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# Enantioselective 1,4-additions of ClMeAl(CH=CHR) (R = alkyl, alkenyl, Ph) to cyclohexenones: supporting data

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***General:*** All reactions were carried out under an argon atmosphere in flame or oven-dried glassware. Tetrahydrofuran and diethyl ether were freshly distilled from sodium benzophenone ketyl. Dichloroalane *bis*(tetrahydrofuran) was prepared by literature methods (ref. 6 in main paper) and stored under inert atmospheres; its purity determined by evolved $H_2$ volume on aqueous quench of small samples (<0.1 g). Samples of $AlHCl_2 \bullet (THF)_2$ were normally weighed under inert atmosphere, but larger quantities could be handled promptly in air if necessary. All alkynes and commercially available enones were distilled prior to use. All other commercially available compounds were used without further purification. 3-Ethylcyclohex-2-en-1-one[1] was prepared according to literature procedure. Phosphoramidates and SimplePhos Ligands prepared according to literature procedures.[2] Flash column chromatography was carried out using Davisil silica gel 60 (0.035 - 0.070 mm particle size). Thin layer chromatography was carried out using Merck $F_{254}$ aluminium backed-silica-plates.

Proton (400.1 MHz) and carbon-13 (100.6 MHz) NMR spectra were recorded on Bruker DPX400, AV400 or AV(III)400 instruments; assignments $H^n$ refer to protons attached to carbon $C^n$ in the numbering schemes provided. Numbering was assigned using ChemDraw Ultra 12 and used for NMR assignment purposes only. Chemical shifts are quoted as parts per million and referenced to $CHCl_3$ (7.26 ppm for $^1H$ and 77.1 ppm for $^{13}C$ nuclei).[3] Carbon-13 NMR spectra were recorded with broadband proton decoupling. Infra-red spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Mass spectrometry was carried out using either a Bruker MicroTOF or a Micromass AutoSpec instrument. GC analysis was carried out using a Varian 3400 with CP400 autosampler instrument and HPLC assay was carried out using a Varian ProStar with UV detector. Optical rotation was recorded using an ADP 440 machine with the $[\alpha]_D$ being quoted at 25 $^oC$.

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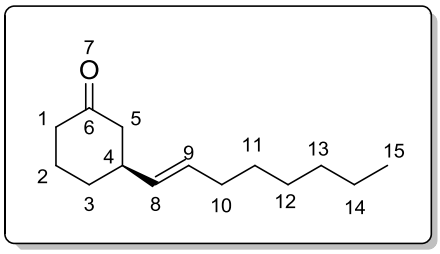
**General procedure 1:** volatile alkyne hydroalumination and conjugate addition

A 1.5 mL vial (glass screw cap vial, 854171, Supelco) was charged with decamethylzirconocene dichloride (21.6 mg, 0.05 mmol, 0.05 equiv.) and dichloroalane *bis*(tetrahydrofuran) (340 mg, 1.40 mmol, 1.4 equiv.) under an inert atmosphere. Neat alkyne (1.00 mmol) and tetrahydrofuran (1.0 mL) were injected through the septum (9mm AG3 CenterGuide, CR246713, Varian) and mixture was heated for 2 h at 80 ºC. The solution was transferred to a flame-dried Schlenk tube and solvent removed *in vacuo* and replaced with toluene (1.0 mL). To this was added methyllithium (330 μL, 0.65 mmol, 2 M in diethyl ether) and the mixture stirred for 30 min. In a Radleys carousel tube, CuTC (9.50 mg, 0.05 mmol) and ligand **L2** (47.9 mg, 0.075 mmol) were dissolved in *t*-butylmethyl ether (1.0 mL) and stirred for 15 mins. The alane mixture was transferred to the copper mixture *via* syringe and enone (0.5 mmol) in toluene (0.5 mL) was added over 0.5 h. The reaction was stirred for a further 0.5 h at 25 $^{o}$C and then quenched with water and HCl (1 M). The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 x 5 mL). The combined organic phases were dried ($Na_2SO_4$), filtered, and concentrated. The crude was purified by flash chromatography (pentane/diethyl ether 4:1).

**General procedure 2:** Zirconium-catalysed hydroalumination and conjugate addition (neat conditions)

A dried Schlenk tube was charged dichloroalane bis(tetrahydrofuran) (158 mg, 0.65 mmol), decamethylzirconocene dichloride (14.0 mg, 0.03 mmol) and 1-octyne (134 μL, 1.40 mmol) and the mixture melted at 80 $^{o}$C for 1.5 h. The excess alkyne was removed under vacuum (0.1 mmHg). The resulting alane was diluted with toluene (1.0 mL) and methyllithium added (330 μL, 0.65 mmol, 2M in diethyl ether) and the mixture stirred for 30 min. In a Radleys carousel tube, CuTC (9.50 mg, 0.05 mmol) and ligand **L2** (47.9 mg, 0.075 mmol) were and stirred for 15 mins in *t*-butylmethyl ether (1.0 mL). The previously prepared alane mixture was transferred to the CuTC/**L2** catalyst *via* syringe and enone (0.5 mmol) in toluene (0.5 mL) was added over 0.5 h. The reaction was stirred for a further 0.5 h at 25 $^{o}$C and then quenched with water and HCl (1 M). The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 x 5 mL). The combined organic phases were dried ($Na_2SO_4$), filtered, and concentrated. The crude was purified by flash chromatography (pentane/diethyl ether 4:1).

## (*S*)-(*E*)-3-(oct-1-en-1-yl)cyclohexanone (2a)[4]




Prepared according to general procedure 2 from 1-octyne (134 μL, 1.40 mmol) and cyclohexenone (48 μL, 0.5 mmol) to yield title compound as a colourless oil in 88% e.e. (67.7 mg, 65%, 0.325 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.56.

**$^{1}$H NMR** $\delta_H$: 0.83 (3H, t, *J* = 7.0 Hz, C$^{15}$**H**$_3$), 1.20–1.32 (8H, m, C$^{11}$**H**$_2$-C$^{14}$**H**$_2$), 1.39–1.49 (1H, m, *c*-hex), 1.58–1.69 (1H, m, *c*-hex), 1.83–1.92 (1H, m, *c*-hex), 1.91–2.02 (3H, m, *c*-hex), 2.11–2.17 (1H, m, *c*-hex), 2.19–2.25 (1H, m, *c*-hex), 2.26–2.44 (3H, m, *c*-hex and C$^{10}$**H**$_2$), 5.31 (1H, dd, *J* = 16.0, 6.0 Hz, C$^{8}$**H**), 5.38 (1H, dt, *J* = 16.0, 6.5 Hz, C$^{9}$**H**).

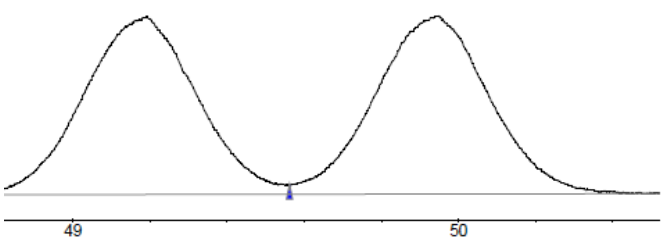
**$^{13}$C NMR** $\delta_C$: 14.1 (C15), 22.6 (C2), 25.0 (C14), 28.8 (C12), 29.4 (C11), 31.6 (C3), 31.7 (C13), 32.5 (C10), 41.3 (C1), 41.6 (C4), 47.7 (C5), 130.0 (C9), 133.0 (C8), 211.4 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 2956, 2927, 2855, 1713, 1455, 1226, 975, 737 cm$^{-1}$.

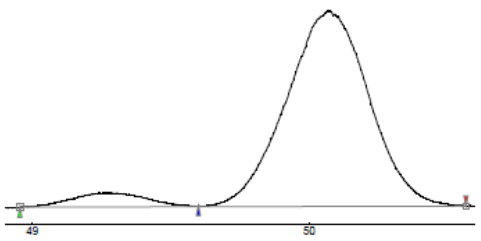
**HRMS** (EI) calc. for $C_{14}H_{24}O$ 208.1827 found 208.1833.

**GC**: (Lipodex A); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL min$^{-1}$, $t_i$= 75 °C (7 min), (5 °C min$^{-1}$) $t_f$ = 115 °C (90 min), (0.7 °C min$^{-1}$) $t_f$ = 140 °C: (*R*)-enantiomer: $t_R$ = 49.19 min; (*S*)-enantiomer: $t_R$ = 49.95 min.

**$[\alpha]_D^{25}$**: +104.9 (*c* = 2.00, $CHCl_3$).

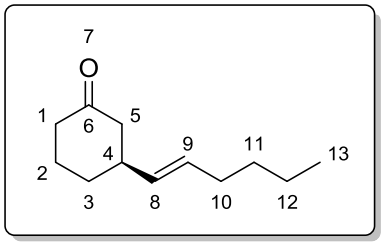



| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 49.19 | 49.71 | 1674.2 | 570.0 | 49.712 |
| 2 | UNKNOWN | 49.95 | 50.29 | 1671.8 | 576.6 | 50.288 |
| | | | | | | |
| Total | | | 100.00 | 3346.0 | 1146.5 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 49.27 | 6.11 | 282.5 | 88.2 | 6.114 |
| 2 | UNKNOWN | 50.07 | 93.89 | 3927.9 | 1354.7 | 93.886 |
| | | | | | | |
| Total | | | 100.00 | 4210.3 | 1442.9 | 100.000 |

## (*S*)-(*E*)-3-(hex-1-en-1-yl)cyclohexanone (2b)[5]




Prepared according to general procedure 1 from 1-hexyne (91 μL, 0.75 mmol) and cyclohexenone (48 μL, 0.5 mmol) to yield title compound as a colourless oil in 90% e.e. (62.2 mg, 69%, 0.345 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.58.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.87 (3H, t, *J* = 7.0 Hz, $C^{13}\boldsymbol{H}_3$), 1.25–1.33 (4H, m, $C^{11}\boldsymbol{H}_2$ & $C^{12}\boldsymbol{H}_2$), 1.42–1.51 (1H, m, *c*-hex), 1.61–1.71 (1H, m, *c*-hex), 1.85–1.90 (1H, m, *c*-hex), 1.96–1.99 (2H, m, $C^{10}\boldsymbol{H}_2$), 2.01–2.06 (1H, m, *c*-hex), 2.14–2.28 (2H, m, *c*-hex), 2.30–2.41 (3H, m, *c*-hex). 5.34 (1H, dd, *J* = 15.0, 6.0 Hz, $C^8\boldsymbol{H}$), 5.41 (1H, dt, *J* = 15.0, 6.0 Hz, $C^9\boldsymbol{H}$).

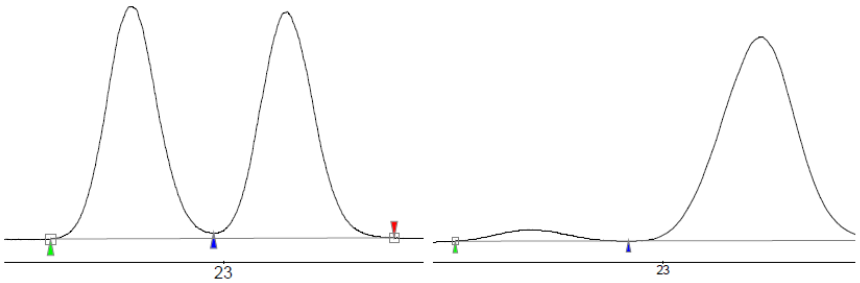
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 14.0 (C13), 22.2 (C12), 25.1 (C2), 31.6 (C11), 31.7 (C3), 32.3 (C10), 41.4 (C4), 41.7 (C1), 47.8 (C5), 130.1 (C9), 133 (C8), 211.8 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 2956, 2927, 2855, 1713, 1455, 1226, 975, 737 $cm^{-1}$.

**HRMS** (EI): calc. for $C_{12}H_{20}O$ 180.1514, found 180.1511.

**GC**: (Lipodex A); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL $min^{-1}$, $t_i$= 75 °C (7 min), (5 °C $min^{-1}$) $t_f$ = 115 °C (90 min), (0.7 °C $min^{-1}$) $t_f$ = 140 °C: (*R*)-enantiomer: $t_R$ = 22.84 min; (*S*)-enantiomer: $t_R$ = 23.12 min.

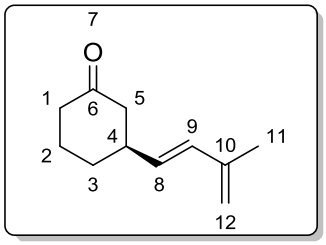
**$[\alpha]_D^{25}$**: -7.8 (*c* = 2.00, $CHCl_3$).




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 22.84 | 49.95 | 4681.3 | 500.5 | 49.951 |
| 2 | UNKNOWN | 23.11 | 50.05 | 4570.5 | 501.5 | 50.049 |
| | | | | | | |
| Total | | | 100.00 | 9251.8 | 1001.9 | 100.000 |

| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 22.84 | 4.60 | 1060.6 | 101.1 | 4.603 |
| 2 | UNKNOWN | 23.12 | 95.40 | 19276.8 | 2094.6 | 95.397 |
| | | | | | | |
| Total | | | 100.00 | 20337.3 | 2195.6 | 100.000 |

## (*S*)-(*E*)-3-(3-methylbuta-1,3-dien-1-yl)cyclohexanone (2c)[6]




Prepared according to general procedure 1 from 2-methyl-1-buten-3-yne (71 µL, 0.75 mmol) and cyclohexenone (48 µL, 0.5 mmol) to yield title compound as a colourless oil in 90% e.e. (57.5 mg, 70%, 0.35 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.35.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 1.49–1.59 (1H, m, *c*-hex), 1.64–1.76 (1H, m, *c*-hex), 1.83 (3H, s, C$^{11}$**H**$_3$), 1.92–1.97 (1H, m, *c*-hex), 2.04–2.10 (1H, m, *c*-hex), 2.20–2.30 (2H, m, *c*-hex), 2.36–2.40 (1H, m, *c*-hex), 2.43–2.48 (1H, m, *c*-hex), 2.52–2.61 (1H, m, *c*-hex), 4.92 (2H, app. s, C$^{12}$***H***$_2$), 5.58 (1H, dd, *J* = 16.0, 7.0 Hz, C$^8$***H***), 6.14 (1H, d, *J* = 16.0 Hz, C$^9$**H**).

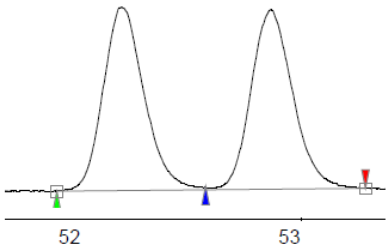
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 18.6 (C11), 25.0 (C2), 31.5 (C3), 41.3 (C4), 41.7 (C1), 47.4 (C5), 115.8 (C12), 132.0 (C8), 132.8 (C9), 141.6 (C10), 210.9 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3083, 2942, 1707, 1608, 1448 cm$^{-1}$.

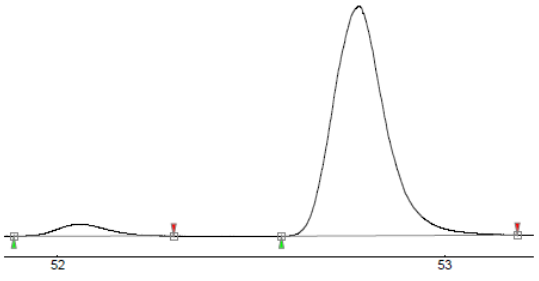
**HRMS** (EI): calc. for $C_{11}H_{16}O$ 164.1201, found 164.1199.

**GC**: (Lipodex A); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL min$^{-1}$, $t_i$=50 °C, (1.0 °C min$^{-1}$) $t_f$ = 160 (30 min): (*R*- enantiomer: $t_R$ = 38.56 min; (*S*)-enantiomer: $t_R$ = 38.70 min.

**$[\alpha]_D^{25}$**: -5.2 (*c* = 2.00, $CHCl_3$).

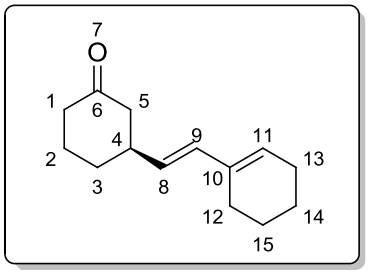



| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 52.23 | 50.07 | 3134.1 | 261.8 | 50.070 |
| 2 | UNKNOWN | 52.97 | 49.93 | 3072.3 | 261.1 | 49.930 |
| | | | | | | |
| Total | | | 100.00 | 6206.4 | 522.9 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 52.06 | 4.77 | 769.3 | 119.6 | 4.766 |
| 2 | UNKNOWN | 52.78 | 95.23 | 15287.7 | 2388.8 | 95.234 |
| | | | | | | |
| Total | | | 100.00 | 16057.0 | 2508.4 | 100.000 |

## (*S*)-(*E*)-3-(2-(cyclohex-1-en-1-yl)vinyl)cyclohexanone (2d)




Prepared according to general procedure 1 from 1-ethynylcyclohexene (88 µL, 0.75 mmol) and cyclohexenone (48 µL, 0.5 mmol) to yield title compound as a colourless oil in 82% e.e. (40.8 mg, 40%, 0.20 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.31.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 1.50 - 1.54 (1H, m, *c*-hex), 1.56 - 1.68 (5H, m, *c*-hex), 1.89 - 1.96 (1H, m, *c*-hex), 2.06 - 2.11 (5H, m, *c*-hex), 2.18 - 2.31 (2H, m, *c*-hex), 2.32 - 2.39 (1H, m, *c*-hex), 2.41 - 2.46 (1H, m, *c*-hex), 2.49 - 2.55 (1H, m, *c*-hex), 5.46 (1H, dd, *J* = 16.0, 7.0 Hz, C$^8$***H***), 5.69 (1H, app. s, C$^{11}$***H***), 6.02 (1H, d, *J* = 16.0 Hz, C$^9$***H***).

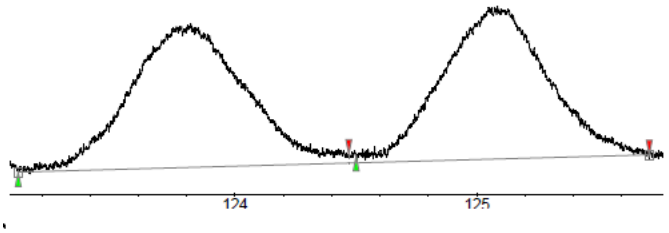
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 22.6 (C15), 22.7 (C2), 24.7 (C14), 25.2 (C13), 25.9 (C12), 31.8 (C3), 41.2 (C4), 42.0 (C1), 47.8 (C5), 128.8 (C11), 129.0 (C9), 132.8 (C8), 135.3 (C10), 211.4 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3011, 2935, 2861, 2837, 1706, 1448 cm$^{-1}$.

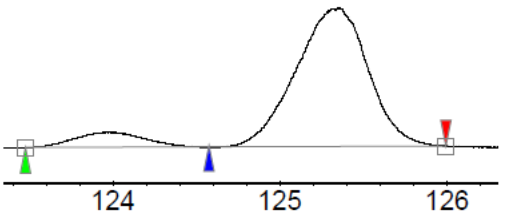
**HRMS** (EI): calc. for $C_{14}H_{20}O$ 204.1514, found 204.1522.

**GC**: (Lipodex A); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL min$^{-1}$, $t_i$= 75 °C (7 min), (5 °C min$^{-1}$) $t_f$ = 115 °C (90 min), (0.7 °C min$^{-1}$) $t_f$ = 140 °C: (*R*)-enantiomer: $t_R$ = 123.96 min; (*S*)- enantiomer: $t_R$ = 125.36 min.

