

Supporting information

Isoquinoline- and Piperazinedione-Derived α -Acylamino Peroxide Moieties in Asymmetric Oxidation of Sulphides and Epoxidation of Naphthoquinones

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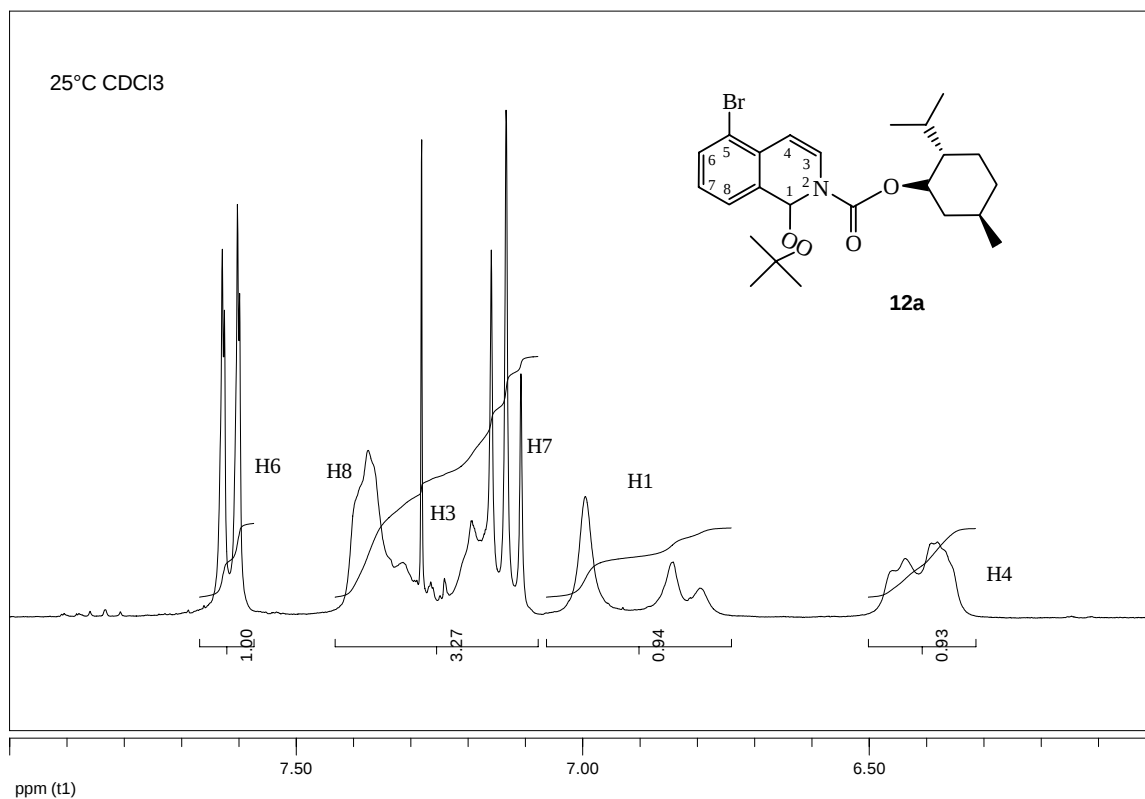
