Synthesis of Axially Chiral Diaryl Ethers via NHCs-Catalyzed Desymmetrization Followed By Kinetic Resolution

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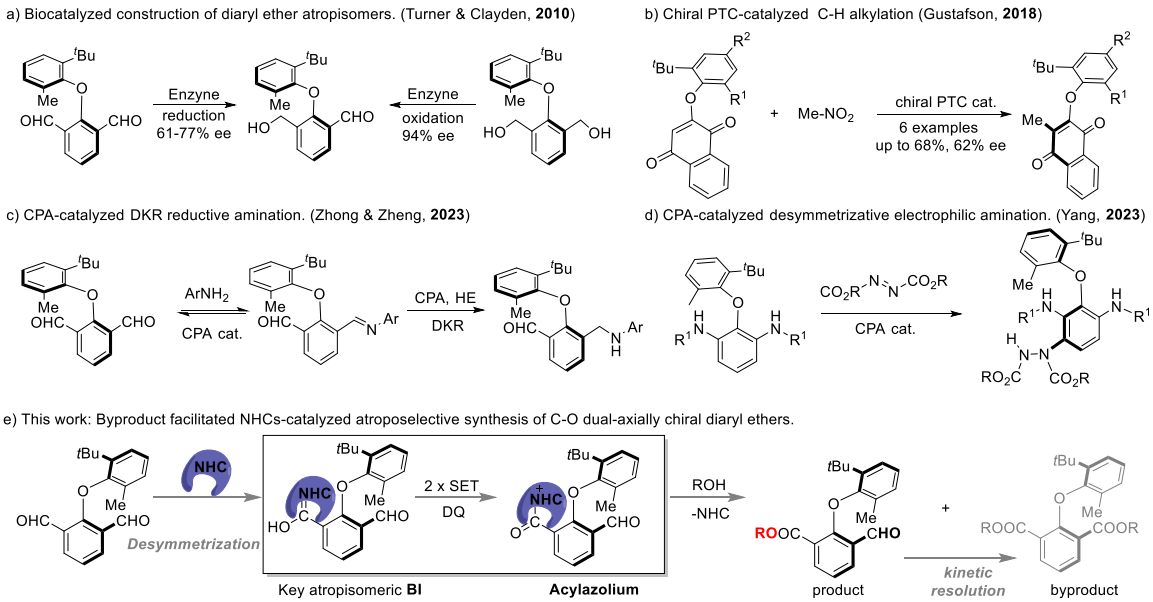
Abstract: Axially chiral diaryl ethers bearing two potential axes, found unique applications in bioactive molecules. However, only very few catalytic methods have been developed to construct structurally diverse diaryl ethers. We herein describe an NHC-catalyzed atroposelective esterification of biaryl dialdehydes leading to the synthesis of flexible axially chiral diaryl ethers. Mechanistic studies indicate that coupling proceeds through NHC-catalyzed desymmetrization of the dialdehydes and matched kinetic resolution. This protocol features excellent enantioselectivity, mild conditions, good functional-group tolerance, and applicability to late-stage functionalization and provides a modular platform for the synthesis of axially chiral diaryl ethers. and their derivatives.

Atropisomerically enriched chiral frameworks found widespread applications in material science,[1] bioactive molecules,[2] and asymmetric catalysis.[3] Accordingly, significant progress has been achieved in the catalytic construction of axial chiral scaffolds, including biaryl atropisomers,[4] axially chiral styrenes,[5] amines,[6] amides,[7] boranes[8], etc. As distinctive atropisomers, axially chiral diaryl ethers bearing two potential axes, found unique applications in bioactive molecules.[9] However, constructing C-O axially chiral diaryl ether received limited attention from organic chemists, probably owing to the challenges in more flexible dual-axial chirality control. In 1998, Fuji and coworkers[10a] discovered the first atropisomerism in diaryl ether.[10] In 2008, the Clayden group[11] pioneered the first enantioselective synthesis of an axially chiral diaryl ether, that with sole dual-axial chirality. Developing a catalytic methodology for the asymmetric construction of diaryl ether-type atropisomers is highly desirable but more challenging. In this regard, Turner, Clayden, and co-workers[12] developed unprecedented biocatalyzed enantioselective construction of diaryl ether atropisomers via desymmetrizative oxidation/reduction of diols/dialdehydes (Scheme 1a). Even with the conceptual breakthrough, only one example of axially chiral diaryl ether was obtained. The Gustafson group[13] developed the first organocatalyzed chiral induction through enantioselective C-H alkylation, although yields and enantioselectivity were not high (Scheme 1b). Very recently, the Zheng[14] and Yang[15] groups developed elegant chiral phosphoric acid (CPA) catalyzed asymmetric reductive amination (DKR) (Scheme 1c) and electrophilic amination (remote desymmetrization) (Scheme 1d) of axially prochiral diaryl ether, leading to highly enantioselective construction of diaryl ether-type atropisomers. Despite those significant processes, the development of a novel catalytic methodology for direct access to diaryl ether-type atropisomers was still in its emerging area and in great demand.

