Supporting Information

Rh-Catalyzed [7+1] Cycloaddition of Buta-1,3-dienylcyclopropanes and CO for the Synthesis of Cyclooctadienones

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1. General Methods of Synthesis

Unless otherwise noted, air- and moisture-sensitive reactions were carried out in oven-dried (110 ºC) glassware capped with rubber septa under a positive pressure of dry argon from a balloon. Likewise, air- and moisture-sensitive reagents, solvents, and solutions were transferred via syringe or stainless steel cannula under a dry inert atmosphere. Stirring was achieved using oven-dried (110 ºC) Teflon-coated magnetic stir bars cooled under a stream of dry nitrogen or argon. Reaction temperatures refer to the external temperature or to the temperature of the bath in which the reaction vessel was partially immersed. Reactions were stirred using Teflon-coated magnetic stir bars. Room temperature indicates an ambient indoor temperature in the range of 10-30 ºC. Elevated temperatures were maintained using thermostat-controlled silicone oil baths. Temperatures of 0 ºC and –78 ºC refer to the bath temperatures achieved with an ice/water slurry or a dry ice/acetone mixture, respectively. Organic solutions were concentrated using a Büchi rotary evaporator with a membrane vacuum pump.

Tetrahydrofuran and diethyl ether were distilled from sodium and benzophenone prior to use. Dioxane (extra dry, water < 50 ppm，purchased from Alfa Aesar), $[Rh(CO)_2Cl]_2$ (purchased from Across) was commercially available and used as received. Analytical TLC was performed with 0.25 mm silica gel 60F plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Varian Mercury Plus 300 (^{1}H at 300 MHz, ^{13}C at 75 MHz) or Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, td = triplet of doublets, br = broad, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm^{-1}). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded

on Waters micromass GCT (EI, 70 eV) and Bruker APEX IV (ESI) mass spectrometers.

Abbreviations:

THF: tetrehydrofuran

PDC: pyridinium dichromate

DIBAL-H: diisobutylaluminum hydride

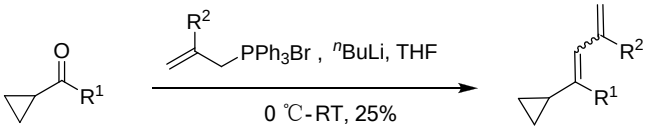
DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene

TEA: triethylamine

TBSOTf: *tert*-butyldimethylsilyl trifluoromethanesulfonate

DCM: dichloromethane

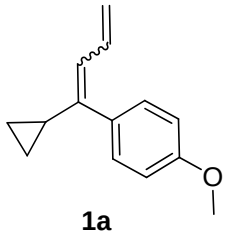
2. General Procedure for the Synthesis of BDCPs 1a-1g, and 1i-1l



1a-1g, 1i-1l

To an oven-dried round-bottomed flask with a stir bar was added allyltriphenylphosphonium bromide (12 mmol, 1.2 equiv.) and THF (40 mL). The solution was cooled to 0 ℃ and 4.8 mL (12 mmol, 1.2 equiv.) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 ℃, ketone (10 mmol, 1.0 equiv.) in 6 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 24 hours. The reaction was then quenched with 10 mL brine and diluted with 50 mL of diethyl ether. The organic layer was separated and the aqueous layer was extracted by diethyl ether in one time. The combined organic layers were dried over Na_2SO_4, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford the buta-1,3-dienylcyclopropane.

1-(1-Cyclopropylbuta-1,3-dienyl)-4-methoxybenzene (**1a**)



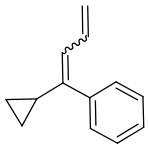
1a

A 2.5:1 mixture of (*Z*:*E*)-1-(1-cyclopropylbuta-1,3-dienyl)-4-methoxybenzene (820 mg, 4.1 mmol, 41 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a doublet at 6.05 ppm for the (*Z*)-1-(1-cyclopropylbuta-1,3-dienyl)-4-methoxybenzene and a quartet at 5.25 ppm for the (*E*)-olefin. The *Z* (**1a-*Z***) and *E* (**1a-*E***) isomers of **1a** were obtained as pure compounds by flash chromatography. The determination of the *Z* and *E* isomers were deduced by analogy to the *Z* and *E* isomers of **1b**.[1]

IR (film): 3002, 2834, 1630, 1607, 1509, 1464, 1287, 1245, 1179, 1119, 1036 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.15-7.13 (d, J = 8.4 Hz, 2H), 6.89-6.86 (d, J = 8.4 Hz, 2H), 6.32-6.23 (dt, J = 17.2 and 10.4 Hz, 1H), 6.07-6.04 (d, J = 10.8 Hz, 1H), 5.16-5.11 (dd, J = 16.8 and 1.6 Hz, 1H), 4.90-4.87 (dd, J = 10.4 and 1.6 Hz, 1H), 3.81 (s, 3H), 1.64-1.56 (m, 1H), 0.74-0.69 (m, 2H), 0.54-0.50 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.6, 144.8, 134.8, 132.1, 130.1, 125.0, 115.1, 113.3, 55.2, 18.5, 6.1. HRMS (ESI+) for $C_{14}H_{17}O$ $(M+H)^+$: calculated: 201.1274, found: 201.1271.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39-7.37 (d, J = 8.8 Hz, 2H), 7.13-7.03 (dt, J = 16.8 and 10.8 Hz, 1H), 6.85-6.83 (d, J = 8.8 Hz, 2H), 6.36-6.33 (d, J = 10.8 Hz, 1H), 5.27-5.23 (dd, J = 17.2 and 1.6 Hz, 1H), 5.18-5.14 (dd, J = 10.4 and 1.6 Hz, 1H), 3.80 (s, 3H), 1.82-1.75 (m, 1H), 0.91-0.86 (m, 2H), 0.41-0.37 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.6, 141.7, 134.3, 133.9, 129.1, 128.1, 116.9, 113.2, 55.2, 11.6, 7.2.

(1-Cyclopropylbuta-1,3-dienyl)benzene (**1b**)



1b

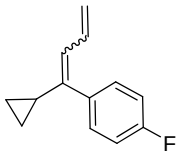
A 2.9:1 mixture of (*Z*:*E*)-(1-cyclopropylbuta-1,3-dienyl)benzene[1] (1292 mg, 7.6 mmol, 76 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of

one of the olefinic protons : a doublet at 6.08 ppm for the (*Z*)-(1-cyclopropylbuta-1,3-dienyl)-benzene and a doublet at 6.39 ppm for the (*E*)-olefin. The NMR signals of *Z* and *E* isomers were determined by the analysis of NOESY study and the previous report.[1]

IR (film): 3095, 3020, 3015, 1635, 1610, 1025 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33-7.19 (m, 5H), 6.28-6.19 (dt, J = 16.8 and 10.4 Hz, 1H), 6.09-6.07 (d, J = 10.8 Hz, 1H), 5.17-5.12 (dd, J = 16.8 and 1.6 Hz, 1H), 4.91-4.88 (dd, J = 10.0 and 1.6 Hz, 1H), 1.67-1.60 (m, 1H), 0.75-0.70 (m, 2H), 0.54-0.50 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.3, 139.8, 134.5, 129.0, 127.9, 127.0, 125.3, 115.4, 18.5, 6.1. HRMS (EI+) for $C_{13}H_{14}$ $(M)^+$: calculated: 170.1096, found: 170.1098.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43-7.22 (m, 5H), 7.14-7.04 (dt, J = 16.8 and 10.8 Hz, 1H), 6.40-6.37 (d, J = 11.2 Hz, 1H), 5.30-5.26 (dd, J = 16.8 and 1.2 Hz, 1H), 5.22-5.18 (dd, J = 10.0 and 1.2 Hz, 1H), 1.87-1.80 (m, 1H), 0.91-0.87 (m, 2H), 0.41-0.37 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.3, 141.8, 133.8, 130.3, 127.8, 127.0, 126.8, 117.6, 11.6, 7.2.

1-(1-Cyclopropylbuta-1,3-dienyl)-4-fluorobenzene (**1c**)



1c

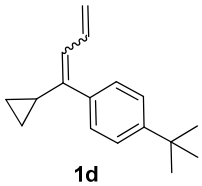
A 2.9:1 mixture of (*Z*:*E*)-1-(1-cyclopropylbuta-1,3-dienyl)-4-fluorobenzene (1524 mg, 8.1 mmol, 81 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a doublet at 6.08 ppm for the (*Z*)-1-(1-cyclopropylbuta-1,3-dienyl)-4-fluorobenzene and a doublet at 6.33 ppm for the (*E*)-olefin.

IR (film): 3075, 3007, 2917, 2849, 1632, 1603, 1507, 1420, 1223, 1158, 1094, 1022 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18-6.96 (m, 4H), 6.25-6.15 (dt, J = 16.8 and 10.8 Hz, 1H), 6.09-6.06 (d, J = 11.2 Hz, 1H), 5.18-5.13 (dd, J = 16.8 and 2.0 Hz, 1H), 4.93-4.90 (dd, J = 10.0 and 2.0 Hz, 1H), 1.64-1.57 (m, 1H), 0.75-0.71 (m, 2H), 0.52-0.48 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.2, 160.7, 144.1, 134.2, 130.6, 130.5, 125.7, 115.8, 115.0, 114.7, 18.5, 6.1. HRMS (EI+) for $C_{13}H_{13}F$ $(M)^+$: calculated: 188.1001, found: 188.1004.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.36 (m, 2H),

7.11-7.02 (dt, J = 16.8 and 10.8 Hz, 1H), 7.05-6.96 (m, 2H), 6.35-6.32 (d, J = 10.8 Hz, 1H), 5.30-5.26 (dd, J = 16.8 and 2.0 Hz, 1H), 5.22-5.19 (dd, J = 10.0 and 2.0 Hz, 1H), 1.84-1.77 (m, 1H), 0.92-0.87 (m, 2H), 0.39-0.35 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.0, 162.4, 141.3, 137.9, 135.7, 135.6, 133.7, 130.3, 128.6, 128.5, 117.8, 114.8, 114.6, 11.7, 7.2.

1-tert-Butyl-4-(1-cyclopropylbuta-1,3-dienyl)benzene (**1d**)



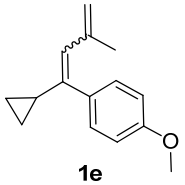
1d

A 1.9:1 mixture of (*Z*:*E*)-1-tert-butyl-4-(1-cyclopropylbuta-1,3-dienyl)benzene (1584 mg, 7.0 mmol, 70 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a doublet at 6.04 ppm for the (*Z*)-1-tert-butyl-4-(1-cyclopropylbuta-1,3-dienyl)benzene and a doublet at 6.40 ppm for the (*E*)-olefin.

IR (film): 3084, 2963, 2903, 2870, 1670, 1631, 1510, 1462, 1420, 1394, 1363, 1269, 1202, 1116, 1100, 1022 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (d, J = 8.4, 2H), 7.17-7.14 (d, J = 8.4 Hz, 2H), 6.35-6.26 (dt, J = 16.8 and 10.8 Hz, 1H), 6.06-6.04 (d, J = 10.8, 1H), 5.16-5.12 (dd, J = 16.8 and 1.6 Hz, 1H), 4.91-4.88 (dd, J = 10.0 and 1.6 Hz, 1H), 1.66-1.59 (m, 1H), 1.33 (s, 9H), 0.75-0.70 (m, 2H), 0.56-0.53 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.8, 145.2, 134.8, 128.6, 126.6, 124.9, 124.7, 115.2, 34.5, 31.4, 18.5, 6.3. HRMS (EI+) for $C_{17}H_{22}$ $(M)^+$: calculated: 226.1722, found: 226.1724.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (d, J = 8.8, 2H), 7.33-7.31 (d, J = 8.8, 2H), 7.14-7.05 (dt, J = 16.8 and 10.8 Hz, 1H), 6.42-6.35 (d, J = 10.8 Hz, 1H), 5.29-5.24 (dd, J = 16.8 and 2.0 Hz, 1H), 5.19-5.16 (dd, J = 10.8 and 2.0 Hz, 1H), 1.84-1.77 (m, 1H), 1.31 (s, 9H), 0.92-0.86 (m, 2H), 0.43-0.39 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.7, 142.0, 138.8, 136.9, 134.0, 129.8, 124.7, 117.2, 34.4, 31.3, 11.6, 7.3.

1-(1-Cyclopropyl-3-methylbuta-1,3-dienyl)-4-methoxybenzene (**1e**)



1e

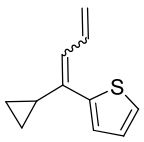
A 2.0:1 mixture of (*Z*:*E*)-1-(1-cyclopropyl-3-methylbuta-1,3-dienyl)-4-methoxybenzene (535 mg,

2.5 mmol, 25 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a singlet at 6.10 ppm for the (*Z*)-1-(1-cyclopropyl-3-methylbuta-1,3-dienyl)-4-methoxybenzene and a singlet at 6.02 ppm for the (*E*)-olefin.

IR (film): 3001, 2918, 2835, 1608, 1509, 1455, 1434, 1329, 1286, 1245, 1174, 1036 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.05-7.03 (d, J = 8.8 Hz, 2H), 6.83-6.81 (d, J = 8.8 Hz, 2H), 6.10 (s, 1H), 4.77 (s, 1H), 4.74 (s, 1H), 3.80 (s, 3H), 1.64-1.57 (m, 1H), 1.36 (s, 3H), 0.65-0.61 (m, 2H), 0.43-0.39 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.5, 142.6, 142.4, 130.2, 128.9, 127.4, 116.0, 113.0, 55.1, 22.4, 20.1, 5.1. HRMS (ESI+) for $C_{15}H_{19}O$ $(M+H)^+$: calculated: 215.1430, found: 215.1430.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (d, J = 8.8 Hz, 2H), 6.83-6.81 (d, J = 8.8 Hz, 1H), 6.02 (s, 1H), 5.13 (s, 1H), 5.08 (s, 1H), 3.80 (s, 3H), 2.00 (s, 3H), 1.97-1.91 (m, 1H), 0.82-0.77 (m, 2H), 0.39-0.35 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.4, 141.9, 141.8, 135.0, 132.0, 130.7, 115.4, 113.1, 55.2, 23.8, 13.3, 8.0.

2-(1-Cyclopropylbuta-1,3-dienyl)thiophene (**1f**)



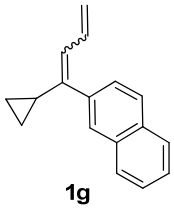
1f

A 4.0:1 mixture of (*Z*:*E*)-2-(1-cyclopropylbuta-1,3-dienyl)thiophene (1250 mg, 7.1 mmol, 71 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a doublet at 6.11 ppm for the (*Z*)-2-(1-cyclopropylbuta-1,3-dienyl)thiophene and a doublet at 6.55 ppm for the (*E*)-olefin.

IR (film): 3081, 3007, 1618, 1432, 1381, 1304, 1237, 1098, 1022 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29-7.27 (dd, J = 4.8 and 1.2 Hz, 1H), 7.06-7.04 (dd, J = 3.6 and 1.2 Hz, 1H), 7.03-7.01 (dd, J = 4.8 and 3.6 Hz, 1H), 6.78-6.68 (dt, J = 16.8 and 10.8 Hz, 1H), 6.13-6.10 (d, J = 10.8 Hz, 1H), 5.29-5.24 (dd, J = 16.8 and 1.6 Hz, 1H), 5.07-5.05 (dd, J = 10.4 and 1.6 Hz, 1H), 1.74-1.68 (m, 1H), 0.81-0.76 (m, 2H), 0.65-0.62 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.1, 136.5, 134.2, 126.8, 126.7, 126.6, 125.1, 117.3, 19.3, 6.5. HRMS (ESI+) for $C_{11}H_{13}S$ $(M+H)^+$: calculated: 177.0733, found: 177.0730.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.24-7.23 (d, J = 2.8 Hz, 1H), 7.15-7.14 (d, J = 5.2 Hz, 1H), 7.10-7.04 (dt, J = 17.2 and 10.4 Hz, 1H), 6.98-6.96 (dd, J = 5.2 and 2.8 Hz, 1H), 6.57-6.54 (d, J = 10.4 Hz, 1H), 5.31-5.26 (dd, J = 17.2 and 1.2 Hz, 1H), 5.21-5.18 (dd, J = 10.4 and 1.2 Hz, 1H), 0.98-0.92 (m, 2H), 0.90-0.83 (m, 1H), 0.62-0.58 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.7, 135.3, 133.6, 128.8, 127.3, 124.3, 124.0, 117.9, 12.0, 7.3.

2-(1-Cyclopropylbuta-1,3-dienyl)naphthalene (**1g**)



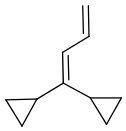
1g

A 2.2:1 mixture of (*Z*:*E*) 2-(1-cyclopropylbuta-1,3-dienyl)naphthalene (1125 mg, 5.1 mmol, 51 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a doublet at 6.21 ppm for the (*Z*)-2-(1-cyclopropylbuta-1,3-dienyl) naphthalene and a doublet at 6.58 ppm for the (*E*)-olefin.

IR (film): 3056, 3006, 1629, 1599, 1502, 1416, 1130, 1051, 1021 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88-7.83 (m, 3H), 7.69 (s, 1H), 7.53-7.46 (m, 2H), 7.41-7.39 (dd, J = 8.4 and 1.6, 1H), 6.37-6.27 (dt, J = 16.8 and 10.8 Hz, 1H), 6.22-6.20 (d, J = 10.8 Hz, 1H), 5.25-5.20 (dd, J = 16.8 and 2.0 Hz, 1H), 4.96-4.93 (dd, J = 10.0 and 2.0 Hz, 1H), 1.79-1.72 (m, 1H), 0.83-0.78 (m, 2H), 0.68-0.60 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.2, 137.3, 134.6, 133.9, 132.5, 130.9, 127.9, 127.6, 127.5, 127.4, 126.0, 125.8, 125.7, 115.6, 18.6, 6.3. HRMS (EI+) for $C_{17}H_{16}$ $(M)^{+}$: calculated: 220.1252, found: 220.1254.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.88-7.79 (m, 3H), 7.64-7.61 (dd, J = 8.4 and 1.6 Hz, 1H), 7.53-7.45 (m, 2H), 7.24-7.14 (dt, J = 16.8 and 10.8 Hz, 1H), 6.60-6.57(d, J = 10.8 Hz, 1H), 5.40-5.35 (dd, J = 16.8 and 1.6 Hz, 1H), 5.30-5.27 (dd, J = 10.8 and 1.6 Hz, 1H), 1.98-1.93 (m, 1H), 1.01-0.97 (m, 2H), 0.50-0.45 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.2, 139.3, 134.6, 133.9, 133.3, 133.1, 128.1, 127.7, 127.5, 127.2, 126.0, 125.6, 125.4, 117.9, 11.7, 7.4.

Buta-1,3-diene-1,1-diyldicyclopropane (**1i**)

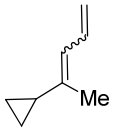


1i

Buta-1,3-diene-1,1-diyldicyclopropane[2] (400 mg, 3.0 mmol, 30 %) as a colorless liquid was obtained.

IR (film): 3083, 3009, 1633, 1421, 1288, 1049, 1020 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.88-6.78 (dt, J = 16.8 and 10.3 Hz, 1H), 5.78-5.75 (d, J = 10.8 Hz, 1H), 5.13-5.08 (dd, J = 16.8 and 2.0 Hz, 1H), 5.01-4.98 (dd, J = 10.1 and 2.0 Hz, 1H), 1.88-1.81 (m, 1H), 1.03-0.98 (m, 1H), 0.80-0.75 (m, 2H), 0.75-0.70 (m, 2H), 0.60-0.55 (m, 2H), 0.44-0.40 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.8, 133.1, 123.5, 114.9, 13.1, 5.6, 5.3. HRMS (EI+) for $C_{10}H_{14}$ $(M)^+$: calculated: 134.1096, found: 134.1098.

Penta-2,4-dien-2-ylcyclopropane (**1j**)



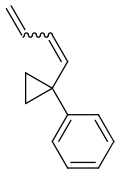
1j

A 0.3:1 mixture of (*Z*:*E*)-penta-2,4-dien-2-ylcyclopropane[3] (280 mg, 2.6 mmol, 26 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of the methyl protons : a singlet at 1.49 ppm for the (*Z*)-penta-2,4-dien-2-ylcyclopropane and a singlet at 1.62 ppm for the (*E*)-olefin.

IR (film): 2955, 2921, 1644, 1460, 1015 cm^{-1}. (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.63-6.53 (dt, J = 16.8 and 10.8 Hz, 1H), 5.93-5.90 (d, J = 10.8 Hz, 1H), 5.10-5.05 (dd, J = 16.8 and 2.0 Hz, 1H), 4.96-4.93 (dd, J = 10.8 and 2.0 Hz, 1H), 1.62 (s, 3H), 1.47-1.40 (m, 1H), 0.64-0.58 (m, 2H), 0.55-0.51 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.0, 133.2, 123.9, 114.1, 19.1, 14.0, 4.9. HRMS (EI+) for C_8H_{12} $(M)^+$: calculated: 108.0939, found: 108.0941.

Additional signals for the (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.86-6.76 (dt, J = 16.8 and 10.8 Hz, 1H), 5.95-5.93 (d, J = 10.8 Hz, 1H), 5.12-5.07 (dd, J = 16.8 and 2.0 Hz, 1H), 5.00-4.97 (dd, J = 10.8 and 2.0 Hz, 1H), 1.90-1.85 (m, 1H), 1.49 (s, 3H), 0.73-0.58 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 139.1, 132.8, 126.8, 114.4, 19.0, 12.9, 4.7.

(1-(Buta-1,3-dienyl)cyclopropyl)benzene (**1k**)



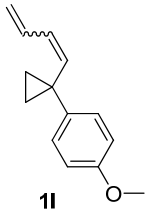
1k

A 3.0:1 mixture of (*Z*:*E*)-(1-(buta-1,3-dienyl)cyclopropyl)benzene (1160 mg, 6.8 mmol, 68 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a doublet of the triplets at 6.59 ppm for the (*Z*)-(1-(buta-1,3-dienyl)-cyclopropyl)benzene and a doublet of the triplets at 6.29 ppm for the (*E*)-olefin.

IR (film): 2928, 2861, 1600, 1500, 1089, 1005 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.32-7.12 (m, 5H), 6.66-6.53 (dt, J = 16.8 and 11.1 Hz, 1H), 6.13-6.06 (t, J = 11.1 Hz, 1H), 5.72-5.68 (d, J = 10.5 Hz, 1H), 5.18-5.11 (dd, J = 16.8 and 1.6 Hz, 1H), 5.06-5.01 (dd, J = 10.2 and 1.6 Hz, 1H), 1.10-1.00 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 144.9, 135.0, 133.3, 132.0, 128.3, 126.7, 125.6, 118.0, 23.9, 17.5. HRMS (EI+) for $C_{13}H_{14}$ $(M)^+$: calculated: 170.1096, found: 170.1098.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.32-7.12 (m, 5H), 6.36-6.21 (dt, J = 16.8 and 8.4 Hz, 1H), 5.62-5.55(m, 2H), 5.62-5.59 (d, J = 8.4 Hz, 1H), 4.98-4.92 (dd, J = 16.8 and 1.8 Hz, 1H), 4.90-4.86 (dd, J = 10.0 and 1.6 Hz, 1H), 1.14-1.08 (m, 2H), 0.98-0.78 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.3, 136.8, 129.9, 128.8, 128.2, 126.5, 114.5, 114.6, 22.7, 15.3

1-(1-(Buta-1,3-dienyl)cyclopropyl)-4-methoxybenzene (**1l**)



1l

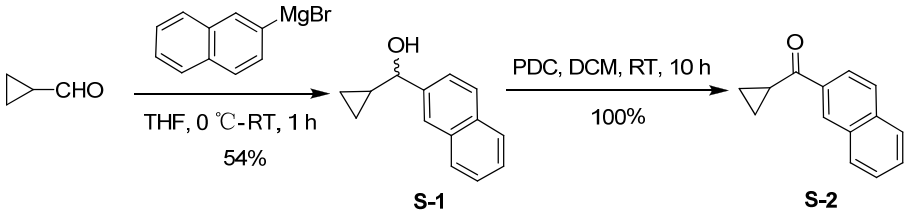
A 5.4:1 mixture of (*Z*:*E*)-1-(1-(buta-1,3-dienyl)cyclopropyl)-4-methoxybenzene (1480 mg, 7.4 mmol, 74 %) as a colorless liquid was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of the methyl protons : a singlet at 3.77 ppm for the (*Z*)-1-(1-(buta-1,3-dienyl)-cyclopropyl)-4-methoxybenzene and a singlet at 3.80 ppm for the (*E*)-olefin.

IR (film): 3089, 2962, 1684, 1513, 1246, 1183, 1038, 1006 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18-7.16 (d, J = 8.4 Hz, 2H), 6.82-6.80 (d, J = 8.4 Hz, 2H), 6.62-6.52 (dt, J = 16.8 and

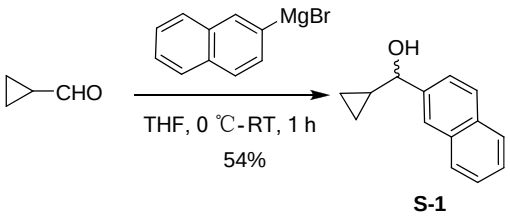
10.8 Hz, 1H), 6.07-6.01 (t, J = 10.8 Hz, 1H), 5.65-5.62 (d, J = 10.4 Hz, 1H), 5.15-5.11 (d, J = 16.8 Hz, 1H), 5.04-5.01 (d, J = 10.0 Hz, 1H), 3.77 (s, 3H), 1.10 (br s, 2H), 1.01 (br s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.6, 136.8, 135.6, 133.2, 131.2, 128.1, 117.5, 113.6, 65.7, 23.6, 15.1. HRMS (ESI+) for $C_{14}H_{17}O$ $(M+H)^+$: calculated: 201.1274, found: 201.1273.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.24-7.22 (d, J = 8.8 Hz, 2H), 6.86-6.84 (d, J = 8.4 Hz, 2H), 6.33-6.24 (dt, J = 16.8 and 10.0 Hz, 1H), 5.62-5.55 (dd, J = 15.2 and 10.0 Hz, 1H), 5.55-5.51 (d, J = 15.2 Hz, 1H), 4.96-4.92 (d, J = 16.8 Hz, 1H), 4.88-4.86 (d, J = 10.0 Hz, 1H), 3.80 (s, 3H), 1.06 (br s, 2H), 0.96 (br s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.1, 142.7, 136.8, 135.0, 130.9, 128.6, 114.2, 113.5, 55.1, 27.4, 16.8.

3. Synthesis of Cyclopropyl(naphthalen-2-yl)methanone (S-2)



Cyclopropyl(naphthalen-2-yl)methanol (**S-1**)



Cyclopropanecarbaldehyde (0.70 g, 10.0 mmol, in 80 mL THF) was cooled to 0 ^{o}C. Naphthalen-2-ylmagnesium bromide (12.0 mmol, in 80 mL THF, prepared by the literature[4] method) was added slowly to the above cyclopropanecarbaldehyde solution. The solution was then stirred under 0 ^{o}C for 30 minutes before it was poured into the mixture of 50 g ice and 50 mL water. After extracted with Et_2O, washed with water, and brine, dried over $MgSO_4$, and concentrated in vacuo, the crude mixture was purified by flash column chromotography to afford 1.07 g (54%) **S-1** as a light yellow liquid.

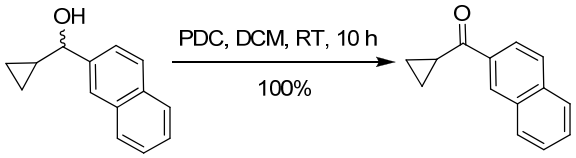
IR (film): 3372, 2917, 1602, 1508, 1363, 1270, 1028 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84-7.82 (m, 4H), 7.57-7.55 (d, J = 9.6 Hz, 1H), 7.49-7.44 (m, 2H), 4.16-4.14 (d, J = 8.4 Hz, 1H), 2.17 (br s, 1H), 1.33-1.23 (m, 1H), 0.70-0.63 (m, 1H),

0.60-0.48 (m, 2H), 0.45-0.39 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.2, 133.3, 133.0, 128.1, 128.0, 127.6, 126.0, 125.7, 124.5, 124.4, 78.6, 19.2, 3.7, 2.9.

HRMS (ESI+) for $C_{14}H_{14}NaO$ $(M+Na)^+$: calculated: 221.0937, found: 221.0935.

Cyclopropyl(naphthalen-2-yl)methanone (**S-2**)[5]



S-1 **S-2**

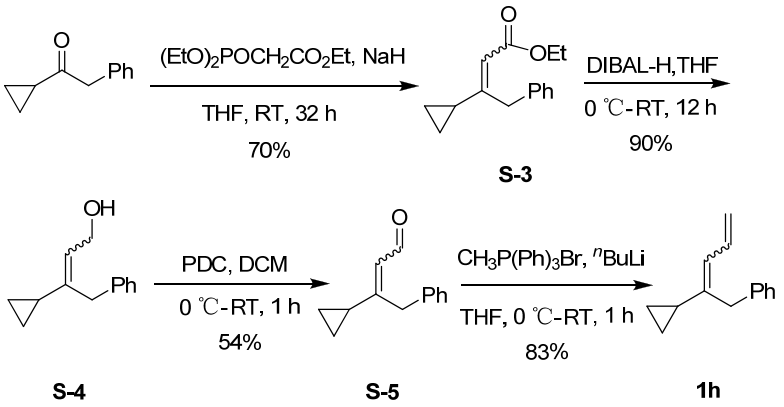
Cyclopropyl(naphthalen-2-yl)methanol (**S-1**) (0.99 g, 5.0 mmol) was dissolved in 100 mL anhydrous CH_2Cl_2 and cooled to 0 °C. Then PDC (3.70 g, 10.0 mmol) was added in batches and the resulting solution was stirred for 10 h at room temperature. The product mixture was filtered through a short silica gel column. Then the filtrate was concentrated to afford 0.98 g (70%) **S-2** as a white solid (melting point: 117-118 °C).

IR (film): 3082, 3021, 2927, 1660, 1392, 1278, 1220, 1125, 1040 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.08-8.05 (dd, J = 8.4 and 1.6 Hz, 1H), 7.99-7.97 (d, J = 8.0 Hz, 1H), 7.92-7.88 (t, J = 8.4 Hz, 2H), 7.62-7.54 (m, 2H), 2.88-2.82 (m, 1H), 1.33-1.29 (m, 2H), 1.13-1.08 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.4, 135.5, 135.4, 132.6, 129.5, 128.3, 128.2, 127.8, 126.7, 124.0, 17.2, 11.7.

HRMS (ESI+) for $C_{14}H_{13}O$ $(M+H)^+$: calculated: 197.0961, found: 197.0960.

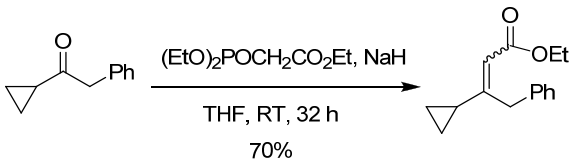
4. Synthesis of (2-Cyclopropylpenta-2,4-dienyl)benzene (1h)



S-3

S-4 **S-5** **1h**

Ethyl-3-cyclopropyl-4-phenylbut-2-enoate (**S-3**)



S-3

To a flask containing NaH (0.48 g, 20.0 mmol) and 80 mL THF at 0 °C was added triethyl phosphonoacetate (4.48 g, 20.0 mmol). After stirring at room temperature for 30 min, 1-cyclopropyl-2-phenylethanone (3.2 g, 20.0 mmol, prepared by literature[6] method) was added dropwise and the reaction was allowed to stir for 32 hours. After quenching with brine, extracting with Et_2O, and drying over $MgSO_4$, concentration of the organic phase in vacuo gave a crude oil that was further purified by flash chromatography to afford 3.22 g (70%) **S-3** as a colorless oil.

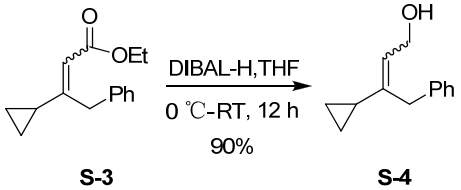
A 0.9:1 mixture of (*Z*:*E*)-Ethyl-3-cyclopropyl-4-phenylbut-2-enoate was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of the olefinic proton: a singlet at 5.55 ppm for the (*Z*)-Ethyl-3-cyclopropyl-4-phenylbut-2-enoate and a singlet at 5.61 ppm for the (*E*)-olefin.

IR (film): 2982, 1709, 1637, 1239, 1153, 1037 cm^{-1}.

(*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.11 (m, 5H), 5.55 (s, 1H), 4.17-4.10 (q, J = 7.2 Hz, 2H), 3.25-3.16 (m, 1H), 3.08 (s, 2H), 1.27-1.23 (t, J = 7.2 Hz, 3H), 0.90-0.80 (m, 2H), 0.73-0.69 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.1, 162.3, 138.0, 128.9, 128.5, 126.4, 118.4, 59.5, 37.6, 13.7, 7.0. HRMS (ESI+) for $C_{15}H_{19}O_2$ $(M+H)^+$: calculated: 231.1380, found: 231.1376.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.11 (m, 5H), 5.61 (s, 1H), 4.19-4.12 (q, J = 7.2 Hz, 2H), 4.08 (s, 2H), 1.46-1.37 (m, 1H), 1.29-1.24 (t, J = 7.2 Hz, 3H), 0.78-0.74 (m, 2H), 0.60-0.54 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.7, 163.1, 139.0, 128.7, 128.3, 126.0, 112.7, 59.6, 37.4, 18.1, 14.2, 8.4.

3-Cyclopropyl-4-phenylbut-2-en-1-ol (**S-4**)



S-3 **S-4**

To a Schlenk flask charged with ethyl 3-cyclopropyl-4-phenylbut-2-enoate (**S-3**) **(**2.99 g, 13 mmol) in THF at 0 °C was added DIBAL-H (29 mL, 1 M in toluene, 29 mmol) dropwise. The reaction was warmed to room temperature overnight and was quenched with ethylacetate and aqueous potassium tartrate tetrahydrate. Stirring was continued until the solution was clear. Extracted with Et_2O, washed with brine, dried over $MgSO_4$, evaporation and purification by flash column chromatography to provide 2.20 g (90%) **S-4** as a clear, colorless oil.

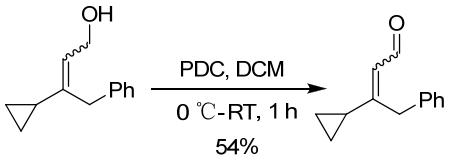
A 0.67:1 mixture of (*Z*:*E*)-3-cyclopropyl-4-phenylbut-2-en-1-ol was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the methylene protons : a singlet at 3.34 ppm for the (*Z*)-3-cyclopropyl-4-phenylbut-2-en-1-ol and a singlet at 3.13 ppm for the (*E*)-olefin.

IR (film): 3354, 3083, 3025, 2923, 1657, 1602, 1494, 1452, 1029 cm^{-1}.

(*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 2H), 7.20-7.16 (m, 3H), 5.53-5.50 (t, J = 7.2 Hz, 1H), 4.23-4.21 (d, J = 7.2 Hz, 2H), 3.43 (s, 2H), 1.57-1.50 (m, 1H), 1.52 (br s, 1H), 0.58-0.54 (m, 2H), 0.43-0.39 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.9, 139.8, 128.4, 127.8, 122.6, 59.3, 36.4, 17.0, 5.8. HRMS (ESI+) for $C_{13}H_{16}NaO$ $(M+Na)^+$: calculated: 211.1093, found: 211.1094.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 2H), 7.20-7.16 (m, 3H), 5.42-5.38 (td, J = 6.8 and 0.8 Hz, 1H), 4.35-4.33 (d, J = 6.8 Hz, 2H), 3.13 (s, 2H), 1.52 (br s, 1H), 1.33-1.26 (m, 1H), 0.67-0.62 (m, 2H), 0.52-0.48 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.0, 139.7, 128.9, 128.4, 128.2, 126.0, 59.2, 40.2, 12.1, 5.1.

3-Cyclopropyl-4-phenylbut-2-enal (**S-5**)



S-4 **S-5**

3-Cyclopropyl-4-phenylbut-2-en-1-ol (**S-4**) (2.10 g, 11.2 mmol) was dissolved in 100 mL anhydrous CH_2Cl_2 and cooled to 0 ^{o}C. Then PDC (6.3 g, 16.8 mmol) was added in batches and the resulting solution was stirred for 1 hour at room temperature. The product mixture was filtered through a short silica gel column. Then the filtrate was concentrated to get 1.12 g (54%) **S-5** as a light yellow liquid.

A 0.5:1 mixture of (*Z*:*E*)-3-cylopropyl-4-phenylbut-2-enal was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the methylene protons : a singlet at 3.23 ppm for the (*Z*)-3-cyclopropyl-4-phenylbut-2-enal and a singlet at 3.94 ppm for the (*E*)-olefin.

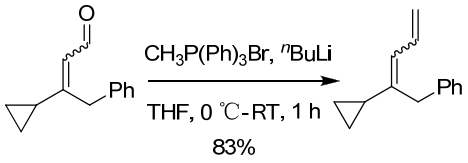
IR (film): 2989, 2901, 1668, 1613, 1491, 1449, 1261, 1159, 1030 cm^{-1}.

(*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.25-10.23 (d, J = 8.0 Hz, 1H), 7.34-7.21 (m, 3H), 7.13-7.12 (d, J = 7.2 Hz, 2H), 5.77-5.75 (d, J = 8.0 Hz, 1H), 3.23 (s, 2H), 2.46-2.39 (m, 1H), 0.99-0.93 (m, 2H), 0.92-0.85 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ191.0, 166.0, 137.2, 130.0, 129.0, 128.7, 124.1, 39.2, 13.2, 7.4. HRMS (ESI+) for $C_{13}H_{15}O$ $(M+H)^+$: calculated: 187.1117,

found: 187.1119.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.05-10.03 (d, J = 8.0 Hz, 1H), 7.34-7.21 (m, 5H), 5.86-5.84 (d, J = 8.0 Hz, 1H), 3.94 (s, 2H), 1.50-1.43 (m, 1H), 0.92-0.85 (m, 2H), 0.72-0.68 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 190.7, 167.9, 137.7, 128.7, 128.5, 126.8, 124.1, 36.8, 18.3, 10.0.

(2-Cyclopropylpenta-2,4-dienyl)benzene (**1h**)



S-5 **1h**

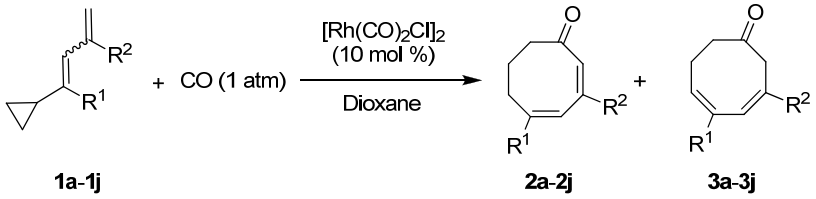
To a flask containing methyltriphenylphosphonium bromide (2.68 g, 7.5 mmol) and 80 mL THF at 0 °C was added n-butyllithium (7.5 mL, 1 M in hexane, 7.5 mmol). After stirring at 0 °C for 30 minutes, 3-cyclopropyl-4-phenylbut-2-enal (**S-5**) (9.30 g, 5.0 mmol, in 10 mL THF) was added dropwise and the reaction was allowed to stir for 1 hour. After quenching with brine, extracting with Et_2O, and drying over $MgSO_4$, concentration of the organic phase in vacuo gave a crude oil which was further purified by flash chromatography to afford 0.76 g (83%) **1h** as a colorless oil.

A 0.8:1 mixture of (*Z*:*E*)-(2-cyclopropylpenta-2,4-dienyl)benzene was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the methylene protons : a singlet at 3.51 ppm for the (*Z*)- (2-cyclopropylpenta-2,4-dienyl)benzene and a singlet at 3.17 ppm for the (*E*)-olefin.

IR (film): 3084, 3027, 1637, 1602, 1494, 1453, 1422, 1030 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.28-7.16 (m, 5H), 6.72-6.63 (dt, J = 16.4 and 10.5 Hz, 1H), 5.99-5.97 (d, J = 10.9 Hz, 1H), 5.20-5.16 (d, J = 16.4 Hz, 1H), 5.04-5.02 (d, J = 8.4 Hz, 1H), 3.51 (s, 2H), 1.36-1.29 (m, 1H), 0.60-0.55 (m, 2H), 0.45-0.42 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.5, 140.0, 133.1, 128.8, 128.5, 128.3, 125.9, 115.7, 36.5, 17.3, 6.1. HRMS (EI+) for $C_{14}H_{16}$ $(M)^+$: calculated: 184.1252, found: 184.1254.

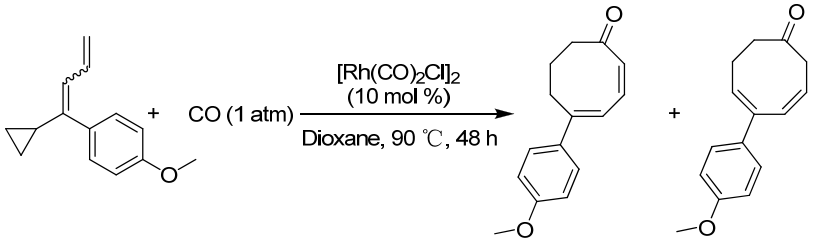
Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.28-7.16 (m, 5H), 6.93-6.84 (dt, J = 16.8 and 10.8 Hz, 1H), 5.89-5.86 (d, J = 10.8 Hz, 1H), 5.13-5.08 (d, J = 16.8 Hz, 1H), 5.06-5.04 (d, J = 8.4 Hz, 1H), 3.17 (s, 2H), 1.72-1.65 (m, 1H), 0.69-0.65 (m, 2H), 0.54-0.50 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.6, 140.0, 133.1, 129.3, 128.2, 126.0, 124.6, 115.7, 40.5, 12.5, 5.5.

5. General Procedure for the Rhodium(I)-Catalyzed [7+1] Cycloadditions



1a-1j **2a-2j** **3a-3j**

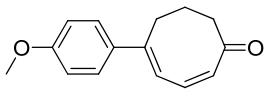
To an oven-dried Schlenk tube with a stir bar was added 7.8 mg $[Rh(CO)_2Cl]_2$ (0.02 mmol, 0.1 equvi), and the flask was purged with CO gas three times. Then a solution of buta-1,3-dienylcyclopropane (0.2 mmol, 1.0 equvi) in dried dioxane was added via cannula, and the solution was bubbled with CO gas for 3 min. Then the solution stirred under balloon pressured CO (1 atm) at indicated temperature until TLC showed the reaction was complete. The solvent was removed in vacuo, and the residue purified by flash chromatography on silica gel to give the final products..



1a (*Z*/*E* = 2.5) **2a** **3a**

39.0 mg 28.5 mg (64%) 4.5 mg (10%)

5-(4-Methoxyphenyl)cycloocta-2,4-dienone (**2a**)



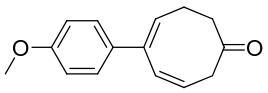
2a Yellow oil.

IR (film): 2917, 2848, 1653, 1605, 1581, 1512, 1462, 1403, 1285, 1248, 1206, 1182, 1126, 1027 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (d, J = 8.8 Hz, 2H), 6.93-6.91 (d, J = 8.8 Hz, 2H), 6.68-6.63 (dd, J = 12.4 and 6.4 Hz, 1H), 6.56-6.54 (d, J = 6.4 Hz, 1H), 5.98-5.95 (d, J = 12.4 Hz, 1H), 3.84 (s, 3H), 2.76-2.73 (t, J = 6.4 Hz, 2H), 2.69-2.66 (t, J = 6.4 Hz, 2H), 2.23-2.16 (p, J = 6.4

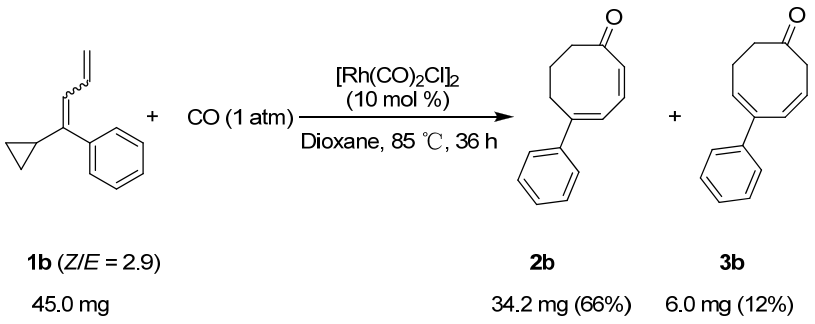
Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.6, 159.9, 148.4, 138.9, 133.1, 130.5, 127.4, 123.4, 114.1, 55.3, 38.7, 32.6, 29.8. HRMS (ESI+) for $C_{15}H_{17}O_2$ $(M+H)^+$: calculated: 229.1223, found: 229.1222.

5-(4-Methoxyphenyl)cycloocta-3,5-dienone (**3a**)



3a Yellow oil.

IR (film): 2921, 2851, 1706, 1659, 1632, 1606, 1511, 1470, 1289, 1247, 1179, 1116, 1035 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (d, J = 8.4, 2H), 6.89-6.86 (d, J = 8.4 Hz, 2H), 6.35-6.31 (t, J = 7.6 Hz, 1H), 6.24-6.21 (d, J = 10.8, 1H), 6.12-6.05 (dt, J = 10.8 and 7.6 Hz, 1H), 3.82 (s, 3H), 3.22-3.20 (d, J = 7.6, 2H), 2.56-2.51 (m, 2H), 2.42-2.39 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.7, 159.3, 138.1, 132.3, 131.4, 127.6, 127.1, 125.8, 113.8, 55.3, 44.3, 39.6, 26.0. HRMS (ESI+) for $C_{15}H_{17}O_2$ $(M+H)^+$: calculated: 229.1223, found: 229.1222.

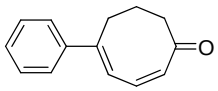


1b (*Z*/*E* = 2.9) 45.0 mg

2b 34.2 mg (66%)

3b 6.0 mg (12%)

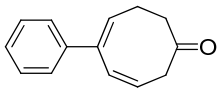
5-Phenylcycloocta-2,4-dienone (**2b**)



2b Yellow oil.

IR (film): 2938, 1654, 1588, 1492, 1449, 1405, 1344, 1250, 1207, 1126, 1025 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.41-7.33 (m, 3H), 6.69-6.64 (dd, J = 12.0 and 6.4 Hz, 1H), 6.61-6.59 (d, J = 6.4 Hz, 1H), 6.01-5.98 (d, J = 12.0 Hz, 1H), 2.78-2.74 (t, J = 6.8 Hz, 2H), 2.71-2.67 (t, J = 6.8 Hz, 2H), 2.24-2.17 (p, J = 6.8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.6, 148.8, 140.9, 138.6, 130.9, 128.7, 128.4, 126.2, 125.1, 38.6, 32.6, 30.0. HRMS (ESI+) for $C_{14}H_{15}O$ $(M+H)^+$: calculated: 199.1117, found: 199.1115.

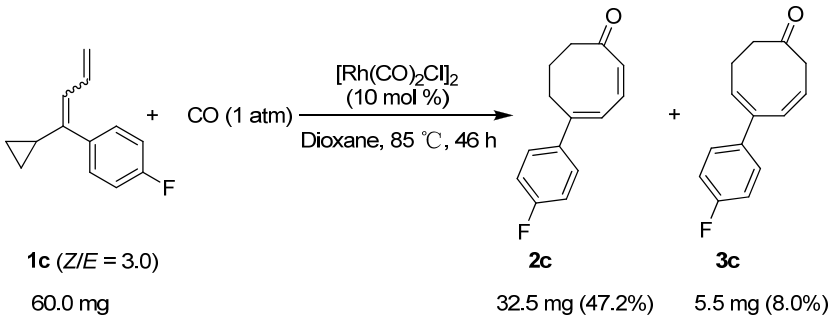
5-Phenylcycloocta-3,5-dienone (**3b**)



3b Yellow oil.

IR (film): 3020, 2923, 2855, 1705, 1654, 1491, 1445, 1420, 1342, 1277, 1206, 1116 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 5H), 6.44-6.40 (t, J = 8.0 Hz, 1H), 6.26-6.24 (d, J = 10.4 Hz, 1H), 6.14-6.07 (dt, J = 10.4 and 7.6 Hz, 1H), 3.24-3.22 (d, J = 7.6 Hz, 2H), 2.59-2.54 (m, 2H), 2.45-2.42 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.6, 139.7, 138.8, 131.2, 128.4, 127.6, 127.5, 127.3, 126.4, 44.3, 39.5, 26.0. HRMS (ESI+) for $C_{14}H_{15}O$ $(M+H)^+$: calculated: 199.1117, found: 199.1115.

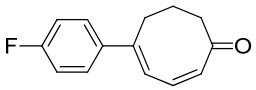


1c (*Z*/*E* = 3.0) 60.0 mg

2c 32.5 mg (47.2%)

3c 5.5 mg (8.0%)

5-(4-Fluorophenyl)cycloocta-2,4-dienone (**2c**)

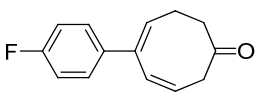


2c Yellow oil.

IR (film): 2935, 1654, 1601, 1583, 1508, 1450, 1400, 1234, 1163, 1127, 1012 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (m, 2H), 7.10-7.05 (m, 2H), 6.67-6.63 (dd, J = 12.4 and 6.0 Hz, 1H), 6.55-6.53 (d, J = 6.0 Hz, 1H), 6.01-5.98 (d, J = 12.4 Hz, 1H), 2.75-2.72 (t, J = 6.8 Hz, 2H), 2.70-2.66 (t, J = 6.8 Hz, 2H), 2.22-2.15 (p, J = 6.8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.3, 164.0, 161.6, 147.7, 138.3, 137.0, 136.9, 131.0, 128.0, 127.9, 125.0, 124.9, 115.7, 115.5, 38.6, 32.3, 30.1. HRMS (ESI+) for $C_{14}H_{13}FNaO$ $(M+Na)^+$: calculated: 239.0843, found: 239.0844.

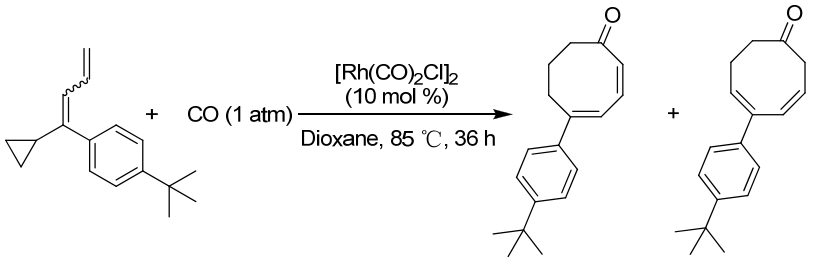
5-(4-Fluorophenyl)cycloocta-3,5-dienone (**3c**)



3c Yellow oil.

IR (film): 2918, 2849, 1706, 1601, 1507, 1423, 1342, 1223, 1159, 1116, 1013 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$):: δ 7.35-7.31 (dd, J = 8.8 and 5.2 Hz, 2H), 7.04-7.00 (t, J = 8.8 Hz, 2H), 6.37-6.33 (t, J = 8.0 Hz, 1H), 6.21-6.19 (d, J = 10.8 Hz, 1H), 6.13-6.07 (dt, J = 10.8 and 7.2 Hz, 1H), 3.23-3.21 (d, J = 7.2 Hz, 2H), 2.59-2.54 (m, 2H), 2.45-2.42 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.4, 163.7, 161.2, 137.7, 135.9, 135.8, 130.8, 128.1, 128.0, 127.6, 127.4, 115.3, 115.1, 44.3, 39.5, 25.9. HRMS (ESI+) for $C_{14}H_{13}FNaO$ $(M+Na)^+$: calculated: 239.0843, found: 239.0844.

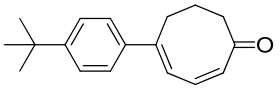


1d (*Z*/*E* = 1.9) 46.0 mg

2d 26.0 mg (50.3%)

3d 4.5 mg (8.7%)

5-(4-*tert*-Butylphenyl)cycloocta-2,4-dienone (**2d**)

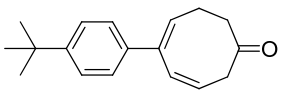


2d Yellow oil.

IR (film): 2955, 2924, 2868, 1656, 1584, 1460, 1400, 1365, 1270, 1250, 1128, 1015 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.49-7.46 (dt, J = 8.4 and 2.0 Hz, 2H), 7.43-7.39 (dt, J = 8.4 and 2.0 Hz, 2H), 6.68-6.64 (dd, J = 12.4 and 6.4 Hz, 1H), 6.62-6.60 (d, J = 6.4 Hz, 1H), 6.00-5.97 (d, J = 12.4 Hz, 1H), 2.77-2.74 (t, J = 6.8 Hz, 2H), 2.69-2.66 (t, J = 6.8 Hz, 2H), 2.24-2.17 (p, J = 6.8 Hz, 2H), 1.34 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.6, 151.7, 148.6, 138.8, 137.8, 130.8, 125.9, 125.6, 124.4, 38.7, 34.6, 32.6, 31.2, 29.8. HRMS (ESI+) for $C_{18}H_{23}O$ $(M+H)^+$: calculated: 255.1743, found: 255.1742.

5-(4-*tert*-Butylphenyl)cycloocta-3,5-dienone (**3d**)

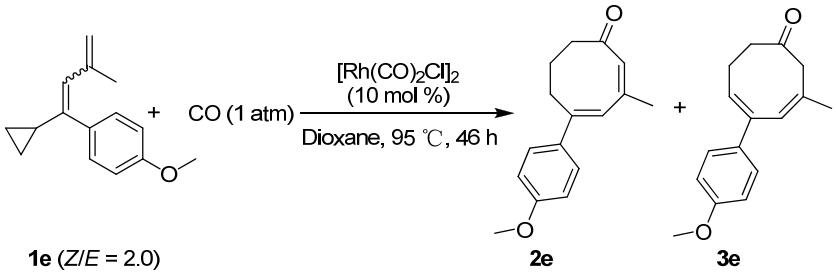


3d Yellow oil.

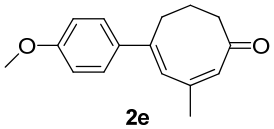
IR (film): 2959, 2917, 2849, 1707, 1656, 1507, 1462, 1363, 1341, 1270, 1204, 1113, 1074, 1023

cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39-7.30 (m, 4H), 6.44-6.39 (t, J = 7.8 Hz, 1H), 6.27-6.24 (d, J = 10.5 Hz, 1H), 6.14-6.07 (dt, J = 10.5 and 7.5 Hz, 1H), 3.22-3.20 (d, J = 7.5 Hz, 2H), 2.59-2.52 (m, 2H), 2.43-2.39 (m, 2H), 1.33 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.8, 150.7, 138.4, 136.7, 131.3, 127.1, 126.8, 126.1, 125.3, 44.2, 39.5, 34.5, 31.3, 25.9. HRMS (ESI+) for $C_{18}H_{23}O$ $(M+H)^+$: calculated: 255.1743, found: 255.1742.



5-(4-Methoxyphenyl)-3-methylcycloocta-2,4-dienone (**2e**)

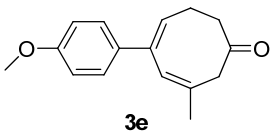


Yellow oil.

IR (film): 2934, 1642, 1605, 1586, 1571, 1511, 1462, 1447, 1372, 1343, 1289, 1250, 1182, 1119, 1031 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.49-7.46 (d, J = 8.8 Hz, 2H), 6.93-6.91 (d, J = 8.8 Hz, 2H), 6.43 (s, 1H), 5.98 (s, 1H), 3.84 (s, 3H), 2.75-2.71 (t, J = 6.8 Hz, 2H), 2.66 (br s, 2H), 2.11-2.08 (t, J = 6.4 Hz, 2H), 2.05 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 204.2, 159.8, 149.7, 146.2, 133.1, 129.4, 127.5, 126.5, 114.0, 55.3, 38.2, 31.3, 29.9, 26.8. HRMS (ESI+) for $C_{16}H_{19}O_2$ $(M+H)^+$: calculated: 243.1380, found: 243.1373.

5-(4-Methoxyphenyl)-3-methylcycloocta-3,5-dienone (**3e**)

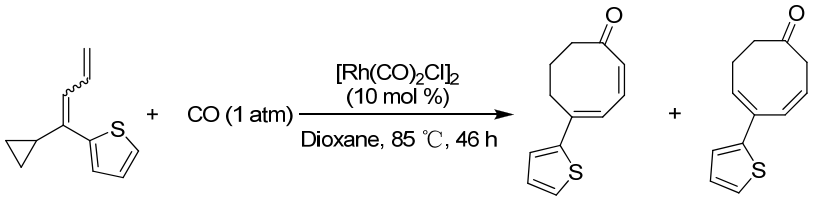


Yellow oil.

IR (film): 2926, 1701, 1648, 1607, 1574, 1510, 1442, 1289, 1246, 1178, 1117, 1034 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (d, J = 8.8 Hz, 2H), 6.88-6.86 (d, J = 8.8 Hz, 2H),

6.33-6.29(t, J = 7.6 Hz, 1H), 5.94 (s, 1H), 3.82 (s, 3H), 3.22 (s, 2H), 2.53-2.48 (m, 2H), 2.39-2.36 (m, 2H), 2.00 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.8, 159.3, 140.0, 136.1, 132.7, 127.5, 126.0, 125.1, 113.7, 55.3, 48.9, 39.4, 26.4, 23.7. HRMS (ESI+) for $C_{16}H_{19}O_2$ $(M+H)^+$: calculated: 243.1380, found: 243.1374.

