

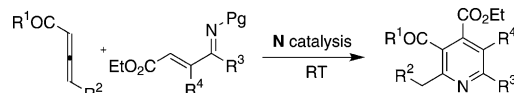
# Organocatalytic Synthesis of Highly Functionalized Pyridines at Room Temperature\*\*

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Substituted pyridines are important building blocks for many natural products, bioactive molecules, and functional materials.<sup>[1]</sup> Thus, their synthesis has drawn extensive attention from the organic community during the past few decades. Accordingly various significant methodologies have been disclosed.<sup>[2,3]</sup> Among them, the traditional thermal condensation of carbonyl compounds represents a typical method for pyridine synthesis, while modern synthetic strategies mainly rely on transition metal catalyzed cycloaddition reactions. However, these existing methodologies either require high temperature or toxic metals as catalysts. Thus, the development of a more general, operationally simple, and environmentally benign method for pyridine synthesis is highly desirable.

Recently, the Rauhut–Currier reaction has emerged as a powerful tool for new C–C bond formation, and demonstrated its high efficiency for the construction of carbocycles and N-containing heterocycles with good stereocontrol.<sup>[4,5]</sup> Among existing methodologies, however, the majority rely on the use of air-sensitive phosphine catalysts. The alternative and newly developed thiol catalyst proved to be a promising catalytic system, albeit still lacking in efficiency.<sup>[6]</sup> In contrast, amines are more stable and easier to handle when compared to phosphines, and has shown its efficiency in numerous nucleophilic catalysis.<sup>[7]</sup> Unfortunately, the amine-catalyzed cross-Rauhut–Currier reactions are rarely documented.<sup>[8]</sup> Herein, we report a novel aza-Rauhut–Currier/cyclization/desulfonation cascade reaction of allenates with 1-aza-1,3-dienes by using *N,N,N',N'*-tetramethylethane-1, 2-diamine (TMEDA) as a catalyst, which enables a facile entry into the synthesis of highly functionalized pyridines (Scheme 1). To the best of our knowledge, this is the first example of an amine-catalyzed aza-Rauhut–Currier reaction.

Our first trial was conducted with benzyl allenate and *N*-4-methoxybenzenesulfonyl-1-aza-1,3-diene, in the presence of 20 mol % 1, 4-diazabicyclo[2, 2, 2]octane (DABCO) as the catalyst (Table 1). To our delight, the pyridine **3a**, having



**Scheme 1.** Amine-catalyzed synthesis of highly functionalized pyridines.

**Table 1:** Amine-catalyzed synthesis of tetrasubstituted pyridines.<sup>[a]</sup>

| Entry             | Catalyst           | Solvent                         | <i>t</i> [h] | Yield [%] <sup>[b]</sup> |
|-------------------|--------------------|---------------------------------|--------------|--------------------------|
| 1                 | DABCO              | toluene                         | 48           | 56                       |
| 2 <sup>[c]</sup>  | DABCO              | toluene                         | 48           | 55                       |
| 3                 | DMAP               | toluene                         | 24           | n.d.                     |
| 4                 | pyridine           | toluene                         | 24           | n.d.                     |
| 5                 | NEt <sub>3</sub>   | toluene                         | 24           | 50                       |
| 6                 | DIPEA              | toluene                         | 72           | 39                       |
| 7                 | 4-methylmorpholine | toluene                         | 72           | 36                       |
| 8                 | quinine            | toluene                         | 72           | 28                       |
| 9                 | NBu <sub>3</sub>   | toluene                         | 72           | 36                       |
| 10                | DBU                | toluene                         | 24           | 30                       |
| 11                | TMEDA              | toluene                         | 24           | 77                       |
| 12                | TMEDA              | MeCN                            | 24           | 69                       |
| 13                | TMEDA              | CH <sub>2</sub> Cl <sub>2</sub> | 24           | 68                       |
| 14                | TMEDA              | CHCl <sub>3</sub>               | 24           | 57                       |
| 15                | TMEDA              | THF                             | 24           | 37                       |
| 16 <sup>[d]</sup> | TMEDA              | toluene                         | 24           | 60                       |
| 17 <sup>[e]</sup> | TMEDA              | toluene                         | 24           | 55                       |

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.05 mmol), and catalyst (20 mol %) were stirred at room temperature. [b] Yield of isolated product. [c] *N*-tosyl-1-aza-1,3-diene was used. [d] Used 10 mol % TMEDA. [e] Used 5 mol % TMEDA. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DIPEA = , DMAP = 4-(*N,N*-dimethylamino)pyridine, n.d. = not detected, PMP = *para*-methoxyphenyl.

multiple functional groups, was obtained with a modest yield (entry 1). Different *N*-protecting groups turned out to have no significant influence on the reaction outcome (entry 2). To improve the chemical yield, various amines were then examined. Trialkylamines proved to be superior to aromatic ones (entries 5–10), and afforded moderate product yields; and the aromatic amines did not catalyze this reaction (entries 3 and 4). Surprisingly, when TMEDA was employed, the reaction yield was significantly elevated (entry 11). Subsequent investigation of solvent effects indicated toluene to be the best choice (entries 12–15). Additionally, the catalyst loading can be further decreased to 10 mol %, though slightly lower yield was obtained (entry 16). Using 5 mol % of catalyst is still efficient enough to promote this reaction (entry 17).

