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SUPPORTING INFORMATION

Mild and Selective Transformations of Amines and Alcohols Through Bioinspired Oxidation with Nitrous Oxide or Oxygen

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1. General experimental proceedings

The oxidation of benzylamines was monitored using gas chromatography with flame-ionization detection (GC-FID) on a Clarus 500 gas chromatograph/mass spectrometer. The GC was equipped with a BP-20 (SGE) column measuring 30 m × 0.22 mm × 0.25 μm. An internal standard, hexadecane (11.7 μL, 40 μmol), was added to each analysis for quantification. The calibration curves for benzylamine and benzonitrile were established using GC-FID method **1**, involving a temperature program of 10 minutes: 1 minute at 100 °C, followed by a ramp of 20°C/min to 260 °C, and then holding at 260 °C for 1 minute. These calibration curves enabled the determination of benzylamine and benzonitrile quantities in the reactions. Distinct benzylamines with varying retention times were also analysed using different GC-FID methods: GC-FID method **2** (27 min.): 1 min. at 100 °C, 20°C/min. to 200 °C, hold at 200 °C for 0 min, followed by a ramp of 10°C/min. to 260 °C, and then holding at 260 °C for 15 min. GC-FID method **3** (35 min.): 1 min. at 100 °C, 20°C/min. to 200 °C, hold at 200 °C for 0 min, followed by a ramp of 10°C/min. to 260 °C, and then holding at 260 °C for 23 min. GC-FID method **4** (60 min.): 1 min. at 100 °C, followed by a ramp of 20°C/min. to 260 °C, and then holding at 260 °C for 51 min. The oxidation of benzyl alcohols was tracked through 1H nuclear magnetic resonance (NMR) analysis on a Bruker 400 MHz Avance II NMR spectrometer with a 5 mm BBO probe (d1 time = 1s). Deuterated $CDCl_3$ was used as the solvent, and cyclohexane (20 μL, 0.184 mmol) served as an internal standard. For comprehensive analysis, all reactions underwent GC-MS analysis on a Clarus 600 (GC-MS) equipped with a Zebron ZB-5 (Phenomenex) column measuring 30 m × 0.25 mm × 0.25 μm. The applied method involved a 14-minute temperature

program: 2 minutes at 80 °C, followed by a ramp of 10°C/min. to 120 °C, holding for 0 minutes, further ramping at 30°C/min. to 300 °C, and then maintaining at 300 °C for 2 minutes. The complex $[RuCl_2(p\text{-cymene})]_2$ was purchased from Sigma-Aldrich, while deuterated $CDCl_3$ and tert-butanol, as well as benzylamines and benzyl alcohols, were purchased from Tokyo Chemical Industry (TCI, Japan) and used without additional purification. The oxygen and nitrous oxide cylinders were obtained from Air Liquide. Silica (200 mesh) were used for column chromatography and monitored with TLC.

1.1. General procedure for the synthesis of the ruthenium complex $[RuCl_2(p\text{-cymene})]_2$ (**Ru-I; Ru_2**)

Adapted from Ref. 1, a 10 mL microwave vessel equipped with a stirring bar and a pressure cap with teflon-coated septa was charged with 0.0835 g (0.32 mmol) of ruthenium(III) trichloride hydrate, along with 10 equiv. of α-phellandrene (3.2 mmol; 0.436 g) and 5.5 mL of ethanol. The reaction mixture was heated to 130 °C for 4 minutes. Afterwards the reaction mixture was cooled to -32°C. The resultant precipitated complex was separated by filtration and washed with n-pentane (10 mL), and air-dried. The complex yield is approx. 83%. The obtained analytical data are in agreement with the literature.

1.2. General procedure for the synthesis of the ruthenium complex $\{[(p\text{-cymene})Ru](\mu\text{-H})(\mu\text{-Cl})(\mu\text{-HCO}_2)[Ru(p\text{-cymene})]\}BF_4$ (**Ru-II**)

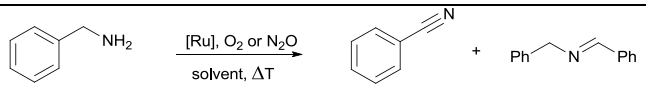
Adapted from Ref. 2, a 20 mL vial equipped with a stirring bar and screwcap was charged with 171 mg (279 µmol) of $[RuCl_2(p\text{-cymene})]_2$. Additionally, 40 mg (475 µmol) of $NaHCO_3$ and 192 mg (4.2 mmol) of HCO_2H were introduced into the vial. Subsequently, 2,5 mL of distilled water was added to the solution. The resulting mixture was stirred for 20 minutes at 95°C (or alternatively, 60 minutes at 80°C). After cooling to room temperature, a solution containing 56 mg (510 µmol) of $NaBF_4$ dissolved in 1 mL distilled water was added. The ensuing precipitate was separated through filtration and subsequently washed for 3 times with distilled water. The final product, a red-orange powder-like solid was dried on air. The typical yield of this process falls within the range of 80 to 85%. The NMR data are consistent with the findings reported in Ref. 2.

2. Oxidation of Benzylamines

2.1. Optimisation of the benzylamine oxidation with ruthenium complexes **Ru-I** ($[RuCl_2(p\text{-cymene})]_2$ and **Ru-II** $\{[(p\text{-cymene})Ru](\mu\text{-H})(\mu\text{-Cl})(\mu\text{-HCO}_2)[Ru(p\text{-cymene})]\}BF_4$)

General procedure: A 20 mL screw-cap vial with teflon-coated septa was loaded with 120 µL (1 mmol) of benzylamine, 1 mL of the chosen solvent (if any) and 6.1 mg (0.01 mmol) of Ru complex **I** or 6.4 mg (0.01 mmol) of complex **II**. The mixture was stirred under O_2 or N_2O atmosphere (balloons). The specific conditions of catalyst, solvent, oxidant, temperature and time are given on Table 1. Following the completion of the reaction, the reaction products were analysed by NMR spectroscopy, GC and GC-MS. Reactions with water as solvent were extracted (3x1.5mL) with DCM followed by microfiltration through a Pasteur pipette with glass wool and $MgSO_4$. To 0.9mL of this solution hexadecane as internal was added for GC and GC-MS analysis. For NMR analysis DCM was carefully evaporated, internal standard and $CDCl_3$ added. The acquired product data were then cross-referenced with authentic samples or established literature data to ensure accuracy and reliability. The conversion was determined by GC (internal standard hexadecane) or NMR (internal standard cyclohexane) for quantification.

Table 1. Benzylamine oxidation optimisation parameters.



Entry	Catalyst	Solvent	Oxidant	T [°C]	t [h]	Con. [%]	**2** (**3**)*[%]
1	**Ru-I**	*t*-BuOH	O_2	35	20	10	61 (39)
2		*t*-BuOH	N_2O	35	20	6	n.d
3		*t*-BuOH	O_2	65	20	20	55 (45)
4		*t*-BuOH	N_2O	65	20	10	30 (70)
5	**Ru-II**	*t*-BuOH	O_2	35	20	17	55 (45)
6		*t*-BuOH	N_2O	35	20	10	42 (58)
7		*t*-BuOH	O_2	65	20	>99	71 (29)
8		*t*-BuOH	N_2O	65	20	>99	67 (33)
9		neat	O_2	65	70	>99	40 (60)
10		neat	N_2O	65	70	>99	43 (57)
11		H_2O	O_2	65	70	>99	41 (59)
12		H_2O	N_2O	65	70	>99	50 (50)
13		*t*-BuOH	O_2	65	70	>99	91 (9)
14		*t*-BuOH	N_2O	65	70	>99	89 (11)
15	**Ru-II**	*t*-BuOH	O_2	65	4	26	67 (33)
16		*t*-BuOH	N_2O	65	4	19	67 (33)
17[)]		*t*-BuOH	O_2	65	8	57	74 (26)
18		*t*-BuOH	N_2O	65	8	21	67 (33)
19		*t*-BuOH	O_2	65	16	>99	70 (30)
20		*t*-BuOH	N_2O	65	16	>99	69 (31)
21		*t*-BuOH	O_2	65	24	>99	85 (15)
22		*t*-BuOH	N_2O	65	24	>99	77 (23)
23		*t*-BuOH	O_2	65	48	>99	74 (26)
24		*t*-BuOH	N_2O	65	48	>99	67 (33)

Reaction conditions: Benzylamine (1 mmol, except neat conditions; 4.5 mmol), solvent (1mL, except neat conditions, no solvent added), 65°C, time varying, [Ru] = [(p-cymene)Ru](μ-H)(μ-Cl)(μ-HCO_2)[Ru(p-cymene)]}BF_4 ($RuBF_4$, 0.01 mmol), oxidant gas varying (balloon). Conversions and yields were determined by GC and GC-MS analysis with

hexadecane as internal standard. Imine quantities and benzylamine conversions were also checked by 1H NMR analysis with cyclohexane as internal standard. *Nitrile **2** yield, the side-product is the secondary imine **3** (in brackets).

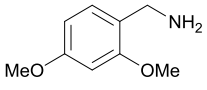
2.2. Procedure for the oxidation of benzylamines with **Ru-II** {[(*p*-cymene)Ru](*μ*-H)(μ-Cl)(μ-HCO_2)[Ru(*p*-cymene)]}BF_4)

A 20 mL screw-cap vial was loaded with 1 mmol of benzylamine, 1 mL of *tert*-butanol (*t*-BuOH), and 6.4 mg (0.01 mmol) of the complex {[(*p*-cymene)Ru](*μ*-H)(*μ*-Cl)(*μ*-HCO_2)[Ru(*p*-cymene)]}BF_4). The mixture was stirred for 24 hours at 65 °C under O_2 atmosphere (balloon). The resulting products were identified through NMR and GC-MS analyses and compared to authentic samples or literature data. Conversions were quantified using either GC or NMR with internal standard (vide supra). Results are summarized in Table 5 of the manuscript.

The following products were exemplary isolated by column chromatography with silica.

- Benzonitrile: 73 mg (0.71 mmol), yellowish liquid, 71% yield, Rf=0.6 (1:4, EtOAc:hexane).
- 3-Bromobenzonitrile: 131 mg (0.72 mmol), yellowish liquid, 72% yield, Rf=0.71 (1:4, EtOAc:hexane).
- 2,4-dimethoxybenzonitrile: 119 mg (0.89 mmol), light yellowish liquid, 89% yield, Rf=0.66 (1:1, EtOAc:hexane).

2.3. **Selected GC chromatograms for benzylamine oxidation**



2,4-Dimethoxybenzylamine

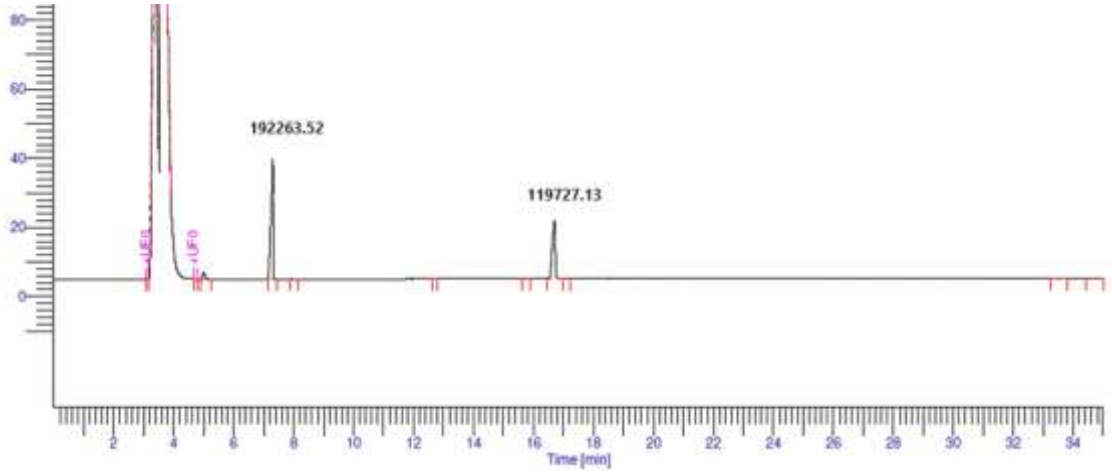


Figure 1: **GC-FID,** 3 – 4.7 min.: solvents (chloroform and ^{t}BuOH), 4.99 min.: *p*-cymene (from catalyst), 7.3 min.: hexadecane (internal standard), 16.7 min.: 2,4-dimethoxybenzonitrile

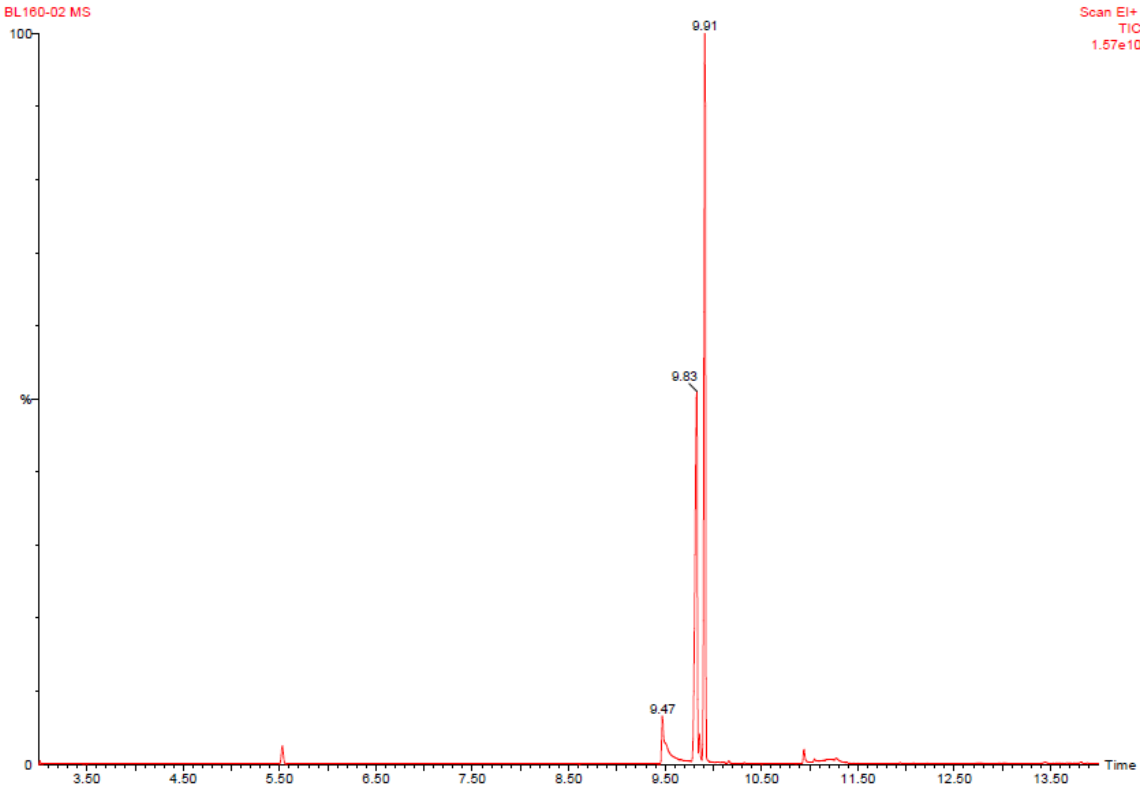


Figure 2 GC-MS, Ca. 5.5 min.: *p*-cymene (from catalyst), 9.47 min.: 2,4-dimethoxybenzylamine, 9.83 min.: 2,4-dimethoxybenzonitrile, 9.91 min.: hexadecane (internal standard), 10.5-11 min: 2,4 dimethoxybenzamide.

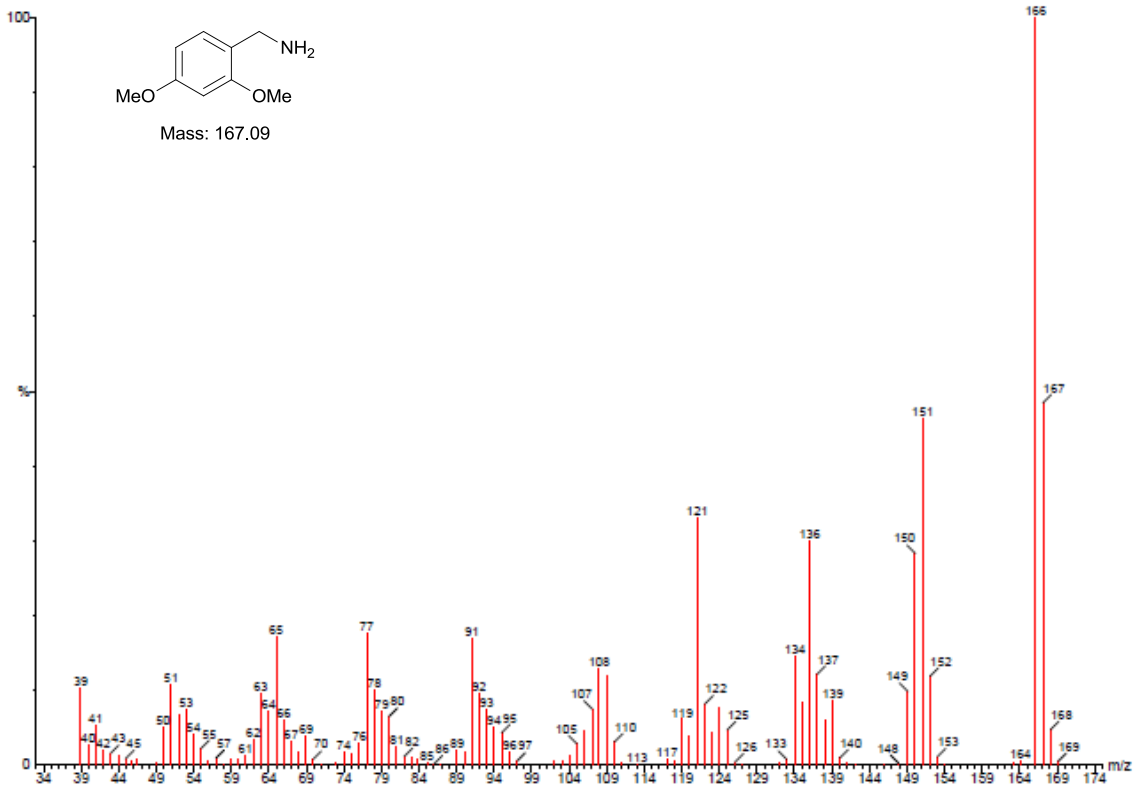


Figure 3: MS of 2,4-dimethoxybenzylamine

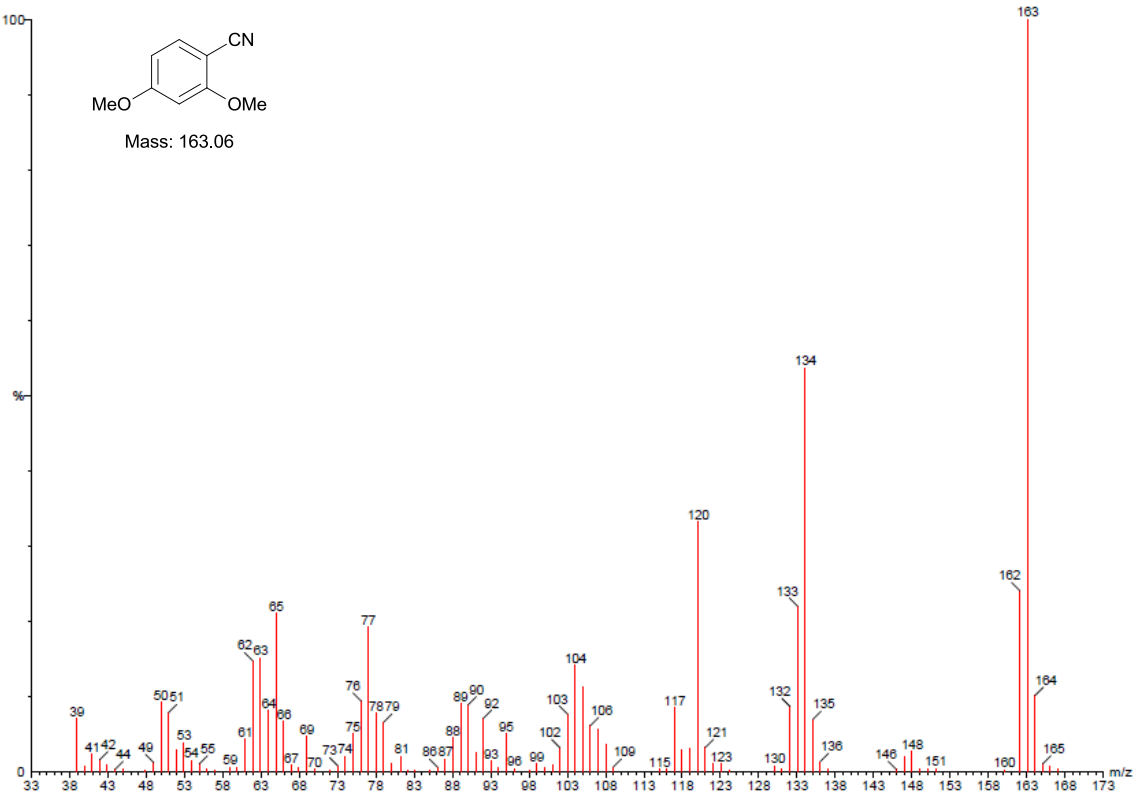


Figure 4 MS of 2,4-dimethoxybenzonitrile

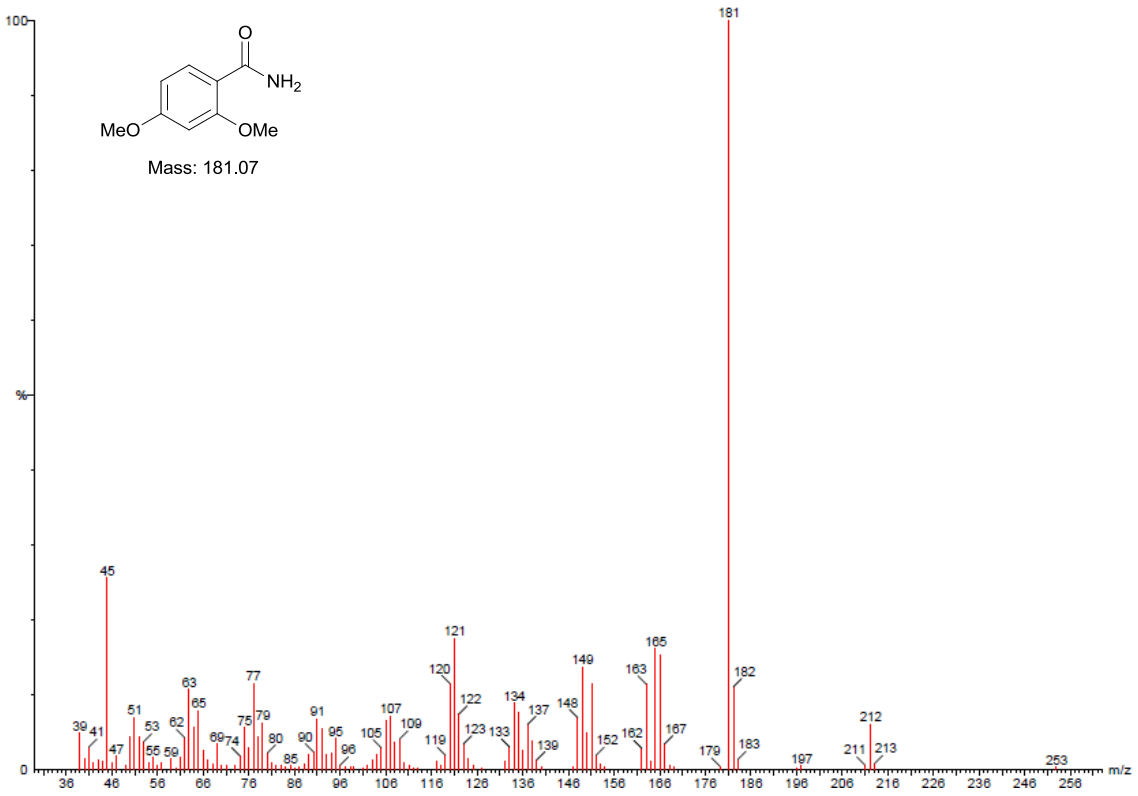
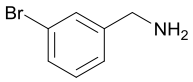


Figure 5 MS of 2,4-dimethoxybenzamide



3-Bromobenzylamine

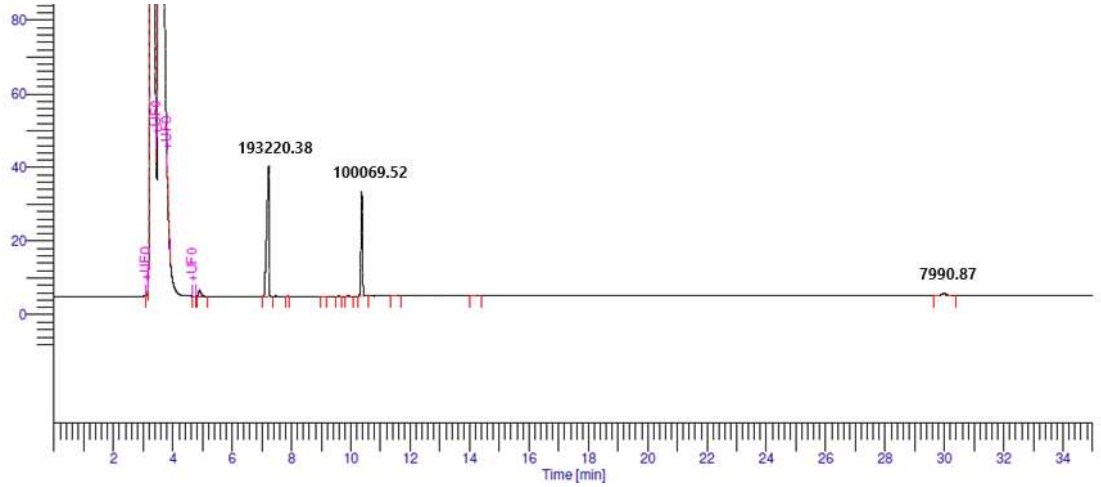


Figure 6 **GC-FID,** 3 – 4.7 min.: solvents (chloroform and ^{t}BuOH), 4.99 min.: *p*-cymene (from catalyst), 7.2 min.: hexadecane (internal standard), 10.4 min.: 3-bromobenzonitrile, 30 min.: imine

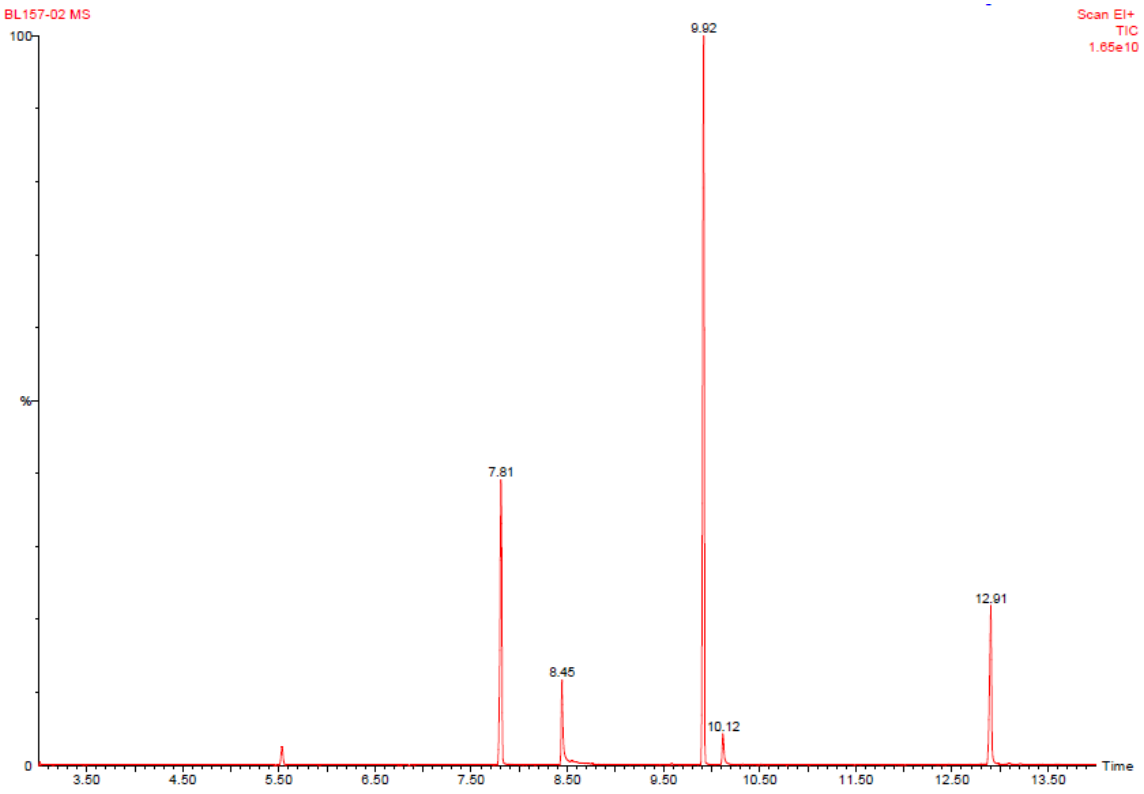


Figure 7 **GC-MS,** Ca. 5.5 min.: *p*-cymene (from catalyst), 7.81 min.: 3-bromobenzonitrile, 8.45 min.: 3-bromobenzylamine, 9.92 min.: hexadecane (internal standard), 10.12 min.: 3-bromobenzamide, 12.91 min.: *N*-(3-bromobenzyl)-1-(3-bromophenyl)methanimine

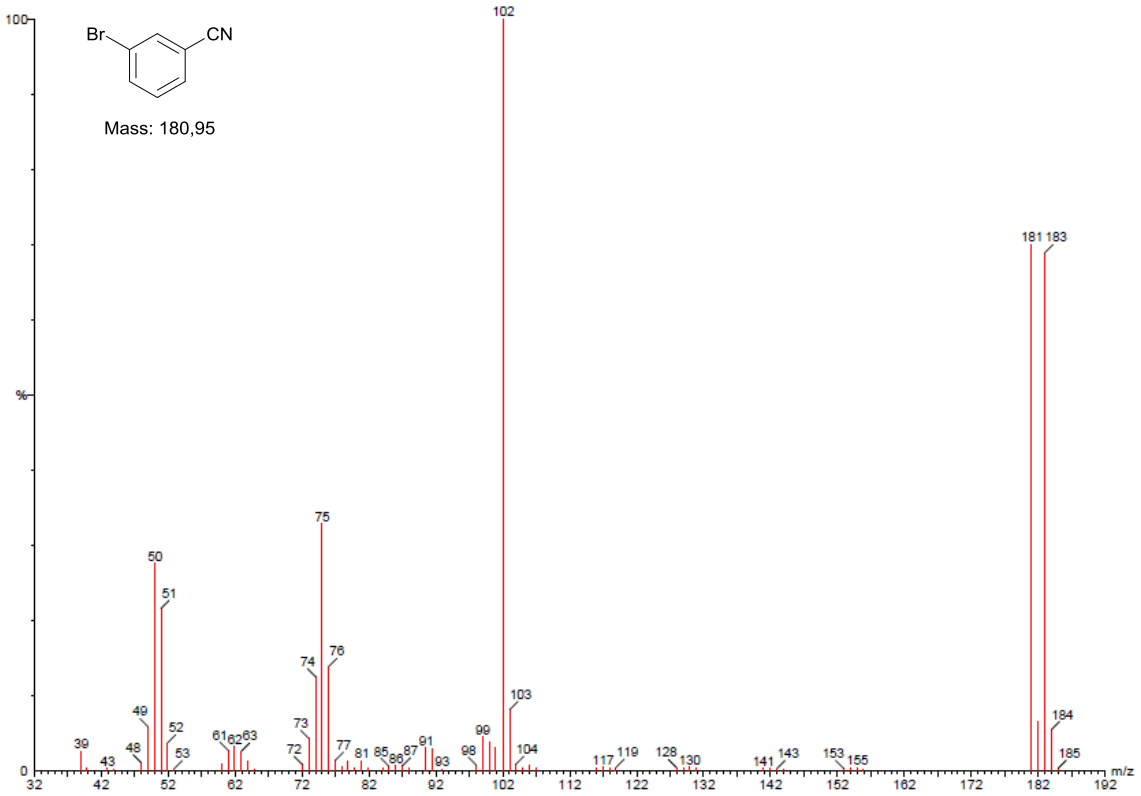


Figure 8 MS of 3-bromobenzonitrile

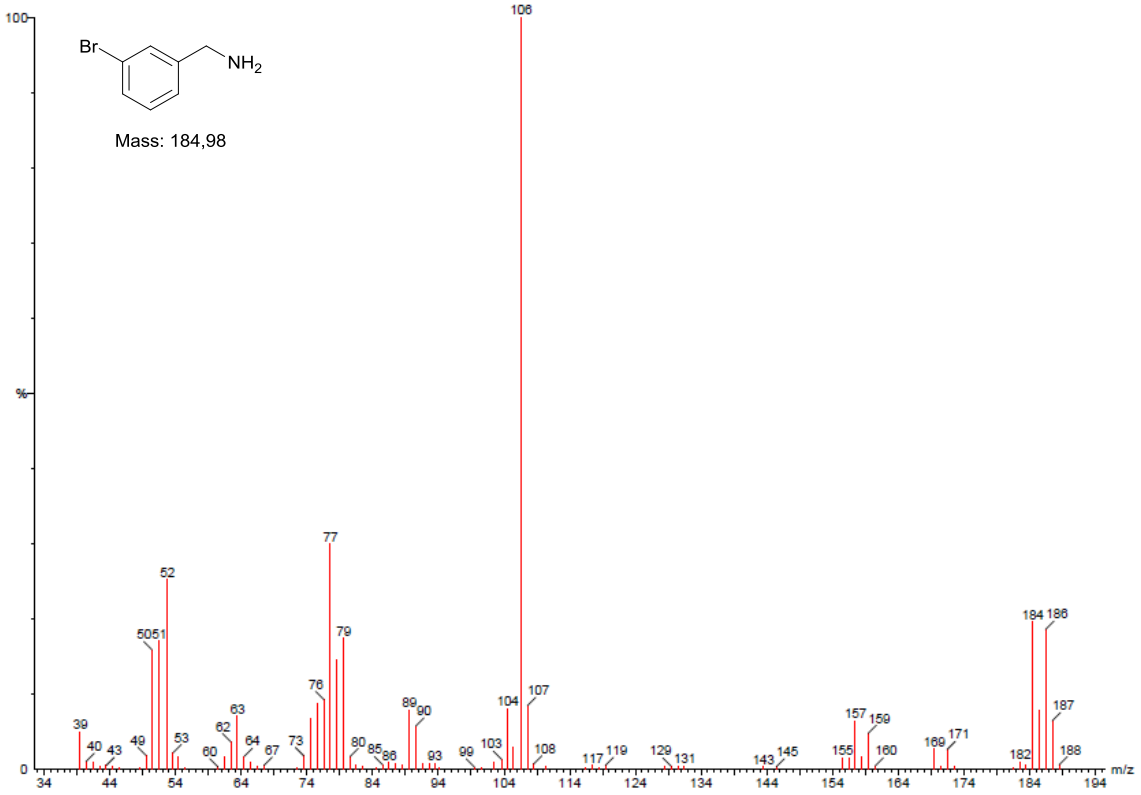


Figure 9 MS of 8.45 min.: 3-Bromobenzylamine

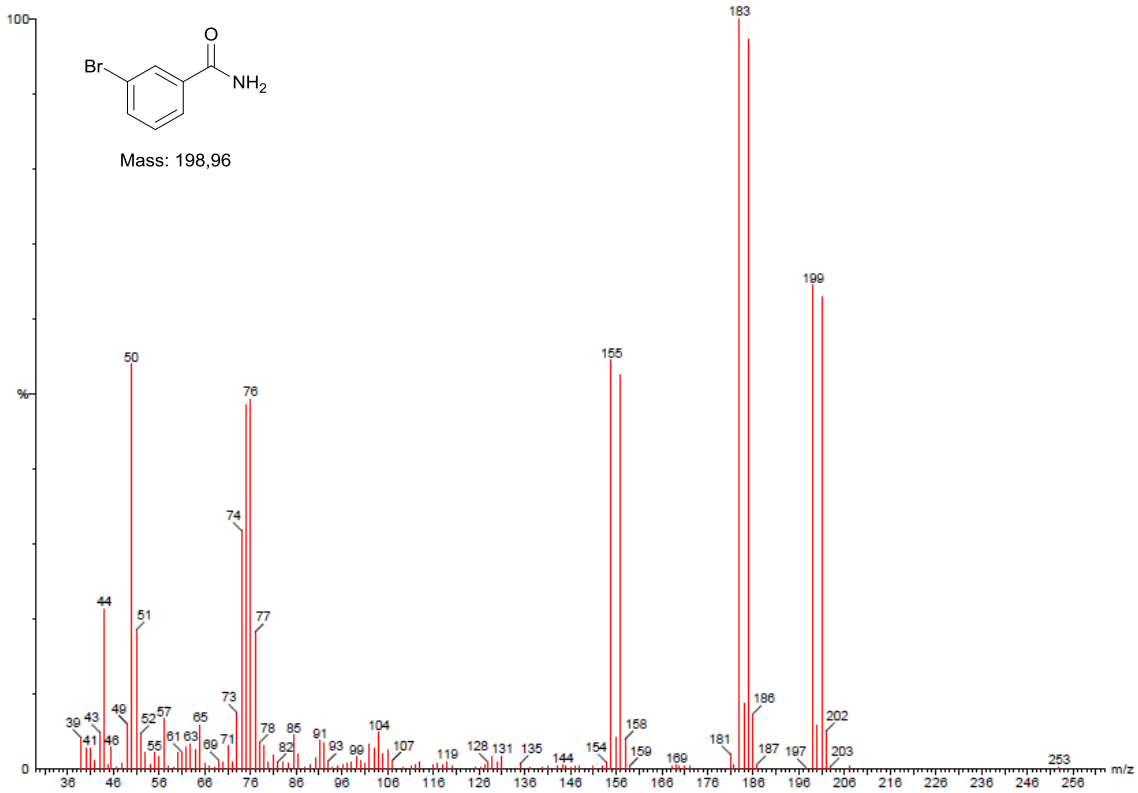


Figure 10 MS of3-bromobenzamide

12.91 min.: *N*-(3-bromobenzyl)-1-(3-bromophenyl)methanimine

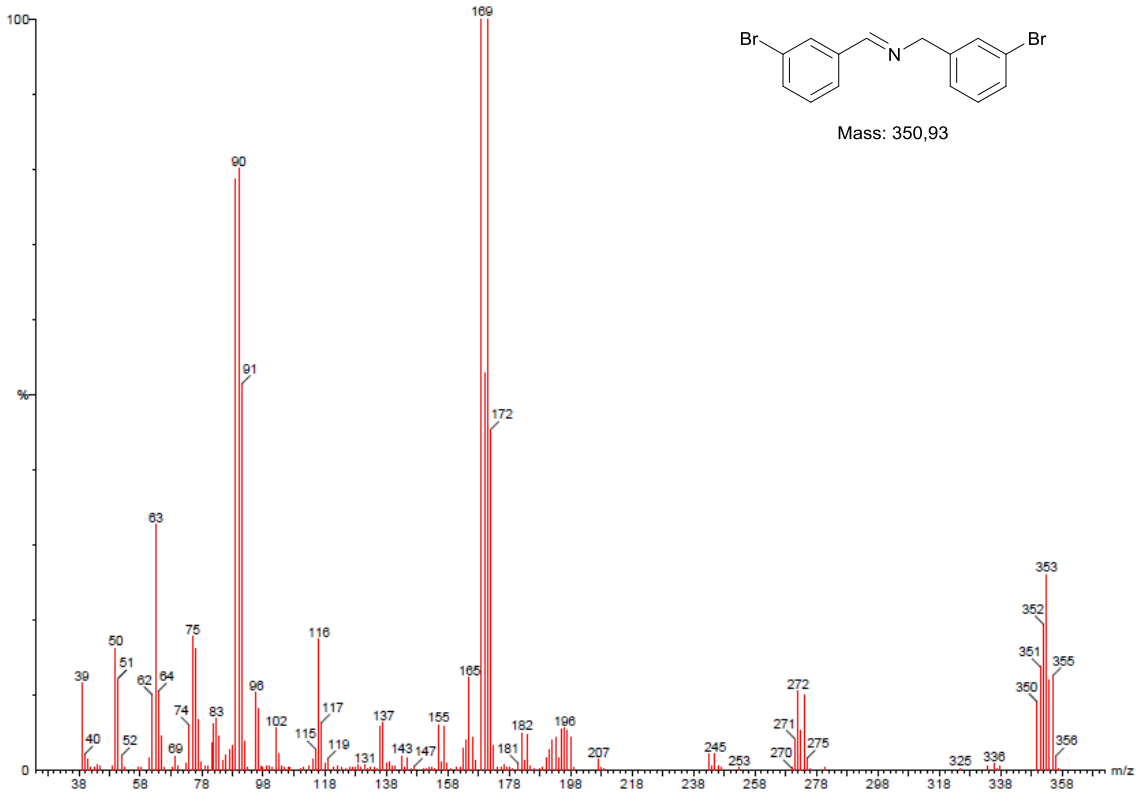
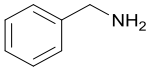