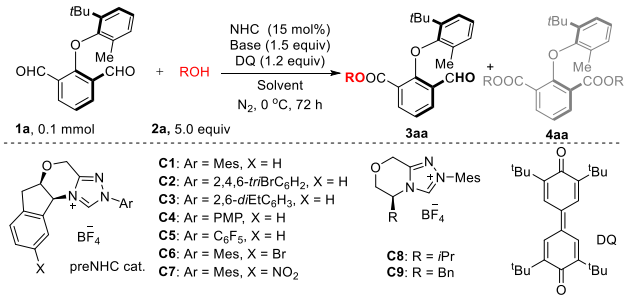
On the other hand, N-heterocyclic carbenes catalysis (NHCs) exhibit unique reactivity in activating the carbonyl group.[16,17] NHCs-catalyzed transformations provide attractive alternatives for constructing axial chiral compounds via desymmetrization,[18] or (dynamic) kinetic resolution[19] strategy. NHCs-catalyzed desymmetrization of axially prochiral dialdehydes provides chiral-NHC-bounded atropisomeric Breslow intermediates (BI) as a critical intermediate, leading to direct access to highly atropisomerically enriched aldehydes via two step single electron oxidation and nucleophilic coupling. However, for NHCs, chiral induction of flexible dual-axial chirality was a gap. As part of our continued interests in NHCs-catalyzed transformations[20] and asymmetric catalysis, we now report an asymmetric esterification approach to flexible axially chiral diaryl ethers by chiral NHCs-catalyzed desymmetrization[21] followed by kinetic resolution from dicarbaldehydes and alcohols/phenols (Scheme 1e).[22, 23] The matched kinetic resolution could improve the enantioselectivity, leading to excellent chiral induction for challenging C-O axially chiral diaryl ethers.

To probe the feasibility of our designed reaction, we commenced our investigation employing dicarbaldehydes (**1a**) and MeOH (**2a**) as the model esterification reaction. Encouragingly, in initial study, treatment of **1a** and **2a** in DCM employing **C1** as the catalyst, DQ (1.2 equiv) as oxidant, and Cs_2CO_3 (1.5 equiv) as the base at 0 °C under N_2 atmosphere for 72 h, desired esterification product **3aa** was determined in 91% yield and 90% ee, along with 5% diester byproduct **4aa** (Table 1, entry 1). Next, a series of NHCs were screened (entries 2–11), and C1 was proven to be the best choice for this atroposelective esterification. Switching the Mes group of C1 to 2,4,6-*tri*BrC_6H_2 (entry 2) or C_6F_5 (entry 5) had nearly no reactivity. The screening of various solvents indicated DCM was the best solvent for this esterification (entries 12–18). Most of the solvent, such as DCE, MTBE, EtOAc, or toluene, gives acceptable yield and enantioselectivity. THF exhibits excellent chiral induction, delivering **3aa** in 68% yield and 98% ee; however, diester **4aa** was identified with a 19% yield because of high activity. Switching catalyst loading to 15 mol% caused an increased yield of diester **4aa** (11%), and **3aa** was isolated in 88% yield and 94% ee (entry 19). This result indicates that the formation of byproduct **4aa** could impact the enantioselectivity of **3aa**. Unfortunately, the screen of various bases failed to afford improved results (entries 20-23); thus, entry 19 was identified as standard conditions for the variation of the substrate.



