

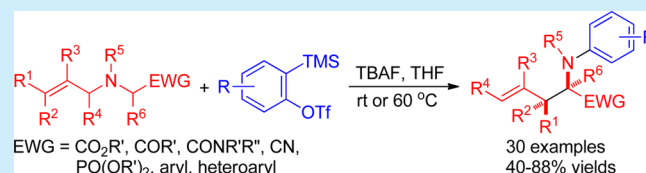
# Aryne-Mediated [2,3]-Sigmatropic Rearrangement of Tertiary Allylic Amines

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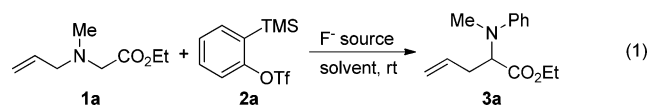
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**S** Supporting Information

**ABSTRACT:** A new strategy has been established for the [2,3]-sigmatropic rearrangement of quaternary allylic ammonium ylides via in situ activation of tertiary allylic amines with arynes under mild conditions. Using 2-(trimethylsilyl)aryl triflates as aryne precursors, a range of tertiary allylic amines bearing electron-withdrawing groups underwent [2,3]-sigmatropic rearrangement to furnish structurally diverse homoallylic amines in moderate to good yields. The reaction enabled construction of quaternary stereocenters with excellent enantiopurity and functionalized cyclopropanes with extremely high diastereoselectivity.

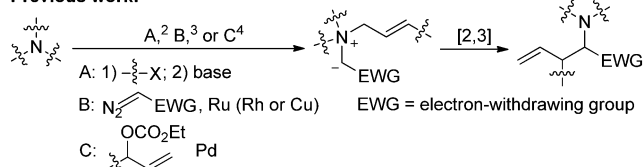


The [2,3]-sigmatropic rearrangement of quaternary allylic ammonium ylides constitutes a powerful strategy for the construction of functionalized homoallylic amines, which serve as versatile building blocks in chemical synthesis.<sup>1</sup> In general, quaternary allylic ammonium ylides are generated in situ by addition of bases to ammonium salts, which are prepared via *N*-alkylation of tertiary amines (Scheme 1).<sup>2</sup> Alternatively, quaternary allylic ammonium ylides are formed either through metal carbenoid-mediated coupling between tertiary allylic amines and diazo compounds<sup>3</sup> or through palladium-catalyzed *N*-alkylation of tertiary amines with allylic carbonates.<sup>4–7</sup> These methods focus on the introduction of alkyl groups to the nitrogen atom of tertiary amines to access quaternary allylic ammonium ylides. To expand the scope for the [2,3]-sigmatropic rearrangement of quaternary allylic ammonium

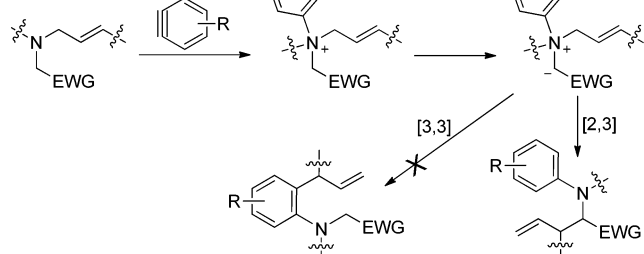


## Scheme 1. [2,3]-Sigmatropic Rearrangement of Quaternary Allylic Ammonium Ylides

### Previous work:



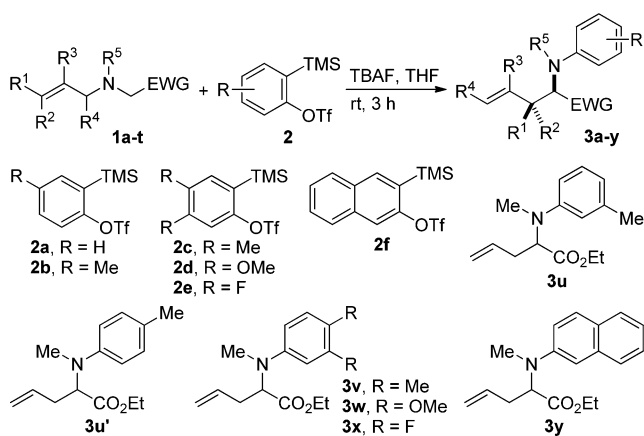
### This work:



ylides, alongside our interests in exploring the synthetic utilities of C–N bond cleavage,<sup>8</sup> we have developed a new strategy to execute the rearrangement through *N*-arylation of tertiary allylic amines in the absence of metals (Scheme 1).

