Supplementary Material

Selective catalytic synthesis of new terpenic chlorides using NaDCC as an eco-friendly and highly stable FAC agent

Salim Adam Labyad[1], Ayoub Abdelkader Mekkaoui[2]*, Mouhsine Laayati[1,2], Hamza Orfi[1], Larbi El Firdoussi[2], Soufiane El Houssame[1]*

[1] Laboratoire des Sciences des Matériaux, Mathématiques et Environnement, Université Sultan Moulay Slimane, Faculté Polydisciplinaire de Khouribga, BP 145, Khouribga 25000, Morocco.

[2] Laboratoire de Chimie Moléculaire, Equipe de Chimie de Coordination et de Catalyse, Département de Chimie, Faculté des Sciences Semlalia, BP 2390, Marrakech 40001, Morocco.

* Corresponding authors. E-mail addresses: mekk.ayoub@gmail.com (A. A. Mekkaoui) hous_soufiane@hotmail.com (S. El Houssame)

List of supplementary materials:

- Spectral data of terpenic chlorinated compounds.
- NMR and MS spectra of terpenic chlorinated compounds.

❖ Spectral data of terpenic chlorinated compounds

Carvone monochloride b

^{1}H NMR (300 MHz) d 6.70 (m, 1H, =CH), 5.20 (s, 1H, =CH_2), 4.99 (s, 1H, =CH_2), 4.03 (s, 2H, –CH_2Cl), 2.91 (m, 1H, CH), 2.53 (m, 2H, CH_2), 2.27 (m, 2H, CH_2), 1.75 (s, 3H, –CH_3).
^{13}C NMR (75 MHz) d 198.94 (C=O), 146.57 (=C–), 144.11 (=CH–), 135.6 (=C–), 115.16 (=CH_2), 46.95 (CH_2Cl), 43.02 (CH_2), 37.81 (CH), 31.38 (CH_2), 15.67 (CH_3).
MS (EI): m/z = 184.0176 $[M]^+$.

Carvone dichloride c

^{1}H NMR (300 MHz) d 6.75 (m, 1H, =CH), 3.53 (m, 2H, –CH_2Cl), 2.61(m, 2H, CH_2), 2.48 (m, 1H, CH), 2.32 (m, 2H, CH_2), 1.75 (s, 3H, CH_3), 1.24 (s, 3H, CH_3).
^{13}C NMR (75 MHz) d 199.60 (C=O), 144.56 (=CH–), 135.20 (=C–), 72.79 (–C–Cl), 52.29 (CH_2Cl), 41.57 (CH), 39.23 (CH_2), 26.26 (CH_2), 21.82 (CH_3), 15.55 (CH_3).
MS (EI): m/z = 220.0758 $[M]^+$.

Carvone vinyl allyl dichloride d

^{1}H NMR (300 MHz) d 6.73 (m, 1H, =CH), 6.12 (s, 1H, =CHCl), 4.24 (m, 2H, –CH_2Cl), 3.01 (m 1H, CH), 2.56 (m, 1H, CH_2), 2.37 (m, 1H, CH_2), 1.76 (s, 3H, CH_3), 1.17 (m, 2H, CH_2).
^{13}C NMR (75 MHz) d 197.97 (C=O), 143.70 (=CH–), 139.70 (=C–), 135.77 (=C–), 119.94 (=CHCl), 42.65 (–CH2Cl), 39.57 (CH2), 39.26 (CH), 31.15 (CH2), 15.63 (CH3).
MS (EI): m/z = 219.061 $[M]^+$.

Carvone trichloride e

^{1}H NMR (300 MHz) d 6.55 (m, 1H, =CH_2), 3.44–3.97 (m, 4H, –CH_2Cl), 2.10–2.62 (m, 4H), 1.44–1.70 (m, 4H).
13C NMR (75 MHz) d 197.44 (C=O), 143.04 (=CH–), 135.54 (=C–), 73.22 (–C–Cl), 50.80 (CH_2Cl), 49.89 (CH_2Cl), 41.04 (CH_2), 39.32 (–CH), 29.69 (CH_2), 15.54 (CH_3).
MS (EI): m/z = 254.048 $[M]^+$.

Limonene oxide monochloride g

^{1}H NMR (300 MHz) d 4.96 (s, 1H, =CH_2), 4.95 (s, 1H, =CH_2), 4.02 (s, 2H, –CH_2Cl), 2.99 (m, 1H, –O–CH–), 2.36 (m, 1H, CH), 1.35–1.93 (m, 6H), 1.30 (s, 3H, –CH_3).
^{13}C NMR (75 MHz) d 148.76 (=C–), 113.65 (=CH_2), 58.97 (O–CH), 57.12 (O–C), 47.37 (CH_2Cl), 32.42 (CH), 30.70 (CH_2), 28.46 (CH_2), 24.66 (CH_2), 22.96 (CH_3).
MS (EI): m/z = 185.0668 $[M]^+$.

Limonene oxide dichloride h

^{1}H NMR (300 MHz) d 3.55 (s, 2H, –CH_2Cl), 3.02 (m, 1H, –O–CH–), 2.05 (m, 1H, CH), 2.01–1.50 (m, 6H), 1.33 (s, 3H, –CH_3), 1.13 (s, 3H, –CH_3).
^{13}C NMR (75 MHz) d 73.37 (–C–Cl), 58.78 (O–CH), 57.66 (O–C), 53.23 (CH_2Cl), 39.78 (CH), 30.58 (CH_2), 24.89 (CH_2), 22.85 (CH_3), 22.96 (CH_3), 20.45 (CH_2).
MS (EI): m/z = 220.9909 $[M]^+$.

Nootkatone monochloride j

^{1}H NMR (300 MHz) d 5.66 (m, 1H, =CH), 5.09 (s, 1H, =CH_2), 4.90 (s, 1H, =CH_2), 4.01 (s, 2H, –CH_2Cl), 2.47 (m, 2H, CH_2), 2.29 (m, 1H, CH), 2.15 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 1.27 (m, 1H, CH), 1.04–1.97 (m, 2H, CH_2), 1.04 (s, 3H, –CH_3), 0.87 (d, 3H, –CH_3).

^{13}C NMR (75 MHz) d 199.08 (C=O), 169.58 (=C–), 148.67 (=C–), 124.74 (=CH–), 113.80 (=CH_2), 47.70 (CH_2Cl), 44.17 (CH_2), 41.95 (CH_2), 40.30 (CH), 39.35 (–C–), 35.72 (CH), 32.85 (CH_2), 31.91 (CH_2), 16.67 (CH_3), 14.87 (CH_3).
MS (EI): m/z = 252.107 $[M]^+$.

Nootkatone vinyl allyl dichloride <u>k</u>

^1H NMR (300 MHz) d 6.07 (s, 1H, =CHCl), 5.77 (S, 1H, =CH), 4.26 (m, 2H, –CH_2Cl), 2.60 (m, 2H, CH_2), 2.30 (m, 2H, CH_2), 2.12 (m, 1H, CH), 2.00 (m, 2H, CH_2) 1.41 (m, 1H, CH), 1.24 (m, 2H, CH_2), 1.13 (s, 3H, CH_3), 0.96 (m, 3H, CH_3).
^{13}C NMR (75 MHz) d 199.25 (C=O), 168.76 (=C–), 141.67 (=C–), 125.10 (=CH–), 118.79 (=CHCl), 43.87 (CH_2Cl), 41.97 (CH_2), 40.38 (CH_2), 40.32 (–C–), 39.41 (–CH), 37.42 (–CH), 32.68 (CH_2), 31.59 (CH_2), 16.74 (CH_3), 14.89 (CH_3).
MS (EI): m/z = 286.088 $[M]^+$.

Nootkatone dichloride <u>l</u>

^1H NMR (300 MHz) d 5.76 (m, 1H, =CH), 3.57 (m, 1H, CH_2Cl), 3.64 (m, 1H, CH_2Cl), 2.40 (m, 1H, CH), 2.23–2.50 (m, 2H, CH_2), 2.06 (m, 2H, CH_2), 1.99–2.29 (m, 2H, CH_2), 1.87–2.12 (m, 2H, CH_2), 1.25 (m, 1H, CH), 1.19 (s, 3H, –CH_3), 1.10 (m, 3H, –CH_3), 0.98 (m, 3H, –CH_3).
^{13}C NMR (75 MHz) d 199.50 (C=O), 170.08 (=C–), 124.62 (=CH–), 73.33 (–CCl), 53.47 (CH_2Cl), 42.04 (CH_2), 40.53 (CH), 39.96 (CH), 39.68 (CH), 32.72 (CH_2), 27.70 (CH_2), 26.67 (CH_2), 21.22 (CH_3), 16.75 (CH_3), 14.96 (CH_3).
MS (EI): m/z = 288.097 $[M]^+$.

Pulegone monochloride <u>n</u>

^1H NMR (300 MHz) d 5.15 (s, 1H, =CH_2), 5.08 (s, 1H, =CH_2), 2.51–2.82 (m, 2H, CH_2), 1.99–2.31 (m, 1H, CH), 1.88–2.19 (m, 2H, CH_2), 1.79 (m, 3H, CH_3), 1.10–1.52 (m, 2H, CH_2), 0.97 (m, 3H, CH_3).
^{13}C NMR (75 MHz) d 203.90 (C=O), 143.44 (=C–), 115.29 (=CH_2), 76.09 (–C–Cl), 45.56 (CH_2), 37.97 (CH_2), 34.42 (CH), 29.64 (CH_2), 21.50 (CH_3), 20.61 (CH_3).
MS (EI): m/z = 187.099 $[M]^+$.

Pulegone monochloride <u>n</u>'

1H NMR (300 MHz) d 5.20 (s, 1H, =CH_2), 5.14 (s, 1H, =CH_2), 2.35–2.80 (m, 2H, CH_2), 2.30 (m, 2H, CH_2), 1.96 (m, 1H, CH), 1.90 (m, 3H, –CH_3), 1.84 (m, 2H, CH_2), 1.06 (d, 3H, –CH_3).
^{13}C NMR (75 MHz) d 203.37 (C=O), 141.35 (=C–), 115.22 (=CH_2), 77.96 (–C–Cl), 46.76 (CH_2), 38.46 (CH_2), 33.87 (CH), 30.53 (CH_2), 20.58 (CH_3), 18.02 (CH_3).
MS (EI): m/z = 187.093 $[M]^+$.

Pulegone vinyl allyl dichloride <u>o</u>

^1H NMR (300 MHz) d 5.71 (s, 1H, =CH_2), 5.57 (s, 1H, =CH_2), 4.22 (m, 2H, –CH_2Cl), 2.84 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 1.83–2.00 (m, 3H), 1.06 (m, 3H, CH_3).
^{13}C NMR (75 MHz,) d 203.53 (C=O), 144.26 (=C–), 119.82 (=CH_2), 74.28(–C–Cl), 45.23(CH_2), 44.42(–CH_2Cl), 38.29 (CH_2), 34.57 (-CH), 29.43 (CH_2), 21.81 (CH_3).
MS (EI): m/z = 221.055 $[M]^+$.

Pulegone vinyl allyl dichloride <u>o</u>'

^1H NMR (300 MHz) d 5.72 (s, 1H, =CH_2), 5.53 (s, 1H, =CH_2)), 4.05–4.25 (m, 2H, –CH_2Cl), 2.68–2.89 (m, 2H, CH_2), 2.12–2.44 (m, 2H, CH_2), 1.94 (m, 1H, CH), 1.19–1.67 (m, 2H, CH_2), 0.91–1.04 (m, 3H, CH_3).
^{13}C NMR (75 MHz,) d 202.49 (C=O), 142.86 (=C–), 119.97 (=CH_2), 77.37 (–C–Cl), 47.54 (CH_2), 43.48 (–CH_2Cl), 39.03 (CH_2), 34.48 (–CH), 31.08 (CH_2), 21.10 (CH_3).

MS (EI): m/z = 221.054 $[M]^+$.

Perillyl aldehyde monochloride q

^{1}H NMR (300 MHz) d 9.43 (s, 1H, HC=O), 6.83 (m, 1H, =CH), 5.23 (s, 1H, =CH_2), 5.02 (s, 1H, =CH_2), 4.09 (s, 2H, –CH_2Cl), 2.02–2.53 (m, 2H, CH_2), 2.25 (m, 1H, CH), 1.42–1.72 (m, 2H, CH_2), 0.87–1.24 (m, 2H, –CH_2).
^{13}C NMR (75 MHz) d 193.74 (HC=O), 149.82 (=CH–), 148.25 (=C–), 141.15 (=C–), 114.20 (=CH_2), 47.56 (CH_2Cl), 36.21 (CH), 32.13 (CH_2), 26.51 (CH_2), 21.46 (CH_2).
MS (EI): m/z = 184.0441 $[M]^+$.

Perillyl aldehyde vinyl allyl dichloride r

^{1}H NMR (300 MHz) d 9.45 (s, 1H, HC=O), 6.82 (m, 1H, =CH), 6.12 (m, 1H, =CHCl), 4.29 (s, 2H, –CH_2Cl), 1.58–2.59 (m, 2H, CH_2), 1.99 (m, 1H, CH), 1.26 (m, 2H, –CH_2), 0.87–2.30 (m, 2H, CH_2).
^{13}C NMR (75 MHz) d 193.51 (HC=O), 148.79 (=CH–), 141.26 (=C–), 141.10 (=C–), 119.00 (=CHCl), 40.11 (CH_2Cl), 37.86 (CH), 31.81 (CH_2), 26.28 (CH_2), 21.40 (CH_2).
MS (EI): m/z = 218.0015 $[M]^+$.

Limona ketone Dichloride u

^{1}H NMR (300 MHz) d 4.00 (m, 1H, –CHCl), 2.78 (m, 1H, CH), 1.90–2.30 (m, 2H, CH_2), 2.12 (m, 3H), 1.70–1.84 (m, 2H, CH_2), 1.53–1.70 (m, 2H, CH_2), 1.30 (m, 3H, CH_3).
^{13}C NMR (75 MHz) d 210.96 (C=O), 71.54 (–C–Cl), 64.75(–CHCl), 44.65 (CH), 32.64 (CH_2), 31.81 (CH_2), 28.14 (CH_3), 27.29 (CH_3), 23.28 (CH_2).
MS (EI): m/z = 207.066 $[M]^+$.

Limona ketone epoxide v

^{1}H NMR (300 MHz) 2.97 (m, 1H), 2.22 (m, 1H), 2.08 (s, 3H, CH_3), 2.06–1.94 (m, 3H), 1.37–1.72 (m, 3H), 1.28 (s, 3H, CH_3).
^{13}C NMR (75 MHz) d 210.46 (C=O), 58.22 (O–CH), 57.51(O–C), 46.38 (CH), 29.71 (CH_2), 27.87 (CH_2), 26.03 (CH_3), 23.04 (CH_2), 21.78 (CH_3).
MS (EI): m/z = 154.0931 $[M]^+$.

❖ NMR and MS spectra of terpenic chlorinated compounds

➢ Derivatives of carvone **a**

- Carvone monochloride **b**

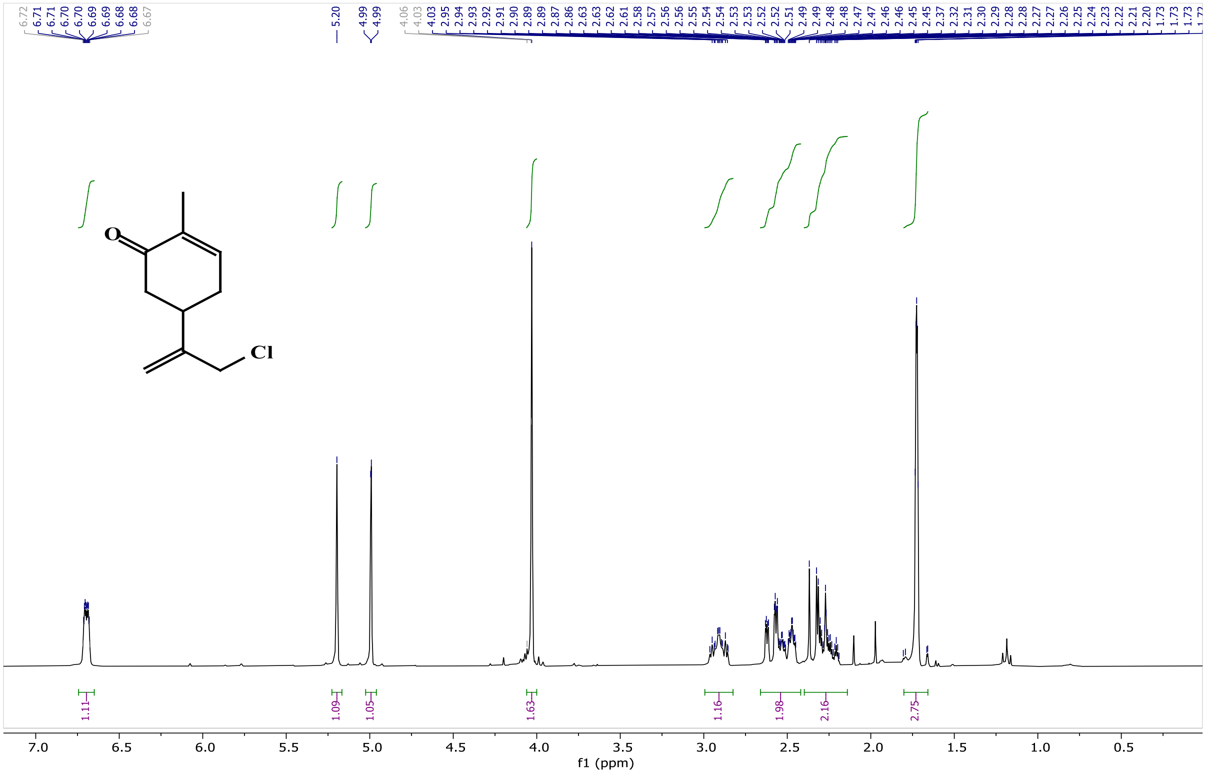

Figure S1: ^{1}H NMR spectrum of the carvone monochloride **b**.

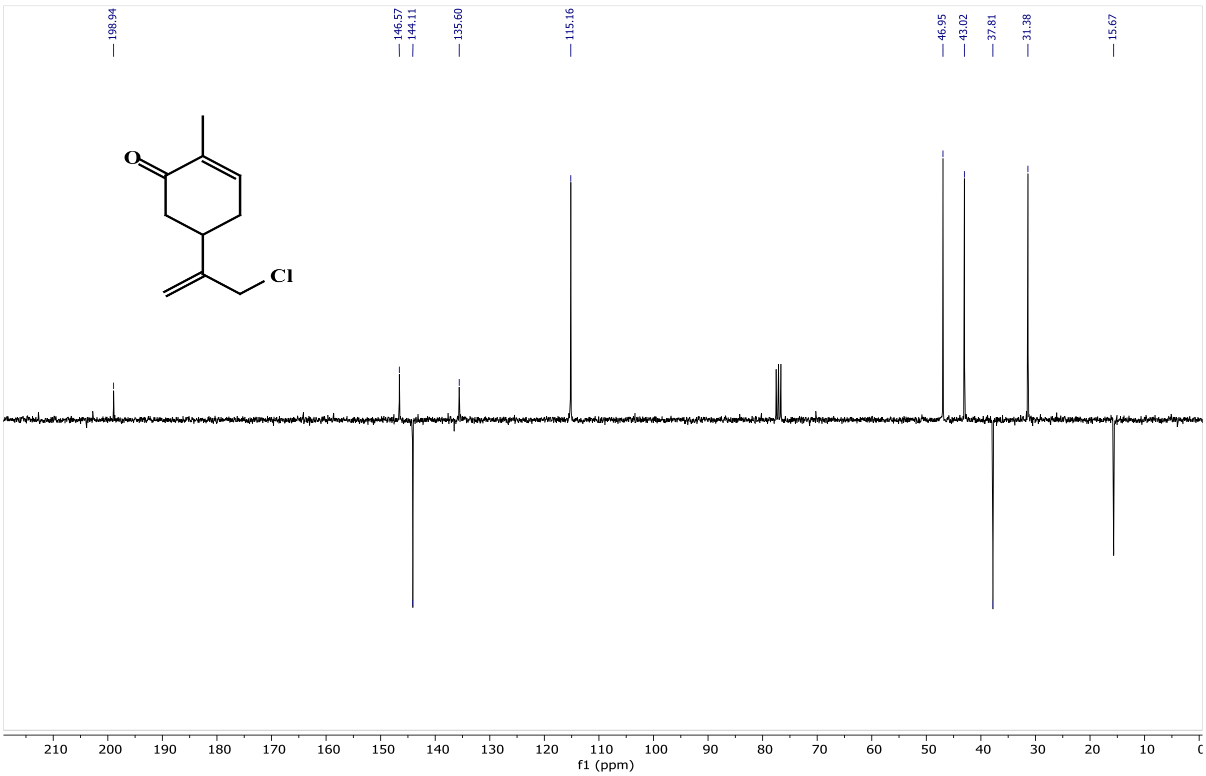

Figure S2: APT spectrum of the carvone monochloride **b**.

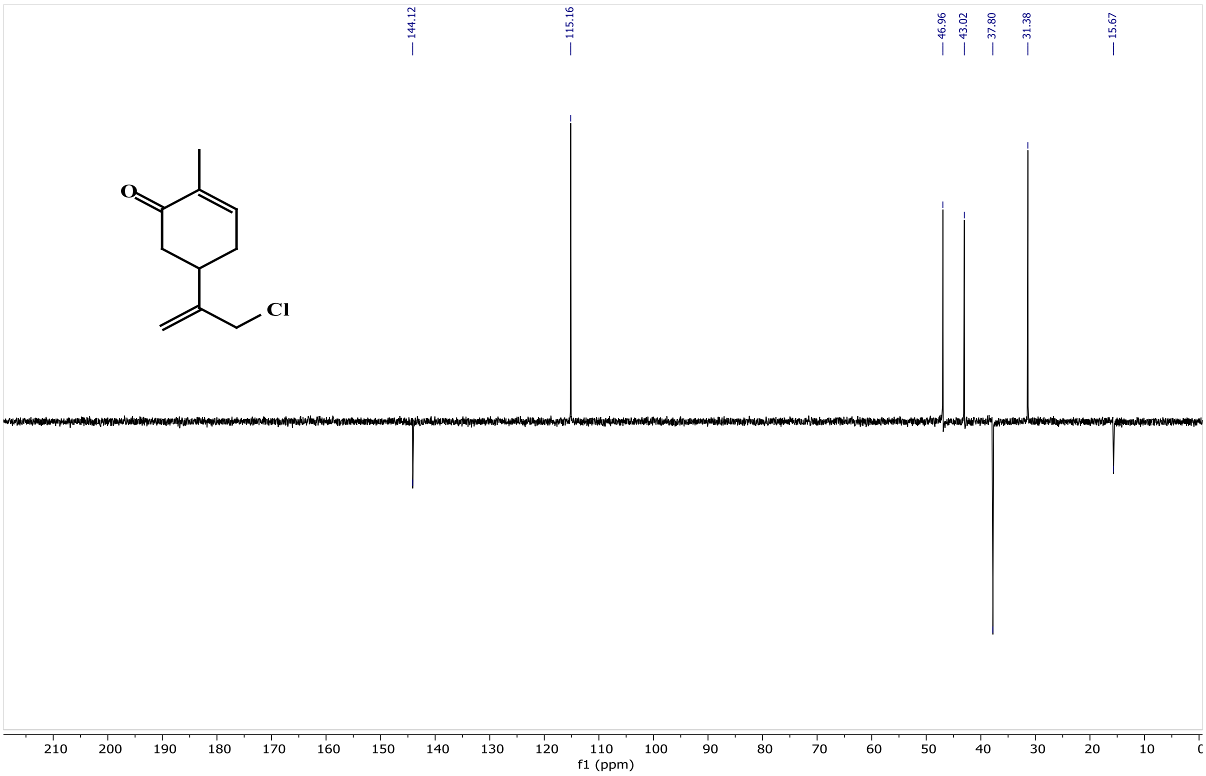

Figure S3: DEPT 135 spectrum of the carvone monochloride **b**.