Figure 11 MS of N-(3-bromobenzyl)-1-(3-bromophenyl)methanimine



Benzylamine

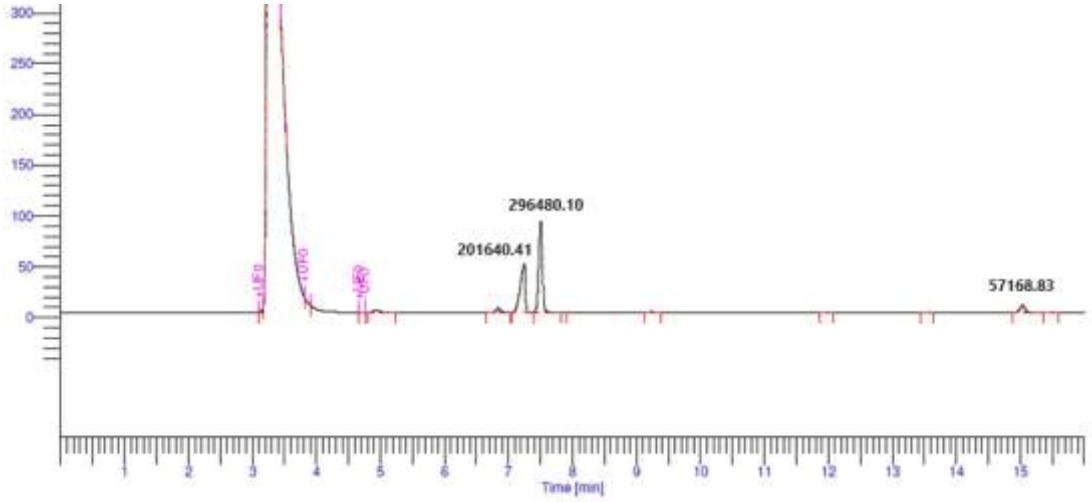


Figure 12 **GC-FID,** 3 – 4.7 min.: Solvents (Chloroform and ^{t}BuOH), 4.99 min.: *p*-cymene (from catalyst), 7.3 min.: hexadecane (internal standard), 7.5 min.: benzonitrile, 15 min.: imine

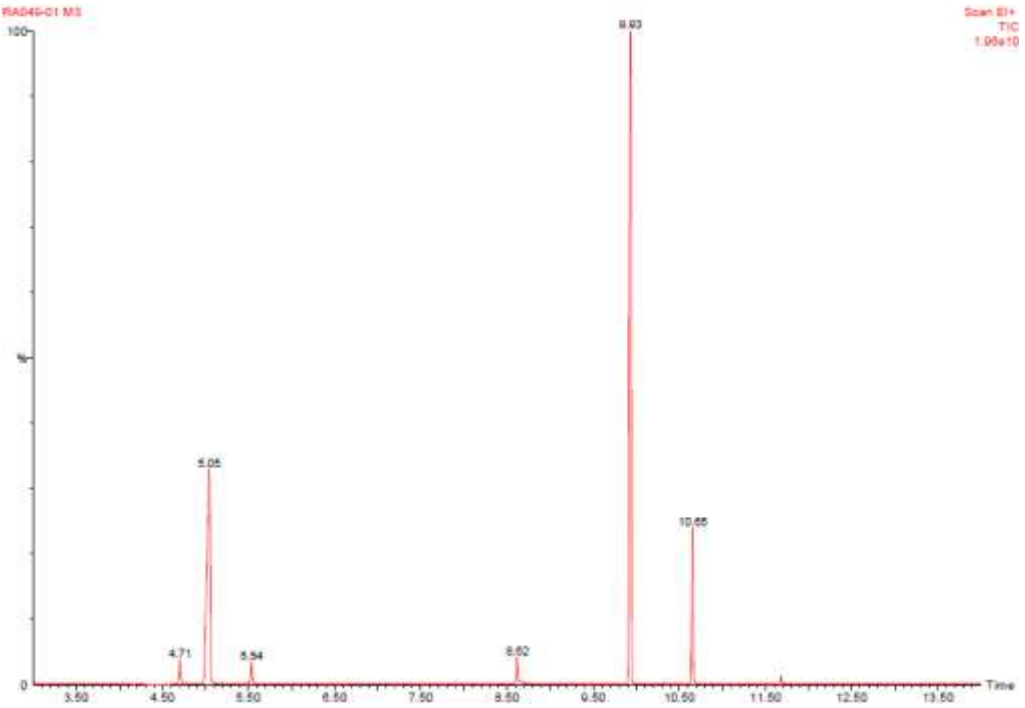


Figure 13 **GC-MS,**), 4.71 min.: benzylamine, 5.05 min.: benzonitrile,

5.54 min.: *p*-cymene (from catalyst), 8.62 min. benzylamide, 9.92 min.: hexadecane (internal standard), 10.65 min.: *N*-benzyl-1-phenylmethanimine,

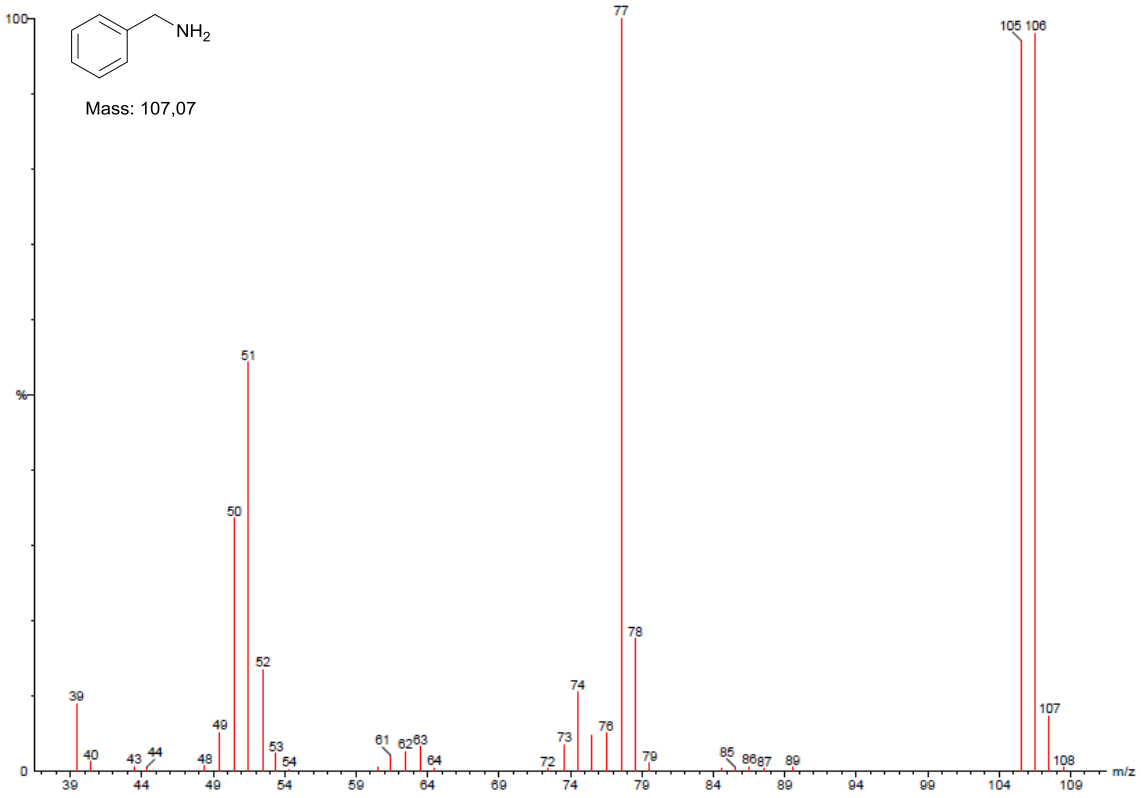


Figure 14 MS of benzylamine

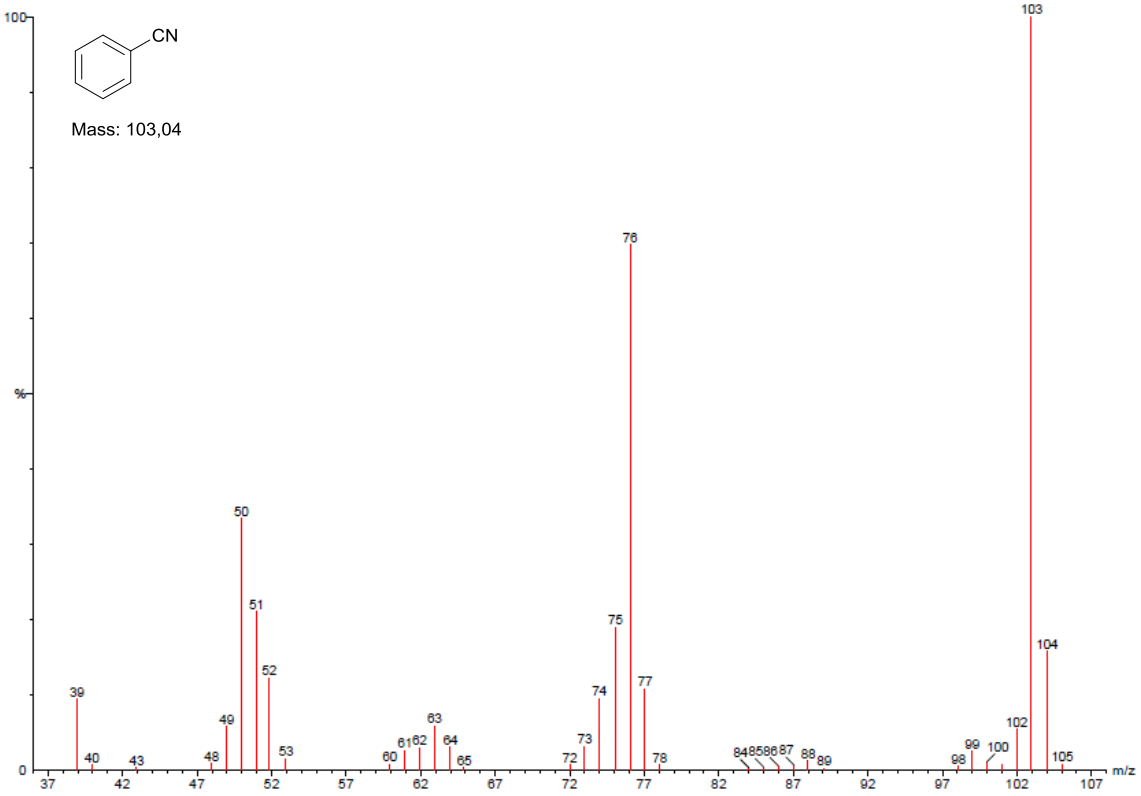


Figure 15 MS of benzonitrile

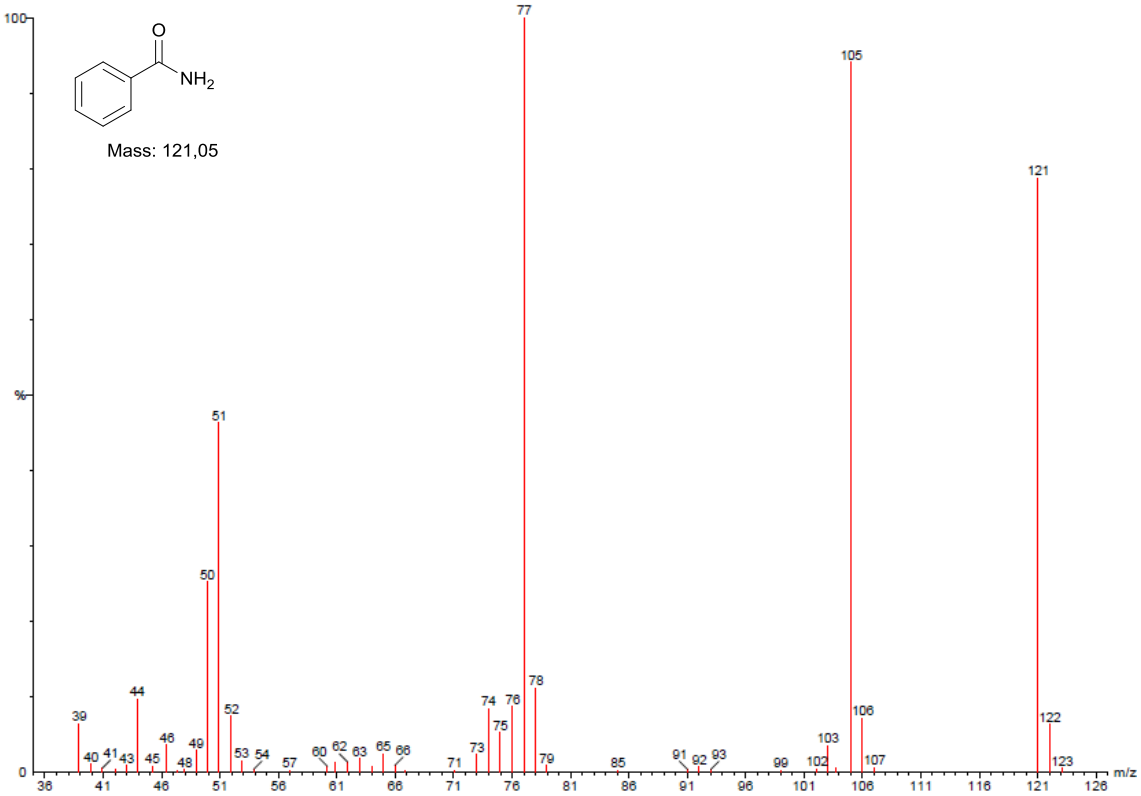


Figure 16 MS of benzylamide

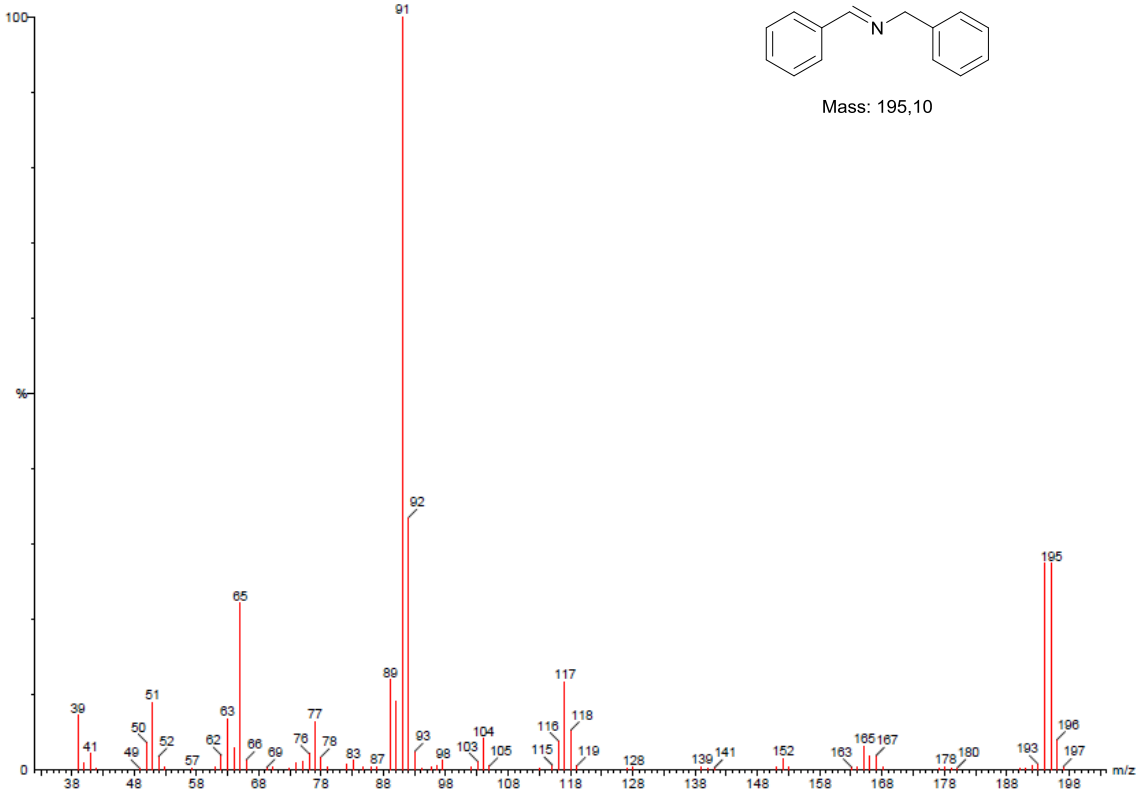


Figure 17 MS of N-benzyl-1-phenylmethanimine

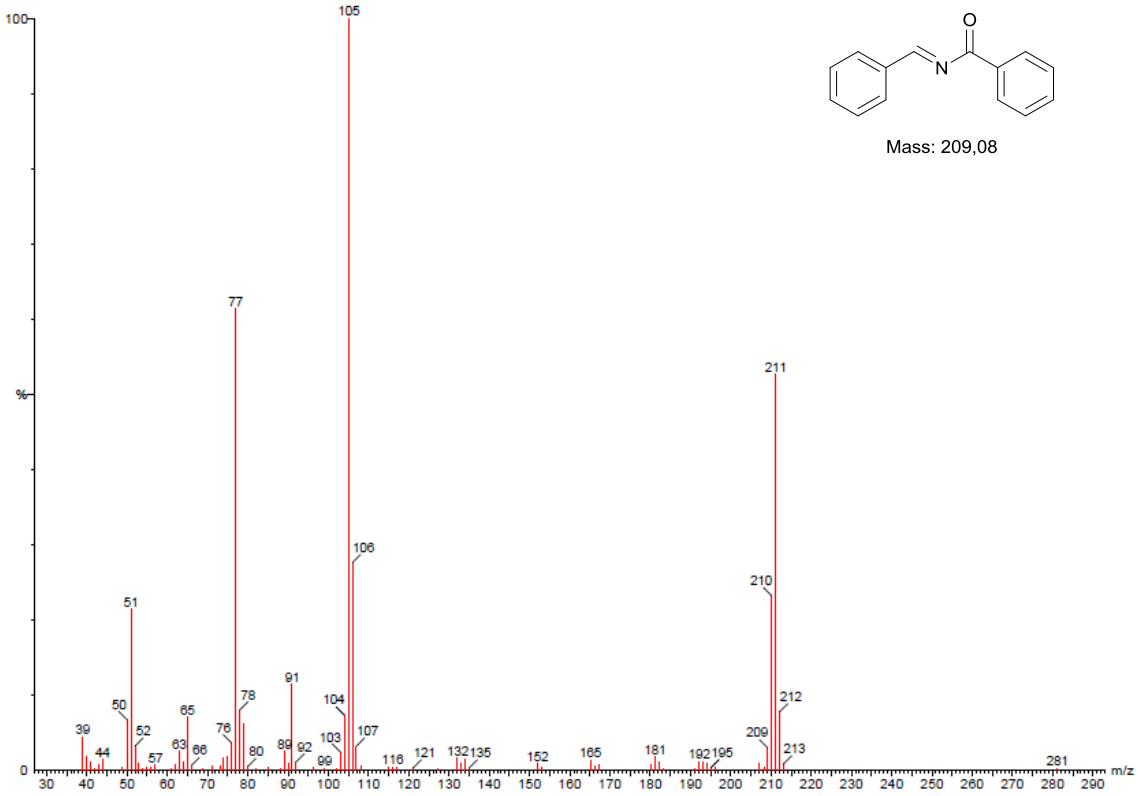
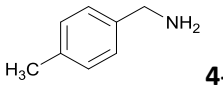


Figure 18 MS of *N*-benzylidenebenzamide



4-methylbenzylamine

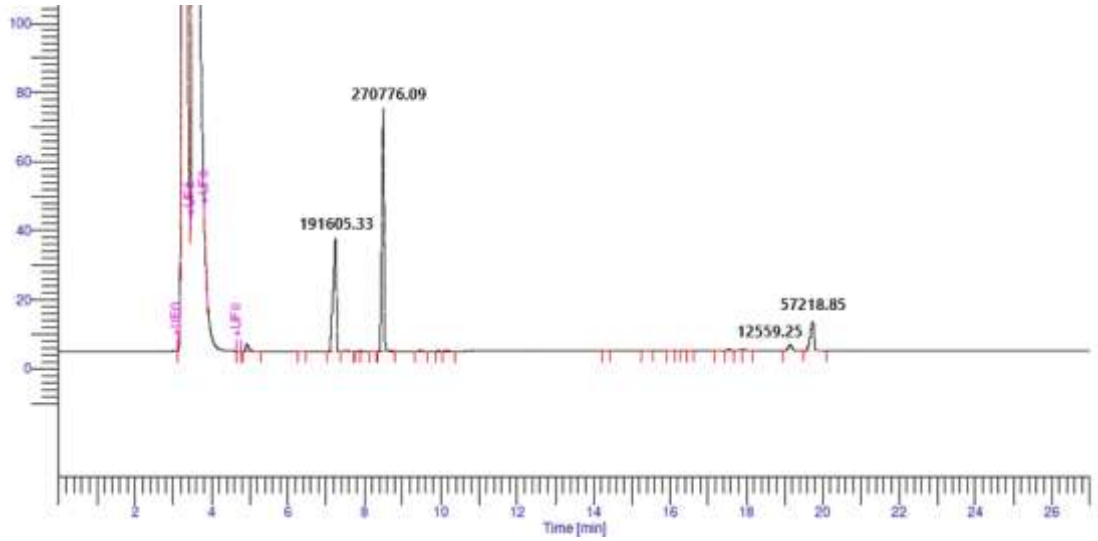


Figure 19 **GC-FID,** 3 – 4.7 min.: solvents (chloroform and ^{t}BuOH), 4.99 min.: *p*-cymene (from catalyst), 7.3 min.: hexadecane (internal standard), 8.5 min.: benzonitrile, 19.2 min.: amide, 19.7 min.: imine

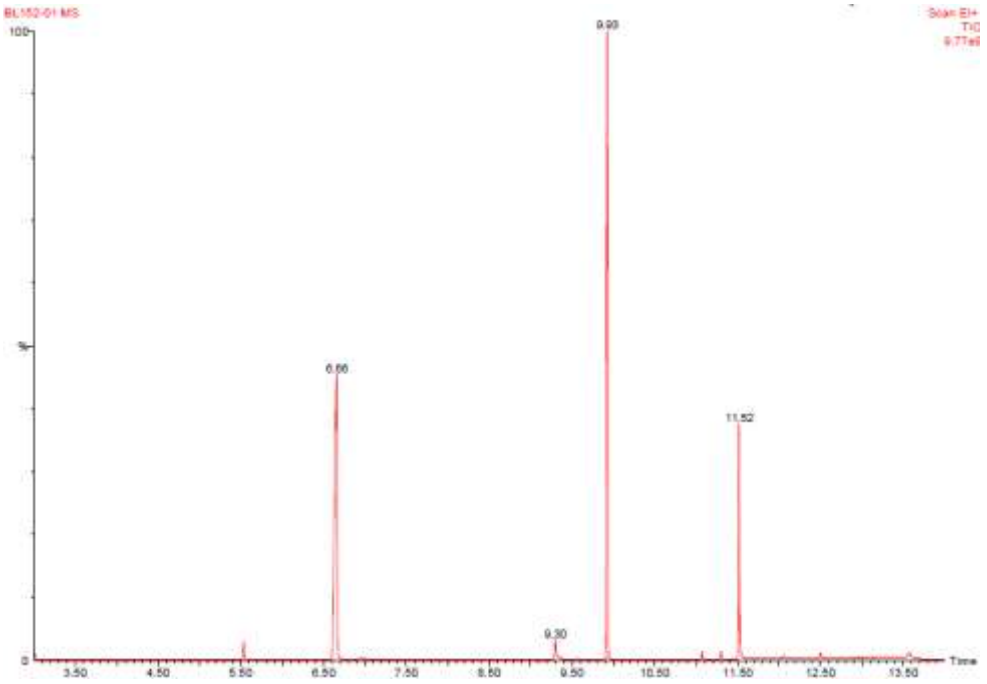


Figure 20 GC-MS, Ca. 5.5 min.: *p*-cymene (from catalyst), 6.66 min.: 4-methylbenzonitrile, 9.3 min.: 4-Methylbenzamide, 9.92 min.: hexadecane (internal standard), 11.52 min.: *N*-(4-methylbenzyl)-1-(p-tolyl)methanimine

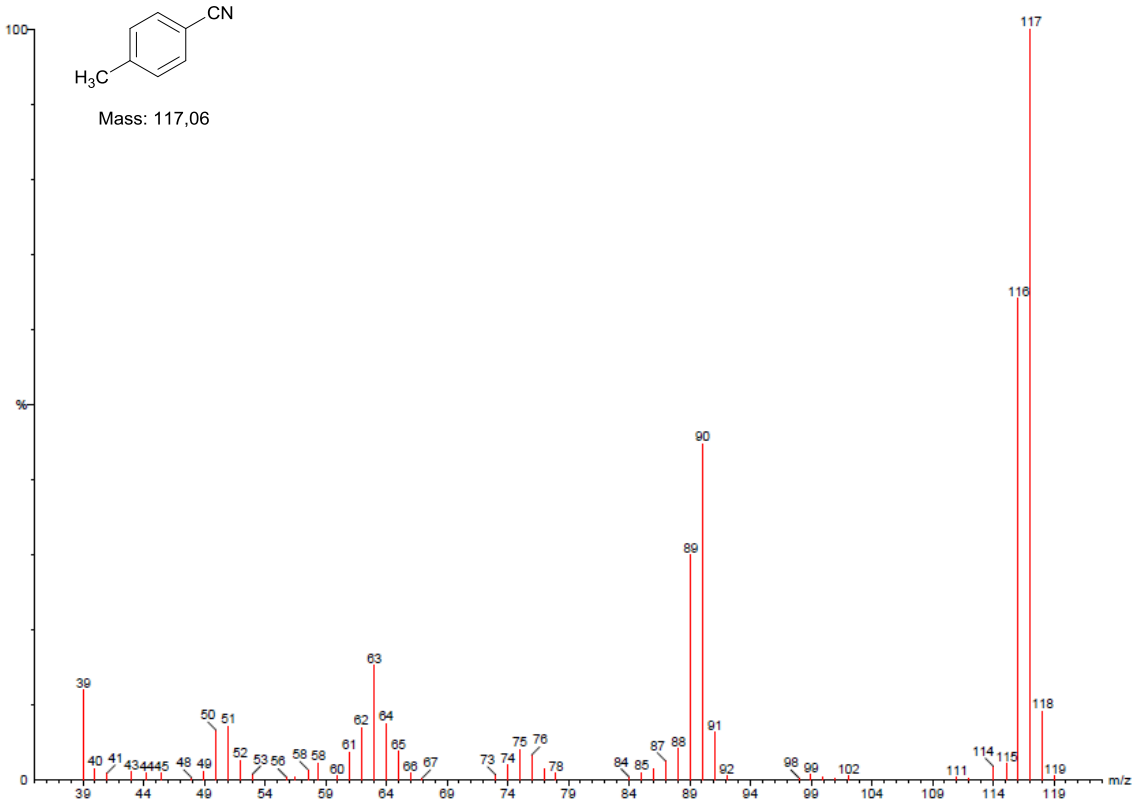


Figure 21 MS of 4-methylbenzonitrile

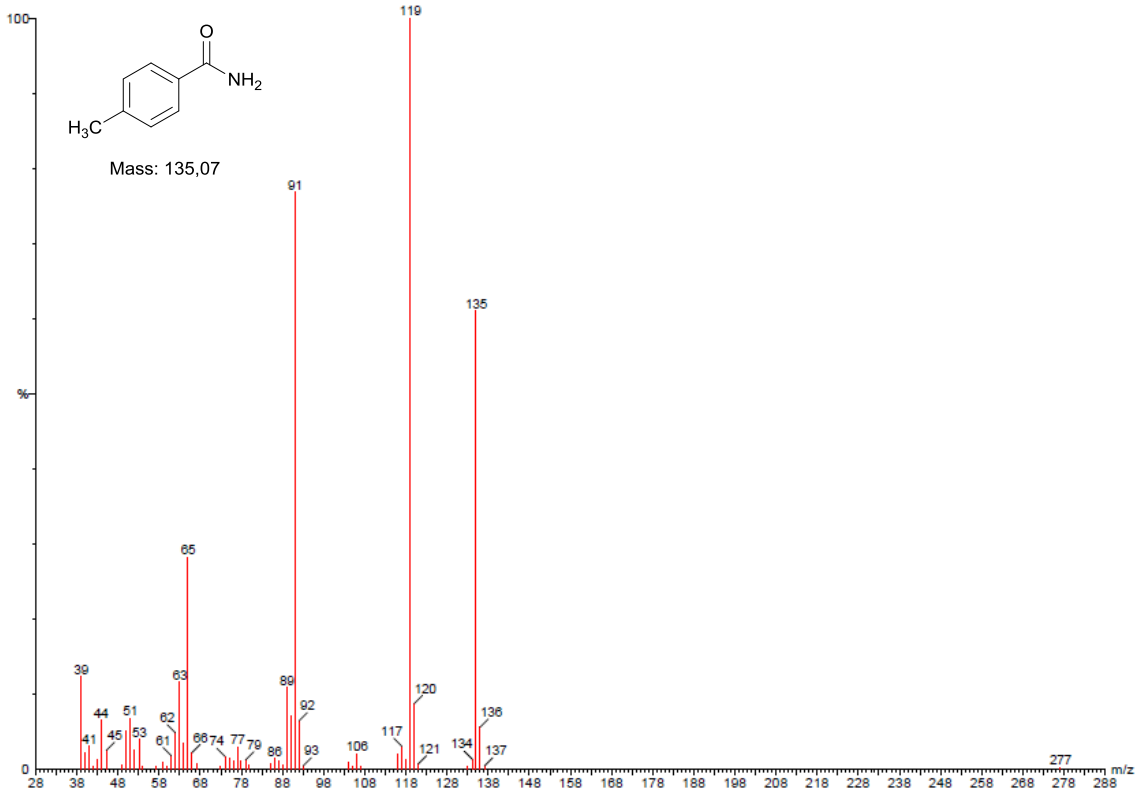


Figure 22 4-methylbenzamide

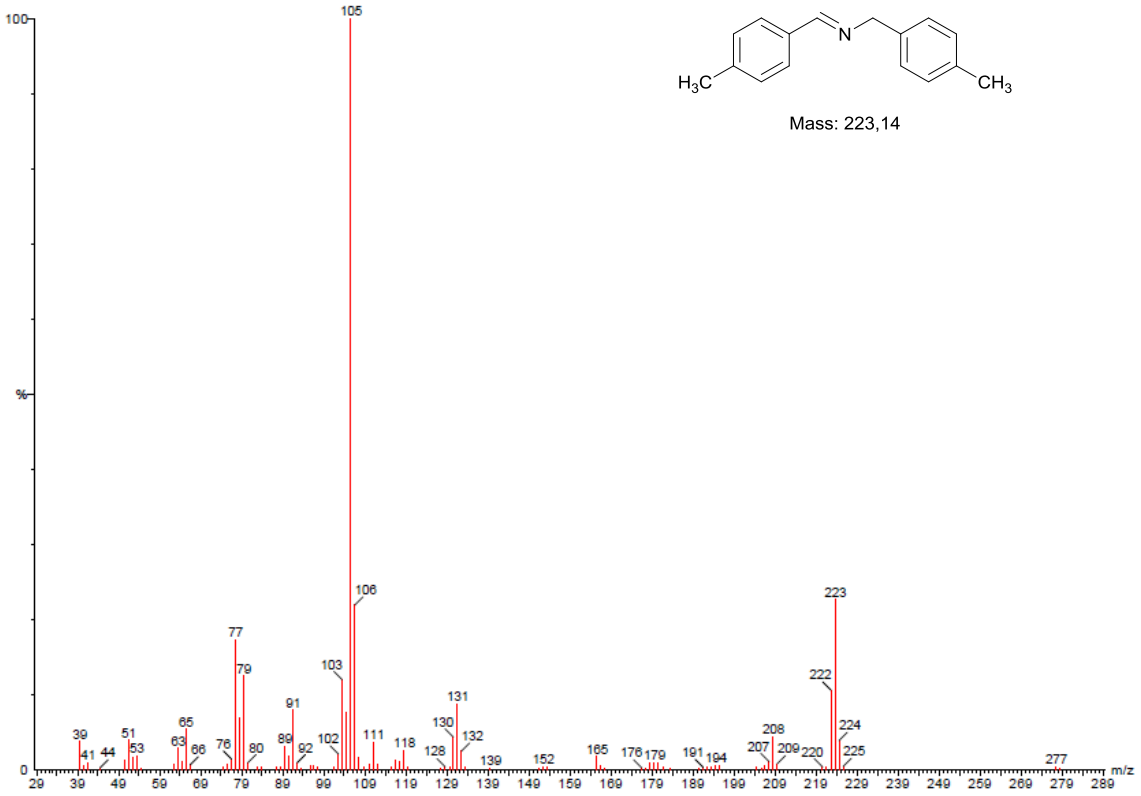
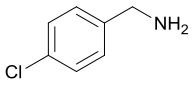


Figure 23 *N*-(4-methylbenzyl)-1-(p-tolyl)methanimine



4-Chlorobenzylamine

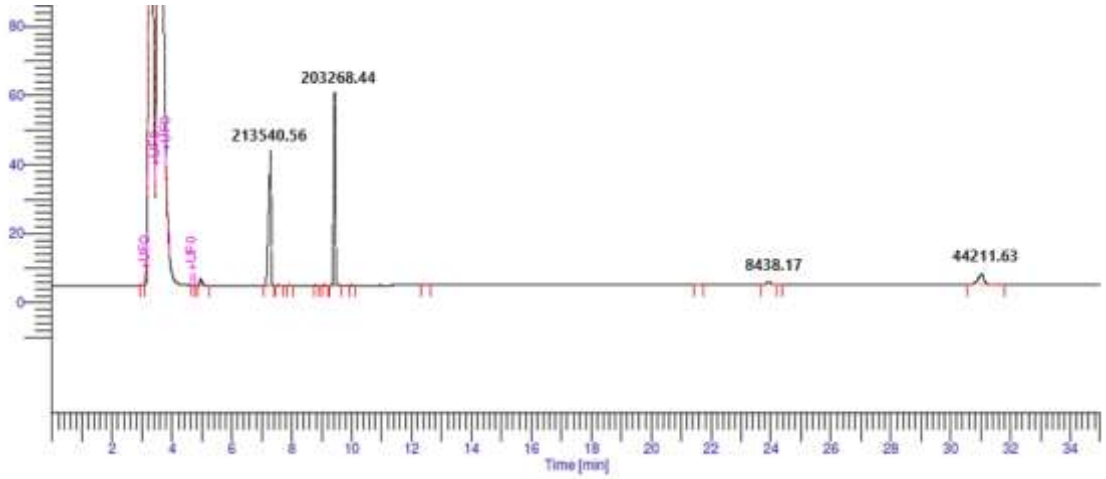


Figure 24 **GC-FID,** 3 – 4.7 min.: solvents (chloroform and ^{t}BuOH), 4.99 min.: *p*-cymene (from catalyst),7.3 min.: hexadecane (Internal Standard),9.4 min.: benzonitrile, 23.9 min.: amide,31 min.: imine

