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Photocatalyzed cascade Meerwein addition/cyclization of *N*-benzylacryamides toward azaspirocycles†

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A visible-light-induced cascade Meerwein Addition/cyclization of alkenes involving C-F bond cleavage was developed. This method offers rapid entry to azaspirocyclic cyclohexadienones from *N*-benzylacrylamides *via* C-F bond cleavage applying H_2O as the external oxygen source, allowing for the incorporation of various aromatic moieties orignated from aryldiazonium salts.

Azaspirocycles are important structural motifs present in a broad range of biologically active molecules,[1] such as pronuciferine,[1d] NO and ROS inhibitors,[1e] and Eryrhatinone.[1f] Dearomatization reaction has been widely identified as a rapid entry for synthesis of more valuable and complex azaspirocyclic skeletons from simple aromatic molecules.[2-4] In this context, many research groups reported Lewis-acid-catalyzed[2] and transition-metal-catalyzed[3] dearomative cyclization toward azaspirocyclic ring systems, whereas only a handful of examples employing the photocatalysis strategy are disclosed for this purpose.[4] Of note, photoredox catalysis has recently emerged as a powerful synthetic strategy for the assembly of diverse molecules for its merits such as eco-friendliness, sustainability, convenience.[5] Thus, the development of mild photocatalysis protocol in dearomative spirocyclization is of high interest for the synthetic practitioners.

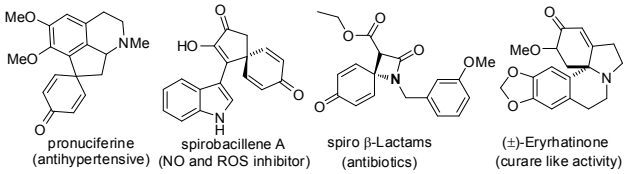
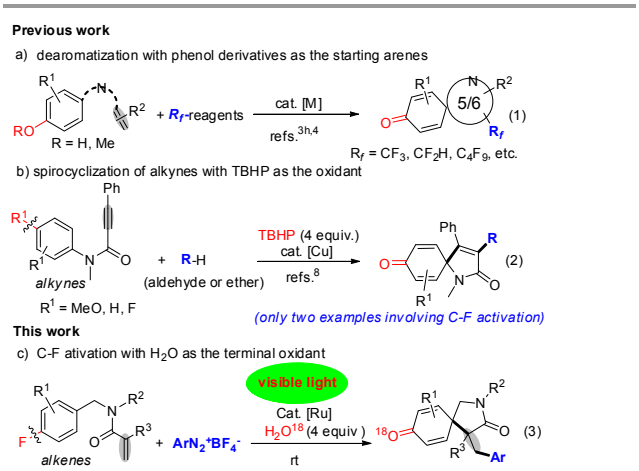


Figure 1 Selected examples of biologically active azaspirocycle molecules.



Scheme 1 Dearomative spirocyclization leading to azaspirocyclic Cyclohexadienones.

On the other hand, expanding the diversity of starting aromatic molecules for the dearomative reactions toward desired azaspirocyclic cyclohexadienones has recently attracted substantial attentions.[6] Notably, these successes were mainly limited to the utilization of phenol or its derivatives as the starting aromatic molecules to introduce carbonyl moieties without the requirement of external O-atom (eqn (1), Scheme 1).[4-6] Aryl fluorides are readily available molecules and function as versatile synthons (e.g., Sanger's reagent) despite commonly high stability and chemical inertness of C-F bond, which are promising to act as alternative starting arenes in the dearomative spirocyclization *via* C-F cleavage.[7] In this regard, a rare example involving the oxidative C-F cleavage of alkynes (e.g., *N*-arylpropiolamides) was recently disclosed by Li's group.[8] However, excess hazardous oxidant TBHP (*tert*-butyl hydroperoxide) as the external oxygen source was required to form the carbonyl group (eqn (2)). In addition, these TBHP-mediated oxidative spirocyclization involving C-F cleavage exhibited a very limited substrate scope, and only