Inspired by previous reports that tertiary amines are able to undergo nucleophilic addition to arynes, particularly those generated in situ from 2-(trimethylsilyl)aryl triflates under mild conditions,<sup>9,10</sup> we envisioned that the zwitterion generated from a tertiary allylic amine and an aryne would undergo proton transfer to furnish a quaternary allylic ammonium ylide, which would undergo the [2,3]-sigmatropic rearrangement to furnish a functionalized homoallylic amine (Scheme 1). Since the quaternary allylic ammonium ylide bears an *N*-aryl group, it is necessary for us to minimize or even obviate a possible reaction pathway of the aza-Claisen rearrangement, which was disclosed previously by Greaney and co-workers.<sup>10a</sup> Using 2-(trimethylsilyl)phenyl triflate (2a) as a benzyne precursor, we surveyed a few fluoride sources, such as CsF, KF, and tetrabutylammonium fluoride (TBAF), in the model reaction of tertiary allylic amine 1a in acetonitrile under air at room temperature (eq 1) and found that the use of TBAF furnished  $\gamma,\delta$ -unsaturated  $\alpha$ -amino ester 3a in the best yield (76%).<sup>11</sup> The reaction was compatible with moisture and air, and importantly, the corresponding aza-Claisen rearrangement was not observed at all. We then examined some other common solvents such as toluene, 1,2-dichloroethane, ethyl acetate, tetrahydrofuran, 1,2-dimethoxyethane, acetonitrile, *N,N*-dimethylformamide, and dimethyl sulfoxide and, to our delight, found that the yield

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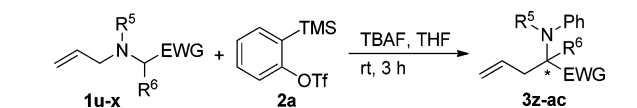
Table 1. Aryne-Mediated [2,3]-Sigmatropic Rearrangement of Tertiary Allylic Amines<sup>a</sup>

entry	1	2	3	yield (%) <sup>b</sup>
1		<b>2a</b>	<b>3a</b>	85
2	<b>1b</b> , EWG = COMe	<b>2a</b>	<b>3b</b>	62
3	<b>1c</b> , EWG = COPh	<b>2a</b>	<b>3c</b>	74
4 <sup>c</sup>	<b>1d</b> , EWG = CONH <sub>2</sub>	<b>2a</b>	<b>3d</b>	69
5 <sup>c</sup>	<b>1e</b> , EWG = CONHMe	<b>2a</b>	<b>3e</b>	53
6 <sup>c</sup>	<b>1f</b> , EWG =	<b>2a</b>	<b>3f</b>	51
7	<b>1g</b> , EWG = CN	<b>2a</b>	<b>3g</b>	88
8 <sup>c</sup>	<b>1h</b> , EWG = PO(OEt) <sub>2</sub>	<b>2a</b>	<b>3h</b>	60
9	<b>1i</b> , EWG =	<b>2a</b>	<b>3i</b>	78
10	<b>1j</b> , EWG = 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	<b>3j</b>	43
11	<b>1k</b> , R <sup>1</sup> = R <sup>2</sup> = H, R <sup>3</sup> = Me	<b>2a</b>	<b>3k</b>	63
12	<b>1l</b> , R <sup>1</sup> = R <sup>2</sup> = Me, R <sup>3</sup> = H	<b>2a</b>	<b>3l</b>	57
13	<b>1m</b> , R <sup>1</sup> = Ph, R <sup>2</sup> = R <sup>3</sup> = H	<b>2a</b>	<b>3m</b> , 94:6 dr <sup>c</sup>	66
14	<b>1n</b>	<b>2a</b>	<b>3n</b> , 56:44 dr <sup>c</sup>	59
15	<b>1o</b> , R <sup>5</sup> = (CH <sub>2</sub> ) <sub>2</sub> Me	<b>2a</b>	<b>3o</b>	71
16	<b>1p</b> , R <sup>5</sup> = allyl	<b>2a</b>	<b>3p</b>	78
17	<b>1q</b> , R <sup>5</sup> = propargyl	<b>2a</b>	<b>3q</b>	50
18	<b>1r</b> , R <sup>5</sup> = CH <sub>2</sub> CO <sub>2</sub> Et	<b>2a</b>	<b>3r</b>	42
19 <sup>d</sup>	<b>1s</b> , R <sup>5</sup> = Ph	<b>2a</b>	<b>3s</b>	63
20 <sup>c</sup>	<b>1t</b>	<b>2a</b>	<b>3t</b>	61
21	<b>1a</b>	<b>2b</b>	<b>3u/3u'</b> (56:44) <sup>c</sup>	76
22	<b>1a</b>	<b>2c</b>	<b>3v</b>	80
23	<b>1a</b>	<b>2d</b>	<b>3w</b>	75
24	<b>1a</b>	<b>2e</b>	<b>3x</b>	40
25	<b>1a</b>	<b>2f</b>	<b>3y</b>	75