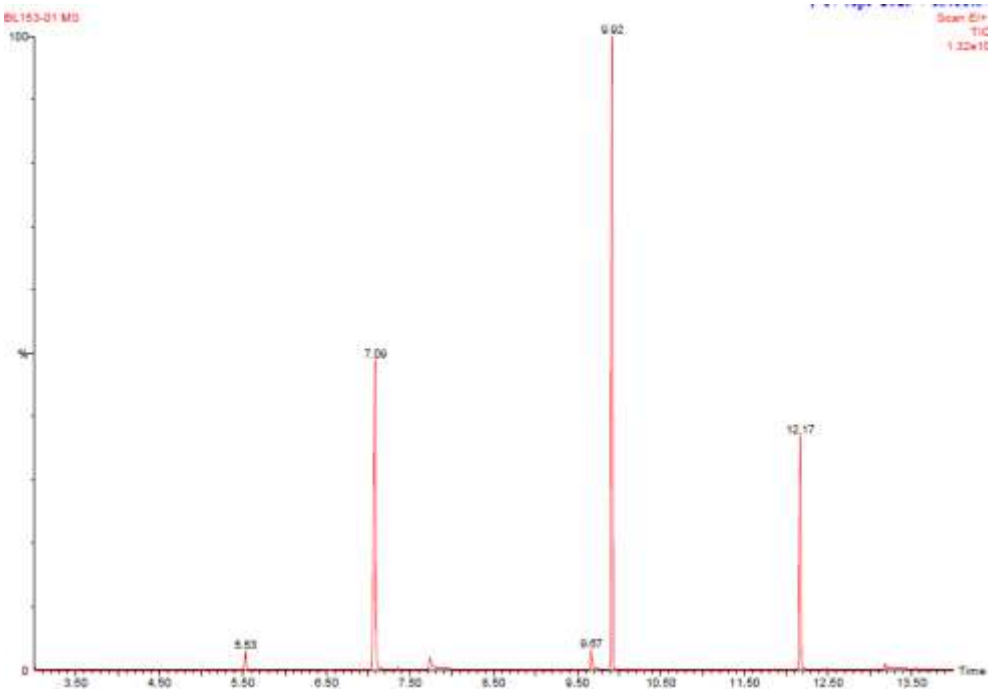


Figure 25 **GC-MS,** Ca. 5.5 min.: *p*-cymene (from catalyst), 7.09 min.: 4-chlorobenzonitrile, 7.74 min.: 4-chlorobenzylamine, 9.67 min.: 4-chlorobenzamide, 9.92 min.: hexadecane (internal standard), 12.17 min.: *N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine

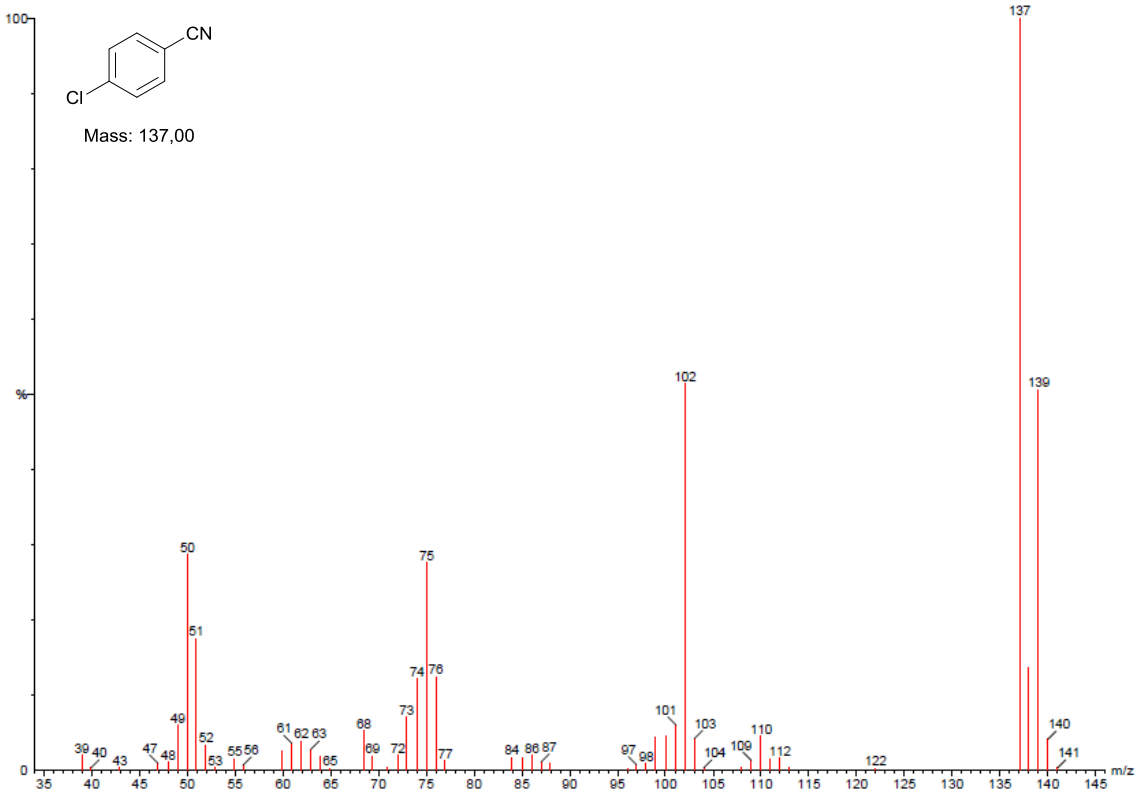


Figure 26 4-MS of chlorobenzonitrile

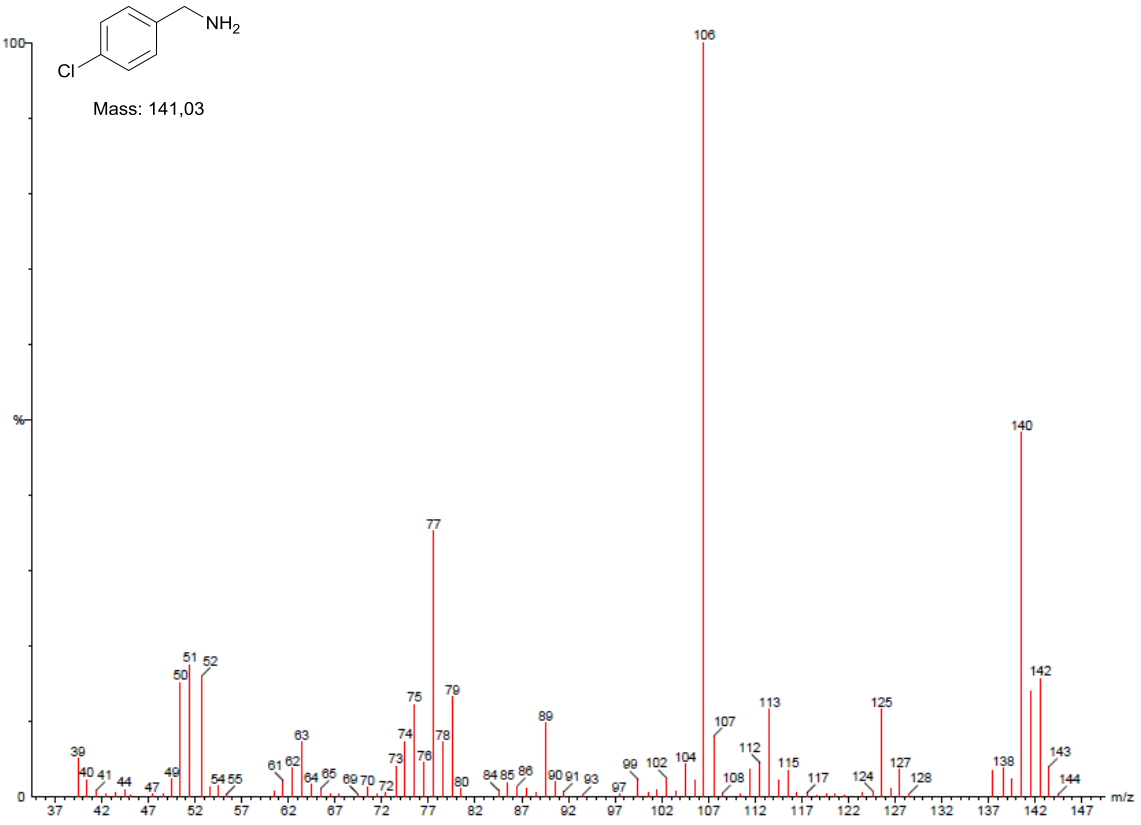


Figure 27 MS of -chlorobenzylamine

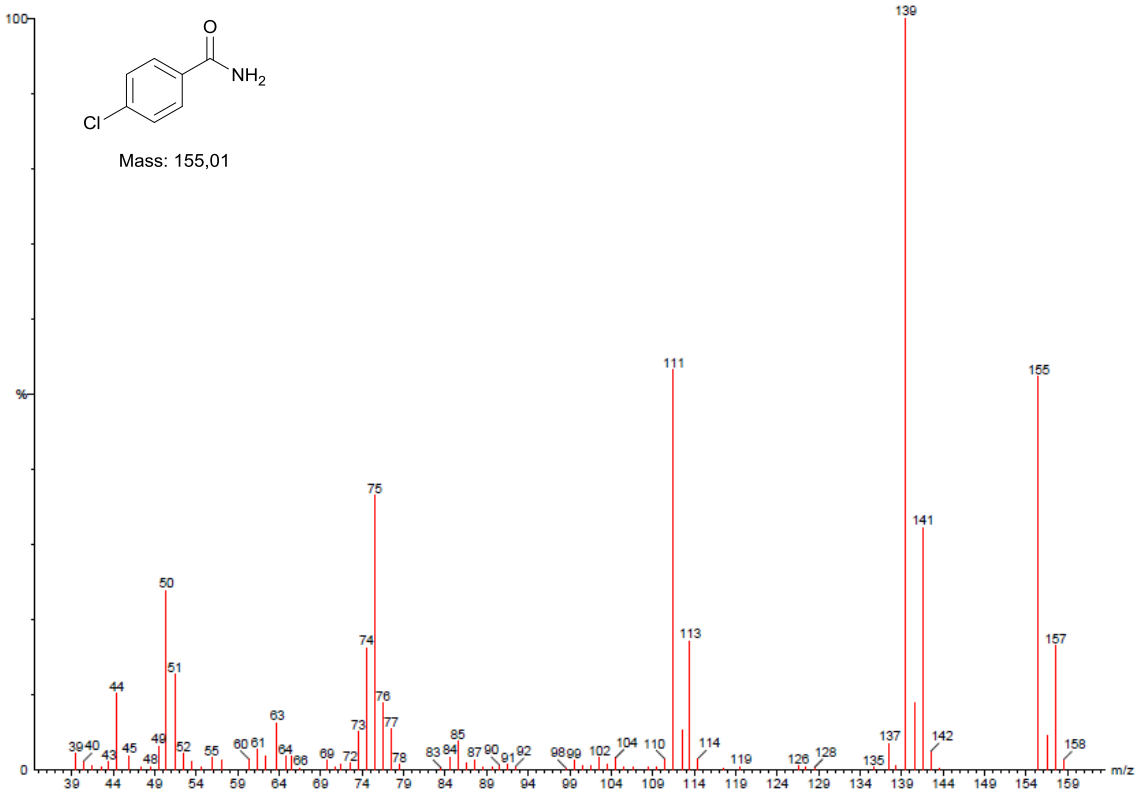


Figure 28 MS of 4-chlorobenzamide

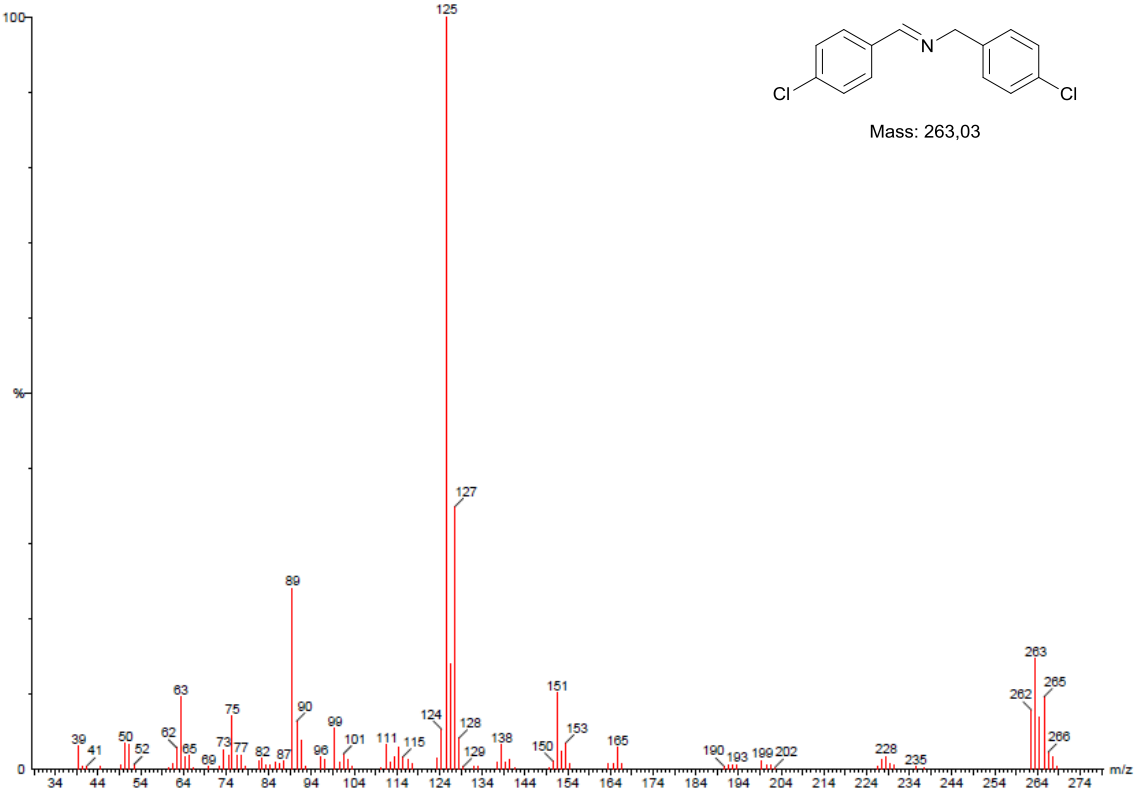
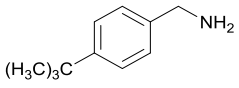


Figure 29 MS of -(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine



4-Tertbutylbenzylamine

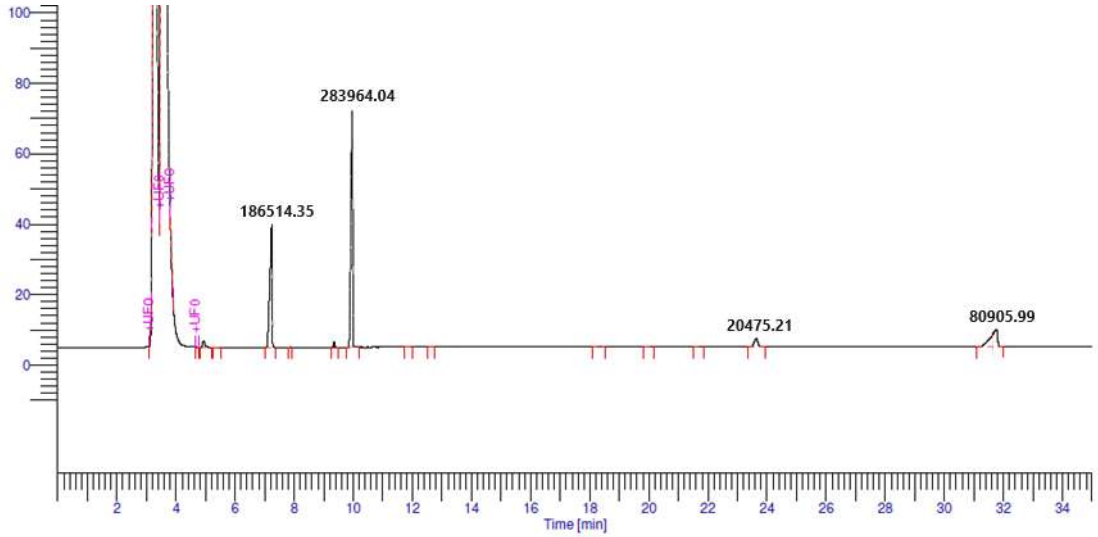


Figure 30 **GC-FID,**3 – 4.7 min.: Solvents (Chloroform and ^{t}BuOH),4.9 min.: *p*-cymene (from catalyst),7.2 min.: hexadecane (internal standard),9.34 min.: benzylamine,9.95 min.: benzonitrile,23.6 min.: benzamide,31.7 min.: imine

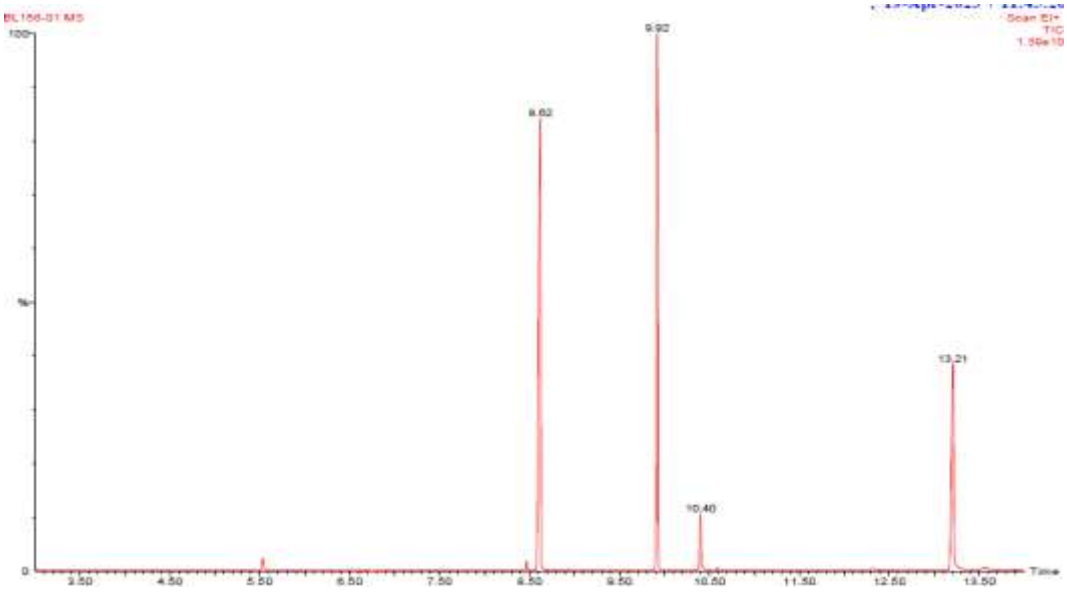


Figure 31 **GC-MS,**Ca. 5.5 min.: *p*-cymene (from catalyst), 8.47 min.: 4-tertbutylbenzylamine, 8.62 min.: 4-tertbutylbenzonitrile, 9.92 min.: hexadecane (internal standard), 10.4 min.: 4-tertbutylbenzamide, 13.21 min.: *N*-(4-(tert-butyl)benzyl)-1-(4-(tert-butyl)phenyl)methanimine

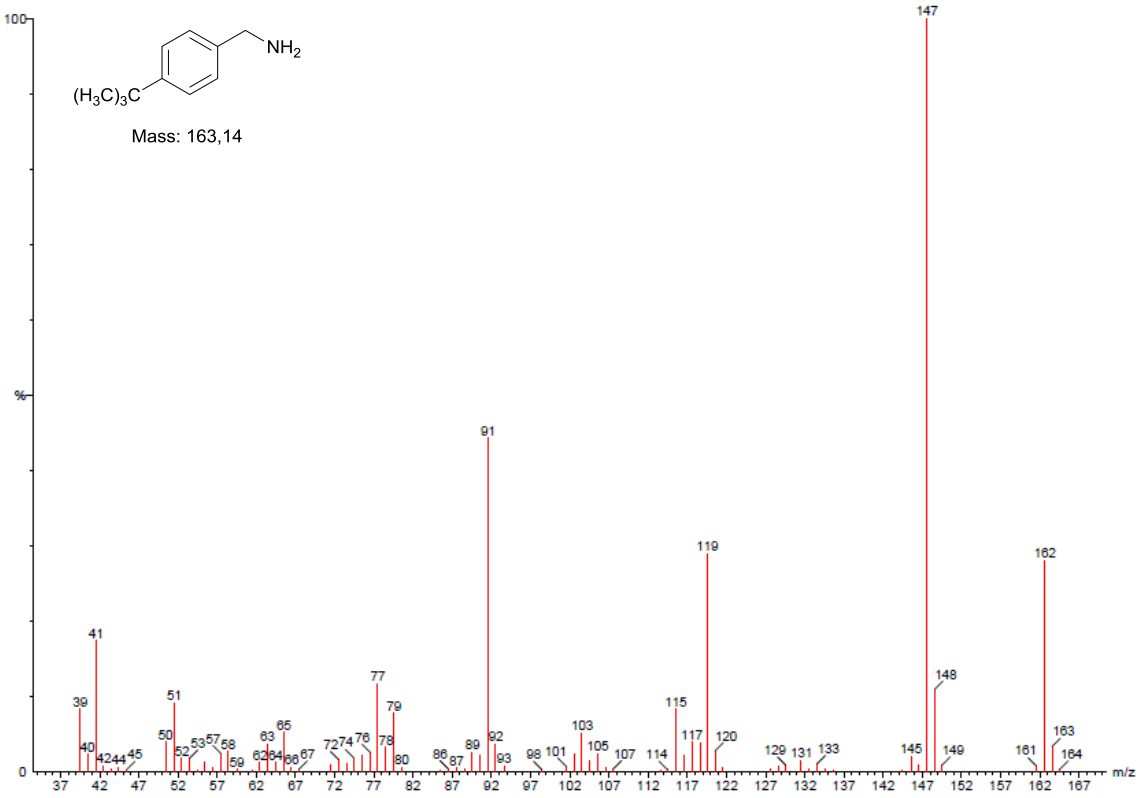


Figure 32 MS of 4-tertbutylbenzylamine

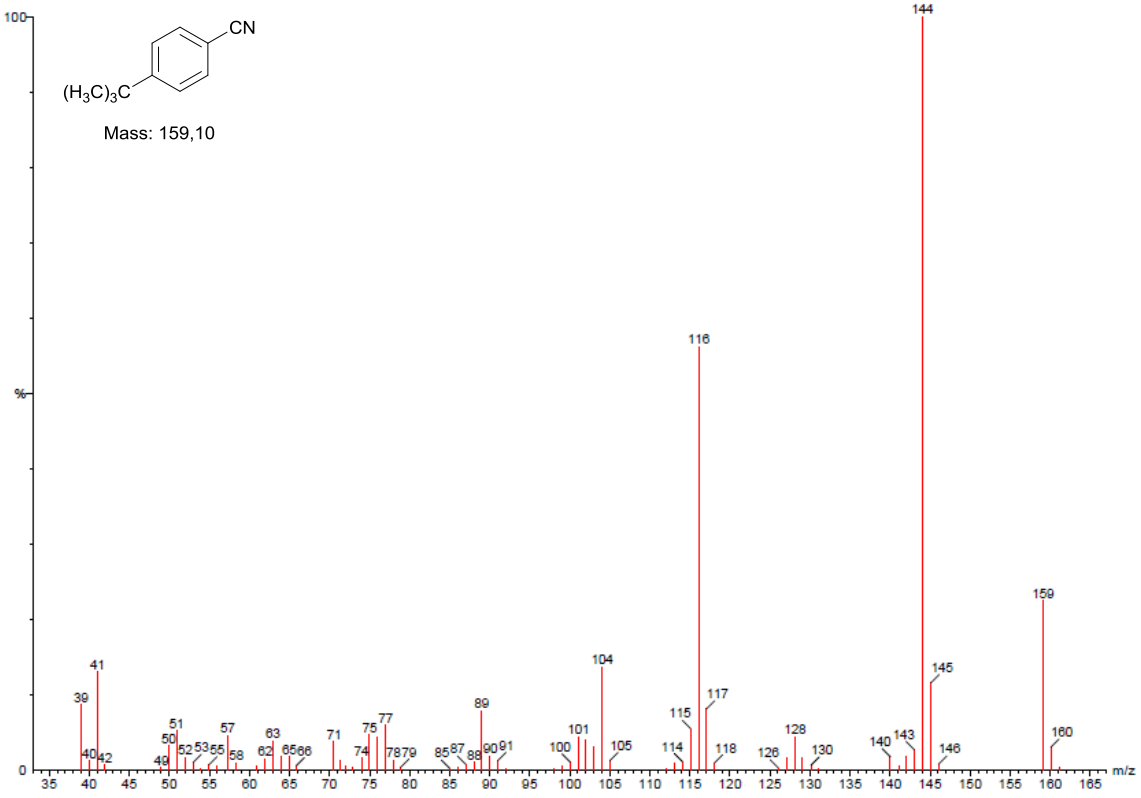


Figure 33 MS of 4-tertbutylbenzonitrile

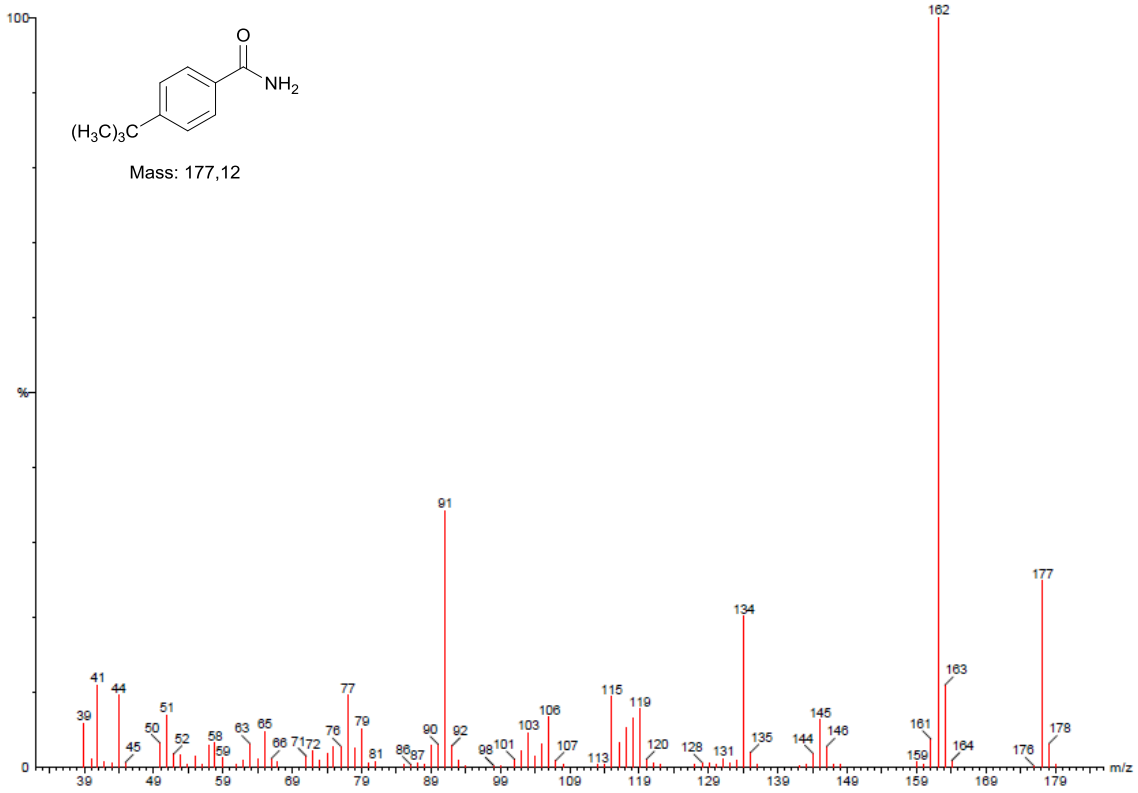


Figure 34 MS of 4-tertbutylbenzamide

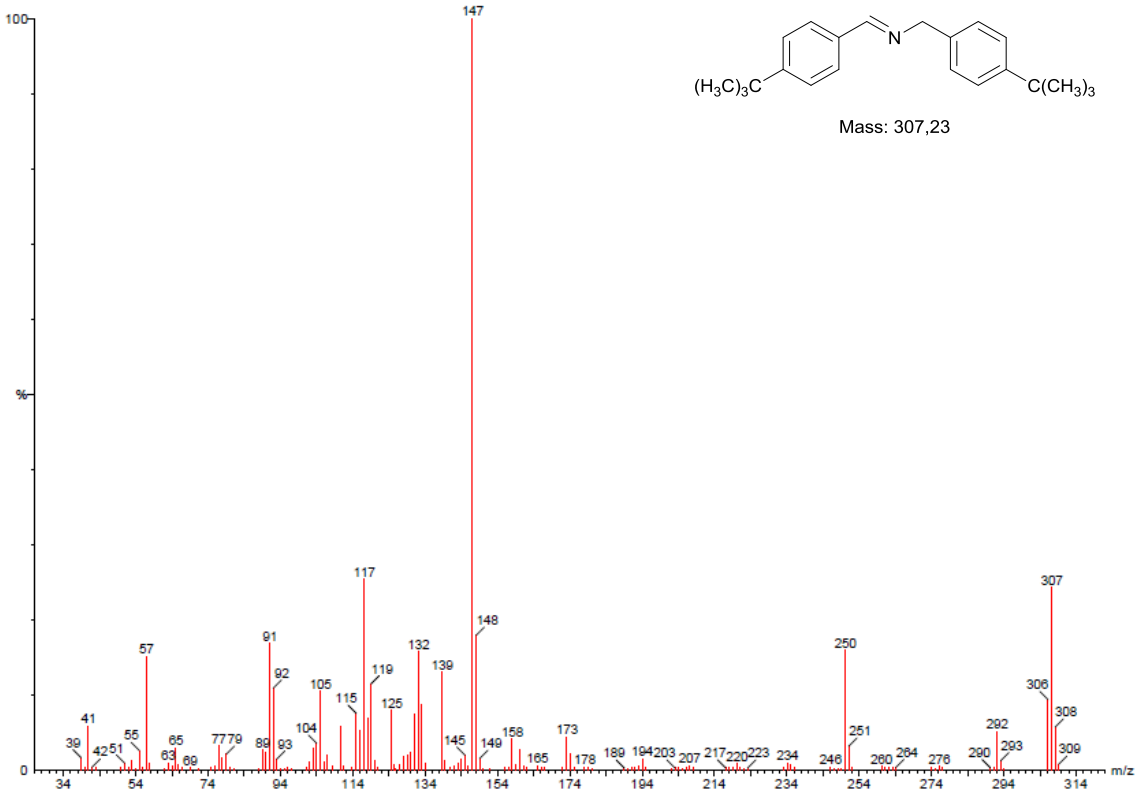
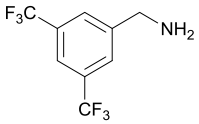


Figure 35 MS of *N*-(4-(tert-butyl)benzyl)-1-(4-(tert-butyl)phenyl)methanimine



3,5-Bis(trifluoromethyl)benzylamine

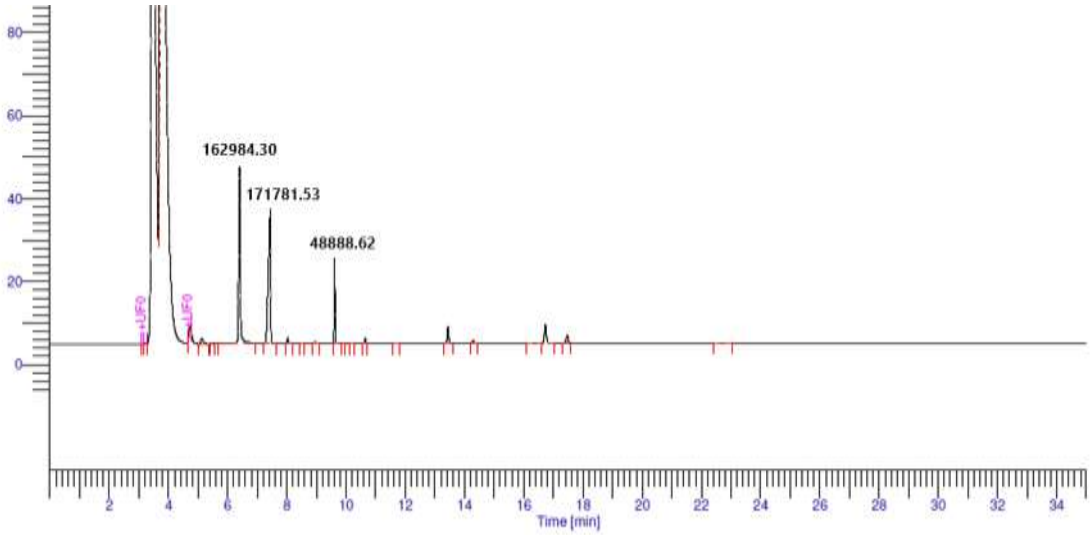


Figure 36 **GC-FID,** 3 – 4.7 min.: solvents (chloroform and ^{t}BuOH),5.1 min.: *p*-cymene (from catalyst), 6.4 min.: 3,5-bis(trifluoromethyl)benzonitrile,7.4 min.: hexadecane (internal standard), 9.6 min.: 3,5-bis(trifluoromethyl)benzylamine. The small signals of 4.7 min., 8 min. and between 10.6 and 17.5 min. were neglected.

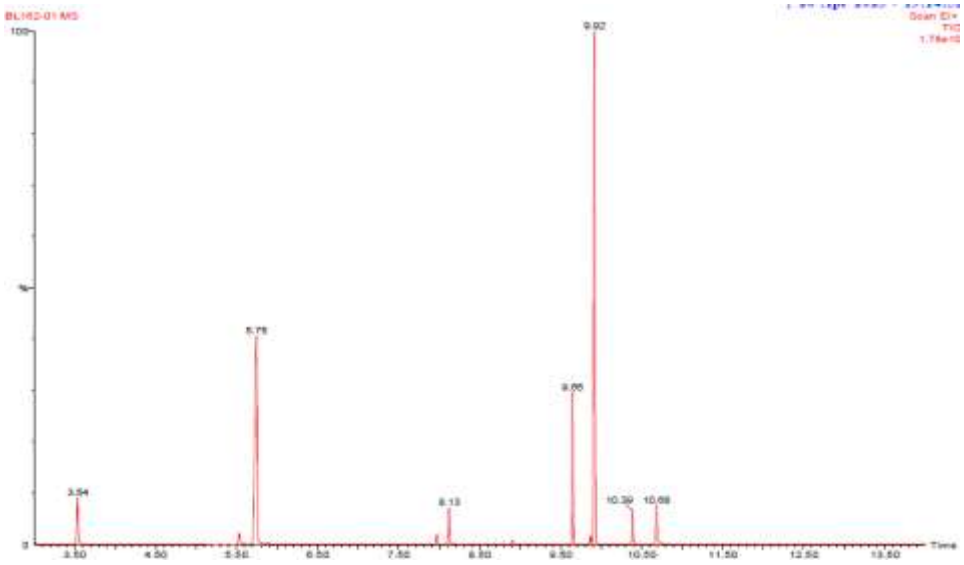


Figure 37 **GC-MS,** ca. 5.5 min.: *p*-cymene (from catalyst), 3.54 min.: 3,5-bis(trifluoromethyl)benzonitrile, 5.75 min.: 3,5-Bis(trifluoromethyl)benzylamine, 8.13 min.: 3,5-Bis(trifluoromethyl)benzylamide, 9.65 min.: *N*-(3,5-bis(trifluoromethyl)benzyl)-1-(3,5-bis(trifluoromethyl)phenyl)methanimine, 9.92 min.: hexadecane (internal standard), 10.39 min.: *N*-(3,5-bis(trifluoromethyl)benzylidene)-3,5-bis(trifluoromethyl)benzamide, 10.68 min.: *N*-(3,5-bis(trifluoromethyl)benzyl)-3,5-bis(trifluoromethyl)benzimidic acid.

