

Metal-Free One-Pot Synthesis of (Tetrahydro)Quinolines through Three-Component Assembly of Arenediazonium Salts, Nitriles, and Styrenes

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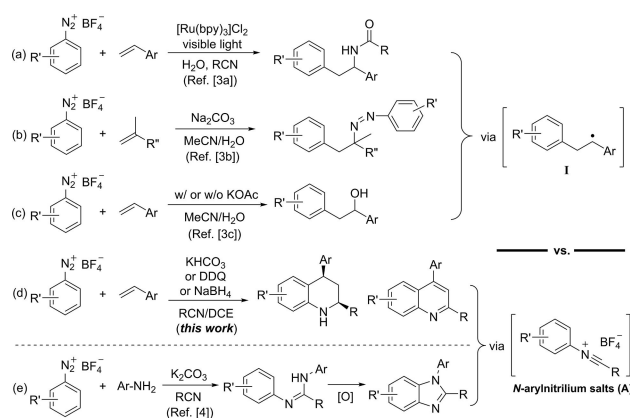
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Abstract: A highly efficient and convenient metal-free, one-pot synthesis of diversely substituted (tetrahydro)quinolines has been achieved through a three-component assembly reaction of arenediazonium salts, nitriles, and styrenes. In sharp contrast to the prior works with the same reagent blend, the formation of *N*-arylnitrilium intermediates from arenediazonium salts and nitriles was followed by reaction with styrenes, leading to 3,4-dihydroquinolinium salts as a common intermediate. These could be further transformed to quinolines and tetrahydroquinolines depending on the reaction conditions. The advantages of this protocol include its simplicity, metal-free and mild conditions, readily available starting materials, and good functional group tolerance.

Keywords: multicomponent reactions; nitrogen heterocycles; one-pot reaction; quinolines; tetrahydroquinolines

Arenediazonium salts can be easily prepared from inexpensive and readily available anilines, and thus they have been used as useful and versatile precursors in a variety of organic transformations.^[1] For instance, they have been employed as the most convenient and cost-effective aryl radical source for intermolecular alkene functionalization, namely, the Meerwein arylation reaction.^[2] König's group reported the intermolecular amino-arylation of styrenes through a photo-redox-catalyzed Meerwein arylation under the Ritter reaction conditions (Scheme 1a).^[3a] In addition, Heinrich and co-workers demonstrated a base- or thermally-induced amino- and hydroxy-arylation of alkenes (Scheme 1b–c).^[3b–c]

Recently, our group reported a highly effective one-pot, three-component reaction to construct a wide



Scheme 1. (a)–(d) Various outcomes of the reaction of arenediazonium salts with alkenes in nitrile solvents and (e) our previous work.

range of *N*-arylbenzimidazoles through in situ generation of *N,N'*-diarylamidines from arenediazonium salts, nitriles, and free anilines (Scheme 1e).^[4] This reaction proceeded via the formation of *N*-arylnitrilium intermediates (**A**)^[5] by an initial attack of nitriles to arenediazonium salts, followed by the addition of anilines as a second nucleophile to afford *N,N'*-diarylamidines. Therefore, we reasoned that other second nucleophiles (instead of anilines) could be used to construct other heterocyclic scaffolds with this strategy. Given the low cost, diversity, and wide availability of styrenes, we were interested in utilizing these reagents to develop a new one-pot, three-component reaction for the facile formation of quinoline derivatives (Scheme 1d).

