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Supporting Information

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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.

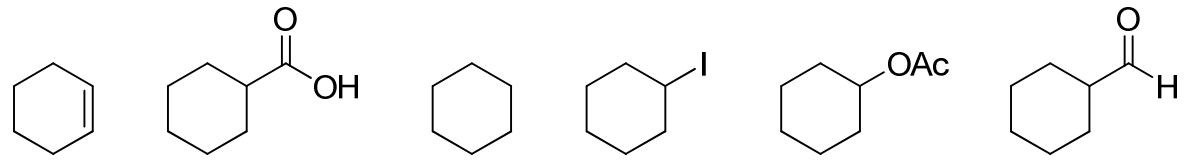
NMR Spectroscopy. NMR spectra were recorded with spectrometers *Bruker AV-600, AV-III-400* or *-300* at ambient temperature at the frequency noted. Chemical shifts δ are given in ppm relative to tetramethylsilane (^{1}H, ^{2}H and ^{13}C).

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.

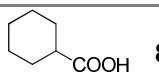
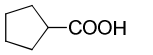
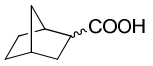
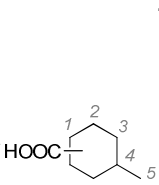
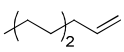
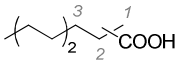
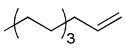
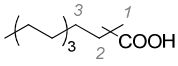
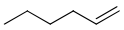
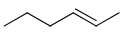
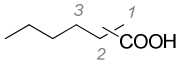
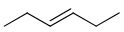
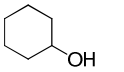
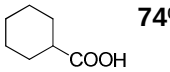
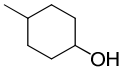
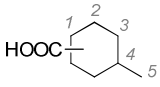
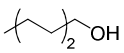
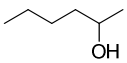
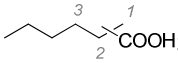
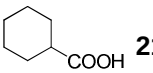
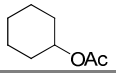
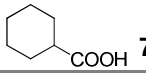
Entry	Reaction time [h]	Conv. [%]	Yield of **CA** [%]	Yield of **CH** [%]	Yield of **CI** [%]	Yield of **CAc** [%]	GC at page
1	1	40	3	2	15	2	S54
2	2	63	27	3	11	4	S55
3	3	80	47	4	11	5	S56
4	6	90	70	5	9	3	S57
5	9	96	77	5	3	1	S58
6	12	98	81	5	3	1	S59
7	16	>99	85	5	1	<1	S60
8	20	>99	85	5	2	1	S61

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* **12**% *endo*		S64
4		96	 **44%** COOH at *1* **20%** COOH at *2/3* **9%** COOH at *5*		S65
5		98	**46%** COOH at *1* **20%** COOH at *2/3* **8%** COOH at *5*		S66
6		99	**52%** COOH at *1* **18%** COOH at *2/3* **7%** COOH at *5*	**75%** yellowish oil	S67
7		99	 **42%** COOH at *1* **22%** COOH at *2* **10%** COOH at *3*		S69
8		98	 **31%** COOH at *1* **17%** COOH at *2* **6%** COOH at *3* **7%** COOH at *4*		S70
9		93	**53%** COOH at *1* **26%** COOH at *2* **11%** COOH at *3*	**76**% yellowish oil	S71
10		97	 **43%** COOH at *1* **24%** COOH at *2* **11%** COOH at *3*		S73
11		93	**45%** COOH at *1* **23%** COOH at *2* **10%** COOH at *3*		S74
12		>99	 **74**%	**73**% yellowish oil, solidifies upon standing (mp_{Lit} = 29℃)	S75
13		99	 **48%** COOH at *1* **19%** COOH at *2/3* **7%** COOH at *5*		S77
14		> 99	**41%** COOH at *1* **15%** COOH at *2* **6%** COOH at *3*	**55**% yellowish oil	S78
15		> 99	 **37%** COOH at *1* **19%** COOH at *2* **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.

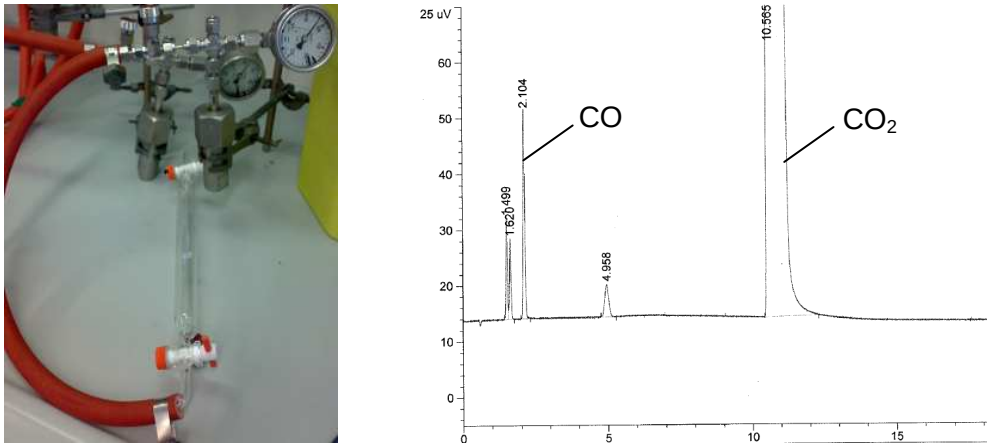


Figure 2.1. *Left*: Gas tube to trap the gas phase from the autoclave after the reaction. *Right*: Part of the GC chromatogram taken from the gas phase analysis after the reaction.

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

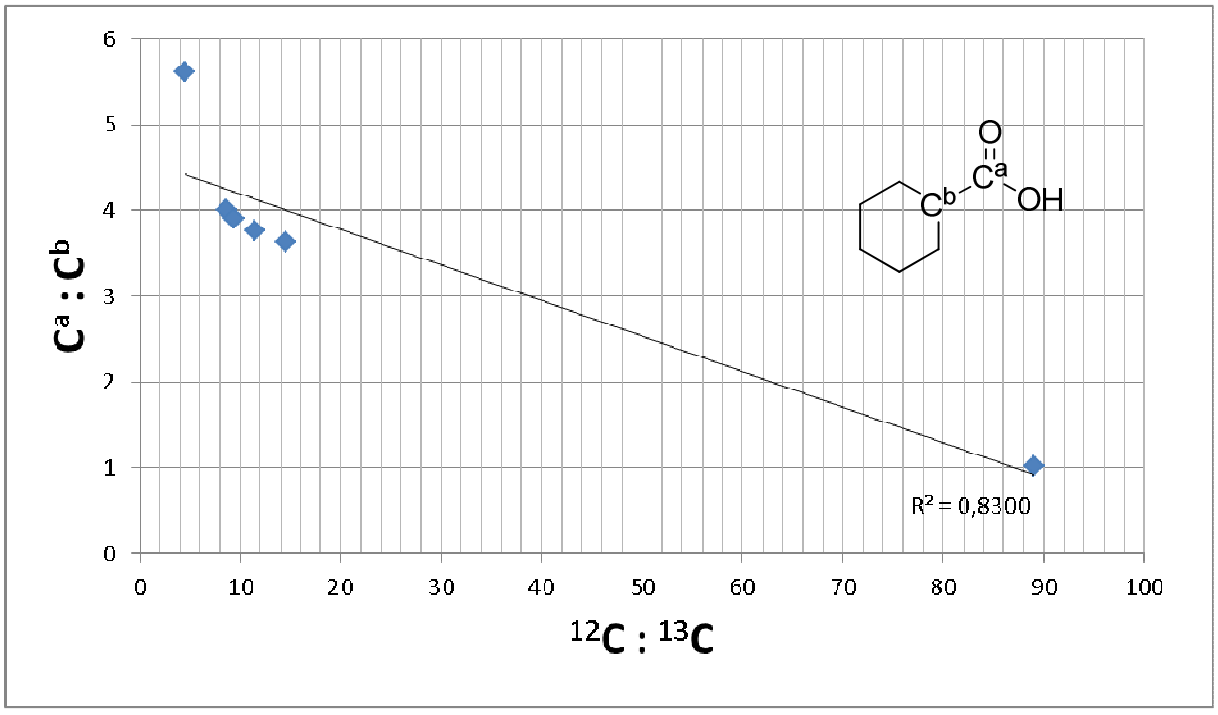


Figure S2.2. Diagram of the ratios of ^{12}C:^{13}C in CO_2 versus the product data obtained from ^{13}C NMR spectroscopy.

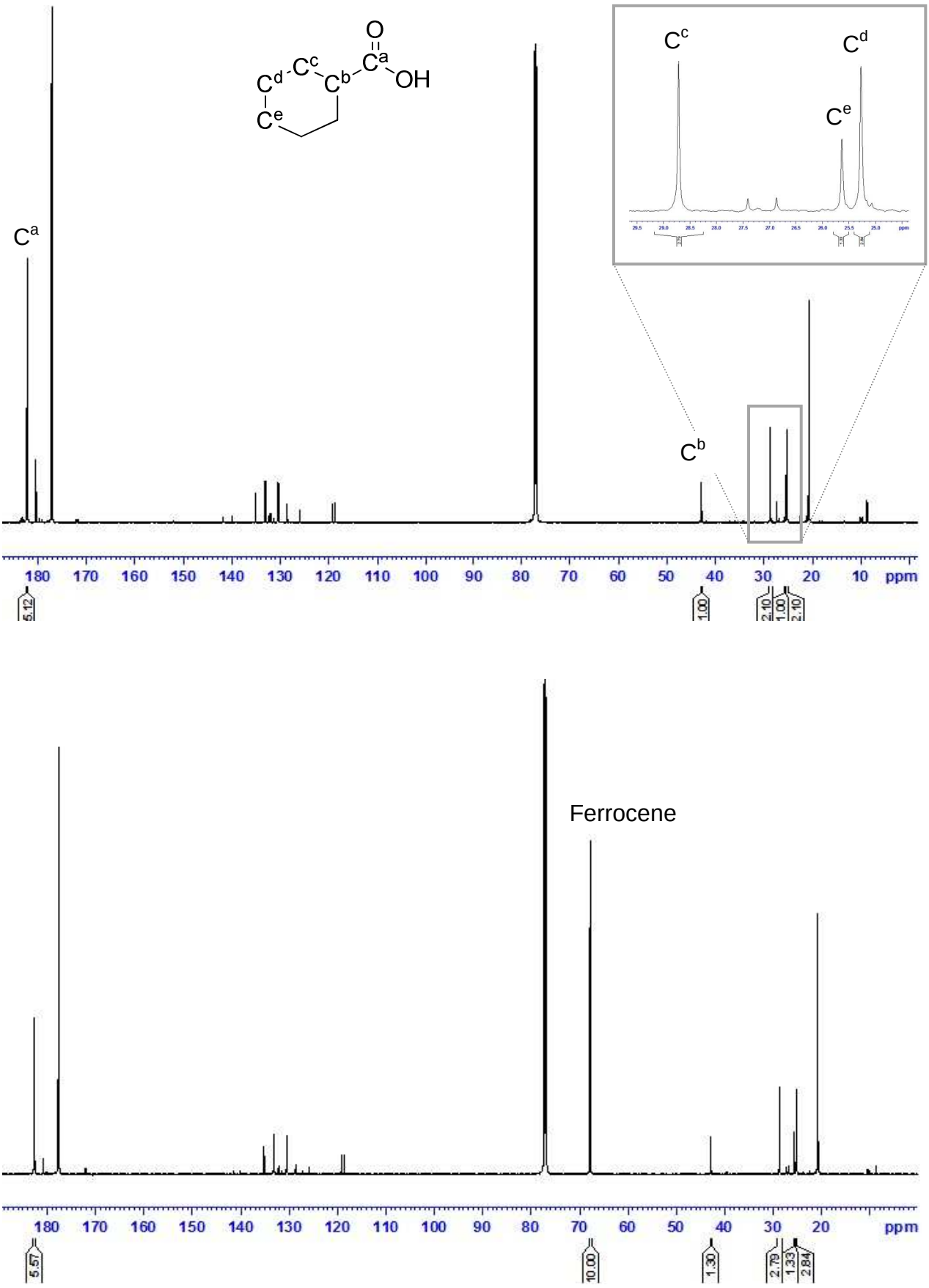


Figure S2.3. ^{13}C NMR spectra of one labeling experiment without (*top*) and with addition of ferrocene (*bottom*) as external NMR standard.

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.

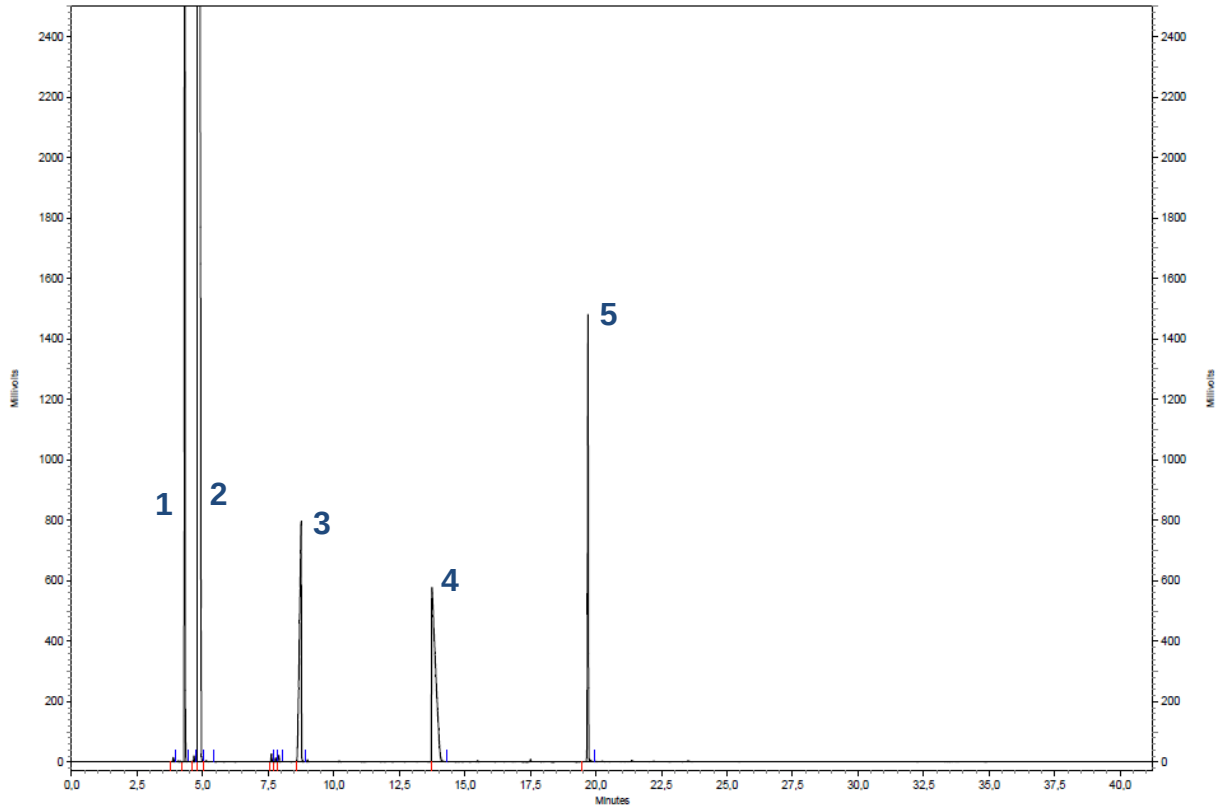
Procedure for the $H_2{}^{18}O$ labelling experiments: Under an argon atmosphere, $[RhCl(CO)_2]_2$ (46 µmol), cyclohexene (1.88 mmol) and **CI**+LiI (184+ 736 µmol) were weighed into a Schlenk tube along with acetic acid (0.65 mL) and $H_2{}^{18}O$ (0.3 mL). The red brownish solution was transferred 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

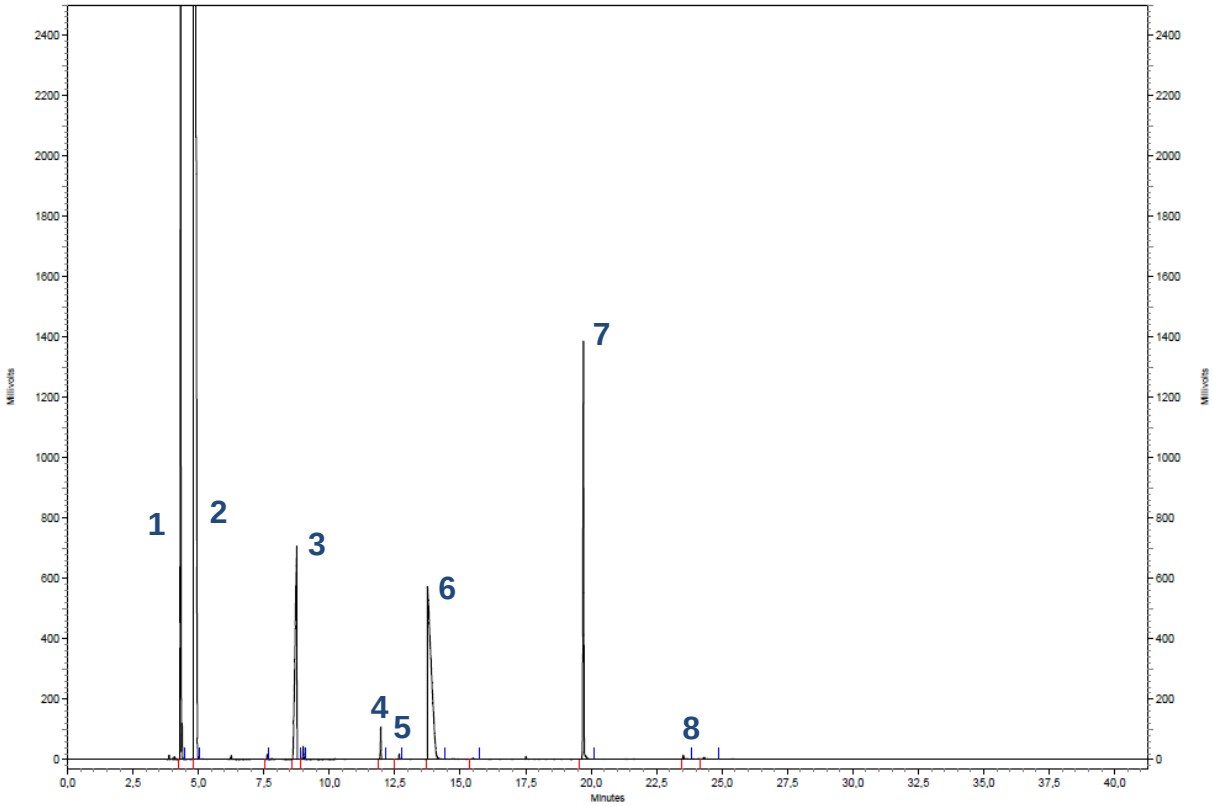
S3.1 Gaschromatograms to Table S2.1

Entry 1



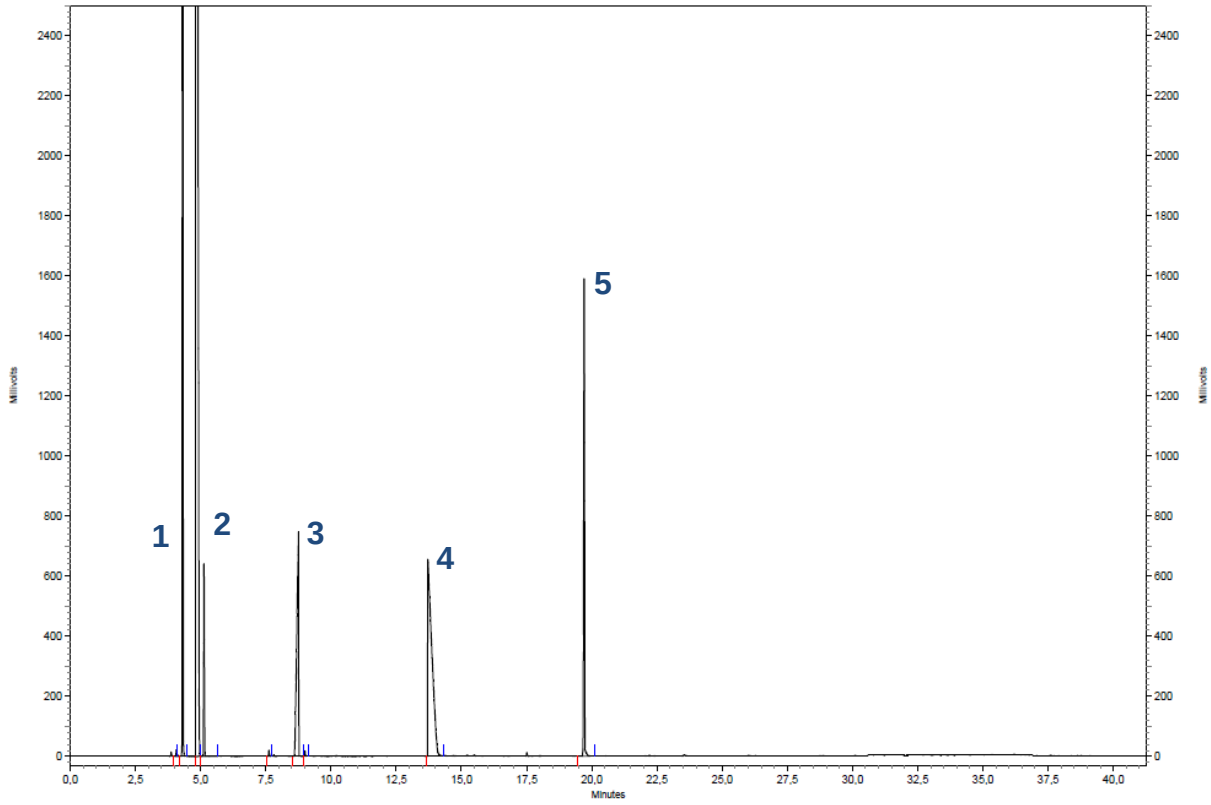
Entry	Retention Time [min]	Substance	Area
1	4.317	**CE**	58098986
2	4.798	CH_2Cl_2 (Solv.)	538231322
3	8.760	*n*-Dodecane (Stand.)	38862081
4	13.745	CH_3COOH (Solv.)	57959547
5	19.703	1-Phenylethanol (Stand.)	28757687

Entry 2



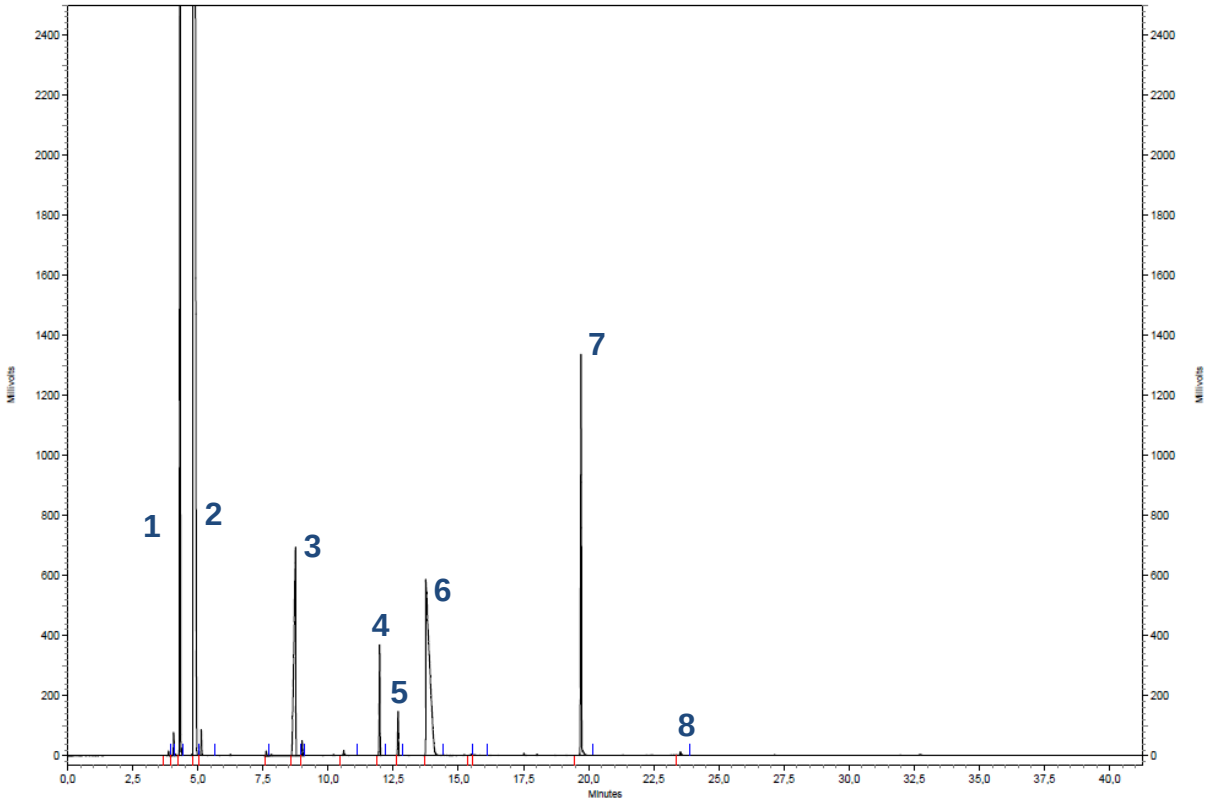
Entry	Retention Time [min]	Substance	Area
1	4.318	**CE**	50062542
2	4.798	CH_2Cl_2 (Solv.)	542094021
3	8.753	*n*-Dodecane (Stand.)	32665215
4	11.963	**CAc**	1747061
5	12.668	**CI**	310187
6	13.745	CH_3COOH (Solv.)	56923094
7	19.703	1-Phenylethanol (Stand.)	27072815
8	23.312	**CA**	308705

Entry 3



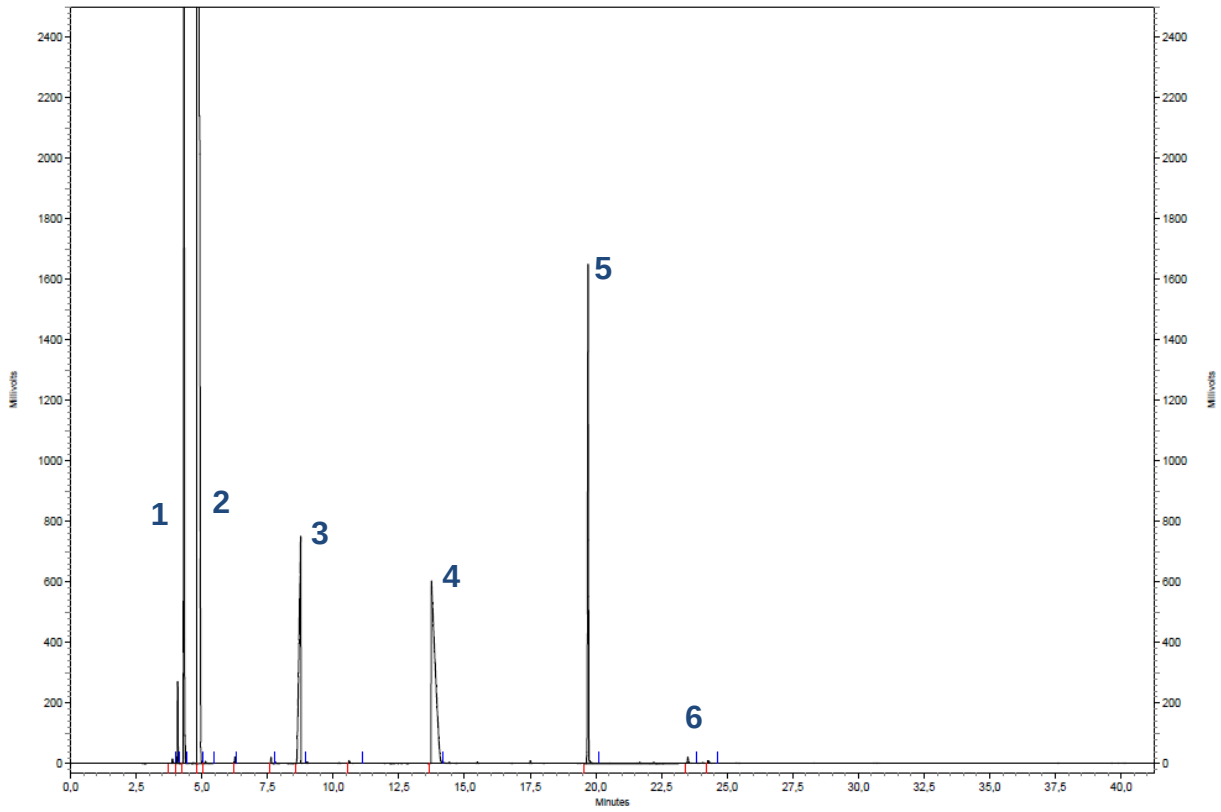
Entry	Retention Time [min]	Substance	Area
1	4.310	**CE**	66855521
2	4.790	CH_2Cl_2 (Solv.)	535246491
3	8.753	*n*-Dodecane (Stand.)	34948061
4	13.715	CH_3COOH (Solv.)	71609064
5	19.708	1-Phenylethanol (Stand.)	32276946

Entry 4



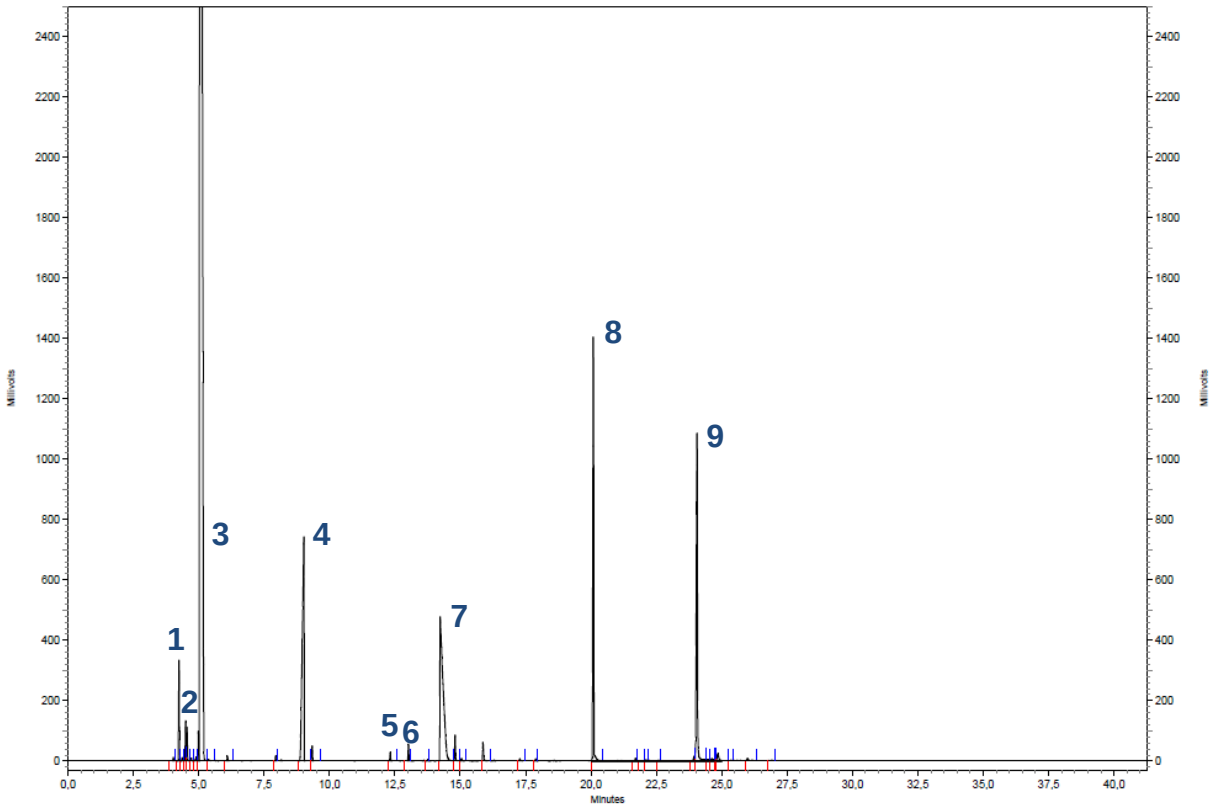
Entry	Retention Time [min]	Substance	Area
1	4.313	**CE**	48194395
2	4.792	CH_2Cl_2 (Solv.)	538476658
3	8.752	*n*-Dodecane (Stand.)	32378855
4	11.983	**CAc**	6877451
5	12.687	**CI**	2662651
6	13.750	CH_3COOH (Solv.)	59668788
7	19.710	1-Phenylethanol (Stand.)	25406361
8	23.525	**CA**	423929

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

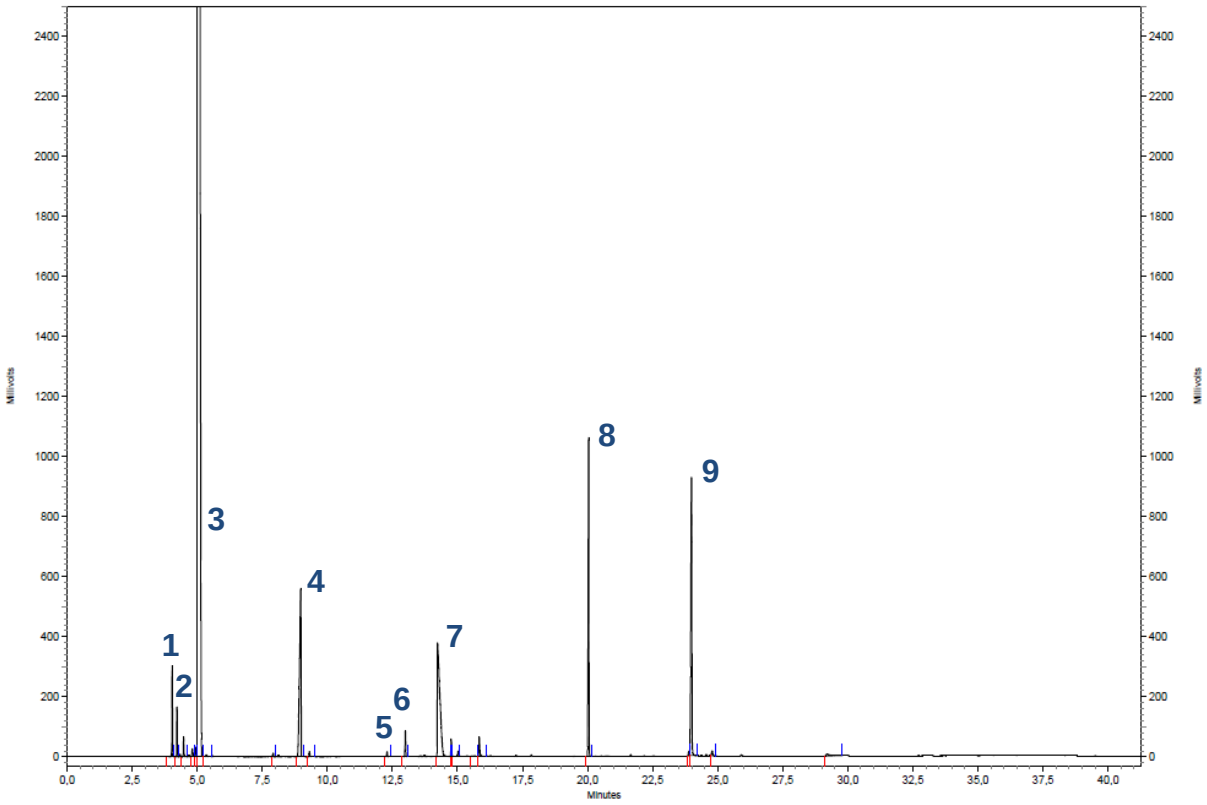
Entry 6



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

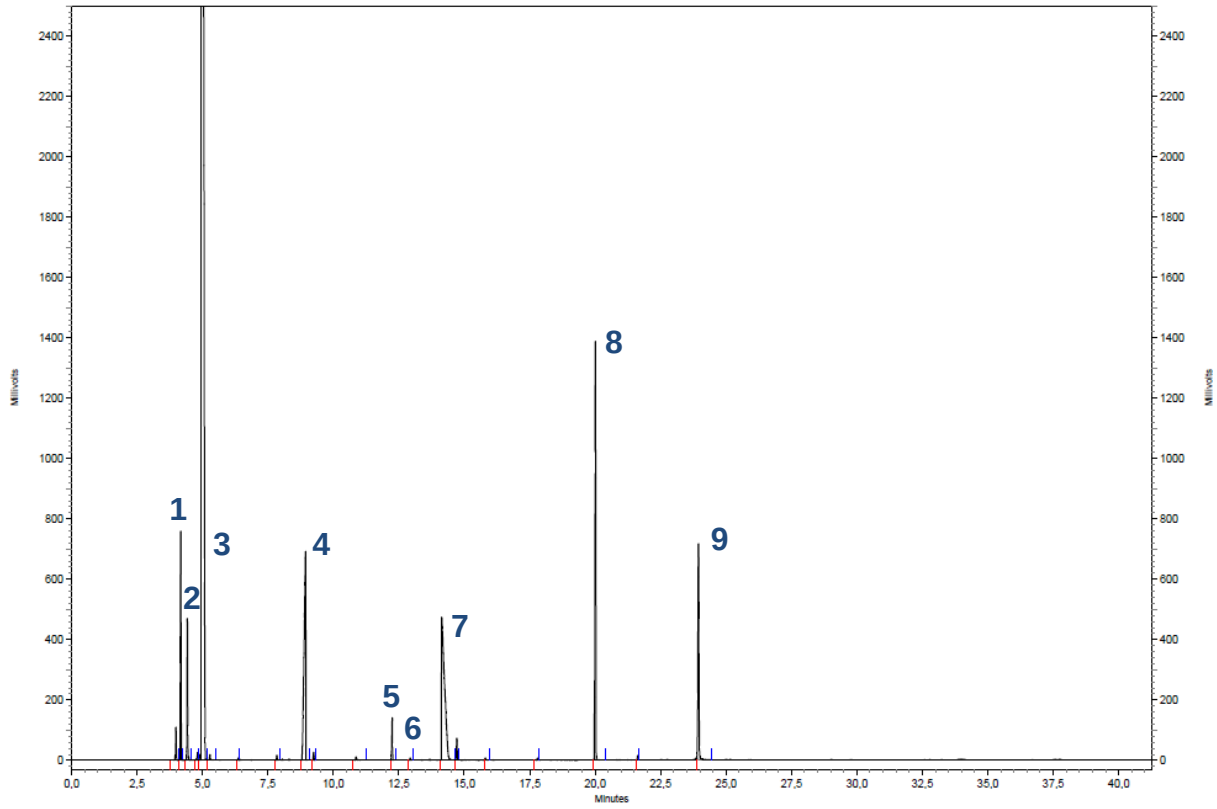
S3.2 Gaschromatograms to Table S2.2

Entry 1



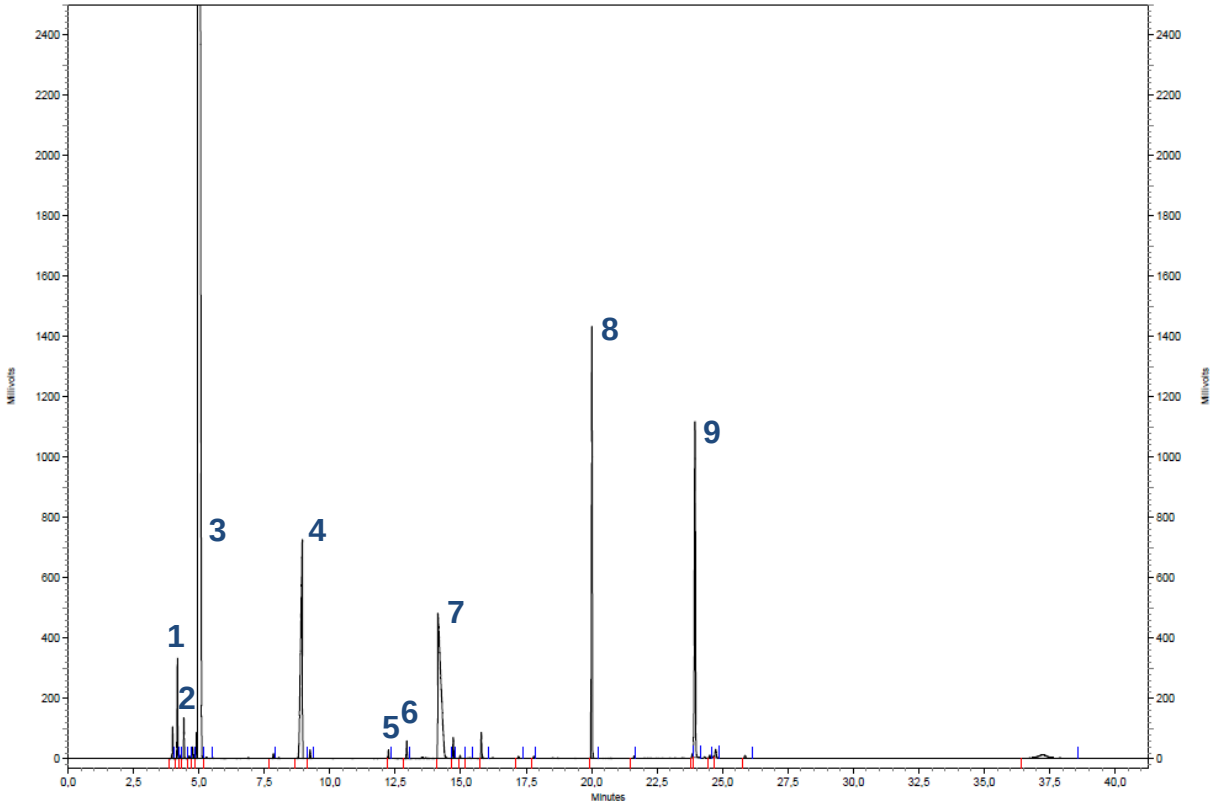
Entry	Retention Time [min]	Substance	Area
1	4.222	**CH**	1991545
2	4.477	**CE**	927542
3	5.017	CH_2Cl_2 (Solv.)	392085582
4	8.980	*n*-Dodecane (Stand.)	20293940
5	12.293	**CAc**	267475
6	13.000	**CI**	1517506
7	14.235	CH_3COOH (Solv.)	25382742
8	20.038	1-Phenylethanol (Stand.)	18798006
9	23.992	**CA**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

