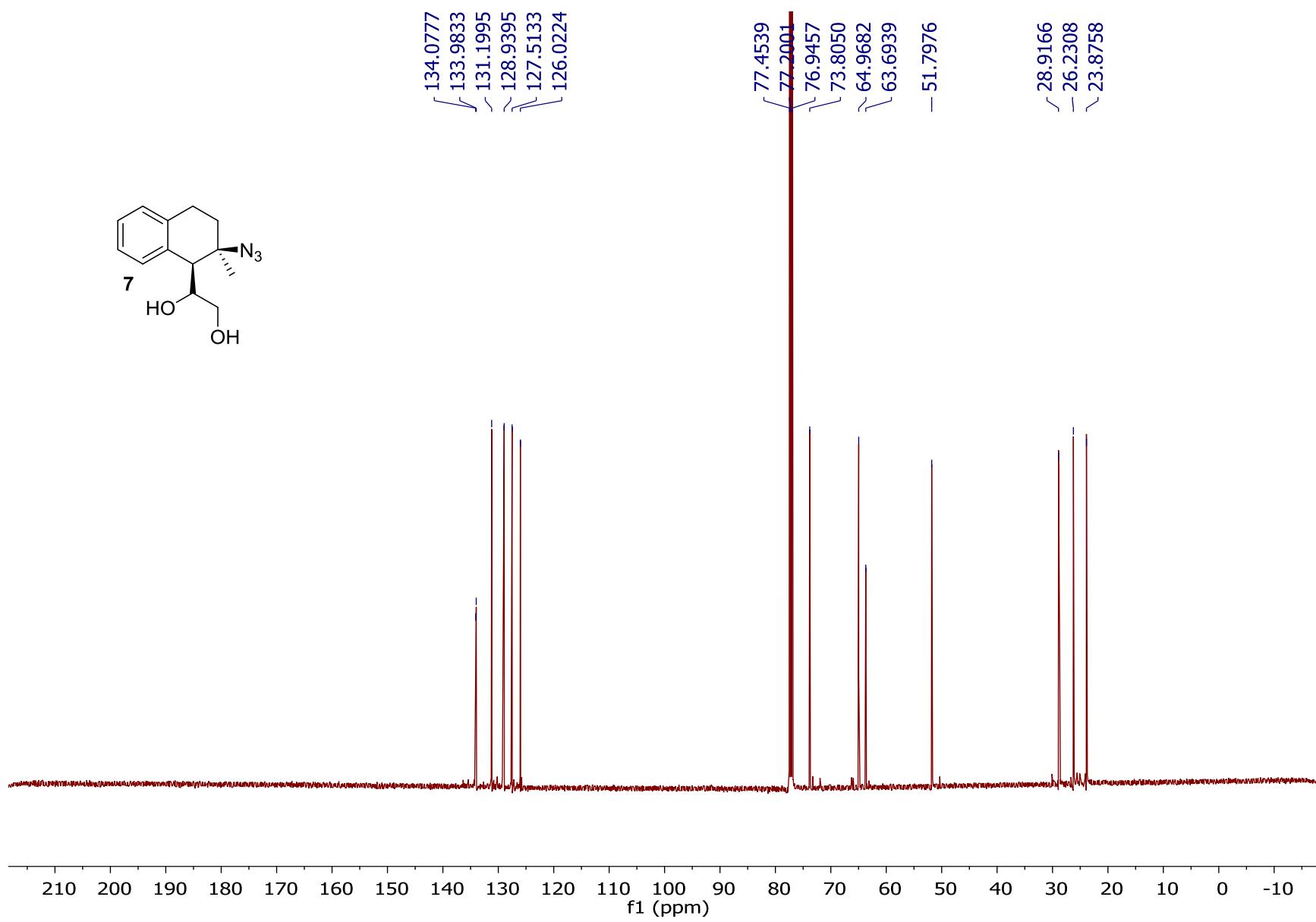
Compound 5e, 101 MHz ^{13}C NMR in CDCl_3



