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ZnBr<sub>2</sub>/Oxone-mediated *ipso*-cyclization of *N*-(3-phenylprop-2-yn-1-yl)aniline†Keke Huang,<sup>a</sup> Jia-Ni Li,<sup>b</sup> Guanyinsheng Qiu,<sup>id</sup>\*<sup>bd</sup> Wenlin Xie<sup>c</sup> and Jin-Biao Liu<sup>id</sup>\*<sup>a</sup>

In this work, a selective synthetic strategy towards 1-azaspiro[4.5]deca-3,6,9-trien-8-ones from *N*-tosyl-*N*-(prop-2-yn-1-yl)aniline is developed. The transformation proceeds smoothly in a mixed solvent including acetonitrile and water when ZnBr<sub>2</sub> and Oxone are employed. Mechanism studies show that the reaction proceeds in a regioselective manner *via* a radical *ipso*-cyclization pathway.

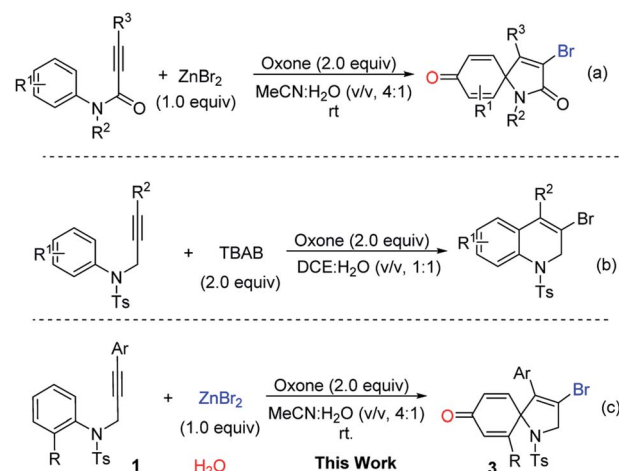
Quaternary carbons are ubiquitous in many useful architectures.<sup>1</sup> Consequently, tremendous effort has been made towards its synthetic methodology development.<sup>2</sup> Among these established achievements, *ipso*-cyclization of arene served as a powerful tool towards quaternary carbon-containing spirocycles.<sup>3</sup> Electrophilic *ipso*-cyclization was initially developed at the beginning of the new century.<sup>4</sup> To date, many unprecedented advances on electrophilic *ipso*-cyclization have already been witnessed, and a series of spirocyclic compounds were achieved accordingly. In the past years a particular emphasis of synthetic chemists was put on radical *ipso*-cyclization.<sup>5</sup> Compared to electrophilic *ipso*-cyclization, the radical way was able to be applicable for more substrates with a broader functional group tolerance.

Recently, a formal 6-*endo* radical cyclization of aryl propiolate was developed to construct substituent-shifted isocoumarin derivatives.<sup>6</sup> Mechanism studies suggested the above formal 6-*endo*-cyclization was constituted by radical  $\alpha$ -addition of propiolate, radical *ipso*-cyclization, and ester migration, which caused the shift of the substituents in core of isocoumarin. To provide a hint on this *ipso*-cyclization, many elegant examples were developed on electrophilic and/or radical *ipso*-cyclization of propiolates, leading to spirocycles 1-oxaspiro[4.5]deca-3,6,9-triene-2,8-diones.<sup>7</sup>

As an important analog of propiolate, *N*-aryl propiolamides was reasonable to be investigated for *ipso*-cyclization.<sup>8</sup> Pleasingly, electrophilic/radical *ipso*-cyclization of *N*-aryl propiolamides was also reached so far. Particularly, for radical pathways, many radical precursors were recognized as efficient

reaction partners. One example from our group indicated that bromo radical was also compatible for the *ipso*-cyclization of *N*-aryl propiolamides, and a series of bromo-containing 1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione was observed (Scheme 1, eqn (a)).<sup>9</sup> As we know, bromo group served as a versatile building block for structural elaboration through these classical transformations with/without metal catalysis. Interestingly, bromo radical was *in situ* generated in the presence of Oxone and bromo anion. In the process, bromo anion occurred to be oxidized into bromo radical through a single electron oxidation, and triggered the radical *ipso*-cyclization of *N*-aryl propiolamides for the synthesis of 1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione as desired.

