Chapter 4. Approach to Asymmetric Synthesis of BINOL

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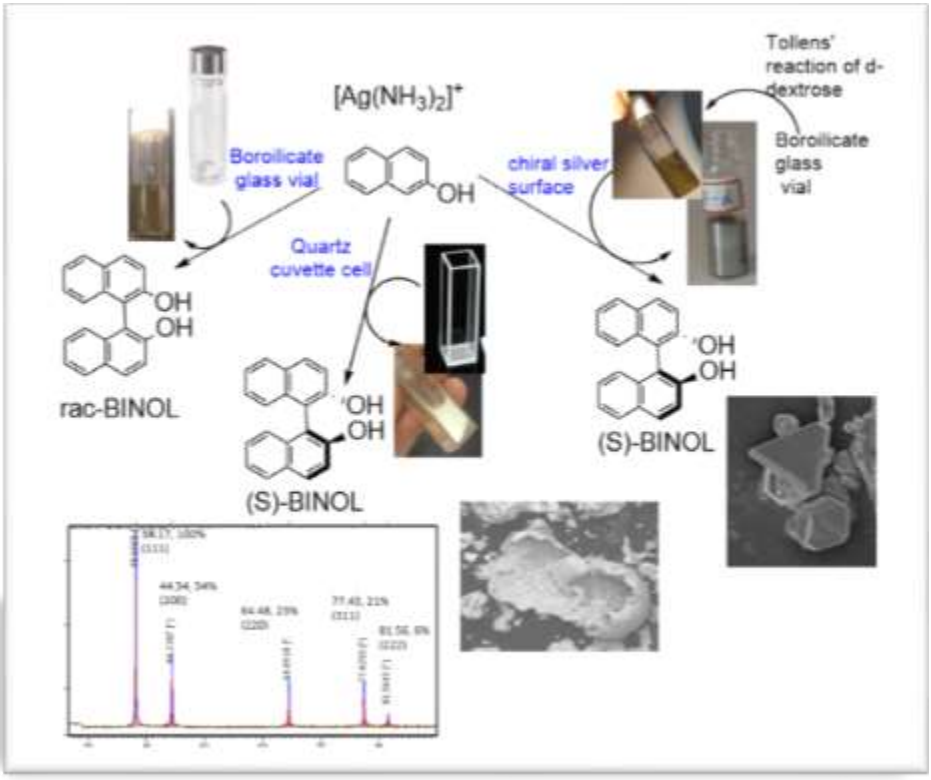


Abstract

This chapter describes three different approaches to obtain optically active/ stereo-selective BINOL by modifying the Tollens' reactions. In the 1st approach, the C-C oxidative coupling reaction of 2-naphthol and modified Tollens' reactions were attempted in the presence of chiral amines and amino acids to obtain optical pure BINOL, possibly due to asymmetric synthesis and/ or chiral resolution. In the 2nd approach, the Quartz surface has been investigated for the asymmetric synthesis of BINOL without using any expensive and toxic organic reagents. In the 3rd approach, freshly generated **silver-coated surface,** obtained from Traditional Tollens' Reaction with (*d)*-glucose, have been explored for the asymmetric synthesis of BINOL.

Up to 57% of enantiomerically excess of (*S*)-BINOL is obtained with 90-92% yield using the 2nd and 3rd approaches. Observed experimental symmetric induction in these approaches is proposed to follow cohesion-adhesion interaction, as discussed in Chapter 3. The silver coating and silver particles were analyzed using optical and electron microscopy as well as P-XRD analysis. Details of these experiments and support for possible mechanisms were discussed.

In short, aggregate formation of Silver, cohesive interaction, during Tollens' test is correlated as a driving force for enantiomerically enriched BINOL synthesis. Although the attempt is in the primary stage but promising, its in-depth analysis will be provided in due course. If successful, these experiments open up a totally new scope for asymmetric synthesis/ enantio-selective C-C oxidative coupling reactions.

4.1 Introduction

Chirality is a geometric property, where the object is non-superimposable to its mirror image, and can not be converted to its mirror image by any translation or rotation alone.[1] Chiral objectives do not contain improper rotation axis (Sn), planes of symmetry, and inversion center in structure. In chemistry, a molecule/ions are non-super-imposable to its mirror image is called chiral.[1] Chirality for organic compounds is defined by the presence of asymmetric carbon atom/center, axial chirality, and chiral propeller arrangement. All living organisms on earth naturally form selectively *L*-amino acids and *D*-sugars.[1] Naturally available some mineral crystallizes in twisted forms shows chiral properties, such as Quartz ($P3_121$ and $P3_221$), cinnabar, sodium chlorate, and sodium bromate ($P2_13$ space group), as shown in the Figure F4.1.1.[1,2]

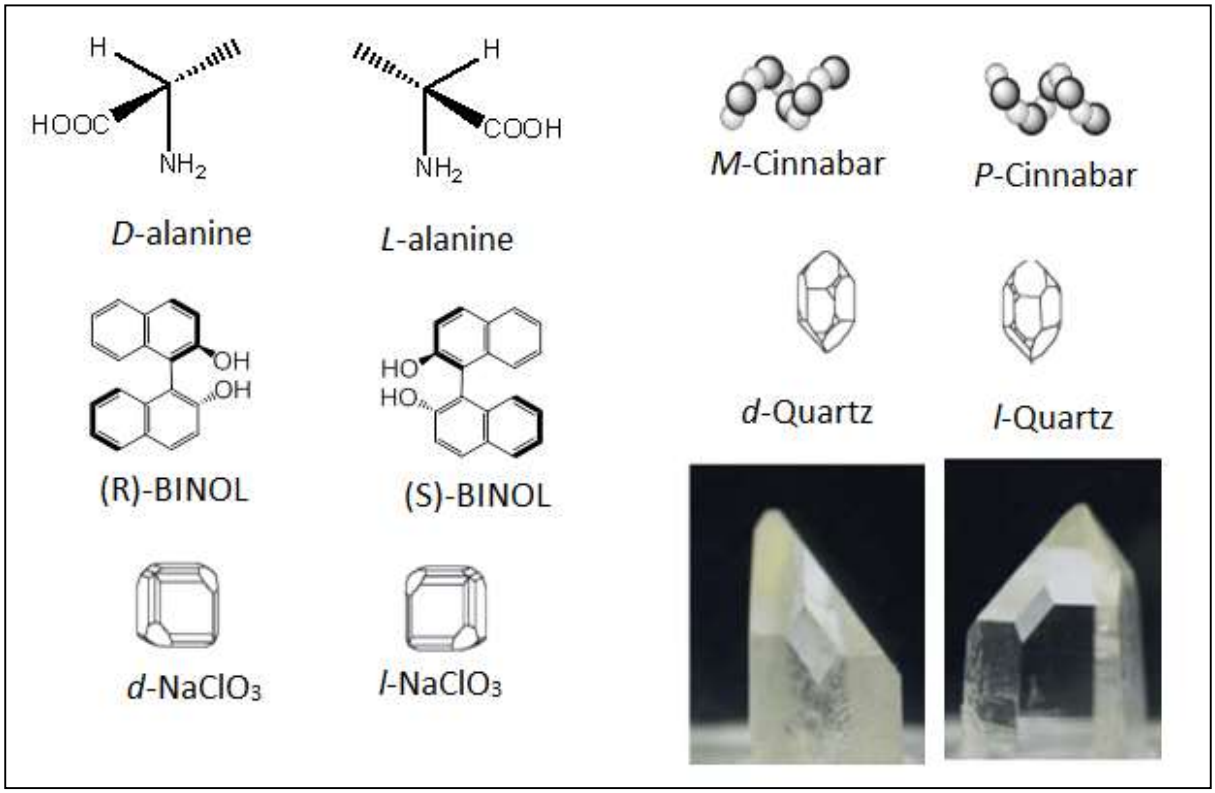


Figure F4.1.1: Chiral compounds: amino acid, axially chiral BINOL, diagram of chiral crystals of achiral compounds/minerals; photographs of optically pure Quartz crystals (from reference[3])

In 1922 Christie and Kenner identified the chirality in biaryls containing hindered rotation around the single bonds joining aryls, due to high-energy barrier to axial rotation, which restricts the isolation of the conformers.[1] These compounds were defined as **Atropisomers** by Kuhn.[4] 1,1'-Bi-2-naphthol (BINOL) is available in two stable enantiomeric forms (due to atropisomers), having barriers of rotation 23.8 kcal/mol.[5,6] BINOL and its derivatives are widely used in the induction of chirality in asymmetric reactions in modern chemistry.[5,6] They are also known as the most privileged molecular entities in material, organic, and physical chemistry.[5,7,8] They are used in numerous applications in pharmaceuticals for the preparation of chiral auxiliaries, chiral complex, ligands, polymers, and catalysts.[5,7–11]

Optically pure BINOL can be synthesized by the asymmetric synthesis method, which has been reported by aerobic oxidative coupling of 2-naphthol using asymmetric catalysts.[9] In these chemical reaction or reaction sequence of chemical reaction results in preferential formation of one of the stereo-selective products (or enantio-selective) over another (enantiomeric or diastereomeric). The organometallic compounds and chiral transition metal complexes such as copper complex of chiral amine/amino acid[12–22], iron salan complexes/schiff base[23–28], vanadium-based chiral mono- or dinuclear-complexes[29–39], and ruthenium-complexes[5], were well reported as asymmetric catalysts for the enantioselective synthesis of BINOL. However, the Asymmetric processes are lengthy multiple steps, and catalyst recovery and reactivation are tricky, thus generally not efficient economically and chemically.

Optically pure BINOL can be obtained by chiral resolution, which is a separation of the enantiomers from a racemic mixture with at least recovery of one of the enantiomers. Even though the main disadvantage of 50% by-product formation, the resolution methods are still considered as a special technique to obtain enantiomerically pure compounds. The chiral resolution of BINOL from racemic BINOL can be done by physical separation of diastereomers or by chemically kinetic resolution using biocatalyst/enzymes. Chiral compounds such as 1,2-cyclohexanediamine[40], threo-(1S,2S)-N-benzyl-N,N-dimethyl[1,3-dihydroxy-1-(4-nitrophenyl)]-2-propylammonium chloride[41], Chiral N-benzylcinchoninium chloride[42] and Proline[43], chiral cyclohexanediamine[44], camphor[45], N-(3-chloro-2-hydroxypropyl)-N,N,N-trimethylammonium chlorid[46] were reported as an efficient chiral derivatizing agent for resolution of (*Rac)*-BINOL.

The chiral reagent reacts only with one enantiomer, due to a difference in activation energy, known as the **chemical resolution method.**[47] The chemical reaction of (*Rac)*-BINOL with chiral reagents such as chiral diamine[40], tetrahydro-1,4-epoxynaphthalene-1-acetyl-chloride[48], campher[49], menthol[50] forms selectively one diastereomer, which can be separated easily.
Apart from that, the biological compounds such as plant cell culture[51], camellia sinensis cell culture[52], isolated enzymes, and living cell[53] were also reported to obtain optically pure BINOL, by the Bio-Catalysis method and enzymatic resolution methods.

In this chapter, to obtain optically pure BINOL three different approaches were designed. The optical purity of BINOL mixtures was calculated based on specific optical rotation (SOR) data obtained from polarimetry analysis, by knowing limitations. The calculations for %ee calculations are shown in the experimental section and table T4.4.

4.2 Present Strategy

i. Efforts were directed on using Tollens' reagent for exploring stereo-selectivity in C-C oxidative coupling reactions of 2-naphthol, by keeping our experiments in Chapter 3 in mind.

ii. To achieve stereo-selective BINOL formation, reactions were attempted using external chiral reagent/ additive- Asymmetric synthesis/resolution.

iii. A devised novel strategy where BINOL generation was studied in the quartz cuvette.

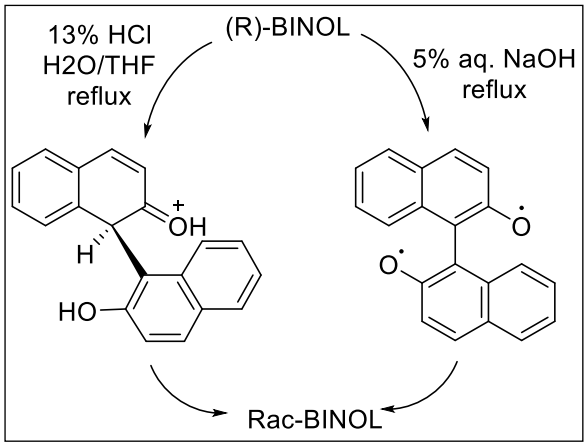
iv. To support the above strategy, the Tollens' Reaction was also performed on a freshly prepared thin silver-coated surface on borosilicate glass, obtained after oxidation of *D*- and *L*-glucose.

4.3 Result and Discussion

Effect of chiral additive on the chirality of oxidative homo-coupling reaction: axially chiral BINOL

The chiral BINOL can be obtained using asymmetric synthesis and chiral resolution methods. The C-C oxidative coupling of 2-naphthol using silver ammine complex resulted in the racemic BINOL, and crystals were also obtained, as shown in chapter 2. The racemization of BINOL was reported in the literature under basic or acid conditions, as shown in schemes S4.3.1[5,54]; thus, the addition of sodium hydroxide was avoided in the present set of Tollens' reactions.

Scheme S4.3.1: Racemization of optically pure BINOL under harsh conditions



In 1st approach to achieve optically pure BINOL formation, the silver complexes were prepared by replacing ammonia with chiral additives (total 16) as shown in scheme S4.3.2. The silver nitrate gets dissolved in alcohol on vigorous stirring after the addition of these chiral additives, resulted in silver complex formation. The 2-naphthol solution (ethanol /methanol) was added to these reagents and kept for 48 hours at 30°C in the dark (refer to section 4.5.4 for detailed experimental procedure). No conversion was observed in most cases. These reactions were also performed at a higher temperature, at 70°C for 3 hours. These reaction mixtures were kept aside at room temperature to check in-situ crystallization. The organic components were separated from silver and attempted for ex-situ crystallization. This strategy also did not yield any quality crystals of BINOL. Interestingly, the nature of the silver particles differs but with no success of organic components (precipitates) as noted in table T4.1.

