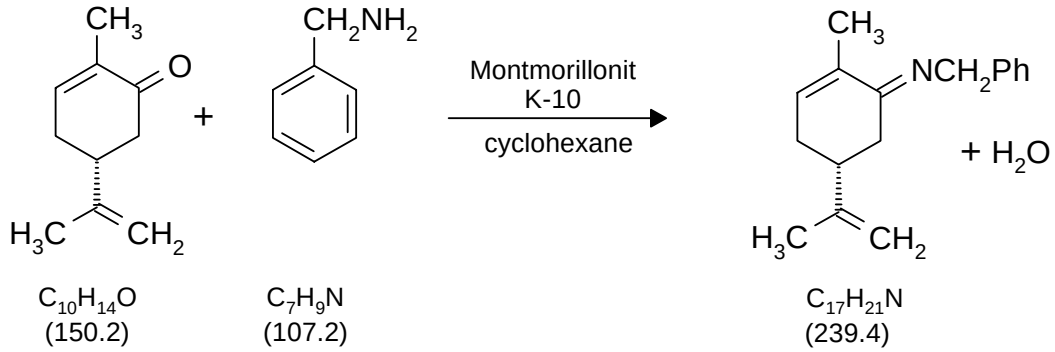
2006 Reaction of (R)-(–)-carvone with benzylamine in the presence of Montmorillonite K-10 to a Schiff's base



$C_{10}H_{14}O$ (150.2) | C_7H_9N (107.2) | $C_{17}H_{21}N$ (239.4)

Classification

Reaction types and substance classes

Reaction of the carbonyl group in ketones

ketone, amine, Schiff's base, natural product, acid catalyst

Work methods

removal of water by azeotropic distillation, stirring with magnetic stir bar, filtering, distilling under reduced pressure, evaporating with rotary evaporator, heating with oil bath

Instruction (batch scale 100 mmol)

Equipment

250 mL round bottom flask, water separator, reflux condenser, heatable magnetic stirrer, magnetic stir bar, rotation evaporator, distillation apparatus, vacuum pump, oil bath

Substances

(R)-(–)-carvone (bp. 230 °C)	15.0 g (15.6 mL, 100 mmol)
benzylamine (bp. 185 °C)	11.8 g (12.0 mL, 110 mmol)
cyclohexane (bp. 81 °C)	170 mL
Montmorillonite K-10	3 g

Reaction

150 mL cyclohexane, 15.0 g (15.6 mL, 100 mmol) carvone, 11.8 g (12.0 mL, 110 mmol) benzylamine and 3.0 g montmorillonite K-10 are filled in a 250 mL round bottom flask with a water separator and reflux condenser. Under stirring with a magnetic stirrer the reaction mixture is heated to reflux until no more water is separated (3-4 hours).

Work up

After cooling down to room temperature the suspension is filtered through a folded filter paper into a 250 mL round bottom flask and the residue is washed with 20 mL cyclohexane. If

the filtrate is not clear, the filtration is repeated. The solvent is evaporated at a rotary evaporator. A yellow liquid remains as crude product.
Crude yield: 22.3 g; GC purity 90%

The crude product is transferred into a 50 mL round bottom flask and is fractional distilled under reduced pressure (0.1 hPa).
Yield: 16.8 g (70.2 mmol, 70%), light yellowish opalescent liquid; bp 128-130 C (0.1 hPa), oil bath temperature up to 175 °C; GC purity 98% (see analytics), distillation residue: 2.20 g, yellow glutinous oil.

Waste management

Recycling
The cyclohexane of the reaction solution is collected and redistilled.
Montmorillonite K-10 can be used again after drying.