<sup>a</sup>Reaction conditions: **1** (0.20 mmol), **2** (0.28 mmol), TBAF (0.30 mmol, 1.0 M in THF), THF (1.0 mL), rt, 3 h. <sup>b</sup>Isolated yields. <sup>c</sup>The reaction was run at 60 °C for 12 h. <sup>d</sup>Replacing TBAF and THF with

Table 1. continued

CsF (0.40 mmol) and MeCN, respectively, 70 °C, 12 h. <sup>e</sup>Determined by <sup>1</sup>H NMR spectroscopic analysis.

Table 2. Reaction of Optically Active Tertiary Allylic Amines<sup>a</sup>

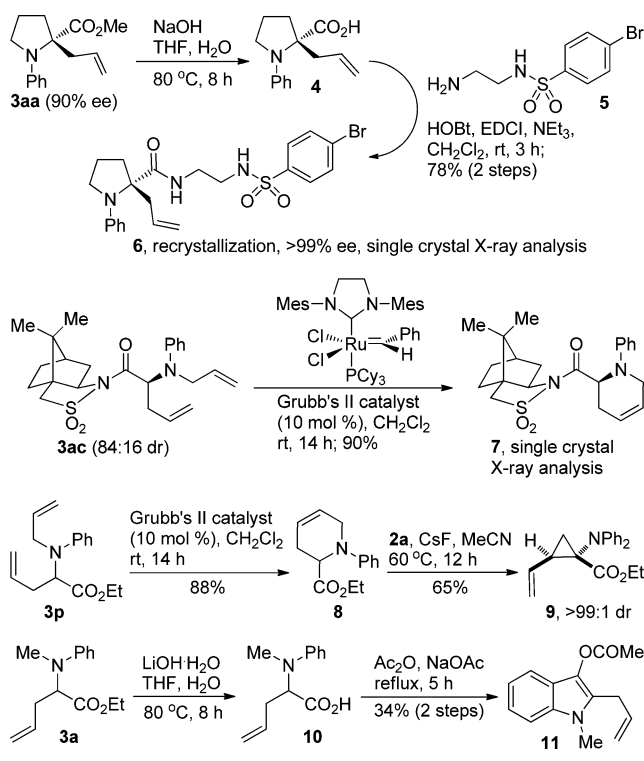
entry	1	3	yield (%) <sup>b</sup>
1	<b>1u</b> , >99% ee	<b>3z</b> , 14% ee <sup>c</sup>	63
2	<b>1v</b> , >99% ee	<b>3aa</b> , 90% ee <sup>c</sup>	60
3	<b>1w</b> , >99% ee	<b>3ab</b> , 90% ee <sup>c</sup>	64
4	<b>1x</b>	<b>3ac</b> , 84:16 dr <sup>d</sup>	66

<sup>a</sup>Reaction conditions: **1** (0.20 mmol), **2a** (0.28 mmol), TBAF (0.30 mmol, 1.0 M in THF), THF (1.0 mL), rt, 3 h. <sup>b</sup>Isolated yields. <sup>c</sup>Determined by HPLC analysis on a chiral stationary phase. <sup>d</sup>Determined by <sup>1</sup>H NMR spectroscopic analysis.

was enhanced to 85% when the reaction was performed in tetrahydrofuran.