Scheme S4.3.2: General Scheme for C-C coupling of 2-naphthol using silver complex in presence of chiral additives

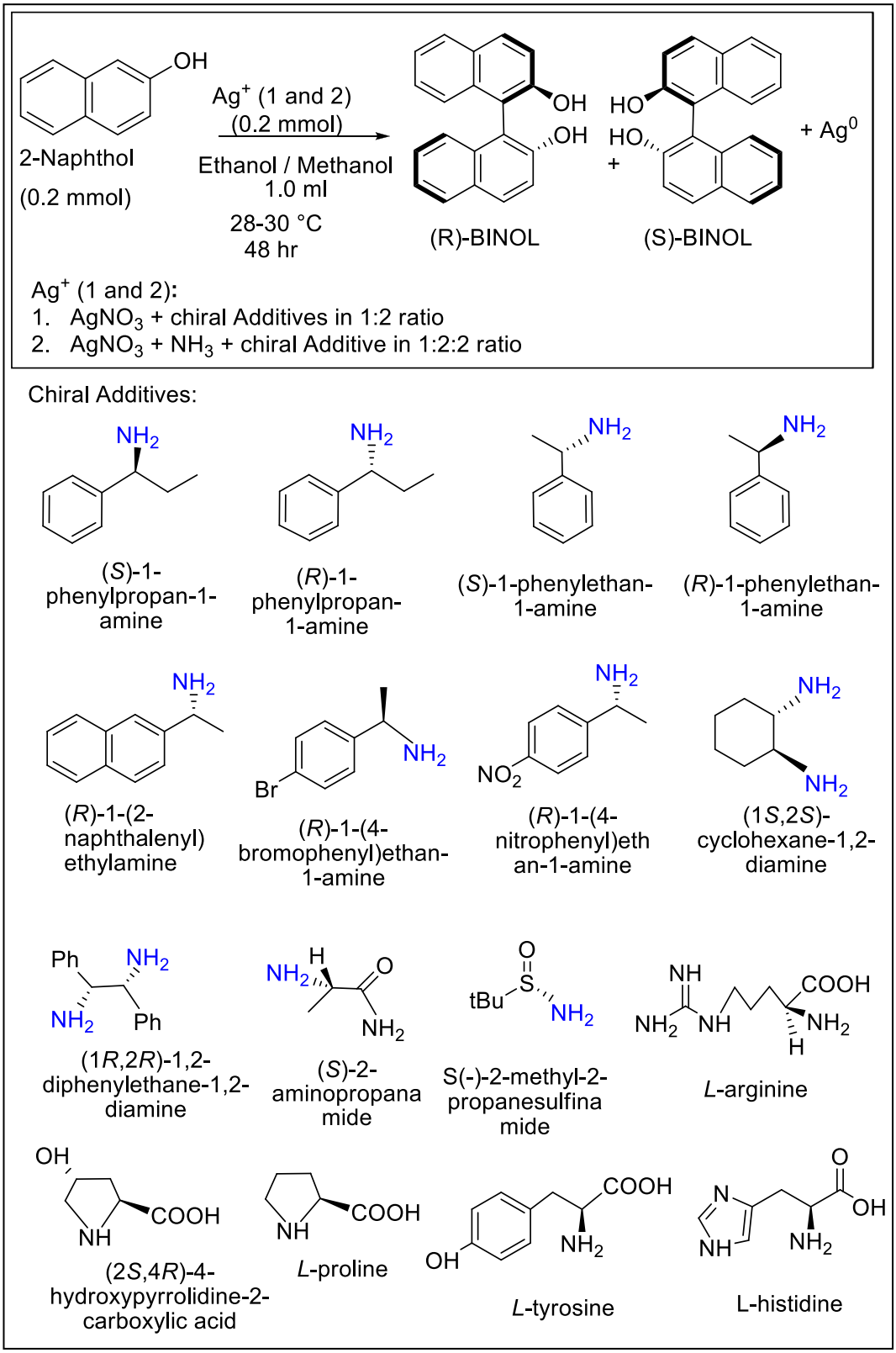


Table T4.1: C-C oxidative coupling reaction of 2-naphthol carried out using chiral additive

	Chiral Additive	In the absence of Ammonia				In the presence of ammonia	
No.	Reaction condition	Room-temperature reaction followed by re-crystallization (I)		Heating reaction followed by re-crystallization (II)		Room temperature reaction (III)	
	Solvent	ethanol	Methanol	ethanol	methanol	Ethanol	Methanol
1	(R)-1-(naphthalen-2-yl)ethan-1-amine	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film
		X	X	X	X	X	X
2	S(-)-2-methyl-2-propanesulfinamide	Ag-part	Ag-part	Blackish Ag-part	Ag-part	Ag-part	Ag-part
		X	X	Rac-CRY	Rac-CRY	Rac-CRY	Rac-CRY
3	(R)-1-(4-nitrophenyl)Ethan-1-amine	Blackish Ag-film	Blackish Ag-film	Ag-part	Blackish Ag-film	Blackish Ag-film	Blackish Ag-film
		X	X	X	X	X	X
4	(R)-1-(4-bromophenyl)ethan-1-amine	Ag-part	Ag-part	Ag-part	Ag-part	Ag-part	Ag-part
		X	X	X	X	X	X
5	(R)-1-phenylpropan-1-amine	Ag-film	-	Ag-film	-	Ag-film	Ag-film
		X	NapC	X	NapC	X	X
6	(1R,2R)-1,2-diphenylethane-1,2-diamine	Ag-part	Ag-part	Ag-part	Ag-part	Ag-part	Ag-part
		X	X	X	X	X	X
7	(1S,2S)-cyclohexane-1,2-diamine	Ag-part	-	Ag-part	-	Ag-part	Ag-part
		X	-	X	-	X	X
8	(R)-1-phenylpropan-1-amine	-	-	-	-	Ag-part	Ag-part
		-	-	-	-	X	X
9	(S)-1-phenylpropan-1-amine	-	-	-	-	Ag-part	Ag-part
		-	-	-	-	X	X
10	(S)-1-phenylethan-1-amine	Ag-part	-	Ag-part	-	Ag-part	Ag-part
		Rac-CRY	X	X	-	X	X
11	(R)-1-phenylethan-1-amine	Ag-part	Ag-part	Ag-part	Ag-part	Ag-part	Ag-part
		X	X	X	X	X	X
12	L-arginine	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film
		X	X	X	X	X	X
13	L- histidine	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film
		X	X	X	X	X	X
14	L-proline	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film
		X	X	X	X	X	X
15	(2S,4R)-4-hydroxypyrrolidine-2-carboxylic acid	-	-	-	-	Ag-part	Ag-part
		NapC	-	NapC	-	X	X
16	L-tyrosine	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film	Ag-film
		Rac-CRY	X	Rac-CRY	X	Rac-CRY	X

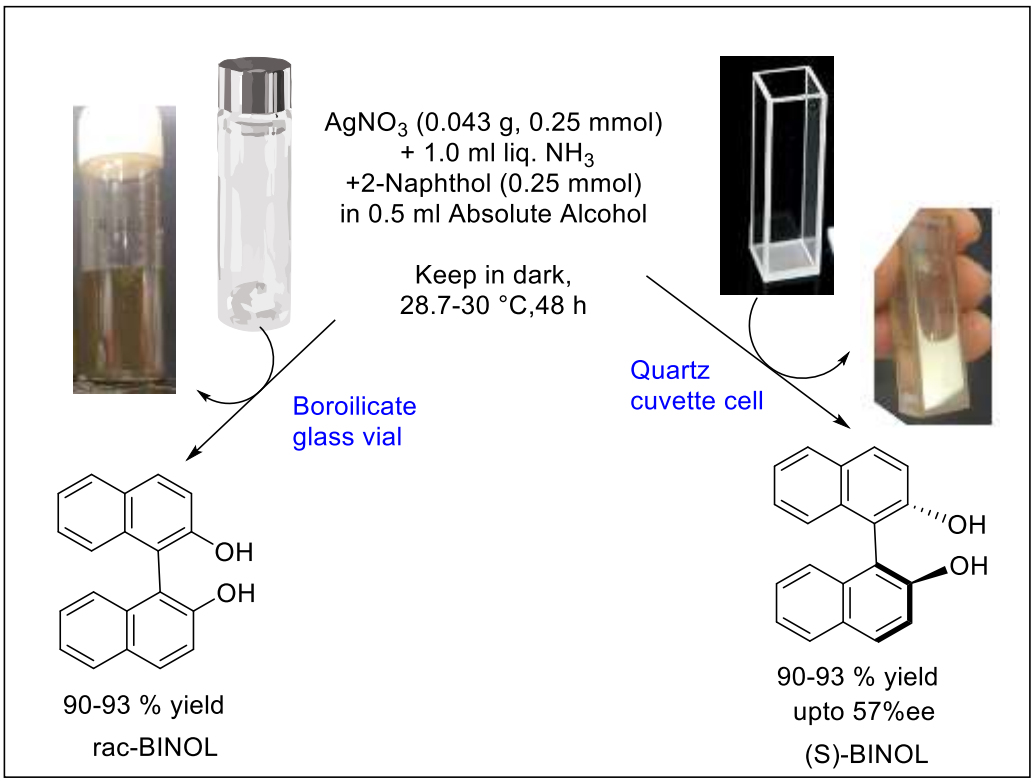
*Reaction carried out $^{(III)}$in the presence of ammonia or $^{(I-II)}$ in the absence of ammonia; carried out at $^{(I)}$ RT/$^{(II)}$ heating; {where observations: Ag-Part = Silver particles, Ag-film =Silver film, NapC =Naphthol crystal, Rac-CRY = (Rac)-BINOL crystal, and X= (Rac)-BINOL obtained in amorphous form}

2-Naphthol was observed un-reacted in numerous cases and could not be converted into the BINOL. Therefore, the C-C oxidative coupling reaction of 2-naphthol was carried out with silver ammine complex in the presence of these chiral additives (total 16), as shown in scheme 4.3.2 (refer to section 4.5.5 for detailed experimental procedure). These reactions resulted in mainly racemic BINOL formation and crystallization, as noted in table T4.1.

Investigation of an active role of Quartz on silver ammine complex-mediated asymmetric C-C oxidative coupling reaction

The literature cites increase in the enantio-selectivity can be achieved by the autocatalysis method, where naturally occurring minerals such as quartz, cinnabar, sodium chlorate, and sodium borate were employed.[55–57] Our 2nd approach, is based on similar lines and is an extension of the hypothesis proposed in the previous chapter-3. Literature also mentions the selective adsorption of a few *L*- and *D*-amino acids on quartz.[58–60] Thus, this part will discuss our attempts to achieve stereo-selectivity in a C-C oxidative coupling reaction by applying a quartz surface.

Scheme S4.3.3: C-C oxidative coupling of 2-naphthol using silver ammine complex in quartz surface



The C-C oxidative coupling reaction of 2-naphthol was attempted in a quartz cuvette, using a silver ammine complex, as shown in scheme S4.3.3. A quartz cuvette of 3.5 ml capacity having 1 cm × 1 cm × 3.5 cm dimensions was used to carry out this reaction (Refer section 4.5.5 for detailed experimental procedure). BINOL was obtained with an average of 92% yield. The optical purity of resultant BINOL was analyzed Polari-metrically, which showed up to 57% ee of S-enantiomer, but the enantio-selectivity was not consistent, as shown in Figure F4.3.1. These experiments were repeated several times, and the reproducibility of the products was confirmed. The repeated experiments confirm the reagent's efficiency and

symmetry breaking capability of quartz surface in cooperative action with silver amine reagent.[61] Remarkably, the Tollens' reaction of 2-naphthol on the quartz surface resulted in enantio-selective BINOL formation, without using any external chiral agent. These inferences are based on polarimetry only.

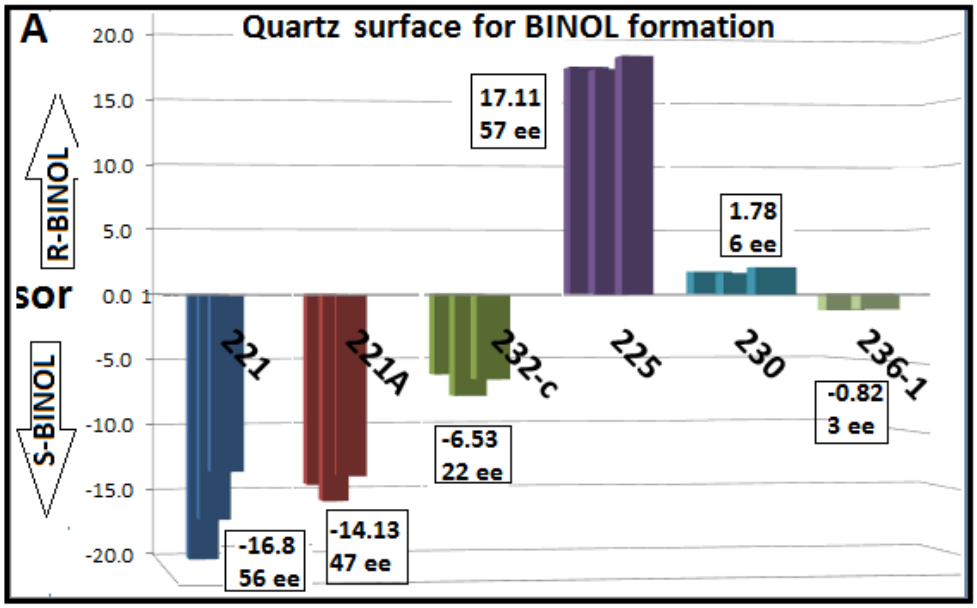
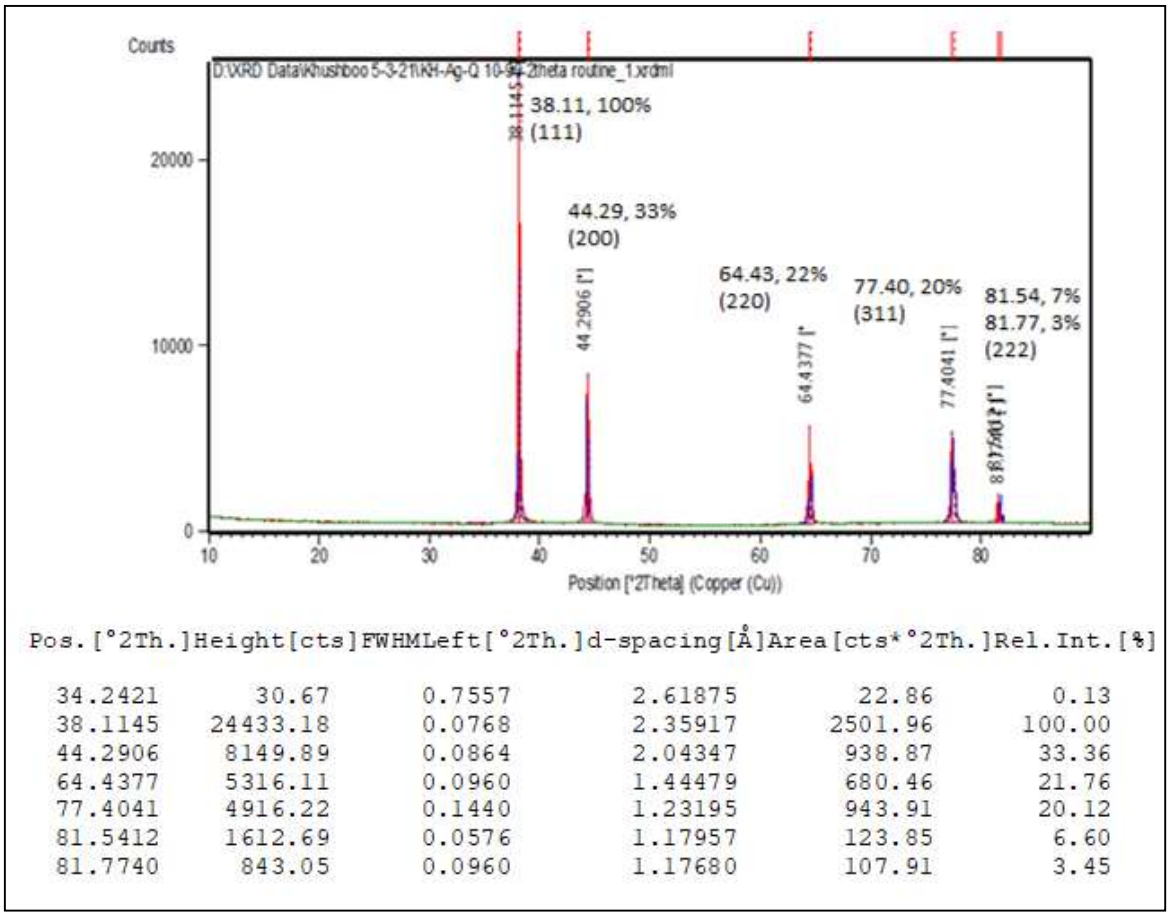


Figure F4.3.1: SOR of BINOL (measured 3 times) obtained using quartz surface in repeated experiments (experiment name) ; in Rectangle values of average SOR and ee%

Analysis of the silver film deposited on the quartz surface was traced to the origin of enantioselectivity. Therefore, The silver obtained was characterized using P-XRD as well as FE-SEM analysis. After washing with ethanol, the silver film gets separated into powder form. This silver powder was washed further with water and dried at room temperature in dark. The P-XRD of these silver powder reflections at 2θ of 38.1º, 44.3º, 64.5º, 77.5º, and 81.5º can be indexed to (111), (200), (220), (311), and (222) reflections of the Face centered cubic-lattice crystalline system for the silver, as shown in F4.3.2. Additional reflection at 2θ of 81.77º was observed with 3.4% intensity (half to the 6.6% to that for 81.54º), which may be due to Cu Kα2 radiation.