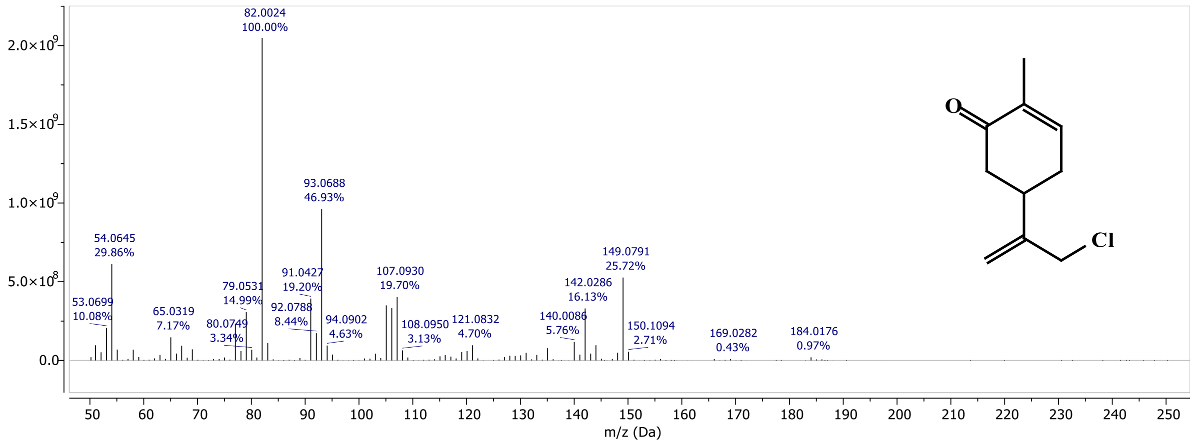

Figure S4: MS spectrum of the carvone monochloride **b**.

- Carvone dichloride **c**

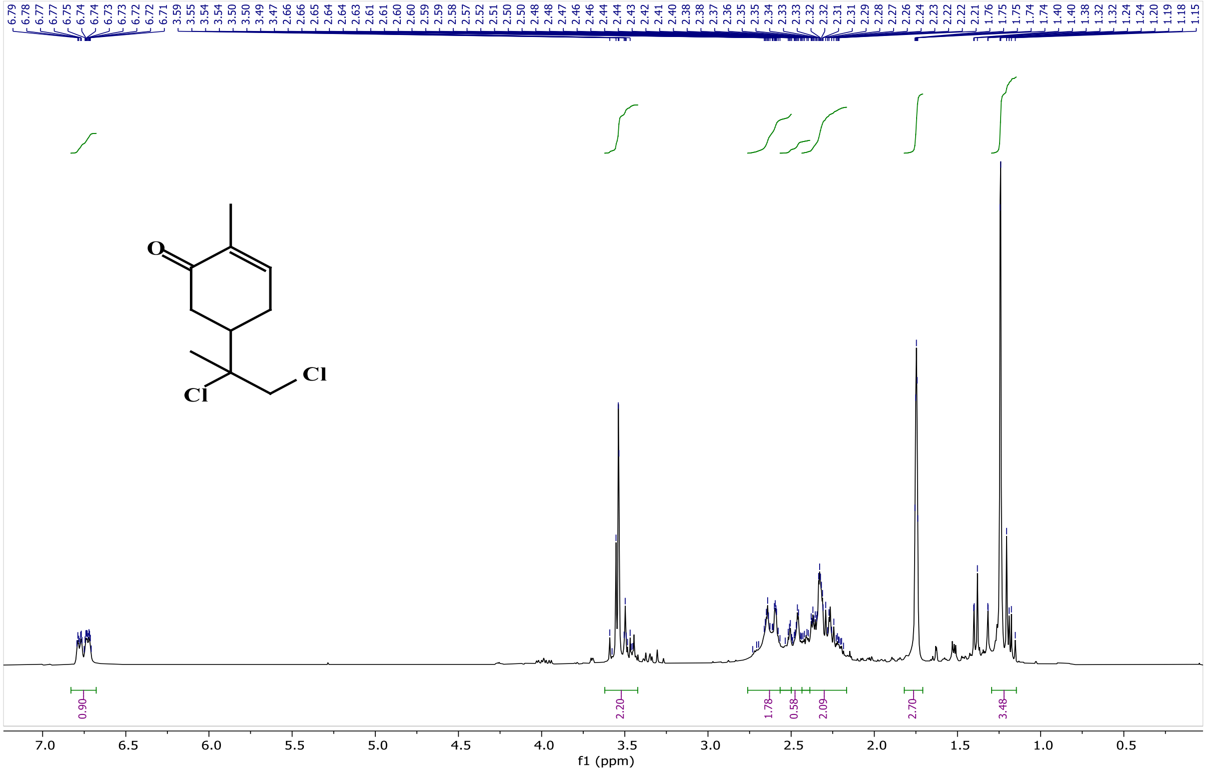

Figure S5: [1]H NMR spectrum of the carvone dichloride **c**.

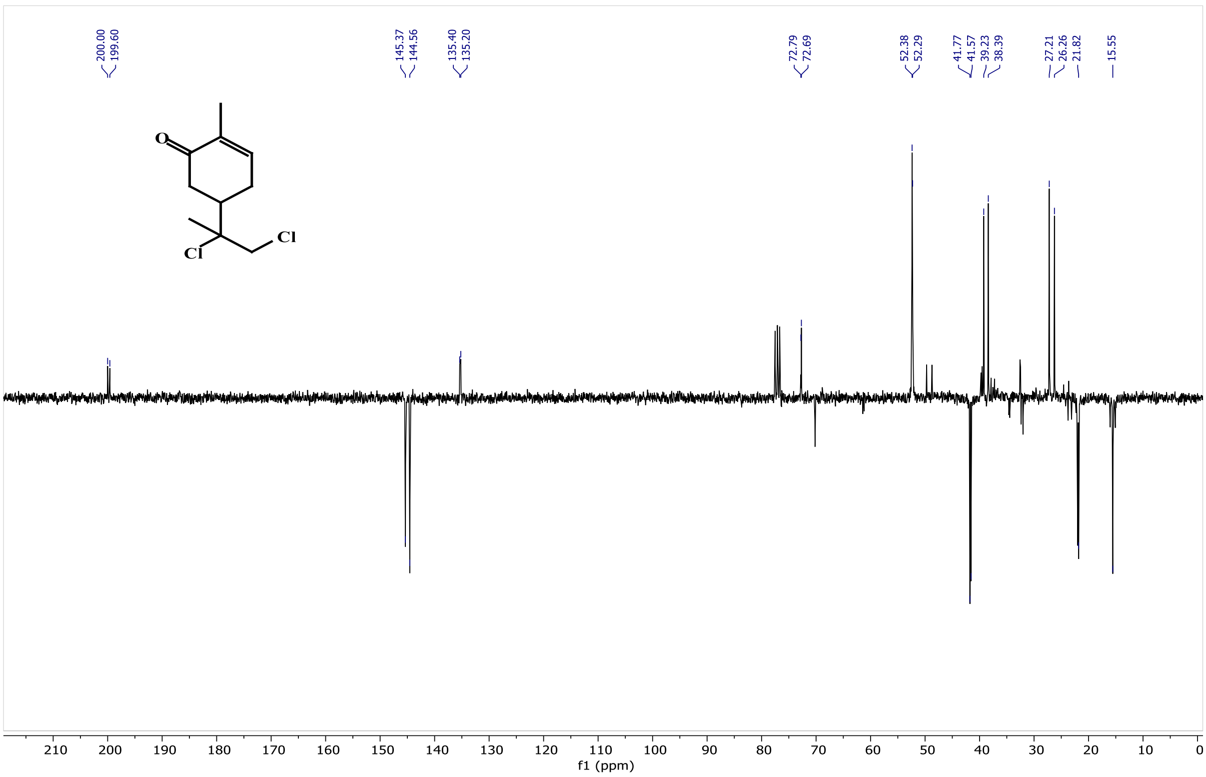

Figure S6: APT spectrum of the carvone dichloride **c**.

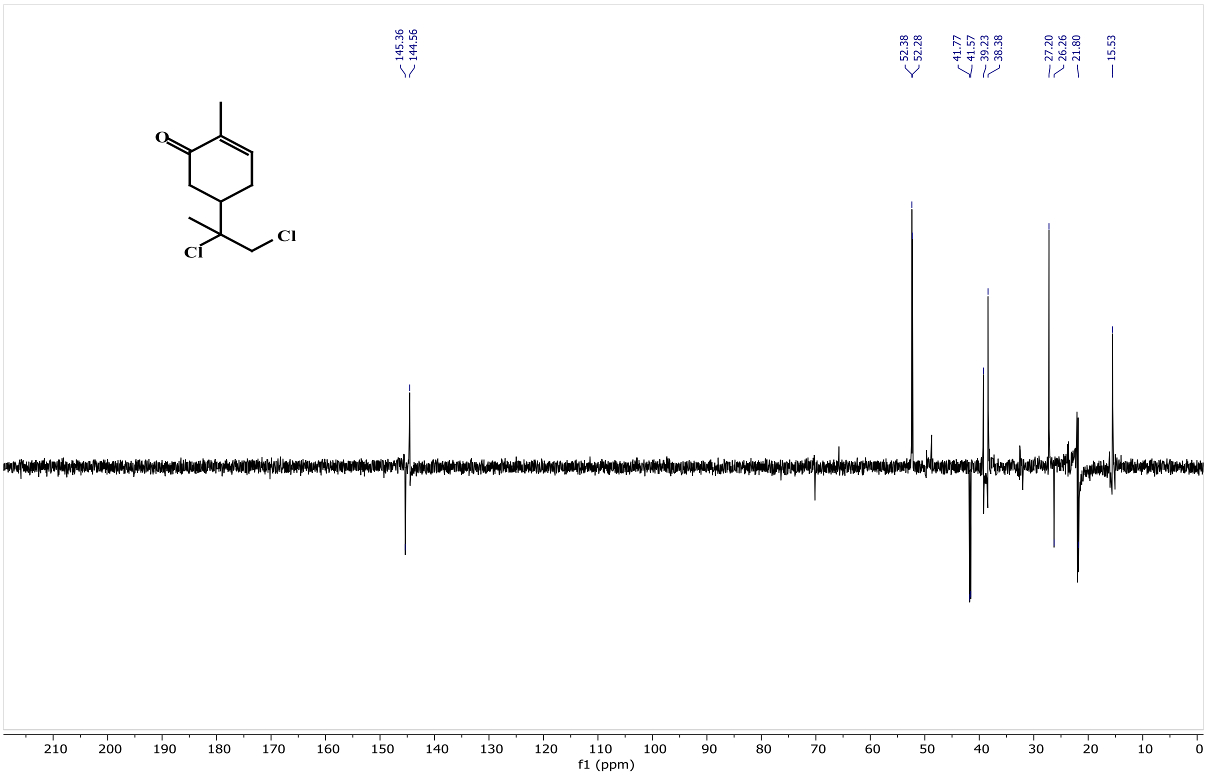

Figure S7: DEPT 135 spectrum of the carvone dichloride **c**.

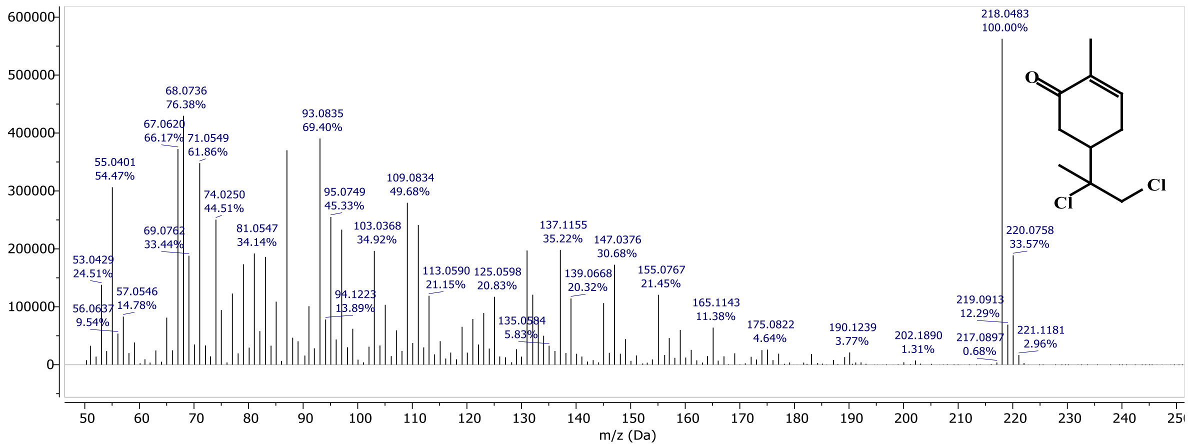

Figure S8: MS spectrum of the carvone dichloride **c**.

- Carvone vinyl allyl dichloride **d**

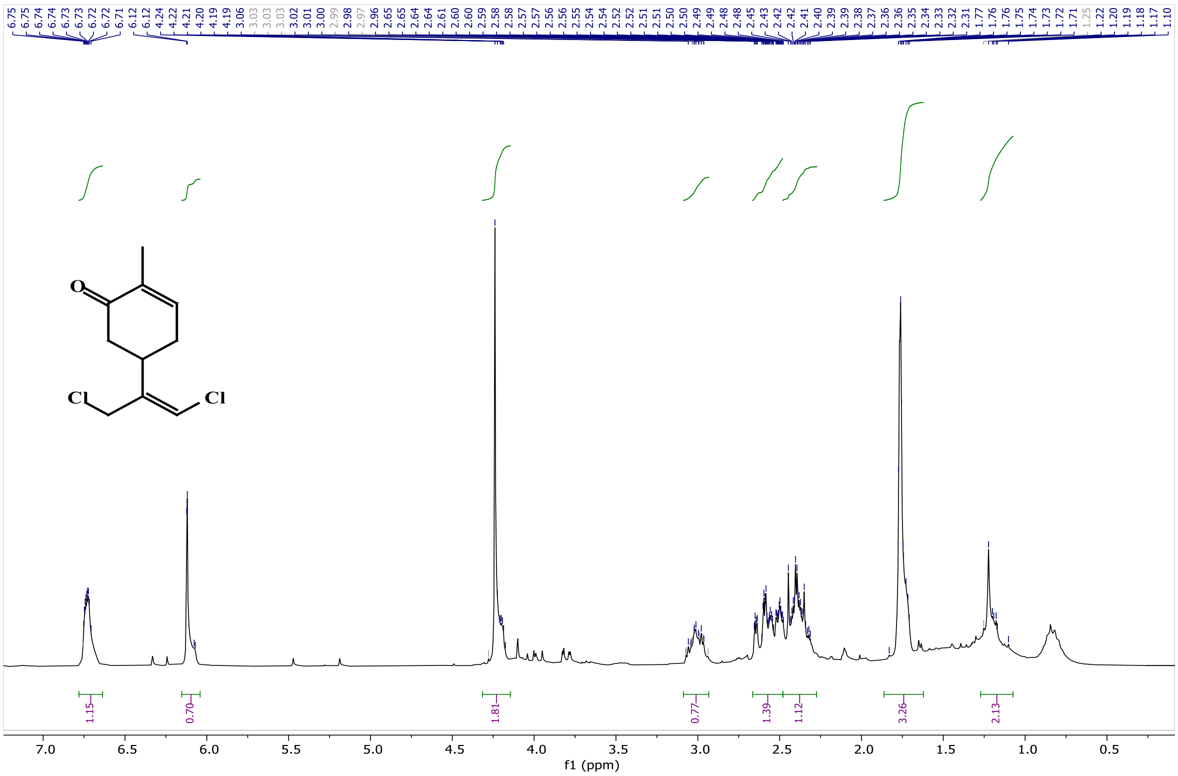

Figure S9: ^{1}H NMR spectrum of the carvone vinyl allyl dichloride **d**.

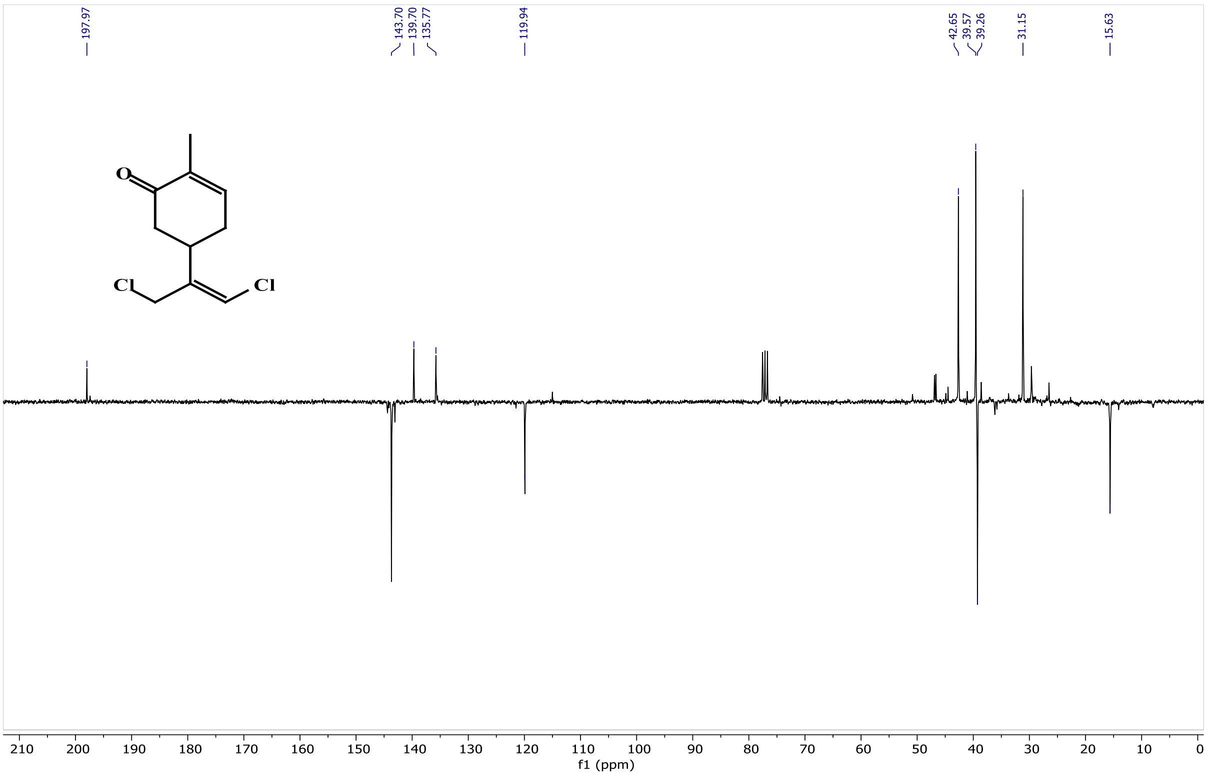

Figure S10: APT spectrum of the carvone vinyl allyl dichloride **d**.

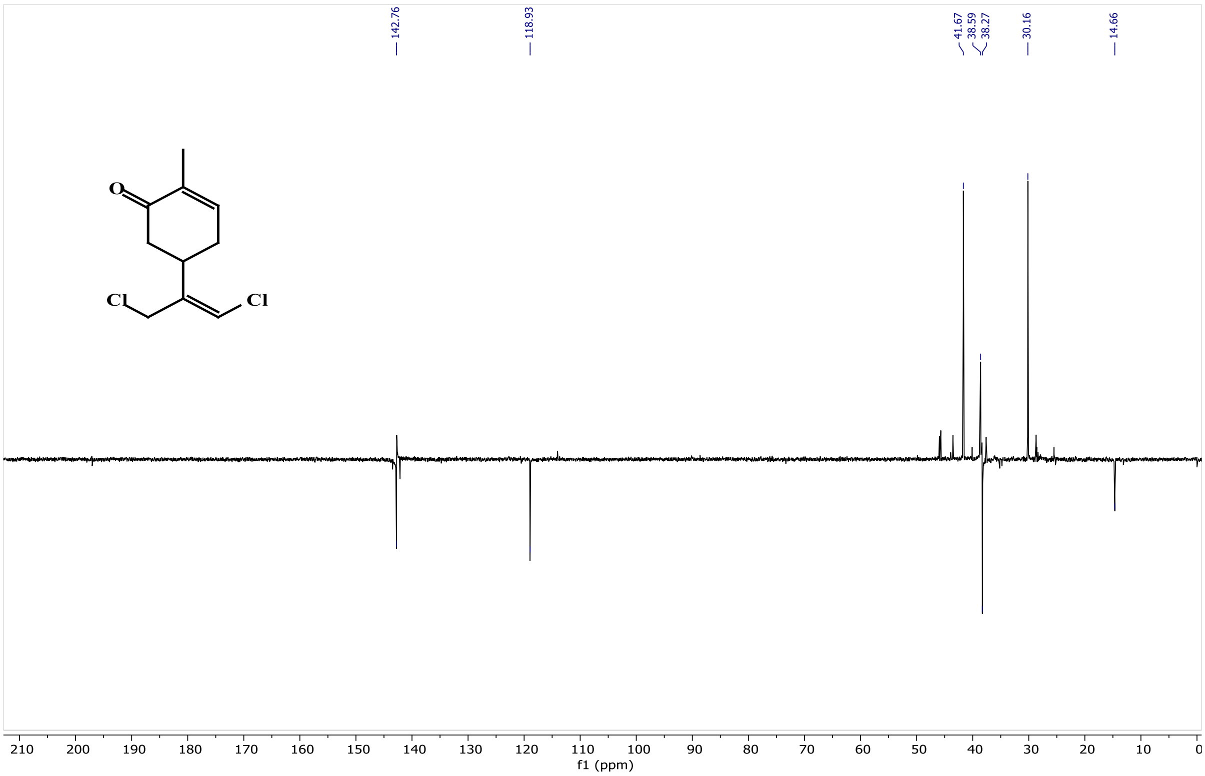

Figure S11: DEPT 135 spectrum of the carvone vinyl allyl dichloride **d**.

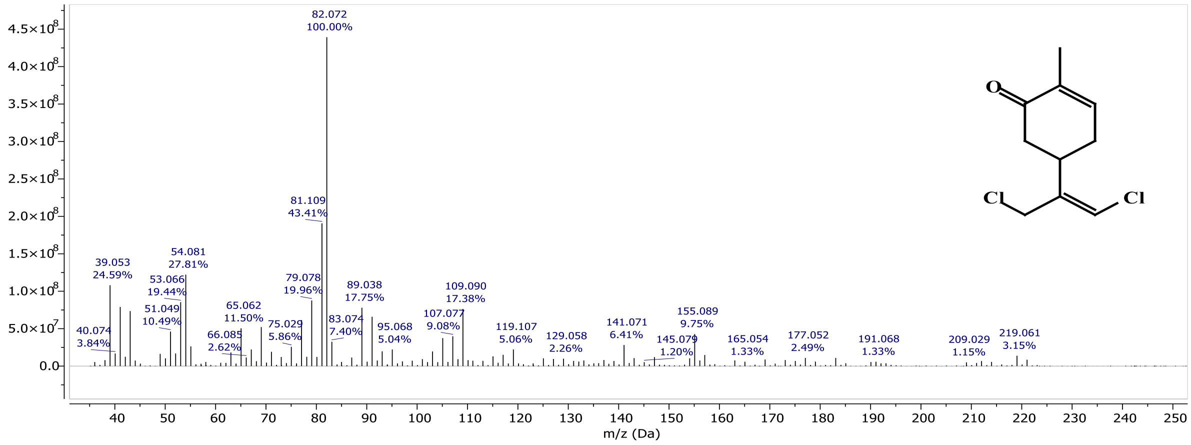

Figure S12: MS spectrum of the carvone vinyl allyl dichloride **d**.

- Carvone trichloride **e**

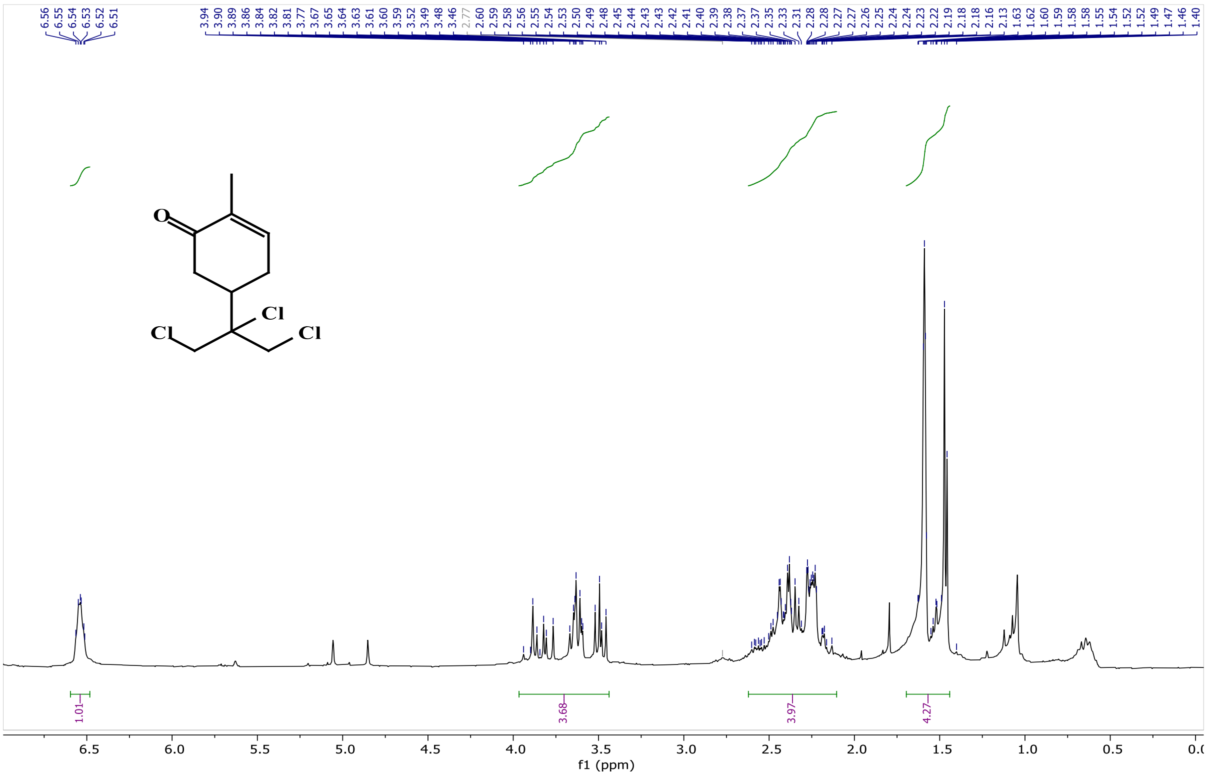

Figure S13: ^{1}H NMR spectrum of the carvone trichloride **e** in a complex mixture.

