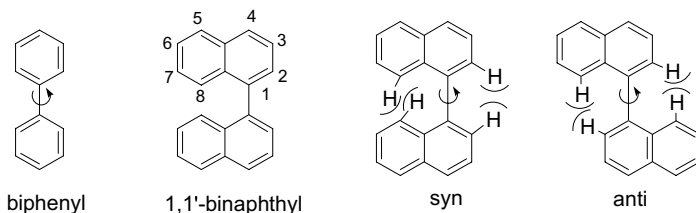


## Chapter 1

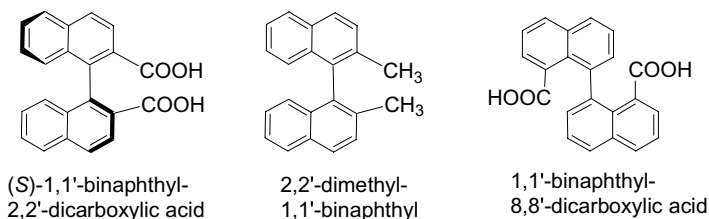
# Introduction About 1,1'-Binaphthyls

1,1'-Binaphthyl compounds represent a special class of biaryl molecules. For a simple unsubstituted biphenyl molecule, its rotation barrier around the phenyl–phenyl bond in gas phase was found to be  $\sim 1.4$  kcal/mol.<sup>1</sup> 1,1'-Binaphthyl incorporated with fused benzene rings to biphenyl has a greatly increased rotation barrier of 23.5 kcal/mol ( $\Delta G^\ddagger$ ).<sup>2</sup> In addition, 1,1'-binaphthyl no longer possesses the plane of symmetry that biphenyl has at the orthogonal conformation. This allows the isolation of the optically active 1,1'-binaphthyl enantiomers. A chiral 1,1'-binaphthyl molecule contains a chiral axis instead of a chiral center. The racemization half-life of the optically active 1,1'-binaphthyl was 14.5 min at 50°C. 1,1'-Binaphthyls have two possible racemization pathways. One goes through a *syn* interaction state where there are close contacts for the 2,2'-H's and 8,8'-H's, and another goes through an *anti* interaction state where there are close contacts for the 2,8'-H's and 2',8-H's. When theoretical rigid models are applied, the *anti* pathway gives lower steric hindrance than the *syn* route. Calculations show that 1,1'-binaphthyl favors the *anti* inversion racemization mechanism.<sup>3,4</sup> However, semi-empirical calculations suggest that 2,2'-dibromo-1,1'-binaphthyl should favor a multi-stage *syn* racemization pathway. The aromatic rings in the transition states of this racemization process are significantly distorted.<sup>3</sup>



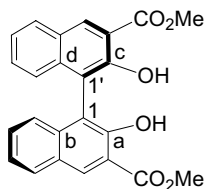
In 1971, Pincock *et al.* discovered that racemic 1,1'-binaphthyl underwent spontaneous resolution to generate the optically active *R* or *S* enantiomer when this compound crystallized from the melt.<sup>5</sup> Out of the 200 crystallization experiments of *rac*-1,1'-binaphthyl examined, the probability to generate the *R* or *S* enriched enantiomer was about the same.

When substituents are introduced to the 2,2'-positions of 1,1'-binaphthyl, the chiral configuration of the 1,1'-binaphthyl compounds becomes very stable. For example, (*S*)-1,1'-binaphthyl-2,2'-dicarboxylic acid did not racemize at 175°C in *N,N*-dimethyl formamide,<sup>6</sup> and 2,2'-dimethyl-1,1'-binaphthyl did not racemize after 40 h at 240°C.<sup>7</sup> This is in sharp contrast to substitution at the 8,8'-positions. For example, 1,1'-binaphthyl-8,8'-dicarboxylic acid underwent racemization in a rate similar to that of the unsubstituted 1,1'-binaphthyl.<sup>2</sup> The half-life for the racemization of the optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid was 51.5 min at 50°C ( $\Delta G^\ddagger = 24.4$  kcal/mol). This is attributed to the steric repulsion of the 1,8-substituents on the naphthalene rings of 1,1'-binaphthyl-8,8'-dicarboxylic acid, which could raise the ground-state energy and cause the deformation of this molecule.



