Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information



69451 Weinheim, Germany

# Carbon Dioxide as a $C_1$ Building Block for the Formation of Carboxylic Acids by Formal Catalytic Hydrocarboxylation**

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# Supporting Information

## Contents

## S1 Material and Methods

**General**. All manipulations involving air-sensitive compounds were carried out under inert atmosphere using schlenk techniques or in a glovebox (*MBraun LabMaster SP*). Argon 4.8 (*Messer*, Germany) was used as inert gas in all cases. Prior to use, all glassware was dried in high vacuum, evacuated and refilled with argon at least three times.

**Autoclaves**. The catalytic runs were performed in 10 mL stainless steel autoclaves. To avoid blind activity, the steel autoclaves were equipped with glas inlets. The autoclaves were evacuated at high vacuum for at least one hour and then charged with an argon atmosphere.

**Solvents and Chemicals.** Acetic acid was pre-dried over molecular sieves (4 Å) and then refluxed for 2 h over anhydrous $CuSO_4$, distilled, and stored over molecular sieves (4 Å) under argon. Methyl iodide was vacuum distilled at low temperatures prior to use and stored at 4°C under argon. All substrates containing stabilizing agents were distilled prior to use and stored under argon over molecular sieves (4 Å). All other substrates were degassed by three freeze-pump-thaw cycles and stored over molecular sieves (3 or 4 Å) under argon. Deionised water was taken from a reverse-osmotic purification system (*Werner EasyPure II*) and degassed by bubbling argon with a frit for at least 1 h. Water contents of all organic solvents were monitored by Carl-Fischer titration (*Metrohm 756 F Coulometer*) and typically kept on the following levels: Acetic acid < 100 ppm, dichloromethane 5 - 10 ppm, tetrahydrofuran 30 - 50 ppm. Deuterated solvents were degassed by three freeze-pump-thaw cycles and stored over molecular sieves 3 Å or 4 Å under argon. All reagents were commercially supplied and used as received unless stated otherwise.

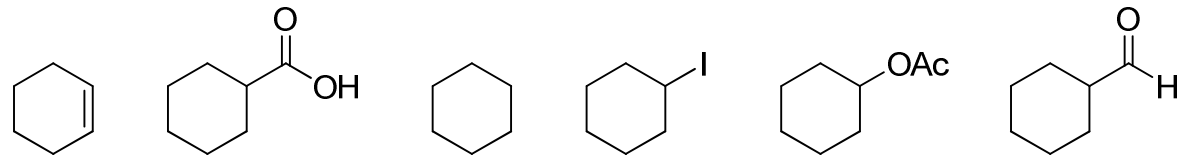
**NMR Spectroscopy**. NMR spectra were recorded with spectrometers *Bruker AV-600, AV-III-400* or *-300* at ambient temperature at the frequency noted. Chemical shifts $\delta$ are given in ppm relative to tetramethylsilane ($^{1}$H, $^{2}$H and $^{13}$C).

**Mass Spectrometry**. High resolution MS analyses were performed on a *LTQ Orbitrap XL* (*Thermo Fisher Scientific*) by direct ESI from organic solutions without acidification in (+) ionisation. Detected masses are given in m/z and correlated to calculated masses of the respective species.

**Gaschromatography**. GC analyses were performed on a *Trace GC Ultra* (*Thermo Scientific*) using a packed *CP-WAX-52-CB* column (length = 60 m, diameter = 0.25 mm) isothermally at 70°C for 5 min, then heated to 200°C at 8°C min$^{-1}$. A constant flow of 2.5 mL min$^{-1}$ He was applied. The gaschromatograph was equipped with a FID detector.

## S2 Catalytic Experiments

The abbreviations for substrates and products are set as follows:




**CE** **CA** **CH** **CI** **CAc** **CAld**

### S2.1 Variation of the Metal Source

General procedure: The according metal precursor (93 µmol per metal atom) and cyclohexene (1.87 mmol) were weighed into a Schlenk tube with acetic acid (0.65 mL). In the runs where methyl iodide was applied as a promotor, 925 µmol $CH_3I$ was added. The red brownish solution was transferred via cannula to a stainless steel autoclave with $PPh_3$ (460 µmol). The autoclave was pressurized with $CO_2$ (4.0 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. To the resulting solution the standards 1- phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and the mixture was analyzed by gas chromatography. Yields were found to be reproducible within $\Delta Y = \pm 2\%$ in two independent runs for selected experiments.

**Table S2.1.** Carboxylation of cyclohexene with $CO_2$ and $H_2$ investigating various metal catalyst precursors. Cf. Table 1 within the manuscript.

| Entry | Cat. precusor | Promotor | Conv. [%] | Yield of **CA** [%] | Yield of **CH** [%] | Yield of **CI** [%] | Yield of **CAc** [%] | GC at page |
|---|---|---|---|---|---|---|---|---|
| 1 | $Fe_2(CO)_9$ | -- | 16 | -- | -- | -- | -- | S15 |
| 2 | $Fe_2(CO)_9$ | $CH_3I$ | 20 | <1 | -- | <1 | 2 | S16 |
| 3 | $Pd(OAc)_2$ | -- | 8 | -- | <1 | -- | -- | S17 |
| 4 | $Pd(OAc)_2$ | $CH_3I$ | 22 | <1 | 2 | 4 | 10 | S18 |
| 5 | $[RhCl(CO)_2]_2$ | -- | 20 | <1 | 5 | -- | -- | S19 |
| 6 | $[RhCl(CO)_2]_2$ | $CH_3I$ | 96 | 69 | 10 | 2 | 1 | S20 |

## S2.2 Variation of the Acidic Additive

General procedure: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and the acidic additive (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. To the resulting red solution the standards 1-phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and the mixture was analysed by gas chromatography. Yields were found to be reproducible within $\Delta Y = \pm 2\%$ in two independent runs for selected experiments.

**Table S2.2.** Carboxylation of cyclohexene with $CO_2$ and $H_2$ investigating the influence of the acidic additive. Cf. Table 1 within the manuscript.

| Entry | Acidic additive[a] | Amount acidic additive [µmol] | $pK_a$ (DMSO) | Ref. for $pK_a$ | Conv. [%] | Yield of **CA** [%] | Yield of **CH** [%] | Yield of **CI** [%] | Yield of **CAc** [%] | GC at page |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | HBTA | 330 | 1.7 | [1] | 97 | 77 | 6 | 5 | <1 | S21 |
| 2 | TFA | 330 | 0.5 | [2] | 85 | 41 | 21 | <1 | 4 | S22 |
| 3 | MSA | 330 | -1.9 | [3] | 96 | 65 | 8 | 2 | <1 | S23 |
| 4 | *p*-TsOH | 330 | -2.8 | [3] | 99 | 75 | 4 | 2 | <1 | S24 |
| 5 | *p*-TsOH·$H_2O$ | 330 | -2.8 | [3] | 99 | 88 | 2 | 1 | <1 | S25 |
| 6 | *p*-TsOH·$H_2O$ | 650 | -2.8 | [3] | 99 | 92 | 5 | 2 | <1 | S27 |
| 7 | *p*-TsOH·$H_2O$ | 1120 | -2.8 | [3] | 99 | 83 | 9 | 2 | <1 | S28 |

[a]: HBTA: *bis*(trifluoromethanesulfon)imide; TFA: trifluoroacetic acid; MSA: methanesulfonic acid; *p*-TsOH: *para*-toluenesulfonic acid; *p*-TsOH·$H_2O$: *para*-toluenesulfonic acid monohydrate.

## S2.3 Variation of the Solvent

General procedure: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with the according solvent (0.65 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and *p*-TsOH·$H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. To the resulting red solution the standards 1-phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and the mixture was analysed by gas chromatography. Yields were found to be reproducible within $\Delta Y = \pm 2\%$ in two independent runs for selected experiments.

**Table S2.3.** Carboxylation of cyclohexene with $CO_2$ and $H_2$ investigating the influence of the solvent.

| Entry | Solvent | Conv. [%] | Yield of **CA** [%] | Yield of **CH** [%] | Yield of **CI** [%] | Yield of **CAc** [%] | GC at page |
|---|---|---|---|---|---|---|---|
| 1 | *neat* | 98 | 59 | 12 | 5 | <1 | S29 |
| 2 | propionic acid | 98 | 77 | 6 | 3 | -- | S30 |
| 3 | tetrahydrofuran | 27 | <1 | 1 | 3 | 2 | S31 |

## S2.4 Variation of the Iodide Source

General procedure: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and the according iodide source (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and *p*-$TsOH \cdot H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. To the resulting red solution the standards 1-phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and the mixture was analysed by gas chromatography. Yields were found to be reproducible within $\Delta Y = \pm 2\%$ in two independent runs for selected experiments.

**Table S2.4.** Carboxylation of cyclohexene with $CO_2$ and $H_2$ investigating the influence of the iodide source. Cf. Table 1 within the manuscript.

| Entry | Iodide source | Amount Iodide source [µmol] | Conv. [%] | Yield of **CA** [%] | Yield of **CH** [%] | Yield of **CI** [%] | Yield of **CAc** [%] | GC at page |
|---|---|---|---|---|---|---|---|---|
| 1 | $I_2$ | 925 | 87 | 47 | 9 | 12 | 4 | S32 |
| 2 | LiI | 925 | 90 | 46 | 15 | <1 | 5 | S33 |
| 3 | NaI | 925 | 36 | 8 | 13 | <1 | 2 | S34 |
| 4 | KI | 925 | 26 | 3 | 21 | <1 | 2 | S35 |
| 5 | $[CH_3PPh_3]I$ | 925 | 26 | 1 | 5 | -- | 3 | S36 |
| 6[a] | **CI** | 925 | 98 | 73 | <1 | 4 | 1 | S37 |
| 7[a] | **CI** | 184 | 91 | 54 | 22 | 1 | 5 | S38 |
| 8[a] | **CI** + LiI | 184 + 736 | 95 | 71 | 11 | 2 | 1 | S39 |

[a]: Conversion and yield calculated for **CE**+**CI** acting both as substrates.

## S2.5 Variation of the Phosphine Ligands

Variation of the phosphine ligand revealed a strong influence on the catalytic performance. Both electronic donating or withdrawing substituents in *para*-position of the phenyl groups showed little effects, and similar yields of **CA** were obtained under otherwise identical conditions ($P(p\text{-Tol})_3$: 66%, $P(p\text{-CF}_3\text{-C}_6\text{H}_4)_3$: 67%). Alkyl phosphines $P^nOct_3$ and $PCy_3$ showed also very good performance with 69% and 81% yield, respectively. A decrease in selectivity towards **CA** results with sterically more demanding ligands like $P^tBu_3$ (32%) or $P(o\text{-Tol})_3$ (5%). The use of bidentate ligands $Ph_2P(CH_2)_nPPh_2$ (n=2: dppe, n=3: dppp) or the tridentate ligand $H_3CC[(CH_2)PPh_2]_3$ (triphos) lead to complete suppression of **CA** formation on the expense of hydrogenation or general loss of activity, respectively. These data strongly suggest dynamic ligand exchange equilibria as important regulators for the system. This is further corroborated by variation of the P/Rh ratio with $PPh_3$ where maximum **CA** yields of >80% was observed in the range of 5:1 to 8:1, with rapid decay to values below 5% above and below these limits.

General procedure: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL). The solution was transferred via cannula to a stainless steel autoclave, in which the phosphine ligand (460 µmol á P atom) and $p$-TsOH·$H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. To the resulting red solution the standards 1-phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and the mixture was analysed by gas chromatography. Yields were found to be reproducible within $\Delta Y = \pm 2\%$ in two independent runs for selected experiments.

**Table S2.5.** Carboxylation of cyclohexene with $CO_2$ and $H_2$ investigating different phosphine ligands.

| Entry | Ligand[a] | Amount ligand [µmol] | Conv. [%] | Yield of **CA** [%] | Yield of **CH** [%] | Yield of **CI** [%] | Yield of **CAc** [%] | GC at page |
|---|---|---|---|---|---|---|---|---|
| 1 | $P^tBu_3$ | 460 | 74 | 32 | 10 | 4 | 6 | S40 |
| 2 | $P(cyclohexyl)_3$ | 460 | >99 | 81 | 5 | 3 | 1 | S41 |
| 3 | $P(n\text{-octyl})_3$ | 460 | 99 | 69 | 5 | 2 | <1 | S42 |
| 4 | $P(p\text{-tolyl})_3$ | 460 | 95 | 66 | 2 | 1 | <1 | S43 |
| 5 | $P(o\text{-tolyl})_3$ | 460 | 73 | 5 | <1 | 10 | 11 | S44 |
| 6 | $P(p\text{-CF}_3\text{-Ph})_3$ | 460 | 98 | 67 | 21 | 1 | <1 | S45 |
| 7 | tppms[c] | 460 | 98 | 76 | 3 | 3 | <1 | S46 |
| 8 | $P(OPh)_3$ | 460 | 40 | <1 | <1 | 4 | 15 | S47 |
| 9 | $O=PPh_3$ | 460 | 74 | 29 | <1 | 13 | 6 | S48 |
| 10 | dppe | 230 | 32 | <1 | -- | 15 | 6 | S49 |
| 11 | dppp | 230 | 38 | <1 | <1 | 14 | 9 | S50 |
| 12 | triphos | 155 | 33 | <1 | <1 | 10 | 11 | S51 |
| 13 | $PPh_3$ | 46 | 68 | 27 | 3 | 22 | 10 | S52 |
| 14 | $PPh_3$ | 690 | 51 | 4 | 22 | -- | 6 | S53 |

[a] dppe: $Ph_2P(CH_2)_2PPh_2$; dppp: $Ph_2P(CH_2)_3PPh_2$; triphos: $H_3CC[(CH_2)PPh_2]_3$.

## S2.6 Conversion Time Profile

General procedure: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which the $PPh_3$ (460 µmol) and *p*-TsOH·$H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After the according time interval, the autoclave was cooled to 0°C and then carefully vented. To the resulting red solution the standards 1-phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and the mixture was analysed by gas chromatography. Yields were found to be reproducible within $\Delta Y = \pm 2\%$ in two independent runs for selected experiments.

**Table S2.6.** Conversion/yield time profile of the carboxylation of cyclohexene with $CO_2$ and $H_2$. Cf. Figure 1 within the manuscript.

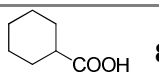
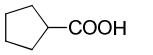
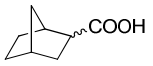
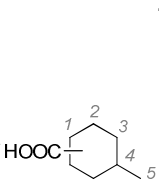
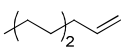
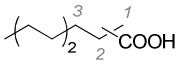
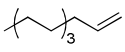
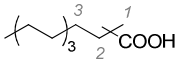
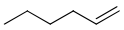
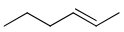
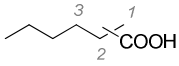
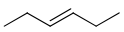
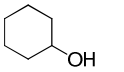
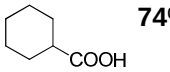
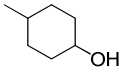
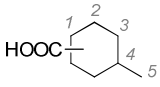
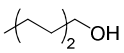
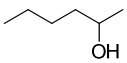
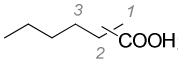
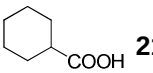
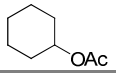
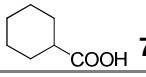
| Entry | Reaction time [h] | Conv. [%] | Yield of **CA** [%] | Yield of **CH** [%] | Yield of **CI** [%] | Yield of **CAc** [%] | GC at page |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 40 | 3 | 2 | 15 | 2 | S54 |
| 2 | 2 | 63 | 27 | 3 | 11 | 4 | S55 |
| 3 | 3 | 80 | 47 | 4 | 11 | 5 | S56 |
| 4 | 6 | 90 | 70 | 5 | 9 | 3 | S57 |
| 5 | 9 | 96 | 77 | 5 | 3 | 1 | S58 |
| 6 | 12 | 98 | 81 | 5 | 3 | 1 | S59 |
| 7 | 16 | >99 | 85 | 5 | 1 | <1 | S60 |
| 8 | 20 | >99 | 85 | 5 | 2 | 1 | S61 |

## S2.7 Substrate Scope

General procedure: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), the according substrate (1.88 mmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and *p*-TsOH·$H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C in an aluminium cylinder. After 16 h the autoclave was cooled to 0°C and then carefully vented. To the resulting red solution the standards 1-phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and the mixture was analysed by gas chromatography. GC Yields were found to be reproducible within $\Delta Y = \pm 2\%$ in two independent runs for selected experiments.

Aqueous work-up to isolate the carboxylic acid products was performed as follows: After the reaction the autoclave was cooled to 0°C and then carefully vented. The reaction mixture was transferred to a round bottom flask with additional dichloromethane and the solvent was evaporated in vacuo. The residual solid was re-dissolved in dichloromethane (15 mL) and the resulting solution was extracted four times with saturated $NaHCO_3$ solution (4 x 10 mL). The aqueous phases were combined and concentrated hydrochloric acid was added dropwise until pH 1 was reached. Subsequently, the combined aqueous phases were re-extracted with dichloromethane (5 x 10 mL). The combined dichloromethane phases were dried over $Na_2SO_4$ and the solvent was removed in vacuo to obtain the carboxylic acid products as slightly yellowish oils or low-melting solids, in agreement with literature melting points. No impurities were detectable by GC chromatography, and only trace amounts of phosphonium ions were detected by $^1H$ NMR and $^{31}P$-NMR spectroscopy. The $^1H$ NMR spectra are depicted at the according pages for the products along with the GC data (see pages: S26, S63, S68, S72, S76, S79). Completely colorless cyclohexane carboxylic acid was obtained upon recrystallization from pentane at -78°C in 65% yield.

**Table S2.7.** Carboxylation with $CO_2$ and $H_2$ investigating different substrates. Cf. Table 2 within the manuscript.

| Entry | Substrate | Conv. [%] | product **yield** [%] | Isolated **yield** | GC at page |
|---|---|---|---|---|---|
| 1 |  | 98 |  **88**% | **86**% yellowish oil, solidifies upon standing ($mp_{Lit}$ = 29℃) | S25 |
| 2 |  | 98 |  **91**% | **81**% yellowish oil ($mp_{Lit}$ = 4℃) | S62 |
| 3 |  | 91 |  **50**% *exo*<br>**12**% *endo* | | S64 |
| 4 |  | 96 |  **44%** COOH at *1*<br>**20%** COOH at *2/3*<br>**9%** COOH at *5* | | S65 |
| 5 |  | 98 | **46%** COOH at *1*<br>**20%** COOH at *2/3*<br>**8%** COOH at *5* | | S66 |
| 6 |  | 99 | **52%** COOH at *1*<br>**18%** COOH at *2/3*<br>**7%** COOH at *5* | **75%** yellowish oil | S67 |
| 7 |  | 99 |  **42%** COOH at *1*<br>**22%** COOH at *2*<br>**10%** COOH at *3* | | S69 |
| 8 |  | 98 |  **31%** COOH at *1*<br>**17%** COOH at *2*<br>**6%** COOH at *3*<br>**7%** COOH at *4* | | S70 |
| 9 |  | 93 | **53%** COOH at *1*<br>**26%** COOH at *2*<br>**11%** COOH at *3* | **76**% yellowish oil | S71 |
| 10 |  | 97 |  **43%** COOH at *1*<br>**24%** COOH at *2*<br>**11%** COOH at *3* | | S73 |
| 11 |  | 93 | **45%** COOH at *1*<br>**23%** COOH at *2*<br>**10%** COOH at *3* | | S74 |
| 12 |  | >99 |  **74**% | **73**% yellowish oil, solidifies upon standing ($mp_{Lit}$ = 29℃) | S75 |
| 13 |  | 99 |  **48%** COOH at *1*<br>**19%** COOH at *2/3*<br>**7%** COOH at *5* | | S77 |
| 14 |  | > 99 | **41%** COOH at *1*<br>**15%** COOH at *2*<br>**6%** COOH at *3* | **55**% yellowish oil | S78 |
| 15 |  | > 99 |  **37%** COOH at *1*<br>**19%** COOH at *2*<br>**8%** COOH at *3* | | S80 |
| 16 |  | 80 |  **21**% | | S81 |
| 17 |  | 95 |  **71**% | | S82 |

## S2.8 Detection of CO and Control Experiments with CO

**Procedure for the detection of CO gas**: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and *p*-$TsOH \cdot H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented into an evacuated gas tube (Figure S2.1 *left*). To the resulting red solution the standards 1-phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and both, the gas phase in the gas tube as well as the liquid reaction mixture, were analysed by gas chromatography.

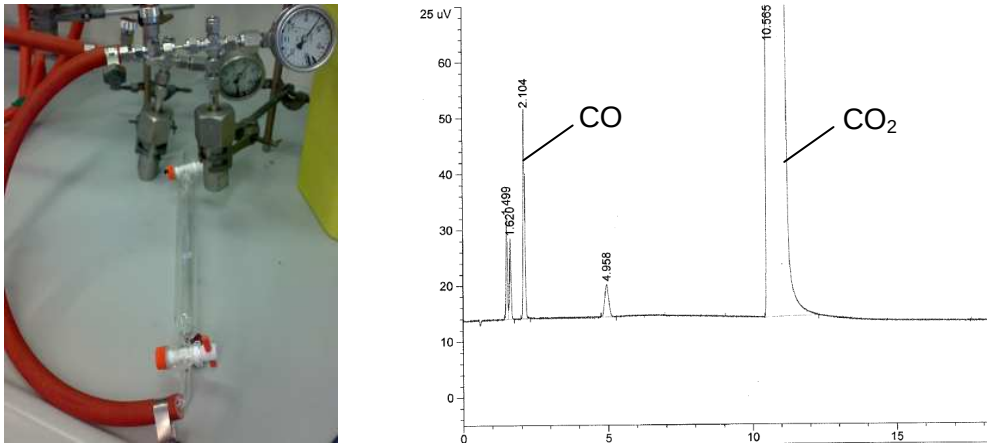



**Figure 2.1.** *Left*: Gas tube to trap the gas phase from the autoclave after the reaction. *Right*: Part of the GC chromatogram taken from the gas phase analysis after the reaction.

**Control Experiments applying CO gas**: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol), and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and *p*-$TsOH \cdot H_2O$ (330 µmol) were deposited already. The autoclave was pressurized with CO and in some experiments additional $H_2$ was added at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. To the resulting red solution the standards 1-phenylethanol (100 mg) and *n*-dodecane (100 mg) were added and the reaction mixture was analysed by gas chromatography.

**Table S2.8.** Control Experiments applying CO gas instead of $CO_2$.

| Entry | CO [bar] | $H_2$ [bar] | Total pressure [bar] | Conv. [%] | Yield of **CA** [%] | Yield of **CH** [%] | Yield of **Cl** [%] | Yield of **CAc** [%] | GC at page |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 30 | -- | 30 | 91 | 32 | <1 | <1 | 7 | S83 |
| 2 | 30 | 10 | 40 | 96 | 53 | <1 | <1 | 5 | S84 |
| 3 | 5 | 10 | 15 | 95 | 79 | <1 | <1 | 1 | S85 |

## S2.9 Labelling Experiments

**Procedure for the $^{13}CO_2$ labelling experiments**: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and *p*-TsOH·$H_2O$ (330 µmol) were already deposited. The autoclave was cooled to different inlet temperatures, then pressurized with $^{13}CO_2$ and weighed. Afterwards, un-labelled $CO_2$ was pressurized to reach the total amount of $CO_2$ between 4.0 and 4.4 g. Then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. The resulting red solution was analysed by $^1H$ and $^{13}C$ NMR spectroscopy. The analysis of the $^{13}C$ labelling experiments were conducted by comparing the initial ratios of $^{12}C$:$^{13}C$ in $CO_2$ with product $^{13}C$ NMR spectra (Figure S2.2). As internal reference the NMR signal of the ring carbon atom $C^b$ was applied to determine the relative intensity of the signal of $C^a$. For comparison also Ferrocene was added as external NMR standard (Figure S2.3).

**Table S2.9.** Labelling experiments using different ratios of $^{13}CO_2$ and un-labelled $CO_2$.

| Entry | Inlet Temp. $^{13}CO_2$ [°C] | Amount $^{13}CO_2$ [g] | Amount $CO_2$ [g] | Ratio $^{12}C$:$^{13}C$ | Ratio $C^a$:$C^b$ determined. by $^{13}C$ NMR | Conv. [%] | Yield of **CA** [%] | $^{13}C$ NMR at page |
|---|---|---|---|---|---|---|---|---|
| 1 | 20 | -- | 4.30 | 89.1:1 | 1.0:1 | **99** | **86** | S87 |
| 2 | 20 | 0.22 | 3.85 | 14.5:1 | 3.6:1 | **99** | **84** | S87 |
| 3 | 0 | 0.30 | 4.00 | 11.5:1 | 3.8:1 | **99** | **85** | S88 |
| 4 | -40 | 0.38 | 4.05 | 9.4:1 | 3.9:1 | **99** | **81** | S88 |
| 5 | -40 | 0.39 | 3.77 | 8.6:1 | 4.0:1 | **98** | **87** | S89 |
| 6 | -40 | 0.38 | 1.83 | 4.5:1 | 5.6:1 | **98** | **75** | S89 |

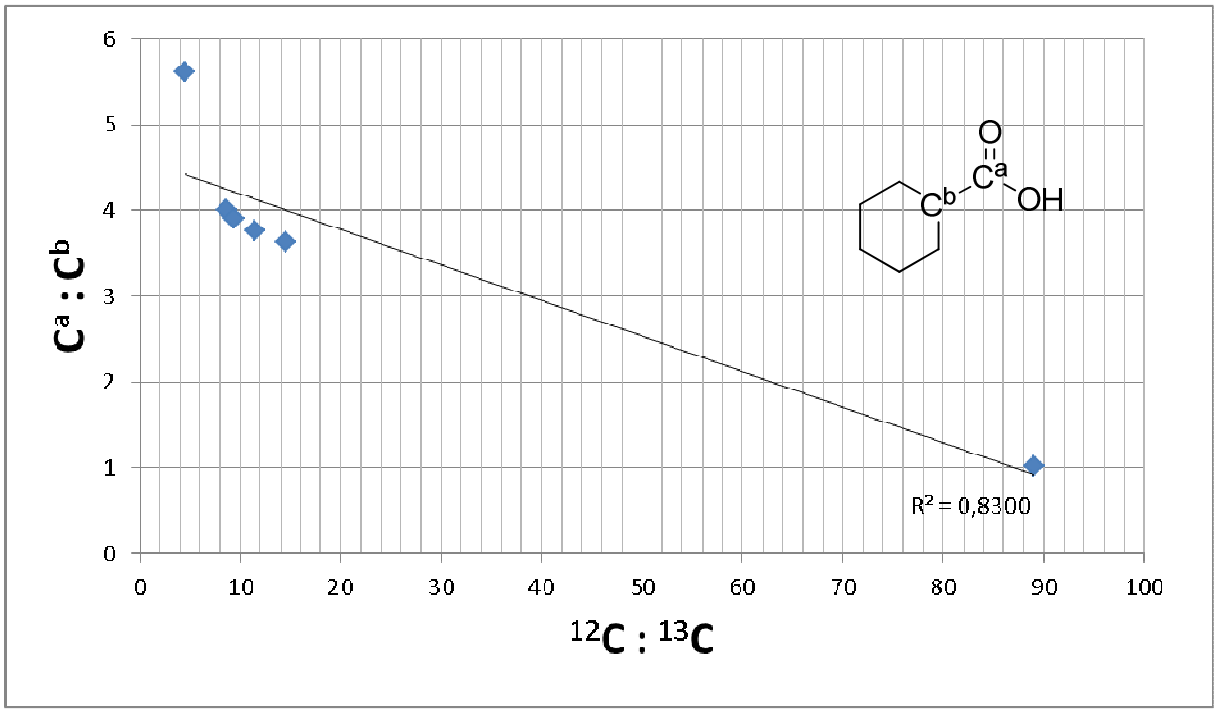



**Figure S2.2.** Diagram of the ratios of $^{12}C$:$^{13}C$ in $CO_2$ versus the product data obtained from $^{13}C$ NMR spectroscopy.

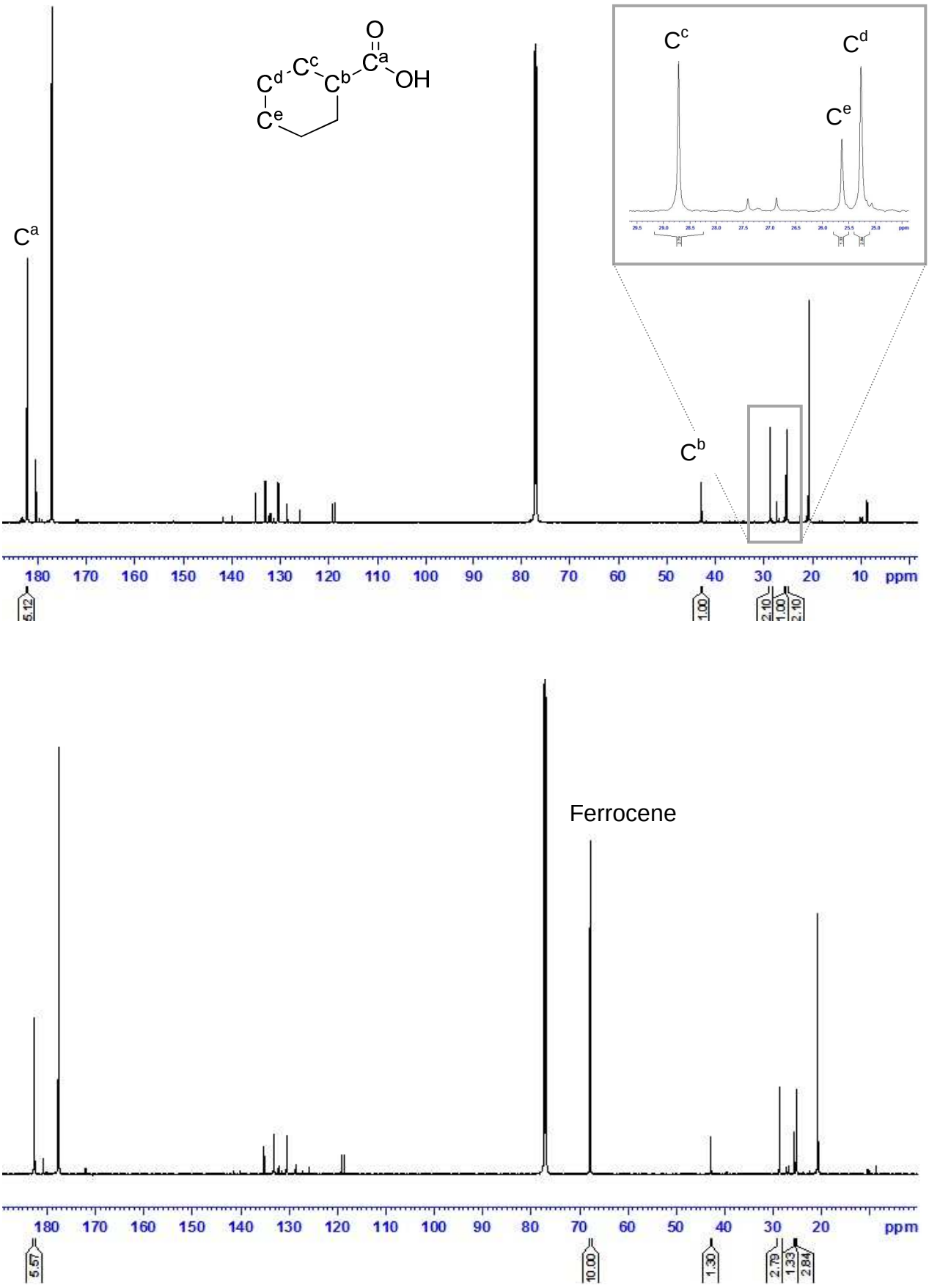



**Figure S2.3.** $^{13}$C NMR spectra of one labeling experiment without (*top*) and with addition of ferrocene (*bottom*) as external NMR standard.

**Procedure for the $D_2$ labelling experiments**: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube without addition of acetic acid. The red brownish solution was transferred via cannula to a stainless steel autoclave, in which the $PPh_3$ (460 µmol) and *p*-$TsOH \cdot H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with 10 bar of $D_2$ and then $CO_2$ (4.1 g) was added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C in an aluminium cylinder. After 16 h, the autoclave was cooled to 0°C and then carefully vented. The resulting red solution was analysed by $^1H$ and $^2H$ NMR spectroscopy. The according spectra are depicted on page 90.

**Procedure for the $D_2O$ labelling experiments**: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and $CH_3I$ (925 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL) and $D_2O$ (0.1 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and *p*-$TsOH \cdot H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. The resulting red solution was analysed by $^1H$ and $^2H$ NMR spectroscopy. The according spectra are depicted on page 91.

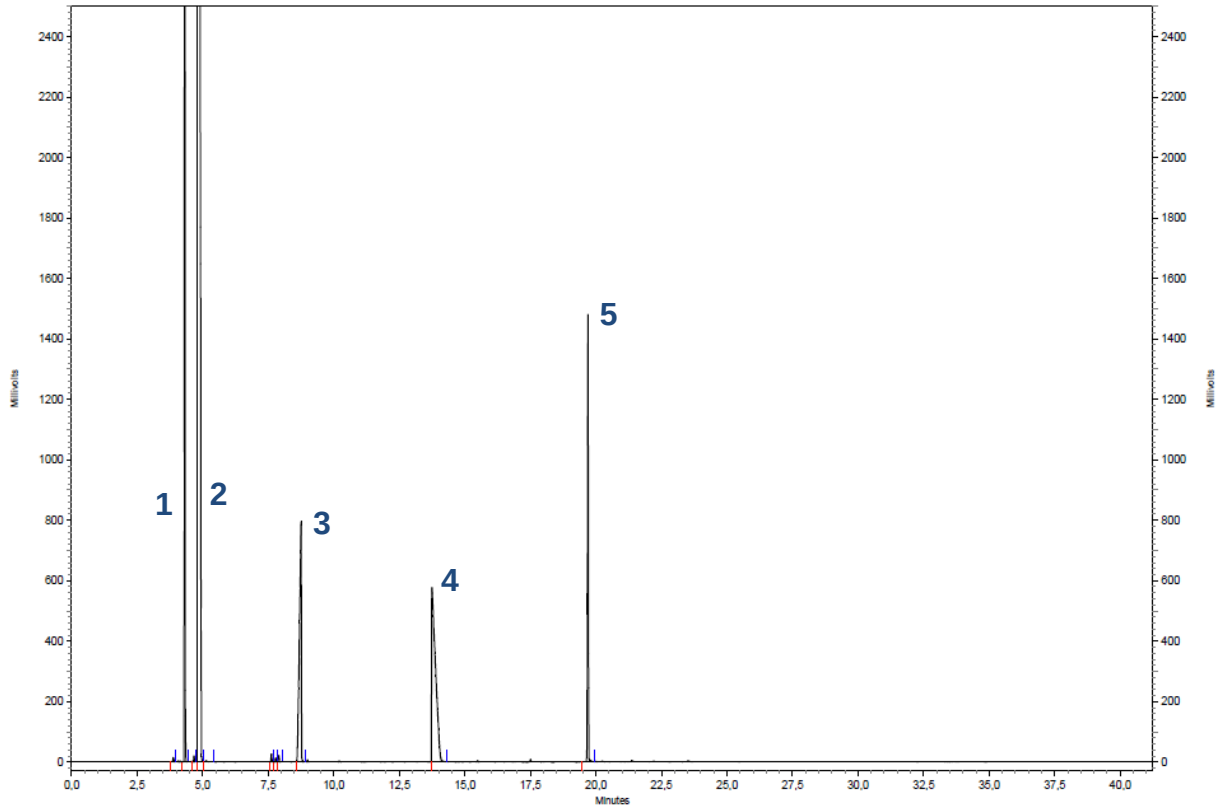
**Procedure for the $H_2{}^{18}O$ labelling experiments**: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and **CI**+LiI (184+ 736 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL) and $H_2{}^{18}O$ (0.3 mL). The red brownish solution was transferred via cannula to a stainless steel autoclave, in which $PPh_3$ (460 µmol) and *p*-$TsOH \cdot H_2O$ (330 µmol) were already deposited. The autoclave was pressurized with $CO_2$ (4.1 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. The resulting red solution was analysed by mass spectrometry. Masses were found to be reproducible in accurancy and intensity for the labelled compounds during 3 min of measuring time. The according spectra are depicted on page 92.

**Procedure for the $H_2{}^{18}O$ control experiment**: Under an argon atmosphere, cyclohexane carboxylic acid (1.88 mmol) was weighed into a Schlenk tube along with acetic acid (0.65 mL) and $H_2{}^{18}O$ (0.2 mL). The solution was transferred via cannula to a stainless steel autoclave. The autoclave was pressurized with $CO_2$ (4.5 g) and then additional 10 bar of $H_2$ were added up to a total pressure of 70 bar at room temperature. The reaction mixture was stirred and heated to 180°C. After 16 h the autoclave was cooled to 0°C and then carefully vented. The resulting solution was analysed by mass spectrometry. Masses were found to be reproducible in accurancy and intensity for the labelled compounds during 3 min of measuring time. The according spectra are depicted on page 93.

## S3 Gaschromatographic Data

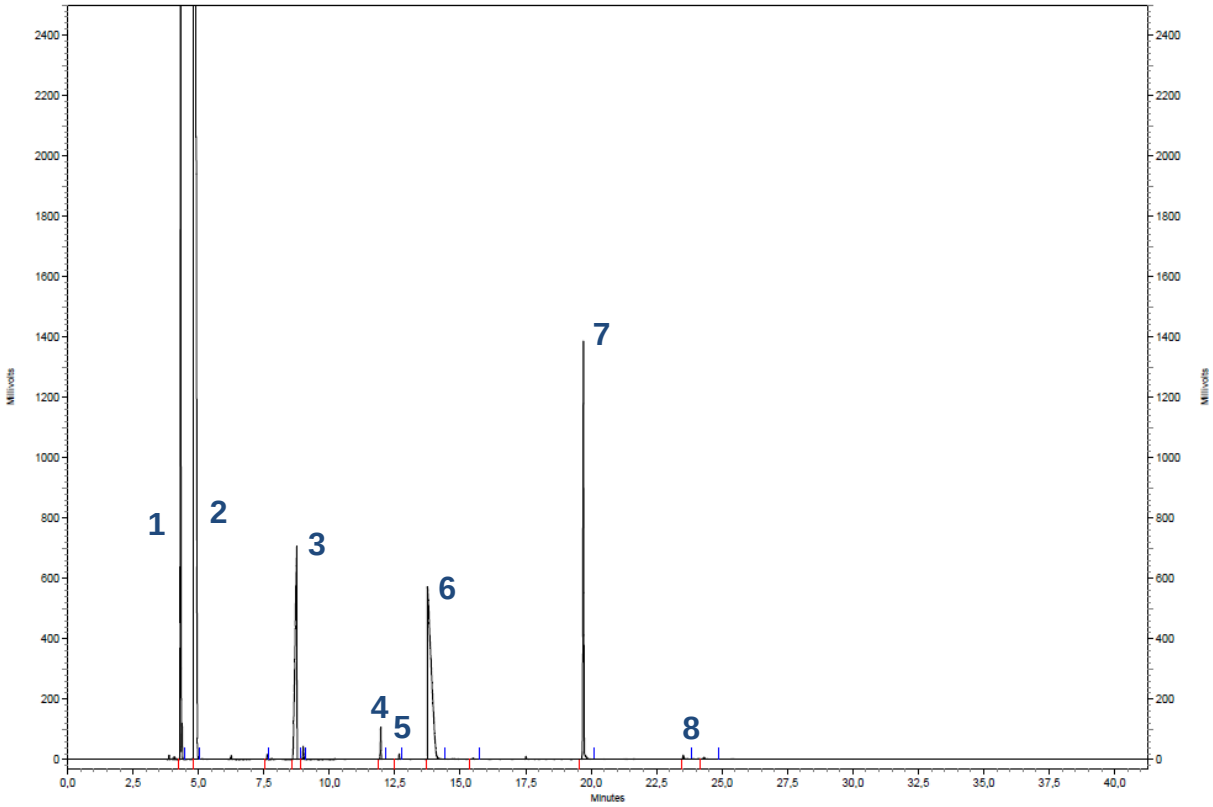
### S3.1 Gaschromatograms to Table S2.1

Entry 1



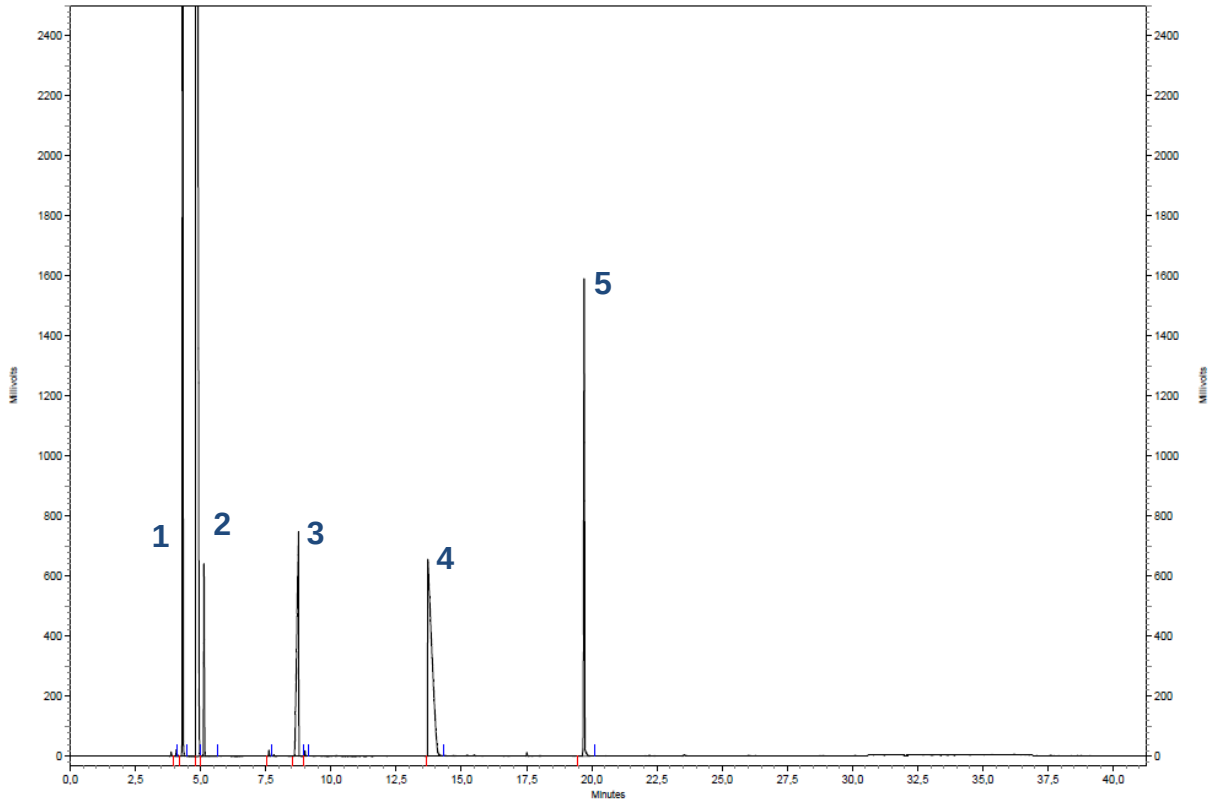

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.317 | **CE** | 58098986 |
| 2 | 4.798 | $CH_2Cl_2$ (Solv.) | 538231322 |
| 3 | 8.760 | *n*-Dodecane (Stand.) | 38862081 |
| 4 | 13.745 | $CH_3COOH$ (Solv.) | 57959547 |
| 5 | 19.703 | 1-Phenylethanol (Stand.) | 28757687 |

Entry 2



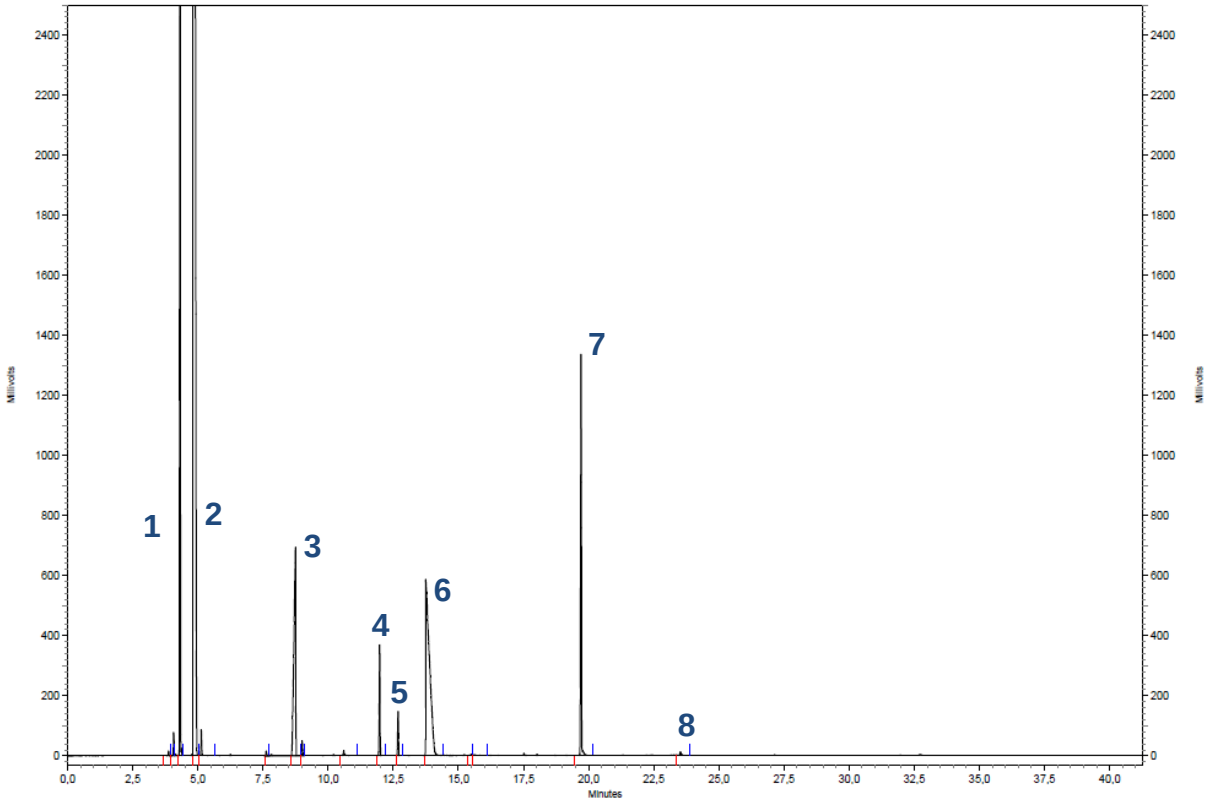

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.318 | **CE** | 50062542 |
| 2 | 4.798 | $CH_2Cl_2$ (Solv.) | 542094021 |
| 3 | 8.753 | *n*-Dodecane (Stand.) | 32665215 |
| 4 | 11.963 | **CAc** | 1747061 |
| 5 | 12.668 | **CI** | 310187 |
| 6 | 13.745 | $CH_3COOH$ (Solv.) | 56923094 |
| 7 | 19.703 | 1-Phenylethanol (Stand.) | 27072815 |
| 8 | 23.312 | **CA** | 308705 |