Quinolines and tetrahydroquinolines are an important class of *N*-heterocycles due to their wide range of biological activities and multiple applications. Consequently, a diverse range of synthetic methods have been developed to synthesize these materials over the

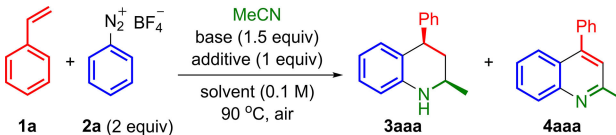
years.^[6] However, most of the known methods have several drawbacks, such as the use of expensive transition metal catalysts and reagents, troublesome operation, harsh reaction conditions, and low yields, limiting their practical utility. Thus, the development of more efficient and economical synthetic strategies is highly desirable. The realization of our proposed method would provide another new and potentially powerful route for the expedient synthesis of a diverse range of quinoline derivatives using simple, inexpensive, readily available chemical feedstocks (anilines, nitriles, styrenes) via a metal-free one-pot reaction. Considering the previously reported, related reaction systems with the same reagent blend as shown in Scheme 1a–c,^[3] however, the challenge with this strategy would be the competing reactions of styrenes with the arenediazonium salts, which lead to undesired products via intermediate **I**.

Herein, we report a highly effective and convenient one-pot synthesis of diversely substituted quinoline derivatives under metal-free conditions (Scheme 1d). In sharp contrast to the related prior works (Scheme 1a–c),^[3] this new protocol involves the initial formation of *N*-arylnitrilium intermediates from arenediazonium salts and nitriles. Then the following reaction with styrenes leads to 3,4-dihydroquinolinium salts as a common intermediate, which can be further selectively transformed to quinolines and/or tetrahydroquinolines depending on the reaction conditions.^[7]

In light of our recent success in the one-pot synthesis of *N*-arylbenzimidazoles in the presence of a base such as K₂CO₃,^[4] we began our studies on the proposed reaction using styrene (**1a**) and phenyldiazonium salt (**2a**) as the test substrates in the presence of K₂CO₃ in MeCN solvent (Table 1, entry 1). Much to our delight, both tetrahydroquinoline **3aaa** and quinoline **4aaa** were obtained in low yields, while the absence of base gave no desired products (Table 1, entries 1 vs. 2). A variety of other inorganic and organic bases were examined (Table S1), and KHCO₃ appeared preferable. After scrupulous examination of the reaction parameters (Tables S2–S3), we could find an optimal condition as entry 5 in Table 1. In stark contrast to the previous works under similar reaction conditions using base promoters (Scheme 1b–c),^[3b–c] these findings suggest that arenediazonium salts indeed initially react with nitriles more favorably rather than styrenes under our reaction conditions, leading to *N*-arylnitrilium salts (**A**).

A series of control experiments were performed to gain insight into the mechanism of this reaction. We speculated that this reaction might proceed through a disproportionation reaction of the initially generated 3,4-dihydroquinolines to quinolines and tetrahydroquinolines.^[8] Gratifyingly, 3,4-dihydroquinolinium salt **5aaa** was successfully obtained in the absence of KHCO₃ under otherwise identical conditions (Scheme

Table 1. Optimization studies.

						
Entry	Base	Additive	Solvent	<i>t</i> [h]	3aaa [%] ^[a]	4aaa [%] ^[a]
1 ^[b]	–	–	MeCN	2	–	–
2 ^[b–c]	K ₂ CO ₃	–	MeCN	2	18 (16)	20 (20)
3 ^[b]	KHCO ₃	–	MeCN	3	25	23
4	KHCO ₃	–	MeCN	3	(19)	(75)
5	KHCO₃	–	MeCN/DCE 12	(15)	(73)	
6	KHCO ₃	DDQ	MeCN/DCE 12	–		(85)
7	KHCO ₃	NaBH ₄	MeCN/DCE 5	18 (17)	4	
8^[d]	–	DDQ	MeCN/DCE 12	–	(84)	
9^[d]	–	NaBH₄	MeCN/DCE 4	(80)	–	

