



Synthesis and characterization of optically active cyclic 6,6'-dinitro-1,1'-binaphthyl-2,2'-diethers

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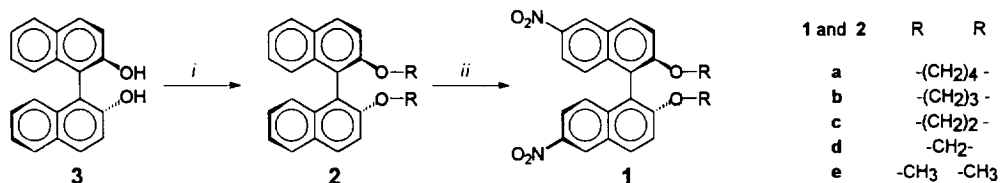
Abstract: A series of racemic and enantiomerically pure 6,6'-dinitro-1,1'-binaphthyl-2,2'-diethers **1** have been synthesized by the nitration of the corresponding cyclic ethers and both the reactivity of nitration and the (chir)optical properties proved to be very sensitive for the chain length of the ether bridge. © 1997 Elsevier Science Ltd

Introduction

The chirality of 1,1'-binaphthyls is often used in a large variety of applications, e.g. in chiral catalysts.¹ More recently, this type of molecule substituted with electron-donating and -accepting groups has been investigated for their interesting nonlinear optical properties.^{2,3} The dihedral angle between the two naphthyl fragments of the 1,1'-binaphthyl-2,2'-diol unit can be fixed by using a bridging chain between the two phenolic positions, as is demonstrated for a number of acetals.⁴ As a result, the optical properties of these systems changed drastically⁵ and it is suggested that the charge-transfer properties are different for open chains and bridging chains.^{2,3} In our effort to understand the influence of chirality on nonlinear optical properties⁶ and to study the conformational dependence on the length of the bridging chain, we have synthesized a series of cyclic 6,6'-dinitro-1,1'-binaphthyl-2,2'-diethers **1**.

Results and discussion

(*RS*)-, (*R*)- and (*S*)-6,6'-dinitro-1,1'-binaphthyl 2,2'-ethers **1** were prepared *via* nitration of the corresponding 1,1'-binaphthyl 2,2'-ethers **2** (cf. Scheme 1, only *R* shown). The latter compounds were prepared from 1,1'-binaphthol **3** by adaptation of a literature procedure (cf. Table 1).⁷ Contrary to an earlier report⁵, no racemization was observed in the etherification reaction of (*R*)-(+)- and (*S*)-(–)-binaphthol **3** when using DMF as solvent, as was evident from HPLC analysis (Pirkle column). Nitrations of **2** were allowed to proceed, until 400 MHz ¹H NMR indicated more than 95% selectivity for the formation of dinitro products.



Scheme 1. Reagents and conditions (only *R* shown): *i*, X(CH₂)_nX (X=Br for **2a** and **2b**, X=OTs for **2c** and X=I for **2d**); K₂CO₃, DMF, 80°C and MeI, K₂CO₃, DMF, 50°C for **2e**; *ii*, HNO₃, HOAc, 16 h at room temp. for **1a** and **1e**, 16 h at room temp., then 2 h at 80°C for **1b**, 48 h at 80°C for **1c**, 168 h at 80°C for **1d**.

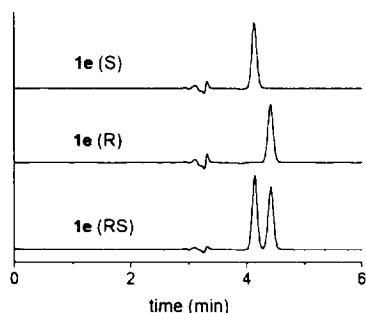
The reactivity of **2** towards nitration decreased with decreasing length of the connecting carbon bridge (Scheme 1, *ii*). The selectivity for formation of the desired 6,6'-dinitro product **1** was determined