Entry 3



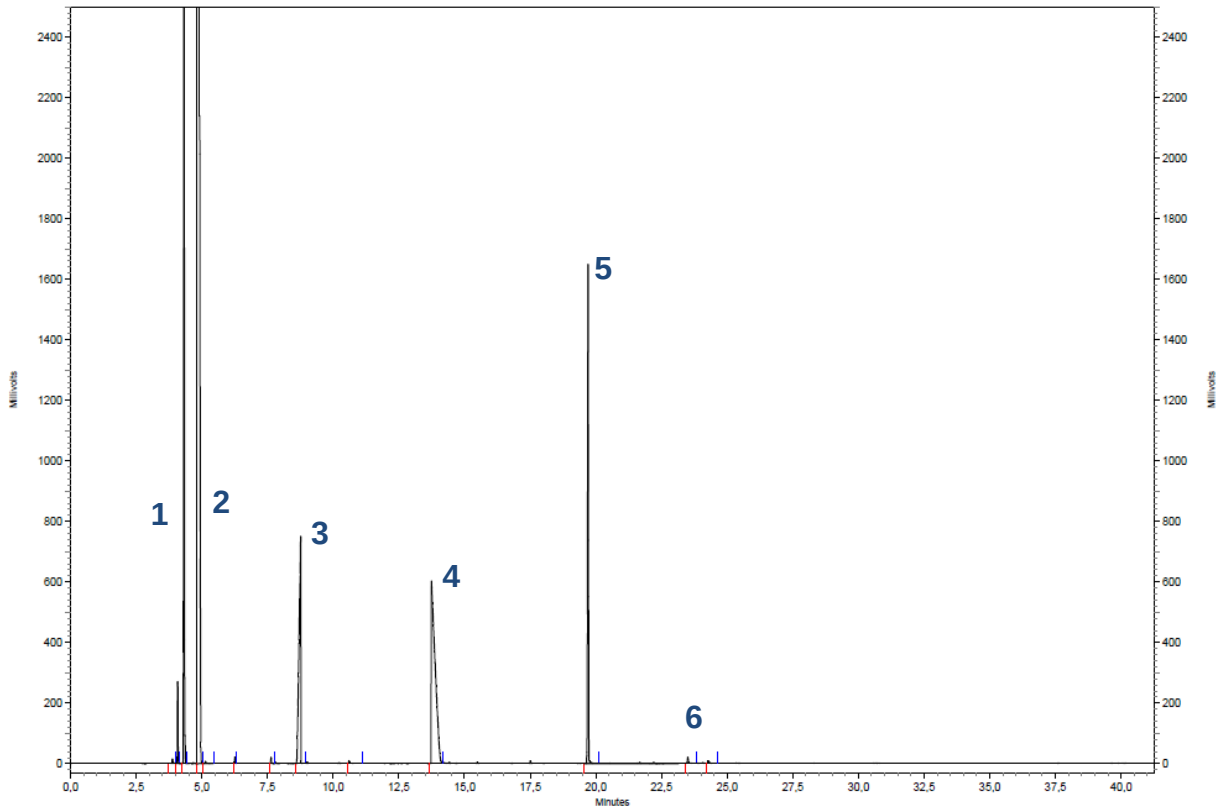

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.310 | **CE** | 66855521 |
| 2 | 4.790 | $CH_2Cl_2$ (Solv.) | 535246491 |
| 3 | 8.753 | *n*-Dodecane (Stand.) | 34948061 |
| 4 | 13.715 | $CH_3COOH$ (Solv.) | 71609064 |
| 5 | 19.708 | 1-Phenylethanol (Stand.) | 32276946 |

Entry 4



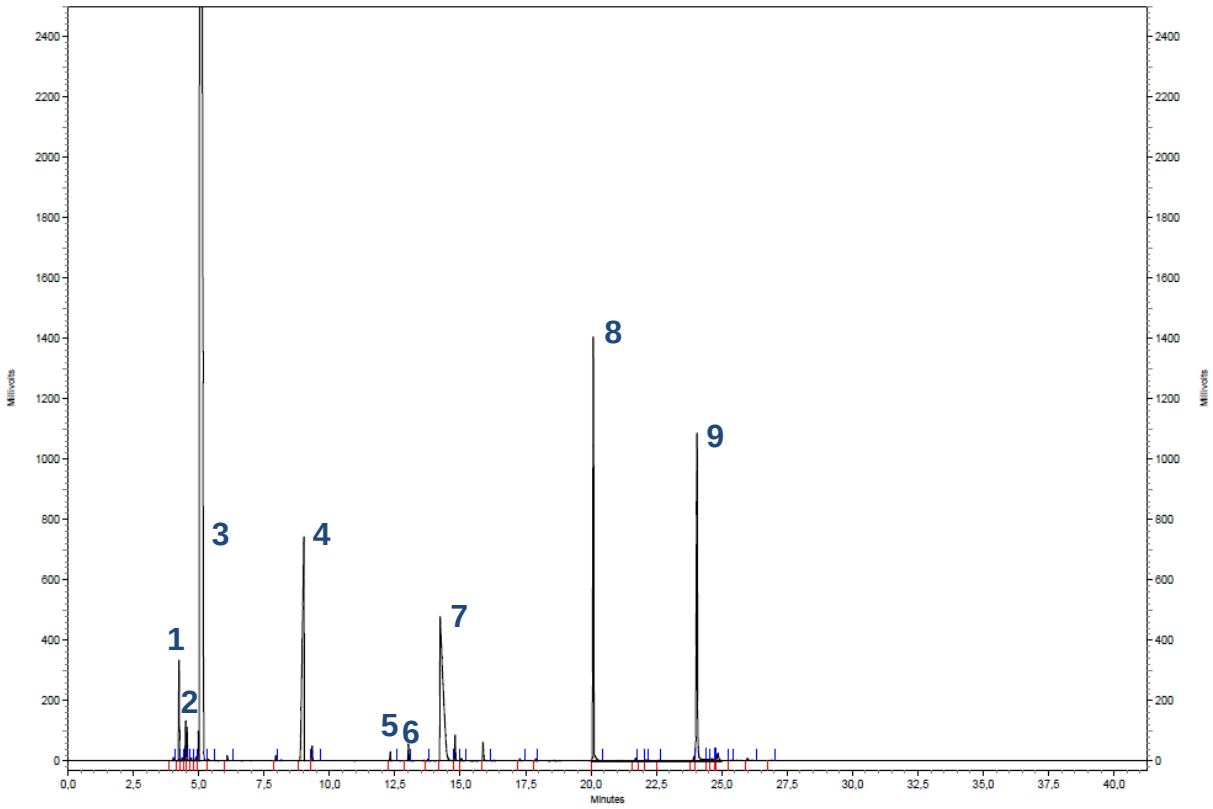

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.313 | **CE** | 48194395 |
| 2 | 4.792 | $CH_2Cl_2$ (Solv.) | 538476658 |
| 3 | 8.752 | *n*-Dodecane (Stand.) | 32378855 |
| 4 | 11.983 | **CAc** | 6877451 |
| 5 | 12.687 | **CI** | 2662651 |
| 6 | 13.750 | $CH_3COOH$ (Solv.) | 59668788 |
| 7 | 19.710 | 1-Phenylethanol (Stand.) | 25406361 |
| 8 | 23.525 | **CA** | 423929 |

Entry 5




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.320 | **CE** | 53071059 |
| 2 | 4.798 | $CH_2Cl_2$ (Solv.) | 544635844 |
| 3 | 8.765 | *n*-Dodecane (Stand.) | 35663246 |
| 4 | 13.740 | $CH_3COOH$ (Solv.) | 62411720 |
| 5 | 19.707 | 1-Phenylethanol (Stand.) | 32192435 |
| 6 | 23.292 | **CA** | 350399 |

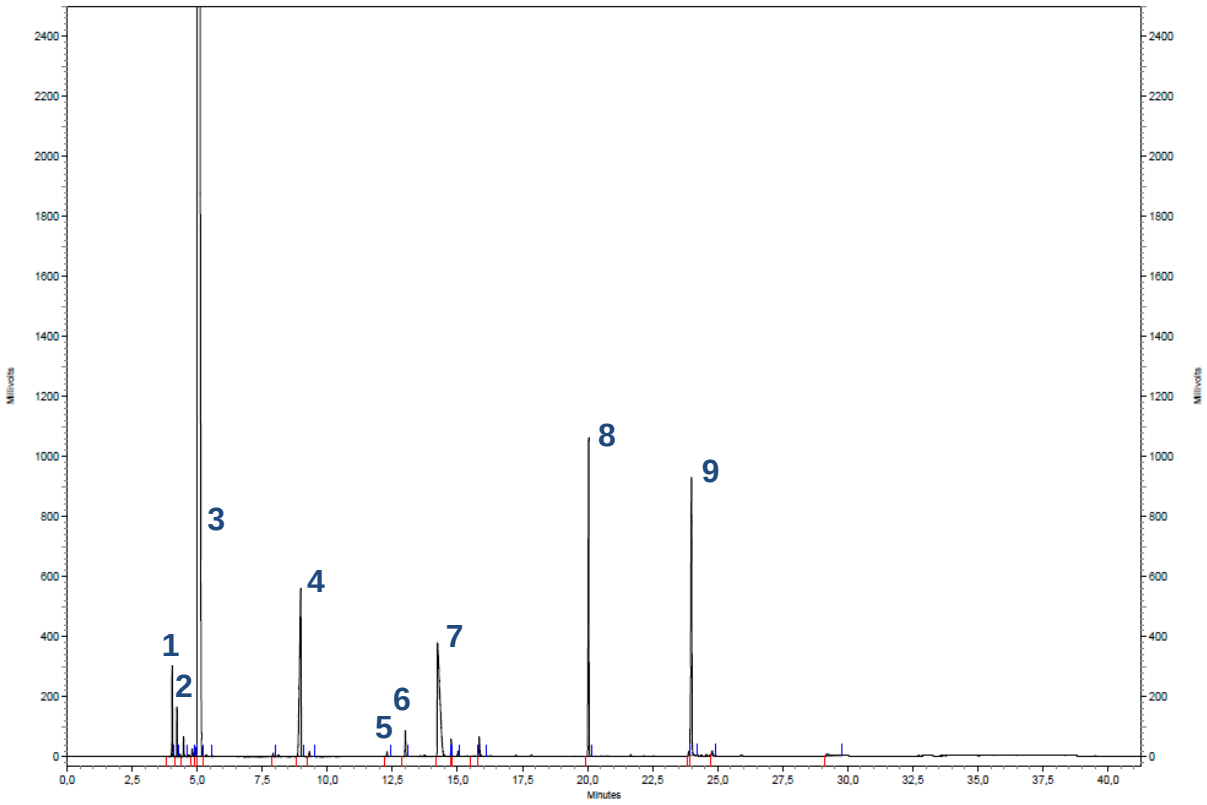
Entry 6




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.245 | **CH** | 4433844 |
| 2 | 4.502 | **CE** | 2031212 |
| 3 | 5.028 | $CH_2Cl_2$ (Solv.) | 522589517 |
| 4 | 9.023 | *n*-Dodecane (Stand.) | 33671343 |
| 5 | 12.323 | **CAc** | 529990 |
| 6 | 13.022 | **CI** | 1042924 |
| 7 | 14.232 | $CH_3COOH$ (Solv.) | 39395166 |
| 8 | 20.090 | 1-Phenylethanol (Stand.) | 28037869 |
| 9 | 24.053 | **CA** | 30891976 |

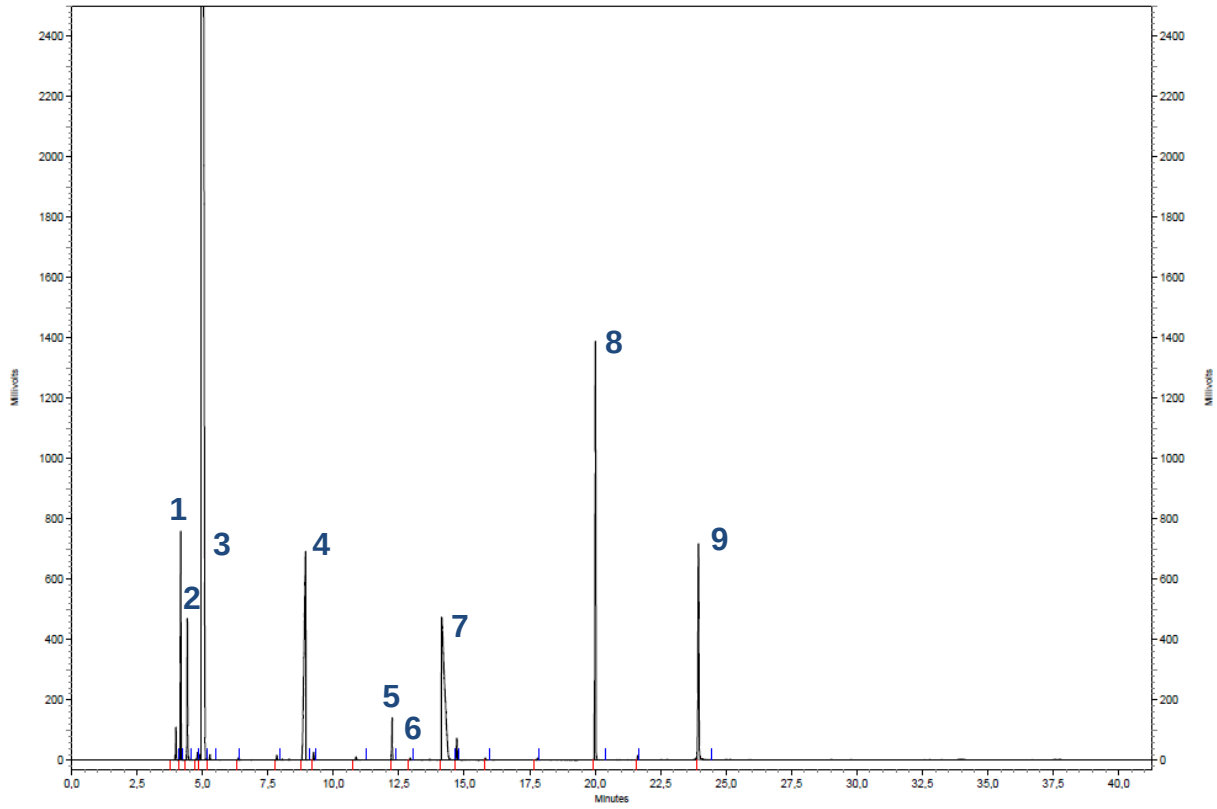
## S3.2 Gaschromatograms to Table S2.2

Entry 1



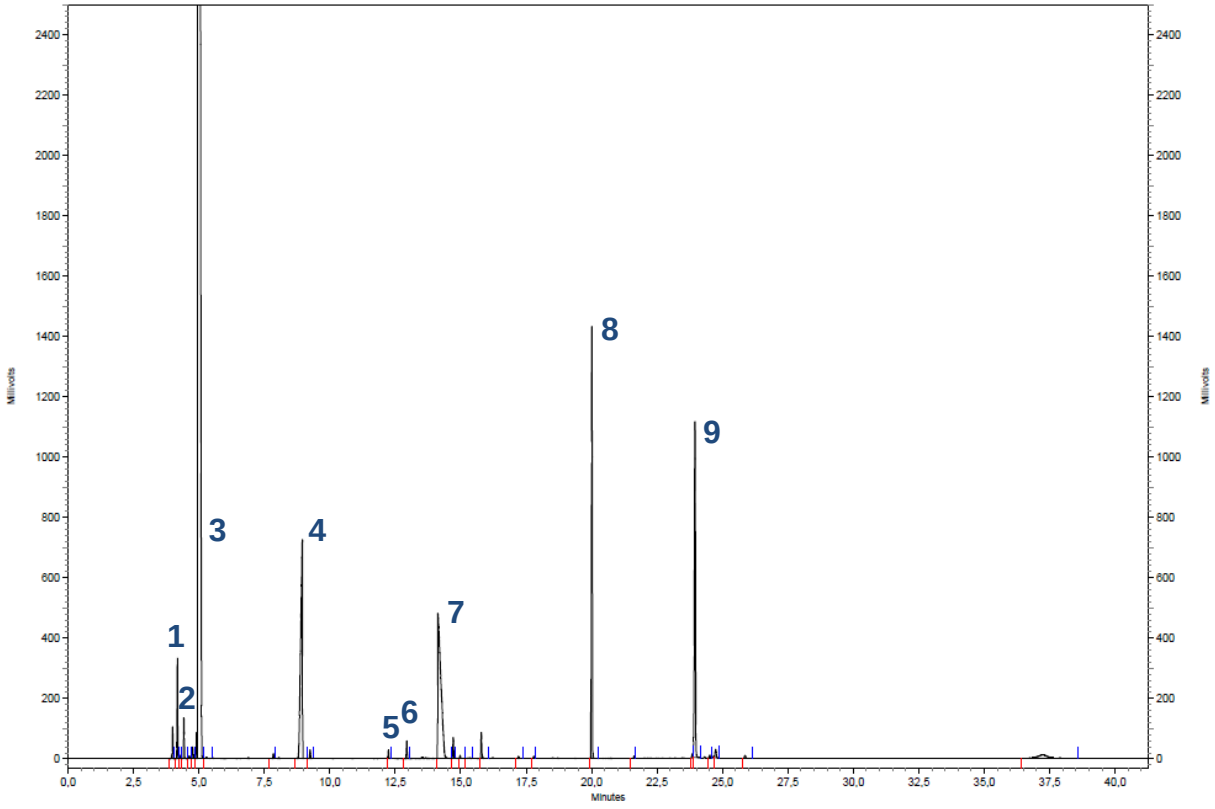

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.222 | **CH** | 1991545 |
| 2 | 4.477 | **CE** | 927542 |
| 3 | 5.017 | $CH_2Cl_2$ (Solv.) | 392085582 |
| 4 | 8.980 | *n*-Dodecane (Stand.) | 20293940 |
| 5 | 12.293 | **CAc** | 267475 |
| 6 | 13.000 | **CI** | 1517506 |
| 7 | 14.235 | $CH_3COOH$ (Solv.) | 25382742 |
| 8 | 20.038 | 1-Phenylethanol (Stand.) | 18798006 |
| 9 | 23.992 | **CA** | 22530242 |

Entry 2



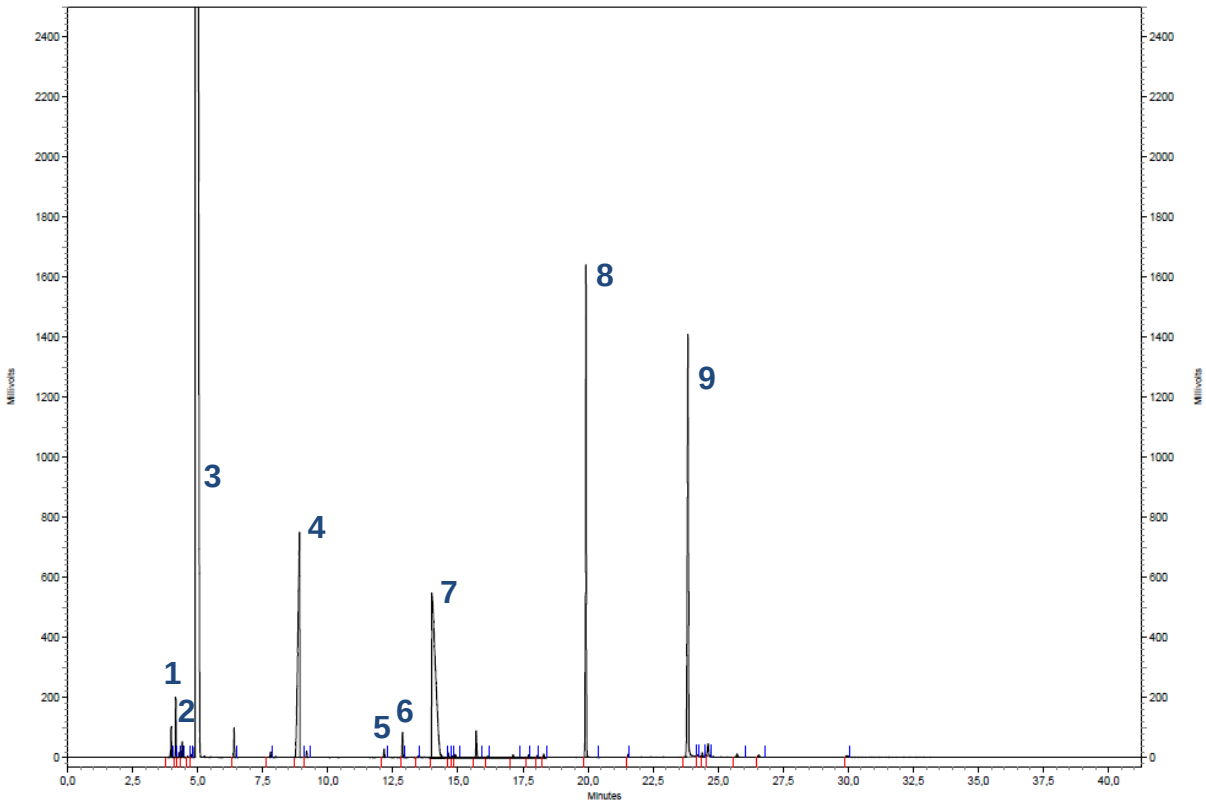

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.170 | **CH** | 10035533 |
| 2 | 4.422 | **CE** | 7333320 |
| 3 | 4.930 | $CH_2Cl_2$ (Solv.) | 565209382 |
| 4 | 8.943 | *n*-Dodecane (Stand.) | 30628600 |
| 5 | 12.245 | **CAc** | 2297911 |
| 6 | 12.937 | **CI** | 130155 |
| 7 | 14.135 | $CH_3COOH$ (Solv.) | 38394893 |
| 8 | 20.012 | 1-Phenylethanol (Stand.) | 26627134 |
| 9 | 23.948 | **CA** | 16921950 |

Entry 3



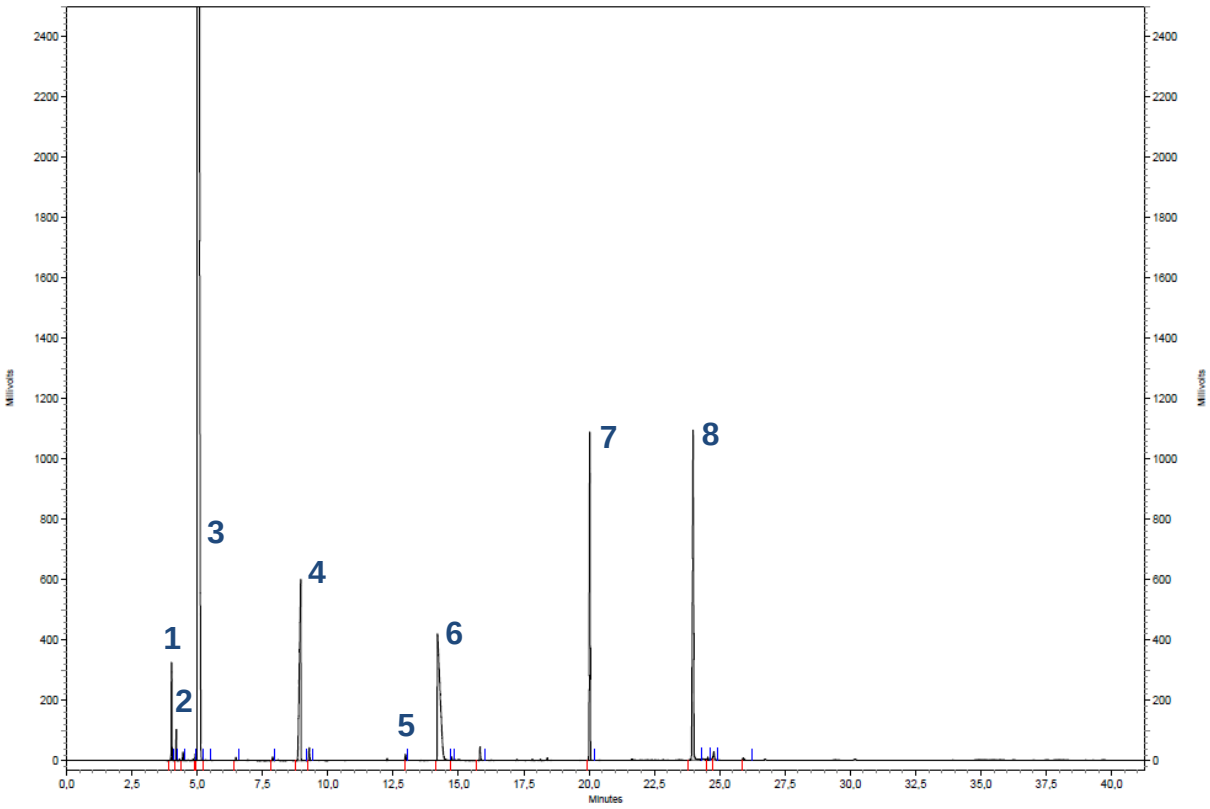

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.177 | **CH** | 4374561 |
| 2 | 4.428 | **CE** | 2088590 |
| 3 | 4.938 | $CH_2Cl_2$ (Solv.) | 551017028 |
| 4 | 8.952 | *n*-Dodecane (Stand.) | 33888780 |
| 5 | 12.238 | **CAc** | 444846 |
| 6 | 12.942 | **CI** | 1018953 |
| 7 | 14.128 | $CH_3COOH$ (Solv.) | 39703195 |
| 8 | 20.012 | 1-Phenylethanol (Stand.) | 27529373 |
| 9 | 23.953 | **CA** | 28584714 |

Entry 4




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.158 | **CH** | 2679301 |
| 2 | 4.407 | **CE** | 848160 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.915 | *n*-Dodecane (Stand.) | 35139425 |
| 5 | 12.163 | **CAc** | 456082 |
| 6 | 12.873 | **CI** | 1462056 |
| 7 | 14.005 | $CH_3COOH$ (Solv.) | 52063194 |
| 8 | 19.925 | 1-Phenylethanol (Stand.) | 32487728 |
| 9 | 23.840 | **CA** | 40158028 |

Entry 5




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.200 | **CH** | 1272338 |
| 2 | 4.453 | **CE** | 408694 |
| 3 | 4.988 | $CH_2Cl_2$ (Solv.) | 425538821 |
| 4 | 8.963 | *n*-Dodecane (Stand.) | 22961031 |
| 5 | 12.972 | **CI** | 360050 |
| 6 | 14.195 | $CH_3COOH$ (Solv.) | 31496254 |
| 7 | 20.025 | 1-Phenylethanol (Stand.) | 19652325 |
| 8 | 23.982 | **CA** | 28968611 |

Data of the isolated product to Entry 5

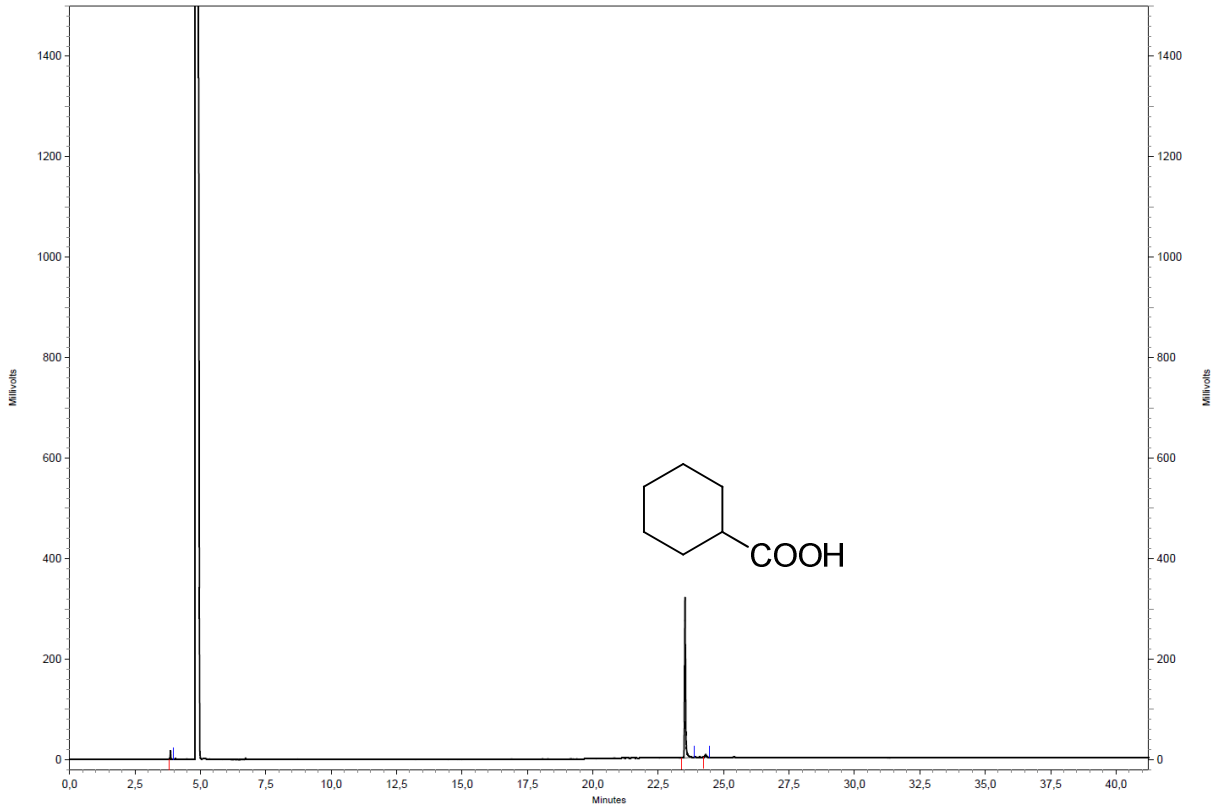



**Figure 3.1.** GC chromatogram of the isolated cyclohexane carboxylic acid.

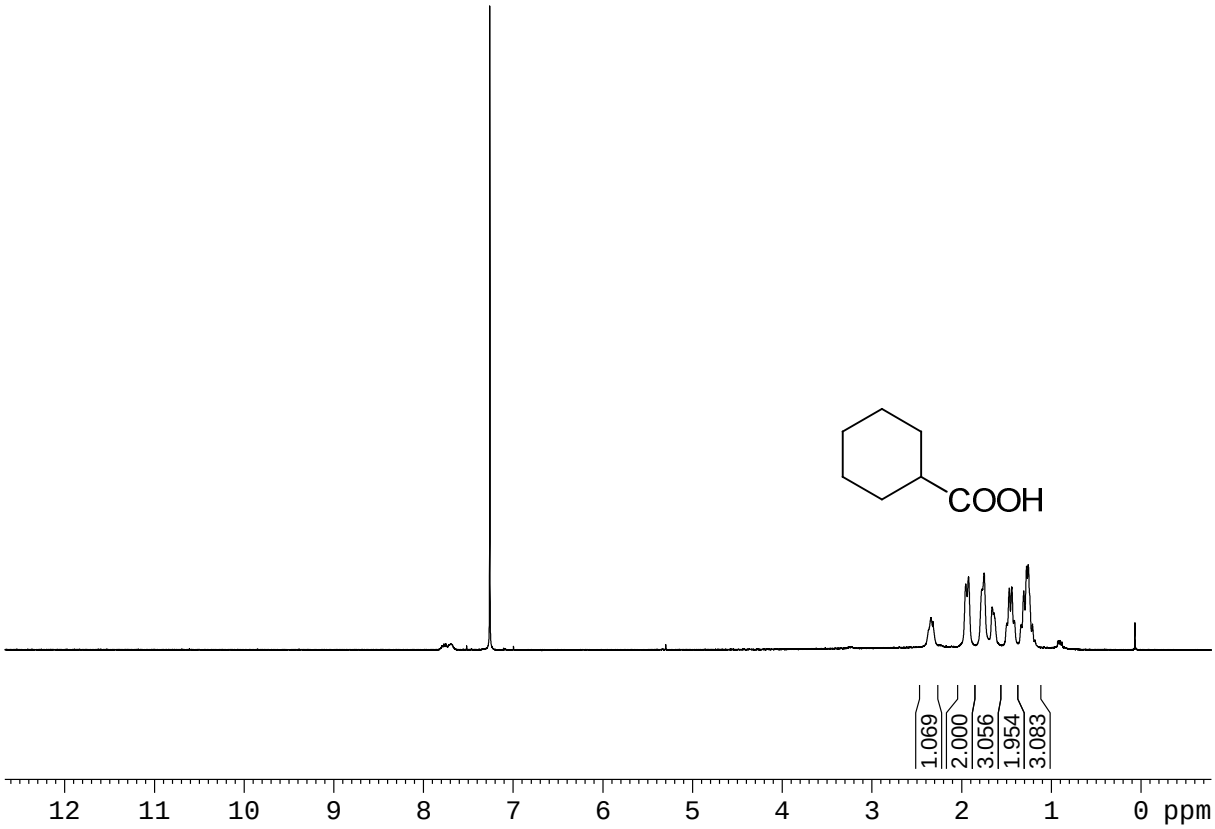
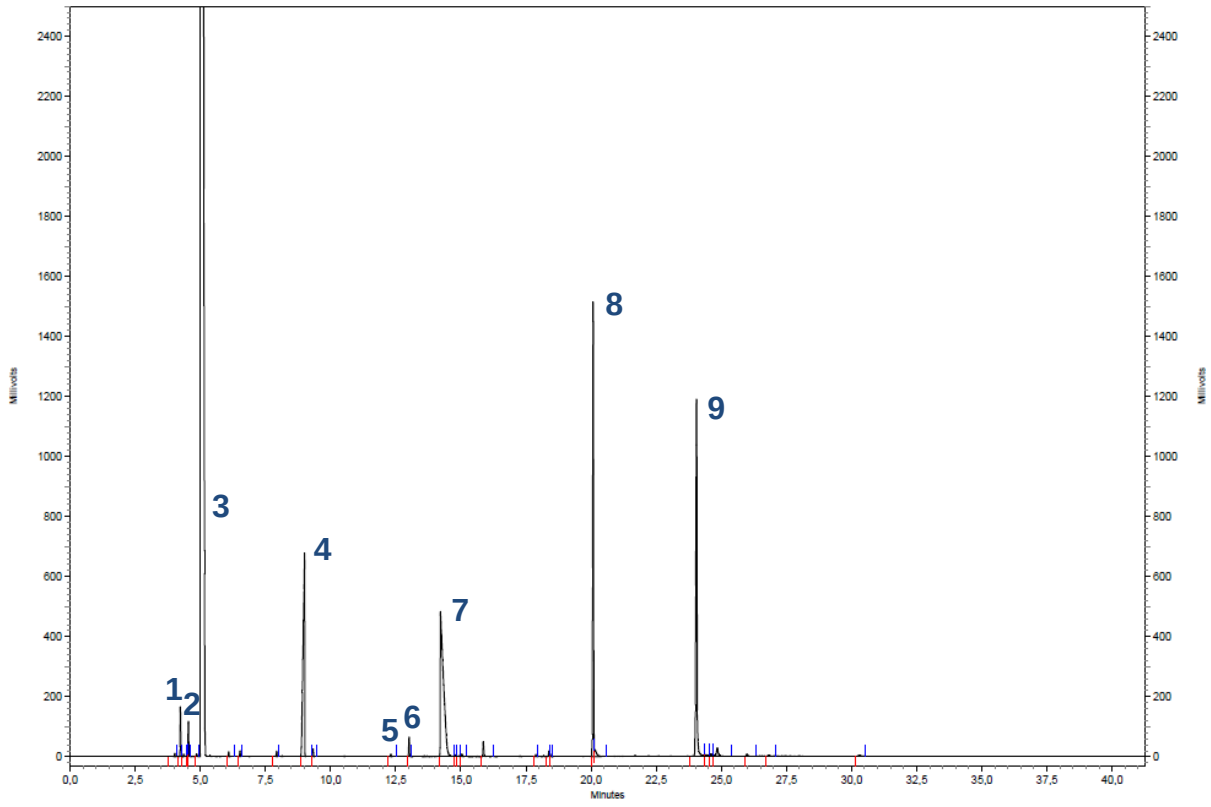


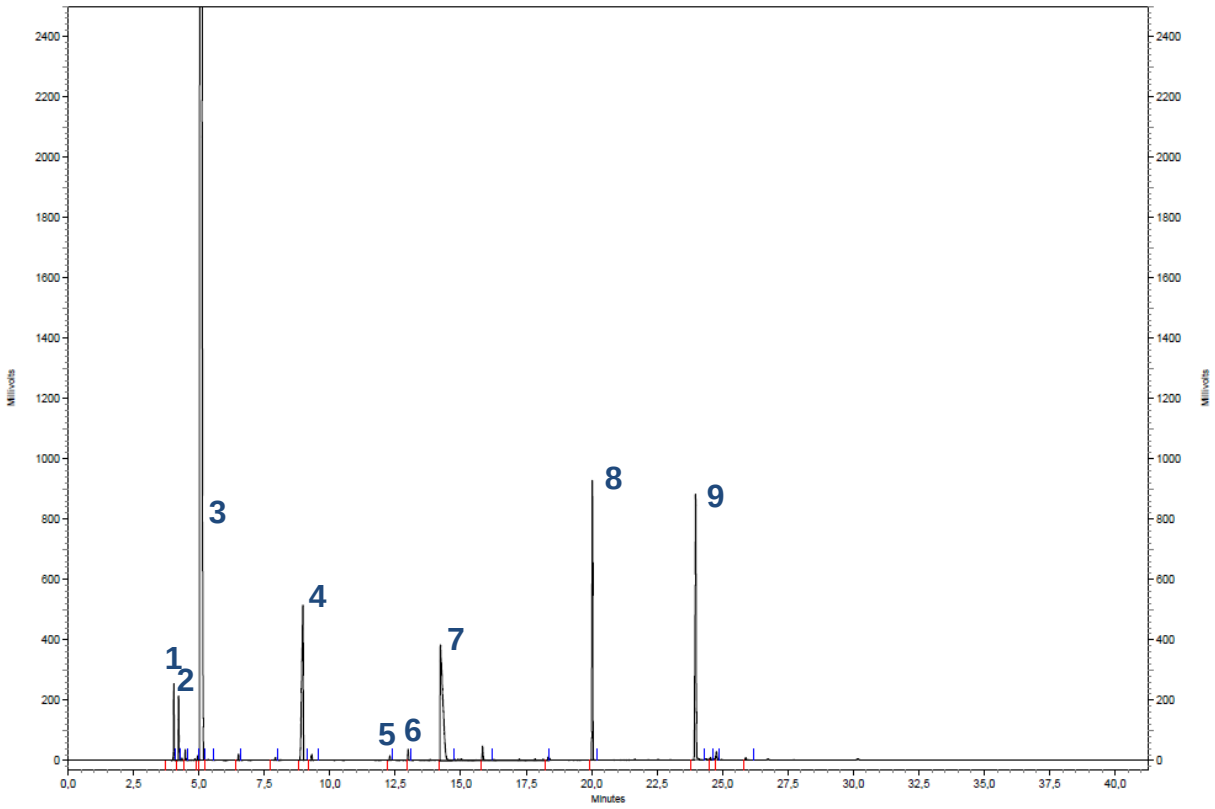

**Figure 3.2.** $^{1}$H NMR spectrum of the isolated product measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

Entry 6




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.235 | **CH** | 2177669 |
| 2 | 4.542 | **CE** | 1783739 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 9.005 | *n*-Dodecane (Stand.) | 29490788 |
| 5 | 12.312 | **CAc** | 161523 |
| 6 | 13.012 | **CI** | 1204964 |
| 7 | 14.213 | $CH_3COOH$ (Solv.) | 41830295 |
| 8 | 20.083 | 1-Phenylethanol (Stand.) | 29884818 |
| 9 | 24.048 | **CA** | 35487518 |

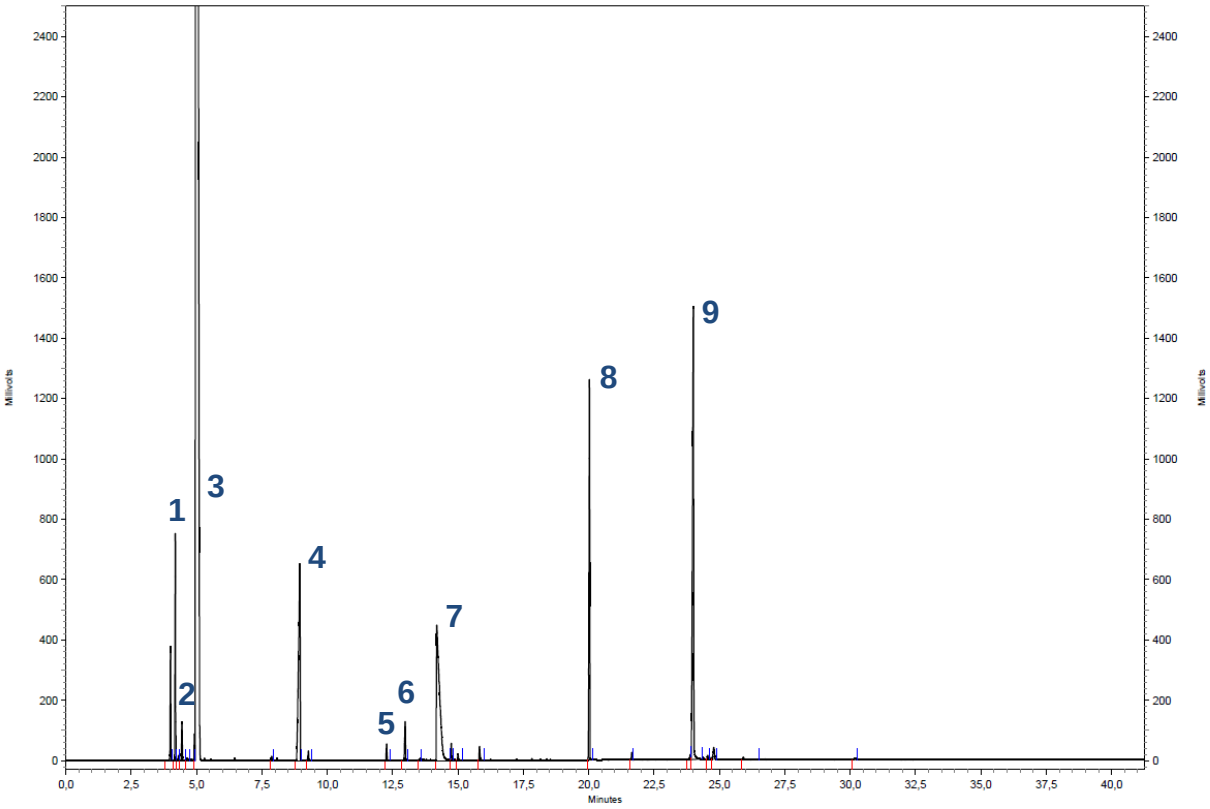
Entry 7




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.227 | **CH** | 2539880 |
| 2 | 4.480 | **CE** | 485270 |
| 3 | 5.032 | $CH_2Cl_2$ (Solv.) | 329568598 |
| 4 | 8.973 | *n*-Dodecane (Stand.) | 17638402 |
| 5 | 12.290 | **CAc** | 247847 |
| 6 | 12.993 | **CI** | 622962 |
| 7 | 14.225 | $CH_3COOH$ (Solv.) | 26212605 |
| 8 | 20.030 | 1-Phenylethanol (Stand.) | 16186723 |
| 9 | 23.975 | **CA** | 21811311 |

