Pergamon

Tetrahedron 58 (2002) 233–238

TETRAHEDRON

Nucleophilic aromatic substitution on 1-alkoxy-2-nitronaphthalene by 1-naphthyl Grignard reagents for the synthesis of 2-nitro-1,1′-binaphthyls

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Received 19 September 2001; accepted 16 November 2001

Abstract—Treatment of 1-methoxy-2-nitronaphthalene with 1-naphthyl- and 2-methoxy-1-naphthylmagnesium bromide in diethyl ether–benzene at room temperature provides a facile entry to the corresponding 2-nitro-1,1′-binaphthyls in high yields. Induction of axial chirality into the binaphthyl bond has been achieved by using 1-menthoxy-2-nitronaphthalene as the substrate, giving 2-methoxy-2′-nitro-1,1′-binaphthyl of 78% ee. Also reported is the optical resolution of 2-amino-1,1′-binaphthyls, which can be easily prepared by reduction of the 2-nitro-1,1′-binaphthyls, by preparative LC on a cellulose-derived chiral stationary phase, or on silica gel after conversion into the diastereomeric menthyl carbamates.

1. Introduction

In the past two decades, an increasing attention has been paid to the development of new methods for the construction of 1,1′-binaphthyl framework,[1,2] especially in a non-racemic form, because of the remarkable chiral recognition ability exhibited by this class of atropisomeric binaphthyl derivatives bearing substituents at the 2 and 2′ position. Previously, we reported a convenient synthesis of 1,1′-binaphthyl-2-carboxylates by the reaction of 1-alkoxy-2-naphthoates with 1-naphthyl Grignard reagents.[3] The alkoxy displacement reaction is supposed to proceed via a chelation-assisted conjugate addition of the naphthyl carbanion, followed by elimination of the alkoxide, the net nucleophilic aromatic substitution (S_NAr) process being closely related to the oxazoline-mediated Meyers reaction.[4–6] As we had noticed that the 2-ester or -oxazoline substituent can be replaced by a phosphinoyl[7] or sulfonyl function[8] to carry out the binaphthyl coupling, our next attention was directed toward the possibility to use nitro group as the 2-substituent considering the potential importance of nitroarenes in organic synthesis.[9] Herein, we report facile synthesis of 2-nitro-1,1′-binaphthyls **3** by the reaction of readily available 1-alkoxy-2-nitronaphthalenes **1** with 1-naphthylmagnesium bromides **2**.[10]

Keywords: asymmetric synthesis; biaryls; coupling reactions; nitro compounds.

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2. Results and discussion

2.1. Synthesis of 2-nitro-1,1′-binaphthyls

Although it had been common understanding that the reaction of Grignard reagents with nitro compounds was of little synthetic use because it generally led to complex mixtures of products,[11,12] intensive studies by Bartoli et al. since the later half of 1970's showed that the reaction of *alkyl* Grignard reagents with nitroarenes sometimes proceeds through a 1,4- or 1,6-conjugate manner to give the nuclear addition products selectively, affording a useful synthetic tool even though under specified conditions.[13] Actually, they reported the reaction of 1-methoxy-2-nitronaphthalene (**1a**) with several alkylmagnesium bromides to give the conjugate addition products to the carbon atom bearing the methoxy group.[14] On the contrary, only limited successful results have yet been found in the literature on the reaction of *aryl* Grignard reagents with nitroarenes,[12,15] probably due to the tendency that these reagents essentially undergo reductive 1,2-addition to the nitro function followed by many subsequent reactions to give, in general, intractable products.[16]

We have found, however, that the reaction of nitro naphthalene **1a** with 1.5 equiv. of 2-methoxy-1-naphthylmagnesium bromide (**2a**) proceeds quite smoothly in diethyl ether–benzene at room temperature to give directly 2-methoxy-2′-nitro-1,1′-binaphthyl (**3a**) in an excellent yield (91%) after chromatography on silica gel (Scheme 1), the result being somewhat different from those of the reactions of alkyl Grignard reagents reported by Bartoli et al.