Pos.[°2Th.]	Height[cts]	FWHMLeft[°2Th.]	d-spacing[Å]	Area[cts*°2Th.]	Rel.Int.[%]
34.2421	30.67	0.7557	2.61875	22.86	0.13
38.1145	24433.18	0.0768	2.35917	2501.96	100.00
44.2906	8149.89	0.0864	2.04347	938.87	33.36
64.4377	5316.11	0.0960	1.44479	680.46	21.76
77.4041	4916.22	0.1440	1.23195	943.91	20.12
81.5412	1612.69	0.0576	1.17957	123.85	6.60
81.7740	843.05	0.0960	1.17680	107.91	3.45

Figure F4.3.2: P-XRD data of silver particles obtained from C-C oxidative coupling reaction of 2-Naphthol in Quartz surface

This silver was further analyzed by optical microscopy, SEM, and FE-SEM. The optical microscopy of silver particles at 100X magnification shows hollow spherical morphology of particles with ~100 µm radius. Similarly, broken spheres were clearly observed in Scanning Electron Microscope at 100X magnification. At 550X magnification, the SEM images of silver spheres were observed made up of small spherical particles, and gaps between them were clearly observed as shown in Figure F4.3.3. These silver particles were further analyzed using FE-SEM on magnification at 25,000X can be fitted to uniform five-fold twinned decahedron rod shape (0.3 to 0.5 µm broad) with some regular dodecagon-shaped particles, as shown in Figure F4.3.4.

Figure F4.3.3: Silver particles obtained from C-C oxidative coupling reaction of 2-Naphthol in quartz surface: optical microscopic images A) at 8x B) at 100X; SEM images C) at 100X, D) at 550X resolution.

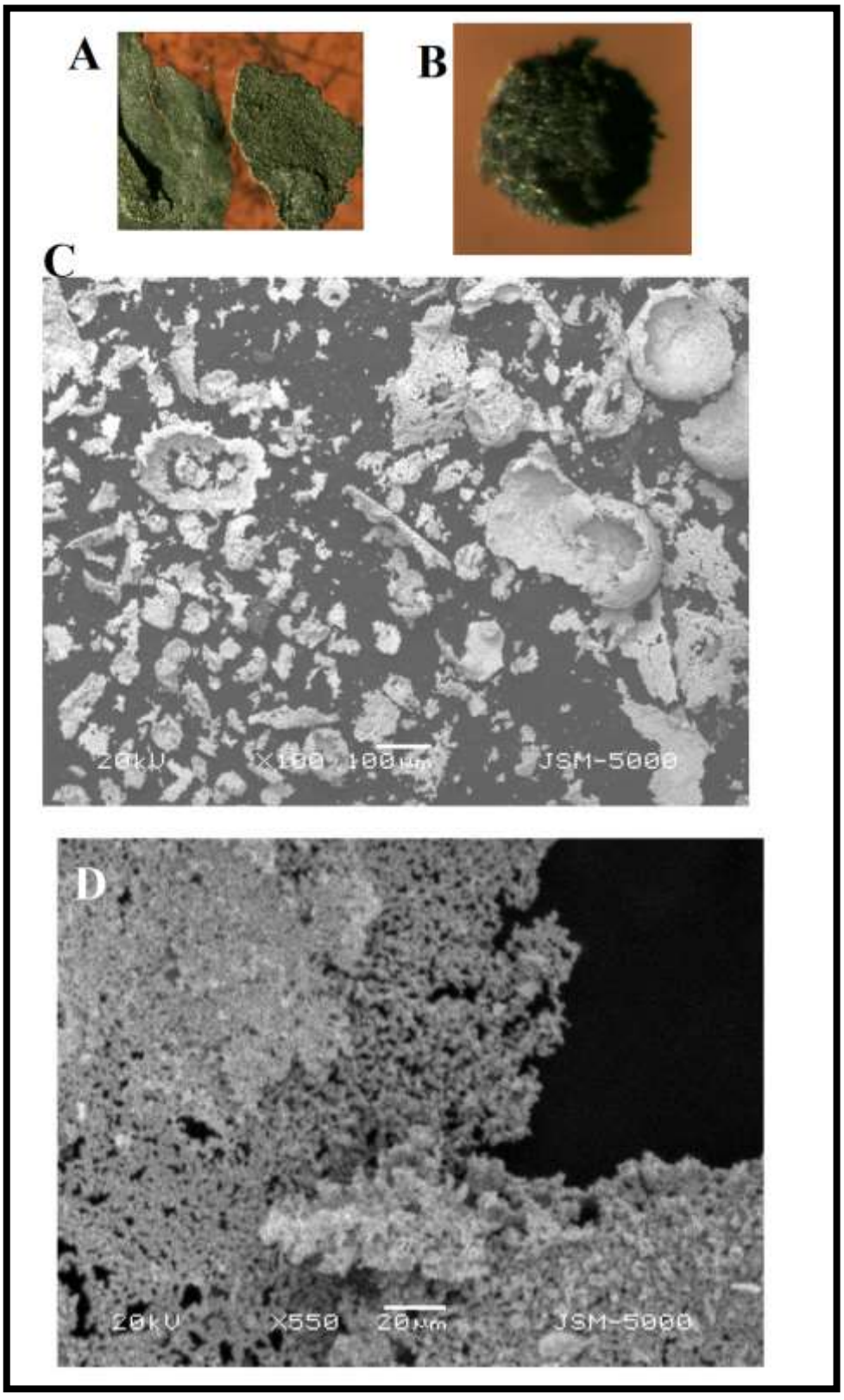
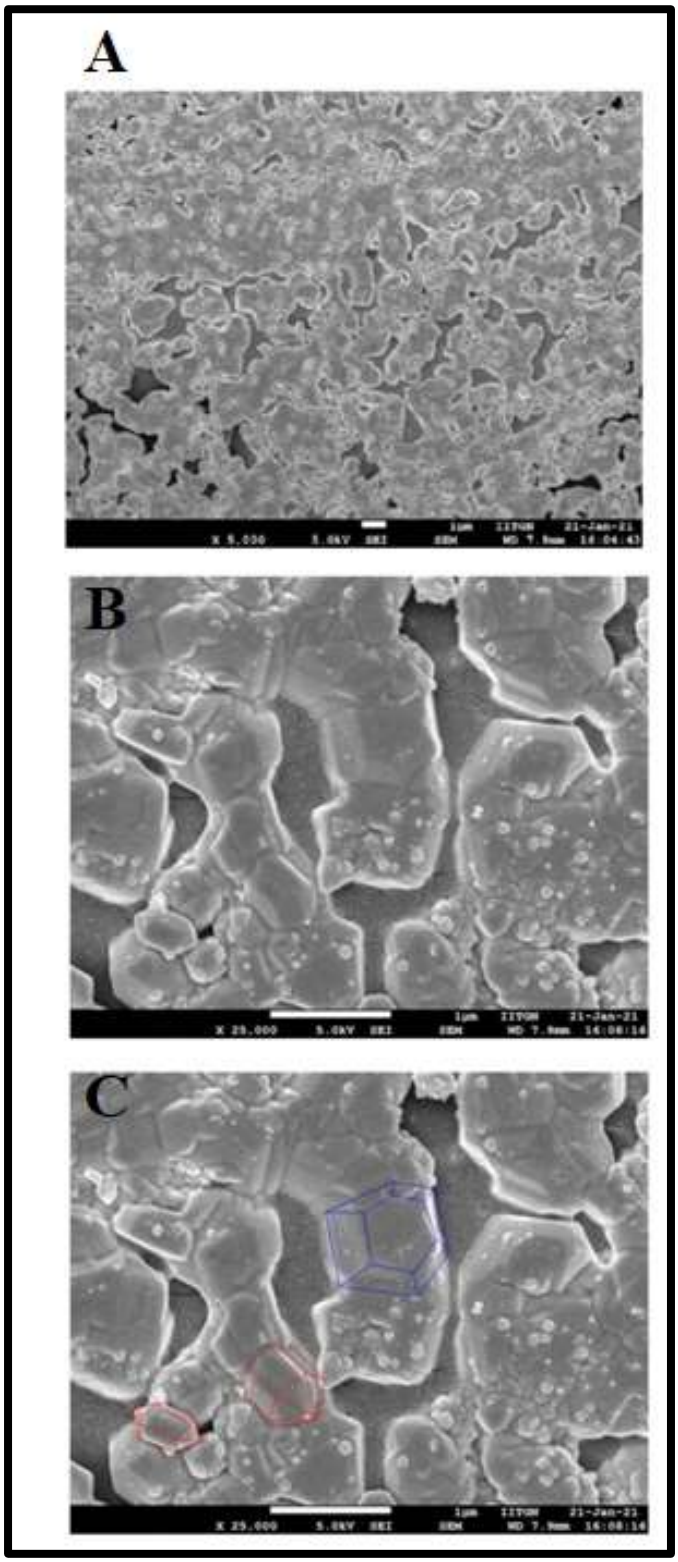


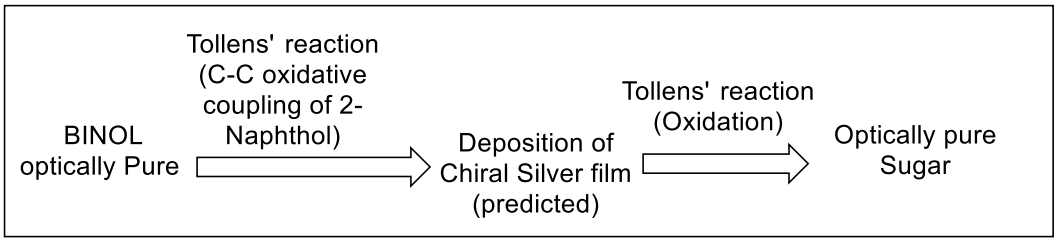
Figure F4.3.4: Silver particles obtained from C-C oxidative coupling reaction of 2-Naphthol in quartz surface; FESEM image at A) 5000X and B) 25,000X resolution; C) image B marked with shapes of silver particles



Considering the difference between optically pure quartz crystal and quartz cuvette, one more experiment was planned. Where, chiral Ag-surface was ‘Imagined’ and generated by Tollens’ reaction, and then studied stereo-selectivity, an approach-III, next section.

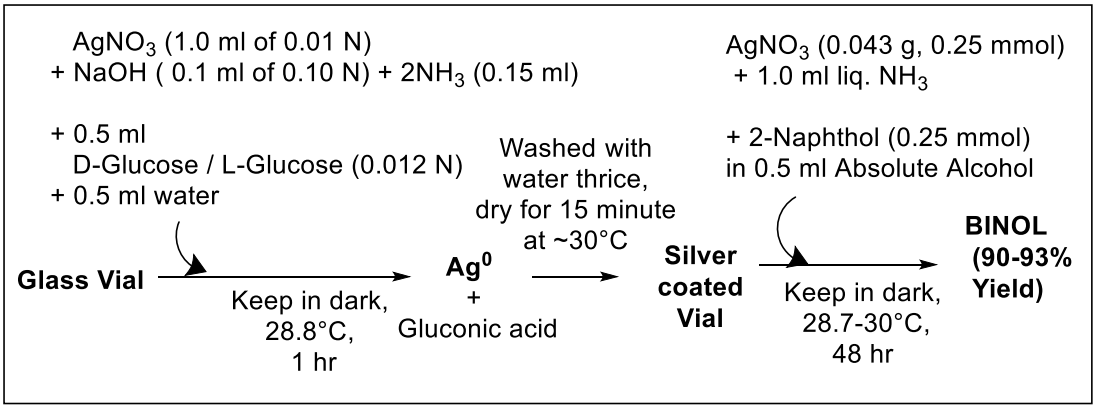
Approach-III: Exploring 'hypothetical' generation of chiral silver surface and therein asymmetric BINOL formation using Tollens reaction.

Scheme S4.3.4: A proposed retro-synthetic strategy for generation of optically pure BINOL in chiral Silver surface obtained after Tollens' reaction on sugar



Recently Silver has been synthesized hierarchically by the redox reaction of Cu and $AgNO_3$ in the presence of (1*S*,2*S*)-(+)-Diaminocyclohexane or (1*R*,2*R*)-(−)-Diaminocyclohexane.[62] Inspired by this work and our efforts in Approach-II, we proposed a retro-synthetic scheme S4.3.4 to prepare the chiral Silver coated surface and then for stereo-selective BINOL formation.

Scheme S4.3.5: Two consecutive Tollens' reactions: First for oxidation of glucose for obtaining 'chiral' silver surface and then oxidative coupling of 2-naphthol



Tollens' reaction of diluted optically pure *D*-Glucose and *L*-Glucose was carried out in a clean borosilicate vial. In this thought experiment, a thin chiral film formation was expected, due to the use of optically pure glucose. In this experiment after 1 hour the silver–coating was observed. The reaction mixture was decanted. This silver-coated vial was washed with alcohol and water rapidly to remove all organics. The vial was dried at room temperature to maintain a clean thin silver-coated surface. FE-SEM studies for these thin films were carried out. But, to complete our thought experiment, we continued C-C oxidative coupling of 2-naphthol using silver ammine complex in the same silver-coated vial, as shown in scheme S4.3.5 (Refer to section 4.5.6 for detailed experimental procedure).

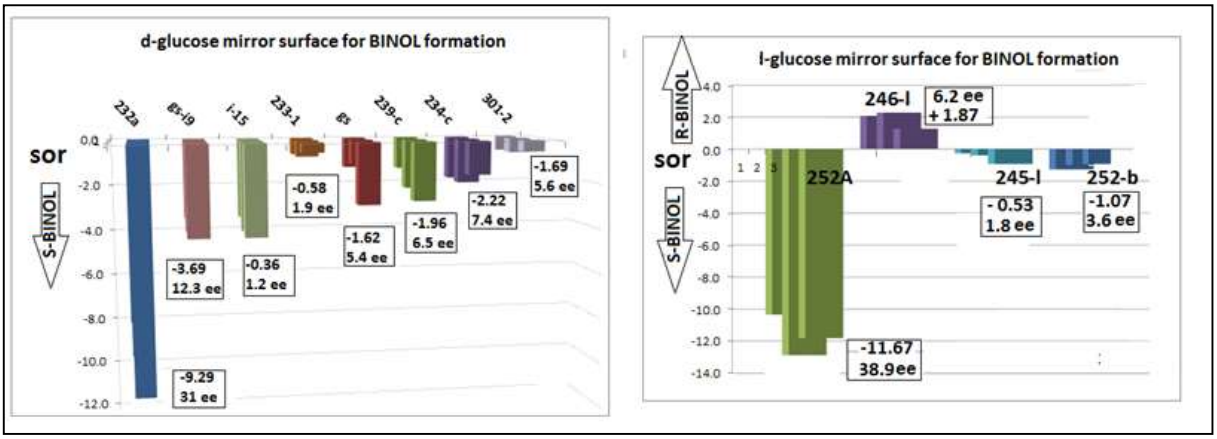


Figure F4.3.5: SOR of BINOL obtained from C-C oxidative coupling reaction of 2-Naphthol in silver coated surface using *D/L*-glucose in repeated reaction; in rectangle value of average SOR and %ee of BINOL

In all attempts, BINOL was obtained with a 90-93% yield. To our expectations, (*S)*-BINOL was obtained with up to 39% enantiomeric excess.