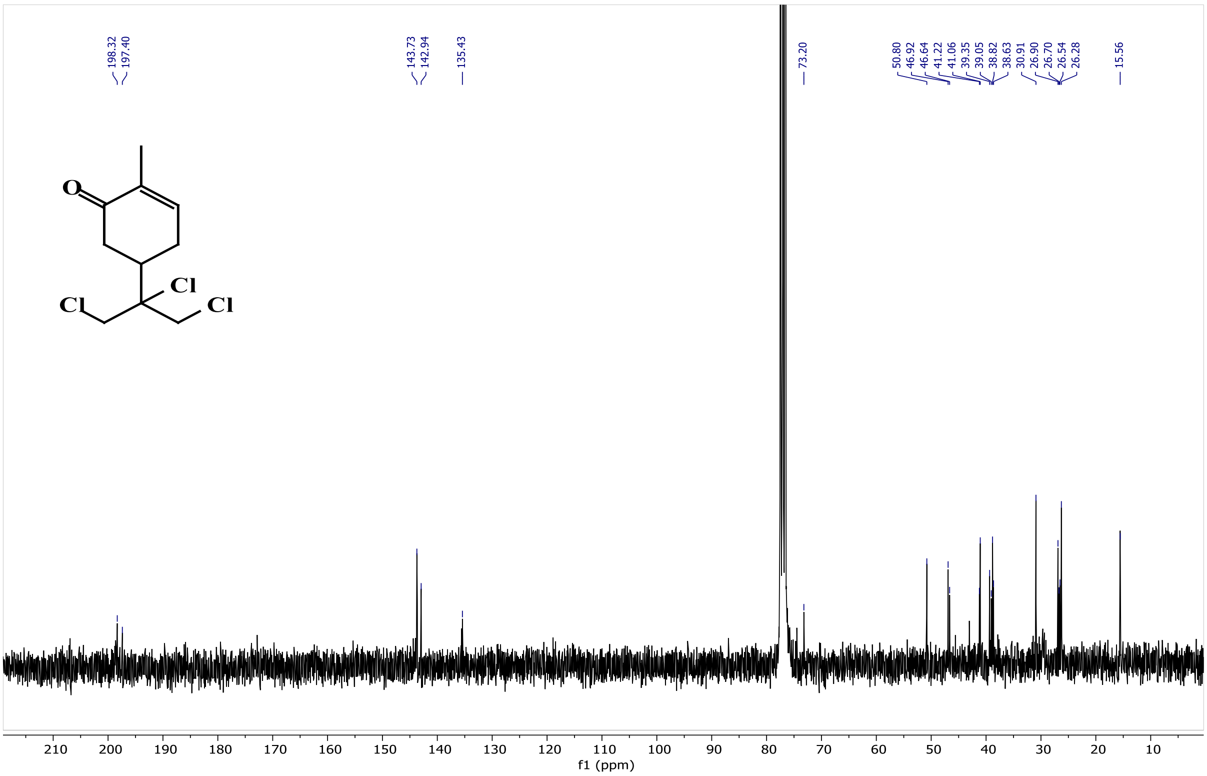

Figure S14: ^{13}C spectrum of the carvone trichloride **e** in a complex mixture.

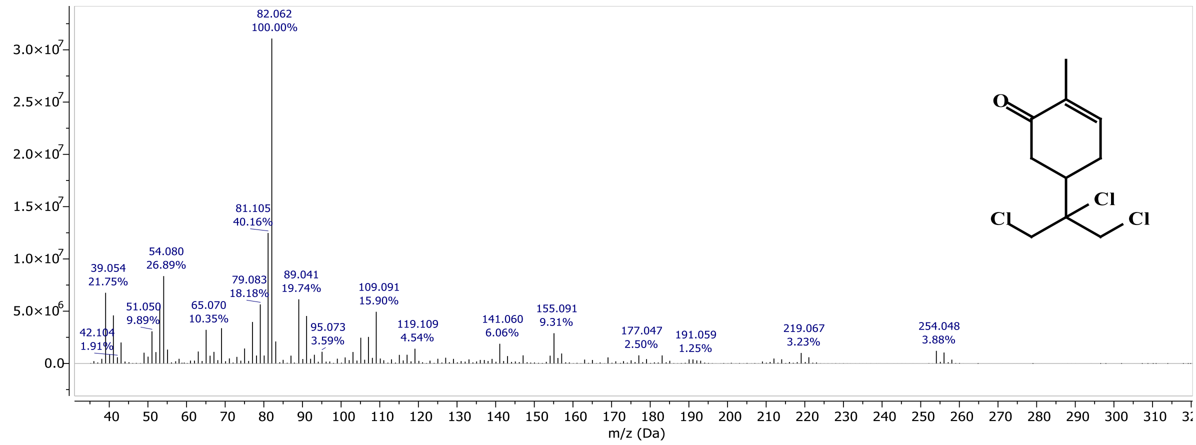

Figure S15: MS spectrum of the carvone trichloride **e**.

➢ Derivatives of limonene oxide **f**

- Limonene oxide monochloride **g**

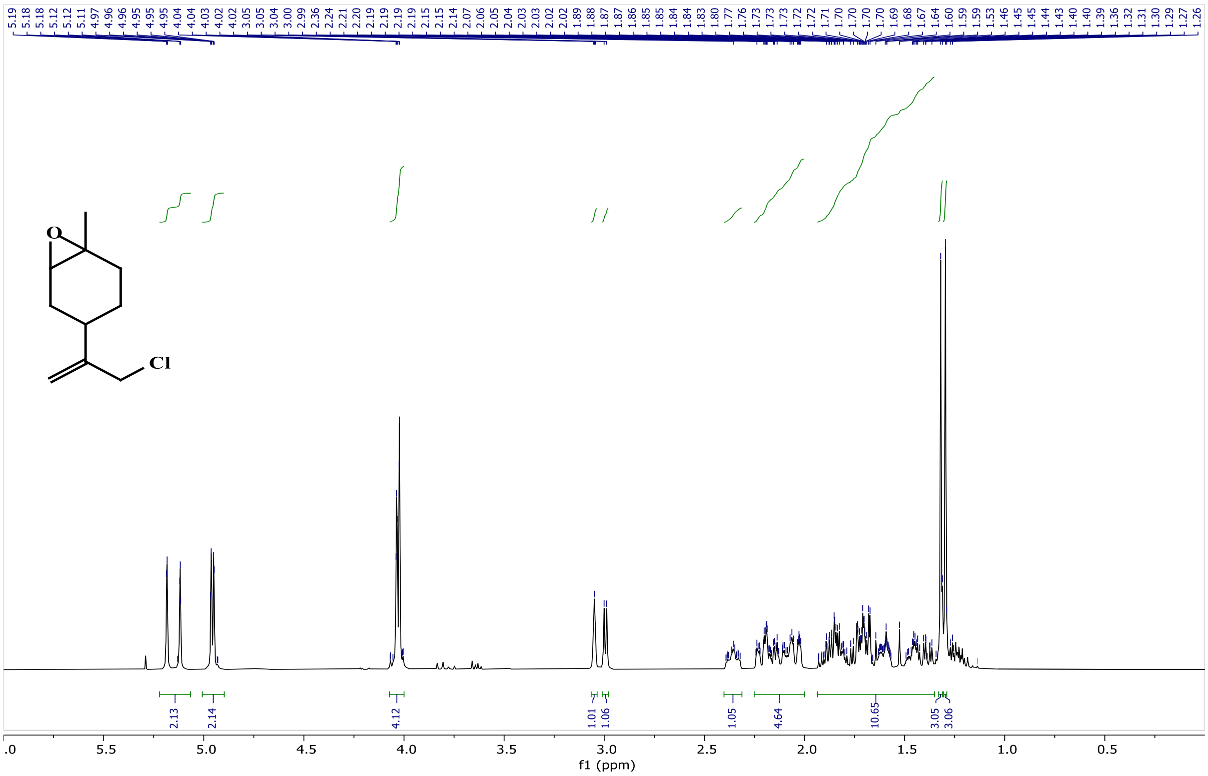

Figure S16: ^{1}H NMR spectrum of the limonene oxide monochloride **g**.

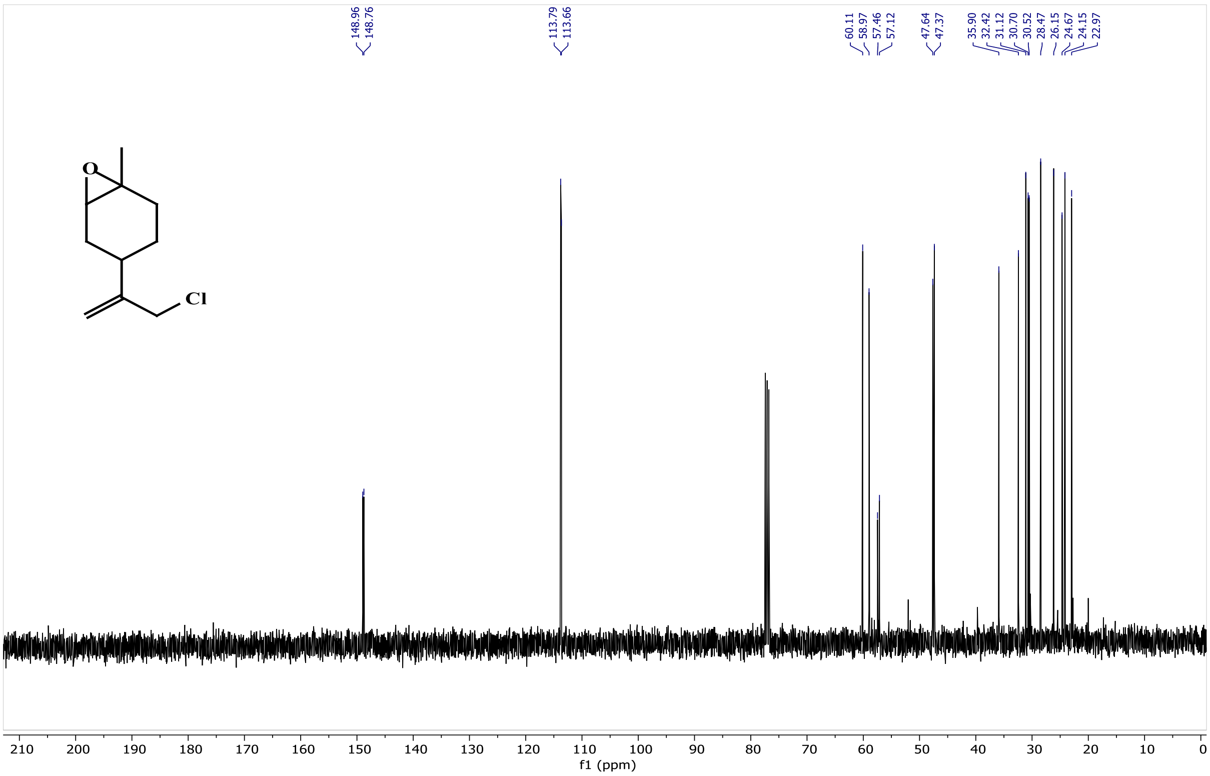

Figure S17: ^{13}C spectrum of the limonene oxide monochloride **g.**

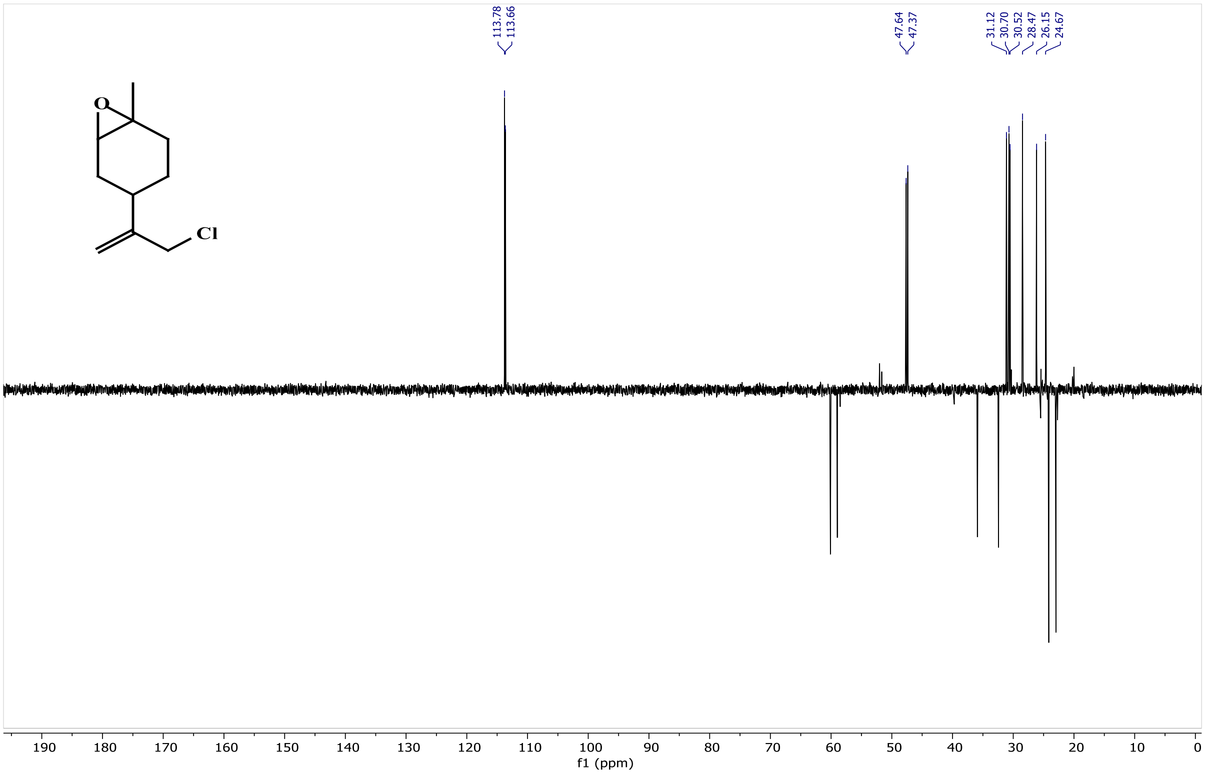

Figure S18: DEPT 135 spectrum of the limonene oxide monochloride **g.**

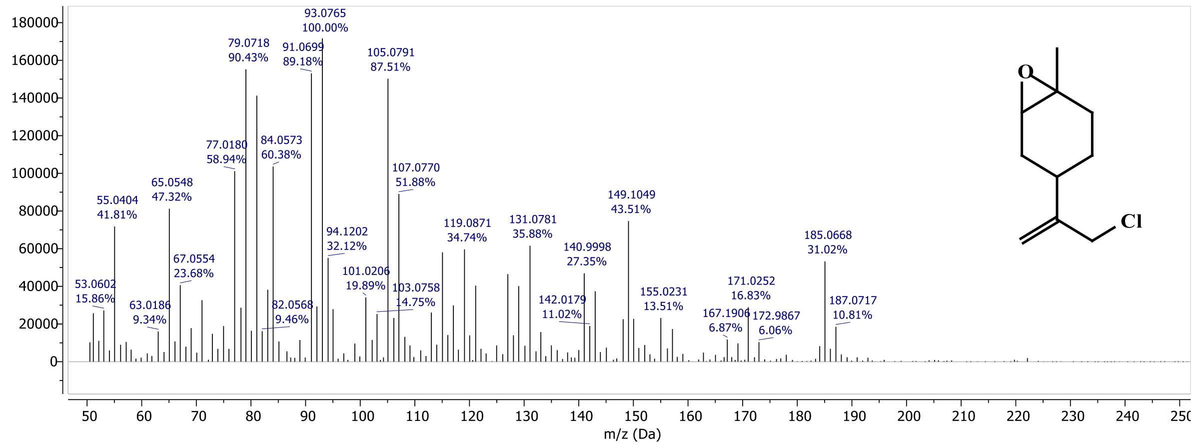

Figure S19: MS spectrum of the limonene oxide monochloride **g**.

- Limonene oxide dichloride **h**

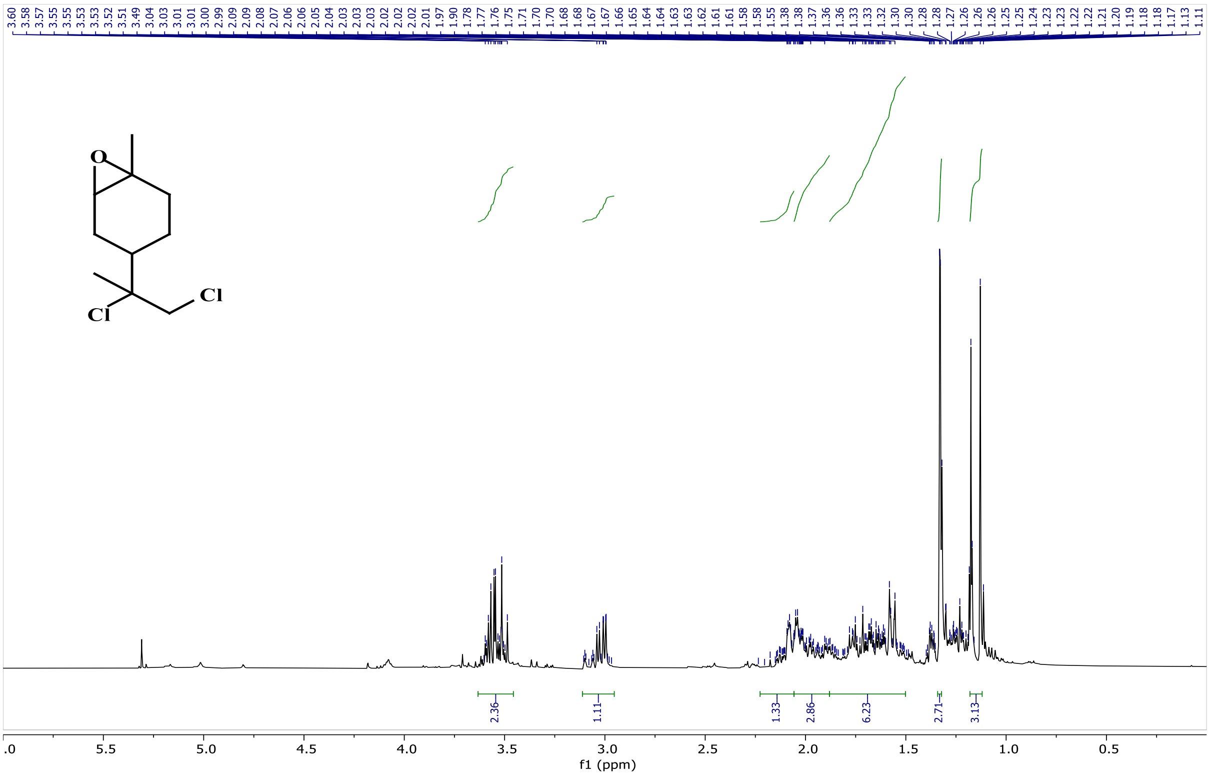

Figure S20: ^{1}H NMR spectrum of the limonene oxide dichloride **h**.

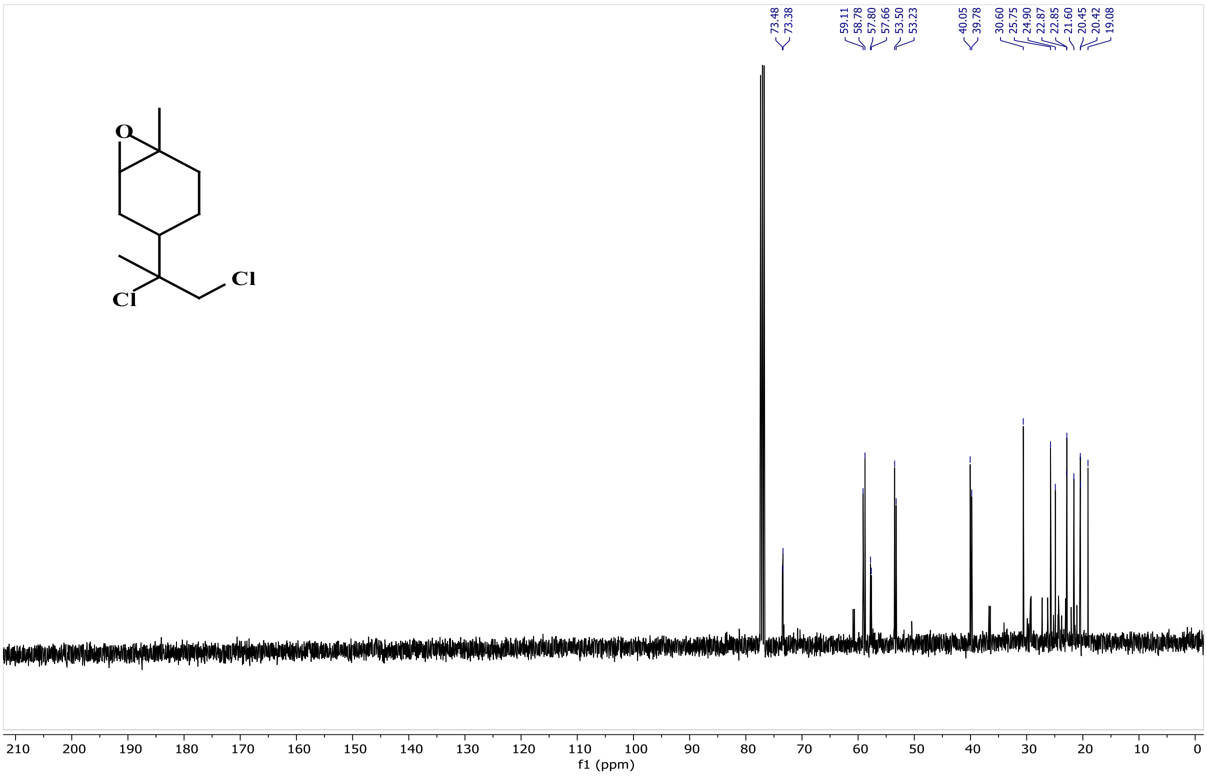

Figure S21: ^{13}C spectrum of the limonene oxide dichloride **h**.

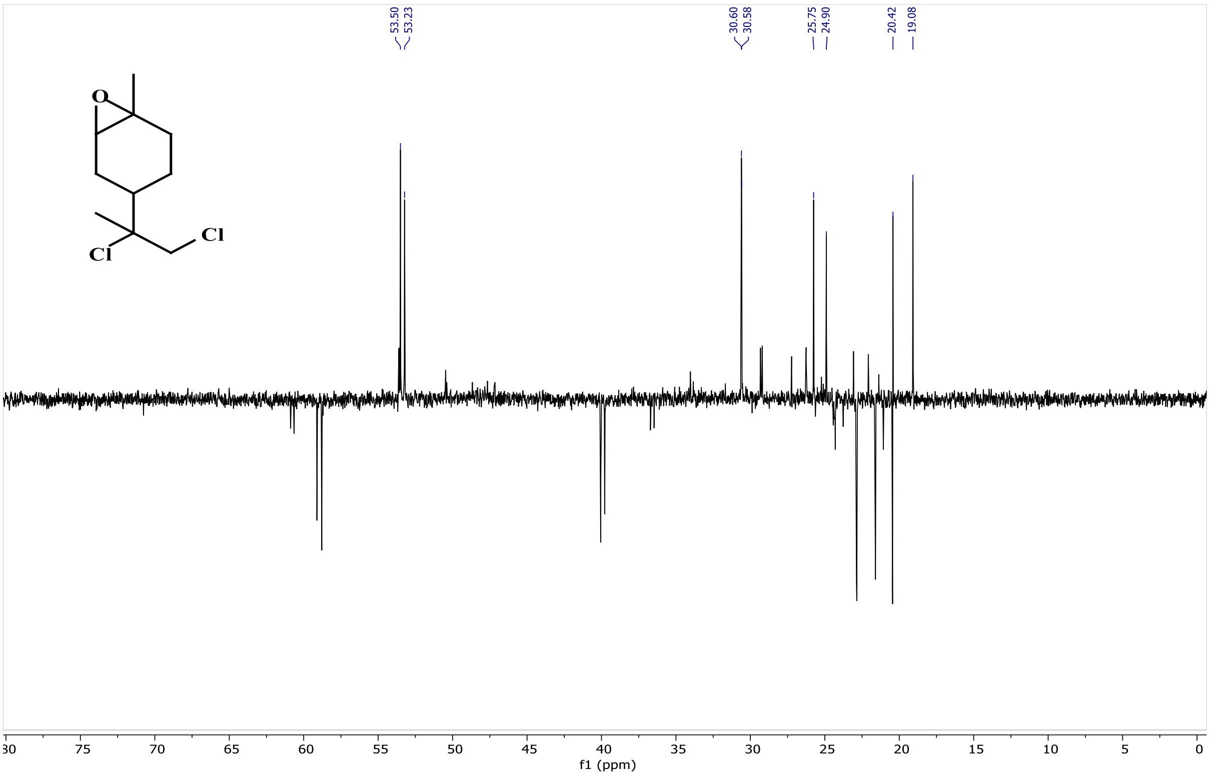

Figure S22: DEPT 135 spectrum of the limonene oxide dichloride **h**.