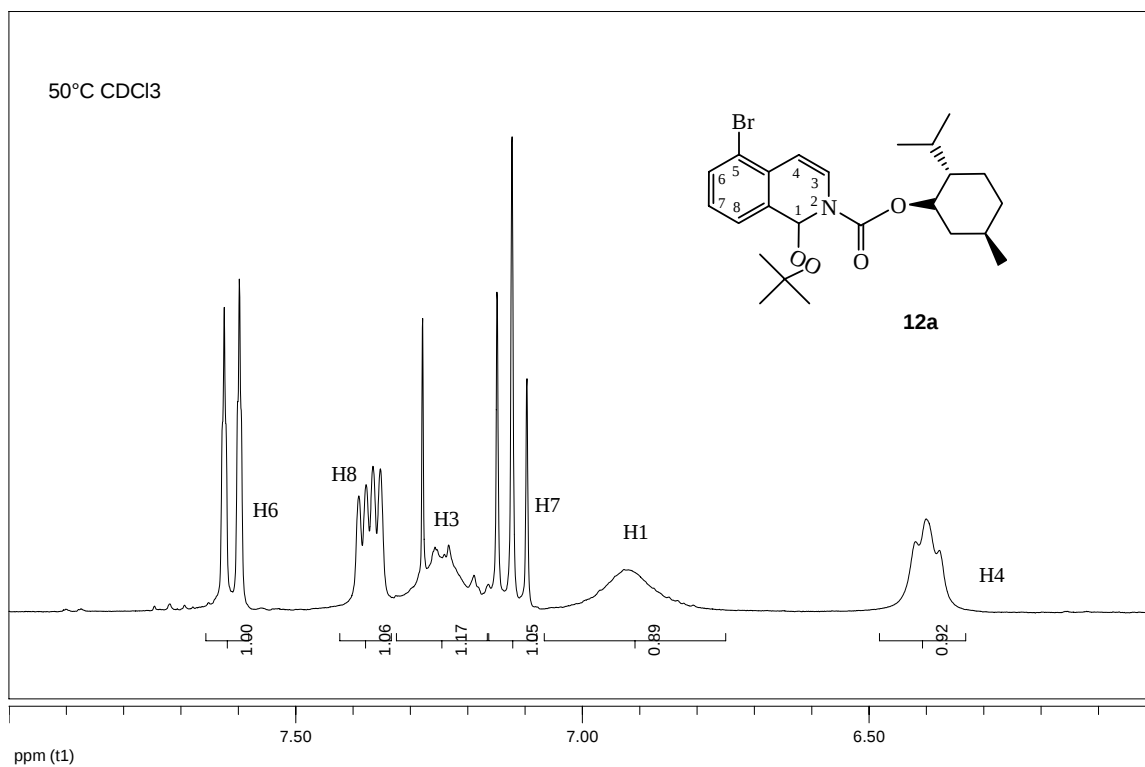
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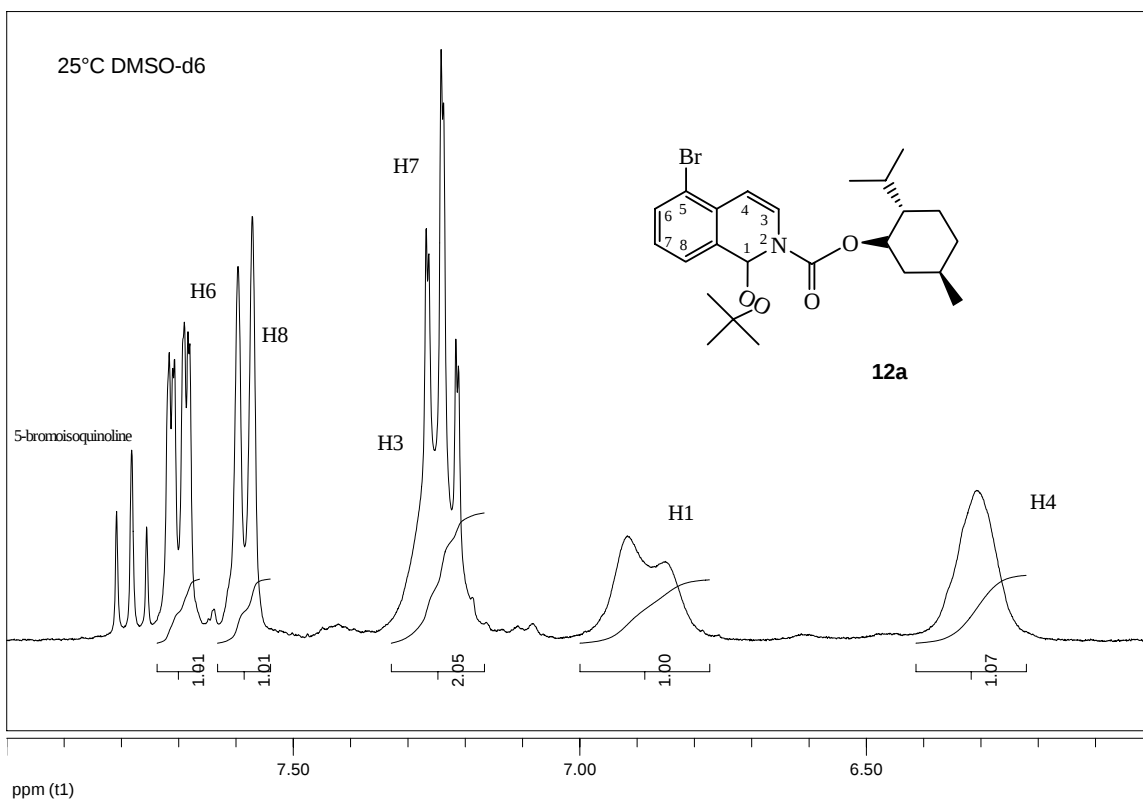
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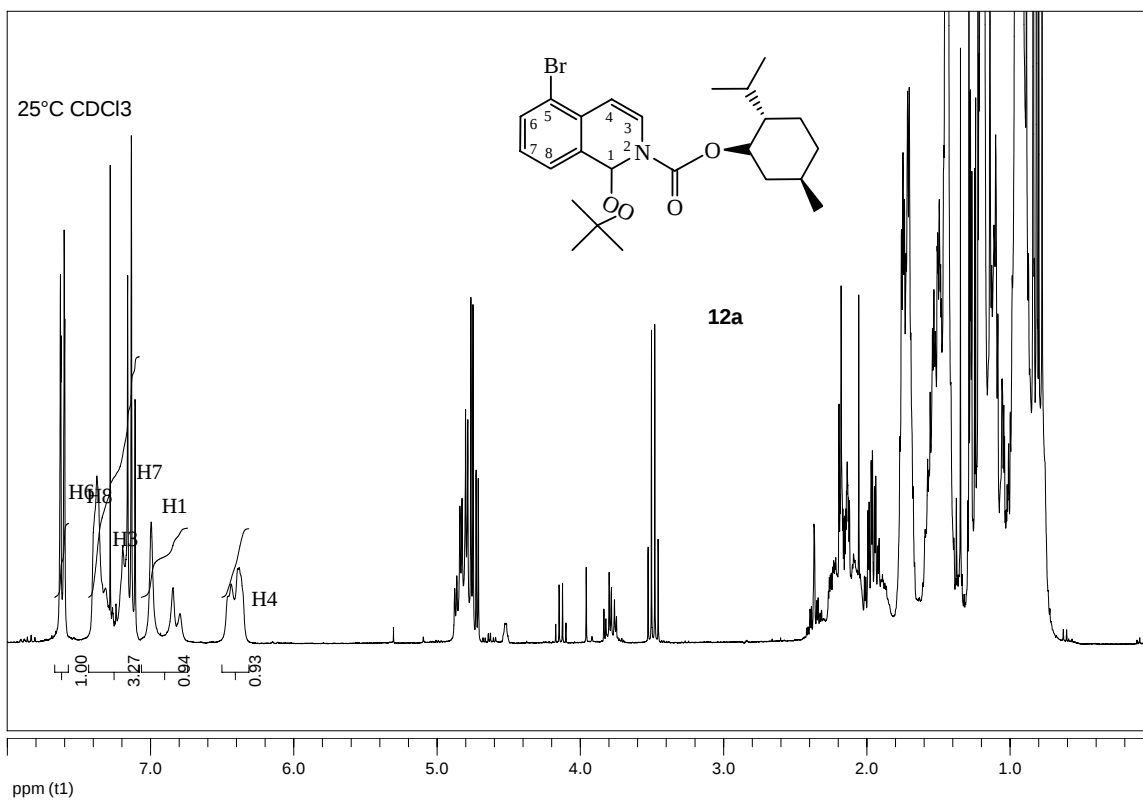
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NMR-Spectra

