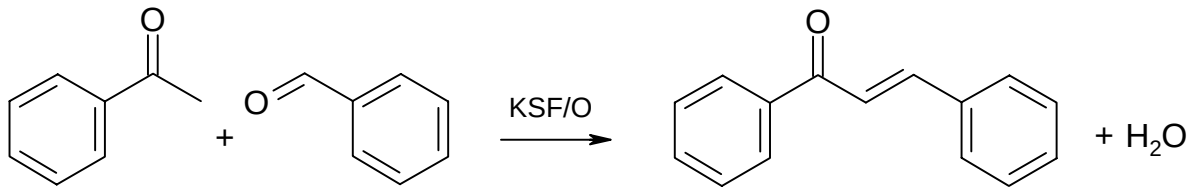
4013 Synthesis of benzalacetophenone from benzaldehyde and acetophenone



C_8H_8O (120.2) + C_7H_6O (106.1) → $C_{15}H_{12}O$ (208.3) + H_2O

Classification

Reaction types and Substance classes
reaction of the carbonyl group in aldehydes, aldol condensation
aldehyde, ketone, aromatics, acid catalyst

Work methods
stirring with magnetic stir bar, distilling under reduced pressure, heating with oil bath

Instruction (batch scale 10 mmol)

Equipment
10 mL round bottom flask, reflux condenser, heatable magnetic stirrer, magnetic stir bar, electronic temperature control, short path distillation apparatus (kugelrohr distillation apparatus), vacuum pump, oil bath

Substances

acetophenone (bp 202 °C)	1.20 g (1.17 mL, 10.0 mmol)
benzaldehyde (freshly distilled) (bp 179 °C)	2.12 g (2.02 mL, 200 mmol)
montmorillonite KSF/O (Fluka)	1.0 g

Reaction
1.20 g (1.17 mL, 10.0 mmol) acetophenone, 2.12 g (2.02 mL, 20.0 mmol) benzaldehyde and 1.0 g montmorillonite KSF/O are placed in a 10 mL round bottom flask with magnetic stirrer and reflux condenser, which is used as a waterless air cooler.The reaction mixture is heated under stirring in the oil bath up to 80°C (bath temperature) and stirred at this temperature for 22 hours.

Work up
The reaction mixture is cooled to room temperature. In a short path distillation apparatus first the not reacted educts are distilled at about 10 hPa and subsequently the product at $2.5 \cdot 10^{-2}$ hPa and 160 °C.

Yield: 1.77 g (8.50 mmol, 85%); yellow solid, mp 51-53 °C.

Comments
Without the excess of benzaldehyd the yield is lower. Neither an extension of the reaction time nor an increase in reaction temperature leads to a quantitative reaction of the educts. Increasing the reaction temperature to 100 °C is leading to more side products.

Waste management

Recycling

Waste	Disposal
distilled educts	organic solvents, halogen free
distillation residue	solid waste, free from mercury

Time
3 hours
Additionally 22 hours of heating

Break

Before distillation

Degree of difficulty
Easy

Instruction (batch scale 100 mmol)

Equipment
100 mL round bottom flask, reflux condenser, heatable magnetic stirrer, magnetic stir bar, elektronic temperature control, hot-air gun, distillation apparatus for solids, vacuum pump, oil bath

Substances

acetophenone (bp 202 °C)	12.0 g(11.7 mL, 100 mmol)
benzaldehyde (freshly distilled) (bp 179 °C)	21.2 g (20.2 mL, 200 mmol)
montmorillonite KSF/O (Fluka)	10 g

Reaction
12.0 g (11.7 mL, 100 mmol) acetophenone, 21.2 g (20.2 mL, 200 mmol) benzaldehyde and 10 g montmorillonite KSF/O are placed in a 100 mL round-bottom flask with magnetic stirrer and reflux condenser, which is used as waterless air cooler, heated under stirring in the oil bath to 80° C (bath temperature) and stirred at this temperature for 24 hours.

