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Axial-to-Central Chirality Transfer for Construction of Quaternary Stereocenters via Dearomatization of BINOLs

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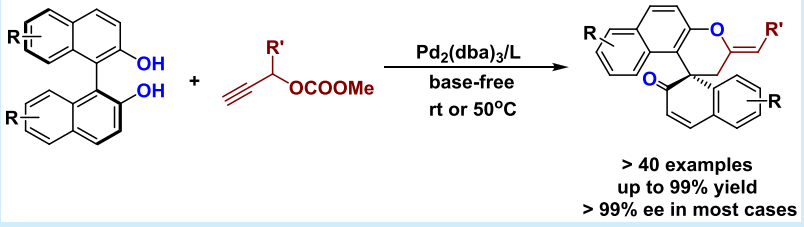
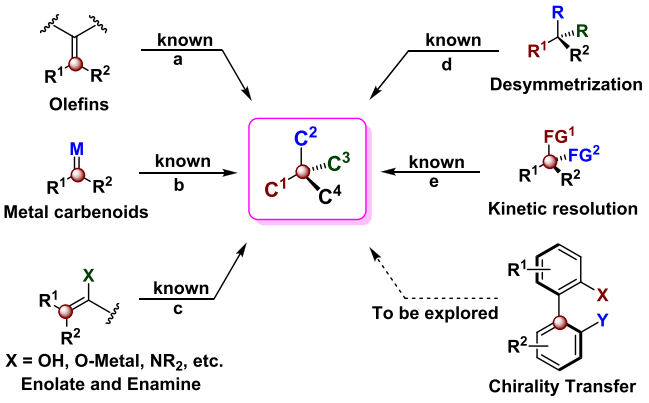
Supporting Information



ABSTRACT: All-carbon quaternary stereocenters are versatile building blocks, and their asymmetric construction has attracted much attention. Herein, we disclose an axial-to-central chirality transfer strategy for the synthesis of chiral quaternary stereocenters via dearomatization of (*S*)-BINOLs. The reaction proceeded smoothly with a wide range of propargyl carbonates to afford chiral *spiro*-compounds in high yields with excellent enantioselectivities. In addition, the strategy was extended to kinetic resolution of *rac*-BINOLs albeit with moderate **s** value.

All-carbon quaternary stereocenters are widely dispersed in natural products and pharmaceuticals.[1] Correspondingly, considerable progress has been made in developing efficient catalytic systems for their asymmetric synthesis.[2] The challenges associated with enantioselective construction of quaternary carbon stereocenters could be addressed by several known synthetic strategies. First, C−C bond formation reactions occur on a sp^2-hybridized prochiral carbon such as olefins, metal carbenoids, enolates and enamines, etc. (Scheme 1, a−c). Second, desymmetrization occurs on prochiral molecules with a prochiral quaternary carbon or kinetic resolutions occur on racemic compounds bearing quaternary stereocenters (Scheme 1, d and e).[3−5] Nevertheless, few research studies have been reported to generate all-carbon quaternary stereocenters via chirality transfer strategy (Scheme 1, to be explored).[6]

Scheme 1. Synthetic Strategies to All-Carbon Quaternary Stereocenters



Axially chiral compounds, especially atropisomeric biaryls, have received increasing attention from chemists due to their promising performance in asymmetric catalysis and drug discovery.[7] However, atropisomeric biaryls are less explored as for their memory of chirality.[8] Basically, two reasons contribute to these constraints: (a) the multistep procedures and high cost during the preparation of desired enantiopure biaryls; (b) dearomatization of biaryls[9] usually require harsh conditions with the risk of racemization. Recently, an axial-to-central chirality transfer strategy has been reported by palladium catalyzed dynamic kinetic resolution of racemic biaryls (Scheme 2, a).[10] A central-to-helical-to-axial-to-central chirality transfer of 2,2′-biphenol by a photoresponsive catalyst was also reported by the Feringa group (Scheme 2, b). Moreover, the chiral switch system was successfully applied to creation of other stereogenic elements.[11]

Inspired by these precedents, we sought to explore a new catalytic system to generate an all-carbon quaternary stereocenter via dearomatization of biaryls. Taking the efficiency of palladium-catalyzed asymmetric dearomatization reactions, we envisioned that this goal might be achieved through dearomatization of (*S*)- or (*R*)-BINOLs. We hypothesized that propargyl carbonate is the suitable partner because of its dual electrophilic property during the palladium catalysis (Scheme 2, c).[12] Herein, we present palladium-catalyzed dearomatizations of enantiopure BINOLs