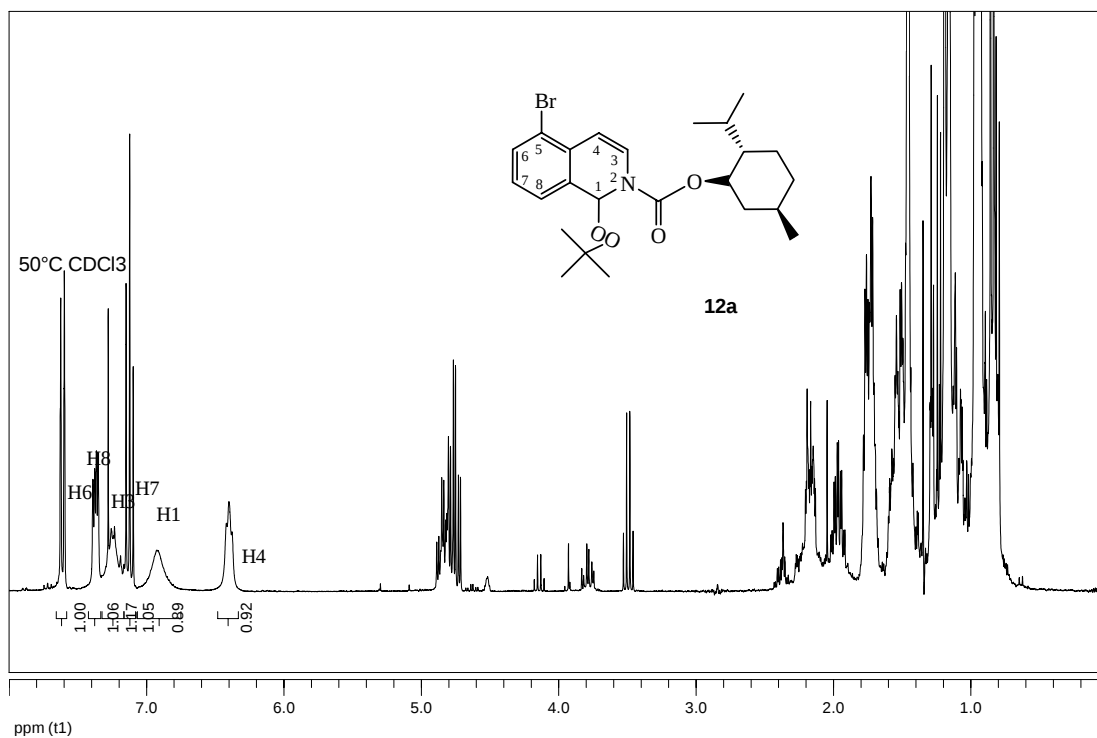
¹H-NMR spectrum in CDCl₃ at 25 °C (part)¹H-NMR spectrum in CDCl₃ at 50 °C (part)