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Under the optimized reaction conditions, a variety of 2,3,4,6-tetrasubstituted pyridines and 2,3,4,5,6-pentasubstituted pyridines were efficiently synthesized in good chemical yields (Table 2). Generally, aromatic groups, such as the

**Table 2:** TMEDA-catalyzed synthesis of highly substituted pyridines.<sup>[a,b]</sup>

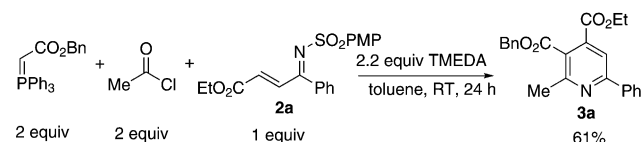
| $  \begin{array}{c}  \text{R}^1\text{OC} \\    \\  \text{C}=\text{C} \\    \\  \text{R}^2  \end{array}  +  \begin{array}{c}  \text{EtO}_2\text{C} \\    \\  \text{C}=\text{C} \\    \\  \text{R}^4 \\    \\  \text{N}=\text{SO}_2\text{PMP} \\    \\  \text{R}^3  \end{array}  \xrightarrow[\text{toluene, RT}]{20 \text{ mol\% TMEDA}}  \begin{array}{c}  \text{R}^1\text{OC} \\    \\  \text{C}=\text{C} \\    \\  \text{R}^2 \\    \\  \text{N}=\text{C} \\    \\  \text{R}^3 \\    \\  \text{R}^4  \end{array}  $ |                                                                                                                                                                                                                                                                     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <br><b>3a:</b> R = H, 77%<br><b>3a:</b> R = H, 79% <sup>[c]</sup><br><b>3b:</b> R = 2-F, 67%<br><b>3c:</b> R = 3-F, 64%<br><b>3d:</b> R = 3-Br, 54%<br><b>3e:</b> R = 3-Me, 61%<br><b>3f:</b> R = 3-MeO, 65%<br><b>3g:</b> R = 3-TsNH, 61%<br><b>3h:</b> R = 4-Me, 61%<br><b>3i:</b> R = 4-I, 56%<br><b>3j:</b> R = 4-Br, 67%<br><b>3k:</b> R = 4-Cl, 56%                                                                                                                                                             | <br><b>3n:</b> 61%<br><br><b>3s:</b> 45%<br><br><b>3o:</b> 70%<br><br><b>3t:</b> 92%<br><br><b>3p:</b> 88%<br><br><b>3u:</b> 65%<br><br><b>3l:</b> 57%<br><br><b>3q:</b> 51%<br><br><b>3v:</b> 45%<br><br><b>3m:</b> 67%<br><br><b>3r:</b> 50%<br><br><b>3w:</b> 0% |

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), and TMEDA (20 mol %) in 0.4 mL toluene were stirred at room temperature. [b] Yield of isolated product. [c] Used 30 mol % TMEDA. Ts = 4-toluenesulfonyl.

phenyl ring in **3a**, can be readily installed at the 6-position. Notably, the yield of **3a** could be slightly improved to 79%, but at the expense of a higher catalyst loading. Fluorinated N-containing heterocycles were frequently found with superior biological activities. This methodology provided facile access to the preparation of fluorinated pyridine derivatives, regardless of their substitution patterns (**3b,c**). Both *meta*- and *para*-substituted phenyl moieties, possessing either electron-withdrawing or electron-donating substituents, were efficiently introduced at the 6-position of the pyridine ring (**3d–h**). Halogenated biaryl systems (**3i–k**) can also be readily constructed by this strategy, where the iodo, bromo, and chloro functionalities enable further transformations such as coupling. The more bulky 1-naphthyl and 2-naphthyl groups were well-tolerated in this reaction (**3l,m**). 6-Furyl-, thiophenyl-, and 6-(1-tosyl-1*H*-indol-3-yl)-substituted pyridines

