[4+2+2] Cycloaddition Catalyzed by a New Cationic Rhodium-Bisphosphine Monooxide Complex

*Gino Martin R. Canlas and Scott R. Gilbertson, Ph.D.**

Contribution from the Department of Chemistry, University of Houston,
4800 Calhoun Road, Houston, TX 77204

SUPPLEMENTARY MATERIAL

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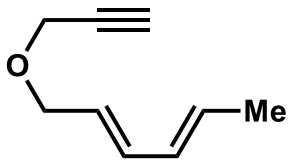
Materials and Methods

Unless stated otherwise, all reactions were carried out under inert atmosphere with anhydrous solvents in dry conditions. Dry dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene (PhMe) and diethyl ether (Et_2O) were obtained by passing into activated alumina columns. Unless noted all reagents were obtinated form commercial sources and used with out further purfication. Unless otherwise stated, yields are reported for pure, isolated compounds. NMR spectra were obtained using either a JEOL ECX-400 or ECA-500 spectrometers and referenced against tetramethylsilane. Reactions were monitored by thin layer chromatography (TLC) on 250 μm SiliCycle SiliaPlate glass-backed plates (extra hard layer, 60 Å, with F-254 indicator), using UV, acidic *p*-anisaldehyde tincture, basic aqueous permanganate ($KMnO_4$) solution, or ethanolic phosphomolybdic acid (PMA) solution as visualizing agents. High resolution mass spectra of the submitted samples were obtained using Autospec HR Chemical Ionization or Agilent 6150 HR Electrospray Ionization mass spectrometers by Dr. Ian Riddington and Jordan Dinser (University of Texas at Austin Mass Spectrometry Facility). Catalyst structure was solved by Dr. James Korp (University of Houston).

[1]: (2*E*,4*E*)-1-(prop-2-ynyloxy)hexa-2,4-diene



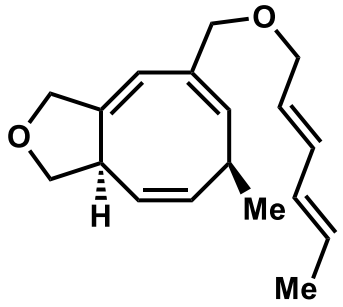
To a stirring suspension of NaH (1.10 g, 46 mmol, 2.0 equiv) in 25 mL THF at 0 ˚C was slowly added a solution of (*2E,4E*)-hexa-2,4-dien-1-ol (2.45 g, 25 mmol, 1.0 equiv.) in 25 mL THF. The resulting yellow suspension was allowed to stir for 2 hours before addition of 80% propargyl bromide solution in toluene (5.0 mL, 2.0 equiv.). The resulting mixture was then allowed to stir overnight at room temperature. The mixture was then cooled to 0 ˚C, diluted with Et_2O and slowly quenched with saturated aqueous NH_4Cl. The layers were separated, and the aqueous layer was extracted with Et_2O four times. The ethereal layers were combined and dried over anhydrous $MgSO_4$, following filtration the solvent was removed *in vacuo*. The resulting crude product was purified by silica gel chromatography to provide 2.55 g (75%) of pure dienyne.

Physical state: yellow liquid, 2.55 g (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (dd, *J* = 15.2, 10.4 Hz, 1H), 6.06 (ddd, *J* 14.8, 10.5, 1.4 Hz, 1H), 5.73 (dq, *J* = 13.6, 6.7 Hz, 1H), 5.60 (dt, *J* = 15.1, 6.5 Hz, 1H), 4.13 (d, *J* = 2.3 Hz, 2H), 4.08 (d, *J* = 6.5 Hz, 2H), 2.42 (t, *J* = 2.4 Hz, 1H), 1.76 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.44, 130.80, 130.72, 125.66, 79.93, 74.45, 70.15, 56.89, 18.28; HRMS (*m/z*): calcd for, $[C_9H_{11}O]^+$, 135.0810; found, 135.0811

[4+2+2] Dimerization of Acyclic Dienynes

In a Schlenk vacuum tube containing a small stir bar under argon was added 30.0 mg (0.04 mol, 0.04 equiv) Rh catalyst, then, the dienyne (1.0 mmol) dissolved in 6 mL CH_2Cl_2. The resulting mixture was subjected to three cycles of freeze-pump-thaw degassing before backfilling with argon. The tube was sealed and placed in an oil bath at 60 ˚C. [Note: the oil bath used only allows the submersion of the tube to the same level (or slightly above) of the solution inside.] After 24 hours the tube was removed from the oil back and after reaching room temperature was opened. Purification by column chromatography and subsequent solvent removal *in vacuo* provided the pure desired [4+2+2] homodimer.

[2]: (3a*R*,6*S*)-8-{[(2*E*,4*E*)-hexa-2,4-dien-1-yloxy]methyl}-6-methyl-1,3,3a,6-tetrahydrocycloocta[*c*]furan



Physical state: creamy white solid, 109 mg (80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.17 (dd, *J* = 15.2, 10.5 Hz, 1H), 6.12-5.99 (m, 1H), 5.75 (d, *J* = 2.2 Hz, 1H), 5.70 (dd, *J* = 14.9, 6.9 Hz, 1H), 5.65-5.54 (m, 2H), 5.42 (d, *J* = 6.4 Hz, 1H), 5.06 (dd, *J* = 10.1, 5.7 Hz, 1H), 4.46 (d, *J* = 13.6 Hz, 1H), 4.31 (d, *J* = 13.7 Hz, 1H), 4.20 (dd, *J* = 7.9, 7.9 Hz, 1H), 4.13 (d, *J* = 5.3 Hz, 1H), 3.93 (d, *J* = 6.4 Hz, 2H), 3.87-3.76 (m, 3H), 3.65 (dd, *J* = 8.2, 8.2 Hz, 1H), 1.75 (d, *J* = 6.7 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.31, 137.23, 137.05, 133.53, 130.95, 130.16, 126.84, 120.83, 117.31, 76.70, 75.37, 74.25, 70.20, 42.58, 32.54, 20.37, 18.27; HRMS (*m*/z): calcd for $[C_{18}H_{24}O_2]^+$, 272.1776; found, 272.1771

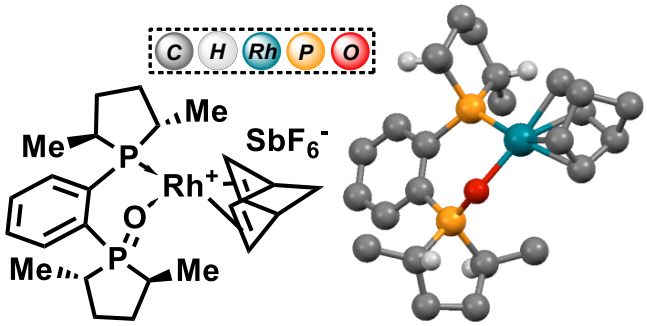
Discovery of Active Rhodium Bisphosphine Monoxide Complex 3

It was previously discovered that preformed mixture 3 (1:2:1 ratio of $[Rh(nbd)Cl]_2$:(*S,S*)-Me-DuPHOS:$AgSbF_6$) was capable of catalyzing the [4+2+2] reaction. However, since this mixture was not capable of providing a well-defined, discrete, and crystallized precatalyst, a series of experiments was performed using [4+2+2] dimerization of substrate **1** as the base reaction. With the goal of finding a well-defined precatalyst, a series of systems were investigated where other rhodium sources or metals, solvents, ligands or additives were investigated. Most conditions failed, especially those that were significantly different from the previous ligand. Based on the observation that the desired [4+2+2] product formed as the catalyst aged led to the idea that oxidation of the complex (metal or ligand) may be responsible for this reaction and subsequently, the discovery and isolation of the first Rh-BozPHOS complex, which catalyzes the [4+2+2] reaction. The results are summarized in the table below:

Complex or Catalyst Mixture	Solvent, Conditions	% Yield (2a)
Rh/nbd/CHIRAPHOS/SbF_6	6:1 CH_2Cl_2:EtOAc, rt	-
$Rh(cod)_2OTf$, PPh_3	benzene, rt, slow addition	-
$[Rh(cod)Cl]_2$, PPh_3	benzene, rt	-
[Rh(cod){(*S,S*)-Et-DuPHOS}]OTf	6:1 CH_2Cl_2:EtOAc, rt	trace
$[Rh(nbd)Cl]_2$, $AgSbF_6$	6:1 CH_2Cl_2:EtOAc, rt (*in situ*)	-
$[Rh(nbd)Cl]_2$, $AgSbF_6$, (*S,S*)-Me-DuPHOS	6:1 CH_2Cl_2:EtOAc, rt (*in situ*)	trace
$[Rh(nbd)Cl]_2$, SDS	H_2O, rt, 10 mins	-
[Rh(nbd){(2*S*,4*S*)-dppp}]PF_6	CH_2Cl_2, 65 °C, 24 h	trace
Rh/nbd/Xyl-BINAP/SbF_6	CH_2Cl_2, 65 °C, 24 h	trace
Rh/nbd/$MePh_2P$=O/SbF_6	CH_2Cl_2, 65 °C, 24 h	-
Rh/cod/RajPHOS/SbF_6	CH_2Cl_2, 65 °C, 24 h	-
Rh/cod/MOP/SbF_6	CH_2Cl_2, 65 °C, 24 h	-
Rh(nbd)(SIPr)Cl	CH_2Cl_2, 65 °C, 24 h	-
Rh(nbd)(IPr)Cl, AgOTf	PhH, 60 °C, 3 h	trace
Ir/cod/DuPHOS/SbF_6	CH_2Cl_2, 65 °C, 24 h	trace
Ni(cod), phosphine or NHC	PhMe, 65 °C, 24 h	-
Rh/nbd/dppf/SbF_6	CH_2Cl_2, 65 °C, 24 h	12
[Rh(cod){(*S,S*)-Me-DuPHOS}]BF_4	6:1 CH_2Cl_2:EtOAc, rt	30
Rh/nbd/DuPHOS/SbF_6 **(3)**	CH_2Cl_2, 60 °C, 24 h	83
[Rh(nbd){(*S,S*)-Me-BozPHOS}]SbF_6	CH_2Cl_2, 60 °C, 24 h	80

Catalyst Preparation

[3]: [Rh(nbd){(*S,S*)-Me-BozPHOS}]SbF_6, (*O,P*)-{[1-(2S,5S)-2,5-dimethylphospholanyl]-[2-(2S,5S)-2,5-dimethylphospholanyl-1-oxide]benzene}norbornadienerhodium (I) hexafluoroantimonate



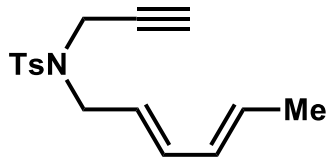
Small Scale: In a screw-cap vial covered with a septum and equipped with a small stir bar under argon were placed 104 mg $[Rh(nbd)Cl]_2$ (0.23 mmol, 1.0 equiv.) and 147 mg (*S,S*)-Me-BozPHOS (0.46 mmol, 2.0 equiv.) THF (14 mL) was added to dissolve the solids, and the mixture was allowed to stir for an hour before the addition of 158 mg $AgSbF_6$ (0.46 mmol, 2.0 equiv.) The resulting mixture was allowed to stir for 2 hours under argon before being doubly filtered using 2.7 and 0.7 µm glass microfiber syringe filters (Whatman) into a pre-weighed container. Most of the solvent was removed by a steady stream of nitrogen gas overnight prior to subjecting the mixture to vacuum to obtain 278.8 mg (82%) of fluffy yellow solids. Single crystal X-ray quality crystals were obtained by very carefully adding pentane over a saturated CH_2Cl_2 solution of the complex and allowing the crystals to form slowly in a vial saturated with pentane vapors.

Scale-up Procedure: To a stirred solution of $[Rh(nbd)Cl]_2$ (392 mg, 0.85 mmol, 1.0 equiv.) and (*S,S*)-Me-BozPHOS (548 mg , 1.70 mmol, 2.0 equiv.) in 25 mL anhydrous THF in a flame-dried 100 mL round bottomed flask equipped with an egg-shaped stir bar, was added 20 mL of ~0.085 M $AgSbF_6$ in anhydrous THF. The mixture was allowed to stir for 3 h while protected from light using aluminum foil. The mixture was sequentially filtered through 2.7 µm, then 0.7 µm glass microfiber syringe filters (Whatman) into a pre-weighed collection flask. Most of the solvent was removed by a steady stream of nitrogen gas overnight prior to subjecting the mixture to high vacuum to obtain 1.227 g (96%) of dried yellow powder. Single crystal X-ray quality crystals were obtained by very carefully adding pentane over a saturated CH_2Cl_2 solution of the complex and allowing the crystals to form slowly in a vial saturated with pentane vapors.

Physical state: yellow solid, 1.227 g (96%); thin, yellow, prismatic crystals obtained after recrystallization; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.73 – 7.65 (m, 2H), 7.64 – 7.60 (m, 1H), 7.37 (dddd, J = 12.9, 7.7, 3.3, 1.6 Hz, 1H), 5.29 – 5.27 (m, 1H), 5.21 (dd, J = 7.7, 3.7 Hz, 1H), 3.95 (d, J = 13.8 Hz, 2H), 3.77 – 3.69 (m, 2H), 2.54 – 2.15 (m, 8H), 2.06 (dq, J = 20.8, 7.0 Hz, 1H), 1.83 – 1.55 (m, 5H), 1.60 (dd, J =

18.8, 7.2 Hz, 3H), 1.41 – 1.32 (m, 3H), 1.12 – 1.05 (m, 3H), 0.94 (dd, J = 17.4, 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 135.03, 134.95, 133.19, 133.16, 132.53, 132.46, 132.42, 132.35, 131.05, 130.96, 64.95, 64.91, 53.03, 52.93, 52.43, 52.08, 50.49, 50.39, 43.97, 43.77, 40.33, 39.79, 37.00, 36.96, 36.35, 35.75, 35.20, 34.06, 33.85, 33.14, 33.06, 32.63, 32.56, 18.56, 18.48, 14.08, 14.06, 13.65, 12.91, 12.88; ^{31}P NMR (202 MHz, $CDCl_3$) δ 77.73 (dd, J = 14.97, 0.75 Hz), 37.50 (dd, J = 169.94, 14.97 Hz); HRMS (*m/z*): calcd for $[C_{25}H_{36}OP_2Rh]^+$; 517.12909; found, 517.12804

[4]: *N*-[(2*E*,4*E*)-hexa-2,4-dien-1-yl]-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide



To an anhydrous THF solution (120 mL) of 1.26 g of (*2E,4E*)-2,4-hexadien-1-ol (12.9 mmol, 1.0 equiv.), 2.70 g of 4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (12.9 mmol, 1.0 equiv.) and 3.39 g of PPh_3 (12.9 mmol, 1.0 equiv.) under argon in a round-bottom flask diisopropylazodicarboxylate (1.1 equiv.) was slowly added. The resulting mixture was stirred at room temperature for 5 hours under argon, then, the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography to obtain 2.40 g (64%) of pure tosylamide dienyne.

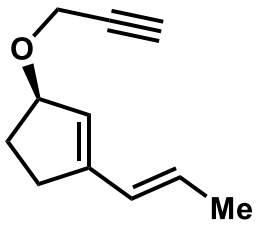
Physical state: white solid, 2.40 g (64%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.73 (dd, J = 8.5, 1.6, 1H), 7.29 (d, J = 8.2, 1H), 6.18 (dd, J = 15.1, 10.5, 1H), 6.02 (ddd, J = 14.9, 10.5, 1.4, 1H), 5.71 (dq, J = 13.7, 6.8, 1H), 5.40 (m, 1H), 4.07 (d, J = 2.4, 1H), 3.83 (d, J = 7.0, 1H), 2.43 (s, 2H), 2.00 (t, J = 2.5, 1H), 1.75 (d, J = 7.0, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.64, 136.16, 135.68, 131.12, 130.46, 129.60, 127.92, 123.44, 76.72, 73.78, 48.34, 35.74, 21.71, 18.25; HRMS (*m/z*): calcd for $[C_{16}H_{18}NO_2S]^+$, 288.1058; found, 288.1056

Syntheses of Cyclic Dienyne Ethers

To a suspension of sodium hydride (2.0 equiv.) in anhydrous THF in a flame-dried round bottom flask equipped with an egg-shaped stir bar under argon at 0 $^{\circ}$C was slowly added a solution of dienol in anhydrous THF (approximate diene concentration is 0.25 M in solution). The resulting mixture was stirred for two hours prior to addition of 80% propargyl bromide solution in toluene at 0 $^{\circ}$C and left overnight, wherein it slowly warmed up to room temperature. The resulting mixture was diluted with diethyl ether and then slowly quenched with aqueous NH_4Cl. The layers were separated and the aqueous layer was

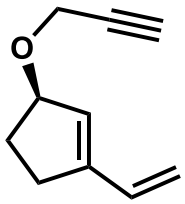
extracted five times with diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate and filtered. The solvent was removed *in vacuo* and the resulting crude material was purified by silica gel column chromatography.

[5]: (±)-(E)-1-(prop-1-enyl)-3-(prop-2-ynyloxy)cyclopent-1-ene



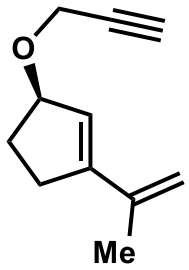
Physical state: yellow liquid, 987.2 mg (78%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.28 (d, *J* = 15.1 Hz, 1H), 5.73 (dq, *J* = 15.6, 6.8 Hz, 1H), 5.67 (s, 1H), 4.77-4.73 (m, 1H), δ 4.15 (dd, *J* = 15.7, 2.4 Hz, 1H), δ 4.12 (dd, *J* = 15.8, 2.6 Hz, 1H), 2.64-2.53 (m, 1H), 2.42-2.38 (m, 1H), 2.37-2.28 (m, 1H), 2.22 (dddd, *J* = 13.9, 9.0, 7.2, 4.8 Hz, 1H), 1.88 (ddd, *J* = 13.6, 8.5, 4.4 Hz, 1H), 1.79 (dd, *J* = 6.6, 1.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.26, 129.33, 127.89, 125.95, 84.24, 80.69, 73.94, 55.72, 30.08, 29.84, 18.54; HRMS (*m/z*): calcd for $[C_{11}H_{13}O]^+$, 161.0966; found, 161.0962

[6]: (±)-1-vinyl-3-(prop-2-ynyloxy)cyclopent-1-ene



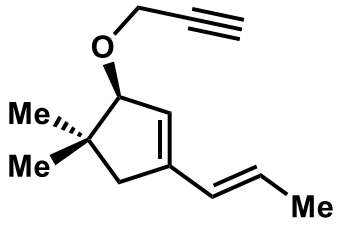
Physical state: yellow liquid, 122.2 mg (52%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (dd, *J* = 17.5, 10.6 Hz, 1H), 5.83 (d, *J* = 1.4 Hz, 1H), 5.22 (d, *J* = 17.7 Hz, 1H), 5.19 (d, *J* = 10.7 Hz, 1H), 4.78 (dd, *J* = 6.3, 3.0 Hz, 1H), δ 4.18 (dd, *J* = 15.8, 2.4 Hz, 1H), 4.14 (dd, *J* = 15.6, 2.4 Hz, 1H), 2.67-2.57 (m, 1H), 2.42 (t, *J* = 2.3 Hz, 1H), 2.39-2.31 (m, 1H), 2.26 (dddd, *J* = 13.8, 9.1, 7.3, 4.7 Hz, 1H), 1.91 (ddd, *J* = 13.6, 8.6, 4.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.28, 133.24, 129.03, 117.07, 84.17, 80.55, 74.07, 55.91, 29.98, 29.20; HRMS (*m/z*): calcd for $[C_{10}H_{12}O]^+$, 148.0888; found, 148.0885

[7]: (±)-1-(prop-1-en-2-yl)-3-(prop-2-ynyloxy)cyclopent-1-ene



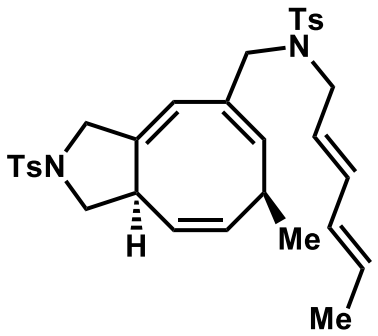
Physical state: yellow liquid, 382.8 mg (56%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (d, *J* = 1.6 Hz, 1H), 5.01 (s, 2H), 4.80 (d, *J* = 2.7 Hz, 1H), δ 4.19 (dd, *J* = 15.6, 2.4 Hz, 1H), 4.15 (dd, *J* = 15.6, 2.4 Hz, 1H), 2.72-2.62 (m, 1H), 2.45-2.35 (m, 2H), 2.26 (dddd, *J* = 13.7, 9.0, 7.4, 4.7 Hz, 1H), 1.94 (s, 3H), 1.94-1.87 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.87, 139.72, 125.95, 115.09, 84.63, 80.59, 77.41, 77.16, 76.91, 74.05, 55.94, 30.69, 30.24, 20.67; HRMS (*m*/*z*): calcd for $[C_{11}H_{14}O]^+$, 162.1045; found, 162.1042

[8]: (±)-4,4-dimethyl-(E)-1-(prop-1-enyl)-3-(prop-2-ynyloxy)cyclopent-1-ene



Physical state: yellow liquid, 563.0 mg (45%) with recovered starting material, 537 mg (54%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (d, *J* = 15.4 Hz, 1H), 5.65 (dq, *J* = 15.4, 6.8 Hz, 1H), 5.61 (s, 1H), 4.17 (d, *J* = 2.5 Hz, 2H), 4.13 (s, 1H), 2.40 (t, *J* = 2.3 Hz, 1H), 2.34 (d, *J* = 15.6 Hz, 1H), 2.12 (d, *J* = 15.7 Hz, 1H), 1.78 (d, *J* = 6.8 Hz, 3H), 1.11 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.47, 128.67, 128.40, 125.42, 90.90, 80.87, 73.86, 57.02, 45.56, 42.07, 29.15, 23.26, 18.50; HRMS (*m*/*z*): calcd for $[C_{13}H_{17}O]^+$, 189.1279; found, 189.1276

[9]: (3a*R*,6*R*)- 8-{(2*E*,4*E*)-hexa-2,4-dien-1-yl[(4-methylphenyl)sulfonyl]amino}-6-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,6-tetrahydro-1*H*-cycloocta[*c*]pyrrole



The same dimerization procedure above was used: Physical state: white solid, 421.5 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.01-5.77 (m, 2H), 5.71-5.54 (m, 2H), 5.48 (tt, *J* = 10.3, 5.2 Hz, 1H), 5.23 (d, *J* = 6.7 Hz, 1H), 5.15-5.03 (m, 1H), 4.95 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.02 (s, 1H), 3.91 (d, *J* = 14.6 Hz, 1H), 4.14-3.53 (m, 6H), 3.48 (d, *J* = 13.8 Hz, 1H), 2.92 (dd, *J* = 8.7, 8.7 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H), 1.71 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.28, 144.01, 143.40, 138.53, 137.39, 134.87, 132.22, 130.47, 130.38, 129.93, 129.76, 128.70, 128.09, 127.64, 127.27, 123.97, 121.53, 120.18, 77.48, 77.16, 76.84, 54.87, 54.77, 54.54, 48.29, 41.36, 32.91, 21.73, 21.65, 20.11, 18.21; HRMS (*m*/*z*): calcd for $[C_{32}H_{38}N_2NaO_4S_2]^+$, 601.21650; found, 601.21530

Cycloadditions Involving a Secondary External Alkyne

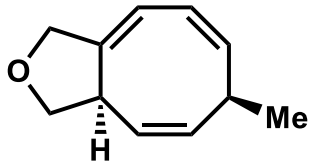
A. [4+2+2] Cycloaddition of Dienynes with Acetylene and Propyne

In a flame-dried 100 mL Schlenk storage tube containing a small stir bar under argon was added (0.04 equiv) Rh catalyst, dissolved in 5 mL CH_2Cl_2, this was followed by the addition of the dienyne (1.0 equiv.) in 15 mL CH_2Cl_2. The resulting mixture was subjected to three cycles of freeze-pump-thaw de-gassing before backfilling (while solution is still frozen) with acetylene or propyne gas. The gaseous alkyne was bubbled directly into the mixture until the temperature is approximately 0 ˚C . The tube was sealed and placed in an oil bath at 60 ˚C. [Note: the oil bath used only allows the submersion of the tube to the same level (or slightly above) of the solution inside.] The reaction was heated in the oil bath for 24 hours after which upon cooling to room temperature was carefully opened. Filtration of the crude mixture though a short pad of Celite 545, or column chromatography gave the analytically pure desired [4+2+2] products.

B. [4+2+2] Cycloaddition of Dienynes with Nongaseous External Alkynes

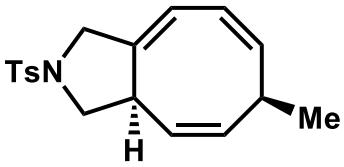
In a flame-dried 100 mL Schlenk vacuum tube containing a small stir bar under argon was added 30.0 mg (0.04 mol, 0.04 equiv) Rh catalyst dissolved in 5 mL CH_2Cl_2. To this was added the external alkyne (5.0 equiv.) and dienyne (162.5 mg) in 15 mL CH_2Cl_2. The resulting mixture was subjected to three cycles of freeze-pump-thaw degassing method before backfilling with argon. The tube was sealed and placed in an oil bath at 60 ˚C. [Note: the oil bath used only allows the submersion of the tube to the same level (or slightly above) of the solution inside.] The reaction was left in the oil bath for 24 hours before very carefully venting. Purification of the crude product by column chromatography gave the analytically pure desired [4+2+2] product.

