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Unexpected Decarboxylation-Triggered *o*-Hydroxyl-Controlled Redox Condensation of Phenylglycines with 2-Nitrophenols in Aqueous Media

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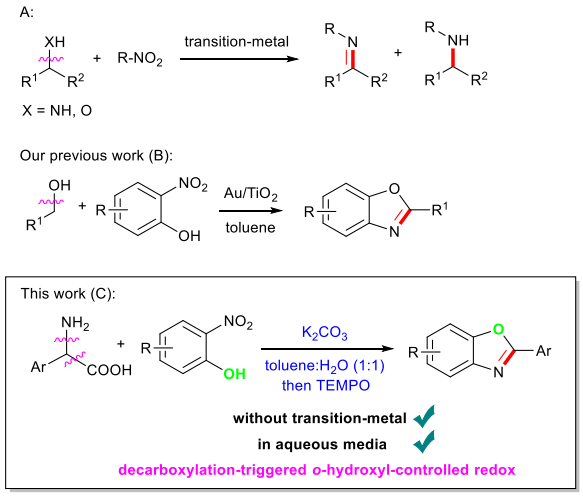
Abstract. A decarboxylation-triggered and *o*-hydroxyl-controlled hydrogen-transfer strategy for the one-pot synthesis of benzoxazoles from readily available amino acids and 2-nitrophenols is reported. On the basis of this autoredox reaction, the C-N bond can be efficiently constructed to afford the desired products in moderate to good yields under transition-metal-free conditions in aqueous media.

Keywords: Amino acids; Benzoxazoles; Decarboxylation; Hydrogen-transfer; C-N bond formation

Nitrogen-containing compounds are extraordinarily valuable building blocks that represent significant biological activity in both naturally produced and synthetically derived pharmaceuticals.[1] Consequently, efforts directed toward exploring new and improved approaches for C-N bond formation have attracted much interest. After the pioneering work of silica gel-catalyzed *N*-alkylation derived from alcohols and anilines reported by Brown et al.,[2] the hydrogen-transfer (borrowing hydrogen) strategy reveals an efficient and practical protocol for C-N bond construction by use of alcohols (or amines) as hydrogen donor and the source of electrophile and amines as nucleophile in the past several decades.[3] On the other hand, hydrogenation of nitro-compounds is deemed as an essential transformation in fields of chemistry and chemical engineering because the reduction products of amines thus obtained are one of the most fundamental nitrogen-containing chemical materials.[4] In this context, the hydrogen-transfer strategy directly employing inexpensive and readily available nitroaromatic compounds instead of amines as a hydrogen acceptor and the source of nucleophile has been extensively developed for C-N bond formation (Scheme 1A).[5] Despite many remarkable advantages achieved in these C-N bond formation approaches, transition-metal catalysts are usually necessary for hydrogenation of nitro compounds by active species of transition-metal–hydride (MH_2). The development of mild and transition-metal-free hydrogen-transfer catalytic systems for C-N bond formation has rarely been reported and is therefore highly desired.[6]



Scheme 1. Hydrogen-transfer strategy for C-N bond formation.

Benzoxazoles are versatile reagents because of their comprehensive application in synthetic, medicinal, biological and material chemistry.[7] Usually, these compounds can be obtained by traditional condensation of various carboxylic acid derivatives with 2-aminophenols,[8] transition-metal-catalyzed intramolecular coupling of anilides or o-haloanilides,[9] oxidative cyclization of alcohols or amines with 2-aminophenols,[10] hydrogen-transfer redox cyclization of 2-nitrophenols with alcohols or amines,[11] and other alternative processes.[12]

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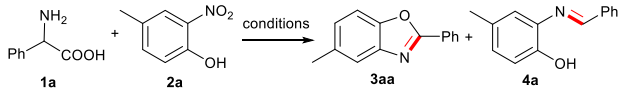
Recently, we developed an Au/TiO_2-catalyzed efficient protocol for the selective synthesis of benzoxazoles via a hydrogen-transfer strategy (Scheme 1B).[11b] As the logical extension for benzoxazole synthesis, and inspired by our continuous research on green synthesis in water,[13] we herein describe a novel and practical hydrogen-transfer strategy for the synthesis benzoxazoles starting from readily available amino acids and 2-nitrophenols (Scheme 1C). With the assistance of potassium carbonate, autoredox condensation of amino acids with 2-nitrophenols could be achieved via a decarboxylation-triggered hydrogen-transfer strategy without a transition-metal catalyst. Further experiments indicated that the hydroxy in 2-nitrophenols played a key role in nitro group reduction.