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Table 1. Synthesis of 1,1'-binaphthyl 2,2'-diethers **2** and their 6,6'-dinitro derivatives **1**

	n	Compound 2			Compound 1			
		yield ^a (%)	^R [α] _D ^b	^S [α] _D ^b	selectivity ^c (%)	yield ^a (%)	^R [α] _D ^b	^S [α] _D ^b
a	4	76	-217	+217	37	24	-558	+558
b	3	77	-431	+431	14	4	-734	+734
c	2	63	-523	+523	50	44	-753	+753
d	1	80	-779	+779	5	2	-998	+998
e	-	84	+54	-54	-	7	-53±10	- ^d

a) Average yields after column chromatography, followed by crystallization. b) At 27 °C (c=1 [except **1e**: c=0.06], CHCl₃); average of 3-5 measurements, the error is ±1. c) As determined by 400 MHz ¹H NMR. d) Not enough compound left for an accurate measurement.

**Figure 1.** HPLC chromatograms for **1e** (*R*), (*S*) and (*RS*).

with ¹H NMR spectroscopy of the mixture (see experimental section). A remarkable effect was found as the selectivity was highest for the compounds with an even number of carbon atoms in the connecting bridge (**2a** and **2c**, Table 1). For **2b** and **2d** a preferred substitution at the 3-position took place. The dimethoxy compound **1e** could only be prepared in a two-step nitration, otherwise the undesired isomers could not be removed. All 6,6'-dinitro-1,1'-binaphthyl 2,2'-ethers **1** were purified by column chromatography, followed by crystallization. HPLC analysis (Chiralpack OT) of the (*R*)- and (*S*)-6,6'-dinitro products **1**, obtained after column chromatography and before crystallization, indicated that no racemization had occurred during the nitration. In Figure 1 a typical HPLC chromatogram is shown for (*R*)-, (*S*)- and (*RS*)-**1e**.

The strong decrease in reactivity towards nitration in the series of binaphthyl ethers **1a** to **1d** may be explained by assuming that the ether oxygens become progressively less capable of donating electrons into the aromatic ring systems and thereby of stabilizing intermediates in electrophilic aromatic substitution. For the 6,6'-dinitro-1,1'-binaphthyl 2,2'-ethers **1** this implies that the extent of charge-transfer from the ether oxygens to the nitro groups would also be decreased by shortening the length of the connecting carbon bridge.

Evidence for this notion was found by recording the UV spectra of compounds **1** (Figure 2). The λ_{max} at 260 and 280 nm may be attributed to naphthalene transitions, while the λ_{max} at 353–363 nm stems from the nitro group. These maxima show little positional variation. However, the position of a fourth band, corresponding with the charge-transfer maximum λ_{CT}, is gradually shifted from 332 nm for **1a** to 306 nm for **1d**. The λ_{CT} of **1a**–**1e** may be compared with those of 2-methoxy-6-nitronaphthalene **4** and 2-nitronaphthalene **5**. While the λ_{CT} of **1a** and **1e** compares favorably with that of **4**, indicating a significant extent of charge-transfer, the λ_{CT} of **1c** and **1d** are approximately

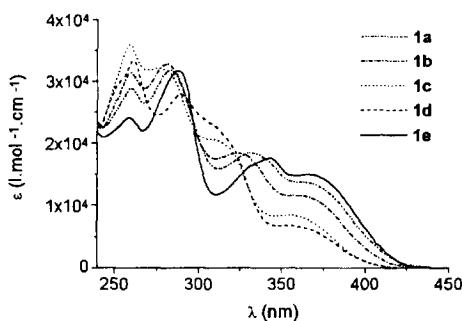


Figure 2. UV Spectra of (*S*)-6,6'-dinitro-1,1'-binaphthyl-2,2'-diethers **1**, as recorded in CHCl₃.

