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Transition-metal-free aerobic C–O bond formation *via* C–N bond cleavage†

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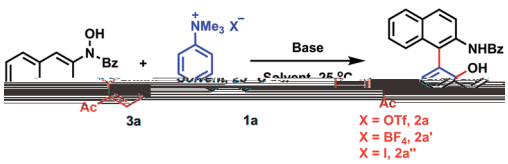
through a S_NAr pathway/C–N bond cleavage to generate a *N*,*O*-diarylhydroxylamine intermediate,[16] which could undergo a cascade [3,3]-sigmatropic rearrangement and rearomatization to form NOBIN-type (2-amino-2′-hydroxy-1,1′-binaphthyl) products (Scheme 1c).

Results and discussion

We began our investigation by conducting the reaction of *N*-hydroxy-*N*-(naphthalene-2-yl)-benzamide **1a** and 4-acetyl-*N*,*N*,*N*-trimethylbenzenaminium trifluoromethanesulfonate **2a** in the presence of various organic bases in DMF at room temperature under air. We found that the expected biaryl product **3a** was obtained in 34% yield in the presence of *t*BuOK while *t*BuONa and NaHDMS were ineffective (Table 1, entries 1–3). The screening of solvents revealed that the polar solvent DMSO was more efficient than other less polar solvents (DCE, THF, toluene and 1,4-dioxane), which is in accordance with other reported S_NAr reactions[15,16b] (Table 1, entries 4–8). When we increased the amount of aryltrimethylammonium salt **2a** from 1.2 to 1.5 equivalents, the yield of the target product was slightly decreased (Table 1, entry 9). To our delight, the corresponding biaryl product **3a** was obtained in 80% yield when we employed 2.0 equivalents of *t*BuOK rather than 1.5 equivalents (Table 1, entry 10). Other frequently used inorganic bases, including K_3PO_4, KOH, NaOH, Na_2CO_3 and K_2CO_3, were also examined and the results showed that *t*BuOK is the best option (Table 1, entries 11–15). It is worth noting that the inert atmosphere does not affect the efficiency of this cascade transformation (Table 1, entry 16). In addition, other quaternary ammonium salts **2a′** and **2a″** with different anions rather than $^-$OTf were also investigated and they were found to be less effective than **2a** (Table 1, entries 17 and 18). Finally, we found that 1.5 equivalents of aryltrimethylammonium salt **2a**, and 2.0 equivalents of *t*BuOK in DMSO at room temperature were the optimal reaction conditions (Table 1, entry 10).

Table 1 Optimization of reaction conditions[a]