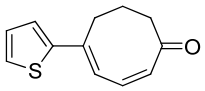


1f (*Z*/*E* = 4.0) 55.0 mg

2f 27.0 mg (42%)

3f 3.2 mg (5%)

5-(Thiophen-2-yl)cycloocta-2,4-dienone (**2f**)

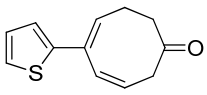


2f Yellow oil.

IR (film): 2931, 1653, 1605, 1576, 1450, 1428, 1406, 1342, 1250, 1127, 1058 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (dd, J = 5.0 and 0.8 Hz, 1H), 7.22-7.21 (dd, J = 3.8 and 0.8 Hz, 1H), 7.06-7.04 (dd, J = 5.0 and 3.8 Hz,1H), 6.71-6.69 (d, J = 6.2 Hz, 1H), 6.64-6.59 (dd, J = 12.3 and 6.2 Hz, 2H), 5.98-5.95 (d, J = 12.3 Hz, 1H), 2.80-2.77 (t, J = 6.6 Hz, 2H), 2.69-2.66 (t, J = 6.6 Hz, 2H), 2.28-2.21 (p, J = 6.6 Hz, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.5, 144.8, 142.4, 137.8, 130.9, 128.1, 126.2, 125.1, 122.9, 38.7, 32.2, 30.0. HRMS (ESI+) for $C_{12}H_{13}OS$ $(M+H)^+$: calculated: 205.0682, found: 205.0683.

5-(Thiophen-2-yl)cycloocta-3,5-dienone (**3f**)

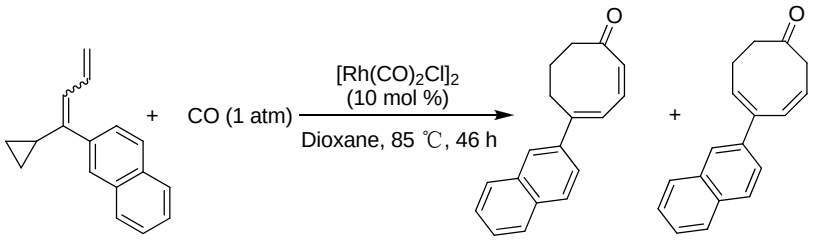


3f Yellow oil.

IR (film): 2921, 2850, 1747, 1704, 1653, 1577, 1427, 1339, 1249, 1226, 1210, 1174, 1128, 1115, 1067, 1024 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.20-7.18 (d, J = 5.2 Hz, 1H), 7.00-6.98 (dd, J = 5.2 and 3.6 Hz, 1H), 6.94-6.93 (d, J = 3.6 Hz, 1H), 6.48-6.44 (t, J = 7.6 Hz, 1H), 6.33-6.31 (d, J = 10.8 Hz, 1H), 6.11-6.05 (dt, J = 10.8 and 7.6 Hz, 1H), 3.23-3.21 (d, J = 7.6 Hz, 2H), 2.55-2.50 (m, 2H),

2.43-2.40 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.2, 143.9, 132.8, 130.0, 127.7, 127.5, 126.3, 124.4, 124.2, 44.3, 39.3, 25.6. HRMS (ESI+) for $C_{12}H_{13}OS$ $(M+H)^+$: calculated: 205.0682, found: 205.0680.

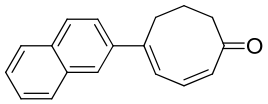


1g (*Z*/*E* = 2.2) 77.0 mg

2g 57.0 mg (66%)

3g 3.5 mg (4%)

5-(Naphthalen-2-yl)cycloocta-2,4-dienone (**2g**)

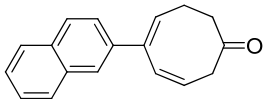


2g White solid, melting point: 91-92℃.

IR (film): 2942, 1654, 1582, 1506, 1448, 1435, 1404, 1344, 1249, 1196, 1127 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.94-7.93 (d, J = 1.5 Hz, 1H), 7.86-7.81 (m, 3H), 7.67-7.63 (dd, J = 8.7 and 2.1 Hz,1H), 7.51-7.46 (m, 2H), 6.74-6.66 (m, 2H), 6.04-6.00 (d, J = 11.1 Hz, 1H), 2.89-2.84 (t, J = 6.6 Hz, 2H), 2.74-2.69 (t, J = 6.6 Hz, 2H),. 2.28-2.21 (p, J = 6.6 Hz, 2H), ^{13}C-NMR (75 MHz, $CDCl_3$): δ 205.5, 148.6, 138.5, 137.9, 133.3, 133.1, 131.0, 128.3, 127.5, 126.5, 125.5, 125.4, 123.9, 38.7, 32.5, 29.8. HRMS (ESI+) for $C_{18}H_{17}O$ $(M+H)^+$: calculated: 249.1274, found: 249.1270.

5-(Naphthalen-2-yl)cycloocta-3,5-dienone (**3g**)

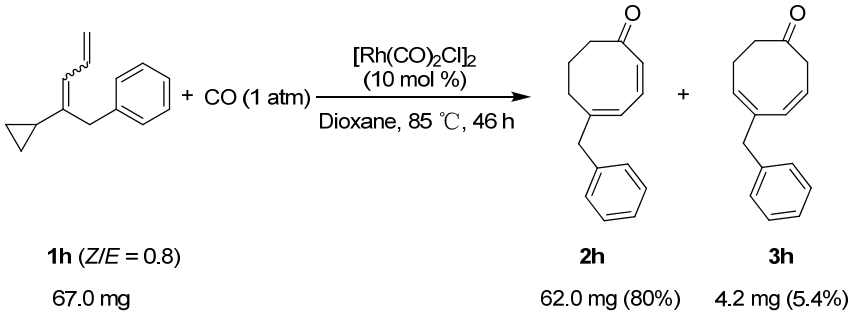


3g Yellow oil.

IR (film): 3362, 2918, 2849, 1705, 1653, 1632, 1426, 1339, 1276, 1114, 1020 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ7.83-7.80 (m, 3H), 7.74 (s, 1H), 7.60-7.57 (dd, J = 8.8 and 2.0 Hz, 1H), 7.49-7.44 (m, 2H), 6.60-6.56 (t, J = 8.0 Hz, 1H), 6.38-6.35 (d, J = 10.8 Hz, 1H), 6.21-6.14 (dt, J = 10.8 and 8.0 Hz, 1H), 3.28-3.26 (d, J = 8.0 Hz, 2H), 2.67-2.60 (m, 2H), 2.48-2.44 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.5, 138.6, 136.9, 133.4, 132.9, 131.2, 128.1, 128.0, 127.6,

127.5, 127.4, 126.3, 126.0, 125.6, 124.3, 44.4, 39.5, 26.1. HRMS (ESI+) for $C_{18}H_{17}O$ $(M+H)^+$: calculated: 249.1274, found: 249.1273.

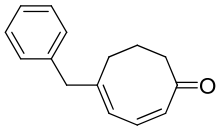


1h (*Z*/*E* = 0.8) 67.0 mg

2h 62.0 mg (80%)

3h 4.2 mg (5.4%)

5-Benzylcycloocta-2,4-dienone (**2h**)

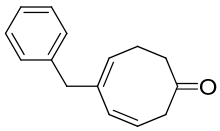


2h Yellow oil.

IR (film): 2928, 1654, 1629, 1592, 1494, 1449, 1435, 1408, 1344, 1251, 1192, 1128, 1076, 1030 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34-7.20 (m, 5H), 6.49-6.44 (dd, J = 12.4 and 5.6 Hz,1H), 6.05-6.04 (d, J = 5.6 Hz, 1H), 5.89-5.86 (d, J = 12.4 Hz, 1H), 3.54 (s, 2H), 2.58-2.55 (t, J = 6.8 Hz, 2H), 2.27-2.24 (t, J = 6.8 Hz, 2H), 1.93-1.86 (p, J = 6.8 Hz, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$): δ 205.9, 151.1, 138.5, 138.3, 130.5, 129.2, 128.6, 126.7, 125.1, 45.1, 38.8, 31.9, 30.5. HRMS (ESI+) for $C_{15}H_{16}NaO$ $(M+Na)^+$: calculated: 235.1093, found: 235.1091.

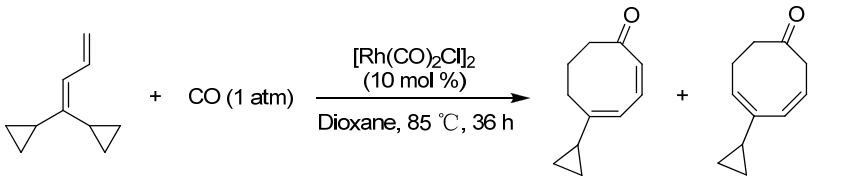
5-Benzylcycloocta-3,5-dienone (**3h**)



3h Yellow oil.

IR (film): 3023, 2923, 1706, 1494, 1453, 1430, 1334, 1278, 1113, 1075, 1029 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): 7.31-7.26 (m, 2H), 7.22-7.17 (m, 3H), 5.88-5.85 (d, J = 10.8 Hz, 1H), 5.80-5.70 (m, 2H), 3.40 (s, 2H), 3.08-3.06 (d, J = 7.2 Hz, 2H), 2.45-2.39 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 209.4, 139.2, 138.1, 131.4, 128.8, 128.3, 127.2, 126.2, 125.8, 44.5, 43.8, 40.2, 25.2. HRMS (ESI+) for $C_{15}H_{16}NaO$ $(M+Na)^+$: calculated: 235.1093, found: 235.1093.

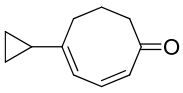


1i 57.8 mg

2i 35.5 mg (51.5%)

3i 8.0 mg (11.6%)

5-Cyclopropylcycloocta-2,4-dienone (**2i**)

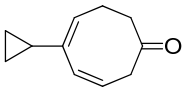


2i Yellow oil.

IR (film): 3012, 2941, 2863, 1654, 1625, 1589, 1449, 1410, 1344, 1251, 1206, 1127, 1019 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.48-6.44 (dd, J = 12.3 and 6.0 Hz,1H), 6.05-6.04 (d, J = 6.0 Hz, 1H), 5.87-5.84 (d, J = 12.3 Hz, 1H), 2.61-2.58 (t, J = 6.5 Hz, 2H), 2.14-2.05 (m, 4H), 1.62-1.55 (m, 1H), 0.86-0.81 (m, 2H), 0.63-0.59 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 206.0, 153.8, 138.7, 129.7, 121.6, 38.6, 33.1, 28.3, 18.6, 7.2. HRMS (ESI+) for $C_{11}H_{15}O$ $(M+H)^+$: calculated: 163.1117, found: 163.1115.

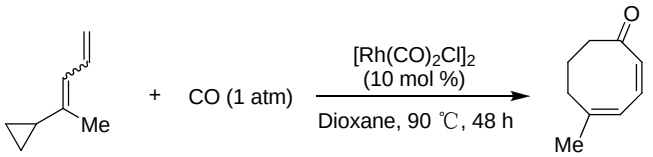
5-Cyclopropylcycloocta-3,5-dienone (**3i**)



3i Yellow oil.

IR (film): 3002, 2925, 2856, 1706, 1657, 1428, 1278, 1117, 1022 cm^{-1}.

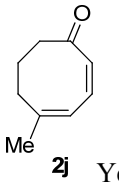
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.86-5.78 (m, 3H), 3.13-3.12 (d, J = 6.0 Hz, 2H), 2.36-2.35 (d, J = 4.0 Hz, 4H), 1.50-1.44 (m, 1H), 0.63-0.59 (m, 2H), 0.47-0.43 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 209.5, 139.7, 129.7, 126.4, 123.9, 44.4, 40.2, 25.0, 16.8, 4.5. HRMS (ESI+) for $C_{11}H_{15}O$ $(M+H)^+$: calculated: 163.1117, found: 163.1116.



1j (*Z*/*E* = 0.3) **2j**

22.0 mg 3.5 mg (12.5%)

5-Methylcycloocta-2,4-dienone (**2j**)

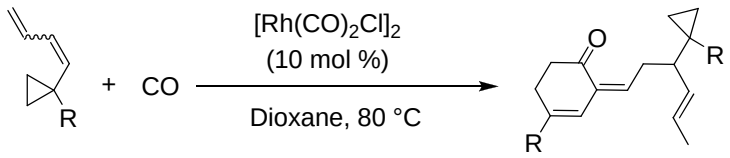


2j Yellow oil.

IR (film): 2933, 2862, 1654, 1631, 1591, 1451, 1406, 1343, 1306, 1250, 1192, 1130, 1052, 1011 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.46-6.42 (dd, J = 12.4 and 5.6 Hz,1H), 6.06-6.05 (d, J = 5.6 Hz, 1H), 5.88-5.86 (d, J = 12.4 Hz, 1H), 2.62-2.58 (t, J = 6.8 Hz, 2H), 2.28-2.25 (t, J = 6.8 Hz, 2H), 2.14-2.07 (p, J = 6.8 Hz, 2H),1.98 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 206.2, 148.8, 138.6, 130.3, 124.1, 38.8, 32.1, 31.6, 24.9. HRMS (ESI+) for $C_9H_{12}NaO$ $(M+Na)^+$: calculated: 159.0780, found: 159.0778.

6. General Procedure for the Synthesis of 4k and 4l

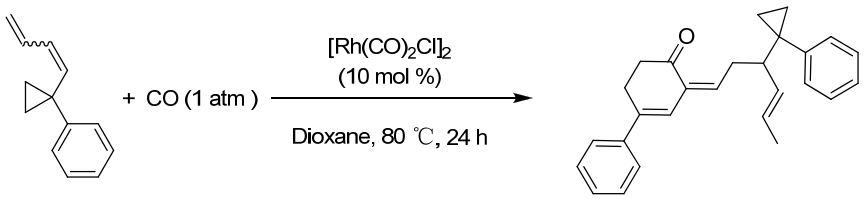


1k R = Ph (*Z*/*E*=3.0) 100% convn, 66% yield **4k**

1l R = 4-$MeOC_6H_4$ (*Z*/*E*=5.4) 100% convn, 69% yield **4l**

To an oven-dried Schlenk tube with a stir bar was added 7.8 mg $[Rh(CO)_2Cl]_2$ (0.02 mmol, 0.1 equiv), and the flask was purged with CO gas three times. Then a solution of buta-1,3-dienylcyclopropane (0.2 mmol, 1.0 equiv) in dried dioxane was added via cannula, and the solution was bubbled with CO gas for 3 min. Then the solution stirred under balloon pressured CO (1 atm) at indicated temperature until TLC showed the reaction was complete. The

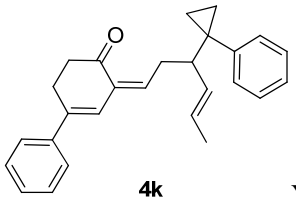
solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel.



1k (*Z*/*E* = 3.0)
85 mg

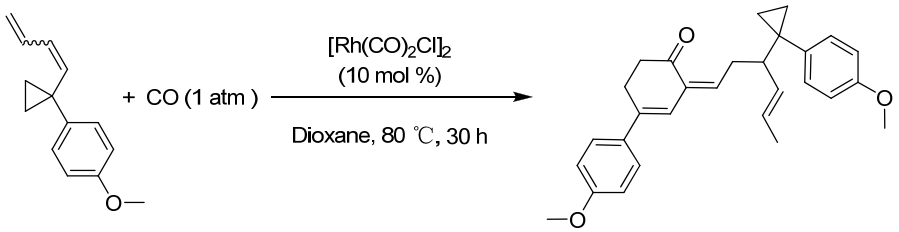
4k
61 mg (66%)

(*Z*)-4-Phenyl-2-((*E*)-3-(1-phenylcyclopropyl)hex-4-enylidene)cyclohex-3-enone (**4k**)



4k Yellow oil.

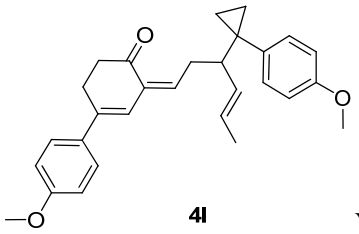
IR (film): 3026, 2916, 2849, 1698, 1622, 1590, 1495, 1445, 1377, 1322, 1238, 1189, 1019 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48-7.19 (m, 10H), 6.76 (s, 1H), 6.66-6.62 (t, J = 8.0 Hz, 1H), 5.46-5.37 (dq, J = 15.2 and 6.4 Hz, 1H), 5.26-5.20 (ddd, J = 15.2, 8.7 and 1.5 Hz, 1H), 2.91-2.88 (t, J = 6.8 Hz, 2H), 2.71-2.67 (t, J = 6.8 Hz, 2H), 2.53-2.46 (ddd, J = 15.3, 8.2 and 5.2 Hz, 1H), 2.18-2.10 (ddd, J = 15.3, 9.0 and 7.3 Hz, 1H), 1.89-1.83 (dt, J = 5.2 and 9.0 Hz, 1H), 1.68-1.66 (dd, J = 6.4 and 1.5 Hz, 3H), 0.88-0.67 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.8, 143.1, 140.6, 137.9, 136.7, 131.7, 131.6, 131.1, 128.5, 127.8, 127.7, 126.8, 126.4, 125.2, 120.9, 51.3, 38.2, 31.0, 30.6, 26.6, 18.1, 12.7, 11.0. HRMS (ESI+) for $C_{27}H_{28}NaO$ $(M+Na)^+$: calculated: 391.2032, found: 391.2042.



1l (*Z*/*E* = 5.4)
180 mg

4l
133 mg (69%)

(*Z*)-4-(4-Methoxyphenyl)-2-((*E*)-3-(1-(4-methoxyphenyl)cyclopropyl)hex-4-enylidene)cyclohex-3-enone (**4l**)



4l Yellow oil.

IR (film): 2916, 2849, 1697, 1606, 1589, 1512, 1463, 1441, 1376, 1288, 1246, 1180, 1109, 1034 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43-7.41 (d, J = 8.8 Hz, 2H), 7.26-7.24 (d, J = 8.8 Hz, 2H), 6.96-6.94 (d, J = 8.8 Hz, 2H), 6.84-6.82 (d, J = 8.8 Hz, 2H), 6.73-6.72 (d, J = 1.2 Hz, 1H), 6.65-6.61 (t, J = 8.0 Hz, 1H), 5.47-5.39 (dq, J = 15.2 and 6.4 Hz, 1H), 5.30-5.24 (ddd, J = 15.2, 8.4 and 1.6 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 2.92-2.89 (t, J = 6.8 Hz, 2H), 2.73-2.70 (t, J = 6.8 Hz, 2H), 2.54-2.47 (ddd, J = 15.6, 8.4 and 5.2 Hz, 1H), 2.20-2.12 (ddd, J = 15.6, 8.8 and 7.4 Hz, 1H), 1.85-1.80 (ddd, J = 8.8, 8.8 and 5.2 Hz, 1H), 1.71-1.69 (dd, J = 6.4 and 1.6 Hz, 3H), 0.79-0.67 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.0, 159.4, 158.1, 137.3, 135.8, 135.2, 133.1, 132.1, 132.0, 131.7, 126.5, 126.4, 119.4, 113.9, 113.1, 55.3, 55.2, 51.5, 38.2, 31.0, 29.8, 26.6, 18.0, 12.8, 11.2. HRMS (ESI+) for $C_{29}H_{33}O_3$ $(M+H)^+$: calculated: 429.2424, found: 429.2416.

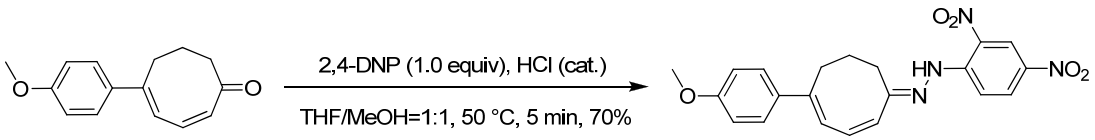
7. Structure Determination

The structures of **2a** and **4l** were identified by ^{1}H NMR and ^{13}C NMR of **2a** and **4l**, and confirmed by the crystallographic data of hydrazone derivatives of **2a** and **4l**, respectively. Then the structures of cycloadducts **2b-2j** were deduced by analogy to **2a**, and the structure of **4k** was deduced by analogy to **4l**.

Synthesis of the Hydrazone Derivatives of 2a

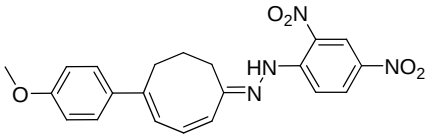
A flame-dried round-bottomed flask with a stir bar was charged with 2,4-dinitrophenylhydrazine (168 mg, 0.85 mmol, 1.5 equiv), MeOH/THF(1:1, 2mL). The suspension was heated at 50 ℃, until the suspension became clear. Then the red brown solution was allowed to cool to room temperature and **2a** (120 mg, 0.57 mmol, 1 equiv, in 1 mL THF) and one drop of concentrated hydrochloric acid was added afterwards. The resulting solution was heated at 50 ℃ for 5 minutes and allowed to cool to room temperature. The solvent was removed in vacuo and the residue was purified by flash chromatography to afford 150 mg (70%) **5a** as a red

brown solid.



2a **5a**

(*E*)-1-(2,4-Dinitrophenyl)-2-((2*Z*,4*E*)-5-(4-methoxyphenyl)cycloocta-2,4-dienylidene)hydrazone (**5a**)

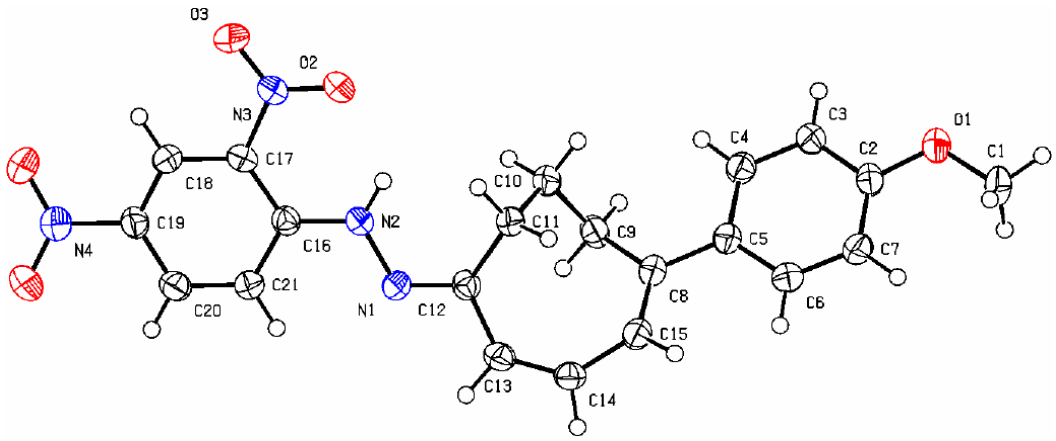


5a

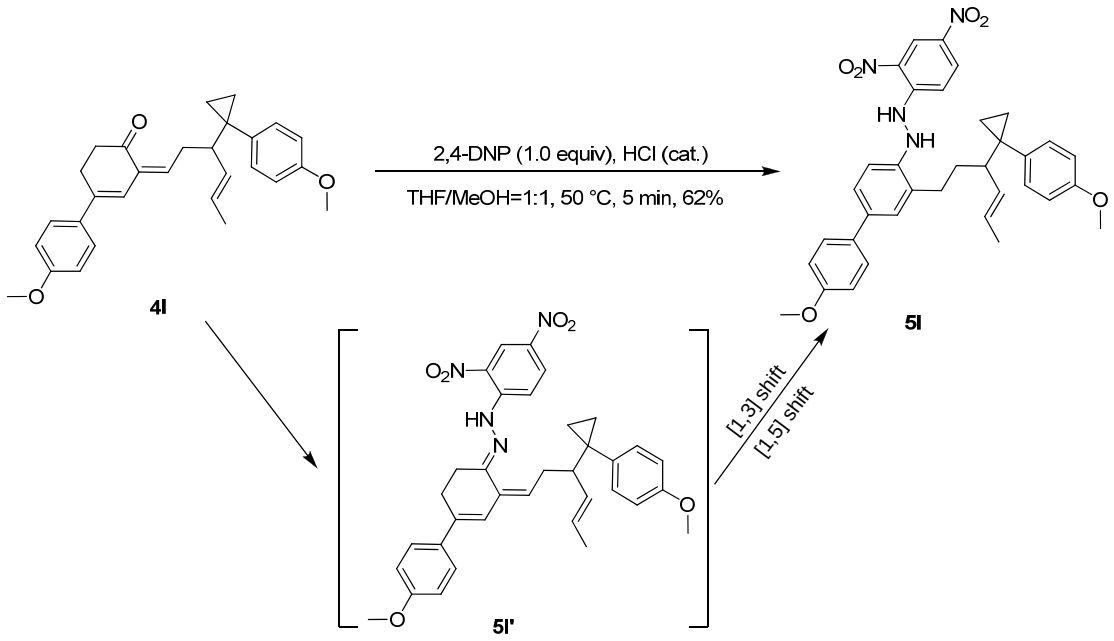
Brown solid, melting point: 207-208℃.

IR (film): 3056, 2957, 2927, 1731, 1617, 1590, 1512, 1416, 1335, 1265, 1180, 1134, 1088 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 11.45 (s, 1H), 9.15-9.14 (d, J = 2.0 Hz, 1H), 8.35-8.32 (dd, J = 9.6 and 2.0 Hz, 1H), 8.06-8.04 (d, J = 9.6 Hz, 1H), 7.48-7.46 (d, J = 8.5 Hz, 2H), 6.92-6.90 (d, J = 8.5 Hz, 2H), 6.58-6.56 (d, J = 5.8 Hz, 1H), 6.41-6.38 (d, J = 12.3 Hz, 1H), 6.35-6.31 (dd, J = 12.3 and 5.8 Hz, 1H), 3.84 (s, 3H), 2.71 (br s, 4H), 2.2.08 (br s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.9, 158.8, 144.6, 143.7, 138.4, 133.4, 131.9, 130.0, 129.91, 129.88, 127.3, 124.1, 123.4, 116.7, 114.2, 55.4, 29.8, 26.7, 24.7. HRMS (ESI+) for $C_{21}H_{21}N_4O_5$ $(M+H)^+$: calculated: 409.1507, found: 409.1508.

The ORTEP Diagrams of Cycloadducts 5a (CCDC: 787186)

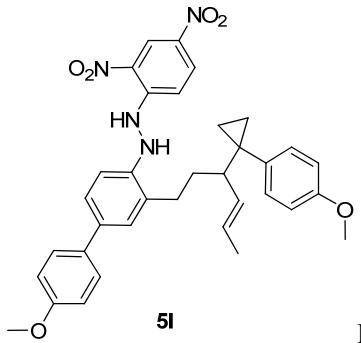


Synthesis of the Hydrazone Derivatives of 4l



A flame-dried round-bottomed flask with a stir bar was charged with 2,4-dinitrophenylhydrazine (35 mg, 0.18 mmol, 1.5 equiv), MeOH/THF(1:1, 2mL). The suspension was heated at 50 ℃, until the suspension became clear. Then the red brown solution was allowed to cool to room temperature and **4l** (50 mg, 0.12 mmol, 1 equiv, in 1 mL THF) and one drop of concentrated hydrochloric acid was added afterwards. The resulting solution was heated at 50 ℃ for 5 minutes and allowed to cool to room temperature. The solvent was removed in vacuo and the residue was purified by flash chromatography to afford 44 mg (62%) **5l** as a red brown solid. This hydrazine **5l** should be generated from the isomerization of hydrazone **5l'** through simultaneous [1,3] hydrogen shift and [1,5] hydrogen shift.

(*E*)-1-(2,4-Dinitrophenyl)-2-(4'-methoxy-3-(3-(1-(4-methoxyphenyl)cyclopropyl)hex-4-enyl)-biphenyl-4-yl)hydrazine (**5l**)



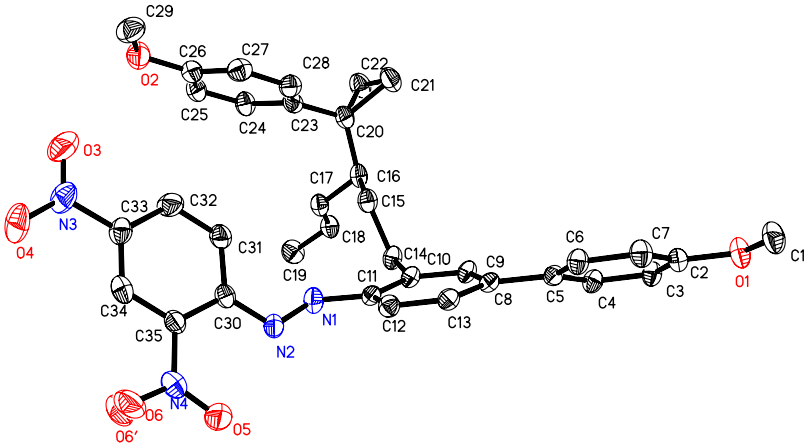
Brown solid, melting point: 165-166℃.

IR (film): 3333, 2916, 2851, 1621, 1610, 1593, 1513, 1493, 1465, 1425, 1335, 1313, 1275, 1244,

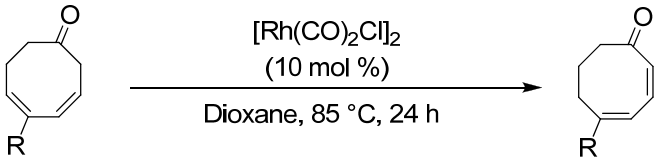
1180, 1139, 1110, 1060, 1031 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 9.16-9.15 (d, J = 2.5 Hz, 1H), 8.26-8.23 (dd, J = 9.5 and 2.5 Hz, 1H), 7.45-7.43 (d, J = 8.7 Hz, 2H), 7.39-7.36 (d, J = 9.5 Hz, 1H), 7.30-7.25 (m, 2H), 7.24-7.22 (d, J = 8.8 Hz, 2H), 6.96-6.94 (d, J = 8.7 Hz, 2H), 6.79-6.77 (d, J = 8.8 Hz, 2H), 6.77-6.74 (d, J = 8.8 Hz, 1H), 5.70 (s, 1H), 5.56-5.48 (dt, J = 15.2 and 6.4 Hz, 1H), 5.32-5.26 (ddd, J = 15.2, 9.0 and 1.2 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 2.62-2.47 (m, 2H), 1.95-1.86 (m, 1H), 1.75-1.73 (dd, J = 6.4 and 1.2 Hz, 3H), 1.69-1.64 (td, J = 10.0 and 3.6 Hz, 1H), 1.57-1.48(m, 1H), 0.78-0.66(m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.9, 158.1, 150.0, 141.9, 137.9, 135.3, 134.6, 133.1, 132.8, 131.8, 130.5, 130.1, 128.5, 127.8, 127.6, 127.0, 125.4, 123.7, 115.2, 114.2, 113.1, 112.1, 55.3, 5.1, 51.6, 32.4, 29.8, 29.5, 18.1, 12.8, 11.4. HRMS (ESI+) for $C_{35}H_{36}N_4NaO_6$ $(M+Na)^+$: calculated: 631.2533, found: 631.2520.

The ORTEP Diagrams of Cycloadducts 5l (CCDC: 764829)



8. Isomerization of 3a and 3c

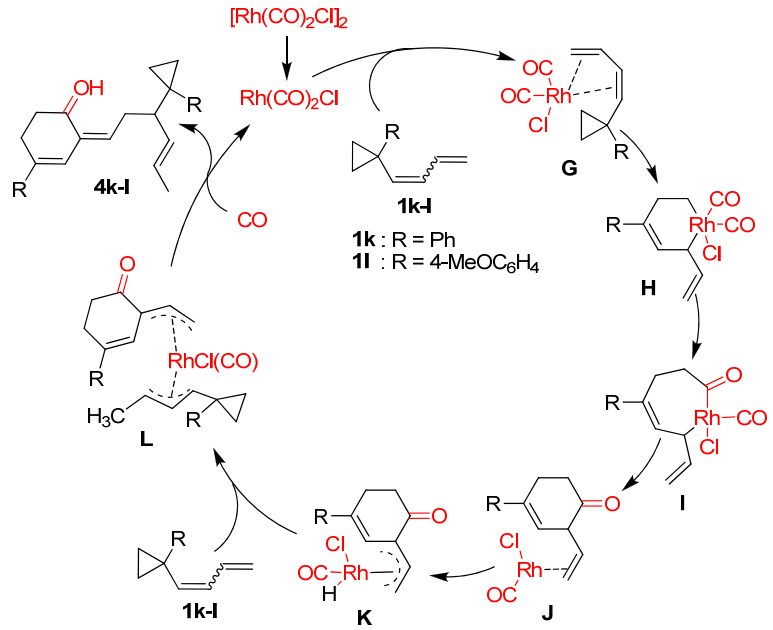


3a R = 4-$MeOC_6H_4$ 86% convn, 86% yield **2a**
3c R = 4-FC_6H_4 90% convn, 76% yield **2c**

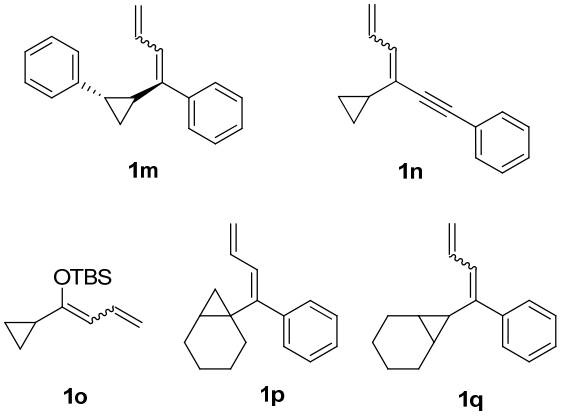
To an oven-dried Schlenk tube with a stir bar was added 7.8 mg $[Rh(CO)_2Cl]_2$ (0.02 mmol, 0.1 equvi), and the flask was purged with Ar gas three times. Then a solution of **3a** or **3c** (0.2 mmol, 1.0 equvi) in dried dioxane was added via cannula, and the solution was bubbled with Ar gas for 3 min. The resulting solution was stirred under balloon pressured Ar (1 atm) at indicated temperature until TLC showed the reaction was complete. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel to give the final product. We also used sodium ethanolate[7] or DBU[8] as base to promote the isomerization of **3a** and **3c**. The starting materials were untouched by DBU, but decomposed when treated with sodium ethanolate.

9. The Proposed Mechanism for the Reaction of 1k-l to 4k-l

We propose the following pathway accounting for the formation of **4k-l**. The active catalyst $Rh(CO)_2Cl$, generated by disassociation of its precursor $[Rh(CO)_2Cl]_2$, coordinates to buta-1,3-dienylcyclopropane **1k-l,** giving the intermediate **G**. Ring opening of the cyclopropane ring converts **G** to the six-membered rhodacycle intermediate **H**, which undergoes CO coordination, CO insertion, and reductive elimination to give intermediate **J**. The process of **G** to **J** can be regarded as a formal [5+1] reaction of BDCP and CO. However, the reaction does not stop at the [5+1] process. Instead, intermediate **J** undergoes an allylic C-H activation[9] process to generate intermediate **K**, which then adds its Rh-H bond to the diene part of BDCP **1k-l,** giving a bisallylic Rh complex **L**. Finally reductive elimination from **L** produces **4k-l**, accompanied with the regeneration of the active catalyst for the next catalytic cycle.

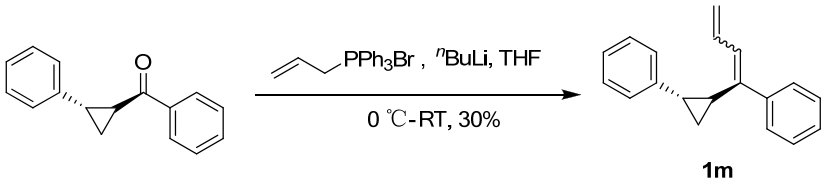


10. Unsuccessful Substrates for the [7+1] Reaction



In all these unsuccessful cases, only starting materials were recovered under the standard [7＋1] reaction conditions.

Synthesis of (2-(1-Phenylbuta-1,3-dienyl)cyclopropyl)benzene (1m)



To an oven-dried round-bottomed flask with a stir bar was added allyltriphenylphosphonium bromide (2.25 mmol, 2.0 equiv) and THF (10 mL). The solution was cooled to 0 ℃ and 0.9 mL (2.25 mmol, 2.0 equiv) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 ℃, phenyl(-2-phenylcyclopropyl)methanone[10] (1.12 mmol, 1.0 equiv) in 6 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 24 hours. The reaction was then quenched with 10 mL brine and diluted with 50 mL of diethyl ether. The organic layer was separated and the aqueous layer was extracted by diethyl ether in one time. The combined organic layers were dried over Na_2SO_4, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford 83 mg (30%) **1m** as a colorless oil.

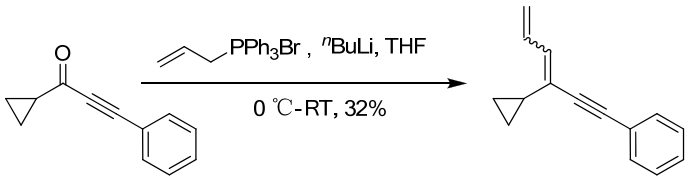
A 4:1 mixture of (*Z*:*E*)-(2-(1-phenylbuta-1,3-dienyl)cyclopropyl)benzene was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a

doublet at 6.14 ppm for the (*Z*)-(2-(1-phenylbuta-1,3-dienyl)cyclopropyl)benzene and a doublet at 6.46 ppm for the (*E*)-olefin.

IR (film): 3026, 1604, 1497, 1442, 1418, 1029 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.39-7.06 (m, 10H), 6.34-6.21 (dt, J = 16.8 and 10.8 Hz, 1H), 6.16-6.12 (d, J = 10.8 Hz, 1H), 5.22-5.15 (dd, J = 16.8 and 1.8 Hz, 1H), 4.96-4.92 (dd, J = 10.8 and 1.8 Hz, 1H), 2.04-1.85 (m, 2H), 1.30-1.19 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.8, 142.3, 139.5, 134.4, 129.0, 128.3, 128.0, 127.1, 125.8, 125.7, 125.6, 116.1, 30.8, 25.3, 15.5. HRMS (EI+) for $C_{19}H_{18}$ $(M)^+$: calculated: 246.1409, found: 246.1412.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.45-7.06 (m, 10H), 7.04-6.91 (dt, J = 16.8 and 10.8 Hz, 1H), 6.48-6.44 (d, J = 10.8 Hz, 1H), 5.34-5.27 (dd, J = 16.8 and 1.8 Hz, 1H), 5.18-5.15 (dd, J = 10.8 and 1.8 Hz, 1H), 2.14-2.09 (m, 1H), 2.04-1.85 (m, 1H), 1.43-1.32 (m, 1H), 1.14-1.05 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.5, 141.4, 141.2, 133.8, 130.7, 128.4, 128.0, 127.0, 126.1, 125.8, 125.6, 118.3, 25.3, 24.3, 18.0.

Synthesis of (3-Cyclopropylhexa-3,5-dien-1-ynyl)benzene (1n)



1n

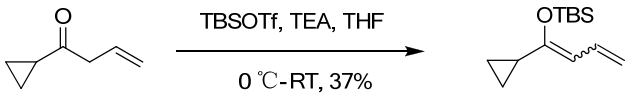
To an oven-dried round-bottomed flask with a stir bar was added allyltriphenylphosphonium bromide (9.9 mmol, 1.2 equiv) and THF (40 mL). The solution was cooled to 0 ℃ and 4.0 mL (10.0 mmol, 1.2 equiv) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 ℃, 1-cyclopropyl-3-phenylprop-2-yn-1-one[11] (8.3 mmol, 1.0 equiv) in 6 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 24 hours. The reaction was then quenched with 10 mL brine and diluted with 50 mL of diethyl ether. The organic layer was separated and the aqueous layer was extracted by diethyl ether in one time. The combined organic layers were dried over Na_2SO_4, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford 498 mg (32%) **1n** as a colorless oil.

A 2.5:1 mixture of (*Z*:*E*)-(3-cyclopropylhexa-3,5-dien-1-ynyl)benzene was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a doublet at 6.44 ppm for the (*Z*)-(3-cyclopropylhexa-3,5-dien-1-ynyl)benzene and a doublet at 6.54 ppm for the (*E*)-olefin.

IR (film): 3005, 1616, 1489, 1442, 1420, 1026 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45-7.39 (m, 1H), 7.33-7.28 (m, 4H), 6.97-6.87 (dt, J = 16.8 and 10.8 Hz, 1H), 6.45-6.43 (d, J = 10.8 Hz, 1H), 5.30-5.24 (dd, J = 16.8 and 1.6 Hz, 1H), 5.14-5.11 (dd, J = 10.8 and 1.6 Hz, 1H), 1.63-1.57 (m, 1H), 0.86-0.81 (m, 2H), 0.78-0.72 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 134.9, 134.3, 131.5, 128.3, 128.2, 127.6, 123.1, 116.9, 95.9, 84.6, 16.4, 6.1. HRMS (EI+) for $C_{15}H_{14}$ $(M)^+$: calculated: 194.1096, found: 194.1097.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45-7.39 (m, 5H), 6.90-6.83 (dt, J = 16.8 and 10.8 Hz, 1H), 6.55-6.52 (d, J = 10.8 Hz, 1H), 5.35-5.29 (dd, J = 16.8 and 1.6 Hz, 1H), 5.22-5.18 (dd, J = 10.8 and 1.6 Hz, 1H), 1.93-1.86 (m, 1H), 0.92-0.87 (m, 2H), 0.82-0.77 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 135.3, 132.1, 131.5, 128.2, 128.0, 126.9, 123.4, 118.6, 90.4, 88.1, 11.1, 6.5.

Synthesis of *tert*-Butyl(1-cyclopropylbuta-1,3-dienyloxy)dimethylsilane (1o)



1o

To an oven-dried round-bottomed flask with a stir bar was added 1-cyclopropylbut-3-en-1-one[12] (220 mg, 2.0 mmol, 1.0 equiv), THF (15 mL), and TEA (1.26 mL, 9.0 mmol, 4.5 equiv). The solution was cooled to 0 ℃ and TBSOTf (0.9 mL, 4.0 mmol, 2.0 equiv) was added dropwise. The solution was stirred for 4 hours at 0 ℃. Then pentane (40 mL) and TEA (5 mL) were added. The resulted solution was washed with brine (10 mL), and then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford 83 mg (37%) **1o** as a colorless oil.

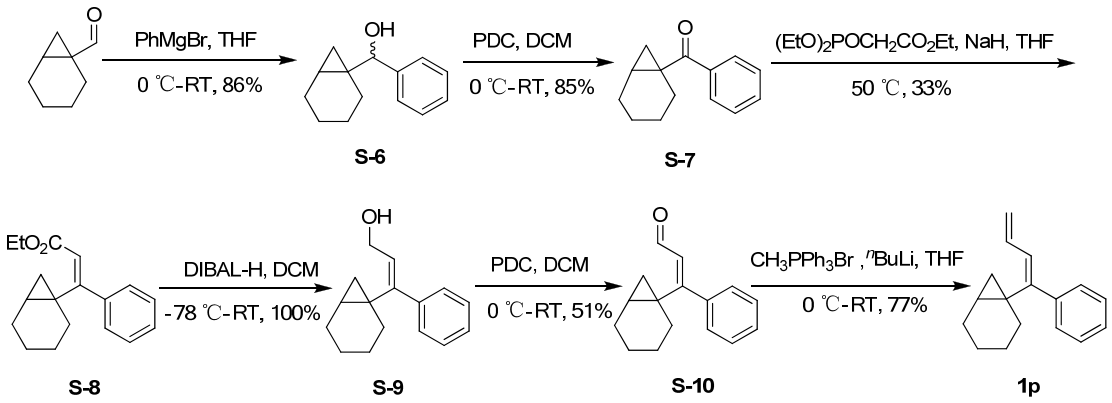
A 0.7:1 mixture of (*Z*:*E*)-*tert*-butyl(1-cyclopropylbuta-1,3-dienyloxy)dimethylsilane was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a

doublet at 5.27 ppm for the (*Z*)-*tert*-butyl(1-cyclopropylbuta-1,3-dienyloxy)dimethylsilane and a doublet at 5.66 ppm for the (*E*)-olefin.

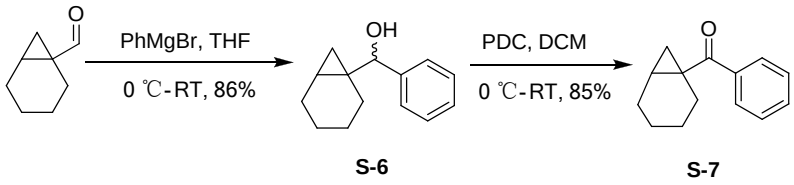
IR (film): 2957, 2930, 2858, 1637, 1472, 1254, 1229 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.00-6.90 (dt, J = 16.8 and 10.8 Hz, 1H), 5.29-5.26 (d, J = 10.8 Hz, 1H), 5.08-5.04 (dd, J = 16.8 and 1.8 Hz, 1H), 4.92-4.89 (dd, J = 10.8 and 1.8 Hz, 1H), 1.18-1.11 (m, 1H), 1.00 (s, 9H), 0.85-0.82 (m, 4H), 0.14 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.2, 132.7, 112.2, 108.4, 26.5, 19.0, 17.0, 7.3, -3.1. HRMS (ESI+) for $C_{13}H_{25}OSi$ $(M+H)^+$: calculated: 225.1669, found: 225.1669.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.75-6.65 (dt, J = 16.8 and 10.8 Hz, 1H), 5.67-5.65 (d, J = 10.8 Hz, 1H), 5.12-5.07 (dd, J = 16.8 and 1.8 Hz, 1H), 4.95-4.92 (dd, J = 10.8 and 1.8 Hz, 1H), 1.73-1.66 (m, 1H), 0.87 (s, 9H), 0.47-0.39 (m, 4H), 0.09 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.5, 133.5, 111.6, 109.6, 26.3, 18.8, 12.5, 5.5, -3.9.

Synthesis of (*Z*)-1-(1-Phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane (1p)



Bicyclo[4.1.0]heptan-1-yl(phenyl)methanone (**S-7**)



Bicyclo[4.1.0]heptane-1-carbaldehyde[13] (0.80 g, 6.5 mmol, in 50 mL THF) was cooled to 0 ^{o}C. Phenylmagnesium bromide (10.0 mmol, 1M solution in THF) was added slowly to the above bicyclo[4.1.0]heptane-1-carbaldehyde solution. The solution was then stirred under 0 ^{o}C for 30 minutes before it was poured into the mixture of 50 g ice and 50 mL water. After extracted with

Et_2O, washed with water, and brine, dried over $MgSO_4$, and concentrated in vacuo, the crude mixture was purified by flash column chromotography to afford 1.13 g (86%) diastereoisomer **S-6** as a light yellow liquid.

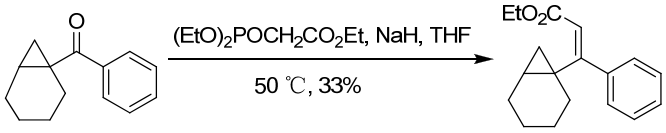
Diastereoisomer bicyclo[4.1.0]heptan-1-yl(phenyl)methanol (**S-6**) (1.13 g, 5.6 mmol) was dissolved in 60 mL anhydrous CH_2Cl_2 and cooled to 0 ^oC. Then PDC (2.52 g, 6.7 mmol) was added in batches and the resulting solution was stirred for 10 h at room temperature. The product mixture was filtered through a short silica gel column. Then the filtrate was concentrated to afford 0.95 g (85%) **S-7** as a colorless oil.

IR (film): 2930, 2857, 1670, 1447, 1302, 1260 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.81-7.77 (m, 2H), 7.52-7.40 (m, 3H), 2.28-2.19 (dt, J = 14.4 and 5.1 Hz, 1H), 1.98-1.75 (m, 3H), 1.69-1.61 (m, 1H), 1.52-1.16 (m, 5H), 0.76-0.73 (dd, J = 6.3 and 4.2 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 204.6, 137.7, 131.6, 128.2, 128.1, 29.0, 27.1, 22.8, 21.6, 20.2, 19.5, 18.9.

HRMS (ESI+) for $C_{14}H_{16}NaO$ $(M+Na)^+$: calculated: 223.1093, found: 223.1091.

(*E*)-Ethyl 3-(bicyclo[4.1.0]heptan-1-yl)-3-phenylacrylate (**S-8**)



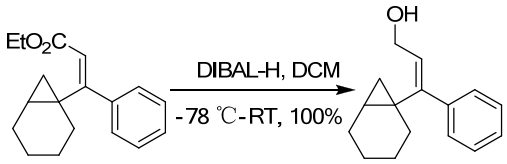
S-7 **S-8**

To a flask containing NaH (0.18 g, 7.5 mmol) and 40 mL THF at 0 °C was added triethyl phosphonoacetate (1.68 g, 7.5 mmol). After stirring at room temperature for 30 min, bicyclo[4.1.0]heptan-1-yl(phenyl)methanone (**S-7**) (0.60 g, 3.0 mmol) was added dropwise and the reaction was allowed to stir for 32 hours. After quenching with brine, extracting with Et_2O, and drying over $MgSO_4$, concentration of the organic phase in vacuo gave a crude oil that was further purified by flash chromatography to afford 0.27 g (33%) **S-8** as a colorless oil.

IR (film): 2929, 2856, 1721, 1613, 1446, 1260, 1154, 1038 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.60-7.55 (m, 2H), 7.36-7.31 (m, 3H), 6.13 (s, 1H), 4.28-4.17 (m, 2H), 2.21-2.11 (m, 1H), 2.01-1.92 (m, 2H), 1.76-1.65 (m, 1H), 1.58-1.42 (m, 2H), 1.40-1.20 (m, 5H), 1.02-0.94 (m, 1H), 0.75-0.64 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.1, 162.8, 140.6, 128.5, 128.2, 127.1, 118.5, 59.9, 30.5, 23.2, 22.4, 21.7, 20.7, 20.0, 19.8, 14.4. HRMS (ESI+) for $C_{18}H_{23}O_2$ $(M+H)^+$: calculated: 271.1693, found: 271.1689.

(*E*)-3-(Bicyclo[4.1.0]heptan-1-yl)-3-phenylprop-2-en-1-ol (**S-9**)



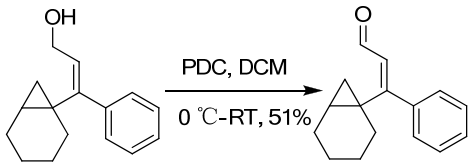
S-8 **S-9**

To a Schlenk flask charged with (*E*)-ethyl 3-(bicyclo[4.1.0]heptan-1-yl)-3-phenylacrylate (**S-8**) **(**190 mg, 0.7 mmol) in THF at 0 °C was added DIBAL-H (2.8 mL, 1 M in toluene, 2.8 mmol) dropwise. The reaction was warmed to room temperature overnight and was quenched with ethylacetate and aqueous potassium tartrate tetrahydrate. Stirring was continued until the solution was clear. Extracted with Et_2O, washed with brine, dried over $MgSO_4$, evaporation and purification by flash column chromatography to give 168 mg (100%) **S-9** as a colorless oil.

IR (film): 2927, 2855, 1493, 1447, 1024 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.49-7.45 (m, 2H), 7.32-7.20 (m, 3H), 5.96-5.92 (t, J = 6.3 Hz, 1H), 4.57-4.54 (dd, J = 6.3 and 3.6 Hz, 2H), 2.04-1.90 (m, 3H), 1.77-1.70 (m, 1H), 1.60 (br s, 1H), 1.46-1.20 (m, 4H), 0.97-0.92 (m, 1H), 0.66-0.61 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 148.8, 141.3, 128.7, 128.0, 126.8, 126.4, 60.3, 31.7, 23.2, 21.8, 20.9, 20.3, 19.8, 19.1. HRMS (ESI+) for $C_{16}H_{20}NaO$ $(M+Na)^+$: calculated: 251.1406, found: 251.1405.

(*E*)-3-(Bicyclo[4.1.0]heptan-1-yl)-3-phenylacrylaldehyde (**S-10**)



S-9 **S-10**

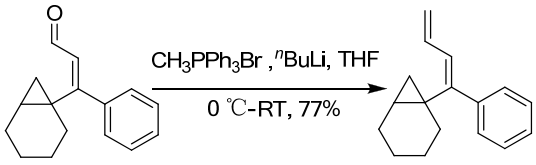
(*E*)-3-(Bicyclo[4.1.0]heptan-1-yl)-3-phenylprop-2-en-1-ol (**S-9**) (168 mg, 0.7 mmol) was dissolved in 20 mL anhydrous CH_2Cl_2 and cooled to 0 ^oC. Then PDC (570 mg, 1.5 mmol) was added in batches and the resulting solution was stirred for 1 hour at room temperature. The product mixture was filtered through a short silica gel column. Then the filtrate was concentrated to get 87 mg (51%) **S-10** as a light yellow liquid.

IR (film): 2931, 2855, 1664, 1590, 1447, 1136 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.50-10.46 (d, J = 8.4 Hz, 1H), 7.65-7.60 (m, 2H), 7.42-7.37 (m, 3H), 6.32-6.30 (d, J = 8.4 Hz, 1H), 2.11-1.98 (m, 3H), 1.86-1.79 (m, 1H), 1.55-1.43 (m, 3H), 1.37-1.13 (m, 2H), 0.89-0.87 (d, J = 7.5 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 193.1, 168.7,

138.8, 129.7, 128.5, 127.6, 127.3, 33.1, 22.5, 21.6, 21.3, 20.2, 19.8, 19.7. HRMS (ESI+) for $C_{16}H_{19}O$ $(M+H)^+$: calculated: 227.1430, found: 227.1427.

(*E*)-1-(1-Phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane (**1p**)

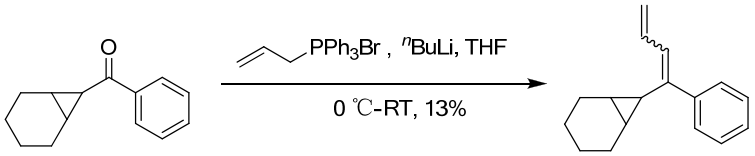


S-10 **1p**

To an oven-dried round-bottomed flask with a stir bar was added methyltriphenylphosphonium bromide (544 mg, 1.5 mmol, 4.0 equiv) and THF (10 mL). The solution was cooled to 0 ℃ and 0.61 mL (1.5 mmol, 4.0 equiv) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 ℃, aldehyde (**S-10**) (86 mg, 0.4 mmol, 1.0 equiv) in 2 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 2 hours. The reaction was then quenched with 8 mL brine and diluted with 40 mL of diethyl ether. The organic layer was separated and the aqueous layer was extracted by diethyl ether in one time. The combined organic layers were dried over Na_2SO_4, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford 66 mg (77%) **1p** as a colorless oil.

IR (film): 2928, 2855, 1492, 1447, 1029 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54-7.52 (d, J = 7.2 Hz, 2H), 7.32-7.28 (t, J = 7.2 Hz, 2H), 7.23-7.21 (d, J = 7.2 Hz, 1H), 7.12-7.03 (dt, J = 16.8 and 10.8 Hz, 1H), 6.46-6.43 (d, J = 10.8 Hz, 1H), 5.32-5.28 (dd, J = 16.8 and 1.6 Hz, 1H), 5.22-5.19 (dd, J = 10.8 and 1.6 Hz, 1H), 2.13-1.94 (m, 3H), 1.81-1.74 (m, 1H), 1.51-1.25 (m, 5H), 1.02-0.96 (m, 1H), 0.68-0.67 (d, J = 7.6 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.3, 141.4, 134.4, 129.0, 128.0, 126.7, 126.3, 117.7, 31.8, 23.4, 22.0, 21.0, 20.4, 20.0, 19.4. HRMS (EI+) for $C_{17}H_{20}$ $(M)^+$: calculated: 224.1565, found: 224.1568.

Synthesis of 7-(1-phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane (1q)



1q

To an oven-dried round-bottomed flask with a stir bar was added allyltriphenylphosphonium bromide (3.0 mmol, 1.5 equiv) and THF (20 mL). The solution was cooled to 0 ℃ and 1.2 mL (3.0 mmol, 1.5 equiv) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 ℃, bicyclo[4.1.0]heptan-7-yl(phenyl)methanone[14] (2.0 mmol, 1.0 equiv) in 6 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 24 hours. The reaction was then quenched with 10 mL brine and diluted with 50 mL of diethyl ether. The organic layer was separated and dried over Na_2SO_4, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford 56 mg (13%) **1q** as a colorless oil.

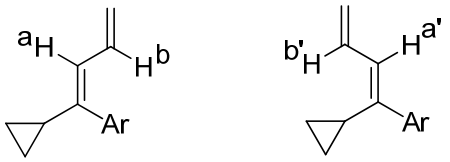
A 1.3:1 mixture of (*Z*:*E*)-7-(1-phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane was obtained. The (*Z*):(*E*)-ratio was determined using ^{1}H-NMR by integration of one of the olefinic protons : a doublet at 5.97 ppm for the (*Z*)-7-(1-phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane and a doublet at 6.39 ppm for the (*E*)-olefin.

