Supporting Information

Ruthenium-catalyzed α-prenylation of ketones using prenol

Raman Vijaya Sankar, Deepsagar Manikpuri and Chidambaram Gunanathan*

School of Chemical Sciences, National Institute of Science Education and Research (NISER), An OCC of Homi Bhabha National Institute, Bhubaneswar-752050, India.

*To whom the correspondence should be addressed. E-mail: gunanathan@niser.ac.in

Index

General Experimental: All catalytic reactions were performed under inert atmosphere using standard Schlenk techniques. All stoichiometric reactions were performed in nitrogen atmosphere MBRAUN glove box. Ru-Macho [Carbonylchlorohydrido{bis[2-(diphenylphosphinomethyl)ethyl]amino}ethyl]amino}ruthenium(II)] (**1**) was purchased from Sigma-Aldrich and stored inside glove box. Chemicals (ketones and Prenol) were purchased from Acros, Sigma-Aldrich, Alfa-aesar, Himedia Chemicals and used without further purification. Dry solvents were prepared according to standard procedures. Infrared (IR) spectra were recorded in Perkin-Elmer FT-IR and Thermo-Nicolet FT-IR spectrophotometers. High-resolution mass spectra (HRMS) were obtained on Bruker micrOTOF-Q II Spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$, $[M]^+$. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded at Bruker AV-700 (^{1}H at 700 MHz, ^{13}C at 175 MHz) and Bruker AV-400 (^{1}H at 400 MHz, ^{13}C at 100.6 MHz). ^{1}H NMR chemical shifts are referenced in parts per million (ppm) with respect to tetramethyl silane (TMS, δ 0.00 ppm) and ^{13}C $\{^1H\}$ NMR chemical shifts are referenced in parts per million (ppm) with respect to $CDCl_3$ (δ 77.160 ppm). Coupling constants are reported in Hertz (Hz).^{1}H NMR spectroscopy abbreviations: s, Singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; td, triplet of doublets; qd, quartets of doublets; ddd, doublets of doublets of doublets; m, multiplet; br, broad. Assignment of spectra was done based on one-dimensional (dept-135) NMR techniques.

GC Method: Gas chromatography data were obtained using a gas chromatograph equipped with a SH-Rtx-1 capillary column (30 m × 250 μm). The instrument was set to an injection volume of 1μL, an inlet split ratio of 10:1, and inlet and detector temperatures of 300 and 330 °C, respectively. The temperature program used for all of the analyses is as follows: 50 °C, 1

min; 12 °C/min to 320 °C, 7 min. Response factor for all of the necessary compounds with respect to standard mesitylene was calculated from the average of three independent GC runs.

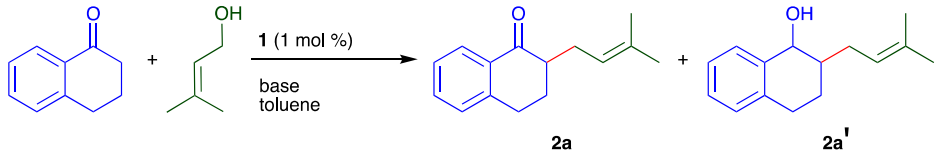
General optimization procedure for α-prenylation of cyclic ketones using prenols:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), base (0.20-0.25 mmol) tetralone (0.5 mmol), prenol (0.75-1 mmol), and toluene (1.5 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 12 h. The completion of the reaction was monitored using GC analysis. After cooling to room temperature, 0.5 mmol of internal standard (mesitylene) was added into the reaction mixture and the conversion of tetralone was calculated using GC analysis. Further the solvent was evaporated, and the reaction was quenched using water (0.5 mL), and extracted by dichloromethane (3 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulted residue was purified by column chromatography over silica gel (100–200 mesh) using hexane/ethyl acetate mixture as eluent. Yields were calculated for isolated pure products.

Initial investigation for catalytic prenylation was tested using tetralone (0.5 mmol) with prenol (3-methyl 2-buten-1-ol, 1 mmol), Ru-Macho catalyst (1 mol %), and KO^{t}Bu (20 mol %) in toluene and the reaction mixture heated at 80 °C for 16 h under nitrogen atmosphere, which resulted in the formation of the desired prenylated ketone product **2a** in 37% and a homoallylic alcohol **2a'** in 10% yield (entry 1, Table S1). Reaction performed with increased base KO^{t}Bu (30 mol %) provided the product **2a** in 54% yield (entry 2, Table S1). When the reaction was performed using 50 mol % base for 12 h, an increase in the formation of product **2a** (79%) was observed (entry 3, Table S1). Next, increasing the reaction temperature to 100 °C resulted in optimal conditions from which 95% yield of **2a** with a minor amount (3%) of **2a'** was obtained.

From this condition, further experiments using decreased amounts of base (30 mol %) and prenol (1.5 equiv.) delivered the products in diminished yields (entries 5,6, Table S1). Employing the milder bases such as K_2CO_3 and Cs_2CO_3 failed to provide the desired reaction (entry 7,8, Table S1). Control experiment carried out without using a catalyst and base KO^{t}Bu (50 mol %) alone resulted in an unidentified complex reaction mixture (entry 9, Table S1).

Table S1. Optimization of reaction condition for *α* -Prenylation of tetralone[a]



entry	base (mol %)	temp (°C)	time (h)	**2a** (%)[b]	**2a'** (%)[b]
1	KO^{t}Bu (20)	80	16	37	10
2	KO^{t}Bu (30)	80	16	54	10
3	KO^{t}Bu (50)	80	12	79	12
4	**KO^{t}Bu (50)**	**100**	12	**95**	**3**
5	KO^{t}Bu (30)	100	12	88	6
6[c]	KO^{t}Bu (30)	100	12	72	16
7	Cs_2CO_3 (30)	100	12	-	-
8	K_2CO_3 (50)	100	12	-	-
9	KO^{t}Bu (50)	100	12	-	-

[a]Reaction conditions: tetralone (0.5 mmol, 1 equiv), prenol (1 mmol, 2 equiv), toluene (2 mL), catalyst 1, and base were heated at an indicated temperature under nitrogen flow. [b]Yields were calculated for pure isolated products after column chromatography. [c]Prenol (0.75 mmol, 1.5 equiv) was used.

General procedure for the α-prenylation of cyclic ketones using prenol:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol, 1 mol %), KO^{t}Bu (0.25 mmol, 50 mol %), tetralone (0.5 mmol), prenol (1 mmol), and toluene (1.5 mL) were added under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 12 h. The completion of the reaction

was monitored using GC analysis. Upon completion, reaction mixture was cooled to room temperature, 0.5 mmol of internal standard (mesitylene) was added into the reaction mixture and the conversion of cyclic ketones was calculated using GC analysis. Further, the solvent was evaporated the reaction was quenched using water (0.5 mL), and extracted by dichloromethane (3 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulted residue was purified by column chromatography over silica gel (100–200 mesh) using hexane/ethyl acetate mixture as eluent. Yields were calculated for isolated pure products.

General procedure for α-prenylation of simple acetophenone derivatives using prenol:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.0025 mmol, 0.5 mol %), NaO^{t}Bu (0.25 mmol, 50 mol %), acetophenone derivatives (0.5 mmol), prenol (1 mmol), and toluene (1.5 mL) were added under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was refluxed at 125 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 8 h. The completion of the reaction was monitored using GC analysis. Upon completion, reaction mixture was cooled to room temperature, 0.5 mmol of internal standard (mesitylene) was added into the reaction mixture and the conversion of acetophenone was calculated using GC analysis. Further, the solvent was evaporated and the reaction was quenched by water (0.5 mL) and extracted with dichloromethane (3 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulted residue was purified by column chromatography over silica gel (100–200 mesh) using hexane/ethyl acetate mixture as eluent. Yields were calculated for isolated pure products.

Experimental procedure for gram-scale synthesis:

A Schlenk flask (50 mL) was equipped with a stir bar, catalyst **1** (0.08 mmol, 1 mol %, 48 mg), KO^{t}Bu (4 mmol, 50 mol %, 448 mg), tetralone (8 mmol, 1.06 g), prenol (16 mmol, 1.62 g), and toluene (20 ml) were added under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 12 h. Upon completion, reaction mixture was cooled to room temperature. Further, the solvent was evaporated the reaction was quenched using water (5 mL), and extracted by dichloromethane (10 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulted residue was purified by column chromatography over silica gel (100–200 mesh) using hexane/ethyl acetate mixture as eluent. Yield was calculated for isolated pure products.

Mechanistic studies

General procedure for control experiment of tetralone with 3-methyl-2-butanal:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol, 1 mol %), KO^{t}Bu (0.25 mmol, 50 mol %), Tetralone (0.5 mmol), 3-methyl-2-butanal (1 mmol) and toluene (1.5 mL) were added under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 12 h. The completion of the reaction was monitored using GC analysis. After cooling to room temperature, 0.5 mmol of internal standard (mesitylene) was added into the reaction mixture and the conversion of tetralone was calculated using GC analysis. Further, the solvent was evaporated the reaction was quenched with water (0.5 mL) and extracted with dichloromethane (3 x 3 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was

purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent. Yields were calculated for isolated pure products.

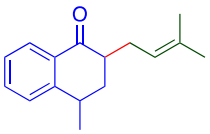
Spectral data of the α-prenylated products:

2-(3-Methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2a): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 102 mg, 95%. IR (DCM): 2927, 1688, 1600, 1455, 1220, 1156, 933, 740 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 1H, ArC*H*), 7.47 (t, *J* = 7.4 Hz, 1H, ArC*H*), 7.33-7.24 (m, 2H, ArC*H*), 5.20 (t, *J* = 6.7 Hz, 1H, Olefinic C*H*), 3.00 (t, *J* = 5.9 Hz, 2H, CH_2), 2.69-2.64 (m, 1H, CH_2), 2.51 (ddd, J_1 = 11.4 Hz, J_2 = 7.9 Hz, J_3 = 4.0 Hz, 1H, CH_2), 2.30-2.19 (m, 2H, CH_2), 1.93-1.85 (m, 1H, C*H*), 1.74 (s, 3H, CH_3), 1.66 (s, 3H, CH_3). ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 200.0, 144.1, 133.5, 133.1, 132.6, 128.7, 127.4, 126.5, 121.8, 48.1, 28.7, 28.1, 28.0, 25.9, 17.9. HRMS (ESI) m/z calcd for $C_{17}H_{22}O$ $(M+H)^+$: 215.1436, found: 215.1480.

5,7-Dimethyl-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2b): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 69 mg, 57%. IR(DCM): 2924, 1683, 1611, 1451, 1377, 1287, 1157, 871 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H, ArC*H*), 7.16 (s, 1H, ArC*H*), 5.18 (t, *J* = 6.8 Hz, 1H, Olefinic C*H*), 2.89 (dt, J_1 = 17.2 Hz, J_2 = 4.4 Hz, 1H, CH_2), 2.73 (ddd, J_1 = 16.5 Hz, J_2 = 10.8 Hz, J_3 = 5.0 Hz, 1H, CH_2), 2.63-2.59 (m, 1H, CH_2), 2.45 (ddd, J_1 = 11.7 Hz, J_2 = 8.1 Hz, J_3 = 4.0 Hz, 1H, CH_2), 2.29 (s, *J* = 23.8 Hz, (2*3= 6H), ArCH_3), 2.20 (qd, J_1 = 9.2 Hz, J_2 = 4.8 Hz, 2H, CH_2), 1.87-1.78 (m, 1H, C*H*), 1.72 (s, 3H, CH_3), 1.63 (s, 3H, CH_3). ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 200.8, 139.6, 136.2, 135.7, 135.7, 133.5, 132.7, 125.4, 122.0, 47.5, 28.1, 27.5, 26.0,

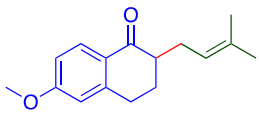
25.3, 21.0, 19.4, 18.0. HRMS (ESI) m/z calcd for $C_{17}H_{22}O$ $(M+H)^+$: 265.1568, found: 265.1572.

4-Methyl-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2c): Purified by



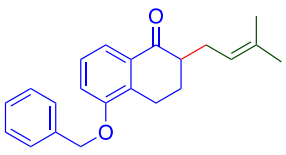
silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 81 mg, 72%. IR (DCM): 2963, 2855, 1683, 1600, 1470, 1377, 1265, 894, 780 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99-7.93 (m, 1H, ArC*H*), 7.41 (qd, J_1 = 7.4 Hz, J_2=1.4 Hz, 1H, ArC*H*), 7.26-7.19 (m, 2H, ArC*H*), 5.13-5.07 (m, 1H, Olefinic C*H*), 3.12-2.97 (m, 1H), 2.69-2.41 (m, 2H), 2.21-1.88 (m, 2H), 1.65 (s, 3H), 1.56 (s, 3H), 1.48 (d, J = 12.2 Hz, 1H), 1.33 (dd, J_1 = 14.2 Hz, J_2 =7.0 Hz, 3H). ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$): δ 200.1, 148.8, 148.2, 133.5, 133.4, 133.3, 131.6, 128.1, 127.5, 127.4, 126.5, 126.4, 126.3, 121.9, 121.8, 48.4, 43.2, 37.7, 34.6, 33.1, 31.5, 28.4, 28.1, 25.9, 21.6, 20.3, 17.9. HRMS (ESI) m/z calcd for $C_{16}H_{20}O$ $(M+H)^+$: 251.1389, found: 251.1406.

6-Methoxy-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2d): Purified by



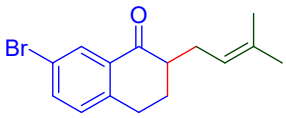
silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 99 mg, 81% IR (DCM): 2927, 16767, 1600, 1495, 1352, 1251, 1154, 1029, 856, 830 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.7 Hz, 1H, ArC*H*), 6.72 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1H, ArC*H*), 6.59 (s, J = 2.0 Hz, 1H, ArC*H*), 5.11-5.07 (m, 1H, Olefinic C*H*), 3.75 (s, 3H), 2.86-2.83 (m, 2H), 2.59-2.52 (m, 1H), 2.39-2.31 (m, 1H), 2.17-2.06 (m, 2H), 1.79-1.69 (m, 1H), 1.63 (s, 3H), 1.55 (s, 3H). ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$): δ 198.8, 163.4, 146.6, 133.4, 129.9, 126.2, 122.0, 113.1, 112.4, 55.4, 47.7, 29.0, 28.2, 28.0, 25.9, 17.9. HRMS (ESI) m/z calcd for $C_{16}H_{20}O$ $(M+H)^+$: 251.1389, found: 251.1406.

5-(Benzyloxy)-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2e): Purified



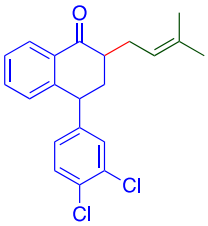
by silica-gel column chromatography using ethyl acetate/hexane

(1:99) mixture as eluent. Colorless liquid. Yield: 112 mg, 70%. IR (DCM): 2926, 1684, 1582, 1454, 1377, 1265, 1189, 1041, 905, 795 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.8 Hz, 1H, ArC*H*), 7.45-7.32 (m, 5H, ArC*H*), 7.24 (t, J = 7.9 Hz, 1H, ArC*H*), 7.06 (d, J = 8.0 Hz, 1H, ArC*H*), 5.20-5.16 (m, 1H, Olefinic C*H*), 5.10 (s, 2H), 3.18-3.11 (m, 1H), 2.84-2.75 (m, 1H), 2.64-2.45 (m, 2H), 2.25-2.18 (m, 2H), 1.87-1.80 (m, 1H), 1.72 (s, 3H), 1.63 (s, 3H). ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$): δ 200.4, 156.0, 137.0, 133.9, 133.6, 128.7, 128.1, 127.3, 126.9, 121.9, 119.5, 115.5, 70.4, 47.7, 28.1, 27.3, 26.0, 22.3, 18.0. HRMS (ESI) m/z calcd for $C_{22}H_{25}O_2$ $(M+H)^+$:321.1855, found: 321.1859.



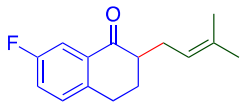
7-Bromo-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2f): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 113 mg, 77%. IR (DCM): 2927, 1687, 1589, 1473, 1404, 1212, 850,772 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 2.3 Hz, 1H, ArC*H*), 7.47 (dd, J_1 = 8.2 Hz, J_2 = 2.2 Hz, 1H, ArC*H*), 7.04 (d, J = 8.2 Hz, 1H, ArC*H*), 5.10-5.05 (m, 1H, Olefinic C*H*), 2.88-2.81 (m, 2H), 2.58-2.53 (m, 1H), 2.43-2.36 (m, 1H), 2.17-2.10 (m, 2H), 1.80-1.72 (m, 1H), 1.64 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.7, 142.9, 135.9, 134.2, 133.9, 130.6, 130.3, 121.5, 120.6, 47.9, 28.2, 28.0, 27.7, 25.9, 18. HRMS (ESI) m/z calcd for $C_{15}H_{17}OBr$ $(M+H)^+$:315.0368, found: 315.0355.

4-(3,4-Dichlorophenyl)-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2g): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 124 mg, 69%. IR (DCM): 2927, 1700, 1491, 1437, 1271, 1159, 892 cm^{-1} .^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J_1 = 11.7, J_2 = 7.9 Hz, 1H, ArC*H*), 7.51-7.14 (m, 4H, ArC*H*), 7.06-7.04 (m, 1H, ArC*H*), 6.88-6.78 (m, 1H, ArC*H*), 5.18-5.03 (m, 1H, Olefinic C*H*), 4.38-4.19 (m, 1H), 2.80-2.48 (m, 2H), 2.38-2.20 (m, 2H), 1.96 (q, J = 13.2 Hz, 1H), 1.70-1.62 (m,



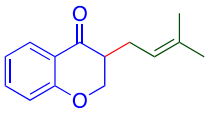
6H). ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 199.4, 199.0, 145.8, 145.1, 144.3, 143.9, 134.1, 134.1, 133.9, 133.4, 133.0, 132.9, 132.8, 132.8, 131.2, 130.9, 130.9, 130.9, 130.6, 130.5, 129.7, 129.0, 128.3, 128.0, 127.9, 127.8, 127.6, 127.3, 121.5, 121.1, 48.4, 46.0, 43.4, 42.5, 38.2, 35.9, 28.2, 28.0, 26.0, 26.0, 18.1, 18.0. HRMS (ESI) m/z calcd for $C_{21}H_{20}Cl_2O$ $(M+H)^+$: 381.0789, found: 381.0803.

7-Fluoro-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2h): Purified by



silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 92 mg, 79% . IR (DCM): 2928, 1687, 1588, 1435, 1352, 1271, 1160, 892, 734 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, J_1 = 9.3 Hz, J_2 = 2.6 Hz, 1H, ArC*H*), 7.11 (ddd, J_1 = 19.7 Hz, J_2 = 8.2 Hz, J_3 = 4.0 Hz, 2H, ArC*H*), 5.10-5.07 (m, 1H, Olefinic C*H*), 2.87 (dd, J_1 = 9.7 Hz, J_2 = 4.5 Hz, 2H), 2.58-2.53 (m, 1H), 2.43-2.38 (m, 1H), 2.19-2.11 (m, 2H), 1.82-1.71 (m, 1H), 1.64 (s, 3H), 1.56 (s, 3H). ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 199.1, 199.1, 162.8, 160.3, 139.9, 139.9, 134.2, 134.2, 133.8, 130.6, 130.5, 121.6, 120.6, 120.4, 113.4, 113.2, 47.8, 28.1, 28.0, 25.9, 18.0. HRMS (ESI) m/z calcd for $C_{15}H_{17}FO$ $(M+H)^+$: 233.1348, found: 233.1336.

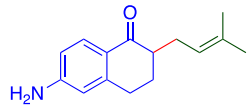
3-(3-Methylbut-2-en-1-yl)chroman-4-one (2i): Purified by silica-gel column



chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 30 mg, 28%. IR (DCM): 2924, 1695, 1605, 1479, 1269, 1125, 1014, 827, 780 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 1H, ArC*H*), 7.42 (td, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H, ArC*H*), 6.99-6.90 (m, 2H, ArC*H*), 5.11 (td, J_1 = 7.4 Hz, J_2 = 1.1 Hz, 1H, Olefinic C*H*), 4.43 (dd, J_1 = 11.4 Hz, J_2 = 4.5 Hz, 1H, CH_2), 4.21 (dd, J_1 = 11.4 Hz, J_2 = 8.7 Hz, 1H, CH_2), 2.63 (tt, J_1 = 9.0 Hz, J_2 = 4.5 Hz, 1H, CH_2), 2.51-2.45 (m, 1H, CH_2), 2.23 (dt, J_1 = 14.8 Hz, J_2 = 8.9 Hz, 1H, C*H*), 1.68 (s, 3H, CH_3),

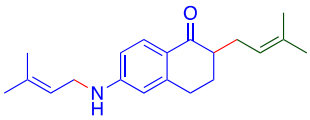
1.58 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.4, 161.7, 135.8, 135.1, 127.5, 121.4, 120.7, 120.2, 117.8, 70.1, 46.4, 25.9, 25.1, 17.9. HRMS (ESI) m/z calcd for $C_{14}H_{16}O_2$ $(M+H)^+$: 239.1058, found: 239.1043.

6-Amino-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2j): Purified by



silica-gel column chromatography using ethyl acetate/hexane (5:95) mixture as eluent. Colorless liquid. Yield: 42 mg, 36%. IR (DCM): 3350, 3232, 2923, 2855, 1633,1582, 1362, 1274, 893 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, J_1 = 8.4 Hz, J_2 = 3.4 Hz, 1H, ArC*H*), 6.48 (dd, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H, ArC*H*), 6.35 (d, J = 2.1 Hz, 1H, ArC*H*), 5.11 (td, J_1 = 7.4 Hz, J_2 = 1.4 Hz, 1H, Olefinic C*H*), 4.06 (s, 2H, NH_2), 2.78 (dd, J_1 = 7.4 Hz, J_2 = 4.9 Hz, 2H, CH_2), 2.58 (dt, J_1 = 13.2 Hz, J_2 = 6.1 Hz, 1H, CH_2), 2.35 (ddt, J_1 = 10.9 Hz, J_2 = 8.8 Hz, J_3 = 4.4 Hz, 1H, CH_2), 2.19-2.05 (m, 2H, CH_2), 1.79-1.71 (m, 1H, C*H*), 1.66 (s, 3H, CH_3), 1.57 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.6, 151.2, 146.8, 133.3, 130.1, 124.0, 122.3, 113.3, 112.5, 47.7, 28.9, 28.4, 28.0, 26.0, 18.0. HRMS (ESI) m/z calcd for $C_{15}H_{19}NO$ $(M+H)^+$: 252.1364, found: 252.1375.

2-(3-Methylbut-2-en-1-yl)-6-((3-methylbut-2-en-1-yl)amino)-3,4-dihydronaphthalen-1(2H)-one (2j'): Purified by silica-gel column chromatography using ethyl acetate/hexane



(2:98) mixture as eluent. Colorless liquid. Yield: 64 mg, 46%. IR (DCM): 3438, 2924, 1652, 1597, 1354, 1273, 1229, 1126, 759 cm^{-1} .^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.7 Hz, 1H, ArC*H*), 6.43-6.41 (m, 1H, ArC*H*), 6.24 (s, 1H, ArC*H*), 5.26-5.23 (m, 1H, Olefinic C*H*), 5.14-5.10 (m, 1H, Olefinic C*H*), 4.26 (s, 1H, N*H*), 3.68 (d, J = 6.8 Hz, 2H, CH_2), 2.80 (t, J = 6.1 Hz, 2H, CH_2), 2.60-2.55 (m, 1H, CH_2), 2.35 (dt, J_1 = 9.9 Hz, J_2 = 4.9 Hz, 1H, C*H*), 2.19-2.06 (m, 2H, CH_2), 1.76-1.73 (m, 1H, C*H*), 1.67 (d, J = 17.0 Hz, 9H, CH_3), 1.57 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.4, 152.0, 146.7, 136.8, 133.2, 129.8, 122.9, 122.4, 120.5, 111.7, 109.7, 47.5, 41.4, 29.1, 28.4, 28.0, 26.0, 25.8, 18.1, 18.0. HRMS (ESI) m/z calcd for $C_{20}H_{27N}O$ $(M+H)^+$: 320.1990, found: 320.2000.

2-(3-Methylbut-2-en-1-yl)-2,3-dihydro-1H-inden-1-one (2k): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 80 mg, 80%. IR (DCM): 2926, 1699, 1608, 1436, 1267, 1092, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 1H, ArC*H*), 7.60 (t, *J* = 7.4 Hz, 1H, ArC*H*), 7.47 (d, *J* = 7.6 Hz, 1H, ArC*H*), 7.38 (t, *J* = 7.4 Hz, 1H, ArC*H*), 5.14 (t, *J* = 6.7 Hz, 1H, Olefinic C*H*), 3.28 (dd, J_1 = 17.3 Hz, J_2 = 7.7 Hz, 1H), 2.85-2.61 (m, 3H, CH_2 & C*H*), 2.27 (dt, J_1 = 14.9 Hz, J_2 = 7.7 Hz, 1H, C*H*), 1.68 (d, *J* = 19.2 Hz, 6H, CH_3). ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$): 208.8, 154.0, 136.9, 134.8, 134.7, 134.0, 127.4, 126.7, 124.0, 121.1, 47.7, 32.3, 29.7, 25.9, 18.1. HRMS (ESI) m/z calcd for $C_{14}H_{16}O$ $(M+H)^+$: 223.1098, found: 223.1103

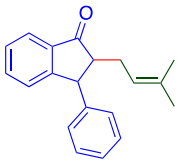
5,6-Dimethoxy-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1H-inden-1-one (2l):

Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 120 mg, 93%. IR (DCM): 3438, 1700, 1576, 1507, 1456, 1387, 1312, 778 cm^{-1} .^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 1H, ArC*H*), 6.90 (s, 1H, ArC*H*), 5.13 (t, *J* = 6.7 Hz, 1H, Olefinic C*H*), 3.96 (d, *J* = 22.3 Hz, 6H, CH_2), 3.19 (dd, J_1 = 17.6 Hz, J_2 = 8.1 Hz, 1H, CH_2), 2.76-2.73 (m, 2H, CH_2), 2.62 (t, *J* = 7.1 Hz, 1H, CH_2), 2.27 (dd, J_1 = 14.8 Hz, J_2 = 7.6 Hz, 1H, C*H*), 1.69 (d, *J* = 18.1 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.3, 155.4, 149.3, 149.2, 133.7, 129.5, 121.1, 107.4, 104.2, 56.2, 56.0, 47.7, 31.9, 29.8, 25.8, 17.9. HRMS (ESI) m/z calcd for $C_{16}H_{20}O_3$ $(M+H)^+$: 260.1412, found: 260.1430.

6-(3-Methylbut-2-en-1-yl)-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-one (2m): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 91 mg, 75%.IR (DCM): 2913, 1699, 1471, 1383, 1037, 940, 869, 735 cm^{-1} .^1H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 1H, ArC*H*),

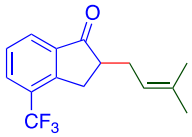
6.75 (s, 1H, ArC*H*), 6.01 (s, 2H, ArC*H*), 5.04 (t, J = 7.3 Hz, 1H, Olefinic C*H*), 3.11-3.05 (m, 1H, CH_2), 2.69-2.60 (m, 2H, CH_2), 2.52 (dt, J_1 = 13.6, J_2 = 6.3 Hz, 1H, CH_2), 2.16 (dt, J_1 = 15.1 Hz, J_2 = 7.8 Hz, 1H, C*H*), 1.63 (s, 3H, CH_3), 1.58 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.7, 154.3, 151.5, 148.3, 134.0, 131.4, 121.1, 105.8, 102.5, 102.2, 48.1, 32.2, 29.9, 25.9, 18.0. HRMS (ESI) m/z calcd for $C_{15}H_{16}O_3$ $(M+H)^+$: 267.1018, found: 267.0992.

2-(3-Methylbut-2-en-1-yl)-3-phenyl-2,3-dihydro-1H-inden-1-one (2n):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as an eluent. Colorless liquid. Yield: 95 mg, 69%. IR (DCM): 3478, 2926, 2811, 1735, 1694, 1472, 1376, 1286, 1094, 744 cm^{-1} .^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.6 Hz, 1H, ArC*H*), 7.49-7.45 (m, 1H, ArC*H*), 7.33 (t, J = 7.4 Hz, 1H, ArC*H*), 7.24-7.21 (m, 2H, ArC*H*), 7.18-7.15 (m, 1H, ArC*H*), 7.11 (d, J = 7.7 Hz, 1H, ArC*H*), 7.03-7.00 (m, 2H, ArC*H*), 4.99 (t, J = 7.4 Hz, 1H, Olefinic C*H*), 4.11 (d, J = 4.5 Hz, 1H, C*H*), 2.66 (dt, J_1 = 7.5 Hz, J_1 = 4.6 Hz, 1H, CH_2), 2.48 (ddt, J_1 = 30.3 Hz, J_2 = 14.8 Hz, J_3 = 7.4 Hz, 2H, C*H*), 1.60 (s, 3H, CH_3), 1.57 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.3, 156.7, 143.3, 136.2, 134.8, 133.8, 128.5, 127.9, 127.6, 126.6, 126.5, 123.1, 120.5, 58.0, 50.1, 28.0, 25.5, 17.8. HRMS (ESI) m/z calcd for $C_{20}H_{20}O$ $(M+H)^+$: 299.1411, found: 299.1420.

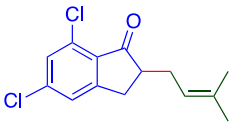
2-(3-Methylbut-2-en-1-yl)-4-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one (2o): Purified



by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as an eluent. Colorless liquid. Yield: 68 mg, 51%. IR (DCM): 3445, 2973, 17212, 1699, 1486, 1377, 1163, 1059, 811, 708 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.7 Hz, 1H, ArC*H*), 7.83 (d, J = 7.6 Hz, 1H, ArC*H*), 7.51-7.47 (m, 1H, ArC*H*), 5.09 (t, J = 7.3 Hz, 1H, Olefinic C*H*), 3.44 (dd, J_1 = 18.1 Hz, J_2 = 8.1 Hz, 1H, CH_2), 2.94 (dd,

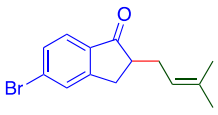
J_1 = 18.1 Hz, J_2 = 3.6 Hz, 1H, CH_2), 2.76 (tt, J_1 = 8.5 Hz, J_2 = 4.2 Hz, 1H, CH_2), 2.64-2.57 (m, 1H, CH_2), 2.26 (dt, J_1 = 15.0 Hz, J_2 = 7.7 Hz, 1H, CH), 1.67 (s, 3H, CH_3), 1.63 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.3, 151.3, 138.4, 134.7, 131.3, 131.3, 127.8, 127.5, 120.4, 47.3, 31.0, 29.6, 25.9, 18.0. HRMS (ESI) m/z calcd for $C_{15}H_{15}F_3O$ $(M+H)^+$: 291.0987, found: 291.0967.

5,7-Dichloro-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1*H*-inden-1-one (2p): Purified by



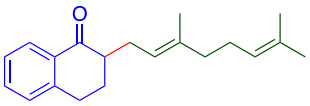
silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 41 mg, 31%. IR (DCM): 2942, 1654, 1635, 1457, 1036, 875, 737 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.25 (m, 2H, ArCH), 5.04- 4.99 (m, 1H, Olefinic CH), 3.16 -3.09 (m, 1H, CH_2), 2.55 -2.48 (m, 2H, CH_2), 2.24 -2.16 (m, 1H, CH), 1.62 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.1, 157.2, 141.0, 134.6, 132.8, 131.5, 129.3, 125.4, 120.5, 48.4, 31.5, 29.7, 25.9, 18.0. HRMS (ESI) m/z calcd for $C_{14}H_{14}Cl_2O$ $(M+H)^+$: 269.0500, found: 269.0521.

5-Bromo-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1H-inden-1-one (2q):



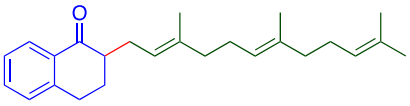
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 99 mg, 71%. IR (DCM): 2923, 1716, 1699, 1575, 1432, 1316, 1199,1057,868 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 11.9 Hz, 2H, ArCH), 7.46-7.44 (m, 1H, ArCH), 5.03 (t, J = 7.1 Hz, 1H, Olefinic CH), 3.19 (dd, J_1 = 17.3 Hz, J_2 = 7.8 Hz, 1H, CH_2), 2.77-2.64 (m, 2H, CH_2), 2.56-2.50 (m, 1H, CH_2), 2.24-2.16 (m, 1H, CH), 1.63 (s, 3H, CH_3), 1.58 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.5, 155.6, 135.8, 134.4, 131.0, 130.1, 130.0, 125.23, 120.6, 47.7, 31.9, 29.6, 25.9, 18.1. HRMS (ESI) m/z calcd for $C_{14}H_{15}BrO$ $(M+H)^+$: 301.0212, found: 301.0198.

(*E*)-2-(3,7-Dimethylocta-2,6-dien-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2r): Purified



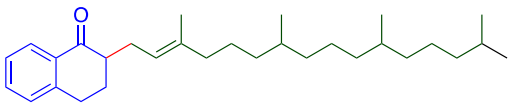
by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 134 mg, 95%. IR (DCM): 2925, 1682, 1456, 1282, 1220, 74 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, J_1 = 7.8 Hz, J_2 = 0.8 Hz, 1H, ArC*H*), 7.38 (dd, J_1 = 7.5 Hz, J_2 = 1.4 Hz, 1H, ArC*H*), 7.25-7.15 (m, 2H, ArC*H*), 5.14-4.99 (m, 2H, Olefinic C*H*), 2.91 (dd, J_1 = 7.5 Hz, J_2 = 4.7 Hz, 2H, CH_2), 2.63-2.58 (m, 1H, CH_2), 2.46-2.40 (m, 1H, CH_2), 2.22-2.13 (m, 2H, CH_2), 2.03-1.94 (m, 4H, CH_2), 1.78 (ddt, J_1 = 13.3 Hz, J_2 = 11.5 Hz, J_3 = 7.6 Hz, 1H, C*H*), 1.60-1.53 (m, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 144.2, 144.2, 137.3, 137.2, 133.2, 132.7, 131.7, 131.4, 128.8, 128.7, 127.5, 126.6, 124.4, 124.3, 122.6, 121.9, 48.2, 48.1, 39.9, 32.1, 29.8, 28.8, 28.2, 28.0, 28.0, 27.9, 26.7, 26.6, 25.8, 23.6, 17.8, 16.2. HRMS (ESI) m/z calcd for $C_{20}H_{26}O$ $(M+H)^+$: 283.2058, found: 283.2056.

2-((2*E*,6*E*)-3,7,11-Trimethyldodeca-2,6,10-trien-1-yl)-3,4-dihydronaphthalen-1(2H)-one



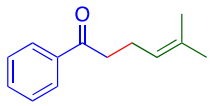
(2s): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 152 mg, 87%. IR (DCM): 2925, 1700, 1600, 1454, 1375, 1220, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.8 Hz, 1H, ArC*H*), 7.37 (td, J_1 = 7.4 Hz, J_2 = 1.3 Hz, 1H, ArC*H*), 7.22 (t, J = 7.5 Hz, 1H, ArC*H*), 7.15 (d, J = 7.7 Hz, 1H, ArC*H*), 5.13-5.00 (m, 3H, Olefinic C*H*), 2.90 (dd, J_1 = 7.2 Hz, J_2 = 4.5 Hz, 2H, CH_2), 2.59 (td, J_1 = 9.9 Hz, J_2 = 4.5 Hz, 1H, CH_2), 2.44-2.40 (m, 1H, CH_2), 2.20-2.12 (m, 2H, CH_2), 2.04-1.94 (m, 7H, CH_2), 1.89 (q, J = 7.5 Hz, 1H, CH_2), 1.81-1.76 (m, 1H, C*H*), 1.61-1.52 (m, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.0, 144.2, 137.2, 137.2, 135.1, 133.2, 132.7, 131.6, 131.3, 128.7, 127.5, 126.6, 125.1, 124.4, 124.2, 121.9, 121.8, 48.1, 40.2, 39.9, 39.8, 32.1, 28.8, 28.7, 28.0,

28.0, 28.0, 26.8, 26.7, 26.6, 26.5, 25.8, 25.8, 23.6, 23.5, 17.8, 17.7, 16.3, 16.2, 16.1.HRMS (ESI) m/z calcd for $C_{25}H_{35}O$ $(M+H)^+$:351.2688, found: 351.2709.



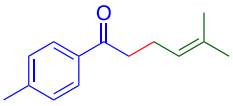
(*E*)-2-(3,7,11,15-Tetramethylhexadec-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (2t): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 202 mg, 95% . IR (DCM): 2925, 1686.92, 1455, 1282, 1219, 742 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.8 Hz, 1H, ArC*H*), 7.38 (t, *J* = 7.4 Hz, 1H, ArC*H*), 7.21 (q, *J* = 6.9 Hz, 1H, ArC*H*), 7.16 (d, *J* = 7.6 Hz, 1H, ArC*H*), 5.12 (t, *J* = 7.2 Hz, 1H, Olefinic C*H*), 2.91 (dd, J_1 = 7.5 Hz, J_2 = 4.7 Hz, 2H, CH_2), 2.60 (dt, J_1 = 14.3 Hz, J_2 = 5.4 Hz, 1H, CH_2), 2.43 (ddd, J_1 = 11.8 Hz, J_2 = 8.3 Hz, J_3 = 3.9 Hz, 1H, CH_2), 2.17 (ddd, J_1 = 19.9 Hz, J_2 = 11.2 Hz, J_3 = 5.7 Hz, 2H, CH_2), 1.91 (t, *J* = 7.4 Hz, 2H, CH_2), 1.82-1.76 (m, 1H, CH_2), 1.56 (s, 3H, CH_2), 1.46 (dt, J_1 = 13.2 Hz, J_2 = 6.6 Hz, 1H, CH_2), 1.33-1.25 (m, 4H, CH_2), 1.20 (ddd, J_1 = 13.1 Hz, J_2 = 9.8 Hz, J_3 = 4.2 Hz, 7H, CH_2), 1.10-1.06 (m, 2H, CH_2), 1.02-0.95 (m, 4H, CH_2), 0.79 (d, *J* = 14.1 Hz, 13H, C*H* & CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.0, 144.1, 137.6, 133.1, 132.6, 128.7, 128.7, 127.5, 126.6, 122.2, 121.5, 48.1, 40.2, 39.4, 37.5, 37.5, 37.4, 36.7, 34.7, 32.9, 32.8, 32.8, 32.7, 31.7, 28.8, 28.7, 28.1, 28.1, 28.0, 27.8, 27.0, 25.57, 25.4, 24.9, 24.6, 23.6, 22.8, 22.7, 19.8, 16.2. HRMS (ESI) m/z calcd for $C_{30}H_{49}O$ $(M+H)^+$:425.3783, found: 425.3783.

5-Methyl-1-phenylhex-4-en-1-one (3a):[1] Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 54 mg, 58% . IR (DCM): 1697, 1458, 1435, 1185, 735 cm^{-1} . ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.9 Hz, 2H, ArC*H*), 7.56 (d, *J* = 7.4 Hz, 1H, ArC*H*), 7.48 (t, *J* = 7.6 Hz, 2H, ArC*H*), 5.20 (td, J_1 = 7.1 Hz, J_2 = 0.8 Hz, 1H, Olefinic C*H*), 3.02 (t, *J* = 7.5 Hz, 2H, CH_2), 2.44 (q, *J* = 7.4 Hz, 2H, CH_2), 1.71 (s, 3H, CH_3), 1.66 (s, 3H, CH_3). ^{13}C NMR (101



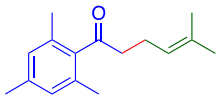
MHz, $CDCl_3$): δ 200.2, 137.1, 133.0, 132.9, 128.7, 128.2, 123.0, 38.9, 25.8, 23.0, 17.8.HRMS (ESI) m/z calcd for $C_{15}H_{19}O$ $(M+H)^+$: 215.1436, found: 215.1480.

5-Methyl-1-(p-tolyl)hex-4-en-1-one (3b):[1] Purified by silica-gel column chromatography



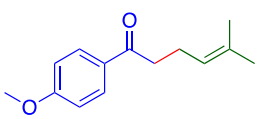
using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 70 mg, 71%. IR (DCM): 1695, 1456, 1436, 1180, 831, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.1 Hz, 2H, ArC*H*), 7.19 (d, *J* = 8.1 Hz, 2H, ArC*H*), 5.13-5.09 (m, 1H, Olefinic C*H*), 2.90 (t, *J* = 7.5 Hz, 2H, CH_2), 2.37-2.32 (m, 5H, CH_2 & ArCH_3), 1.63 (s, 3H, CH_3), 1.57 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 143.7, 134.6, 132.8, 129.3, 128.3, 123.1, 38.7, 25.8, 23.1, 21.7, 17.8. HRMS (ESI) m/z calcd for $C_{14}H_{18}O$ $(M+H)^+$: 225.1255, found: 225.1259.

1-Mesityl-5-methylhex-4-en-1-one (3c):[1] Purified by silica-gel column chromatography



using ethyl acetate/hexane (1:99) mixture as an eluent. Colorless liquid. Yield: 61 mg, 53% . IR (DCM):3443, 1696, 1558, 1457, 1434, 850, 702 cm^{-1} . ^1H NMR (400 MHz, $CDCl_3$): δ 6.75 (s, 2H, ArC*H*), 5.06 (t, *J* = 7.3 Hz, 1H, Olefinic C*H*), 2.64 (t, *J* = 7.4 Hz, 2H, CH_2), 2.31 (d, *J* = 7.3 Hz, 2H, CH_2), 2.19 (s, 3H, ArCH_3), 2.10 (s, 6H, ArCH_3), 1.60 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 210.7, 139.8, 138.3, 133.0, 132.6, 128.5, 122.8, 44.9, 25.8, 22.2, 21.1, 19.2, 17.8. HRMS (ESI) m/z calcd for $C_{16}H_{22}O$ $(M+H)^+$: 253.1535, found: 253.1563.

