OL | Organic Letters

Letter

Cite This: Org. Lett. 2019, 21, 2894−2898

pubs.acs.org/OrgLett

Cascade Approach to Highly Functionalized Biaryls by a Nucleophilic Aromatic Substitution with Arylhydroxylamines

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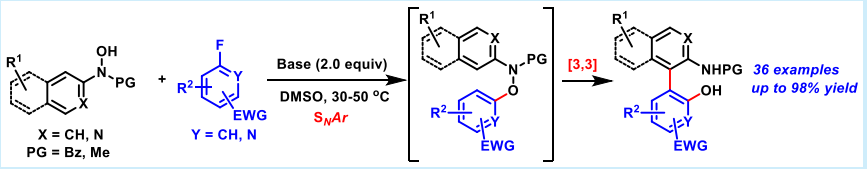
Supporting Information



ABSTRACT: A transition-metal free synthesis of highly functionalized 2-hydroxy-2′-amino-1,1′-biaryls from *N*-arylhydroxylamines has been developed. This operationally simple and readily scalable approach relies on a cascade of reactions that initially generates transient *N*,*O*-diarylhydroxylamines, via direct *O*-arylation, which then undergo rapid [3,3]-sigmatropic rearrangement and subsequent rearomatization to form NOBIN-type products. These structurally diverse functionalized biaryls are obtained under mild conditions in good to excellent isolated yields.

The biaryl motif is a privileged structure because of its presence in a large number of bioactive natural products, pharmaceuticals, catalysts, as well as organic functional materials (Figure 1).[1] In particular, axially chiral biaryl

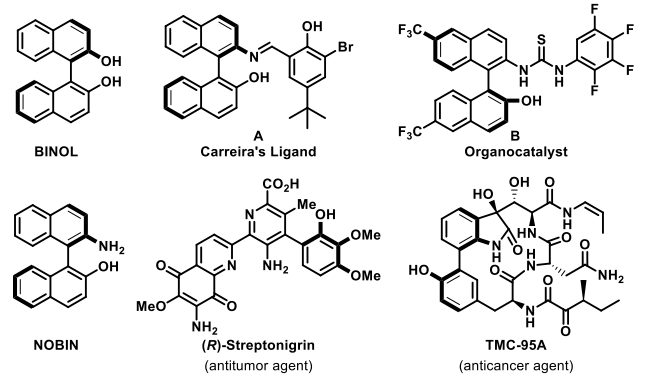


Figure 1. Representative examples of important biaryl compounds.

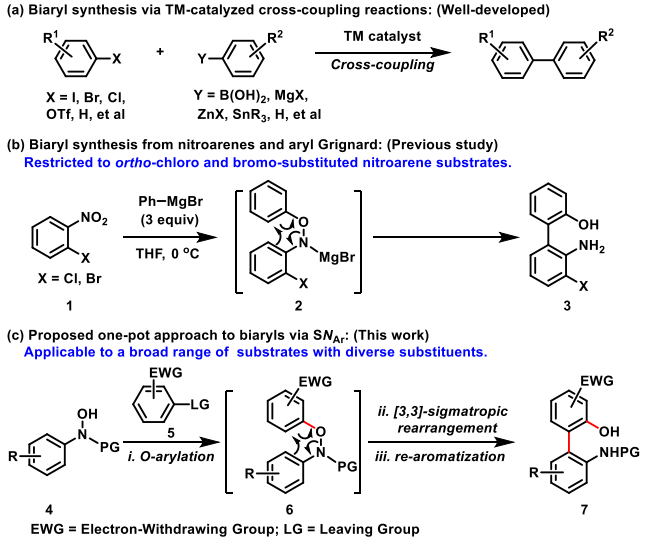
molecules, as exemplified by BINOL, BINAP, NOBIN, BINAM, and their derivatives, are of increasing importance due to their extensive applications as chiral catalysts and ligands.[1a,c,2] For instance, chiral BINAP, MAP (monodentate aminophosphine ligand), and phosphoric acids, which were derived from BINOL, have been intensively evaluated in asymmetric catalysis;[2d,3] the NOBIN-derived ligand (Figure 1, Compound **A**) has been successfully employed in a series of asymmetric aldol reactions in the presence of titanium catalysts.[4] A NOBIN derived organocatalyst **B** was found to be an efficient catalyst to promote the enantioselective [2 + 2] photocycloaddition of 4-alkenyl-substituted coumarins (Figure 1. Compound **B**).[5] In view of the importance of the biaryl motif, it is not surprising that much attention has been devoted to develop novel strategies for the construction of biaryl unit and numerous methods have been reported.[6] Among these methods, transition-metal-catalyzed cross-coupling of aryl (pseudo)halides with organometallic reagents has been well developed and widely applied in biaryl synthesis,[7] for instance, Suzuki,[8] Kumada, Negishi, and Stille reactions (Scheme 1a). During the past two decades, transition-metal-catalyzed direct dehydrogenative C−H/C−H cross-coupling[9] and oxidative homocoupling[6a,d,l] of two aromatic compounds were found to be efficient alternative approaches to biaryls from the viewpoint of atom and step economy (Scheme 1a).[10] However, the generally harsh conditions, employment of expensive metal catalysts/ligands, and scarcity of specific starting materials often limit the versatility and utility of these methods for biaryl synthesis. In addition, the heavy metal residues in the products pose a serious challenge in both the development of pharmaceuticals and novel functional materials. Thus, there is need for the continued development of alternative and more efficient synthetic strategies that allow the expedient and greener construction of structurally diverse biaryls in the absence of transition metals.