IR (film): 2925, 2852, 1624, 1448, 1077, 1018 cm^{-1}. (*Z*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40-7.18 (m, 5H), 6.30-6.21 (dt, J = 16.8 and 10.8 Hz, 1H), 5.99-5.96 (d, J = 10.8 Hz, 1H), 5.13-5.09 (dd, J = 16.8 and 2.0 Hz, 1H), 4.87-4.84 (dd, J = 10.8 and 2.0 Hz, 1H), 1.99-1.78 (m, 4H), 1.50-1.48 (t, J = 3.6 Hz, 1H), 1.34-1.15 (m, 6H), 1.13-1.10 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.0, 140.5, 134.7, 128.9, 127.8, 126.8, 123.7, 114.8, 31.4, 23.3, 21.4, 19.4. HRMS (EI+) for $C_{17}H_{20}$ $(M)^+$: calculated: 224.1565, found: 224.1568.

Additional signals for the (*E*)-isomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40-7.18 (m, 5H), 7.01-6.91 (dt, J = 16.8 and 10.8 Hz, 1H), 6.40-6.38 (d, J = 10.8 Hz, 1H), 5.30-5.25 (dd, J = 16.8 and 1.6 Hz, 1H), 5.21-5.18 (dd, J = 10.8 and 1.6 Hz, 1H), 1.99-1.67 (m, 5H), 1.34-1.15 (m, 6H), 0.93-0.91 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.0, 142.1, 134.3, 129.9, 128.1, 126.7, 126.0, 117.4, 24.6, 23.4, 21.5, 19.8.

11. References

[1] Kataoka, F.; Nishida, S.; Tsuji, T.; Murakami, M. *J. Am. Chem. Soc.* **1981**, *103*, 6878.



Usually, in the ^{1}H NMR spectra, ^{a}H is in the upfield compared with $^{a'}$H, and ^{b}H is also in the upfield compared with $^{b'}$H.

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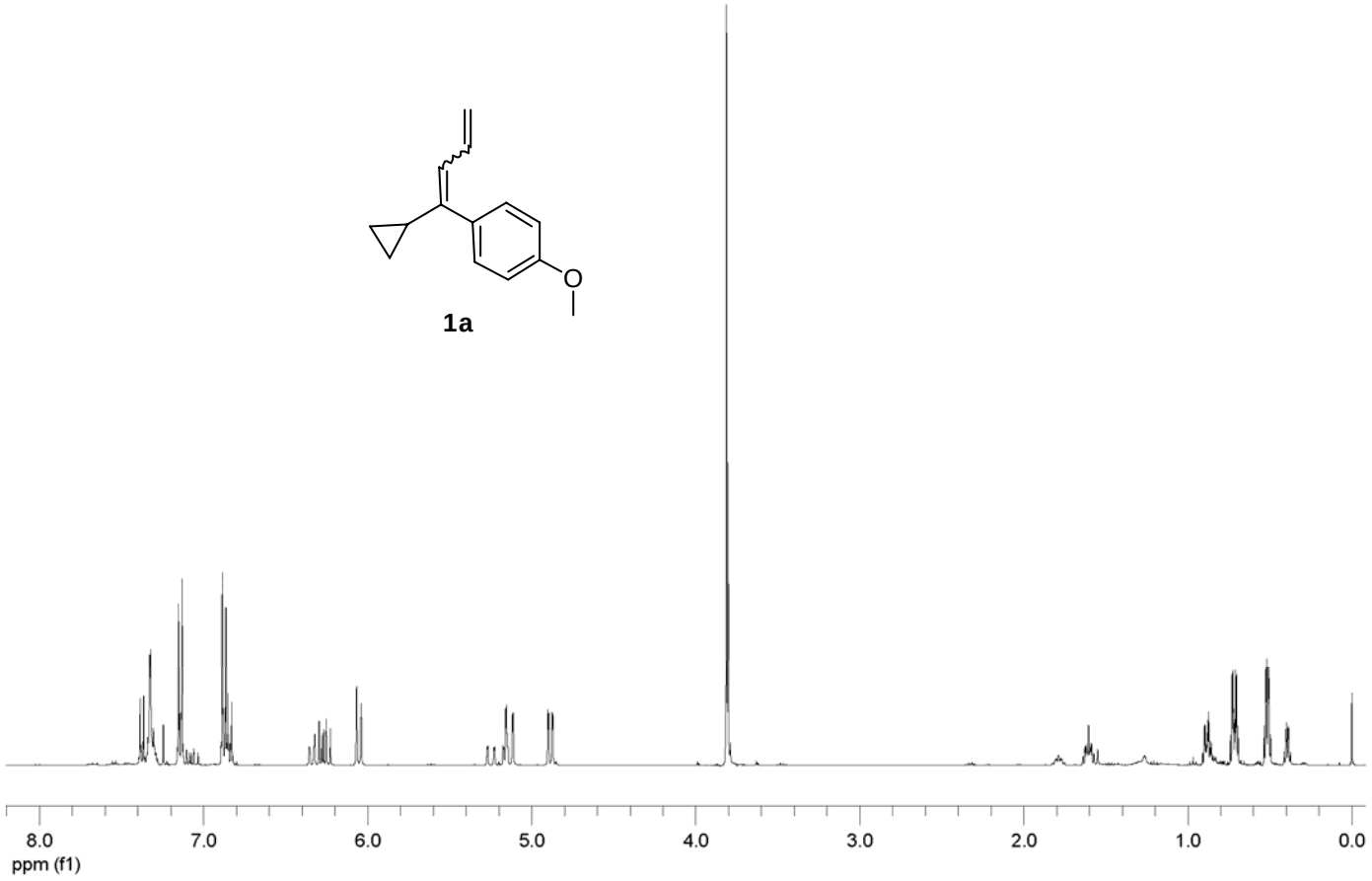
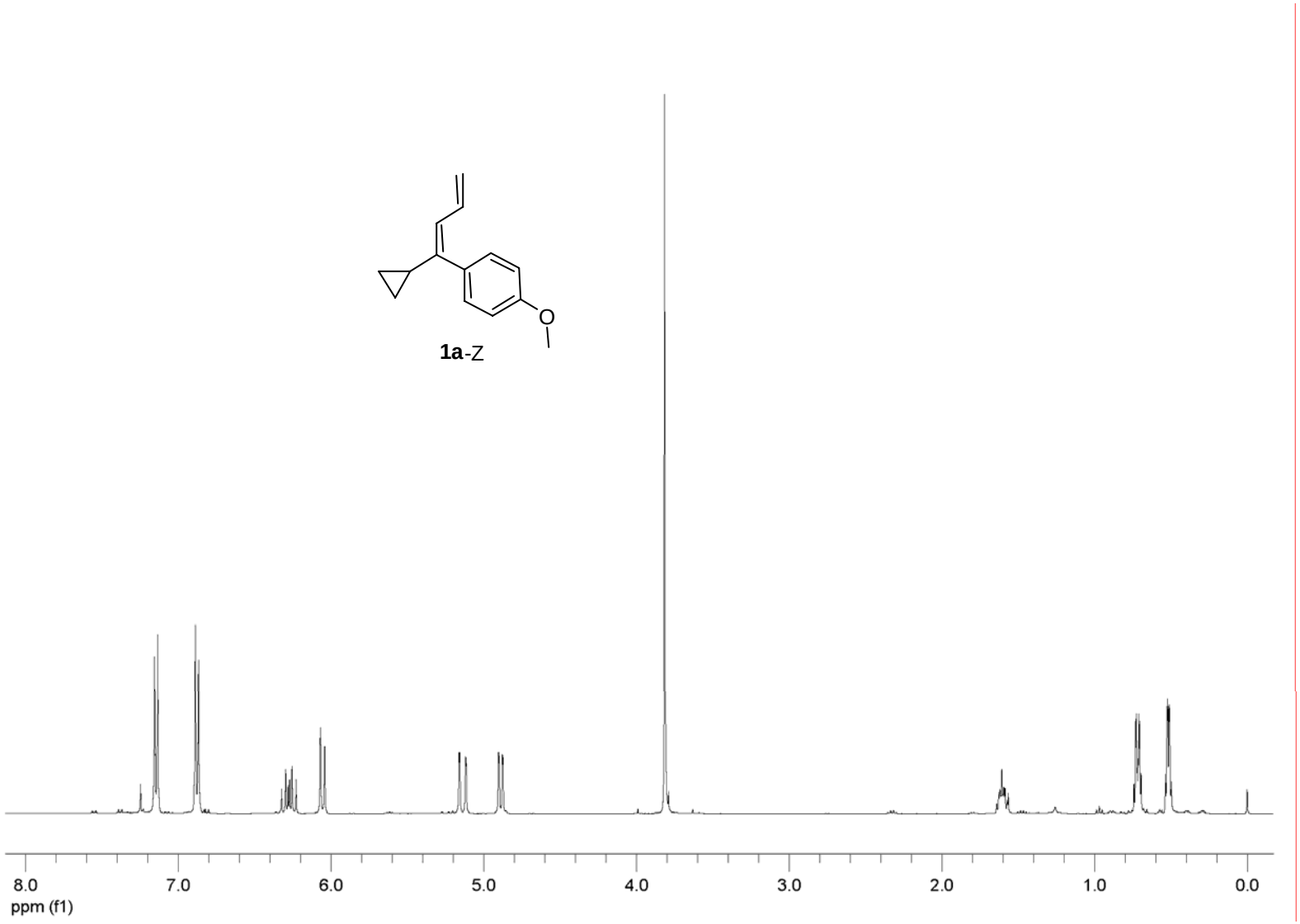
12. ^{1}H and ^{13}C Spectra for all New Compounds





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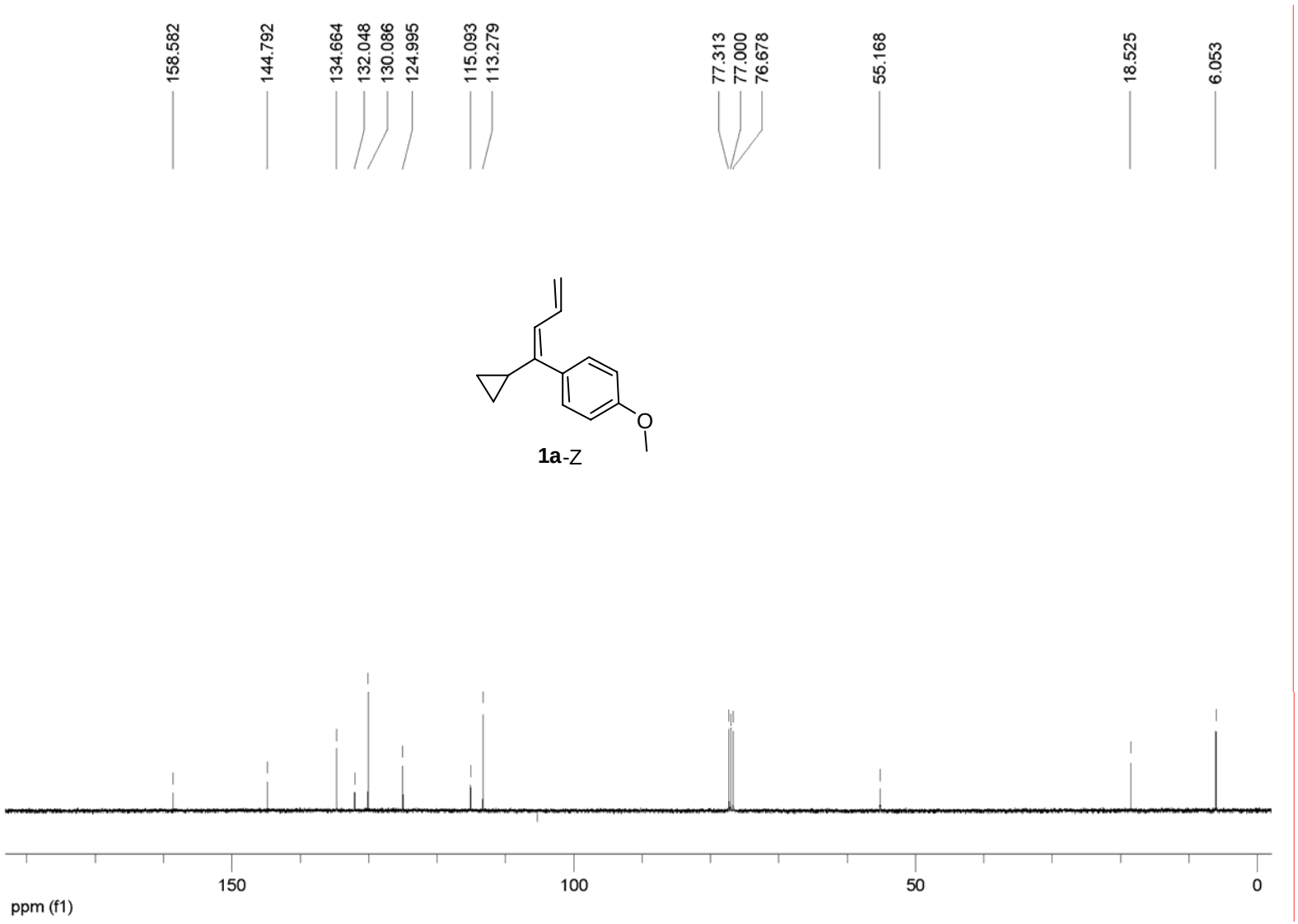
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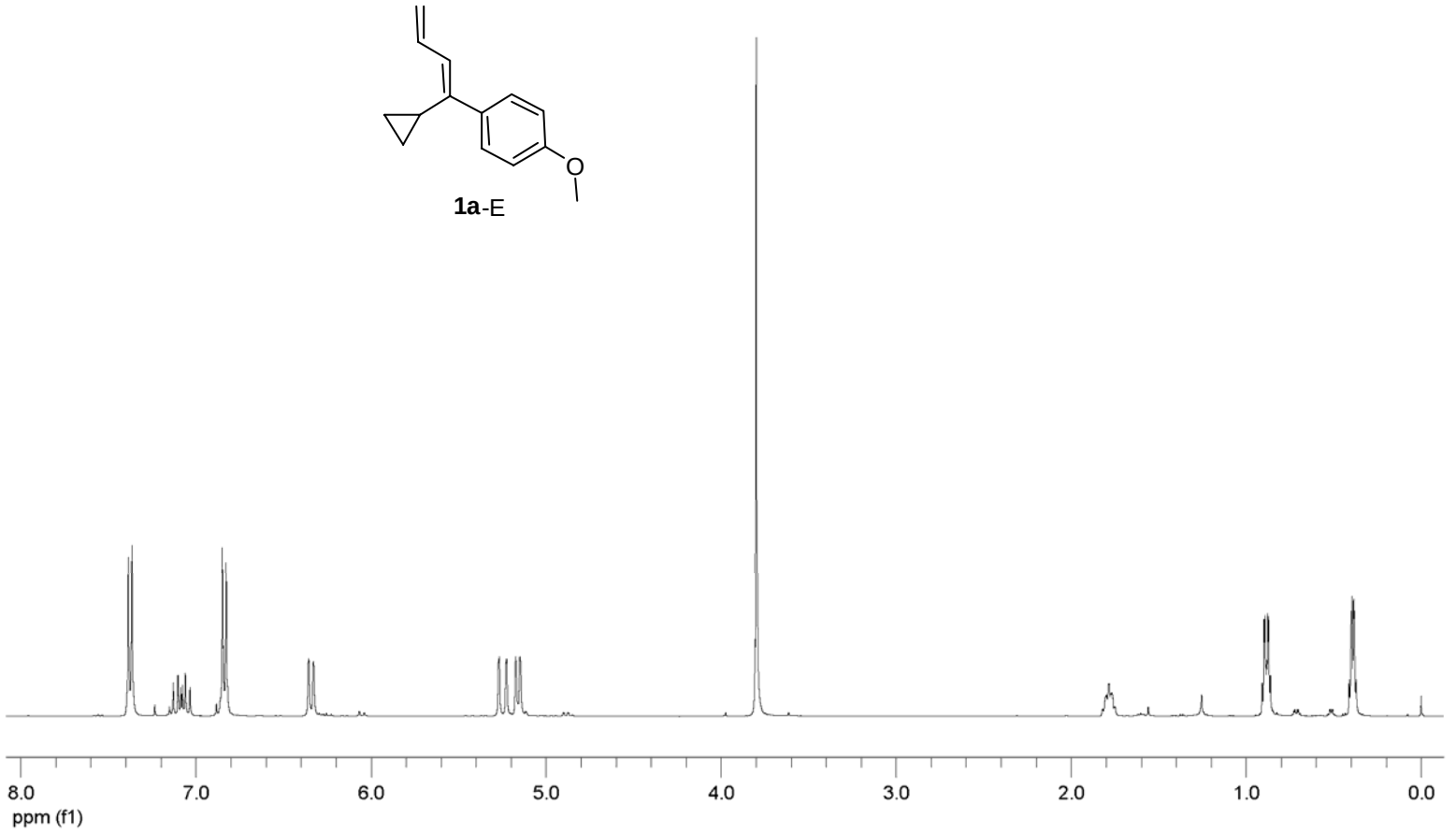
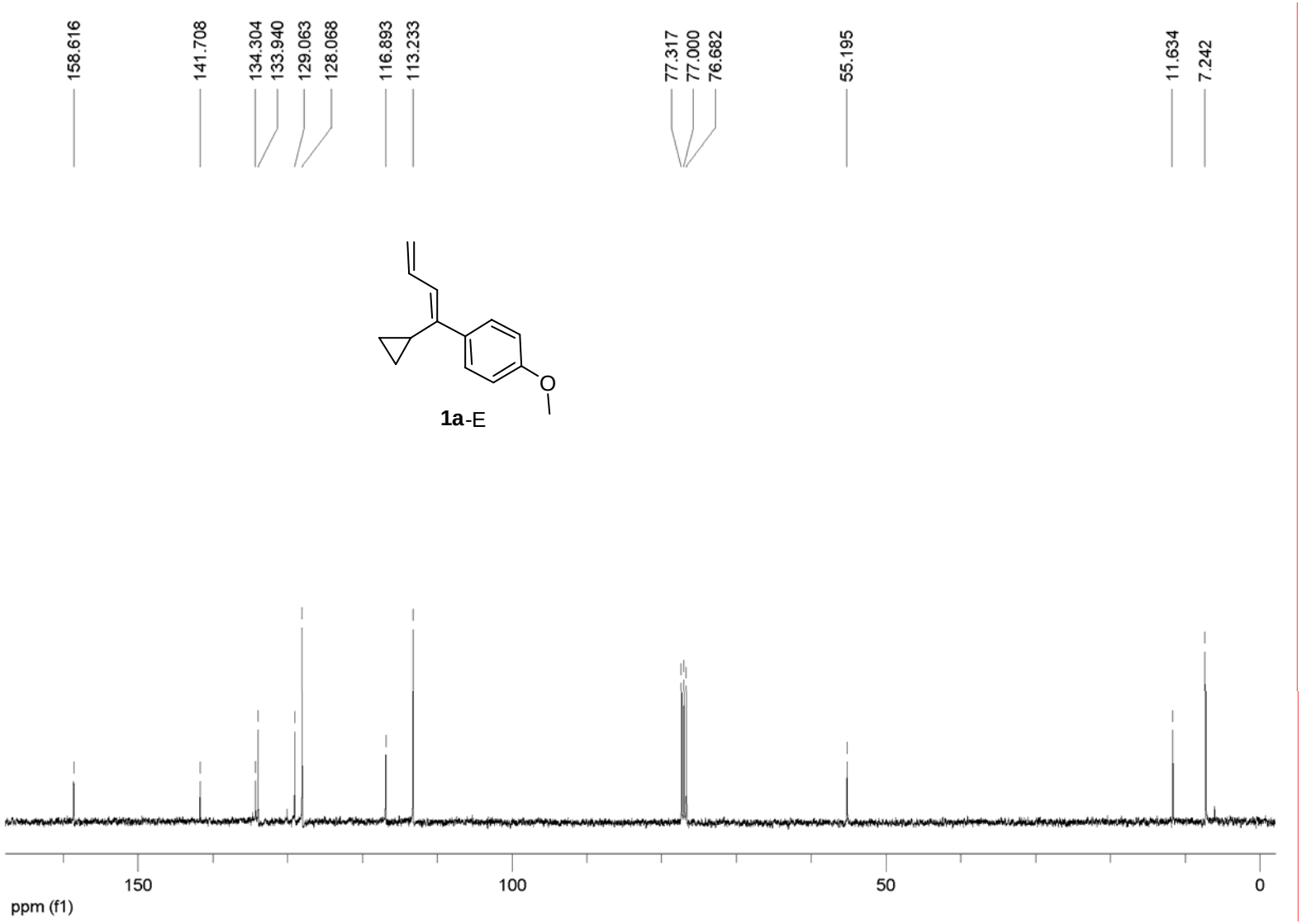
100
50
0
ppm (f1)

1a-Z



1a-E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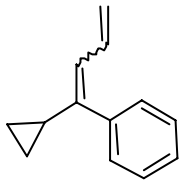
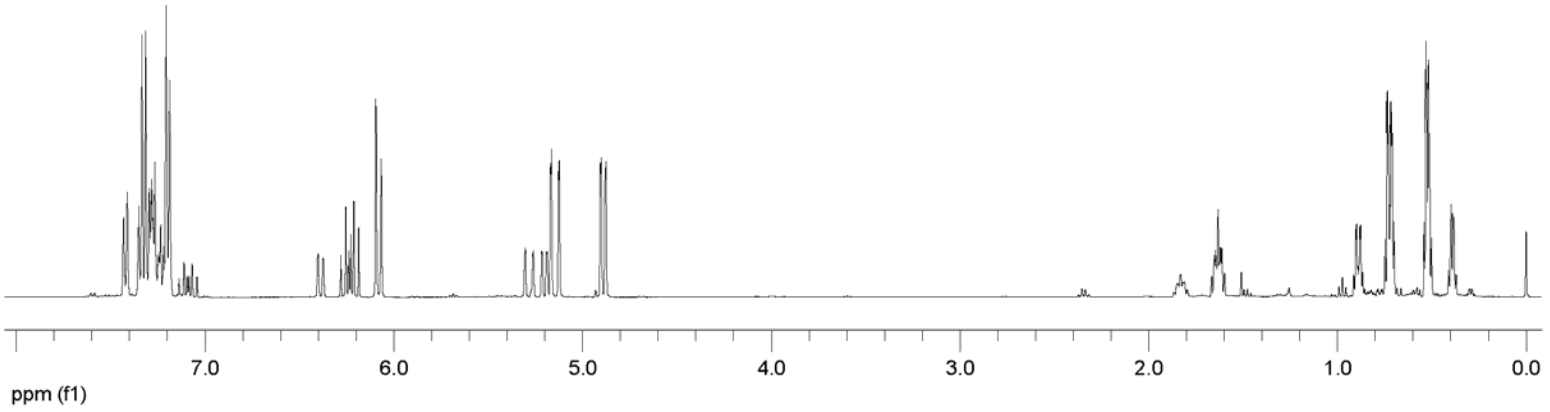
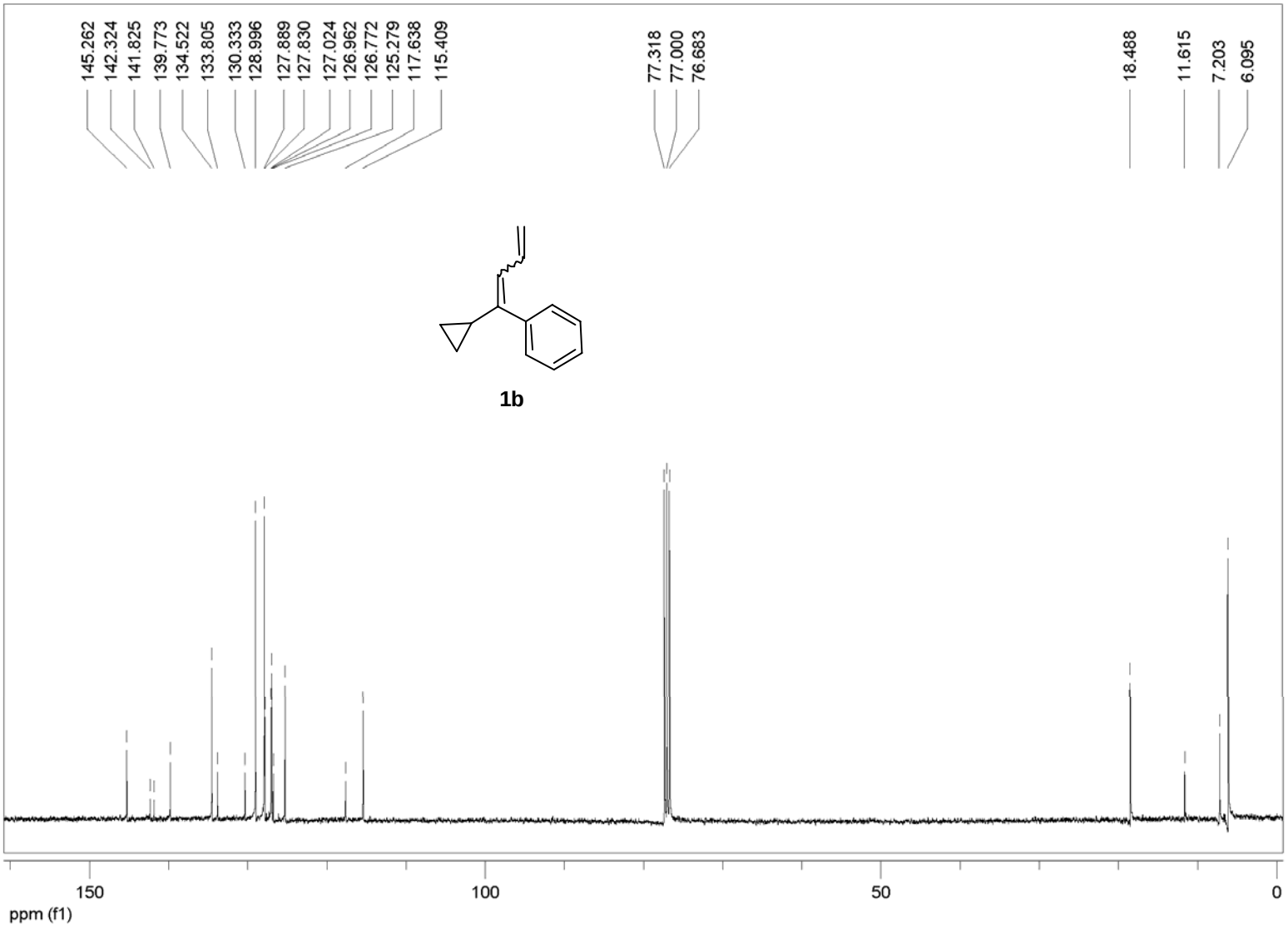
50
0
ppm (f1)

1a-E



1b

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127.830
127.024
126.962
126.772
125.279
117.638
115.409
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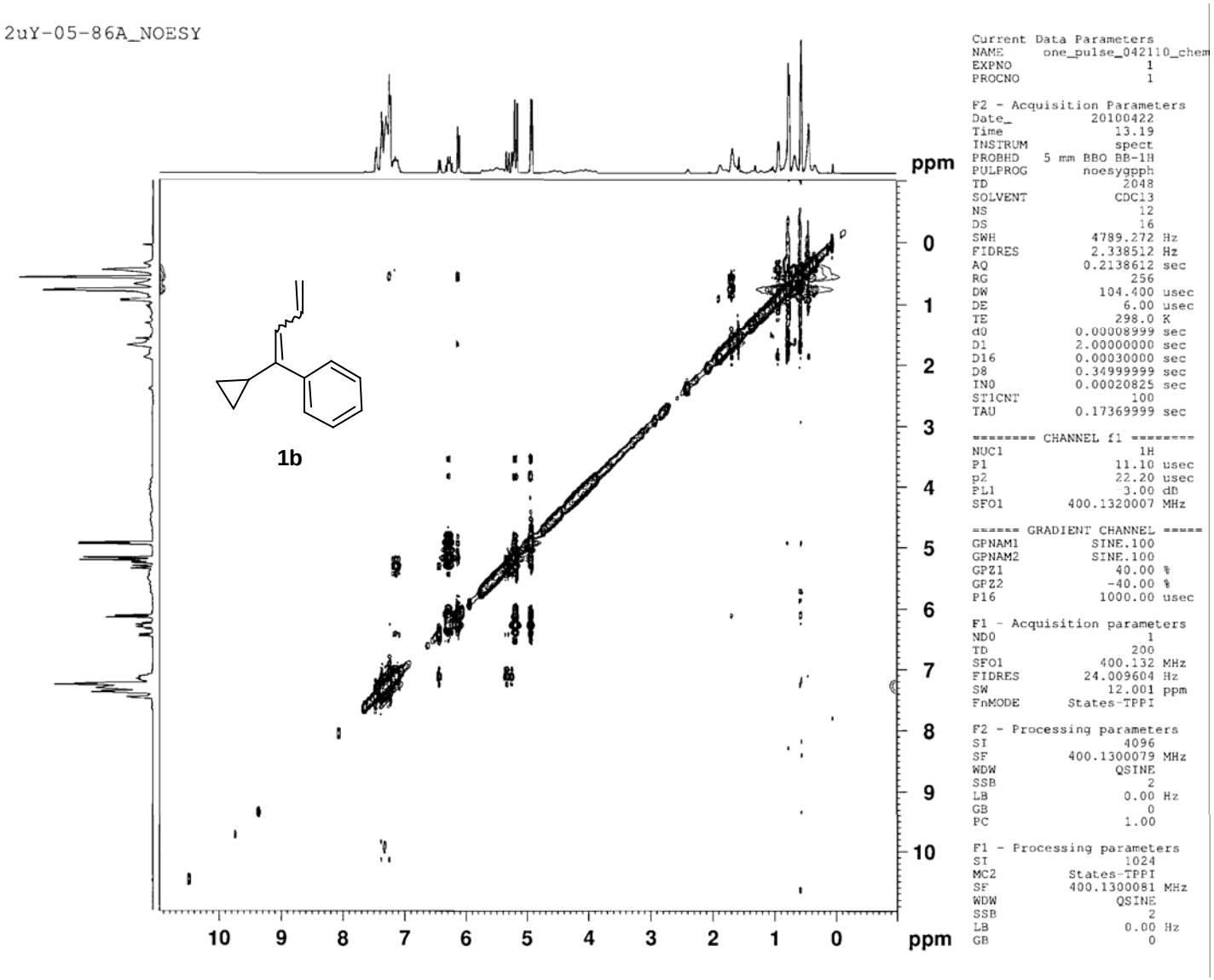
77.000
76.683
18.488
11.615
7.203
6.095
1b
150
100
50
0
ppm (f1)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ppm
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PROCNO 1
F2 - Acquisition Parameters
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Time 13.19
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PULPROG noesygpph
TD 2048
SOLVENT CDCl3
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DS 16
SWH 4789.272 Hz
FIDRES 2.338512 Hz
AQ 0.2138612 sec
RG 256
DW 104.400 usec
DE 6.00 usec
TE 298.0 K
d0 0.00008999 sec
D1 2.00000000 sec
D16 0.00030000 sec
D8 0.34999999 sec
IN0 0.00020825 sec
ST1CNT 100
TAU 0.17369999 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.10 usec
p2 22.20 usec
PL1 3.00 dB
SFO1 400.1320007 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec
F1 - Acquisition parameters
ND0 1
TD 200
SFO1 400.132 MHz
FIDRES 24.009604 Hz
SW 12.001 ppm
FnMODE States-TPPI
F2 - Processing parameters
SI 4096
SF 400.1300079 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
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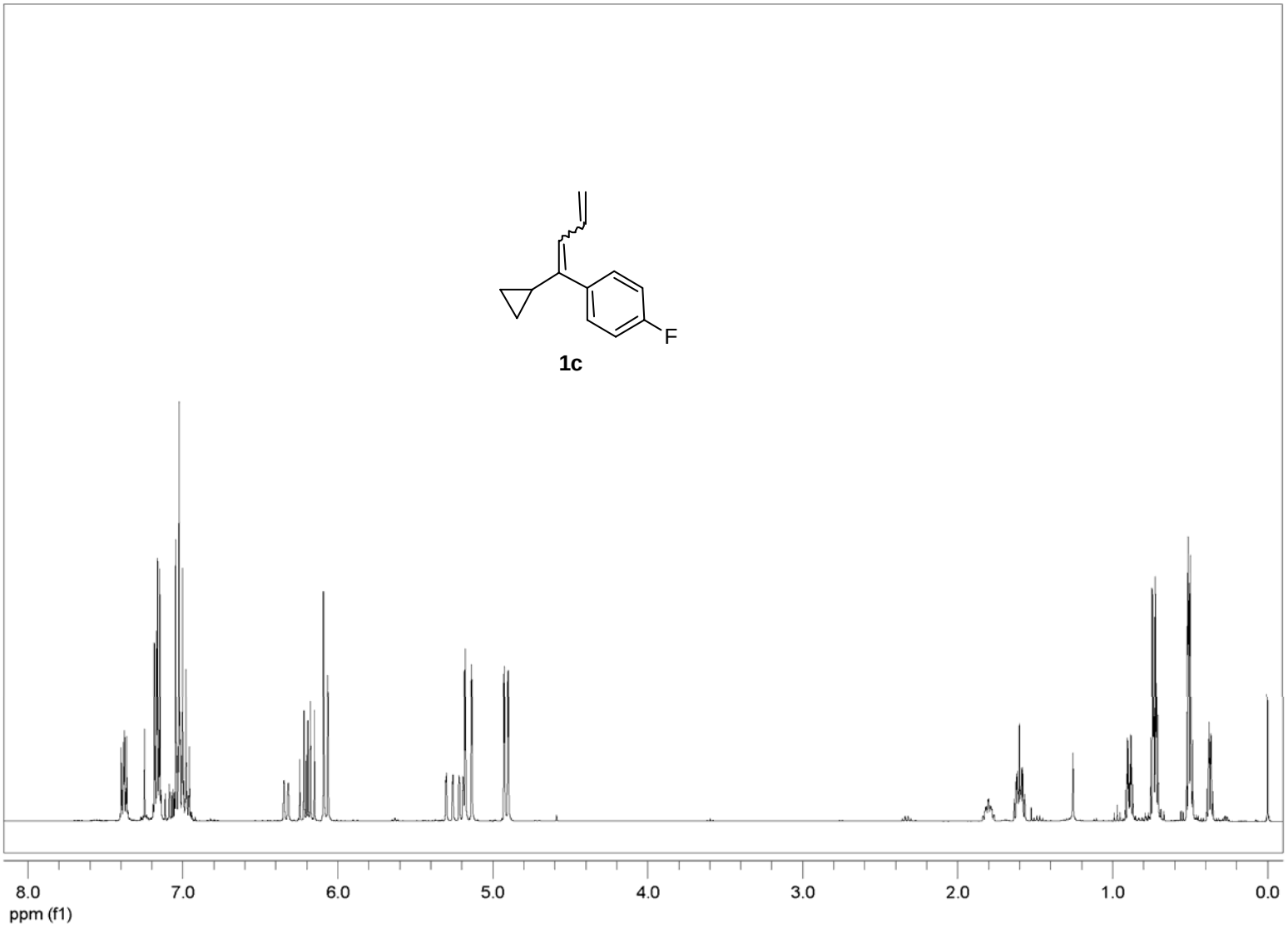
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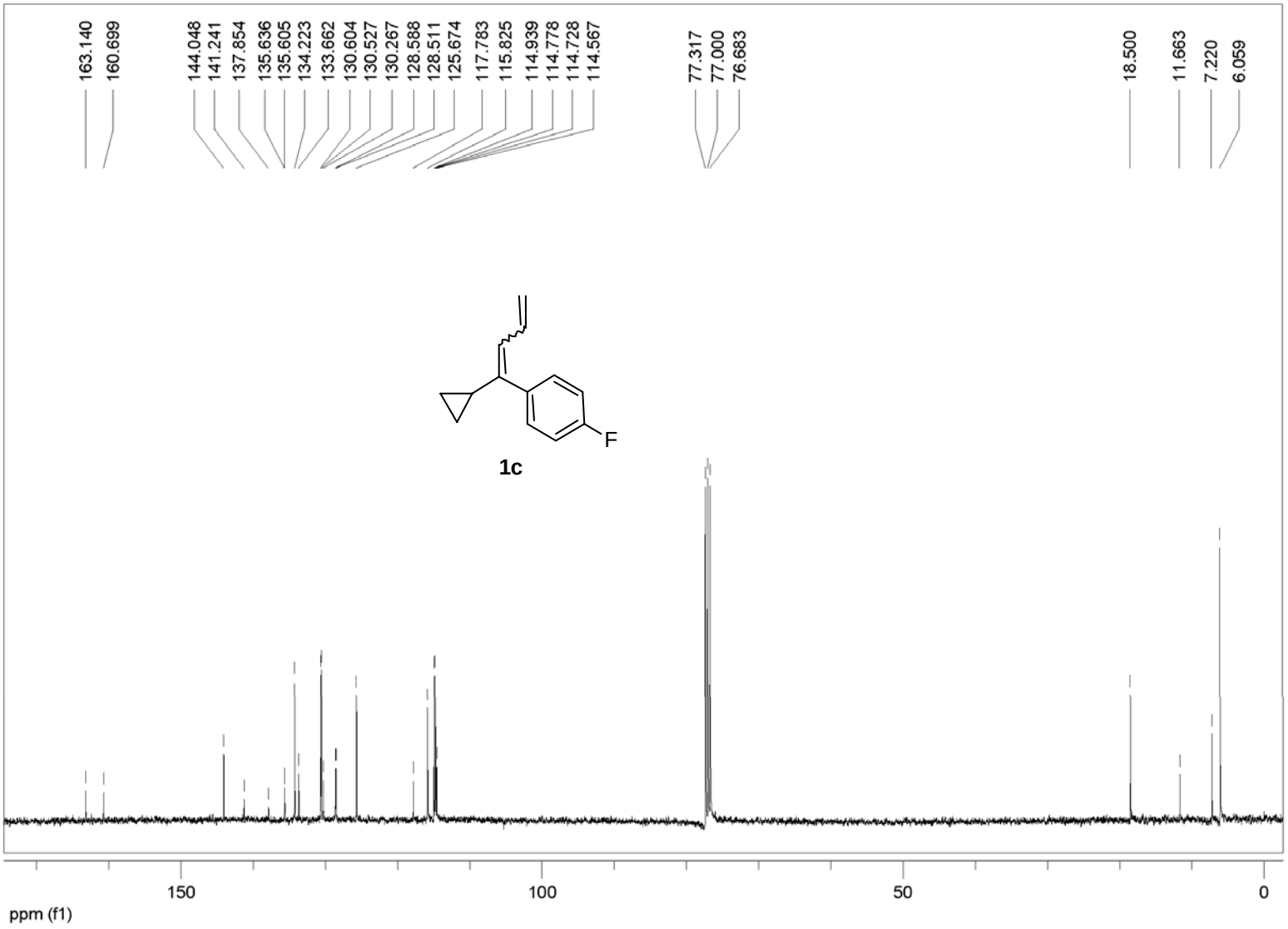
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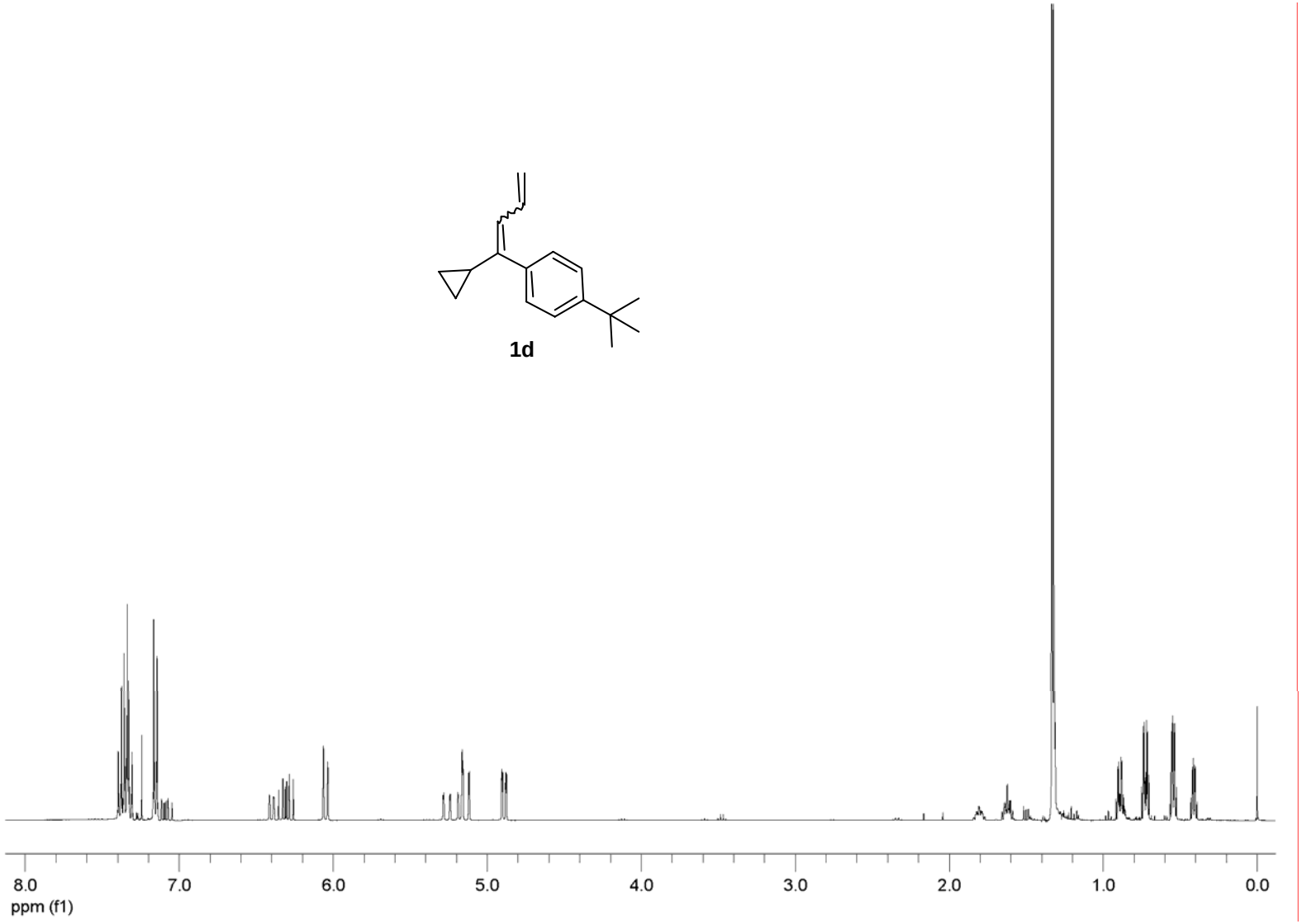
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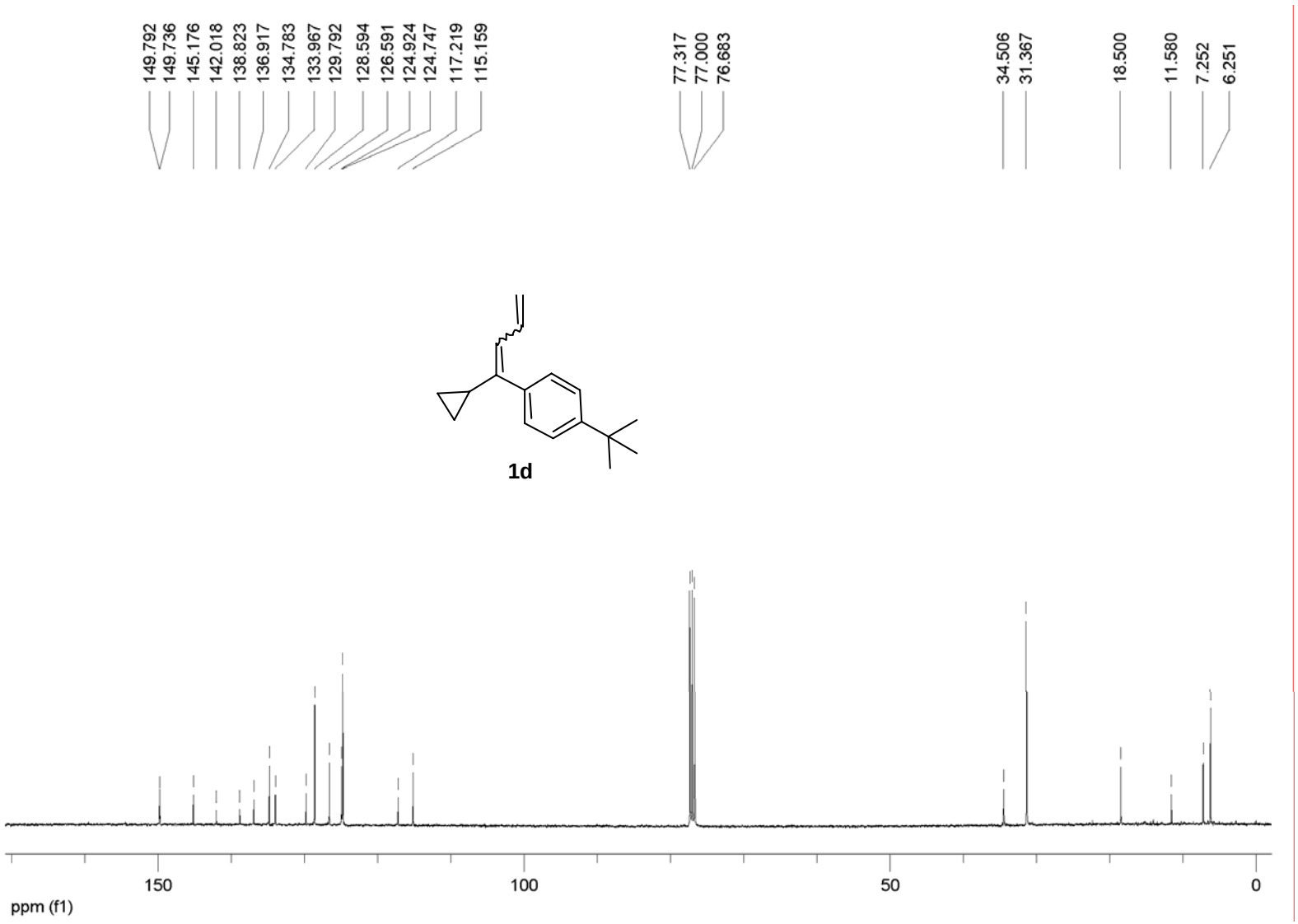
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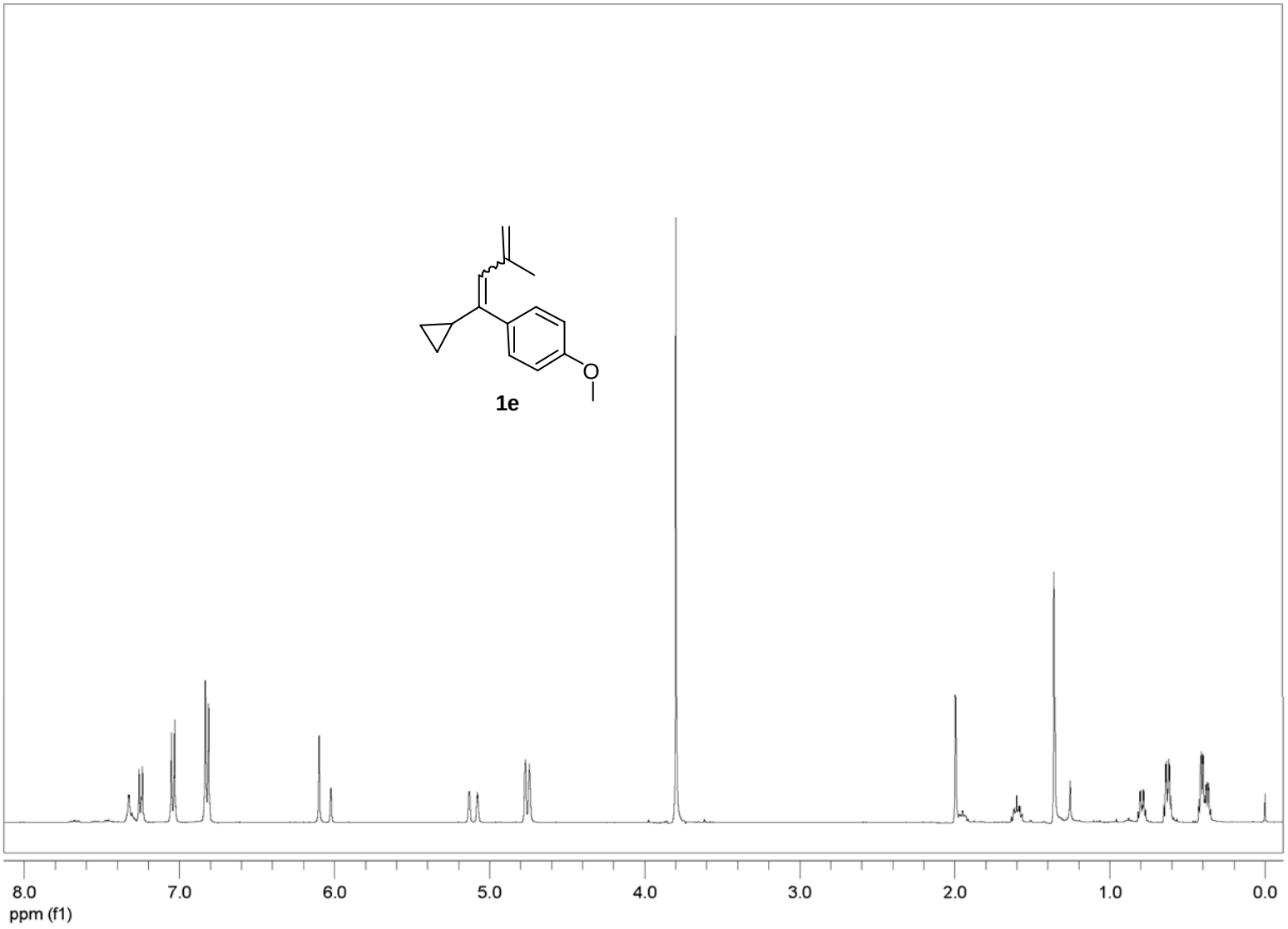
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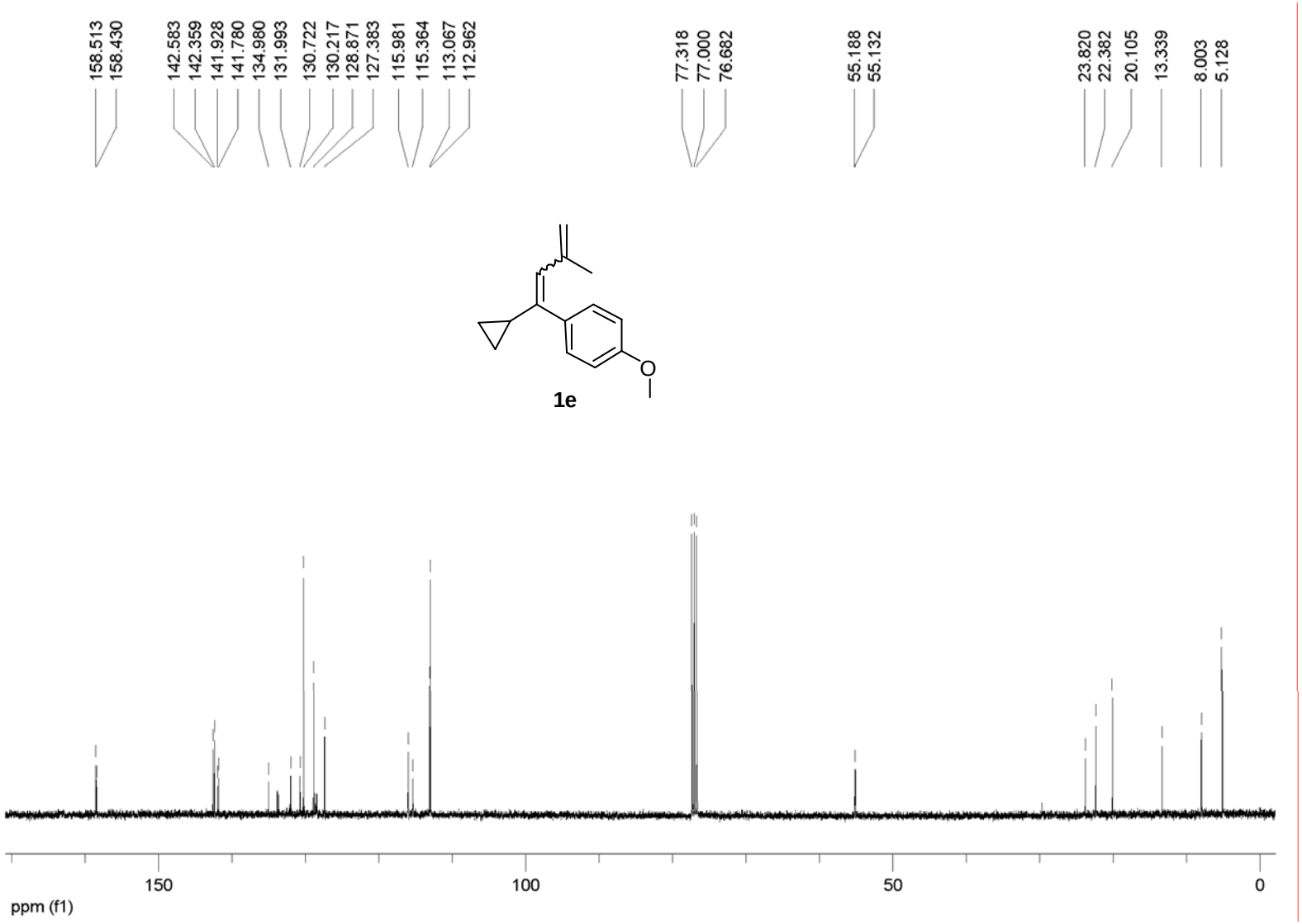
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115.981
115.364
113.067
112.962
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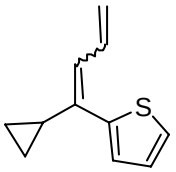
ppm (f1)

1e



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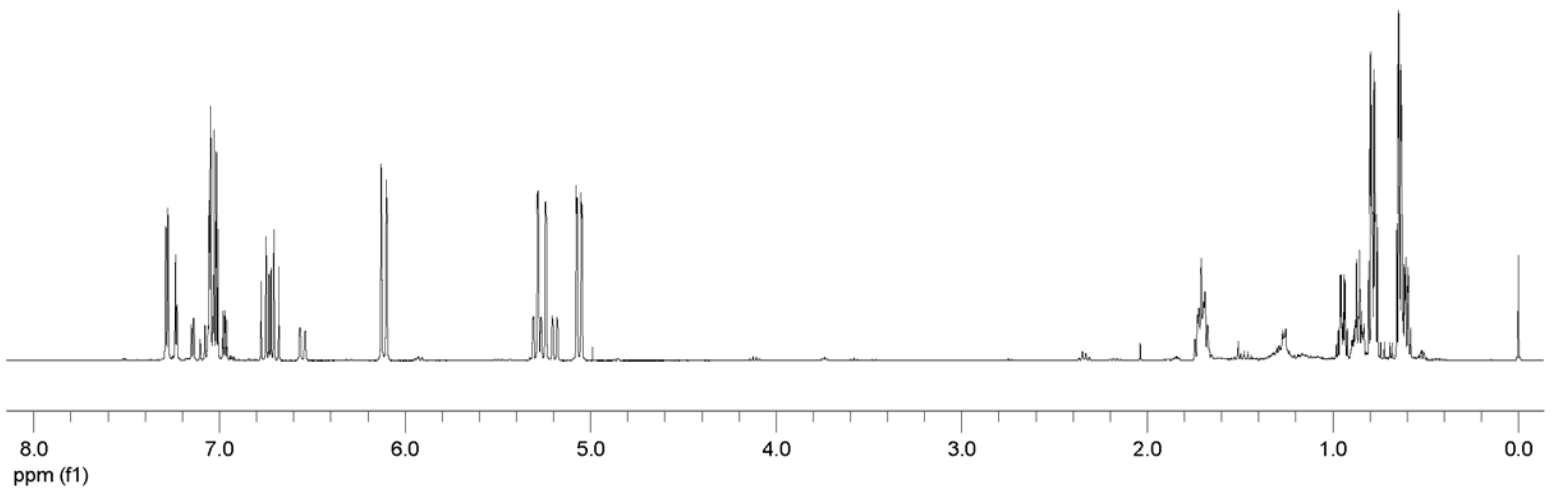

