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Supporting Information

Towards an efficient methodology for the synthesis of functionalized dihydropyrans by silyl-Prins cyclization: access to truncated natural products

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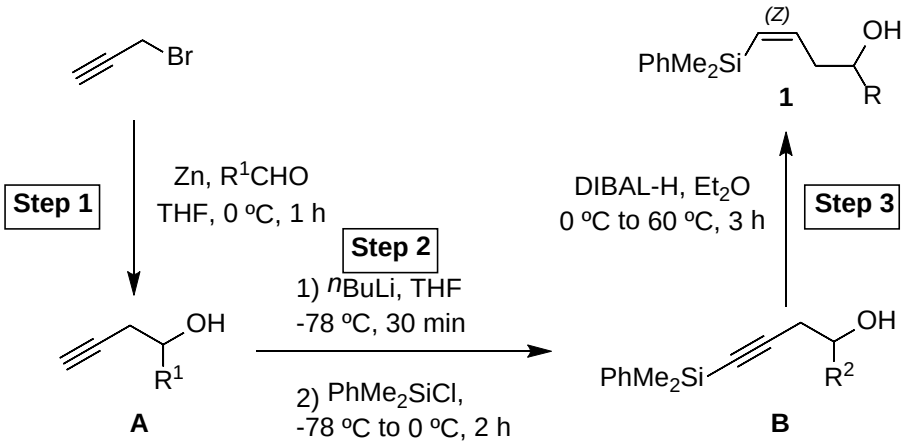
1. GENERAL PROCEDURES

Unless otherwise noted, experiments were carried out with dry solvents under nitrogen atmosphere. Dichloromethane was dried with preactivated molecular sieves. Flash column chromatography was performed using Silica Gel 60 (230-400 mesh ASTM). Thin layer chromatography (TLC) was performed using aluminium backed plate, pre-coated with silica gel (0.20 mm, silica gel 60) with a fluorescent indicator (254 nm) from Macherey. NMR spectra were recorded at nuclear magnetic resonance service of the Laboratory of Instrumental Techniques (L.T.I., www.laboratoriotecnicasinstrumentales.es) University of Valladolid at Varian 400 MHz (^{1}H, 399.85 MHz; ^{13}C, 100.61 MHz), Varian 500 MHz (^{1}H, 500.12 MHz; ^{13}C, 100.61 MHz) spectrometers at room temperature (25 °C). Chemical shifts (δ) were reported in parts per million (ppm) relative to the residual solvent peaks recorded, rounded to the nearest 0.01 for ^{1}H-NMR and 0.1 for ^{13}C-NMR (reference: $CDCl_3$ [^{1}H: 7.26, ^{13}C: 77.2]). Spin-spin coupling constants (*J*) in ^{1}H-NMR were given in Hz to the nearest 0.1 Hz, and peak multiplicity was indicated as follows s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). ^{13}C NMR were recorded with complete proton decoupling. Carbon types, structure assignments and attribution of peaks were determined from two-dimensional correlation experiments (HSQC, COSY and HMBC). Relative stereochemistry was assigned based on the 2D-NOE experiments. High-resolution mass spectra (HRMS) were measured at mass spectrometry service of the Laboratory of Instrumental Techniques, University of Valladolid, on a UPLC-MS system (UPLC: Waters ACQUITY H-class UPLC; MS: Bruker Maxis Impact) by electrospray ionization (ESI positive).

2. EXPERIMENTAL SECTION

2.1. Synthesis of *Z*-vinylsilyl alcohols **1**

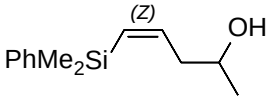


Step 1. To a suspension of 2.35 g of Zn (36 mmol, 1.2 equiv.) in 25 mL THF (1.4 M), cooled at 0 °C and under nitrogen atmosphere, 2.82 mL of propargyl bromide (30 mmol, 1 equiv.) and the corresponding aldehyde (36 mmol, 1.2 equiv.) were added dropwise. The mixture was stirred at 0 °C for one hour. Then, the reaction was quenched with 20 mL of NH_4Cl sat. and the aqueous phase was extracted three times with diethyl ether (3 x 20 mL). The organic phases were combined, washed with NaCl sat. (50 mL) and dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the resulting crude product **1** was used in the next step without further purification.

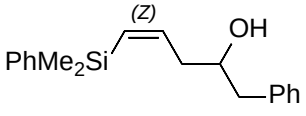
Step 2. To a solution of alkynyl alcohol **A** (12 mmol, 1 equiv.) in THF (0.8 M), cooled to -78 °C and under nitrogen atmosphere, 16.5 mL of *n*-BuLi 1.6 M (26.4 mmol, 2.2 equiv.) were added dropwise and the mixture was stirred at -78 ºC for 30 minutes. Then, 3.92 mL of chloro(dimethyl)phenylsilane (26.4 mmol, 2.2 equiv.) was added into the reaction and the temperature was allowed to rise to 0 °C. When the starting material was consumed, the reaction was quenched slowly with 15 mL HCl 1 M. The phases were separated and the aqueous phase was extracted three times with diethyl ether (3 x 15 mL). The organic phases were combined, washed with NaCl sat. (40 mL) and dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure. The crude mixture was purified by column chromatography in silica gel, using a mixture of hexane-ethyl acetate (8:1) and yielding alkynylsilyl alcohols **B.**

Step 3. To a solution of alkynylsilyl alcohol **B** (6 mmol, 1 equiv.) in Et_2O (0.5 M) was added dropwise 16.4 mL of DIBAL-H 1.1 M at 0 °C and under nitrogen atmosphere. The resulting mixture was stirred at reflux (60 °C) for three-four hours. When the starting material was consumed, the reaction was quenched at 0 °C with 15 mL of HCl 1 M. The phases were separated and the aqueous phase was

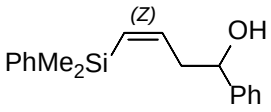
extracted three times with diethyl ether (3 x 15 mL). The organic phases were combined, washed with NaCl sat. (40 mL) and dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure. The crude mixture is purified by column chromatography in silica gel, using a mixture of hexane-ethyl acetate (8:1) to afford Z-vinylsilyl alcohols **1**.



(*Z*)-5-(dimethyl(phenyl)silyl)pent-4-en-2-ol (**1a**) was obtained as a yellow oil in 83% chemical yield (1.1 g from 6 mmol of corresponding alkynyl alcohol **B**), following the general procedure 1, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58 – 7.52 (m, 2H, Ar-*H*), 7.40 – 7.33 (m, 3H, Ar-*H*), 6.46 (dt, *J* = 14.1, 7.5 Hz, 1H, =C*H*), 5.84 (dt, *J* = 14.1, 1.4 Hz, 1H, *H*C=), 3.81 – 3.73 (m, 1H, *H*C-OH), 2.21 (ddd, *J* = 7.5, 6.3, 1.3 Hz, 2H, CH_2), 1.10 (d, *J* = 6.2 Hz, 3H, CH_3), 0.41 (s, 3H, Si-CH_3), 0.40 (s, 3H, Si-CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.1 (=CH), 139.5 (C), 133.9 (CH), 130.6 (HC=), 129.1 (CH), 128.0 (CH), 67.7 (CH), 43.1 (CH_2), 23.0 (CH_3), -0.7 (CH_3), -0.8 (CH_3).

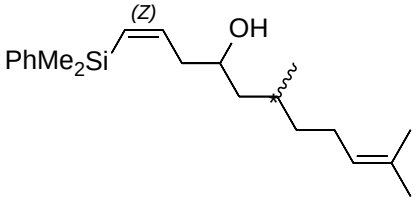


(*Z*)-5-(dimethyl(phenyl)silyl)-1-phenylpent-4-en-2-ol (**1b**) was obtained as a yellow oil in 63% chemical yield (1.1 g from 6 mmol of corresponding alkynyl alcohol **B**) following the general procedure 1. **^{1}H NMR (500 MHz, $CDCl_3$)** 7.58 – 7.50 (m, 2H, Ar-*H*), 7.40 – 7.34 (m, 3H, Ar-*H*), 7.33 – 7.27 (m, 2H, Ar-*H*), 7.25 – 7.12 (m, 3H, Ar-*H*), 6.53 (dt, *J* = 14.1, 7.4 Hz, 1H, =C*H*), 5.86 (dt, *J* = 14.1, 1.4 Hz, 1H, *H*C=), 3.83 – 3.76 (m, 1H, *H*C-OH), 2.68 (dd, *J* = 13.6, 4.6 Hz, 1H, C*H*H-Ph), 2.58 (dd, *J* = 13.6, 8.1 Hz, 1H, CH*H*-Ph), 2.33 – 2.21 (m, 2H, CH_2), 0.39 (s, 3H, Si-CH_3), 0,38 (s, 3H, Si-CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.1 (=CH), 139.6 (C), 138.4 (C), 133.9 (CH), 130.6 (HC=), 129.6 (CH), 129.1 (CH), 128.7 (CH), 128.0 (CH), 126.6 (CH), 72.4 (CH), 43.6 (CH_2), 40.7 (CH_2), - 0.8 (CH_3), -0.9 (CH_3).



(*Z*)-4-(dimethyl(phenyl)silyl)-1-phenylbut-3-en-1-ol (**1c**) was obtained as a yellow oil in 70% chemical yield (1.2 g from 6 mmol of corresponding alkynyl alcohol **B**) following the general procedure 1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 – 7.53 (m, 2H, Ar-*H*), 7.38 – 7.34 (m, 3H, Ar-*H*), 7.33 – 7.29 (m, 2H, Ar-*H*), 7.27 – 7.25 (m, 1H, Ar-*H*), 7.22 – 7.19 (m, 2H, Ar-*H*), 6.46 (ddd, *J* = 14.1, 7.9, 6.9 Hz, 1H, C=C*H*), 5.86 (dt, *J* = 14.1, 1.3 Hz, 1H, *H*C=C), 4.66 – 4.61 (m, 1H, *H*C-OH), 2.57 – 2.43 (m, 2H, CH_2), 0.39 (s, 3H, Si-CH_3), 0.38 (s, 3H, Si-CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.8 (=CH),

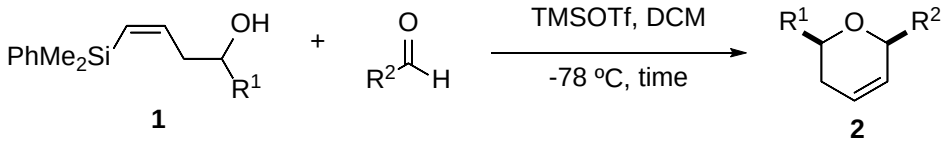
144.0 (C), 139.5 (C), 133.9 (CH), 131.0 (HC=), 129.1 (CH), 128.5 (CH), 128.1 (CH), 127.7 (CH), 125.9 (CH), 73.9 (CH), 43.3 (CH_2), -0.8 (CH_3), -0.8 (CH_3).



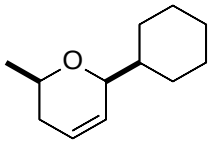
((*Z*)-1-(dimethyl(phenyl)silyl)-6,7,10-trimethylundeca-1,9-dien-4-ol (**1d**) was obtained as a yellow oil in 63% chemical yield (0.6 g from 2.75 mmol of corresponding alkynyl alcohol **B**) following the general procedure 1. **^{1}H NMR (400 MHz, $CDCl_3$)** (both diastereomers **a** + **b)** δ 7.58 – 7.53 (m, 2H, Ar-*H*), 7.37 – 7.32 (m, 3H, Ar-*H*), 6.47 (ddd, *J* = 14.1, 7.9, 7.0 Hz, 1H, =C*H*), 5.83 (dt, *J* = 14.1, 1.0 Hz, 1H, *H*C=), 5.09 (t, *J* = 7.3 Hz, 1H, =CH), 3.72 – 3.61 (m, 1H, *H*C-OH), 2.30 – 2.08 (m, 2H, CH_2), 2.03 – 1.86 (m, 2H, CH_2), 1.76 – 1.53 (m, 1H, C*H*), 1.68 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.40 – 1.01 (m, 4H, CH_2), 0.87 (d, *J* = 6.3 Hz, 3H, CH_3), 0.41 (s, 3H, Si-CH_3), 0.40 (s, 3H, Si-CH_3).

Distinguishable signals of epimer: 0.85 (d, *J* = 6.3 Hz, 3H, CH_3).

2.2. TMSOTf-promoted cyclization of *Z*-vinylsilyl alcohols **1**

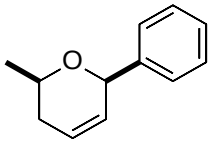


A solution of the *Z*-vinylsilyl alcohol **1** (1.0 equiv.) and the corresponding aldehyde (1.2 equiv.) in dichloromethane (0.05 M) was cooled to -78 °C (under nitrogen). The Lewis acid TMSOTf (1.0 equiv) was then added dropwise and the mixture stirred at this temperature for 30 min while monitored by TLC. When starting materials were consumed, it was quenched with 5 mL of $NaHCO_3$ (sat). Phases are then separated, extracting the aqueous phase three times with dichloromethane (3 x 10 mL). The organic phases are combined, washed with NaCl sat. (20 mL) and dried over anhydrous Na_2SO_4. The solvent is then evaporated under reduced pressure. The crude mixture is purified by column chromatography in silica gel, using mixtures of hexane-ethyl acetate and yielding dihydropyrans **2.** Compounds **2a-b, 2d-h** have been previously described.

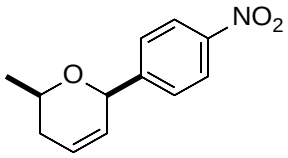


(2*R**,6*S**)-6-cyclohexyl-2-methyl-3,6-dihydro-2*H*-pyran (**2c**). Following the general procedure, compound **2c** was obtained from vinylsilyl alcohol **1a** (79.3 mg, 0.36 mmol) and cyclohexaldehyde as a colourless oil (42.2 mg, 65%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.84 – 5.77 (m, 1H, *H*C=), 5.65 (dq, *J* = 10.3, 1.9 Hz, 1H, =C*H*), 3.96 – 3.89 (m, 1H, O-C*H*), 3.69 – 3.59 (m, 1H, *H*C-O),

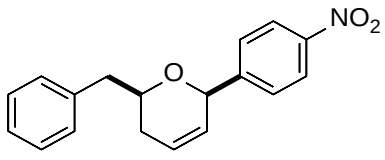
1.94 – 1.89 (m, 2H), 1.80 – 1.69 (m, 4H), 1.68 – 1.61 (m, 1H), 1.51 – 1.42 (m, 1H), 1.28 – 1.22 (m, 1H), 1.21 (d, *J* = 6.2 Hz, 3H, C*H*$_3$), 1.18 – 1.04 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 128.7 (=CH), 125.3 (HC=), 79.2 (O-CH), 70.0 (HC-O), 42.9 (CH), 33.3 (CH_2), 28.6 (CH_2), 28.4 (CH_2), 26.8 (CH_2), 26.6 (CH_2), 26.4 (CH_2), 21.9 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{12}H_{20}NaO$ ([M+Na]$^+$): 203.1406, found 203.1408.



(2*R**,6*R**)-2-methyl-6-phenyl-3,6-dihydro-2*H*-pyran (**2i**). Following the general procedure, compound **2i** was obtained from vinylsilyl alcohol **1a** (79.3 mg, 0.36 mmol) and benzaldehyde as a colourless oil (22 mg, 35%). **^{1}H NMR (500 MHz, CDCl$_3$)** δ (ppm) 7.39 -7.31 (m, 4H, Ar-*H*), 7.29 – 7.25 (m, 1H, Ar-*H*), 5.93 – 5.88 (m, 1H, *H*C=), 5.73 (ddt, *J* = 10.1, 2.8, 1.5 Hz, 1H, =C*H*), 5.20 – 5.16 (m, 1H, O-C*H*), 3.95 – 3.85 (m, 1H, *H*C-O), 2.16 – 2.08 (m, 1H, C*H*H), 2.08 – 2.01 (m, 1H, CH*H*), 1.30 (d, *J* = 6.2 Hz, 3H, C*H*$_3$). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 141.8 (C), 130.2 (=CH), 128.6 (CH), 127.9 (CH), 127.4 (CH), 124.8 (HC=), 77.9 (O-CH), 70.7 (CH-O), 32.8 (CH_2), 22.0 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{12}H_{14}NaO$ ([M+Na]$^+$): 197.0937, found 197.0936.

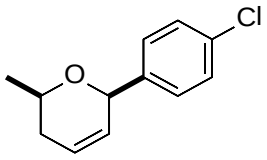


(2*R**,6*R**)-2-methyl-6-(4-nitrophenyl)-3,6-dihydro-2*H*-pyran (**2j**). Following the general procedure, compound **2j** was obtained from vinylsilyl alcohol **1a** (79.3 mg, 0.36 mmol) and 4-nitrobenzaldehyde as yellow solid (54 mg, 68%). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.20 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.55 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 5.98 – 5.91 (m, 1H, *H*C=), 5.70 – 5.65 (m, 1H, =C*H*), 5.31 – 5.27 (m, 1H, O-C*H*), 3.96 – 3.87 (m, 1H, *H*C-O), 2.14 – 2.07 (m, 2H, C*H*$_2$), 1.32 (d, *J* = 6.2 Hz, 3H, C*H*$_3$). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 149.2 (C), 147.5 (C), 128.7 (=CH), 127.9 (CH), 125.9 (HC=), 123.9 (CH), 76.8 (O-CH), 70.7 (CH-O), 32.5 (CH_2), 21.8 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{12}H_{13}NNaO_3$ ([M+Na]$^+$): 242.0788, found 242.0794. **Melting point**: 65.5 – 67.5 °C.

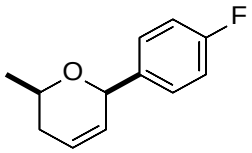


(2*S**,6*R**)-2-benzyl-6-(4-nitrophenyl)-3,6-dihydro-2*H*-pyran (**2k**). Following the general procedure, compound **2k** was obtained from vinylsilyl alcohol **1b** (80 mg, 0.27 mmol) and 4-nitrobenzaldehyde as yellow solid (53 mg, 67%). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.21 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.54 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.31 – 7.22 (m, 5H, Ar-*H*), 5.94 – 5.88 (m, 1H, *H*C=), 5.72 – 5.65 (m, 1H, =C*H*), 5.30 – 5.26 (m, 1H, O-C*H*), 4.04 – 3.96 (m, 1H, *H*C-O), 3.05 (dd, *J* =

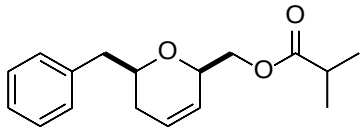
13.9, 6.4 Hz, 1H, Ph-C*H*H), 2.82 (dd, *J* = 13.9, 6.4 Hz, 1H, Ph-CH*H*), 2.22 – 2.13 (m, 1H, C*H*H), 2.06 – 1.97 (m, 1H, CH*H*). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.2 (C), 147.5 (C), 138.2 (C), 129.6 (CH), 128.8 (=CH), 128.4 (CH), 127.7 (CH), 126.5 (CH), 125.8 (HC=), 123.9 (CH), 76.7 (O-CH), 75.3 (CH-O), 42.5 (CH_2), 30.4 (CH_2). **HRMS (ESI+)** m/z calc. for $C_{18}H_{17}NNaO_3$ ([M+Na]$^+$): 318.1101, found 318.1104. **Melting point**: 83.7 – 85.5 °C.



(2*R**,6*R**)-6-(4-chlorophenyl)-2-methyl-3,6-dihydro-2*H*-pyran (**2l**). Following the general procedure, compound **2l** was obtained from vinylsilyl alcohol **1a** (79.3 mg, 0.36 mmol) and 4-chlorobenzaldehyde as white solid (51 mg, 68%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 (s, 4H, Ar-*H*), 5.94 – 5.88 (m, 1H, *H*C=), 5.67 (ddt, *J* = 10.1, 2.6, 1.5 Hz, 1H, =C*H*), 5.17 – 5.12 (m, 1H, O-C*H*), 3.93 – 3.84 (m, 1H, *H*C-O), 2.14 – 2.00 (m, 2H, CH_2), 1.29 (d, *J* = 6.2 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.4 (C), 133.5 (C), 129.7 (=CH), 128.7 (CH), 128.7 (CH), 125.2 (HC=), 77.1 (O-CH), 70.6 (HC-O), 32.6 (CH_2), 21.9 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{12}H_{13}ClNaO$ ([M+Na]$^+$): 231.0547, found 231.0551. **Melting point**: 39.0 – 40.1 °C.

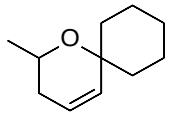


(2*R**,6*R**)-6-(4-fluorophenyl)-2-methyl-3,6-dihydro-2*H*-pyran (**2m**). Following the general procedure, compound **2m** was obtained from vinylsilyl alcohol **1a** (79.3 mg, 0.36 mmol) and 4-fluorbenzaldehyde as a colourless oil (35 mg, 50%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (dd, $^3J_{H\text{-}H}$ = 8.8 Hz, $^4J_{H\text{-}F}$ = 5.5 Hz, 2H, Ar-*H*), 7.02 (t, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 8.8 Hz, 2H, Ar-*H*), 5.94 – 5.88 (m, 1H, *H*C=), 5.71 – 5.66 (m, 1H, =C*H*), 5.18 – 5.14 (m, 1H, O-C*H*), 3.93 – 3.85 (m, 1H, *H*C-O), 2.16 – 1.98 (m, 2H, CH_2), 1.29 (d, *J* = 6.3 Hz, 3H, C*H*). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.5 (d, $^1J_{C\text{-}F}$ = 245.4 Hz, C), 137.6 (d, $^4J_{C\text{-}F}$ = 3.1 Hz, C), 129.9 (=CH), 129.1 (d, $^3J_{C\text{-}F}$ = 8.2 Hz, CH), 125.1 (HC=), 115.4 (d, $^2J_{C\text{-}F}$ = 21.4 Hz, CH), 77.2 (O-CH), 70.7 (CH-O), 32.7 (CH_2), 21.9 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{12}H_{13}FNaO$ ([M+Na]$^+$): 215.0843, found 215.0846.

