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TETRAHEDRON: *ASYMMETRY*

Chiral enrichment of 2-amino-2′-hydroxy-1,1′-binaphthyl

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Abstract

A new synthetic procedure for the formation of 2-amino-2′-hydroxy-1,1′-binaphthyl, and a new purification procedure through the formation of Schiff bases, purification of the Schiff bases, and breakdown of the Schiff bases through amine exchange, are described. Through the new purification procedure, greater than 99% purity of the compound can be obtained easily and reliably. A set of procedures were examined to compare the efficiency and reliability to resolve 2-amino-2′-hydroxy-1,1′-binaphthyl into enantiomers. A new procedure was discovered to enrich enantiomeric excess from less than 10% to 95–99% in one step. Even a racemic mixture from an achiral procedure can be enriched to 67% e.e. in about 4% yield. The X-ray crystal structure of the racemic mixture [rhombohedral, space group *Iba2*, a=15.718(2) Å, b=21.703(2) Å, c=8.5398(9) Å, V=2913.2(5) Å^3, $R1$=0.0705, Z=8, d_{calcd}=1.301 g/cm^3, $F(000)$=1200 e] was solved to elucidate the intriguing behavior of this compound.

1. Introduction

Compared with the asymmetric ligands based on BINAP and 1,1′-bi-2-naphthol,[1] asymmetric ligands based on 2,2′-diamine-1,1′-binaphthyl, 2-amino-2′-hydroxy-1,1′-binaphthyl, and 2-amino-2′-thiol-1,1′-binaphthyl, are scarce,[2] but promising results have been obtained in the catalysis of Mukaiyama reactions.[2c] One of the problems is the availability of the chiral starting material. There are several methods available for the synthesis or resolution of the chiral 2-amino-2′-hydroxy-1,1′-binaphthyl compound. Cross coupling of 2-naphthol and 2-naphthylamine under controlled conditions, using a combination of $CuCl_2$ and chiral benzylamine in methanol, generates a precipitate and solution of 46% e.e., but opposite in sign for their chirality, at 1 mmol scale.[3] After repeated recrystallization in benzene, approximately 20% of both optically pure isomers have been isolated. Since the racemic mixture of 2-amino-2′-hydroxy-1,1′-binaphthyl is available in high yield,[4] resolution into enantiomers via crystallization of diastereoisomeric salts with (1*S*)-(+)-10-camphorsulfonic acid has been developed.[5] In our hands, the former methods give greatly reduced e.e. on a large scale, and variable results on a

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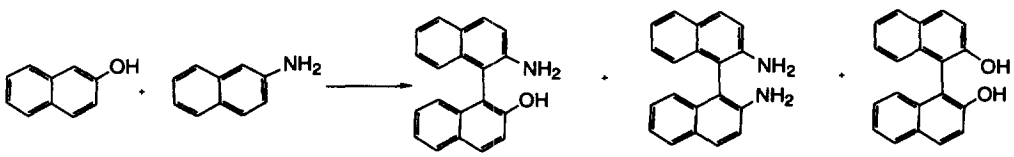
small scale depending on unidentified changes to the experimental conditions. The latter method is very sensitive to impurities such as 2,2′-diamine-1,1′-binaphthyl in the racemic mixture, which happens to be difficult to remove, as described in the original literature.[5] Here we report our effort on the improved synthesis, purification, and resolution of the 2-amino-2′-hydroxy-1,1′-binaphthyl into its enantiomers.