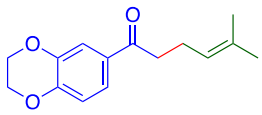
1-(4-Methoxyphenyl)-5-methylhex-4-en-1-one (3d): [1] Purified by silica-gel column



chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 95 mg, 88% . IR (DCM): 2925, 1678, 1511, 1258, 1171, 1031, 97, 841 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.8 Hz, 2H, ArC*H*), 6.95 (d, *J* = 8.8 Hz, 2H, ArC*H*), 5.19 (td, J_1 = 7.2, *J* = 1.0 Hz, 1H, Olefinic C*H*), 3.88 (s, 3H, ArOCH_3), 2.96 (t, *J* = 7.5 Hz, 2H, CH_2), 2.43 (q, *J* = 7.4 Hz, 2H, CH_2), 1.71 (s, 3H, CH_3), 1.65

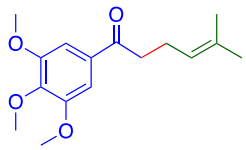
(s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.6, 163.3, 132.6, 130.3, 130.1, 123.1, 113.6, 55.4, 38.4, 25.7, 23.1, 17.6. HRMS (ESI) m/z calcd for $C_{14}H_{18}O_2$ $(M+H)^+$: 241.1208, found: 241.1199.

1-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-5-methylhex-4-en-1-one (3e): Purified by silica-



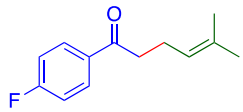
gel column chromatography using ethyl acetate/hexane (1:99) mixture as an eluent. Colorless liquid. Yield: 68 mg, 55% . IR (DCM): 3445, 1683, 1582, 1457, 1319, 1260, 1066, 893, 738 cm^{-1} .^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H, ArC*H*), 6.83 (d, *J* = 8.9 Hz, 1H, ArC*H*), 5.09 (t, *J* = 7.2 Hz, 1H, Olefinic C*H*), 4.25-4.20 (m, 4H, CH_2), 2.84 (t, *J* = 7.5 Hz, 2H, CH_2), 2.32 (q, *J* = 7.4 Hz, 2H, CH_2), 1.62 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.6, 147.9, 143.3, 132.7, 131.0, 123.17, 122.2, 117.6, 117.2, 64.7, 64.2, 38.5, 25.8, 23.2, 17.8. HRMS (ESI) m/z calcd for $C_{15}H_{18}O_3$ $(M+H)^+$: 269.1153, found: 269.1157.

5-Methyl-1-(3,4,5-trimethoxyphenyl)hex-4-en-1-one (3f) : Purified by silica-gel column



chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 64 mg, 46% . IR (DCM): 2928, 1700, 1585, 1456, 1322, 1231, 1154, 1004, 895, 835 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 2H, ArC*H*), 5.12-5.09 (m, 1H, Olefinic C*H*), 3.84 (s, 9H, ArOCH_3), 2.89 (t, *J* = 7.5 Hz, 2H, CH_2), 2.34 (q, *J* = 7.4 Hz, 2H, CH_2), 1.63 (s, 3H, CH_3), 1.58 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 153.1, 142.5, 132.9, 132.4, 123.0, 105.6, 61.0, 56.3, 38.6, 25.8, 23.2, 17.8. HRMS (ESI) m/z calcd for $C_{16}H_{22}O_4$ $(M+H)^+$: 301.1404, found: 301.1410.

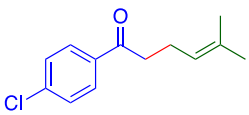
1-(4-Fluorophenyl)-5-methylhex-4-en-1-one (3g): Purified by silica-gel column



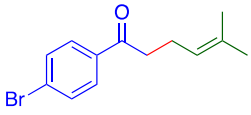
chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 68 mg, 66% . IR (DCM): 3438, 1696, 1558, 1457,

1407, 850, 807, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, J_1 = 8.1 Hz, J_2 = 5.8 Hz, 2H, ArC*H*), 7.05 (t, *J* = 8.5 Hz, 2H, ArC*H*), 5.09 (td, J_1 = 7.2 Hz, J_2 = 1.0 Hz, 1H, Olefinic C*H*), 2.90 (t, *J* = 7.5 Hz, 2H, CH_2), 2.34 (d, *J* = 7.3 Hz, 2H, CH_2), 1.62 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 167.0, 164.4, 133.5, 133.5, 133.0, 130.8, 130.7, 122.9, 115.8, 115.6, 38.7, 25.8, 23.0, 17.8. HRMS (ESI) m/z calcd for $C_{13}H_{25}OF$ $(M+H)^+$: 229.1000, found: 229.0999.

1-(4-Chlorophenyl)-5-methylhex-4-en-1-one (3h):[1] Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as an eluent. Colorless liquid. Yield: 83 mg, 75% . IR (DCM): 3438, 1684, 1635, 1362, 1093, 912, 734 cm^{-1} .^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.6 Hz, 2H, ArC*H*), 7.36 (d, *J* = 8.6 Hz, 2H, ArC*H*), 5.10-5.06 (m, 1H, Olefinic C*H*), 2.91-2.87 (m, 2H, CH_2), 2.34 (q, *J* = 7.2 Hz, 2H, CH_2), 1.62 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 139.4, 135.4, 133.1, 129.6, 129.0, 122.8, 38.8, 25.8, 23.0, 17.8. HRMS (ESI) m/z calcd for $C_{13}H_{16}ClO$ $(M+H)^+$: 223.0890, found: 223.0900.



1-(4-Bromophenyl)-5-methylhex-4-en-1-one (3i): [1] Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as an eluent. Colorless liquid. Yield: 76 mg, 57% . IR (DCM): 3446, 2925, 1683, 1585, 1483, 1259, 1070, 978, 789 cm^{-1} .^1H NMR (400 MHz, $CDCl_3$): δ 7.76-7.72 (m, 2H, ArC*H*), 7.54-7.50 (m, 2H, ArC*H*), 5.10-5.05 (m, 1H, Olefinic C*H*), 2.90-2.86 (m, 2H, CH_2), 2.36-2.30 (m, 2H, CH_2), 1.61 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.1, 135.8, 133.1, 131.9, 129.9, 129.7, 128.1, 122.8, 38.8, 25.8, 22.9, 17.8. HRMS (ESI) m/z calcd for $C_{13}H_{15}BrO$ $(M+H)^+$: 289.0203, found: 289.0201.



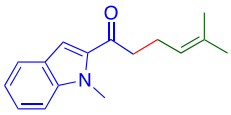
5-Methyl-1-(5-methylfuran-2-yl)hex-4-en-1-one (3j): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 39 mg, 42% . IR (DCM): 2924, 1674, 1516, 1456, 1375, 1026, 796 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 3.4 Hz, 1H, ArC*H*), 6.15-6.14 (m, 1H, ArC*H*), 5.17-5.13 (m, 1H, Olefinic C*H*), 2.78 (t, *J* = 7.6 Hz, 2H, CH_2), 2.42-2.37 (m, 5H, CH_2 & ArCH_3), 1.69 (s, 3H, CH_3), 1.64 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 188.7, 157.7, 151.6, 132.9, 122.9, 119.1, 108.9, 38.4, 25.8, 23.4, 17.8, 14.2. HRMS (ESI) m/z calcd for $C_{12}H_{16}O_2$ $(M+H)^+$: 215.1048, found: 215.1054.

5-Methyl-1-(1-methyl-1H-pyrrol-2-yl)hex-4-en-1-one (3k): Purified by silica-gel column chromatography using ethyl acetate/hexane (3:97) mixture as eluent. Colorless liquid. Yield: 84 mg, 89% . IR (DCM): 3446, 1700, 1683, 1558, 1456, 1418, 1274, 764, 749 cm^{-1} .^1H NMR (400 MHz, $CDCl_3$): δ 6.87 (dd, J_1 = 4.1 Hz, J_2 = 1.7 Hz, 1H, ArC*H*), 6.71 (d, *J* = 2.1 Hz, 1H, ArC*H*), 6.04 (dd, J_1 = 4.0 Hz, J_2 = 2.5 Hz, 1H, ArC*H*), 5.12-5.06 (m, 1H, olefinic C*H*), 3.86 (s, 3H, N-CH_3), 2.71 (d, *J* = 7.9 Hz, 2H, CH_2), 2.33-2.27 (m, 2H, CH_2), 1.61 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.2, 132.5, 130.8, 123.3, 119.0, 107.8, 39.2, 37.7, 25.7, 23.8, 17.7. HRMS (ESI) m/z calcd for $C_{12}H_{17}NO$ $(M+H)^+$: 214.1207, found: 214.1213.

5-Methyl-1-(thiophen-2-yl)hex-4-en-1-one (3l): Purified by silica-gel column chromatography using ethyl acetate/hexane (2:98) mixture as eluent. Colorless liquid. Yield: 58 mg, 60% . IR (DCM): 2925, 1661, 1519, 1416, 1354, 1233, 1062, 854 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, J_1 = 3.7 Hz, J_2 = 0.8 Hz, 1H, ArC*H*), 7.54 (dd, J_1 = 4.9 Hz, J_2 = 0.8 Hz, 1H, ArC*H*), 7.05 (dd, J_1 = 4.8 Hz, J_2 = 3.9 Hz, 1H, ArC*H*), 5.11-5.07 (m, 1H, Olefinic C*H*), 2.85 (t, *J* = 7.5 Hz, 2H, CH_2), 2.35 (q, *J* = 7.4 Hz, 2H, CH_2), 1.61 (s, 3H, CH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.1, 144.5,

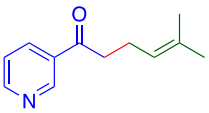
133.4, 133.1, 131.8, 128.1, 122.8, 39.6, 25.8, 23.4, 17.8. HRMS (ESI) m/z calcd for $C_{11}H_{14}OS(M+H)^+$: 217.0648, found: 217.0658.

5-Methyl-1-(1-methyl-1H-indol-2-yl)hex-4-en-1-one (3m): Purified by silica-gel column



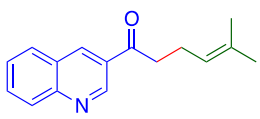
chromatography using ethyl acetate/hexane (5:95) mixture as eluent. Colorless liquid. Yield: 82 mg, 68% . IR (DCM): 3442, 1695, 1576, 1456, 1539, 1506, 1456, 776 cm^{-1} .^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34-8.31 (m, 1H, ArC*H*), 7.64 (s, 1H, ArC*H*), 7.27-7.22 (m, 3H, ArC*H*), 5.15 (t, *J* = 7.2 Hz, 1H, Olefinic C*H*), 3.76 (s, 3H, N-C*H*$_3$), 2.80 (dd, J_1 = 8.5 Hz, J_2 = 6.8 Hz, 2H, C*H*$_2$), 2.41 (t, *J* = 7.6 Hz, 2H, C*H*$_2$), 1.64-1.59 (m, 6H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.4, 135.3, 126.4, 123.5, 123.3, 122.7, 122.6, 116.6, 109.6, 40.0, 33.5, 25.8, 23.7, 17.8. HRMS (ESI) m/z calcd for $C_{16}H_{19}NO$ $(M+H)^+$: 264.1364, found: 264.1375.

5-Methyl-1-(pyridin-3-yl)hex-4-en-1-one (3n): Purified by silica-gel column



chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 35 mg, 37% . IR (DCM): ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, *J* = 2.2 Hz, 1H, ArC*H*), 8.70 (dd, J_1 = 4.7 Hz, J_2 =1.6 Hz, 1H, ArC*H*), 8.16 (d, *J* = 7.9 Hz, 1H, ArC*H*), 7.34 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H, ArC*H*), 5.15-4.95 (m, 1H, Olefinic C*H*), 2.94 (t, *J* = 7.4 Hz, 2H, C*H*$_2$), 2.37 (d, *J* = 7.4 Hz, 2H, C*H*$_2$), 1.62 (s, 3H, C*H*$_3$), 1.56 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 153.4, 149.7, 135.4, 123.7, 122.5, 39.1, 29.8, 25.8, 22.7, 17.8, 14.2. HRMS (ESI) m/z calcd for $C_{12}H_{15}NO$ $(M+H)^+$: 190.1237, found: 190.1226.

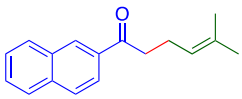
5-Methyl-1-(quinolin-3-yl)hex-4-en-1-one (3o): Purified by silica-gel column



chromatography using ethyl acetate/hexane (5:95) mixture as eluent. Colorless liquid. Yield: 72 mg, 60% . IR (DCM): 3446, 2923, 1683, 1616, 1436, 1375, 1126, 949, 751 cm^{-1} .^{1}H NMR (400 MHz, $CDCl_3$): δ 9.44 (s, 1H, ArC*H*),

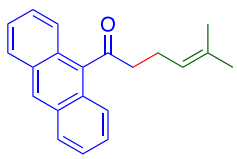
8.72 (s, 1H, ArC*H*), 8.17 (d, *J* = 8.4 Hz, 1H, ArC*H*), 7.95 (d, *J* = 8.2 Hz, 1H, ArC*H*), 7.85 (t, *J* = 7.7 Hz, 1H, ArC*H*), 7.64 (t, *J* = 7.5 Hz, 1H, ArC*H*), 5.24-5.20 (m, 1H, Olefinic C*H*), 3.14 (t, *J* = 7.4 Hz, 2H, CH_2), 2.51 (q, *J* = 7.3 Hz, 2H, CH_2), 1.71 (s, 3H, CH_3), 1.67 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 149.9, 149.3, 137.1, 133.4, 132.0, 129.6, 129.4, 129.3, 127.6, 127.0, 122.6, 39.2, 25.8, 22.9, 17.9. HRMS (ESI) m/z calcd for $C_{16}H_{17n}O$ $(M+H)^+$: 240.1388, found: 240.1399.

5-Methyl-1-(naphthalen-2-yl)hex-4-en-1-one (3p): [1] Purified by silica-gel column



chromatography using ethyl acetate/hexane (1:99) mixture as eluent. Colorless liquid. Yield: 77 mg, 65%. IR (DCM): 2966, 1700, 1456, 1374, 1181, 1123, 862, 747 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H, ArC*H*), 7.99-7.94 (m, 1H, ArC*H*), 7.89-7.87 (m, 1H, ArC*H*), 7.83-7.79 (m, 2H, ArC*H*), 7.54-7.45 (m, 2H, ArC*H*), 5.19-5.11 (m, 1H, olefinic C*H*), 3.06 (t, 2H, CH_2), 2.41 (q, *J* = 7.4 Hz, 2H, CH_2), 1.63 (s, 3H, CH_3), 1.58 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 135.6, 134.4, 132.9, 132.6, 129.7, 129.6, 128.4, 128.4, 127.8, 126.8, 124.0, 123.0, 38.9, 25.8, 23.1, 17.8. HRMS (ESI) m/z calcd for $C_{17}H_{18}O$ $(M+H)^+$: 261.1255, found: 261.1264.

1-(4a,10-Dihydroanthracen-9-yl)-5-methylhex-4-en-1-one (3q): Purified by silica-gel



column chromatography using ethyl acetate/hexane (2:98) mixture as eluent. Colorless liquid. Yield: 109 mg, 76% . IR (DCM): 2926, 1699, 1674, 1331, 1269, 1109, 936, 889, 735 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.94-7.90 (m, 2H, ArC*H*), 7.73-7.71 (m, 2H, ArC*H*), 7.42-7.38 (m, 4H, ArC*H*), 5.15-5.14 (m, 1H, Olefinic C*H*), 3.01 (q, J_1 = 8.6 Hz, J_2 = 8.0 Hz, 2H, CH_2), 2.50 (q, *J* = 7.4 Hz, 2H, CH_2), 1.62 (s, 3H, CH_3), 1.57 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 210.4, 136.8, 133.3, 131.2, 128.9, 128.2, 127.1, 126.7, 125.5, 124.5, 122.7, 46.5, 25.8, 22.5, 17.9. HRMS (ESI) m/z calcd for $C_{21}H_{20}O$ $(M+H)^+$: 311.1411, found: 311.1425.

(*E*)-5,9-Dimethyl-1-phenyldeca-4,8-dien-1-one (3r): Purified by silica-gel column chromatography using ethyl acetate/hexane (1:99) mixture as an eluent. Colourless liquid. Yield: 69 mg, 54% . IR (DCM): 2976,1716, 1581, 1377, 1265, 1025, 896 cm^{-1} .^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.9 Hz, 2H, ArC*H*), 7.50-7.46 (m, 1H, ArC*H*), 7.38 (t, *J* = 7.7 Hz, 2H, ArC*H*), 5.12 (t, *J* = 7.2 Hz, 1H, Olefinic C*H*), 5.03-4.99 (m, 1H, Olefinic C*H*), 2.93 (t, *J* = 7.5 Hz, 2H, CH_2), 2.37 (q, *J* = 7.4 Hz, 2H, CH_2), 1.95 (td, J_1 = 18.1 Hz, J_2 = 10.4 Hz, 4H, CH_2), 1.56 (t, *J* = 14.8 Hz, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 137.1, 136.5, 133.0, 131.4, 128.6, 128.1, 124.3, 122.8, 39.8, 38.8, 26.7, 25.7, 23.0, 17.8, 16.1. HRMS (ESI) m/z calcd for $C_{20}H_{16}O(M+H)^+$: 283.2058, found: 283.2090.

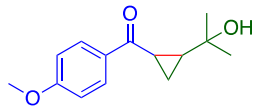
Spectral Data of Functionalized Compounds Prepared from α-Prenylated Ketones:

5-Methyl-1-phenylhex-4-en-1-ol (4a): Purified by silica-gel column chromatography using ethyl acetate/hexane (2:98) mixture as eluent. Colourless liquid. Yield: 76 mg, 80% . ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 6.2 Hz, 4H, ArC*H*), 7.20 (dd, J_1 = 8.6 Hz, J_2 = 4.3 Hz, 1H, ArC*H*), 5.08-5.05 (m, 1H, Olefinic C*H*), 4.59 (t, *J* = 6.6 Hz, 1H, C*H*), 1.98 (t, *J* = 7.2 Hz, 2H, CH_2), 1.81-1.65 (m, 3H, CH_2 & *OH*), 1.62 (s, 3H, CH_3), 1.51 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8, 132.4, 128.5, 127.5, 126.0, 123.9, 74.3, 39.1, 25.8, 24.6, 17.8.

3,5-Dibromo-2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyran (4b):[2] Purified by silica-gel column chromatography using ethyl acetate/hexane (2:98) mixture as an eluent. Colorless liquid. Yield: 81 mg, 47%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.38 (m, 2H, ArC*H*), 7.34-7.22 (m, 3H, ArC*H*), 4.13 (dd, J_1 = 9.1 Hz, J_2 = 6.0 Hz, 1H, C*H*), 3.06 (s, 1H, CH_2), 2.94 (dd, J_1 = 17.5 Hz, J_2 = 9.0 Hz, 1H, CH_2), 1.43 (d, *J* = 11.9 Hz,

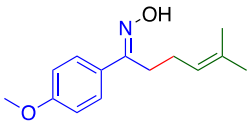
6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.59, 135.28, 129.17, 129.09, 127.99, 92.51, 77.96, 51.89, 40.95, 26.88, 20.66.

(2-(2-Hydroxypropan-2-yl)cyclopropyl)(4-methoxyphenyl)methanone (4d):[3] Purified by



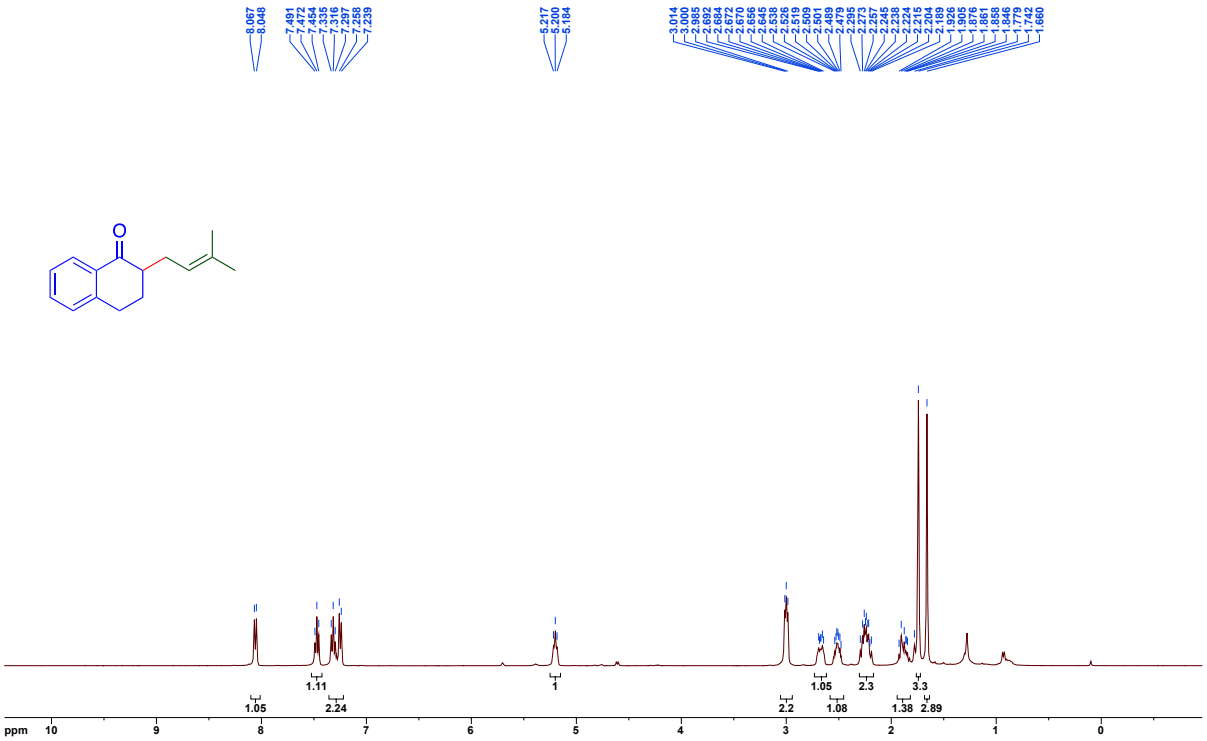
silica-gel column chromatography using ethyl acetate/hexane (2:98) mixture as an eluent. Colorless liquid. Yield: 84 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.6 Hz, 2H, ArCH), 6.88 (d, J = 8.6 Hz, 2H, ArCH), 3.81 (s, 3H, ArOCH_3), 2.68 (dt, J_1 = 8.4 Hz, J_2 = 4.3 Hz, 1H, CH), 1.70-1.65 (m, 1H, CH_2), 1.44-1.41 (m, 1H, OH), 1.30 (dt, J_1 = 8.8 Hz, J_2 = 4.3 Hz, 1H, CH_2), 1.25 (d, J = 4.0 Hz, 6H, CH_3), 1.11-1.07 (m, 1H, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.7, 163.5, 131.0, 130.4, 113.8, 68.9, 55.6, 36.4, 29.9, 29.6, 20.7, 14.1.

(E)-1-(4-Methoxyphenyl)-5-methylhex-4-en-1-one oxime (4e):[4] Purified by silica-gel



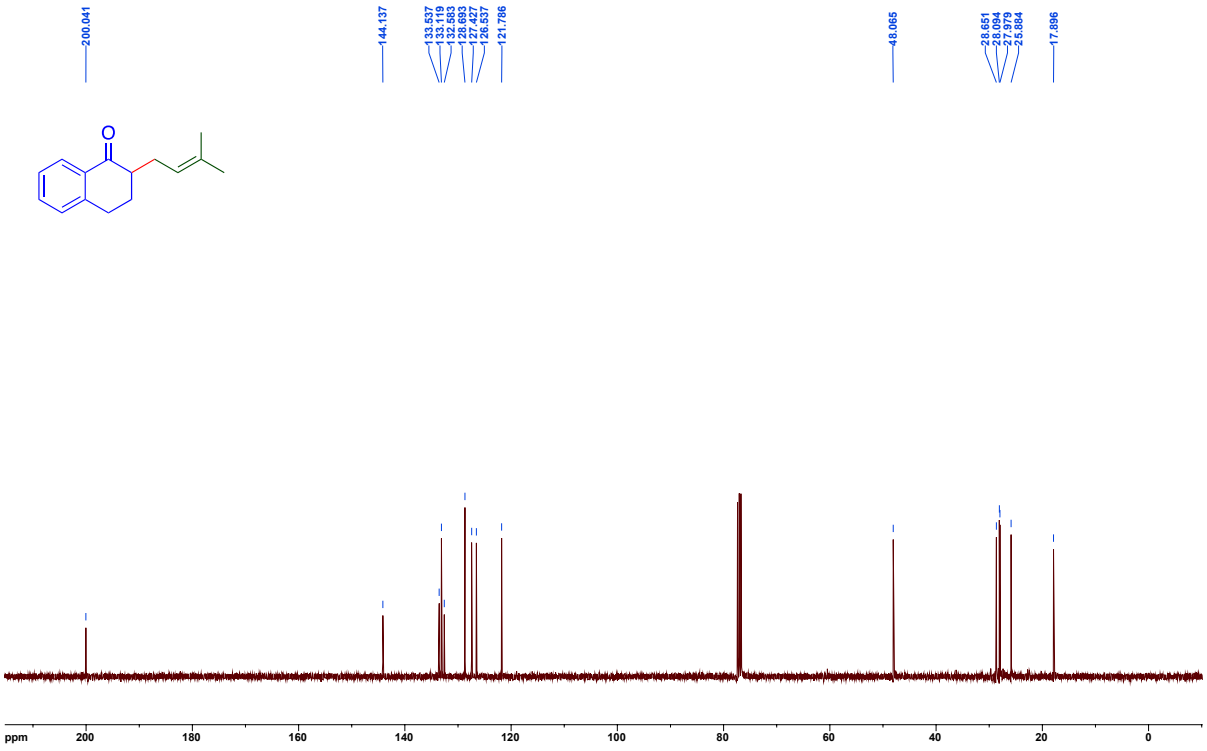
column chromatography using ethyl acetate/hexane (2:98) mixture as an eluent. White solid. Yield: 110 mg, 95% . ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H, OH), 7.49 (d, J = 8.7 Hz, 2H, ArCH), 6.84 (d, J = 8.7 Hz, 2H, ArCH), 5.12 (t, J = 6.8 Hz, 1H, ArCH), 3.76 (s, 3H, ArOCH_3), 2.74 (t, J = 8.0 Hz, 2H, CH_2), 2.20 (q, J = 7.8 Hz, 2H, CH_2), 1.61 (s, 3H, CH_3), 1.51 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 158.1, 131.8, 127.5, 126.8, 126.8, 122.5, 113.2, 113.1, 54.5, 25.7, 24.8, 24.1, 16.9.

^{1}H and ^{13}C NMR spectra of *α*-prenylated products:

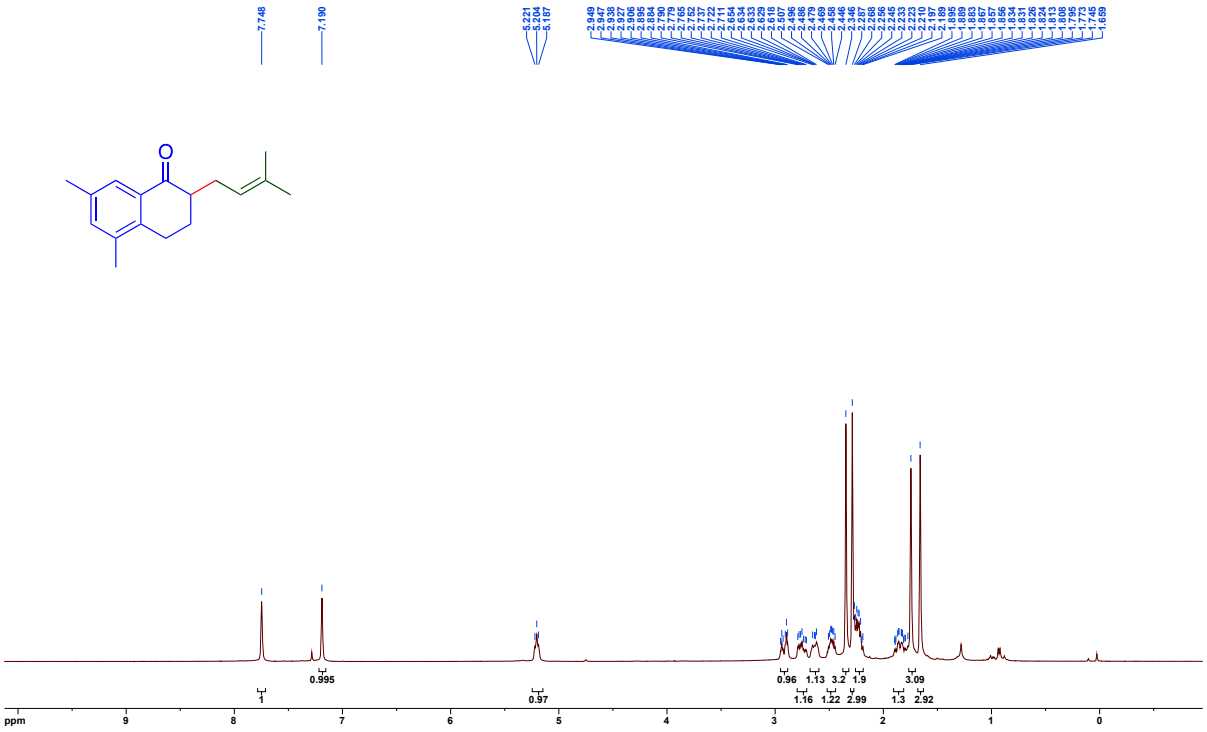


^{1}H NMR spectrum of 2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1-one (**2a**, 400 MHz, $CDCl_3$)

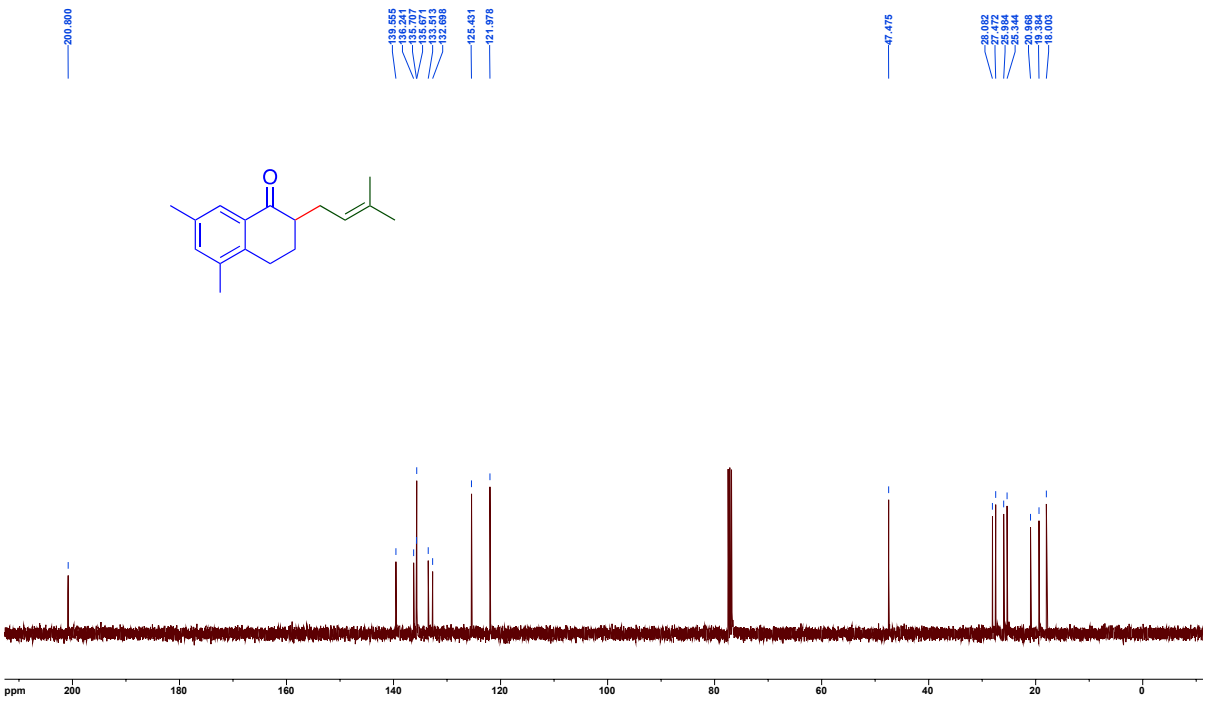
^{13}C NMR spectrum of 2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1-one (**2a,** 101 MHz, $CDCl_3$):


200.041
144.137
133.537
131.149
132.583
128.693
127.427
126.837
121.786
48.065
28.651
28.094
27.979
25.884
17.896
O
ppm
200
180
160
140
120
100
80
60
40
20
0

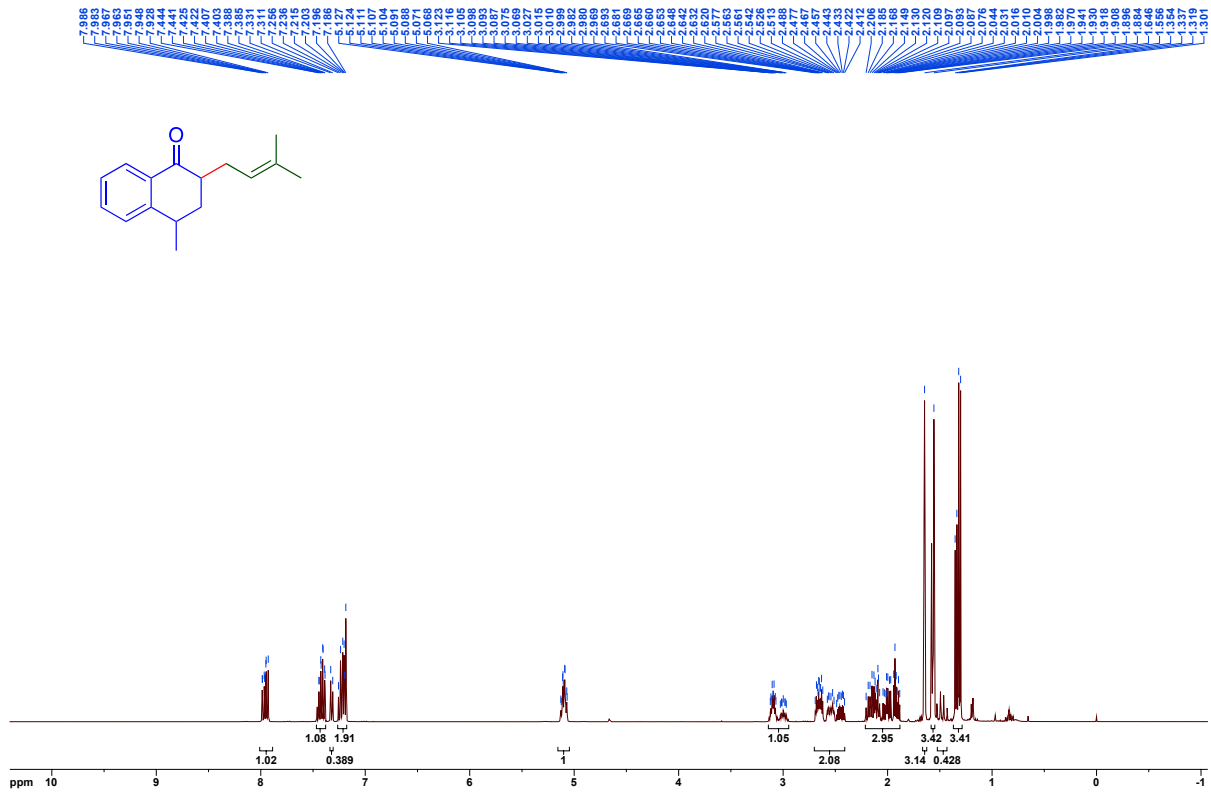
^{1}H NMR spectrum of 5,7-dimethyl-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2b,** 400 MHz, $CDCl_3$)



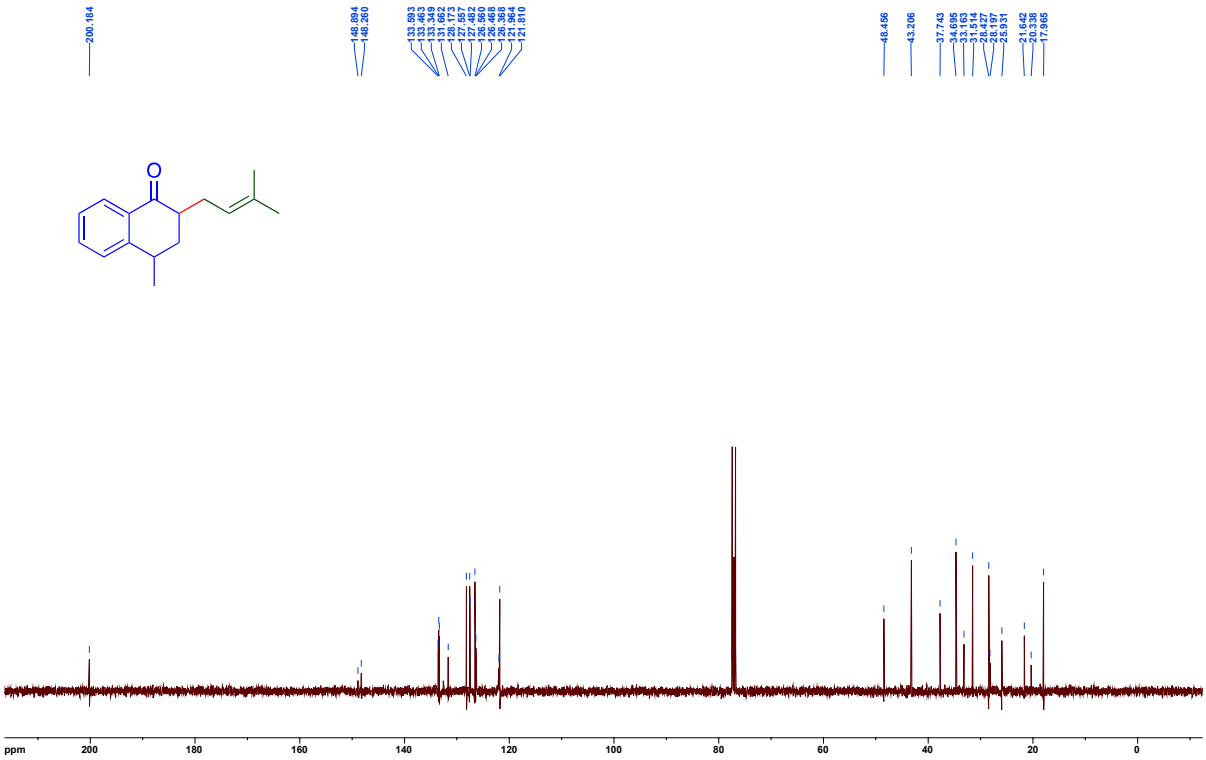
^{13}C NMR spectrum of 5,7-dimethyl-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2b,** 101 MHz, $CDCl_3$):



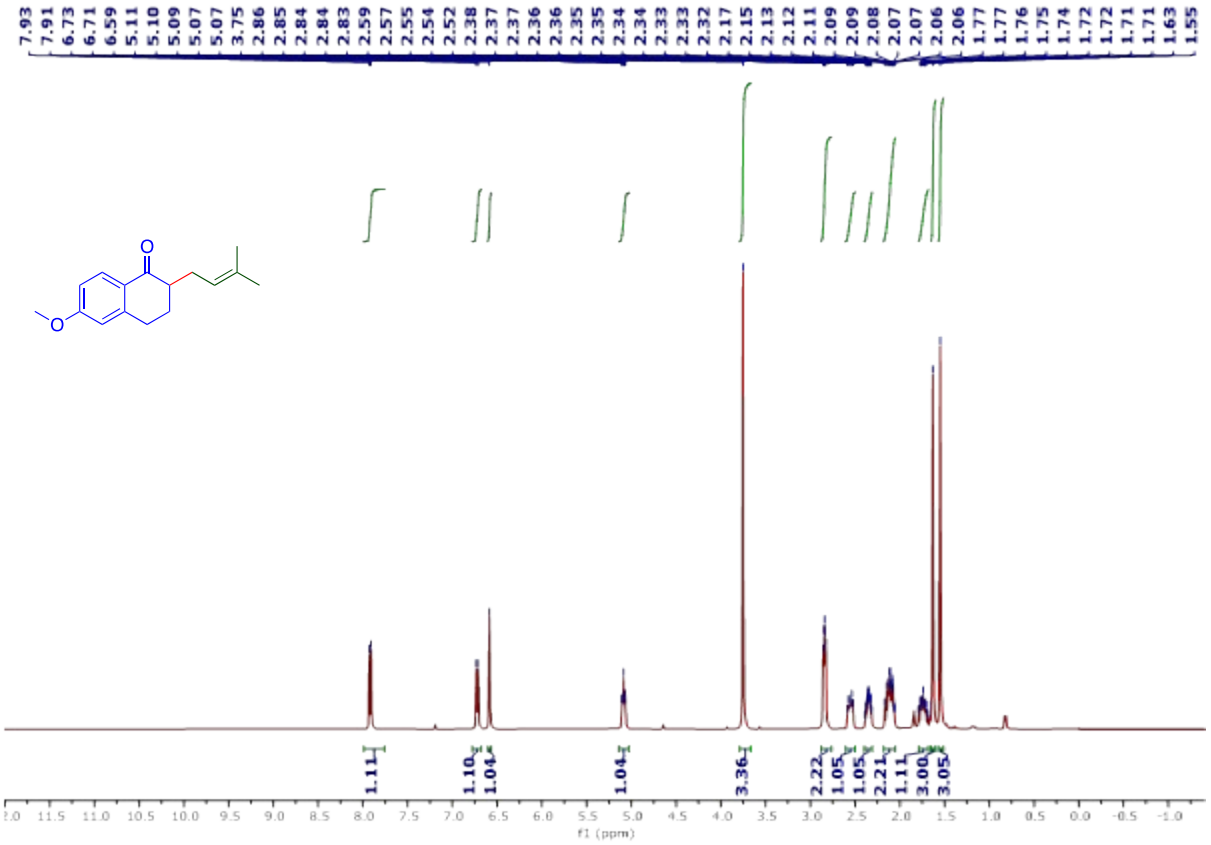
^{1}H NMR spectrum of 4-methyl-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2c,** 400 MHz, $CDCl_3$)