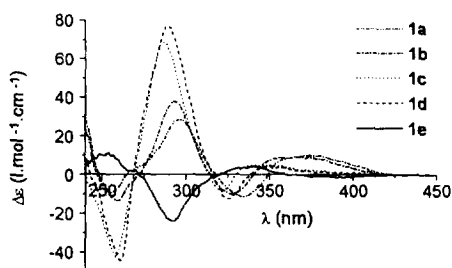


Figure 3. CD Spectra of (*S*)-6,6'-dinitro-1,1'-binaphthyl-2,2'-diethers **1**, as recorded in CHCl₃.

equal to that of **5**, indicating little, if any, donation by the ether oxygens in **1c** and **1d**. The λ_{CT} of **1b** is intermediate in nature. Thus, by decreasing the length of the connecting carbon bridge in **1** the extent of charge-transfer is strongly reduced.

The CD spectra of (*S*)-6,6'-dinitro-1,1'-binaphthyl 2,2'-ethers **1** are presented in Figure 3. Evidently, the extent of chirality is strongly increased by shortening the length of the connecting carbon bridge (see also $[\alpha]$ in Table 1). Most remarkable, open chain **1e** shows low specific rotations and even opposite CD Cotton effects. This can be the result of more conformational flexibility in **1e**, while in **1a–1d** the torsional angle between the naphthalene rings is fixed. This rationalization is in agreement with AM1 and PM3 calculations.

Conclusion

With the series of bridged push-pull binaphthyls, we have shown that the length of the ether bridge dramatically influences the character of the electron-donating capability of the ether. This dependence has profound effect in both the chemistry and the absorption data. In separate papers we discussed the nonlinear optical properties in connection with semi-empirical calculations.^{8,9}

Experimental

General

All chemical reagents were of the highest purity commercially available and used as received. Regular and flash column chromatography was performed using Merck silica gel 60 (0.063–0.200 mm and 0.040–0.063 mm respectively). ¹H and ¹³C NMR spectra were taken on a Bruker AM 400 spectrometer operating at 400.1 and 100.6 MHz respectively. Melting point determinations were done on a Jenaval optical microscope equipped with a Linkam THMS 600 hotstage and given uncorrected.

Synthesis

All syntheses of binaphthalenes were performed with both enantiomers as well as with the racemic compound, but only described for the racemic compound. Enantiomeric purity was checked with HPLC as described in the text. 2-Methoxy-6-nitronaphthalene **4** was prepared by amination¹⁰ of the known Grignard reagent derived from 6-bromo-2-methoxynaphthalene¹¹ to yield 2-amino-6-methoxynaphthalene **4a**, followed by oxidation with sodium perborate. The preparation of **2a** is described in detail and the synthesis of **2b–2e** was carried out in a similar fashion using the conditions and reagents as described in the text.

2,2'-(1,4-Butylenedioxy)-1,1'-binaphthalene **2a**⁵

1,1'-Bi-2-naphthol (4.30 g, 15 mmol) and K₂CO₃ (4.56 g, 33 mmol) were stirred in anhydrous DMF (75 ml) at 80°C. 1,4-Dibromobutane (3.56 g, 16.5 mmol) in anhydrous DMF (50 ml) was added dropwise over a period of 1 h after which it was stirred at 80°C for 16h. The reaction mixture was then poured into water (500 ml) and extracted with dichloromethane (3×150 ml). The organic layer was subsequently washed with 0.5 N KOH, water, 0.5N HCl, water and brine and dried over MgSO₄. Filtration, evaporation of the solvent, column chromatography (dichloromethane/hexane: 3/7) and crystallization from toluene yielded **2a** (3.88 g, 11.40 mmol, 76%).