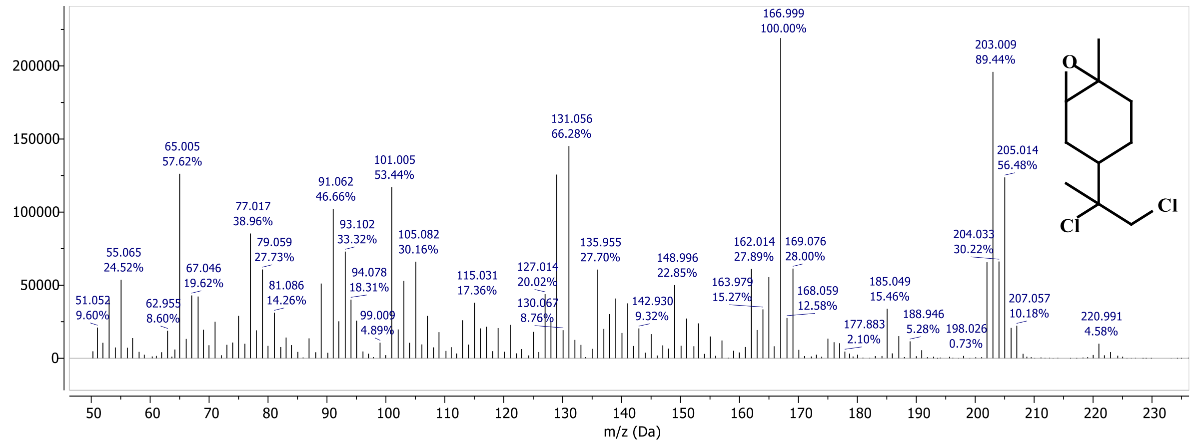

Figure S23: MS spectrum of the limonene oxide dichloride **h**.

➢ Derivatives of nootkatone i

- Nootkatone monochloride j

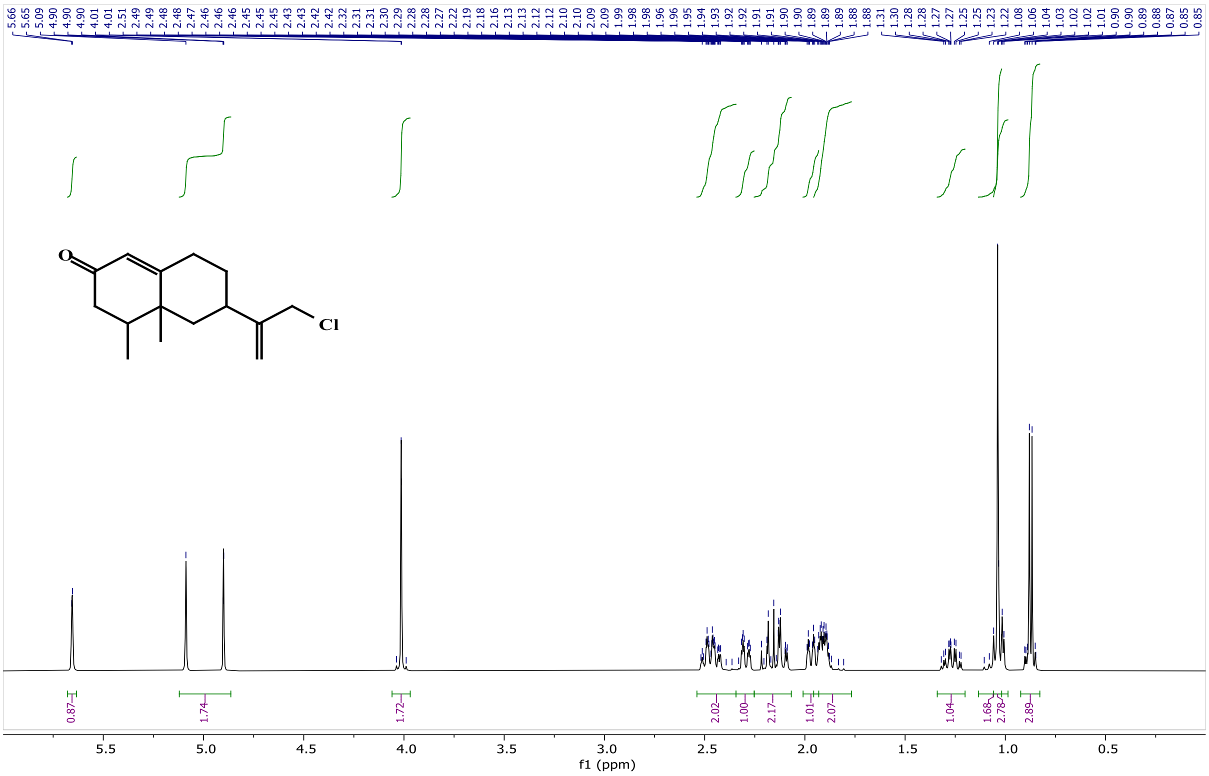

Figure S24: [1]H NMR spectrum of the nootkatone monochloride **j**.

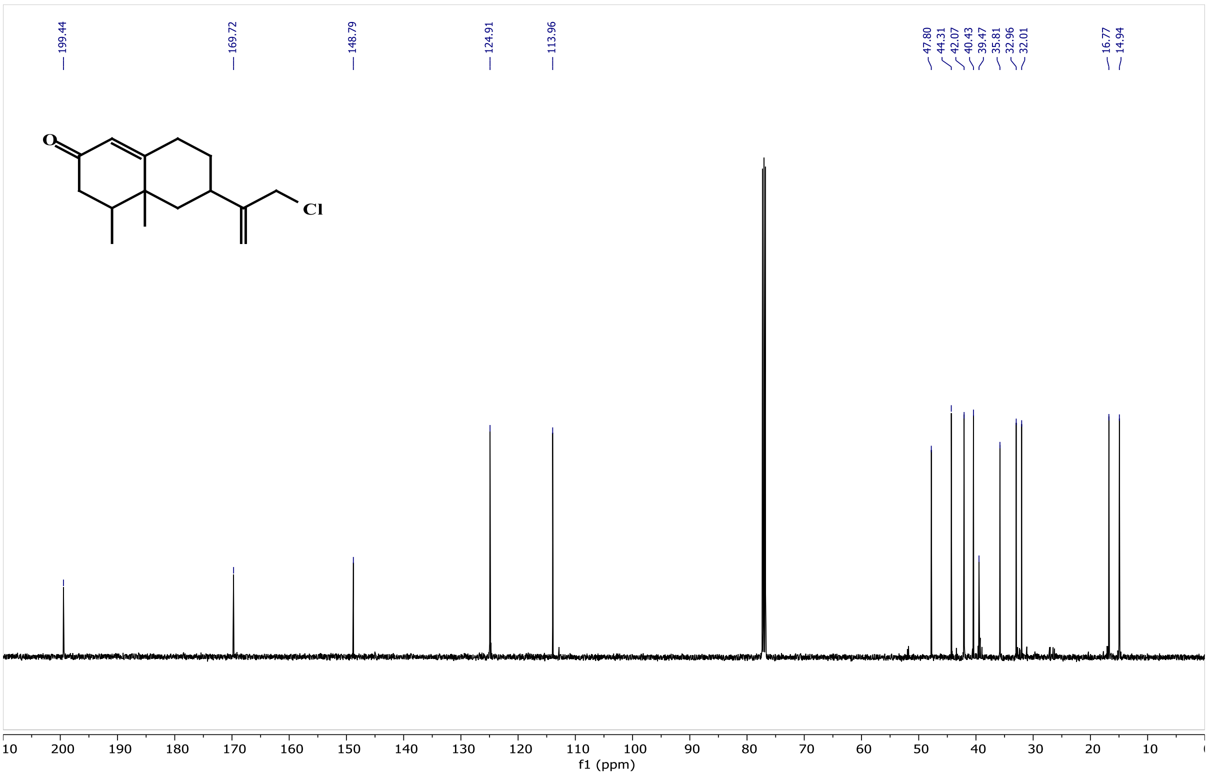

Figure S25: ^{13}C spectrum of the nootkatone monochloride **j**.

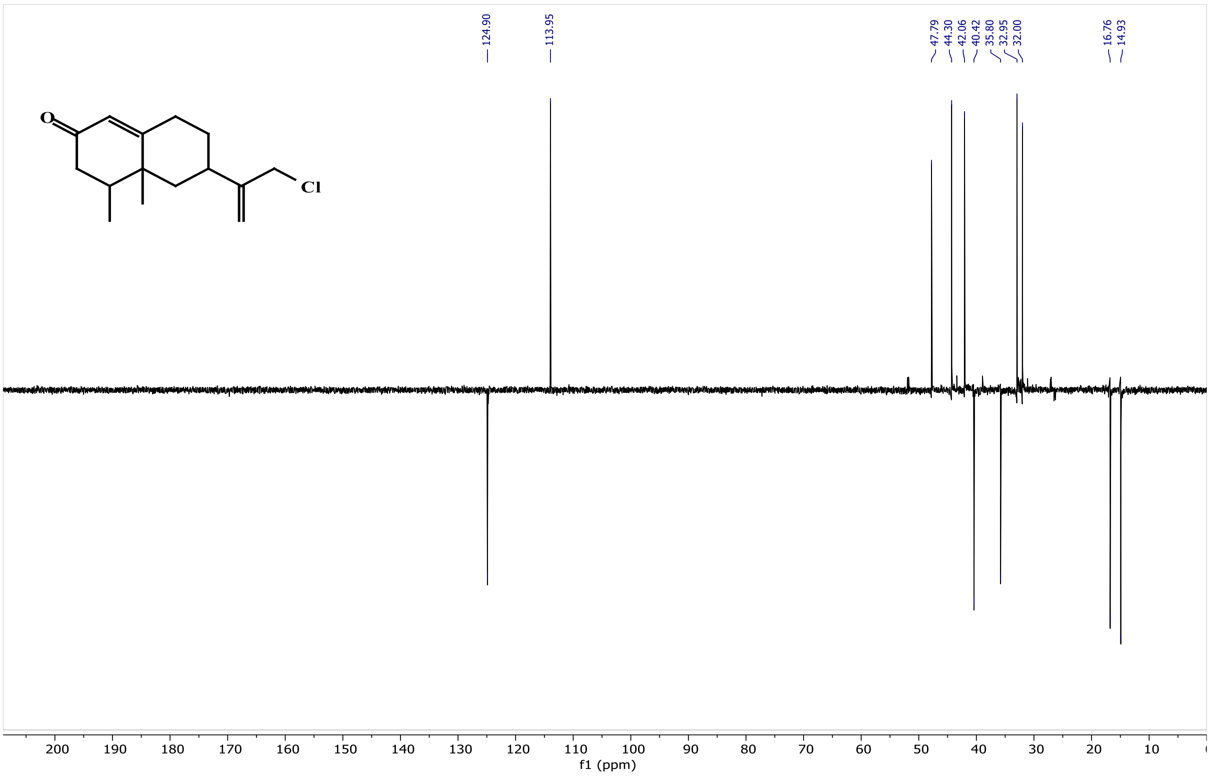

Figure S26: DEPT 135 spectrum of the nootkatone monochloride **j**.

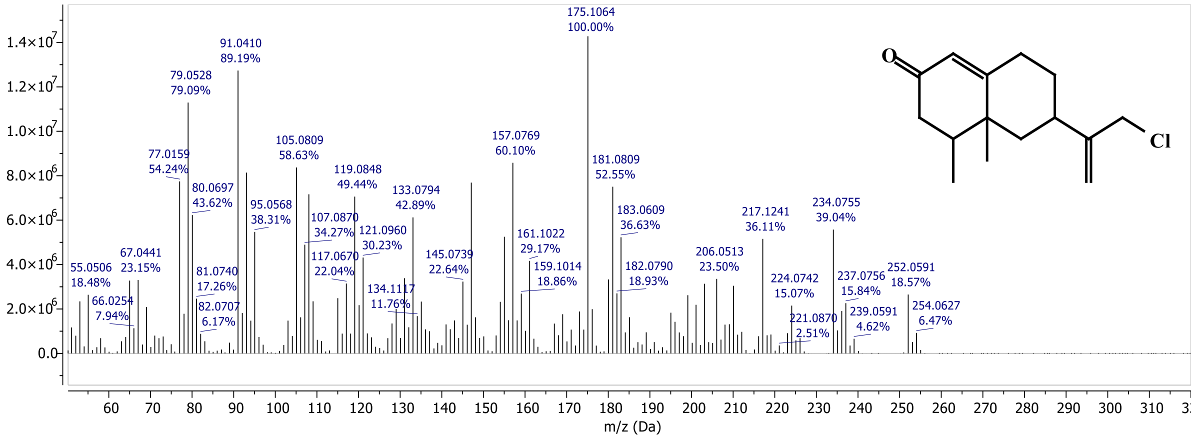

Figure S27: MS spectrum of the nootkatone monochloride **j.**

- Nootkatone vinyl allyl dichloride **k**

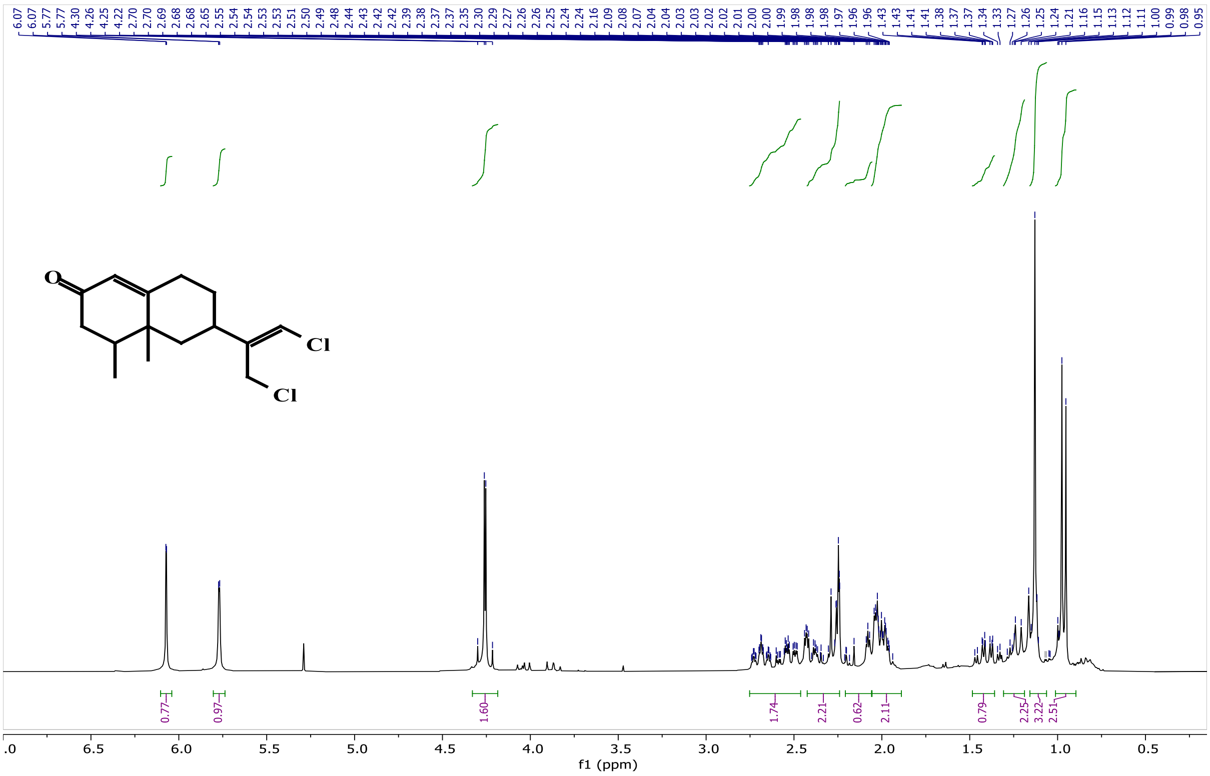

Figure S28: ^{1}H NMR spectrum of the nootkatone vinyl allyl dichloride **k.**

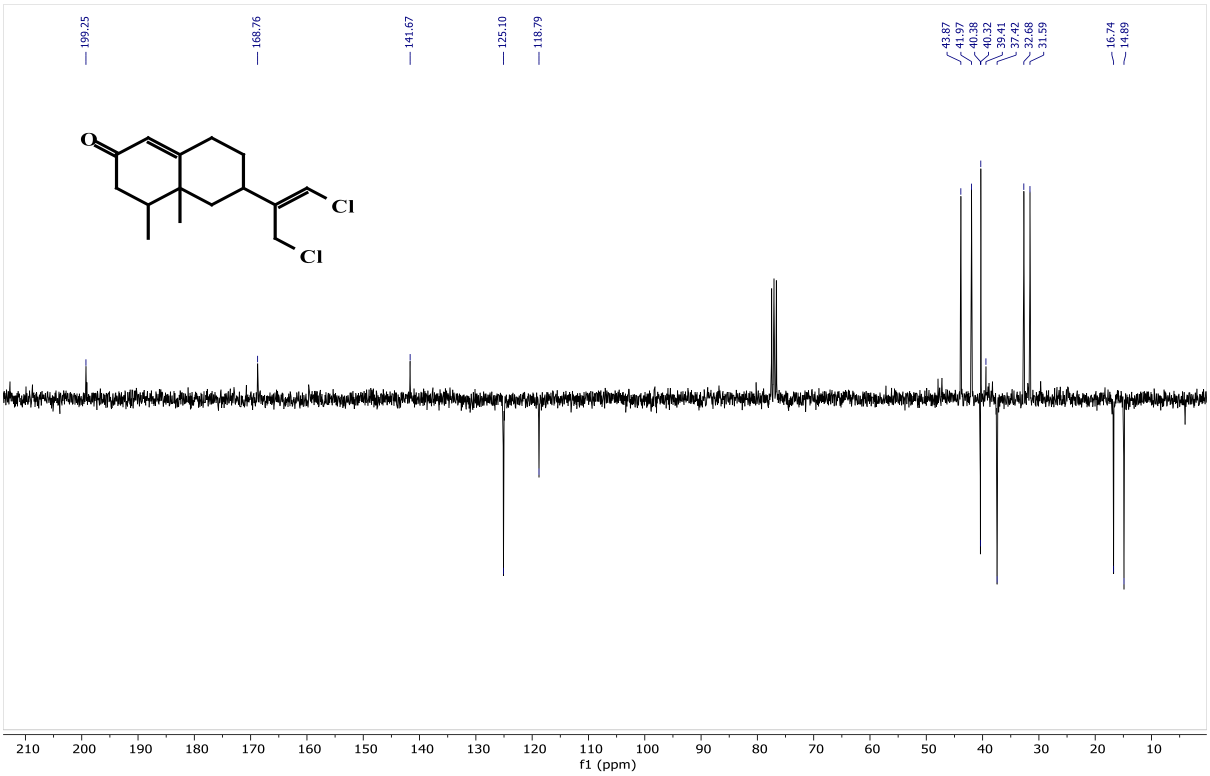

Figure S29: APT spectrum of the nootkatone vinyl allyl dichloride **k**.

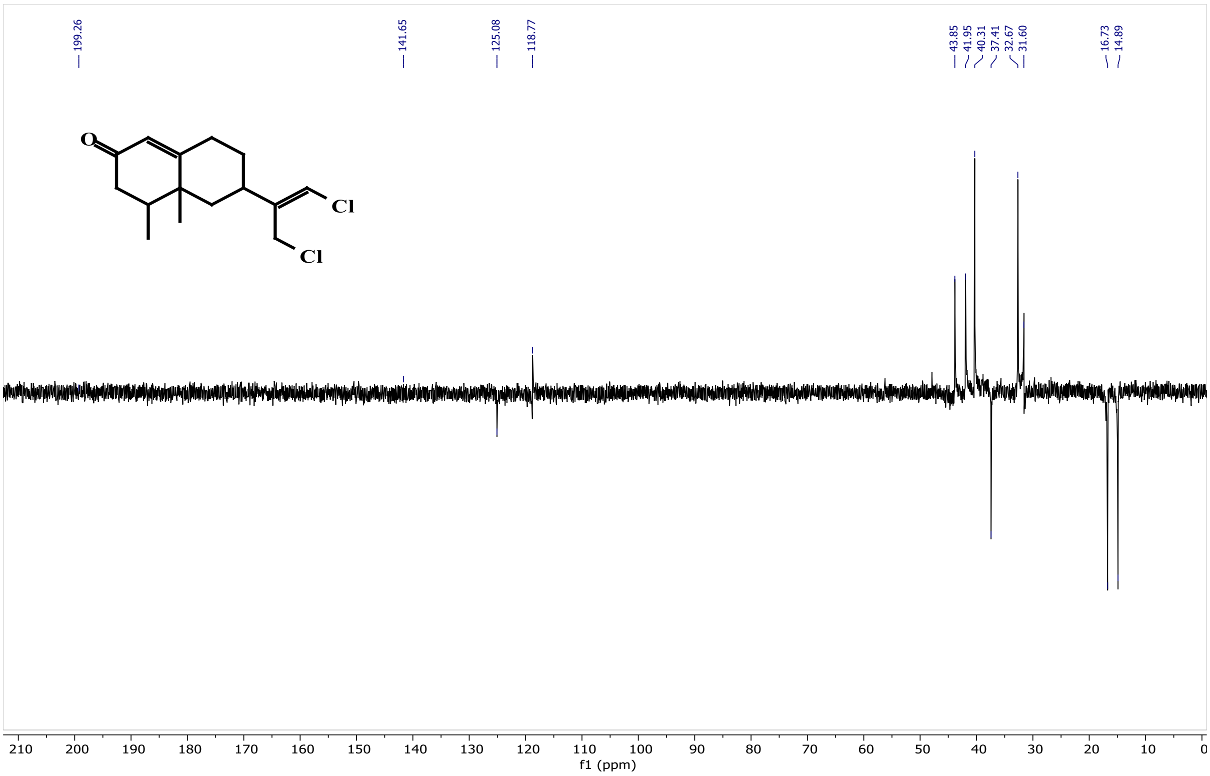

Figure S30: DEPT 135 spectrum of the nootkatone vinyl allyl dichloride **k**.

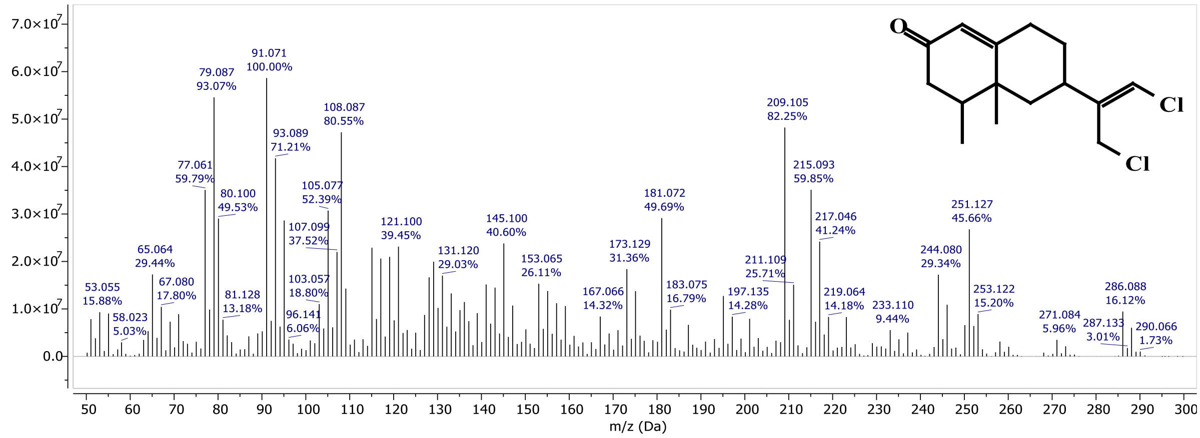

Figure S31: MS spectrum of the nootkatone vinyl allyl dichloride **k**.