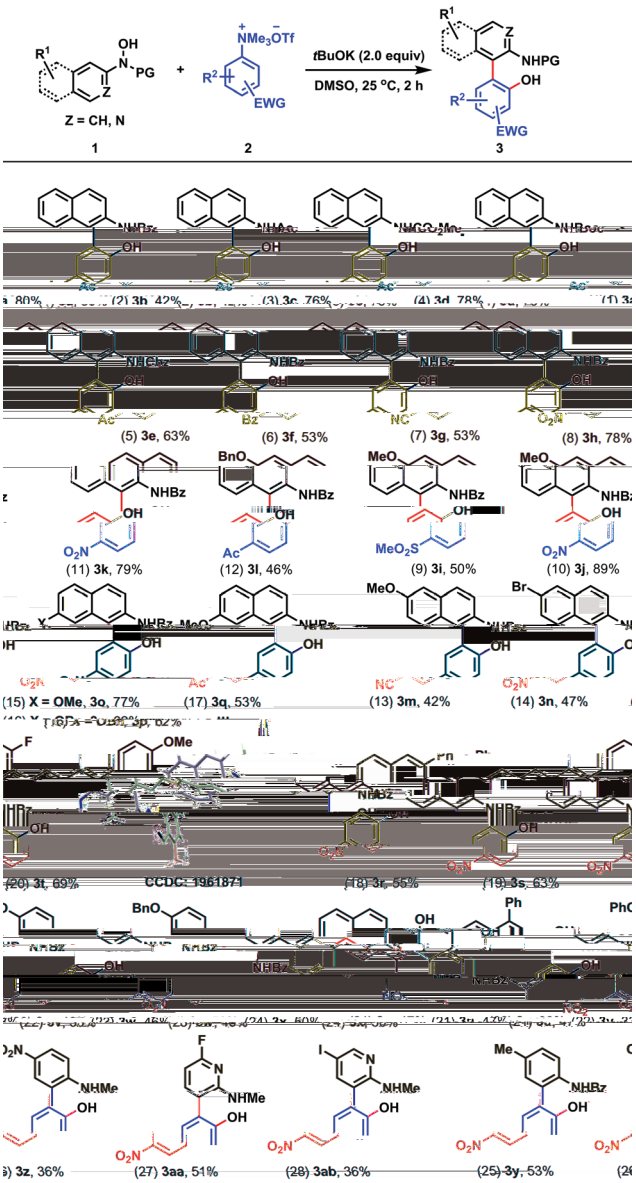


Entry	Base	Solvent	Yield[b] (%)
1	*t*BuOK	DMF	34
2	*t*BuONa	DMF	Trace
3	NaHMDS	DMF	N.P.
4	*t*BuOK	DMSO	51
5	*t*BuOK	DCE	Trace
6	*t*BuOK	THF	27
7	*t*BuOK	Toluene	26
8	*t*BuOK	1,4-Dioxane	24
9[c]	*t*BuOK	DMSO	36
10[d]	***t*BuOK**	**DMSO**	**80**
11[d]	K_3PO_4	DMSO	N.P.
12[d]	KOH	DMSO	25
13[d]	NaOH	DMSO	Trace
14[d]	Na_2CO_3	DMSO	N.P.
15[d]	K_2CO_3	DMSO	Trace
16[d,e]	*t*BuOK	DMSO	75
17[f]	*t*BuOK	DMSO	30
18[g]	*t*BuOK	DMSO	15

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.2 equiv.), base (1.5 equiv.), solvent (2 mL) under air at 25 °C for 2 h. [b] Yields of the isolated products. [c] 1.5 equivalents of **2a** were employed. [d] 1.5 equivalents of **2a** and 2.0 equivalents of base were employed. [e] Under N_2. [f] 1.5 equivalents of **2a′** and 2.0 equivalents of base were employed. [g] 1.5 equivalents of **2a″** and 2.0 equivalents of base were employed. Bz = benzoyl, Ac = acetyl, N.P. = no product.

We next investigated the scope and limitation of this reaction. In most cases, this cascade protocol proceeded smoothly to generate NOBIN analogues in moderate to good yields and excellent regioselectivities under the optimized reaction conditions (Scheme 2). We first investigated various protecting groups on the nitrogen atom of the arylhydroxylamine and the benzoyl group was found to be the best choice to afford a good yield of the expected biaryl product (Scheme 2, entries 1–5). The reaction of arylhydroxylamine **1a** and aryltrimethylammonium salts with diverse substituents on the phenyl ring revealed that strong electron-withdrawing groups, such as Bz, CN, NO_2, and SO_2Me, afforded the expected products in moderate to good yields (Scheme 2, entries 6–9). Nevertheless, the reactions of **1a** and aryltrimethylammonium salts with *para*-substituted weak electron-withdrawing groups (F, Cl, Br, CO_2Et *etc.*) or electron-donating groups (Me) or electron-neutral ammonium salts (phenyl, naphthyl) usually showed weak reactivity or complex reaction mixtures were obtained (for more details, see the ESI†).

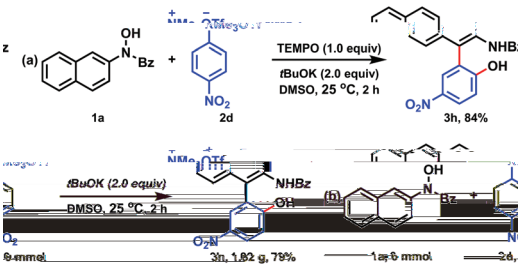
Subsequently, we turned our attention to explore the substrate scope of arylhydroxylamines in this tandem transformation (Scheme 2, entries 10–28). The variation of different substituents at the 6-, 7-, 3-position of 2-naphthalenylhydroxylamines was then evaluated. Both electron-donating groups and electron-withdrawing groups were well tolerated in this tandem reaction to afford the corresponding NOBIN-type biaryl products in moderate to good yields (Scheme 2, entries 10–20). 1-Naphthalenylhydroxylamines were amenable to this transformation as well (Scheme 2, entries 21 and 22). To our delight, this cascade protocol was also suitable to substituted phenylhydroxylamines albeit with relatively lower yields than the corresponding naphthylhydroxylamines under standard reaction conditions (Scheme 2, entries 23–26). Notably, phenylhydroxylamine with a strong electron-withdrawing group (NO_2) is applicable to this transformation when the protecting group was switched to an electron-donating group (Me) (Scheme 2, entry 26). We delightfully found that heteroarylhydroxylamines, such as *N*-(6-fluoropyridin-2-yl)-*N*-methylhydroxylamine **1t** and *N*-(5-iodopyridin-2-yl)-*N*-methylhydroxylamine **1u**, can also be introduced into this cascade reaction to afford heterobiaryl products in moderate yields (Scheme 2, entries 27 and 28). The structure of **3q** was explicitly confirmed by the single crystal X-ray diffraction study (Scheme 2, entry 17).