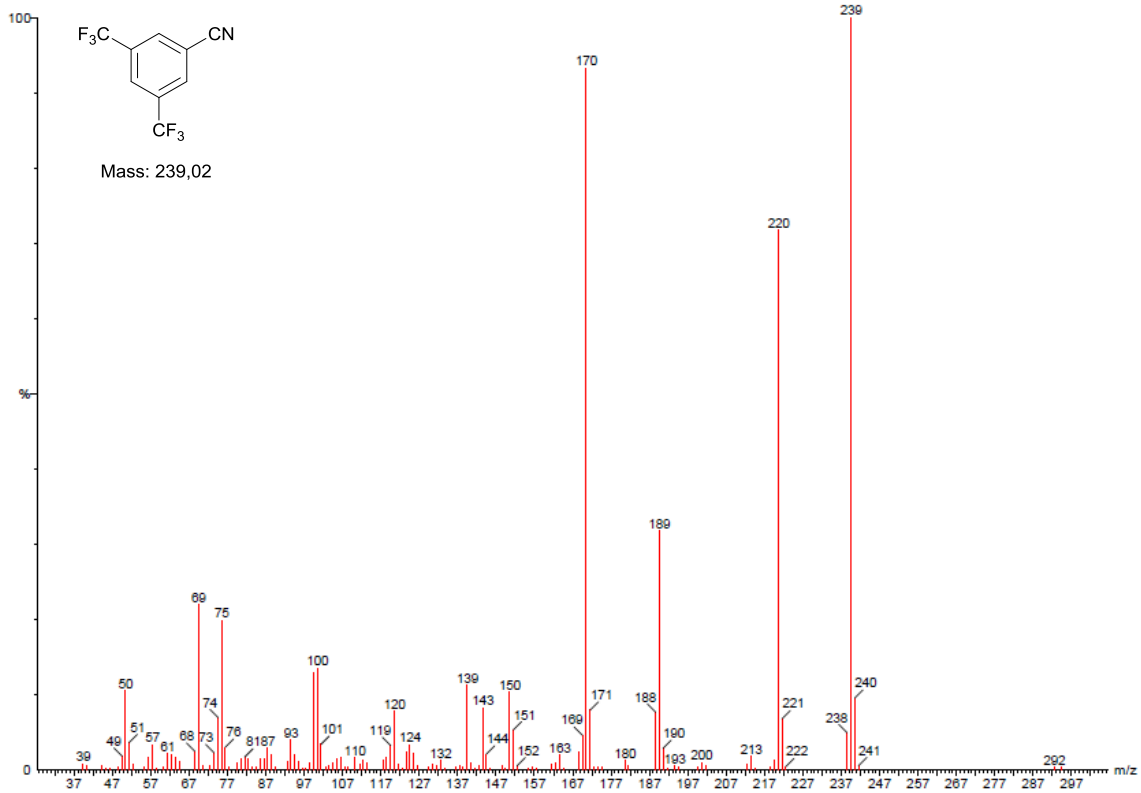


Figure 38 MS of 3,5-bis(trifluoromethyl)benzonitrile

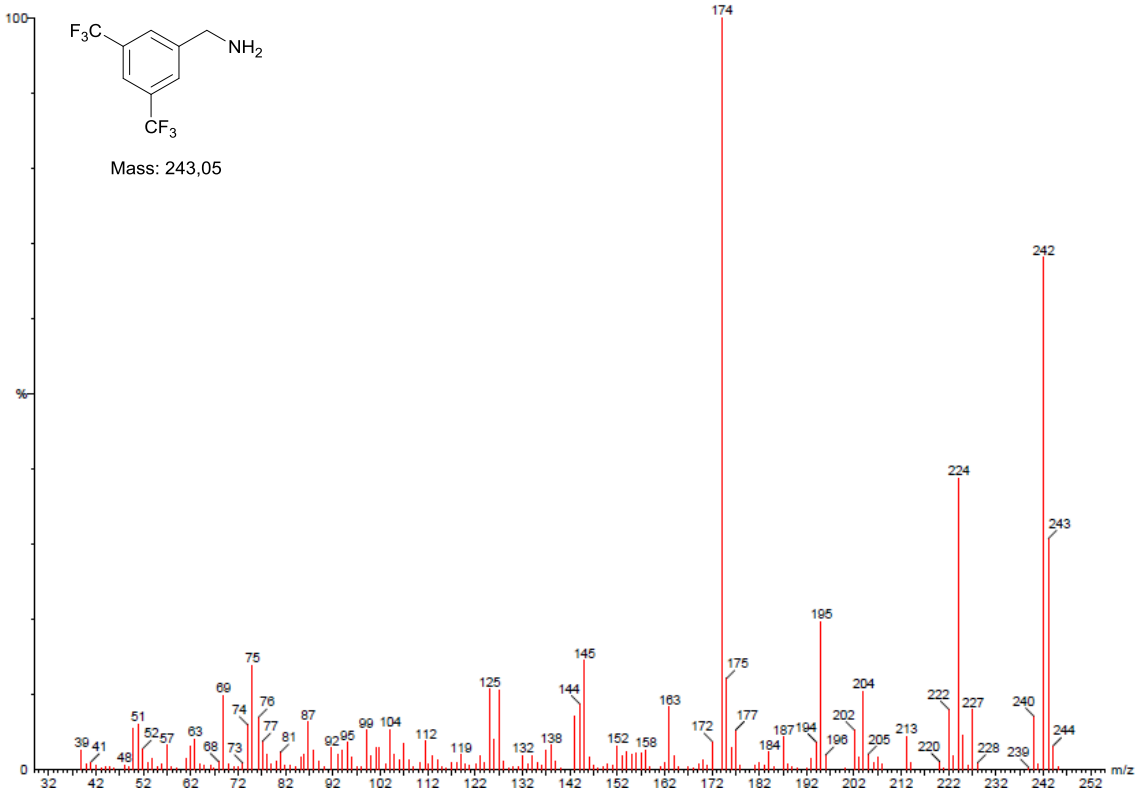


Figure 39 MS of 3,5-Bis(trifluoromethyl)benzylamine

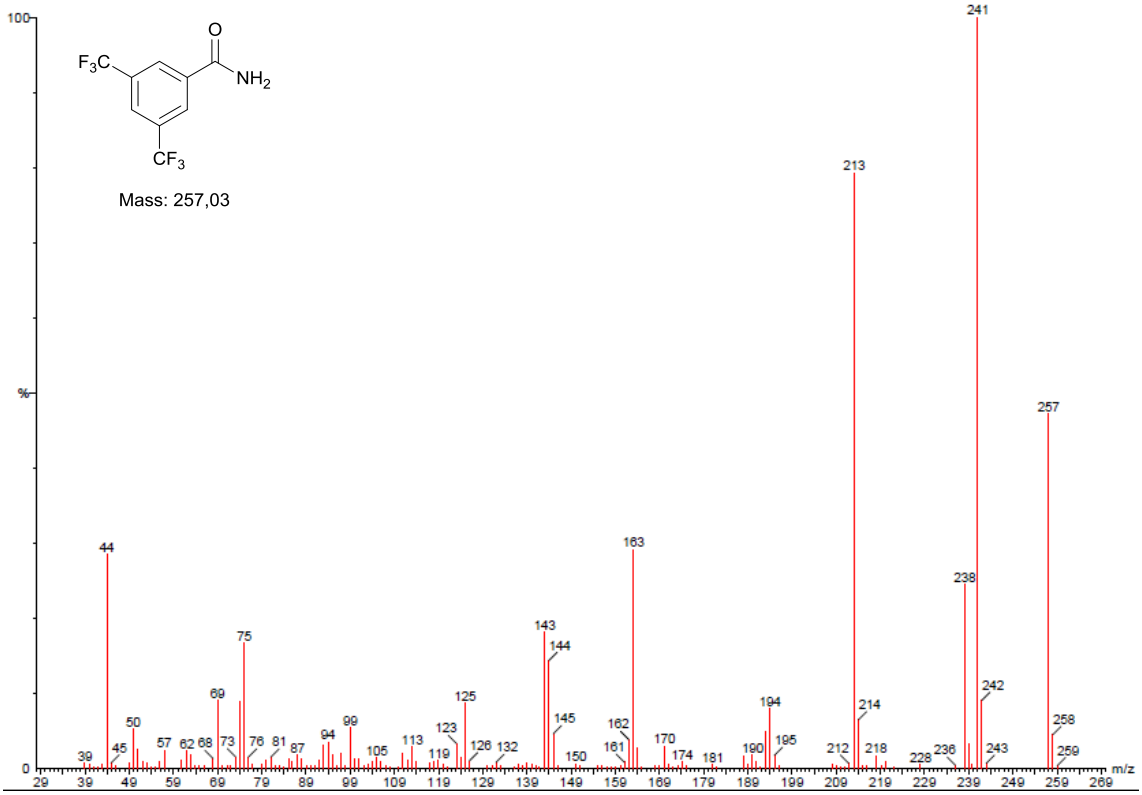


Figure 40 MS of 3,5-bis(trifluoromethyl)benzylamide

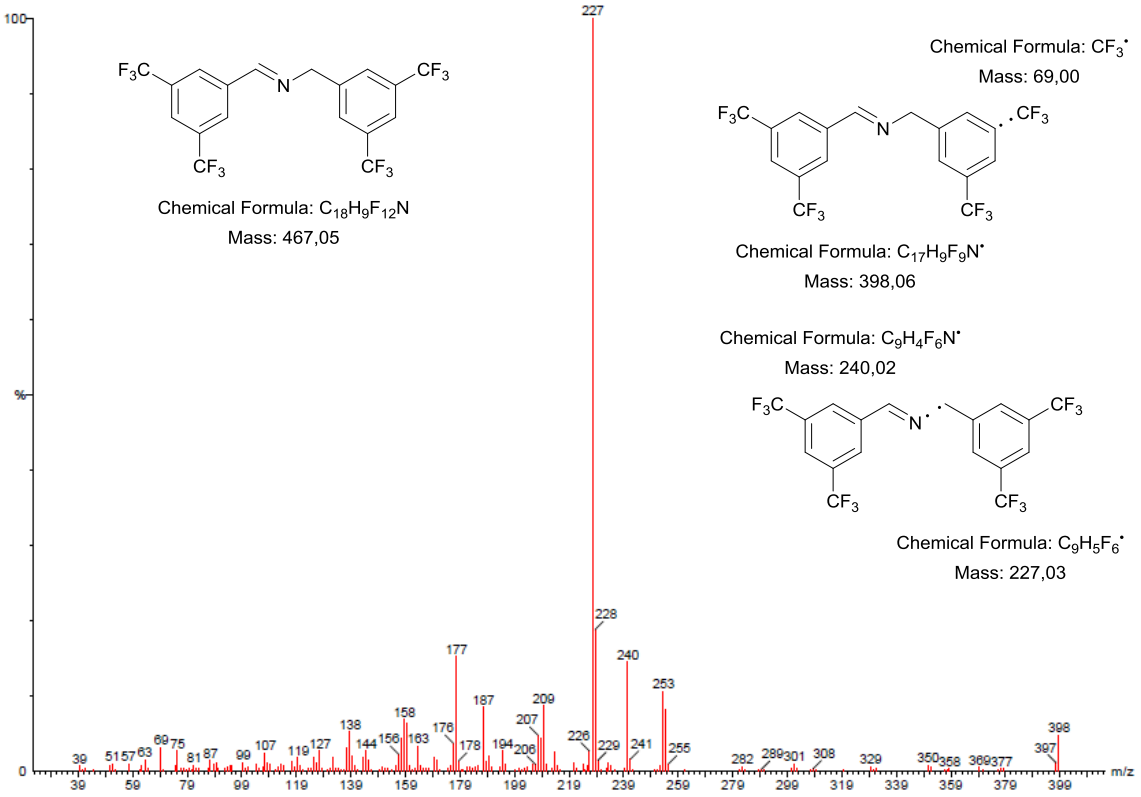


Figure 41. MS of N-(3,5-bis(trifluoromethyl)benzyl)-1-(3,5-bis(trifluoromethyl)phenyl) methanimine

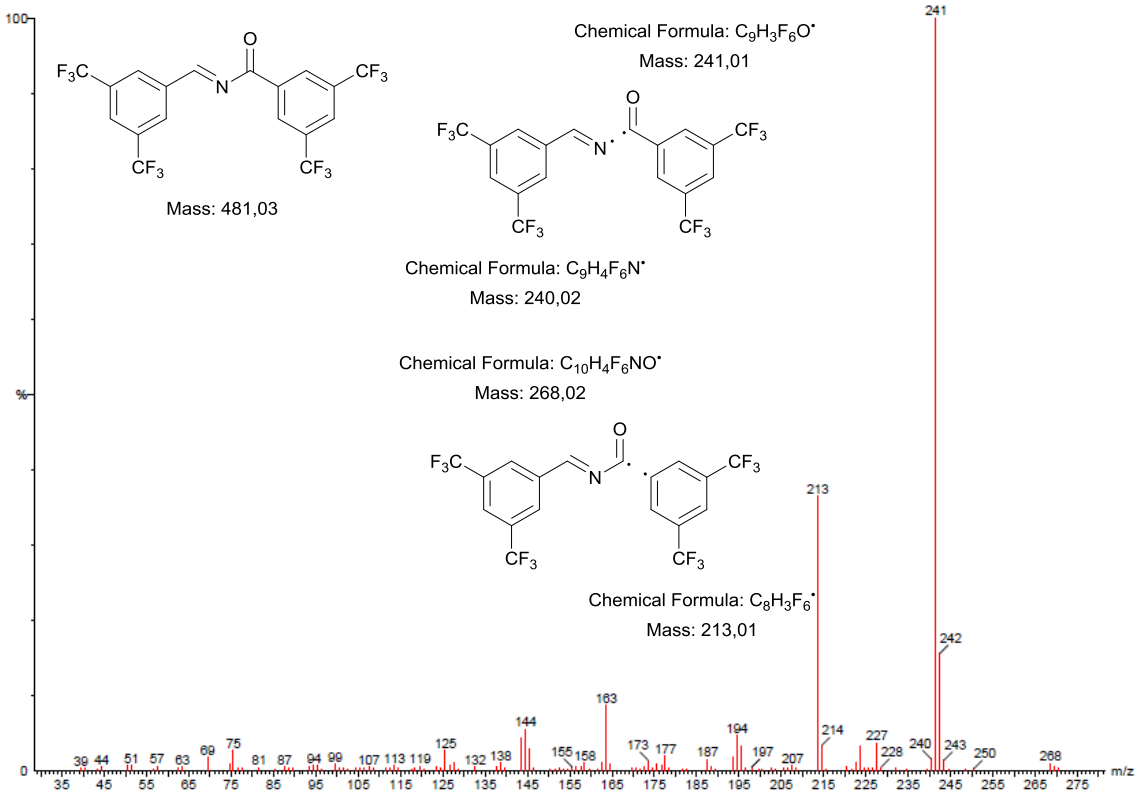


Figure 42. MS of *N*-(3,5-bis(trifluoromethyl)benzylidene)-3,5-bis(trifluoromethyl)benzamide

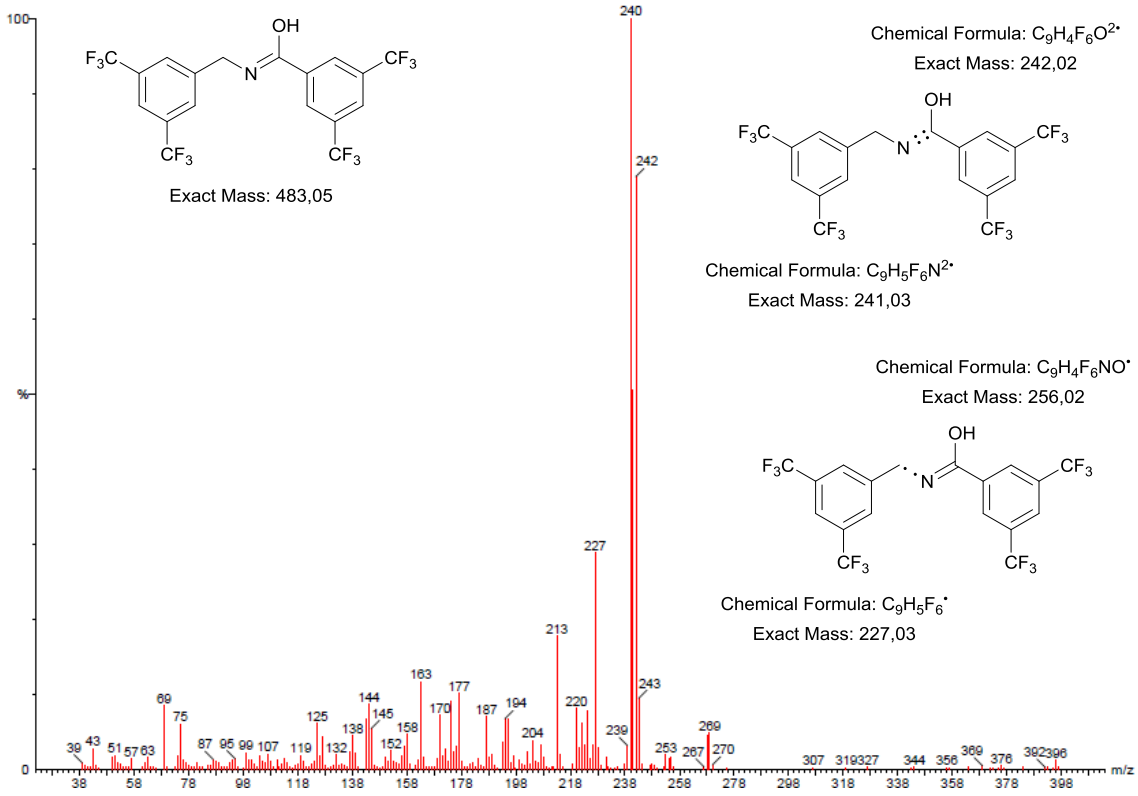
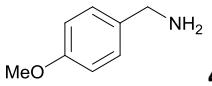


Figure 43. MS of N-(3,5-bis(trifluoromethyl)benzyl)-3,5-bis(trifluoromethyl)benzimidic acid



4-methoxybenzylamine

GC-FID

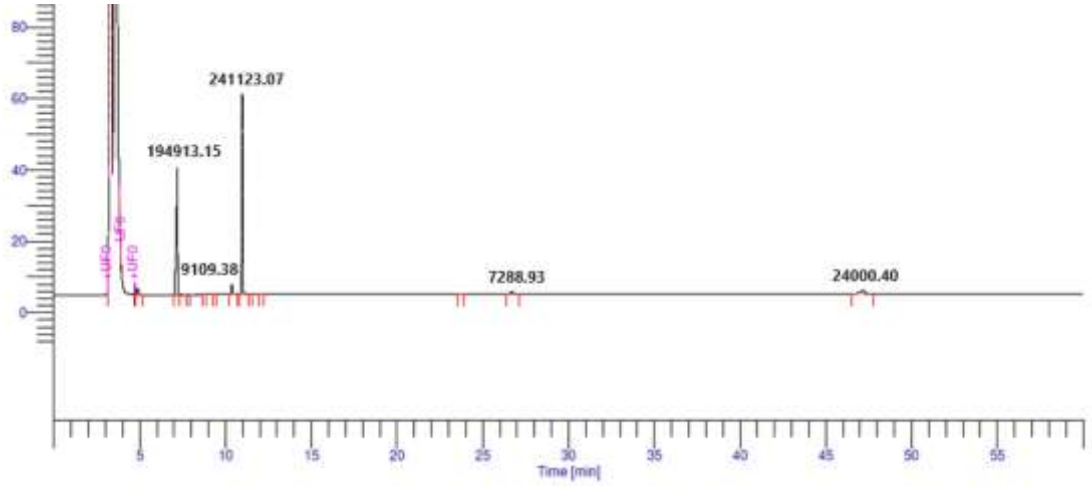


Figure 44 **GC-FID**, 3 – 4.7 min.: solvents (chloroform and ^{t}BuOH), 4.9 min.: *p*-cymene (from catalyst), 7.2 min.: hexadecane (internal standard), 10.4 min.: 4-methoxybenzylamine, 11 min.: 4-methoxybenzonitrile, 26.7 min.: 4-methoxybenzamide, 47.2 min.: *N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine

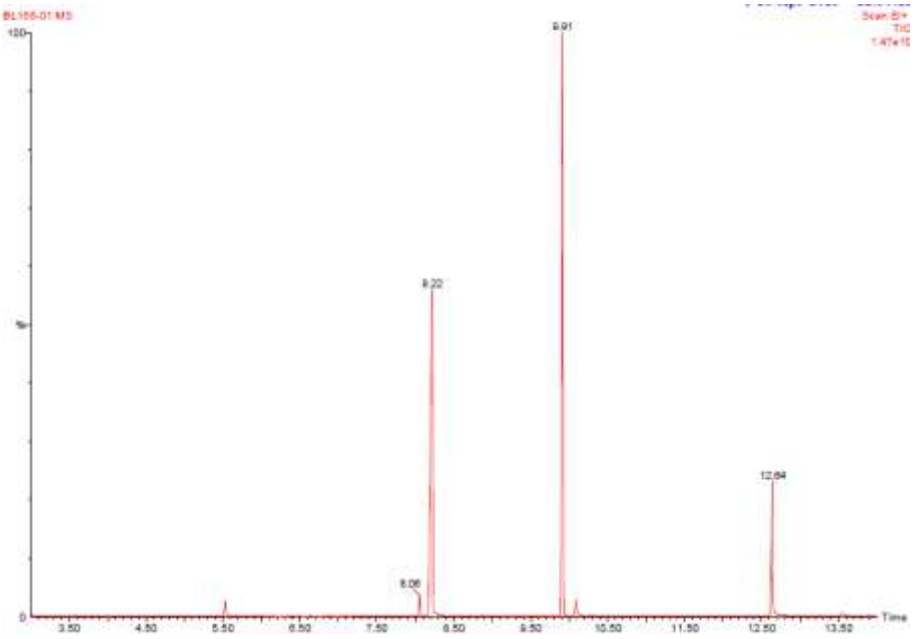


Figure 45 **GC-MS,** ca. 5.5 min.: *p*-cymene (from catalyst), 8.06 min.: 4-methoxybenzylamine, 8.22 min.: 4-methoxybenzonitrile, 9.92 min.: hexadecane (internal standard), 10.09 min.: 4-methoxybenzylamide, 12.64 min.: *N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine

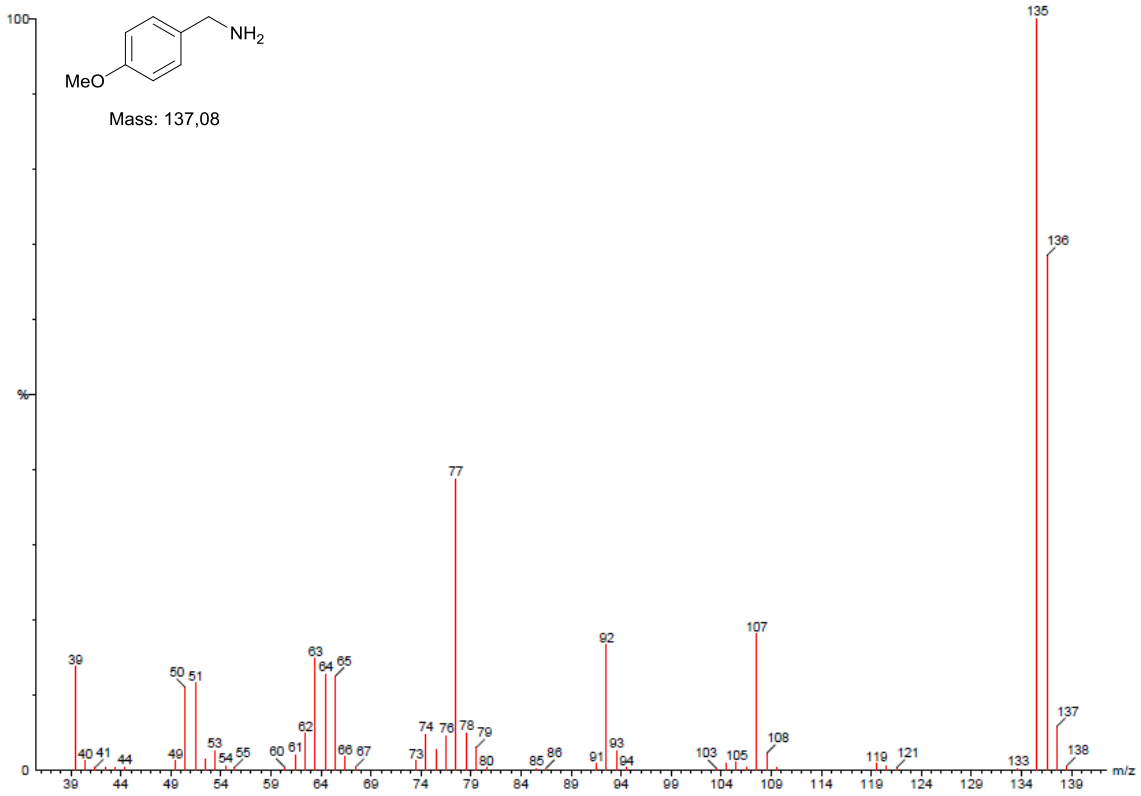


Figure 46 MS of 4-methoxybenzylamine

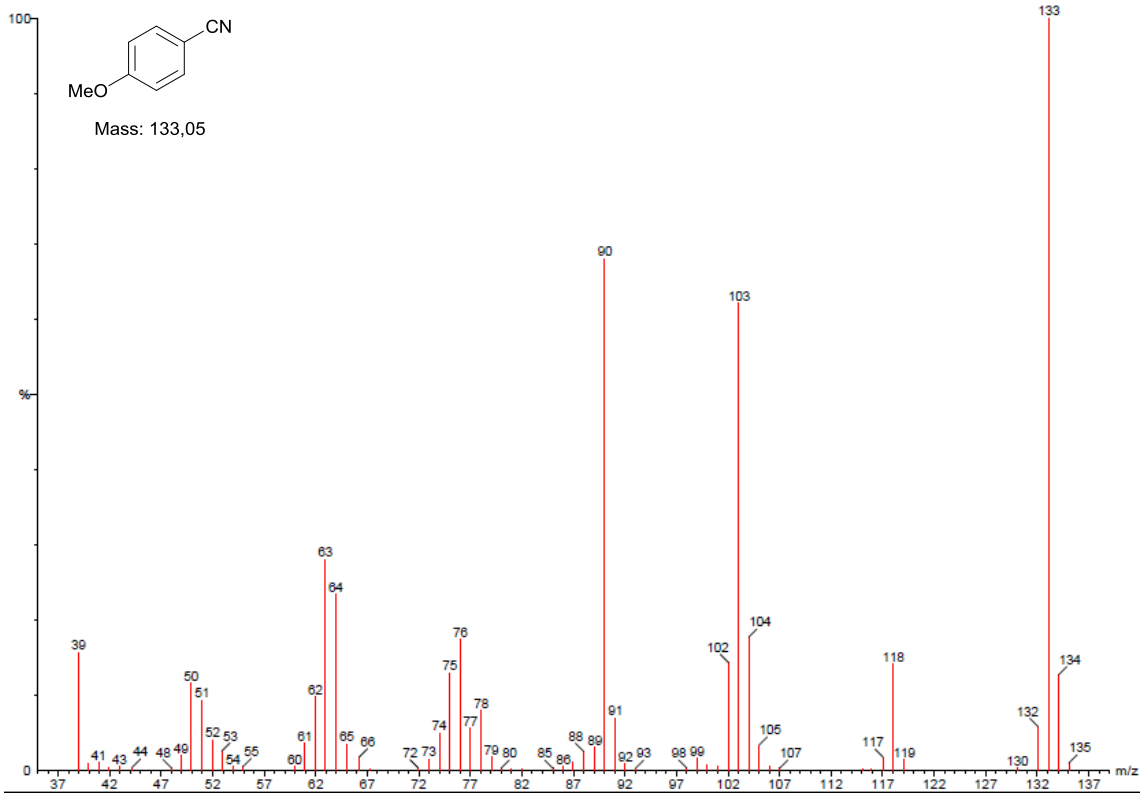


Figure 47 MS of 4-methoxybenzonitrile

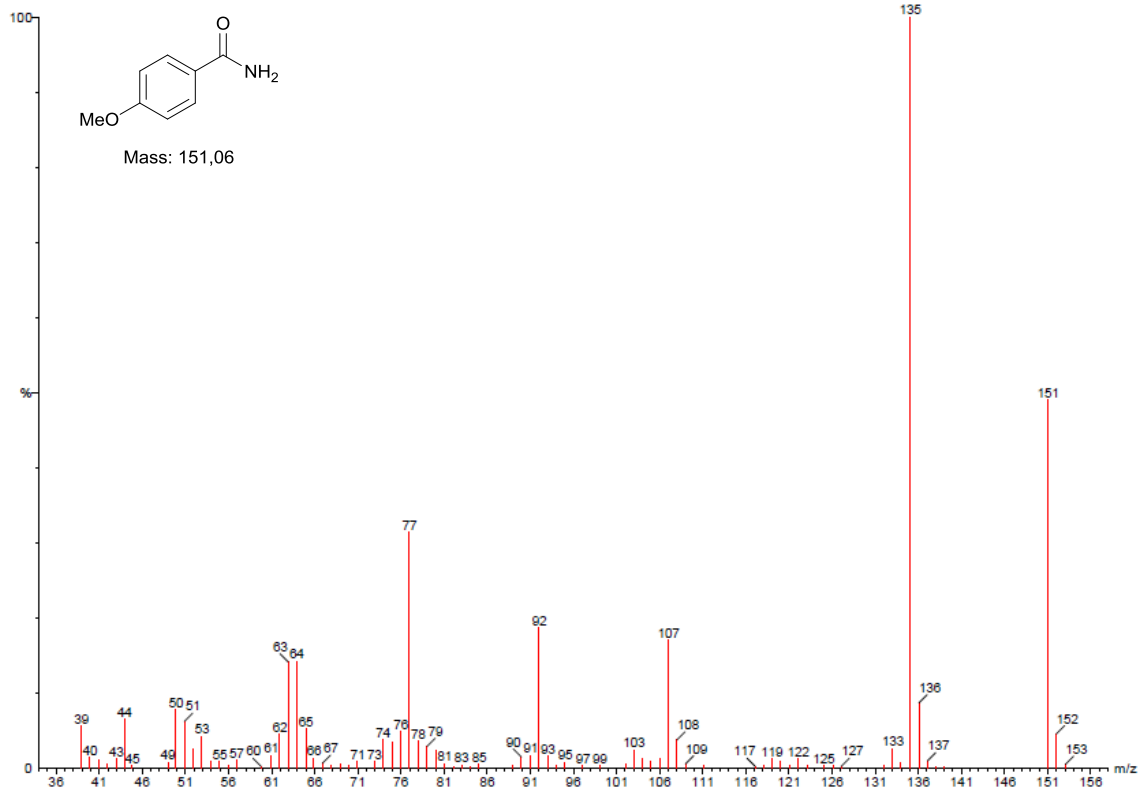


Figure 48 MS of 4-methoxybenzylamide

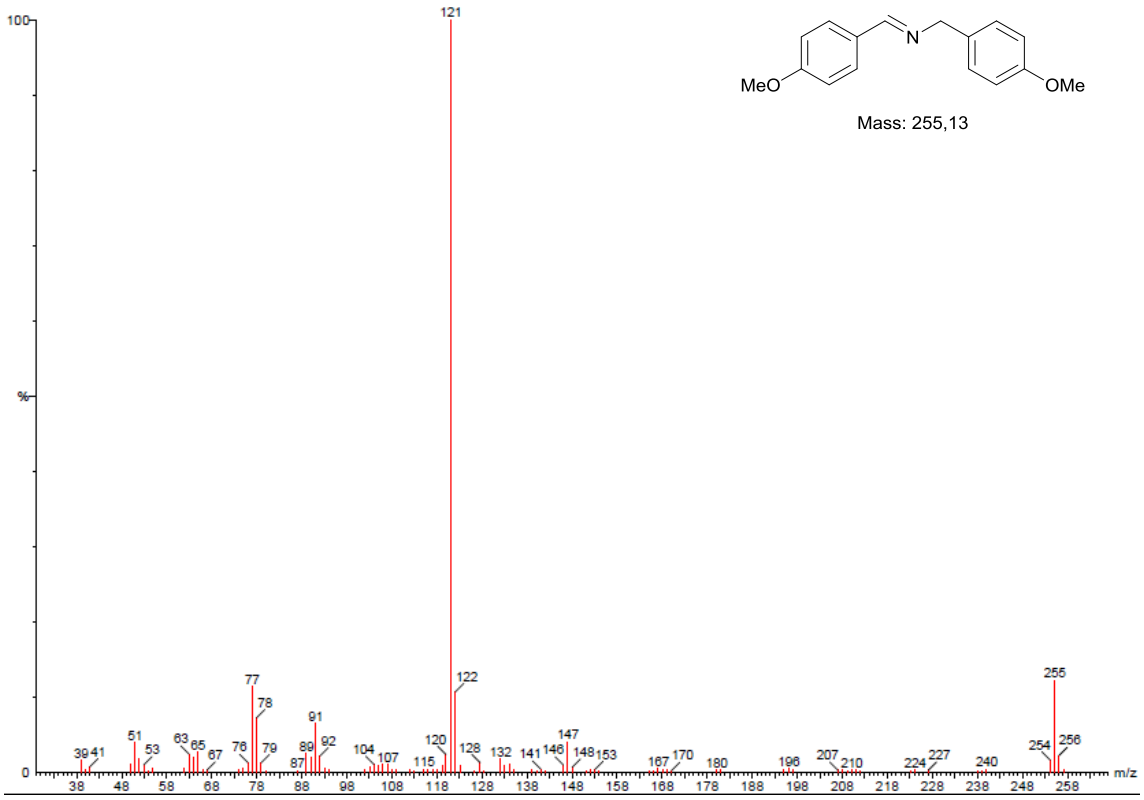
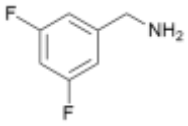


Figure 49 MS of *N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine



3,5-difluorobenzylamine

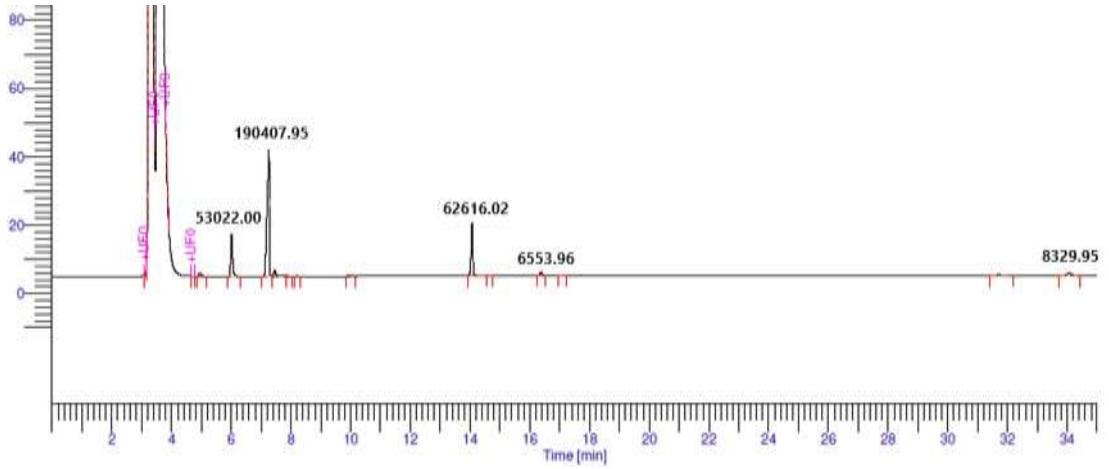
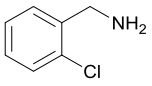


Figure 50 **GC-FID**, 3 – 4.7 min.: solvents (chloroform and ^{t}BuOH), 4.99 min.: p-cymene (from catalyst), 6.0 min.: 3,5-difluorobenzylamine, 7.3 min.: hexadecane (internal standard), 13.9 min.: 3,5-difluorobenzonitrile, 16.4 min.: 3,5-difluorobenzamide, 34 min.: N-(3,5-difluorobenzyl)-1-(3,5-difluorophenyl)methanimine



2-Chlorobenzylamine

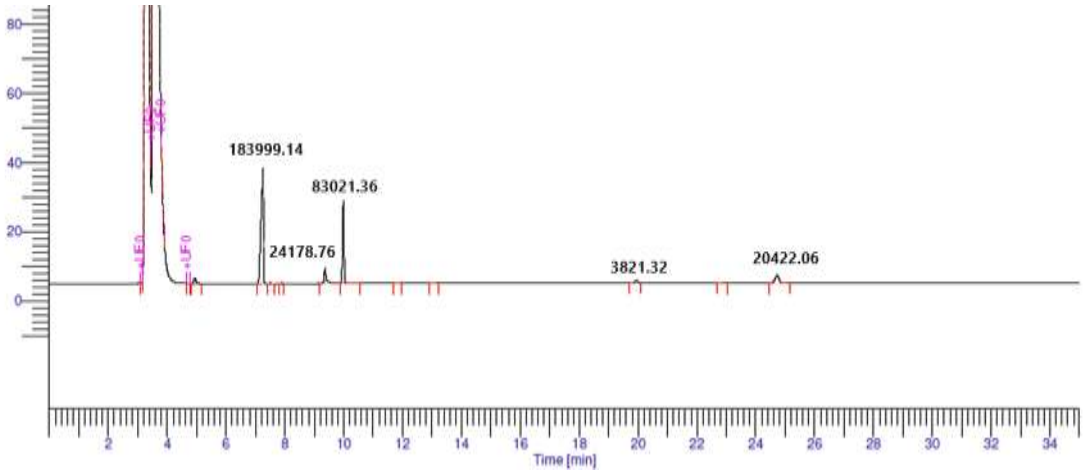
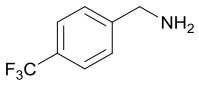


Figure 51 GC-FID, 3 – 4.7 min.: Solvents (Chloroform and ^{t}BuOH), 4.99 min.: p-cymene (from catalyst), 7.3 min.: hexadecane (internal standard), 9.4 min.: 2-chlorobenzylamine, 10 min.: 2-chlorobenzonitrile, 20 min.: 2-chlorobenzamide, 24.7 min.: N-(2-chlorobenzylidene)-2-chlorobenzylamine



4-Trifluorobenzylamine

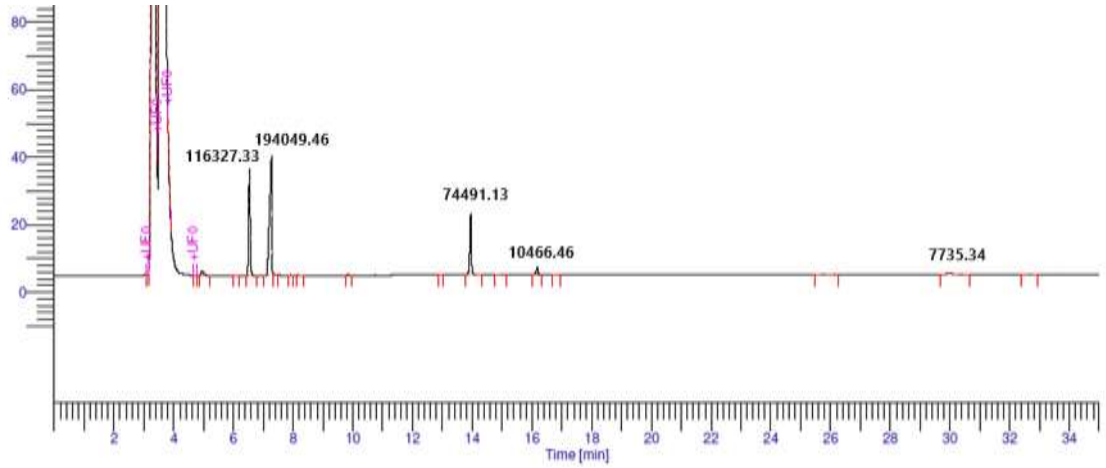


Figure 52 GC-FID, 3 – 4.7 min.: Solvents (Chloroform and ^{t}BuOH), 4.99 min.: p-cymene (from catalyst), 6.5 min.: benzylamine, 7.3 min.: hexadecane (internal standard), 13.9 min.: **4-trifluoro**benzonitrile, 16.2 min.: **4-trifluoro**benzamide, 30 min.: N-(4-(trifluoromethyl)benzyl)-1-(4-(trifluoromethyl)phenyl)methanimine

3. Benzylamine oxidation in a sealed vessel with nitrous oxide

3.1. Optimisation of the benzylamine oxidation with the ruthenium complex {[(*p*-cymene)Ru](*μ*-H)(*μ*-Cl)(*μ*-HCO_2)[Ru(*p*-cymene)]}BF_4 (**Ru-II; $RuBF_4$**) in sealed vessel with N_2O(flask with high-vacuum teflon valve)

A 50 mL tube equipped with high-vacuum teflon valve was charged with 120 µL (1 mmol) of benzylamine and 1 or 2 mL of tert-butanol. 3.2, 6.4 or 12.8 mg (0.005, 0.01 or 0.02 mmol) of complex **$RuBF_4$** was employed as catalyst. The mixture was stirred under N_2O. 100 mL of N_2O was condensed into to the tube at -196°C. The specific conditions of catalyst, solvent, oxidant, temperature and time are given in Table 4 of the manuscript. The reaction products were identified by NMR spectroscopy and gas chromatography-mass spectrometry (GC-MS) and compared with authentic samples or literature data. The product selectivity was determined with GC-FID with hexadecane as internal standard. In addition, benzylamine and imine were also quantified by NMR with cyclohexane as an internal standard. Results are summarized in Table 4 of the manuscript.

