OL Organic Letters

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Carbene-Catalyzed Direct O-Functionalization of Ketone: Atroposelective Access to Non-C_2-Symmetric Binaphthyls

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Cite This: https://doi.org/10.1021/acs.orglett.3c03141 Read Online

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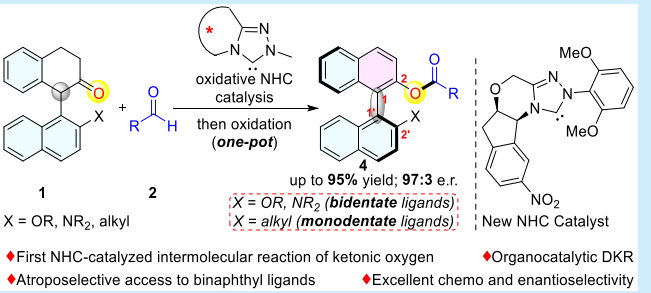
ABSTRACT: Disclosed here is NHC-catalyzed direct intermolecular trapping of the ketone oxygen atom with the acyl azolium intermediate. The overall reaction is a dynamic kinetic resolution process that converts ketone to the corresponding enol ester with well-controlled axial chirality. Our reaction eventually affords non-C_2-symmetric binaphthyl derivatives with important applications, such as in the area of asymmetric catalysis.



Ketones are common functional moieties and basic building blocks in chemistry and related sciences.[1] Multiple atoms (e.g., carbonyl carbon, oxygen, α-carbon, and even remote carbon atoms) of ketones can participate in useful chemical transformations. In the area of *N*-heterocyclic carbene (NHC), a proven powerful organic catalyst,[2] ketones as substrates have mainly been found in two types of reactions (Figure 1a). One is to use the ketone carbonyl carbon atoms as electrophilic centers to react with nucleophilic NHC-bound intermediates, such as acyl anion and azolium enolate intermediates,[3] and the other is to use the ketone α-carbon atoms as nucleophilic centers to react with electrophilic NHC-bound intermediates, such as α,β-unsaturated acyl azolium intermediates.[4] In contrast, the direct intermolecular reaction of the oxygen atoms of ketones as nucleophilic centers[5] in NHC catalysis has not been developed. The reported reactions involving ketone oxygen atoms are intramolecular reactions or reactions that start with ketone α-carbon atoms as the initial key steps followed by intramolecular cyclization involving ketone oxygen atoms.[2,4] There are three main challenges for direct use of ketone oxygen atoms in NHC-catalyzed reactions: (i) the low concentration of the tautomeric enol form of ketone, (ii) the potential competing side reactions from the ketone α-carbon atoms,[4] and (iii) the instability of the resulting enol ester product that may behave as an activated ester to react with the NHC catalyst.[6]

Here, we report the first NHC-catalyzed direct enantioselective intermolecular reaction of ketone oxygen atoms with acyl azolium intermediates (Figure 1b). The enol ester products from our reactions undergo smooth oxidations to afford axially chiral non-C_2-symmetric binaphthyl derivatives with excellent optical purities. Key steps include ketone−enol tautomerization, facile interconversion of the two enantiomeric enol intermediates, and enantioselective acylation (Figure 1b). The overall reaction is a base and NHC-mediated dynamic kinetic resolution (DKR)[7] process that converts ketone to the corresponding enol ester. The NHC-catalyzed step can be combined with an oxidation step in a one-pot strategy to eventually afford non-C_2-symmetric binaphthyl derivatives (Figure 1b). It is worth mentioning that axially chiral 2,2′-disubstituted binaphthyls are highly stable against racemization and serve as essential structural components in chiral ligands, materials, and natural products.[8] Indeed, their applications depend upon the properties of functional groups at the 2,2′ positions.[8b] For instance, those with two coordinating groups are used as bidentate ligands (e.g., BINOLs[9] and NOBINs[10]), while substituting one coordinating group with a non-coordinating group (source of monodentate ligands) can be crucial for the success of certain metal-catalyzed reactions.[11] To access these chiral binaphthyl scaffolds, several DKR methods have been developed,[12,13] including chiral phase-transfer catalyst-mediated atroposelective biaryl synthesis,[13c] which employ similar ketone functionalization methods as ours. However, when it comes to the substitution of one of the coordinating groups at 2,2′ positions by a non-coordinating group (such as alkyl), these elegant methods (including the prior approach for atroposelective enolate trapping[13c]) suffer from poor yields and enantioselectivities.[13] Our NHC-