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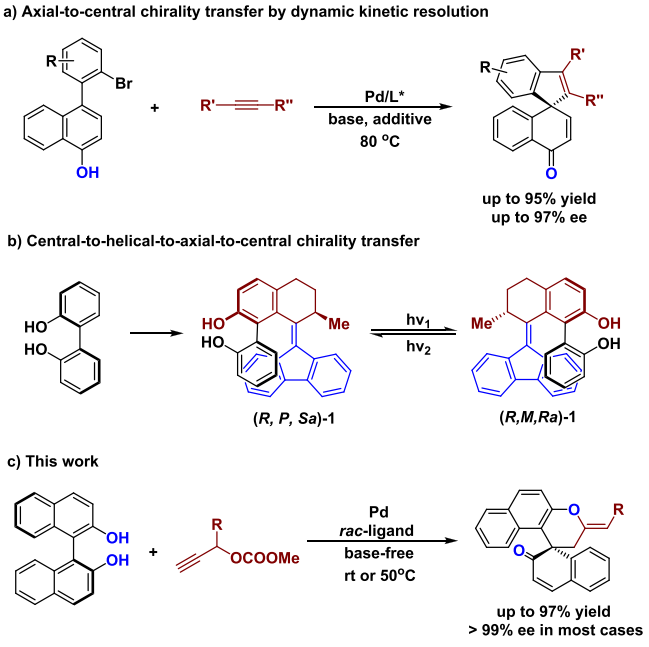
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 2. Axial-to-Central Chirality Transfer of Biaryls

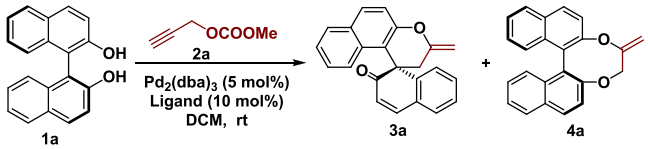


to form all-carbon quaternary stereocenters via axial-to-central chirality transfer.

We initiated our optimization by examining the reaction parameters involving solvents, catalyst ligands, and leaving groups using (*S*)-BINOL and methyl prop-2-yn-1-yl carbonate as model substrates. Screening of solvents and catalysts disclosed that DCM was the best solvent in the presence of $Pd_2(dba)_3$ (see SI for details). When (*R*)-BINAP (**L1**) was used as a ligand, more than 20:1 ratio of **3a**/**4a** was obtained albeit with moderate yield of the reaction (Table 1, entry 1). Upon switching the ligand to **L2**–**L5**, **3a** was generated in low yield with decreased ratio of **3a**/**4a** (Table 1, entries 2–5). Reaction conducted with $Pd_2(dba)_3$/**L6** afforded **3a** in an improved yield while maintaining excellent **3a**/**4a** ratio at shorter reaction time (Table 1, entry 6). Ultimately, the change in ligand such as **L7** and **L8** gave us both high yields of **3a** along with high ratio of **3a**/**4a** (Table 1, entries 7 and 8). It is noteworthy that when the reaction was performed in toluene with **L1** as a ligand, diether product **4a** was obtained exclusively (Table 1, entry 9). This observation highlights the importance of the reaction system affording the different selectivity between **3a** and **4a**. Interestingly, **4a** could undergo palladium-catalyzed isomerization to deliver dearomatizative product **3a** (see SI for details). Finally, different leaving groups were also examined but resulted in decreased yield of **3a** (Table 1, entries 10 and 11).

