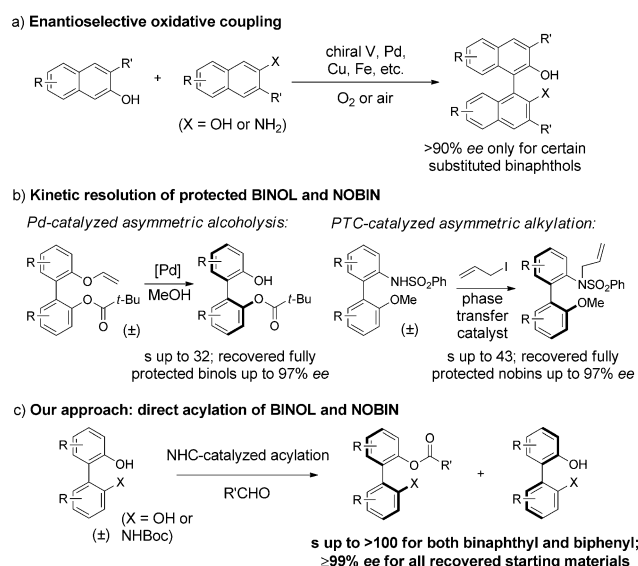


Kinetic Resolution of 1,1'-Biaryl-2,2'-Diols and Amino Alcohols through NHC-Catalyzed Atroposelective Acylation**

Shenci Lu, Si Bei Poh, and Yu Zhao*

Abstract: We present here a highly efficient NHC-catalyzed kinetic resolution of a wide range of 1,1'-biaryl-2,2'-diols and amino alcohols to provide them in uniformly $\geq 99\%$ ee. This represents the first highly enantioselective catalytic acylation of axially chiral alcohols. The aldehyde backbone that is incorporated into the chiral acyl azolium intermediate was found to have a significant effect on the enantioselectivity of the process.

Axially chiral biaryls are important structural motifs in natural products, pharmaceuticals and materials,^[1] and also find wide application as chiral catalysts in organic synthesis.^[2] Accordingly, the development of efficient enantioselective syntheses of them has attracted extensive attention and great progress has been reported in recent years from the Tanaka group,^[3b,c] the Miller group,^[3d,e] the Buchwald group,^[3f] and many others.^[3] In particular, one class of axially chiral alcohols including 1,1'-bi-2-naphthol (BINOL) and 2-amino-2'-hydroxy-1,1'-binaphthyl (NOBIN) has proven to be privileged chiral backbones for asymmetric catalysis.^[4,5] The preparation of these axially chiral alcohols in enantiopure form, however, still relies on conventional optical resolution, which requires the stoichiometric use of chiral compounds.^[6] Whereas the oxidative coupling of 2-naphthols (or 2-naphthylamines) represents a straightforward way to prepare BINOL and NOBIN analogues from achiral precursors, the current state-of-the-art catalytic systems can only produce binaphthols with certain specific substitution patterns in high ee (and not biphenols at all; see (a) in Scheme 1).^[7] The catalytic kinetic resolution of these axially chiral diols and amino alcohols has surprisingly been underdeveloped.^[8] Only a few highly enantioselective examples were reported on orthogonally protected BINOL and NOBIN analogues, either using asymmetric Pd-catalyzed alcoholysis by the Tsuji group^[8c] or using *N*-alkylation under phase transfer catalysis by the Maruoka group^[8d] (see (b) in Scheme 1). Although the catalytic asymmetric acylation of alcohols (or other group transfer reactions in general) has great potential to provide an efficient, direct kinetic resolution of free BINOL and NOBIN, no successful catalytic system along those lines has



Scheme 1. Catalytic approaches to enantioenriched BINOL and NOBIN. s = selectivity factor.

been reported^[9] despite the great success of asymmetric acylation of alcohols that possess central chirality.^[10,11] We report here the first example of a highly efficient and enantioselective acylative kinetic resolution of free BINOLs and *N*-Boc-protected NOBINs to access a wide range of them with $\geq 99\%$ ee (see (c) in Scheme 1).

