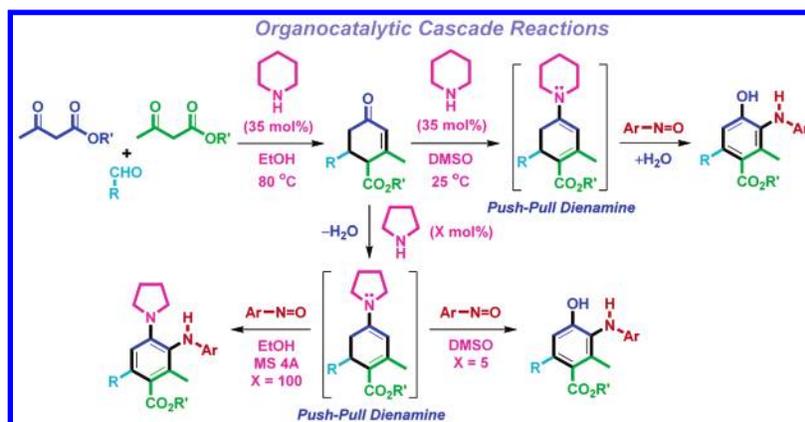


## Organocatalytic Cascade Reactions Based on Push–Pull Dienamine Platform: Synthesis of Highly Substituted Anilines

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A practical and novel one-pot organocatalytic selective process for the cascade synthesis of highly substituted *o*-hydroxydiarylamines and *o*-pyrrolidin-1-yl diarylamines is reported. Direct combination of amine-catalyzed cascade Knoevenagel/Michael/aldol condensation/decarboxylation and cascade enamine amination/isoaromatization of alkyl acetoacetates, aldehydes, and nitrosoarenes furnished the highly functionalized anilines with high yields.

Arylamines are of considerable importance in a variety of industries. As such, the development of new and more general methods for their preparation is of significant interest.<sup>1</sup> Recently, palladium catalysis has emerged for the reactions of aryl halides with primary and secondary amines in the presence of strong base to provide a general route to a variety of arylamines in good yields (Scheme 1).<sup>2</sup>

Herein, we discovered a metal-free, novel, and green technology for the synthesis of highly substituted *o*-hydroxydiarylamines, *o*-pyrrolidin-1-yl diarylamines, and *o*-alkoxydiaryl-

### SCHEME 1. Synthesis of Highly Substituted Anilines

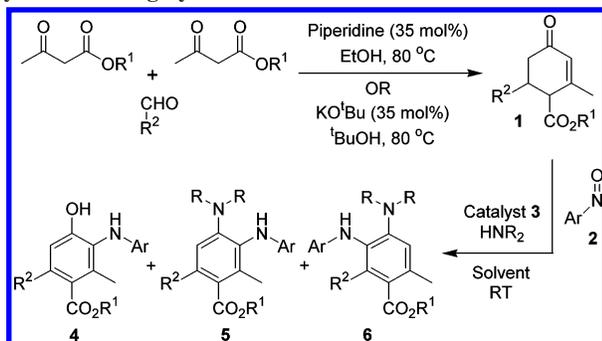


amines by using direct organocatalytic cascade enamine amination/isoaromatization (EA/IA) and enamine amination/isoaromatization/alkylation (EA/IA/A) reactions from commercially available enones, nitrosobenzenes, and alkyl halides (Scheme 1). Direct combination of amine-catalyzed cascade Knoevenagel/Michael/aldol condensation/decarboxylation (K/M/A/DC) and cascade enamine amination/isoaromatization (EA/IA) of alkyl acetoacetates, aldehydes, and nitrosoarenes has been developed in one pot as shown in Scheme 2. *o*-Hydroxydiarylamines are useful materials as additives for rubbers and plastics, antioxidants, antibacterial activity, anti-fibrilliant activity, and hair dyes.<sup>3</sup>

In continuation of our recent discovery of in situ generation and application of novel push–pull dienamines<sup>4</sup> in tandem reactions, we initiated our studies of the cascade EA/IA reaction by screening a number of known and novel organocatalysts for