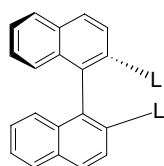
The absolute configurations for chiral binaphthyl compounds were originally proposed by Mislow on the basis of the study of optical properties, stereochemical mechanisms and thermal analysis.<sup>8</sup> This was later confirmed by Yamada and coworkers from the X-ray analysis of (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthalenyl-3,3'-dicarboxylic acid dimethyl ester and its chemical correlation with other binaphthyl molecules.<sup>9</sup> In this compound, its dihedral angle between the two naphthalene rings is  $\sim 77^\circ$ . The absolute configuration of an axially chiral 1,1'-binaphthyl molecule is designated as *R* or *S* according to the following steps: (i) start from one of the naphthalene rings arbitrarily and assign the priority of the two

carbons directly connected to the carbon 1 as  $a > b$ ; (ii) move to the other naphthalene ring and assign the priority of the two carbons directly connected to the carbon 1' as  $c > d$ ; and (iii) determine the *R* or *S* configuration on the basis of the arrangement of  $a > b > c > d$  according to the Cahn–Ingold–Prelog *R–S* notation system.



(*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthalenyl  
-3,3'-dicarboxylic acid dimethyl ester

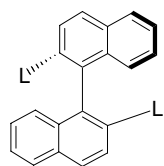
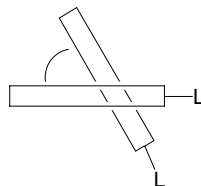
An optically pure 1,1'-binaphthyl molecule can exist in two conformations, *i.e.* *cisoid* and *transoid*, as shown in Fig. 1.1. In the (*S*)-*cisoid*



(*S*)-*cisoid*

L = OH, CH<sub>2</sub>OH, OCH<sub>2</sub>COOH, NH<sub>2</sub>, OCH<sub>3</sub>, OCH<sub>2</sub>Ph or CH<sub>3</sub>

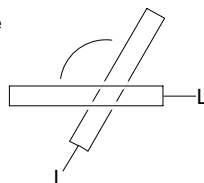
dihedral angle  
< 90°



(*S*)-*transoid*

L = CH<sub>2</sub>Br or CHBr<sub>3</sub>

dihedral angle  
> 90°

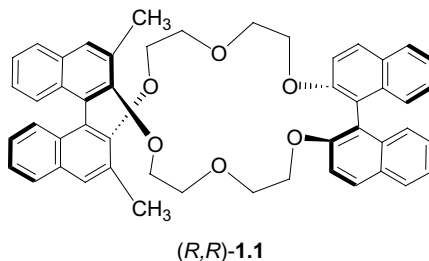


**Figure 1.1.** Conformations of 2,2'-substituted 1,1'-binaphthyls.

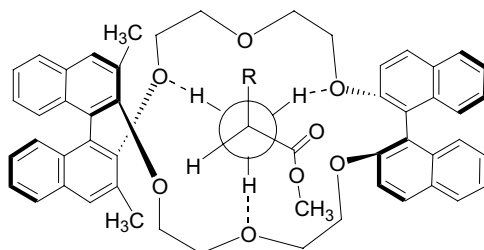
conformation, the dihedral angle between the two naphthalene rings is less than  $90^\circ$ , whereas, in the (*S*)-transoid conformation, the dihedral angle is greater than  $90^\circ$ . The crystal structure of *rac*-1,1'-binaphthyl shows that it exists in the cisoid conformation with a dihedral angle of  $68^\circ$ .<sup>10,11</sup> However, its optically active crystals exist in the transoid conformation with a dihedral angle of  $103^\circ$ . The study of various 2,2'-substituted 1,1'-binaphthyl molecules has indicated that when the 2,2'-substituents L are either small or capable of intramolecular hydrogen bonding, *e.g.* when L = OH, CH<sub>2</sub>OH, OCH<sub>2</sub>COOH, NH<sub>2</sub>, OCH<sub>3</sub>, CH<sub>3</sub> or OCH<sub>2</sub>Ph, the cisoid conformation is preferred.<sup>12–15</sup> When the 2,2'-substituents are large, *e.g.* when L = CH<sub>2</sub>Br or CHBr<sub>2</sub>, the transoid conformation is preferred. The CD spectra of the binaphthyl molecules that have the same *R* or *S* configuration but with the opposite cisoid or transoid conformation are found to be almost mirror images of each other. That is, the conformation of the binaphthyl molecules strongly influences their CD signals. The dynamics of the atropisomerization of 1,1'-binaphthyl in liquid crystalline solvents was also studied.<sup>16</sup>