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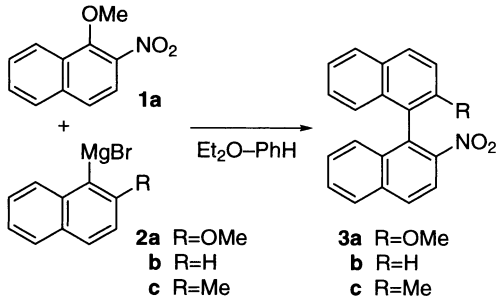
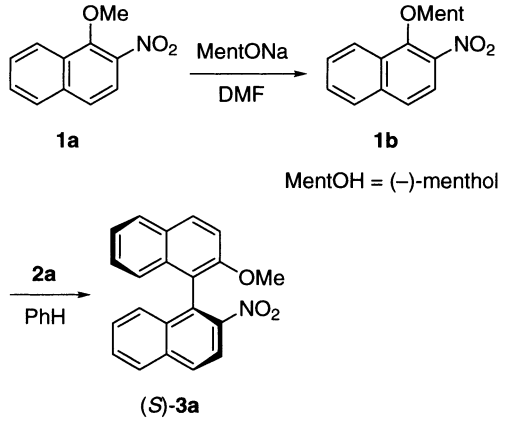


Scheme 1.

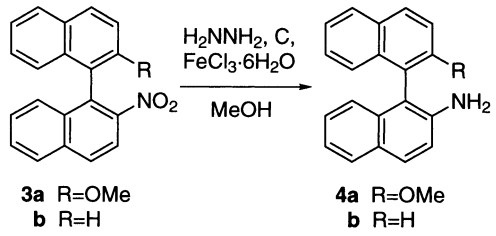
in that they required acid treatment of the conjugate adducts for demethoxylation.[14] Treatment of 1-naphthylmagnesium bromide (**2b**) with the substrate **1a** also gave the coupling product **3b** in good yield (72%), while the reaction of 2-methyl-1-naphthylmagnesium bromide (**2c**) with **1a** was rather sluggish probably due to the steric demands imposed by the 2-methyl group and the yield of the coupling product **3c** was low (13%) accompanied by the formation of many by-products.

2.2. Induction of axial chirality by using a chiral leaving group

It is known that displacement of enantiomeric menthoxy leaving group can induce axial chirality in the oxazoline-[6] and the ester-mediated[3,17] binaphthyl coupling reactions. The method was applied to the nitro-mediated S_NAr reaction. Treatment of the substrate **1a** with sodium (−)-menthoxide in DMF at room temperature for 1 h displaced the 1-methoxy group by (−)-menthoxy moiety to give 1-(−)-menthoxy-2-nitronaphthalene (**1b**) in a moderate yield (34%), recovering substantial amount of the unchanged starting **1a** (57%) (Scheme 2). Elongation of the reaction period did not improve the yield of **1b** by the concurrent formation of unidentified, colored by-products. Treatment of the (−)-menthoxy substrate **1b** with the naphthyl Grignard reagent **2a** under the standard conditions gave the binaphthyl product **3a** only in a low yield (9%) but induced axial twist of *S* conformation with rather high stereoselectivity (85% ee). The product yield was improved to 51% with a slight loss of axial chirality (78% ee) by using benzene as the solvent instead of the mixed solvent, which may indicate the importance of the



Scheme 2.



Scheme 3.

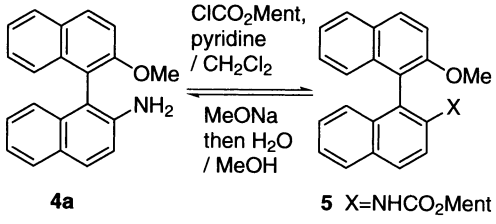
chelation between the substrate and the Grignard reagent to proceed the S_NAr reaction. The direction of the induced axial twist is the same as that of the reaction of 1-(−)-menthoxy-2-naphthoates with Grignard **2a**,[3] and thus it may be concluded that the mechanism of the 2-nitro-mediated binaphthyl coupling and thus of the asymmetric induction is similar to that of the ester-mediated S_NAr reaction.[18]

2.3. Reduction of 2-nitro-1,1′-binaphthyls to 2-amino derivatives and their optical resolution

Atropisomeric 2-amino-1,1′-binaphthyls, which may be derived from these nitro binaphthyls **3a**,**b**, are very useful as a chiral selector[19,20] or for the synthesis of other atropisomeric 1,1′-binaphthyls by derivatization of the amino function without racemization of the binaphthyl axis.[21,22] Thus, we next studied optical resolution of amino binaphthyls **4a**,**b**.[23] The amines **4a**,**b** were readily prepared by the reduction of the nitro compounds **3a**,**b** by use of a conventional method such as hydrazine reduction (Scheme 3)[24] or nickel-catalyzed sodium borohydride reduction.[25]

Optical resolution of amine **4a** was first examined by use of several commonly used chiral acids as resolving agents, among which (2*R*,3*R*)-(+)-tartaric acid and (1*S*)-(+)-10-camphorsulfonic acid may be useful: both acids gave diastereomeric salts of up to 30% optical purity by one crystallization in ethanol, but several variations of the crystallization conditions including the change of the solvent, crystallization temperature and the like did not so much improve the efficiency. It should be noted, however, that enantiomeric enrichment of partially optically active amine **4a** is possible by repeated crystallization, as exemplified by the result that one crystallization of amine (*S*)-**4a** of 70% ee from ethanol gave the amine of 93% ee as crystals.