3.2. Selected ^{1}H NMR analysis of benzylamine oxidation in sealed vessel (Table 4)

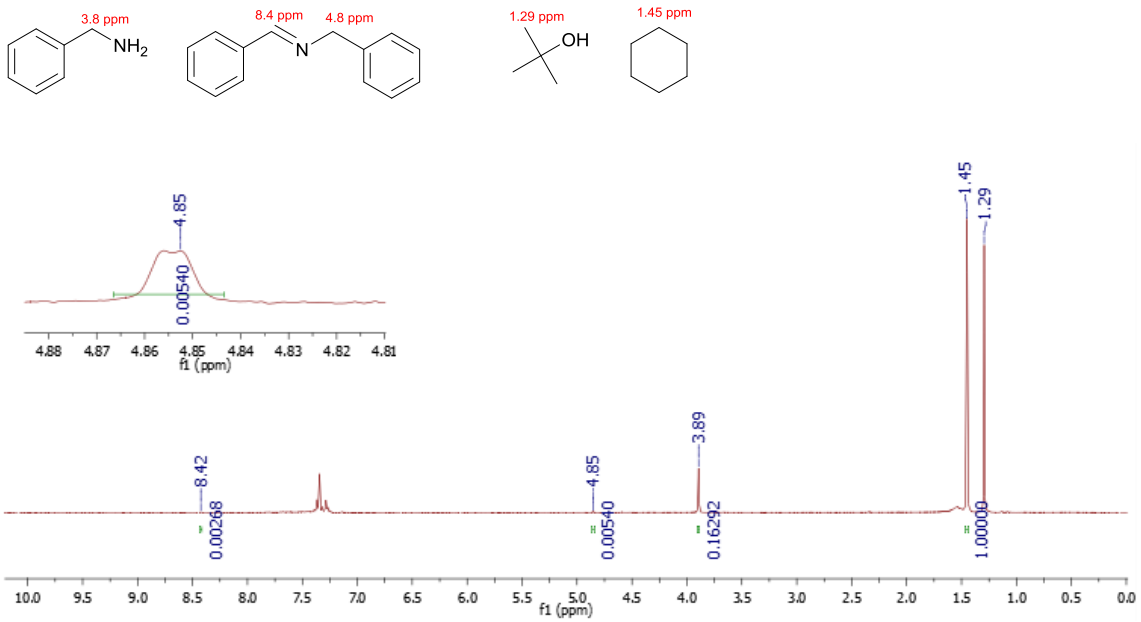


Figure 53 Entry 1

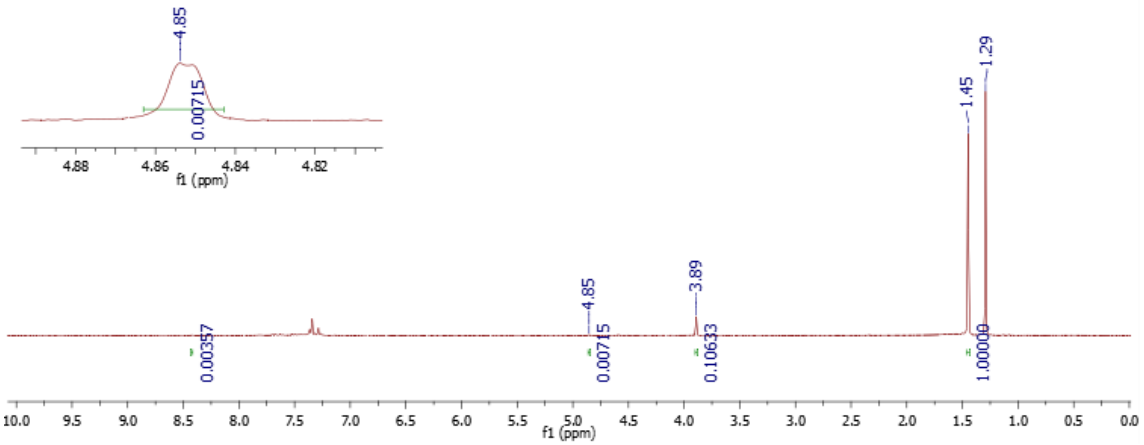


Figure 54 Entry 2

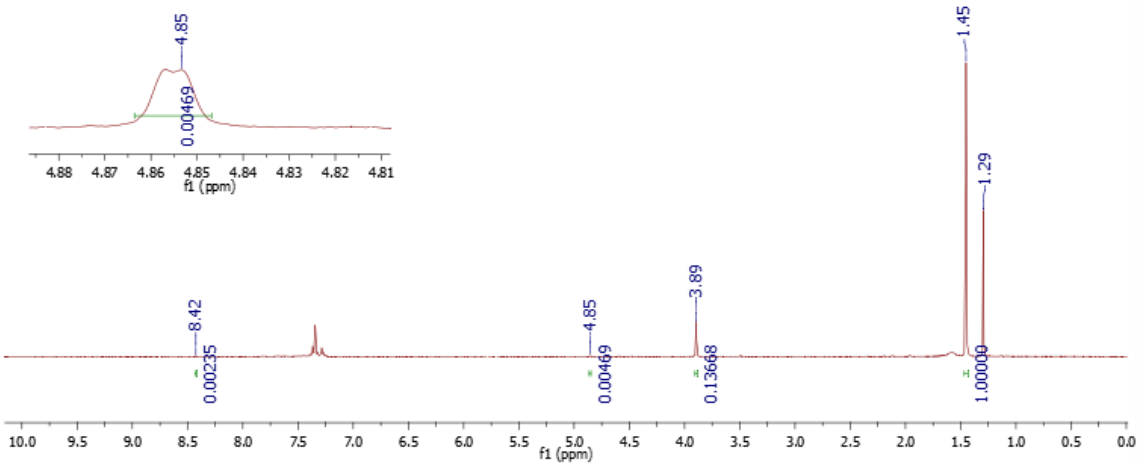


Figure 55 Entry 3

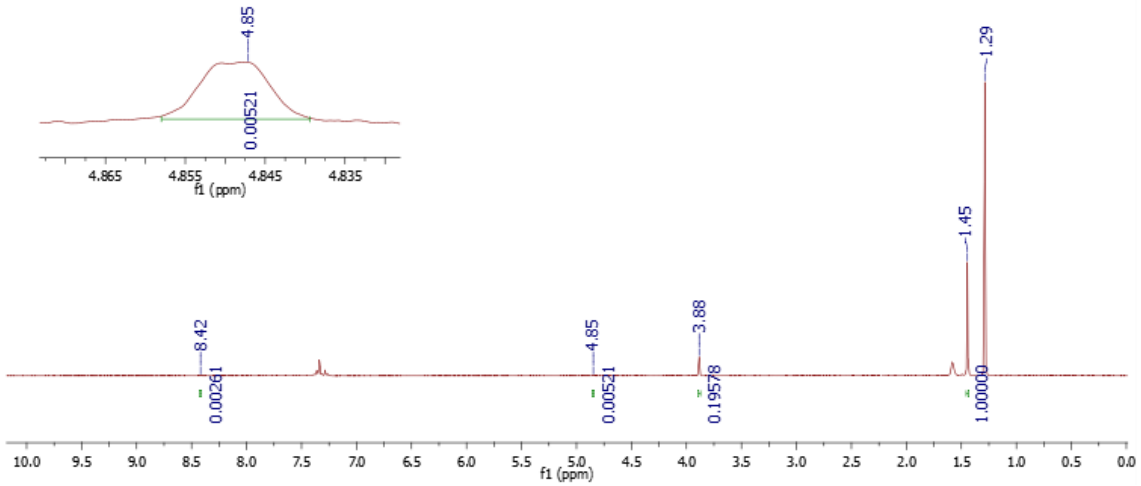


Figure 56 Entry 4

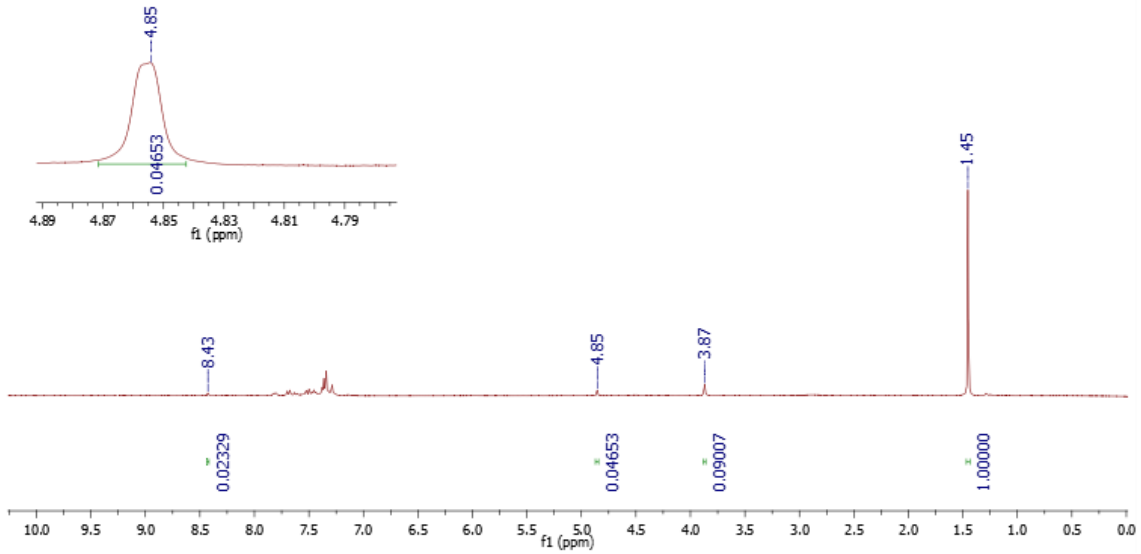


Figure 57 Entry 5

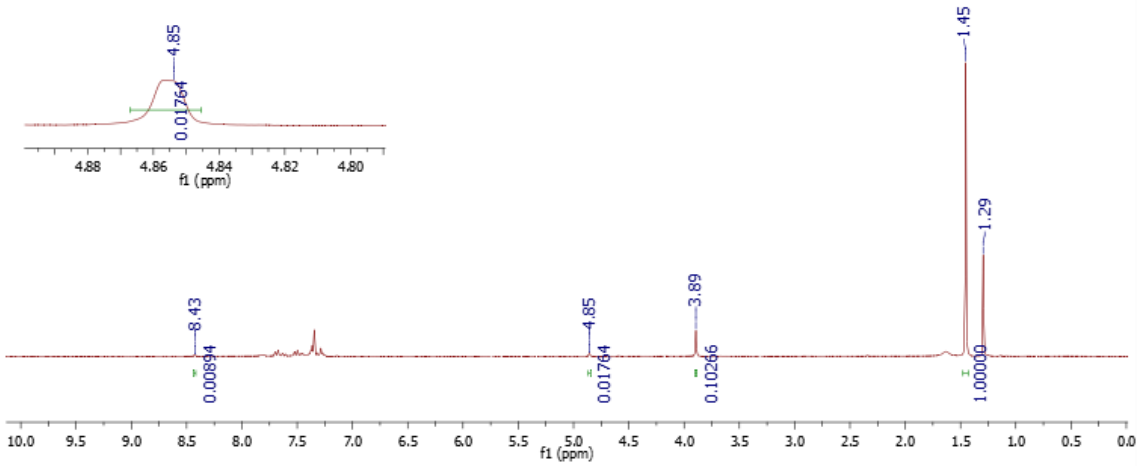


Figure 58 Entry 6

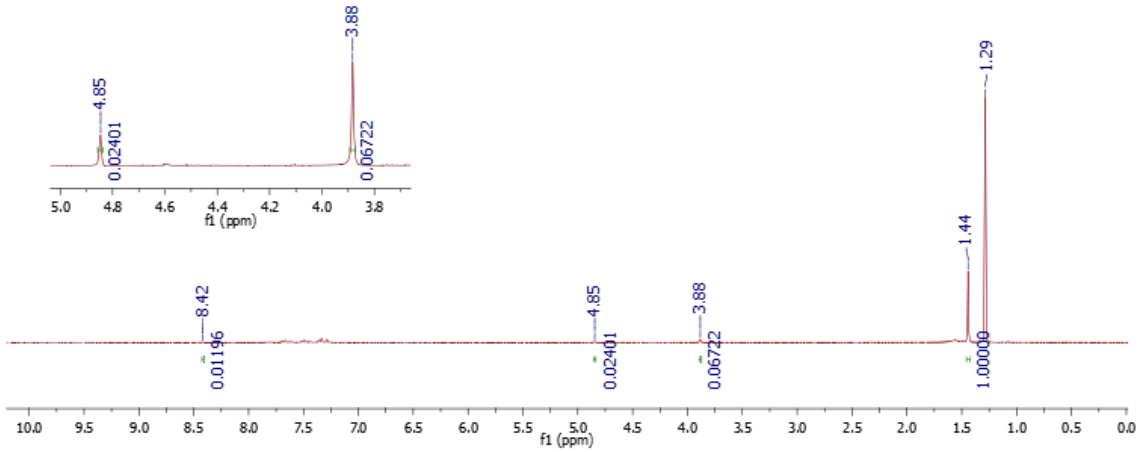


Figure 59 Entry 7

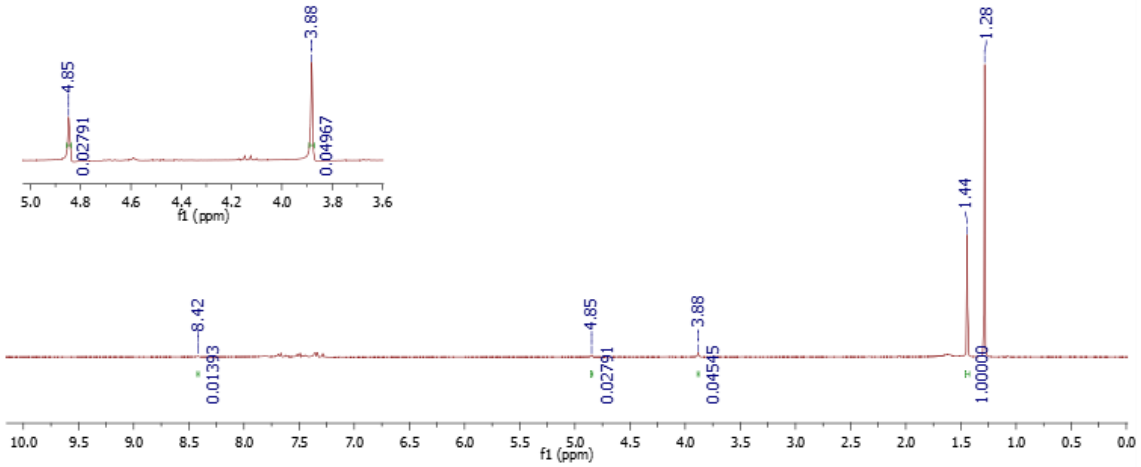


Figure 60 Entry *8*

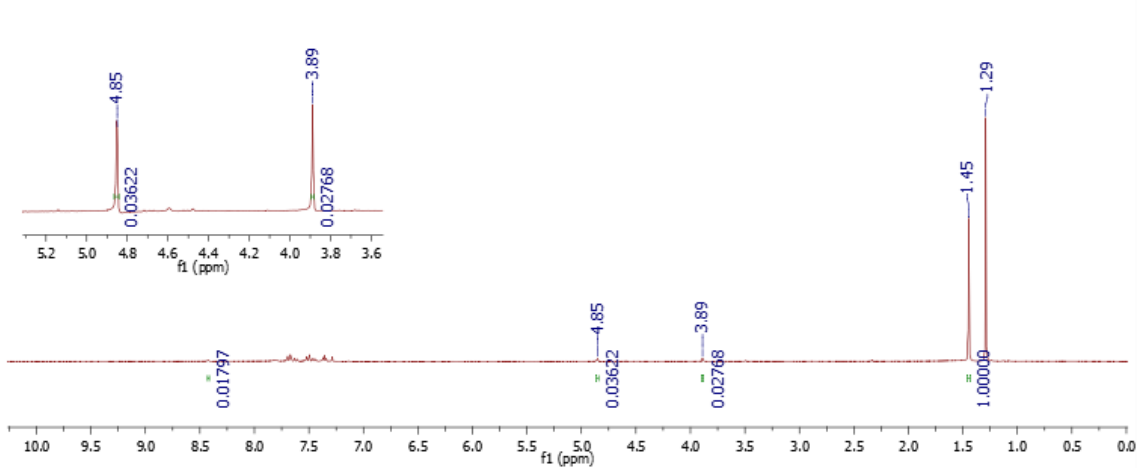


Figure 61 Entry 9

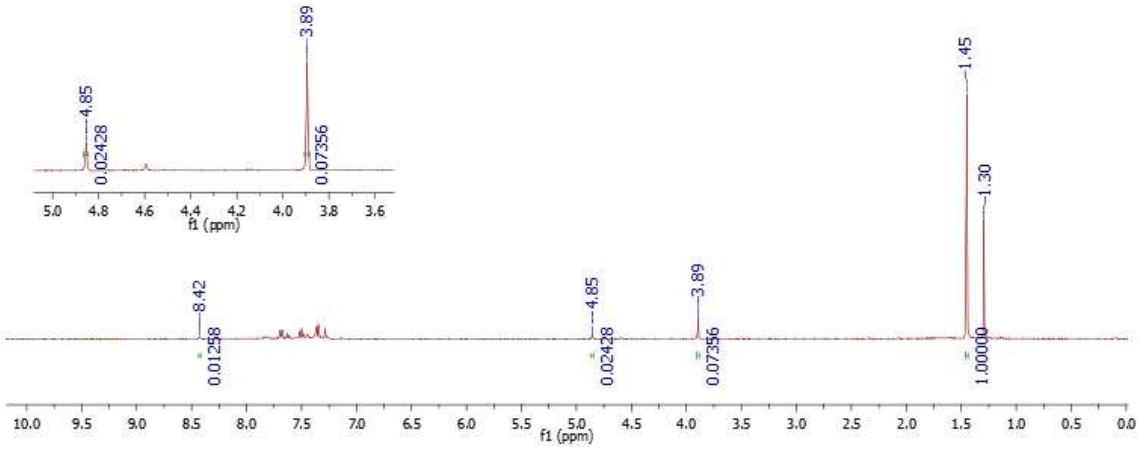


Figure 62 Entry 10

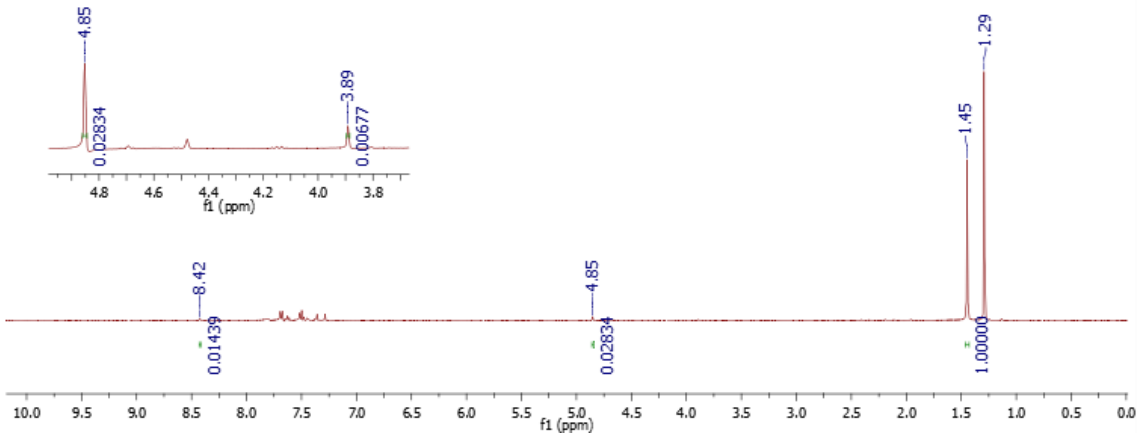


Figure 63 Entry 11

3.3. **Selected GC-FID analysis of benzylamine oxidation (Table 4)**

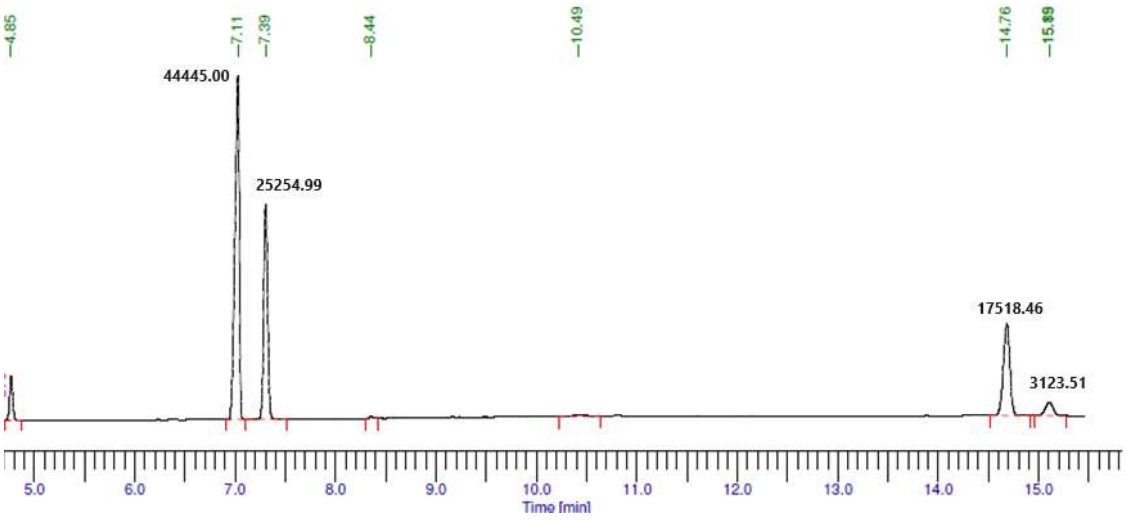


Figure 64 Entry 5 4.85 min.: p-cymene (from catalyst), 7.11 min.: hexadecane (internal standard), 7.39 min.: benzonitrile, 14.76 min.: imine.

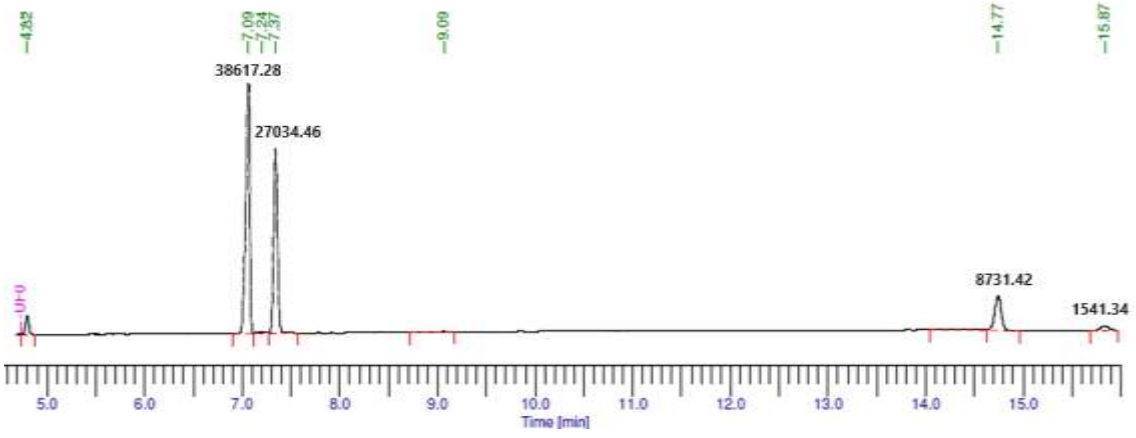


Figure 65 Entry 6 4.82 min.: p-cymene (from catalyst), 7.09 min.: hexadecane (internal standard), 7.37 min.: benzonitrile, 14.77 min.: imine.

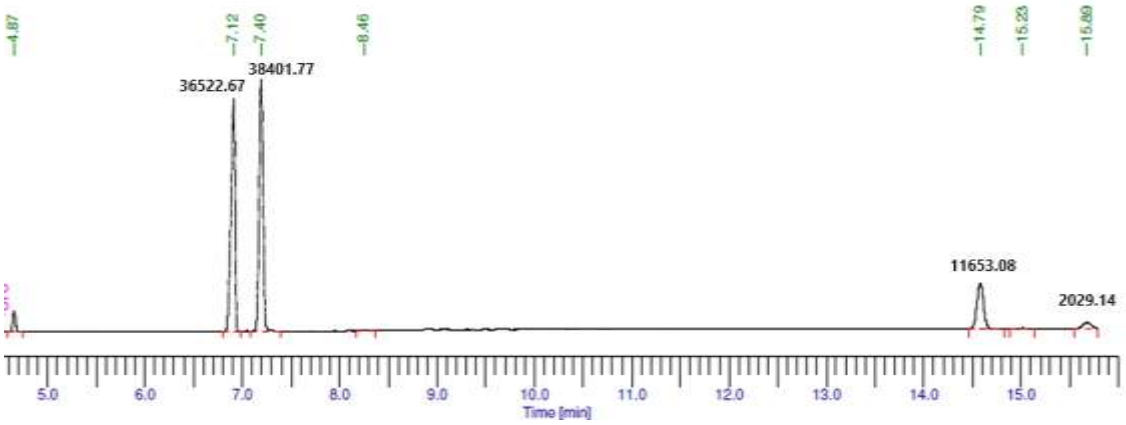


Figure 66 Entry 7 4.87 min.: p-cymene (from catalyst), 7.12 min.: hexadecane (internal standard), 7.40 min.: benzonitrile, 14.79 min.: imine.

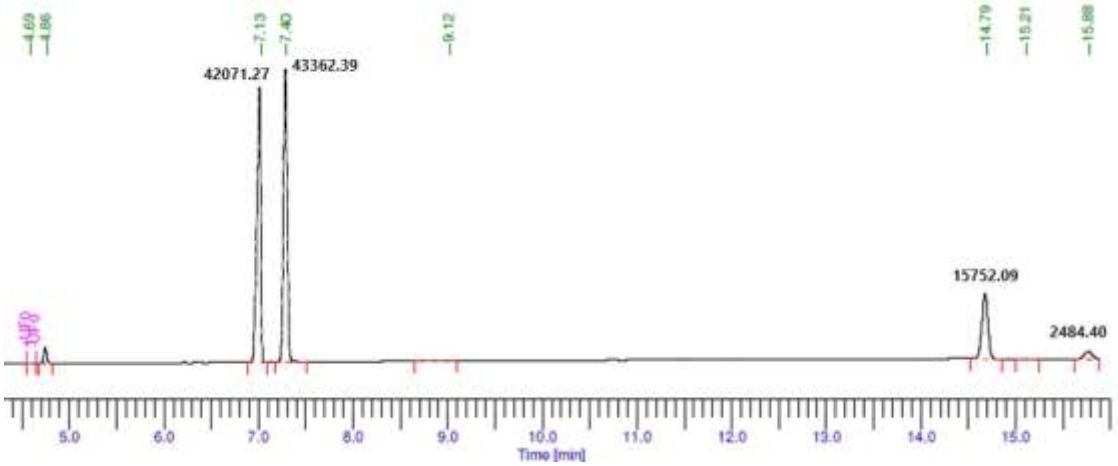


Figure 67 Entry 8 4.86 min.: p-cymene (from catalyst), 7.13 min.: hexadecane (internal standard), 7.40 min.: benzonitrile, 14.79 min.: imine.

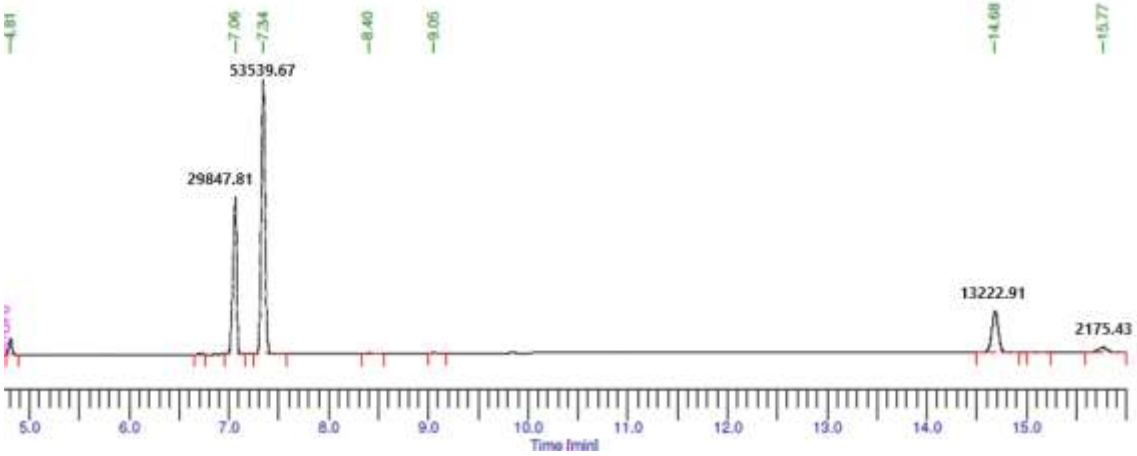


Figure 68 Entry 9 4.81 min.: p-cymene (from catalyst), 7.06 min.: hexadecane (internal standard), 7.34 min.: benzonitrile, 14.68 min.: imine.

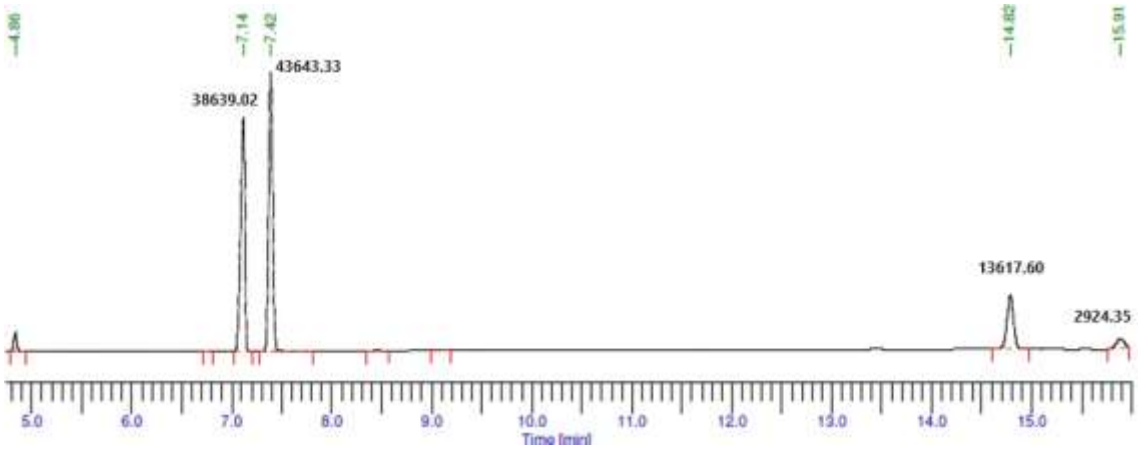


Figure 69 Entry 10 4.86 min.: p-cymene (from catalyst), 7.14 min.: hexadecane (internal standard), 7.42 min.: benzonitrile, 14.82 min.: imine.

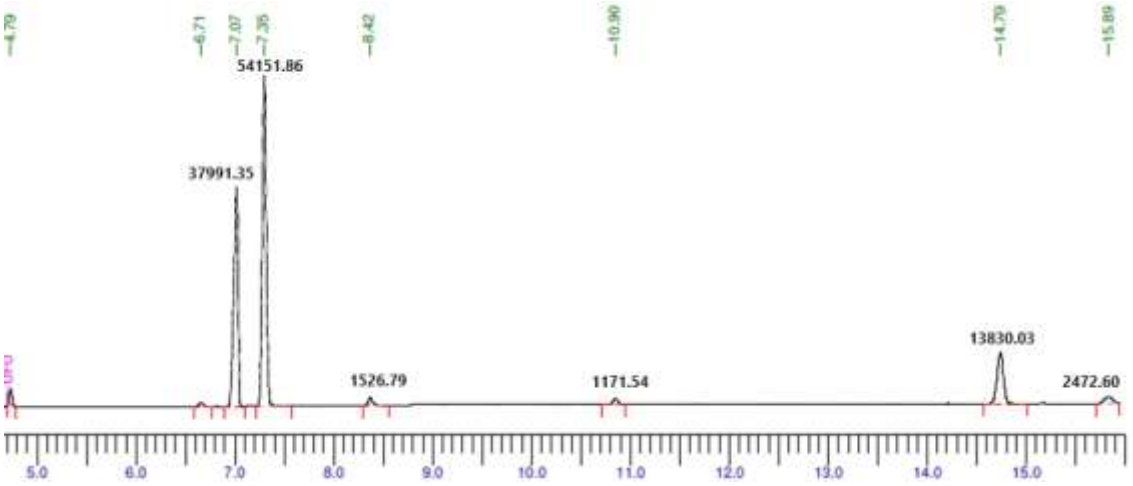


Figure 70 Entry 11 4.79 min.: p-cymene (from catalyst), 7.07 min.: hexadecane (internal standard), 7.35 min.: benzonitrile, 14.79 min.: imine.

3.4. Procedure for the oxidation of benzylamines with **Ru-II** {[(*p*-cymene)Ru](*μ*-H)(μ-Cl)(μ-HCO_2)[Ru(*p*-cymene)]}BF_4) in sealed vessel with N_2O

A 50 mL high vacuum tube was equipped with 1 mmol of benzylamines, 2 mL of tert-butanol and, 6.4 mg (0.01 mmol) of **Ru-II** {[(*p*-cymene)Ru](*μ*-H)(*μ*-Cl)(*μ*-HCO_2)[Ru(*p*-cymene)]}BF_4). 100 mL of N_2O was condensed into to the tube at -196°C. The mixture was stirred for 12 hours at 95 °C. After reaction time, the mixture was transferred to a round-bottom flask. The reaction products were identified by NMR spectroscopy and gas chromatography-mass spectrometry (GC-MS) and compared with authentic samples or literature data. The product selectivity was determined with GC-FID with hexadecane as internal standard. In addition benzylamine and imine were also quantified by NMR with cyclohexane as an internal standard. Results are summarized in Table 6 of the manuscript.