Scheme 1 Catalytic asymmetric construction of diaryl ether-type atropisomers.

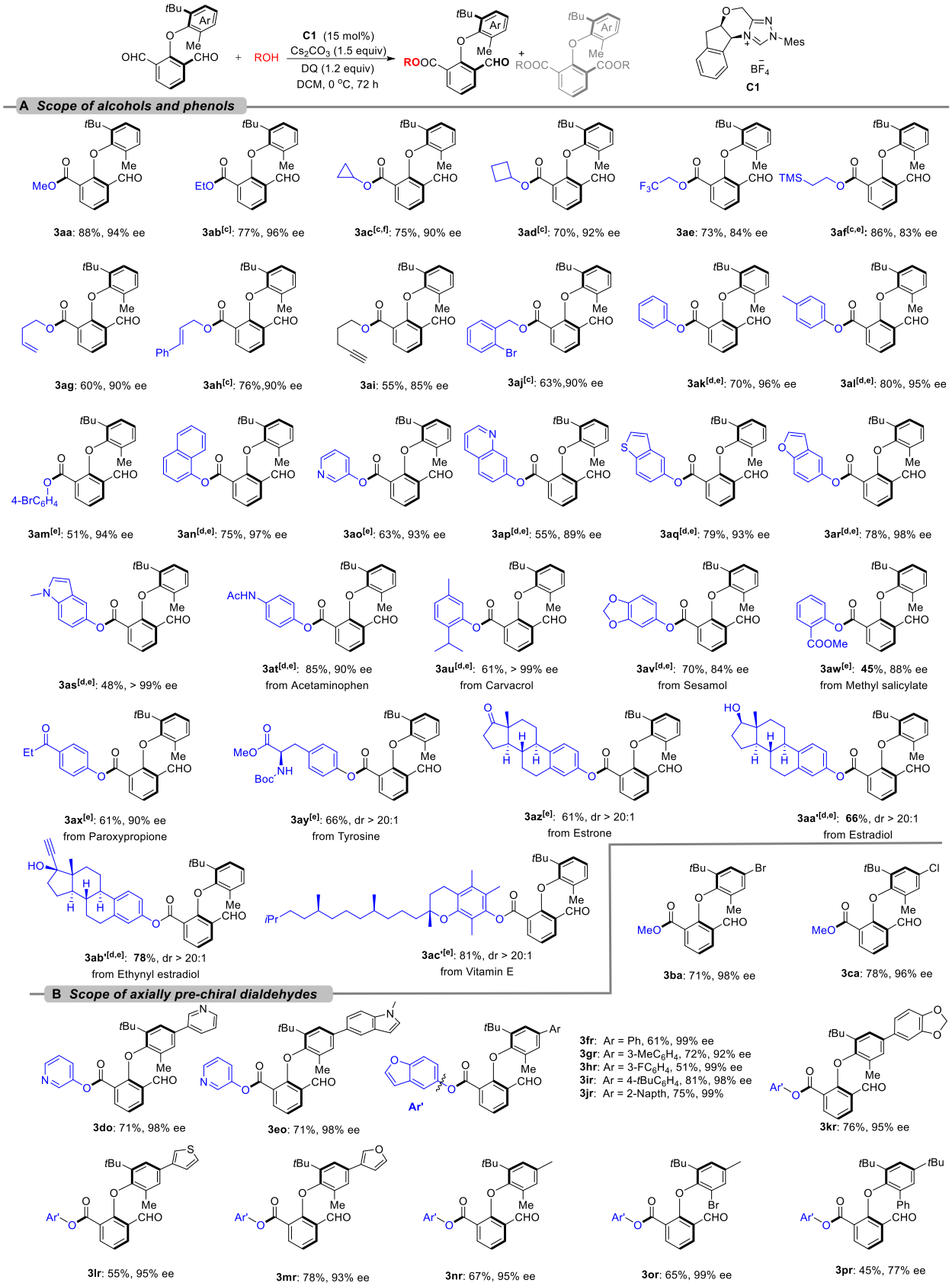
Table 1 Optimization of the reaction conditions[a]