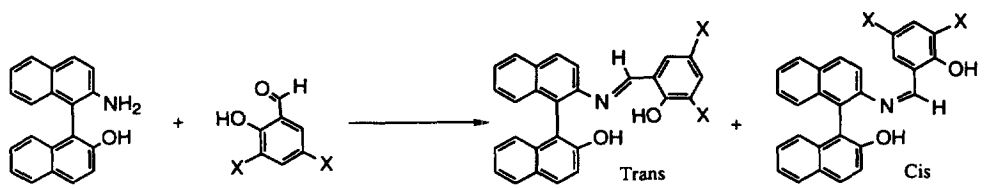
2. Results and discussion

2.1. Solid state synthesis

Coupling of 2-naphthol and 2-aminonaphthalene with $FeCl_3 \cdot 6H_2O$ could be accomplished in the solid state without any solvent. The reaction products were a mixture of 2-amino-2′-hydroxy-1,1′-binaphthyl, 1,1′-bi-2-naphthol, and 2,2′-diamine-1,1′-binaphthyl (Scheme 1). Pure 2-amino-2′-hydroxy-1,1′-binaphthyl was obtained by the Schiff base purification procedure described below in 33% yield (Scheme 2). A similar procedure to the solid state synthesis was used for the synthesis of binaphthol.[6]



Scheme 1. Reaction scheme for the synthesis of 2-amino-2′-hydroxy-1,1′-binaphthyl



Scheme 2. Reaction scheme for the formation of Schiff bases. When X=H, trans:cis ratio=3:1. When X=*tert*-butyl, only the trans isomer is observed

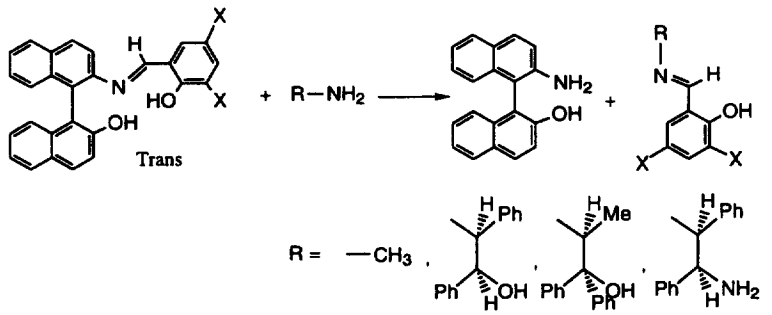
2.2. Schiff base purification procedure

Since the mixture of 2-amino-2′-hydroxy-1,1′-binaphthyl, 1,1′-bi-2-naphthol, and 2,2′-diamine-1,1′-binaphthyl is close on TLC and a silica gel column, purification of 2-amino-2′-hydroxy-1,1′-binaphthyl through derivatives has been designed here. Transformation of 2-amino-2′-hydroxy-1,1′-binaphthyl by salicylaldehyde or 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde into their corresponding Schiff bases gave 95% and 95% yields, respectively. These Schiff bases are well separated from those of 2,2′-diamine-1,1′-binaphthyl, and unreacted 1,1′-bi-2-naphthol. Greater than 99% pure Schiff bases of 2-amino-2′-hydroxy-1,1′-binaphthyl can be easily obtained through a silica gel column. Schiff base exchange with methylamine hydrochloride in methanol precipitates 2-amino-2′-hydroxy-1,1′-binaphthyl in 90% yield. This procedure produces greater than 99% pure 2-amino-2′-hydroxy-1,1′-binaphthyl, as checked by GC–MS. However, Schiff bases generated from acetic acid at 80°C for 2 hours are contaminated with an impurity which is difficult to separate on a column.

2.3. Resolution

2.3.1. Kinetic resolution

After formation of the Schiff base of 2-amino-2′-hydroxy-1,1′-binaphthyl, chiral amines were applied to perform a kinetic resolution on the amine exchange of the Schiff base (Scheme 3). The reaction was followed by HPLC on a chiral column (Chiralcel OD) with UV–vis detection. The effect of variations of amines and pH on the kinetic resolution were determined. Among the amines tested, (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine, (*S*)-(−)-2-amino-1,1-diphenyl-1-propanol, (1*S*,2*R*)-(+)-norephedrine (erythro-α-(1-aminoethyl)benzyl alcohol), and (*R*)-(+)-α-methylbenzylamine, 2-amino-1,2-diphenylethanol was the most effective. When acetic acid and triethyl amine were used to adjust the pH values, the optimal conditions occurred when 1 equiv. of acetic acid was added: the rate and efficiency of the kinetic resolution was best under these conditions. The results are summarized in Table 1, where % e.e. of the starting Schiff bases remaining, and % e.e. for the resulting 2-amino-2′-hydroxy-1,1′-binaphthyl are correlated with the percentage of the conversion. The efficiency of the kinetic resolution as determined by the ratio of the effective rate constants of the two enantiomers with the chiral aminoalcohol is 0.47±0.03.