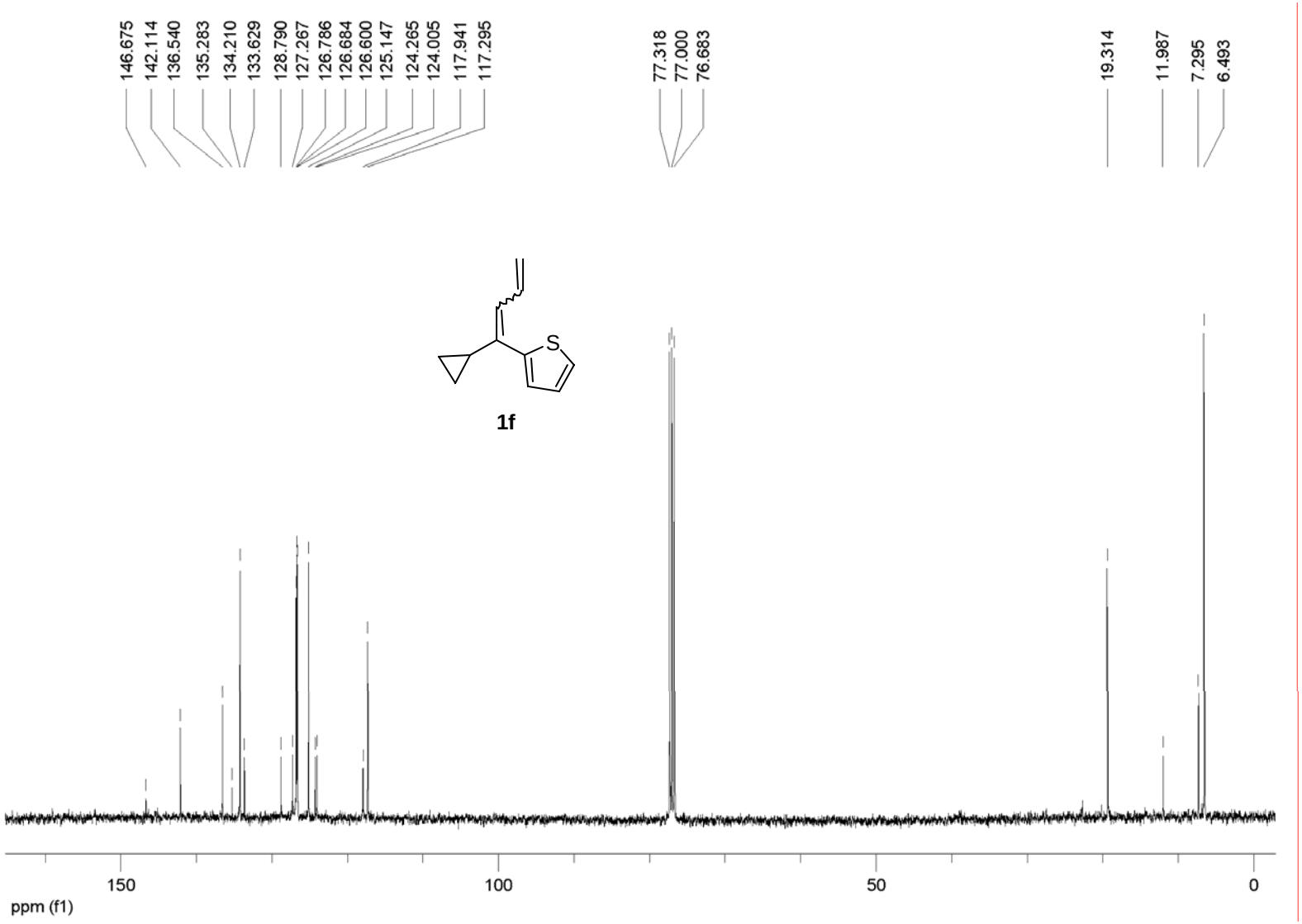
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124.005
117.941
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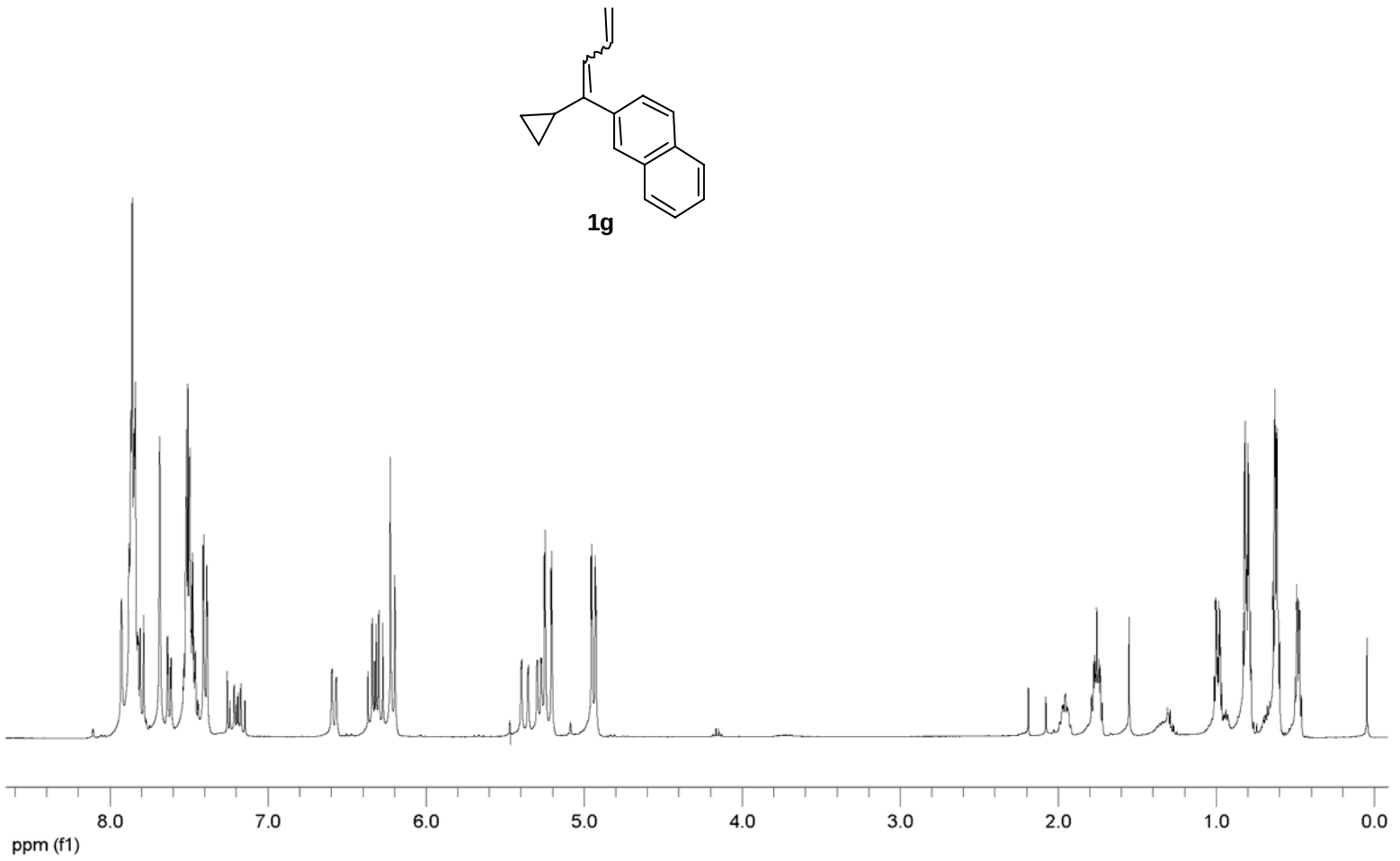
ppm (f1)



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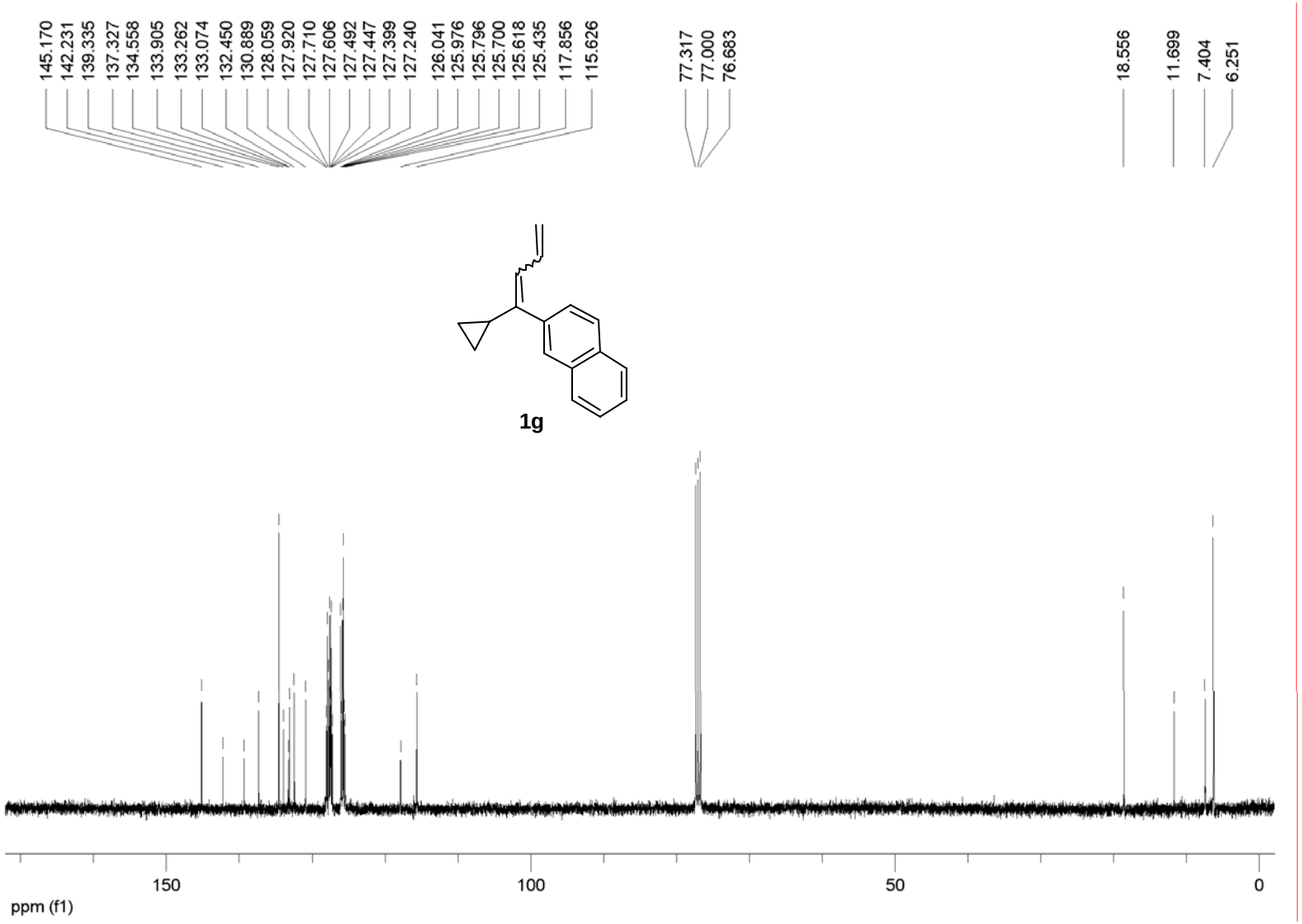
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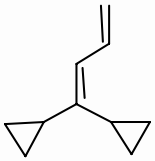
ppm (f1)



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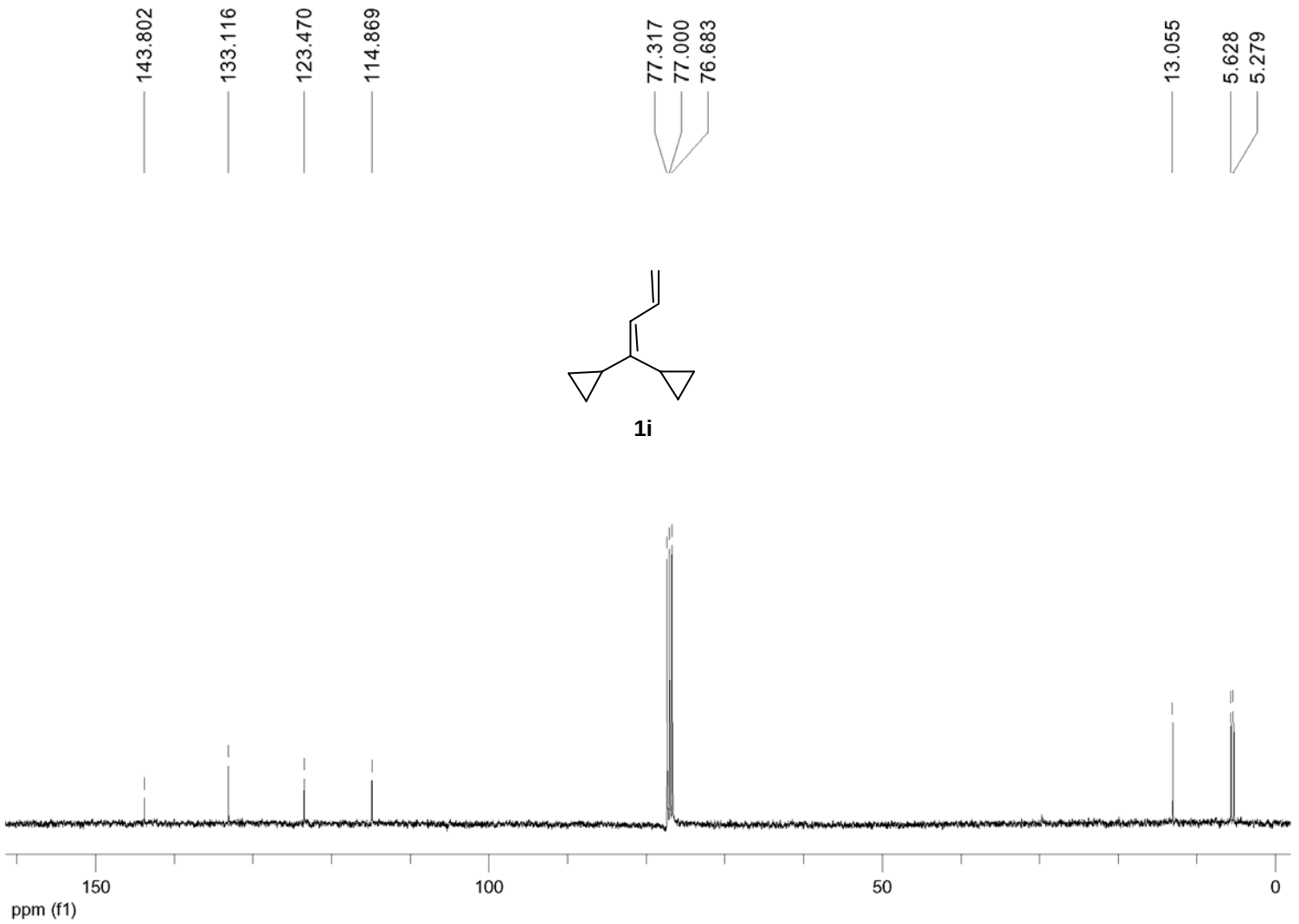
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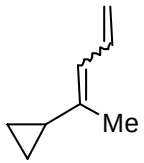
50
0
ppm (f1)

1i



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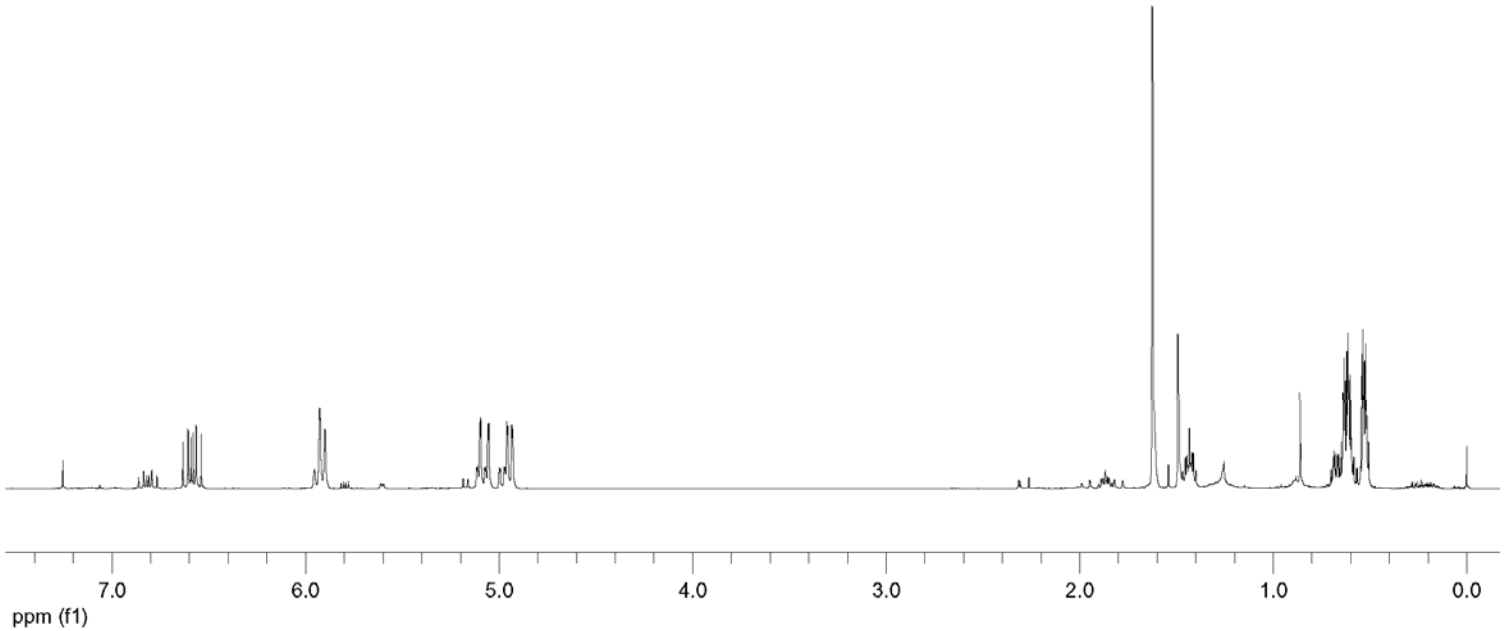

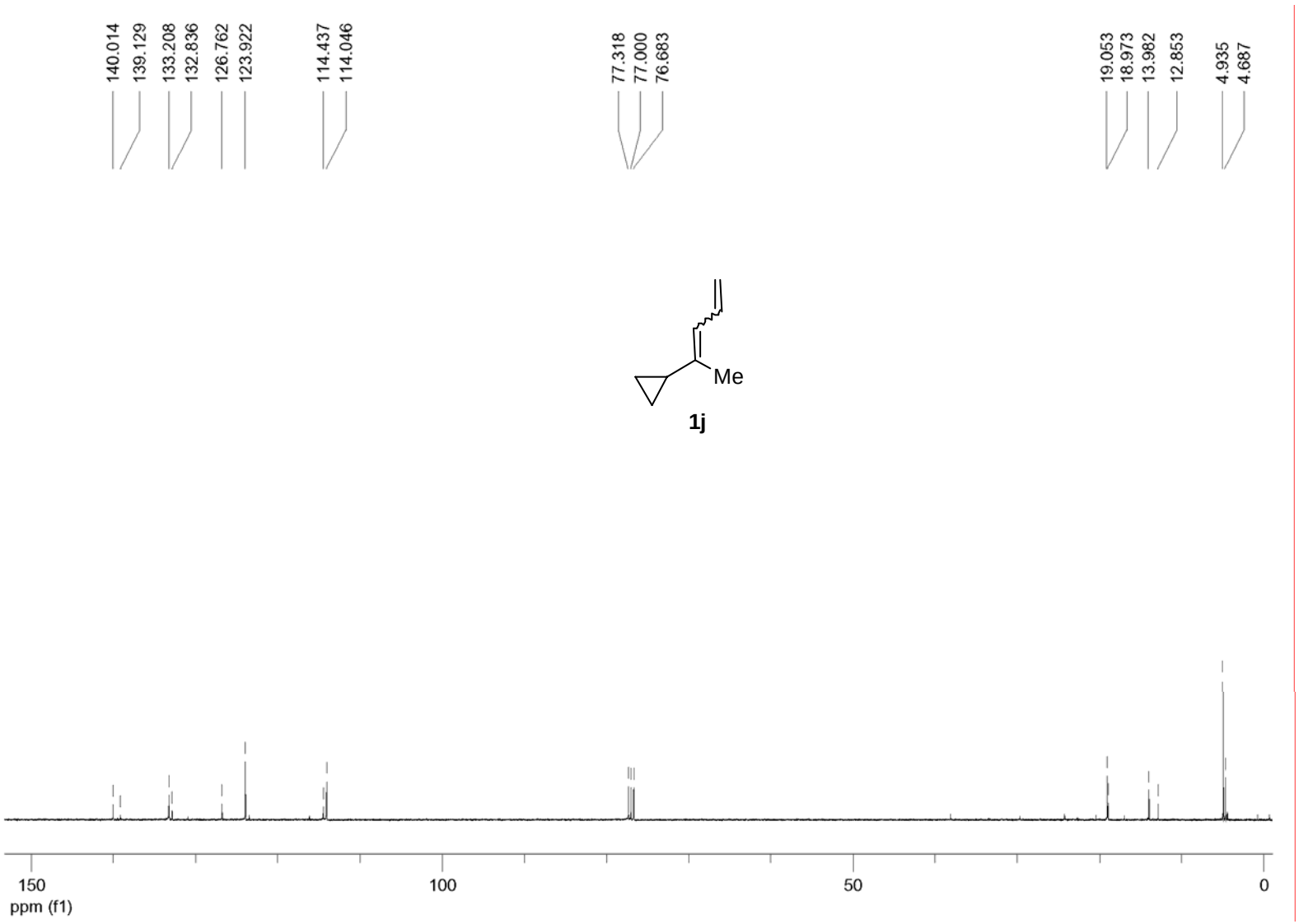
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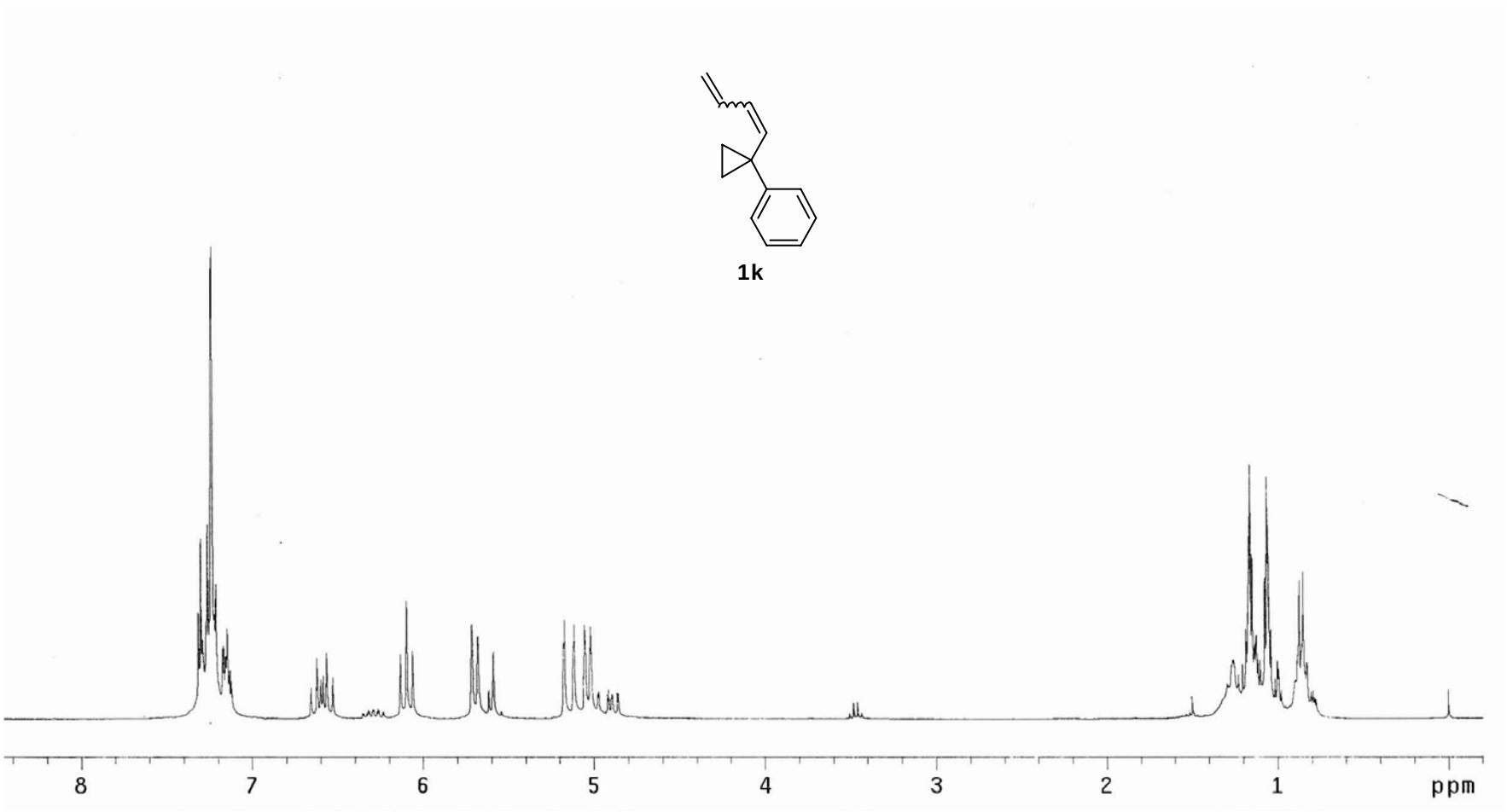
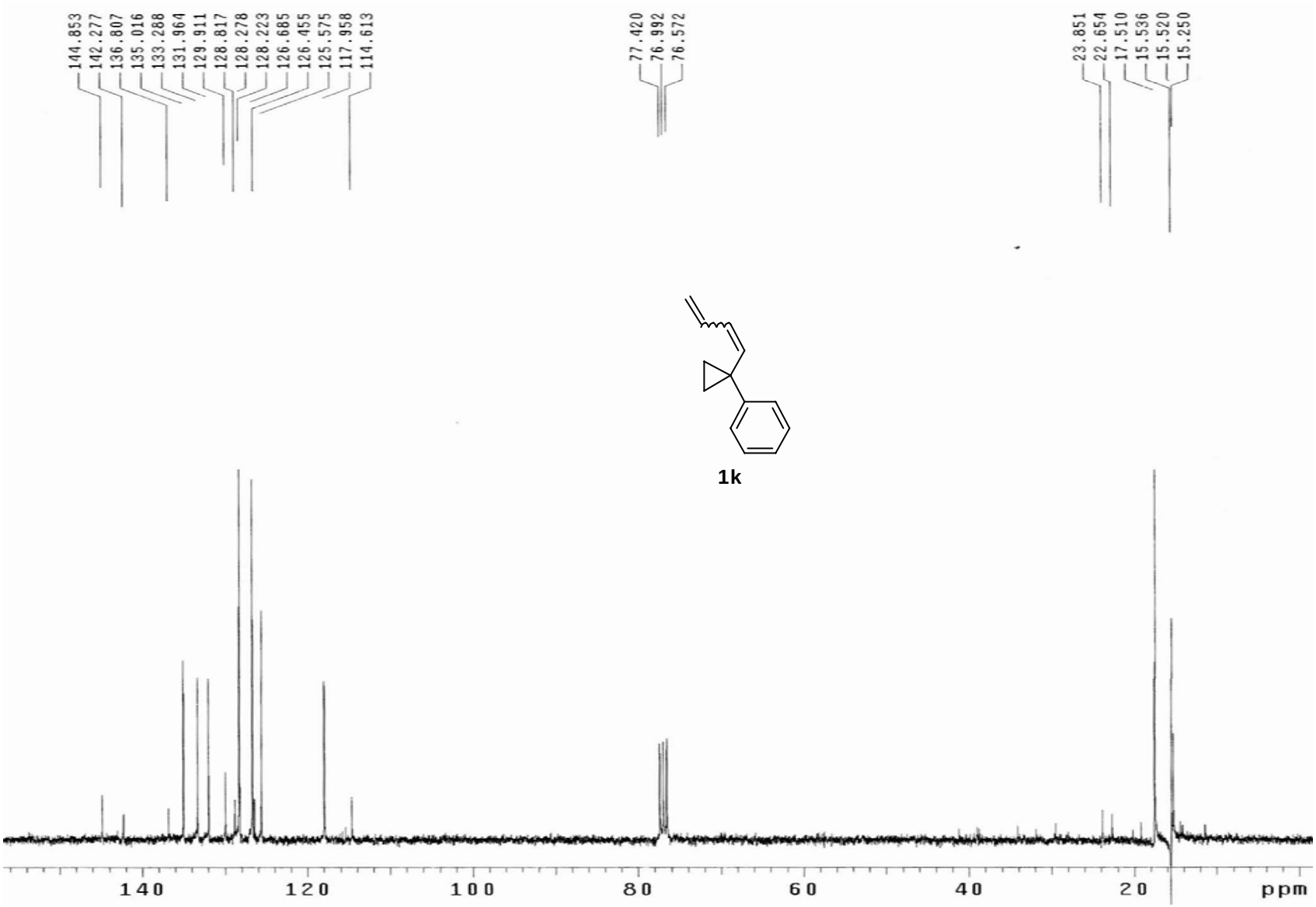
0

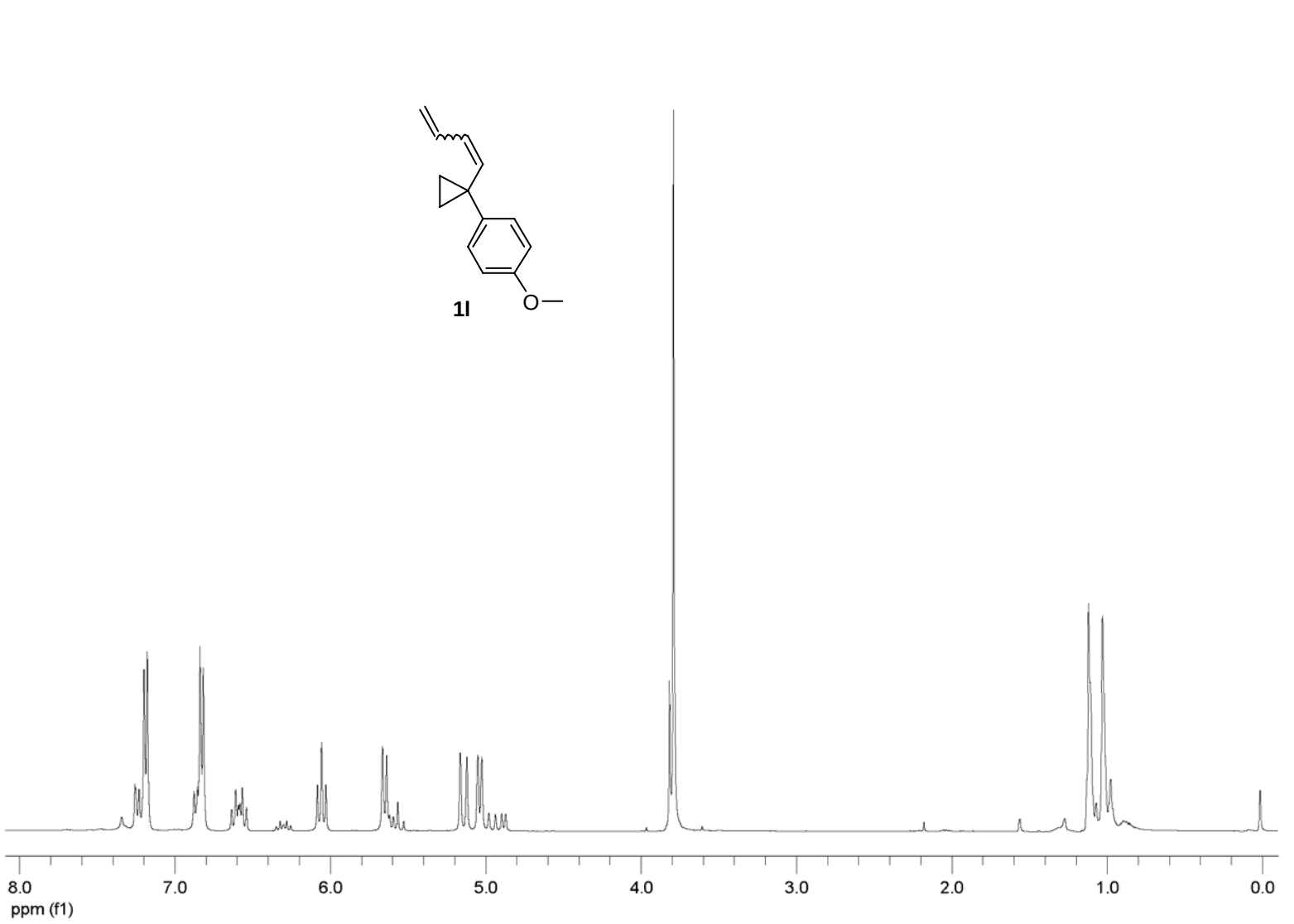
1j

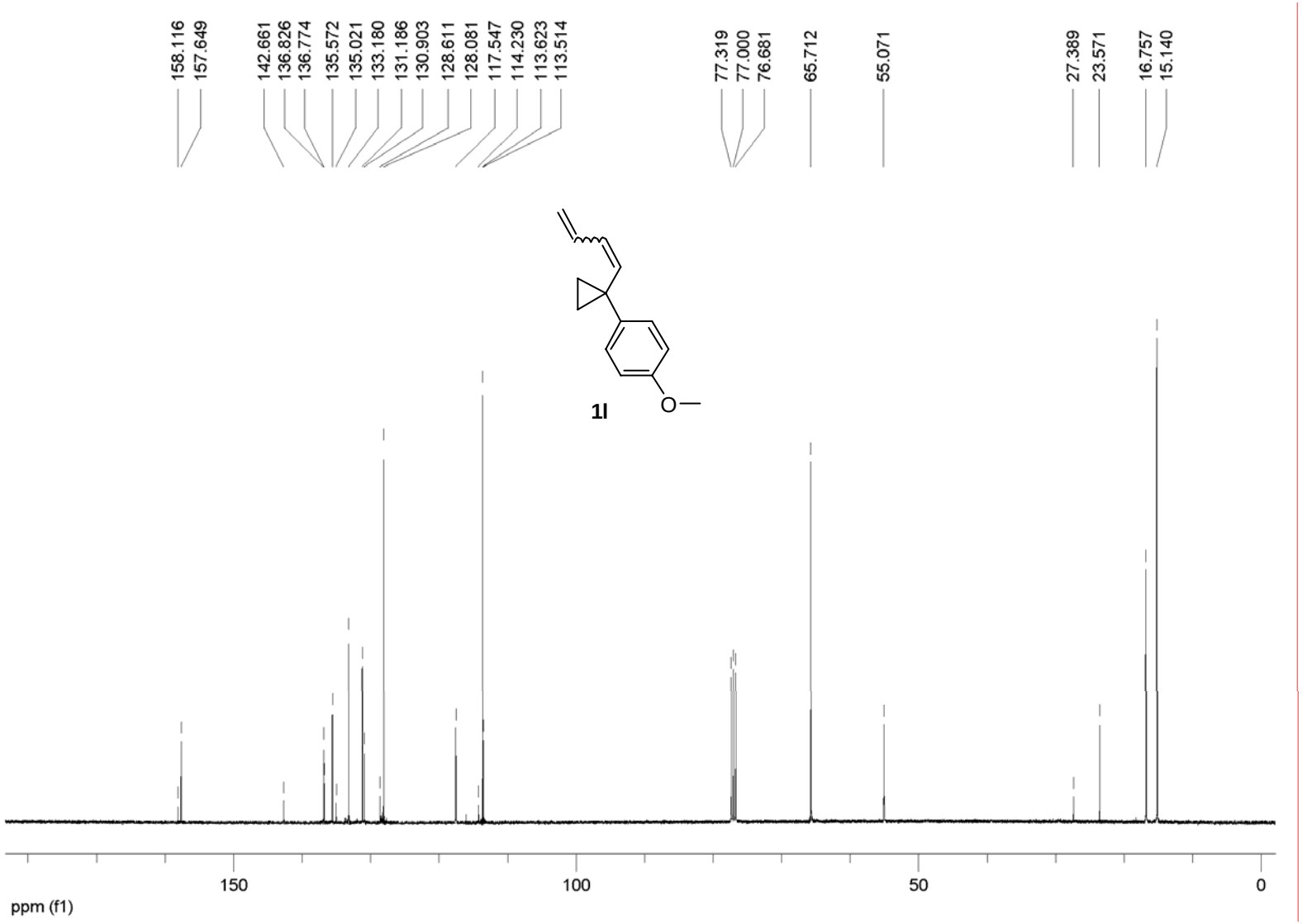


1k

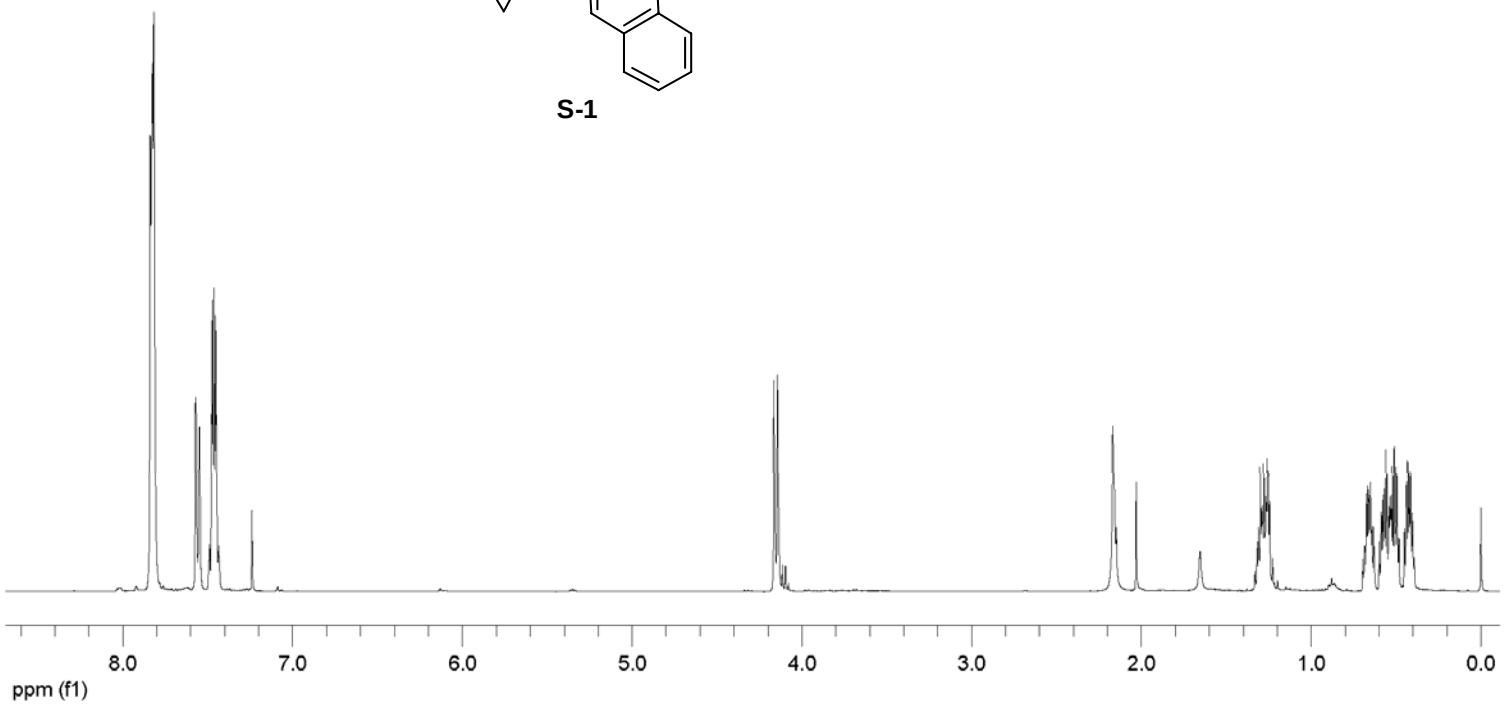

144.853
142.277
136.807
135.016
133.288
131.964
129.911
128.817
128.278
128.223
126.685
126.455
125.575
117.958
114.613
77.420
76.992
76.572
23.851
22.654
17.510
15.536
15.520
15.250
140
120
100
80
60
40
20
ppm

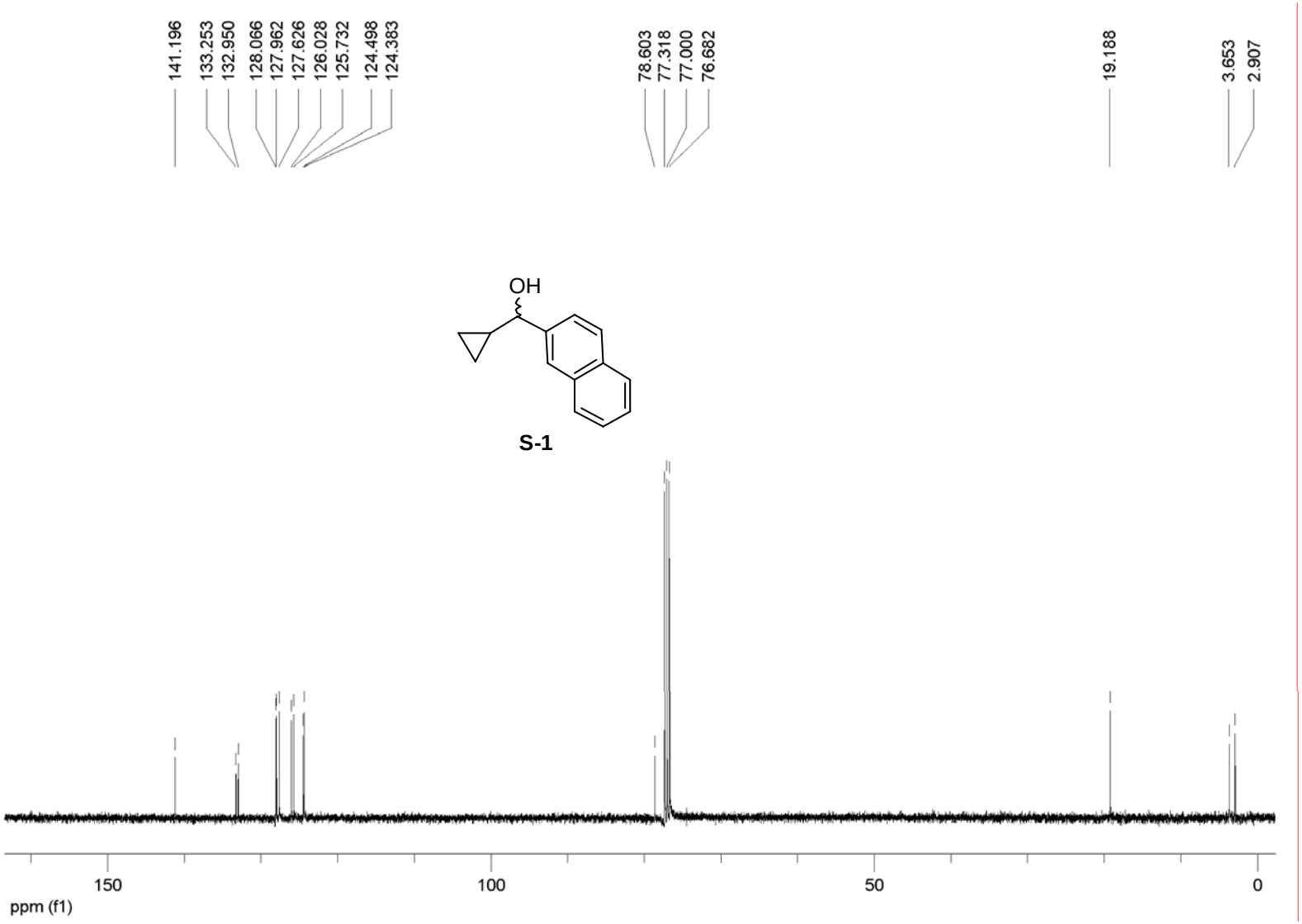
1k

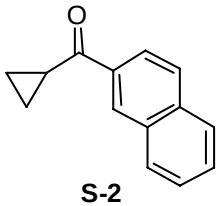

1l
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


158.116
157.649
142.661
136.826
136.774
135.572
135.021
133.180
131.186
130.903
128.611
128.081
117.547
114.230
113.623
113.514
77.319
77.000
76.681
65.712
55.071
27.389
23.571
16.757
15.140
1l
O
150
100
50
0
ppm (f1)

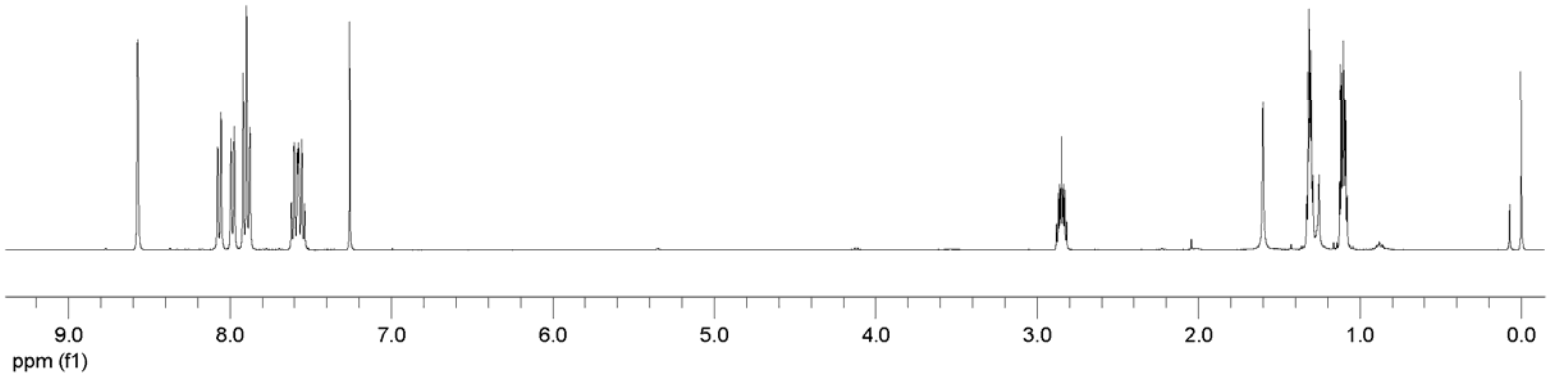
S-1

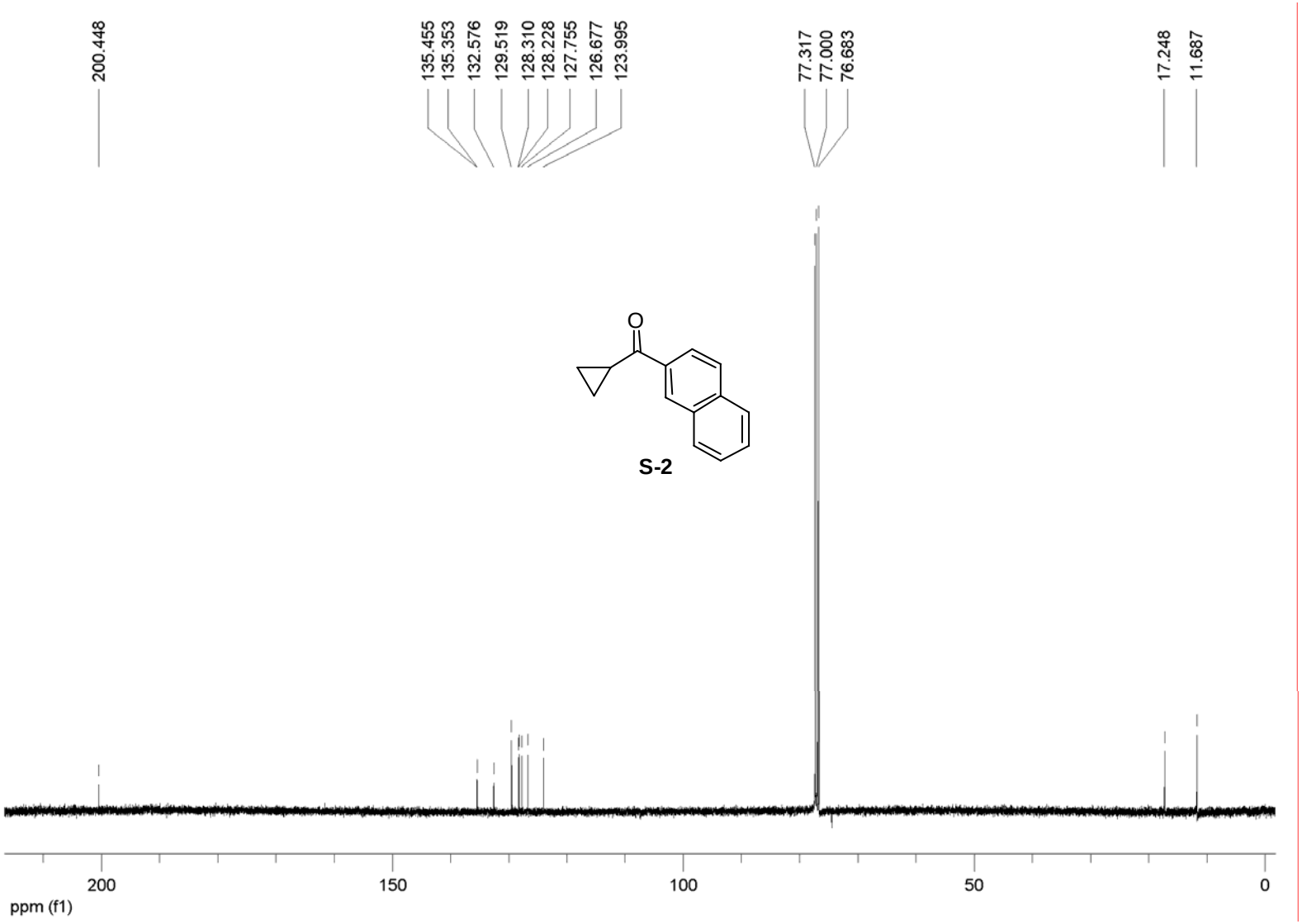


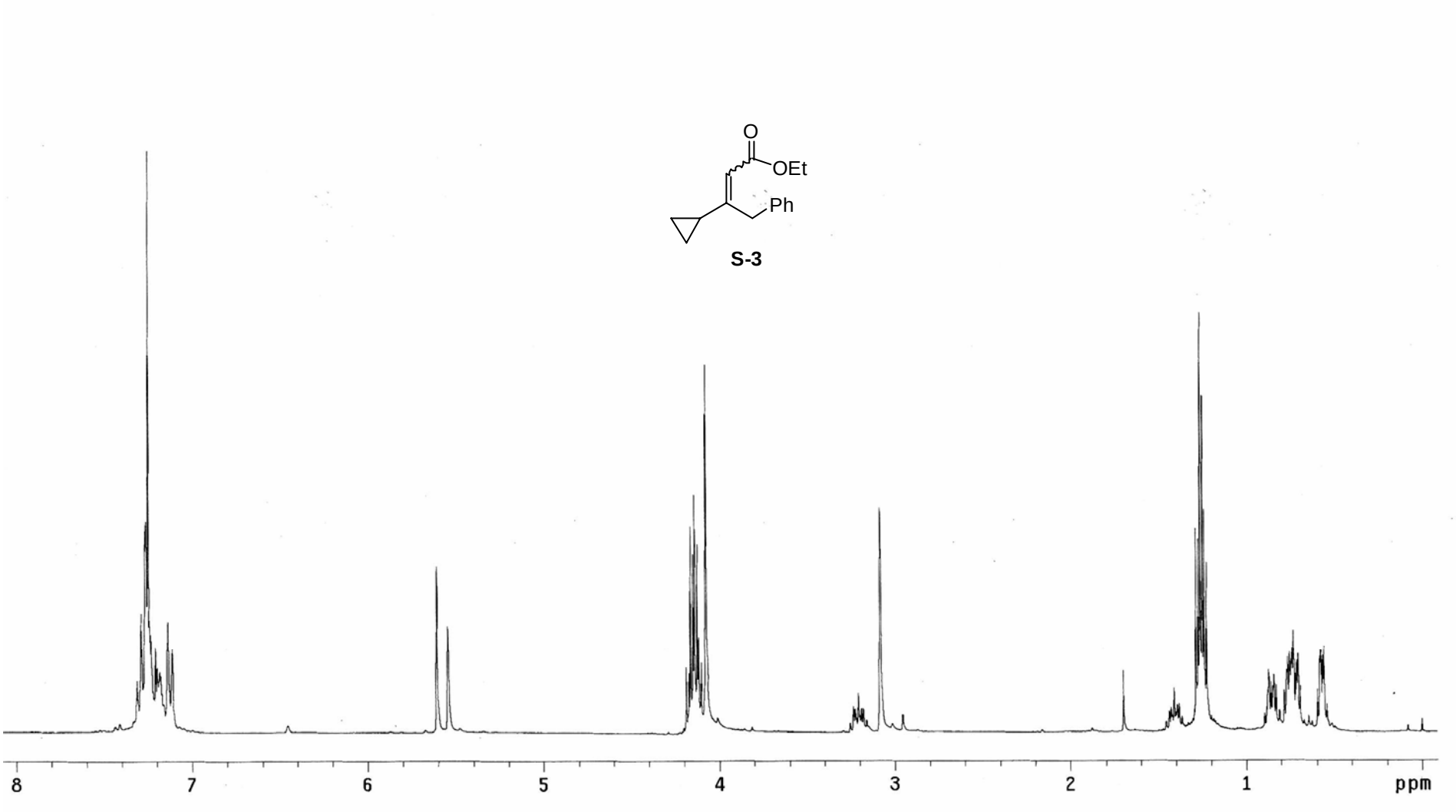

141.196
133.253
132.950
128.066
127.962
127.626
126.028
125.732
124.498
124.383
78.603
77.318
77.000
76.682
19.188
3.653
2.907
OH
S-1
150
100
50
0
ppm (f1)



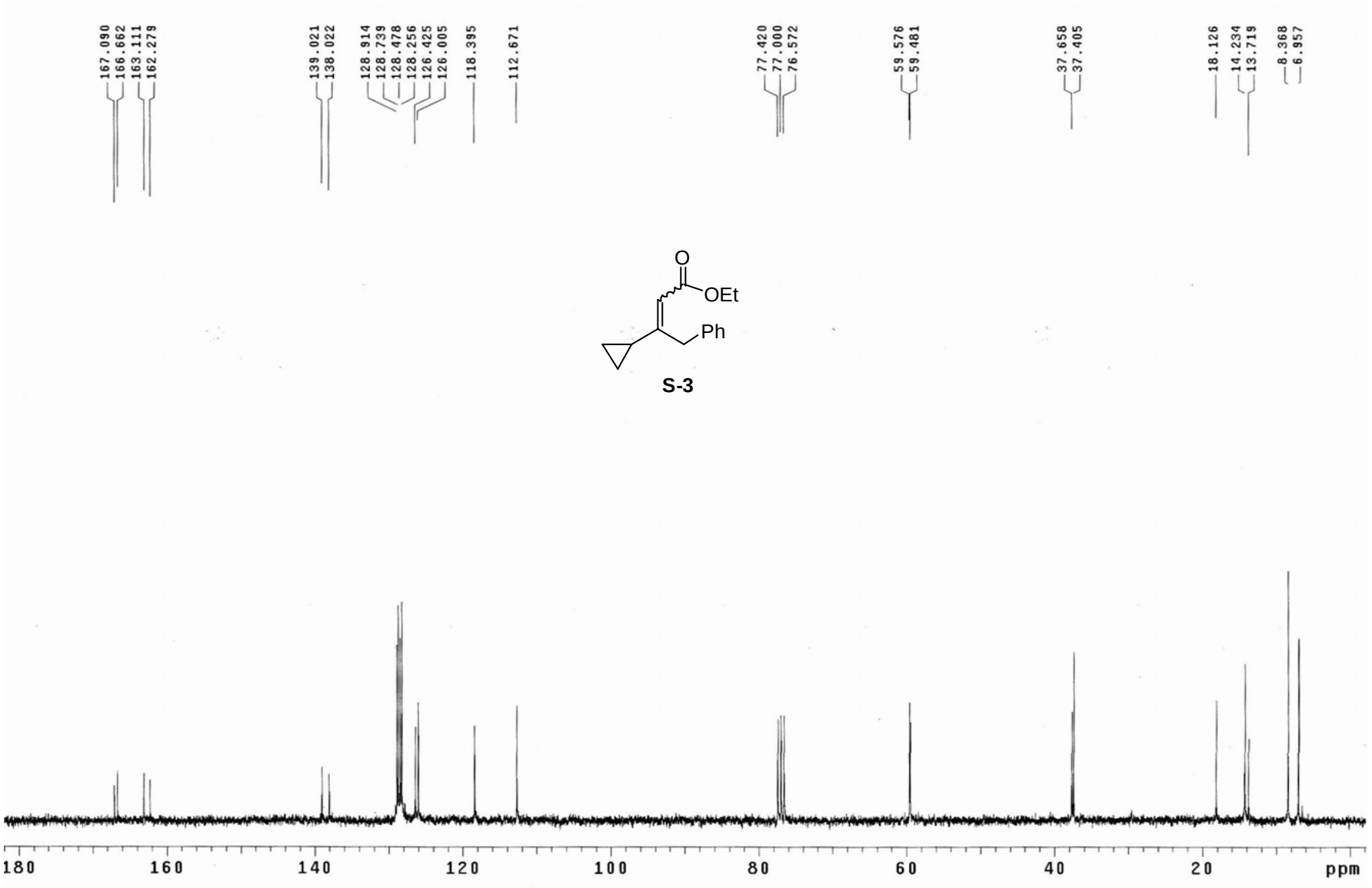
S-2



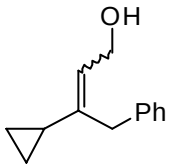

200.448
135.455
135.353
132.576
129.519
128.310
128.228
127.755
126.677
123.995
77.317
77.000
76.683
17.248
11.687
O
S-2
200
150
100
50
0
ppm (f1)