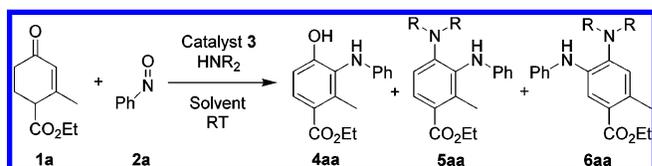
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**SCHEME 2. Organocatalytic Cascade Approach to the Synthesis of Highly Substituted Anilines**


the amination of a variety of Hagemann's esters **1** with different nitrosoarenes **2** as shown in Scheme 2. For developing this novel cascade EA/IA reaction, we need a library of Hagemann's esters **1**, and we synthesized these esters **1** in good yields with minor modifications of known methods of direct piperidine- or KO<sup>t</sup>Bu-catalyzed cascade K/M/A/DC reactions (Scheme 2 and Table S1, see the Supporting Information).<sup>5</sup>

We initiated our studies of the cascade EA/IA reaction by screening a number of known and novel organocatalysts for the amination of Hagemann's ester **1a** using 0.5–1.0 equiv of nitrosobenzene **2a** as shown in Table 1.<sup>6</sup> Proline-catalyzed the formation of *o*-hydroxydiarylamine **4aa** in moderate yields in DMSO and DMF solvents (Table 1, entries 1 and 2) (in all

**TABLE 1. Optimization of Direct Organocatalytic Cascade Synthesis of *o*-Hydroxydiarylamines<sup>a</sup>**


entry	catalyst (20 mol %)	solvent (0.3 M)	Hagemann's ester <b>1a</b> (equiv)	time (h)	products yield <sup>b</sup> (%)		
					<b>4aa</b>	<b>5aa</b>	<b>6aa</b>
1	proline	DMSO	1.0	6	46		
2	proline	DMF	1.0	6	32		
3	<b>diamine<sup>c</sup></b>	<b>DMSO</b>	<b>2.0</b>	<b>1</b>	<b>90</b>		
4	glycine	DMSO	2.0	36	30		
5	piperidine	DMSO	2.0	1	87		
6	<b>morpholine</b>	<b>DMSO</b>	<b>2.0</b>	<b>1</b>	<b>88</b>		
7	benzylamine	DMSO	2.0	1	83		
8	<b>pyrrolidine</b>	<b>DMSO</b>	<b>2.0</b>	<b>1</b>	<b>88</b>	<b>4</b>	<b>4</b>
9 <sup>d</sup>	<b>pyrrolidine</b>	<b>DMSO</b>	<b>2.0</b>	<b>1</b>	<b>85</b>	<b>2</b>	<b>2</b>
10	pyrrolidine	DMSO	1.0	1	70	2	2
11	pyrrolidine	CH <sub>3</sub> CN	2.0	10	40	10	10
12	pyrrolidine	EtOH	2.0	10	35	10	10
13	<b>4aa</b> (5 mol %)	DMSO	2.0	72	35		
14		DMSO	2.0	72			

<sup>a</sup> Reactions were carried out in solvent (0.3 M) with 1.0–2.0 equiv of **1a** relative to the **2a** in the presence of 20 mol % of catalyst. <sup>b</sup> Yield refers to the column purified product. <sup>c</sup> (*S*)-1-(2-Pyrrolidinylmethyl)pyrrolidine. <sup>d</sup> 5 mol % of pyrrolidine used.

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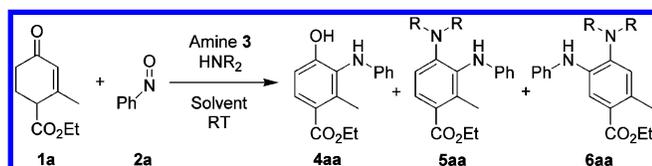
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compounds denoted **4xy**, **5xy**, and **6xy**, **x** is incorporated from reactant enones **1** and **y** is incorporated from the reactant nitrosoarenes **2**). Interestingly, catalyst diamine generated the cascade product **4aa** in very good yield in DMSO (Table 1, entry 3). Secondary amines like piperidine and morpholine catalysts also furnished the cascade product **4aa** in very good yields with excellent regioselectivity in DMSO solvent (entries 5 and 6). The primary amine, benzylamine, also catalyzed the formation of cascade product **4aa** in good yield (entry 7). The simple amine, pyrrolidine, catalyzed the cascade EA/IA reaction to produce **4aa** in 88% yield, which was accompanied by 1:1 regioisomers of *o*-pyrrolidin-1-yl diaryl amines **5aa** and **6aa** in 8% yield (entry 8). Amine-catalyzed cascade EA/IA reactions are solvent dependent and also autocatalyzed reactions as shown in Table 1, entries 10–14. The use of 5 mol % of **4aa** catalyzed the cascade EA/IA reaction of **1a** and **2a** to produce product **4aa** in 35% yield. This is a good demonstration of the involvement of autocatalysis in the present reactions (Table 1, entry 13). We envisioned the optimized condition to be 25 °C in DMSO under 5 mol % of pyrrolidine catalysis to furnish *o*-hydroxydiarylamine **4aa** in 85% yield (entry 9).