[10]: (3a*R*,6*R*)-6-methyl-1,3,3a,6-tetrahydrocycloocta[*c*]furan



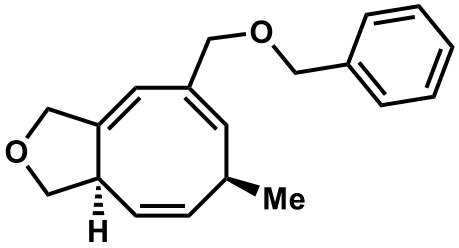
Physical state: yellow liquid, 79.0 mg (45%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72-5.66 (m, 1H), 5.54-5.48 (m, 2H), 5.34 (dd, *J* = 11.8, 5.7 Hz, 1H), 5.08-5.04 (m, 1H), 4.41 (d, *J* = 13.7 Hz, 1H), 4.28 (d, *J* = 13.6 Hz, 1H), 4.25-4.15 (m, 2H), 3.88-3.75 (m, 1H), 3.67 (dd, *J* = 7.3, 7.3 Hz, 1H),, 1.11 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.90, 139.46, 135.69, 122.68, 120.90, 115.76, 75.40, 74.07, 42.08, 32.38, 20.46; HRMS (*m/z*): calcd for $[C_{11}H_{14}O]^+$, 162.1045, found 162.1044

[11]: (3a*R*,6*R*)-6-methyl-2-[(4-methylphenyl)sulfonyl]-2,3,3a,6-tetrahydro-1*H*-cycloocta[*c*]pyrrole



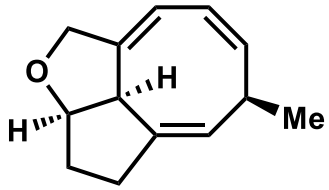
Physical state: white solid, 307.4 mg (99%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.67-5.63 (m, 1H), 5.49-5.41 (m, 1H), 5.56-5.39 (m, 1H), 5.35 (dd, *J* = 11.5, 5.8 Hz, 1H), 4.95 (dd, *J* = 9.8, 6.5 Hz, 1H), 4.14 (d, *J* = 6.3 Hz, 1H), 3.96 (d, *J* = 14.6 Hz, 1H), 3.72-3.59 (m, 3H), 2.94 (dd, *J* = 8.7, 8.7 Hz, 1H), 2.96-2.91 (m, 1H), 2.44 (s, 3H), 1.07 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.22, 144.02, 139.98, 136.33, 131.99, 129.83, 128.20, 122.71, 121.31, 119.03, 54.87, 54.70, 40.75, 32.64, 21.71, 20.29; HRMS (*m/z*): calcd for $[C_{18}H_{22}NO_2S]^+$, 316.1371; found, 316.1375

[12]: (3a*R*,6*S*)-8-[(benzyloxy)methyl]-6-methyl-1,3,3a,6-tetrahydrocycloocta[*c*]furan



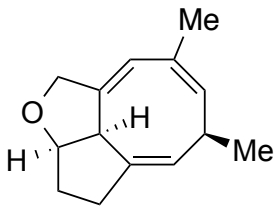
Physical state: yellow liquid, 128.6 mg (45%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 5.79 (q, *J* = 2.2 Hz, 1H), 5.59 (td, *J* = 9.6, 2.2 Hz, 1H), 5.44 (d, *J* = 6.3 Hz, 1H), 5.07 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.51-4.47 (m, 1H), 4.45 (s, 2H), 4.31 (d, *J* = 13.7 Hz, 1H), 4.21 (t, *J* = 7.9 Hz, 1H), 4.17-4.10 (m, 1H), 3.86 (s, 2H), 3.88-3.79 (m, 1H), 3.66 (t, *J* = 8.2 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.37, 138.41, 137.40, 137.08, 130.88, 128.50, 128.04, 127.75, 120.86, 117.27, 76.84, 75.37, 74.24, 71.61, 42.59, 32.58, 20.36; HRMS (*m/z*): calcd for $[C_{19}H_{21}O_2]^+$, 281.1542; found, 281.1545

[13]: (2a*R*,6*R*,9b*R*)-6-methyl-1,2a,3,4,6,9b-hexahydro-2-oxacycloocta[*cd*]pentalene

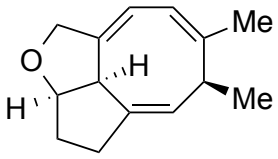


Physical state: orange waxy solid, 182.1 mg (97%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.69 (m, 1H), 5.57 (dd, *J* = 11.9, 7.3, 1H), 5.42 (dd, *J* = 11.9, 5.9, 1H), 5.33 (dd, *J* = 8.2, 1.6, 1H), 4.66 (m, 1H), 4.33 (d, *J* = 12.5, 1H), 4.25 (d, *J* = 12.6, 1H), 4.15 (s, 1H), 3.59 (dd, *J* = 14.0, 7.0, 1H), 2.62 (m, 1H), 2.20 (ddd, *J* = 16.4, 7.8, 2.9, 1H), 1.90 (m, 1H), 1.72 (m, 1H), 1.07 (d, *J* = 7.0, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.32, 139.11, 139.05, 125.67, 123.88, 116.53, 86.50, 74.34, 49.01, 33.57, 31.95, 30.01, 21.29; HRMS (*m/z*): calcd for $[C_{13}H_{16}O]^+$, 188. 1201, found 188.1199

[14]: (2a*R*,6*R*,9b*R*)-6,8-dimethyl-1,2a,3,4,6,9b-hexahydro-2-oxacycloocta[*cd*]pentalene (major regioismer)



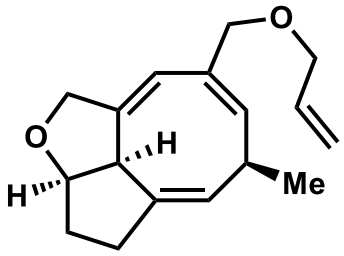
major product



minor product

Physical state: yellow liquid, 87.8 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 – 5.71 (m, 1H), 5.46 – 5.41 (m, 1H), 5.36 – 5.32 (m, 1H), 4.66 – 4.60 (m, 1H), 4.34 (s, 2H), 3.79 – 3.74 (m, 1H), 3.25 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.66 – 2.53 (m, 2H), 2.33 (ddd, *J* = 14.4, 8.4, 4.1 Hz, 1H), 2.25 (dd, *J* = 22.9, 2.7 Hz, 1H), 1.78 (br. s, 3H), 1.03 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.33, 139.49, 134.38, 130.15, 126.28, 120.61, 86.68, 72.76, 49.96, 34.48, 31.09, 31.05, 25.62, 21.35; HRMS (*m*/*z*): calcd for $[C_{14}H_{18}O]^+$, 202.1358; found, 202.1355

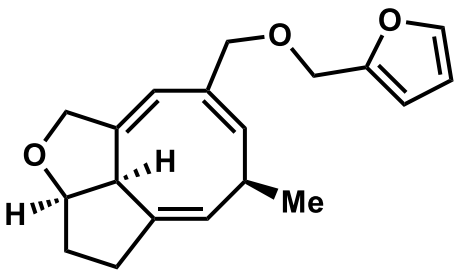
[15]: (2a*R*,6*S*,9b*R*)-6-methyl-8-[(prop-2-en-1-yloxy)methyl]-1,2a,3,4,6,9b-hexahydro-2-oxacycloocta[*cd*]pentalene



Physical state: yellow liquid, 21.1 mg (16%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (ddd, *J* = 22.8, 10.8, 5.7 Hz, 1H), 5.80 (q, *J* = 1.9 Hz, 1H), 5.55 (d, *J* = 7.1 Hz, 1H), 5.40 (dq, *J* = 7.9, 1.7 Hz, 1H), 5.26 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.3, 1.1 Hz, 1H), 4.66-4.62 (m, 1H), 4.41-4.31 (m, 2H), 3.98-3.87 (m, 4H), 3.84 (d, *J* = 11.5 Hz, 1H), 3.50-3.40 (m, 1H), 2.65-2.56 (m, 1H), 2.29 (ddd, *J* = 15.7, 8.1, 3.4 Hz, 1H), 1.94-1.86 (m, 1H), 1.75 (dddd, *J* = 13.4, 10.1, 8.2, 5.0 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.86, 139.60, 134.97, 134.71, 134.22, 125.70, 117.64, 117.23, 86.62,

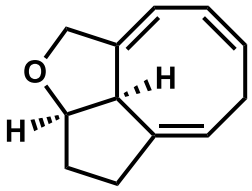
77.41, 77.16, 76.91, 76.40, 73.57, 70.74, 49.86, 33.97, 31.38, 30.62, 21.27; HRMS (*m*/*z*): calcd for $[C_{17}H_{22}O_2]^+$, 258.1620; found, 258.1610

[16]: (2a*R*,6*S*,9b*R*)-8-[(furan-2-ylmethoxy)methyl]-6-methyl-1,2a,3,4,6,9b-hexahydro-2-oxacycloocta[*cd*]pentalene



Physical state: yellow liquid, 29.0 mg (29%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 1.5 Hz, 1H), 6.34 (dd, *J* = 3.0, 2.0 Hz, 1H), 6.29 (d, *J* = 3.1 Hz, 1H), 5.79 (d, *J* = 1.9 Hz, 1H), 5.56 (d, *J* = 7.1 Hz, 1H), 5.42-5.38 (m, 1H), 4.67-4.63 (m, 1H), 4.40 (q, *J* = 12.9 Hz, 2H), 4.36 (dd, *J* = 22.8, 13.0 Hz, 2H), 3.98-3.84 (m, 3H), 3.46 (dq, *J* = 14.4, 7.0 Hz, 1H), 2.61 (dt, *J* = 22.4, 8.3 Hz, 1H), 2.29 (ddd, *J* = 11.7, 8.0, 3.3 Hz, 1H), 1.94-1.87 (m, 1H), 1.75 (dddd, *J* = 13.3, 10.1, 8.1, 5.0 Hz, 1H), 1.07 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.97, 148.01, 142.88, 139.63, 135.29, 133.90, 125.66, 117.56, 110.38, 109.41, 86.62, 76.30, 73.61, 63.35, 49.87, 33.99, 31.39, 30.61, 21.28; HRMS (*m*/*z*): calcd for $[C_{19}H_{22}O_3]^+$, 298.1569; found, 298.1564

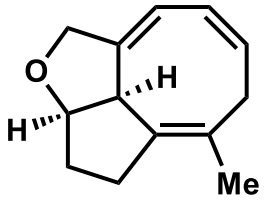
[17]: (2a*R*,9b*R*)-1,2a,3,4,6,9b-hexahydro-2-oxacycloocta[*cd*]pentalene



Physical state: yellow liquid, 93.0 mg (82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19-6.13 (m, 1H), 5.89 (s, 1H), 5.62-5.55 (m, 1H), 5.43 (dt, *J* = 10.4, 7.4 Hz, 1H), 4.62 (dt, *J* = 5.8, 3.8 Hz, 1H), 4.44 (dq, *J* = 13.2, 1.7 Hz, 1H), 4.36 (dt, *J* = 13.2, 2.0 Hz, 1H), 3.47 (s, 1H), 2.84 (dt, *J* = 16.0, 8.2 Hz, 1H), 2.71-2.53 (m, 2H), 2.49-2.40 (m, 1H), 1.87 (ddd, *J* = 8.1, 7.5, 3.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.25,

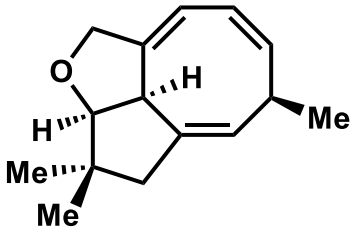
141.48, 130.64, 124.91, 118.22, 116.74, 86.75, 77.42, 77.16, 76.91, 71.31, 51.09, 31.93, 30.20, 28.26; HRMS (*m/z*): calcd for $[C_{12}H_{13}O]^+$, 173.0966; found 173.0969

[18]: (2a*R*,9b*R*)-5-methyl-1,2a,3,4,6,9b-hexahydro-2-oxacycloocta[*cd*]pentalene



Physical state: yellow liquid, 66.3 mg (70%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.10 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.86-5.82 (m, 1H), 5.47 (dt, *J* = 10.4, 7.6 Hz, 1H), 4.56-4.52 (m, 1H), 4.44-4.38 (m, 1H), 4.38-4.33 (m, 1H), 3.50 (s, 1H), 2.82 (dd, *J* = 14.9, 7.6 Hz, 1H), 2.73-2.65 (m, 1H), 2.58-2.47 (m, 1H), 2.42 (dd, *J* = 16.3, 9.6 Hz, 1H), 1.98 (dddd, *J* = 13.9, 8.2, 2.9, 1.4 Hz, 1H), 1.79 (ddd, *J* = 12.1, 8.4, 3.5 Hz, 1H), 1.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.83, 133.44, 130.35, 125.94, 125.58, 116.24, 87.12, 77.41, 77.16, 76.91, 71.76, 52.01, 35.42, 30.03, 29.68, 22.91; HRMS (*m/z*): calcd for $[C_{13}H_{16}O]^+$, 188.1201; found, 188.1196

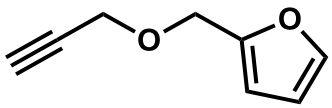
[19]: (2a*S*,6*R*,9b*R*)-3,3,6-trimethyl-1,2a,3,4,6,9b-hexahydro-2-oxacycloocta[*cd*]pentalene



Physical state: yellow liquid, 106.3 mg (85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.67 (m, 1H), 5.58 (m, 1H), 5.42 (dd, *J* = 11.9, 6.0, 1H), 5.29 (d, *J* = 7.9, 1H), 4.29 (d, *J* = 12.9, 1H), 4.24 (d, *J* = 12.3, 1H), 4.17 (s, 1H), 3.96 (m, 1H), 3.58 (m, 1H), 2.52 (d, *J* = 14.8, 1H), 1.88 (d, *J* = 14.8, 1H), 1.10 (s, 3H), 1.07 (d, *J* = 7.0, 3H), 0.86 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.04, 139.06, 138.85, 126.19, 124.18, 116.21, 93.37, 74.59, 48.67, 43.62, 41.29, 33.34, 26.29, 22.01, 21.49; HRMS (*m/z*): calcd for $[C_{15}H_{20}O]^+$, 216.1514, found 216.1513

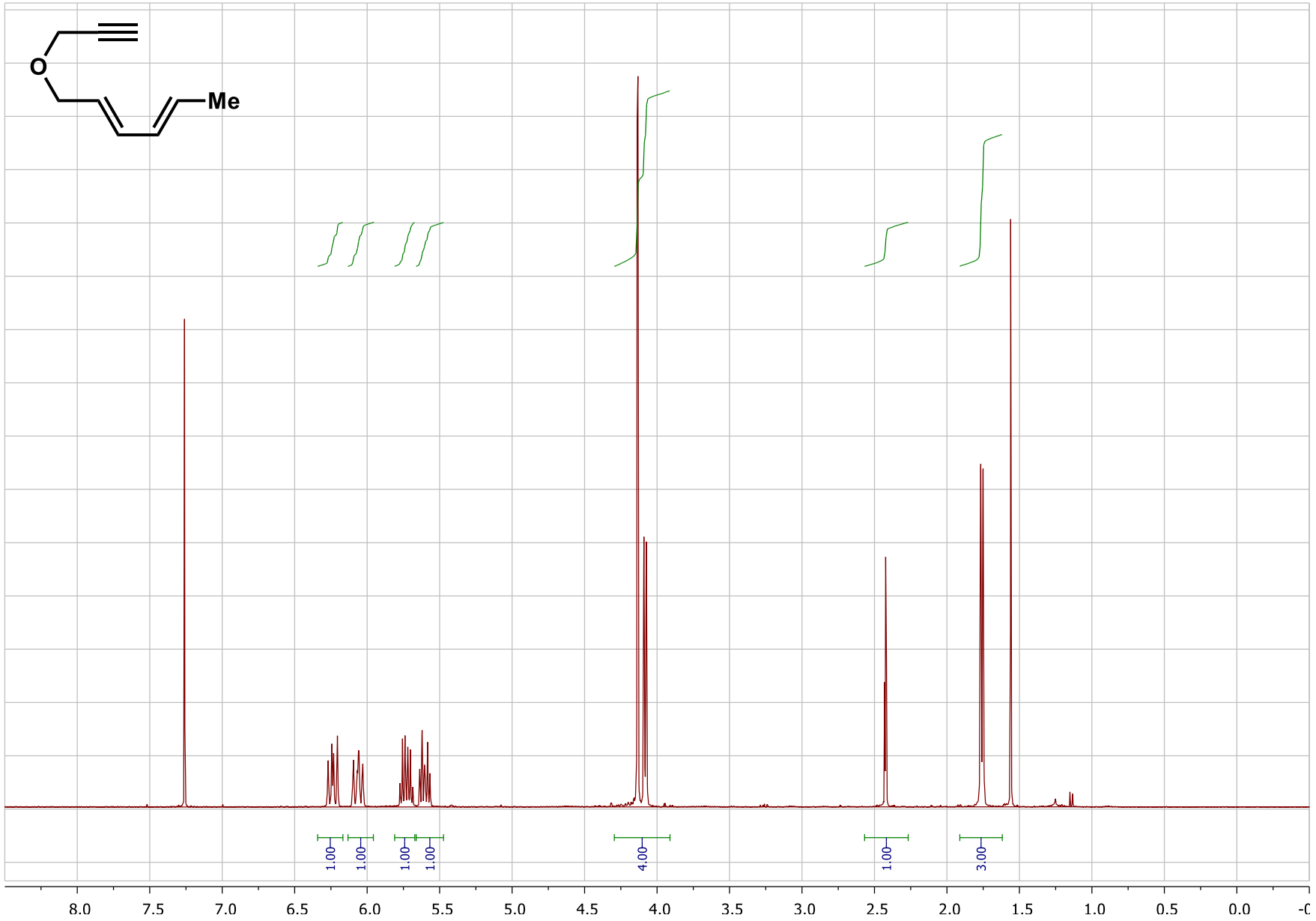
Miscellaneous compounds also synthesized (using the same method as the syntheses of the other cyclic dienynes above)

[20]: [2-(prop-2-ynyloxy)methyl]furan

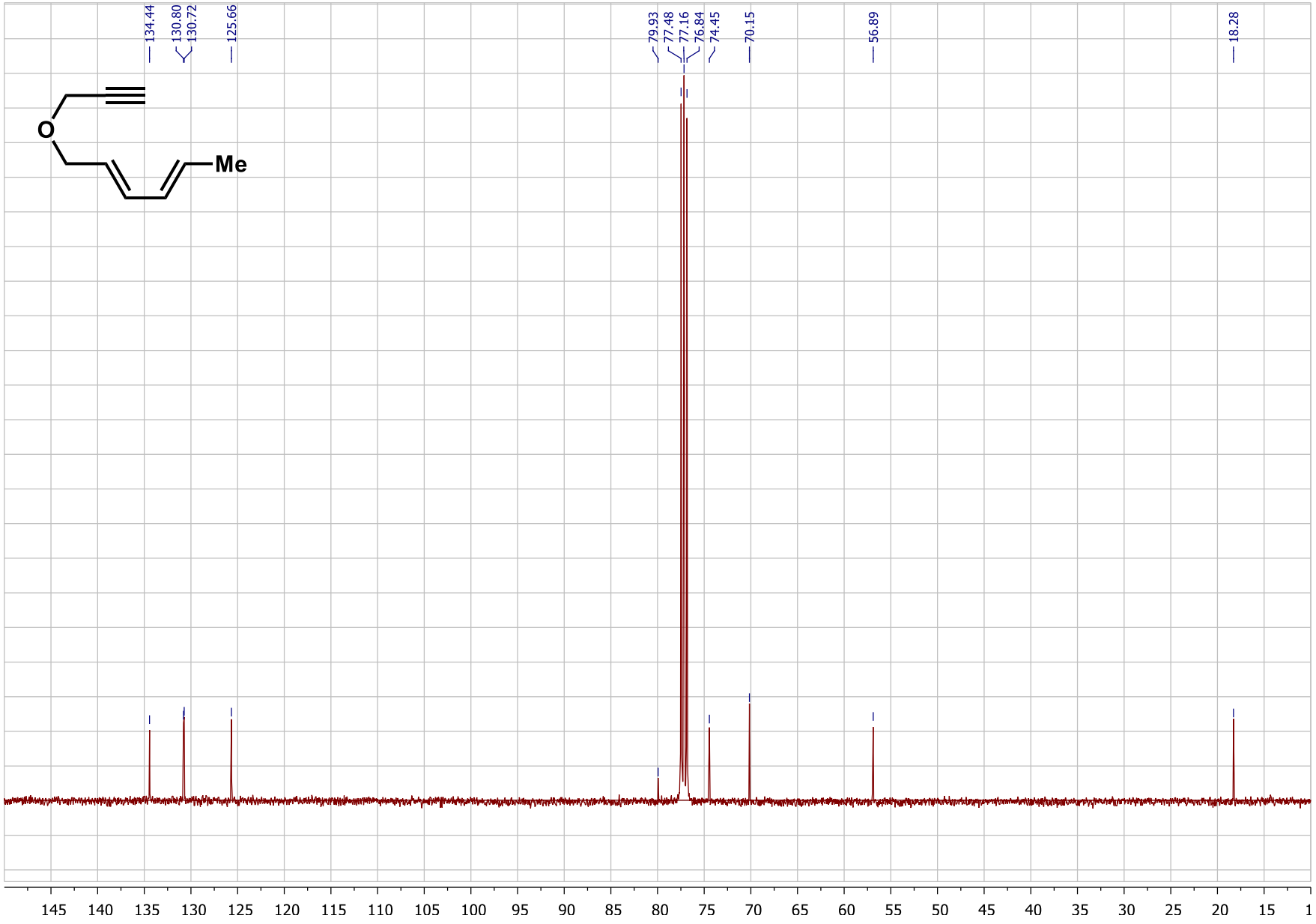


Physical state: yellow liquid, 5.5829 g (82%), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.9 Hz, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.35 (dd, *J* = 3.2, 1.9 Hz, 1H), 4.57 (s, 2H), 4.16 (d, *J* = 2.3 Hz, 2H), 2.47 (t, *J* = 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.90, 143.28, 110.48, 110.27, 79.42, 74.97, 63.17, 56.88; HRMS (*m/z*): calcd for $[C_8H_8O_2]^+$, 136.0524; found, 136.0522

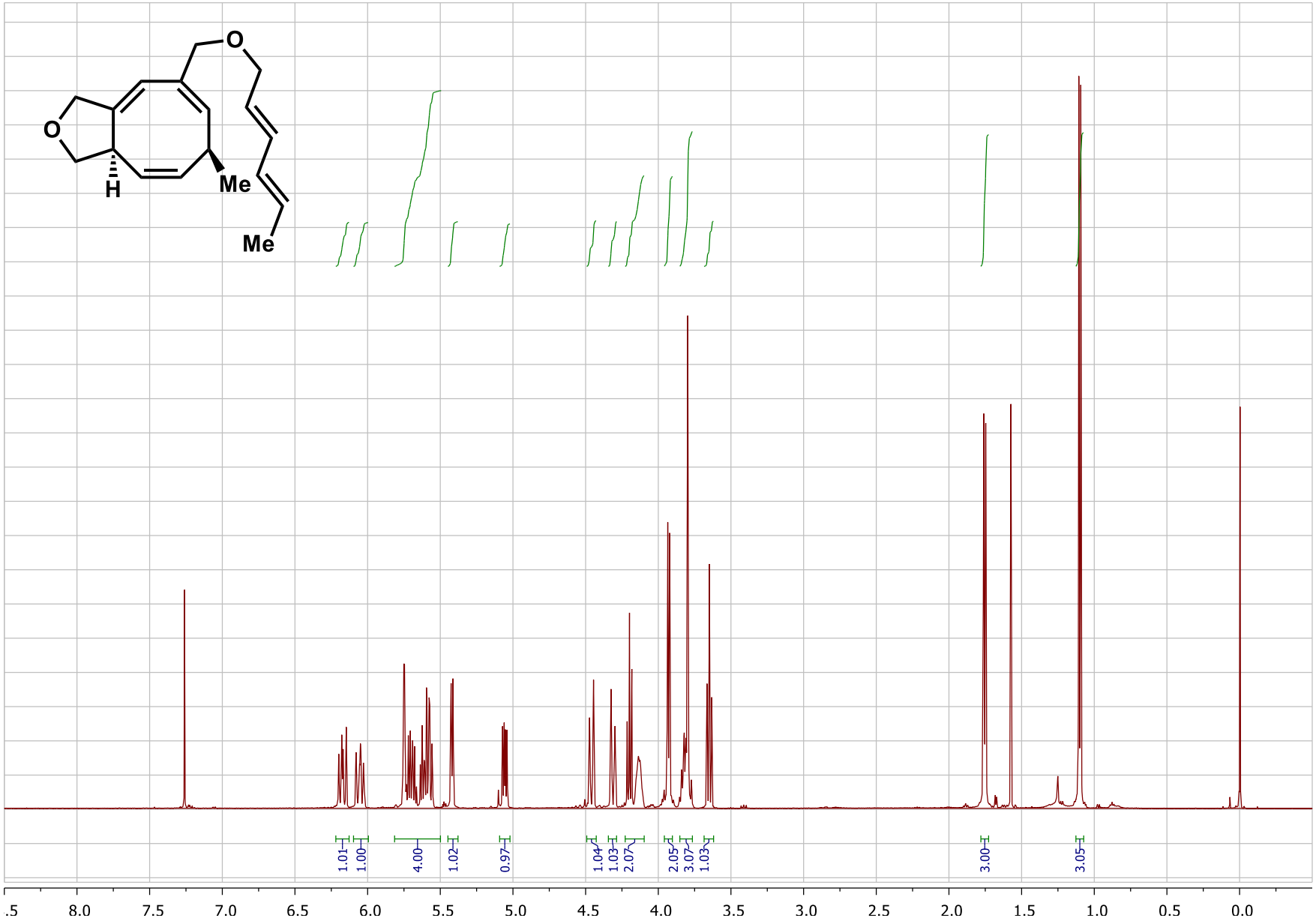
[1]: (^{1}H NMR, 400 MHz, $CDCl_3$)



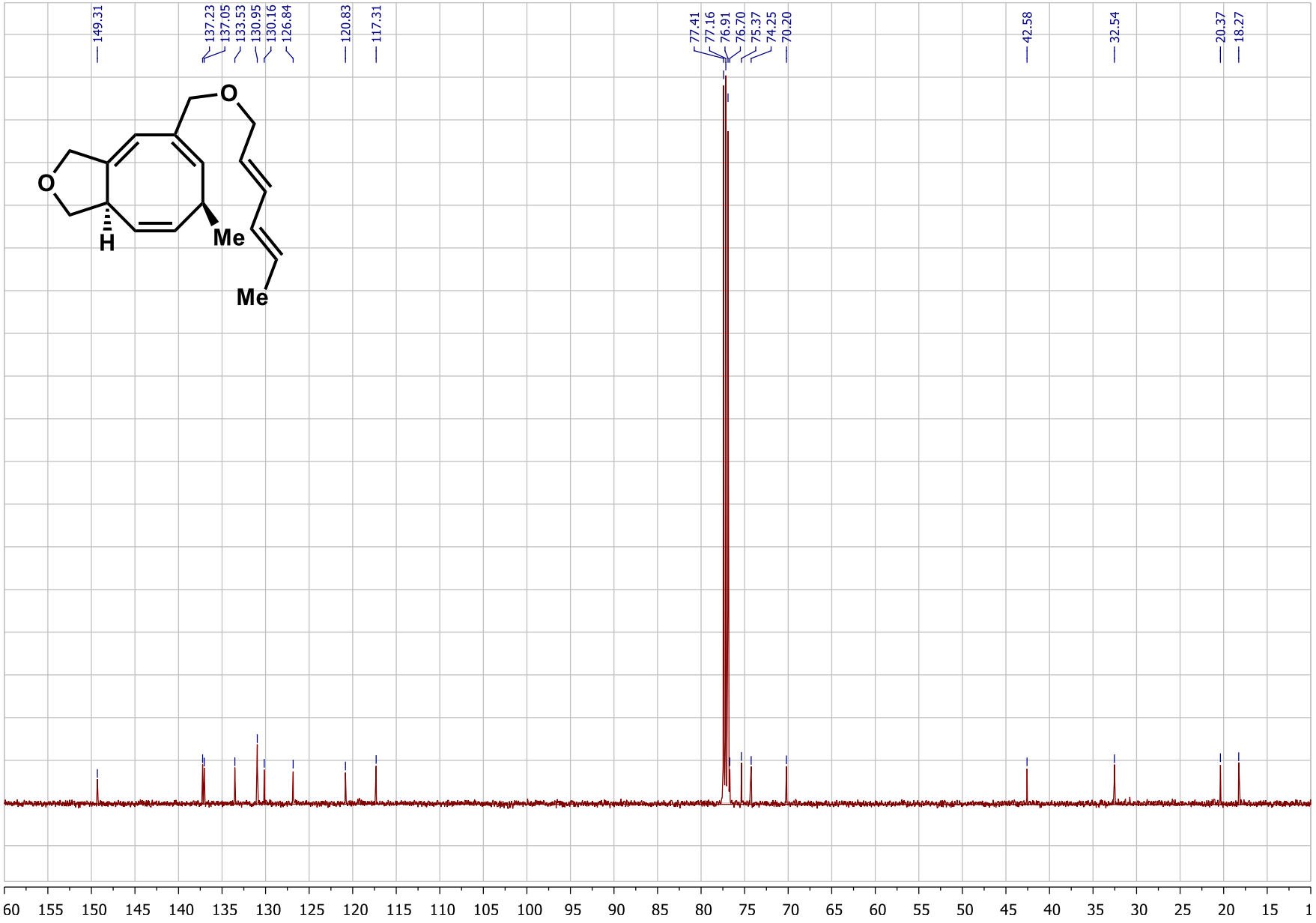
[1]: (^{1}H NMR, 101 MHz, $CDCl_3$)