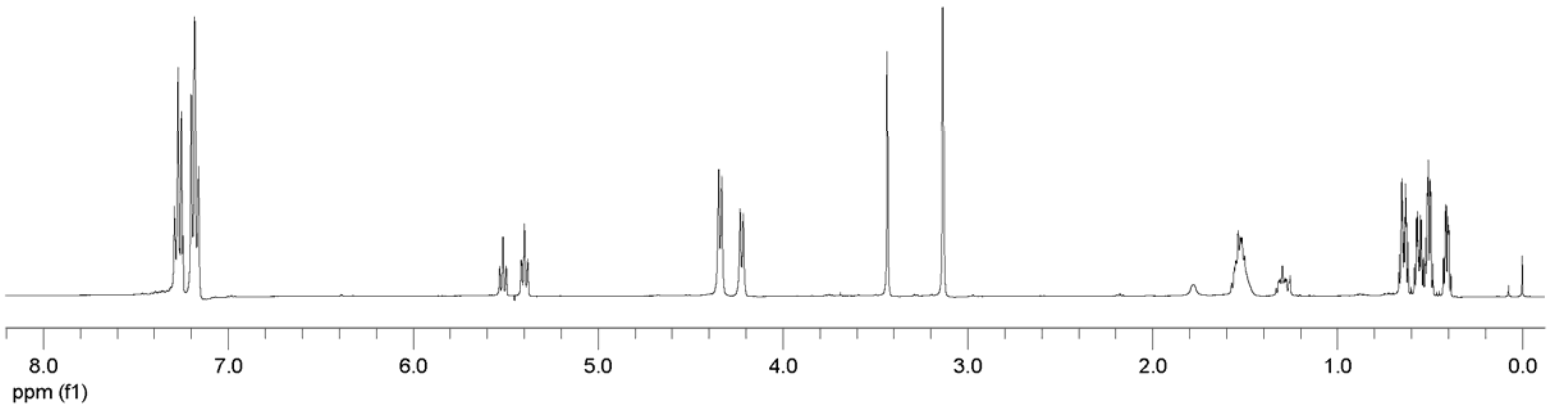
S-3

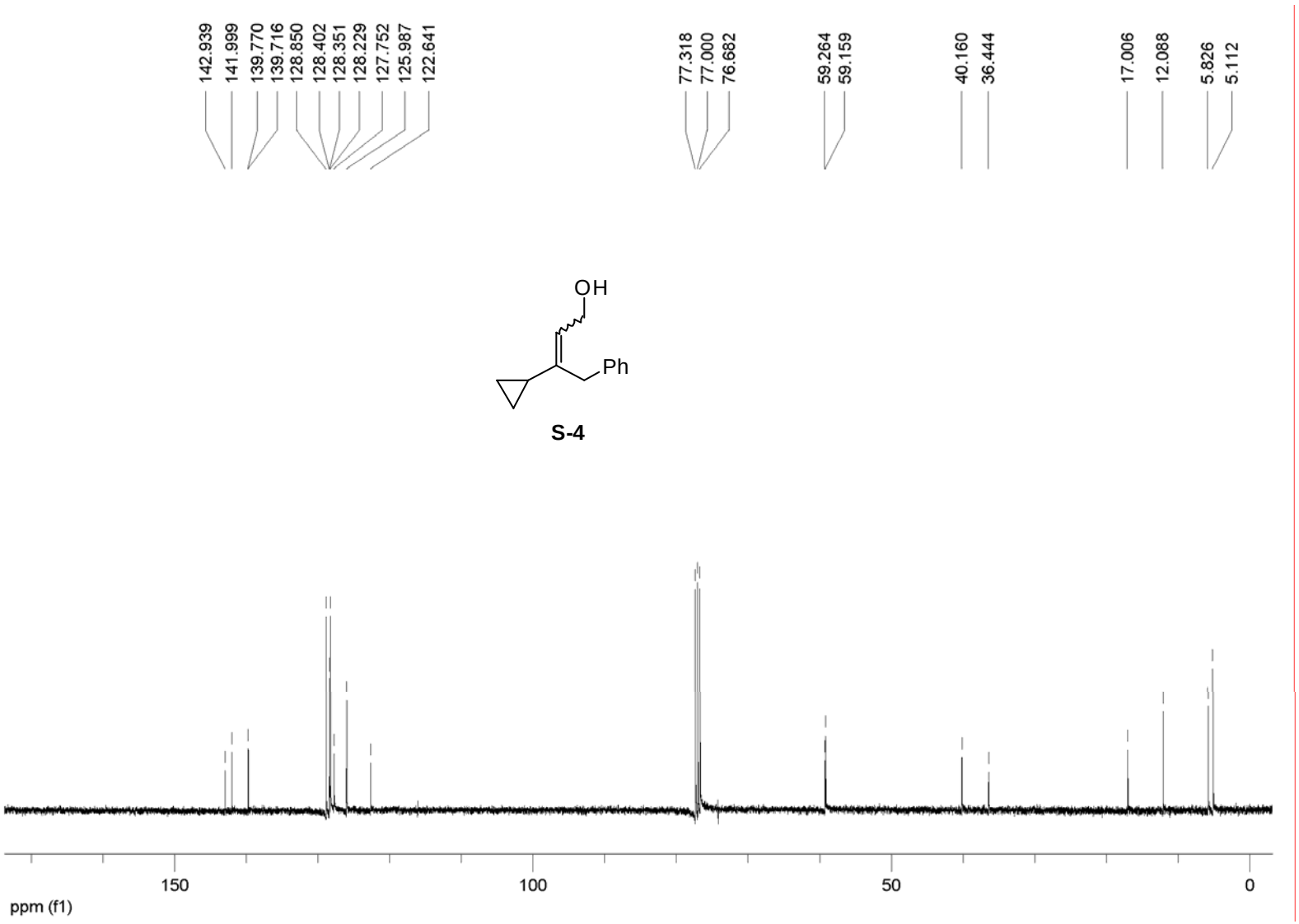

167.090
166.662
163.111
162.279
139.021
138.022
128.914
128.739
128.478
128.256
126.425
126.005
118.395
112.671
77.420
77.000
76.572
59.576
59.481
37.658
37.405
18.126
14.234
13.719
8.368
6.957
O
OEt
Ph
180
160
140
120
100
80
60
40
20
ppm

S-3

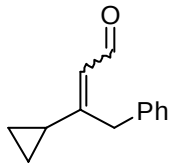


S-4

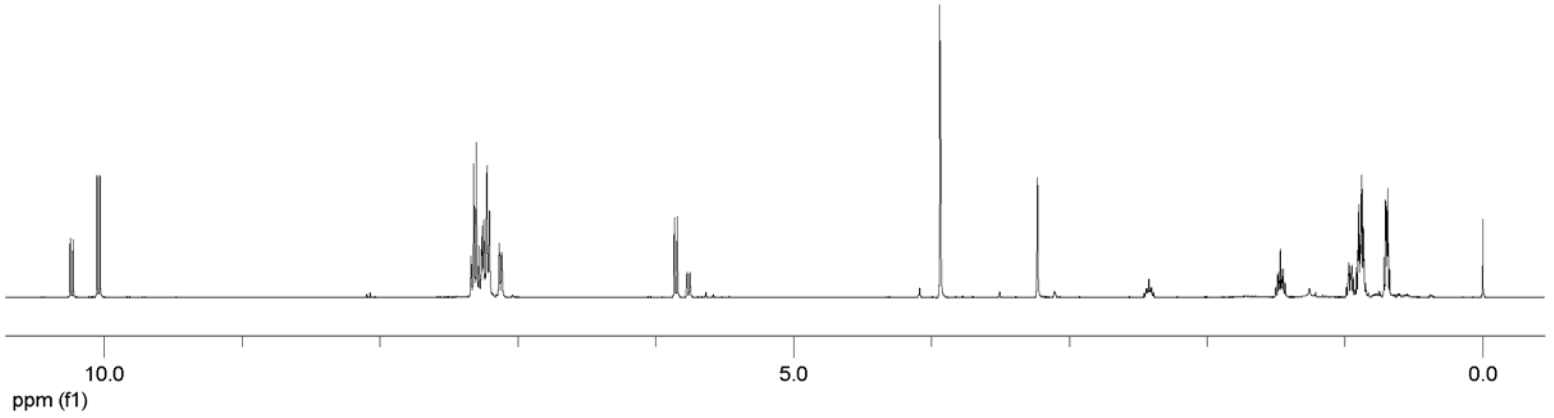


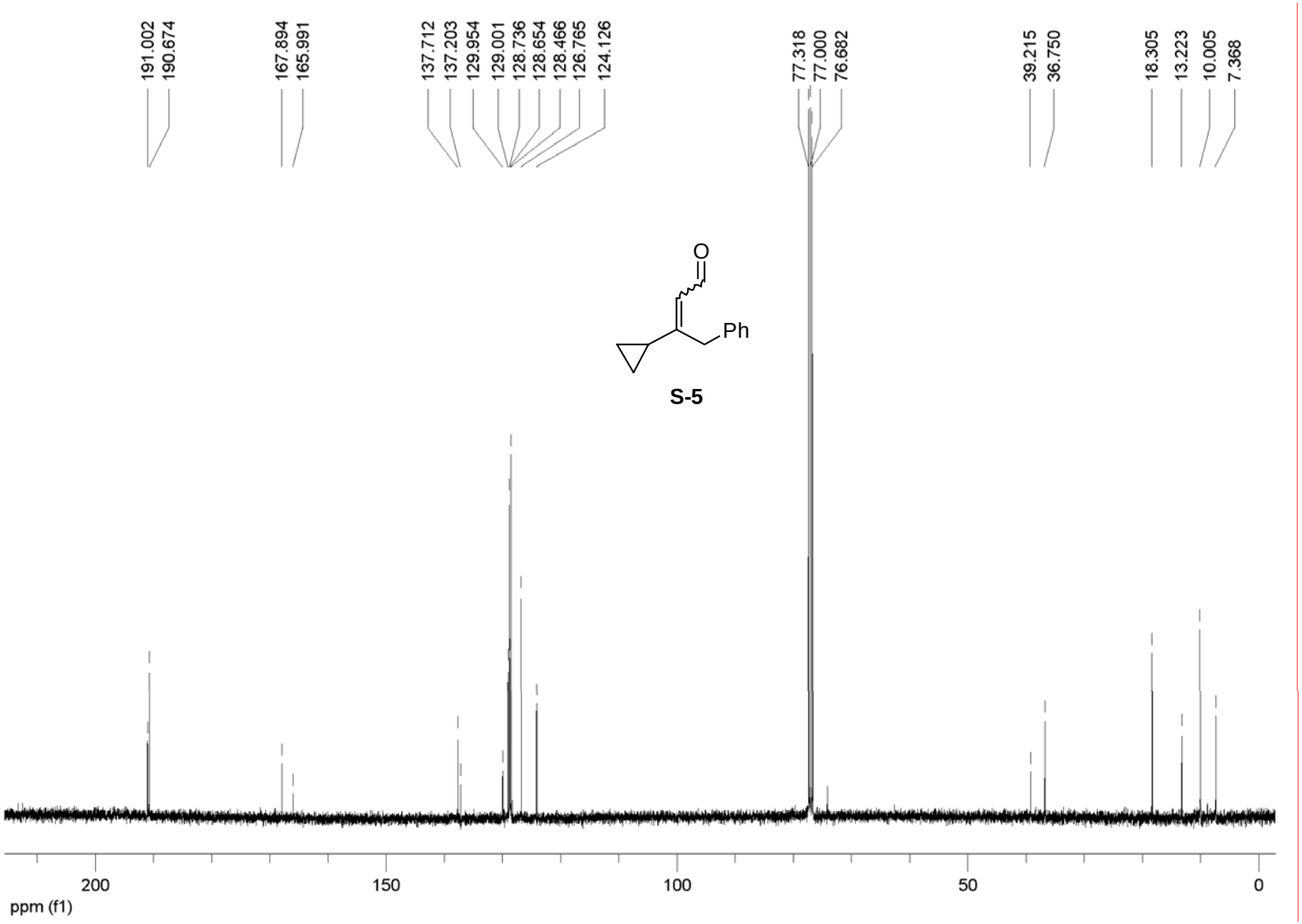

142.939
141.999
139.770
139.716
128.850
128.402
128.351
128.229
127.752
125.987
122.641
77.318
77.000
76.682
59.264
59.159
40.160
36.444
17.006
12.088
5.826
5.112
OH
Ph
150
100
50
0
ppm (f1)

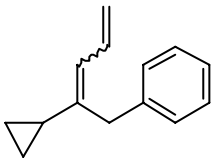
S-4



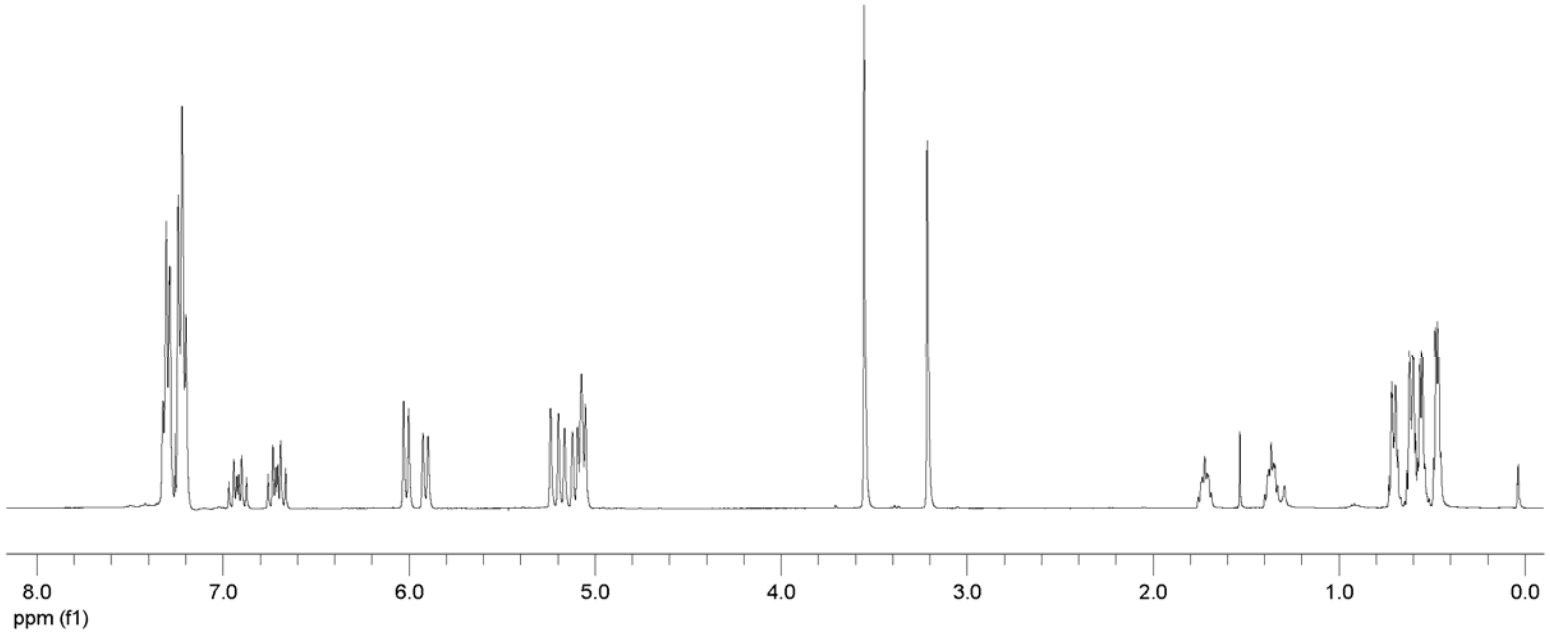
S-5

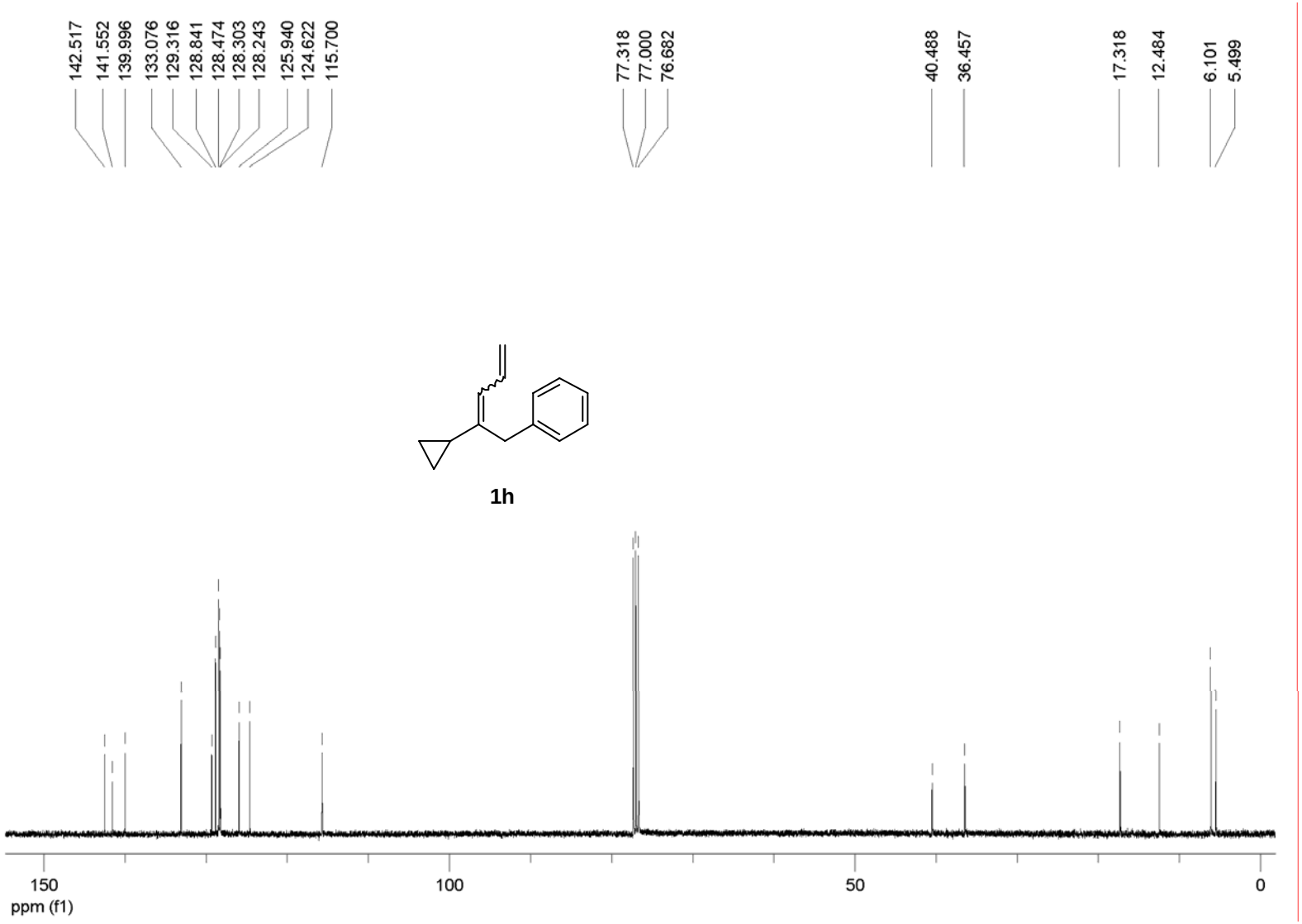



191.002
190.674
167.894
165.991
137.712
137.203
129.954
129.001
128.736
128.654
128.466
126.765
124.126
77.318
77.000
76.682
39.215
36.750
18.305
13.223
10.005
7.368
O
Ph
S-5
200
150
100
50
0
ppm (f1)

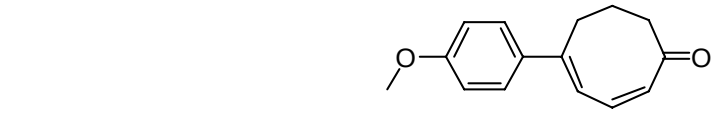


1h

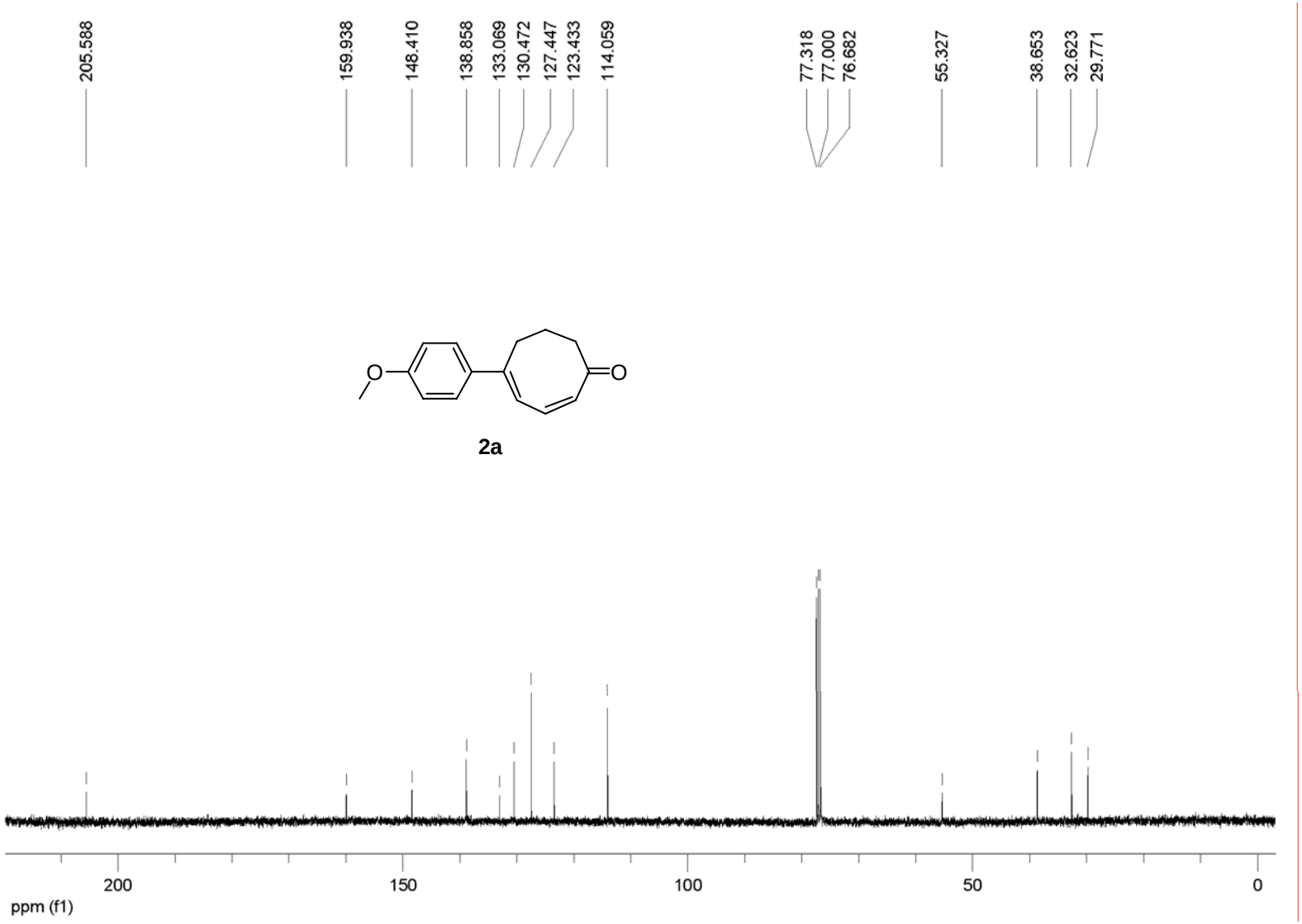



142.517
141.552
139.996
133.076
129.316
128.841
128.474
128.303
128.243
125.940
124.622
115.700
77.318
77.000
76.682
40.488
36.457
17.318
12.484
6.101
5.499
150
100
50
0
ppm (f1)

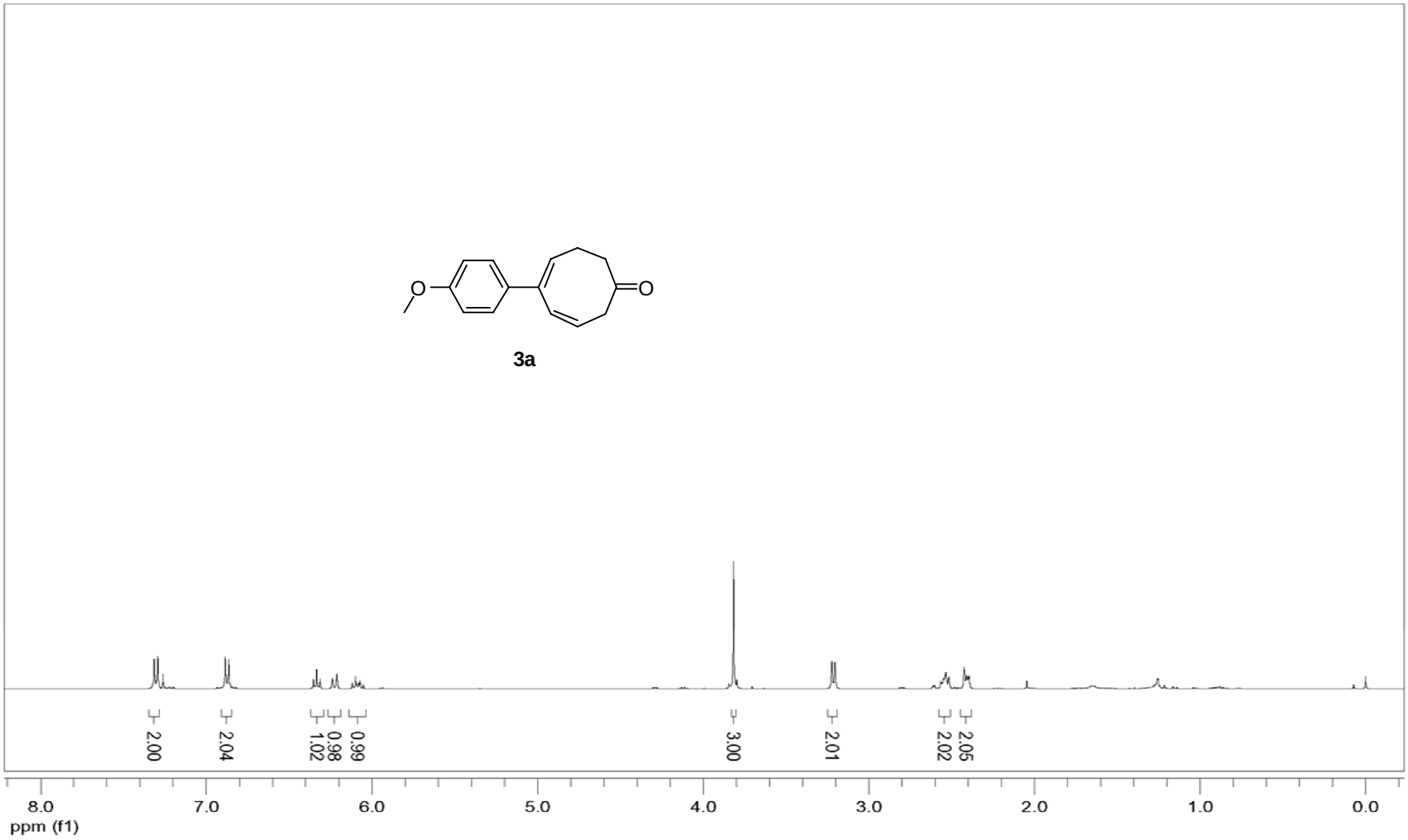
1h

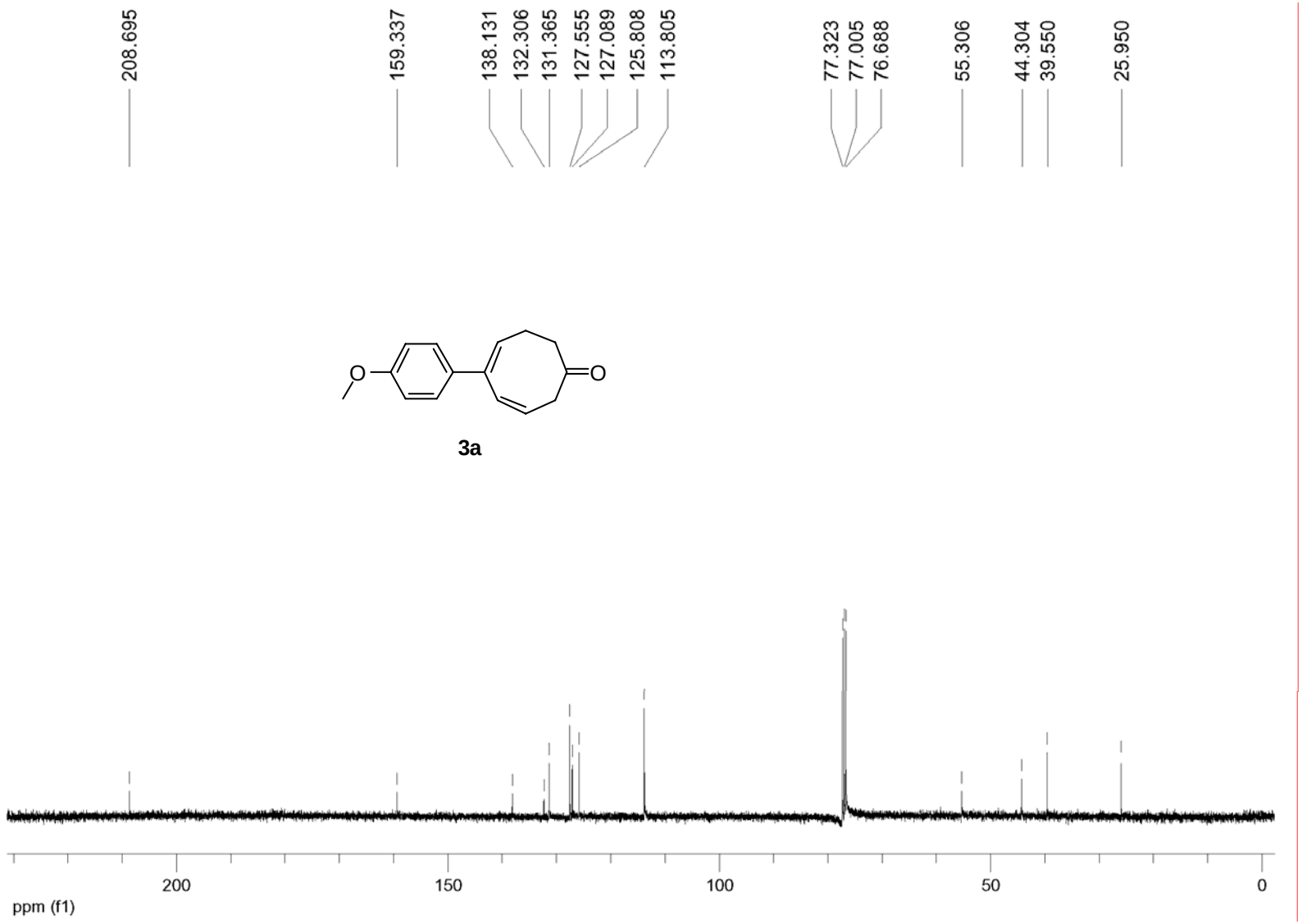


2a

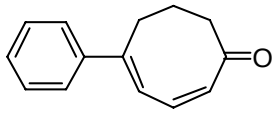

205.588
159.938
148.410
138.858
133.069
130.472
127.447
123.433
114.059
77.318
77.000
76.682
55.327
38.653
32.623
29.771
O
O
200
150
100
50
0
ppm (f1)

2a

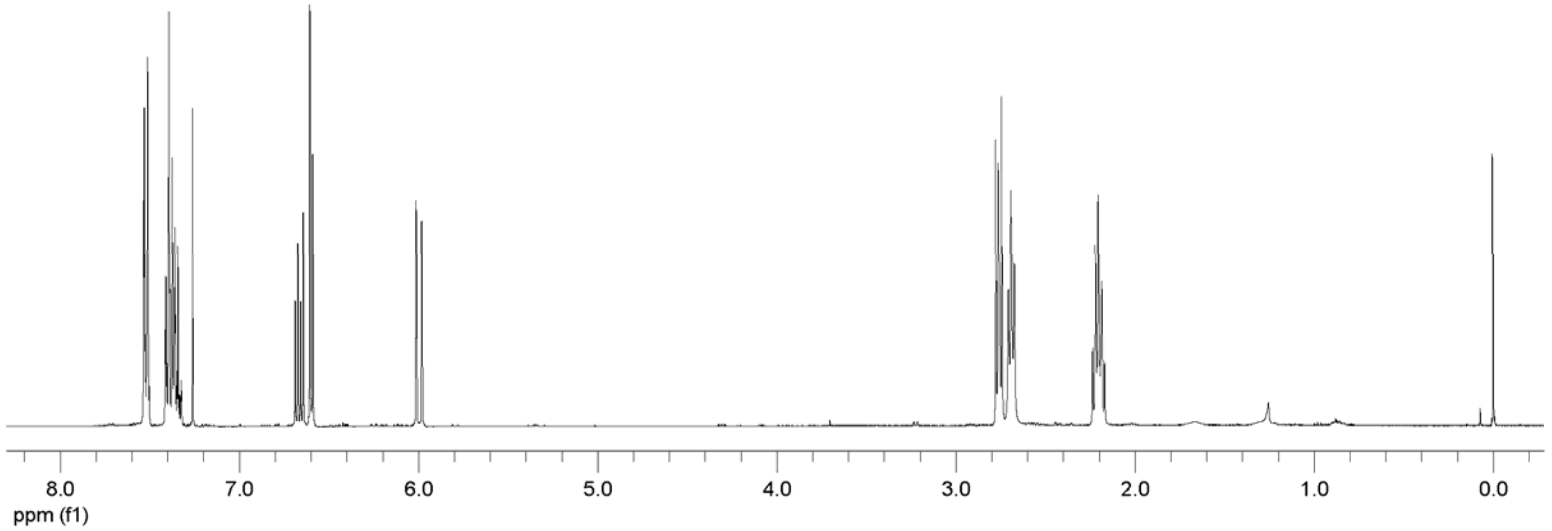

O
O
3a
2.00
2.04
1.02
0.98
0.99
3.00
2.01
2.02
2.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

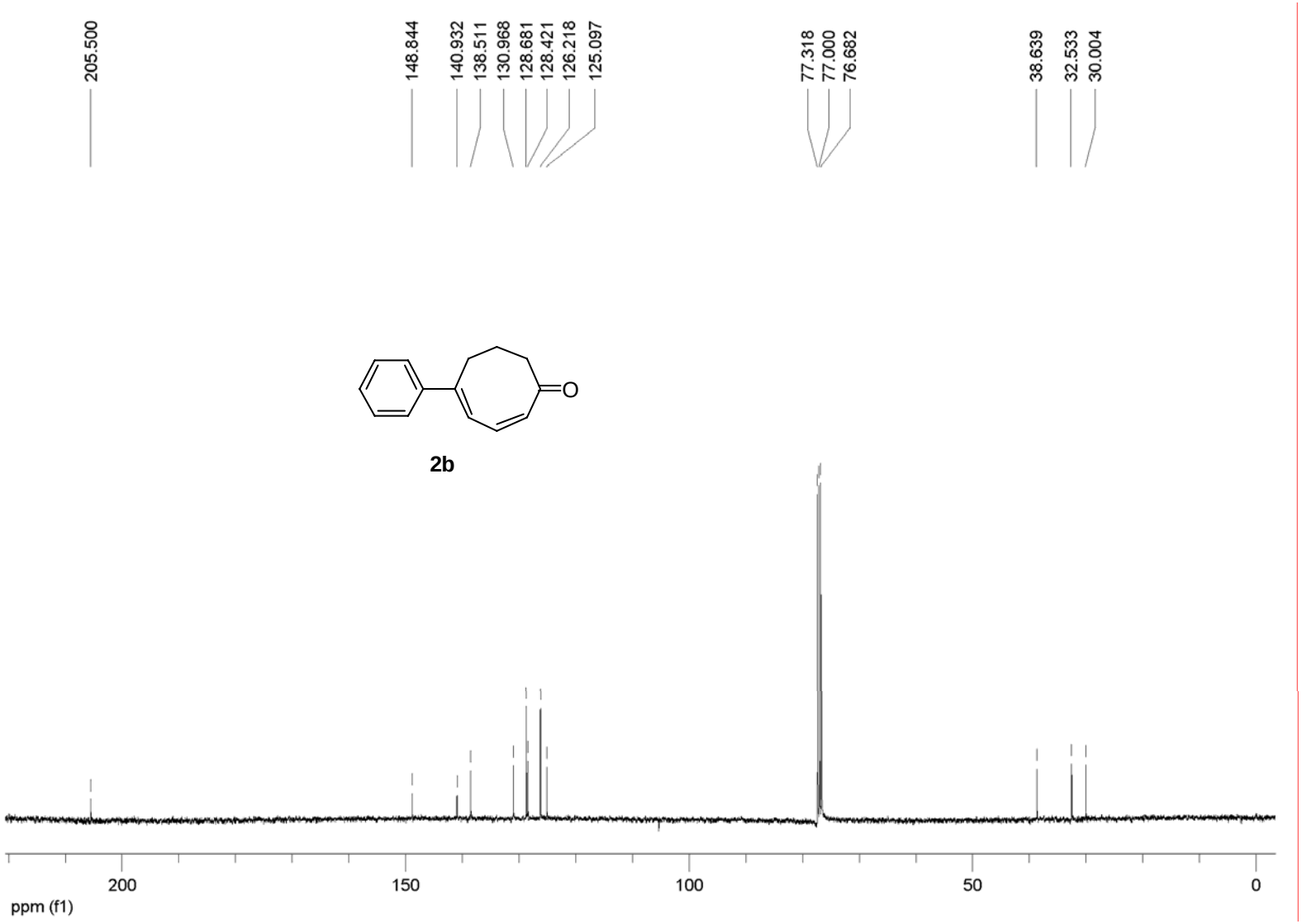

208.695
159.337
138.131
132.306
131.365
127.555
127.089
125.808
113.805
77.323
77.005
76.688
55.306
44.304
39.550
25.950
O
O
200
150
100
50
0
ppm (f1)

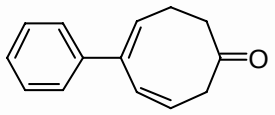
3a



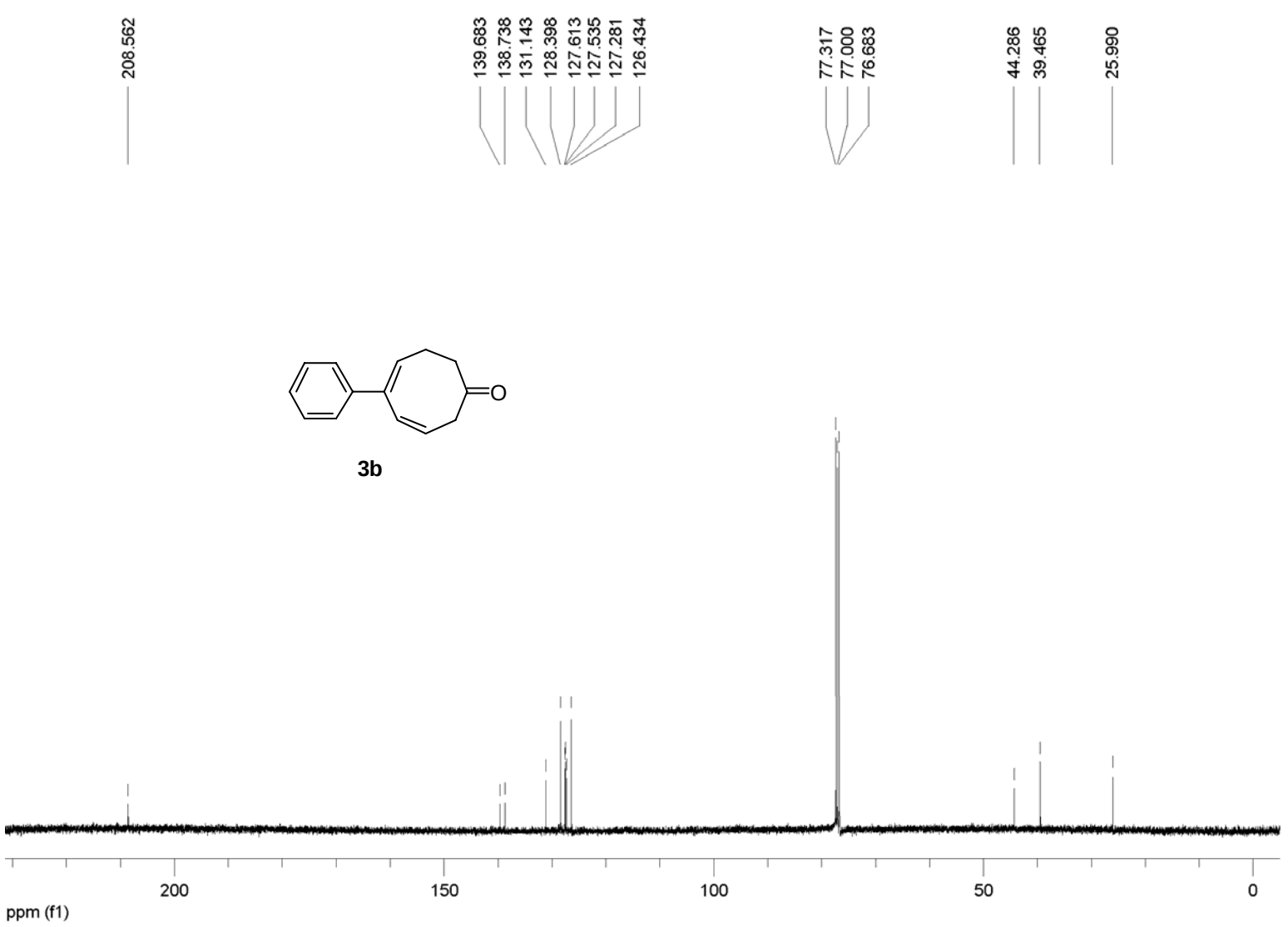
2b

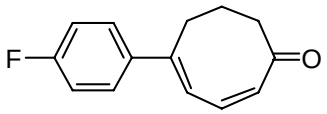



205.500
148.844
140.932
138.511
130.968
128.681
128.421
126.218
125.097
77.318
77.000
76.682
38.639
32.533
30.004
O
2b
200
150
100
50
0
ppm (f1)

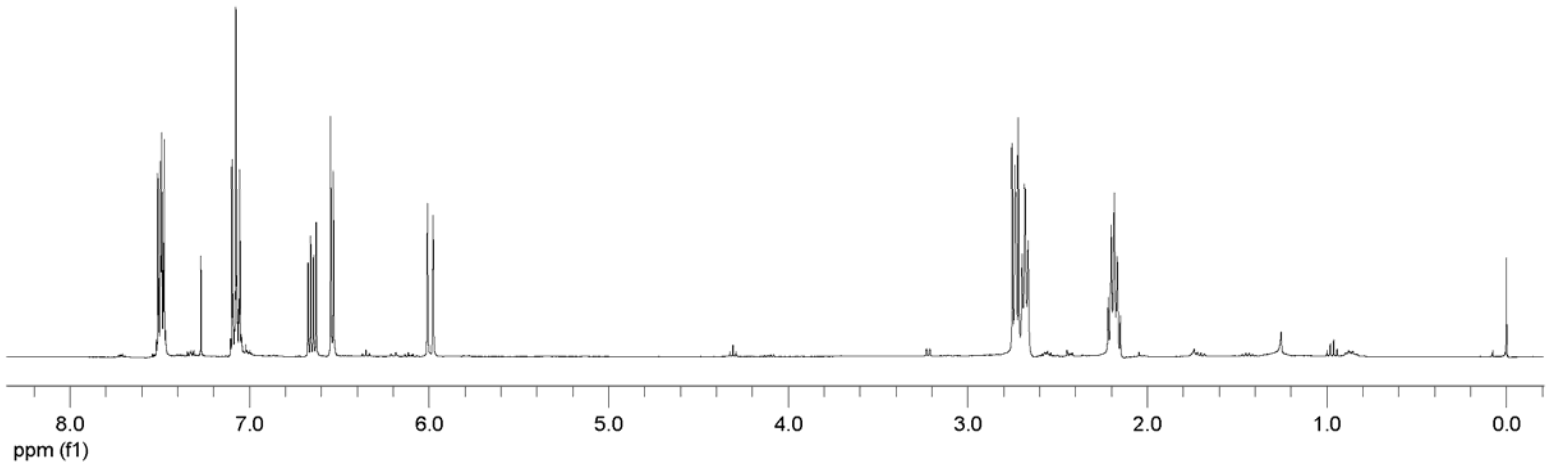


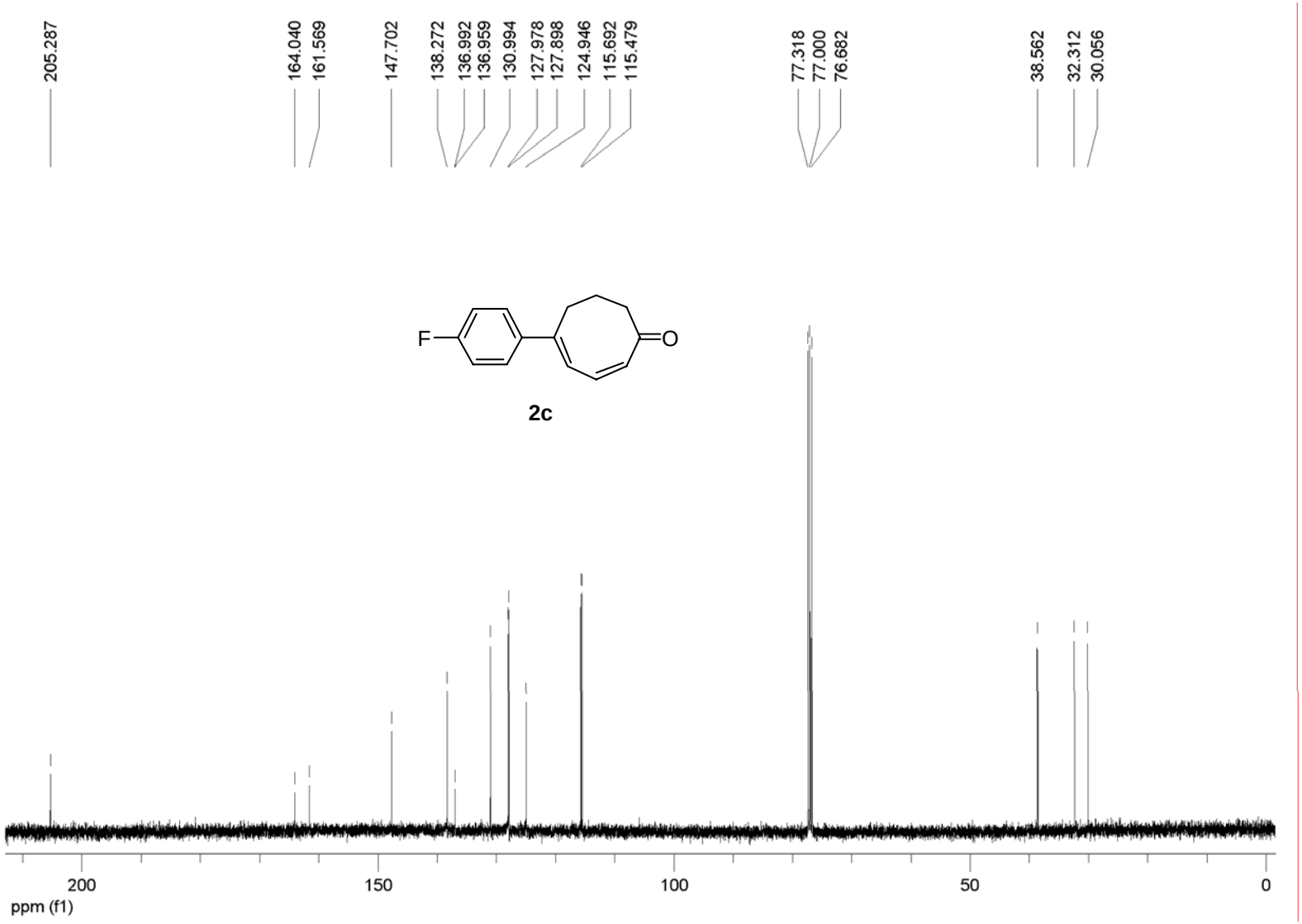
3b

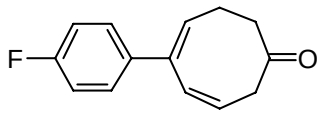

208.562
139.683
138.738
131.143
128.398
127.613
127.535
127.281
126.434
77.317
77.000
76.683
44.286
39.465
25.990
O
3b
200
150
100
50
0
ppm (f1)



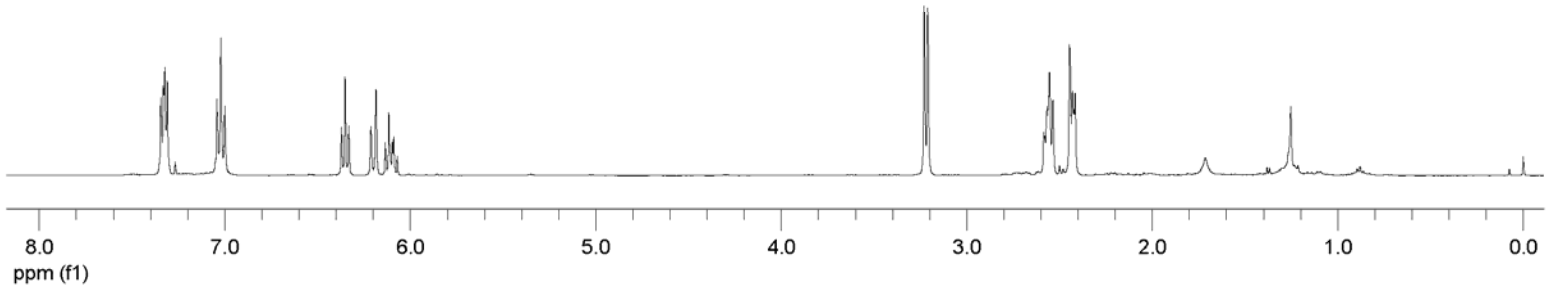
2c

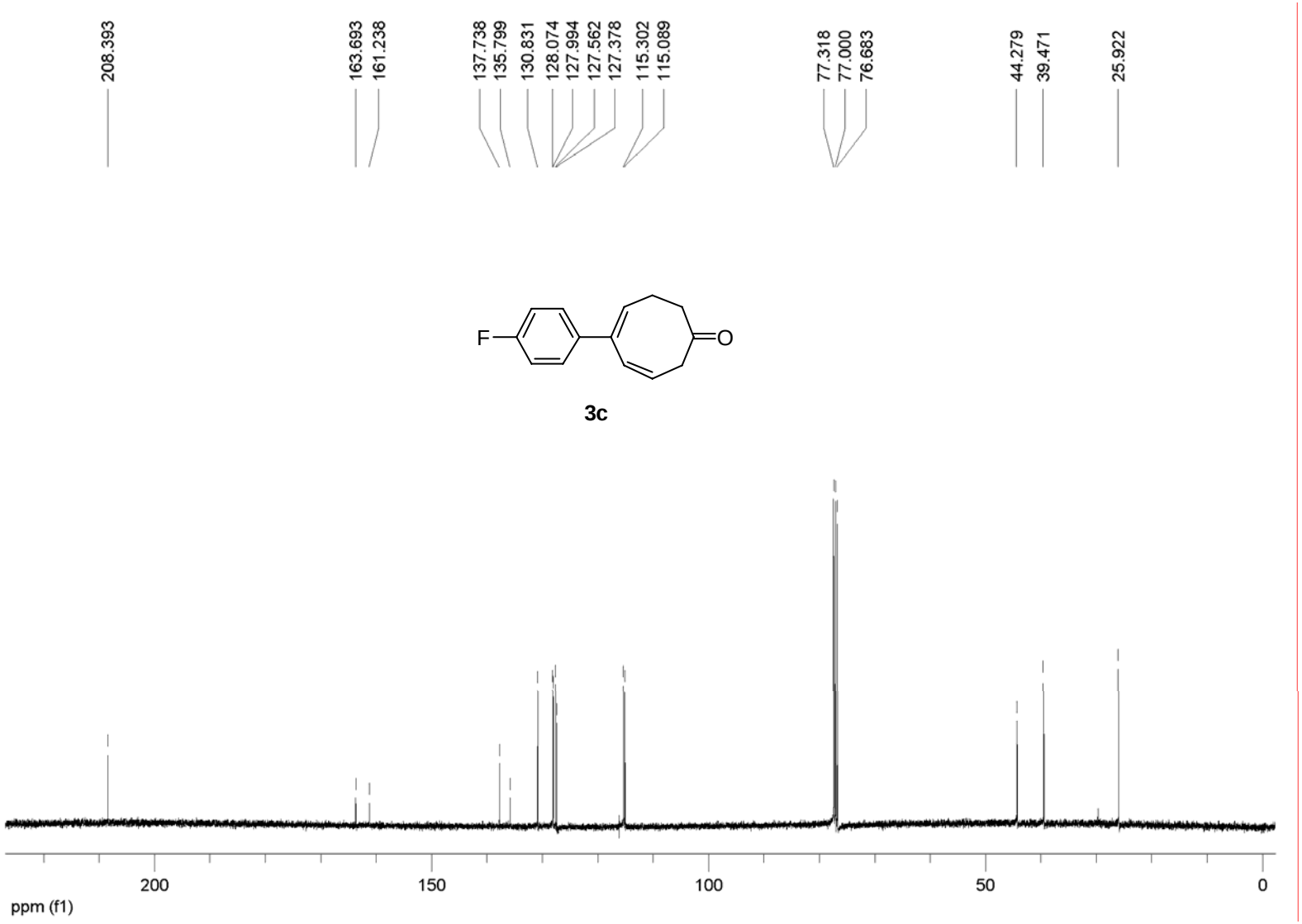



205.287
164.040
161.569
147.702
138.272
136.992
136.959
130.994
127.978
127.898
124.946
115.692
115.479
77.318
77.000
76.682
38.562
32.312
30.056
F
O
2c
200
150
100
50
0
ppm (f1)

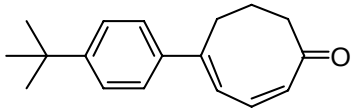


3c

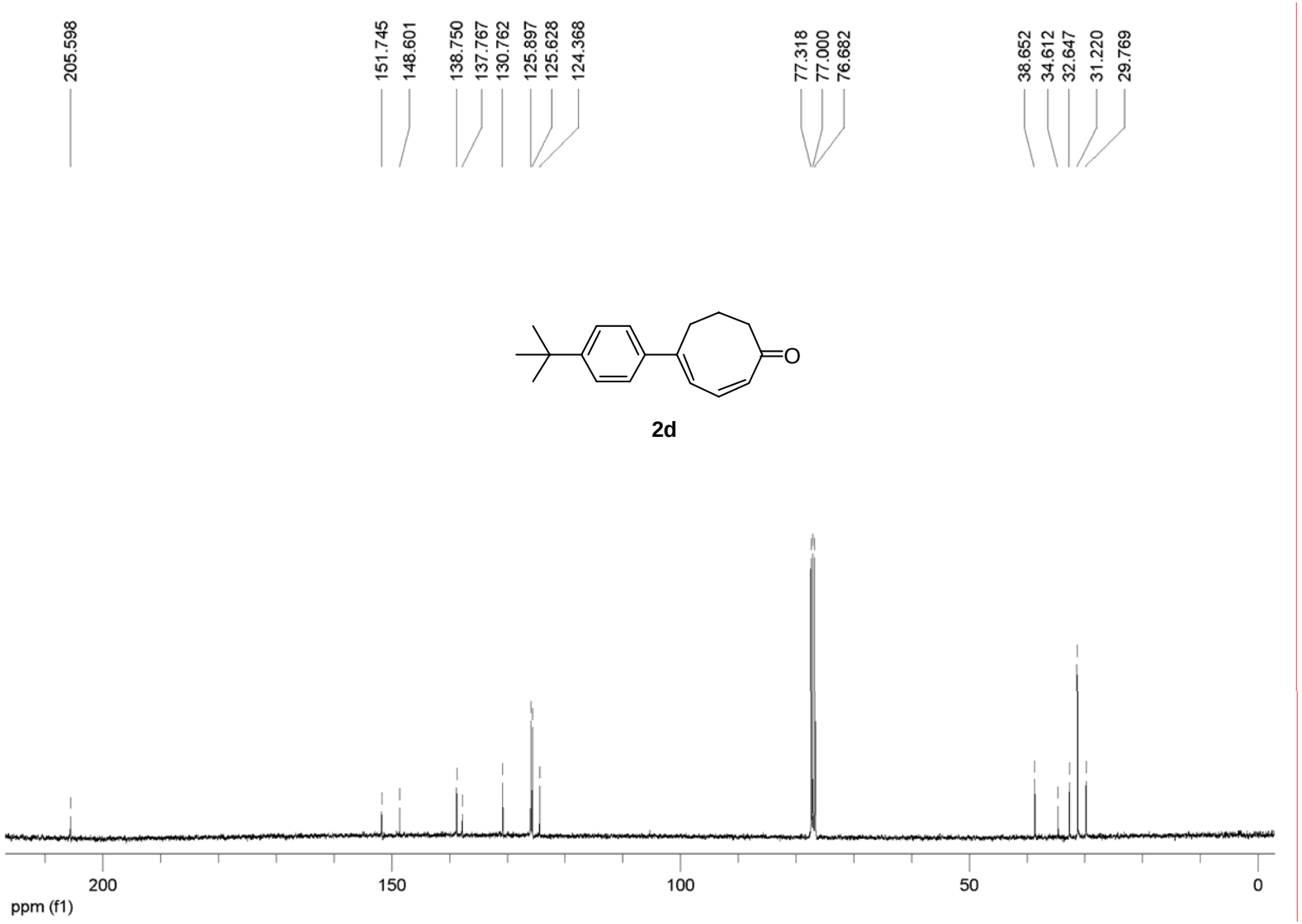



208.393
163.693
161.238
137.738
135.799
130.831
128.074
127.994
127.562
127.378
115.302
115.089
77.318
77.000
76.683
44.279
39.471
25.922
F
O
200
150
100
50
0
ppm (f1)