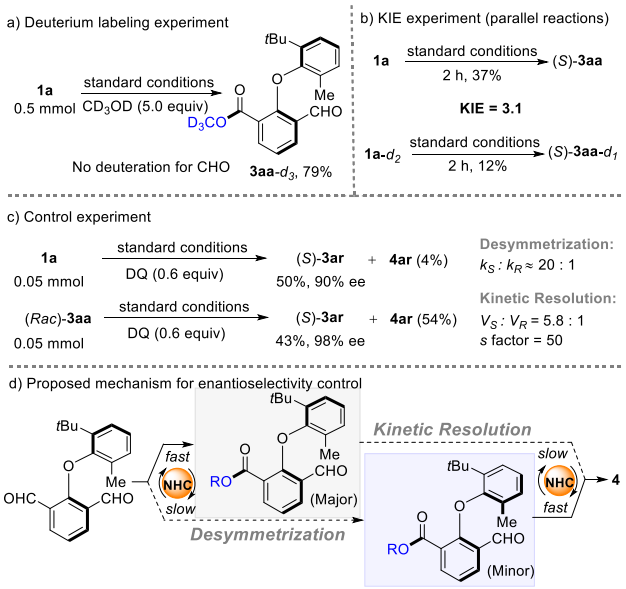
Entry	NHC Cat.	Solvent	Base	3aa (%) Yield	*ee*	4aa (%)
1	C1	DCM	Cs_2CO_3	91	90	5
2	C2	DCM	Cs_2CO_3	7	35	trace
4	C3	DCM	Cs_2CO_3	73	86	2
5	C4	DCM	Cs_2CO_3	84	-67	11
6	C5	DCM	Cs_2CO_3	9	-40	trace
7	C6	DCM	Cs_2CO_3	74	91	2
8	C7	DCM	Cs_2CO_3	40	87	trace
9	C8	DCM	Cs_2CO_3	59	-16	31
11	C9	DCM	Cs_2CO_3	60	41	35
12	C1	$CHCl_3$	Cs_2CO_3	83	75	6
13	C1	DCE	Cs_2CO_3	86	91	10
14	C1	THF	Cs_2CO_3	68	98	19
15	C1	MTBE	Cs_2CO_3	87	91	8
16	C1	EtOAc	Cs_2CO_3	81	90	12
17	C1	MeCN	Cs_2CO_3	82	80	16
18	C1	Toluene	Cs_2CO_3	79	93	11
19[b]	C1	**DCM**	**Cs_2CO_3**	**89 (88)**	**94**	**11**
20[b]	C1	DCM	K_2CO_3	80	89	11
21[b]	C1	DCM	K_3PO_4	90	90	10
22[b]	C1	DCM	DBU	80	91	9
23[b]	C1	DCM	DMAP	82	89	8

[a] Conditions: **1a** (0.1 mmol), **2a** (5.0 equiv), NHCs. (10 mol%), base (1.5 equiv) and DQ (1.2 equiv), solvent (1.0 mL), 0 °C, N_2 atmosphere, 72 h. Yields were determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture employing CH_2Br_2 as the internal standard; *ee* was determined by chiral-phase HPLC analysis. [b] **NHC-1** (15 mol%).

After the optimized conditions in the hands, the scope and limitation of the atroposelective esterification system has been examined (Scheme 2). First, the substrate scope of the alcohols were evaluated by the coupling with 2-(2-(tert-butyl)-6-methylphenoxy)isophthalaldehyde (**1a**) (Scheme 2A). A series of alcohols bearing primary alkyl (**3aa**, **3ab**), secondary alkyl (**3ac**, **3ad**), strained rings (**3ac**, **3ad**), trifluoromethyl (**3ae**), TMS (**3af**), terminal (**3ag**) and internal (**3ah**) alkenyl, alkynyl (**3ai**), and benzyl group (**3aj**) were well tolerated, and delivering diaryl ether-type atropisomers in 55-88% yield and 83-96% ee. Phenol was also a suitable substrate, generating **3ak**-**3am** with up to 96% ee. Fused ring (**3an**), pyridine (**3ao**), isoquinoline (**3ap**), benzothiophene (**3aq**) and benzofuran (**3ar**), indole (**3as**) substituted phenols were all well tolerated, offering desired products with high enantioselectivity (in most cases >90% ee) and moderate yield (48%-79%). Mild conditions and broad functional group tolerance encouraged us to carry out late-stage functionalization of natural products and bioactive compounds. Natural products include carvacrol (**3au**), and sesamol (**3av**); bioactive molecules such as methyl salicylate (**3aw**), paroxypropione (**3ax**), tyrosine (**3ay**), estrone (**3az**), estradiol (**3aa'**), and ethynyl estradiol (**3ab'**); Drugs such as acetaminophen (**3at**), and vitamin E (**3ac'**) were well tolerated in this system and delivered the axially chiral diaryl ethers in acceptable yields with good to excellent stereoselectivity (84-99% *ee*, or 20:1 *dr*).