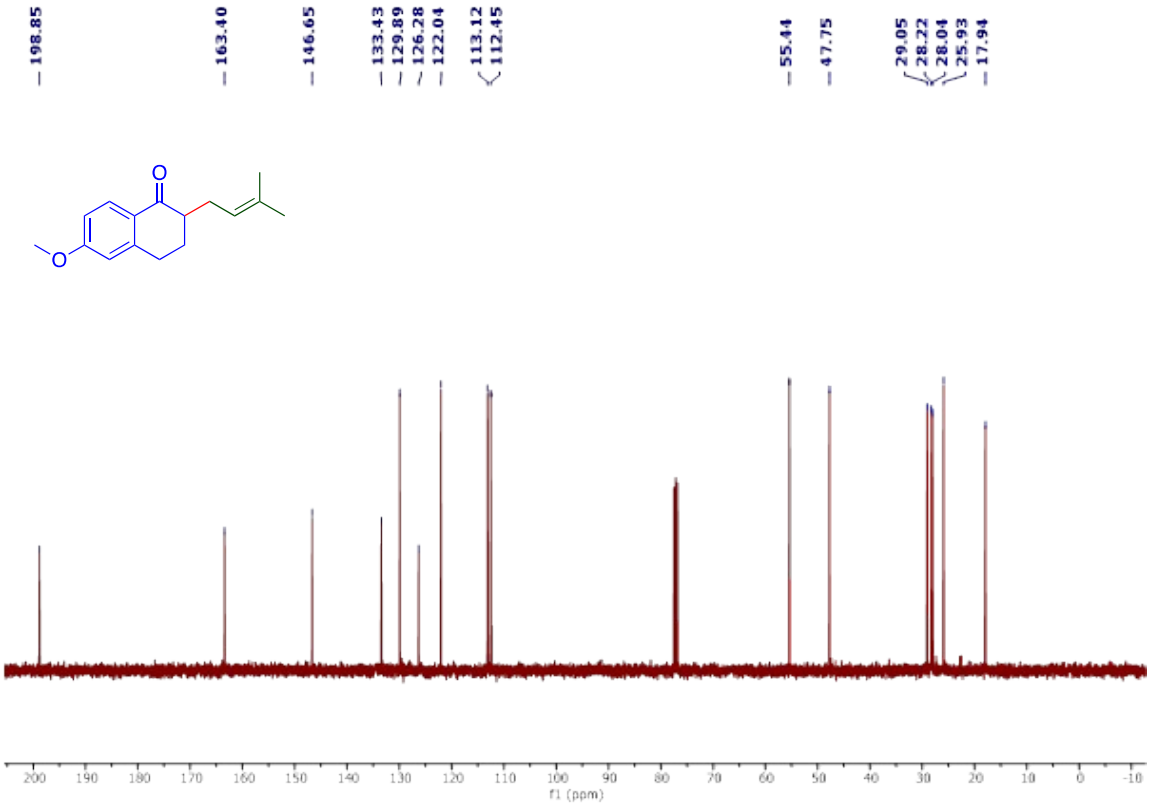
^{13}C NMR spectrum of 4-methyl-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2c,** 101 MHz, $CDCl_3$):



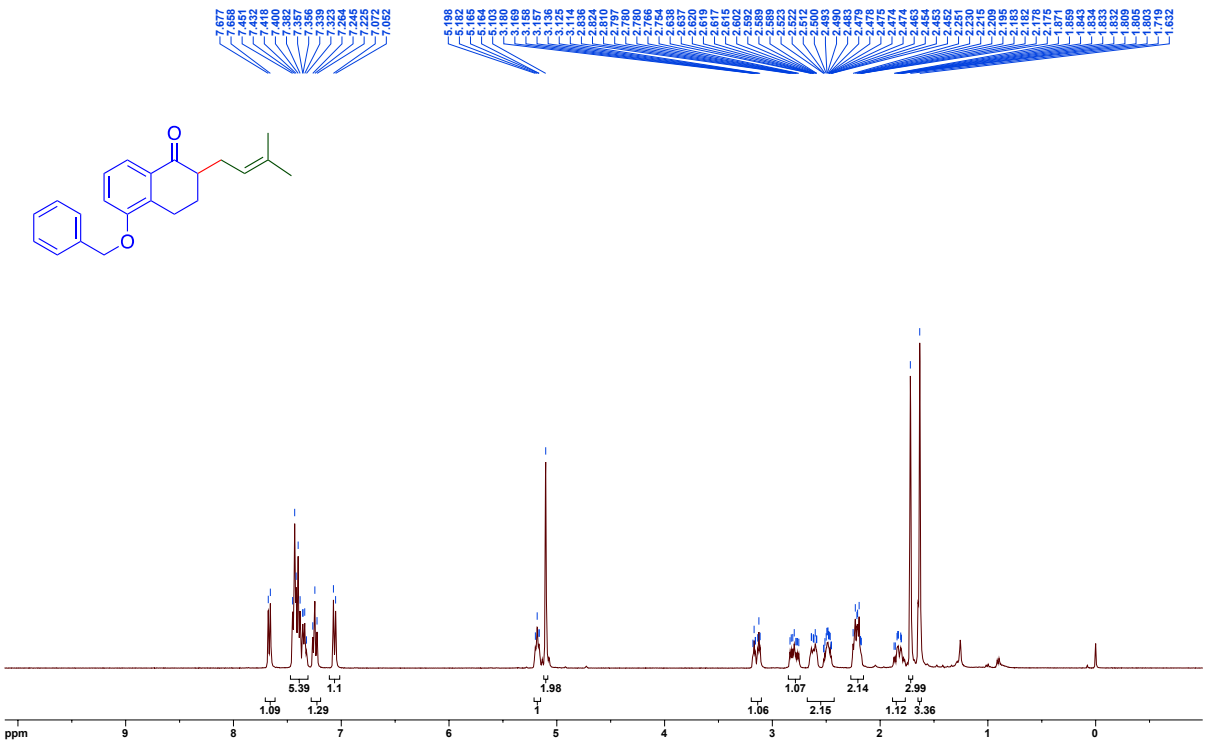
^{1}H NMR spectrum of 6-methoxy-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2d,** 400 MHz, $CDCl_3$)



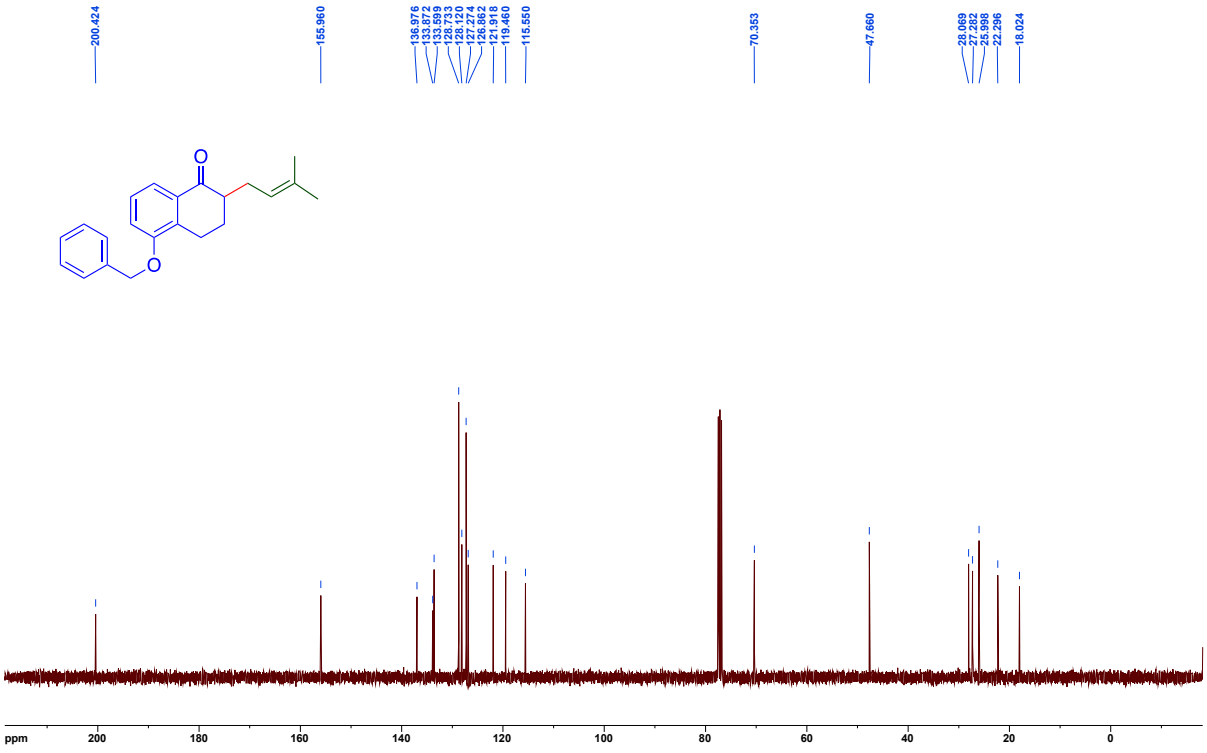
^{13}C NMR spectrum of 6-methoxy-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2d,** 101 MHz, $CDCl_3$):



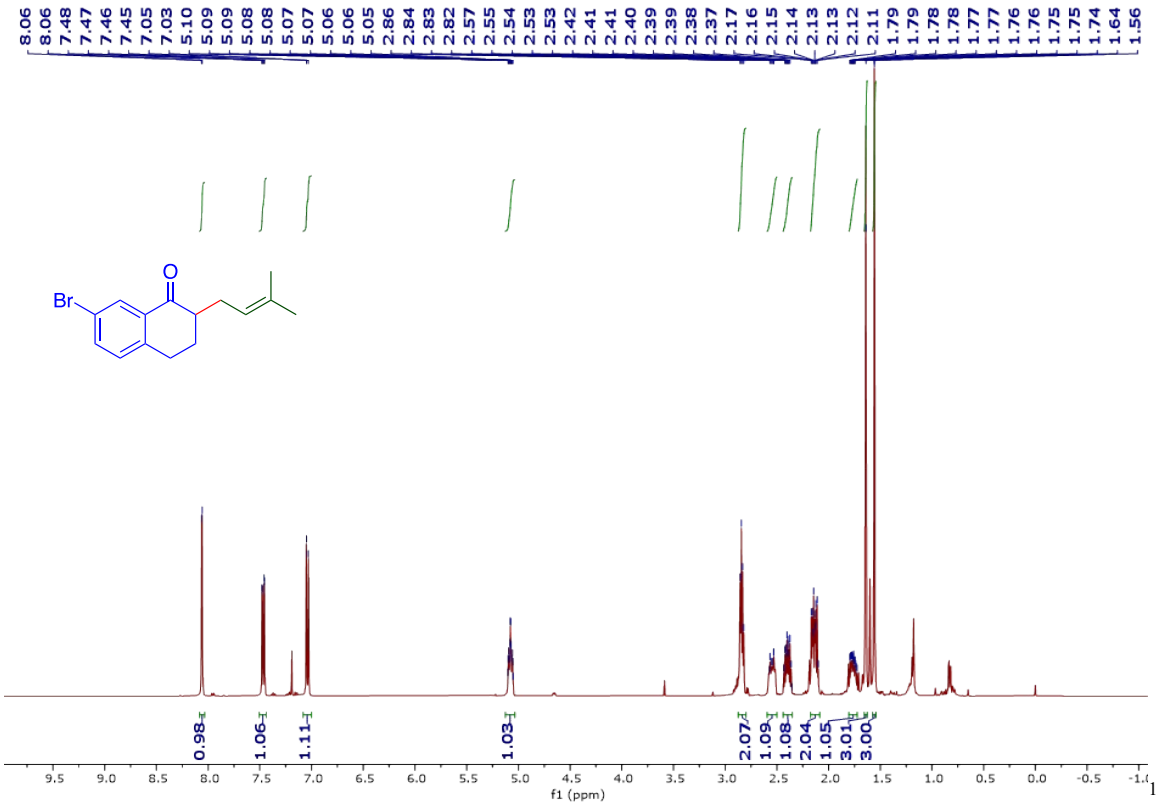
^{1}H NMR spectrum of 5-(benzyloxy)-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2e,** 400 MHz, $CDCl_3$)



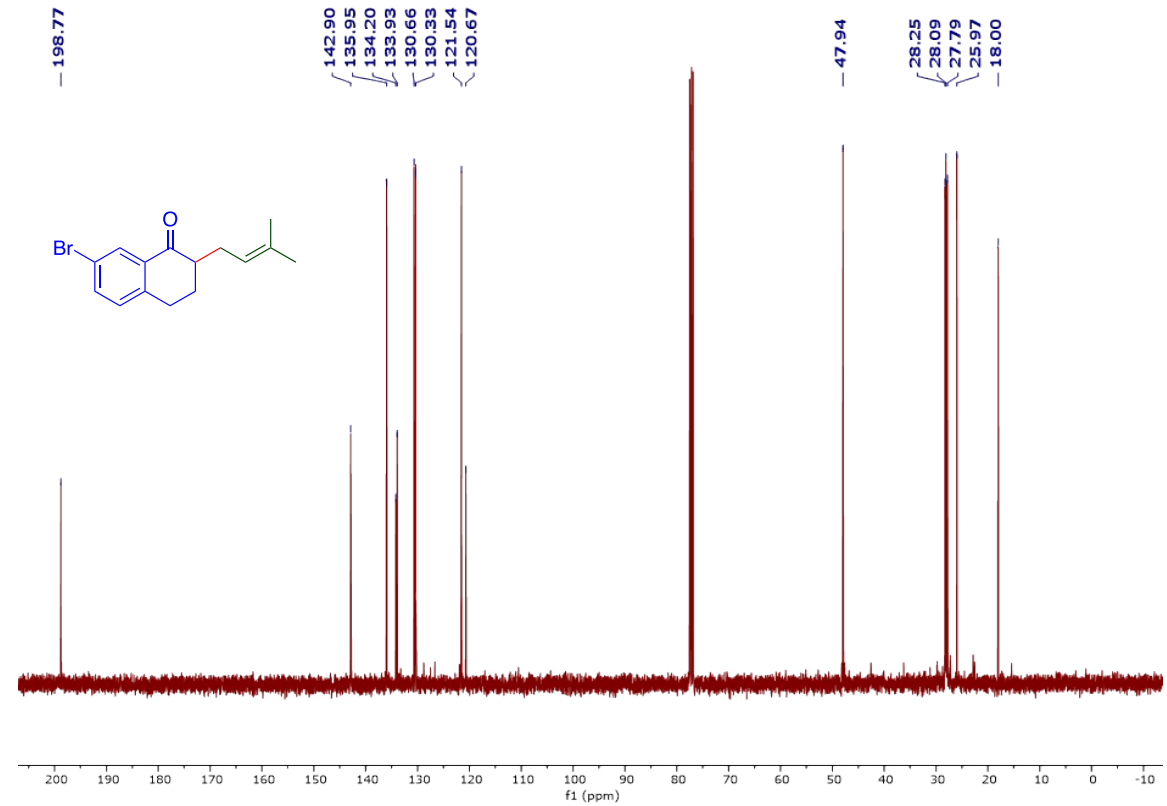
^{13}C NMR spectrum of 5-(benzyloxy)-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2e,** 101 MHz, $CDCl_3$):



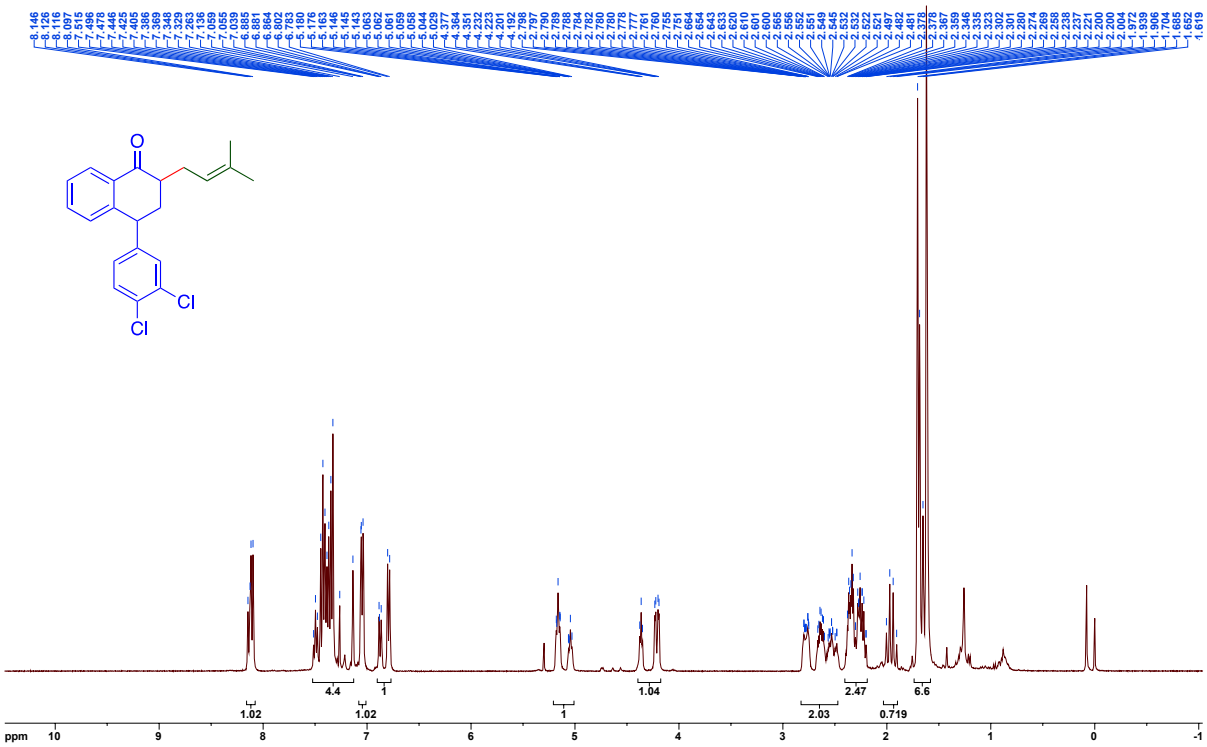
^{1}H NMR spectrum of 7-bromo-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2f,** 400 MHz, $CDCl_3$)



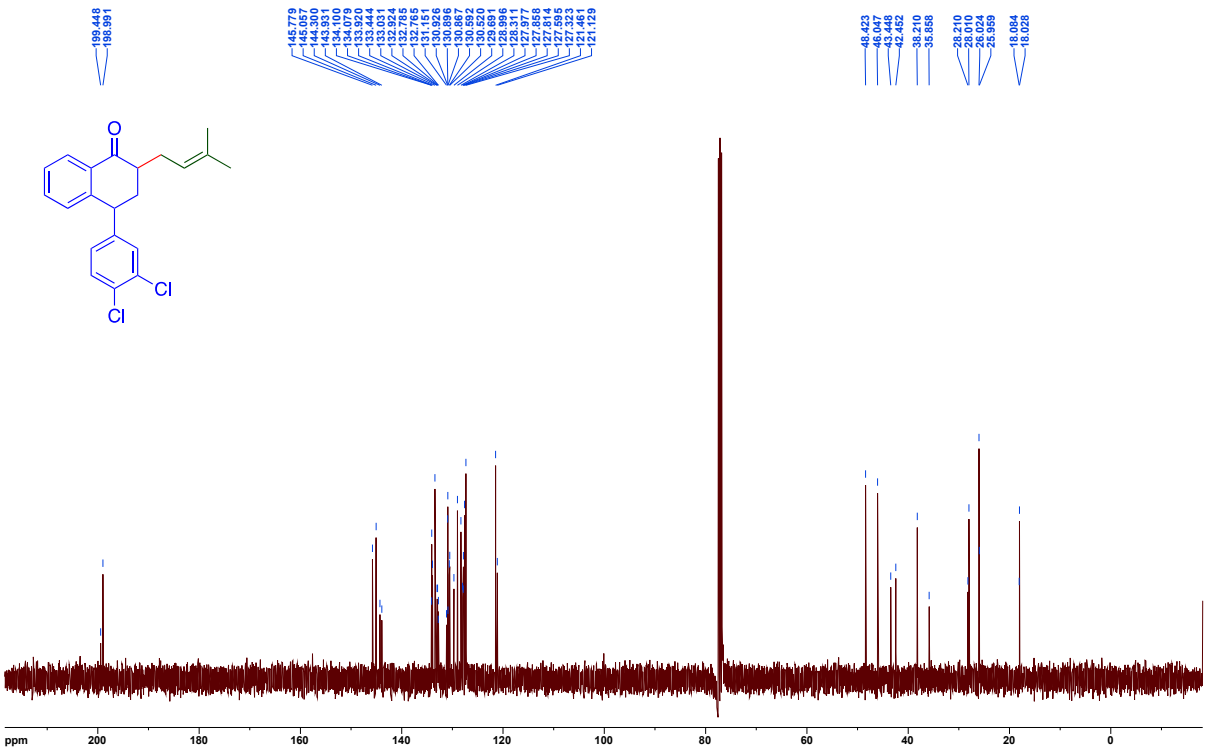
^{13}C NMR spectrum of 7-bromo-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2f,** 101 MHz, $CDCl_3$):



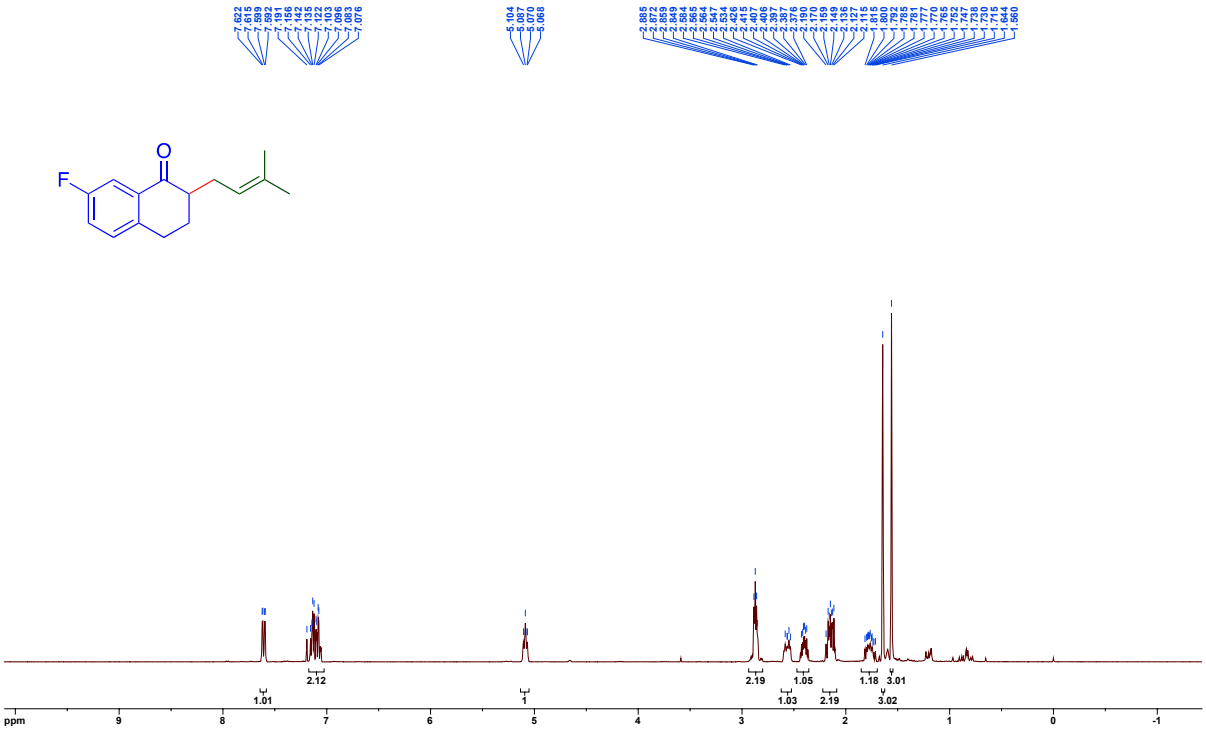
^{1}H NMR spectrum of 4-(3,4-dichlorophenyl)-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2g,** 400 MHz, $CDCl_3$):



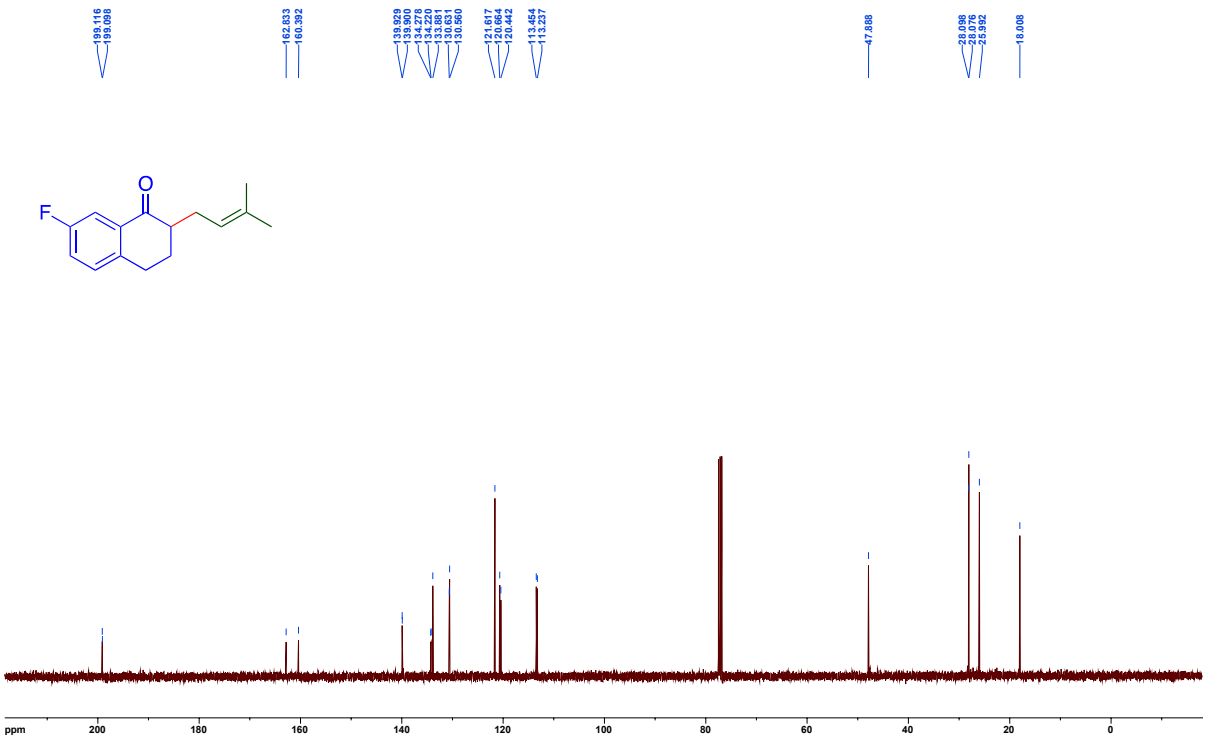
^{13}C NMR spectrum of 4-(3,4-dichlorophenyl)-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2g,** 101 MHz, $CDCl_3$):



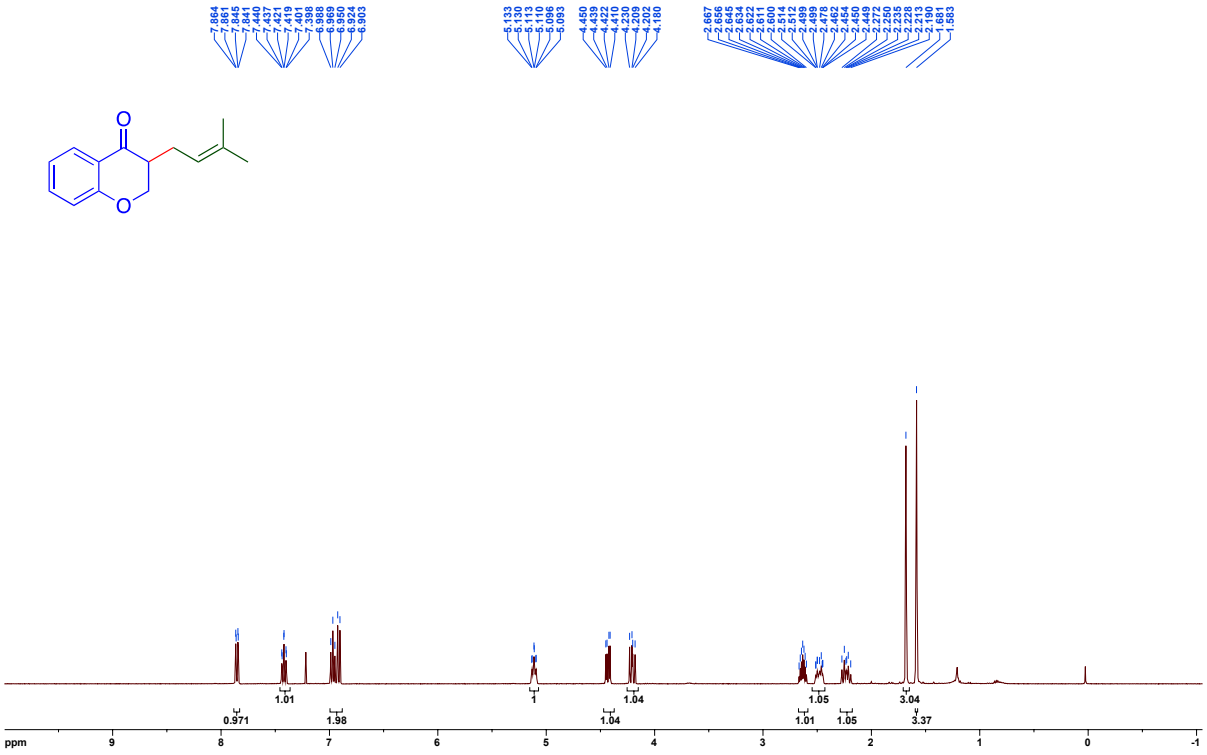
[1]HNMR spectrum of 7-fluoro-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2h,** 400 MHz, $CDCl_3$**):**



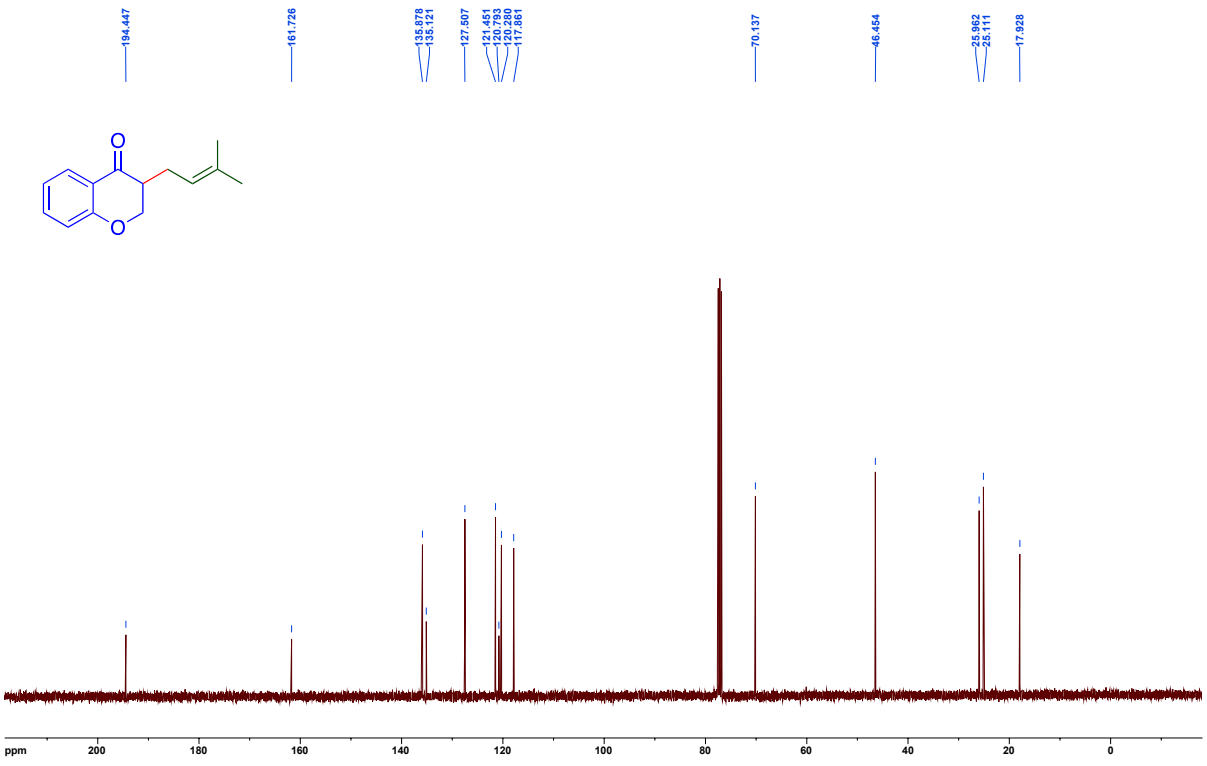
[13]C NMR spectrum of 7-fluoro-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2h,** 101 MHz, $CDCl_3$):



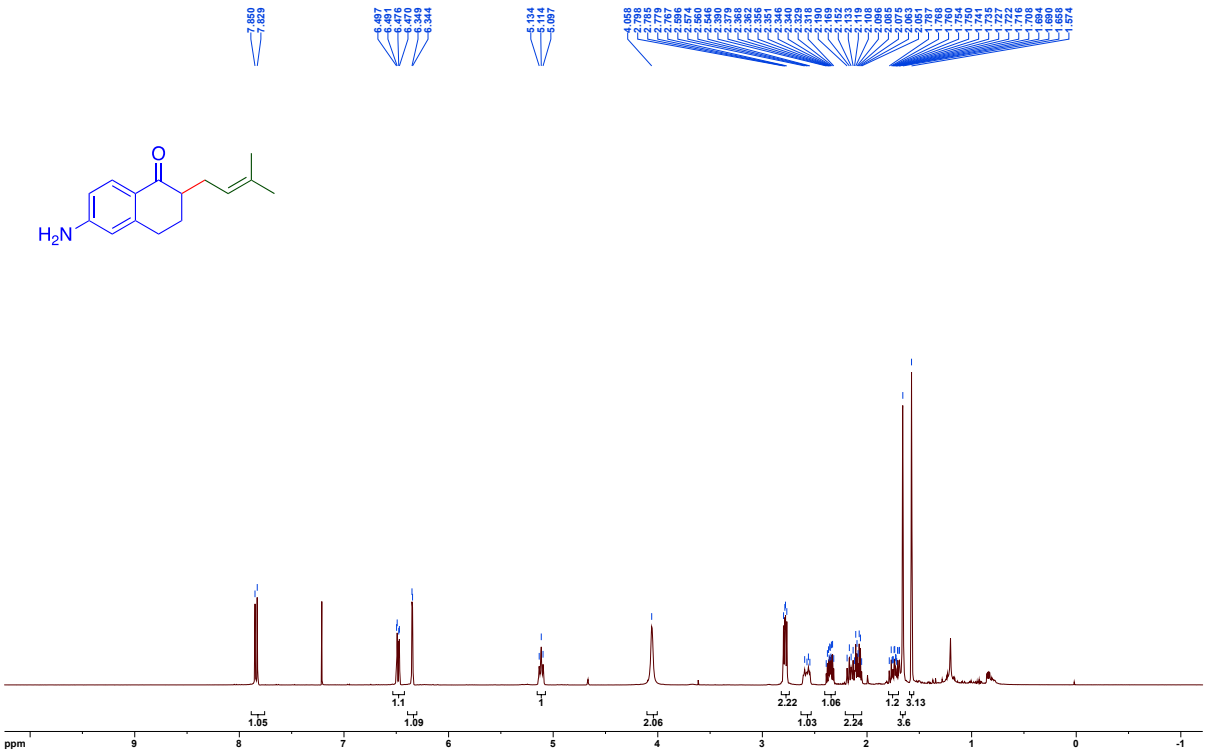
^{1}H NMR spectrum of 3-(3-methylbut-2-en-1-yl)chroman-4-one **(2i,** 400 MHz, $CDCl_3$) **:**



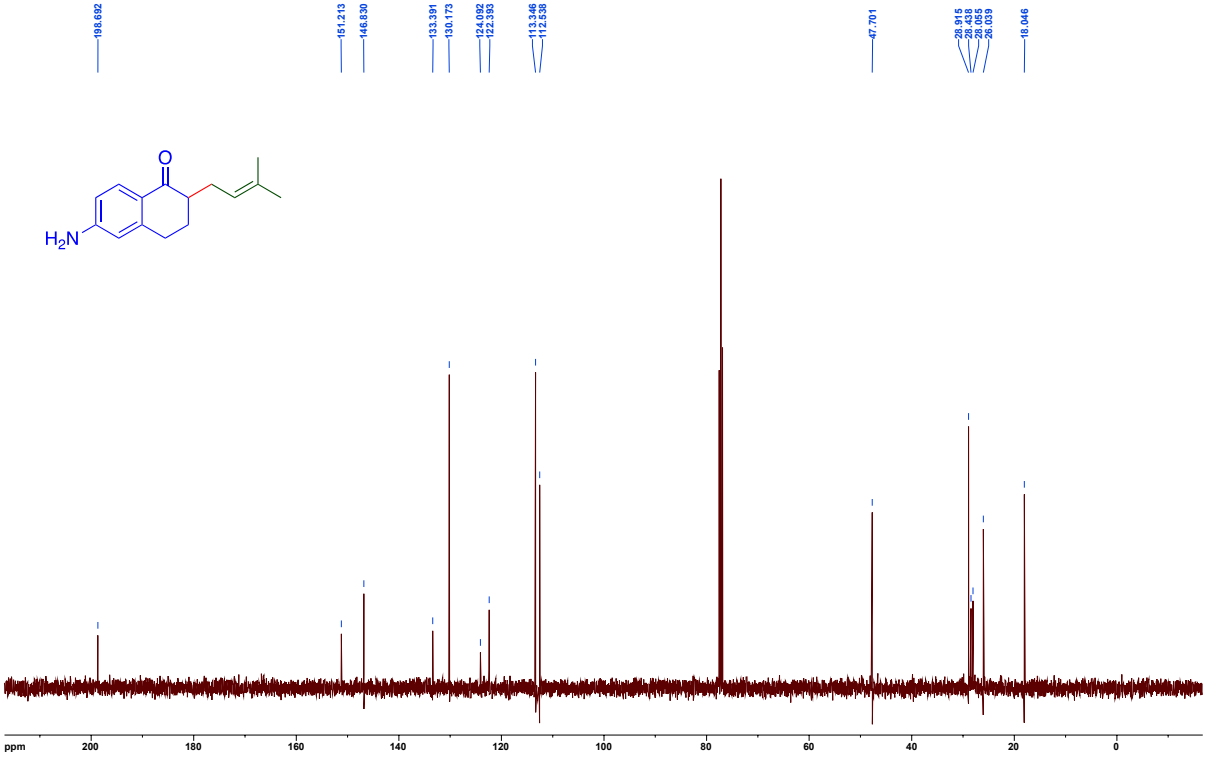
^{13}C NMR spectrum of 3-(3-methylbut-2-en-1-yl)chroman-4-one **(2i,** 101 MHz, $CDCl_3$):



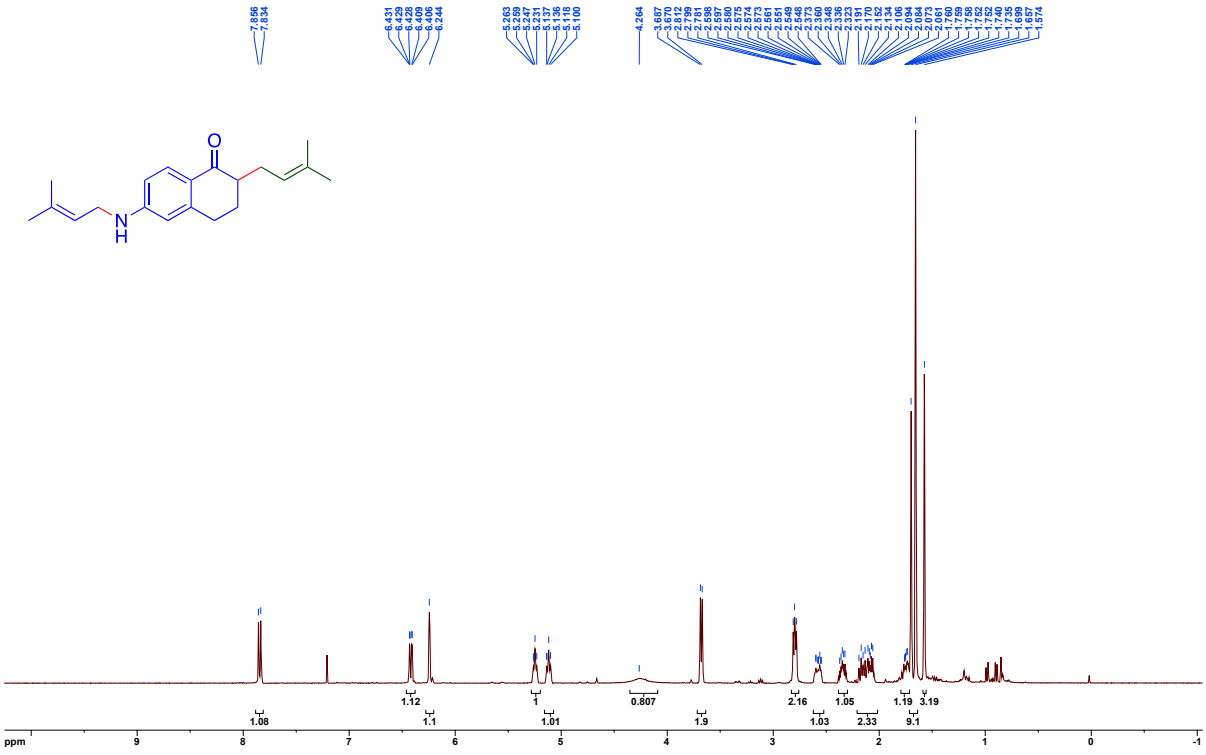
^{1}H NMR spectrum of 6-amino-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2j,** 400 MHz, $CDCl_3$) :