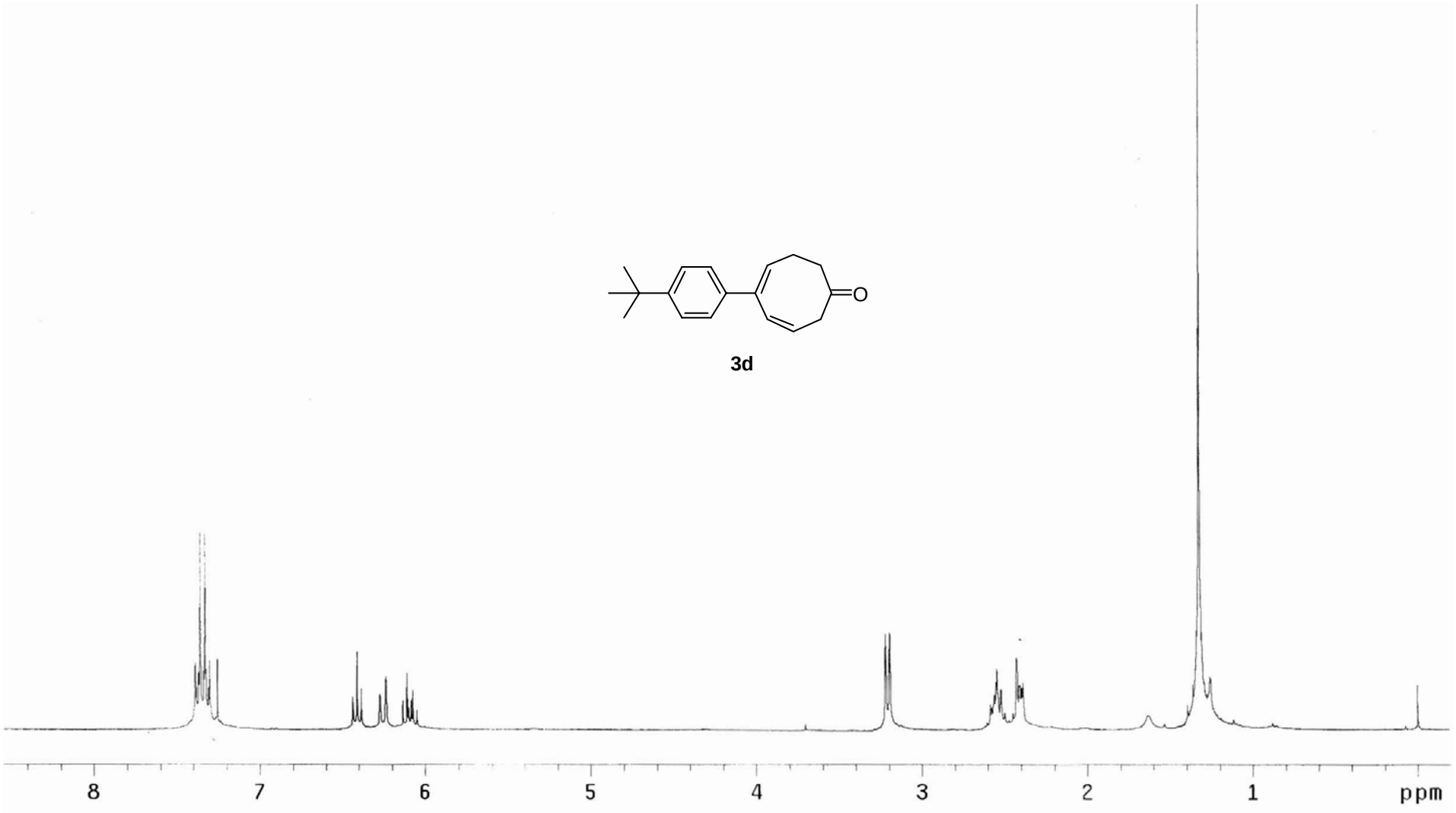
3c



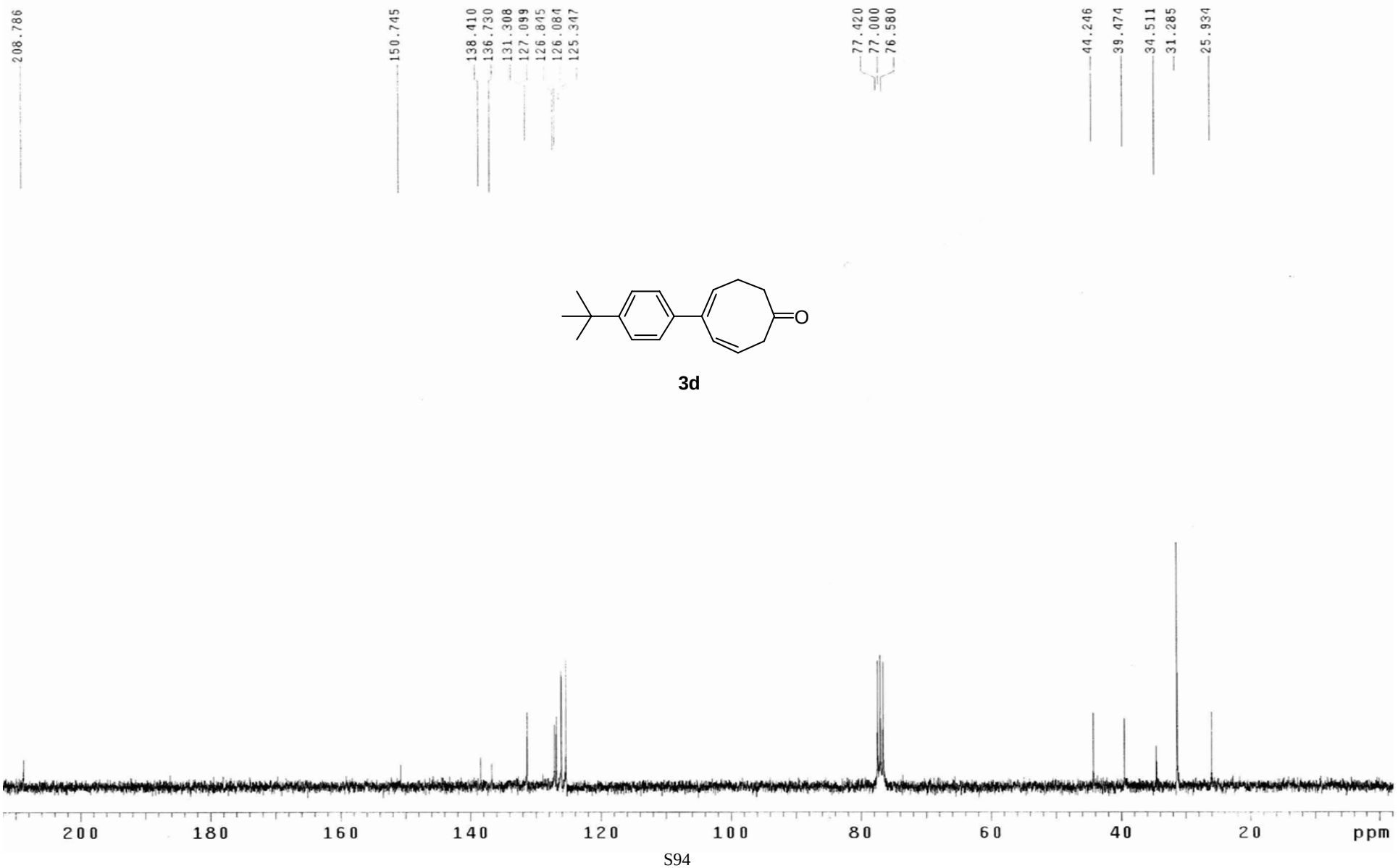
2d


205.598
151.745
148.601
138.750
137.767
130.762
125.897
125.628
124.368
77.318
77.000
76.682
38.652
34.612
32.647
31.220
29.769
O
200
150
100
50
0
ppm (f1)

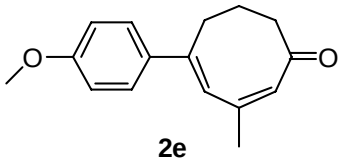
2d



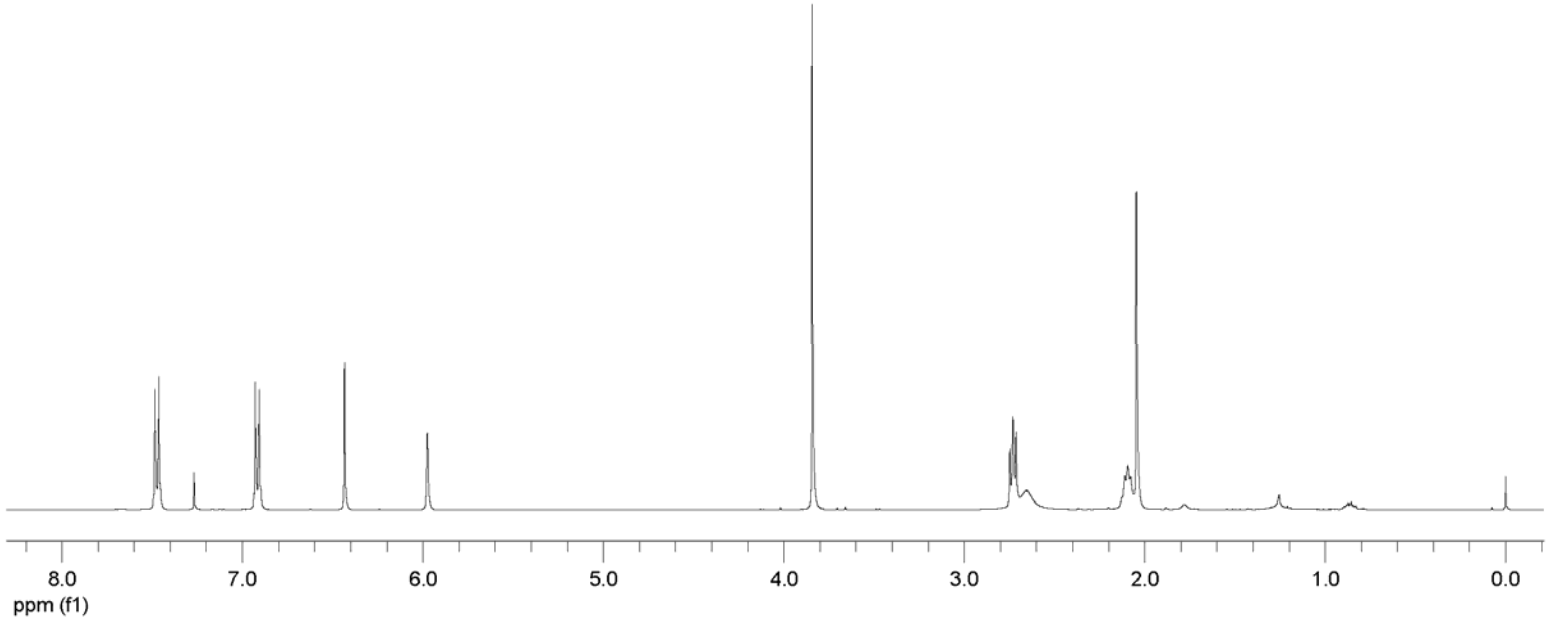
3d

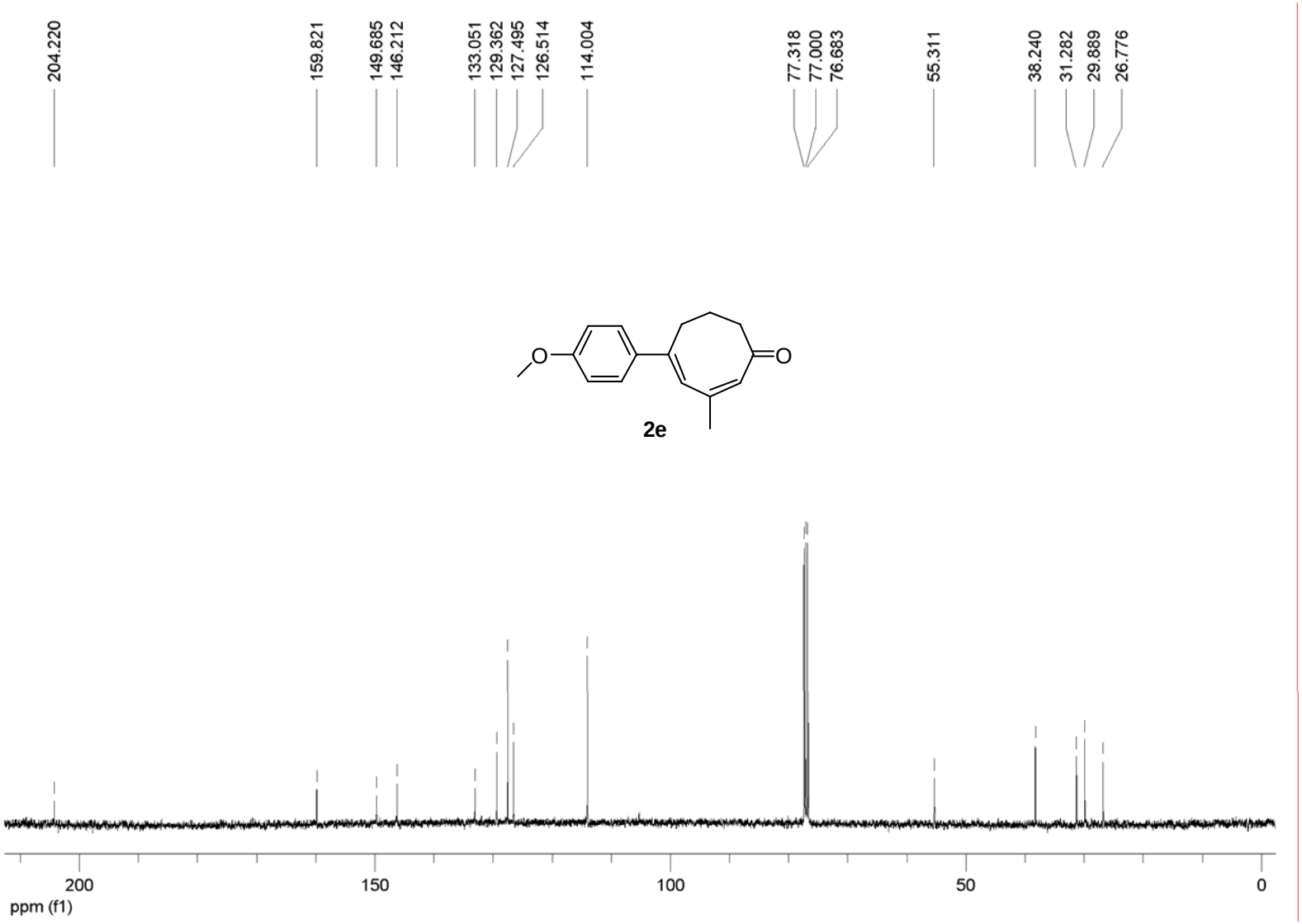

208.786
150.745
138.410
136.730
131.308
127.099
126.845
126.084
125.347
77.420
77.000
76.580
44.246
39.474
34.511
31.285
25.934
O
200
180
160
140
120
100
80
60
40
20
ppm

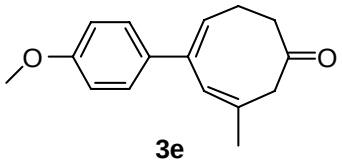
3d



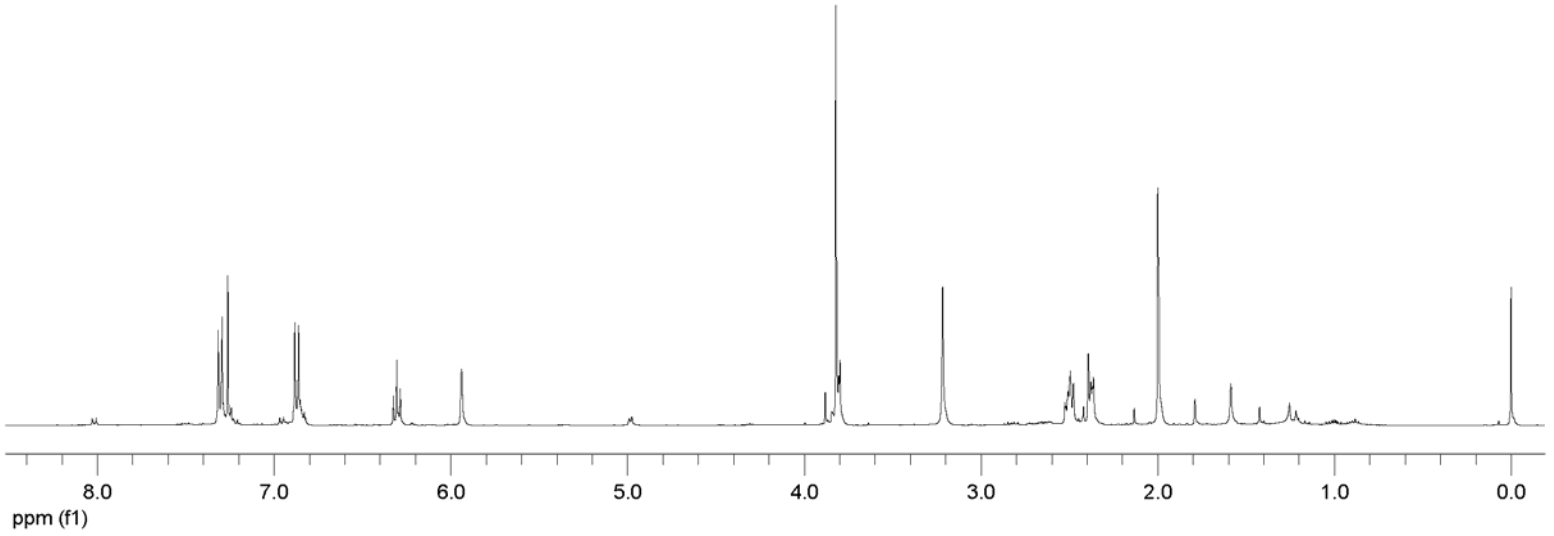
2e

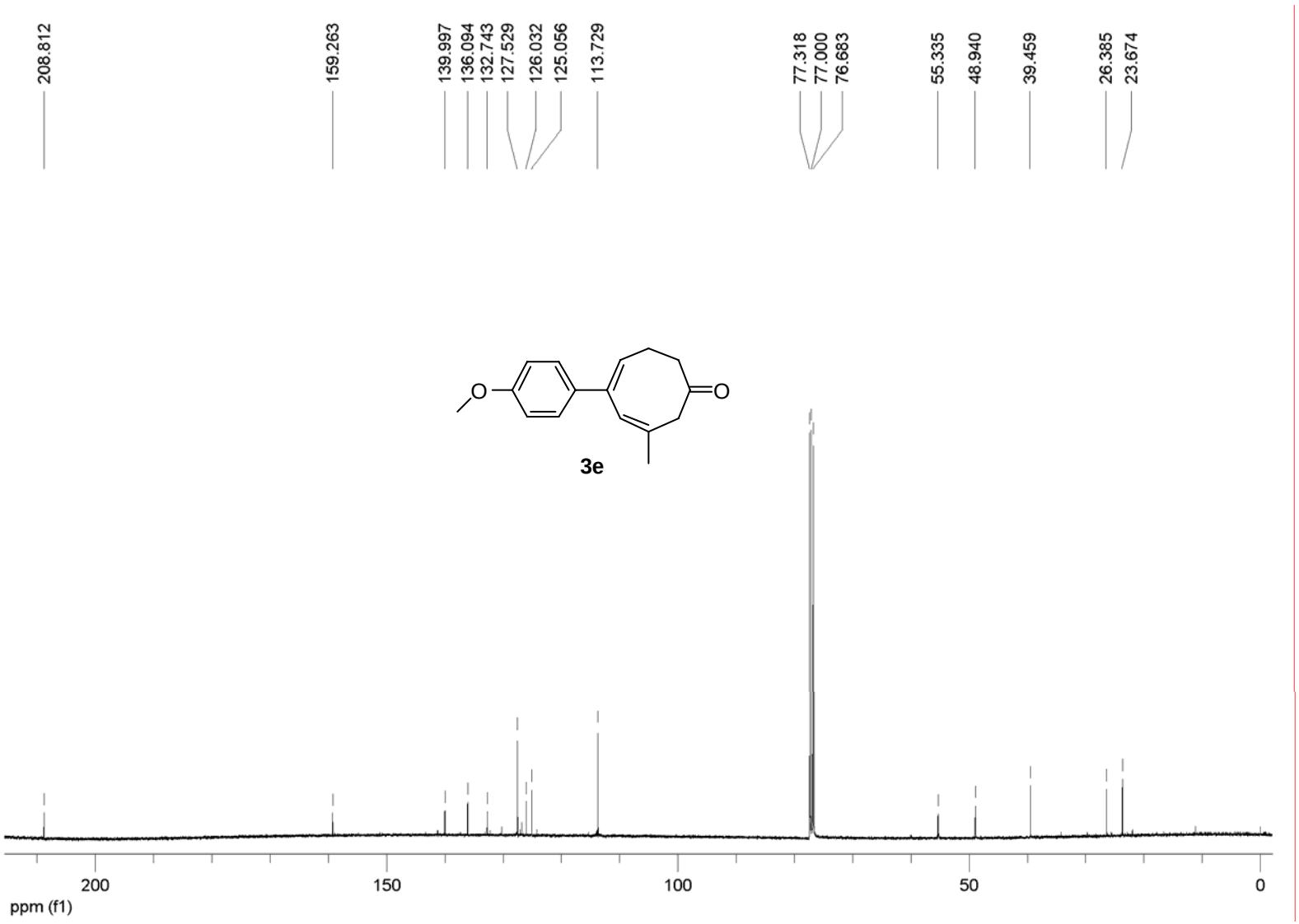


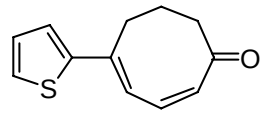

204.220
159.821
149.685
146.212
133.051
129.362
127.495
126.514
114.004
77.318
77.000
76.683
55.311
38.240
31.282
29.889
26.776
O
O
2e
200
150
100
50
0
ppm (f1)



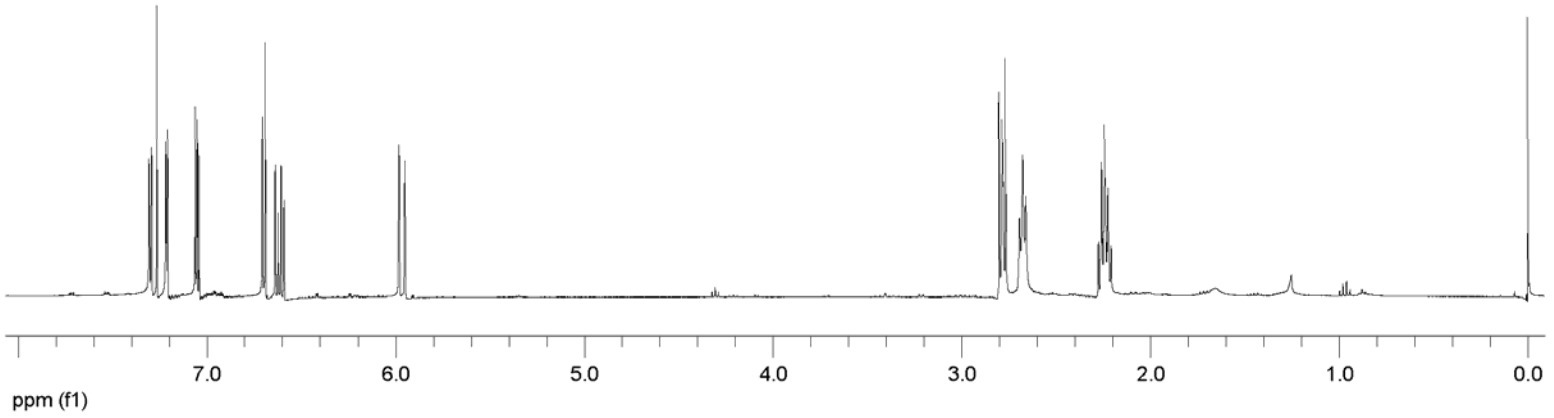
3e

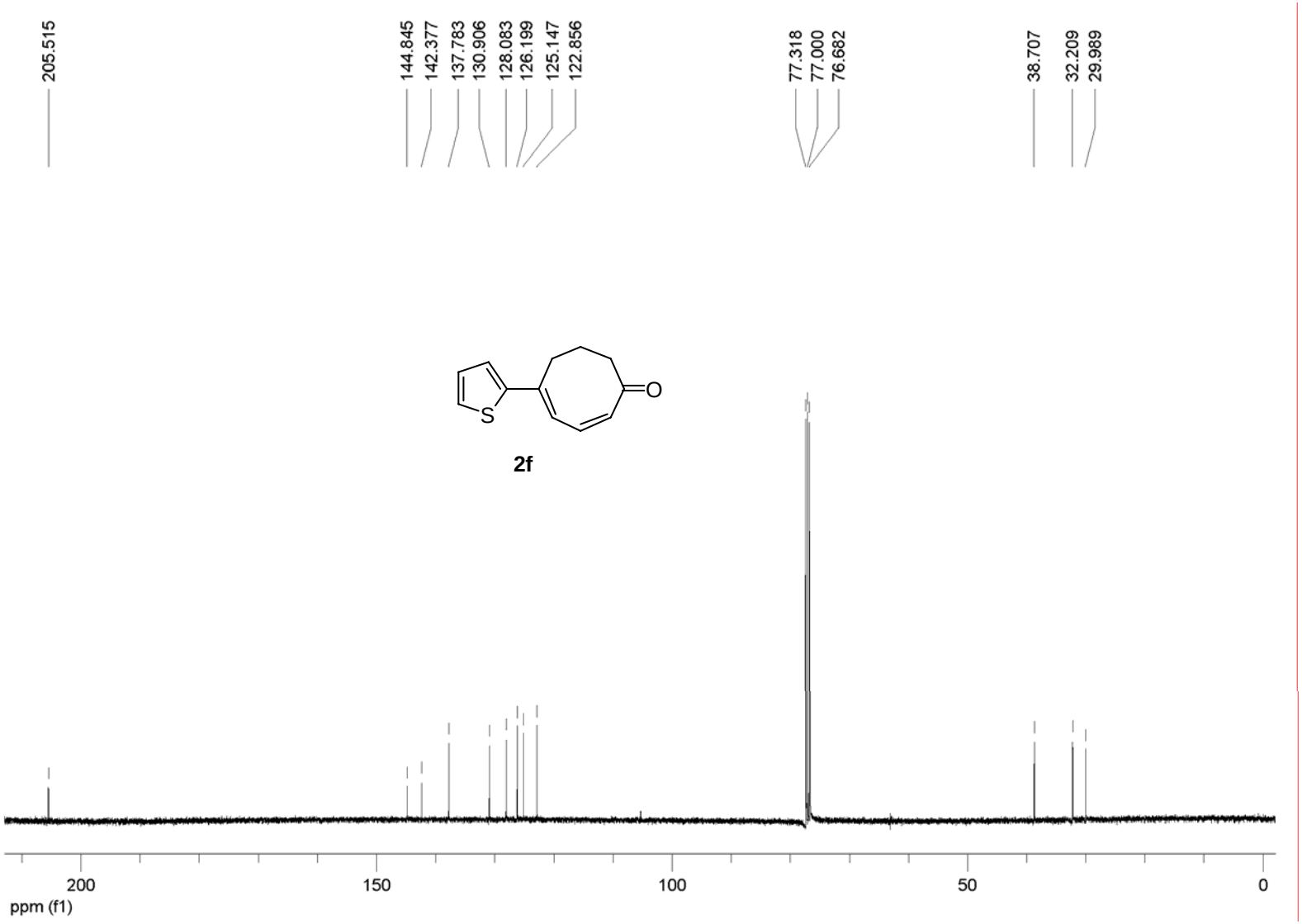


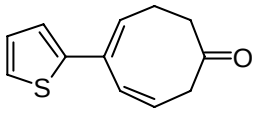

208.812
159.263
139.997
136.094
132.743
127.529
126.032
125.056
113.729
77.318
77.000
76.683
55.335
48.940
39.459
26.385
23.674
O
O
3e
200
150
100
50
0
ppm (f1)



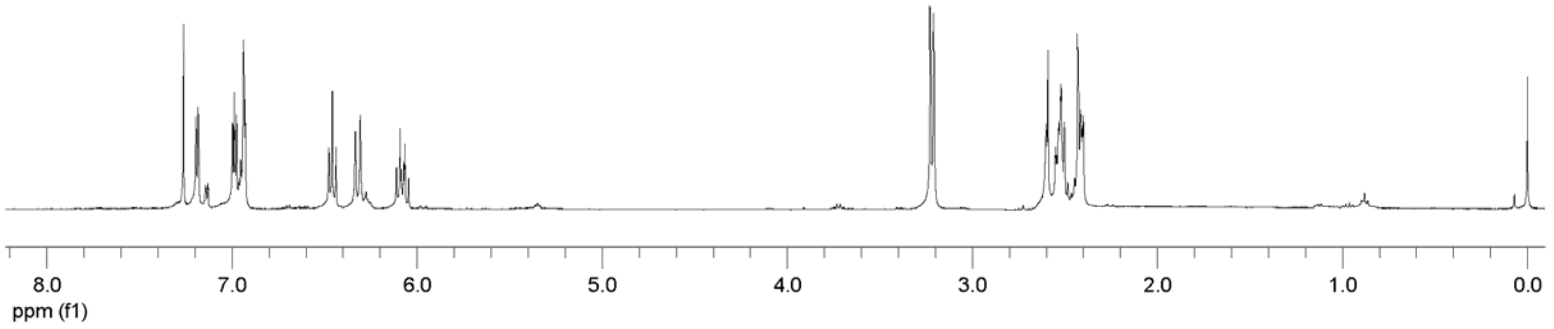
2f

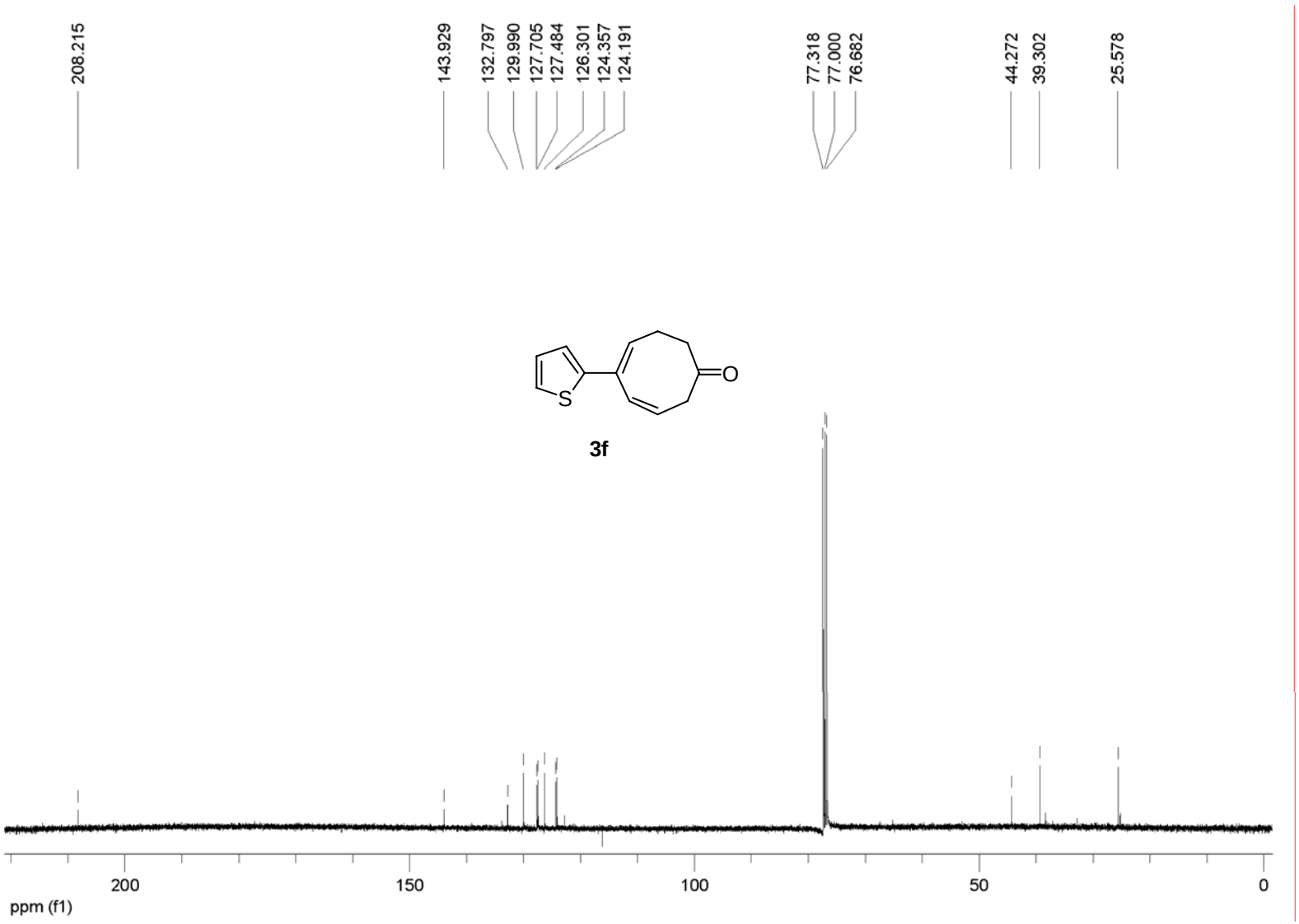


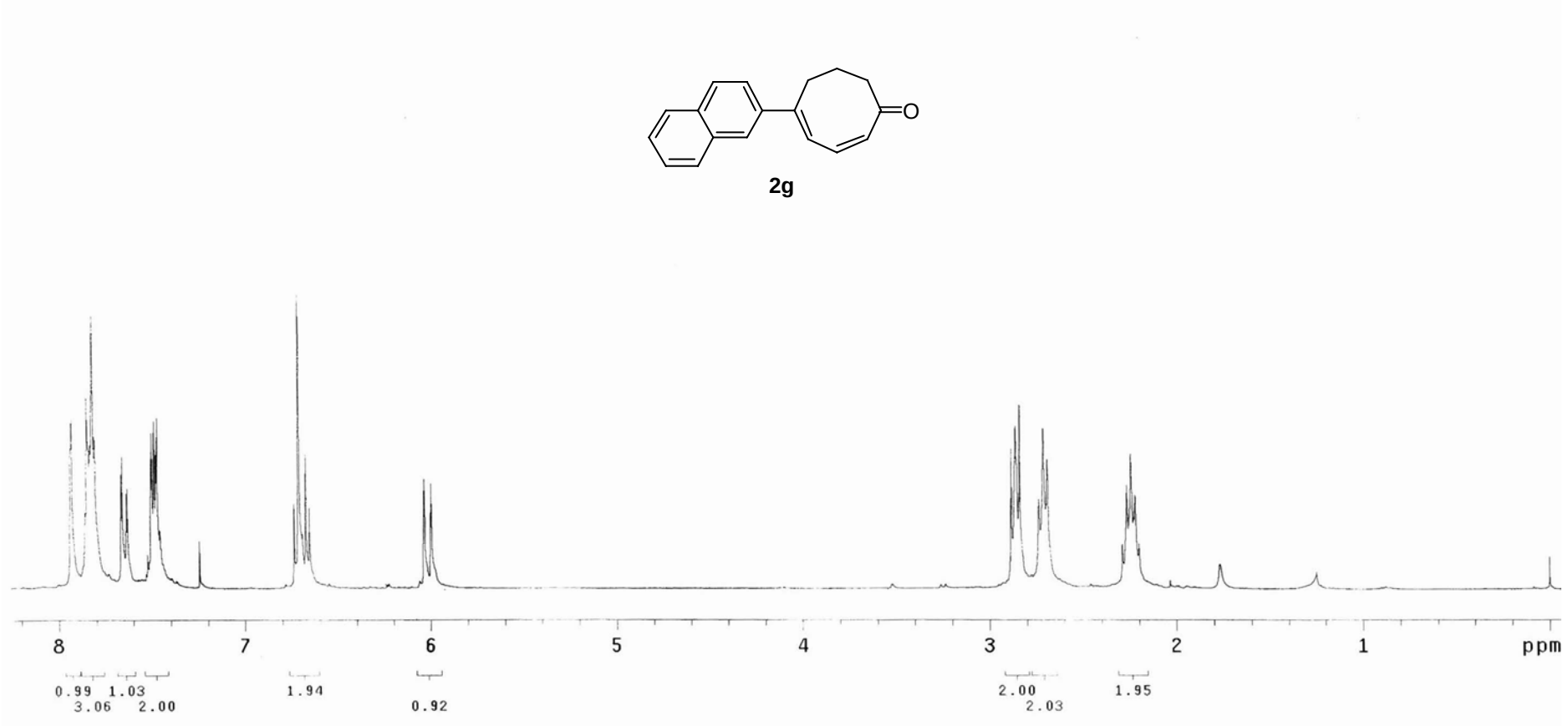

205.515
144.845
142.377
137.783
130.906
128.083
126.199
125.147
122.856
77.318
77.000
76.682
38.707
32.209
29.989
S
O
2f
200
150
100
50
0
ppm (f1)

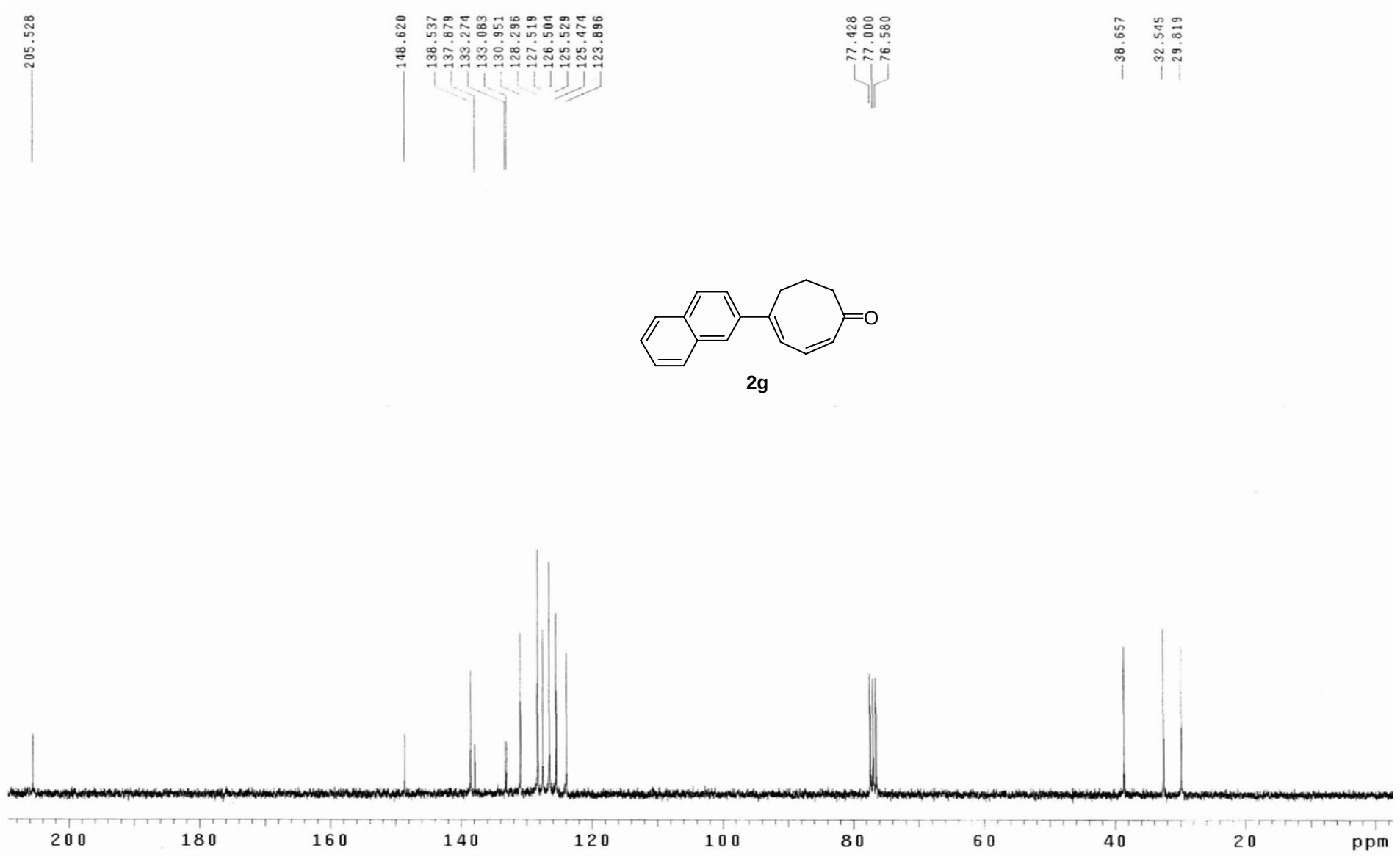


3f

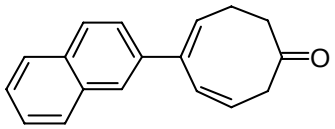



208.215
143.929
132.797
129.990
127.705
127.484
126.301
124.357
124.191
77.318
77.000
76.682
44.272
39.302
25.578
S
O
3f
200
150
100
50
0
ppm (f1)

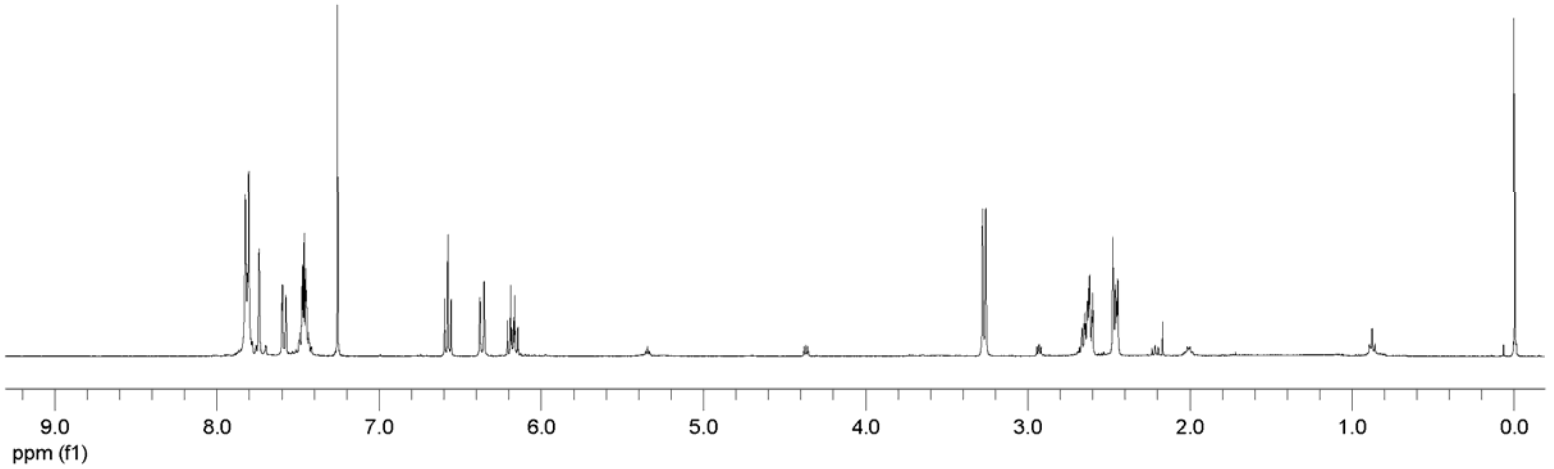

O
2g
8
7
6
5
4
3
2
1
ppm
0.99
1.03
3.06
2.00
1.94
0.92
2.00
2.03
1.95

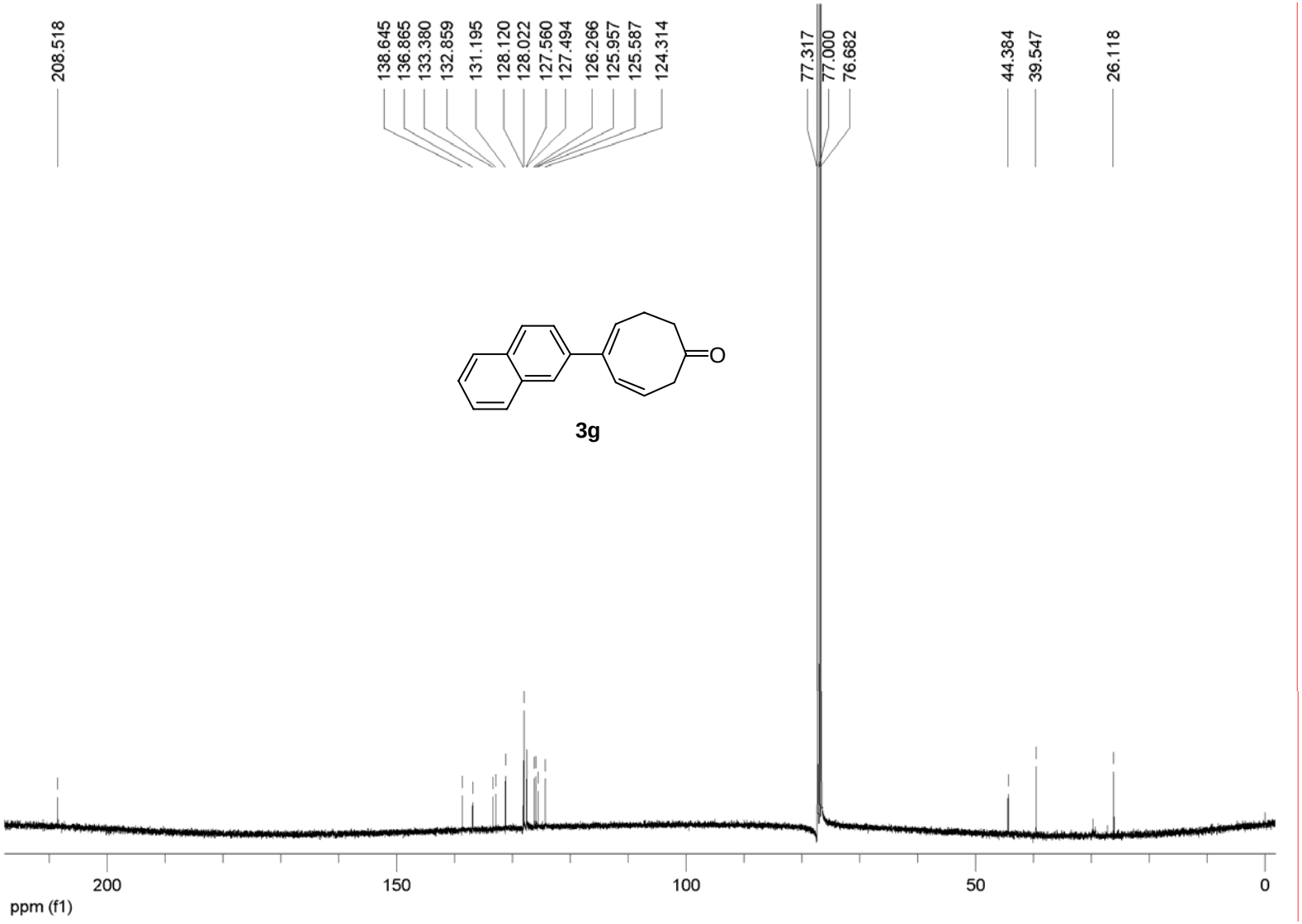

205.528
148.620
138.537
137.879
133.274
133.083
130.951
128.296
127.519
126.504
125.529
125.474
123.896
77.428
77.000
76.580
38.657
32.545
29.819
O
200
180
160
140
120
100
80
60
40
20
ppm

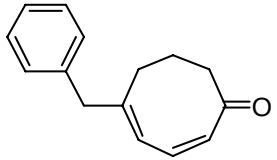
2g



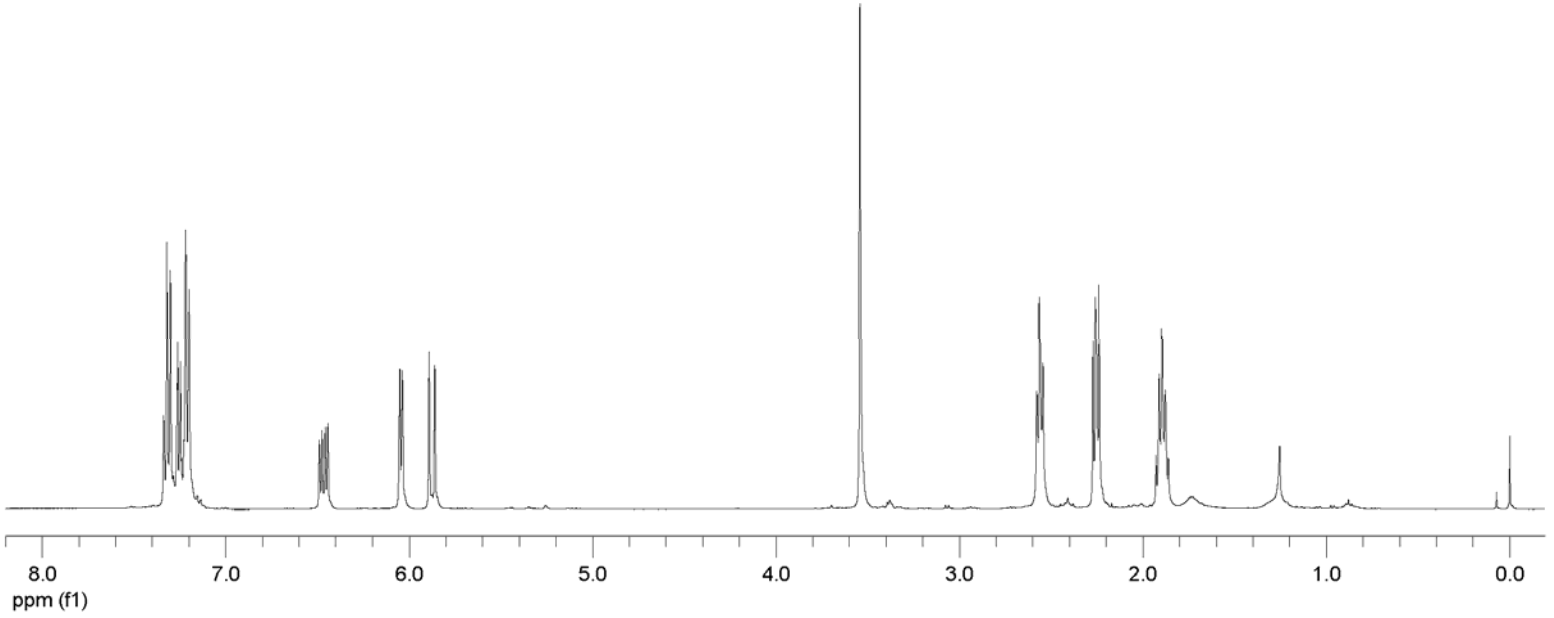
3g

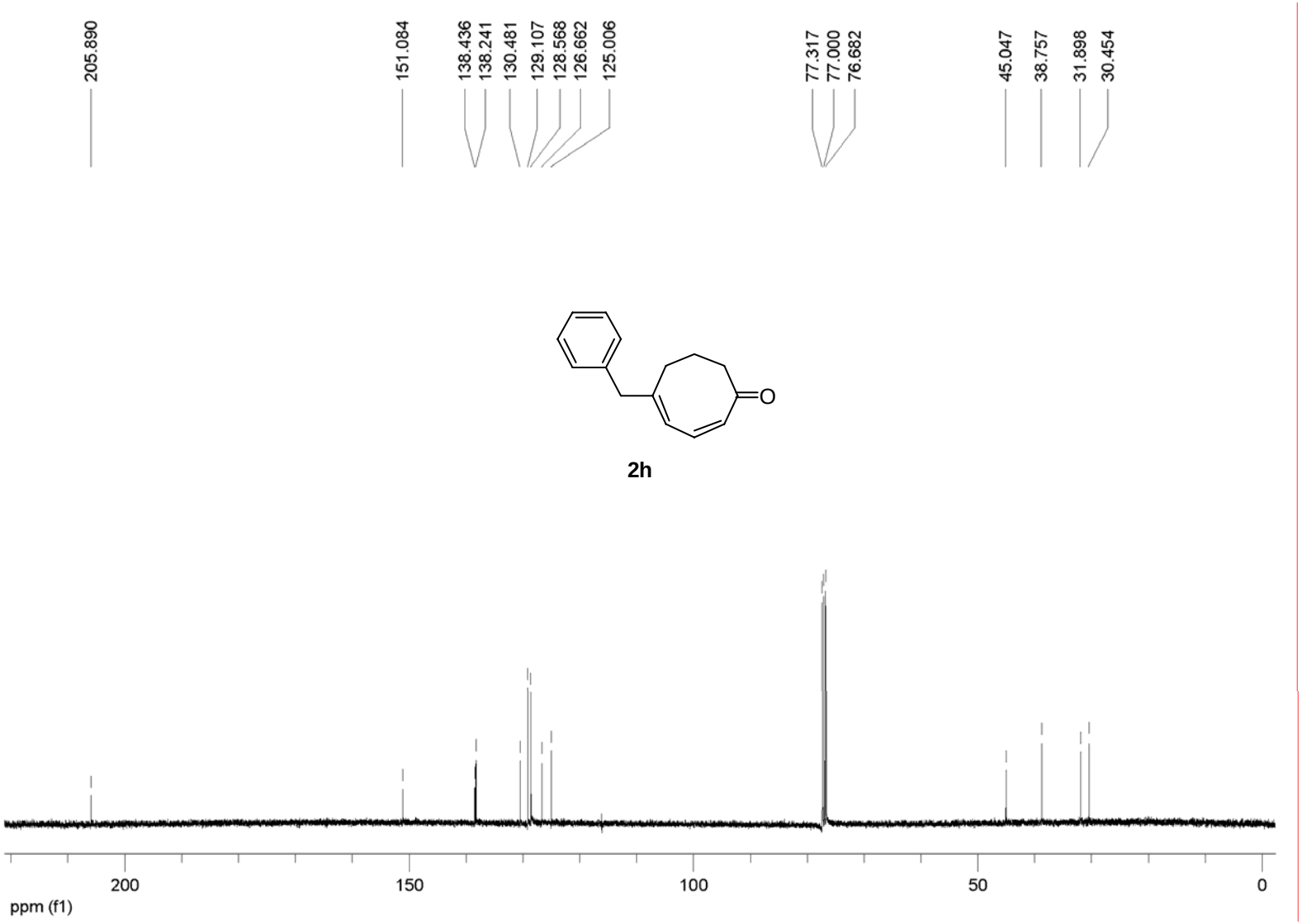



208.518
138.645
136.865
133.380
132.859
131.195
128.120
128.022
127.560
127.494
126.266
125.957
125.587
124.314
77.317
77.000
76.682
44.384
39.547
26.118
O
3g
200
150
100
50
0
ppm (f1)