Work up
The reaction mixture is cooled to room temperature. In a solid distillation apparatus first the not reacted educts are distilled at 10 hPa and then the product at $9 \cdot 10^{-3}$ hPa and 175 °C oil

bath temperature. If using a water cooler for distillation, the water should be kept at about 60 °C. The possibly in the distillation apparatus crystallized product is dissolved again with a hot-air gun.
Yield: 15.6 g (74.9 mmol, 75%); yellow solid, mp 52-54 °C.

Comments
Without the excess of benzaldehyde the yield is lower. Neither an extension of the reaction time nor an increase in reaction temperature leads to a quantitative reaction of the educt. Increasing the reaction temperature up to 100 °C is leading to more side products.

Waste management

Waste disposal

Waste	Disposal
distilled educt	organic solvents, halogen free
distillation residue	solid waste, free from mercury

Time
5 hours
Additionally 24 hours of heating

Break
Before distillation

Degree of difficulty
Easy

Analytics

Reaction monitoring with GC

Sample preparation:

Using a pipette, a drop is taken from the reaction mixture or from the product and diluted with 10 mL dichlormethane. 10 mg of solid substances are dissolved in 10 mL dichloromethane.
0.2 µL from this solution are injected.

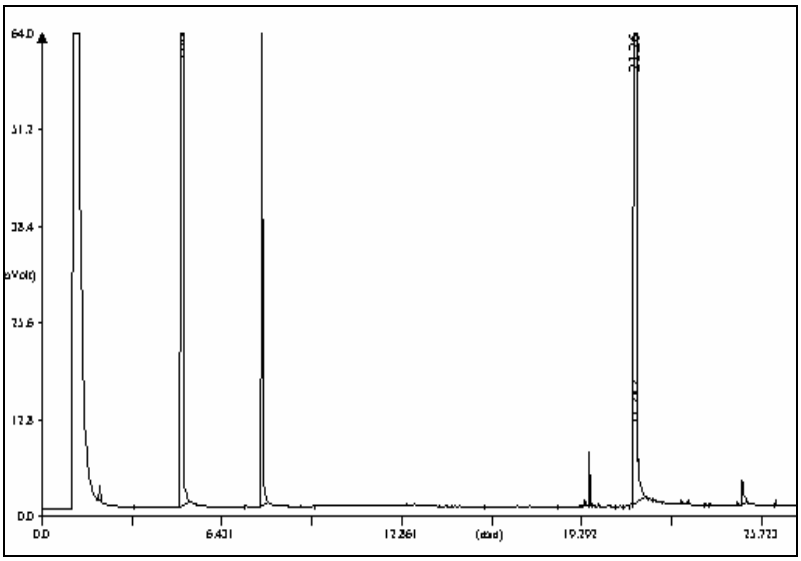
GC conditions:

column:	DB-1, 28 m, internal diameter 0.32 mm, film 0.25 µm
inlet:	on-column injection
carrier gas:	hydrogen (40 cm/s)
oven:	60 °C (5 min), 10 °C/min to 240 °C (30 min)
detector:	FID, 270 °C

Percent concentration was calculated from peak areas.

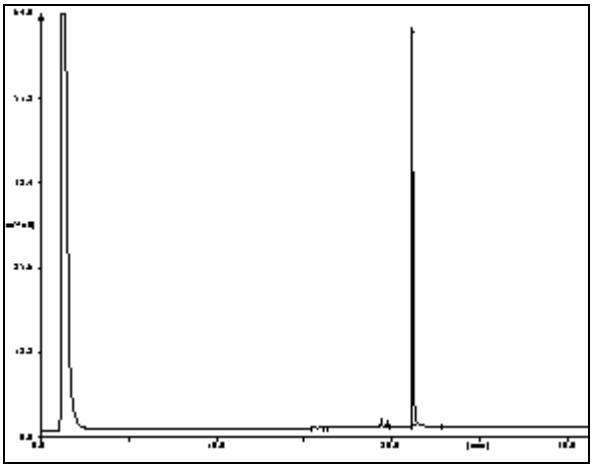
GC of the crude product

GC conditions as specified under "reaction monitoring"