**$[\alpha]_D^{25}$**: +5.5 (c = 2.00, $CHCl_3$).

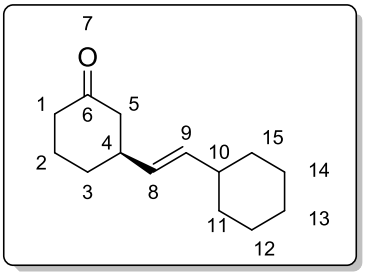



| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 123.82 | 50.61 | 284.9 | 159.2 | 50.612 |
| 2 | UNKNOWN | 125.09 | 49.39 | 310.8 | 155.3 | 49.388 |
| | | | | | | |
| Total | | | 100.00 | 595.7 | 314.5 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 123.96 | 9.23 | 586.8 | 280.0 | 9.228 |
| 2 | UNKNOWN | 125.36 | 90.77 | 5541.3 | 2753.9 | 90.772 |
| | | | | | | |
| Total | | | 100.00 | 6128.2 | 3033.9 | 100.000 |

## (*S*)–(*E*)-3-(2-cyclohexylvinyl)cyclohexanone (2e)[7]




Prepared according to general procedure 1 from cyclohexylacetylene (98 μL, 0.75 mmol) and cyclohexenone (48 μL, 0.5 mmol) to yield title compound as a colourless oil in 82% e.e. (52.6 mg, 51%, 0.255 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.42.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.98–1.08 (2H, m, *c*-hex), 1.11–1.31 (4H, m, *c*-hex), 1.63–1.71 (6H, m, *c*-hex), 1.86–1.93 (2H, m, *c*-hex), 2.00–2.07 (1H, m, *c*-hex), 2.14–2.21 (1H, m, *c*-hex), 2.23–2.29 (1H, m, *c*-hex), 2.32–2.36 (1H, m, *c*-hex), 2.37–2.45 (2H, m, *c*-hex), 5.28–5.40 (2H, m, C$^8$***H*** & C$^9$***H***).

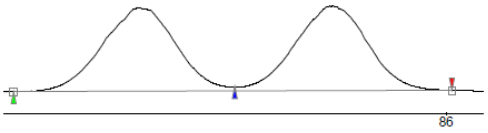
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 25.1 (C2), 26.2 (C12 & C14), 26.3 (C13), 31.8 (C3), 32.2 (C11 & C15), 40.7 (C4), 41.4 (C10), 41.7 (C1), 47.9 (C5), 130.4 (C8), 135.9 (C9), 211.6 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3011, 2935, 2861, 2837, 1706, 1448 cm$^{-1}$.

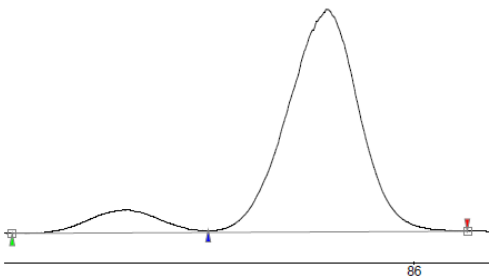
**HRMS** (EI): Calc. for $C_{14}H_{22}O$ 206.1671, found 206.1667.

**GC**: (Lipodex A); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL min$^{-1}$, $t_i$=50 °C, (1.0 °C min$^{-1}$) $t_f$ = 160 (30 min): (*R*)-enantiomer: $t_R$ = 85.42 min; (*S*)-enantiomer: $t_R$ = 85.83 min.

**$[\alpha]_D^{25}$**: +3.6 (c=2.00, $CHCl_3$).

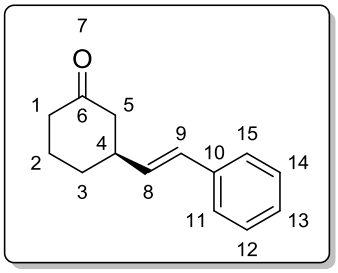



| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 85.40 | 49.96 | 7992.1 | 1338.3 | 49.959 |
| 2 | UNKNOWN | 85.78 | 50.04 | 8100.2 | 1340.5 | 50.041 |
| | | | | | | |
| Total | | | 100.00 | 16092.2 | 2678.8 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 85.42 | 9.38 | 1200.6 | 199.3 | 9.375 |
| 2 | UNKNOWN | 85.83 | 90.62 | 11705.5 | 1926.3 | 90.625 |
| | | | | | | |
| Total | | | 100.00 | 12906.1 | 2125.5 | 100.000 |

## (*S*)-(*E*)-3-styrylcyclohexanone (2f)[7]




Prepared according to general procedure 1 from phenylacetylene (82 µL, 0.75 mmol) and cyclohexenone (48 µL, 0.50 mmol) to yield title compound as a colourless oil in 80% e.e. (51.9 mg, 52%, 0.26 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.36.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 1.60–1.67 (1H, m, *c*-hex), 1.70–1.80 (1H, m, *c*-hex), 1.99–2.06 (1H, m, *c*-hex), 2.07–2.14 (1H, m, *c*-hex), 2.27–2.45 (3H, m, *c*-hex), 2.51–2.56 (1H, m, *c*-hex), 2.66–2.70 (1H, m, *c*-hex), 6.16 (1H, dd, *J* = 16.0, 7.0 Hz, C$^8$***H***), 6.39 (1H, d, *J* = 16.0 Hz, C$^9$***H***), 7.21–7.24 (1H, m, C$^{13}$***H***), 7.29–7.36 (4H, m, C$^{11}$***H***, C$^{12}$***H***, C$^{14}$***H***, C$^{15}$***H***).

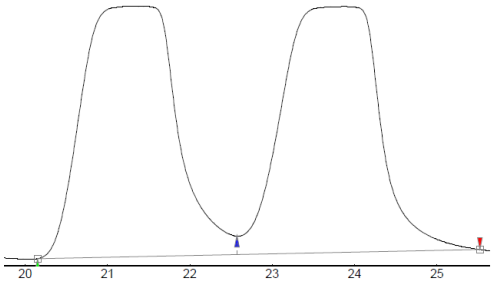
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 25.1 (C2), 31.5 (C3), 41.4 (C1), 42.1 (C4), 47.5 (C5), 126.3 (C11 & C15), 127.5 (C13), 129.2 (C12 & C14), 129.7 (C9), 133.0 (C8), 137.2 (C10), 211.1 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3402, 3058, 3026, 2936, 2865, 1711, 1598, 1493, 1448, 1223 cm$^{-1}$.

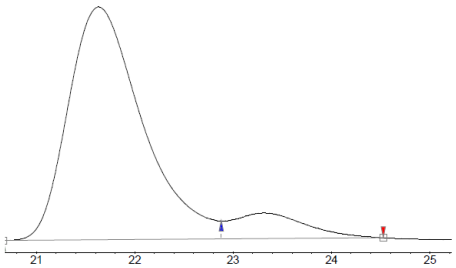
**HRMS** (EI): Calc. for $C_{14}H_{16}O$ 200.1201, found 200.1203.

**HPLC**: (Chircel OD-H); eluent 2% isopropanol/hexane, 1.0 mL/min, 254 nm: (*S*)-enantiomer: $t_R$ = 21.6 min; (*R*)-enantiomer: $t_R$ = 23.3 min.

**$[\alpha]_D^{25}$**: +85.5 (*c* = 2.00, $CHCl_3$).

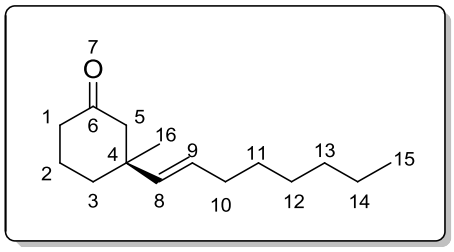



| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 21.22 | 49.74 | 2553.6 | 3374.5 | 49.739 |
| 2 | UNKNOWN | 23.77 | 50.26 | 2507.6 | 3409.8 | 50.261 |
| | | | | | | |
| Total | | | 100.00 | 5061.1 | 6784.3 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [mAU] | Area [mAU.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 21.63 | 90.14 | 953.9 | 832.3 | 90.141 |
| 2 | UNKNOWN | 23.31 | 9.86 | 105.3 | 91.0 | 9.859 |
| | | | | | | |
| Total | | | 100.00 | 1059.2 | 923.4 | 100.000 |

## (S, E)-3-methyl-3-(oct-1-en-1-yl)cyclohexanone (3a)[8]




Prepared according to general procedure 2 from 1-octyne (134 µL, 1.4 mmol) and 3-methyl-cyclohexenone (55 µL, 0.5 mmol) to yield title compound as a colourless oil in 94% e.e. (58.8 mg, 53%, 0.26 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.44.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.87 (3H, t, $J$ = 7.0 Hz, $C^{15}\boldsymbol{H}_3$), 1.04 (3H, s, $C^{16}\boldsymbol{H}_3$), 1.25–1.31 (8H, m, $C^{11}\boldsymbol{H}_2$-$C^{14}\boldsymbol{H}_2$), 1.57–1.62 (1H, m, *c*-hex), 1.66–1.72 (1H, m, *c*-hex), 1.79–1.86 (2H, m, *c*-hex), 1.94–1.99 (2H, m, *c*-hex), 2.14 (1H, d, $J$ = 14.0 Hz, $C^5\boldsymbol{H}$), 2.19–2.32 (2H, m, $C^{10}\boldsymbol{H}_2$), 2.42 (1H, dt, $J$ = 14.0, 1.5 Hz, $C^5\boldsymbol{H}$), 5.28 (1H, d, $J$ = 16.0 Hz, $C^8\boldsymbol{H}$), 5.35 (1H, dt, $J$ = 16.0, 6.0 Hz, $C^9\boldsymbol{H}$).

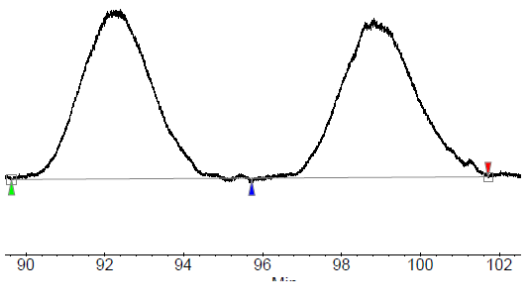
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 14.2 (C15), 22.3 (C2), 22.7 (C14), 28.2 (C16), 28.8 (C12), 29.5 (C11), 31.7 (C13), 32.8 (C10), 37.2 (C3), 40.9 (C4), 41.0 (C1), 52.4 (C5), 128.9 (C9), 137.7 (C8), 211.9 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 2956, 2927, 2855, 1713, 1455, 1226, 975, 737 $cm^{-1}$.

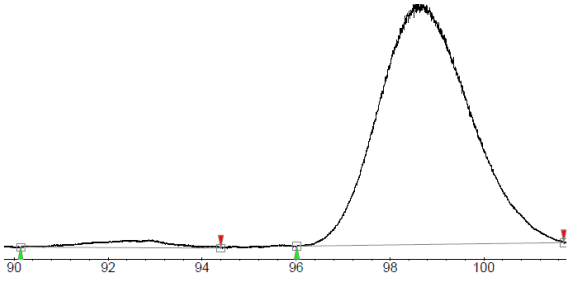
**HRMS** (EI): calc. for $C_{15}H_{26}O$ 222.1984 found 122.1980.

**GC**:(octakis(2,6-di-*O*-methyl-3-*O*-pentyl-γ-cyclodextrin); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL $min^{-1}$, $t_i$= 75 °C (7 min), (5 °C $min^{-1}$) $t_f$ = 115 °C (90 min), (0.7 °C $min^{-1}$) $t_f$ = 170 °C (*R*)-enantiomer: $t_R$ = 92.94 min; (*S*)-enantiomer: $t_R$ = 98.54 min.

**$[\alpha]_D^{25}$**: +12.7 ($c$ = 2.00, $CHCl_3$).

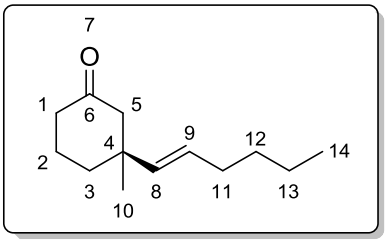



| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 92.40 | 50.12 | 876.8 | 1828.5 | 50.124 |
| 2 | UNKNOWN | 98.82 | 49.88 | 829.0 | 1819.5 | 49.876 |
| | | | | | | |
| Total | | | 100.00 | 1705.8 | 3648.0 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 92.94 | 2.70 | 130.8 | 248.5 | 2.704 |
| 2 | UNKNOWN | 98.54 | 97.30 | 4009.6 | 8940.6 | 97.296 |
| | | | | | | |
| Total | | | 100.00 | 4140.4 | 9189.1 | 100.000 |

## (*S*)-(*E*)-3-(hex-1-en-1-yl)-3-methylcyclohexanone (3b)[9]




Prepared according to general procedure 1 from 1-hexyne (91 μL, 0.75 mmol) and 3-methyl-cyclohexenone (55 μL, 0.5 mmol) to yield title compound as a colourless oil in 92% e.e. (66.1 mg, 68%, 0.34 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.47.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.90 (3H, t, $J$ = 7.0 Hz, $C^{14}\boldsymbol{H}_3$), 1.06 (3H, s, $C^{10}\boldsymbol{H}$), 1.28–1.38 (4H, m, $C^{12}\boldsymbol{H}_2$ & $C^{13}\boldsymbol{H}_2$), 1.57–1.65 (1H, m, *c*-hex), 1.65–1.74 (1H, m, *c*-hex), 1.81–1.90 (2H, m, *c*-hex), 1.97–2.02 (2H, m, *c*-hex), 2.17 (1H, d, $J$ = 14.0 Hz, $C^5\boldsymbol{H}$), 2.22–2.33 (2H, m, $C^{11}\boldsymbol{H}_2$), 2.44 (1H, dt, $J$ = 14.0, 1.0 Hz, $C^5\boldsymbol{H}$), 5.30 (1H, d, $J$ = 16.0 Hz, $C^8\boldsymbol{H}$), 5.37 (1H, dt, $J$ = 16.0, 6.0 Hz, $C^9\boldsymbol{H}$).

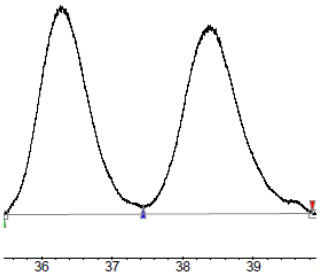
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 13.9 (C14), 22.1 (C2), 22.2 (C13), 28.1 (C10), 31.6 (C12), 32.4 (C11), 37.1 (C3), 40.7 (C4), 40.9 (C1), 52.4 (C5), 128.7 (C9), 137.5 (C8), 211.7 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 2956, 2927, 2855, 1713, 1455, 1226, 975, 737 $cm^{-1}$.

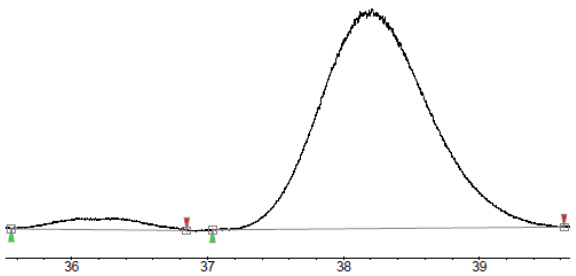
**HRMS** (EI): calc. for $C_{13}H_{22}O$ 194.1671, found 194.1666.

**GC**:(octakis(2,6-di-*O*-methyl-3-*O*-pentyl-γ-cyclodextrin); $T_{inj}$ = 250 °C, $T_{det}$ = 25 °C, flow = 2.0 mL $min^{-1}$, $t_i$=50 °C, (1.0 °C $min^{-1}$) $t_f$ = 160 (30 min): (*R*)-enantiomer: $t_R$ = 36.30 min; (*S*)-enantiomer: $t_R$ = 38.22 min.

**$[\alpha]_D^{25}$**: +59.6 (*c* = 2.0, $CHCl_3$).

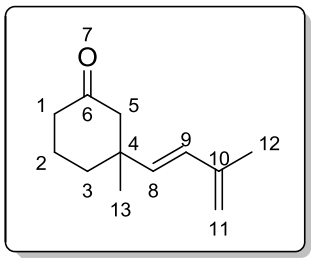



| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 36.27 | 49.02 | 1558.6 | 1262.9 | 49.024 |
| 2 | UNKNOWN | 38.39 | 50.98 | 1409.9 | 1313.2 | 50.976 |
| | | | | | | |
| Total | | | 100.00 | 2968.5 | 2576.2 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 36.30 | 4.01 | 138.5 | 102.4 | 4.011 |
| 2 | UNKNOWN | 38.22 | 95.99 | 2642.9 | 2450.0 | 95.989 |
| | | | | | | |
| Total | | | 100.00 | 2781.4 | 2552.4 | 100.000 |

## (*S*)-(*E*)-3-methyl-3-(3-methylbuta-1,3-dien-1-yl)cyclohexanone (3c)




Prepared according to general procedure 1 from 2-methyl-1-buten-3-yne (71 µL, 0.75 mmol)) and 3-methyl-cyclohexenone (55 µL, 0.5 mmol) to yield title compound as a colourless oil in 98% e.e. (51.0 mg, 57%, 0.29 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.31.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 1.09 (3H, s, $C^{13}\boldsymbol{H}_3$), 1.60–1.69 (1H, m, *c*-hex), 1.74–1.79 (1H, m, *c*-hex), 1.81 (3H, s, $C^{12}\boldsymbol{H}_3$), 1.83–1.92 (2H, m, *c*-hex), 2.20 (1H, d, *J* = 14.0 Hz, $C^5\boldsymbol{H}$), 2.24–2.34 (2H, m, *c*-hex), 2.47 (1H, dt, *J* = 14.0, 1.0 Hz, $C^5\boldsymbol{H}$), 4.93 (2H, app. s, $C^{11}\boldsymbol{H}_2$), 5.52 (1H, d, *J* = 16.0 Hz, $C^8$H), 6.08 (1H ,d, *J* = 16.0 Hz, $C^9$H).

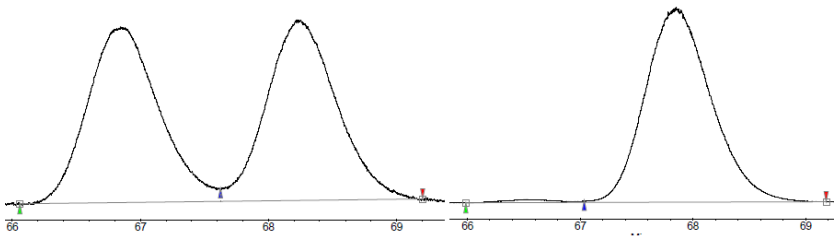
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 18.7 (C12), 22.3 (C2), 22.7 (C13), 37.2 (C3), 41.0 (C1), 41.1 (C4), 52.5 (C5), 116.0 (C11), 130.7 (C9), 137.5 (C8), 141.7 (C10), 211.4 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3010, 2959, 2929, 2872, 1704, 1455, 1378, 972, 892 $cm^{-1}$.

**HRMS** (EI): calc. for $C_{12}H_{18}O$ 178.1358, found 178.1356.

**GC**:(octakis(2,6-di-O-methyl-3-O-pentyl-γ-cyclodextrin); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL $min^{-1}$, $t_i$=50 °C, (1.0 °C $min^{-1}$) $t_f$ = 160 (30 min): (*R*)-enantiomer: $t_R$ = 66.51 min; (*S*)-enantiomer: $t_R$ = 67.85 min.

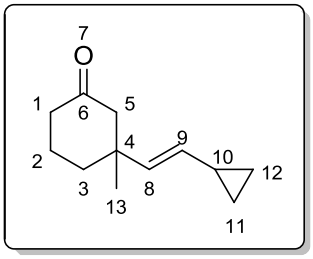
**$[\alpha]_D^{25}$**: +29.0 (*c* = 2.00, $CHCl_3$)




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 66.84 | 49.85 | 1284.3 | 827.5 | 49.850 |
| 2 | UNKNOWN | 68.22 | 50.15 | 1317.0 | 832.5 | 50.150 |
| | | | | | | |
| Total | | | 100.00 | 2601.3 | 1660.0 | 100.000 |

| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 66.51 | 1.24 | 193.6 | 107.1 | 1.236 |
| 2 | UNKNOWN | 67.85 | 98.76 | 12681.7 | 8563.0 | 98.764 |
| | | | | | | |
| Total | | | 100.00 | 12875.4 | 8670.2 | 100.000 |

## (*S*)-(*E*)-3-(2-cyclopropylvinyl)-3-methylcyclohexanone (3g)




Prepared according to general procedure 1 from cyclopropylacetylene (71 µL, 0.75 mmol) and 3-methyl-cyclohexenone (55 µL, 0.5 mmol) to yield title compound as a colourless oil in 94% e.e. (26.3 mg, 30%, 0.15 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.42.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.29–0.32 (2H, m, *c*-propyl), 0.63–0.67 (2H, m, *c*-propyl), 1.03 (3H, s, $C^{13}\boldsymbol{H}_3$), 1.24–1.34 (1H, m, $C^{10}\boldsymbol{H}$), 1.55–1.61 (1H, m, *c*-hex), 1.66–1.71 (1H, m, *c*-hex), 1.80–1.87 (2H, m, *c*-hex), 2.13 (1H, d, $J$ = 14.0 Hz, $C^5\boldsymbol{H}$), 2.17–2.31 (2H, m, *c*-hex), 2.37 (1H, dt, $J$ = 14.0, 1.5 Hz, $C^5\boldsymbol{H}$), 4.86 (1H, dd, $J$ = 16.0, 8.5 Hz, $C^9\boldsymbol{H}$), 5.38 (1H, d, $J$ = 16.0 Hz, $C^8\boldsymbol{H}$).