Because of the highly stable chiral configuration of the 2,2'-substituted 1,1'-binaphthyls, these molecules have been extensively used to control many asymmetric processes and have demonstrated outstanding chiral discrimination properties.<sup>17–19</sup> A great number of 1,1'-binaphthyl molecules are *C*<sub>2</sub> symmetric with two identical naphthyl units. The rigid structure and the *C*<sub>2</sub> symmetry of the chiral binaphthyl molecules are found to be important for their roles in chiral induction. Many binaphthyl-based *C*<sub>1</sub> symmetric catalysts or reagents have also been prepared and studied.

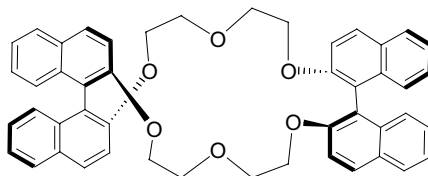
Since the early 1970s, extensive studies on the use of chiral binaphthyl-based compounds including crown ethers, cyclophanes and cyclic amides as hosts for molecular recognition have been conducted in Cram's laboratory.<sup>20–42</sup> These macrocycles either undergo complexation-induced organization in the presence of guests or have pre-organized cavities based on the rigid structures. They interact with the functional groups of guest molecules through weak forces such as hydrogen bonding,  $\pi$ - $\pi$  stacking, and van der Waals forces. The chirality of the binaphthyl units in these hosts leads to their enantioselective complexation with chiral guest molecules. Such a chiral recognition has been applied to the resolution of racemic molecules including amino acids, amino esters, amines, sugars and other chiral alkyl or aryl compounds.



For example, the bisbinaphthyl macrocyclic ether (*R,R*)-**1.1** was synthesized and its specific optical rotation was  $[\alpha]_{578} = +152$ .<sup>22,23</sup> This compound was found to be an excellent chiral host in the differentiation of the enantiomeric salts of chiral amines, chiral amino acids and amino esters.<sup>22,26,27</sup> The chiral recognition factors,  $D_A/D_B$ , ( $D_A$  is the distribution coefficient of the enantiomer more complexed;  $D_B$  is that of the less complexed.) as high as 52 for  $\text{PhCH}(\text{NH}_3^+)\text{CO}_2\text{HClO}_4^-$ , 48 for  $p\text{-HOC}_6\text{H}_4\text{CH}(\text{NH}_3^+)\text{CO}_2\text{HClO}_4^-$ , and 31 for  $\text{PhCH}(\text{CO}_2\text{CH}_3)\text{NH}_3^+\text{PF}_6^-$  were observed when (*R,R*)-**1.1** or (*S,S*)-**1.1** was used to extract these ammonium salts from their water solution into the organic phase (chloroform or chloroform/acetonitrile solution). The D-enantiomers of the amino acid or ester salts bind with the host (*R,R*)-**1.1** more favorably than the L-enantiomers do. Such a high chiral recognition is due to the complementary complexation between the host and the guest. According to the Corey–Pauling–Koltun (CPK) model, the preferred complex between (*R,R*)-**1.1** and an *R* chiral amino ester has a structure as shown by **1.2**. In this host–guest complex, the binding between the crown ether and the amino ester salt involves three O–H–N hydrogen bonds and a  $\pi$ – $\pi$  attractive interaction of the ester group with a naphthalene ring. This four-point binding is essential for the observed high chiral discrimination.