Entry 2



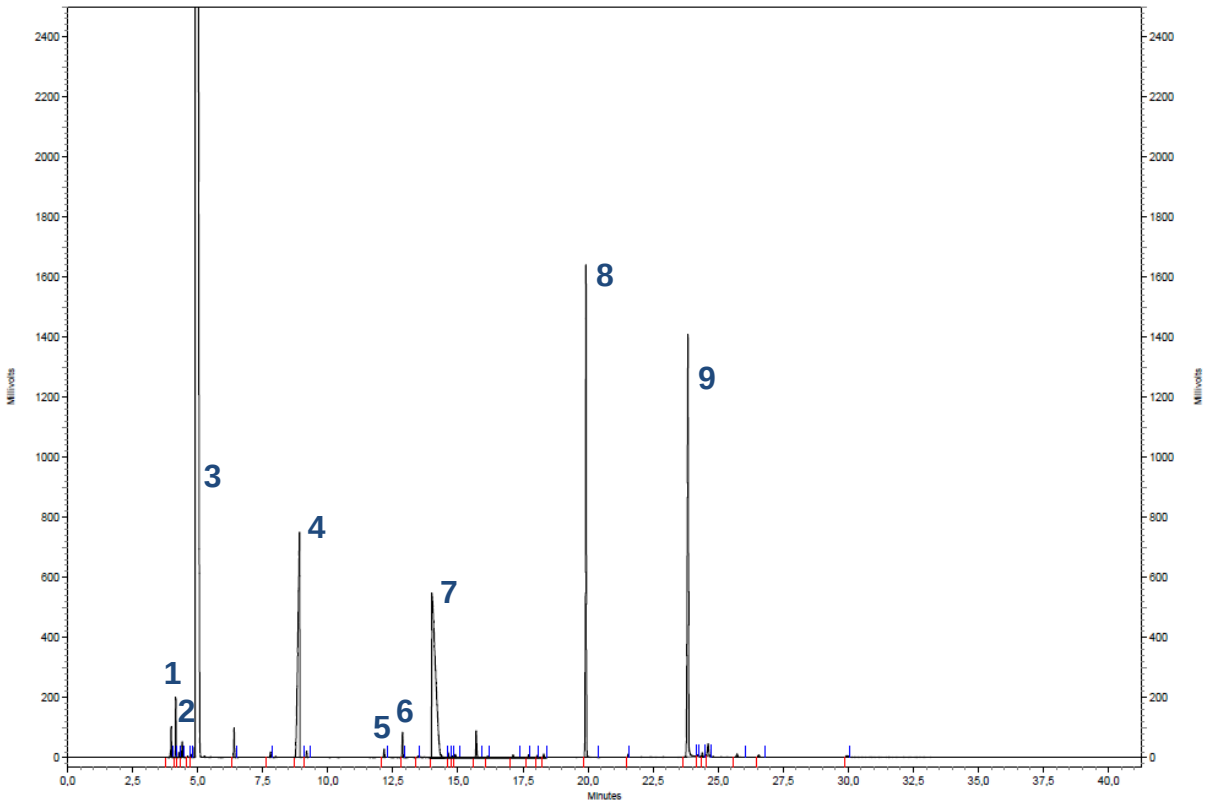
Entry	Retention Time [min]	Substance	Area
1	4.170	**CH**	10035533
2	4.422	**CE**	7333320
3	4.930	CH_2Cl_2 (Solv.)	565209382
4	8.943	*n*-Dodecane (Stand.)	30628600
5	12.245	**CAc**	2297911
6	12.937	**CI**	130155
7	14.135	CH_3COOH (Solv.)	38394893
8	20.012	1-Phenylethanol (Stand.)	26627134
9	23.948	**CA**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

Entry 3



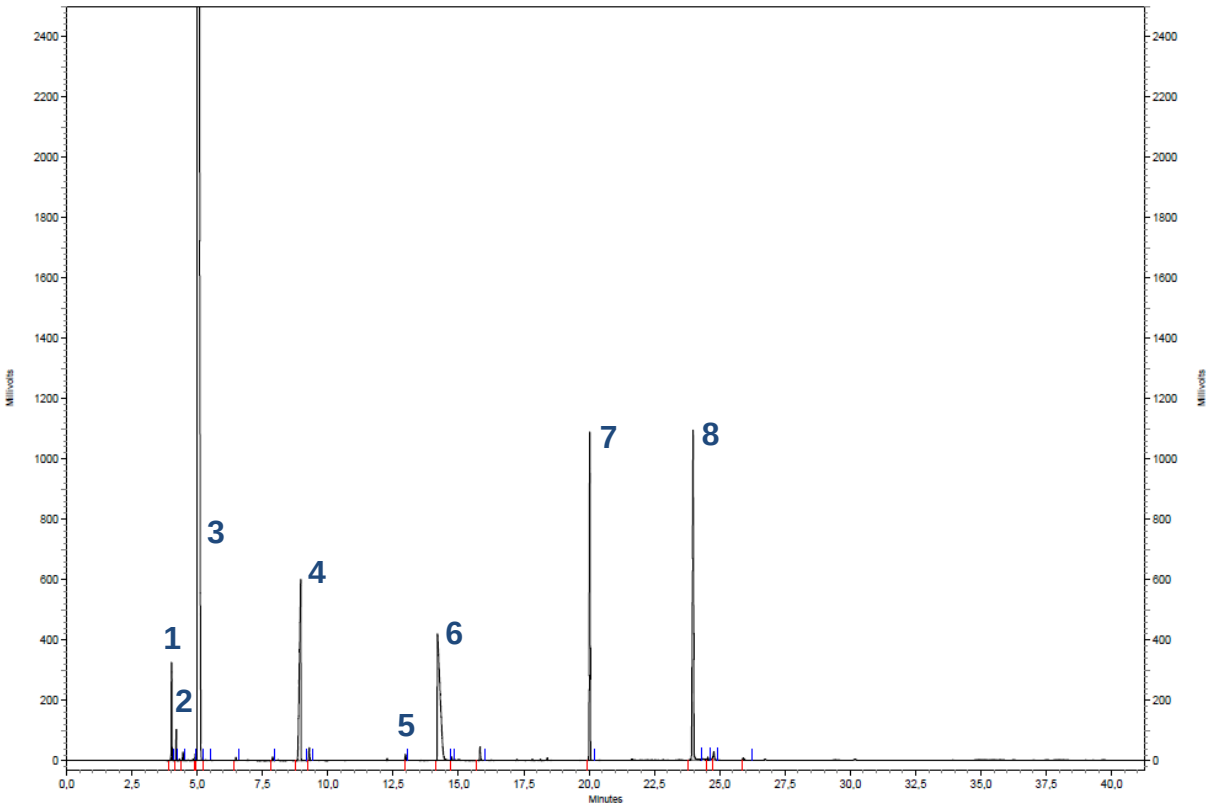
Entry	Retention Time [min]	Substance	Area
1	4.177	**CH**	4374561
2	4.428	**CE**	2088590
3	4.938	CH_2Cl_2 (Solv.)	551017028
4	8.952	*n*-Dodecane (Stand.)	33888780
5	12.238	**CAc**	444846
6	12.942	**CI**	1018953
7	14.128	CH_3COOH (Solv.)	39703195
8	20.012	1-Phenylethanol (Stand.)	27529373
9	23.953	**CA**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

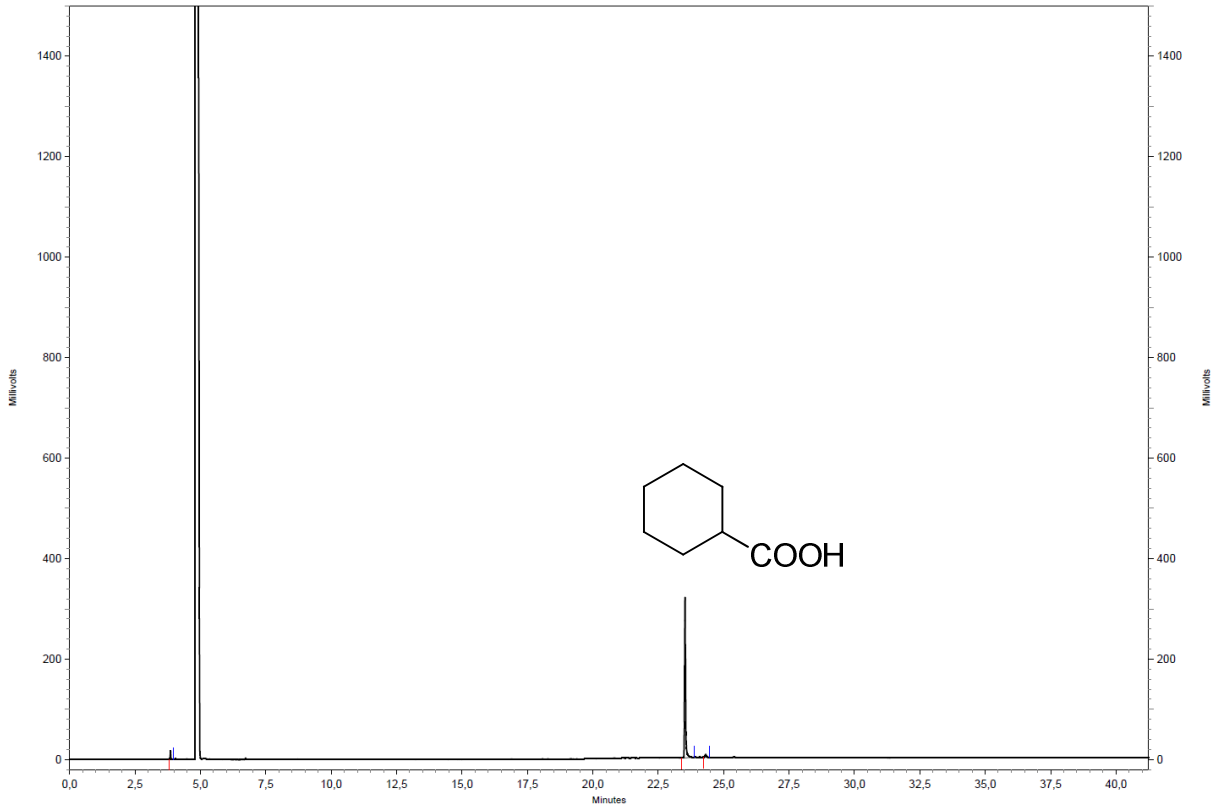


Figure 3.1. GC chromatogram of the isolated cyclohexane carboxylic acid.

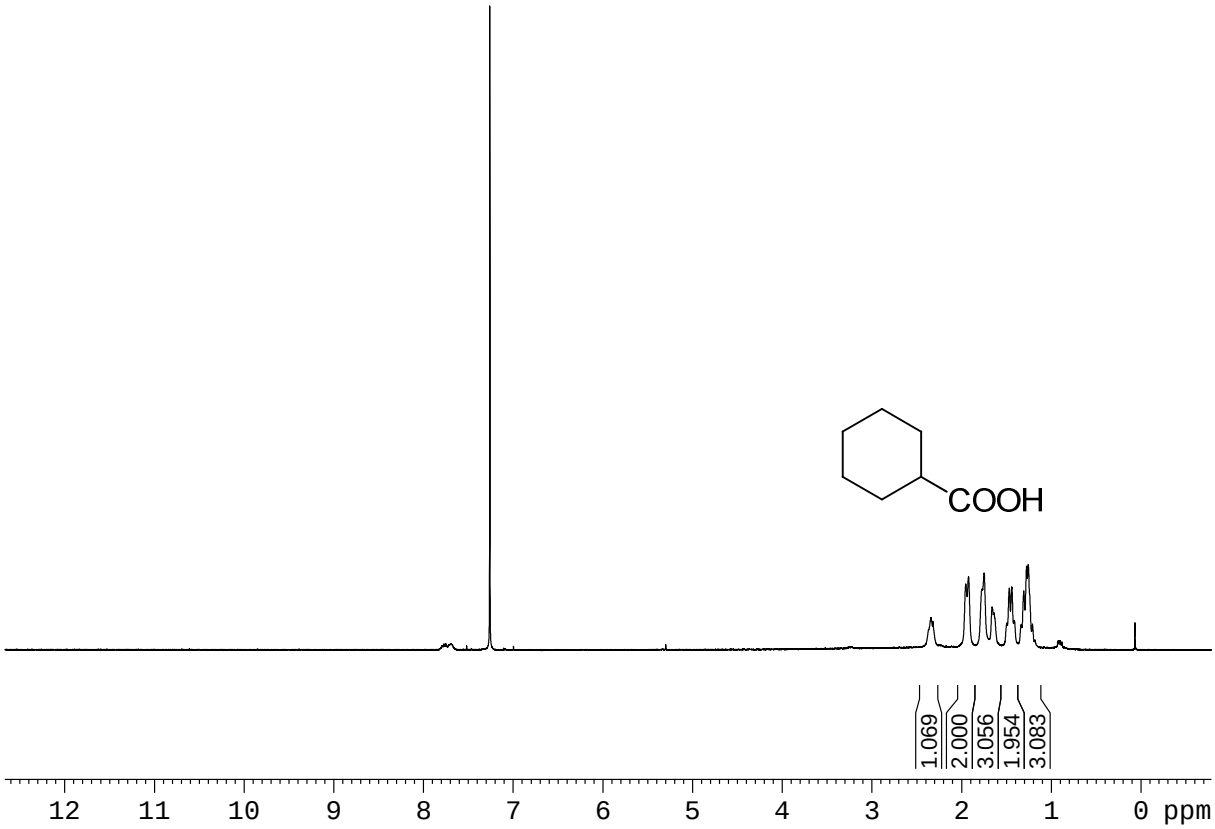
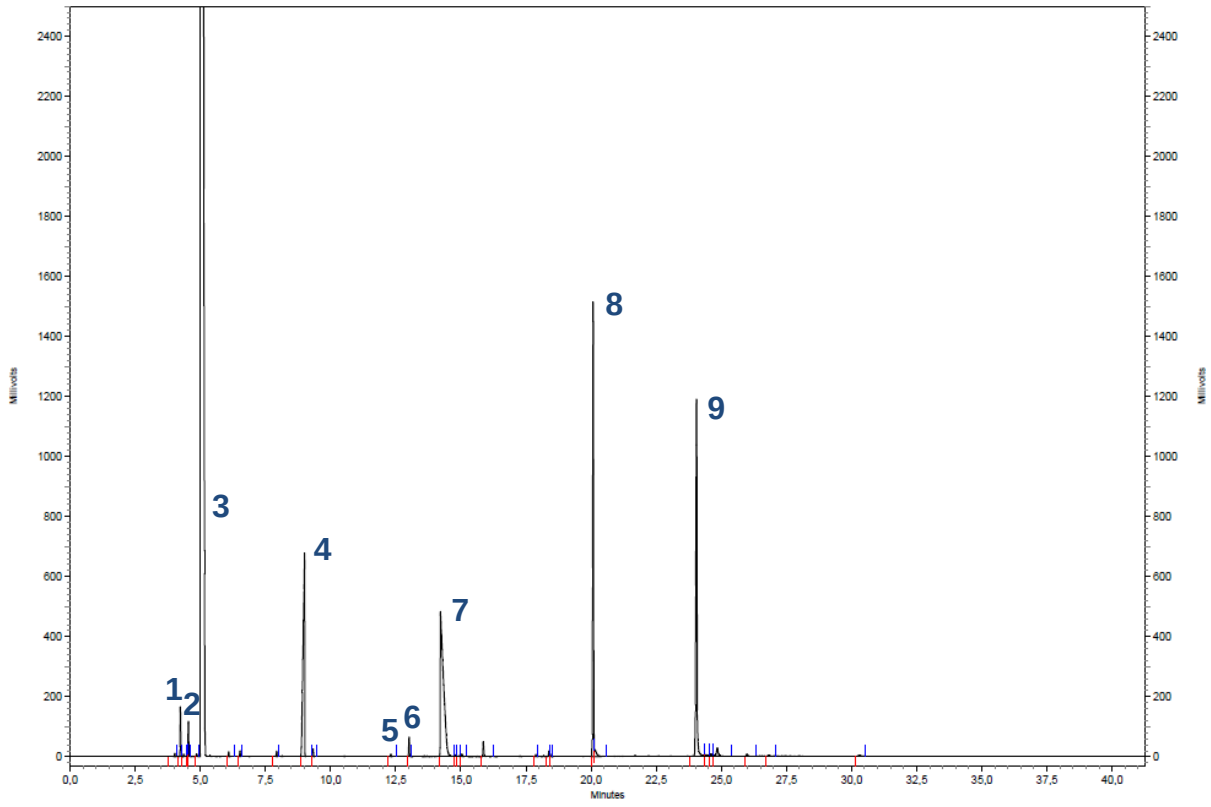


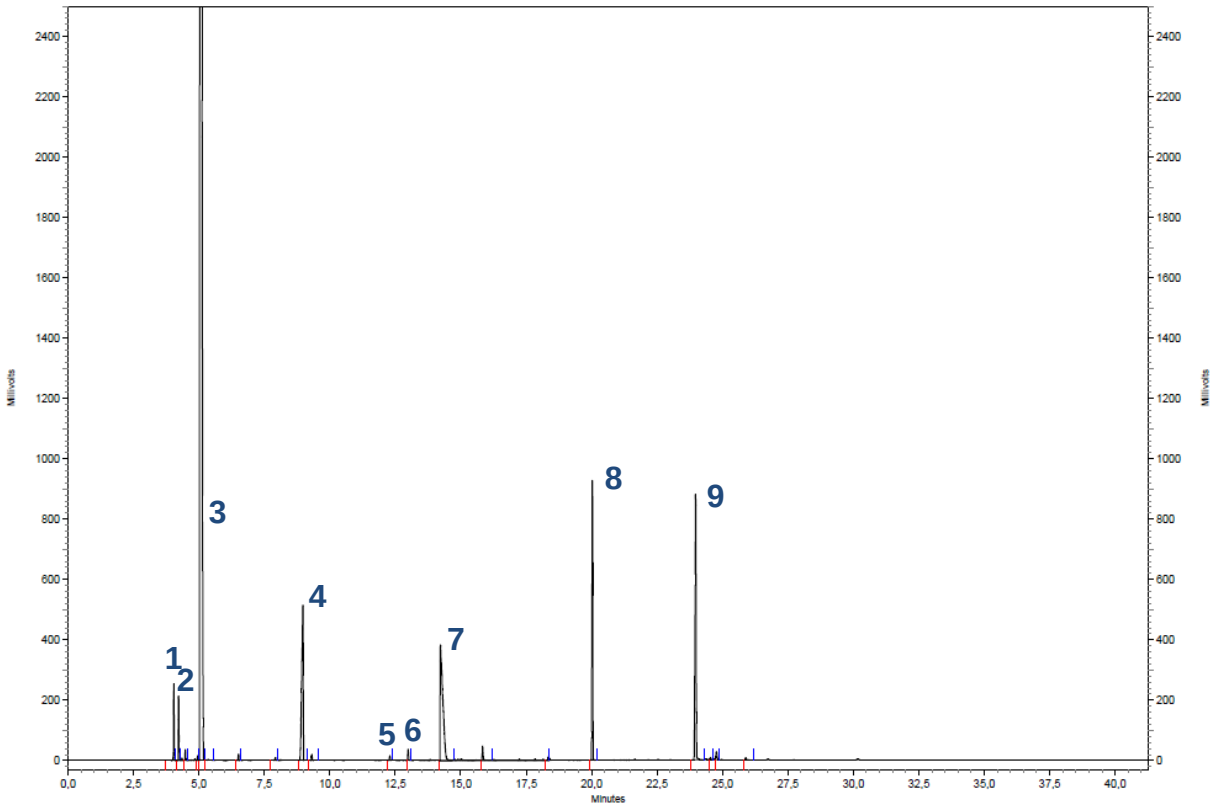
Figure 3.2. ^{1}H NMR spectrum of the isolated product measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

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

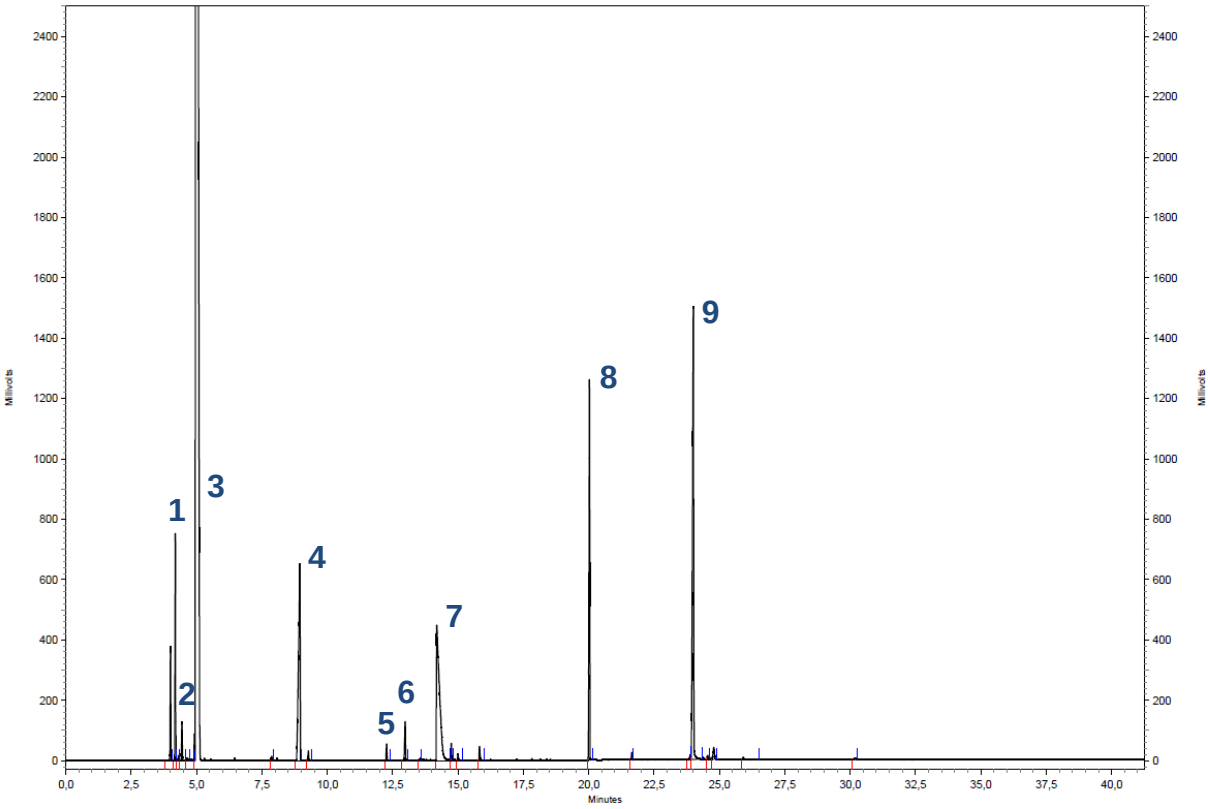
Entry 7



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

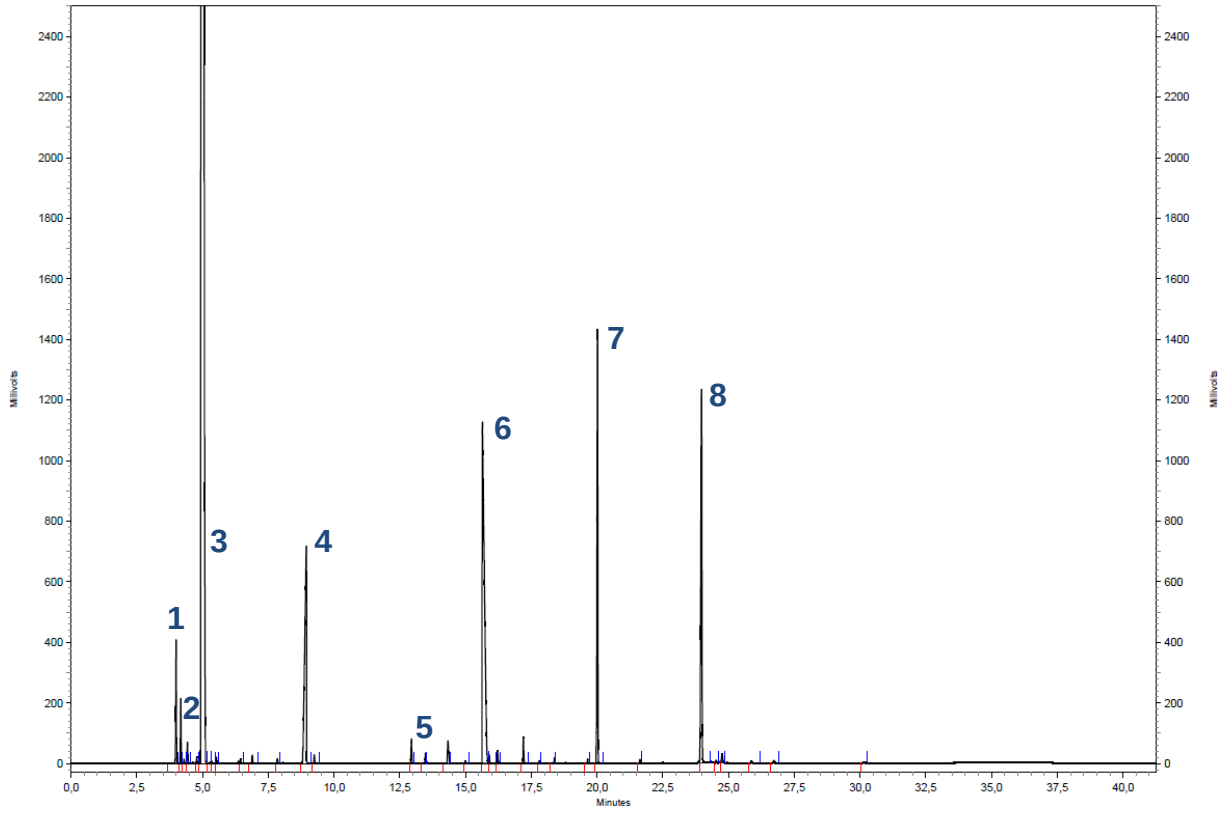
S3.3 Gaschromatograms to Table S2.3

Entry 1



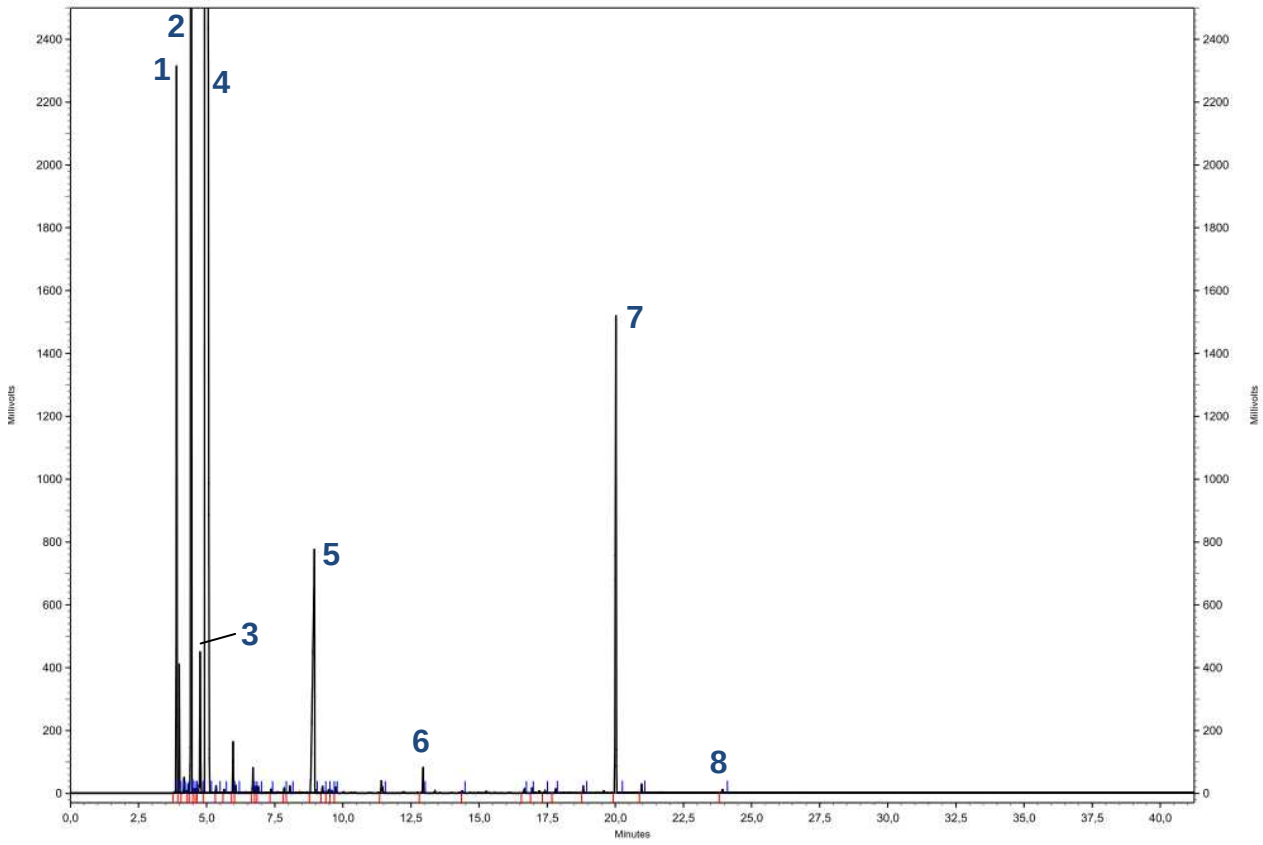
Entry	Retention Time [min]	Substance	Area
1	4.183	**CH**	9605788
2	4.438	**CE**	1889030
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	8.955	*n*-Dodecane (Stand.)	26190459
5	12.268	**CAc**	890076
6	12.973	**CI**	2287680
7	14.185	CH_3COOH (Solv.)	35089734
8	20.027	1-Phenylethanol (Stand.)	23278985
9	23.998	**CA**	43927273

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

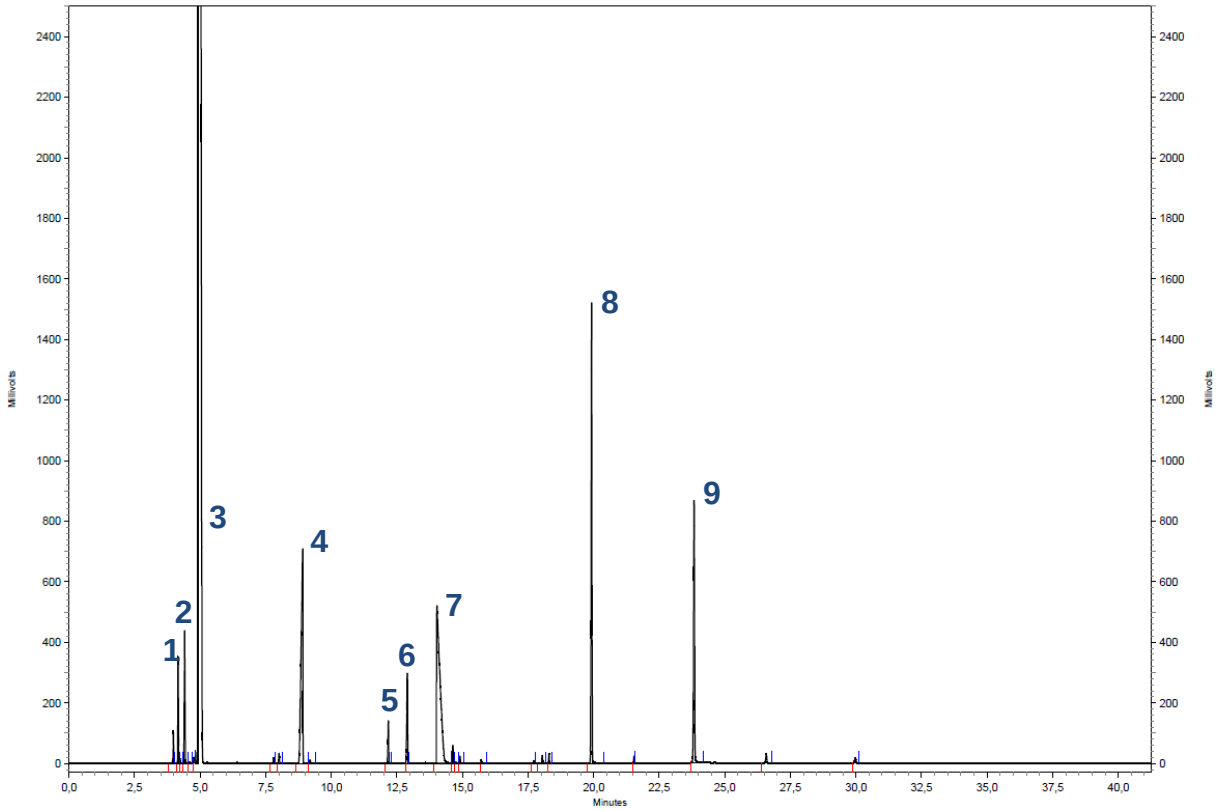
Entry 3



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

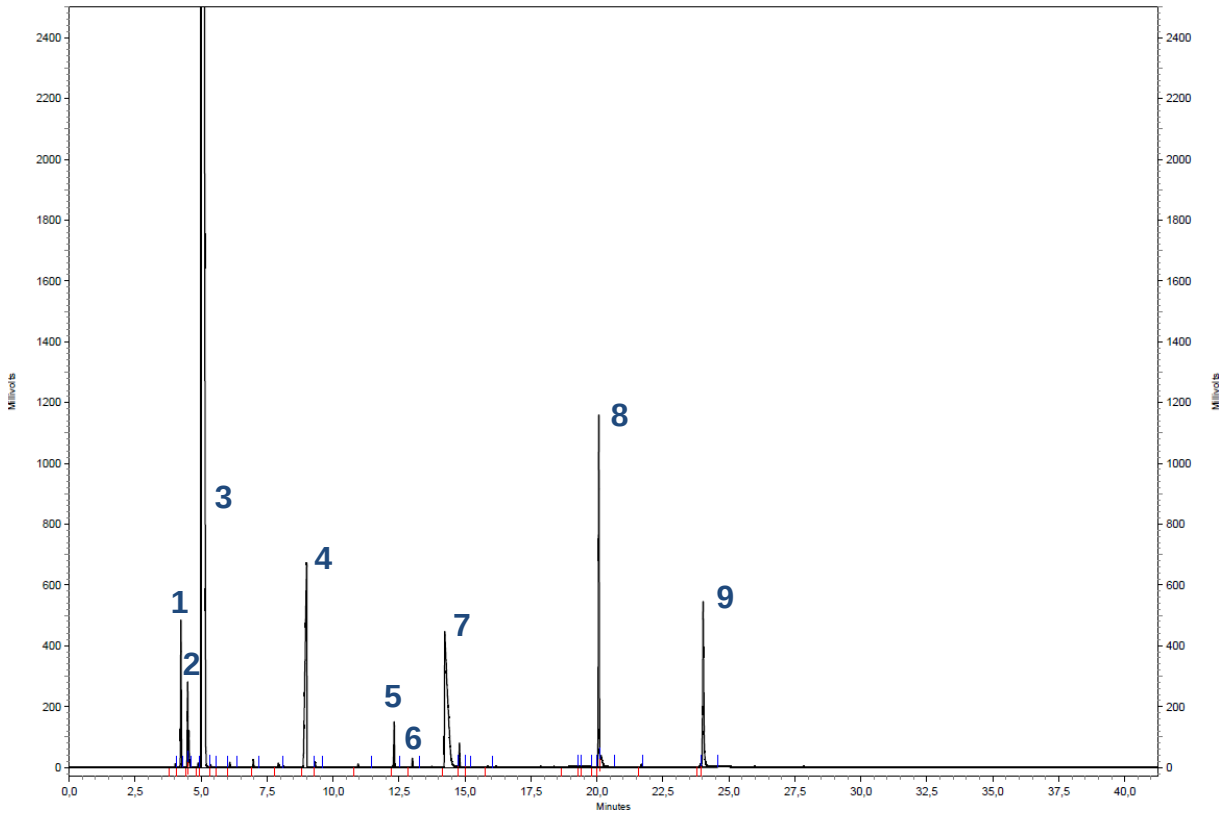
S3.4 Gaschromatograms to Table S2.4

Entry 1



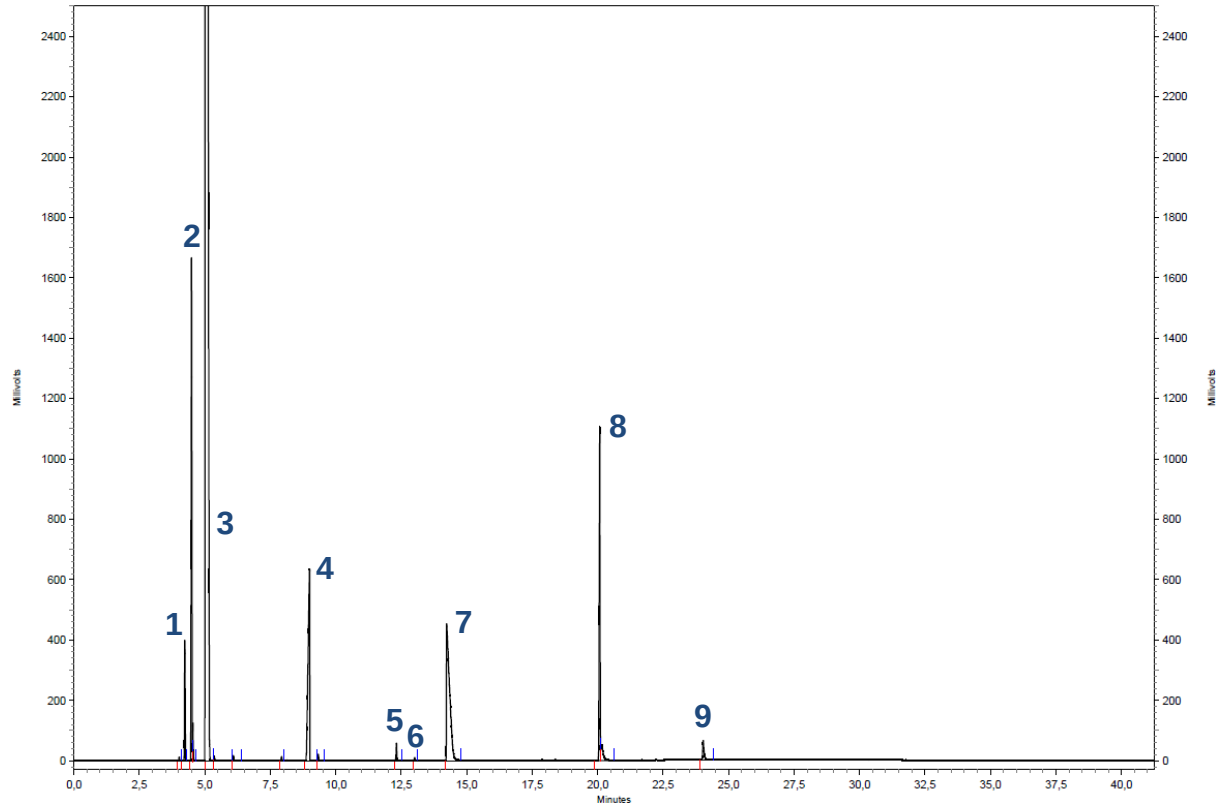
Entry	Retention Time [min]	Substance	Area
1	4.162	**CH**	4623719
2	4.412	**CE**	6724551
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	8.910	*n*-Dodecane (Stand.)	30930081
5	12.173	**CAc**	2314710
6	12.898	**CI**	6311692
7	14.028	CH_3COOH (Solv.)	46117037
8	19.927	1-Phenylethanol (Stand.)	29236760
9	23.833	**CA**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

