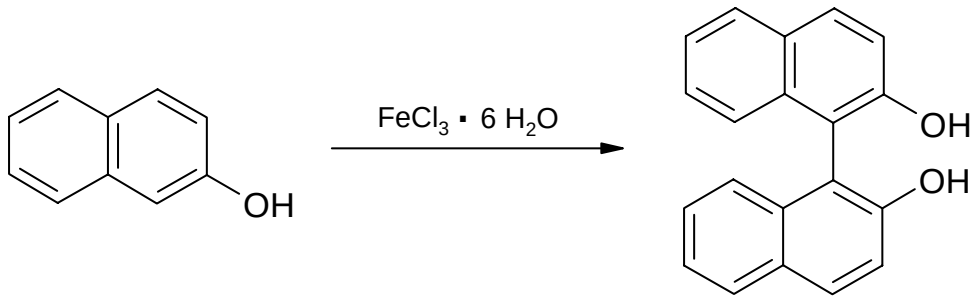
4016 Synthesis of (±)-2,2'-dihydroxy-1,1'-binaphthyl (1,1'-bi-2-naphthol)



$C_{10}H_7OH$		$C_{20}H_{14}O_2$
(144.2)	(270.3)	(286.3)

Classification

Reaction types and substance classes
oxidative coupling
naphthol, aromatics

Work methods
heating under reflux, stirring with magnetic stir bar, removal of water by azeotropic distillation, filtering, evaporating with rotary evaporator, heating with oil bath

batch scale of 100 mmol, additional:
stirring with KPG-stirrer, heating with regulatable heating mantle as alternative to oil bath

Instruction (batch scale 10 mmol)

Equipment
250 mL two-neck flask, reflux condenser, addition funnel with pressure balance and elongated outlet, 100 mL round bottom flask, heatable magnetic stirrer, magnetic stir bar, Buechner funnel (Ø = 5.5 cm), suction flask, water separator, desiccator, oil bath

Substances

2-naphthol (mp 122-123 °C)	1.44 g (10.0 mmol)
iron(III) chloride hexahydrate	2.70 g (10.0 mmol)
toluene (bp 111 °C)	about 30 mL
water	120 mL

Reaction

The reaction apparatus consists of a 250 mL two-neck flask with magnetic stir bar, a reflux condenser and an addition funnel with elongated outlet, which dips into the reaction solution in the flask. An oil bath serves as heating source.

In the reaction flask 1.44 g (10.0 mmol) 2-naphthol are dissolved in 100 mL water under stirring and heating to boiling at an oil bath temperature of 130 °C. Under strong stirring, the solution of 2.70 g (10.0 mmol) iron(III) chloride hexahydrate in 20 mL water is slowly transferred from the addition funnel within a period of 20 minutes directly into the reaction solution. Then it is stirred for one further hour at an oil bath temperature of 100 °C.

Work up

From the hot reaction solution the precipitated solid is sucked off over a Buechner funnel. The solid is rinsed with 20 mL water back into the reaction flask, stirred and heated under ref1ux for 10 minutes, and then again sucked off. For purification and removal of residual water the so obtained crude product is heated with 30 mL toluene under reflux and under stirring with a magnetic stir bar in a 100 mL round bottom flask with a water separator for 2 hours. After cooling down to room temperature, the flask is stored in the refrigerator for crystallization. The precipitated product is sucked off and dried in the desiccator.

Yield: 0.930 g (3.25 mmol, 66%); mp 216 °C

A further crystal fraction can be obtained through evaporating the mother liquor at a rotary evaporator to 50% of its volume and again cooling in the refrigerator.

Yield: 0.110 g (0.384 mmol, 8%); mp 212 °C

Total yield: 1.04 g (3.63 mmol, 73%); light-brown solid

Comments

The product is used as educt in NOP 4014.