3.5. Selected ^{1}H-NMR and GC-FID analysis of benzylamine oxidation (Table 6)

Entry 1 2,4-dimethoxybenzylamine

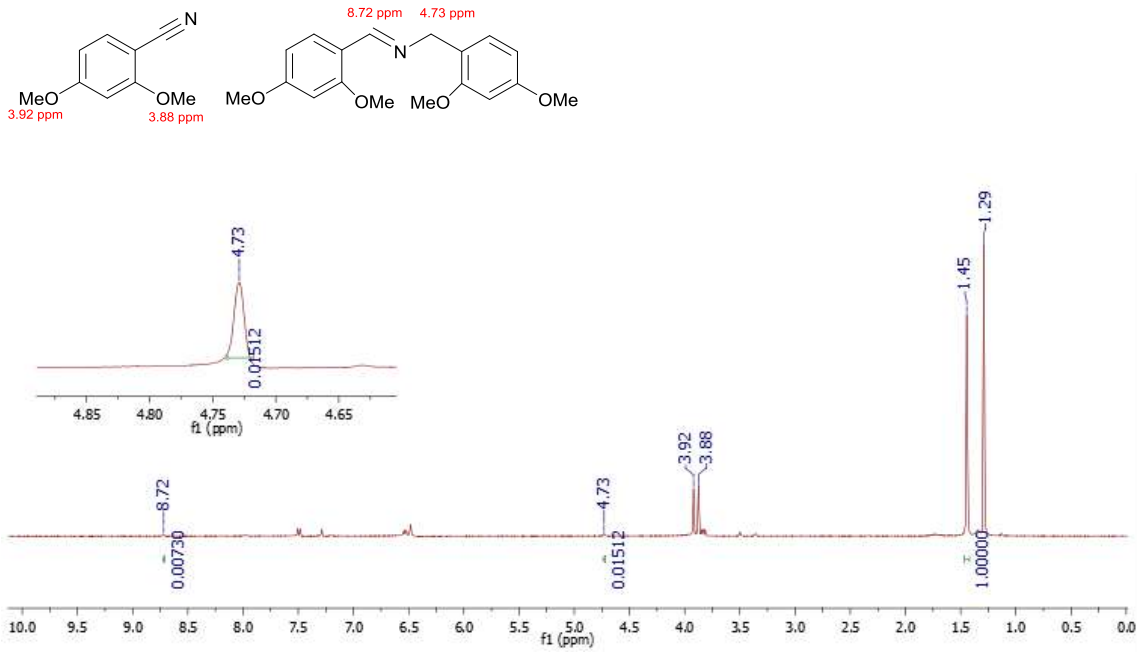


Figure 71 Entry 1 2,4-dimethoxybenzylamine NMR

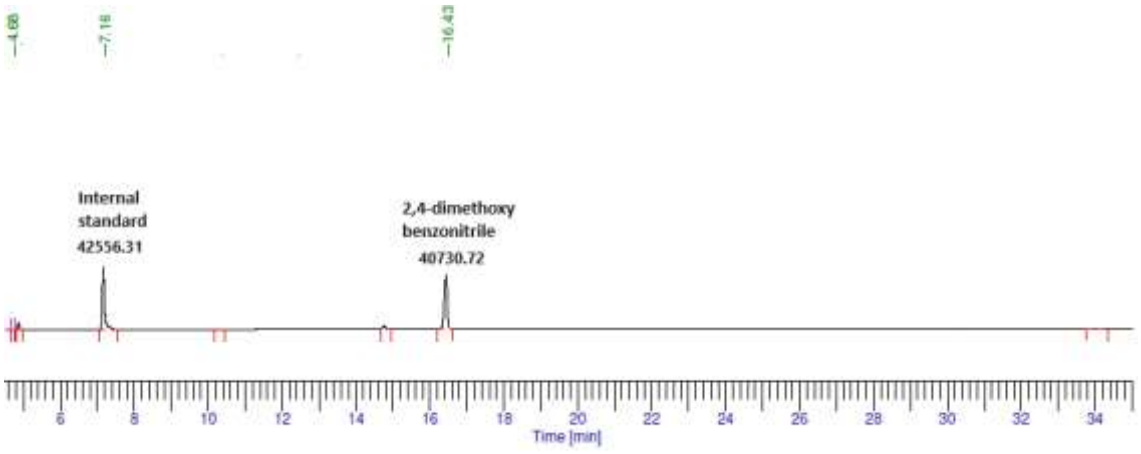


Figure 72 Entry 1 2,4-dimethoxybenzylamine GC-FID

Entry 2 4-methoxybenzylamine

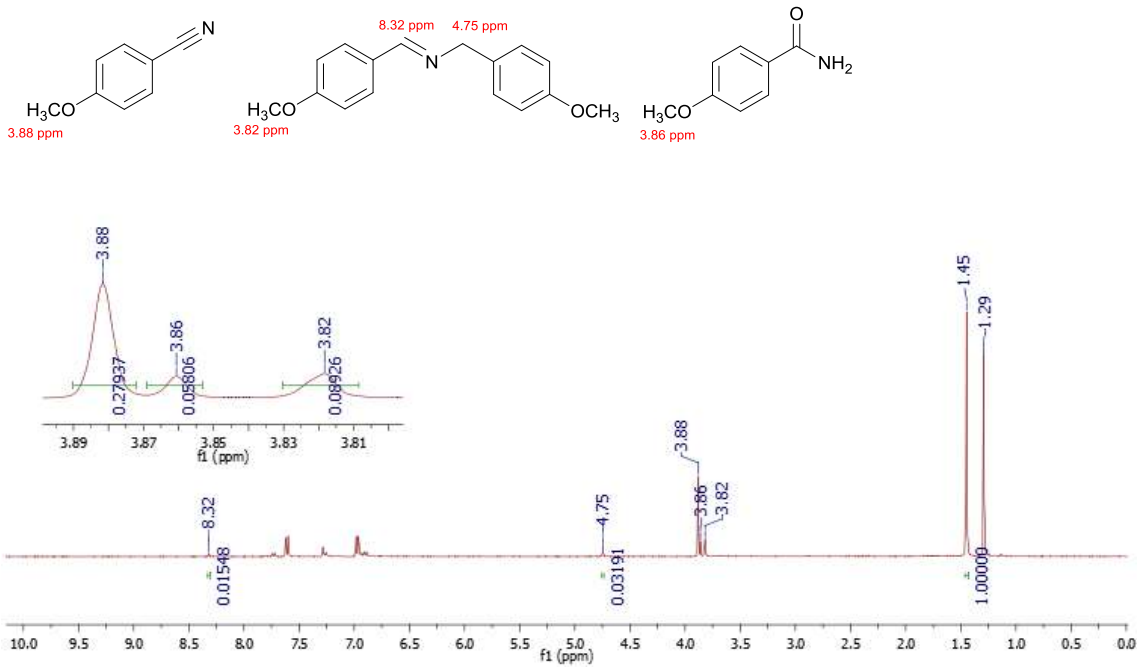


Figure 73 Entry 2 4-methoxybenzylamine NMR

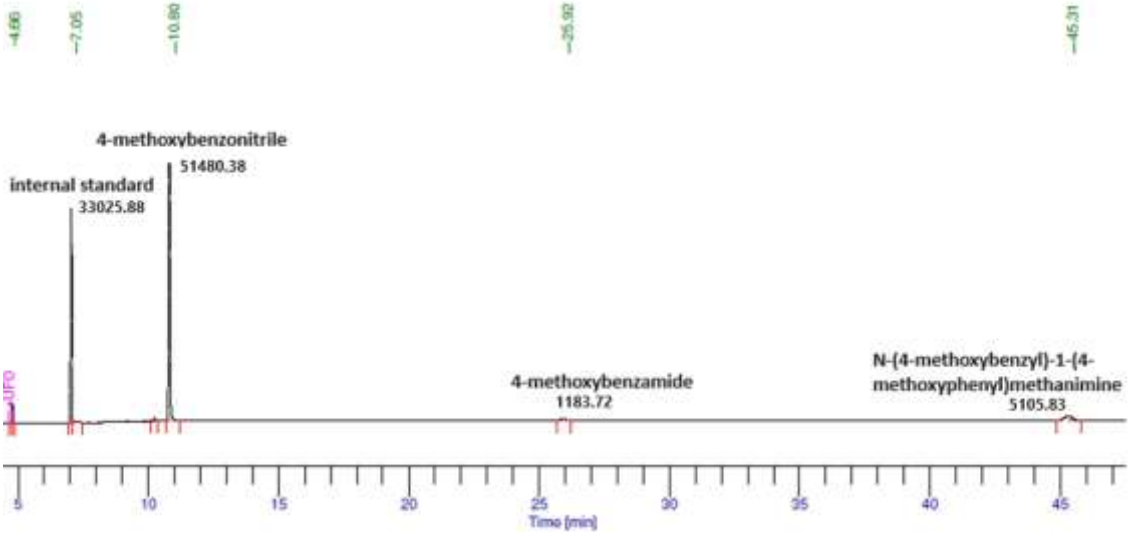


Figure 74 Entry 2 4-methoxybenzylamine GC-FID

Entry 4 4-chlorobenzylamine

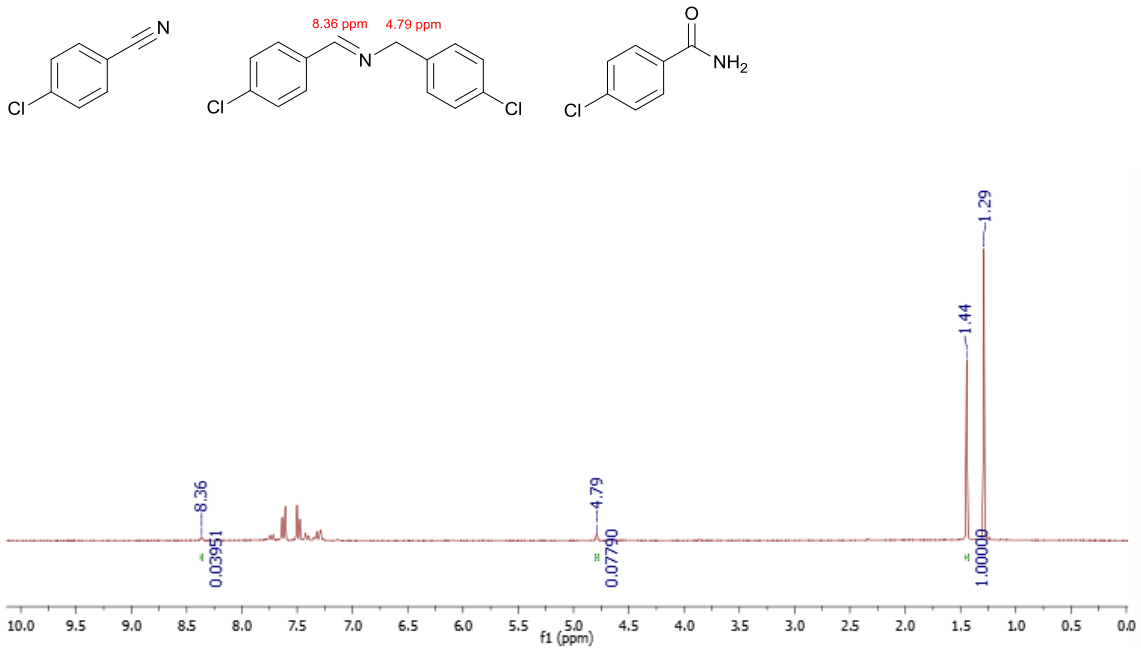


Figure 75 Entry 4 4-chlorobenzylamine NMR

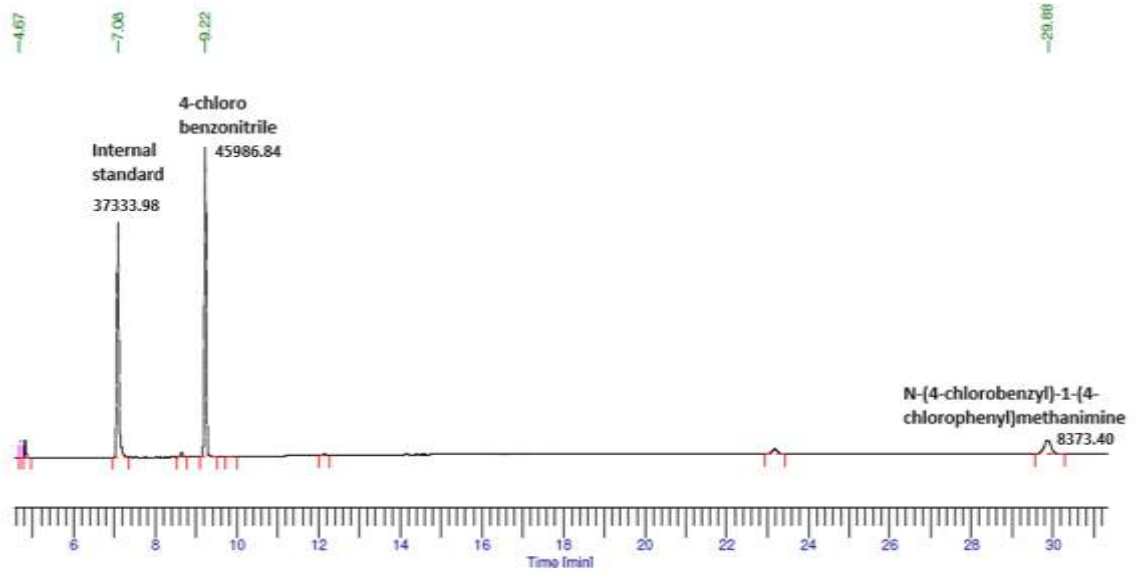


Figure 76 Entry 4 4-chlorobenzylamine GC-FID

Entry 5 4-tertbuthylbenzylamine

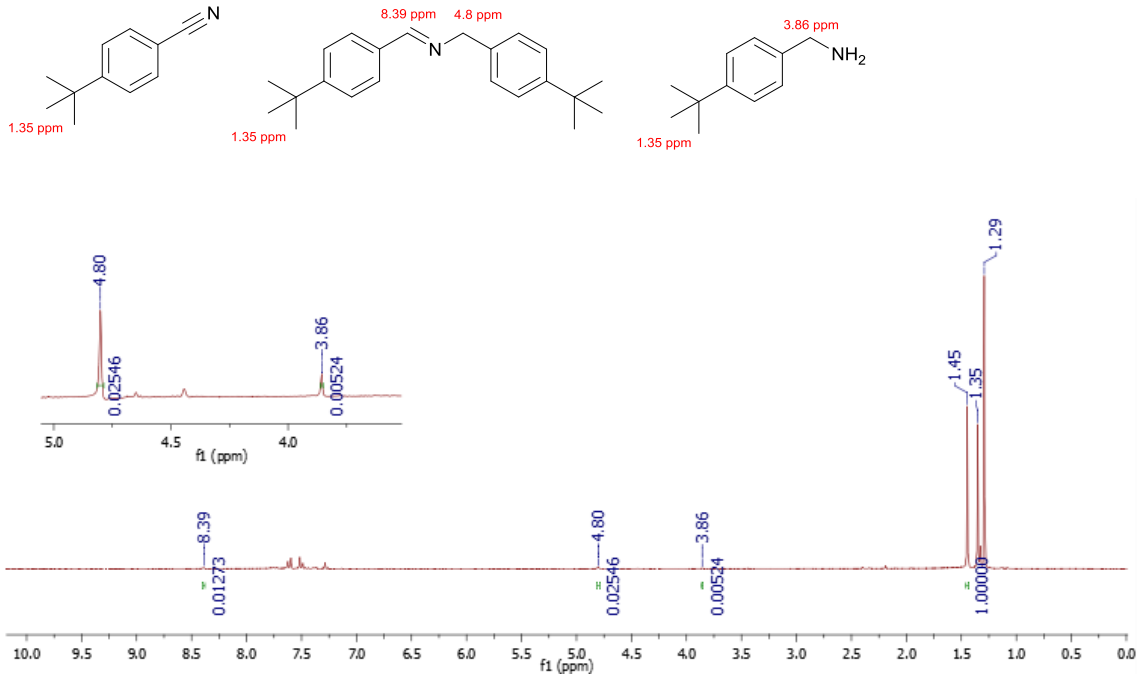


Figure 77 Entry 5 4-tertbuthylbenzylamine NMR

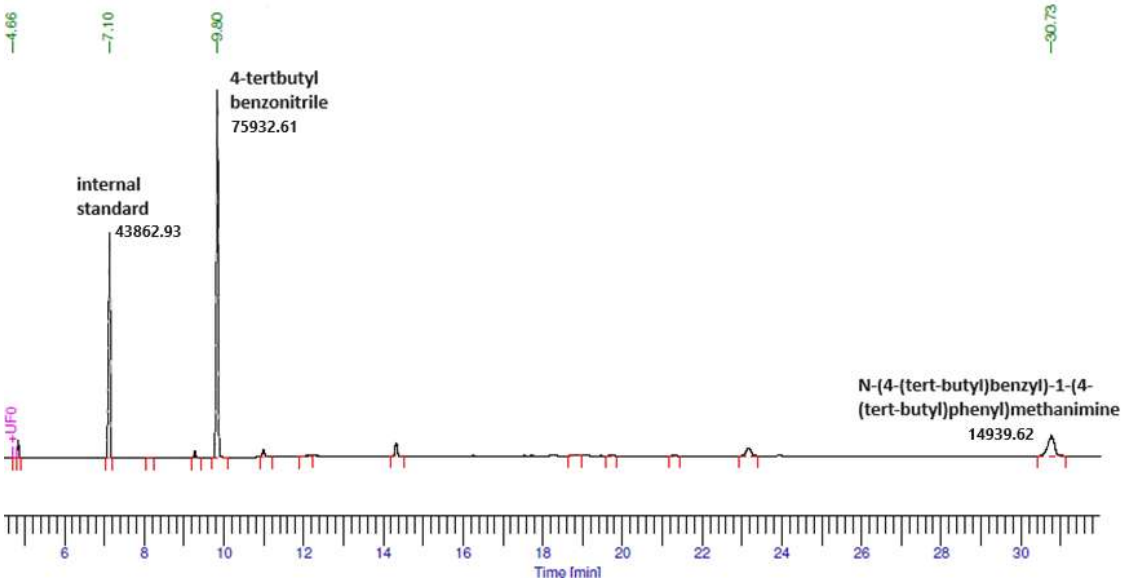


Figure 78 Entry 5 4-tertbuthylbenzylamine GC-FID

Entry 6 refer Table 4 of the manuscript

Entry 7 3-bromobenzylamine

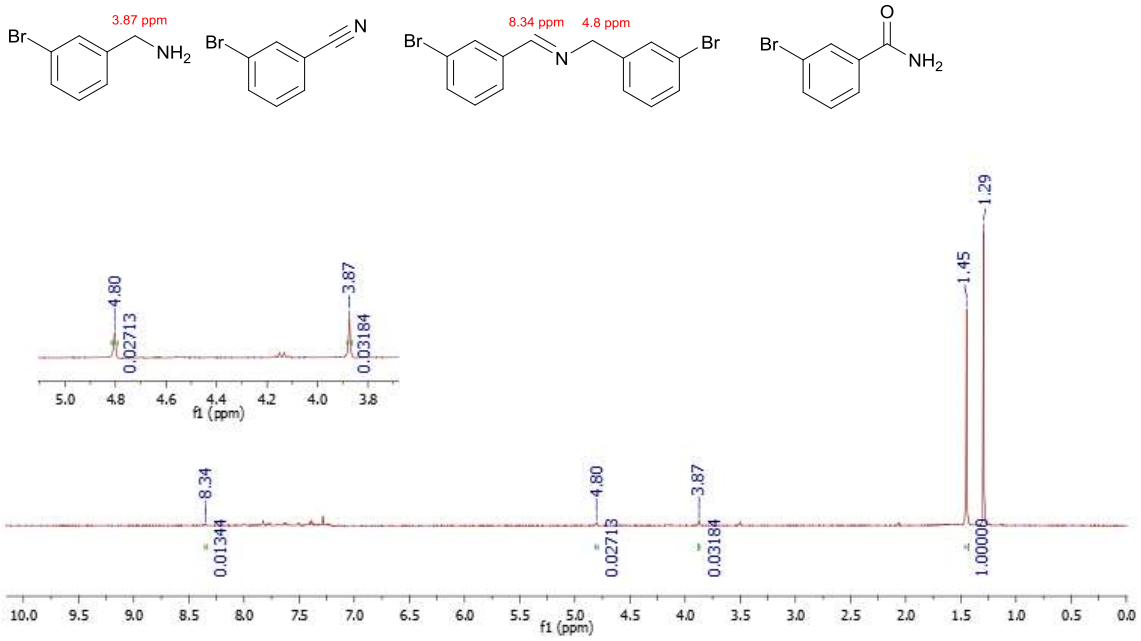


Figure 79 Entry 7 3-bromobenzylamine NMR

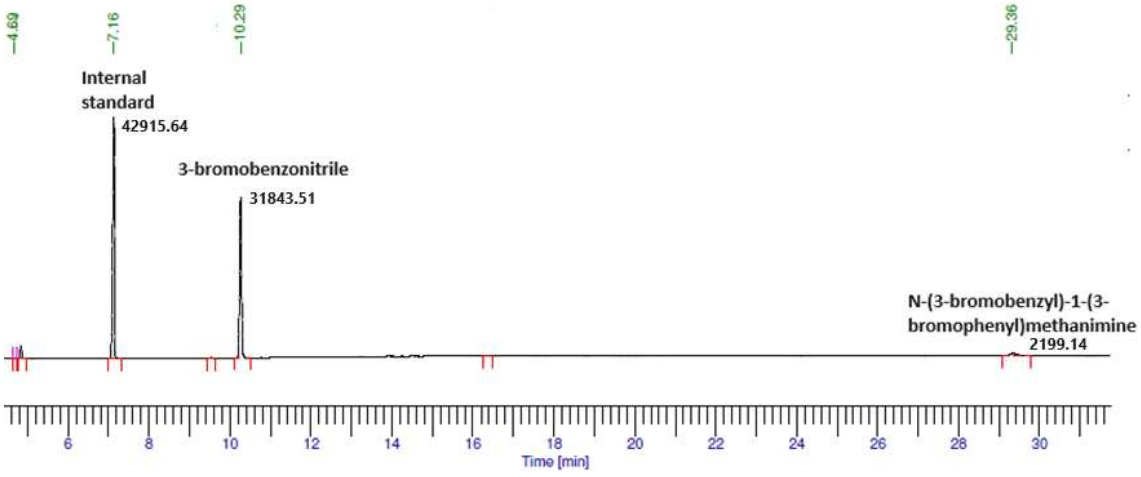


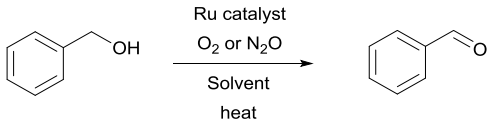
Figure 80 Entry 7 3-bromobenzylamine GC-FID

4. Oxidation of benzyl alcohols

4.1. Optimisation of benzyl alcohol oxidation with ruthenium complex **Ru-II** {[(*p*-cymene)Ru](*μ*-H)(*μ*-Cl)(*μ*-HCO_2)[Ru(*p*-cymene)]}BF_4)

A 20 mL screw-cap vial was equipped with stirring bar, 52 µL (0.5 mmol) of benzyl alcohol, 1 mL of solvent, and 6.4 mg (0.01 mmol) of **Ru-II**. The mixture was stirred under O_2 or N_2O atmosphere (balloon), as specified in Table 2, which outlines the precise conditions for the catalyst, solvent, oxidant, temperature, and reaction time. Products were analysed by NMR, GC and GC-MS and compared with authentic samples or literature data. Reactions with water as solvent were extracted (3x1.5mL) with DCM followed by microfiltration through a Pasteur pipette with glass wool and $MgSO_4$. To 0.9mL of this solution hexadecane as internal was added for GC and GC-MS analysis. For NMR analysis DCM was carefully evaporated, internal standard and $CDCl_3$ added. Conversions were quantified using either GC with hexadecane as internal standard or NMR techniques with cyclohexane as internal standard.

Table 2. Optimisation of benzyl alcohol oxidation to benzaldehyde.



Entry	Cat. [mol%]	Solvent	Oxidant	T [°C]	t [h]	Conv. [%]	CHO Selectivity [%]
1	2	*t*-BuOH	O_2	65	20	6	100
2	2	H_2O	O_2	65	20	14	32
3	2	H_2O	O_2	95	20	45	39
4	2	H_2O	O_2	95	48	100	50
5	4	H_2O	O_2	95	20	14	100
6	4	toluene	O_2	65	48	18	100
7	2	toluene	O_2	95	20	45	100
8	2	toluene	O_2	80	48	31	95
9[b]	2	toluene	O_2	95	5	59	100
10[b]	2	toluene	O_2	95	16	100	96

[b] Reactions performed in a 50 mL tube with a high vacuum teflon valve with 4.5 mmol O_2 condensed into the tube at -196°C.

4.2. Procedure for the oxidation of benzyl alcohols with **Ru-II** {[(*p*-cymene)Ru](*μ*-H)(*μ*-Cl)(*μ*-HCO_2)[Ru(*p*-cymene)]}BF_4)

A 50 mL tube with a high vacuum teflon valve was equipped with stirring bar, 0.5 mmol of benzyl alcohol, 1 mL of toluene and 6.4 mg (0.01 mmol) of **Ru-II** {[(*p*-cymene)Ru](*μ*-H)(*μ*-Cl)(*μ*-HCO_2)[Ru(*p*-cymene)]}BF_4). 4.5 mmol of oxygen was condensed into to the tube at -196°C. The mixture was then stirred for 16 hours at 95°C. After reaction time, the mixture was transferred to a round-bottom flask, and 1 mL of methanol was added to help in solubilization and evaporation. The reactions were analyzed using 1H NMR and GC-MS for product identification and compared to authentic samples or literature data. Reactions with water as solvent were extracted (3x1.5mL) with DCM followed by microfiltration through a Pasteur pipette with glass wool and $MgSO_4$. To 0.9mL of this solution hexadecane as internal was added for GC and GC-MS analysis. For NMR analysis DCM was carefully evaporated, internal standard and $CDCl_3$ added. Conversions were quantified via NMR using cyclohexane as internal standard. Results are summarized in Table 7 of the manuscript.

The following products were exemplary isolated by column chromatography with silica.

- Benzaldehyde: 46 mg (0.43 mmol), colourless liquid, 86% yield, Rf=0.8 (1:1, EtOAc:hexane).
- 3-Bromobenzaldehyde: 85 mg (0.46 mmol), colourless liquid, 92% yield, Rf=0.8 (1:1, EtOAc:hexane).
- 4-Fluorobenzaldehyde: 59 mg (0.475 mmol), colourless liquid, 95% yield, Rf=0.83 (1:1, EtOAc:hexane).

4.3. GC-MS for qualitative analysis of benzyl alcohols oxidation

Entry 1 benzaldehyde

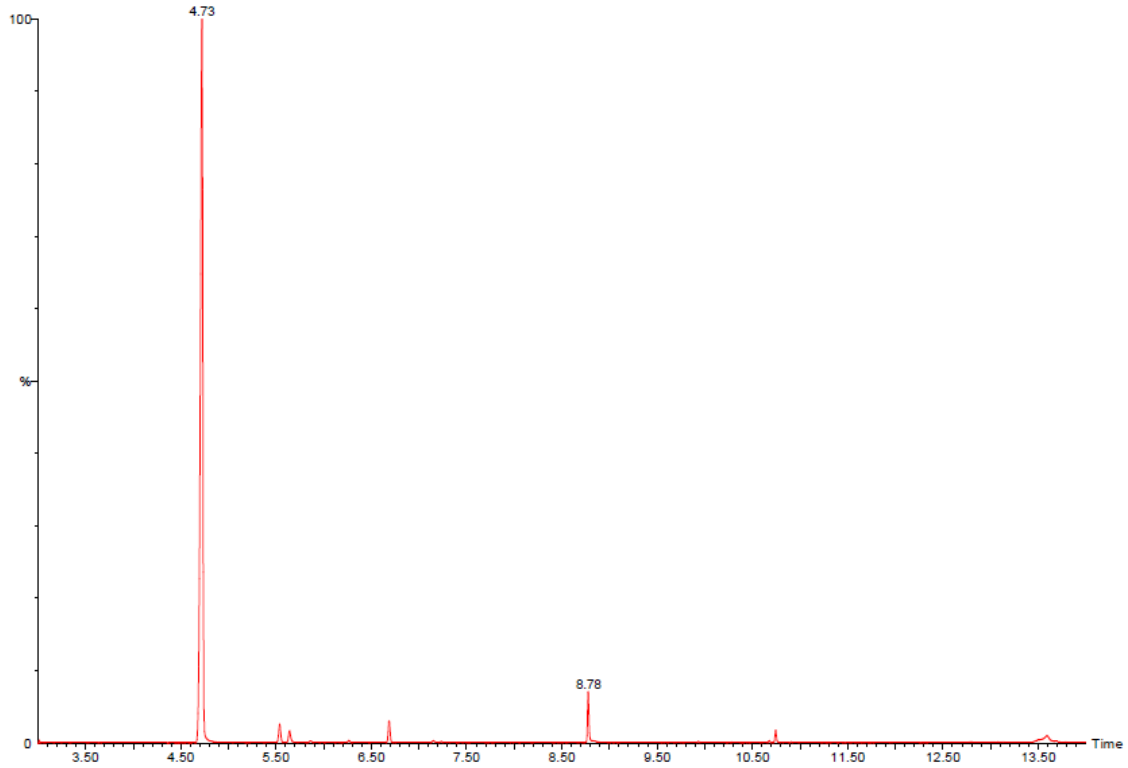


Figure 81 Entry 1, 4.73 min.: benzaldehyde, 8.78 min.: (E)-4-phenylbut-3-en-2-one.(impurity)