m.p. 264–267°C (256.5–257.5°C)⁴; Elem. anal. found (calc.): C 84.80 (84.68), H 5.94 (5.92); ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, J=9.0 Hz, 2H, H-4), 7.85 (dd, J=1.3 Hz, J=8.1 Hz, 2H, H-5), 7.49 (d, J=9.0 Hz, 2H, H-3), 7.32 (ddd, J=1.3 Hz, J=6.8 Hz, J=8.1 Hz, 2H, H-6), 7.18 (ddd, J=1.3 Hz, J=6.8 Hz, J=8.5 Hz, 2H, H-7), 7.09 (dd, J=1.3 Hz, J=8.5 Hz, 2H, H-8), 4.52 (ddd, J=2.7 Hz, J=4.8 Hz, J=11.4 Hz, 2H, OCH₂), 4.10 (ddd, J=2.0 Hz, J=9.5 Hz, J=11.4 Hz, 2H, OCH₂), 1.79–1.89 (m, 2H, OCH₂CH₂), 1.67–1.77 (m, 2H, OCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 153.3 (C_q), 134.1 (C_q), 129.8 (C_q), 129.4, 127.9, 126.4, 125.8, 124.0, 122.4 (C_q), 117.4, 70.3 (OCH₂), 25.3 (OCH₂CH₂).

2,2'-(1,3-Propylenedioxy)-1,1'-binaphthalene **2b**⁵

Yield: 77%; m.p. (cryst. from toluene/hexane: 1/1) 280–284°C (272.5–273.5°C)⁴; Elem. anal. found (calc.): C 84.93 (84.64), H 5.55 (5.56); ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, J=8.9 Hz, 2H, H-4), 7.88 (dd, J=1.3 Hz, J=8.2 Hz, 2H, H-5), 7.46 (d, J=8.9 Hz, 2H, H-3), 7.36 (ddd, J=2.3 Hz, J=5.7 Hz, J=8.1 Hz, 2H, H-6), 7.21–7.27 (m, 4H, H-7 and H-8), 4.40 (dt, J=4.5 Hz, J=11.8 Hz, 2H, OCH₂), 4.33 (dt, J=5.6 Hz, J=11.8 Hz, 2H, OCH₂), 1.96 (tt, J=4.5 Hz, J=5.6 Hz, 2H, OCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 154.6 (C_q), 133.6 (C_q), 130.4 (C_q), 129.6, 128.1, 126.3, 126.1, 124.2, 123.9 (C_q), 119.2, 71.9 (OCH₂), 30.6 (OCH₂CH₂).

2,2'-(1,2-Ethylenedioxy)-1,1'-binaphthalene **2c**^{5,7}

Yield: 63%; m.p. (cryst. from toluene/hexane: 1/1) 233–237°C (197.5–198.5°C)⁴; Elem. anal. found (calc.): C 84.65 (84.59), H 5.21 (5.16); ¹H NMR (400 MHz, CDCl₃): δ 7.98 (d, J=8.8 Hz, 2H, H-4), 7.89 (dd, J=1.3 Hz, J=8.2 Hz, H-5), 7.45 (d, J=8.8 Hz, 2H, H-3), 7.39 (ddd, J=2.1 Hz, J=5.8 Hz, J=8.2 Hz, 2H, H-6), 7.26 (dd, J=1.4 Hz, J=8.2 Hz, 2H, H-8), 7.22 (ddd, J=1.2 Hz, J=5.8 Hz, J=8.2 Hz, 2H, H-7), 4.41 (m, 2H, OCH₂), 4.19 (m, 2H, OCH₂); ¹³C NMR (100 MHz, CDCl₃): δ 156.5 (C_q), 132.9 (C_q), 130.9 (C_q), 130.7, 128.0, 127.0, 126.2, 124.7, 124.2 (C_q), 122.4, 72.9 (OCH₂).

2,2'-Methylenedioxy-1,1'-binaphthalene **2d**⁵

Yield: 80%; m.p. (cryst. from toluene/hexane: 1/1) 185–189°C (178.5–179.5°C)⁴; Elem. anal. found (calc.): C 84.52 (84.54), H 4.75 (4.73); ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, J=8.7 Hz, 2H, H-4), 7.88 (dd, J=0.6 Hz, J=8.1 Hz, 2H, H-5), 7.51 (dd, J=0.6 Hz, J=8.5 Hz, 2H, H-8), 7.44 (d, J=8.8 Hz, 2H, H-3), 7.40 (ddd, J=1.2 Hz, J=6.4 Hz, J=8.1 Hz, 2H, H-6), 7.25 (ddd, J=1.4 Hz, J=7.0 Hz, J=8.5 Hz, 2H, H-7), 5.66 (s, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 151.2 (C_q), 132.1 (C_q), 131.7 (C_q), 130.3, 128.3, 126.8, 126.0 (C_q), 126.0, 124.9, 120.9, 103.1 (OCH₂).