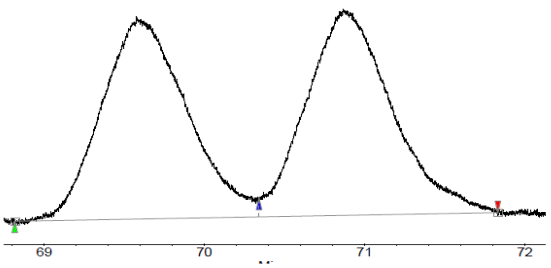
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 6.72 (C11 & C12), 13.9 (C10), 22.3 (C2), 28.0 (C13), 37.2 (C3), 40.8 (C4), 41.0 (C1), 52.5 (C5), 132.3 (C9), 136.4 (C8), 211.8 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3038, 3010, 2959, 2873, 1704, 1454, 1426, 1313, 1291, 1241, 968 $cm^{-1}$.

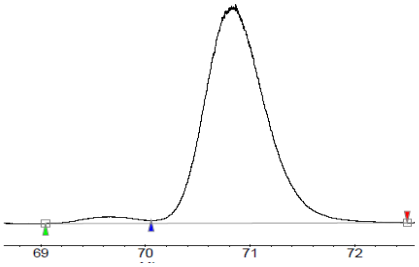
**HRMS** (EI): calc. for $C_{12}H_{18}O$ 178.1358 found 178.1361.

**GC**:(octakis(2,6-di-*O*-methyl-3-*O*-pentyl-γ-cyclodextrin); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL $min^{-1}$, $t_i$=50 °C, (1.0 °C $min^{-1}$) $t_f$ = 160 (30 min): (*R*)-enantiomer: $t_R$ = 69.64 min; (*S*)-enantiomer: $t_R$ = 70.86 min.

**$[\alpha]_D^{25}$**: +37.4 (*c* = 2.00, $CHCl_3$).

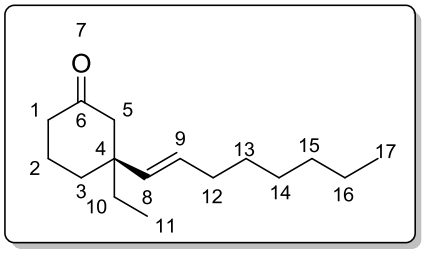



| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 69.60 | 49.30 | 677.1 | 421.0 | 49.305 |
| 2 | UNKNOWN | 70.87 | 50.70 | 699.0 | 432.9 | 50.695 |
| | | | | | | |
| Total | | | 100.00 | 1376.1 | 853.9 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 69.64 | 2.63 | 668.5 | 391.7 | 2.625 |
| 2 | UNKNOWN | 70.86 | 97.37 | 21766.6 | 14527.7 | 97.375 |
| | | | | | | |
| Total | | | 100.00 | 22435.0 | 14919.4 | 100.000 |

## (*S*)-(*E*)-3-ethyl-3-(oct-1-en-1-yl)cyclohexanone (4a)




Prepared according to general procedure 2 from 1-octyne (134 μL, 0.75 mmol) and 3-ethyl-cyclohexenone (59 μL, 0.5 mmol) to yield title compound as a colourless oil in 88% e.e. (70.9 mg, 60%, 0.29 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.50.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.78 (3H, t, *J* = 7.5 Hz, $C^{11}\boldsymbol{H}_3$), 0.87 (3H, t, *J* = 7.0 Hz, $C^{17}\boldsymbol{H}_3$), 1.19–1.32 (8H, m, $C^{13}\boldsymbol{H}_2$-$C^{16}\boldsymbol{H}_2$), 1.34–1.40 (2H, m, $C^{10}\boldsymbol{H}_2$), 1.60–1.69 (2H, m, *c*-hex), 1.76–1.86 (2H, m, *c*-hex), 1.96–2.02 (2H, m, *c*-hex), 2.10 (1H, d, *J* = 14.0 Hz, $C^5\boldsymbol{H}$), 2.16–2.32 (2H, m, $C^{12}\boldsymbol{H}_2$), 2.49 (1H, d, *J* = 14.0 Hz, $C^5\boldsymbol{H}$), 5.12 (1H, d, *J* = 16.0 Hz, $C^8\boldsymbol{H}$), 5.31 (1H, dt, *J* = 16.0, 7.0 Hz, $C^9\boldsymbol{H}$).

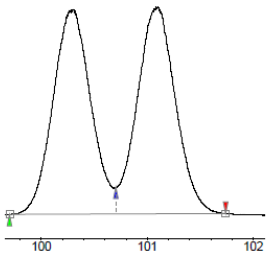
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 7.9 (C11), 14.1 (C17), 21.7 (C2), 22.6 (C16), 28.7 (C14), 29.5 (C13), 31.7 (C10), 32.9 (C15), 34.2 (C3), 35.3 (C12), 41.2 (C1), 44.1 (C4), 49.8 (C5), 131.1 (C9), 135.3 (C8), 211.9 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3038, 3010, 2959, 2873, 1704, 1454, 1426, 1313, 1291, 1241, 968 $cm^{-1}$

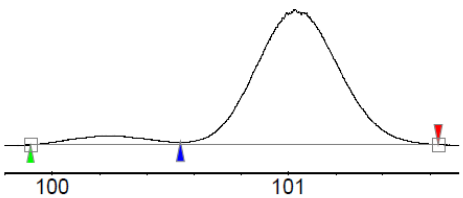
**HRMS** (EI): calc. for $C_{16}H_{28}O$ 236.2140 found 236.2138.

**GC**:(octakis(2,6-di-*O*-methyl-3-*O*-pentyl-γ-cyclodextrin); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL $min^{-1}$, $t_i$=50 °C, (1.0 °C $min^{-1}$) $t_f$ = 160 (30 min): (*R*)-enantiomer: $t_R$ = 100.24 min; (*S*)-enantiomer: $t_R$ = 101.02 min.

**$[\alpha]_D^{25}$**: +69.1 (*c*=2.00, $CHCl_3$).

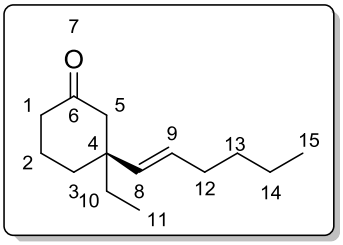



| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 100.31 | 49.52 | 15500.3 | 6437.7 | 49.517 |
| 2 | UNKNOWN | 101.08 | 50.48 | 15696.7 | 6563.3 | 50.483 |
| | | | | | | |
| Total | | | 100.00 | 31197.0 | 13001.0 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 100.24 | 5.63 | 652.6 | 240.7 | 5.629 |
| 2 | UNKNOWN | 101.02 | 94.37 | 9764.9 | 4036.2 | 94.371 |
| | | | | | | |
| Total | | | 100.00 | 10417.5 | 4276.9 | 100.000 |

## (*S*)-(*E*)-3-ethyl-3-(oct-1-en-1-yl)cyclohexanone (4b)[10]




Prepared according to general procedure 1 from 1-hexyne (71 μL, 0.75 mmol)) and 3-ethyl-cyclohexenone (59 μL, 0.5 mmol) to yield title compound as a colourless oil in 96% e.e. (47.9 mg, 46%, 0.23 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.55.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.80 (3H, t, *J* = 7.0 Hz, $C^{11}\boldsymbol{H}_3$), 0.90 (3H, t, *J* = 7.0 Hz, $C^{15}\boldsymbol{H}_3$), 1.25–1.36 (4H, m, $C^{13}\boldsymbol{H}_2$ & $C^{14}\boldsymbol{H}_2$), 1.36–1.42 (2H, m, $C^{10}\boldsymbol{H}_2$), 1.60–1.71 (2H, m, *c*-hex), 1.79–1.90 (2H, m, *c*-hex), 2.00–2.06 (2H, m, *c*-hex), 2.13 (1H, d, *J* = 14.0 Hz, $C^5\boldsymbol{H}$), 2.18–2.33 (2H, m, $C^{12}\boldsymbol{H}_2$), 2.49 (1H, dt, *J* = 14.0, 1.5 Hz, $C^5\boldsymbol{H}$), 5.14 (1H, d, *J* = 16.0 Hz, $C^8\boldsymbol{H}$), 5.34 (1H, dt, *J* = 16.0, 6.5 Hz, $C^9\boldsymbol{H}$).

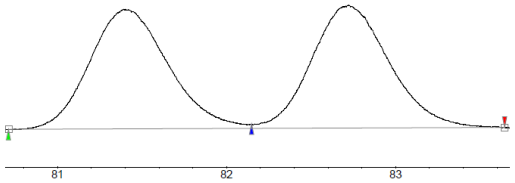
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 7.8 (C11), 13.9 (C15), 21.7 (C2), 22.1 (C14), 31.7 (C10), 32.6 (C13), 34.2 (C3), 35.3 (C12), 41.2 (C1), 44.1 (C4), 49.8 (C5), 131.0 (C9), 135.3 (C8), 211.9 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3038, 3010, 2959, 2873, 1704, 1454, 1426, 1313, 1291, 1241, 968 $cm^{-1}$.

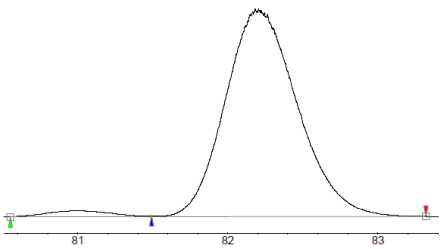
**HRMS** (EI): calc. for $C_{14}H_{24}O$ 208.1827 found 208.1820.

**GC**:(octakis(2,6-di-*O*-methyl-3-*O*-pentyl-γ-cyclodextrin); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL $min^{-1}$, $t_i$=50 °C, (1.0 °C $min^{-1}$) $t_f$ = 160 (30 min): (*R*)-enantiomer: $t_R$ = 81.01 min; (*S*)-enantiomer: $t_R$ = 82.19 min.

**$[\alpha]_D^{25}$**: +31.8 (*c* = 2.00, $CHCl_3$).




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 81.40 | 49.66 | 2414.7 | 1298.7 | 49.656 |
| 2 | UNKNOWN | 82.72 | 50.34 | 2484.9 | 1316.6 | 50.344 |
| | | | | | | |
| Total | | | 100.00 | 4899.6 | 2615.3 | 100.000 |




| Index | Name | Time [Min] | Quantity [% Area] | Height [uV] | Area [uV.Min] | Area % [%] |
|---|---|---|---|---|---|---|
| 1 | UNKNOWN | 81.01 | 2.42 | 1032.4 | 493.5 | 2.420 |
| 2 | UNKNOWN | 82.19 | 97.58 | 35813.8 | 19896.6 | 97.580 |
| | | | | | | |
| Total | | | 100.00 | 36846.1 | 20390.1 | 100.000 |

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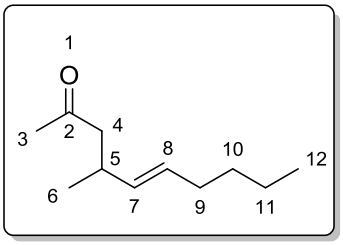
## (*E*)-4-methyldec-5-en-2-one (5)




Prepared according to general procedure 1 from 1-hexyne (71 μL, 0.75 mmol), 3-penten-2-one (49 μL, 0.5 mmol), trimethylaluminium (0.37 mL, 0.75 mmol) and tricyclohexylphosphine (24.5 mg, 0.075 mmol) to yield title compound as a yellow oil (18.5 mg, 22%, 0.11 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.64.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.58 (3H, t, *J* = 7.0 Hz, $C^{12}\boldsymbol{H}_3$), 0.99 (3H, d, *J* = 6.5 Hz, $C^{6}\boldsymbol{H}_3$), 1.25-1.34 (4H, m, $C^{10}\boldsymbol{H}_2$ & $C^{11}\boldsymbol{H}_2$), 1.96 (2H, app q, *J* = 6.0 Hz, $C^{9}\boldsymbol{H}_2$), 2.11 (3H, s, $C^{3}\boldsymbol{H}_3$), 2.33 (1H, dd, *J* = 15.5, 7.0 Hz, $C^{4}\boldsymbol{H}$), 2.42 (1H, dd, *J* = 15.5, 7.0 Hz, $C^{4}\boldsymbol{H}$), 5.30 (1H, dd, *J* = 15.5, 7.0 Hz, $C^{7}\boldsymbol{H}$), 5.40 (1H, dt, *J* = 15.5, 6.0 Hz, $C^{8}\boldsymbol{H}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 14.1 (C12), 20.7 (C6), 22.3 (C11), 30.7 (C5), 31.8 (C3), 32.9 (C9), 51.3 (C4), 129.6 (C8), 134.4 (C7), 208.6 (C2).

**IR** ($CHCl_3$) $\nu_{max}$: 3010, 2961, 2930, 2873, 1710, 1457, 1360, 971 $cm^{-1}$.

**HRMS** ($ESI^+$): calc. for $C_{14}H_{24}O$ 219.1597 found $[M+MeOH+H_2O+H^+]$ 219.1717.

**GC:**(octakis(6-*O*-pentyl-2,3-di-*O*-methyl-γ-cyclodextrin); $T_{inj}$ = 250 °C, $T_{det}$ = 250 °C, flow = 2.0 mL $min^{-1}$, $t_i$=70 °C, (45 min)(20 °C $min^{-1}$) $t_f$ = 170 (10 min): enantiomer 1: $t_R$ = 29.37 min; enantiomer 2: $t_R$ = 30.39 min.

Maximum 39% enantioselectivity was obtained in asymmetric runs broadly analogous to Table 1 but due to the low chemical yield (11%) this was not further optimised.

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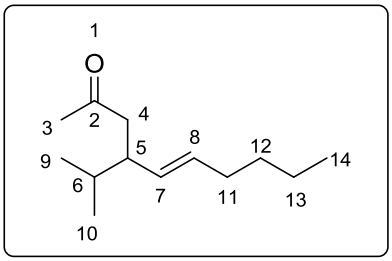
## (*E*)-4-isopropyldec-5-en-2-one (6)




Prepared according to general procedure 1 from 1-hexyne (71 μL, 0.75 mmol), 5-methyl-3-hexen-2-one (66 μL, 0.5 mmol), trimethylaluminium (0.37 mL, 0.75 mmol) and tricyclohexylphosphine (24.5 mg, 0.075 mmol) to yield title compound as a yellow oil (18.5 mg, 22%, 0.11 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.60.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.82-0.92 (9H, m, $C^9\boldsymbol{H}_3$, $C^{10}\boldsymbol{H}_3$, $C^{14}\boldsymbol{H}_3$), 1.19-1.34 (4H, m, $C^{12}\boldsymbol{H}_2$ & $C^{13}\boldsymbol{H}_2$), 1.54-1.60 (1H, m, $C^6\boldsymbol{H}$), 1.97 (2H, app q, $J$ = 6.5 Hz, $C^{11}\boldsymbol{H}_2$), 2.10 (3H, s, $C^3\boldsymbol{H}_3$), 2.31-2.47 (3H, m, $C^4H_2$ & $C^5\boldsymbol{H}$), 5.19 (1H, dd, $J$ = 15.0, 8.5 Hz, $C^7\boldsymbol{H}$), 5.38 (1H, dt, $J$ = 15.0, 6.5 Hz, $C^8\boldsymbol{H}$).

**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 14.1 (C14), 18.9 (C10), 20.6 (C9), 22.3 (C13), 30.7 (C5), 31.8 (C3), 32.0 (C12), 32.4 (C11), 45.2 (C6), 47.3 (C4), 130.3 (C8), 132.5 (C7), 209.3 (C2).

**IR** ($CHCl_3$) $\nu_{max}$: 3010, 2961, 2930, 2873, 1706, 1466, 1369, 1358, 973 $cm^{-1}$.

**HRMS** (ESI): calc. for $C_{13}H_{24}O$ 196.1827, found [M+H] 197.1907.

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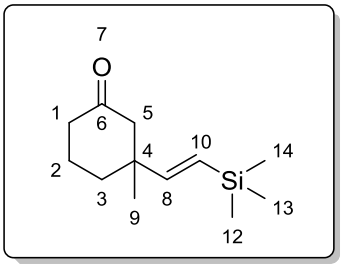
## (E)-3-methyl-3-(2-(trimethylsilyl)vinyl)cyclohexanone (8)




Prepared according to general procedure 1 from trimethylsilylacetylene (104 µL, 0.75 mmol) and 3-methyl-cyclohexenone (55 µL, 0.5 mmol) trimethylaluminium (0.37 mL, 0.75 mmol) and tricyclohexylphosphine (24.5 mg, 0.075 mmol) to yield title compound as a colourless oil (21.1 mg, 20%, 0.10 mmol) $\mathbf{R_f}$ (pentane/diethyl ether 4:1) 0.36.

**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.06 (9H, s, Si(C***H***$_3$)$_3$), 1.05 (3H, s, C$^9$***H***$_3$), 1.56-1.62 (1H, m, c-hex), 1.69-1.85 (3H, m, c-hex), 2.16 (1H, d, *J* = 14.0 Hz, C$^5$H), 2.20-2.30 (2H, m, c-hex), 2.47 (1H, dt, *J* = 14.0, 1.0 Hz, C$^5$***H***), 5.60 (1H, d, *J* = 19.0 Hz, C$^{10}$***H***), 5.88 (1H, d, *J* = 19.0 Hz, C$^8$***H***).

**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 1.06 (Si(***C***H$_3$)$_3$), 22.2 (C9), 27.1 (C2), 36.5 (C3), 41.0 (C1), 42.9 (C4), 51.8 (C5), 127.1 (C10), 153.3 (C8), 211.6 (C6).

**IR** ($CHCl_3$) $\nu_{max}$: 3010, 2958, 1705, 1612, 1248, 867, 841 cm$^{-1}$.

**HRMS** (EI): Calculated for $C_{12}H_{22}OSi$ [M+] 210.1440, found 210.1436.

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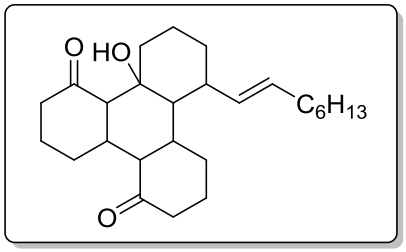
## Footnote tetracyclic compound



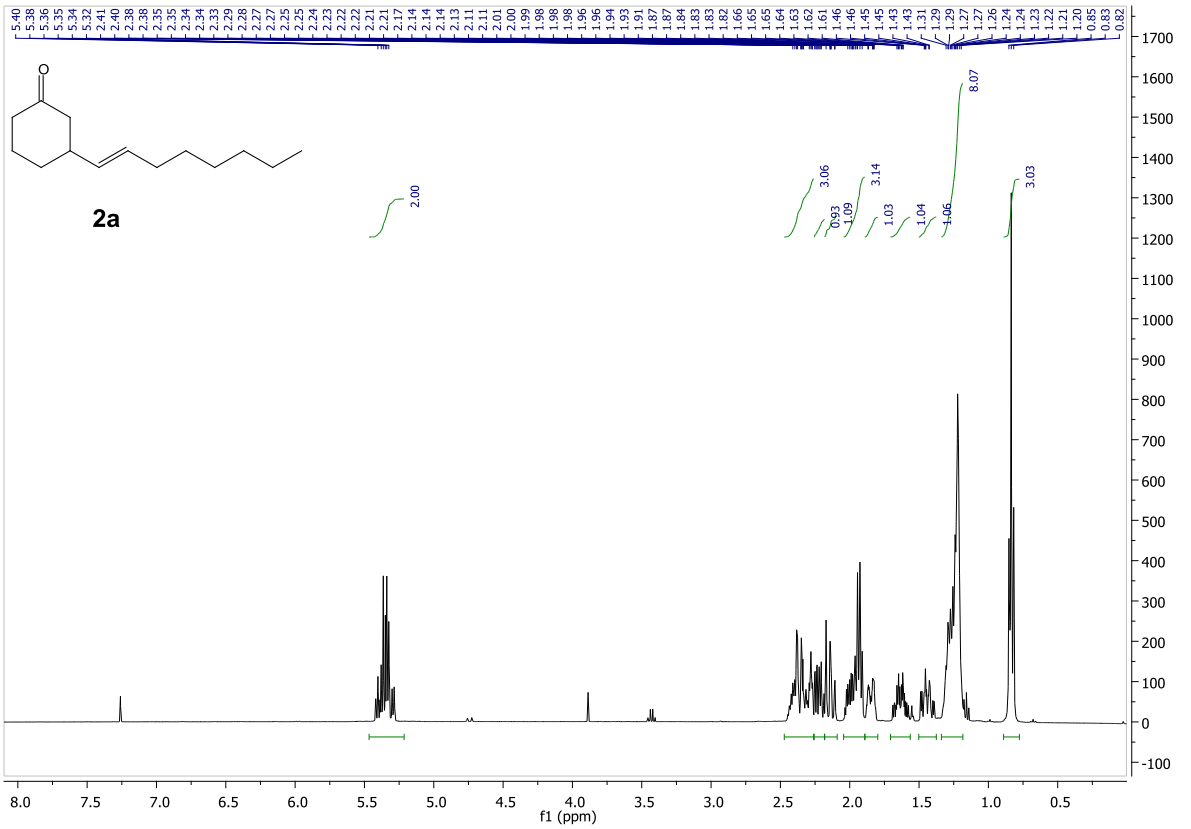

Racemic tetracycle was identified in early optimisation studies using CuTC/$PCy_3$ or **L1** as the major mass balance element. It was isolatedwas purified by flash chromatography (pentane/diethyl ether 4:1) $\mathbf{R_f}$ 0.28.