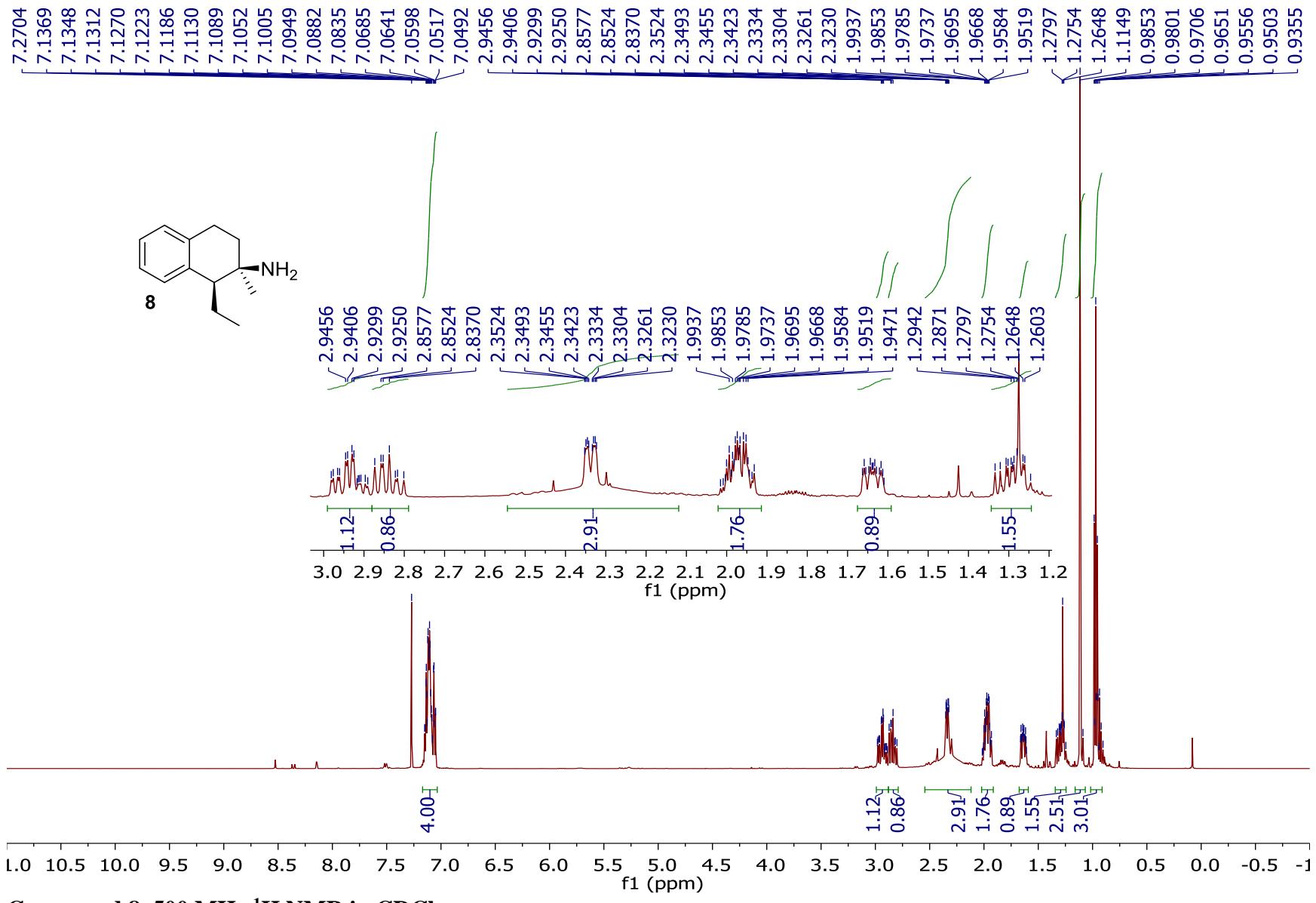
Compound 5f, 500 MHz ^1H NMR in CDCl_3



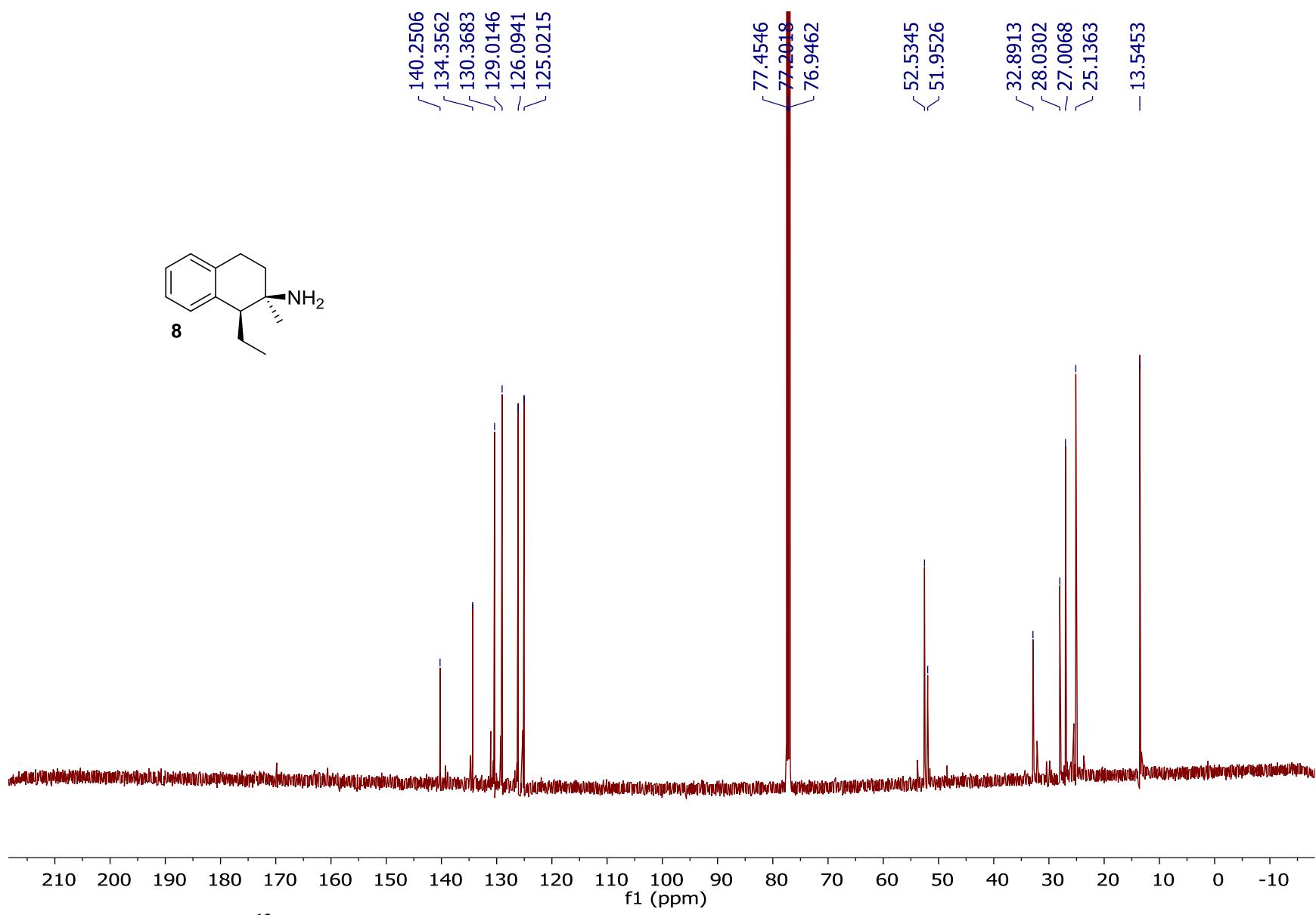




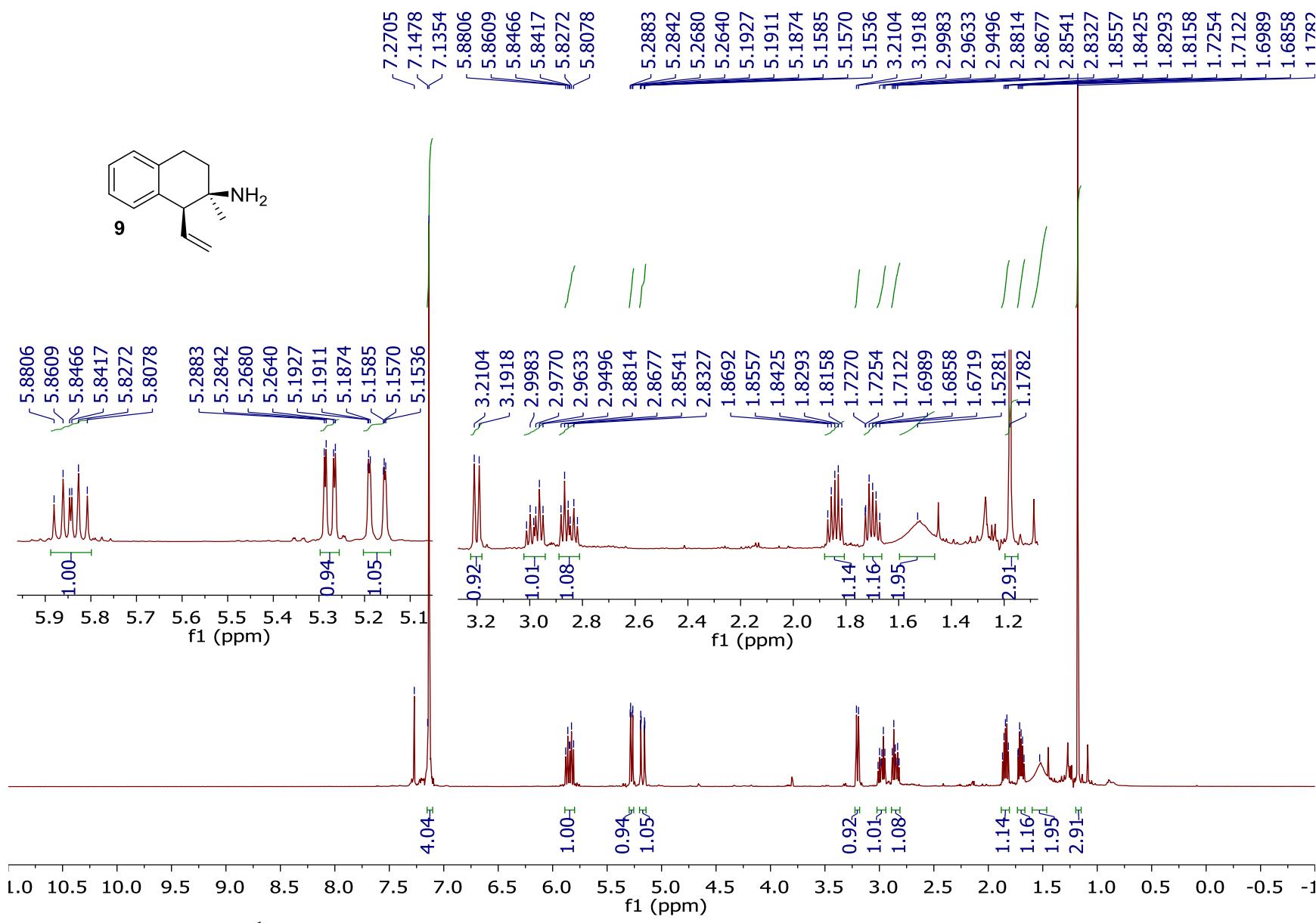
Compound 7, 126 MHz ^{13}C NMR in CDCl_3