Waste management

Waste disposal

Waste	Disposal
aqueous phases	solvent water mixtures, containing halogen
mother liquor (toluene)	organic solvents, halogen free

Time

5-6 hours

Break

Before heating at the water separator

Degree of difficulty

Medium

Instruction (batch scale 100 mmol)

Equipment

2 L three-neck flask, reflux condenser, addition funnel with pressure balance and elongated outlet, 500 mL round bottom flask, KPG-stirrer, Buechner funnel (Ø = 10 cm), suction flask, heatable magnetic stirrer, magnetic stir bar, water separator, desiccator, oil bath, regulatable heating mantle as alternative to oil bath

Substances

2-naphthol (mp 122-123 °C)	14.4 g (100 mmol)
iron(III) chloride hexahydrate	27.0 g (100 mmol)
toluene (bp 111 °C)	about 200 mL
water	1.5 L

Reaction

The reaction apparatus consists of a 2 L three-neck flask with KPG stirrer, a reflux condenser and an addition funnel with elongated outlet, which dips into the reaction solution in the flask. As heating source serves an oil bath or alternatively a regulatable heating mantle.
In the reaction flask 14.4 g (100 mmol) 2-naphthol are dissolved in 1 L water under stirring and heating to boiling at an oil bath temperature of 130 °C. Under strong stirring, the solution of 27.0 g (100 mmol) iron(III) chloride hexahydrate in 200 mL water is slowly transferred from the addition funnel within a period of one hour directly into the reaction solution. Then it is stirred for one further hour at an oil bath temperature of 100 °C.

Work up

From the hot reaction solution the precipitated solid is sucked off over a Buechner funnel. The solid is rinsed with 500 mL water back into the reaction flask, stirred and heated under ref1ux for 10 minutes, and then again sucked off. For purification and removal of residual water the so obtained crude product is heated with 200 mL toluene under reflux and under stirring with a magnetic stir bar in a 500 mL round bottom flask with a water separator for 2 hours. After cooling down to room temperature, the flask is stored in the refrigerator for crystallization. The precipitated product is sucked off and dried in the desiccator.
Yield: 9.80 g (34.2 mmol, 68%); mp 216 °C, light-brown solid

To check the completeness of crystallization, the mother liquor is evaporated at a rotary evaporator to 50% of its volume and cooled again in the refrigerator

Comments

The product is used as educt in NOP 4014.

Waste management

Waste disposal

Waste	Disposal
aqueous phases	solvent water mixtures, containing halogen
mother liquor (toluene)	solvent, halogen free

Time
6-7 hours

Break
Before heating at the water separator

Degree of difficulty
Medium

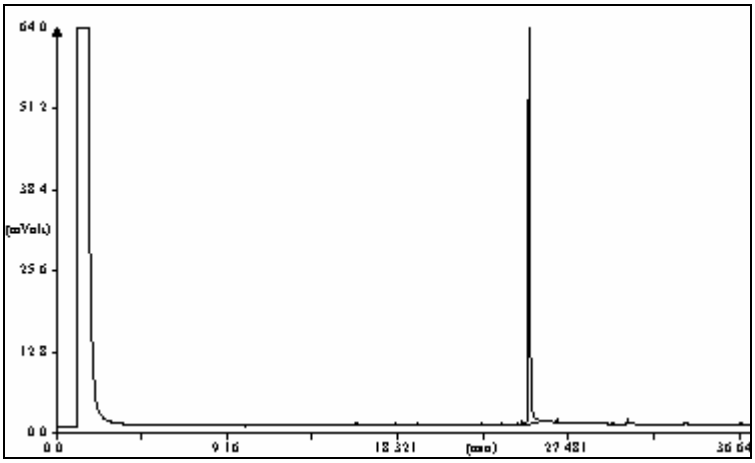
Analytics

GC-conditions:

column:	DB-1, 28 m, internal diameter 0.32 mm, film 0.25 µm
inlet:	on-column-injection
carriergas:	hydrogen (40 cm/s)
oven:	90 °C (5 min), 10 °C/min at 240 °C (30 min)
detector:	FID, 270 °C