Entry 2



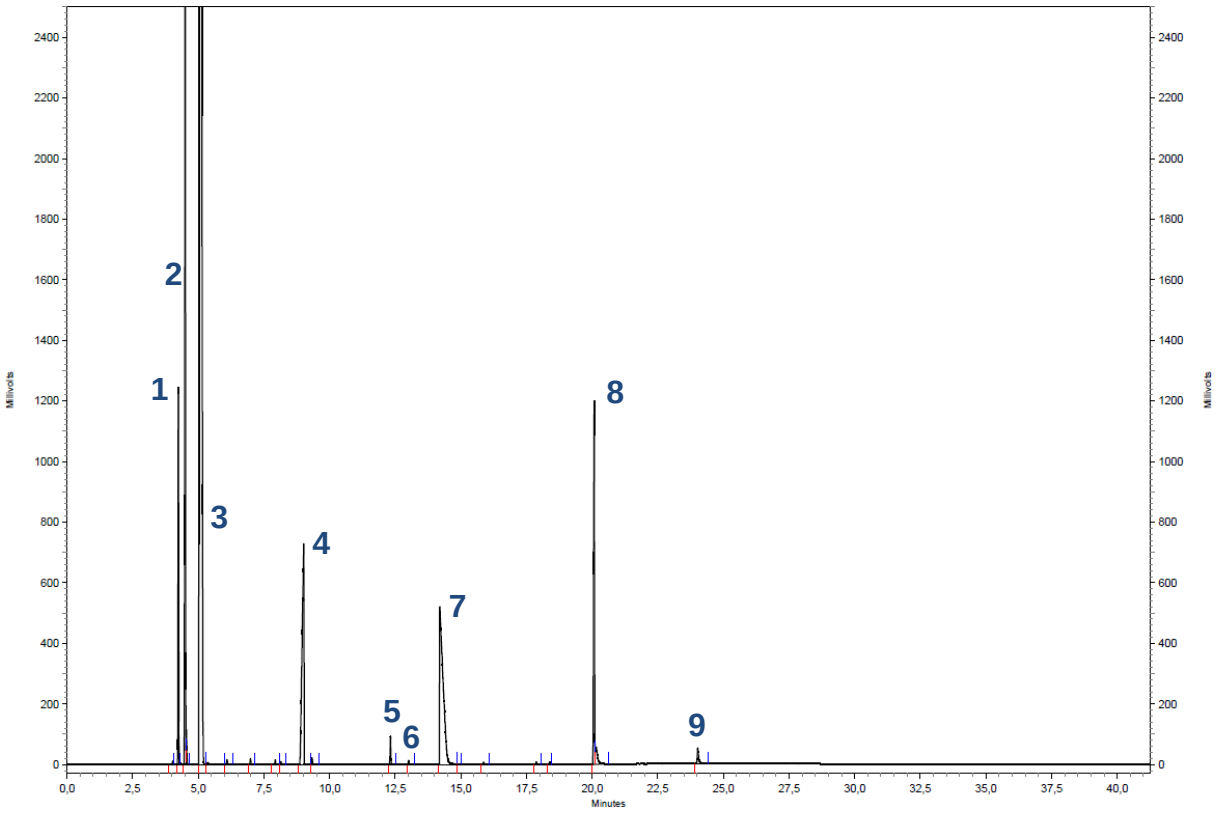
Entry	Retention Time [min]	Substance	Area
1	4.233	**CH**	6407863
2	4.490	**CE**	4261870
3	5.012	CH_2Cl_2 (Solv.)	538587171
4	9.002	*n*-Dodecane (Stand.)	29123450
5	12.315	**CAc**	2617854
6	13.007	**CI**	553475
7	14.233	CH_3COOH (Solv.)	35607530
8	20.073	1-Phenylethanol (Stand.)	21793779
9	24.027	**CA**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

Entry 3



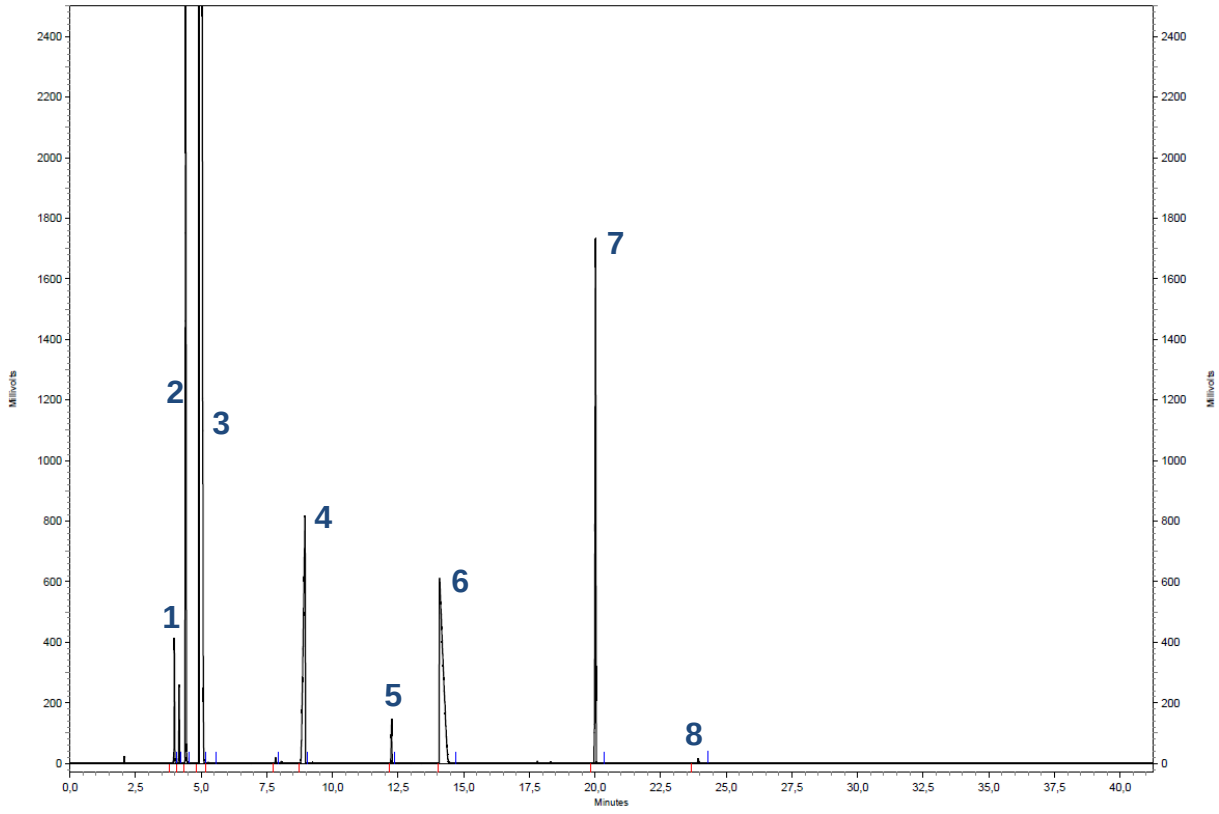
Entry	Retention Time [min]	Substance	Area
1	4.235	**CH**	5144918
2	4.492	**CE**	25230166
3	5.013	CH_2Cl_2 (Solv.)	544970234
4	8.998	*n*-Dodecane (Stand.)	26142032
5	12.317	**CAc**	991745
6	13.010	**CI**	195450
7	14.233	CH_3COOH (Solv.)	37599694
8	20.078	1-Phenylethanol (Stand.)	20853886
9	24.028	**CA**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

Entry 4



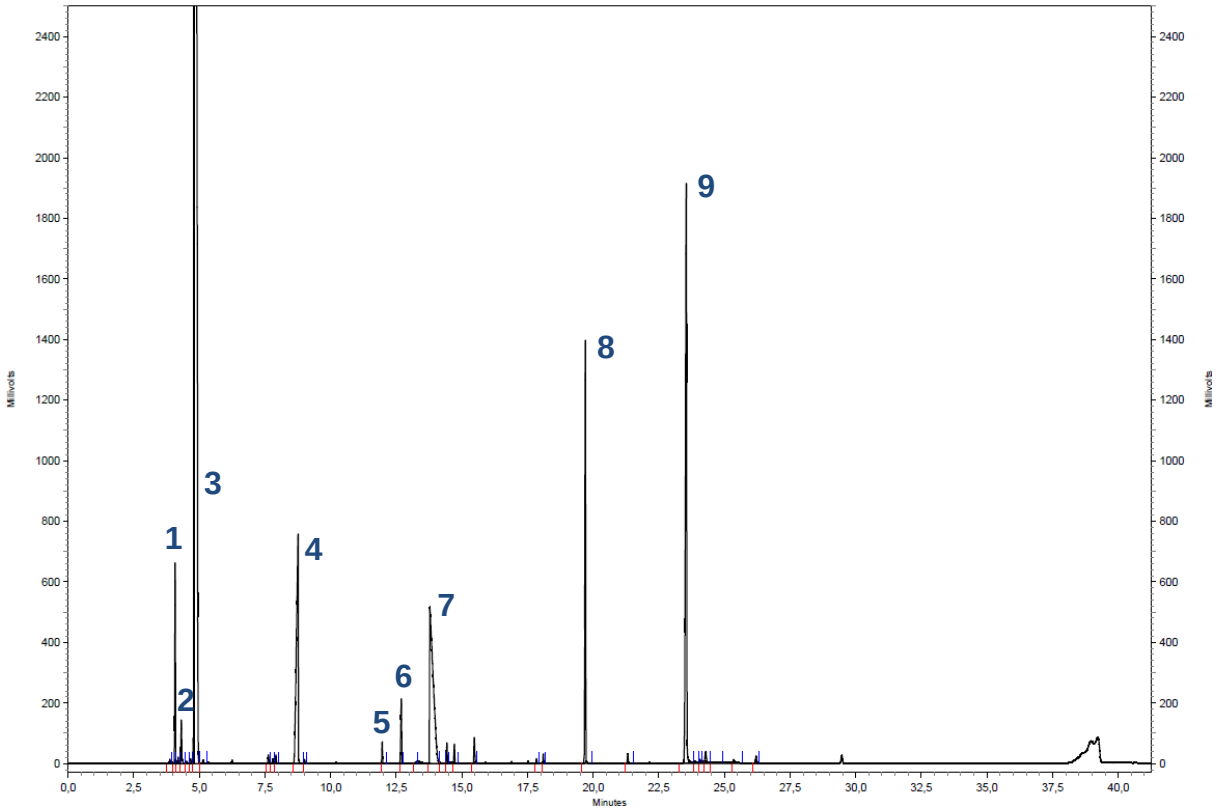
Entry	Retention Time [min]	Substance	Area
1	4.240	**CH**	16346362
2	4.498	**CE**	55861908
3	5.022	CH_2Cl_2 (Solv.)	522642505
4	9.015	*n*-Dodecane (Stand.)	32957009
5	12.320	**CAc**	1666006
6	13.010	**CI**	265242
7	14.200	CH_3COOH (Solv.)	47136194
8	20.075	1-Phenylethanol (Stand.)	23201249
9	24.025	**CA**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

Entry 5



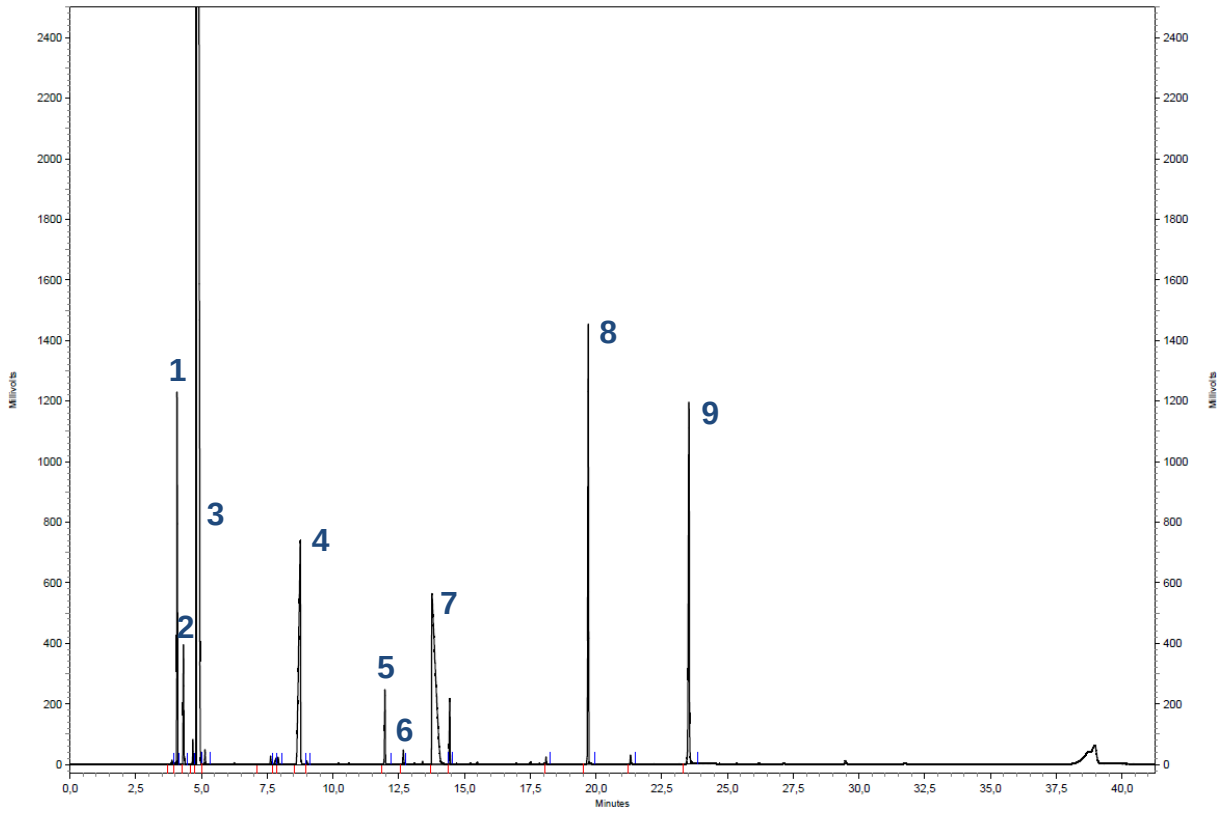
Entry	Retention Time [min]	Substance	Area
1	4.158	**CH**	3365695
2	4.412	**CE**	46005793
3	4.922	CH_2Cl_2 (Solv.)	544941656
4	8.960	*n*-Dodecane (Stand.)	40741507
5	12.252	**CAc**	2408441
6	14.080	CH_3COOH (Solv.)	58967864
7	20.022	1-Phenylethanol (Stand.)	34575327
8	23.937	**CA**	356243

Entry 6



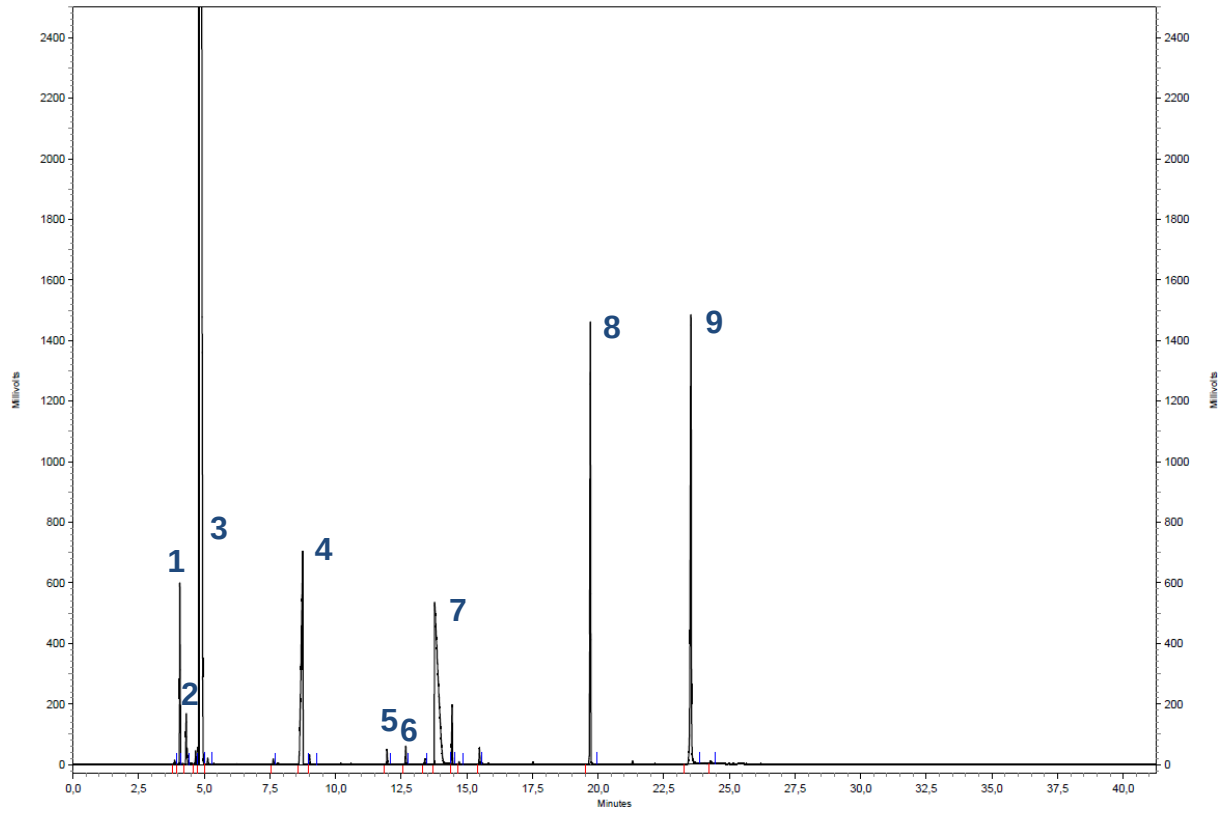
Entry	Retention Time [min]	Substance	Area
1	4.073	**CH**	8443705
2	4.313	**CE**	2321799
3	4.795	CH_2Cl_2 (Solv.)	539046412
4	8.762	*n*-Dodecane (Stand.)	35617834
5	11.963	**CAc**	1153530
6	12.692	**CI**	4076805
7	13.777	CH_3COOH (Solv.)	47859651
8	19.705	1-Phenylethanol (Stand.)	25810587
9	23.548	**CA**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

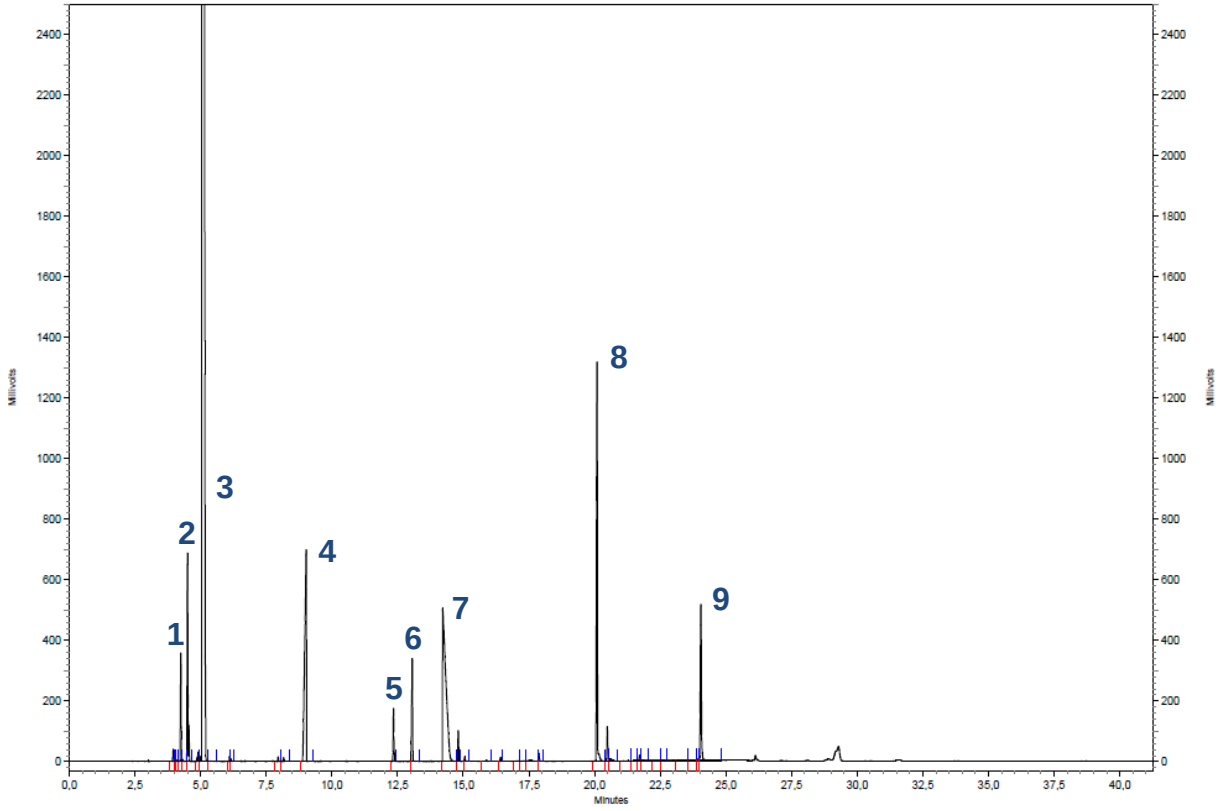
Entry 8



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

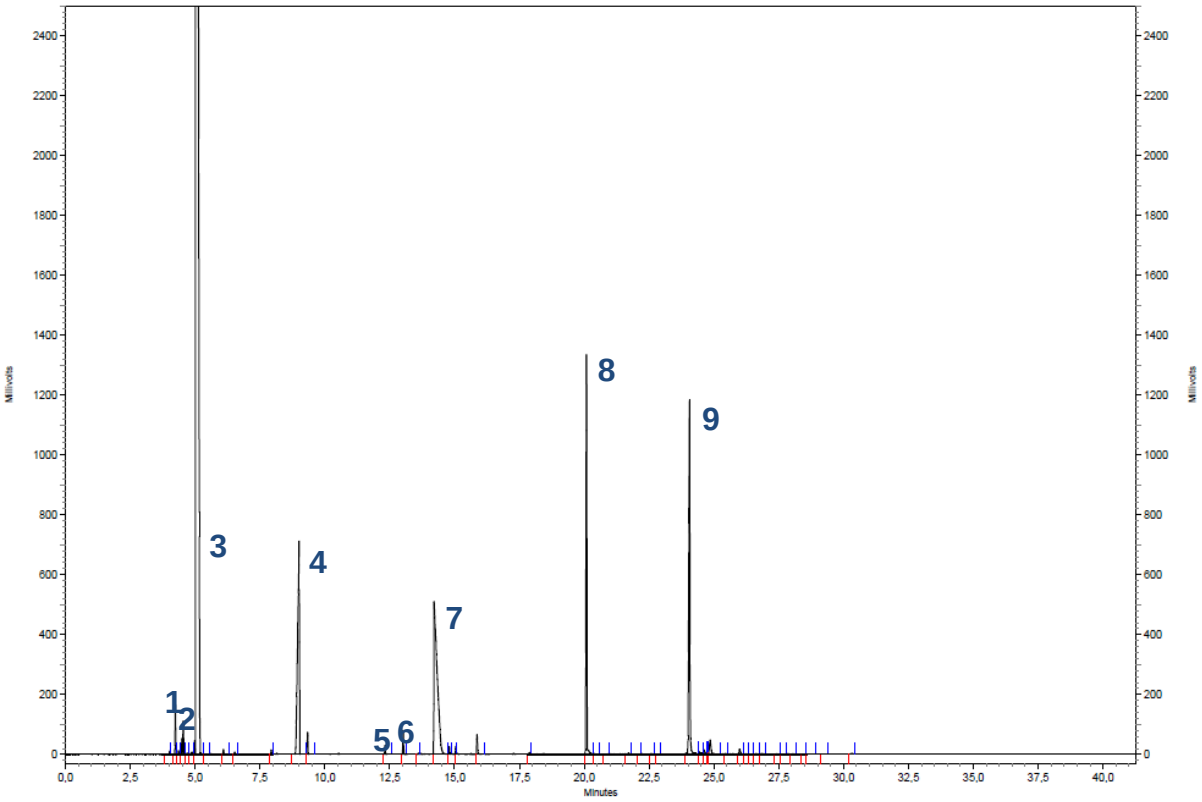
S3.5 Gaschromatograms to Table S2.5

Entry 1



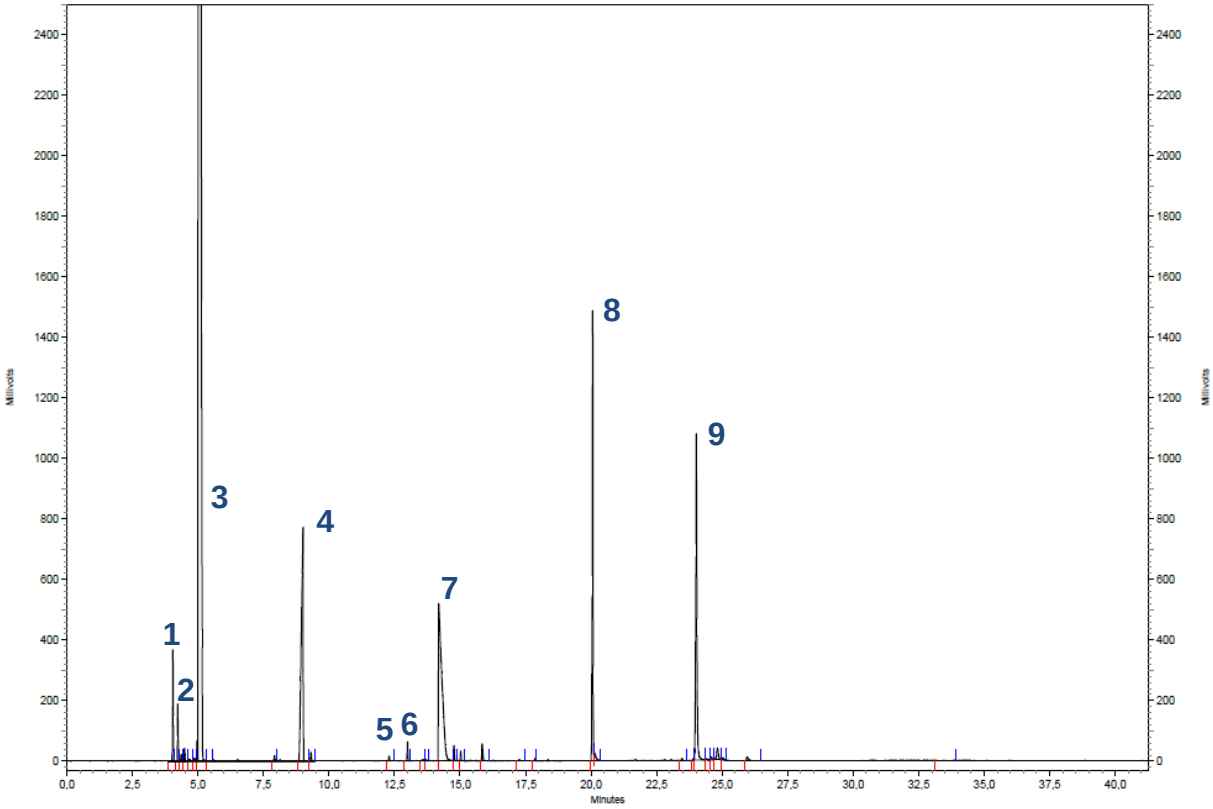
Entry	Retention Time [min]	Substance	Area
1	4.245	**CH**	4755632
2	4.502	**CE**	12208263
3	5.027	CH_2Cl_2 (Solv.)	538971362
4	9.023	*n*-Dodecane (Stand.)	30517966
5	12.347	**CAc**	3354729
6	13.058	**CI**	7869117
7	14.218	CH_3COOH (Solv.)	44047706
8	20.092	1-Phenylethanol (Stand.)	26530706
9	24.047	**CA**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

Entry 2



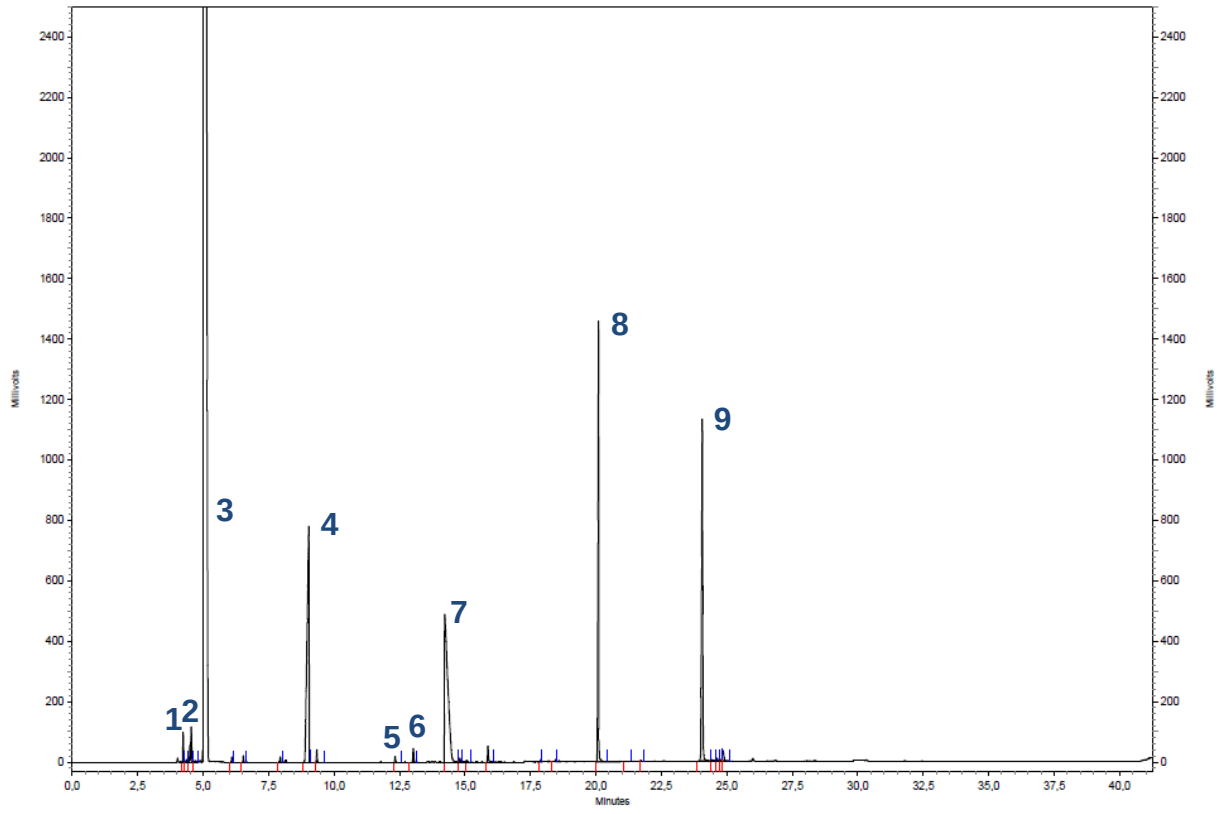
Entry	Retention Time [min]	Substance	Area
1	4.237	**CH**	2212263
2	4.543	**CE**	2549632
3	5.018	CH_2Cl_2 (Solv.)	523505336
4	9.013	*n*-Dodecane (Stand.)	31575593
5	12.322	**CAc**	543484
6	13.022	**CI**	1491064
7	14.212	CH_3COOH (Solv.)	44837575
8	20.087	1-Phenylethanol (Stand.)	26305575
9	24.058	**CA**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

Entry 3



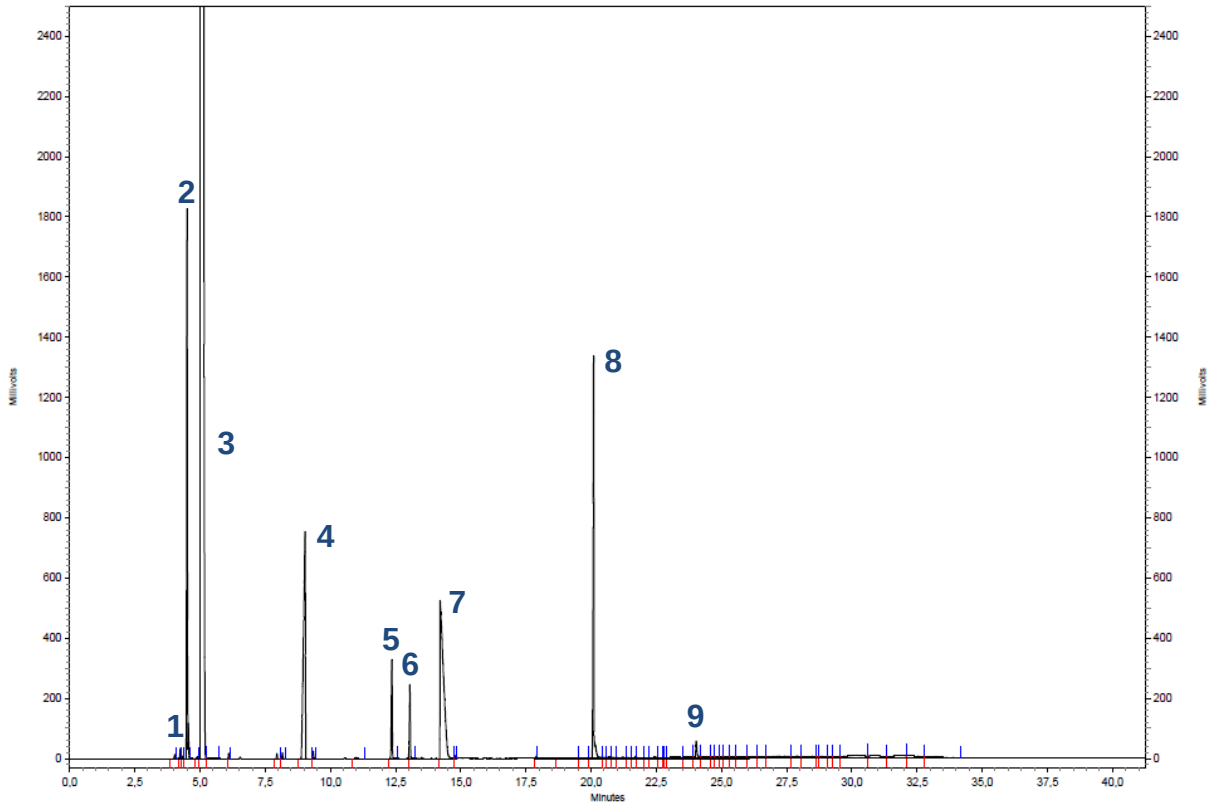
Entry	Retention Time [min]	Substance	Area
1	4.230	**CH**	2536833
2	4.485	**CE**	677684
3	5.012	CH_2Cl_2 (Solv.)	516660834
4	9.012	*n*-Dodecane (Stand.)	36570073
5	12.295	**CAc**	275615
6	12.998	**CI**	1168625
7	14.185	CH_3COOH (Solv.)	45849429
8	20.062	1-Phenylethanol (Stand.)	29227806
9	24.018	**CA**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