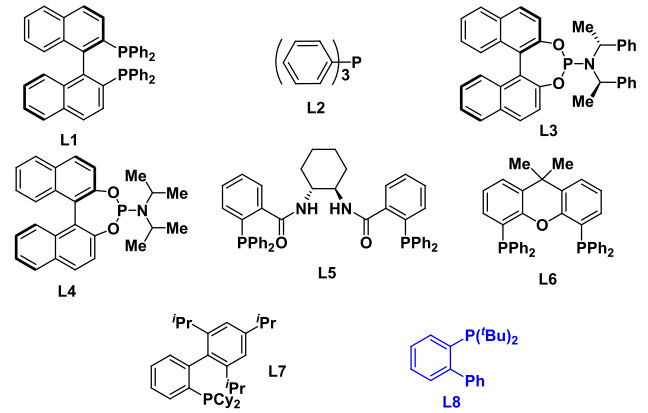
With the optimized reaction conditions in hand, we then explored the scope and limitations of the reaction (Schemes 3 and 4). Delightfully, the reaction tolerated broad substituent groups on arylpropargyl carbonates regardless of electron effect and steric hindrance of aryl group.[13] For example, **3b** was obtained in excellent yield with >99% ee.[14] Various substituted groups at the *para*-positions of arenes were well tolerated to generate products **3** in good to excellent yields (Schemes 3, **3c**–**3j**). Moreover, a range of *meta*- and *ortho*-substituted, electron-poor and electron-rich analogues gave high yields of dearomative products (**3k**–**3p**). The substrates bearing multifunctional groups at aryl group of

Table 1. Optimization of Reaction Conditions[a]



entry	ligand	*t* (h)	leaving group	yield (**3a**, %)[b]	yield (**4a**, %)[b]	**3a**/**4a**[c]
1	L1	1.0	OCOOMe	62	trace	>20:1
2	L2	2.0	OCOOMe	38	47	45:56
3	L3	2.0	OCOOMe	46	24	66:34
4	L4	2.0	OCOOMe	39	26	60:40
5	L5	20	OCOOMe	37	43	46:54
6	L6	0.5	OCOOMe	77	trace	93:7
7	L7	0.5	OCOOMe	96	trace	>20:1
8	L8	0.2	OCOOMe	99	trace	>20:1
9[d]	L1	1.0	OCOOMe	trace	45	<1:20
10	L8	10	OBoc	52	trace	>20:1
11	L8	8.0	OBz	37	trace	>20:1

[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol), $Pd_2(dba)_3$ (5 mol %), ligand (10 mol %), DCM (1.0 mL), rt. [b]Yield of isolated products. **3a** were obtained in >99% ee in all cases. [c]Determined by HPLC. [d]Toluene as solvent.



2 also underwent smoothly to generate the desired products (**3q**–**3u**). Steric hindrance was then proved to be uninfluential to this reaction since hindered arylpropargyl carbonates delivered the corresponding products in excellent yields (**3v** and **3w**). Finally, we noticed that heterocycle was compatible with the reaction system (**3x**). More importantly, in all cases, the reaction of (*S*)-BINOL with arylpropargyl carbonates delivered the desired products in high *Z*/*E* selectivity of **3**. Meanwhile, the products were obtained in absolute configuration of *S* without erosion of ee value.

To showcase the generality of this method, alkylpropargyl carbonates were synthesized and subjected to the reaction system (Scheme 4).[15] The nonfunctional linear alkylpropargyl carbonates were compatible with the reaction, leading to the products in good to excellent yields (**6a** and **6b**). The alkyl groups could be changed to branched or cyclic substituents which gave moderate to good yields, albeit with decreased *Z*/*E* ratio in some cases (**6c**–**6h**). A variety of functional alkylpropargyl carbonates were tolerated, affording the desired products with moderate to high *Z*/*E* ratios (**6i**–**6m**). Lastly, selected natural available aldehydes were used to synthesize the corresponding propargyl carbonates which could also be treated as candidates for the reaction. The products were obtained with moderate yields with high *Z*/*E* ratios (**6n**–**6p**).