Received: October 8, 2023
Revised: November 3, 2023
Accepted: November 9, 2023

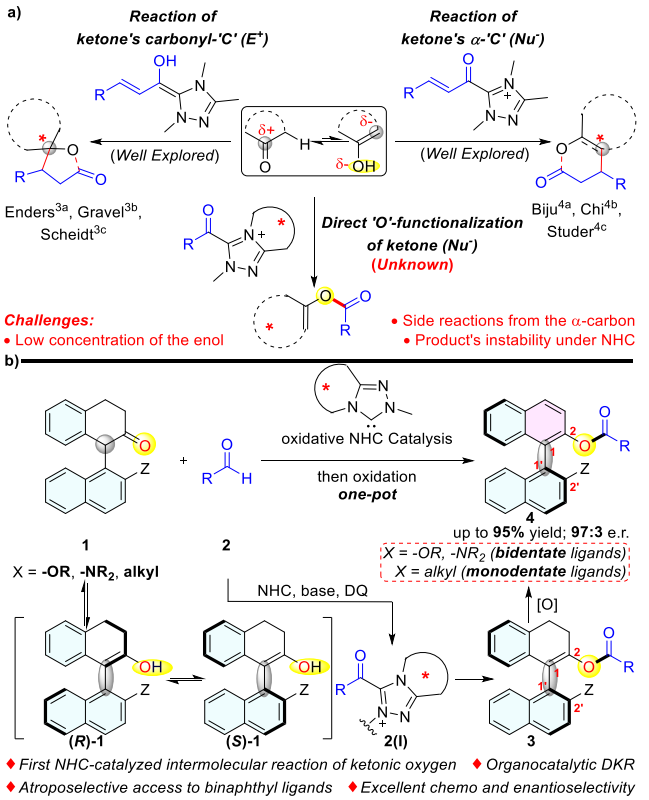
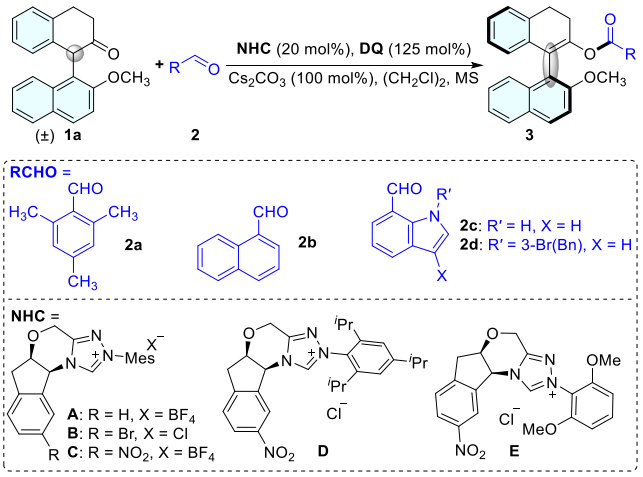


Figure 1. Modes of intermolecular ketone functionalizations via NHC catalysis and its application in atropo-enriched binaphthyl preparation: (a) intermolecular reaction modes of ketones via NHC catalysis and (b) direct O-functionalization of ketones: access to axially chiral binaphthyls (this work).

catalyzed DKR method solves the above-mentioned issue and gives access to the derivatives of BINOLs,[9] NOBINs,[10] and monoalkylated BINOLs,[11b,c] by tolerating both coordinating (alkoxy and protected amine) and non-coordinating (alkyl) groups at 2′ positions. Diverse 2′-functional group tolerance together with good to excellent yields and optical purities makes our DKR method a general approach toward the asymmetric synthesis of 2,2′-disubstituted binaphthyls.