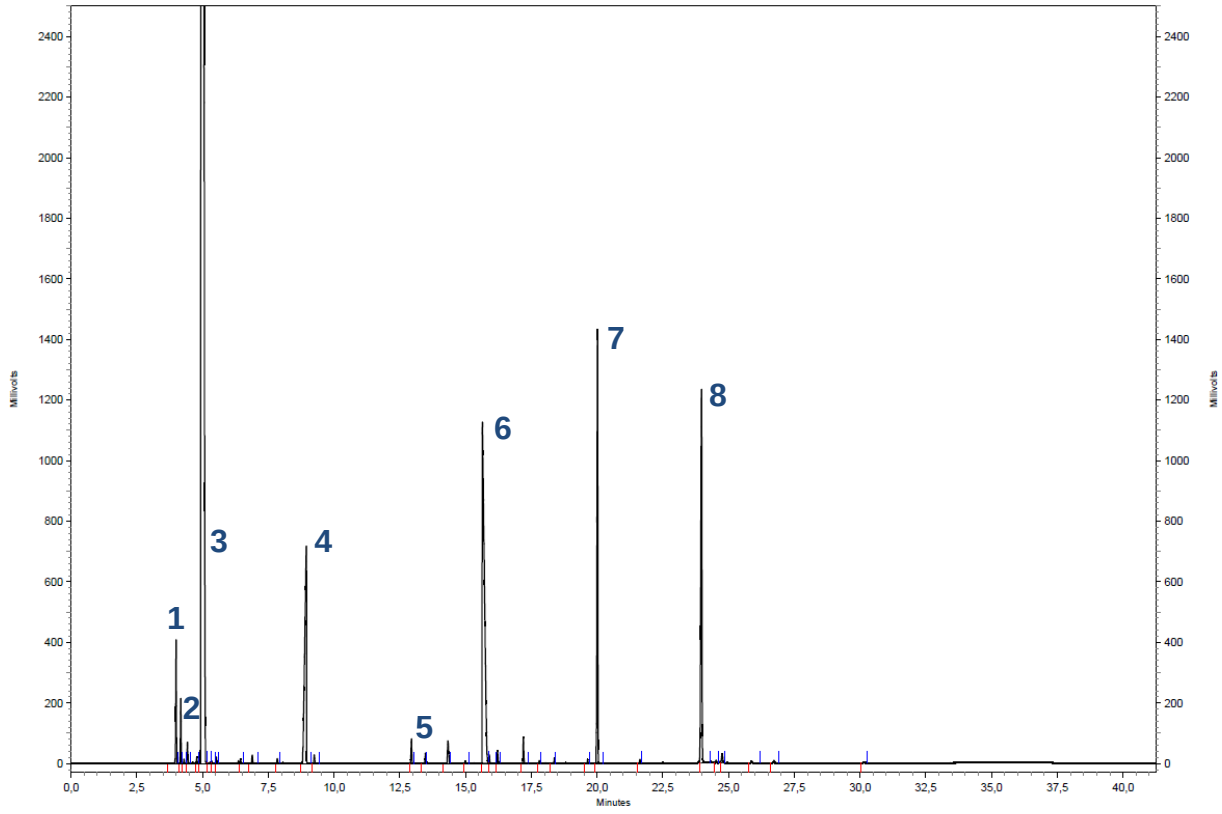
## S3.3 Gaschromatograms to Table S2.3

Entry 1



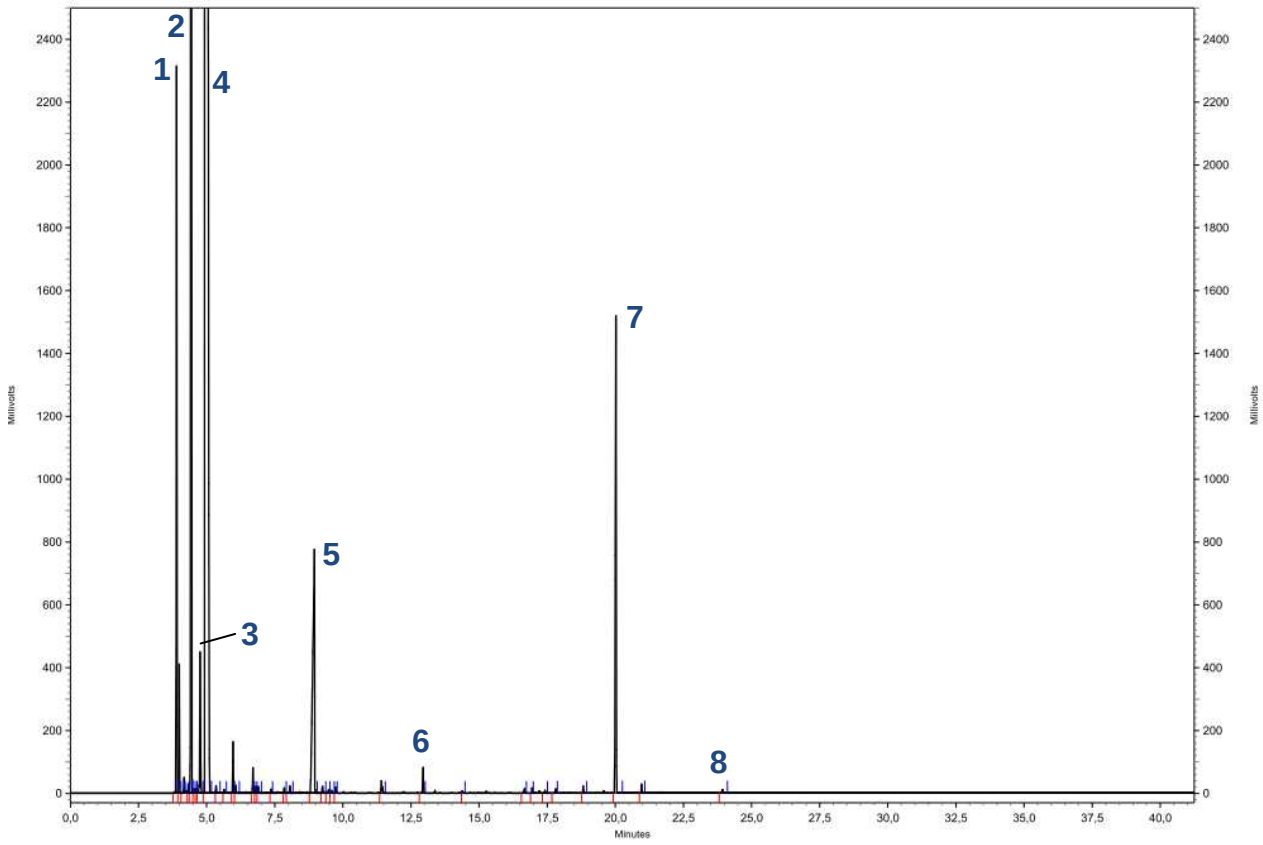

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.183 | **CH** | 9605788 |
| 2 | 4.438 | **CE** | 1889030 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.955 | *n*-Dodecane (Stand.) | 26190459 |
| 5 | 12.268 | **CAc** | 890076 |
| 6 | 12.973 | **CI** | 2287680 |
| 7 | 14.185 | $CH_3COOH$ (Solv.) | 35089734 |
| 8 | 20.027 | 1-Phenylethanol (Stand.) | 23278985 |
| 9 | 23.998 | **CA** | 43927273 |

Entry 2




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.172 | **CH** | 2823840 |
| 2 | 4.425 | **CE** | 1093745 |
| 3 | 4.935 | $CH_2Cl_2$ (Solv.) | 554829493 |
| 4 | 8.947 | *n*-Dodecane (Stand.) | 32640783 |
| 5 | 12.945 | **CI** | 1468257 |
| 6 | 15.624 | Propionic acid (Solv.) | 63238146 |
| 7 | 20.018 | 1-Phenylethanol (Stand.) | 27675391 |
| 8 | 23.973 | **CA** | 33090337 |

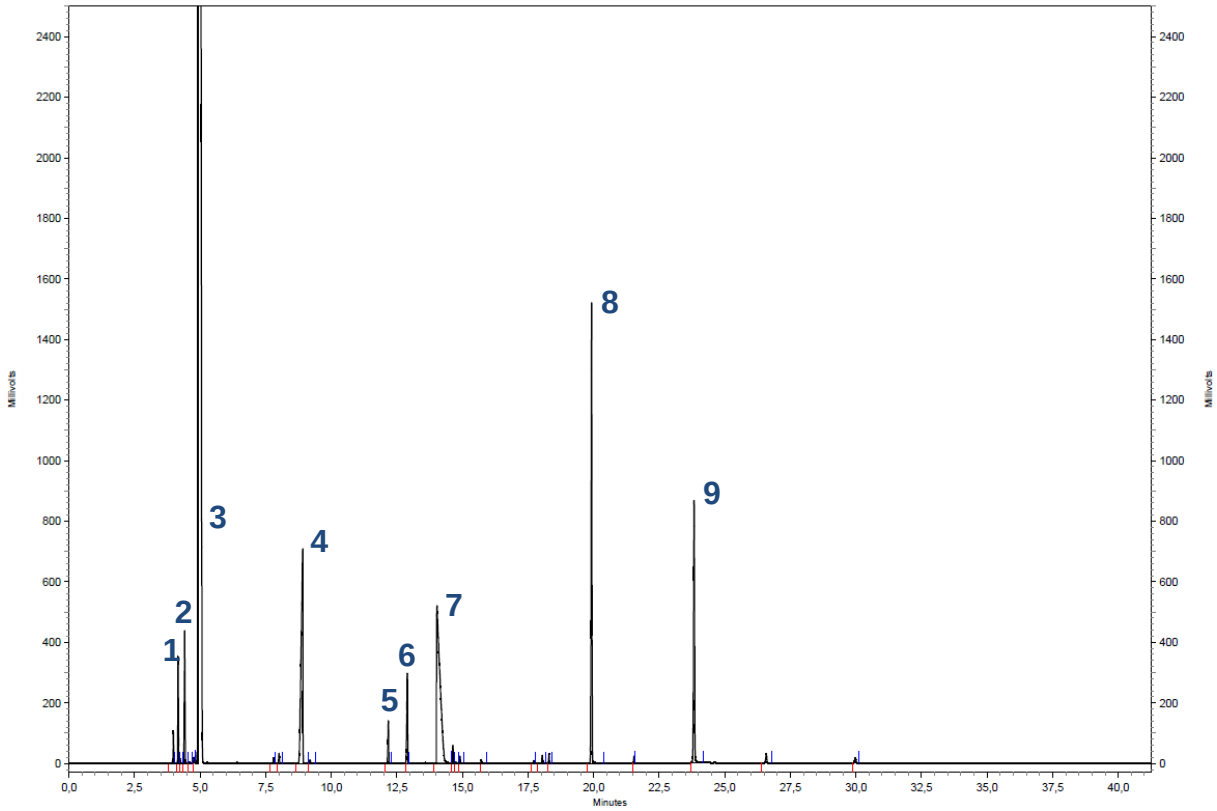
Entry 3




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.175 | **CH** | 689970 |
| 2 | 4.430 | THF (Solv.) | 102123861 |
| 3 | 4.520 | **CE** | 473567 |
| 4 | 4.938 | $CH_2Cl_2$ (Solv.) | 555651727 |
| 5 | 8.960 | *n*-Dodecane (Stand.) | 36062420 |
| 6 | 12.945 | **CI** | 1450316 |
| 7 | 20.020 | 1-Phenylethanol (Stand.) | 29402117 |
| 8 | 23.932 | **CA** | 239182 |

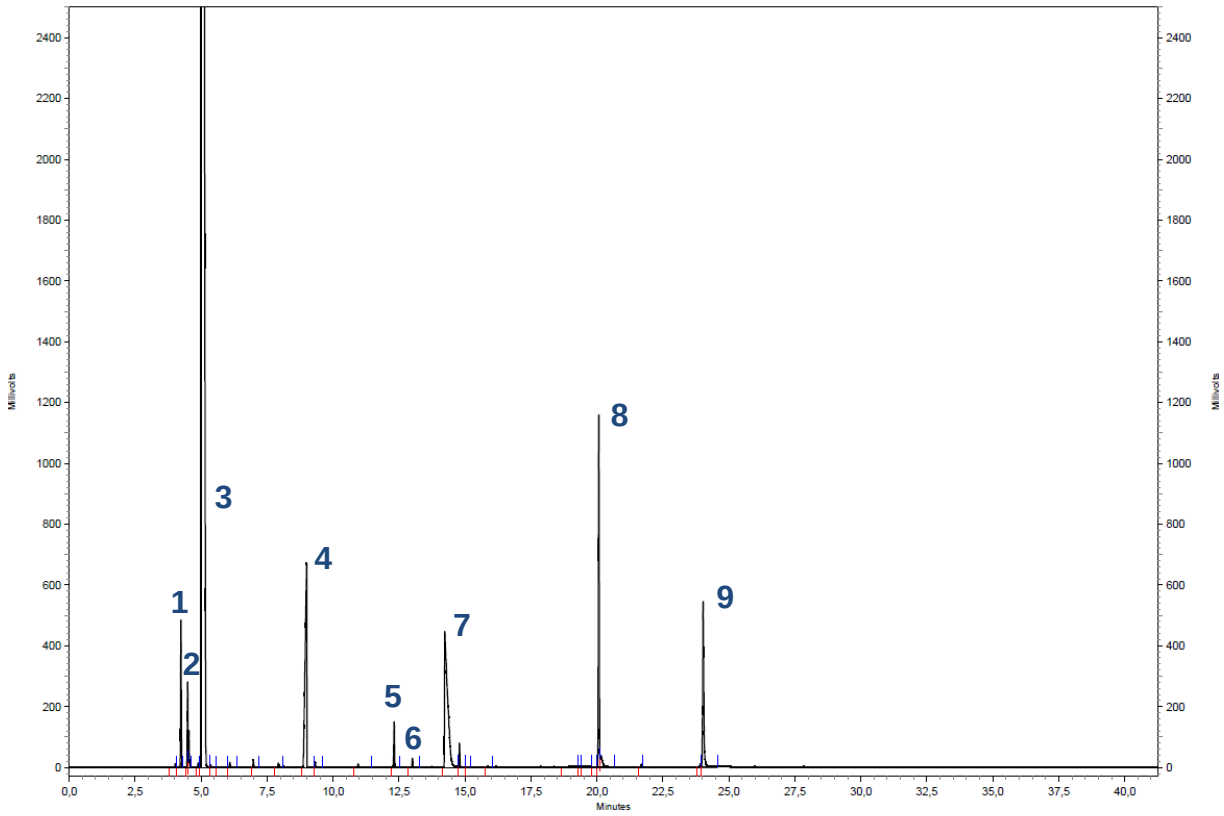
## S3.4 Gaschromatograms to Table S2.4

Entry 1



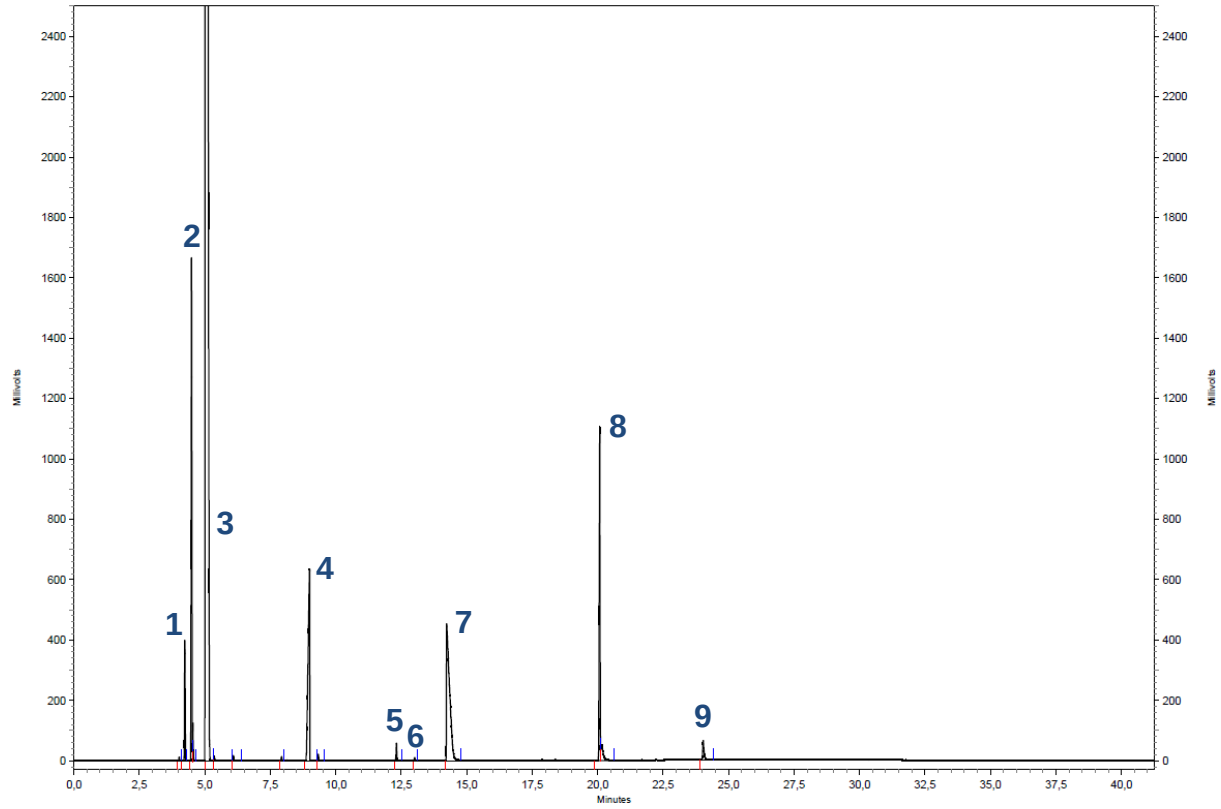

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.162 | **CH** | 4623719 |
| 2 | 4.412 | **CE** | 6724551 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.910 | *n*-Dodecane (Stand.) | 30930081 |
| 5 | 12.173 | **CAc** | 2314710 |
| 6 | 12.898 | **CI** | 6311692 |
| 7 | 14.028 | $CH_3COOH$ (Solv.) | 46117037 |
| 8 | 19.927 | 1-Phenylethanol (Stand.) | 29236760 |
| 9 | 23.833 | **CA** | 21649809 |

Entry 2



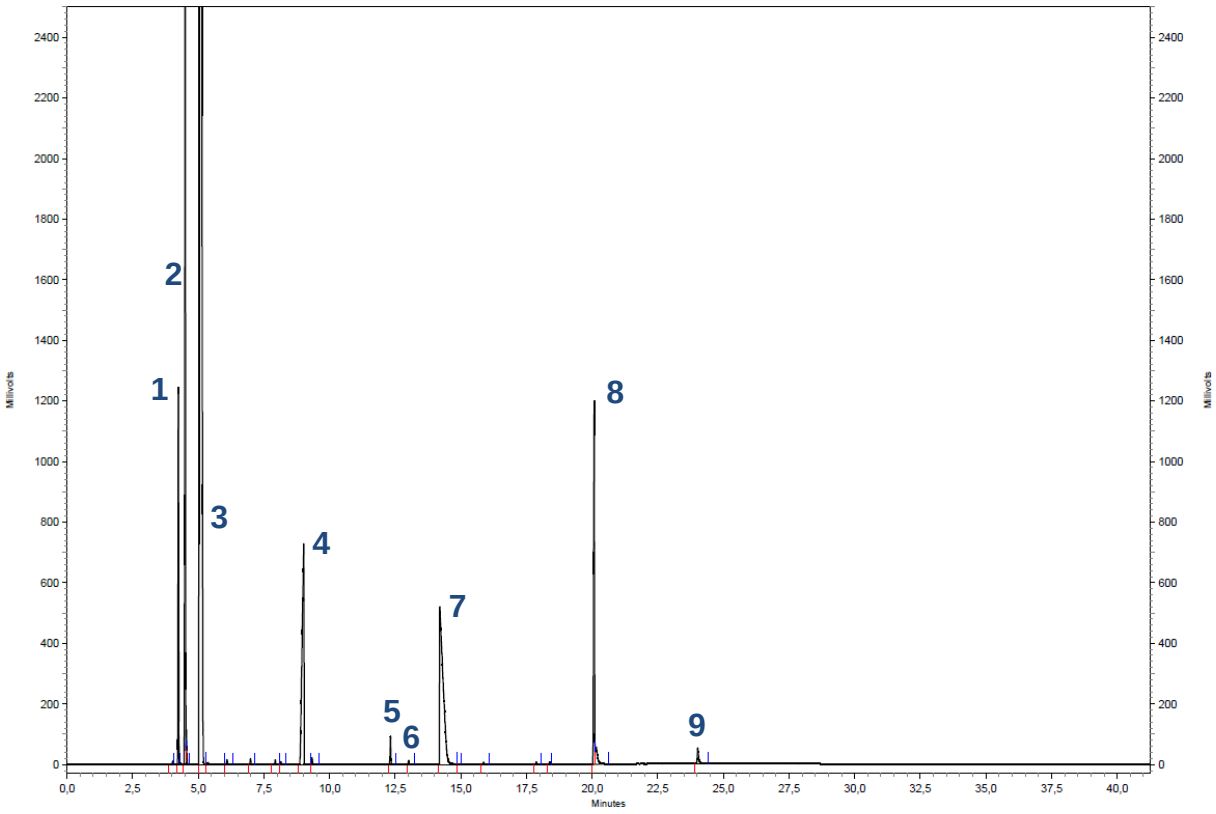

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.233 | **CH** | 6407863 |
| 2 | 4.490 | **CE** | 4261870 |
| 3 | 5.012 | $CH_2Cl_2$ (Solv.) | 538587171 |
| 4 | 9.002 | *n*-Dodecane (Stand.) | 29123450 |
| 5 | 12.315 | **CAc** | 2617854 |
| 6 | 13.007 | **CI** | 553475 |
| 7 | 14.233 | $CH_3COOH$ (Solv.) | 35607530 |
| 8 | 20.073 | 1-Phenylethanol (Stand.) | 21793779 |
| 9 | 24.027 | **CA** | 16019251 |

Entry 3



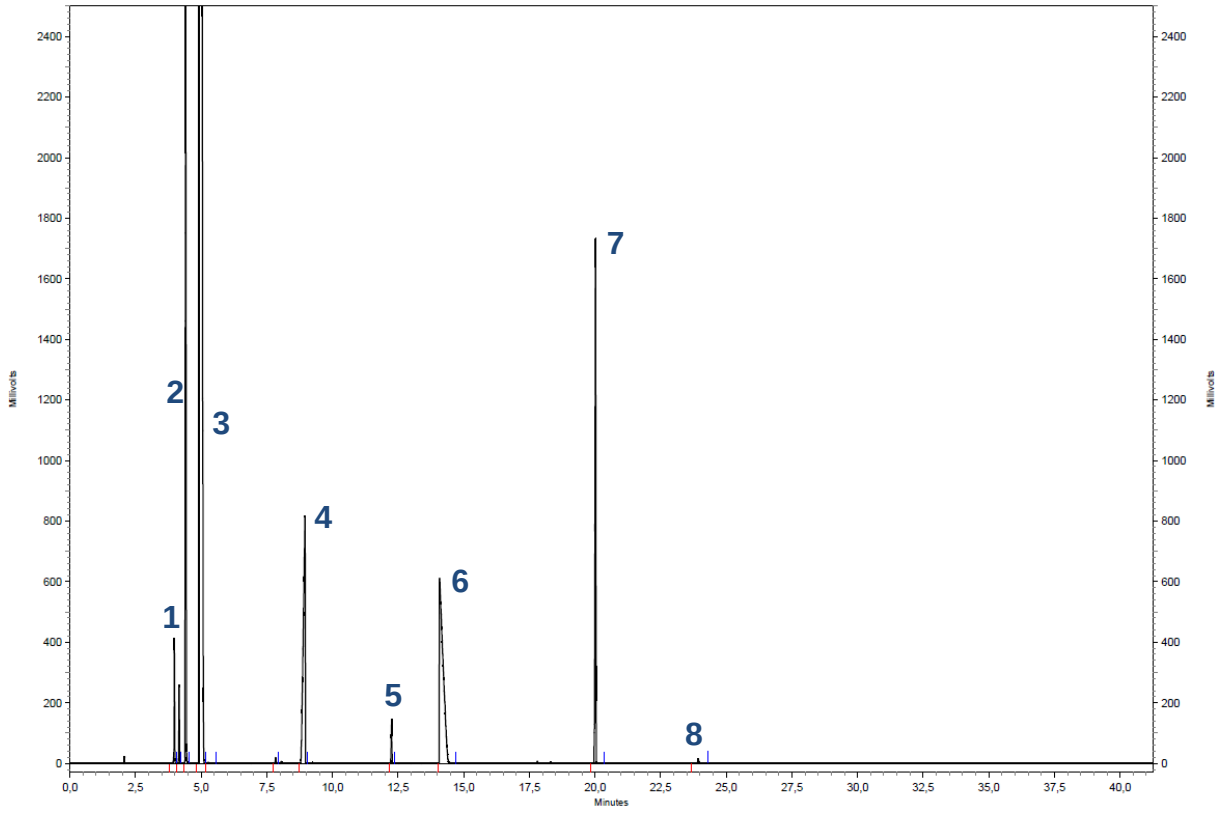

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.235 | **CH** | 5144918 |
| 2 | 4.492 | **CE** | 25230166 |
| 3 | 5.013 | $CH_2Cl_2$ (Solv.) | 544970234 |
| 4 | 8.998 | *n*-Dodecane (Stand.) | 26142032 |
| 5 | 12.317 | **CAc** | 991745 |
| 6 | 13.010 | **CI** | 195450 |
| 7 | 14.233 | $CH_3COOH$ (Solv.) | 37599694 |
| 8 | 20.078 | 1-Phenylethanol (Stand.) | 20853886 |
| 9 | 24.028 | **CA** | 2439710 |

Entry 4



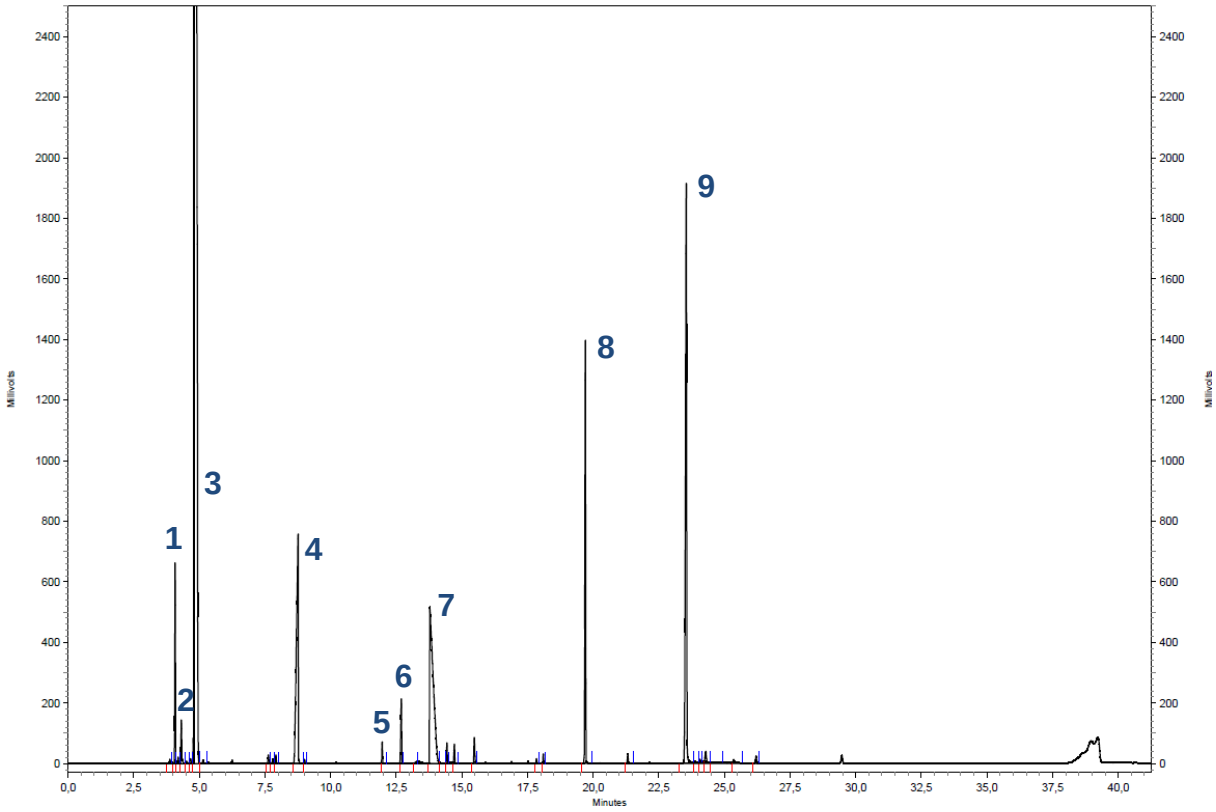

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.240 | **CH** | 16346362 |
| 2 | 4.498 | **CE** | 55861908 |
| 3 | 5.022 | $CH_2Cl_2$ (Solv.) | 522642505 |
| 4 | 9.015 | *n*-Dodecane (Stand.) | 32957009 |
| 5 | 12.320 | **CAc** | 1666006 |
| 6 | 13.010 | **CI** | 265242 |
| 7 | 14.200 | $CH_3COOH$ (Solv.) | 47136194 |
| 8 | 20.075 | 1-Phenylethanol (Stand.) | 23201249 |
| 9 | 24.025 | **CA** | 1839809 |

Entry 5



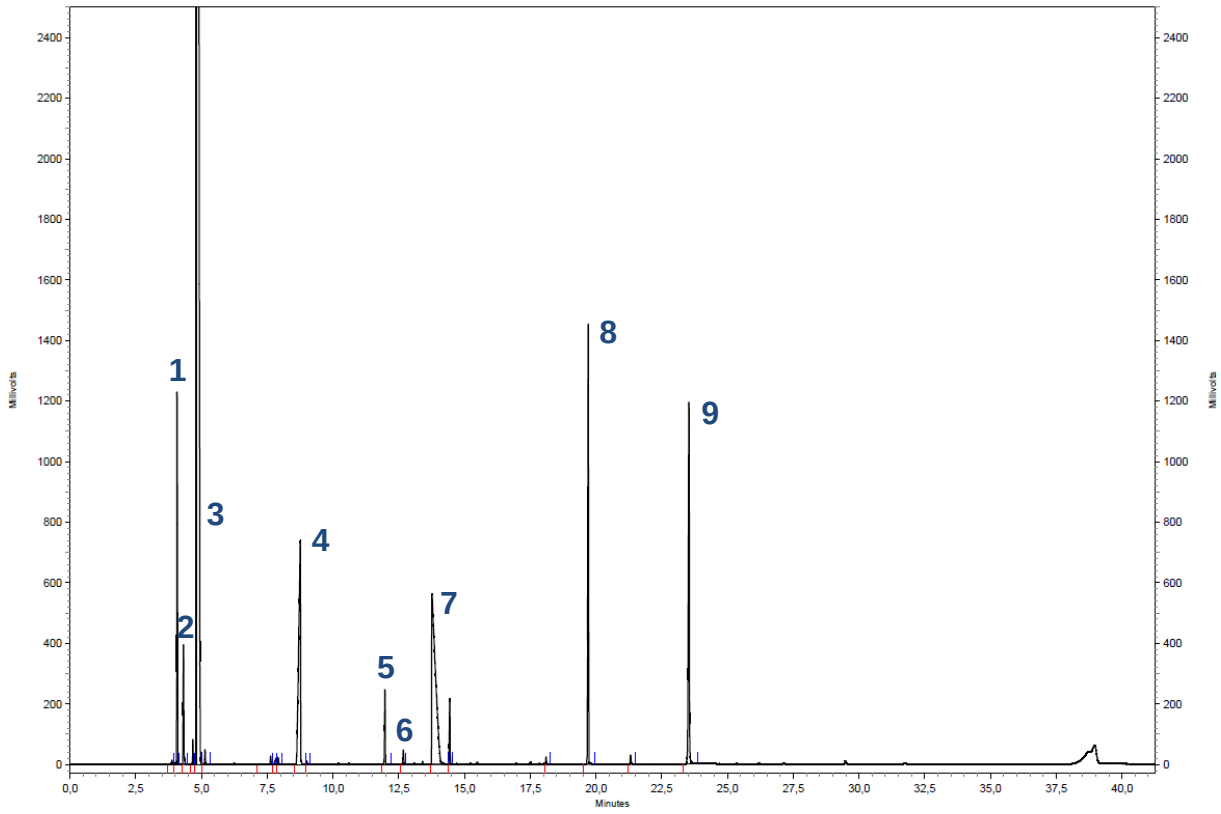

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.158 | **CH** | 3365695 |
| 2 | 4.412 | **CE** | 46005793 |
| 3 | 4.922 | $CH_2Cl_2$ (Solv.) | 544941656 |
| 4 | 8.960 | *n*-Dodecane (Stand.) | 40741507 |
| 5 | 12.252 | **CAc** | 2408441 |
| 6 | 14.080 | $CH_3COOH$ (Solv.) | 58967864 |
| 7 | 20.022 | 1-Phenylethanol (Stand.) | 34575327 |
| 8 | 23.937 | **CA** | 356243 |

Entry 6



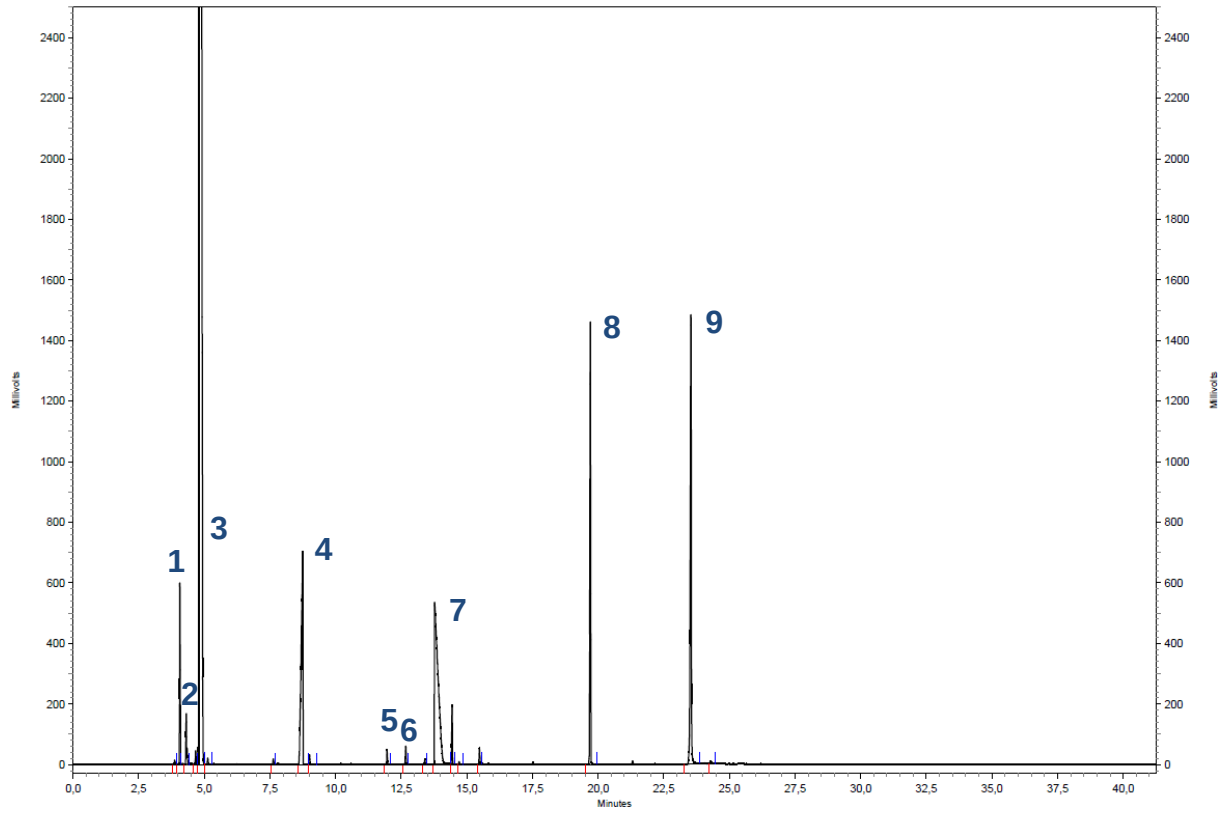

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.073 | **CH** | 8443705 |
| 2 | 4.313 | **CE** | 2321799 |
| 3 | 4.795 | $CH_2Cl_2$ (Solv.) | 539046412 |
| 4 | 8.762 | *n*-Dodecane (Stand.) | 35617834 |
| 5 | 11.963 | **CAc** | 1153530 |
| 6 | 12.692 | **CI** | 4076805 |
| 7 | 13.777 | $CH_3COOH$ (Solv.) | 47859651 |
| 8 | 19.705 | 1-Phenylethanol (Stand.) | 25810587 |
| 9 | 23.548 | **CA** | 57425083 |

Entry 7




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.072 | **CH** | 15599781 |
| 2 | 4.312 | **CE** | 6099375 |
| 3 | 4.792 | $CH_2Cl_2$ (Solv.) | 544760547 |
| 4 | 8.758 | *n*-Dodecane (Stand.) | 34454803 |
| 5 | 11.977 | **CAc** | 4301103 |
| 6 | 12.675 | **CI** | 813872 |
| 7 | 13.757 | $CH_3COOH$ (Solv.) | 56141915 |
| 8 | 19.705 | 1-Phenylethanol (Stand.) | 27244280 |
| 9 | 23.535 | **CA** | 30588932 |

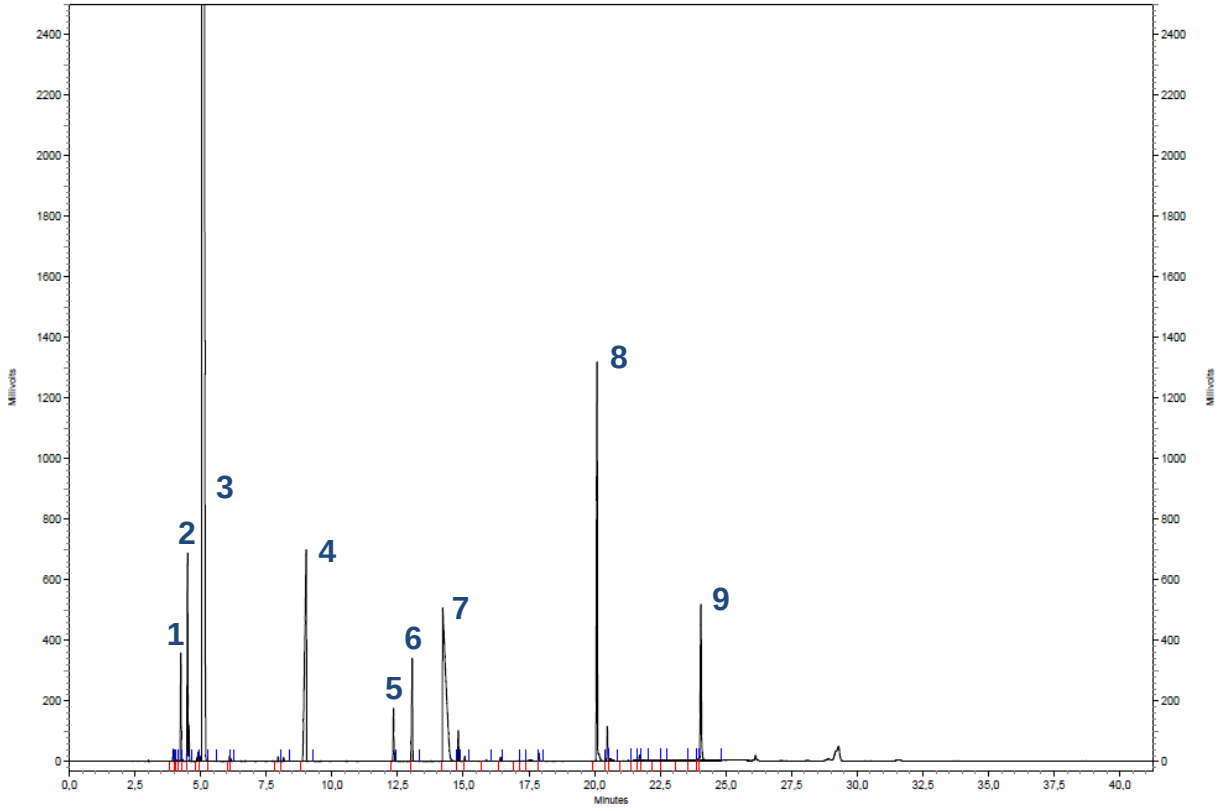
Entry 8




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.070 | **CH** | 7688845 |
| 2 | 4.310 | **CE** | 3263295 |
| 3 | 4.788 | $CH_2Cl_2$ (Solv.) | 552348130 |
| 4 | 8.753 | *n*-Dodecane (Stand.) | 31910631 |
| 5 | 11.962 | **CAc** | 787350 |
| 6 | 12.675 | **CI** | 1050554 |
| 7 | 13.773 | $CH_3COOH$ (Solv.) | 50790928 |
| 8 | 19.705 | 1-Phenylethanol (Stand.) | 27606546 |
| 9 | 23.537 | **CA** | 40727922 |

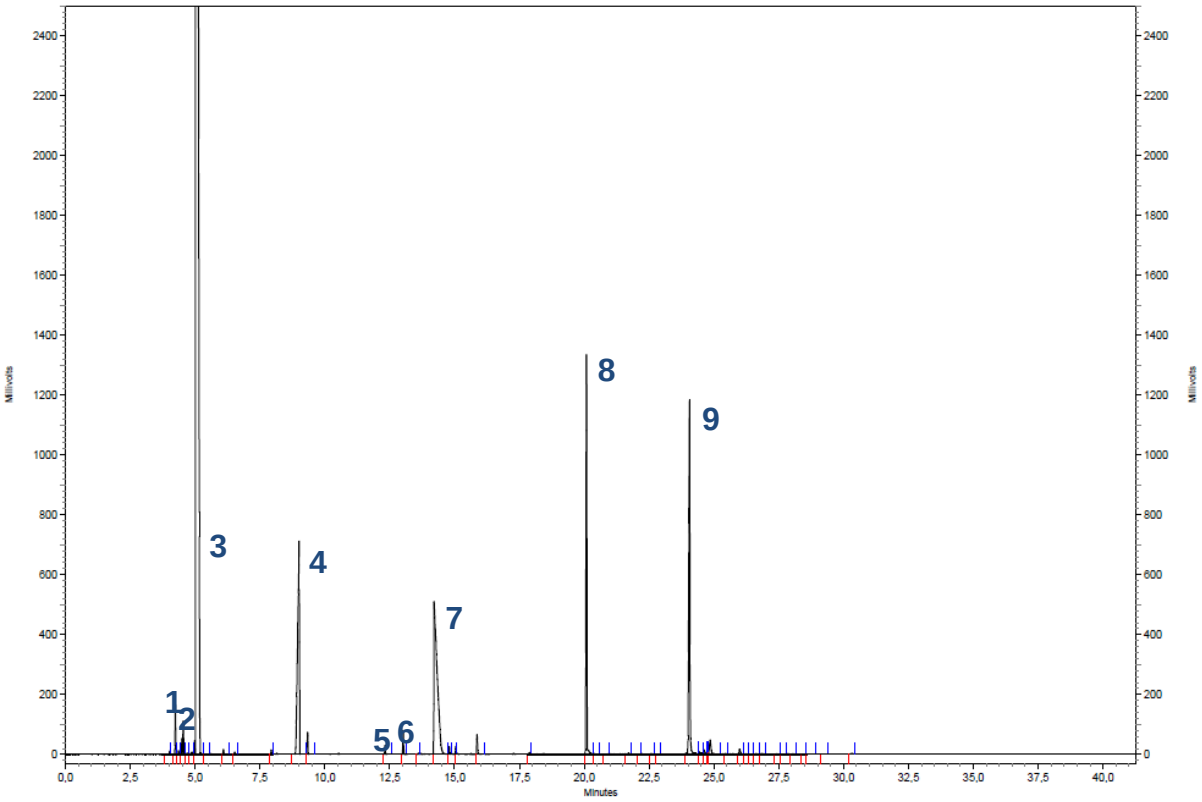
## S3.5 Gaschromatograms to Table S2.5

Entry 1



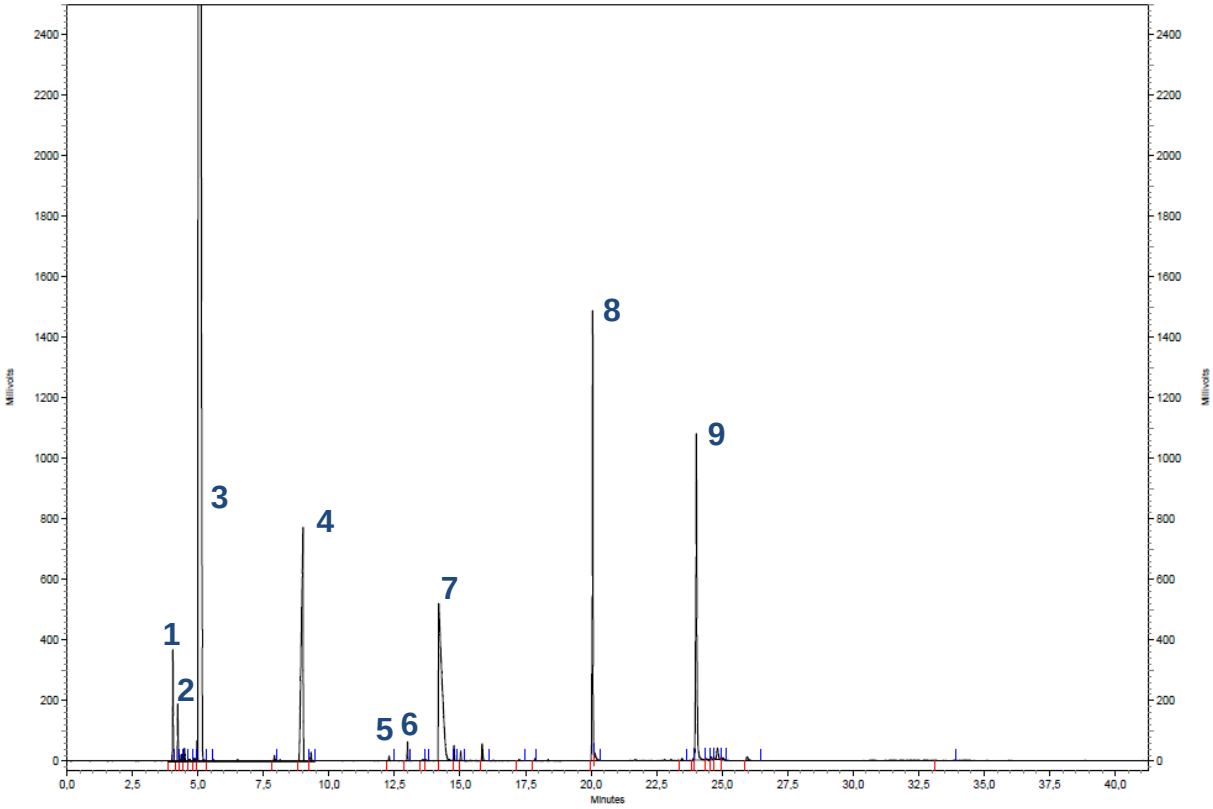

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.245 | **CH** | 4755632 |
| 2 | 4.502 | **CE** | 12208263 |
| 3 | 5.027 | $CH_2Cl_2$ (Solv.) | 538971362 |
| 4 | 9.023 | *n*-Dodecane (Stand.) | 30517966 |
| 5 | 12.347 | **CAc** | 3354729 |
| 6 | 13.058 | **CI** | 7869117 |
| 7 | 14.218 | $CH_3COOH$ (Solv.) | 44047706 |
| 8 | 20.092 | 1-Phenylethanol (Stand.) | 26530706 |
| 9 | 24.047 | **CA** | 13544121 |