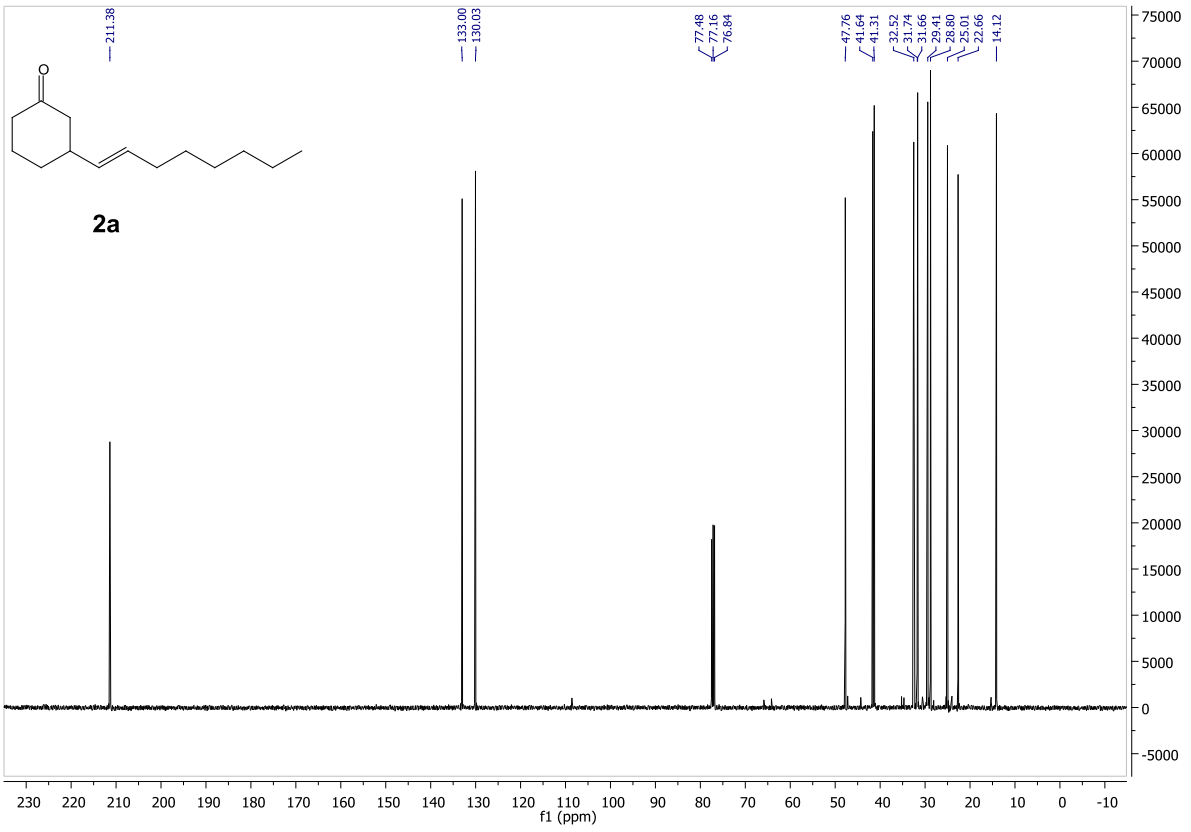
**$^1$H NMR** ($CDCl_3$) $\delta_H$: 0.89 (3H, t, *J* = 7.0 Hz, C***H***$_3$), 0.99–1.18 (3H, m), 1.27- 1.32 (8H, m, C***H***$_2$), 1.41–1.54 (3H, m), 1.66–2.45 (16H, m), 2.50 (1H, d, J = 10.5 Hz), 2.61 (1H, m), 2.97 (1H, app t, J = 11.0 Hz), 4.42 (1H, s), 5.20 (1H, app dd, *J* = 15.0, 8.0 Hz), 5.45 (1H, dt, *J* = 15.0, 7.0 Hz).

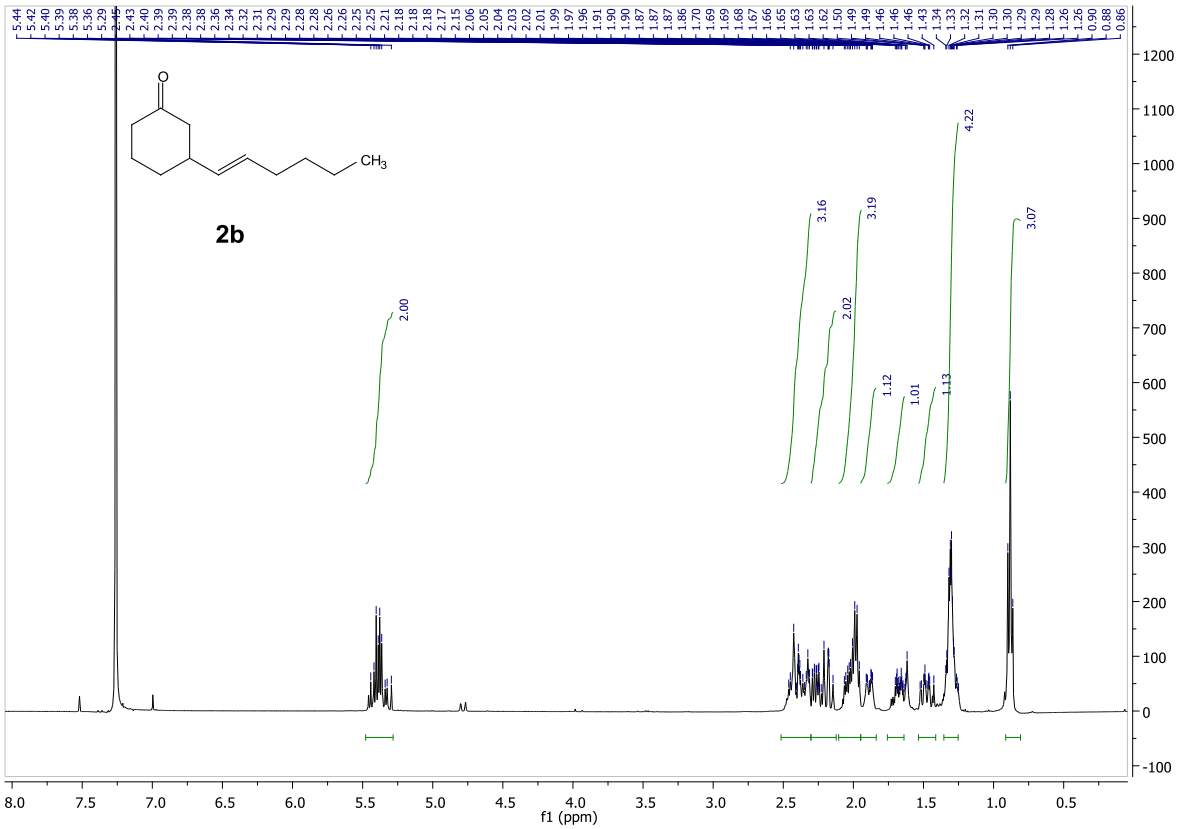
**$^{13}$C NMR** ($CDCl_3$) $\delta_C$: 14.2, 20.6, 20.7, 22.7, 27.6, 28.8, 29.8, 31.8, 32.8, 34.4. 38.1, 41.9, 45.5, 55.1, 55.9, 75.5, 130.7, 134.8, 213.7, 219.3 ppm.

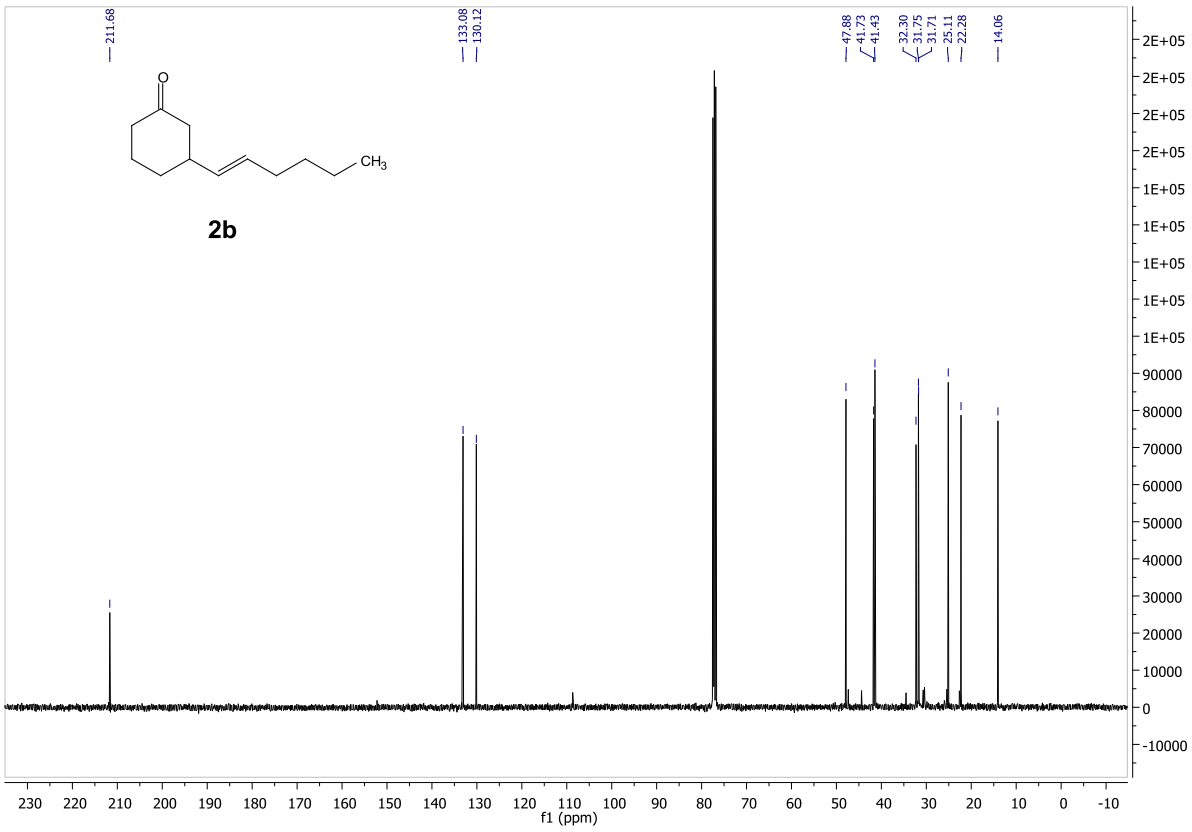
**IR** ($CHCl_3$) $\nu_{max}$: 3598, 3546, 3047. 3005, 2976, 2950, 2925, 2862, 1705, 1478, 1436, 1323, 1118 $cm^{-1}$.

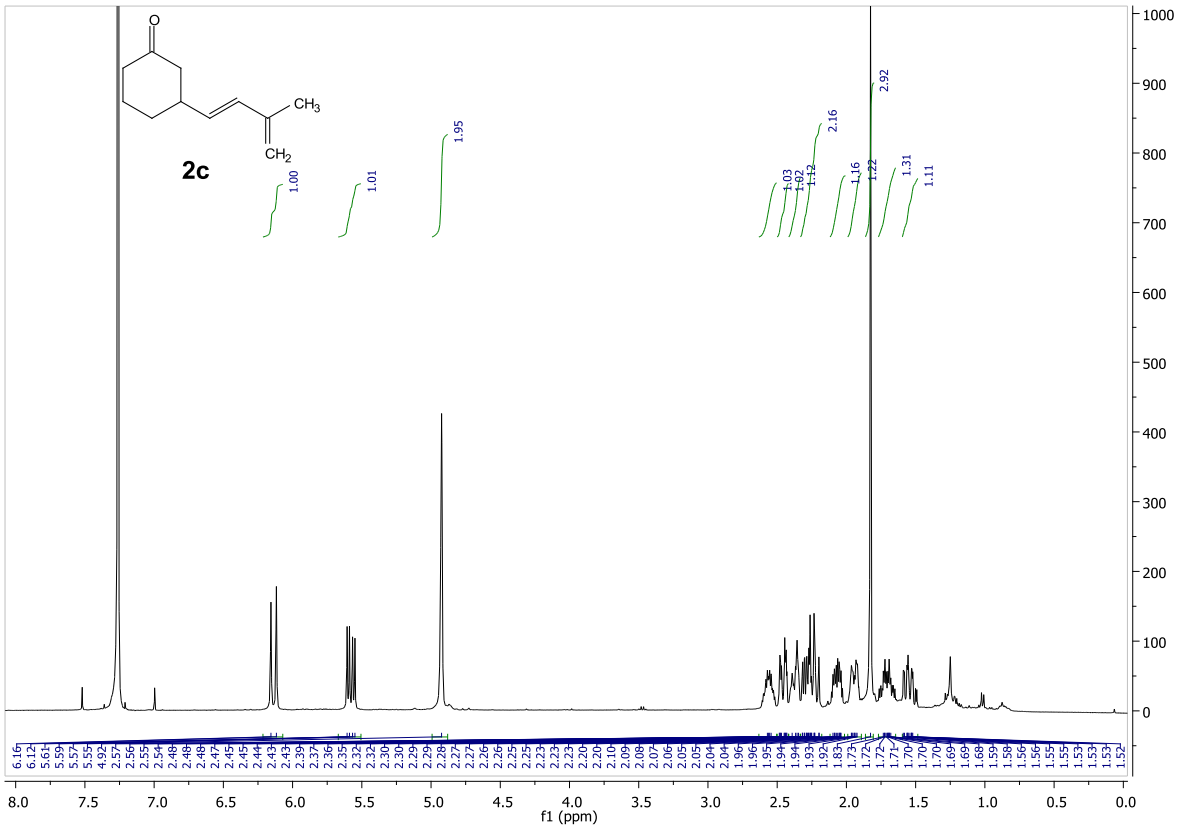
**HRMS** (ESI): calc. for $[M+Na]^+$ 422.2989 found 422.2982.


2a
f1 (ppm)


2a
f1 (ppm)


2b
CH3
f1 (ppm)


2b
CH3
f1 (ppm)


O
CH3
CH2
2c
1.00
1.01
1.95
1.03
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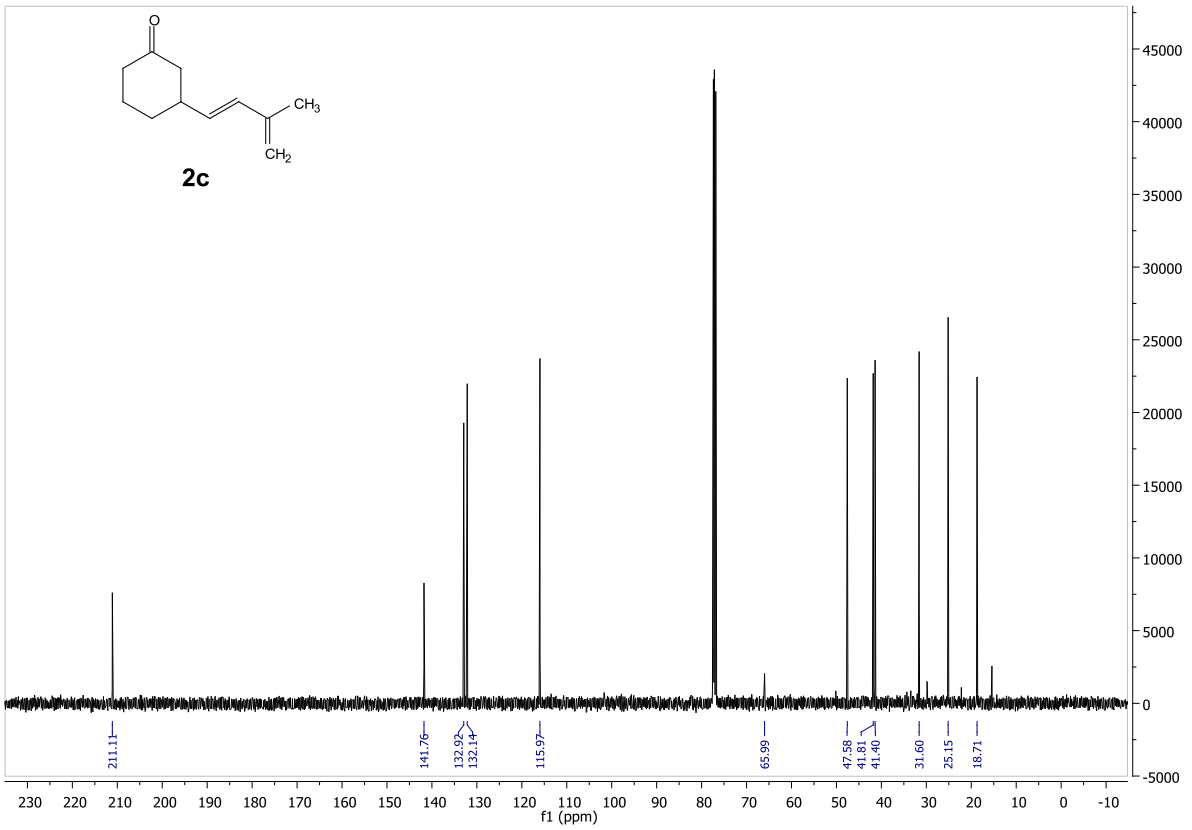
1.43
2.16
1.16
1.22
2.92
1.31
1.11
f1 (ppm)