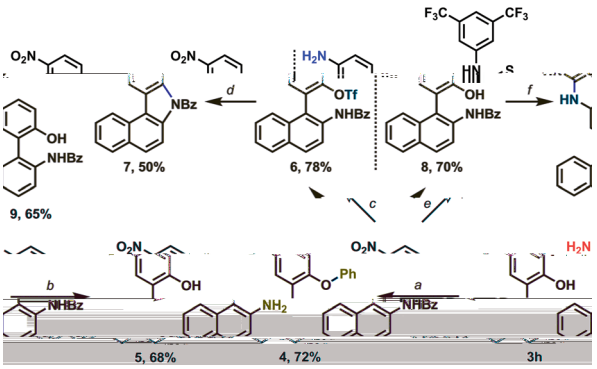
Scheme 2 Substrate scope. Reaction conditions: **1** (0.3 mmol), **2** (0.45 mmol), *t*BuOK (0.6 mmol), DMSO (3 mL) under air at 25 °C for 2 hours. Yields of isolated products are given. Bn = benzyl.

In order to gain deeper insight into the mechanism of this cascade reaction, a control experiment was conducted in the presence of a radical scavenger, such as TEMPO, and it was found that the reaction still proceeded smoothly to generate the corresponding biary product in 84% yield (Scheme 3a). This result suggested that a radical pathway can be excluded and a nucleophilic aromatic substitution mechanism is more likely in this cascade reaction.

Finally, the usefulness and practicality of this cascade protocol were exemplified by scale-up synthesis and the synthetic transformations of these biaryl products (Schemes 3b and 4). This method is synthetically practical since it is readily scalable and grams of the NOBIN-type product can be prepared in good yield



Scheme 3 Large scale reaction and control experiments. TEMPO = 2,2,6,6-Tetramethylpiperidine 1-oxyl.



Scheme 4 Synthetic transformations of biaryl products. (a) $Cu(OAc)_2$, phenylboronic acid, Et_3N, 30 °C, 16 h. (b) Hydrazine hydrate, 150 °C, 8 h. (c) Tf_2O, pyridine, CH_2Cl_2, 0 °C, 12 h. (d) $Pd(OAc)_2$, Cs_2CO_3, toluene, reflux, 16 h. (e) $SnCl_2$, iPrOH, 100 °C, 8 h. (f) Isothiocyanate, THF, 30 °C, 12 h.

under mild conditions (Scheme 3b). As shown in Scheme 4, the biaryl product **3h** can be further *O*-arylated with arylboronic acid through a Chan–Lam reaction (Scheme 4a).[17] Biaryl diamine **5** can be generated in good yield *via* the simultaneous reduction of the nitro group and deprotection of amine in one pot while hydrazine hydrate was employed (Scheme 4b).[18] Palladium-catalyzed intramolecular aminantion/cyclization of compound **6**, which is prepared from **3h** in good yield,[19] affords benzocarbazole **7** in moderate yield (Scheme 4c and d).[20] Reduction of **3h** with $SnCl_2$ gave arylaniline **8** in 70% yield,[21] which can be further converted into the corresponding thiourea in 65% yield in the presence of isothiocyanate (Scheme 4e and f).[22]

Conclusions

In conclusion, we have presented a general, operationally simple, cascade S_NAr-[3,3] rearrangement–rearomatization approach to achieve the efficient construction of NOBIN-type biaryls, which are difficult to synthesize by employing conventional methods, from (hetero)arylhydroxylamines and aryltrimethylammonium salts in the presence of a base under mild conditions. A broad range of functional groups can be well tolerated and this method provides an efficient strategy to produce structurally diverse NOBIN analogues. The transform-

ation of biaryl products presented great potential to synthesize novel atropoisomeric biaryl compounds and heterocycles. Further extension of the potential applications of biaryl products and studies of related transformation are currently undergoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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