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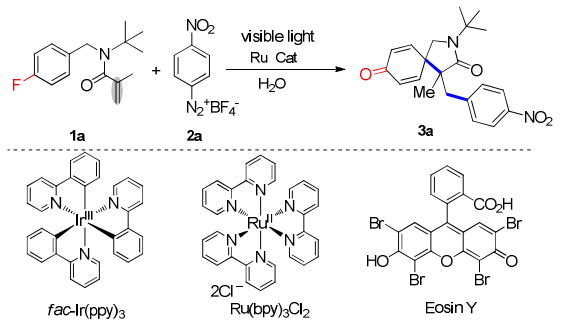
two examples using *N*-(*p*-fluoroaryl)propiolamides have been demonstrated in Li's works.[8a] From a diversification perspective, exploiting new starting arenes in the dearomatization involving C-F cleavage, leading to azaspirocyclic cyclohexadienones, with clean and safe oxygen source arguably remains synthetically interesting. As the continuation of our interest in photocatalysis and Meerwein cyclization,[9] we herein want to demonstrate a visible-light-induced dearomative Meerwein cyclization of alkenes with aryldiazonium salts involving C-F bond cleavage employing H_2O as the oxygen source,[10,11] allowing for the general synthesis of 2-azaspiro[4.5]deca-6,9-diene-3,8-diones (eqn (3)). Notably, it is arguably of practically interest to introduce the carbonyl group into azaspirocyclic core using clean, non-toxic and cost-effective water as an oxygen source by cost-effective Ru-based photoredox catalysis.

Our preliminary investigation was concentrated on the reactions between *N*-(*p*-fluorobenzyl)acrylamides **1a** and 4-nitrophenyldiazonium tetrafluoroborate **2a** under irradiation from 5 W blue LEDs (Table 1). Delightedly, the initial experiment using 5 mol% $Ru(bpy)_3Cl_2$ as the photocatalyst, DMF as the solvent, and K_3PO_4 as the base led to the desired product **3a** in a yield of 48% (Table 1, entry 1). Inspired by the results, several typical photocatalyst such as *fac*-Ir(ppy)$_3$, $Ru(bpy)_3Cl_2•6H_2O$ and Eosin Y were subsequently investigated (entries 2-4). Unfortunately, none of them gave better results than $Ru(bpy)_3Cl_2$, and Eosin Y was completely inefficient for the reaction. In order to improve the yield further, several bases were sequentially examined, and the results showed that K_2CO_3 was the optimal to increase the yield to 75% (entry 7), whereas the use of the K_2HPO_4, KH_2PO_4, KOAc, Et_3N and etc. gave inferior yields (entries 5-10). In addition, the photocatalyst $Ru(bpz)_3[PF_6]_2$ with higher redox potential cannot improve the reaction yield further (entry 8). Next, the Further solvent screening turned out that DMF was the optimal medium among these solvents such as dioxane, DMSO, CH_3CN, CH_2Cl_2 (entries 11-14). Given that the visible-light irradiation and Ru catalyst are necessary for the dearomative spirocyclization, two control experiments were designed and conducted. Expectedly, the cyclization reactions were found to be restrained seriously with the removal of either the light irradiation or Ru catalyst (entries 15 and 16). Remarkably, small amount of water plays significant role in the reactions, and should function as an oxygen source in the C-F carbonylation process. The conditions investigation showed that 4 equiv. of H_2O gave the best results, whereas no reaction took place in the absence of H_2O (for detail, see SI). Interestingly, ethanol was also observed to be a viable oxygen source instead of H_20 in the reaction, and afforded a slightly decreased reaction yield (entry 18).

With the optimal conditions in hand, we targeted to investigate the scope of substrate in the dearomative cyclization leading to azaspirocyclic cyclohexadienones (Scheme 2). Initially, we screened the scope of aryldiazonium

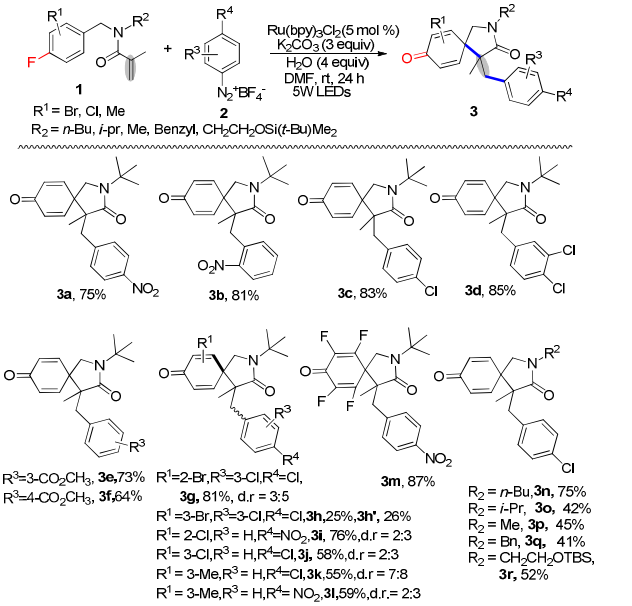
Table 1 Optimization of reaction conditions for the synthesis of **3a**[a]