We inclined to rely on more product-saving procedures for the optical resolution. Therefore, chromatographic resolution was investigated after converting into a mixture of diastereomeric carbamates **5**, as interconversion between the



Scheme 4.

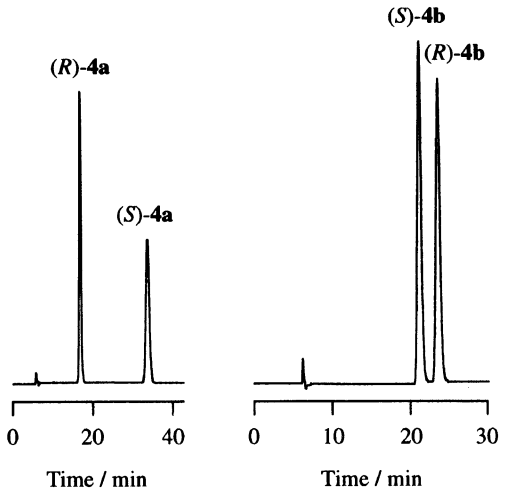


Figure 1. Enantiomer resolutions of **4a**,**b** on a chiral HPLC. Conditions: Column, Daicel CHIRALPAK AD (250 mm×4.6 mm i.d.); eluent, hexane–2-propanol (17:3 for **4a** and 19:1 for **4b**).

amine **4a** and the carbamate **5** was rather easy (Scheme 4). Actually, the mixture was separable into each diastereomer on a silica gel column by preparative LC. Alternatively, direct separation of the enantiomers by chiral chromatographic method seemed to be also attractive, as these amino binaphthyls **4a**,**b** were separated very well on a cellulose-derived chiral column (Daicel CHIRALPAK AD) in HPLC (Fig. 1). Thus, preparative optical resolution of the racemates **4a**,**b** in several hundred mg scale was readily carried out by use of a 20 mm i.d. column equipped with the stationary phase (see Section 3).

In conclusion, we have shown here a facile route for the first synthesis of two 2-nitro-1,1′-binaphthyls **3a**,**b**, showing that nitro function can also take part in the chelation-assisted S_NAr process for the displacement of an *ortho* alkoxy substituent,[8] which is somewhat different from the mechanism of the reaction of nitroarenes with alkyl Grignard reagents as proposed by Bartoli et al.[13]

3. Experimental

3.1. General

Melting points were taken using a Mitamura Riken MP-P apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-250T spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. Microanalyses were carried out in the Microanalytical Laboratory of Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. Preparative LC was carried out on a Shimadzu LC-8A with UV detection at 254 nm. A YMC silica gel column (S-5 120A SIL; 250 mm×20 mm i.d.) was used for the separation of diastereomers **5** and a Daicel CHIRALPAK AD (250 mm×20 mm i.d.) for the enantiomer resolutions of amines **4a**,**b**. Merck silica gel 60GF_{254} was used for analytical and preparative TLC (PLC). Silica gel columns were prepared by use of Merck silica gel 60 (70–230 mesh). Water- and air-sensitive reactions were routinely carried out under nitrogen. Grignard reactions were performed by a similar procedure to that described in the previous paper.[3] Diethyl ether and benzene were distilled from sodium diphenylketyl just before use. Other solvents for experiments requiring anhydrous conditions were purified by usual methods. 1-Methoxy-2-nitronaphthalene (**1a**) was prepared from 1-hydroxy-2-nitrosonaphthalene according to the literature procedure.[26]