Scheme 3. Reaction scheme for kinetic resolution of 2-amino-2′-hydroxy-1,1′-binaphthyl

2.3.2. Camphorsulfonic acid resolution

Methods used in the past research[7] were modified and used to resolve 2-amino-2′-hydroxy-1,1′-binaphthyl, due to the difference in solubility of diastereoisomers in chlorobenzene/ethanol. The camphorsulfonic acid resolution procedure is extremely difficult to reproduce. Apparently, controlling the amount of ethanol, and the rate of its evaporation in the resolution, are critical for a successful resolution. Under identical conditions, the optical purity of 2-amino-2′-hydroxy-1,1′-binaphthyl generated from the precipitate could range from 30% e.e. in the (*R*)-(+) form to 95% e.e. in the (*S*)-(−) form.

Other conditions were also examined. The resolution temperature varied from RT to 110°C with the bottle opened, generating a white precipitate over time, resulting in a compound of about 15–40% e.e.

Table 1
The corresponding e.e. of the starting Schiff base (X=*tert*-butyl) and resulting 2-amino-2′-hydroxy-1,1′-binaphthyl at different conversions of the reaction when 2-amino-1,2-diphenylethanol was used

Reaction Times (hrs.)	Conversion (%)	Starting Schiff base (yield/e.e.)	1,1'-Binaphthyl-2-amino-2'-hydroxy (yield/e.e.)
12	60	0.40 (33.8)	0.60 (29.9)
18	76	0.24 (56.2)	0.76 (34.5)
24	89	0.11 (69.8)	0.89 (27.7)

as determined by HPLC. Pure enantiomer crystal seeding at various temperatures did not increase the selectivity of the crystallization of one enantiomer. Recrystallization of the camphorsulfonate salt, after its formation from either ethanol at room temperature or from chlorobenzene/ethanol at 110°C, was also attempted. The salt is not soluble in chlorobenzene/ethanol (10/1 v/v) even at 110°C. Increasing the percentage of ethanol (about 10/2–3) is needed to ensure a homogeneous solution at 110°C. A white precipitate is formed during the cooling process to room temperature. A low e.e. (about 10%) was obtained after it was broken down by the base.

The effect of temperature on the e.e.% value during the breakdown of the camphorsulfonate salt with pyridine in hot water was also studied. Optically pure camphorsulfonate salt was synthesized with optically pure 2-amino-2′-hydroxy-1,1′-binaphthyl in methanol at room temperature. The breakdown of the salt follows the same conditions as described above but under different temperatures. Breaking down the enantiomeric salt at 95°C resulted in a greater than 90% yield with only a 30% e.e. However, no dramatic e.e. loss was observed at 70°C. Breakdown at room temperature produced a milky water solution which was difficult to filter, unless it was allowed to stand for a long time.

Among the bases evaluated in the breakdown, such as Na_2CO_3, pridine, and $NaHCO_3$, pyridine is the best base. A water solution of Na_2CO_3, for example, generates low recovery of the material. An unknown compound, whose structure has not yet been determined, could be extracted by CH_2Cl_2 from the water solution and purified by silica gel chromatography.