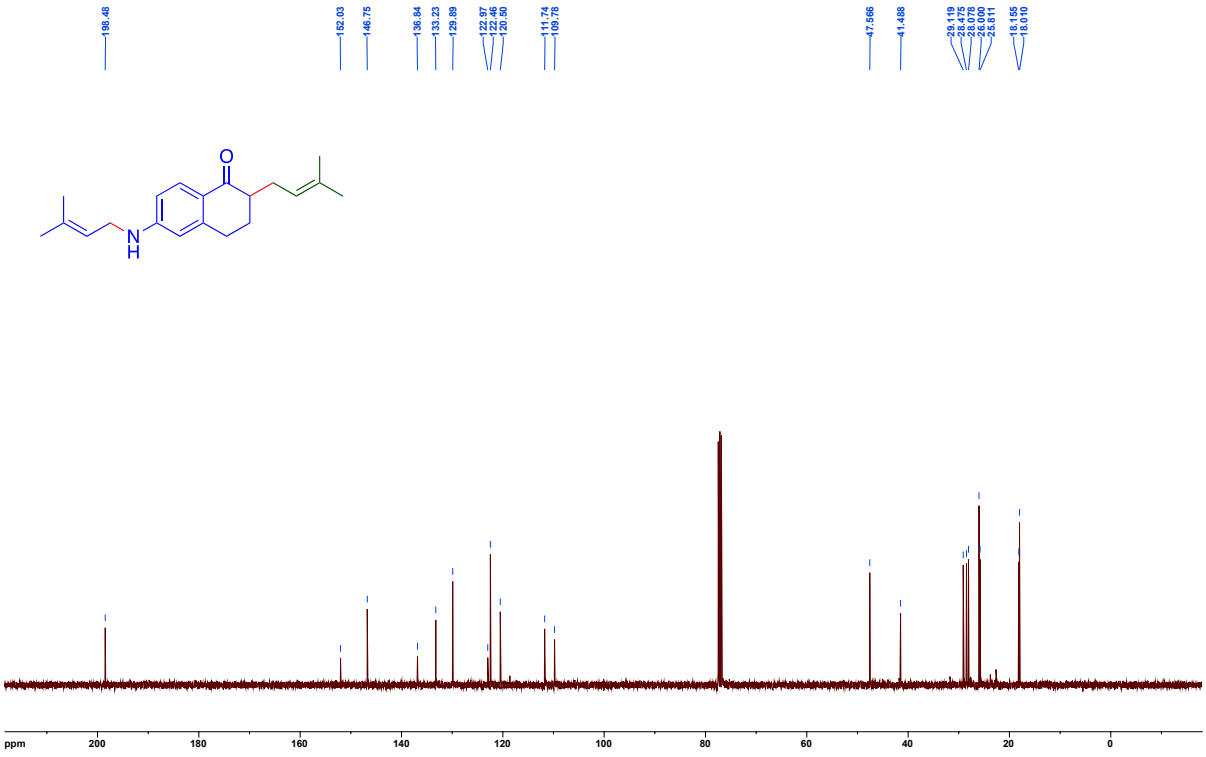
^{13}C NMR spectrum of 6-amino-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2j,** 101 MHz, $CDCl_3$):



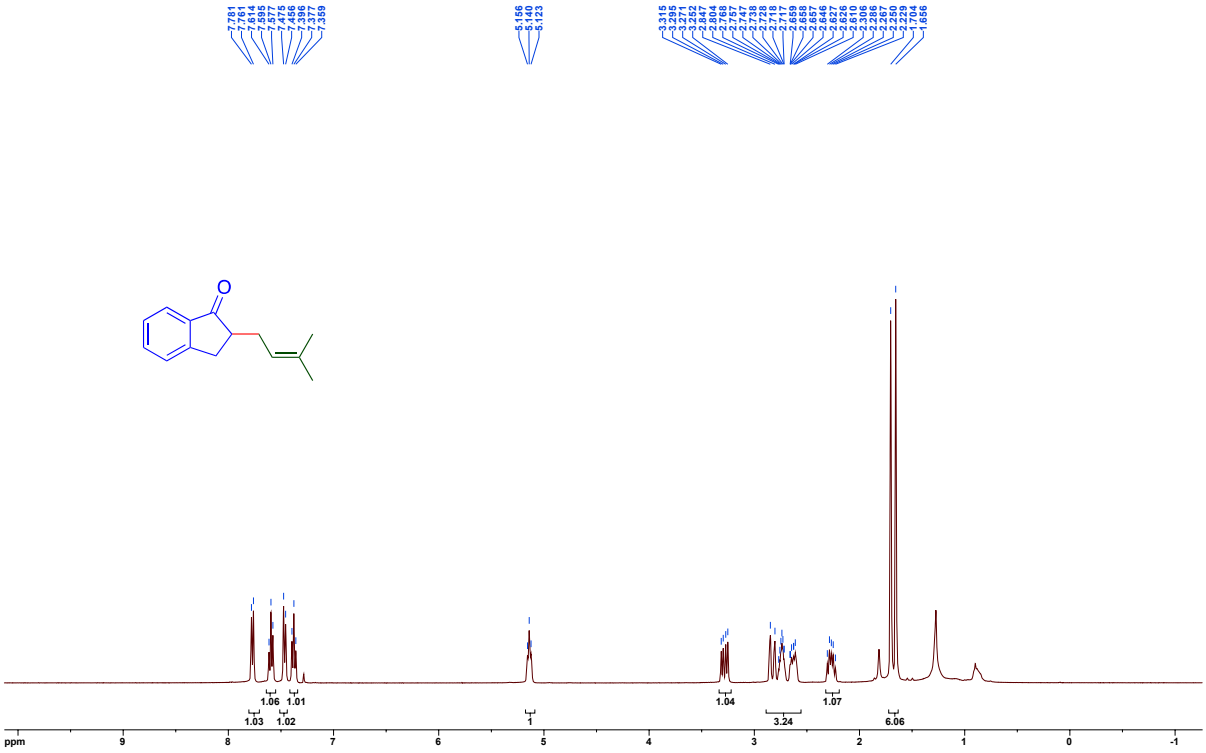
^{1}H NMR spectrum of 2-(3-methylbut-2-en-1-yl)-6-((3-methylbut-2-en-1-yl)amino)-3,4-dihydronaphthalen-1(2H)-one **(2j',** 400 MHz, $CDCl_3$) :



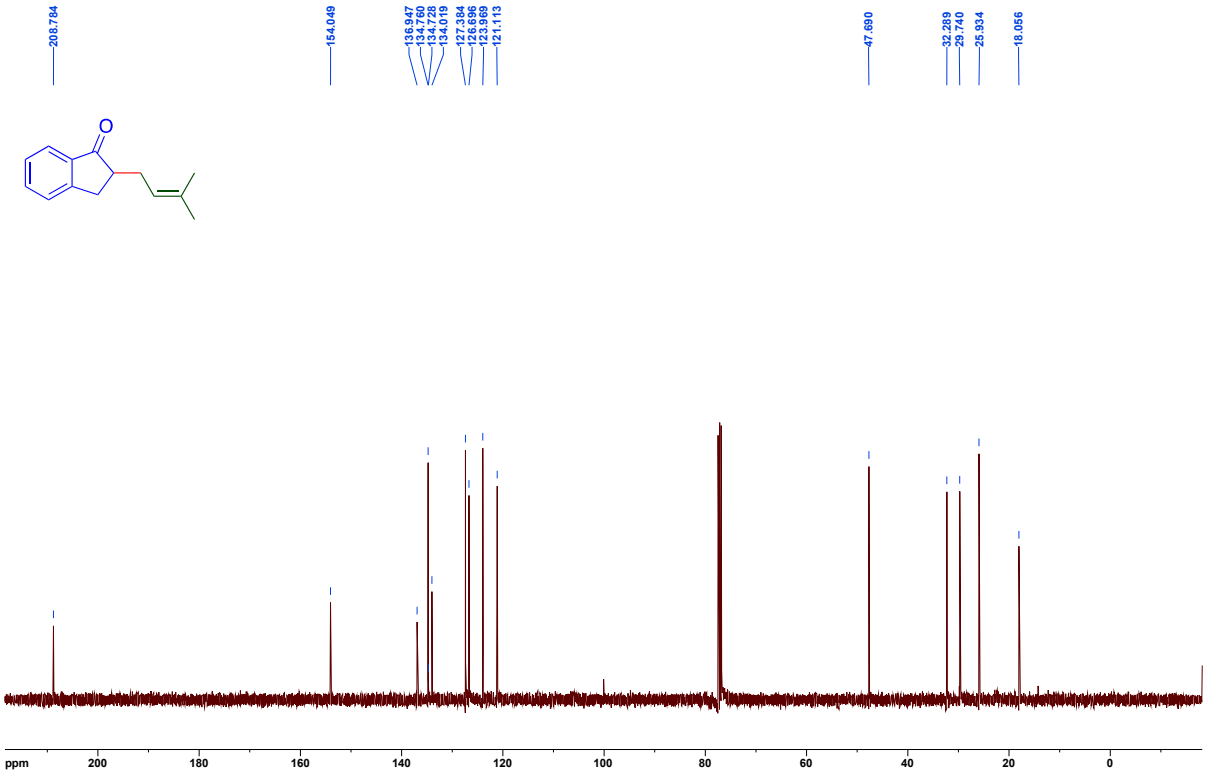
^{13}C NMR spectrum of 2-(3-methylbut-2-en-1-yl)-6-((3-methylbut-2-en-1-yl)amino)-3,4-dihydronaphthalen-1(2H)-one **(2j',** 101 MHz, $CDCl_3$):



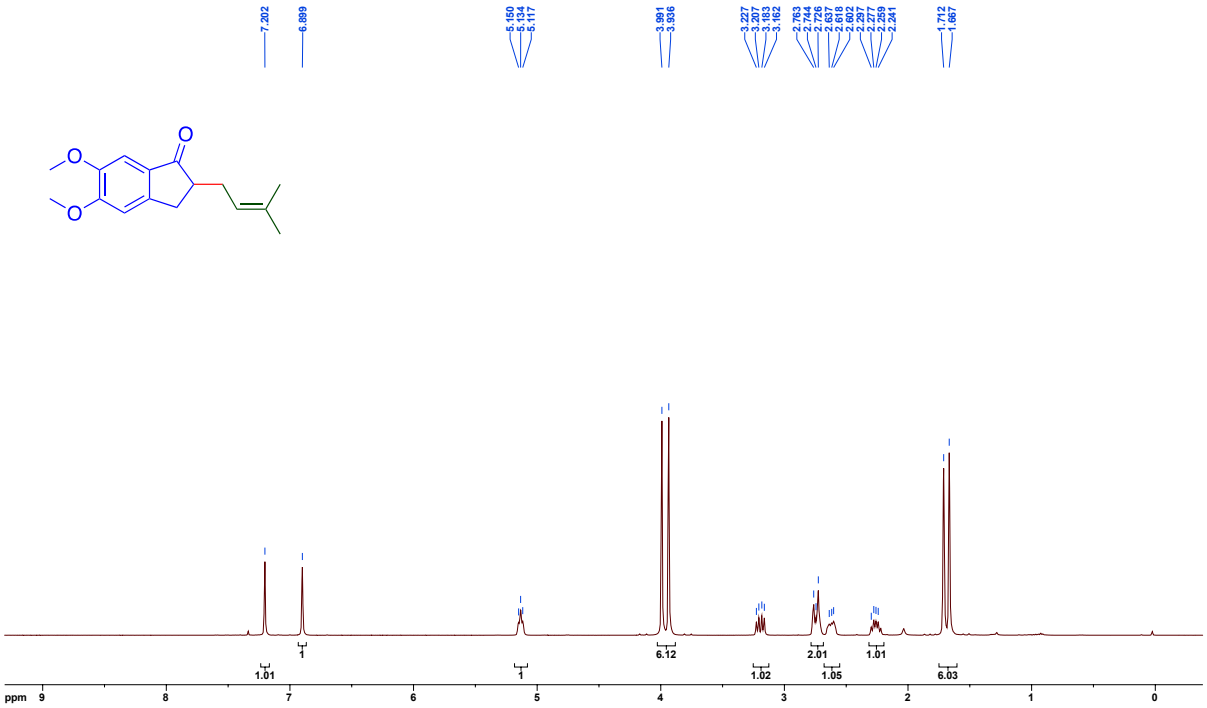
^{1}H NMR spectrum of 2-(3-methylbut-2-en-1-yl)-2,3-dihydro-inden-1-one **(2k,** 400 MHz, $CDCl_3$):



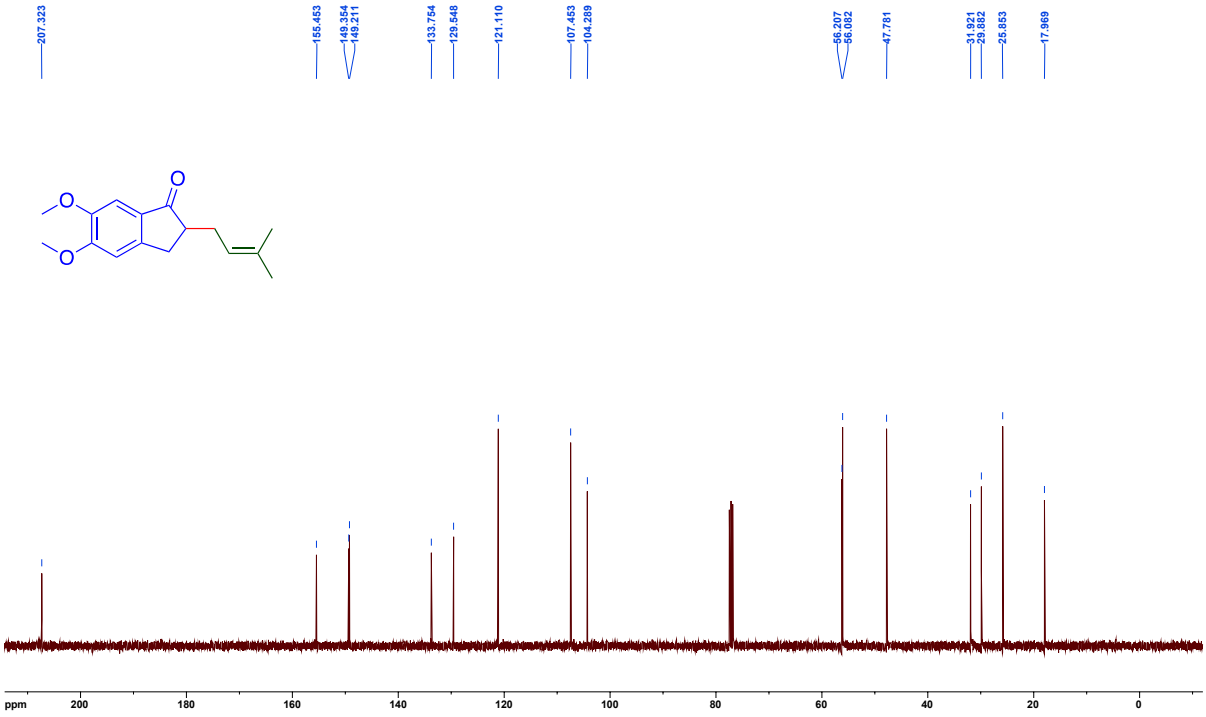
^{13}C NMR spectrum of 2-(3-methylbut-2-en-1-yl)-2,3-dihydro-inden-1-one **(2k,** 101 MHz, $CDCl_3$):



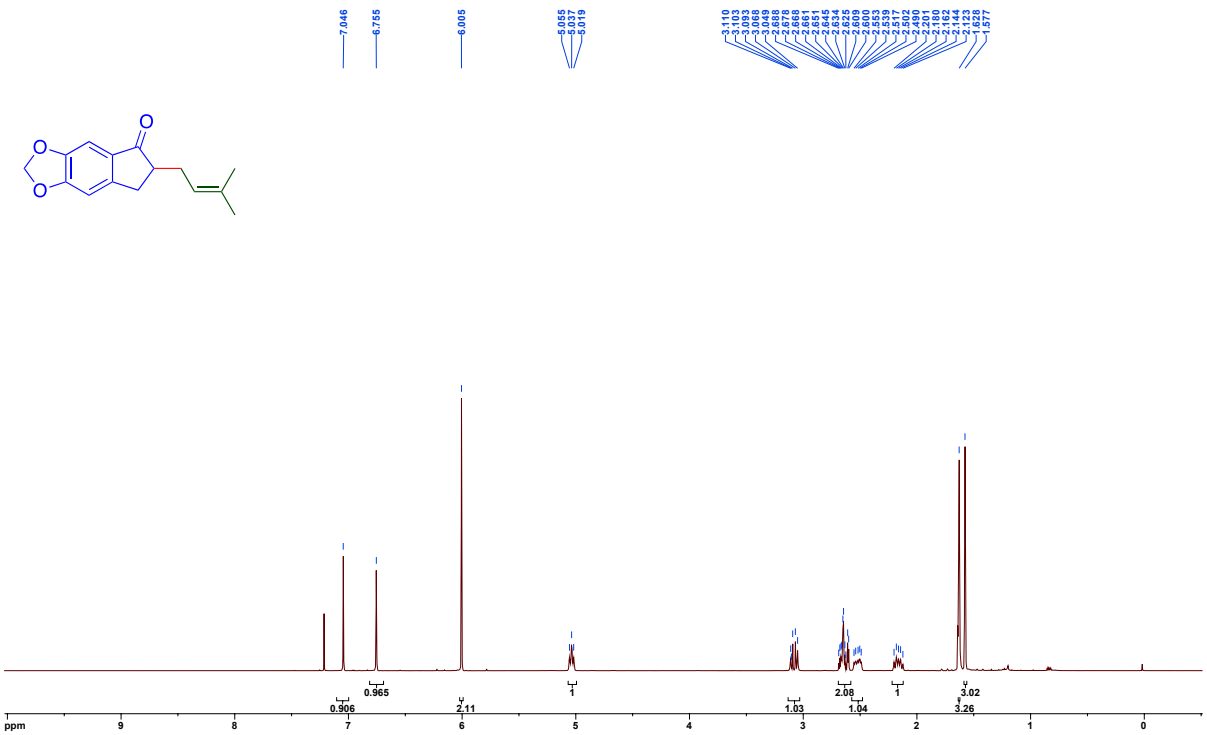
^{1}H NMR spectrum of 5,6-dimethoxy-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1H-inden-1-one **(2l,** 400 MHz, $CDCl_3$) :



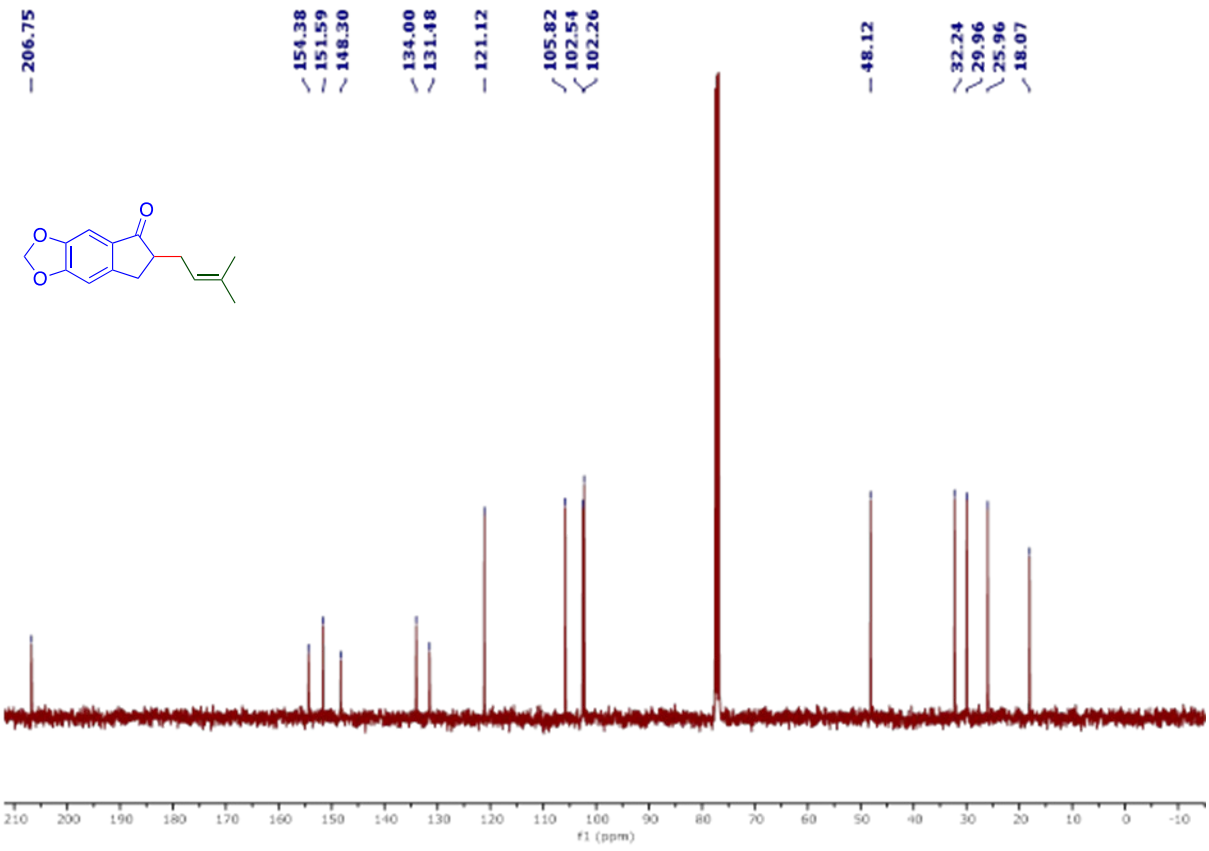
^{13}C NMR spectrum of 5,6-dimethoxy-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1H-inden-1-one **(2l,** 101 MHz, $CDCl_3$):


207.323
155.453
149.354
149.211
133.754
129.548
121.110
107.453
104.289
66.207
66.082
47.781
31.921
29.882
25.853
17.969
O
O
O
ppm
200
180
160
140
120
100
80
60
40
20
0

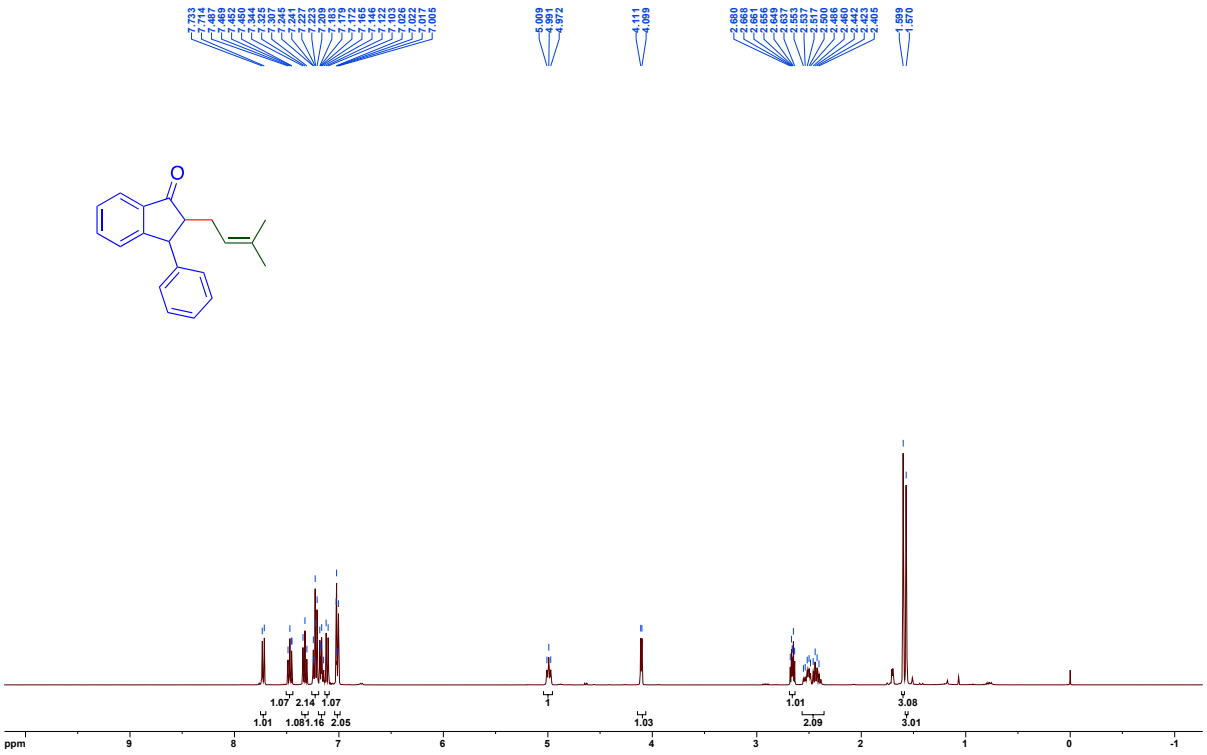
^{1}H NMR spectrum of 6-(3-methylbut-2-en-1-yl)-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-one **(2m,** 400 MHz, $CDCl_3$) :



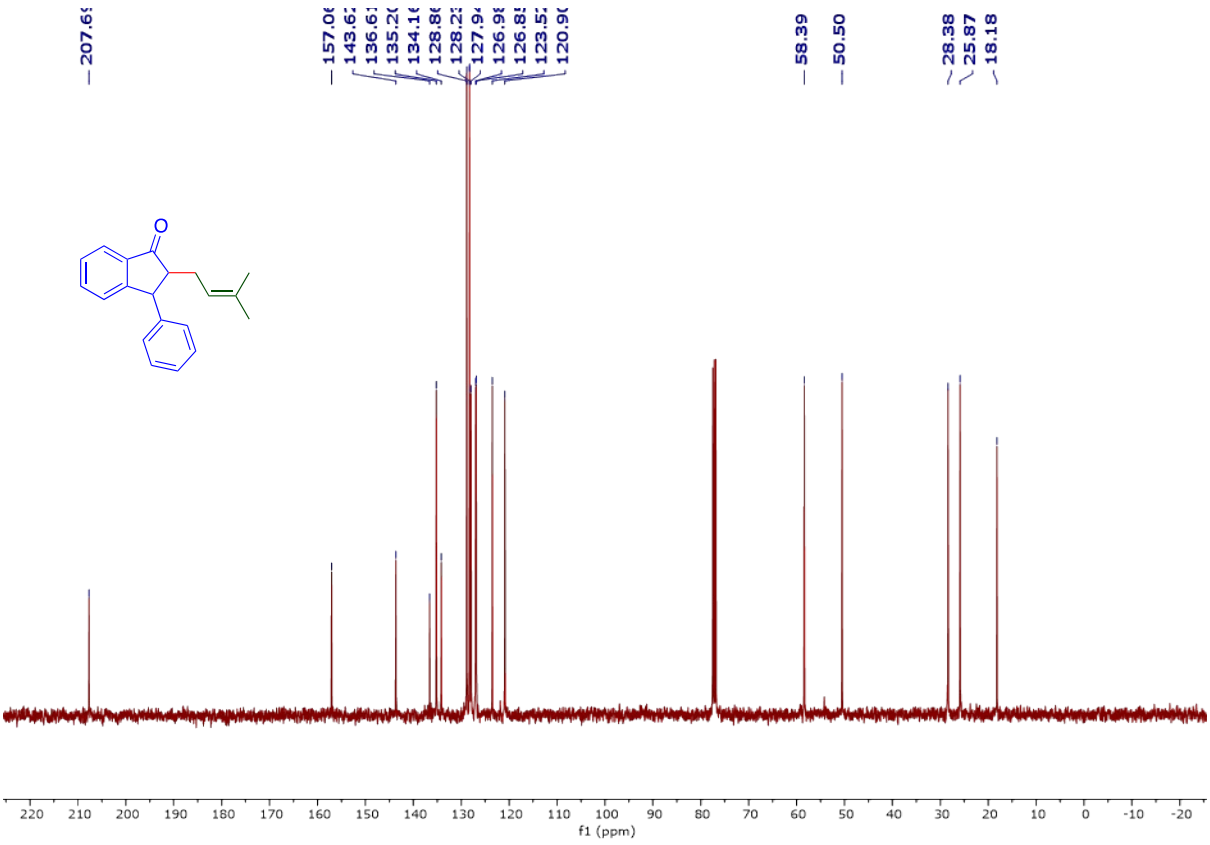
^{13}C NMR spectrum of 6-(3-methylbut-2-en-1-yl)-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-one **(2m,** 101 MHz, $CDCl_3$):



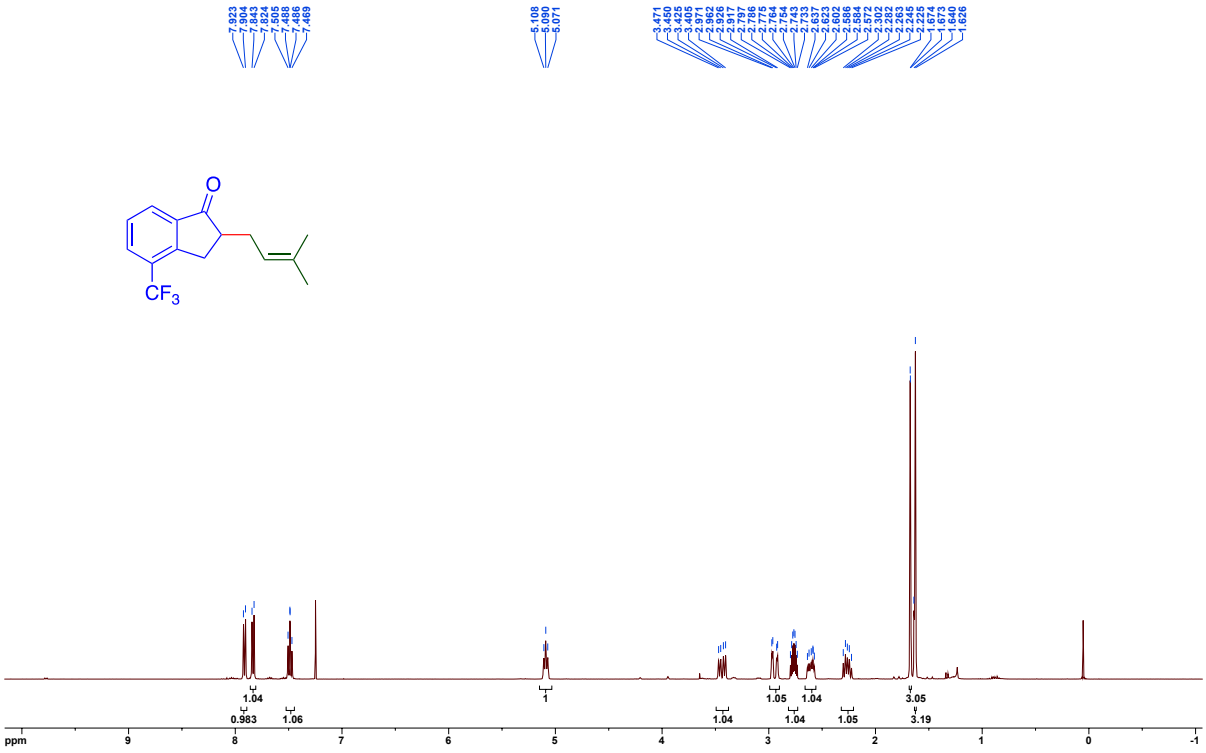
^{1}H NMR spectrum of 2-(3-methylbut-2-en-1-yl)-3-phenyl-2,3-dihydro-1H-inden-1-one **(2n,** 400 MHz, $CDCl_3$) :



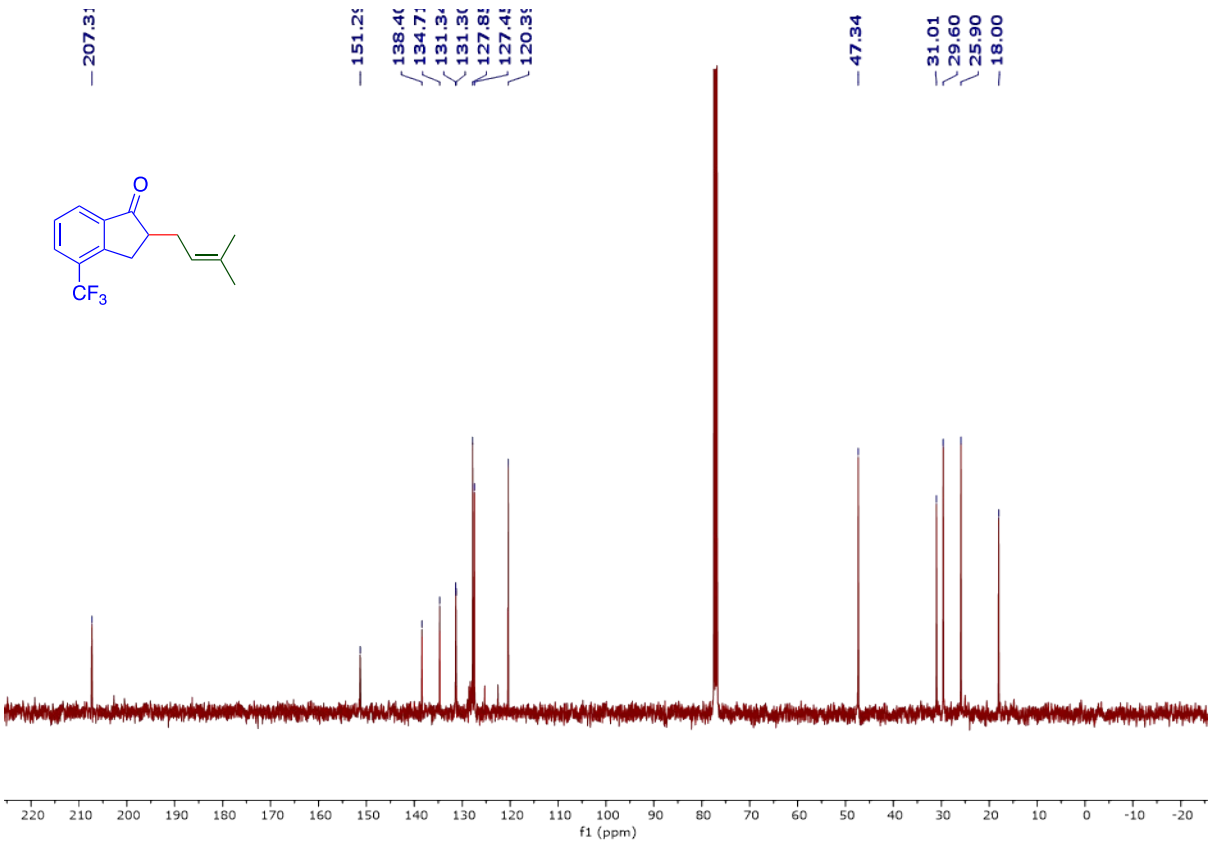
^{13}C NMR spectrum of 2-(3-methylbut-2-en-1-yl)-3-phenyl-2,3-dihydro-1H-inden-1-one **(2n,** 101 MHz, $CDCl_3$):



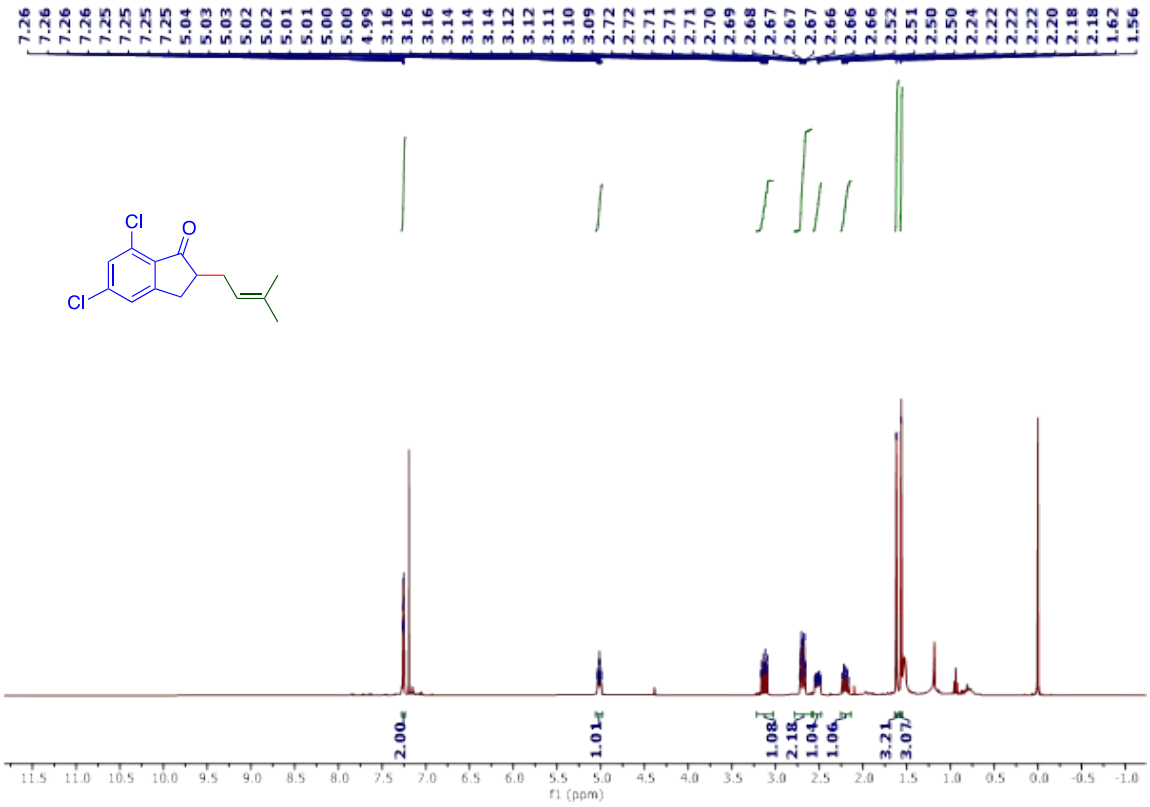
^{1}H NMR spectrum of 2-(3-methylbut-2-en-1-yl)-4-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one **(2o,** 400 MHz, $CDCl_3$) **:**



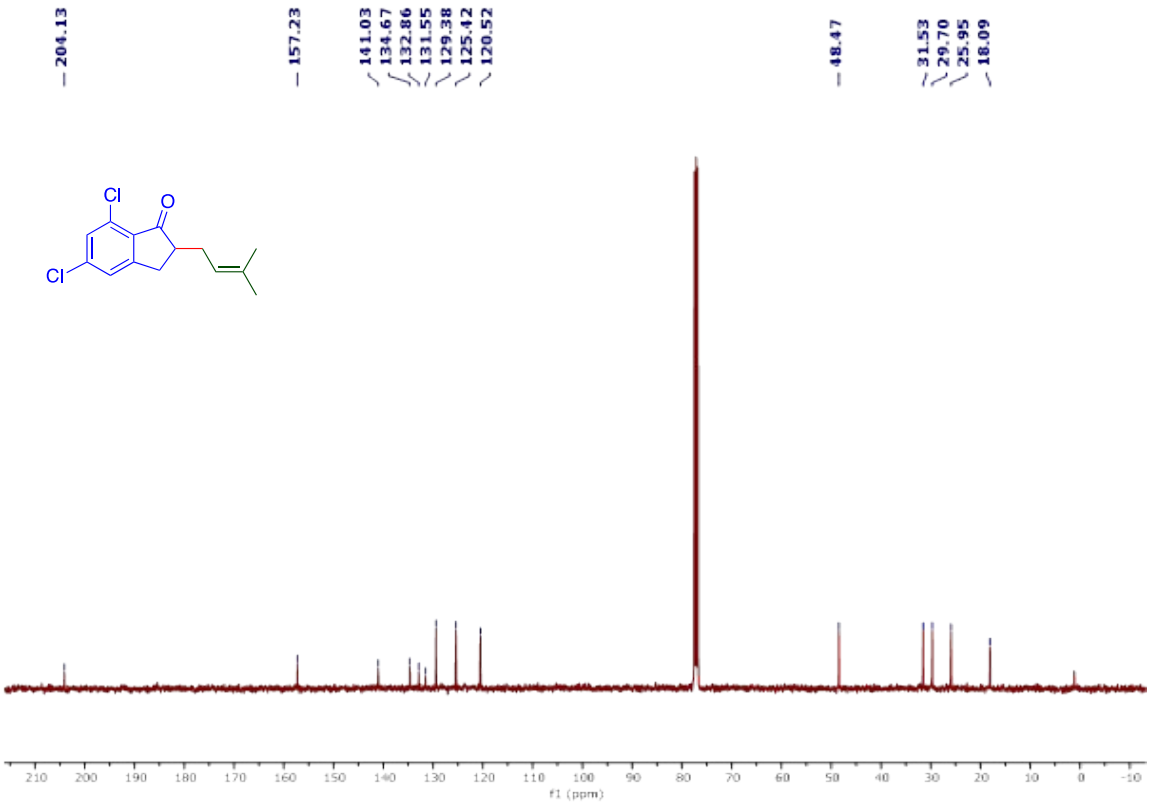
^{13}C NMR spectrum of 2-(3-methylbut-2-en-1-yl)-4-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one **(2o,** 101 MHz, $CDCl_3$):