Table 1. Optimization of reaction conditions.[a]



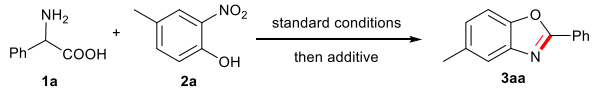
1a 2a 3aa 4a

Entry	Catalyst	Base	Solvent	T	Yield[b] [%] 3aa	4a
1	Au/TiO_2	–	toluene:H_2O (1:1)	140	n.d.	trace
2	Au/TiO_2	Cs_2CO_3	toluene:H_2O (1:1)	140	trace	56
3	Au/ZrO_2	Cs_2CO_3	toluene:H_2O (1:1)	140	trace	55
4	Au/C	Cs_2CO_3	toluene:H_2O (1:1)	140	5	52
5	Au/CeO_2	Cs_2CO_3	toluene:H_2O (1:1)	140	trace	53
6	Pd/C	Cs_2CO_3	toluene:H_2O (1:1)	140	7	51
7	Pt/C	Cs_2CO_3	toluene:H_2O (1:1)	140	5	51
8	Ni/ZrO_2	Cs_2CO_3	toluene:H_2O (1:1)	140	trace	49
9	–	Cs_2CO_3	toluene:H_2O (1:1)	140	trace	45
10	–	K_2CO_3	toluene:H_2O (1:1)	140	trace	49
11	–	Na_2CO_3	toluene:H_2O (1:1)	140	trace	44
12	–	KOH	toluene:H_2O (1:1)	140	trace	38
13	–	*t*-BuOK	toluene:H_2O (1:1)	140	trace	47
14	–	K_2CO_3	toluene:H_2O (1:1)	120	trace	< 5
15	–	K_2CO_3	toluene:H_2O (1:1)	150	trace	68
16[c]	–	K_2CO_3	toluene:H_2O (1:1)	150	trace	75
17[d]	–	K_2CO_3	toluene:H_2O (1:1)	150	trace	87
18[d]	–	K_2CO_3	toluene	150	n.d.	11
19[d]	–	K_2CO_3	acetone	150	n.d.	20
20[d]	–	K_2CO_3	1,4-dioxane	150	trace	78
21[d]	–	K_2CO_3	DMSO	150	trace	46
22[d]	–	K_2CO_3	DMF	150	32	n.d.
23[d]	–	K_2CO_3	H_2O	150	trace	80

[a] Reaction conditions: **1a** (0.75 mmol), **2a** (0.25 mmol), catalyst (5 mol%), base (0.25 mmol), solvent (2.0 ml), 20 h, argon atmosphere. [b] NMR yield. [c] Base (0.50 mmol). [d] Base (0.75 mmol).

To optimize reaction conditions, 2-amino-2-phenylacetic acid (**1a**) and 4-methyl-2-nitrophenol (**2a**) were employed as the model substrates in a mixed solvent of toluene and water (1:1) at 140 °C (Table 1). In the beginning, we chose Au/TiO_2 as the catalyst since heterogeneous gold catalysts have exhibited excellent catalytic performance for hydrogen-transfer reactions. No desired product was obtained without a base (Entry 1). However, the reaction could proceed smoothly to afford the intermediate **4a** in 56% yield in the presence of Cs_2CO_3 (Entry 2). Additionally, other heterogeneous nano-catalysts could also provide **4a** in moderate yields, with an interesting finding that the final product **3aa** was obtained in very low yields when activated carbon served as the support (Entries 3-8). To our surprise, this reaction was still performed readily in the absence of nano-catalysts (Entry 9). Encouraged by this result, different bases were then investigated (Entries 10-13). When K_2CO_3 was used as the base, **4a** was achieved in 49% yield (Entry 10). Further studies showed that high reaction temperature and excess bases were necessary (Entries 14-17). Subsequently, various solvents were tested (Entries 18-23). The reaction in acetone, toluene, and DMSO represented low activity. It is interesting that **3aa** could be selectively achieved in 32% yield when the reaction was carried out in DMF (Entry 22). After the solvent screening, the mixed solvent of toluene and water (1:1) was confirmed as the optimal solvent (Entry 17).