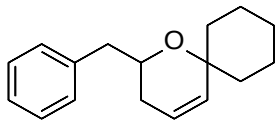


((2*R**,6*S**)-6-benzyl-2-(isobutyryloxymethyl)-5,6-dihydro-2*H*-pyran (**2n**). Following the general procedure, compound **2n** was obtained from vinylsilyl alcohol **1b** (80 mg, 0.27 mmol) and 2-(isobutyryloxymethyl)acetaldehyde as colourless oil (52 mg, 70%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8 7.31 – 7.17 (m, 5H, Ar-*H*), 5.92 – 5.85 (m, 1H, *H*C=), 5.63 – 5.57 (m, 1H, =C*H*), 4.39 – 4.32 (m, 1H, O-C*H*), 4.15 (dd, *J* = 11.3, 6.3 Hz, 1H, *H*HC-O), 4.11 (dd, *J* = 11.3, 4.8 Hz, 1H, H*H*C-

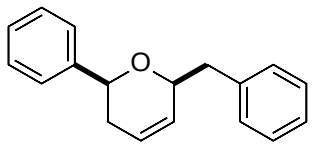
O), 3.83 – 3.74 (m, 1H, *H*C-O), 2.78 (dd, *J* = 13.8, 7.0 Hz, 1H, Ph-C*H*H), 2.72 (dd, *J* = 13.8, 6.2 Hz, 1H, Ph-CH*H*), 2.62 – 2.54 (m, 1H, C*H*), 2.11 – 2.01 (m, 1H, C*H*H), 1.96 – 1.87 (m, 1H, CH*H*), 1.17 (d, *J* = 7.0 Hz, 3H, CH_3), 1.16 (d, *J* = 7.0 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.1 (C), 138.6 (C), 129.5 (CH), 128.3 (CH), 127.1 (HC=), 126.3 (=CH), 126.1 (CH), 74.8 (CH-O), 73.4 (O-CH), 66.2 (CH_2-O), 42.4 (CH_2), 34.1 (CH), 30.8 (CH_2), 19.2 (CH_3), 19.1 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{17}H_{22}NaO_3$ ([M+Na]$^+$): 297.1461, found 297.1469.



2-methyl-1-oxaspiro[5.5]undec-4-ene (**2o**). Following the general procedure, compound **2o** was obtained from vinylsilyl alcohol **1a** (79.3 mg, 0.36 mmol) and cyclohexanone as a colourless oil (44 mg, 73%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.73 – 5.63 (m, 2H, 2x*H*C=), 3.79 (sext, *J* = 6.2, 1H, *H*C-O), 1.92 – 1.87 (m, 2H, CH_2), 1.78 – 1.25 (m, 10H, 5xCH_2), 1.21 (d, *J* = 6.2 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.7 (=CH), 123.2 (HC=), 73.5 (O-C), 63.8 (HC-O), 38.3 (CH_2), 33.9 (CH_2), 33.2 (CH_2), 25.9 (CH_2), 22.1 (CH_2), 21.9 (CH_3), 21.8 (CH_2). Volatil compound. No HRMS.

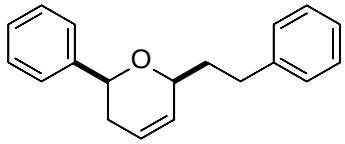


2-benzyl-1-oxaspiro[5.5]undec-4-ene (**2p**). Following the general procedure, compound **2p** was obtained from vinylsilyl alcohol **1b** (80 mg, 0.27 mmol) and cyclohexanone as a colourless oil (46 mg, 70%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 – 7.24 (m, 4H, Ar-*H*), 7.22 – 7.17 (m, 1H, Ar-*H*), 5.67 (ddd, *J* = 10.2, 5.7, 2.0 Hz, 1H, *H*C=), 5.59 (ddd, *J* = 10.2, 2.7, 1.3 Hz, 1H, =C*H*), 3.84 – 3.77 (m, 1H, *H*C-O), 2.87 (dd, *J* = 13.5, 7.9 Hz, 1H, Ph-C*H*H), 2.73 (dd, *J* = 13.5, 5.2 Hz, 1H, Ph-CH*H*), 2.00 (ddt, *J* = 17.1, 10.3, 2.5 Hz, 1H, C*H*H_{Cy}), 1.89 (dddd, *J* = 17.1, 5.7, 3.3, 1.3 Hz, 1H, CHH_{Cy}), 1.71 – 1.63 (m, 2H, CH_2), 1.62 – 1.56 (m, 1H, C*H*H), 1.49 – 1.43 (m, 2H, CH_{2Cy}), 1.42 – 1.32 (m, 1H, CHH_{Cy}), 1.27 – 1.09 (m, 2H, CH_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.4 (C), 135.4 (=CH), 129.7 (CH), 128.1 (CH), 126.1 (CH), 123.9 (HC=), 73.5 (O-C), 69.1 (HC-O), 42.9 (CH_2), 38.3 (CH_2), 33.1 (CH_2), 31.5 (CH_2), 25.7 (CH_2), 21.6 (CH_2), 21.1 (CH_2). **HRMS (ESI+)** m/z calc. for $C_{17}H_{22}NaO$ ([M+Na]$^+$): 265.1563, found 265.1569.

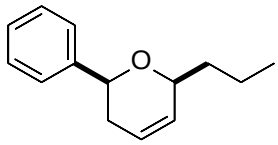


(2*S**,6*S**)-6-benzyl-2-phenyl-3,6-dihydro-2*H*-pyran (**2q**). Following the general procedure, compound **2q** was obtained from vinylsilyl alcohol **1c** (80 mg, 0.28 mmol) and phenylacetaldehyde as a colourless oil (35 mg, 50%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 – 7.33 (m, 4H, Ar-*H*), 7.32 – 7.26 (m, 5H, Ar-*H*), 7.25 – 7.20 (m, 1H, Ar-*H*), 5.92 – 5.82 (m, 1H, *H*C=), 5.76 – 5.69 (m, 1H, =C*H*), 4.62 (dd, *J* = 9.2, 4.8 Hz, 1H, *H*C-O), 4.59 – 4.52 (m, 1H, O-C*H*), 3.08 (dd, *J* = 13.5, 6.4

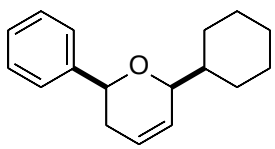
Hz, 1H, Ph-C*H*H), 2.84 (dd, *J* = 13.5, 7.2 Hz, 1H, Ph-CH*H*), 2.27 – 2.22 (m, 2H, CH_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.0 (C), 138.3 (C), 129.9 (CH), 129.5 (=CH), 128.4 (CH), 128.3 (CH), 127.4 (CH), 126.4 (CH), 125.8 (CH), 125.2 (=CH), 76.5 (O-CH), 75.8 (HC-O), 42.2 (CH_2), 33.4 (CH_2). **HRMS (ESI+)** m/z calc. for $C_{18}H_{18}NaO$ ([M+Na]$^+$): 273.1250, found 273.1256.



(2*S**,6*S**)-6-phenethyl-2-phenyl-3,6-dihydro-2*H*-pyran (**2r**). Following the general procedure, compound **2r** was obtained from vinylsilyl alcohol **1c** (80 mg, 0.28 mmol) and 3-phenylpropionaldehyde as a colourless oil (58 mg, 78%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.37 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 7.28 (t, *J* = 7.3 Hz, 3H, Ar-*H*), 7.23 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.18 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 5.96 – 5.89 (m, 1H, *H*C=), 5.76 – 5.70 (m, 1H, =C*H*), 4.63 (dd, *J* = 9.2, 4.7 Hz, 1H, *H*C-O), 4.39 – 4.33 (m, 1H, O-C*H*), 2.89 – 2.78 (m, 2H, CH_2-Ph), 2.31 – 2.25 (m, 2H, CH_2), 1.99 – 1.91 (m, 2H, CH_2-CH_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.2 (C), 143.1 (C), 130.4 (=CH), 128.7 (CH), 128.4 (CH), 127.4 (CH), 125.8 (CH), 125.2 (HC=), 75.6 (HC-O), 74.7 (O-CH), 37.3 (CH_2), 33.4 (CH_2), 31.4 (CH_2). **HRMS (ESI+)** m/z calc. for $C_{19}H_{20}NaO$ ([M+Na]$^+$): 287.14096, found 287.1409.

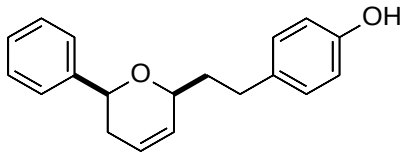


(2*S**,6*S**)-2-phenyl-6-propyl-3,6-dihydro-2*H*-pyran (**2s**). Following the general procedure, compound **2s** was obtained from vinylsilyl alcohol **1c** (80 mg, 0.28 mmol) and propionaldehyde as a colourless oil (42 mg, 75%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 – 7.38 (m, 2H, Ar-*H*), 7.37 – 7.32 (m, 2H, Ar-*H*), 7.29 – 7.24 (m, 1H, Ar-*H*), 5.92 – 5.87 (m, 1H, *H*C=), 5.75 – 5.70 (m, 1H, =C*H*), 4.61 (dd, *J* = 9.2, 4.8 Hz, 1H, *H*C-O), 4.37 – 4.30 (m, 1H, O-C*H*), 2.29 – 2.23 (m, 2H, CH_2), 1.67 – 1.57 (m, 2H, CH_2), 1.56 – 1.44 (m, 2H, CH_2), 0.96 (t, *J* = 7.2 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.3 (C), 130.8 (=CH), 128.4 (CH), 127.3 (CH), 125.9 (CH), 124.7 (HC=), 75.6 (HC-O), 75.4 (O-CH), 37.9 (CH_2), 33.4 (CH_2), 18.4 (CH_2), 14.4 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{14}H_{18}NaO$ ([M+Na]$^+$): 225.1250, found 225.1553.

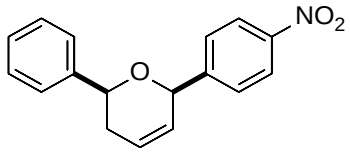


(2*S**,6*S**)-6-cyclohexyl-2-phenyl-3,6-dihydro-2*H*-pyran (**2t**). Following the general procedure, compound **2t** was obtained from vinylsilyl alcohol **1c** (80 mg, 0.28 mmol) and cyclohexanecarbaldehyde as a colourless oil (52 mg, 76%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 – 7.37 (m, 2H, Ar-*H*), 7.36 – 7.31 (m, 2H, Ar-*H*), 7.28 – 7.23 (m, 1H, Ar-*H*), 5.96 – 5.89 (m, 1H, *H*C=), 5.75

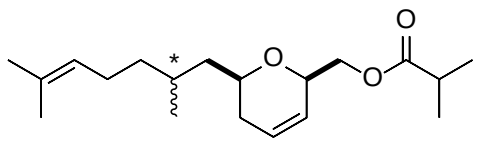
(dq, *J* = 10.3, 1.9 Hz, 1H, =C*H*), 4.59 (t, *J* = 6.9 Hz, 1H, *H*C-O), 4.17 – 4.10 (m, 1H, O-C*H*), 2.26 – 2.19 (m, 2H, CH_{2Cy}), 1.87 – 1.62 (m, 4H), 1.71 – 1.65 (m, 1H, C*H*H), 1.61 – 1.55 (m, 1H), 1.32 – 1.11 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.6 (C), 129.2 (=CH), 128.4 (CH), 127.2 (CH), 125.8 (CH), 125.2 (HC=), 79.6 (O-CH), 75.4 (HC-O), 43.1 (CH), 33.7 (CH_2), 28.8 (CH_2), 28.2 (CH_2), 26.8 (CH_2), 26.6 (CH_2), 26.5 (CH_2). **HRMS (ESI+)** m/z calc. for $C_{17}H_{22}NaO$ ([M+Na]$^+$): 265.1563, found 265.1569.



(2*S**,6*S**)-6-(4-hydroxyphenethyl)-2-phenyl-3,6-dihydro-2*H*-pyran (**2u**). Following the general procedure, compound **2u** was obtained from vinylsilyl alcohol **1c** (80 mg, 0.28 mmol) and 3-(4-hydroxyphenyl)propanal as a yellow viscous oil (40 mg, 51%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 – 7.40 (m, 2H, Ar-*H*), 7.40 – 7.35 (m, 2H, Ar-*H*), 7.32 – 7.27 (m, 1H, Ar-*H*), 7.09 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 6.74 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 5.96 – 5.91 (m, 1H, *H*C=), 5.73 (ddt, *J* = 10.2, 2.8, 1.5 Hz, 1H, =C*H*), 4.86 (br s, 1H, O*H*), 4.63 (dd, *J* = 9.7, 4.3 Hz, 1H, *H*C-O), 4.39 – 4.32 (m, 1H, O-C*H*), 2.77 (td, *J* = 7.5, 3.0 Hz, 2H, CH_2-Ph), 2.35 – 2.25 (m, 2H, CH_2), 1.95 – 1.87 (m, 2H, CH_2-CH_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.7 (C), 143.1 (C), 134.7 (C), 130.4 (=CH), 129.7 (CH), 128.5 (CH), 127.4 (CH), 125.9 (CH), 125.1 (HC=), 115.3 (CH), 75.6 (HC-O), 74.7 (O-CH), 37.5 (CH_2), 33.3 (CH_2), 30.4 (CH_2). **HRMS (ESI+)** m/z calc. for $C_{19}H_{20}NaO_2$ ([M+Na]$^+$): 303.1356, found 303.1362.



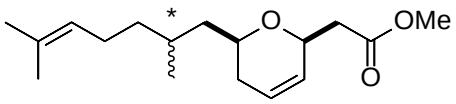
(2*S**,6*R**)-6-(4-nitrophenyl)-2-phenyl-3,6-dihydro-2*H*-pyran (**2v**). Following the general procedure, compound **2w** was obtained from vinylsilyl alcohol **1c** (80 mg, 0.28 mmol) and 4-nitrobenzaldehyde as a yellow oil (61 mg, 77%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 7.63 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 7.46 – 7.42 (m, 2H, Ar-H), 7.40 – 7.35 (m, 2H, Ar-*H*), 7.33 – 7.28 (m, 1H, Ar-*H*), 6.09 – 6.02 (m, 1H, *H*C=), 5.80 (ddt, *J* = 10.2, 2.8, 1.5 Hz, 1H, =C*H*), 5.52 – 5.48 (m, 1H, O-C*H*), 4.84 (dd, *J* = 10.4, 3.5 Hz, 1H, *H*C-O), 2.52 – 2.43 (m, 1H, C*H*H), 2.41 – 2.33 (m, 1H, CH*H*). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.0 (C), 147.6 (C), 142.1 (C), 129.0 (CH), 128.7 (=CH), 127.9 (CH), 127.8 (CH), 126.0 (CH), 125.9 (HC=), 123.9 (CH), 77.4 (O-CH), 76.3 (CH-O), 32.9 (CH_2). **HRMS (ESI+)** m/z calc. for $C_{17}H_{15}NNaO_3$ ([M+Na]$^+$): 304.0944, found 304.0939.



(2*R**,6*R**)-2-(isobutyryloxymethyl)-6-(2,6-dimethylhept-5-en-1-yl)-3,6-dihydro-2*H*-pyran (**2w**). Following the general procedure, compound **2w**, as a mixture of epimers, was obtained from vinylsilyl alcohol **1d** (70 mg, 0.21 mmol) and 2-

(isobutyryloxy)acetaldehyde as a yellow oil (26 mg, 40%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.95 – 5.87 (m, 1H, *H*C=), 5.63 – 5.57 (m, 1H, =C*H*), 5.12 – 5.07 (m, 1H, =CH), 4.37 – 4.29 (m, 1H, O-C*H*), 4.16 – 4.05 (m, 2H, H_2C-O), 3.68 – 3.58 (m, 1H, *H*C-O), 2.57 (sept, *J* = 7.2 Hz, 1H), 2.07 – 1.86 (m, 4H), 1.66 – 1.59 (m, 1H), 1.68 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.53 – 1.29 (m, 2H), 1.26 – 1.10 (m, 2H), 1.18 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 0.92 (d, *J* = 6.7 Hz, 3H, CH_3).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.2 (C), 131.3 (C), 127.5 (CH), 126.2 (CH), 125.1 (CH), 73.4 (O-CH), 72.5 (HC-O), 66.3 (CH_2), 43.4 (CH_2), 37.7 (CH_2), 34.1 (CH), 31.9 (CH_2), 29.4 (CH), 25.9 (CH_3), 25.7 (CH_2), 20.1 (CH_3), 19.2 (CH_3), 19.1 (CH_3), 17.8 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{19}H_{32}NaO_3$ ([M+Na]$^+$): 331.2444, found 331.2244.

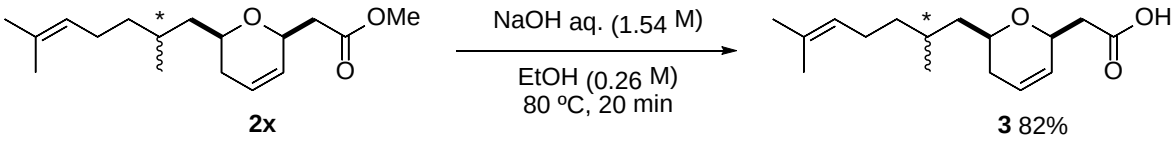
Distinctive signals of epimer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.89 (d, *J* = 6.5 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.1 (C), 131.2 (C), 127.4 (CH), 125.0 (CH), 71.9 (HC-O), 43.2 (CH_2), 37.3 (CH_2), 31.5 (CH_2), 25.6 (CH_2), 19.4 (CH_3).



Methyl 2-((2*S**,6*R**)-6-(2,6-dimethylhept-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-yl)acetate (**2x**). Following the general procedure, compound **2x**, as a mixture of epimers, was obtained from vinylsilyl alcohol **1d** (70 mg, 0.21 mmol) and methyl 3,3-dimethoxypropionate as a yellow oil (27 mg, 46%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.87 – 5.80 (m, 1H, *H*C=), 5.67 – 5.61 (m, 1H, =C*H*), 5.09 (t, *J* = 7.0 Hz, 1H, =CH), 4.57 – 4.47 (m, 1H, O-C*H*), 3.69 (s, 3H, O-C*H*$_3$), 3.67 – 3.59 (m, 1H, *H*C-O), 2.56 (ddd, *J* = 15.0, 8.2, 1.4 Hz, 1H, C*H*H), 2.44 (dd, *J* = 15.0, 6.0 Hz, 1H, CH*H*), 2.05 – 1.85 (m, 4H), 1.68 (s, 3H, CH_3), 1.62 – 1.54 (m, 1H) 1.60 (s, 3H, CH_3), 1.48 – 1.37 (m, 1H), 1.38 – 1.28 (m, 1H), 1.26 – 1.11 (m, 2H), 0.90 (d, *J* = 6.5 Hz, 3H, CH_3).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8 (C), 131.2 (C), 129.0 (CH), 126.2 (CH), 125.1 (CH), 72.9 (HC-O), 71.9 (O-CH), 51.8 (O-CH_3), 43.3 (CH_2), 40.7 (CH_2), 37.6 (CH_2), 31.8 (CH_2), 29.5 (CH), 25.9 (CH_3), 25.7 (CH_2), 20.1 (CH_3), 17.8 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{17}H_{28}NaO_3$ ([M+Na]$^+$): 303.1931, found 303.1937.

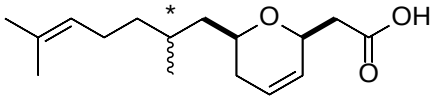
Distinctive signals of epimer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.88 (d, *J* = 6.5 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7 (C), 126.1 (CH), 125.0 (CH), 72.1 (HC-O), 71.8 (O-CH), 51.7 (O-CH_3), 43.2 (CH_2), 37.3 (CH_2), 31.4 (CH_2), 28.9 (CH), 25.6 (CH_2), 19.4 (CH_3).

2.3. Synthesis of carboxylic acid **3**



2x **3** 82%

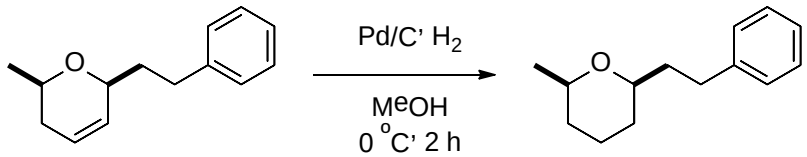
A solution of 72 mg (0.26 mmol, 1.0 equiv.) of the 2,6-*cis*-dihydropyran **2x** in 1 mL ethanol (0.26 M) was added a solution of NaOH 1.54 M. Then, the mixture was stirred at 80 °C for 20 min while monitored by TLC. When starting material was consumed, the heating was stopped and 5 mL of NaOH 2 M was added. The aqueous phase was washing two times with diethyl ether. Then, HCl 1 M was added dropwise to the aqueous phase until pH = 3. The organic compound **3** was dissolved in diethyl ether and extracted three times. The organic phases were combined, washed with NaCl sat., dried over anhydrous Na_2SO_4 and then, concentrated in *vacuo* to afford the crude carboxylic acid **3** (mixture of epimers) as a viscous white oil (56 mg) in 82% yield.