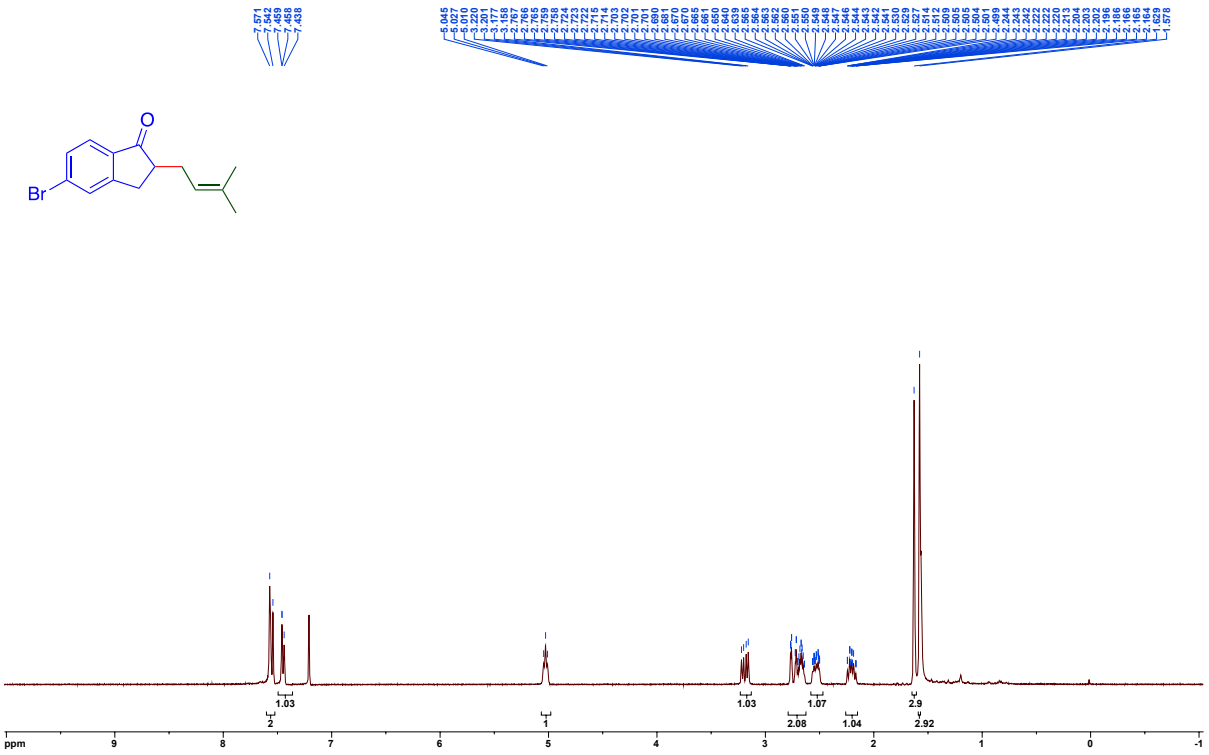
^{1}H NMR spectrum of 5,7-Dichloro-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1*H*-inden-1-one **(2p,** 101 MHz, $CDCl_3$):



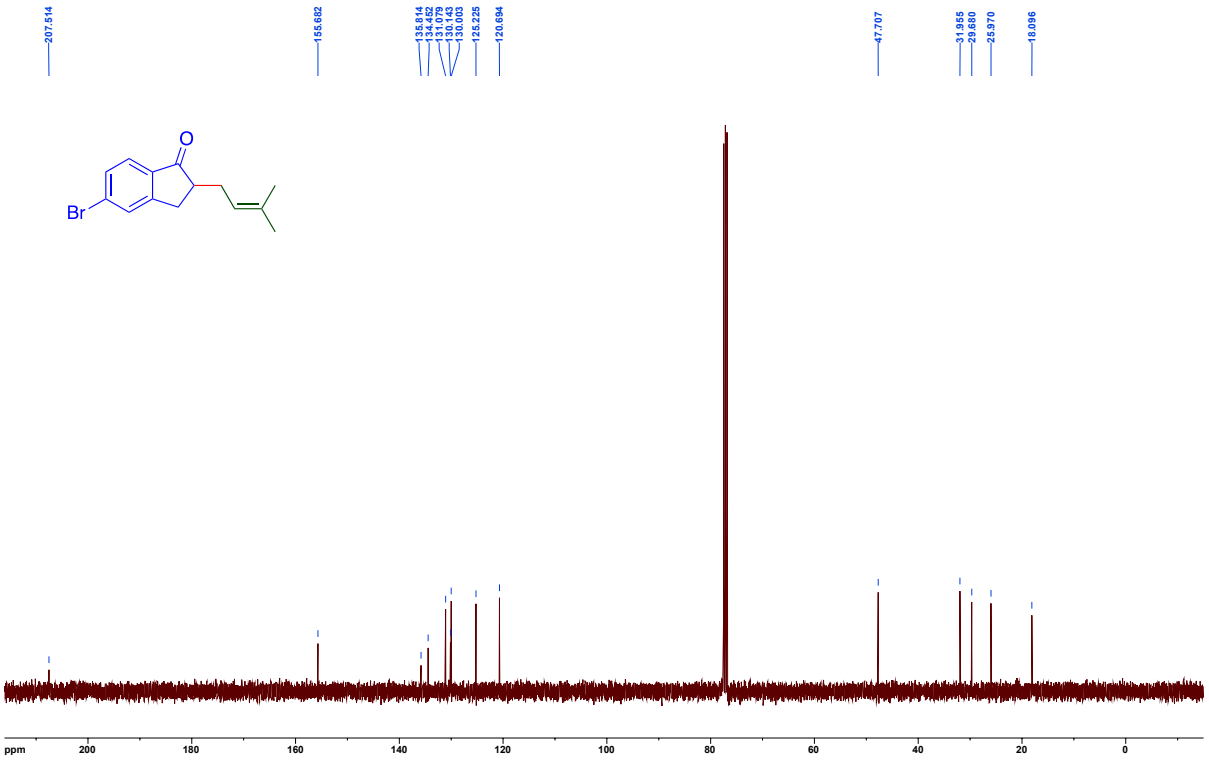
^{13}C NMR spectrum of 5,7-Dichloro-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1*H*-inden-1-one **(2p,** 101 MHz, $CDCl_3$):



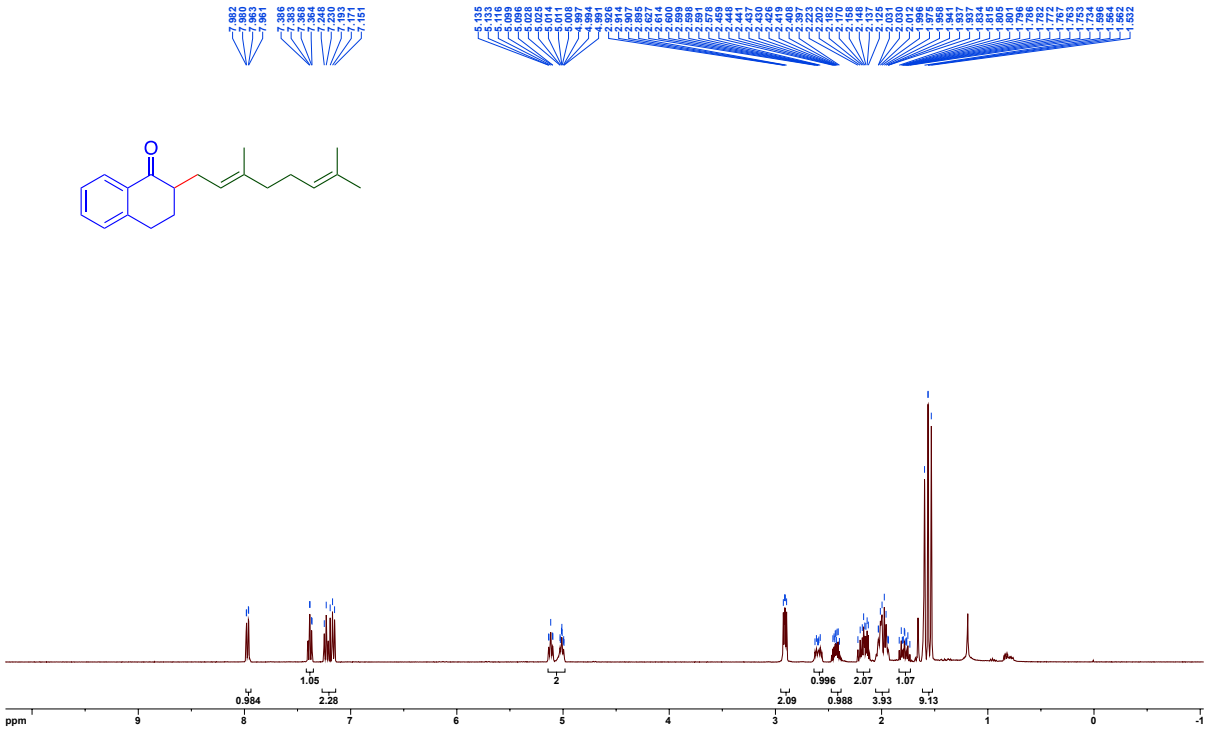
^{1}H NMR spectrum of 5-bromo-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1H-inden-1-one **(2q,** 400 MHz, $CDCl_3$) :



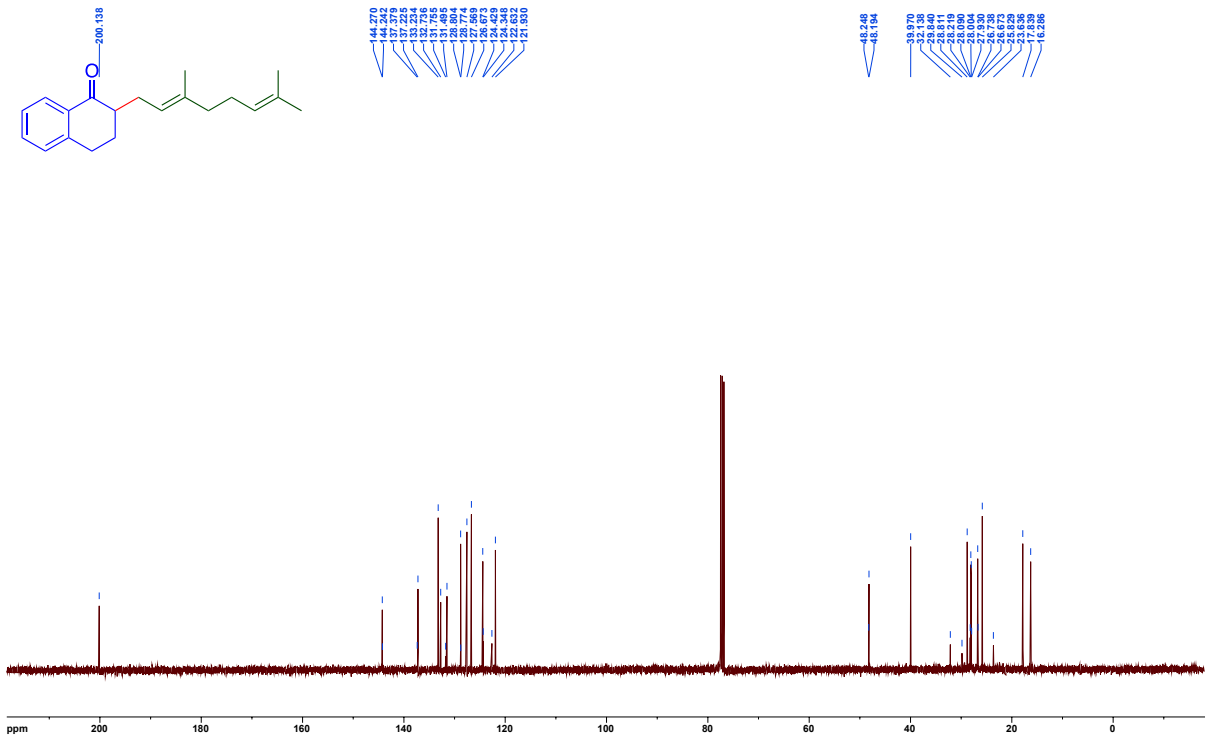
^{13}C NMR spectrum of 5-bromo-2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1H-inden-1-one **(2q,** 101 MHz, $CDCl_3$):



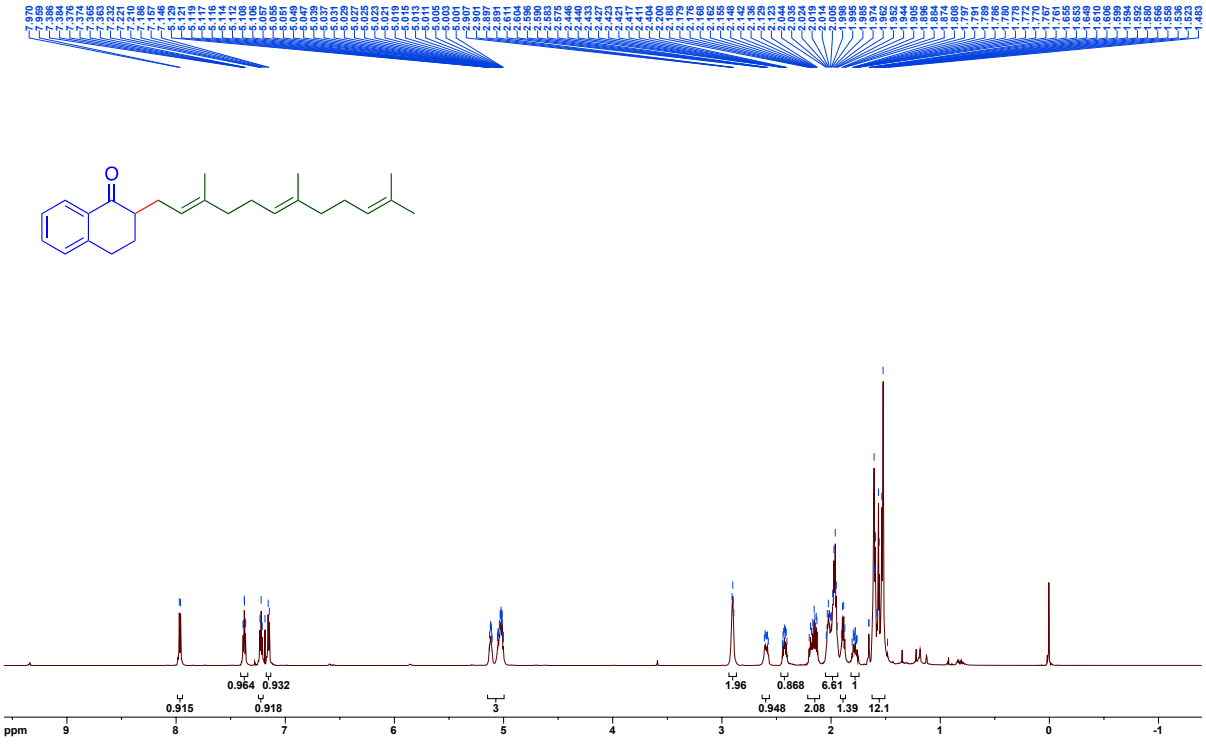
^{1}H NMR spectrum of (*E*)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2r,** 400 MHz, $CDCl_3$) :



^{13}C NMR spectrum of (*E*)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2r,** 101 MHz, $CDCl_3$):

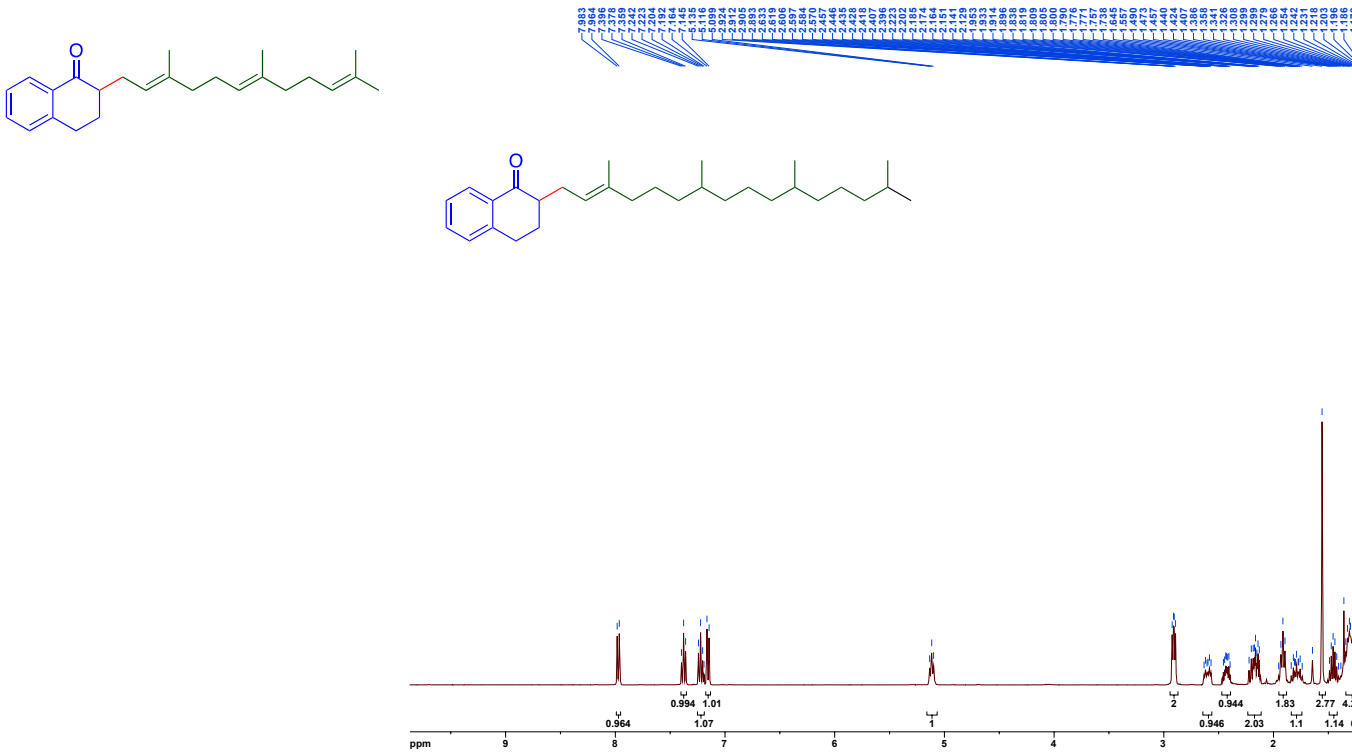


^{1}H NMR spectrum of 2-((2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2s,** 400 MHz, $CDCl_3$) :

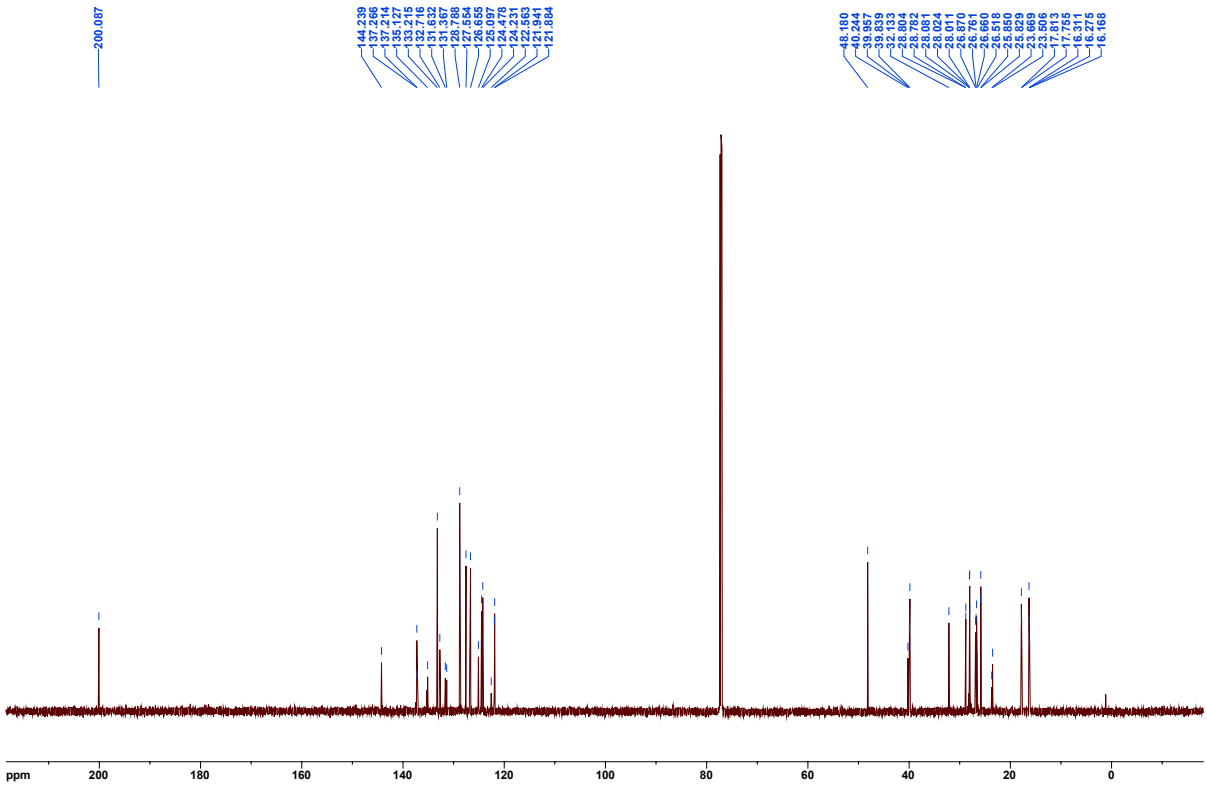


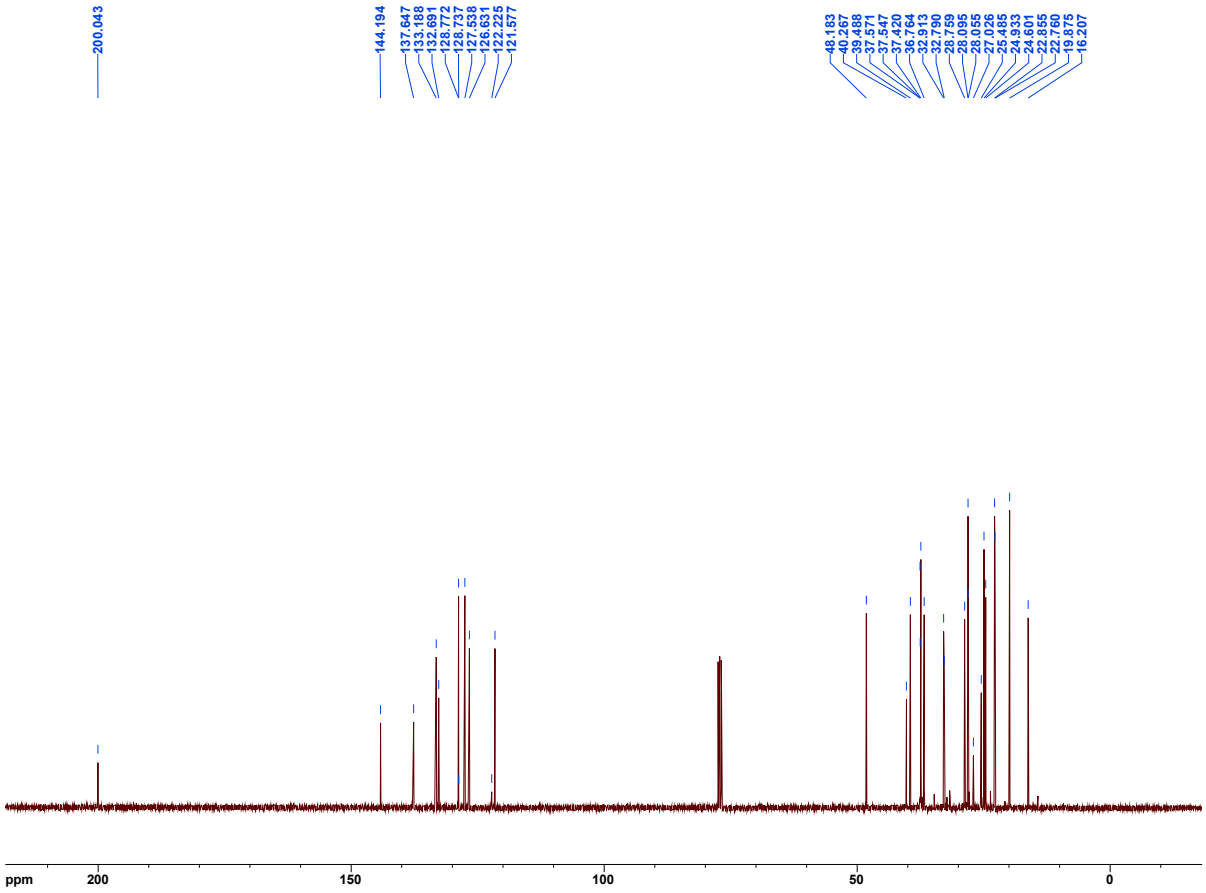
^{13}C NMR spectrum of 2-((2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2s,** 101 MHz, $CDCl_3$):

^{1}H NMR spectrum of (*E*)-2-(3,7,11,15-tetramethylhexadec-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2t,** 400 MHz, $CDCl_3$) :

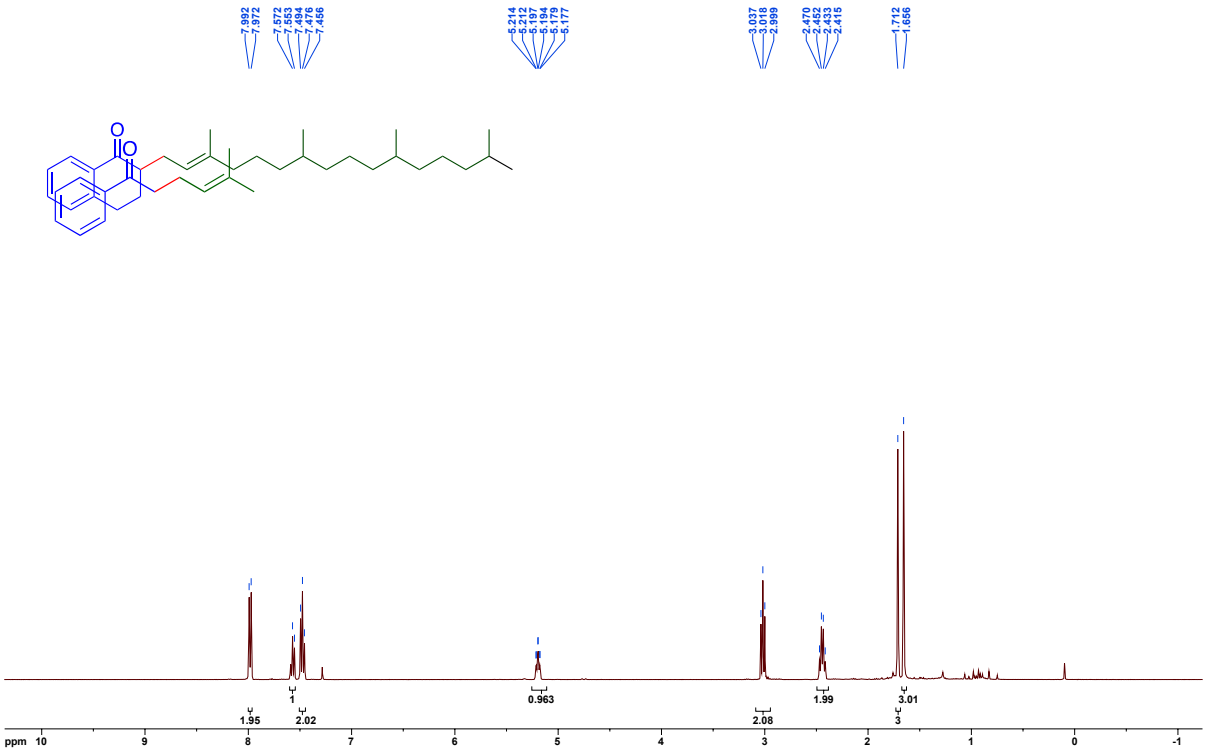


^{13}C NMR spectrum of (*E*)-2-(3,7,11,15-tetramethylhexadec-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one **(2t,** 101 MHz, $CDCl_3$):

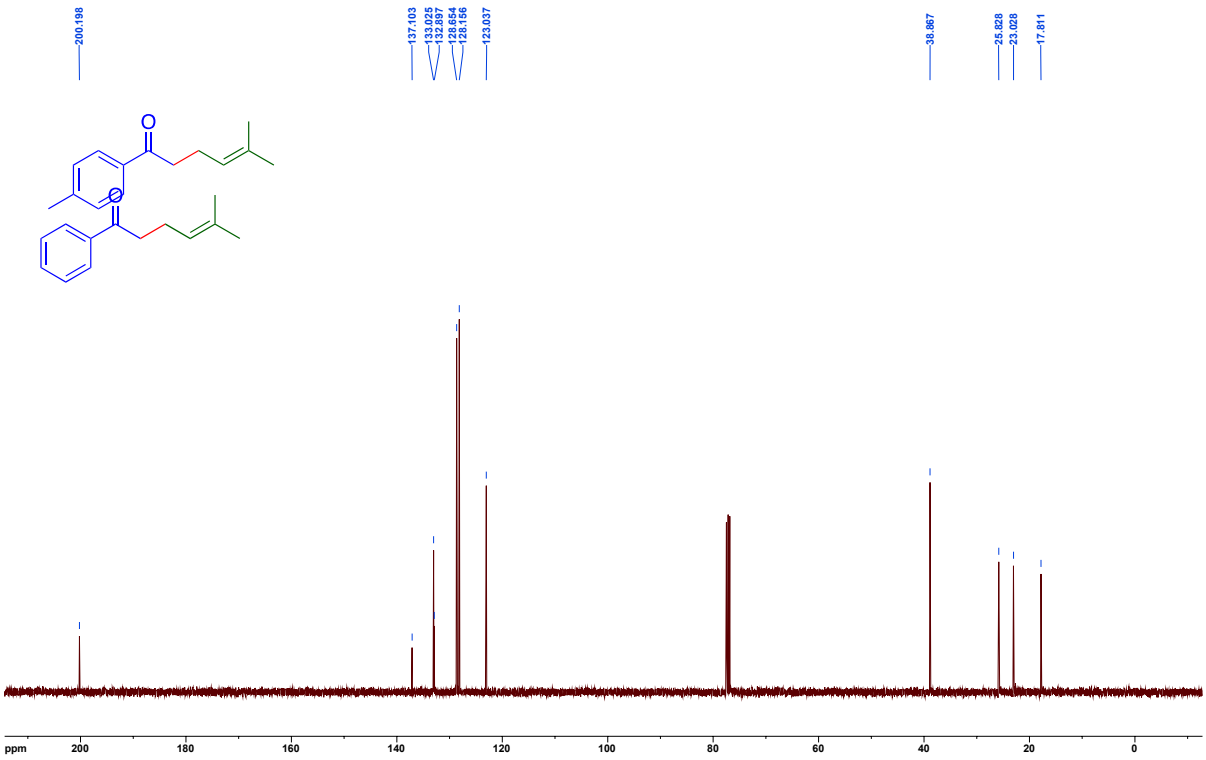




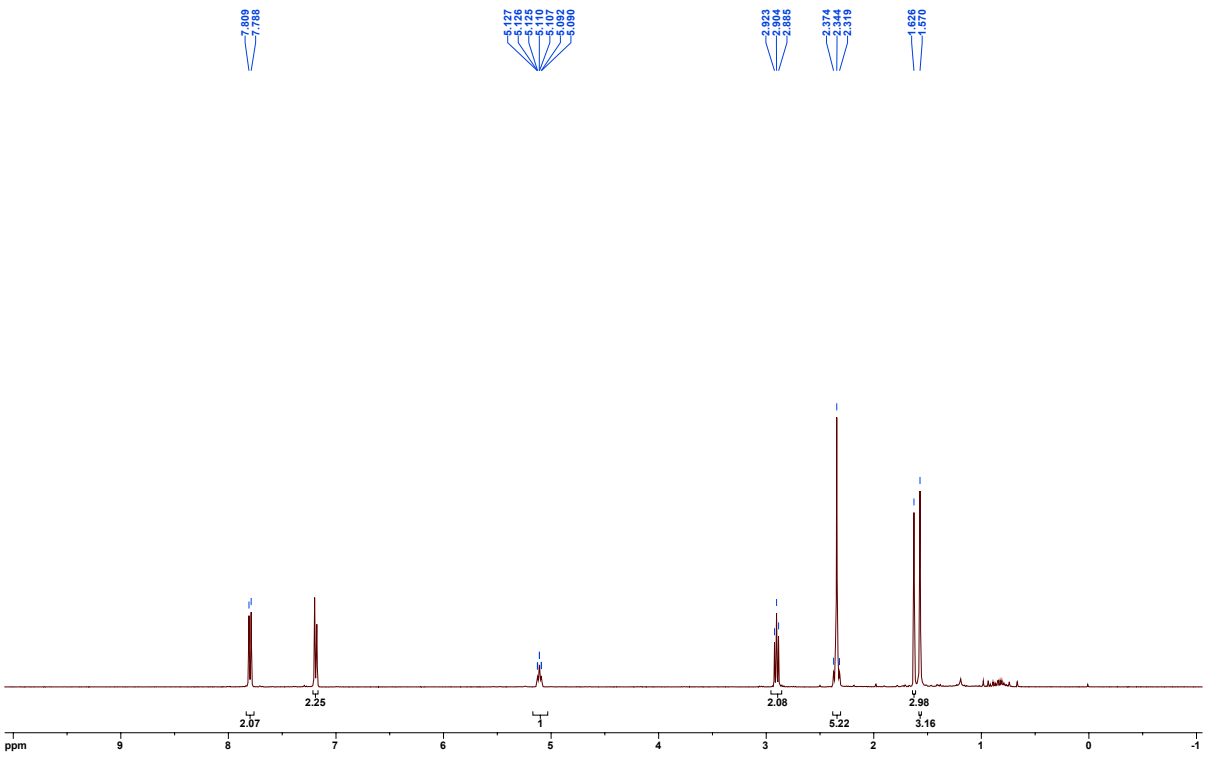
^{1}H NMR spectrum of 5-methyl-1-phenylhex-4-en-1-one (**3a**, 400 MHz, $CDCl_3$) :



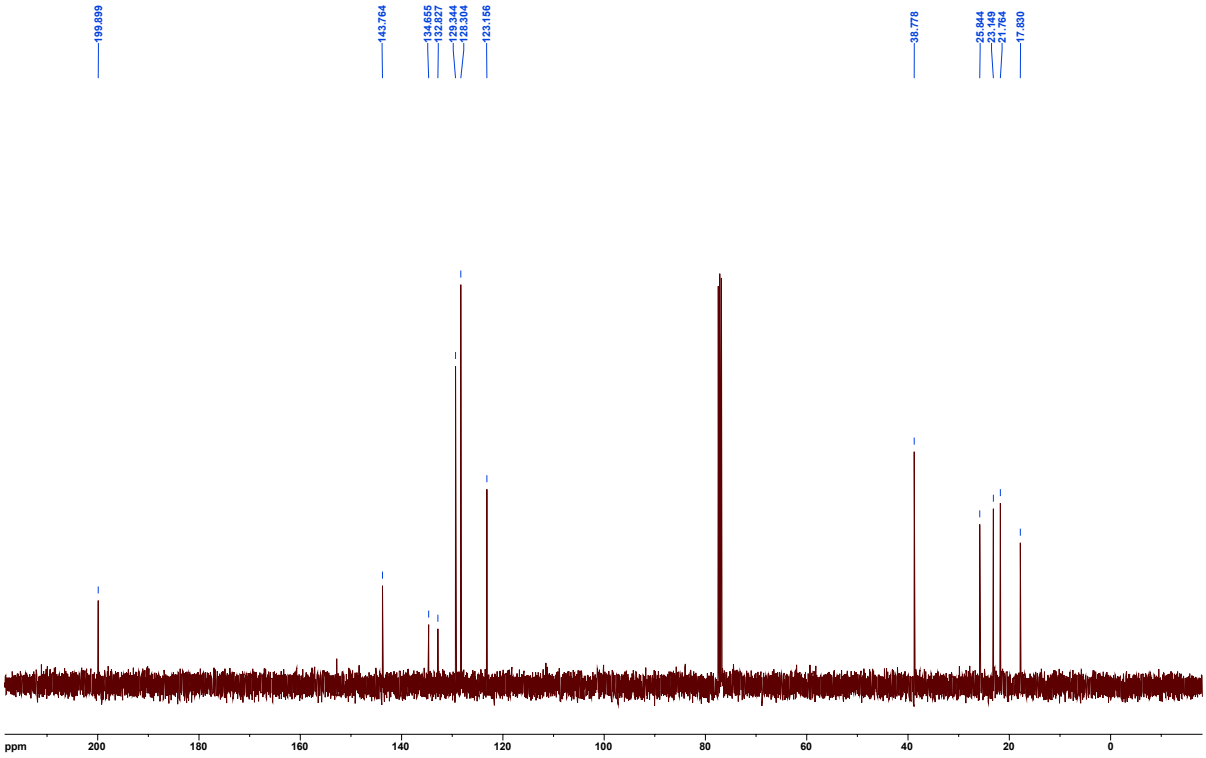
^{13}C NMR spectrum of 5-methyl-1-phenylhex-4-en-1-one (**3a**, 101 MHz, $CDCl_3$):



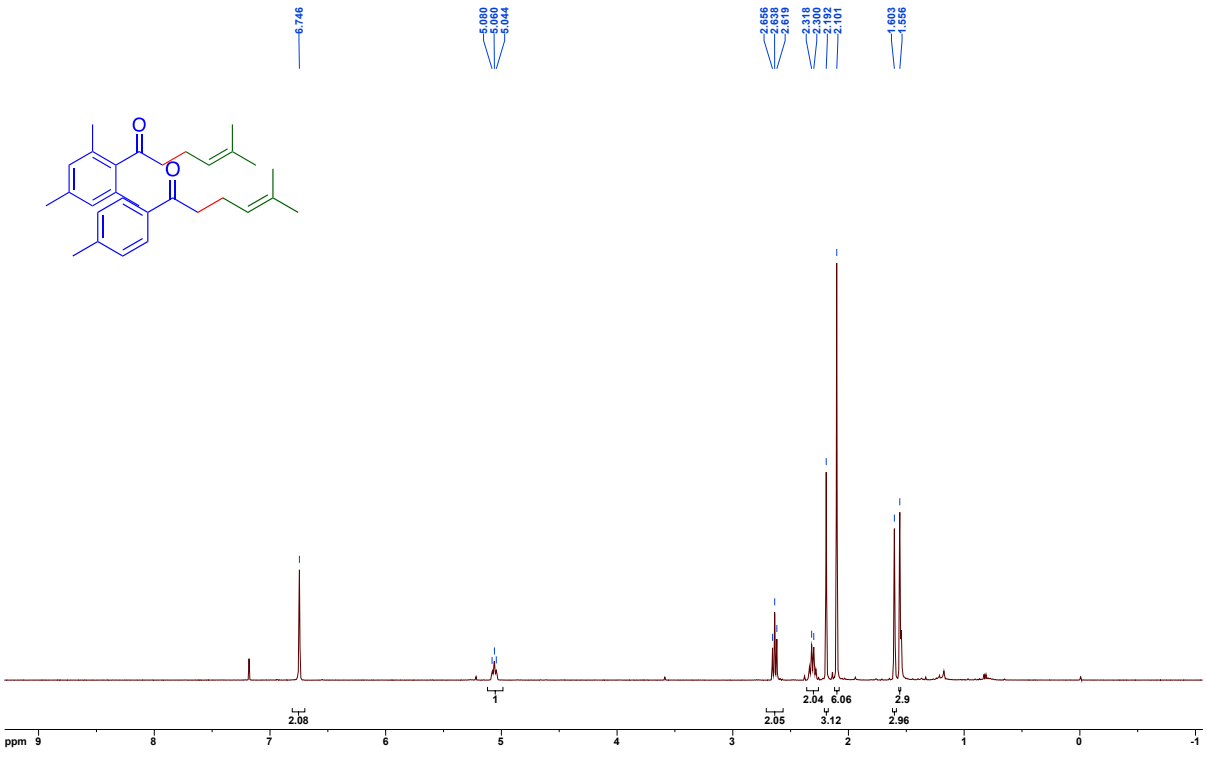
^{1}H NMR spectrum of 5-methyl-1-(p-tolyl)hex-4-en-1-one (**3b**, 400 MHz, $CDCl_3$) :