Table 2. Screening of the additive for the synthesis of **3aa**.[a]



1a 2a 3aa

Entry	Additive	Yield[b] [%]
1[c]	activated carbon	14
2	I_2	17
3	SnO	19
4	$Cu(OAc)_2 \cdot H_2O$	49
5	$FeCl_3$	trace
6	$Co(OAc)_2$	45
7	CuCl	17
8	CuI	trace
9	TEMPO	63
10	4-OH-TEMPO	56
11	4-oxo-TEMPO	43
12	4-acetamido-TEMPO	45
13	NHPI	27

[a] Reaction conditions: **1a** (0.75 mmol), **2a** (0.25 mmol), K_2CO_3 (0.75 mmol), 2.0 ml of toluene and H_2O (1:1), 150 °C, 20 h, argon atmosphere; then added additive (20 mol%), 8 h, air atmosphere. [b] Isolated yield. [c] Activated carbon (20 mg).

With the optimized conditions in hand, we then studied the impact of additives on cyclization for the synthesis of **3aa** (Table 2). The obtained result in Table 1 indicated that activated carbon might promote **3aa** synthesis due to its acidity. Therefore, we firstly employed activated carbon as the additive (Entry 1). As a result, **3aa** was obtained in 14% yield.

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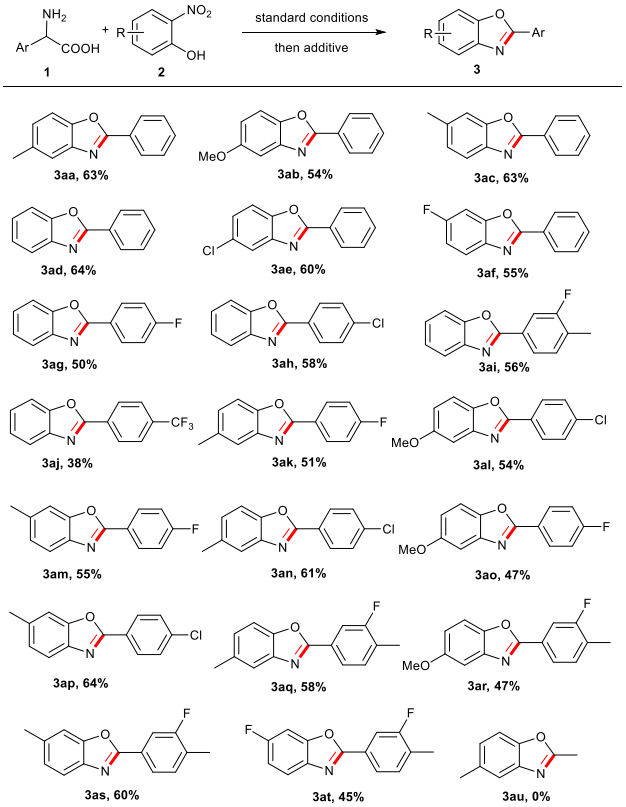
Interestingly, molecular iodine could also give the product (Entry 2). Subsequently, different metal salts used as Lewis acids were investigated, and a moderate yield of 49% was received in the presence of $Cu(OAc)_2 \cdot H_2O$ (Entries 3-8). A catalyst of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added, with a satisfactory result that **3aa** could be obtained in 63% yield via oxidative cyclization (Entry 9). Relatively low yields were achieved when other additives such as 4-OH-TEMPO, 4-oxo-TEMPO, 4-acetamido-TEMPO, and NHPI (2-hydroxyisoindoline-1,3-dione) were added (Entries 10-13).