These consecutive Tollens' reaction experiments were repeated several times, and the reproducibility of the stereo-selectivity in BINOL was confirmed.[63] But the consistency in the selectivity values was not observed. The results of repeated experiments are presented in the graphical format in Figure F4.3.5, showing the trend of SOR. To understand these inconsistencies in the results, the experimental procedure was carried out with at most care and repeated several times, as shown in section 4.5.6. In these methods, the racemic BINOL formation was observed when coupling reactions were carried out 1) in the presence of light 2) carried out more than 35°C temperature, Or on the surface having 1) thick coating or 2) prepared at more than 30°C reaction temperature. In general, using dextrorotatory *D*-Glucose, levorotatory (*S*)-BINOL is obtained, which is opposite to starting material's optical activity. This is clearly observed in polarimetry. The levorotatory (*L)*-Glucose resulted in the levorotatory (*S)*-BINOL formation instead of expected dextro-rotatory (*R)*-BINOL. In repetitive experiments, only once opposite (*R*)-BINOL is observed due to unknown reasons, and we could not reproduce it again. The silver-coated surface and silver particles formed after the coupling reaction were analyzed using FE-SEM and P-XRD.

Figure F4.3.6: FE-SEM Images silver obtained from Tollens's reaction of *D*-Glucose: A 5,000X, B 7,500X, and C 50,000X resolution.

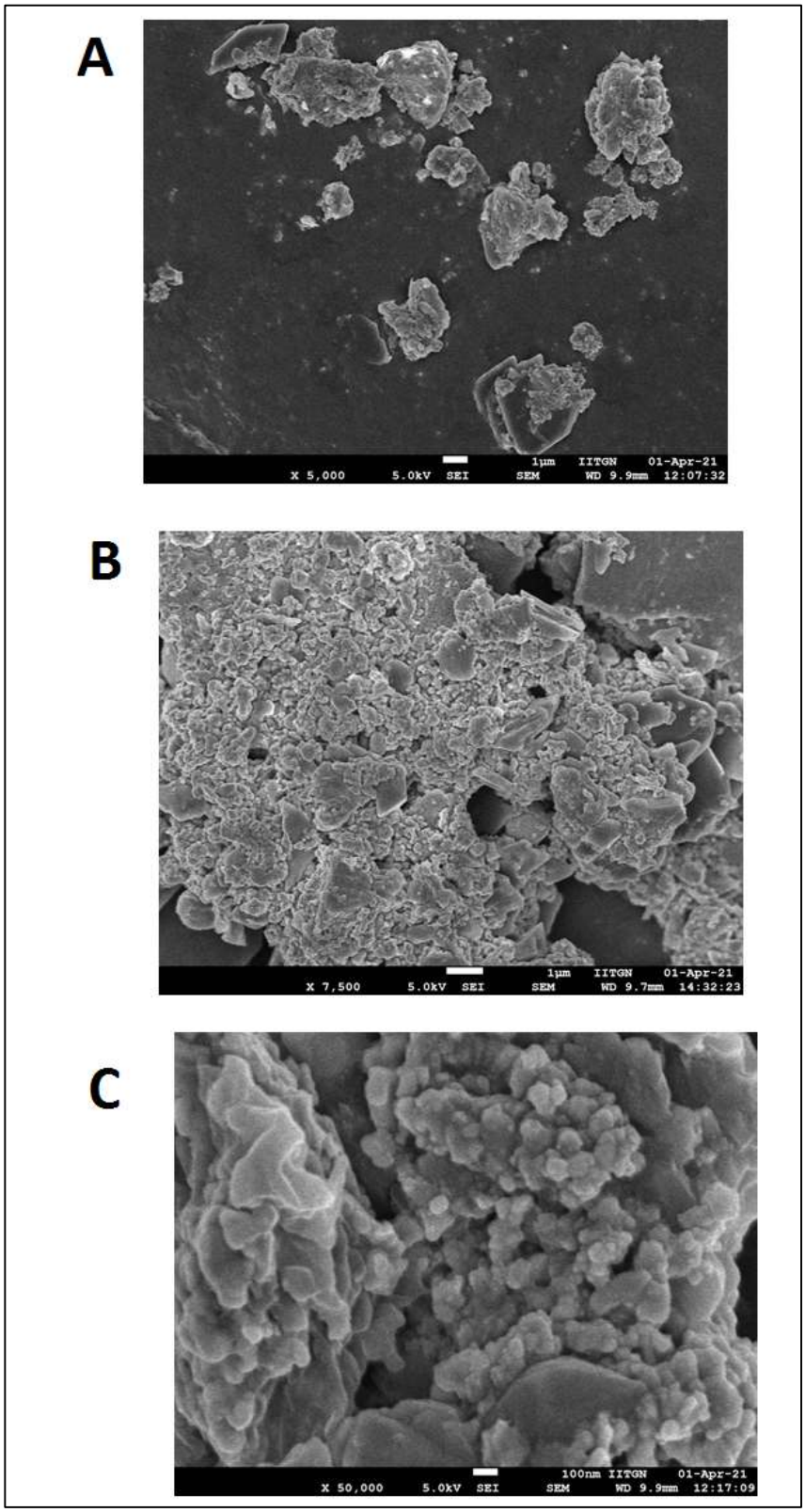


Figure F4.3.7: FE-SEM Images silver obtained from C-C oxidative coupling reaction of 2-Naphthol in the silver-coated surface (using *D*-Glucose) A) 5,000X, B) 10,000X, C) 50,000X resolution and D) images of crystal shapes and possible growth.

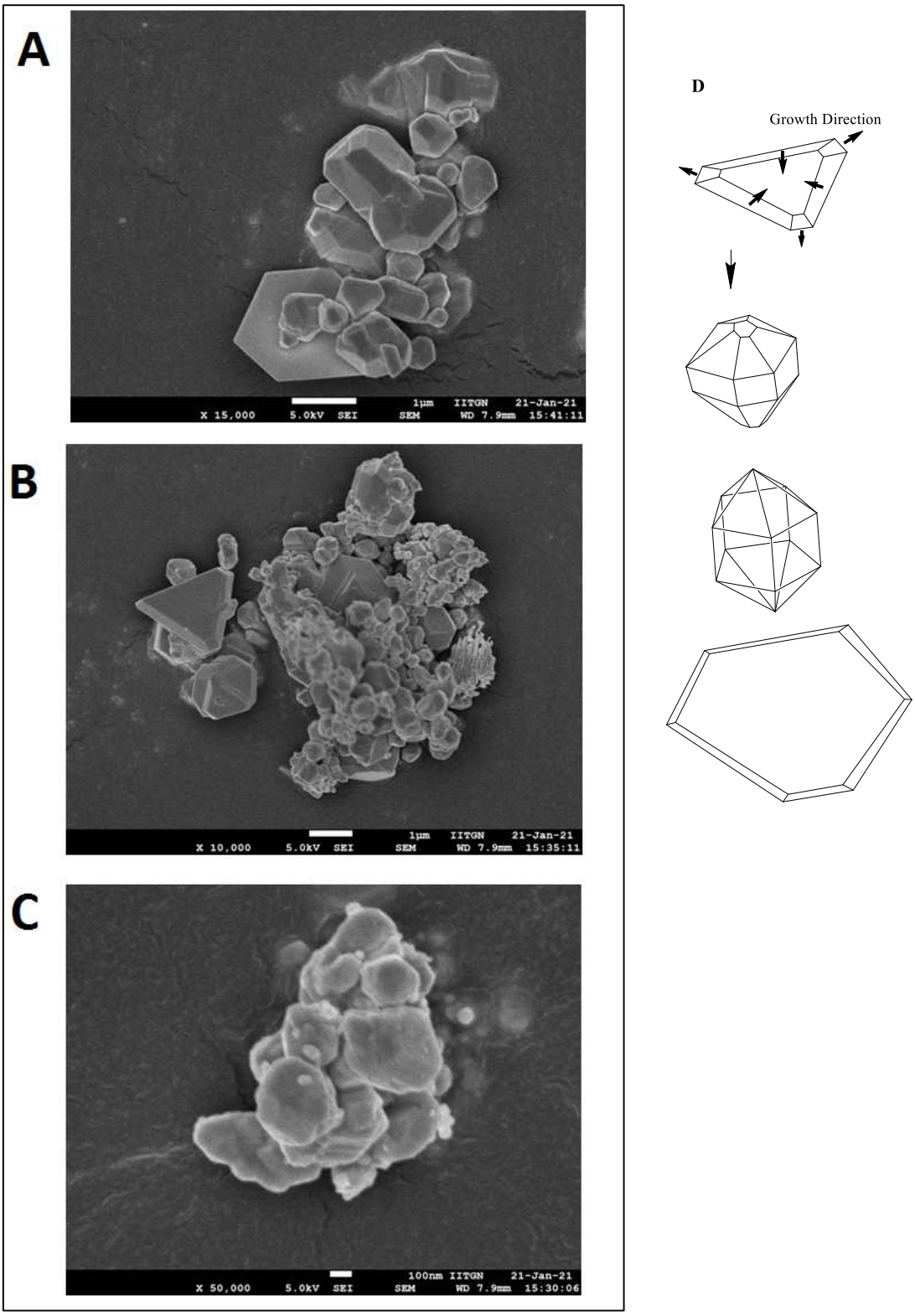


Figure F4.3.8: FE-SEM Images of silver obtained from Tollens's reaction of *L*-Glucose: A) 1,000X, B) 6,000X, and C) 10,000X resolution

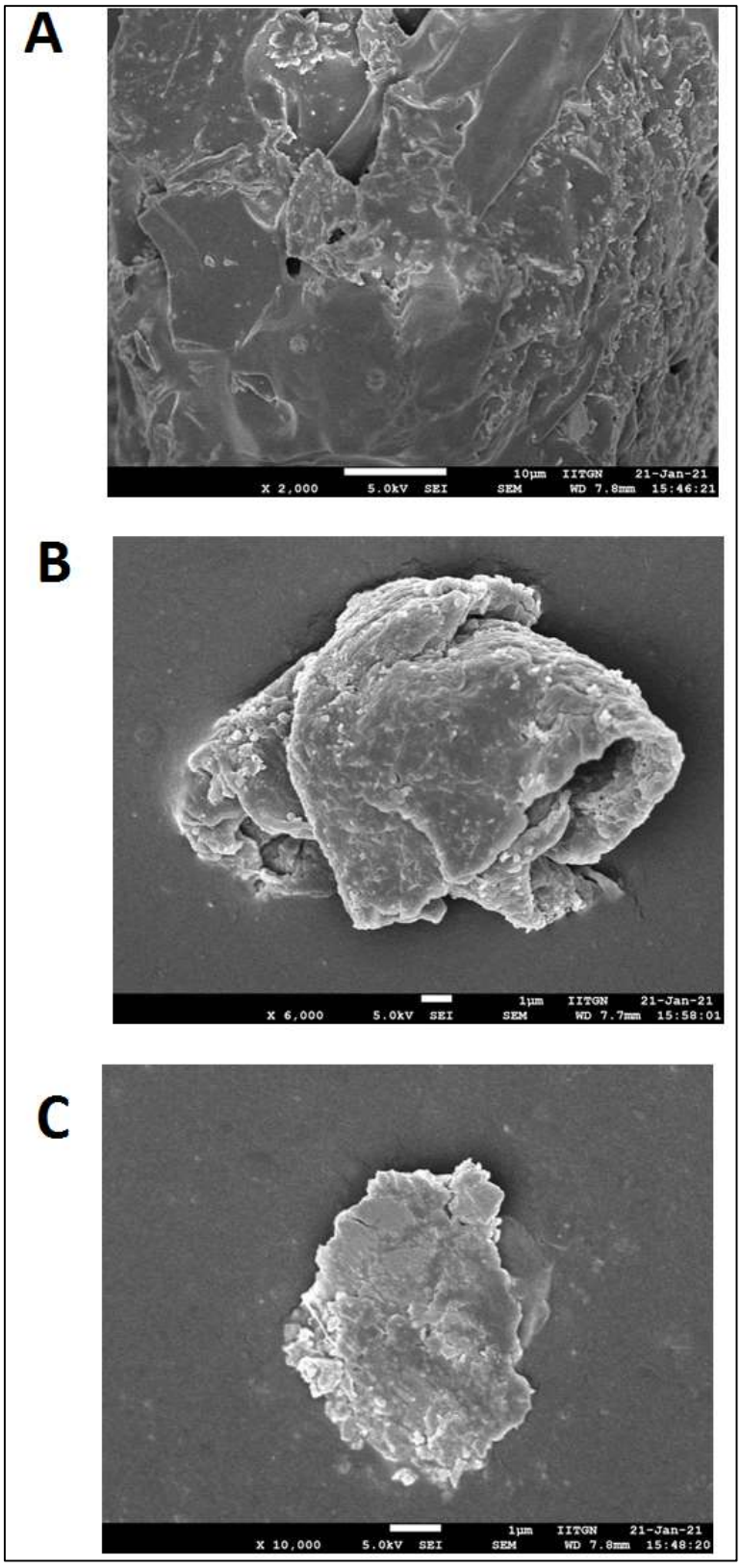
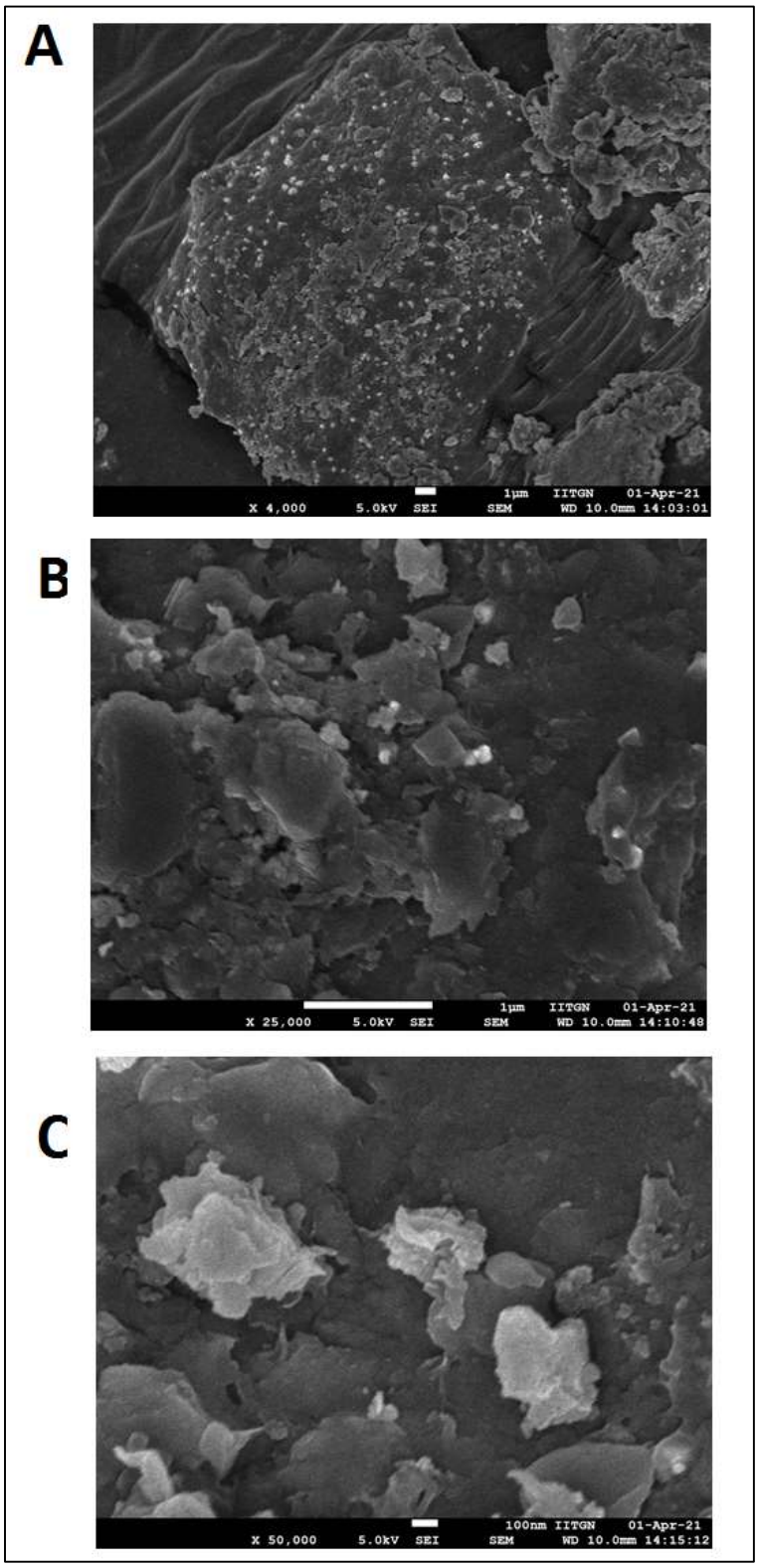
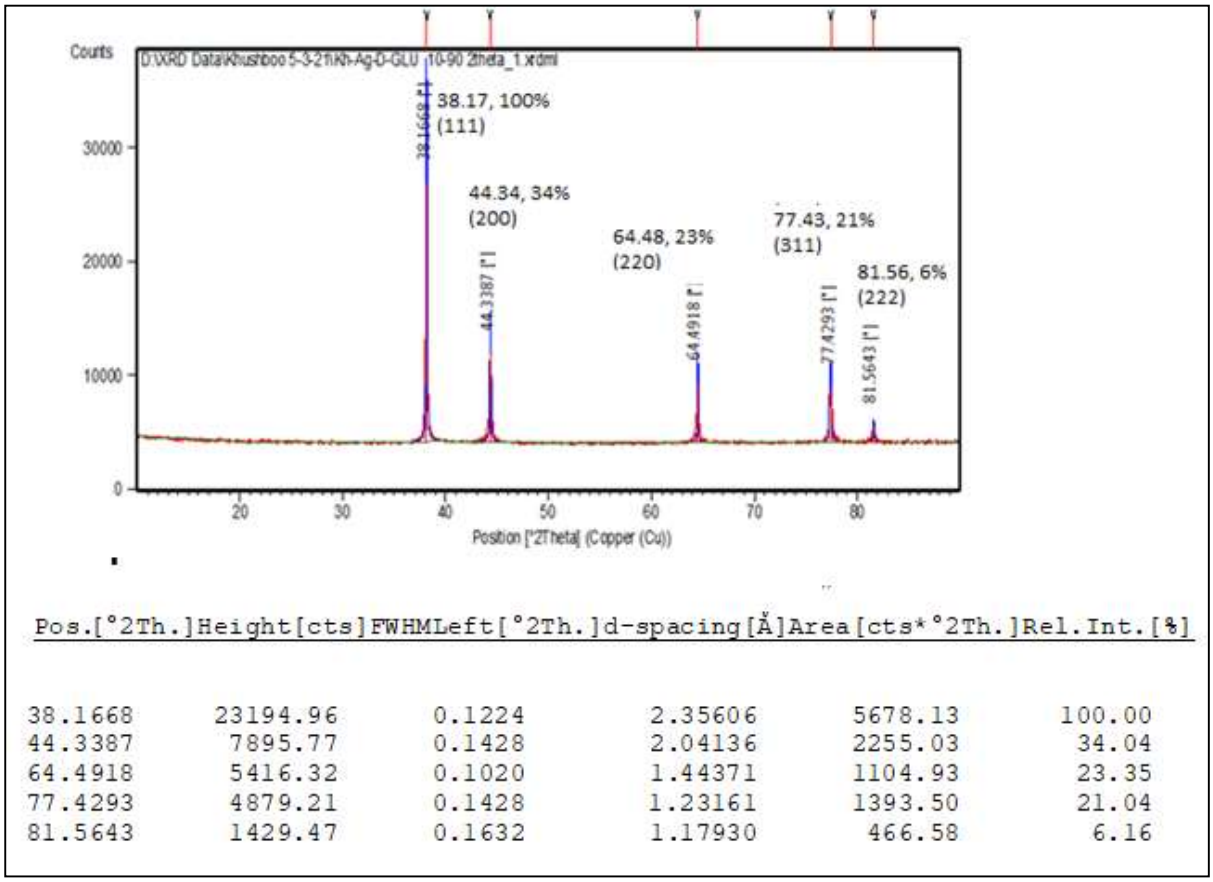