Entry 2



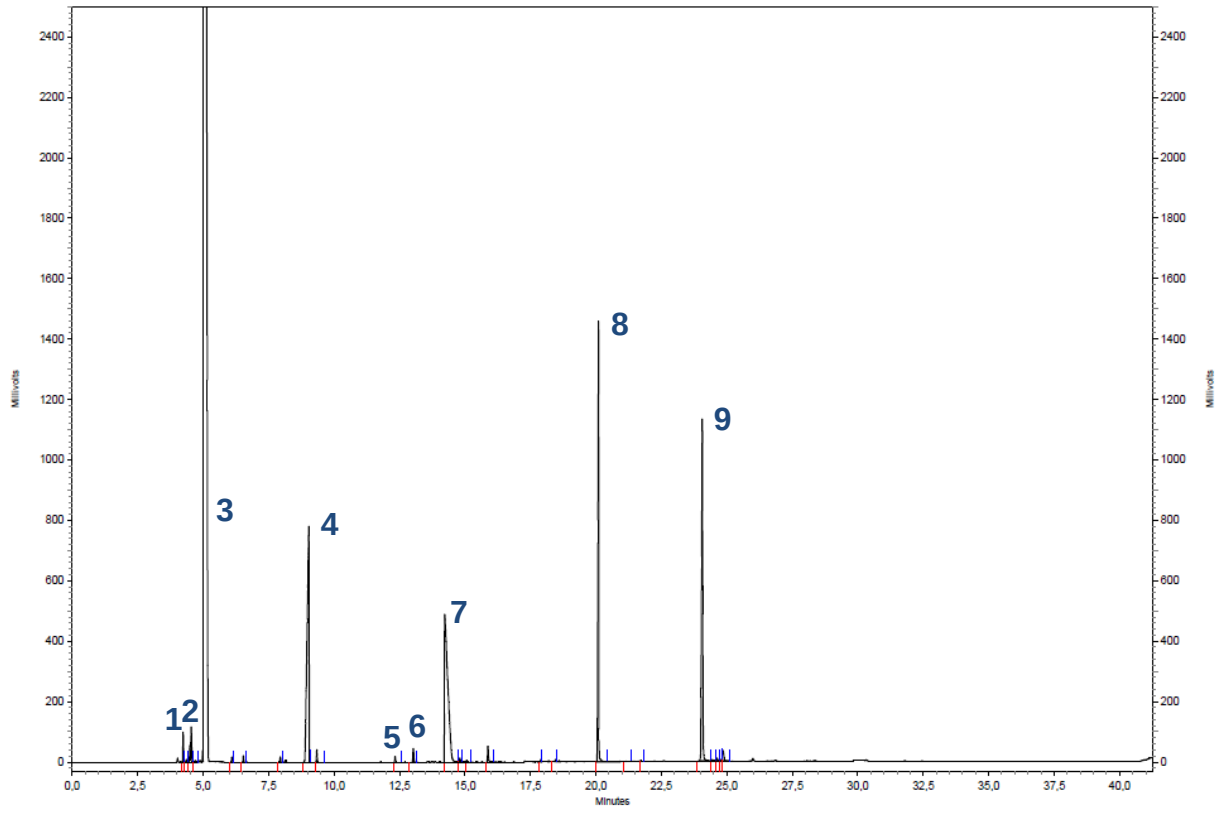

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.237 | **CH** | 2212263 |
| 2 | 4.543 | **CE** | 2549632 |
| 3 | 5.018 | $CH_2Cl_2$ (Solv.) | 523505336 |
| 4 | 9.013 | *n*-Dodecane (Stand.) | 31575593 |
| 5 | 12.322 | **CAc** | 543484 |
| 6 | 13.022 | **CI** | 1491064 |
| 7 | 14.212 | $CH_3COOH$ (Solv.) | 44837575 |
| 8 | 20.087 | 1-Phenylethanol (Stand.) | 26305575 |
| 9 | 24.058 | **CA** | 34121033 |

Entry 3



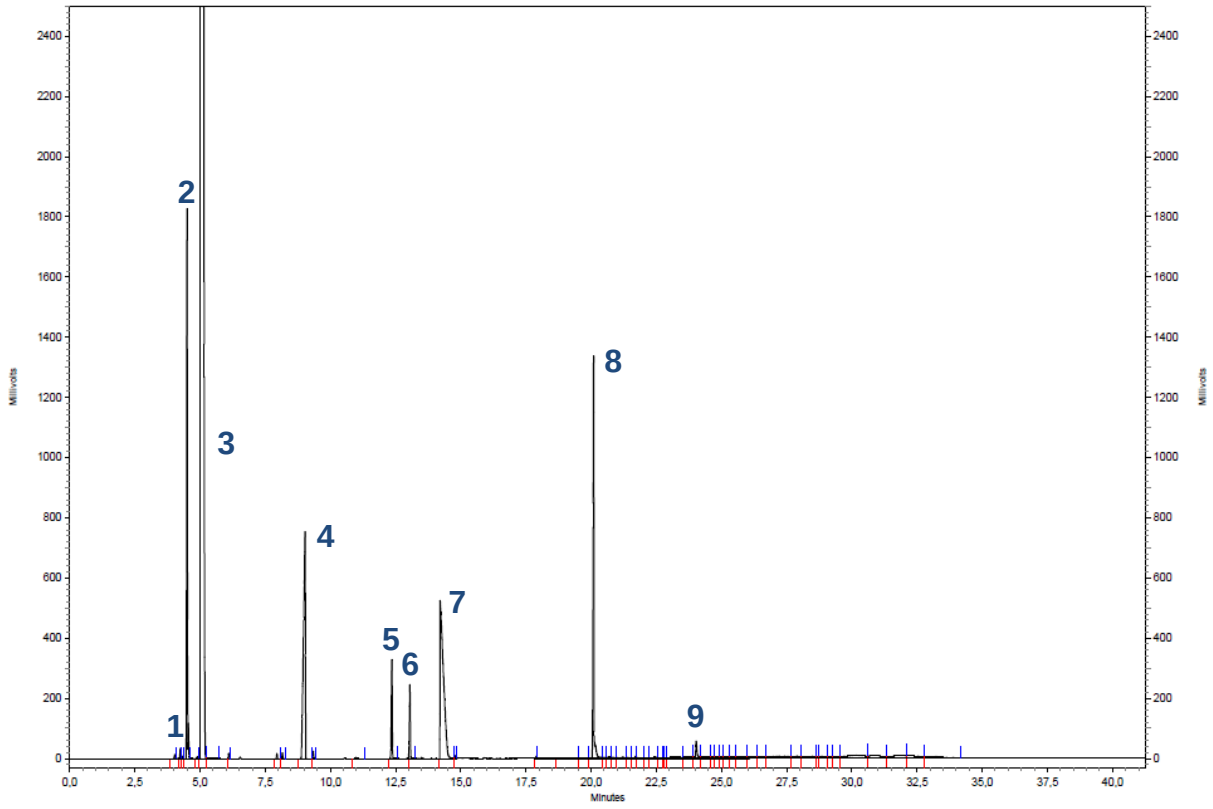

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.230 | **CH** | 2536833 |
| 2 | 4.485 | **CE** | 677684 |
| 3 | 5.012 | $CH_2Cl_2$ (Solv.) | 516660834 |
| 4 | 9.012 | *n*-Dodecane (Stand.) | 36570073 |
| 5 | 12.295 | **CAc** | 275615 |
| 6 | 12.998 | **CI** | 1168625 |
| 7 | 14.185 | $CH_3COOH$ (Solv.) | 45849429 |
| 8 | 20.062 | 1-Phenylethanol (Stand.) | 29227806 |
| 9 | 24.018 | **CA** | 33012551 |

Entry 4



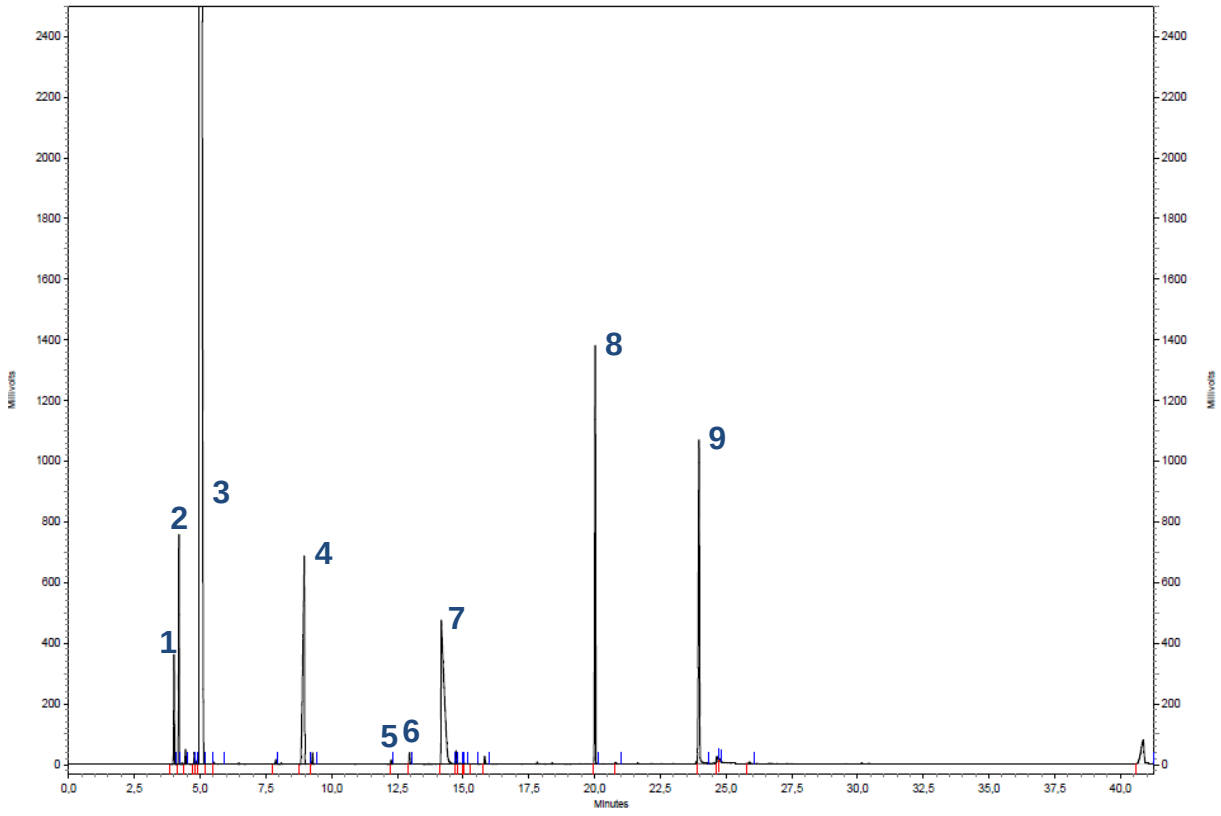

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.242 | **CH** | 1300713 |
| 2 | 4.550 | **CE** | 2590549 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 9.037 | *n*-Dodecane (Stand.) | 37018450 |
| 5 | 12.333 | **CAc** | 326345 |
| 6 | 13.030 | **CI** | 821294 |
| 7 | 14.228 | $CH_3COOH$ (Solv.) | 41566839 |
| 8 | 20.098 | 1-Phenylethanol (Stand.) | 29190086 |
| 9 | 24.063 | **CA** | 32288328 |

Entry 5



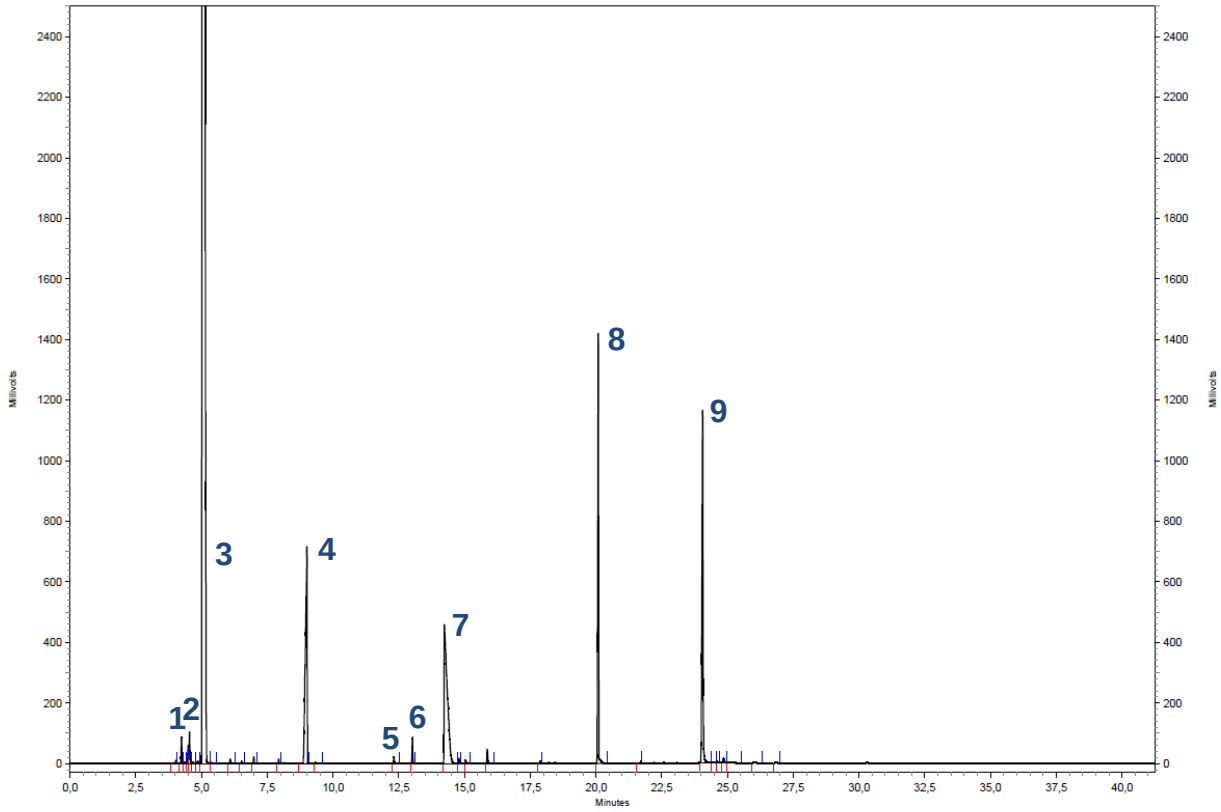

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.243 | **CH** | 463012 |
| 2 | 4.502 | **CE** | 29574068 |
| 3 | 5.027 | $CH_2Cl_2$ (Solv.) | 534155611 |
| 4 | 9.033 | *n*-Dodecane (Stand.) | 35038431 |
| 5 | 12.358 | **CAc** | 6954729 |
| 6 | 13.052 | **CI** | 5116405 |
| 7 | 14.210 | $CH_3COOH$ (Solv.) | 47295142 |
| 8 | 20.093 | 1-Phenylethanol (Stand.) | 28523371 |
| 9 | 24.033 | **CA** | 2112362 |

Entry 6



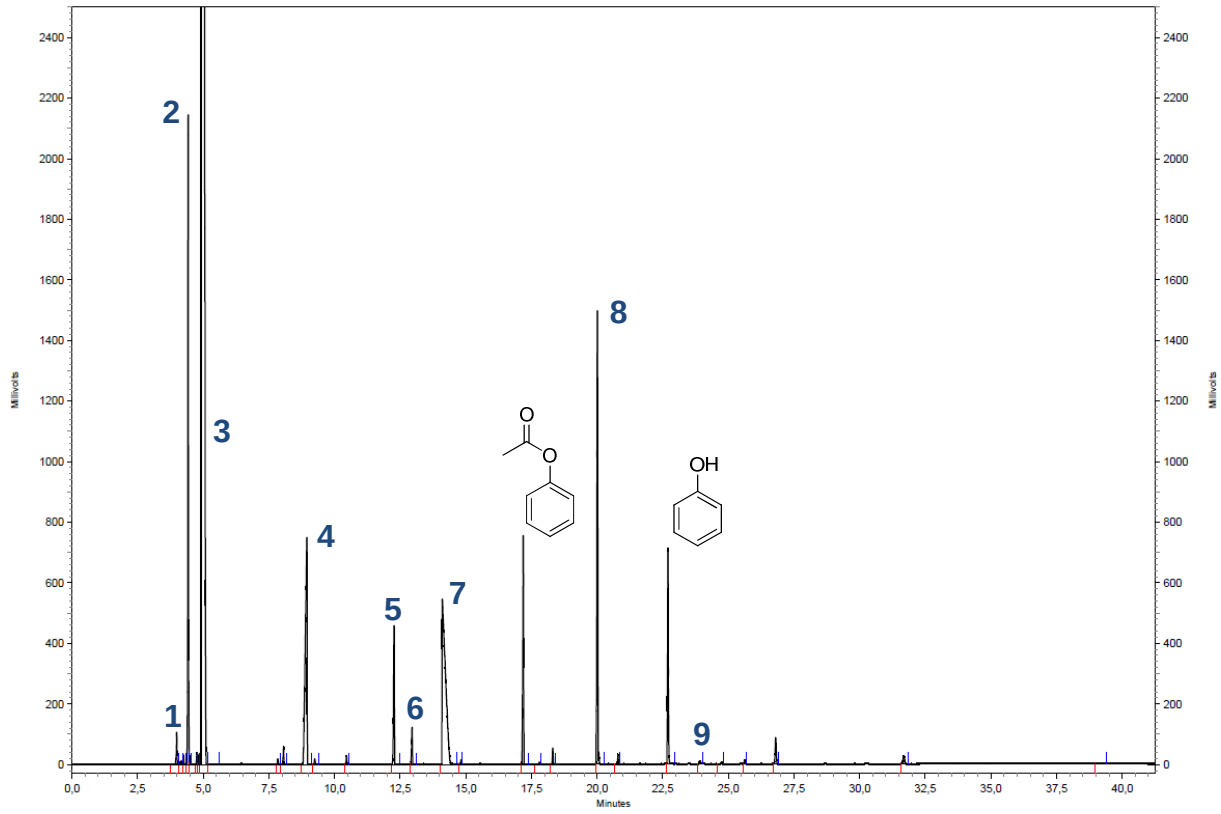

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.192 | **CH** | 9516376 |
| 2 | 4.445 | **CE** | 736403 |
| 3 | 4.970 | $CH_2Cl_2$ (Solv.) | 481626659 |
| 4 | 8.968 | *n*-Dodecane (Stand.) | 29571531 |
| 5 | 12.267 | **CAc** | 227325 |
| 6 | 12.967 | **CI** | 669337 |
| 7 | 14.170 | $CH_3COOH$ (Solv.) | 38218067 |
| 8 | 20.027 | 1-Phenylethanol (Stand.) | 25971566 |
| 9 | 23.975 | **CA** | 27930573 |

Entry 7




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.238 | **CH** | 1331223 |
| 2 | 4.543 | **CE** | 1804530 |
| 3 | 5.018 | $CH_2Cl_2$ (Solv.) | 545775329 |
| 4 | 9.012 | *n*-Dodecane (Stand.) | 31634188 |
| 5 | 12.318 | **CAc** | 376806 |
| 6 | 13.020 | **CI** | 1531813 |
| 7 | 14.233 | $CH_3COOH$ (Solv.) | 37546431 |
| 8 | 20.085 | 1-Phenylethanol (Stand.) | 27903054 |
| 9 | 24.057 | **CA** | 32949156 |

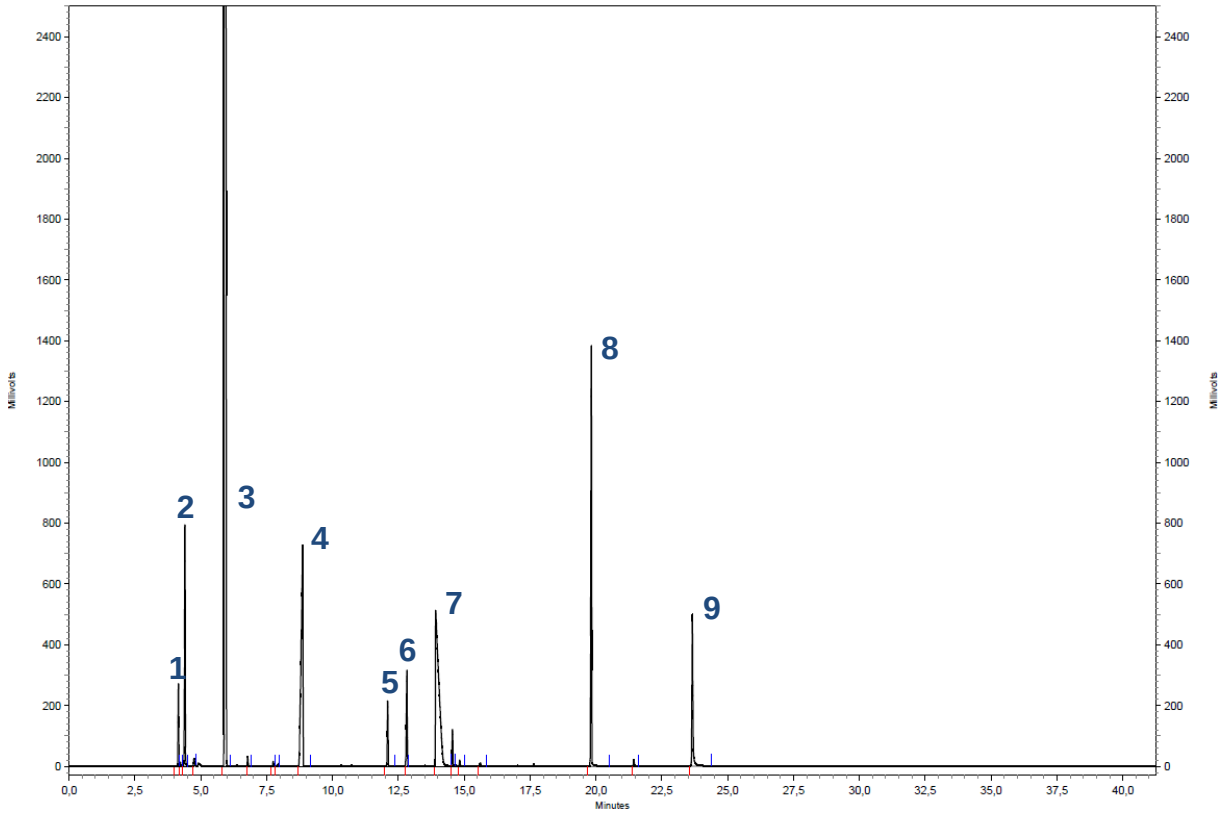
Entry 8




Phenol and acetic acid phenyl ester derive from ligand decomposition under reaction conditions.

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.168 | **CH** | 262557 |
| 2 | 4.422 | **CE** | 32763520 |
| 3 | 4.932 | $CH_2Cl_2$ (Solv.) | 553455134 |
| 4 | 8.952 | *n*-Dodecane (Stand.) | 34844775 |
| 5 | 12.270 | **CAc** | 9424417 |
| 6 | 12.952 | **CI** | 2149744 |
| 7 | 14.107 | $CH_3COOH$ (Solv.) | 48125055 |
| 8 | 20.013 | 1-Phenylethanol (Stand.) | 29333737 |
| 9 | 23.935 | **CA** | 356222 |

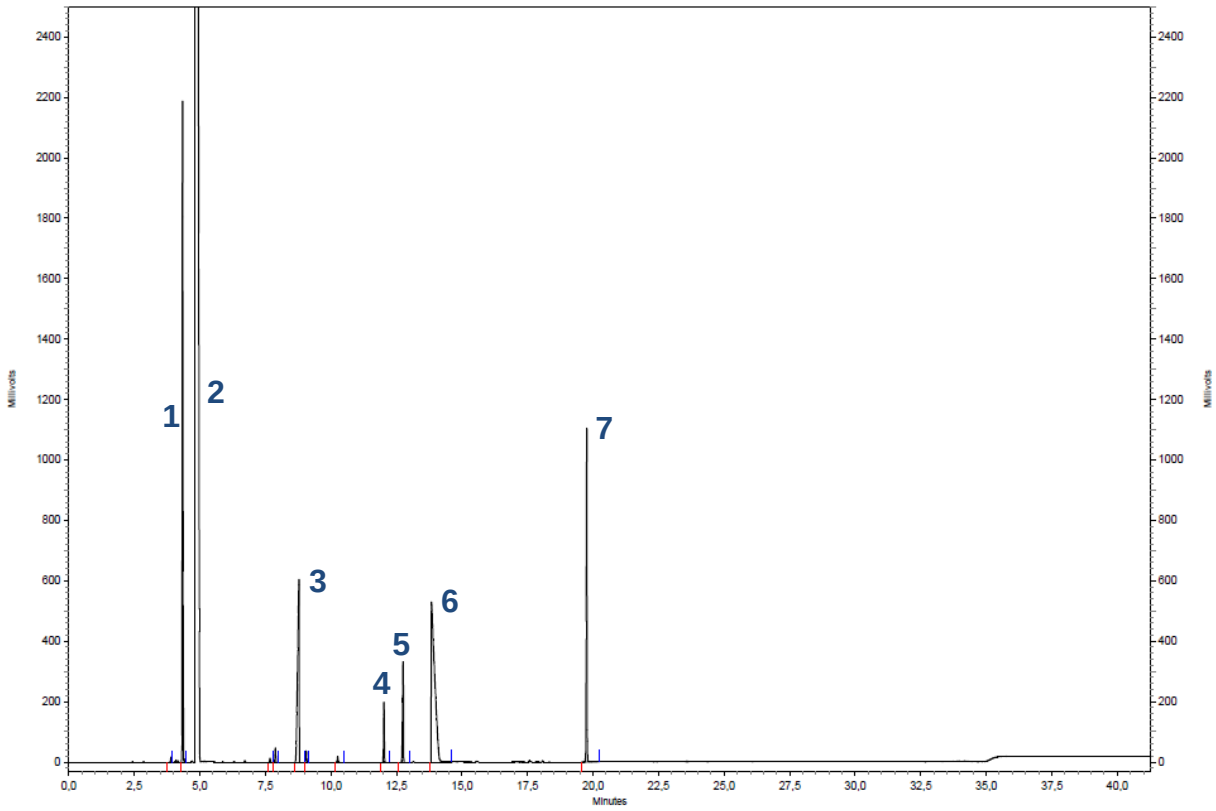
Entry 9




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.148 | **CH** | 3958223 |
| 2 | 4.393 | **CE** | 13722225 |
| 3[a] | 5.892 | $CDCl_3$ (Solv.) | 386368933 |
| 4 | 8.872 | *n*-Dodecane (Stand.) | 33464320 |
| 5 | 12.095 | **CAc** | 3811090 |
| 6 | 12.825 | **CI** | 6818725 |
| 7 | 13.913 | $CH_3COOH$ (Solv.) | 46197680 |
| 8 | 19.825 | 1-Phenylethanol (Stand.) | 26247824 |
| 9 | 23.663 | **CA** | 13232421 |

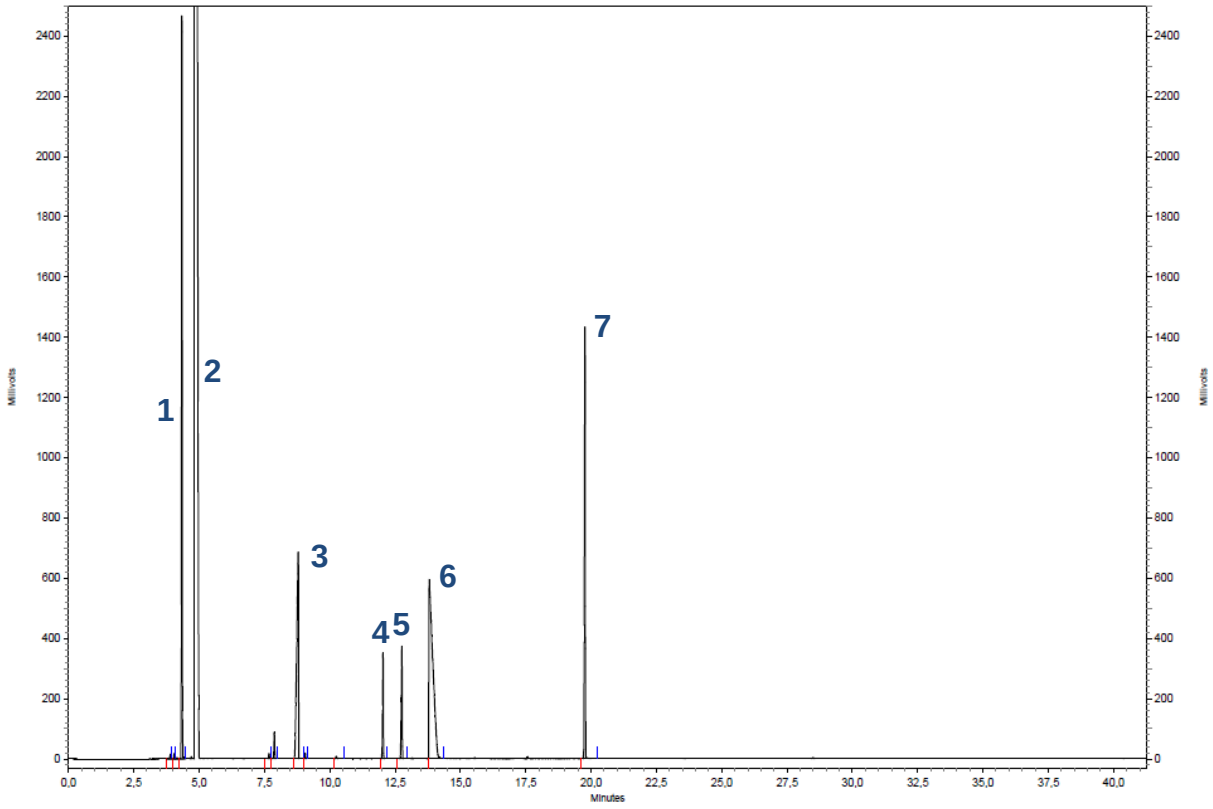
[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

Entry 10



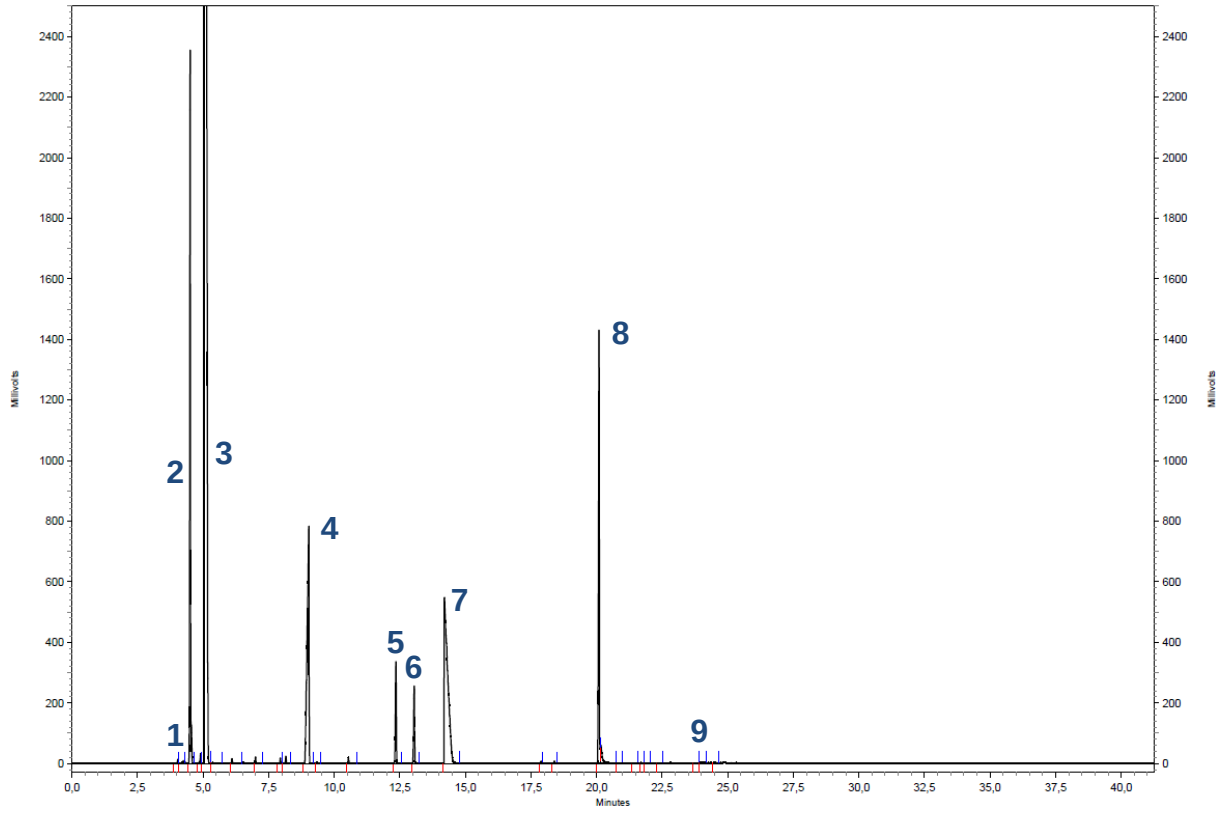

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.345 | **CE** | 32798302 |
| 2 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 3 | 8.783 | *n*-Dodecane (Stand.) | 23821426 |
| 4 | 12.027 | **CAc** | 3374657 |
| 5 | 12.757 | **Cl** | 7129707 |
| 6 | 13.835 | $CH_3COOH$ (Solv.) | 48159978 |
| 7 | 19.758 | 1-Phenylethanol (Stand.) | 19839278 |

Entry 11



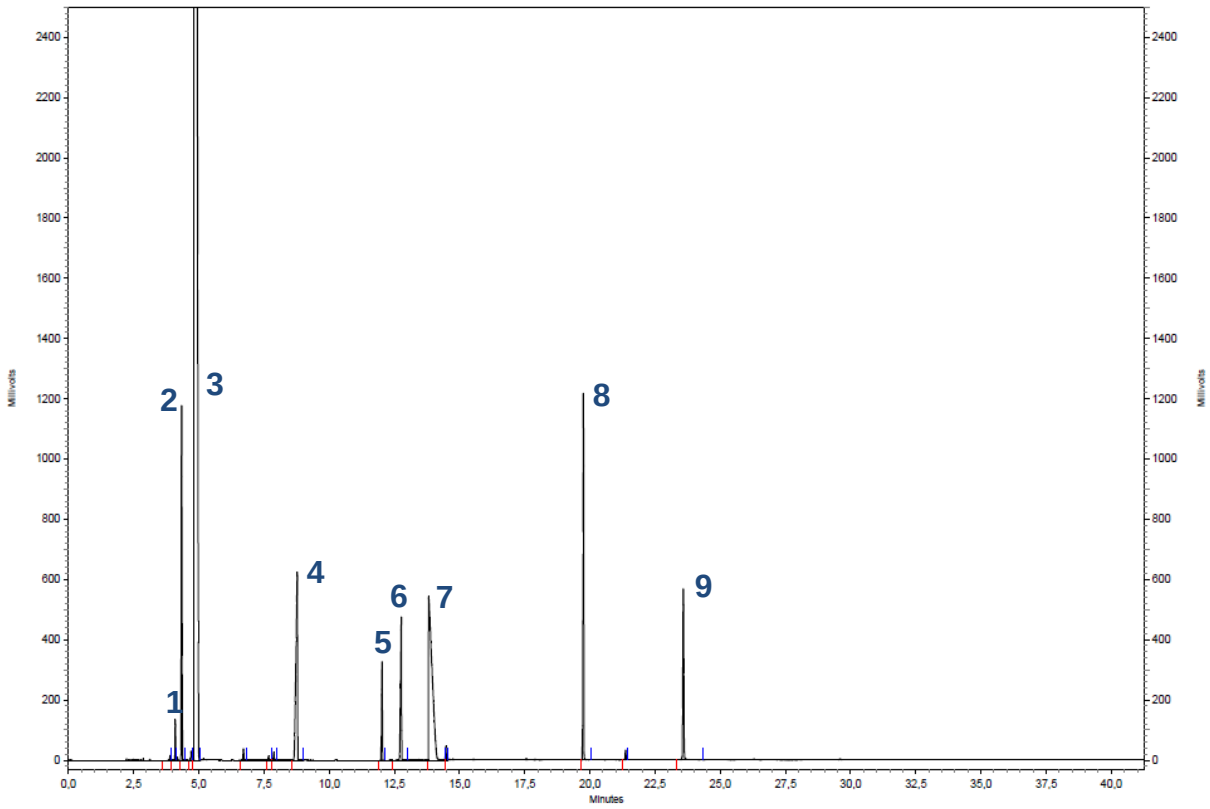

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.338 | **CE** | 36838685 |
| 2 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 3 | 8.795 | *n*-Dodecane (Stand.) | 30001100 |
| 4 | 12.038 | **CAc** | 6531078 |
| 5 | 12.762 | **Cl** | 8435655 |
| 6 | 13.803 | $CH_3COOH$ (Solv.) | 59775994 |
| 7 | 19.765 | 1-Phenylethanol (Stand.) | 27215247 |

Entry 12



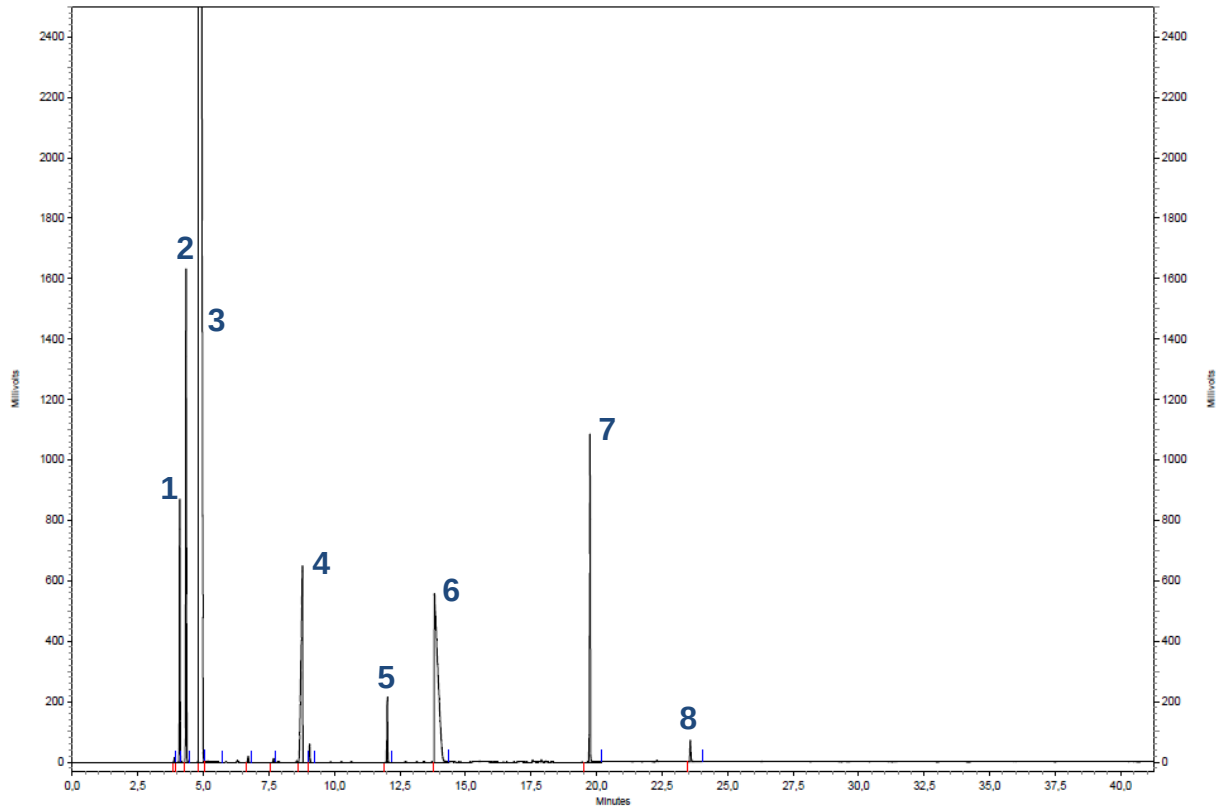

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.245 | **CH** | 182931 |
| 2 | 4.503 | **CE** | 38260389 |
| 3 | 5.028 | $CH_2Cl_2$ (Solv.) | 527915450 |
| 4 | 9.032 | *n*-Dodecane (Stand.) | 37414196 |
| 5 | 12.352 | **CAc** | 7412775 |
| 6 | 13.048 | **CI** | 5515266 |
| 7 | 14.200 | $CH_3COOH$ (Solv.) | 50794739 |
| 8 | 20.093 | 1-Phenylethanol (Stand.) | 28896099 |
| 9 | 24.042 | **CA** | 213664 |

Entry 13




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.102 | **CH** | 1704673 |
| 2 | 4.345 | **CE** | 17177792 |
| 3 | 4.828 | $CH_2Cl_2$ (Solv.) | 564983185 |
| 4 | 8.782 | *n*-Dodecane (Stand.) | 25360706 |
| 5 | 12.030 | **CAc** | 6017472 |
| 6 | 12.765 | **CI** | 11665187 |
| 7 | 13.820 | $CH_3COOH$ (Solv.) | 50357720 |
| 8 | 19.753 | 1-Phenylethanol (Stand.) | 21901588 |
| 9 | 23.585 | **CA** | 12788526 |

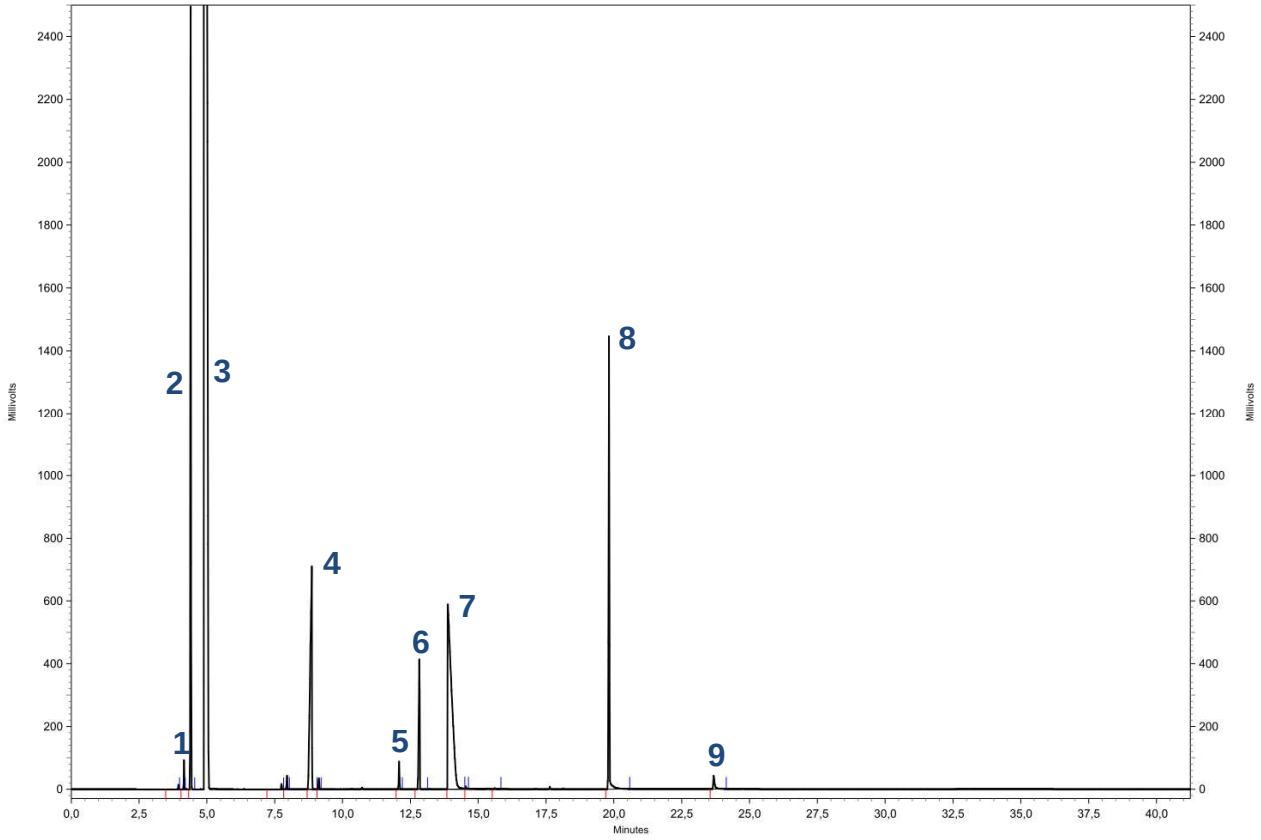
Entry 14




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.103 | **CH** | 12078281 |
| 2 | 4.345 | **CE** | 26052188 |
| 3 | 4.833 | $CH_2Cl_2$ (Solv.) | 543849939 |
| 4 | 8.783 | *n*-Dodecane (Stand.) | 26618126 |
| 5 | 12.022 | **CAc** | 3729234 |
| 6 | 13.822 | $CH_3COOH$ (Solv.) | 52073206 |
| 7 | 19.752 | 1-Phenylethanol (Stand.) | 19140448 |
| 8 | 23.578 | **CA** | 1678163 |