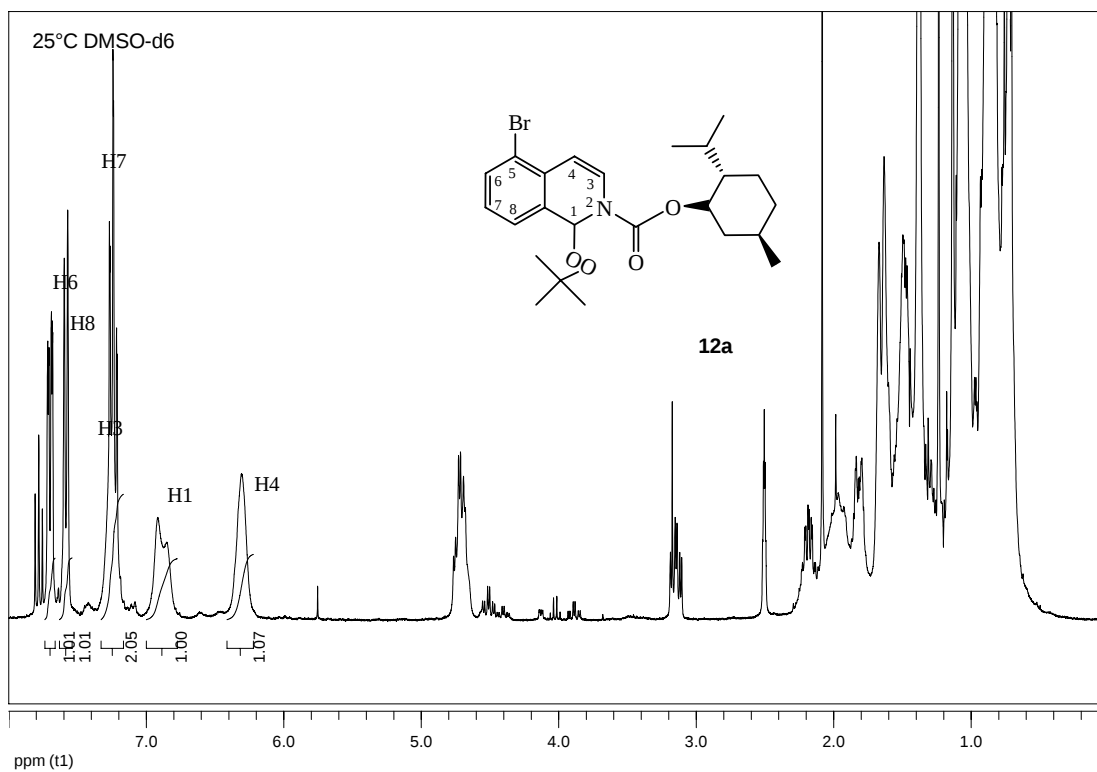
¹H-NMR spectrum in DMSO-d₆ at 25 °C (part)