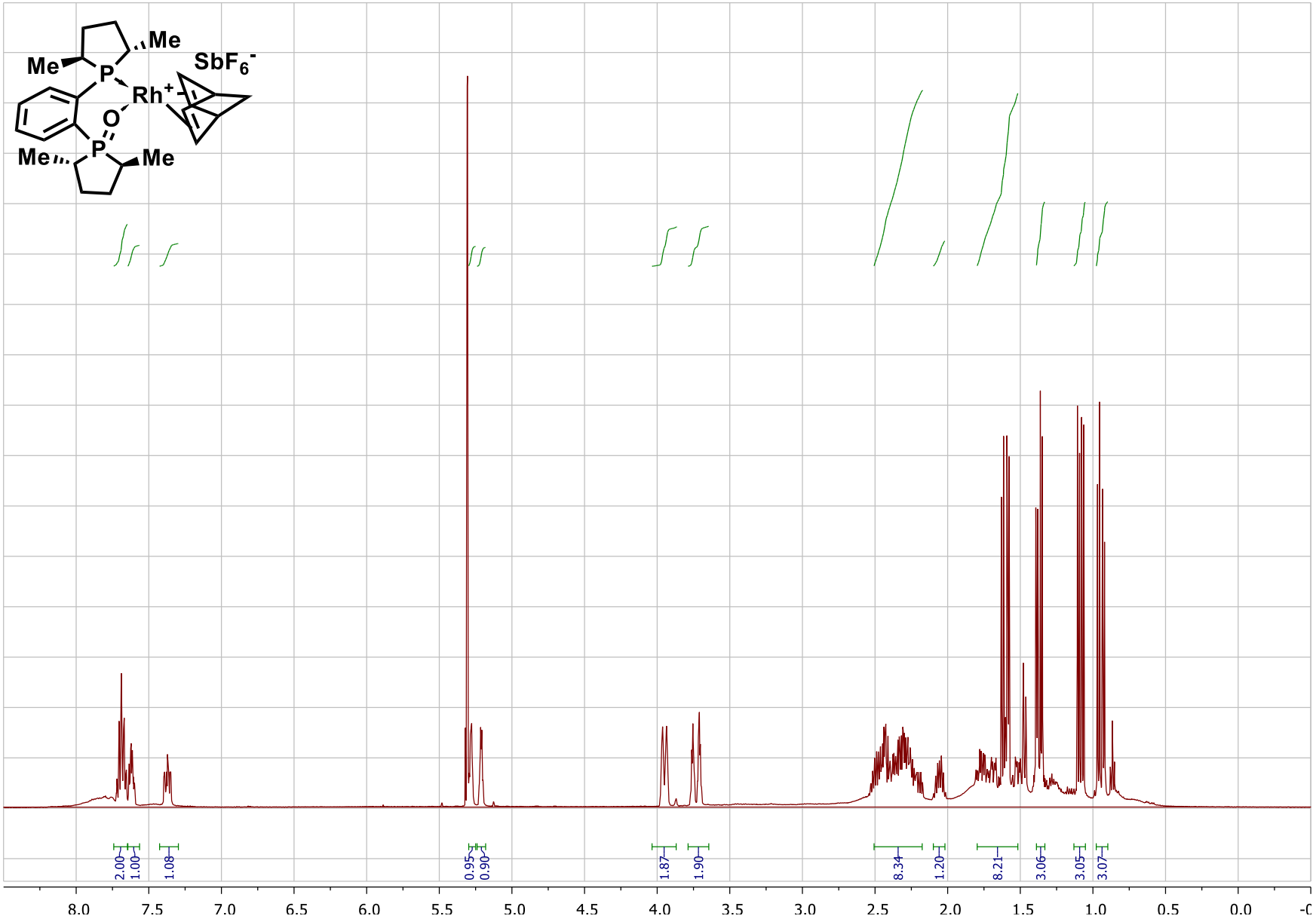
[2]: (^{1}H NMR, 500 MHz, $CDCl_3$)



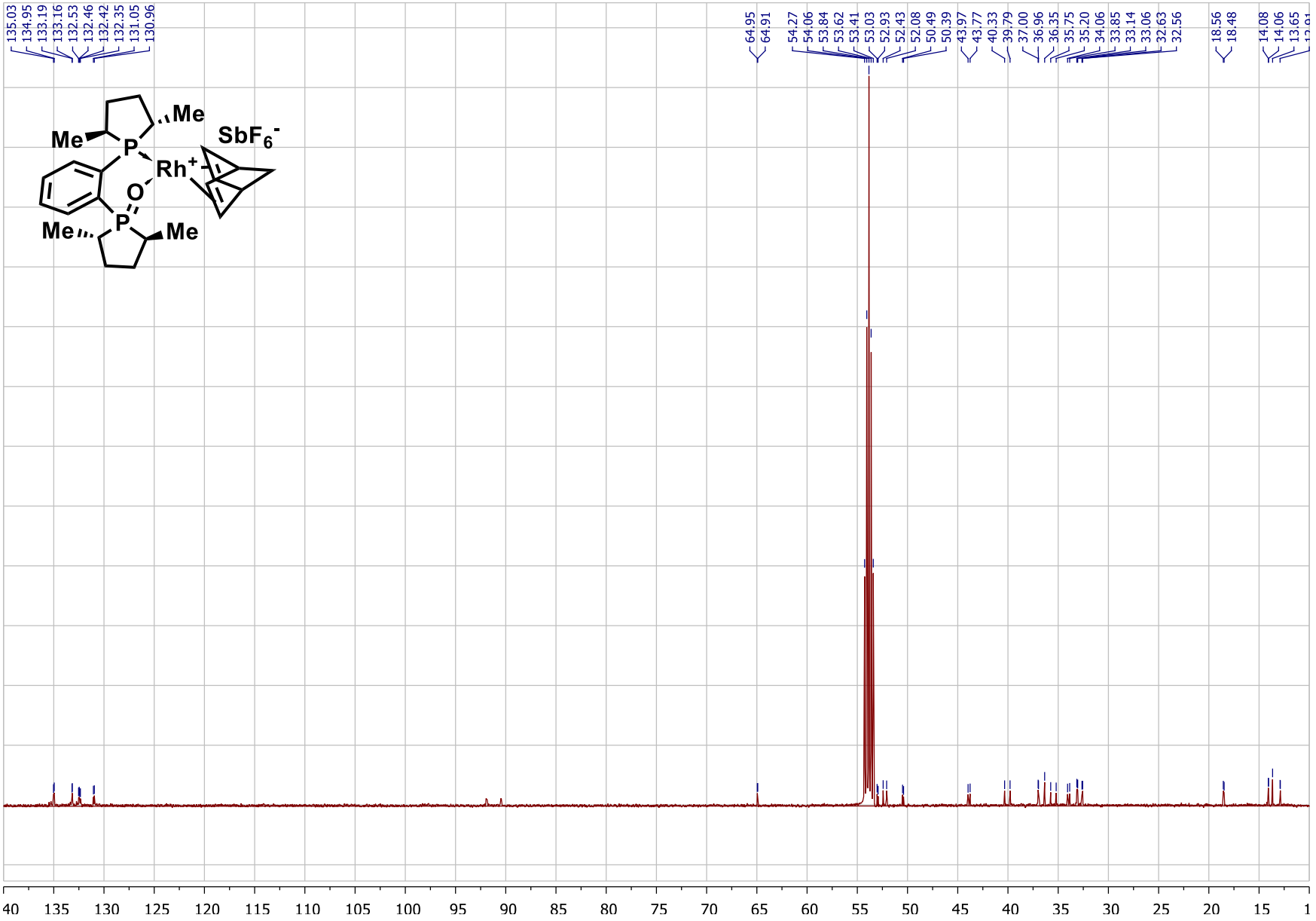
[2]: (^{13}C NMR, 126 MHz, $CDCl_3$)



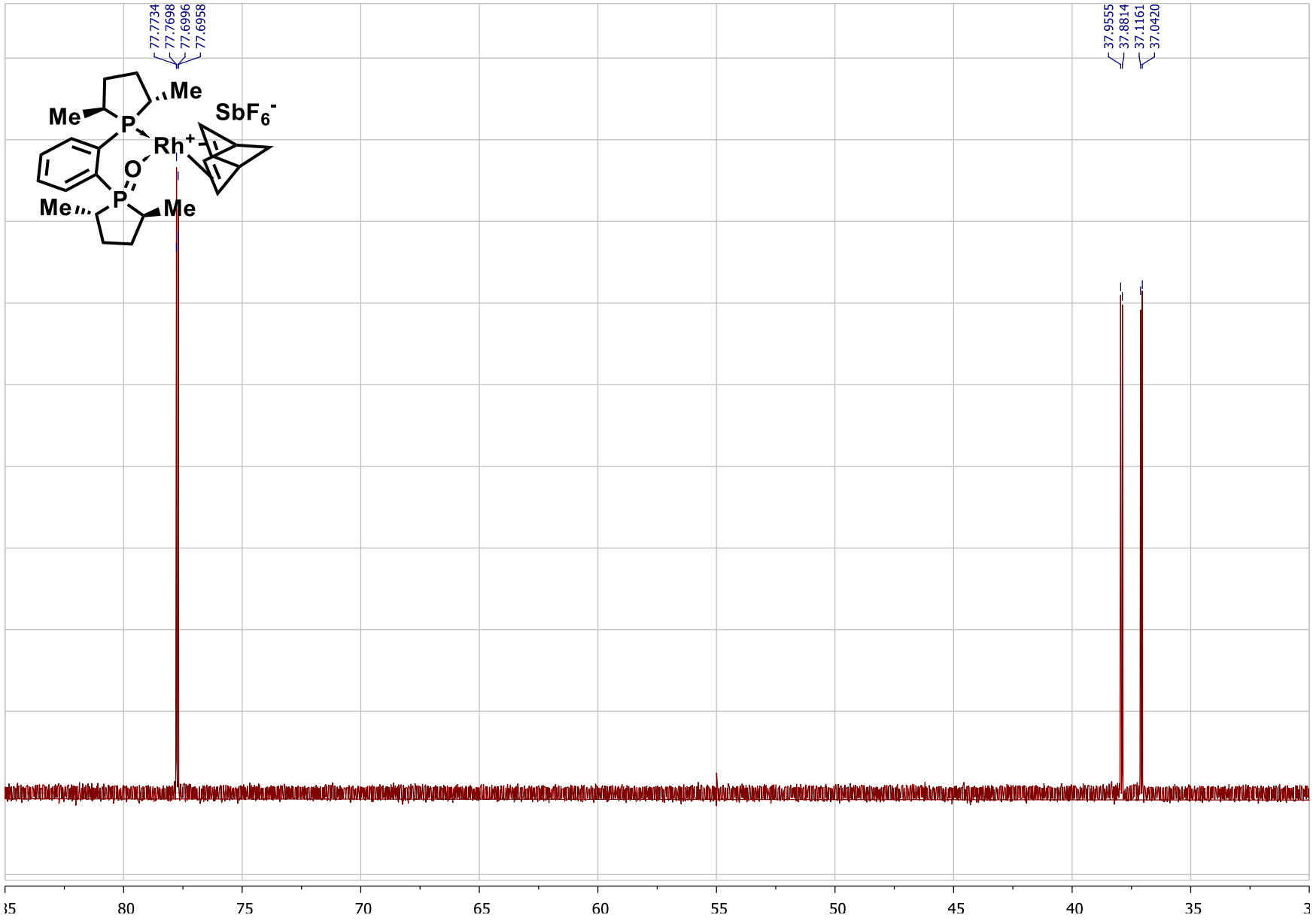
[3]: (^{1}H NMR, 500 MHz, CD_2Cl_2)



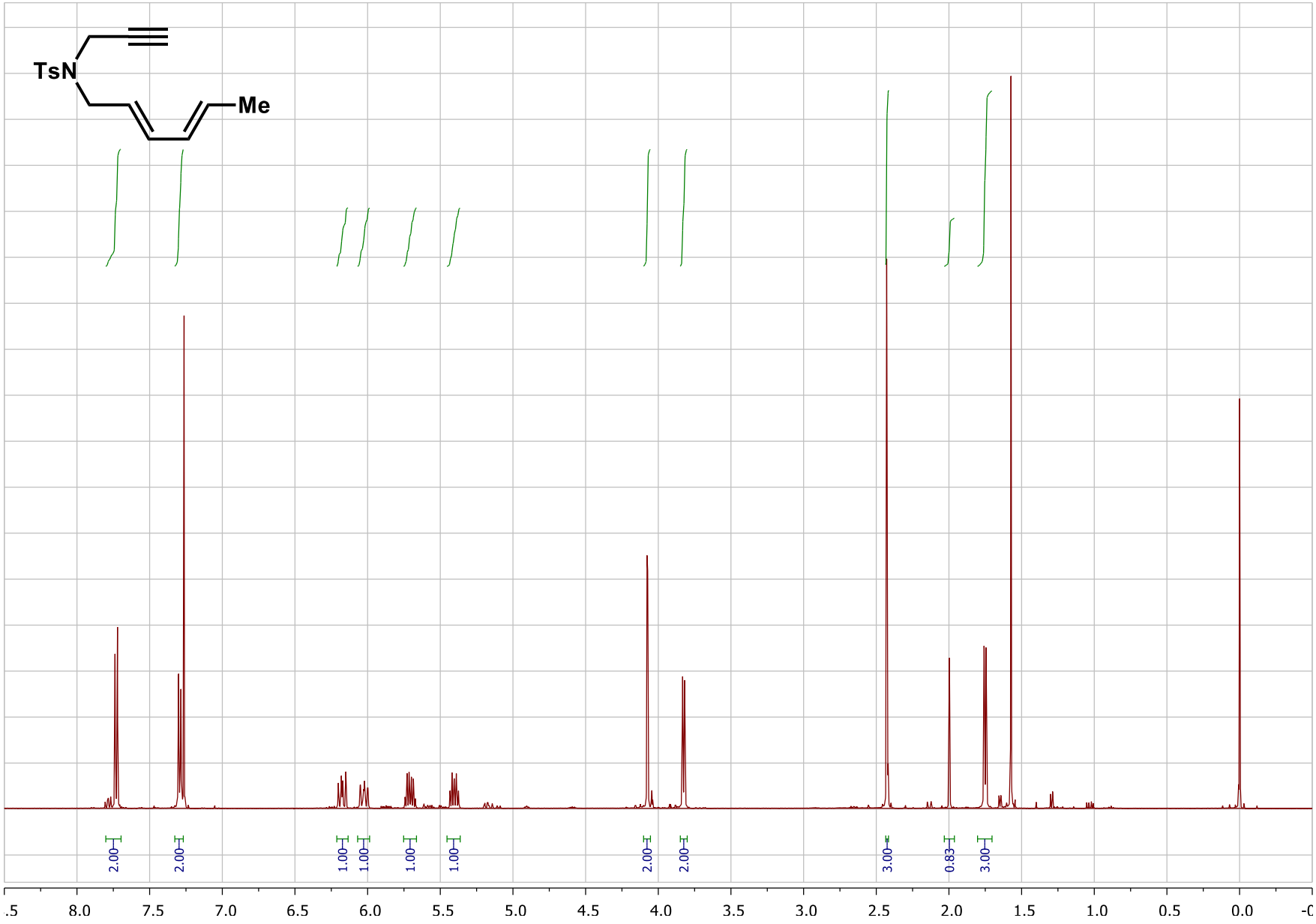
[3]: (^{13}C NMR, 126 MHz, CD_2Cl_2)



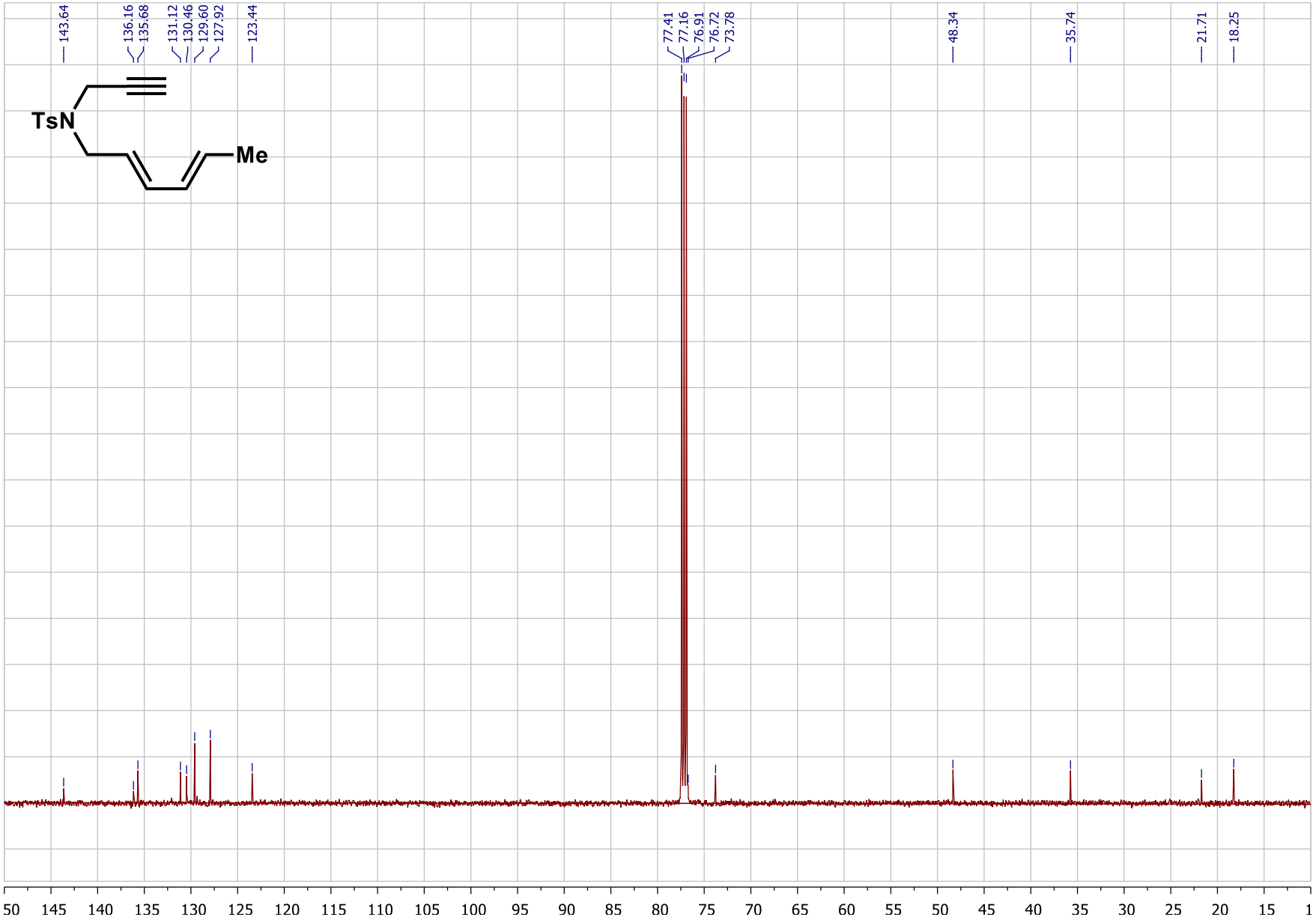
[3]: (^{31}P NMR, 202 MHz, CD_2Cl_2)



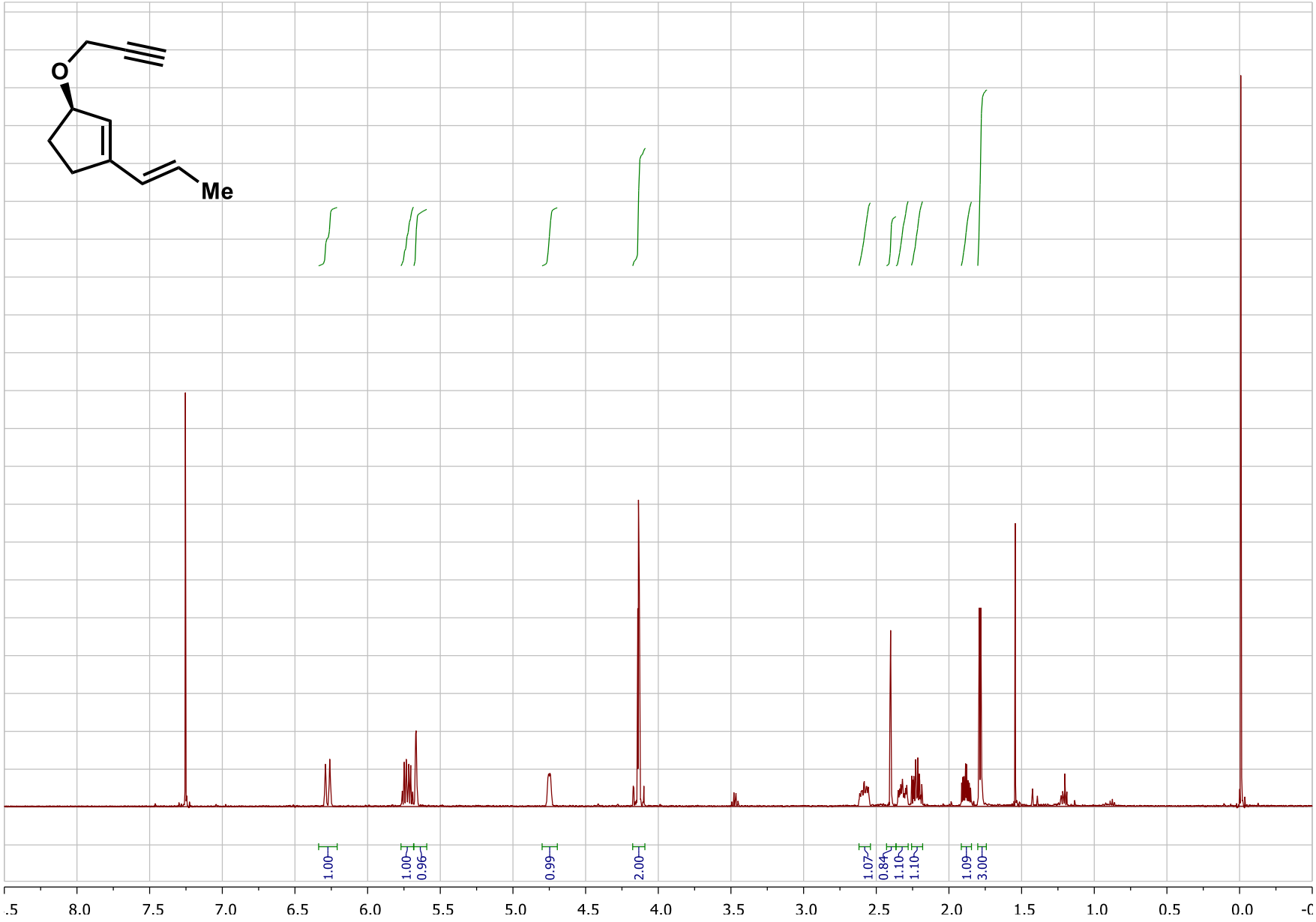
[4]: (^{1}H NMR, 500 MHz, $CDCl_3$)



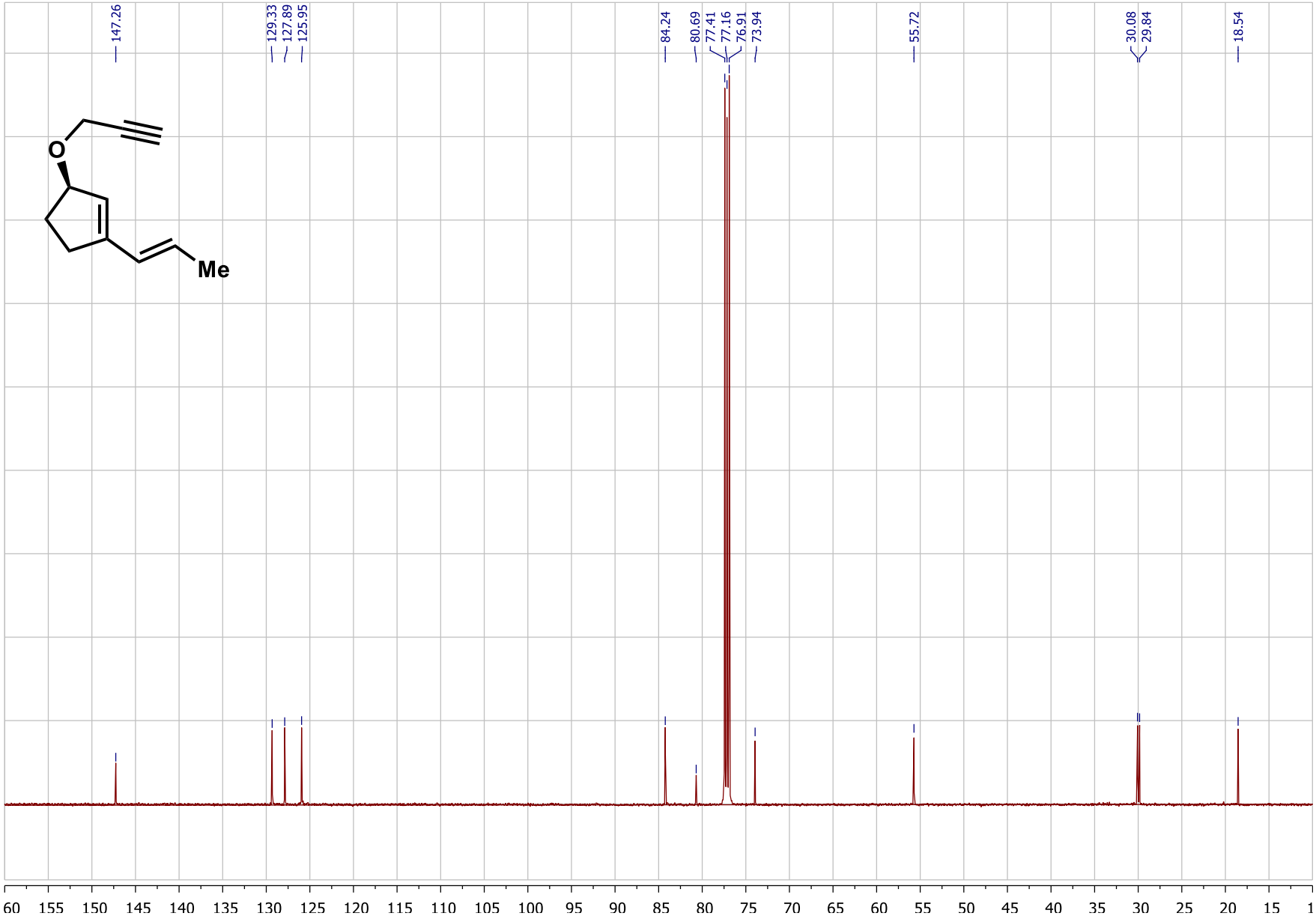
[4]: (^{13}C NMR, 126 MHz, $CDCl_3$)