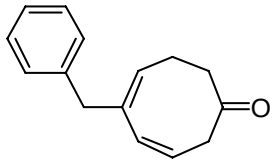


2h

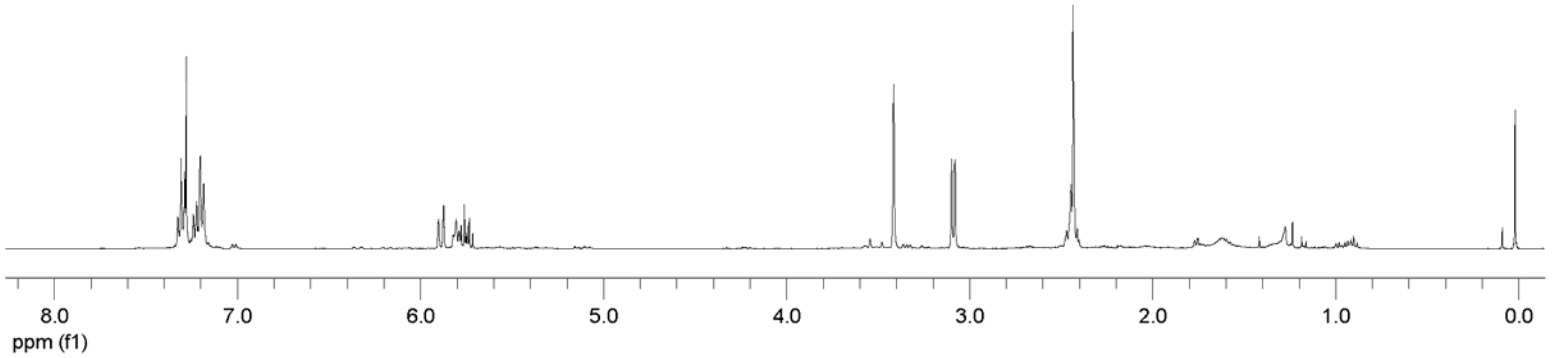


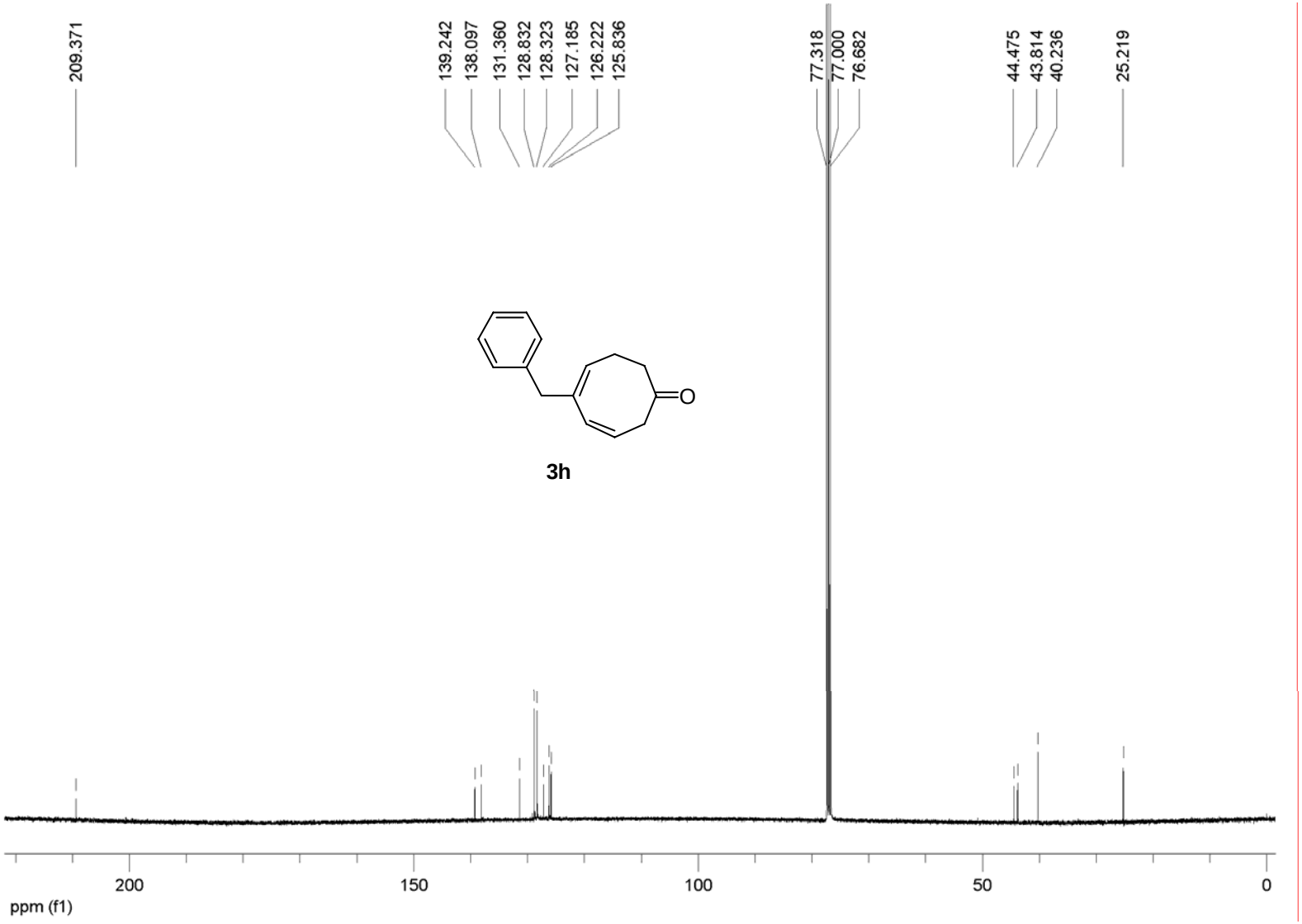

205.890
151.084
138.436
138.241
130.481
129.107
128.568
126.662
125.006
77.317
77.000
76.682
45.047
38.757
31.898
30.454
O
200
150
100
50
0
ppm (f1)

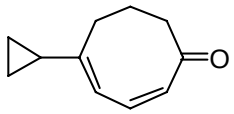
2h



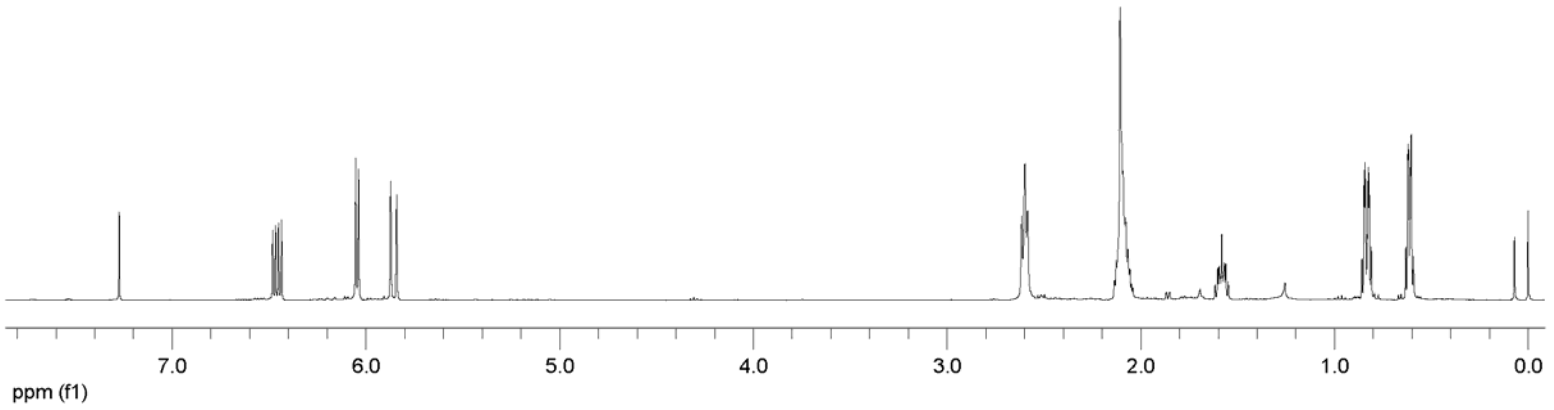
3h

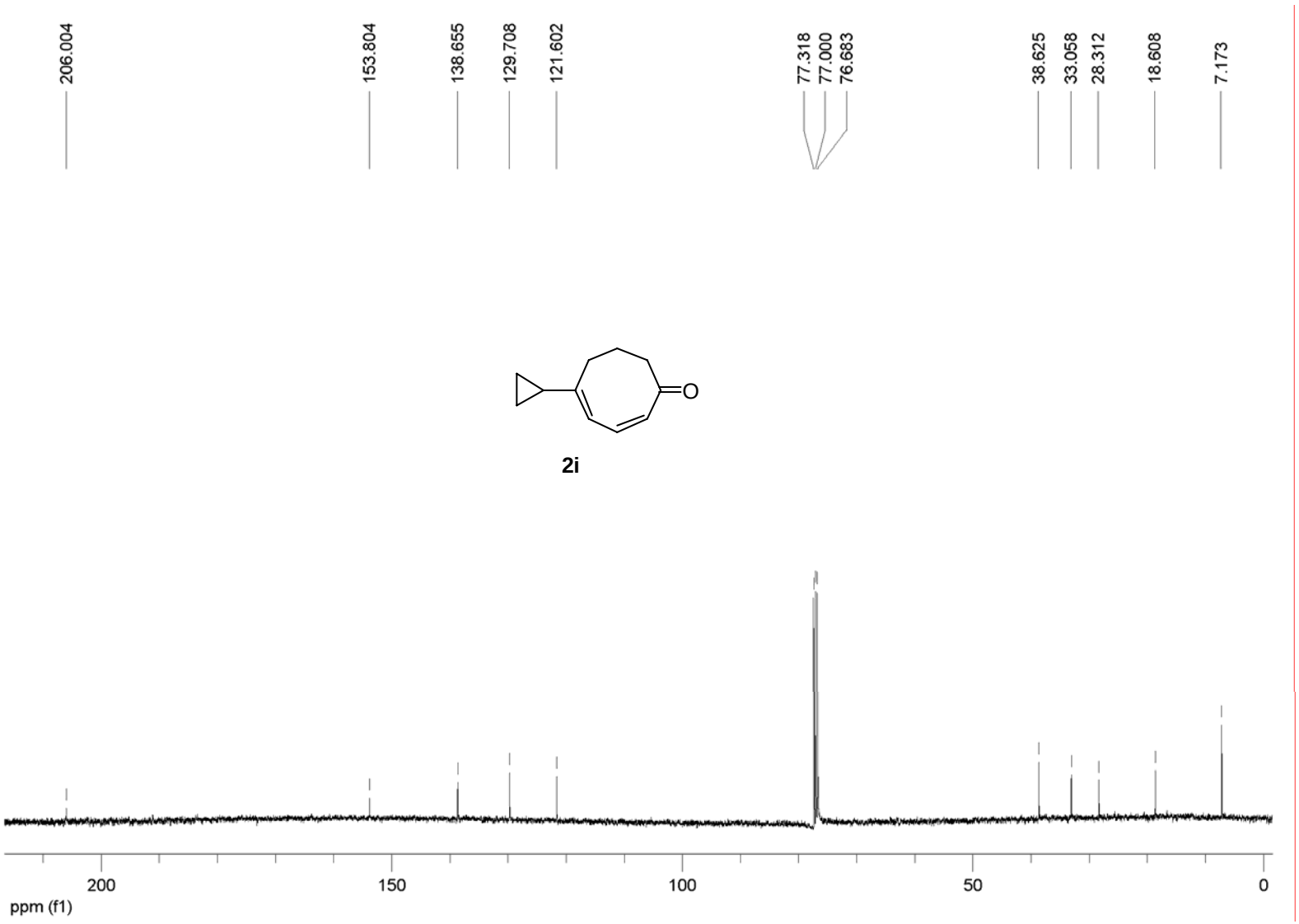



209.371
139.242
138.097
131.360
128.832
128.323
127.185
126.222
125.836
77.318
77.000
76.682
44.475
43.814
40.236
25.219
O
3h
200
150
100
50
0
ppm (f1)

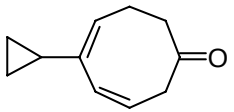


2i

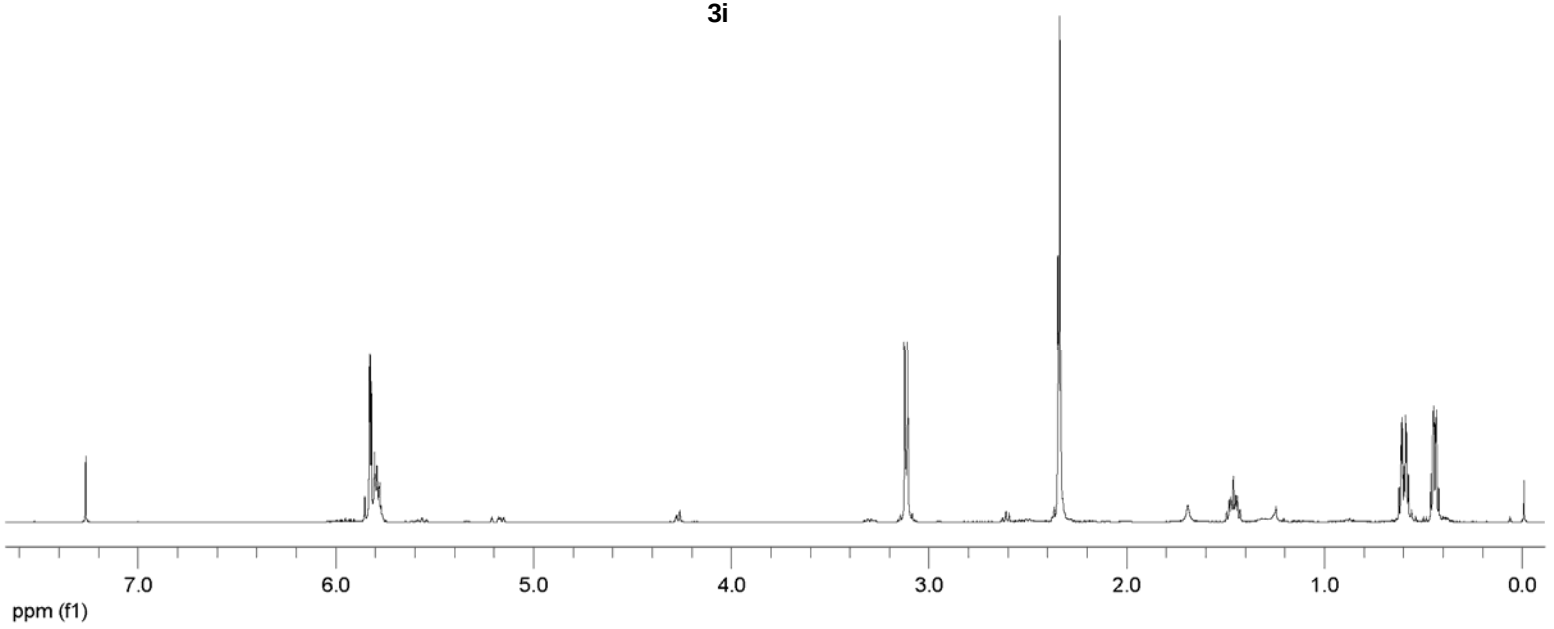


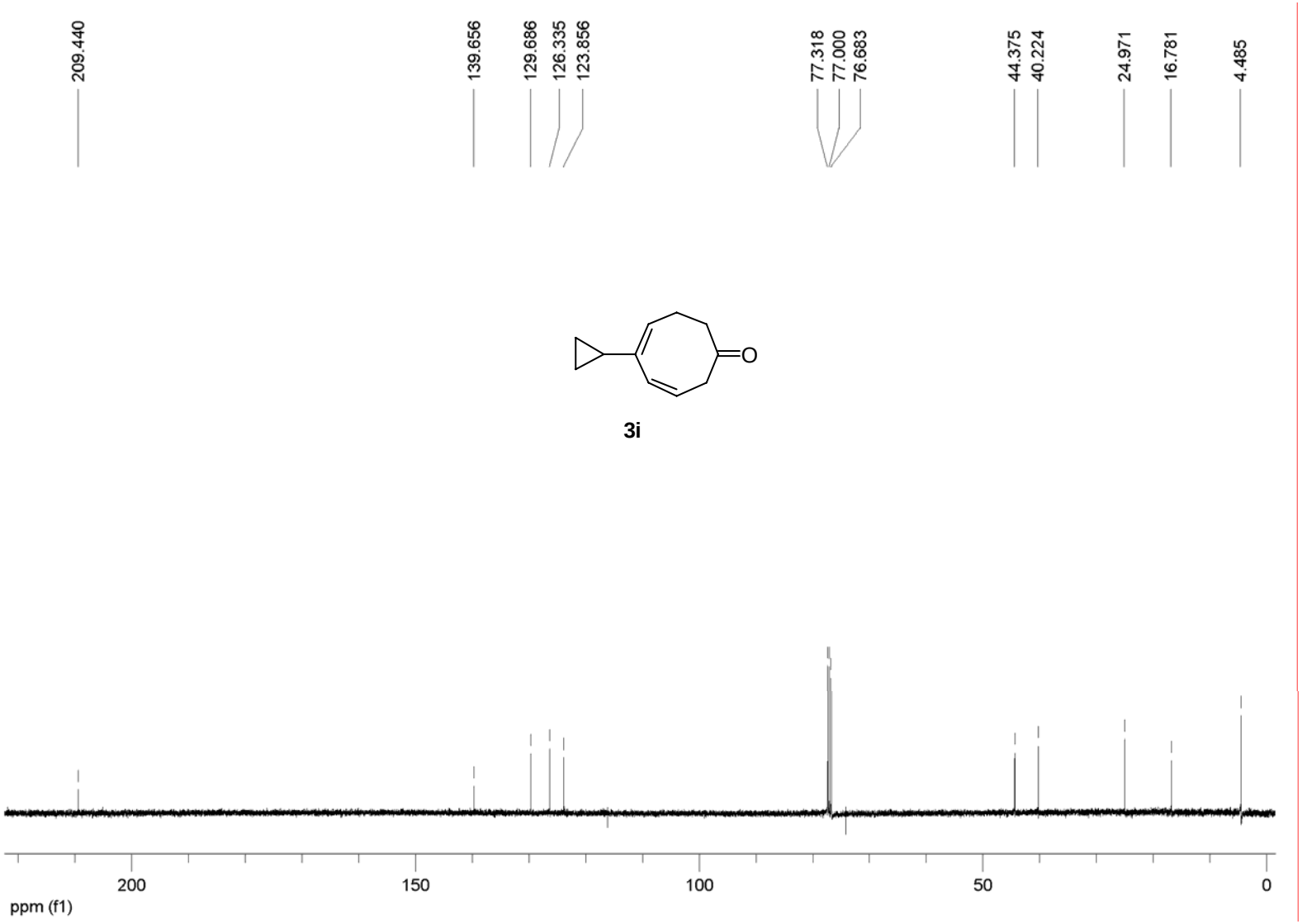

206.004
153.804
138.655
129.708
121.602
77.318
77.000
76.683
38.625
33.058
28.312
18.608
7.173
O
200
150
100
50
0
ppm (f1)

2i

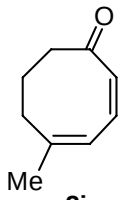


3i

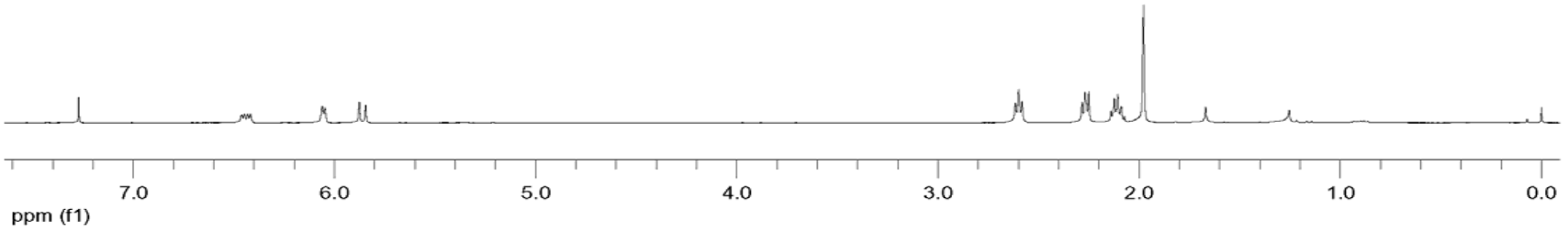


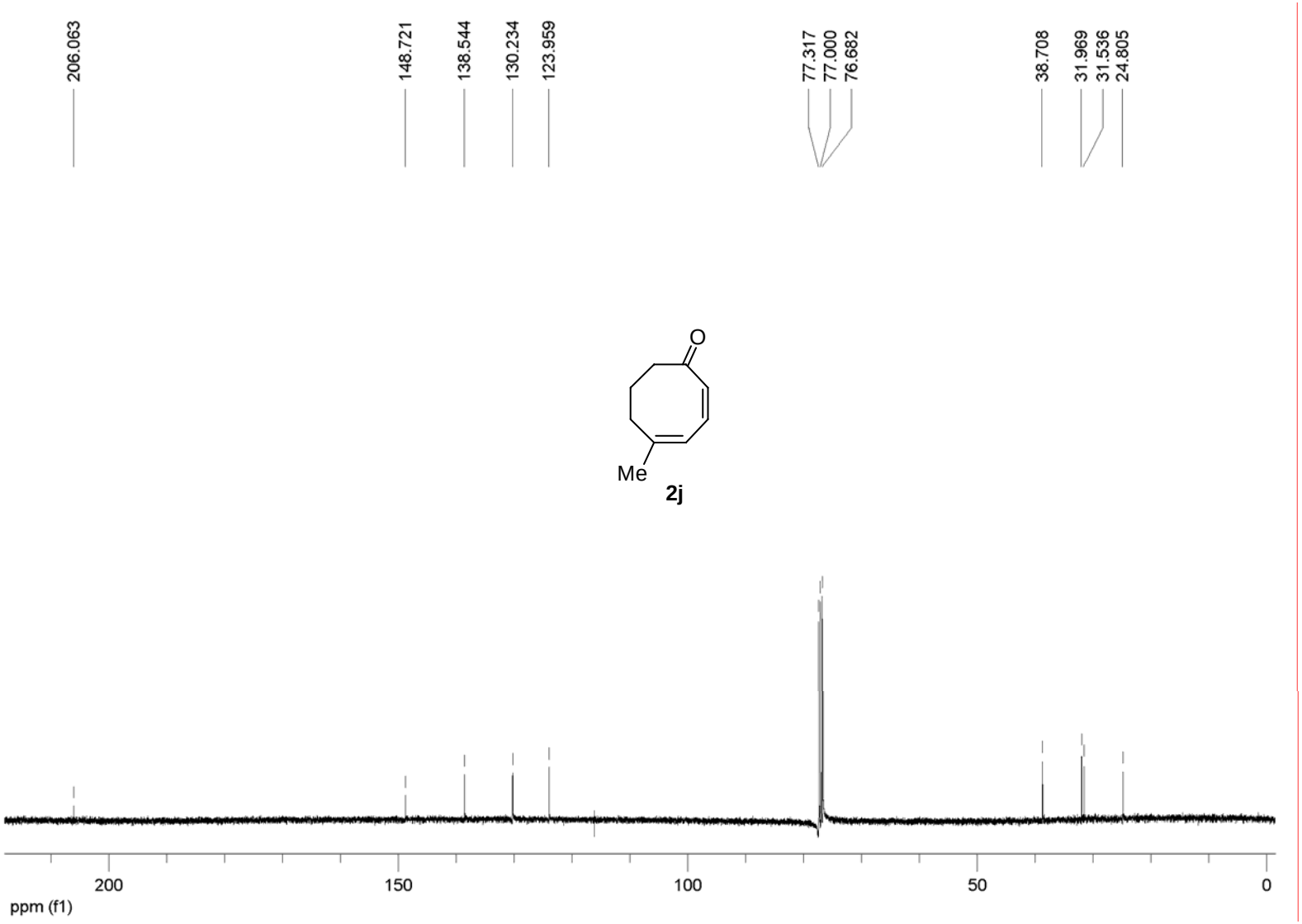

209.440
139.656
129.686
126.335
123.856
77.318
77.000
76.683
44.375
40.224
24.971
16.781
4.485
O
200
150
100
50
0
ppm (f1)

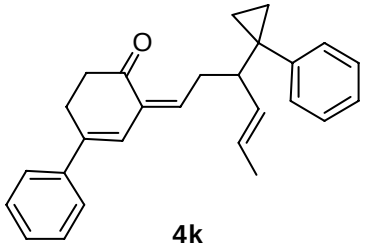
3i



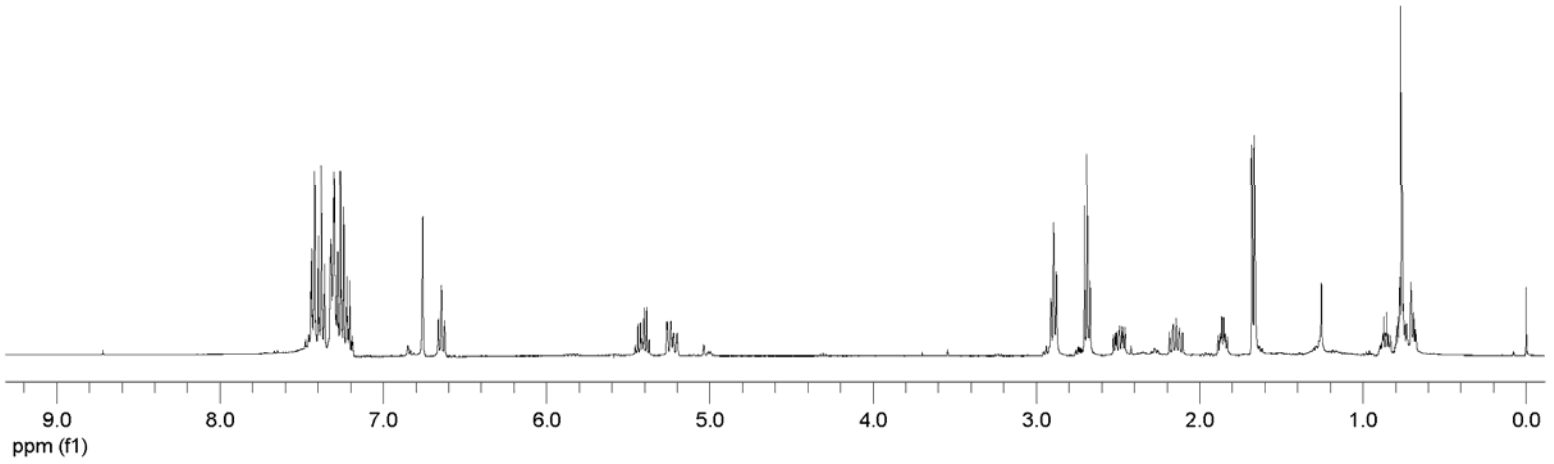
2j

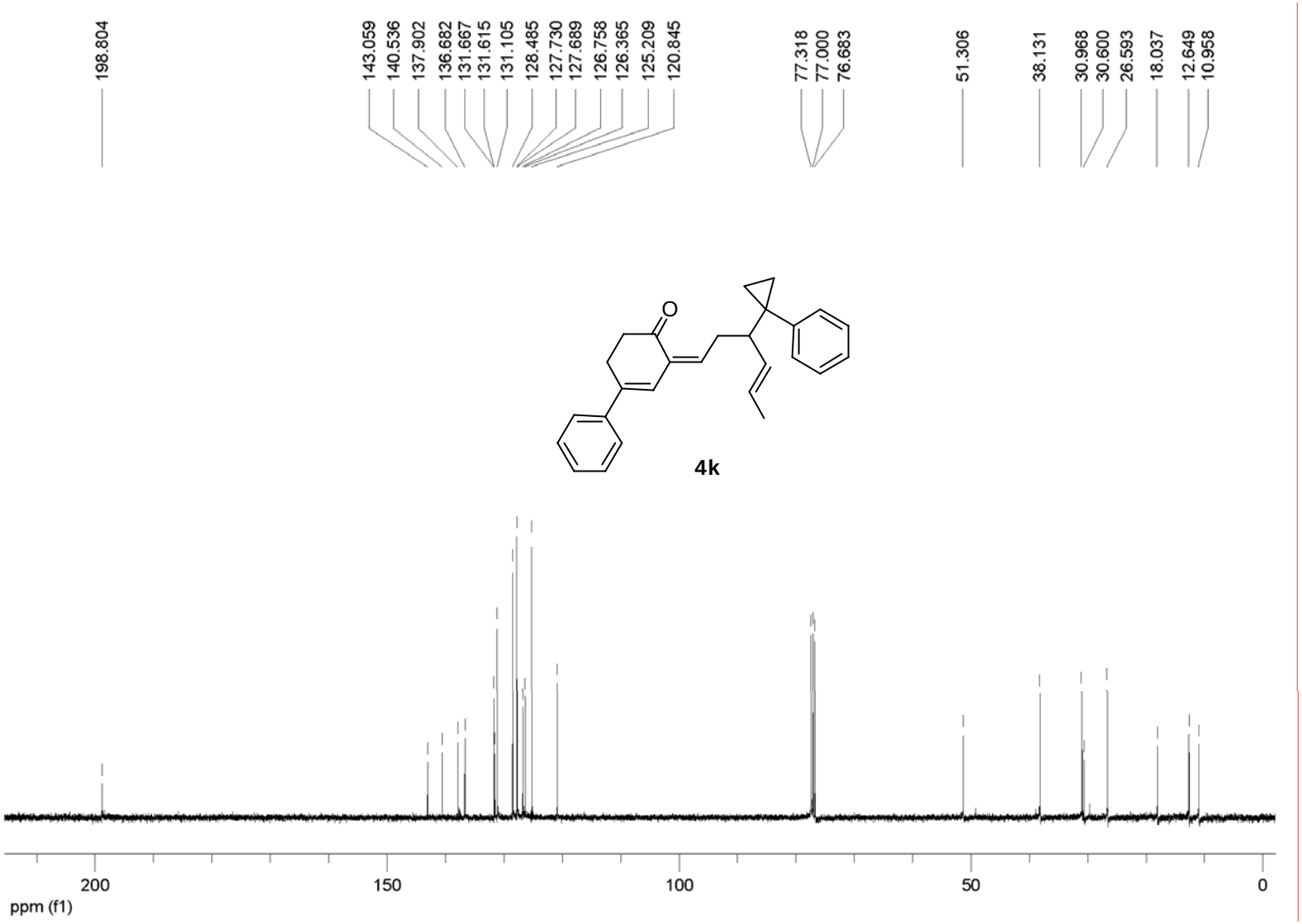


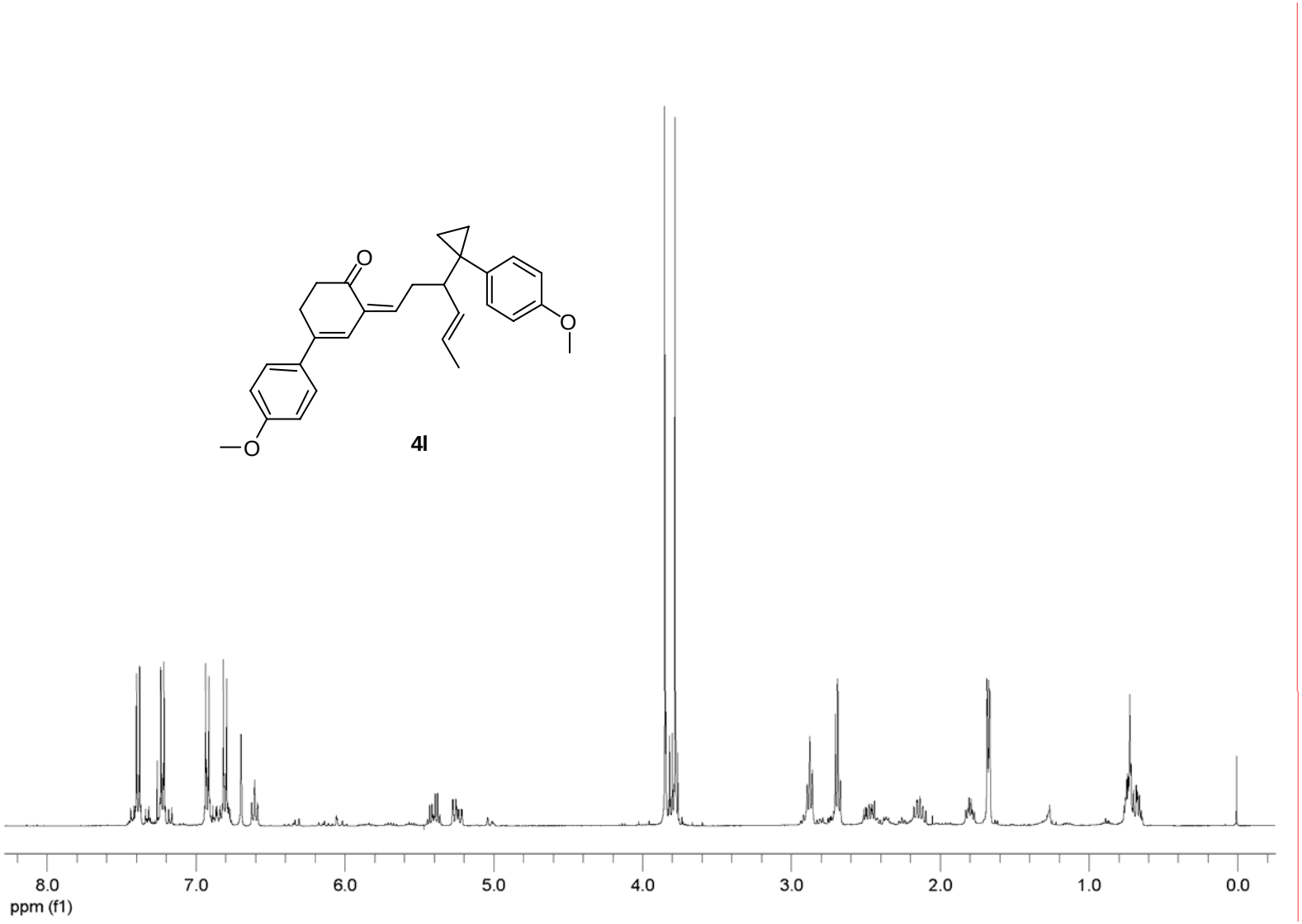

206.063
148.721
138.544
130.234
123.959
77.317
77.000
76.682
38.708
31.969
31.536
24.805
O
Me
2j
200
150
100
50
0
ppm (f1)

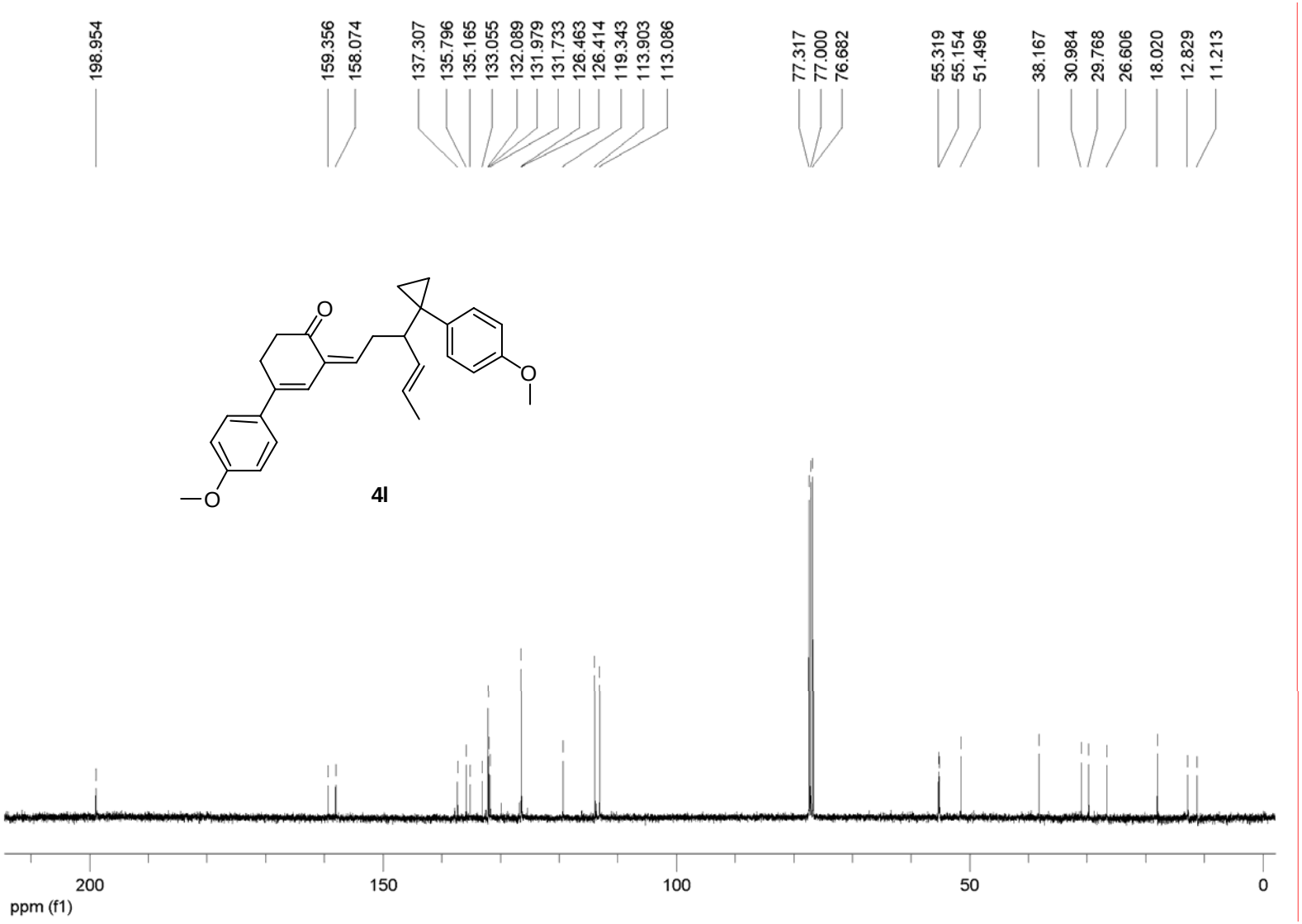


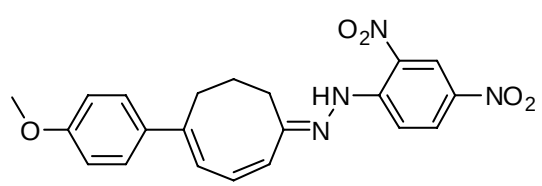
4k



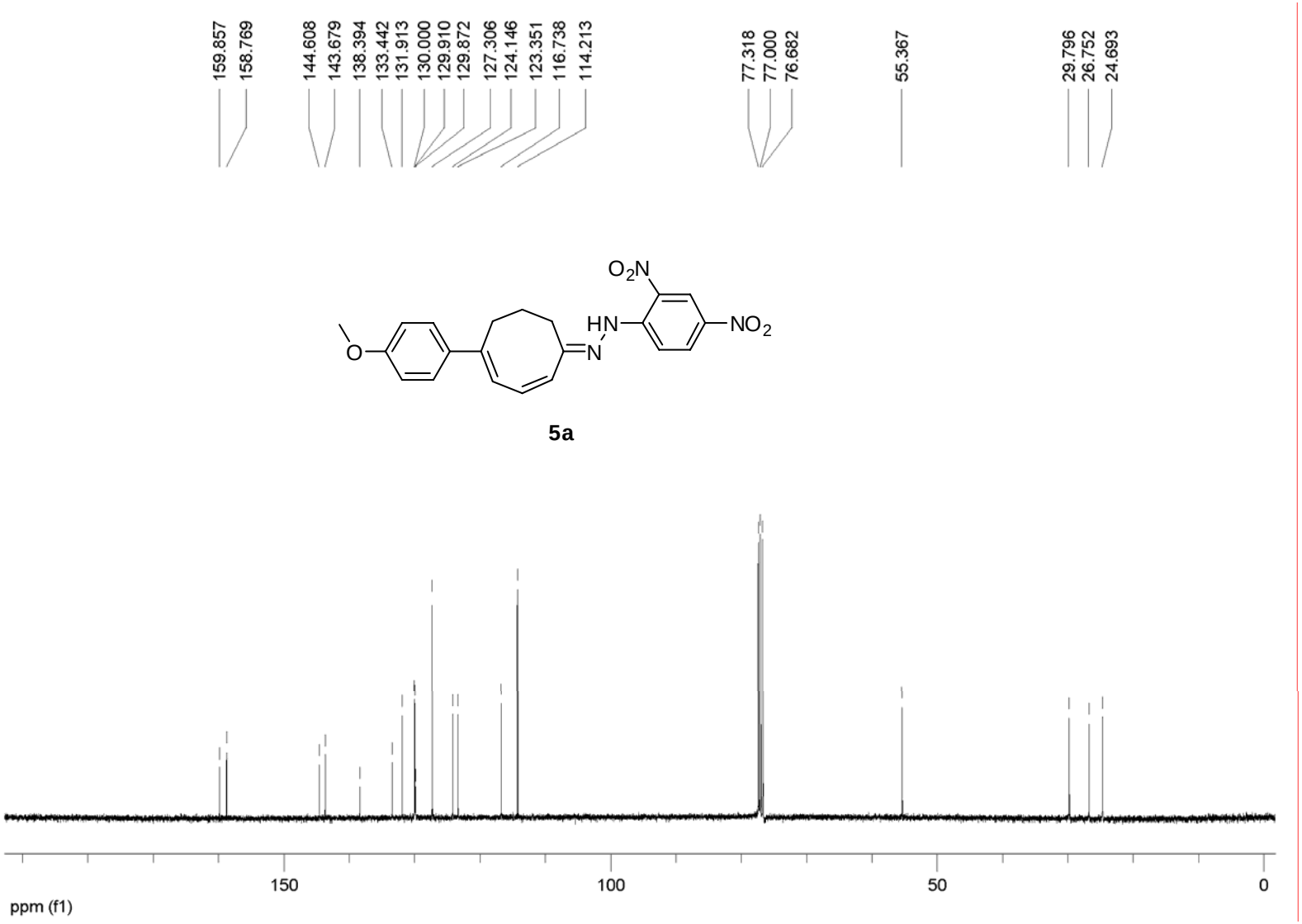

198.804
143.059
140.536
137.902
136.682
131.667
131.615
131.105
128.485
127.730
127.689
126.758
126.365
125.209
120.845
77.318
77.000
76.683
51.306
38.131
30.968
30.600
26.593
18.037
12.649
10.958
O
4k
200
150
100
50
0
ppm (f1)


O
O
O
4l
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

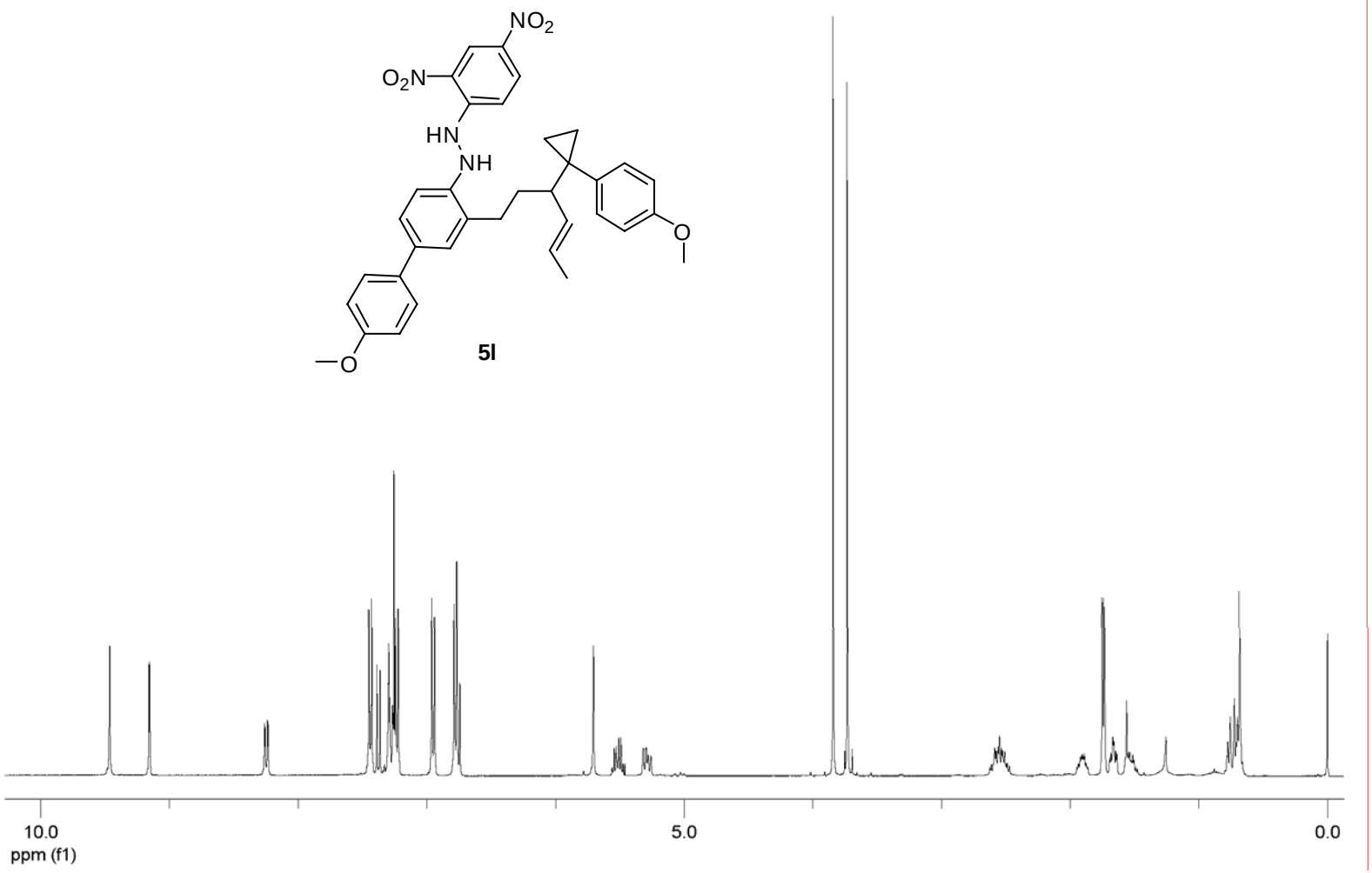

198.954
159.356
158.074
137.307
135.796
135.165
133.055
132.089
131.979
131.733
126.463
126.414
119.343
113.903
113.086
77.317
77.000
76.682
55.319
55.154
51.496
38.167
30.984
29.768
26.606
18.020
12.829
11.213
O
O
O
4l
200
150
100
50
0
ppm (f1)

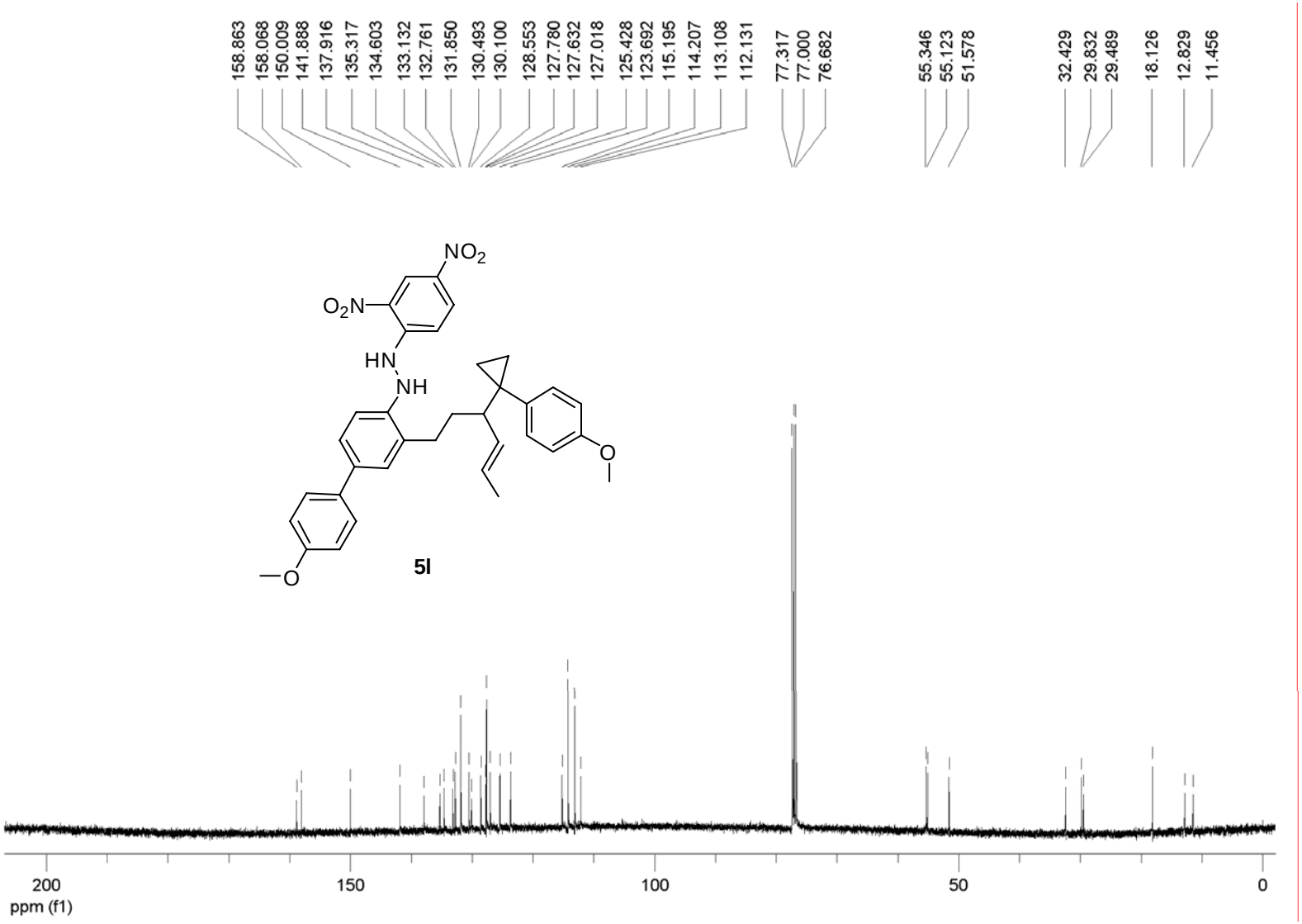


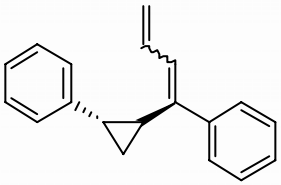
5a


159.857
158.769
144.608
143.679
138.394
133.442
131.913
130.000
129.910
129.872
127.306
124.146
123.351
116.738
114.213
77.318
77.000
76.682
55.367
29.796
26.752
24.693
O2N
HN
NO2
O
N
150
100
50
0
ppm (f1)

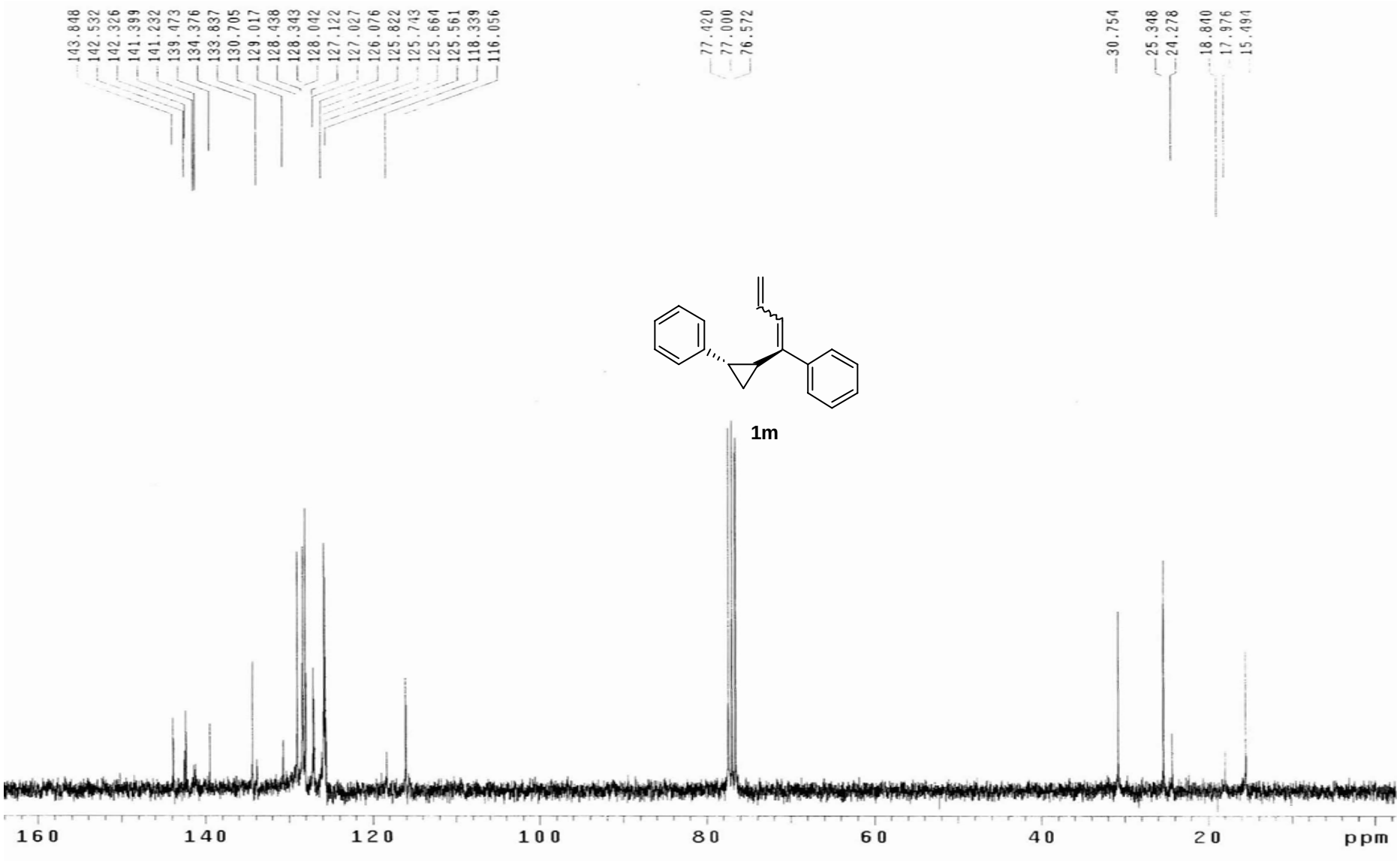
5a


NO2
O2N
HN
NH
O
O
5l
10.0
ppm (f1)
5.0
0.0


158.863
158.068
150.009
141.888
137.916
135.317
134.603
133.132
132.761
131.850
130.493
130.100
128.553
127.780
127.632
127.018
125.428
123.692
115.195
114.207
113.108
112.131
77.317
77.000
76.682
55.346
55.123
51.578
32.429
29.832
29.489
18.126
12.829
11.456
NO2
O2N
HN
NH
O
O
5l
200
150
100
50
0
ppm (f1)