Figure F4.3.9: FE-SEM Images silver obtained from C-C oxidative coupling reaction of 2-Naphthol in the silver-coated surface (using *L*-Glucose) A) 4,000X, B) 25,000X, and C) 50,000X resolution

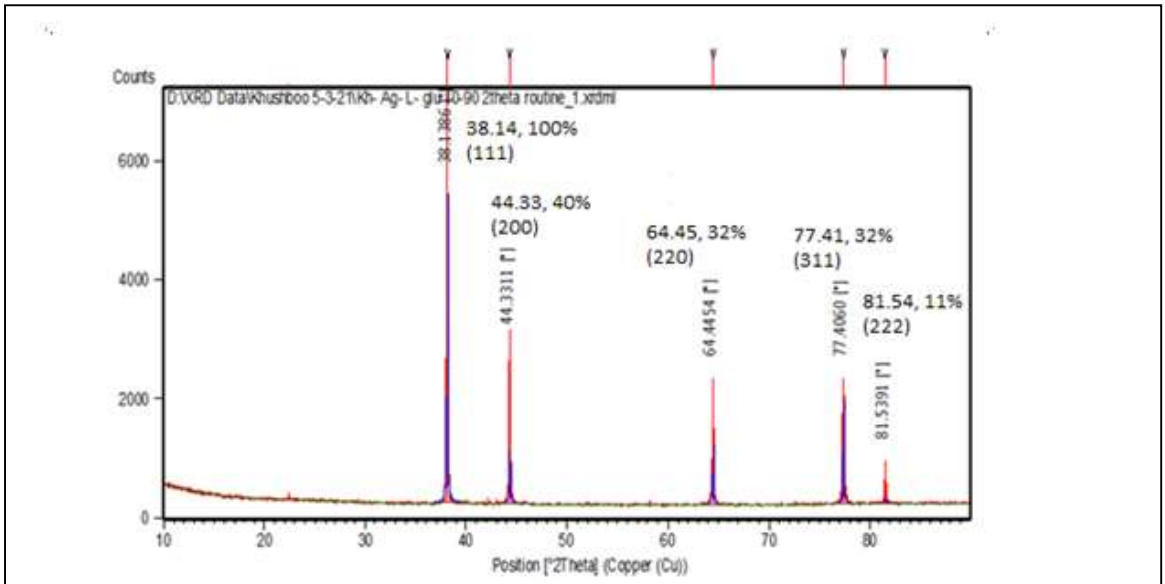


The thin silver film formed by Tollens' reaction of *D*- and *L*-glucose was observed non-crystalline or layered shape in the FE-SEM analysis, as shown in Figures F4.3.6, and F4.3.8. The silver particles obtained after coupling reaction of 2-naphthol in silver-coated surface (from the *D*-glucose reaction) results in different crystalline shapes like hexagons and truncated triangular, and five-fold twinned decahedron rod shapes, as shown in image F4.3.7. These images mimic the micro-crystalline morphology of silver after coupling. On the other hand, the silver particles obtained from the coupling reaction of 2-naphthol in silver-coated surface (from the *L*-glucose reaction) were of layered shape attached from the horizontal plane, as shown in image F4.3.9.



Pos.[°2Th.]	Height[cts]	FWHMLeft[°2Th.]	d-spacing[Å]	Area[cts*°2Th.]	Rel.Int.[%]
38.1668	23194.96	0.1224	2.35606	5678.13	100.00
44.3387	7895.77	0.1428	2.04136	2255.03	34.04
64.4918	5416.32	0.1020	1.44371	1104.93	23.35
77.4293	4879.21	0.1428	1.23161	1393.50	21.04
81.5643	1429.47	0.1632	1.17930	466.58	6.16

Figure F4.3.10: P-XRD data of silver obtained from C-C oxidative coupling reaction of 2-Naphthol carried out in Silver coated surface (obtained from Tollens' reaction of *D*-Glucose)



Pos.[°2Th.]	Height[cts]	FWHMLeft[°2Th.]	d-spacing[Å]	Area[cts*°2Th.]	Rel.Int.[%]
22.4050	103.01	0.0768	3.96494	10.55	1.54
38.1386	6683.74	0.1344	2.35773	1197.73	100.00
44.3311	2679.46	0.0960	2.04170	342.97	40.09
64.4454	2170.99	0.1056	1.44464	305.68	32.48
77.4060	2129.35	0.0960	1.23192	272.56	31.86
81.5391	710.66	0.0576	1.17960	54.58	10.63

Figure F4.3.11: P-XRD data of silver obtained from C-C oxidative coupling reaction of 2-Naphthol carried out in Silver coated surface (obtained from Tollens' reaction of *L*-Glucose)

The silver particles obtained from the C-C oxidative coupling reaction of 2-naphthol on silver-coated surfaces were characterized using P-XRD, as shown in F4.3.10, and F4.3.11. The reflections at 2θ of 38.1º, 44.3º, 64.5º, 77.5º, and 81.5º can be indexed to the (111), (200), (220), (311), and (222) reflections of the Face centered cubic-lattice crystalline system of silver particles.

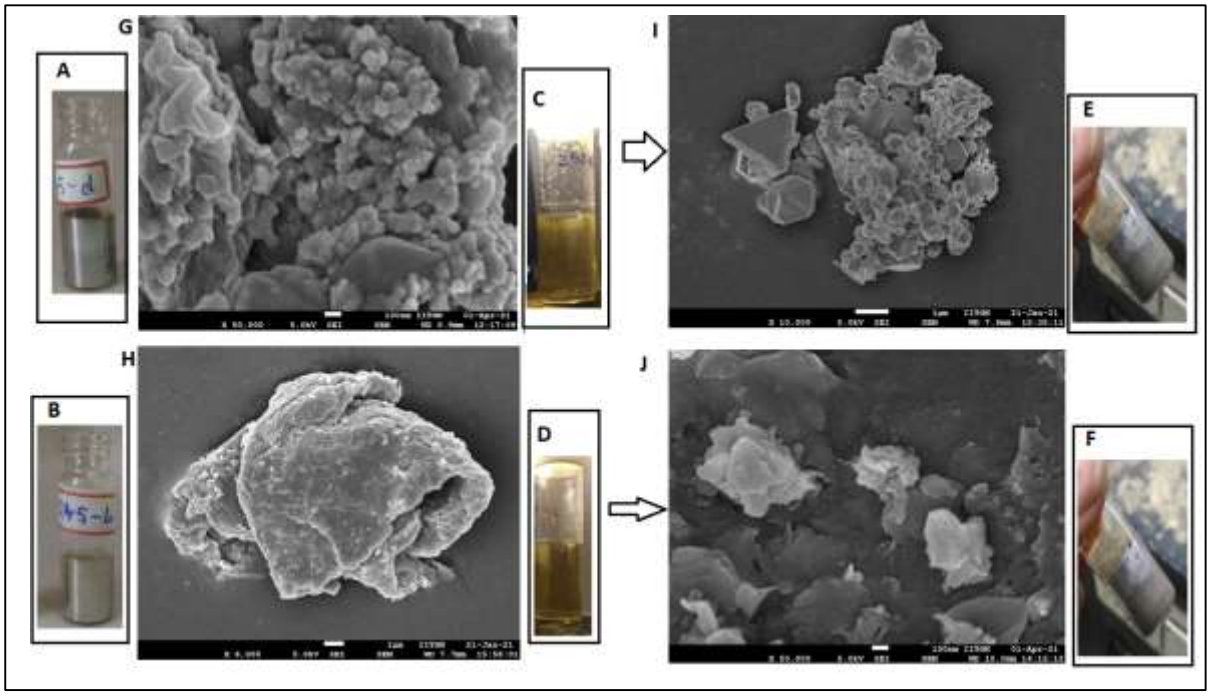


Figure F4.3.12: Images of silver obtained *D*-glucose (upper) and *L*-Glucose (lower): silver coated vial in the reflection mode (A –B) and transmission mode (C-D), after C-C coupling (E-F); And FE-SEM images of Silver film (G-H), silver after coupling reaction (I-J)

These experimental results indicates the source of chirality can be silver coating, which directed the reaction towards the chiral organic product formation. The P-XRD shows the FCC lattice structure of silver, but generally, the FCC Ag structure with high symmetry has no chirality. Still, it has been reported that there exist chiral kink sites in particular high Miller index surface, especially (111) plane, and thus broadness in peak is reported for (111) plane.[62] The comparison of silver-coated surface for *L*- and *D*-glucose, and silver particles obtained after coupling reactions and vials is shown in image F4.3.12. The morphology of silver was different, but to confirm the chiral morphology of silver further analysis is required.

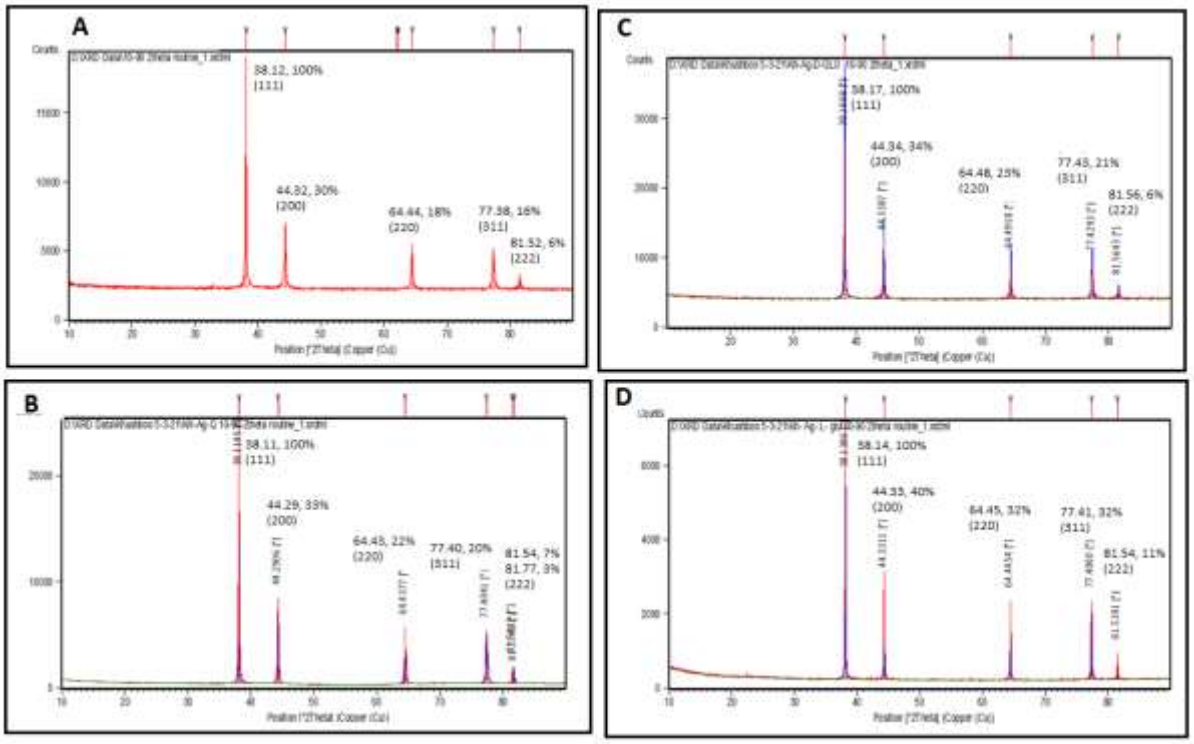
Comparison of surface directed stereoselective reactions

The stereo-selectivity in the coupling reaction of 2-naphthol carried out in four different surfaces, (i) borosilicate glass surface, (ii) quartz surface, (iii and iv) silver-coated surface generated after the Tollens reaction of *D*-glucose and *L*-glucose, are compared and shown in Figure F4.3.13, and table T4.2. These surfaces yielded mainly *Rac*-BINOL, (*S*)-BINOL, (*S*)-BINOL, and (*R*)/(*S*)-BINOL, respectively. Interestingly, the case (ii) and (iii) shows similarities with respect to - (a) crystalline nature of silver particles, (b) relative intensities at (200), (220), (311), and (222) planes, and (c) promising and consistent formation of (*S*)-BINOL, as highlighted in table T4.2. On the other hand, P-XRD on the other two surfaces, viz., (iv) shows intense peaks, while the borosilicate glass surface (i) offered the least intense peaks for all above planes except at (111).