In the recent past, several transition-metal free approaches to biaryls have been reported[10,11] including: (1) SET-type (single

Received: March 15, 2019
Published: April 3, 2019

DOI: 10.1021/acs.orglett.9b00927
Org. Lett. 2019, 21, 2894−2898

Scheme 1. Synthetic Strategies to Biaryl Compounds



electron transfer) cross-coupling between aryl halides and arenes[12] or aryl metal reagents,[13] (2) Brønsted acid-catalyzed atroposelective BINAM synthesis through benzidine rearrangement,[14] (3) Brønsted acid-catalyzed arylation of 2-naphthols with quinone derivatives for the synthesis of axially chiral biaryldiols,[15] (4) a similar strategy to NOBIN analogues using 2-naphthylamines as nucleophiles instead of 2-naphthols with quinone derivatives,[16] (5) Brønsted acid-catalyzed arylation of indole derivatives for the synthesis of axially biaryls,[17] (6) regioselective strategies to biaryls from aryl sulfoxides[18] or aryliodanes[19] with phenols via a [3,3]-sigmatropic rearrangement, (7) and others,[20] a restricted range of substrates could engage among these transformations.

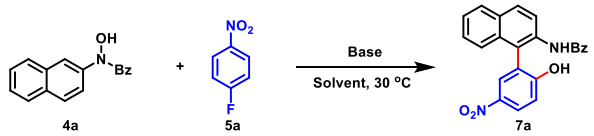
In 2013, Kurti and Ess and co-workers described the reaction of 2-halonitroarenes **1** with excess (3 equiv) arylmagnesium reagents at low temperature to generate halogenated 2-amino-2′-hydroxy-1,1′-biaryls **3** upon aqueous workup conditions.[21] The key intermediate was presumed to be an *N*,*O*-biarylhydroxylamine **2** that could undergo a facile [3,3]-sigmatropic rearrangement, followed by an intramolecular proton-transfer/rearomatization to afford the final biaryl product **3** (Scheme 1 b). The mechanistic pathway for the generation of **2** is analogous to the Bartoli indole synthesis.[22]

This approach allows the rapid preparation of multihalogen-substituted and axially chiral NOBIN-type biaryls. While powerful, there are two main limitations of this method: (a) the best results are obtained with *ortho*-halogen-substituted nitroarene substrates, in the absence of this structural motif, complex reaction mixtures are usually obtained; (b) three equivalents of the same aryl Grignard reagent is required, which limits the scope of potential substrates, especially those with base- and Grignard-sensitive functional groups such as nitriles, esters, ketones, and aldehydes. Given this background, it became clear to us that if the key intermediate *N*,*O*-biarylhydroxylamines **2** could be obtained via a different process, the structural diversity of the NOBIN-type biaryl products would be dramatically improved.

Thus, we envisioned that the direct *O*-arylation of arylhydroxylamines **4** with electron-deficient haloarenes would occur via a nucleophilic aromatic substitution (S_NAr)[23] pathway to form transient intermediate *N*,*O*-diarylhydroxylamines[24] **6**, which are expected to undergo the [3,3]-rearrangement/rearomatization cascade to afford the corresponding biaryl products **7** (Scheme 1c). This new approach utilizes *N*-protected arylhydroxylamines, which are readily prepared from the corresponding nitroarenes using well-developed protocols.[25]