2-((2*S**,6*R**)-6-(2,6-dimethylhept-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-yl)acetic acid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.95 – 5.85 (m, 1H, *H*C=), 5.65 – 5.59 (m, 1H, =C*H*), 5.09 (t, *J* = 7.2 Hz, 1H, =CH), 4.58 – 4.49 (m, 1H, O-C*H*), 3.80 – 3.70 (m, 1H, *H*C-O), 2.66 (ddd, *J* = 15.8, 4.8, 2.0 Hz, 1H, C*H*H), 2.57 (dd, *J* = 15.8, 7.5 Hz, 1H, CH*H*), 2.10 – 1.91 (m, 4H), 1.69 (s, 3H, CH_3), 1.64 – 1.56 (m, 1H), 1.60 (s, 3H, CH_3), 1.52 – 1.12 (m, 4H), 0.92 (d, *J* = 6.6 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.7 (C), 131.4 (C), 128.2 (CH), 126.6 (CH), 124.9 (CH), 73.2 (HC-O), 71.5 (O-CH), 43.2 (CH_2), 40.5 (CH_2), 37.6 (CH_2), 31.6 (CH_2), 29.3 (CH), 25.8 (CH_3), 25.6 (CH_2), 20.1 (CH_3), 17.8 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{16}H_{26}NaO_3$ ([M+Na]$^+$): 289.1774, found 289.1774.

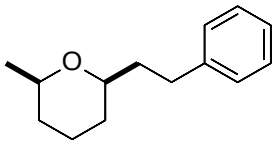
Distinctive signals of epimer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.91 (d, *J* = 6.5 Hz, 3H, CH_3). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.5 (C), 131.3 (C), 126.5 (CH), 72.6 (HC-O), 71.4 (O-CH), 43.1 (CH_2), 37.2 (CH_2), 31.2 (CH_2), 28.8 (CH), 25.5 (CH_2), 19.5 (CH_3).

2.4. Synthesis of tetrahydropyran **4**



2b **4**, 80%

To a stirred solution of **2b** (130 mg, 0.64 mmol) in MeOH (3 mL) at 0 ºC was added Pd/C (10 wt.%, 7 mg). The mixture was stirred at 0 °C under hydrogen atmosphere for 2 hours. The catalyst was then removed by filtration through celite and the filtrate was concentrated under reduced pressure to afford the desired product **4** as a colourless oil in 80% yield (104 mg).

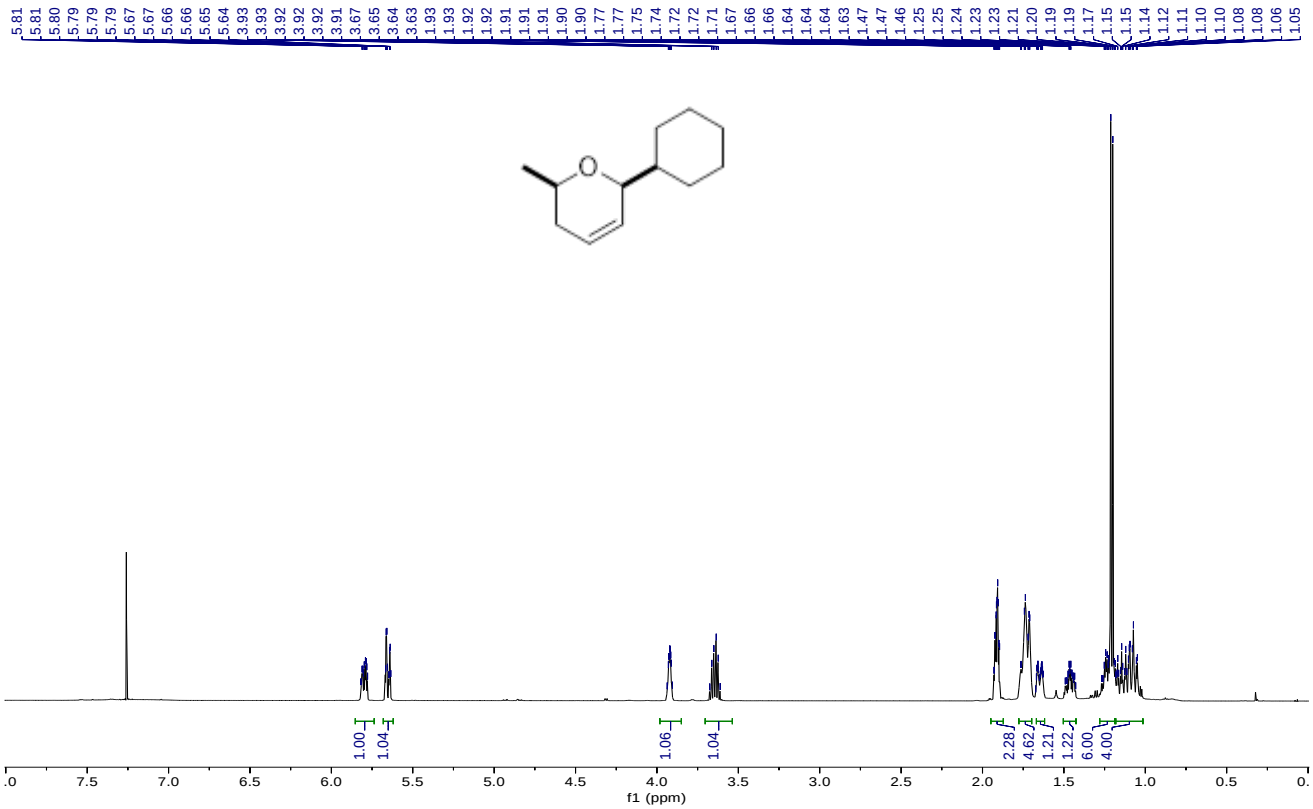


(2*R**,6*R**)-2-methyl-6-phenethyltetrahydro-2*H*-pyran (**4**). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.24 (m, 2H, Ar-*H*), 7.22 – 7.14 (m, 3H, Ar-*H*), 3.46 – 3.35 (m, 1H, O-C*H*), 3.30 – 3.22 (m, 1H, *H*C-O), 2.82 – 2.73 (m, 1H, C*H*H-Ph), 2.73 – 2.63 (m, 1H, CH*H*-Ph), 1.91 – 1.73 (m, 2H), 1.74 – 1.62 (m, 1H), 1.57 – 1.51 (m, 2H), 1.45 (tt, *J* = 13.0, 3.9 Hz, 1H), 1.31 – 1.13 (m, 2H), 1.20 (d, *J* = 6.2 Hz, 3H, C*H*$_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.6 (C), 128.7 (CH), 128.4 (CH), 125.7 (CH), 76.9 (O-CH), 74.0 (CH-O), 38.2 (CH_2), 33.5 (CH_2), 31.9 (CH_2), 31.5 (CH_2), 23.9 (CH_2), 22.4 (CH_3). **HRMS (ESI+)** m/z calc. for $C_{14}H_{20}NaO$ ($[M+Na]^+$): 227.1406, found 227.1403.

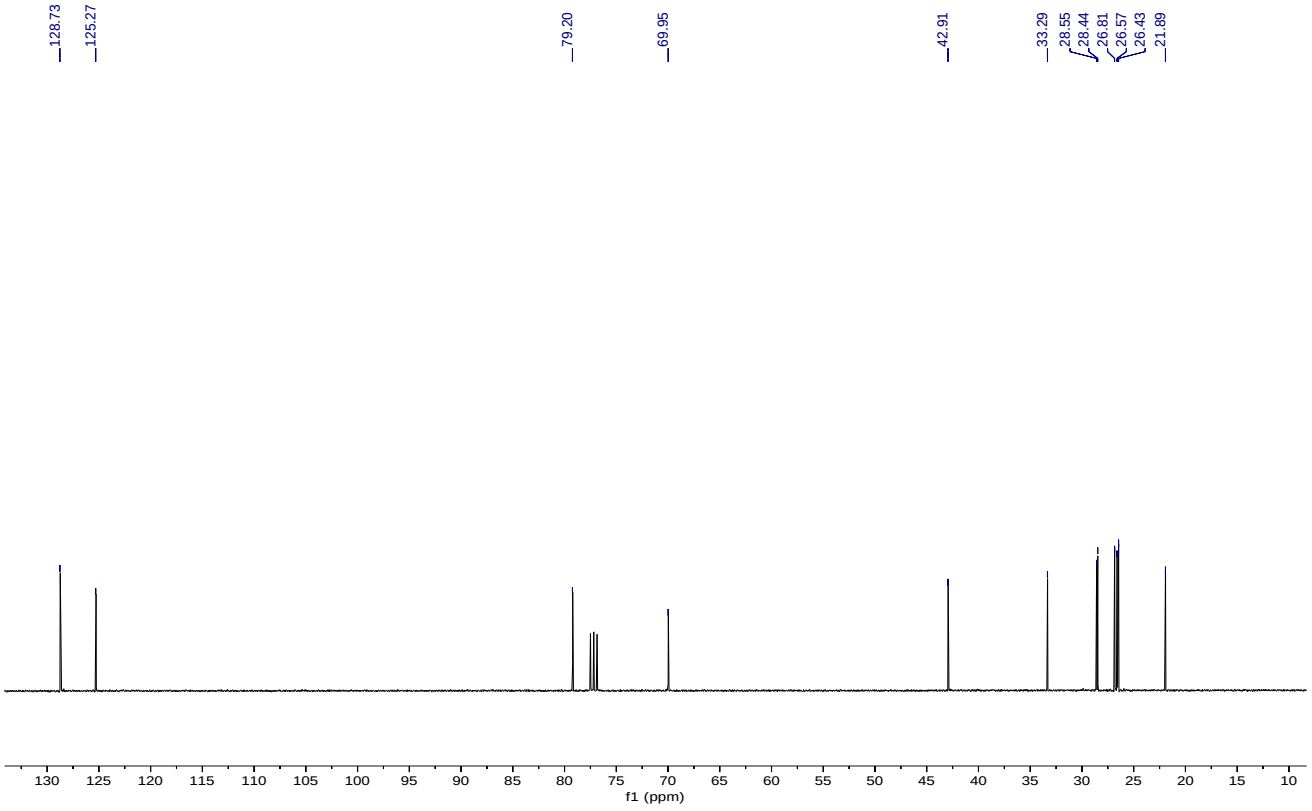
3. ^{1}H and ^{13}C SPECTRA for new compounds

Compound 2c

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

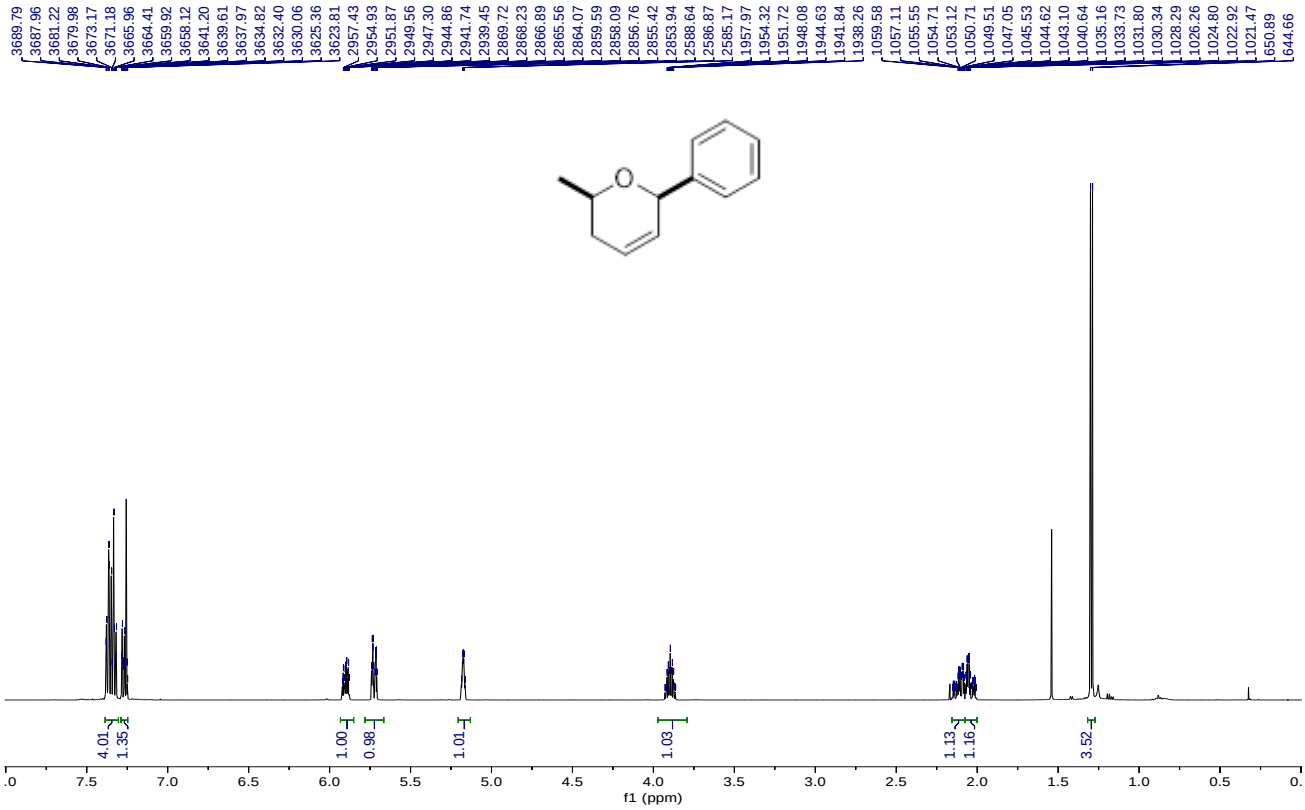


^{13}C NMR (101 MHz, $CDCl_3$)

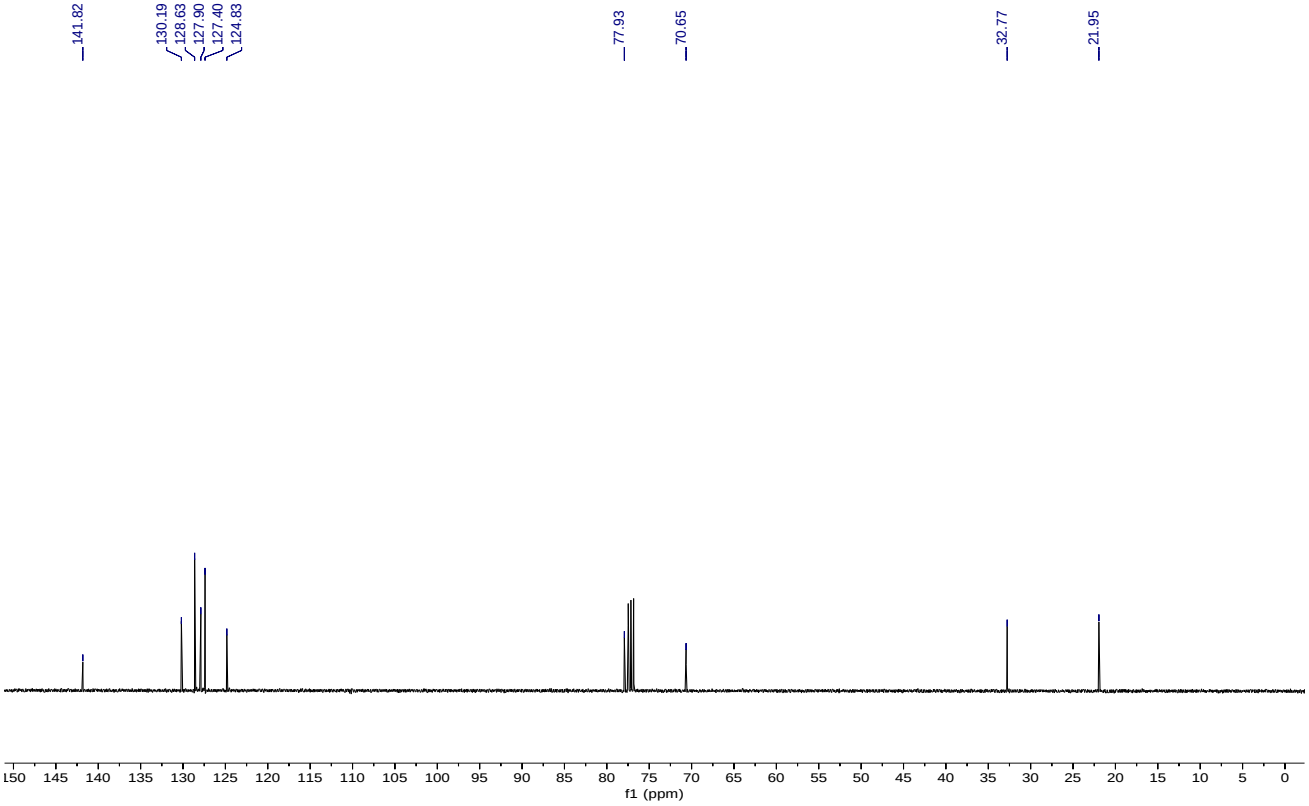


Compound 2i

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

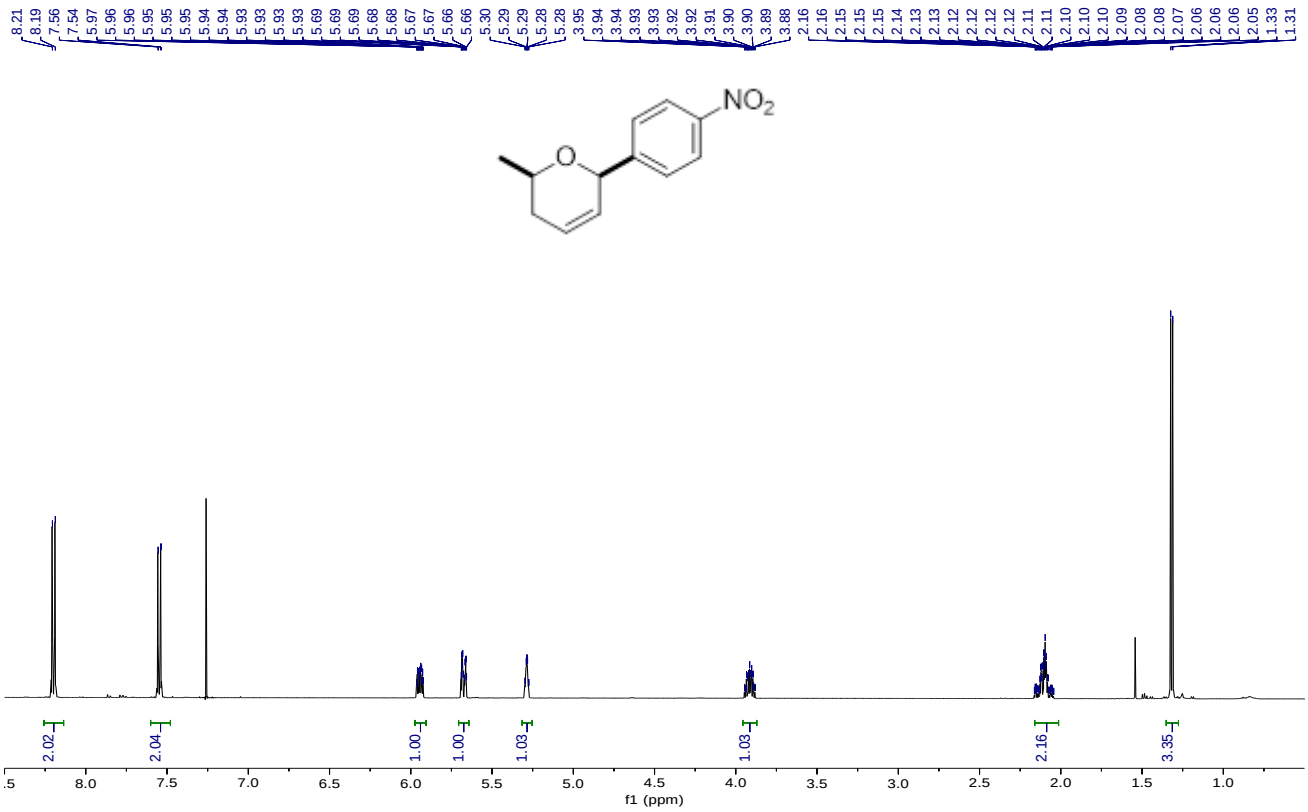


^{13}C NMR (101 MHz, $CDCl_3$)