We started our investigation with racemic **1a** as the model substrate for the atroposelective synthesis of enol ester intermediate **3**, an immediate precursor to chiral binaphthyl (BINOL) derivative **4**. Various aldehydes (**2**) were employed to couple with compound **1a** in the presence of $(CH_2Cl)_2$ as the solvent and Cs_2CO_3 as the base to find out the optimal reaction conditions. Key results of optimized conditions are briefed in Table 1 (see the Supporting Information for details). We were pleased to observe that aldehyde **2a** coupled with compound **1a** in the presence of aminoindanol-derived NHC catalyst **A**,[14a] resulting in the formation of enol ester **3a** in 8% yield and 62:38 enantiomeric ratio (er) value (entry 1 in Table 1). The introduction of a bromide (−Br) group in the aminoindanol skeleton of catalyst **A** (to obtain catalyst **B**[14b]) improved both the yield and er value (entry 2 in Table 1). Further modification of catalyst **B** by replacing the −Br group with the nitro ($-NO_2$) group (to obtain catalyst **C**[14b]) resulted in improved enantioselectivity with a diminishing yield (entry 3 in Table 1). Unfortunately, switching of *N*-mesityl substitution of catalyst **C** by a more electron-rich and bulky *N*-(1,3,5-triisopropyl)phenyl group (to obtain catalyst **D**[14b]) was unable to produce compound **3a** (entry 4 in Table 1). However, changing to the *N*-2,6-dimethoxyphenyl group instead (to design catalyst **E**) afforded compound **3a** in 75:25 er and 39% yield (entry 5 in Table 1). It is well-known that stereoelectronic properties of the acyl azolium intermediate have a prominent influence on the reaction outcomes. Therefore, we shifted our focus onto the screening of various aldehydes using catalyst **E** (entries 6−8 in Table 1). 1-Naphthaldehyde **2b** as an acyl azolium source showed a sharp increase in the yield (91%) with an inferior er (61.5:38.5) (entry 6 in Table 1). An improved yield from sterically bulky

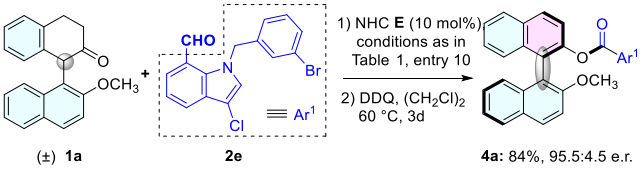
Table 1. Optimization of Reaction Conditions[a]



entry	NHC	aldehyde	product	yield (%)[b]	er[c]
1	**A**	**2a**	**3a**	8	62:38
2	**B**	**2a**	**3a**	24	67:33
3	**C**	**2a**	**3a**	11	73:27
4	**D**	**2a**	**3a**	–	–
5	**E**	**2a**	**3a**	39	75:25
6	**E**	**2b**	**3b**	91	61.5:38.5
7	**E**	**2c**	**3c**	76	84:16
8	**E**	**2d**	**3d**	74	87:13
9[d]	**E**	**2d**	**3d**	87	88.5:11.5
10[d,e]	**E**	**2d**	**3d**	81	94.5:5.5

[a]Reaction conditions: compound **1a** (0.05 mmol), compound **2** (1.25 equiv), NHC·HX (20 mol %), base (1.0 equiv), and 3,3,5,5-tetra-*tert*-butyl diphenoquinone (DQ, 1.25 equiv) in $(CH_2Cl)_2$ (0.025 M) at room temperature for 24 h. [b]Yields were determined by ^{1}H nuclear magnetic resonance (NMR) analysis. [c]The er values were determined via chiral-phase HPLC analysis. [d]DBU in place of Cs_2CO_3 was used. [e]The reaction was carried out at −20 °C for 3 days with 1.6 equiv of compound **2d**, and DQ.