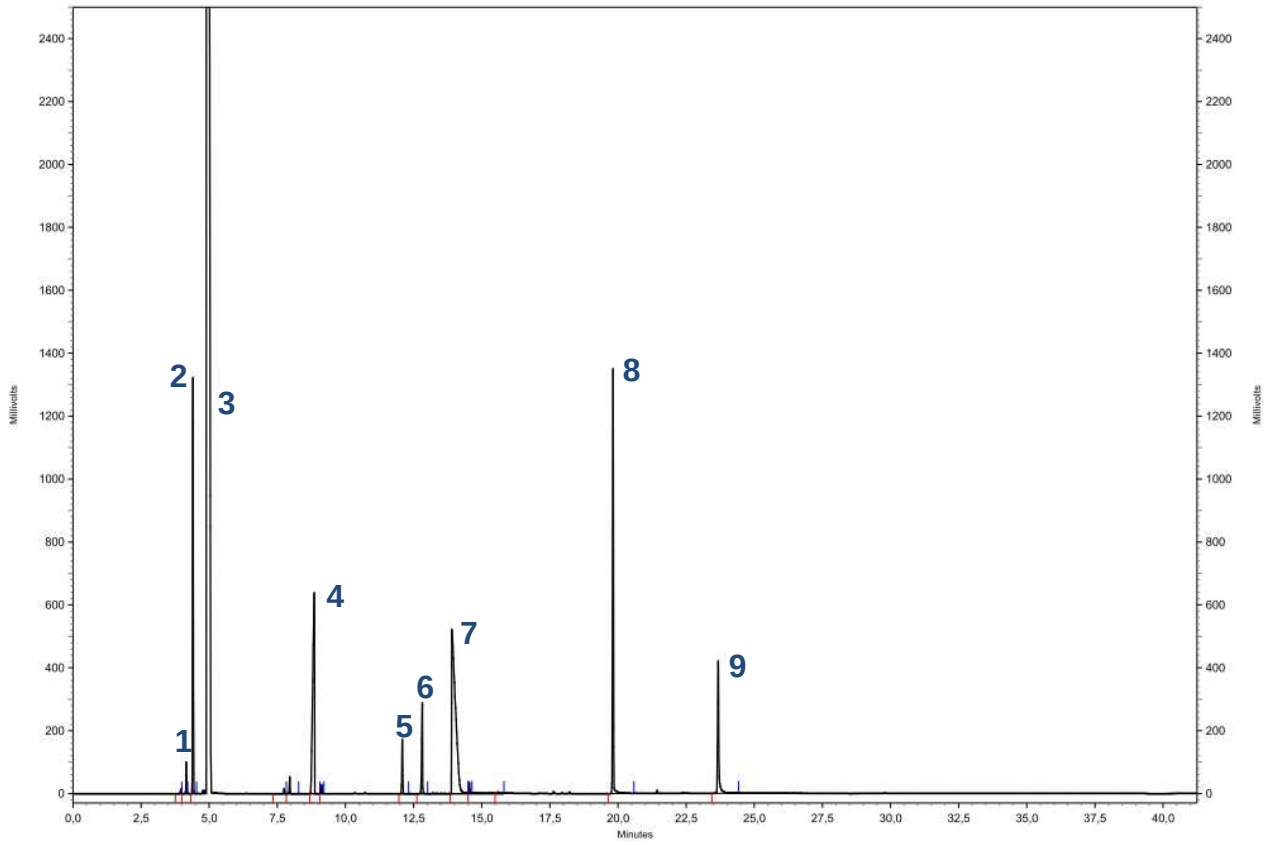
## S3.6 Gaschromatograms to Table S2.6

Entry 1



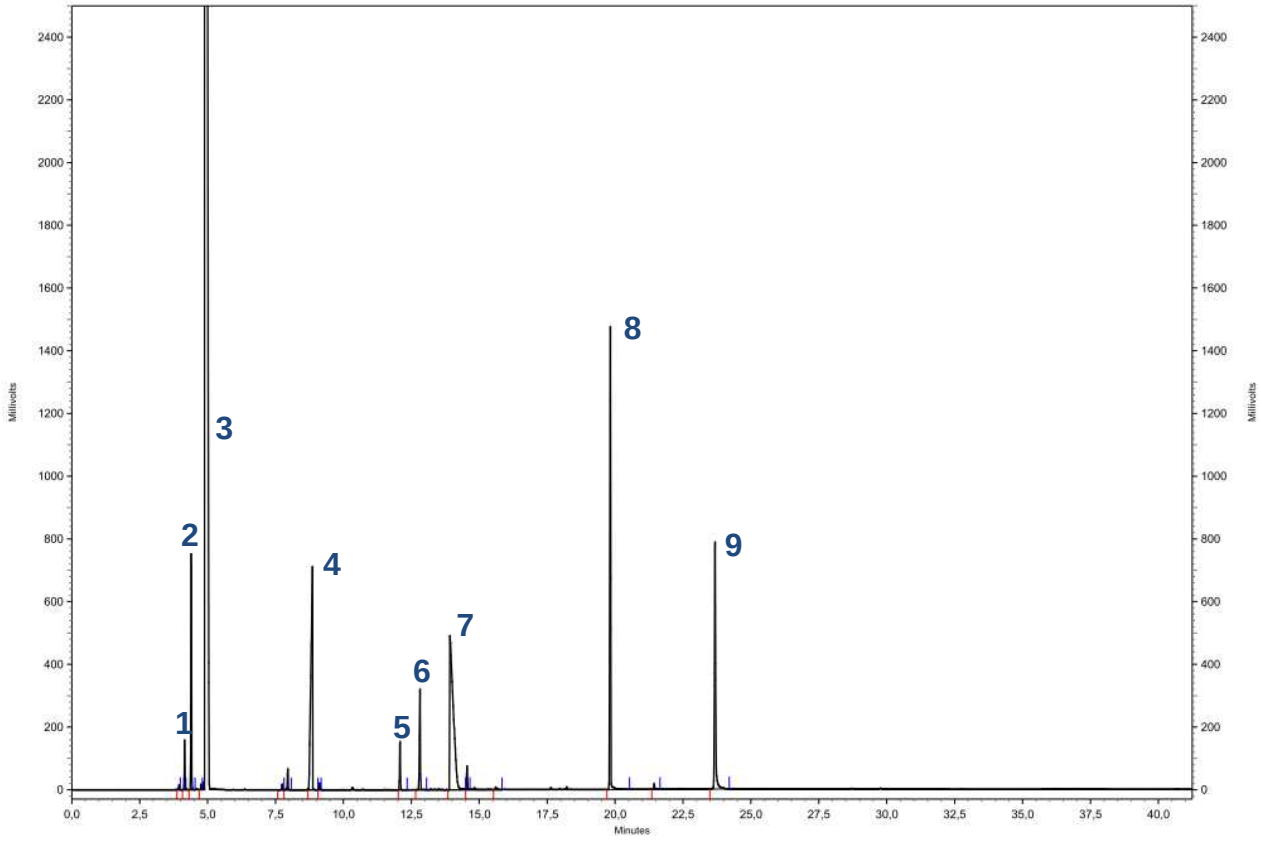

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.157 | **CH** | 1253709 |
| 2 | 4.403 | **CE** | 38041907 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.868 | *n*-Dodecane (Stand.) | 32513740 |
| 5 | 12.085 | **CAc** | 1519053 |
| 6 | 12.832 | **CI** | 9855061 |
| 7 | 13.880 | $CH_3COOH$ (Solv.) | 59349994 |
| 8 | 19.823 | 1-Phenylethanol (Stand.) | 29204886 |
| 9 | 23.680 | **CA** | 1587142 |

Entry 2



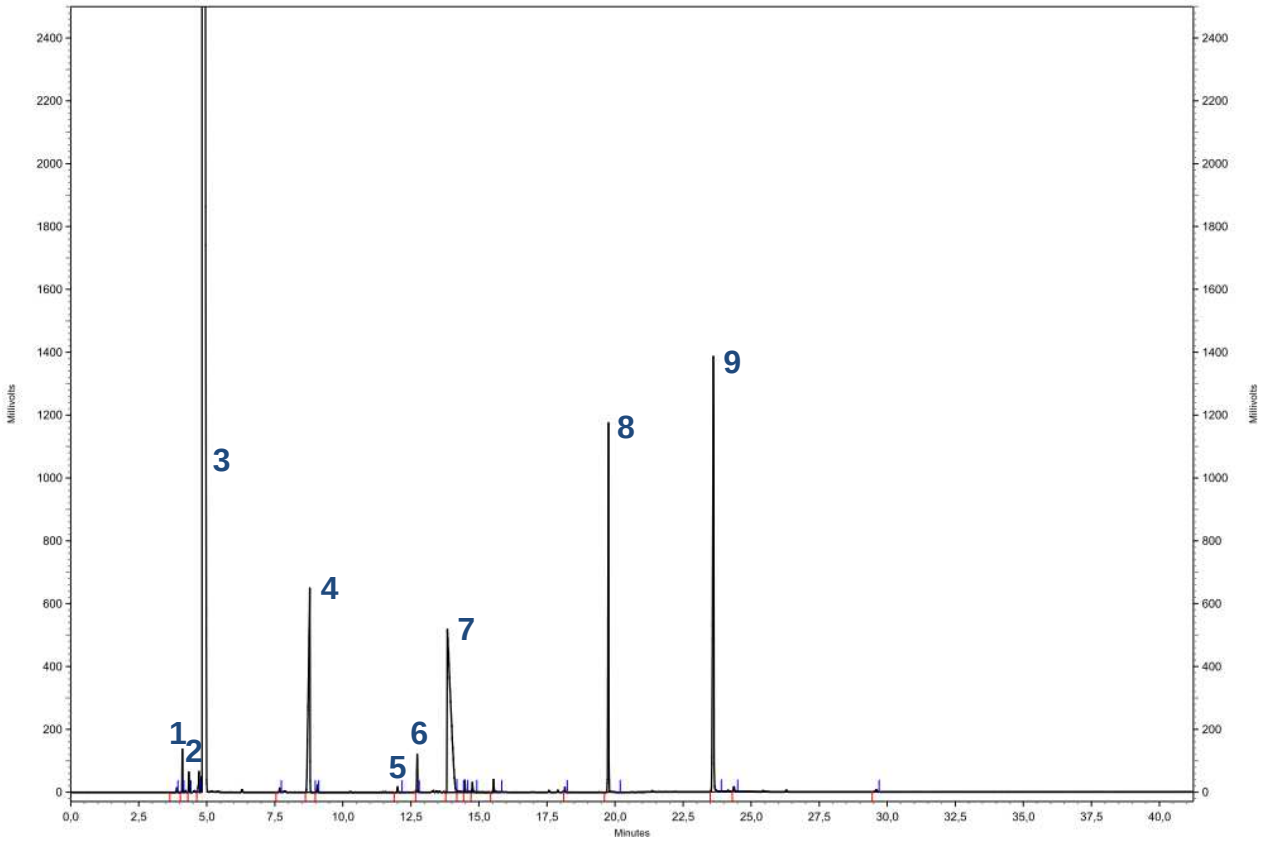

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.158 | **CH** | 1360010 |
| 2 | 4.403 | **CE** | 20203678 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.857 | *n*-Dodecane (Stand.) | 27430014 |
| 5 | 12.085 | **CAc** | 3046430 |
| 6 | 12.818 | **CI** | 6202747 |
| 7 | 13.907 | $CH_3COOH$ (Solv.) | 48552998 |
| 8 | 19.820 | 1-Phenylethanol (Stand.) | 26169017 |
| 9 | 23.675 | **CA** | 12613377 |

Entry 3



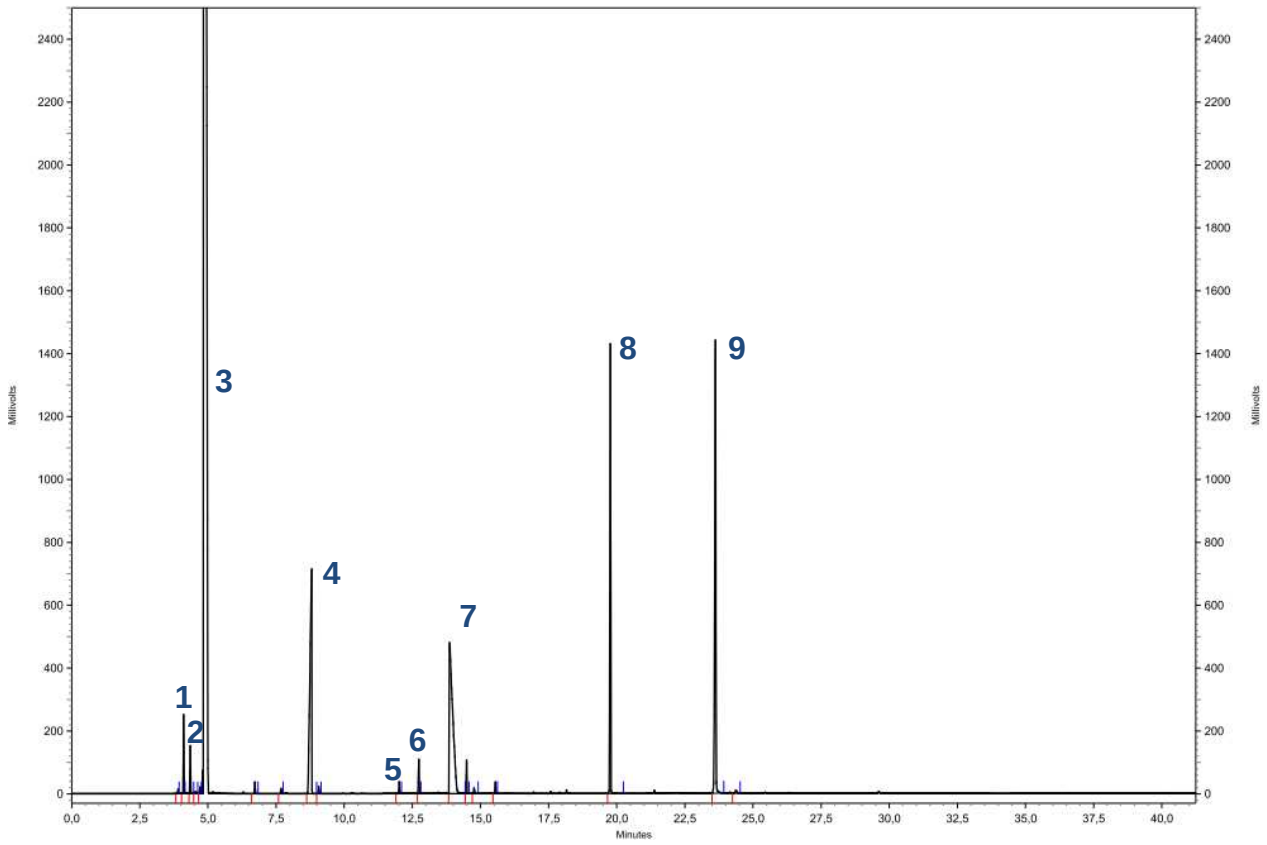

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.152 | **CH** | 2035683 |
| 2 | 4.397 | **CE** | 11078406 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.862 | *n*-Dodecane (Stand.) | 30954072 |
| 5 | 12.082 | **CAc** | 2552132 |
| 6 | 12.822 | **CI** | 6986287 |
| 7 | 13.922 | $CH_3COOH$ (Solv.) | 43032339 |
| 8 | 19.827 | 1-Phenylethanol (Stand.) | 29246822 |
| 9 | 23.683 | **CA** | 21673896 |

Entry 4



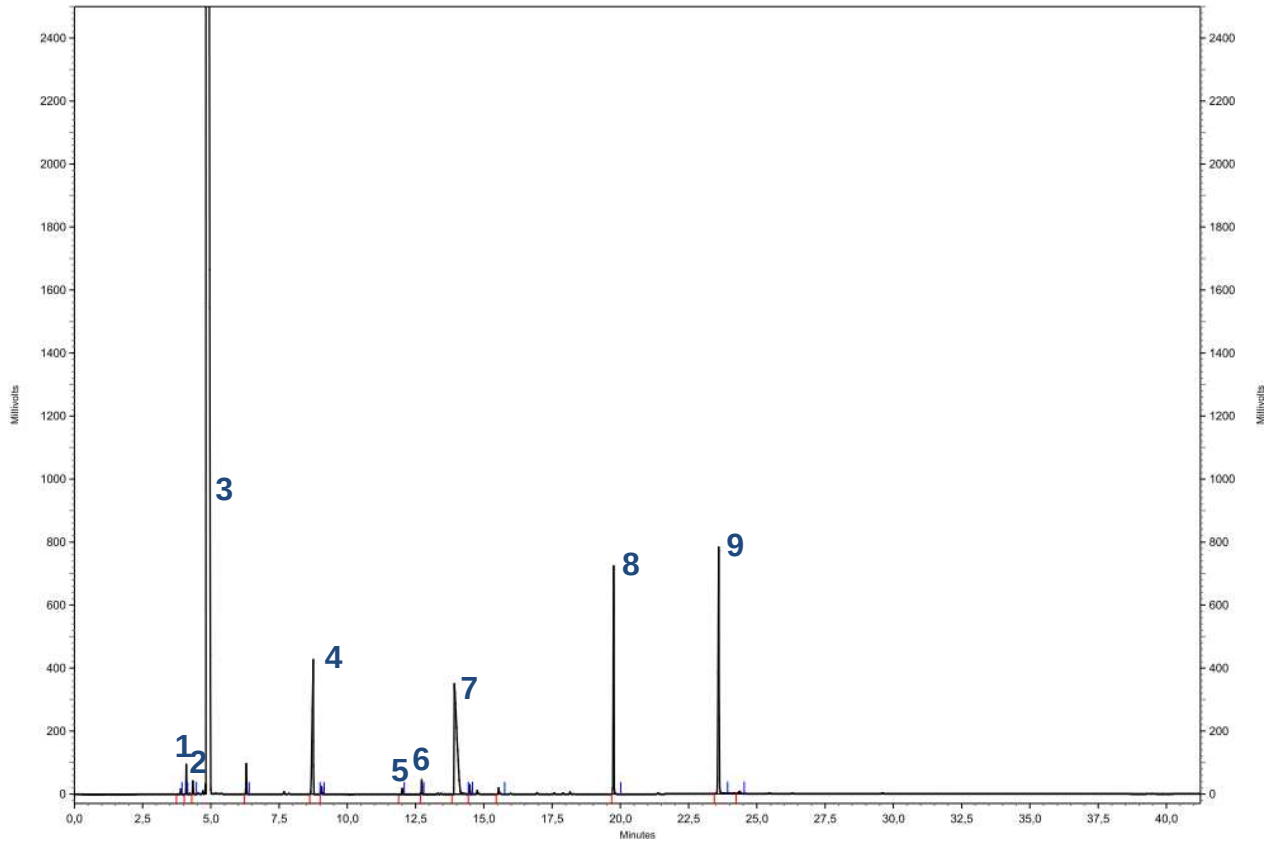

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.105 | **CH** | 1755261 |
| 2 | 4.347 | **CE** | 954342 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.788 | *n*-Dodecane (Stand.) | 26385371 |
| 5 | 12.012 | **CAc** | 280721 |
| 6 | 12.735 | **CI** | 2112889 |
| 7 | 13.838 | $CH_3COOH$ (Solv.) | 46449859 |
| 8 | 19.758 | 1-Phenylethanol (Stand.) | 20877781 |
| 9 | 23.612 | **CA** | 37072381 |

Entry 5



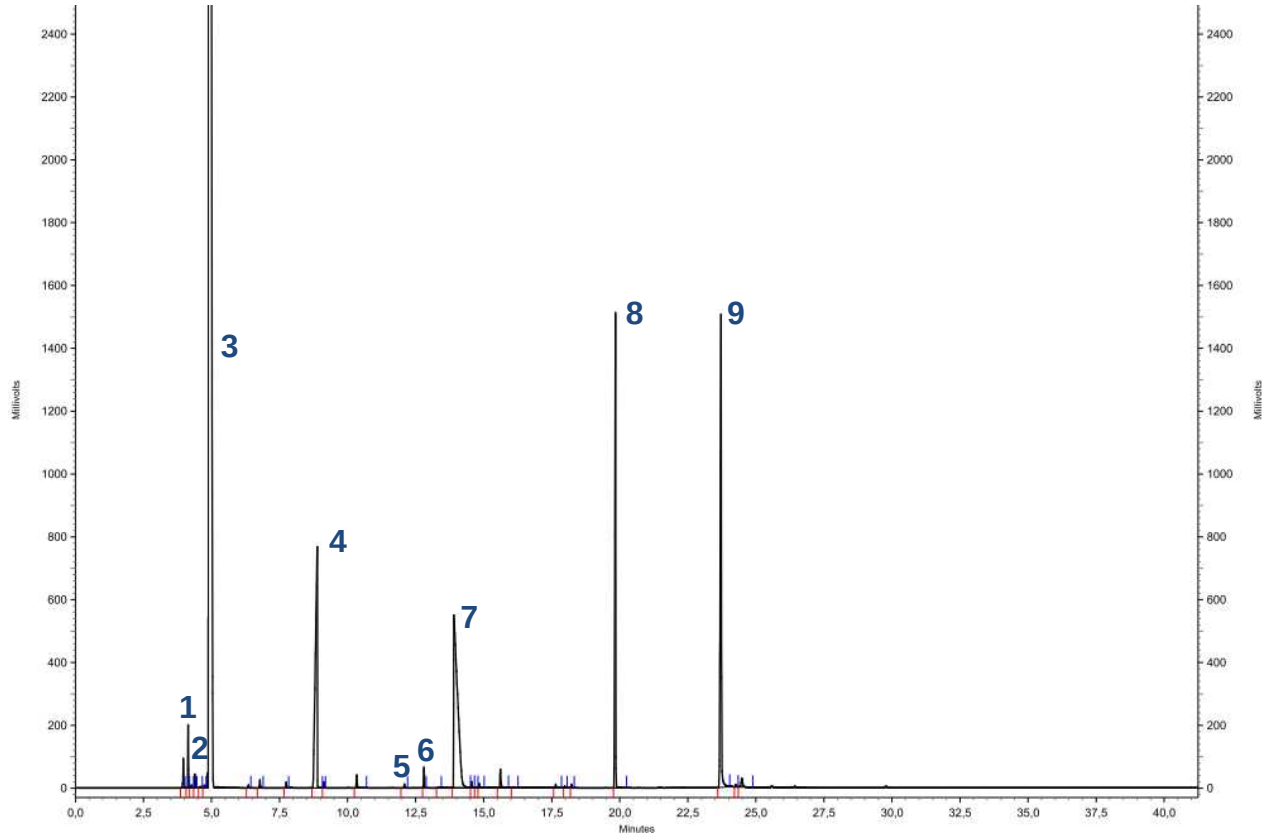

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.108 | **CH** | 3238297 |
| 2 | 4.352 | **CE** | 2280269 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.807 | *n*-Dodecane (Stand.) | 32192057 |
| 5 | 12.018 | **CAc** | 629956 |
| 6 | 12.738 | **CI** | 1930831 |
| 7 | 13.865 | $CH_3COOH$ (Solv.) | 40637845 |
| 8 | 19.768 | 1-Phenylethanol (Stand.) | 26679121 |
| 9 | 23.623 | **CA** | 38750777 |

Entry 6



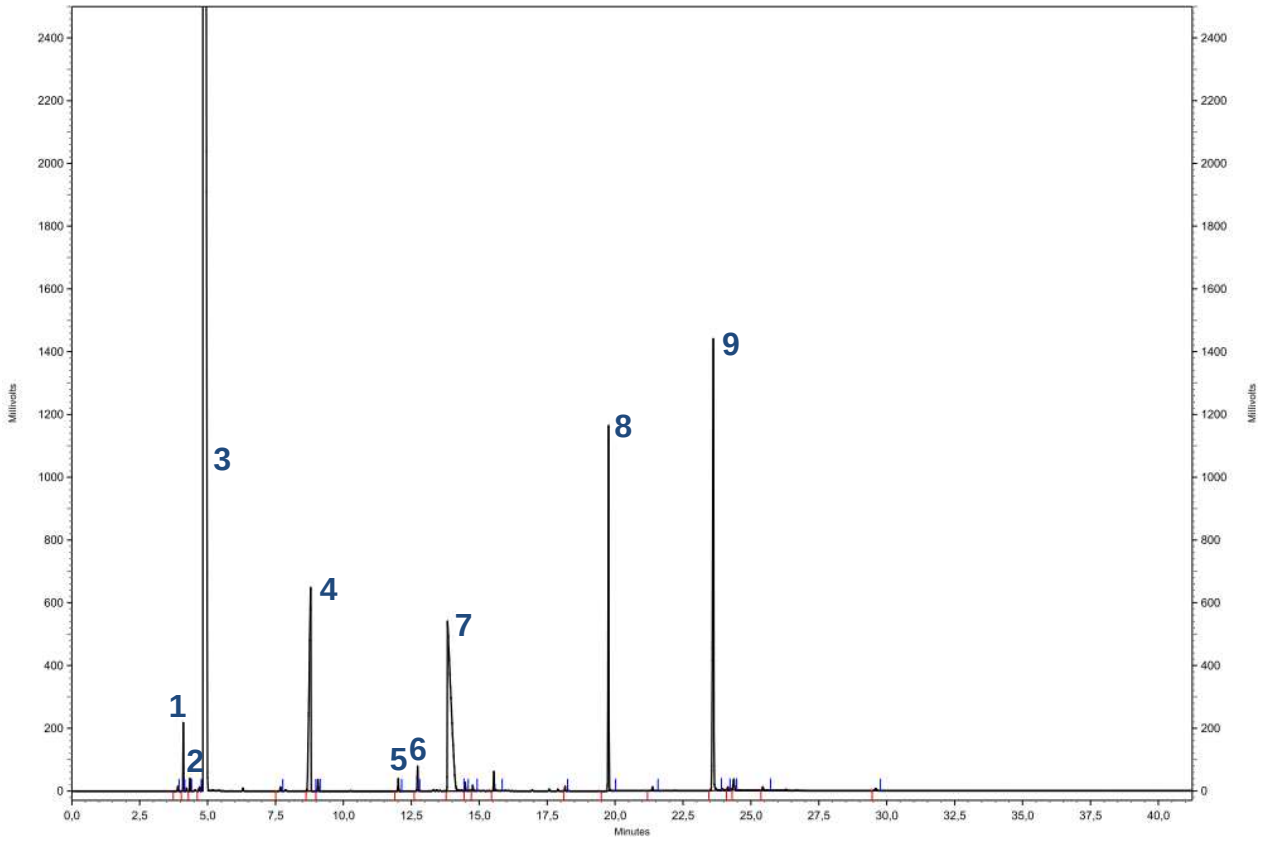

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.100 | **CH** | 1214717 |
| 2 | 4.343 | **CE** | 641059 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.750 | *n*-Dodecane (Stand.) | 12656494 |
| 5 | 12.010 | **CAc** | 298821 |
| 6 | 12.727 | **CI** | 793040 |
| 7 | 13.922 | $CH_3COOH$ (Solv.) | 23583787 |
| 8 | 19.753 | 1-Phenylethanol (Stand.) | 12066681 |
| 9 | 23.602 | **CA** | 18100772 |

Entry 7




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.145 | **CH** | 2645996 |
| 2 | 4.390 | **CE** | 690070 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.887 | *n*-Dodecane (Stand.) | 38410164 |
| 5 | 12.088 | **CAc** | 206428 |
| 6 | 12.805 | **CI** | 1165824 |
| 7 | 13.907 | $CH_3COOH$ (Solv.) | 52427679 |
| 8 | 19.838 | 1-Phenylethanol (Stand.) | 29284032 |
| 9 | 23.720 | **CA** | 43379657 |

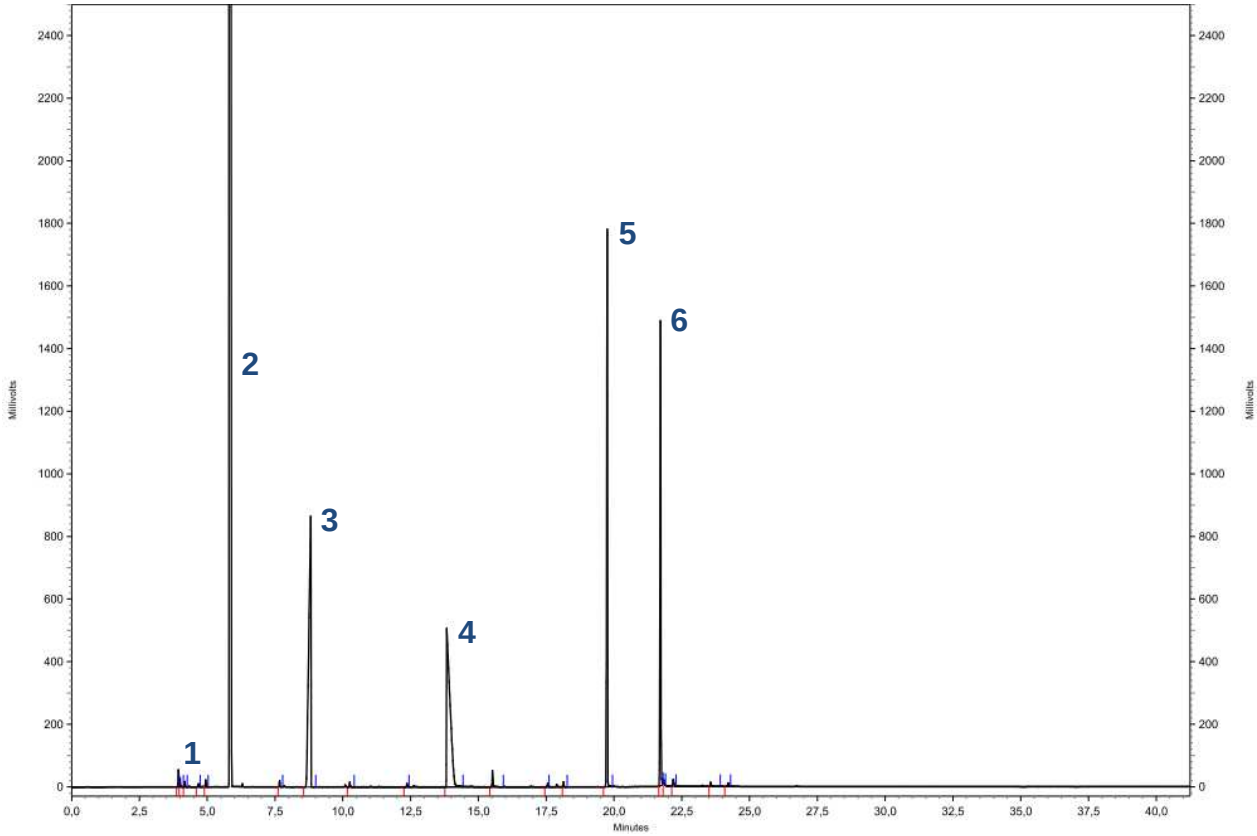
Entry 8




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.107 | **CH** | 2784368 |
| 2 | 4.348 | **CE** | 601856 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.797 | *n*-Dodecane (Stand.) | 27777498 |
| 5 | 12.017 | **CAc** | 634682 |
| 6 | 12.733 | **CI** | 1348814 |
| 7 | 13.832 | $CH_3COOH$ (Solv.) | 50006752 |
| 8 | 19.762 | 1-Phenylethanol (Stand.) | 20877959 |
| 9 | 23.617 | **CA** | 38595273 |

## S3.7 Gaschromatograms to Table S2.7

Entry 2




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 3.997 | **Cyclopentene** | 497410 |
| 2[a] | *cutted* | $CD_2Cl_3$ (Solv.) | -- |
| 3 | 8.817 | *n*-Dodecane (Stand.) | 44779679 |
| 4 | 13.832 | $CH_3COOH$ (Solv.) | 44799715 |
| 5 | 19.752 | 1-Phenylethanol (Stand.) | 35436584 |
| 6 | 21.715 | **Cyclopentane carboxylic acid** | 28834332 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

Data of the isolated product to Entry 2

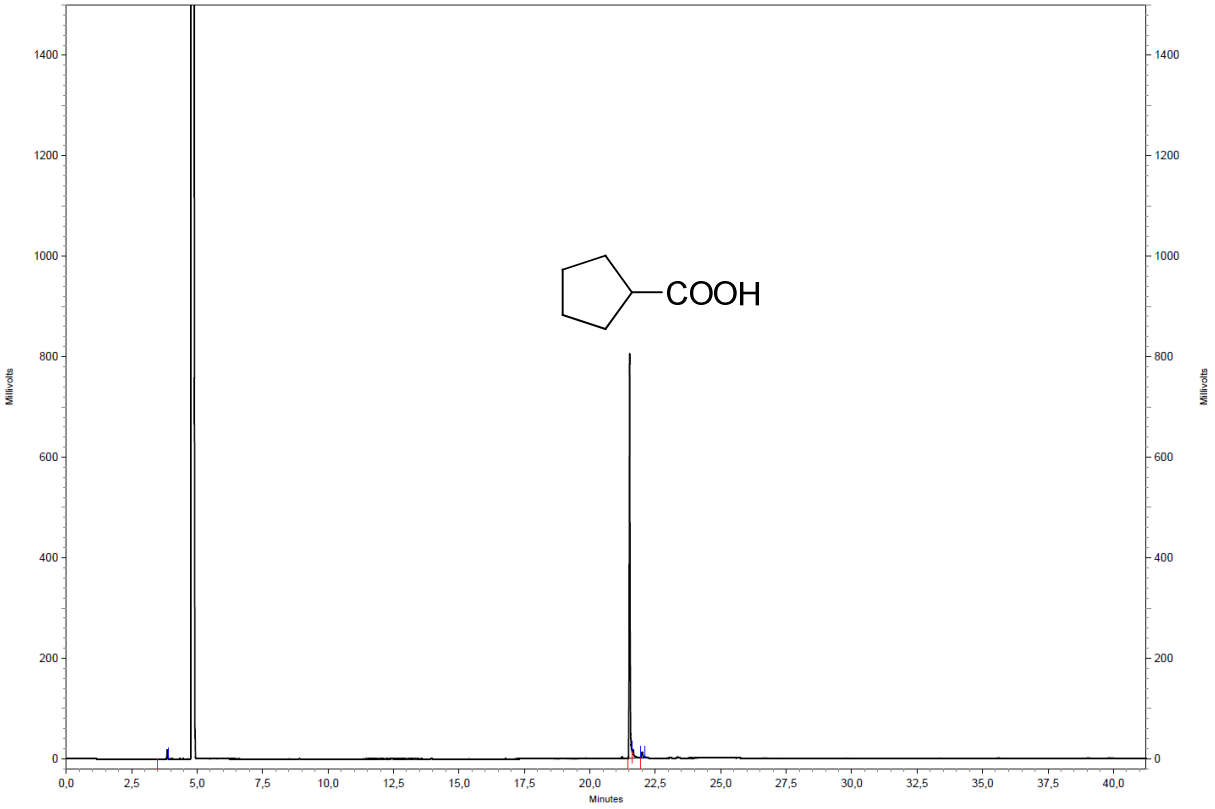



**Figure 3.3** GC Chromatogram of the isolated cyclopentane carboxylic acid.

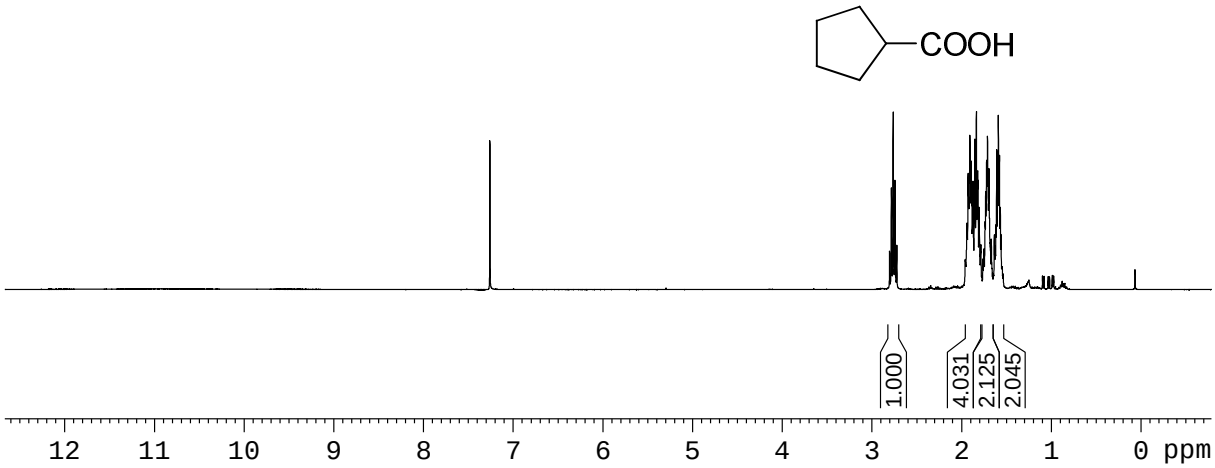
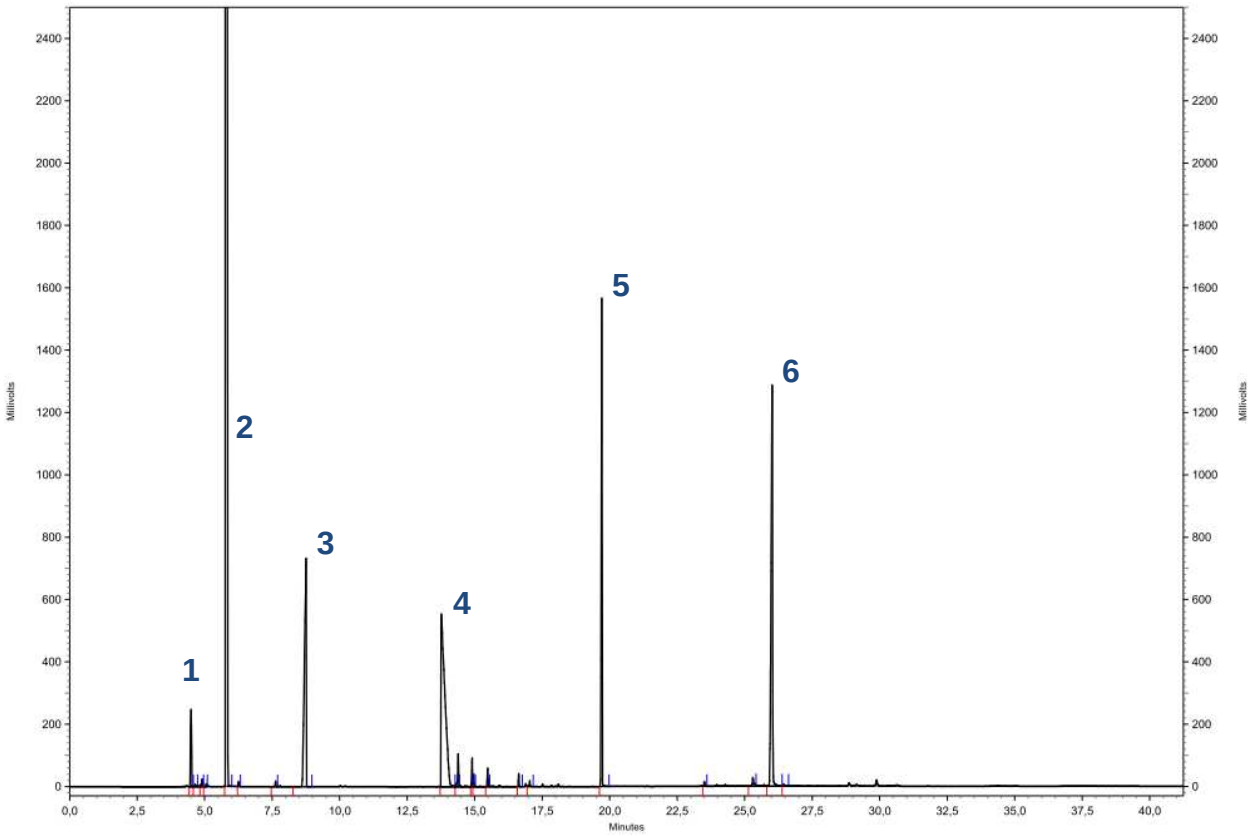



**Figure 3.4.** $^{1}$H NMR spectrum of the isolated product measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

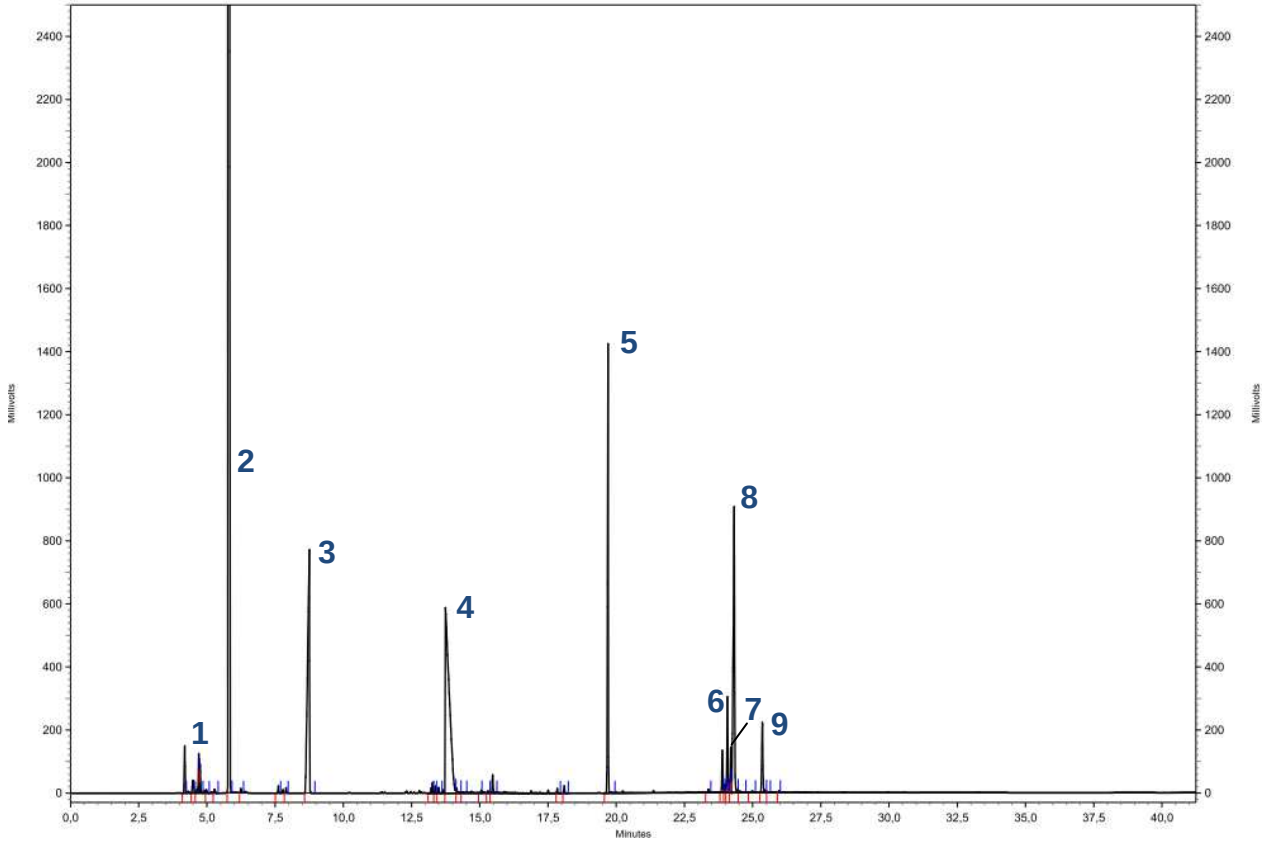
Entry 3




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.497 | **Norbornene** | 6705878 |
| 2[a] | 5.780 | $CDCl_3$ (Solv.) | 371538304 |
| 3 | 8.757 | *n*-Dodecane (Stand.) | 33373713 |
| 4 | 13.765 | $CH_3COOH$ (Solv.) | 53248514 |
| 5 | 19.708 | 1-Phenylethanol (Stand.) | 30539476 |
| 6 | 26.017 | ***exo/endo*-Norbornane carboxylic acid** | 47434972 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