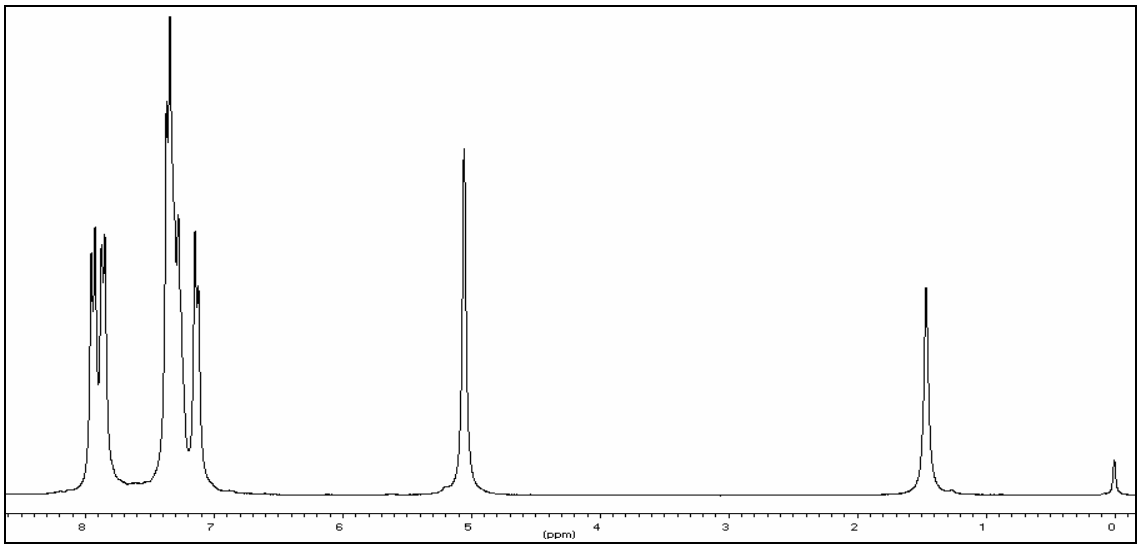
Percent concentration was calculated from peak areas.