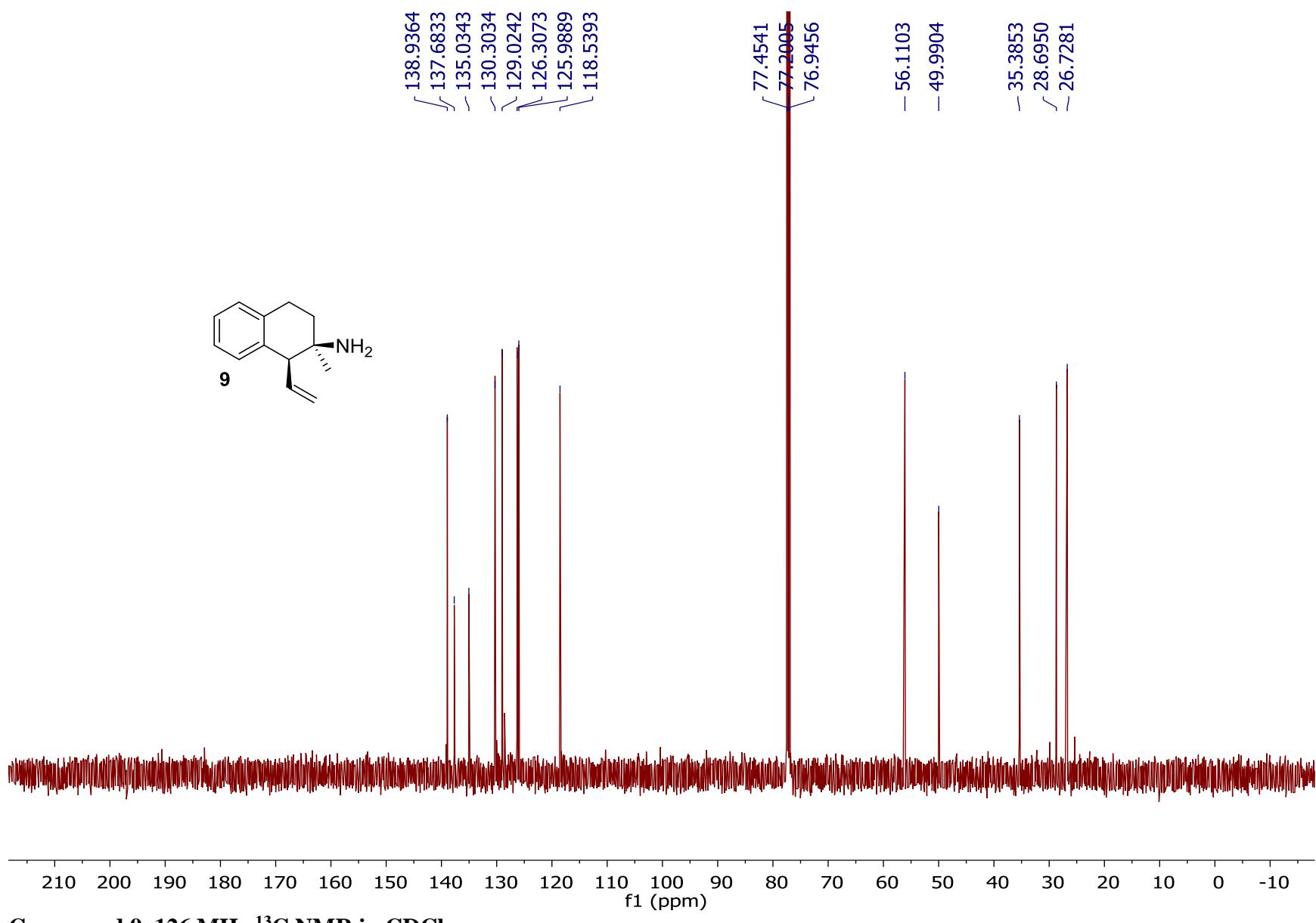
Compound 8, 500 MHz ^1H NMR in CDCl_3



Compound 8, 126 MHz ^{13}C NMR in CDCl_3

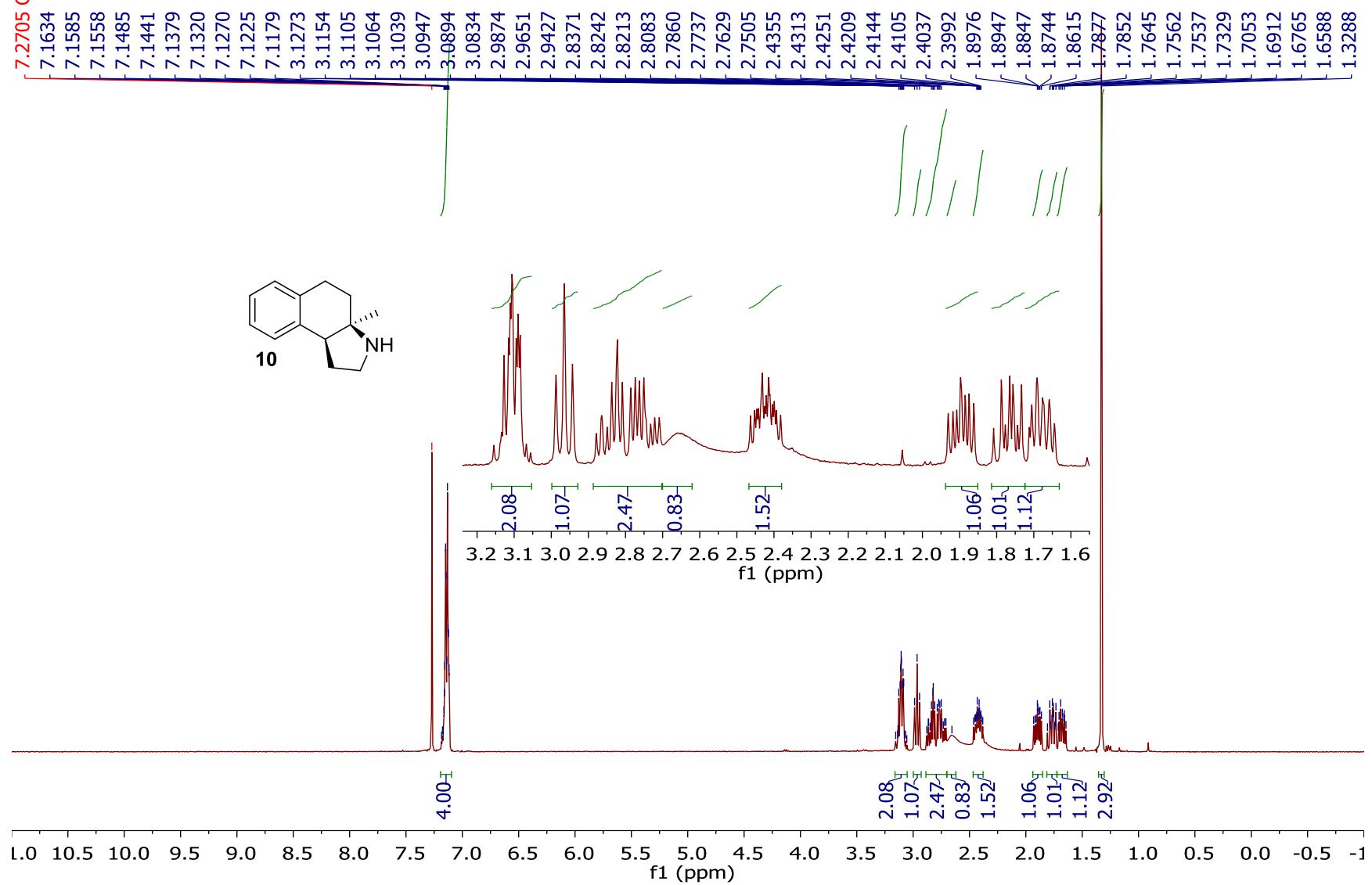


Compound 9, 500 MHz ^1H NMR in CDCl₃

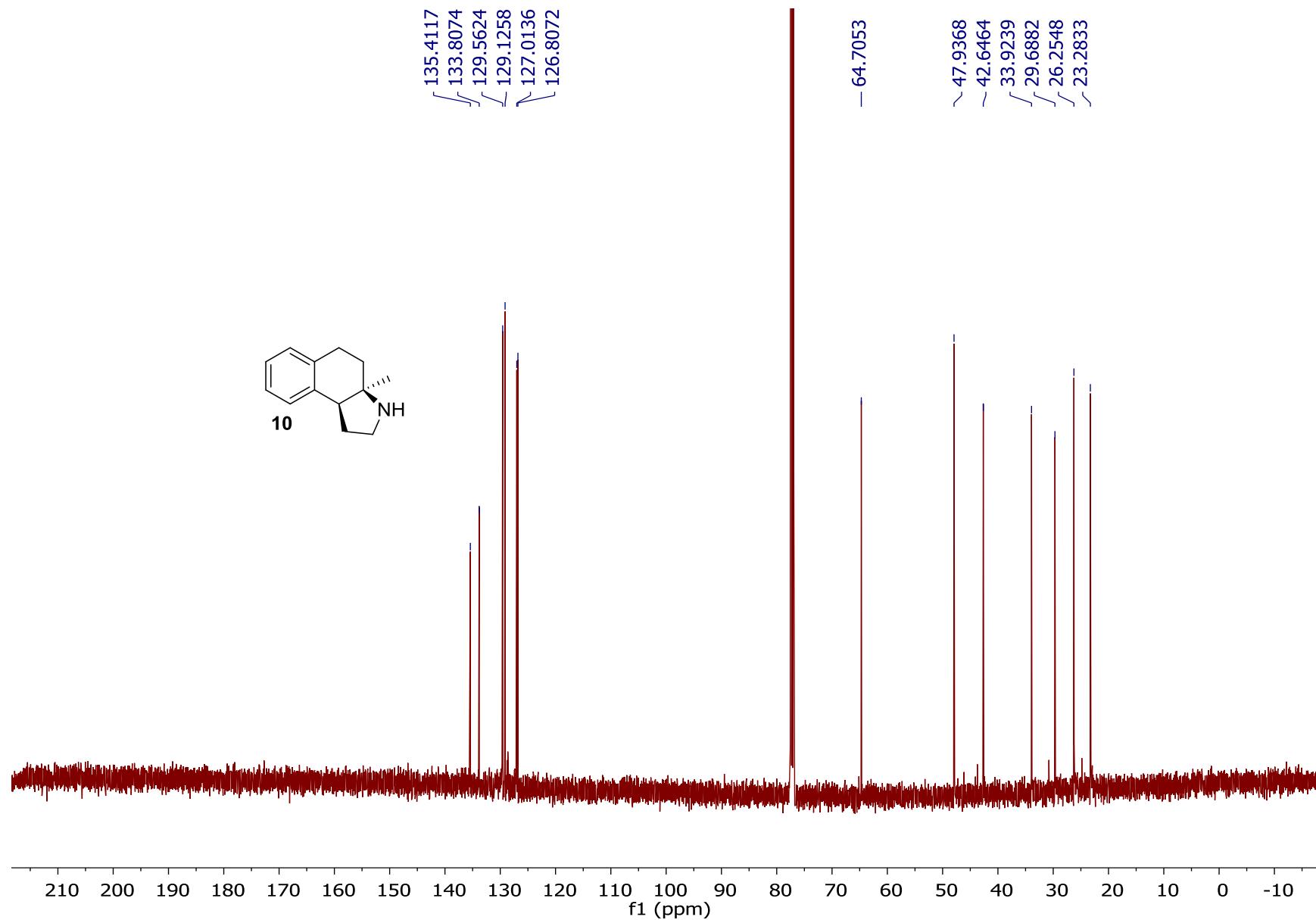


Compound 9, 126 MHz ^{13}C NMR in CDCl_3