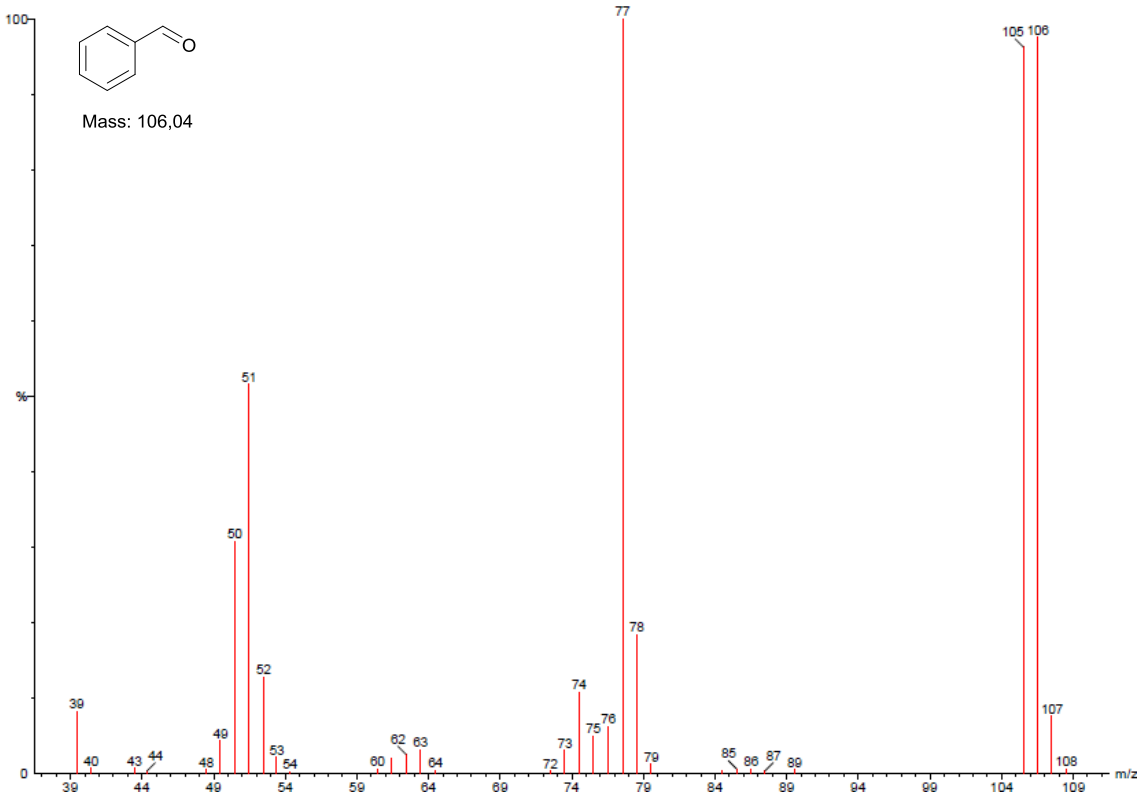


Figure 82 Entry 1, benzaldehyde

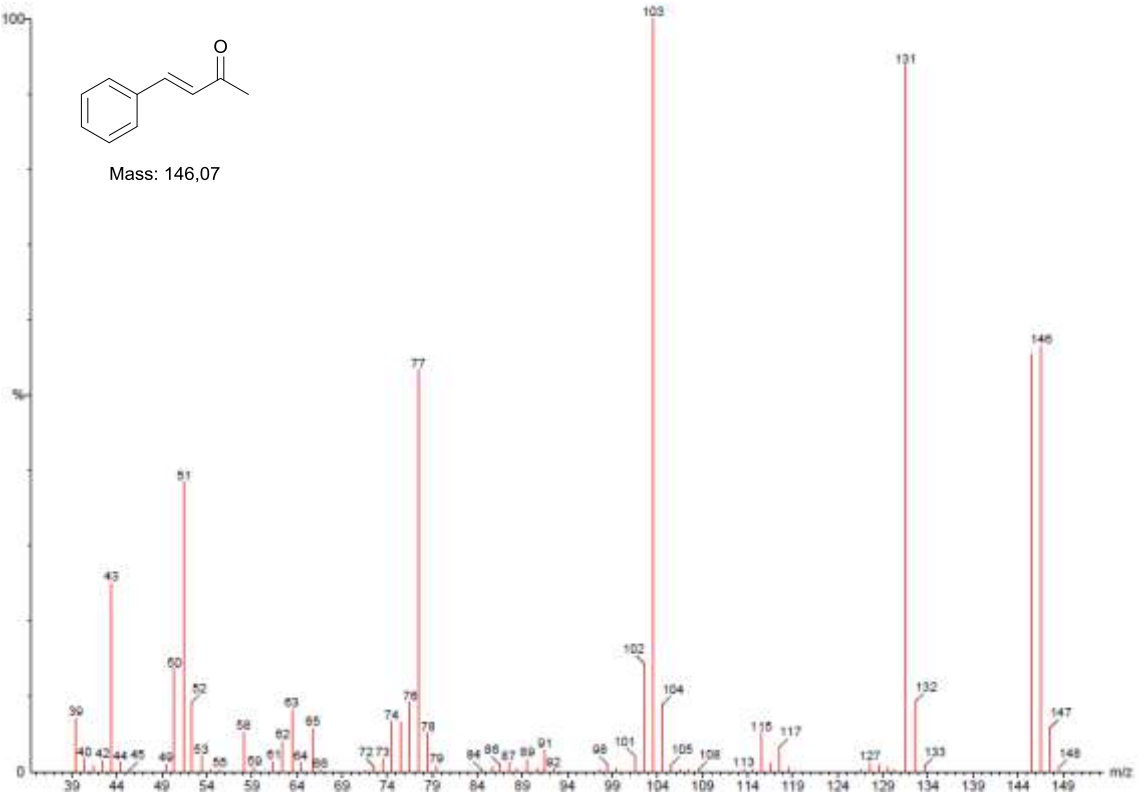


Figure 83. Entry 1, (E)-4-phenylbut-3-en-2-one

Entry 2 4-bromobenzaldehyde

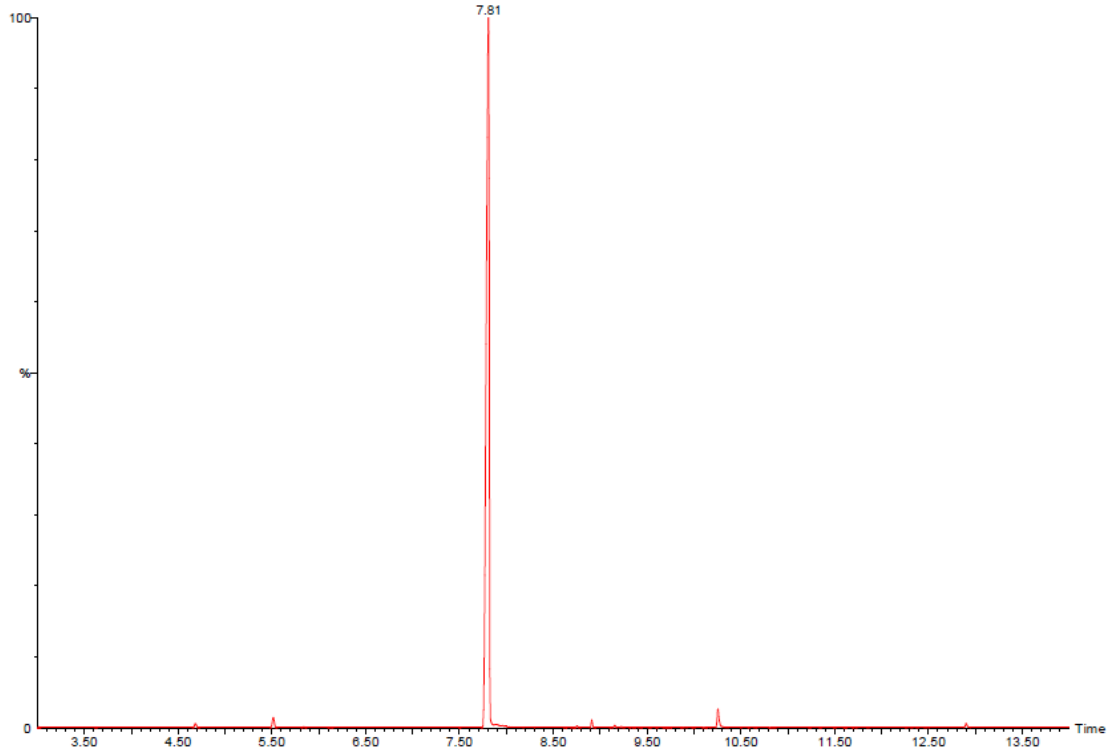


Figure 84 Entry 2, 7.81 min.: 4-bromobenzaldehyde

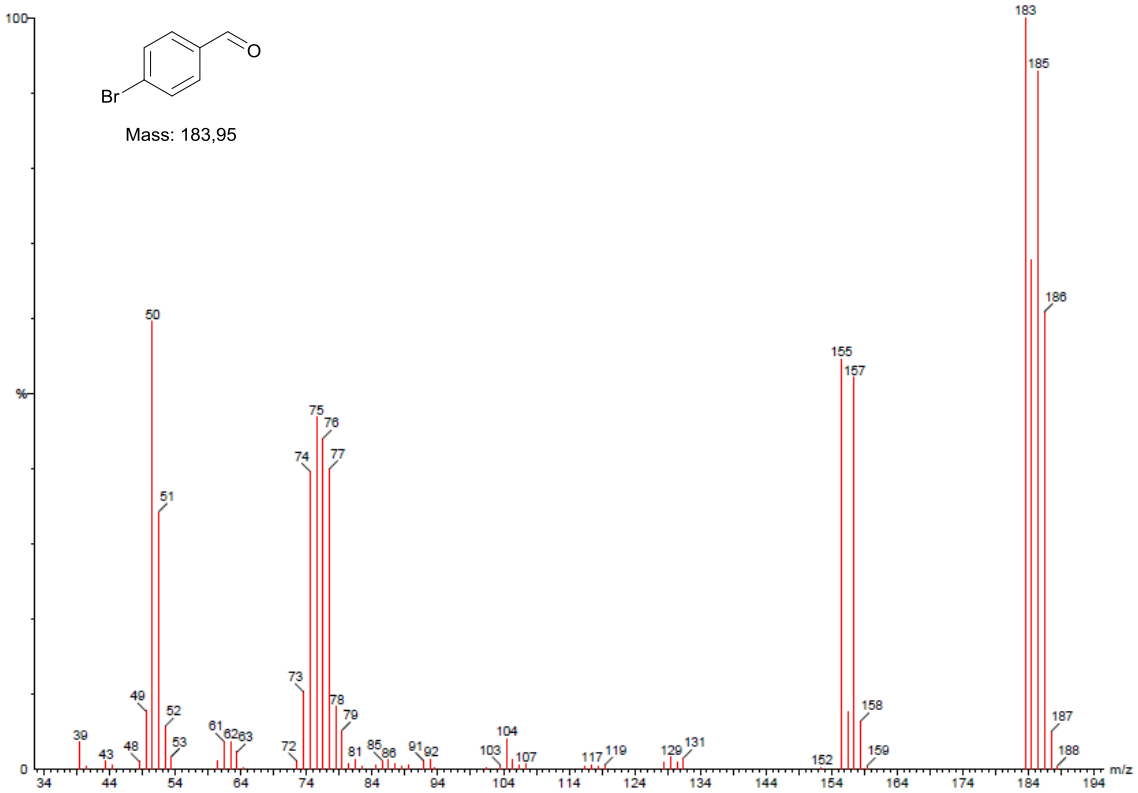


Figure 85 Entry 2, 4-bromobenzaldehyde

Entry 3 4-fluorobenzyl alcohol

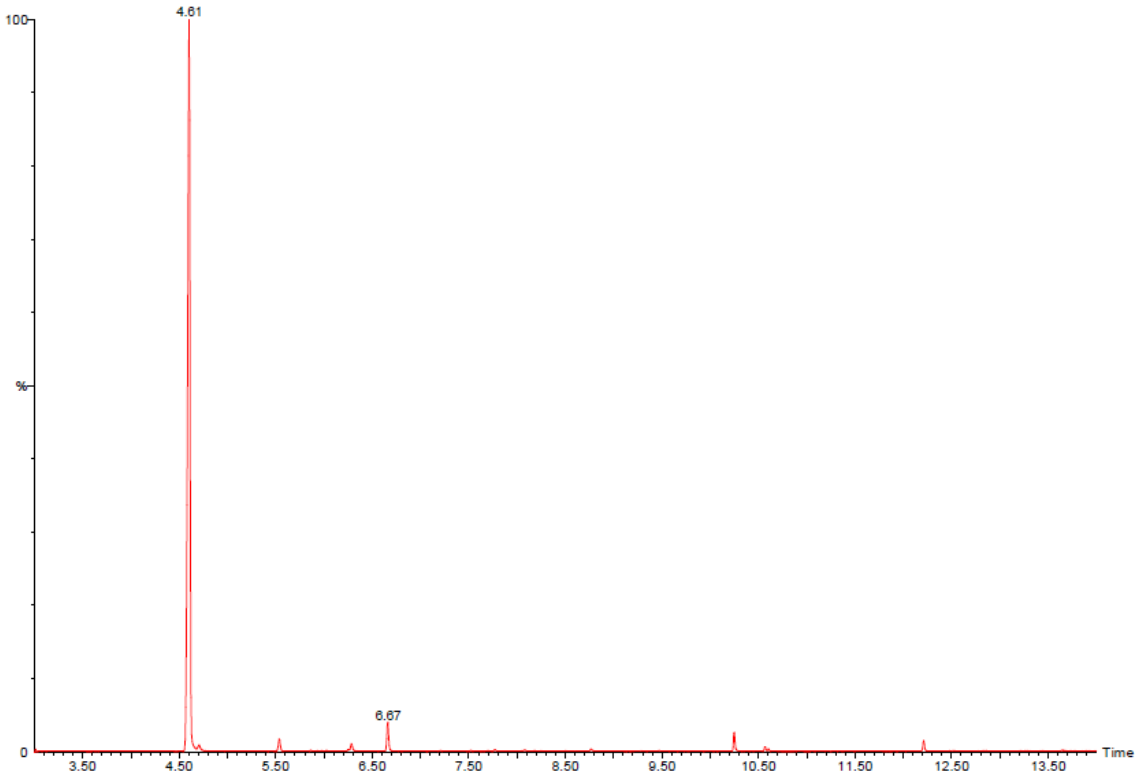


Figure 86 Entry3, 4.61 min.: 4-fluorobenzaldehyde

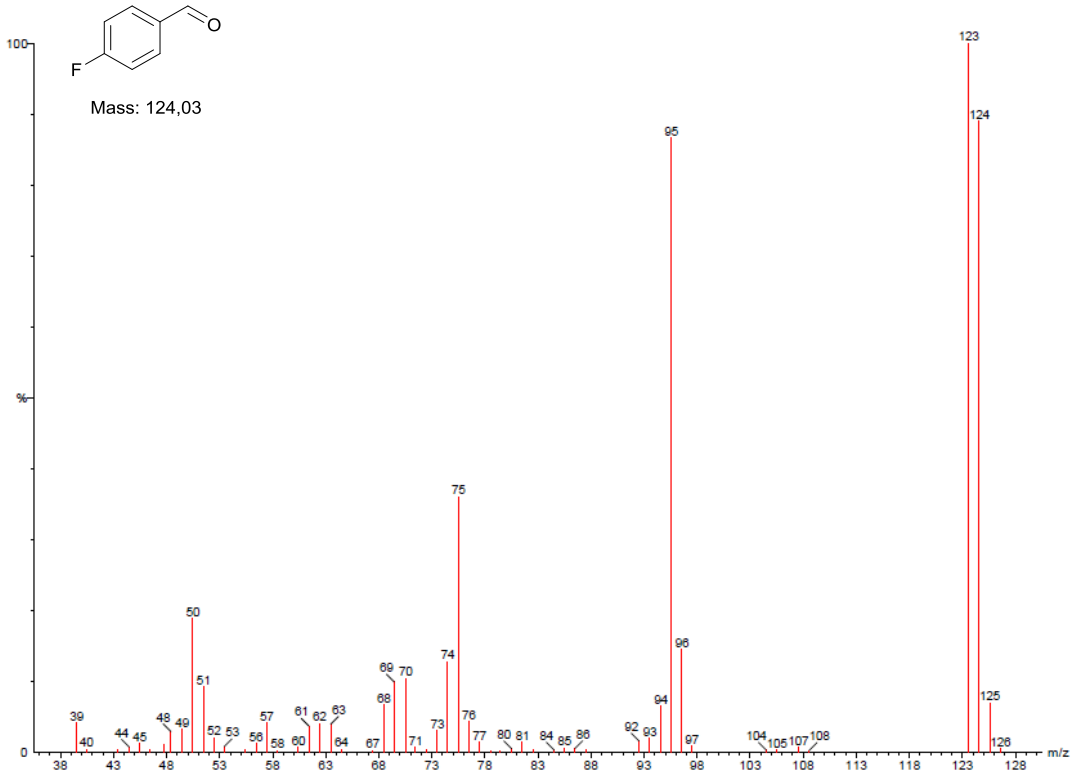


Figure 87 Entry3, 4-fluorobenzaldehyde

Entry 4 of 3,5-difluorobenzyl alcohol

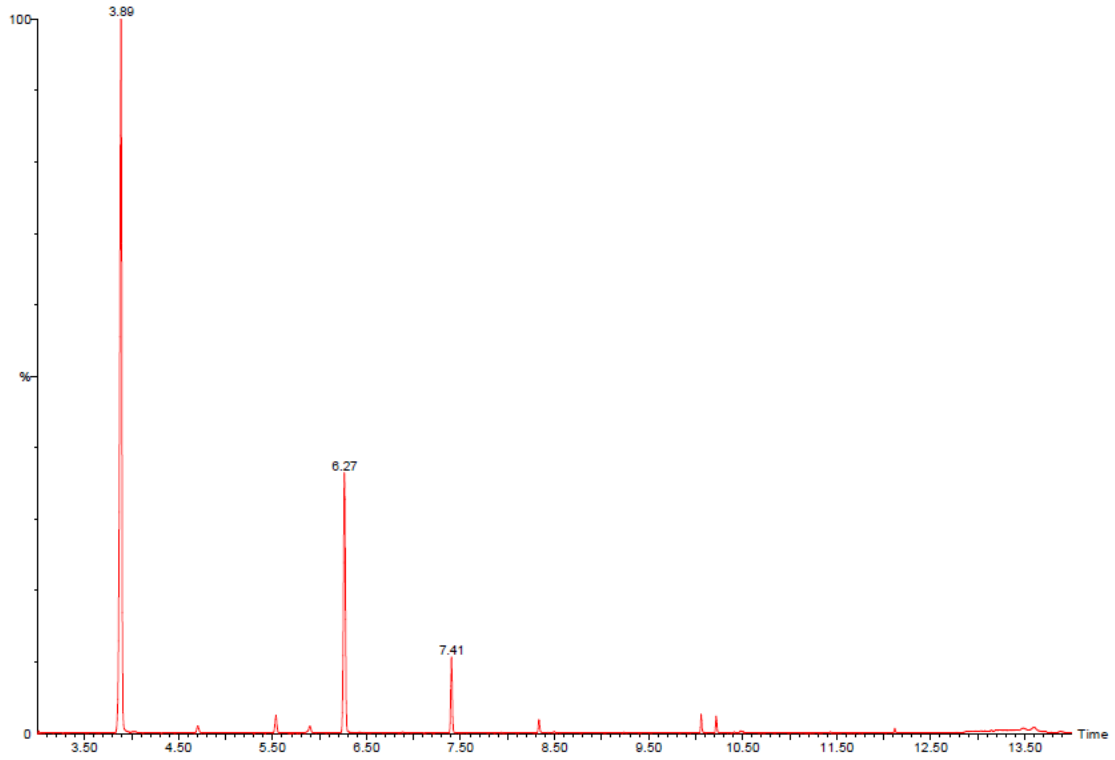


Figure 88 Entry 4, 3.89 min.: 3,5-difluorobenzaldehyde, 6.27 min.: 3,5-difluorobenzyl 3,5-difluorobenzoate, 7.41 min.: 3,5-difluorobenzyl acetate (impurity).

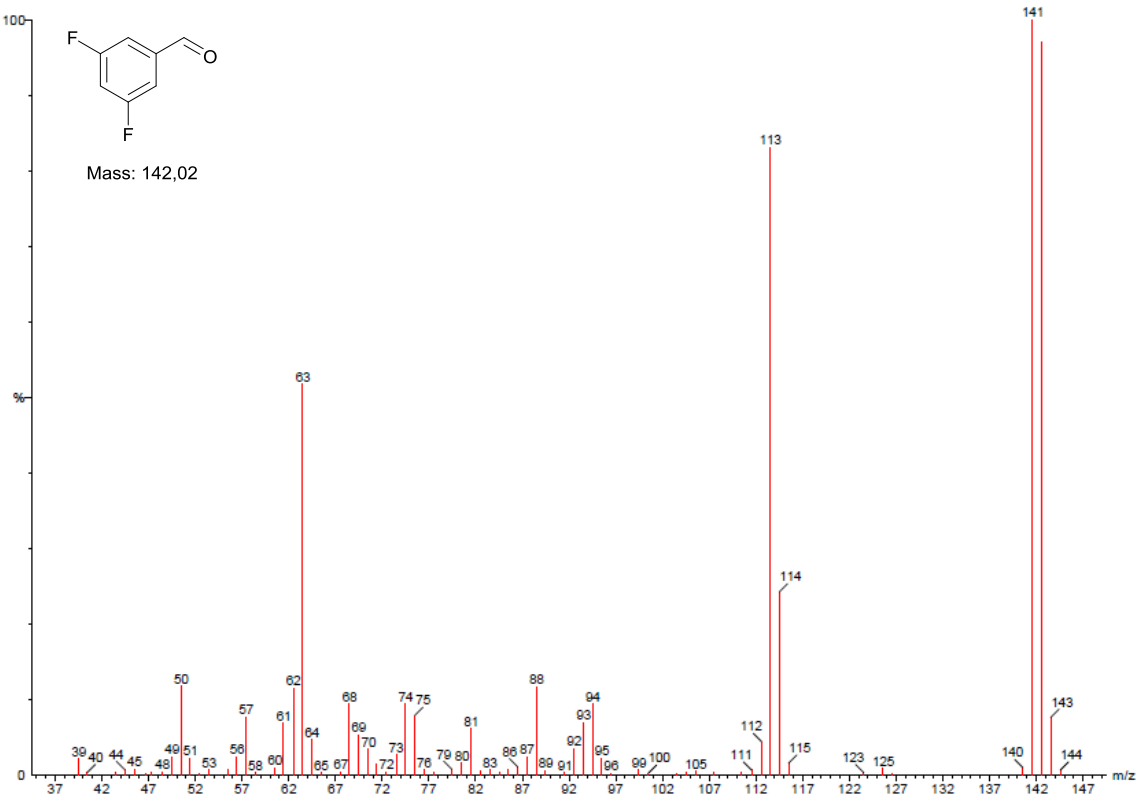


Figure 89 Entry 4, 6.27 min.: 3,5-difluorobenzaldehyde

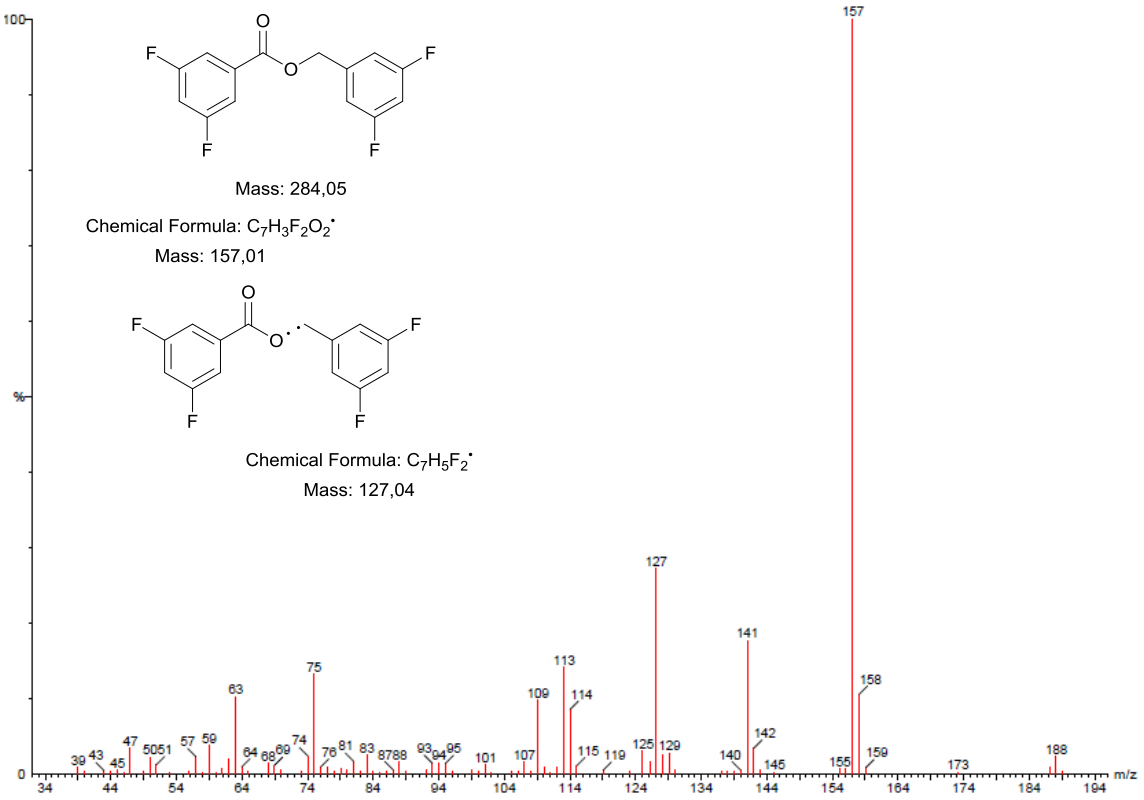


Figure 90 Entry 4, 3,5-difluorobenzyl 3,5-difluorobenzoate

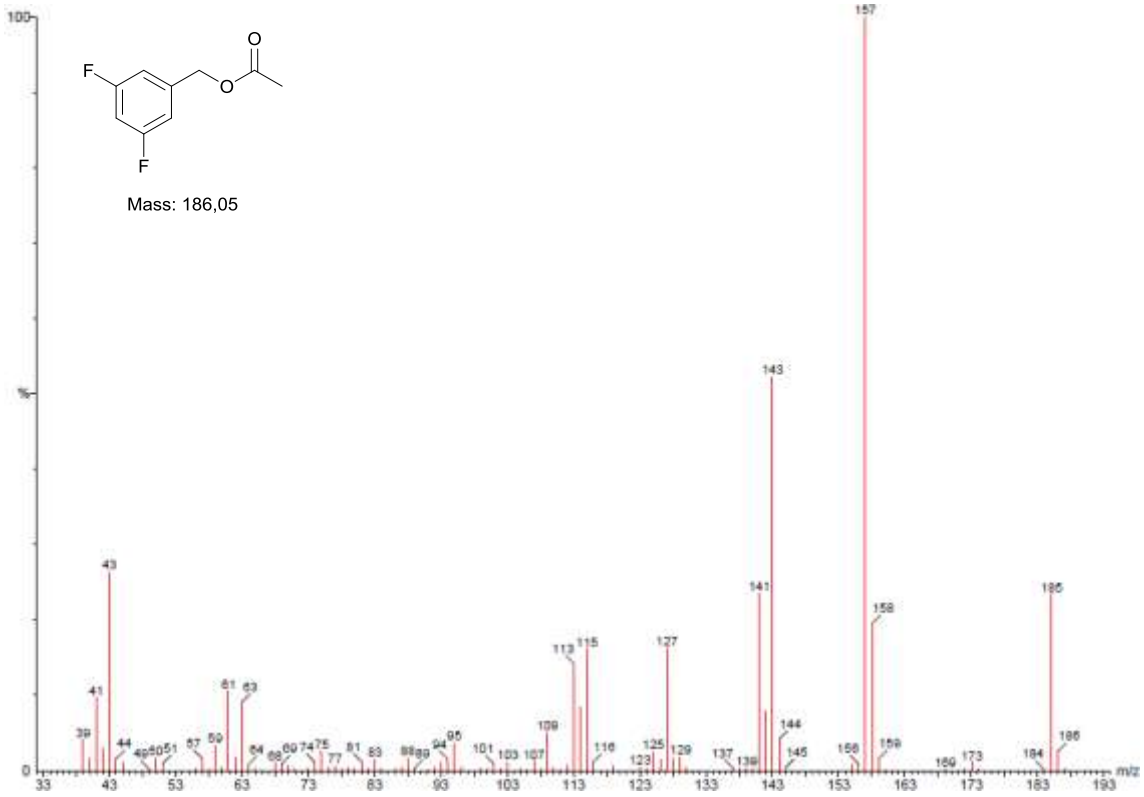


Figure 91. Entry 4, 7.41 min.: 3,5-difluorobenzyl acetate

Entry 5 4-chlorobenzyl alcohol

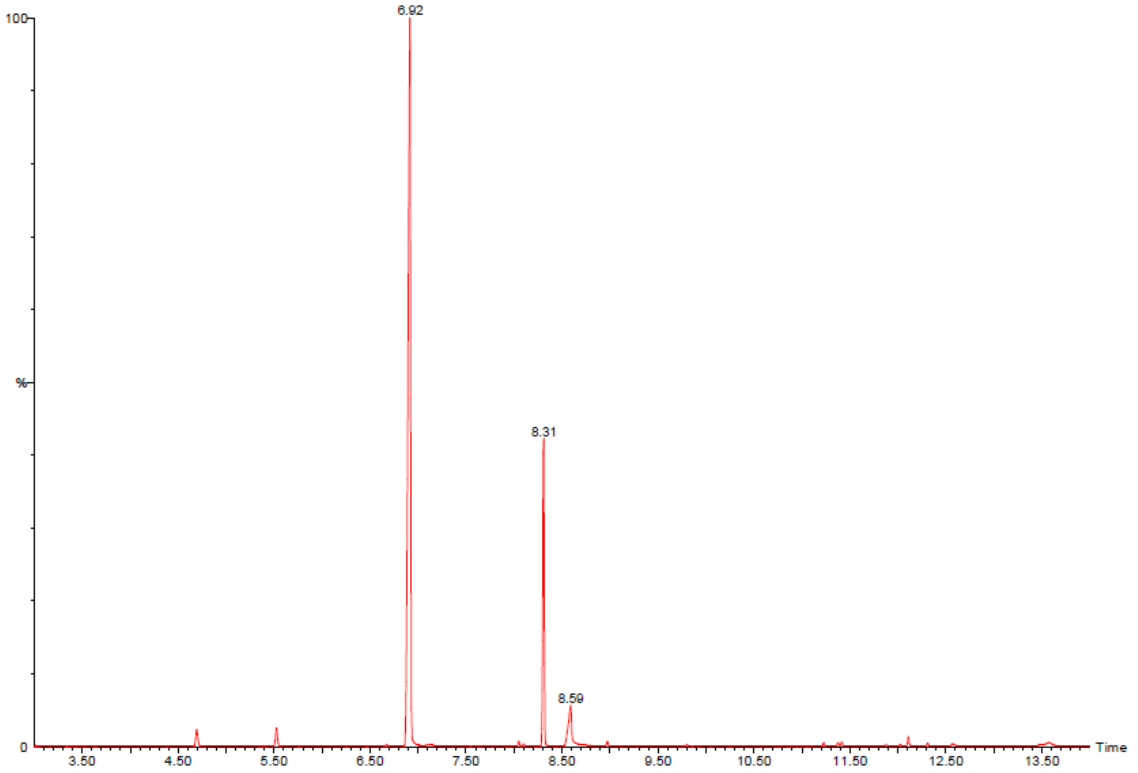


Figure 92 Entry 5, 6.92 min.: 4-chlorobenzaldehyde, 8.31 min.: 4-chlorobenzyl 4-chlorobenzoate

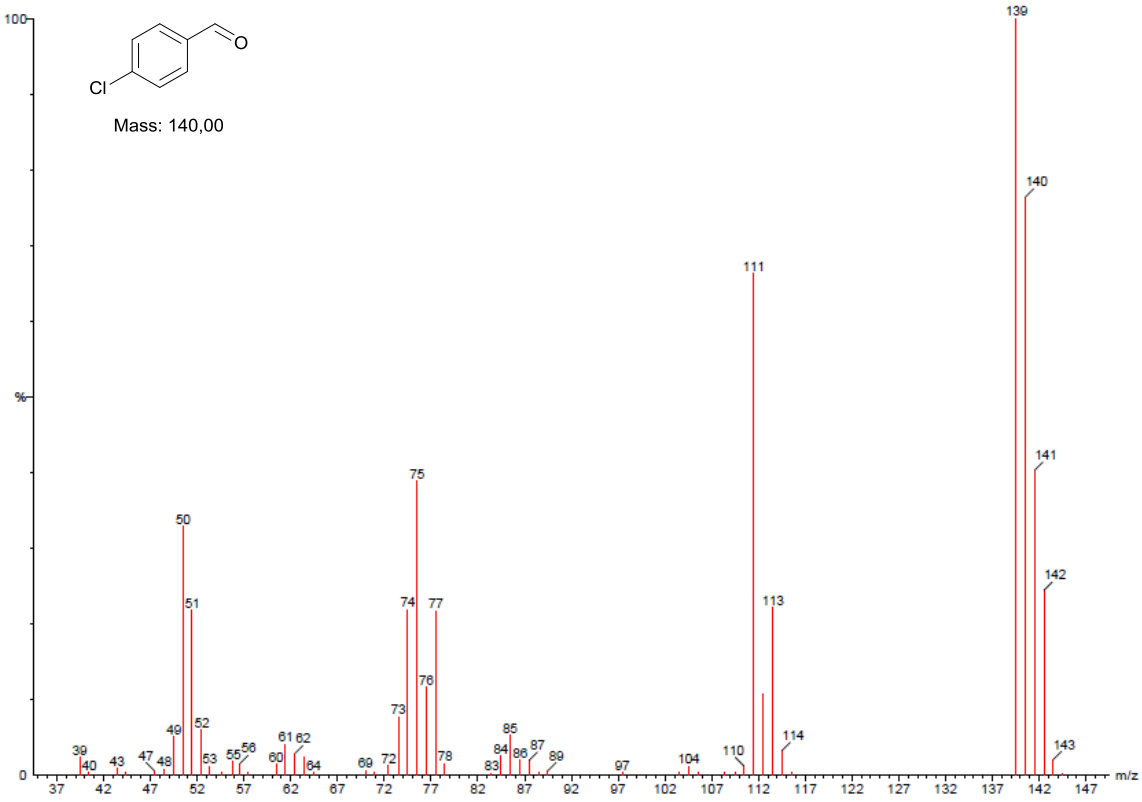


Figure 93 Entry 5 4-chlorobenzaldehyde

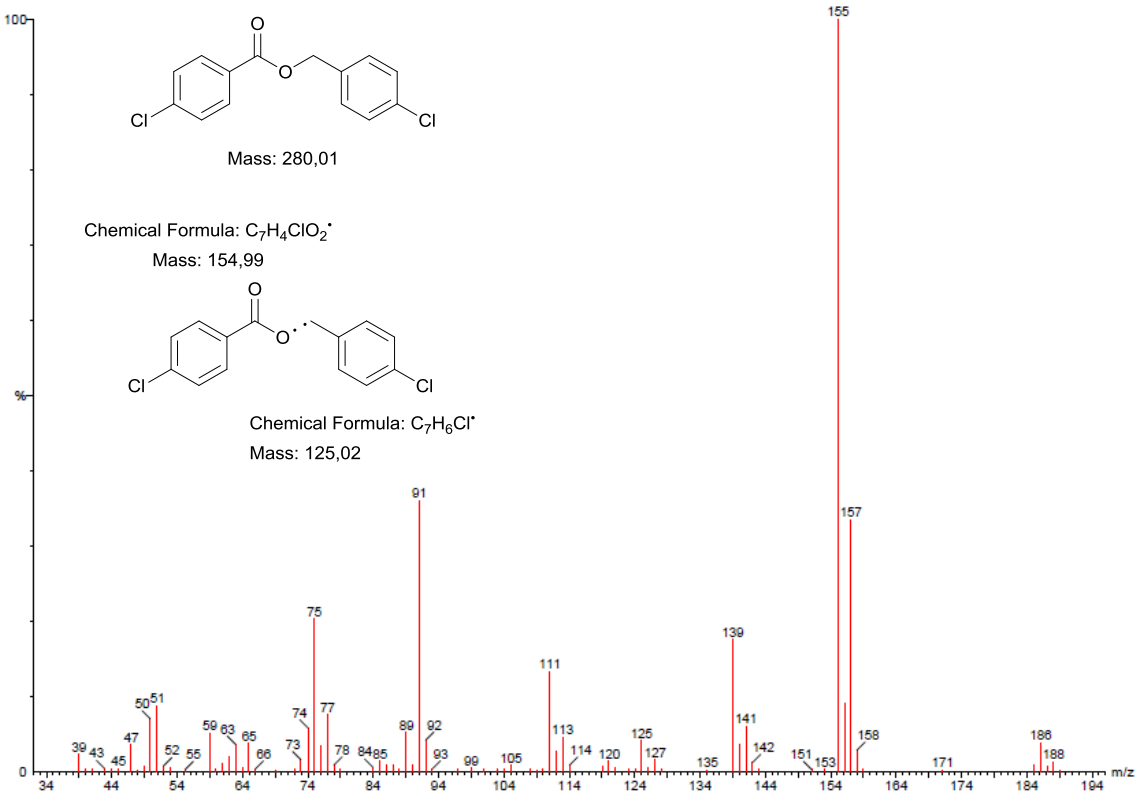


Figure 94 Entry 5 4-chlorobenzyl 4-chlorobenzoate

Entry 9 2-methoxybenzyl alcohol

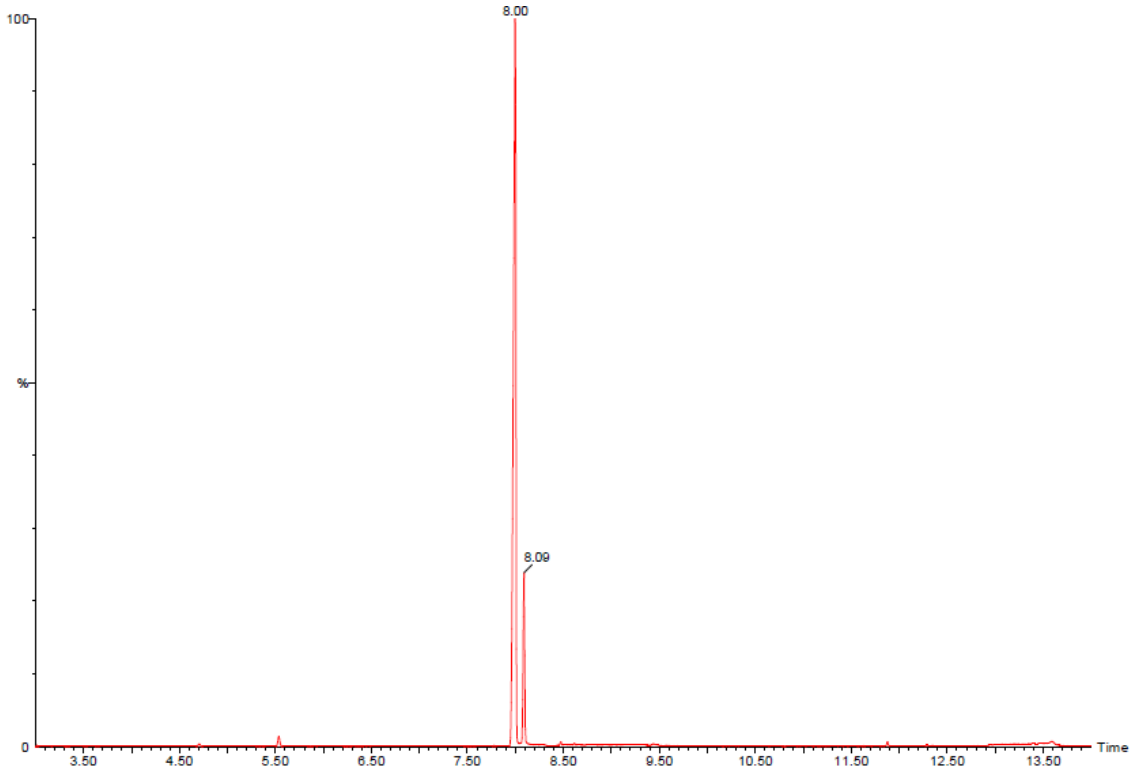


Figure 95 Entry 9 8.00 min.: 2-methoxybenzaldehyde, 8.09 min.: 2-methoxybenzyl alcohol

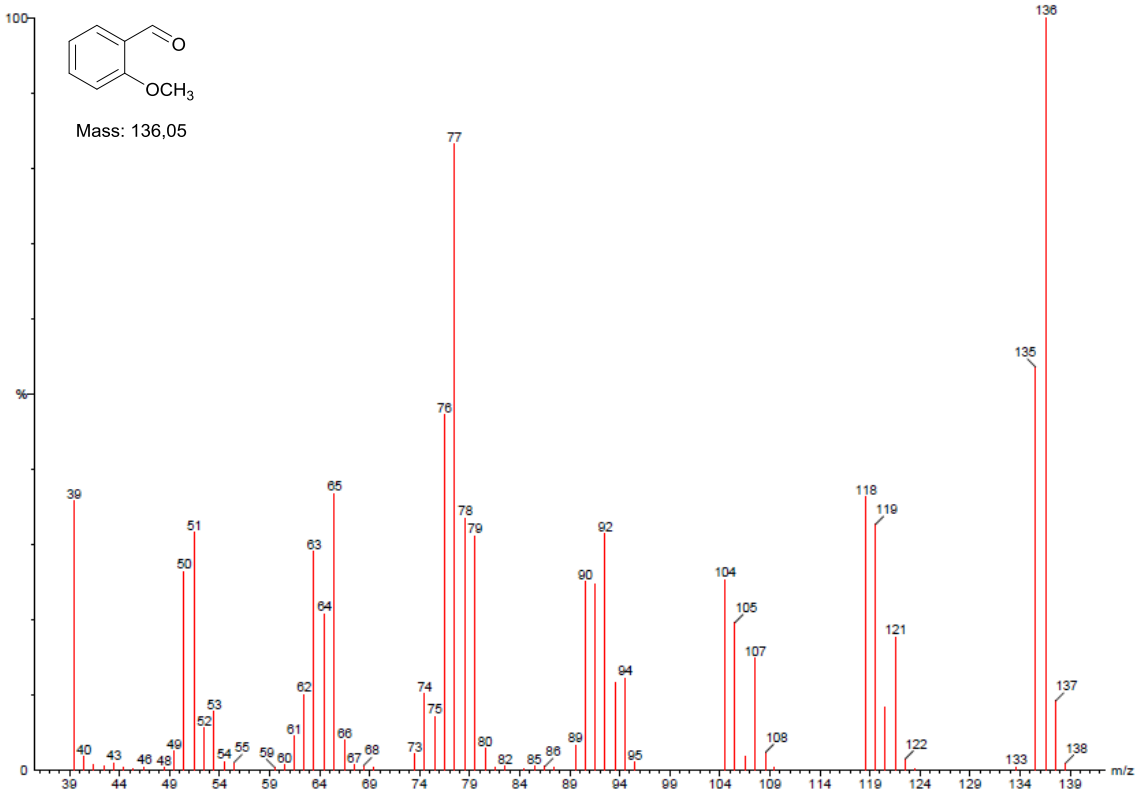


Figure 96 Entry 9 2-methoxybenzaldehyde

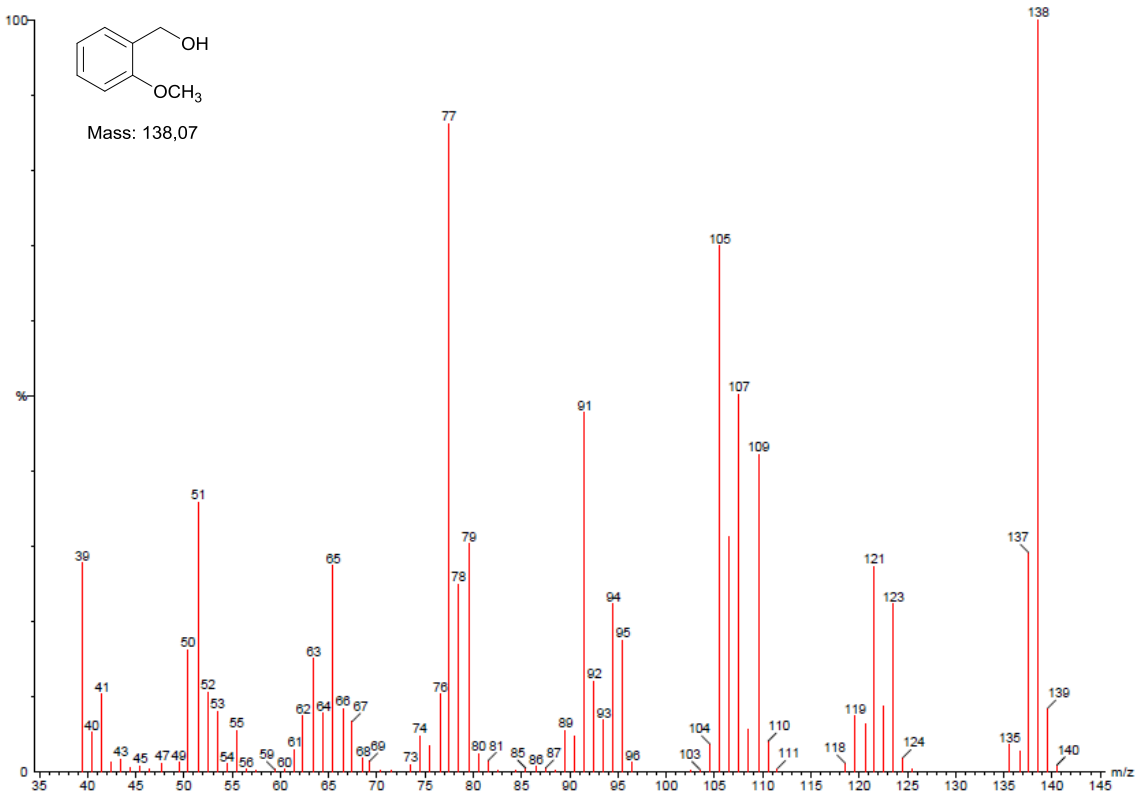


Figure 97 Entry 9 2-methoxybenzyl alcohol

Entry 10 4-methoxybenzyl alcohol

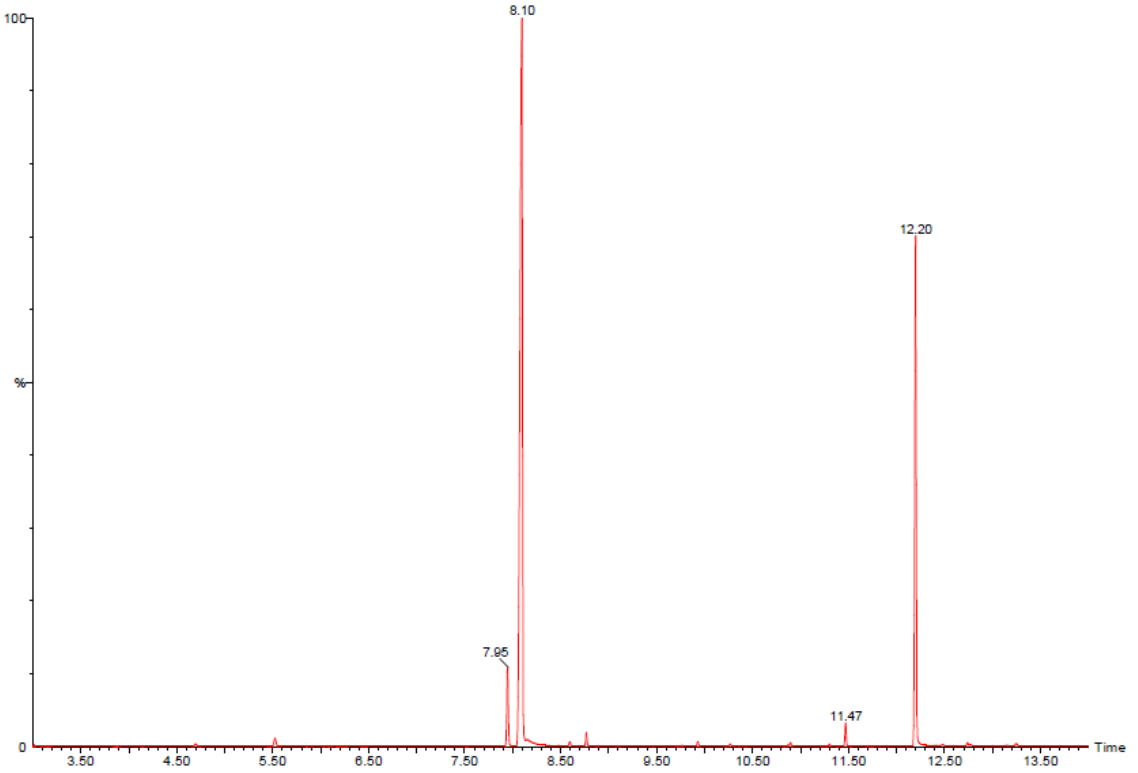


Figure 98 Entry 10 7.95 min.: 4-methoxybenzoic acid, 8.10 min.: 4-methoxybenzaldehyde, 12.20 min.: 4-methoxybenzyl 4-methoxybenzoate.

