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Access to P-Stereogenic Phosphinates via N-Heterocyclic Carbene-Catalyzed Desymmetrization of Bisphenols

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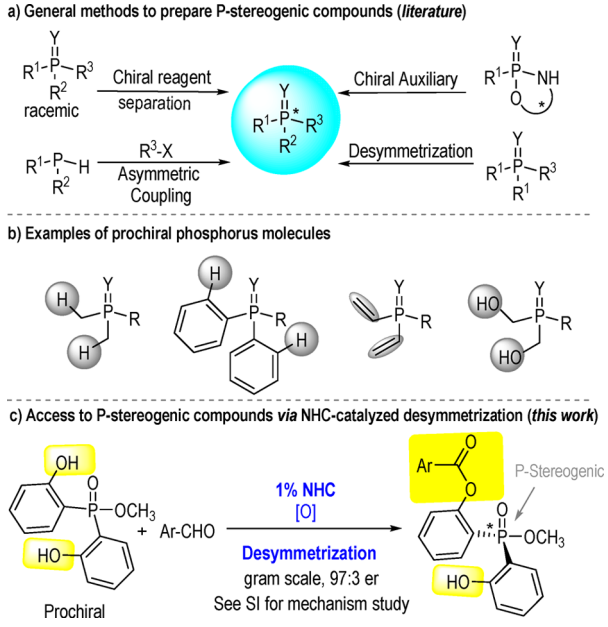
Supporting Information

ABSTRACT: A carbene-catalyzed desymmetrization of prochiral bisphenol compounds bearing remote P-stereogenic centers is disclosed. The catalytic reactions can be performed on gram scales with 1 mol % N-heterocyclic carbene (NHC) catalyst, providing efficient access to enantiomerically enriched P-stereogenic phosphinates. The chiral phosphinates prepared with our method can find widespread applications as asymmetric organic catalysts and ligands.

Phosphorus compounds with P-stereogenic center(s) have found wide applications as ligands[1] and organic catalysts.[2] Having the phosphorus atoms directly coordinated to metals or intimately involved in key organocatalytic steps can likely induce better stereocontrol in organic synthesis.[1,2] Thus, the preparation of enantiomerically enriched phosphorus compounds with P-stereogenic centers has received considerable attention. In the 1970s, Knowles prepared a diphosphine ligand with stereogenic phosphorus centers (DiPAMP) by using L-menthol to form separable diastereomeric phosphinates as a key step.[3] The use of a chiral reagent such as L-menthol has become one of the common methods in preparing phosphorus compounds with P-stereogenic centers.[4] Other alternative methods[5] developed over the years include resolution of diastereomeric mixtures,[6] the use of chiral auxiliaries,[7] metal-catalyzed asymmetric couplings,[8] and desymmetrization of prochiral phosphorus molecules[9] (Scheme 1a). In particular, approaches for the desymmetrization of prochiral phosphorus molecules include deprotonation of dimethylphosphine−borane adducts or phosphine sulfides,[9a,b] asymmetric catalytic C−H activation of diphenylphosphinamides,[9c,d] olefin metathesis of divinyl phosphinates,[9e] and lipase-catalyzed monoacetylation of diol or diacetate phosphine−borane percursors[9f] (Scheme 1b). Despite the elegant progress, efficient preparation of phosphorus compounds with P-stereogenic centers still remains challenging. Compared with the synthesis of chiral carbon centers, the construction of P-stereogenic centers is much less developed.