In the investigation of EA/IA cascade reactions under pyrrolidine catalysis, product **4aa** was accompanied by interesting diamination products **5aa** and **6aa** with good conversion in EtOH via self-catalysis (Table 1, entry 12). To further exploit formation of this novel structure, we initiated our studies of the cascade EA/IA reaction by screening a number of known amines for the diamination of Hagemann's ester **1a** by 0.5 to 1.0 equiv of both nitrosobenzene **2a** and amines **3** as shown in Table 2.

The use of proline, diamine, and glycine as reagents in cascade reactions did not furnish the expected diamination products **5/6** in EtOH via self-catalysis and produced only amination product **4aa** (not shown in Table 2). Interestingly, pyrrolidine as reagent in self-catalyzed cascade reactions in

**TABLE 2.** Optimization of Direct Self-Catalyzed Cascade Synthesis of *o*-Aminodiarylamines

entry	amine <b>3</b>	solvent (0.3 M)	Hagemann's ester <b>1a</b> (equiv)	time (h)	products yield <sup>a</sup>		
					<b>4aa</b>	<b>5 &amp; 6</b>	ratio <b>5/6</b>
1 <sup>b</sup>	pyrrolidine	DMSO	2.0	0.5	85	11	2:1
2 <sup>b</sup>	pyrrolidine	MeOH	2.0	1	35	45	1:1
3 <sup>b</sup>	pyrrolidine	EtOH	2.0	1	35	45	3:1
4 <sup>b</sup>	pyrrolidine	DCM	2.0	0.5	35	45	10:1
5 <sup>c</sup>	pyrrolidine	MeOH	1.0	1	10	80	10:1
6 <sup>c</sup>	pyrrolidine	EtOH	1.0	1	10	80	10:1
7 <sup>c</sup>	piperidine	EtOH	1.0	0.5	85	-	-
8 <sup>d</sup>	pyrrolidine	EtOH	2.0	1	10	90	33:1

<sup>a</sup> Yield refers to the column purified product. <sup>b</sup> All reactants pyrrolidine (0.3 mmol), nitrosobenzene **2a** (0.3 mmol), and Hagemann's ester **1a** (0.6 mmol) were mixed at the same time in solvent (0.3 M) and stirred at room temperature. <sup>c</sup> To the mixture of Hagemann's ester **1a** (0.3 mmol) and amine **3** (0.6 mmol) in solvent (0.5 mL) was added a 0.5 mL solution of nitrosobenzene **2a** (0.3 mmol) over a period of 0.5 h and the mixture stirred at rt. <sup>d</sup> To the mixture of Hagemann's ester **1a** (0.6 mmol), pyrrolidine (0.3 mmol), and MS 4A (300 mg) in solvent (0.5 mL) was added a 0.5 mL solution of nitrosobenzene **2a** (0.3 mmol) over a period of 0.5 h and the mixture stirred at rt.

DMSO furnished the amination product **4aa** as the major product and diamination products **5/6** as minor products (Table 2, entry 1). The same reaction in protic solvents furnished the amination **4aa** and diamination **5aa/6aa** products with poor regioselectivity (entries 2 and 3). Slow addition of nitrosobenzene **2a** to Hagemann's ester **1a** under pyrrolidine self-catalysis in EtOH furnished the expected *o*-pyrrolidin-1-yl-diarylamines **5aa** and **6aa** in 80% yield with good selectivity (entry 6). We envisioned the optimized condition to be slow addition of **2a** to the mixture of **1a**, **3**, and MS 4A at 25 °C in EtOH to furnish *o*-pyrrolidin-1-yl-diarylamines **5aa/6aa** in 90% yield with 33:1 regioselectivity (entry 8). A mechanistic aspect of this cascade EA/IA reaction is discussed in the next section.