Scheme 2. Substrate scope for desymmetrizing esterification of axially pre-chiral dialdehydes.[a,b] [a] Unless otherwise noted, all the reactions were carried out with **1** (0.1 mmol), **2** (0.5 mmol), NHC-1 (15 mol%), DQ (1.2 equiv), Cs_2CO_3 (1.5 equiv), and dry DCM (1.0 mL) at 0 °C under N_2 atmosphere for 72 h. [b] Isolated yield, *ee* was determined by chiral-phase HPLC analysis. [c] THF was used instead of DCM. [d] Reactions were performed at -20 °C. [e] Reactions were carried out with **2** (.0 equiv). [f] Reactions were carried out with **C1** (10 mol%)



Scheme 3. Mechanistic studies and proposed mechanism.

Then, the scope of axially prochiral dialdehydes was explored (Scheme 2B). Dicarbaldehydes bearing halogen (**3ba**, **3ca**), pyridinyl (**3do**), indolyl (**3eo**), substituted aryl (**3fr-3ir**, **3kr**), naphthyl (**3jr**), thienyl (**3lr**), furyl (**3mr**) on the aromatic ring could delivering the desired products with excellent enantioselectivity (in all cases > 90% *ee*). Dicarbaldehydes with electro-donating methyl groups were well tolerated, giving the desired products **3nr** and **3or** excellent *ee*. When the blocking group methyl of dicarbaldehyde was switched to bromine, nearly no reduction of *ee* was detected (**3nr** VS **3or**); however, when changing to the phenyl group, a drop in *ee* value to 77% was observed.

A series of mechanistic investigations were then conducted to probe the catalytic cycle and enantio-determining step of this esterification reaction (Scheme 3). Isotope exchange experiments resulted in no deuterium incorporation at the aldehyde group of ***3aa-d₃***; reversible formation of Breslow intermediate could be excluded (Scheme 3a). Parallel KIE experiment employing 1a and ***1a-d₂*** in the coupling with MeOH gives KIE = 3.1 (Scheme 3b), indicating that BI formation might be involved in the rate-determine step. While optimizing the conditions, we found that the formation of diester byproducts could increase the *ee* value of the main product. We carried out a control experiment, and the results were shown in Scheme 3c. when the esterification carried out with 60 mol% DQ, 50% (***S-3aa***) was obtained with 4% 4aa. Furthermore, racemic 3aa could undergo efficient kinetic resolution, delivering ***S-3aa*** (43%, 98% ee). Efficient kinetic resolution (s factor = 50) could improve the enantioselectivity of esterification products.

In summary, we have developed NHCs-catalyzed facile and robust desymmetrization of readily accessible dialdehydes, leading to direct access to axially chiral diaryl ether derivatives. Mechanistic studies indicate the esterification proceeds *via* irreversible rate- and enantio-determination activation of aldehyde followed by oxidative esterification and tandem kinetic resolution. The synthetic value of the esterification was further highlighted by the late-stage functionalization of natural products, bioactive molecules, and medicines (10 examples, up to 99% ee/ > 20:1 dr). This protocol features excellent enantioselectivity (up to 99.9% *ee*), mild conditions, good functional group tolerance, and broad substrate scope. The NHCs-catalyzed desymmetrization-functionalization strategy may provide modularized platforms for the synthesis of value-added axially chiral aldehydes and their derivatives.

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