O
CH3
CH2
2c
211.11
141.76
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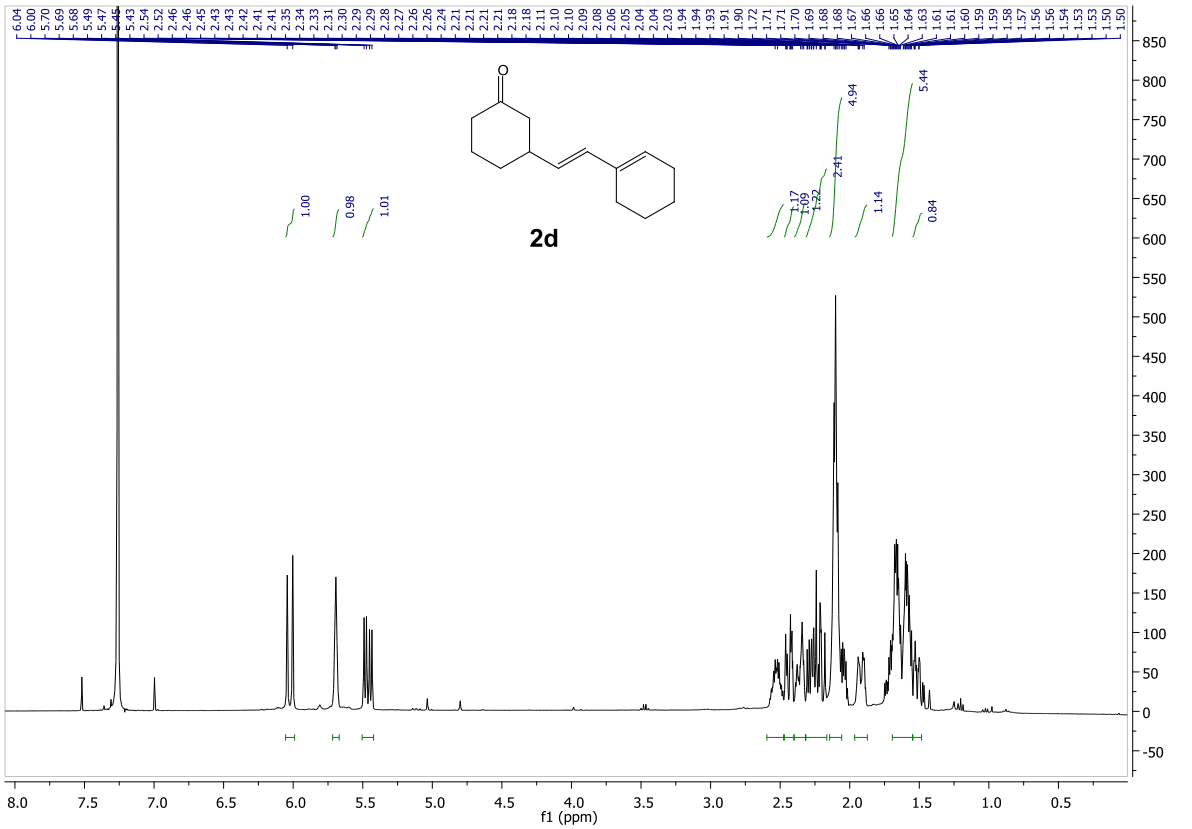
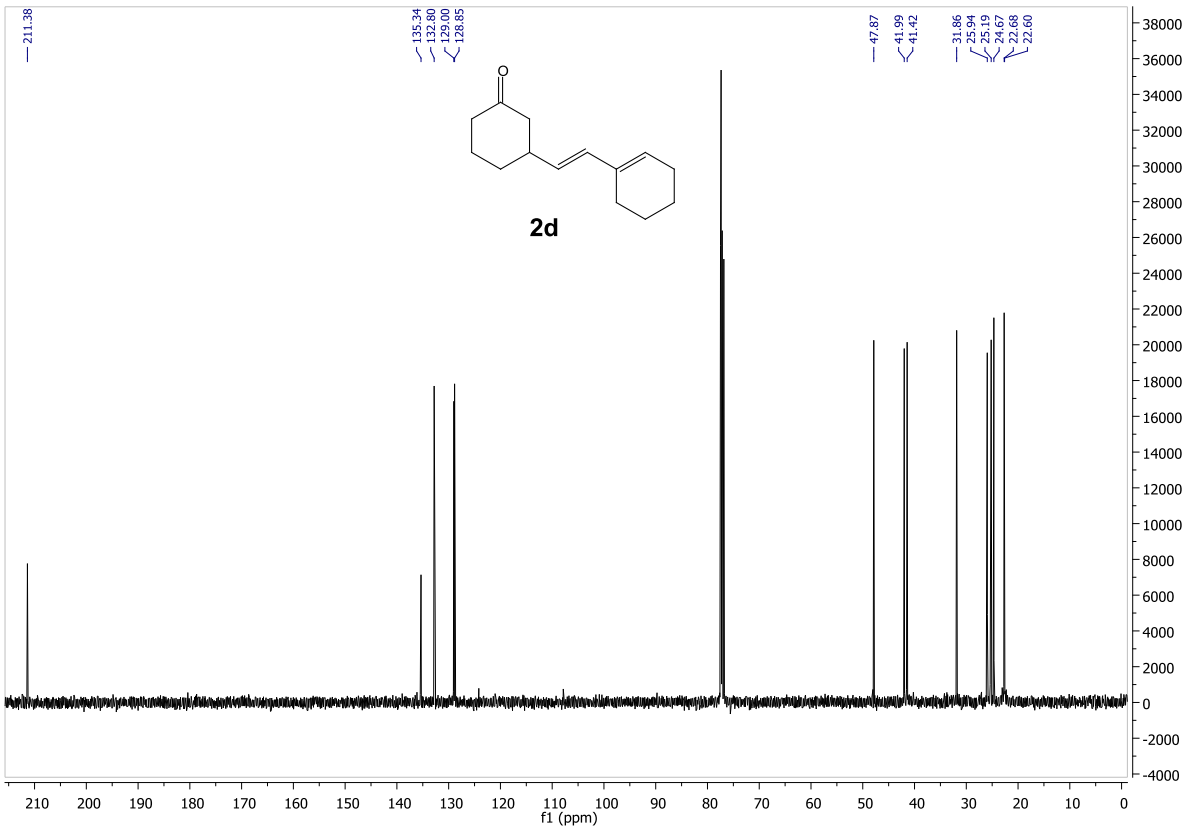
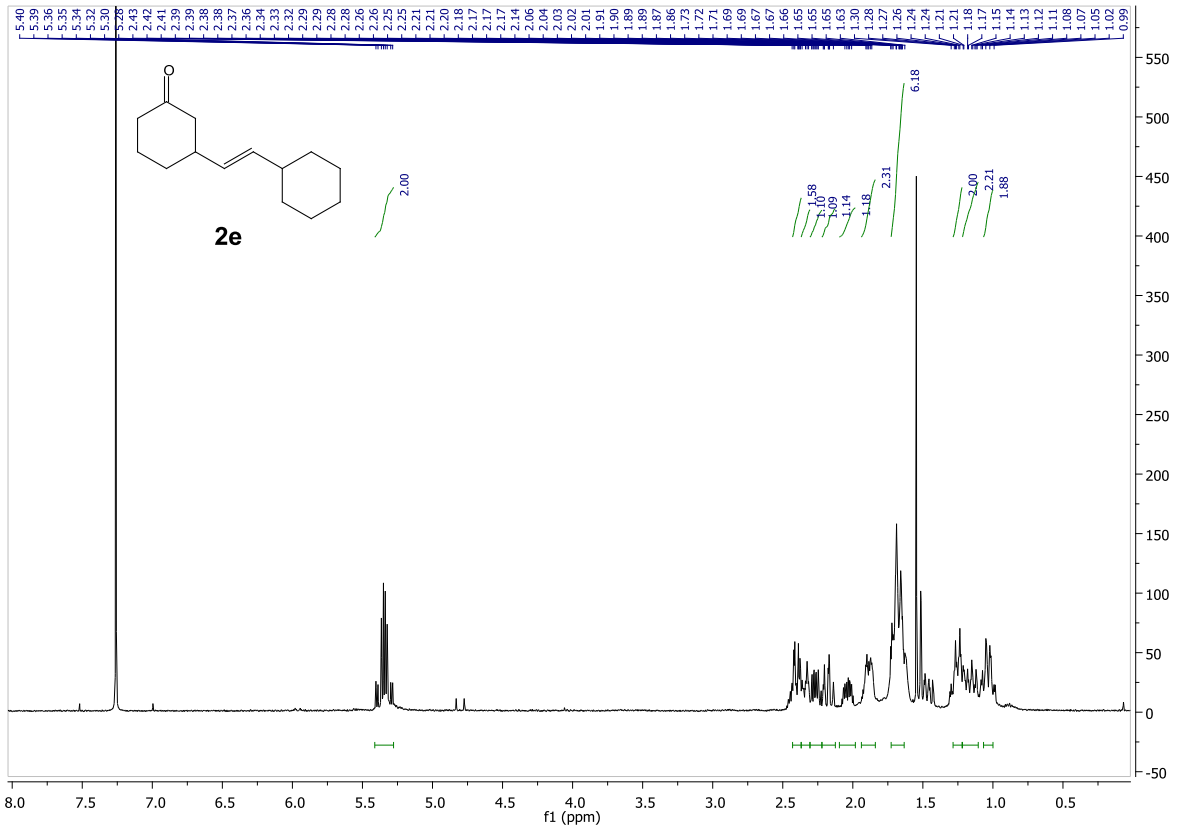
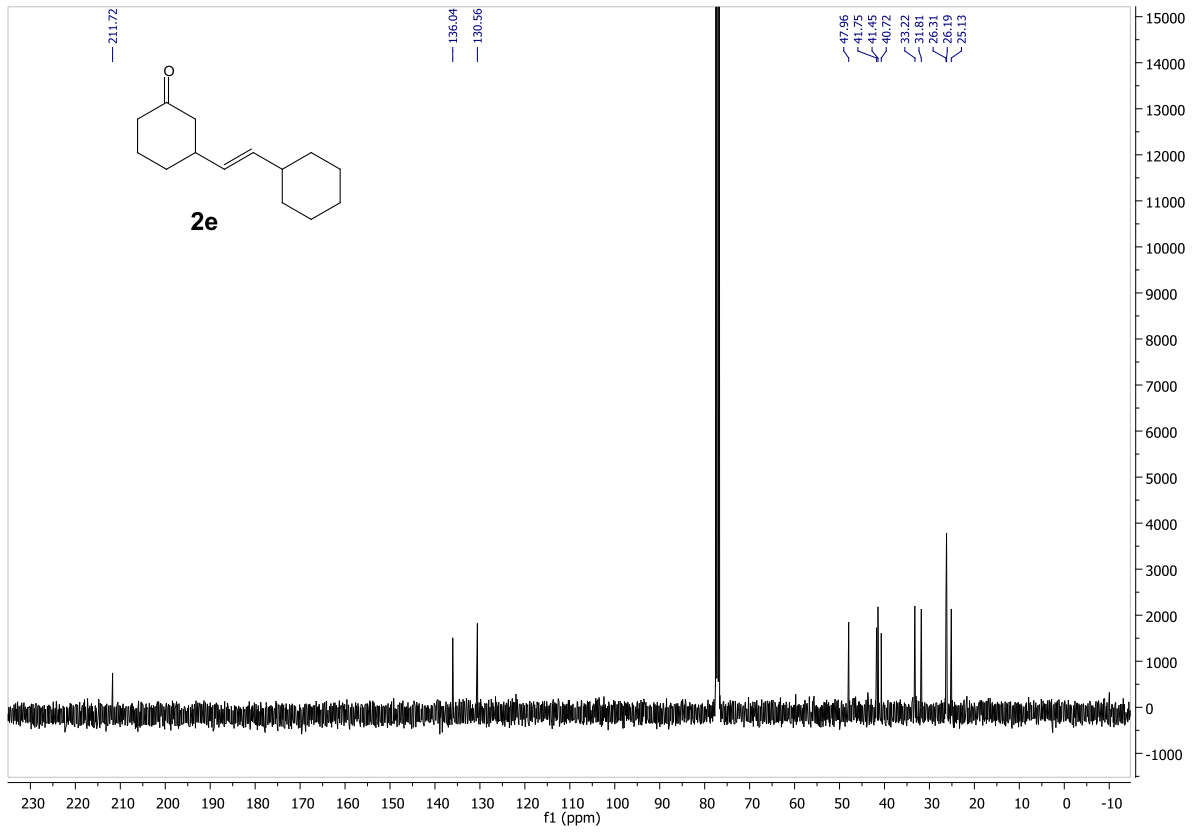
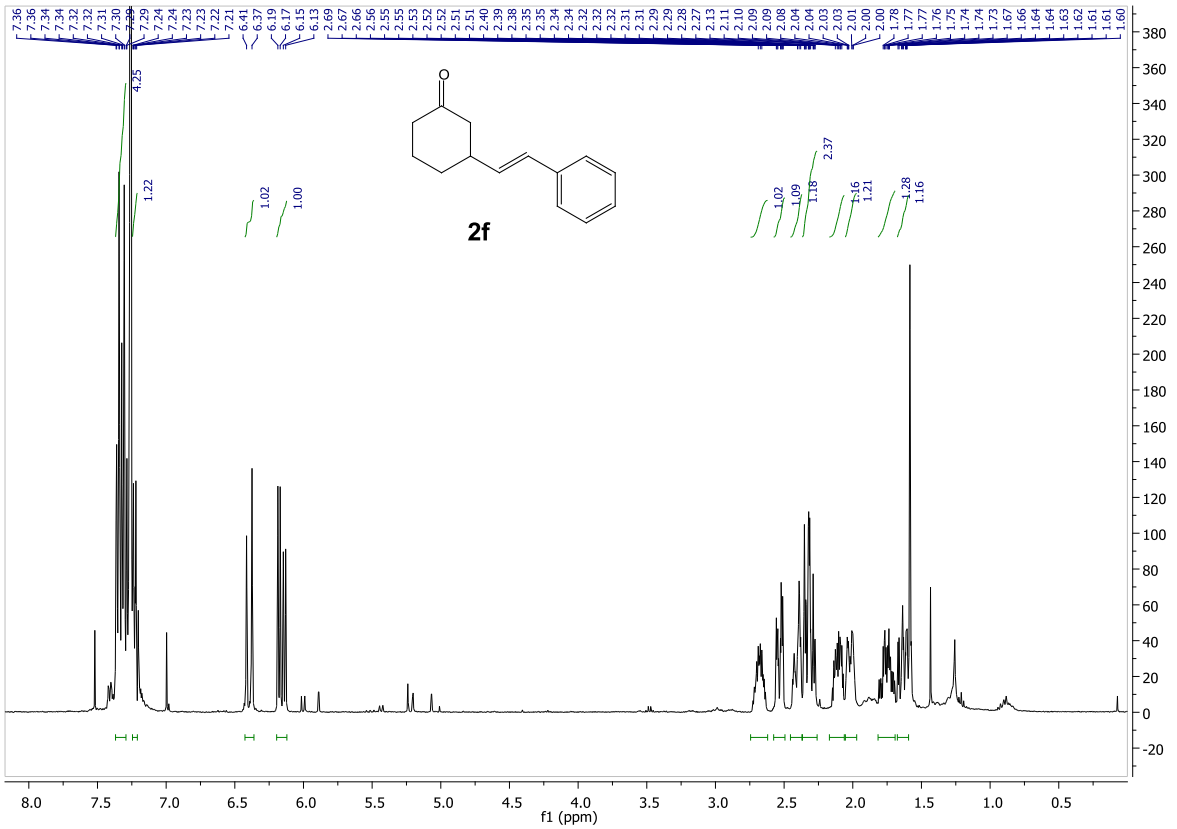
132.14
115.97
65.99
47.58
41.81
41.40
31.60
25.15
18.71
f1 (ppm)

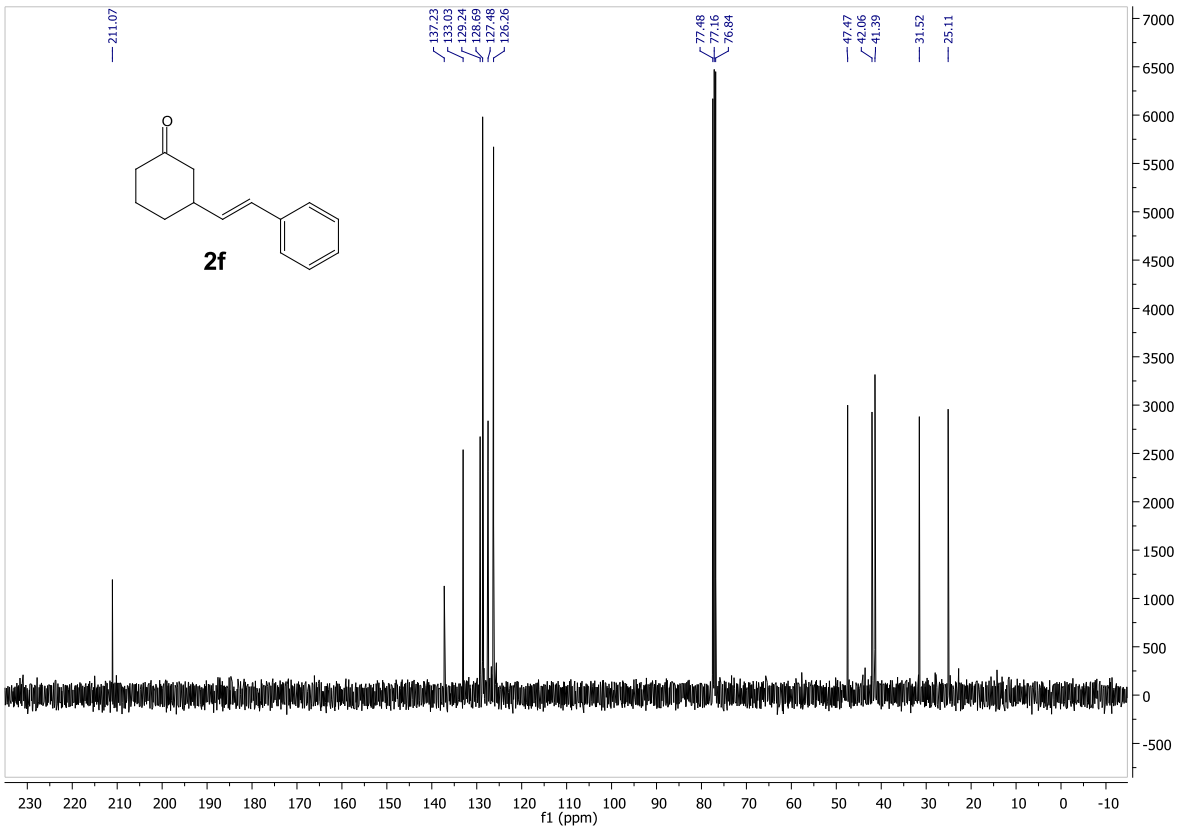

2d
f1 (ppm)

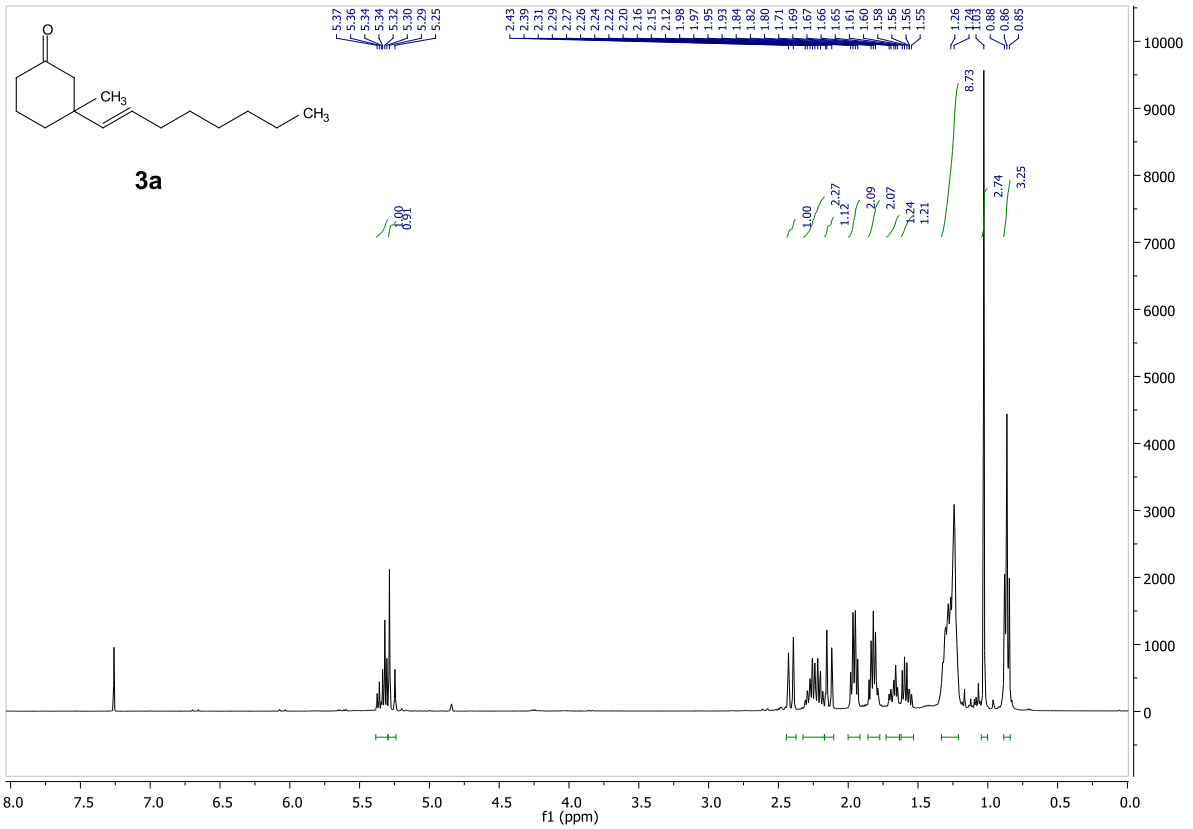

2d
f1 (ppm)