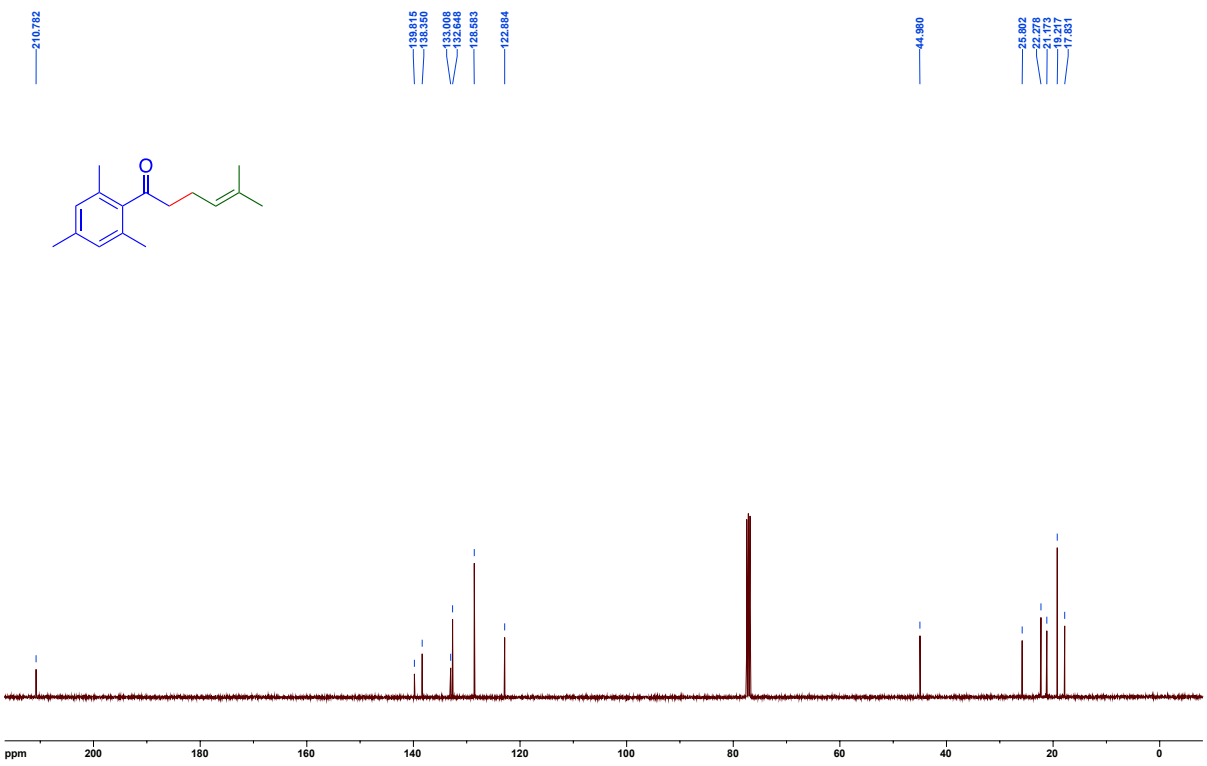
^{13}C NMR spectrum of 5-methyl-1-(p-tolyl)hex-4-en-1-one (**3b,** 101 MHz, $CDCl_3$):



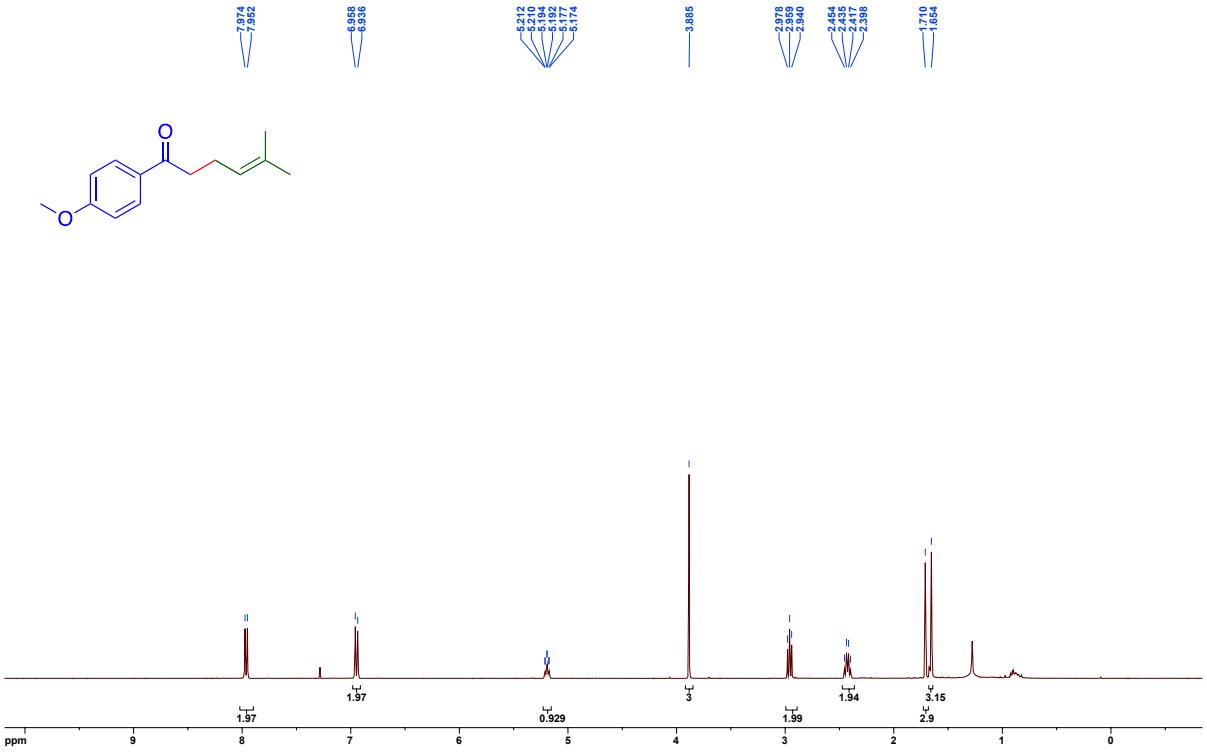
^{1}H NMR spectrum of 1-mesityl-5-methylhex-4-en-1-one (**3c**, 400 MHz, $CDCl_3$) :



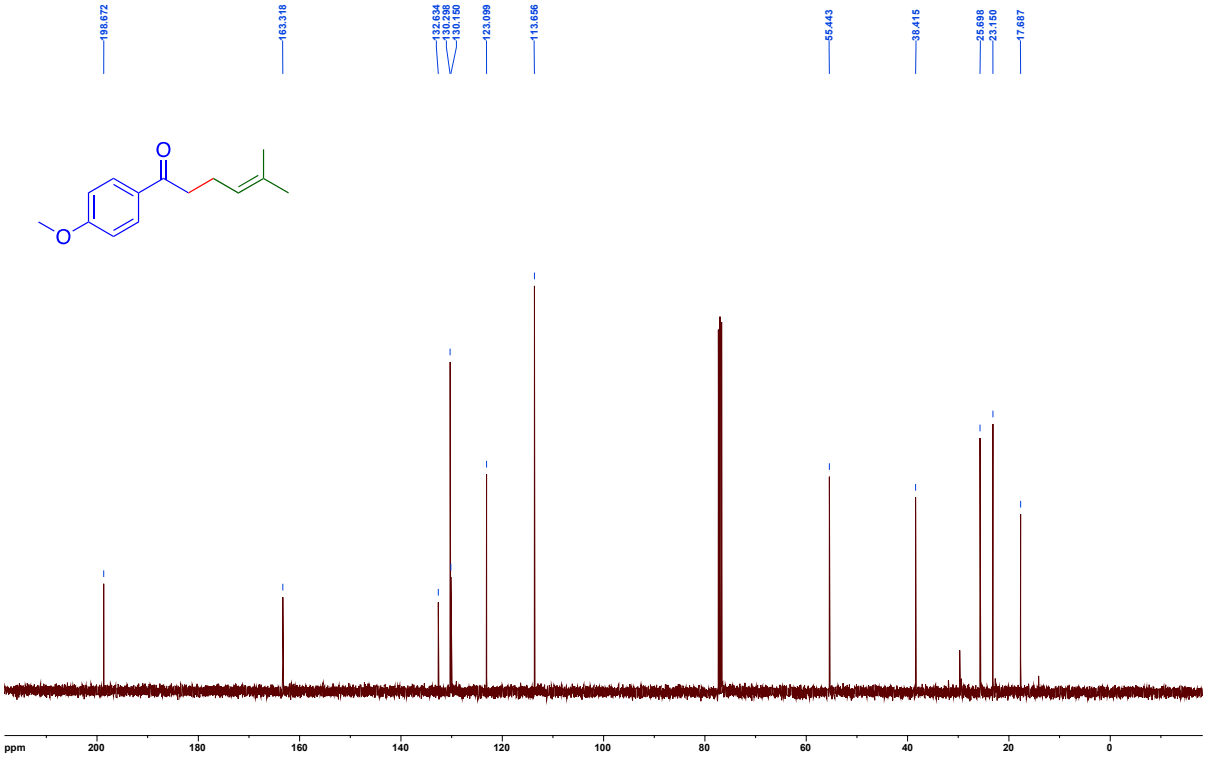
^{13}C NMR spectrum of 1-mesityl-5-methylhex-4-en-1-one (**3c**, 101 MHz, $CDCl_3$):



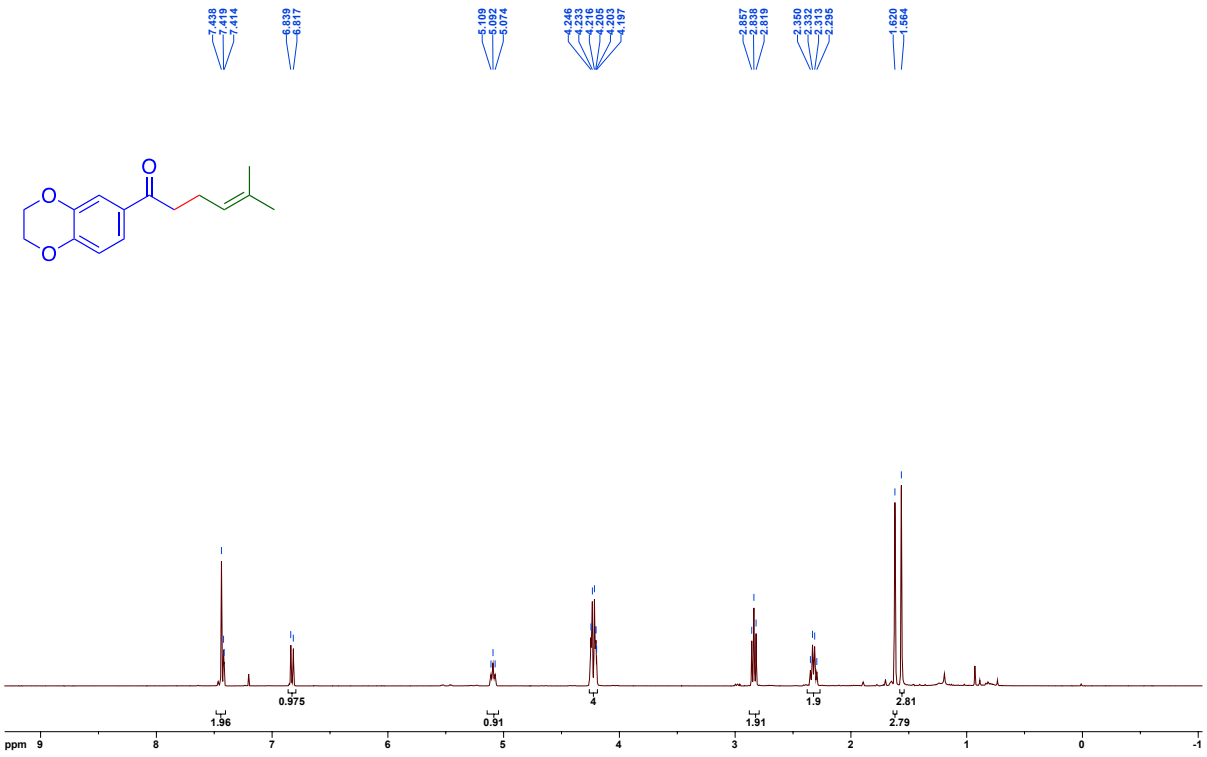
^{1}H NMR spectrum of 1-(4-methoxyphenyl)-5-methylhex-4-en-1-one (**3d**, 400 MHz, $CDCl_3$) :



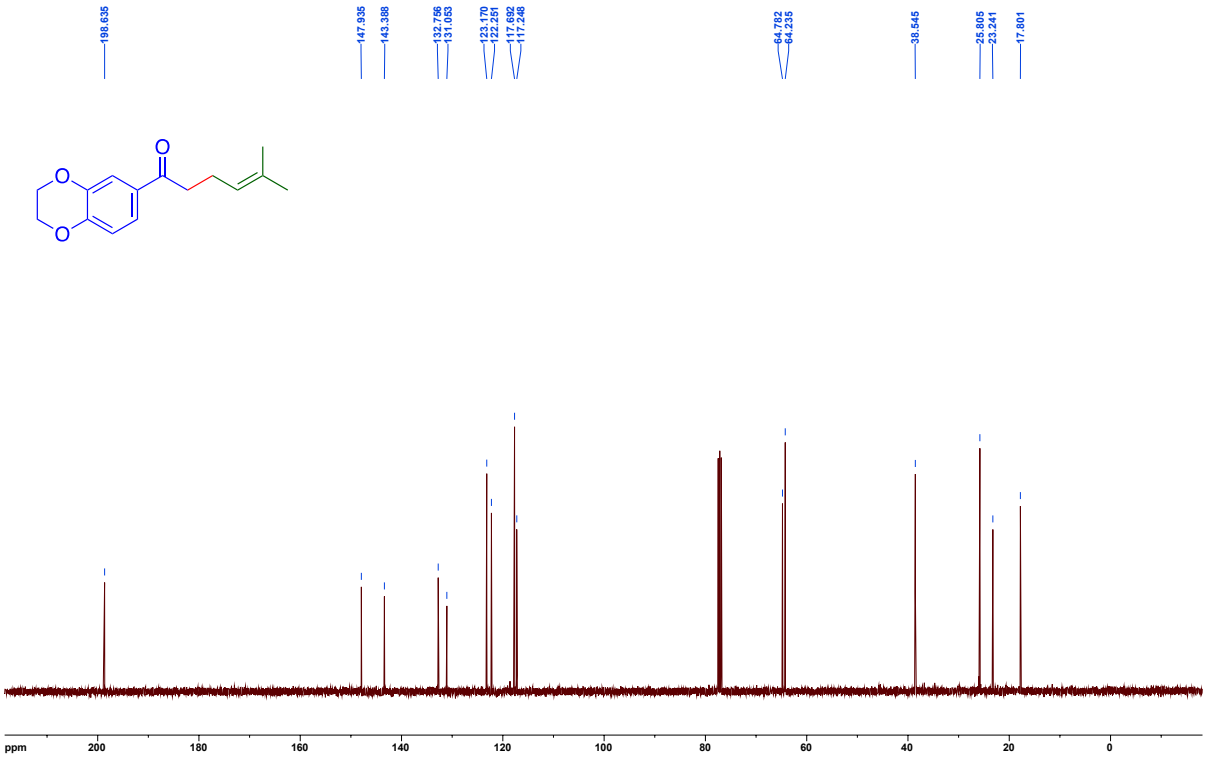
^{13}C NMR spectrum of 1-(4-methoxyphenyl)-5-methylhex-4-en-1-one (**3d**, 101 MHz, $CDCl_3$):



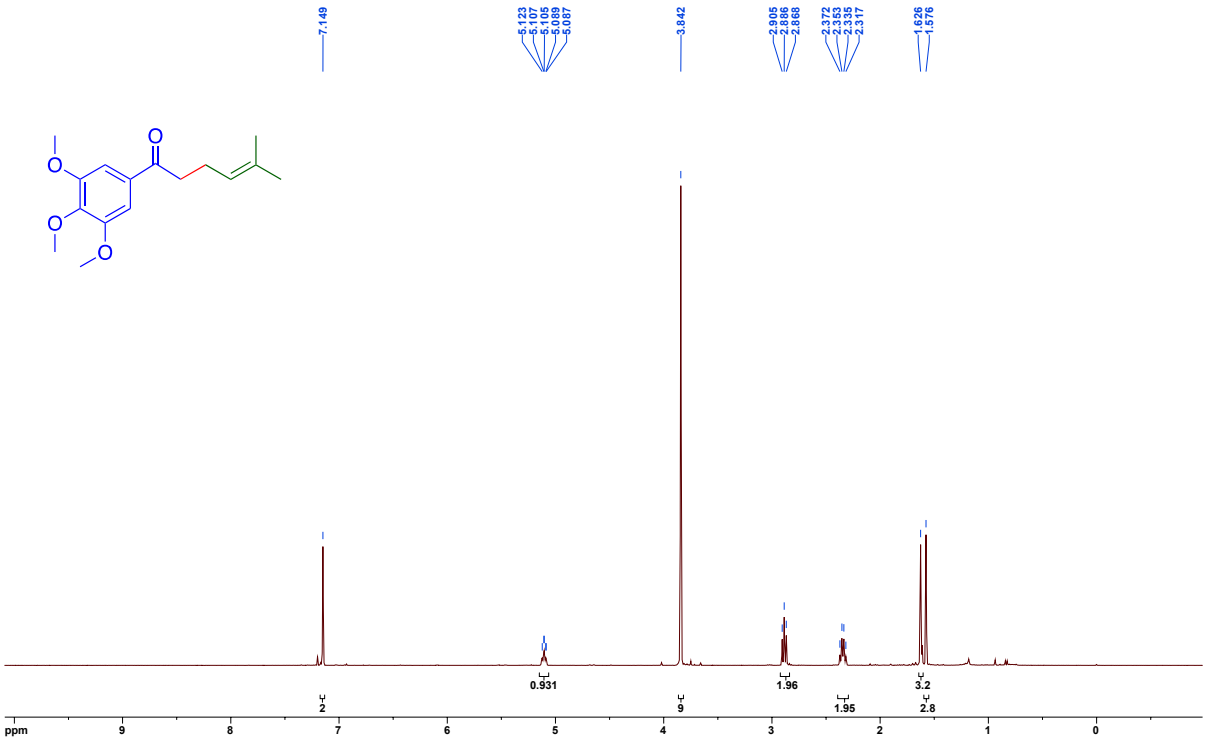
^{1}H NMR spectrum of 1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-methylhex-4-en-1-one **(3e,** 400 MHz, $CDCl_3$) :



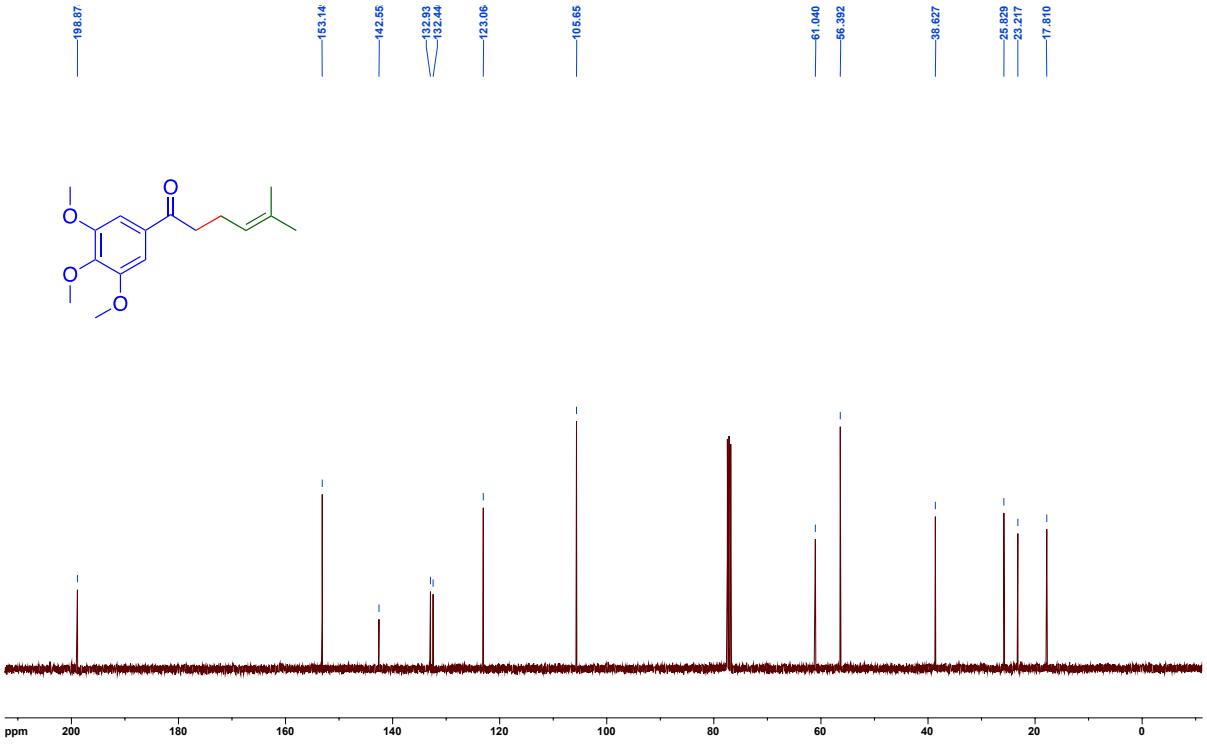
^{13}C NMR spectrum of 1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-methylhex-4-en-1-one **(3e,** 101 MHz, $CDCl_3$):



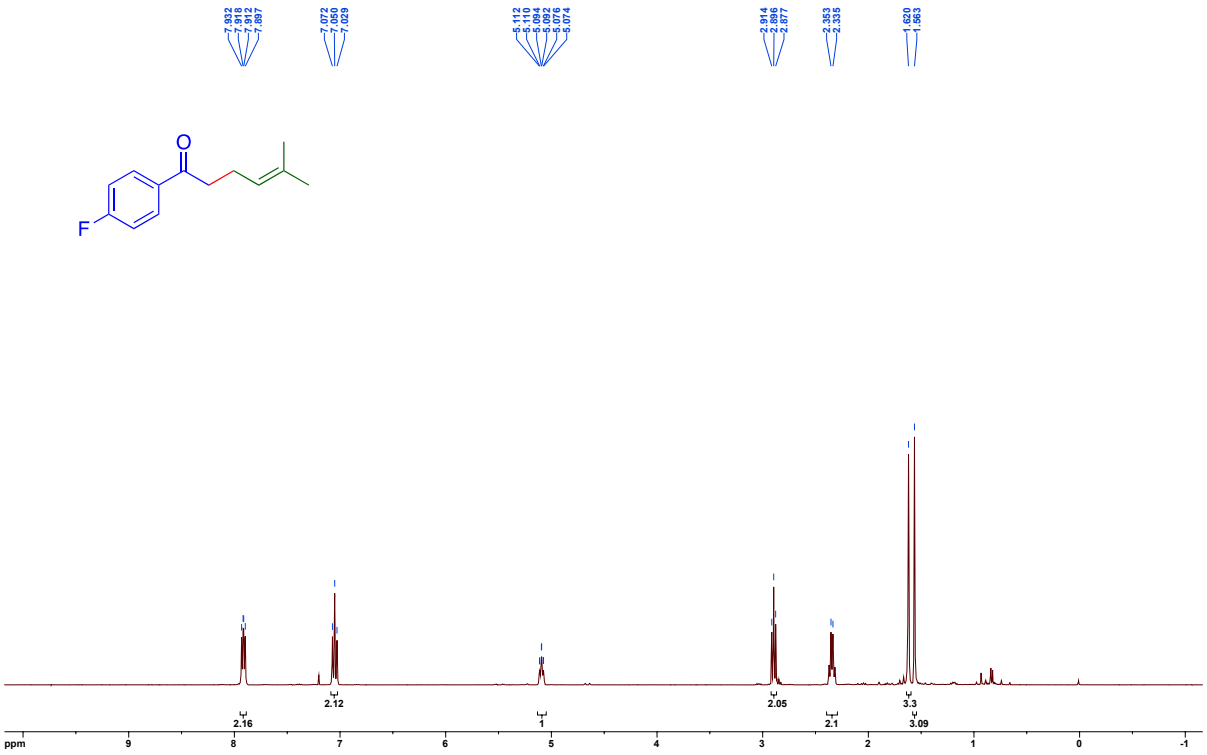
^{1}H NMR spectrum of 5-methyl-1-(3,4,5-trimethoxyphenyl)hex-4-en-1-one **(3f,** 400 MHz, $CDCl_3$) :



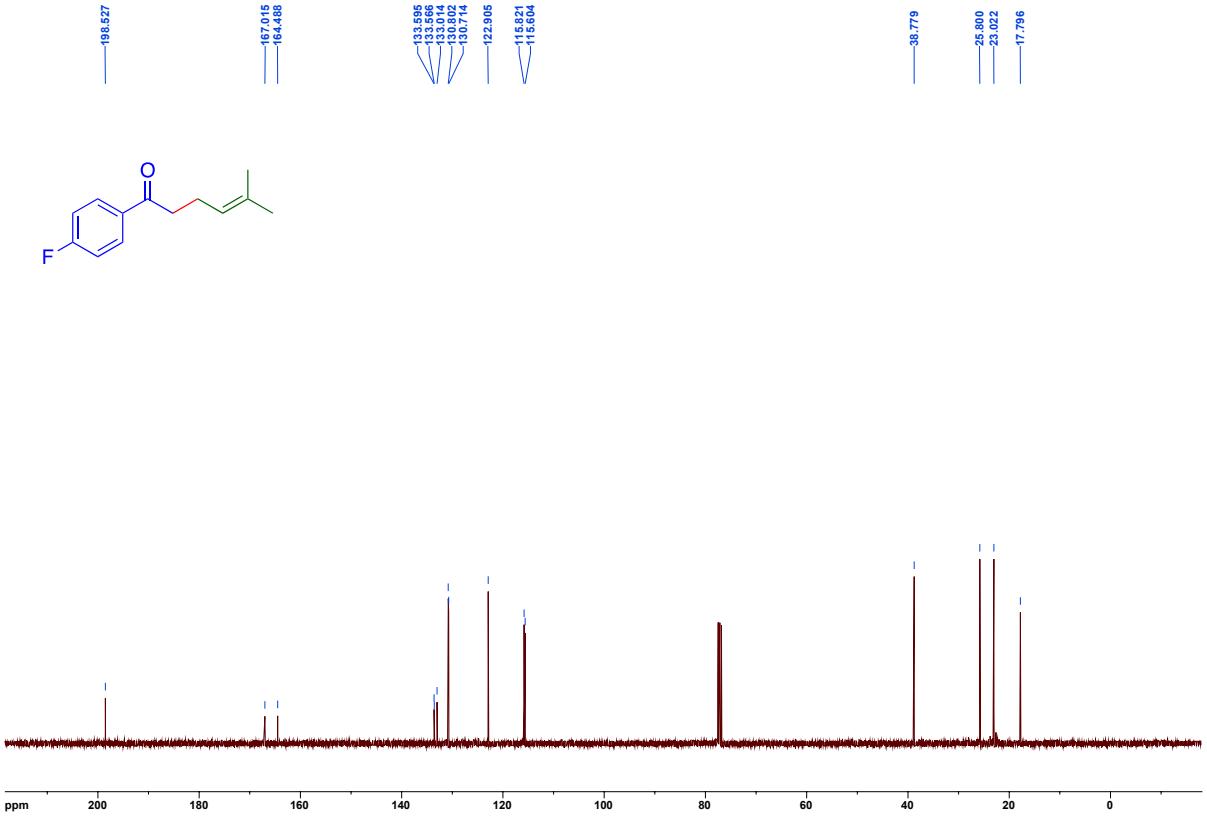
^{13}C NMR spectrum of 5-methyl-1-(3,4,5-trimethoxyphenyl)hex-4-en-1-one **(3f,** 101 MHz, $CDCl_3$):



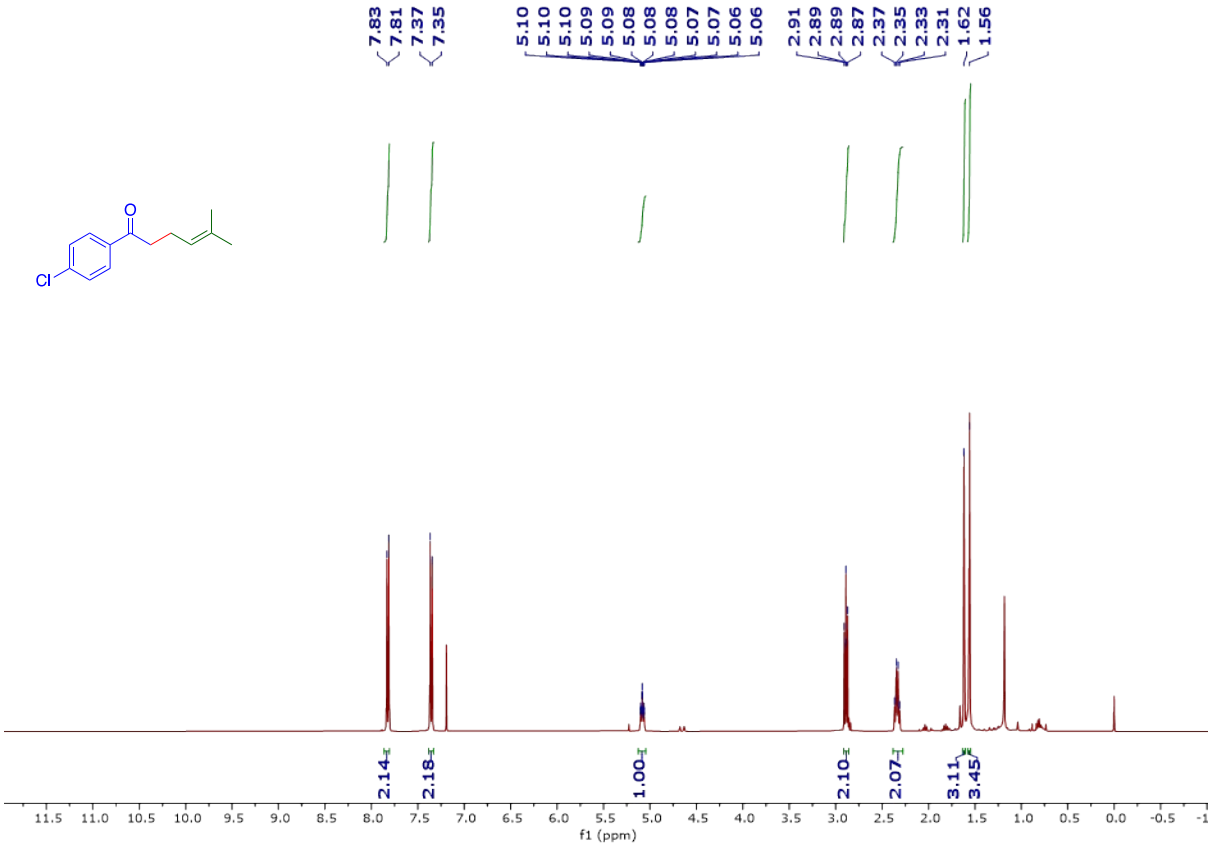
^{1}H NMR spectrum of 1-(4-fluorophenyl)-5-methylhex-4-en-1-one **(3g,** 400 MHz, $CDCl_3$) :



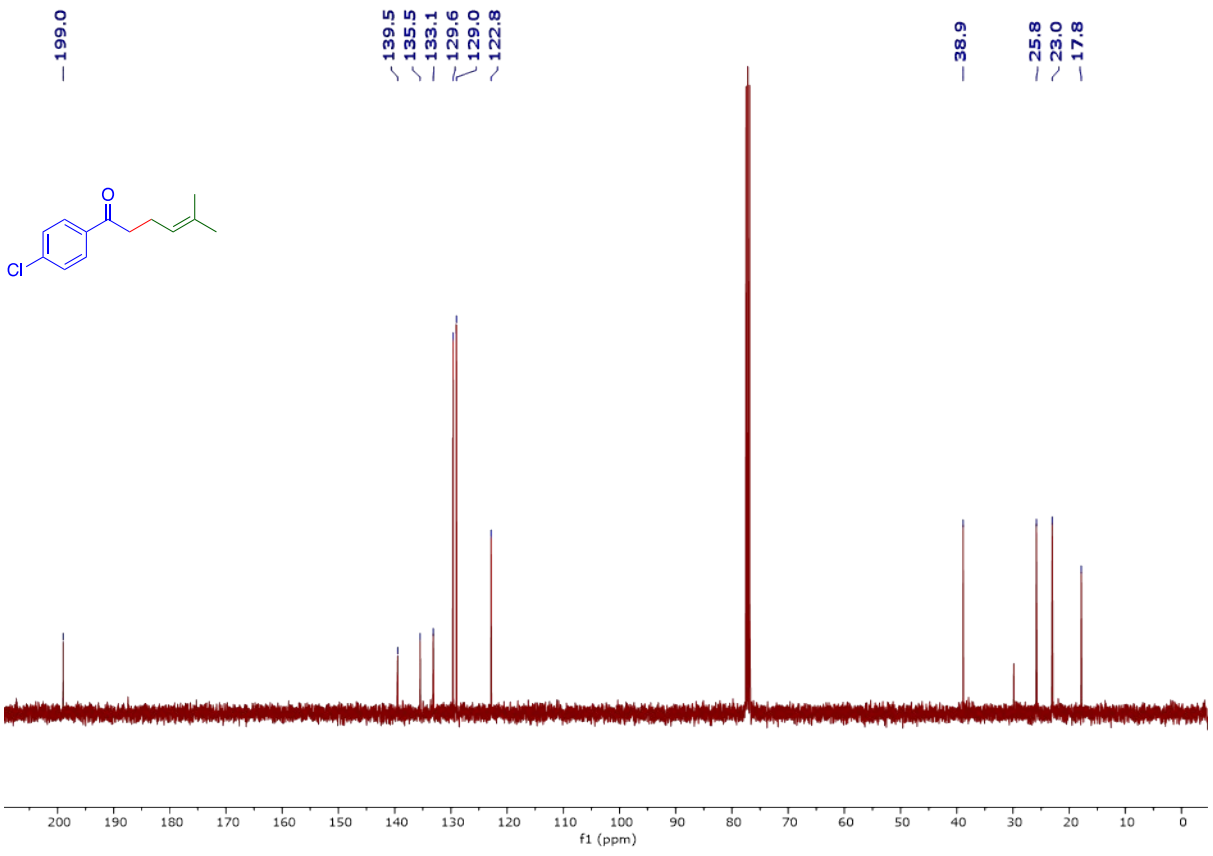
^{13}C NMR spectrum of 1-(4-fluorophenyl)-5-methylhex-4-en-1-one **(3g,** 101 MHz, $CDCl_3$):



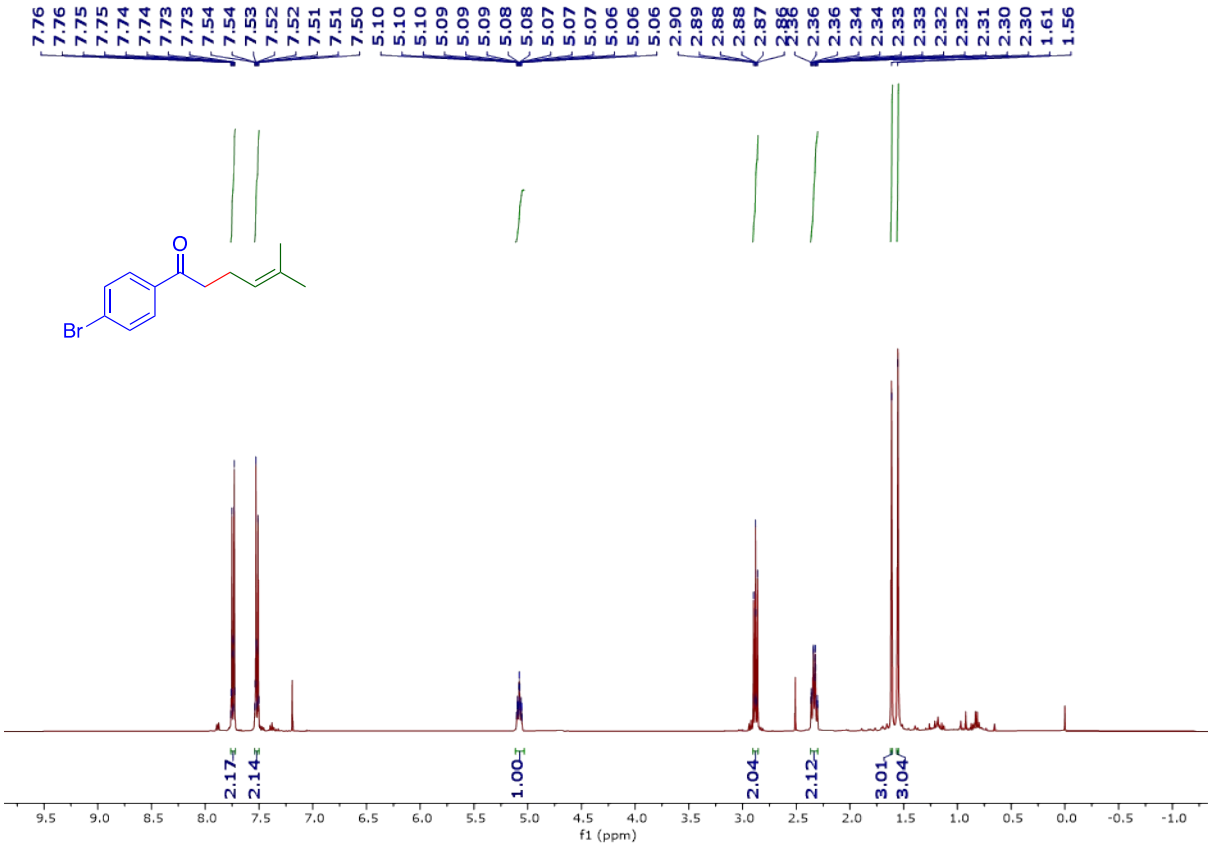
^{1}H NMR spectrum of 1-(4-chlorophenyl)-5-methylhex-4-en-1-one **(3h,** 400 MHz, $CDCl_3$) :



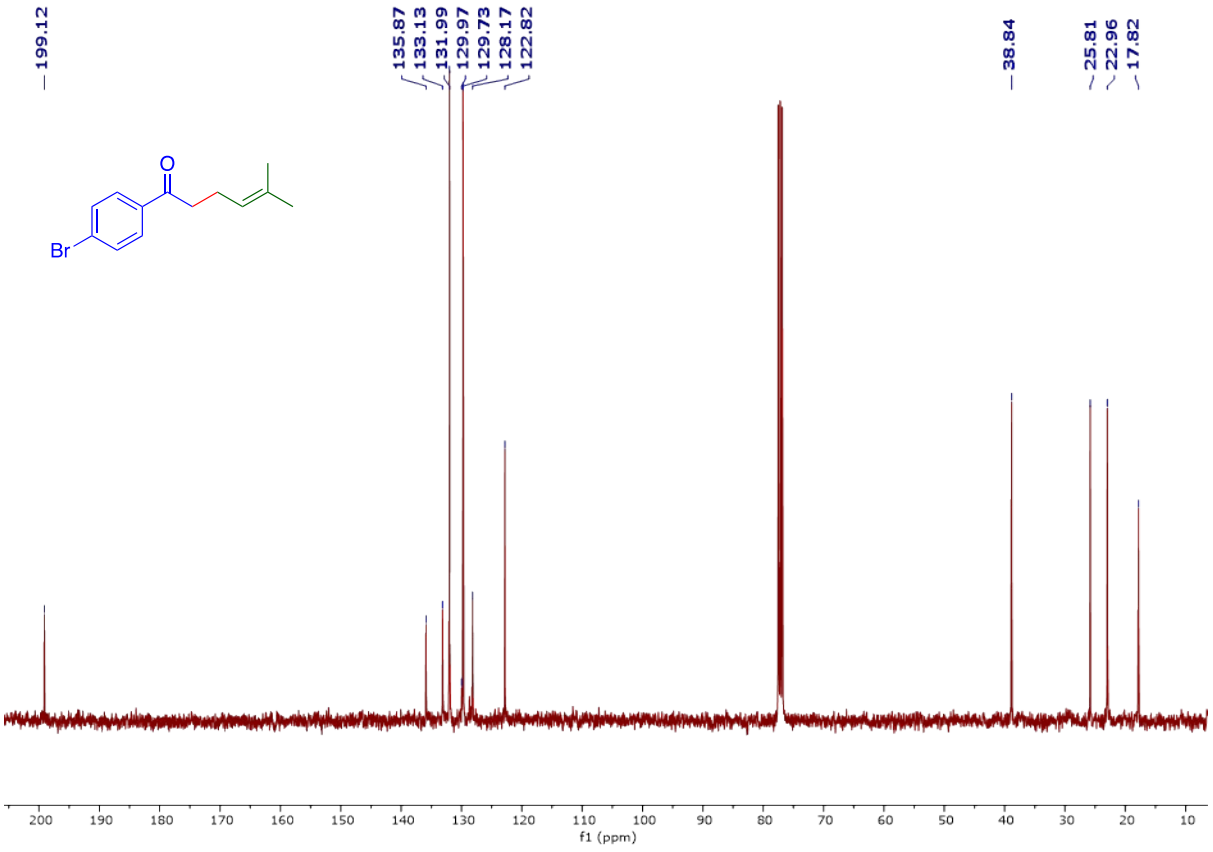
^{13}C NMR spectrum of 1-(4-chlorophenyl)-5-methylhex-4-en-1-one **(3h,** 101 MHz, $CDCl_3$)