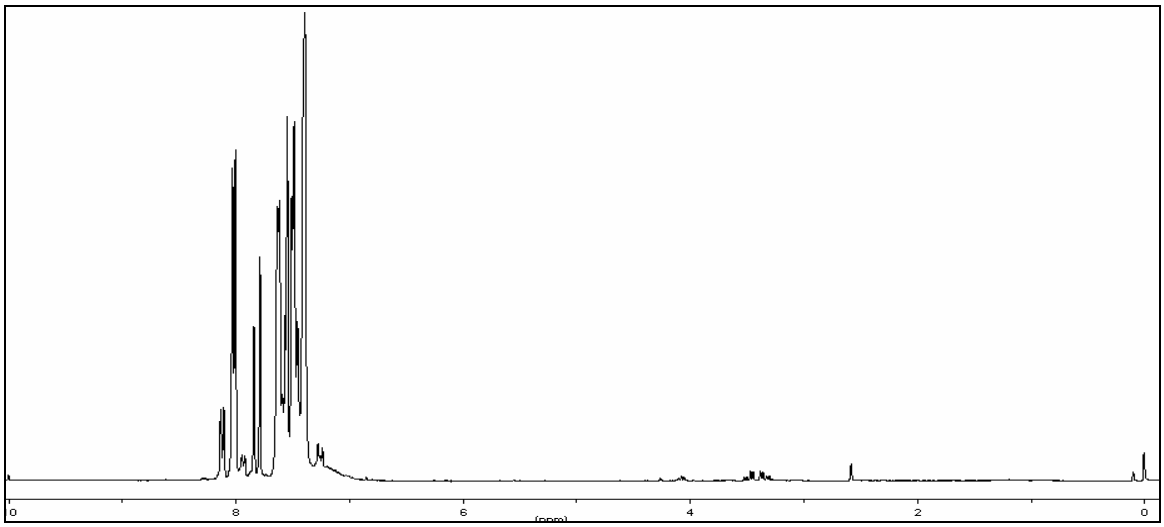
Retention time (min)	Substance	Peak area %
5.06	educt (benzaldehyde)	36.7
7.87	educt (acetophenone)	8.3
21.35	product (benzalacetophenone)	54.3

GC of the pure product

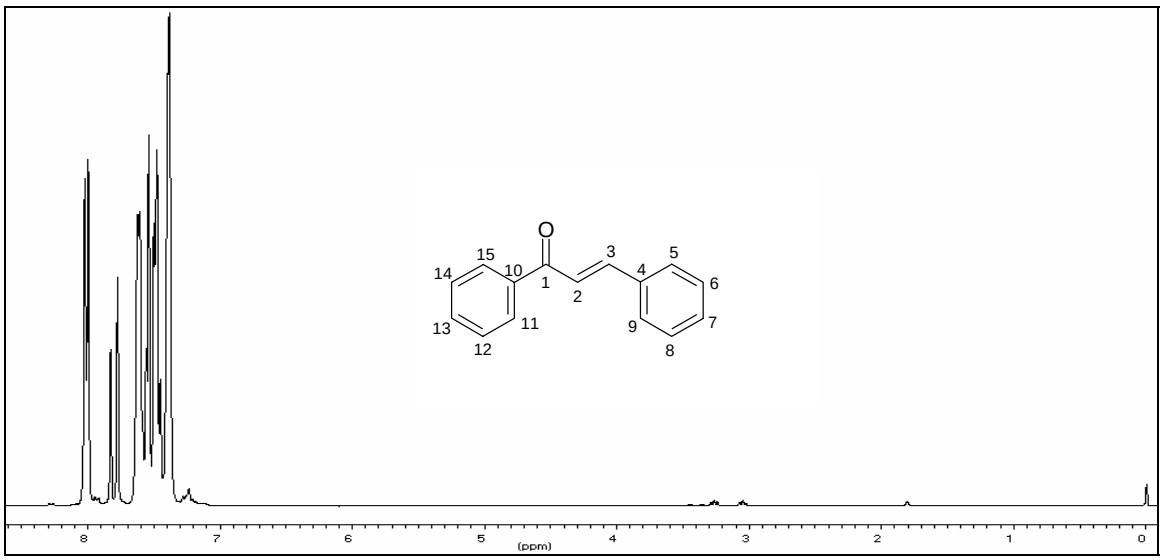


Retention time (min)	Substance	Peak area %
21.17	product (benzalacetophenone)	97.2
19.39	byproduct	1.5
19.69	byproduct	1.3