With an efficient organocatalytic cascade protocol in hand, the scope of the auto- and self-catalyzed EA/IA cascade reactions was investigated with various Hagemann's esters **1a–m** and nitrosoarenes **2a–c**.<sup>7</sup> A series of 6-substituted Hagemann's esters **1a–m** were reacted with 0.5 equiv of nitrosoarenes **2a–c** catalyzed by 5 mol % of pyrrolidine or piperidine at 25 °C in DMSO (Table 3). The *o*-hydroxydiarylamines **4** were obtained as single isomers with excellent yields. The reaction of **1a** with 1-methyl-2-nitrosobenzene **2b** furnished the *o*-hydroxydiarylamine **4ab** as a single isomer, in good yield (Table 3). Synthesis of *o*-hydroxydiarylamines **4ac** from **1a**, **2c**, and **3** at 25 °C required a longer reaction time (12 h), but reaction at 65 °C furnished the product **4ac** with good yield within 2.5 h (Table 3). Both aliphatic- and aromatic-substituted Hagemann's esters **1d–m** generated the expected *o*-hydroxydiarylamines **4** with nitrosoarenes **2a–c** in excellent yield (Table

3). The rates of EA/IA cascade reactions are accelerated by in situ generated products **4**, and these reactions are ideal examples for the biomimetic autocatalysis of functionalized amines in organic reactions.<sup>8</sup> Structure and regiochemistry of *o*-hydroxydiarylamines **4** was confirmed by X-ray structure analysis on **4aa** as shown in Figure S1 (see the Supporting Information).<sup>9</sup>

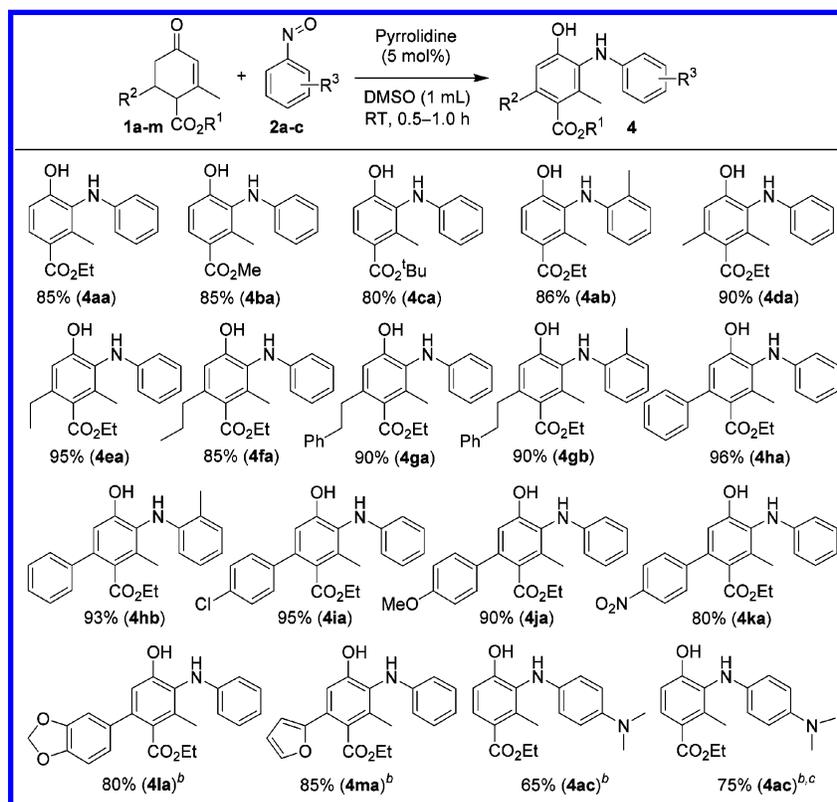
With the success of cascade synthesis of highly functionalized *o*-hydroxydiarylamines **4**, we continued our investigation for generation of a highly functionalized diversity-oriented library of cascade *o*-pyrrolidin-1-yl-diarylamines **5** under self-catalysis. The results in Table 4 demonstrate the broad scope of this novel green methodology covering a structurally diverse group of Hagemann's esters **1a–m**, pyrrolidine, and nitrosobenzenes **2a–c**. Cascade EA/IA reaction of Hagemann's esters **1b,c**, nitrosobenzene **2a**, and pyrrolidine furnished the regioselective diamines **5ba** and **5ca** in 11:1 ratio with >85% yield (Table 4). Unexpectedly, cascade product **5ab** furnished with moderate yield in 3:1 isomeric ratio from **1a**, pyrrolidine, and **2b**. 4-*N,N*-Dimethylnitrosobenzene **2c** did not furnish the expected cascade EA/IA product **5ac** at 25 °C, but gave only <5% of expected **5ac** along with 40% of *o*-hydroxydiarylamines **4ac** at 65 °C in EtOH; this may be due to the electronic factor of the NMe<sub>2</sub> group. Interestingly, all 6-substituted Hagemann's esters **1d–m** furnished the expected *o*-pyrrolidin-1-yl-diarylamines **5da–ma** with good yields as single isomers in self-catalyzed EA/IA cascade reactions as shown in Table 4. The structure and regiochemistry of *o*-pyrrolidin-1-yl-diarylamines **5** were confirmed by X-ray structure analysis on **5ia** (Figure S2, see the Supporting Information).<sup>9</sup>