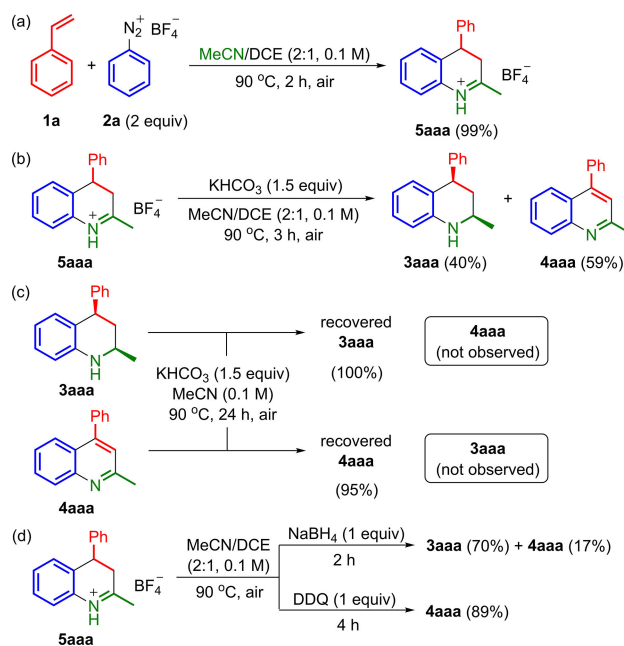
^[a] Yields were determined by ¹H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields.

^[b] Using 1 equiv. **2a**.

^[c] Using 1 equiv. base.

^[d] Additives were added after 2 h.

me **2a**). Subjecting **5aaa** to the standard reaction conditions (i.e., entry 5 in Table 1) led to the formation of **3aaa** and **4aaa** in 40% and 59% yields,



Scheme 2.

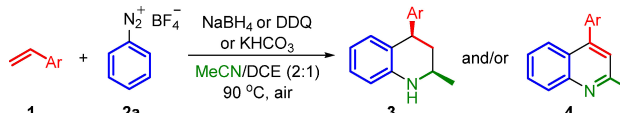
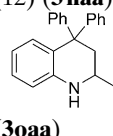
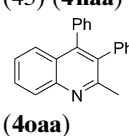
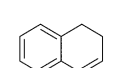
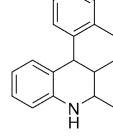
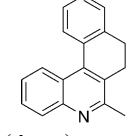
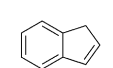
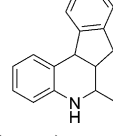
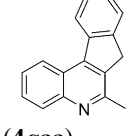
respectively (Scheme 2b). However, no reaction occurred with both **3aaa** and **4aaa** (Scheme 2c). These results suggest that **5aaa** generated from the three-component assembly reaction of **1a**, **2a**, and MeCN is a likely intermediate in this process. The reason why the formation of **3aaa** was in much lower yield than **4aaa** under the standard conditions in the one-pot reaction (Table 1, entry 5) remains unclear at this point.

Although the combined yield of **3aaa** and **4aaa** is high under the reaction conditions as shown in entry 5 in Table 1, selective formation of either **3aaa** or **4aaa** in high yields would be preferable. Therefore, to investigate both the oxidation and reduction of 3,4-dihydroquinolinium salts prior to the disproportionation, various oxidants and reductants were introduced to the reaction mixture as an additive (Table S4).^[8a-c,9] To our delight, the use of DDQ as an oxidant gave the desired **4aaa** in good yields without the formation of **3aaa**, regardless of the presence of KHCO₃ (Table 1, entries 6 and 8). In contrast, the absence of KHCO₃ was beneficial to the selective and high-yielding formation of **3aaa** in the presence of NaBH₄ as a reductant (Table 1, entries 7 vs. 9). On the other hand, reaction of **5aaa** in the presence of NaBH₄ or DDQ indeed afforded **3aaa** and/or **4aaa** (Scheme 2d), which further supports that 3,4-dihydroquinolinium salt **5aaa** is a likely intermediate in this process.