A range of tertiary allylic amines bearing various electron-withdrawing groups were examined in the reaction with 2-(trimethylsilyl)aryl triflates in the presence of TBAF under air at room temperature or at 60 °C (Table 1). The electron-withdrawing group could be an ester, a ketone, an amide, a cyano, a phosphonate, a benzoxazole, or a *p*-nitrophenyl group (entries 1–10). Although amides were reported previously to undergo addition<sup>12</sup> or insertion<sup>13</sup> to arynes, in our case they were well tolerated even at 60 °C due to their much lower nucleophilicity relative to tertiary amines. The reaction proceeded smoothly with the substrates having substituents at the  $\alpha$ -,  $\beta$ -, and/or  $\gamma$ -positions of the allyl moiety (entries 11–14). While excellent diastereoselectivity was observed for an amine having an acyclic allylic group, the reaction with an amine having a cyclic allylic group exhibited poor diastereoselectivity (entries 13 and 14). A variety of functional groups, such as allyl, propargyl, and ethoxycarbonylmethyl, were also successfully introduced as *N*-substituents, which were not involved in the rearrangement (entries 15–20). Nevertheless, introduction of an *N*-phenyl group decreased the nucleophilicity of the amine and consequently required relatively harsh reaction conditions by replacing TBAF and tetrahydrofuran with CsF and acetonitrile, respectively, and elevating the temperature to 70 °C (entry 19). The reaction was further extended to a few 2-(trimethylsilyl)aryl triflates bearing either

### Scheme 2. Chemical Transformations of the Products and Structure Determination



electron-donating or electron-withdrawing groups (entries 21–25). In accordance with previous reports on the addition to an unsymmetrical aryne,<sup>9</sup> poor regioselectivity was obtained from the reaction with aryne precursor **2b** (entry 21).

The aryne-mediated [2,3]-sigmatropic rearrangement was further applied to optically active tertiary allylic amines (Table 2). While poor efficiency of chirality transfer was observed for the [2,3]-sigmatropic rearrangement of L-alanine derivative **1u**, the reaction of either L-proline derivative **1v** or L-pipecolic acid derivative **1w** proceeded smoothly to construct a quaternary stereocenter with inversion of configuration and excellent retention of enantiopurity (entries 1–3). The high efficiency of chirality transfer in the latter two cases was attributable to the highly diastereoselective attack of the cyclic tertiary amine on the benzyne intermediate, generated in situ from 2-(trimethylsilyl)phenyl triflate (**2a**). On the other hand, the aryne-mediated [2,3]-sigmatropic rearrangement could be affected significantly by a chiral auxiliary such as camphorsultam and provided an optically active functionalized homoallylic amine with good diastereoselectivity (entry 4).

The functionalized homoallylic amines we obtained from the above processes were amenable to a number of chemical transformations (Scheme 2). Basic hydrolysis of ester **3aa** followed by condensation with amine **5** led to the formation of amide **6** in 78% yield (two steps). An 84:16 mixture of diene **3ac** and its diastereomer underwent ring-closing metathesis in the presence of Grubbs' II catalyst to furnish cyclic allylic amine **7**,<sup>14</sup> which was separated from its diastereomer through silica gel chromatography. Both amide **6** and cyclic allylic amine **7** were subjected to single-crystal X-ray analysis, which allowed us to determine the absolute configuration of ester **3aa** and diene **3ac**, respectively.<sup>11</sup> Cyclic allylic amine **8**, prepared by ring-closing metathesis of diene **3p**, was treated with 2-(trimethylsilyl)phenyl triflate (**2a**) and CsF to furnish function-

alized cyclopropane **9** as a single diastereomer, whose relative stereochemistry was determined by 2D NOESY spectroscopic analysis. To our knowledge, this type of ring-contraction reaction has never been reported previously. Finally, basic hydrolysis of ester **3a** followed by treatment with acetic anhydride and sodium acetate provided a facile access to functionalized indole **11**.<sup>15</sup>

In summary, we have established a new strategy for the [2,3]-sigmatropic rearrangement of quaternary allylic ammonium ylides via in situ activation of tertiary allylic amines with aryne under mild conditions. Using 2-(trimethylsilyl)aryl triflates as aryne precursors, a range of tertiary allylic amines bearing various electron-withdrawing groups smoothly underwent [2,3]-sigmatropic rearrangement to furnish structurally diverse homoallylic amines in moderate to good yields. The reaction proved useful for the construction of quaternary stereocenters with excellent enantiopurity and functionalized cyclopropanes with extremely high diastereoselectivity. It is noteworthy that the reaction proceeds in the absence of metals, is compatible with moisture and air, and tolerates a wide variety of functional groups.

### ■ ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02344.

Experimental procedures, characterization data, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra and HPLC traces, and crystal data of compounds **6** and **7** (PDF)

X-ray data for compound **6** (CIF)

X-ray data for compound **7** (CIF)

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#### Notes

The authors declare no competing financial interest.

### ■ ACKNOWLEDGMENTS

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