Here we report an asymmetric access to phosphinates bearing P-stereogenic centers via N-heterocyclic carbene[10] (NHC)-mediated desymmetrization[11] of bis(hydroxyphenyl) phosphinates (Scheme 1c). The P-stereogenic phosphinates, which can be readily prepared on gram scales (e.g., 5 g) using this approach,

Scheme 1. Access to P-Stereogenic Compounds



can be transformed to chiral ligands and organic catalysts. Although desymmetrization of diols[11a,d,12] has enjoyed remarkable success, desymmetrization of the related prochiral bisphenols[13] and diols with remote hydroxyl groups[14] is much more challenging. In these bisphenol substrates, the prochiral center(s) are remote from the enantiotopic sites (e.g., the reactive phenol hydroxyl units) that are difficult to differentiate. In this regard, Miller and co-workers have systematically designed peptide catalysts for the desymmetrization of challenging bisphenol compounds.[13c−e] Fu has designed planar-chiral dimethylaminopyridines for the desymmetrization of *meso*-diols in which the two alcohol units are separated by multiple carbons, including an aromatic unit.[14a]

We tested our designs by using bis(2-hydroxyphenyl) phosphinate (**1a**) as the model prochiral bisphenol substrate, aryl aldehydes (**2a−c**) as acylation reagents, and quinone (first used by Studer in NHC catalysis[15]) as an oxidant. Key results of

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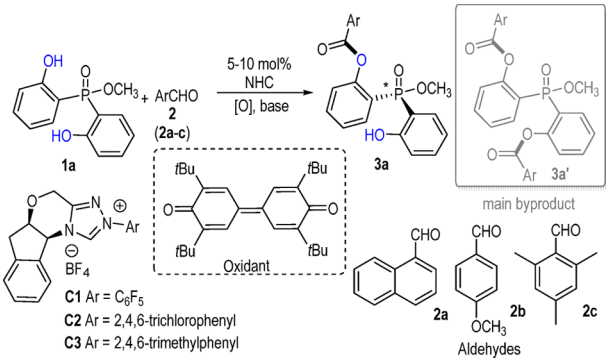
condition optimizations are summarized in Table 1. We first examined the reactions at room temperature. To our delight, the reaction catalyzed by aminoindanol-derived NHC catalyst **C1** (first developed by Rovis[16]) went to completion in less than 5 min with the formation of the desired monoester product **3a** in 90% yield with 87:13 e.r. (entry 1). The main side product was a diester adduct in which both hydroxyl groups were acylated. Changing the substrate from 1-naphthaldehyde (**2a**) to *p*-methoxybenzaldehyde (**2b**) led to a similar e.r. and slightly dropped yield (entry 2). Mesitaldehyde (**2c**) was also an effective acylating reagent (entry 3). Changing the *N*-C_6F_5 group in catalyst **C1** to an *N*-$C_6H_2Cl_3$ substituent (**C2**) led to similar reaction efficiency and product stereoselectivity (reaction for 5 min, 87% yield, 88:12 e.r.; entry 4). NHC catalyst **C3** with an *N*-mesityl substituent could also catalyze the reaction, but a much longer reaction time (18 h) was required (entry 5). We then chose catalyst **C1** and aldehyde **2a** as model catalyst and acylation reagent for further optimizations (entries 6–14). Decreasing the reaction temperature (−40 °C) improved the product e.r., albeit with a longer reaction time (88% yield, 97:3 e.r.; entry 8). Replacing Et_3N with other common bases (such as Cs_2CO_3, K_2CO_3, NaOAc) was tolerated in this reaction (entries 9–11). Common solvents such as CH_2Cl_2, toluene, and CH_3CN could also be used (entries 12–14).