2,2'-Dimethoxy-1,1'-binaphthalene 2e⁵

Yield: 84%; m.p. (cryst. from toluene/hexane: 1/1) 200–204°C (198–202°C)¹²; Elem. anal. found (calc.): C 84.07 (84.05), H 5.81 (5.77); ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, J=9.0 Hz, 2H, H-4), 7.85 (dd, J=0.9 Hz, J=8.1 Hz, 2H, H-5), 7.44 (d, J=9.0 Hz, 2H, H-3), 7.30 (ddd, J=1.3 Hz, J=6.7 Hz, J=8.1 Hz, 2H, H-6), 7.19 (ddd, J=1.3 Hz, J=6.7 Hz, J=8.4 Hz, 2H, H-7), 7.10 (dd, J=1.3 Hz, J=8.4 Hz, 2H, H-8), 3.74 (s, 6H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 154.9 (C_q), 134.0 (C_q), 129.4, 129.2 (C_q), 127.9, 126.3, 125.2, 123.5, 119.5 (C_q), 114.2, 56.9 (OCH₃).

The preparation of **1a** is described in detail and the synthesis of **1b–1e** was carried out in a similar fashion using the conditions and reagents as described in the text.

2,2'-(1,4-Butylenedioxy)-6,6'-dinitro-1,1'-binaphthalene 1a

2a (3.4 g, 10 mmol) was suspended in glacial acetic acid (50 ml). Nitric acid (100%, 1.29 g, 20.5 mmol) in glacial acetic acid (2 ml) was added dropwise in 5 minutes. The resulting mixture was then stirred at room temperature for 16 hours after which it was poured into water (100 ml) and extracted with dichloromethane (3×50 ml). The organic layer was then washed with 1 N KOH, water and brine and dried over MgSO₄. Filtration and evaporation of the solvent yielded a yellow solid. The mono- and dinitro isomers were isolated by flash column chromatography (gradient: dichloromethane/hexane: 3/7 to 1/1; elution took place in the following order: 3-, 6- and 8-mononitro (when still present) and 3,3'-, 3,6'-, 6,6'-, 3,8'-, 6,8'- and 8,8'-dinitro) and characterized by ¹H NMR spectroscopy. These data were then used to analyze the composition of the crude reaction mixture. Crystallization of the 6,6'-dinitro isomer from toluene/hexane (1/1) yielded pure **1a** (1.03 g, 2.39 mmol, 24%).

m.p. >300°C; Elem. anal. found (calc.): C 66.79 (66.97), H 4.18 (4.22), N 6.41 (6.51); ¹H NMR (400 MHz, CDCl₃): δ 8.87 (d, J=2.3 Hz, 2H, H-5), 8.19 (d, J=9.1 Hz, 2H, H-4), 7.98 (dd, J=2.3 Hz, J=9.5 Hz, 2H, H-7), 7.65 (d, J=9.1 Hz, 2H, H-3), 7.14 (d, J=9.5 Hz, 2H, H-8), 4.56–4.62 and 4.18–4.28 (each m, 4H, OCH₂), 1.82–1.92 (m, 4H, CH₂CH₂); ¹³C NMR (100 MHz, CDCl₃/MeOD: 10/1): δ 157.2 (C_q), 146.9 (C_q), 136.4 (C_q), 132.1, 127.9 (C_q), 126.5, 125.1, 121.0 (C_q), 119.8, 118.9, 70.7 (OCH₂), 25.8 (CH₂CH₂).