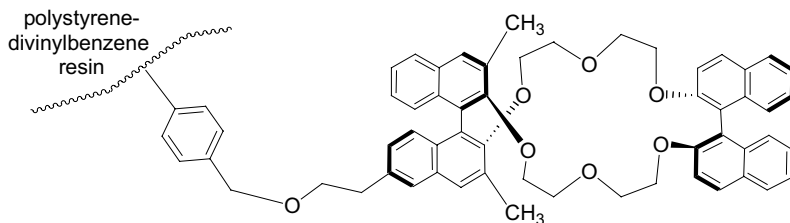


**1.2, a (*R,R*)-1.1-(*R*)-amino ester complex**

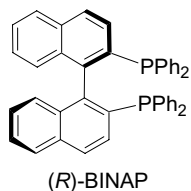
**(*R,R*)-1.3**

A single crystal X-ray structure of (*S,S*)-**1.3** complexed with the hexafluorophosphate salt of (*R*)-phenylglycine methyl ester, the less stable diastereomeric complex, was obtained.<sup>28</sup> Analysis of this structure indicates that the introduction of substituents at the 3,3'-positions of (*S,S*)-**1.3** would increase the steric interaction between the two binaphthyl units in this unfavorable diastereomeric complex and further destabilize it, leading to the observed much higher chiral recognition capability of (*S,S*)-**1.1** over (*S,S*)-**1.3**. The crown ethers made of monobinaphthyl units generally showed lower enantioselectivity than the bisbinaphthyl hosts.<sup>29</sup> A liquid-liquid extraction machine was designed to use (*S,S*)-**1.1** and (*R,R*)-**1.1** to catalytically resolve racemic amino ester salts. Up to 90% optical purity of the enantiomers could be continuously removed from this device.<sup>30</sup>

Macrocycle (*R,R*)-**1.1** was also covalently bound to polymer resins to prepare the polymeric material (*R,R*)-**1.4** as a chiral stationary phase for enantioselective chromatography.<sup>31</sup> The chromatography columns made of (*R,R*)-**1.4** gave baseline separation for the enantiomers of a number of amino acid and amino ester salts. The chiral recognition behavior of the immobilized host parallels that of the macrocycle itself.

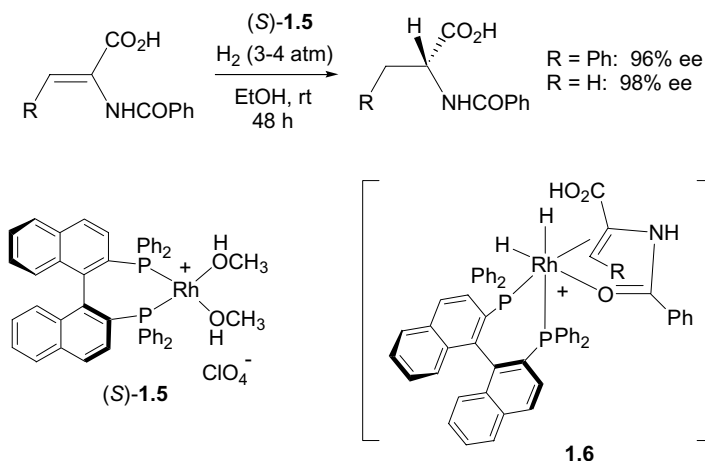
**(*R,R*)-1.4**

Besides the study of the binaphthyl-based crown ethers for chiral recognition, another important milestone in the development of the binaphthyl