^{1}H NMR spectrum of the crude product (300 MHz, $CDCl_3$)

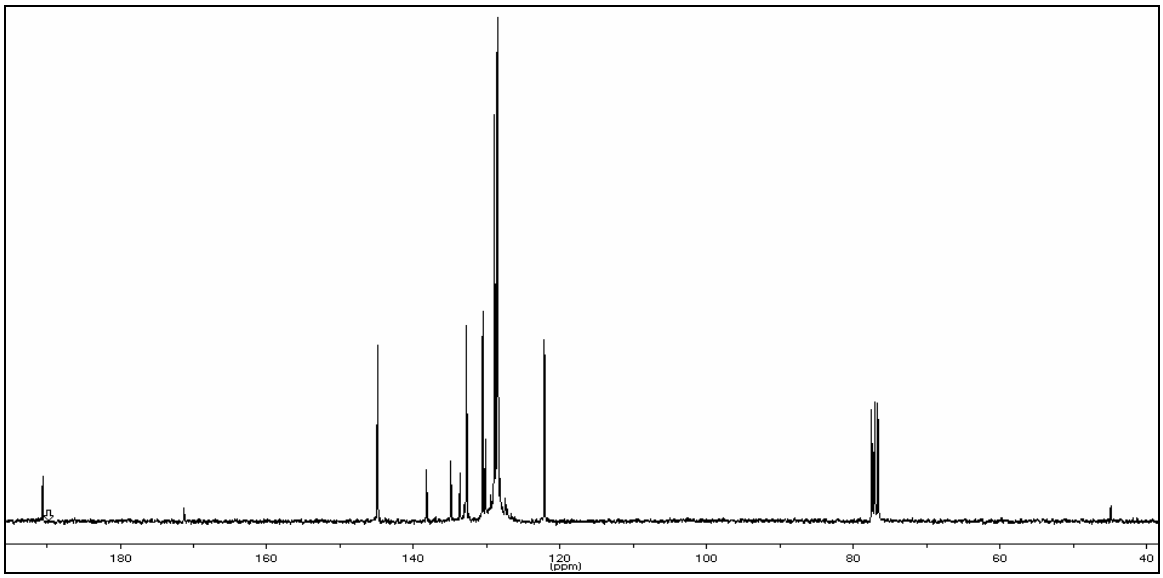


^{1}H NMR spectrum of the pure product (300 MHz, $CDCl_3$)