entry	catalyst	base	solvent	yield of **3a** (%)[b]
1	$Ru(bpy)_3Cl_2$	K_3PO_4	DMF	48
2	*fac*-Ir(ppy)$_3$	K_3PO_4	DMF	36
3	$Ru(bpy)_3Cl_2•6H_2O$	K_3PO_4	DMF	12
4	Eosin Y	K_3PO_4	DMF	0
5	$Ru(bpy)_3Cl_2$	K_2HPO_4	DMF	25
6	$Ru(bpy)_3Cl_2$	KH_2PO_4	DMF	27
7	**$Ru(bpy)_3Cl_2$**	**K_2CO_3**	**DMF**	**75**
8	$Ru(bpz)_3[PF_6]_2$	K_2CO_3	DMF	51
9	$Ru(bpy)_3Cl_2$	KOAc	DMF	32
10	$Ru(bpy)_3Cl_2$	Et_3N	DMF	21
11	$Ru(bpy)_3Cl_2$	K_2CO_3	dioxane	64
12	$Ru(bpy)_3Cl_2$	K_2CO_3	DMSO	55
13	$Ru(bpy)_3Cl_2$	K_2CO_3	CH_3CN	26
14	$Ru(bpy)_3Cl_2$	K_2CO_3	CH_2Cl_2	11
15	none	K_2CO_3	DMF	0
16[c]	$Ru(bpy)_3Cl_2$	K_2CO_3	DMF	0
17[d]	$Ru(bpy)_3Cl_2$	K_2CO_3	DMF	trace
18[e]	$Ru(bpy)_3Cl_2$	K_2CO_3	DMF	69

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (2 equiv.), photocatalyst (5 mol%), base (3 equiv.), H_2O (4 equiv.) and solvent (2 mL) were irradiated with a 5 W blue LEDs at room temperaturefor 24 h. DMF = *N*,*N*-dimethyl formamide, DMSO = dimethyl sulfoxide. [b] Yield of the isolated product. [c] Without light irradiation. [d] Without the addition of external water. [e] Ethanol (4 equiv.) in stead of H_2O.

Scheme 2 Substrate scope in the spirocyclizaction involving C-F bond cleavage[a,b]



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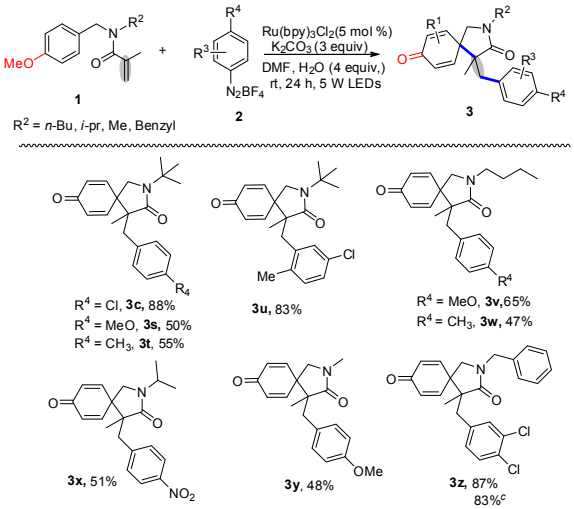
[a] Reaction conditions: **1** (0.3 mmol), **2** (2 equiv), $Ru(bpy)_3Cl_2$ (5 mol%), K_2CO_3 (3 equiv.), H_2O (4 equiv.) and DMF (2 mL) were irradiated with a 5 W blue LEDs at room temperature for 24 h. [b] Yield of the isolated product.

tetrafluoroborates. Gratifyingly, the optimal conditions were compatible with various aryldiazonium tetrafluoroborates with 2/4-NO_2, 4-Cl, 3,4-2Cl, 3/4-CO_2Me substituents, thereby affording a series of azaspirocyclic cyclohexadienones in moderate to good yield (**3a**-**3f**). Next, we embarked on investigating the scope of the *N*-(fluorobenzyl)acrylamides with different substituents on the aromatic ring. Of note, the cyclization of the benzylacrylamides bearing Br or Cl at 2/3-position of aromatic ring proceeded smoothly, leading to corresponding diastereoisomers in moderate yields (**3g** and **3i**, **3h** and **3j**). To our delight, perfluorinated aryl ring were also tolerated under the reaction system, affording the corresponding polyfluoroazaspirocycle **3m** *via* site-selective C-F cleavage. Further screening revealed that a series of substituents on the *N*-atom such as *n*-butyl, *i*-propyl, methyl, benzyl and CH_2CH_2OTBS groups were also compatible with the optimal conditions (**3n**-**3r**).