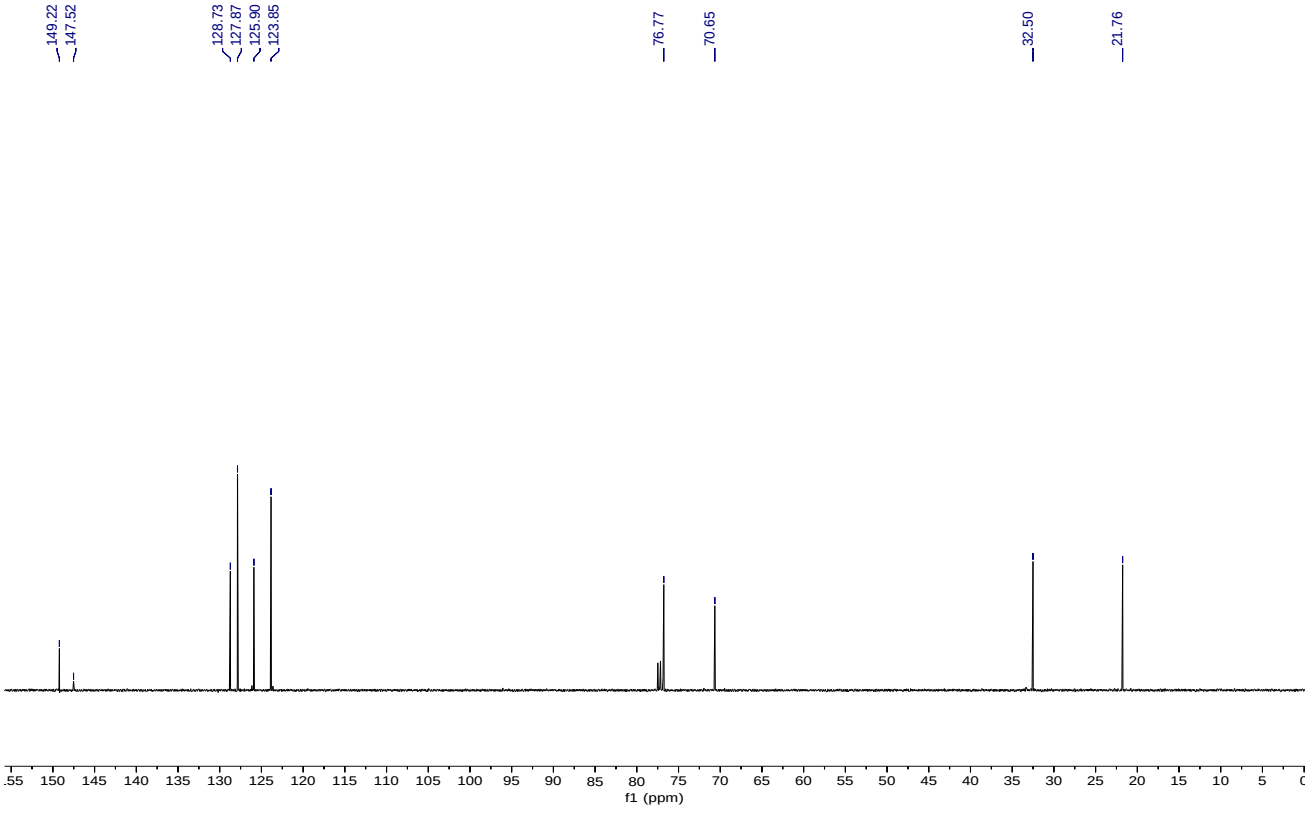


Compound 2j

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

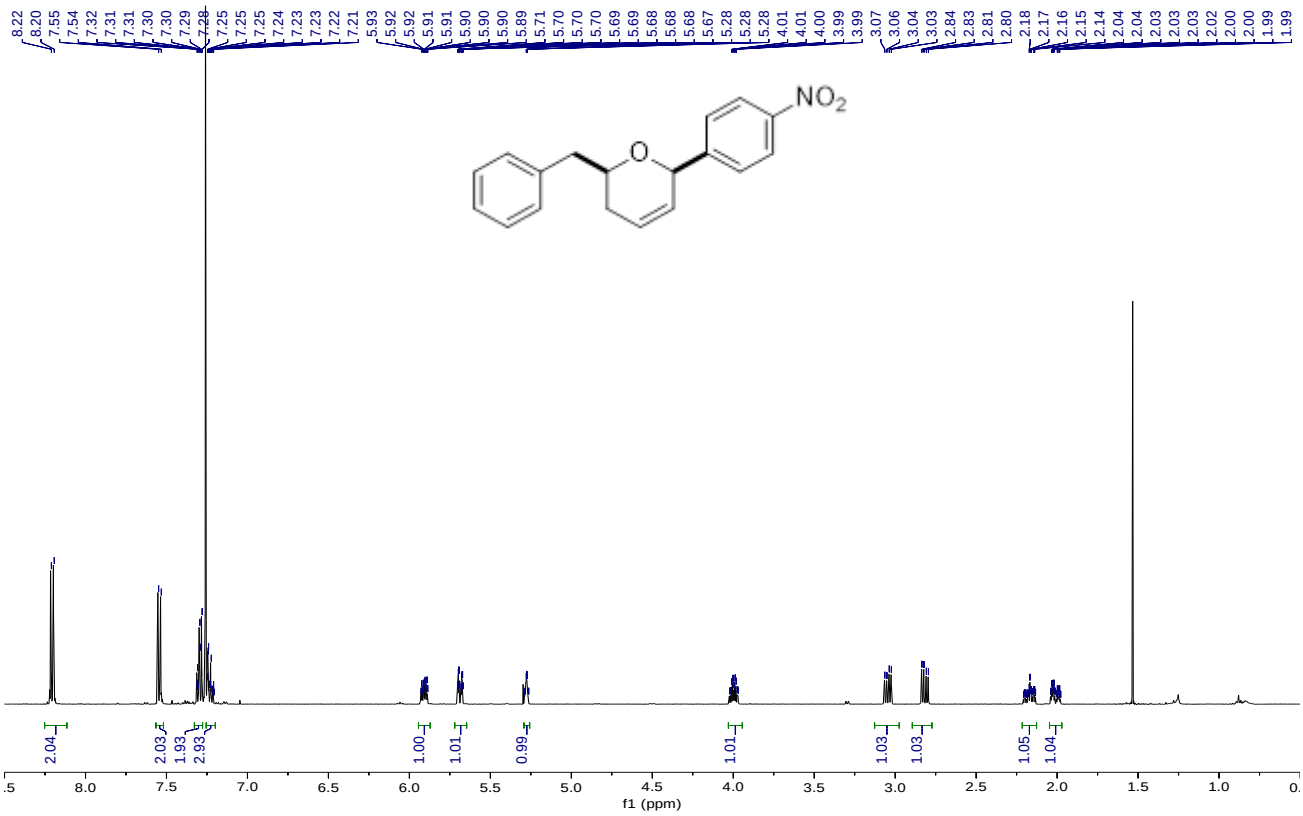


^{13}C NMR (101 MHz, $CDCl_3$)

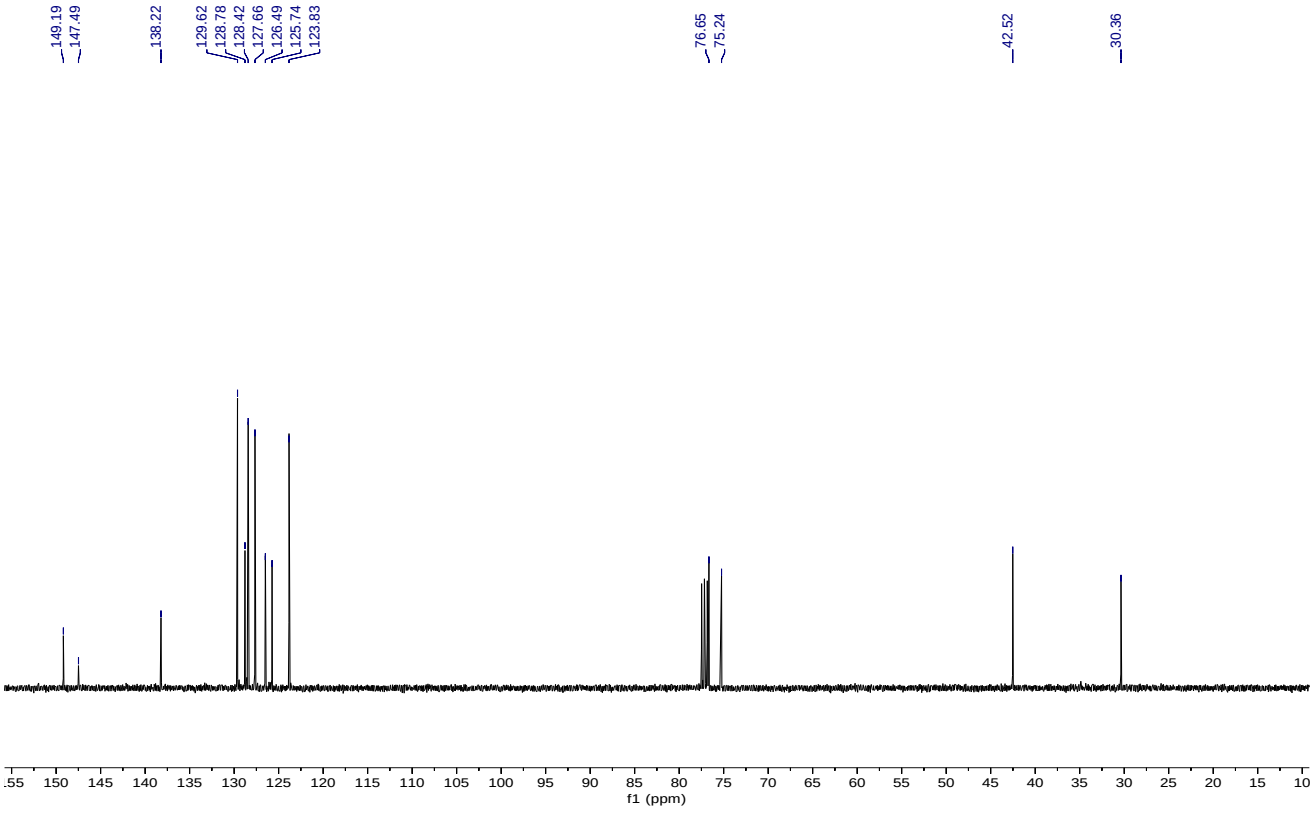


Compound 2k

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

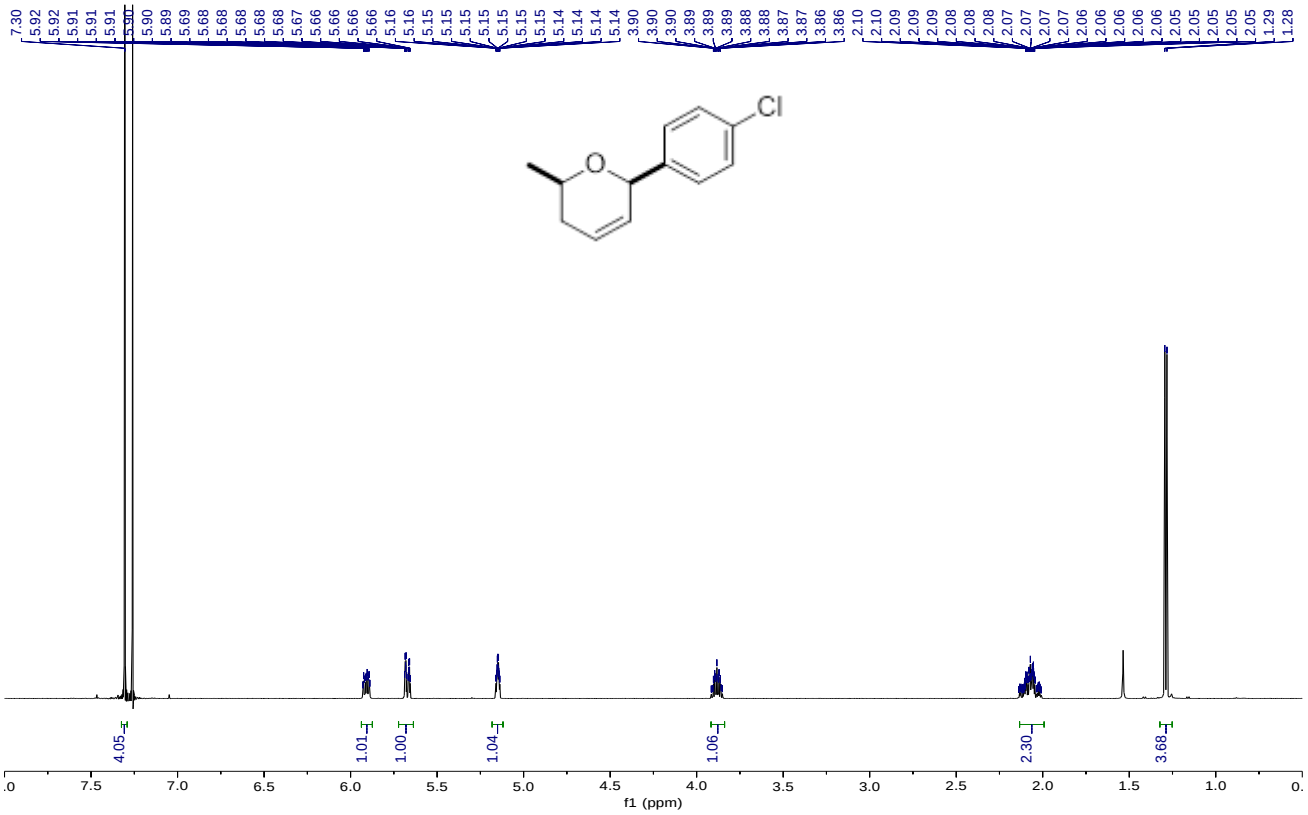


^{13}C NMR (101 MHz, $CDCl_3$)

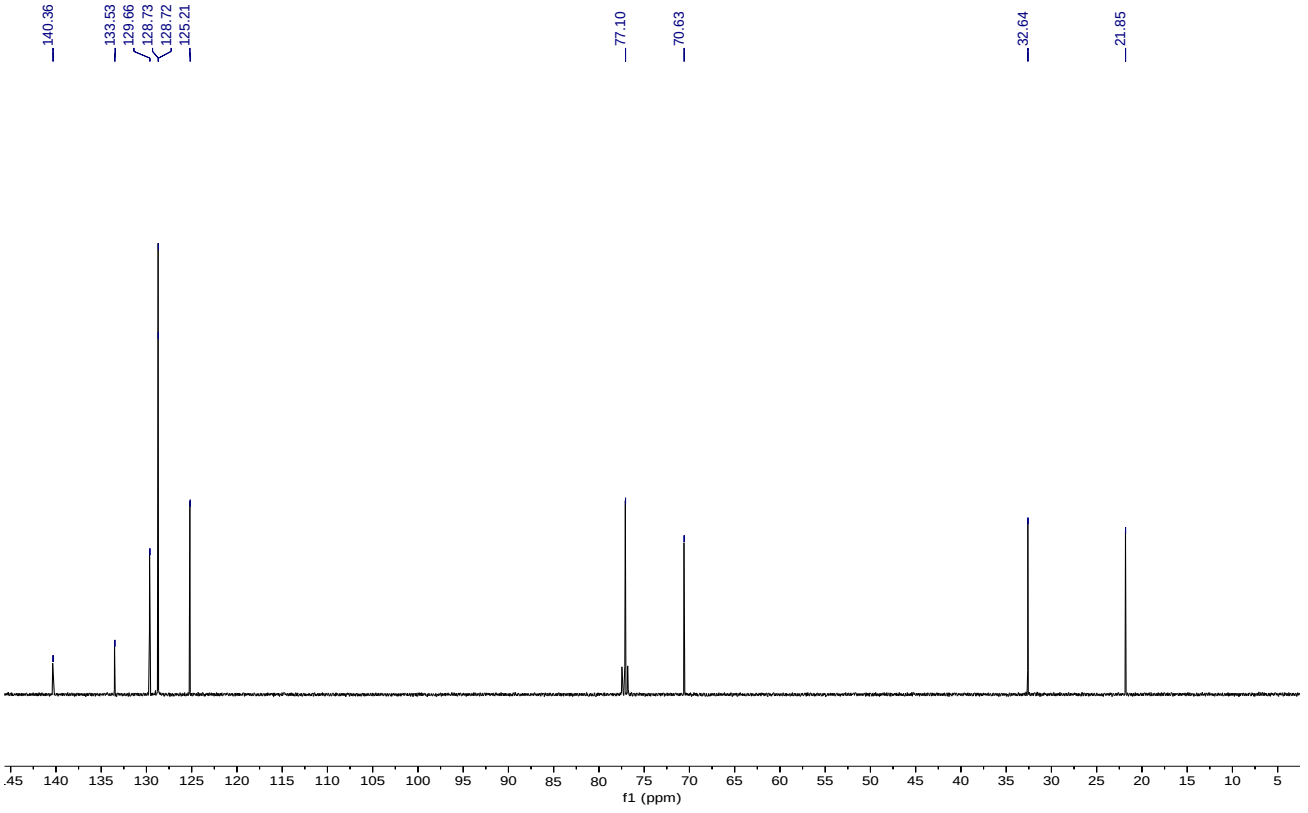


Compound 2l

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

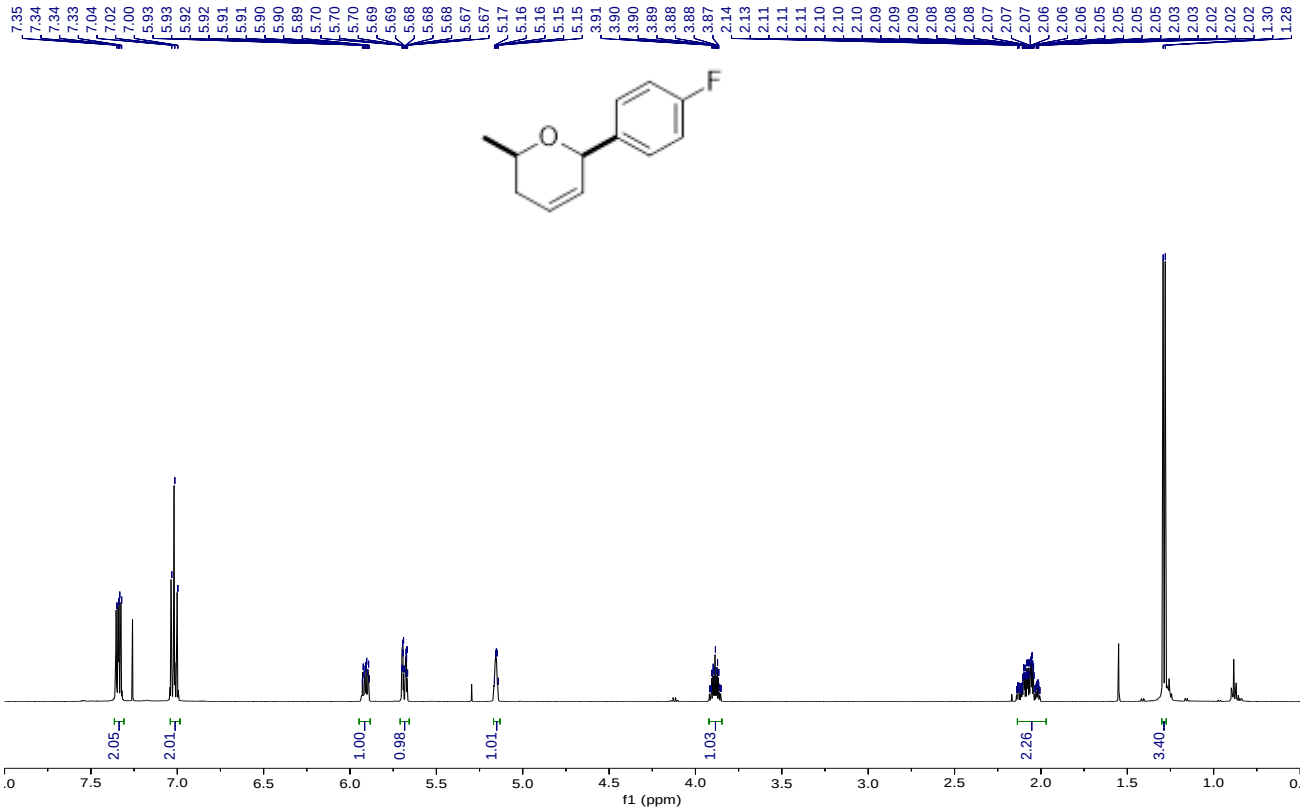


^{13}C NMR (101 MHz, $CDCl_3$)