2.3.3. *Enantiomer enrichment*

Enantiomerically pure 2-amino-2′-hydroxy-1,1′-binaphthyl from a low e.e. mixture through recrystallization from benzene has been described.[3] However, the efficiency is low and requires multiple steps which take a long time. We have found that greater than 95% e.e. in nearly the calculated amount of one enantiomer 2-amino-2′-hydroxy-1,1′-binaphthyl can be extracted from the wet solid by the Soxhlet extractor with pentane in a one step process overnight. Mixtures with less than 10% e.e. are suitable for this procedure. The enantiomeric excess changes sharply after the theoretical amount of one enantiomer was extracted. In fact, we have obtained 4% of 67% e.e. of one enantiomer of 2-amino-2′-hydroxy-1,1′-binaphthyl from the racemic mixture completely free of the chiral source from its synthesis. That corresponds to about 3% e.e. from the total racemic mixture. The origin of the chirality is unknown at this moment.

2.3.4. *Other resolution procedures*

A number of other chiral compounds have been tested for resolution of 2-amino-2′-hydroxy-1,1′-binaphthyl via co-crystallization by either possible hydrogen bonding interaction or salt formation such as (8*S*,9*R*)-(−)-N-benzylcinchonidinum chloride in methanol,[8] (*S*)-(−)-2-amino-1,1-diphenyl-1-propanol, (1*S*,2*R*)-(+)-norephedrine (erythro-α-(1-aminoethyl)benzyl alcohol), 2-amino-1,2-diphenylethanol, (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine, and (−)-sparteine. Recrystallization from chiral (*R*)-(+)-α-methylbenzylamine as solvent also gave racemic mixtures of both isomers.

2.4. *X-Ray crystal structure of racemic 2-amino-2′-hydroxy-1,1′-binaphthyl*

After 2 days, crystals of the racemic mixture were grown from the reaction of the Schiff bases with methyl ammonium hydrogen chloride and triethyl amine in methanol. The ORTEP of the compound is shown in Fig. 1 and the experimental details given in Section 4.6. Overall, the bond distances and angles are normal for these types of compounds. The two naphthyl planes adopt an 85.8° dihedral angle. No hydrogen bonding and π-stacking interactions were found either intra- or intermolecularly in the crystal

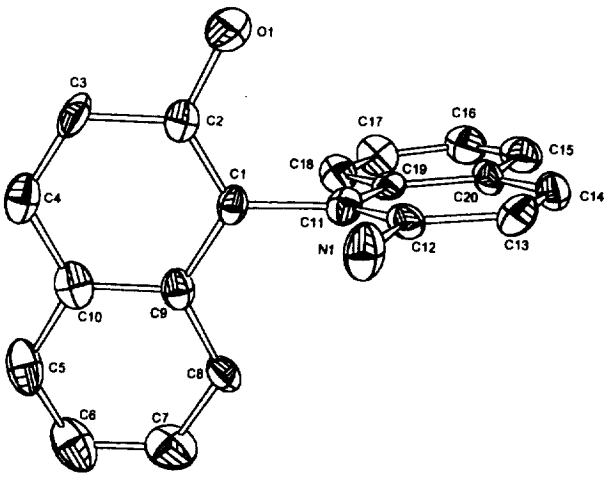


Fig. 1. Molecular structure of 2-amino-2′-hydroxy-1,1′-binaphthyl with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity)

structure. This may explain why the presence of water is critical for the chiral enrichment procedure described above. Intermolecular hydrogen bonding through a water molecule may be possible for 2-amino-2′-hydroxy-1,1′-binaphthyl.

3. Conclusion

We have generated an optimized purification procedure for 2-amino-2′-hydroxy-1,1′-binaphthyl through the formation of stable Schiff bases, which could be broken down easily with methylamine HCl salts under mild conditions. A number of resolution procedures were evaluated, and we found that a modified procedure from the literature gave the best results, but was difficult to repeat. A novel enantiomeric enrichment procedure was discovered which could enrich enantiomeric mixtures from as low as 10% e.e. to 90–95% e.e. in one single step through pentane extraction in a Soxhlet extractor. An X-ray diffraction study of the single crystals revealed the molecular structure of the compound, and no hydrogen bonding is found in the crystal lattice. The structural information of the compound is used to explain such intriguing observations as the importance of the wet solid for the enantiomeric enrichment procedure.

