

# Supporting Information

for

## Elucidation of the regio- and chemoselectivity of enzymatic allylic oxidations with *Pleurotus sapidus* – conversion of selected spirocyclic terpenoids and computational analysis

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\*Corresponding author

## Computational details, experimental procedures, analytical data, NMR spectra and chromatograms of new compounds.

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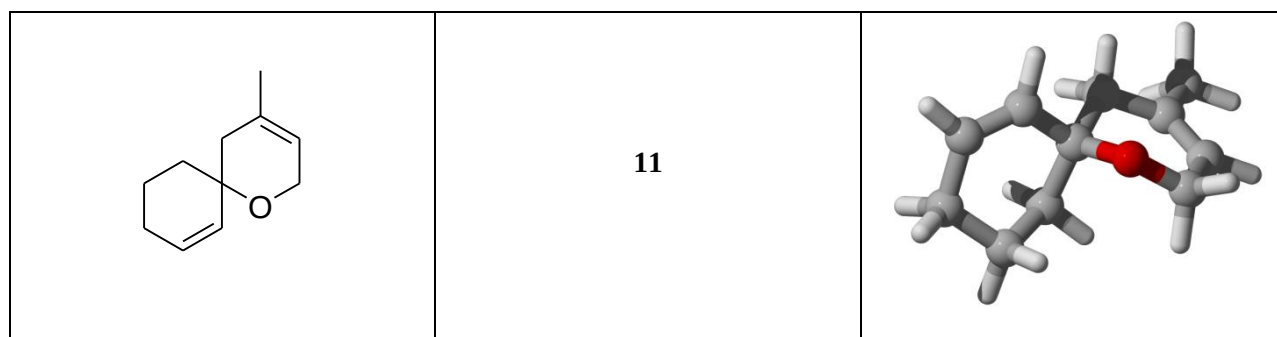
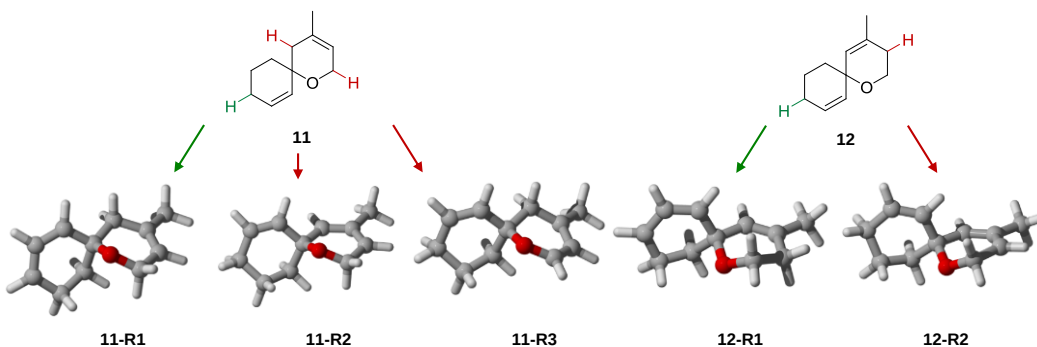
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## Computational details

All calculations have been conducted using the Gaussian09 suite of programs [1-5]. Density functional theory calculations were initially carried out at the B3LYP/6-31+G\*\* level of theory [6,7], as this level has previously provided adequate results in the calculation of BDEs of not highly activated bonds, e.g., strong bonds. Nevertheless, it has also been reported that the popular hybrid density functional B3LYP has (also) limitations concerning prediction of BDE values of weaker bonds. Therefore, a CBS-QB3 calculation [8-13] has been applied to smaller model systems (Table 1) of the allylic substructures in the compounds of interest to obtain accurate thermodynamic properties. Solvent effects were modeled using the implemented polarized continuum model (PCM) [14-16] applied as full optimizations and frequency analysis in the dielectric field (B3LYP/6-31G\* + PCM) for substrate and product structures. As a rough model for the Tris-buffer used in the experiments we have chosen water as the solvent. Stationary points were confirmed as ground states by calculated harmonic vibrational frequencies [17]. Approximate free energies were obtained through thermochemical analysis of the frequency calculations, using the thermal correction to the Gibbs free energy as reported in Gaussian09. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. All energies reported in this paper are enthalpies in kcal mol<sup>-1</sup> at 298 K if not stated otherwise. Frequencies remained unscaled. Population analysis on B3LYP/6-31+G\*\* level of theory has been done with the NBO program as implemented in Gaussian09 [18].

## Results obtained at B3LYP/6-31+G\*\* level of theory

Table 1 DFT results



### xyz-matrix

28

XYZ file generated by gabedit : coordinates in Angstrom

```

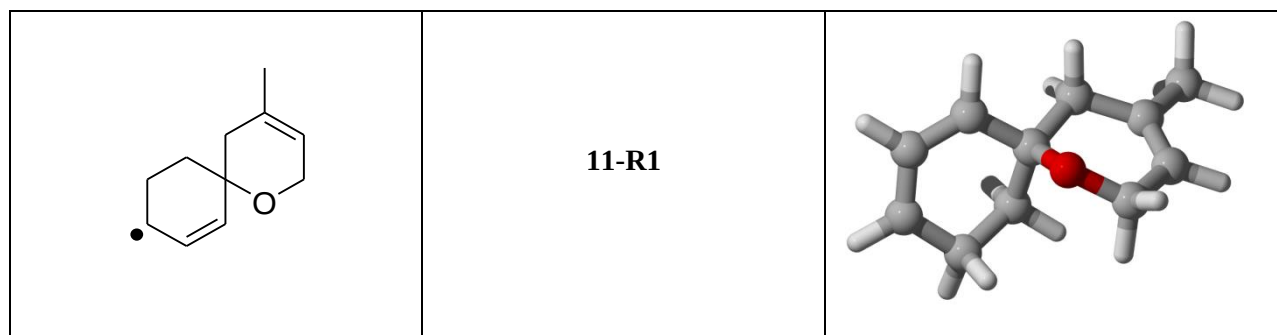
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C    -0.2917240000   -0.1404450000   -0.4332200000
C    -0.8011330000    0.2477120000    0.9732410000
O     0.0360540000    1.0362310000   -1.2176400000
C     1.1071200000    1.8352620000   -0.7235890000
C     2.2687960000    1.0443630000   -0.1935040000
C     2.2216250000   -0.2815440000   -0.0157030000
C     0.9600890000   -1.0427690000   -0.3620040000
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H    -2.5051350000    1.2153290000    1.9121800000
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H    -3.3921210000   -1.3833710000   -1.4745470000
H    -1.0739330000   -1.3328120000   -2.1305860000
H    -0.8374680000   -0.6609720000    1.5892240000
  
```

|   |               |               |               |
|---|---------------|---------------|---------------|
| H | -0.0869980000 | 0.9205950000  | 1.4583130000  |
| H | 0.7403730000  | 2.5332600000  | 0.0507770000  |
| H | 1.4202660000  | 2.4525770000  | -1.5745710000 |
| H | 3.1668170000  | 1.6081900000  | 0.0560980000  |
| H | 1.0996230000  | -1.5406830000 | -1.3326010000 |
| H | 0.7911800000  | -1.8456230000 | 0.3676840000  |
| H | 3.6700440000  | -1.8668190000 | -0.2286520000 |
| H | 3.1338580000  | -1.6031830000 | 1.4278740000  |
| H | 4.2652530000  | -0.4596370000 | 0.6739200000  |

### thermodynamic data

Zero-point correction= 0.247266 (Hartree/Particle)  
 Thermal correction to Energy= 0.258291  
 Thermal correction to Enthalpy= 0.259235  
 Thermal correction to Gibbs Free Energy= 0.211116  
 Sum of electronic and zero-point Energies= -503.784513  
 Sum of electronic and thermal Energies= -503.773489  
 Sum of electronic and thermal Enthalpies= -503.772544  
 Sum of electronic and thermal Free Energies= -503.820663

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 162.080                 | 44.664               | 101.275             |



### xyz-matrix

27

XYZ file generated by gabedit : coordinates in Angstrom

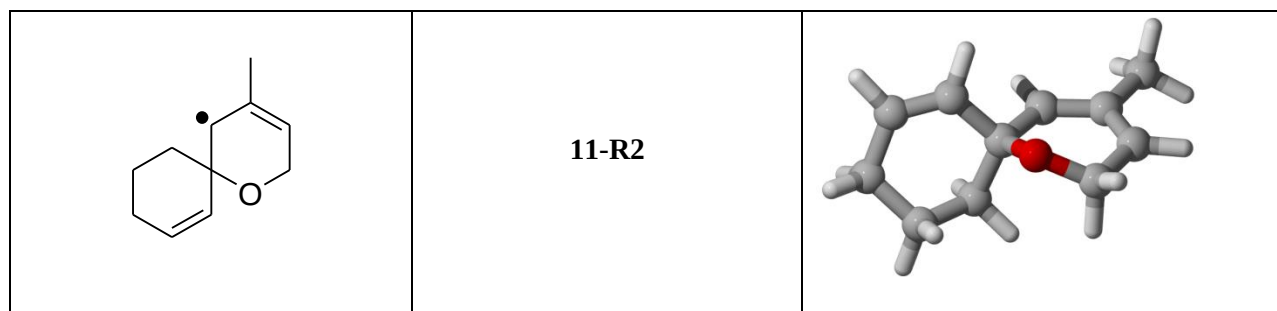
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| C | -2.8473980000 | -0.9080070000 | -0.7123570000 |
| C | -1.5040530000 | -1.0861140000 | -1.0236970000 |
| C | -0.4178750000 | -0.2755980000 | -0.3609330000 |
| C | -0.9100090000 | 0.2194560000  | 1.0185660000  |
| O | -0.1807960000 | 0.8460800000  | -1.2591870000 |
| C | 0.8503110000  | 1.7460510000  | -0.8620020000 |
| C | 2.0752480000  | 1.0694900000  | -0.3164710000 |
| C | 2.1123050000  | -0.2363040000 | -0.0241560000 |
| C | 0.8849180000  | -1.0939050000 | -0.2457890000 |

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | 3.3426950000  | -0.9292280000 | 0.4988530000  |
| H | -2.6475830000 | 1.1360270000  | 1.9478150000  |
| H | -2.1977570000 | 1.8572160000  | 0.4107680000  |
| H | -4.3422680000 | 0.1654360000  | 0.4029620000  |
| H | -3.5866040000 | -1.5142280000 | -1.2323250000 |
| H | -1.2099950000 | -1.7806020000 | -1.8059110000 |
| H | -0.9802500000 | -0.6529060000 | 1.6801530000  |
| H | -0.1741540000 | 0.8950000000  | 1.4660470000  |
| H | 0.4631480000  | 2.4768680000  | -0.1287640000 |
| H | 1.0977940000  | 2.3147470000  | -1.7666910000 |
| H | 2.9484320000  | 1.7006230000  | -0.1558570000 |
| H | 1.0207200000  | -1.6811560000 | -1.1656870000 |
| H | 0.7854140000  | -1.8253090000 | 0.5675590000  |
| H | 3.6422420000  | -1.7519870000 | -0.1644240000 |
| H | 3.1566020000  | -1.3740840000 | 1.4854480000  |
| H | 4.1881770000  | -0.2403950000 | 0.5874870000  |

### thermodynamic data

Zero-point correction= 0.233624 (Hartree/Particle)  
 Thermal correction to Energy= 0.244624  
 Thermal correction to Enthalpy= 0.245568  
 Thermal correction to Gibbs Free Energy= 0.196949  
 Sum of electronic and zero-point Energies= -503.157689  
 Sum of electronic and thermal Energies= -503.146689  
 Sum of electronic and thermal Enthalpies= -503.145745  
 Sum of electronic and thermal Free Energies= -503.194364

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 153.504                 | 44.670               | 102.327             |



### xyz-matrix

27

XYZ file generated by gabedit : coordinates in Angstrom

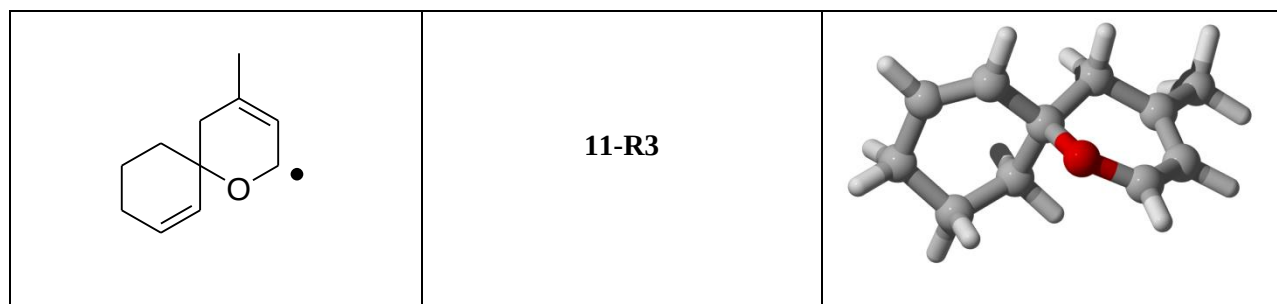
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| C | -2.4213050000 | 0.8355010000  | 0.7379220000  |
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| C | -1.1440680000 | -0.8755800000 | -1.1538410000 |
| C | -0.2397510000 | -0.0653380000 | -0.2417520000 |
| C | -0.9982500000 | 0.3559600000  | 1.0451930000  |
| O | 0.1201650000  | 1.0966870000  | -1.0288540000 |

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | 1.2574410000  | 1.8360280000  | -0.5876290000 |
| C | 2.4475360000  | 0.9727770000  | -0.3086990000 |
| C | 2.2769750000  | -0.3668990000 | 0.0289920000  |
| C | 0.9858460000  | -0.8792680000 | 0.1055440000  |
| C | 3.4742870000  | -1.2550480000 | 0.3005520000  |
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| H | -2.3690610000 | 1.6824210000  | 0.0434720000  |
| H | -4.1816290000 | 0.0947890000  | -0.3099190000 |
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| H | -0.6479870000 | -1.3677390000 | -1.9871960000 |
| H | -1.0372690000 | -0.5063360000 | 1.7244580000  |
| H | -0.4201560000 | 1.1307280000  | 1.5609550000  |
| H | 1.0011350000  | 2.4372270000  | 0.3058080000  |
| H | 1.4670080000  | 2.5488200000  | -1.3930190000 |
| H | 3.4352120000  | 1.4260820000  | -0.3318950000 |
| H | 0.8156370000  | -1.9008940000 | 0.4361110000  |
| H | 3.2176340000  | -2.0714770000 | 0.9826030000  |
| H | 4.2986030000  | -0.6879830000 | 0.7445410000  |
| H | 3.8453430000  | -1.7049510000 | -0.6281060000 |

### thermodynamic data

Zero-point correction= 0.233171 (Hartree/Particle)  
 Thermal correction to Energy= 0.244558  
 Thermal correction to Enthalpy= 0.245502  
 Thermal correction to Gibbs Free Energy= 0.195131  
 Sum of electronic and zero-point Energies= -503.154862  
 Sum of electronic and thermal Energies= -503.143474  
 Sum of electronic and thermal Enthalpies= -503.142530  
 Sum of electronic and thermal Free Energies= -503.192901

|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 153.463     | 44.981         | 106.015        |



### xyz-matrix

27

XYZ file generated by gabedit : coordinates in Angstrom

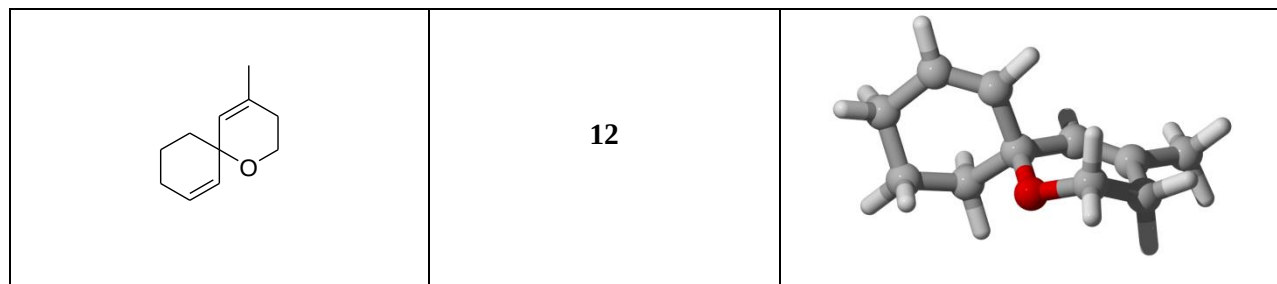
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|   |               |               |               |
|---|---------------|---------------|---------------|
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| C | -0.7280770000 | 0.1601810000  | 0.9894400000  |
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| C | 1.2361650000  | 1.9157060000  | -0.6232140000 |
| C | 2.2957770000  | 1.1692870000  | -0.1278860000 |
| C | 2.2321620000  | -0.2174180000 | -0.0445590000 |
| C | 0.9931040000  | -0.8722170000 | -0.5984200000 |
| C | 3.3595380000  | -1.0732760000 | 0.4453370000  |
| H | -2.4164420000 | 0.8974570000  | 2.1367550000  |
| H | -2.1308000000 | 1.7544870000  | 0.6217260000  |
| H | -4.1112880000 | 0.3964780000  | 0.2441120000  |
| H | -3.3878320000 | -1.0168780000 | 0.9839390000  |
| H | -3.3798320000 | -0.9977830000 | -1.6698420000 |
| H | -1.0777690000 | -0.8040150000 | -2.3589800000 |
| H | -0.7237330000 | -0.8389700000 | 1.4460210000  |
| H | -0.0030530000 | 0.7660700000  | 1.5411170000  |
| H | 1.2649610000  | 2.9870800000  | -0.7835230000 |
| H | 3.1898170000  | 1.7051930000  | 0.1806330000  |
| H | 1.1461720000  | -1.1143380000 | -1.6636940000 |
| H | 0.7885990000  | -1.8277610000 | -0.0989780000 |
| H | 3.0477980000  | -1.7158840000 | 1.2820760000  |
| H | 4.2064990000  | -0.4680700000 | 0.7839390000  |
| H | 3.7265420000  | -1.7506420000 | -0.3414190000 |

### thermodynamic data

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.233807 (Hartree/Particle) |
| Thermal correction to Energy=                | 0.244924                    |
| Thermal correction to Enthalpy=              | 0.245869                    |
| Thermal correction to Gibbs Free Energy=     | 0.196827                    |
| Sum of electronic and zero-point Energies=   | -503.167329                 |
| Sum of electronic and thermal Energies=      | -503.156211                 |
| Sum of electronic and thermal Enthalpies=    | -503.155267                 |
| Sum of electronic and thermal Free Energies= | -503.204308                 |

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 153.692                 | 44.680               | 103.216             |



xyz-matrix

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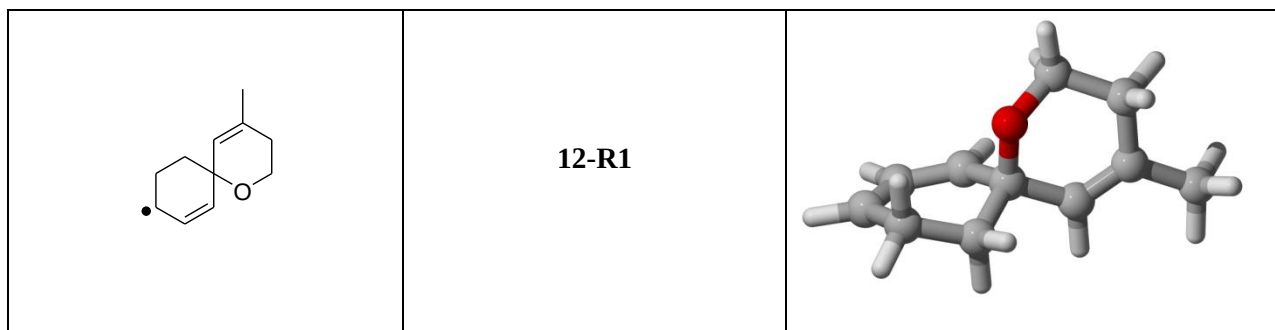
XYZ file generated by gabedit : coordinates in Angstrom

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| C | 2.4171650000  | -0.1116650000 | 1.3726180000  |
| C | 1.0861780000  | 0.0046700000  | 1.2765840000  |
| C | 0.3270960000  | -0.0029510000 | -0.0465860000 |
| C | 1.2376650000  | -0.5119490000 | -1.1829450000 |
| O | -0.0296200000 | 1.3513170000  | -0.4212660000 |
| C | -1.1792130000 | 1.8694850000  | 0.2400690000  |
| C | -2.4279840000 | 1.0681580000  | -0.1237820000 |
| C | -2.1673000000 | -0.4156100000 | 0.0112700000  |
| C | -0.9084620000 | -0.8736530000 | 0.0634310000  |
| C | -3.3687610000 | -1.3219670000 | 0.0717950000  |
| H | 3.2314100000  | -0.2030290000 | -1.9839360000 |
| H | 2.5288740000  | 1.2118010000  | -1.1976260000 |
| H | 4.2225050000  | 0.3908770000  | 0.3391010000  |
| H | 3.7199500000  | -1.2749340000 | 0.1405190000  |
| H | 2.8765970000  | -0.1138860000 | 2.3606630000  |
| H | 0.4896700000  | 0.1069820000  | 2.1806900000  |
| H | 1.3277490000  | -1.6030750000 | -1.0967510000 |
| H | 0.7409150000  | -0.2971050000 | -2.1344160000 |
| H | -1.2607780000 | 2.9115460000  | -0.0819980000 |
| H | -1.0323760000 | 1.8641340000  | 1.3309370000  |
| H | -2.7416630000 | 1.2987490000  | -1.1523620000 |
| H | -3.2616840000 | 1.3652250000  | 0.5283370000  |
| H | -0.7202640000 | -1.9391960000 | 0.1882560000  |
| H | -3.0798870000 | -2.3750450000 | 0.1396710000  |
| H | -3.9972190000 | -1.1975450000 | -0.8203640000 |
| H | -4.0010080000 | -1.0822700000 | 0.9371050000  |

### thermodynamic data

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.247452 (Hartree/Particle) |
| Thermal correction to Energy=                | 0.258529                    |
| Thermal correction to Enthalpy=              | 0.259473                    |
| Thermal correction to Gibbs Free Energy=     | 0.211110                    |
| Sum of electronic and zero-point Energies=   | -503.786426                 |
| Sum of electronic and thermal Energies=      | -503.775349                 |
| Sum of electronic and thermal Enthalpies=    | -503.774405                 |
| Sum of electronic and thermal Free Energies= | -503.822768                 |

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 162.229                 | 44.665               | 101.788             |



### xyz-matrix

27

XYZ file generated by gabedit : coordinates in Angstrom

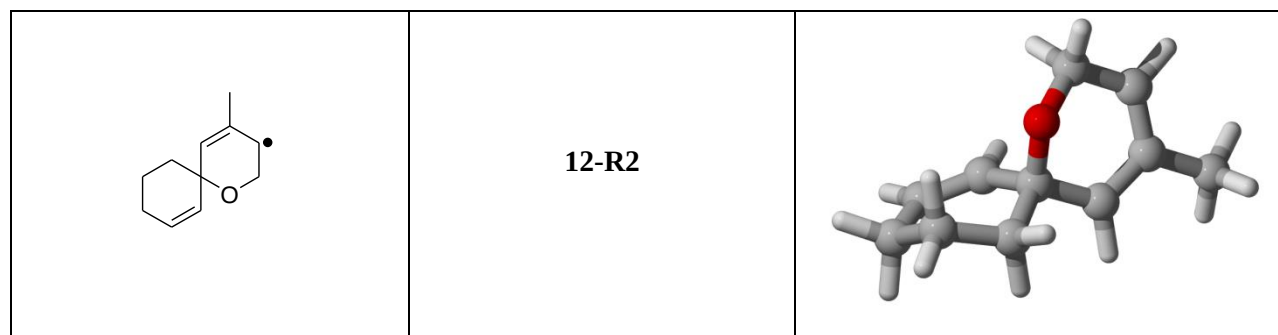
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| C | 2.5871520000  | 0.0188220000  | 1.3630070000  |
| C | 1.1955400000  | -0.0173440000 | 1.3151770000  |
| C | 0.4495730000  | -0.1124090000 | -0.0042770000 |
| C | 1.3521250000  | -0.7762810000 | -1.0645580000 |
| O | 0.1802190000  | 1.2182090000  | -0.5236880000 |
| C | -0.9340270000 | 1.8685810000  | 0.0802700000  |
| C | -2.2302450000 | 1.1145630000  | -0.2130150000 |
| C | -2.0632520000 | -0.3654440000 | 0.0512770000  |
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| C | -3.3197810000 | -1.1870970000 | 0.1716460000  |
| H | 3.3884920000  | -0.7023360000 | -1.8189220000 |
| H | 2.6550190000  | 0.8756830000  | -1.5734200000 |
| H | 4.4573530000  | 0.0385050000  | 0.3027170000  |
| H | 3.0722860000  | 0.1025820000  | 2.3338960000  |
| H | 0.6168700000  | 0.0527060000  | 2.2315430000  |
| H | 1.4602030000  | -1.8360750000 | -0.8027680000 |
| H | 0.8462860000  | -0.7212190000 | -2.0335240000 |
| H | -0.9516760000 | 2.8783600000  | -0.3395100000 |
| H | -0.7839130000 | 1.9564720000  | 1.1669580000  |
| H | -2.5325580000 | 1.2713650000  | -1.2588200000 |
| H | -3.0425830000 | 1.5190360000  | 0.4075670000  |
| H | -0.7158040000 | -1.9570720000 | 0.3677170000  |
| H | -3.0983260000 | -2.2467380000 | 0.3301620000  |
| H | -3.9327660000 | -1.0985940000 | -0.7354510000 |
| H | -3.9421060000 | -0.8373780000 | 1.0061420000  |

### thermodynamic data

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.233799 (Hartree/Particle) |
| Thermal correction to Energy=                | 0.244858                    |
| Thermal correction to Enthalpy=              | 0.245803                    |
| Thermal correction to Gibbs Free Energy=     | 0.196913                    |
| Sum of electronic and zero-point Energies=   | -503.160545                 |
| Sum of electronic and thermal Energies=      | -503.149485                 |
| Sum of electronic and thermal Enthalpies=    | -503.148541                 |
| Sum of electronic and thermal Free Energies= | -503.197431                 |

|             |                |                |
|-------------|----------------|----------------|
| E (Thermal) | CV             | S              |
| KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |

|       |         |        |         |
|-------|---------|--------|---------|
| Total | 153.651 | 44.674 | 102.897 |
|-------|---------|--------|---------|



### xyz-matrix

27

XYZ file generated by gabedit : coordinates in Angstrom

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | 2.6259590000  | 0.0731780000  | -1.0318610000 |
| C | 3.1937190000  | -0.2166740000 | 0.3648300000  |
| C | 2.1563410000  | -0.0246000000 | 1.4408420000  |
| C | 0.8420960000  | 0.0825330000  | 1.2017590000  |
| C | 0.2230650000  | -0.0113210000 | -0.1895410000 |
| C | 1.2439910000  | -0.5685140000 | -1.1985960000 |
| O | -0.1176710000 | 1.3105100000  | -0.6860340000 |
| C | -1.2007350000 | 1.9548990000  | -0.0255410000 |
| C | -2.4007390000 | 1.0701450000  | 0.1281700000  |
| C | -2.2848480000 | -0.3116830000 | 0.0285920000  |
| C | -1.0174030000 | -0.8701940000 | -0.1371790000 |
| C | -3.5126710000 | -1.1979850000 | 0.0865720000  |
| H | 3.3096650000  | -0.2973100000 | -1.8044110000 |
| H | 2.5334420000  | 1.1559220000  | -1.1739970000 |
| H | 4.0592450000  | 0.4264350000  | 0.5715740000  |
| H | 3.5755880000  | -1.2492330000 | 0.4146370000  |
| H | 2.5109690000  | 0.0256280000  | 2.4699370000  |
| H | 0.1534310000  | 0.2279270000  | 2.0313600000  |
| H | 1.3221000000  | -1.6536810000 | -1.0491470000 |
| H | 0.8483850000  | -0.4018040000 | -2.2055590000 |
| H | -1.4394620000 | 2.8272510000  | -0.6454730000 |
| H | -0.8761870000 | 2.3468430000  | 0.9567230000  |
| H | -3.3609130000 | 1.5386120000  | 0.3297040000  |
| H | -0.8863920000 | -1.9488570000 | -0.1675430000 |
| H | -3.2965250000 | -2.1469860000 | 0.5874820000  |
| H | -3.8738870000 | -1.4321440000 | -0.9219710000 |
| H | -4.3305520000 | -0.7089060000 | 0.6246730000  |

### thermodynamic data

|                                            |                             |
|--------------------------------------------|-----------------------------|
| Zero-point correction=                     | 0.233222 (Hartree/Particle) |
| Thermal correction to Energy=              | 0.244635                    |
| Thermal correction to Enthalpy=            | 0.245579                    |
| Thermal correction to Gibbs Free Energy=   | 0.194828                    |
| Sum of electronic and zero-point Energies= | -503.155675                 |
| Sum of electronic and thermal Energies=    | -503.144262                 |

Sum of electronic and thermal Enthalpies= -503.143318  
 Sum of electronic and thermal Free Energies= -503.194069

|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 153.511     | 44.947         | 106.815        |

|  |                          |  |
|--|--------------------------|--|
|  | <b>H (hydrogen atom)</b> |  |
|--|--------------------------|--|

**xyz-matrix**

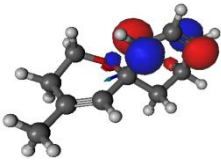
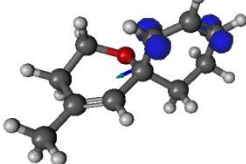
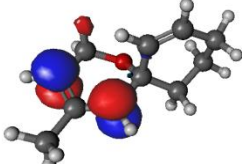
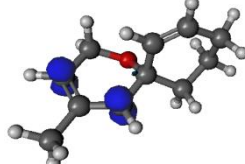
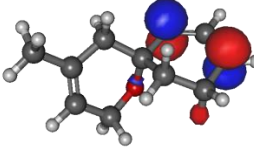
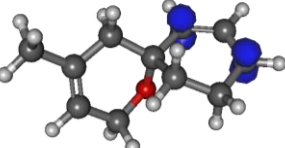
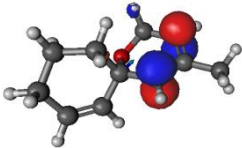
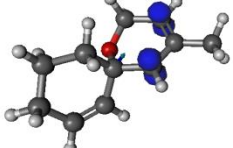
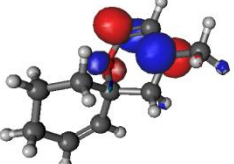
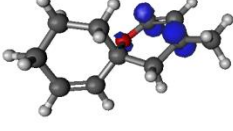
--

### thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
 Thermal correction to Energy= 0.001416  
 Thermal correction to Enthalpy= 0.002360  
 Thermal correction to Gibbs Free Energy= -0.010654  
 Sum of electronic and zero-point Energies= -0.500273  
 Sum of electronic and thermal Energies= -0.498857  
 Sum of electronic and thermal Enthalpies= -0.497912  
 Sum of electronic and thermal Free Energies= -0.510927

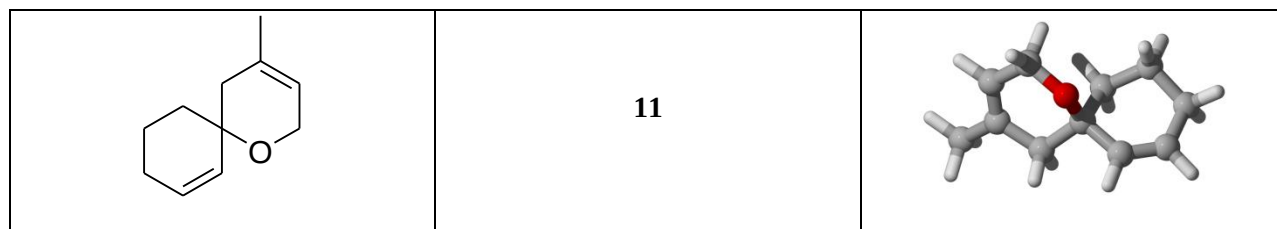
|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 0.889       | 2.981          | 27.39          |

**Population Analysis:** NBO:  $\alpha$ -HOMO (equals SOMO[19]) with energies and spin density distribution

|                                                                                   |                                                                                   |                                                                                    |                                                                                     |                                                                                     |                                                                                     |
|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|  |  |  |  |                                                                                     |                                                                                     |
| <b>12-R1 <math>\alpha</math>-HOMO</b><br>-0.18496                                 | <b>12-R1 spin density</b>                                                         | <b>12-R2 <math>\alpha</math>-HOMO</b><br>-0.184580                                 | <b>12-R2 <math>\alpha</math>-HOMO</b><br>spin density                               |                                                                                     |                                                                                     |
|  |  |  |  |  |  |
| <b>11-R1</b><br>$\alpha$ -HOMO                                                    | <b>11-R1 <math>\alpha</math>-HOMO</b><br>spin density                             | <b>11-R2 <math>\alpha</math>-HOMO</b><br>-0.185170                                 | <b>11-R2 <math>\alpha</math>-HOMO</b><br>spin density                               | <b>11-R3 <math>\alpha</math>-HOMO</b><br>-0.154760                                  | <b>11-R3 <math>\alpha</math>-HOMO</b><br>spin density                               |

Plotted  $\beta$ -LUMOs are similar in shape to  $\alpha$ -HOMOs therefore, we used the  $\alpha$ -HOMOs for further discussions of shape and energy of the SOMO.