- Nootkatone dichloride **l**

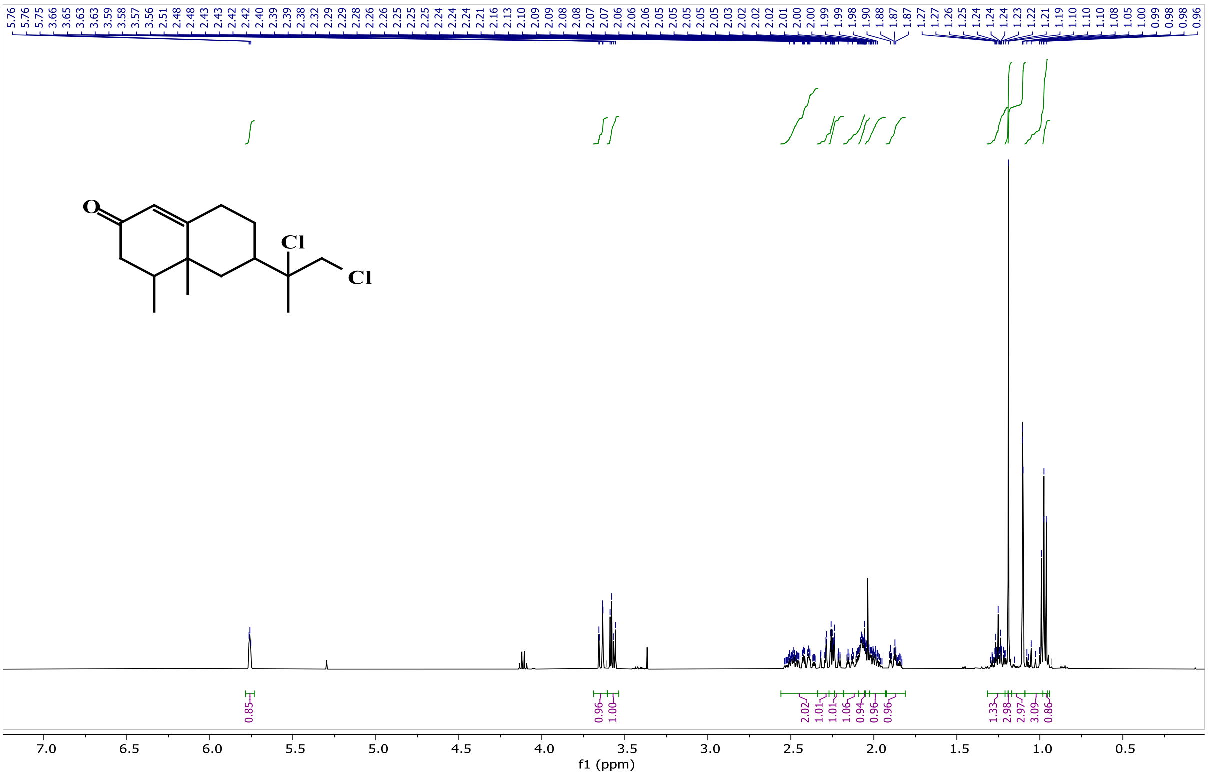

Figure S32: ^{1}H NMR spectrum of the nootkatone dichloride **l**.

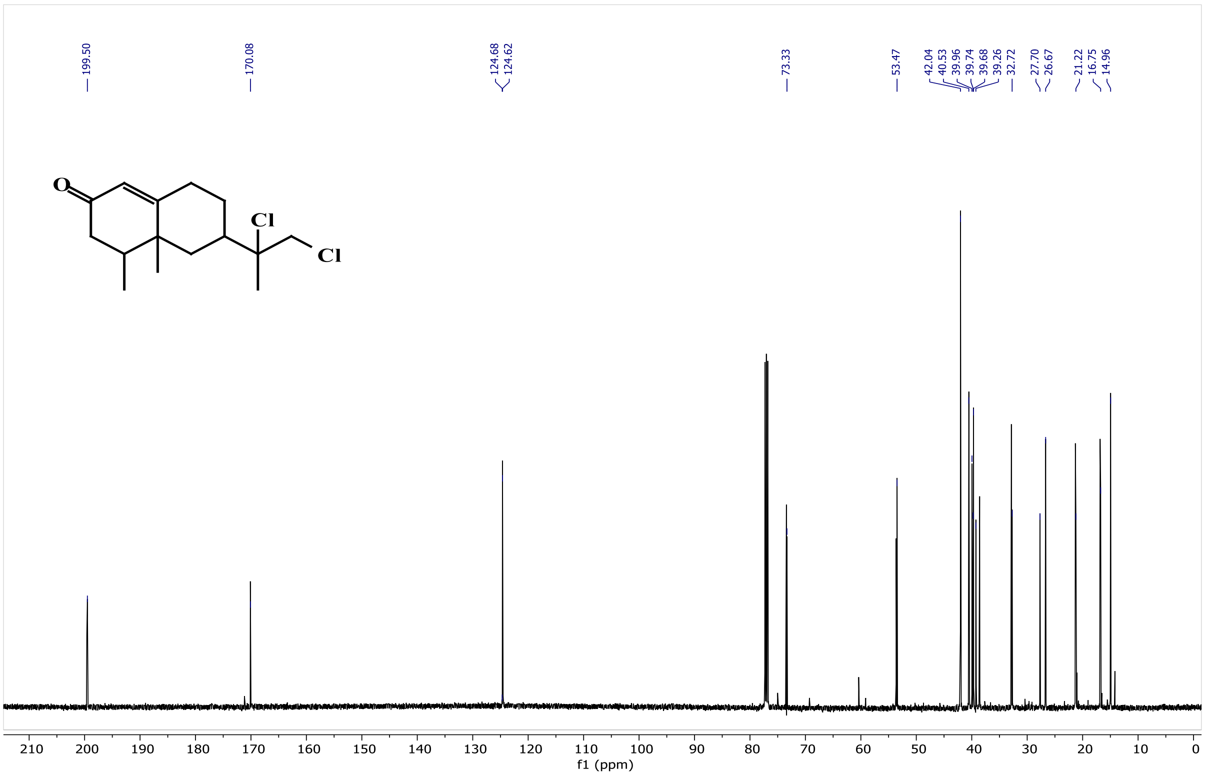

Figure S33: ^{13}C spectrum of the nootkatone dichloride **l**.

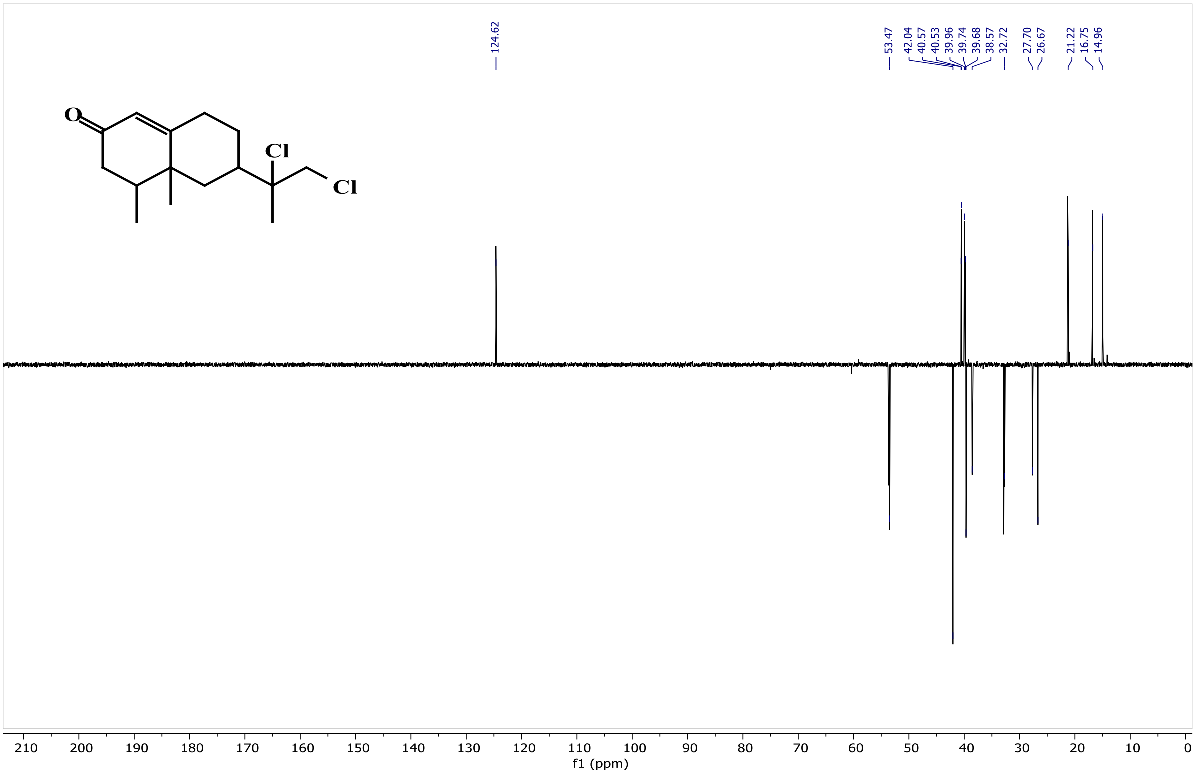

Figure S34: DEPT 135 spectrum of the nootkatone dichloride **l**.

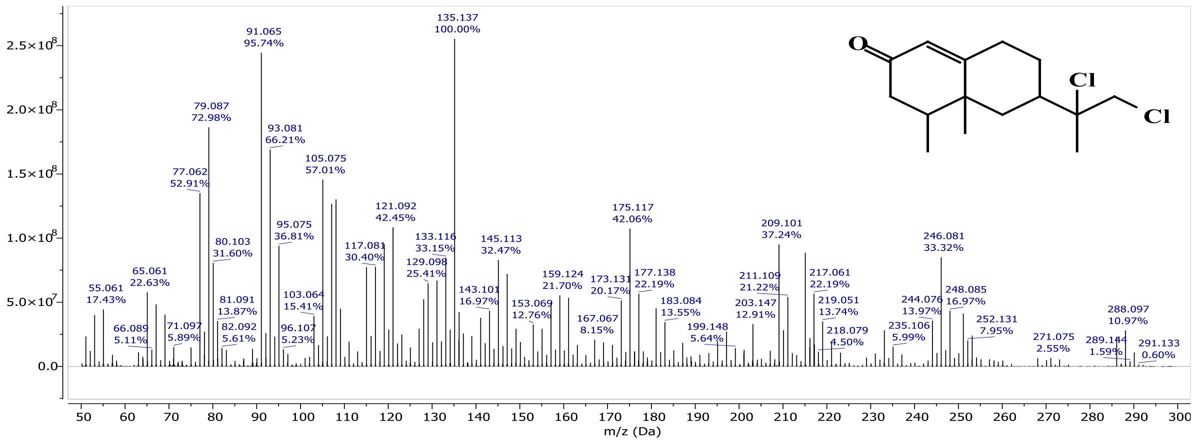

Figure S35: MS spectrum of the nootkatone dichloride **l.**

➢ Derivatives of pulegone m

- Pulegone monochloride **n**

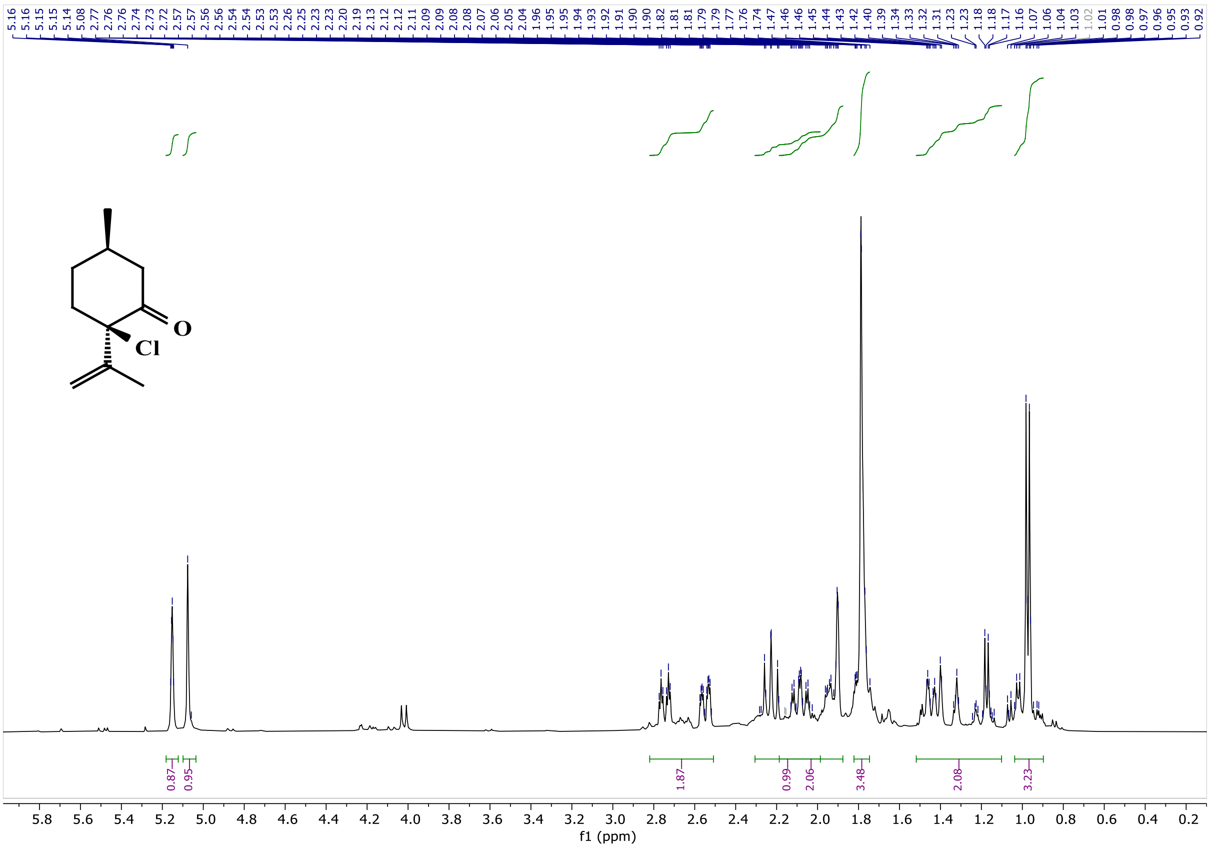

Figure S36: ^{1}H NMR spectrum of the pulegone monochloride **n.**

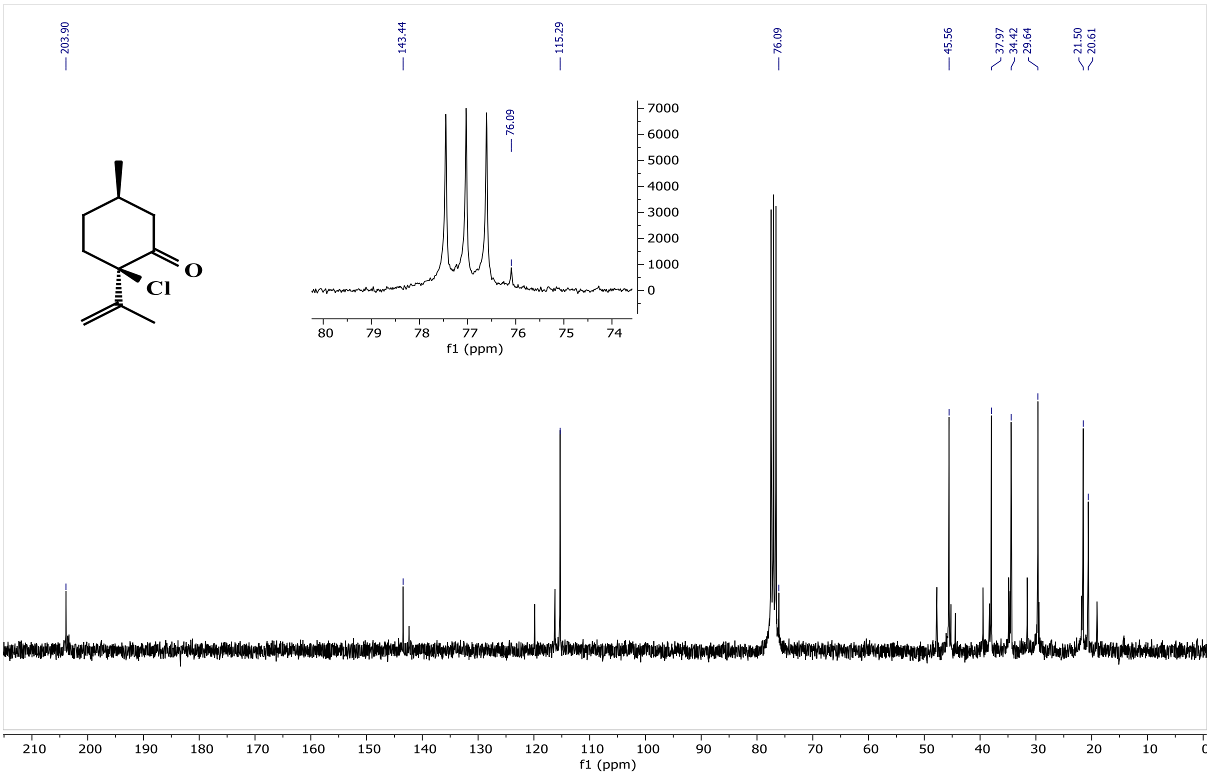

Figure S37: ^{13}C spectrum of the pulegone monochloride **n**.

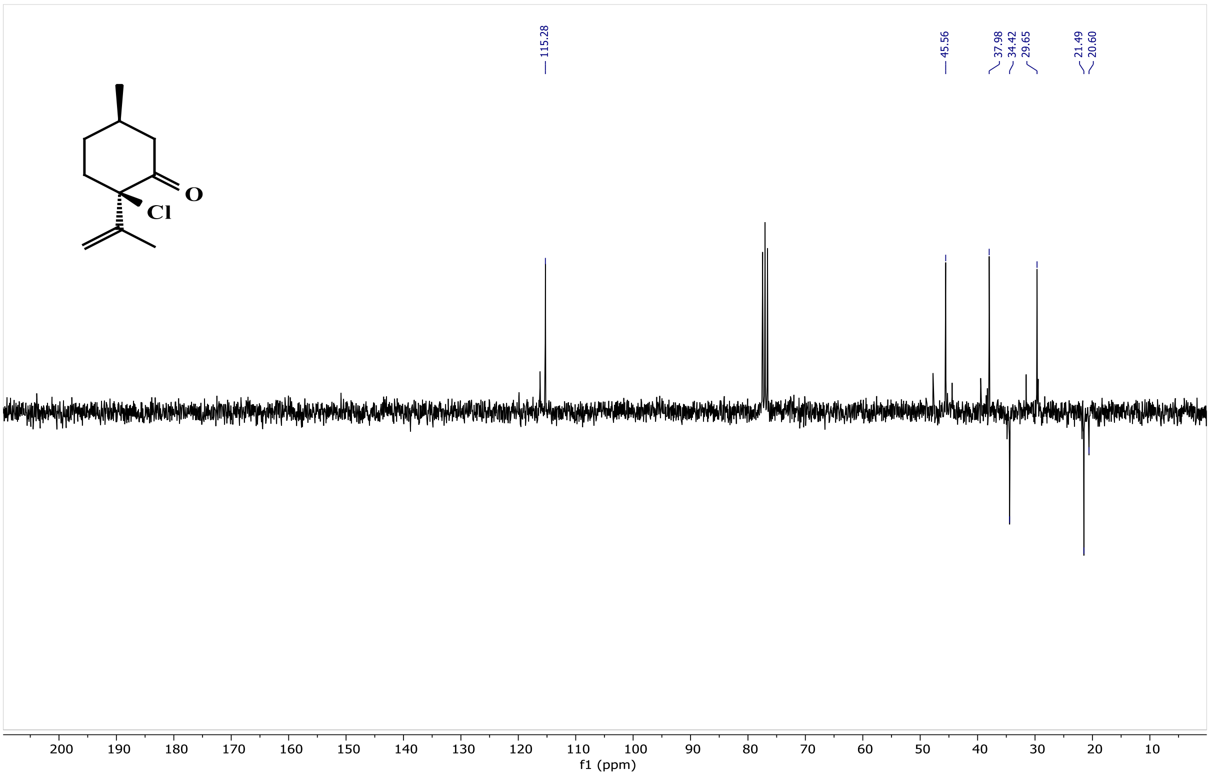

Figure S38: APT spectrum of the pulegone monochloride **n**.

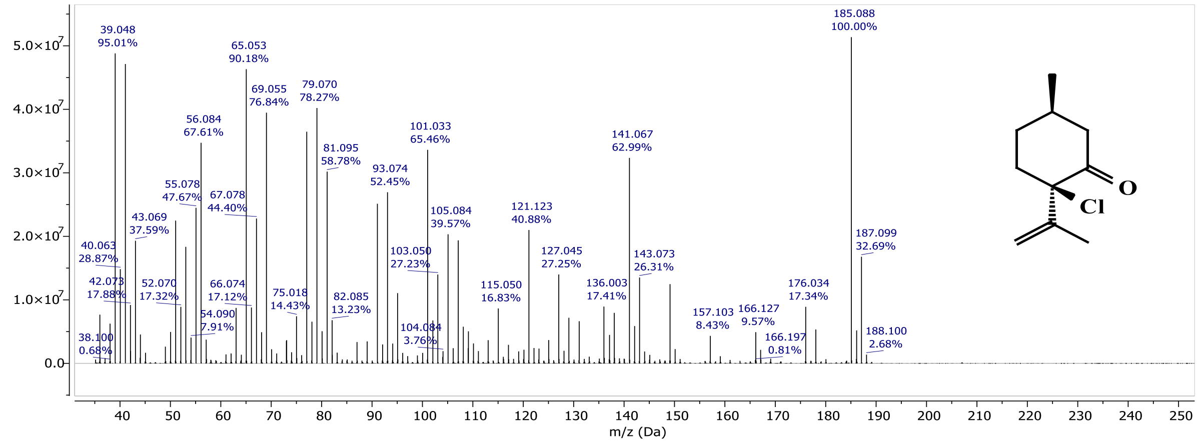

Figure S39: MS spectrum of the pulegone monochloride **n**.

- Pulegone monochloride **n'**

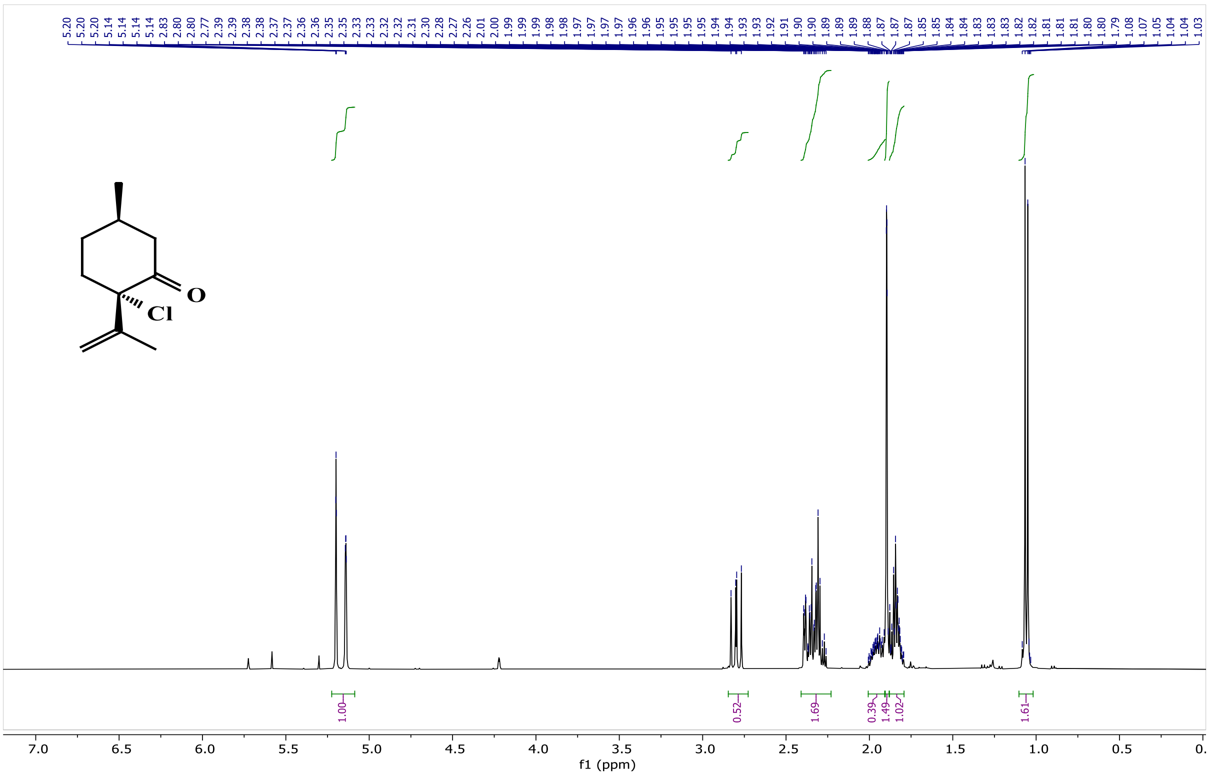

Figure S40: ^{1}H NMR spectrum of the pulegone monochloride **n'**.