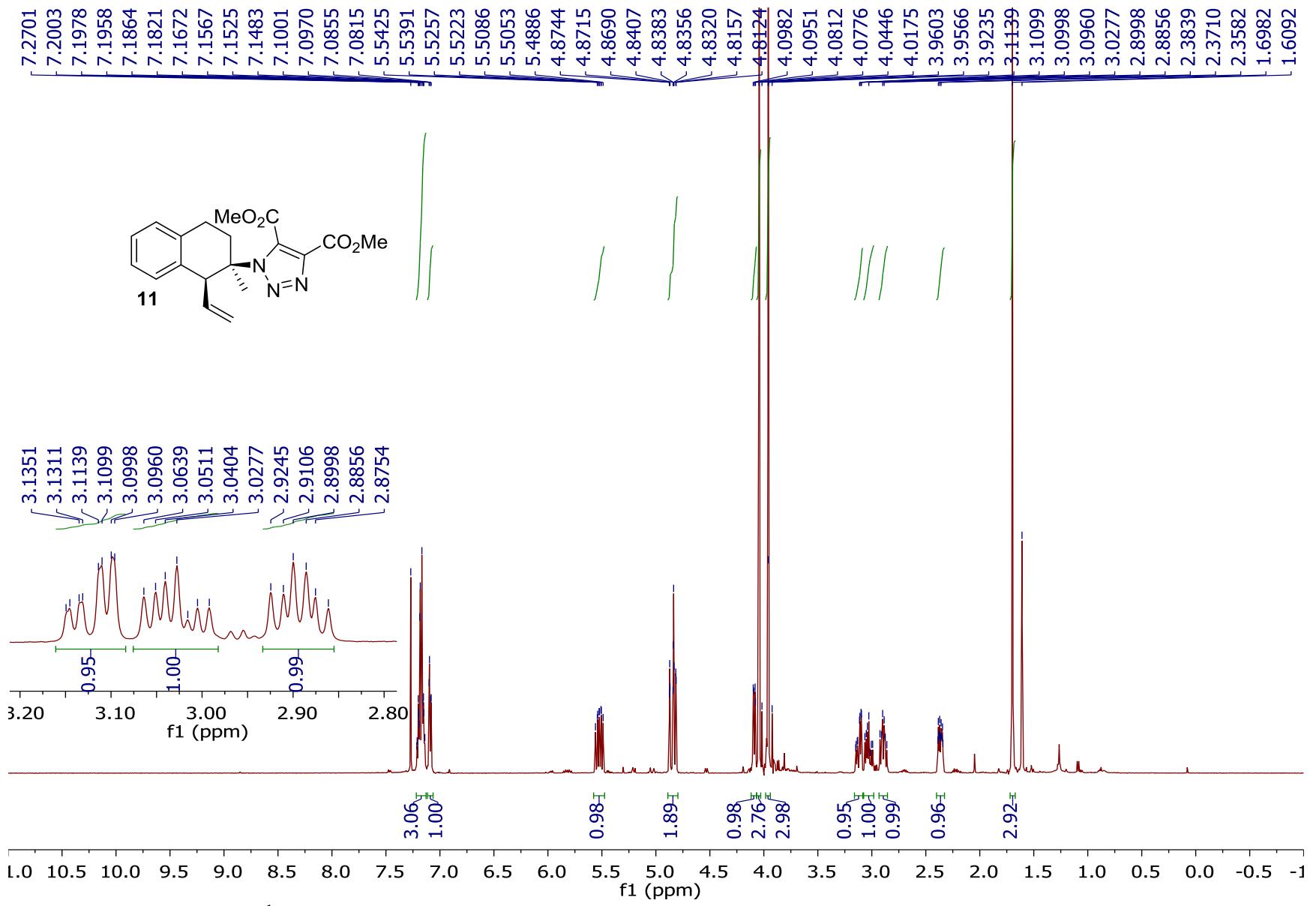
7.2705 CDCl₃

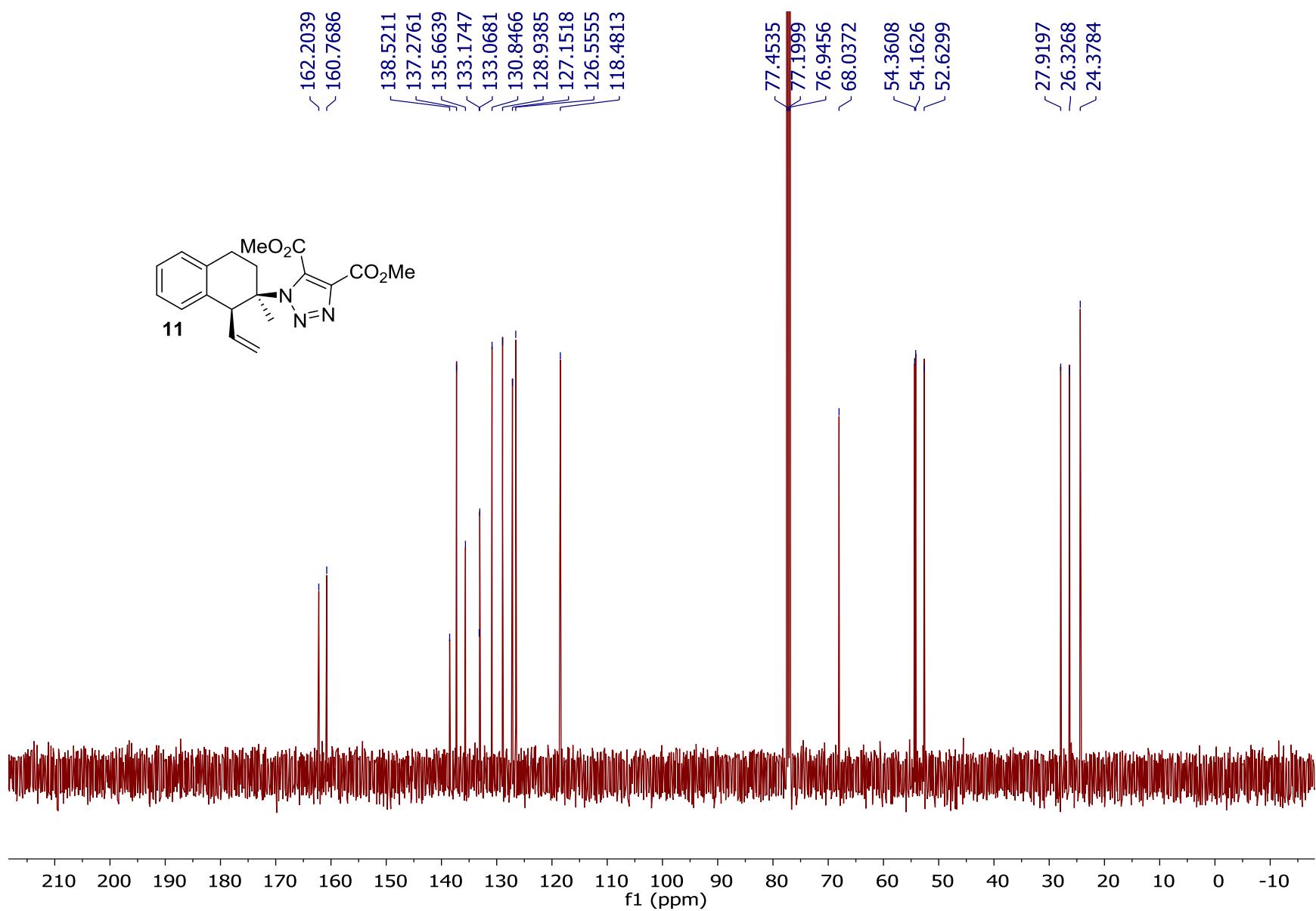


Compound 10, 400 MHz ¹H NMR in CDCl₃

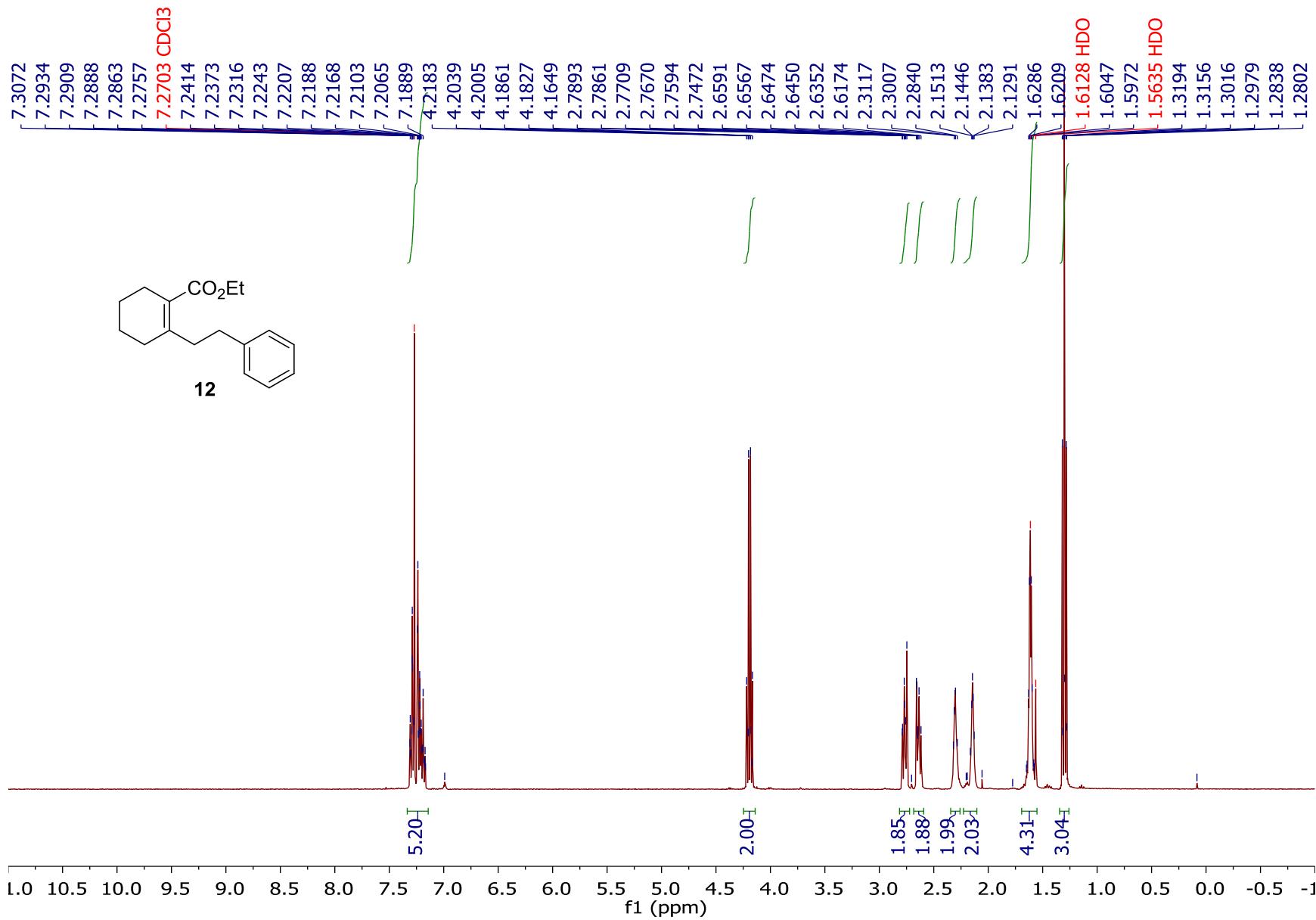


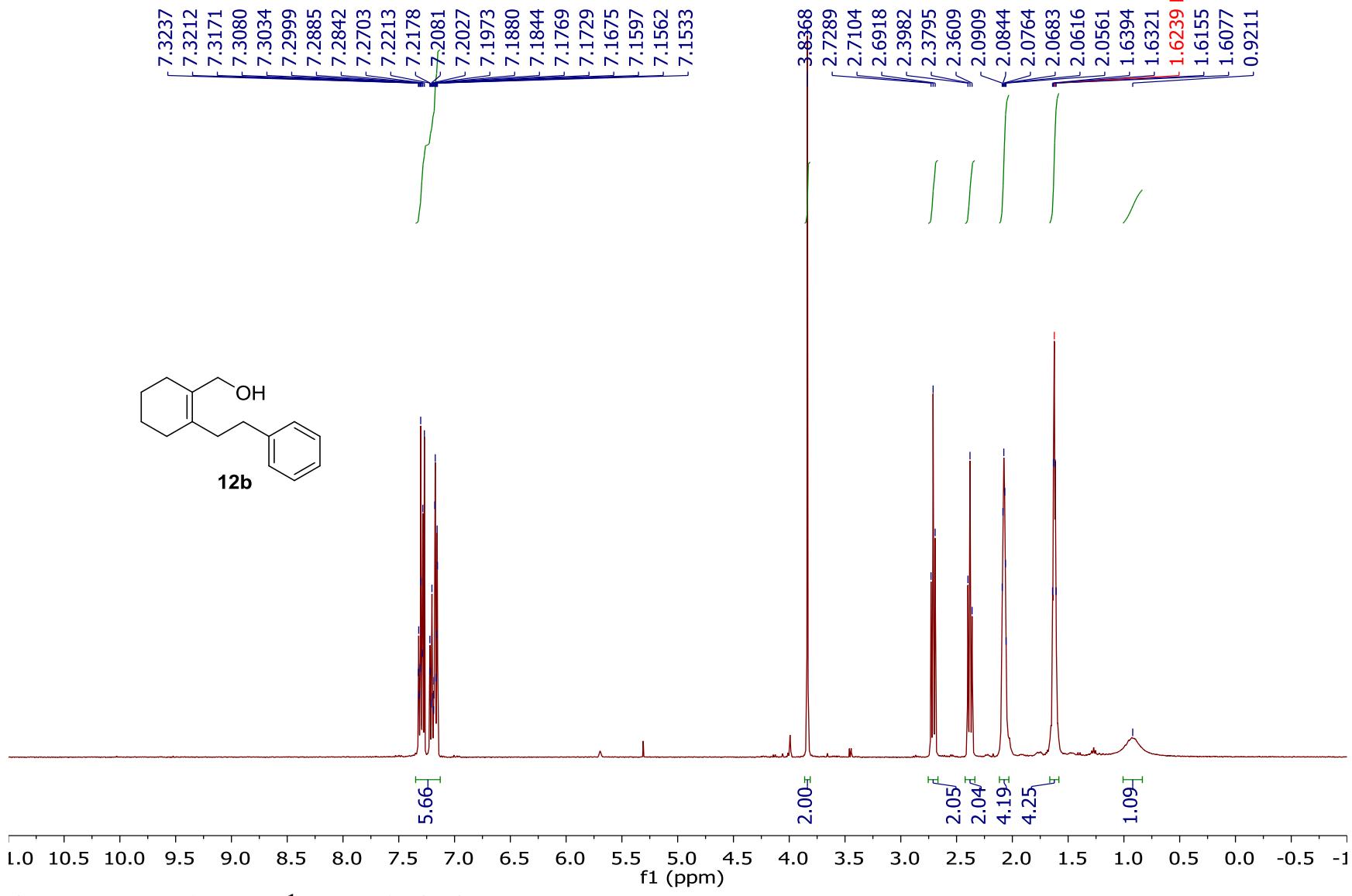
Compound 10, 126 MHz ^{13}C NMR in CDCl_3