Scheme 1. One-Pot Binaphthyl Preparation[a]



[a]Reaction conditions: (1) compound **1a** (0.1 mmol), compound **2e** (1.6 equiv), DBU (1.3 equiv), 4 Å molecular sieve (MS, 100 mg/mL), DQ (1.6 equiv), and NHC·HCl **E** (10 mol %) in $(CH_2Cl)_2$ (0.025 M) at −20 °C for 1 day and (2) DDQ (5 equiv) oxidation at 60 °C for 3 days. The er value was determined via chiral-phase HPLC analysis, with the isolated yield.

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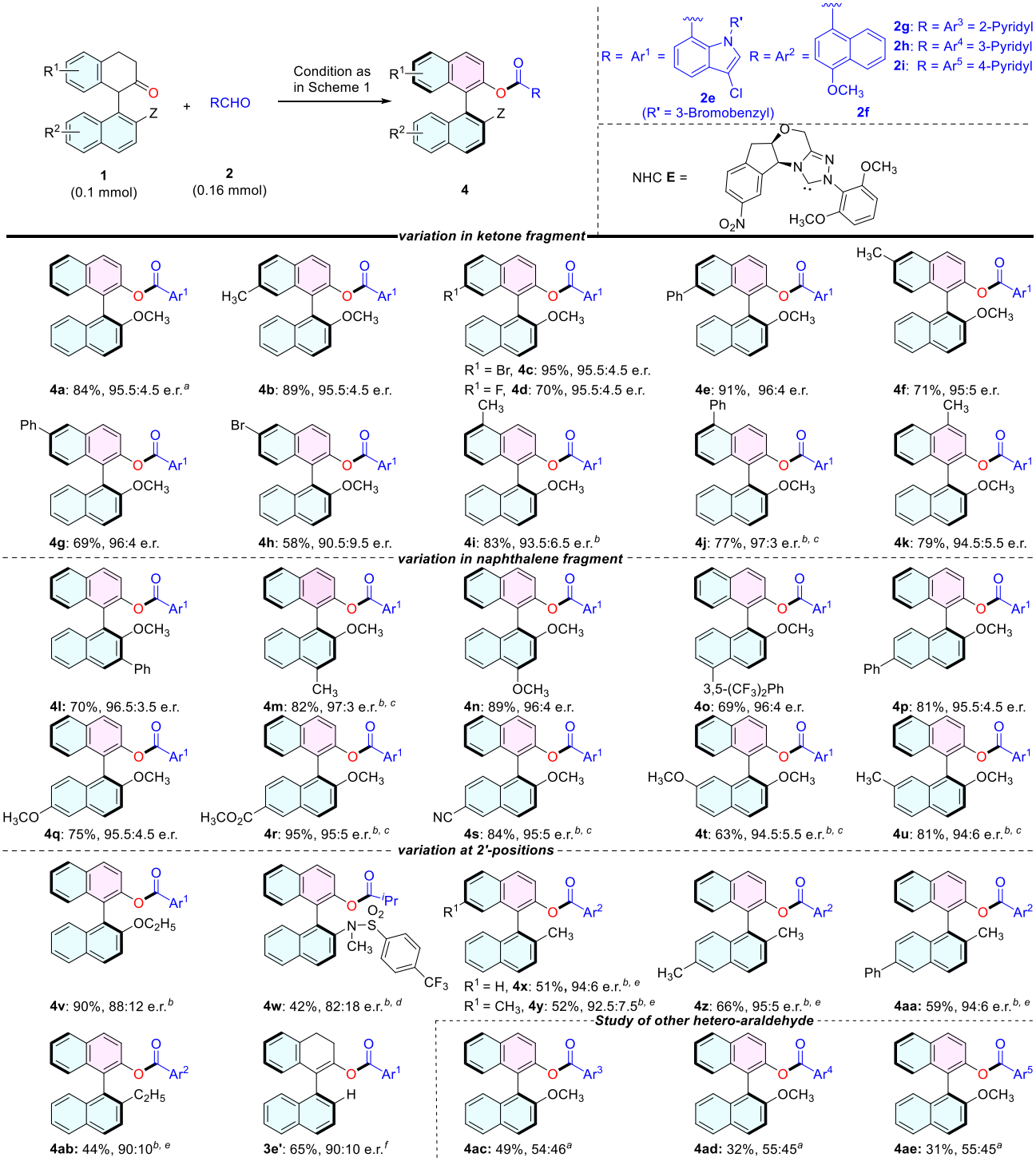
Scheme 2. Substrate Scope[g]