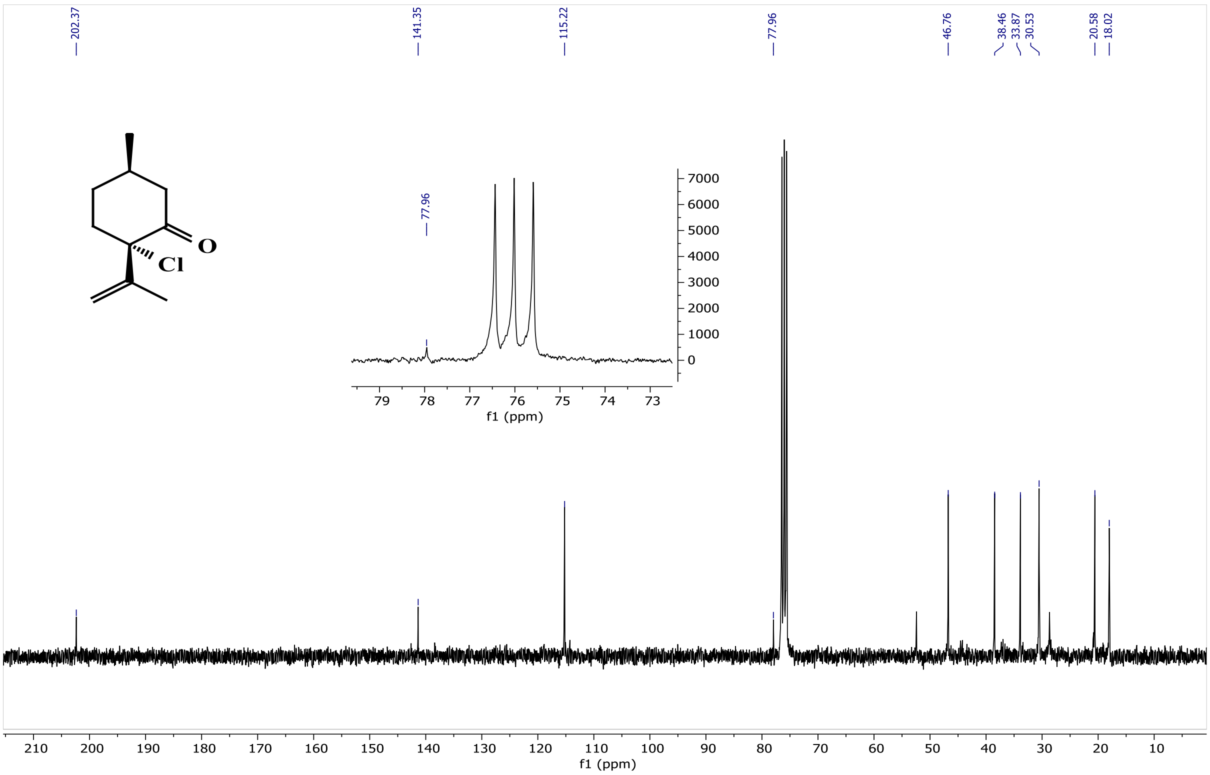

Figure S41: ^{13}C spectrum of the pulegone monochloride **n'**.

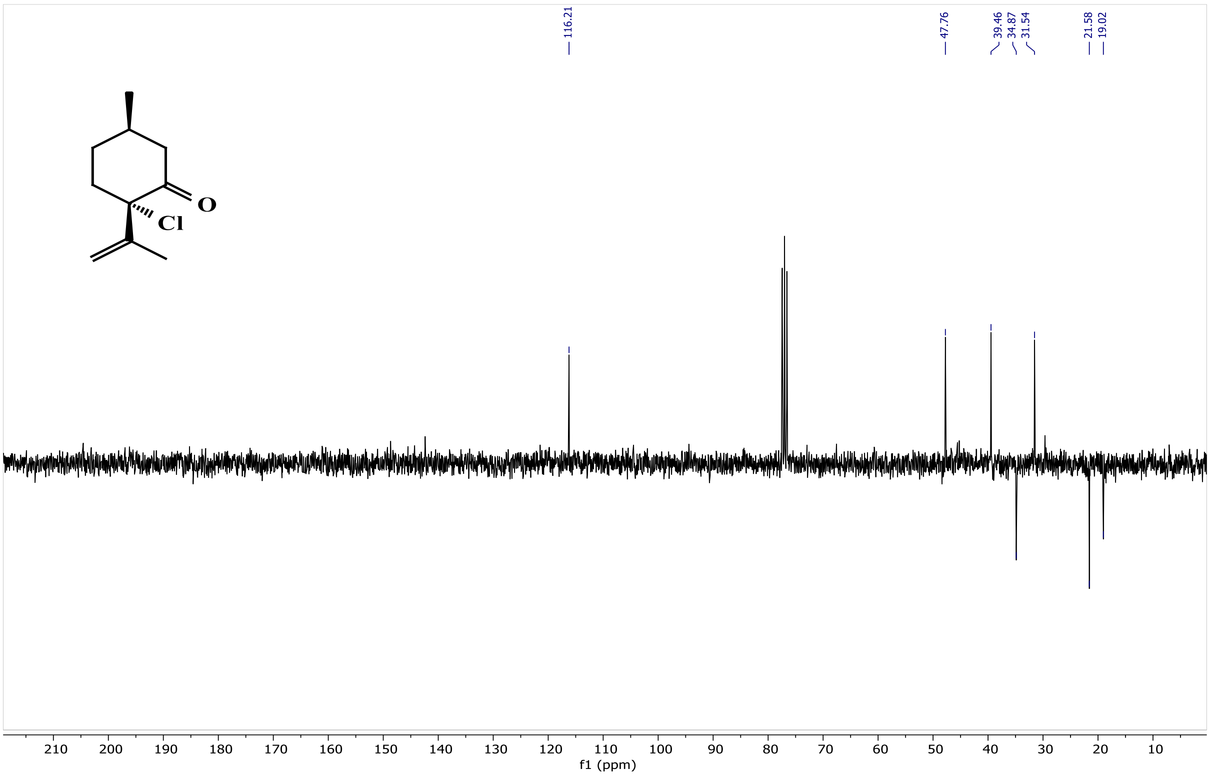

Figure S42: APT spectrum of the pulegone monochloride **n'**.

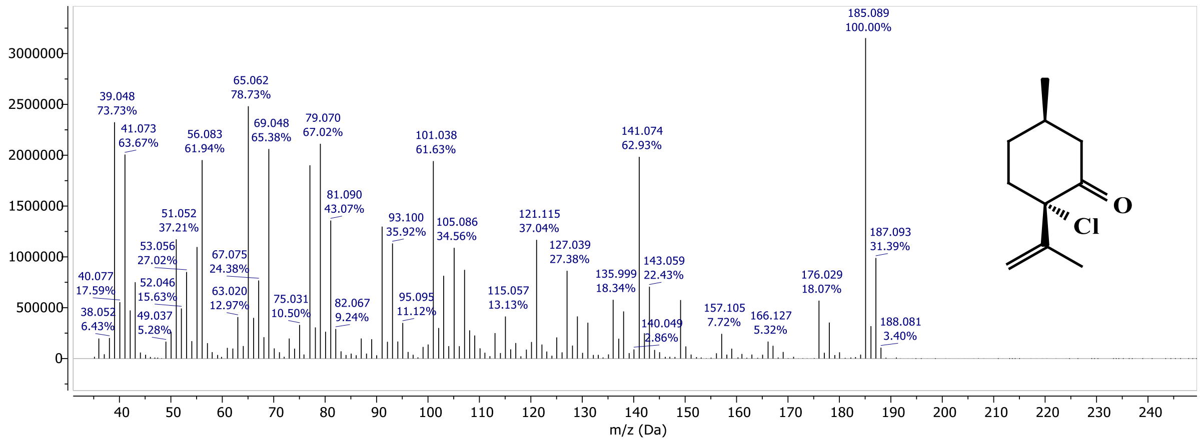

Figure S43: MS spectrum of the pulegone monochloride **n'**.

- Pulegone allyl dichloride **o**

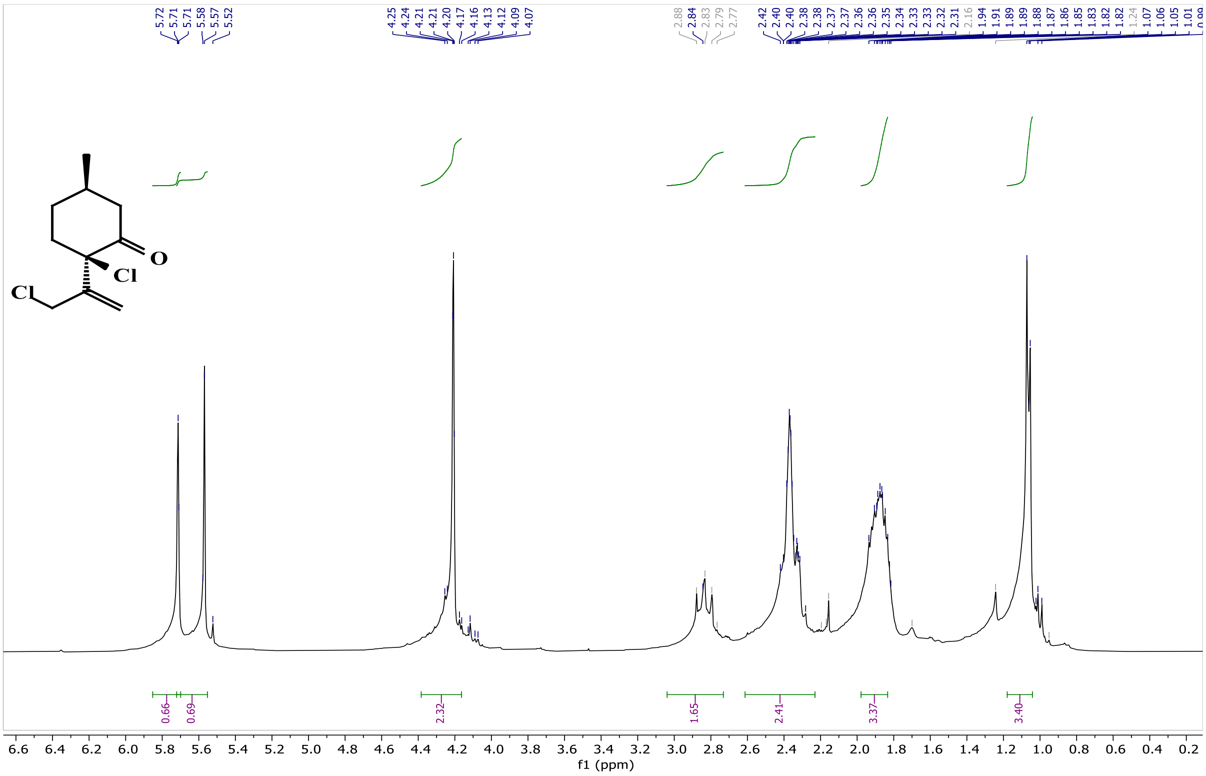

Figure S44: ^{1}H NMR spectrum of the pulegone vinyl allyl dichloride **o**.

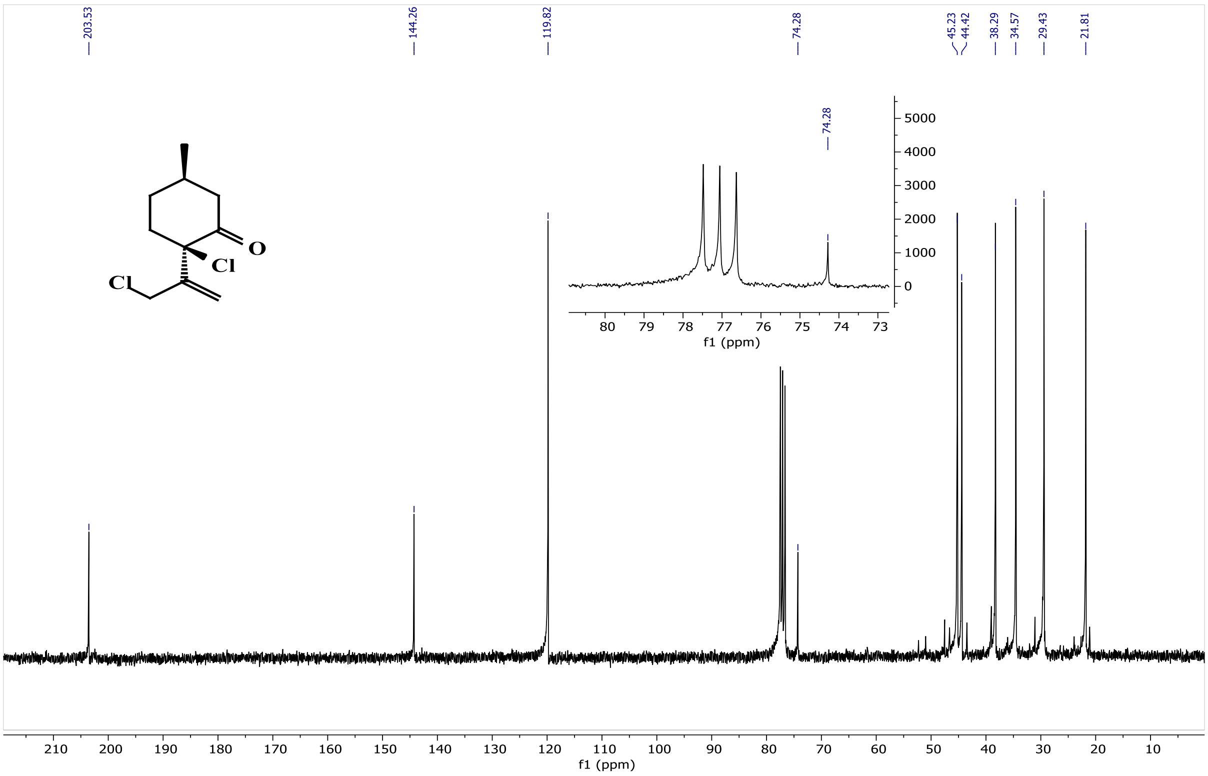

Figure S45: ^{13}C spectrum of the pulegone vinyl allyl dichloride **o**.

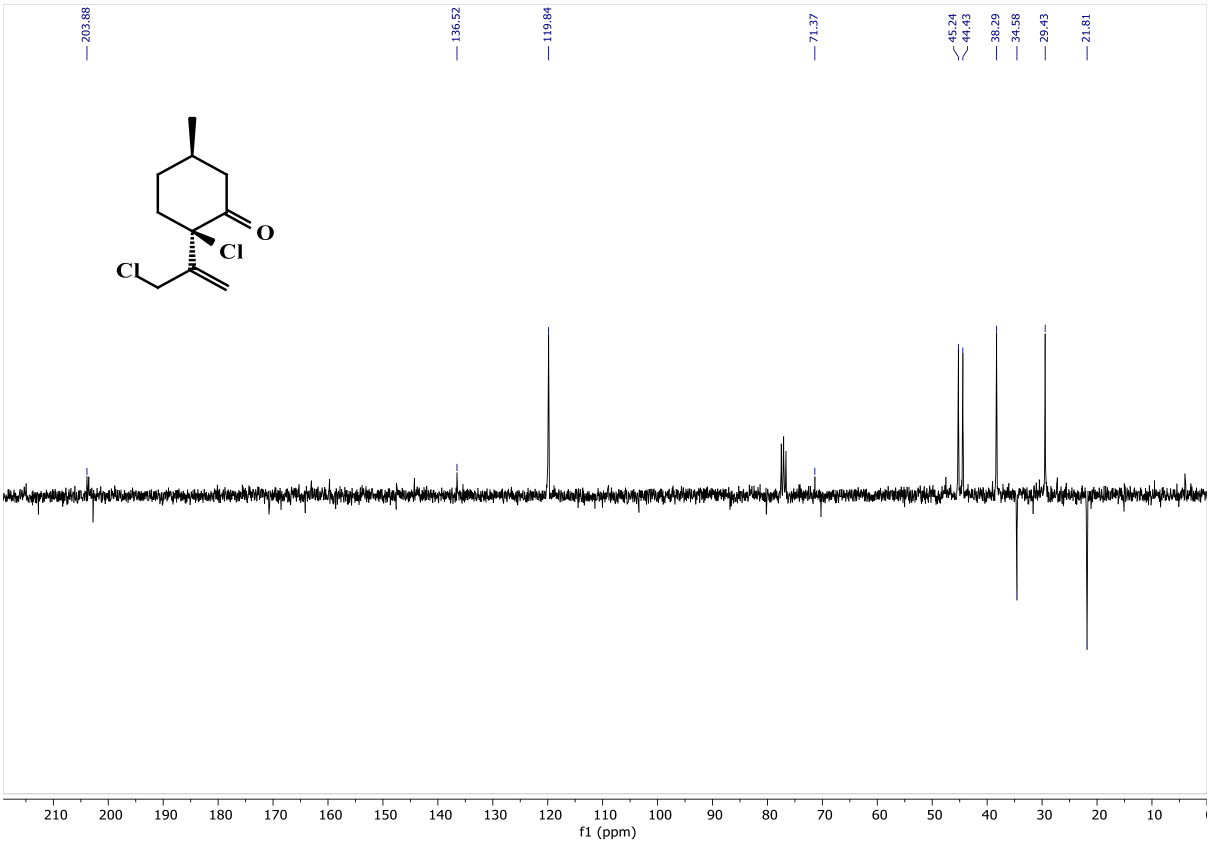

Figure S46: APT spectrum of the pulegone vinyl allyl dichloride **o**.

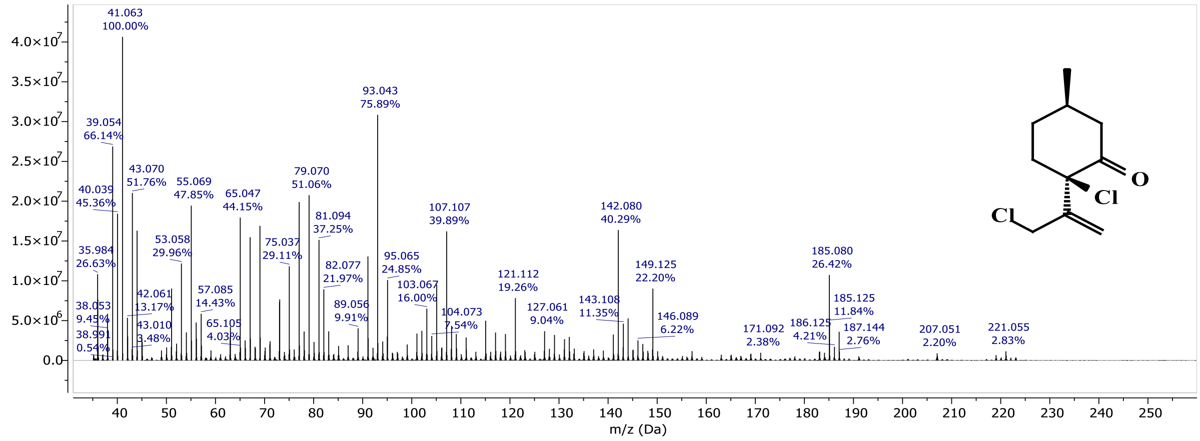

Figure S47: MS spectrum of the pulegone vinyl allyl dichloride **o**.

- Pulegone allyl dichloride **o’**

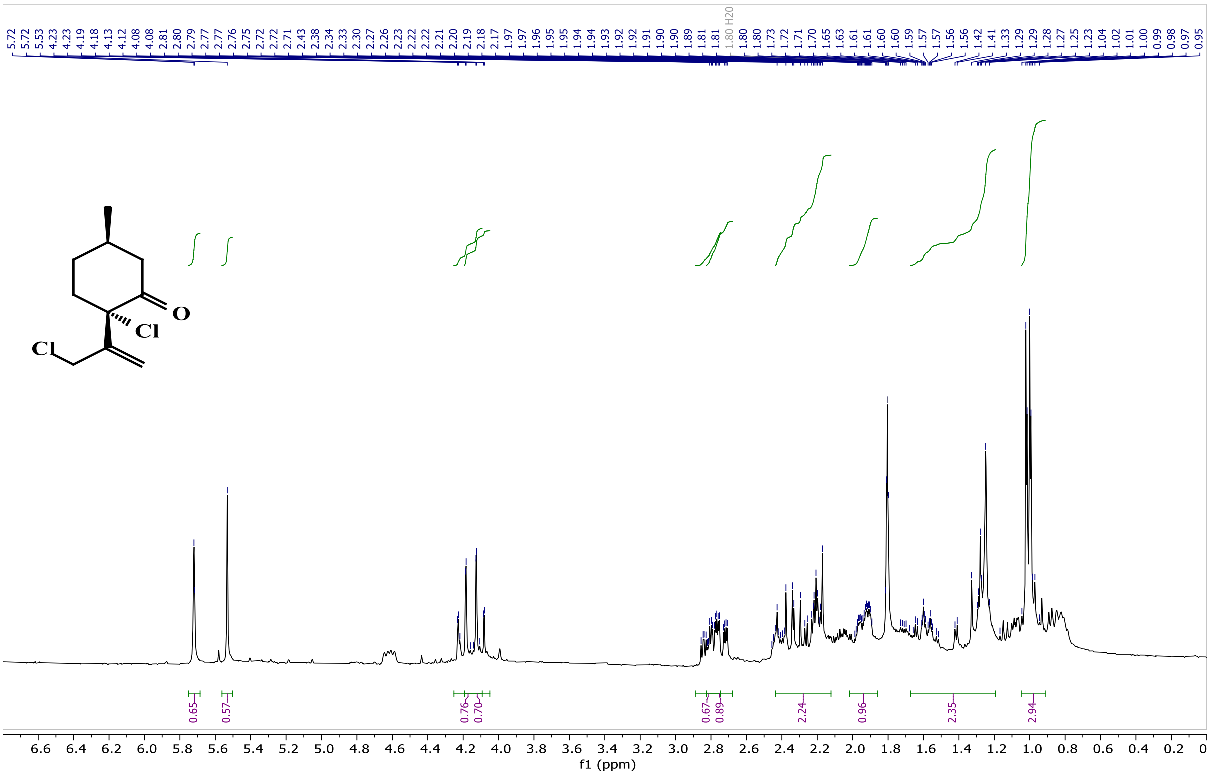

Figure S48: ^{1}H NMR spectrum of the pulegone vinyl allyl dichloride **o’**.

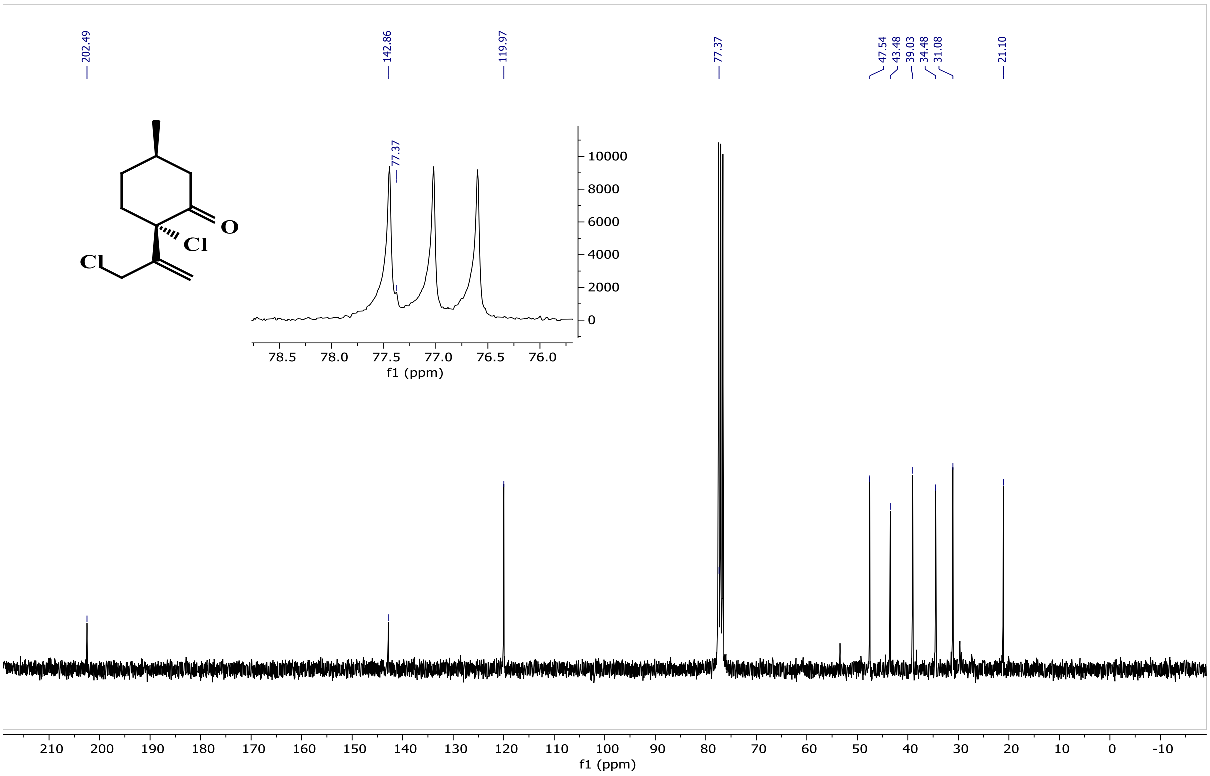

Figure S49: ^{13}C spectrum of the pulegone vinyl allyl dichloride **o'**.