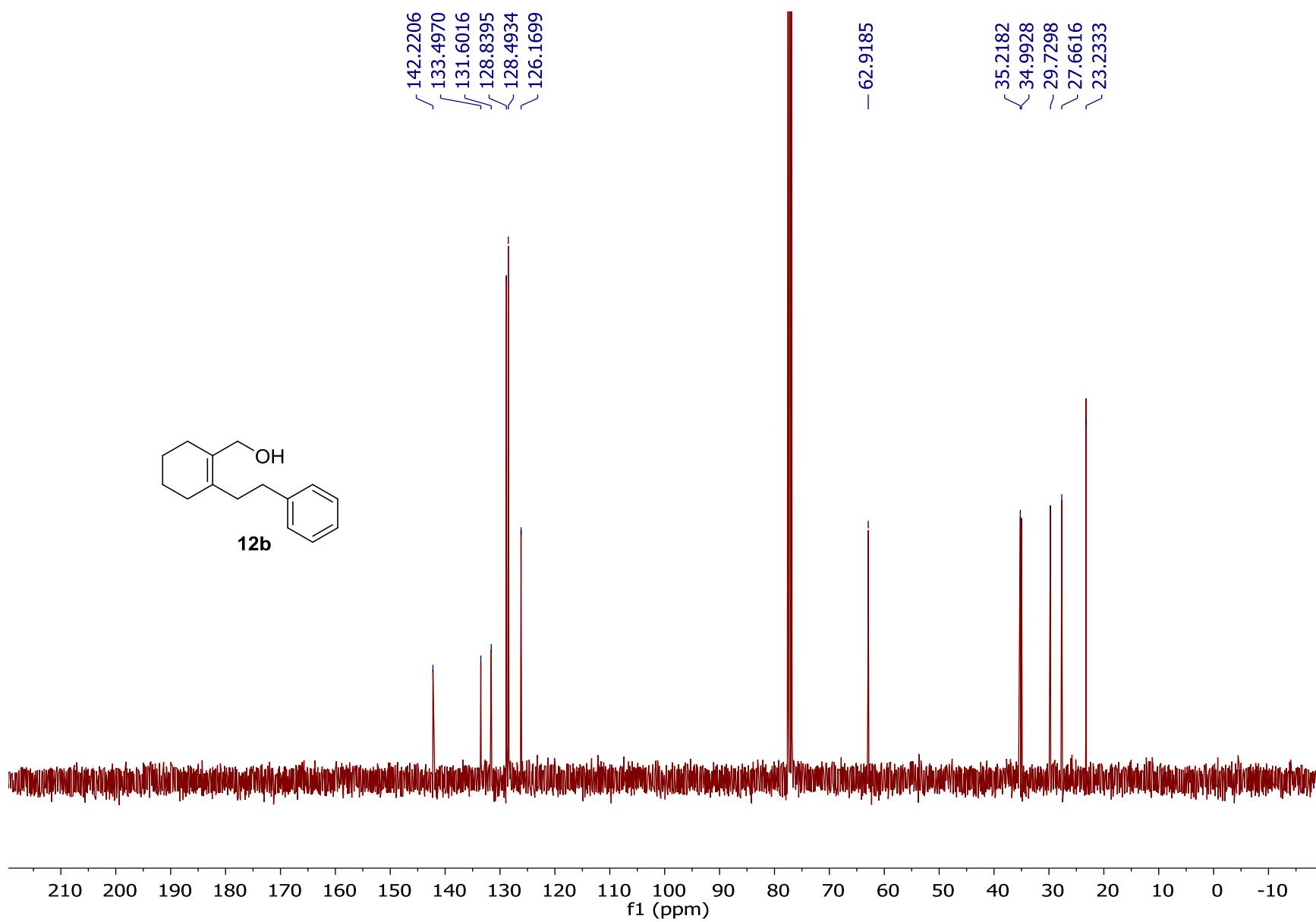


Compound 11, 126 MHz ^{13}C NMR in CDCl_3

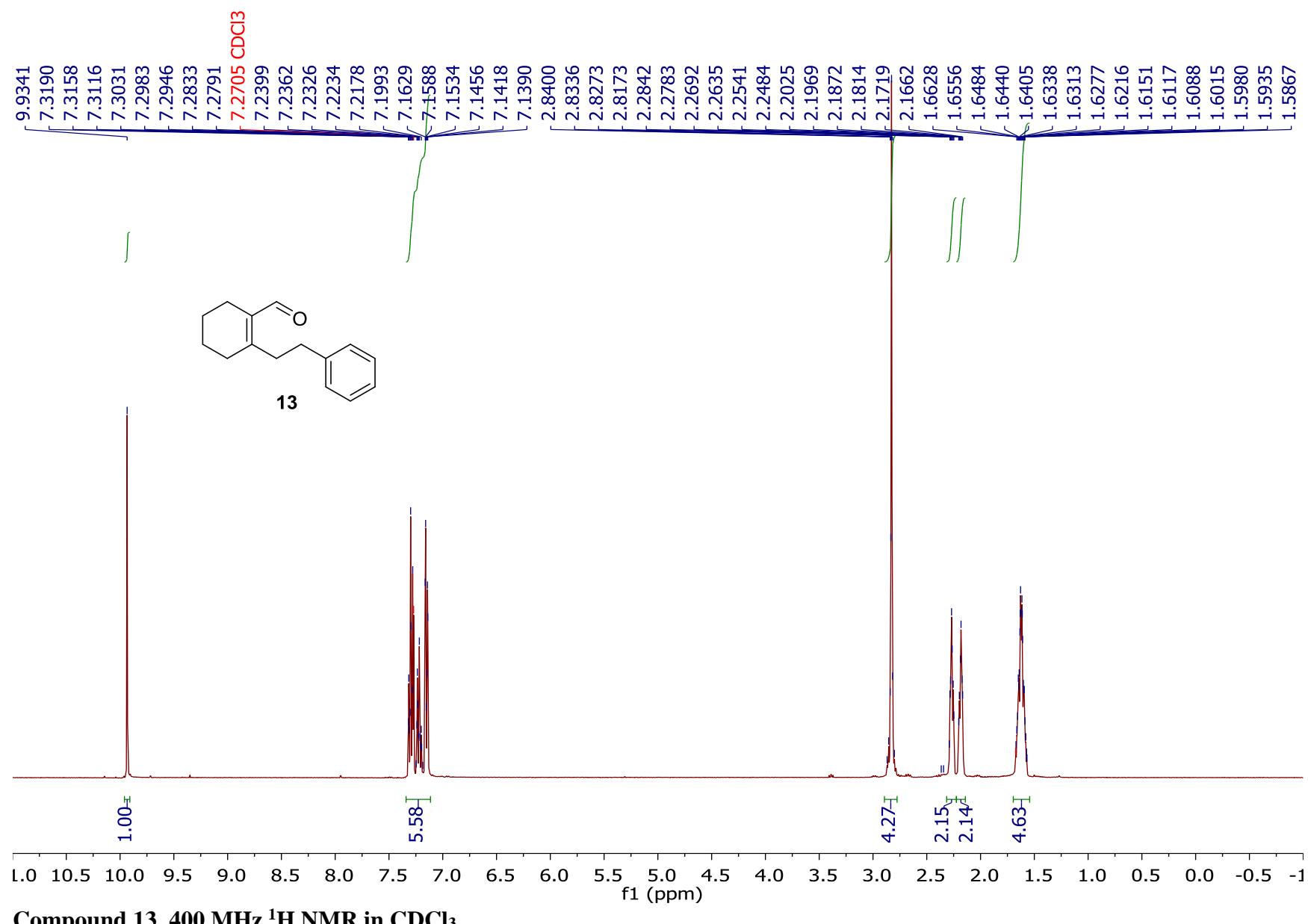


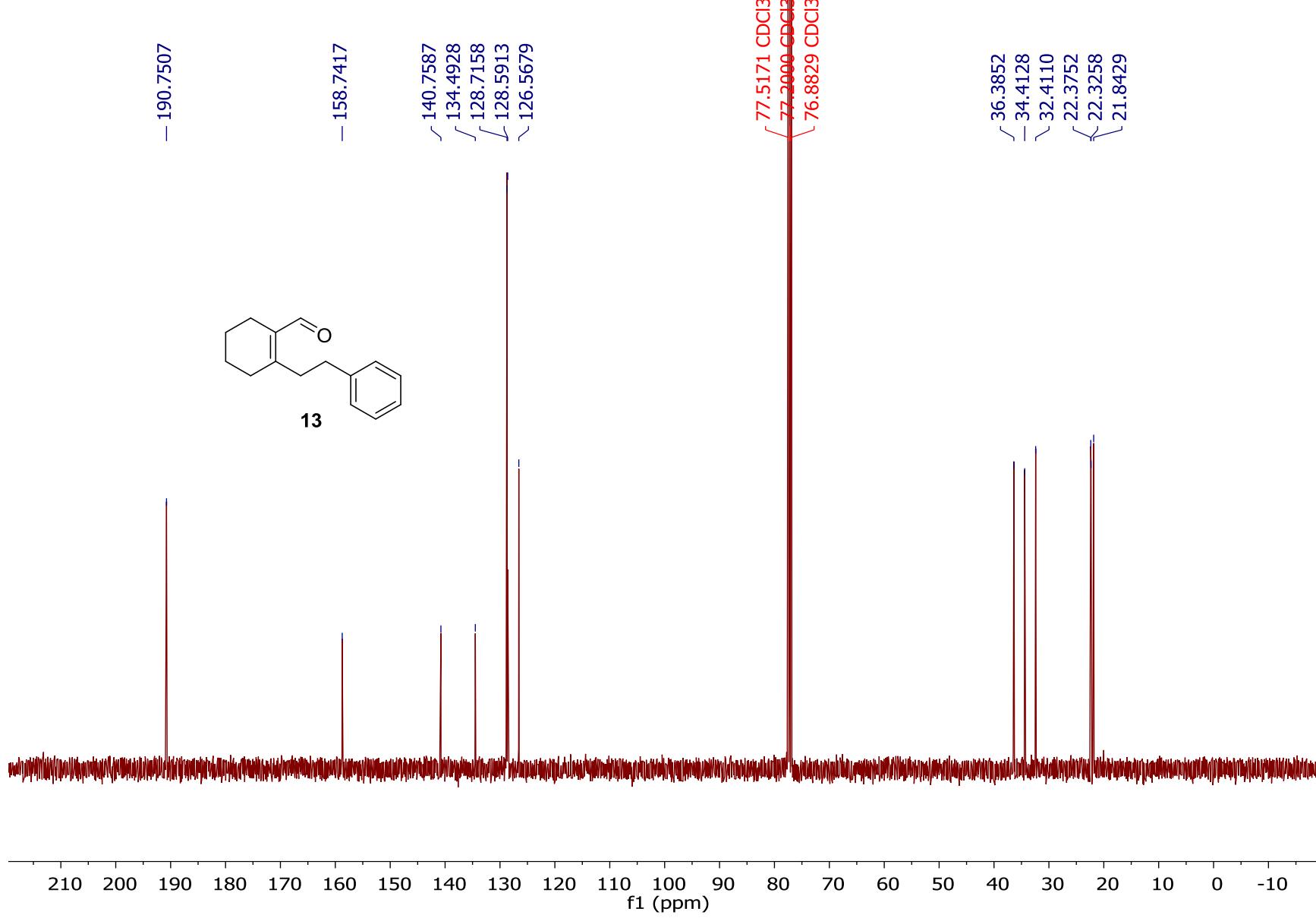


Compound 12b, 400 MHz ¹H NMR in CDCl₃