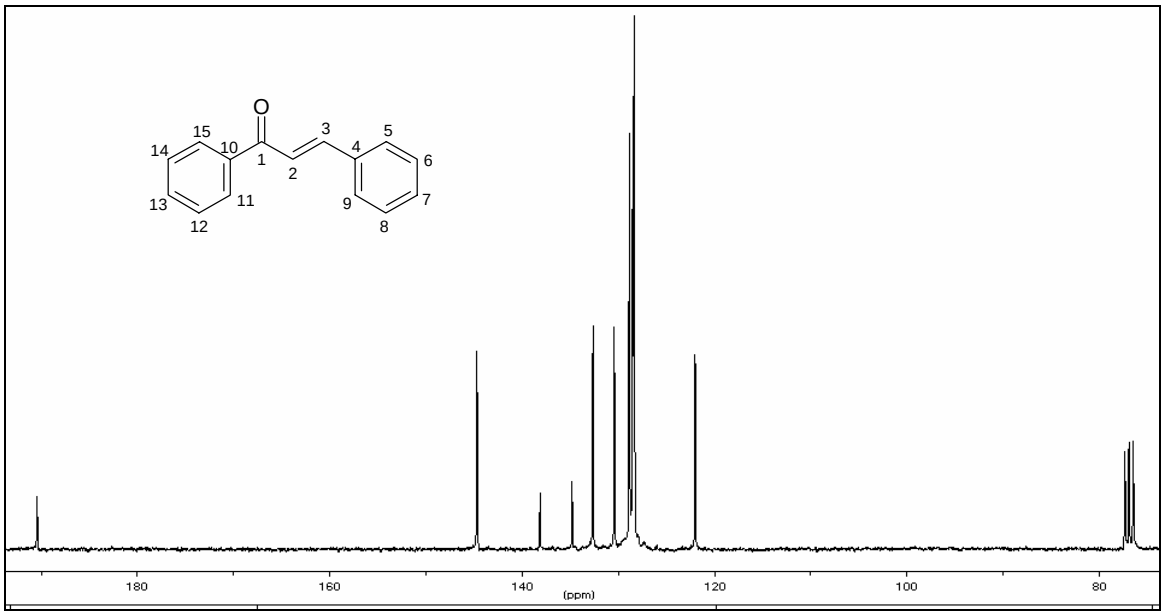


δ (ppm)	Multiplicity	Number of H	Assignment
7.38	m	3	6-H, 7-H, 8-H
7.47	m	2	12-H, 14-H
7.54	m	2	2-H, 13-H
7.61	m	2	5-H, 9-H
7.80	d	1	3-H
8.02	m	2	15-H, 11-H

^{13}C NMR spectrum of the crude product (75.5 MHz, $CDCl_3$)

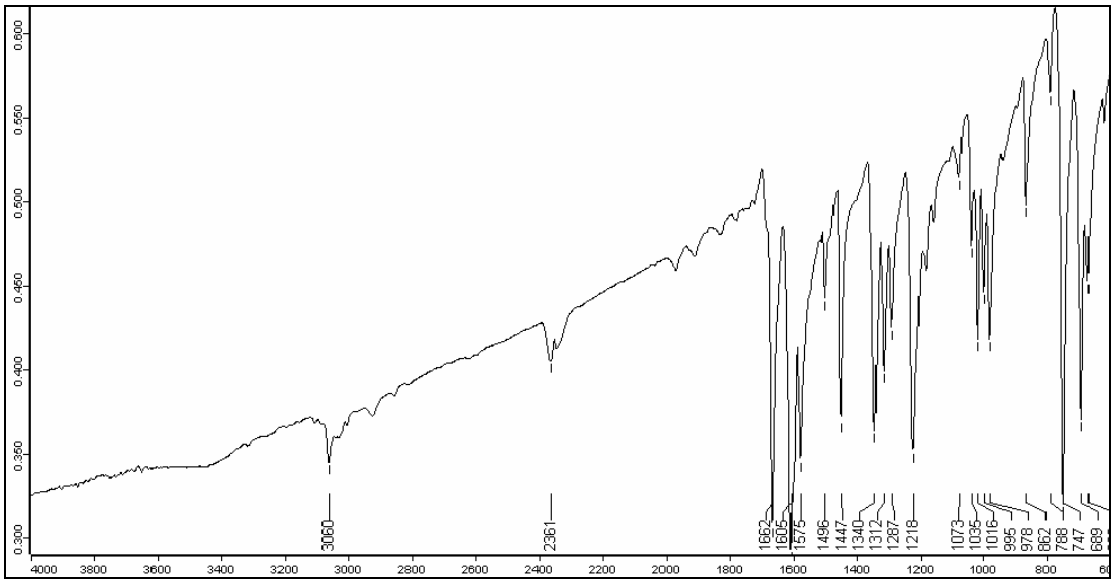


^{13}C NMR spectrum of the pure product (75.5 MHz, $CDCl_3$)



δ (ppm)	Assignment
190.4	C-1
144.7	C-3
138.1	C-10
134.8	C-4
132.7	C-13
130.4	C-7
128.9, 128.5, 128.4, 128.3	C-5, C-6, C-8, C-9, C-11, C-12, C-14, C-15
122.0	C-2
76.5-77.5	solvent

IR spectrum of the pure product (KBr)



cm^{-1}

(cm^{-1})	**Assignment**
3060	C-H-valence, arene, alkene
1662	C=O-valence, ketone
1605	C=C-valence, arene, alkene
1575, 1496	C=C-valence, arene