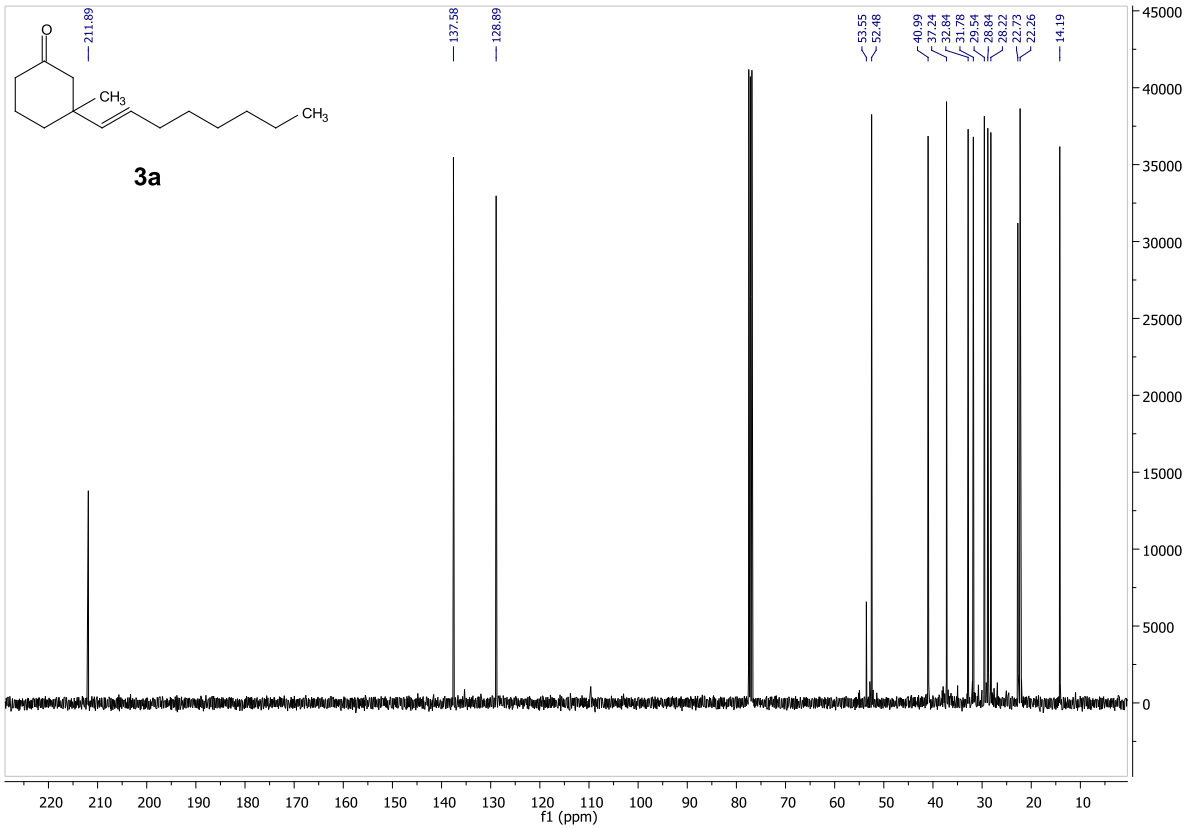

2e
f1 (ppm)

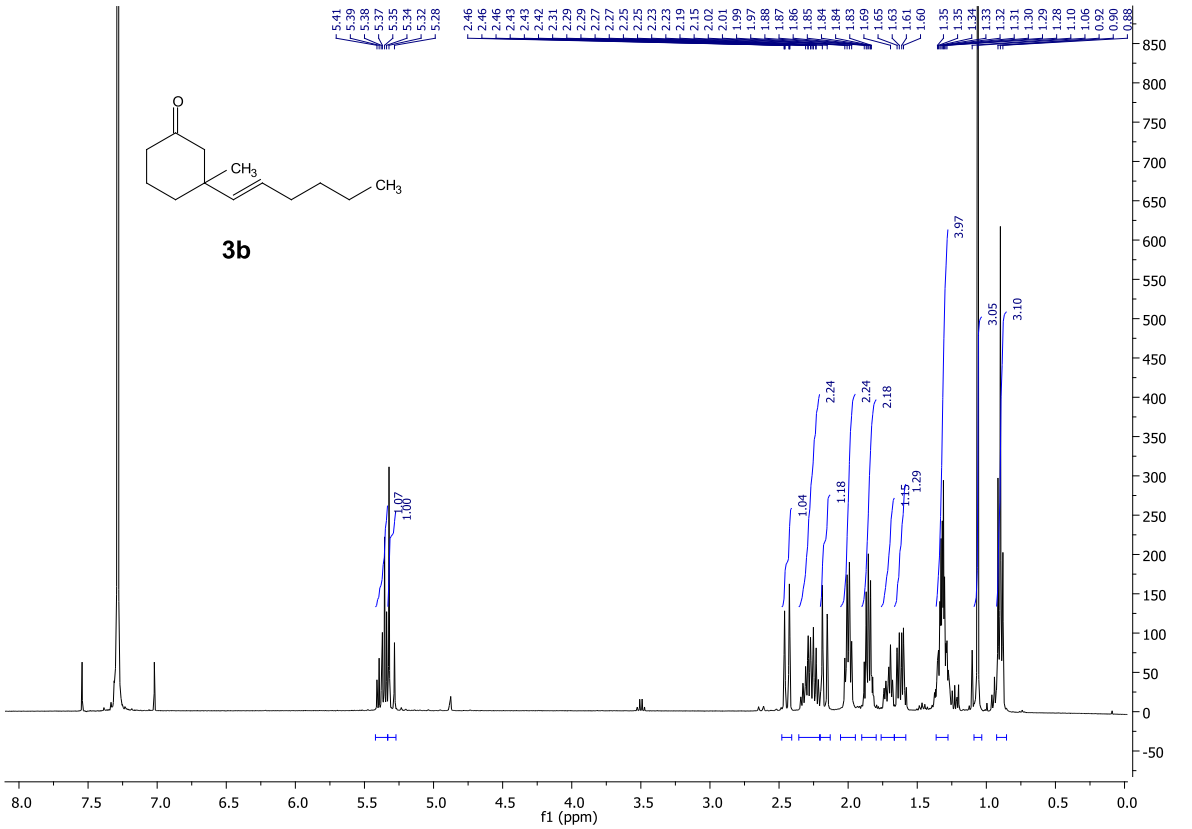

2e
f1 (ppm)

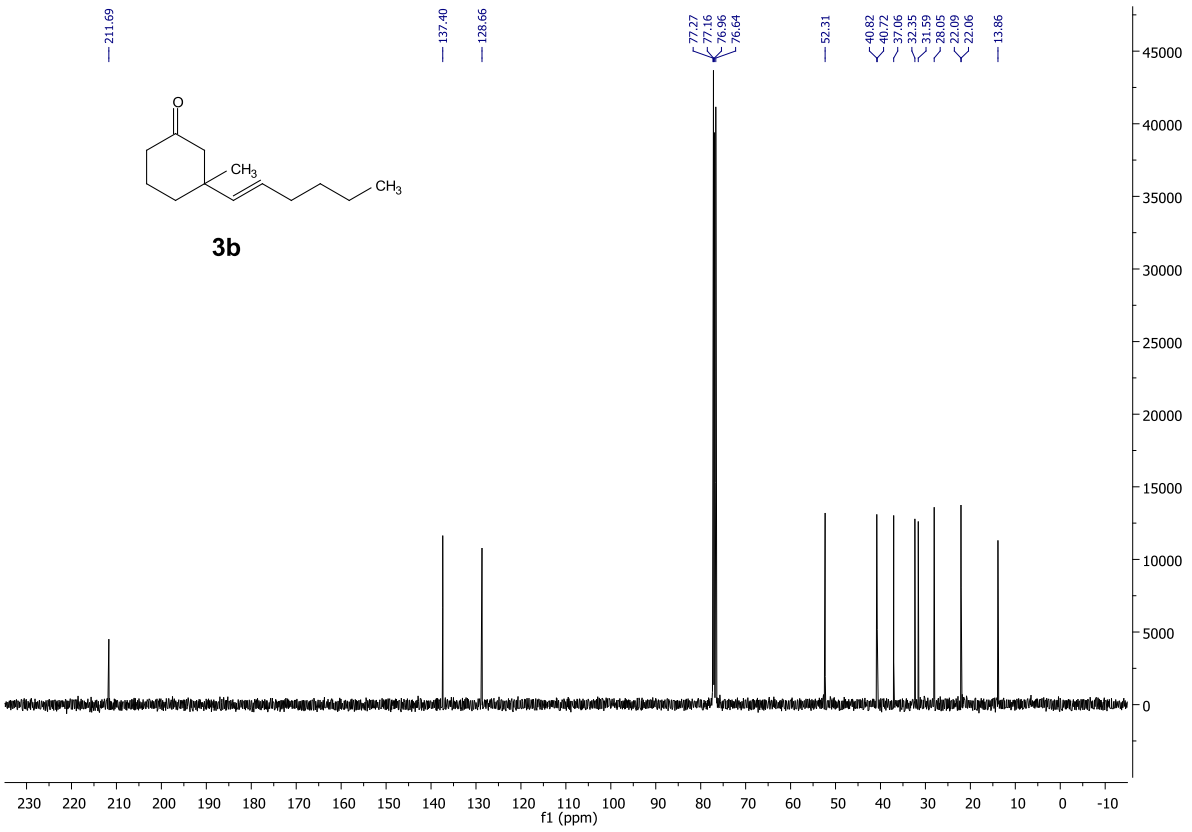

2f
f1 (ppm)

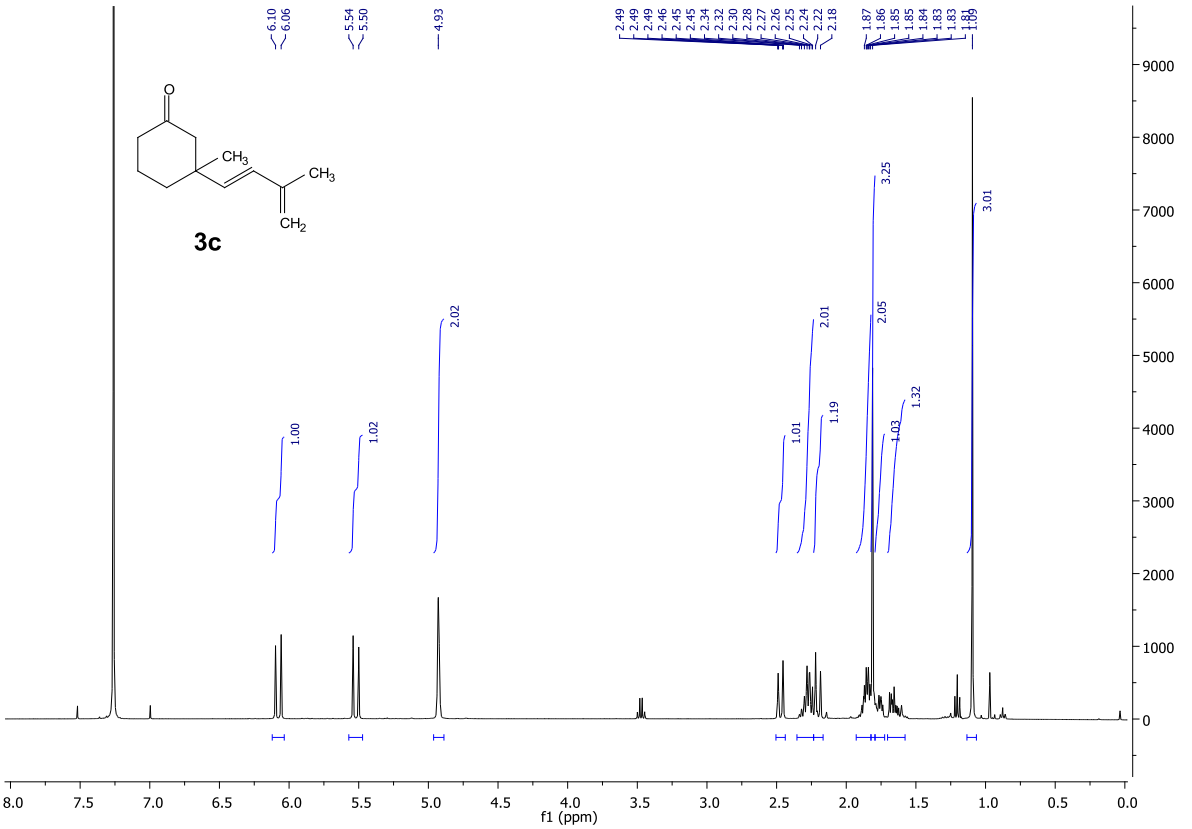

2f
f1 (ppm)

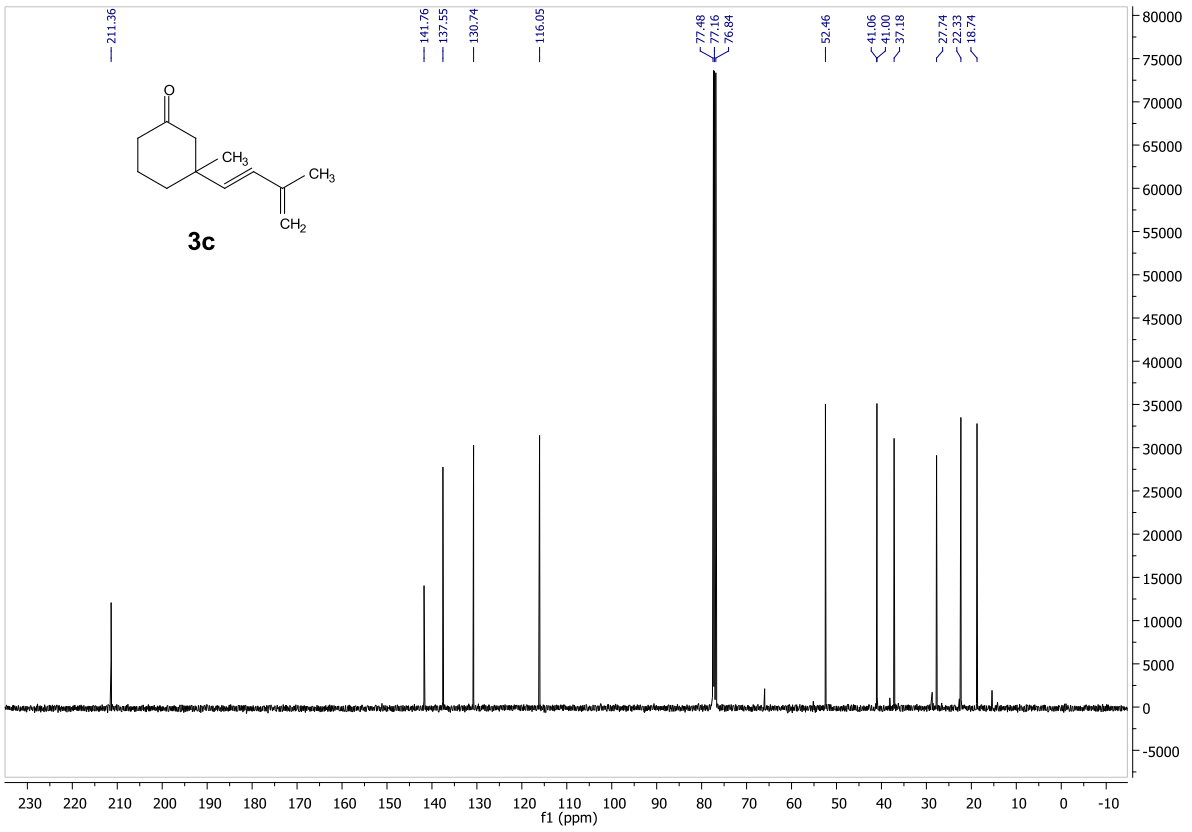

3a
f1 (ppm)

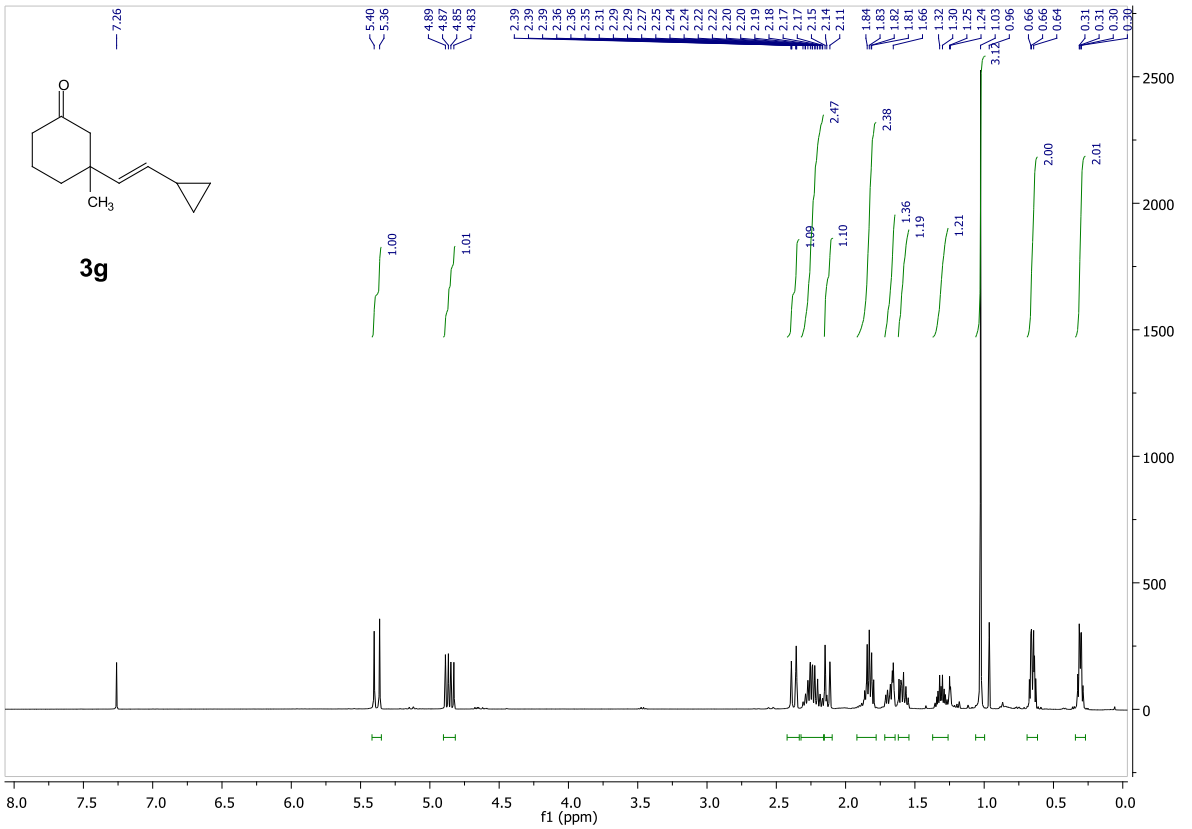

3a
f1 (ppm)

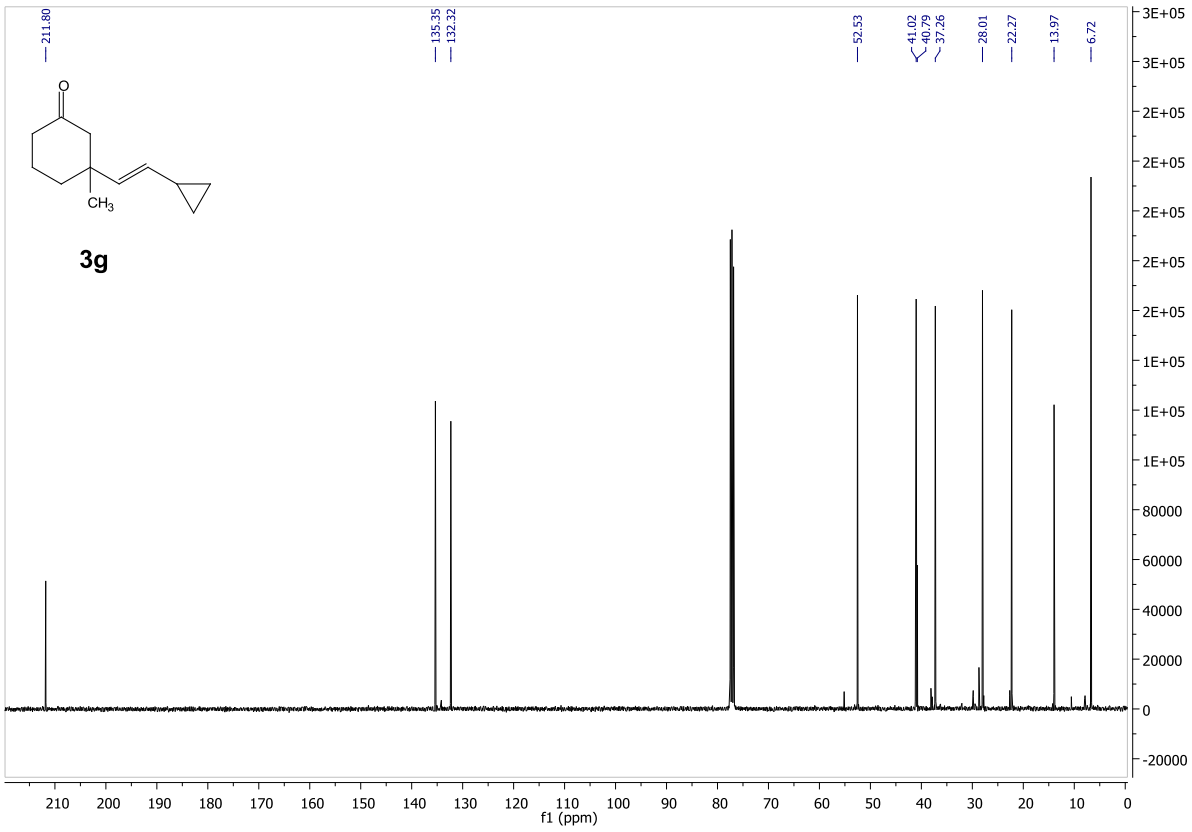

3b
f1 (ppm)