4. Experimental section

4.1. Solid state synthesis of 2-amino-2′-hydroxy-1,1′-binaphthyl

A mixture of 2-naphthol (1 g, 7 mmol), 2-aminonaphthalene (1 g, 7 mmol), and $FeCl_3 \cdot 6H_2O$ (3.8 g, 14 mmol) was finely powdered by agate mortar and pestle. The mixture was then transferred to test tube and kept at 60°C overnight. The solid was extracted by CH_2Cl_2 to obtain a dark green solution and yellow solid. The solvent was removed and the product was purified by a silica gel column to obtain a mixture of 2-amino-2′-hydroxy-1,1′-binaphthyl, 1,1′-bi-2-naphthol, and 2,2′-diamino-1,1′-binaphthyl. ^{1}H NMR for 2-amino-2′-hydroxy-1,1′-binaphthyl in acetone-d_6: δ, 7.93 (d, $^3J_{HH}$=8.9 Hz, 1H), 7.88 (d, $^3J_{HH}$=8.0 Hz, 1H), 7.76 (m, 2H), 7.37 (d, $^3J_{HH}$=8.9 Hz, 1H), 7.28 (t, $^3J_{HH}$=8.9 Hz, 1H), 7.23 (d, $^3J_{HH}$=8.7 Hz, 1H),

7.21 (t, $^3J_{HH}$=7.2 Hz, 1H), 7.13 (m, 2H), 7.08 (d, $^3J_{HH}$=8.6 Hz, 1H), 6.90 (dd, $^3J_{HH}$=8.9 Hz, $^5J_{HH}$=1.7 Hz, 1H), 4.42 (brs, 3H, NH_2 and OH). $^{13}C\{^1H\}$ NMR for 2-amino-2′-hydroxy-1,1′-binaphthyl in acetone-d_6: δ, 154.4 (C2–O), 145.8 (C12–N), 135.8, 135.1, 130.7 (CH), 130.4, 130.3 (CH), 129.3 (CH), 129.1 (CH), 129.1, 127.4 (CH), 127.2 (CH), 125.5 (CH), 124.7 (CH), 124.1 (CH), 122.5 (CH), 119.8 (CH), 119.6 (CH), 116.2, 111.1. High resolution MS for $C_{20}H_{15}NO$, found: 285.114981; calcd: 285.115364.