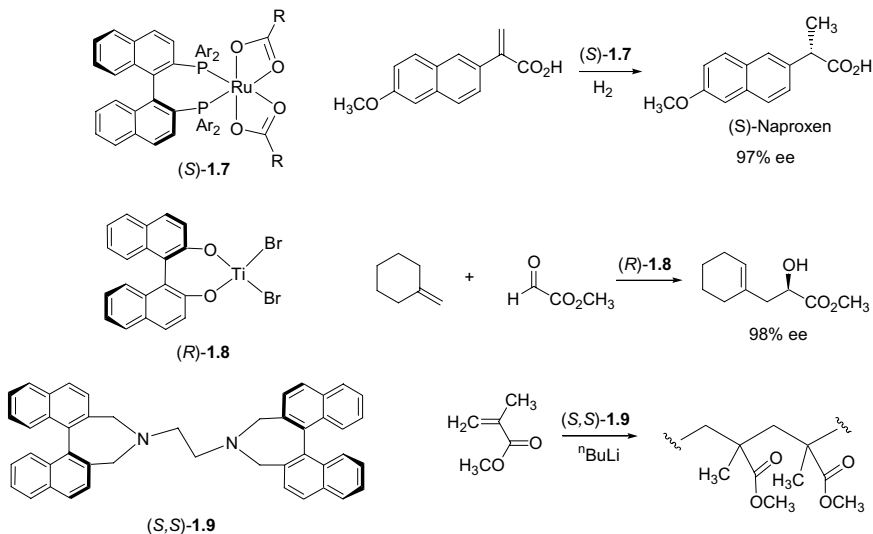


chemistry is the discovery of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP)-based chiral catalysts in asymmetric hydrogenation.<sup>43–46</sup> For example, the rhodium complex of BINAP, (*S*)-**1.5**, catalyzed the hydrogenation of enamides to generate the  $\alpha$ -amino acid derivatives with excellent enantiomeric excess ( $ee = |R - S| / |R + S|$ ) (Scheme 1.1).<sup>43</sup> The dihydride complex **1.6** was proposed as an intermediate for the asymmetric hydrogenation process. From **1.6**, the hydride and alkene ligands can undergo migratory insertion and then reductive elimination to generate the *N*-acyl amino acid product. The stereochemistry for the hydride-alkene reaction is governed by the chelated chiral BINAP ligand.

The ruthenium complex of BINAP, (*S*)-**1.7**, was later found to be a more generally applicable catalyst for the asymmetric hydrogenation of a variety of functional alkenes (Scheme 1.2). Many other binaphthyl-based metal catalysts have been developed for asymmetric catalysis. Scheme 1.2



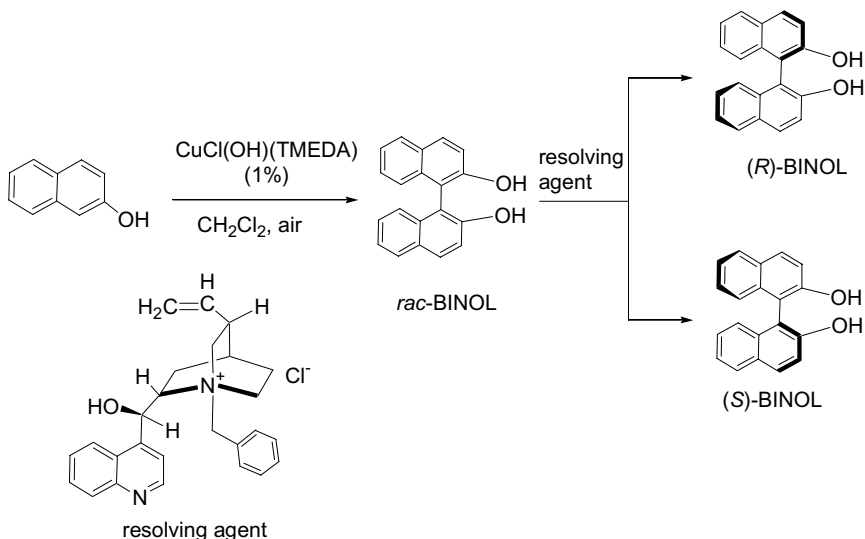
**Scheme 1.1.** Asymmetric hydrogenation catalyzed by a BINAP complex.



**Scheme 1.2.** A few asymmetric reactions catalyzed by binaphthyl complexes.

shows three examples where the chiral binaphthyl complexes (*S*)-1.7, (*R*)-1.8 and (*S,S*)-1.9 are used to carry out asymmetric hydrogenation,<sup>44</sup> asymmetric ene reaction<sup>47</sup> and asymmetric anionic polymerization.<sup>48</sup>