Table T4.2: comparison of silver obtained from C-C oxidative coupling of 2-naphthol on varying surfaces

	The surface used for the coupling reaction	**Borosilicate glass surface (i)**	**Quartz surface (ii)**	**Silver coated surface using *D*-glucose (iii)**	**Silver coated surface using *L*-glucose (iv)**
	The shape of silver particles	-	crystalline particles	crystalline particles	Foils / non-crystalline Planes
2θ	**selectivity** / **Plane**	(*Rac*)-BINOL	(*S*)-BINOL	(*S*)-BINOL	Not clear (*S*)/(*R*)-BINOL
38°	111	100	100	100	100
44°	200	29	33	34	40
64°	220	18	22	23	32
77°	311	16	20	21	31
81.5°	222	5	7	6	11
82°		-	3 (Kα2)	-	-

Figure F4.3.13: P-XRD data of silver obtained from C-C oxidative coupling reaction of 2-Naphthol in A) borosilicate glass surface, B) quartz surface, C) silver-coated surface obtained from oxidation of *D*-glucose), and D) Silver-coated surface (obtained from oxidation of *L*-glucose)



Thus, the present set of experiments shows that the stereoselective organic transformation happens can with the concurrent growth of silver on chiral surfaces. We are presently trying to understand silver particles nucleation, growth, crystallization, and/or film formation using multiple pathways, as shown in Figure F4.3.14.[64] However, all the results indicate the proposed mechanism and hypothesis, where macroscopic forces (adhesive and cohesive interactions) are modulated *in-situ* growth of silver in different morphologies basically to drive stereo-selective BINOL formation.

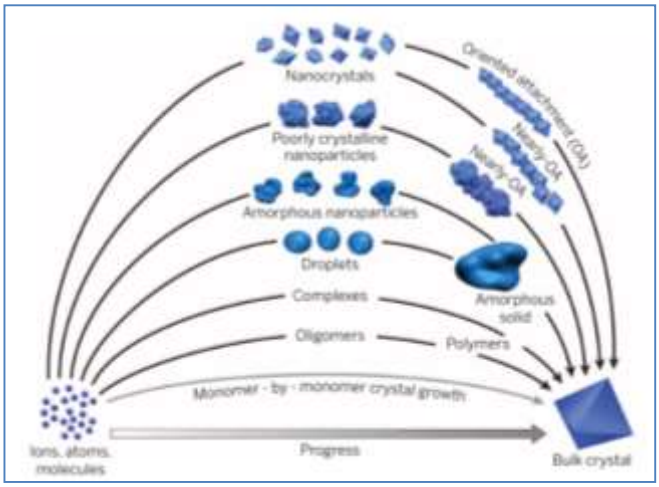


Figure F4.3.14: Possible path for nucleation and growth of any crystals from literature [64]

4.4 Conclusion

In conclusion, the asymmetric synthesis of BINOL was achieved by modifying Tollens' reaction. Attempts were made to use reduced metal's intrinsic cohesive interaction, leading to aggregation for controlling the topology of concurrently oxidizing organic reactant/product on inorganic chiral or crystalline surfaces.

- Reactions of 2-naphthol were carried out with silver complex, using chiral amines, and amino acids (Total 16) as ligand/derivatizing agents, where the formation of optically active BINOL remained elusive.
- Tollens' reaction of 2-naphthol carried out in a quartz cuvette resulted in BINOL formation (90-92 % isolated yield) and more importantly up to 57% enantiomerically enriched (*S*)-enantiomer. These experiments were repeated several times, and the observed optical purity was calculated based on polarimetric analysis.
- On the basis of the above results, Tollens' reaction of optically pure *D*- and *L*-glucose was carried out to generate 'Chial' thin silver film coating on a boro-silicate glass tube.
- Tollens reaction of 2-naphthol carried out in the above 'chiral' silver-coated surface, resulted in BINOL formation (90-92% isolated yield) and more importantly up to 38% enantiomerically enriched (*S*)-enantiomer.
- For all the experiments optical purity of BINOL was measured by using polarimetry analysis.
- The silver formed during all the above experiments was well characterized using optical and electronic microscopically by SEM and FE-SEM showed distinct morphologies.
- During all coupling reactions, silver forms FCC crystalline lattice structures, based on P-XRD analysis.
- The experiment supports the previously proposed hypothesis, "In-situ organizations of Ag^0 due to macroscopic forces (cohesive and adhesive interactions) although not directly relates to BINOL formation but controls enantio-selectivity."

4.5 Experimental

4.5.1 Materials

Silver nitrate was purchased commercially of 99.9999% purity. 2-Naphthol was purchased SRL Pvt. Ltd. commercially And used after purifying by sublimation method. All other reagents were of analytical grade quality, purchased commercially from Sigma-Aldrich, Alfa Aesar, TCI, and used without further purification. Absolute alcohol (99.6 %v/v) was acquired from the Maharaja Sayajirao University of Baroda and was used without further purification. Distilled water was used in preparing the sample solution, which was double-distilled de-ionized in an all-glass distillation setup (specific conductivity of less than 10 μS cm^{-1} at 30°C). All other solvents were purchased commercially from local sources.

4.5.2 Methods and Characterization

- The reaction vessels used were of borosilicate glass, otherwise noted. Glass wares used for the reactions were pre-cleaned and rinsed with dil. HNO_3 and de-ionized water followed by oven drying.
- The products were purified by column chromatography using Fluka chromatographic silica gel (40-60 μm).
- The crystals were analyzed using a single crystal-XRD machine, Oxford X-CALIBUR-S diffractometer equipped with a CCD detector, with CuKα radiation (λ= 1.541841Å) at 293K and processed with CrysAlisPro, Agilent Technologies, and structure was solved using SHELXL program.
- Powder X-ray diffraction (P-XRD) pattern of silver clusters was recorded with X'pert Pan Analytical Powder diffractometer, by using the following instrument parameters: X-ray source: Cu Kα radiation (λ =0.154060 nm); Current 40 mA, Voltage:40kV; 2Θ value from 10° to 90° in continuous scanning mode at 25°C.
- The microscopic FE-SEM images were recorded using Field Emission Scanning Electron Microscope JSM7600F (Jeol) instrument. The optical purity of the BINOL mixture was calculated from specific optical rotation data of mixture analyzed using Rudolph Research Autopol IV Automatic Polarimeter using sodium D-light.

  The optical purity was measured in enantiomeric excess (ee) in %:

$$\textbf{\% ee} = [\alpha]_{obs} \times 100 / [\alpha]_{max}$$

Where the $[\alpha]_{obs}$ is an observed optical rotation of a given sample, and $[\alpha]_{max}$ is a specific optical rotation/ maximum optical rotation of a pure sample.

Where the **Specific Optical Rotation (SOR)**[65] [α] of the sample/compound is the change in orientation of monochromatic plane-polarized light, per unit distance–concentration product, as the light passes through a sample/compound.

$$[\alpha]_{\lambda}^{T} = \alpha / l \times c$$

In this equation, α is the measured rotation in degrees, l is the path length in decimeters, for solution concentration c is used in g/ml, for a liquid sample at a temperature t (given in degrees Celsius) and wavelength λ (in nm). If the wavelength of the light used is 589 nm (the sodium D line), the symbol "D" is used. The sign of the rotation (+ or −) is always given.

- The data were obtained with 0.5 dm path length and 0.3 w/v % g/ml concentration otherwise noted. The specific optical rotation of (*S*)-BINOL and (*R)*-BINOL obtained in absolute alcohol is -30.0°cm^2g^{-1} and +30.0°cm^2g^{-1} (C 0.3, at 28°C, D-light) respectively. And calculations of %ee are shown in table T4.4.

4.5.3 Characterization of organic products

BINOL was characterized using FT-NMR (^{1}H and ^{13}C) spectroscopy, and mass spectrometry analysis, already shown in chapter 2. The crystals obtained from any reaction were separate and analyzed using single-crystal XRD. Crystals were found to be of racemic BINOL and obtained the data is shown in chapter 2. The BINOL was purified using chromatography and further dissolved in ethanol solvent for optical purity analysis. The silver was separated and washed with water and organic solvents for purification.

4.5.4 General procedure for the formation of a silver complex with chiral additives

Herein the additives used are *L*-tyrosine, (*2S,4R*)-4-hydroxypyrrolidine-2-carboxylic acid, *L*-proline, (*1S,2S*)-cyclohexane-1,2-diamine, (*R*)-1-(4-bromophenyl)ethan-1-amine, (*S*)-1-phenylethan-1-amine, *L*-arginine, (*R*)-1-phenylethan-1-amine, (*1R,2R*)-1,2-diphenylethane-1,2-diamine, (*S*)-1-phenylpropan-1-amine, (*R*)-1-phenylpropan-1-amine, *L*- histidine, (*R*)-1-(naphthalen-2-yl)ethan-1-amine, (*S*)-2-methyl-2-propanesulfinamide, (*R*)-1-(4-nitrophenyl)ethan-1-amine, and (*S*)-2-aminopropanamine. Herein, (*R*)-1-(4-nitrophenyl)ethan-1-amine, (*S*)-2-aminopropanamide, and (*R*)-1-(4-bromophenyl)ethan-1-amine were purchased as the hydrochloride salt. Thus salts were neutralized using sodium bicarbonate and extracting it with MDC.

Silver nitrate (0.034 g, 0.20 mmol), additive (0.4 mmol), and 1.0 ml of ethanol were added to the 5 ml borosilicate test tube and stirred until complete dissolution using a magnetic stirrer.

The solution of 2-naphthol (0.029 g, 0.2 mmol in 0.5 ml ethanol) was added to it and immediately kept in the dark at 28-32°C for 48 hr.

4.5.5 The general procedure for C-C oxidative coupling reaction of 2-Naphthol using silver ammine complex in the presence of chiral additives

Silver nitrate (0.034 g, 0.20 mmol) was dissolved in 0.2 ml liquor ammonia into the 5 ml borosilicate test tube. 2-naphthol (0.029 g, 0.2 mmol) solution prepared in 1.0 ml ethanol and 0.5 ml of additive (2 equivalents, 0.4 mmol) solution was added to it and immediately kept in the dark at 28-32°C for 48 hr.

4.5.6 General procedure for C-C oxidative coupling reaction of 2-Naphthol in quartz surface

Silver nitrate (0.043 g, 0.25 mmol) was dissolved in 1.0 ml liquor ammonia into the quartz tube. After 5 minutes, 2-naphthol (0.036 g, 0.25 mmol) in 0.5 ml absolute ethanol was added and mixed by shaking the solution. This solution was kept in the dark at 28-30 °C for 48 hours. The organics were isolated, and BINOL was purified using column chromatography on silica gel using ethyl acetate-hexane mixture.

The reaction conditions used for repeated experiments are shown in T4.3.

4.5.7 General procedure for preparation of the silver-coated surface and C-C oxidative coupling reaction of 2-Naphthol in it

1.0 ml of 0.01 N Silver nitrate solution was added to the oven-dried glass vial (cylindrical shape having 1 cm diameter and 5 ml capacity). After 1 minute, 0.1 ml of 0.10 N sodium hydroxide solution was added into it using a 1.0 ml syringe. After 1 minute, 0.15 ml ammonia solution (0.0025 % w/v) was added slowly using a 1.0 ml syringe and mixed by shaking. After 5 minutes, 0.5 ml 0.012 N glucose solution was added to the vial using a pipette. 0.5 ml water was added to it. This reaction mixture was kept in the dark at 28-30 °C for 1 hour. The solution in the vial was discarded. The vial was washed with water thrice. After ethanol washing, the vial was kept for 1–2 h for drying at room temperature. This silver-coated surface was used instead of quartz for further C–C coupling reaction of BINOL using the same procedure given for experiment 2. The exact stoichiometric of reagents and conditions used in repeated experiments are given in Tables T4.4 (oxidation of *d*/*l*-glucose) and T4.5 (C-C oxidative coupling of BINOL in silver-coated surface).

Table T4.3: Procedure of C-C oxidative coupling reaction of 2-naphthol carried out in quartz vessel*

Quartz									
No.	**name**	**Silver nitrate**	**liq. ammonia**	**Time**	**2-naphthol**		**abolute ethanol**	**Condition**	
		(I)	**(II)**	**(III)**	**(IV)**		**(V)**	**(VI)**	
		wt. mmol equal.			**Wt. mmol equa.**	**solution of BINOL if used**		**Temp.**	**Time**
1	221	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.036 g (0.25) 1 eq		0.5 ml	in dark at ~25°C	48 hr
2	221a	0.0432 g 0.25 mmol 1eq	1.0 ml	5 min	0.037 g (0.25) ~1 eq		0.5 ml	in dark at 25°C	48 hr
3	232c	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.036 g (0.25) 1 eq		0.5 ml	in dark at ~25°C	48 hr
4	225	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.036 g (0.25) 1 eq	in 0.5 ml ethanol		in the dark at 25°C	48 hr
5	230	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.036 g (0.25) 1 eq		0.5 ml + 0.5 ml	in dark at ~25°C	48 hr
6	236-1	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.036 g (0.25) 1 eq	in 0.5 ml ethanol		in the dark at ~25°C	48 hr

*reaction conditions and procedure: Name of experiment, (I) silver nitrate (weight, mol, and mole equivalent) was added to the quartz vial, and dissolved in (II) liq. Ammonia (in ml). After (III) time interval (IV) 2-naphthol (weight, mol, and mole equivalent) was added in it or noted if a solution is added, followed by the addition of (V) absolute ethanol, (VI) conditions.