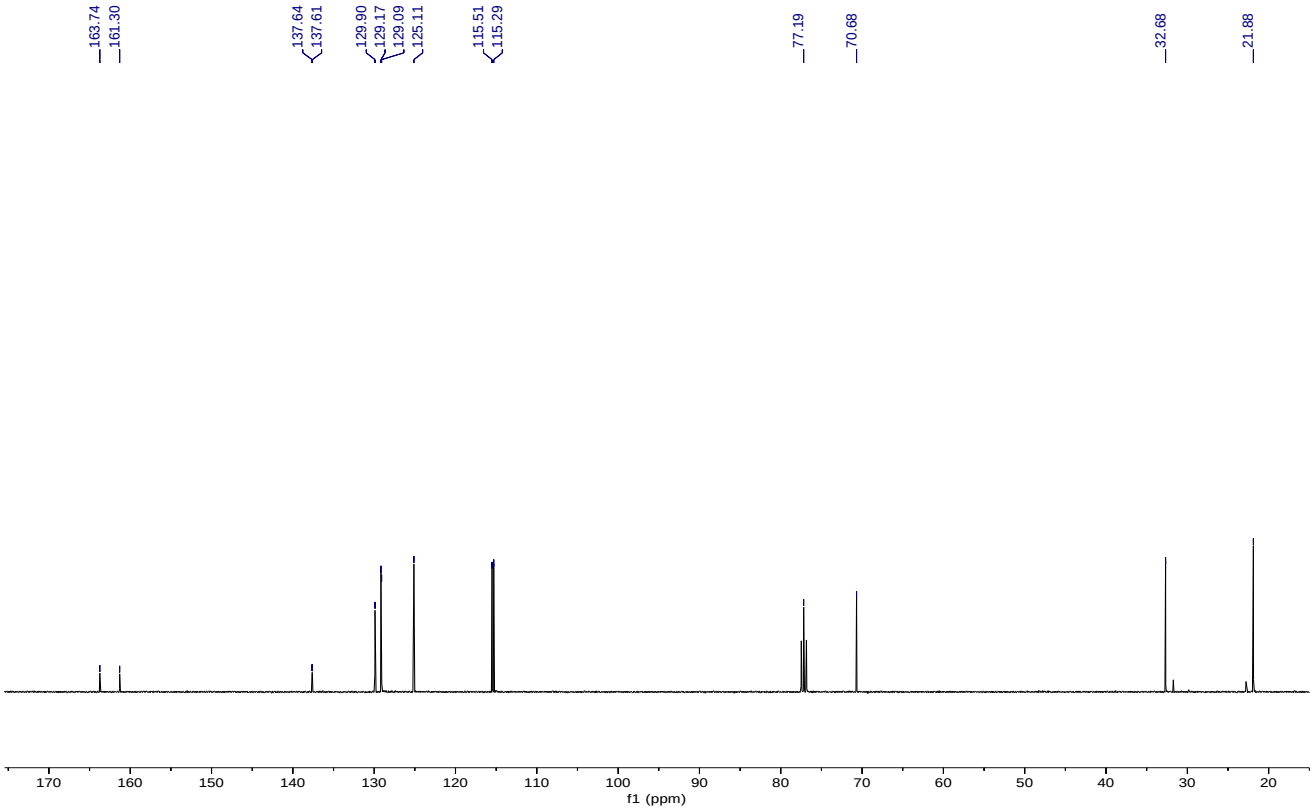


Compound 2m

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

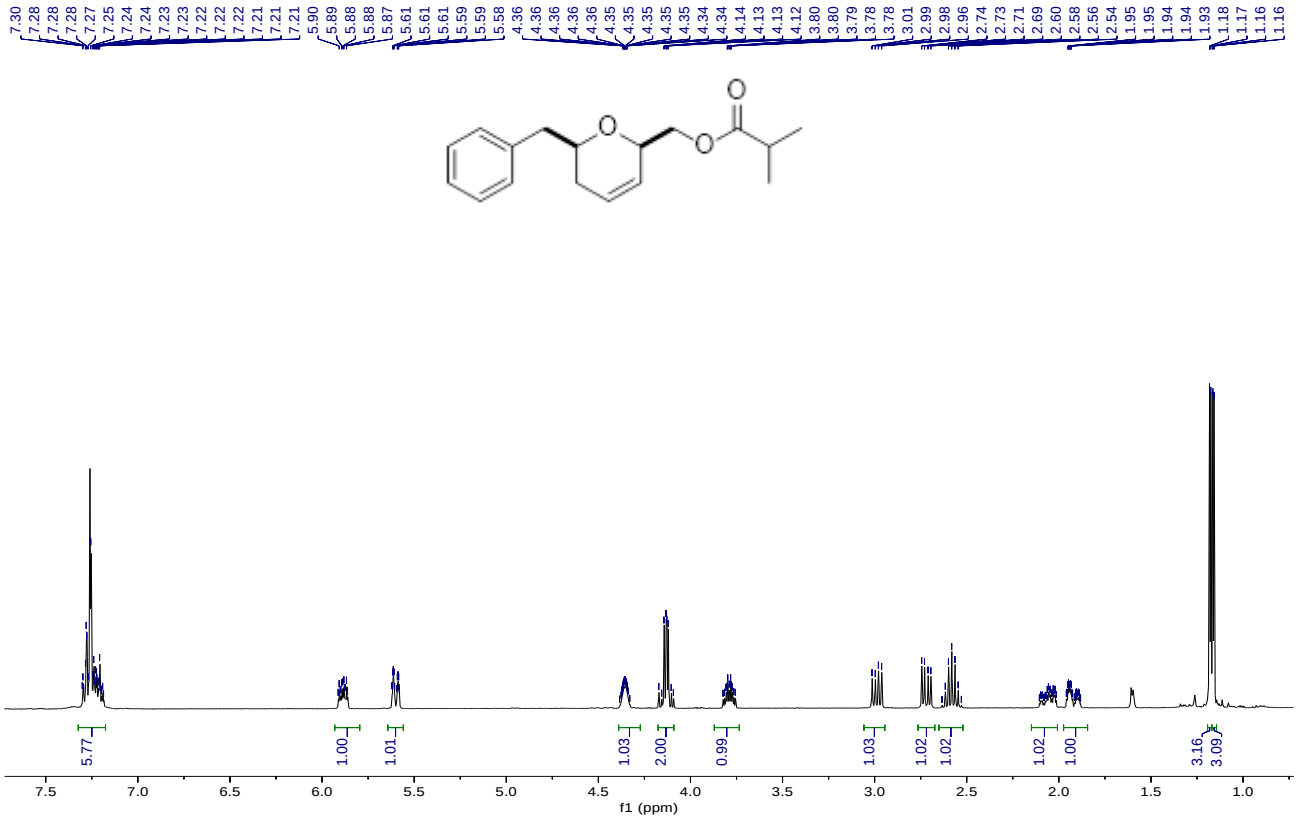


^{13}C NMR (101 MHz, $CDCl_3$)

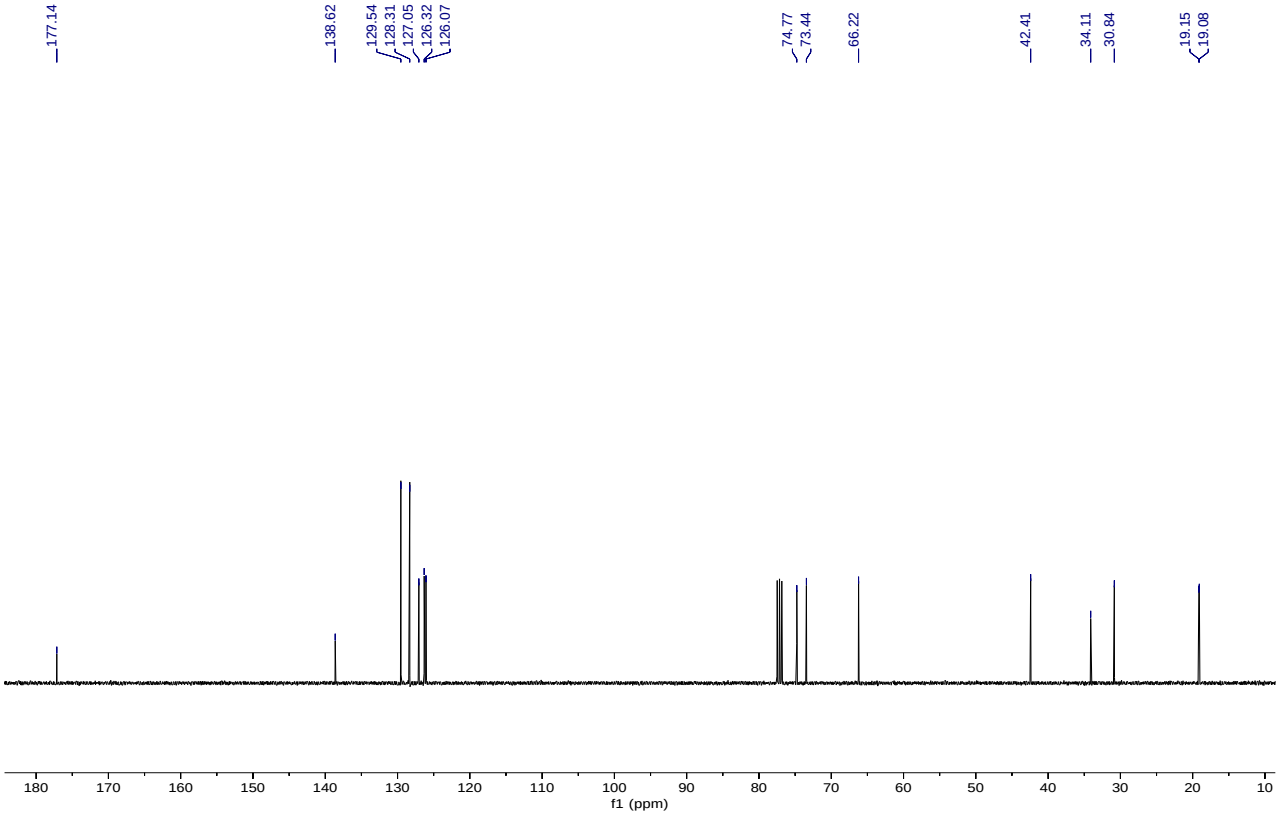


Compound 2n (molecules)

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

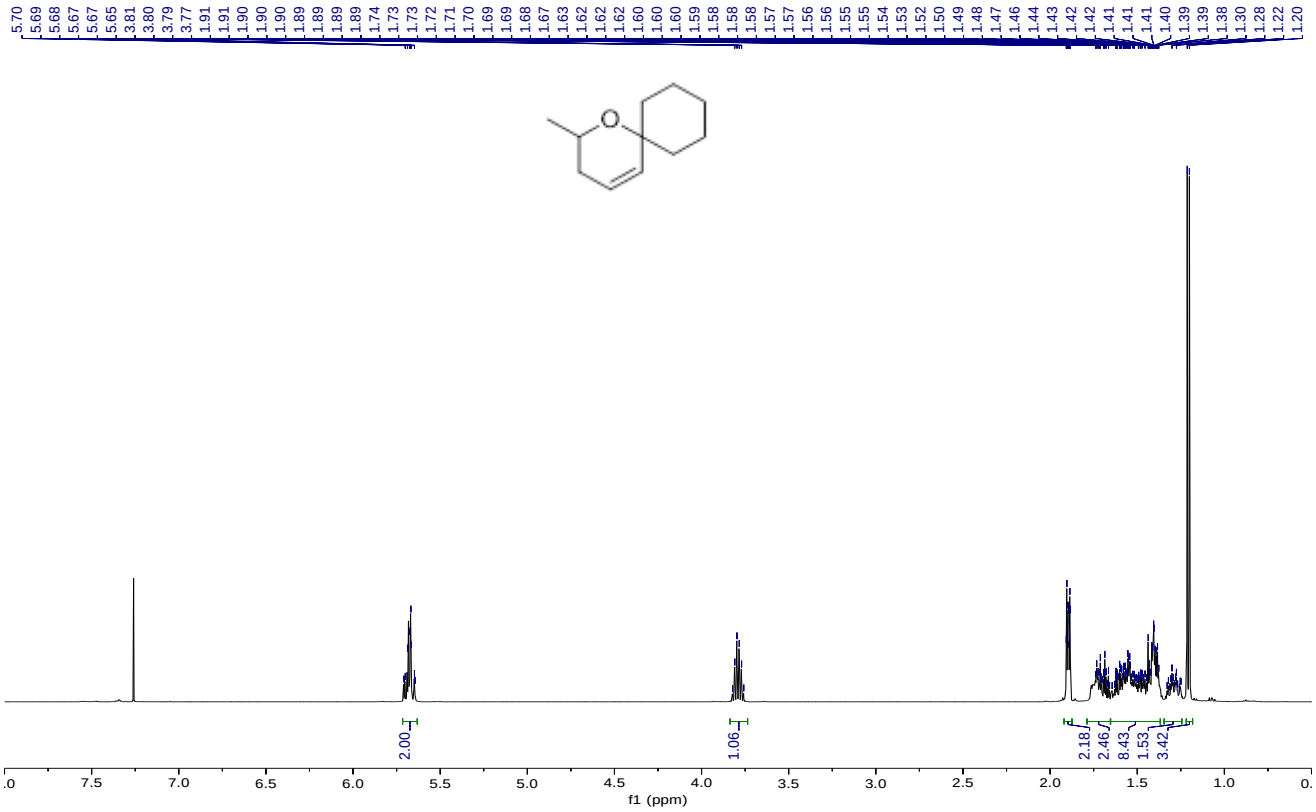


^{13}C NMR (101 MHz, $CDCl_3$)

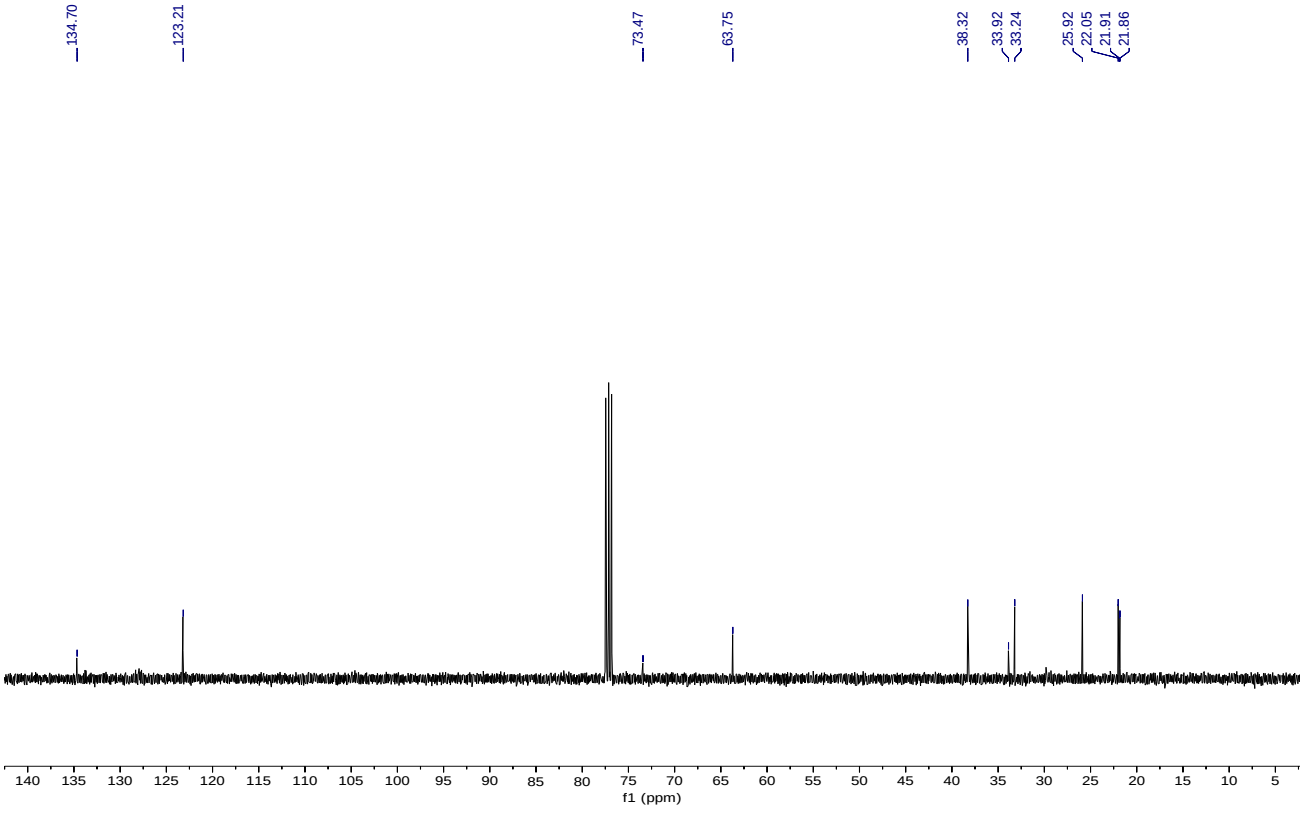


Compound 2o

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

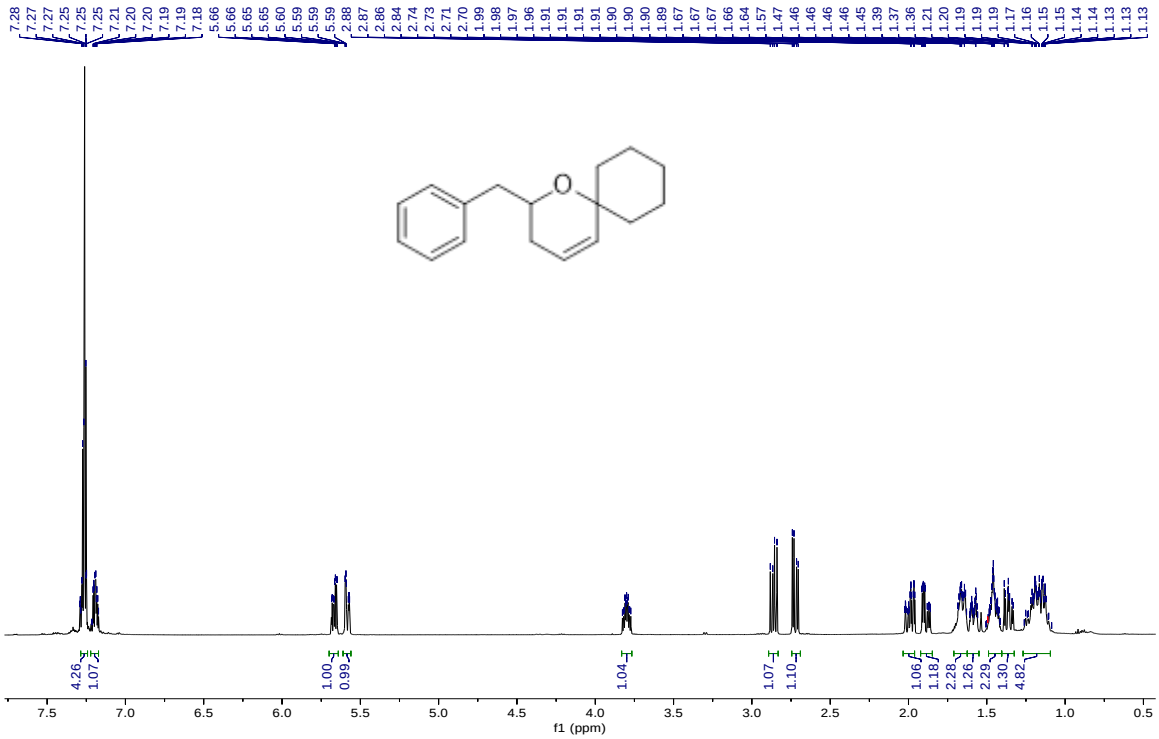


^{13}C NMR (101 MHz, $CDCl_3$)

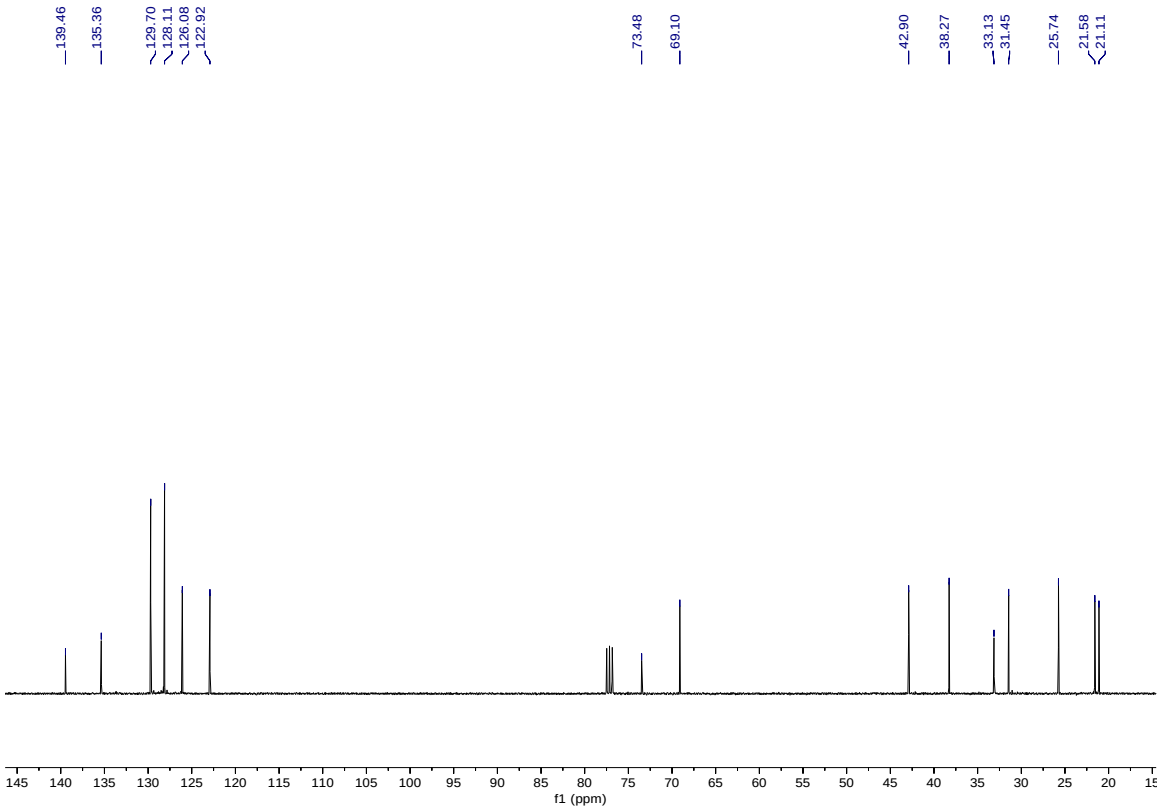


Compound 2p

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

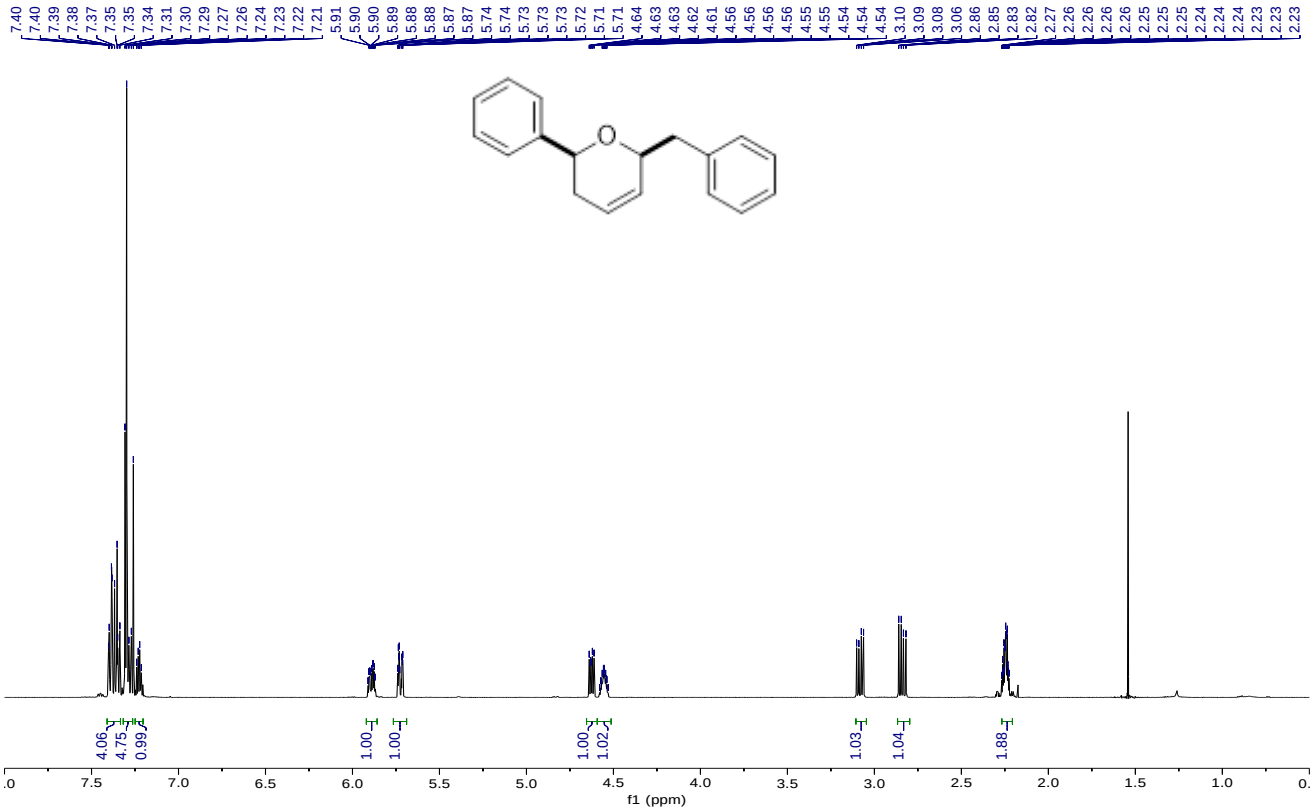


^{13}C NMR (101 MHz, $CDCl_3$)