[a]The catalytic reaction was completed after 1 day. [b]NHC·HCl **E** at 20 mol % was used. [c]The catalytic reaction was performed at −30 °C for 7 days. [d]The catalytic reaction was performed with isobutyraldehyde (3 equiv) and Cs_2CO_3 (5 equiv) in dichloromethane (DCM, 0.025 M) at room temperature for 1 day. [e]The catalytic reaction was performed with compound **1** (1.25 equiv), compound **2f** (0.1 mmol), and Cs_2CO_3 (5 equiv) in CH_3CN (0.025 M) at −30 °C for 7 days. [f]One-pot oxidation was not performed as a result of racemization at the reaction condition. [g]Reaction conditions: (1) compound **1** (0.1 mmol), compound **2** (1.6 equiv), DBU (1.3 equiv), 4 Å MS (100 mg/mL), DQ (1.6 equiv), and NHC·HCl **E** (10 mol %) in DCE (0.025 M) at −20 °C for 5 days and (2) DDQ (5 equiv) oxidation at 60−75 °C for 2−5 days.

2b prompted us to explore more bulky aldehydes with diverse electronic properties to enhance both the yield and enantioselectivity. To our delight, an attempt to carry out the reaction with commercially available indole 7-carbaldehyde (**2c**) resulted in the product **3c** in 76% yield with 84:16 er value (entry 7 in Table 1). Installing a 3-bromobenzyl (see the Supporting Information) protection on indole-7-carbaldehyde (to obtain aldehyde **2d**) further improved the er value to 87:13

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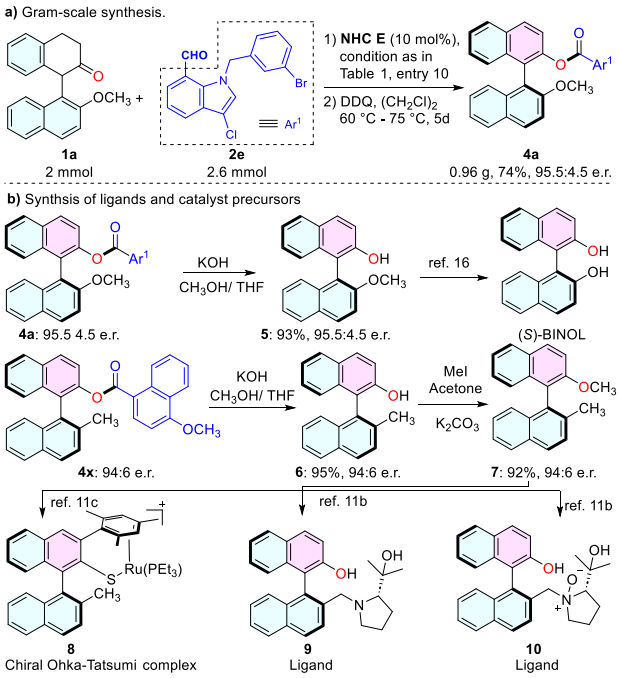

Figure 2. Gram-scale synthesis and applications in synthesizing ligands and the catalyst precursor.

with 74% yield (entry 8 in Table 1). Interestingly, use of strong organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) improved the yield and er value (entry 9 in Table 1) further. Finally, we mannaged to achieve compound **3d** in 81% yield and 94.5:5.5 er value (entry 10 in Table 1) when the reaction was carried out at a lower temperature (−20 °C).