## 1. Results obtained at B3LYP/6-31G\* PCM(solvent=water) level of theory



### xyz-matrix

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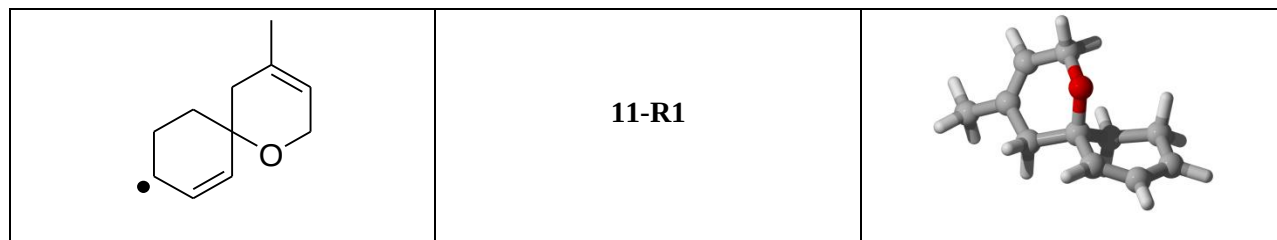
XYZ file generated by gabedit : coordinates in Angstrom

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | -2.1843060000 | 0.8851390000  | 0.9105740000  |
| C | -3.2112880000 | -0.1127410000 | 0.3591600000  |
| C | -2.6801610000 | -0.8447500000 | -0.8467240000 |
| C | -1.3928090000 | -0.8494620000 | -1.2076640000 |
| C | -0.2916420000 | -0.1512940000 | -0.4357150000 |
| C | -0.7935170000 | 0.2442250000  | 0.9700700000  |
| O | 0.0286190000  | 1.0226990000  | -1.2309220000 |
| C | 1.0956010000  | 1.8286080000  | -0.7360880000 |
| C | 2.2593080000  | 1.0451010000  | -0.1997900000 |
| C | 2.2192090000  | -0.2791580000 | -0.0193770000 |
| C | 0.9627170000  | -1.0486960000 | -0.3676350000 |
| C | 3.3866860000  | -1.0753890000 | 0.4996230000  |
| H | -2.4882400000 | 1.2353100000  | 1.9038750000  |
| H | -2.1437870000 | 1.7652670000  | 0.2564570000  |
| H | -4.1477400000 | 0.3976050000  | 0.0965900000  |
| H | -3.4836480000 | -0.8451180000 | 1.1361760000  |
| H | -3.4019090000 | -1.3960190000 | -1.4491810000 |
| H | -1.0817240000 | -1.3762850000 | -2.1090950000 |
| H | -0.8369390000 | -0.6623480000 | 1.5887480000  |
| H | -0.0730200000 | 0.9133500000  | 1.4517110000  |
| H | 0.7271430000  | 2.5301000000  | 0.0335750000  |
| H | 1.4107700000  | 2.4470620000  | -1.5870410000 |
| H | 3.1504960000  | 1.6179820000  | 0.0540580000  |
| H | 1.1041060000  | -1.5475790000 | -1.3383870000 |
| H | 0.7984050000  | -1.8541540000 | 0.3605390000  |
| H | 3.6783580000  | -1.8586220000 | -0.2141380000 |
| H | 3.1293150000  | -1.5894370000 | 1.4360100000  |
| H | 4.2600100000  | -0.4414070000 | 0.6845910000  |

### thermodynamic data

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.248546 (Hartree/Particle) |
| Thermal correction to Energy=                | 0.259530                    |
| Thermal correction to Enthalpy=              | 0.260474                    |
| Thermal correction to Gibbs Free Energy=     | 0.212434                    |
| Sum of electronic and zero-point Energies=   | -503.748051                 |
| Sum of electronic and thermal Energies=      | -503.737066                 |
| Sum of electronic and thermal Enthalpies=    | -503.736122                 |
| Sum of electronic and thermal Free Energies= | -503.784163                 |

|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 162.857     | 44.404         | 101.109        |



### xyz-matrix

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XYZ file generated by gabedit : coordinates in Angstrom

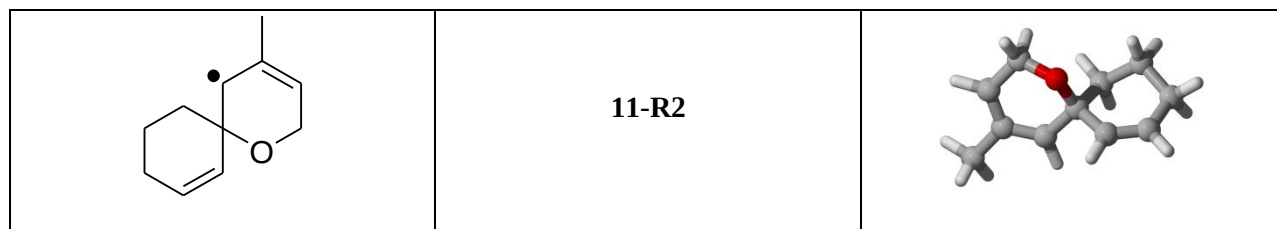
|   |               |               |               |
|---|---------------|---------------|---------------|
| C | -2.2736380000 | 0.9042830000  | 0.9342360000  |
| C | -3.2724690000 | 0.0452570000  | 0.2149940000  |
| C | -2.8496110000 | -0.9102810000 | -0.7001480000 |
| C | -1.5081790000 | -1.1091780000 | -1.0057850000 |
| C | -0.4173810000 | -0.2899380000 | -0.3601180000 |
| C | -0.9014650000 | 0.2159490000  | 1.0170240000  |
| O | -0.1920100000 | 0.8264370000  | -1.2711020000 |
| C | 0.8328380000  | 1.7362000000  | -0.8754500000 |
| C | 2.0624170000  | 1.0707110000  | -0.3267410000 |
| C | 2.1096400000  | -0.2323530000 | -0.0303920000 |
| C | 0.8890530000  | -1.1009940000 | -0.2492680000 |
| C | 3.3435600000  | -0.9113000000 | 0.5016900000  |
| H | -2.6320130000 | 1.1514140000  | 1.9415450000  |
| H | -2.1703690000 | 1.8680190000  | 0.4087470000  |
| H | -4.3332690000 | 0.1972620000  | 0.3964590000  |
| H | -3.5952600000 | -1.5196440000 | -1.2087220000 |
| H | -1.2193170000 | -1.8358800000 | -1.7609990000 |
| H | -0.9783970000 | -0.6522630000 | 1.6835790000  |
| H | -0.1593090000 | 0.8878040000  | 1.4599990000  |
| H | 0.4425610000  | 2.4686290000  | -0.1464070000 |
| H | 1.0788110000  | 2.3067150000  | -1.7808410000 |
| H | 2.9275850000  | 1.7126880000  | -0.1651150000 |
| H | 1.0259020000  | -1.6908500000 | -1.1682970000 |
| H | 0.7972760000  | -1.8335150000 | 0.5642180000  |
| H | 3.6522210000  | -1.7385280000 | -0.1528560000 |
| H | 3.1568540000  | -1.3516800000 | 1.4908540000  |
| H | 4.1839740000  | -0.2149740000 | 0.5889050000  |

### thermodynamic data

|                                            |                             |
|--------------------------------------------|-----------------------------|
| Zero-point correction=                     | 0.234791 (Hartree/Particle) |
| Thermal correction to Energy=              | 0.245747                    |
| Thermal correction to Enthalpy=            | 0.246691                    |
| Thermal correction to Gibbs Free Energy=   | 0.198175                    |
| Sum of electronic and zero-point Energies= | -503.121776                 |
| Sum of electronic and thermal Energies=    | -503.110820                 |
| Sum of electronic and thermal Enthalpies=  | -503.109876                 |

Sum of electronic and thermal Free Energies= -503.158392

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 154.209                 | 44.430               | 102.110             |



#### xyz-matrix

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XYZ file generated by gabedit : coordinates in Angstrom

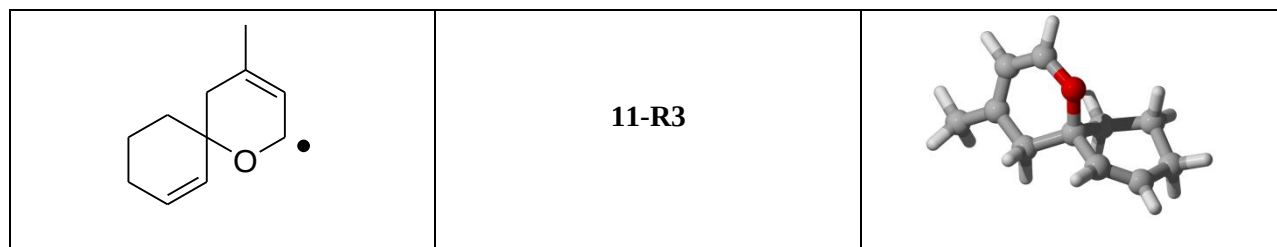
|   |               |               |               |
|---|---------------|---------------|---------------|
| C | -2.4145420000 | 0.8406210000  | 0.7320800000  |
| C | -3.2413440000 | -0.2865390000 | 0.0998270000  |
| C | -2.4686150000 | -0.9972340000 | -0.9812920000 |
| C | -1.1460820000 | -0.8895100000 | -1.1459440000 |
| C | -0.2394580000 | -0.0723150000 | -0.2411950000 |
| C | -0.9955030000 | 0.3535600000  | 1.0443840000  |
| O | 0.1144500000  | 1.0879050000  | -1.0364610000 |
| C | 1.2488880000  | 1.8330980000  | -0.5910530000 |
| C | 2.4432260000  | 0.9741340000  | -0.3159590000 |
| C | 2.2777170000  | -0.3640380000 | 0.0243220000  |
| C | 0.9890520000  | -0.8811600000 | 0.1048900000  |
| C | 3.4774930000  | -1.2471900000 | 0.3011330000  |
| H | -2.9018010000 | 1.2084880000  | 1.6425970000  |
| H | -2.3528990000 | 1.6841080000  | 0.0331530000  |
| H | -4.1786930000 | 0.1062670000  | -0.3162820000 |
| H | -3.5430480000 | -1.0136470000 | 0.8708130000  |
| H | -3.0369910000 | -1.6274080000 | -1.6650540000 |
| H | -0.6496180000 | -1.4034970000 | -1.9672060000 |
| H | -1.0418450000 | -0.5079570000 | 1.7243490000  |
| H | -0.4151500000 | 1.1268360000  | 1.5608580000  |
| H | 0.9912390000  | 2.4313880000  | 0.3030580000  |
| H | 1.4568630000  | 2.5522710000  | -1.3922820000 |
| H | 3.4276900000  | 1.4341060000  | -0.3357300000 |
| H | 0.8231410000  | -1.9015560000 | 0.4417560000  |
| H | 3.2306060000  | -2.0423020000 | 1.0124540000  |
| H | 4.3121590000  | -0.6688570000 | 0.7110660000  |
| H | 3.8330750000  | -1.7295800000 | -0.6182930000 |

#### thermodynamic data

Zero-point correction= 0.234294 (Hartree/Particle)  
 Thermal correction to Energy= 0.245645  
 Thermal correction to Enthalpy= 0.246590  
 Thermal correction to Gibbs Free Energy= 0.196309  
 Sum of electronic and zero-point Energies= -503.118777

Sum of electronic and thermal Energies= -503.107426  
 Sum of electronic and thermal Enthalpies= -503.106482  
 Sum of electronic and thermal Free Energies= -503.156763

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 154.145                 | 44.765               | 105.825             |



#### xyz-matrix

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XYZ file generated by gabedit : coordinates in Angstrom

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | -2.1262160000 | 0.7701550000  | 1.0810640000  |
| C | -3.1553380000 | -0.1195030000 | 0.3715990000  |
| C | -2.6521060000 | -0.5877170000 | -0.9691080000 |
| C | -1.3737560000 | -0.5100620000 | -1.3535920000 |
| C | -0.2610370000 | 0.0139620000  | -0.4766070000 |
| C | -0.7244310000 | 0.1579820000  | 0.9862230000  |
| O | 0.0387880000  | 1.3586010000  | -1.0047900000 |
| C | 1.2300570000  | 1.9107720000  | -0.6368920000 |
| C | 2.2916710000  | 1.1709290000  | -0.1402070000 |
| C | 2.2333650000  | -0.2150680000 | -0.0523050000 |
| C | 0.9952310000  | -0.8769720000 | -0.6011020000 |
| C | 3.3587460000  | -1.0633960000 | 0.4549020000  |
| H | -2.4067580000 | 0.9162480000  | 2.1304850000  |
| H | -2.1146290000 | 1.7608410000  | 0.6096890000  |
| H | -4.1061750000 | 0.4141960000  | 0.2412700000  |
| H | -3.3936840000 | -0.9971680000 | 0.9936770000  |
| H | -3.3854600000 | -1.0134600000 | -1.6533870000 |
| H | -1.0799170000 | -0.8457900000 | -2.3472300000 |
| H | -0.7280490000 | -0.8397060000 | 1.4458630000  |
| H | 0.0055670000  | 0.7601230000  | 1.5364270000  |
| H | 1.2525690000  | 2.9840350000  | -0.7912120000 |
| H | 3.1839640000  | 1.7107460000  | 0.1687100000  |
| H | 1.1453290000  | -1.1252600000 | -1.6657400000 |
| H | 0.7958380000  | -1.8315220000 | -0.0972680000 |
| H | 3.0431620000  | -1.6929110000 | 1.3009120000  |
| H | 4.2061410000  | -0.4534810000 | 0.7864340000  |
| H | 3.7271320000  | -1.7565670000 | -0.3178200000 |

#### thermodynamic data

Zero-point correction= 0.234903 (Hartree/Particle)

Thermal correction to Energy= 0.245981  
 Thermal correction to Enthalpy= 0.246925  
 Thermal correction to Gibbs Free Energy= 0.197979  
 Sum of electronic and zero-point Energies= -503.131411  
 Sum of electronic and thermal Energies= -503.120334  
 Sum of electronic and thermal Enthalpies= -503.119390  
 Sum of electronic and thermal Free Energies= -503.168336

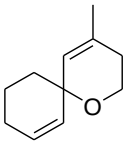
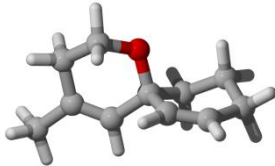
|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 154.355                 | 44.474               | 103.015             |

|  |                          |  |
|--|--------------------------|--|
|  | <b>H (hydrogen atom)</b> |  |
|--|--------------------------|--|

### thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
 Thermal correction to Energy= 0.001416  
 Thermal correction to Enthalpy= 0.002360  
 Thermal correction to Gibbs Free Energy= -0.010654  
 Sum of electronic and zero-point Energies= -0.500282  
 Sum of electronic and thermal Energies= -0.498865  
 Sum of electronic and thermal Enthalpies= -0.497921  
 Sum of electronic and thermal Free Energies= -0.510936

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 0.889                   | 2.981                | 27.392              |

|                                                                                     |           |                                                                                       |
|-------------------------------------------------------------------------------------|-----------|---------------------------------------------------------------------------------------|
|  | <b>12</b> |  |
|-------------------------------------------------------------------------------------|-----------|---------------------------------------------------------------------------------------|

### xyz-matrix

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XYZ file generated by gabedit : coordinates in Angstrom

```

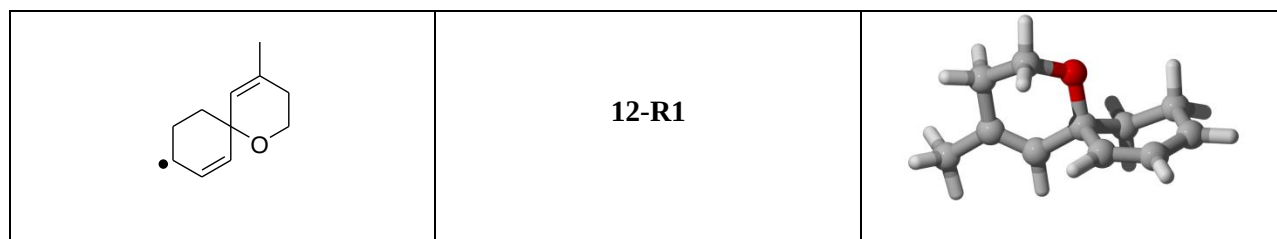
C 2.6344270000 0.1232160000 -1.1240760000
C 3.3364930000 -0.2488380000 0.1885990000
C 2.4146830000 -0.1079350000 1.3726740000
C 1.0857950000 0.0143710000 1.2745990000
C 0.3266620000 0.0034070000 -0.0479910000
C 1.2378570000 -0.5061660000 -1.1842570000
O -0.0315460000 1.3576160000 -0.4233560000
C -1.1848280000 1.8675890000 0.2423320000
C -2.4300740000 1.0658150000 -0.1290790000
C -2.1652080000 -0.4170470000 0.0086390000
  
```

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | -0.9063030000 | -0.8704660000 | 0.0621390000  |
| C | -3.3626070000 | -1.3276400000 | 0.0750810000  |
| H | 3.2347320000  | -0.2003470000 | -1.9825240000 |
| H | 2.5371100000  | 1.2136540000  | -1.1910110000 |
| H | 4.2284220000  | 0.3738010000  | 0.3404270000  |
| H | 3.7073360000  | -1.2855030000 | 0.1402600000  |
| H | 2.8761030000  | -0.1082450000 | 2.3602690000  |
| H | 0.4865090000  | 0.1224690000  | 2.1769740000  |
| H | 1.3254640000  | -1.5978060000 | -1.1025630000 |
| H | 0.7431530000  | -0.2900480000 | -2.1375750000 |
| H | -1.2719060000 | 2.9126810000  | -0.0703610000 |
| H | -1.0405810000 | 1.8543170000  | 1.3329420000  |
| H | -2.7394160000 | 1.2973440000  | -1.1591580000 |
| H | -3.2680880000 | 1.3636960000  | 0.5165730000  |
| H | -0.7132950000 | -1.9354150000 | 0.1886040000  |
| H | -3.0700940000 | -2.3802350000 | 0.1468760000  |
| H | -3.9957050000 | -1.2087390000 | -0.8153300000 |
| H | -3.9951020000 | -1.0855480000 | 0.9402950000  |

### thermodynamic data

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.248741 (Hartree/Particle) |
| Thermal correction to Energy=                | 0.259782                    |
| Thermal correction to Enthalpy=              | 0.260726                    |
| Thermal correction to Gibbs Free Energy=     | 0.212411                    |
| Sum of electronic and zero-point Energies=   | -503.749751                 |
| Sum of electronic and thermal Energies=      | -503.738709                 |
| Sum of electronic and thermal Enthalpies=    | -503.737765                 |
| Sum of electronic and thermal Free Energies= | -503.786081                 |

|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 163.016     | 44.407         | 101.689        |



### xyz-matrix

27

XYZ file generated by gabedit : coordinates in Angstrom

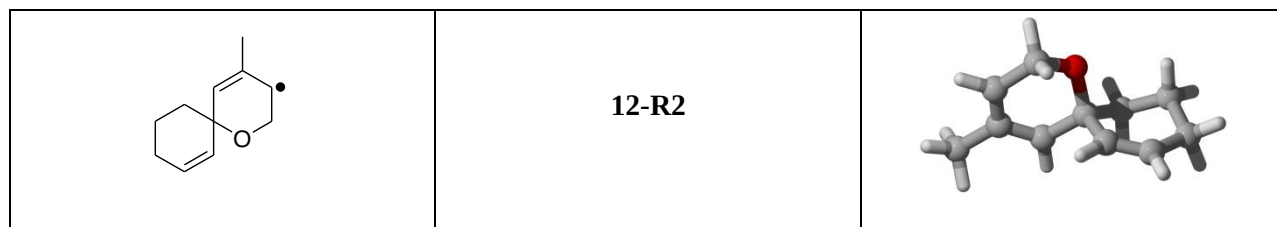
|   |              |               |               |
|---|--------------|---------------|---------------|
| C | 2.7487470000 | -0.1407350000 | -1.1365620000 |
| C | 3.3758020000 | -0.0297380000 | 0.2225070000  |
| C | 2.5861670000 | 0.0296480000  | 1.3623300000  |
| C | 1.1950790000 | -0.0040940000 | 1.3141990000  |
| C | 0.4487050000 | -0.1071010000 | -0.0039690000 |

|   |               |               |               |
|---|---------------|---------------|---------------|
| C | 1.3511100000  | -0.7778810000 | -1.0607270000 |
| O | 0.1795920000  | 1.2211710000  | -0.5301810000 |
| C | -0.9383400000 | 1.8672280000  | 0.0759330000  |
| C | -2.2316590000 | 1.1124180000  | -0.2237180000 |
| C | -2.0622780000 | -0.3656750000 | 0.0499510000  |
| C | -0.8354270000 | -0.8913740000 | 0.1603910000  |
| C | -3.3161480000 | -1.1892640000 | 0.1791040000  |
| H | 3.3897850000  | -0.7223310000 | -1.8112060000 |
| H | 2.6675510000  | 0.8609690000  | -1.5885260000 |
| H | 4.4578030000  | 0.0348860000  | 0.3033920000  |
| H | 3.0706240000  | 0.1190230000  | 2.3338080000  |
| H | 0.6161200000  | 0.0725380000  | 2.2301600000  |
| H | 1.4543670000  | -1.8377090000 | -0.7968530000 |
| H | 0.8470720000  | -0.7276480000 | -2.0317420000 |
| H | -0.9598170000 | 2.8801390000  | -0.3376700000 |
| H | -0.7922880000 | 1.9500140000  | 1.1631360000  |
| H | -2.5275920000 | 1.2657590000  | -1.2722270000 |
| H | -3.0487500000 | 1.5208340000  | 0.3874350000  |
| H | -0.7116800000 | -1.9514730000 | 0.3802890000  |
| H | -3.0925550000 | -2.2478540000 | 0.3465640000  |
| H | -3.9330500000 | -1.1091670000 | -0.7268870000 |
| H | -3.9389440000 | -0.8325830000 | 1.0110790000  |

### thermodynamic data

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.234920 (Hartree/Particle) |
| Thermal correction to Energy=                | 0.245956                    |
| Thermal correction to Enthalpy=              | 0.246900                    |
| Thermal correction to Gibbs Free Energy=     | 0.198035                    |
| Sum of electronic and zero-point Energies=   | -503.124201                 |
| Sum of electronic and thermal Energies=      | -503.113166                 |
| Sum of electronic and thermal Enthalpies=    | -503.112222                 |
| Sum of electronic and thermal Free Energies= | -503.161086                 |

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 154.340                 | 44.466               | 102.845             |



### xyz-matrix

27

XYZ file generated by gabedit : coordinates in Angstrom

|   |              |               |               |
|---|--------------|---------------|---------------|
| C | 2.6278760000 | 0.0744290000  | -1.0288880000 |
| C | 3.1911580000 | -0.2212100000 | 0.3678040000  |
| C | 2.1517180000 | -0.0230150000 | 1.4405640000  |
| C | 0.8399920000 | 0.0878060000  | 1.1978850000  |

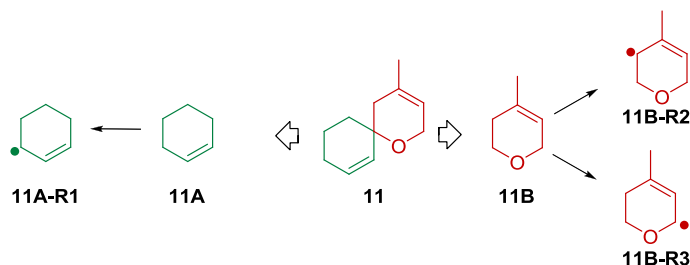
|   |               |               |               |
|---|---------------|---------------|---------------|
| C | 0.2226280000  | -0.0084330000 | -0.1933720000 |
| C | 1.2461190000  | -0.5659560000 | -1.2004050000 |
| O | -0.1190460000 | 1.3133060000  | -0.6924190000 |
| C | -1.2020670000 | 1.9542190000  | -0.0249510000 |
| C | -2.4016930000 | 1.0684730000  | 0.1257060000  |
| C | -2.2834440000 | -0.3120450000 | 0.0248940000  |
| C | -1.0162970000 | -0.8691840000 | -0.1425280000 |
| C | -3.5094170000 | -1.2004910000 | 0.0884900000  |
| H | 3.3140620000  | -0.2912380000 | -1.8016760000 |
| H | 2.5370340000  | 1.1590040000  | -1.1649680000 |
| H | 4.0618740000  | 0.4148050000  | 0.5767260000  |
| H | 3.5663390000  | -1.2564010000 | 0.4146470000  |
| H | 2.5068480000  | 0.0280300000  | 2.4698800000  |
| H | 0.1475720000  | 0.2371580000  | 2.0244040000  |
| H | 1.3239480000  | -1.6514050000 | -1.0539300000 |
| H | 0.8544510000  | -0.4011300000 | -2.2102300000 |
| H | -1.4437320000 | 2.8326060000  | -0.6366740000 |
| H | -0.8791590000 | 2.3424140000  | 0.9590790000  |
| H | -3.3601510000 | 1.5371950000  | 0.3336680000  |
| H | -0.8841230000 | -1.9478250000 | -0.1729290000 |
| H | -3.2885040000 | -2.1498720000 | 0.5879480000  |
| H | -3.8770960000 | -1.4391190000 | -0.9176790000 |
| H | -4.3268900000 | -0.7121340000 | 0.6289580000  |

### thermodynamic data

|                                              |                             |
|----------------------------------------------|-----------------------------|
| Zero-point correction=                       | 0.234314 (Hartree/Particle) |
| Thermal correction to Energy=                | 0.245715                    |
| Thermal correction to Enthalpy=              | 0.246659                    |
| Thermal correction to Gibbs Free Energy=     | 0.195650                    |
| Sum of electronic and zero-point Energies=   | -503.119226                 |
| Sum of electronic and thermal Energies=      | -503.107825                 |
| Sum of electronic and thermal Enthalpies=    | -503.106881                 |
| Sum of electronic and thermal Free Energies= | -503.157890                 |

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 154.188                 | 44.735               | 107.358             |

## 2. Results obtained with composite method CBS-QB3 for model system 11A and 11B



|  |     |  |
|--|-----|--|
|  | 11A |  |
|--|-----|--|

### xyz-matrix

16

XYZ file generated by gabedit : coordinates in Angstrom

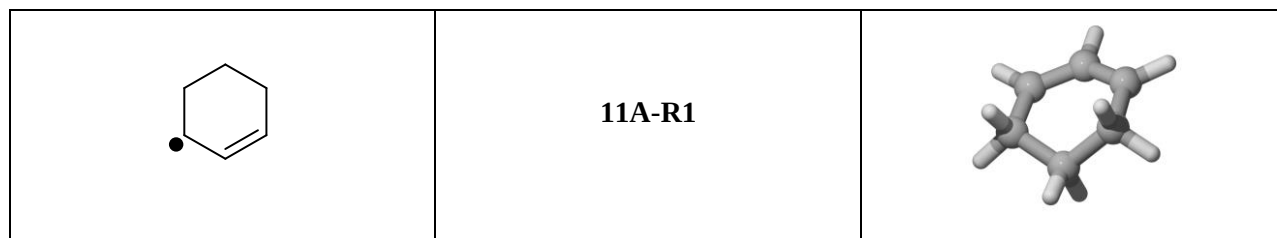
|   |               |               |               |
|---|---------------|---------------|---------------|
| H | 0.7296280000  | -0.2739240000 | -2.1308050000 |
| H | 3.2188580000  | -0.1560800000 | -1.9881000000 |
| C | 1.2316240000  | -0.5035640000 | -1.1882060000 |
| H | 2.4988170000  | 1.2285510000  | -1.1694900000 |
| C | 2.6185590000  | 0.1423940000  | -1.1234880000 |
| H | 1.3265160000  | -1.5934330000 | -1.1194090000 |
| H | -0.0192030000 | 1.3490980000  | -0.3991640000 |
| C | 0.3267990000  | -0.0097600000 | -0.0430230000 |
| H | -0.9104980000 | -0.8757630000 | 0.0574460000  |
| H | 3.7209330000  | -1.2668120000 | 0.1129800000  |
| C | 3.3305300000  | -0.2405080000 | 0.1790360000  |
| H | 4.2078770000  | 0.3962730000  | 0.3397070000  |
| C | 1.0876130000  | -0.0254300000 | 1.2776560000  |
| C | 2.4130560000  | -0.1387300000 | 1.3680890000  |
| H | 0.4922910000  | 0.0565970000  | 2.1822610000  |
| H | 2.8763990000  | -0.1580660000 | 2.3519940000  |