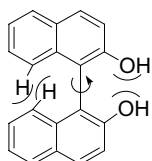
In the study of 1,1'-binaphthyl-based chemistry, 1,1'-bi-2-naphthol (BINOL) often serves as the starting material to chiral binaphthyl compounds.<sup>17–19</sup> The specific optical rotation  $[\alpha]_D$  of (*R*)-BINOL is +35.5 ( $c = 1$ , THF) and its melting point is 205–211°C. The 2,2'-hydroxyl groups of BINOL can be easily converted to other functional groups. The 3,3'-, 4,4'- and 6,6'-positions of this molecule can also be selectively functionalized to prepare a variety of binaphthyl derivatives. Because of the importance of this molecule, great efforts have been devoted to prepare it in the optically pure forms and many methods have been reported.<sup>49–55</sup> Among these methods, the use of (*8S,9R*)-(–)-*N*-benzylcinchonidinium chloride to resolve racemic BINOL into its optically pure (*R*)- and (*S*)-enantiomers received significant attention because of its simplicity and efficiency when used in organic laboratory (Scheme 1.3).<sup>56–59</sup> This method was originally developed by Toda *et al.*<sup>56,57</sup> and was later improved by our laboratory<sup>58</sup> and Cai.<sup>59</sup> Both (*R*)-BINOL and (*S*)-BINOL can be obtained in large scale with high optical purity by using this method. The chiral resolving agent is easily recovered after the resolution.<sup>58</sup> This compound is commercially



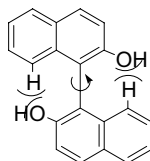
**Scheme 1.3.** Synthesis of racemic BINOL and its optical resolution.

available and can also be synthesized from the reaction of (–)-cinchonidine with benzyl chloride.<sup>60</sup> Racemic BINOL can be produced in large scale from the oxidative coupling of 2-naphthol in air in the presence of a copper catalyst (Scheme 1.3).<sup>58,61</sup>

The chiral configuration of BINOL is thermally stable. After heated at 100°C for 24 h in a dioxane-water solution, (*S*)-BINOL showed no sign of racemization.<sup>62</sup> However, acid or base can promote the thermal racemization of BINOL. In 1.2 N HCl solution, there was 72% racemization for (*S*)-BINOL when it was heated at 100°C for 24 h. In butanol containing 0.67 M KOH, (*S*)-BINOL also underwent 69% racemization after 23 h at 118°C. At 220°C in diphenyl ether, the racemization half-life of BINOL is 60 min ( $\Delta G^\ddagger = 158 \text{ kJ/mol}$ ).<sup>63</sup> The racemization of BINOL might go through an anti pathway as shown by a density functional calculation.<sup>63,64</sup>



syn or cisoid  
racemization path



anti or transoid  
racemization path

The structures of (+)-(*R*)- and racemic BINOL was determined by X-ray analysis of the single crystals of these molecules obtained from the slow evaporation of their toluene and ethanol solutions.<sup>65</sup> In the crystals of (*R*)-BINOL, this molecule has a cisoid conformation with a dihedral angle of 80.8° between the two naphthol rings. In the crystals of racemic BINOL, it has a more orthogonal conformation with a dihedral angle of 91.4°. The C1–C2 bond lengths (1.383–1.367 Å) in both structures are slightly shorter than their C2–C3 bond lengths (1.411–1.407 Å). The C1–C1' bond distances for these two structures are 1.494 and 1.500, respectively. The C1–C2–O bond angles (122.8–123.6°) in both structures are larger than those of C3–C2–O (116.2–114.9°) because of the steric interaction between the OH group and the other naphthol ring at position 1.

While the study of the monomeric chiral binaphthyl compounds continues to be an active research subject in many laboratories, multiple binaphthyl units have also been joined together to extend the chiral differentiation power of the binaphthyl structure and to construct molecular objects and polymers of unique structures and properties. Over a decade ago, our laboratory has stepped on a journey to explore the use of BINOL to construct structurally diverse chiral polymers, dendrimers, macrocycles and functional BINOLs. We have explored the applications of these materials in asymmetric catalysis and chiral sensing and have studied their electrical/optical properties. This is a journey of excitement, dedication and endurance. I am most grateful for the students, post-doctorals and visiting scholars working in my laboratory over these years. Without their intelligence and hardworking, it would be impossible to tell the stories in the following chapters.

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