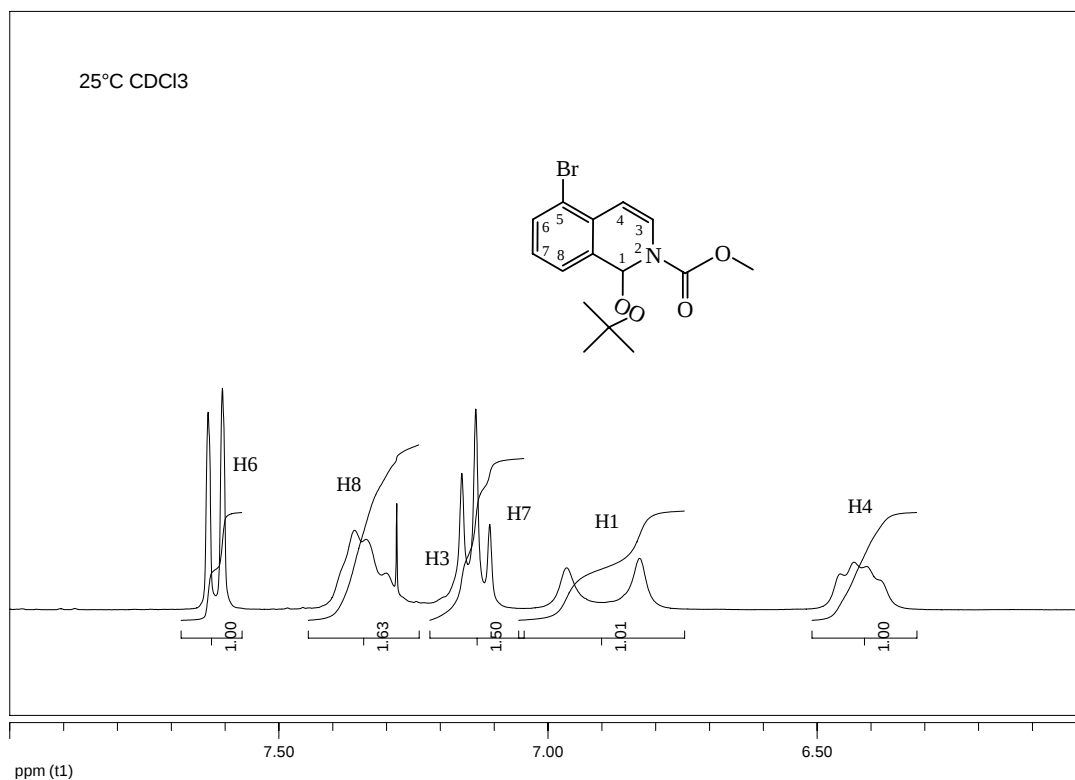
¹H-NMR spectrum in CDCl₃ at 25 °C (total)