Waste Disposal

Waste	Disposal
aquaeous phase from water separator	solvent water mixtures, halogen free
distillation residue	organic solvents, halogen free
Montmorillonite K-10	solid waste, free from mercury

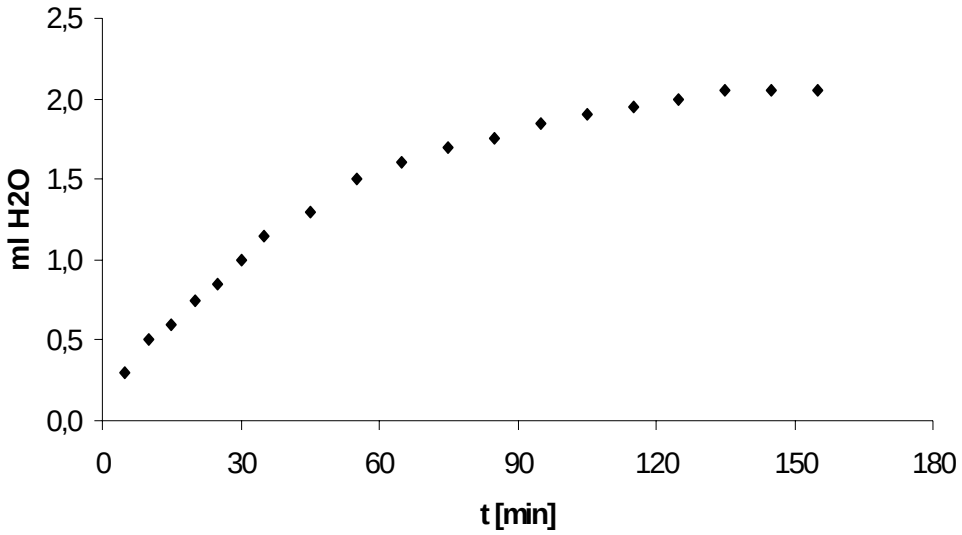
Time
5 hours

Break
After filtration of the montmorillonite K-10

Degree of difficulty
Medium

Analytics

Reaction monitoring using the amount of separated water



Start of water separation is defined as point 0 of the time scale.

The reaction time varies according to the speed of heating and distillation.

GC

GC-conditions

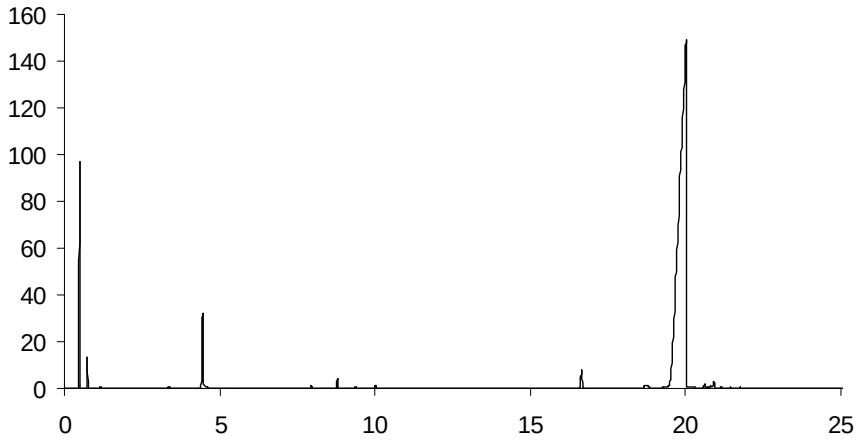
column:	Zebron ZB-1, length 15 m, internal diameter 0.25 mm, film 0.25 µm, (Phenomenex, Torrance, CA, USA)
inlet:	injector temperature 300 °C; split injection
carrier gas:	He, pre-column pressure 100 kPa
oven:	start temperature 50 °C (2 min), 8 °C/min to 200 °C (5 min), 8 °C/min to 250 °C (15 min).
detector:	FID, 256 °C, H_2 33.9 mL/min; synth. air 322 mL/min; make-up-gas N_2
integration:	integrator 4290 (Thermo Separation Products)

Percent concentration was calculated from peak areas.