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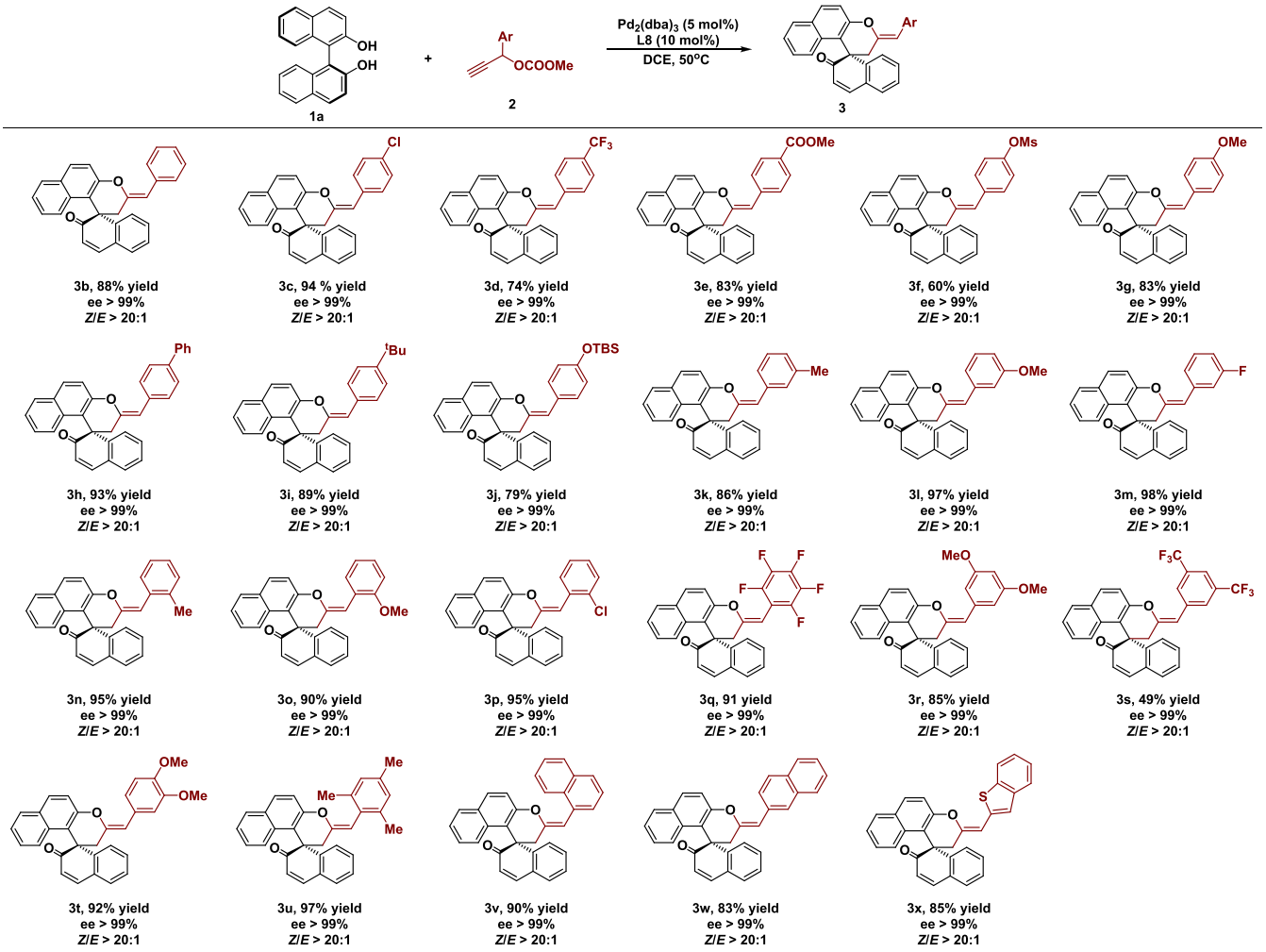
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 3. Substrate Scope of Arylpropargyl Carbonates[a]



[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol), $Pd_2(dba)_3$ (5 mol %), ligand (10 mol %), DCE (1.0 mL), 50 °C, 2 h. Yield of isolated product. % ee was determined by chiral HPLC. *Z*/*E* ratio was determined by ^1H NMR.

With respect to the BINOL derivatives, several disubstituted (*S*)-BINOLs were utilized in the reaction system. As expected, the reaction proceeded smoothly to furnish the desired products in excellent yields (Scheme 5, a). In addition, linear propargyl carbonates were also tested and found compatible to the reaction (Scheme 5, b). A late-stage functionalization was also conducted, and excellent yield was obtained without the erosion of diastereomeric ratio, highlighting the strategy to modify glycoside derivatives (Scheme 5, c).

In light of the axial-to-central chirality transfer reaction system, we investigated the kinetic resolution of *rac*-BINOL using **2a** as the substrate. After evaluating a series of solvents and ligands, **s** factor of 9.4 was obtained with 72% ee of (*S*)-BINOL and 64% ee of (*R*)-**3a** (Scheme 6, see SI for details).