Initially, we chose *N*-hydroxy-*N*-(naphthalen-2-yl)-benzamide **4a** and 4-fluoronitrobenzene **5a** as model substrates to optimize the reaction conditions. The screening of frequently used organic bases revealed that the desired biaryl product **7a** can be afforded in moderate to good yields (Table 1, entries 1−6). Various inorganic bases (NaOH, KOH, Na_2CO_3, K_2CO_3, Cs_2CO_3, K_3PO_4) were then tested (Table 1, entries 7−12), and we found that the use of KOH and K_3PO_4 resulted in excellent yields (Table 1, entries 8 and 12). The yields were slightly decreased when reducing the amount of base (Table 1, entries 13 and 14). Next, a solvent-screen was carried out and we observed that less polar solvents were not as efficient as DMSO (Table 1, entries 15−19). When 4-chloronitrobenzene was used instead of **5a** as the arylating agent, the same biaryl product **7a** was isolated in a much lower yield, presumably because of the significantly lower reactivity of the chloronitroarene compared to the corresponding fluoronitroarene in S_NAr reactions (Table 1, entry 20). The optimization studies revealed that the combination of 2.0 equiv of **5a**, 2.0 equiv of K_3PO_4, in DMSO at 30 °C were an optimal choice for this transformation (Table 1, entry 12).

Table 1. Optimization of Reaction Conditions[a]



entry	base	solvent	time	yield (%)[b]
1	Et_3N	DMSO	24 h	34
2	DIPA	DMSO	24 h	60
3	DBU	DMSO	2 h	58
4	LDA	DMSO	2 h	73
5	*t*BuONa	DMSO	2 h	58
6	*t*BuOK	DMSO	2 h	68
7	NaOH	DMSO	2 h	78
8	KOH	DMSO	2 h	92
9	Na_2CO_3	DMSO	2 h	79
10	K_2CO_3	DMSO	2 h	75
11	Cs_2CO_3	DMSO	12 h	48
12	**K_3PO_4**	**DMSO**	**24 h**	**97**
13[c]	K_3PO_4	DMSO	24 h	83
14[d]	K_3PO_4	DMSO	24 h	77
15	K_3PO_4	CH_2Cl_2	48 h	21
16	K_3PO_4	THF	48 h	34
17	K_3PO_4	acetone	48 h	29
18	K_3PO_4	CH_3CN	48 h	44
19	K_3PO_4	toluene	48 h	0
20[e]	K_3PO_4	DMSO	48 h	21

[a]Unless otherwise noted, all reactions were carried out under the following conditions: **4a** (0.2 mmol), **5a** (2.0 equiv), base (2.0 equiv), solvent (2 mL) at 30 °C. [b]Yields of isolated products. [c]1.5 equiv of **5a** was employed. [d]1.2 equiv of **5a** was employed. [e]2.0 equiv of 4-chloronitrobenzene was employed instead of **5a**. DIPA = diisopropylamine; DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene; LDA = lithium diisopropylamide.

DOI: 10.1021/acs.orglett.9b00927
Org. Lett. 2019, 21, 2894−2898

With the optimized conditions in hand, we next turned our attention to exploring the scope and limitations of this transformation. We were pleased to find that this cascade nucleophilic aromatic substitution followed by [3,3]-rearrangement and rearomatization protocol is applicable to a wide range of arylhydroxylamines and electron-deficient haloarenes, to afford the highly functionalized NOBIN-type biaryls in good to excellent yields under standard conditions (Scheme 2).