### thermodynamic data

|                                          |                             |
|------------------------------------------|-----------------------------|
| Zero-point correction=                   | 0.145723 (Hartree/Particle) |
| Thermal correction to Energy=            | 0.151240                    |
| Thermal correction to Enthalpy=          | 0.152185                    |
| Thermal correction to Gibbs Free Energy= | 0.117076                    |

Sum of electronic and zero-point Energies= -234.565778  
 Sum of electronic and thermal Energies= -234.560261  
 Sum of electronic and thermal Enthalpies= -234.559317  
 Sum of electronic and thermal Free Energies= -234.594426

|       | E (Thermal)<br>KCal/Mol | CV<br>Cal/Mol-Kelvin | S<br>Cal/Mol-Kelvin |
|-------|-------------------------|----------------------|---------------------|
| Total | 94.905                  | 21.515               | 73.893              |



#### xyz-matrix

15

XYZ file generated by gabedit : coordinates in Angstrom

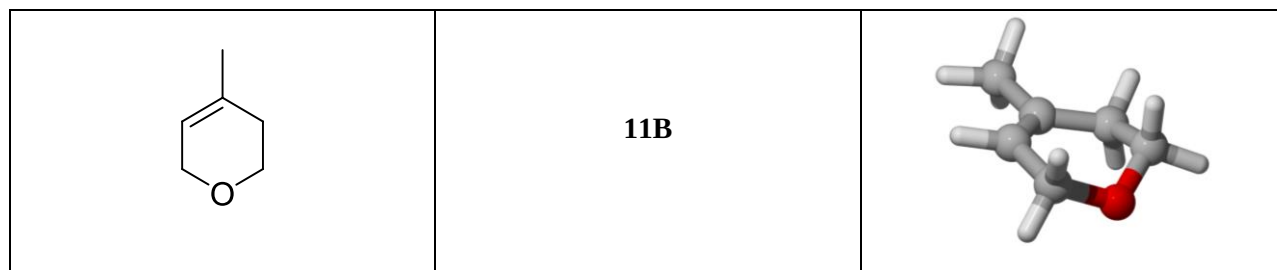
|   |               |               |               |
|---|---------------|---------------|---------------|
| H | 0.8364490000  | -0.6892730000 | -2.0391290000 |
| H | 1.4613520000  | -1.8254240000 | -0.8357820000 |
| H | 3.3773810000  | -0.6456790000 | -1.8386860000 |
| C | 1.3467880000  | -0.7633680000 | -1.0762580000 |
| H | -0.8380330000 | -0.8983840000 | 0.1457970000  |
| C | 2.7327700000  | -0.1043350000 | -1.1382380000 |
| H | 2.6242410000  | 0.9121310000  | -1.5418890000 |
| C | 0.4485420000  | -0.1183620000 | -0.0033240000 |
| H | 0.1881070000  | 1.2191090000  | -0.5011630000 |
| C | 3.3659780000  | -0.0343810000 | 0.2177460000  |
| H | 4.4454780000  | 0.0347700000  | 0.2963250000  |
| C | 1.1959340000  | -0.0498800000 | 1.3151630000  |
| C | 2.5833430000  | -0.0125600000 | 1.3590980000  |
| H | 0.6199290000  | -0.0026800000 | 2.2320770000  |
| H | 3.0709800000  | 0.0501170000  | 2.3282590000  |

#### thermodynamic data

Zero-point correction= 0.131905 (Hartree/Particle)  
 Thermal correction to Energy= 0.137418  
 Thermal correction to Enthalpy= 0.138362  
 Thermal correction to Gibbs Free Energy= 0.102714  
 Sum of electronic and zero-point Energies= -233.938449  
 Sum of electronic and thermal Energies= -233.932936  
 Sum of electronic and thermal Enthalpies= -233.931991

Sum of electronic and thermal Free Energies= -233.967640

| E (Thermal) | CV             | S              |
|-------------|----------------|----------------|
| KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total       | 86.231         | 21.571         |
|             |                | 75.028         |



#### xyz-matrix

17

XYZ file generated by gabedit : coordinates in Angstrom

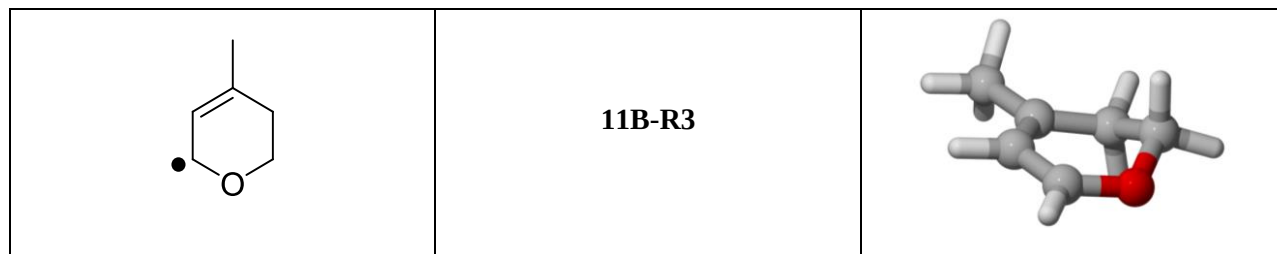
|   |               |               |               |
|---|---------------|---------------|---------------|
| H | 1.4126420000  | 2.4350590000  | -1.5839850000 |
| O | 0.0241020000  | 1.0293970000  | -1.2147570000 |
| C | 1.0969000000  | 1.8270020000  | -0.7297110000 |
| H | 0.7376040000  | 2.5336760000  | 0.0382070000  |
| H | -1.3910290000 | -0.8396980000 | -1.2083440000 |
| C | 2.2578840000  | 1.0419110000  | -0.1948450000 |
| H | 3.1513210000  | 1.6088770000  | 0.0559650000  |
| H | 1.0993680000  | -1.5365320000 | -1.3357380000 |
| C | -0.2927480000 | -0.1468540000 | -0.4311380000 |
| C | 0.9598490000  | -1.0447220000 | -0.3644460000 |
| C | 2.2165460000  | -0.2781980000 | -0.0181440000 |
| H | -0.7956500000 | 0.2396950000  | 0.9760990000  |
| H | 3.6672200000  | -1.8579260000 | -0.2222020000 |
| H | 4.2565430000  | -0.4477020000 | 0.6737710000  |
| C | 3.3827750000  | -1.0776640000 | 0.4938730000  |
| H | 0.7962520000  | -1.8490400000 | 0.3619140000  |
| H | 3.1288340000  | -1.5891180000 | 1.4297260000  |

#### thermodynamic data

|                                            |                             |
|--------------------------------------------|-----------------------------|
| Zero-point correction=                     | 0.149288 (Hartree/Particle) |
| Thermal correction to Energy=              | 0.156101                    |
| Thermal correction to Enthalpy=            | 0.157045                    |
| Thermal correction to Gibbs Free Energy=   | 0.118823                    |
| Sum of electronic and zero-point Energies= | -309.790840                 |
| Sum of electronic and thermal Energies=    | -309.784026                 |
| Sum of electronic and thermal Enthalpies=  | -309.783082                 |

Sum of electronic and thermal Free Energies= -309.821304

|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 97.955      | 25.812         | 80.445         |



#### xyz-matrix

16

XYZ file generated by gabedit : coordinates in Angstrom

|   |               |               |               |
|---|---------------|---------------|---------------|
| H | -2.1608480000 | -1.8103500000 | -0.0385580000 |
| H | -2.0763180000 | 2.2389020000  | -0.1342440000 |
| O | -2.1995150000 | 0.2062140000  | -0.1854030000 |
| C | -1.4670710000 | 1.3470170000  | -0.0851730000 |
| H | -0.1480760000 | -1.3271290000 | -1.3606530000 |
| C | -1.5259930000 | -0.9804060000 | 0.2715880000  |
| C | -0.1077240000 | -1.0987460000 | -0.2849810000 |
| C | -0.0874800000 | 1.3448920000  | 0.0338120000  |
| H | -1.4925020000 | -0.9492100000 | 1.3674760000  |
| H | 0.4057650000  | 2.3039800000  | 0.1543950000  |
| C | 0.6578720000  | 0.1765490000  | -0.0461220000 |
| H | 0.3860240000  | -1.9539190000 | 0.1929690000  |
| H | 2.5859210000  | -0.2692560000 | -0.9057450000 |
| C | 2.1513510000  | 0.1395960000  | 0.0172700000  |
| H | 2.5724860000  | 1.1361140000  | 0.1696120000  |
| H | 2.5061100000  | -0.5042530000 | 0.8337600000  |

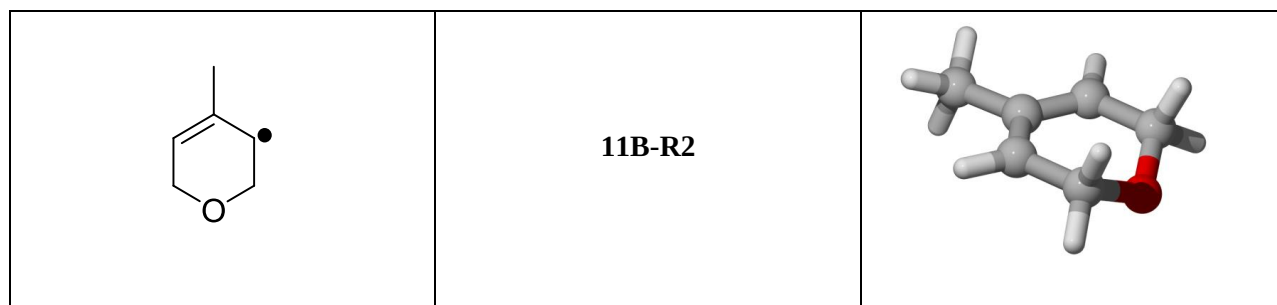
#### thermodynamic data

Thermo

|                                            |                             |
|--------------------------------------------|-----------------------------|
| Zero-point correction=                     | 0.135962 (Hartree/Particle) |
| Thermal correction to Energy=              | 0.142843                    |
| Thermal correction to Enthalpy=            | 0.143787                    |
| Thermal correction to Gibbs Free Energy=   | 0.104739                    |
| Sum of electronic and zero-point Energies= | -309.171471                 |
| Sum of electronic and thermal Energies=    | -309.164590                 |
| Sum of electronic and thermal Enthalpies=  | -309.163646                 |

Sum of electronic and thermal Free Energies= -309.202694

|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 89.635      | 25.802         | 82.183         |



#### xyz-matrix

16

XYZ file generated by gabedit : coordinates in Angstrom

|   |               |               |               |
|---|---------------|---------------|---------------|
| H | -1.8650990000 | -2.0098550000 | -0.5280490000 |
| C | -1.4484150000 | -1.1851800000 | 0.0563370000  |
| O | -2.0110690000 | -0.0000080000 | -0.4908950000 |
| H | -1.7957960000 | -1.3224870000 | 1.0986380000  |
| H | 0.5637800000  | -2.1487270000 | 0.0309510000  |
| C | 0.0502440000  | -1.1935550000 | 0.0027040000  |
| C | -1.4484100000 | 1.1851830000  | 0.0563160000  |
| C | 0.7578530000  | 0.0000020000  | -0.0502740000 |
| H | -1.8650640000 | 2.0098390000  | -0.5281230000 |
| C | 0.0502420000  | 1.1935410000  | 0.0027270000  |
| H | 2.5756780000  | -0.0001630000 | -1.2184010000 |
| H | -1.7958380000 | 1.3225450000  | 1.0985920000  |
| H | 2.7009790000  | -0.8842010000 | 0.3035900000  |
| C | 2.2661830000  | -0.0000010000 | -0.1684230000 |
| H | 0.5637730000  | 2.1487160000  | 0.0309970000  |
| H | 2.7009590000  | 0.8843560000  | 0.3033130000  |

#### thermodynamic data

Zero-point correction= 0.134877 (Hartree/Particle)  
 Thermal correction to Energy= 0.142066  
 Thermal correction to Enthalpy= 0.143010  
 Thermal correction to Gibbs Free Energy= 0.102655  
 Sum of electronic and zero-point Energies= -309.158331

Sum of electronic and thermal Energies= -309.151142  
 Sum of electronic and thermal Enthalpies= -309.150197  
 Sum of electronic and thermal Free Energies= -309.190553

|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 89.148      | 26.198         | 84.936         |

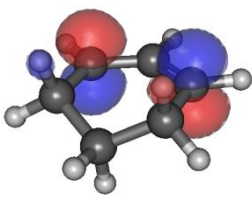
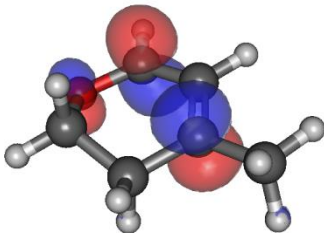
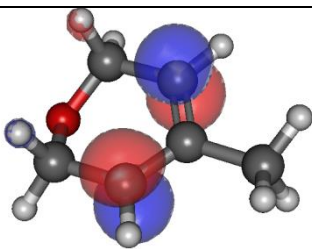
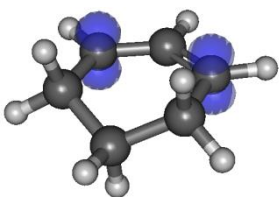
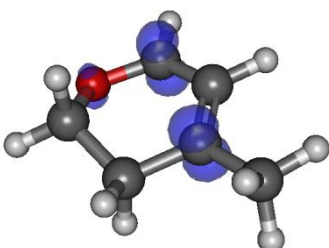
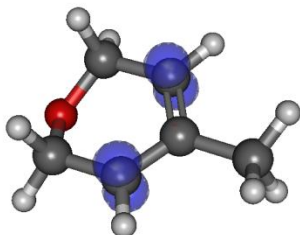
|  |                          |  |
|--|--------------------------|--|
|  | <b>H (hydrogen atom)</b> |  |
|--|--------------------------|--|

### thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
 Thermal correction to Energy= 0.001416  
 Thermal correction to Enthalpy= 0.002360  
 Thermal correction to Gibbs Free Energy= -0.010654  
 Sum of electronic and zero-point Energies= -0.502156  
 Sum of electronic and thermal Energies= -0.500740  
 Sum of electronic and thermal Enthalpies= -0.499795  
 Sum of electronic and thermal Free Energies= -0.512810

|       | E (Thermal) | CV             | S              |
|-------|-------------|----------------|----------------|
|       | KCal/Mol    | Cal/Mol-Kelvin | Cal/Mol-Kelvin |
| Total | 0.889       | 2.981          | 27.392         |

**Population Analysis:** Spin densities and  $\alpha$ -HOMOs of model system at CBS-QB3 level of theory.

| 11A-R1                                                                            | 11B-R3                                                                            | 11B-R2                                                                              |
|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|  |  |  |
| $\alpha$ -HOMO                                                                    | $\alpha$ -HOMO                                                                    | $\alpha$ -HOMO                                                                      |
|  |  |  |
| spin density                                                                      | spin density                                                                      | spin density                                                                        |

**General Methods:** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data were recorded with a 400 or 500 MHz spectrometer at ambient temperature. The samples were dissolved in  $\text{CDCl}_3$ . The coupling constant ( $J$ ) is given in Hz. The chemical shifts  $\delta$  are reported in ppm on a scale downfield from TMS, which was used as an internal standard, and the signal patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), sext (sextet), m (multiplet), and br. (broad). Appropriate 1D and 2D NMR methods (e.g., COSY, HSQC and HMBC) were used for peak assignment. For HRMS  $m/z$  ratios are recorded in atomic mass units. Mass analysis was carried out using APCI or ESI mode. All of the reagents were reagent grade and used without further purification unless otherwise specified. Solvents for the reactions were distilled prior to use. All air or moisture-sensitive reactions were conducted under nitrogen or argon in flame or oven-dried glassware and were magnetically stirred. THF, toluene and diethyl ether were distilled from Na. Column chromatography was carried out with silica gel (40–63  $\mu\text{m}$ ) packed in glass columns. Technical grade ethyl acetate and petroleum ether, which were used for column chromatography, were distilled prior to use.  $R_f$ -values were detected by phosphomolybdic acid.

The filamentous fungus *Pleurotus sapidus* (PSA) was obtained from the German Collection of Microorganisms and Cell Cultures (DSMZ 8266), Braunschweig, Germany.

Production of biomass and lyophilisate were described previously by Fraatz et al. [20]. For all new oxidations with PSA, a parallel positive control experiment with the known substrate valencene and the same batch of PSA-lyophilisate was performed, confirming enzymatic activity of the lyophilisate used.

**Epoxide 4a** [8,21]: The diastereomeric mixture of *cis*- and *trans*-theaspirane **1** was separated by column chromatography (pentane/ $\text{Et}_2\text{O}$ , 95:5) in portions of 500 mg. A solution of theaspirane *trans*-**1** (3.89 g, 20.0 mmol) in 25 mL  $\text{CH}_2\text{Cl}_2$  was added to a solution of *m*-CPBA

(5.80 g, 24.8 mmol) in 40 mL CH<sub>2</sub>Cl<sub>2</sub> at 4 °C under continuous stirring. The solution was stirred for 60 min at 15 °C and subsequently quenched with 2 M aqueous NaOH (100 mL). The reaction mixture was washed with water (40 mL), dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by column chromatography (pentane/Et<sub>2</sub>O, 85:15) to give epoxide **4a** (3.58 g, 17.0 mmol, 85%) and epoxide **4b** (0.31 g, 1.46 mmol, 7%) as colorless crystals; *R*<sub>f</sub> 0.49 (pentane/Et<sub>2</sub>O, 8:2).

**4a:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.07–3.99 (m, 1H, 2-H), 3.03 (br. s, 1H, 7-H), 2.13–2.05 (m, 1H, 4-H), 1.93–1.80 (m, 4H, 4-H, 3-H, 8-H, 8-H), 1.34–1.25 (m, 2H, 9-H, 3-H), 0.98–0.92 (m, 1H, 9-H), 1.29 (s, 3H, 11-H), 1.22 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.1 Hz, 3H, 14-H), 0.84 (s, 3H, 12-H), 0.76 (s, 3H, 13-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 86.8 (C5), 77.2 (C2), 64.7 (C6), 62.8 (C7), 35.8 (C10), 34.4 (C3), 31.7 (C4), 30.0 (C9), 24.3 (C13), 22.1 (C8), 21.7 (C12), 20.8 (C14), 19.9 (C11) ppm. GC–MS *m/z* 210 (34, M<sup>+</sup>), 154 (73, M-56), 153 (22, M-57), 139 (32, M-71), 126 (100, M-84), 125 (82, M-85), 111 (56, M-99), 85 (39, M-125), 69 (66, M-141), 55 (73, M-155), 43 (81, M-167).

**4b:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.35–4.20 (m, 1H, 2-H), 2.95 (br. s, 1H, 7-H), 2.15–2.06 (m, 1H, 3-H), 2.01–1.95 (m, 1H, 8-H), 1.94–1.89 (m, 2H, 4-H), 1.84–1.75 (m, 1H, 8-H), 1.60–1.53 (m, 1H, 9-H), 1.52–1.46 (m, 1H, 3-H), 1.36 (s, 3H, 11-H), 1.23 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.0 Hz, 3H, 14-H), 1.00–0.94 (m, 1H, 9-H), 0.94 (s, 3H, 12-H), 0.92 (s, 3H, 13-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 86.9 (C5), 75.3 (C2), 61.8 (C7), 60.5 (C6), 35.6 (C10), 34.0 (C3), 30.2 (C9), 30.1 (C4), 23.8/23.6/23.6 (C11/C12/C13), 21.6/21.6 (C8/C14) ppm. GC–MS *m/z* 210 (34, M<sup>+</sup>), 154 (73, M-56), 153 (22, M-57), 139 (32, M-71), 126 (95, M-84), 125 (41, M-85), 112 (68, M-99), 83 (39, M-125), 69 (66, M-141), 55 (73, M-155), 43 (100, M-167).

**Allyl alcohol 22** [8,21]: To a magnetically stirred solution of tetramethylpiperidine (3.34 mL, 19.7 mmol) in 50 mL dry toluene was added *n*-BuLi (16.0 mL 1.3 M solution in hexanes, 20.8 mmol) dropwise at 0 °C whereby the solution turned yellow-orange. Stirring was

continued for 30 min. at 0 °C and subsequently diethylaluminium chloride (1 M solution, 20.0 mL, 20.0 mmol) was added. After an additional stirring for 40 min at 0 °C epoxide **4a** (1.03 g, 4.91 mmol) was added and the solution was stirred for 30 min at 0 °C and then 2 h at rt. The reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub> (10 mL) and extracted three times with Et<sub>2</sub>O (30 mL). The combined organic phases were washed with saturated aqueous KHSO<sub>4</sub> and with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was coevaporated three times with MeOH to give allyl alcohol **22** (0.96 g, 4.57 mmol, 93%) as colorless oil; *R*<sub>f</sub> = 0.12 (pentane/Et<sub>2</sub>O, 9:1). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 5.17 (s, 1H, 11-H), 4.94 (s, 1H, 11-H), 4.50–4.47 (m, 1H, 7-H), 3.95–3.87 (m, 1H, 2-H), 2.09–1.83/1.50–1.33 (2 m, 8H, 3-H/4-H/8-H/9-H), 1.17 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.1 Hz, 3H, 14-H), 0.85/0.77 (2 s, 6H, 12-H/13-H) ppm. **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.3 (C6), 106.7 (C11), 90.2 (C5), 73.5 (C2), 71.0 (C7), 37.8 (C10), 34.7 (C9), 33.3/28.6 (C3/C4), 32.3 (C8), 23.7/23.6 (C12/C13), 21.3 (C14) ppm. **GC–MS** *m/z* 192 (51, M-8), 177 (40, M-33), 163 (24, M-47), 153 (63, M-57), 149 (22, M-61), 141 (40, M-69), 136 (29, M-74), 121 (46, M-89), 111 (35, M-99), 93 (76, M-117), 85 (98, M-125), 77 (44, M-133), 55 (100, M-155).

**Vitispirane 23** [8,21]: To a solution of pyridine (50 mL, 620 mmol) and acetic anhydride (25 mL, 264 mmol) was added the allylic alcohol **22** (1.05 g, 4.99 mmol). The resulting solution was stirred at rt for 24 h. The reaction was monitored by TLC. The crude product was concentrated in vacuo and dissolved in dioxane (12 mL). To the resulting solution was added Pd(OAc)<sub>2</sub> (15.7 mg, 0.07 mmol), PPh<sub>3</sub> (184 mg, 0.70 mmol) and CaCO<sub>3</sub> (700 mg, 6.99 mmol) and the resulting heterogeneous mixture was stirred under reflux under nitrogen for 6.5 h. Then the mixture was cooled to rt, diluted with Et<sub>2</sub>O (5 mL) and filtrated. The filtrate was washed successively with saturated aqueous NaHCO<sub>3</sub> (30 mL) and brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by column chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub>, 4:1) to give vitispirane (**23**) (0.64 g, 3.32 mmol, 84%) as colorless oil; *R*<sub>f</sub> = 0.25 (pentane/CH<sub>2</sub>Cl<sub>2</sub>, 9:1). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.07–6.04 (m, 1H, 7-H), 5.61–

5.57 (m, 1H, 8-H), 5.06 (s, 1H, 11-H), 4.85 (s, 1H, 11-H), 4.32–4.28 (m, 1H, 2-H), 2.16–1.94/1.62–1.36 (2m, 6H, 3-H/4-H/9-H), 1.22 (d,  $^3J_{\text{H,H}} = 6.1$  Hz, 3H, 14-H), 0.95/0.88 (2s, 6H, 12-H/13-H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8 (C6), 128.7 (C7), 127.3 (C8), 109.2 (C11), 89.1 (C5), 76.0 (C2), 41.3 (C9), 36.3 (C4), 32.9 (C3), 23.7/23.4 (C12/C13), 21.7 (C14). GC–MS  $m/z$  192 (86,  $\text{M}^+$ ), 177 (60, M- $\text{CH}_3$ ), 163 (12, M-29), 149 (29, M-43), 136 (44, M-56), 135 (31, M-57), 126 (17, M-66), 121 (60, M-71), 119 (34, M-73), 107 (33, M-85), 93 (100, M-99), 91 (56, M-102), 77 (41, M-115), 65 (28, M-127), 55 (37, M-137) ppm.

**Spiroethers 7 and 8** [22]: To a flame-dried round-bottom flask was added dry  $\text{CH}_2\text{Cl}_2$  (40 mL) and cooled to  $-20$  °C. Cyclohexanone (**5**) (2.20 mL, 20.0 mmol) and TMS-ether **6** (3.79 g, 23.9 mmol) were added and stirred for 5 min at  $-20$  °C. The solution was treated with TMSOTf (725  $\mu\text{L}$ , 4.00 mmol) and stirred at  $-20$  °C for 4 h under  $\text{N}_2$ . The reaction was monitored by TLC. The reaction mixture was diluted with saturated aqueous  $\text{NaHCO}_3$  solution (10 mL) and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  mL). The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The resulting bright yellow oil was purified by column chromatography (pentane/ $\text{CH}_2\text{Cl}_2$ , 4:1→1:1) to give spiroether **7** (1.50 g, 9.02 mmol, 45%) and **8** (1.47 g, 8.84 mmol, 44%) as colorless oils; spiroether **7**:  $R_f = 0.34$  (pentane/ $\text{CH}_2\text{Cl}_2$ , 2:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.35 (m, 1H, 3-H), 4.06–4.04 (m, 2H, 2-H), 1.83 (br. s, 2H, 5-H), 1.66 (br. s, 3H, 12-H), 1.72–1.24 (m, 10H, 7-11-H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  130.3 (C4), 118.7 (C3), 70.9 (C6), 60.4 (C2), 40.5 (C5), 35.0 (C7/C11), 26.3 (C9), 23.5 (C12), 22.1 (C8/C10) ppm. GC–MS  $m/z$  166 (17,  $\text{M}^+$ ), 148 (10, M-18), 123 (14, M-43), 110 (14, M-56), 99 (21, M-67), 95 (28, M-71), 81 (25, M-85), 68 (100, M-98), 55 (58, M-111).

**Spiroether 8**:  $R_f = 0.4$  (pentane/ $\text{CH}_2\text{Cl}_2$ , 2:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.34–5.32 (m, 1H, 5-H), 3.76 (t,  $^3J_{\text{H,H}} = 5.6$  Hz, 2H, 2-H), 1.96–1.93 (m, 2H, 3-H), 1.68 (m, 3H, 12-H), 1.66–1.21 (m, 10H, 7-11-H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  130.9 (C4), 128.7 (C5),

72.4 (C6), 58.8 (C2), 35.9 (C7/C11), 30.3 (C3), 25.8 (C9), 23.5 (C12), 21.9 (C8/C10) ppm. **GC-MS**  $m/z$  166 (12,  $M^+$ ), 151 (10, M-15), 137 (5, M-29), 123 (100, M-43), 110 (10, M-56), 79 (9, M-47), 67 (8, M-99), 55 (9, M-111).

**Spiroethers 11 and 12:** To a flame-dried round-bottom flask was added dry  $\text{CH}_2\text{Cl}_2$  (20 mL) and cooled to  $-20\text{ }^\circ\text{C}$ . Cyclohexenon **10** (0.96 g, 9.99 mmol) and TMS-ether **6** (1.58 g, 10 mmol) were added and stirred for 5 min at  $-20\text{ }^\circ\text{C}$ . The solution was treated with TMSOTf (362  $\mu\text{L}$ , 2.00 mmol) and stirred at  $-20\text{ }^\circ\text{C}$  for 5 h under  $\text{N}_2$ . The reaction was monitored by TLC. The reaction mixture was diluted with saturated aqueous  $\text{NaHCO}_3$  solution (10 mL) and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10\text{ mL}$ ). The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The resulting bright yellow oil was purified by column chromatography (pentane/ $\text{Et}_2\text{O}$ , 100:1.5 $\rightarrow$ 100:4) to give spirother **11** (0.61 g, 3.70 mmol, 37%) and **12** (0.49 g, 3.00 mmol, 30%) as colorless oils; Spiroether **11**:  $R_f$  = 0.38 (pentane/ $\text{Et}_2\text{O}$ , 50:1).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.86 (td,  $^3J_{\text{H,H}}$  = 10.0 Hz,  $^3J_{\text{H,H}}$  = 3.6 Hz, 1H, 8-H), 5.72 (d,  $^3J_{\text{H,H}}$  = 10.0 Hz, 1H, 7-H), 5.43 (br.s, 1H, 3-H), 4.17–4.05 (m, 2H, 2-H), 2.11–1.88 (m, 4H, 5-H/9-H), 1.84–1.78 (m, 2H, 10-H/11-H), 1.69 (s, 3H, 12-H), 1.63–1.52 (m, 1H, 10-H/11-H) ppm.  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.1 (C8), 130.4 (C4), 130.2 (C7), 119.3 (C3), 69.2 (C6), 61.3 (C2), 40-4 (C5), 33.9 (C11), 25.8 (C9), 23.6 (C12), 18.9 (C10) ppm. **GC-MS**  $m/z$  164 (11,  $M^+$ ), 149 (12, M- $\text{CH}_3$ ), 136 (82, M-25), 121 (100, M-43), 105 (11, M-59), 91 (34, M-73), 79 (16, M-85), 77 (17, M-87), 67 (8, M-97), 55 (11, M-109).

**Spiroether 12:**  $R_f$  = 0.30 (pentane/ $\text{Et}_2\text{O}$ , 50:1).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.82 (td,  $^3J_{\text{H,H}}$  = 10.0 Hz,  $^3J_{\text{H,H}}$  = 3.8 Hz, 1H, 8-H), 5.59 (d,  $^3J_{\text{H,H}}$  = 10.0 Hz, 1H, 7-H), 5.30–5.29 (m, 1H, 5-H), 3.86–3.81 (m, 1H, 2-H), 3.78–3.72 (m, 1H, 2-H), 2.10–1.89 (m, 4H, 3-H/9-H), 1.85–1.72 (m, 2H, 10-H/11-H), 1.70 (s, 3H, 12-H), 1.65–1.58 (m, 1H, 10-H), 1.56–1.50 (m, 1H, 11-H) ppm.  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.6 (C4), 130.4 (C7), 129.9 (C8), 127.4 (C5), 70.9

(C6), 59.5 (C2), 34.1 (C11), 30.0 (C3), 25.3 (C9), 23.5 (C12), 18.9 (C10) ppm. **GC–MS** *m/z* 164 (11, M<sup>+</sup>), 149 (12, M-CH<sub>3</sub>), 136 (82, M-25), 121 (100, M-43), 105 (11, M-59), 91 (34, M-73), 79 (16, M-85), 77 (17, M-87), 67 (8, M-97), 55 (11, M-109). HRMS: calcd. for C<sub>11</sub>H<sub>16</sub>O [M+H]<sup>+</sup> 165.1274; found 165.1269.