Having determined the optimized conditions for the synthesis of either quinolines (Table 1, entry 8) or tetrahydroquinolines (entry 9) or both (entry 5), we set out to explore the scope of this one-pot process. First, we examined the reaction of various styrenes (**1**) with phenyldiazonium salt (**2a**) and MeCN (Table 2). A wide range of styrenes underwent a one-pot three-component reaction to afford the corresponding tetrahydroquinolines (**3**) and quinolines (**4**) in moderate to good yields irrespective of their electronic properties and the position of their substituents. However, strongly electron-deficient styrenes resulted in no (Ar = C₆F₅, not shown) or low conversion (entry 13), which suggests the involvement of a cationic intermediate (*vide infra*, **B** in Scheme 4). Both naphthyl and heteroaryl moieties could also be incorporated as a substituent at the alkene terminus (entries 8 and 14). Internal and 1,1-disubstituted terminal alkenes proved to be suitable substrates (entries 15–17), while the latter afforded **4oaa** via 1,2-phenyl migration (entry 15). It should be noted that the formation of fused-tetracyclic **4paa–4qaa** could be advantageous compared to other annulation methods using alkynes.^[6,7b-c]

In general, a KHCO₃-promoted reaction afforded both tetrahydroquinolines (**3**) in low yields and quinolines (**4**) in moderate yields, while NaBH₄- and DDQ-mediated reactions led to the selective formation of **3** and **4**, respectively, in much higher yields. It should be

Table 2. Substrate scope: Alkenes.^[a]

			
Entry	Ar	with NaBH ₄ 3 [%]	with DDQ 4 [%]
1	Ph	80, 85 ^[b] (15) (3aaa)	84, 73 ^[b] (73) (4aaa)
2	4-AcOC ₆ H ₄	52 (14) (3baa)	58 (52) (4baa)
3	3-MeOC ₆ H ₄	73 (22) (3caa)	81 (63) (4caa)
4	4-MeC ₆ H ₄	71 (15) (3daa)	62 (69) (4daa)
5	3-MeC ₆ H ₄	72 (11) (3eaa)	89 (71) (4eaa)
6	2-MeC ₆ H ₄	72 (29) (3faa)	73 (64) (4faa)
7	4-PhC ₆ H ₄	48 (14) (3gaa)	66 (65) (4gaa)
8	1-naphthyl	67 (21) (3haa)	86 (63) (4haa)
9	3-BrC ₆ H ₄	82 (21) (3iaa)	83 (53) (4iaa)
10	4-ClC ₆ H ₄	77 (14) (3jaa)	88 (69) (4jaa)
11	3-CF ₃ C ₆ H ₄	62 (3) (3kaa)	76 (46) (4kaa)
12	4-CNC ₆ H ₄	49 (11) (3laa)	65 (40) (4laa)
13	4-NO ₂ C ₆ H ₄	23 (21) (3maa)	36 (28) (4maa)
14	3-thienyl	56 (12) (3naa)	49 (43) (4naa)
15		 81 (3oaa)	 26 (4oaa)
16		 56 (3paa)	 53 (4paa)
17		 56 (3qaa)	 67 (4qaa)

^[a] Reaction conditions (with KHCO₃): **1** (1 equiv.), **2a** (2 equiv.), KHCO₃ (1.5 equiv.) in MeCN/DCE (2:1, 0.1 M) at 90 °C under air. (with NaBH₄ or DDQ): **1** (1 equiv.), **2a** (2 equiv.) in MeCN/DCE (2:1, 0.1 M) at 90 °C for 2 h under air. Subsequently, NaBH₄ or DDQ (1 equiv.) was added to the reaction mixture and stirred at 90 °C under air. Isolated yields of **3** (using NaBH₄) and **4** (using DDQ) are given. Values in parentheses indicate isolated yields of **3** and **4** from the reactions using KHCO₃.