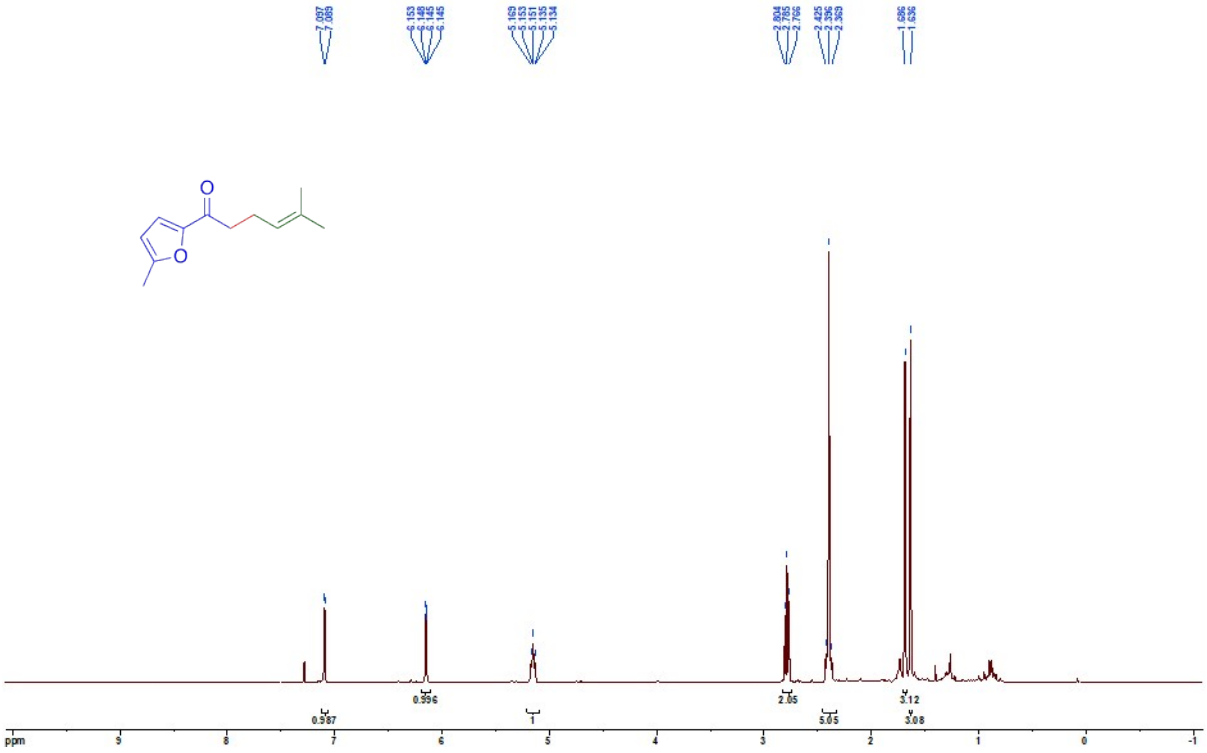
^{1}H NMR spectrum of 1-(4-bromophenyl)-5-methylhex-4-en-1-one **(3i,** 400 MHz, $CDCl_3$) :



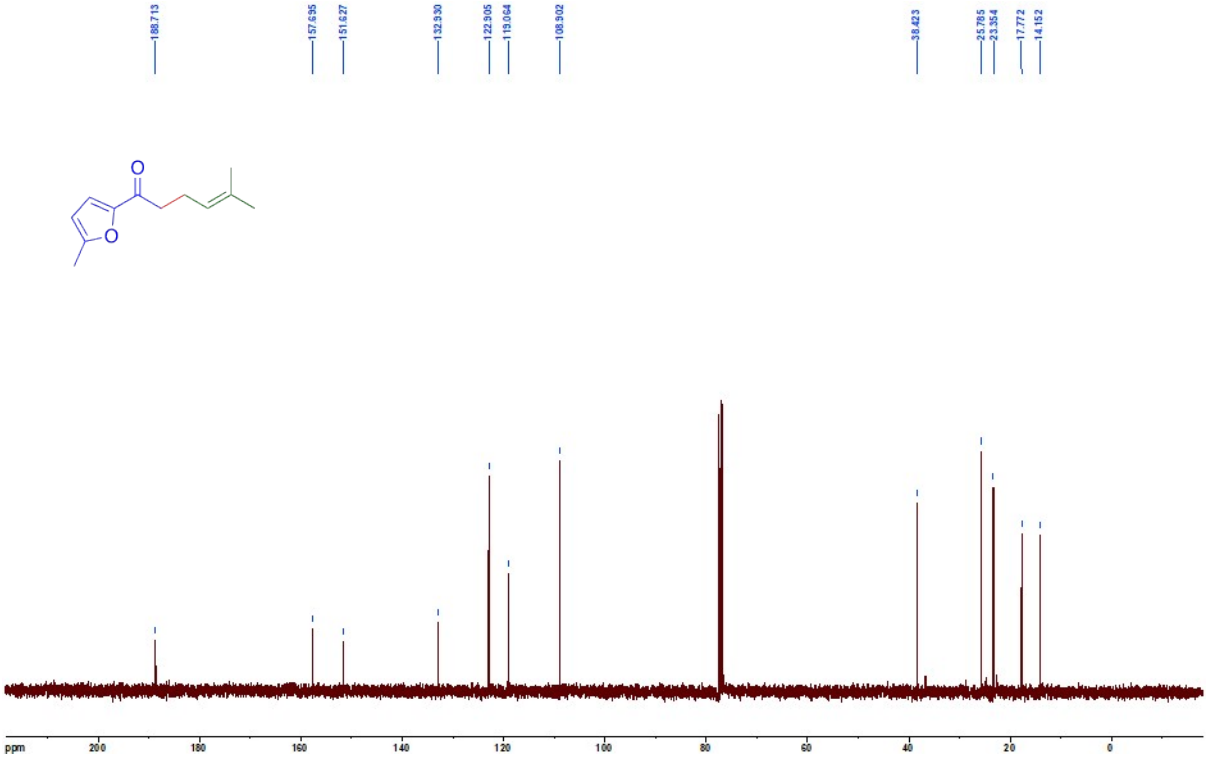
^{13}C NMR spectrum of 1-(4-bromophenyl)-5-methylhex-4-en-1-one **(3i,** 101 MHz, $CDCl_3$):



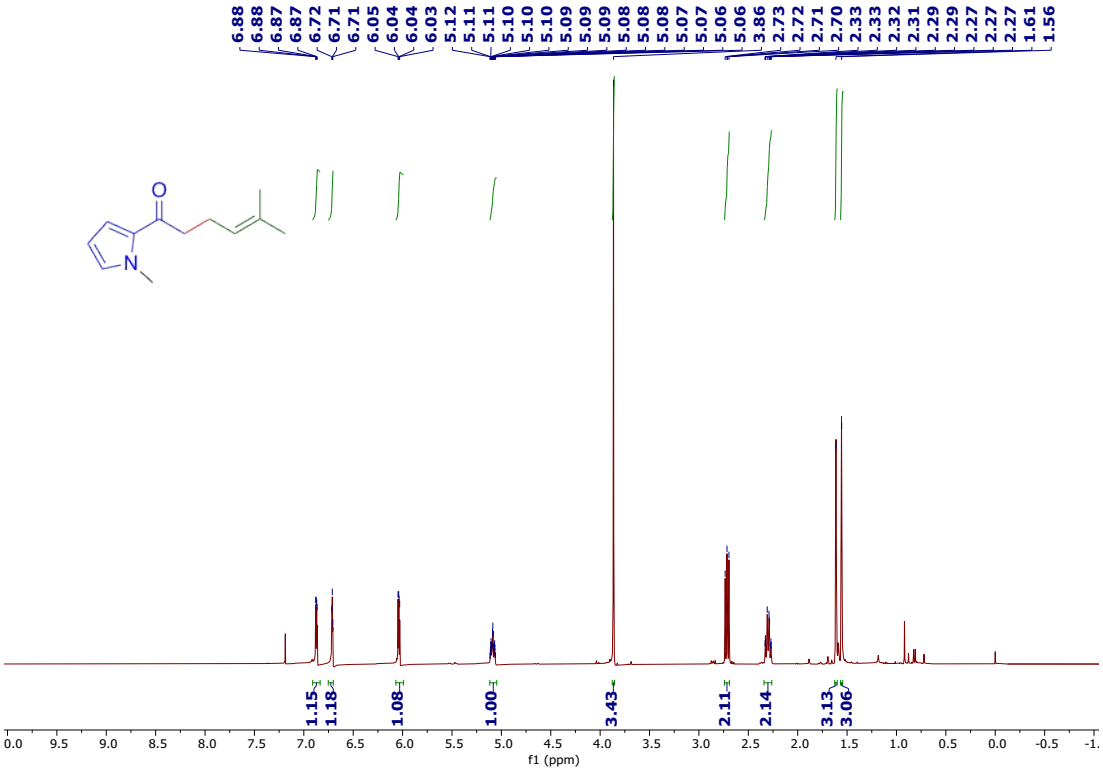
^{1}H NMR spectrum of 5-methyl-1-(5-methylfuran-2-yl)hex-4-en-1-one **(3j,** 400 MHz, $CDCl_3$) **:**



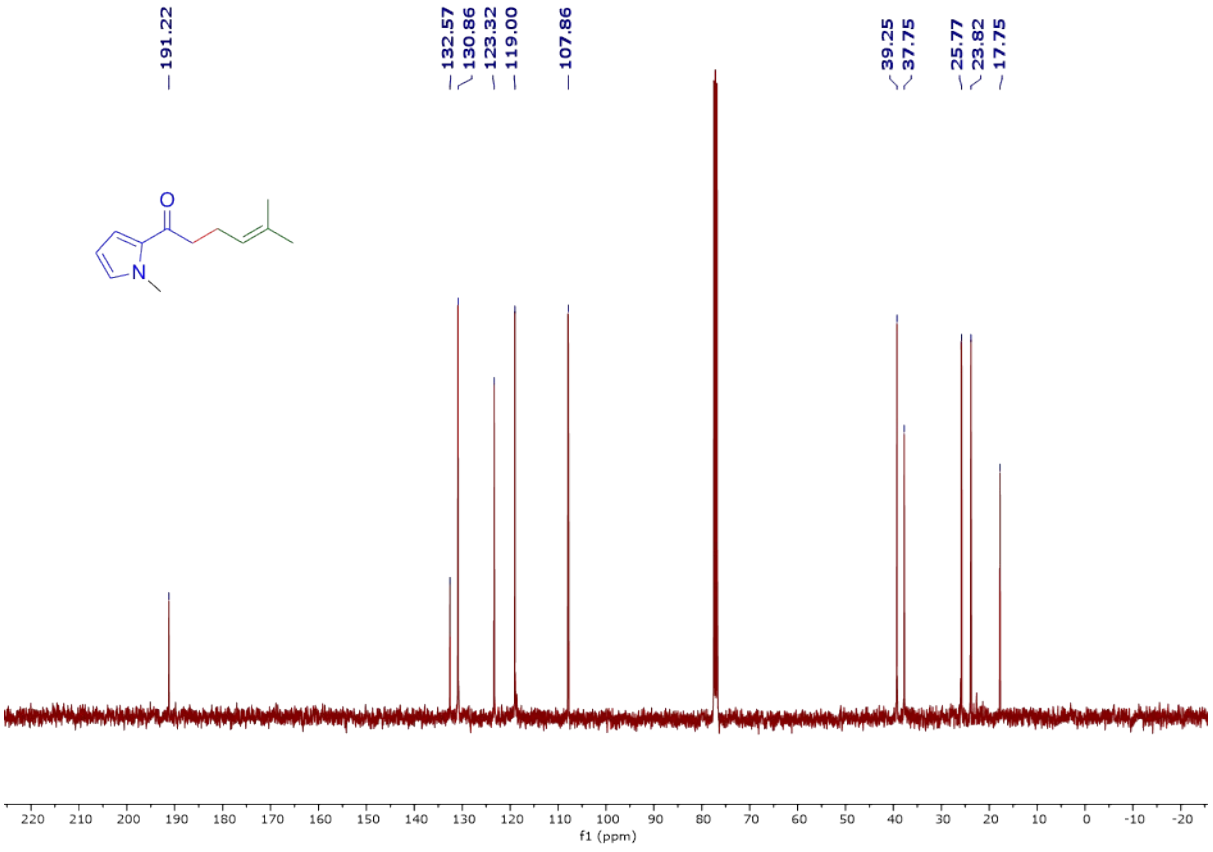
^{13}C NMR spectrum of 5-methyl-1-(5-methylfuran-2-yl)hex-4-en-1-one **(3j,** 101 MHz, $CDCl_3$):



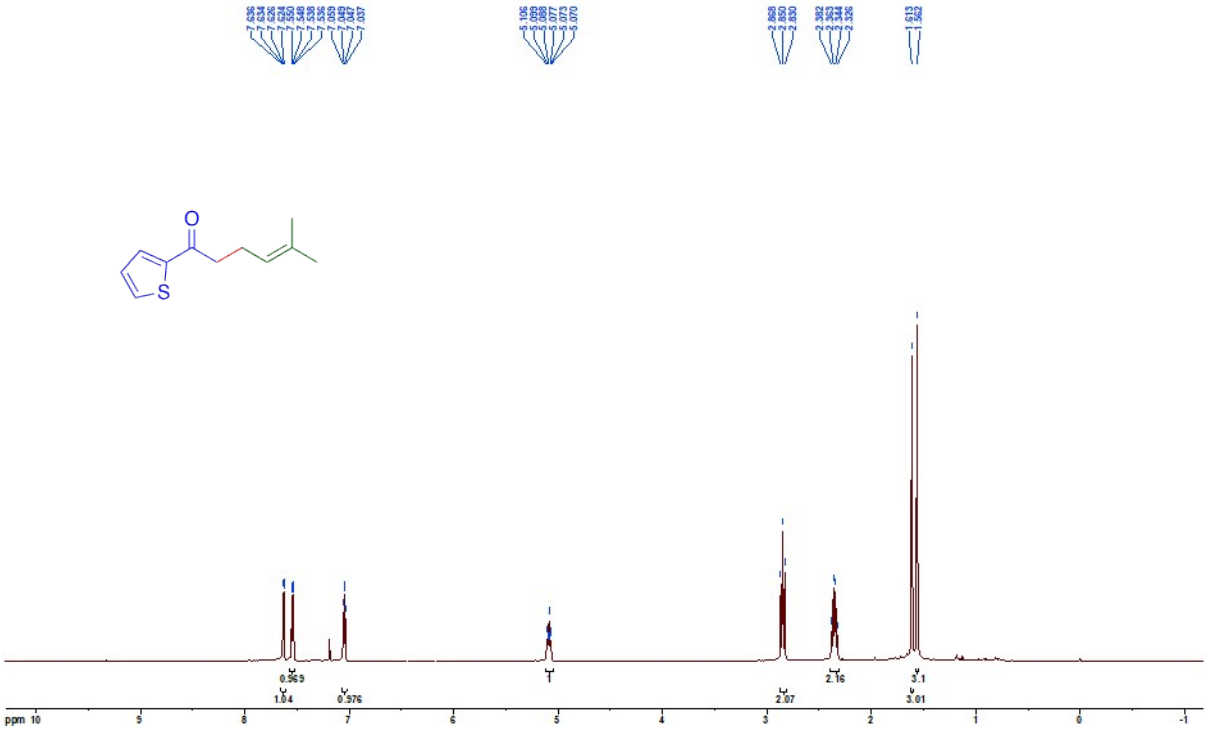
^{1}H NMR spectrum of 5-methyl-1-(1-methyl-1H-pyrrol-2-yl)hex-4-en-1-one (**3k**, 400 MHz, $CDCl_3$) 101 MHz, $CDCl_3$):



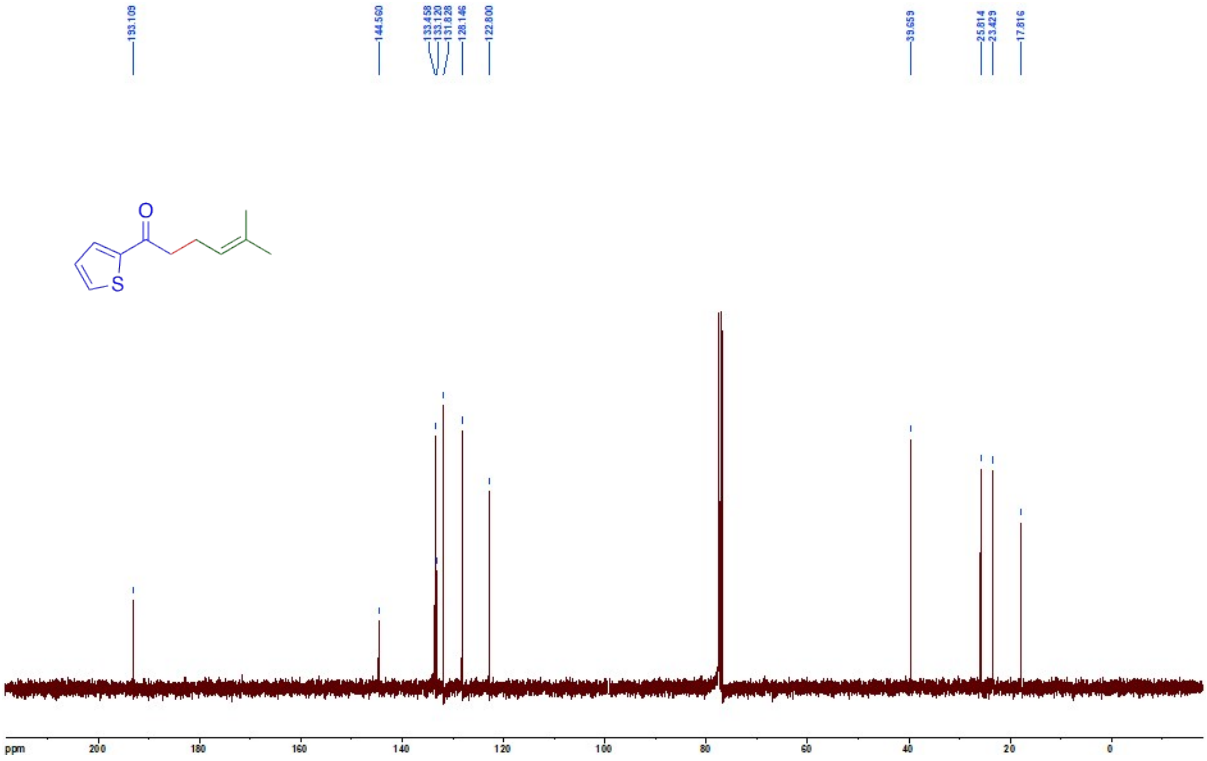
^{13}C NMR spectrum of 5-methyl-1-(1-methyl-1H-pyrrol-2-yl)hex-4-en-1-one (**3k**, 101 MHz, $CDCl_3$):



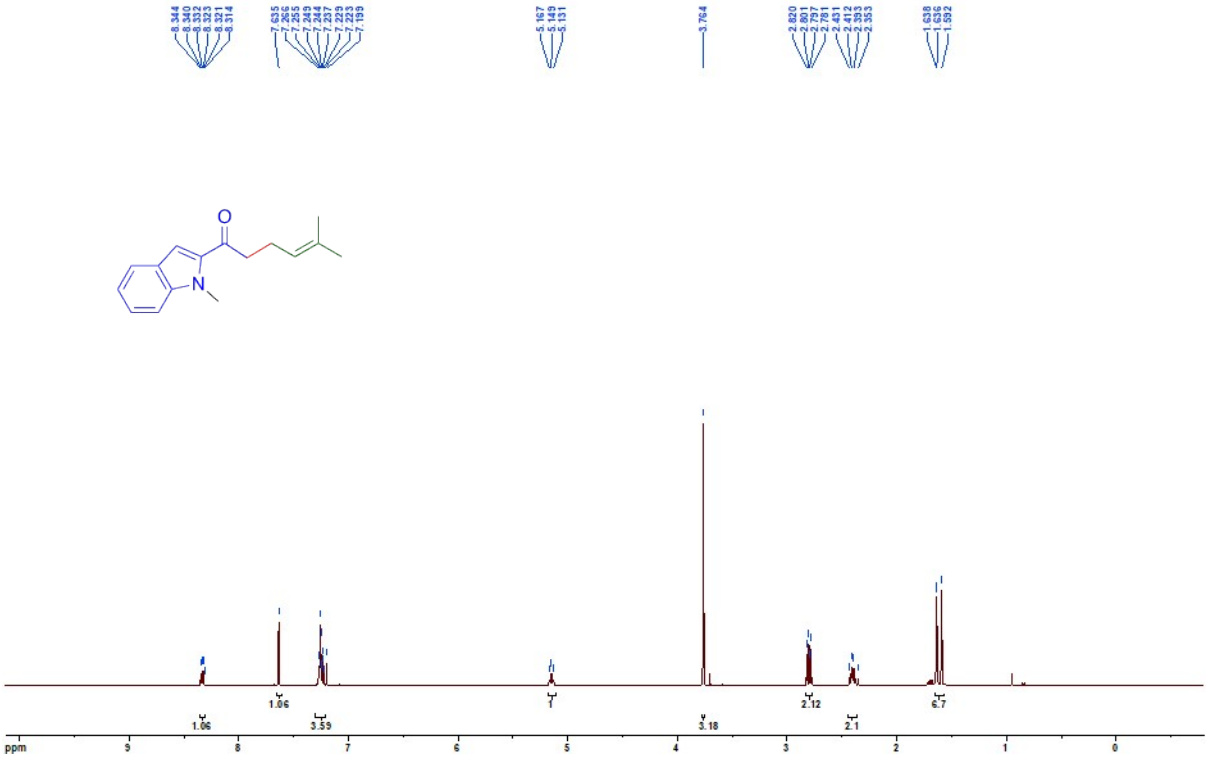
^{1}H NMR spectrum of 5-methyl-1-(thiophen-2-yl)hex-4-en-1-one (**3l**, 400 MHz, $CDCl_3$) **:**



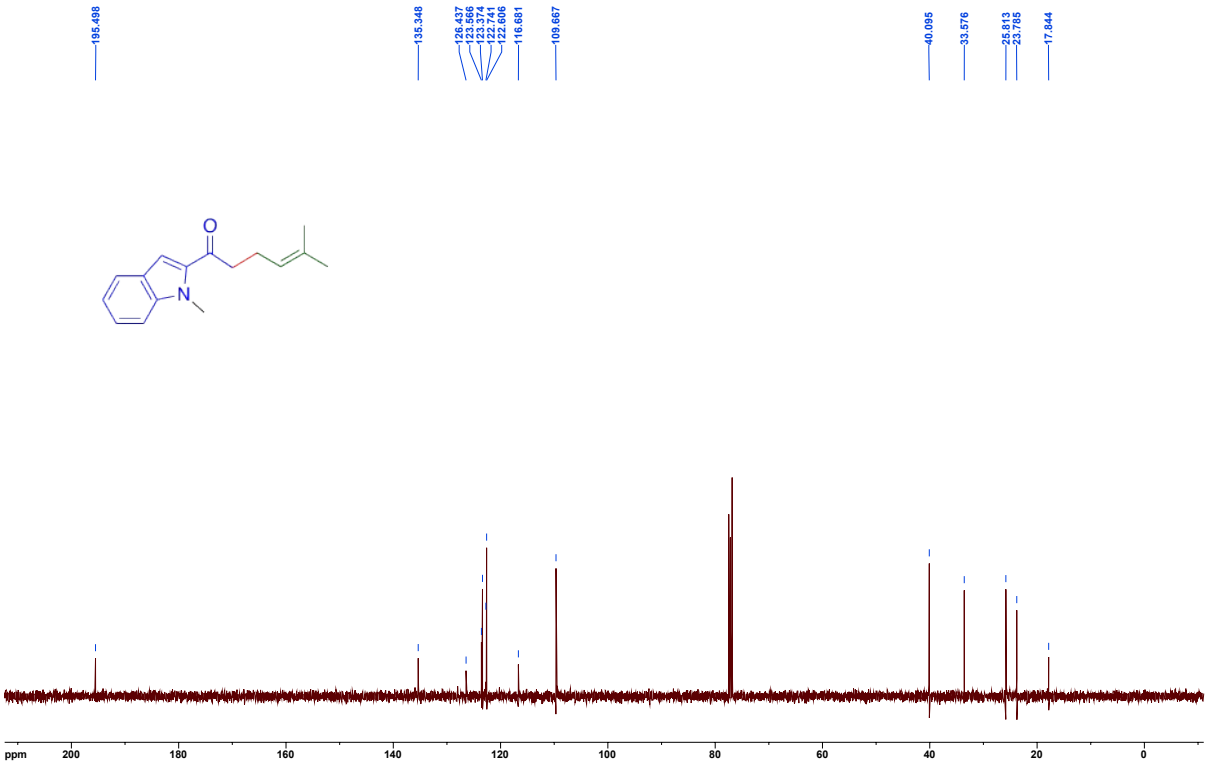
^{13}C NMR spectrum of 5-methyl-1-(thiophen-2-yl)hex-4-en-1-one (**3l**, 101 MHz, $CDCl_3$):



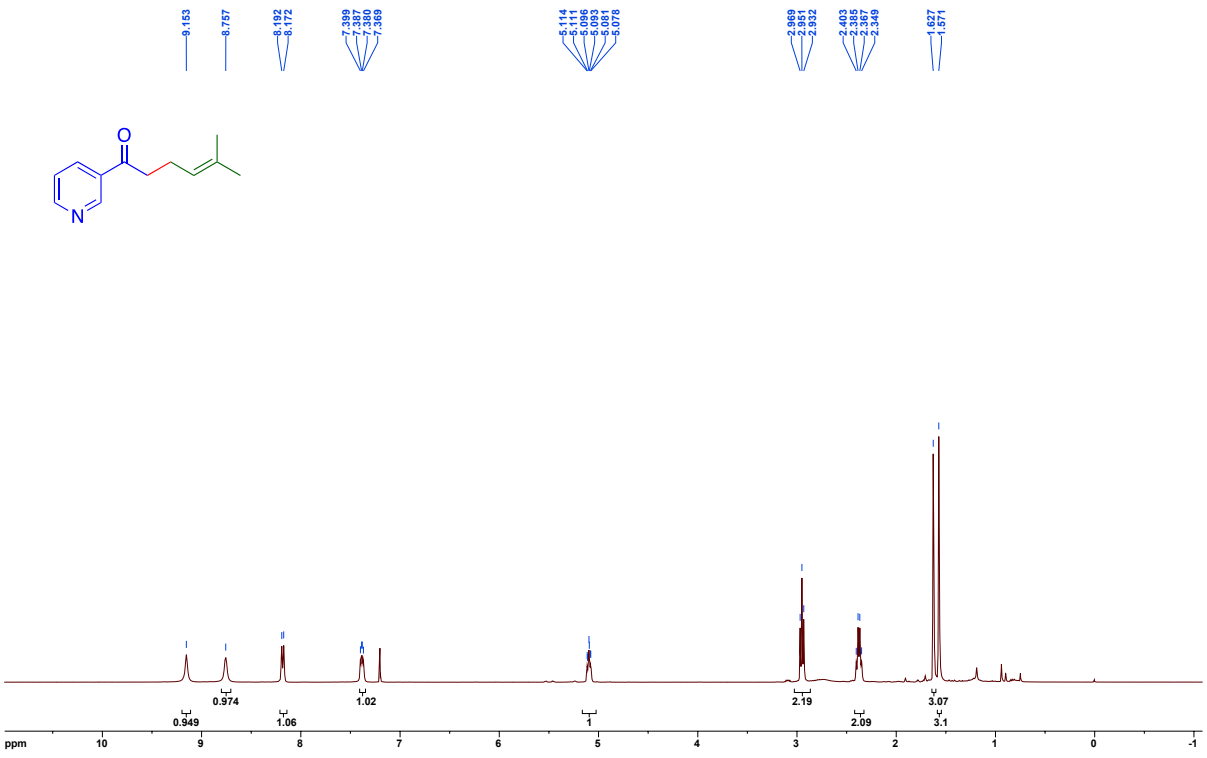
^{1}H NMR spectrum of 5-methyl-1-(1-methyl-1H-indol-2-yl)hex-4-en-1-one **(3m,** 400 MHz, $CDCl_3$) :



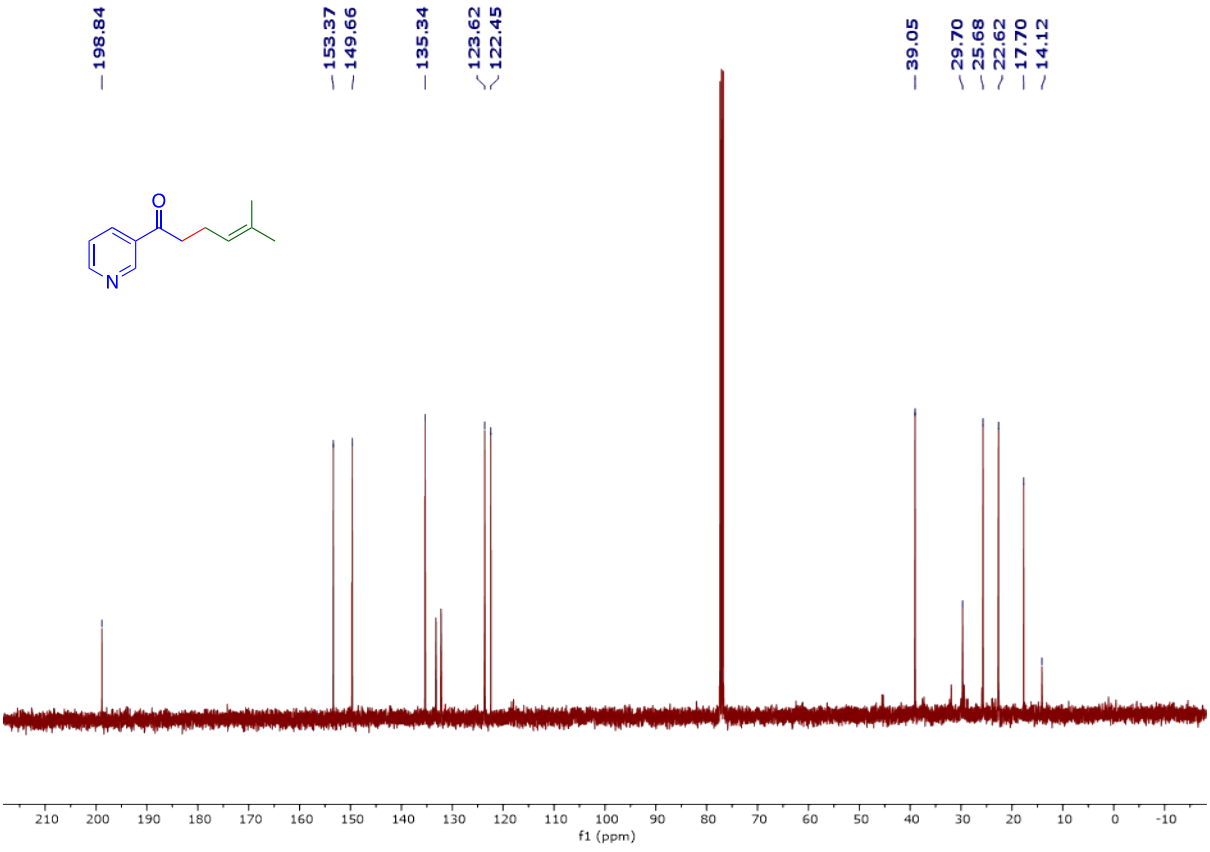
^{3}C NMR spectrum of 5-methyl-1-(1-methyl-1H-indol-2-yl)hex-4-en-1-one **(3m,** 101 MHz, $CDCl_3$):



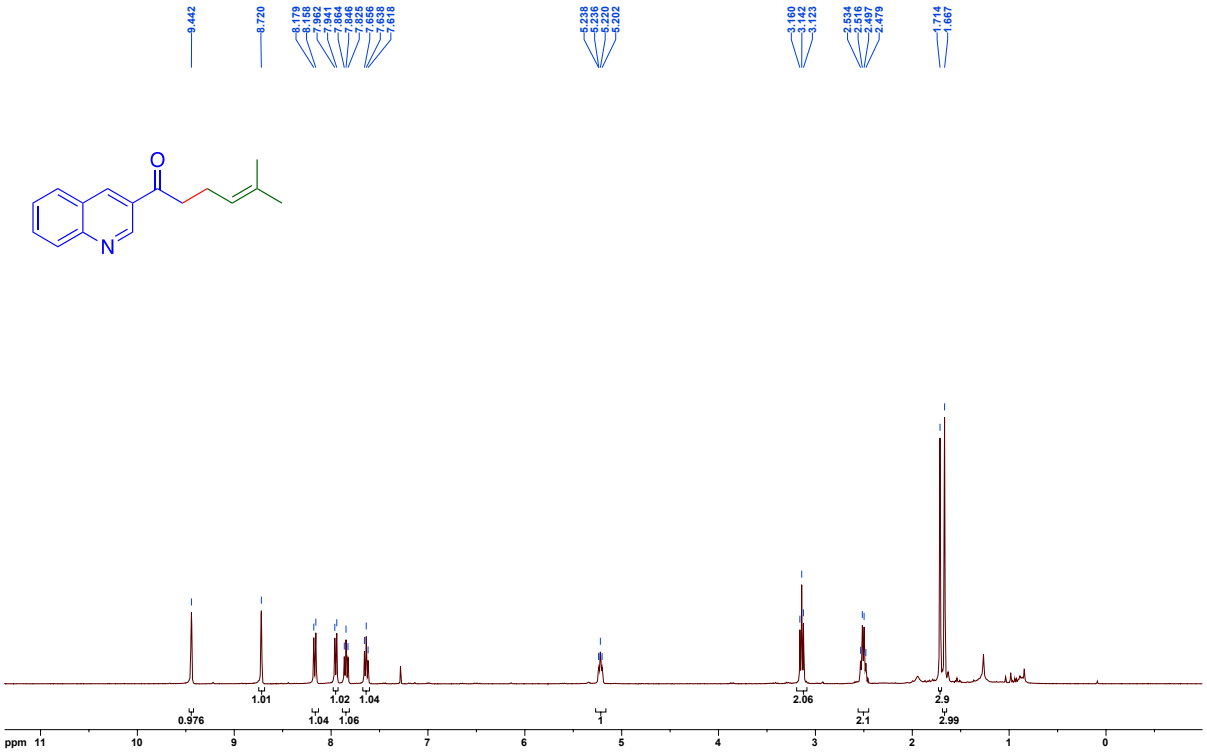
^{1}H NMR spectrum of 5-methyl-1-(pyridin-3-yl)hex-4-en-1-one (**3n**, 400 MHz, $CDCl_3$) :



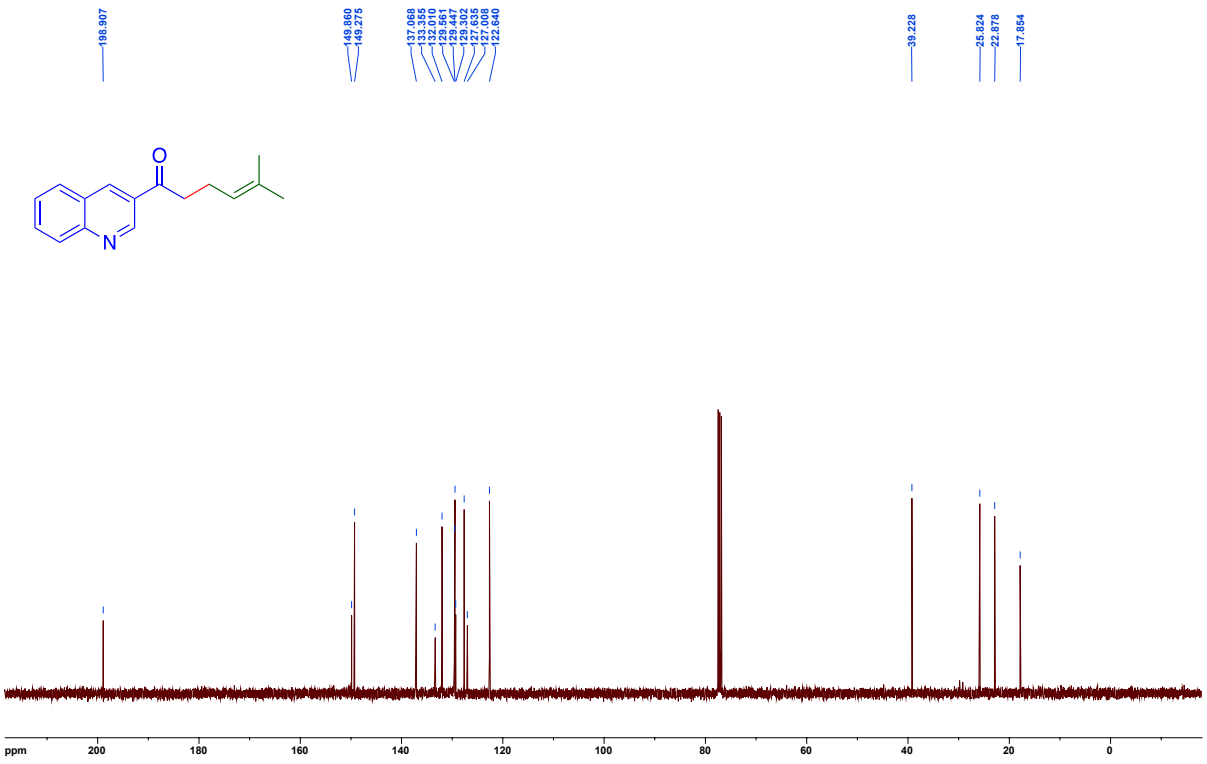
^{13}C NMR spectrum of 5-methyl-1-(pyridin-3-yl)hex-4-en-1-one (**3n**, 101 MHz, $CDCl_3$):



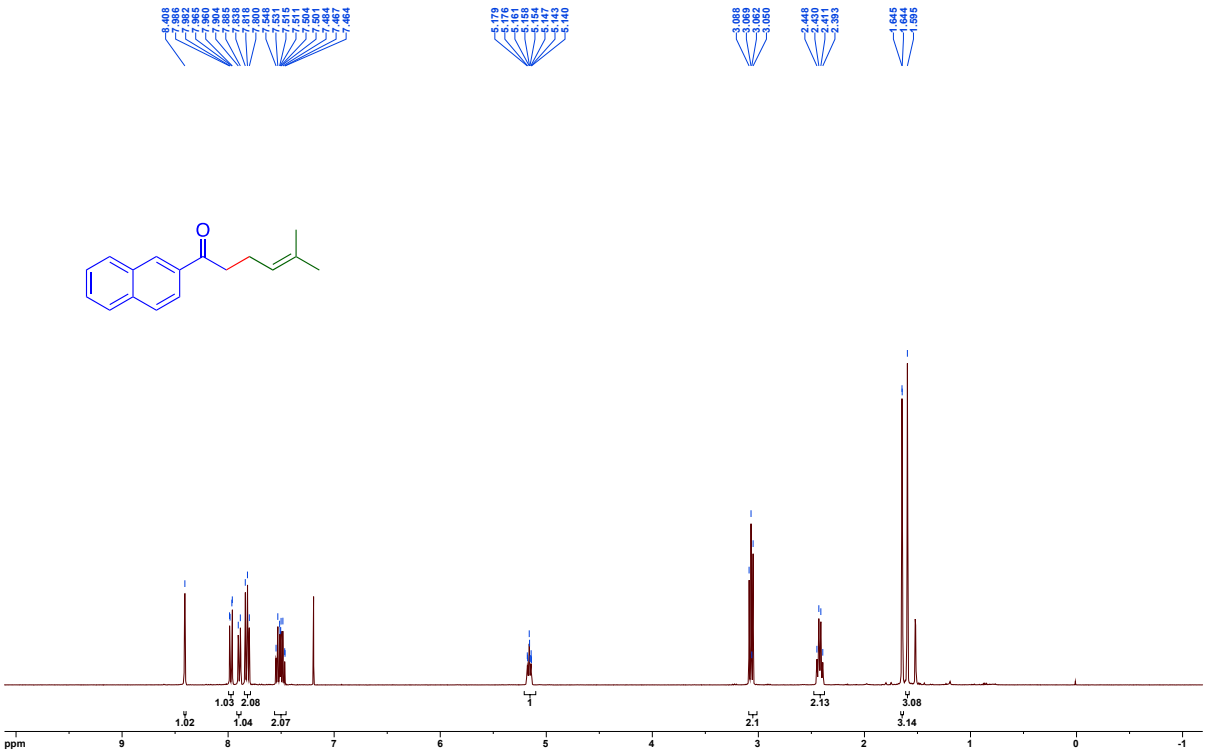
^{1}H NMR spectrum of 5-methyl-1-(quinolin-3-yl)hex-4-en-1-one **(3o,** 400 MHz, $CDCl_3$) :