**General Procedure for biocatalytic oxidations with PSA:** 600 mg PSA lyophilisate were dissolved in 30 mL Tris HCl buffer. The dried biomass was rehydrated by stirring at 900 rpm for 10 min. The substrate was added and the solution was stirred at 900 rpm at rt. The reaction progress was controlled by GC-FID. After 24 h another 400 mg of PSA lyophilisate and 20 mL buffer were added. After 48 h the reaction was stopped by adding 50 mL of Et<sub>2</sub>O and further stirring of the reaction mixture for 30 min. The solution was filtered and the aqueous phase was extracted with Et<sub>2</sub>O three times. The combined organic phases were dried with MgSO<sub>4</sub>, filtered and concentrated in vacuo. The crude product was analyzed with GC–MS and if necessary GCO and if required purified by column chromatography.

#### **Physical and spectral data of the products:**

**Biotransformation of vitispirane 23;** according to the general procedure vitispirane **23** (192 mg, 1.00 mmol) was treated with 1 g PSA-lyophilisate for 48 h. The crude product was purified by column chromatography (Et<sub>2</sub>O, then EtOAc) to afford the enone **24** (18.0 mg, 8%) and the allylic alcohol **26** (36.2 mg, 16%). The diastereomeric mixture **26** was separated via HPLC (conditions: Waters Sunfire 5  $\mu$ m 250\*4.6 mm, flow: 1 mL/min, UV detection at 202 nm, gradient 10–90% MeCN in H<sub>2</sub>O (0.05% TFA)); enone **24**: *R*<sub>f</sub> = 0.25 (Et<sub>2</sub>O). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.94 (d, <sup>4</sup>*J*<sub>H,H</sub> = 1.2 Hz, 1H, 7-H), 4.54 (dd, <sup>2</sup>*J*<sub>H,H</sub> = 15.2 Hz, <sup>4</sup>*J*<sub>H,H</sub> = 1.2 Hz, 1H, 11-H), 4.25–4.18 (m, 1H, 2-H), 4.16 (dd, <sup>2</sup>*J*<sub>H,H</sub> = 15.2 Hz, <sup>4</sup>*J*<sub>H,H</sub> = 1.2 Hz, 1H, 11-H), 2.44–2.37 (m, 2H, 4-H/9-H), 2.25 (dd, <sup>2</sup>*J*<sub>H,H</sub> = 17.4 Hz, <sup>4</sup>*J*<sub>H,H</sub> = 1.2 Hz, 1H, 9-H), 2.10–2.03 (m, 1H, 3-H), 1.93–1.85 (m, 1H, 4-H), 1.60–1.49 (m, 1H, 3-H), 1.31 (d, <sup>3</sup>*J*<sub>H,H</sub> = 5.8 Hz, 3H, 14-H), 1.04/0.98 (2s, 6H, 12-H/13-H) ppm. **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.7 (C8), 167.3 (C6), 123.1 (C7), 89.1 (C5), 78.3 (C2), 62.6 (C11), 50.3 (C9), 41.2 (C10), 34.3

(C3), 33.4 (C4), 24.3/23.1 (C12/C13), 20.7 (C14) ppm. **GC-MS**  $m/z$  224 (1,  $M^+$ ), 168 (100, M-56), 135 (15, M-89), 121 (21, M-103), 112 (33, M-112), 97 (27, M-127), 84 (21, M-140), 67 (21, M-157), 55 (53, M-169). HRMS (APCI): calcd. for  $C_{13}H_{20}O_3$   $[M+H]^+$  225.1485; found 225.1478.

**Allylic alcohol 26a:**  $R_f = 0.1$  (EtOAc).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  5.67 (s, 1H, 7-H), 4.34 (d,  $^2J_{H,H} = 12.0$  Hz, 1H, 11-H), 4.25–4.20 (m, 1H, 2-H), 4.19–4.15 (m, 1H, 8-H), 3.92 (d,  $^2J_{H,H} = 12.0$  Hz, 1H, 11-H), 2.16–2.11 (m, 1H, 4-H), 2.03–1.99 (m, 1H, 3-H), 1.92–1.86 (m, 1H, 9-H), 1.80–1.74 (m, 1H, 4-H), 1.72–1.69 (m, 1H, 9-H), 1.51–1.44 (m, 1H, 3-H), 1.30 (d,  $^3J_{H,H} = 5.0$  Hz, 3H, 14-H), 1.12 (s, 3H, 12-H), 0.89 (s, 3H, 13-H) ppm.  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  144.73 (C6), 125.60 (C7), 89.66 (C5), 77.28 (C2), 64.57 (C11), 64.10 (C8), 42.85 (C9), 35.63 (C10), 34.34 (C3), 33.20 (C4), 24.54 (C13), 23.98 (C12), 20.74 (C14) ppm. **GC-MS**  $m/z$  208 (6, M-18), 170 (34, M-56), 161 (21, M-65), 152 (100, M-74), 126 (72, M-100), 119 (24, M-107), 111 (30, M-115), 105 (44, M-121), 96 (44, M-130), 91 (47, M-135), 77 (32, M-149), 55 (58, M-171). HRMS (ESI): calcd. for  $C_{13}H_{22}O_3$   $[M+Na]^+$  249.1461; found 249.1467.

**Allylic alcohol 26b:**  $R_f = 0.1$  (EtOAc).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  5.64 (s, 1H, 7-H), 4.37–4.31 (m, 2H, 11-H, 8-H), 4.20 (m, 1H, 2-H), 3.87 (d,  $^2J_{H,H} = 12.0$  Hz, 1H, 11-H), 2.22–2.17 (m, 1H, 4-H), 2.02–1.97 (m, 1H, 3-H), 1.92–1.89 (m, 1H, 4-H), 1.89–1.86 (m, 1H, 9-H), 1.53–1.49 (m, 1H, 3-H), 1.49–1.46 (m, 1H, 9-H), 1.30 (d,  $^3J_{H,H} = 5.0$  Hz, 3H, 14-H), 0.99 (s, 3H, 12-H), 0.92 (s, 3H, 13-H) ppm.  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  144.36 (C6), 127.62 (C7), 89.78 (C5), 77.42 (C2), 65.77 (C8), 64.76 (C11), 44.75 (C9), 39.59 (C10), 35.23 (C4), 34.27 (C3), 24.60 (C13), 21.89 (C12), 20.70 (C14) ppm. **GC-MS**  $m/z$  208 (6, M-18), 170 (34, M-56), 161 (21, M-65), 152 (100, M-74), 126 (72, M-100), 119 (24, M-107), 111 (30, M-115), 105 (44, M-121), 96 (44, M-130), 91 (47, M-135), 77 (32, M-149), 55 (58, M-171). HRMS (ESI): calcd. for  $C_{13}H_{22}O_3$   $[M+Na]^+$  249.1461; found 249.1467

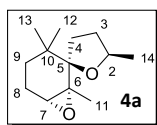
**Biotransformation of spiroether 7;** according to the general procedure, spiroether **7** (150 mg, 0.90 mmol) was treated with 600 mg PSA lyophilisate for 48 h. The crude product was purified by column chromatography (pentane/Et<sub>2</sub>O, 4:1 → 1:1) to afford spirolactone **14** (72.9 mg, 45%) as a colorless oil; *R*<sub>f</sub> = 0.49 (pentane/Et<sub>2</sub>O, 4:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.79–5.78 (m, 1H, 3-H), 2.30 (s, 2H, 5-H), 1.94 (s, 3H, 12-H), 1.96–1.30 (m, 10H, 7-11-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.9 (C2), 154.9 (C4), 116.1 (C3), 80.6 (C6), 40.0 (C5), 36.4 (C7/C11), 25.5 (C9), 23.4 (C12), 21.7 (C8/C10) ppm. GC–MS *m/z* 180 (18, M<sup>+</sup>), 152 (7, M-28), 137 (19, M-43), 124 (29, M-56), 109 (14, M-71), 96 (10, M-84), 82 (100, M-98), 55 (22, M-125). HRMS (APCI): calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> [M+H]<sup>+</sup> 181.1223; found 181.1218.

**Biotransformation of spiroether 8;** according to the general procedure spiroether **8** (125 mg, 0.75 mmol) was treated with 600 mg PSA lyophilisate for 48 h. No conversion was observed.

**Biotransformation of spirodiene 11;** according to the general procedure spiroether **11** (200 mg, 1.21 mmol) was treated with 800 mg PSA lyophilisate for 48 h. The crude product was purified by column chromatography (pentane/Et<sub>2</sub>O, 3:2) to afford spirolactone **17** (69.0 mg, 0.39 mmol, 32%) as a colorless oil; *R*<sub>f</sub> = 0.3 (pentane/Et<sub>2</sub>O, 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.93–5.89 (m, 1H, 8-H), 5.83–5.82 (m, 1H, 3-H), 5.78–5.76 (m, 1H, 7-H), 2.44 (d, <sup>4</sup>*J*<sub>H,H</sub> = 17.8 Hz, 1H, 5-H), 2.33 (d, <sup>2</sup>*J*<sub>H,H</sub> = 17.8 Hz, 1H, 5-H), 2.11–1.56 (m, 6H, 9-11-H), 1.95 (s, 3H, 12-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 164.7 (C2), 154.6 (C4), 132.9 (C8), 127.6 (C7), 116.5 (C3), 78.1 (C6), 40.1 (C5), 34.7 (C11), 25.1 (C9), 23.4 (C12), 18.3 (C10) ppm. GC–MS *m/z* 178 (2, M<sup>+</sup>), 150 (9, M-28), 91 (6, M-87), 82 (100, M-96), 79 (12, M-99), 39 (18, M-139). HRMS (APCI): calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> [M+H]<sup>+</sup> 118.1223; found 118.1218.

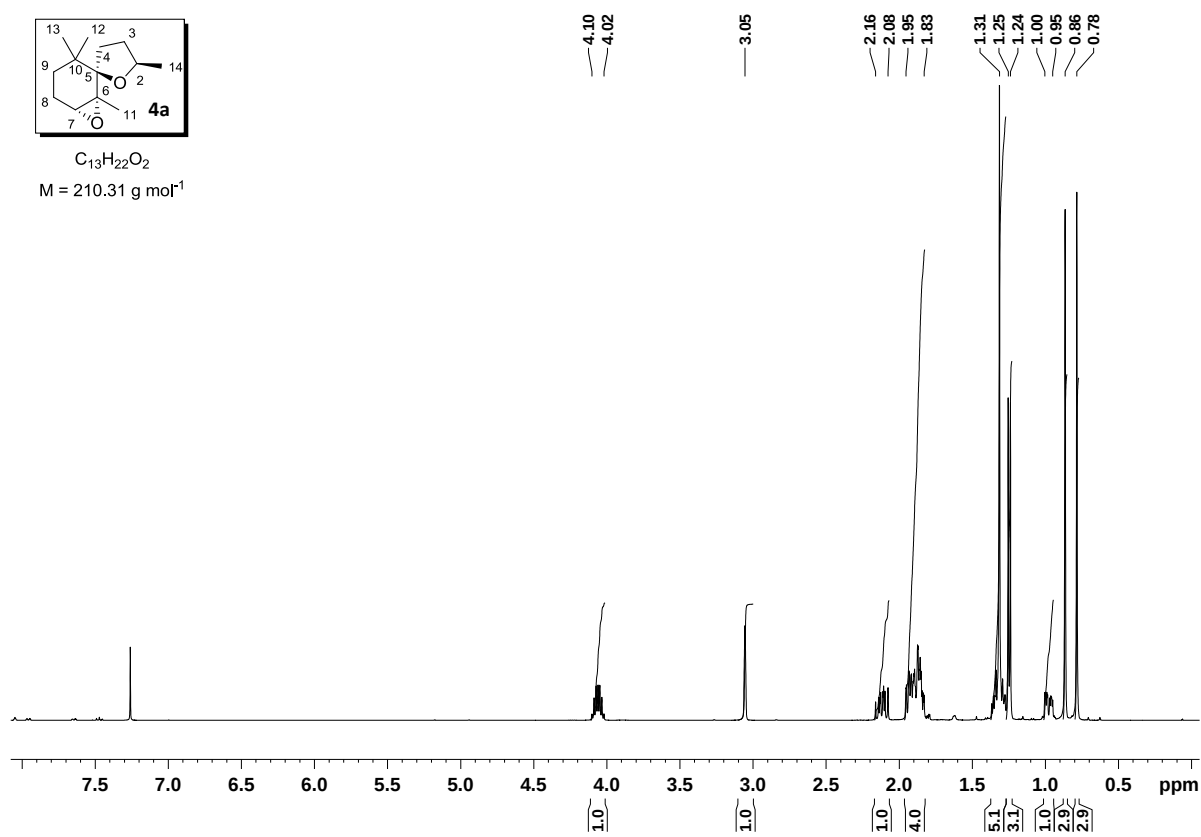
**Biotransformation of spirodiene 12;** according to the general procedure spiroether **12** (100 mg, 0.60 mmol) was treated with 1 g PSA lyophilisate for 7 d. No conversion was observed.

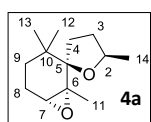
# NMR spectra



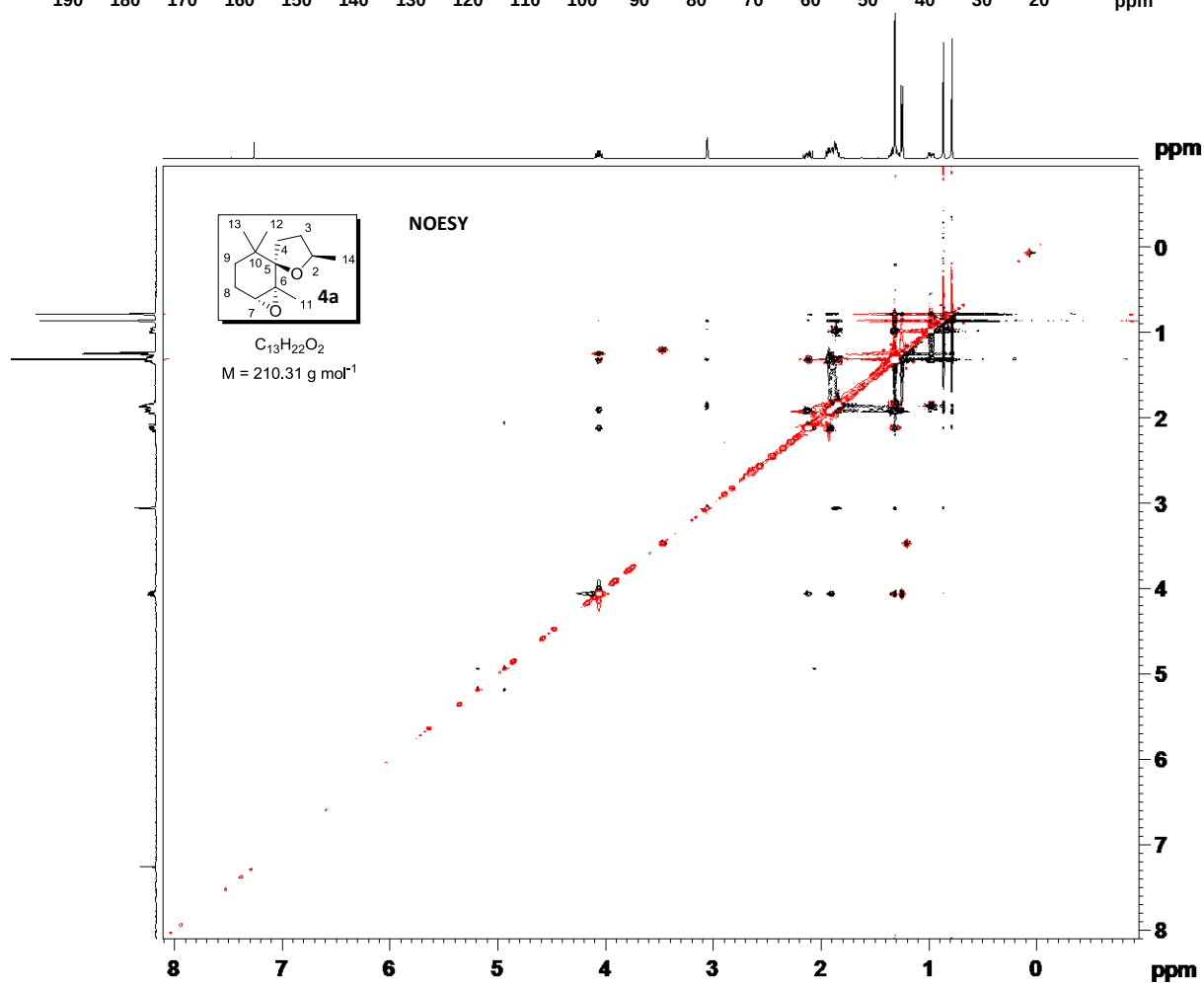
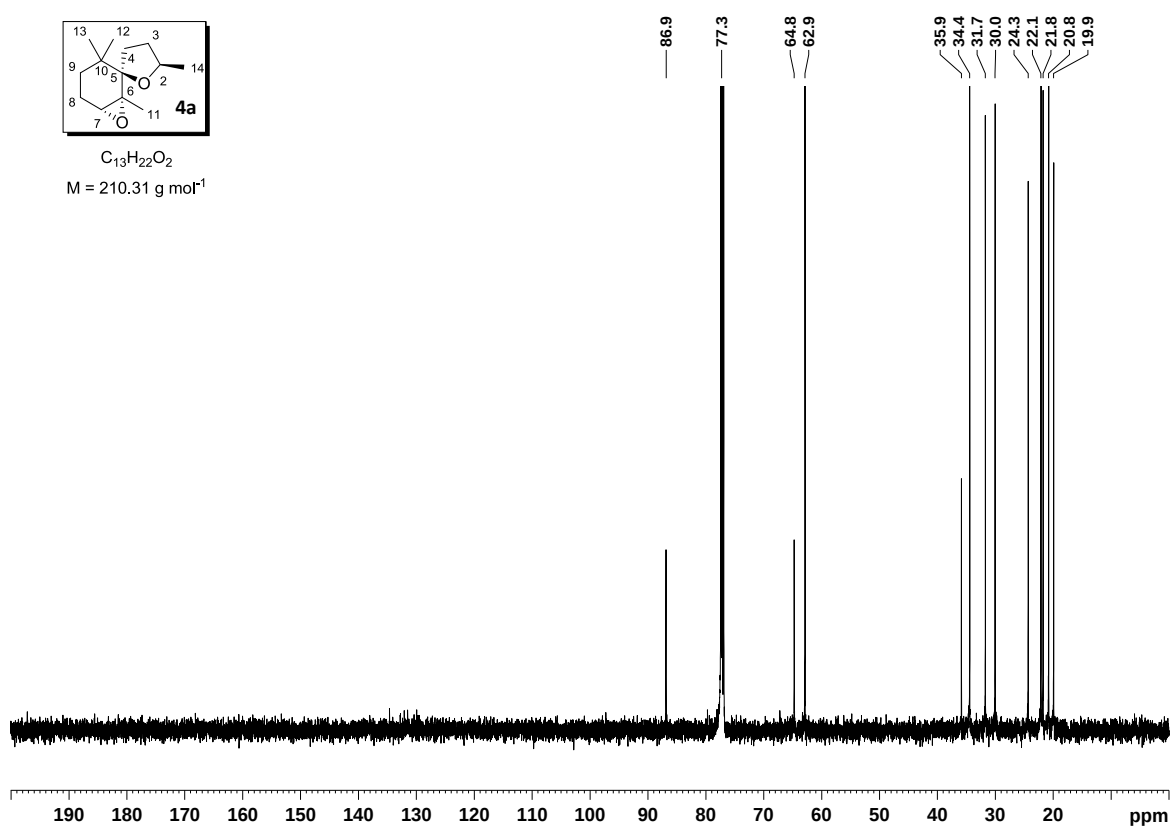
$C_{13}H_{22}O_2$

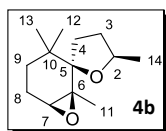
$M = 210.31 \text{ g mol}^{-1}$





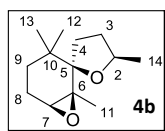
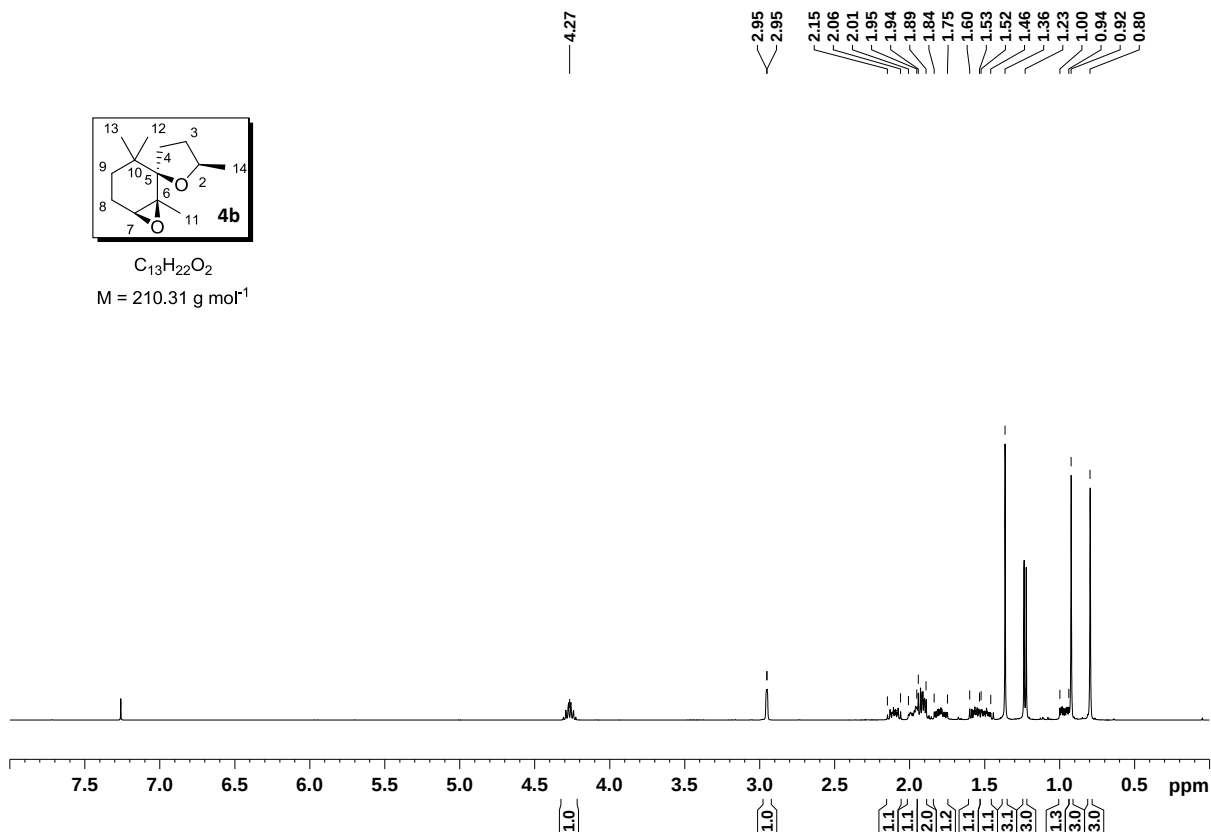
$C_{13}H_{22}O_2$   
 $M = 210.31 \text{ g mol}^{-1}$





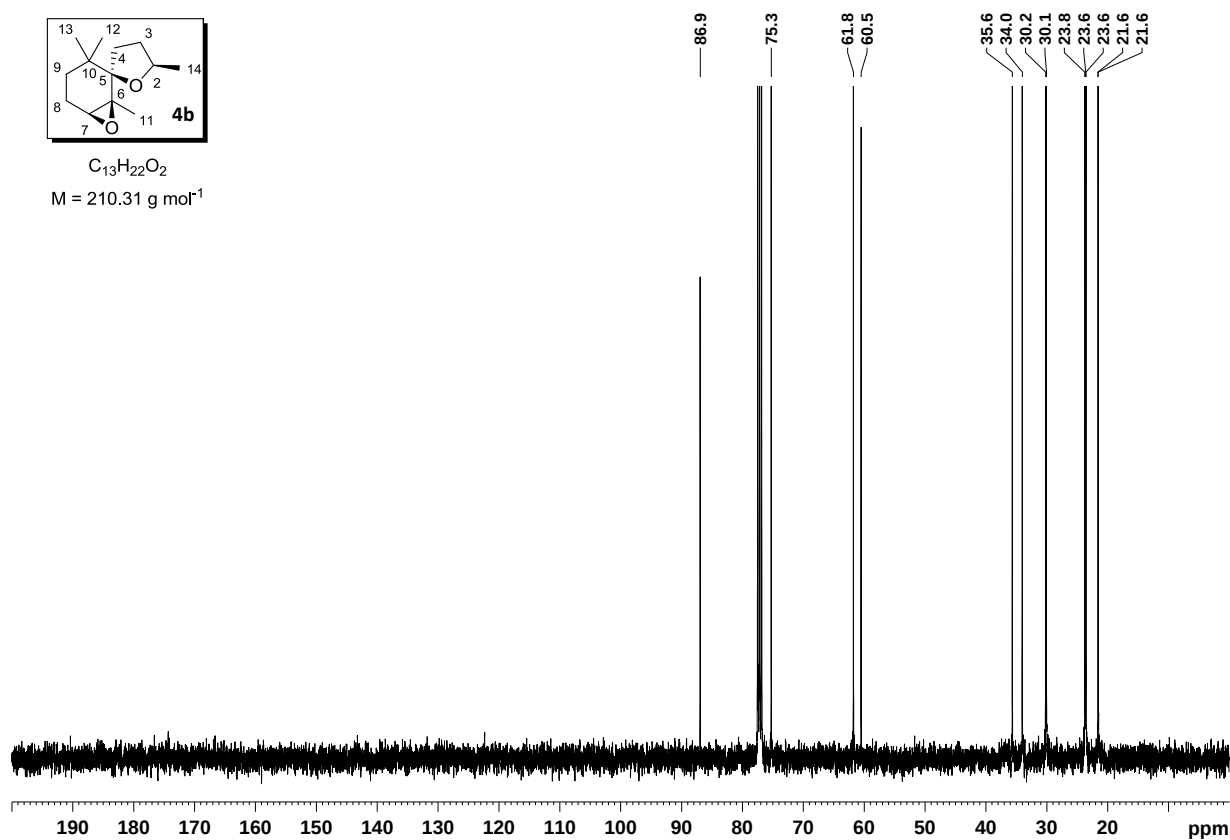
$C_{13}H_{22}O_2$

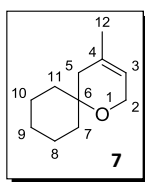
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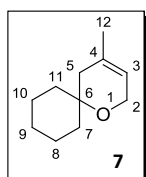
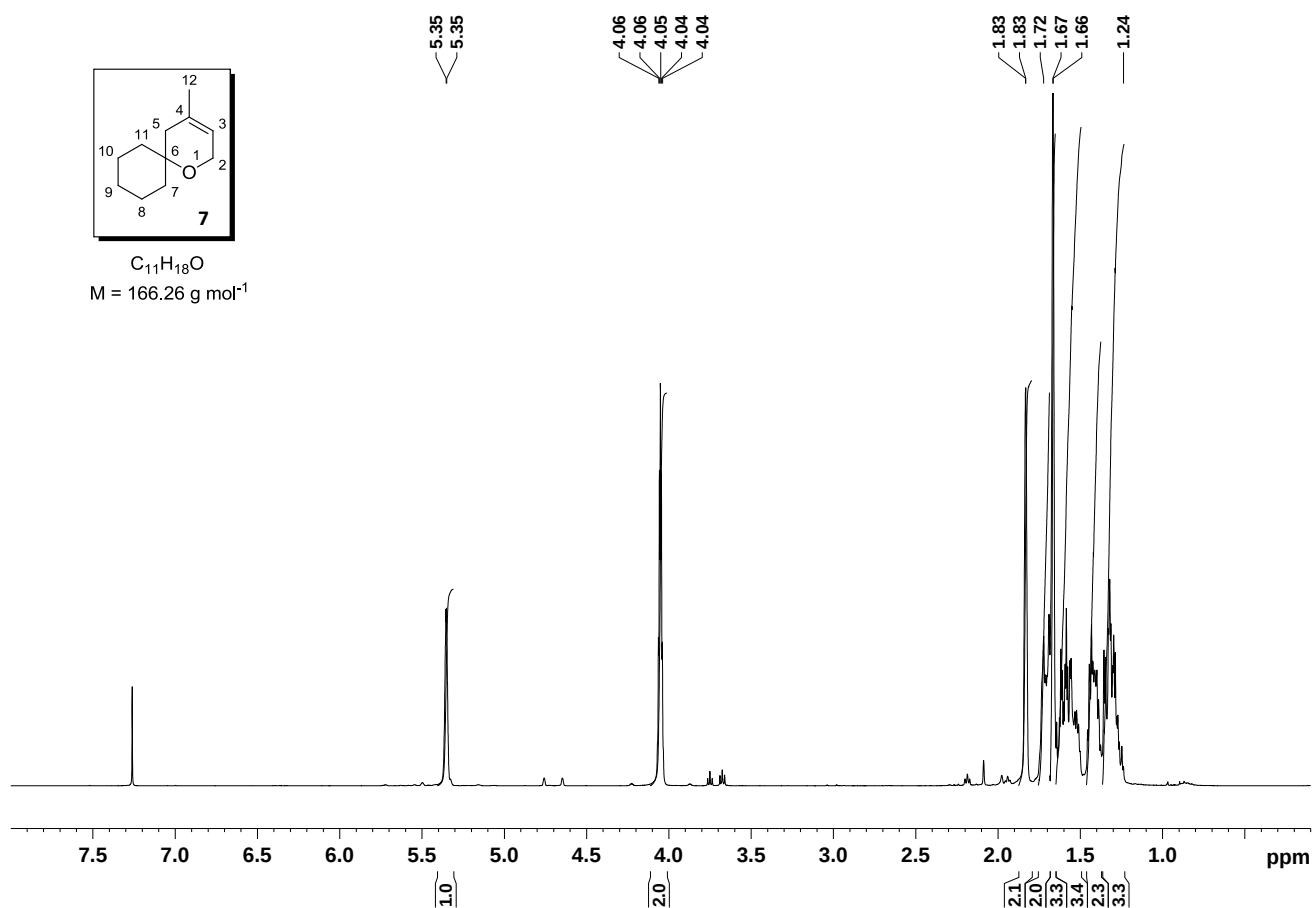
$C_{13}H_{22}O_2$