3.2. Synthesis of 2-nitro-1,1′-binaphthyls 3

3.2.1. 2-Methoxy-2′-nitro-1,1′-binaphthyl (3a). 1-Bromo-2-methoxynaphthalene (3.56 g, 15.0 mmol) was treated with magnesium turnings (1.46 g) in diethyl ether (100 cm^3) under ultrasonic irradiation for 4 h to form a slurry, which was dissolved by the addition of benzene (100 cm^3) to give Grignard reagent **2a**. Two-third aliquot of the solution was added dropwise over a period of 40 min to a solution of 1-methoxy-2-nitronaphthalene (**1a**) (2.04 g, 10.0 mmol) in benzene (140 cm^3) and the mixture was stirred at room temperature for 1 h. The reaction was monitored by TLC and then the remaining Grignard solution was added to the mixture. The resulting mixture was stirred for a further 15 min and then worked up as usual. Chromatography on a silica gel column eluting with hexane–benzene (1:1 to 2:3) afforded binaphthyl **3a** (3.00 g, 91%) as crystals; mp 170–171°C; IR (KBr) 1524 and 1360 cm^{-1}; ^{1}H NMR δ 3.75 (3H, s, OCH_3) and 6.93–8.14 (12H, m, ArH). Found: C, 76.52; H, 4.49; N, 4.13%. Calcd for $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59; N, 4.25%.

3.2.2. 2-Nitro-1,1′-binaphthyl (3b). This compound was prepared by the same procedure as mentioned for the preparation of compound **3a** except the concentrations of the substrate **1a** and the reagent **2b**. Starting from **1a** (4.06 g, 20.0 mmol) in benzene (140 cm^3) and 1.5 equiv. of the Grignard reagent **2b** in diethyl ether–benzene (1:1) (200 cm^3), binaphthyl **3b** (4.30 g, 72%) was obtained as crystals after chromatography on a silica gel column with hexane–benzene (2:3) as the eluent, followed by recrystallization from hexane–dichloromethane; mp 120–121°C; IR (KBr) 1521 and 1348 cm^{-1}; ^{1}H NMR δ 7.17–7.63 (8H, m, ArH) and 7.93–8.06 (5H, m, ArH). Found: C, 80.14; H, 4.49; N, 4.60%. Calcd for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68%.

3.2.3. 2-Methyl-2′-nitro-1,1′-binaphthyl (3c). The Grignard reagent **2c** was prepared from 1-bromo-2-methylnaphthalene (680 mg, 3.08 mmol) and magnesium turnings (127 mg) in diethyl ether (10.5 cm^3) and dissolved by the addition of benzene (10.5 cm^3). Half the quantity of the solution was added to a solution of **1a** (305 mg, 1.50 mmol) in benzene (10.5 cm^3) over a period of 40 min and the mixture was stirred for 1 h. The reaction was monitored by TLC and then each half aliquot of the remaining Grignard reagent was added every 30 min. After 1 h, the mixture was worked up as usual. The crude product was purified by chromatography on a silica gel column with hexane–benzene (2:1) to benzene as the eluent and then by PLC with hexane–benzene (2:1) as the developer to give binaphthyl **3c** (63.1 mg, 13%) as crystals; mp 103–105°C; IR (KBr) 1521 and 1344 cm^{-1}; ^{1}H NMR δ 2.08 (3H, s, CH_3) and 6.93–8.14 (12H, m, ArH). Found: C,

80.58; H, 4.84; N, 4.36%. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47%.

3.3. Asymmetric synthesis of 2-methoxy-2′-nitro-1,1′-binaphthyl (3a)

3.3.1. 1-(−)-Menthoxy-2-nitronaphthalene (1b). Menthyl ether **1b** was prepared by a similar procedure to that described in the previous paper.[3] Sodium (−)-menthoxide was prepared by treatment of (−)-menthol (2.93 g, 18.7 mmol) with NaH (60% dispersion in mineral oil; 722 mg, 18.1 mmol) and was dissolved by the addition of dry DMF (30 cm^3). The solution was added dropwise over a period of 15 min to a solution of compound **1a** (3.05 g, 15.0 mmol) in DMF (30 cm^3) and the mixture was stirred at room temperature for 1 h. The mixture was poured into 2 mol dm^{-3} HCl (120 cm^3) and extracted several times with diethyl ether. The combined extract was washed with 1 mol dm^{-3} Na_2CO_3 and then water, and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column with hexane–ethyl acetate (40:1) as the eluent to give menthyl ether **1b** (1.69 g, 34%) as an oil; $[\alpha]_D^{25}=-267°$ (*c* 1.37, $CHCl_3$); IR (neat) 1525 and 1347 cm^{-1}; ^1H NMR δ 0.72–2.60 (18H, m, menthyl H), 4.22–4.32 (1H, m, OCH) and 7.56–8.38 (6H, m, ArH). Found: C, 73.22; H, 7.78; N, 4.15%. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28%.