After successful demonstration of the piperidine-catalyzed cascade K/M/A/DC and EA/IA reactions, we decided to investigate the combination of these two cascade reactions in one pot. Reaction of 2 equiv of ethyl acetoacetate and benzaldehyde under piperidine catalysis in EtOH at 80 °C for 3–6 h furnished the expected Hagemann's ester **1h**, which on treatment with nitrosobenzene **2a** at 25 °C in same solvent did not furnish the expected *o*-hydroxydiarylamines **4ha** in good yield, but removing the solvent EtOH by vacuum pump and adding solvent DMSO, 20 mol % of piperidine, and nitrosobenzene **2a** to the reaction mixture of cascade K/M/A/DC furnished the expected *o*-hydroxydiarylamines **4ha** in good yield as shown in Table 5. Successful combination of two cascade K/M/A/DC and EA/IA reactions under piperidine catalysis was demonstrated by two more examples as shown in Table 5, and this one-pot synthetic strategy will have a great impact on the synthesis of functionalized small molecules.

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(9) Crystal structure data for **4aa**: C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>, *M<sub>r</sub>* = 271.31, monoclinic, space group *P2<sub>1</sub>/c*, *a* = 10.9755(12) Å, *b* = 8.2031(9) Å, *c* = 16.2285(18) Å, α = 90°, β = 107.064(2)°, γ = 90°, *V* = 1396.8(3) Å<sup>3</sup>, *T* = 293(2) K, 13983 reflections collected. Crystal structure data for **5ia**: C<sub>26</sub>H<sub>27</sub>ClN<sub>2</sub>O<sub>2</sub>, *M<sub>r</sub>* = 434.95, triclinic, space group *P-1*, *a* = 10.602(2) Å, *b* = 10.735(2) Å, *c* = 11.281(2) Å, α = 77.344(3)°, β = 67.507(3)°, γ = 83.509(3)°, *V* = 1156.8(4) Å<sup>3</sup>, *T* = 293(2) K, 12012 reflections collected. CCDC-611665 for **4aa** and CCDC-611666 for **5ia** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail to [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). See the Supporting Information for the crystal structures.

(7) Many of nitrosoarenes **2** are commercially available, and suitable methods are known to prepare them. For excellent methods for synthesis of nitroso compounds, see: (a) Priewish, B.; Ruck-Braun, K. *J. Org. Chem.* **2005**, *70*, 2350–2352. (b) Defoin, A. *Synthesis* **2004**, 706–710. (c) Porta, F.; Prati, L. *J. Mol. Catal.* **2000**, *157*, 123–129. (d) Tollari, S.; Cuscela, M.; Porta, F. *J. Chem. Soc., Chem. Commun.* **1993**, 1510–1511.

TABLE 3. Chemically Diverse Libraries of *o*-Hydroxydiarylamines<sup>a</sup>

<sup>a</sup> Yield refers to the column purified product. <sup>b</sup> Piperidine (5 mol %) used as catalyst. <sup>c</sup> Reaction performed at 65 °C.

