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A practical synthesis of 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN)

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Abstract—A practical synthesis of 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) was realized from BINOL through a single step. Its facile purification procedure makes the process amenable for large scale synthesis of NOBIN.

Chiral 2-amino-2′-hydroxy,-1,1′-binaphthyl (NOBIN), first developed by Kočovský,[1] has proven to be an excellent framework for constructing chiral ligands (Fig. 1). For example, ligand **1**, made from NOBIN by Carreira, has been successfully applied in Ti-catalyzed asymmetric aldol reactions.[2] We have recently developed a NOBIN-derived N,P ligand **2**, which has shown high enantioselectivities in the Cu-catalyzed Michael addition.[3] A Ru complex derived from an *N*,*O*-mixed polydentate ligand **3** has been applied as an excellent catalyst for intermolecular cyclopropanation reactions.[4] Hoveyda has developed an excellent asymmetric metathesis catalyst based on the NOBIN motif.[5] In addition, NOBIN itself has been used as a good phase transfer catalyst by Kagan.[6] However, despite many excellent applications of NOBIN and its derived ligands, a practical synthesis of NOBIN is still not available.

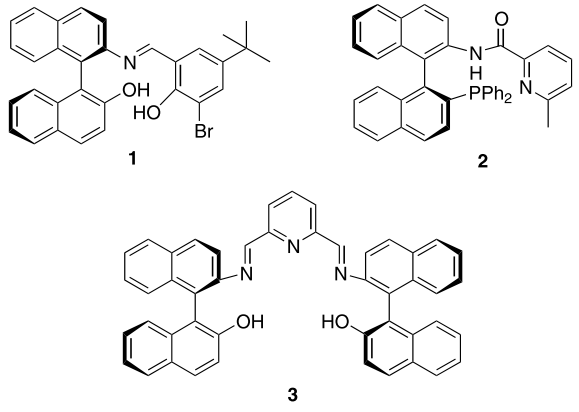
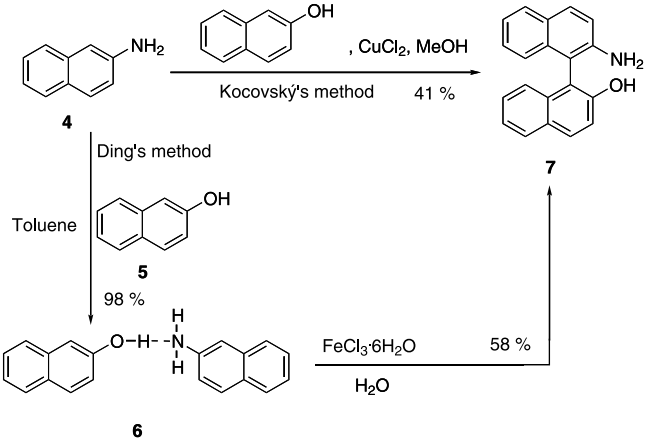


Figure 1.

Several methods have been reported for the synthesis of NOBIN. Kočovský employed a Cu(II)Cl_2-mediated coupling reaction of 2-naphthylamine and 2-naphthol to yield NOBIN in 43% yield (Scheme 1).[1] Ding et al. reported improved conditions for the above coupling reaction by employing the two-component molecular crystal **6** in aqueous solution. The coupling yield increased to 65% when 10 g of molecular crystal was employed.[7,8] Buchwald et al. offered an attractive route to synthesize chiral NOBIN from optically pure BINOL via a palladium-catalyzed amination reaction.[9] However, this process requires several protection and deprotection steps.



Scheme 1.

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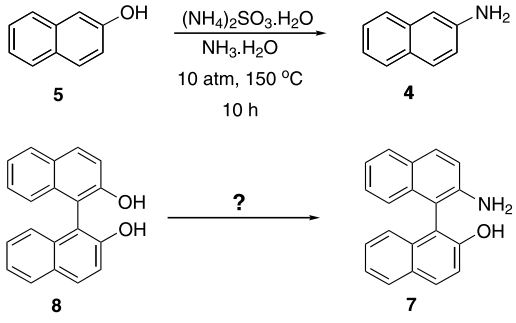
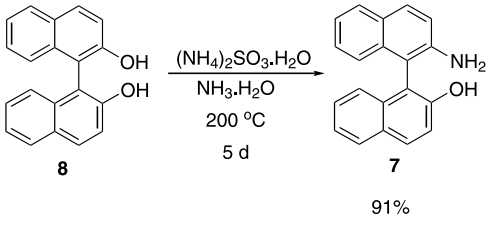
We used both Kočovský and Ding's methods to synthesize NOBIN in a 20 g scale. By using Kočovský's method, a mixture of NOBIN, BINOL, and 1,1′-binaphthyl-2,2′-diamine (BINAM) was obtained. Although the ratio of NOBIN in the mixture was relatively high, the isolated yield decreased to around 40% due to the difficult separation of NOBIN from BINOL and especially BINAM. Using Ding's method also resulted in formation of a mixture of three products. However, since less BINAM was formed in Ding's method, an easier purification procedure allowed us to obtain NOBIN in 58% yield. It is likely that the formation of BINOL and BINAM is unavoidable in the cross-coupling reaction between 2-naphthol and 2-naphthylamine. Since removal of the two by-products from NOBIN is tedious due to their similar properties, a higher yield of NOBIN is unlikely to be obtained.

We have made 2-naphthylamine in high yield from 2-naphthol via a Bucherer reaction.[10] We proposed that NOBIN might be synthesized from BINOL in a similar way (Scheme 2). It was reported that 2-naphthylamine was obtained in high yield when 2-naphthol was heated at 150°C in the presence of concentrated aqueous ammonia and ammonium sulfite for 8 h.[11] However, no reaction was observed when the same conditions were subjected to BINOL. When the temperature was increased to 200°C and more ammonium sulfite was employed, NOBIN was exclusively formed without detectable amounts of BINAM. By extending the reaction time to 5 days and increasing the amount of ammonium sulfite to 10 equiv., the starting material disappeared completely. The produced solid was simply filtered and washed with water. A 91% isolated yield of NOBIN was obtained by recrystallization from benzene (Scheme 3). Unfortunately, racemization took place when enantiomerically pure BINOL was used in this procedure. Importantly, no trace amount of BINAM was observed during the reaction. We assumed that the strong internal hydrogen bond between the hydroxy group and the amino group of NOBIN prevented its further conversion to BINAM.



Scheme 2.



Scheme 3.

A detailed procedure is as follows. To a 125 mL Teflon lined autoclave was added 5.0 g (17.5 mmol) of 1,1′-bi-2-naphthol, 23.5 g (175 mmol) of $(NH_4)_2SO_3 \cdot H_2O$, and 65 mL of concentrated aqueous ammonia. The mixture was stirred at 200°C in an oil-bath for 5 days. It was then cooled down to ambient temperature and filtered. The resulting solid was washed with water followed by recrystallization from benzene to afford 4.5 g (15.8 mmol, 91%) of pure 2-amino-2′-hydroxy-1,1′-binaphthyl.

In summary, we have discovered a practical procedure for the synthesis of NOBIN. This single-step preparation of NOBIN from BINOL is simple and offers high yield. This method may be applicable for a large-scale synthesis of NOBIN. The enantiomerically pure NOBIN can be obtained from racemic NOBIN by the reported resolution methods.[2e,12]

Acknowledgements

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