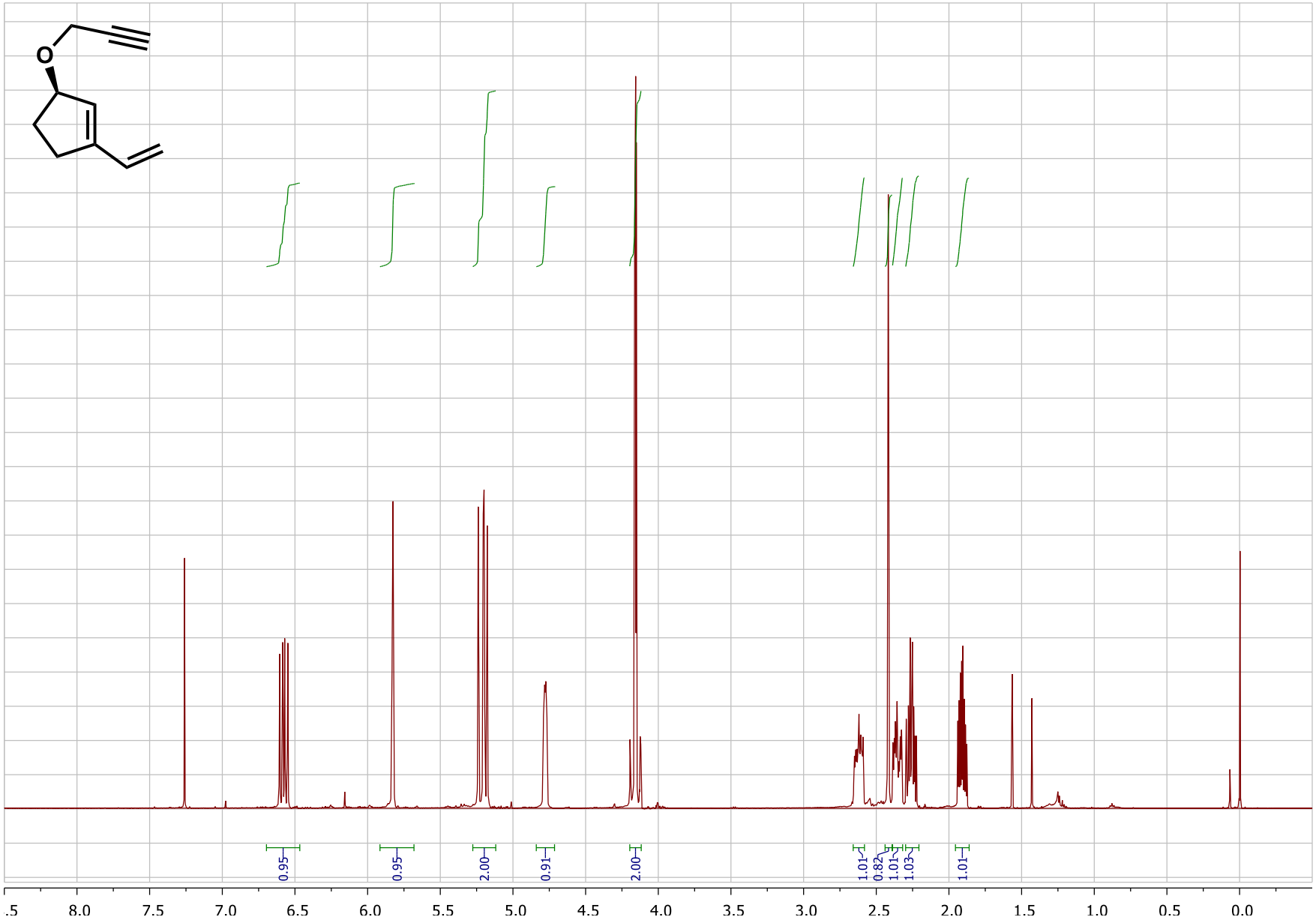
[06]: (^{1}H NMR, 500 MHz, $CDCl_3$)



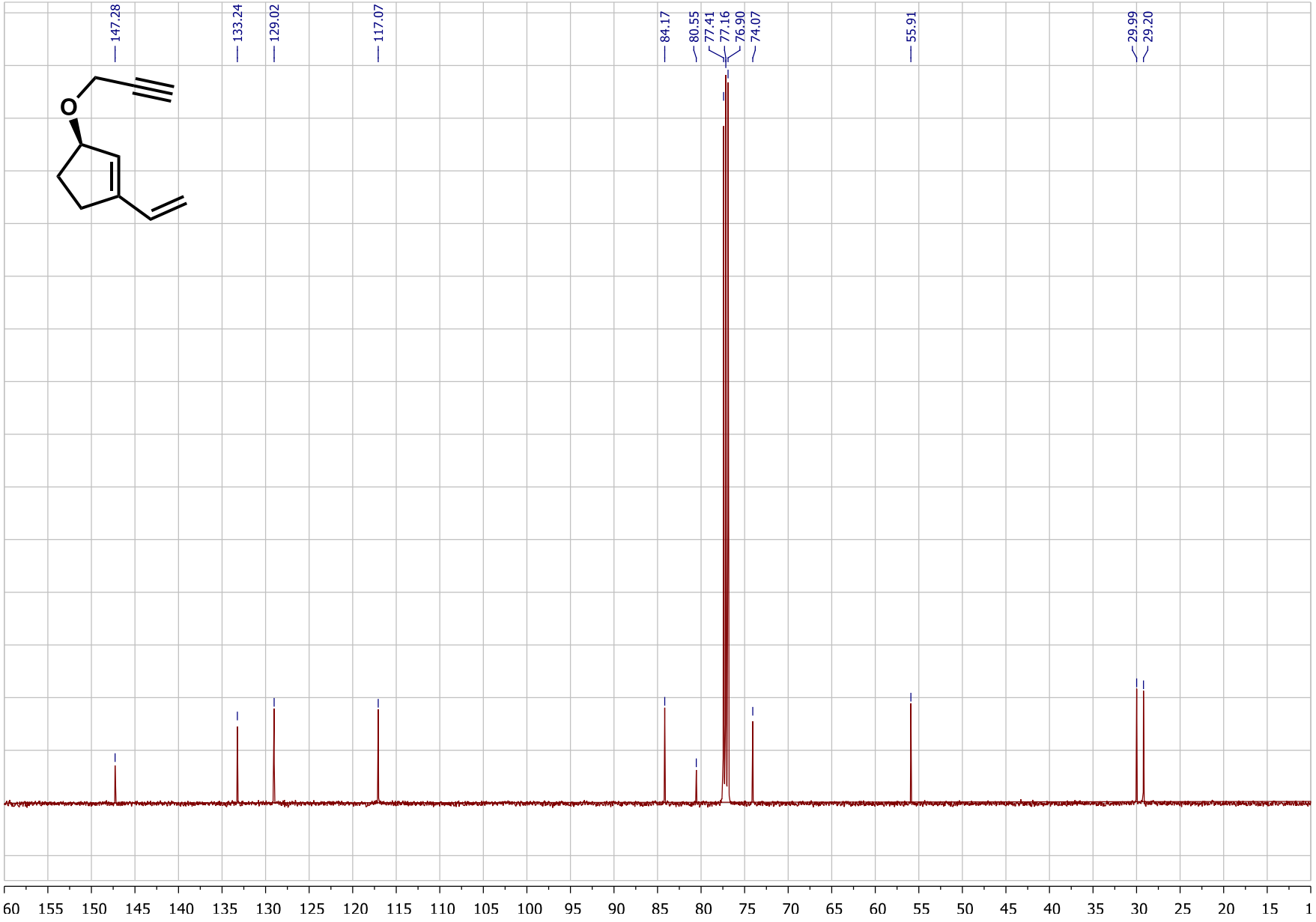
[06]: (^{13}C NMR, 126 MHz, $CDCl_3$)



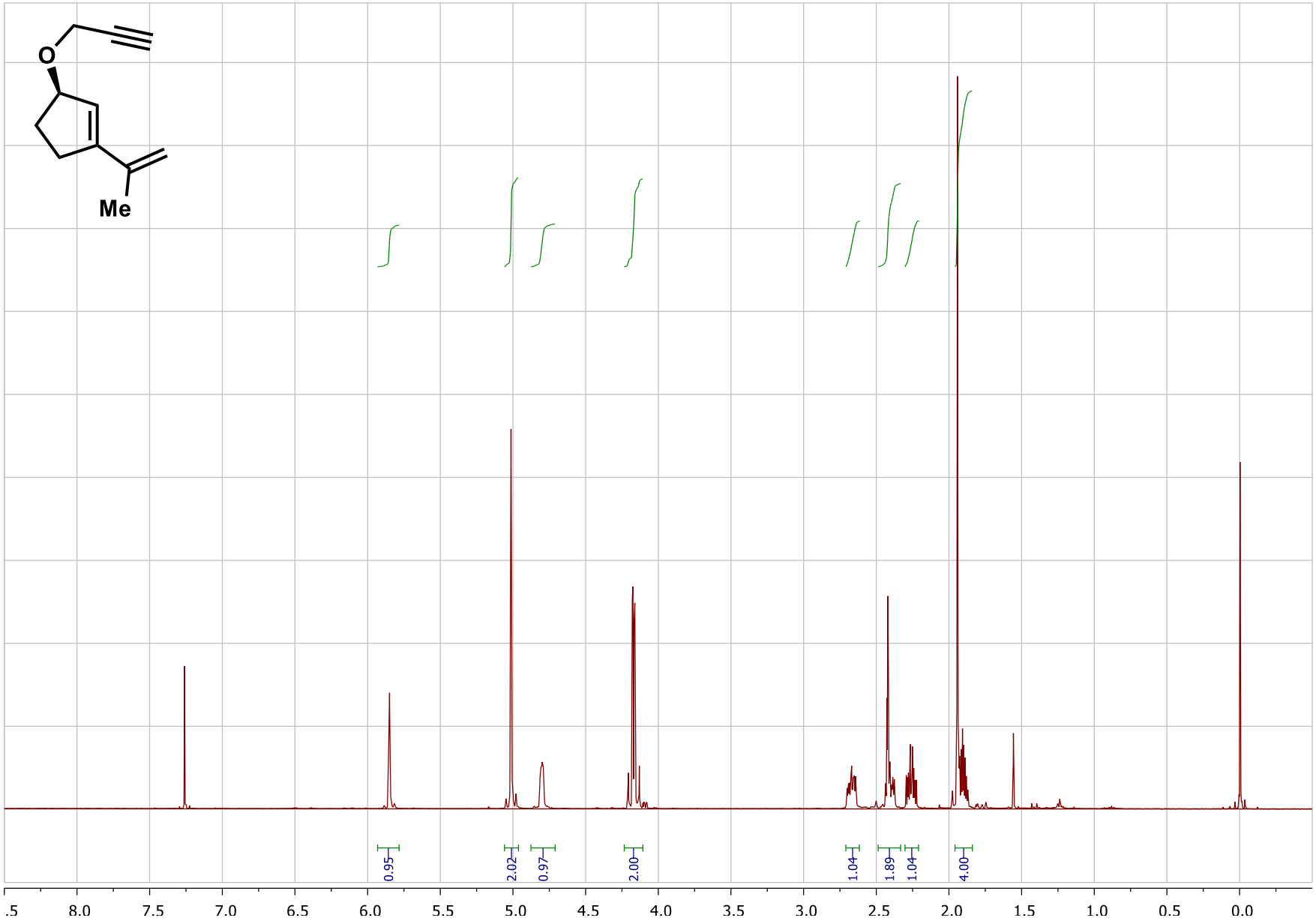
[6]: (^{1}H NMR, 500 MHz, $CDCl_3$)



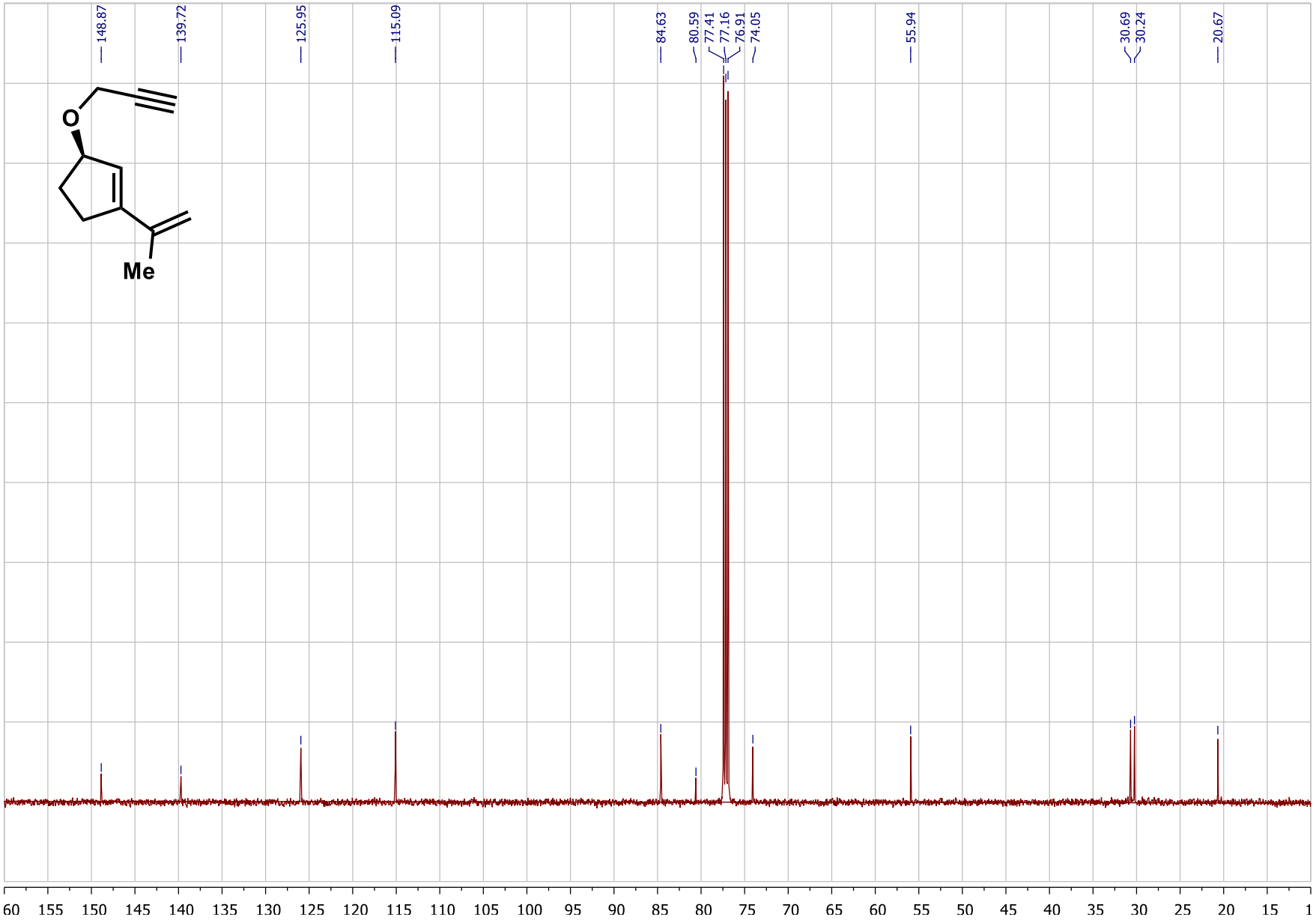
[6]: (^{13}C NMR, 126 MHz, $CDCl_3$)



[07]: (^{1}H NMR, 500 MHz, $CDCl_3$)

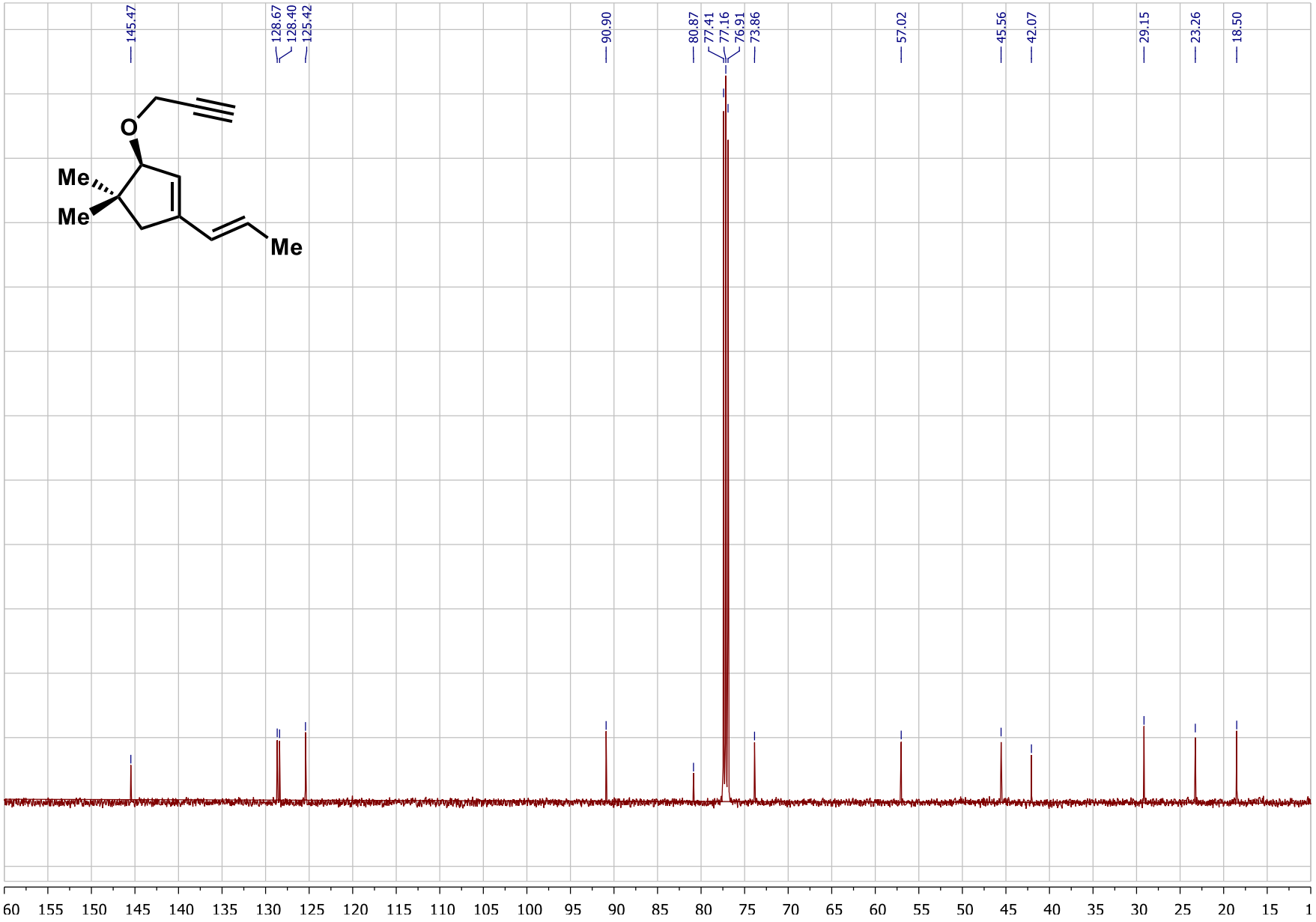


[07]: (^{13}C NMR, 126 MHz, $CDCl_3$)

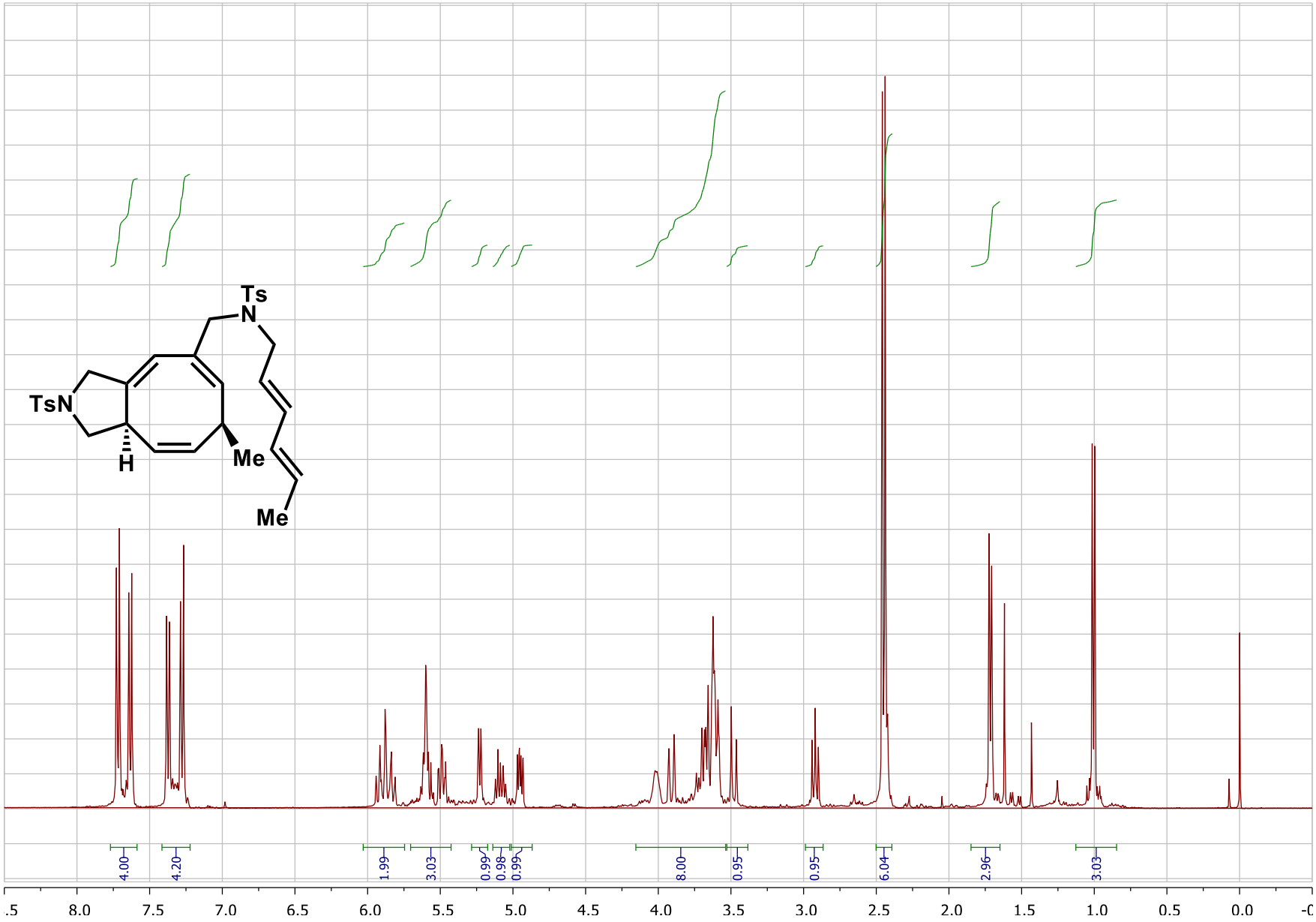


[08]: (^{1}H NMR, 500 MHz, $CDCl_3$)

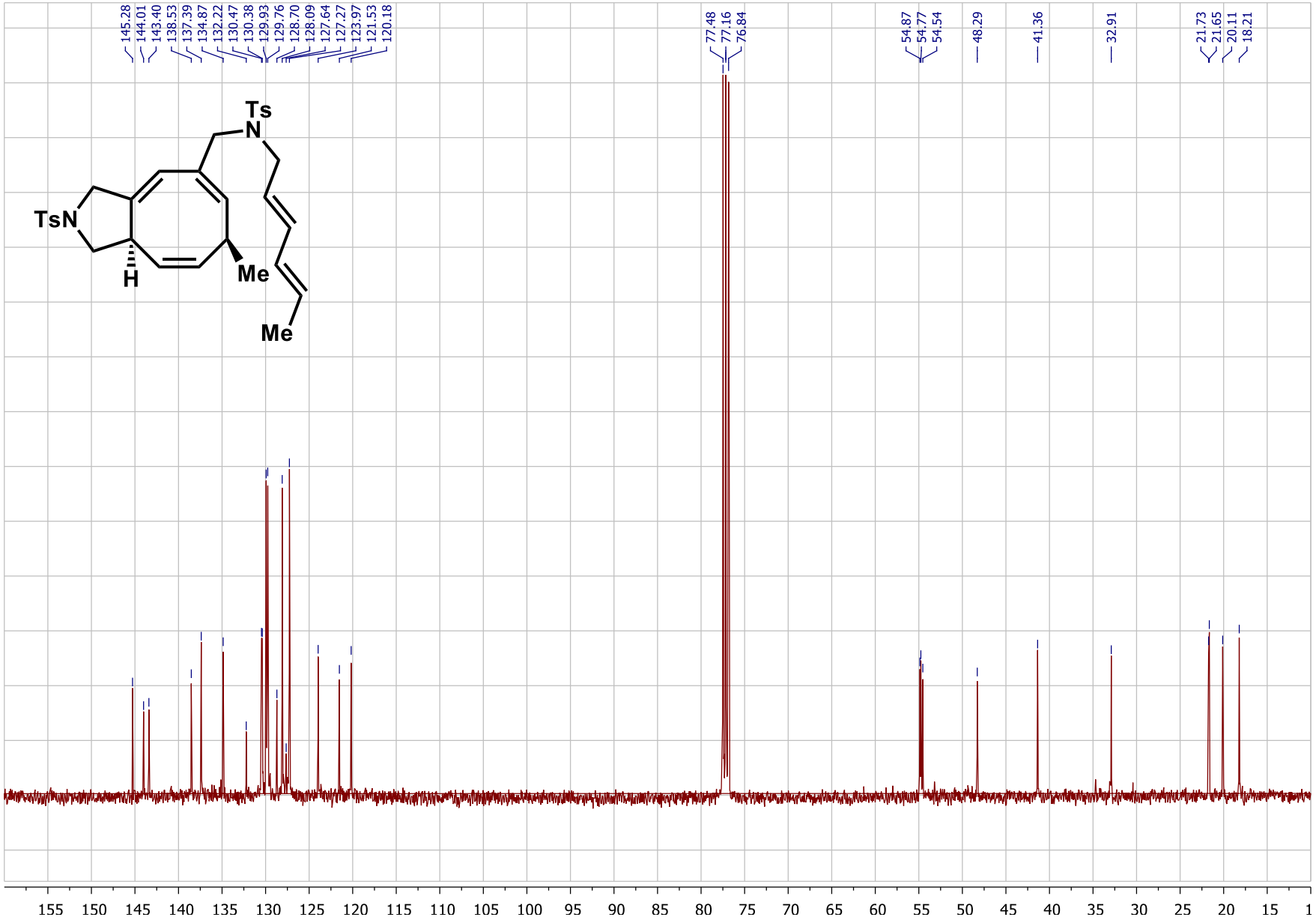
[08]: (^{13}C NMR, 126 MHz, $CDCl_3$)