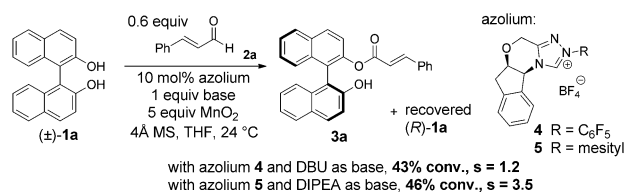
Recent advances in *N*-heterocyclic carbene (NHC) catalysis have led to the catalytic generation of activated carboxylates either through internal redox reaction of functionalized aldehydes (such as α,β -unsaturated aldehydes or α -halo aldehydes) or from simple aldehydes under oxidative conditions.^[12] The chiral acyl azolium species generated in this way has been employed for enantioselective C–C bond formation as well as acylation of the alcohol counterpart.^[13,14] Following the early proof-of-principle reports from the groups of Rovis, Scheidt, and Studer,^[13a–d] we have recently disclosed a highly enantioselective acylative kinetic resolution of oxindole-derived tertiary alcohols, in which oxidative NHC catalysis with the aid of a Lewis acid proved essential to obtain high enantioselectivity.^[13e–f] Takasu, Yamada, and co-workers also reported a NHC-catalyzed asymmetric acylation of cyclic *trans*-diols and amino alcohols with high levels of stereoselectivity, in which a carboxylate salt was identified as a basic cocatalyst for an enhanced rate and selectivity.^[13g] Recognizing the lack of efficient acylation reactions for axially chiral alcohols, we decided to examine NHC catalysis for the kinetic resolution of free BINOL.

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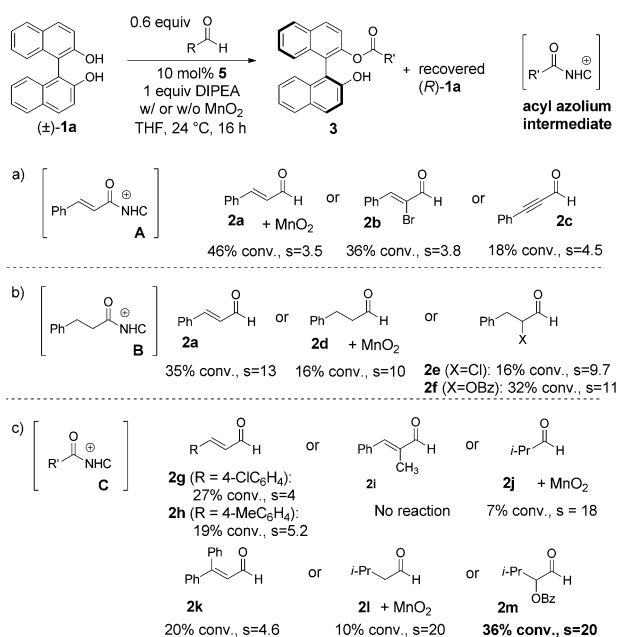
The original conditions were adopted from our previous studies^[13e] using oxidative NHC catalysis and provided very poor selectivity for the resolution of BINOL (selectivity factor $s=1.2$; Scheme 2).^[15] We reasoned that the strong



Scheme 2. Initial catalyst and base optimization.

acidity of the phenol functionality in BINOL may require the use of a weak base. Indeed, DIPEA proved optimal after extensive screening, which, in combination with azolium **5**, led to an improved but still poor selectivity factor of 3.5.

The breakthrough was achieved by screening different aldehydes (Scheme 3). Compounds **2b** and **2c** were tested with the hope that they might provide the same acyl azolium intermediate **A** without the need for MnO_2 and hopefully lead to a different outcome. The results turned out to be similar to those observed in the reaction with **2a** in terms of selectivity. Using **2a** in the absence of MnO_2 (leading to a different acyl azolium ion **B**), however, resulted in a significantly improved s factor of 13 with reasonable conversion. Again, the use of different aldehydes (**2d** + MnO_2 , **2e**, and **2f**) that lead to the same intermediate **B** resulted in similar selectivities (s ranges from 10–13). It was clear at this point that the selectivity of this system was largely influenced by the substituent of the aldehyde; a wider range of aldehydes was then examined. Whereas substituted cinnamaldehydes (**2g**, **2h**) or α -substituted aldehydes (**2i**, **2j**) led to either reduced selectivity or

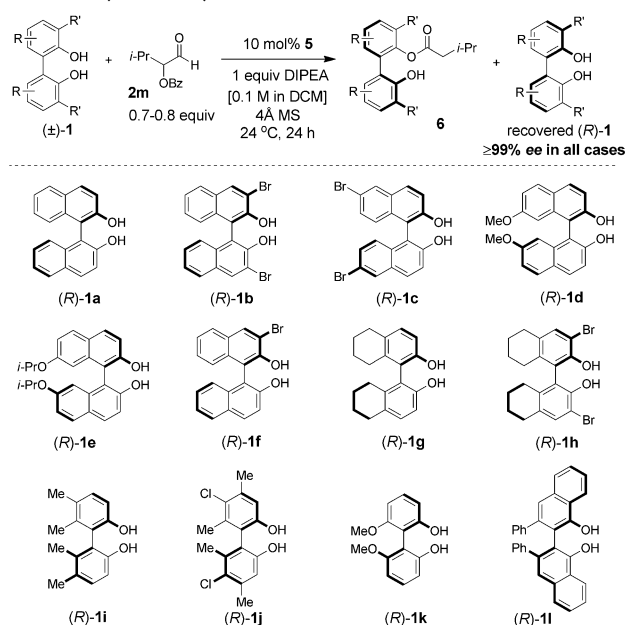


Scheme 3. Effect of the aldehyde on the resolution of **1a**.