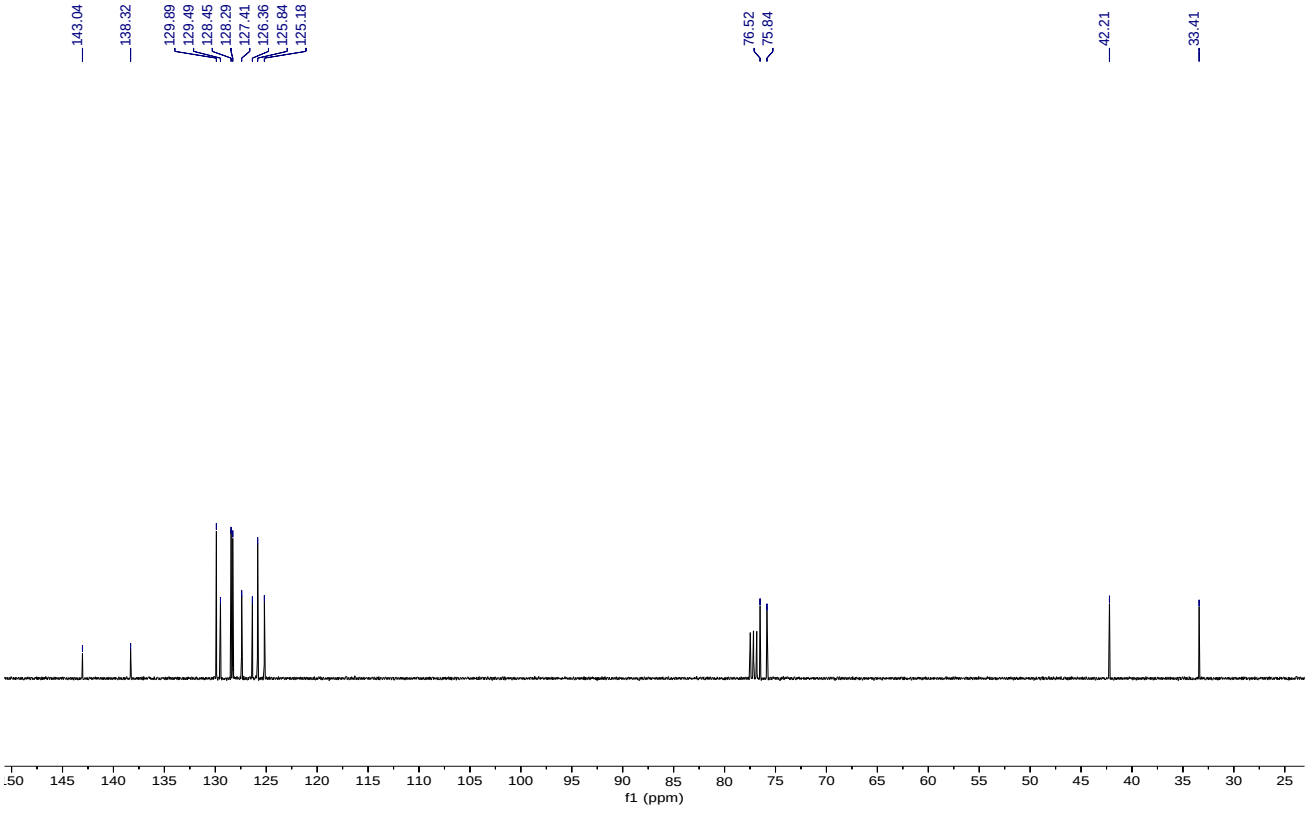


Compound 2q

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

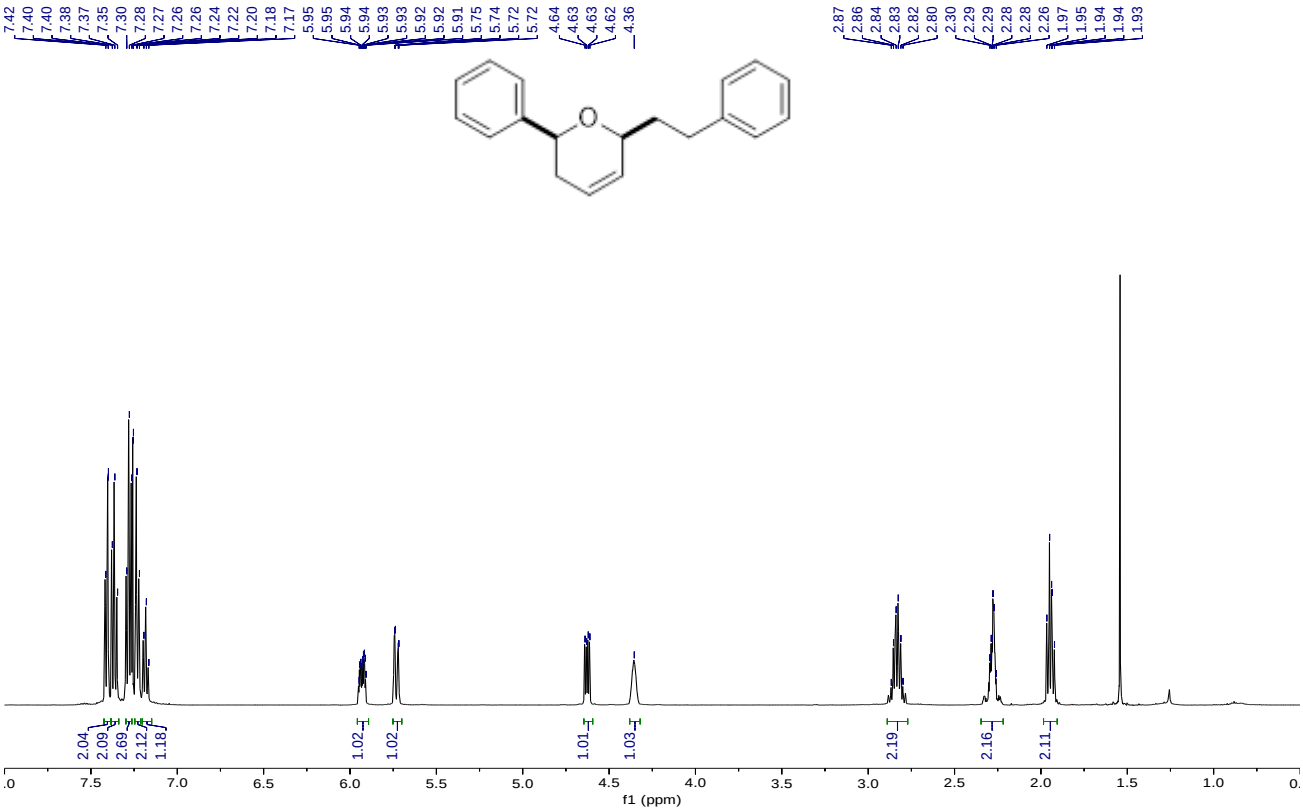


^{13}C NMR (101 MHz, $CDCl_3$)

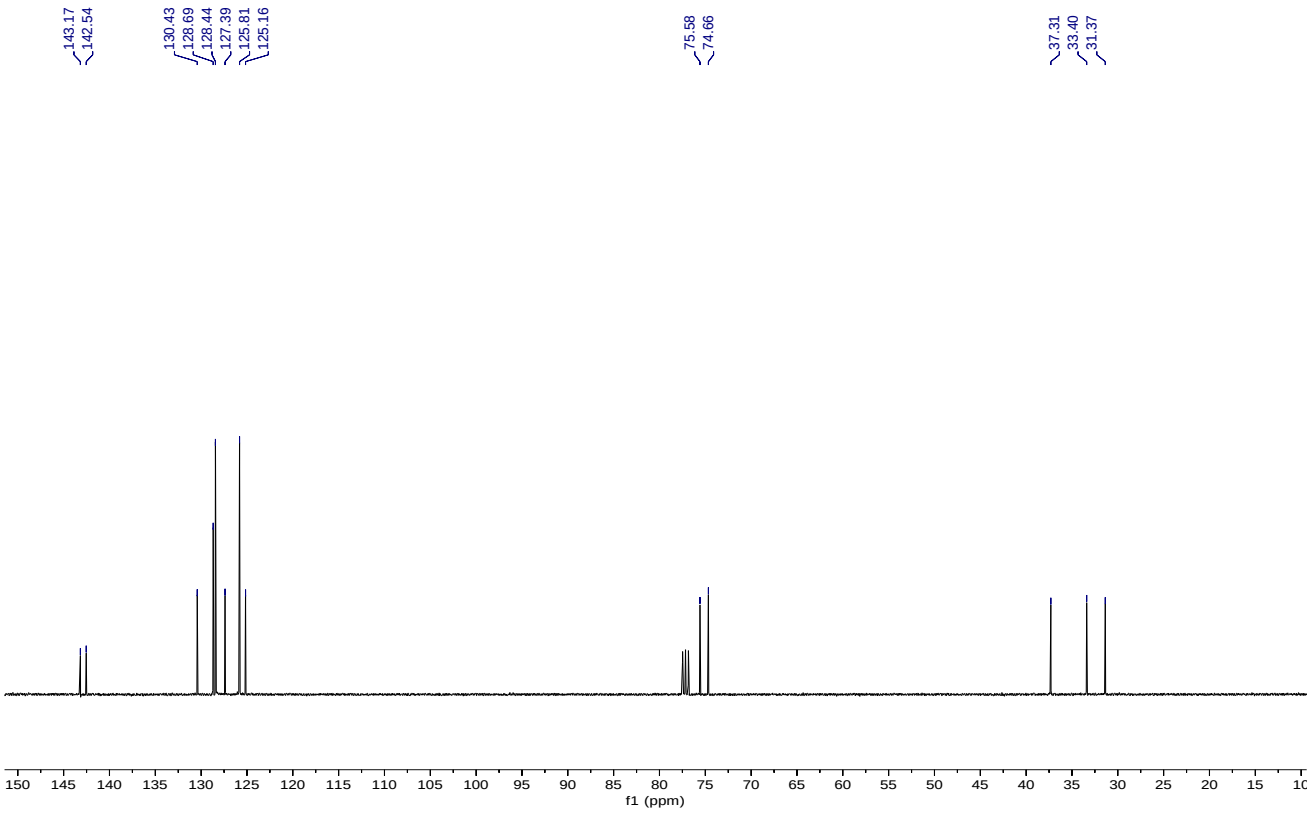


Compound 2r

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

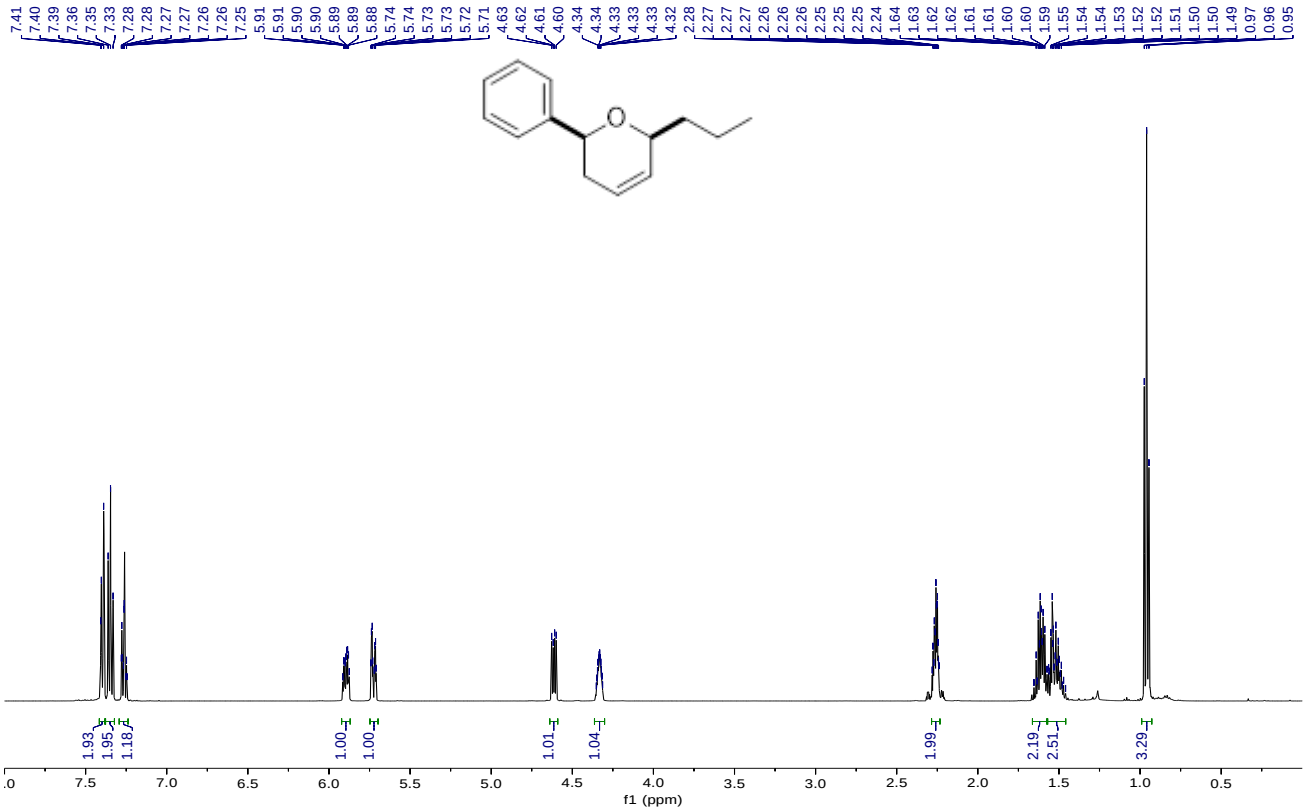


^{13}C NMR (101 MHz, $CDCl_3$)

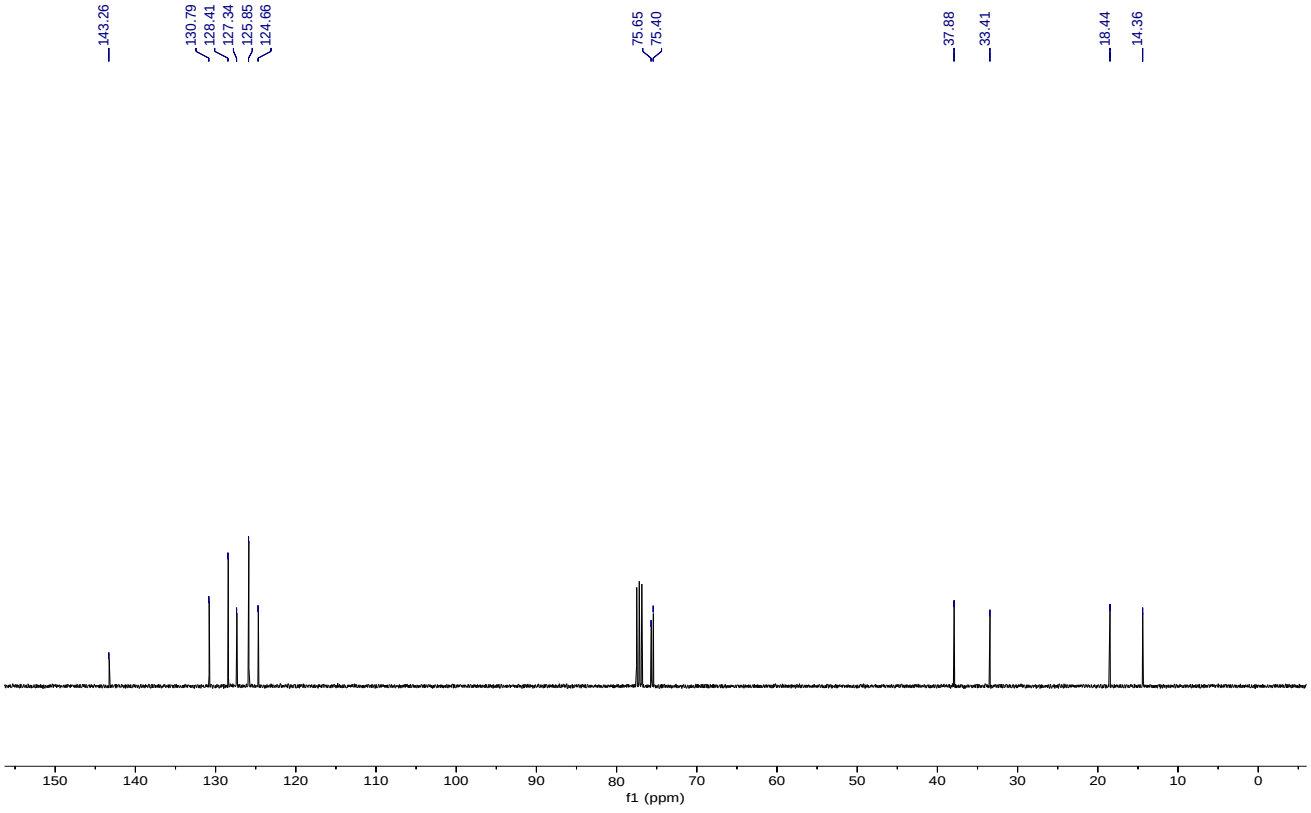


Compound 2s

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

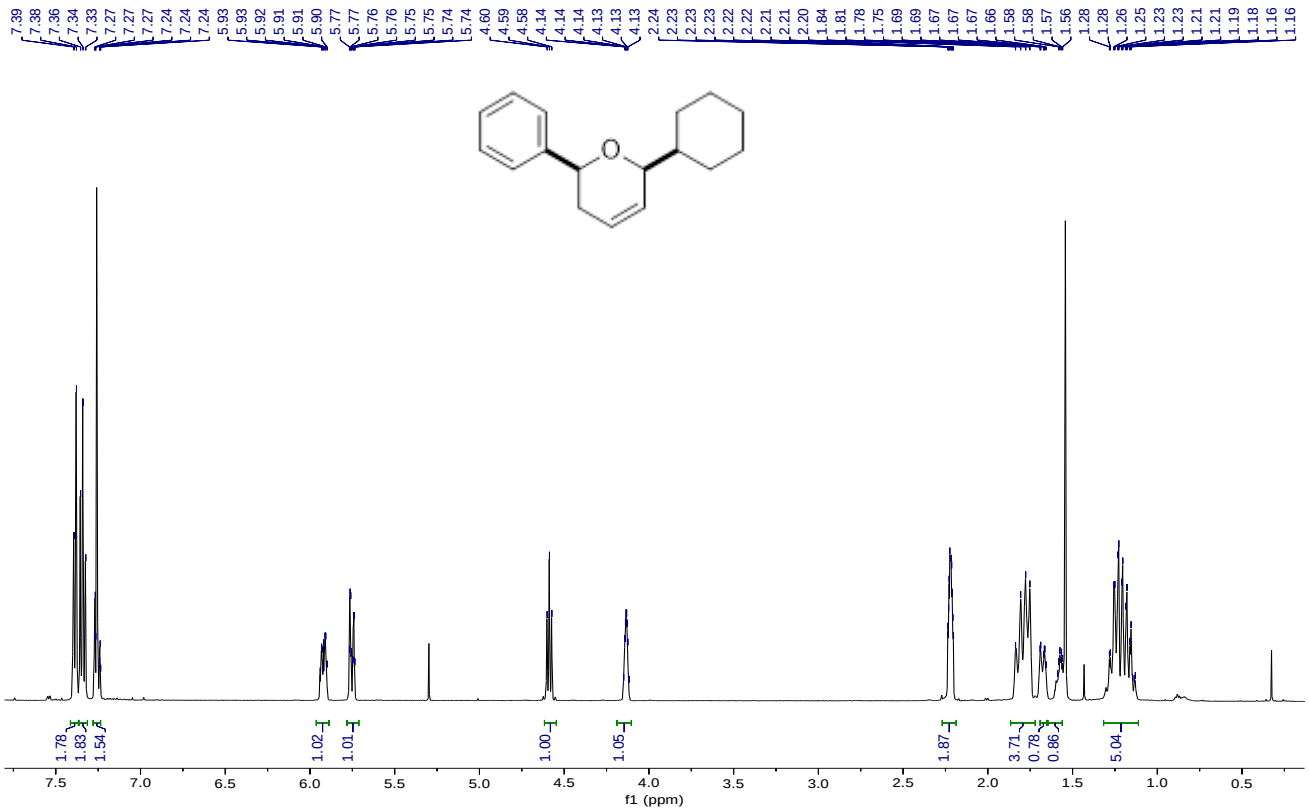


^{13}C NMR (101 MHz, $CDCl_3$)