To further test the practicality of this method, a gram-scale reaction of (*S*)-BINOL with **2a** was carried out (Scheme 7). To our delight, the loading of catalyst could be decreased to 1.0 mol % without the erosion of yield and enantioselectivity. Then several transformations of **3a** were carried out. For example, a Pd/C-catalyzed hydrogenation of product **3a** afforded product **11** in excellent yield with high chemoselectivity. **3a** was transformed into **12** in 94% yield under acidic conditions. The absolute configuration was confirmed by X-ray crystallographic analysis.[16]

Presumably, two competing reactions occur under the reaction conditions (Scheme 8). First, propargyl carbonates are activated by Pd and converted to highly reactive intermediate **I** with a release of CO_2.[12e] Next, the BINOL hydroxy group attacks intermediate **I** to form π-allylpalladium intermediate **II**. Intermediate **III** is formed after the generation of MeOH from intermediate **II**. On the one hand, intermediate **III** would undergo dearomatization to deliver product **3a** directly. On the other hand, the anionic oxygen would attack the π-allylpalladium to afford product **4a** first, and then product **4a** undergoes palladium-catalyzed isomerization to dearomatizative product **3a** (see SI for details).

In summary, we have described herein a novel strategy to construct all-carbon quaternary stereocenter scaffolds by axial-to-central chirality transfer. This new highly chemo- and stereoselective approach allows for the rapid construction of a new class of spirocyclic molecules bearing an all-carbon quaternary stereogenic center with high enantioselectivities (>99% ee). Moreover, limited attempts were conducted to realize the kinetic resolution of *rac*-BINOL with **s** factor of

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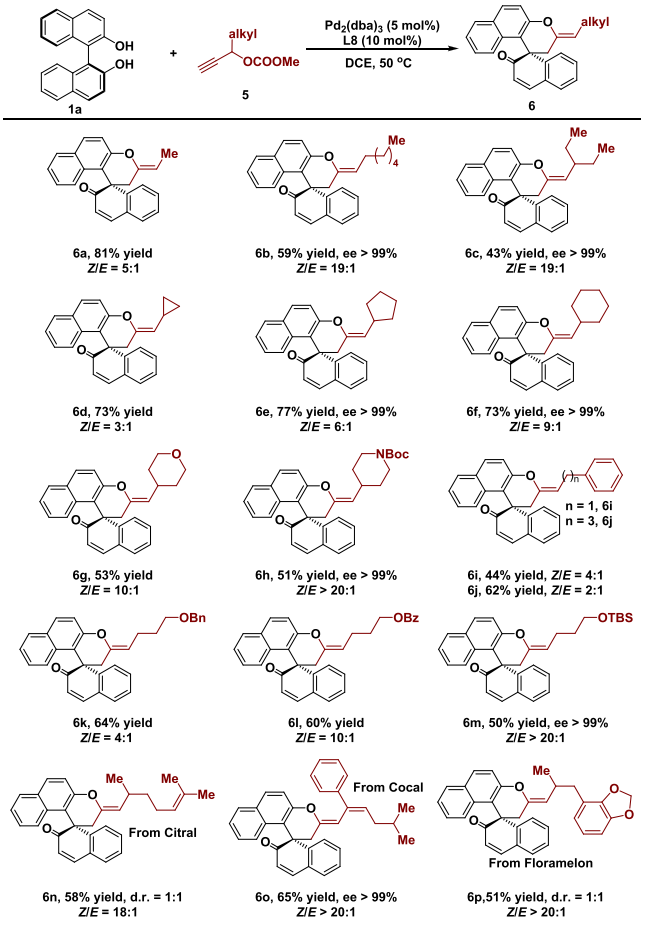
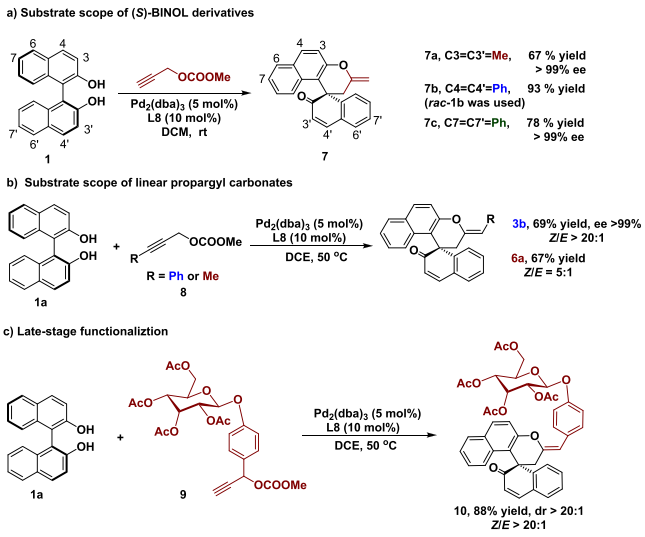
Scheme 4. Substrate Scope of Alkylpropargyl Carbonates[a]