Table T4.4: Procedure for coating of silver in a vial by oxidation of *D/L*-glucose*

Procedure for silver coating using *D*-glucose											
	washing	**Silver nitrate**		**NaOH**		**ammonia**	**time**	***D*-glucose**		**Reaction conditions**	
	(I)	**(II)**		**(III)**		**(IV)**	**(V)**	**(VI)**		**(VII)**	
		Wt. mmol equa.	**sol. of $AgNO_3$ if used**	**Wt. mmol equa.**	**Sol. Of NaOH used**			**Wt. mmol equa.**	***d*-glucose sol.**		
232a	dis. water dil. HNO_3	1.7 mg (0.010) (1 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	2.67 N 0.1 ml	5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	prepared	28.8°C
gs-i9	dis. water dil. HNO_3	1.7 mg (0.010) (1 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	2.67 N 1.0 ml	5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	24-48 hr	27.8°C to 29.2°C
i-15	dis. water dil. HNO_3	1.7 mg (0.010) (1 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	2.67 N 0.1 ml	5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	74 hr	28.8°C
233-1	dis. water dil. HNO_3	1.9 mg (0.010) (~1 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	2.67 N 0.1 ml	5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	24-48 hr	27.8°C to 29.2°C
Gs	dis. Water dil. HNO_3	1.7 mg (0.010) (1 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	2.67 N 0.1 ml	5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	24 hr	27.8°C to 29.2°C
239-c	dis. Water dil. HNO_3	1.7 mg (0.010) (1 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	2.67 N 0.05 ml	5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	24 hr	26°C
234-c	dis. water dil. HNO_3	1.7 mg (0.010) (1 eq)	0.10 N 0.1 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	25% 0.1 ml	+0.8 ml water 5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	24 hr	27.8°C to 29.2°C
301-2	dis. water dil. HNO_3	3.2 mg (0.019) (4 eq)	0.10 N 0.1 ml	0.44 mg (0.011) (2 eq)	0.11 N 0.1ml	2.67 N 0.1 ml	5 min	1.05 mg (0.0058) 1eq	0.58 N 1.0 ml	120 min	32°C
Procedure for silver coating using *L*-glucose											
252a	dis. water dil.HNO_3	1.8 mg (0.010) (~2 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (2 eq)	0.10 N 0.1 ml	2.67 N 0.15 ml	5 min	1.10 mg (0.006) 1eq	0.012 N 0.5 ml + 0.5 ml water	1 hr	28.8°C
246-l	dis. water dil.HNO_3	1.7 mg (0.010) (1 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	2.67 N 0.04 ml	5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	14 hr	31.8°C
245-l	dis. water dil.HNO_3	1.8 mg (0.010) (~1 eq)	0.01 N 1.0 ml	0.40 mg (0.010) (1 eq)	0.10 N 0.1 ml	2.67 N 0.04 ml	5 min	1.80 mg (0.010) 1eq	0.01 N 1.0 ml	25 hr	35.0°C
252b	dis. water dil.HNO_3	2.1 mg (0.012) (~2 eq)	0.012 N 1.0 ml	0.40 mg (0.010) (2 eq)	0.10 N 0.1 ml	2.67 N 0.15 ml	5 min	1.10 mg (0.006) 1eq	0.012 N 0.5 ml +0.5 ml water	6 hr	28.8°C

* Procedure: The borosilicate vial of name used for experiment, (I) washed with solvent. After drying (II) silver nitrate solution was mixed with (in weight, mol, and mole equivalent, normality and volume) (II) Sodium hydroxide solution (weight, mol, and mole equivalent, normality and volume), after 1 minute (IV) ammonia solution added. After (V) time interval (VI) glucose solution (weight, mol, and mole equivalent) was added in it (VII) And were kept in conditions.

Table T4.5: Procedure of C-C oxidative coupling reaction of 2-naphthol carried out in the Silver coated surface (obtained from Tollens' reaction of *D/L*-glucose)*

The procedure of coupling of 2-naphthol on a Silver coated surface (*D*-glucose)									
Name of vial	**washing**	**drying**	**AgNO3**	**liq. Ammonia**	**time**	**2-naphthol**	**Ab. ethanol**	**Reaction Condition**	
	(I)	**(II)**	**(III)**	**(IV)**	**(V)**	**(VI)**	**(VII)**	**(IIX)**	
	Volume*times solvent		**Wt. Mmol equa.**			**Wt. Mmol equa.**			
232a	1.0 ml *3 water 1.0 ml ethanol	1 hr at 28.5°C	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.0360 g (0.25) ~1 eq	0.5 ml	in dark at 28.5°C	48 hr
gs-i9	1.0 ml *3 water 1.0 ml ethanol	1 hr at 28.5°C	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.0360 g (0.25) ~1 eq	0.5 ml	in dark at 28.5°C	48 hr
i-15	1.0 ml *3 water 1.0 ml ethanol	1 hr at 28.5°C	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.0360 g (0.25) ~1 eq	0.5 ml	in dark at 28.5°C	48 hr
233-1	1.0 ml *3 water 1.0 ml ethanol	6 hr at 30°C	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.0360 g (0.25) ~1 eq	0.5 ml	in dark at 30°C	48 hr
Gs	1.0 ml *3 water 1.0 ml ethanol	oven dried at 70°C	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.0360 g (0.25) ~1 eq	0.5 ml	in dark at 28.5°C	48 hr
239-c	1.0 ml *3 water	Imediately at 28.5°C	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.0340 g (0.25) 1 eq	0.5 ml	in dark at 28°C	72 hr
234-c	1.0 ml *3 water 1.0 ml ethanol	1 hr at 28.5°C	0.043 g 0.25 mmol 1eq	1.0 ml	5 min	0.0360 g (0.25) ~1 eq	0.5 ml	in dark at 28.5°C	48 hr
301-2	1.0 ml *3 water 1.0 ml ethanol	1 hr at 30°C	0.0463 g 0.27 mmol 1eq	1.0 ml	5 mint	0.0362 g (0.26) 1 eq	0.5 ml	in dark at 30°C	48 hr
The procedure of coupling of 2-naphthol on the Silver coated surface (*L*-glucose)									
252a	1.0 ml *3 water	15 mint at 28.7°C	0.0441 g 0.25 mmol ~1eq	1.0 ml	3 min	0.0370 g (0.25) ~1 eq	in 0.5 ml	in dark at 28.7°C	49 hr
246-l	1.0 ml *3 water	5 mint at 31.8°C	0.043 g 0.25 mmol 1eq	1.0 ml	3 min	0.0340 g (0.25) ~1 eq	in 0.5 ml	in dark at 31.8°C	48 hr
245-l	1.0 ml *3 water ethanol	1 hr at 35°C	0.043 g 0.25 mmol 1eq	1.0 ml	1 min	0.0360 g (0.25) 1 eq	in 0.5 ml	in dark at 35°C	48 hr
252b	1.0 ml *3 water	15 mint at 28.7°C	0.0428 g 0.25 mmol ~1eq	1.0 ml	3 min	0.0350 g (0.25) ~1 eq	in 0.25 ml +0.25 ml ethanol	in dark at 28.7°C	49 hr

*Name of vial used for the experiment, (I) washing of solvent given with amount, (II) drying conditions and time, (III) silver nitrate (weight, mol, and mole equivalent)was added in (IV) liq. Ammonia (in ml). After (V) time interval (VI) 2-naphthol (weight, mol, and mole equivalent) and (VII) absolute ethanol was added into it. (IIX) This reaction mixture was kept in conditions.

Table T4.6: The polarimetry study and calculation of ee of BINOL *

Ag-surface using reaction of l-Glucose				Silver coated surface using Tollens reaction of d-glucose								Surface
4	3	2	1	8	7	6	5	4	3	2	1	No.
252-b	245-l	246-l	252A	234-c	234-d	239-c	gs	233-1	i-15	gs-i9	232a	name
-0.0019	-0.0004	0.0031	-0.0155	-0.0027	-0.0034	-0.0020	-0.0019	-0.0010	-0.0010	-0.0051	-0.0172	α1
-0.0015	-0.0006	0.0034	-0.0193	-0.0028	-0.0036	-0.0031	-0.0015	-0.0010	-0.0002	-0.0057	-0.0137	α2
-0.0014	-0.0014	0.0019	-0.0177	-0.0021	-0.0030	-0.0037	-0.0039	-0.0006	-0.0004	-0.0058	-0.0109	α3
-0.0016	-0.0008	0.0028	-0.0175	-0.0025	-0.0033	-0.0029	-0.0024	-0.0009	-0.0005	-0.0055	-0.0139	Average α in degree
0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	c in w/v% c = gm/ml *100 %
-1.2667	-0.2667	2.0667	-10.3333	-1.8000	-2.2667	-1.3333	-1.2667	-0.6667	-0.6667	-3.4000	-11.4667	SOR1= 100 α1/L C
-1.0000	-0.4000	2.2667	-12.8667	-1.8667	-2.4000	-2.0667	-1.0000	-0.6667	-0.1333	-3.8000	-9.1333	SOR2= 100 α 2/L C
-0.9333	-0.9333	1.2667	-11.8000	-1.4000	-2.0000	-2.4667	-2.6000	-0.4000	-0.2667	-3.8667	-7.2667	SOR3= 100 α 3/L C
-1.0667	-0.5333	1.8667	-11.6667	-1.6889	-2.2222	-1.9556	-1.6222	-0.5778	-0.3556	-3.6889	-9.2889	cal average Ave SOR= 100 α /LC
0.18	0.35	0.53	1.20	0.25	0.20	0.57	0.86	0.15	0.28	0.25	2.10	SD= stand red devi ation
16.5	66.1	28.3	10.9	14.9	9.2	29.3	52.8	26.6	78.1	6.8	22.7	CV coefficient of variance = SD/AV *100%
3.6	**1.8**	**6.2**	**38.9**	**5.6**	**7.4**	**6.5**	**5.4**	**1.9**	**1.2**	**12.3**	**31.0**	% ee of sample ee =100* SOR of sample / SOR of pure BINOL
S	S	R	S	S	S	S	S	S	S	S	S	Enriched enantiomer

Quartz surface	No.	1	2	3	4	5	6
	name	221	221A	232-c	225	230	236-1
	α 1	-0.0324	-0.0217	-0.0092	0.0262	0.0026	-0.0019
	α 2	-0.0246	-0.0227	-0.0112	0.0251	0.0024	-0.0017
	α 3	-0.0186	-0.0192	-0.0090	0.0257	0.0030	-0.0001
	Average α in degree	-0.0252	-0.0212	-0.0098	0.0257	0.0027	-0.0012
	c in w/v% gm/ml ×100 %	0.3	0.3	0.3	0.3	0.3	0.3
	SOR1= 100 α1/L C	-21.6000	-14.4667	-6.1333	17.4667	1.7333	-1.2667
	SOR2= 100 α 2/L C	-16.4000	-15.1333	-7.4667	16.7333	1.6000	-1.1333
	SOR3= 100 α /L C	-12.4000	-12.8000	-6.0000	17.1333	2.0000	-0.0667
	cal average Ave SOR= 100 α /LC	-16.8000	-14.1333	-6.5333	17.1111	1.7778	-0.8222
	SD= stand red devi ation	4.61	1.20	0.80	0.30	0.20	0.66
	CV coefficient of variance = SD/AV ×100%	27.5	8.5	12.4	2.2	11.4	79.0
	% ee of sample ee =100* SOR of sample / SOR of pure BINOL	**56.0**	**47.1**	**21.8**	**57.0**	**5.9**	**2.7**
	Enriched enantiomer	S	S	S	R	R	S

*****where, the table is showing data obtained from polarimetry and calculation of optical purity based on that, in repeated experiments. The surfaces used for synthesis are noted as silver-coated surface (by Tollens' reaction of d-glucose and l-glucose) and quarts surface, $^{\alpha}$ is observed optical rotation of BINOL sample obtained from reaction (1-3 are 3 measurements and average α value); ^{SOR} specific optical rotation (in $°cm^2g^{-1}$) calculated for repeated observation (and average) (using formula SOR = 100 α1/L C), where ^{C} in weight per volume in % is noted (in gm/ml × 100 %). The standard deviation and coefficient of variance were shown to validate the data. The enantiomeric excess was calculated in % (% ee of sample =100* SOR of sample / SOR of pure BINOL), and enriched enantiomer is noted.

4.6 References

(1) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons, 1994.

(2) Durand, D. J.; Kondepudi, D. K.; Moreira, P. F.; Quina, F. H. Generation of Molecular Chiral Asymmetry through Stirred Crystallization. *Chirality* **2002**, *14* (4), 284–287.

(3) Matsumoto, A.; Kaimori, Y.; Kawasaki, T.; Soai, K. Asymmetric Autocatalysis Initiated by Crystal Chirality of Achiral Compounds. In *Advances in Asymmetric Autocatalysis and Related Topics*; Gyula, P., Róbert, K., Claudi, Z., Eds.; Elsevier: Tokyo, Japan, 2017; pp 337–355.

(4) Bringmann, G.; Gulder, T.; Gulder, T. A. M.; Breuning, M. Atroposelective Total Synthesis of Axially Chiral Biaryl Natural Products. *Chem. Rev.* **2011**, *111* (2), 563–639.

(5) Brunel, J. M. Update 1 of: BINOL: A Versatile Chiral Reagent. *Chem. Rev.* **2007**, *107* (9), PR1–PR45.

(6) Meca, L.; Řeha, D.; Havlas, Z. Racemization Barriers of 1,1‘-Binaphthyl and 1,1‘-Binaphthalene-2,2‘-Diol: A DFT Study. *J. Org. Chem.* **2003**, *68* (14), 5677–5680.

(7) Kim, H. Y.; Takizawa, S.; Sasai, H.; Oh, K. Reversal of Enantioselectivity Approach to BINOLs via Single and Dual 2-Naphthol Activation Modes. *Org. Lett.* **2017**, *19* (14), 3867–3870.

(8) Bringmann, G.; Mortimer, A. J. P.; Keller, P. A.; Gresser, M. J.; Garner, J.; Breuning, M. Atroposelective Synthesis of Axially Chiral Biaryl Compounds. *Angew. Chemie - Int. Ed.* **2005**, *44* (34), 5384–5427.

(9) Wu, L. Y.; Usman, M.; Liu, W. B. Enantioselective Iron/Bisquinolyldiamine Ligand-catalyzed Oxidative Coupling Reaction of 2-naphthols. *Molecules* **2020**, *25* (4), 852.

(10) Hossain, A.; Bhattacharyya, A.; Reiser, O. Copper’s Rapid Ascent in Visible-Light Photoredox Catalysis. *Science* **2019**, *364* (6439).

(11) Marathe, S.; Karnik, A. V. Design, Synthesis, and Characterization of Novel BINOL-Based Heterocyclic Analogues as Potential Sensors. *Synth. Commun.* **2017**, *47* (17), 1577–1581.

(12) Adão, P.; Barroso, S.; Carvalho, M. F. N. N.; Teixeira, C. M.; Kuznetsov, M. L.; Costa Pessoa, J. Amino Acid Derived CuII Compounds as Catalysts for Asymmetric Oxidative Coupling of 2-Naphthol. *Dalt. Trans.* **2015**, *44* (4), 1612–1626.

(13) Caselli, A.; Giovenzana, G. B.; Palmisano, G.; Sisti, M.; Pilati, T. Synthesis of C2-Symmetrical Diamine Based on (1R)-(+)-Camphor and Application to Oxidative Aryl Coupling of Naphthols. *Tetrahedron Asymmetry* **2003**, *14* (11), 1451–1454.

(14) Temma, T.; Habaue, S. Highly Selective Oxidative Cross-Coupling of 2-Naphthol Derivatives with Chiral Copper(I)-Bisoxazoline Catalysts. *Tetrahedron Lett.* **2005**, *46* (34), 5655–5657.