proved to be too bulky for an efficient reaction to take place, β -substituted aldehydes **2i** (+ MnO_2) yielded a good s factor of 20, albeit with low reactivity. Finally, inspired by the pioneering work of the Scheidt group^[16a,b] and Smith group^[16c,d] on the use of α -aryloxy aldehyde in NHC catalysis as well as previous kinetic resolution experiments from the Takasu and Yamada group,^[13g] we examined the use of **2m**, which resulted in a higher conversion with the same selectivity. With this promising lead, further reaction conditions were systematically screened, from which the choice of DCM as solvent and a lower concentration of 0.1M led to further improvement. Under the optimal conditions, an excellent selectivity of 52 was obtained for the resolution of BINOL, which was recovered in 99% ee with 44% yield (entry 1, Table 1).

The scope of this catalytic system turned out to be very broad. Various binaphthyl (entries 1–6) and biphenyl diols (entries 7–12) with different substitution patterns were

Table 1: Scope of axially chiral diols.^[a]

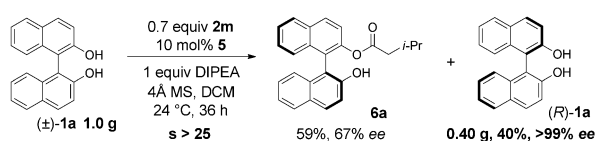


Entry	1	Yield ₁ [%] ^[b]	ee_1 [%] ^[c]	6	Yield ₆ [%] ^[b]	ee_6 [%] ^[c]	Conv. [%]	s
1	1a	44	99	6a	53	82	55	52
2 ^[d]	1b	42	99	6b	54	77	56	38
3	1c	44	99	6c	53	81	55	49
4	1d	43	99	6d	55	77	56	40
5	1e	42	99.4	6e	55	76	57	41
6 ^[e]	1f	42	99	6f	53	76	56	37
7	1g	41	99.1	6g	56	72	58	31
8	1h	43	99	6h	55	76	56	37
9	1i	40	99.4	6i	57	68	59	30
10	1j	38	99.3	6j	58	66	60	26
11 ^[d]	1k	37	99.5	6k	61	60	62	22
12	1l	47	99	6l	50	92	52	116

[a] The reactions were carried out at ambient temperature with 0.7–0.8 equiv **2m**. See the Supporting Information for details. [b] Yields of isolated products. [c] Determined by HPLC. [d] 1.5 equiv of **2m** was used. [e] A mixture of two esters with a ratio of 2:3 was produced with the same ee .

resolved with similarly high selectivity; all substrates examined were recovered in $\geq 99\%$ *ee* with 37–47% isolated yield. For biphenyl diols, the substituents at the 6,6'-positions showed some influence on the selectivity. Whereas **1k** bearing small methoxy groups showed a relatively low selectivity of 22, the widely used VANOL **11**^[17] with phenyl substituents was resolved with an excellent selectivity of >100 . The non- C_2 symmetrical diols such as **1f** could be resolved efficiently as well (entry 6), for which two ester products were formed with the same *ee* and the same axial configuration.

It is also noteworthy that this catalytic procedure is very simple to perform with readily available catalysts at ambient temperature. The reaction can also be easily scaled up. A test reaction with BINOL worked similarly well at gram scale to yield enantiopure BINOL ($>99\%$ *ee*) in 40% yield (Scheme 4).



Scheme 4. Gram-scale resolution of **1a**.

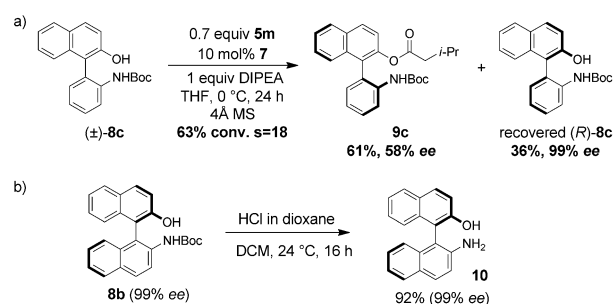
In an effort to extend the scope to axially chiral amino alcohols, it was discovered that the kinetic resolution of unprotected NOBIN using this catalytic system was problematic due to side reaction pathways. To our excitement, the acyl- or Boc-protected NOBIN worked out well with $s=15$ (entries 1 and 2, Table 2). A new catalyst **7** with a bromo substituent proved superior and an excellent selectivity was obtained at 0°C ($s=34$; entry 4); enantiopure **8b** could be isolated with 41% yield. The extension of the method to other NOBIN analogues proved successful (Scheme 5a); **8c** was recovered in 36% yield and, again, in 99% *ee*. As expected, the removal of the Boc group worked out cleanly to yield free NOBIN in a high yield (Scheme 5b). Our method thus represents one of the most straightforward syntheses of NOBIN and its analogues in their enantiopure form.