4.2. 2-Salicylideneaminato-2′-hydroxy-1,1′-binaphthyl

Crude 2-amino-2′-hydroxy-1,1′-binaphthyl (342 mg, 1.20 mmol), salicylaldehyde (196.2 mg, 1.61 mmol), and $MgSO_4$ (150 mg, 1.25 mmol), were suspended in 50 ml absolute ethanol. The mixture was refluxed for 4 days or until the starting material almost disappeared. The $MgSO_4$ solid was filtered and washed with ethanol (3×10 ml). The solvent was removed under vacuum, and the solid was loaded onto a silica gel column (230–300 mesh, Fisher) pre-treated with triethyl amine (10 ml in 100 ml eluate). The column was washed with hexane first (100 ml), then hexane:ethyl acetate (8:2 by volume). The unreacted aldehyde (yellow) came out first, followed by the Schiff-base band (orange). Removal of the solvent afforded 465 mg of product. Yield 95%. ^1H NMR in acetone-d_6, δ, 12.3 (Ph–OH), 8.98 (CH=N), 8.17 (s, 1H), 8.15 (d, $^3J_{HH}$=8.9 Hz, 1H), 8.03 (d, $^3J_{HH}$=8.1 Hz, 1H), 7.93 (d, $^3J_{HH}$=8.9 Hz, 1H), 7.86 (t, $^3J_{HH}$=8.9 Hz, 2H), 7.49 (t, $^3J_{HH}$=7.2 Hz, 1H), 7.46 (d, $^3J_{HH}$=7.2 Hz, 1H), 7.35 (d, $^3J_{HH}$=9.1 Hz, 1H), 7.34 (t, $^3J_{HH}$=9.1 Hz, 1H), 7.26 (d, $^3J_{HH}$=8.2 Hz, 1H), 7.23 (dm, $^3J_{HH}$=7.6 Hz, 1H), 7.16 (t, $^3J_{HH}$=7.3 Hz, 1H), 6.95 (d, $^3J_{HH}$=8.4 Hz, 1H), 6.83 (t, $^3J_{HH}$=7.4 Hz, 1H), 6.62 (d, $^3J_{HH}$=8.3 Hz, 1H). $^{13}C\{^1H\}$ NMR in DMSO-d_6, δ, 162.2 (C=N), 160.0 (C–O), 152.6 (C2–O), 143.3 (C12–N), 133.4, 132.9, 132.7 (CH), 132.4 (CH), 132.2, 129.2 (CH), 129.0 (CH), 128.8, 128.0 (CH), 127.9 (CH), 127.8, 126.4 (CH), 126.0 (CH), 125.9 (CH), 125.5 (CH), 123.7 (CH), 122.2 (CH), 119.1, 118.5 (CH), 118.2 (CH), 117.3 (CH), 116.2 (CH), 115.7. High resolution MS for $C_{27}H_{19}NO_2$, found: 389.141412; calcd: 389.141579.

4.3. 2-(3,5-Di-tert-butyl-salicylideneaminato)-2′-hydroxy-1,1′-binaphthyl

Crude 2-amino-2′-hydroxy-1,1′-binaphthyl (6.00 g, 21.1 mmol), 3,5-di-*tert*-butyl-salicylaldehyde (5.92 g, 25.2 mmol), and $MgSO_4$ (6.00 g, 49.8 mmol), were suspended in 700 ml of absolute ethanol. The mixture was refluxed for 4 days or until the starting material almost disappeared. The $MgSO_4$ solid was filtered and washed with ethanol (3×100 ml). The solvent was removed under a vacuum, and the solid was loaded onto a silica gel column (60×300 mesh, Fisher) pre-treated with triethyl amine (10 ml in 100 ml eluate). The column was washed with hexane first (200 ml), then hexane:ethyl acetate (8:2 by volume). The unreacted aldehyde (yellow) came out first, then the Schiff-base band (orange). Removal of the solvent afforded 9.31 g of product. Yield 88%.

UV: ε_{300}=15171. ^1H NMR in acetone-d_6: δ, 8.96 (s, CH=N), 8.12 (d, $^3J_{HH}$=8.8 Hz, 1H), 8.01 (d, $^3J_{HH}$=8.1 Hz, 1H), 7.95 (d, $^3J_{HH}$=8.9 Hz, 1H), 7.88 (d, $^3J_{HH}$=8.0 Hz, 1H), 7.82 (d, $^3J_{HH}$=8.8 Hz, 1H), 7.46 (t, $^3J_{HH}$=7.6 Hz, 1H), 7.43 (d, $^3J_{HH}$=8.9 Hz, 1H), 7.40 (d, $^3J_{HH}$=8.4 Hz, 1H), 7.38 (d, $^4J_{HH}$=2.0 Hz, 1H), 7.35 (d, $^4J_{HH}$=2.7 Hz, 1H), 7.32 (t, $^3J_{HH}$=8.9 Hz, 1H), 7.23 (t, $^3J_{HH}$=7.6 Hz, 1H), 7.15 (t, $^3J_{HH}$=7.6 Hz, 1H), 7.04 (d, $^3J_{HH}$=8.3 Hz, 1H), 1.29 (s, 3×CH_3), 1.28 (s, 3×CH_3). $^{13}C\{^1H\}$ NMR in acetone-d_6: δ, 164.3 (CH=N), 158.6 (C–O), 153.5 (C2–O), 145.8 (C12–N), 140.8, 136.9, 135.0, 134.7, 133.5, 130.4 (CH), 130.3 (CH), 129.8, 129.0 (CH), 128.9 (CH), 128.7, 128.1 (CH), 127.9 (CH), 127.4 (CH), 127.3 (CH), 127.0 (CH), 126.9, 126.4 (CH), 125.2 (CH), 123.5 (CH), 119.5, 119.1 (CH), 118.7 (CH), 117.2, 35.4 (C), 34.6 (C), 31.8 (CH_3), 29.6 (CH_3). High resolution MS for $C_{35}H_{35}NO_2$, found: 501.266124; calcd: 501.266780.