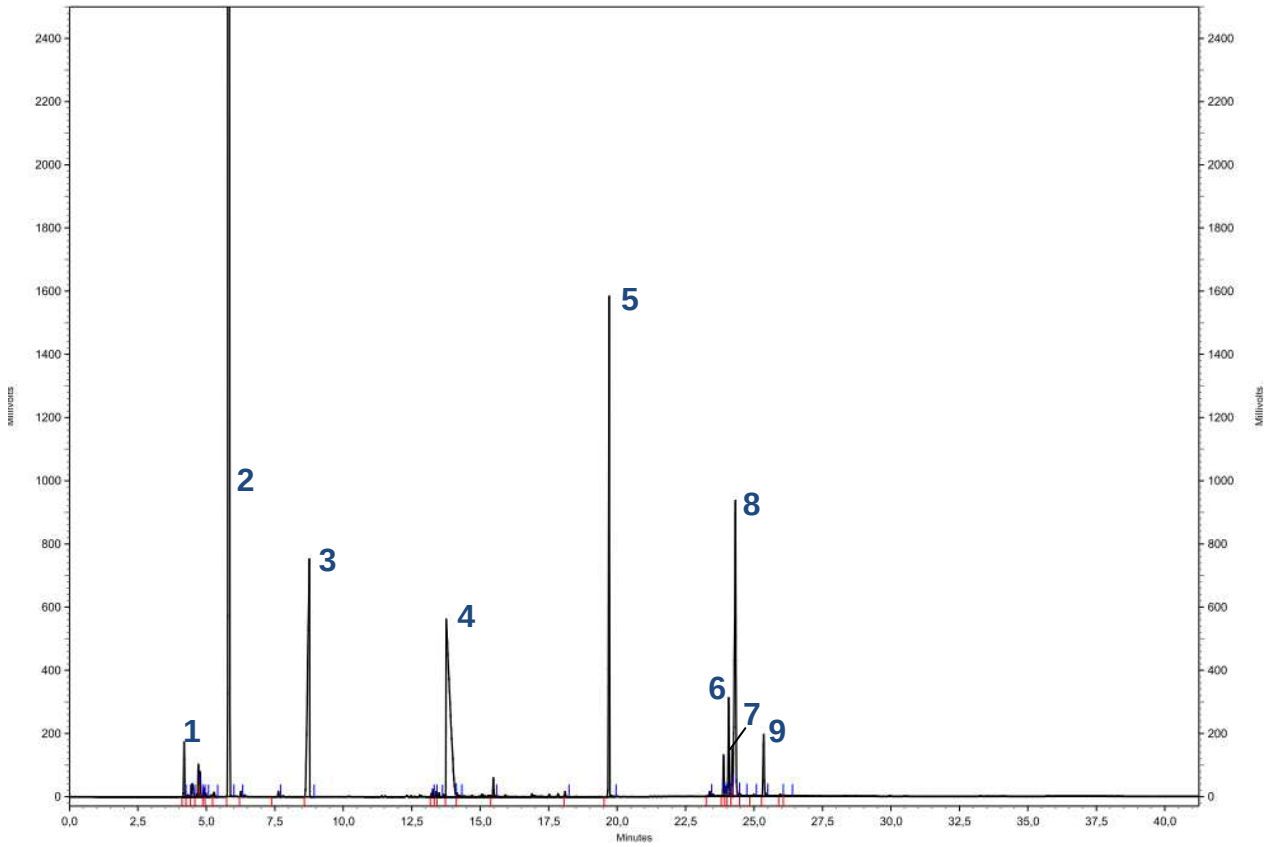
Entry 4




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.702 | **1-Methyl cyclohexene** | 3189899 |
| 2[a] | 5.777 | $CDCl_3$ (Solv.) | 374078246 |
| 3 | 8.753 | *n*-Dodecane (Stand.) | 36190743 |
| 4 | 13.740 | $CH_3COOH$ (Solv.) | 59138955 |
| 5 | 19.698 | 1-Phenylethanol (Stand.) | 26539261 |
| 6 | 24.077 | **2-Methyl cyclohexane carboxylic acid** | 6957721 |
| 7 | 24.202 | **3-Methyl cyclohexane carboxylic acid** | 3302187 |
| 8 | 24.325 | **4-Methyl cyclohexane carboxylic acid** | 31599858 |
| 9 | 25.357 | **Carboxymethyl cyclohexane carboxylic acid** | 6345452 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

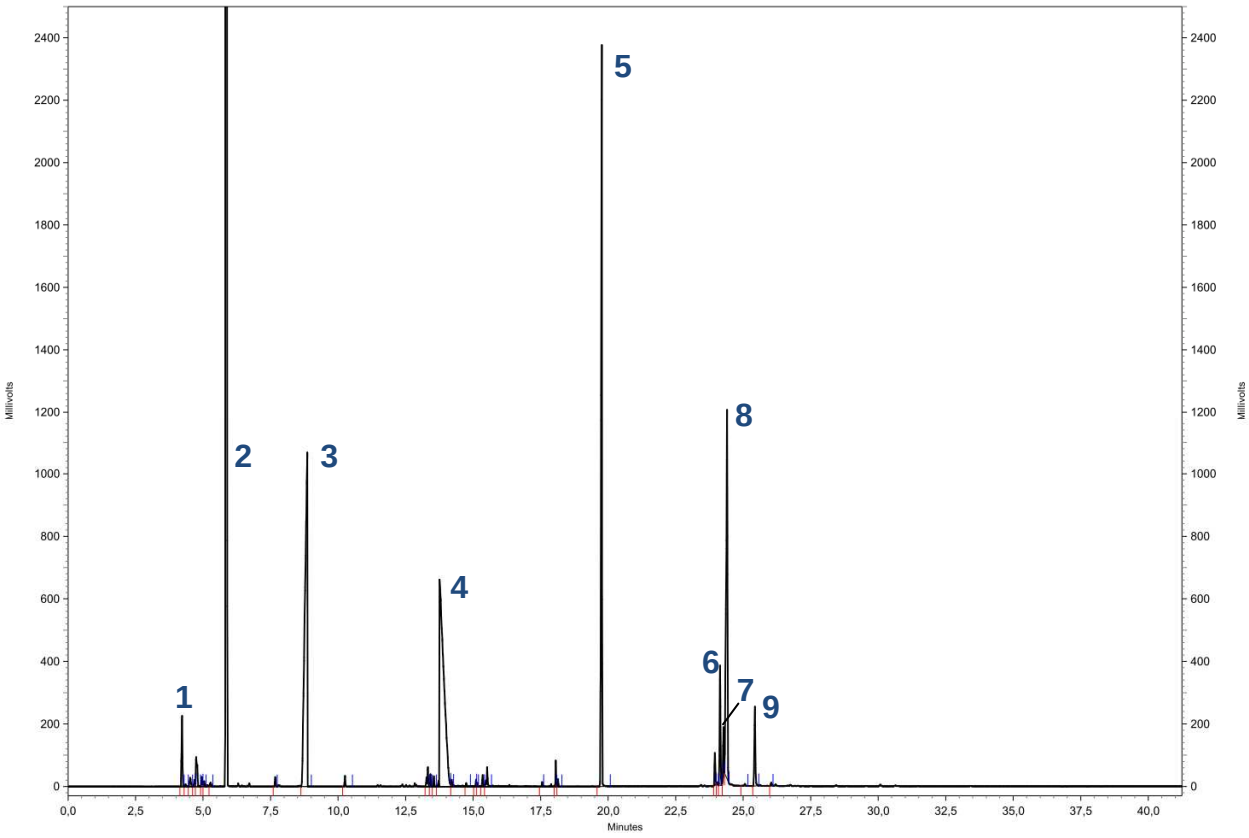
Entry 5




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.492 | **3-Methyl cyclohexene** | 1548035 |
| 2[a] | 5.783 | $CDCl_3$ (Solv.) | 371868926 |
| 3 | 8.762 | *n*-Dodecane (Stand.) | 35212762 |
| 4 | 13.757 | $CH_3COOH$ (Solv.) | 54646215 |
| 5 | 19.708 | 1-Phenylethanol (Stand.) | 29990772 |
| 6 | 24.073 | **2-Methyl cyclohexane carboxylic acid** | 7105626 |
| 7 | 24.200 | **3-Methyl cyclohexane carboxylic acid** | 3443924 |
| 8 | 24.323 | **4-Methyl cyclohexane carboxylic acid** | 32876073 |
| 9 | 25.352 | **Carboxymethyl cyclohexane carboxylic acid** | 5608579 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

Entry 6




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.223 | **4-Methyl cyclohexene** | 4856166 |
| 2[a] | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 3 | 8.862 | *n*-Dodecane (Stand.) | 68225275 |
| 4 | 13.758 | $CH_3COOH$ (Solv.) | 73330100 |
| 5 | 19.765 | 1-Phenylethanol (Stand.) | 54515566 |
| 6 | 24.145 | **2-Methyl cyclohexane carboxylic acid** | 8691609 |
| 7 | 24.272 | **3-Methyl cyclohexane carboxylic acid** | 2237887 |
| 8 | 24.407 | **4-Methyl cyclohexane carboxylic acid** | 41916337 |
| 9 | 25.433 | **Carboxymethyl cyclohexane carboxylic acid** | 6620257 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

Data of the isolated product to Entry 6

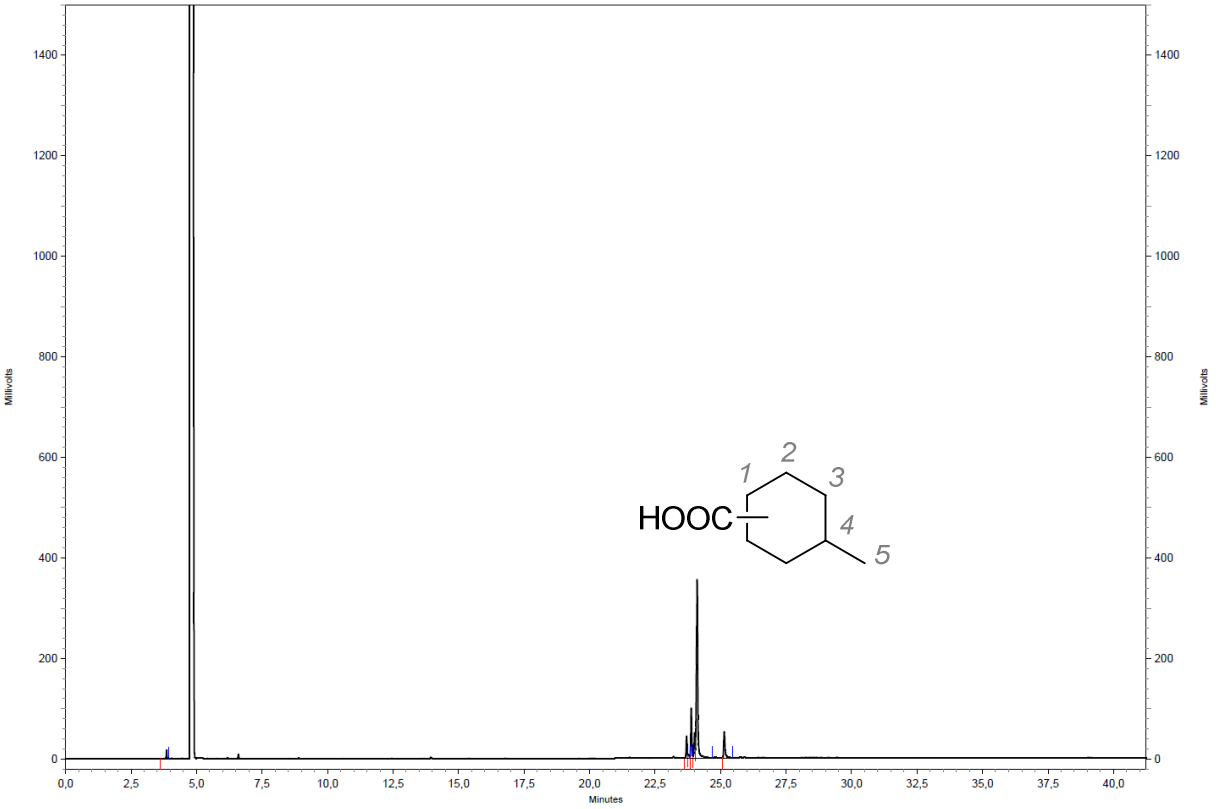



**Figure 3.5** GC Chromatogram of the isolated product mixture.

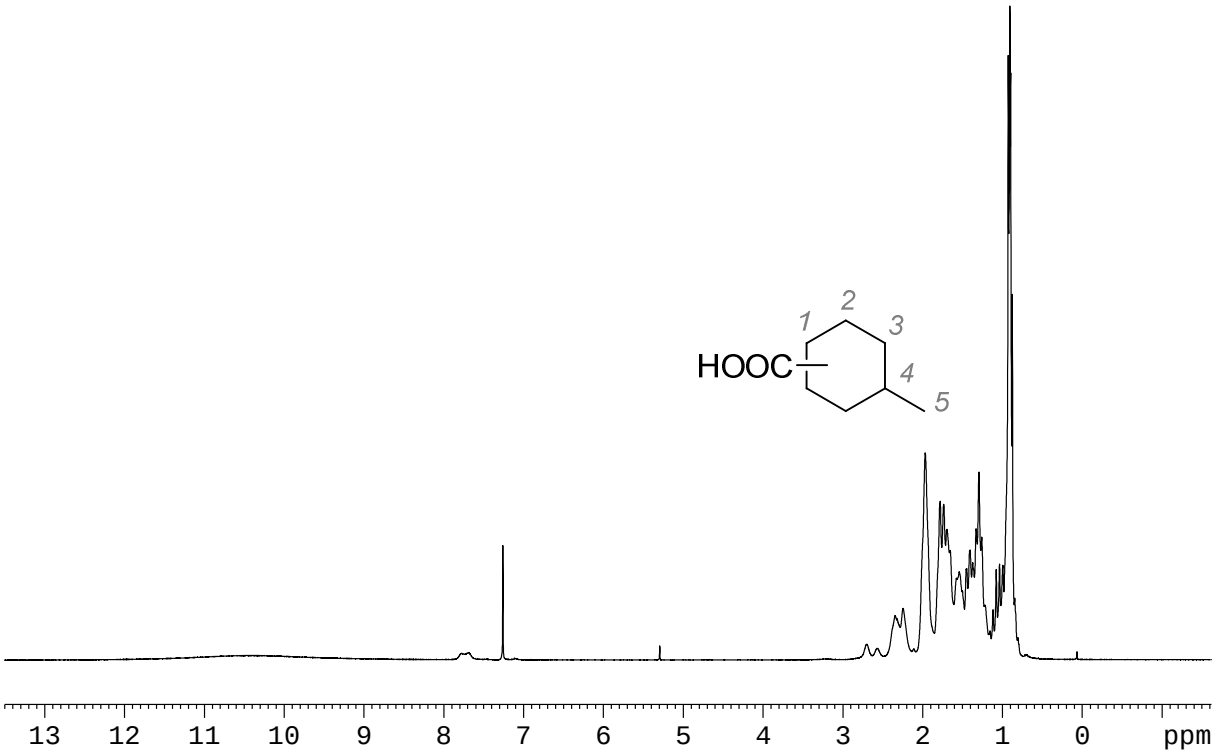
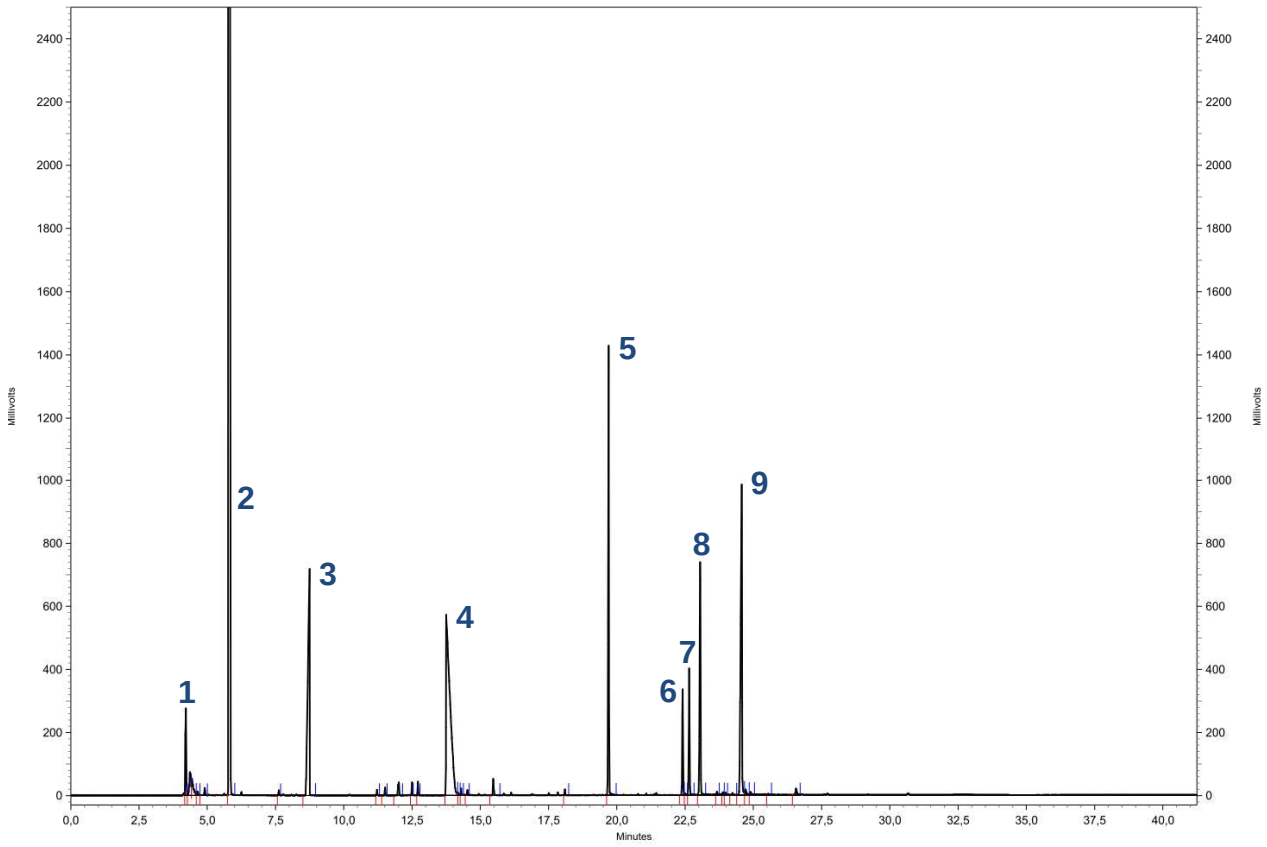



**Figure 3.6.** $^{1}$H NMR spectrum of the isolated product mixture measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

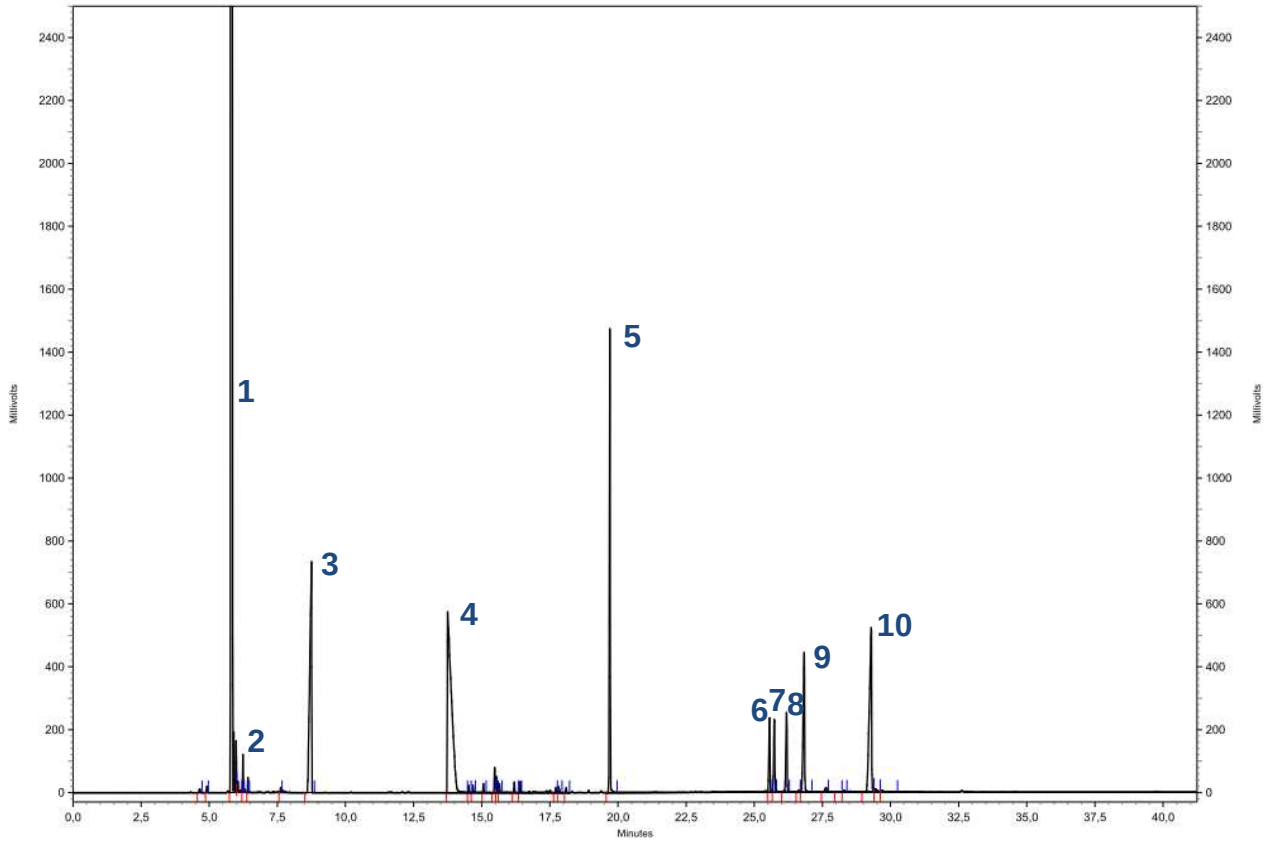
Entry 7




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.908 | **1-Octene** | 553025 |
| 2[a] | 5.780 | $CDCl_3$ (Solv.) | 359078923 |
| 3 | 8.745 | *n*-Dodecane (Stand.) | 32088523 |
| 4 | 13.752 | $CH_3COOH$ (Solv.) | 57547470 |
| 5 | 19.703 | 1-Phenylethanol (Stand.) | 27356427 |
| 6 | 22.410 | **2-Propyl hexanoic acid** | 6277807 |
| 7 | 22.652 | **2-Ethyl heptanoic acid** | 7866978 |
| 8 | 23.055 | **2-Methyl octanoic acid** | 17459174 |
| 9 | 24.573 | ***n*-Nonanoic acid** | 32665607 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

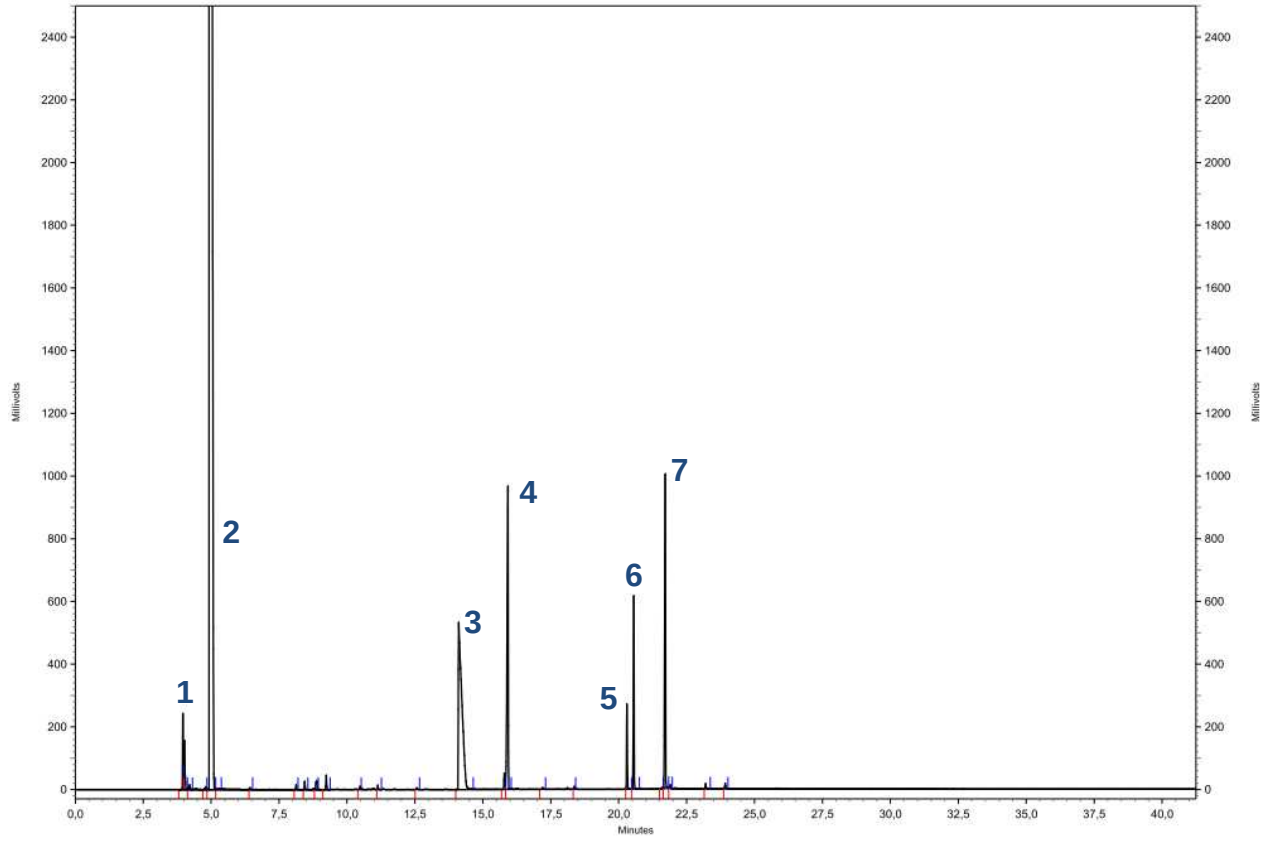
Entry 8




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1[a] | 5.787 | $CDCl_3$ (Solv.) | 374207983 |
| 2 | 6.235 | **1-Decene** | 1708970 |
| 3 | 8.753 | *n*-Dodecane (Stand.) | 33940046 |
| 4 | 13.745 | $CH_3COOH$ (Solv.) | 58204489 |
| 5 | 19.703 | 1-Phenylethanol (Stand.) | 28592481 |
| 6 | 25.562 | **2-Butyl heptanoic acid** | 6474445 |
| 7 | 25.737 | **2-Propyl octanoic acid** | 6161028 |
| 8 | 26.187 | **2-Ethyl nonane carboxylic acid** | 7543975 |
| 9 | 26.830 | **2-Methyl decanoic acid** | 16369660 |
| 10 | 29.290 | ***n*-Undecanoic acid** | 29869254 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

Entry 9




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.022 | **1-Hexene** | 2844752 |
| 2 | 4.928 | $CH_2Cl_2$ (Solv.) | 549670979 |
| 3 | 14.110 | $CH_3COOH$ (Solv.) | 46299377 |
| 4[a] | 15.927 | *n*-Octanol (Stand.) | 26466472 |
| 5 | 20.305 | **2-Ethyl pentanoic acid** | 4229028 |
| 6 | 20.555 | **2-Methyl hexanoic acid** | 9939627 |
| 7 | 21.712 | ***n*-Heptanoic acid** | 19681225 |

[a]: *n*-Octanol was used in this experiment to avoid signal overlap with the substrate peak.

Data of the isolated product to Entry 9

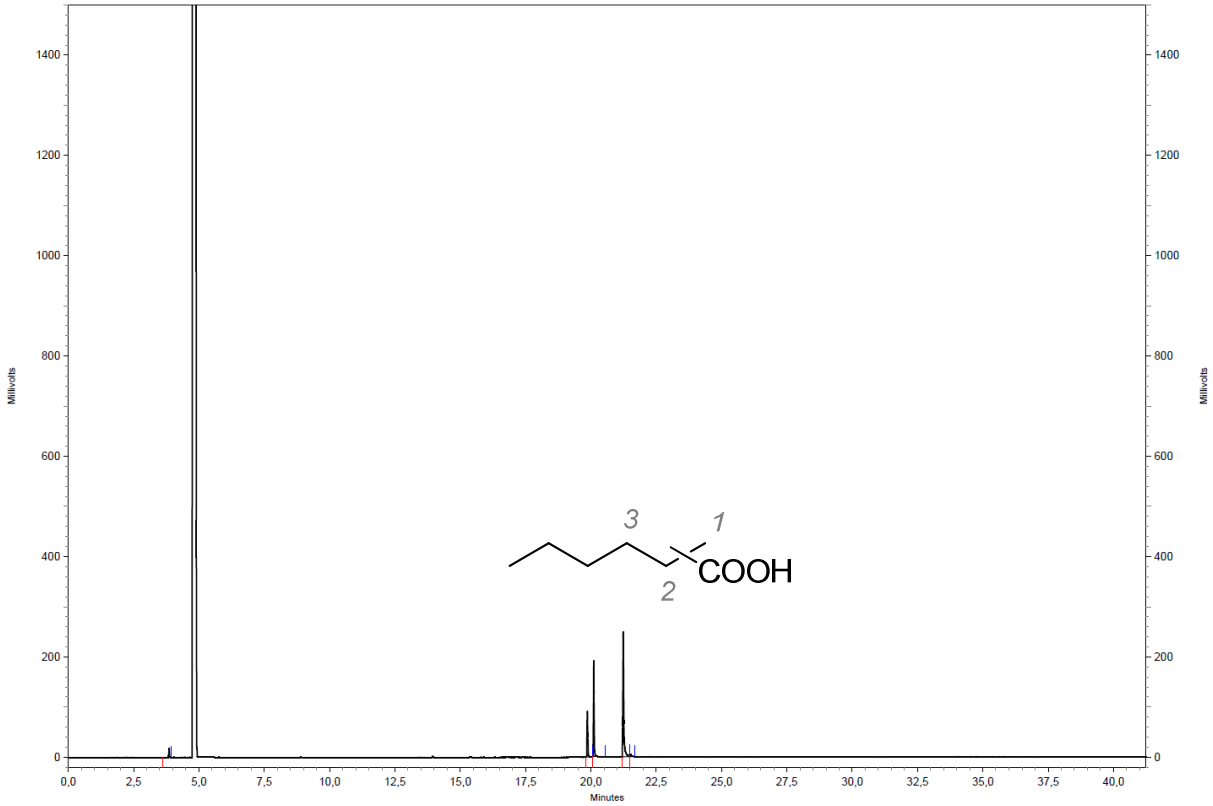



**Figure 3.7** GC chromatogram of the isolated product mixture.

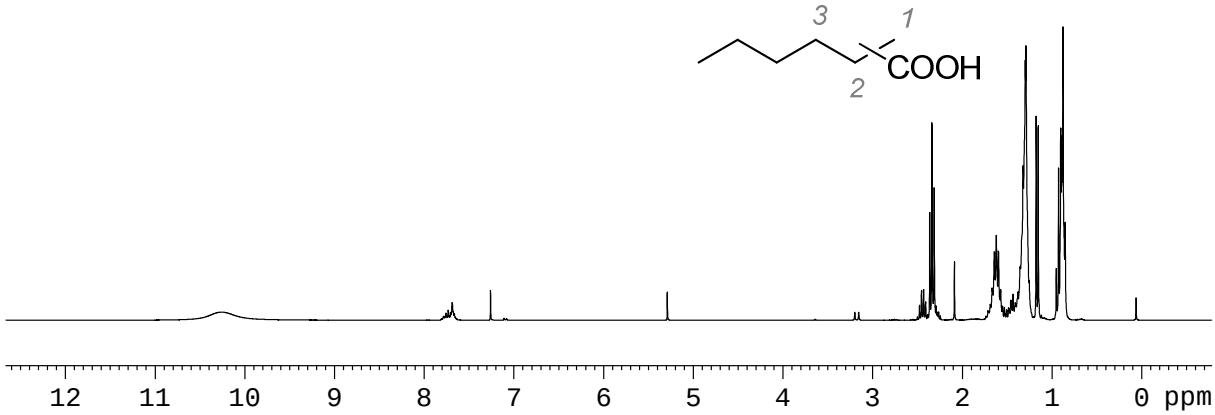
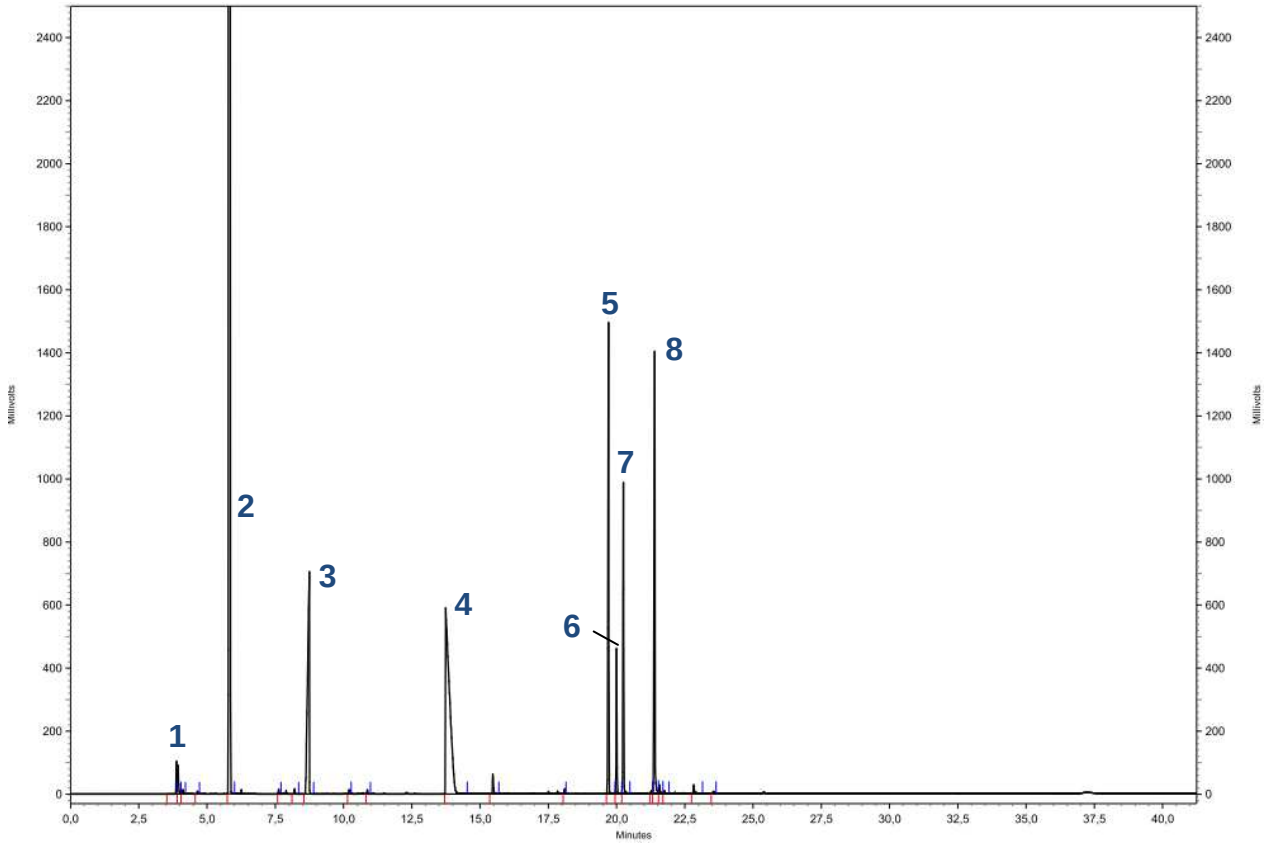



**Figure 3.8.** $^{1}H$ NMR spectrum of the isolated product mixture measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

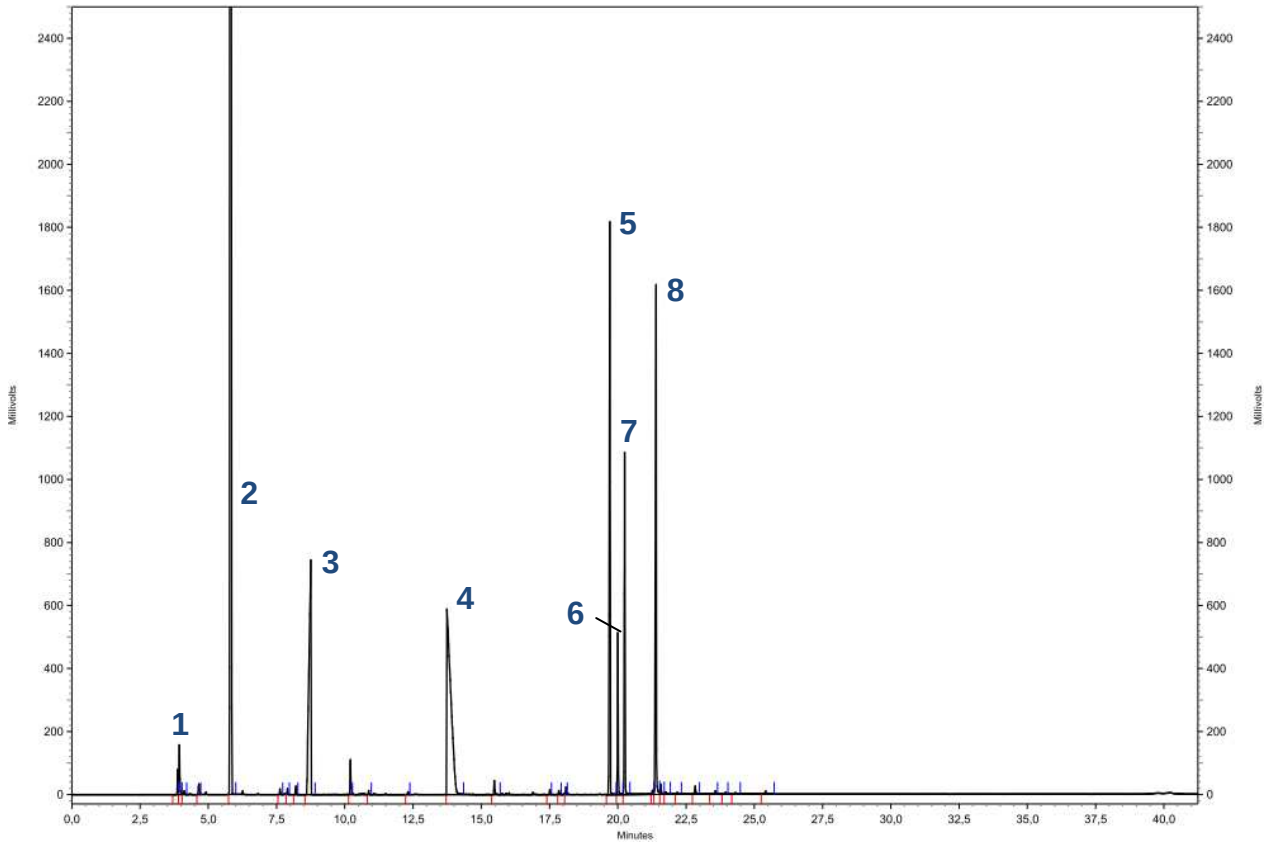
Entry 10




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 3.940 | **2-Hexene** | 1987613 |
| 2[a] | 5.785 | $CDCl_3$ (Solv.) | 369417755 |
| 3 | 8.747 | *n*-Dodecane (Stand.) | 32575311 |
| 4 | 13.738 | $CH_3COOH$ (Solv.) | 60717693 |
| 5 | 19.705 | 1-Phenylethanol (Stand.) | 28888805 |
| 6 | 19.998 | **2-Ethyl pentanoic acid** | 7441529 |
| 7 | 20.250 | **2-Methyl hexanoic acid** | 16837208 |
| 8 | 21.393 | ***n*-Heptanoic acid** | 30026305 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

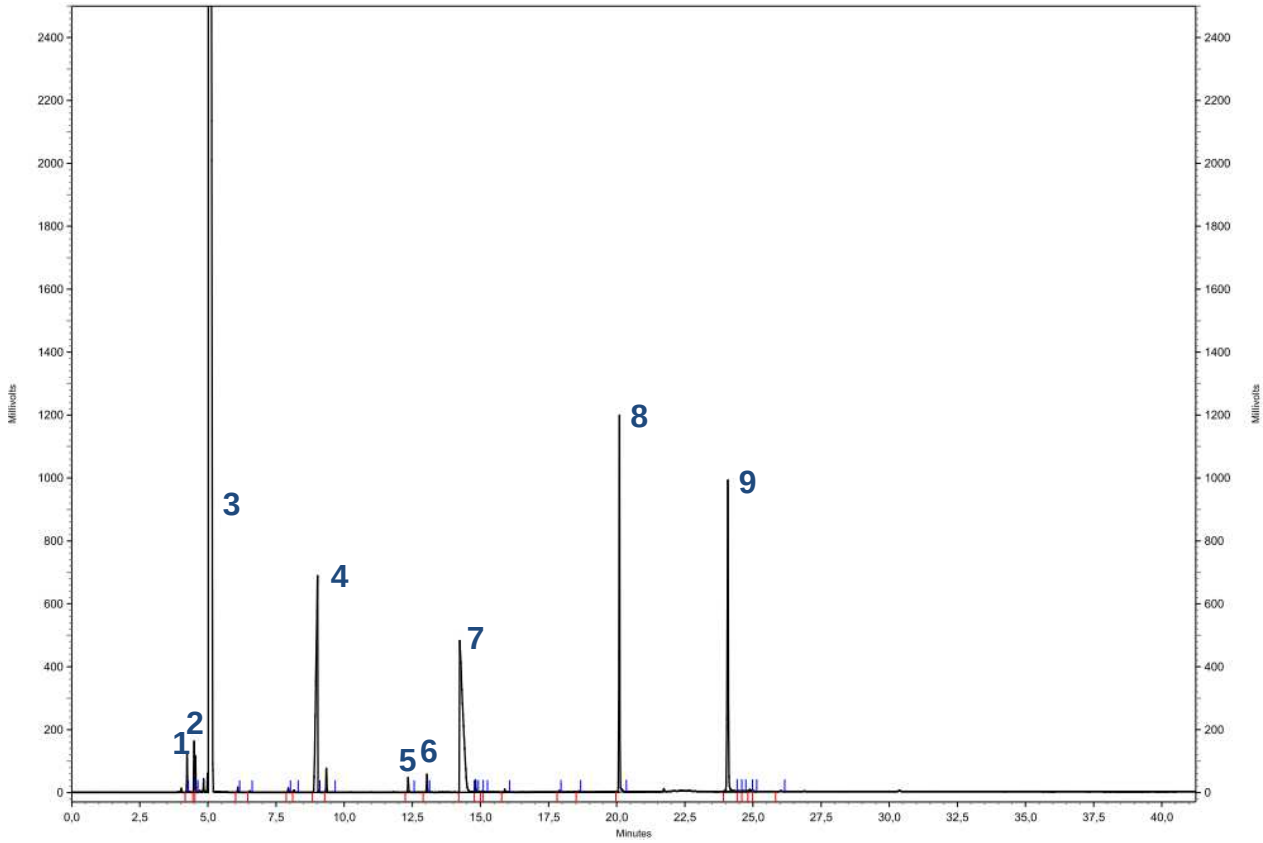
Entry 11




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 3.938 | **3-Hexene** | 3238228 |
| 2[a] | 5.787 | $CDCl_3$ (Solv.) | 367788054 |
| 3 | 8.755 | *n*-Dodecane (Stand.) | 36634777 |
| 4 | 13.740 | $CH_3COOH$ (Solv.) | 59999654 |
| 5 | 19.708 | 1-Phenylethanol (Stand.) | 36647525 |
| 6 | 20.000 | **2-Ethyl pentanoic acid** | 8206306 |
| 7 | 20.252 | **2-Methyl hexanoic acid** | 18575822 |
| 8 | 21.398 | ***n*-Heptanoic acid** | 36340221 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

Entry 12




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.235 | **CH** | 1595466 |
| 2 | 4.545 | **CE** | 1736854 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 9.023 | *n*-Dodecane (Stand.) | 30367527 |
| 5 | 12.347 | **CAc** | 845689 |
| 6 | 13.038 | **CI** | 1050040 |
| 7 | 14.240 | $CH_3COOH$ (Solv.) | 40342430 |
| 8 | 20.102 | 1-Phenylethanol (Stand.) | 22697158 |
| 9 | 24.080 | **CA** | 27697583 |