$M = 210.31 \text{ g mol}^{-1}$

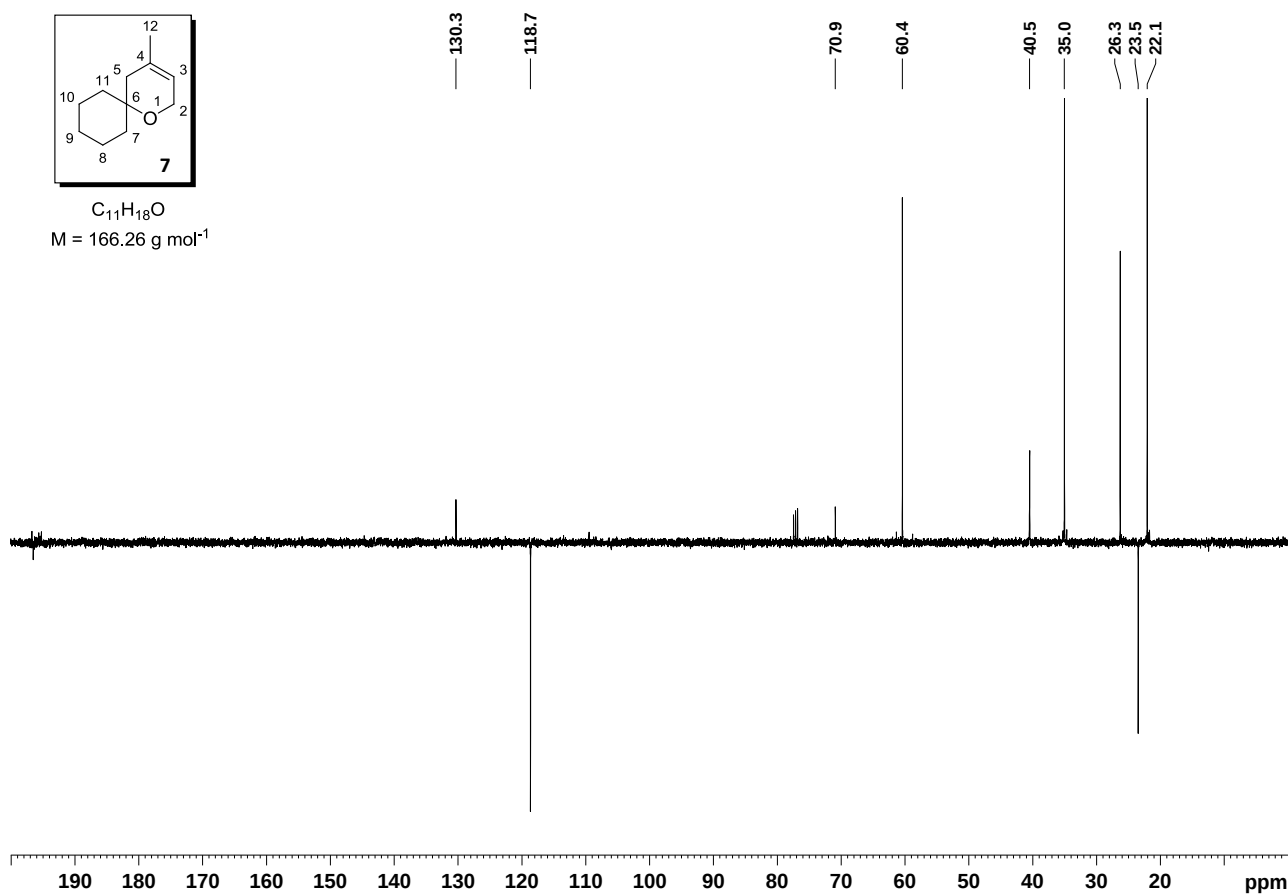


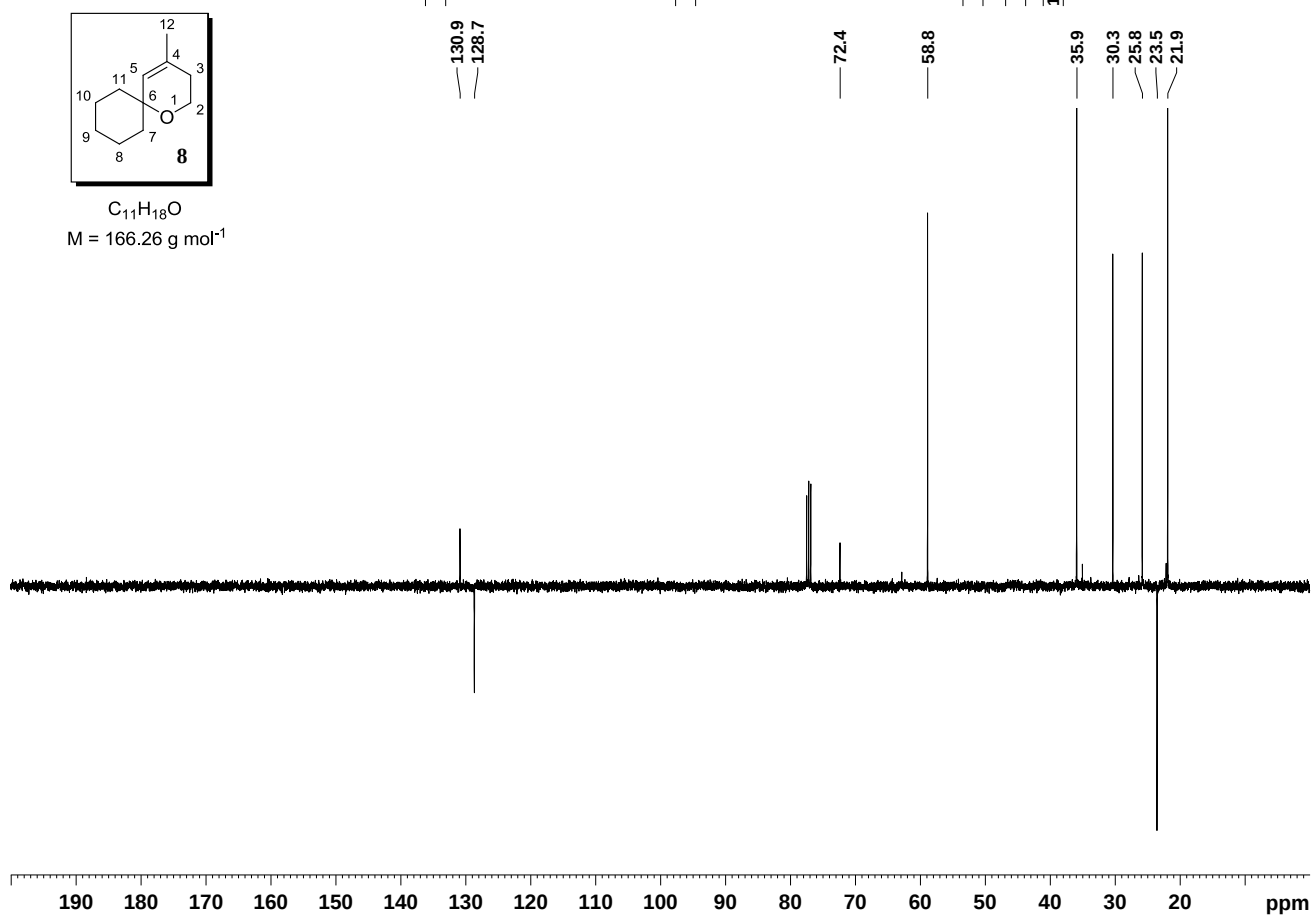
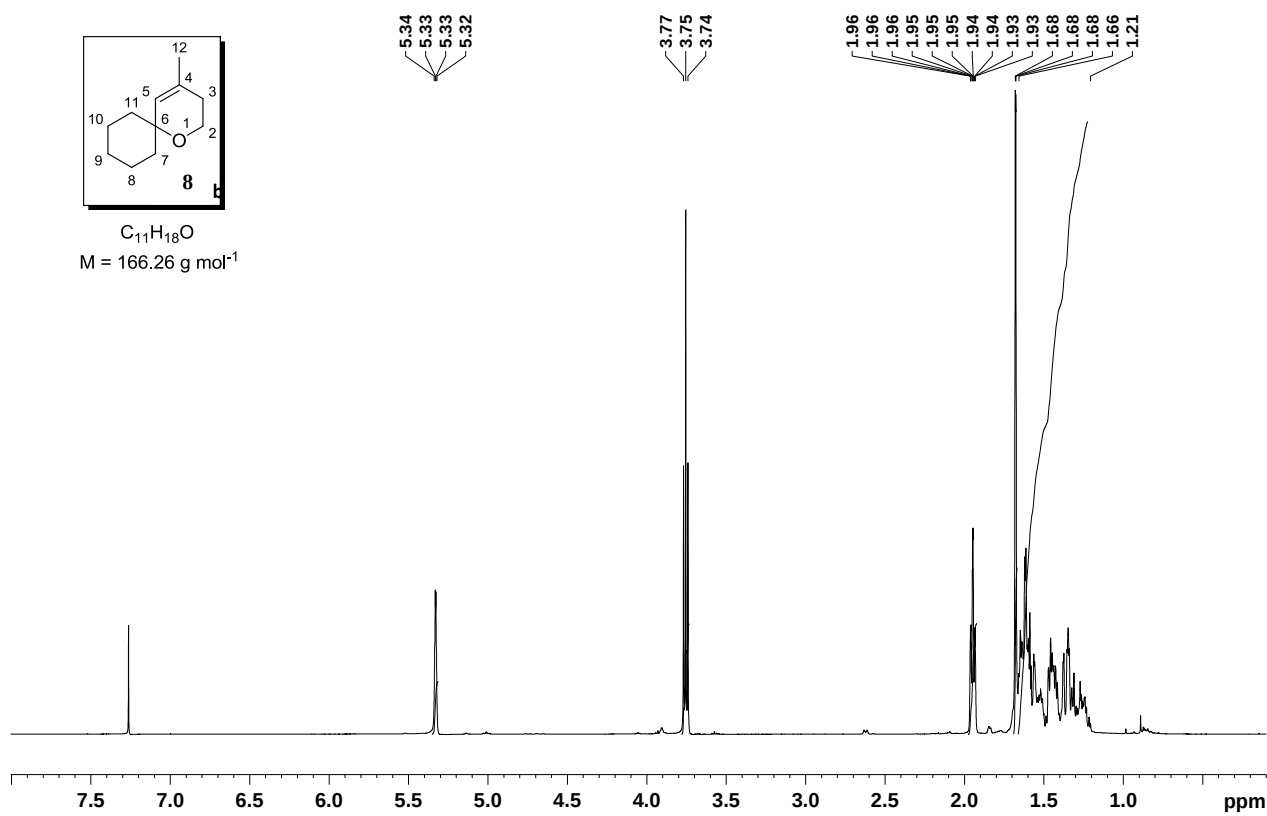


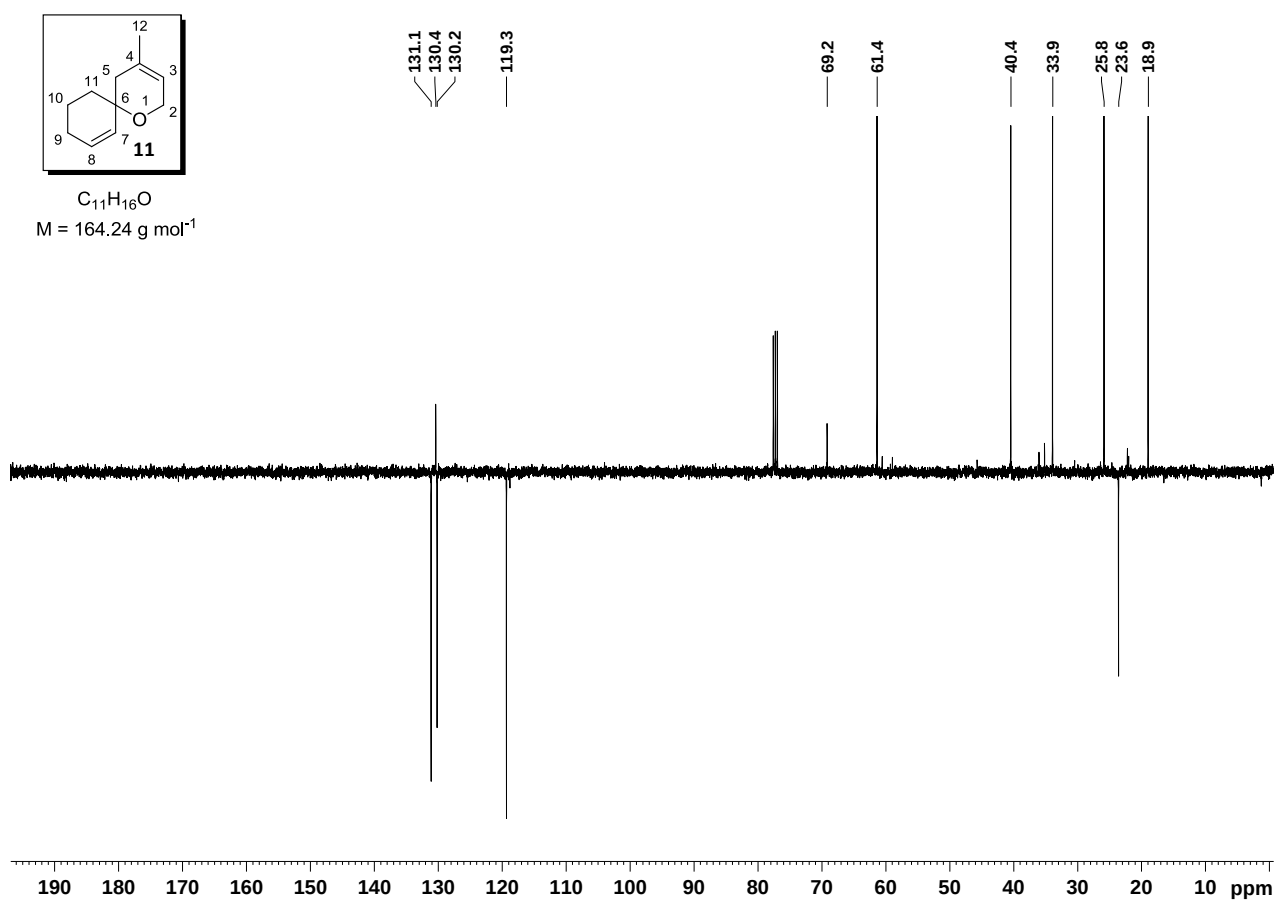
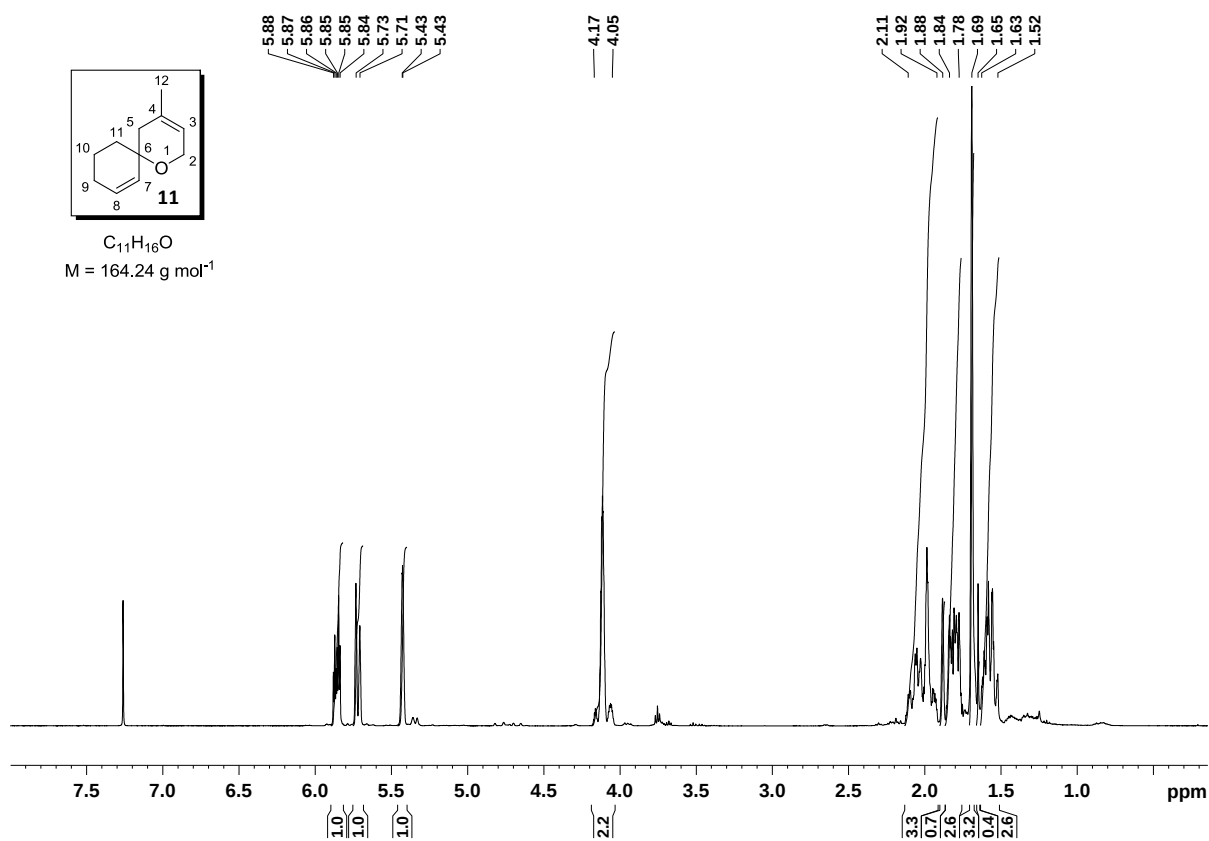
$C_{11}H_{18}O$   
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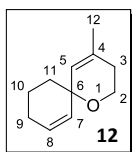


$C_{11}H_{18}O$   
 $M = 166.26 \text{ g mol}^{-1}$

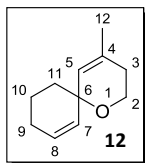
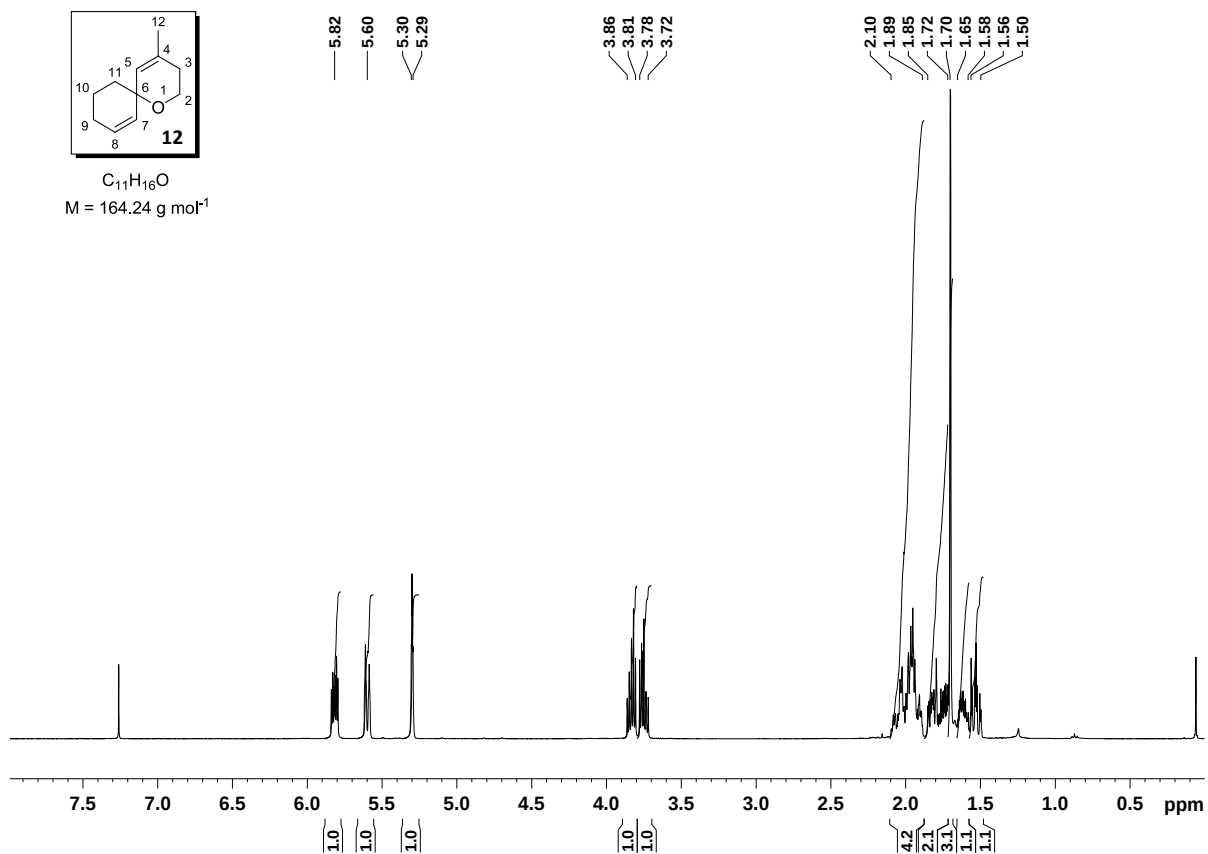




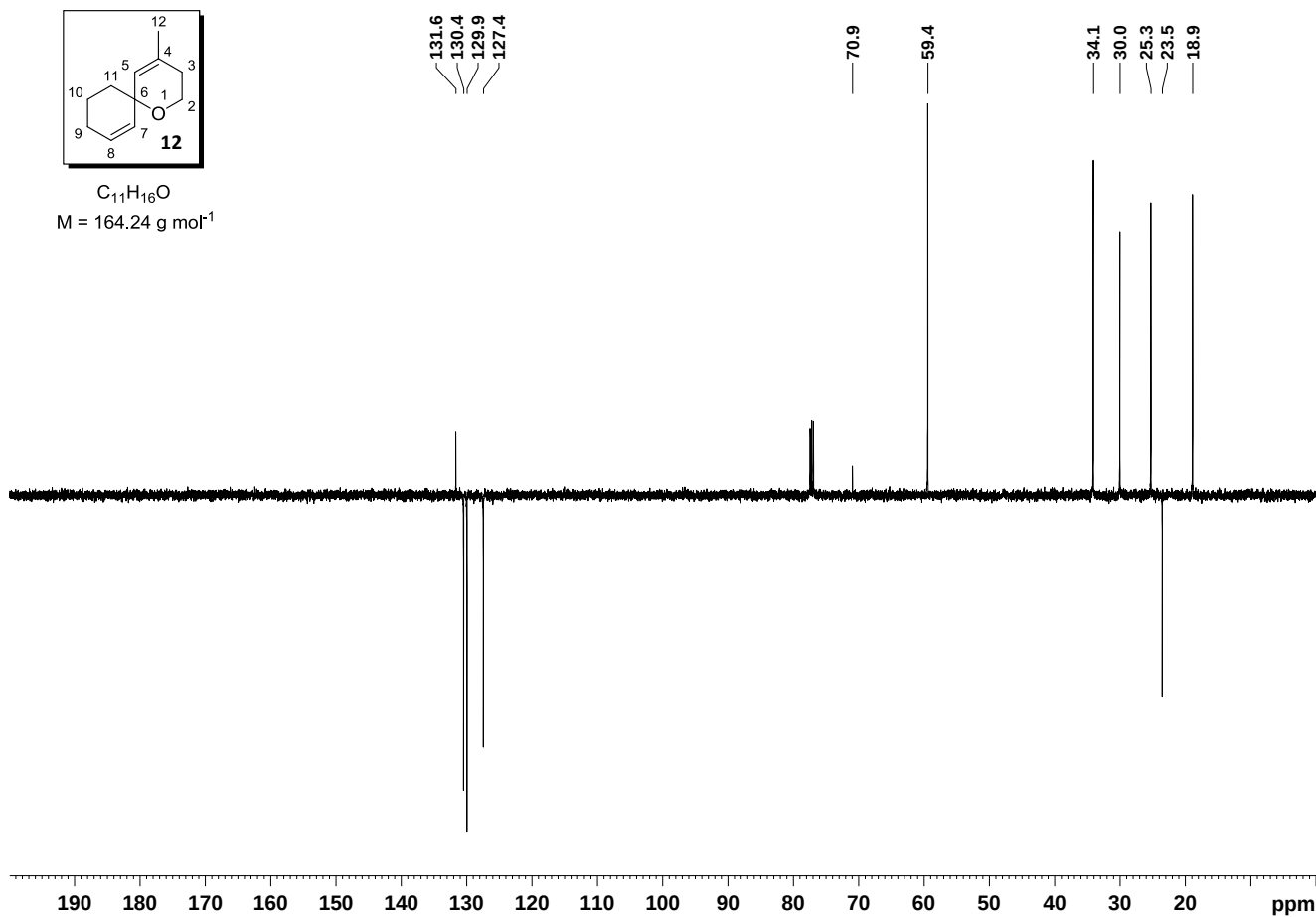


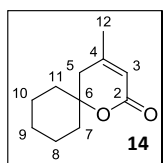


$C_{11}H_{16}O$   
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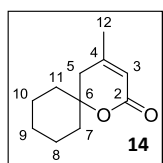
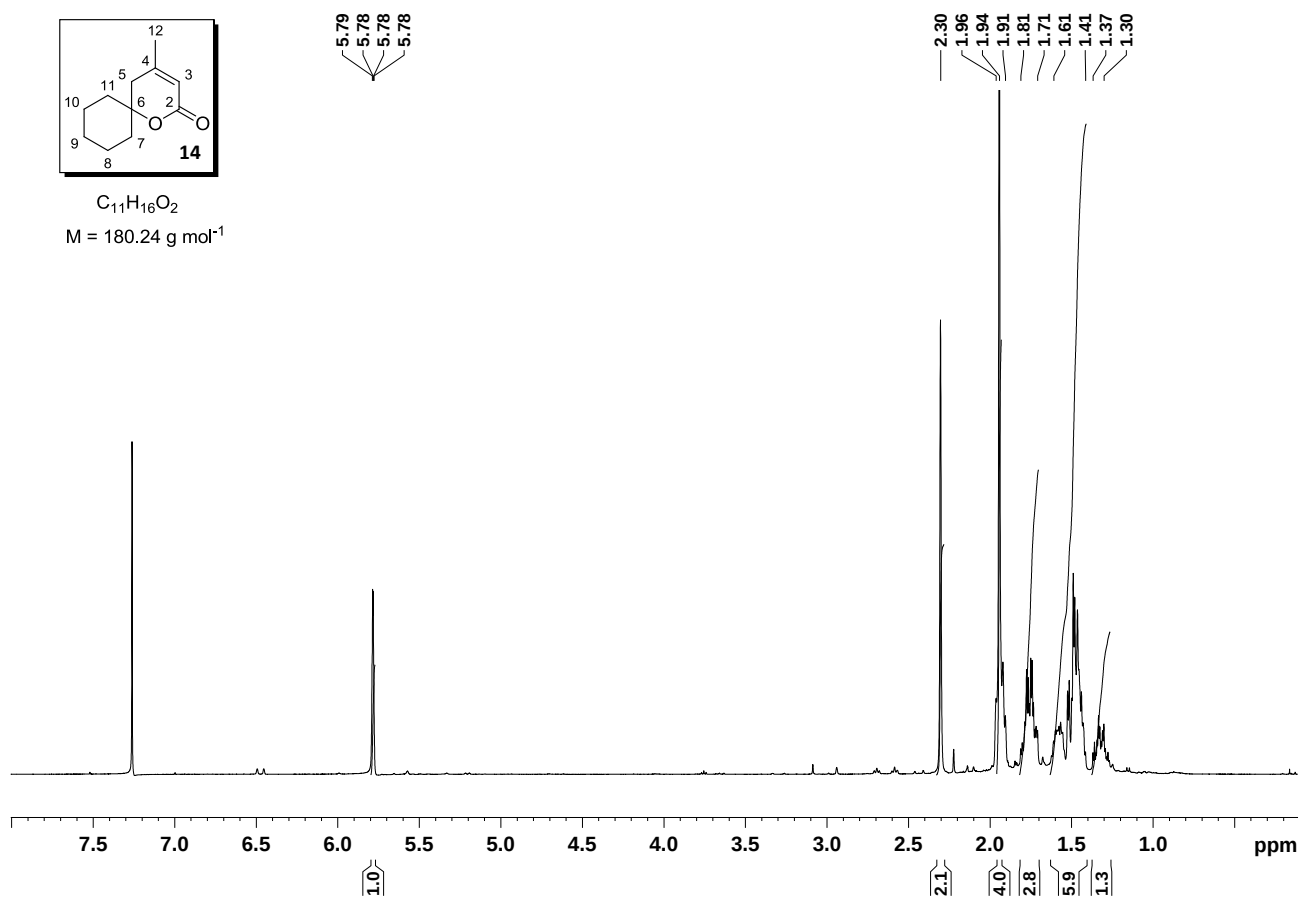