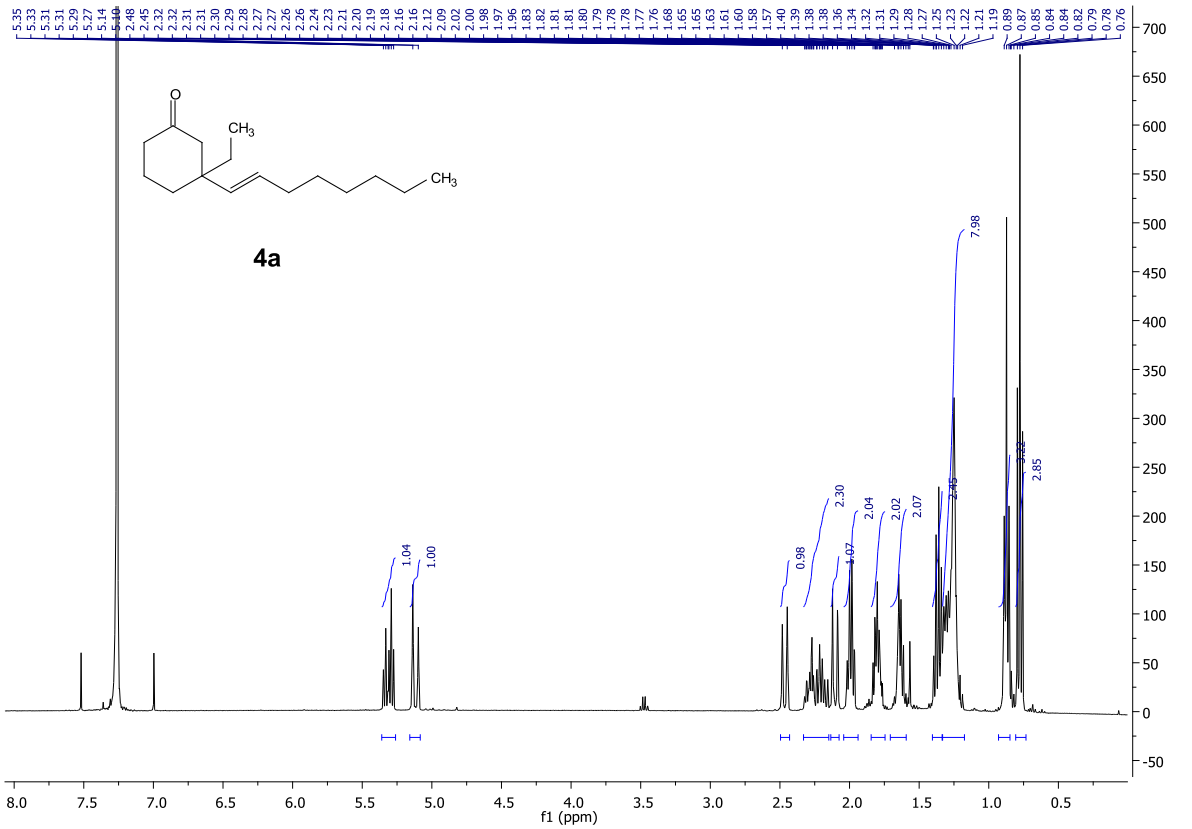

3b
f1 (ppm)

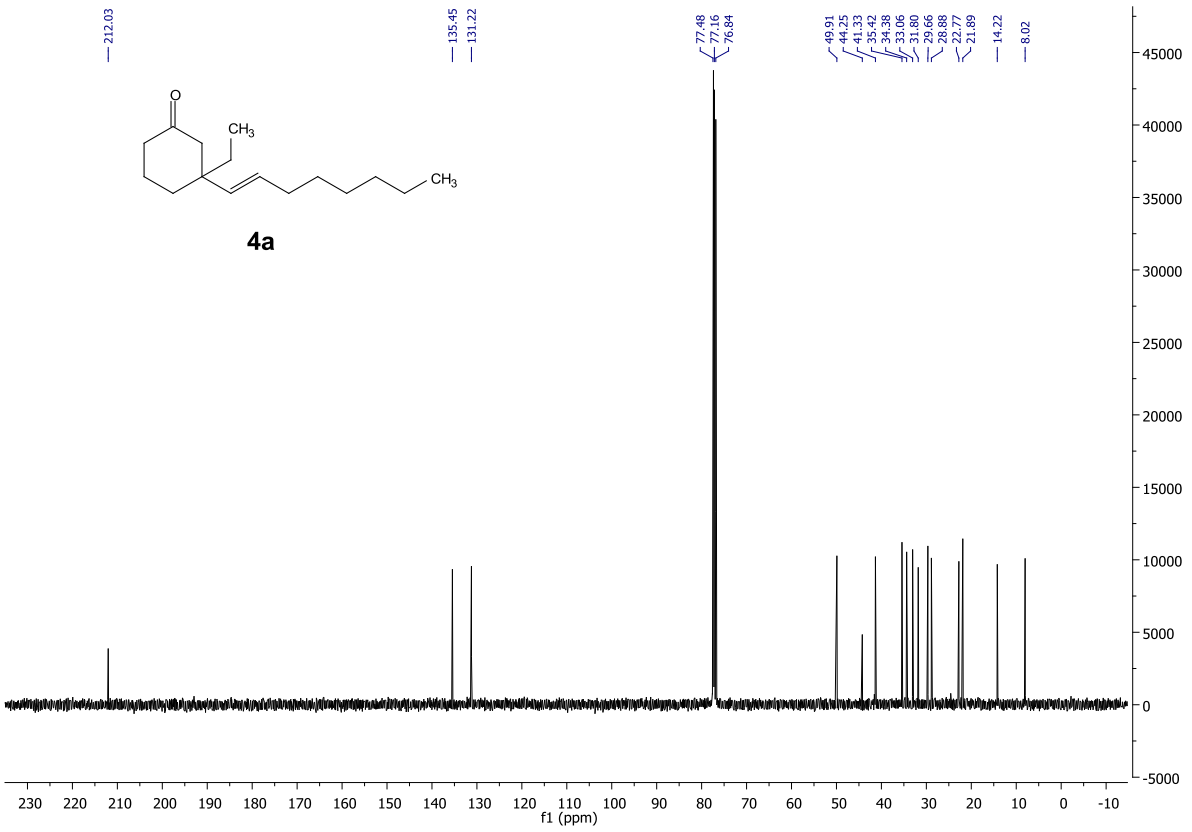

6.10
6.06
5.54
5.50
4.93
2.49
2.34
2.32
2.30
2.28
2.27
2.26
2.25
2.24
2.22
2.18
1.87
1.86
1.85
1.84
1.83
1.81
1.80
3.25
3.01
2.02
2.01
2.05
1.32
1.19
1.00
1.02
1.01
1.03
O
CH3
CH3
CH2
3c
f1 (ppm)

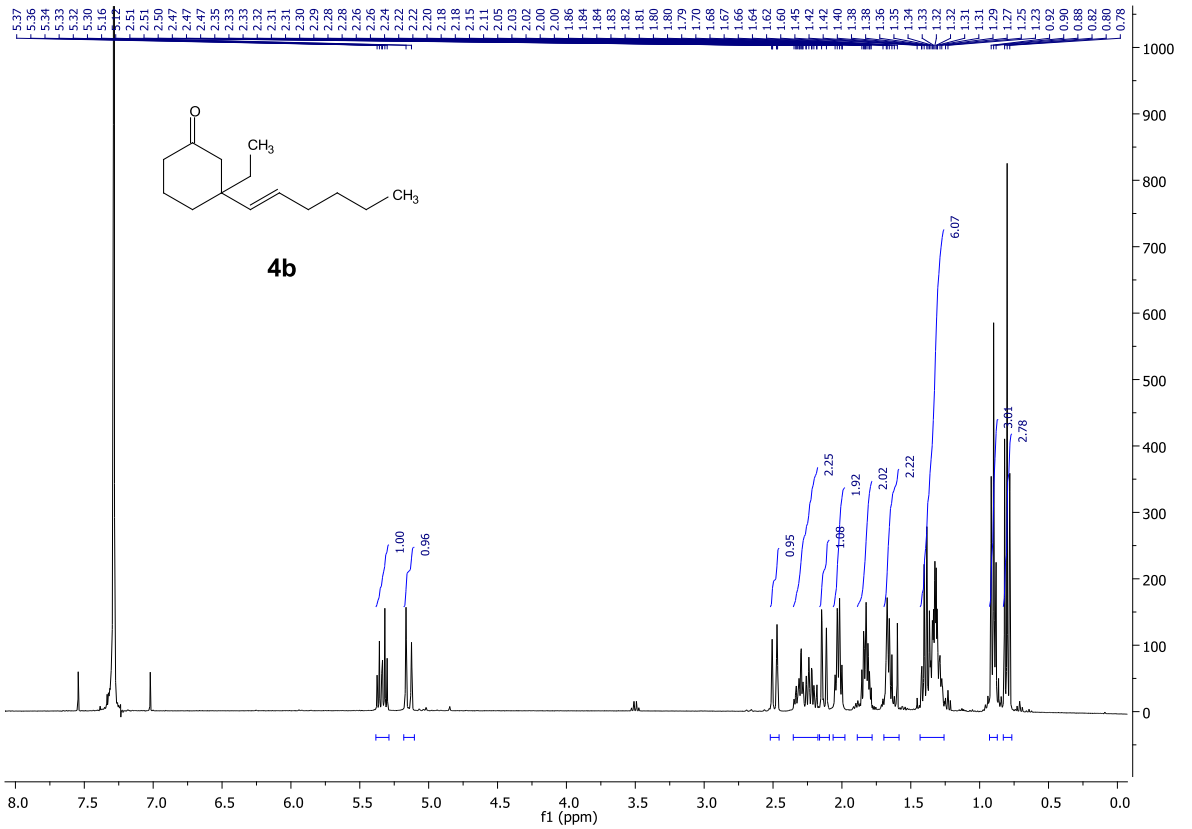

211.36
141.76
137.55
130.74
116.05
77.48
77.16
76.84
52.46
41.06
41.00
37.18
27.74
22.33
18.74
O
CH3
CH3
CH2
3c
f1 (ppm)

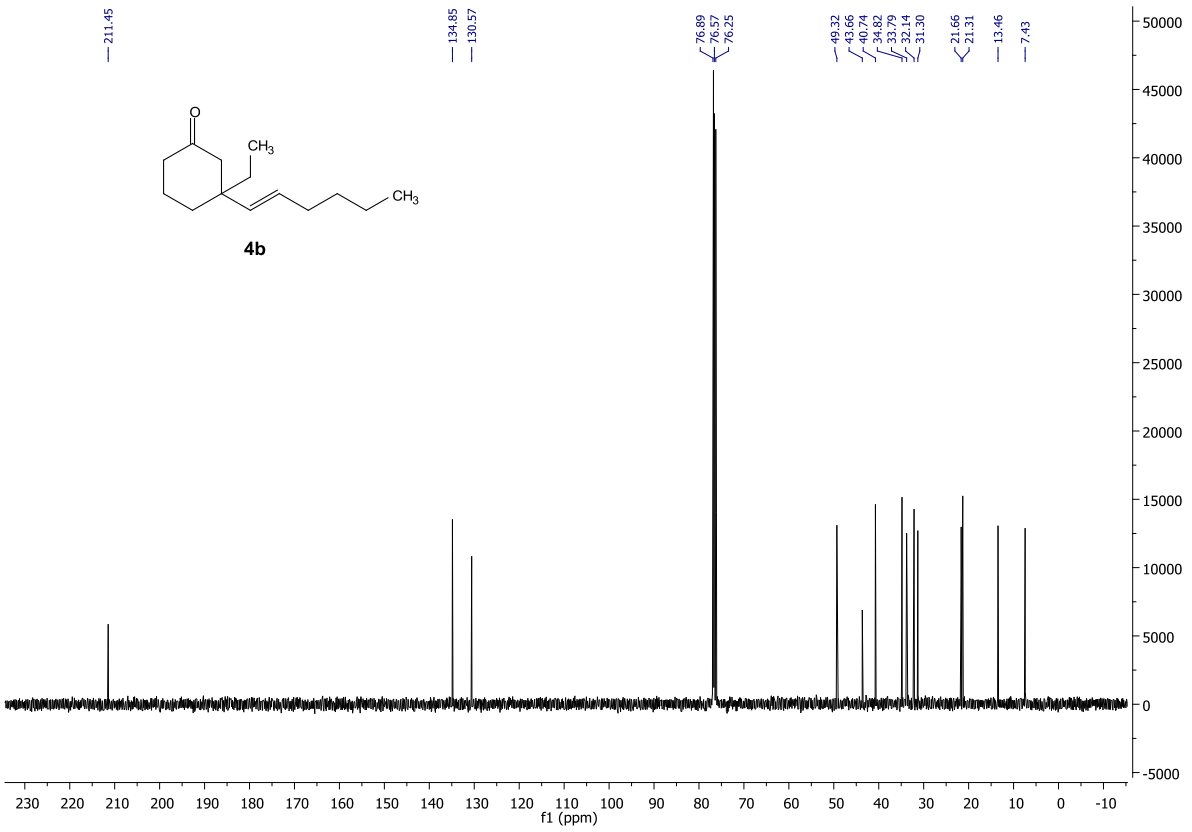

7.26
5.40
5.36
4.89
4.87
4.85
4.83
2.39
2.39
2.38
2.36
2.35
2.31
2.29
2.29
2.27
2.25
2.24
2.24
2.22
2.22
2.20
2.20
2.19
2.18
2.17
2.17
2.15
2.14
2.11
1.84
1.83
1.82
1.81
1.66
1.32
1.30
1.25
1.24
1.03
0.96
0.66
0.66
0.64
0.31
0.31
0.30
0.30
O
CH3
3g
1.00
1.01
1.09
1.10
2.47
2.38
1.36
1.19
1.21
3.12
2.00
2.01
2500
2000
1500
1000
500
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

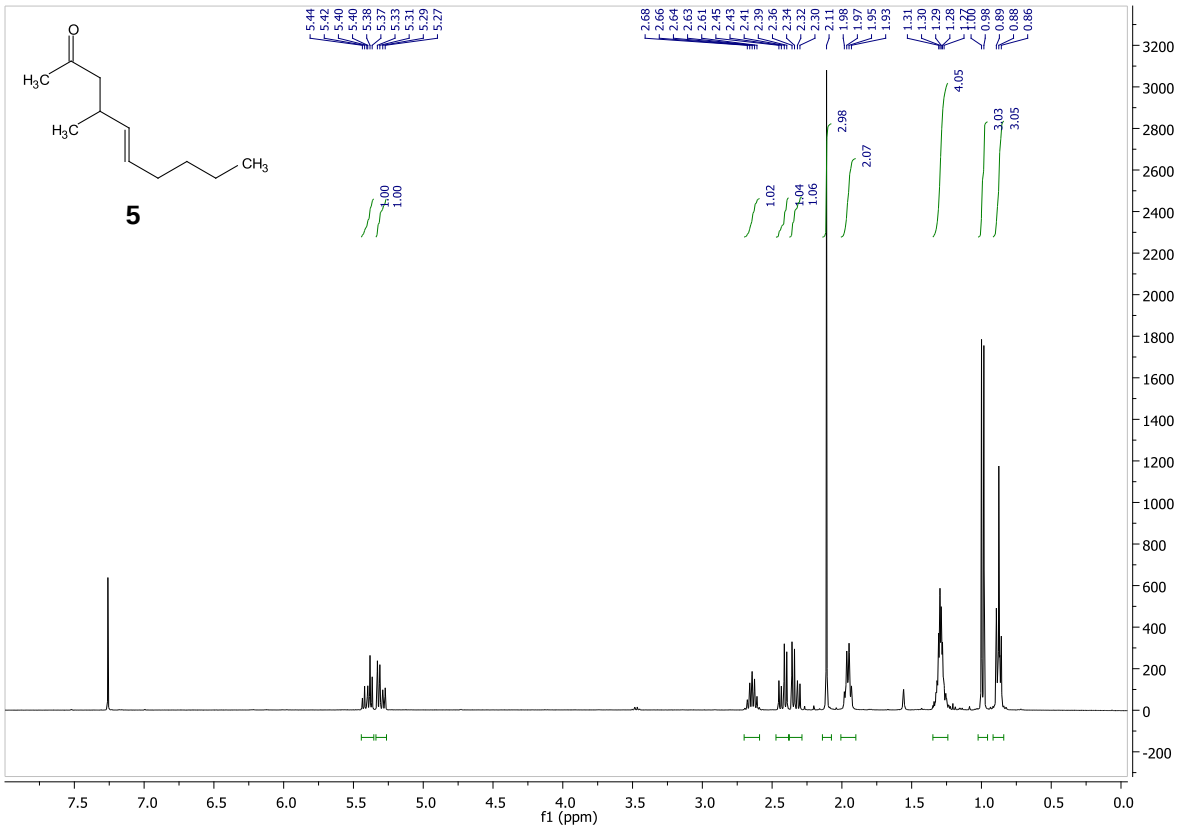

211.80
135.35
132.32
52.53
41.02
40.79
37.26
28.01
22.27
13.97
6.72
O
CH3
3g
3E+05
3E+05
2E+05
2E+05
2E+05
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
80000
60000
40000
20000
0
-20000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

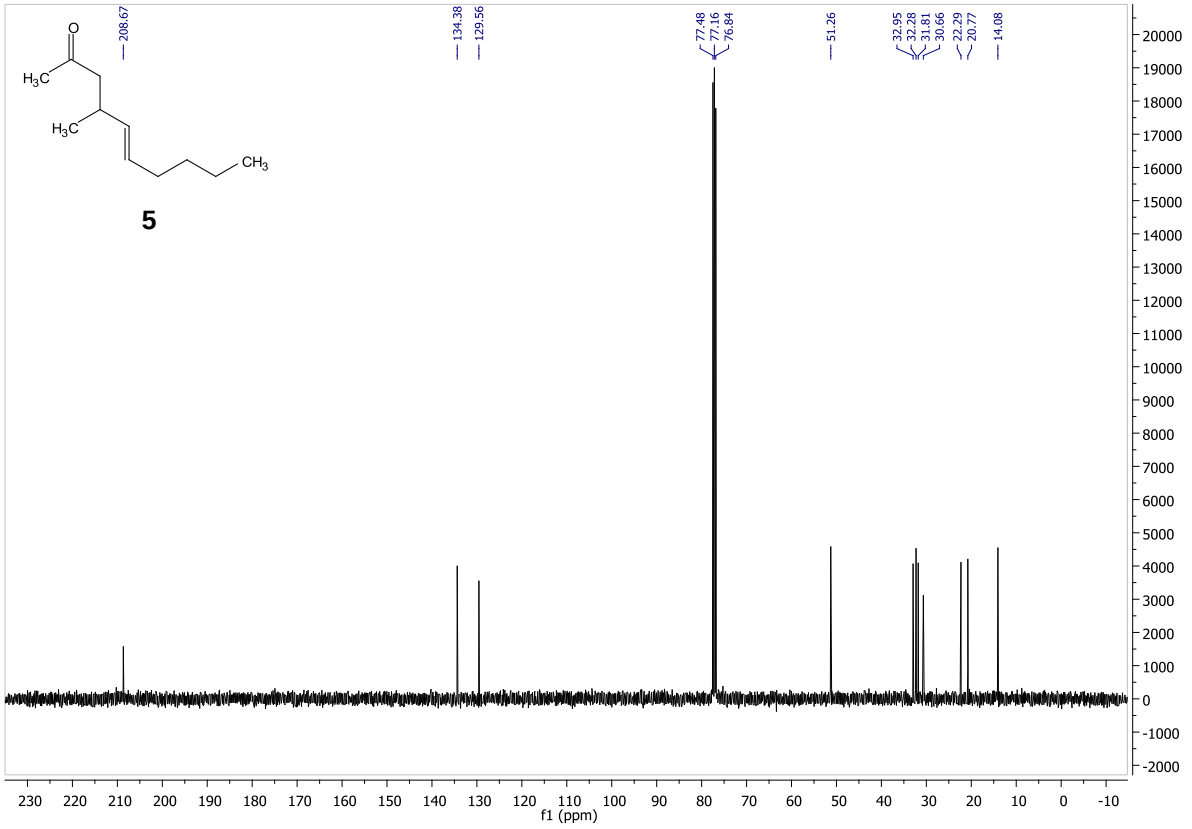

O
CH3
CH3
4a
1.04
1.00
0.98
2.30
1.07
2.04
2.02
2.07
2.45
7.98
2.85
f1 (ppm)