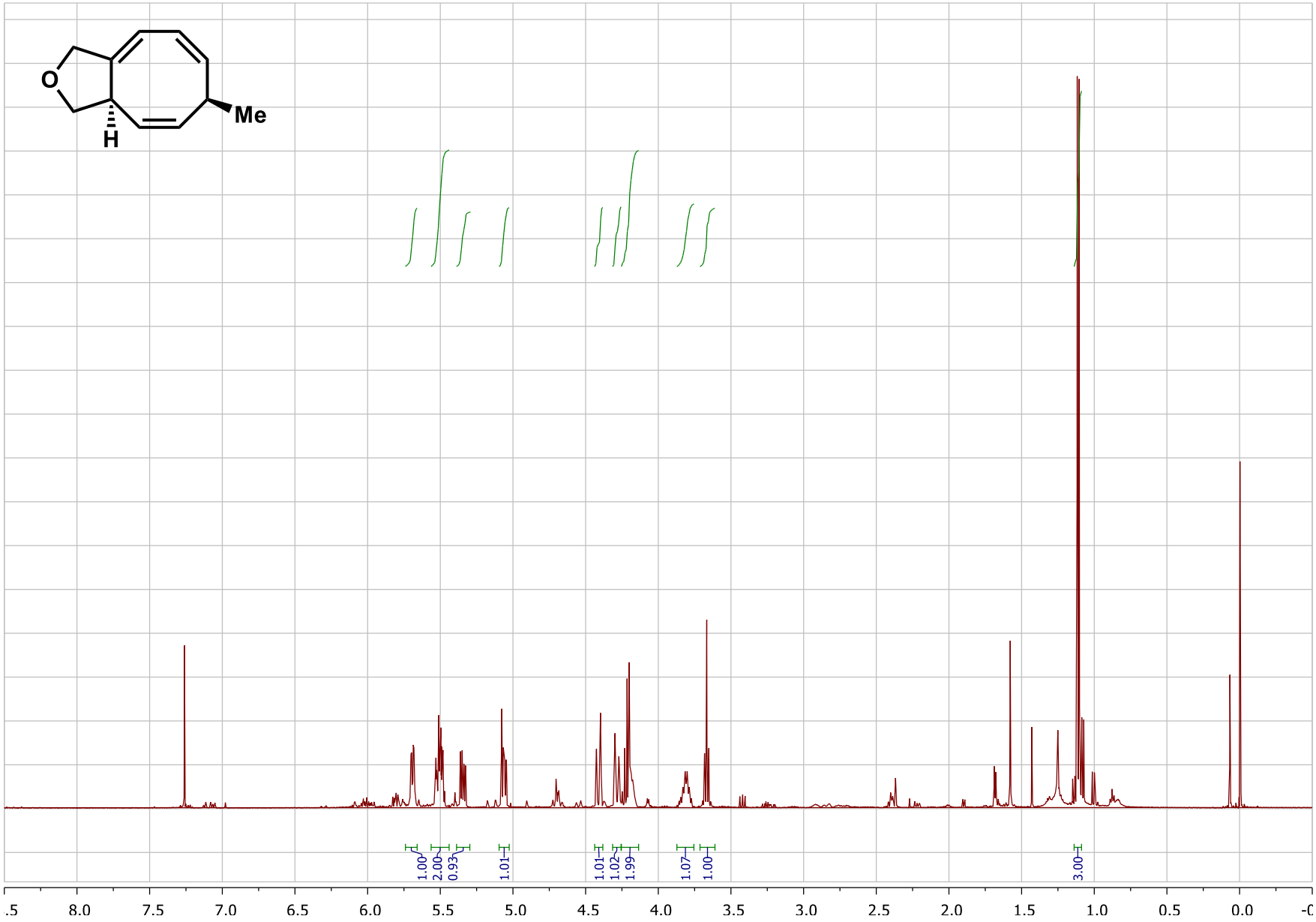
[09]: (^{1}H NMR, 400 MHz, $CDCl_3$)



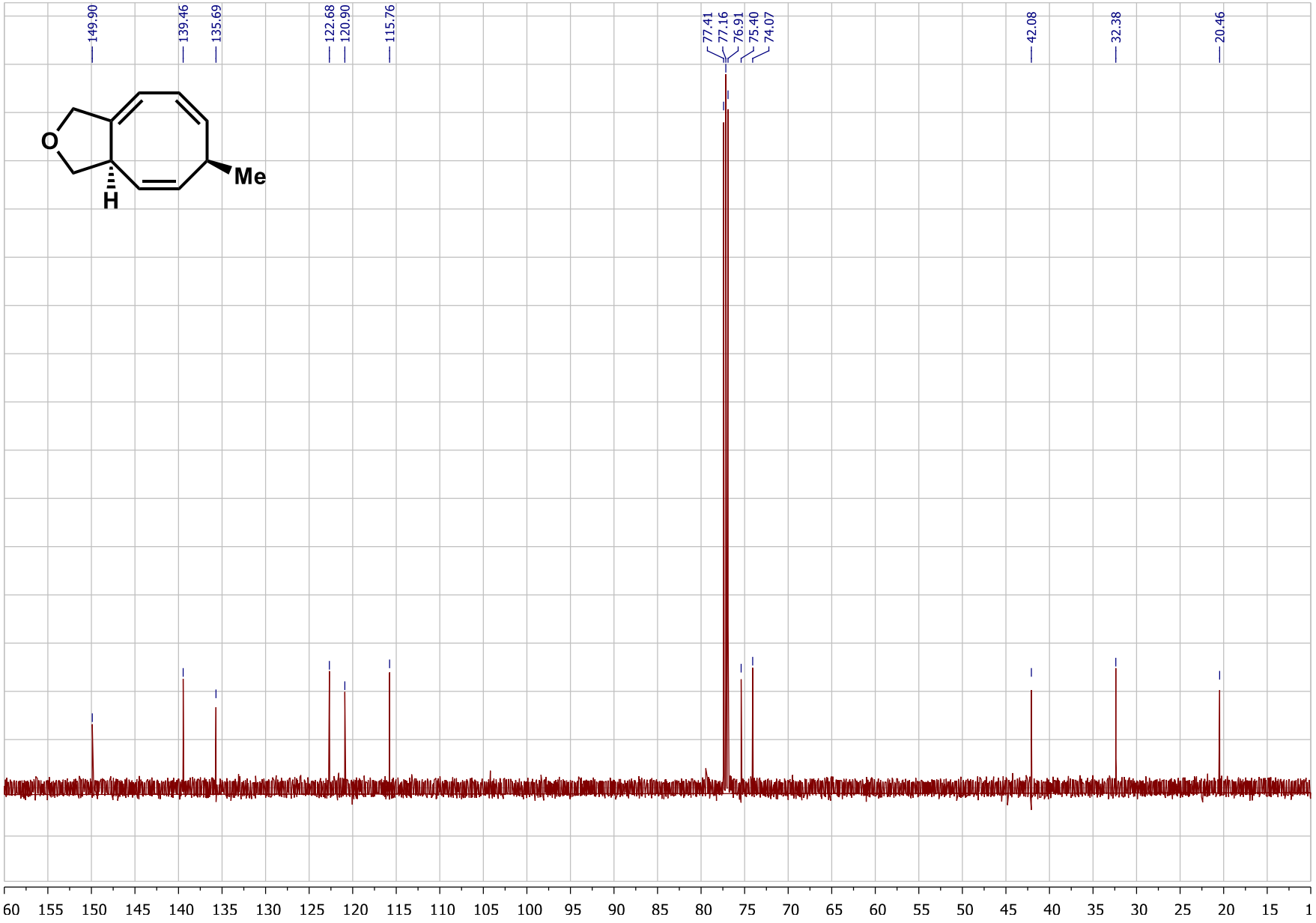
[09]: (^{13}C NMR, 101 MHz, $CDCl_3$)



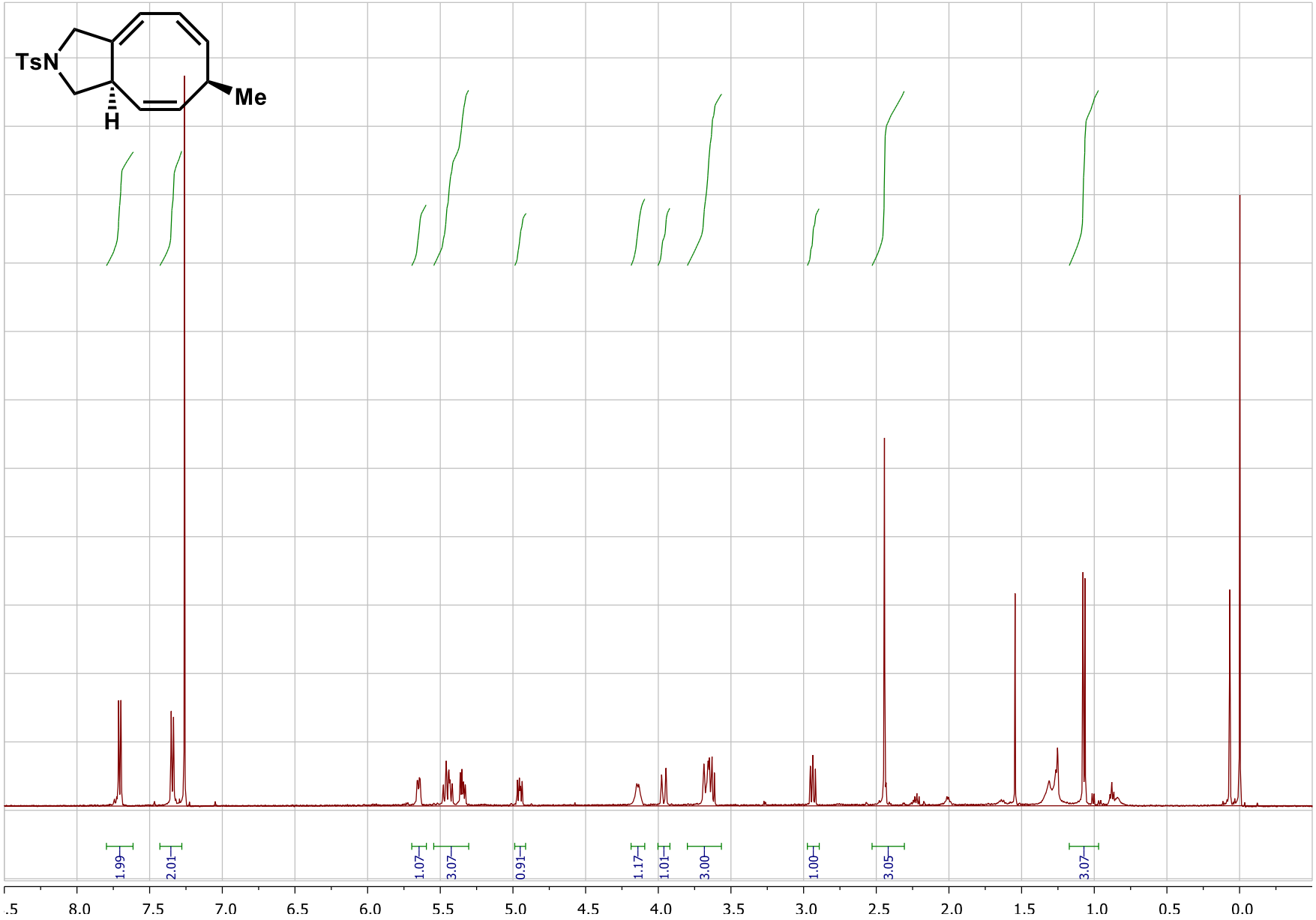
[10]: (^{1}H NMR, 500 MHz, $CDCl_3$)



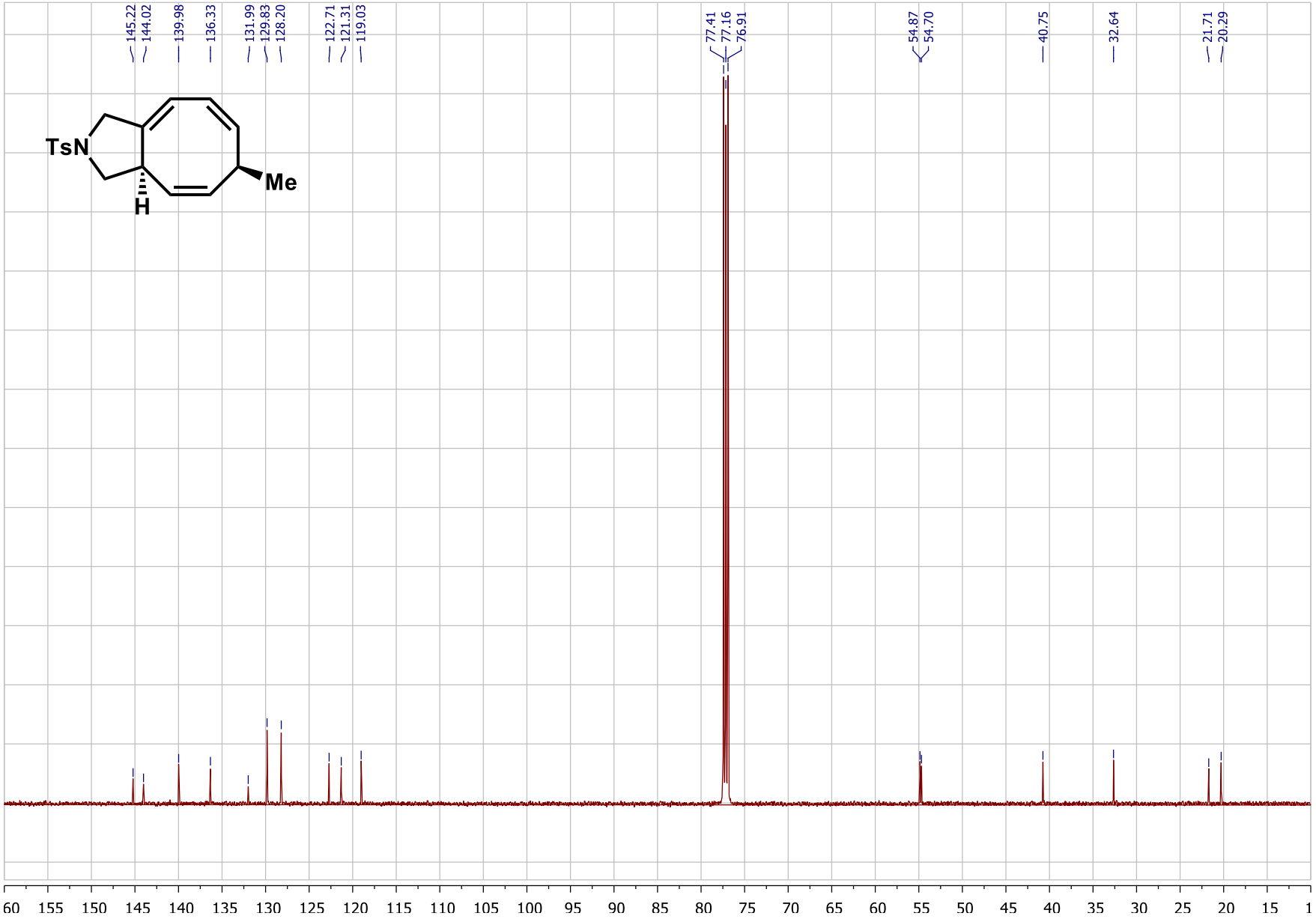
[10]: (^{13}C NMR, 126 MHz, $CDCl_3$)



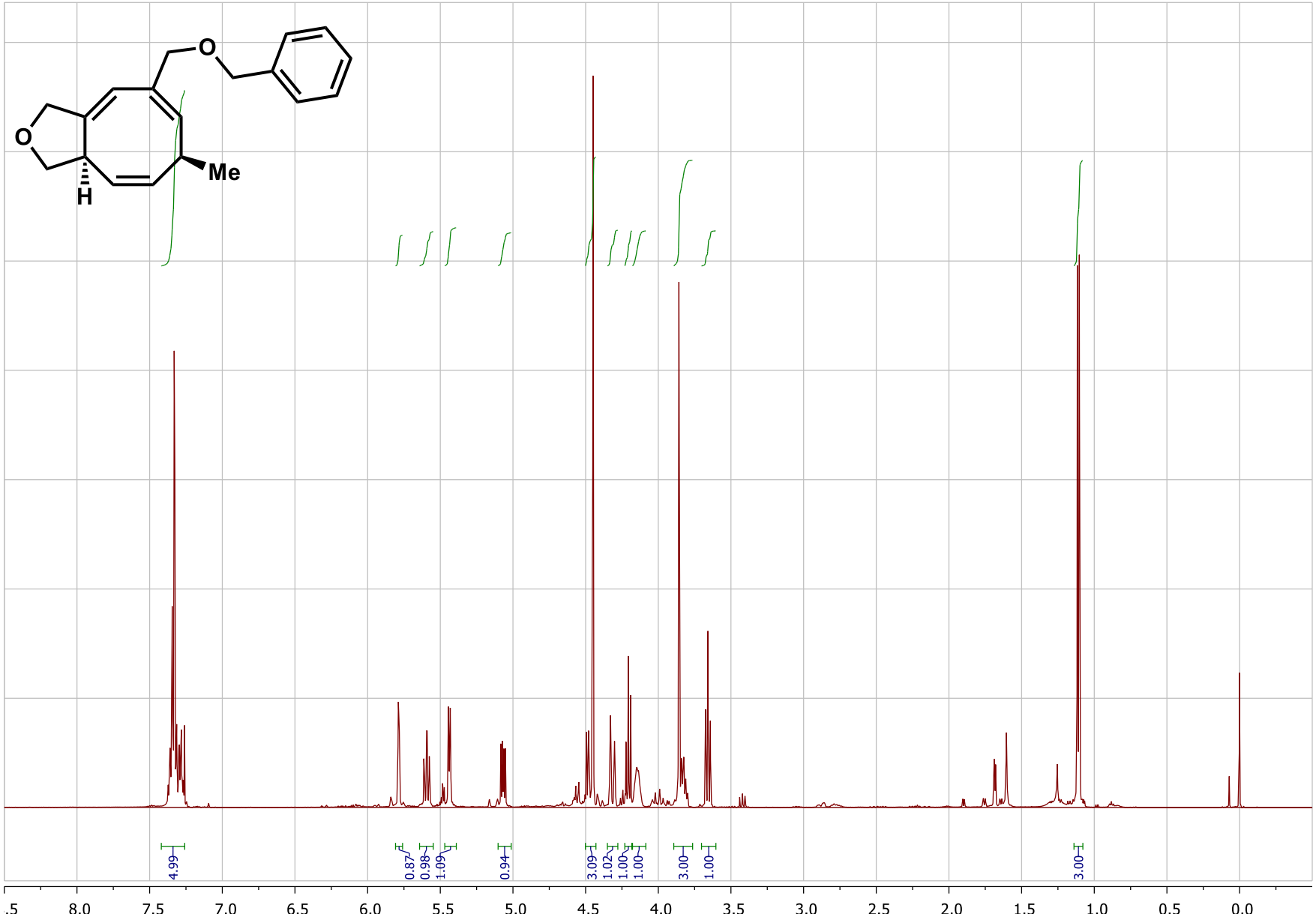
[11]: (^{1}H NMR, 500 MHz, $CDCl_3$)



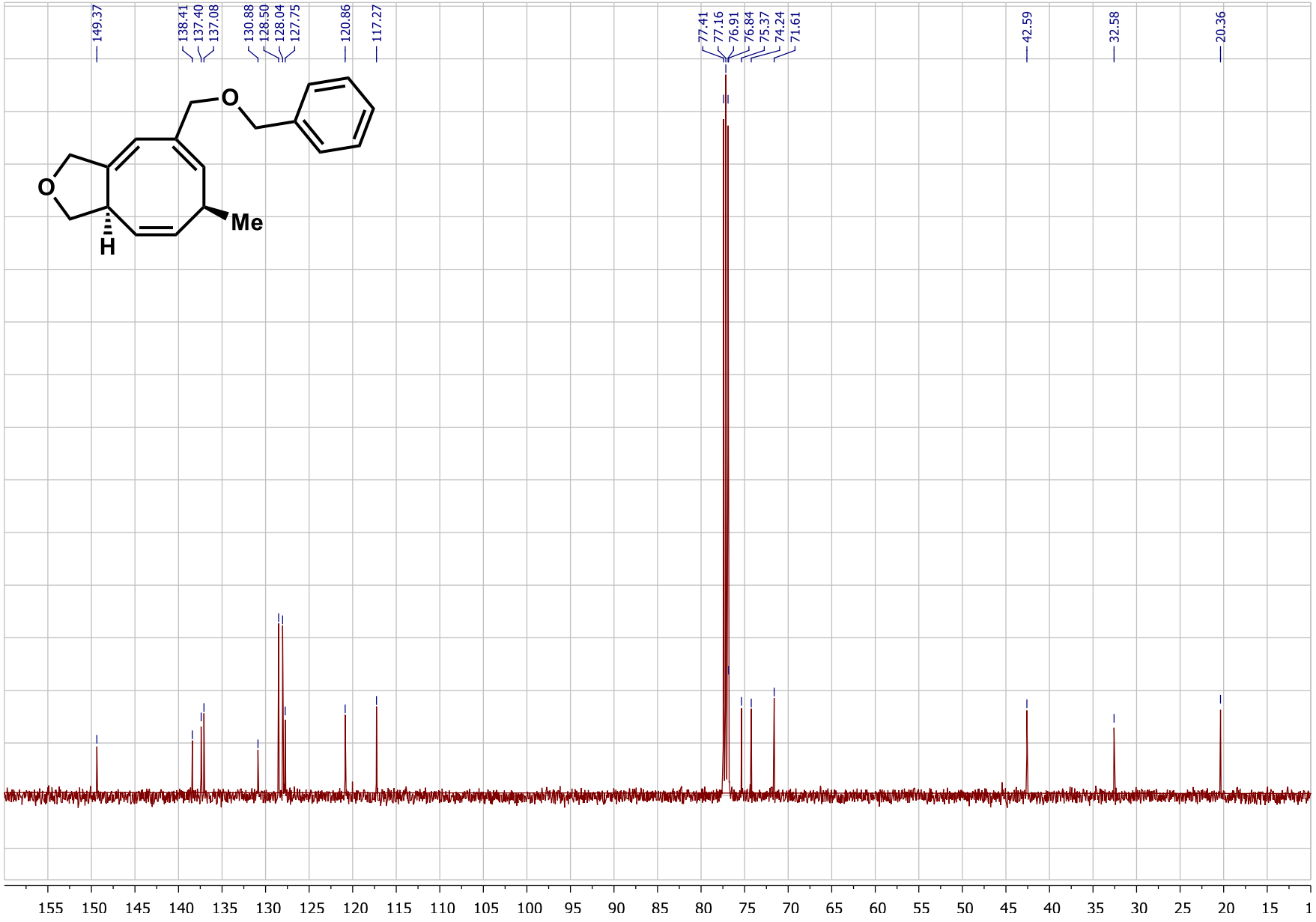
[11]: (^{13}C NMR, 126 MHz, $CDCl_3$)



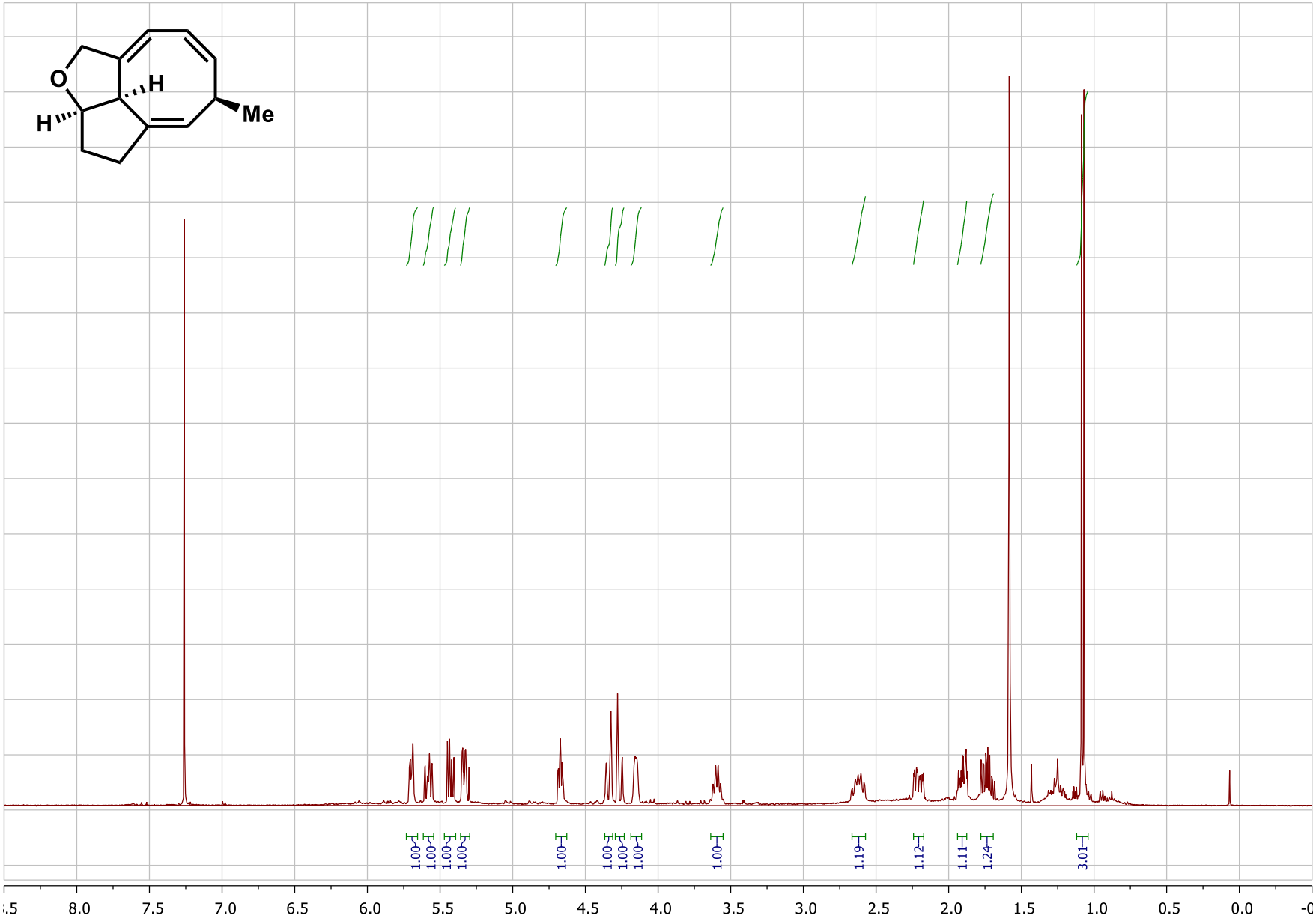
[12]: (^{1}H NMR, 500 MHz, $CDCl_3$)