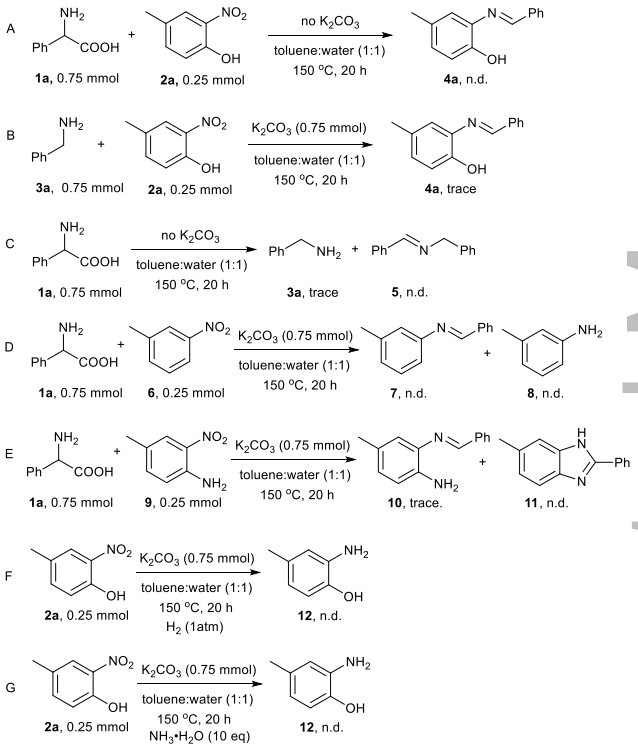
After confirming TEMPO as the additive, the tandem reaction scope of amino acids with 2-nitrophenols was extended as shown in Table 3. Different 2-nitrophenols bearing groups of methyl, methoxyl, chloro and fluoro on the benzene ring smoothly reacted with 2-amino-2-phenylacetic acid to afford the desired product **3aa**-**3af** in moderate to good yields. Reactions of substituted 2-amino-2-phenylacetic acids with 2-nitrophenol could also give the corresponding products **3ag**-**3ai** in acceptable yields. When trifluoromethyl appeared in amino acid, the low yield of 38% of the product was provided (**3aj**). Various substituted amino acids and 2-nitrophenols were employed as starting materials, successfully affording the desired products **3ak**-**3at**. It is noteworthy that many fluorine-containing compounds that construct a crucial skeleton in active drug molecules were also achieved. Unfortunately, the product **3au** was not observed when alanine was employed as the substrate.

Table 3. Scope of substrates.[a],[b]



[a] Reaction conditions: **1** (0.75 mmol), **2** (0.25 mmol), K_2CO_3 (0.75 mmol), 2.0 ml of toluene and H_2O (1:1), 150 °C, 20 h, argon atmosphere; then TEMPO (20 mol%), 8 h, air atmosphere. [b] Isolated yield.

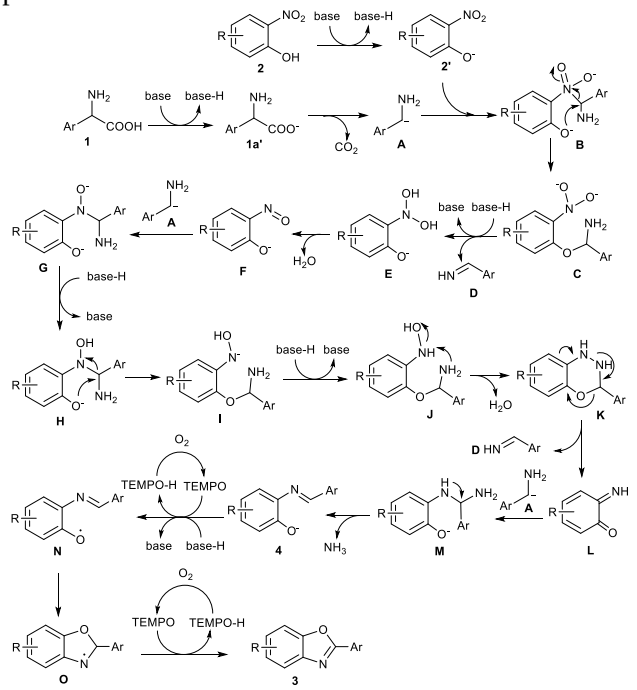
We then performed some control experiments for getting an insight into the base-promoted hydrogen-transfer process (Scheme 2). The reaction of **1a** with **2a** could not give **4a** in the absence of K_2CO_3, which indicated that K_2CO_3 was crucial for this reaction (Scheme 2A). **4a** was not obtained in the reaction of **3a** with **2a** under standard conditions, which implied that **3a** was not the reaction intermediate (Scheme 2B). Further experiments revealed that K_2CO_3 was crucial for decarboxylation of **1a** (Scheme 2C). When the substrate **2a** was replaced by **6** and **9**, transfer-hydrogenation of the nitro group could not take place, which revealed that *o*-hydroxy in 2-nitrophenol was necessary (Scheme 2D and 2E). In addition, reduction of **2a** could not be achieved when H_2 and NH_3 were added to the reaction (Scheme 2F and 2G). This meant that hydrogenation of nitro group did not involve reductants of H_2 and NH_3.[5e,11c]