1m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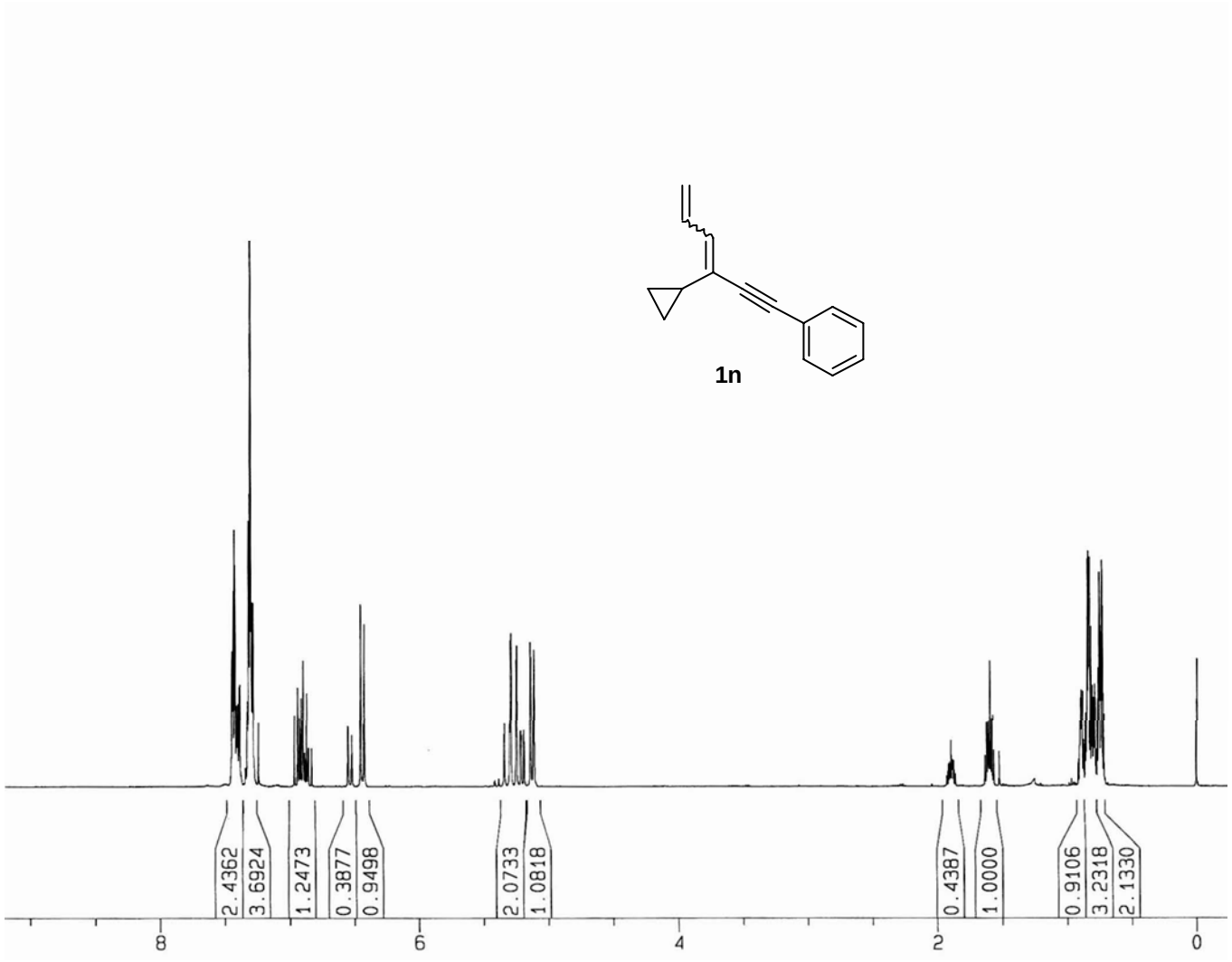
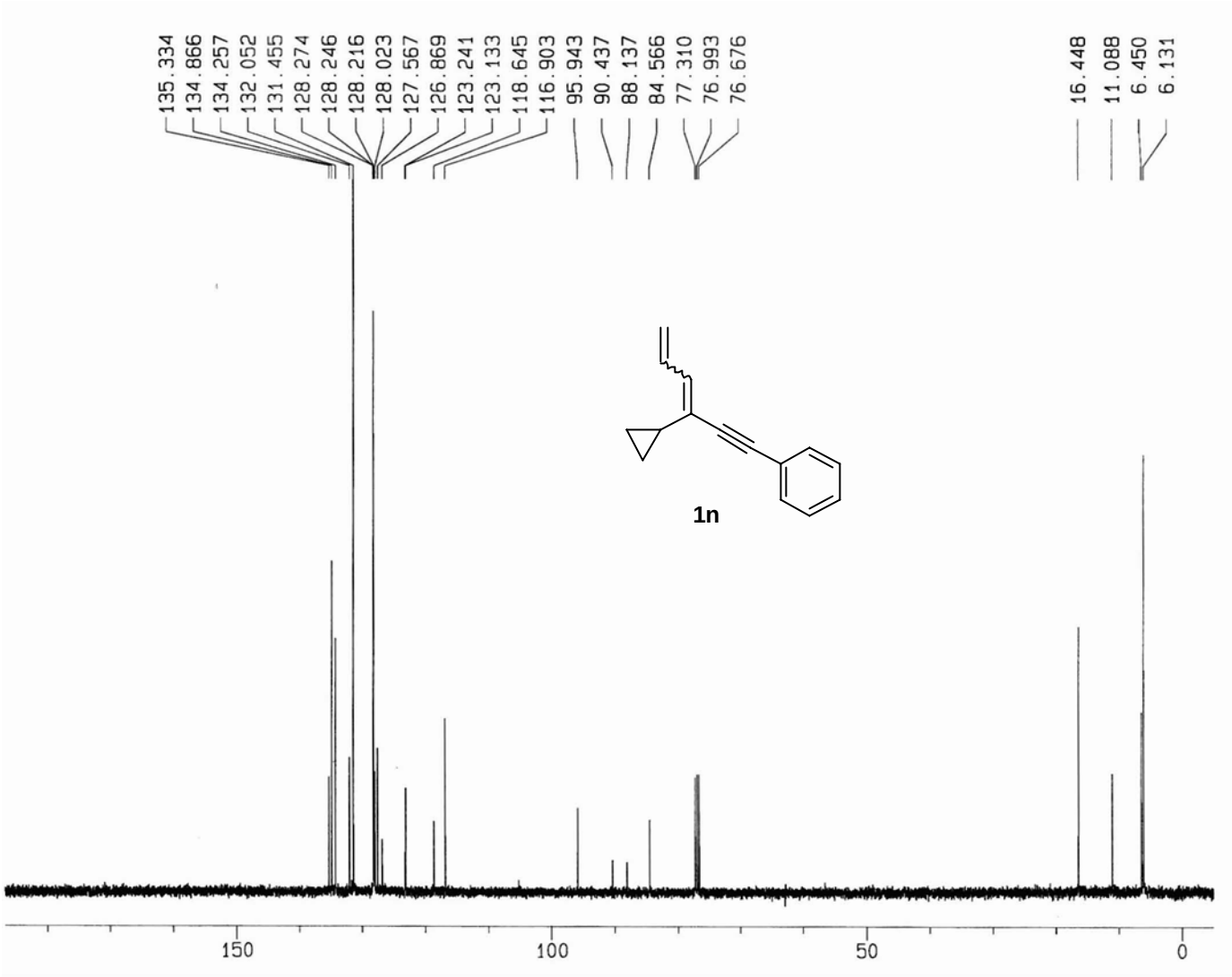
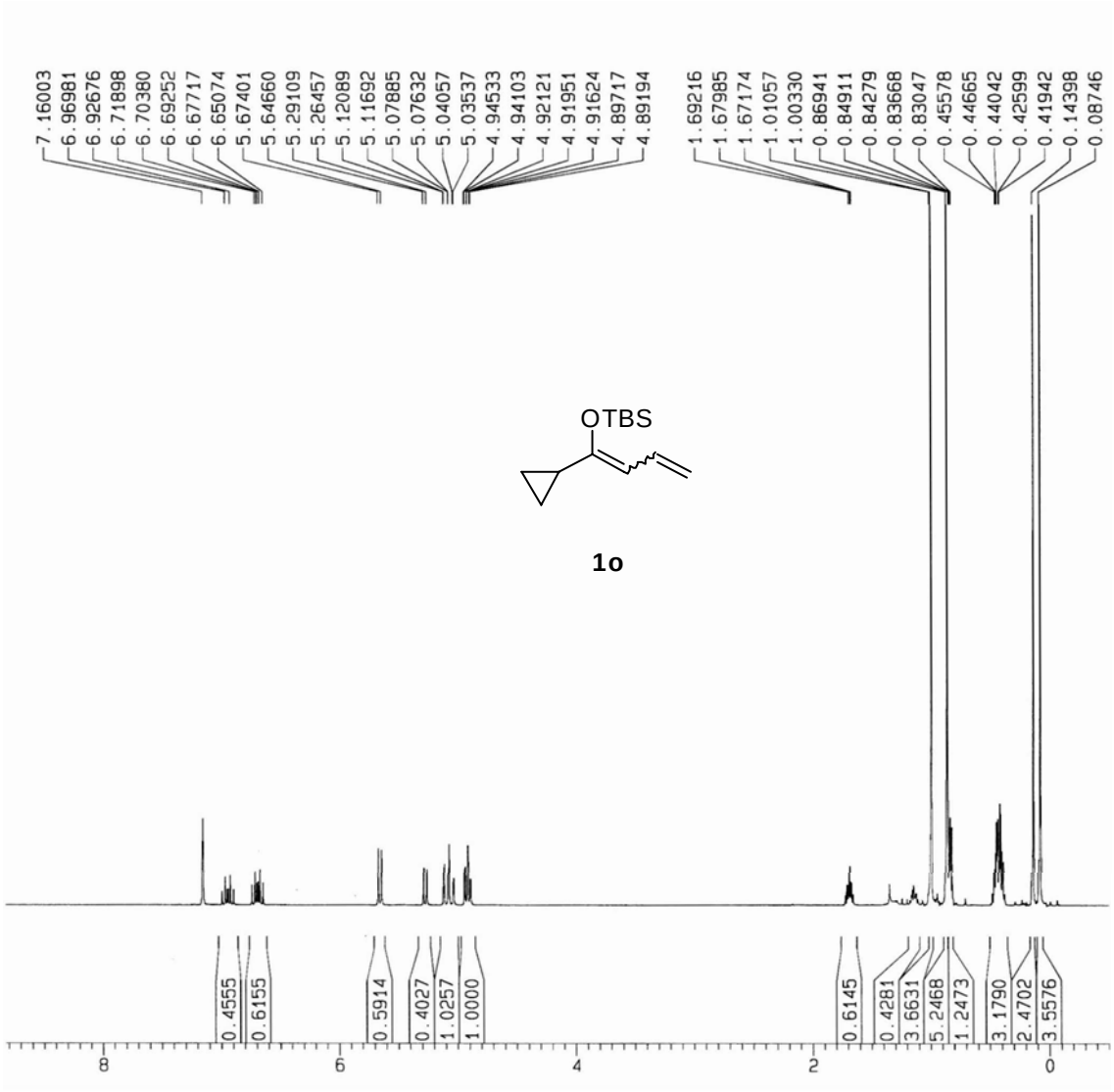
142.326
141.399
141.232
139.473
134.376
133.837
130.705
129.017
128.438
128.343
128.042
127.122
127.027
126.076
125.822
125.743
125.664
125.561
118.339
116.056
77.420
77.000
76.572
30.754
25.348
24.278
18.810
17.976
15.494
160
140
120
100
80
60
40
20
ppm

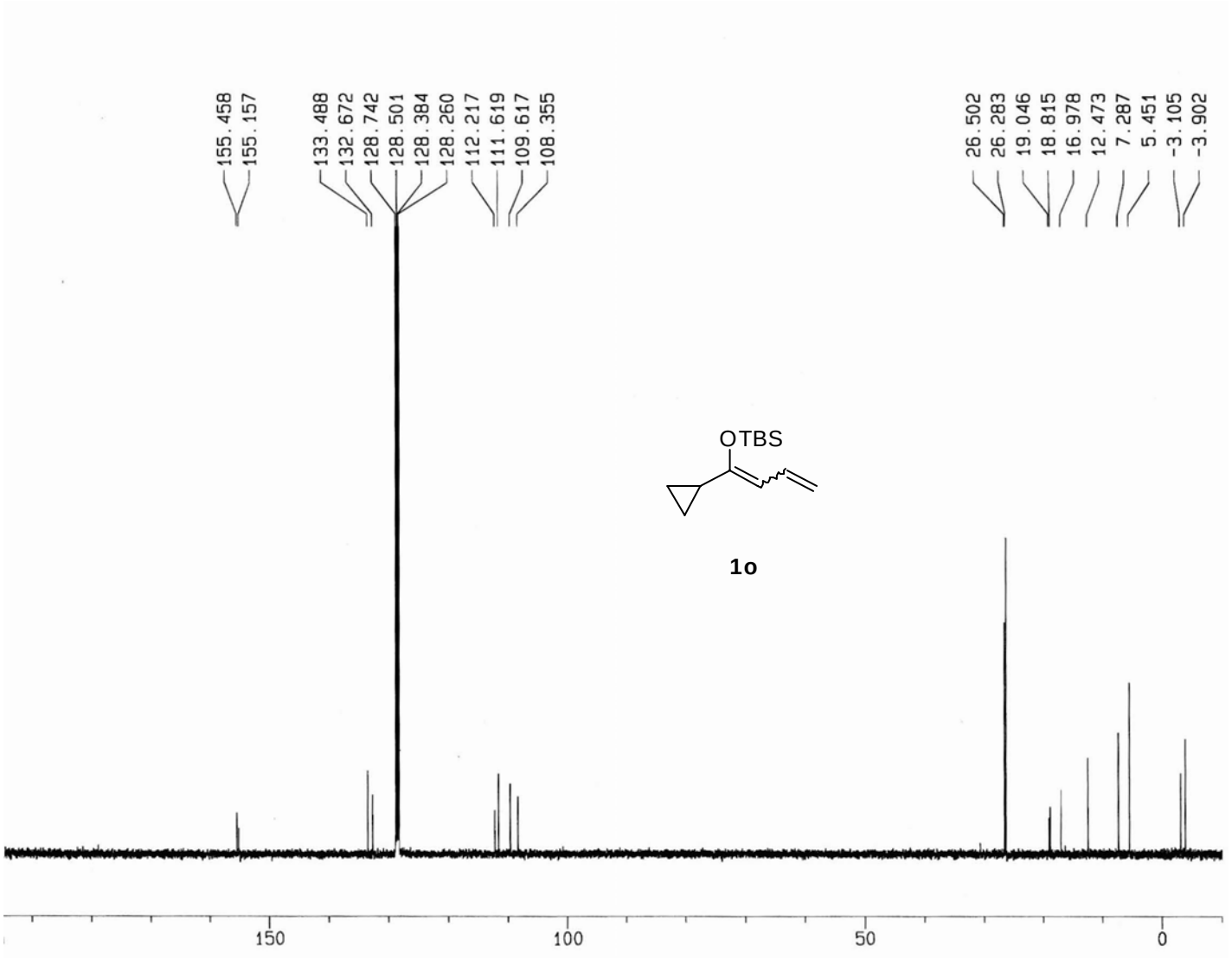
1m

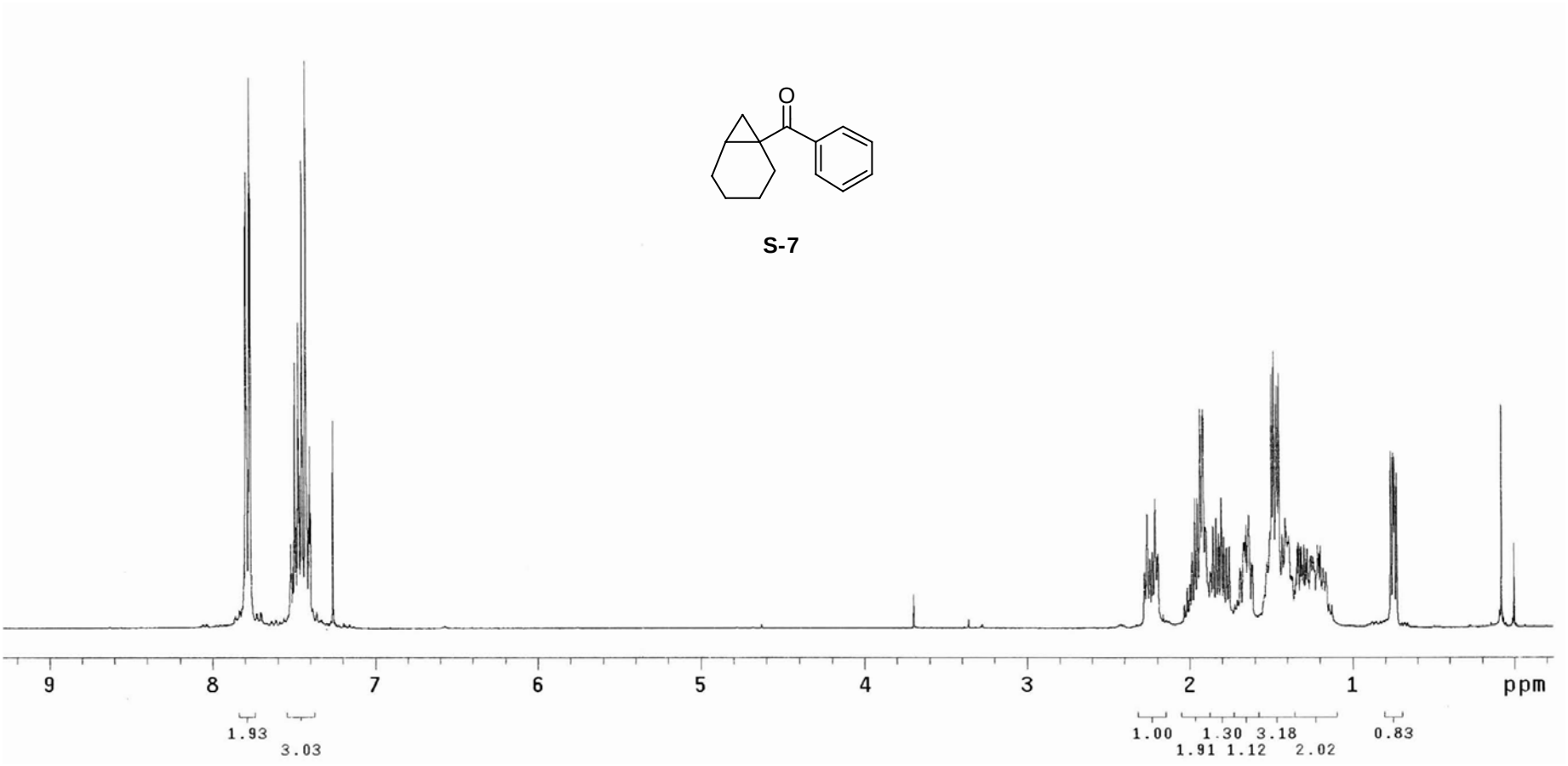

2.4362
3.6924
1.2473
0.3877
0.9498
2.0733
1.0818
0.4387
1.0000
0.9106
3.2318
2.1330
8
6
4
2
0

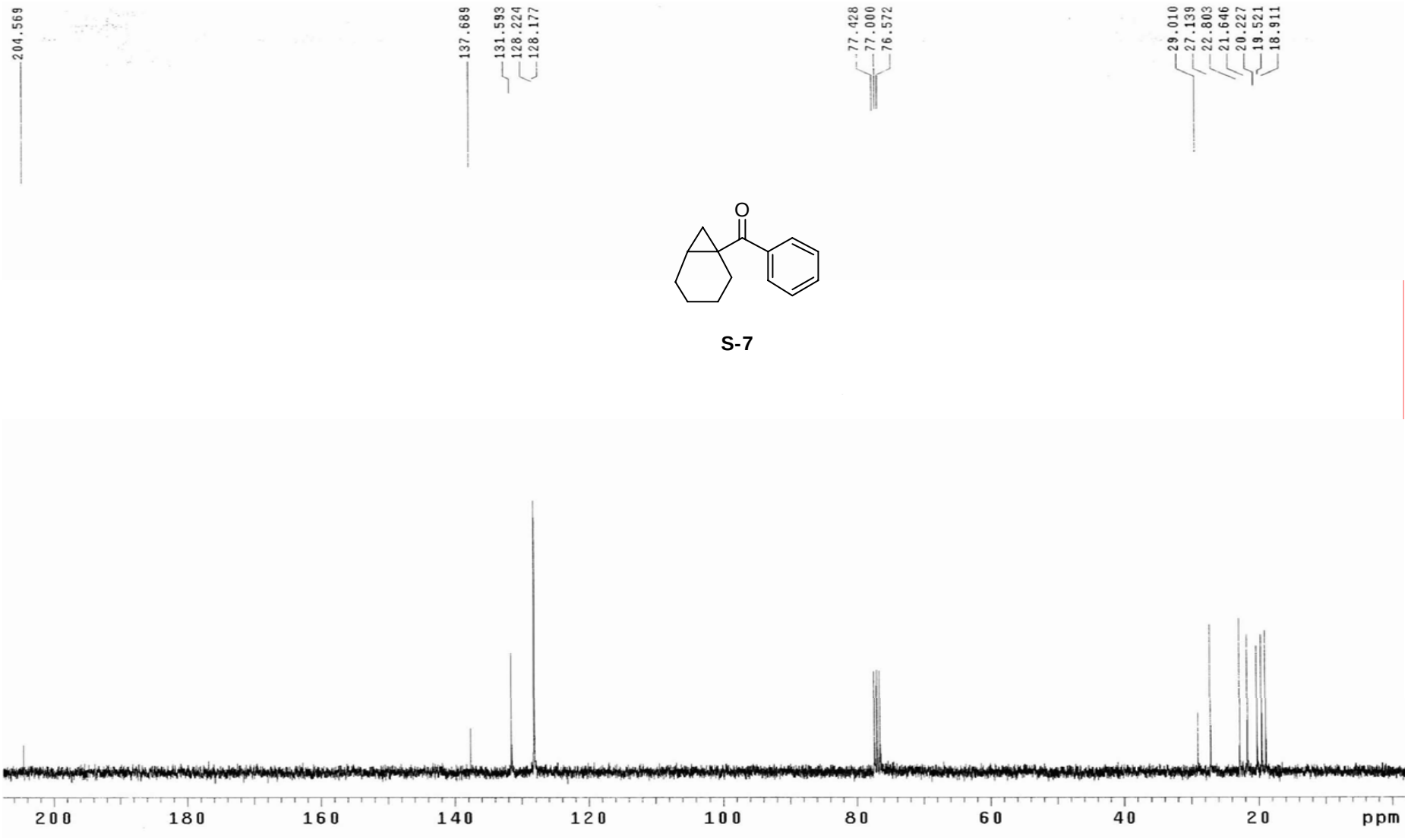
1n


135.334
134.866
134.257
132.052
131.455
128.274
128.246
128.216
128.023
127.567
126.869
123.241
123.133
118.645
116.903
95.943
90.437
88.137
84.566
77.310
76.993
76.676
16.448
11.088
6.450
6.131
1n
150
100
50
0

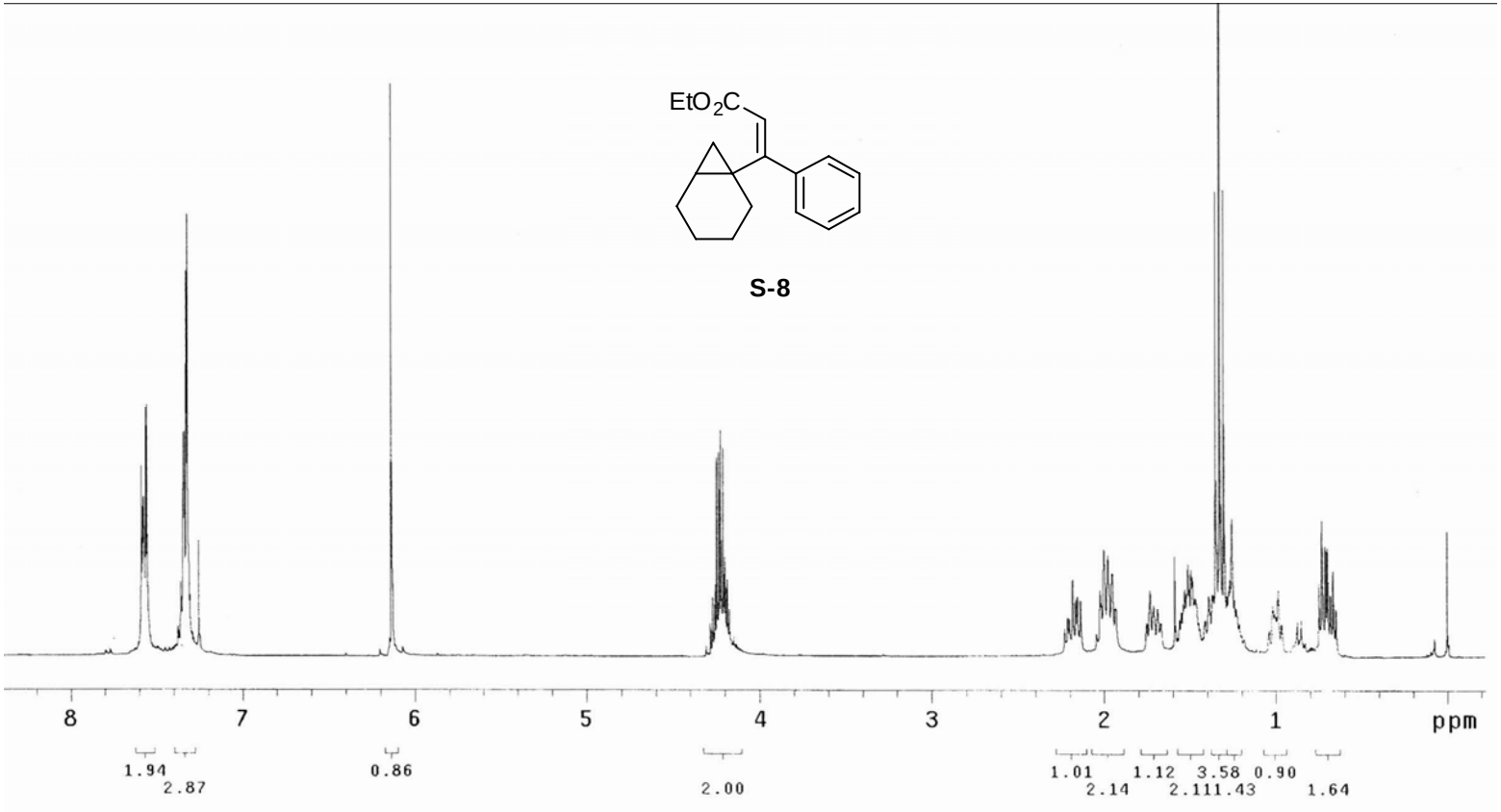

7.16003
6.96981
6.92676
6.71898
6.70380
6.69252
6.67717
6.65074
5.67401
5.64660
5.29109
5.26457
5.12089
5.11692
5.07885
5.07632
5.04057
5.03537
4.94533
4.94103
4.92121
4.91951
4.91624
4.89717
4.89194
1.69216
1.67985
1.67174
1.01057
1.00330
0.86941
0.84911
0.84279
0.83668
0.83047
0.45578
0.44665
0.44042
0.42599
0.41942
0.14398
0.08746
OTBS
1o
0.4555
0.6155
0.5914
0.4027
1.0257
1.0000
0.6145
0.4281
3.6631
5.2468
1.2473
3.1790
2.4702
3.5576
8
6
4
2
0


155.458
155.157
133.488
132.672
128.742
128.501
128.384
128.260
112.217
111.619
109.617
108.355
26.502
26.283
19.046
18.815
16.978
12.473
7.287
5.451
-3.105
-3.902
OTBS
1o
150
100
50
0

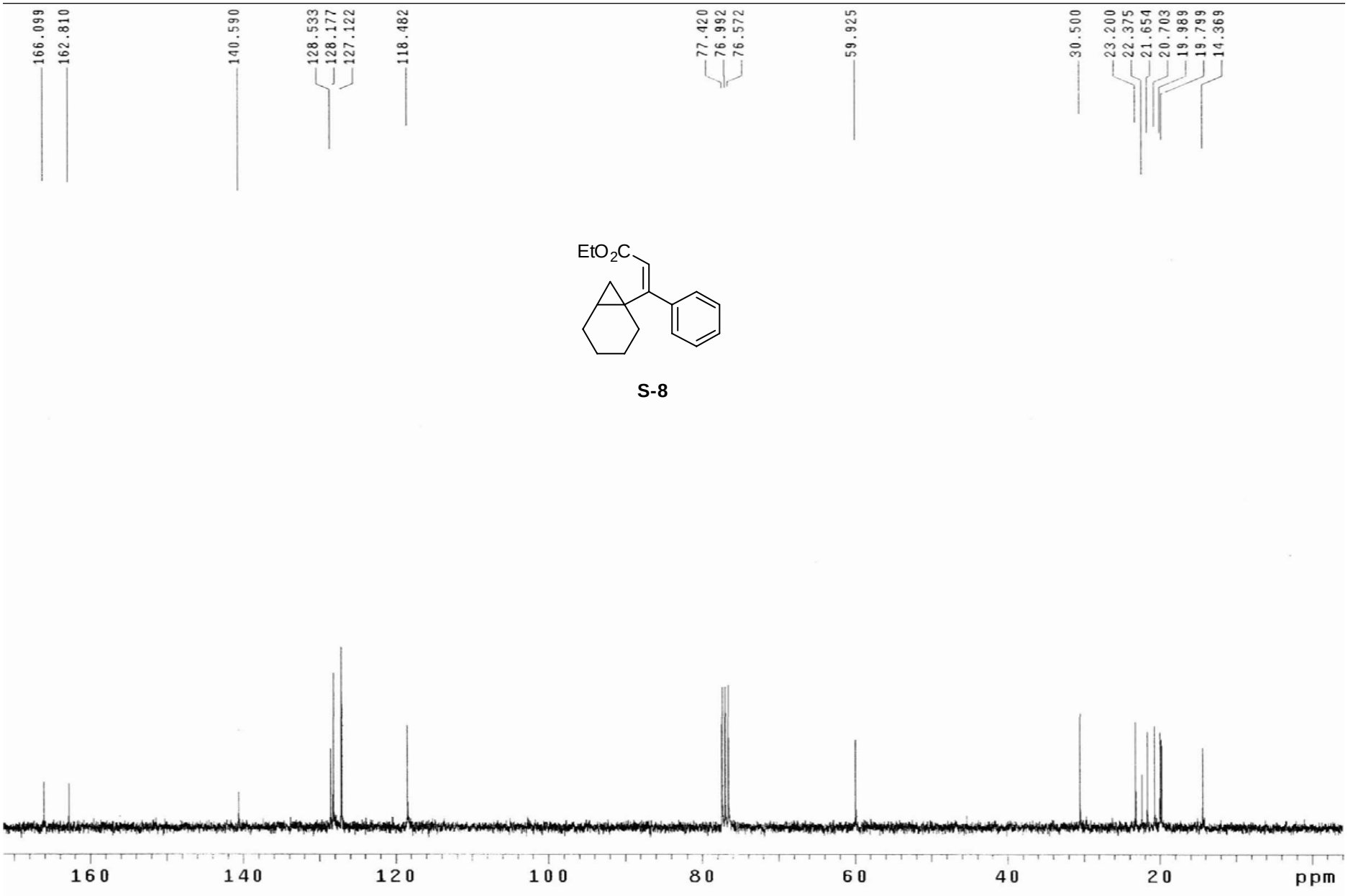

O
S-7
9
8
7
6
5
4
3
2
1
ppm
1.93
3.03
1.00
1.30
3.18
1.91
1.12
2.02
0.83


204.569
137.689
131.593
128.224
128.177
77.428
77.000
76.572
29.010
27.139
22.803
21.646
20.227
19.521
18.911
O
200
180
160
140
120
100
80
60
40
20
ppm

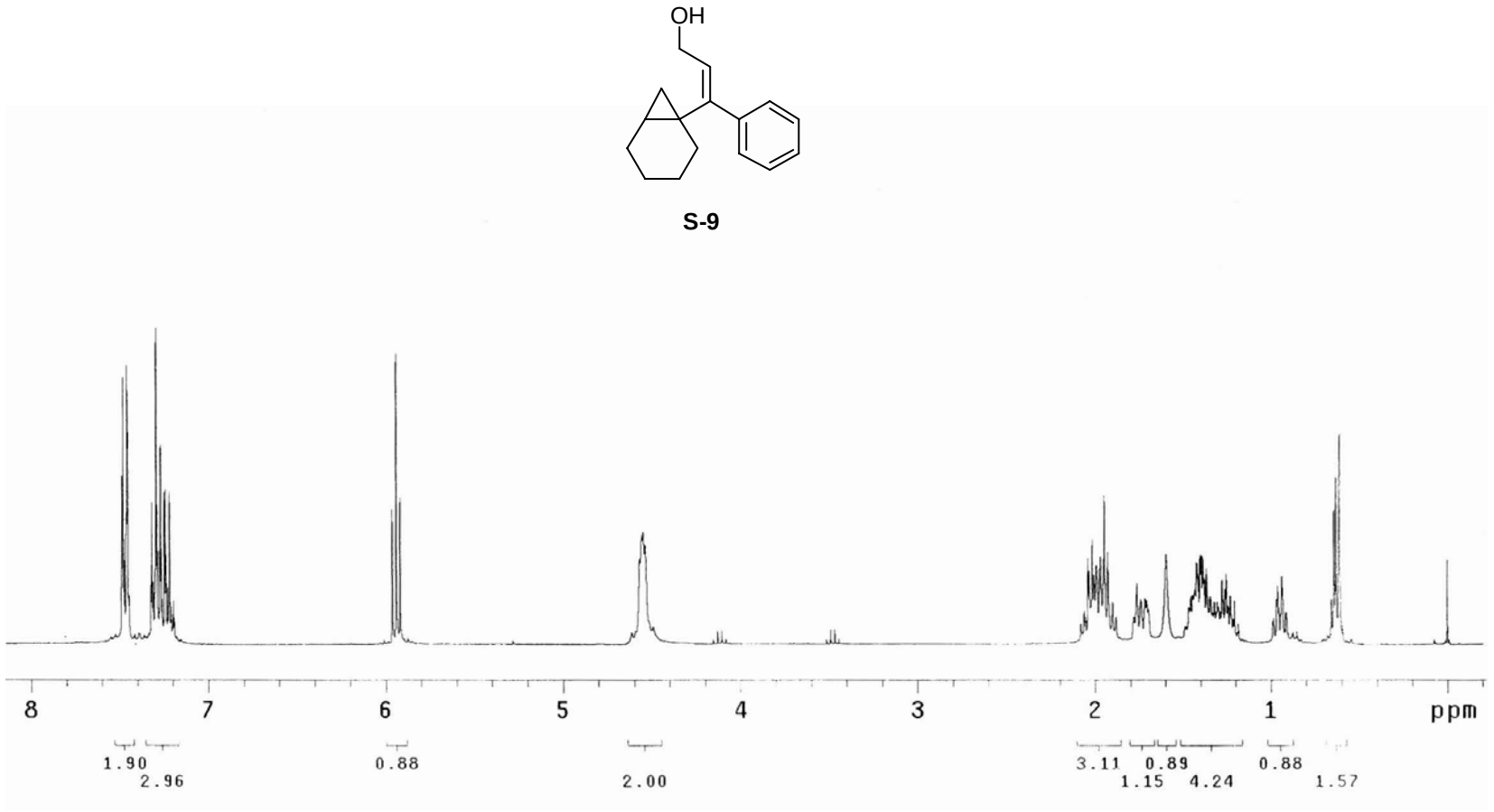
S-7


EtO2C
8
7
6
5
4
3
2
1
ppm
1.94
2.87
0.86
2.00
1.01
2.14
1.12
2.11
3.58
1.43
0.90
1.64

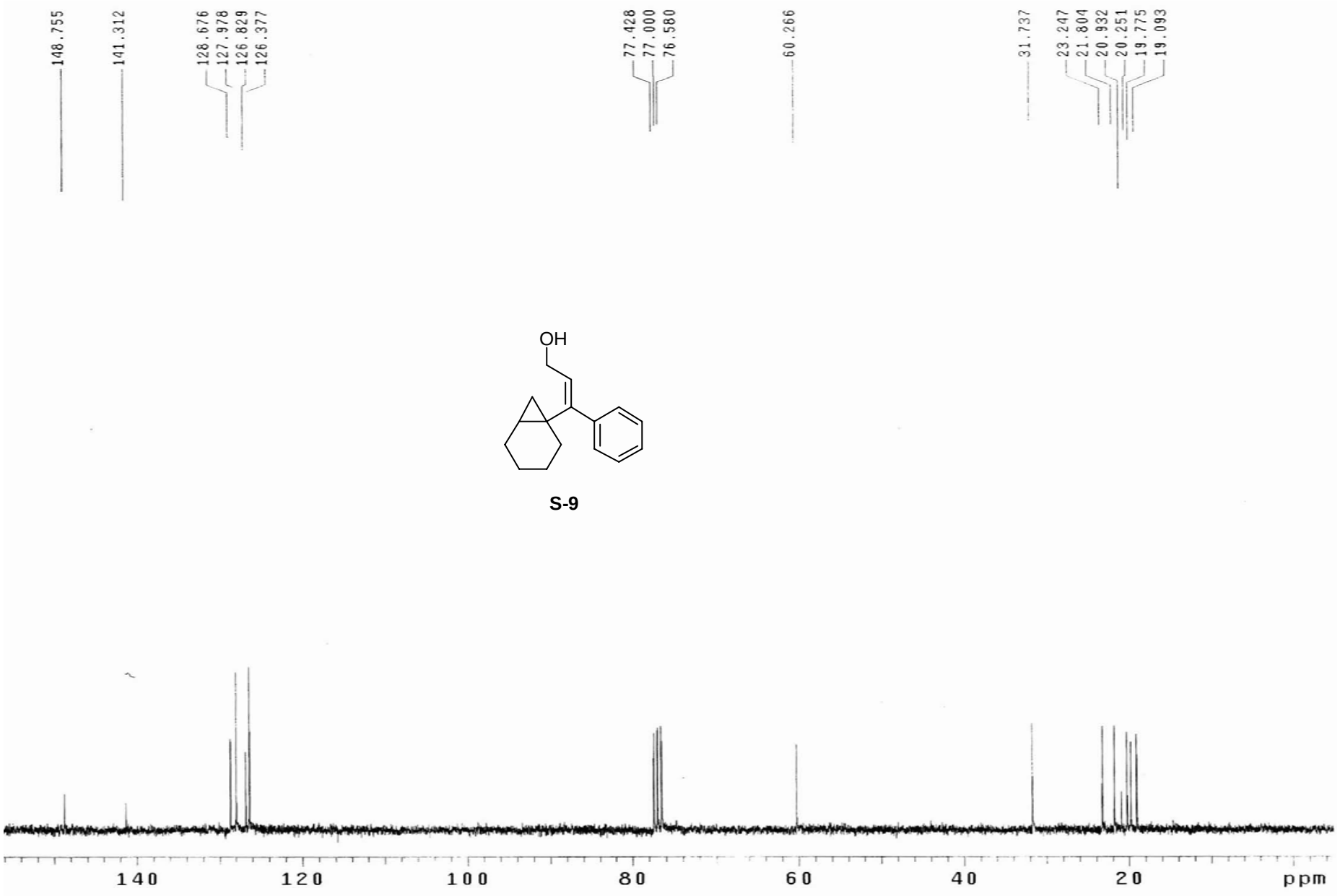
S-8


166.099
162.810
140.590
128.533
128.177
127.122
118.482
77.420
76.992
76.572
59.925
30.500
23.200
22.375
21.654
20.703
19.989
19.799
14.369
EtO2C
160
140
120
100
80
60
40
20
ppm

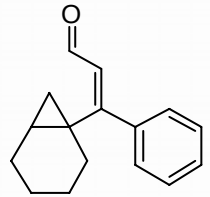
S-8



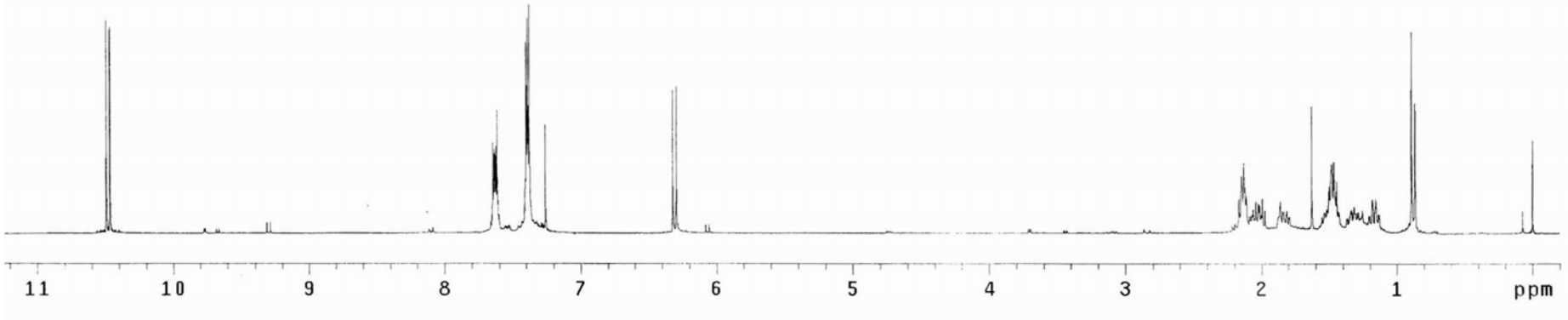
S-9

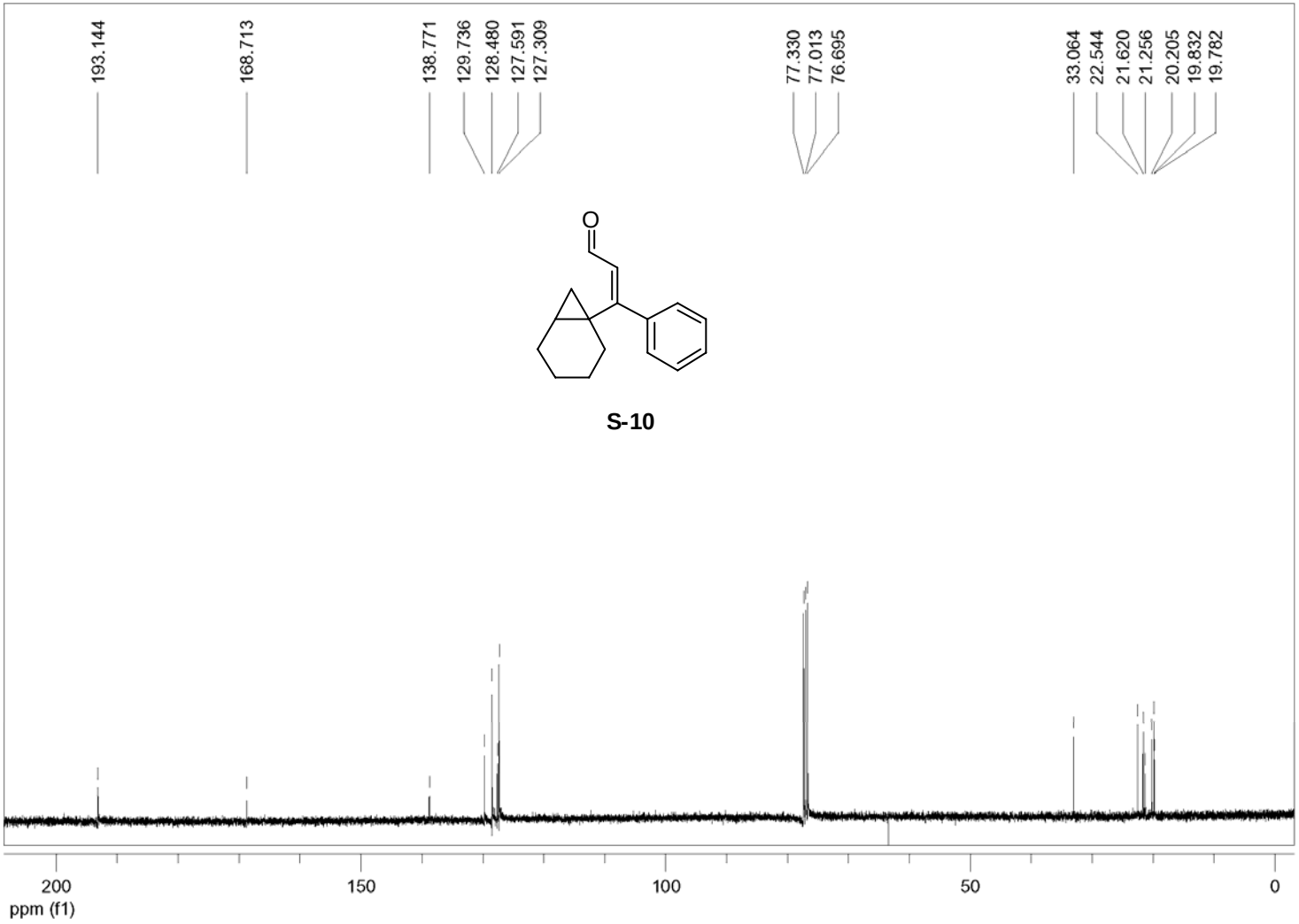

148.755
141.312
128.676
127.978
126.829
126.377
77.428
77.000
76.580
60.266
31.737
23.247
21.804
20.932
20.251
19.775
19.093
OH
140
120
100
80
60
40
20
ppm

S-9

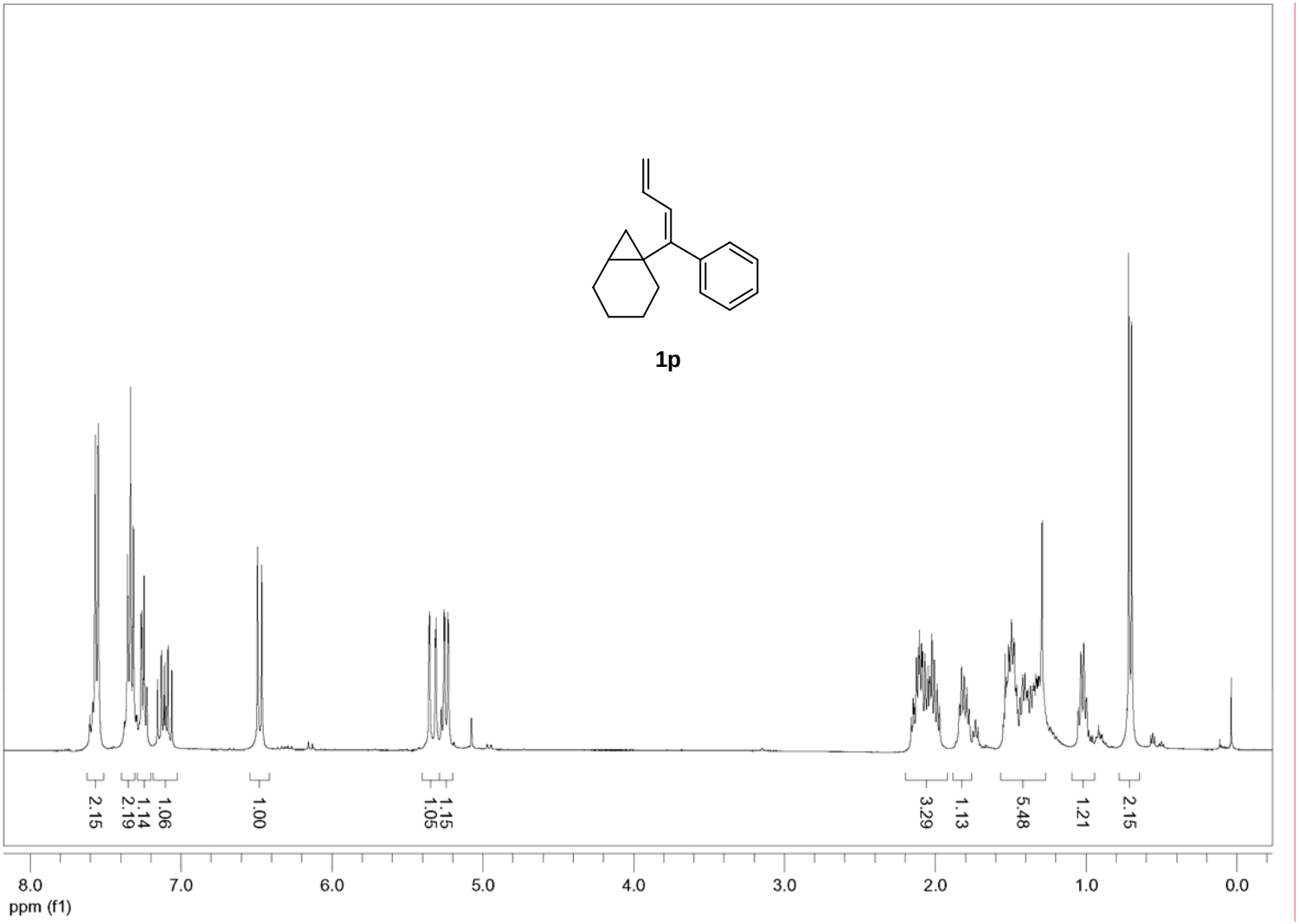


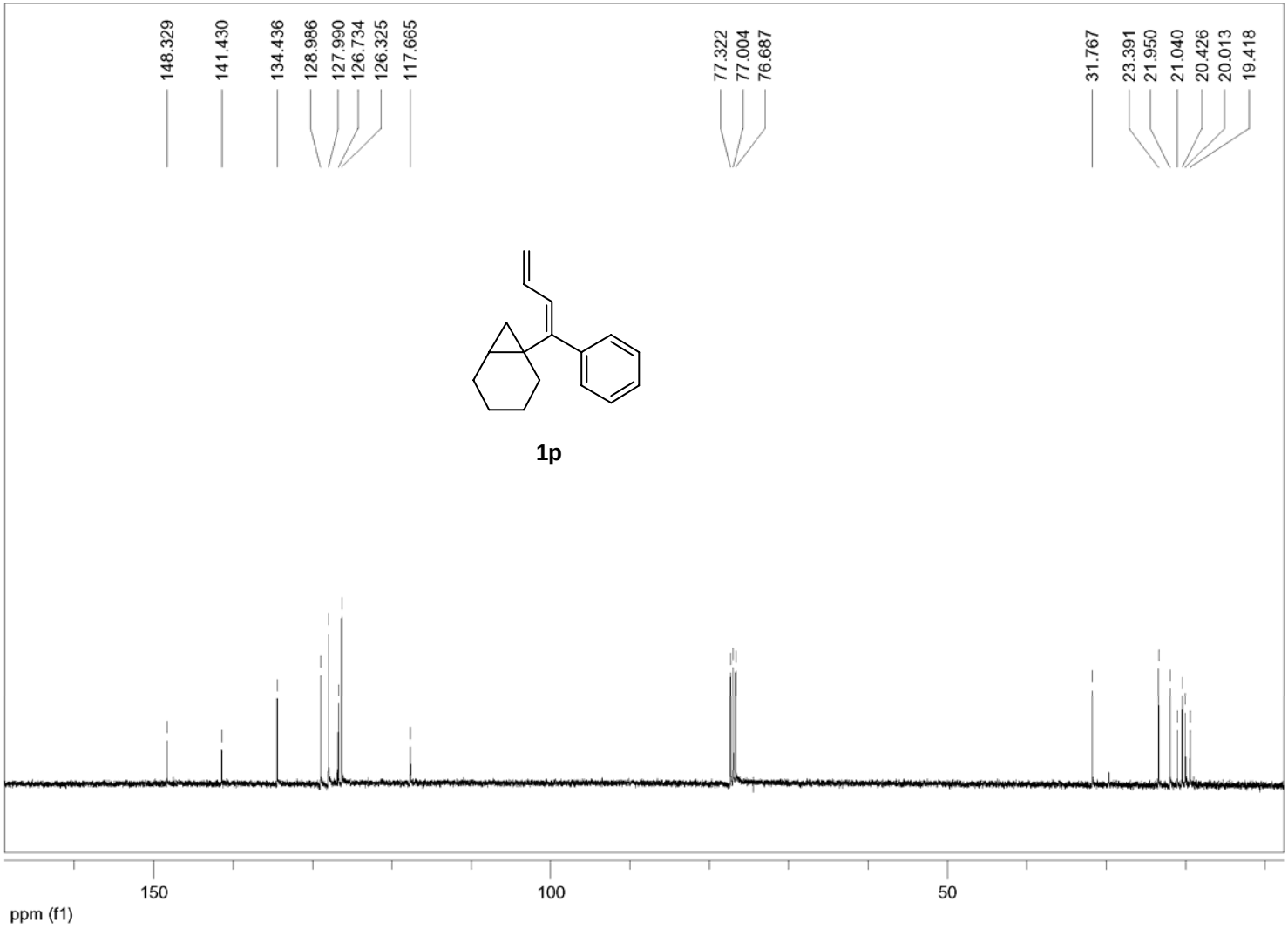
S-10



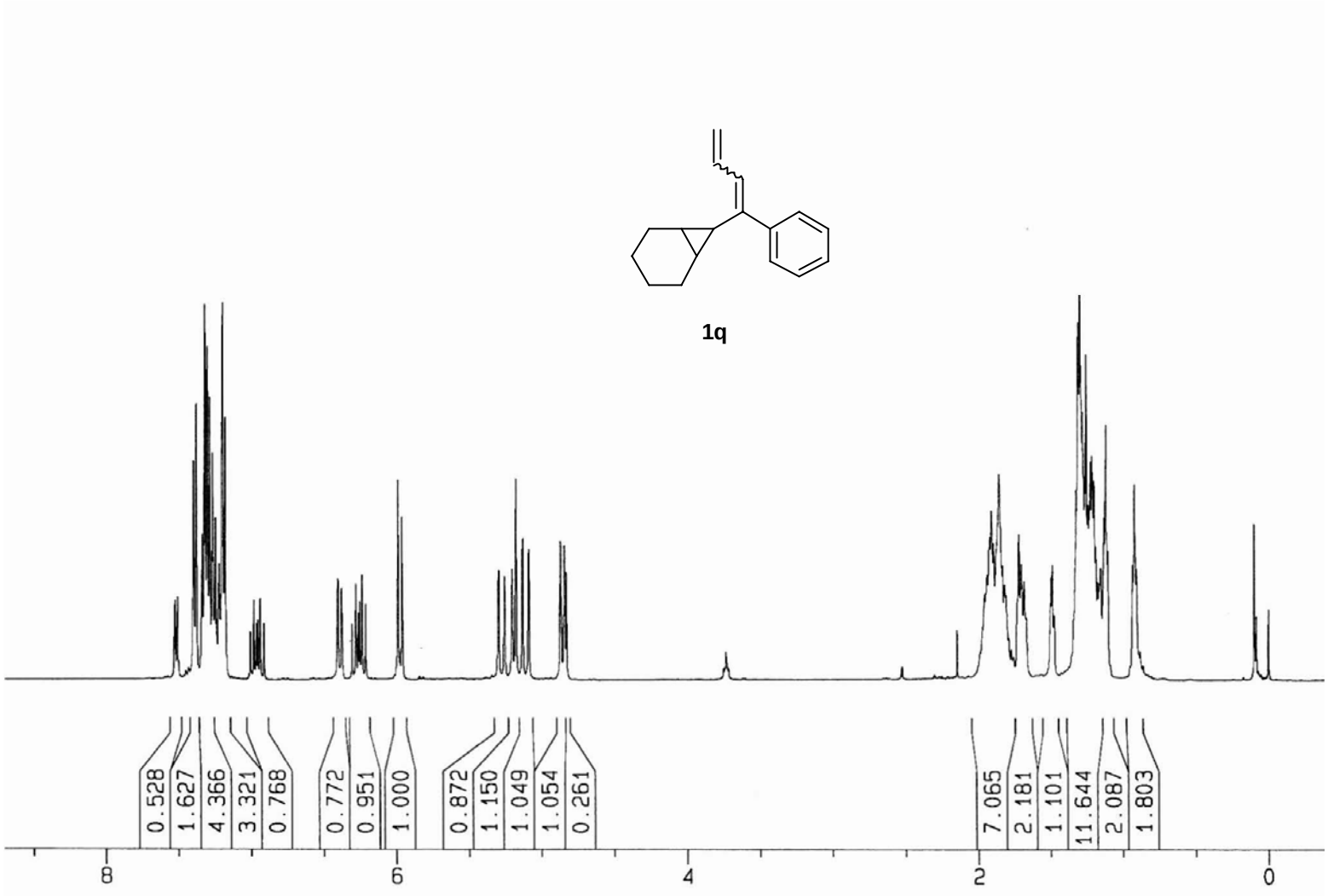

193.144
168.713
138.771
129.736
128.480
127.591
127.309
77.330
77.013
76.695
33.064
22.544
21.620
21.256
20.205
19.832
19.782
O
200
150
100
50
0
ppm (f1)

S-10

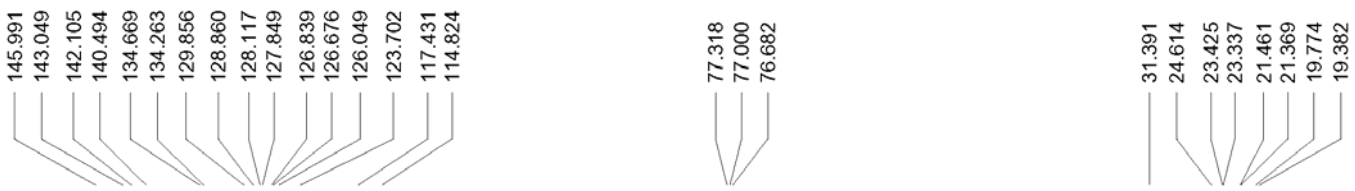

1p
2.15
2.19
1.14
1.06
1.00
1.15
1.05
3.29
1.13
5.48
1.21
2.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

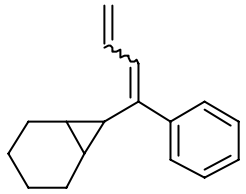

148.329
141.430
134.436
128.986
127.990
126.734
126.325
117.665
77.322
77.004
76.687
31.767
23.391
21.950
21.040
20.426
20.013
19.418
150
100
50
ppm (f1)

1p

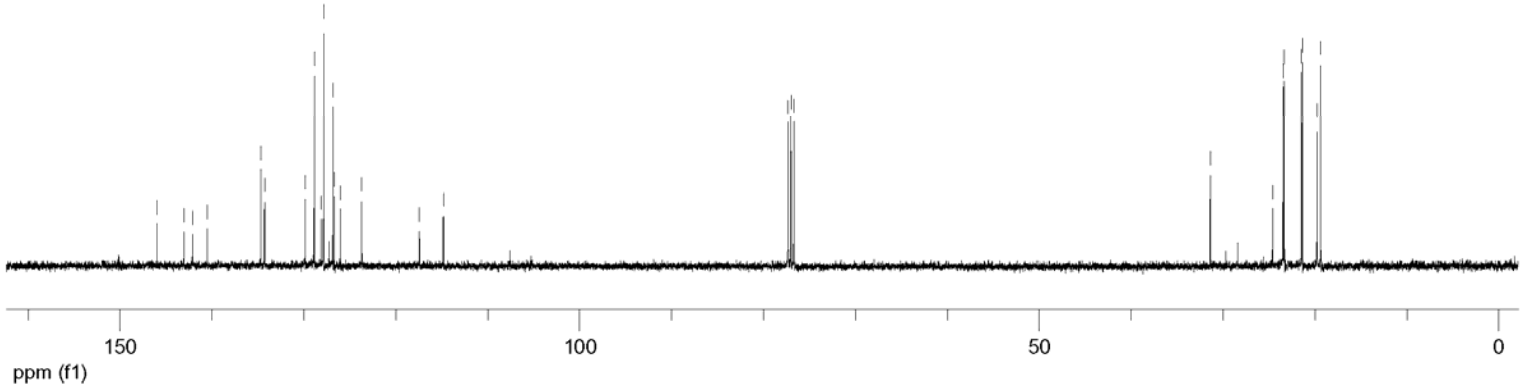

0.528
1.627
4.366
3.321
0.768
0.772
0.951
1.000
0.872
1.150
1.049
1.054
0.261
7.065
2.181
1.101
11.644
2.087
1.803
8
6
4
2
0

1q


145.991
143.049
142.105
140.494
134.669
134.263
129.856
128.860
128.117
127.849
126.839
126.676
126.049
123.702
117.431
114.824
77.318
77.000
76.682
31.391
24.614
23.425
23.337
21.461
21.369
19.774
19.382



1q


150
100
50
0
ppm (f1)