4.4. 2-(3,5-Di-tert-butyl-salicylideneaminato)-1,2-diphenylethanol

2-Amino-1,2-diphenylethanol (30 mg, 0.14 mmol), 3,5-di-*tert*-butyl-salicylaldehyde (16.5 mg, 0.071 mmol), and $MgSO_4$ (1.00 g, 8.3 mmol), were suspended in 10 ml of absolute ethanol. The mixture was refluxed for 1 hour or until the starting material almost disappeared. The $MgSO_4$ solid was filtered and washed with ethanol (3×3 ml). The solvent was removed under vacuum, and the solid was loaded onto a silica gel column (60×300 mesh, Fisher) pre-treated with triethyl amine (10 ml in 100 ml eluate). The column was washed with hexane first (20 ml), then hexane:ethyl acetate (8:2 by volume). Removal of the solvent afforded 28 mg product. Yield 92% based on limiting aldehyde.

UV: ε_{300}=1463. ^{1}H NMR in acetone-d_6: δ, 13.8 (C1–OH), 8.44 (s, CH=N), 7.40 (d, $^4J_{HH}$=2.0 Hz, 1H), 7.36 (d, $^3J_{HH}$=7.6 Hz, 2H), 7.30 (t, $^3J_{HH}$=7.3 Hz, 2H), 7.25 (d, $^3J_{HH}$=7.0 Hz, 1H), 7.20 (m, 5H), 7.17 (d, $^4J_{HH}$=2.1 Hz, 1H), 5.17 (d, $^3J_{HH}$=5.8 Hz, 1H, CH–O), 4.72 (d, $^3J_{HH}$=5.8 Hz, 1H, CH–N), 1.45 (s, 9H, CH_3), 1.27 (s, 9H, CH_3). ^{13}C{^{1}H} NMR in acetone-d_6: δ, 168.3 (CH=N), 159.3 (C–O), 143.0, 142.0, 141.2, 137.4, 129.5 (CH), 129.4 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.0 (CH), 127.8 (CH), 119.6, 81.3 (CH–O, aliphatic), 79.1 (CH–N, aliphatic), 36.1 (C), 35.2 (C), 32.3 (CH_3), 30.3 (CH_3). High resolution MS for $C_{29}H_{35}NO_2$, found: 429.266430; calcd: 429.266780.

4.5. Kinetic resolution of 2-(3,5-di-tert-butyl-salicylideneaminato)-2′-hydroxy-1,1′-binaphthyl

2-(3,5-Di-*tert*-butyl-salicylideneaminato)-2′-hydroxy-1,1′-binaphthyl (5.9 mg, 0.012 mmol), 2-amino-1,2-diphenylethanol (5.0 mg, 0.024 mmol) were dissolved in dried benzene, various amounts of HOAc or triethylamine in benzene were added immediately. The progress of the reaction was followed by HPLC at 300 nm, eluted with hexane:isopropanol (95:5 by volume).