Table 1. Condition Optimizations

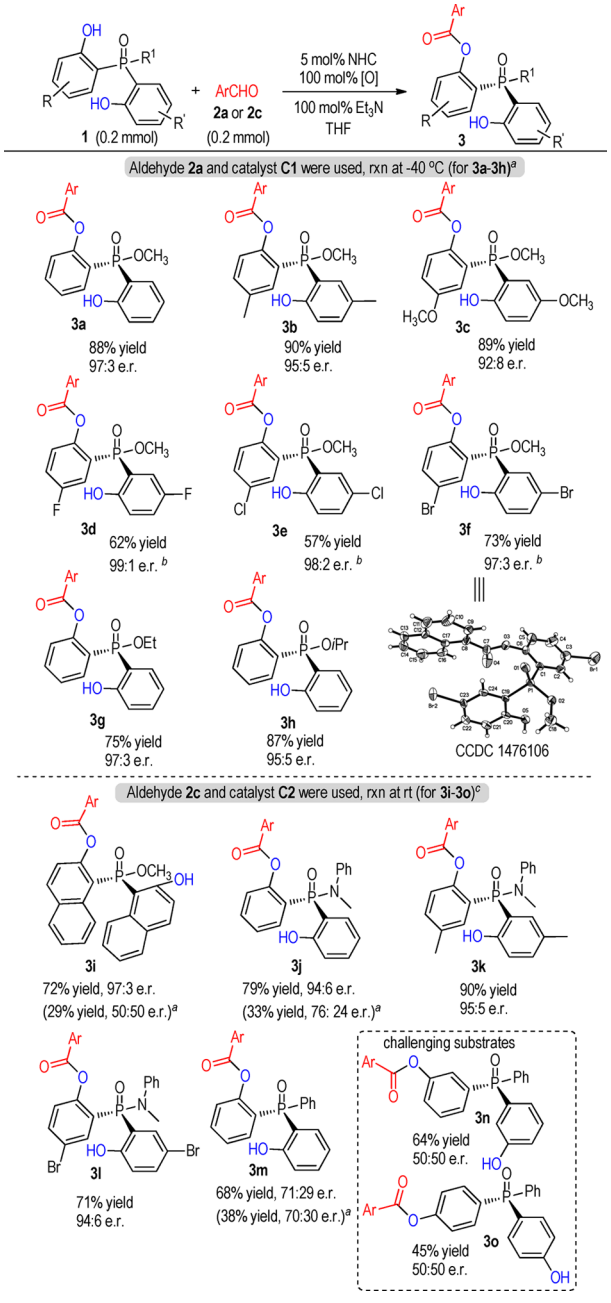


entry[a]	NHC, aldehyde	condition	yield (%)[b]	e.r.[c]
	Entries 1–7: 10 mol % NHC, Et_3N, THF			
1	**C1**, **2a**	rt, <5 min	90	87:13
2	**C1**, **2b**	rt, <5 min	65	87:13
3	**C1**, **2c**	rt, <5 min	63	89:11
4	**C2**, **2a**	rt, 5 min	87	88:12
5	**C3**, **2a**	rt, 18 h	55	80:20
6	**C1**, **2a**	−15 °C, 2 h	96	93:7
7	**C1**, **2a**	−40 °C, 2 h	87	97:3
	Entries 8–14: 5 mol % NHC, −40 °C, 24 h			
8	**C1**, **2a**	Et_3N, THF	88[d]	97:3
9	**C1**, **2a**	Cs_2CO_3, THF	47	87:13
10	**C1**, **2a**	K_2CO_3, THF	65	92:8
11	**C1**, **2a**	NaOAc, THF	70	95:5
12	**C1**, **2a**	Et_3N, DCM	69	93:7
13	**C1**, **2a**	Et_3N, Tol	94	94:6
14	**C1**, **2a**	Et_3N, CH_3CN	56	90:10

[a]Reaction conditions: phosphinate **1a** (0.1 mmol), aldehyde **2** (0.1 mmol), NHC (5–10 mol %), base (0.1 mmol), and oxidant (0.1 mmol) in 1 mL of solvent. [b]Isolated yields after SiO_2 column chromatography. [c]Enantiomeric ratio determined via chiral-phase HPLC analysis. [d]The main byproduct (diester adduct) was formed in ~5% yield.