To synthesize binaphthyl skeletons directly from compound **1a** in one pot, we sought a compatible oxidation method. We tried using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidant, but it led to the decomposition of compound **3d**, likely because the electron-rich indole motif is sensitive to strong oxidative conditions.[15] To solve this issue, we used a more electron-poor aldehyde **2e** obtained by protecting 3-chloro-indole-7-carbaldehyde with 3-bromobenzyl. Contrary to compound **2d**, aldehyde **2e** successfully yielded high enantiopure binaphthyl **4a** from ketone **1a** (84% isolated yield and 95.5:4.5 er) under the one-pot strategy using previously optimized conditions (entry 10 in Table 1) with a reduced NHC loading (10 mol %) (Scheme 1). The absolute stereochemistry of compound **4a** was determined by comparing the high-performance liquid chromatography (HPLC) spectra of the derivative of commercially available (*S*)-BINOL with the derivative of compound **4a** (see the Supporting Information for details).

After achieving the optimized reaction conditions, we moved to evaluate the generality of this protocol (Scheme 2). First, we examined the substituent tolerance in the ketone ring fragment of compound **1**. Various kinds of substitutions (such as methyl, halogens, and phenyl) at the sterically demanding 7 position of the ketone ring fragment worked well, obtaining the desired BINOL derivatives (**4b**−**4e**) in excellent yields and enantioselectivities. The introduction of different groups (such as methyl, phenyl, and bromo) at the 6 and 5 positions of ketone also resulted in the formation of corresponding BINOL derivatives (**4f**−**4j**) with excellent outcomes. Interestingly, our catalytic system worked proficiently with a 4-methyl substitution at the saturated ring part of ketone, yielding compound **4k** in 79% yield with 94.5:5.5 er. Steric and electronic effects on the naphthalene ring fragment of ketone **1** were assessed next. A diverse range of functional groups, such as the aryl nucleus [phenyl, 3,5-bis(trifluoromethyl)], electron-donating groups (methyl and methoxy), and electron-withdrawing groups (methyl carboxylate and nitrile) at different positions (3′, 4′, 5′, and 6′) of the naphthalene ring fragment of ketone (**1**) reacted smoothly to give the corresponding BINOL derivatives (**4l**−**4s**) in good to excellent yields and optical purities. Substitutions at the sterically encumbered 7′ position with methoxy and methyl groups were also found to be tolerable and afforded the product BINOL derivatives **4t** (63% and 94.5:5.5) and **4u** (81% and 94:6), respectively.

To understand the essentiality of the 2′-methoxy group in our catalytic reaction, next, we tested various substitutions at the 2′ position (Scheme 2). We successfully obtained a BINOL derivative with 2′-ethoxy substitution (**4v**) with a satisfactory outcome. We also prepared a NOBIN derivative with a protected amine group at the 2′ position (**4w**) with a moderate result. Notably, for compound **4w**, we conducted the reaction at room temperature using isobutyraldehyde and excess (5 equiv) Cs_2CO_3 to improve the outcome. To analyze the independency of a coordinating group at the 2′ position of ketone (**1**), we synthesized 2′-alkyl-substituted binaphthyls (**4x**−**4ab**) with acceptable results. It is worth mentioning that, for 2′-alkyl substitutions, we switched to 4-methoxy-1-naphthaldehyde (**2f**) to achieve better outcomes. Interestingly, even ketones with no substitution at the 2′ position worked well, yielding the enol ester product (**3e′**) in excellent yield with a good enantiomeric ratio. However, one-pot oxidation was not feasible in this case as a result of racemization under the oxidation conditions.