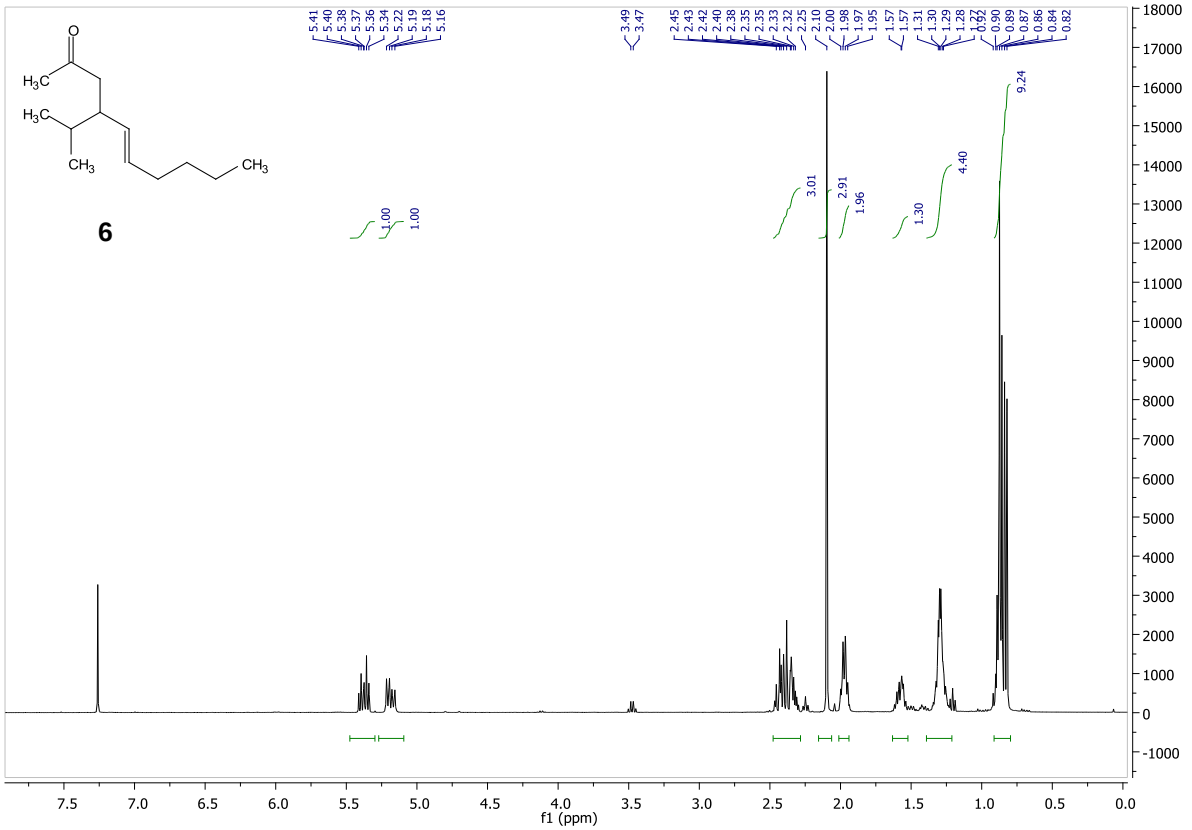

212.03
135.45
131.22
77.48
77.16
76.84
49.91
44.25
41.33
35.42
34.38
33.06
31.80
29.66
28.88
22.77
21.89
14.22
8.02
O
CH3
CH3
4a
f1 (ppm)

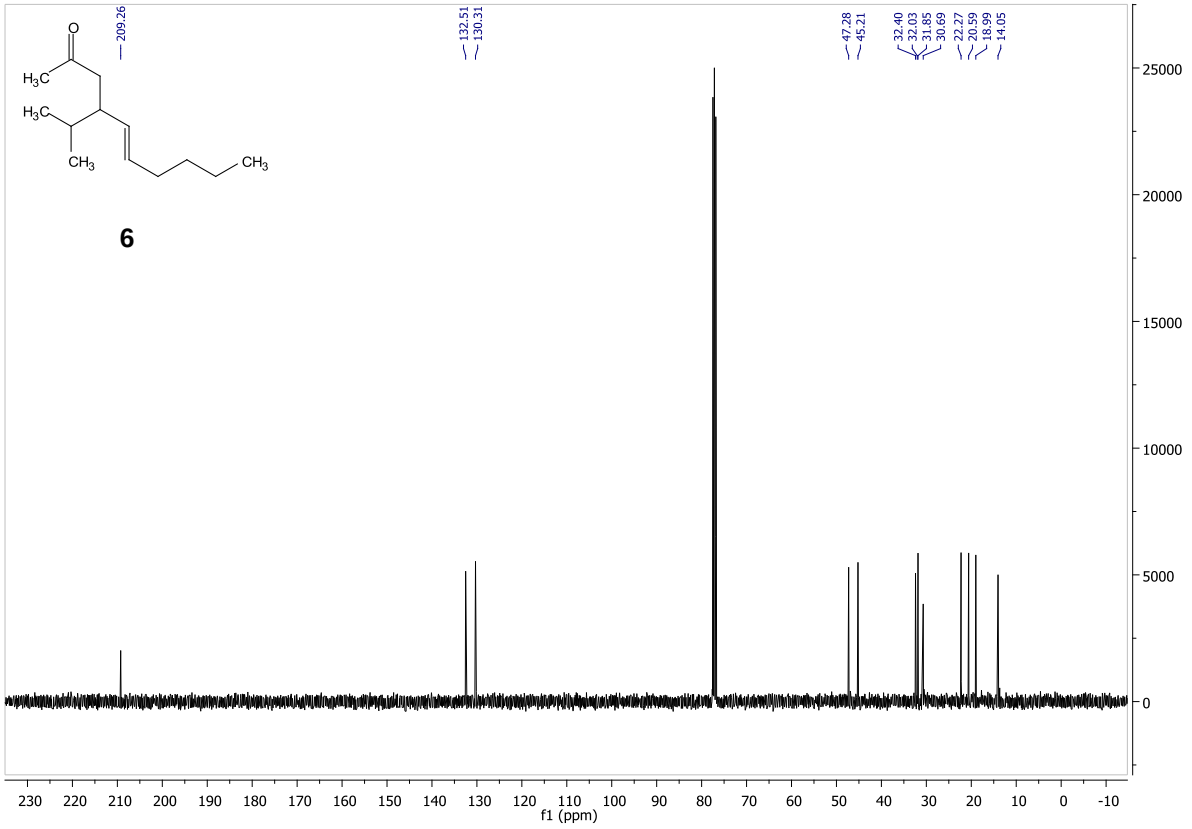

4b
f1 (ppm)

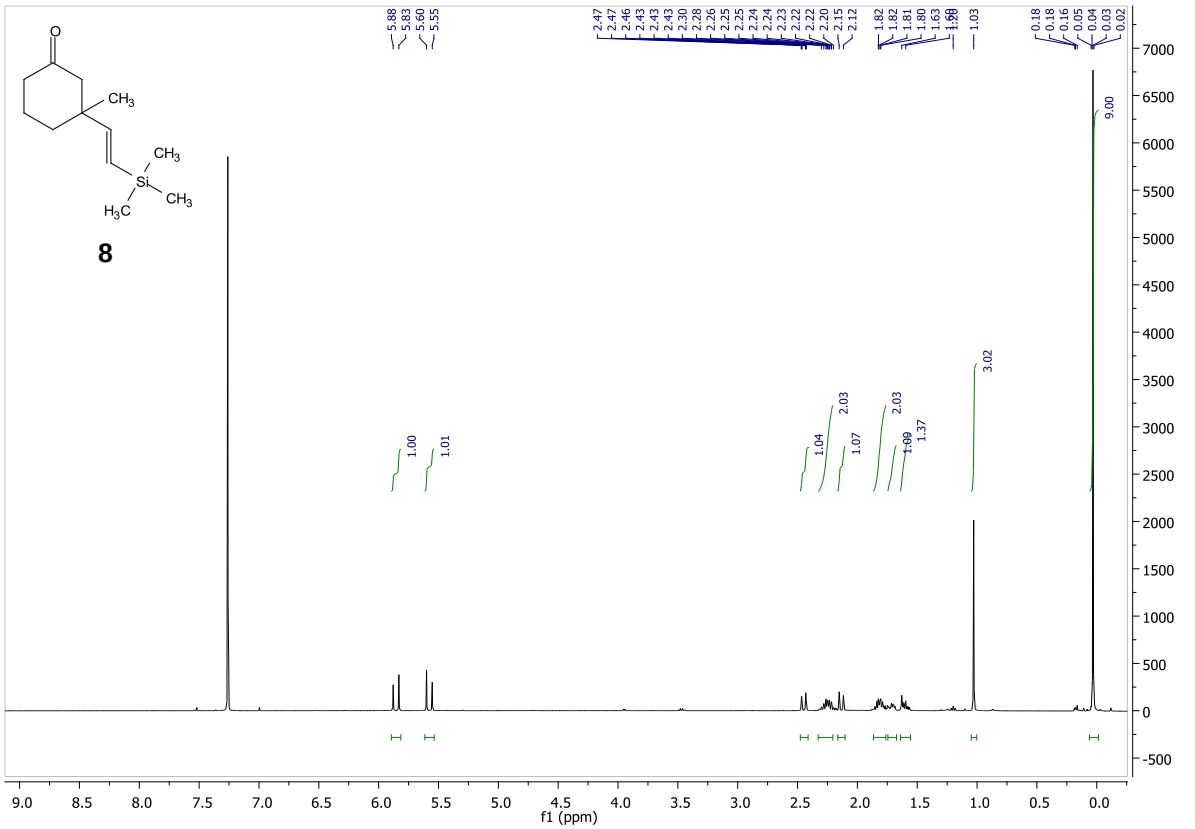

4b
f1 (ppm)

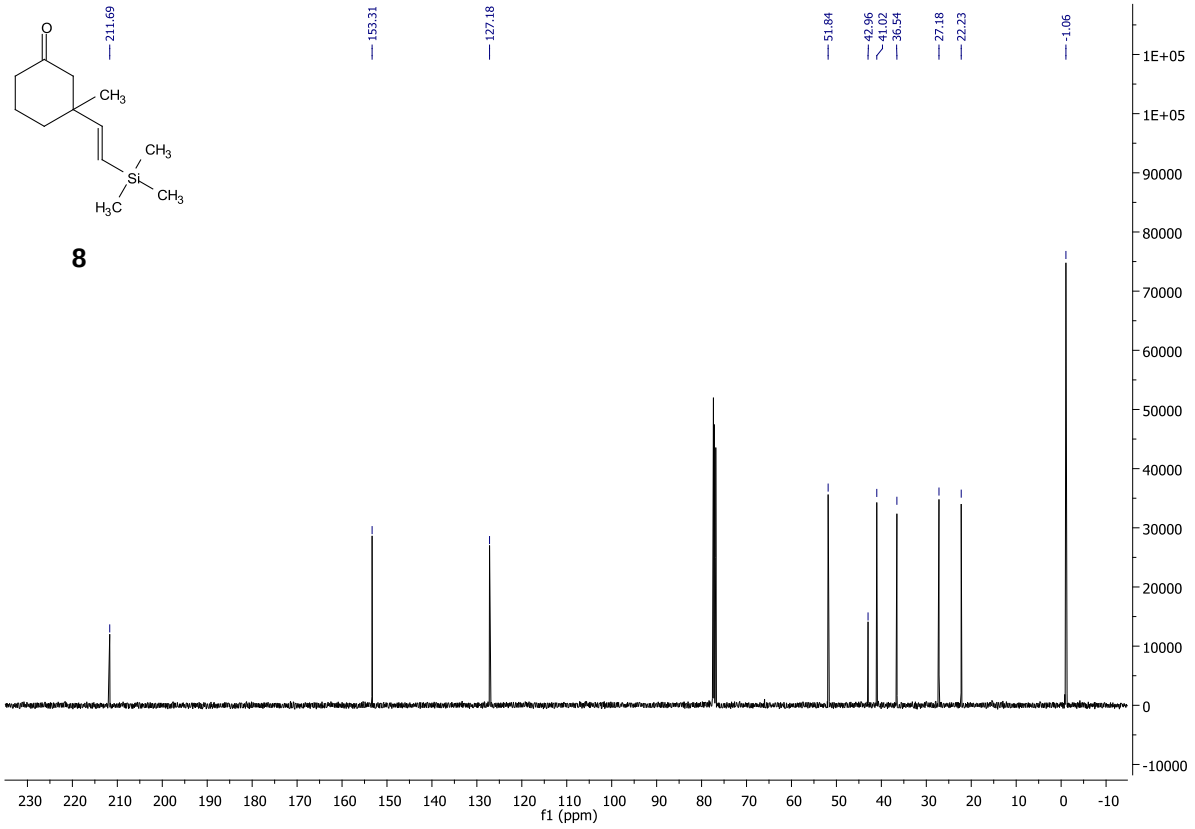

5
f1 (ppm)

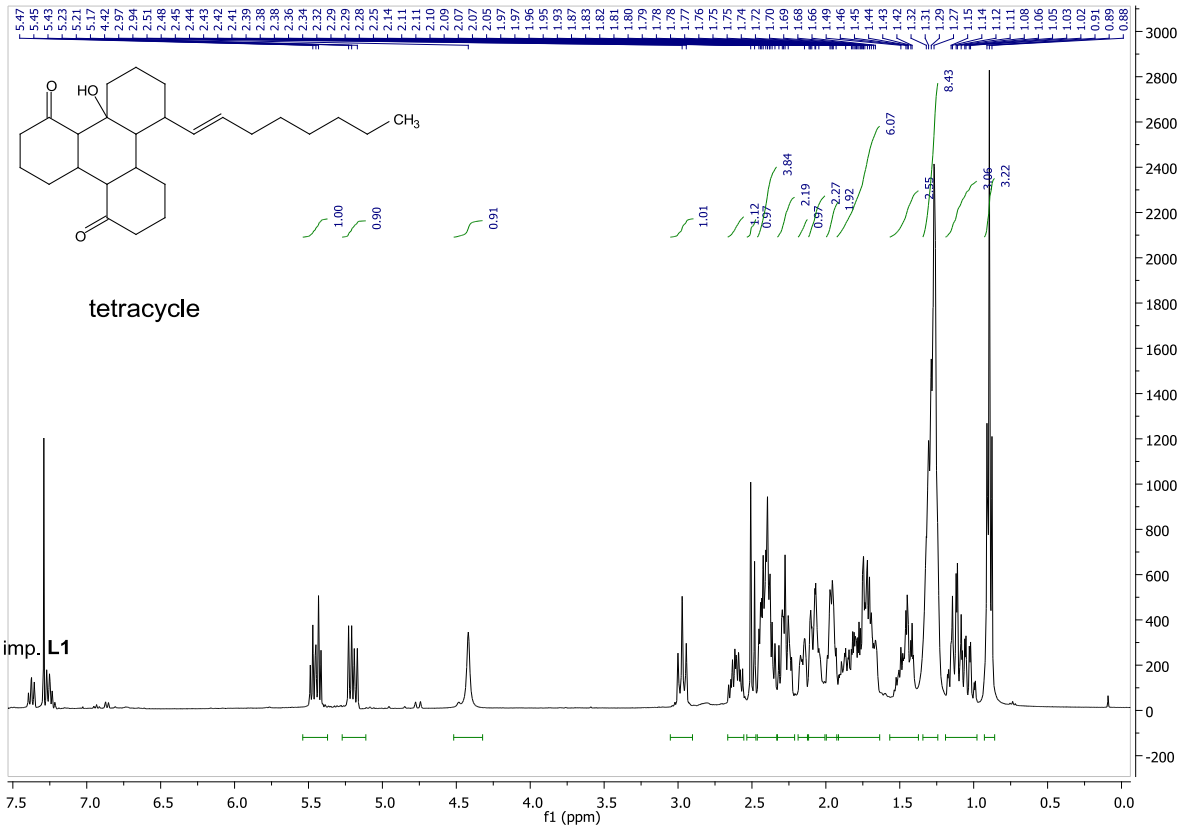

5
f1 (ppm)

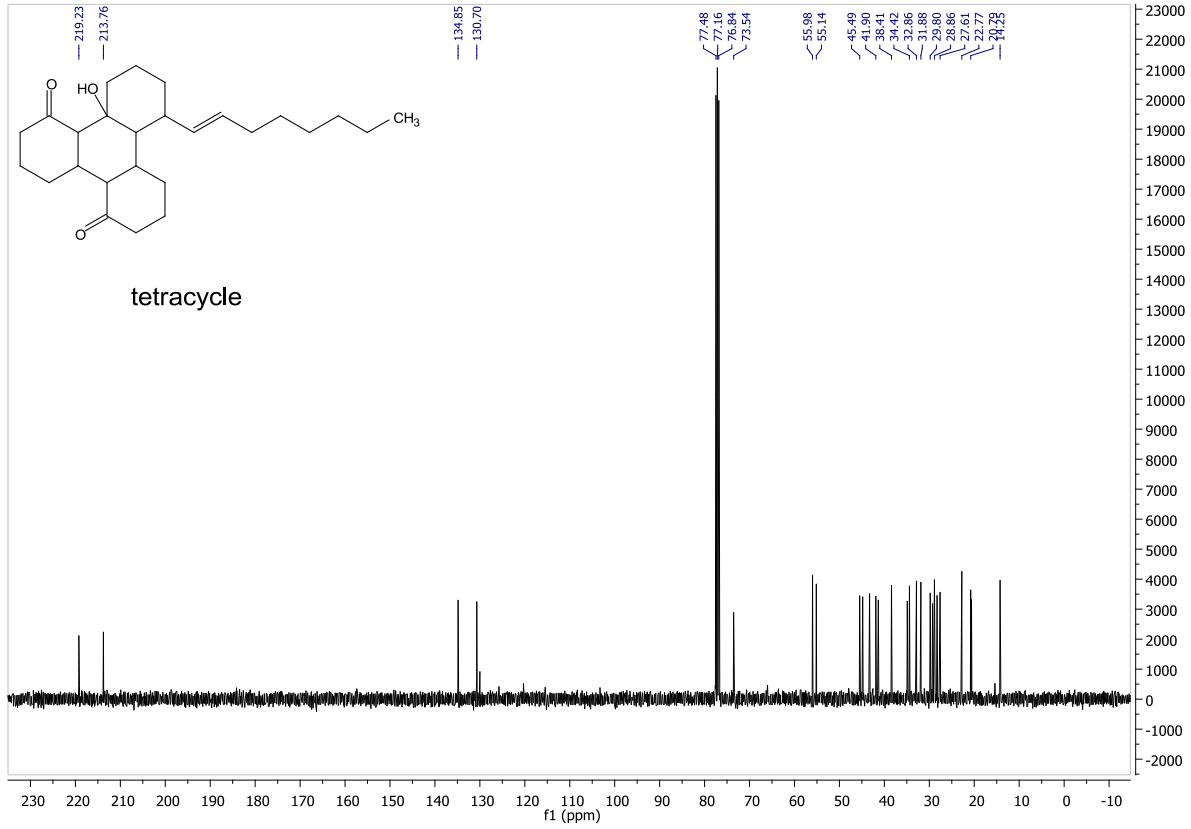

6
f1 (ppm)


6
f1 (ppm)


8
f1 (ppm)


8
f1 (ppm)


tetracycle
imp. L1
f1 (ppm)


tetracycle
f1 (ppm)

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