Entry 4



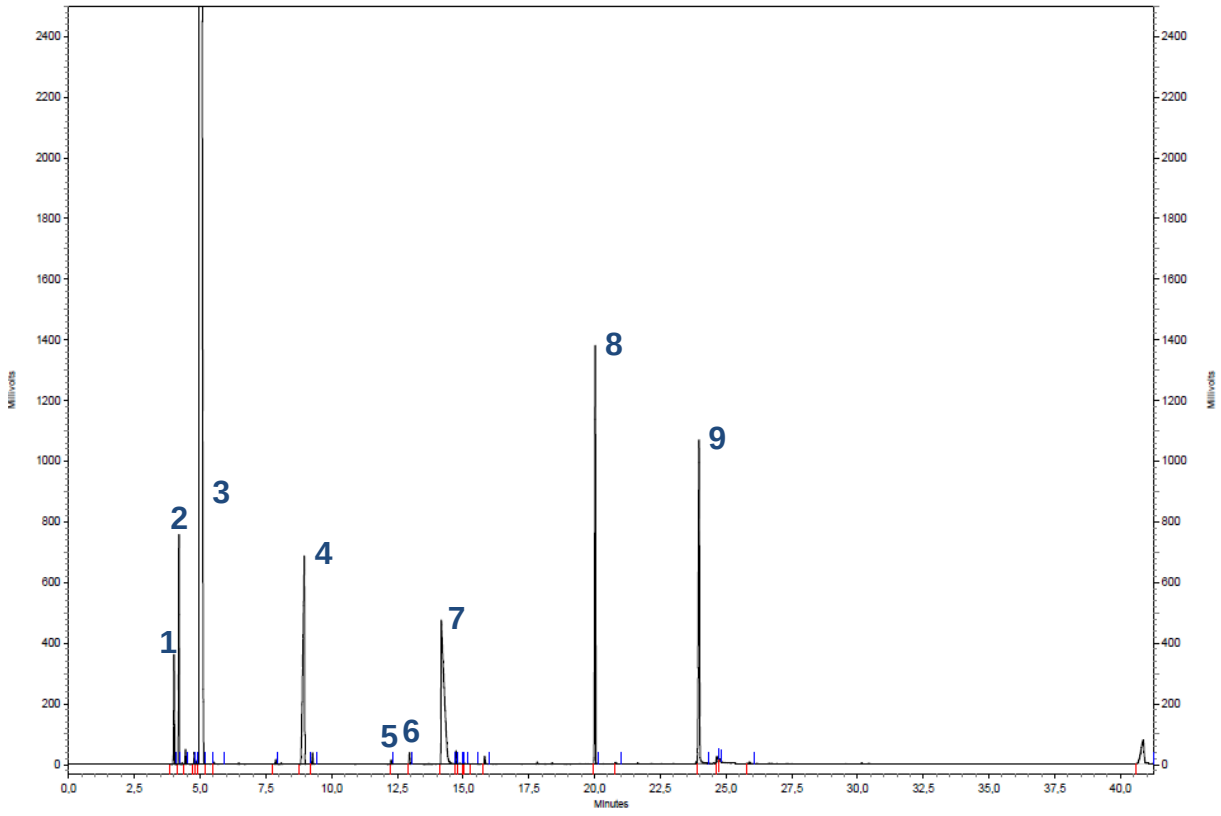
Entry	Retention Time [min]	Substance	Area
1	4.242	**CH**	1300713
2	4.550	**CE**	2590549
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	9.037	*n*-Dodecane (Stand.)	37018450
5	12.333	**CAc**	326345
6	13.030	**CI**	821294
7	14.228	CH_3COOH (Solv.)	41566839
8	20.098	1-Phenylethanol (Stand.)	29190086
9	24.063	**CA**	32288328

Entry 5



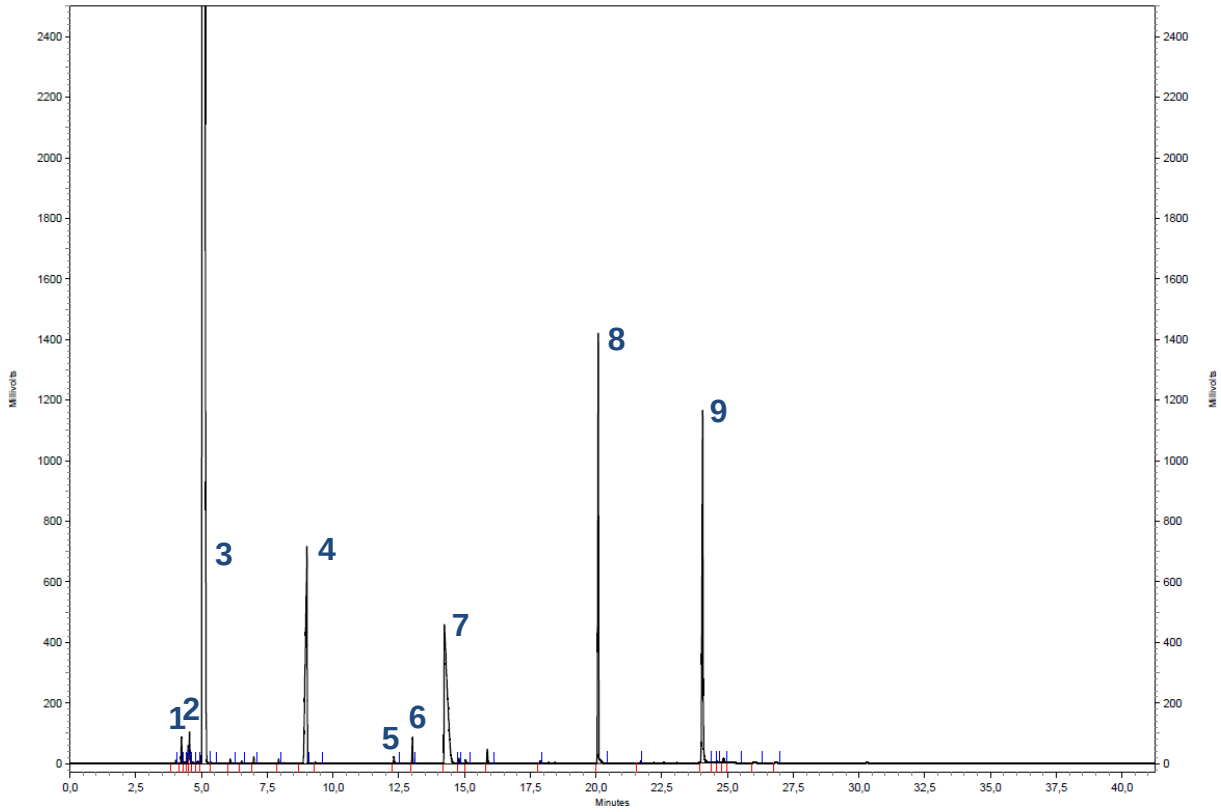
Entry	Retention Time [min]	Substance	Area
1	4.243	**CH**	463012
2	4.502	**CE**	29574068
3	5.027	CH_2Cl_2 (Solv.)	534155611
4	9.033	*n*-Dodecane (Stand.)	35038431
5	12.358	**CAc**	6954729
6	13.052	**CI**	5116405
7	14.210	CH_3COOH (Solv.)	47295142
8	20.093	1-Phenylethanol (Stand.)	28523371
9	24.033	**CA**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

Entry 6



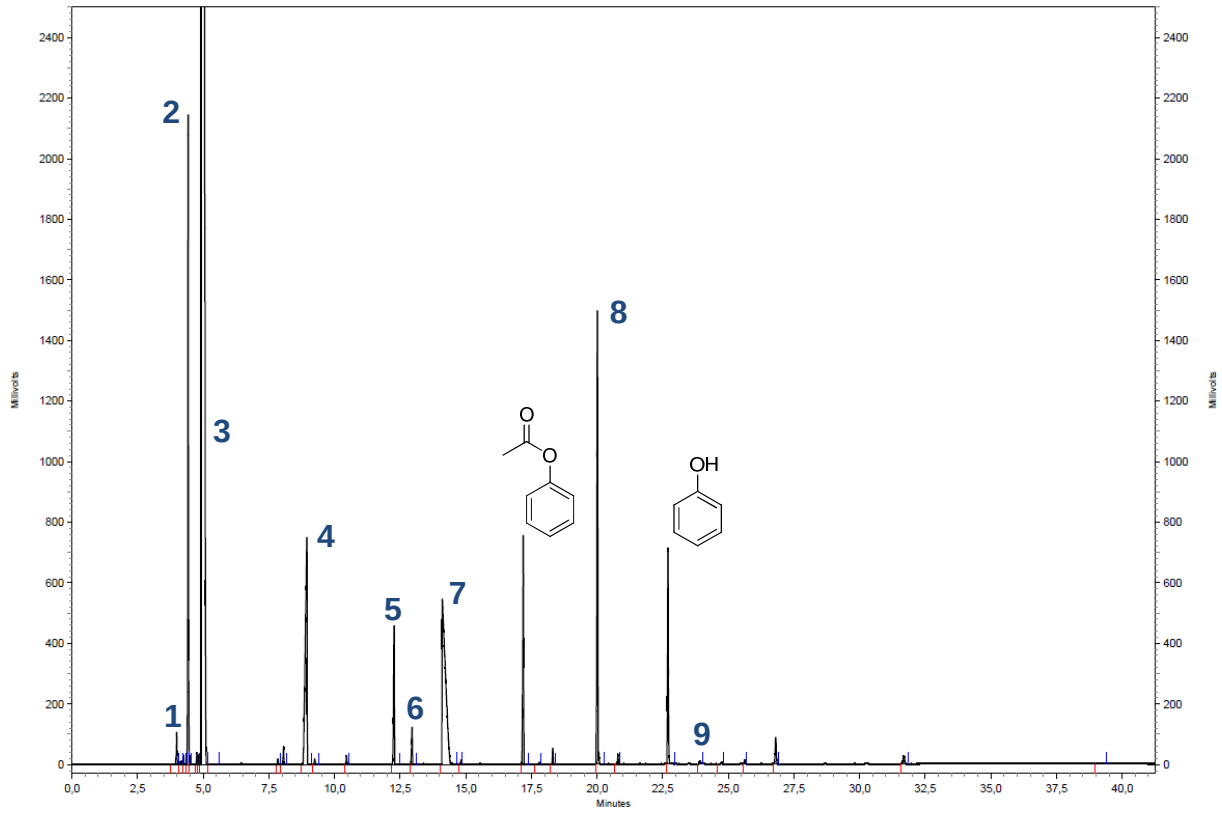
Entry	Retention Time [min]	Substance	Area
1	4.192	**CH**	9516376
2	4.445	**CE**	736403
3	4.970	CH_2Cl_2 (Solv.)	481626659
4	8.968	*n*-Dodecane (Stand.)	29571531
5	12.267	**CAc**	227325
6	12.967	**CI**	669337
7	14.170	CH_3COOH (Solv.)	38218067
8	20.027	1-Phenylethanol (Stand.)	25971566
9	23.975	**CA**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

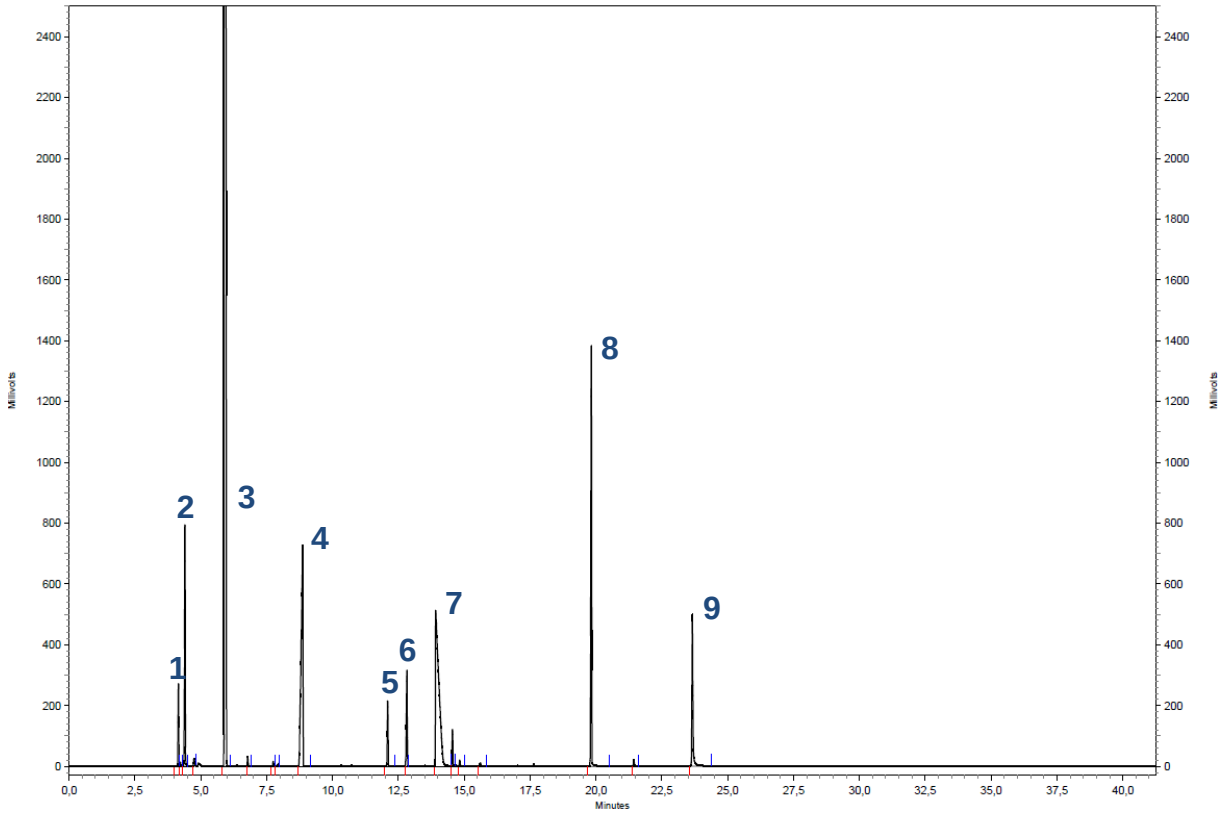
Entry 8



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

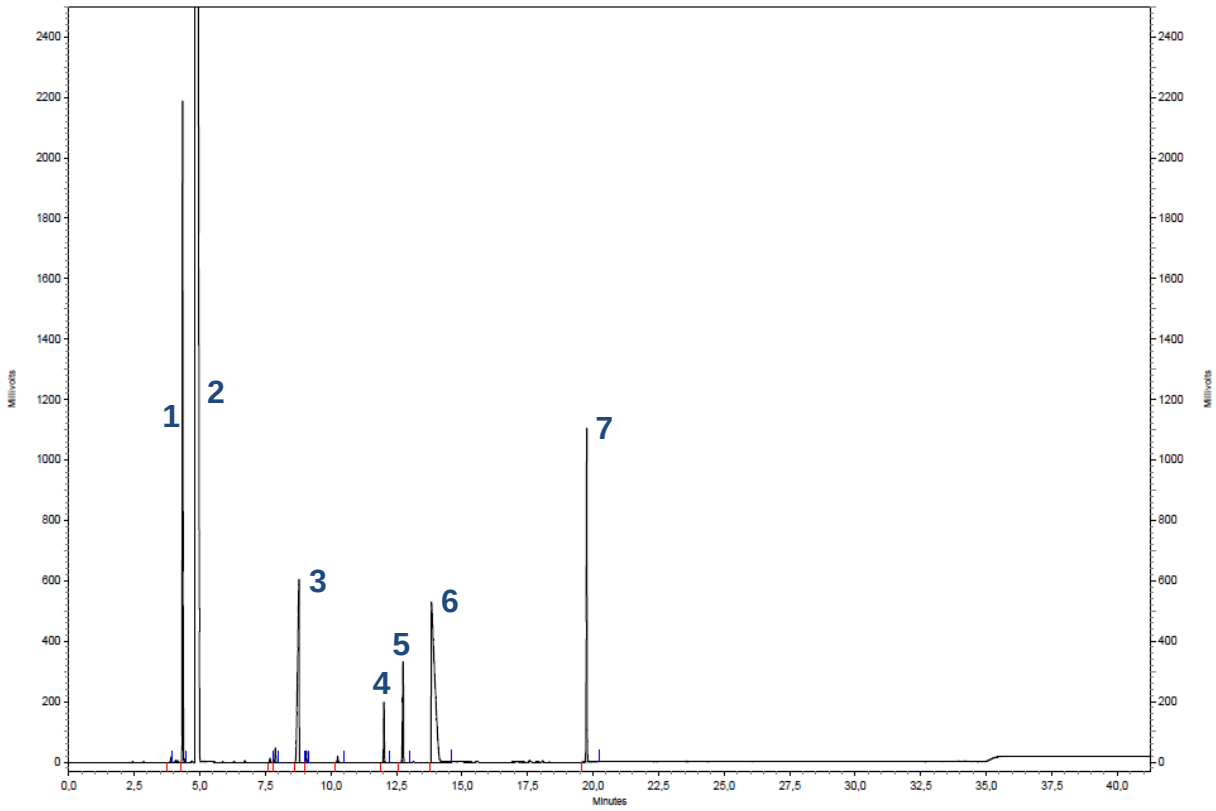
Entry 9



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

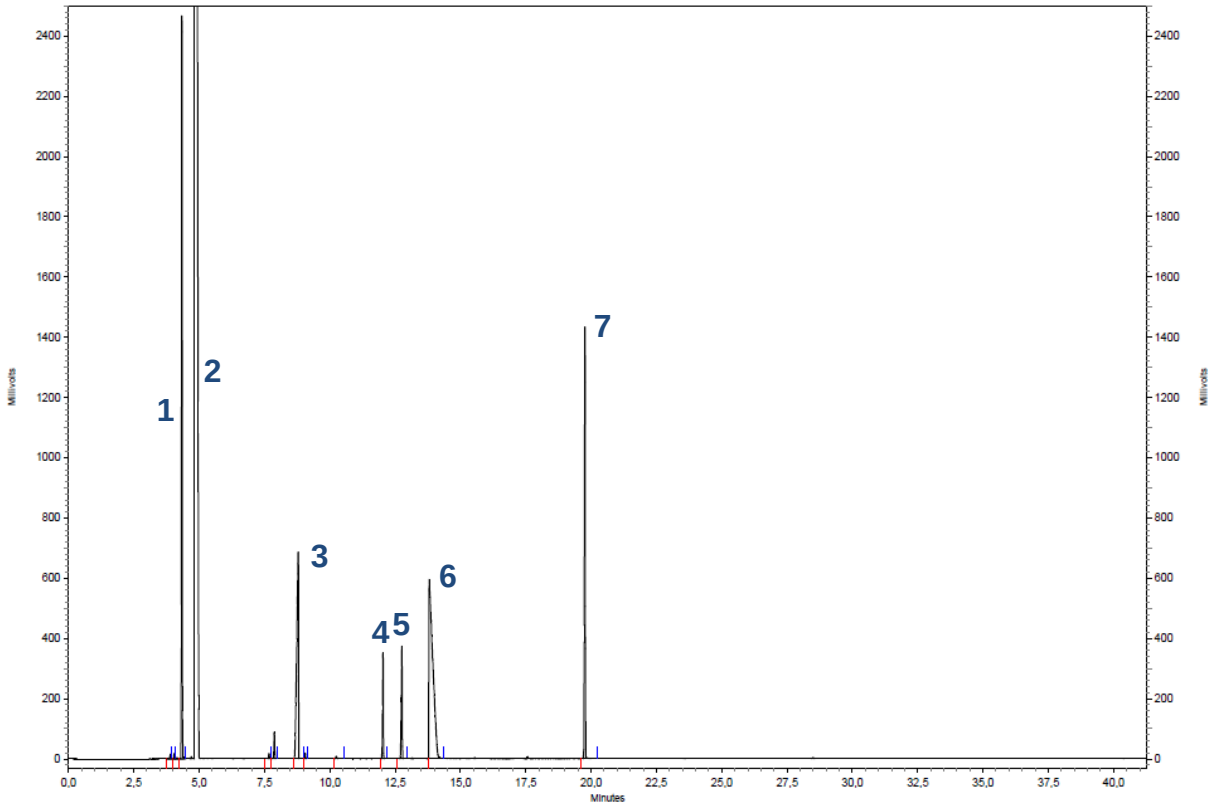
[a]: $CDCl_3$ was used in this experiment to dilute the reaction mixture in order to avoid signal overlap with the substrate peak and allow for simultaneous NMR analysis.

Entry 10



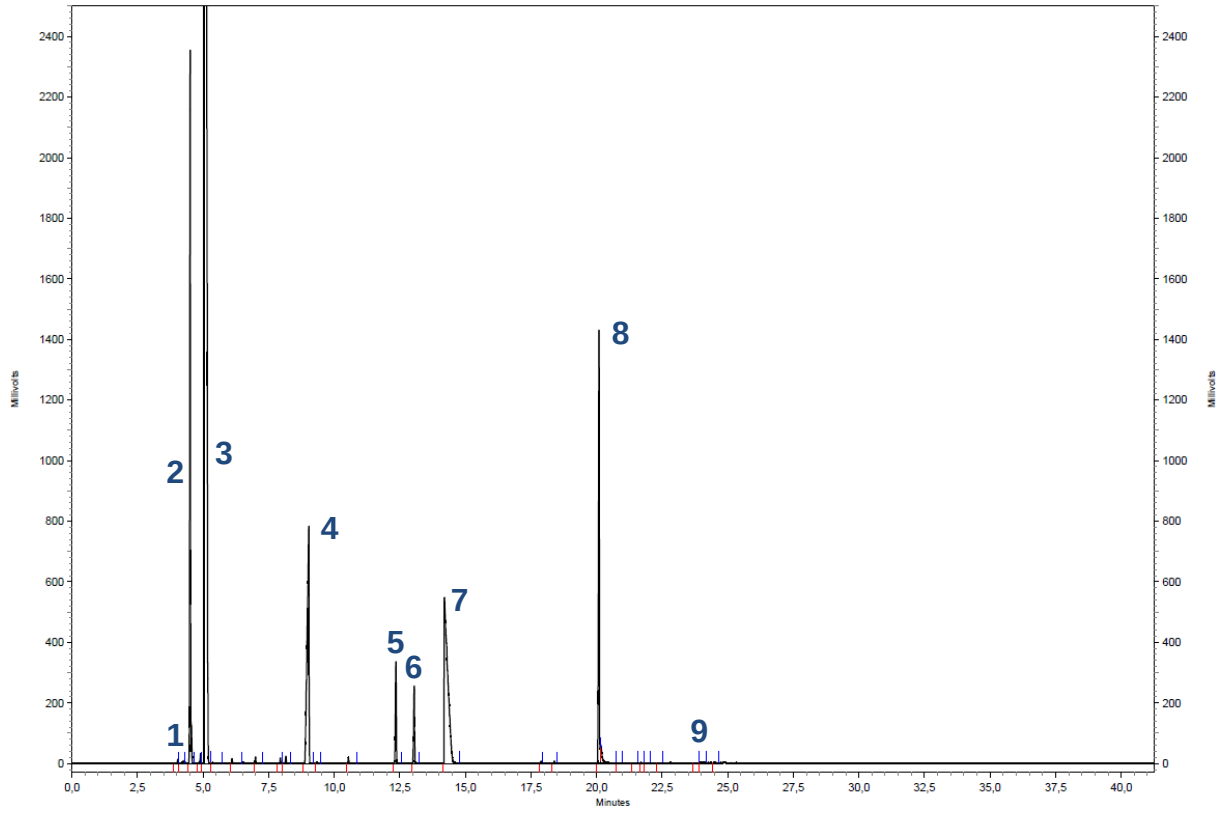
Entry	Retention Time [min]	Substance	Area
1	4.345	**CE**	32798302
2	*cutted*	CH_2Cl_2 (Solv.)	--
3	8.783	*n*-Dodecane (Stand.)	23821426
4	12.027	**CAc**	3374657
5	12.757	**Cl**	7129707
6	13.835	CH_3COOH (Solv.)	48159978
7	19.758	1-Phenylethanol (Stand.)	19839278

Entry 11



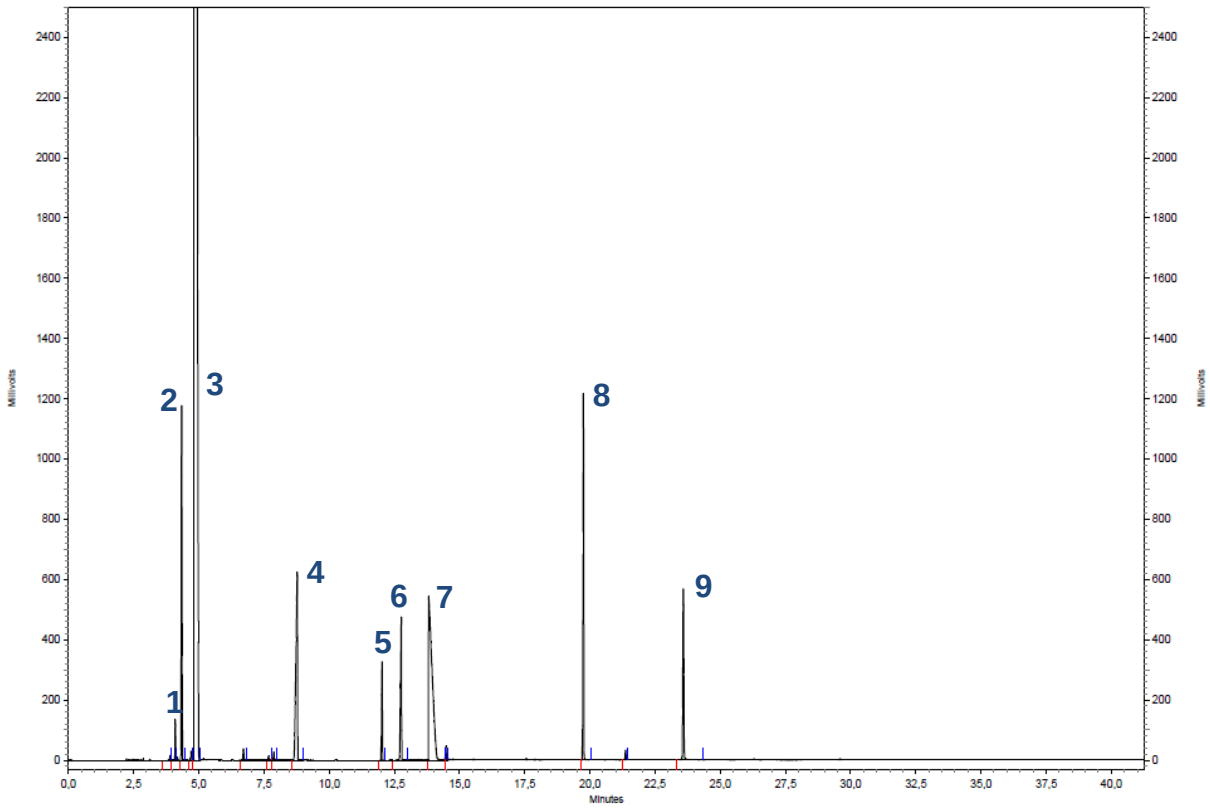
Entry	Retention Time [min]	Substance	Area
1	4.338	**CE**	36838685
2	*cutted*	CH_2Cl_2 (Solv.)	--
3	8.795	*n*-Dodecane (Stand.)	30001100
4	12.038	**CAc**	6531078
5	12.762	**Cl**	8435655
6	13.803	CH_3COOH (Solv.)	59775994
7	19.765	1-Phenylethanol (Stand.)	27215247

Entry 12



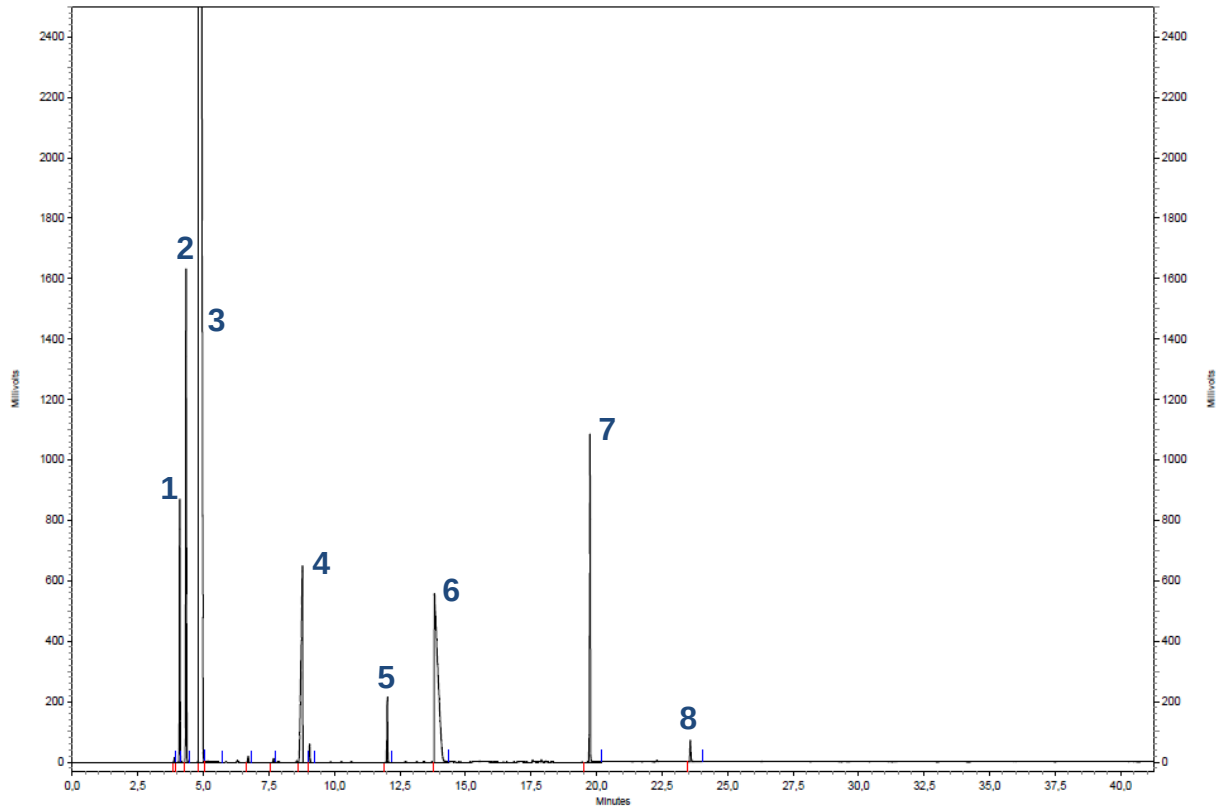
Entry	Retention Time [min]	Substance	Area
1	4.245	**CH**	182931
2	4.503	**CE**	38260389
3	5.028	CH_2Cl_2 (Solv.)	527915450
4	9.032	*n*-Dodecane (Stand.)	37414196
5	12.352	**CAc**	7412775
6	13.048	**CI**	5515266
7	14.200	CH_3COOH (Solv.)	50794739
8	20.093	1-Phenylethanol (Stand.)	28896099
9	24.042	**CA**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

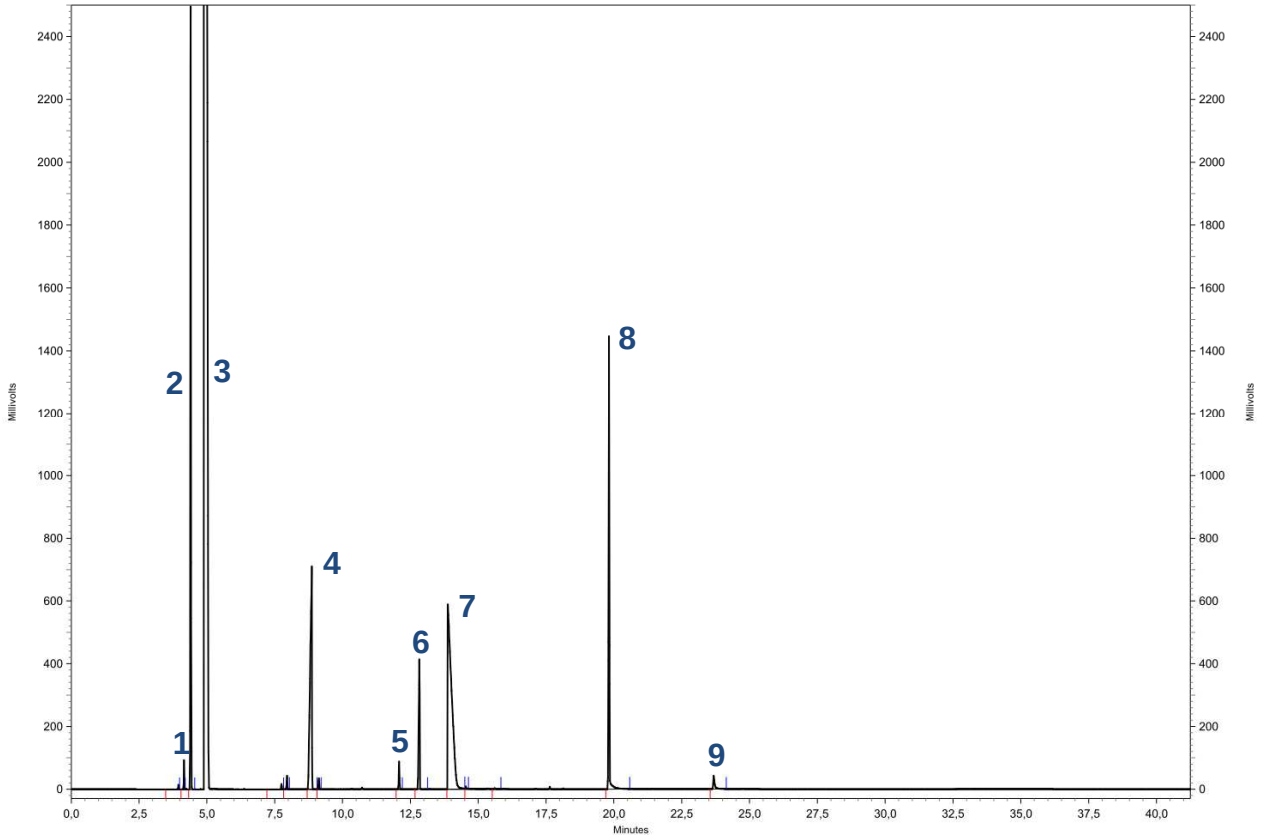
Entry 14



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

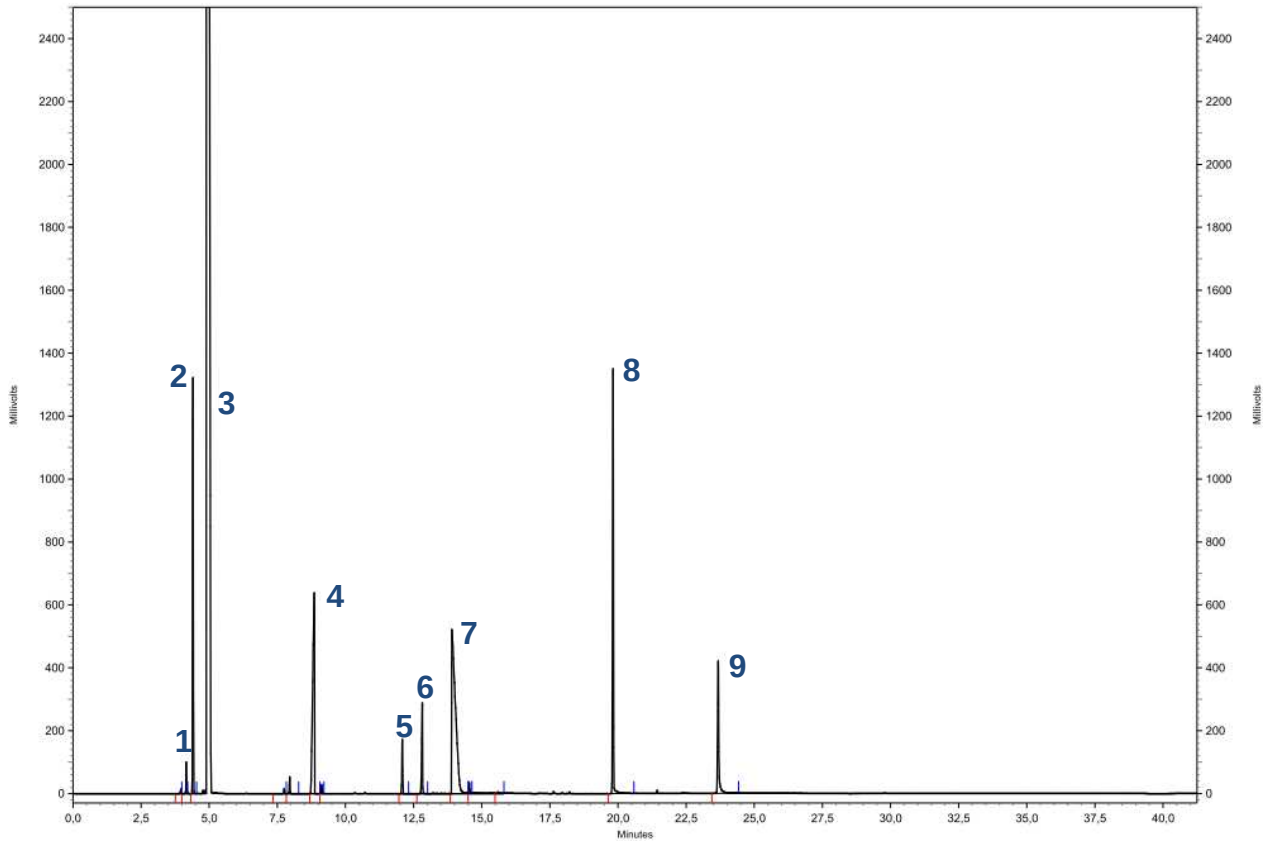
S3.6 Gaschromatograms to Table S2.6

Entry 1



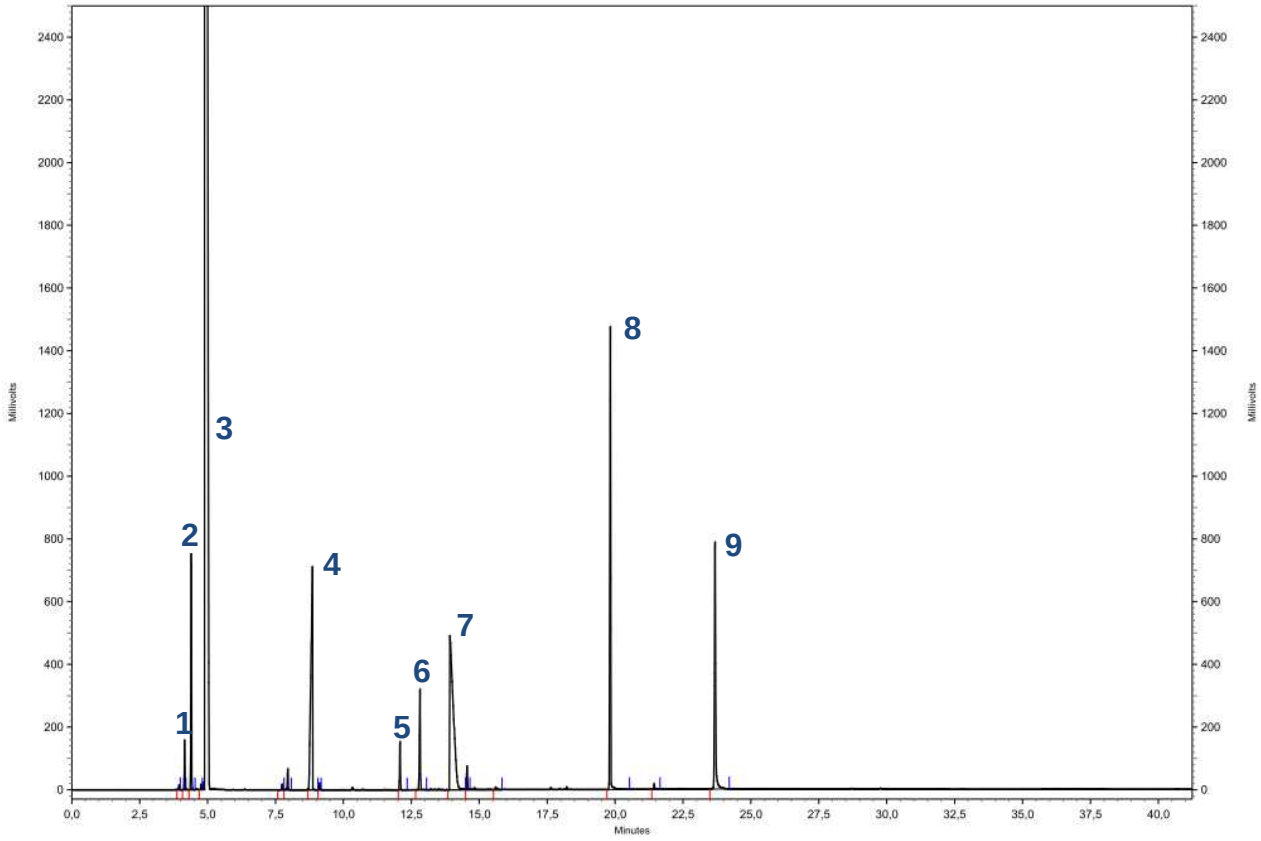
Entry	Retention Time [min]	Substance	Area
1	4.157	**CH**	1253709
2	4.403	**CE**	38041907
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	8.868	*n*-Dodecane (Stand.)	32513740
5	12.085	**CAc**	1519053
6	12.832	**CI**	9855061
7	13.880	CH_3COOH (Solv.)	59349994
8	19.823	1-Phenylethanol (Stand.)	29204886
9	23.680	**CA**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