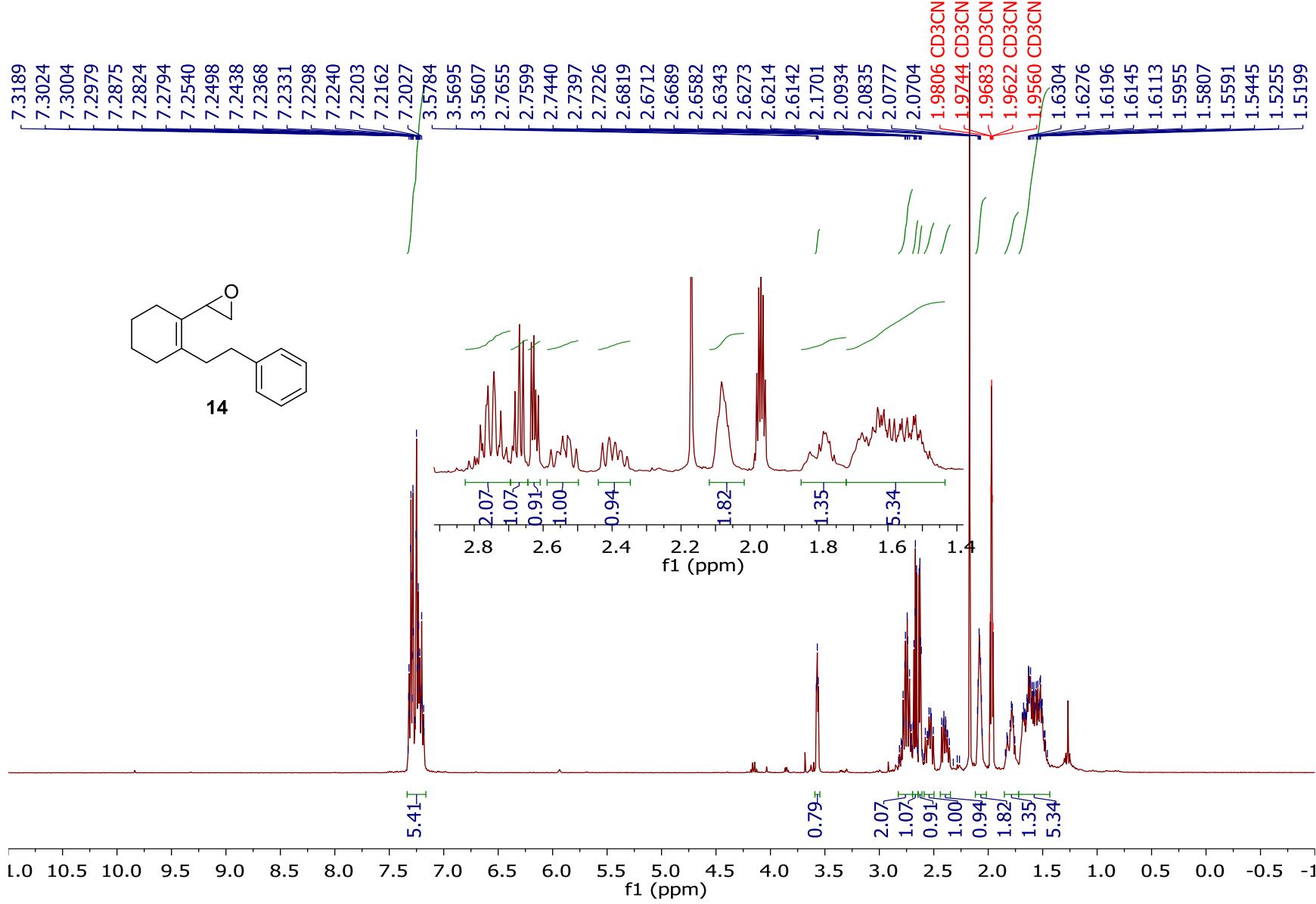


Compound 12b, 101 MHz ^{13}C NMR in CDCl_3

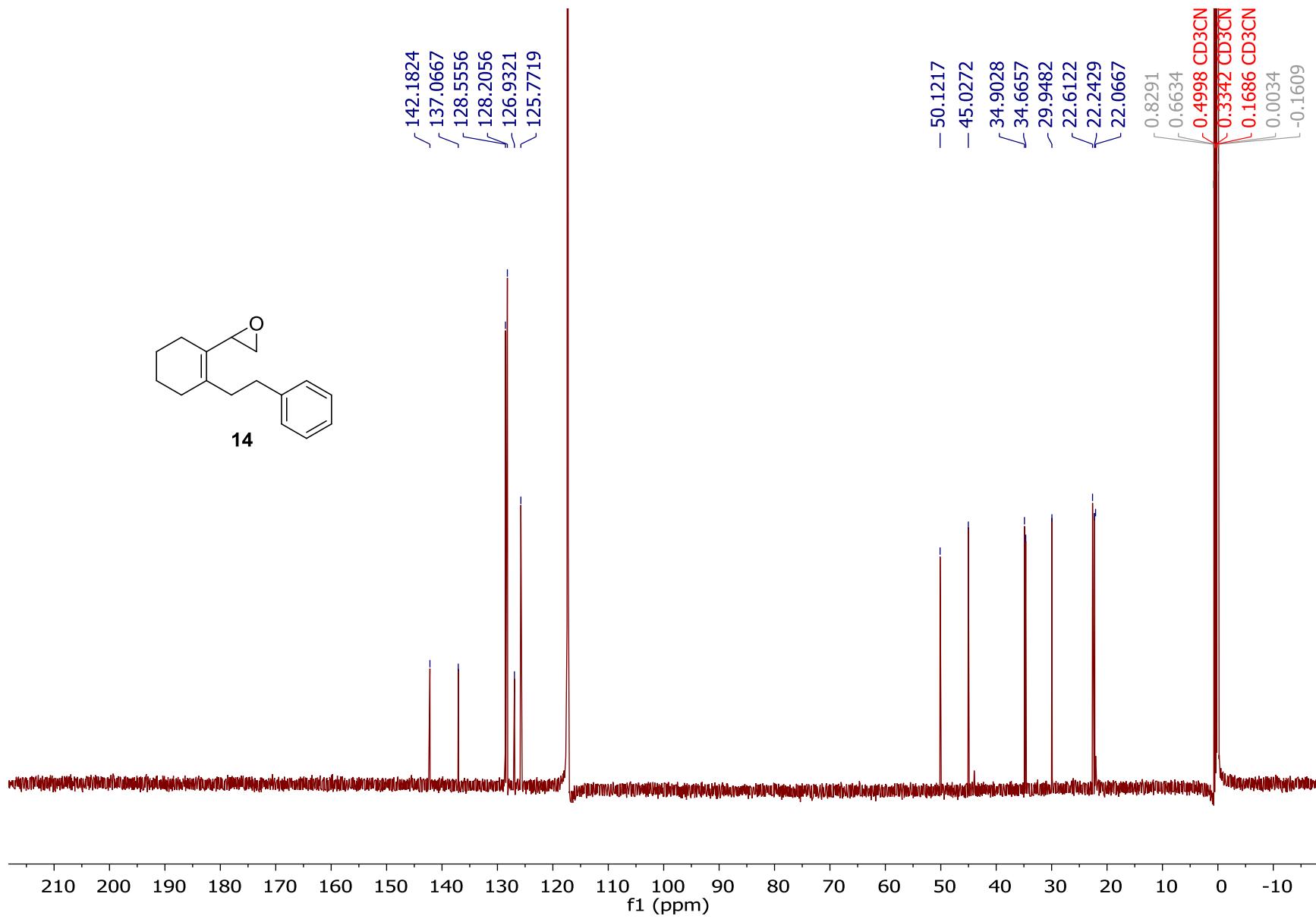




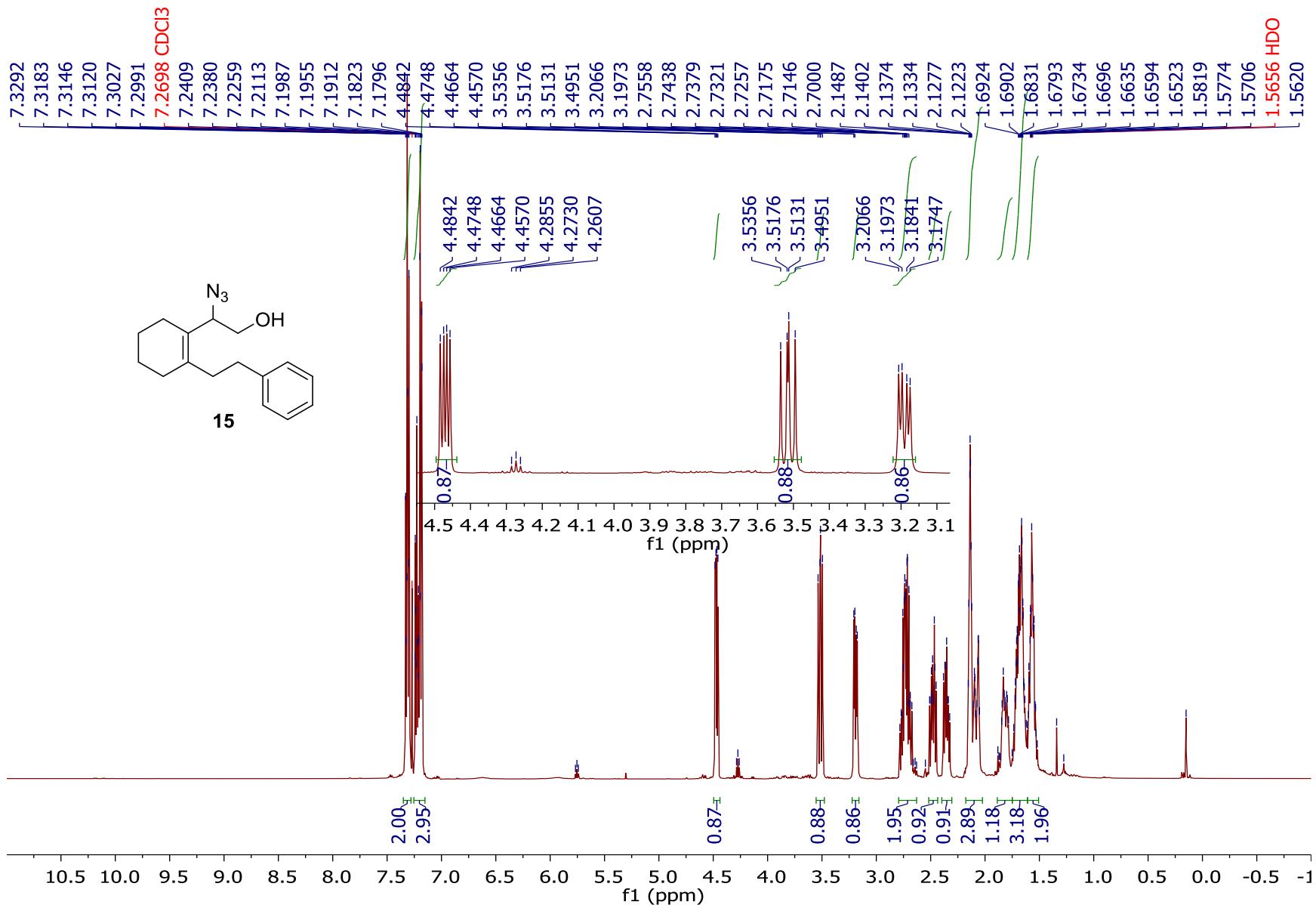
Compound 13, 101MHz ^{13}C NMR in CDCl_3