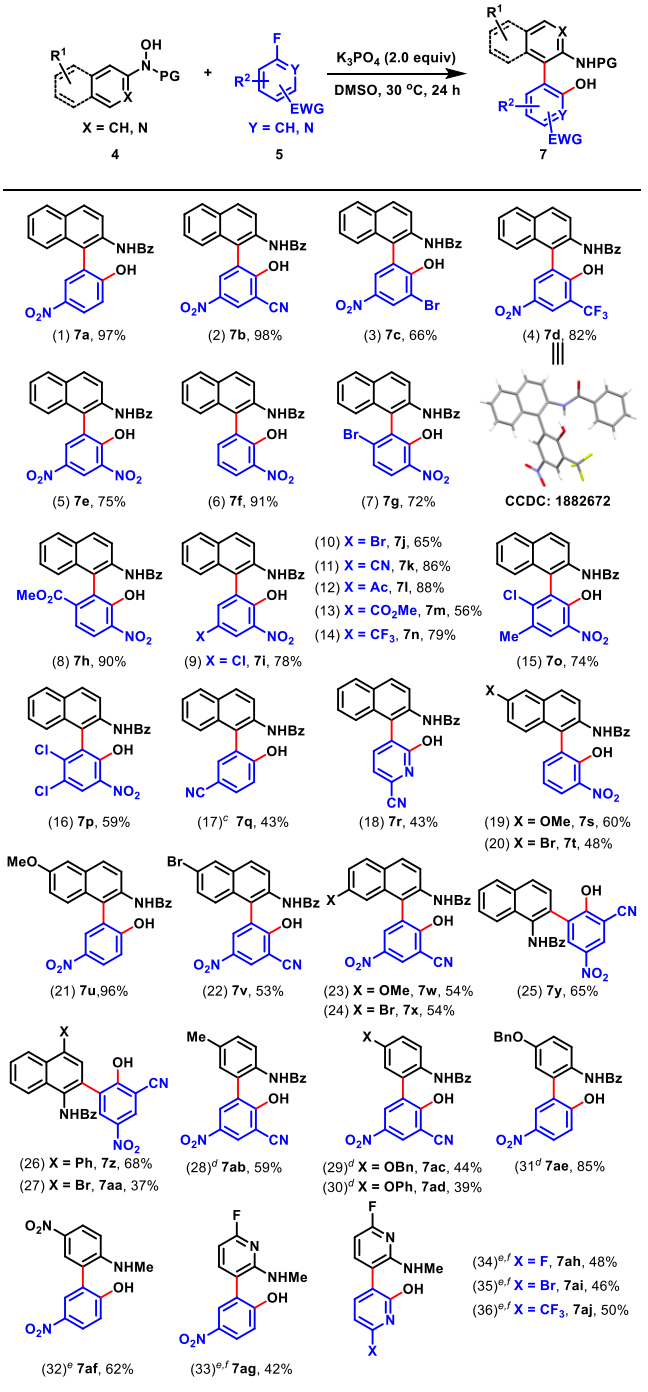
Treatment of *N*-hydroxy-*N*-(naphthalen-2-yl)benzamide **4a** and fluoronitroarenes with different electron-deficient groups, such as Cl, Br, CF_3, NO_2, CN, Ac, CO_2Me, etc., gave the corresponding biaryl products in good to excellent yields (Scheme 2, entries 1−16). However, the reactions of **4a** and fluoronitroarenes with electron-donating groups, such as Me, OMe, usually resulted in complex reaction mixtures under standard reaction conditions. Notably, the reactions of *N*-hydroxy-*N*-(naphthalen-2-yl)benzamide **4a** and 4-fluorobenzonitrile **5q** or 6-fluoropicolinonitrile **5r** also proceeded smoothly to give the desired biaryl products **7q** and **7r** in moderate yields, respectively (Scheme 2, entries 17 and 18).[26]

We next investigated the substrate scope with respect to arylhydroxylamines in this reaction using commercially available 1-fluoro-4-nitrobenzene **5a** and 2-fluoro-5-nitrobenzonitrile **5b** as representative electrophiles (Scheme 2, entries 19−33). Naphthalenyl or phenylhydroxylamines with electron-donating or electron-withdrawing groups were tolerated well and engaged in reactions with fluoronitrobenzene **5a** or **5b** to generate the corresponding biaryl products in moderate to good yields. In general, arylhydroxylamines with electron-donating groups resulted in higher yields of the biaryl products than those arylhydroxylamines with electron-withdrawing groups under the optimal reaction conditions (Scheme 2, entries 19 vs 20, 21 vs 22). An arylhydroxylamine with a strong electron-withdrawing group such as nitro group was also amenable to the optimized reaction conditions once the protecting group of the nitrogen atom was switched to an electron-donating group such as the methyl group instead of a benzoyl group (Scheme 2, entry 32). To our delight, this cascade approach could also be applied to the reactions of heteroarylhydroxylamines such as 6-fuloro-*N*-methylpyridylhydroxylamine with 4-fluoronitrobenzene **5a** to furnish the corresponding biaryl product in moderate yield (Scheme 2, entry 33). In addition, the combination of pyridylhydroxylamines with electron-deficient fluoropyridines gave the bipyridyl products in moderate yields under the optimal reaction conditions (Scheme 2, entries 34−36). The structure of the product was unambiguously confirmed by the single crystal X-ray diffraction of compound **7d** (Scheme 2, entry 4). It is noteworthy that this transformation can be readily scaled up and grams of biaryl products can be synthesized under standard conditions (Scheme 3a).

To gain some mechanistic insight, we conducted several control experiments. The reactions proceeded smoothly to generate the title products in the presence of radical-trapping reagents, for instance, TEMPO and BHT (Scheme 3b). These results revealed that a radical route can be ruled out and a S_NAr pathway is more likely.