Entry 2



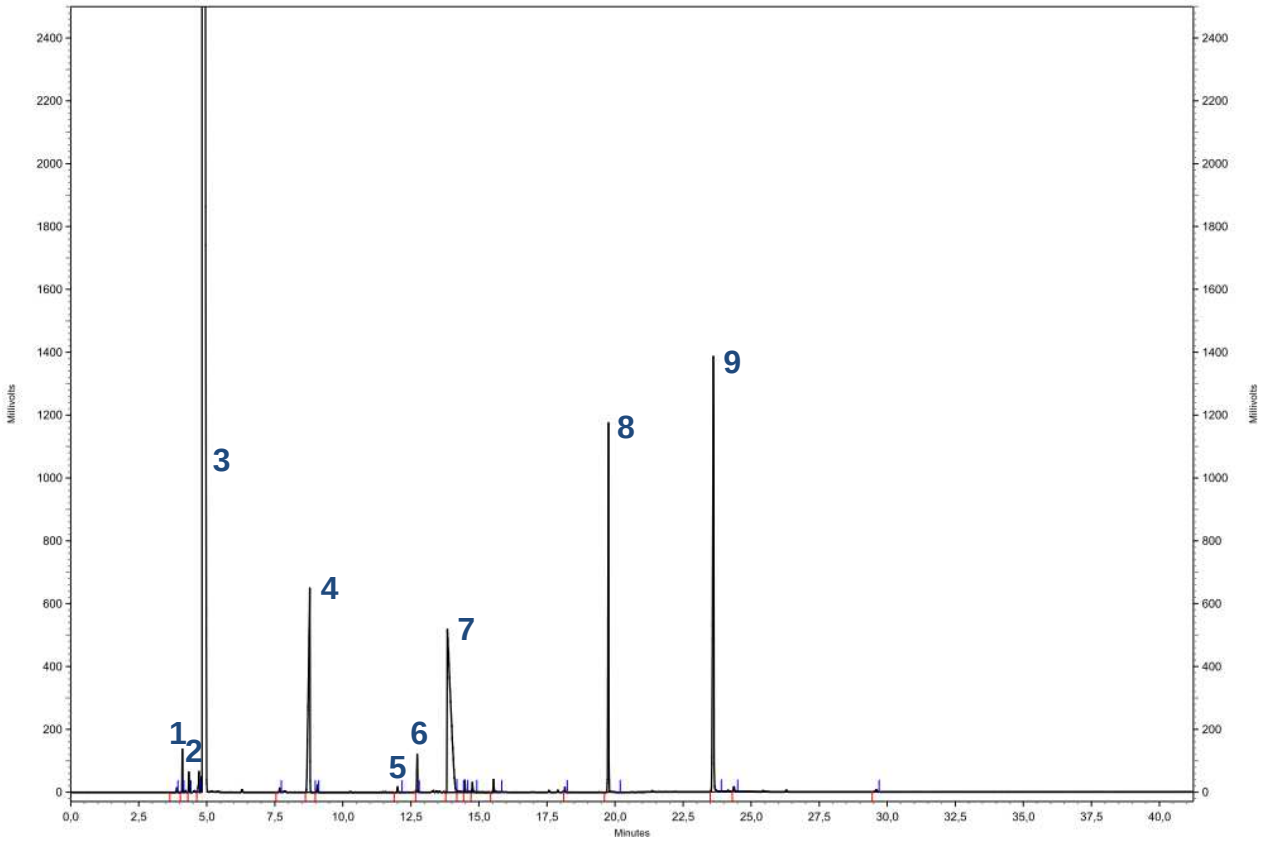
Entry	Retention Time [min]	Substance	Area
1	4.158	**CH**	1360010
2	4.403	**CE**	20203678
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	8.857	*n*-Dodecane (Stand.)	27430014
5	12.085	**CAc**	3046430
6	12.818	**CI**	6202747
7	13.907	CH_3COOH (Solv.)	48552998
8	19.820	1-Phenylethanol (Stand.)	26169017
9	23.675	**CA**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

Entry 3



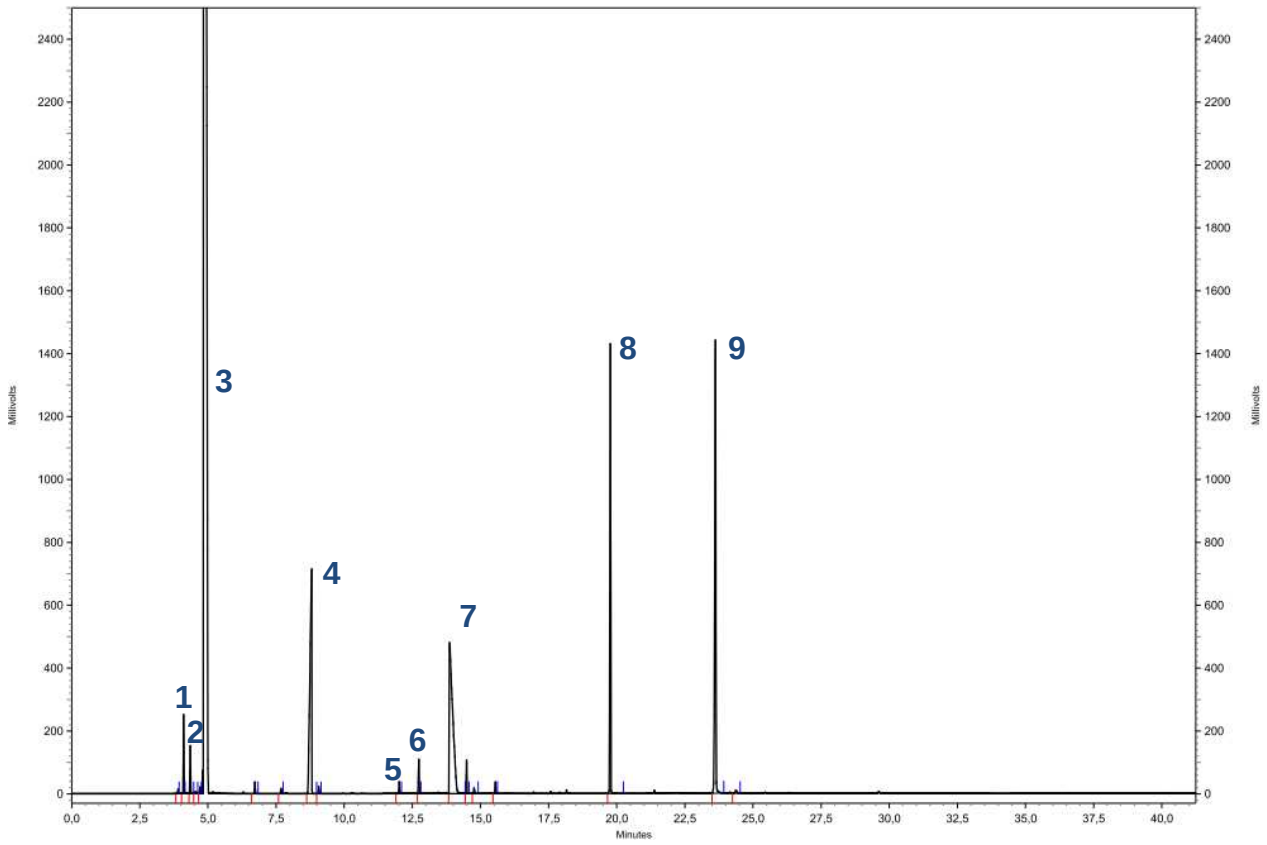
Entry	Retention Time [min]	Substance	Area
1	4.152	**CH**	2035683
2	4.397	**CE**	11078406
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	8.862	*n*-Dodecane (Stand.)	30954072
5	12.082	**CAc**	2552132
6	12.822	**CI**	6986287
7	13.922	CH_3COOH (Solv.)	43032339
8	19.827	1-Phenylethanol (Stand.)	29246822
9	23.683	**CA**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

Entry 4



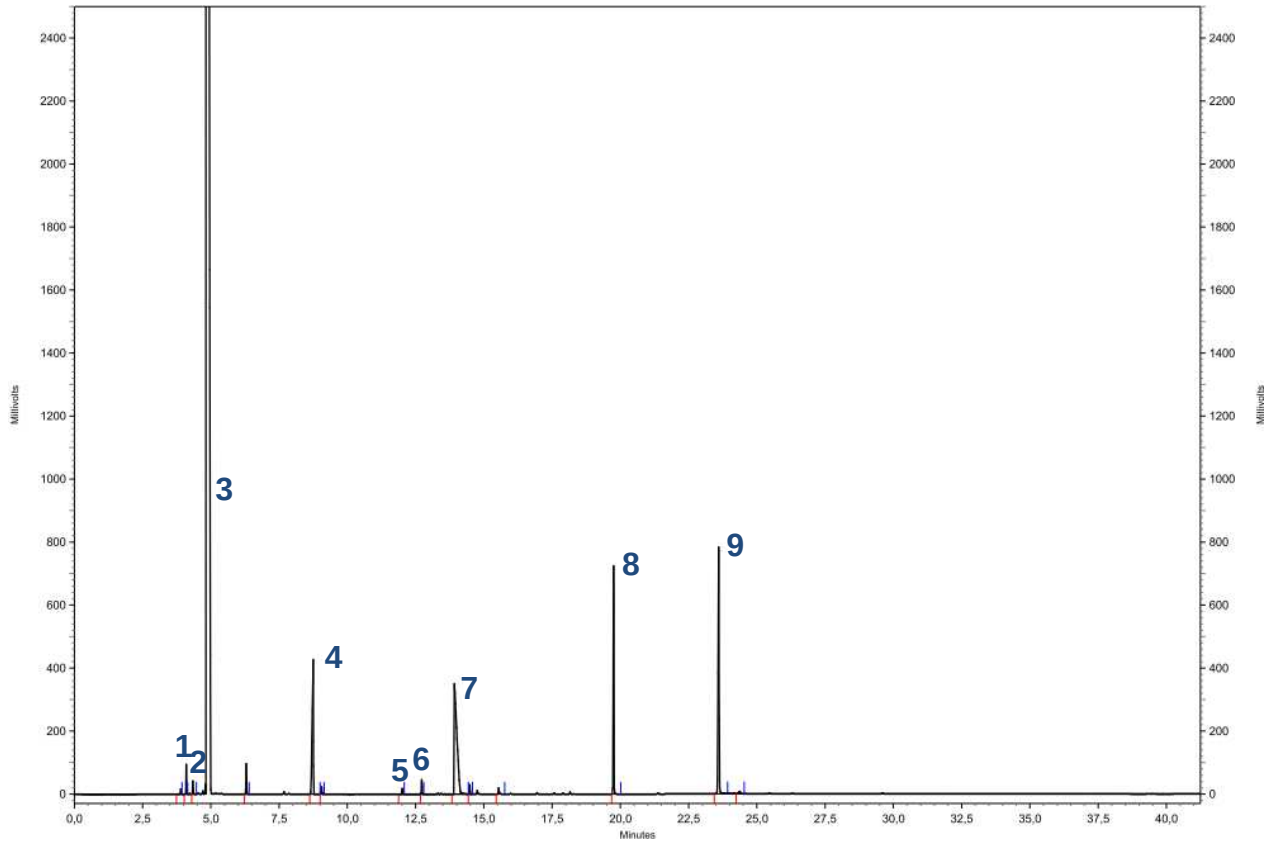
Entry	Retention Time [min]	Substance	Area
1	4.105	**CH**	1755261
2	4.347	**CE**	954342
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	8.788	*n*-Dodecane (Stand.)	26385371
5	12.012	**CAc**	280721
6	12.735	**CI**	2112889
7	13.838	CH_3COOH (Solv.)	46449859
8	19.758	1-Phenylethanol (Stand.)	20877781
9	23.612	**CA**	37072381

Entry 5



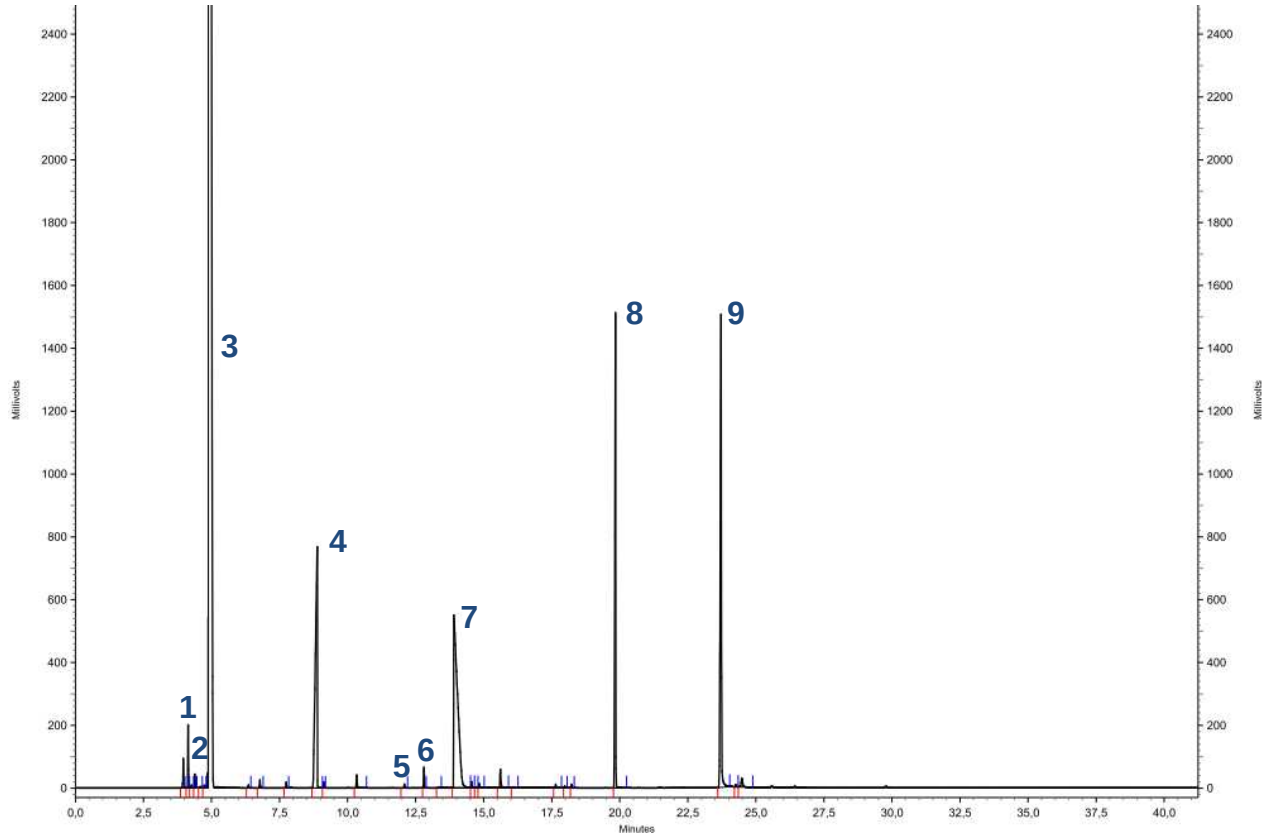
Entry	Retention Time [min]	Substance	Area
1	4.108	**CH**	3238297
2	4.352	**CE**	2280269
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	8.807	*n*-Dodecane (Stand.)	32192057
5	12.018	**CAc**	629956
6	12.738	**CI**	1930831
7	13.865	CH_3COOH (Solv.)	40637845
8	19.768	1-Phenylethanol (Stand.)	26679121
9	23.623	**CA**	38750777

Entry 6



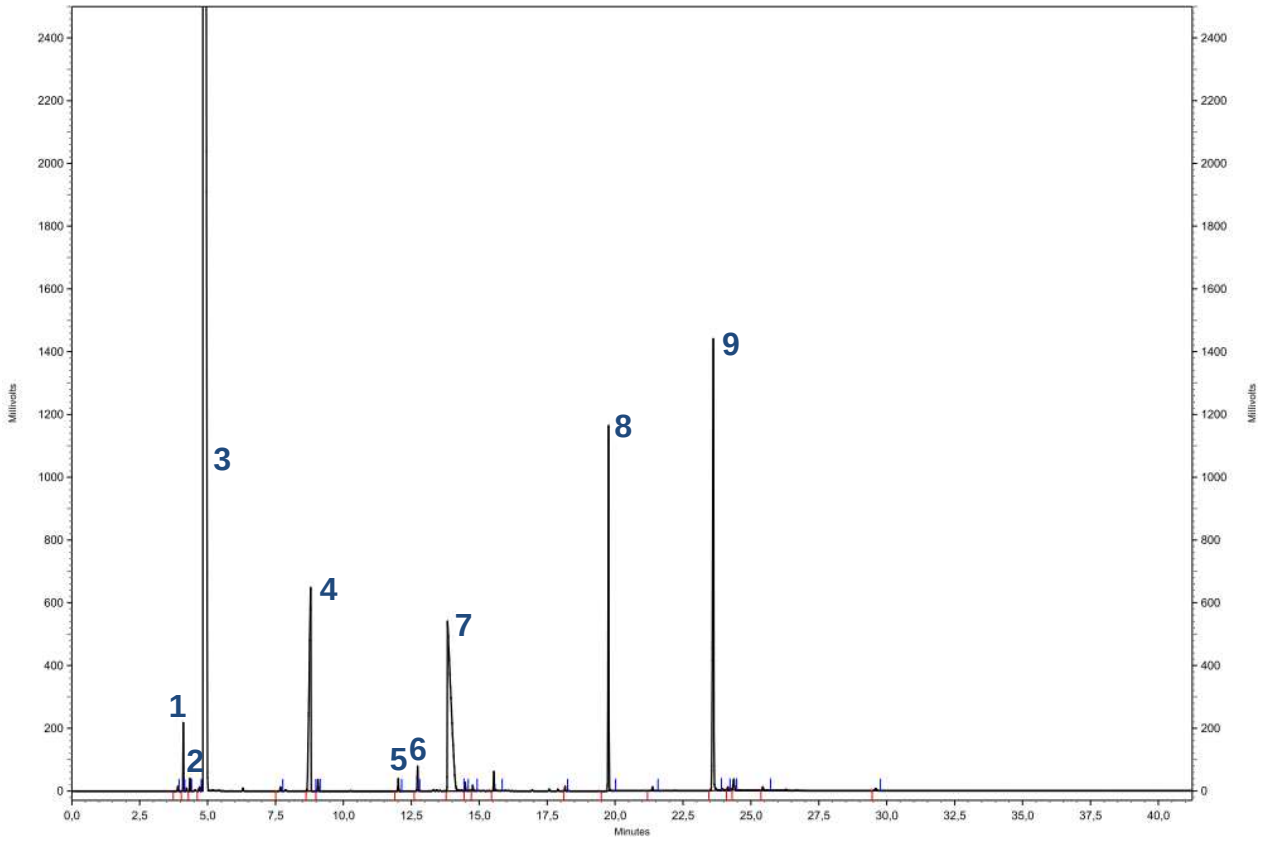
Entry	Retention Time [min]	Substance	Area
1	4.100	**CH**	1214717
2	4.343	**CE**	641059
3	*cutted*	CH_2Cl_2 (Solv.)	--
4	8.750	*n*-Dodecane (Stand.)	12656494
5	12.010	**CAc**	298821
6	12.727	**CI**	793040
7	13.922	CH_3COOH (Solv.)	23583787
8	19.753	1-Phenylethanol (Stand.)	12066681
9	23.602	**CA**	18100772

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

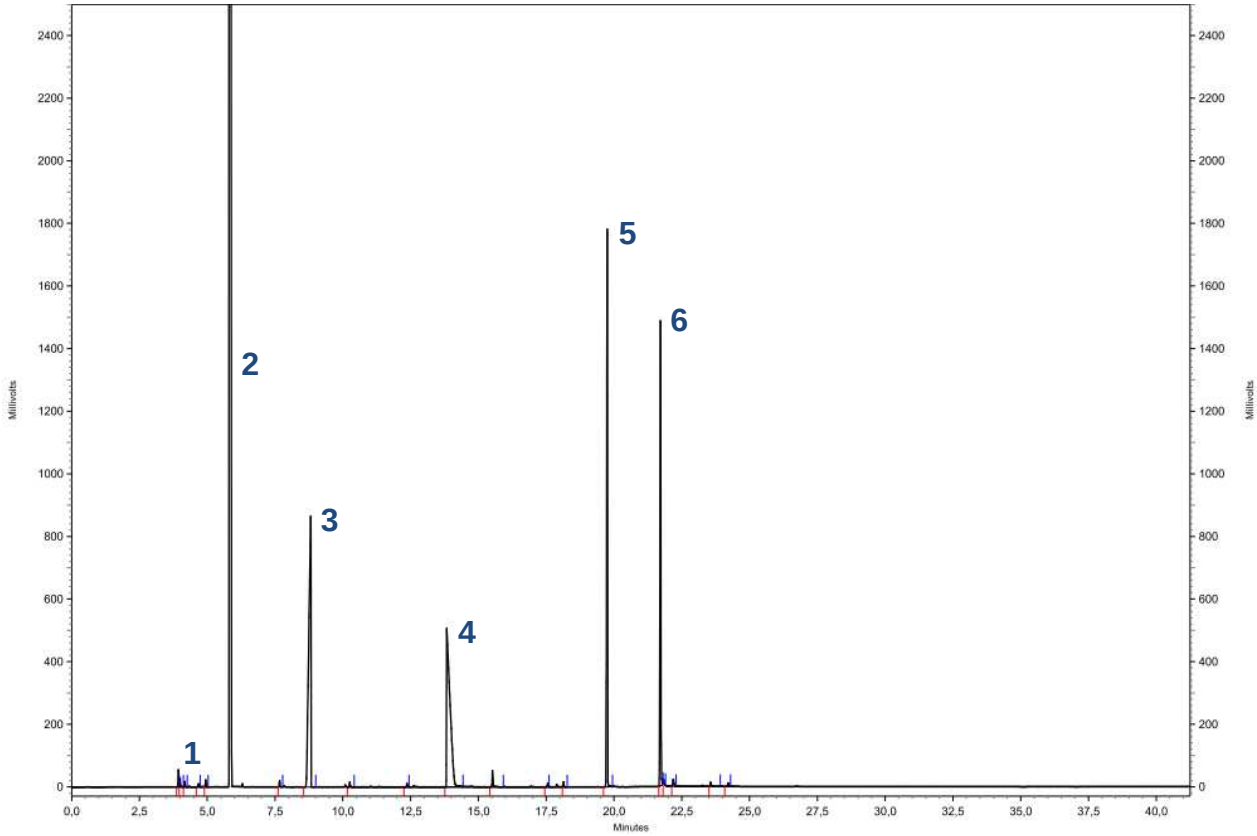
Entry 8



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

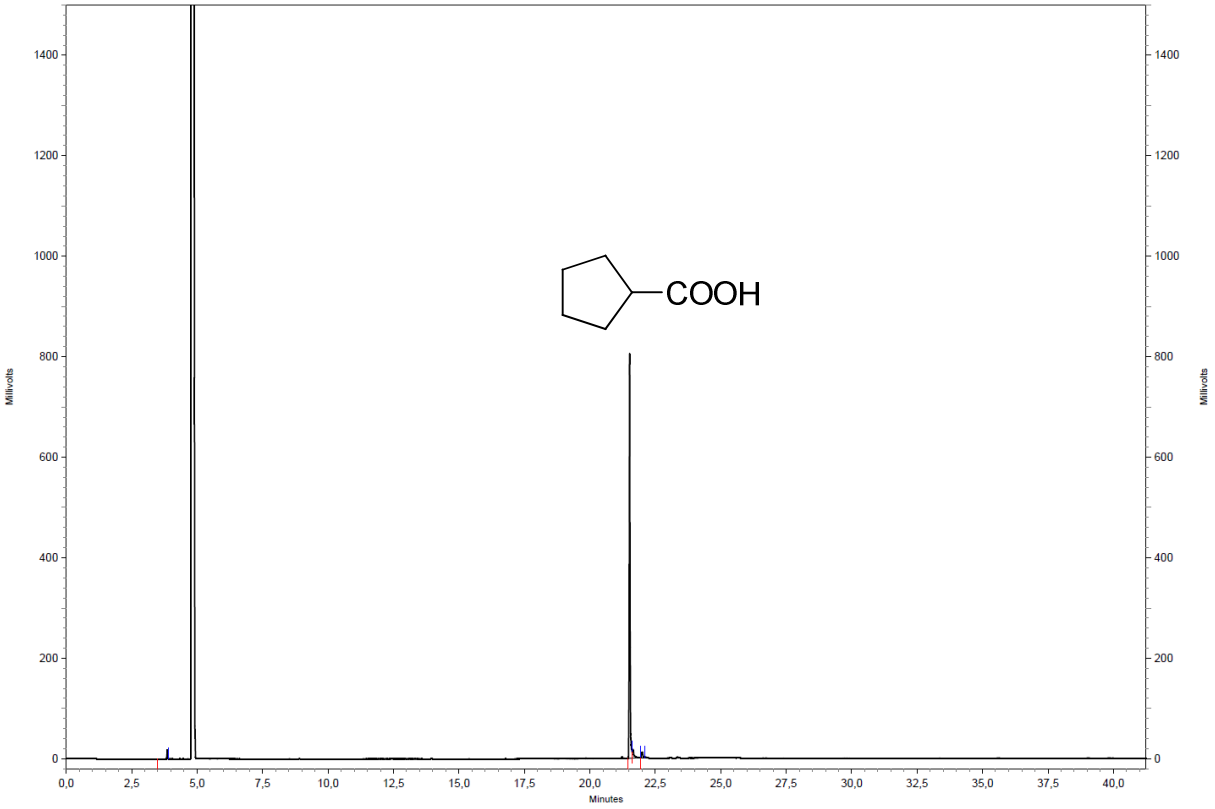


Figure 3.3 GC Chromatogram of the isolated cyclopentane carboxylic acid.

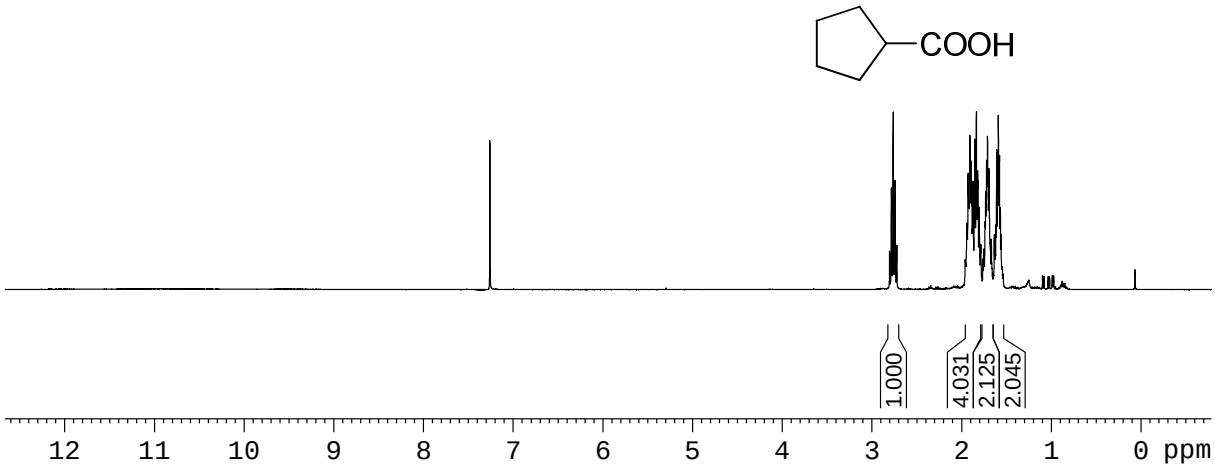
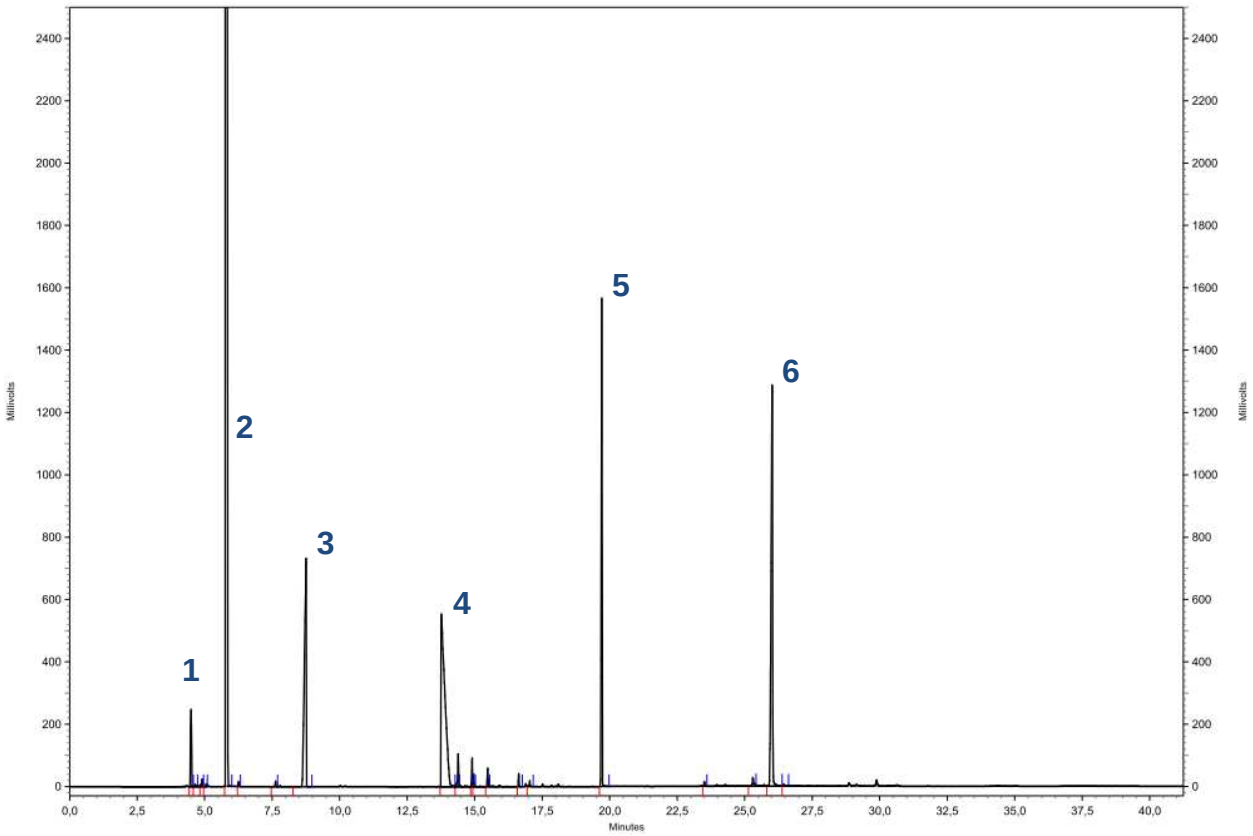


Figure 3.4. ^{1}H NMR spectrum of the isolated product measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

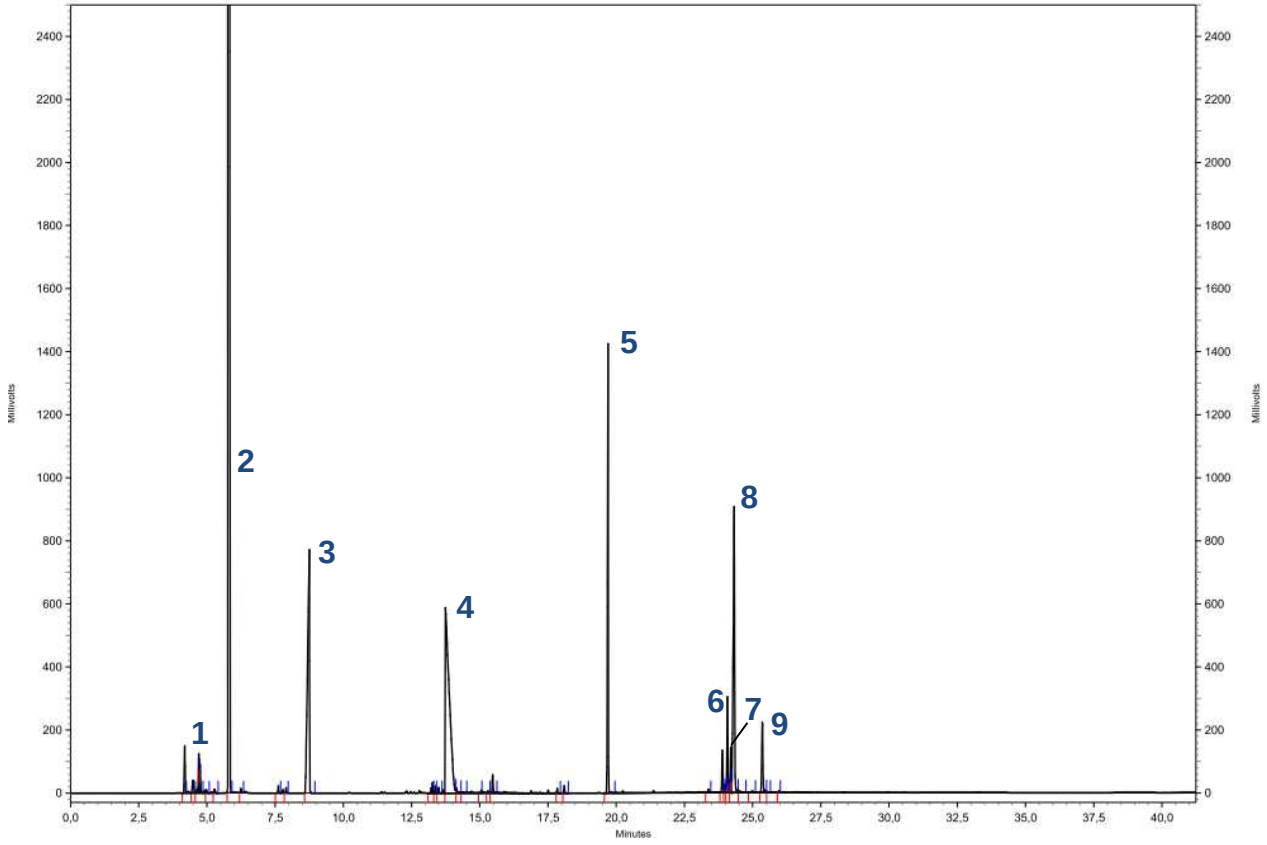
Entry 3



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.

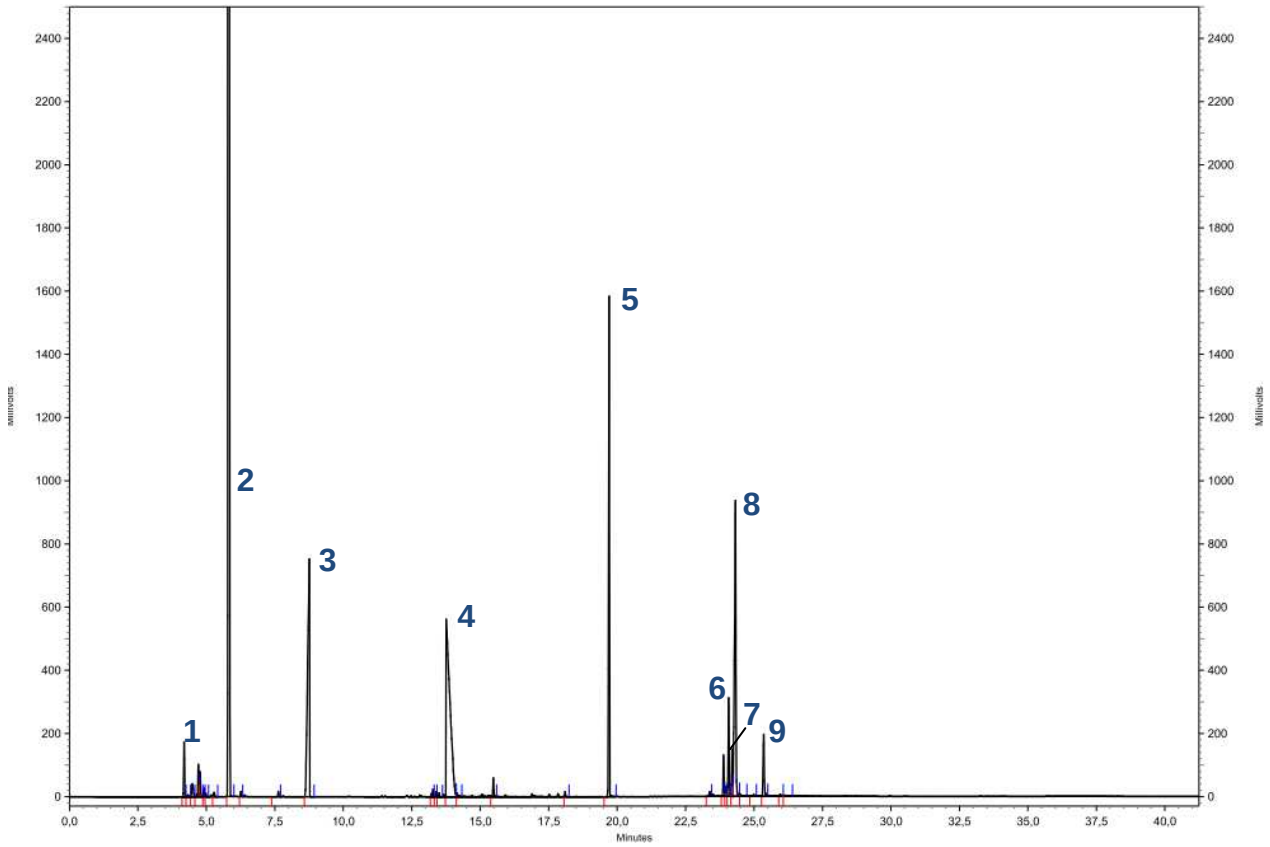
Entry 4



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.