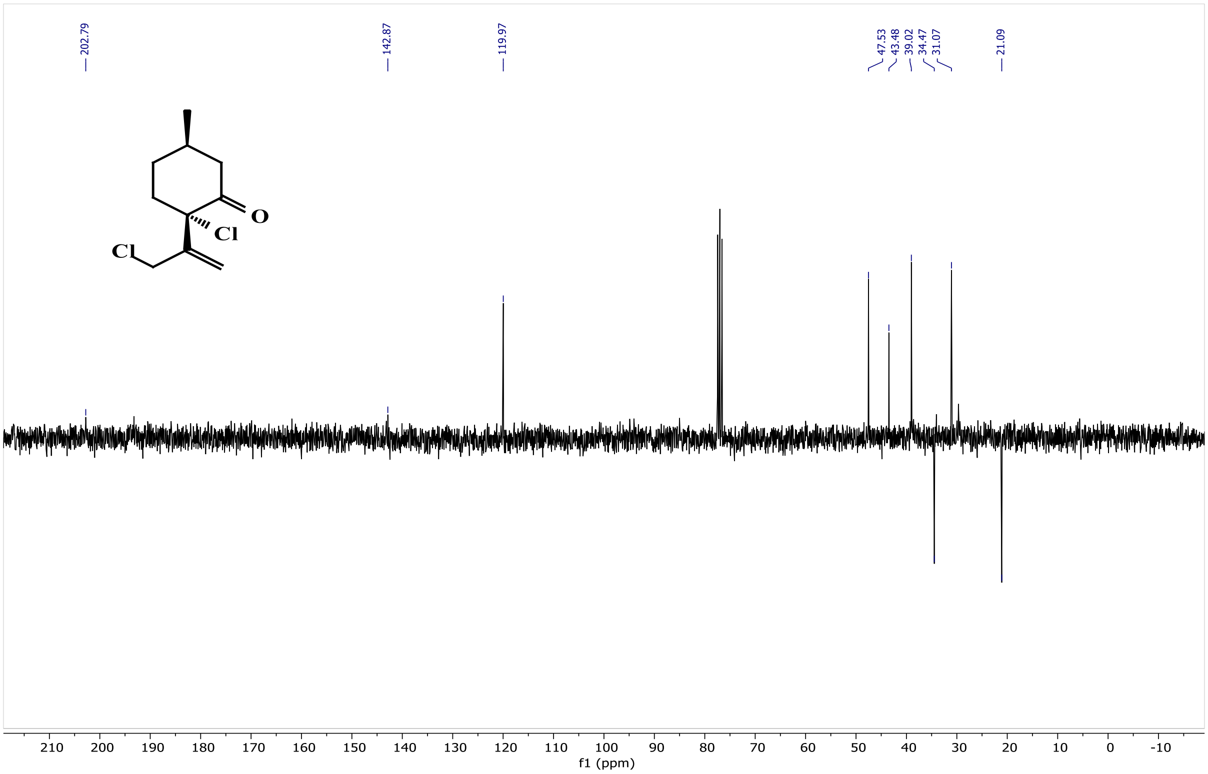

Figure S50: APT spectrum of the pulegone vinyl allyl dichloride **o'**.

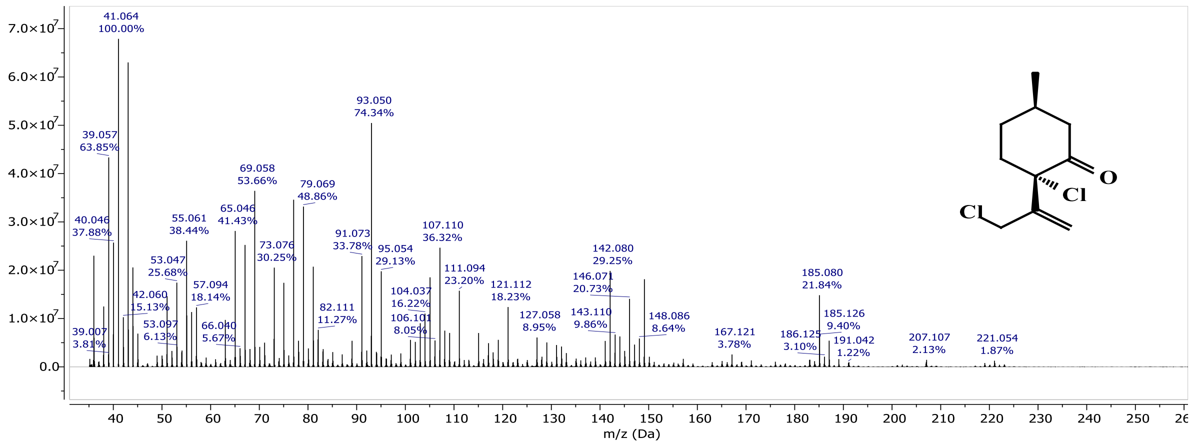

Figure S51: MS spectrum of the pulegone vinyl allyl dichloride **o'**.

➢ Derivatives of both perillyl aldehyde p and perillyl alcohol s

- Perillyl aldehyde monochloride **q**

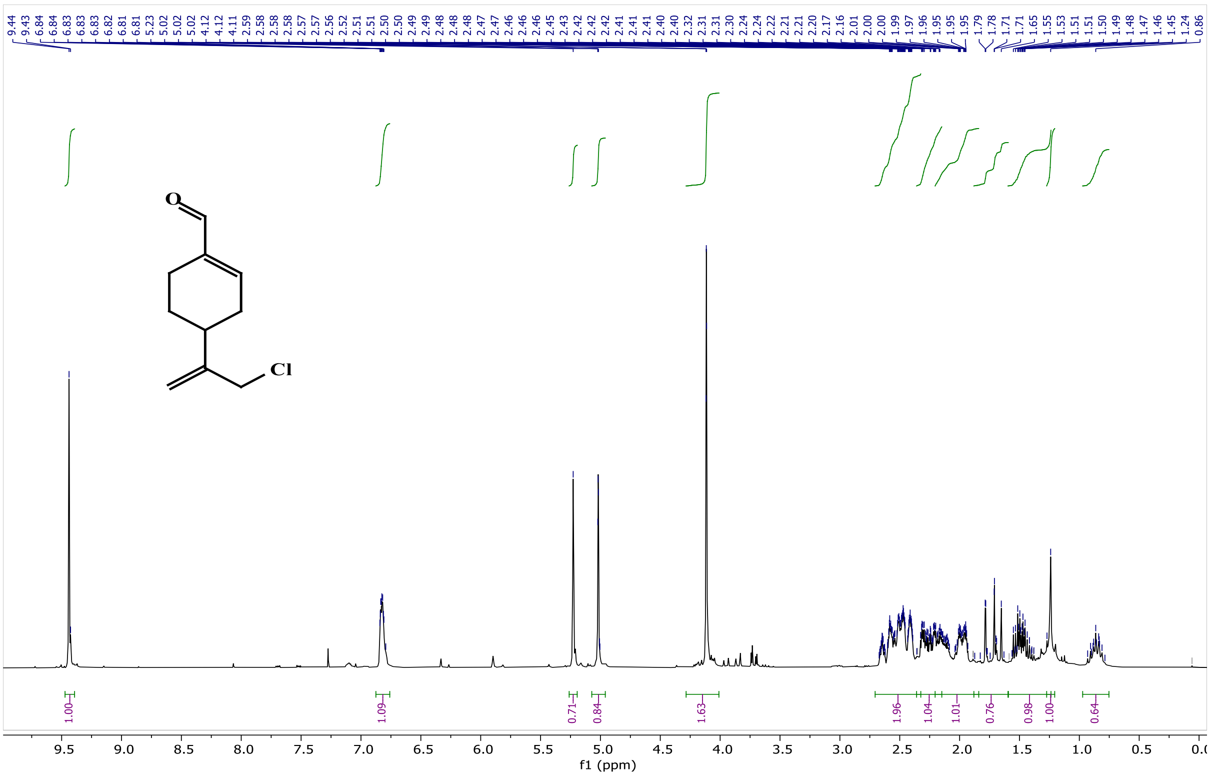

Figure S52: [1]H NMR spectrum of the perillyl aldehyde monochloride **q**.

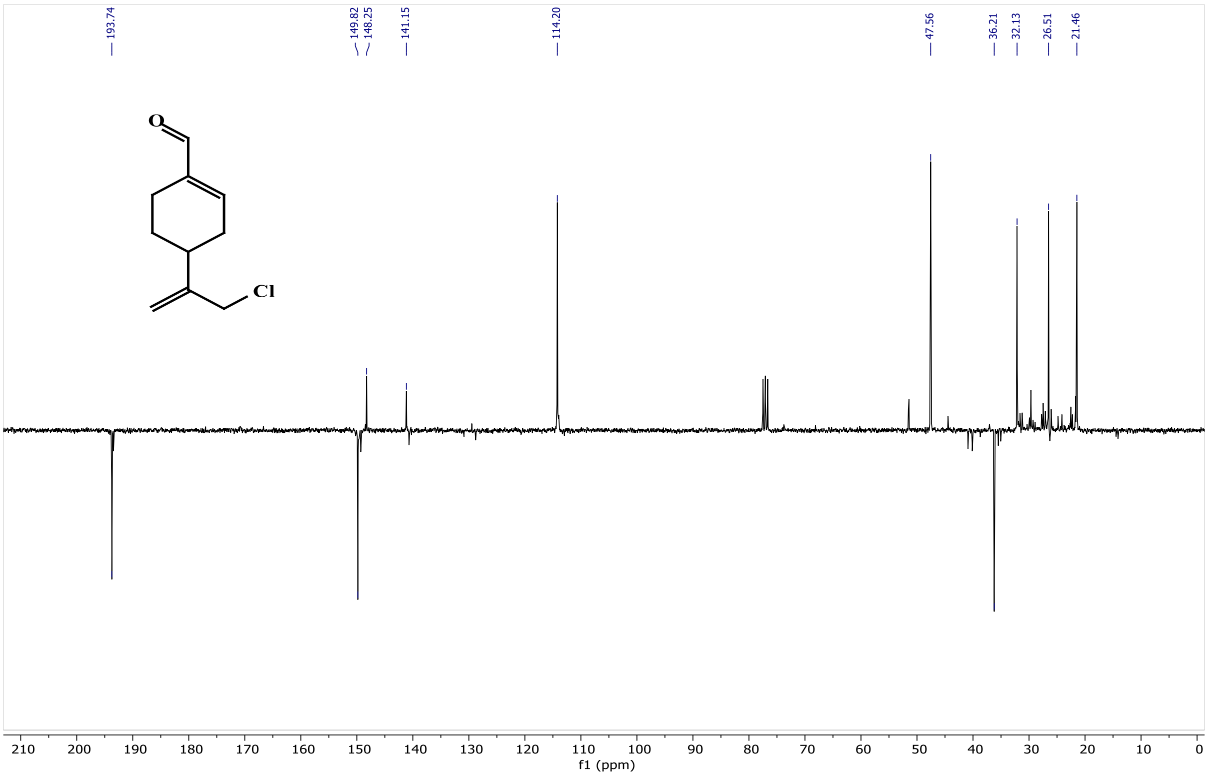

Figure S53: APT spectrum of the perillyl aldehyde monochloride **q**.

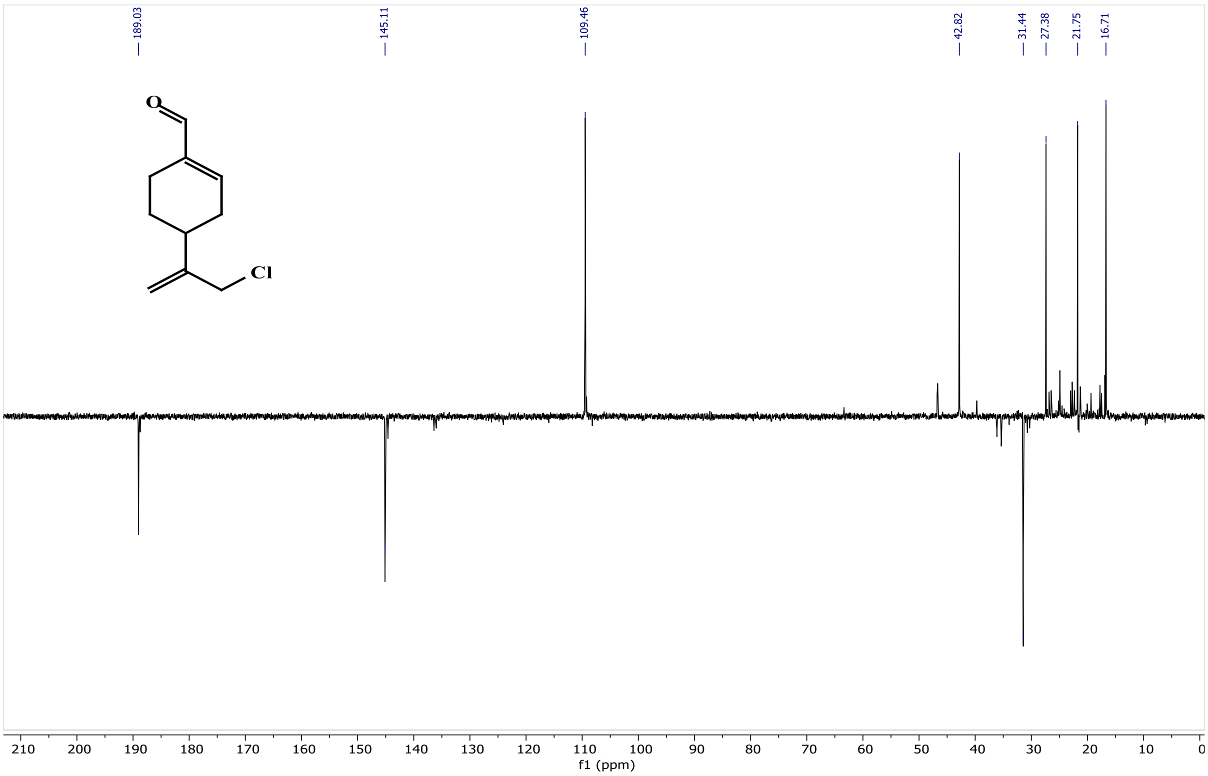

Figure S54: DEPT 135 spectrum of the perillyl aldehyde monochloride **q**.

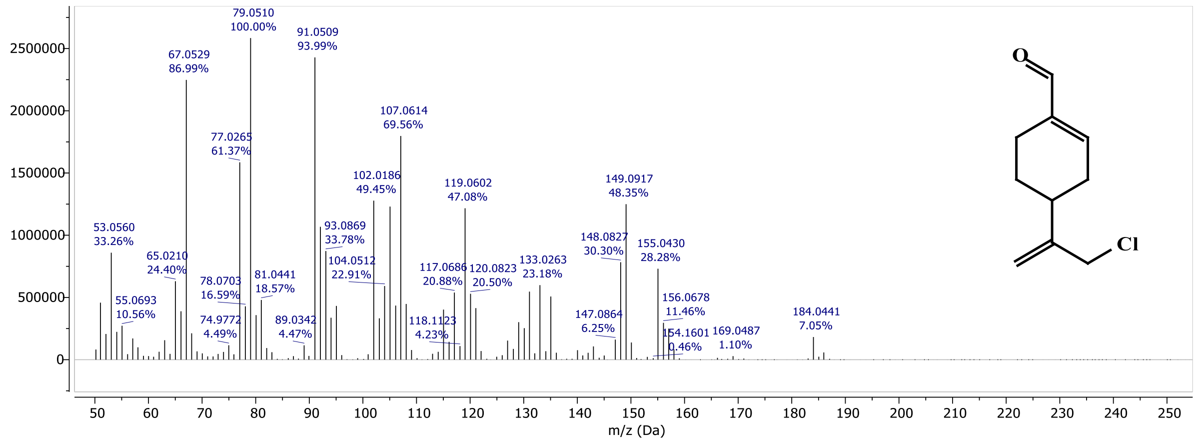

Figure S55: MS spectrum of the perillyl aldehyde monochloride **q**.

- Perillyl aldehyde vinyl allyl dichloride **r**

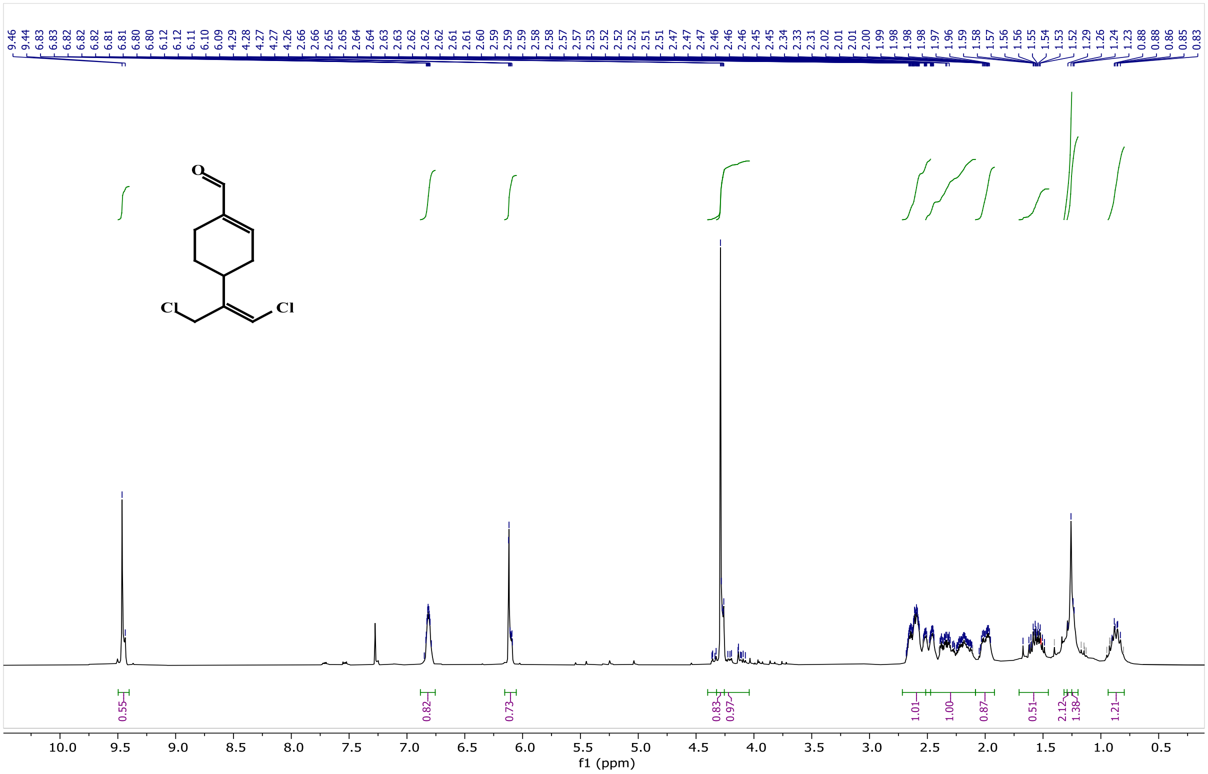

Figure S56: ^{1}H NMR spectrum of the perillyl aldehyde vinyl allyl dichloride **r**.

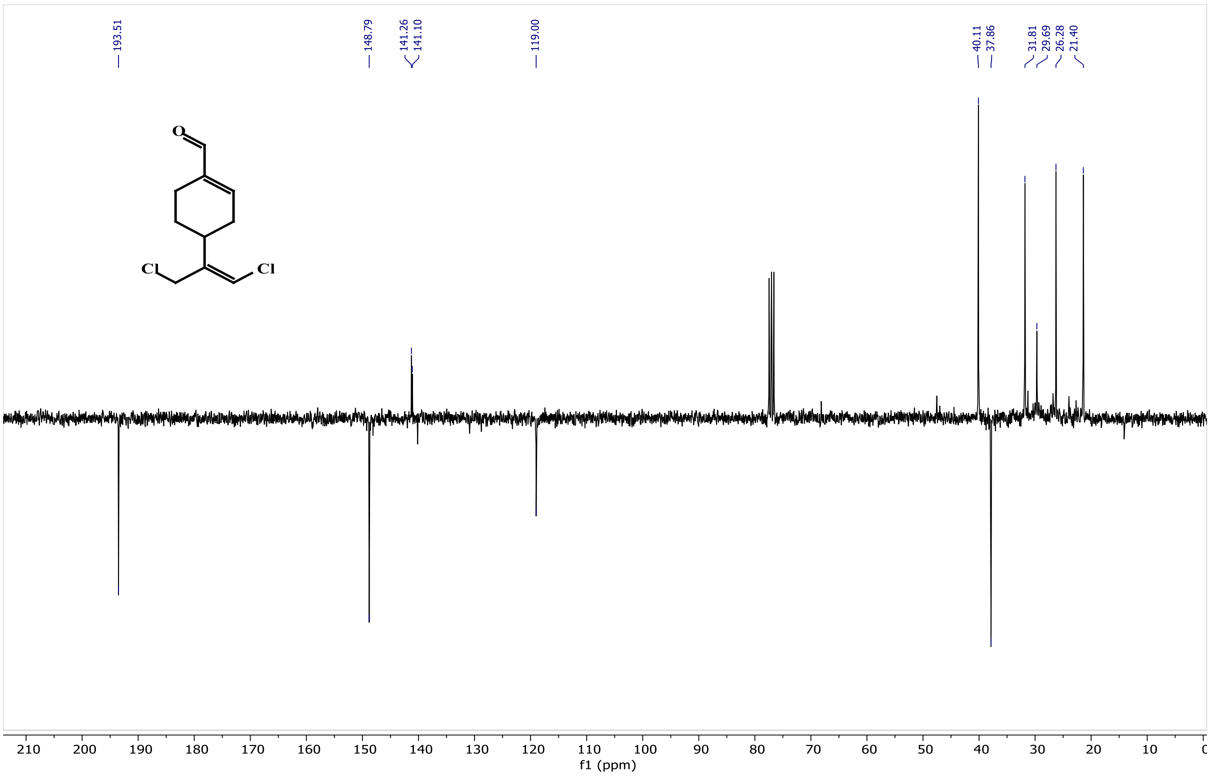

Figure S57: APT spectrum of the perillyl aldehyde vinyl allyl dichloride **r**.

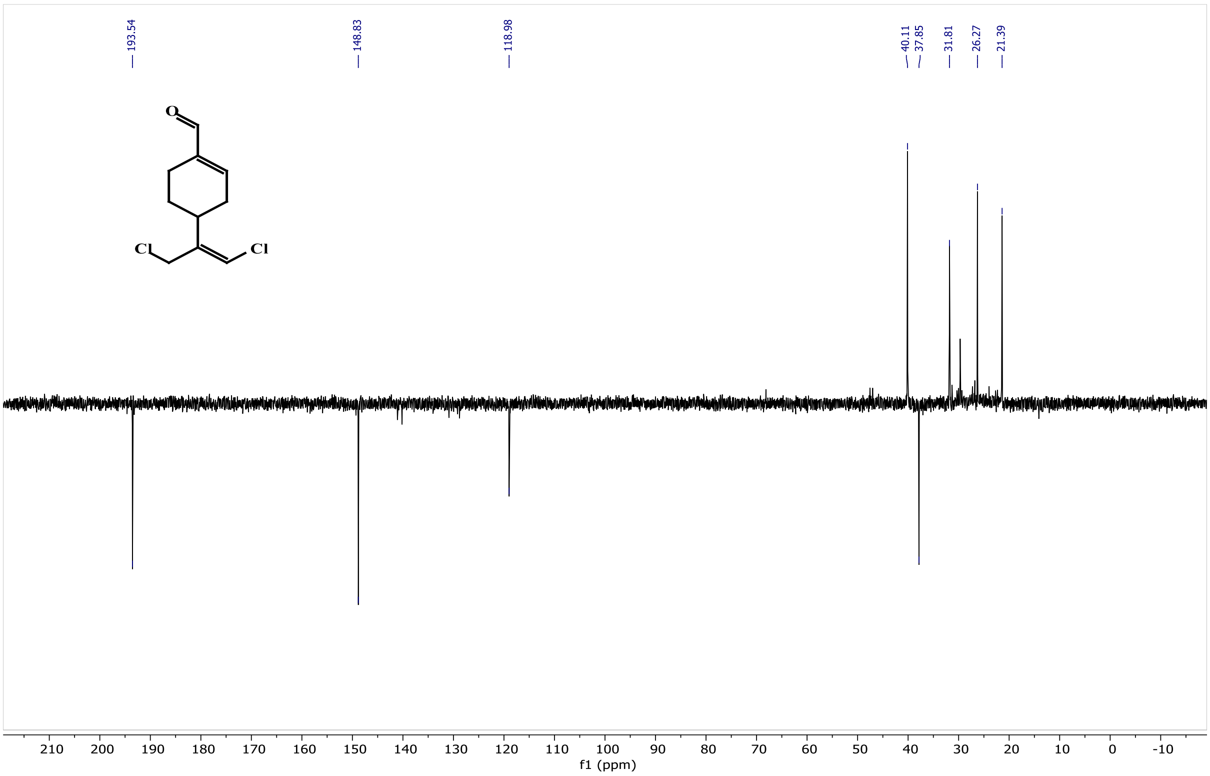

Figure S58: DEPT 135 spectrum of the perillyl aldehyde vinyl allyl dichloride **r**.