Over the past years, our group was focusing intensively on developing a more efficient and more economic system to realize regioselective transformations of alkynes.<sup>10</sup> For instance, we recently reported a base-promoted  $\alpha$ -addition of propiolamides, which led to various azetidin-2-ones with high efficiency and good reaction scope.<sup>10a</sup> In addition, the *ortho*-cyclizative reaction of *ortho*-substituent-free *N*-tosyl-*N*-(prop-2-yn-1-yl)aniline was reported by our group under Oxone and tetrabutylammonium



Scheme 1 Proposed route for the synthesis of trienones.

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bromide (TBAB), where released a distinctive compound 3-bromo-1-tosyl-1,2-dihydroquinoline derivatives (Scheme 1, eqn (b)).<sup>11</sup> As our continuous interest on alkyne-based regioselective transformations and in light of the findings presented in Scheme 1a and b, we would like to disclose the radical *ipso*-cyclization of *N*-(prop-2-yn-1-yl)aniline **1** under mild conditions for the synthesis of 1-azaspiro[4.5]deca-3,6,9-trien-8-one **3** (Scheme 1, eqn (c)). Considering our findings on Oxone chemistry,<sup>12</sup> in this paper we envisioned the radical brominative *ipso*-cyclization of *N*-tosyl-*N*-(prop-2-yn-1-yl)aniline could be activated by Oxone and ZnBr<sub>2</sub>. To reduce the possibility of *ortho*-cyclization, the reaction of 2-iodo-*N*-tosyl-*N*-(3-arylprop-2-yn-1-yl)aniline **1a** was herein employed as the model substrate. 2-Iodo-*N*-tosyl-*N*-(3-arylprop-2-yn-1-yl)aniline was often used as a dual-functional building block.<sup>13</sup>

To our delight, a preliminary result from the model reaction of **1a** and ZnBr<sub>2</sub> was favored to deliver the spirocyclic compound 1-azaspiro[4.5]deca-3,6,9-trien-8-one **3a** as expected, and the reaction yield was 70% at room temperature.

Other reaction condition trials on temperature, solvent, and bromo source were optimized accordingly. The results were presented in Table 1. Based on the results, an increase of reaction temperature to 60 °C did not make positive impact on the reaction outcome, just providing the desired product **3a** in 62% yield (entry 2, Table 1). A similar yield was observed when the loading of ZnBr<sub>2</sub> was used (entry 3, Table 1). The reactions using other solvents, including DCE : H<sub>2</sub>O (v/v = 1 : 1) and THF : H<sub>2</sub>O (v/v = 1 : 1), gave rise to inferior yields (entries 4 and 5, Table 1). Changing the ratio between MeCN and H<sub>2</sub>O did not give better yields, suggesting MeCN : H<sub>2</sub>O (v/v = 4 : 1) being the

best choice (entries 6 and 7, Table 1). The use of TBAB, KBr or NaBr as a replacement of ZnBr<sub>2</sub> was not favourable for the reaction, resulting in lower yield of the desired product **3a** (entries 8–10 Table 1). The use of 2.0 equiv. of TEMPO as a radical scavenger totally shut the model reaction down, probably suggesting the model reaction going through a radical pathway (entry 11, Table 1).