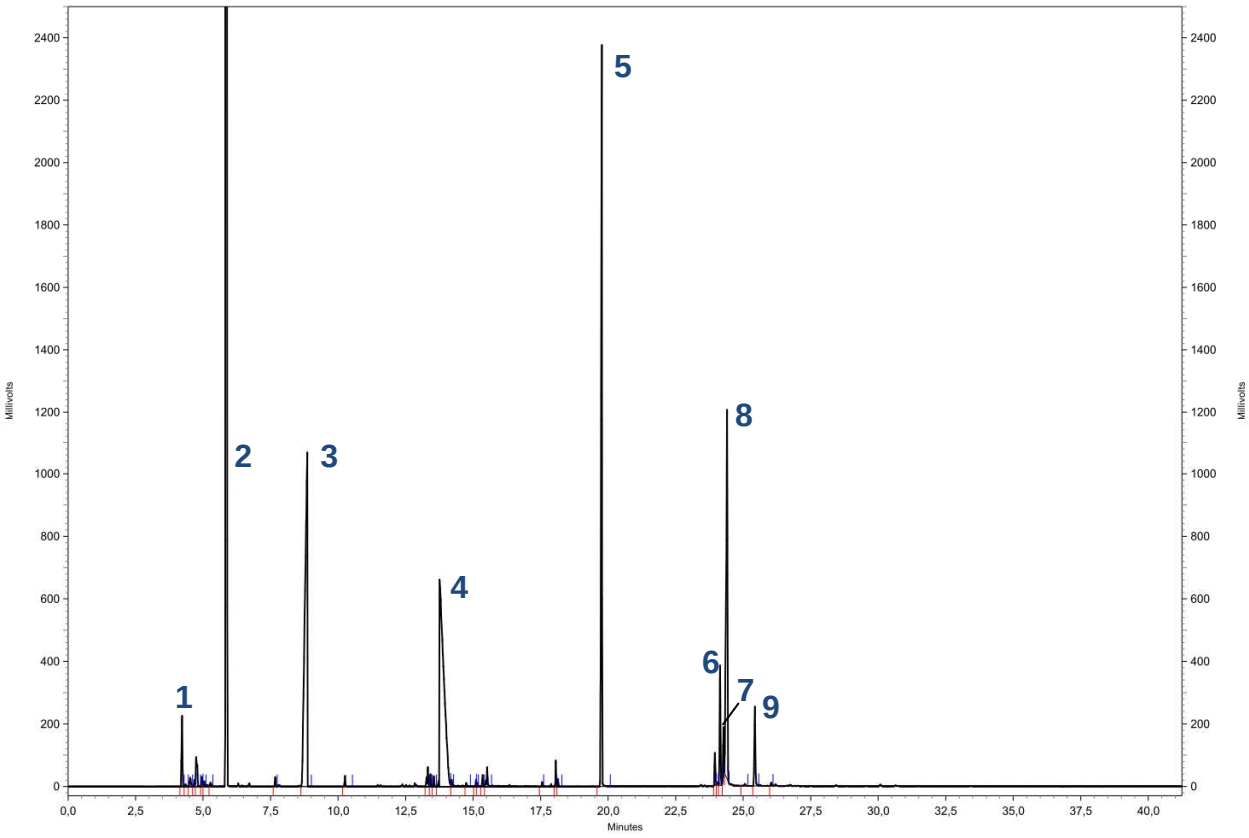
Entry 5



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

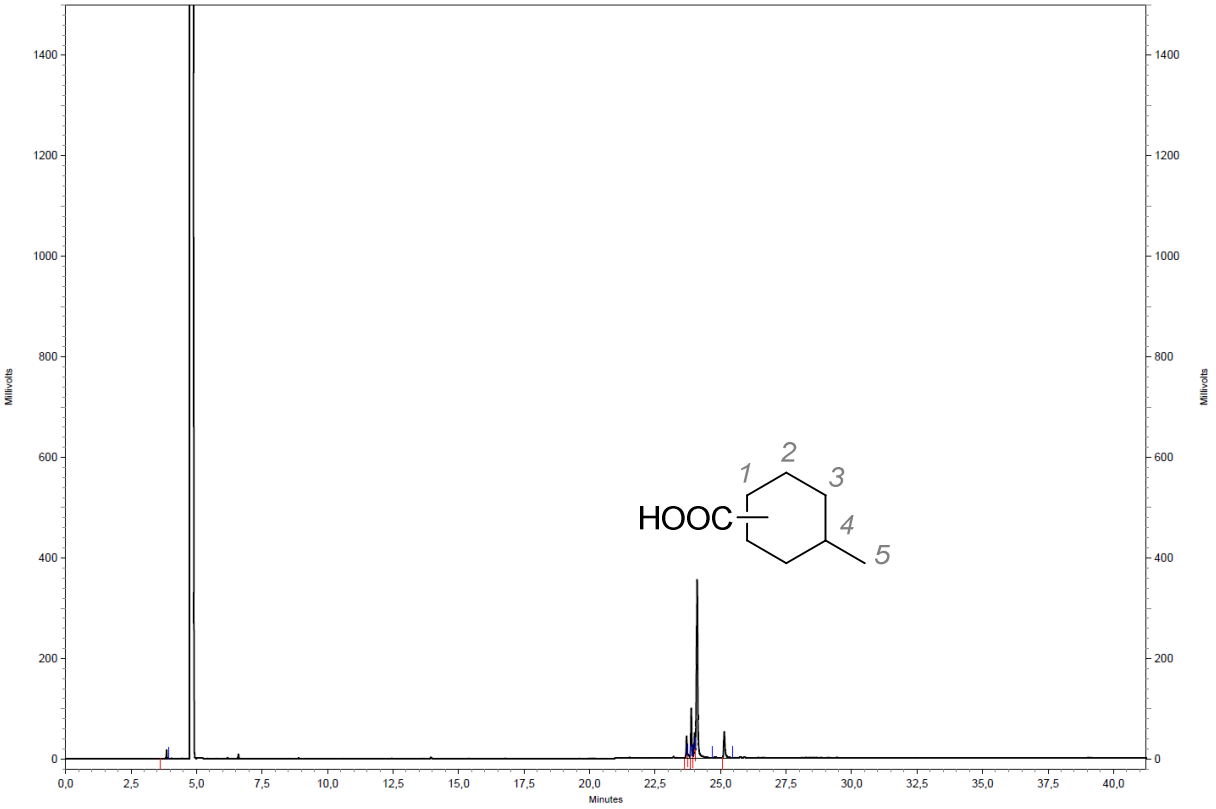


Figure 3.5 GC Chromatogram of the isolated product mixture.

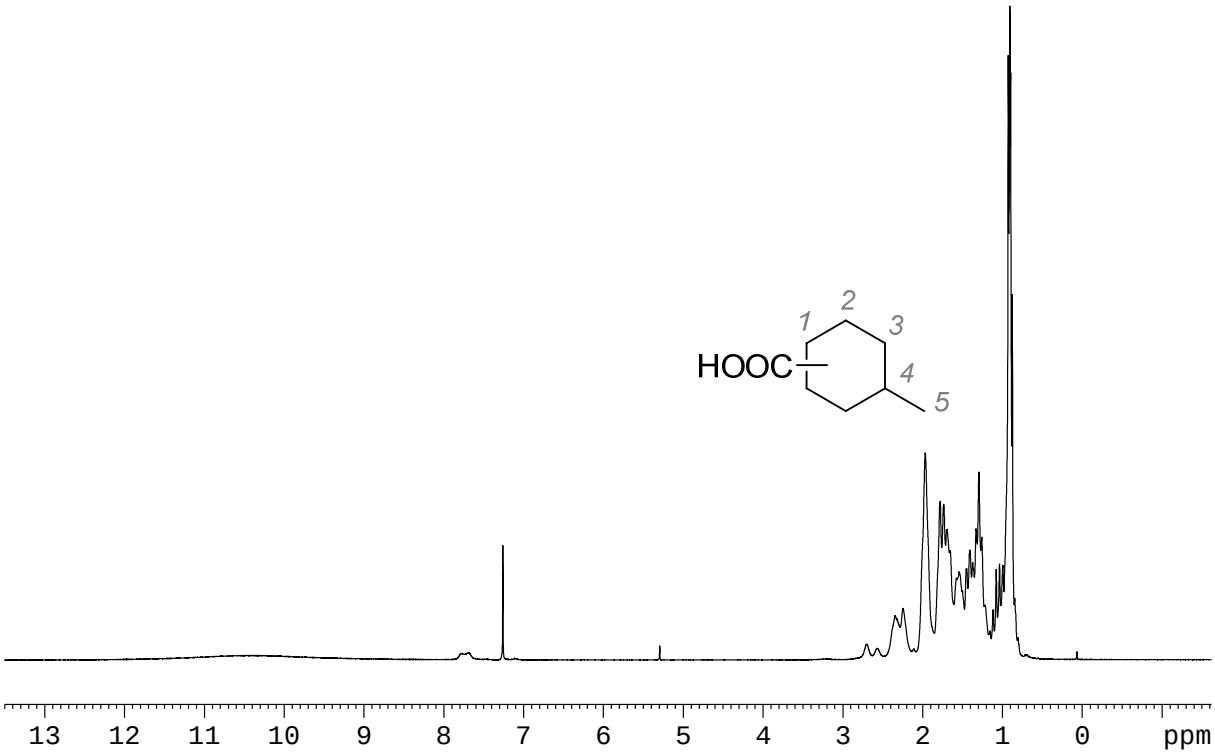
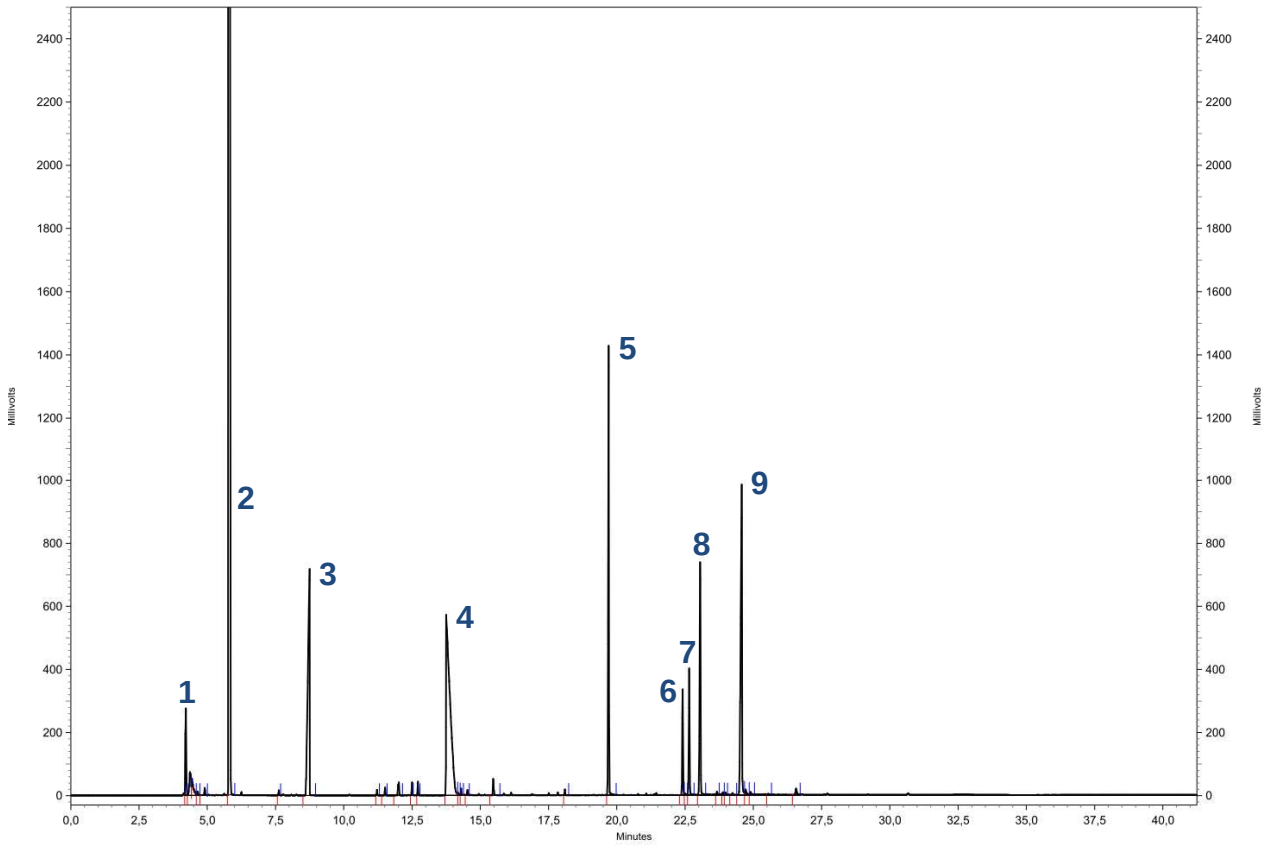


Figure 3.6. ^{1}H NMR spectrum of the isolated product mixture measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

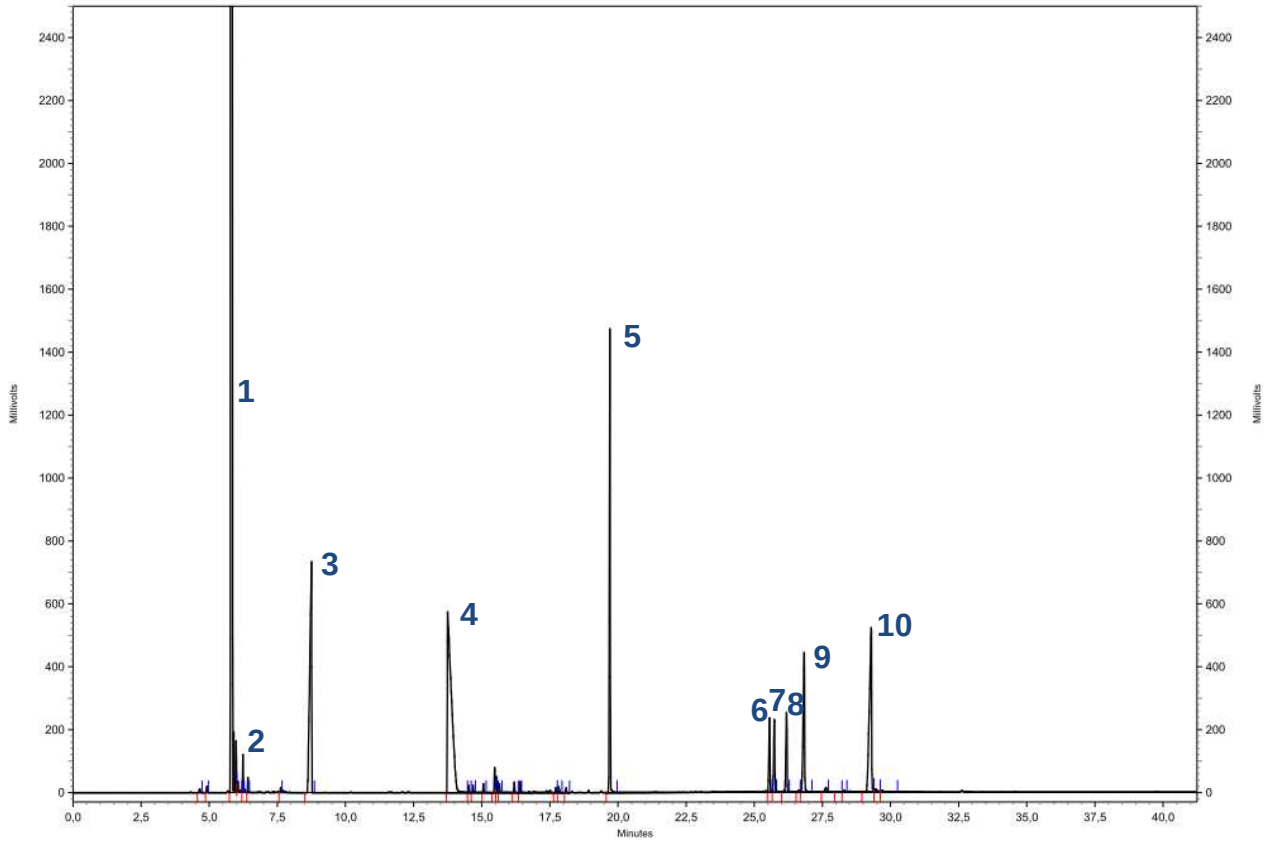
Entry 7



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.

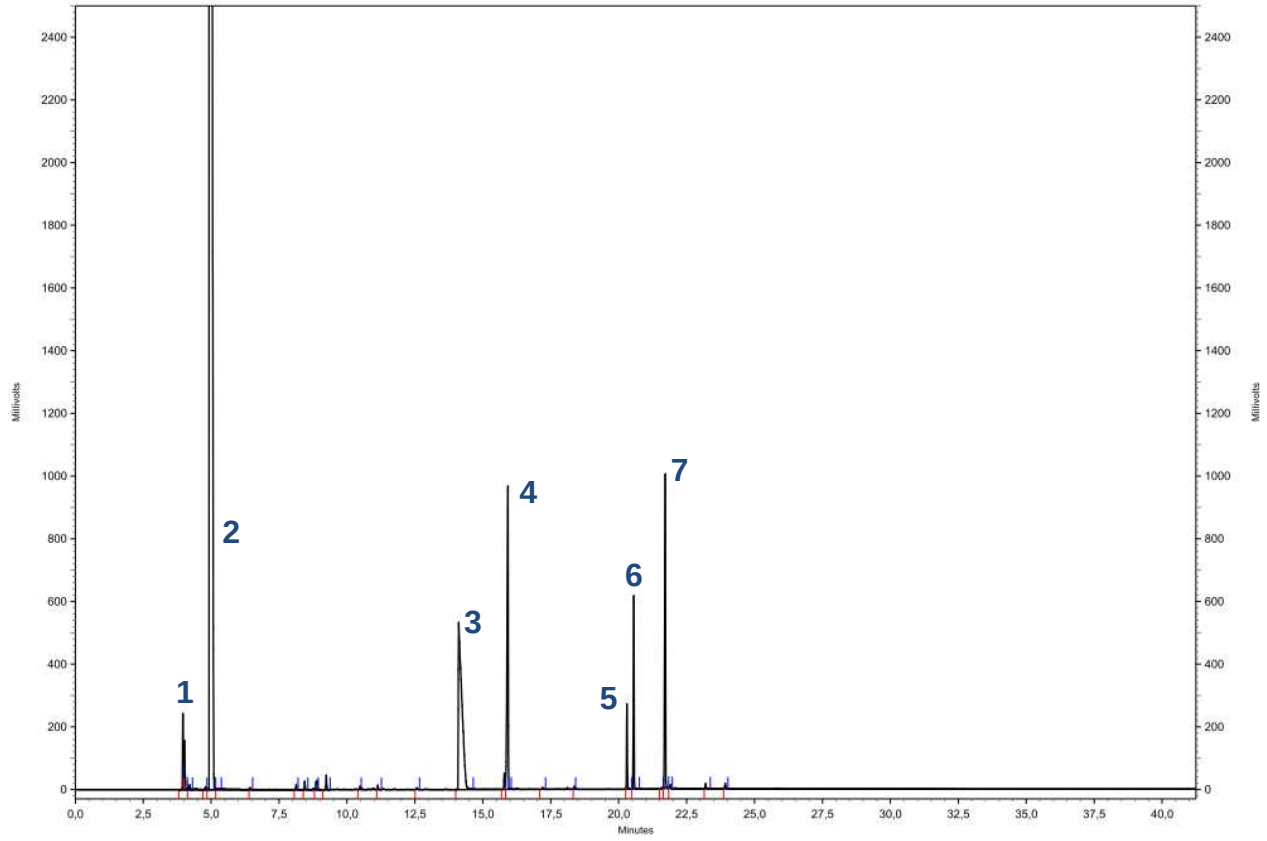
Entry 8



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

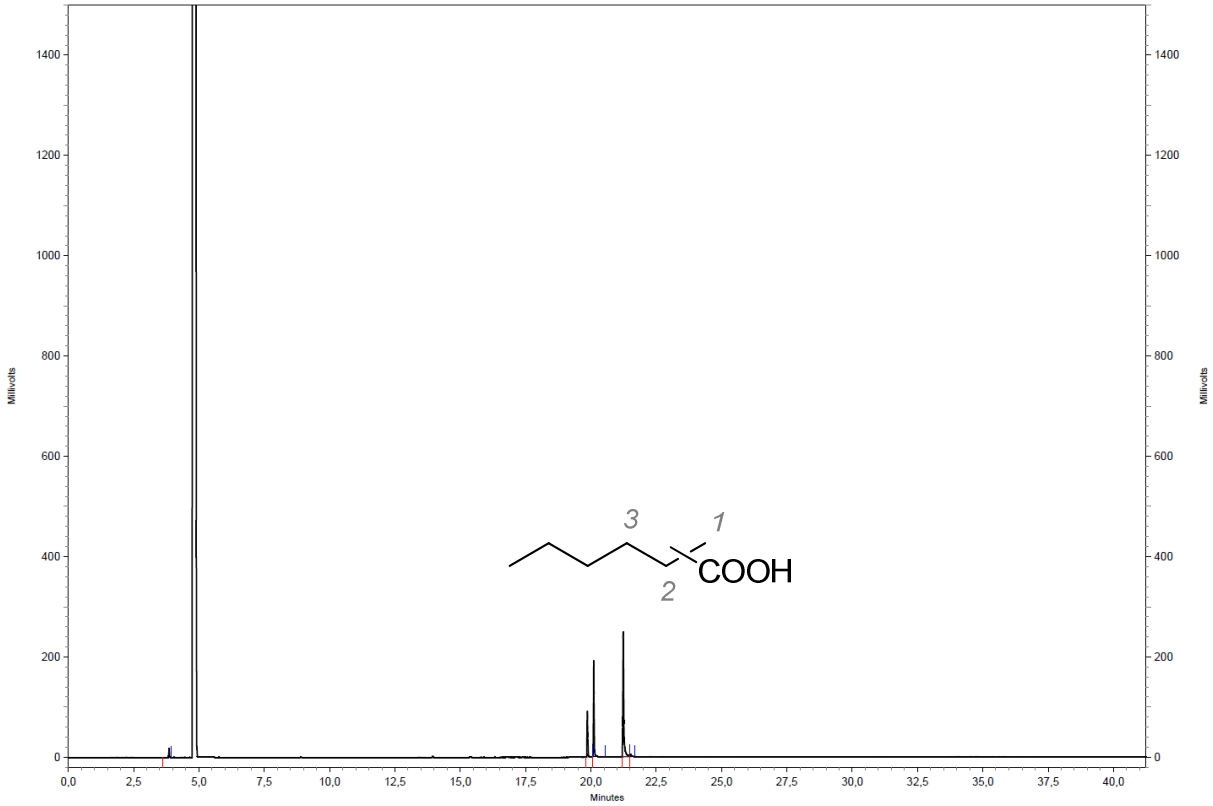


Figure 3.7 GC chromatogram of the isolated product mixture.

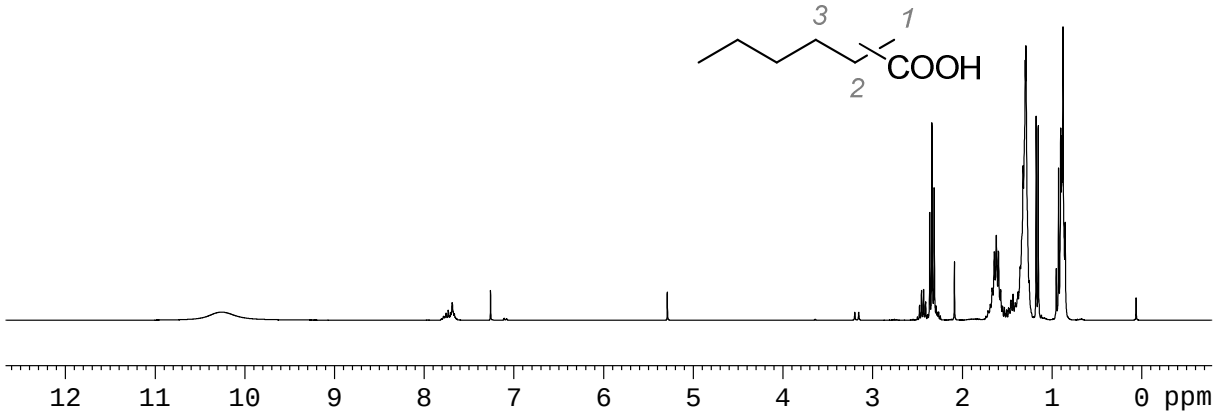
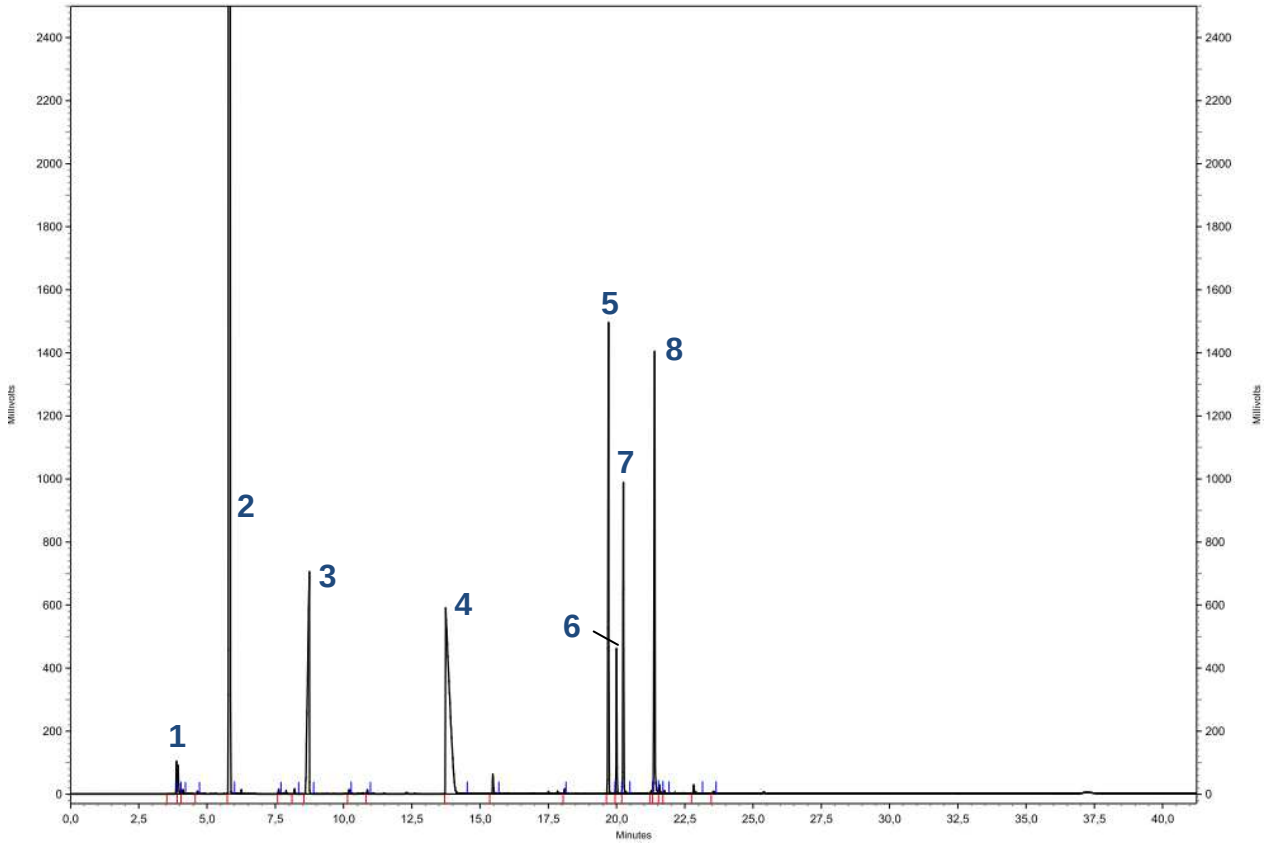


Figure 3.8. ^{1}H NMR spectrum of the isolated product mixture measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

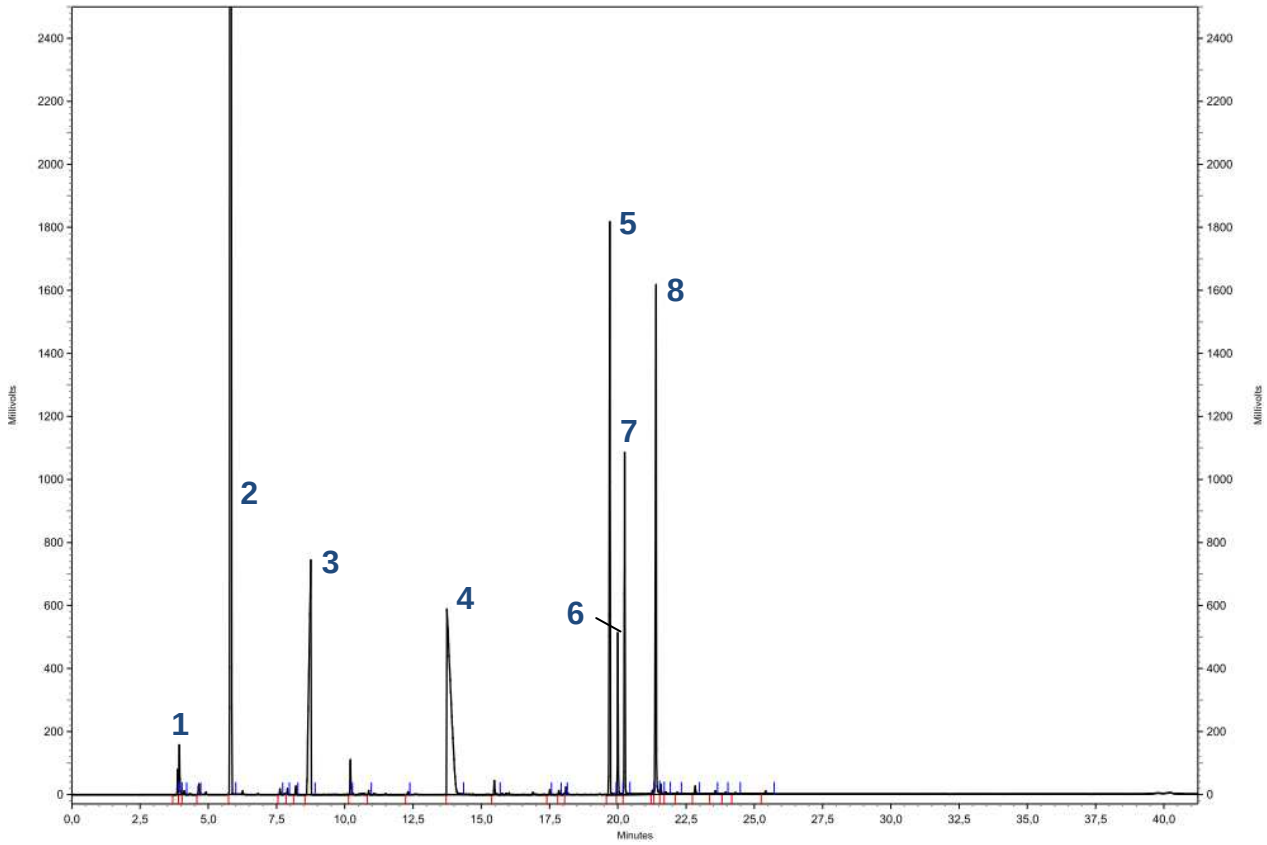
Entry 10



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.

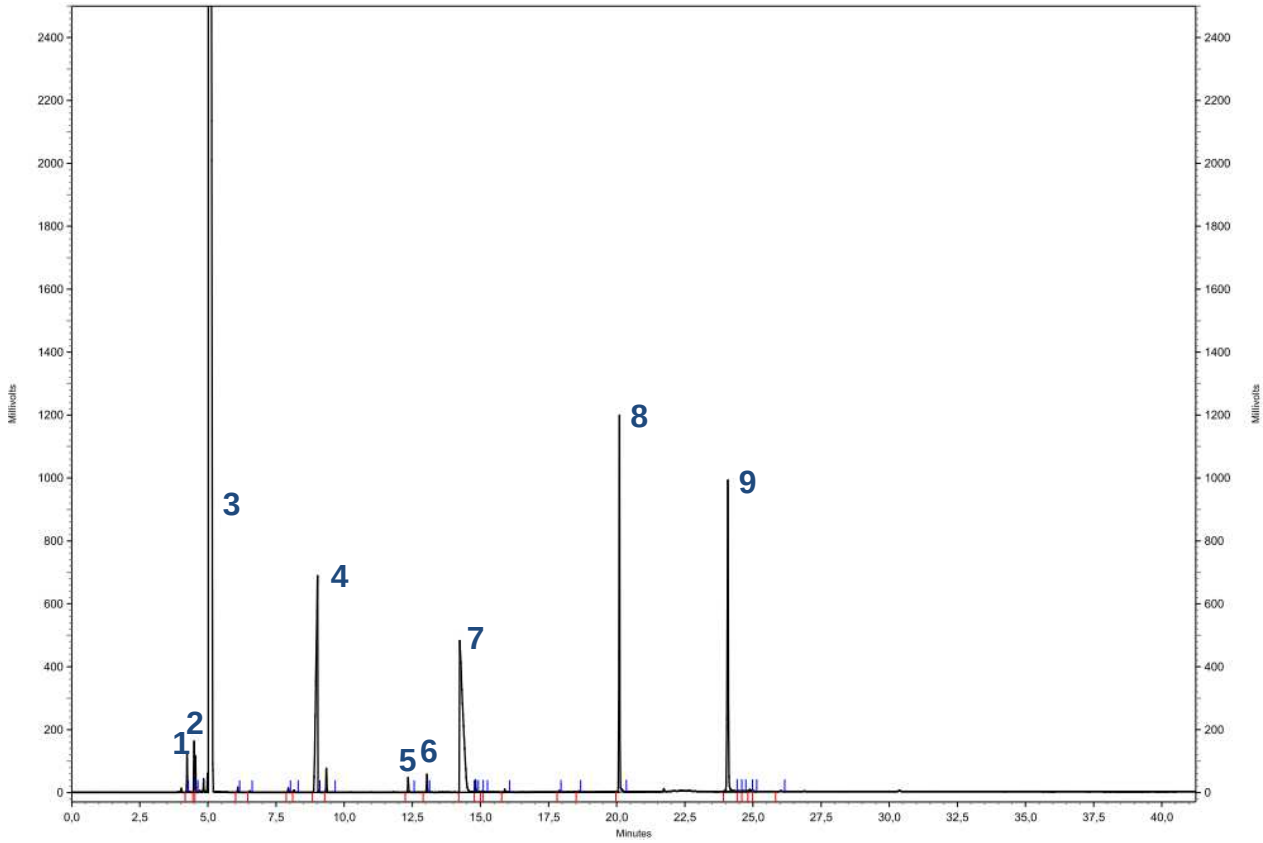
Entry 11



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

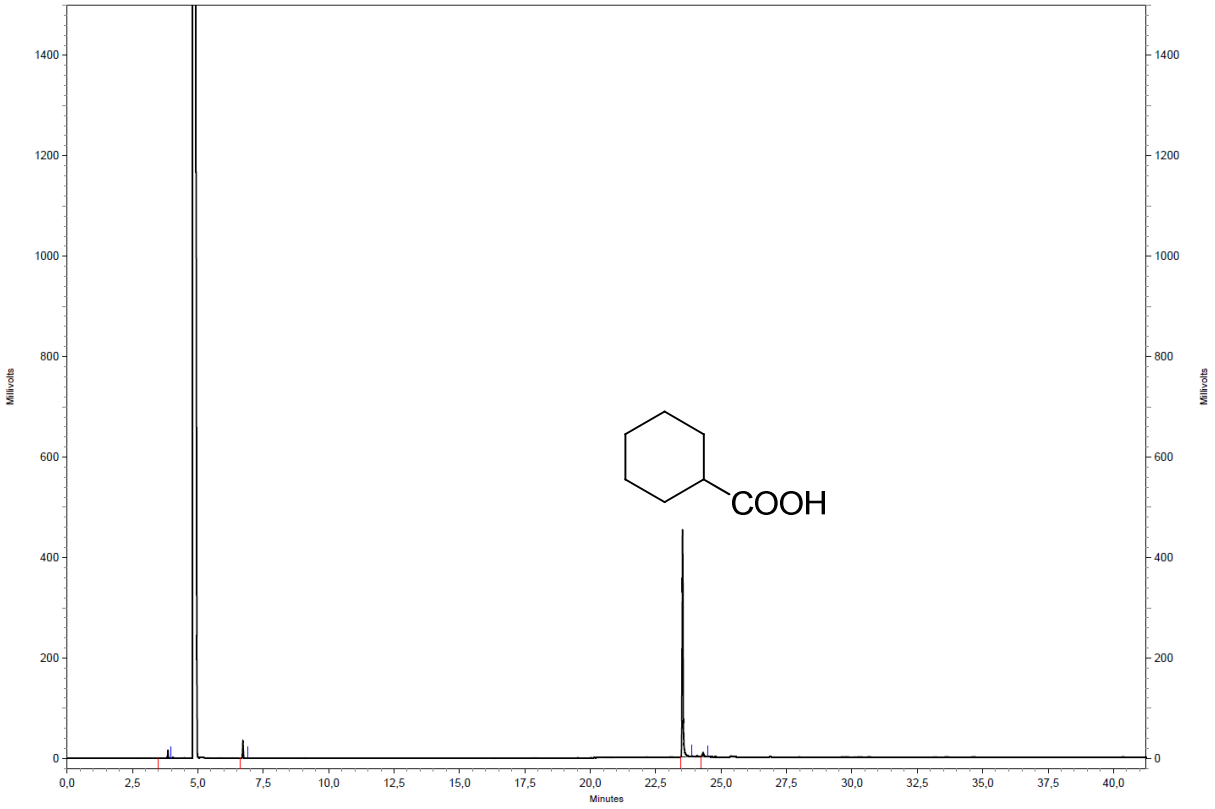


Figure 3.9 GC chromatogram of the isolated cyclohexane carboxylic acid.