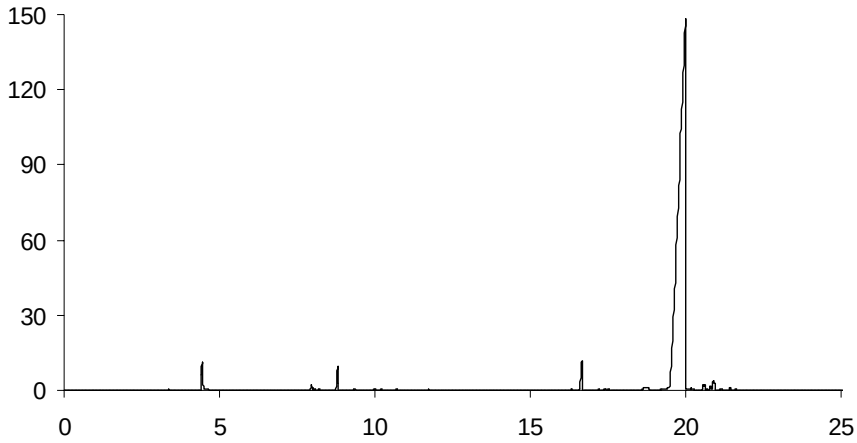
Regarding the GCs on the following page:

Retention time (min)	**Substance**	**Peak area %**		
		crude product	**fore-run**	**pure product** (main fraction)
4.5	benzylamine	3.2	1.4	0
8.8	carvone	0.3	1.0	0
20.0	Schiff's base	90.0	92.9	97.8

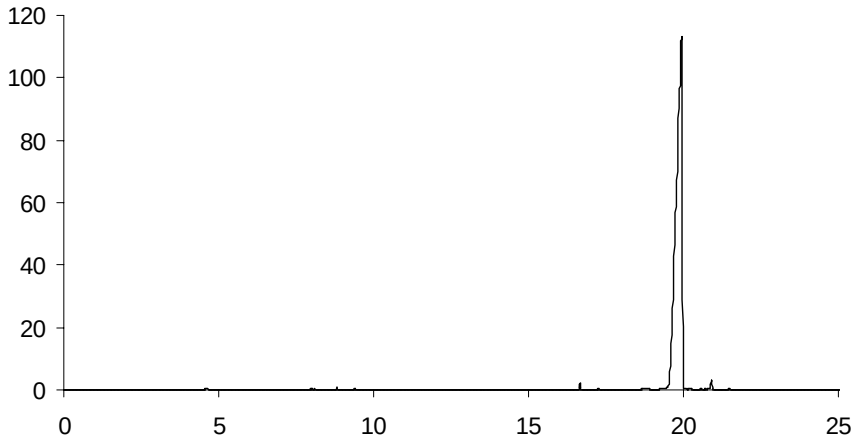
GC of the crude product



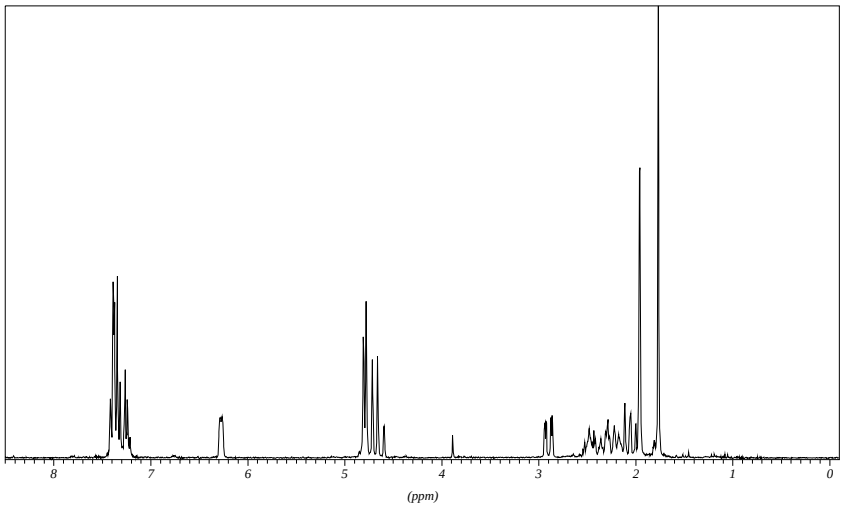
GC of the fore-run



GC of the pure product (mainfraction)