Data of the isolated product to Entry 12

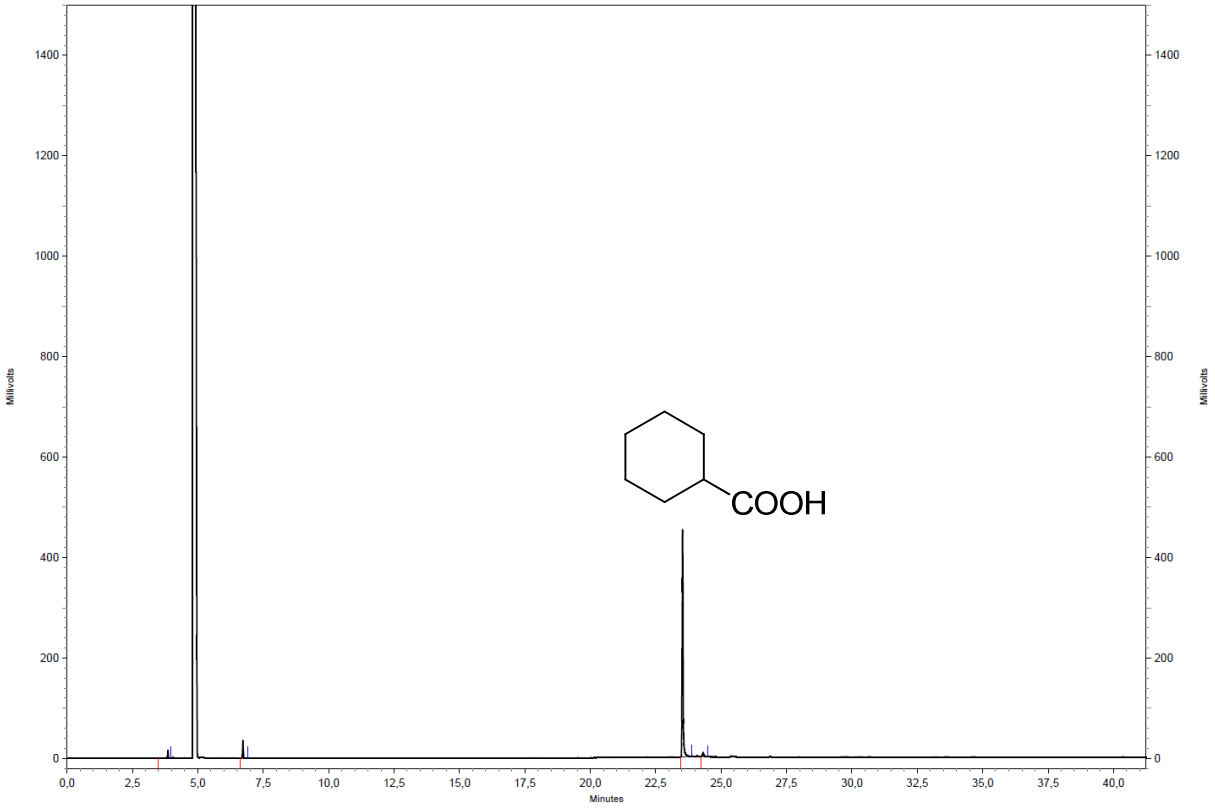



**Figure 3.9** GC chromatogram of the isolated cyclohexane carboxylic acid.

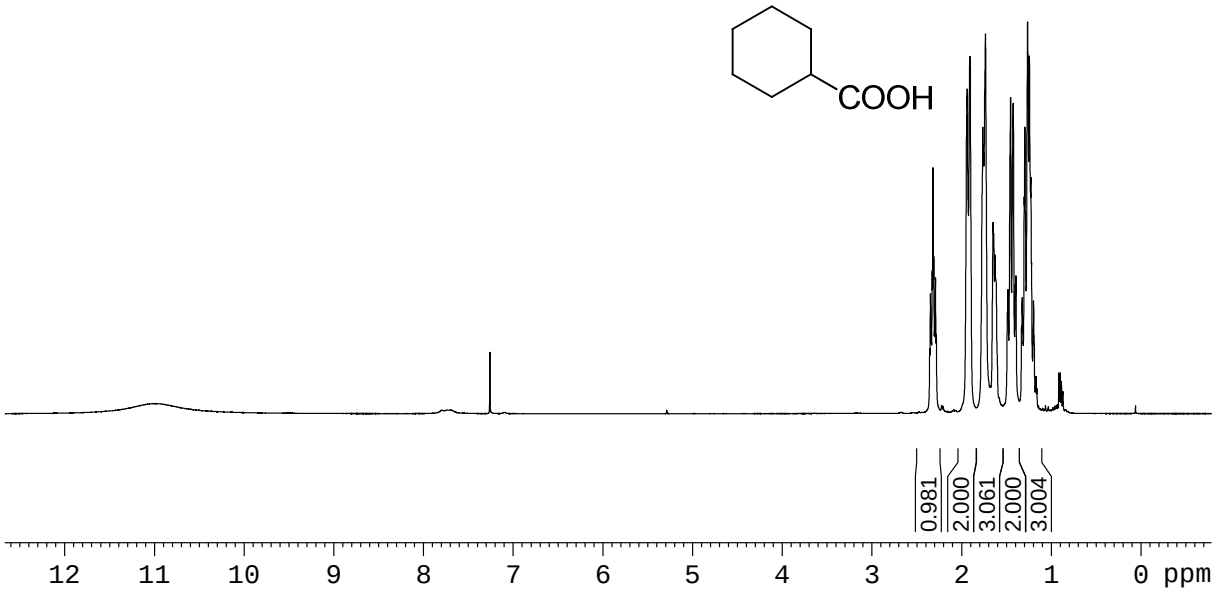
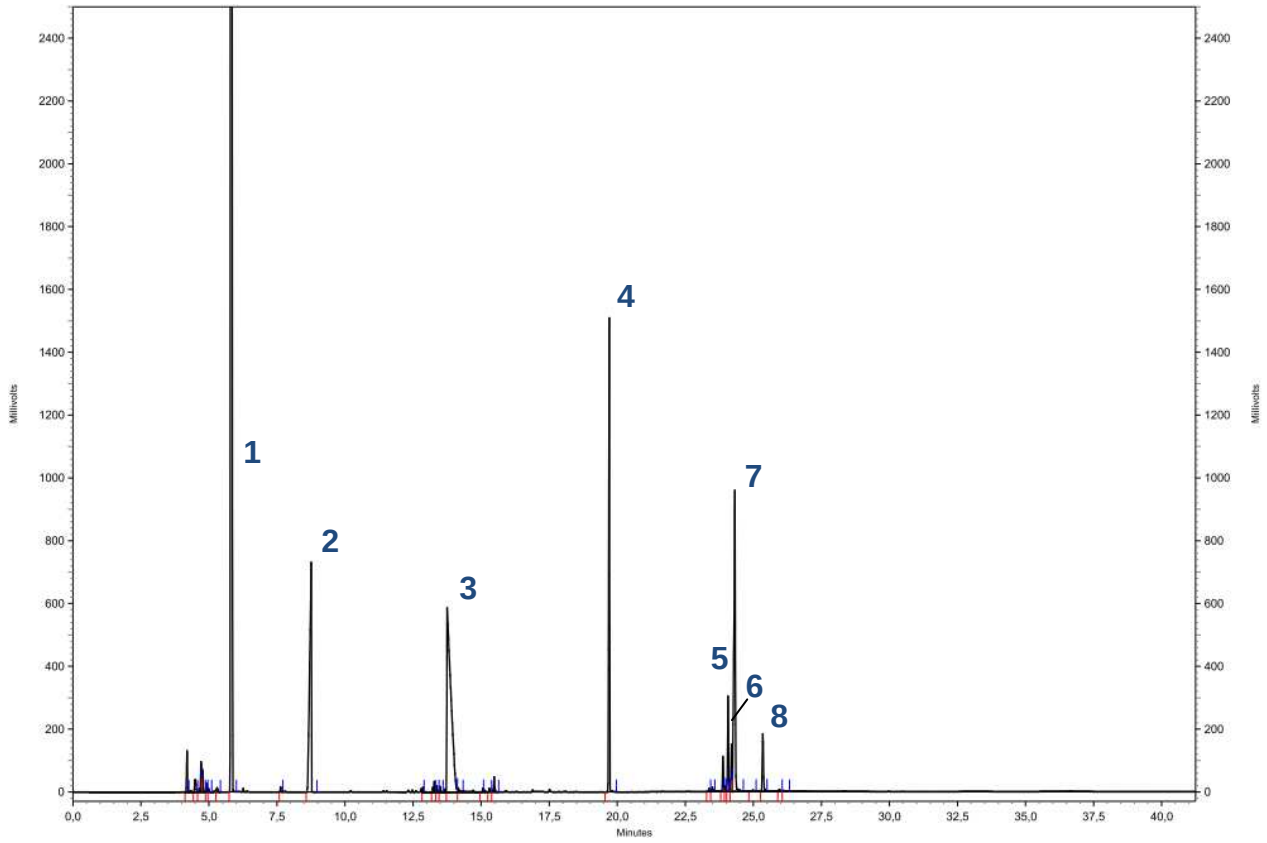



**Figure 3.10.** $^{1}$H NMR spectrum of the isolated product measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

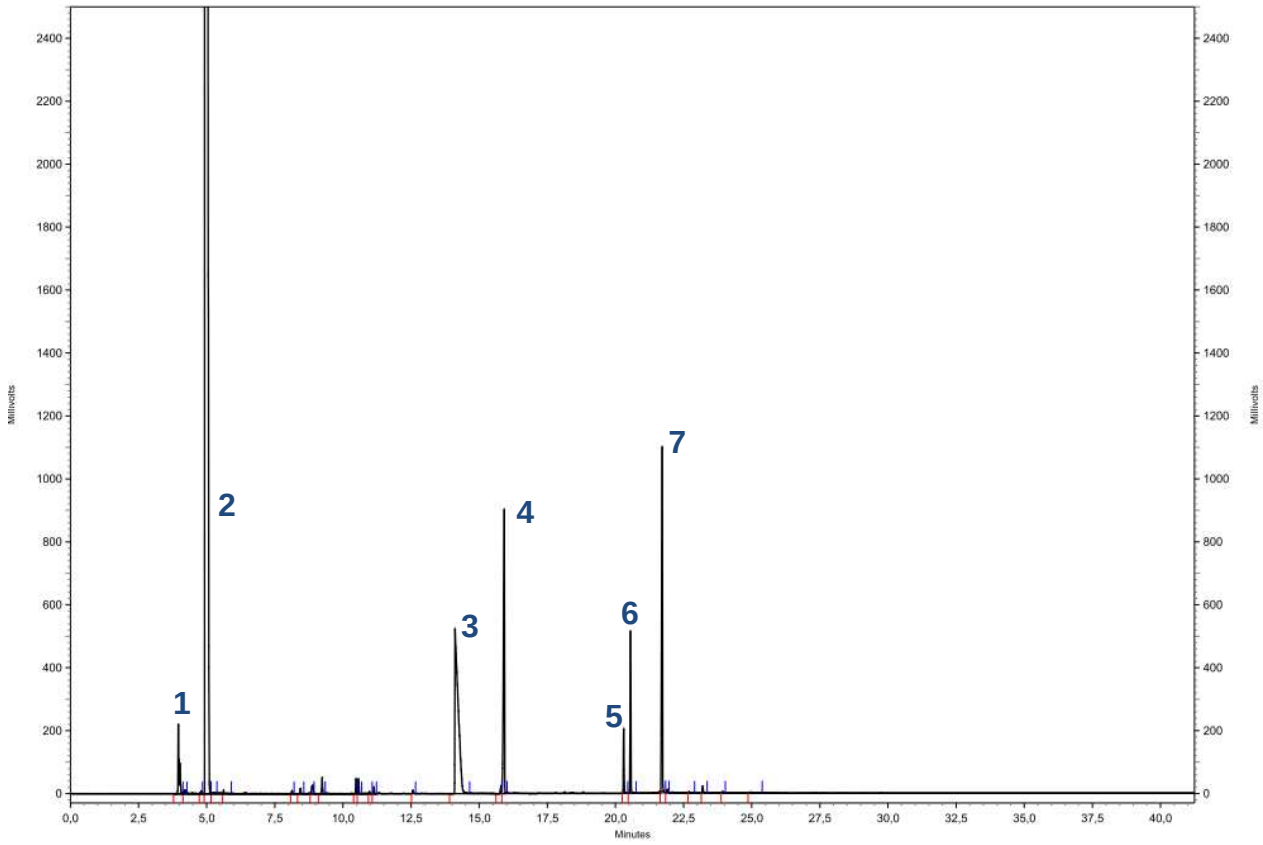
Entry 13




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1[a] | 5.790 | $CDCl_3$ (Solv.) | 367119043 |
| 2 | 8.760 | *n*-Dodecane (Stand.) | 33495695 |
| 3 | 13.747 | $CH_3COOH$ (Solv.) | 59139257 |
| 4 | 19.707 | 1-Phenylethanol (Stand.) | 29286436 |
| 5 | 24.073 | **2-Methyl cyclohexane carboxylic acid** | 7063099 |
| 6 | 24.198 | **3-Methyl cyclohexane carboxylic acid** | 3499874 |
| 7 | 24.325 | **4-Methyl cyclohexane carboxylic acid** | 34118403 |
| 8 | 25.350 | **Carboxymethyl cyclohexane carboxylic acid** | 5247547 |

[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

Entry 14




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 3.958 | **Hexane** | 5716156 |
| 2 | 4.927 | $CH_2Cl_2$ (Solv.) | 556022214 |
| 3 | 14.112 | $CH_3COOH$ (Solv.) | 44565895 |
| 4 | 15.922 | *n*-Octanol (Stand.) | 23743985 |
| 5 | 20.303 | **2-Ethyl pentanoic acid** | 3152384 |
| 6 | 20.552 | **2-Methyl hexanoic acid** | 8133389 |
| 7 | 21.713 | ***n*-Heptanoic acid** | 21904251 |

[a]: *n*-Octanol was used in this experiment to avoid signal overlap with the substrate peak.

Data of the isolated product to Entry 14

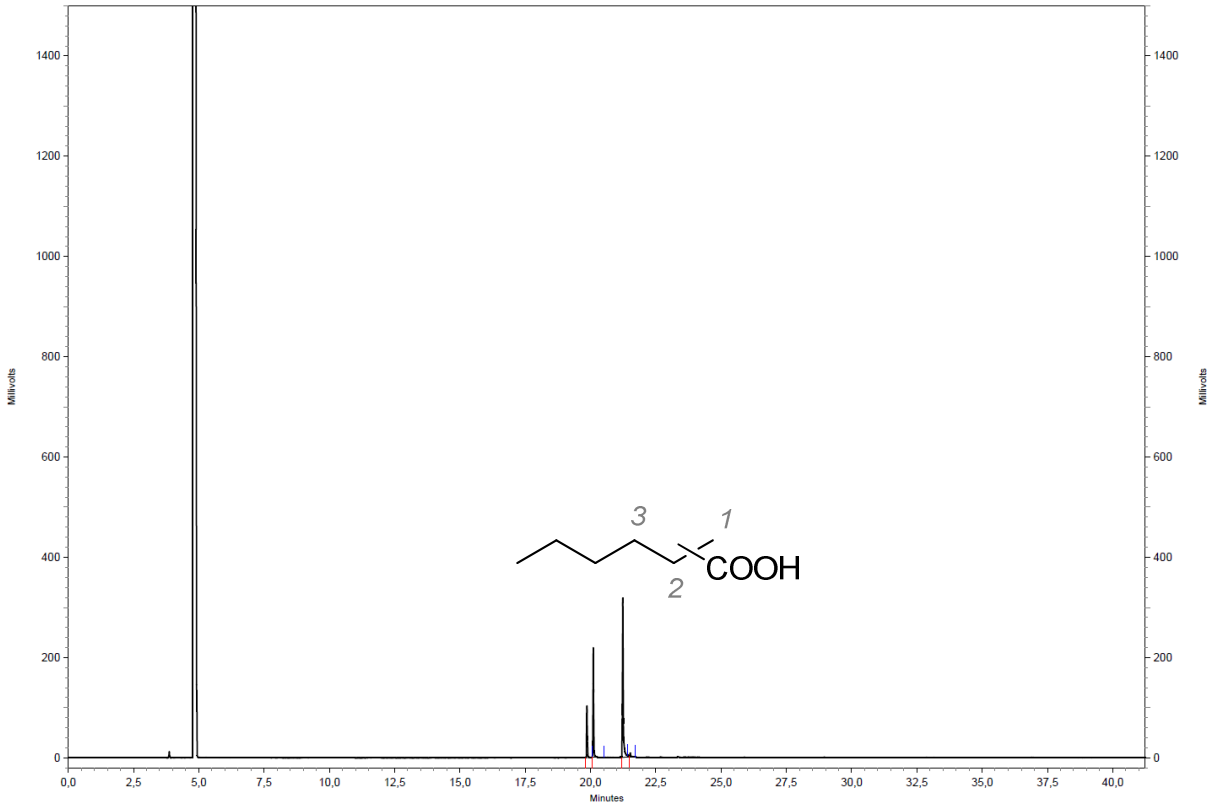



**Figure 3.11** GC chromatogram of the isolated product mixture.

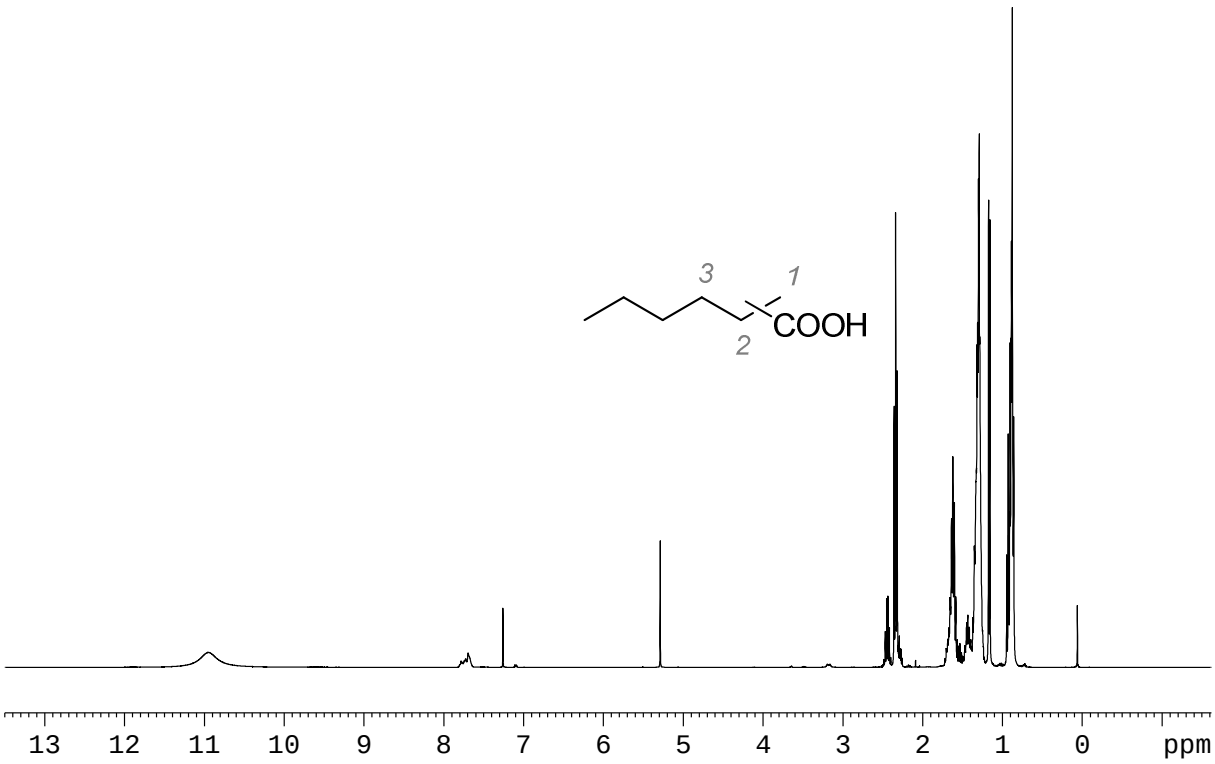
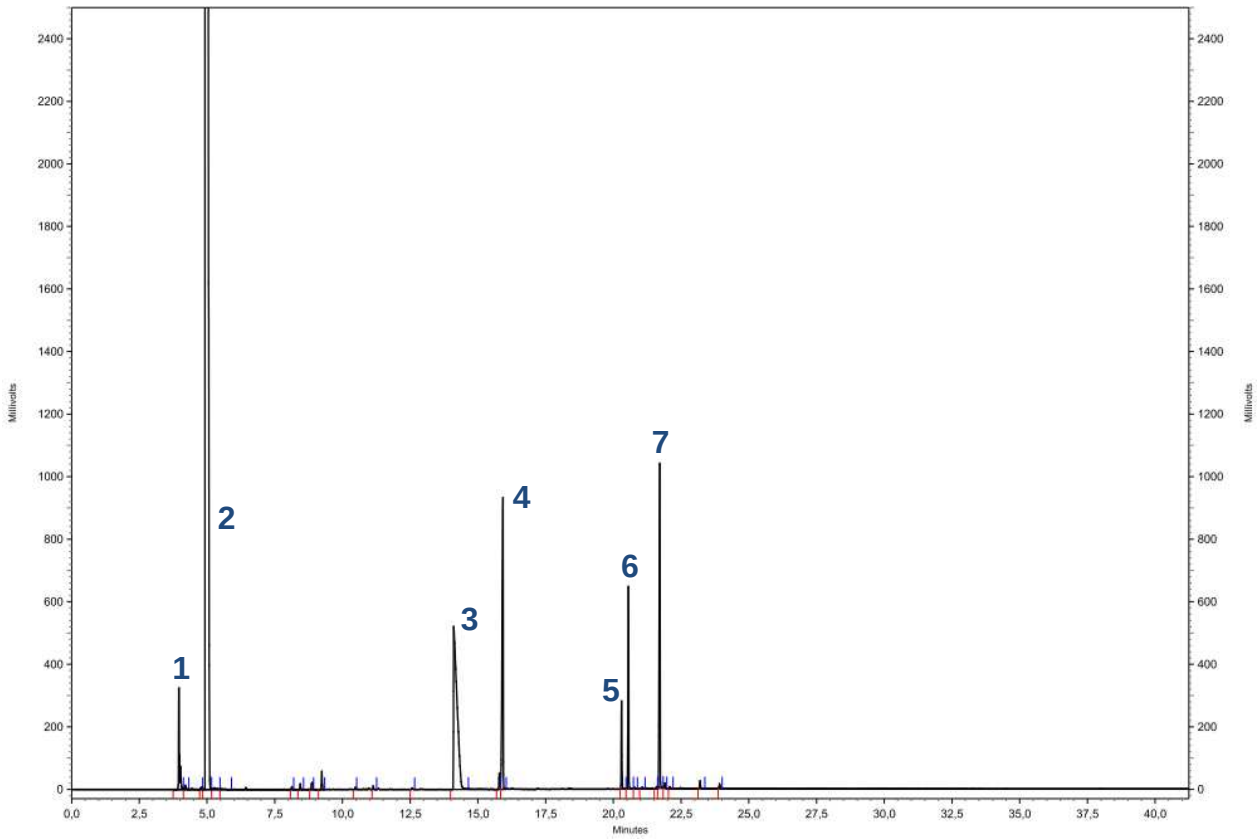



**Figure 3.12.** $^{1}$H NMR spectrum of the isolated product mixture measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

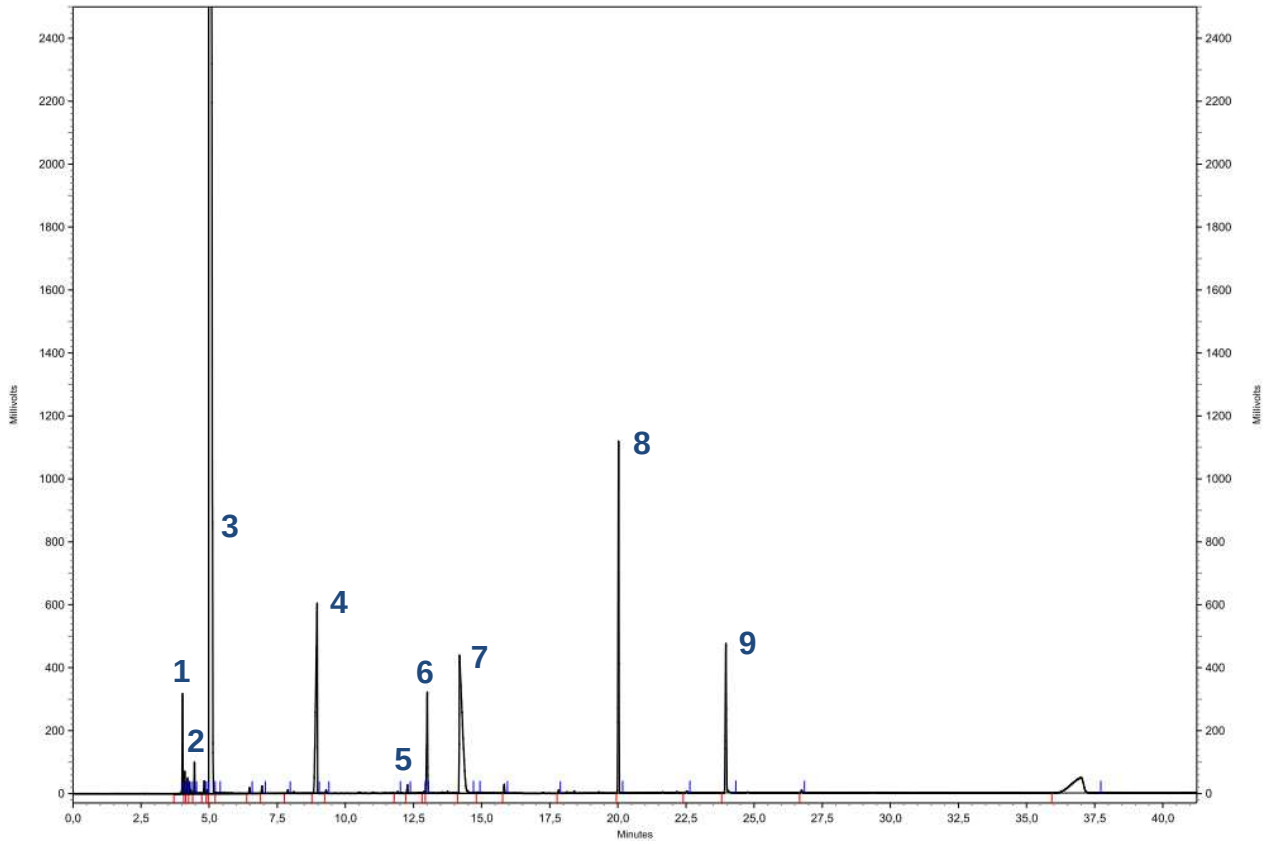
Entry 15




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 3.960 | **Hexane** | 6557964 |
| 2 | 4.927 | $CH_2Cl_2$ (Solv.) | 553192172 |
| 3 | 14.107 | $CH_3COOH$ (Solv.) | 45606092 |
| 4[a] | 15.923 | *n*-Octanol (Stand.) | 25208028 |
| 5 | 20.305 | **2-Ethyl pentanoic acid** | 4348062 |
| 6 | 20.555 | **2-Methyl hexanoic acid** | 10543606 |
| 7 | 21.712 | ***n*-Heptanoic acid** | 20621202 |

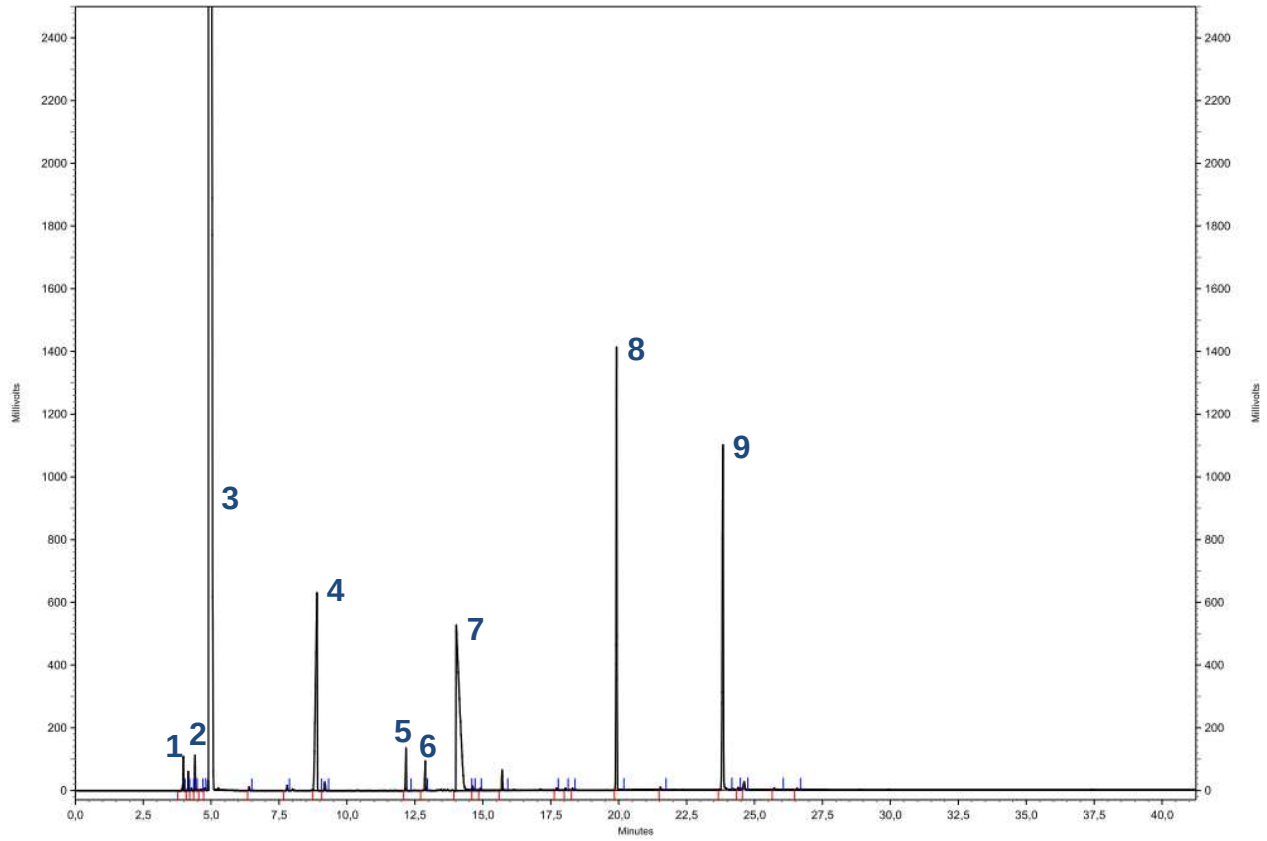
[a]: *n*-Octanol was used in this experiment to avoid signal overlap with the substrate peak.

Entry 16




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.105 | **CH** | 886422 |
| 2 | 4.462 | **CE** | 1521631 |
| 3 | 4.993 | $CH_2Cl_2$ (Solv.) | 442202356 |
| 4 | 8.965 | *n*-Dodecane (Stand.) | 23486393 |
| 5 | 12.275 | **CAc** | 469594 |
| 6 | 13.003 | **CI** | 6920339 |
| 7 | 14.188 | $CH_3COOH$ (Solv.) | 33074464 |
| 8 | 20.025 | 1-Phenylethanol (Stand.) | 20020794 |
| 9 | 23.965 | **CA** | 11015083 |

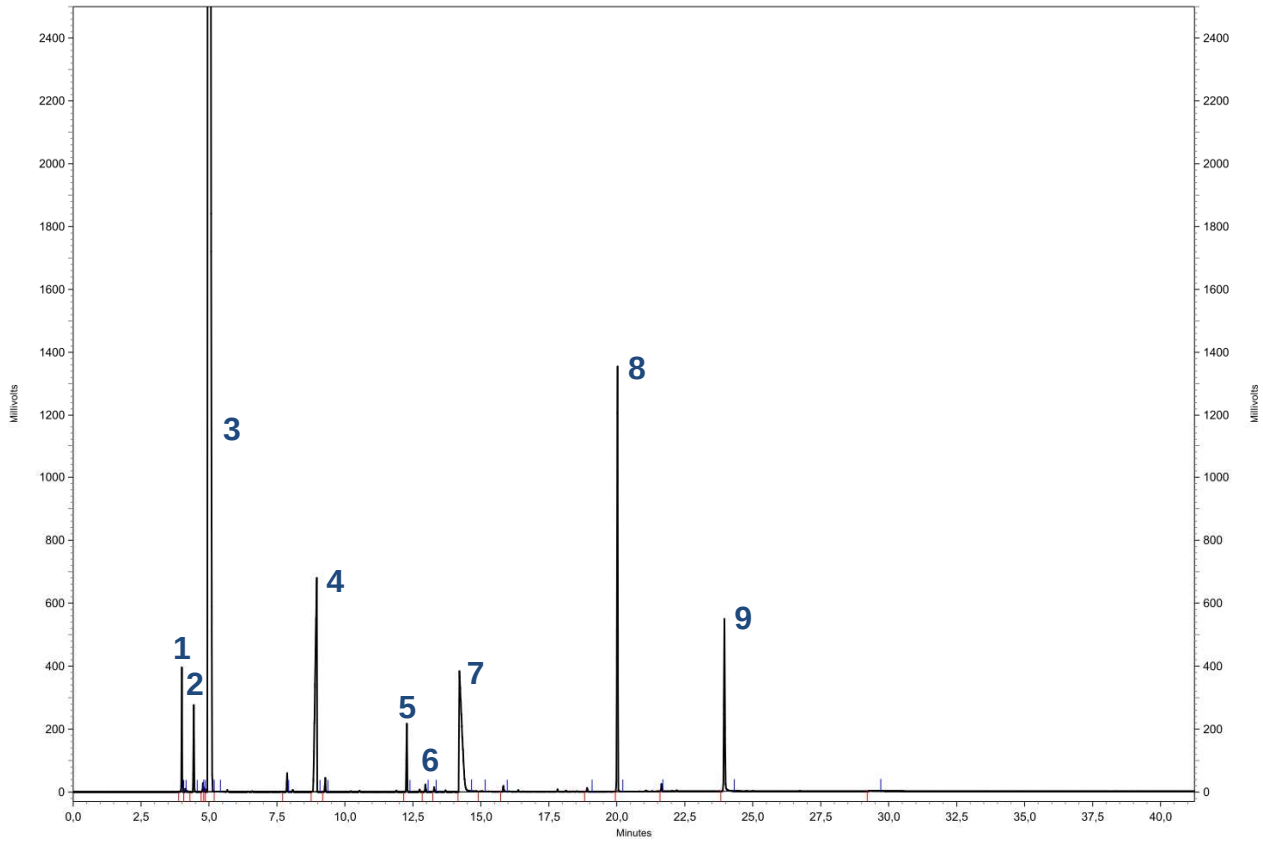
Entry 17




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 3.978 | **CH** | 1532625 |
| 2 | 4.408 | **CE** | 1738139 |
| 3 | *cutted* | $CH_2Cl_2$ (Solv.) | -- |
| 4 | 8.897 | *n*-Dodecane (Stand.) | 25850032 |
| 5 | 12.172 | **CAc** | 2219896 |
| 6 | 12.877 | **CI** | 1660622 |
| 7 | 14.023 | $CH_3COOH$ (Solv.) | 46455180 |
| 8 | 19.925 | 1-Phenylethanol (Stand.) | 27194328 |
| 9 | 23.837 | **CA** | 28915927 |

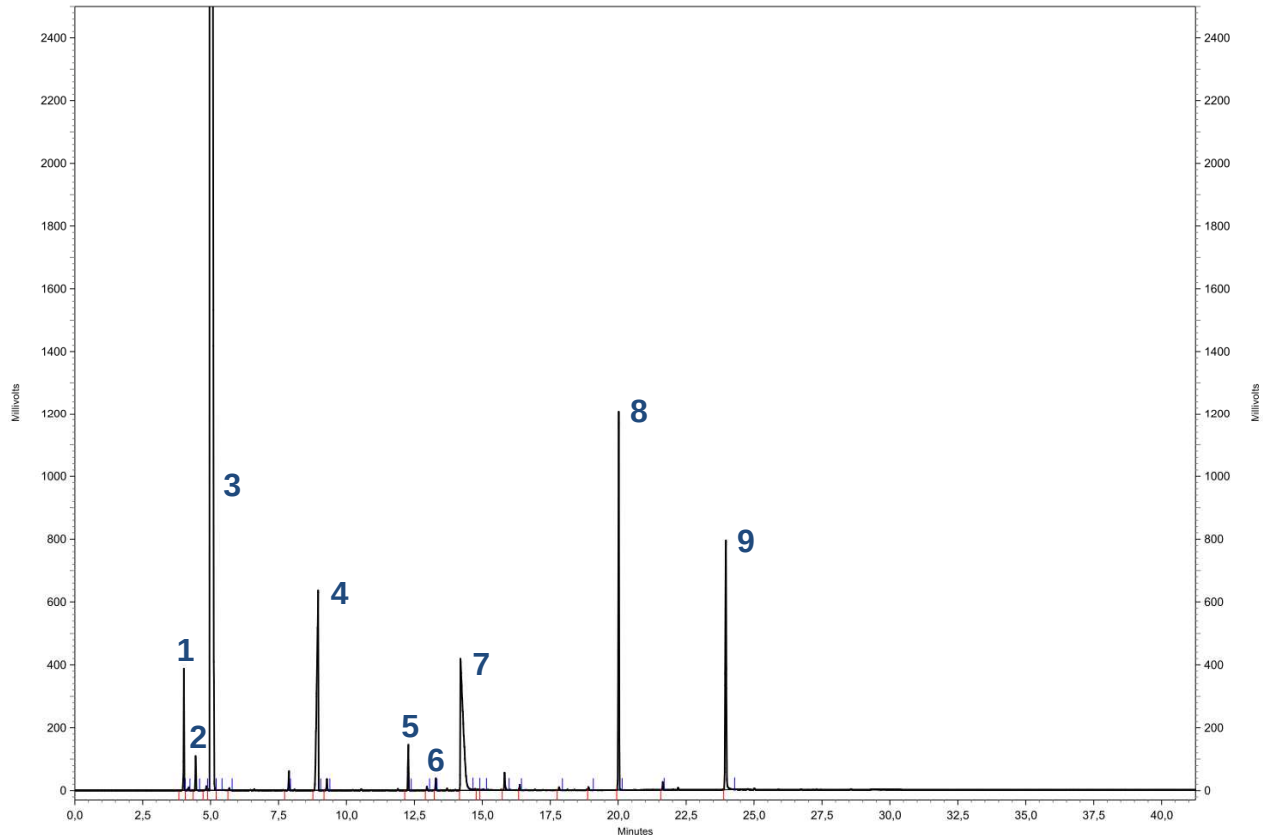
## S3.8 Gaschromatograms to Table S2.8

Entry 1



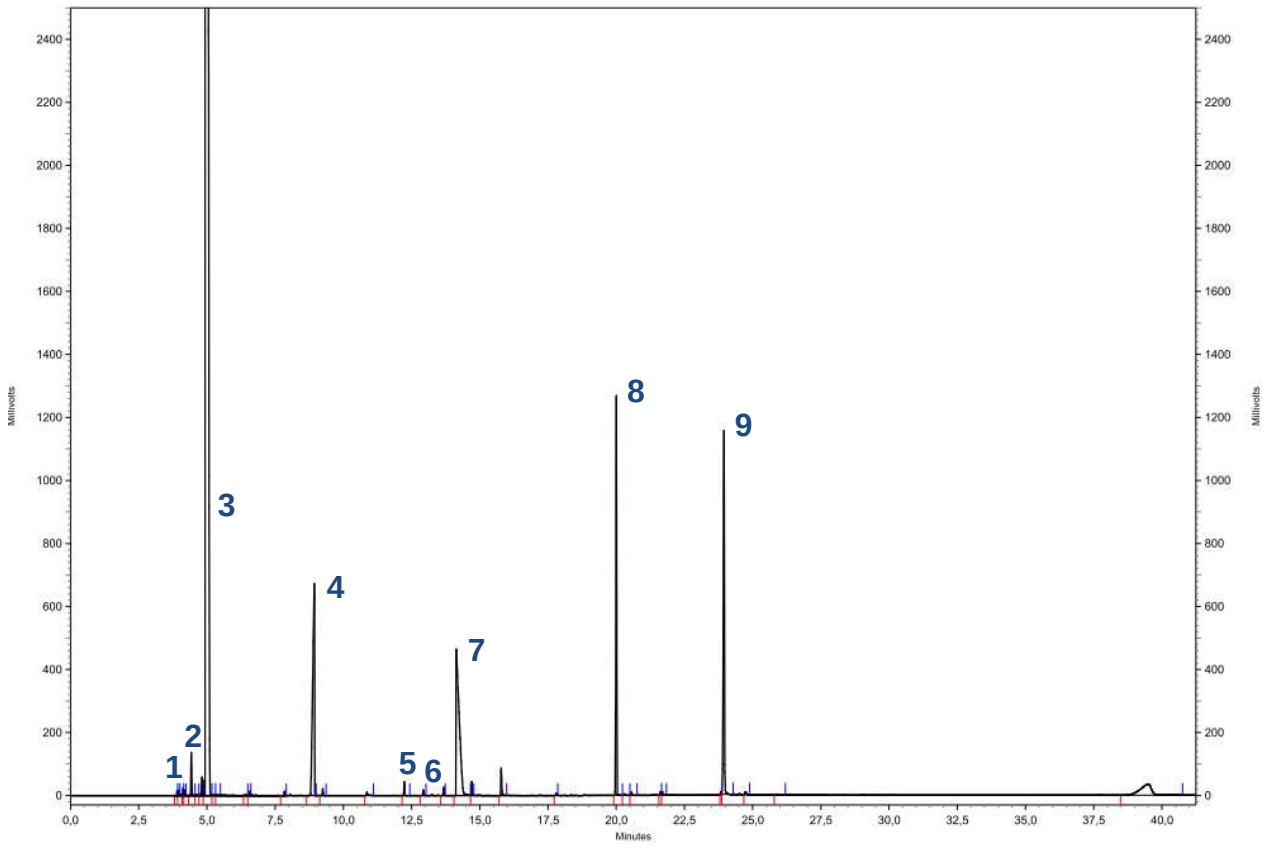

| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.002 | **CH** | 4917794 |
| 2 | 4.437 | **CE** | 4097124 |
| 3 | 4.955 | $CH_2Cl_2$ (Solv.) | 527292253 |
| 4 | 8.963 | *n*-Dodecane (Stand.) | 29266189 |
| 5 | 12.277 | **CAc** | 3705318 |
| 6 | 12.962 | **CI** | 416532 |
| 7 | 14.208 | $CH_3COOH$ (Solv.) | 26990150 |
| 8 | 20.025 | 1-Phenylethanol (Stand.) | 25556688 |
| 9 | 23.960 | **CA** | 13083714 |

Entry 2




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.013 | **CH** | 4803994 |
| 2 | 4.450 | **CE** | 1654564 |
| 3 | 4.972 | $CH_2Cl_2$ (Solv.) | 515167964 |
| 4 | 8.960 | *n*-Dodecane (Stand.) | 25402549 |
| 5 | 12.275 | **CAc** | 2397405 |
| 6 | 12.963 | **CI** | 218698 |
| 7 | 14.195 | $CH_3COOH$ (Solv.) | 31434402 |
| 8 | 20.022 | 1-Phenylethanol (Stand.) | 22217797 |
| 9 | 23.963 | **CA** | 19465837 |

Entry 3




| Entry | Retention Time [min] | Substance | Area |
|---|---|---|---|
| 1 | 4.123 | **CH** | 345223 |
| 2 | 4.428 | **CE** | 2222789 |
| 3 | 4.935 | $CH_2Cl_2$ (Solv.) | 572180609 |
| 4 | 8.937 | *n*-Dodecane (Stand.) | 29129720 |
| 5 | 12.233 | **CAc** | 716350 |
| 6 | 12.933 | **CI** | 322269 |
| 7 | 14.135 | $CH_3COOH$ (Solv.) | 37123096 |
| 8 | 20.007 | 1-Phenylethanol (Stand.) | 23395148 |
| 9 | 23.952 | **CA** | 30421755 |

## S4 NMR and Mass Spectra

### S4.1 Additional NMR Spectra to Table Table S2.7

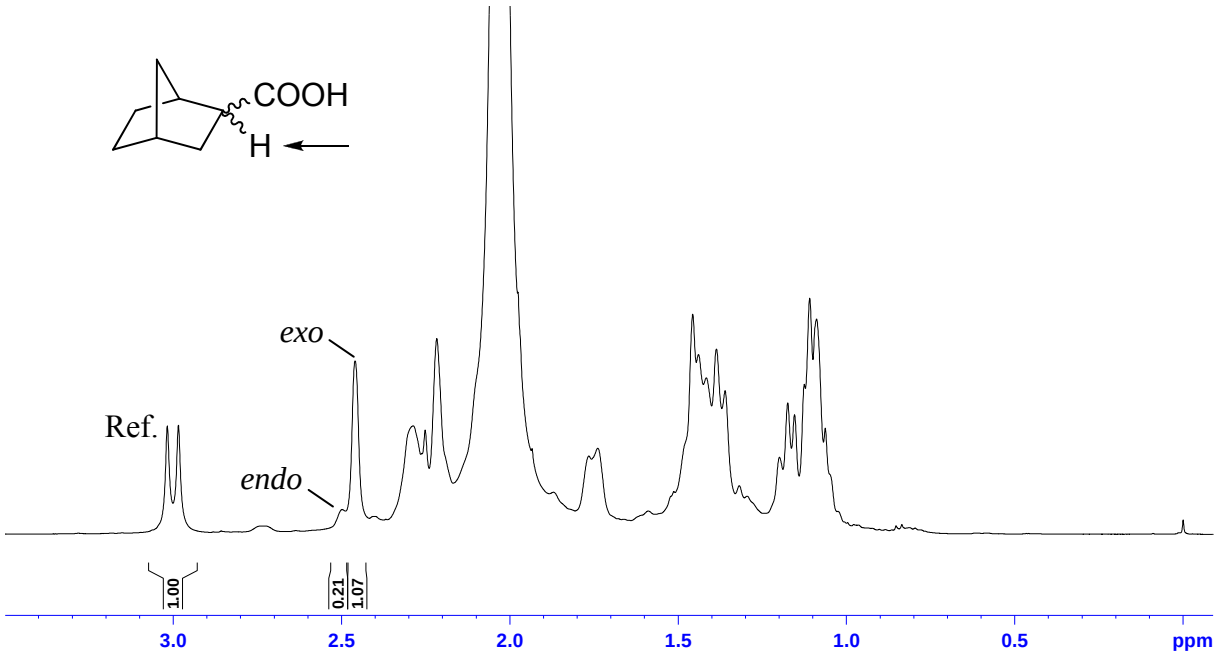



**Figure S4.1.** $^{1}$H NMR spectrum of the reaction mixture after the catalysis with the substrate norbornene indicating the ratio of the integrals for *exo*/*endo* substitution. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