2,2'-(1,3-Propylenedioxy)-6,6'-dinitro-1,1'-binaphthalene 1b

Yield: 4%; m.p. (cryst. from toluene/hexane: 1/1) 264–268°C; Elem. anal. found (calc.): C 66.60 (66.35), H 3.91 (3.87), N 6.45 (6.73); ¹H NMR (400 MHz, CDCl₃): δ 8.89 (d, J=2.4 Hz, 2H, H-5), 8.21 (d, J=8.9 Hz, 2H, H-4), 8.04 (dd, J=2.4 Hz, J=9.3 Hz, 2H, H-7), 7.64 (d, J=8.9 Hz, 2H, H-3), 7.29 (d, J=9.3 Hz, 2H, H-8), 4.40–4.51 (m, 4H, OCH₂), 2.00–2.06 (m, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 158.4 (C_q), 144.3 (C_q), 135.8 (C_q), 132.4, 128.7 (C_q), 126.9, 125.2, 123.1 (C_q), 121.2, 120.0, 72.1 (OCH₂), 30.3 (OCH₂CH₂).

2,2'-(1,2-Ethylenedioxy)-6,6'-dinitro-1,1'-binaphthalene 1c

Yield: 44%; m.p. (cryst. from toluene) 242–245°C; Elem. anal. found (calc.): C 65.76 (65.67), H 3.51 (3.51), N 6.71 (6.96); ¹H NMR (400 MHz, CDCl₃): δ 8.89 (d, J=2.3 Hz, 2H, H-5), 8.23 (d, J=8.8 Hz, 2H, H-4), 8.02 (dd, J=2.3 Hz, J=9.4 Hz, 2H, H-7), 7.63 (d, J=8.8 Hz, 2H, H-3), 7.26 (d, J=9.4 Hz, 2H, H-8), 4.48–4.56 and 4.19–4.27 (each m, 4H, OCH₂); ¹³C NMR (100 MHz, CDCl₃): δ 159.6 (C_q), 144.7 (C_q), 135.4 (C_q), 133.3, 129.5 (C_q), 127.9, 124.9, 124.9, 123.8 (C_q), 120.0, 72.8 (OCH₂).

2,2'-Methylenedioxy-6,6'-dinitro-1,1'-binaphthalene 1d

Yield: 2%; m.p. (R) 226–228°C; Elem. anal. found (calc.): C 64.97 (64.95), H 3.43 (3.11), N 6.79 (7.21); ¹H NMR (400 MHz, CDCl₃): δ 8.94 (d, J=2.3 Hz, 2H, H-5), 8.25 (d, J=8.8 Hz, 2H, H-4), 8.09 (dd, J=2.3 Hz, J=9.3 Hz, 2H, H-7), 7.68 (d, J=8.8 Hz, 2H, H-3), 7.50 (d, J=9.3 Hz, 2H, H-8), 5.79 (s, 2H, OCH₂O); ¹³C NMR (100 MHz, CDCl₃): δ 154.5 (C_q), 144.9 (C_q), 134.5 (C_q), 133.0 (C-4), 130.4 (C_q), 127.8, 125.7 (C_q), 125.3, 123.5, 119.9, 103.5 (OCH₂).

2,2'-Dimethoxy-6,6'-dinitro-1,1'-binaphthalene **1e**

Yield: 7%; m.p. >300°C; Elem. anal. found (calc.): C 65.86 (65.35), H 4.04 (3.99), N 6.52 (6.93); ¹H NMR (400 MHz, CDCl₃): δ 8.87 (d, J=2.3 Hz, 2H, H-5), 8.22 (d, J=9.2 Hz, 2H, H-4), 8.00 (dd, J=2.3 Hz, J=9.3 Hz, 2H, H-7), 7.61 (d, J=9.2 Hz, 2H, H-3), 7.13 (d, J=9.3 Hz, 2H, H-8), 3.84 (s, 6H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 158.0 (C_q), 143.6 (C_q), 136.5 (C_q), 132.5, 127.2 (C_q), 126.1, 125.3, 120.1, 118.4 (C_q), 115.2, 56.5 (OCH₂).