$C_{11}H_{16}O$   
 $M = 164.24 \text{ g mol}^{-1}$

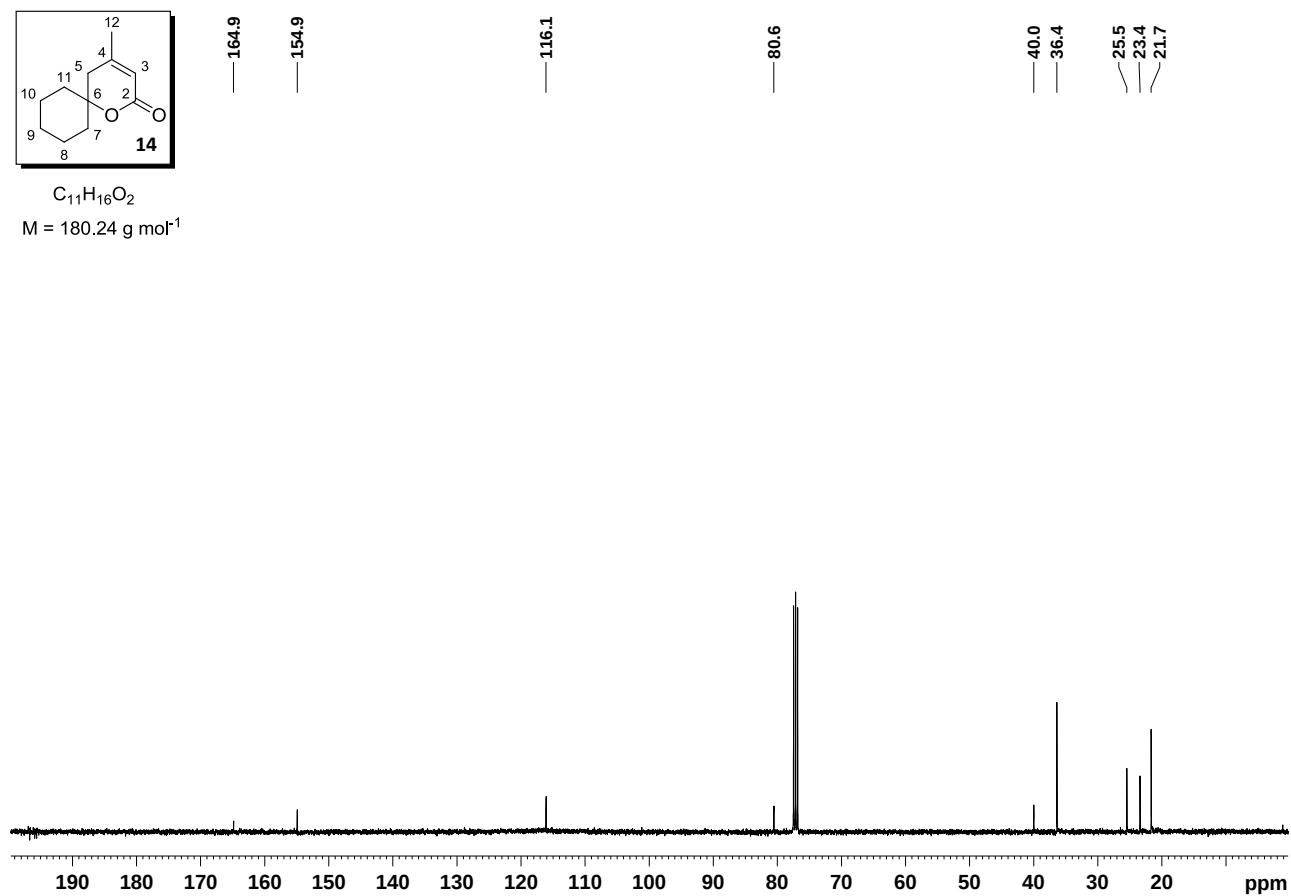


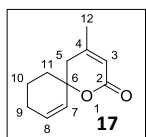


$C_{11}H_{16}O_2$   
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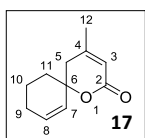
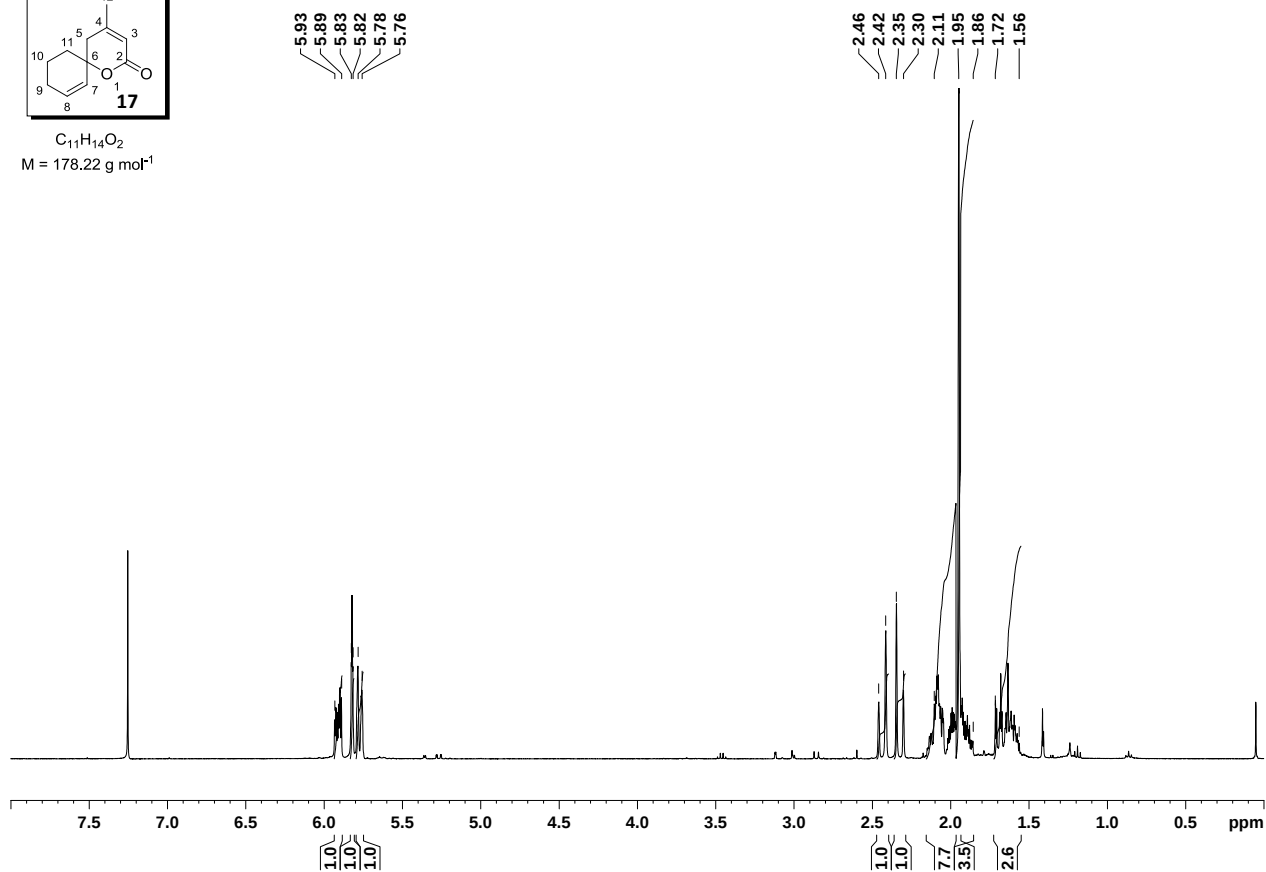


$C_{11}H_{16}O_2$   
 $M = 180.24 \text{ g mol}^{-1}$

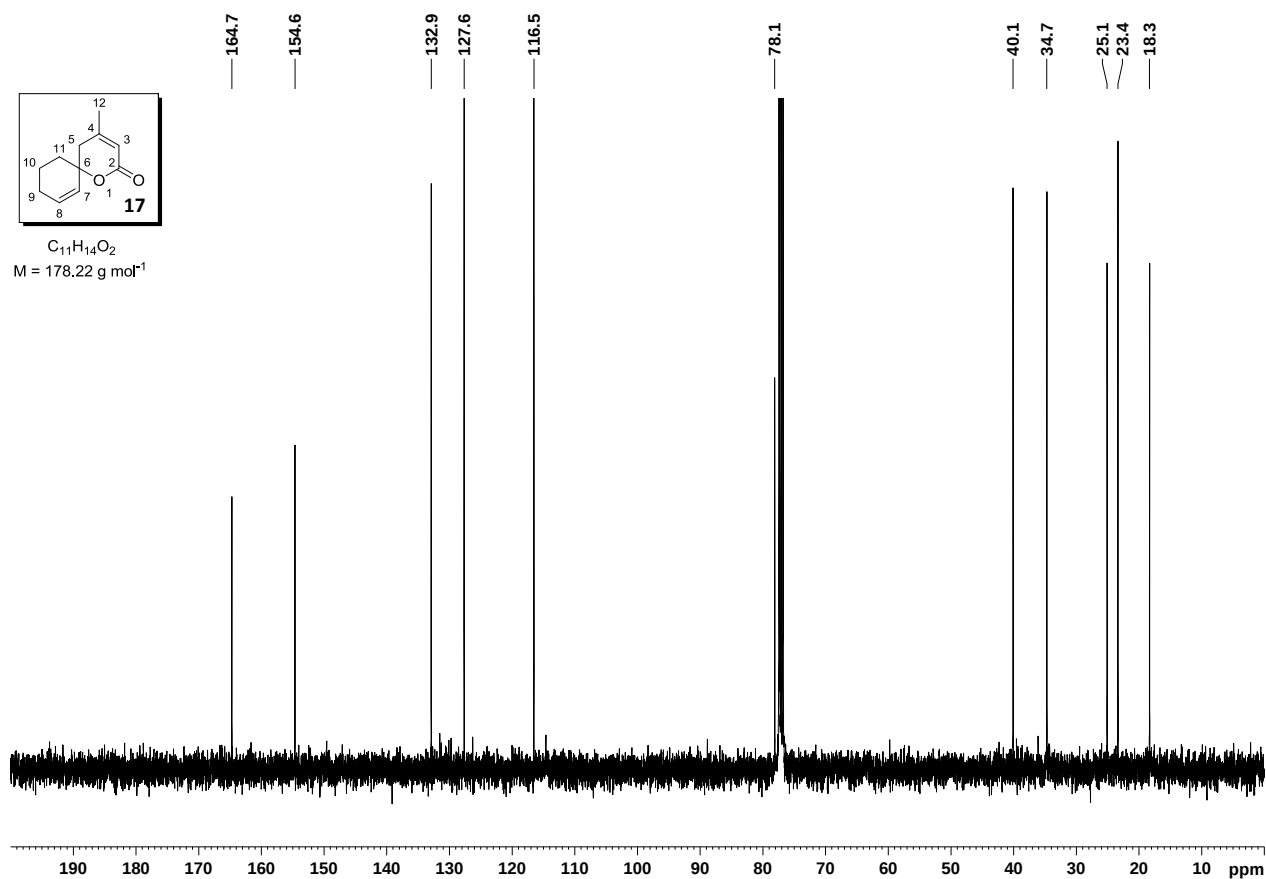


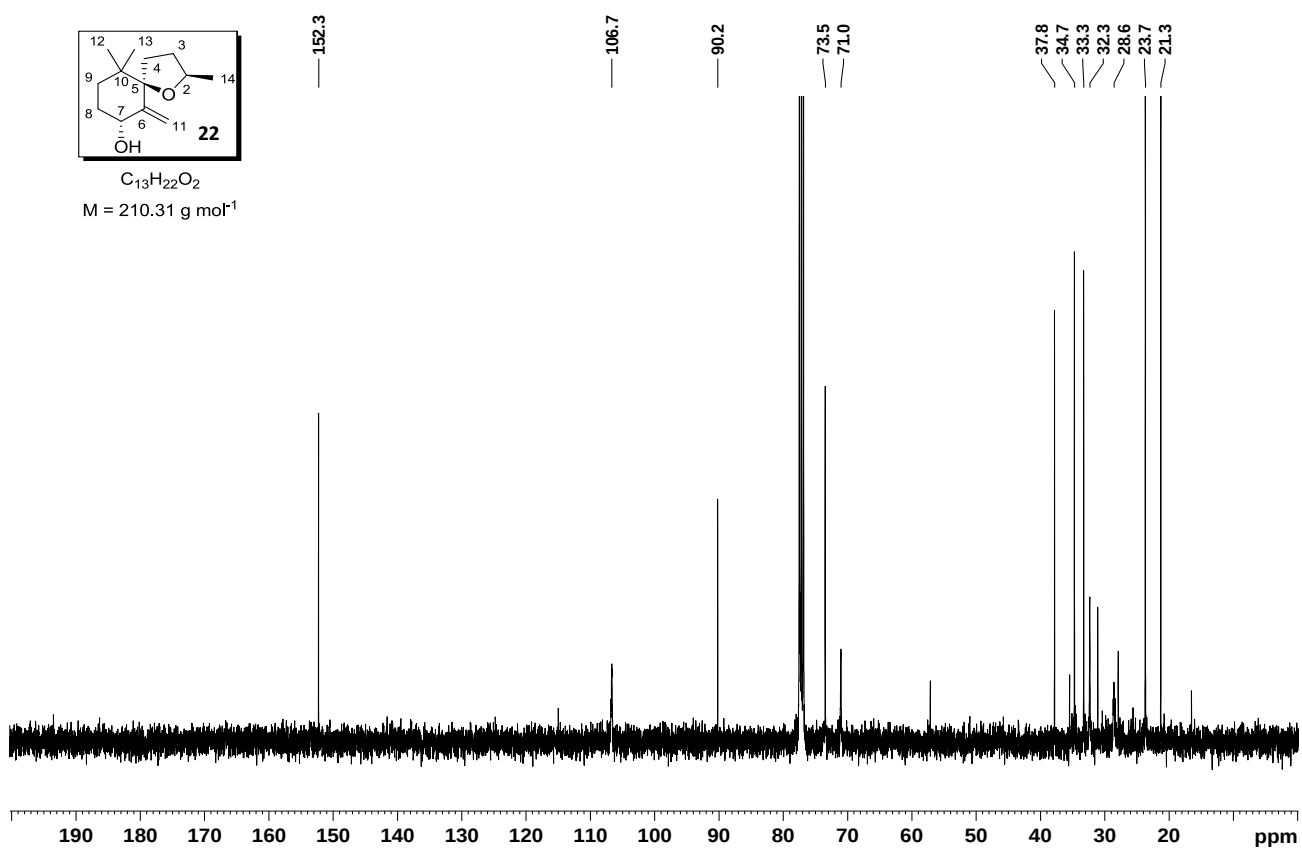
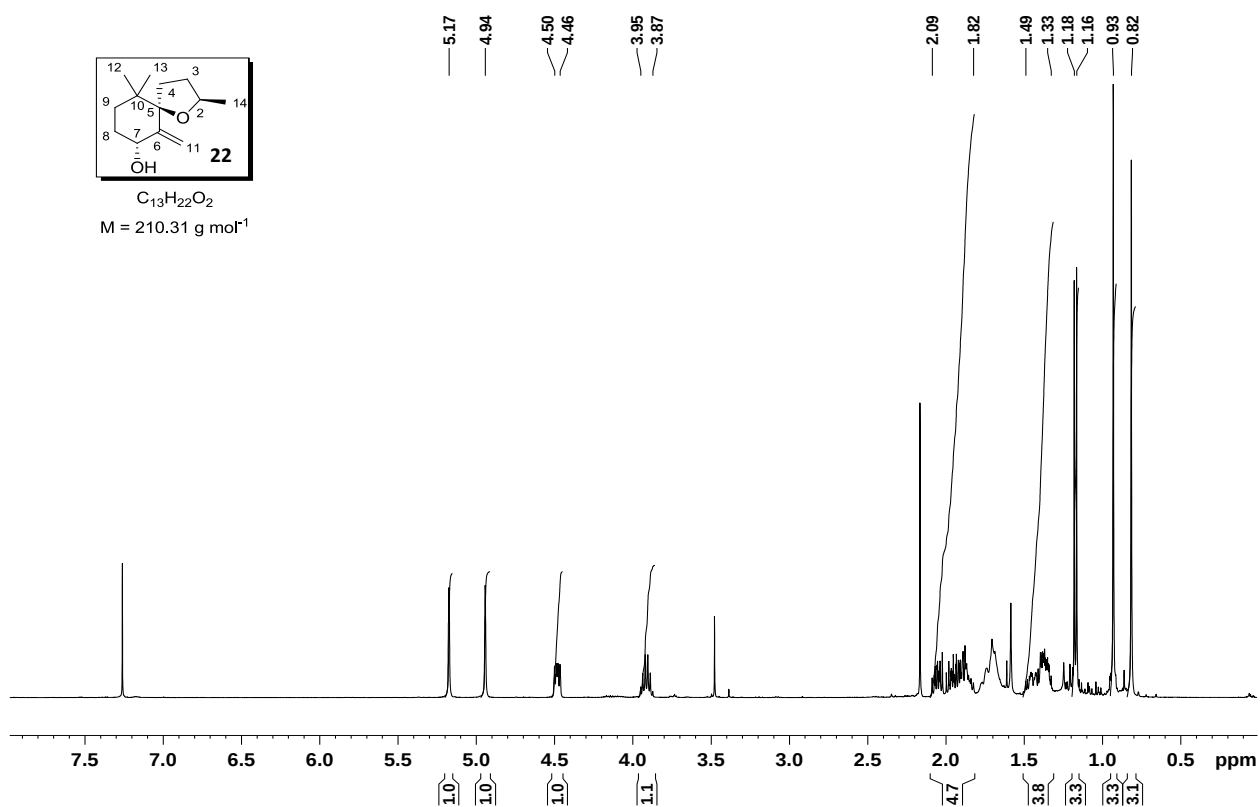


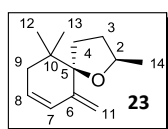
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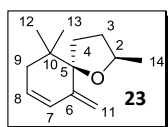
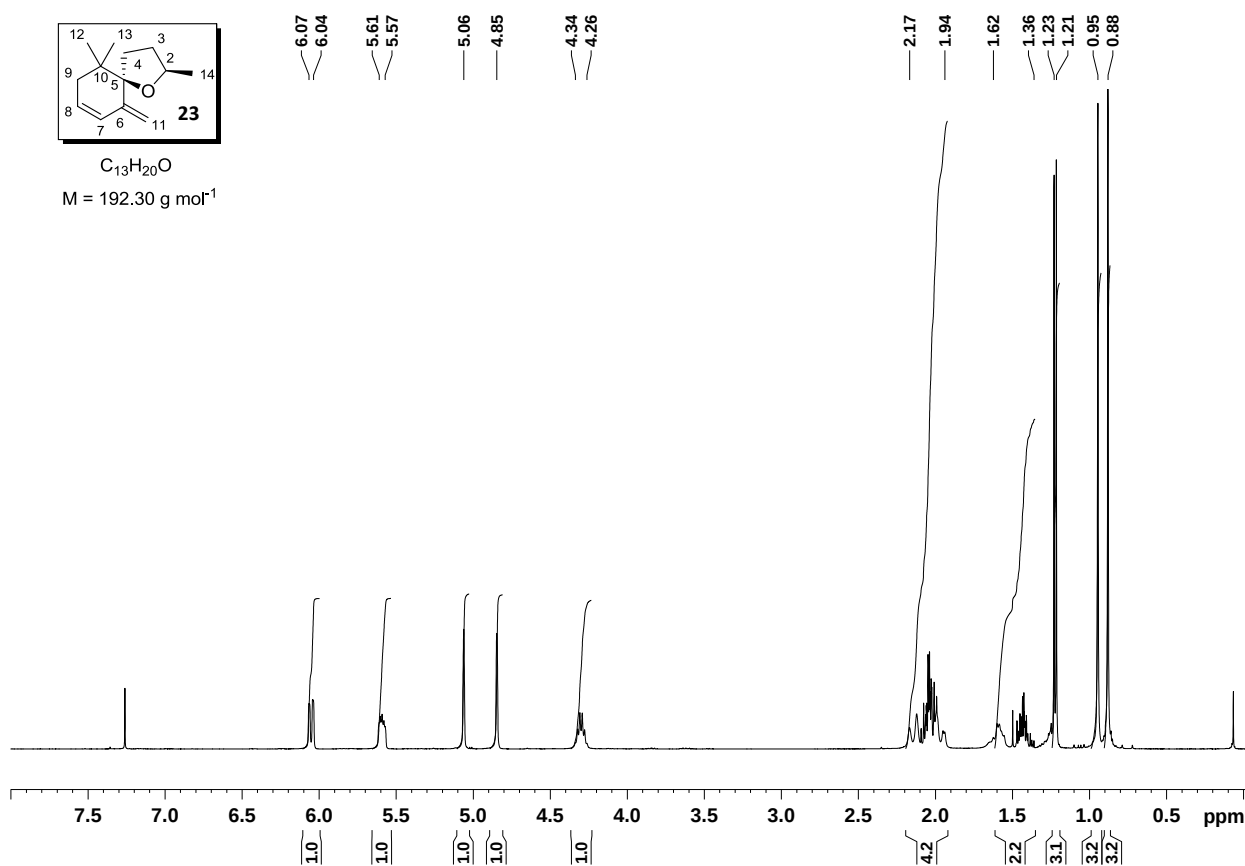
$C_{11}H_{14}O_2$   
 $M = 178.22 \text{ g mol}^{-1}$



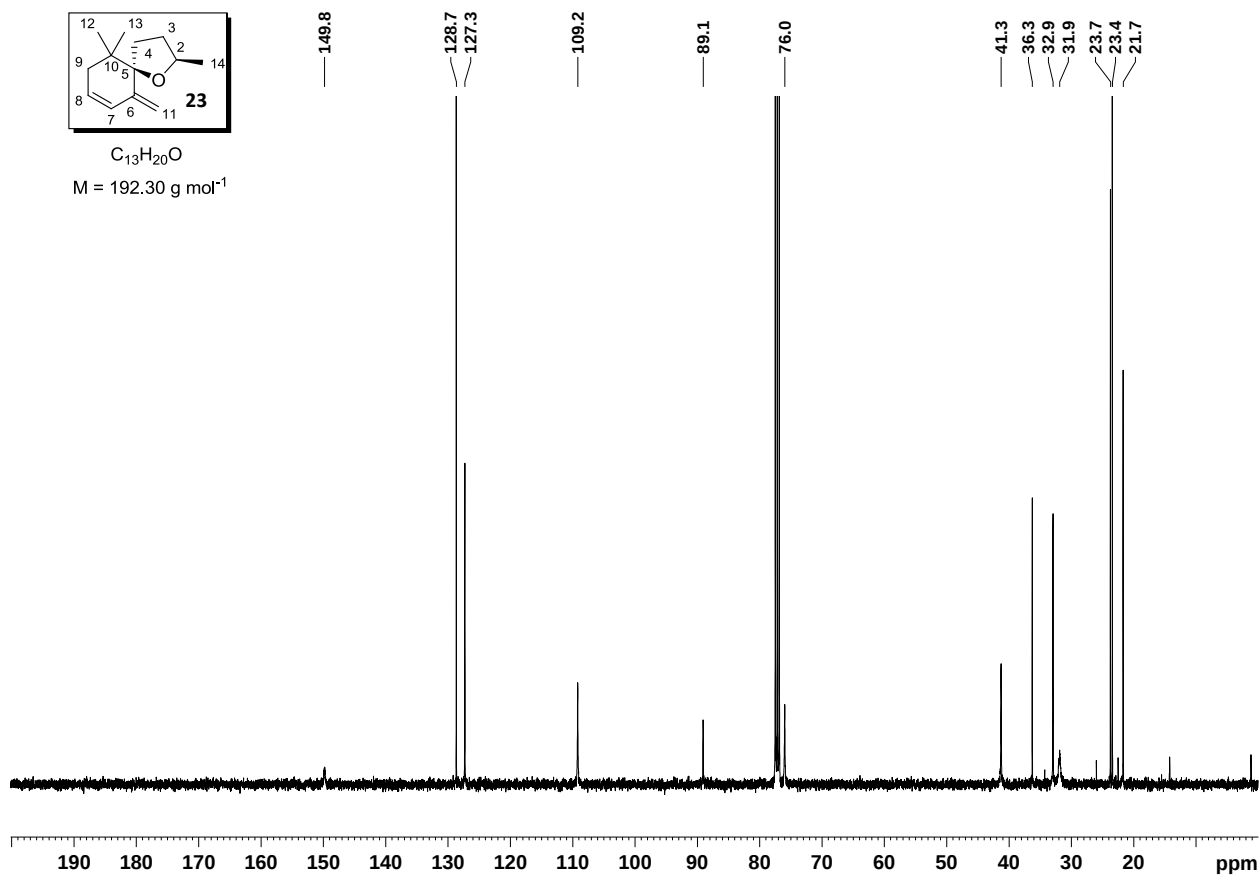


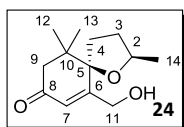


$C_{13}H_{20}O$   
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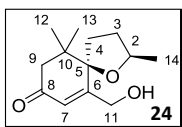
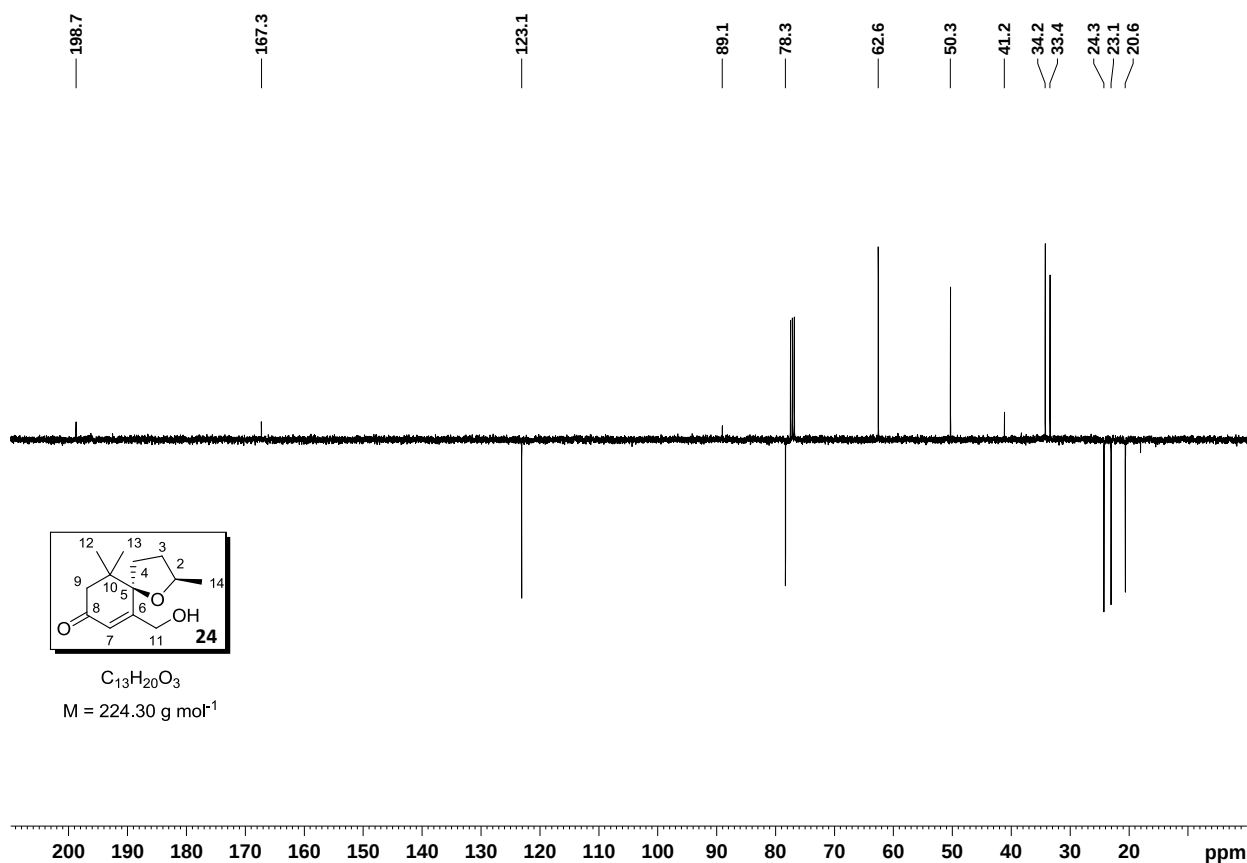
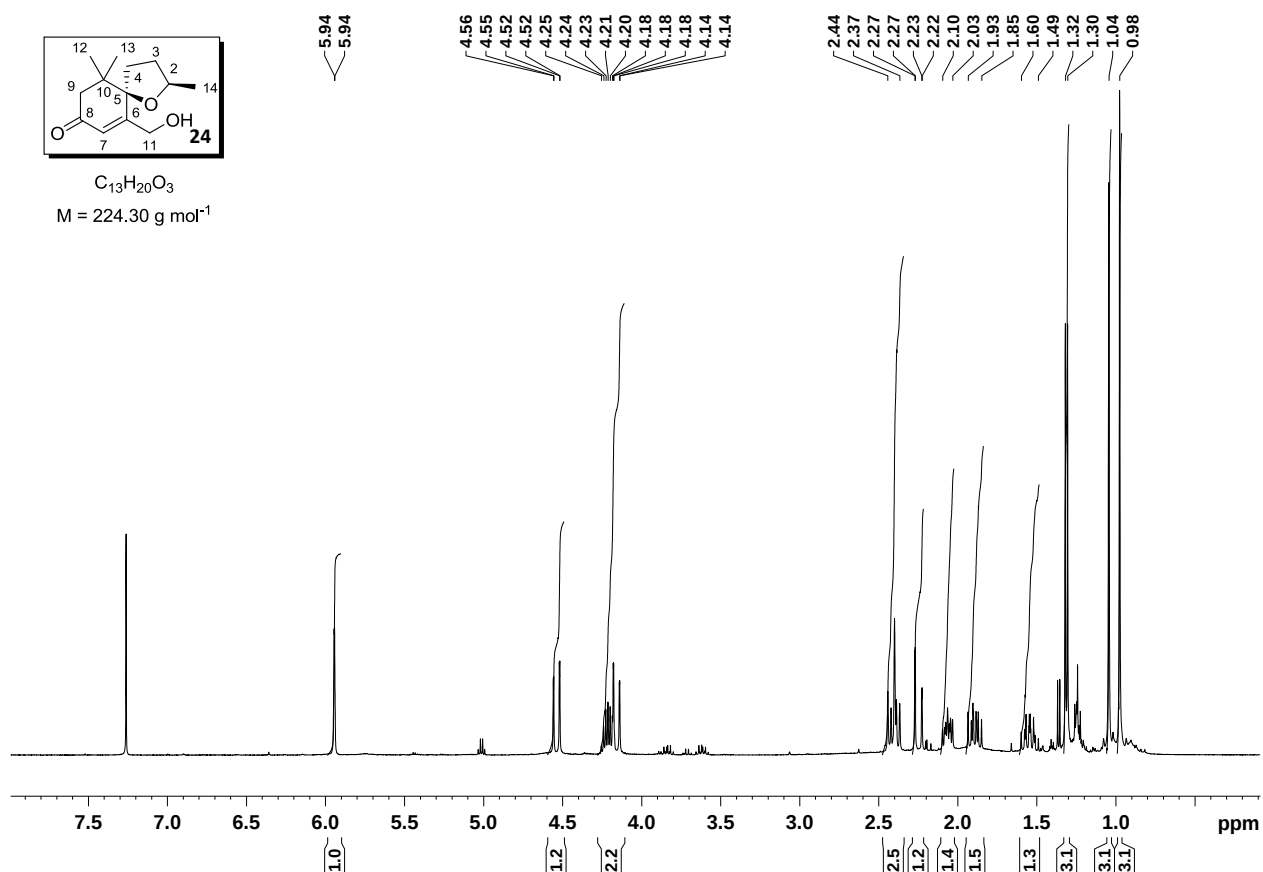


$C_{13}H_{20}O$   
 $M = 192.30 \text{ g mol}^{-1}$





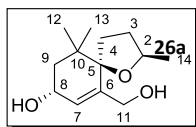
$C_{13}H_{20}O_3$   
 $M = 224.30 \text{ g mol}^{-1}$