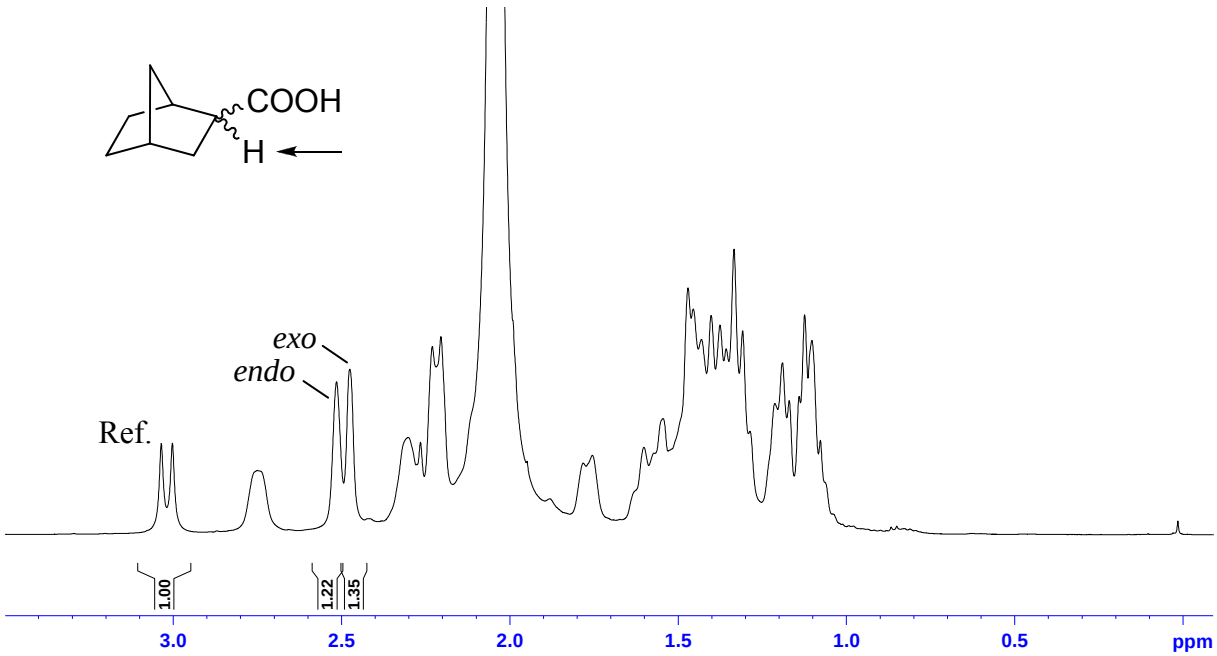



**Figure S4.2.** $^{1}$H NMR spectrum of the reaction mixture after the catalysis with the substrate norbornene indicating the ratio of the integrals for *exo*/*endo* substitution enriched with pure *endo* product. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

## S4.2 NMR Spectra to Table S2.9

Entry 1

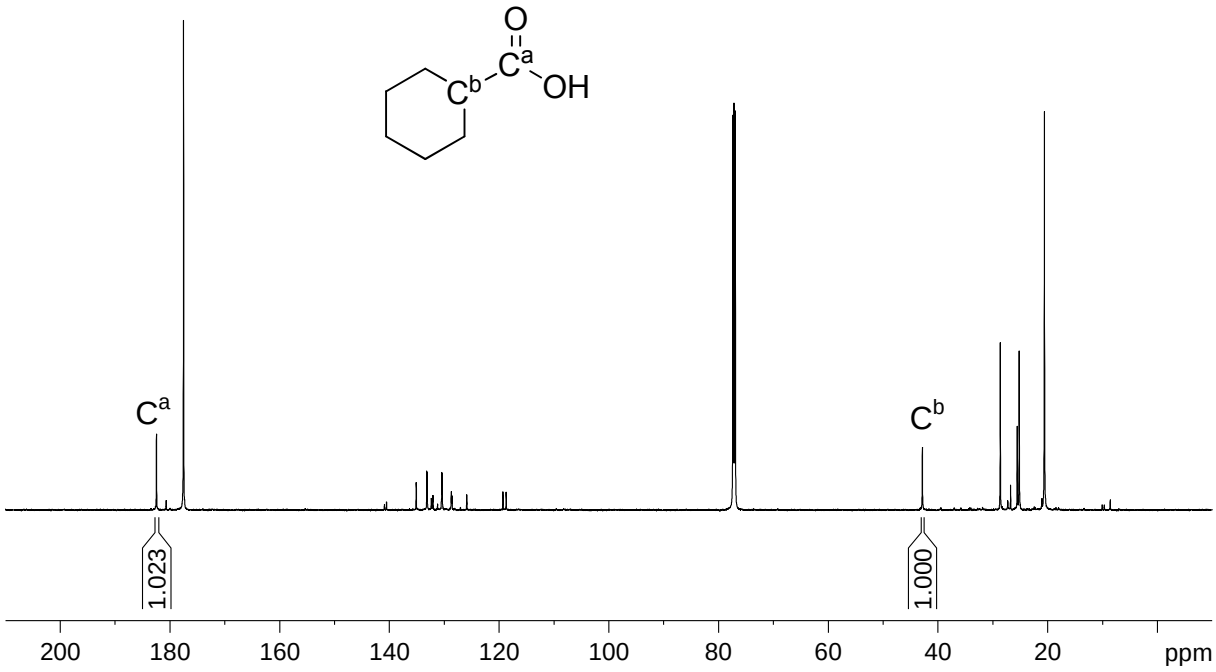



**Figure S4.3.** Quantitative $^{13}C$ NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for $C^a$:$C^b$. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 2

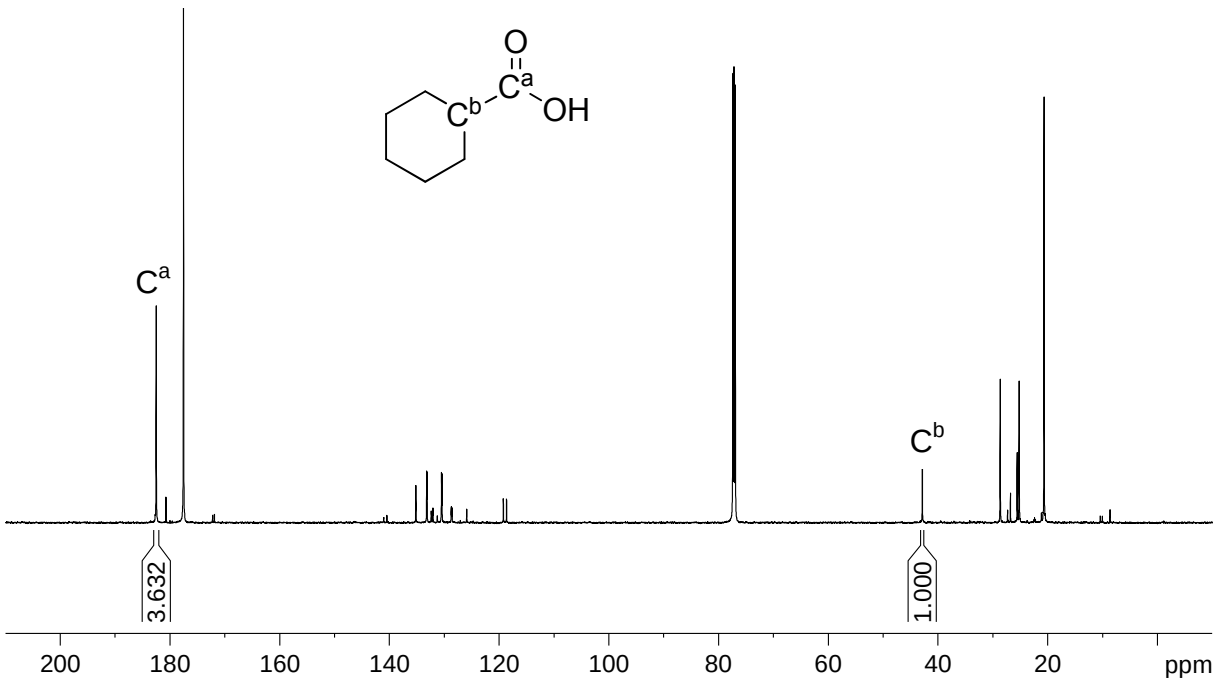



**Figure S4.4.** Quantitative $^{13}C$ NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for $C^a$:$C^b$. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 3

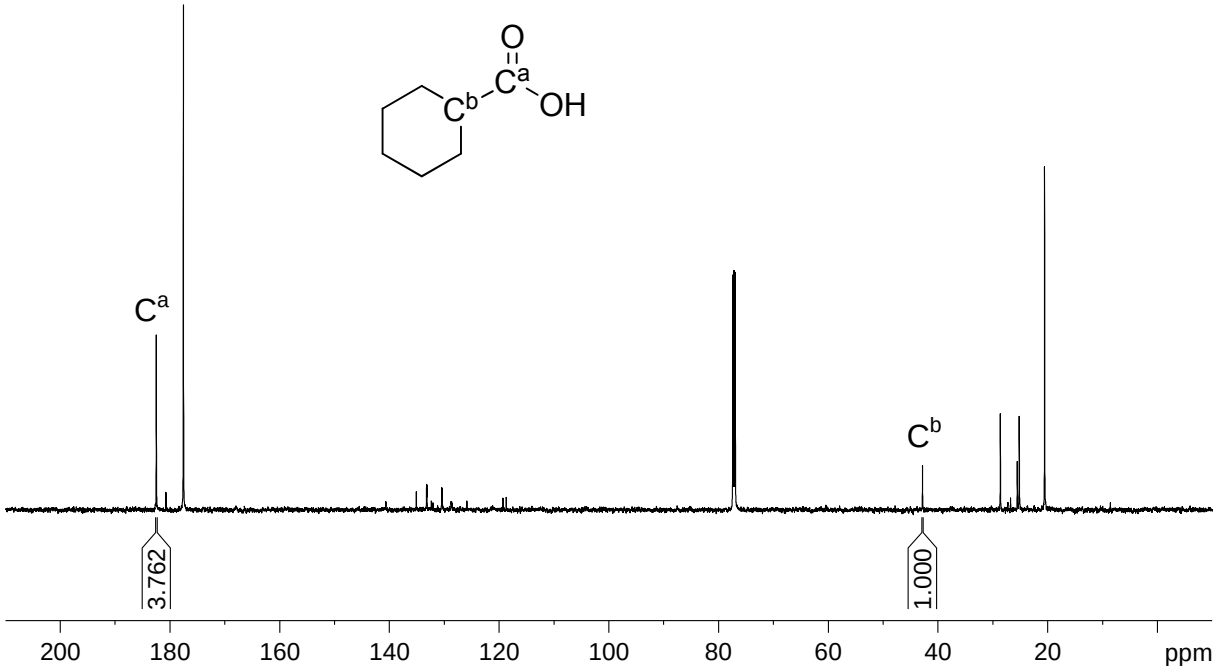



**Figure S4.5 .** Quantitative $^{13}C$ NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for $C^a$:$C^b$. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 4

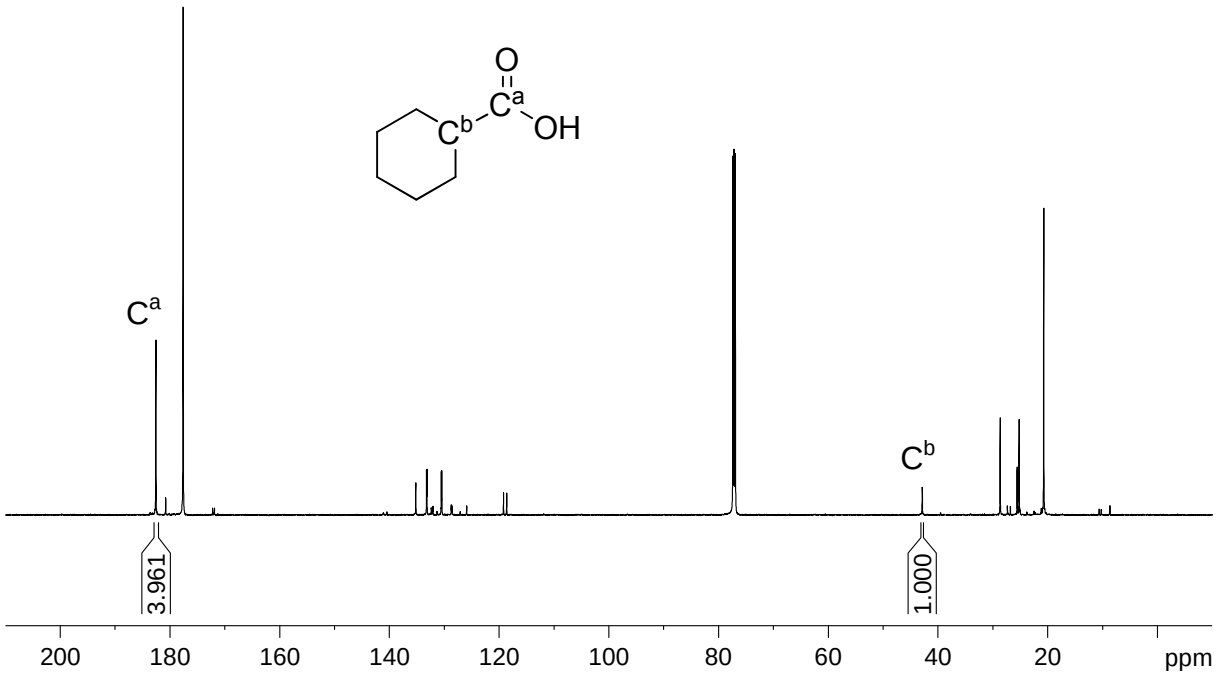



**Figure S4.6.** Quantitative $^{13}C$ NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for $C^a$:$C^b$. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 5

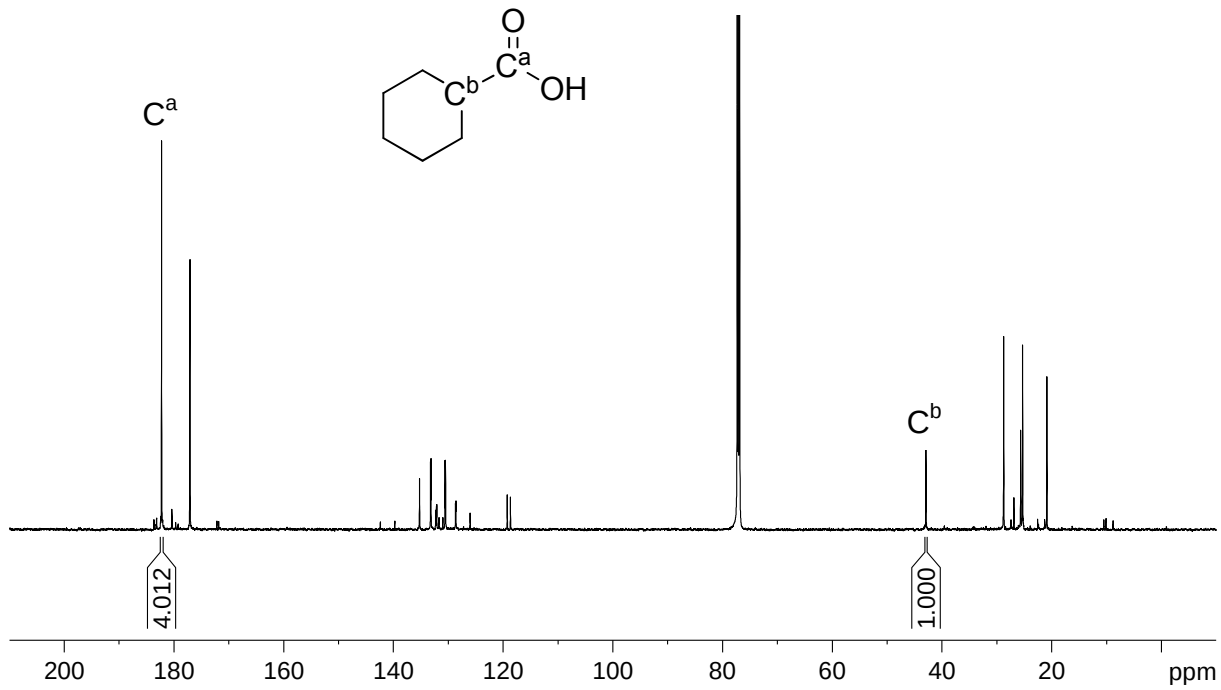



**Figure S4.7.** Quantitative $^{13}C$ NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for $C^a$:$C^b$. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 6

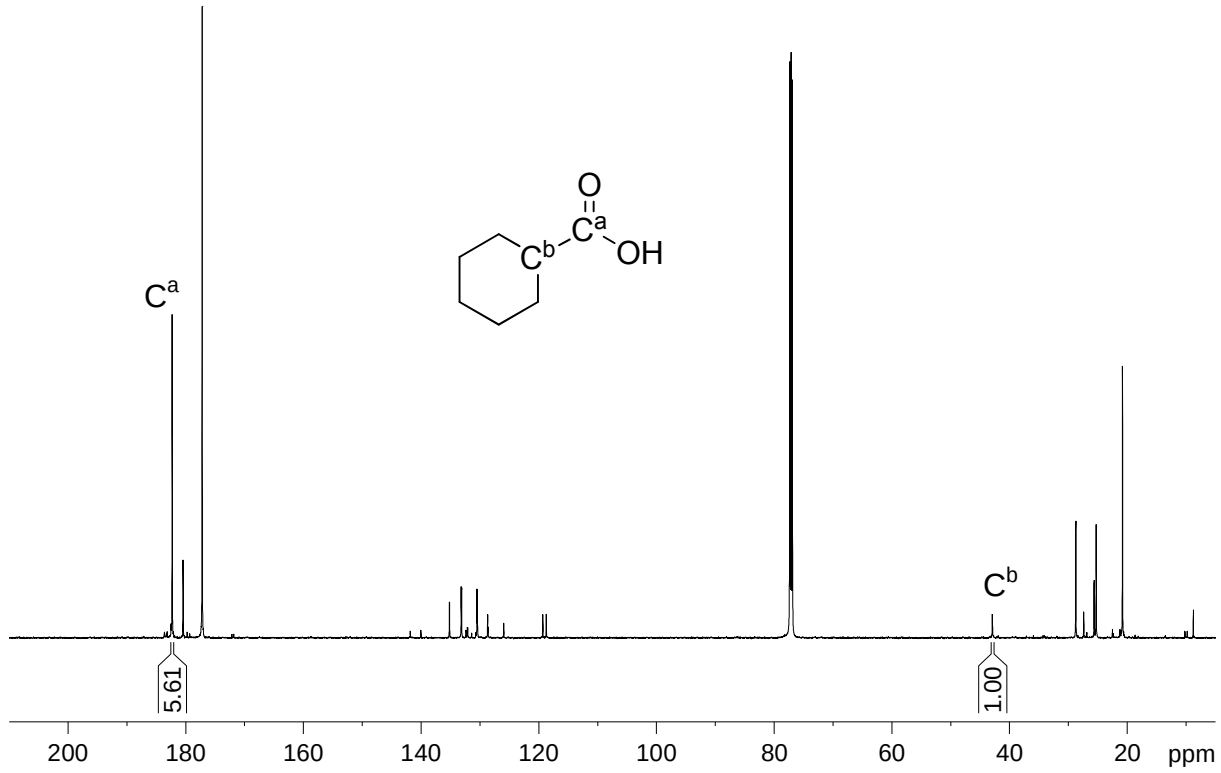



**Figure S4.8.** Quantitative $^{13}C$ NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for $C^a$:$C^b$. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

## S4.3 NMR Spectra to the $D_2$ labelling experiment

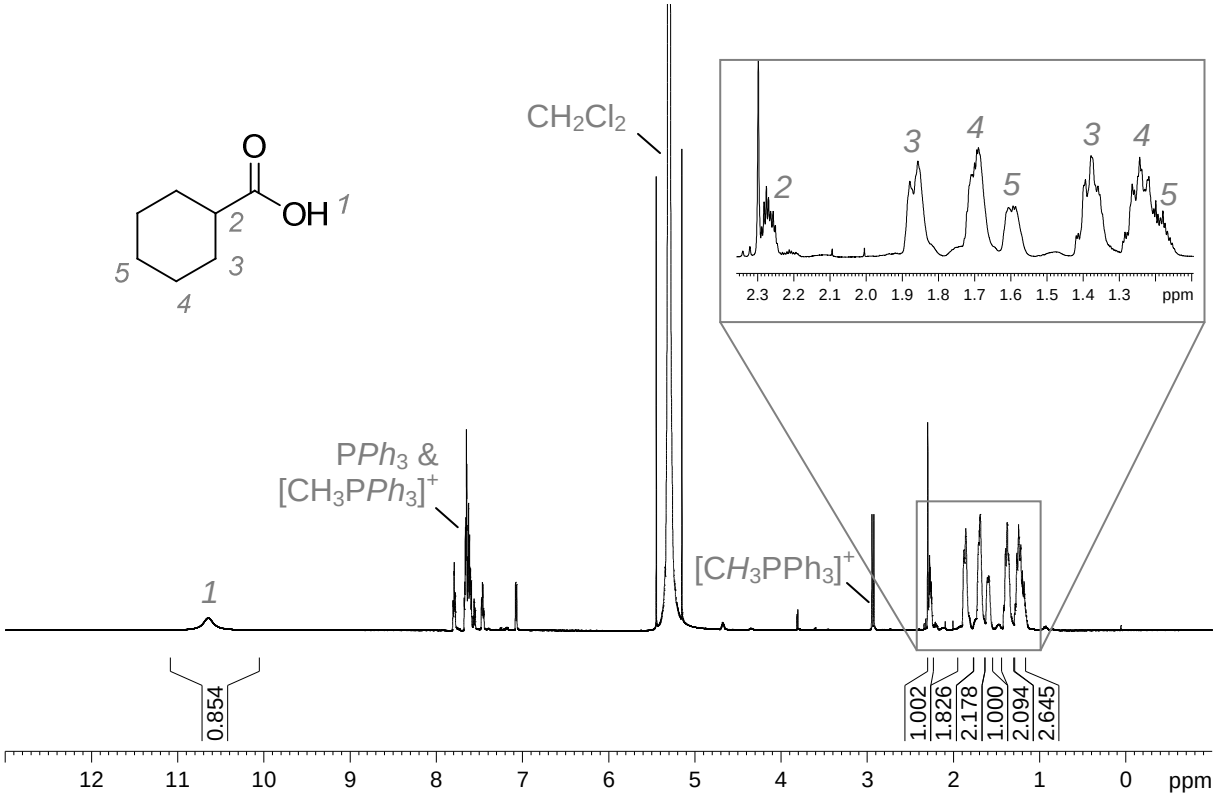



**Figure S4.9.** $^{1}$H NMR spectrum of the reaction mixture after the catalysis with integrals for the cyclohexanoic acid product **CA**. Measured in $CH_2Cl_2$ at ambient temperature with a resonance frequency of 600 Mhz. Signal assignment based on $^{1}$H-$^{13}$C HSQC and HMBC NMR experiment.

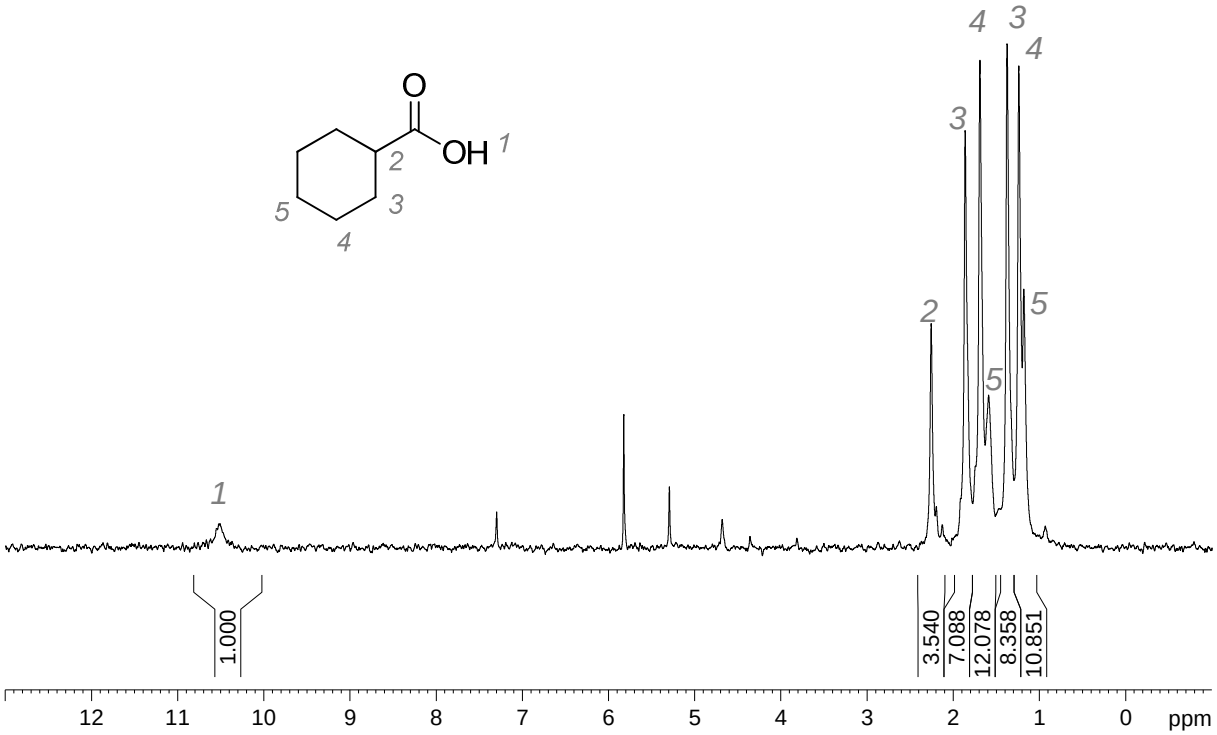



**Figure S4.10.** $^{2}$H NMR spectrum of the reaction mixture after the catalysis with integrals for the cyclohexanoic acid product **CA**. Measured in $CH_2Cl_2$ at ambient temperature with a resonance frequency of 92 Mhz.

## S4.4 NMR Spectra to the $D_2O$ labelling experiments

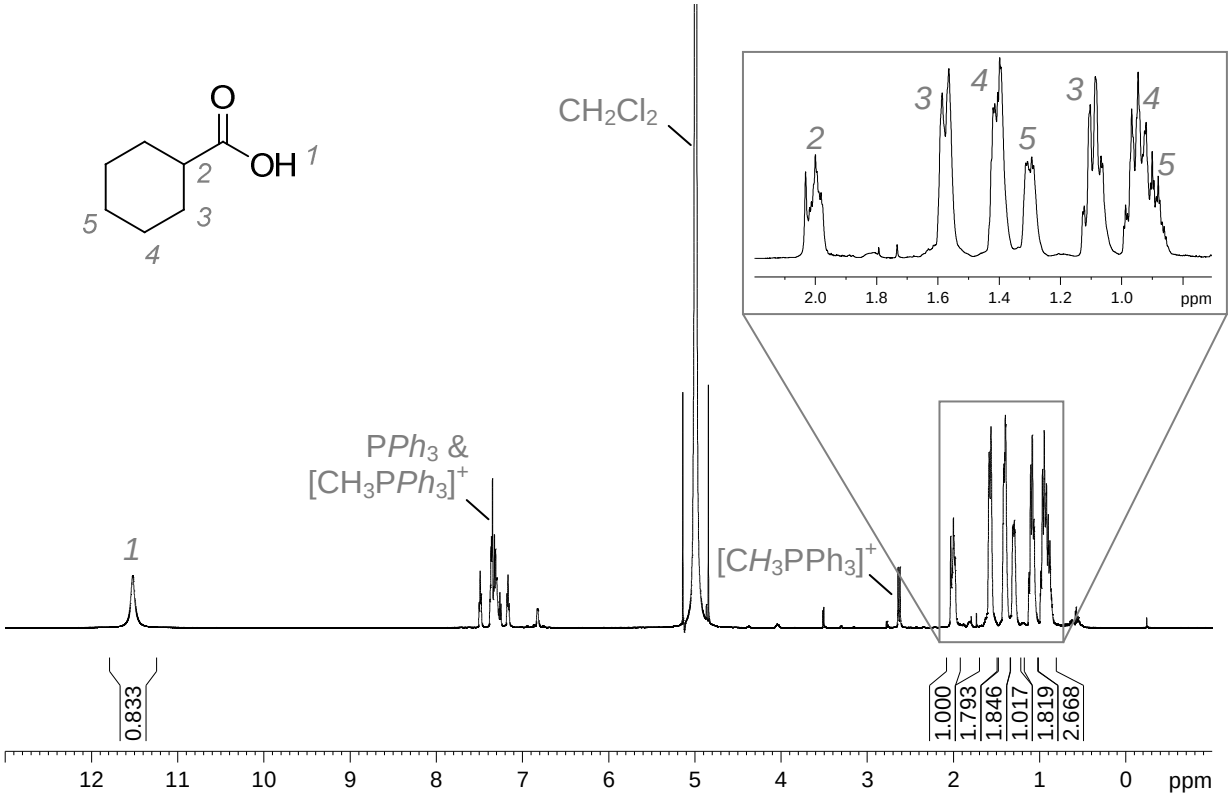



**Figure S4.11.** $^{1}$H NMR spectrum of the reaction mixture after the catalysis with integrals for the cyclohexanoic acid product **CA**. Measured in $CH_2Cl_2$ at ambient temperature with a resonance frequency of 600 Mhz. Signal assignment based on $^{1}$H-$^{13}$C HSQC and HMBC NMR experiment.

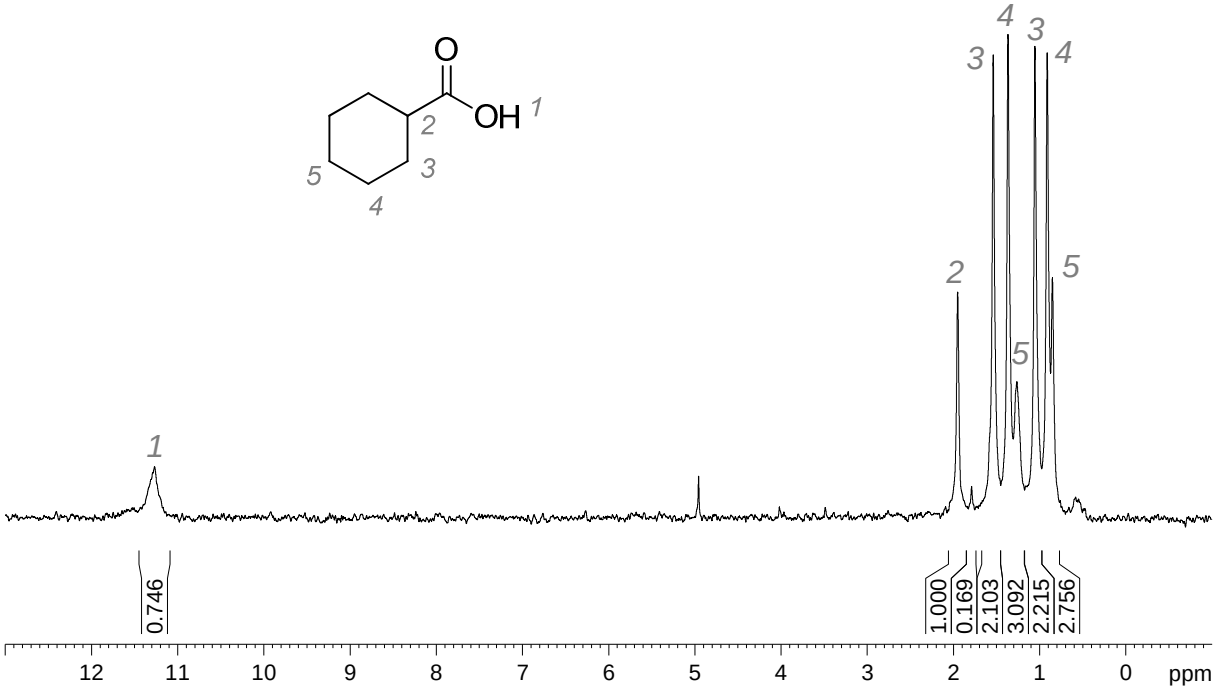



**Figure 4.12.** $^{2}$H NMR spectrum of the reaction mixture after the catalysis with integrals for the cyclohexanoic acid product **CA**. Measured in $CH_2Cl_2$ at ambient temperature with a resonance frequency of 92 Mhz.

## S4.5 Mass Spectra to the $H_2{}^{18}O$ labelling experiments

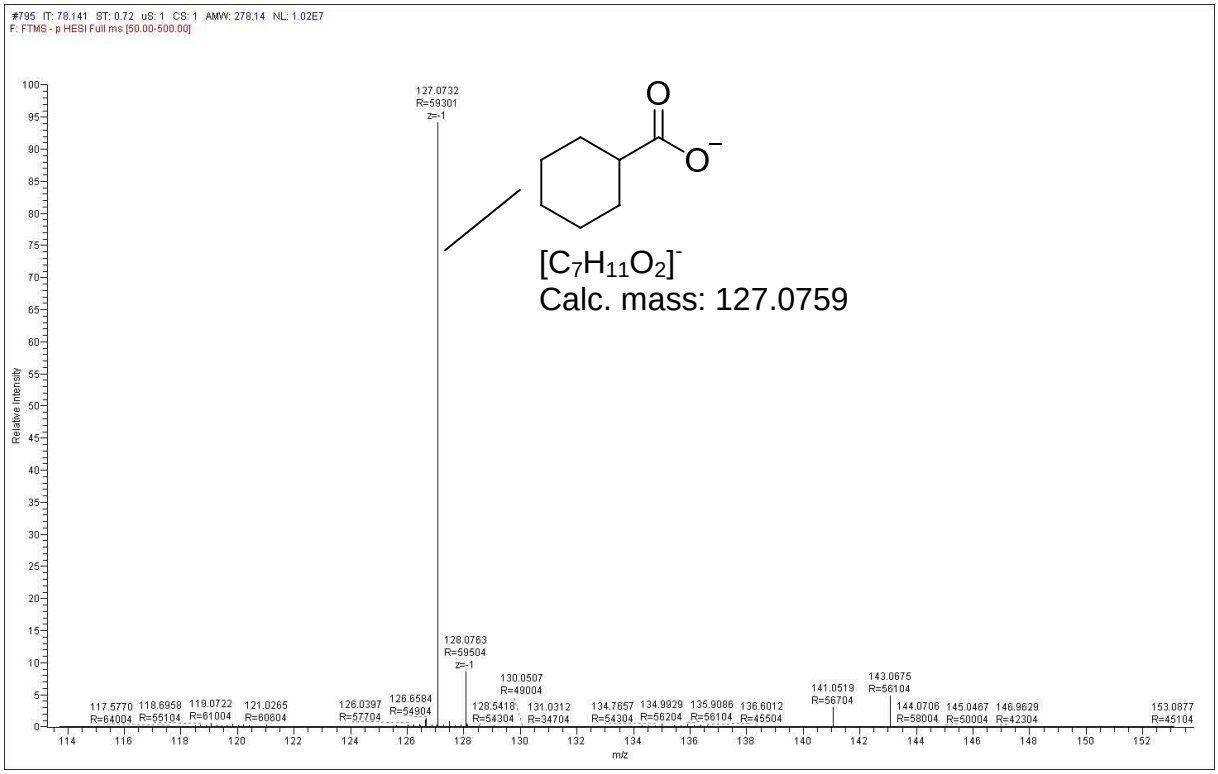



**Figure S4.13.** High resolution mass spectrum of the reaction mixture after the catalysis without addition of $H_2{}^{18}O$ for the cyclohexanoic acid product **CA**. Measured as ESI(-) in Methanol at ambient temperature.

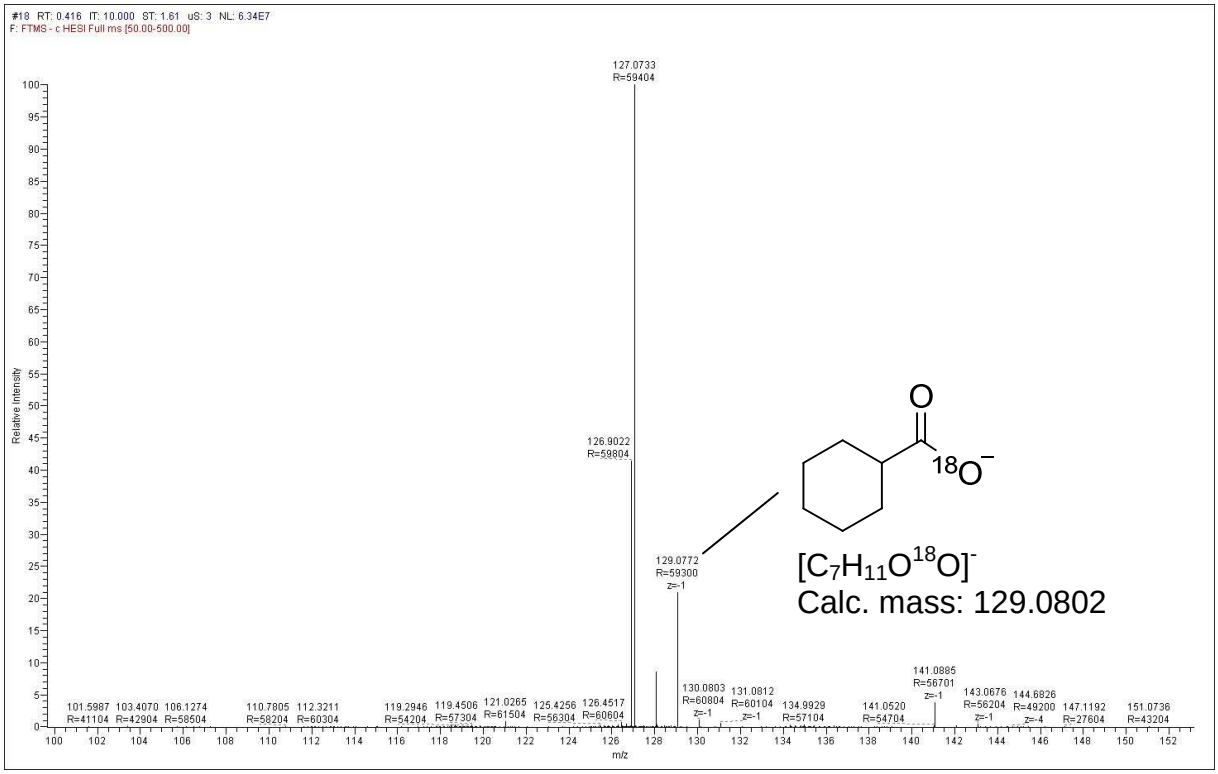



**Figure S4.14.** High resolution mass spectrum of the reaction mixture after the catalysis with addition of $H_2{}^{18}O$ for the cyclohexanoic acid product **CA**. Measured as ESI(-) in Methanol at ambient temperature.

## S4.6 Mass Spectra to the $H_2{}^{18}O$ control experiment

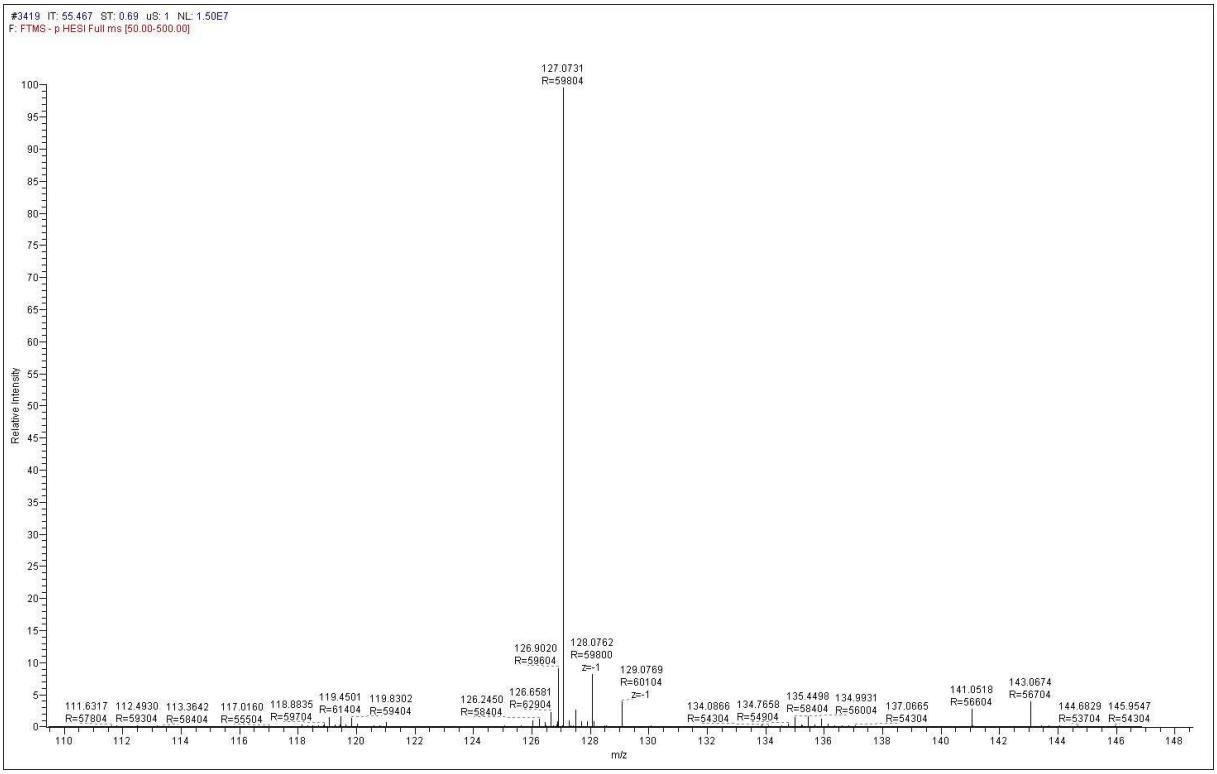



**Figure 4.15.** High resolution mass spectrum of the reaction mixture after the control experiment with addition of $H_2{}^{18}O$ for the cyclohexanoic acid product **CA**. Measured as ESI(-) in Methanol at ambient temperature.

## S5 Crystallographic Details

Crystal data and refinement results have been compiled in Table S5.1. Intensity data were collected at 100 K with a *Bruker APEX* area detector equipped with an *Incoatec microsource* (Mo-$K_\alpha$, $\lambda = 0.71073$ Å, multilayer optics). Temperature was controlled with an *Oxford Cryostream 700* instrument. Intensities were integrated with *SAINT+*[4] and corrected for absorption by multi-scan methods with *SADABS*[5]. The structure was solved by direct methods.[6] The structures were refined by full matrix least squares procedures as implemented in *SHELXL-97*.[6] All non-hydrogen atoms in the target molecule were assigned anisotropic displacement parameters. The hydrogen atoms were included as riding. Isotropic displacement parameters were assigned to all atoms with fractional site occupancies.

**Table S5.1.** Crystallographic data to the structure.

| Parameter | | Parameter | |
|---|---|---|---|
| Empirical formula | $C_{19}H_{15}I_4OPRh$, $C_{19}H_{18}P$ | $V$/Å$^3$ | 3814.5(6) |
| $M$/g mol$^{-1}$ | 1178.09 | $Z$ | 4 |
| Crystal dimensions/mm | 0.01 x 0.12 x 0.30 | $\mu$(Mo $K_\alpha$)/mm$^{-1}$ | 3.798 |
| Crystal shape | Block | Scan range (θ)/° | 1.71 / 30.82 |
| Crystal color | Dark brown | Total reflections | 56229 |
| Crystal system | Monoclinic | Unique reflections | 11273 |
| Space group (no.) | P $2_1/n$ | Variables refined | 416 |
| $a$/Å | 15.4392(15) | $R_{int}$ | 0.0400 |
| $b$/Å | 15.0715(14) | $wR_2$ (all reflections) | 0.0747 |
| $c$/Å | 16.5045(16) | $R_1$ (all/obs.) | 0.0376 / 0.0291 |
| $\alpha$/° | 90.00 | GOF on $F^2$ | 1.084 |
| $\beta$/° | 96.6600(10) | Diff. peak/hole [e/ Å$^{-3}$] | 1.671 / -0.550 |
| $\gamma$/° | 90.00 | | |

Further details on the crystallographic studies including fractional coordinates, displacement parameters and molecular geometry are given in the CIF format. Crystallographic data (excluding structure factors) for all data collections will be deposited at the Cambridge Crystallographic Data Centre as supplementary publications numbers when the manuscript is accepted for publication. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: int. code +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk; web, www:http://www.ccdc.cam.ac.uk).

## S6 References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