With pharmaceutical applications in mind, we extended the two-component cascade EA/IA reactions to a novel amine/ $\text{Cs}_2\text{CO}_3$ -catalyzed three-component EA/IA/A reaction of **1a**, **1d**, and **2a** with allyl and propargyl bromides in one pot as shown in Table 6. *o*-Alkyloxydiarylamines **7** were constructed in good yields with high selectivity as shown in Table 6, and this method will have a great impact on the synthesis of carbazole alkaloids.<sup>1a</sup>

The possible reaction mechanism for regioselective synthesis of cascade products **4** and **5** through reaction of Hagemann's ester **1a**, nitrosoarene **2**, and pyrrolidine **3** is illustrated in Scheme 3. First, reaction of pyrrolidine **3** with Hagemann's ester **1a** generates the imine cation **8**, which will transform into both dienamines **9** (thermodynamic stable product, major) and **15** (kinetic product, minor) on the basis of reaction conditions. The energy difference ( $\Delta H$ ) between the two dienamines **9** and **15** is 4.698 kcal/mol based on AM1 and 4.367 kcal/mol based on PM3 calculations. Minimized structures of **9** and **15** are depicted in the Supporting Information. Since the difference in  $\Delta H$ 's between the two dienamines of **9** and **15** are  $>4$  kcal/mol, formation of thermodynamic stable dienamine **9** will be major under mild organocatalysis conditions. Slow addition of nitrosoarenes **2** to the reaction mixture of **1** and **3** controlled the formation of kinetic dienamine **15**, which may be due the basic nature of nitrosoarenes **2**, and this was supported by results in Tables 2 and 4.

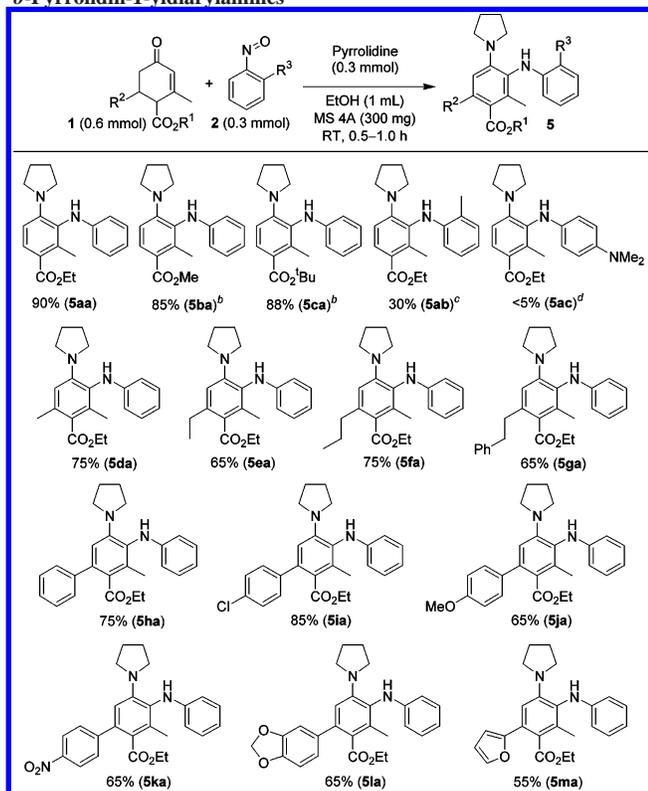
The reaction of push–pull dienamine **9** with **2** furnishes the selectively nitroso aldol product **11**, which will give imine product **12** by losing the hydroxide ion. Hydrolysis followed by isoaromatization of imine product **12** converted into highly substituted *o*-hydroxydiarylamines **4** under amine catalysis. Imine product **12** was transformed into highly substituted *o*-pyrrolidin-

yl-diarylamines **5** via isoaromatization under suitable conditions (EtOH and MS 4A). Hydrolysis of imine **12** is more solvent dependent as shown in Tables 1 and 2, which means this hydrolysis step is faster in DMSO than in EtOH, perhaps due to more interactions with water. In a similar manner, regioisomer **6** was also furnished from kinetic dienamine **15**. As discussed above, these cascade reactions are autocatalyzed and product **4** can catalyze the nitroso aldol reaction of enolate **1a'** of **1a** with **2** to form **17** via hydrogen-bonding transition state **16**, which will transform into the expected product **4** through imine **13** as shown in Scheme 3 (see Table 1, entries 13 and 14).