^{1}H NMR spectrum of the crude product (250 MHz, $CDCl_3$)



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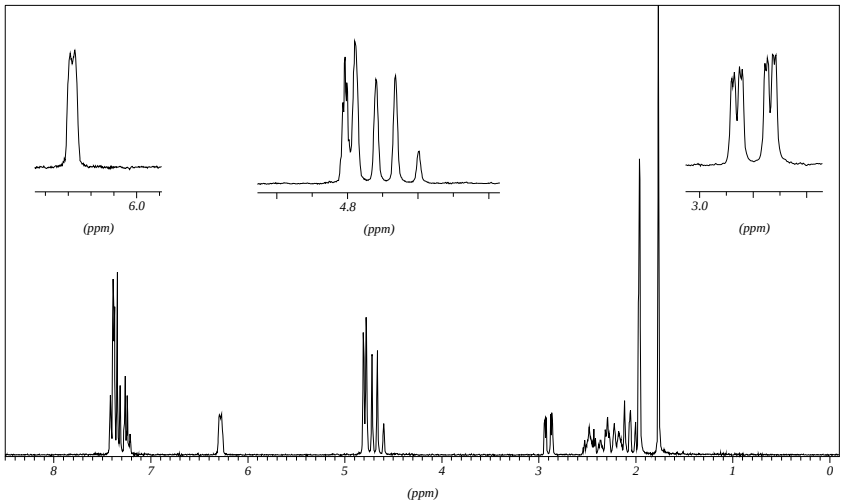
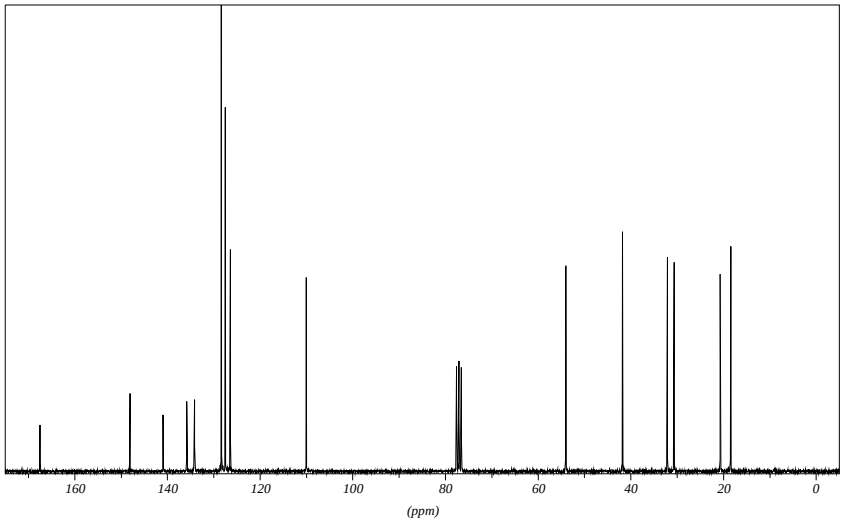