With acceptable conditions in hand (Table 1, entry 8), we moved to examine the substrate scope (Chart 1). Electron-donating substituents such as methyl (**3b**) or methoxyl (**3c**) groups on the phenyl ring were well-tolerated. When halogen atoms were introduced on the phenyl ring of the phosphinate (**3d**, **3e**, and **3f**), esterification of both hydroxyl groups to form the undesired diester adduct became a significant problem under the standard conditions (the desired monoester product was

Chart 1. Substrate Scope



[a]Reaction conditions as in Table 1, entry 8, unless otherwise noted. [b]Slow addition of aldehyde **2a** and Et_3N in 1 mL of THF to the reaction mixture via syringe pump was employed (see the Supporting Information). The absolute configuration of the major enantiomer was assigned on the basis of the X-ray structure of **3f**. [c]Aldehyde **2c** and catalyst **C2** were used, and reactions were carried out at room temperature for 24 h.

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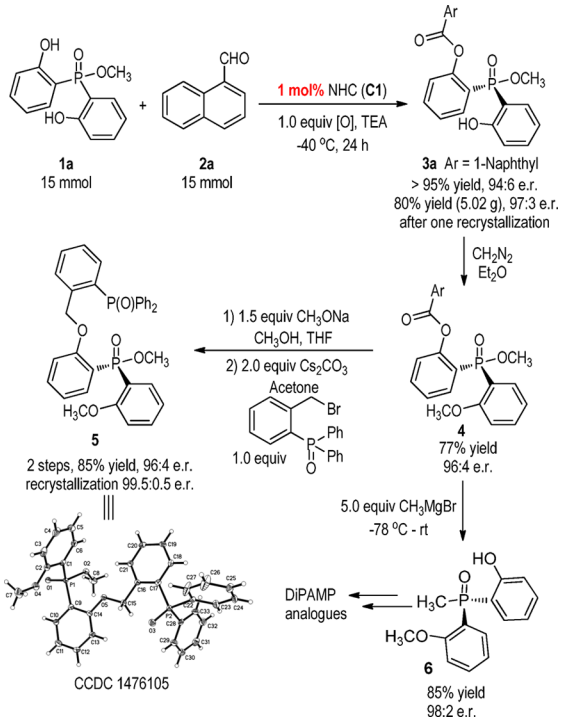
formed in about 30% yield). In these cases (**3d–f**), slow addition of the aldehyde (via syringe pump) was necessary to achieve optimal results. Changing methyl phosphinate (**1a**) to ethyl or isopropyl phosphinate (**3g** and **3h**) did not affect the reaction outcomes. Next, we found that when a sterically congested phosphinate substrate (**3i**) was used, the standard conditions (−40 °C, catalyst **C1**, aldehyde **2a**) led to product in low yield (29%) with nearly no enantiomeric excess (50:50 e.r.). This problem was addressed by running the reaction at room temperature for 24 h using NHC catalyst **C2** and sterically less-bulky aldehyde **2c**. These modified conditions worked effectively for sterically bulky phosphinate derivatives such as phosphinamides **3j**, **3k**, and **3l** and triarylphosphine oxide **3m**. Bis(3-hydroxyphenyl) (**3n**) and bis(4-hydroxyphenyl) (**3o**) phosphine oxides remained very challenging, and no enantioselectivity was obtained under the current conditions.

This approach for catalytic desymmetrization of phosphinates is amenable to large-scale synthesis (Scheme 2). In a gram-scale