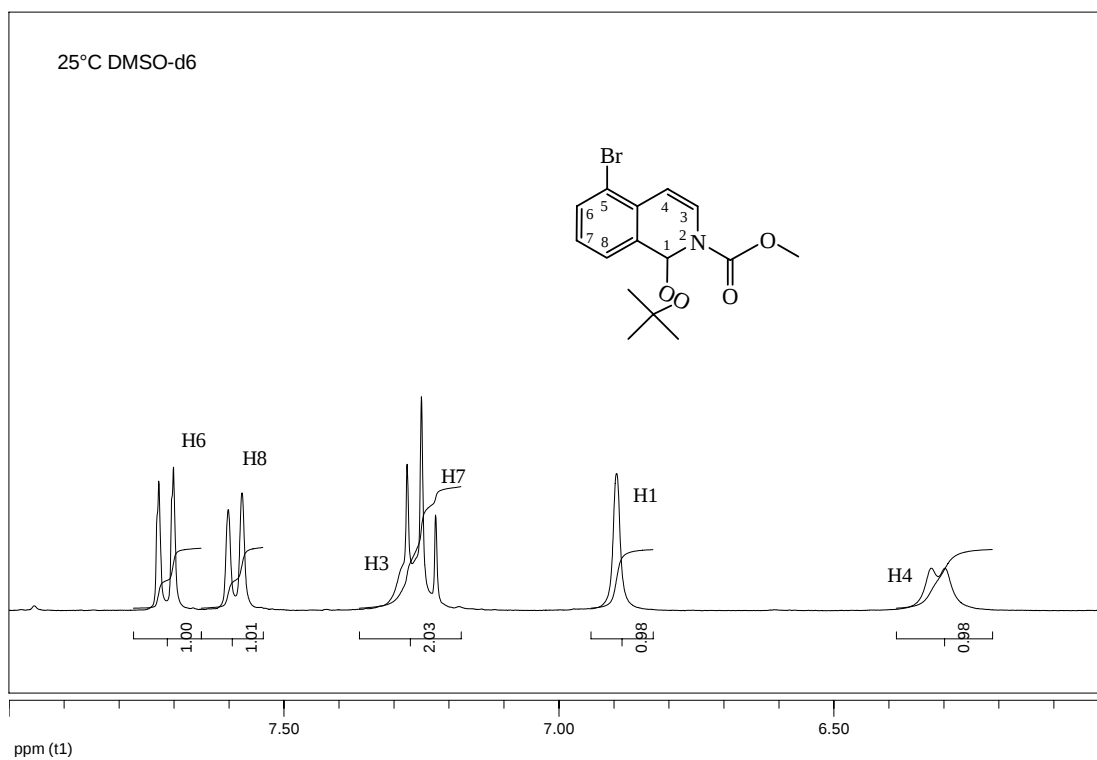
¹H-NMR spectrum in CDCl₃ at 50 °C (total)



¹H-NMR spectrum in DMSO-d₆ at 25 °C (total)



¹H-NMR spectrum of an achiral 2-methyloxycarbonyl peroxide in CDCl₃ at 25 °C (part)



¹H-NMR spectrum of achiral 2-methyloxycarbonyl peroxide in DMSO-d₆ at 25 °C (part)

Table 1. Oxidation of methylphenylsulfide with t-butylhydroperoxide (TBHP) or H₂O₂ in the presence of VO(OiPr)₃