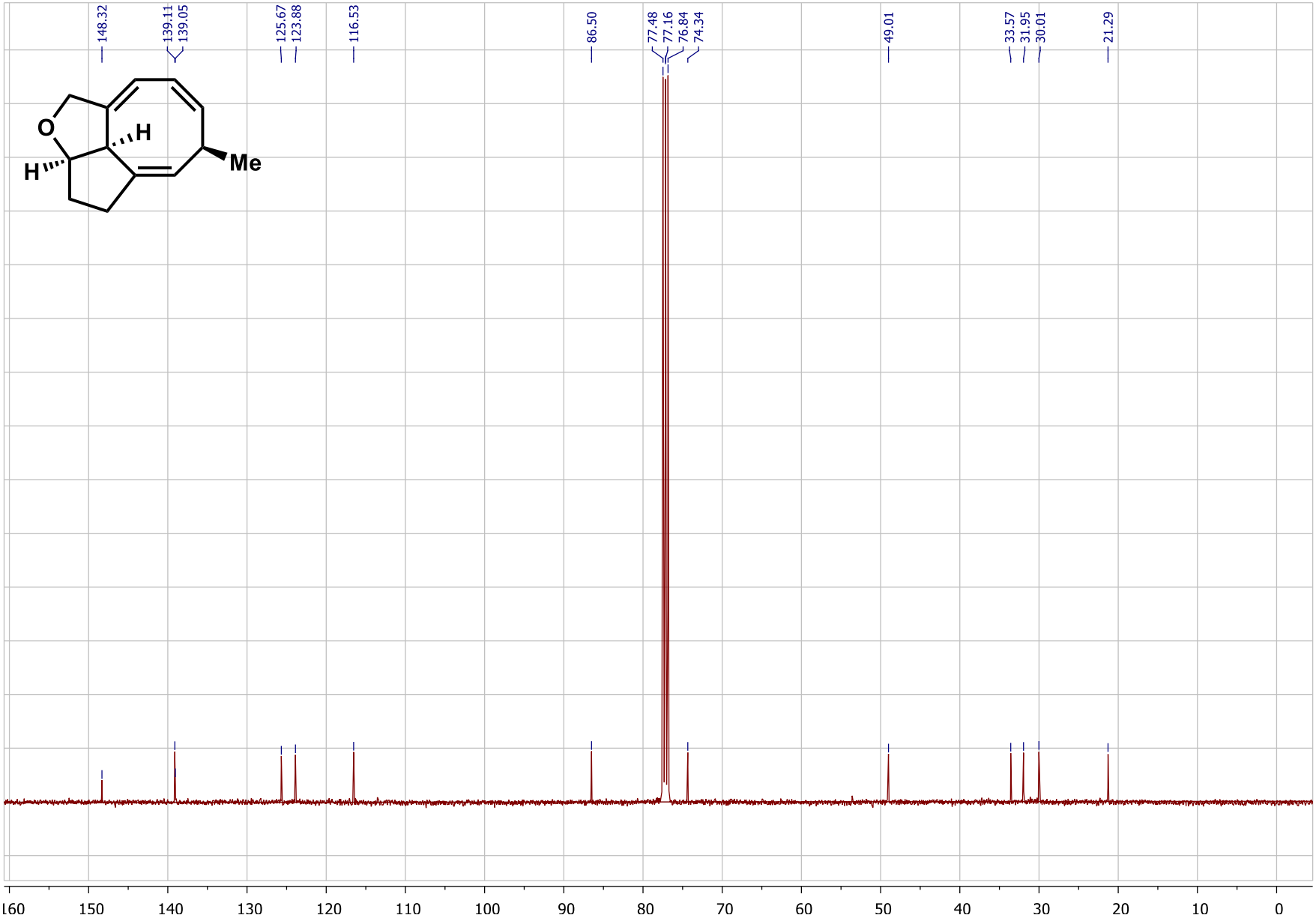
[12]: (^{13}C NMR, 126 MHz, $CDCl_3$)



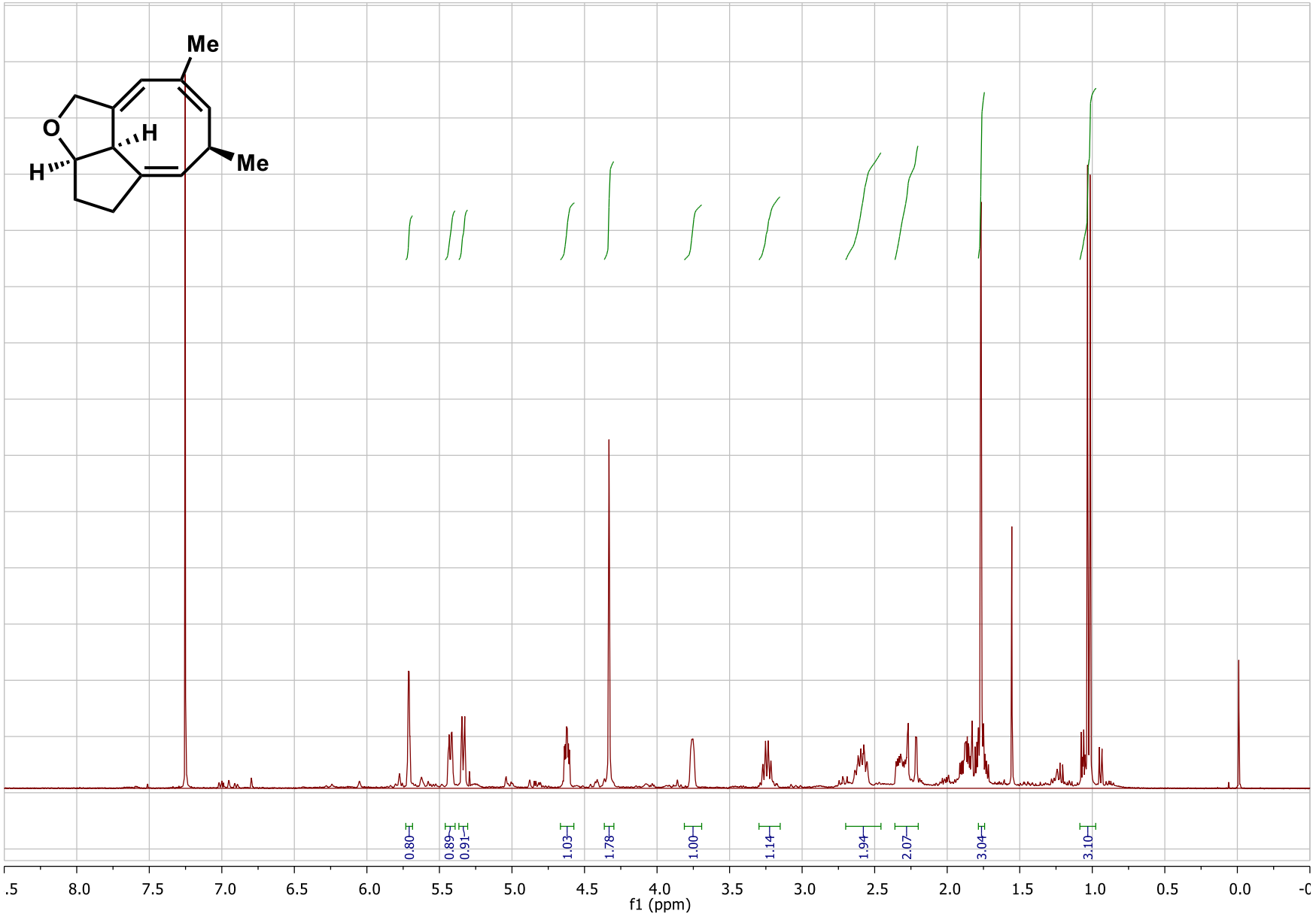
[13]: (^{1}H NMR, 400 MHz, $CDCl_3$)



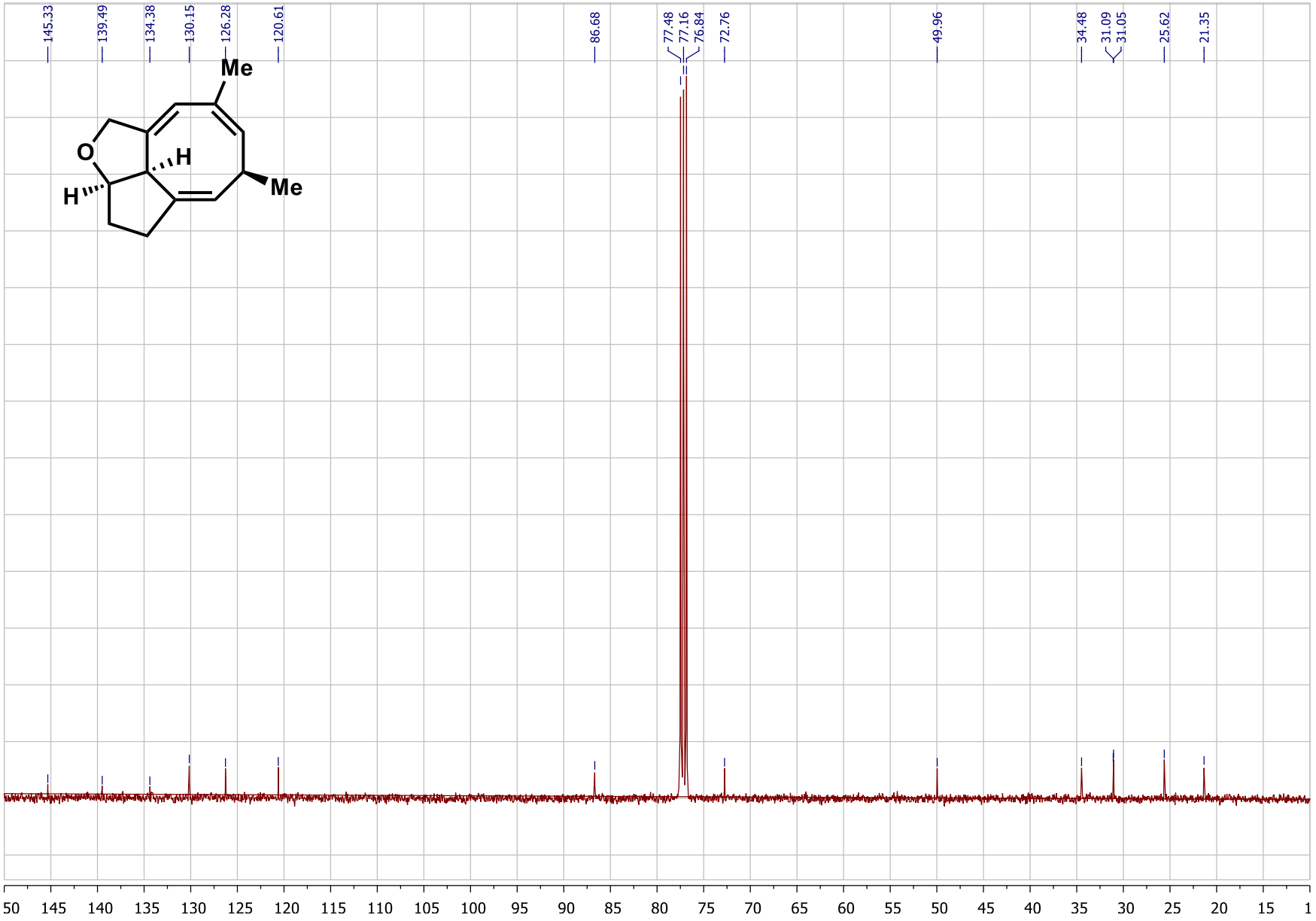
[13]: (^{13}C NMR, 100 MHz, $CDCl_3$)



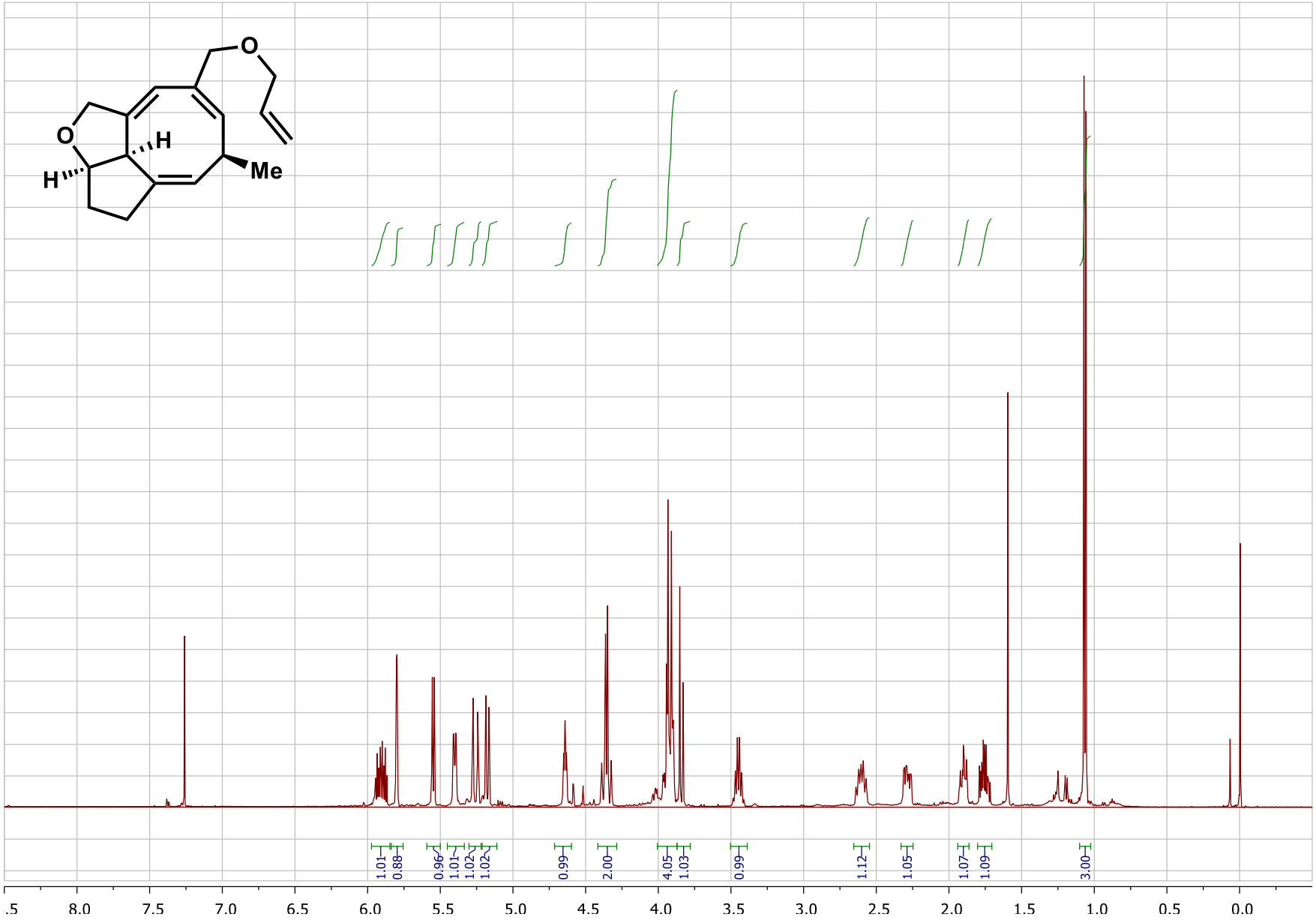
[14]: (^{1}H NMR, 400 MHz, $CDCl_3$)



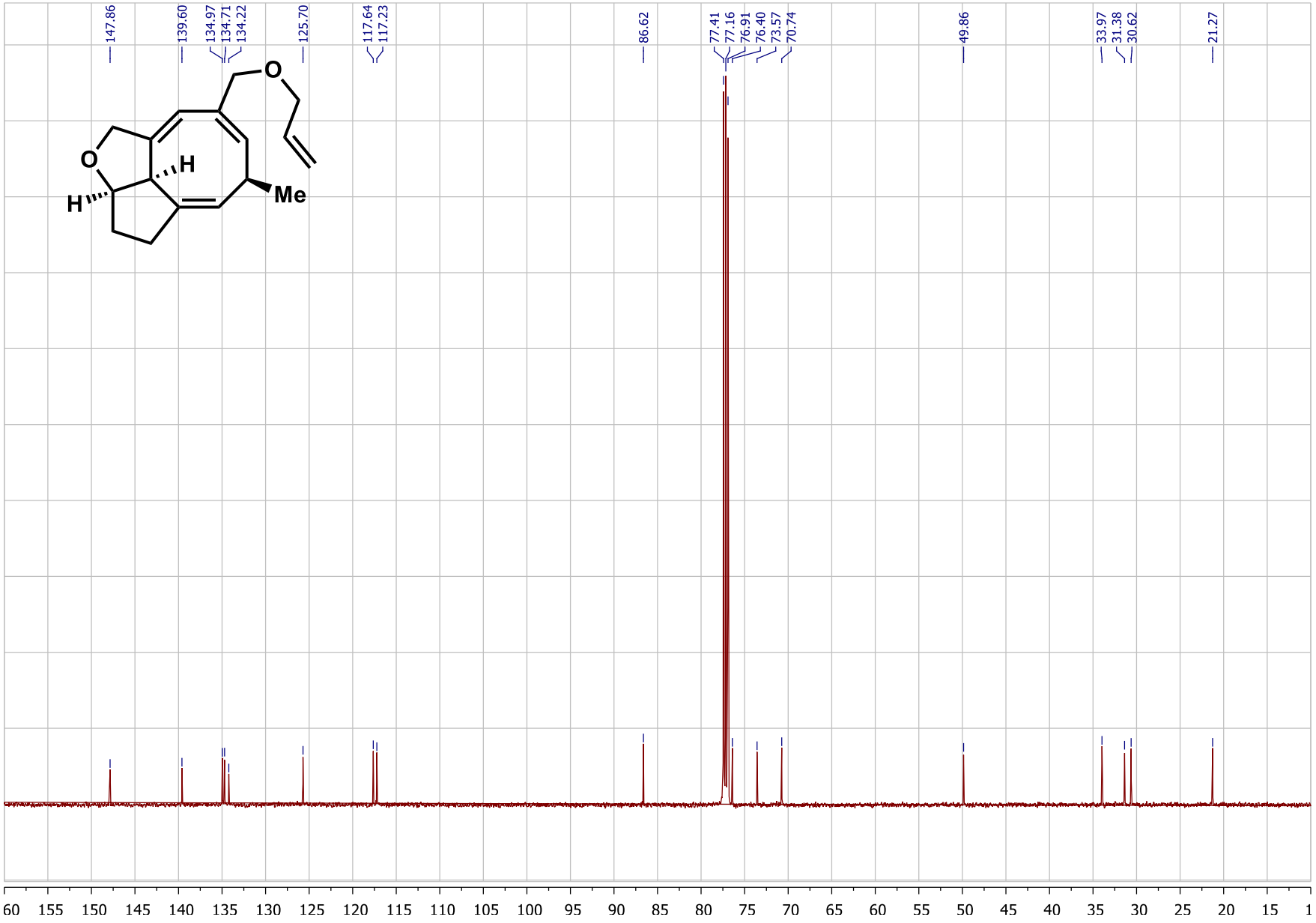
[14]: (^{13}C NMR, 126 MHz, $CDCl_3$)



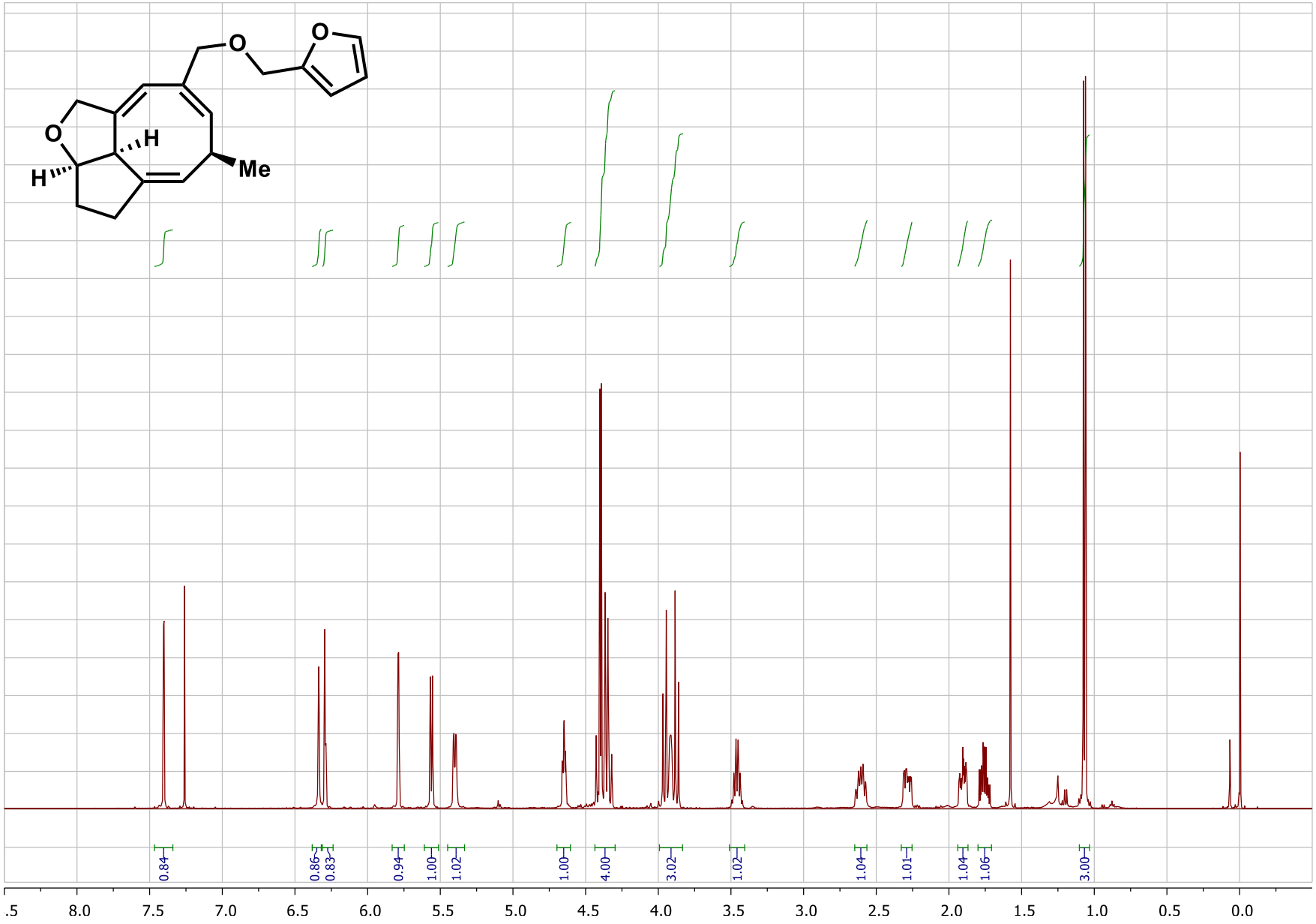
[15]: (^{1}H NMR, 500 MHz, $CDCl_3$)



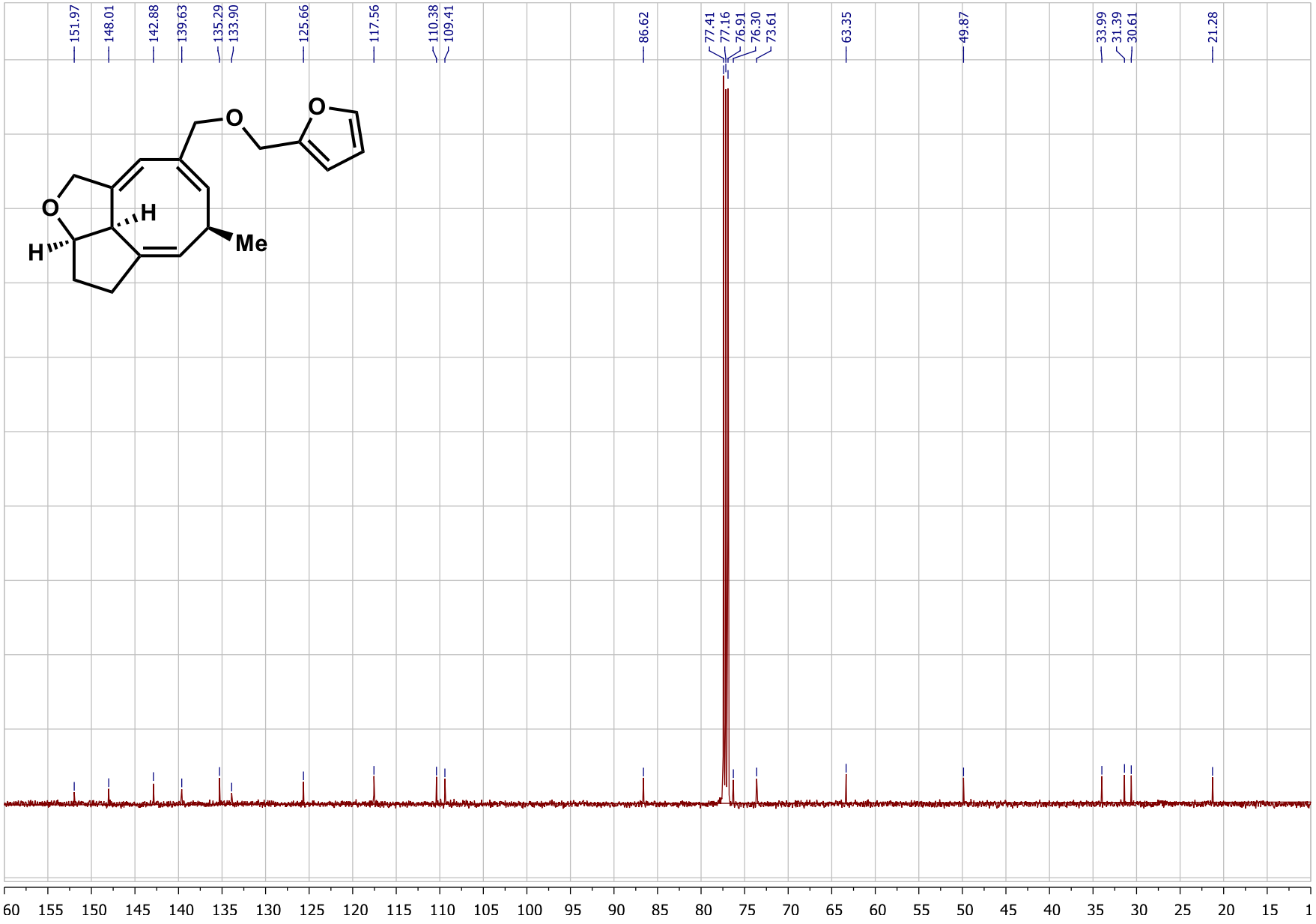
[15]: (^{1}H NMR, 500 MHz, $CDCl_3$)