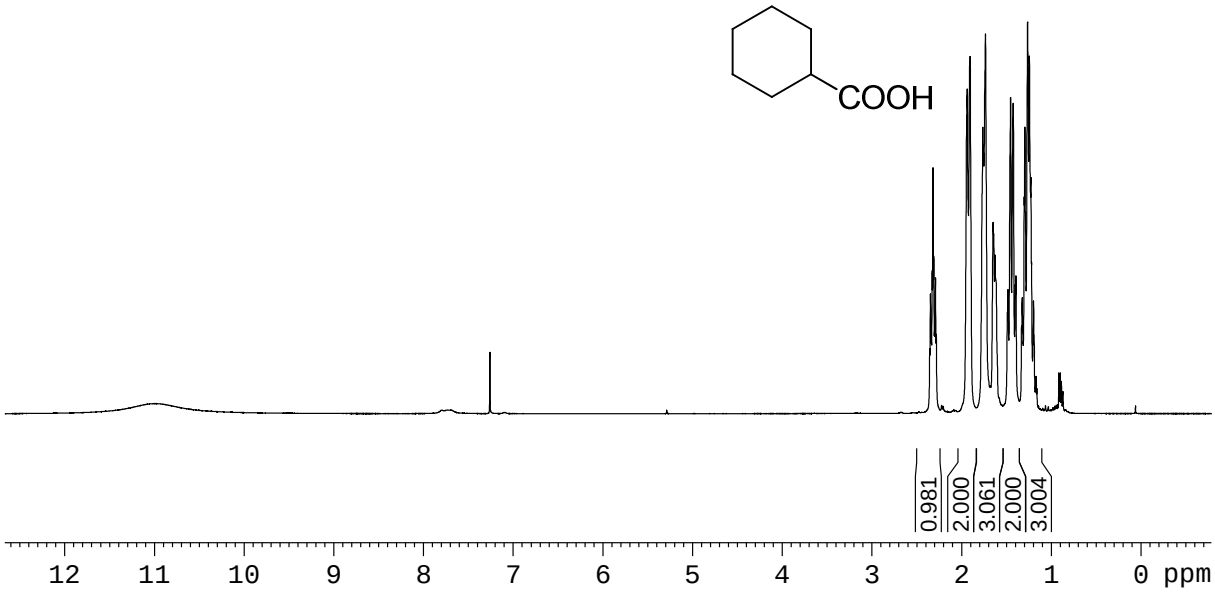
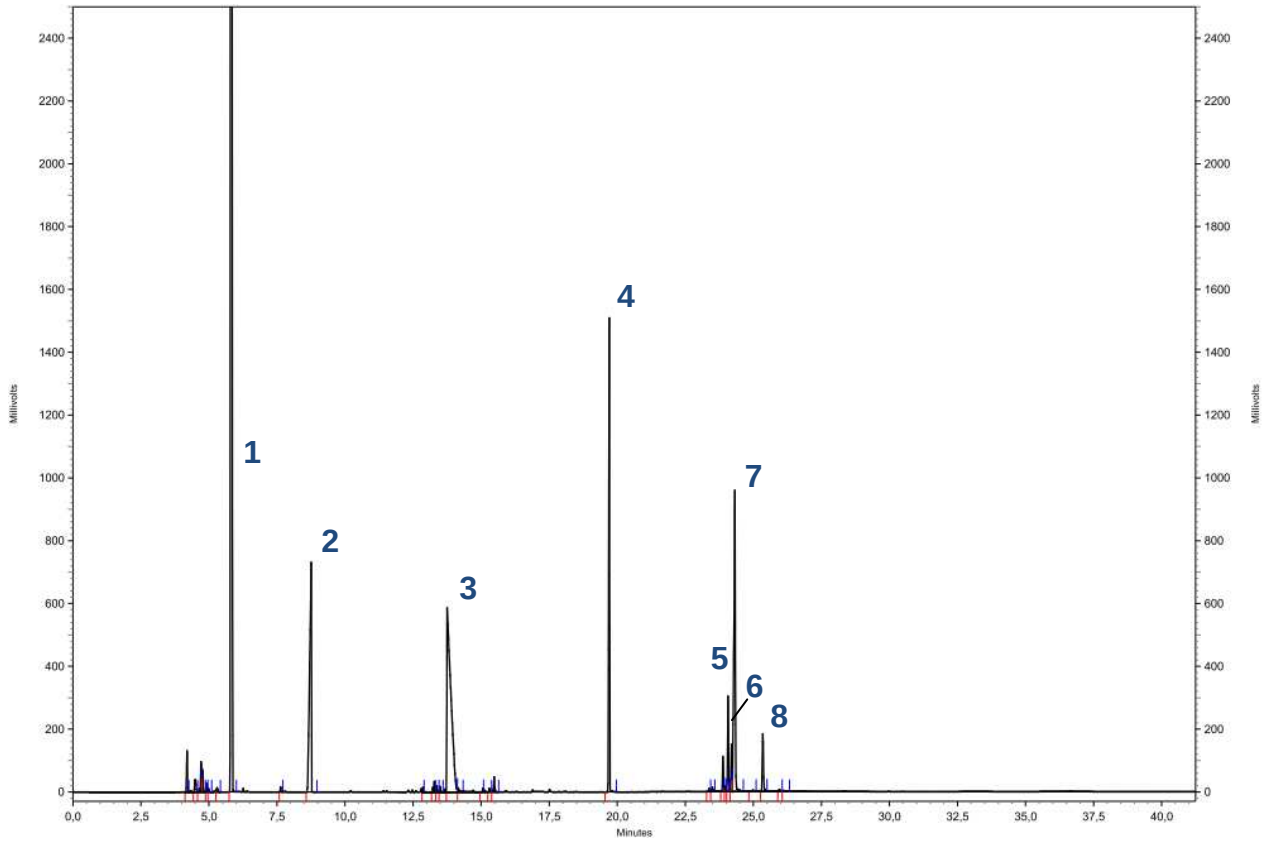


Figure 3.10. ^{1}H NMR spectrum of the isolated product measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

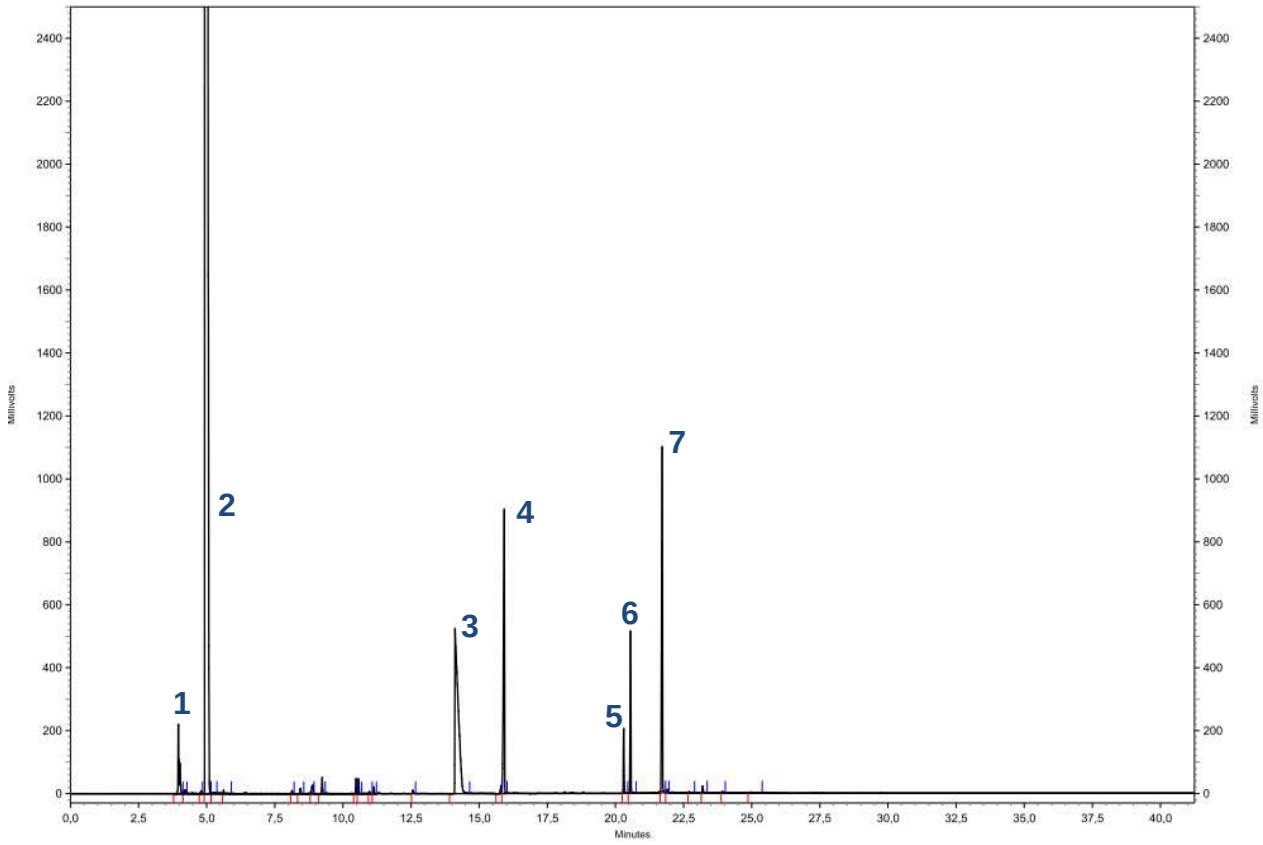
Entry 13



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

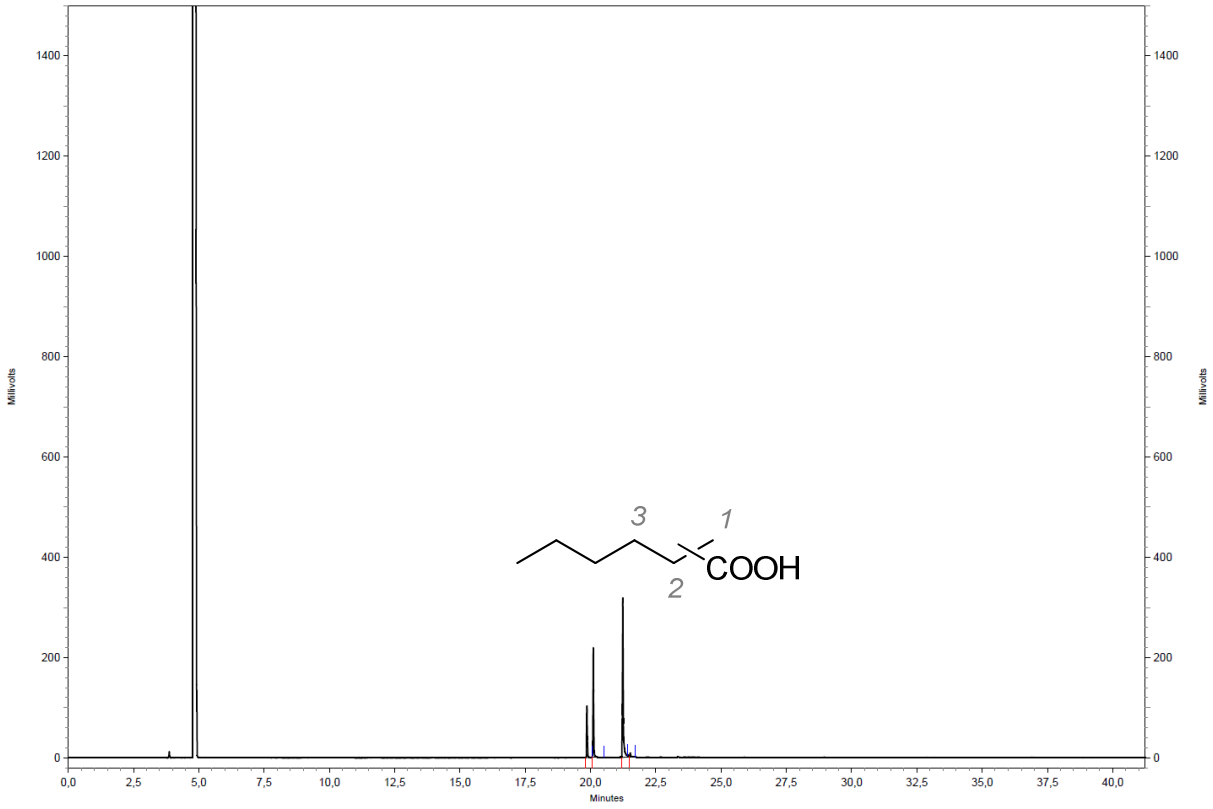


Figure 3.11 GC chromatogram of the isolated product mixture.

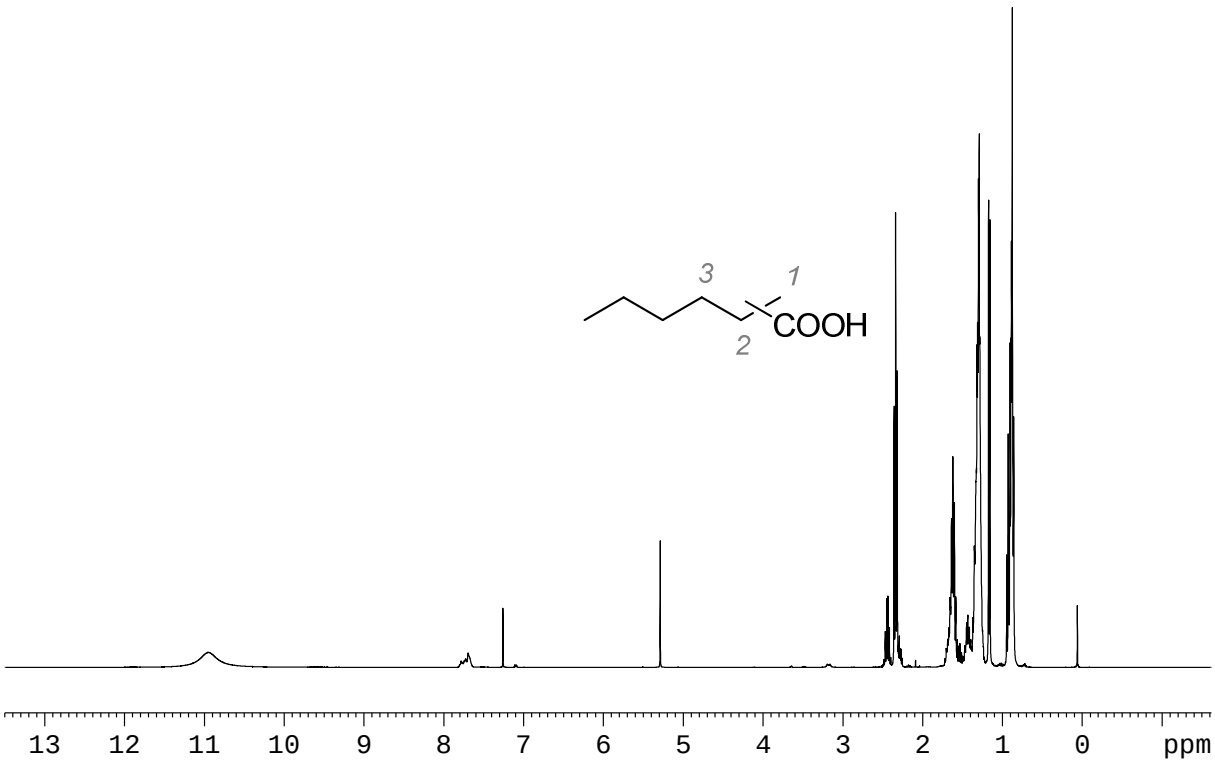
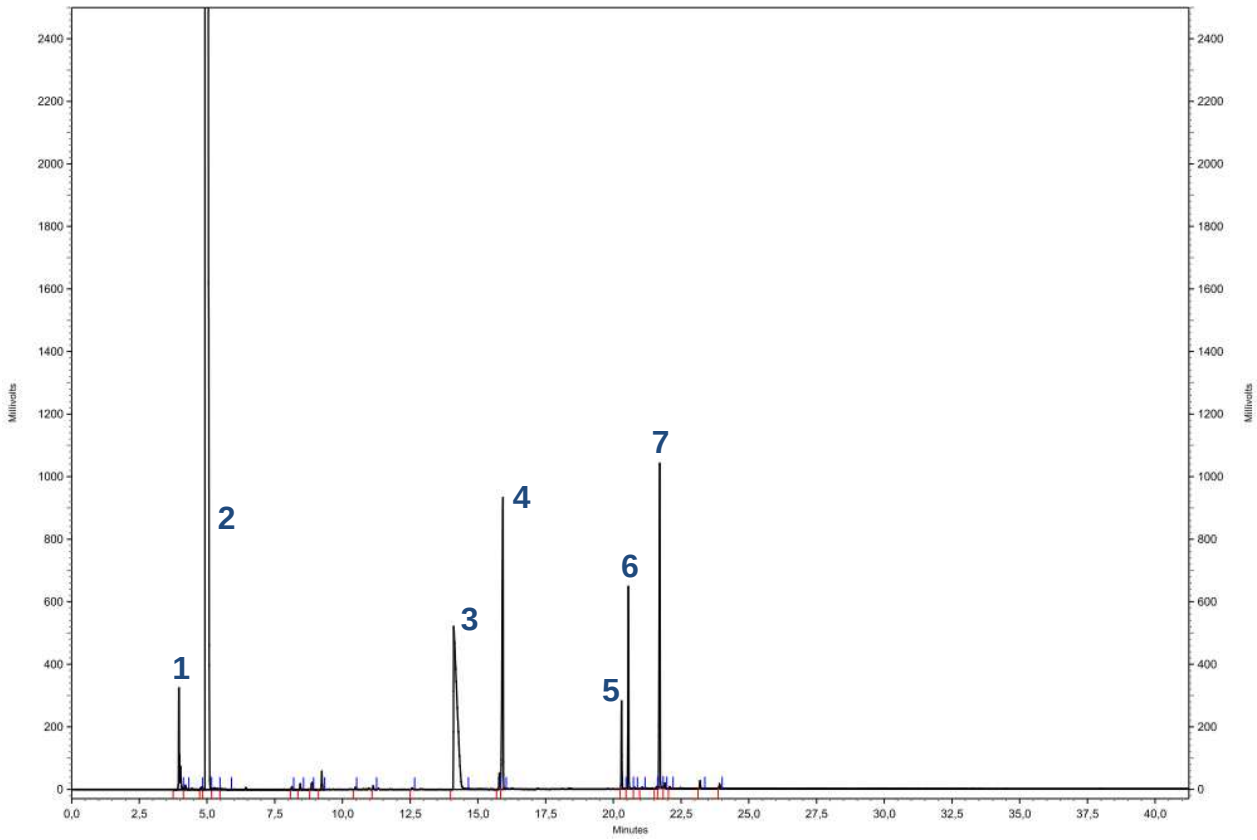


Figure 3.12. ^{1}H NMR spectrum of the isolated product mixture measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

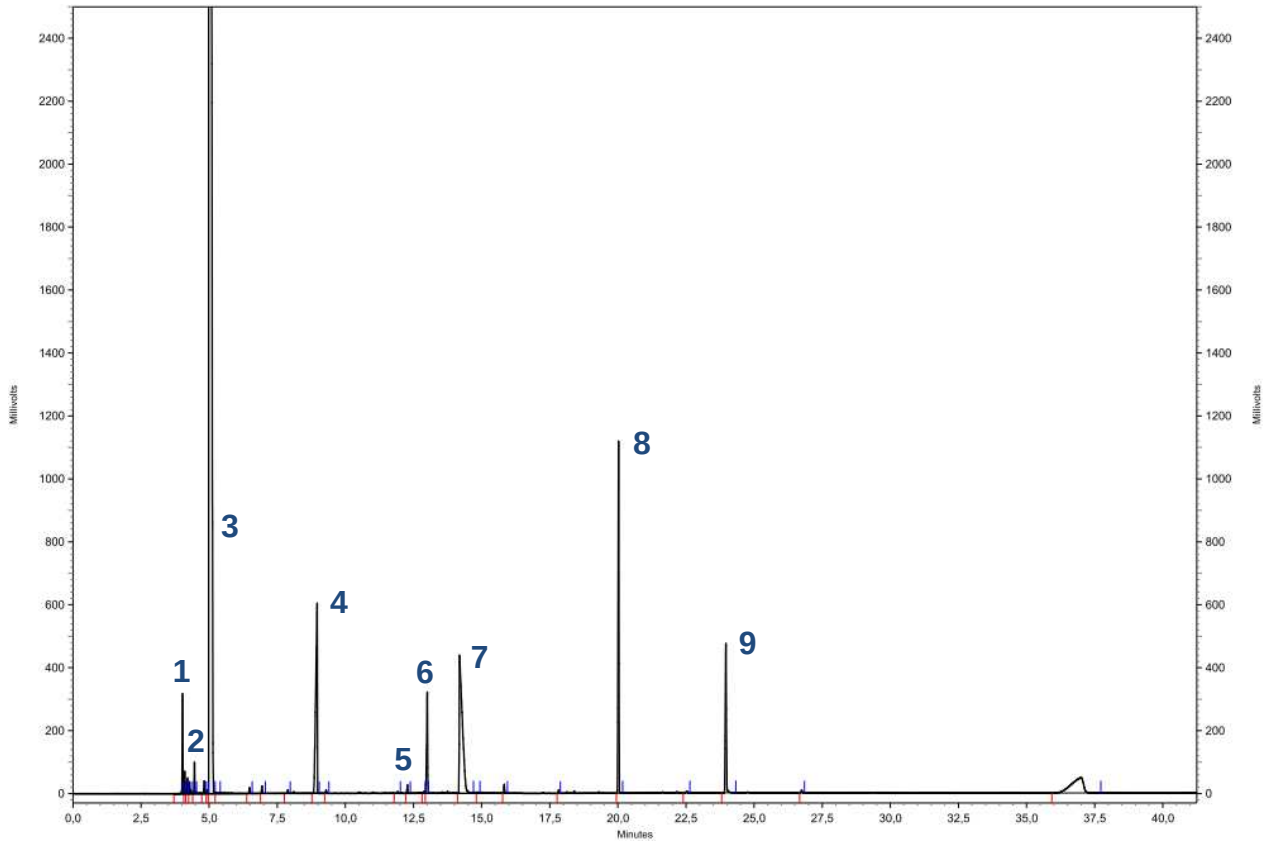
Entry 15



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

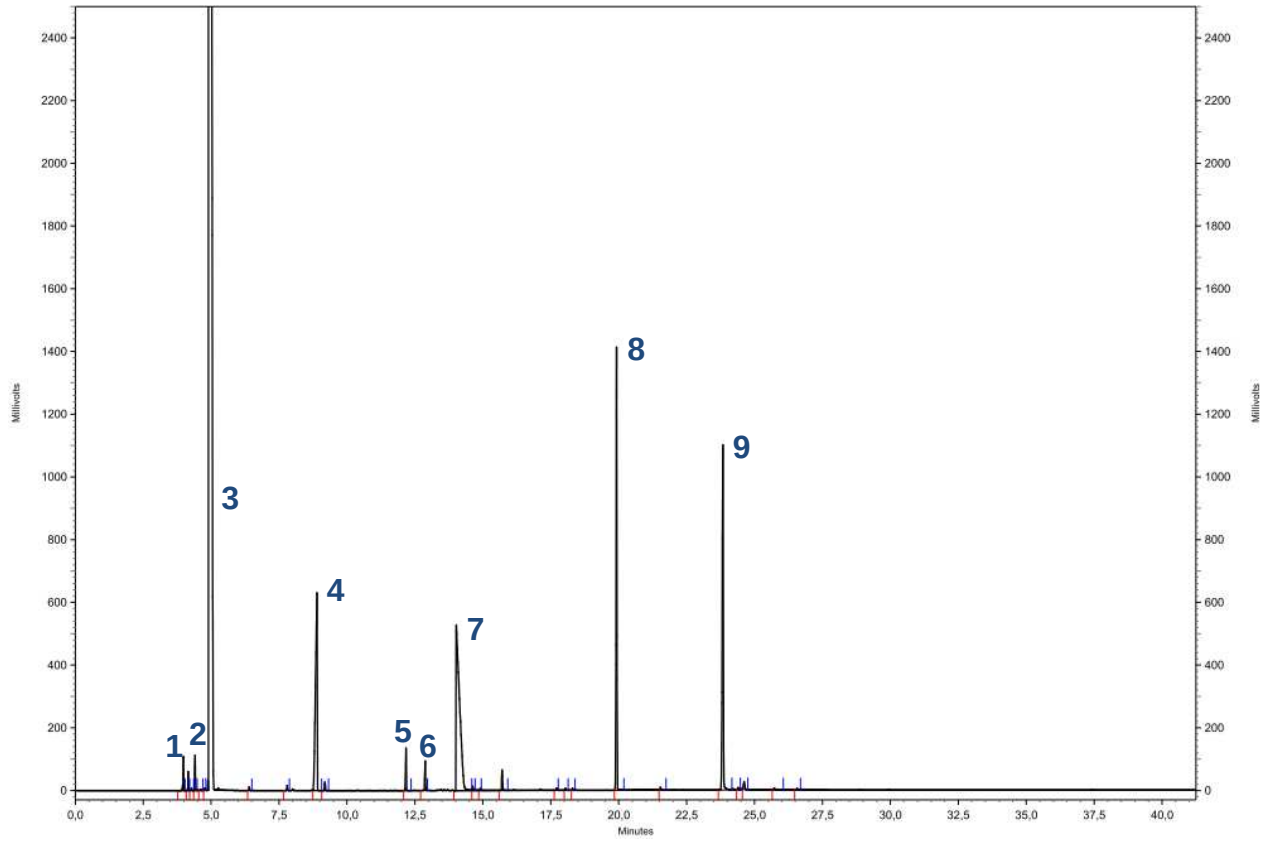
[a]: *n*-Octanol was used in this experiment to avoid signal overlap with the substrate peak.

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

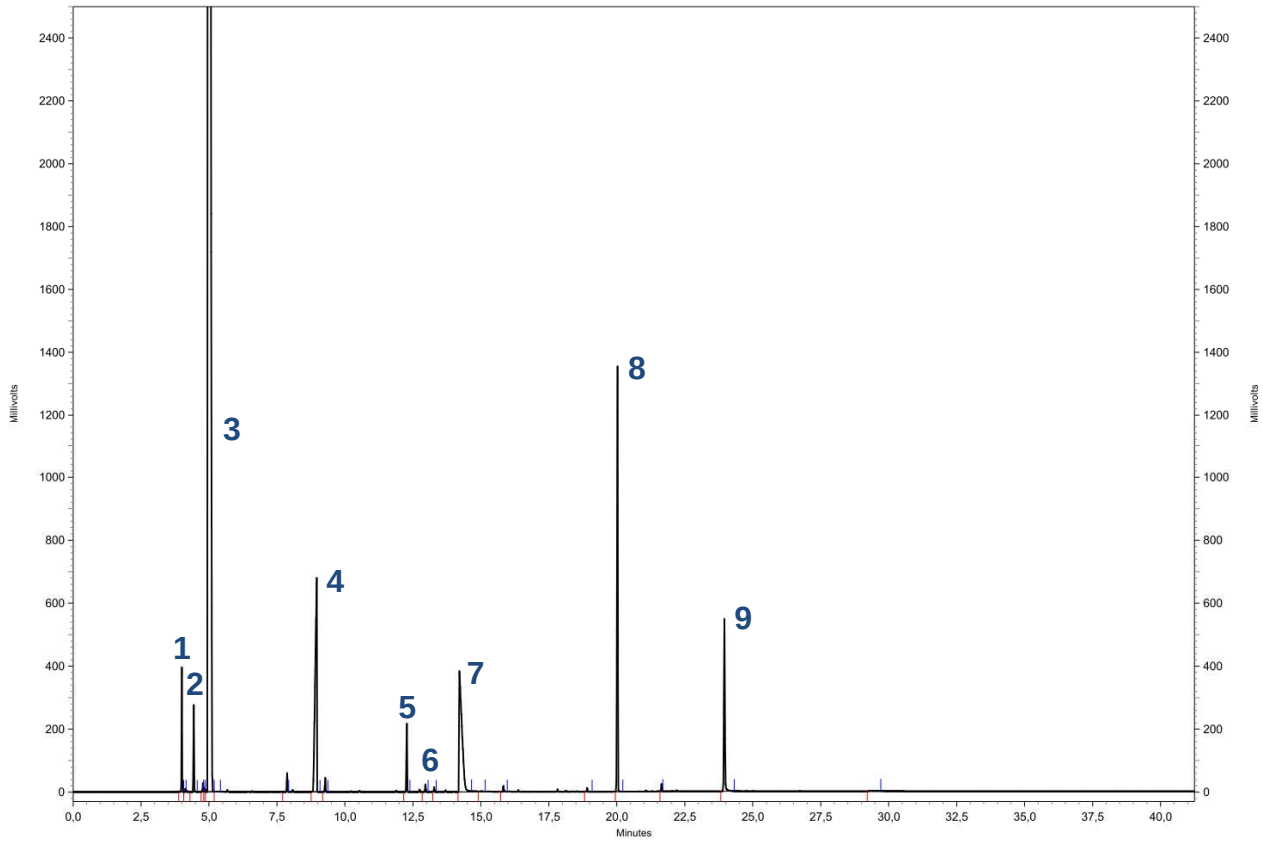
Entry 17



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

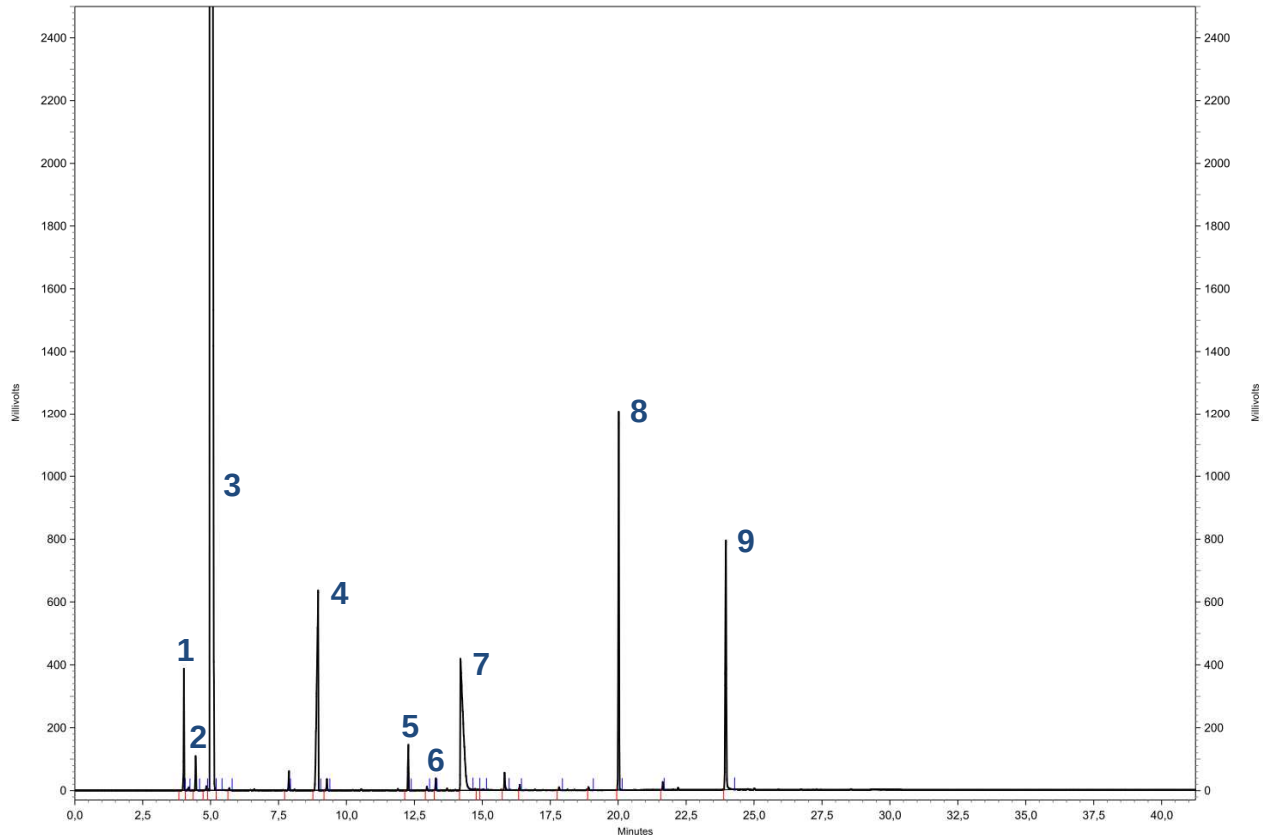
S3.8 Gaschromatograms to Table S2.8

Entry 1



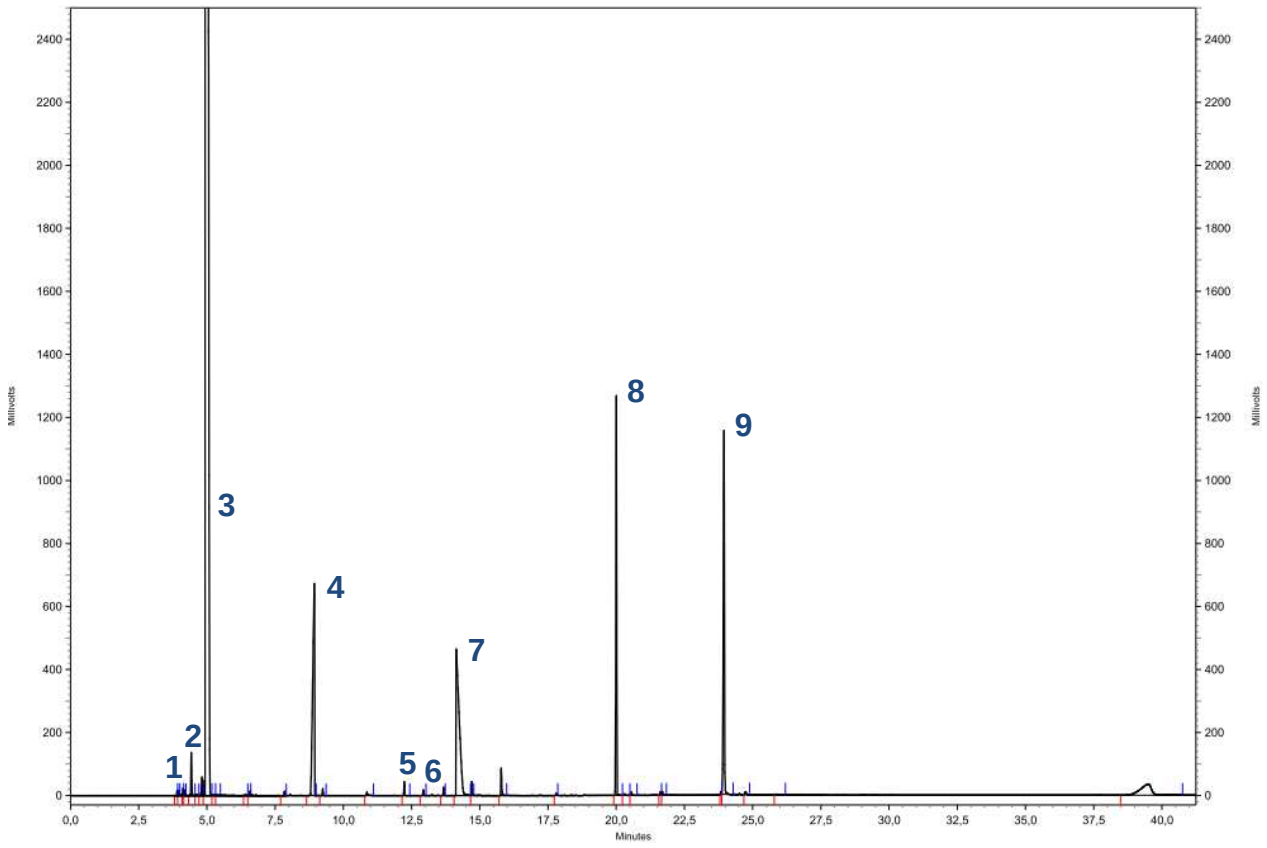
Entry	Retention Time [min]	Substance	Area
1	4.002	**CH**	4917794
2	4.437	**CE**	4097124
3	4.955	CH_2Cl_2 (Solv.)	527292253
4	8.963	*n*-Dodecane (Stand.)	29266189
5	12.277	**CAc**	3705318
6	12.962	**CI**	416532
7	14.208	CH_3COOH (Solv.)	26990150
8	20.025	1-Phenylethanol (Stand.)	25556688
9	23.960	**CA**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

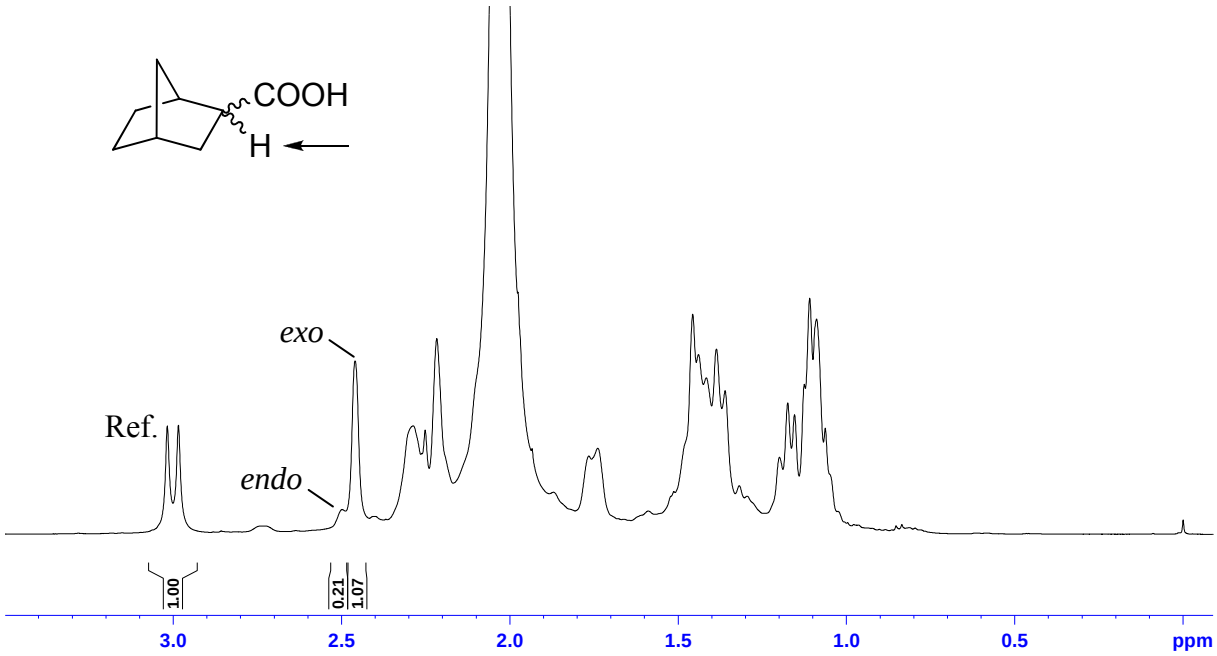


Figure S4.1. ^{1}H NMR spectrum of the reaction mixture after the catalysis with the substrate norbornene indicating the ratio of the integrals for *exo*/*endo* substitution. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

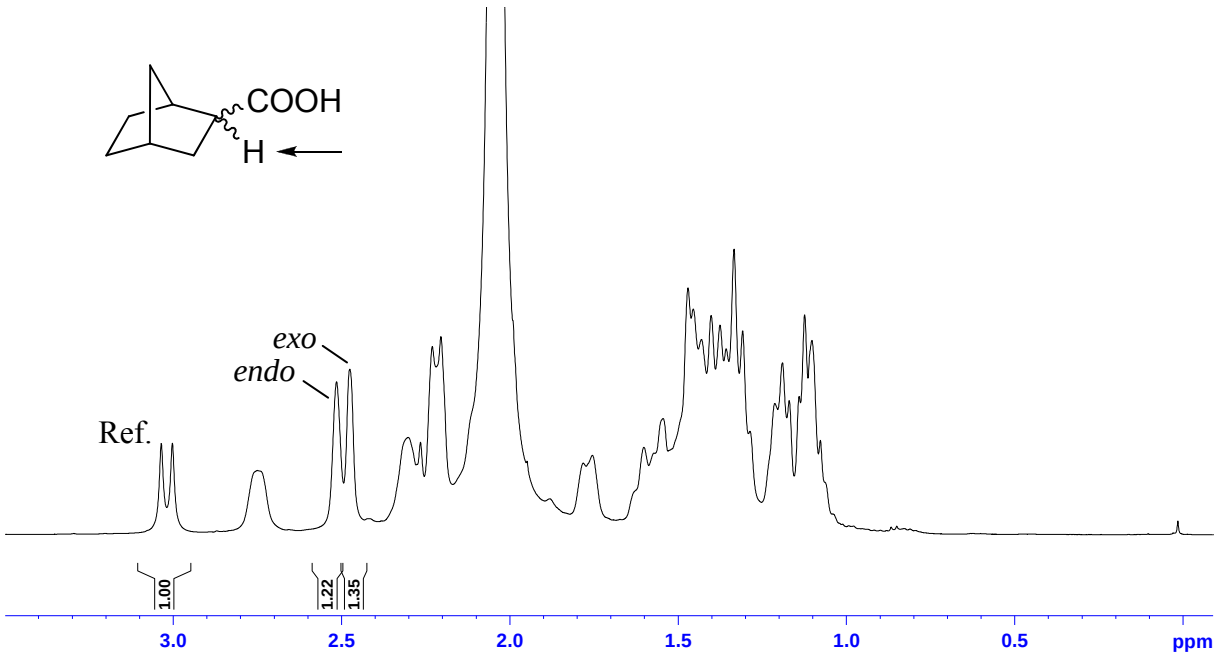


Figure S4.2. ^{1}H NMR spectrum of the reaction mixture after the catalysis with the substrate norbornene indicating the ratio of the integrals for *exo*/*endo* substitution enriched with pure *endo* product. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 400 Mhz.