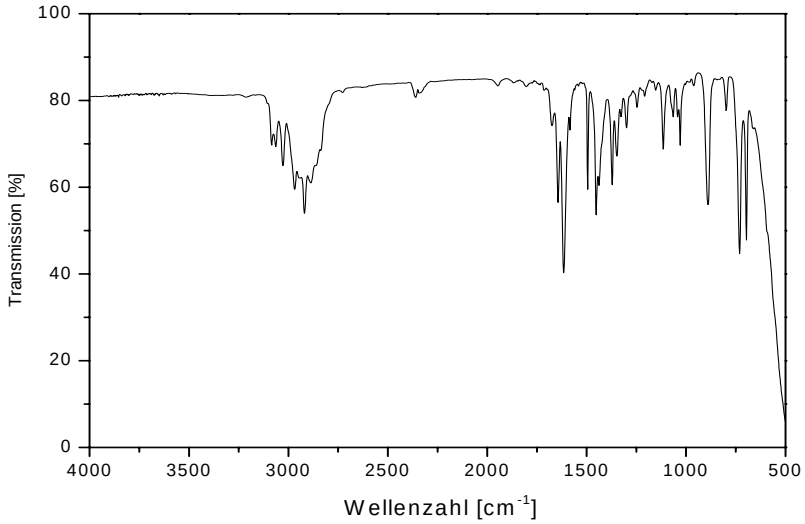
δ (ppm)	Multiplicity	Number of H	Assignment
1.77	s	3	C**H$_3$**
1.96	s	3	C**H$_3$**
2.0 - 2.6	m	4	C**H$_2$** ring
2.90	m	1	tertiary H
4.69	m	2	= N – C**H$_2$** – Ph
4.80	m	2	C**H$_2$** = C
6.29	m	1	–C**H** = C ring
7.2 - 7.5	m	5	C**H** arene

^{13}C NMR spectrum of the pure product (250 MHz, $CDCl_3$)

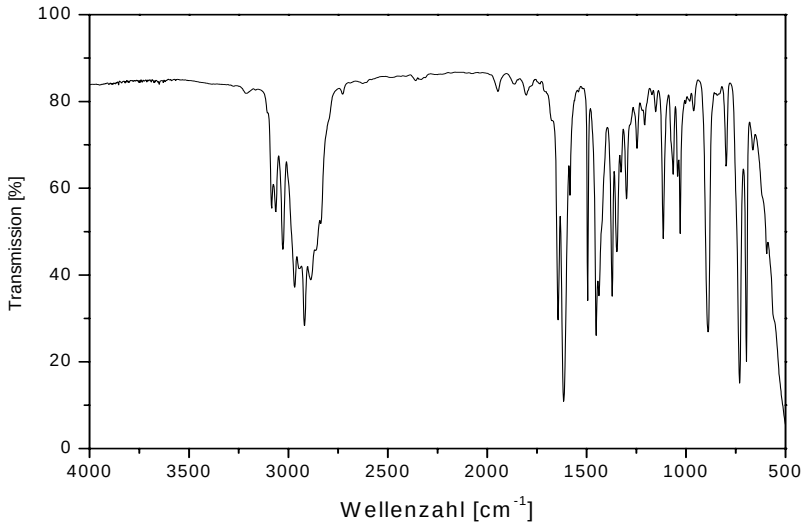


δ (ppm)	Assignment
18.4	**C**H_3
20.7	**C**H_3
30.7	**C**H_2 ring
32.1	**C**H_2 ring
41.7	**C**H – C (CH_3) = CH_2 ring
54.0	**C**H_2 – N =
110.0	**C**H_2 = C
126.4	**C**H arene
127.5	**C**H arene
128.3	**C**H arene
134.2	**C**H = C ring
135.8	CH = **C** (CH_3)– C ring
140.9	$\mathbf{C}_{quart}$ arene
148.1	CH_2 = **C** (CH_3) – C
167.5	**C** = N ring
76.5-77.5	solvent

IR spectrum of the crude product (film)



IR spectrum of the pure product (film)



(cm^{-1})	**Assignment**
3080, 3070, 3030	C – H – valence, arene
2970, 2920	C – H – valence, alkene
1640, 1620	C = C – and C = N – valence
1580, 1500	C = C – valence, arene