$C_{13}H_{20}O_3$   
 $M = 224.30 \text{ g mol}^{-1}$

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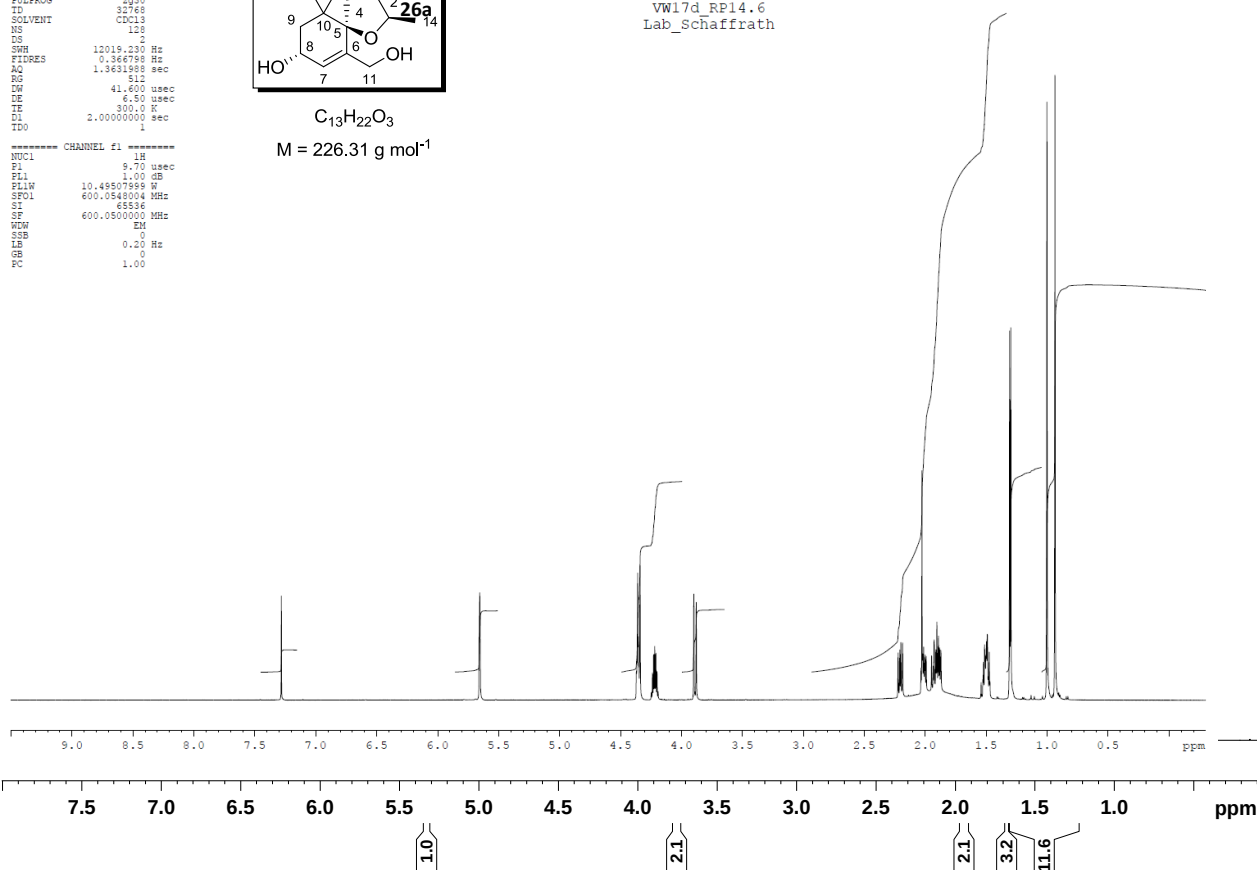
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$C_{13}H_{22}O_3$

$M = 226.31 \text{ g mol}^{-1}$

h913303  
 VW17d\_RP14.6  
 Lab\_Schaffrath

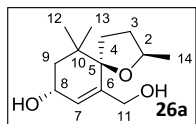


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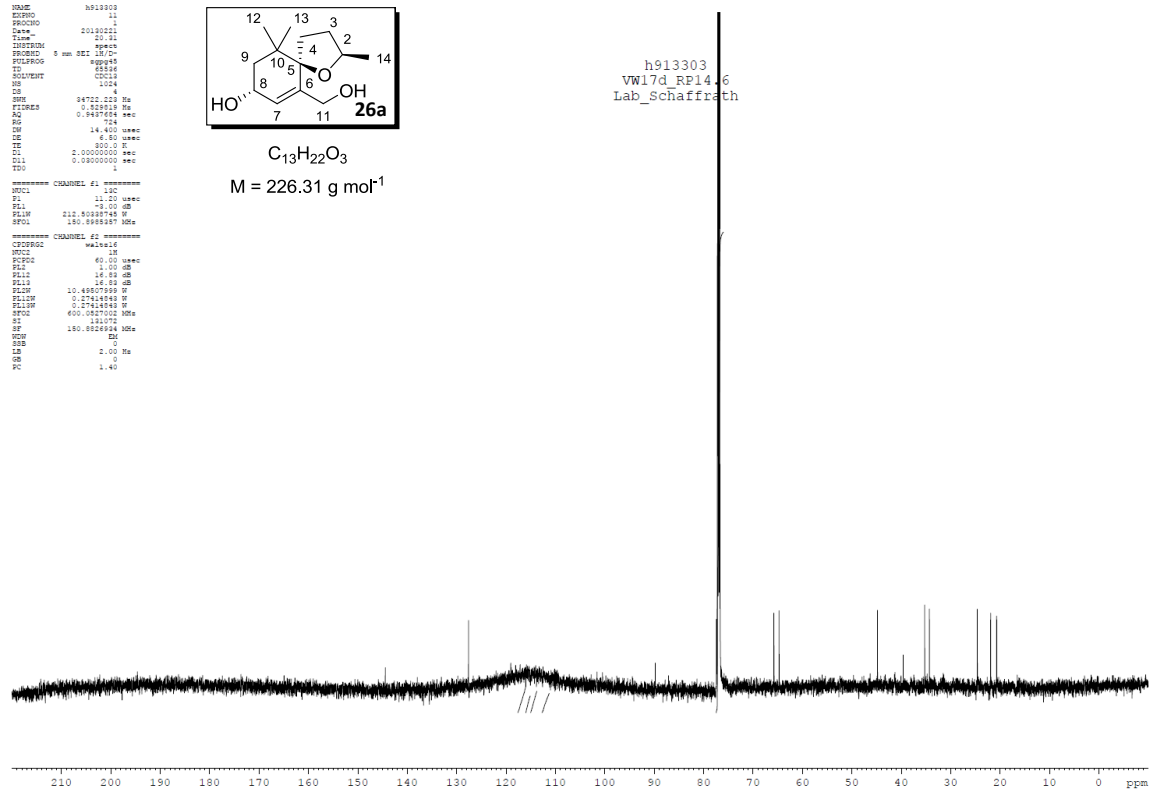
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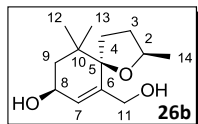
$C_{13}H_{22}O_3$

$M = 226.31 \text{ g mol}^{-1}$

h913303  
 VW17d\_RP14.6  
 Lab\_Schaffrath



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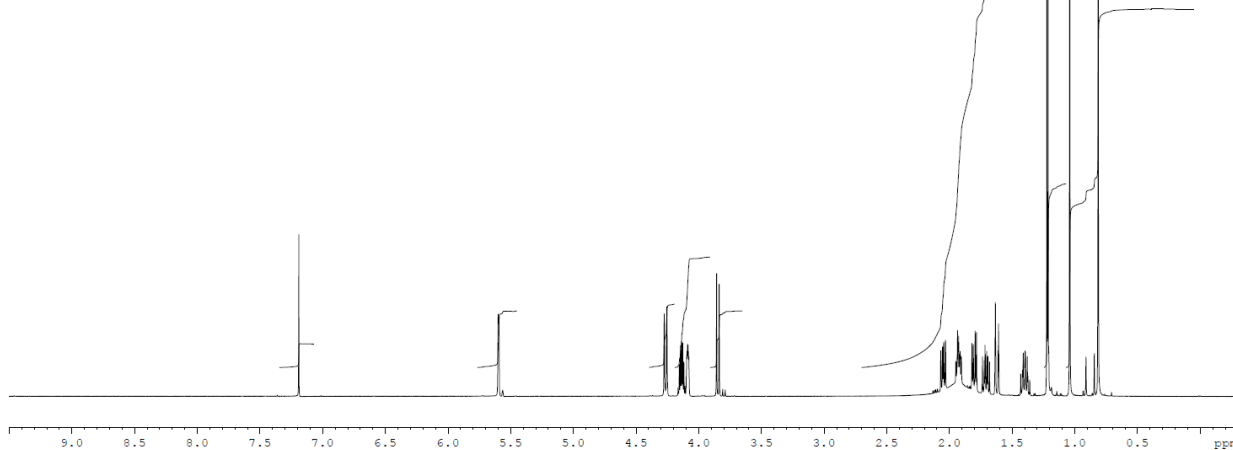


$C_{13}H_{22}O_3$

$M = 226.31 \text{ g mol}^{-1}$

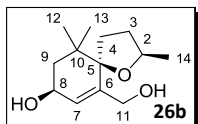
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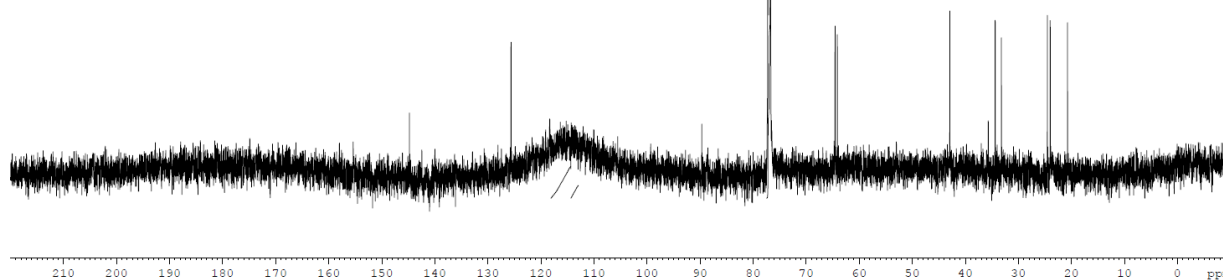


$C_{13}H_{22}O_3$

$M = 226.31 \text{ g mol}^{-1}$

h913304  
 VW17d\_RP15.7  
 Lab\_Schaffrath

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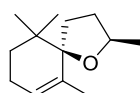
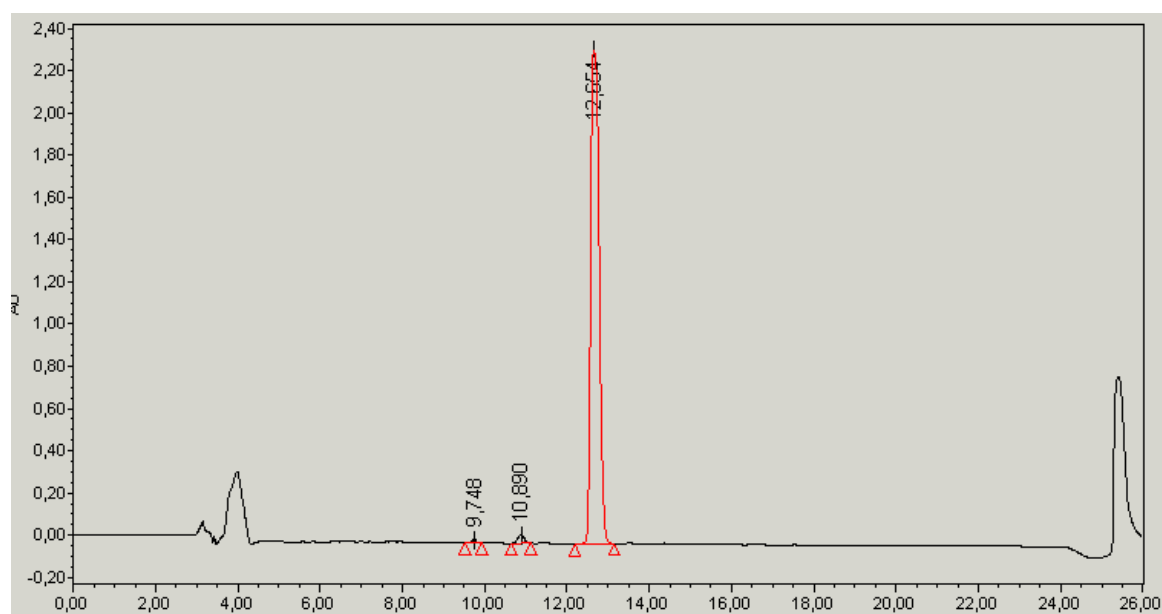
## HPLC analysis, Methods

*Quality control of the compounds:* All measurements were performed on an analytical Waters H-class UPLC system with a quadrupol mass and a PDA detector. For the reversed phase method, a Waters Sunfire C18 phase was used as stationary phase. Mobil phases were H<sub>2</sub>O/MeCN gradients with 0.05% TFA as modifier.

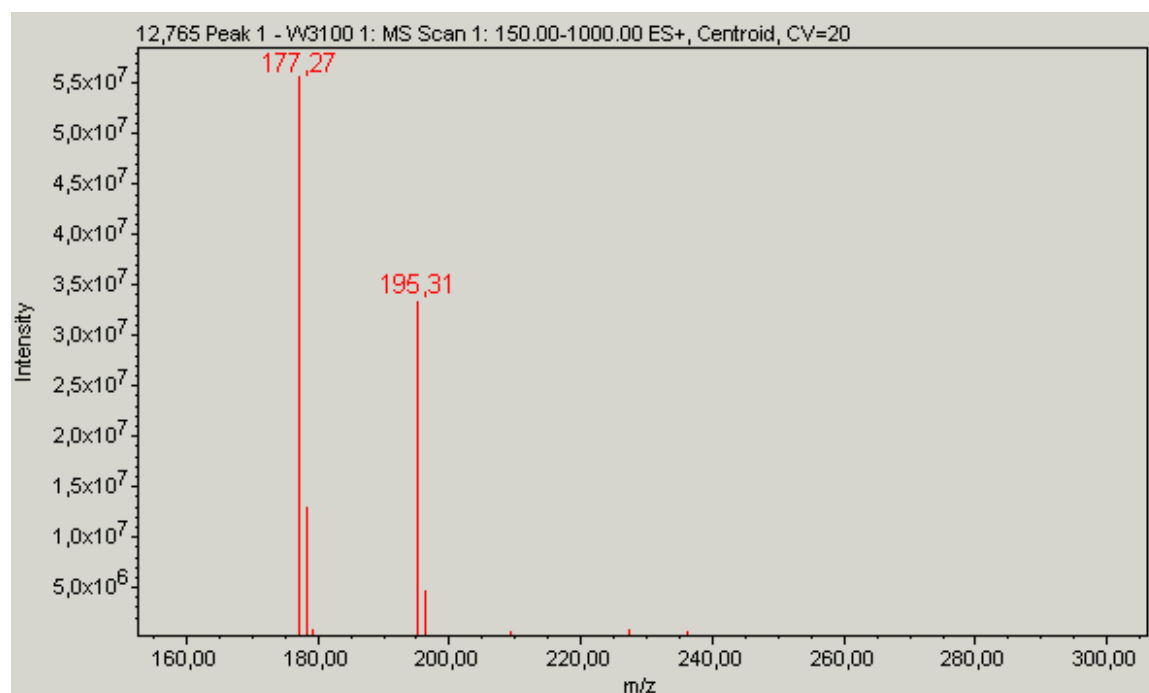
*Separation of enantiomeric mixtures:* The measurements were performed with analytical Waters Alliance HPLC systems with PDA and chiral detectors. For the normal phase method development several commercial and non-commercial (not listed) amylose and cellulose derivatized chiral stationary phases (CSP) were available. Amylose: Daicel Chiralpak AD-H, AS-H, IA, IB, IF, AY, Phenomenex Lux Amylose-2; Cellulose: Daicel Chiralcel OD-H, OJ-H, IC, OZ-H, Phenomenex Lux Cellulose-4. As mobile phase different mixtures of MeOH, EtOH, *iso*-PrOH, MeCN and heptane were used. Modifier was TFA or diethylamine (DEA).

*Separation of the diastereomers:* The reversed phase method development was performed with an analytical Waters H-class UPLC system with a quadrupol mass and a PDA detector. The preparative separation was carried out by a preparative Jasco HPLC with an UV detector. Mobil phase: MeCN/H<sub>2</sub>O gradient, flow rate 30 mL/min, stationary phase: Waters Sunfire C18.

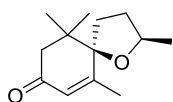
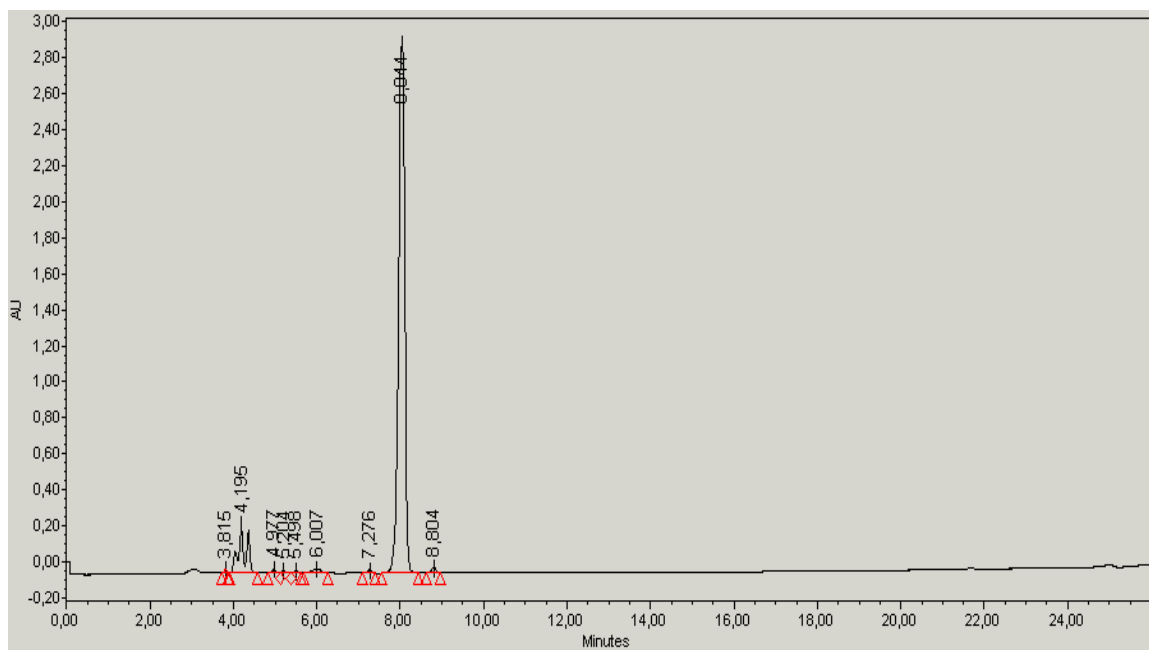
## Chromatographic data



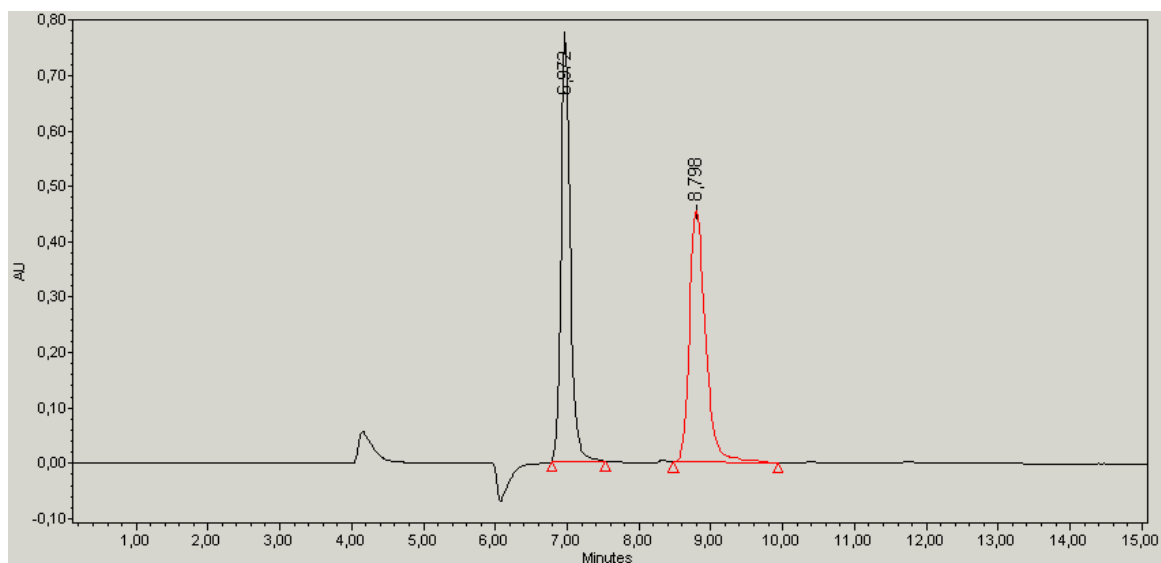
HPLC-chromatogram of theaspiran *trans*-1, Waters Sunfire 5  $\mu\text{m}$  250\*4.6 mm, flow: 1 mL/min, UV detection 210 nm, gradient 90–95% MeCN in H<sub>2</sub>O (0.05% TFA).



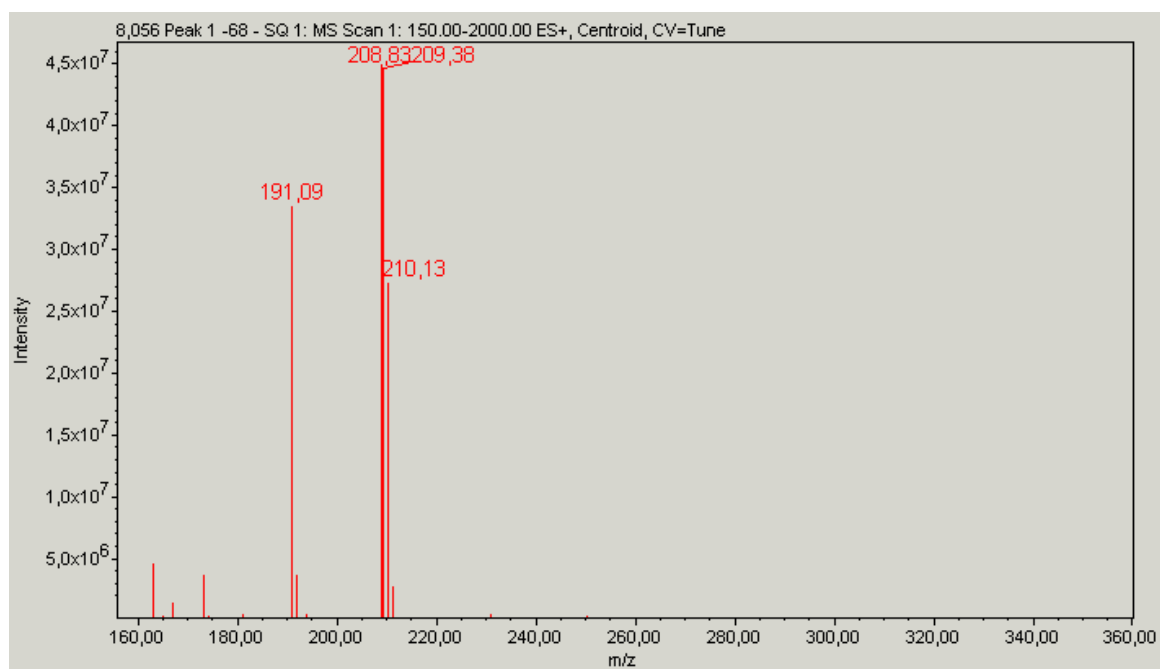
ESI-MS of theaspiran *trans*-1.



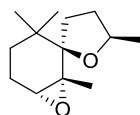
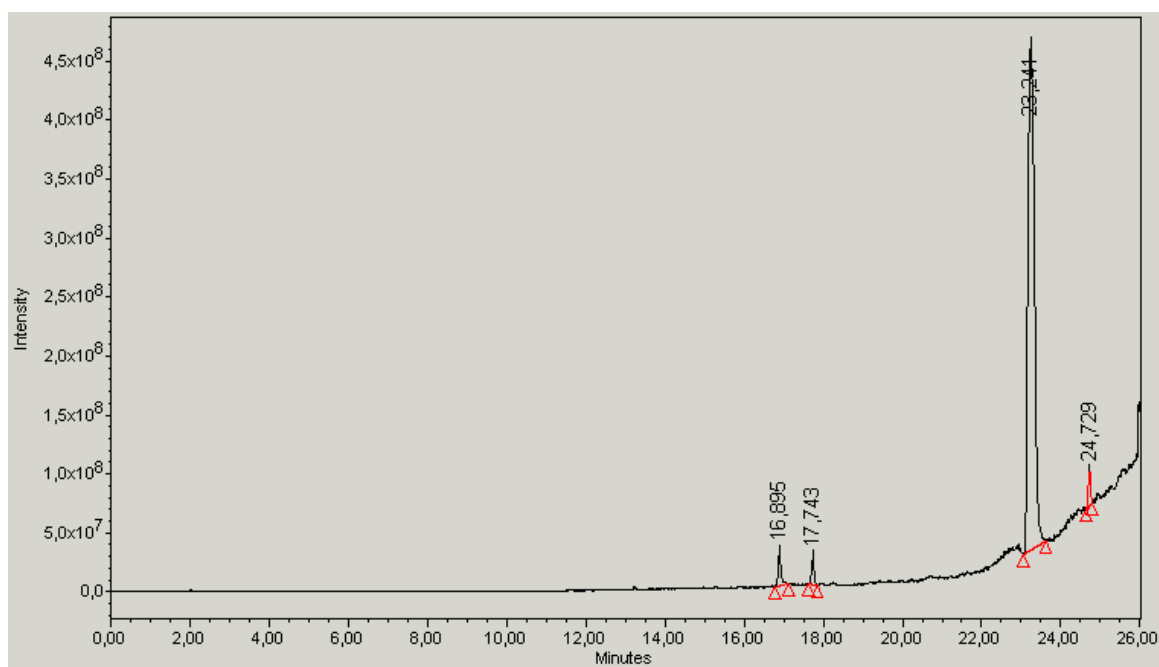
HPLC-chromatogram of enone **2**, Waters Sunfire 5  $\mu\text{m}$  250\*4.6 mm, flow: 1 mL/min, UV detection 239 nm, gradient 50–90% MeCN in H<sub>2</sub>O (0.05% TFA).



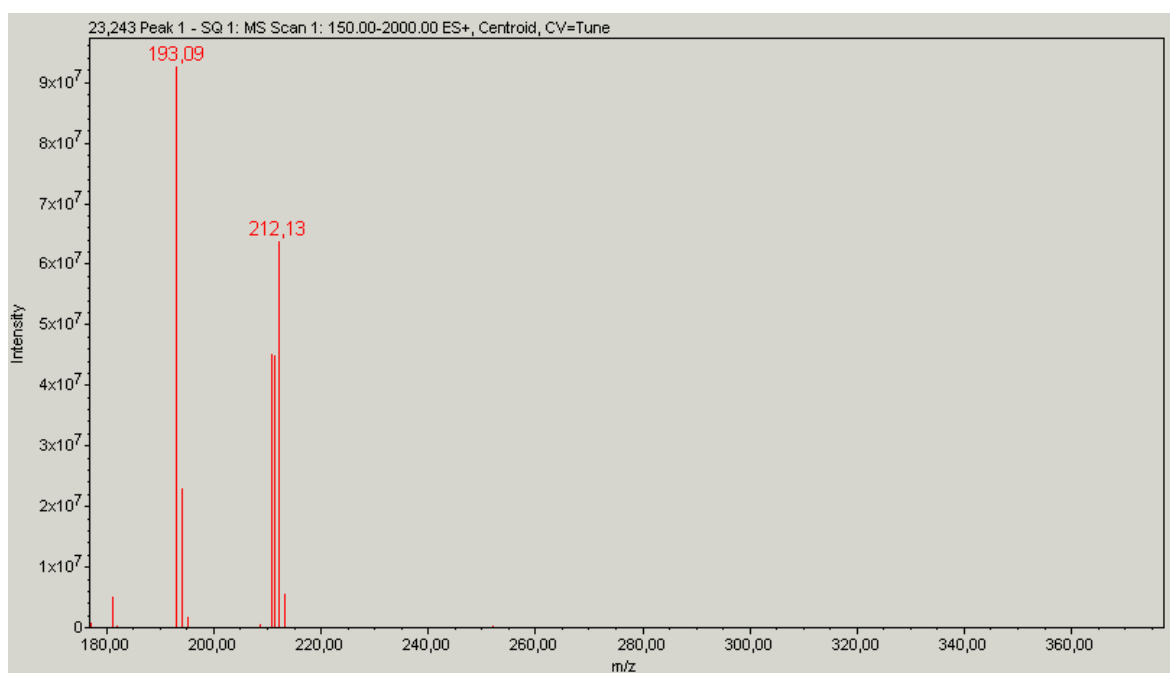
HPLC-chromatogram of enone **2** on a chiral stationary phase, Chiralpak IA 5  $\mu\text{m}$  250\*4.6 mm, flow: 1 mL/min, UV detection 230 nm, isocratic heptane/EtOH/MeOH 50/1/1 + 0.1% TFA.