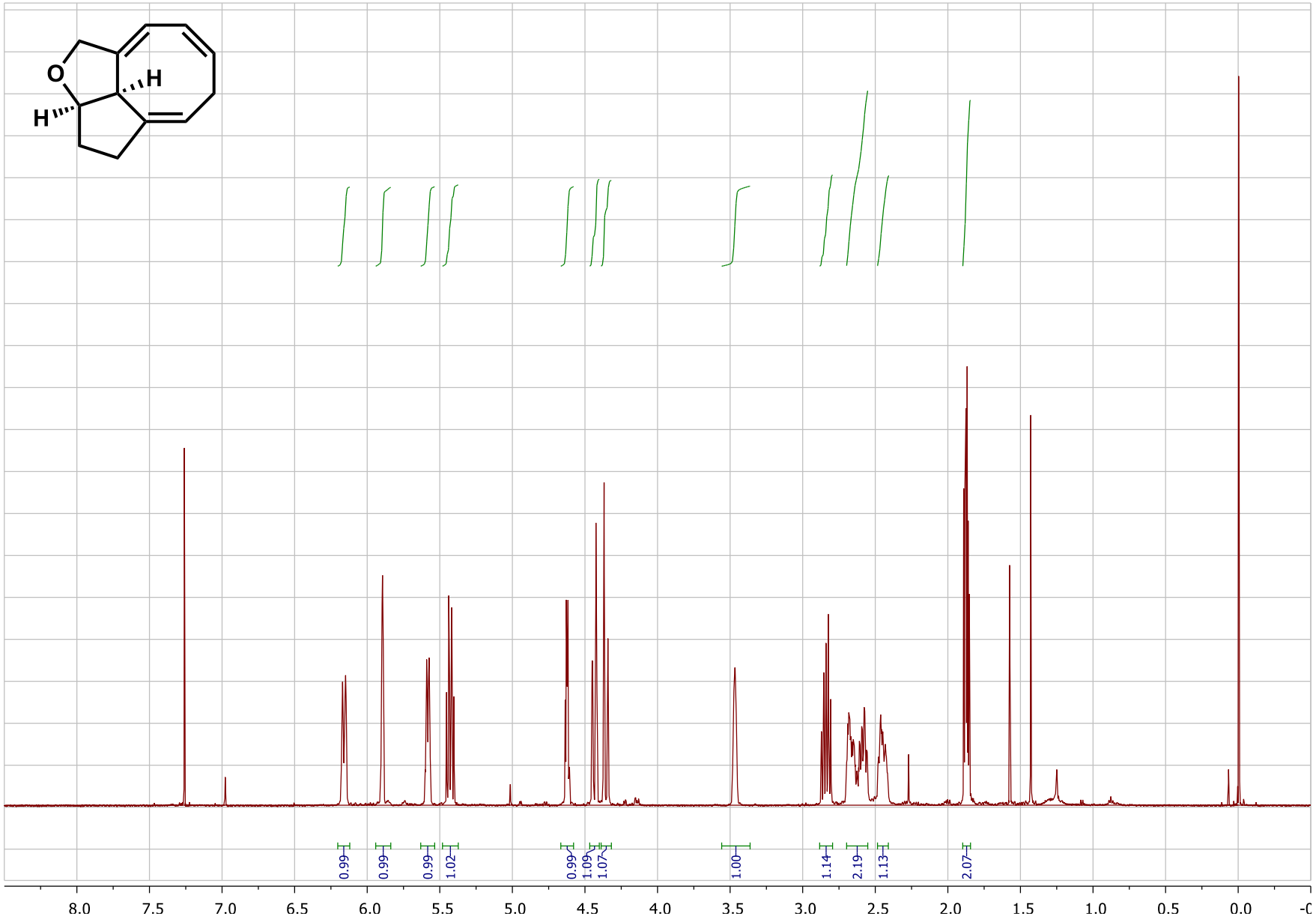
[16]: (^{1}H NMR, 400 MHz, $CDCl_3$)



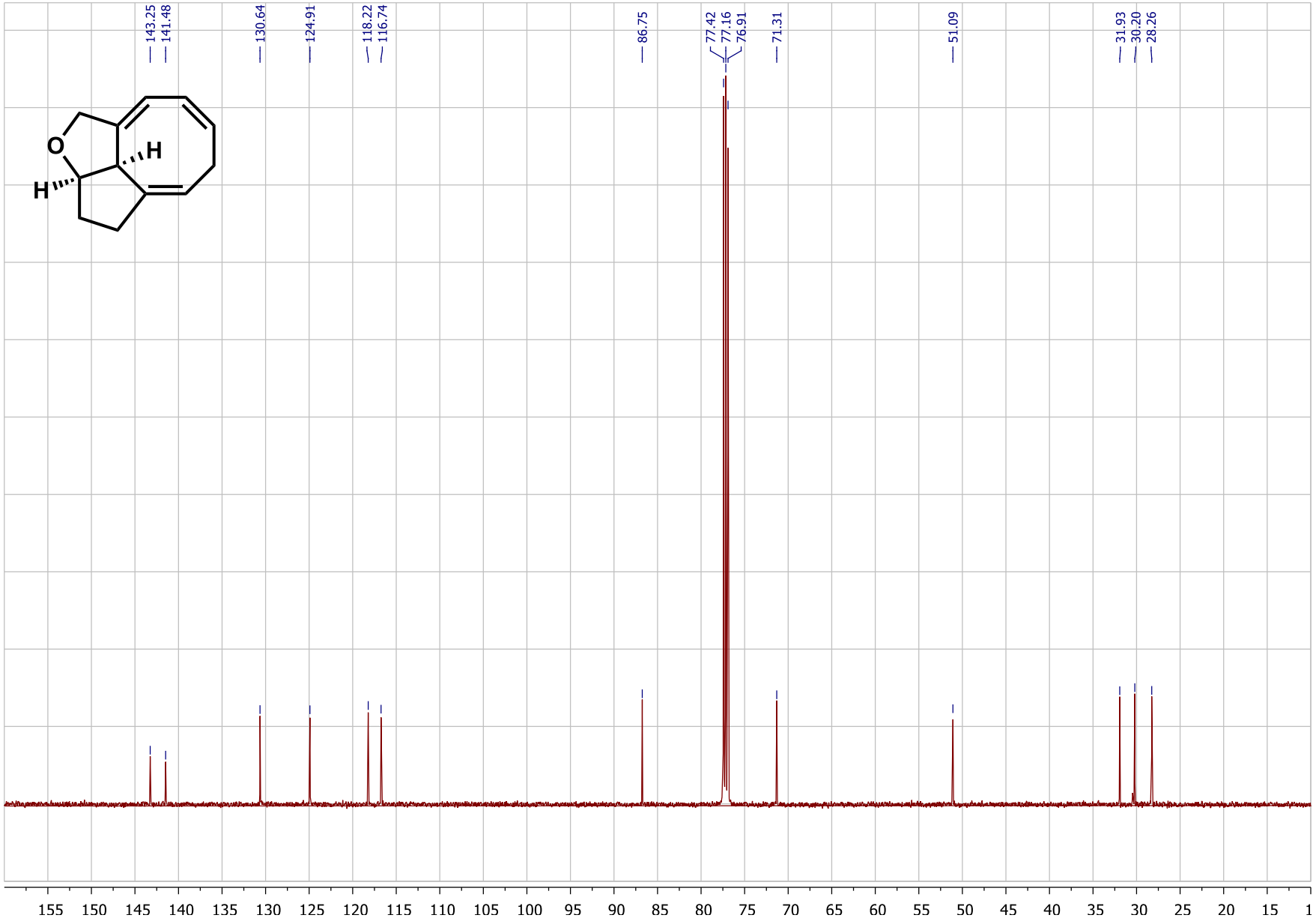
[16]: (^{13}C NMR, 125 MHz, $CDCl_3$)



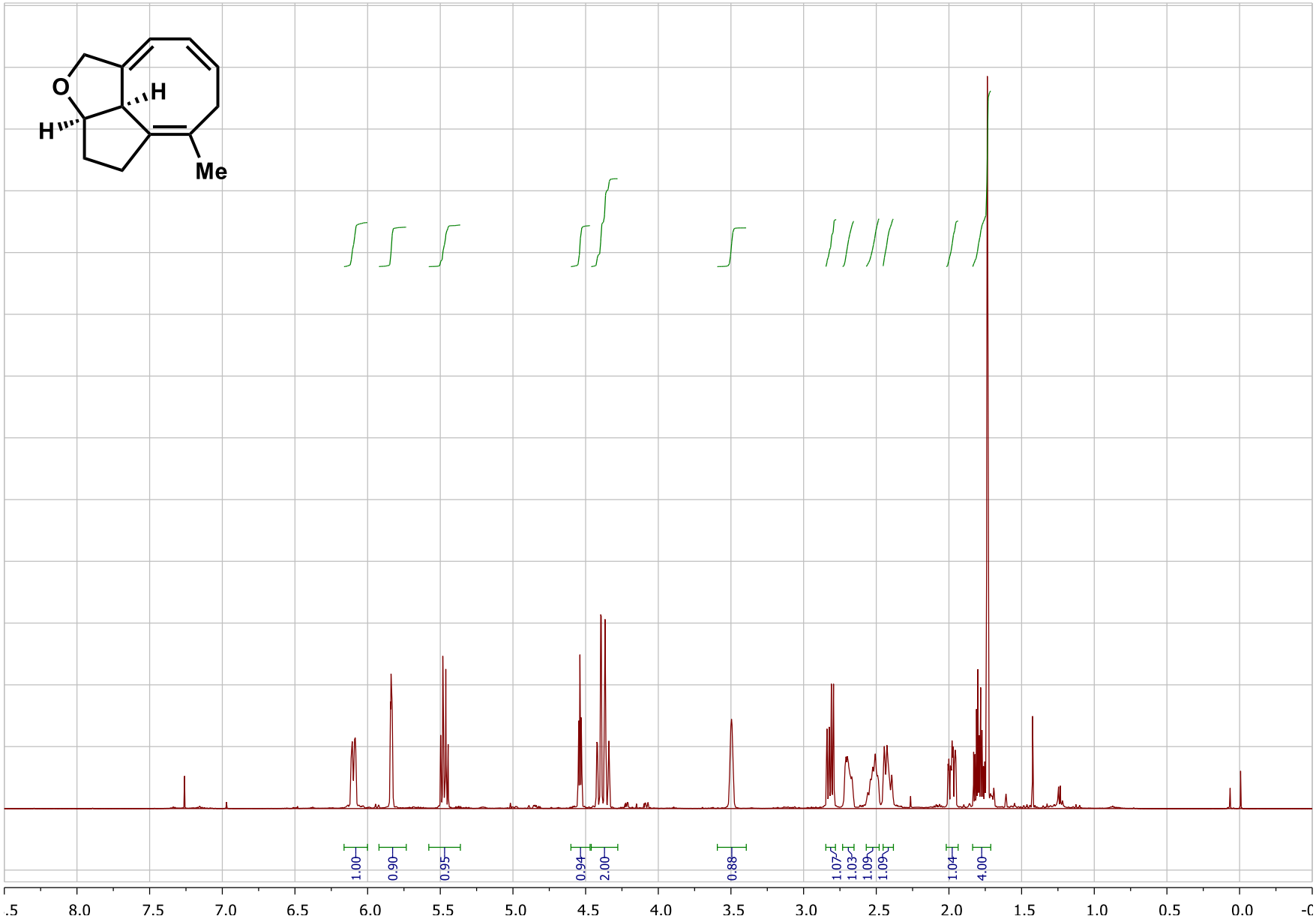
[17]: (^{1}H NMR, 500 MHz, $CDCl_3$)



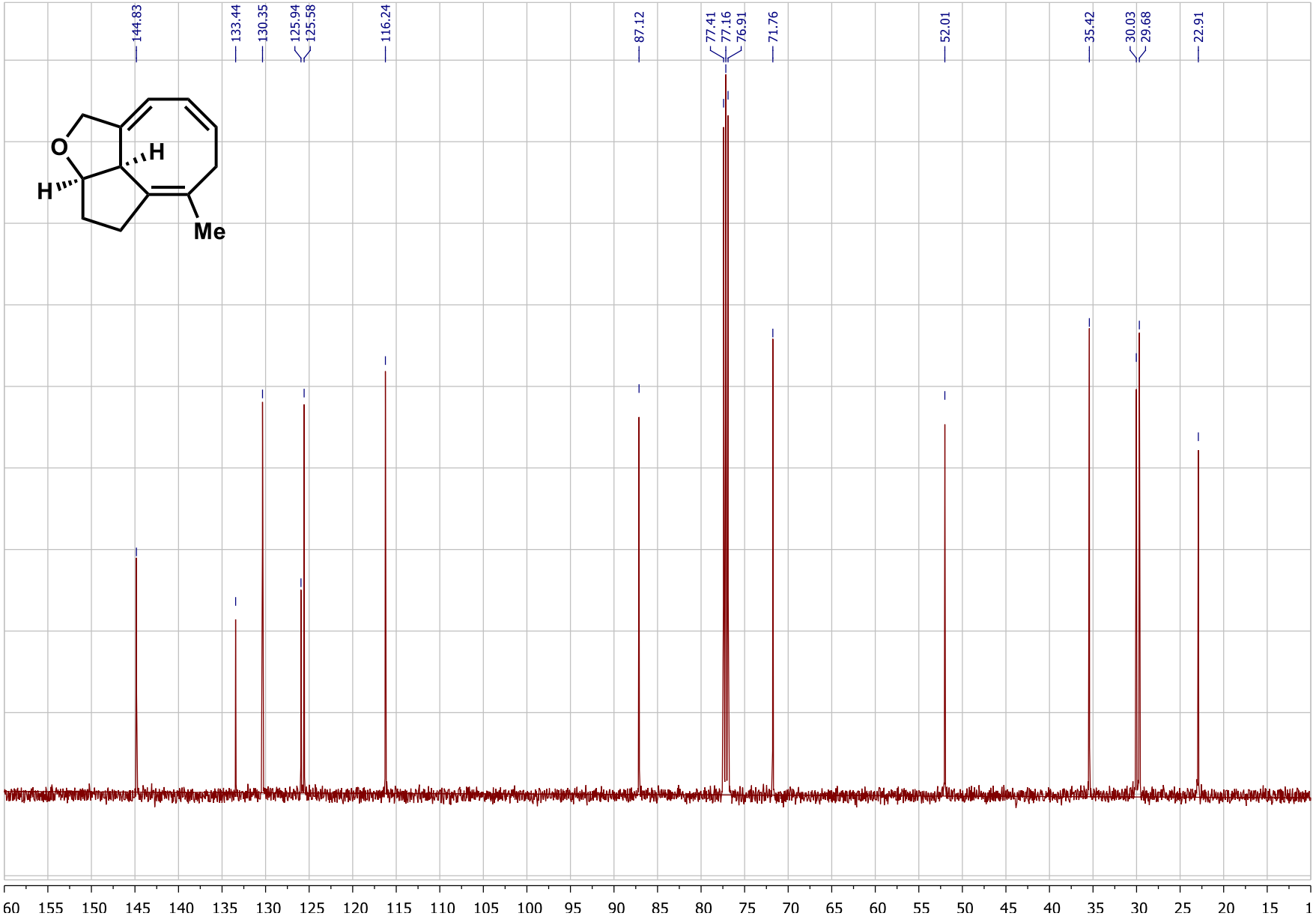
[17]: (^{13}C NMR, 126 MHz, $CDCl_3$)



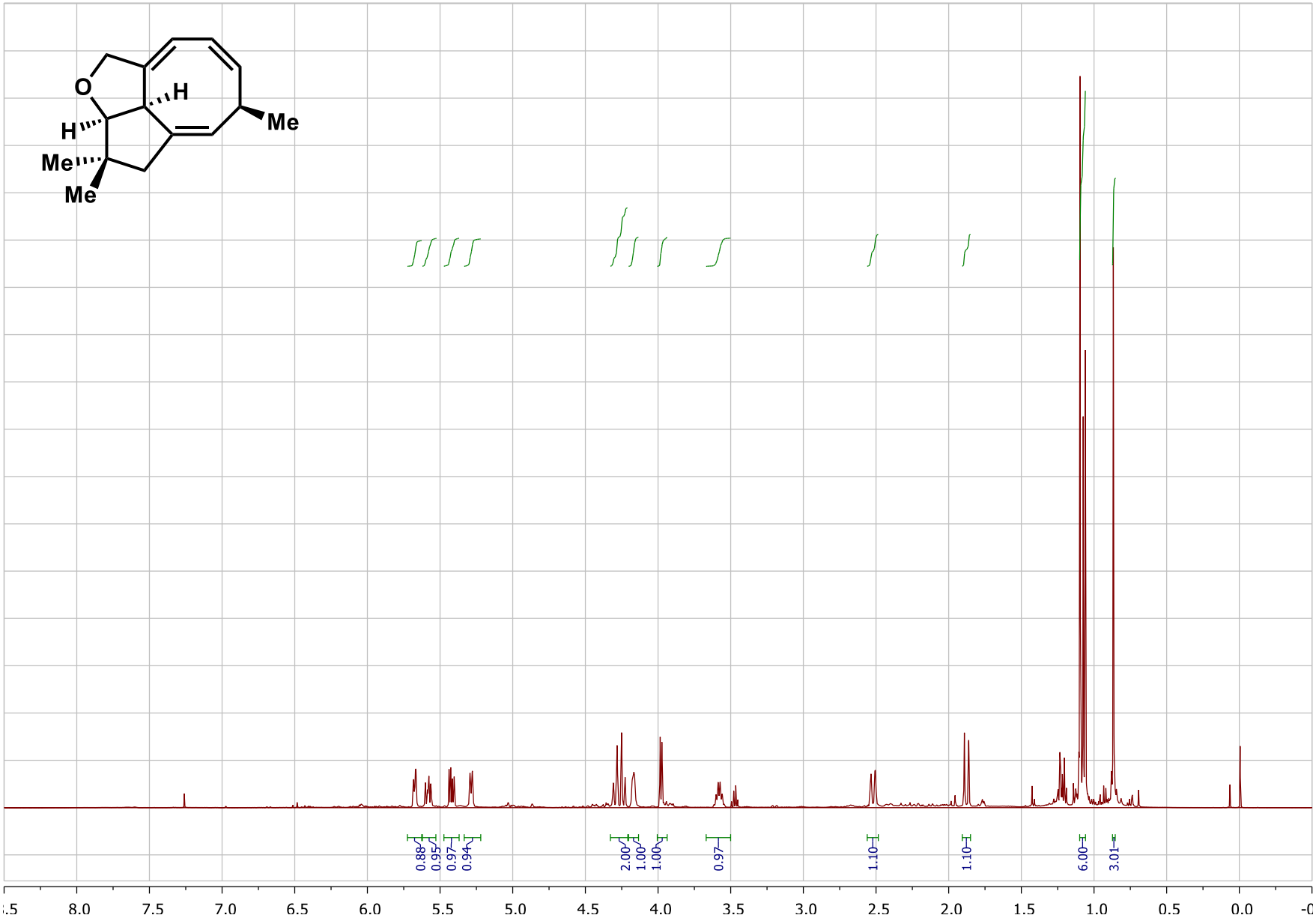
[18]: (^{1}H NMR, 500 MHz, $CDCl_3$)



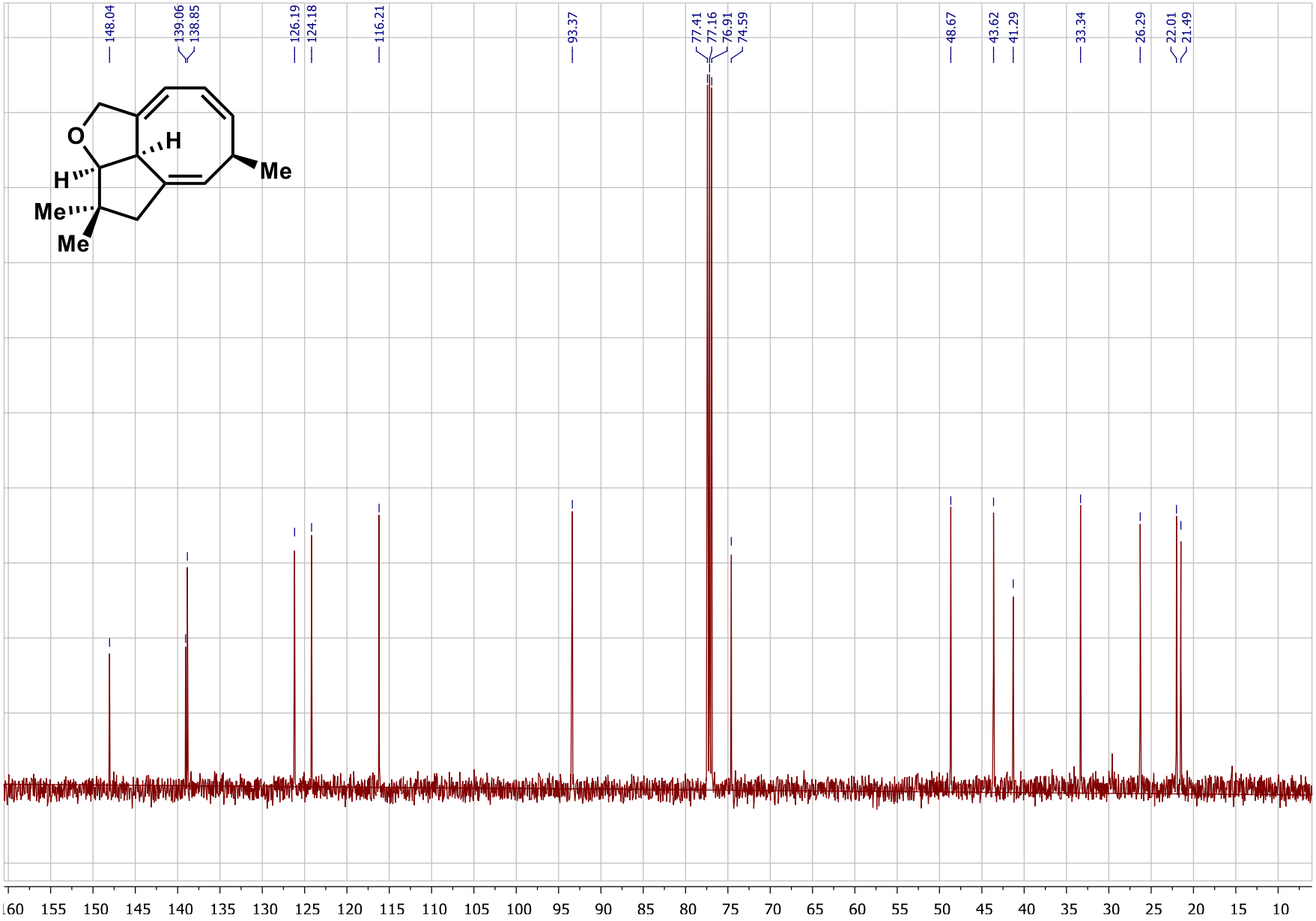
[18]: (^{13}C NMR, 126 MHz, $CDCl_3$)



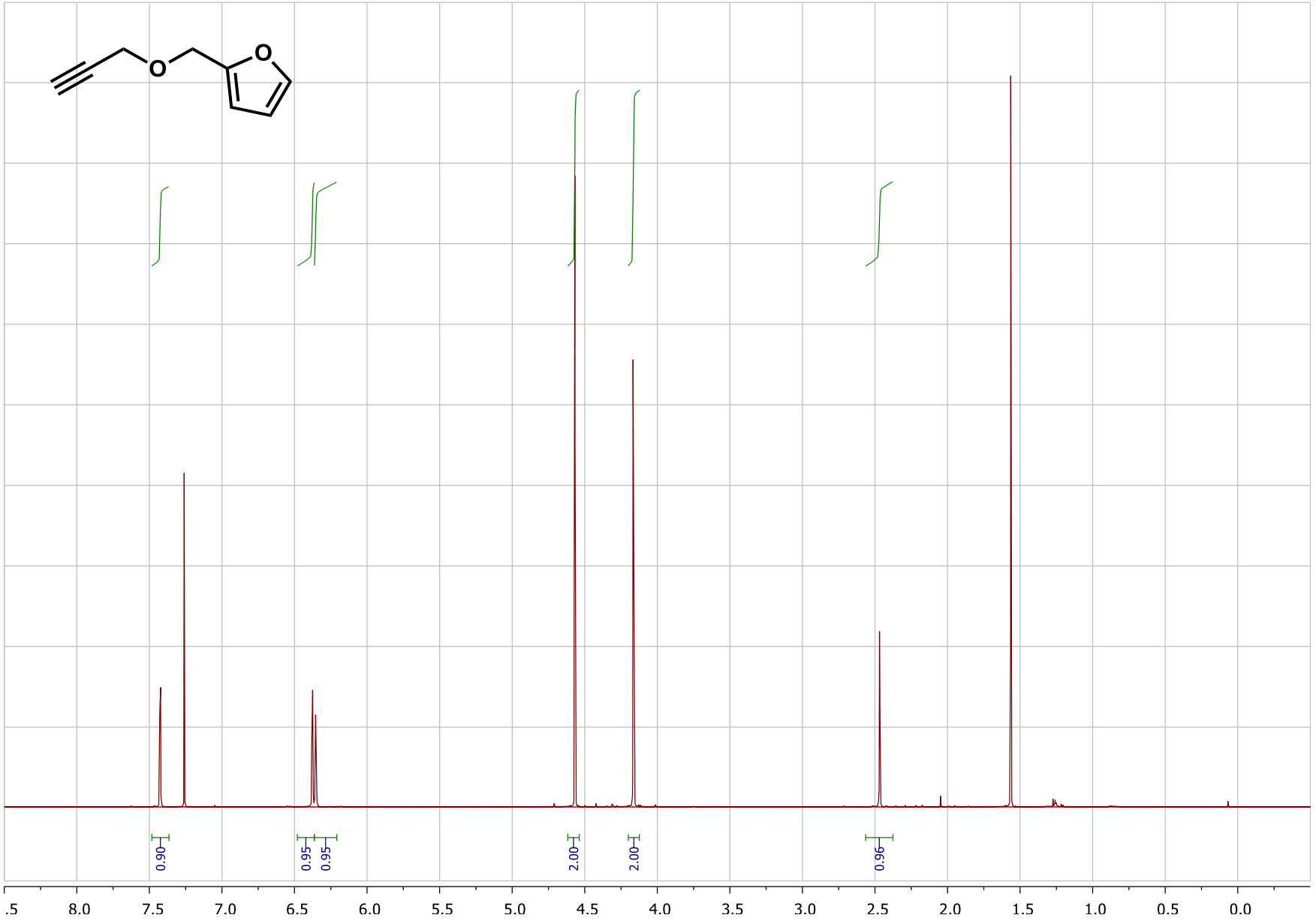
[19]: (^{1}H NMR, 500 MHz, $CDCl_3$)