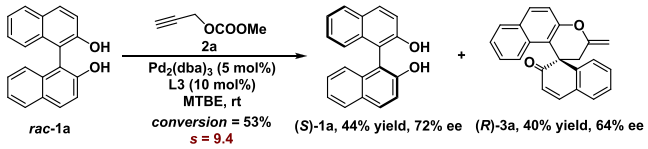
[a]Reaction conditions: **1a** (0.1 mmol), **5** (0.2 mmol), $Pd_2(dba)_3$ (5 mol %), ligand (10 mol %), DCE (1.0 mL), 50 °C, 2 h. Yield of isolated product. % ee was determined by chiral HPLC. The *Z*/*E* ratio and d.r. were determined by ^1H NMR or HPLC.

Scheme 5. Substrate Scope and Late-Stage Functionalization

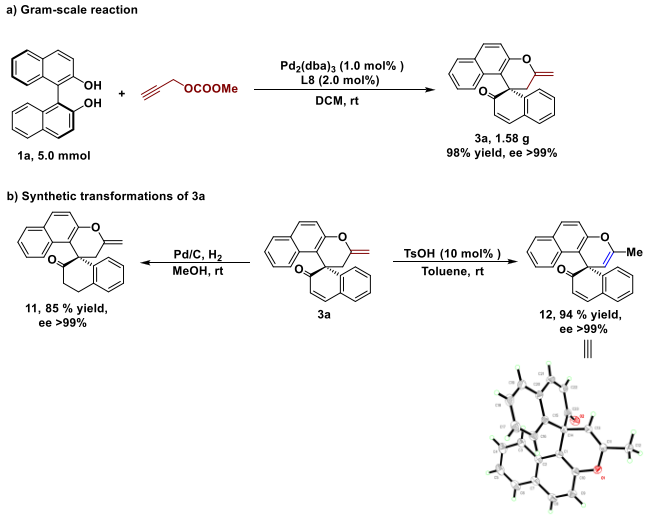


9.4. The synthetic potential of the resulting products was demonstrated with several transformations and late-stage functionalization.

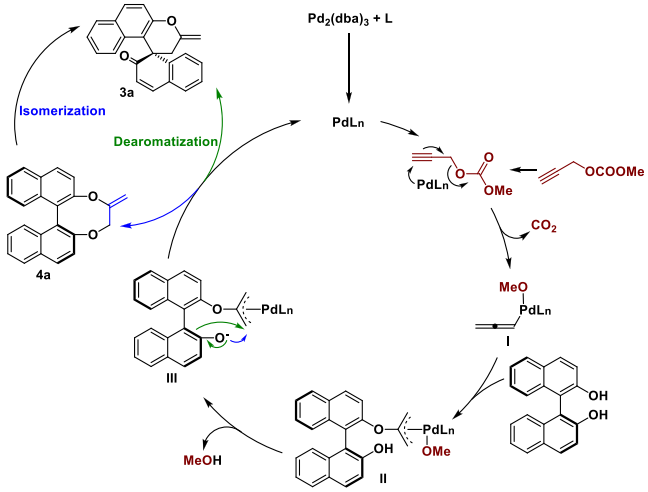
Scheme 6. Kinetic Resolution of *rac*-BINOL



Scheme 7. Gram-Scale Reaction and Synthetic Transformations



Scheme 8. Proposed Mechanism of the Reaction



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03558.

Experimental details, ^1H, ^{13}C NMR and other characterization data, single-crystal X-ray analysis (PDF)

Accession Codes

CCDC 1940195 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cam-

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Notes

The authors declare no competing financial interest.

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(13) The reaction was performed at 50 °C. DCE was used instead of DCM as solvent since low yields were obtained using substituted propargyl carbonates as substrates at room temperature.
(14) The *Z* configuration of **3b** was confirmed by NOE experiment. The absolute configuration was confirmed by transformation of **3a** to **12**. See SI for details.
(15) Due to lower *Z*/*E* ratio of products **6a**, **6d**, **6g**, and **6i**−**6l**, we could not separate the product *Z* from the *Z*/*E* mixture. The HPLC traces were omitted since the spectra were overlapped.
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