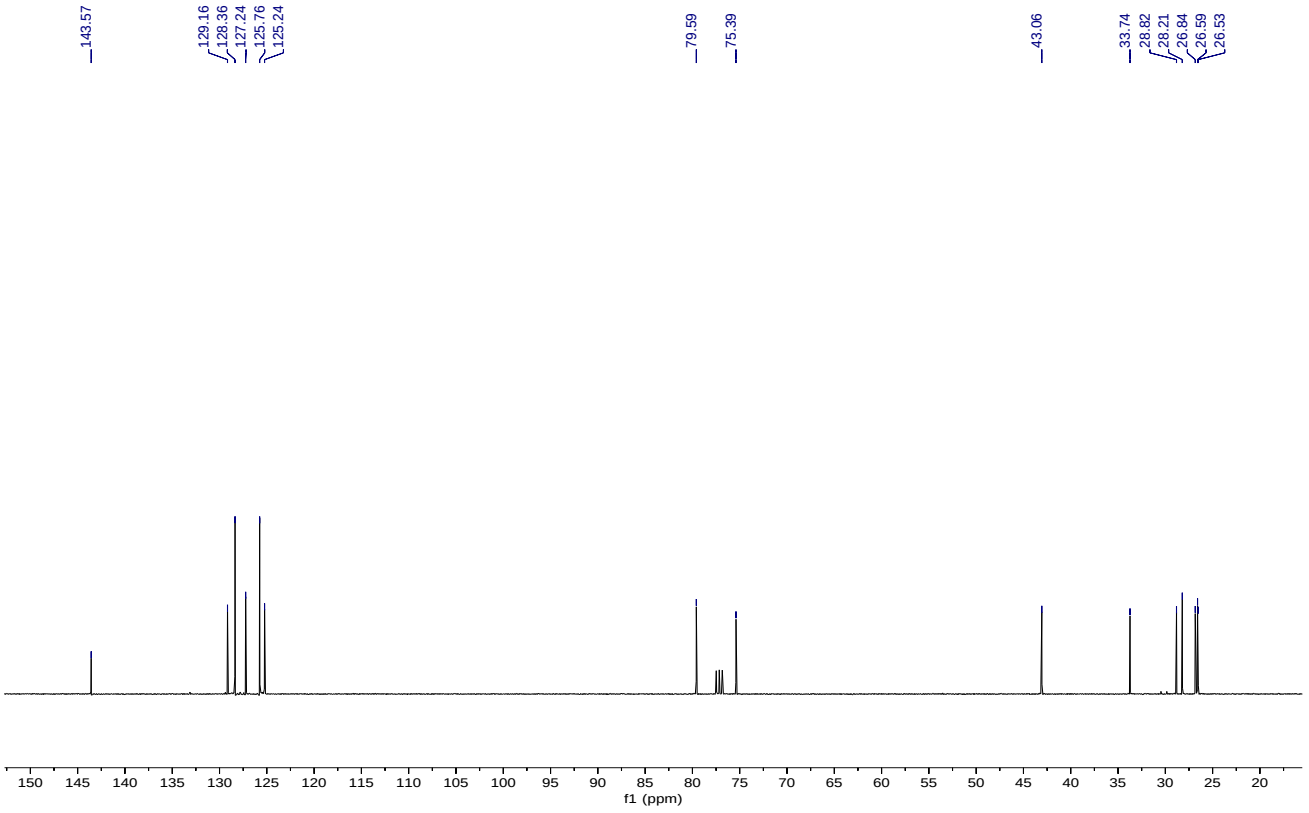


Compound 2t

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

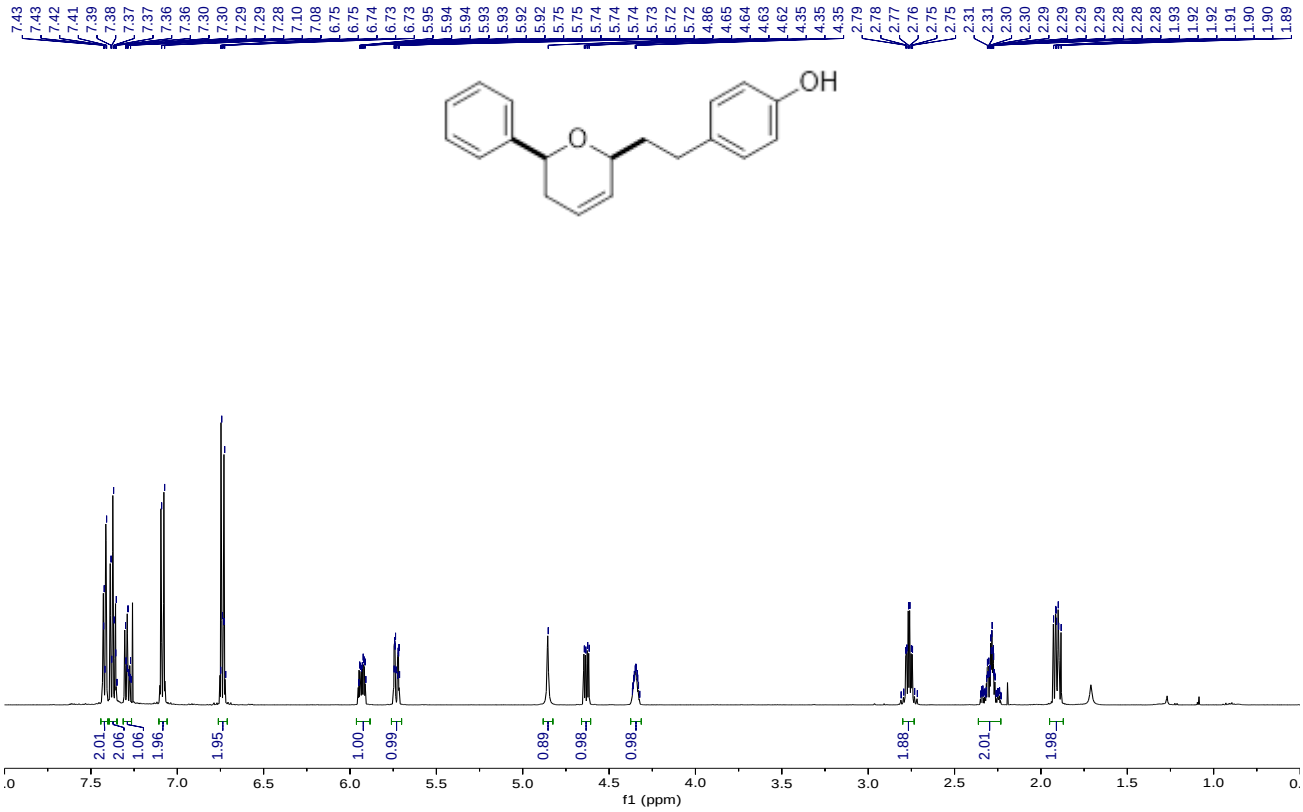


^{13}C NMR (101 MHz, $CDCl_3$)

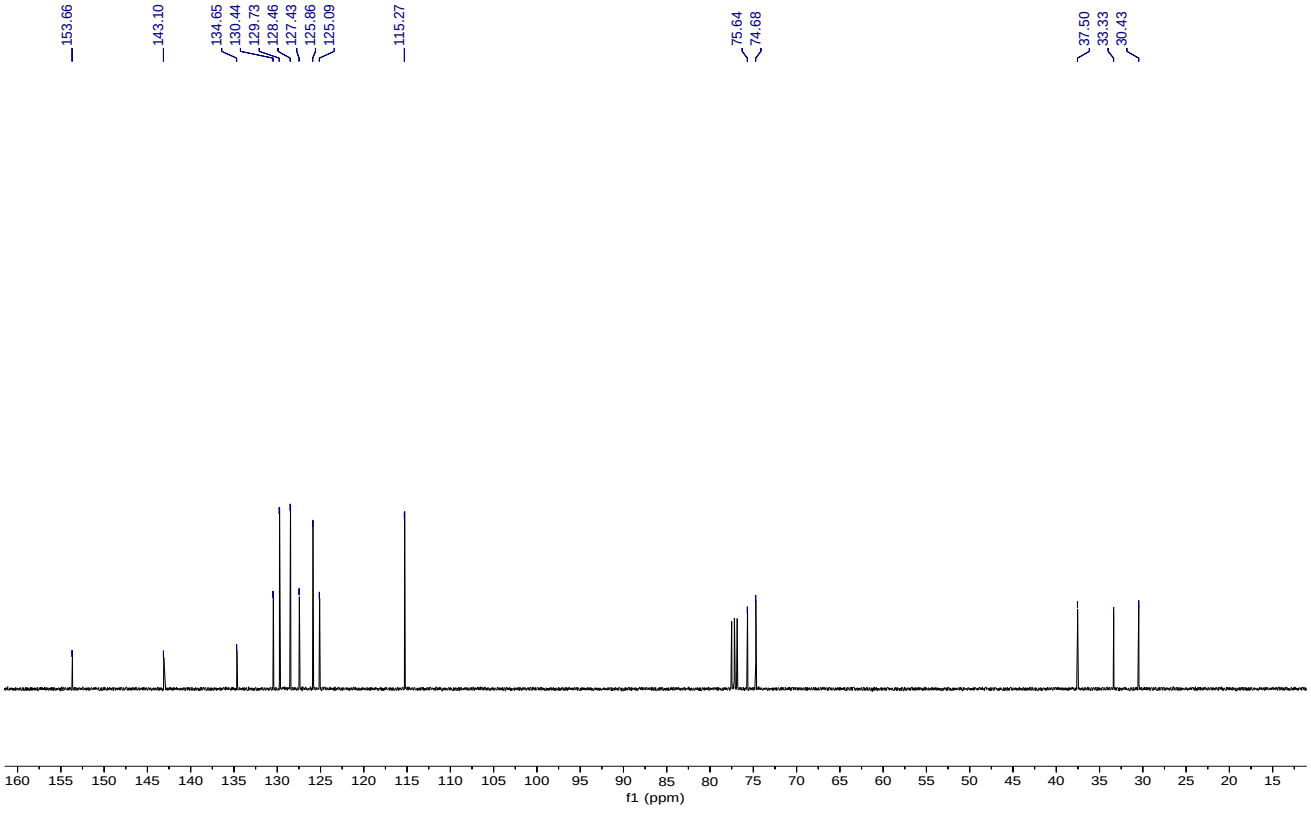


Compound 2u

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

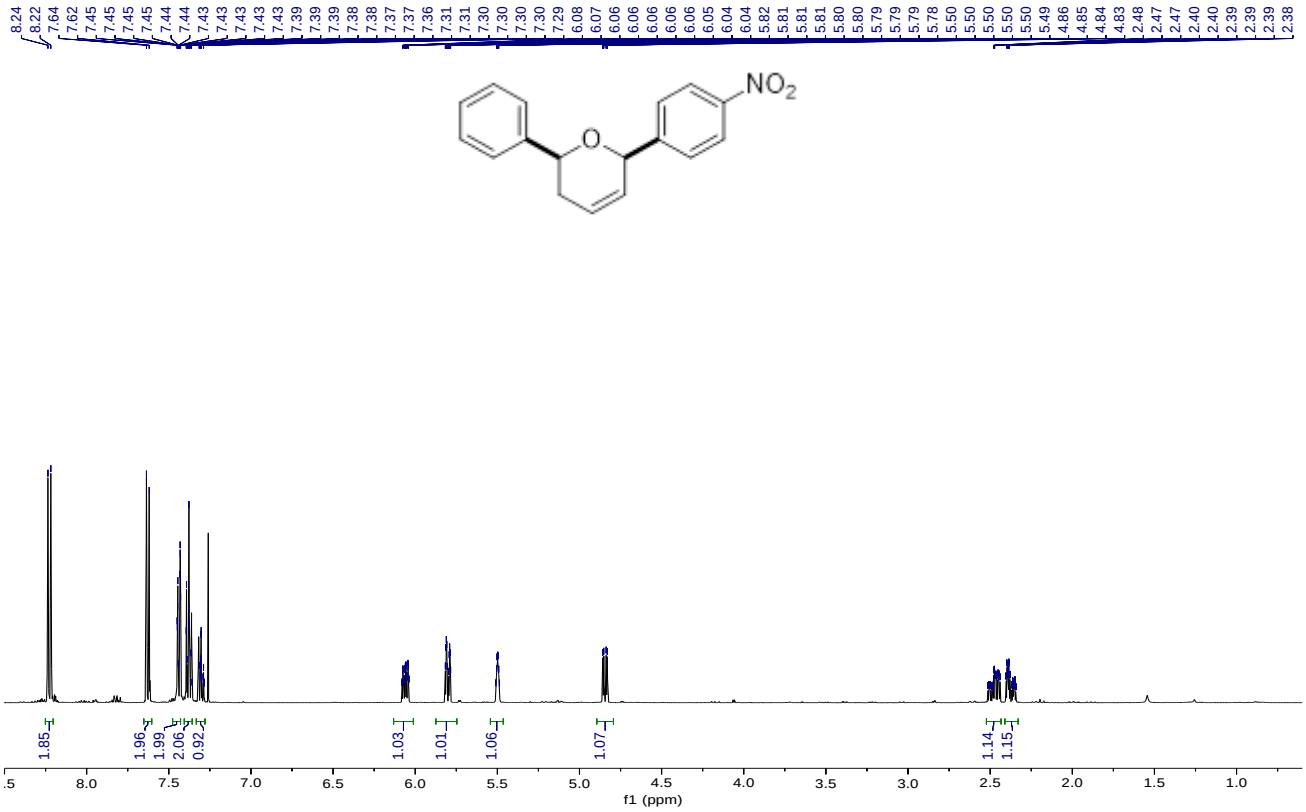


^{13}C NMR (101 MHz, $CDCl_3$)

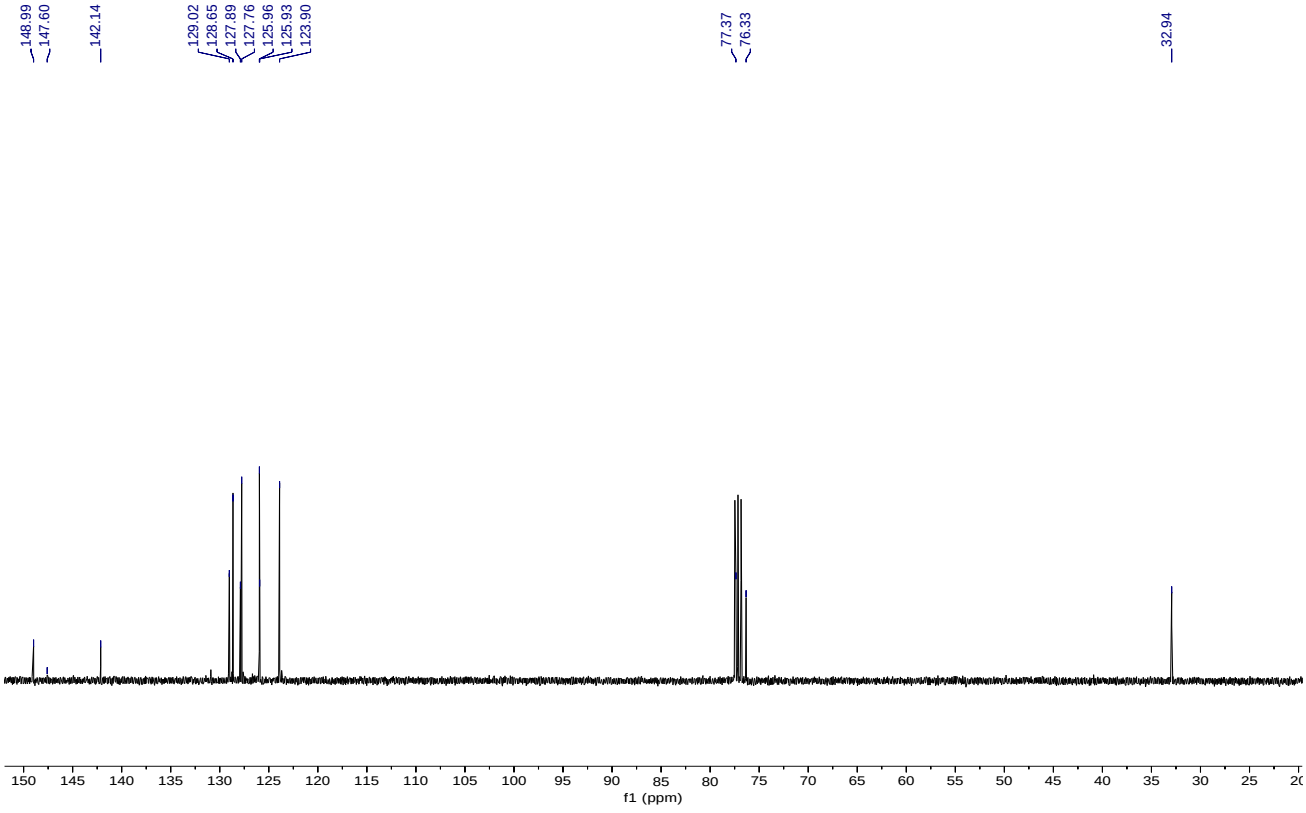


Compound 2v

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

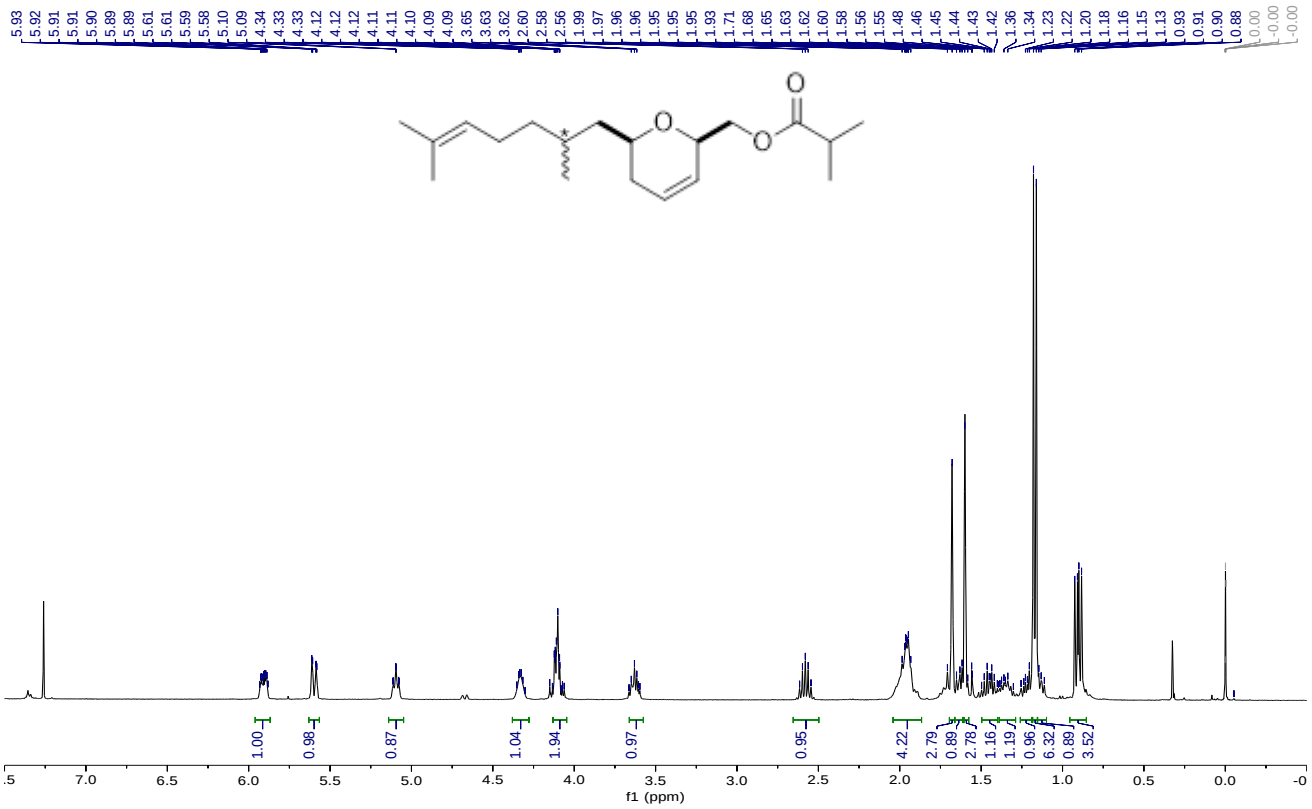


^{13}C NMR (101 MHz, $CDCl_3$)