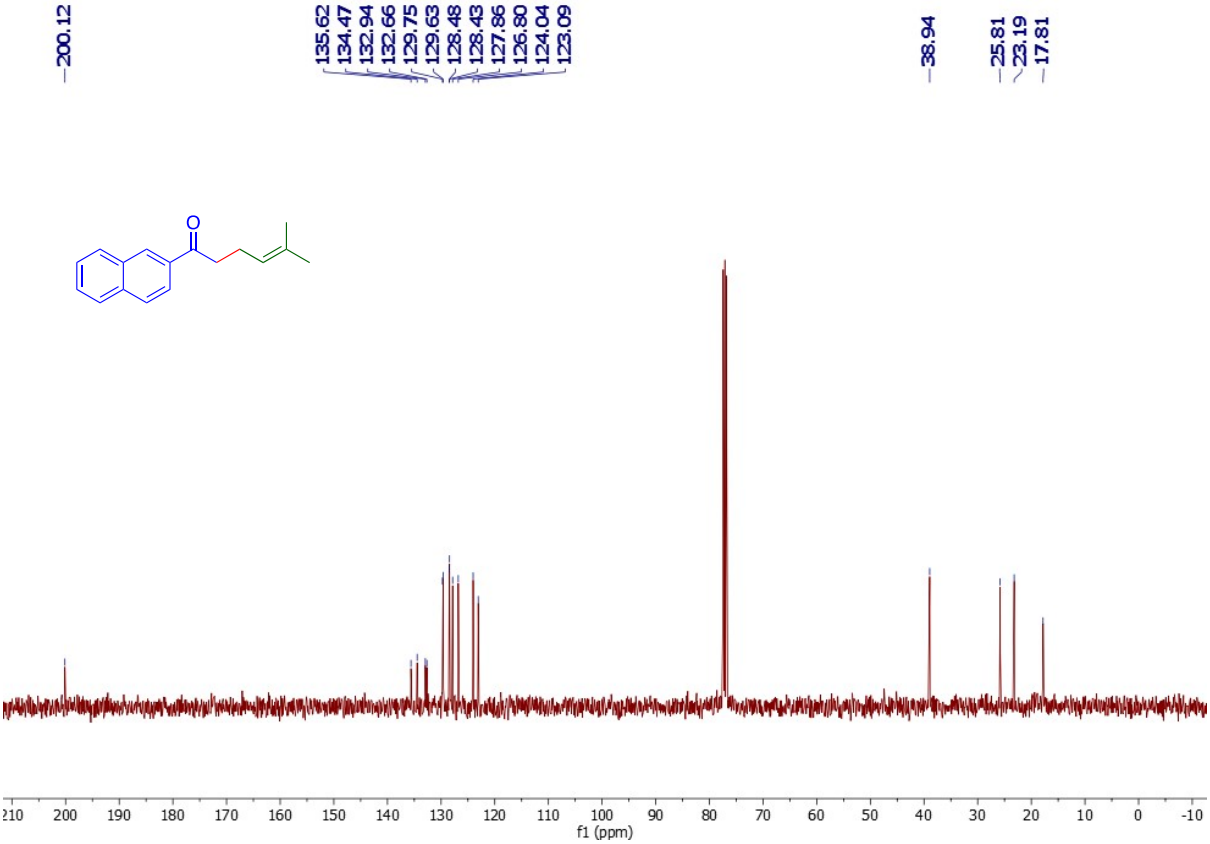
^{13}C NMR spectrum of 5-methyl-1-(quinolin-3-yl)hex-4-en-1-one **(3o,** 101 MHz, $CDCl_3$):



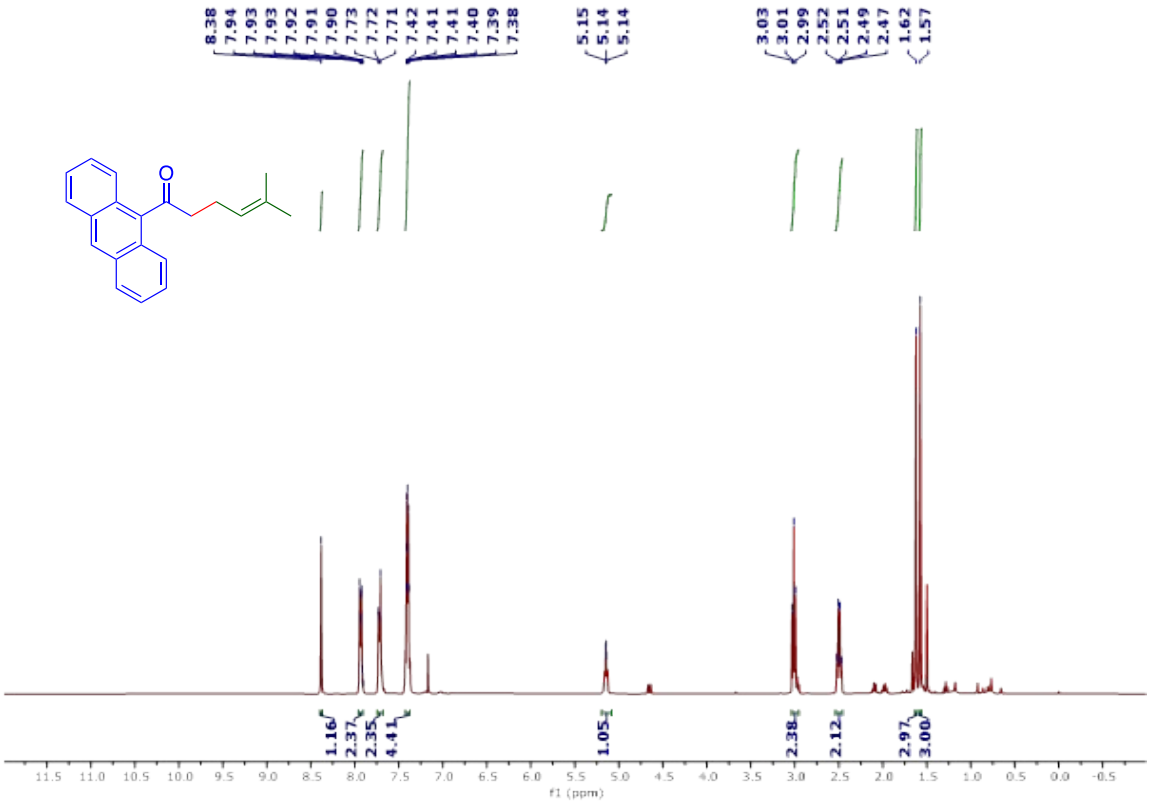
^{1}H NMR spectrum of 5-methyl-1-(naphthalen-2-yl)hex-4-en-1-one **(3p,** 400 MHz, $CDCl_3$) 101 MHz, $CDCl_3$):



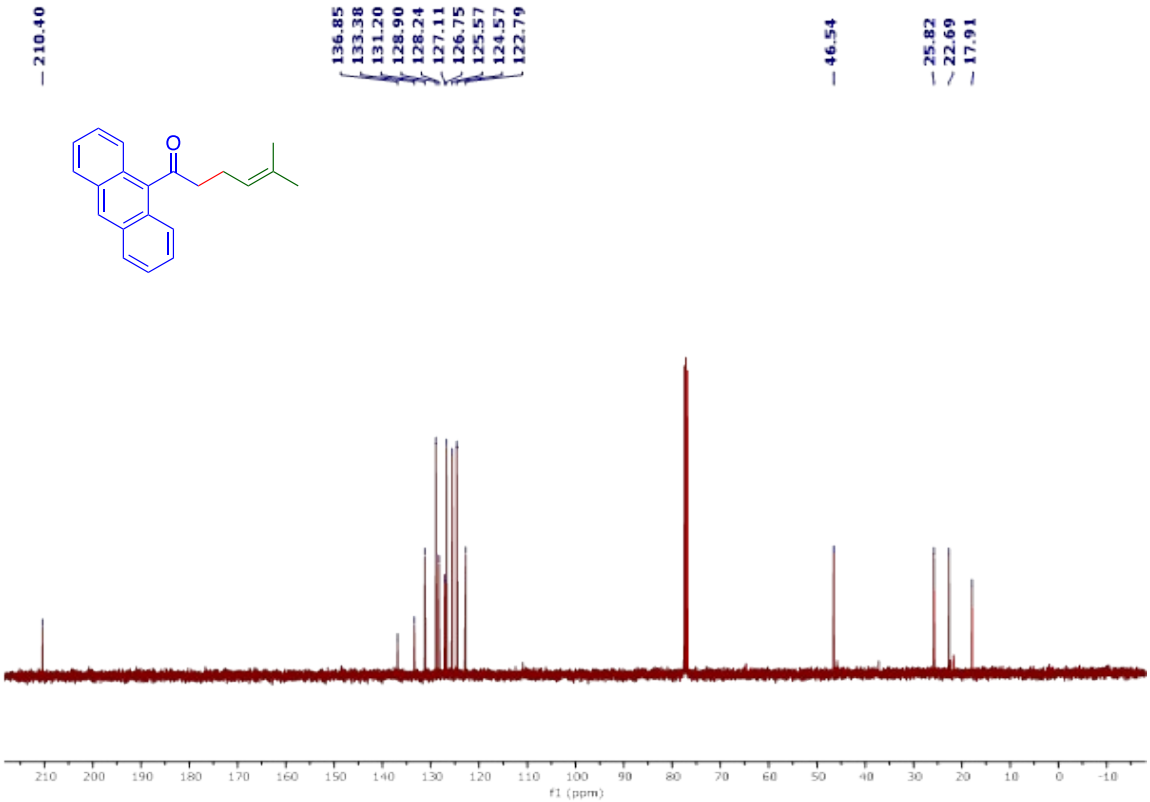
^{13}C NMR spectrum of 5-methyl-1-(naphthalen-2-yl)hex-4-en-1-one **(3p,** 101 MHz, $CDCl_3$):



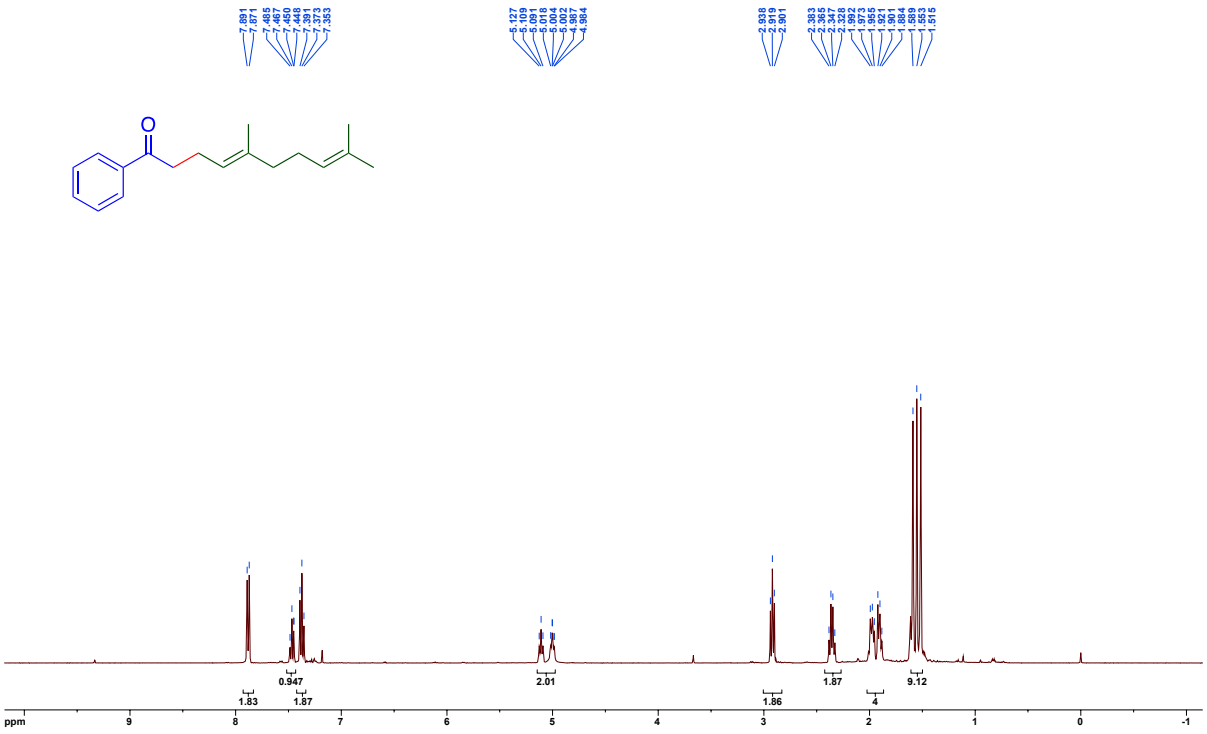
^{1}H NMR spectrum of 1-(4a,10-dihydroanthracen-9-yl)-5-methylhex-4-en-1-one (**3q**, 400 MHz, $CDCl_3$) **:**



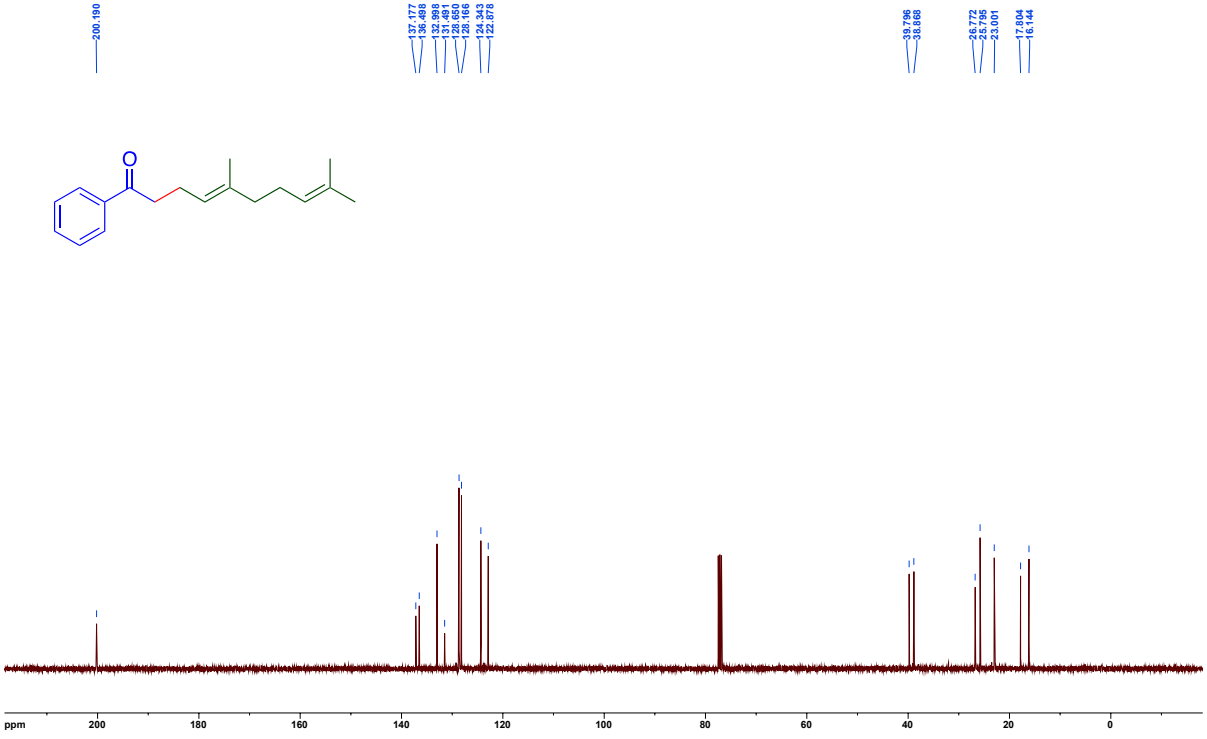
^{3}C NMR spectrum of 1-(4a,10-dihydroanthracen-9-yl)-5-methylhex-4-en-1-one (**3q**, 101 MHz, $CDCl_3$):



^{1}H NMR spectrum of (*E*)-5,9-Dimethyl-1-phenyldeca-4,8-dien-1-one (**3r**, 400 MHz, $CDCl_3$) :

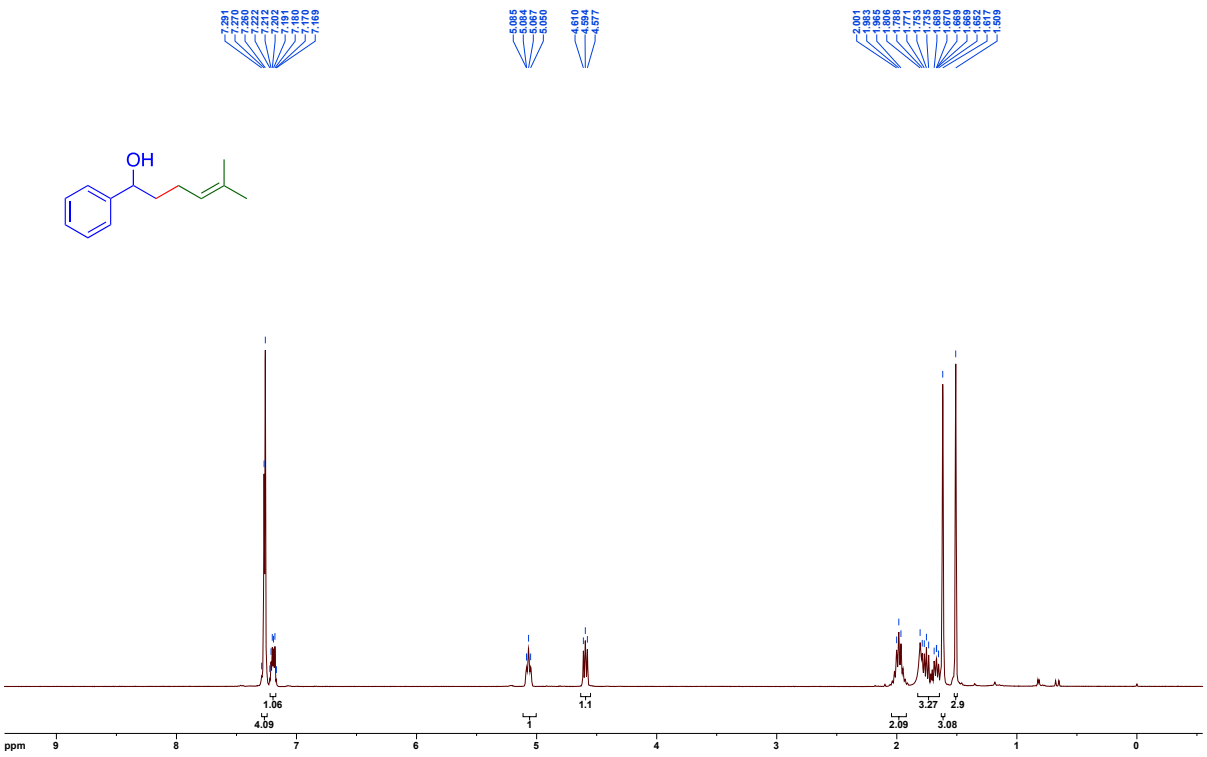


^{13}C NMR spectrum of (*E*)-5,9-Dimethyl-1-phenyldeca-4,8-dien-1-one (**3r,** 101 MHz, $CDCl_3$):

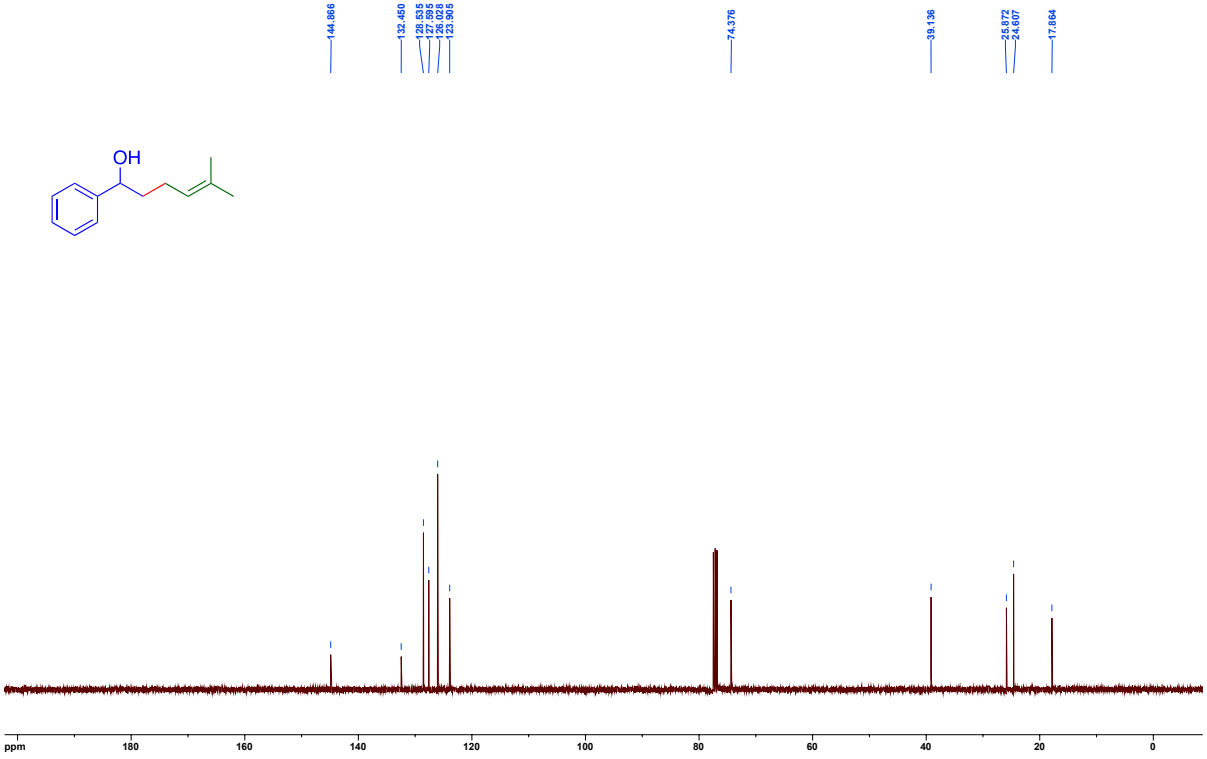


^{1}H & ^{13}C spectra of Functionalized Compounds Prepared from α-Prenylated Ketones:

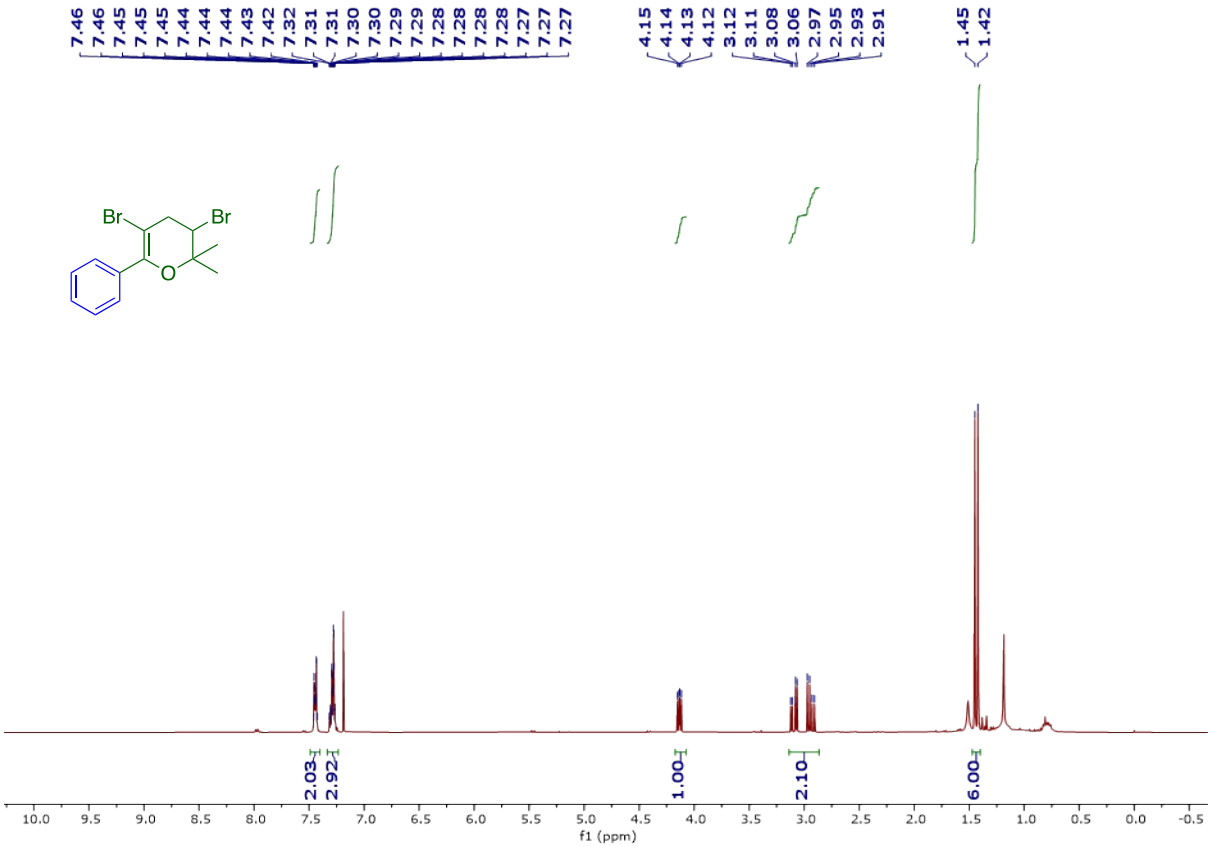
^{1}H NMR spectrum of 5-methyl-1-phenylhex-4-en-1-ol (**4a**, 400 MHz, $CDCl_3$) :



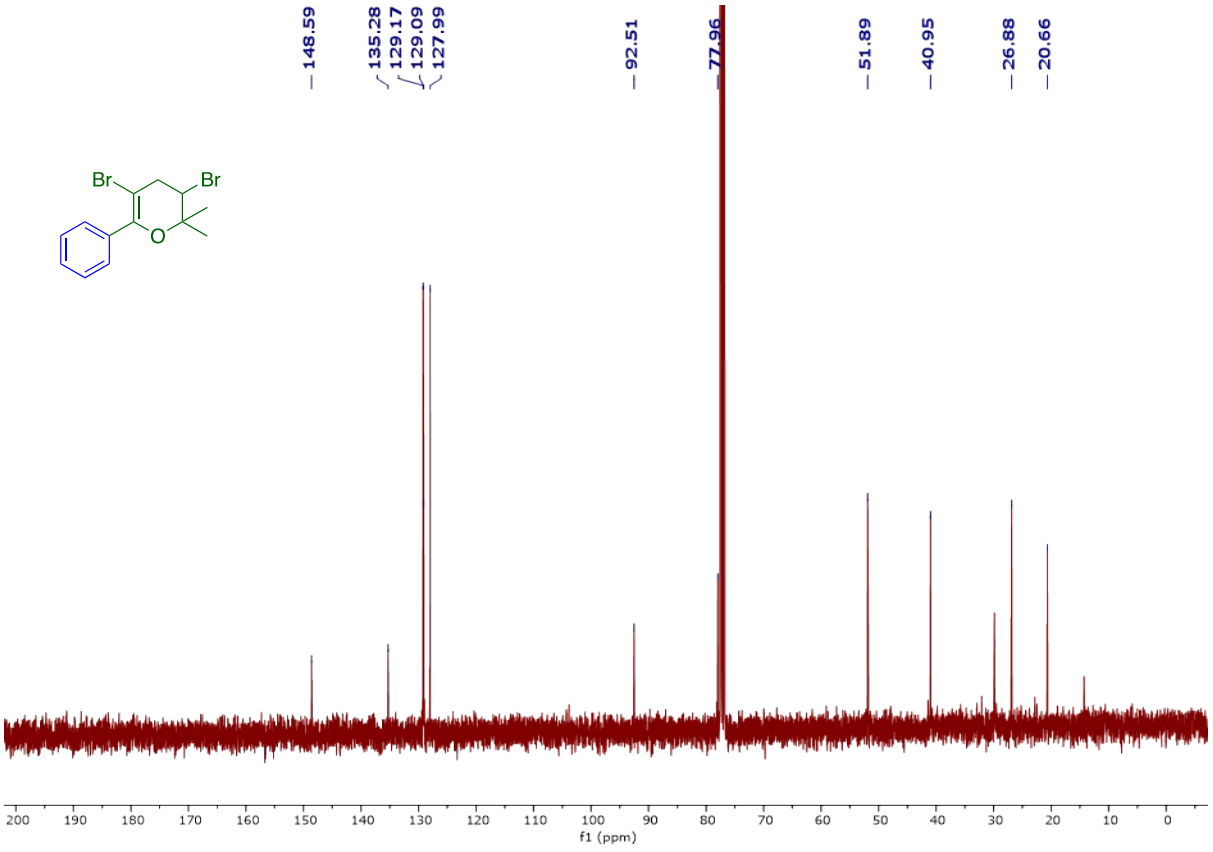
^{13}C NMR spectrum of 5-methyl-1-phenylhex-4-en-1-ol (**4a**, 101 MHz, $CDCl_3$):



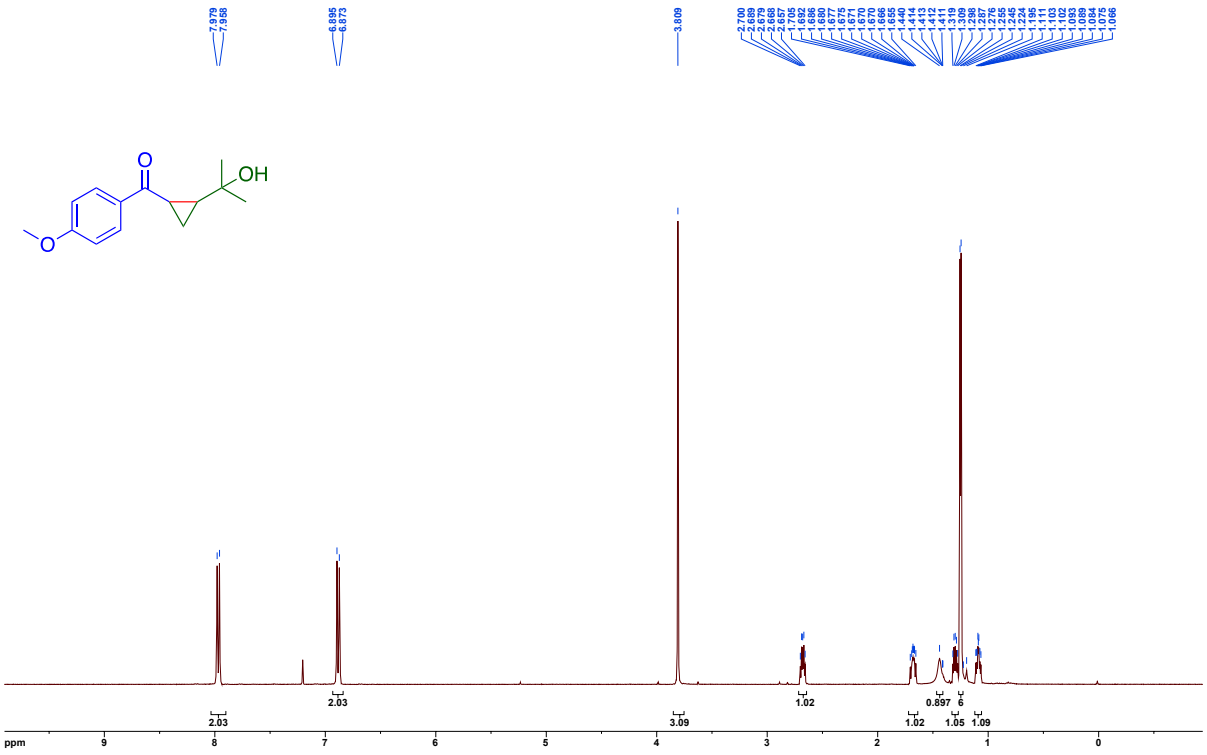
^{1}H NMR spectrum of 3,5-dibromo-2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyran (**4b**, 400 MHz, $CDCl_3$) **:**



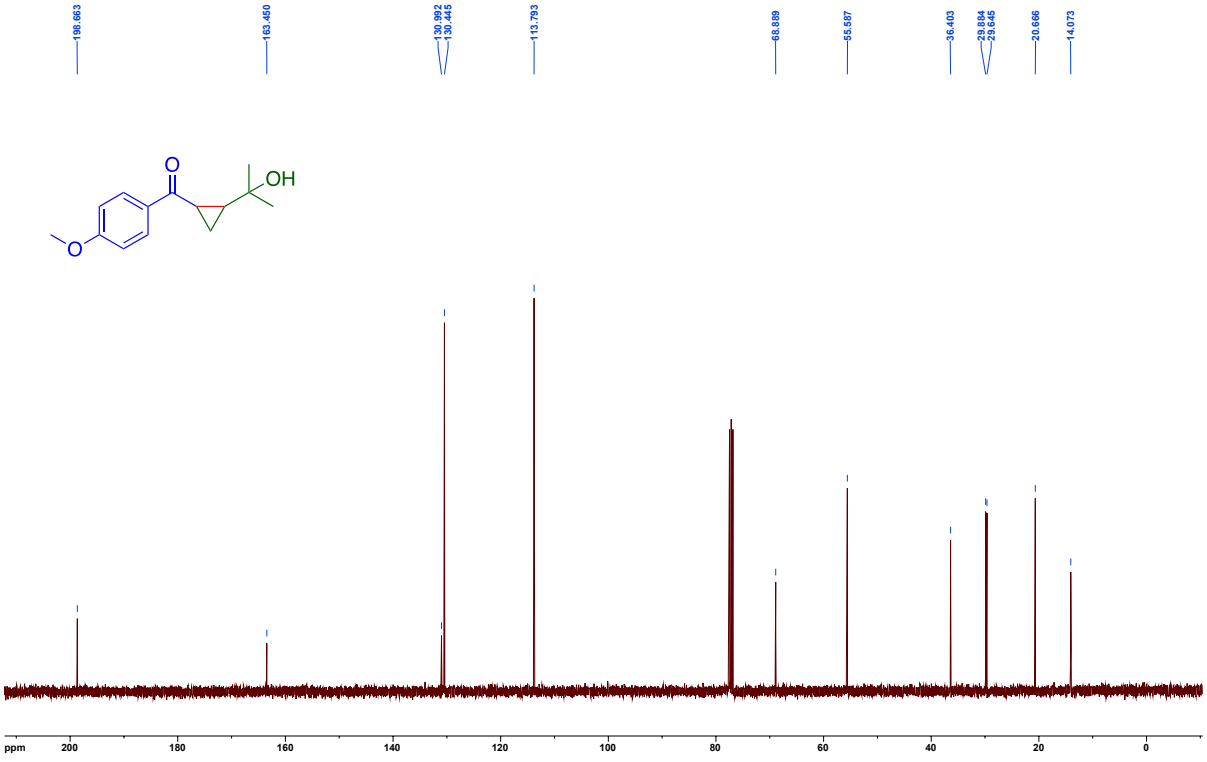
^{13}C NMR spectrum of 3,5-dibromo-2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyran (**4b**):



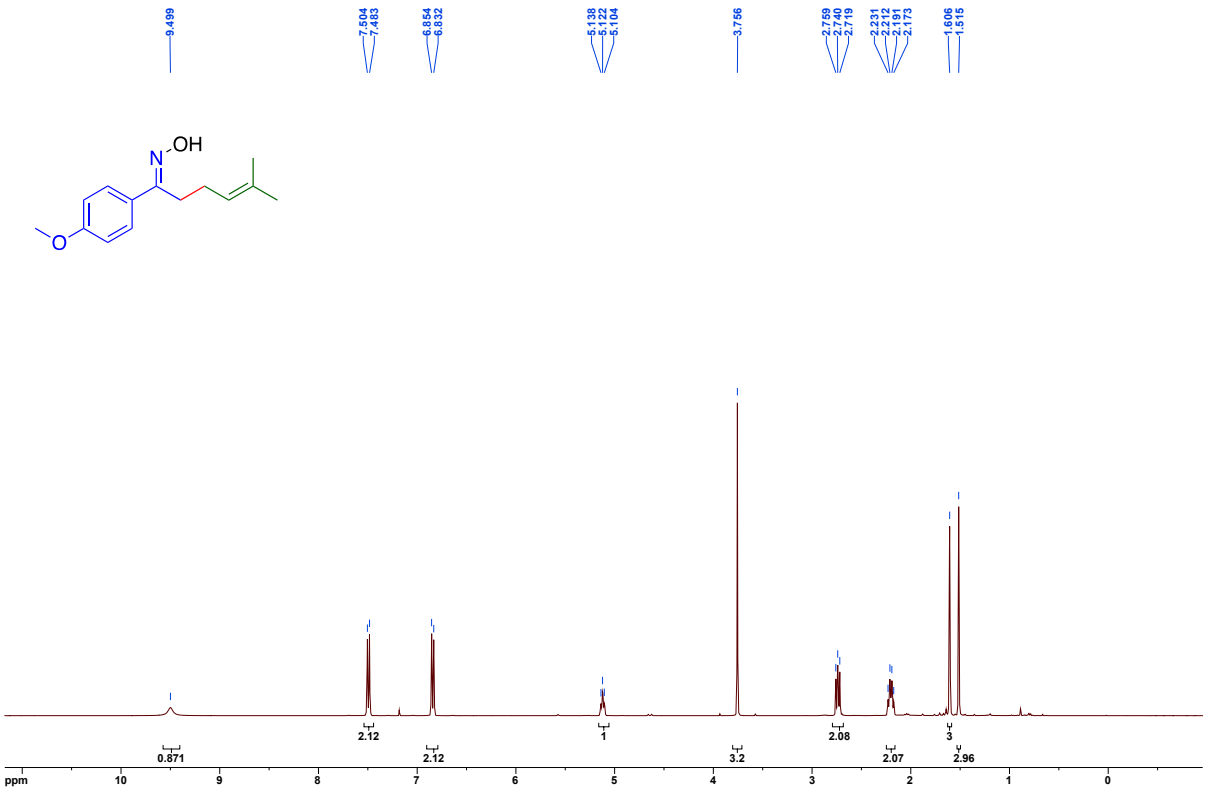
^{1}H NMR spectrum of (2-(2-hydroxypropan-2-yl)cyclopropyl)(4-methoxyphenyl)methanone (**4d**, 400 MHz, $CDCl_3$) **:**



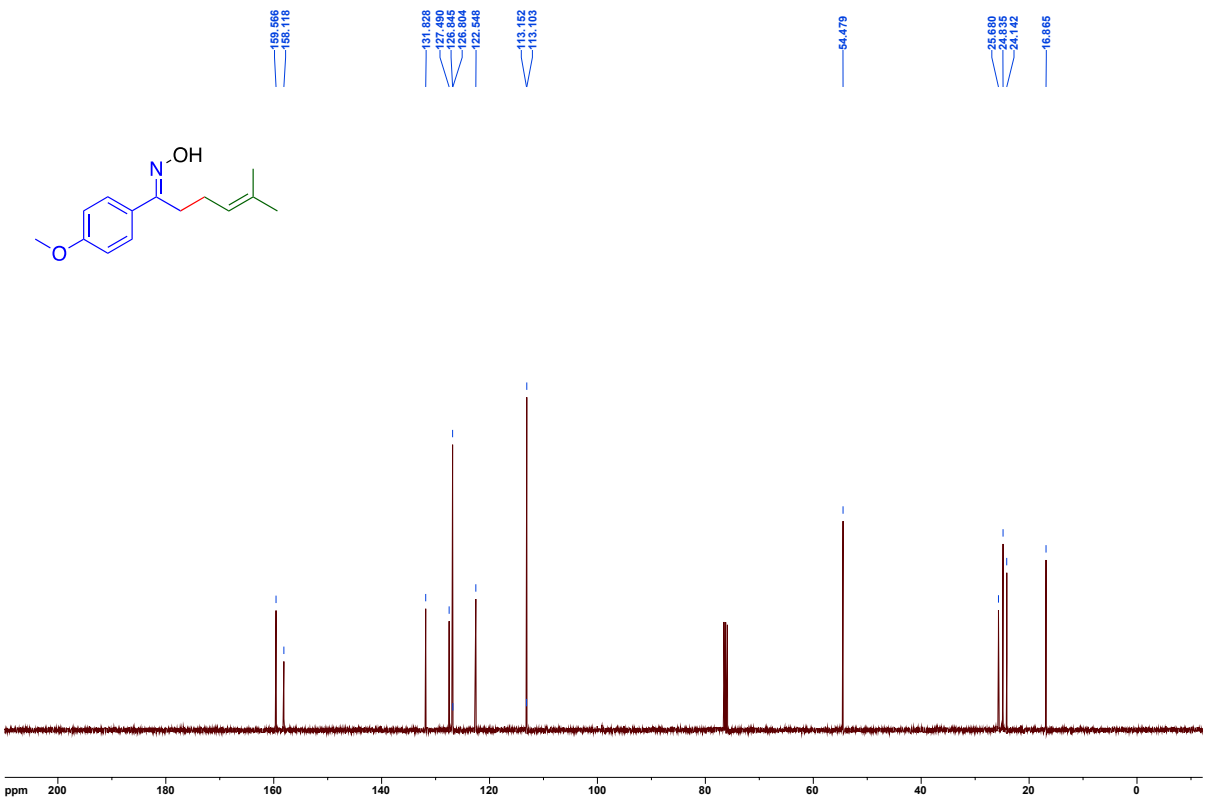
^{13}C NMR spectrum of (2-(2-hydroxypropan-2-yl)cyclopropyl)(4-methoxyphenyl)methanone (**4d**, 101 MHz, $CDCl_3$):



^{1}H NMR spectrum of (*E*)-1-(4-methoxyphenyl)-5-methylhex-4-en-1-one oxime (**4e**, 400 MHz, $CDCl_3$)**:**



^{13}C NMR spectrum of (*E*)-1-(4-methoxyphenyl)-5-methylhex-4-en-1-one oxime (**4e**, 101 MHz, $CDCl_3$):



References:

1) Narender, T.; Sarkar, S.; Rajendar, K.; Tiwari, S. Synthesis of Biaryls via $AlCl_3$ Catalyzed Domino Reaction Involving Cyclization, Dehydration, and Oxidation. *Org. Lett*. **2011**, *13*, 6140-6143.

2) Antonioletti, R.; Magnanti, S.; Scettri, A. Br^+-Induced Cyclization of γ,δ-Unsaturated Ketones: Anew Approach to Bromopyrane Derivatives. *Tetrahedron. Lett*. **1994**, *35*, 2619-2620.

3) Dechoux, L.; Ebel, M.; Jung, L.; Stambach, J, F. A Simple One-Pot Preparation Of (Z)-Cyclopropanes from γ,δ-Ketoalkenes using KOH/DMSO Intramolecular Alkylation Conditions. *Tetrahedron. Lett*. **1993**, *34*, 7405-7408.

4) Chen, F.; Yang, X. L.; Wu, Z. W.; Han, B. Synthesis of Isoxazoline/Cyclic Nitrone-Featured Methylenes Using Unsaturated Ketoximes: A Dual Role of TEMPO. *J. Org. Chem*. **2016**, *81*, 3042-3050.