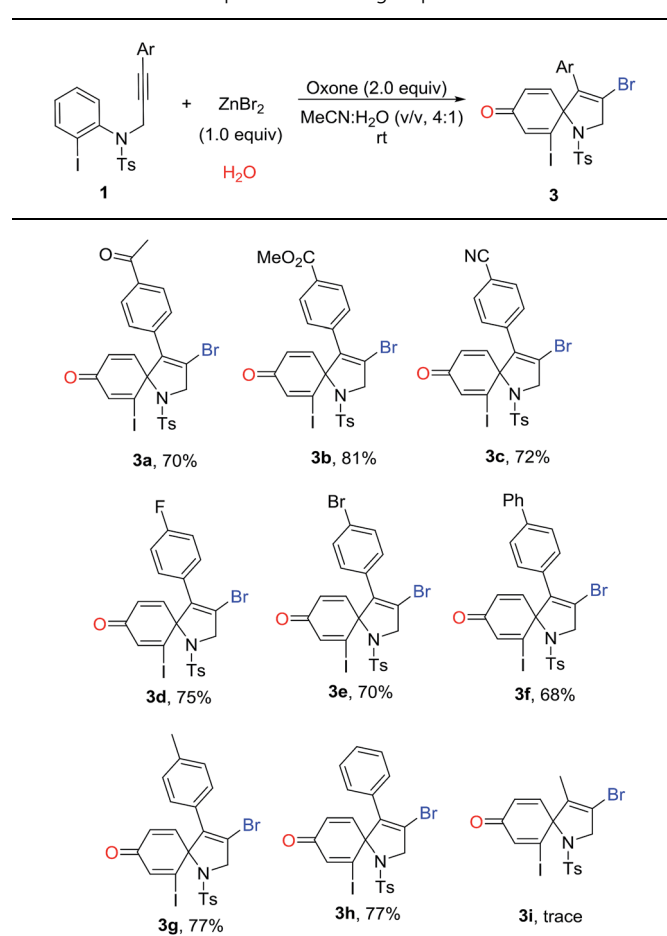
With the optimized conditions in hand, we then explored the reaction generality. The results are illustrated in Table 2. As shown in Table 2, a series of substituted 1-azaspiro[4.5]deca-3,6,9-trien-8-one **3** was achieved in good yields. The substituent Ar effects of aryl alkynes were investigated. The results reveal that both electron-donating groups and electron-deficient groups were compatible for the reactions. For example, the reaction with the substrate containing a 4-cyano-phenyl group on Ar group afforded the desired 1-azaspiro[4.5]deca-3,6,9-trien-8-one **3c** in a 72% yield, while the substrate having a 4-methylphenyl gave the corresponding product **3g** in a 77% yield. Other substituents including 4-acetylphenyl, 4-esterphenyl, 4-fluorophenyl, 4-bromophenyl, and 4-phenylphenyl groups were efficient reaction partners, leading to the corresponding products **3a–3h** in 68–81% yields. However, the

**Table 1** Initial studies for the reaction of regioselective spirocyclization of 2-iodo-*N*-tosyl-*N*-(3-arylprop-2-yn-1-yl)aniline<sup>a</sup>

Entry	Variation of standard conditions	Yield of <b>3a</b> <sup>a,b</sup> (%)
1	—	70
2	60 °C	62
3	1.5 equiv. ZnBr <sub>2</sub>	70
4	DCE : H <sub>2</sub> O (v/v = 1 : 1)	61
5	THF : H <sub>2</sub> O (v/v = 1 : 1)	32
6	MeCN : H <sub>2</sub> O (v/v, 10 : 1)	67
7	MeCN : H <sub>2</sub> O (v/v, 1 : 1)	45
8	2.0 equiv. TBAB	47
9	2.0 equiv. KBr	41
10	2.0 equiv. NaBr	38
11	2.0 equiv. TEMPO	0

<sup>a</sup> Isolated yield based on **1a**. <sup>b</sup> Standard conditions: **1a** (0.2 mmol), ZnBr<sub>2</sub> (1 equiv.), Oxone (2.0 equiv.), solvent (2 mL), rt, overnight; TBAB = *n*-tetrabutyl ammonium bromide; Oxone = 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>.

**Table 2** Reaction scope: effect of Ar group<sup>a</sup>



<sup>a</sup> Isolated yield based on **1**.



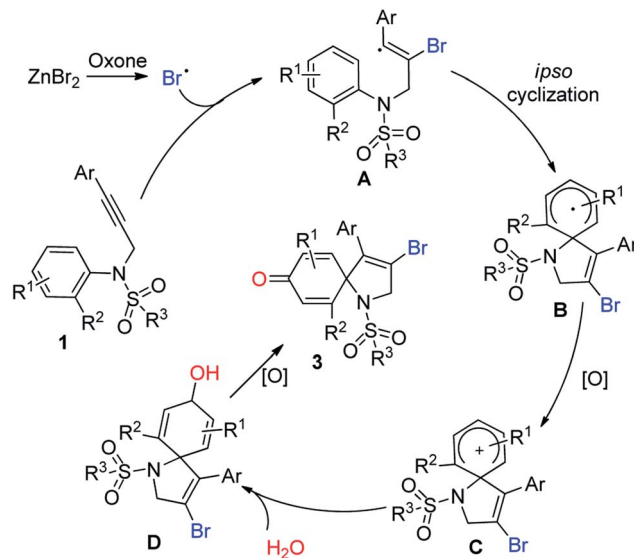
reaction of 2-iodo-*N*-tosyl-*N*-(but-2-yn-1-yl)aniline **1i** became complex, and did not offer the desired product **3i**. It was reasoned that methyl in alkyne took part in the reaction, causing the reaction complex.