To increase the overall efficiency of the process, the ester products generated in these studies were hydrolyzed to the

Table 2: Optimization of NOBIN resolution.^[a]

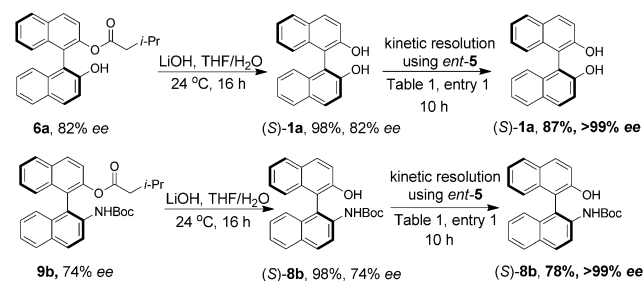
Entry	8	T [°C]	Azolium	Yield ₈ , ^[b]		Yield ₉ , ^[b]		Conv. [%]	s
				ee ₈ ^[c]	ee ₉ ^[c]	ee ₈ ^[c]	ee ₉ ^[c]		
1	8a	24	5	38;95	57;63	60	15		
2	8b	24	5	40;93	53;64	58	15		
3	8b	24	7	41;94	56;70	57	19		
4	8b	0	7	41;99	56;74	57	34		

[a–c] See Table 1.



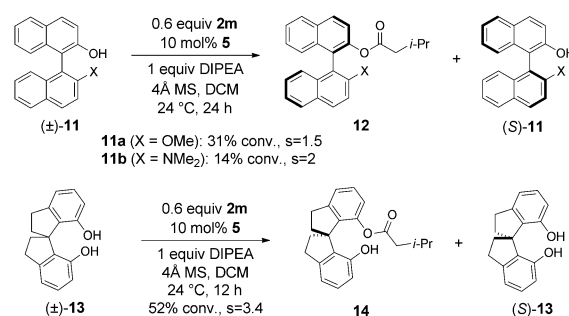
Scheme 5. Resolution of the NOBIN analogue and Boc removal.

enantiomeric BINOL and NOBIN, which was then resolved under similar conditions using the enantiomeric catalyst *ent*-**5** to yield enantiomeric BINOL and NOBIN in $>99\%$ *ee* and high yield (Scheme 6). In this way, the racemic starting materials could be converted to two enantiomers of BINOL or NOBIN in $\geq 99\%$ *ee* with an overall yield of $>84\%$ (Tables 1 and 2, Scheme 6).



Scheme 6. Recycling of the esters to enantiopure BINOL and NOBIN.

During our studies, it was found that an intramolecular H bond interaction between the two phenols (or with aniline) presumably serves as a key element that may increase the nucleophilicity of the substrate and/or help to organize the substrate conformation leading to a better enantioselectivity. When methyl ether **11a** or dimethyl amino derived **11b** was tested, a much lower selectivity as well as lower reactivity was observed (Scheme 7). The spirocyclic diol **13** was also tested, whose rigid structure does not allow H bond interaction between its two phenols. Indeed, a low selectivity ($s=3.4$) was observed using the current catalytic system. Further optimi-



Scheme 7. Importance of intramolecular H bond.

zation is ongoing for the resolution of this unique and highly useful class of compounds.^[18]

In conclusion, we have developed a highly efficient NHC-catalyzed atroposelective kinetic resolution of a wide range of BINOL and NOBIN derivatives that gives them in constantly high *ee*'s of $\geq 99\%$, representing the first highly enantioselective catalytic acylation of axially chiral alcohols.^[19] Mechanistic and computational studies will be performed to better understand the basis for asymmetric induction in this catalytic system.

Experimental Section

To a 4 mL vial the racemic BINOL derivative (0.075 mmol), triazolium salt **5** (0.0075 mmol), and 4 Å MS (25 mg) was added. The mixture was transferred into the glovebox, where aldehyde **2m** (9 μ L, 0.052 mmol), anhydrous DCM (0.75 mL), and DIPEA (18 μ L, 0.075 mmol) were added and the reaction mixture was removed from the glovebox. The vial was then sealed and the reaction mixture was allowed to stir at ambient temperature for 24 h. The crude reaction mixture was directly purified by silica gel column chromatography with hexanes/ethyl acetate (10:1 v/v) as eluent to afford the ester product and the recovered starting material in pure form.

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