With the aim to prepare the tridentate ligand, next, we focused our attention on exploring more heterocyclic aldehydes in our reaction (Scheme 2). Different pyridine-derived aldehydes (**2g**−**2i**) was able to couple with ketone **1a** successfully to give the desired BINOL derivatives (**4ac**−**4ae**) in poor to moderate yields, albeit in a poor er value.

To demonstrate practicality, we performed a gram-scale synthesis of the BINOL derivative, yielding compound **4a** in 74% yield without affecting enantiomeric purity (Figure 2a). Axially chiral binaphthalenes from our catalytic reaction could be easily transformed into essential catalyst precursors and ligands (and their precursor) used in both academia and industry (Figure 2b). For example, compound **5**, the precursor of (*S*)-BINOL,[16] was obtained by hydrolyzing the ester linkage in compound **4a**, yielding 93% of compound **5** with a 95.5:4.5 er value (Figure 2b). Similarly, compound **4x** was converted into versatile intermediate **7** through hydrolysis and subsequent methylation, maintaining excellent yields and enantioselectivity in each step. It should be noted that compound **7** is a versatile intermediate for the chiral Ohka−Tatsumi complex[11c] (**8**) and various other kinds of literature-reported ligands,[11b,d−f] such as ligands **9**[11b] and **10**[11b] (Figure 2b).

In summary, we developed a NHC-catalyzed enantioselective reaction for direct (intermolecular) acylation of ketone oxygen atoms to access axially chiral enol esters. Non-C_2-symmetric binaphthyl derivatives have been facilely accessed through a one-pot oxidation process with our catalytic strategy, which could find important applications in the area of asymmetric catalysis. Key steps involve selective acylation of the racemic mixture of atropisomeric enol by the NHC-

https://doi.org/10.1021/acs.orglett.3c03141
Org. Lett. XXXX, XXX, XXX−XXX

mediated acyl azolium intermediate via DKR. The tolerance of diverse functional groups, specifically the presence of both coordinating (alkoxy and protected amine) and non-coordinating (alkyl) groups at the 2′ position, molded our NHC-catalyzed DKR method into a general approach for making a variety of non-C_2-symmetric binaphthyls. The practicability of our method was demonstrated by the gram-scale synthesis and the effective conversions of our reaction products into chiral BINOL and monoalkylated BINOL derivatives that are precursors of many literature-reported ligands and catalysts. We expect that our study will inspire asymmetric O-functionalization of other carbonyls in the field.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.3c03141.

Experimental procedures, analytical and spectroscopic data for new compounds, chiral-phase HPLC data, and copies of NMR (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge funding support from the National Natural Science Foundation of China (21732002, 22061007, and 22071036), the Frontiers Science Center for Asymmetric Synthesis and Medicinal Molecules, Department of Education, Guizhou Province [Qianjiaohe KY (2020)004], the 10 Talent Plan (Shicengci) of Guizhou Province [(2016) 5649], the Science and Technology Department of Guizhou Province [Qiankehe-jichu-ZK(2022)zhongdian024, (2018)2802, and (2019)1020], the Program of Introducing Talents of Discipline to Universities of China (111 Program, D20023) at Guizhou University, the Singapore National Research Foundation under its NRF Competitive Research Program (NRF-CRP22-2019-0002), the Ministry of Education, Singapore, under its MOE AcRF Tier 1 Award (RG70/21 and RG84/22), MOE AcRF Tier 2 (MOE2019-T2-2-117), and MOE AcRF Tier 3 Award (MOE2018-T3-1-003), the Chair Professorship Grant, and Nanyang Technological University.

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https://doi.org/10.1021/acs.orglett.3c03141
Org. Lett. XXXX, XXX, XXX−XXX