3.3.2. Coupling reaction of menthyl ether 1b with Grignard reagent 2a to binaphthyl 3a. The Grignard reagent **2a** was prepared from 1-bromo-2-methoxynaphthalene (382 mg, 1.61 mmol) and magnesium turnings (78 mg) in THF (5.0 cm^3). The solvent was removed under reduced pressure and the residue was dissolved by the addition of benzene (5.0 cm^3). The Grignard solution was added dropwise to a solution of **1b** (329 mg, 1.00 mmol) in benzene (5.0 cm^3) at 0°C over a period of 2 h and the mixture was allowed to warm to room temperature. After 10 h, the mixture was worked up as usual. The menthol liberated in the reaction was distilled off at 120°C under vacuum and the residue was chromatographed on a silica gel column with hexane–ethyl acetate (9:1) as the eluent to give binaphthyl **3a** (168 mg, 51%) as an amorphous solid, a sample of which was reduced to amine **4a** with $NaBH_4$–nickel(II) complex:[25] To a suspension of $NiCl_2(PPh_3)_2$ (20.3 mg, 31.0 μmol) in 2-propanol (2.0 cm^3) was added $NaBH_4$ (5.1 mg, 0.13 mmol) and the mixture was heated at 60°C. To the hot mixture was added a solution of **3a** (44.5 mg, 135 μmol) in ethanol (4.0 cm^3) and $NaBH_4$ (10.2 mg, 270 μmol), and the resulting mixture was stirred at 60°C for 3 h. After cooling, the mixture was poured into water (30 cm^3) and worked up as usual. The crude product was chromatographed on a silica gel column with hexane–ethyl acetate (4:1) as the eluent to give amine **4a** (34.6 mg, 86%). Absolute configuration and optical purity of the amine was determined to be 78% ee (*S*) by HPLC on a Daicel CHIRALPAK AD with hexane–2-propanol (17:3) as the eluent.

3.4. Reduction of 2-nitro-1,1′-binaphthyls 3 to 2-amino-1,1′-binaphthyls 4

3.4.1. 2-Amino-2′-methoxy-1,1′-binaphthyl (4a). The method is essentially that reported by Hirashima and Manabe.[24] A mixture of nitro compound **3a** (1.50 g, 4.55 mmol), active carbon (200 mg), $FeCl_3·6H_2O$ (14 mg), and methanol (60 cm^3) was refluxed for 10 min. To the mixture was added hydrazine hydrate (730 mg, 14.6 mmol) and the resulting mixture was refluxed for 7 h. The cooled mixture was filtered and the filtrate was evaporated to dryness. The residue was extracted with diethyl ether, washed with water, and then dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column eluting with hexane–benzene (2:3 to 1:3) to hexane–ethyl acetate (3:1 to 7:3) to give amine **4a** as crystals (1.25 g, 92%); mp 139–141°C; IR (KBr) 3465, 3370 and 1615 cm^{-1}; ^1H NMR δ 3.14 (2H, br, NH_2), 3.76 (3H, s, OCH_3) and 6.95–8.01 (12H, m, ArH).

3.4.2. 2-Amino-1,1′-binaphthyl (4b). A mixture of nitro compound **3b** (3.00 g, 10.0 mmol), active carbon (520 mg), $FeCl_3·6H_2O$ (36 mg), and methanol (120 cm^3) was refluxed for 10 min. To the mixture was added hydrazine hydrate (1.87 g, 37.4 mmol) and the resulting mixture was refluxed for 4 h. The reaction was monitored by TLC and then additional hydrazine hydrate (940 mg, 18.8 mmol) was added. The resulting mixture was refluxed for a further 17 h and worked up as above. The crude product was recrystallized form methanol to give amine **4b** as crystals (2.27 g, 84%); mp 199–201°C (lit,[27] 190–191.5°C); IR (KBr) 3470, 3375 and 1614 cm^{-1}; ^1H NMR δ 3.38 (2H, br, NH_2) and 7.00–7.97 (13H, m, ArH).