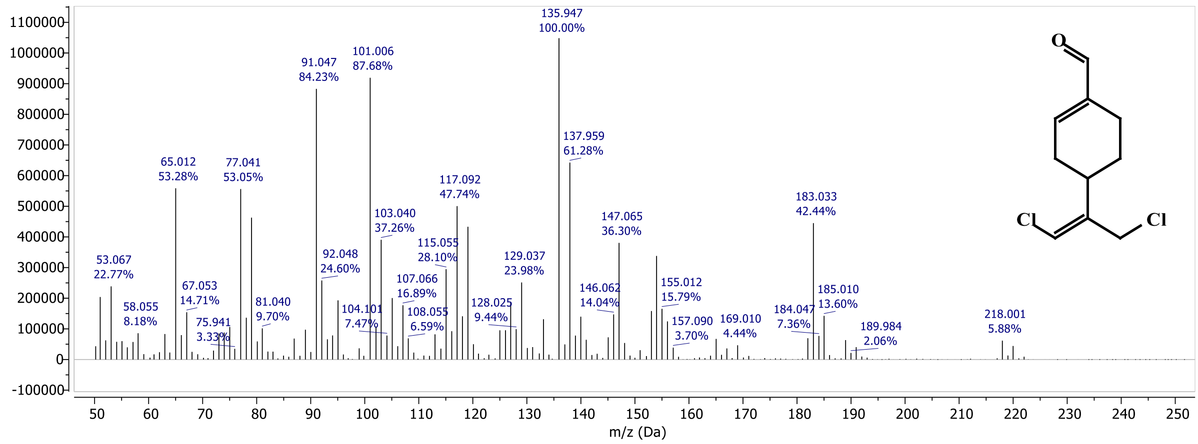

Figure S59: MS spectrum of the perillyl aldehyde vinyl allyl dichloride **r**.

➢ Derivatives of limona ketone t

- Limona ketone dichloride **u**

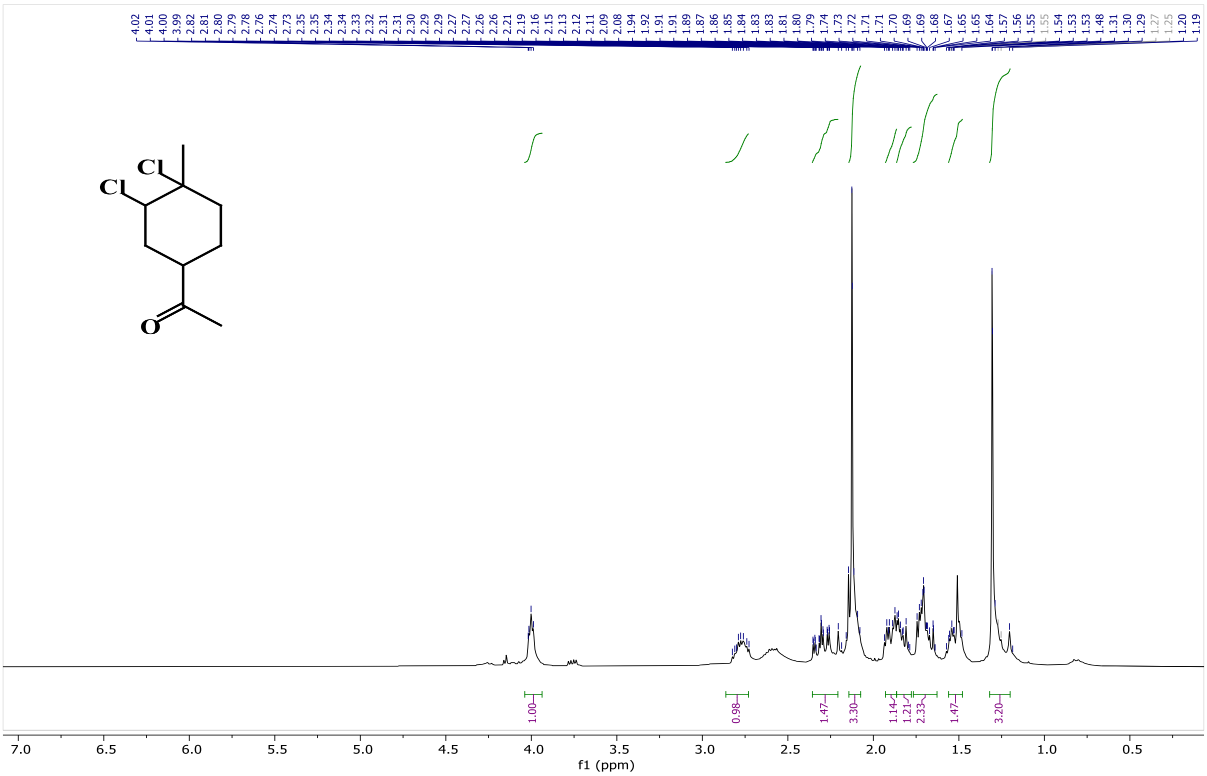

Figure S60: ^{1}H NMR spectrum of the limona ketone dichloride **u**.

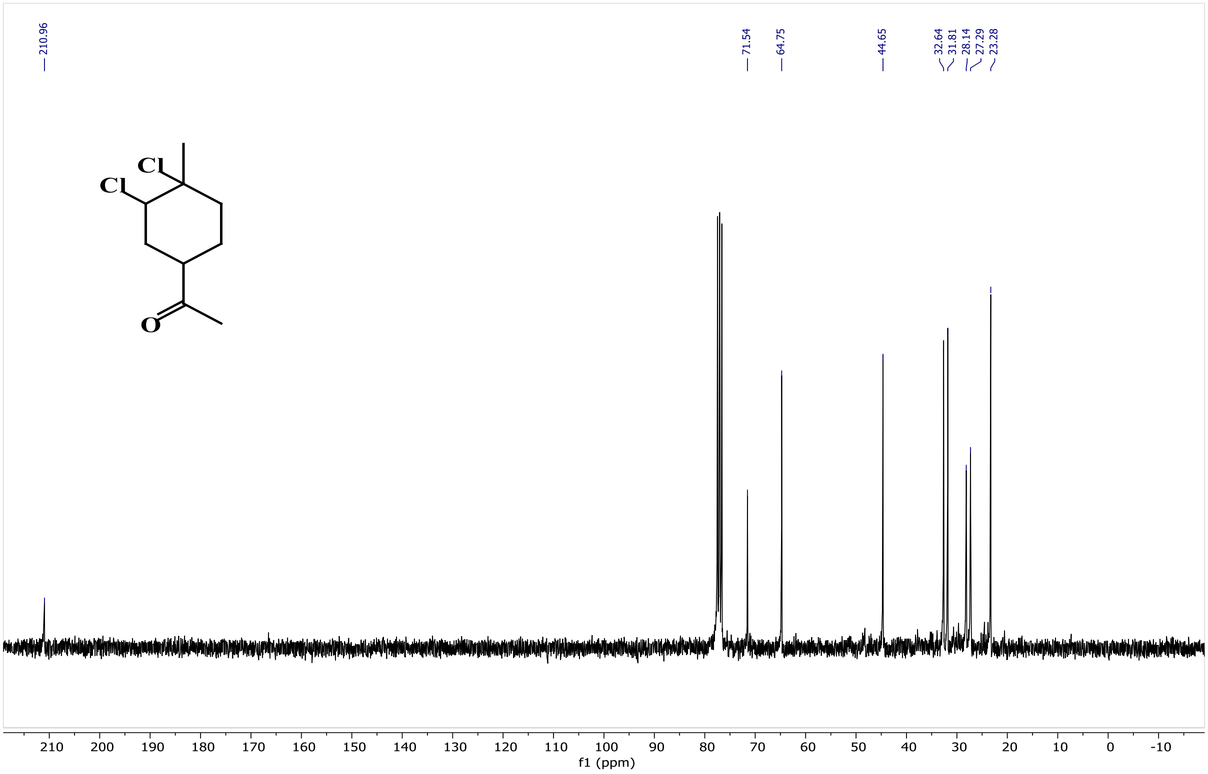

Figure S61: ^{13}C spectrum of the limona ketone dichloride **u**.

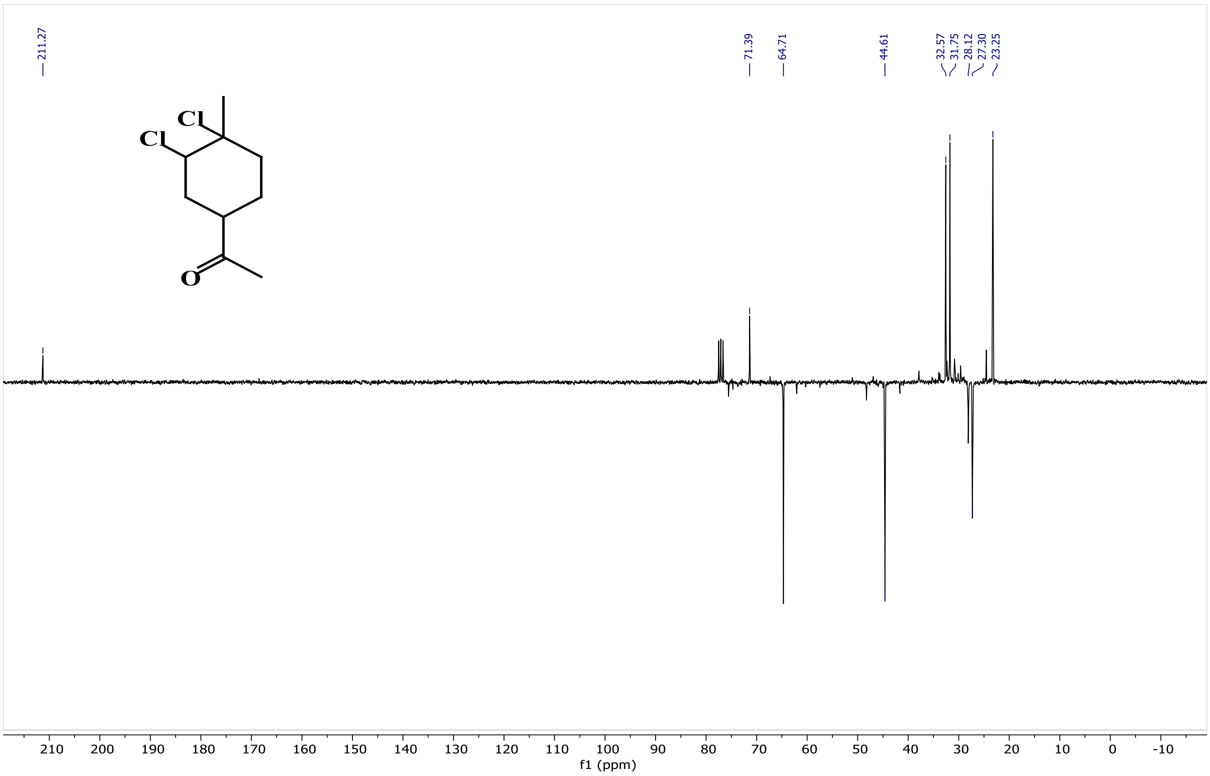

Figure S62: APT spectrum of the limona ketone dichloride **u**.

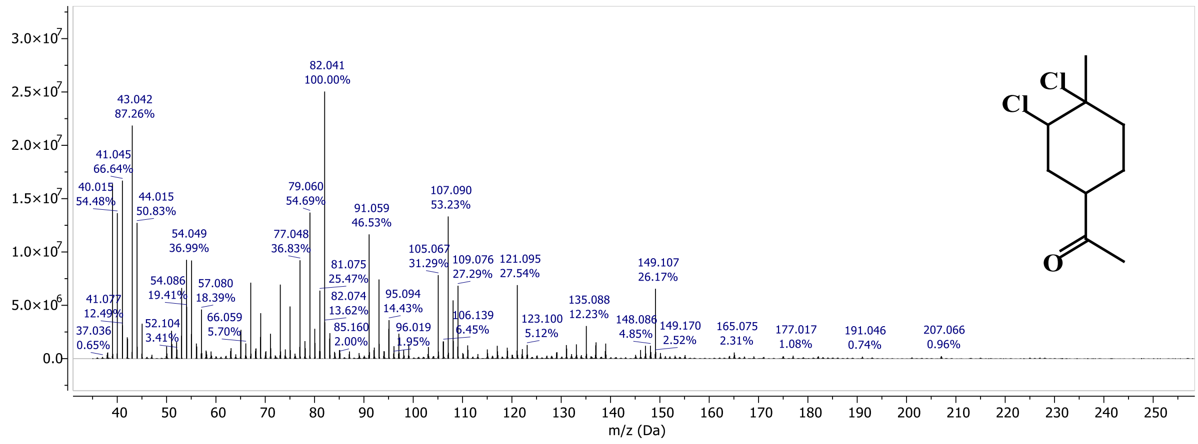

Figure S63: MS spectrum of the limona ketone dichloride **u**.

- Limona ketone epoxide **v**

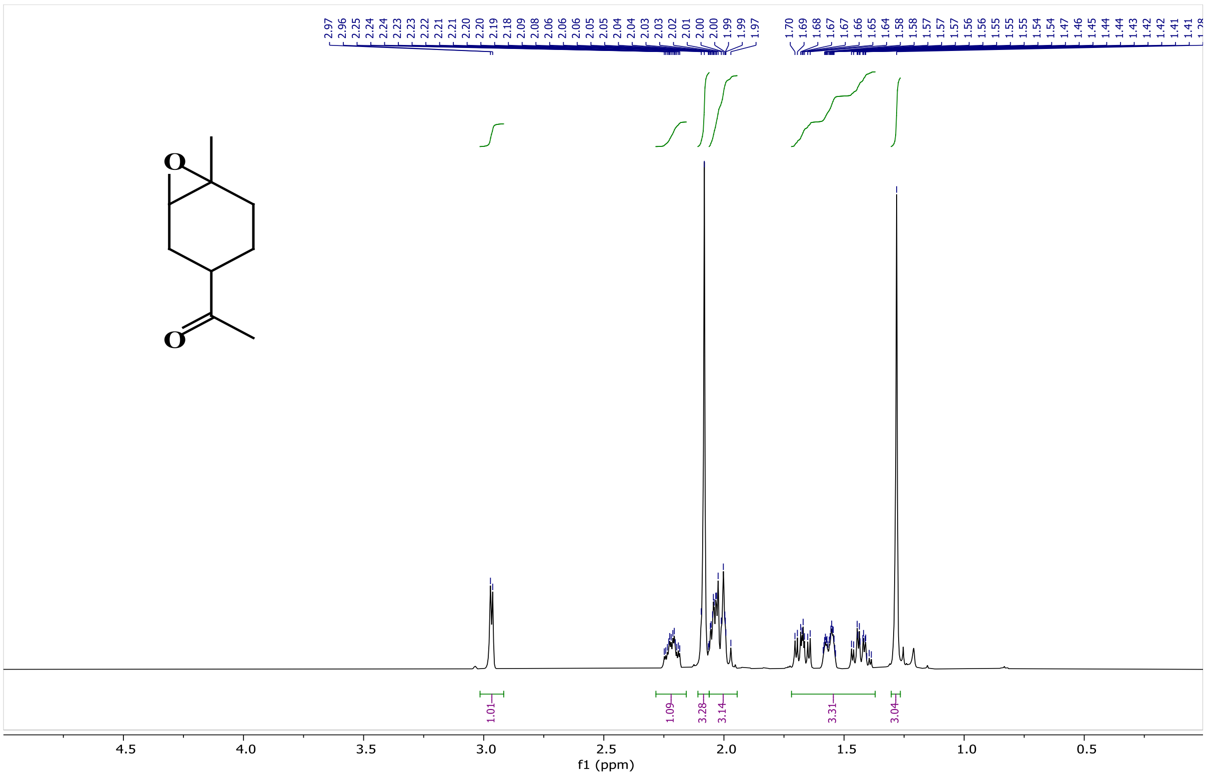

Figure S64: [1]H NMR spectrum of the limona ketone epoxide **v**.

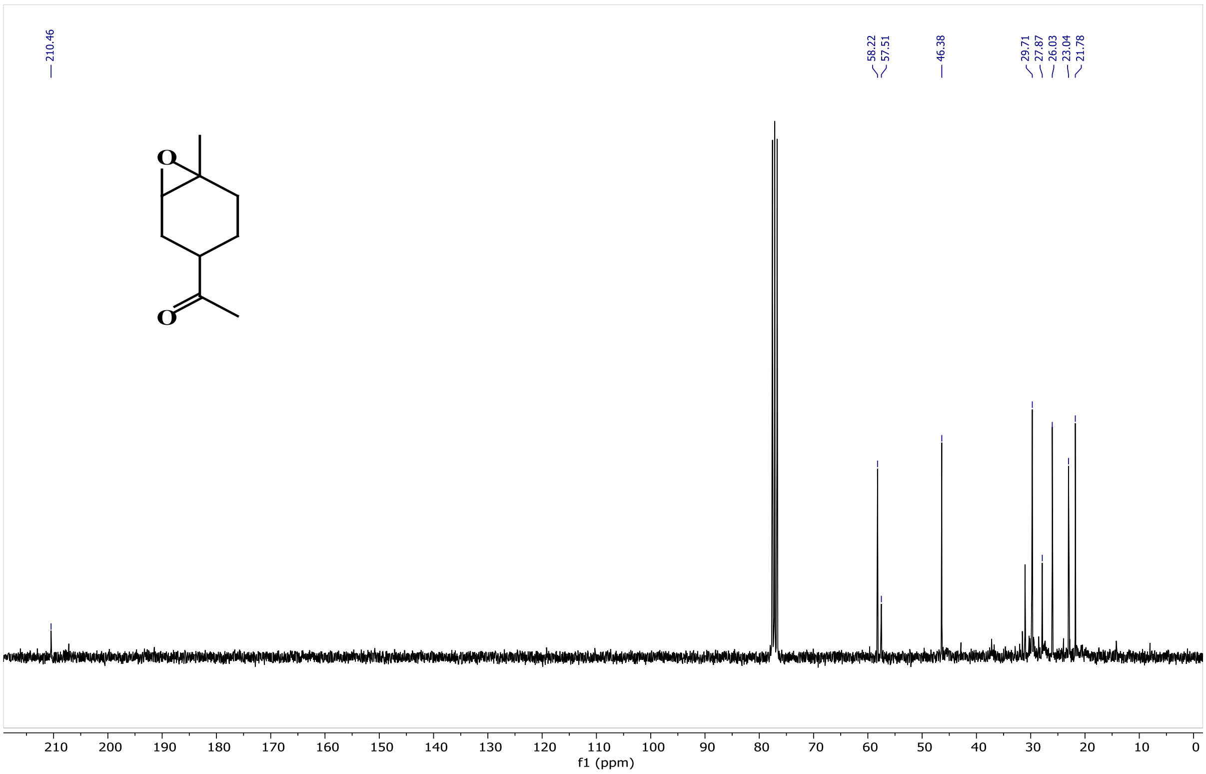

Figure S65: ^{13}C spectrum of the limona ketone epoxide **v**.

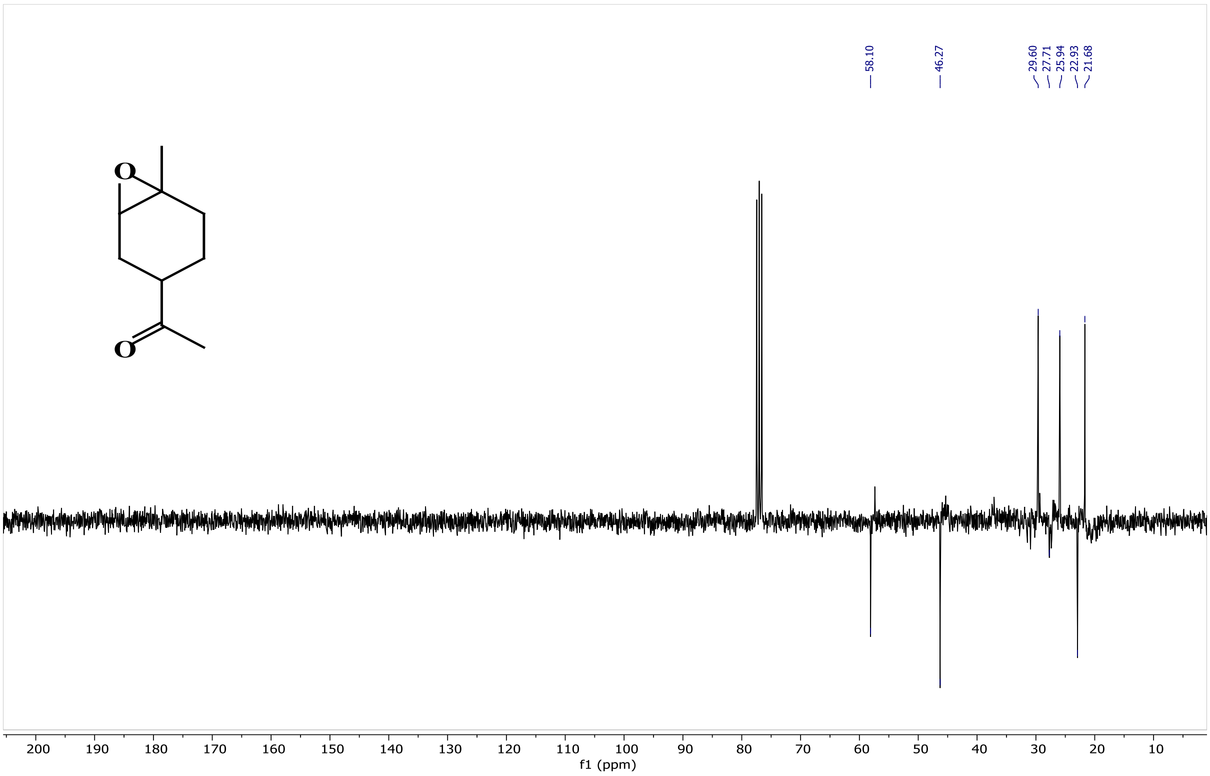

Figure S66: APT spectrum of the limona ketone epoxide **v**.

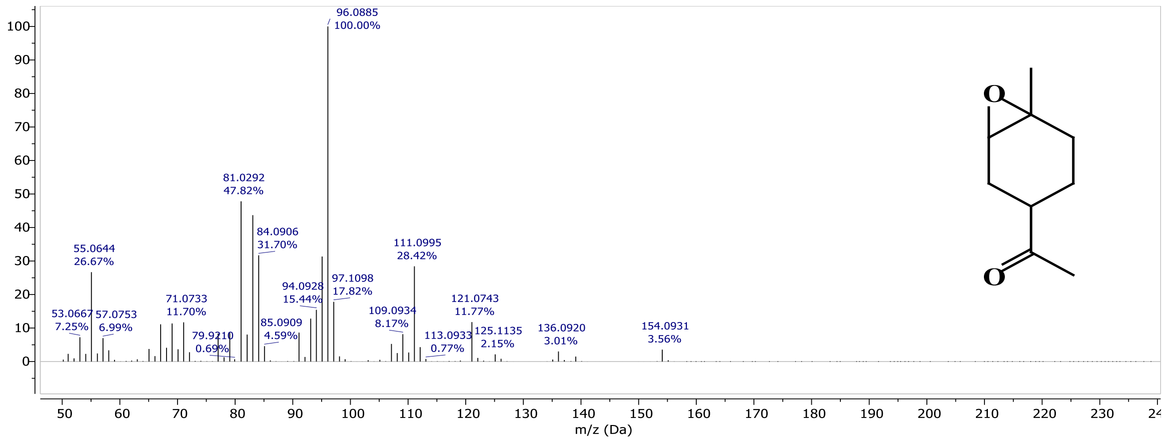

Figure S67: MS spectrum of the limona ketone dichloride v.