(15) Yusa, Y.; Kaito, I.; Akiyama, K.; Mikami, K. Asymmetric Catalysis of Homo-Coupling of 3-Substituted Naphthylamine and Hetero-Coupling with 3-Substituted Naphthol Leading to 3,3'-Dimethyl-2,2'-Diaminobinaphthyl and -2-Amino-2'-Hydroxybinaphthyl. *Chirality* **2010**, *22* (2), 224–228.

(16) Grach, G.; Pieters, G.; Dinut, A.; Terrasson, V.; Medimagh, R.; Bridoux, A.; Razafimahaleo, V.; Gaucher, A.; Marque, S.; Marrot, J.; et al. N-Heterocyclic Pyridylmethylamines: Synthesis, Complexation, Molecular Structure, and Application to Asymmetric Suzuki-Miyaura and Oxidative Coupling Reactions. *Organometallics* **2011**, *30* (15), 4074–4086.

(17) Brussee, J.; Groenendijk, J. L. G.; te Koppele, J. M.; Jansen, A. C. A. On the Mechanism of the Formation of s(-)-(1, 1'-Binaphthalene)-2,2'-Diol via Copper(II)Amine Complexes. *Tetrahedron* **1985**, *41* (16), 3313–3319.

(18) Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S. I.; Noji, M.; Koga, K. Enantioselective Synthesis of Binaphthol Derivatives by Oxidative Coupling of Naphthol Derivatives Catalyzed by Chiral Diamine-Copper Complexes. *J. Org. Chem.* **1999**, *64* (7), 2264–2271.

(19) Sabarinathan, S.; Vasuki, G.; Rao, P. S. Chiral Cu(II) Salen Complexes Catalyzed Aerobic Oxidative Biaryl Coupling-Probing the Reaction by EPR. *Eur. J. Chem.* **2010**, *1* (4), 360–367.

(20) Larionov, V. A.; Peregudova, S. M.; Maleev, V. I.; Belokon, Y. N. A Novel Type of Catalysts for Asymmetric Oxidative Coupling of 2-Naphthol. *Russ. Chem. Bull.* **2016**, *65* (3), 685–688.

(21) Grandbois, A.; Mayer, M. È.; Bédard, M.; Collins, S. K.; Michel, T. Synthesis of C1-Symmetric BINOLs Employing N-Heterocyclic Carbene Copper Complexes. *Chem. - A Eur. J.* **2009**, *15* (38), 9655–9659.

(22) Alamsetti, S. K.; Poonguzhali, E.; Ganapathy, D.; Sekar, G. Enantioselective Oxidative Coupling of 2-Naphthol Derivatives by Copper-(R)-1,1′-Binaphthyl-2,2′-

Diamine-TEMPO Catalyst. *Adv. Synth. Catal.* **2013**, *355* (14–15), 2803–2808.

(23) Egami, H.; Katsuki, T. Iron-Catalyzed Asymmetric Aerobic Oxidation: Oxidative Coupling of 2-Naphthols. *J. Am. Chem. Soc.* **2009**, *131* (17), 6082–6083.

(24) Bania, K. K.; Bharali, D.; Viswanathan, B.; Deka, R. C. Enhanced Catalytic Activity of Zeolite Encapsulated Fe(III)-Schiff-Base Complexes for Oxidative Coupling of 2-Napthol. *Inorg. Chem.* **2012**, *51* (3), 1657–1674.

(25) Zhang, Q.; Cui, X.; Chen, L.; Liu, H.; Wu, Y. Syntheses of Chiral Ferrocenophanes and Their Application to Asymmetric Catalysis. *European J. Org. Chem.* **2014**, *2014* (35), 7823–7829.

(26) Narute, S.; Pappo, D. Iron Phosphate Catalyzed Asymmetric Cross-Dehydrogenative Coupling of 2-Naphthols with β-Ketoesters. *Org. Lett.* **2017**, *19* (11), 2917–2920.

(27) Shalit, H.; Dyadyuk, A.; Pappo, D. Selective Oxidative Phenol Coupling by Iron Catalysis. *J. Org. Chem.* **2019**, *84* (4), 1677–1686.

(28) Narute, S.; Parnes, R.; Toste, F. D.; Pappo, D. Enantioselective Oxidative Homocoupling and Cross-Coupling of 2-Naphthols Catalyzed by Chiral Iron Phosphate Complexes. *J. Am. Chem. Soc.* **2016**, *138* (50), 16553–16560.

(29) Takizawa, S.; Kodera, J.; Yoshida, Y.; Sako, M.; Breukers, S.; Enders, D.; Sasai, H. Enantioselective Oxidative-Coupling of Polycyclic Phenols. *Tetrahedron* **2014**, *70* (9), 1786–1793.

(30) Takizawa, S.; Gröger, H.; Sasai, H. Vanadium in Asymmetric Synthesis: Emerging Concepts in Catalyst Design and Applications. *Chem. - A Eur. J.* **2015**, *21* (25), 8992–8997.

(31) Barhate, N. B.; Chen, C. T. Catalytic Asymmetric Oxidative Couplings of 2-Naphthols by Tridentate N-Ketopinidene-Based Vanadyl Dicarboxylates. *Org. Lett.* **2002**, *4* (15), 2529–2532.

(32) Takizawa, S.; Katayama, T.; Somei, H.; Asano, Y.; Yoshida, T.; Kameyama, C.; Rajesh, D.; Onitsuka, K.; Suzuki, T.; Mikami, M.; et al. Dual Activation in Oxidative Coupling of 2-Naphthols Catalyzed by Chiral Dinuclear Vanadium Complexes. *Tetrahedron* **2008**, *64* (15), 3361–3371.

(33) Noshiranzadeh, N.; Bikas, R.; Emami, M.; Siczek, M.; Lis, T. Oxidative Coupling of 2-Naphthol Catalyzed by a New Methoxido Bridged Dinuclear Oxidovanadium(V) Complex. *Polyhedron* **2016**, *111*, 167–172.

(34) Sako, M.; Takizawa, S.; Yoshida, Y.; Sasai, H. Enantioselective and Aerobic

Oxidative Coupling of 2-Naphthol Derivatives Using Chiral Dinuclear Vanadium(V) Complex in Water. *Tetrahedron Asymmetry* **2015**, *26* (12–13), 613–616.

(35) Mandal, M.; Nagaraju, V.; Karunakar, G. V.; Sarma, B.; Borah, B. J.; Bania, K. K. Electronic, Conjugation, and Confinement Effects on Structure, Redox, and Catalytic Behavior of Oxido-Vanadium(IV) and -(V) Chiral Schiff Base Complexes. *J. Phys. Chem. C* **2015**, *119* (52), 28854–28870.

(36) Guo, Q. X.; Wu, Z. J.; Luo, Z. Bin; Liu, Q. Z.; Ye, J. L.; Luo, S. W.; Cun, L. F.; Gong, L. Z. Highly Enantioselective Oxidative Couplings of 2-Naphthols Catalyzed by Chiral Bimetallic Oxovanadium Complexes with Either Oxygen or Air as Oxidant. *J. Am. Chem. Soc.* **2007**, *129* (45), 13927–13938.

(37) Tada, M.; Taniike, T.; Kantam, L. M.; Iwasawa, Y. Chiral Self-Dimerization of Vanadium Complexes on a SiO2 Surface: The First Heterogeneous Catalyst for Asymmetric 2-Naphthol Coupling. *Chem. Commun.* **2004**, *10* (22), 2542–2543.

(38) Somei, H.; Asano, Y.; Yoshida, T.; Takizawa, S.; Yamataka, H.; Sasai, H. Dual Activation in a Homolytic Coupling Reaction Promoted by an Enantioselective Dinuclear Vanadium(IV) Catalyst. *Tetrahedron Lett.* **2004**, *45* (9), 1841–1844.

(39) Lou, Z.; Liu, Q.; Gong, L.; Cui, X.; Mi, A.; Jiang, Y. Novel Achiral Biphenol-Derived Diastereomeric Oxovanadium(IV) Complexes for Highly Enantioselective Oxidative Coupling of 2-Naphthols. *Angew. Chemie - Int. Ed.* **2002**, *41* (23), 4532–4535.

(40) Kawashima, M.; Hirata, R. Epimerization-Crystallization Method in Optical Resolution of 2,2′-Dihydroxy-1,1′-Binaphthyl, and Kinetic Study. *Bull. Chem. Soc. Jpn.* **1993**, *66* (7), 2002–2005.

(41) Ha, W.; Shan, Z. An Economic, Practical Access to Enantiopure 1,1′-Bi-2-Naphthols: Enantioselective Complexation of Threo-(1S,2S)-N-Benzyl-N,N-Dimethyl[1,3-Dihydroxy-1-(4′-Nitrophenyl)]-2-Propylammonium Chloride. *Tetrahedron Asymmetry* **2006**, *17* (5), 854–859.

(42) Wang, Y.; Sun, J.; Ding, K. Practical Method and Novel Mechanism for Optical Resolution of BINOL by Molecular Complexation with N-Benzylcinchoninium Chloride. *Tetrahedron* **2000**, *56* (26), 4447–4451.

(43) Hu, X.; Shan, Z.; Chang, Q. An Improved and Practical Approach to Essentially Enantiopure BINOLs: Enantioselective Inclusion Complexation of (S)-Proline. *Tetrahedron Asymmetry* **2012**, *23* (18–19), 1327–1331.

(44) Schanz, H. J.; Linseis, M. A.; Gilheany, D. G. Improved Resolution Methods for

(R,R)- and (S,S)-Cyclohexane-1,2-Diamine and (R)- and (S)-BINOL. *Tetrahedron Asymmetry* **2003**, *14* (18), 2763–2769.

(45) Liu, D.; Shan, Z.; Liu, F.; Xiao, C.; Lu, G.; Qin, J. A New and Practical Method for Preparing Enantiomerically Pure [1, 1′-Binaphthalene]-2, 2′-diol: Resolution of Racemic [1, 1′-Binaphthalene]-2, 2′-diol with Threo-(1S, 2S)-2-Amino-1-(4-nitrophenyl) Propane-1, 3-diol- Cyclohexanone Condensate. *Helv. Chim. Acta* **2003**, *86* (1), 157–163.

(46) Toda, F.; Yoshizawa, K.; Hyoda, S.; Toyota, S.; Chatziefthimiou, S.; Mavridis, I. M. Efficient Resolution of 2,2′-Dihydroxy-1,1′-Binaphthyl by Inclusion Complexation with Chiral N-(3-Chloro-2-Hydroxypropyl)-N,N,N-Trimethylammonium Chloride. *Org. Biomol. Chem.* **2004**, *2* (4), 449–451.

(47) Miyaji, R.; Wada, Y.; Matsumoto, A.; Asano, K.; Matsubara, S. Bifunctional Organocatalysts for the Asymmetric Synthesis of Axially Chiral Benzamides. *Beilstein J. Org. Chem.* **2017**, *13* (1), 1518–1523.

(48) Dolsophon, K.; Ruangsupapichat, N.; Soponpong, J.; Sungsuwan, S.; Prabpai, S.; Kongsaeree, P.; Thongpanchang, T. Tetrahydro-1,4-Epoxynaphthalene-1-Carboxylic Acid: A Chiral Resolving Agent for the Resolution and Absolute Configuration Assignment of 7,7'-Disubstituted 1,1'-Bi-2-Naphthols. *Tetrahedron Asymmetry* **2016**, *27* (22–23), 1113–1120.

(49) Li, Z.; Liang, X.; Wu, F.; Wan, B. A Convenient Resolution Method for 1,1′-Bi-2-Naphthol and 4,4′-Dibromo-1,1′-Spirobiindane-7,7′-Diol with Menthyl Chloroformate in the Presence of TBAB. *Tetrahedron Asymmetry* **2004**, *15* (4), 665–669.

(50) Cai, J. X.; Zhou, Z. H.; Li, K. Y.; Yeung, C. H.; Tang, C. C. An Improved Method for the Resolution of 1,1′-Binaphthalene-2,2′-Diol via a Phosphite Using (-)-Menthol as a Resolving Agent. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177* (1), 189–193.

(51) Trotta, F.; Cravotto, G.; Casile, G. A Straightforward Synthesis in Aqueous Medium of Enantiomerically Enriched S(-)2,2′-Dihydroxy-1,1′-Binaphthyl. *Environ. Sci. Pollut. Res.* **2003**, *10* (3), 144–146.

(52) Takemoto, M.; Suzuki, Y.; Tanaka, K. Enantioselective Oxidative Coupling of 2-Naphthol Derivatives Catalyzed by Camellia Sinensis Cell Culture. *Tetrahedron Lett.* **2002**, *43* (47), 8499–8501.

(53) Fürtges, L.; Obermaier, S.; Thiele, W.; Foegen, S.; Müller, M. Diversity in Fungal Intermolecular Phenol Coupling of Polyketides: Regioselective Laccase-Based

Systems. *ChemBioChem* **2019**, *20* (15), 1928–1932.

(54) Cardoso, F. S. P.; Abboud, K. A.; Aponick, A. ChemInform Abstract: Design, Preparation, and Implementation of an Imidazole-Based Chiral Biaryl P,N-Ligand for Asymmetric Catalysis. *ChemInform* **2014**, *45* (12), no-no.

(55) Blackmond, D. G. Autocatalytic Models for the Origin of Biological Homochirality. *Chem. Rev.* **2020**, *120* (11), 4831–4847.

(56) Soai, K. Asymmetric Autocatalysis. Chiral Symmetry Breaking and the Origins of Homochirality of Organic Molecules. *Proc. Japan Acad. Ser. B Phys. Biol. Sci.* **2019**, *95* (3), 89–110.

(57) Han, Z.; Dong, X. Y.; Luo, P.; Li, S.; Wang, Z. Y.; Zang, S. Q.; Mak, T. C. W. Ultrastable Atomically Precise Chiral Silver Clusters with More than 95% Quantum Efficiency. *Sci. Adv.* **2020**, *6* (6), 1–9.

(58) Zaera, F. Chirality in Adsorption on Solid Surfaces. *Chem. Soc. Rev.* **2017**, *46* (23), 7374–7398.

(59) Liu, L.; Corma, A. Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. *Chem. Rev.* **2018**, *118*, 4981–5079.

(60) Bonner, W. A.; Kavasmaneck, P. R. Asymmetric Adsorption of Dl-Alanine Hydrochloride by Quartz. *J. Org. Chem.* **1976**, *41* (12), 2225–2226.

(61) Ghalsasi, P. S.; Bhanderi, K. D. Microscopic Cavity to Macroscopic Suraface for Asymmetric Synthesis. 362870, 201721039245 A, 2017.

(62) Ma, L.; Cao, Y.; Duan, Y.; Han, L.; Che, S. Silver Films with Hierarchical Chirality. *Angew. Chemie - Int. Ed.* **2017**, *56* (30), 8657–8662.

(63) Bhanderi, K.; Ghalsasi, P. S.; Inoue, K. Nonconventional Driving Force for Selective Oxidative C–C Coupling Reaction Due to Concurrent and Curious Formation of Ag0. *Sci. Rep.* **2021**, *11* (1), 1–11.

(64) De Yoreo, J. J.; Gilbert, P. U. P. A.; Sommerdijk, N. A. J. M.; Penn, R. L.; Whitelam, S.; Joester, D.; Zhang, H.; Rimer, J. D.; Navrotsky, A.; Banfield, J. F.; et al. Crystallization by Particle Attachment in Synthetic, Biogenic, and Geologic Environments. *Science* **2015**, *349* (6247), aaa6760.

(65) Chuan-Fu, C.; Zhong, L.; Min, A.; Yong-Ming, C.; Fu, X. Optical Rotatory Feature of (R or S)-1, 1′-Binaphthalene-2, 2′-Diol (BINOL) in Various Solvents. *Chinese J. Chem.* **2010**, *21* (2), 204–207.