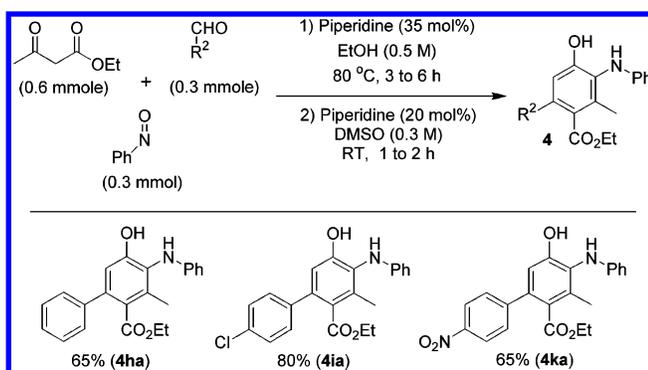
In summary, we have developed the metal-free synthesis of highly substituted anilines **4**, **5**, and **7** from simple starting materials via cascade EA/IA, K/M/A/DC/EA/IA, and EA/IA/A reactions under amine catalysis. The cascade reaction proceeds in good yields with high selectivity using pyrrolidine or piperidine as the catalyst. Furthermore, we have demonstrated the biomimetic auto- and self-catalysis in amine-catalyzed cascade reactions. Further work is in progress to utilize novel EA/IA, K/M/A/DC/EA/IA, and EA/IA/A reactions in synthetic chemistry.

## Experimental Section

**General Experimental Procedures for the Cascade Amination Reactions: Pyrrolidine-Catalyzed, Two-Component, Cascade Enamine Amination/Isoaromatization Reactions.** In an ordinary glass vial equipped with a magnetic stirring bar, to 0.6 mmol of the Hagemann's esters **1** was added 1.0 mL of solvent, and then the catalyst pyrrolidine (0.015 mmol, 2.5  $\mu\text{L}$ ) was added and the reaction mixture was stirred at 25 °C for 0.5 h; then 0.3 mmol of nitrosoarenes **2** was added in one portion, and the reaction mixture

**TABLE 4. Chemically Diverse Libraries of *o*-Pyrrolidin-1-yl-diarylamines<sup>a</sup>**

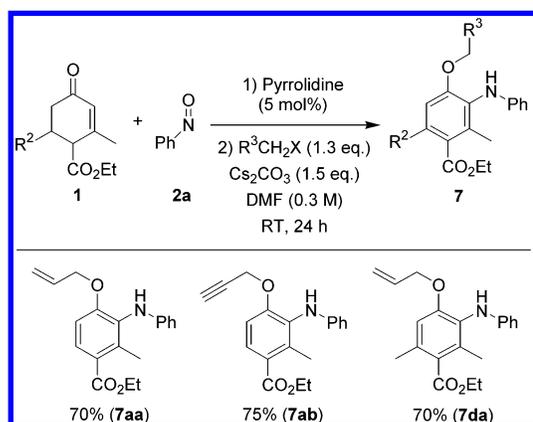
<sup>a</sup> In all reactions, 10–35% of the corresponding substituted *o*-hydroxydiarylamines **4** were isolated. Yield refers to the column purified product. <sup>b</sup> 11:1 ratio of regioisomers **5/6** are isolated. <sup>c</sup> 3:1 ratio of **5/6** are isolated. <sup>d</sup> Reaction performed at 65 °C for 2.5 h, and 40% of product **4ac** was isolated.

**TABLE 5. Combination of Cascade Knoevenagel/Michael/Aldol Condensation/Decarboxylation and Cascade Enamine Amination/Isoaromatization Reactions in One Pot<sup>a,b</sup>**