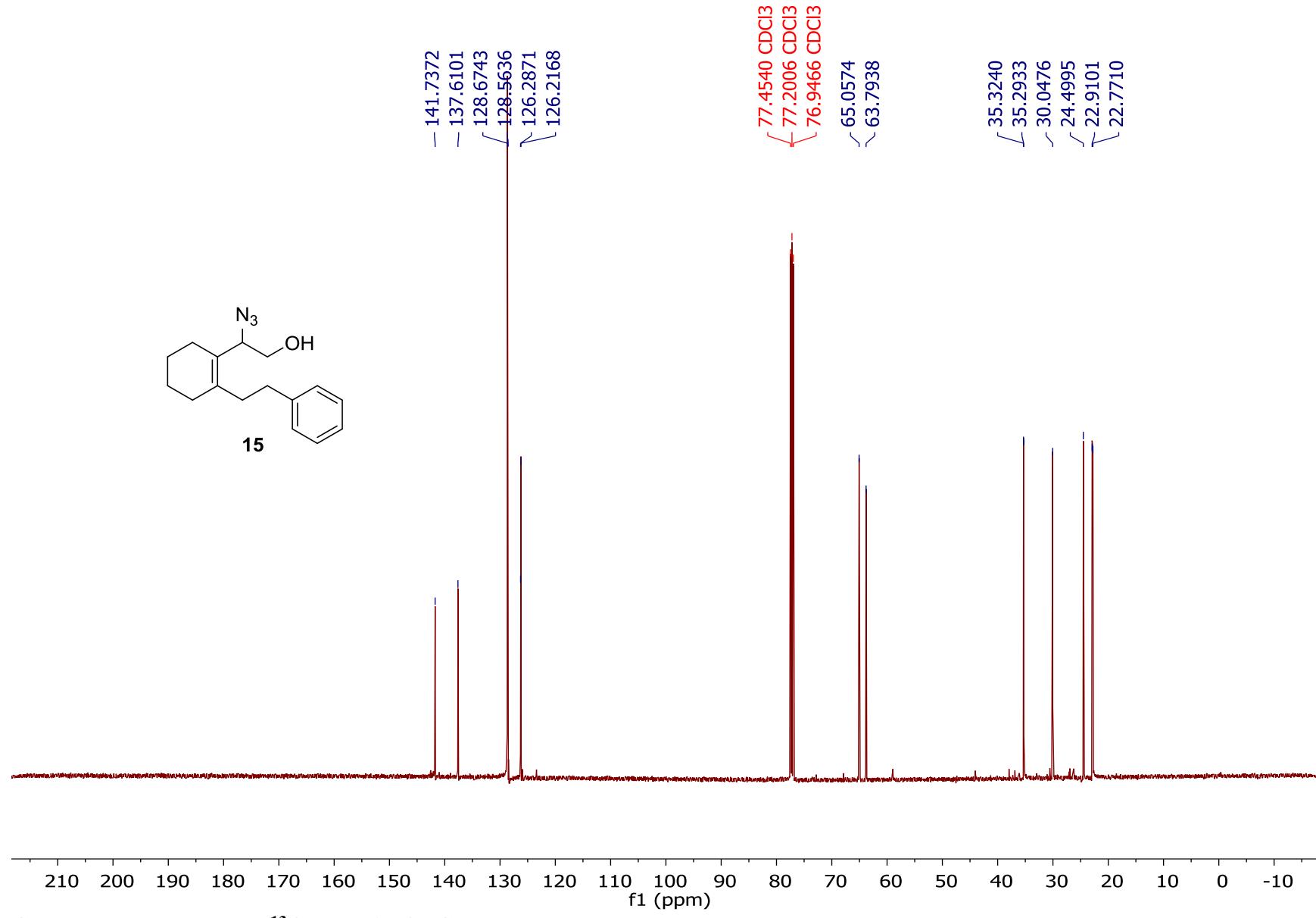
Compound 14, 400 MHz ^1H NMR in CD_3CN



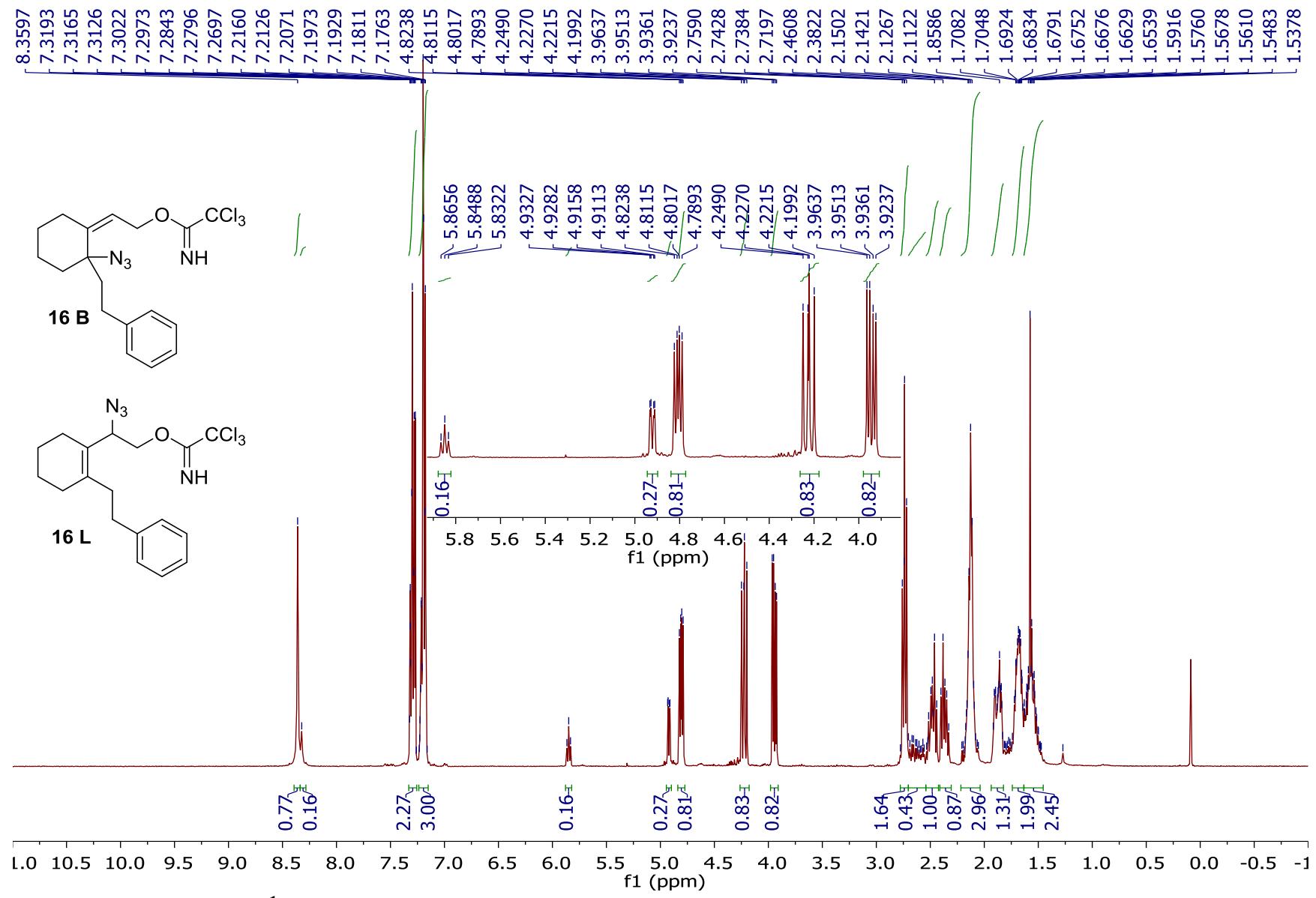
Compound 14, 126 MHz ^{13}C NMR in CD_3CN



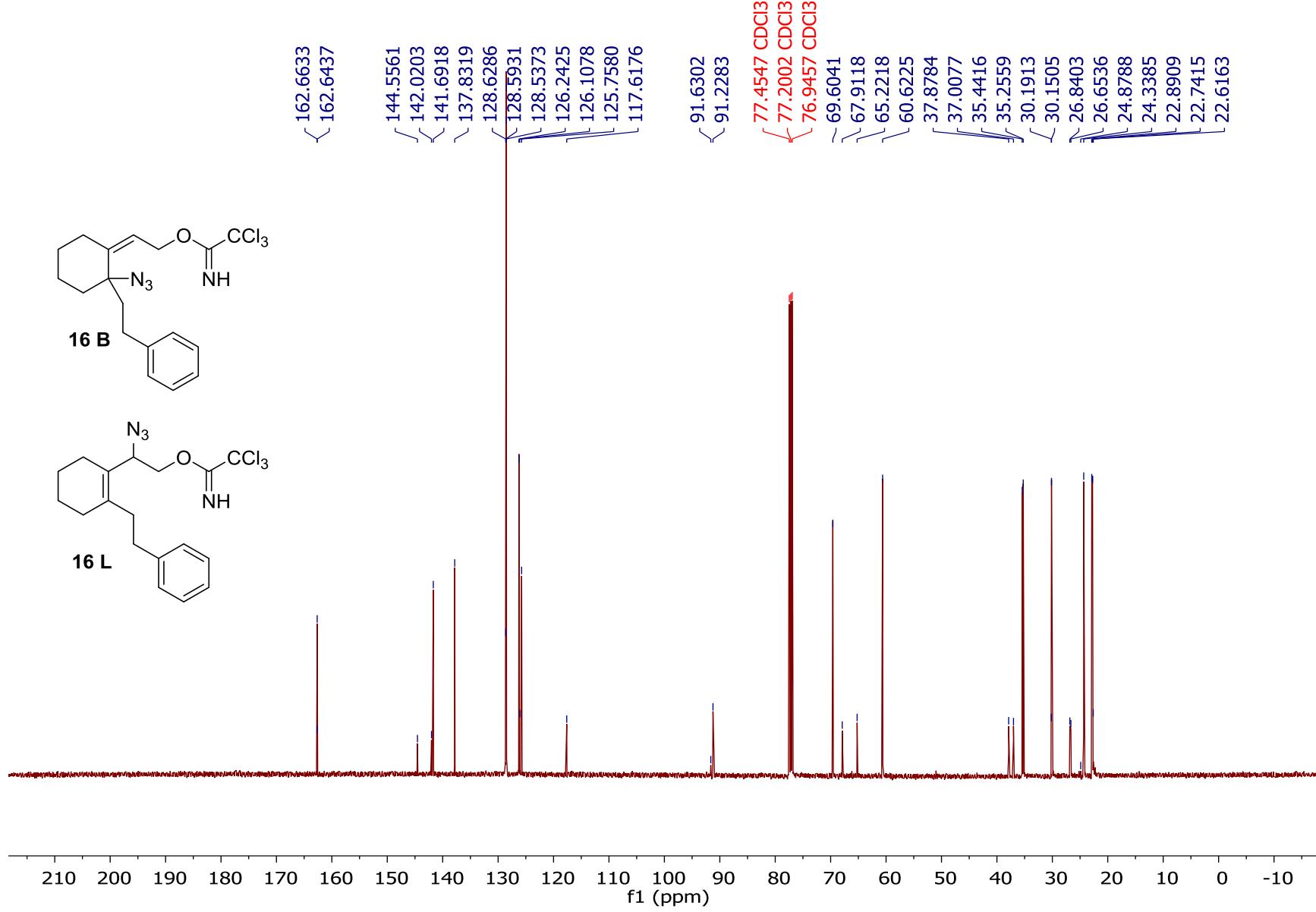
Compound 15, 400 MHz ^1H NMR in CDCl_3



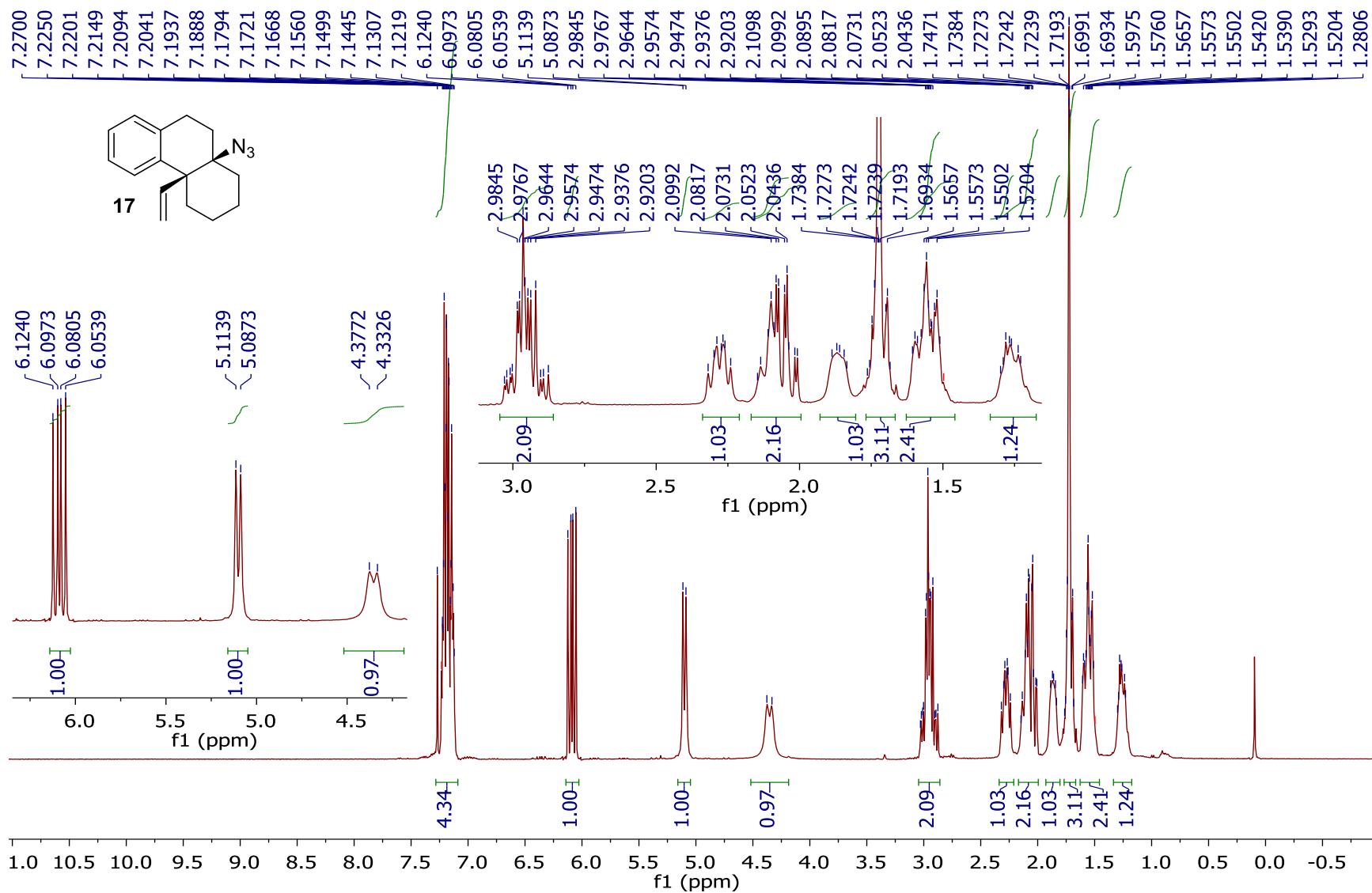
Compound 15, 101 MHz ^{13}C NMR in CDCl_3