S4.2 NMR Spectra to Table S2.9

Entry 1

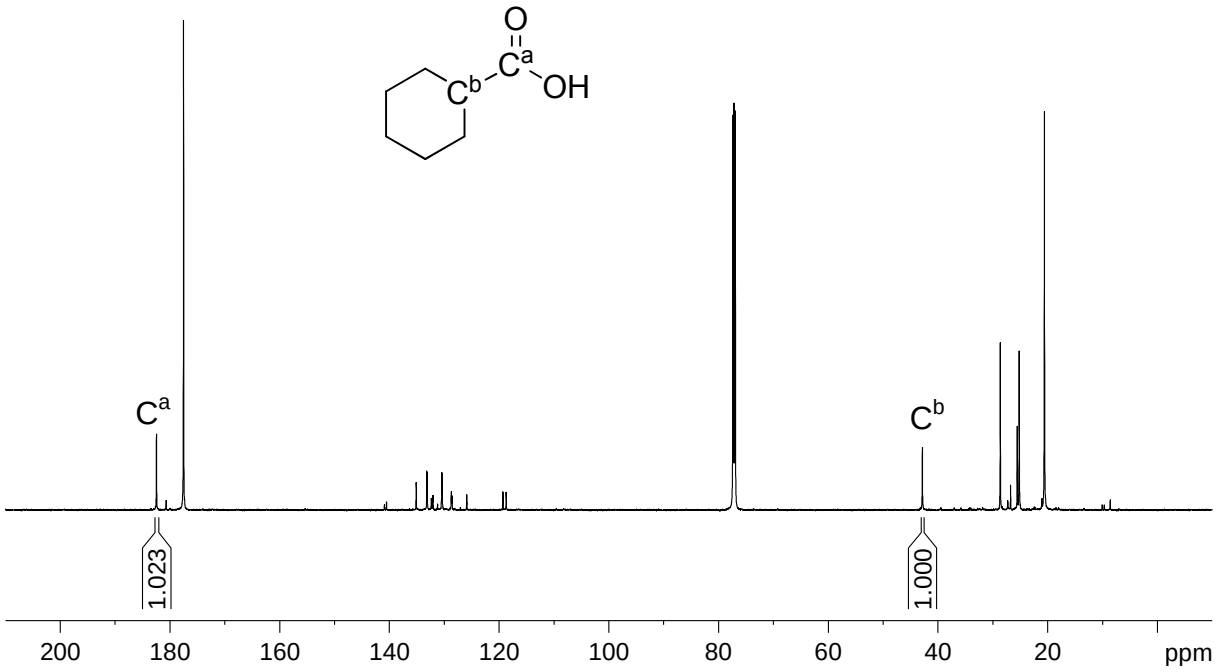


Figure S4.3. Quantitative ^{13}C NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for C^a:C^b. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 2

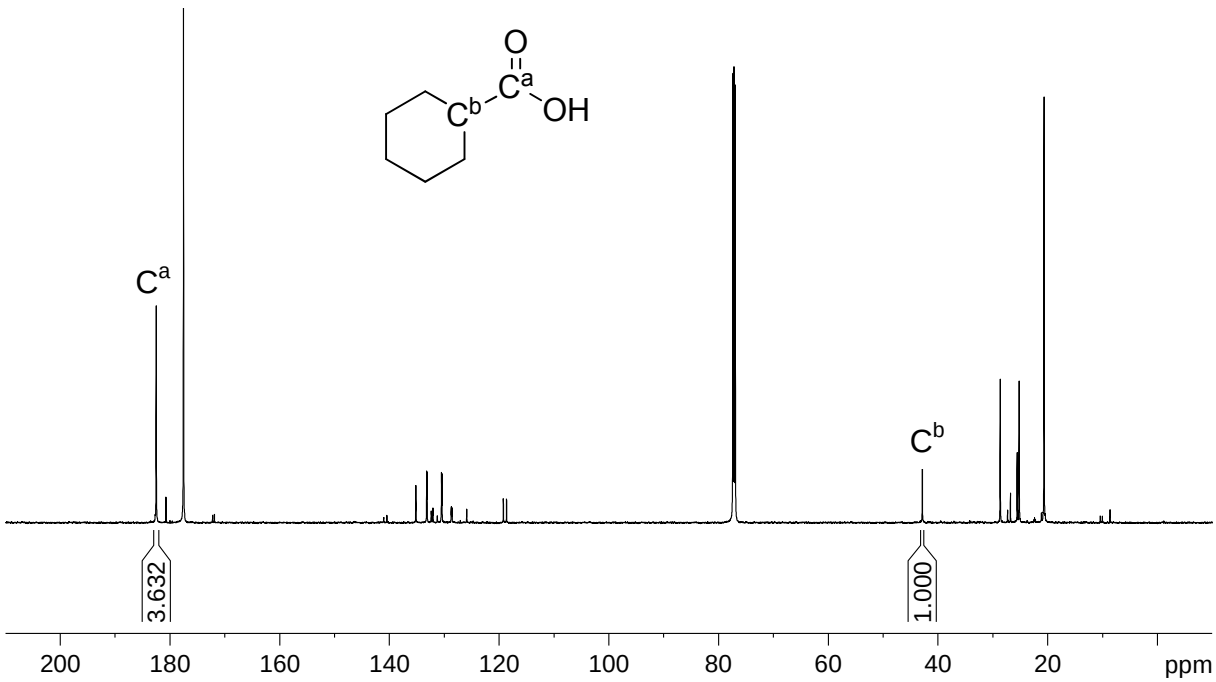


Figure S4.4. Quantitative ^{13}C NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for C^a:C^b. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 3

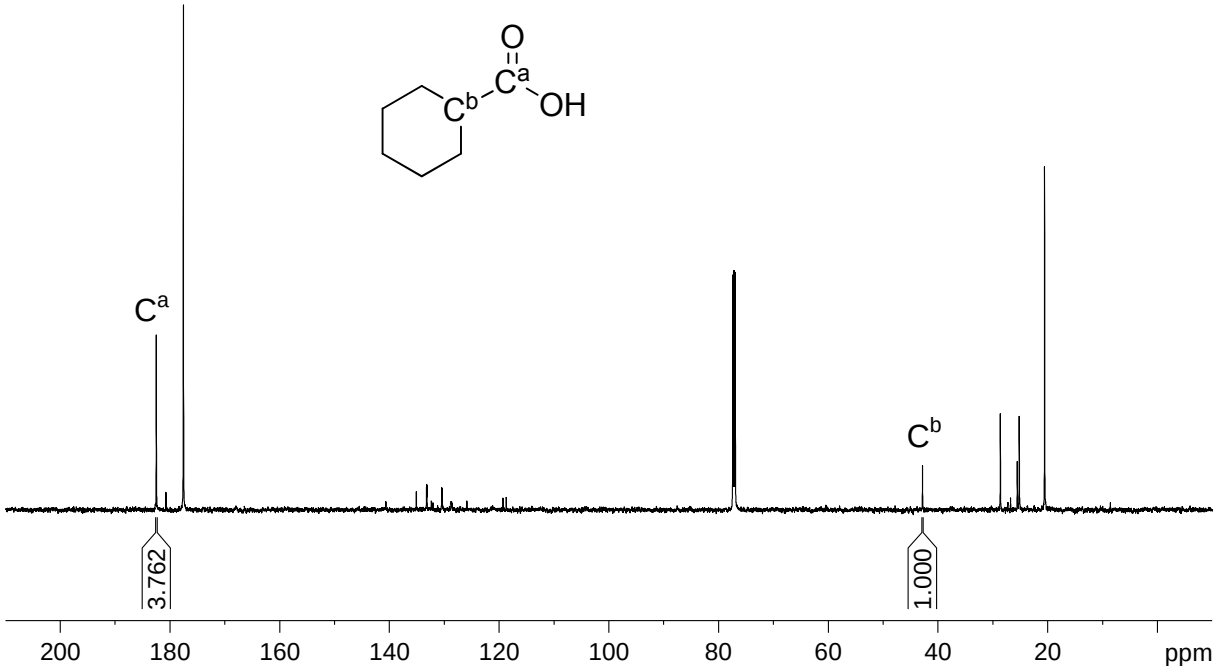


Figure S4.5 . Quantitative ^{13}C NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for C^a:C^b. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 4

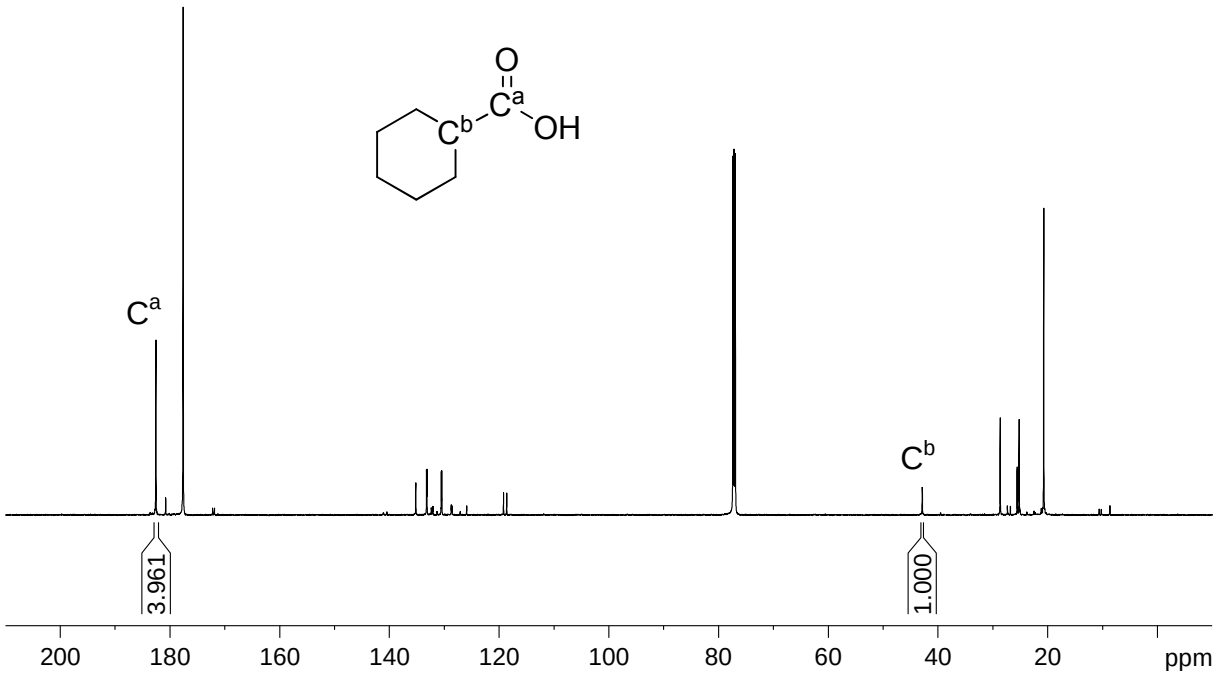


Figure S4.6. Quantitative ^{13}C NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for C^a:C^b. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 5

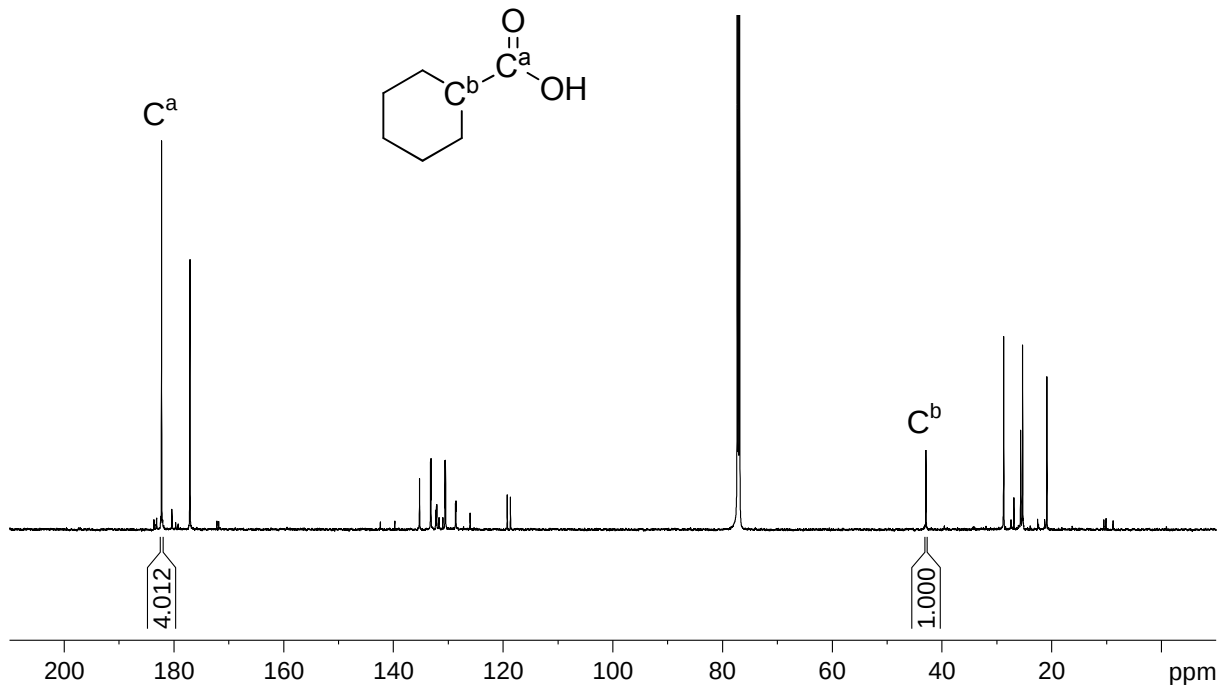


Figure S4.7. Quantitative ^{13}C NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for C^a:C^b. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

Entry 6

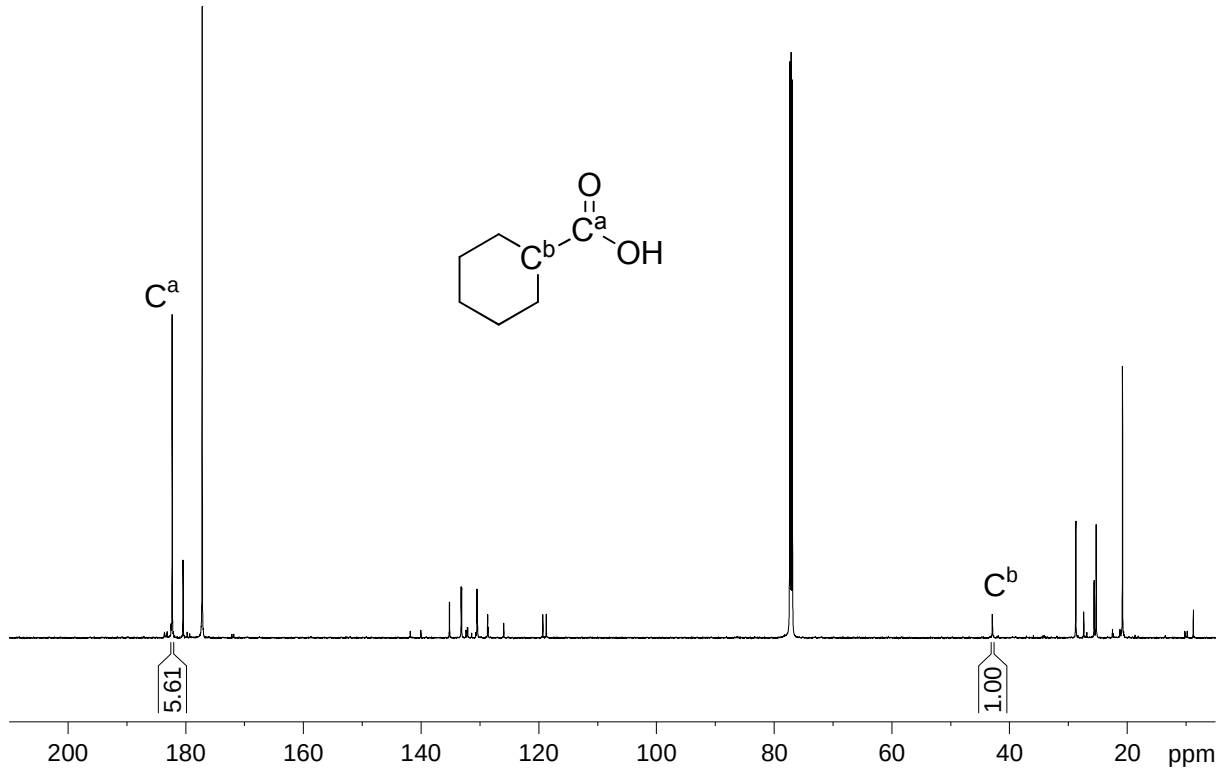


Figure S4.8. Quantitative ^{13}C NMR spectrum of the reaction mixture after the catalysis indicating the ratio of the integrals for C^a:C^b. Measured in $CDCl_3$ at ambient temperature with a resonance frequency of 151 Mhz.

S4.3 NMR Spectra to the D_2 labelling experiment

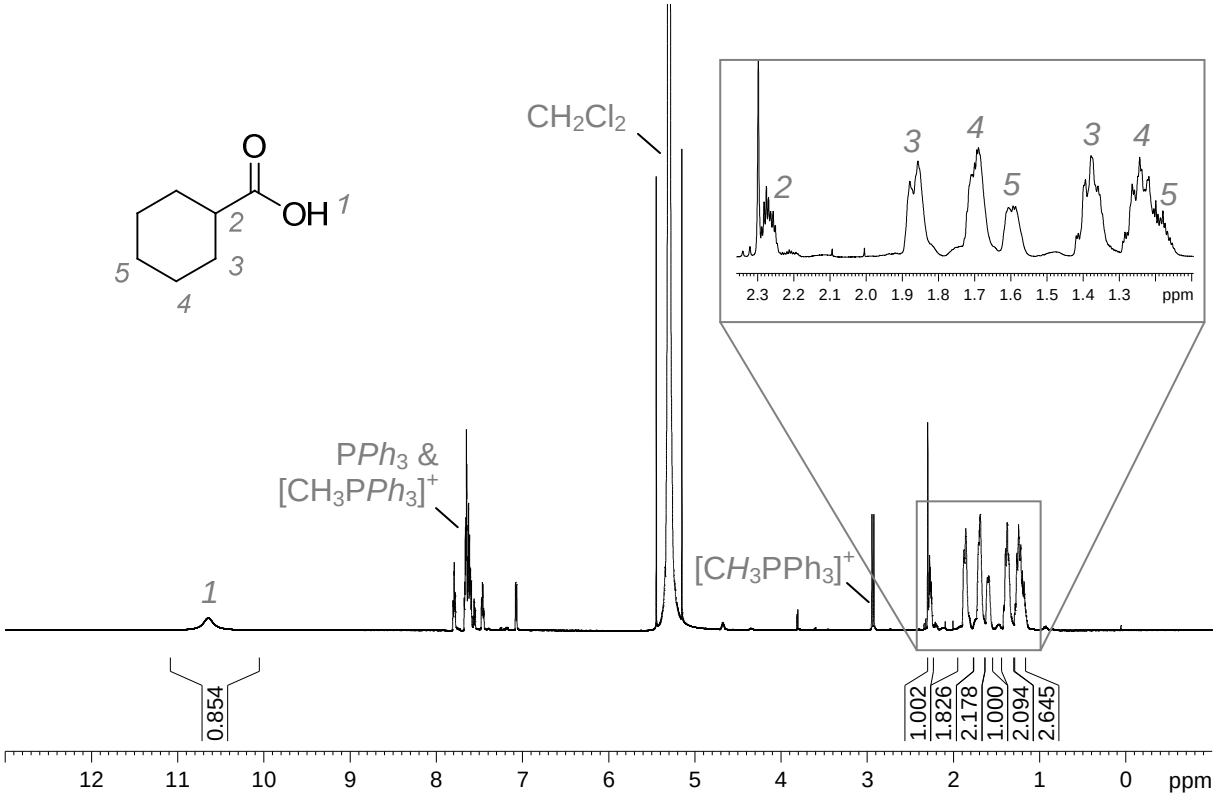


Figure S4.9. ^{1}H NMR spectrum of the reaction mixture after the catalysis with integrals for the cyclohexanoic acid product **CA**. Measured in CH_2Cl_2 at ambient temperature with a resonance frequency of 600 Mhz. Signal assignment based on ^{1}H-^{13}C HSQC and HMBC NMR experiment.

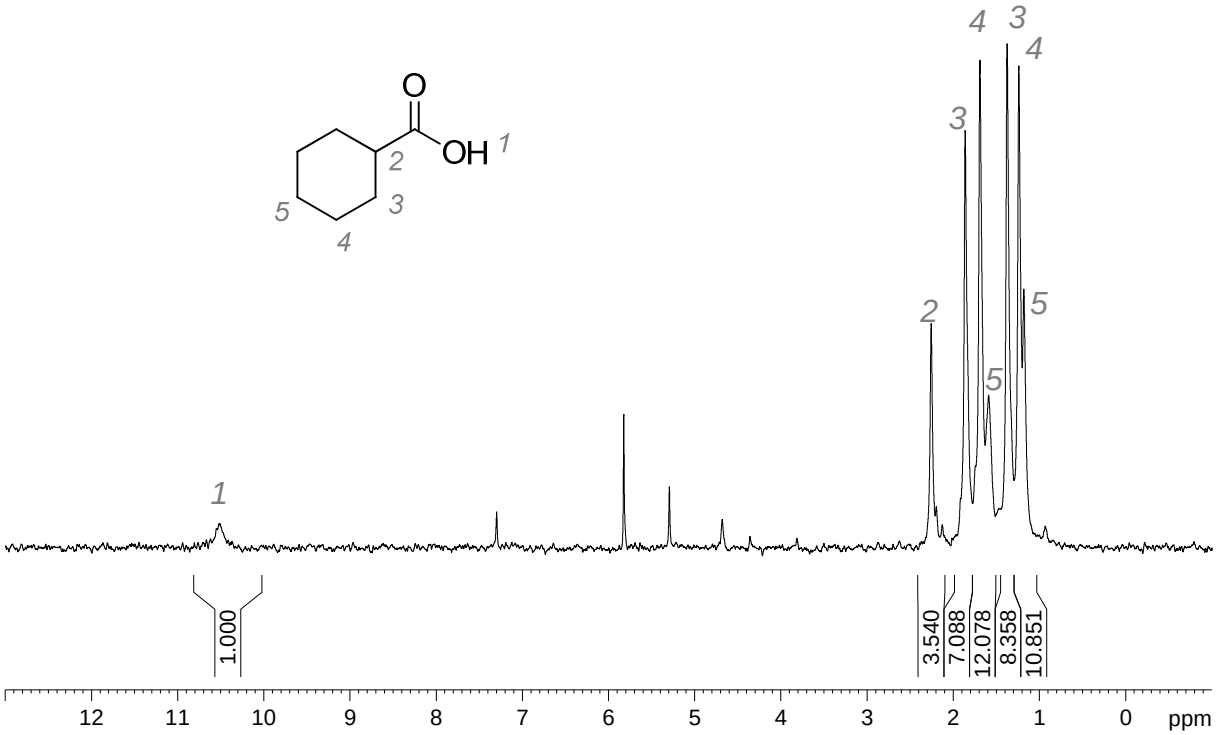


Figure S4.10. ^{2}H NMR spectrum of the reaction mixture after the catalysis with integrals for the cyclohexanoic acid product **CA**. Measured in CH_2Cl_2 at ambient temperature with a resonance frequency of 92 Mhz.

S4.4 NMR Spectra to the D_2O labelling experiments

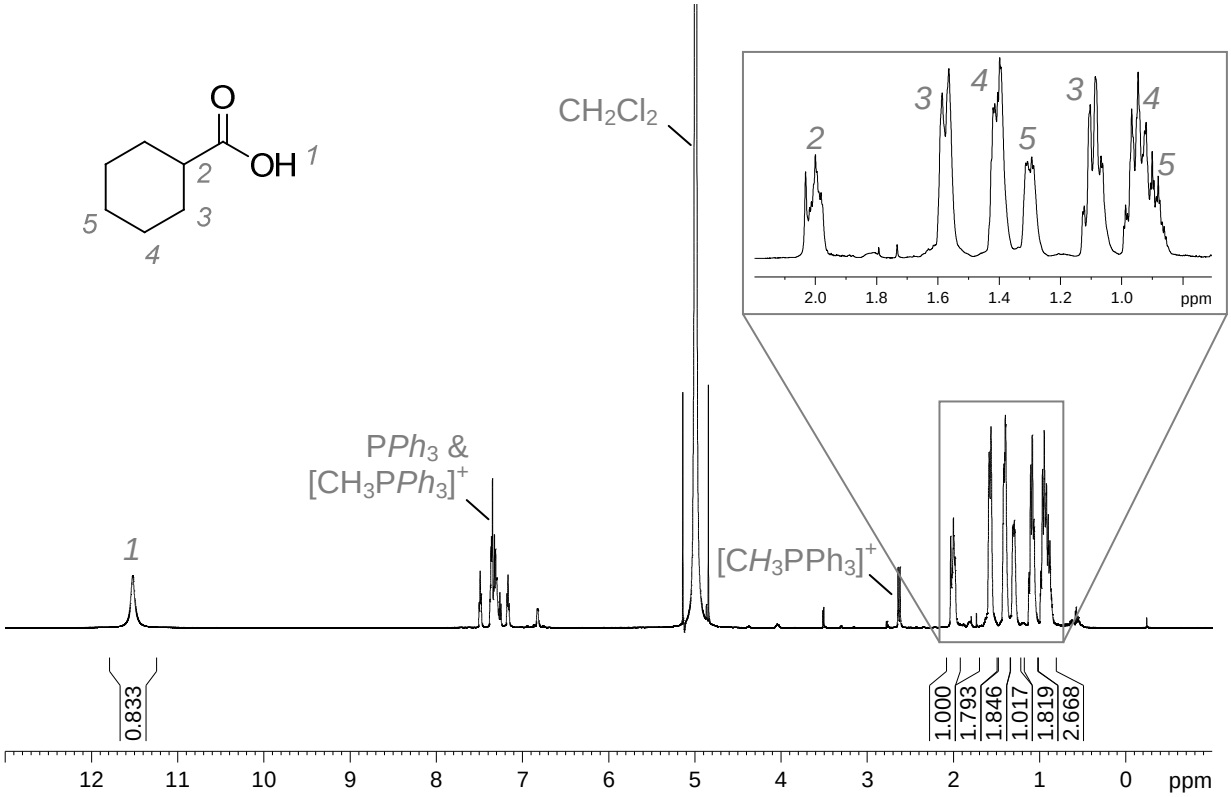


Figure S4.11. ^{1}H NMR spectrum of the reaction mixture after the catalysis with integrals for the cyclohexanoic acid product **CA**. Measured in CH_2Cl_2 at ambient temperature with a resonance frequency of 600 Mhz. Signal assignment based on ^{1}H-^{13}C HSQC and HMBC NMR experiment.

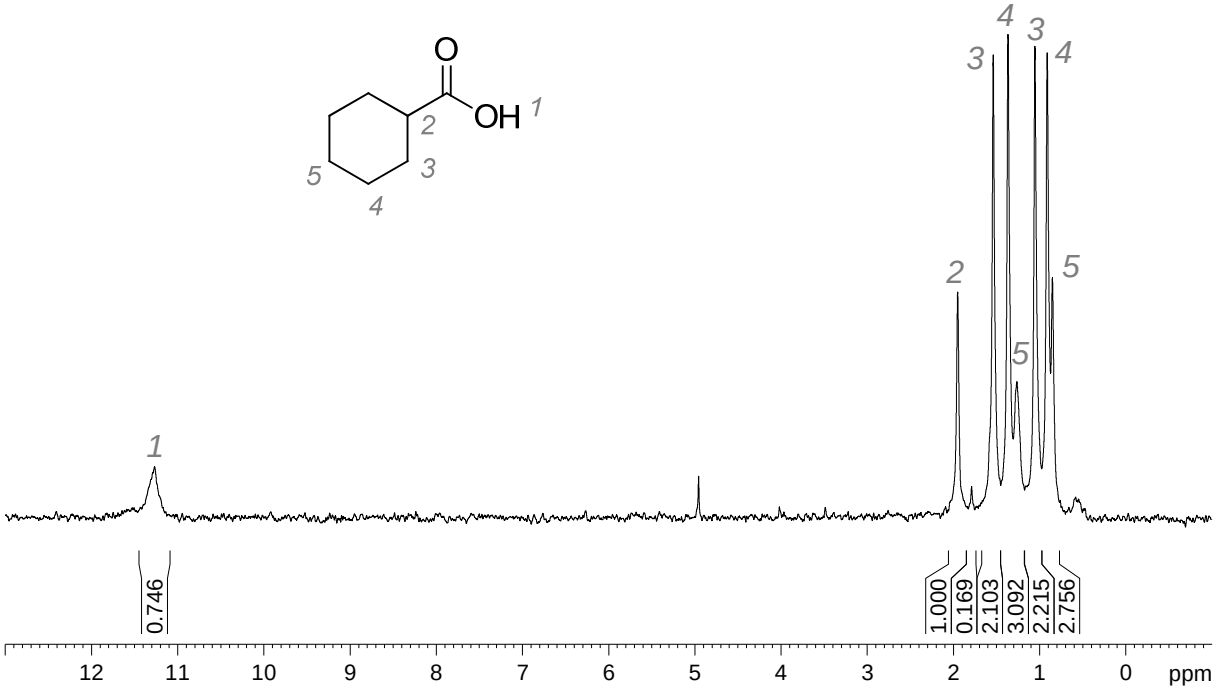


Figure 4.12. ^{2}H NMR spectrum of the reaction mixture after the catalysis with integrals for the cyclohexanoic acid product **CA**. Measured in CH_2Cl_2 at ambient temperature with a resonance frequency of 92 Mhz.

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

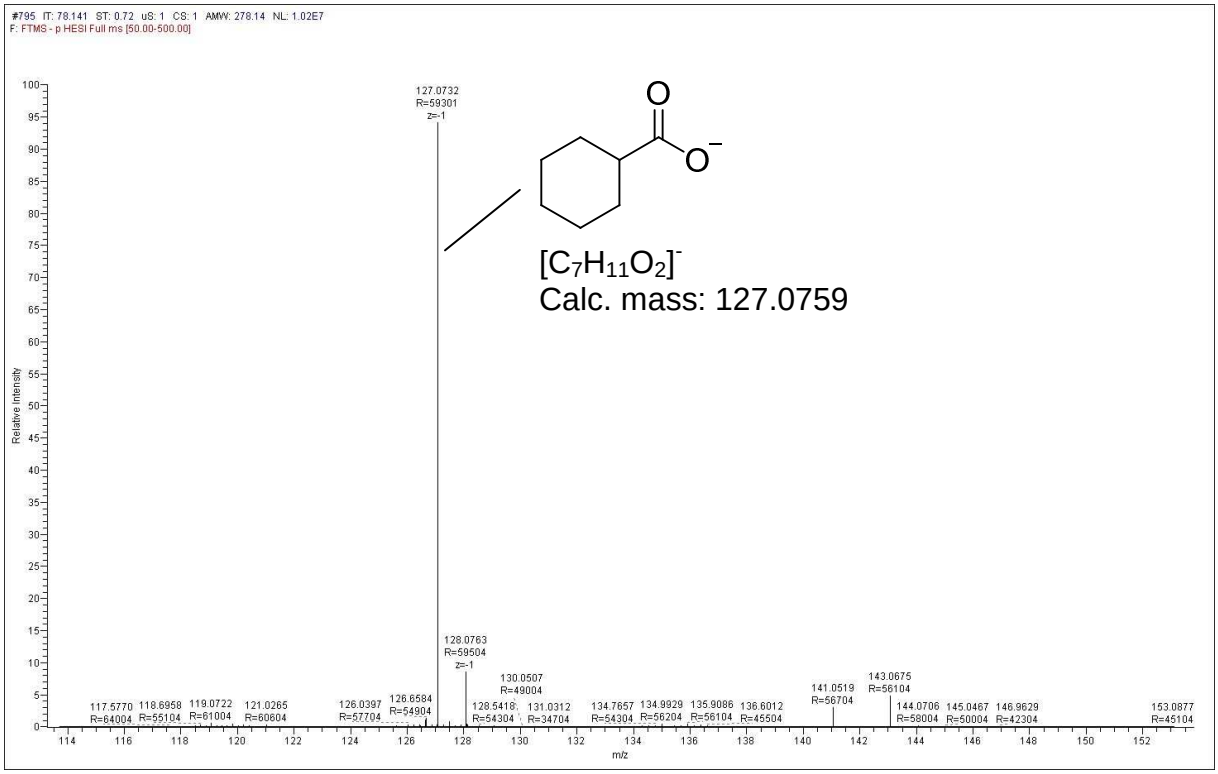


Figure S4.13. High resolution mass spectrum of the reaction mixture after the catalysis without addition of $H_2{}^{18}O$ for the cyclohexanoic acid product **CA**. Measured as ESI(-) in Methanol at ambient temperature.

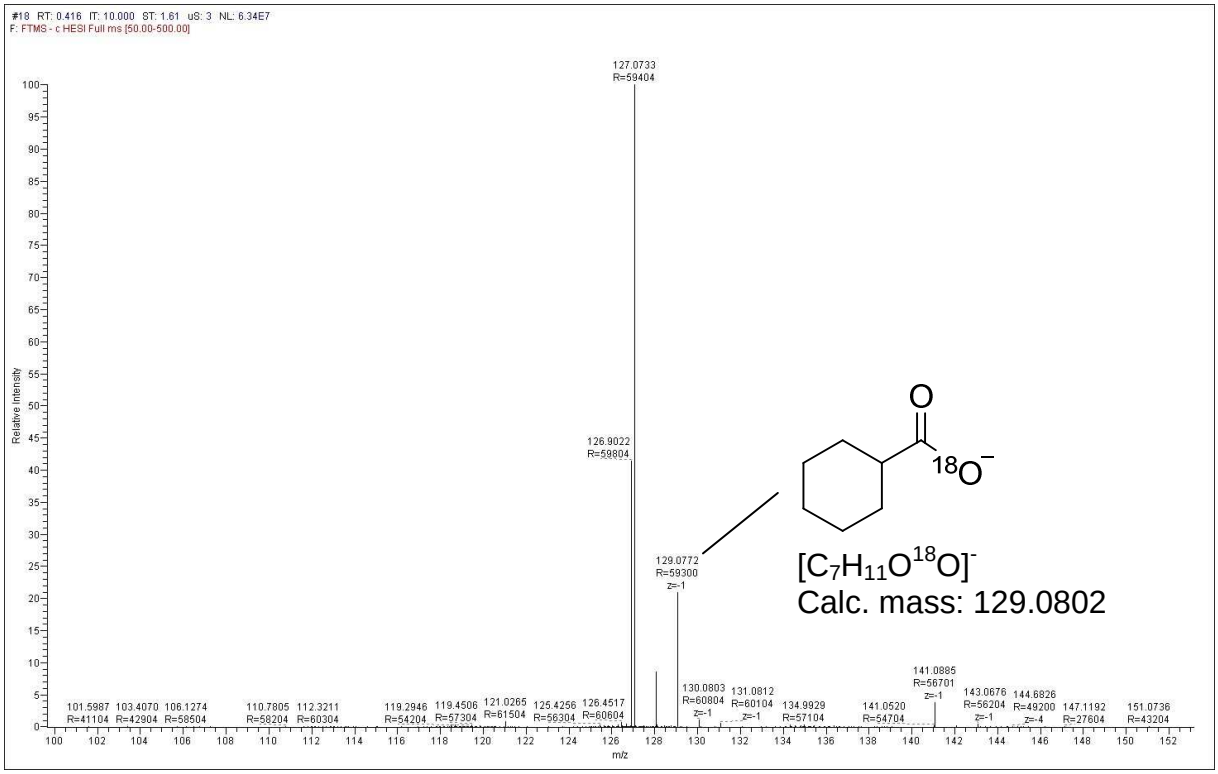


Figure S4.14. High resolution mass spectrum of the reaction mixture after the catalysis with addition of $H_2{}^{18}O$ for the cyclohexanoic acid product **CA**. Measured as ESI(-) in Methanol at ambient temperature.

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

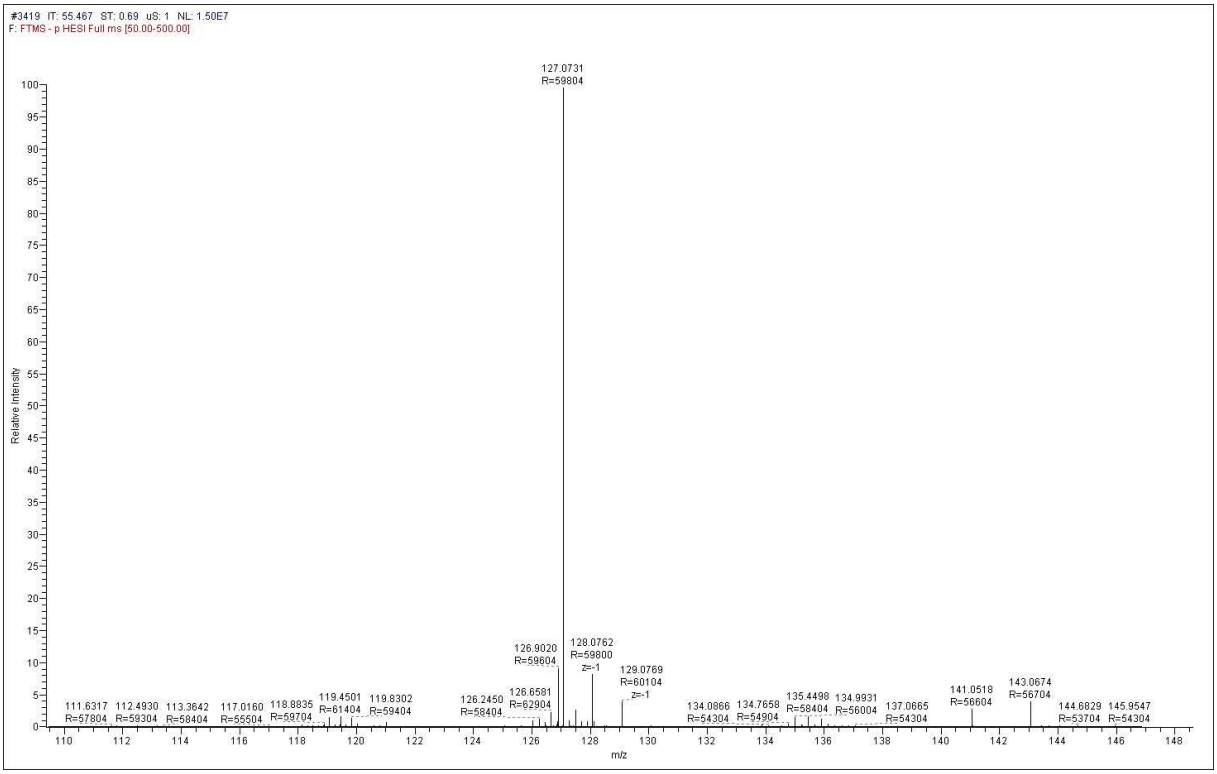


Figure 4.15. High resolution mass spectrum of the reaction mixture after the control experiment with addition of $H_2{}^{18}O$ for the cyclohexanoic acid product **CA**. Measured as ESI(-) in Methanol at ambient temperature.

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_α, $\lambda = 0.71073$ 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	μ(Mo K_α)/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
α/°	90.00	GOF on F^2	1.084
β/°	96.6600(10)	Diff. peak/hole [e/ Å^{-3}]	1.671 / -0.550
γ/°	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

[1] A. Vij, R. L. Kirchmeier, J. n. M. Shreeve, R. D. Verma, *Coord. Chem. Rev.* **1997**, *158*, 413-432.

[2] "Dissociation constants of organic acids and bases" in *CRC Handbook of Chemistry and Physics*, 89th ed. (Ed.: D. R. Lide), CRC Press/Taylor and Francis, Boca Raton, FL, **2009**.

[3] J. P. Guthrie, *Can. J. Chem.* **1978**, *56*, 2342-2354.

[4] SAINT, *Bruker AXS, Program for Reduction of Data collected on Bruker CCD Area Detector Diffractometer V.6.02*, Bruker AXS Inc., Madison, WI, USA, **1999**.

[5] SADABS, *Program for Empirical Absorption Correction of Area Detector Data V 2004/1*, Bruker AXS Inc., Madison, WI, USA, **2004**.

[6] a) G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, Universität Göttingen, **1997**; b) G. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.