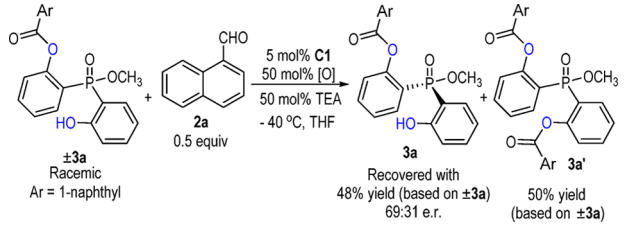
Scheme 2. Synthetic Transformations



(5 g) preparation of chiral phosphinate **3a**, the catalyst loading could be reduced to 1 mol % without affecting the reaction yield and e.r. (>95% yield and 94:6 e.r.; 80% yield and 97:3 e.r. after one recrystallization). The reaction products (e.g., **3a**) could readily undergo further transformations to functional molecules via straightforward processes. For example, the free hydroxyl group of **3a** could be methylated to give **4** in 77% yield with little erosion of the enantiomeric excess. Adduct **4** could react with a Grignard reagent (CH_3MgBr) to afford chiral phosphine oxide **6** in 85% yield with 98:2 e.r. Adduct **4** could also be converted to chiral bidentate Lewis base **5** via a simple hydrolysis of the phenolic ester followed by an alkylation reaction.

Since the monoacylation product **3a** could undergo further acylation to form the diester adduct (**3a′**), we wondered whether this second acylation is a kinetic resolution process that could lead to an improved e.r. of **3a** (Scheme 3). A racemic sample of **3a** was subjected to the catalytic conditions ((±)-**3a** and aldehyde

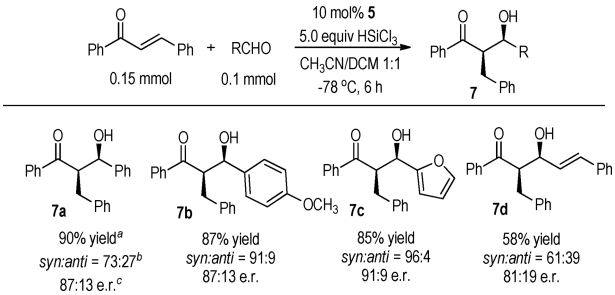
Scheme 3. Kinetic Resolution Is Not a Main Contributor to the Observed Enantioselectivity



2a in a 2:1 molar ratio; Scheme 3). Upon complete consumption of aldehyde **2a** (with the formation of diester **3a′** in 50% yield), the monoester **3a** was recovered in 48% yield with 69:31 e.r. This second acylation is indeed a kinetic resolution process. However, given the low e.r. of **3a** from this process (69:31; Scheme 3) and the good to excellent yields of the monoester products in the reactions (Chart 1), this kinetic resolution process is not a main contributor to the observed e.r. of the monoester product. The enantioselectivity of the monoester product mainly results from catalytic desymmetrization.

We further demonstrated that the newly synthesized P-stereogenic bidentate Lewis base **5** could be directly used as a catalyst in asymmetric reactions of enones and aldehydes (Chart 2). The preliminary results indicated that compound **5** could

Chart 2. Application of P-Stereogenic Phosphinate 5 as a Catalyst



[a]Isolated yield of all diastereomers combined. [b]Determined via chiral-phase HPLC. [c]Enantiomeric ratio of syn diastereomers.

promote the conjugate reduction of chalcone with trichlorosilane to form a trichlorosilyl enolate intermediate that subsequently underwent an aldol reaction with an aldehyde.[17] This tandem process catalyzed by P-stereogenic phosphinate **5** gave *β*-hydroxy ketone products **7a–d** with promising enantioselectivities.

In summary, we have developed a carbene-catalyzed desymmetrization of bisphenols bearing a remote P-stereogenic center. Through the formation of a carboxylic ester from an aldehyde and a phenol hydroxyl group under oxidative NHC catalysis, enantiomerically enriched P-stereogenic phosphinates can be prepared. The reactions can be carried out with a relatively low loading of NHC catalyst (1 mol %). Because of the high efficiency of the ester-forming reaction (the reaction went to completion in less than 5 min at rt), we expect that the NHC catalyst loading can be further reduced for large-scale synthesis. The chiral phosphinates prepared with current method can readily undergo further transformations to useful molecules such as asymmetric organic catalysts. Further studies of catalytic desymmetrization of challenging compounds and evaluation of phosphinates and their derivatives as chiral pesticide scaffolds for agricultural use are in progress.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04624.

Crystallographic data for **3f** (CIF)
Crystallographic data for **5** (CIF)
Experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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