Scheme 2. Control experiments.

Based on the obtained results in control experiments, a possible mechanism of this hydrogen-transfer is proposed as shown in Scheme 3. Firstly, base-promoted decarboxylation of **1** generates carbanion **A**. Then the nucleophilic attack of **A** to **2'** affords **B**, and **B** is readily converted to **C** by oxyanion-induced isomerization. Reduction product of nitroso compound **F** was obtained from **C** through the liberation of imine **D**, followed by dehydration. A second nucleophilic attack of **A** to **F** gives **G**, which can be transformed into **L**[14] via proton-transfer,

dehydration, and liberation of imine D respectively. Subsequently, Michael-type addition of **A** to **L** constructs **M**, which affords intermediate **4** with the release of NH_3. **4** can afford the final product 3 under the catalysis of TEMPO via a single-electron transfer process.[15]



Scheme 3. Proposed mechanism for decarboxylation-triggered *o*-hydroxyl-controlled redox condensation of phenylglycines with 2-nitrophenols.

In summary, we have established a simple and efficient protocol for C-N bond formation via a base-promoted *o*-hydroxyl-controlled hydrogen-transfer strategy. The reaction can be easily carried out by employing easily accessible and stable amino acids and 2-nitrophenols as the substrates. In terms of this auto-catalytic system, decarboxylation and deamination of amino acids and reduction of 2-nitrophenols can be smoothly achieved under transition-metal-free conditions in aqueous media. The present method offers facile and accurate access to various benzoxazoles with the assistance of TEMPO. Detailed mechanistic studies of the reaction are in progress within our laboratories.

Experimental Section

Typical reaction procedure for the synthesis of 3aa in the reaction of 1a with 2a

The solvent of toluene and water (v:v = 1:1, 2.0 ml) was added to the mixture of **1a** (0.75 mmol), **2a** (0.25 mmol), and K_2CO_3 (0.75 mmol) in a Schlenk tube. The tube was vacuumized and degassed with argon for three times. The mixture was stirred at 150 °C for 20 h. When the mixture was cooled down to room temperature, TEMPO (0.05 mmol) was added. Then, the aforementioned mixture continued to be stirred at 150 °C for 8 h. When the reaction was finished, the mixture was acidized with saturated ammonium chloride and extracted by ethyl acetate. The obtained organic phase was evaporated to remove the solvent and the resulting residue was further purified by flash column chromatography using petroleum ether/ethyl acetate (v:v = 50:1) to afford the product **3aa**.

5-Methyl-2-phenylbenzo[d]oxazole (3aa). ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.26-8.23 (m, 2H), 7.56 (s, 1H), 7.54-7.50 (m, 3H), 7.45 (d, J = 8.4 Hz, 1H), 7.17-7.15 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 163.2, 149.1, 142.4, 134.5, 131.5, 129.0, 127.7, 127.4, 126.4, 120.0, 110.1, 21.7; HRMS (ESI-TOF): calcd. for $C_{14}H_{12}NO$ $[M+H]^+$ 210.0919, found 210.0924.

Acknowledgments

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Unexpected Decarboxylation-Triggered *o*-Hydroxyl-Controlled Redox Condensation of Phenylglycines with 2-Nitrophenols in Aqueous Media

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