were also easily prepared (**3n–p**). Additionally, styryl was well-incorporated in this pyridine system (**3q**). A heterocycle (**3r**) could also be prepared using this methodology in modest yield. Moreover, the use of 2,3,4-trisubstituted 1-aza-1,3-diene provided a straightforward entry to the pentasubstituted pyridine **3s**. This protocol could be readily extended to the synthesis of 6-alkyl-substituted pyridine. To our surprise, the more sterically hindered 6-*tert*-butyl-substituted pyridine could be easily prepared with excellent yield (**3t**). Further exploration demonstrated that the size of the 2,3-butadienoate had no significant influence on the reaction outcome (**3u**). Notably, highly unstable 1-phenyl-2,3-butadien-1-one was well tolerated in this transformation (**3v**). Unfortunately,  $\gamma$ -substituted 2,3-butadienoates could not participate in this process (**3w**), possibly because of the lower electrophilicity of  $\gamma$ -substituted 2,3-butadienoates, compared to simple nonsubstituted 2,3-dienoates. Thus, the zwitterionic intermediate **A** could not be formed by nucleophilic addition of the amine catalyst (see Scheme 3). Chalcone-derived N-sulfonyl-1-aza-1,3-diene could not be employed in this transformation, probably because of its lower reactivity.

To further simplify this protocol, a one-pot three component strategy was developed. As shown in Scheme 2, in the presence of TMEDA, the mixture of readily available benzyl

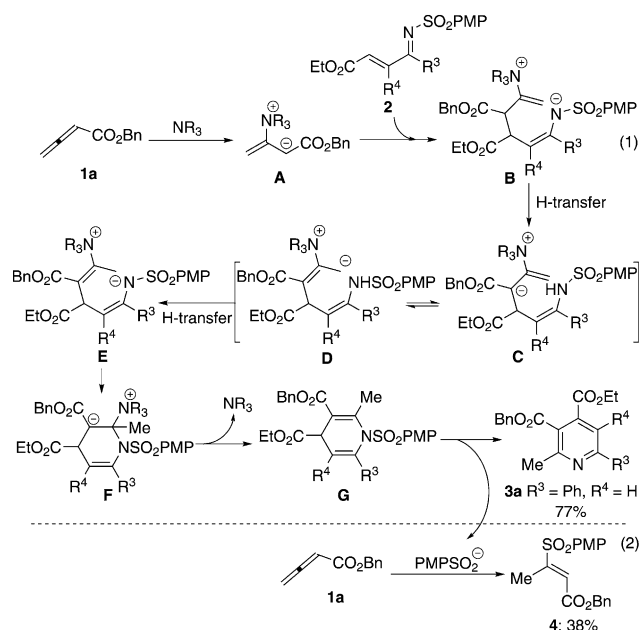


**Scheme 2.** One-pot synthesis of pyridine.

2-(triphenylphosphoranylidene)acetate, acetic chloride, and the N-sulfonyl-1-aza-1,3-diene **2a** were directly converted into the pyridine adduct **3a** in good yield under mild reaction conditions.

Although the detailed mechanism of this reaction is not clear at the current stage, a rational reaction pathway is proposed [Scheme 3, Eq. (1)]. The reaction is believed to be initiated by the nucleophilic addition of TMEDA to the 2,3-butadienoate **1**, thus giving the zwitterionic intermediate **A**. Subsequent nucleophilic attack of the 1-aza-1,3-diene **2** and subsequent intramolecular proton transfer within **B** provides **C**, which is believed to exist in equilibrium with the intermediate **D**. A second intramolecular proton transfer then provides **E**, which undergoes an aza-1,4-addition, thus affording the tetrahydropyridine adduct **F**. After expulsion of the TMEDA catalyst, the dihydropyridine **G** is formed. Further desulfonation delivers the final pyridine adduct. The observation of the side-product **4** provides evidence in support of this mechanism [Scheme 3, Eq. (2)].

In conclusion, a mild, environmentally benign protocol for the synthesis of pyridines has been developed by an amine-catalyzed aza-Rauhut–Currier/cyclization/desulfonation cascade reaction between 2,3-butadienoate and N-sulfonyl-1-aza-1,3-dienes. Readily available TMEDA proved to be an efficient catalyst for this process. In addition, a plausible



**Scheme 3.** Proposed mechanism and reaction pathway.

mechanism has been proposed to account for this unprecedented cascade reaction pathway. A detailed mechanistic study and application of this strategy to the synthesis of complex heterocycles are currently underway in our laboratory and will be reported in due course.

## Experimental Section

General procedure: *N,N,N',N'*-tetramethylethane-1, 2-diamine (TMEDA; 0.02 mmol) was added, under ambient conditions, to a solution of allenates (0.2 mmol) and *N*-sulfonyl-1-aza-1, 3-dienes (0.1 mmol) in 0.4 mL toluene. The reaction mixture was stirred at room temperature. After the reaction was completed, it was directly subjected to column chromatography purification using *n*-hexane/ethyl acetate (15:1→10:1) as the eluent.

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