^[b] Using 1.0 mL of styrene **1a**.

noted that any byproducts derived from the Meerwein-type reaction of aryl radical with styrene (via **I** in Scheme 1) were not observed in this protocol at all. Both terminal and internal aryl-substituted alkenes resulted in the regioselective formation of 4-aryl-substituted **3** and **4**, which further supports an electrophilic process via a benzylic carbocation intermediate (**B** in Scheme 4). This process can tolerate various

functional groups such as halogen, nitro, ester, and cyano groups. In addition, the reactions on a gram scale gave comparable yields (entry 1), thus showing the synthetic potential of this method. Furthermore, from a practical perspective, this newly developed method offers user-friendly access to a diverse array of valuable (tetrahydro)quinolines from the readily available, simple starting materials under air without the need for anhydrous solvents and an inert atmosphere. Comparable or even better product yields were obtained using reagent grade, undistilled solvents under an ambient atmosphere, thereby eliminating the need for precautionary measures to rigorously exclude air and moisture from the reaction mixture. This protocol could be a potentially powerful and effective alternative to the methods known for the synthesis of quinoline derivatives.

Next, we proceeded to explore the scope of arenediazonium salts (**2**) (Table 3). A variety of substituted arenediazonium salts were well tolerated regardless of the position of their substituents, leading to the assembly of diversely substituted **3** and **4**.

Table 3. Reaction of various arenediazonium salts and styrenes.^[a]

Reaction scheme: **1** + **2** $\xrightarrow[\text{MeCN/DCE (2:1), 90 °C, air}]{\text{NaBH}_4 \text{ or DDQ}}$ **3** and/or **4**

Yields and ratios for various arenediazonium salts (**2**):

- R = Me:** 84% (**3aba**), 80% (**4aba**)
- R = Ph:** 67% (**3aca**), 79% (**4aca**)
- R = Cl:** 51% (**3ada**), 52% (**4ada**)
- R = I:** - [b], 87% (**4aea**)
- R = 3-MeC₆H₄:** 81% (**3eba**), 79% (**4eba**)
- R = 4-ClC₆H₄:** 71% (**3bba**), 78% (**4bba**)
- R = Ph:** - [c], 71% (**4ica**)
- R = 3-BrC₆H₄:** 60% (**3ica**)
- Ar = Ph:** 73%^[c] (**3aha**), 88% (**4aha**)
- Ar = 2-MeC₆H₄:** 73%^[c] (**3fha**), 80% (**4fha**)
- Ar = Ph:** 72% (**3aia**), 77% (**4aia**)
- Ar = 3-MeOC₆H₄:** 67% (**3cia**), 49% (**4cia**)
- Ar = 3-MeOC₆H₄:** 83% (**4aja**), 69% (**4aja'**)

Other yields and ratios:

- 3afa** (85%)^[c], **4afa** (90%)
- 3aga** (75%), **3aga'** (71:29)
- 4aga** (80%), **4aga'** (73:27)

^[a] Reaction conditions: **1** (1 equiv.), **2** (2 equiv.) in MeCN/DCE (2:1, 0.1 M) at 90 °C for 2 h under air. Subsequently, NaBH₄ or DDQ (1 equiv.) was added to the reaction mixture and stirred at 90 °C under air. Isolated yields of **3** (using NaBH₄) and **4** (using DDQ) are given.

^[b] **3aaa** was obtained in 66% yield.

^[c] In the reaction using NaBH₄, **4afa**, **4aha**, and **4fha** were also obtained at 5%, 13%, and 15%, respectively.

Subsequently, we investigated this reaction with various nitriles (Table 4). In the case of the DDQ-mediated reaction, various 1°, 2°, and 3° alkyl nitriles as well as aryl nitriles were all well tolerated to afford the desired quinolines **4** in moderate to good yields. It should be noted that the reaction with PhCN gave quinazoline **6bh** as a byproduct as a result of the sequential reaction of **2b** and two equivalents of PhCN,^[10] along with the desired quinoline **4ebh** (entry 7). In contrast, both steric and electronic properties of nitriles seemed to have a great influence on the NaBH₄-mediated reaction. Only simple 1° and 2° alkyl nitriles could afford **3** in good yields along with a small amount of **4** (entries 1–2 and 4), while the reaction with sterically bulky alkyl and aryl nitriles failed to afford the desired **3**, leading to only the corresponding **4** instead (entries 5–7).