2-Amino-6-methoxynaphthalene **4a**

A Grignard reagent was prepared from 2-bromo-6-methoxy-naphthalene (11.86 g, 50.0 mmol) and magnesium (1.34 g, 55.1 mmol) in THF (50 ml) according to a literature procedure.¹¹ This Grignard-suspension was cooled to -70°C and added dropwise to a cooled (-70°C) solution of diphenylphosphorylazide (14.5 g, 52.7 mmol) in THF (400 ml). The resulting mixture was stirred for 1 h at -70°C and then allowed to warm up to -20°C and stirred an additional 40 minutes. After cooling again to -70°C Red-Al® (65 ml ≈ 3.2 M, ≈ 216 mmol) was added dropwise. It was allowed to warm up to 0°C and stirred for 1 h and then stirred an additional 30 minutes at room temperature. Then ice-water (500 ml) was added carefully (H₂ formation) and the resulting suspension was filtered and washed with water. The organic layer was washed with water and then extracted with 0.5 N HCl. Then the water layer was washed with ether and made basic again by the addition of solid KOH. The resulting precipitate was taken up in dichloromethane (500 ml) and the water layer was washed with dichloromethane (2×100 ml). The organic layer was washed with water (2×100 ml), brine (2×100 ml) and dried over K₂CO₃. Filtration, evaporation of the solvent and column chromatography (dichloromethane/methanol: 98:2) yielded **4a** (4.15 g, 24.0 mmol, 48%).

m.p. 151–153°C; ¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, J=8.5 Hz, 1H, H-4), 7.50 (d, J=8.9 Hz, 1H, H-8), 7.06 (dd, J=2.6 Hz, J=8.8 Hz, 1H, H-7), 7.03 (d, J=2.5 Hz, 1H, H-5), 6.95 (d, J=2.1 Hz, 1H, H-1), 6.93 (dd, J=2.3 Hz, J=8.5 Hz, 1H, H-3), 3.87 (s, 3H, OCH₃), 3.69 (br. s, 2H, NH₂); ¹³C NMR (100 MHz, CDCl₃): δ 155.3 (C_q), 142.3 (C_q), 130.2 (C_q), 128.6 (C_q), 127.9, 127.3, 118.9, 118.7, 109.2, 106.1, 55.3 (OCH₃).

2-Methoxy-6-nitronaphthalene **4**

Sodium perborate tetrahydrate (7.3 g, 47.4 mmol) was stirred in acetic acid (30 ml) at 60°C. To this suspension was added dropwise (0.5h) a solution of **4a** (1.73 g, 10.0 mmol) in acetic acid (20 ml). After stirring for 2 h at 60°C the reaction mixture was cooled to 0°C and filtered. The remaining solid was washed with ice-water and diethylether. The two layers were separated, the water layer was extracted with diethylether (2×100 ml) and the combined organic layers were washed with water and dried over MgSO₄. After filtration, evaporation of the solvent and column chromatography (dichloromethane/hexane: 2/8) the resulting solid was taken up into dichloromethane (150 ml) and washed with 1 N KOH (3×50 ml), water (50 ml) and brine (50 ml). Drying over MgSO₄, filtration, evaporation of the solvent and crystallization (ethanol/water: 9/1) yielded **4** (0.33 g, 1.6 mmol, 16%).

m.p. 138.5–139.5°C; ¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, J=2.2 Hz, 1H, H-5), 8.20 (dd, J=2.3 Hz, J=9.0 Hz, 1H, H-7), 7.90 (d, J=9.0 Hz, 1H, H-4), 7.80 (d, J=9.0 Hz, 1H, H-8), 7.27 (dd, J=2.5 Hz, J=9.0 Hz, 1H, H-3), 7.19 (d, J=2.4 Hz, 1H, H-1), 3.97 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 160.7 (C_q), 143.8 (C_q), 137.8 (C_q), 131.5 (C_q), 130.9, 127.8, 124.6, 121.0, 120.0, 105.9, 55.5 (OCH₃).

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