To demonstrate the synthetic utility of this protocol, biaryl product **7f** was further elaborated as shown in Scheme 4. The nitro group of **7f** can be selectively reduced by zinc to furnish the corresponding amine **8** (Scheme 4a).[27] The deprotection of amine and the reduction of nitro group can be achieved in one-pot in the presence of hydrazine hydrate to afford biaryl diamine **9** in 61% yield (Scheme 4b).[28] The biaryl triflate **10**, which is derived from **7f** in good yield,[29] can be converted into carbazole **12** through an intramolecular amination (Scheme 4c,e).[30] The nitro group of biaryl compound **11**, which was methylated from **7f** in moderate yield,[31] could be easily converted into indole **13** through Bartoli indole synthesis (Scheme 4d,f).[32]

Scheme 2. Substrate Scope[a,b]



[a]Reaction conditions: **4** (0.3 mmol), **5** (0.6 mmol), K_3PO_4 (0.6 mmol), DMSO (3 mL) at 30 °C for 24 h. [b]Yields of isolated products. [c]2.0 equiv of *t*BuOK was employed as base. [d]Reaction was run at 50 °C for 12 h. [e]2.0 equiv of Cs_2CO_3 was employed as base. [f]Reaction was run at 50 °C for 3 h. Bz = benzoyl, Bn = benzyl.

DOI: 10.1021/acs.orglett.9b00927
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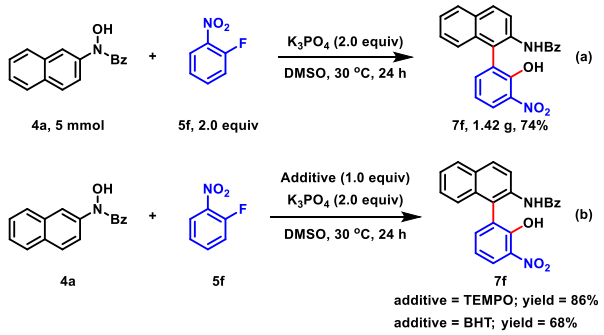
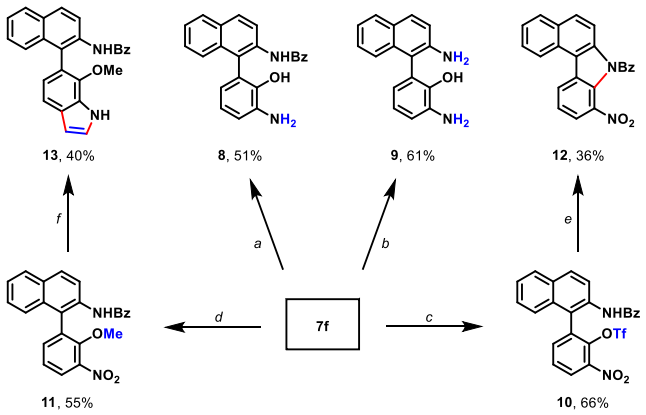
Scheme 3. Large Scale Reaction and Control Experiments[a]



[a]TEMPO = 2,2,6,6-tetramethylpiperidine 1-oxyl ; BHT = 2,6-di-tert-butyl-4-methylphenol.

Scheme 4. Synthetic Applications of Biaryl Products[1]



[1](a) Zn, HCl (2 N), EtOH, 60 °C, 1 h. (b) Hydrazine hydrate, 100 °C, 6 h. (c) Tf_2O, Et_3N, CH_2Cl_2, −40 °C, 2 h. (d) Me_2SO_4, K_2CO_3, MeCN, reflux, 2.5 h. (e) $Pd(OAc)_2$, Cs_2CO_3, toluene, reflux, 16 h. (f) Vinylmagnesium bromide, THF, −45 °C, 0.5 h.

In summary, we have developed a cascade (i.e., nucleophilic aromatic substitution followed by [3,3]-rearrangement and rearomatization) process for the synthesis of highly functionalized biaryls from readily available (hetero)arylhydroxylamines and electron-deficient haloarenes under mild conditions. This transformation is tolerant to a broad range of functional groups and provides ready access to structurally diverse biaryl products in high yields and with excellent regioselectivity. The resulting biaryl products can be transformed into brand new atropoisomeric biaryl compounds and heterocycles. Further investigation and synthetic applications are undergoing in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00927.

Detailed experimental procedures, characterization data, copies of ^1H and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 1882672 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 e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of Shandong University, the National Natural Science Foundation of China (21702122), and the Natural Science Foundation of Shandong Province (ZR2017MB002). We thank Prof. Di Sun at Shandong University for the X-ray diffraction and data analysis.

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DOI: 10.1021/acs.orglett.9b00927
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DOI: 10.1021/acs.orglett.9b00927
Org. Lett. 2019, 21, 2894−2898