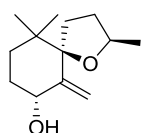
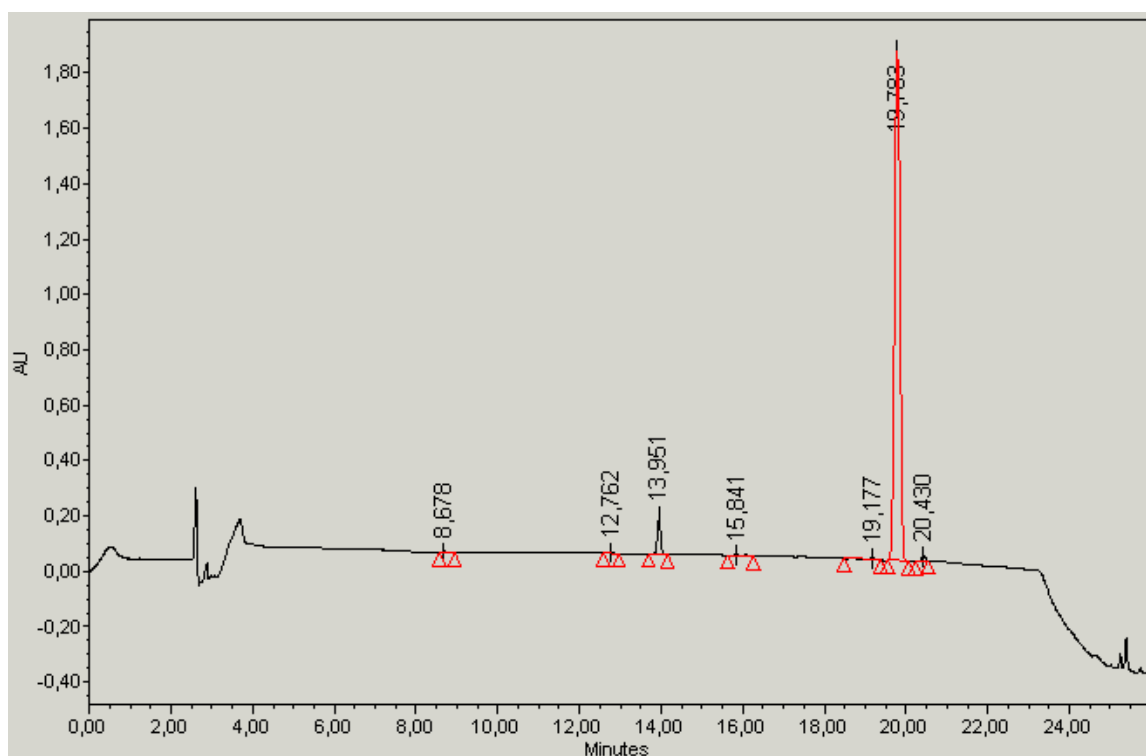
ESI-MS of enone 2.



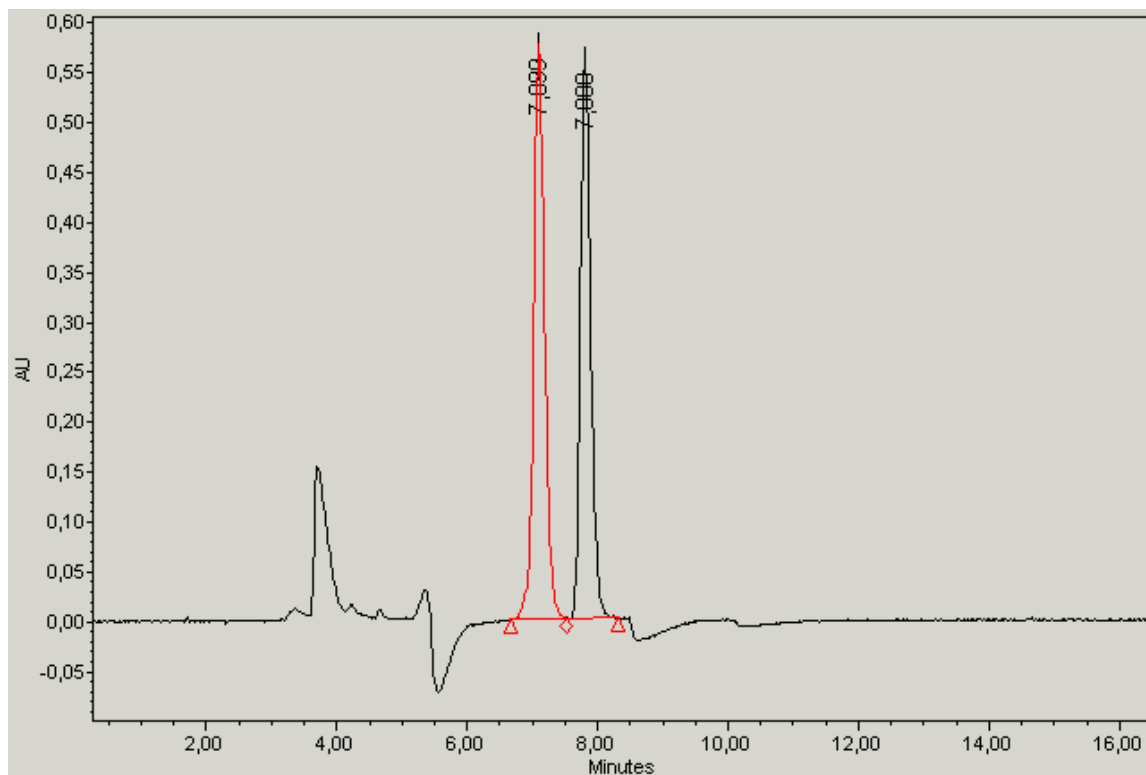
HPLC-chromatogram of epoxide **4a**, Waters Sunfire 5  $\mu\text{m}$  250\*4.6 mm, flow: 1 mL/min, TIC, gradient 10–90% MeCN in  $\text{H}_2\text{O}$  (0.05% TFA).



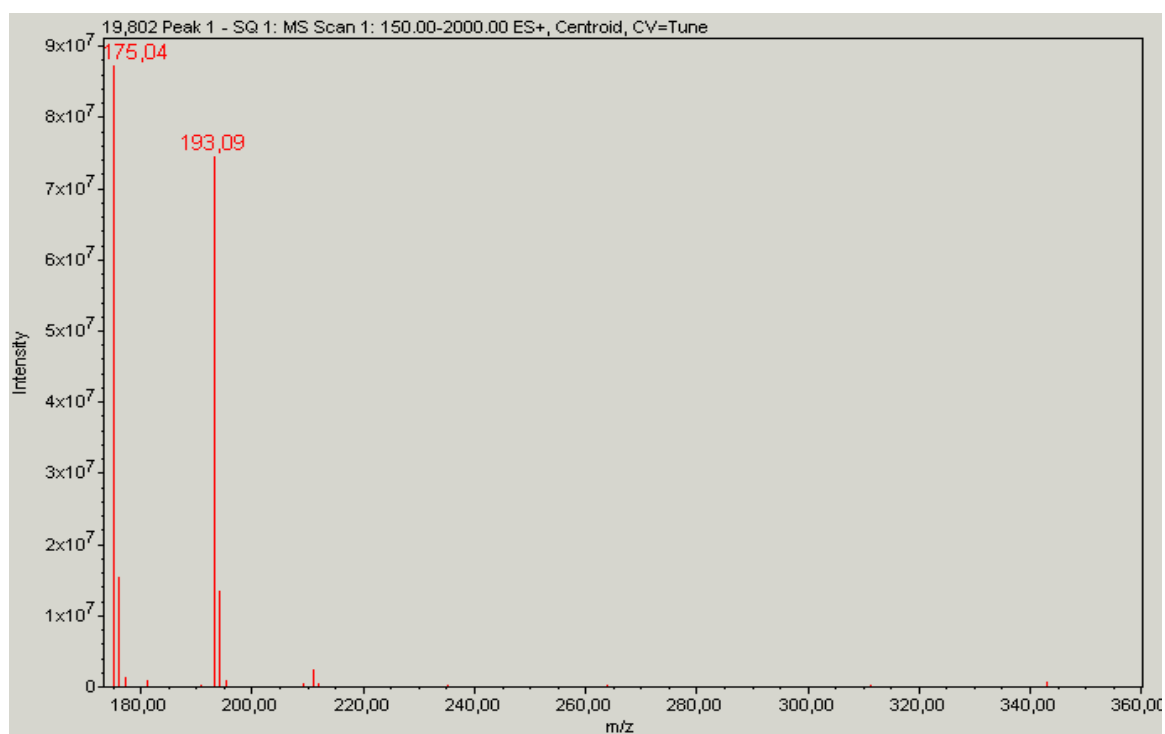
ESI-MS of epoxide **4a**.



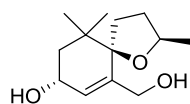
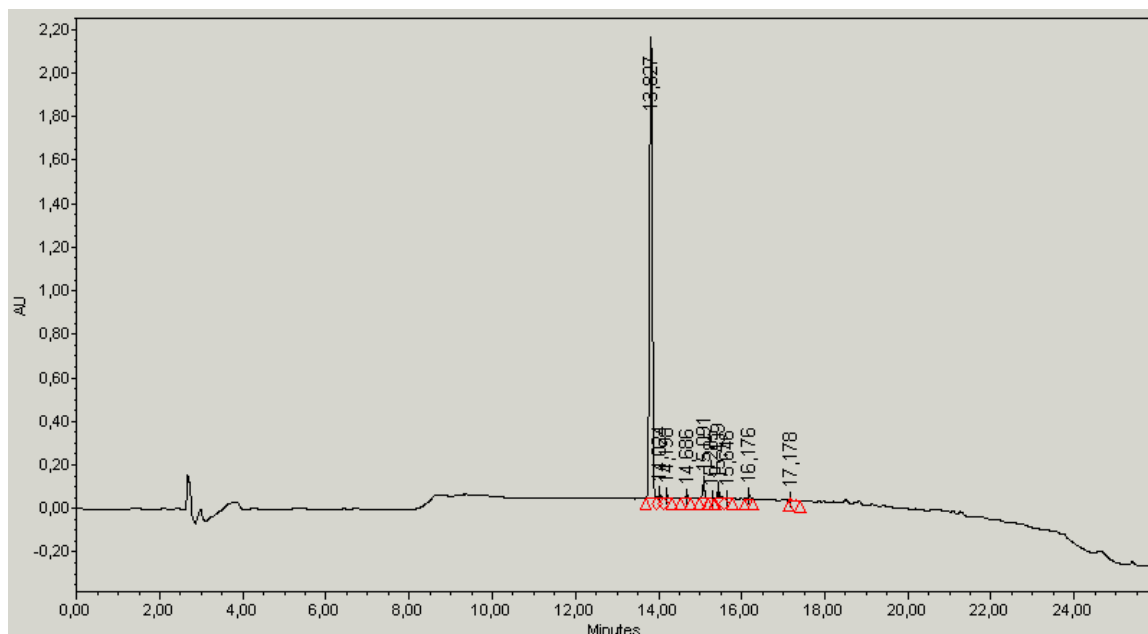
HPLC-chromatogram of allyl alcohol **22**, Waters Sunfire 5  $\mu$ m 250\*4.6 mm, flow: 1 mL/min, UV detection 238 nm, gradient 30–70% MeCN in H<sub>2</sub>O (0.05% TFA).



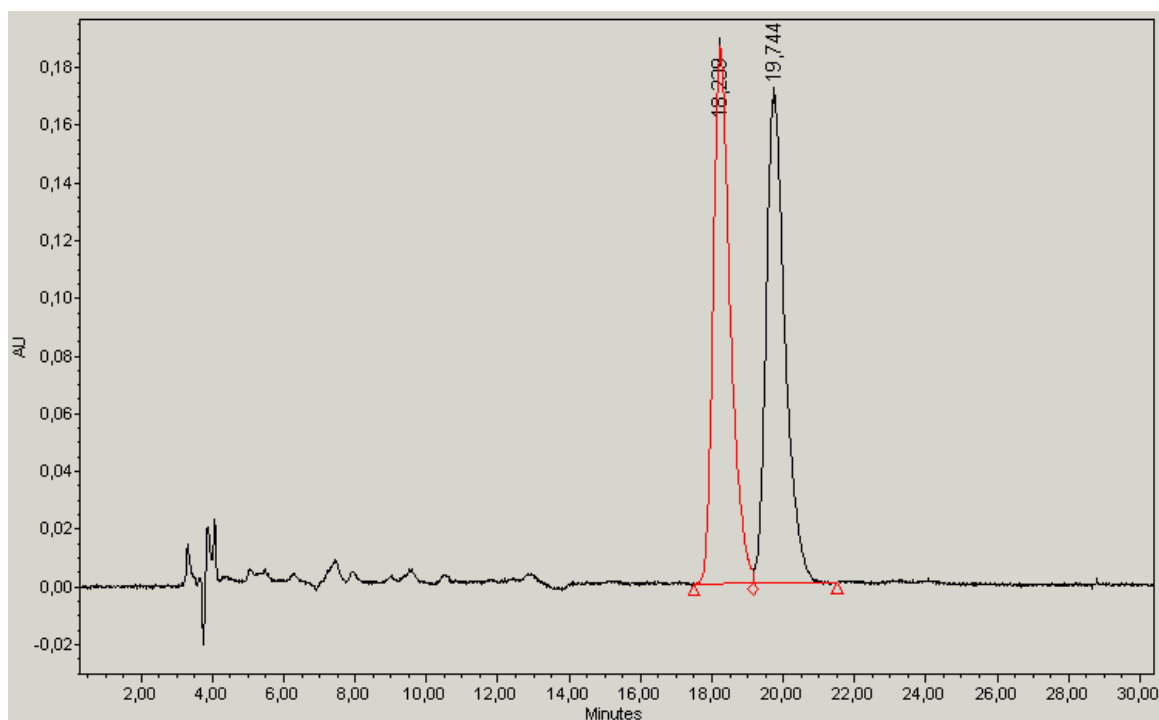
HPLC-chromatogram of allyl alcohol **22** on a chiral stationary phase, Chiralpak OD 5  $\mu$ m 250\*4.6 mm, flow: 1 mL/min, UV detection 202 nm, isocratic heptane/iPrOH 50/1 + 0.1% TFA.



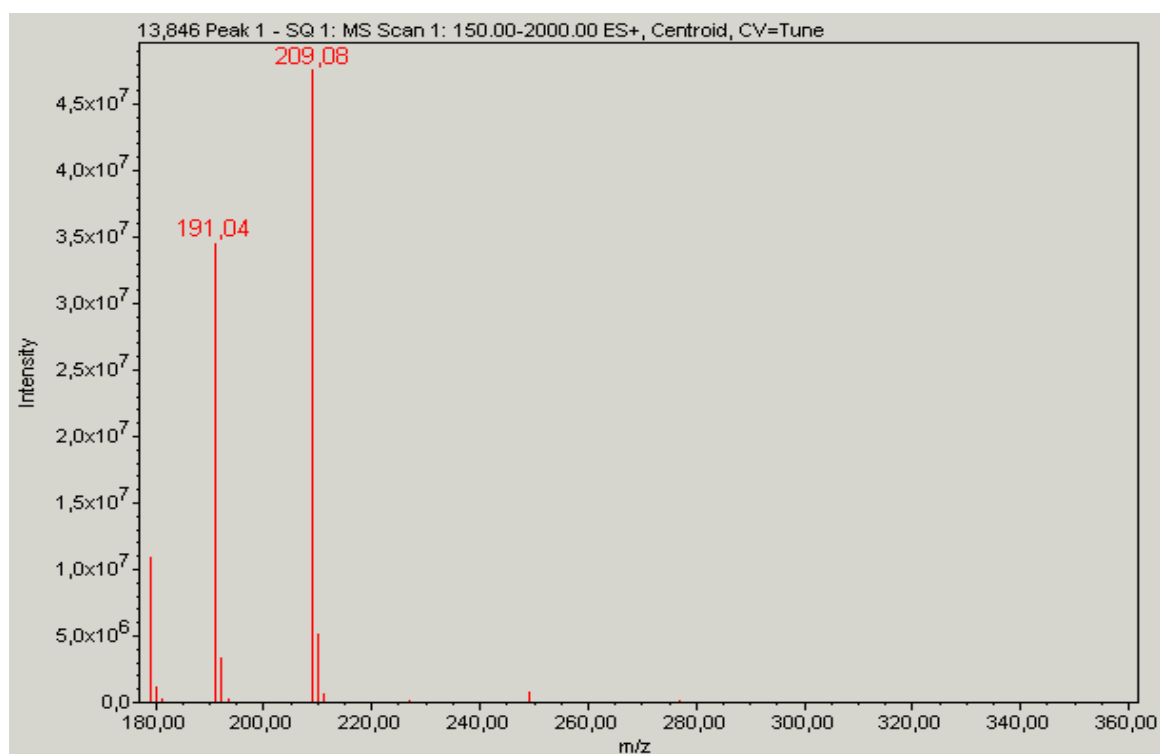
ESI-MS of allyl alcohol **22**.



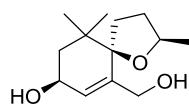
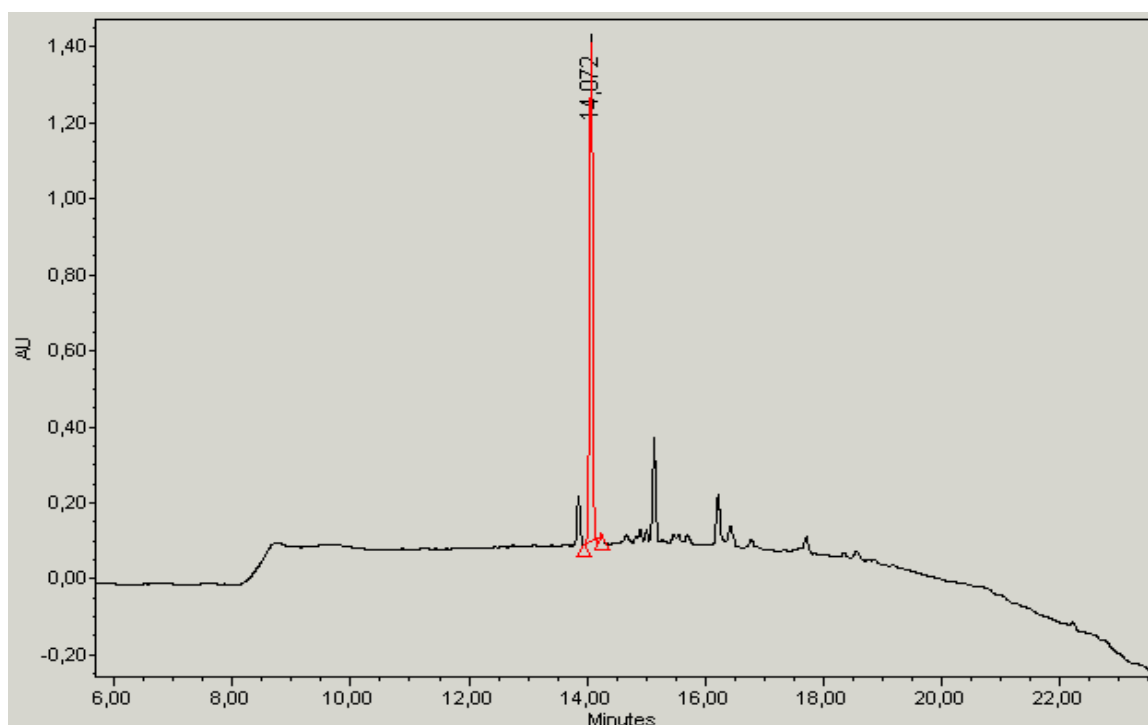
HPLC-chromatogram of diol **26a**, Waters Sunfire 5  $\mu\text{m}$  250\*4.6 mm, flow: 1mL/min, UV detection 208 nm, gradient 10-90% MeCN in  $\text{H}_2\text{O}$  (0.05% TFA).



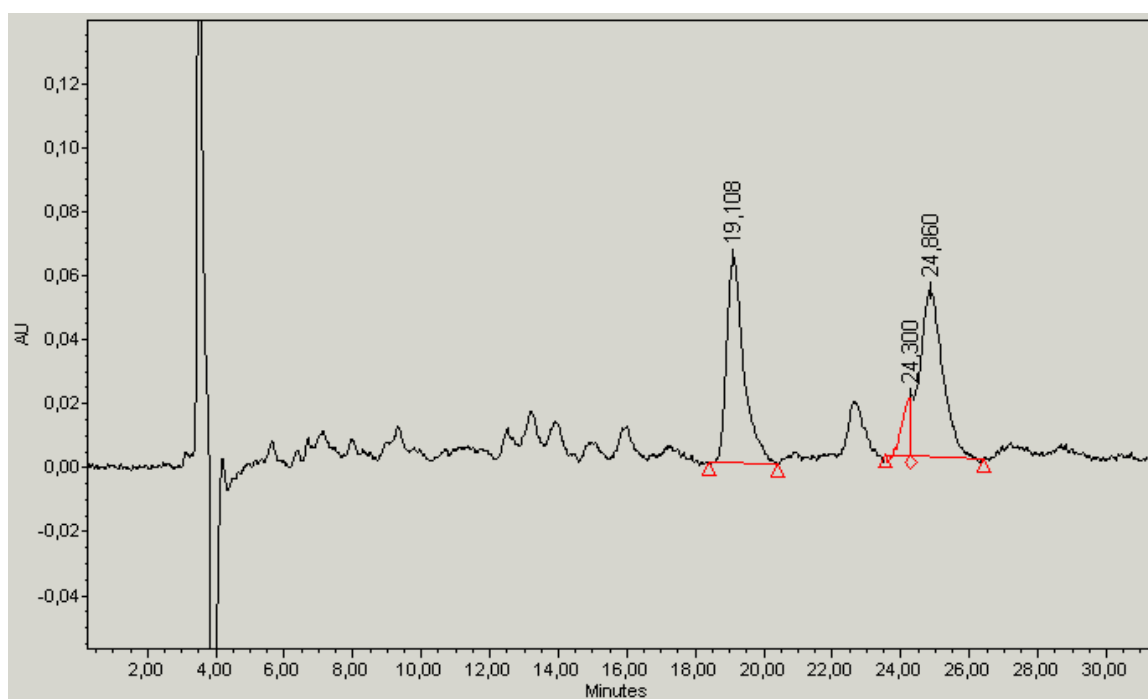
HPLC-chromatogram of diol **26a** on a chiral stationary phase, Chiralpak IC 5  $\mu\text{m}$  250\*4.6 mm, flow: 1 mL/min, UV detection 202 nm, isocratic heptane/EtOH/MeOH 40/1/1 + 0.1% TFA.



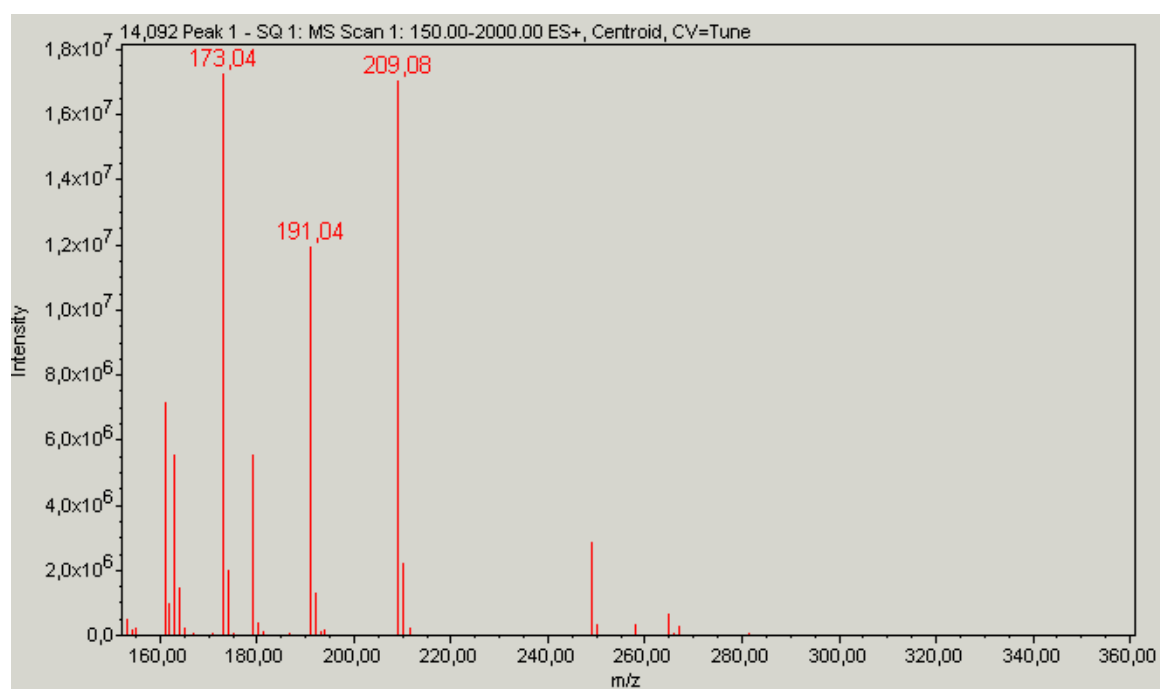
ESI-MS of diol **26a**.



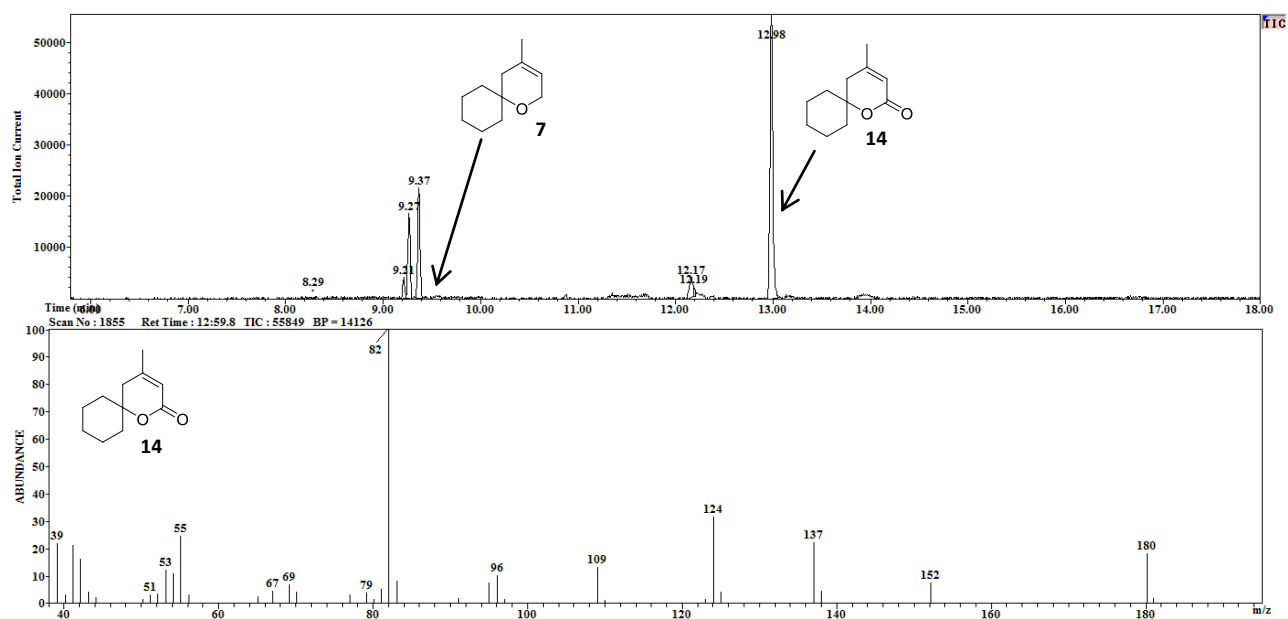
HPLC-chromatogram of diol **26b**, Waters Sunfire 5  $\mu$ m 250\*4.6 mm, flow: 1 mL/min, UV detection 202 nm, gradient 10–90% MeCN in H<sub>2</sub>O (0.05% TFA).



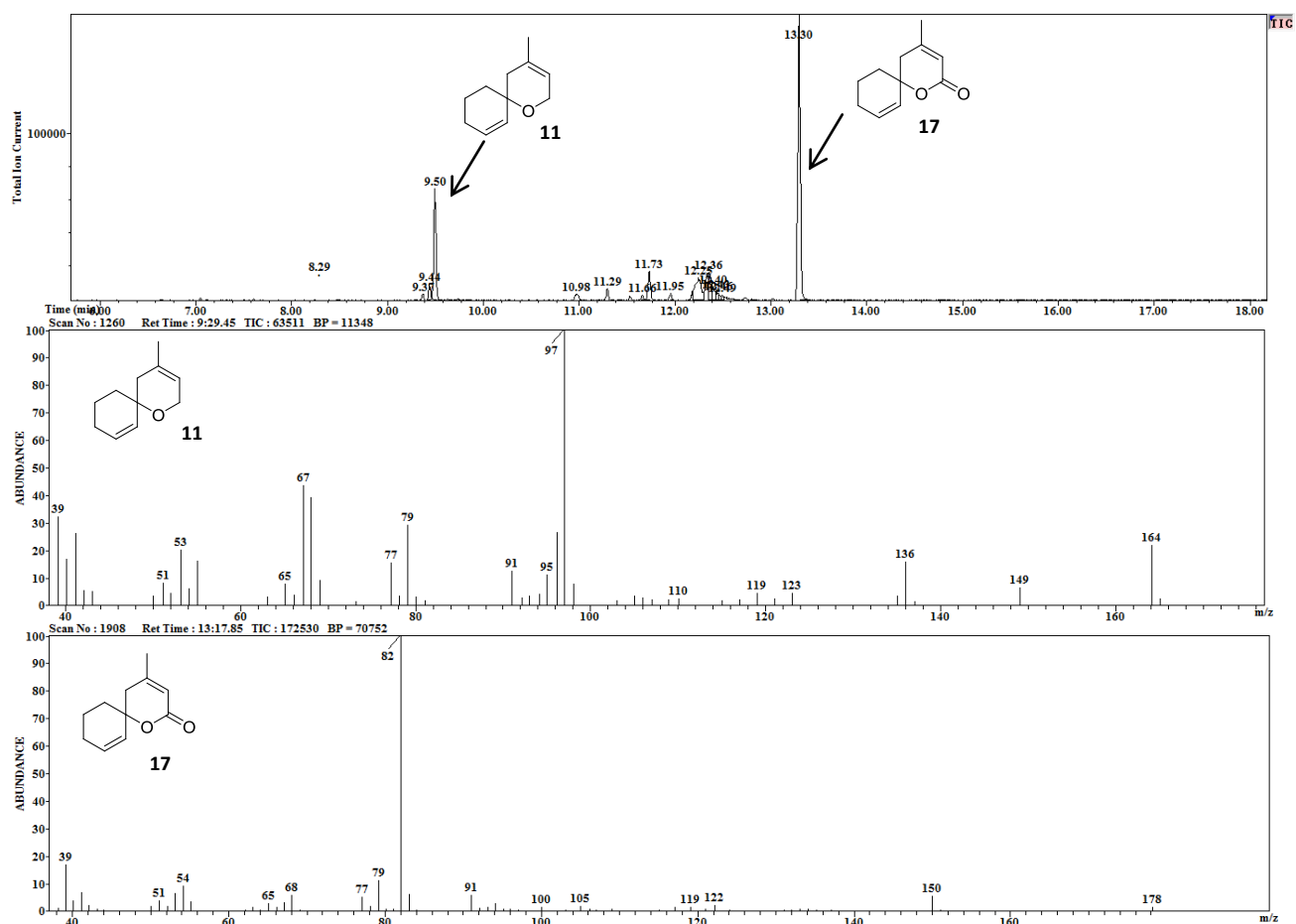
HPLC-chromatogram of diol **26b** on a chiral stationary phase, Chiralpak AS 5  $\mu$ m 250\*4.6 mm, flow: 1 mL/min, UV detection 203 nm, isocratic heptane/EtOH/MeOH 40/1/1 + 0.1% TFA.



ESI-MS of diol **26b**.



GC-MS of the biocatalytic oxidation of spiroether **7** (crude reaction mixture).



GC–MS of the biocatalytic oxidation of spiroether **11** (crude reaction mixture).

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