Table 4. Substrate scope: Nitriles.^[a]

Reaction scheme: **1e** + **2b** $\xrightarrow[\text{RCN/DCE (2:1), 90 °C, air}]{\text{NaBH}_4 \text{ or DDQ}}$ **3** and/or **4**

Yields of **3** and **4** for various nitriles (**2b**):

Entry	R	with NaBH ₄ 3 [%]	with DDQ 4 [%]
1	Et	78 (3ebb) ^[b]	83 (4ebb)
2	<i>n</i> Pr	60 (3ebc) ^[b]	82 (4ebc)
3	CH ₂ CH ₂ OMe	-	49 (4ebd)
4	<i>i</i> Pr	61 (3ebe) ^[b]	80 (4ebe)
5	<i>c</i> Hex	- ^[c]	62 (4ebf)
6	<i>t</i> Bu	- ^[c]	56 (4ebg)
7	Ph	trace ^[d]	47 (4ebh) ^[e]

^[a] Reaction conditions: **1** (1 equiv.), **2b** (2 equiv.) in RCN/DCE (2:1, 0.1 M) at 90 °C for 2 h under air. Subsequently, NaBH₄ or DDQ (1 equiv.) was added to the reaction mixture and stirred at 90 °C under air. Isolated yields of **3** (using NaBH₄) and **4** (using DDQ) are given.

^[b] **4ebb**, **4ebc**, and **4ebe** were also obtained in 13%, 19%, and 20%, respectively.

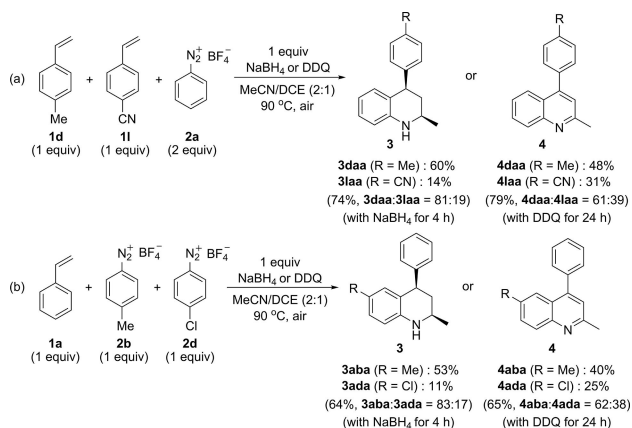
^[c] Only **4ebf** and **4ebg** were obtained in 59% and 55%, respectively.

^[d] **4ebh** and **6bh** were obtained in 21% and 40% yield, respectively.

^[e] **6bh** was also obtained in 51% yield.

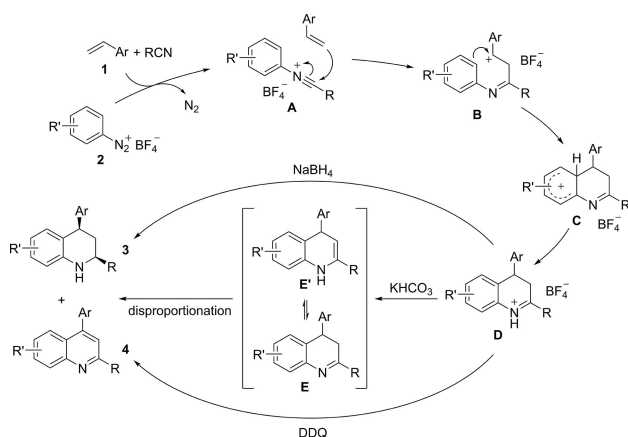
To gain further mechanistic insight into this reaction, we performed competition experiments (Scheme 3). This study revealed an electronic dependence, in which the electron-rich styrenes and arenediazonium salts reacted faster than their electron-deficient counterparts. The former (Scheme 3a) is consistent with the observed electronic dependence in Table 2, where substituents that cannot stabilize positive charge resulted in relatively low yields. The latter (Scheme 3b) may be attributed to the involvement of

aryl cations generated from arenediazonium salts along with the loss of N_2 .