GC of the crude product

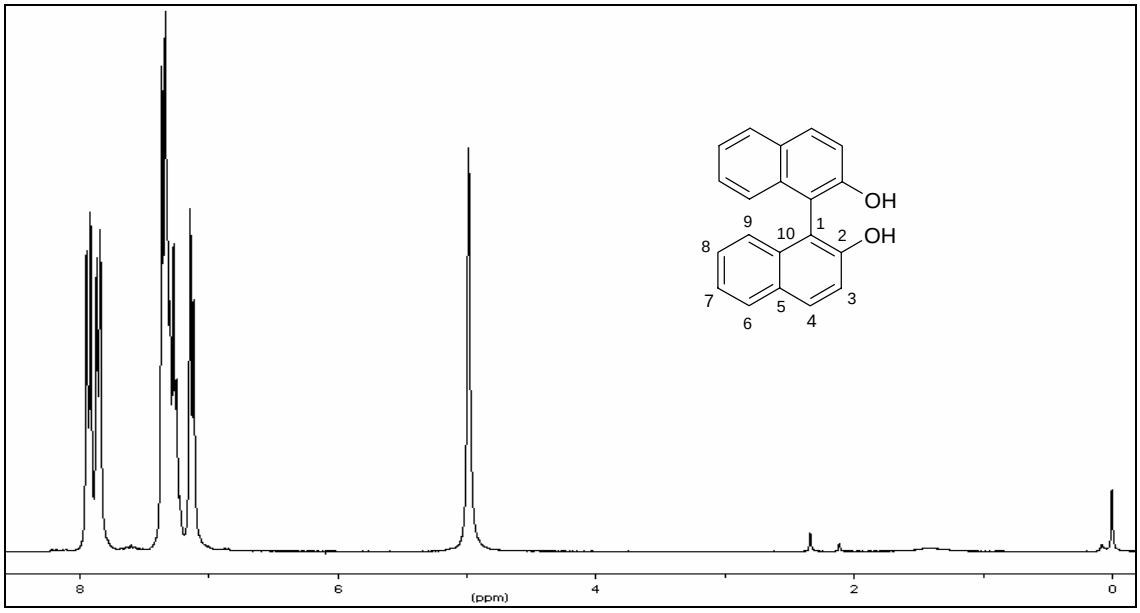


Retention time (min)	Substance	Peak area%
25.39	product	97.8
	impurities	< 1.2

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

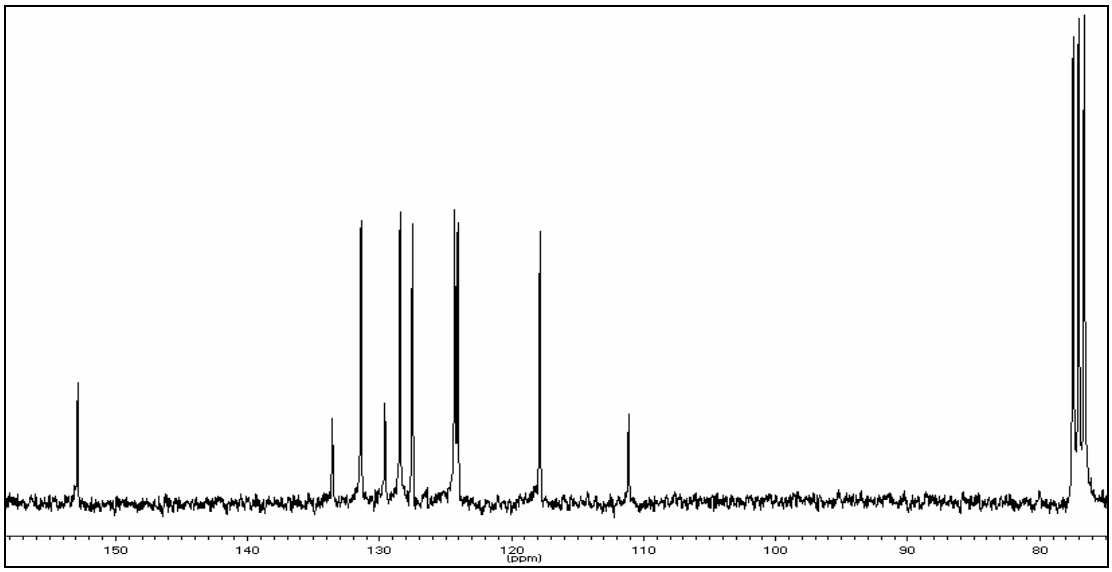


^{1}H NMR spectrum of the pure product (300 MHz, $CDCl_3$)

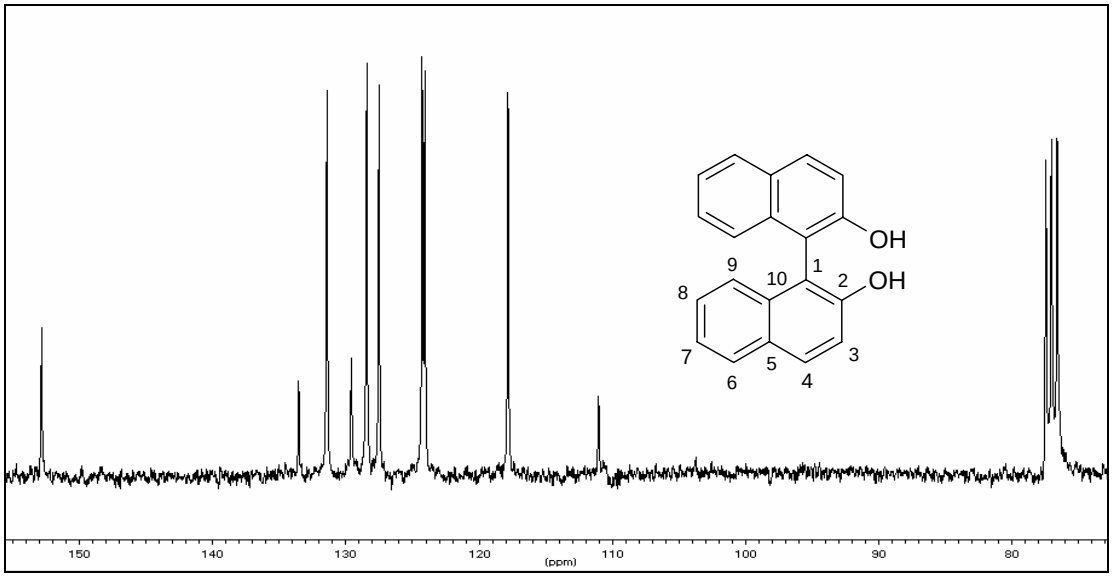


δ (ppm)	Multiplicity	Number of H	Assignment
5.05	s	2	OH
7.13	d	2	3-H
7.40-7-21	m	6	7-H, 8-H, 9-H
7.85	d	2	4-H (6-H)
7.93	d	2	6-H (4-H)

^{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
152.8	C-2
133.5	C-10
131.4	C-5
129.6	C-4
128.4	C-6
127.5	C-8
124.2	C-9
124.0	C-7
117.8	C-3
111.0	C-1
76.5-77.5	solvent