3.5. Optical resolution of amine 4a via (−)-menthyl carbamate 5

3.5.1. (−)-Menthyl (2′-methoxy-1,1′-binaphthyl-2-yl)carbamate (5). A mixture of amine **4a** (999 mg, 3.34 mmol), (−)-menthyl chloroformate (2.42 g, 11.1 mmol), dry pyridine (820 mm^3) and dry dichloromethane (35 cm^3) was stirred at room temperature for 5 h. The mixture was quenched with water (80 cm^3) and 2 mol dm^{-3} NaOH (10 cm^3) was added. After the two layers had been separated, the aqueous layer was extracted several times with diethyl ether, and the combined organic layer was washed with water and then dried over $MgSO_4$. After the solvents had been evaporated, volatiles were removed under reduced pressure by use of a Kugelrohr (75°C/270 Pa) and the residue was chromatographed on a silica gel column with hexane–ethyl acetate (9:1) as the eluent to give a mixture of diastereomeric carbamates **5** as crystals (1.59 g, 99%); mp 72.5–74.0°C; IR (KBr) 1726 cm^{-1}; ^1H NMR δ 0.55–2.02 (18H, m, menthyl H), 3.78 (3H, s, OCH_3), 4.48–4.62 (1H, m, OCH), 6.22, 6.27 [1H: s, NHCO (*R*); s, NHCO (*S*)], and 6.98–8.42 (12H, m, ArH). Found: C, 79.92; H, 7.32; N, 2.89%. Calcd for $C_{32}H_{35}NO_3$: C, 79.80; H, 7.32; N, 2.91%.

3.5.2. Separation of a mixture of diastereomeric carbamates 5 by HPLC. Carbamates **5** (1.27 g) were separated by preparative LC on a silica gel column eluting with hexane–ethyl acetate (97:3) to give diastereomerically pure (*S*)-**5** (314 mg, 99% de) and (*R*)-enriched **5** (496 mg, 71% de). (*S*)-**5**: $[\alpha]_D^{29}=-19.6°$ (*c* 1.04, $CHCl_3$).

3.5.3. Hydrolysis of carbamate (*S*)-5 to amine (*S*)-4a. A

solution of sodium methoxide in methanol was prepared from Na (390 mg, 17.0 mmol) and dry methanol (8.5 cm^3). To the solution was added (*S*)-**5** (161 mg, 334 μmol) and the mixture was refluxed for 8 h. To it was added water (430 mm^3) and the resulting mixture was refluxed for a further 3 h. After cooling, the mixture was poured into water (30 cm^3) and extracted several times with diethyl ether. The combined extract was washed with water and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column with hexane–ethyl acetate (4:1) as the eluent to afford amine (*S*)-**4a** (91.0 mg, 91%) as crystals, spectral data of which were identical with those of the racemate (vide supra). The enantiomeric excess of the sample was determined to be 99% ee by HPLC on a Daicel CHIRALPAK AD with hexane–2-propanol (17:3) as the eluent.

3.6. Chiral HPLC separation of amines 4

3.6.1. (*S*)- and (*R*)-2-Amino-2′-methoxy-1,1′-binaphthyl (4a). Racemic amine **4a** (249 mg) was dissolved in ethanol and a 10th part each of the solution was injected into the preparative LC apparatus equipped with a Daicel CHIRALPAK AD column with hexane–2-propanol (4:1) as the eluent to give enantiomerically pure (*S*)- and (*R*)-**4a** (99% ees) in total yields of 125 and 120 mg, respectively. (*S*)-**4a**: $[\alpha]_D^{23}=-116°$ (*c* 0.88, THF) {lit,[21] $[\alpha]_D^{21}=-117°$ (*c* 1.00, THF)}. (*R*)-**4a**: $[\alpha]_D^{31}=+116°$ (*c* 0.99, THF).

3.6.2. (*S*)- and (*R*)-2-Amino-1,1′-binaphthyl (4b). By preparative LC on a Daicel CHIRALPAK AD with hexane–2-propanol (9:1) as the eluent, 20 mg each of the racemic amine **4b** (200 mg) was resolved into (*S*)-enriched **4b** of 50% ee in a total yield of 120 mg and (*R*)-enriched **4b** of 80% ee in 73.0 mg yield. Each sample was resolved again by the same procedure to give enantiomerically pure (*S*)-**4b** (53.7 mg, 98% ee) and (*R*)-**4b** (43.0 mg, 99% ee), respectively. (*S*)-**4b**:[6] $[\alpha]_D^{27}=+68.9°$ (*c* 0.99, THF). (*R*)-**4b**: $[\alpha]_D^{24}=-73.7°$ (*c* 0.97, THF).

Acknowledgements

We are grateful to Drs Yoichiro Ueda and Akito Ichida of Daicel Chemical Industries, Ltd, for valuable suggestions. This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 07555587 and 08405058).

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