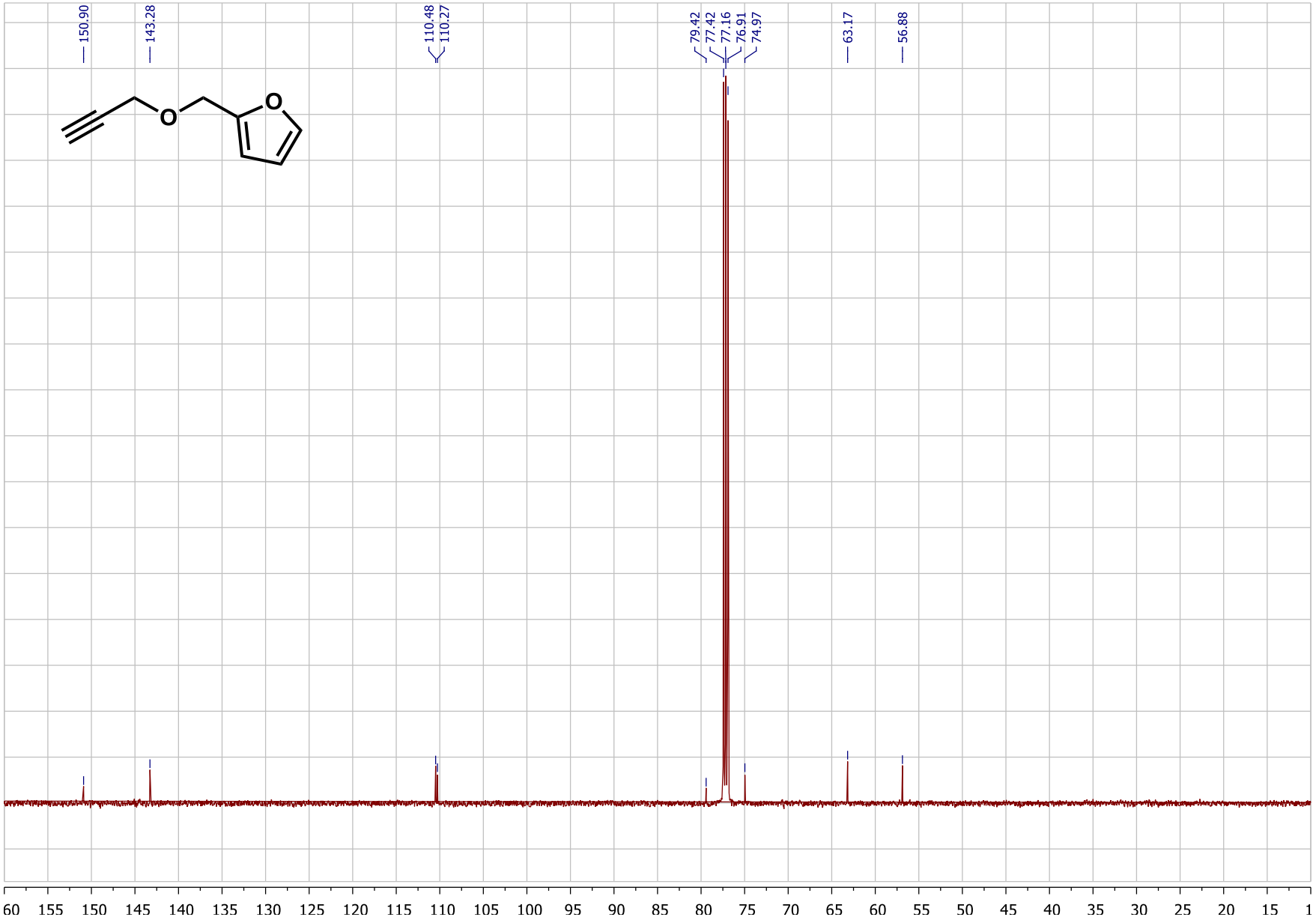
[19]: (^{13}C NMR, 125 MHz, $CDCl_3$)



[20]: (^{1}H NMR, 500 MHz, $CDCl_3$)



[20]: (^{13}C NMR, 126 MHz, $CDCl_3$)



Crystallographic Information: [Rh(nbd){(*S*,*S*)-Me-BozPHOS}]SbF_6

General	
Origin	
Code	k1261
Database dates	
Common name	
Systematic name	
Structural formula	
Analytical formula	

Bibliographic data	
Author(s)	
Publication title	
Citation	
Mineral name	
Compound source	
Structure type	
Creation method	SHELXL-97
Comments	

Phase data	
Formula sum	C25 H36 F6 O P2 Rh Sb
Formula weight	753.14 g/mol
Crystal system	orthorhombic
Space-group	P 21 21 21 (19)
Cell parameters	a=9.2068(7) Å b=14.9966(12) Å c=21.0120(17) Å
Cell ratio	a/b=0.6139 b/c=0.7137 c/a=2.2822
Cell volume	2901.14(40) $Å^3$
Z	4
Calc. density	1.72421 g/cm^3
Meas. density	
Melting point	
RAll	0.047
RObs	
Pearson code	oP344
Formula type	NOP2Q25R36...
Wyckoff sequence	a86

Atomic parameters

Atom	Ox.	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U [$Å^2$]
Rh		4a	1		0.60580(5)	0.74142(3)	0.29555(2)	
P1		4a	1		0.80189(18)	0.68861(11)	0.17463(7)	
P2		4a	1		0.76994(17)	0.6449(1)	0.33863(6)	
O1		4a	1		0.7322(5)	0.7596(3)	0.21594(17)	
C1		4a	1		0.6792(9)	0.6269(5)	0.1225(3)	
H1		4a	1		0.71600	0.56510	0.11870	0.0680
C2		4a	1		0.6972(10)	0.6726(6)	0.0576(3)	
H2A		4a	1		0.66780	0.63220	0.02330	0.0800
H2B		4a	1		0.63670	0.72630	0.05550	0.0800
C3		4a	1		0.8567(10)	0.6971(6)	0.0508(3)	
H3A		4a	1		0.87050	0.73690	0.01430	0.0820
H3B		4a	1		0.91520	0.64330	0.04400	0.0820
C4		4a	1		0.9030(7)	0.7437(5)	0.1122(3)	
H4		4a	1		0.85980	0.80400	0.10930	0.0610
C5		4a	1		0.5231(10)	0.6226(7)	0.1479(5)	
H5A		4a	1		0.46360	0.58780	0.11910	0.1290
H5B		4a	1		0.48410	0.68250	0.15120	0.1290
H5C		4a	1		0.52310	0.59490	0.18960	0.1290
C6		4a	1		1.0664(9)	0.7602(6)	0.1210(4)	
H6A		4a	1		1.10480	0.79010	0.08370	0.1100
H6B		4a	1		1.11580	0.70360	0.12680	0.1100
H6C		4a	1		1.08180	0.79730	0.15830	0.1100
C7		4a	1		0.9077(7)	0.6070(4)	0.2184(3)	

C8	4a	1		1.0079(8)	0.5602(5)	0.1818(3)	
H8	4a	1		1.01330	0.57140	0.13780	0.0640
C9	4a	1		1.0993(8)	0.4977(5)	0.2084(3)	
H9	4a	1		1.16460	0.46590	0.18250	0.0730
C10	4a	1		1.0948(8)	0.4819(5)	0.2736(3)	
H10	4a	1		1.15840	0.44060	0.29240	0.0730
C11	4a	1		0.9954(7)	0.5279(5)	0.3100(3)	
H11	4a	1		0.99150	0.51630	0.35400	0.0580
C12	4a	1		0.9006(7)	0.5906(4)	0.2847(3)	
C13	4a	1		0.6939(7)	0.5593(4)	0.3922(3)	
H13	4a	1		0.59670	0.58240	0.40380	0.0550
C14	4a	1		0.7813(9)	0.5646(6)	0.4538(3)	
H14A	4a	1		0.72170	0.54490	0.48980	0.0840
H14B	4a	1		0.86680	0.52590	0.45110	0.0840
C15	4a	1		0.8274(9)	0.6596(7)	0.4631(3)	
H15A	4a	1		0.90140	0.66310	0.49660	0.0890
H15B	4a	1		0.74400	0.69580	0.47620	0.0890
C16	4a	1		0.8891(8)	0.6946(5)	0.4005(3)	
H16	4a	1		0.98730	0.66890	0.39510	0.0600
C17	4a	1		0.664(1)	0.4675(5)	0.3637(5)	
H17A	4a	1		0.62150	0.42920	0.39590	0.1160
H17B	4a	1		0.75440	0.44160	0.34880	0.1160
H17C	4a	1		0.59710	0.47340	0.32830	0.1160
C18	4a	1		0.9033(10)	0.7945(6)	0.3971(6)	
H18A	4a	1		0.96680	0.81500	0.43090	0.1350
H18B	4a	1		0.80830	0.82160	0.40200	0.1350
H18C	4a	1		0.94390	0.81130	0.35620	0.1350
C19	4a	1		0.4059(9)	0.8076(6)	0.2585(3)	
H19	4a	1		0.38240	0.81290	0.21270	0.0740
C20	4a	1		0.4873(8)	0.8699(5)	0.2918(4)	
H20	4a	1		0.52710	0.92510	0.27270	0.0700
C21	4a	1		0.4353(10)	0.8627(7)	0.3617(4)	
H21	4a	1		0.45810	0.91310	0.39040	0.0870
C22	4a	1		0.4962(8)	0.7698(6)	0.3802(3)	
H22	4a	1		0.53740	0.75660	0.42270	0.0700
C23	4a	1		0.4177(7)	0.7086(6)	0.3459(3)	
H23	4a	1		0.39790	0.64760	0.36160	0.0760
C24	4a	1		0.3054(9)	0.7630(7)	0.3077(4)	
H24	4a	1		0.22090	0.72980	0.29070	0.0880
C25	4a	1		0.273(1)	0.8396(8)	0.3518(4)	
H25A	4a	1		0.22440	0.82090	0.39110	0.1120
H25B	4a	1		0.21840	0.88770	0.33120	0.1120
Sb	4a	1	0.44	0.26240(17)	0.49848(14)	0.48825(8)	0.0381(5)
F1	4a	1	0.44	0.0773(3)	0.4543(4)	0.4721(3)	0.0734(12)
F2	4a	1	0.44	0.4475(3)	0.5427(4)	0.5044(3)	0.0734(12)
F3	4a	1	0.44	0.2119(7)	0.5175(4)	0.57288(12)	0.0734(12)
F4	4a	1	0.44	0.3129(7)	0.4795(5)	0.40363(13)	0.0734(12)
F5	4a	1	0.44	0.1992(7)	0.6128(2)	0.4679(3)	0.0734(12)
F6	4a	1	0.44	0.3256(7)	0.3842(2)	0.5086(3)	0.0734(12)
Sb'	4a	1	0.27	0.2615(2)	0.47414(17)	0.48658(13)	0.0345(6)
F1'	4a	1	0.27	0.0837(5)	0.4335(6)	0.4561(4)	0.0724(19)
F2'	4a	1	0.27	0.4392(5)	0.5148(6)	0.5170(4)	0.0724(19)
F3'	4a	1	0.27	0.2751(11)	0.3746(4)	0.5390(4)	0.0724(19)
F4'	4a	1	0.27	0.2478(11)	0.5737(4)	0.4341(4)	0.0724(19)
F5'	4a	1	0.27	0.1664(9)	0.5359(6)	0.5511(4)	0.0724(19)
F6'	4a	1	0.27	0.3565(9)	0.4123(6)	0.4221(3)	0.0724(19)
Sb"	4a	1	0.29	0.2688(3)	0.4905(3)	0.47900(13)	0.0424(10)
F1"	4a	1	0.29	0.0941(6)	0.4314(6)	0.4648(5)	0.0731(19)
F2"	4a	1	0.29	0.4435(6)	0.5495(6)	0.4932(5)	0.0731(19)
F3"	4a	1	0.29	0.2557(10)	0.4645(7)	0.56536(17)	0.0731(19)
F4"	4a	1	0.29	0.2820(11)	0.5165(6)	0.39264(16)	0.0731(19)
F5"	4a	1	0.29	0.1682(9)	0.5964(4)	0.4923(5)	0.0731(19)
F6"	4a	1	0.29	0.3695(9)	0.3846(4)	0.4657(4)	0.0731(19)

Anisotropic displacement parameters, in Å^2						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**

Rh	0.0395(2)	0.0535(3)	0.0319(2)	0.0114(2)	0.0030(2)	0.0049(2)
P1	0.0428(9)	0.0442(9)	0.0258(7)	-0.0003(7)	0.0000(6)	0.0008(6)
P2	0.0345(8)	0.0430(8)	0.0271(7)	0.0054(7)	0.0010(6)	0.0001(6)
O1	0.054(2)	0.041(2)	0.0336(18)	0.009(2)	0.0050(18)	0.0022(17)
C1	0.067(5)	0.055(4)	0.048(4)	0.002(4)	-0.015(4)	-0.009(3)
C2	0.083(6)	0.079(6)	0.038(4)	0.013(5)	-0.020(4)	-0.011(4)
C3	0.097(7)	0.085(6)	0.024(3)	0.012(5)	0.002(4)	0.006(3)
C4	0.058(4)	0.057(4)	0.037(3)	-0.001(4)	0.010(3)	0.009(3)
C5	0.071(6)	0.104(8)	0.082(6)	-0.023(5)	-0.012(5)	-0.020(5)
C6	0.077(5)	0.080(6)	0.063(5)	-0.022(5)	0.028(4)	0.009(4)
C7	0.042(3)	0.041(3)	0.033(3)	-0.002(3)	0.006(3)	-0.003(2)
C8	0.064(4)	0.059(4)	0.036(3)	0.015(4)	0.010(3)	-0.002(3)
C9	0.066(4)	0.065(4)	0.050(4)	0.026(4)	0.013(4)	-0.006(3)
C10	0.061(4)	0.072(5)	0.051(4)	0.030(4)	0.003(3)	0.000(3)
C11	0.052(4)	0.059(4)	0.033(3)	0.016(3)	0.005(3)	0.007(3)
C12	0.042(3)	0.047(3)	0.033(3)	0.006(3)	0.006(3)	0.000(2)
C13	0.042(4)	0.048(4)	0.048(4)	0.006(3)	0.009(3)	0.007(3)
C14	0.063(5)	0.108(7)	0.039(4)	0.035(5)	0.007(3)	0.028(4)
C15	0.062(5)	0.123(8)	0.038(4)	0.024(5)	-0.010(4)	-0.007(4)
C16	0.037(3)	0.068(4)	0.044(4)	0.010(3)	-0.006(3)	-0.014(3)
C17	0.080(6)	0.054(5)	0.099(7)	-0.006(4)	0.016(5)	0.007(4)
C18	0.061(5)	0.071(6)	0.137(9)	0.002(5)	-0.002(6)	-0.039(6)
C19	0.061(4)	0.082(5)	0.041(4)	0.026(4)	-0.005(4)	0.012(4)
C20	0.057(4)	0.053(4)	0.066(4)	0.018(3)	-0.004(4)	0.003(4)
C21	0.068(5)	0.097(7)	0.053(4)	0.027(5)	0.001(4)	-0.010(4)
C22	0.047(4)	0.100(6)	0.029(3)	0.023(4)	0.011(3)	0.005(3)
C23	0.037(4)	0.107(6)	0.046(4)	0.016(4)	0.011(3)	0.025(4)
C24	0.051(4)	0.100(7)	0.070(5)	0.008(4)	-0.006(4)	0.024(5)
C25	0.067(6)	0.146(9)	0.066(5)	0.058(6)	0.003(5)	-0.003(6)

Selected geometric informations			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Rh—O1	2.056(4)	C16—C18	1.506(11)
Rh—C23	2.088(7)	C19—C20	1.387(11)
Rh—C22	2.089(6)	C19—C24	1.541(11)
Rh—C20	2.216(7)	C20—C21	1.549(11)
Rh—C19	2.231(7)	C21—C25	1.547(14)
Rh—P2	2.2799(15)	C21—C22	1.551(11)
P1—O1	1.516(4)	C22—C23	1.373(11)
P1—C4	1.809(6)	C23—C24	1.542(10)
P1—C7	1.814(6)	C24—C25	1.506(13)
P1—C1	1.826(7)	Sb—F4	1.8598
P2—C12	1.843(6)	Sb—F2	1.8599
P2—C13	1.846(6)	Sb—F5	1.8599
P2—C16	1.857(7)	Sb—F1	1.8601
C1—C5	1.534(12)	Sb—F3	1.8601
C1—C2	1.535(11)	Sb—F6	1.8601
C2—C3	1.520(12)	Sb'—F3'	1.8599
C3—C4	1.528(10)	Sb'—F1'	1.8599
C4—C6	1.536(11)	Sb'—F6'	1.8600
C7—C8	1.392(9)	Sb'—F5'	1.8600
C7—C12	1.416(8)	Sb'—F2'	1.8600
C8—C9	1.378(10)	Sb'—F4'	1.8600
C9—C10	1.391(10)	Sb"—F4"	1.8599
C10—C11	1.379(9)	Sb"—F5"	1.8599
C11—C12	1.389(9)	Sb"—F2"	1.8600
C13—C17	1.526(11)	Sb"—F1"	1.8600
C13—C14	1.525(10)	Sb"—F6"	1.8600
C14—C15	1.499(13)	Sb"—F3"	1.8600
C15—C16	1.527(11)		
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
O1—Rh—C23	155.9(3)	C21—C20—Rh	93.3(5)
O1—Rh—C22	160.0(3)	C25—C21—C22	100.5(8)
C23—Rh—C22	38.4(3)	C25—C21—C20	100.7(7)
O1—Rh—C20	97.7(2)	C22—C21—C20	100.9(6)
C23—Rh—C20	79.3(3)	C23—C22—C21	106.1(7)
C22—Rh—C20	67.4(3)	C23—C22—Rh	70.8(4)
O1—Rh—C19	97.1(2)	C21—C22—Rh	98.3(4)

C23—Rh—C19	66.3(3)	C22—C23—C24	105.9(8)
C22—Rh—C19	79.0(3)	C22—C23—Rh	70.8(4)
C20—Rh—C19	36.3(3)	C24—C23—Rh	99.7(5)
O1—Rh—P2	91.83(12)	C25—C24—C19	101.5(8)
C23—Rh—P2	101.5(2)	C25—C24—C23	102.5(7)
C22—Rh—P2	96.4(2)	C19—C24—C23	100.2(6)
C20—Rh—P2	153.2(2)	C24—C25—C21	93.6(6)
C19—Rh—P2	165.4(2)	F4—Sb—F2	90.000
O1—P1—C4	108.2(3)	F4—Sb—F5	90.000
O1—P1—C7	114.2(2)	F2—Sb—F5	90.000
C4—P1—C7	113.6(3)	F4—Sb—F1	90.000
O1—P1—C1	116.0(3)	F2—Sb—F1	180.000
C4—P1—C1	96.6(3)	F5—Sb—F1	90.000
C7—P1—C1	107.1(3)	F4—Sb—F3	180.0(4)
C12—P2—C13	108.4(3)	F2—Sb—F3	90.000
C12—P2—C16	102.8(3)	F5—Sb—F3	90.000
C13—P2—C16	94.4(3)	F1—Sb—F3	90.000
C12—P2—Rh	118.0(2)	F4—Sb—F6	90.000
C13—P2—Rh	115.6(2)	F2—Sb—F6	90.000
C16—P2—Rh	114.5(2)	F5—Sb—F6	180.000
P1—O1—Rh	127.8(2)	F1—Sb—F6	90.000
C5—C1—C2	115.4(7)	F3—Sb—F6	90.000
C5—C1—P1	113.0(5)	F3'—Sb'—F1'	90.000
C2—C1—P1	103.8(5)	F3'—Sb'—F6'	90.000
C3—C2—C1	107.2(6)	F1'—Sb'—F6'	90.000
C2—C3—C4	107.5(6)	F3'—Sb'—F5'	90.000
C3—C4—C6	116.7(6)	F1'—Sb'—F5'	90.000
C3—C4—P1	105.1(5)	F6'—Sb'—F5'	180.000
C6—C4—P1	119.3(5)	F3'—Sb'—F2'	90.000
C8—C7—C12	119.1(6)	F1'—Sb'—F2'	180.000
C8—C7—P1	114.6(4)	F6'—Sb'—F2'	90.000
C12—C7—P1	126.3(5)	F5'—Sb'—F2'	90.000
C9—C8—C7	121.6(6)	F3'—Sb'—F4'	180.000
C8—C9—C10	119.8(6)	F1'—Sb'—F4'	90.000
C11—C10—C9	118.8(6)	F6'—Sb'—F4'	90.000
C10—C11—C12	122.9(6)	F5'—Sb'—F4'	90.000
C11—C12—C7	117.8(5)	F2'—Sb'—F4'	90.000
C11—C12—P2	118.3(4)	F4"—Sb"—F5"	90.000
C7—C12—P2	123.9(5)	F4"—Sb"—F2"	90.000
C17—C13—C14	118.4(6)	F5"—Sb"—F2"	90.000
C17—C13—P2	117.2(5)	F4"—Sb"—F1"	90.000
C14—C13—P2	106.3(5)	F5"—Sb"—F1"	90.000
C15—C14—C13	108.1(6)	F2"—Sb"—F1"	180.000
C14—C15—C16	108.6(6)	F4"—Sb"—F6"	90.000
C18—C16—C15	114.5(7)	F5"—Sb"—F6"	180.000
C18—C16—P2	114.7(6)	F2"—Sb"—F6"	90.000
C15—C16—P2	104.2(5)	F1"—Sb"—F6"	90.000
C20—C19—C24	106.2(7)	F4"—Sb"—F3"	180.0(6)
C20—C19—Rh	71.2(4)	F5"—Sb"—F3"	90.000
C24—C19—Rh	93.9(4)	F2"—Sb"—F3"	90.000
C19—C20—C21	105.3(7)	F1"—Sb"—F3"	90.000
C19—C20—Rh	72.4(4)	F6"—Sb"—F3"	90.000

Atoms 1,2,3,4	Tors. an. 1,2,3,4 [°]	Atoms 1,2,3,4	Tors. an. 1,2,3,4 [°]
O1—Rh—P2—C12	-20.5(3)	C13—C14—C15—C16	-46.9(8)
C23—Rh—P2—C12	139.2(4)	C14—C15—C16—C18	164.6(8)
C22—Rh—P2—C12	177.8(3)	C14—C15—C16—P2	38.5(7)
C20—Rh—P2—C12	-131.8(5)	C12—P2—C16—C18	107.2(6)
C19—Rh—P2—C12	107.4(8)	C13—P2—C16—C18	-142.9(6)
O1—Rh—P2—C13	-151.2(3)	Rh—P2—C16—C18	-22.1(7)
C23—Rh—P2—C13	8.6(4)	C12—P2—C16—C15	-126.8(5)
C22—Rh—P2—C13	47.2(3)	C13—P2—C16—C15	-16.8(5)
C20—Rh—P2—C13	97.6(5)	Rh—P2—C16—C15	103.9(5)
C19—Rh—P2—C13	-23.3(8)	O1—Rh—C19—C20	-93.4(5)
O1—Rh—P2—C16	100.7(3)	C23—Rh—C19—C20	104.8(5)
C23—Rh—P2—C16	-99.5(4)	C22—Rh—C19—C20	66.7(5)
C22—Rh—P2—C16	-61.0(3)	P2—Rh—C19—C20	139.2(7)
C20—Rh—P2—C16	-10.5(5)	O1—Rh—C19—C24	160.8(5)

C19—Rh—P2—C16	-131.4(8)	C23—Rh—C19—C24	-1.0(5)
C4—P1—O1—Rh	-179.0(3)	C22—Rh—C19—C24	-39.1(6)
C7—P1—O1—Rh	-51.4(4)	C20—Rh—C19—C24	-105.8(7)
C1—P1—O1—Rh	73.9(4)	P2—Rh—C19—C24	33.5(11)
C23—Rh—O1—P1	-75.0(7)	C24—C19—C20—C21	0.0(8)
C22—Rh—O1—P1	163.3(6)	Rh—C19—C20—C21	-88.6(5)
C20—Rh—O1—P1	-156.1(4)	C24—C19—C20—Rh	88.6(5)
C19—Rh—O1—P1	-119.5(4)	O1—Rh—C20—C19	91.5(5)
P2—Rh—O1—P1	49.0(3)	C23—Rh—C20—C19	-64.3(5)
O1—P1—C1—C5	-26.9(8)	C22—Rh—C20—C19	-102.5(5)
C4—P1—C1—C5	-140.9(7)	P2—Rh—C20—C19	-158.6(4)
C7—P1—C1—C5	102.0(7)	O1—Rh—C20—C21	-163.4(5)
O1—P1—C1—C2	98.9(5)	C23—Rh—C20—C21	40.8(5)
C4—P1—C1—C2	-15.0(6)	C22—Rh—C20—C21	2.6(5)
C7—P1—C1—C2	-132.2(5)	C19—Rh—C20—C21	105.1(7)
C5—C1—C2—C3	161.9(7)	P2—Rh—C20—C21	-53.5(8)
P1—C1—C2—C3	37.7(8)	C19—C20—C21—C25	-33.6(8)
C1—C2—C3—C4	-48.5(9)	Rh—C20—C21—C25	-106.3(6)
C2—C3—C4—C6	169.7(7)	C19—C20—C21—C22	69.4(7)
C2—C3—C4—P1	35.1(7)	Rh—C20—C21—C22	-3.3(6)
O1—P1—C4—C3	-131.3(5)	C25—C21—C22—C23	34.4(7)
C7—P1—C4—C3	100.7(5)	C20—C21—C22—C23	-68.8(7)
C1—P1—C4—C3	-11.2(6)	C25—C21—C22—Rh	106.7(6)
O1—P1—C4—C6	95.5(7)	C20—C21—C22—Rh	3.5(7)
C7—P1—C4—C6	-32.5(7)	O1—Rh—C22—C23	146.0(6)
C1—P1—C4—C6	-144.4(7)	C20—Rh—C22—C23	101.7(5)
O1—P1—C7—C8	-160.3(5)	C19—Rh—C22—C23	65.5(5)
C4—P1—C7—C8	-35.6(6)	P2—Rh—C22—C23	-100.5(4)
C1—P1—C7—C8	69.8(6)	O1—Rh—C22—C21	41.7(9)
O1—P1—C7—C12	17.0(7)	C23—Rh—C22—C21	-104.2(7)
C4—P1—C7—C12	141.7(6)	C20—Rh—C22—C21	-2.6(5)
C1—P1—C7—C12	-112.9(6)	C19—Rh—C22—C21	-38.7(5)
C12—C7—C8—C9	0.6(11)	P2—Rh—C22—C21	155.3(5)
P1—C7—C8—C9	178.1(6)	C21—C22—C23—C24	-1.6(7)
C7—C8—C9—C10	-1.5(12)	Rh—C22—C23—C24	-94.9(5)
C8—C9—C10—C11	1.7(12)	C21—C22—C23—Rh	93.3(5)
C9—C10—C11—C12	-1.1(12)	O1—Rh—C23—C22	-152.0(5)
C10—C11—C12—C7	0.2(11)	C20—Rh—C23—C22	-66.9(5)
C10—C11—C12—P2	178.4(6)	C19—Rh—C23—C22	-102.6(5)
C8—C7—C12—C11	0.1(10)	P2—Rh—C23—C22	85.8(4)
P1—C7—C12—C11	-177.1(5)	O1—Rh—C23—C24	-48.4(10)
C8—C7—C12—P2	-178.0(5)	C22—Rh—C23—C24	103.6(8)
P1—C7—C12—P2	4.8(9)	C20—Rh—C23—C24	36.7(6)
C13—P2—C12—C11	-42.5(6)	C19—Rh—C23—C24	1.0(6)
C16—P2—C12—C11	56.6(6)	P2—Rh—C23—C24	-170.7(5)
Rh—P2—C12—C11	-176.4(5)	C20—C19—C24—C25	34.7(8)
C13—P2—C12—C7	135.6(6)	Rh—C19—C24—C25	106.3(5)
C16—P2—C12—C7	-125.3(6)	C20—C19—C24—C23	-70.4(8)
Rh—P2—C12—C7	1.8(6)	Rh—C19—C24—C23	1.2(7)
C12—P2—C13—C17	-37.9(7)	C22—C23—C24—C25	-33.0(8)
C16—P2—C13—C17	-143.0(6)	Rh—C23—C24—C25	-105.7(7)
Rh—P2—C13—C17	97.2(6)	C22—C23—C24—C19	71.4(8)
C12—P2—C13—C14	97.1(5)	Rh—C23—C24—C19	-1.3(7)
C16—P2—C13—C14	-8.0(5)	C19—C24—C25—C21	-52.2(7)
Rh—P2—C13—C14	-127.9(4)	C23—C24—C25—C21	51.0(8)
C17—C13—C14—C15	166.1(7)	C22—C21—C25—C24	-51.3(7)
P2—C13—C14—C15	31.8(7)	C20—C21—C25—C24	52.1(8)