4.6. Recovery of 2-amino-2′-hydroxy-1,1′-binaphthyl from Schiff base

2-(3,5-Di-*tert*-butyl-salicylideneaminato)-2′-hydroxy-1,1′-binaphthyl (9.31 g, 18.6 mmol), methyl ammonium chloride (3.77 g, 55.9 mmol), and triethyl amine (5.6 g, 55 mmol) were dissolved in 100 ml of methanol. Everything was soluble at the beginning. After 10 min, there was a large amount of white precipitate. The mixture was stirred overnight or until the Schiff base disappeared as checked by TLC. The precipitate was filtered and washed with hexane. The product was extracted with THF to remove a small amount of the co-precipitated methyl ammonium chloride. Removal of the solvent generated 5.3 g of 2-amino-2′-hydroxy-1,1′-binaphthyl. Yield >99%. Recrystallization from toluene generated the product in greater than 99% purity as determined by GC–MS.

The X-ray quality crystals were grown from a small scale reaction by combining solutions of the above compounds without stirring at RT. $C_{20}H_{15}NO$; space group *Iba2*, a=15.718(2) Å, b=21.703(2) Å, c=8.5398(9) Å, V=2913.2(5) Å^3, crystal dimensions 0.3×0.2×0.2 mm, Z=8, d_{calcd}=1.301 g/cm^3, F(000)=1200 e, Siemens SMART/CCD diffractometer, Mo-Kα radiation (λ=0.71073 Å), T=−60°C. Data were corrected for Lorentz and polarization effects as well as for absorption effects [empirical, absorption coefficient=0.080 mm^{-1}]. 5329 reflections were measured, 1761 [R(int)=0.0986] unique reflections. Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were calculated in idealized geometry and included with isotropic contributions. Refined parameters (200) *wR2* [unique data]=0.1166, *R1* [$Fo^3 2\sigma(Fo)$]=0.0705, {$wR2=[\sum w(Fo^2-Fc^2)^2]/\sum[w(Fo^2)^2]^{1/2}$, $R1=\sum(||Fo|-|Fc||)/\sum|Fo|$, $w=q/2\sigma^2(Fo^2)+(ap)^2+bp$, $p=(Fo^2+2Fc^2)/3$; a=0.0304, b=4.14}, ρ_{final}=+0.253/−0.279 e Å^3. The structure was solved by

direct methods and refined by full matrix least-square calculations (SHELX-93, Sheldrick, G. M. SHELXL-93, Göttingen, 1993).

Acknowledgements

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References

1. (a) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*, VCH: New York, 1993. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*, John Wiley & Sons, Inc.: New York, 1994.
2. (a) Kabuto, K.; Yoshida, T.; Yamaguchi, S.; Miyano, S.; Hashimoto, H. *J. Org. Chem.* **1985**, *50*, 3013–3015. (b) Ho, C.-W.; Cheng, W.-C.; Cheng, M.-C.; Peng, S.-M.; Cheng, K.-F.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1996**, 405–414. (c) Carreira, E. M.; Singer, R. A.; Lee, W. *J. Am. Chem. Soc.* **1994**, *116*, 8837–8838. (d) Lin, J.-H.; Che, C.-M.; Lai, T.-F.; Poon, C.-K.; Cui, Y. X. *J. Chem. Soc., Chem. Commun.* **1991**, 468–470.
3. Smrcina, M.; Lorenc, M.; Hanus, V.; Sedmera, P.; Kocovsky, P. *J. Org. Chem.* **1992**, *57*, 1917–1920.
4. Smrcina, M.; Lorenc, M.; Hanus, V.; Kocovsky, P. *Synlett.* **1991**, 231.
5. Smrcina, M.; Vyskocil, S.; Polivkova, J.; Polakova, J. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1520–1524.
6. Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007–3009.
7. Smrcina, M.; Vyskocil, S.; Polivkova, J.; Polakova, J. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1520–1524.
8. Hu, Q.-S.; Vitharana, D.; Pu, L. *Tetrahedron: Asymmetry* **1995**, *6*, 2123–2126.