Subsequently, we explored the tolerance of substituents on ring of aniline (Table 3). Encouragingly, it seemed that R<sup>1</sup> substituents could be replaced by methyl and chloro. The corresponding products **3j–3l** were obtained in 50–65% yields. For instance, the reaction using the substrate with 5-methyl substituent produced a desired 1-azaspiro[4.5]deca-3,6,9-trien-8-one **3j** in a 65% yield, while using the substrate substituted by 5-chlorogave rise to **3k** in a 62% yield. Surprising, the reaction was suppressed by the presence of the 3-chloro group in substituent R<sup>1</sup>, resulting in a decreased yield of **3l** in 50% yield. The substituent effect of R<sup>2</sup> on the ring of aniline was also exploited. Beside iodo function, it was pleased to find the R<sup>2</sup> could be also replaced by bromo and methyl, and the yield of corresponding products **3m** and **3n** were 75% and 68%, respectively. It was noteworthy that 1-azaspiro[4.5]deca-3,6,9-trien-8-ones **3b** and **3n** has been synthesized under the standard conditions of Scheme 1b.<sup>11</sup> Compared to our previous finding, this results were highlighted by a higher efficiency, indicating a broader reaction scope simultaneously.

Table 3 Reaction scope: substituent effect<sup>a</sup>

<b>Substituent effect of R<sup>1</sup>:</b>	
	<b>3j</b> , 65%
	<b>3k</b> , 62%
	<b>3l</b> , 50%
<b>Substituent effect of R<sup>2</sup>:</b>	
	<b>3m</b> , 75%
	<b>3n</b> , 68%
<b>Substituent effect of N-protecting group:</b>	
	<b>3o</b> , 72%
	<b>3p</b> , 68%
	<b>3q</b> , 61%

<sup>a</sup> Isolated yield based on **1**.



Scheme 2 Proposed mechanism.

Finally, various *N*-protecting groups were screened. Pleasingly, *N*-tosyl could be replaced with 4-bromophenylsulfonyl, 2-naphthalenesulfonyl, and 2-thiophenesulfonyl. The desired 1-azaspiro[4.5]deca-3,6,9-trien-8-ones **3o–3q** were detected in 61–72% yields. However, when acetyl group or hydrogen atom attached on the nitrogen atom, no desired product was observed.

Enlightened by the above information and the previous results, a plausible mechanism was proposed in Scheme 2. As illustrated in Scheme 2, bromo anion was oxidized into bromo radical,<sup>14</sup> which occurred to undergo regioselective radical  $\alpha$ -addition to form an intermediate **A**.<sup>15</sup> Radical *ipso*-cyclization of the intermediate **A** then took place. Followed by oxidation, the spiro intermediate **B** was converted into a spirocation intermediate **C**. Thanks to the use of water as a mixed solvent, herein the intermediate **C** was trapped by water to afford hydroxyl-linked species **D**. Oxidation again provided the final targeted molecules **3**.

In conclusion, we have developed a selective synthetic strategy towards 1-azaspiro[4.5]deca-3,6,9-trien-8-ones from *N*-tosyl-*N*-(prop-2-yn-1-yl)aniline. The transformation proceeded smoothly in a mixed solvent system of MeCN/H<sub>2</sub>O when ZnBr<sub>2</sub> and Oxone was employed as the promoters. Mechanism studies showed that the reaction proceeded in a regioselective manner *via* a radical *ipso*-cyclization pathway. It was believed that the products were synthetically versatile since iodo and bromo groups in the product 1-azaspiro[4.5]deca-3,6,9-trien-8-ones was ready to be structurally elaborated through some classical transformations.

## Conflicts of interest

There are no conflicts to declare.

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