Nr.	Oxidizing reagent	Reaction conditions		ee % (R)-Sulfoxide 2(R)
		Temperature / °C	Equivalents of reagents 7d:8:VO(OiPr)₃:1	
1	TBHP (CH ₂ Cl ₂)	-40	1:1:1:1	2
2	TBHP (CH ₂ Cl ₂)	0	1:1:1:1	4
3	TBHP (CH ₂ Cl ₂)	25	1:1:1:1	6
4	H ₂ O ₂ (eth)	-40	1:1:1:1	2
5	H ₂ O ₂ (eth)	0	1:1:1:1	8
6	H ₂ O ₂ (eth)	25	1:1:1:1	50 ^a
7 ^b	TBHP (CH ₂ Cl ₂)	-40	1:2:1:1	2
8 ^b	TBHP (CH ₂ Cl ₂)	0	1:2:1:1	2
9 ^b	H ₂ O ₂ (eth)	-40	1:2:1:1	2
10 ^{c, d}	H ₂ O ₂ (eth)	0	1:1:1:1	2
11 ^c	H ₂ O ₂ (eth)	0	1:1:1:1	2
12 ^c	H ₂ O ₂ (eth)	0	1:1:1:2	2
13 ^c	H ₂ O ₂ (eth)	0	1:2:1:1	50
14 ^e	H ₂ O ₂ (eth)	0	1:1:1:2	10
15 ^e	H ₂ O ₂ (eth)	0	1:2:1:2	8
16 ^f	H ₂ O ₂ (eth)	0	1:1:1:2	4
17 ^f	H ₂ O ₂ (eth)	0	1:2:1:2	4
18 ^g	H ₂ O ₂ (eth)	0	1:1:1:2	28
19 ^h	H ₂ O ₂ (eth)	0	1:2:1:2	6

^a Opposite configuration of major isomer. ^b H₂O₂ was added before **1**. ^c 4 equ. H₂O₂; ^d VO(OEt)₃.

^e H₂O₂ added dropwise within 3 h. ^f addition of H₂O₂ after 2 h. ^g sequence of addition: **7** + **8**, after 0,5 h VO(OiPr)₃, after 0.5 h **1**, after 0.5 h H₂O₂. ^h H₂O₂ added within 1 h.

Analysis of reaction mixtures

General Remarks. ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, with a Bruker AC 300 in CDCl_3 with TMS as internal standard. Silica gel (0.04–0.063 mm, Merck) was used for preparative column chromatography. Bromoisoquinolines **4a-c** and the substituted 2-methylnaphthoquinones **18** were synthesized according to literature procedures.^[1-6] All other materials were purchased from commercial suppliers.

The EI high resolution mass spectra were recorded on a Varian (MAT 711) at 70 eV and the ESI spectra were recorded on a Finnigan LTQ FT system.

The enantiomeric excesses were determined on a HPLC high pressure gradient system 322 (Kontron) equipped with a K-2800 DAD (Knauer) and a chiral detector by IBZ Messtechnik. Chiracel columns by the Daicel Chemical Industries LTD were used. Mobile phase: *n*-hexane : *i*-propanol.

HPLC-Measuring conditions. Methyl phenyl sulphide OB (50 mm) solvent: 9:1; flow: 2.0 ml/min; S: 0.6 min; SO (R): 1.8 min; SO (S): 2.6 min; SO_2 : 7.7 min. methyl 4-methylphenyl sulphide OB (50 mm) solvent: 9:1; flow: 2.0 ml/min; S: n.b.; SO (R): 1.5 min; SO (S): 3.3 min; SO_2 : 9.9 min. methyl 4-nitrophenyl sulphide OB (50 mm) solvent: 9:1; flow: 2.0 ml/min; S: 1.6; SO (R): 10.4 min; SO (S): 13 min; SO_2 : 33.7 min. methyl 4-chlorophenyl sulphide OB (50 mm) solvent: 9:1; flow: 2.0 ml/min; S: 0.6; SO (R): 1.7 min; SO (S): 2.5 min; SO_2 : 7.4 min. 2-methylnaphthoquinone AD (250 mm) solvent: 9:1; flow: 0.7 ml/min; olefin: 10.1 min; epoxide a: 11.8 min; epoxide b: 12.7 min. 2-*tert*-butyl-naphthoquinone AD (250 mm) solvent: 99:1; flow: 0.7 ml/min; olefin: 7.4 min; epoxide a: 10.2 min; epoxide b: 11.7 min. 2-benzhydryl-naphthoquinone AD (250 mm) solvent: 97:3; flow: 0.7 ml/min; olefin: 15.9 min; epoxide a: 20.3 min; epoxide b: 29.5min.

References

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