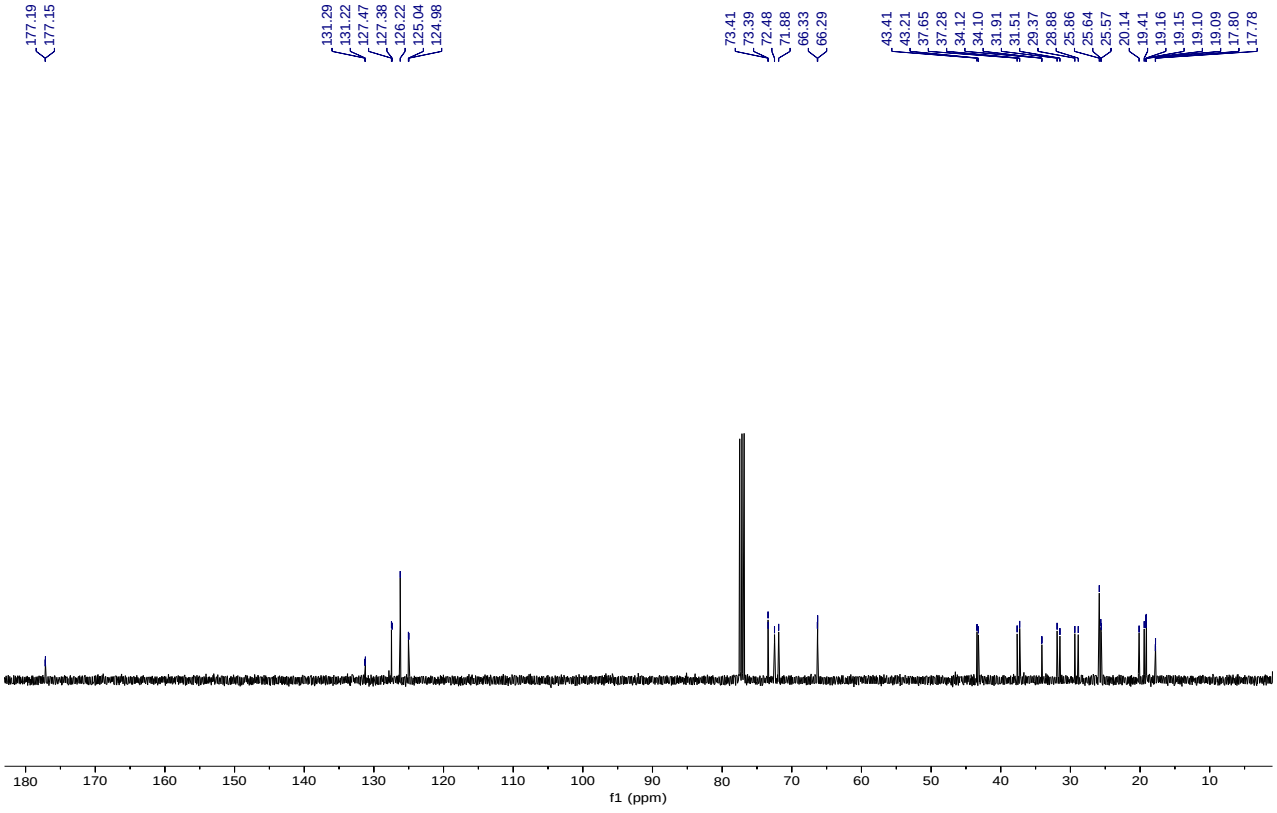


Compound 2x

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

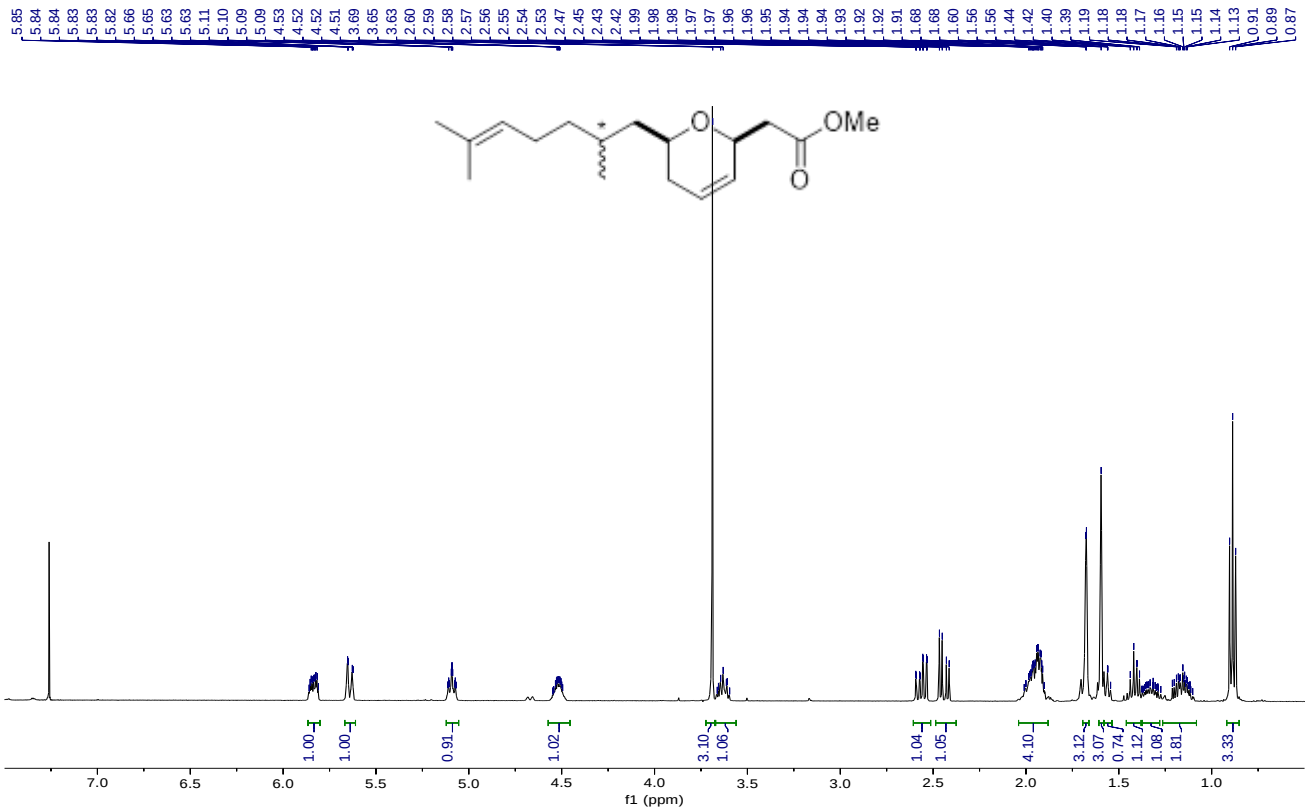


^{13}C NMR (101 MHz, $CDCl_3$)

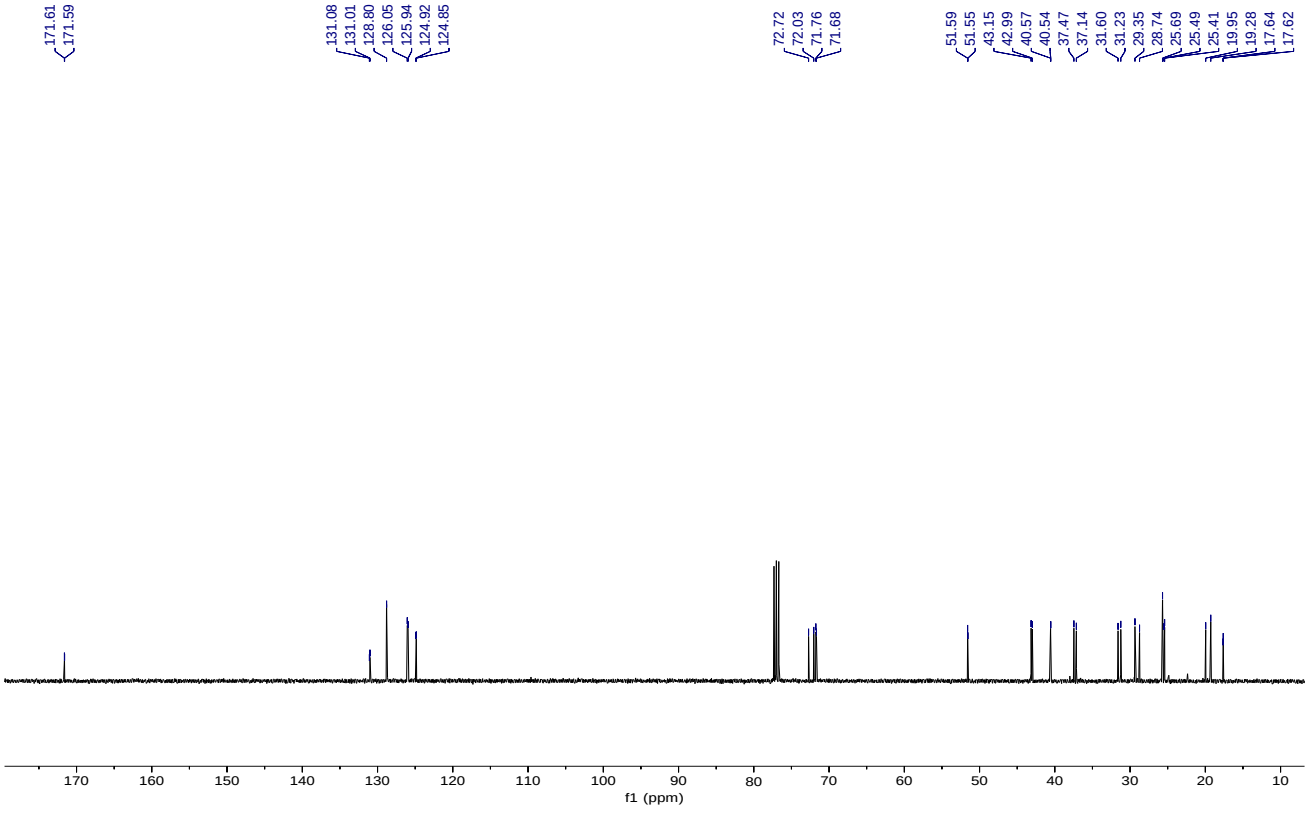


Compound 2y

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

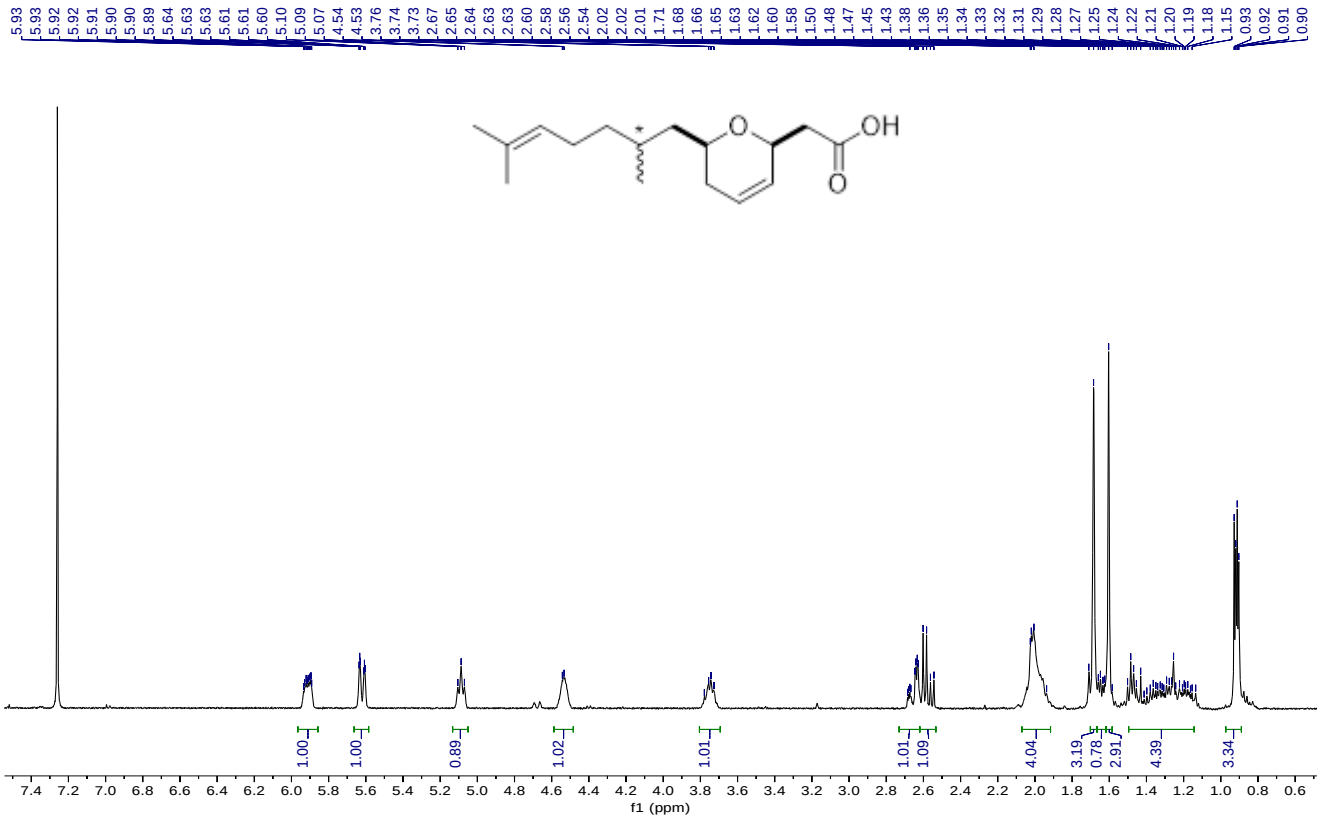


^{13}C NMR (101 MHz, $CDCl_3$)

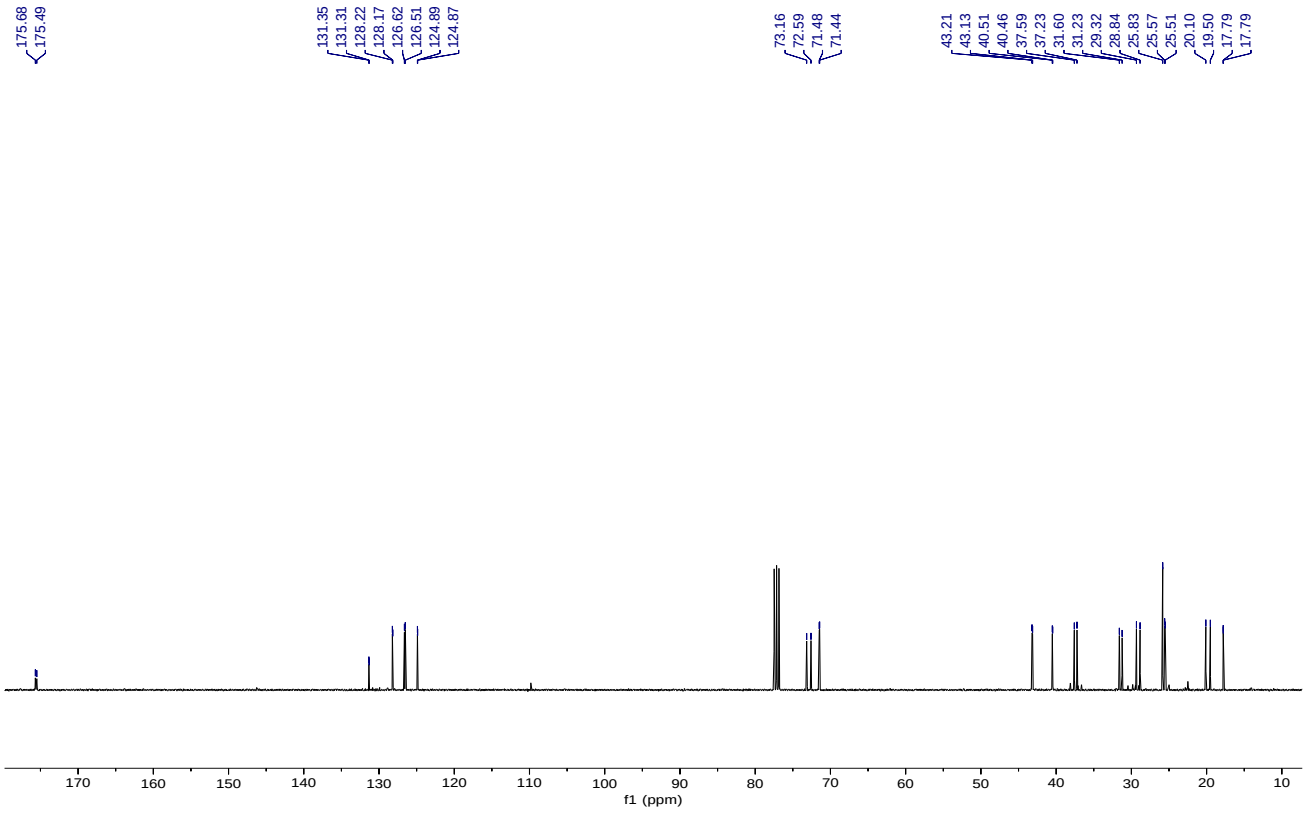


Compound 3

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

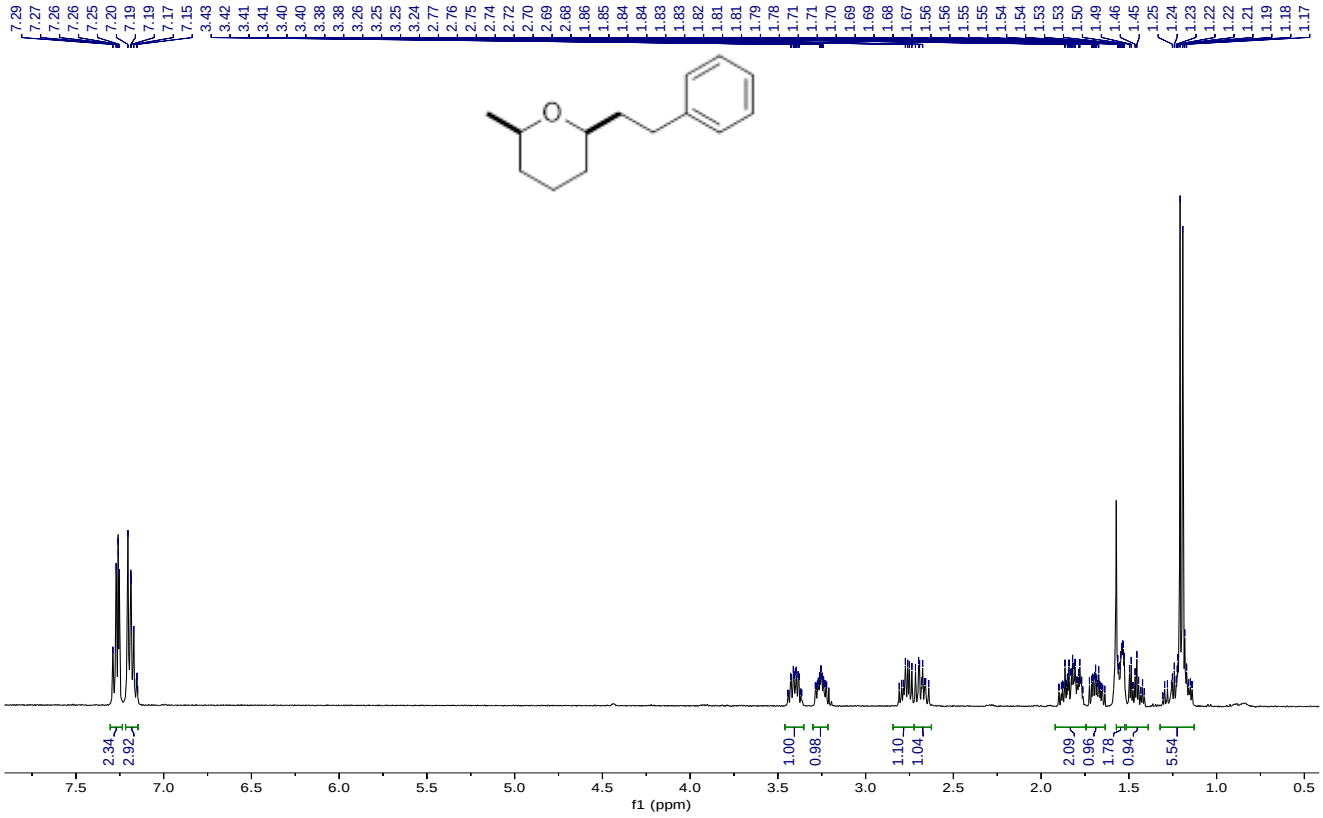


^{13}C NMR (101 MHz, $CDCl_3$)



Compound 4

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



^{13}C NMR (101 MHz, $CDCl_3$)