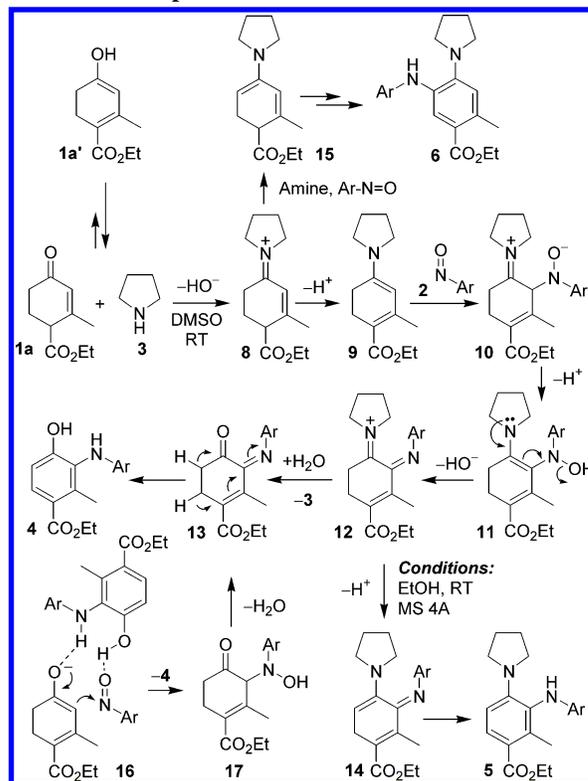
<sup>a</sup> See the Experimental Section. <sup>b</sup> Yield refers to the column purified product.

was stirred at 25 °C for the time indicated in Tables 1 and 3. The crude reaction mixture was directly loaded onto a silica gel column with or without aqueous workup, and pure cascade products **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Self-Catalyzed, Three-Component, Cascade Enamine Amination/Isoaromatization Reactions.** In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of the pyrrolidine, 0.6 mmol of Hagemann's esters **1**, and 300 mg of MS 4A was added 0.5 mL of solvent, and then the 0.5 mL solution of nitrosoarene (**2**) was added dropwise for 0.5 h and the

**TABLE 6. Amine–Cs<sub>2</sub>CO<sub>3</sub>-Catalyzed Enamine Amination/Isoaromatization/Alkylation Reactions in One Pot<sup>a,b</sup>**

<sup>a</sup> See the Experimental Section. <sup>b</sup> Yield refers to the column purified product.

**SCHEME 3. Proposed Reaction Mechanism**

reaction mixture was stirred at 25 °C for the time indicated in Tables 2 and 4. The crude reaction mixture was worked up with aqueous NH<sub>4</sub>Cl solution, and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and concentrated. Pure cascade products **5** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Piperidine-Catalyzed Combination of Cascade Knoevenagel/Michael/Aldol Condensation/Decarboxylation and Cascade Enamine Amination/Isoaromatization Reactions in One Pot.** To a stirred solution of ethyl acetoacetate (0.6 mmol) and aldehydes (0.3 mmol) in EtOH (1 mL) was added a catalytic amount of piperidine (0.1 mmol, 35 mol %), and the reaction mixture was stirred at 80 °C for 3 h. Solvent ethanol and piperidine were evaporated by vacuum pump, then catalyst piperidine (0.06 mmol, 20 mol %), nitrosobenzene **2a** (0.3 mmol), and solvent DMSO (1 mL) were added, and

the reaction mixture was stirred at 25 °C for 1–2 h. The crude reaction mixture was worked up with aqueous NH<sub>4</sub>Cl solution, and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and concentrated. Pure one-pot products **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Pyrrolidine/Cs<sub>2</sub>CO<sub>3</sub>-Catalyzed Three-Component Enamine Amination/Isoaromatization/Alkylation Reactions in One Pot.**

In an ordinary glass vial equipped with a magnetic stirring bar, to 0.6 mmol of the Hagemann's esters **1** was added 1.0 mL of solvent, and then the catalyst pyrrolidine (0.015 mmol, 2.5 μL) was added and the reaction mixture was stirred at 25 °C for the 0.5 h. A 0.3 mmol portion of nitrosoarenes **2** was added in one portion, and the reaction mixture was stirred at 25 °C for the time indicated in Table 6. To the reaction mixture were added alkyl halide (0.39 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (0.45 mmol), and stirring was continued at rt for 24 h. The crude reaction mixture was worked up with aqueous NH<sub>4</sub>Cl solution, and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and concentrated. Pure one-pot products **7** were obtained

by column chromatography (silica gel, mixture of hexane/ethyl acetate).

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**Supporting Information Available:** General experimental procedures, compound characterization, X-ray crystal structures, and analytical data (<sup>1</sup>H NMR, <sup>13</sup>C NMR, and HRMS) for all new compounds. Copies of <sup>13</sup>C NMR spectra of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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