Scheme 3. Competition experiments.

Based on our experimental findings, we proposed a plausible mechanism outlined in Scheme 4. *N*-Arylnitrilium salt **A** generated from an arenediazonium salt and a nitrile undergoes an electrophilic addition to a styrene to afford a benzylic carbocation intermediate **B**. Subsequent electrophilic cyclization of **B** to produce **C** followed by the deprotonation gives a 3,4-dihydroquinolinium salt **D**. Under basic conditions, a disproportionation reaction of the free bases, 3,4-dihydroquinoline **E** and its enamine tautomer **E'**, leads to the formation of tetrahydroquinoline **3** and quinoline **4**. On the other hand, **D** reacts with either NaBH₄ or DDQ to afford either **3** or **4**, respectively.



Scheme 4. Proposed mechanism.

In summary, we developed a highly efficient and convenient one-pot reaction for the three-component assembly of diversely substituted (tetrahydro)quinolines under metal-free mild conditions. The formation

of 3,4-dihydroquinolinium salts as a common intermediate for the synthesis of quinolines and tetrahydroquinolines is involved as a result of the reaction between styrenes and *N*-arylnitrilium intermediates generated from arenediazonium salts and nitriles. To the best of our knowledge, this is the first example of the synthesis of both quinolines and tetrahydroquinolines using arenediazonium salts as a C₂ building block for a benzene ring fused to a pyridine/piperidine ring, offering new access to *N*-heterocycles from arenediazonium salts. This facile and simple procedure employs readily available starting materials and has significantly improved the efficiency and practicality of the synthesis of quinoline derivatives.

Experimental Section

General Procedure for the KHCO₃-Promoted Reaction. To a solution of **1** (0.12–0.15 mmol, 1.0 equiv.) and KHCO₃ (0.18–0.23 mmol, 1.5 equiv.) in MeCN/CICH₂CH₂Cl (1.2–1.5 mL, 2:1, 0.1 M) was added **2** (0.24–0.30 mmol, 2.0 equiv.). After being stirred at 90 °C for the reported time under air (closed flask), the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding products **3** and **4**.

General Procedure for the NaBH₄-Mediated Reaction. To a solution of **1** (0.12–0.15 mmol, 1.0 equiv.) in R'CN/CICH₂CH₂Cl (1.2–1.5 mL, 2:1, 0.1 M) was added **2** (0.24–0.30 mmol, 2.0 equiv.). After being stirred at 90 °C for 2 h under air (closed flask), the reaction mixture was cooled to 25 °C and then NaBH₄ (0.12–0.15 mmol, 1.0 equiv.) was added. After being stirred at 90 °C for additional 1–22 h (the reported time = initial 2 h + additional time after adding NaBH₄) under air (closed flask), the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding product **3** (In some cases, along with a small amount of **4**, or only **4** instead of **3** was obtained. See Tables S6–S8 for details).

General Procedure for the DDQ-Mediated Reaction. To a solution of **1** (0.12–0.15 mmol, 1.0 equiv.) in R'CN/CICH₂CH₂Cl (1.2–1.5 mL, 2:1, 0.1 M) was added **2** (0.24–0.30 mmol, 2.0 equiv.). After being stirred at 90 °C for 2 h under air (closed flask), the reaction mixture was cooled to 25 °C and then DDQ (0.12–0.15 mmol, 1.0 equiv.) was added. After being stirred at 90 °C for additional 10–22 h (the reported time = initial 2 h + additional time after adding DDQ) under air (closed flask), the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding product **4**.

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