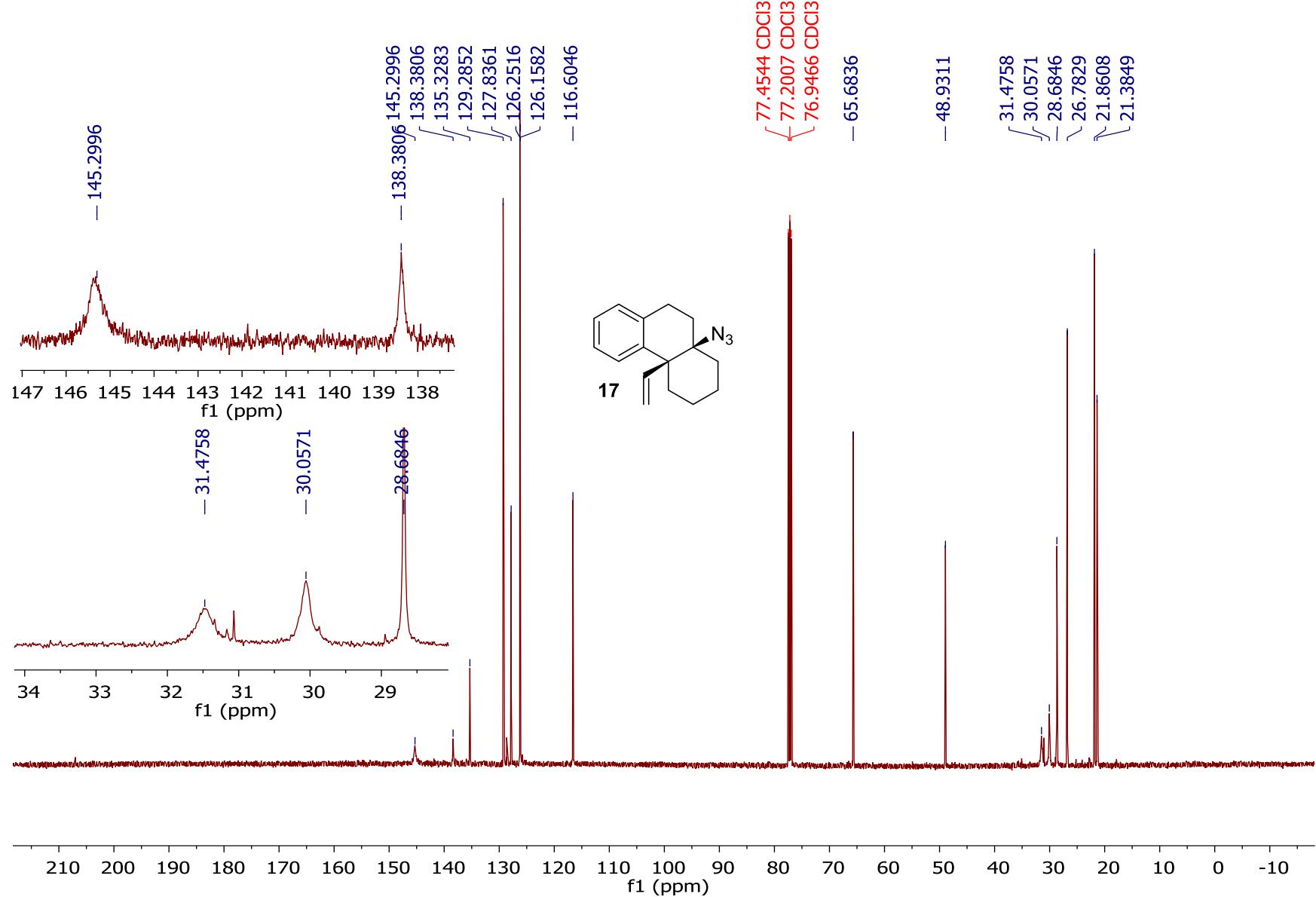
Compound 16, 400 MHz ^1H NMR in CDCl_3

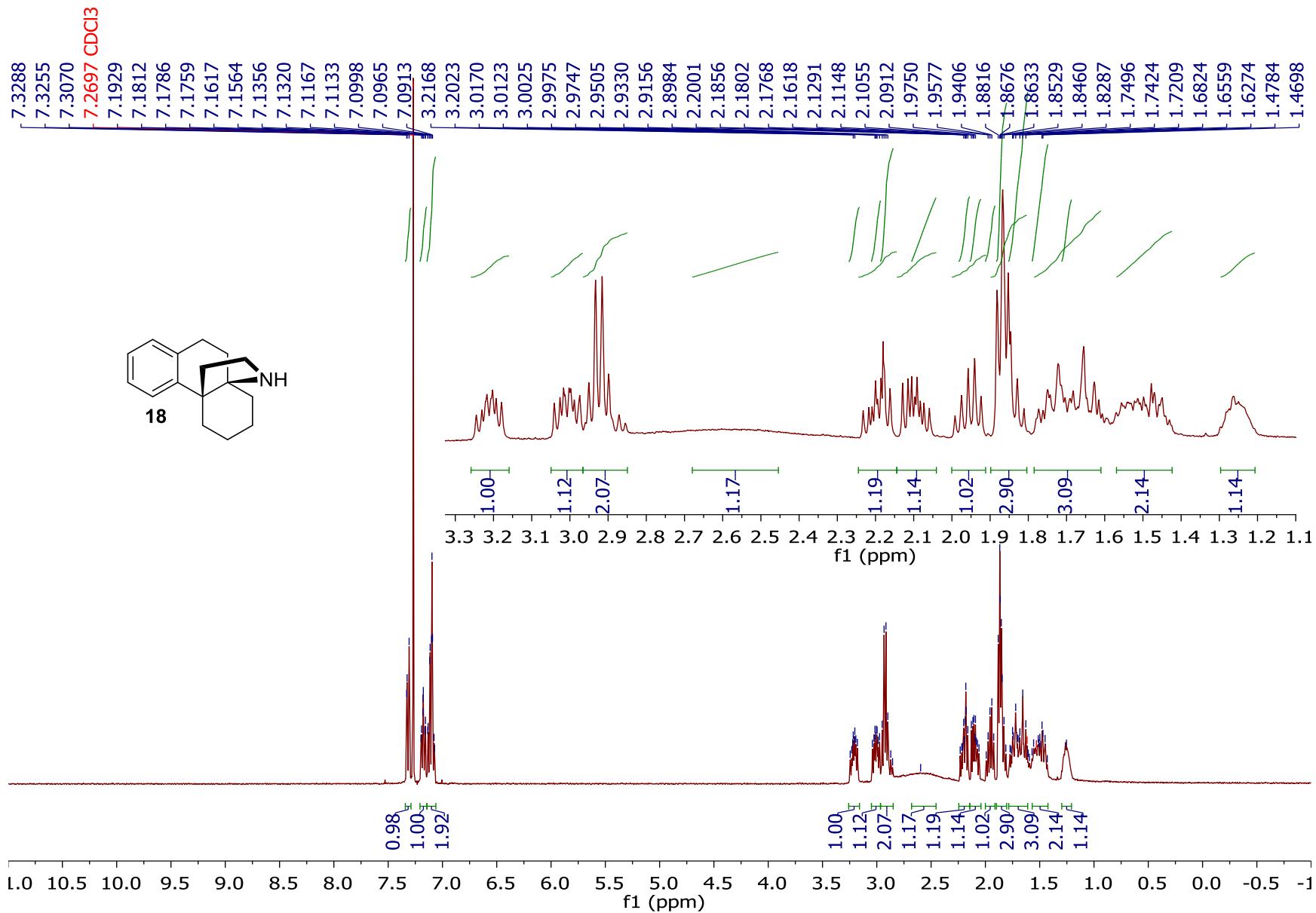


Compound 16, 126 MHz ^{13}C NMR in CDCl_3

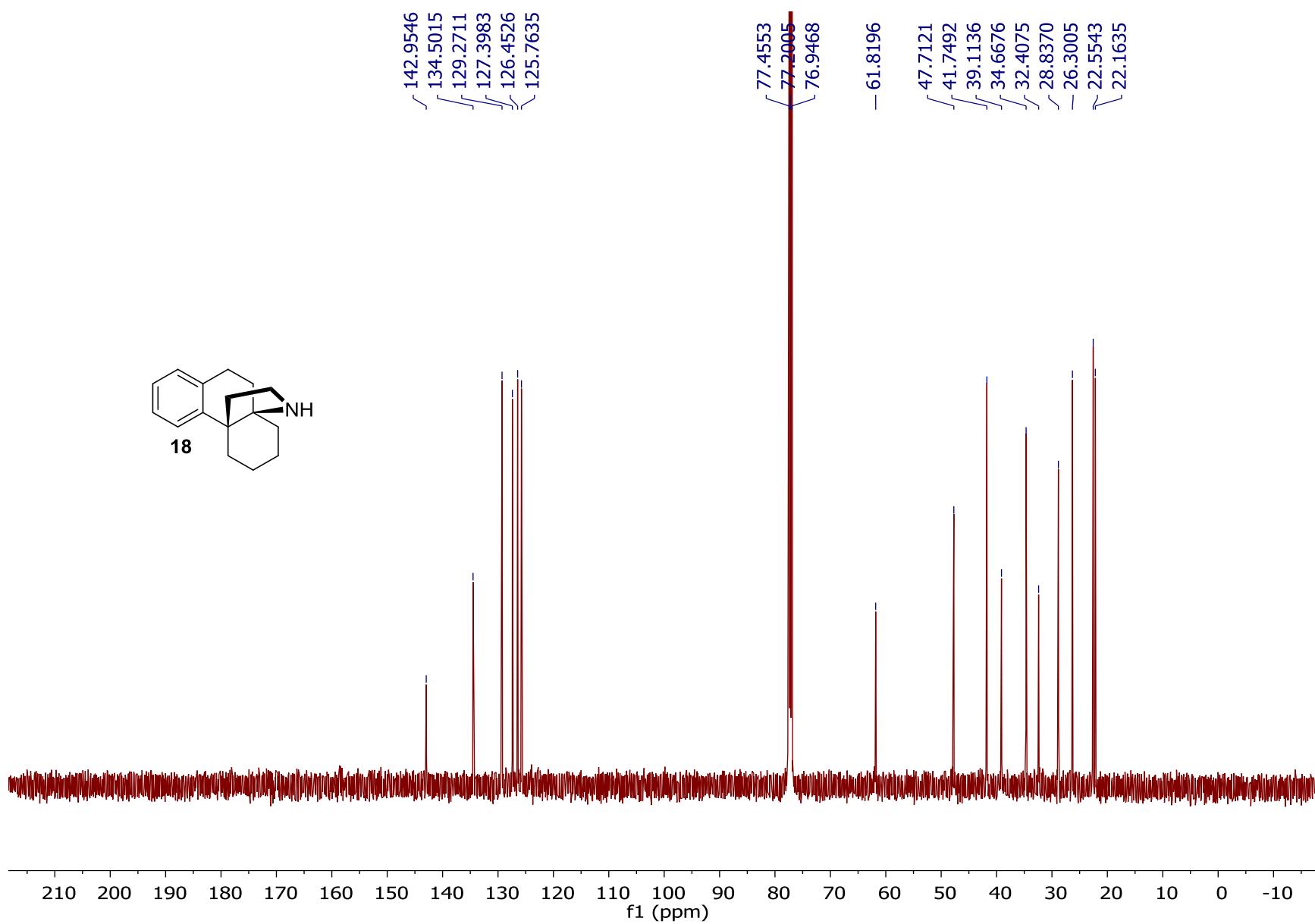


Compound 17, 400 MHz ^1H NMR in CDCl_3





Compound 18, 400 MHz ¹H NMR in CDCl₃



Compound 18, 126 MHz ^{13}C NMR in CDCl_3