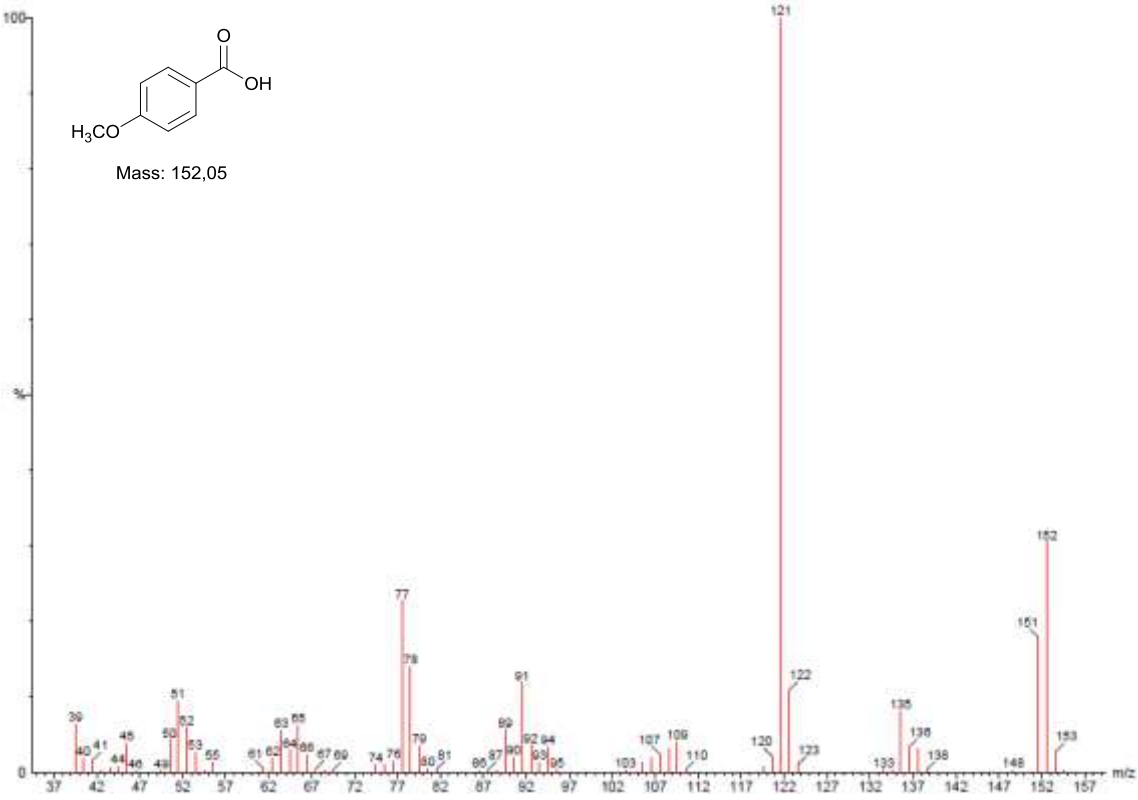


Figure 99. Entry 10, 7.95 min.: 4-methoxybenzoic acid

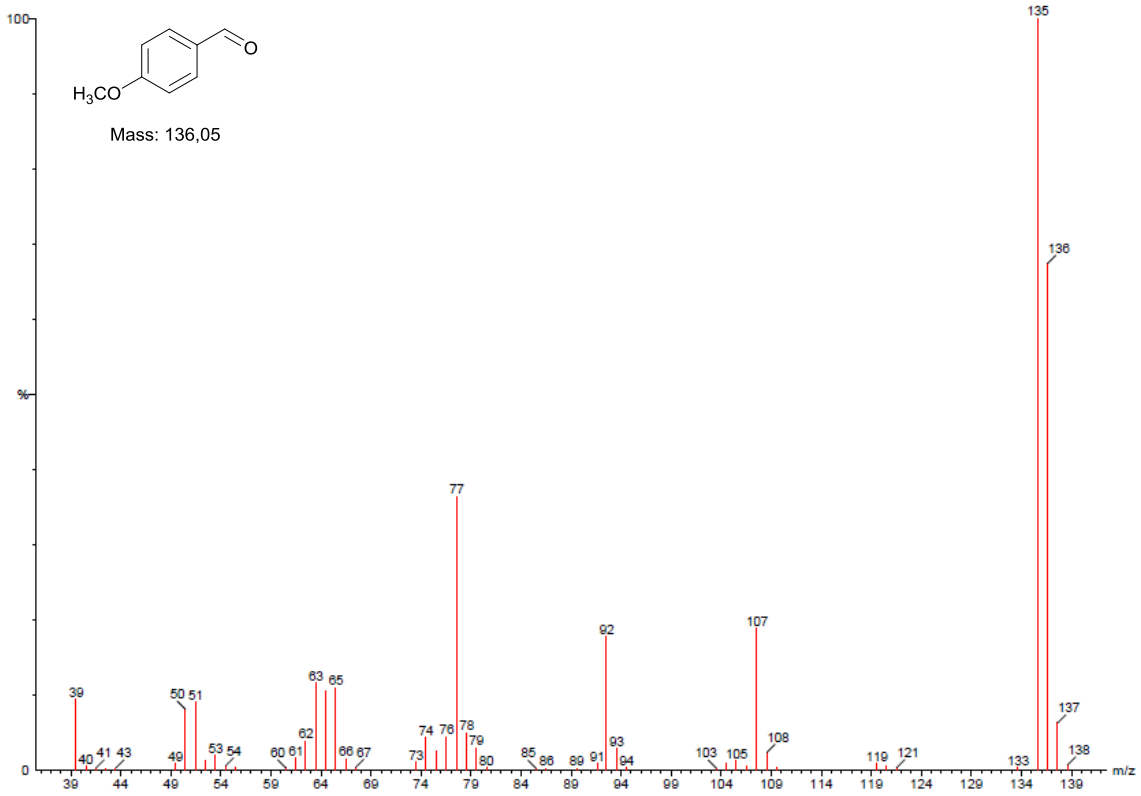


Figure 100 Entry 10, 8.10 min.: 4-methoxybenzaldehyde

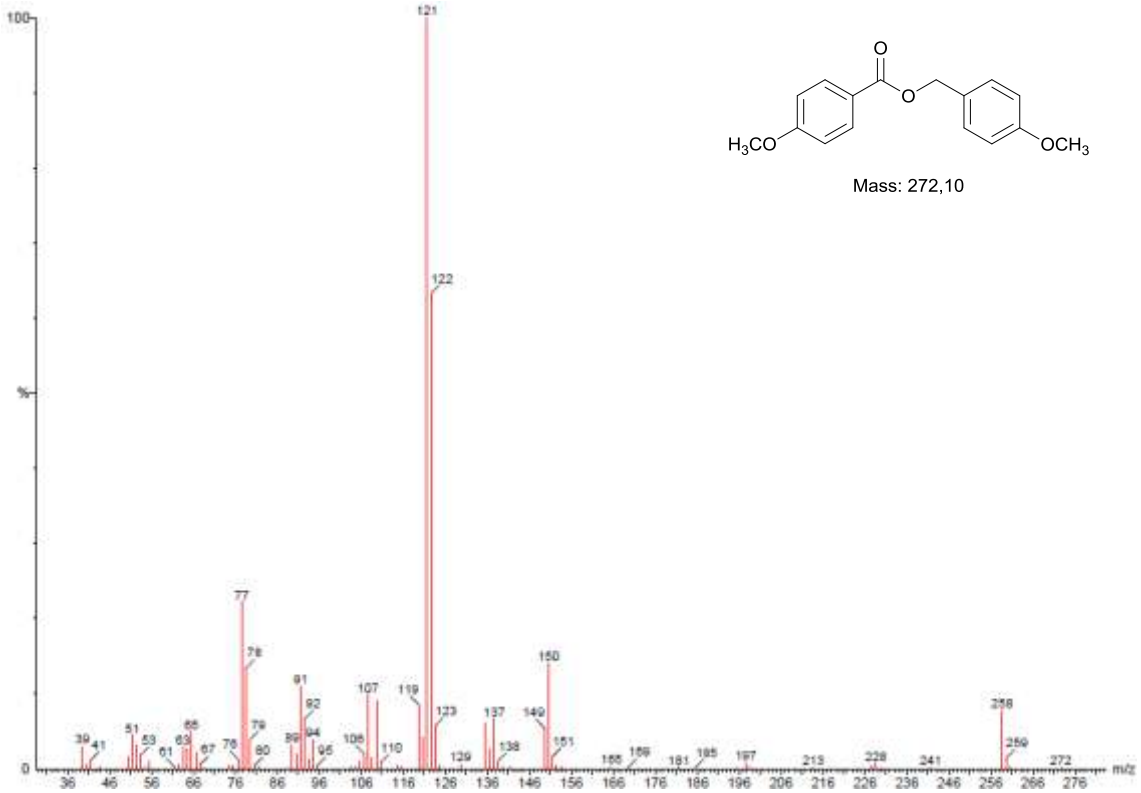


Figure 101. Entry 10, 12.20 min.: 4-methoxybenzyl 4-methoxybenzoate

^{1}H NMR spectrum for benzyl alcohols oxidation

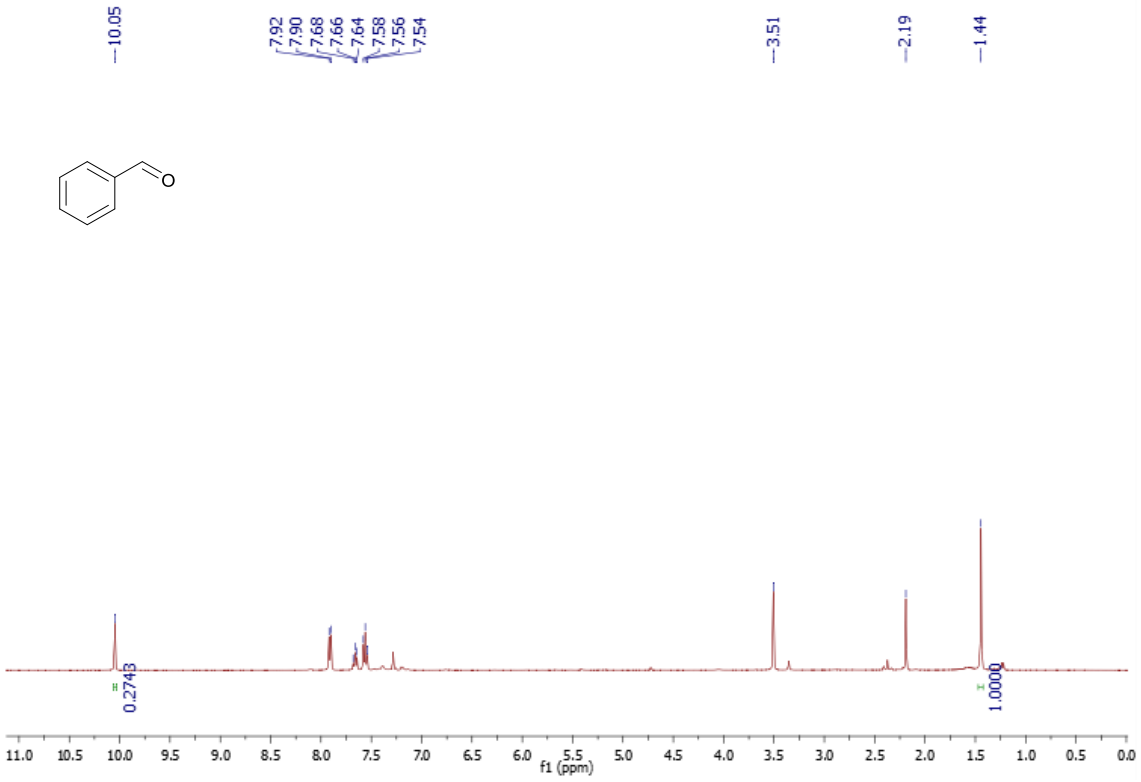


Figure 102 Benzyl alcohol oxidation; note: toluene (2.19 ppm)/ methanol (3.51 ppm). ^{1}H NMR (400 MHz) $CDCl_3$

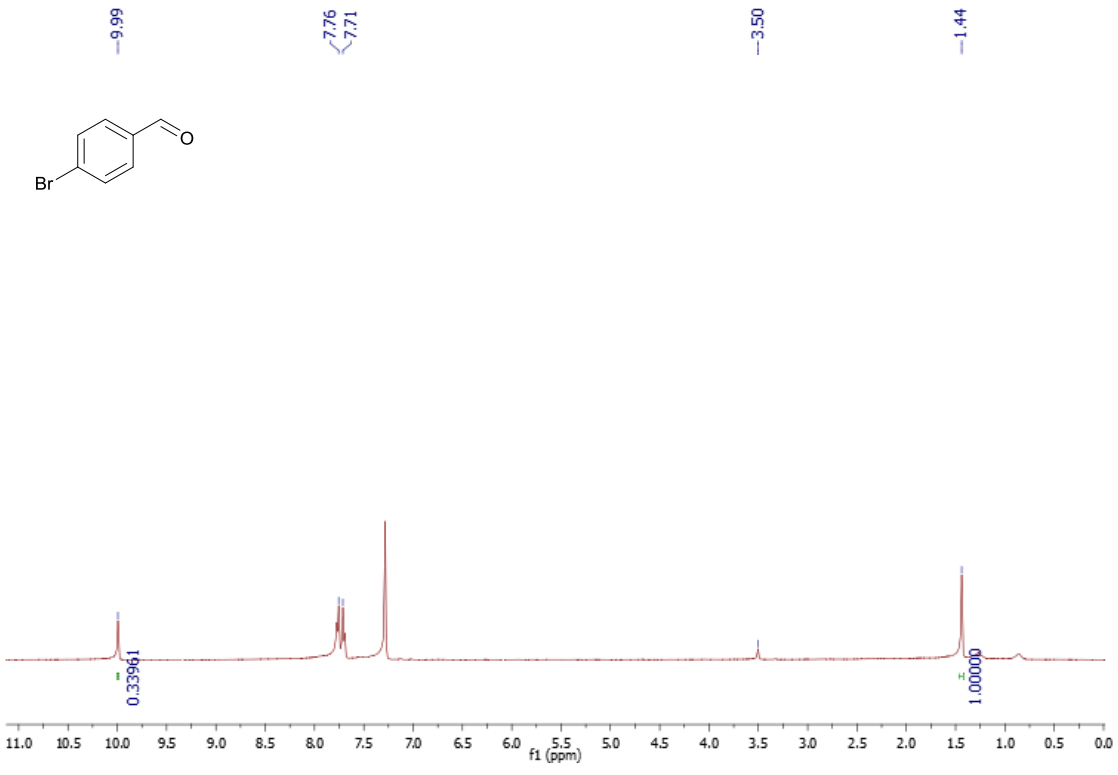


Figure 103 **4-bromobenzyl alcohol oxidation,** ^{1}H NMR (400 MHz) $CDCl_3$

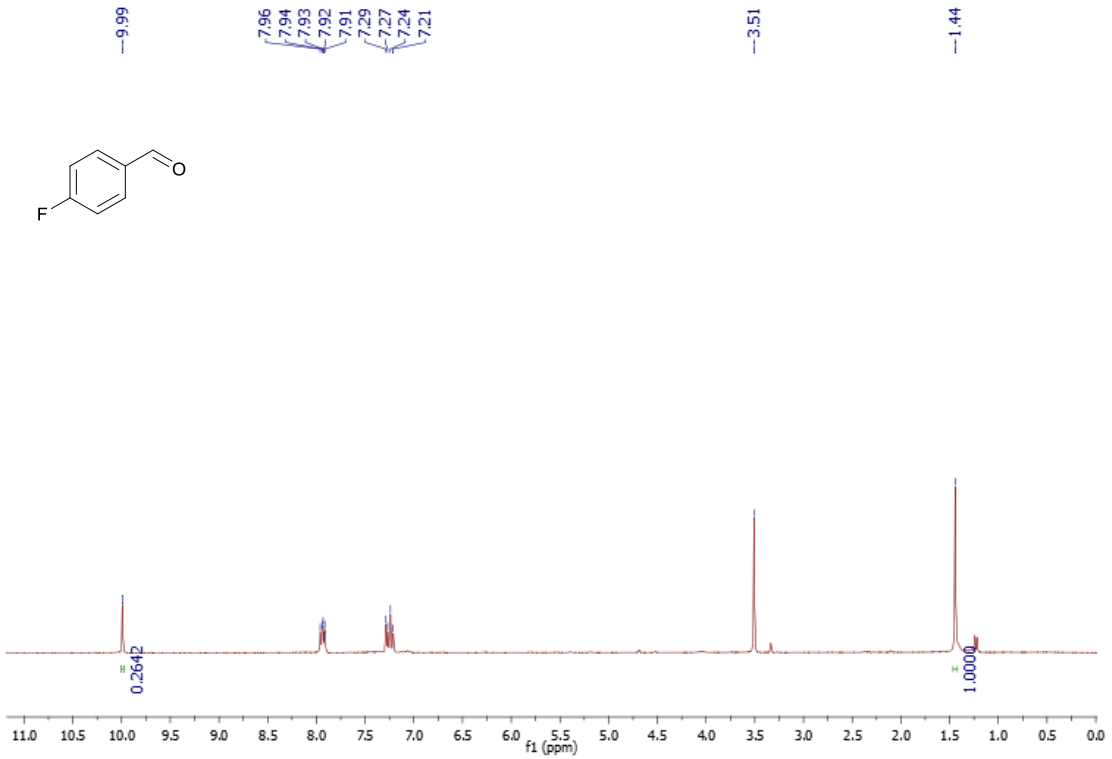


Figure 104 **4-fluorobenzyl alcoho oxidationl,** ^{1}H NMR (400 MHz) $CDCl_3$

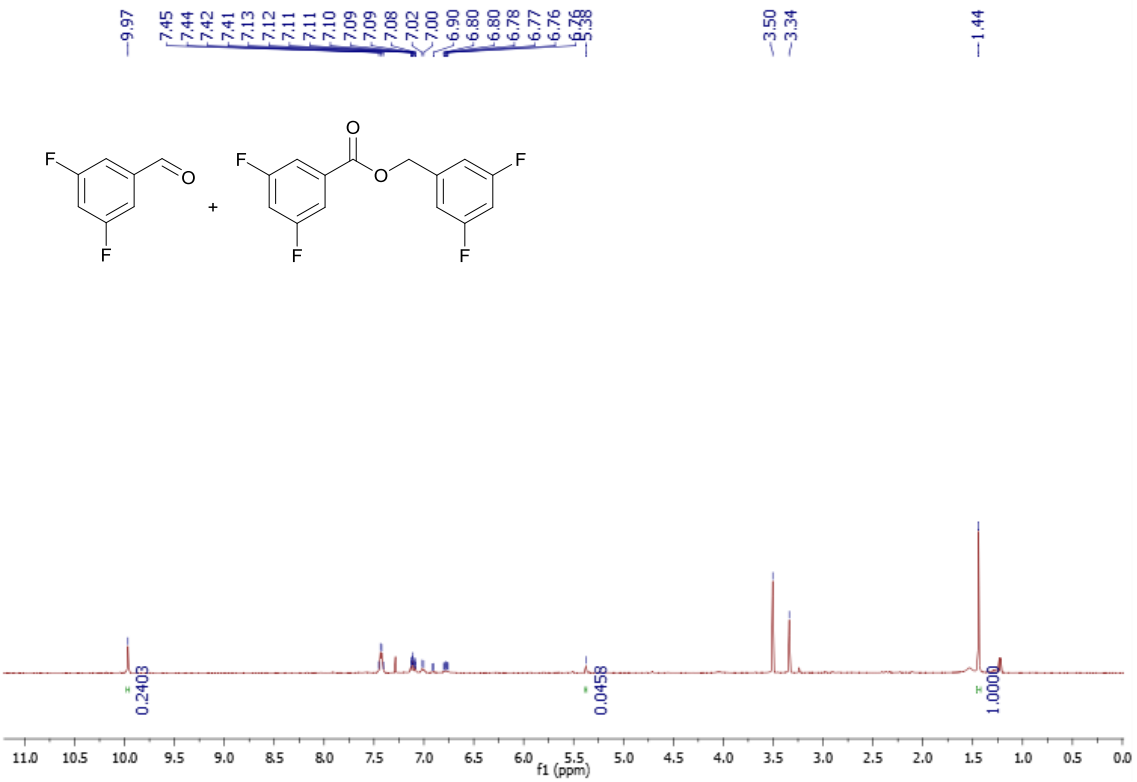


Figure 105 **3,5-difluorobenzyl alcohol oxidation,** ^{1}H NMR (400 MHz) $CDCl_3$

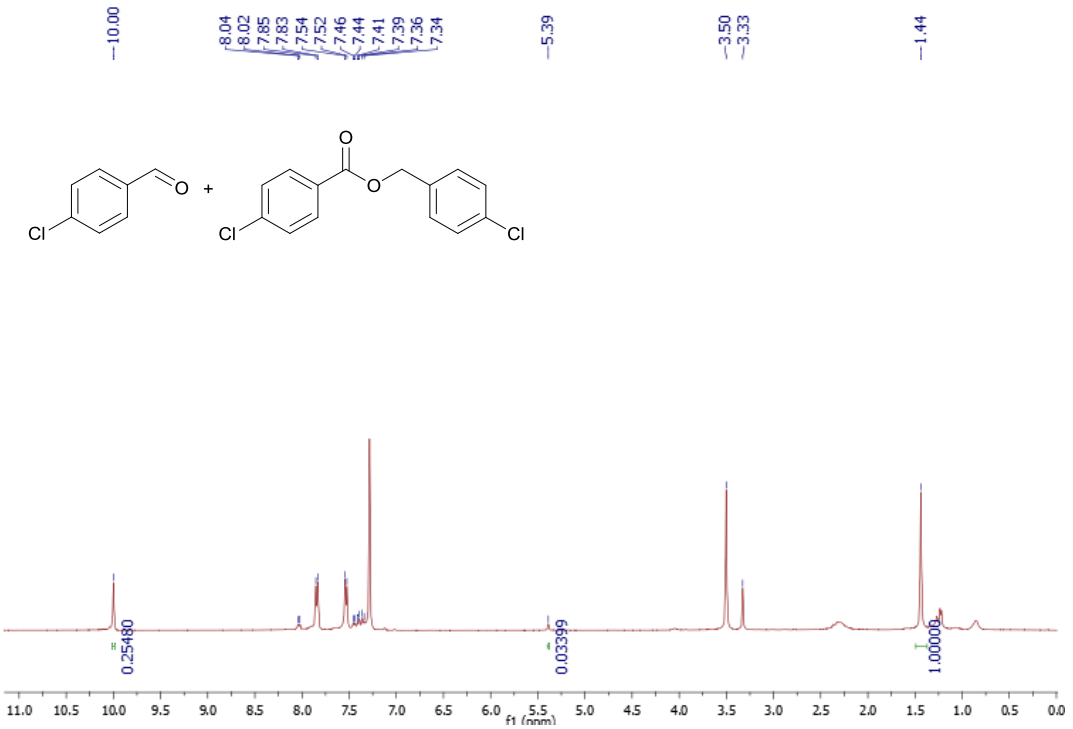


Figure 106 **4-chlorobenzyl alcohol oxidation,** ^{1}H NMR (400 MHz) $CDCl_3$

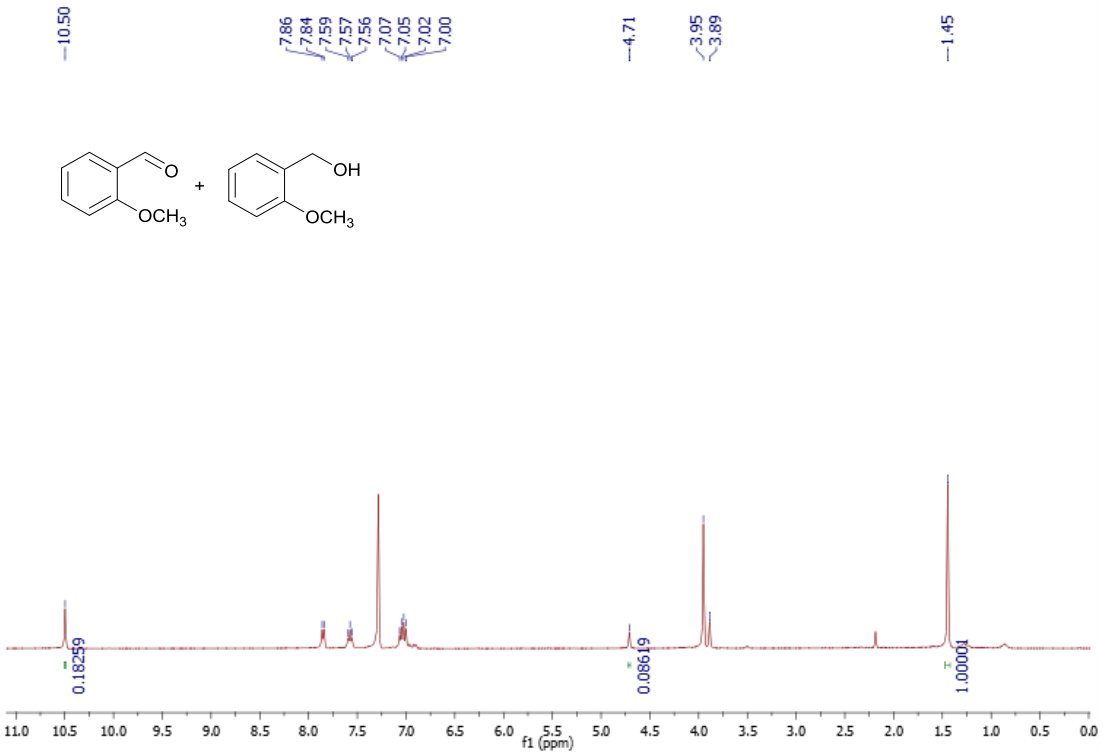


Figure 107 **2-methoxybenzyl alcohol oxidation,** ^{1}H NMR (400 MHz) $CDCl_3$

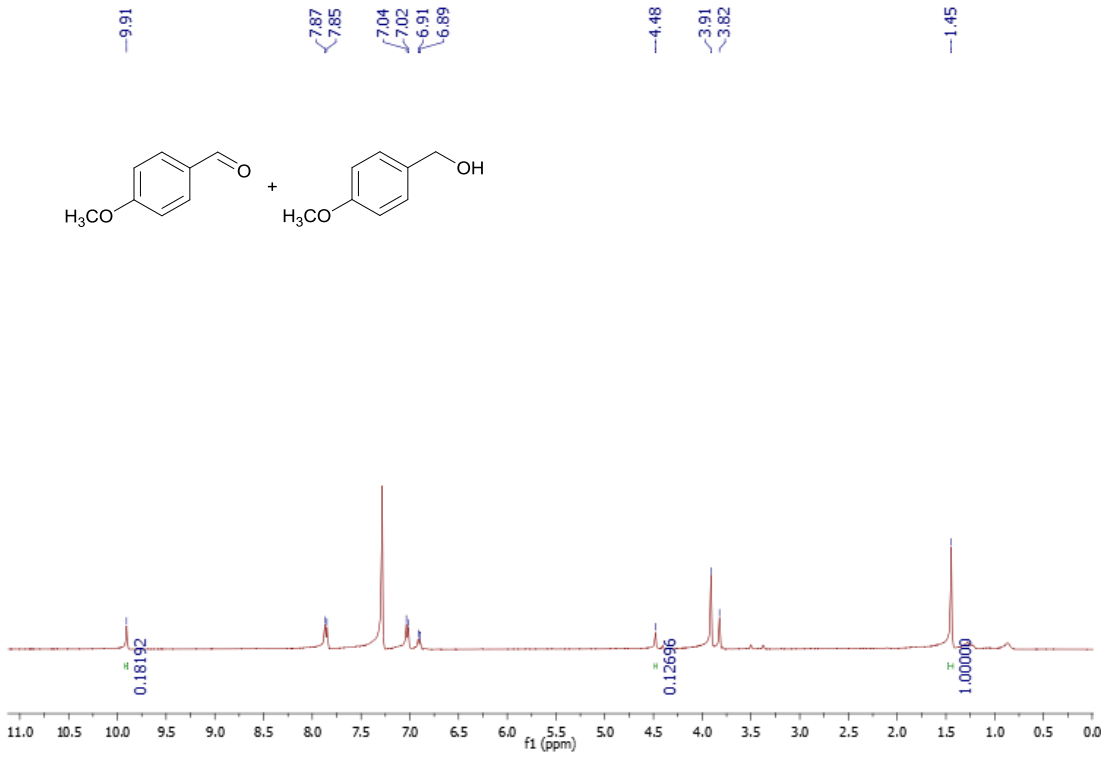


Figure 108 **4-methoxybenzyl alcohol oxidation,** ^{1}H NMR (400 MHz) $CDCl_3$

4.4. NMR spectrum of control experiments

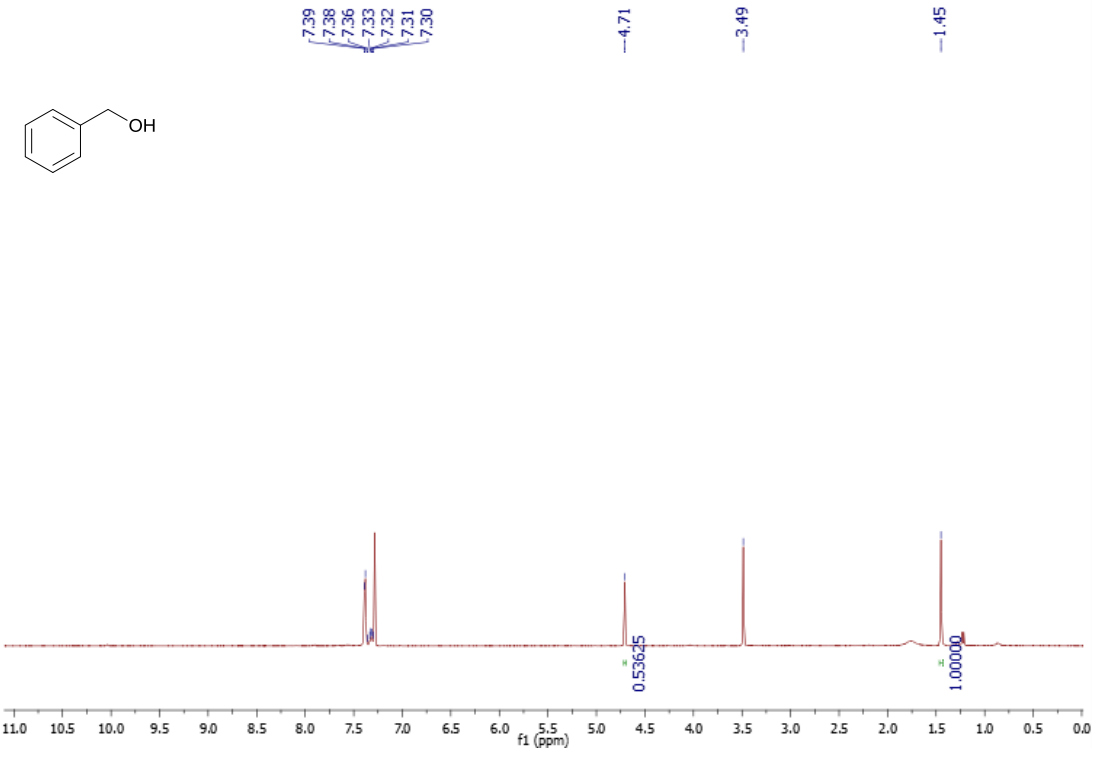


Figure 109 **Test for oxidation of benzyl alcohol without catalyst,** ^{1}H NMR (400 MHz) $CDCl_3$

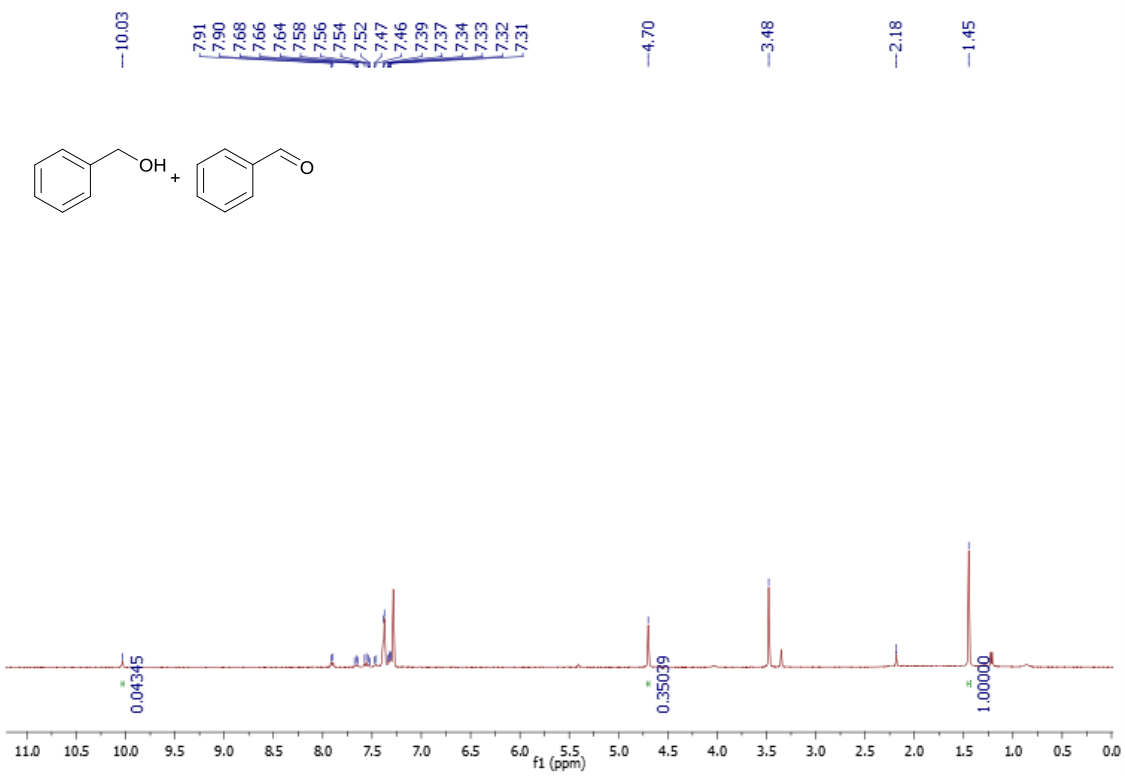


Figure 110 **Test for oxidation of benzyl alcohol without O_2** ^{1}H NMR (400 MHz) $CDCl_3$

5. References

1. L. E. Heim, S. Vallazza, D. Van der Waals, M. H. G. Prechtl, Green Chem., **2016**, **18**, 1469-1474.

2. L. E. Heim, N. E. Schlörer, J.-H. Choi, M. H. G. Prechtl, Nat Commun., **2014**, **5**, Article 3621.