Next, to further explore the application of this cyclization system, the dearomatization reactivity of *N*-benzylacrylamides with a *para*-methoxyl substituent is also investigated under the optimal conditions (Scheme 3). Expectedly, a series of substituents such as *t*-butyl, *n*-butyl, *i*-propyl, Me, and benzyl on *N*-atom of the acrylamides moiety was well tolerated and furnished a series of azaspirocyclic cyclohexadienones in moderate to good yields (Scheme 3). Aryldiazonium tetrafluoroborates irrespective of with electron-donating substituents (e.g., MeO, CH_3) or electron-withdrawing substituents (e.g., Cl and NO_2) were compatible with the optimal conditions. Of note, the yields in the dearomatization were commonly higher comparing with above-mentioned examples involving C-F bond cleavage leading to the same

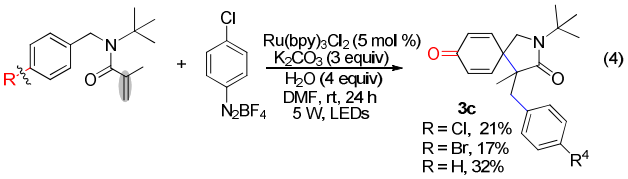
Scheme 3 Dearomative Meerwein cyclization of *N*-(*p*-methoxyl)benzylacrylamides[a,b]

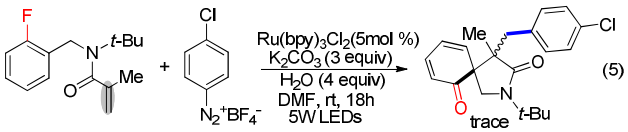


[a] Reaction conditions: **1** (0.3 mmol), **2** (2 equiv.), $Ru(bpy)_3Cl_2$ (5 mol%), K_2CO_3 (3 equiv.), H_2O (4 equiv.)and DMF (2 mL) were irradiated with a 5 W blue LEDs at room temperature for 24 h. [b] Yield of the isolated product. [c] Without the addition of H_2O.

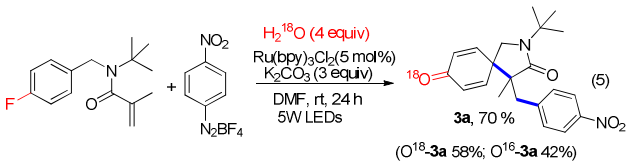
products (e.g., **3c**). The dearomatization of *N*-(methoxybenzyl)acrylamides could also work without the H_2O as the additive, suggesting that the carbonyl group thereby formed in these reactions should arise from the MeO substituent (**3z**).[4c]

In addition, we also investigated the reactivity of *N*-benzylacrylamides with other *para*-substituents on the phenyl moiety under the standard conditions (eqn (4)). In the presence of *p*-$ClC_6H_4N_2^+BF_4^-$, these reactions did work to give desired azaspirocyclic cyclohexadienones **3c** *via* C-X (x = Cl, Br, H) activation, but only in low yields (<32%), which suggested that the dearomative spirocyclization involving C-F cleavage would be more reactive to afford synthetically useful yields. In addition, the reaction using *N*-(*ortho*-fluorobenzyl)acrylamide as a substrate failed to afford the expected azaspirocycles *via* the *ortho*-position C-F cleavage (eqn(5)), and yielded a small amount of azaspirocycle *via* the C-H cleavage at the 4-position as well (<10%).





Finally, the O^{18}-labelled control experiment was designed and conducted (eqn (6)). Expectedly, we found that the azaspirocyclic cyclohexadienone **3a** containing O^{18}-atom thereby obtained was increased as the main product with the addition 4 equiv of $H_2{}^{18}O$ in the reaction mixture, which suggested that the oxygen atom of newly-formed carbonyl group should originate from H_2O in the C-F cleavage process (for detail, see SI).[11,12]



On the basis of above experimental results and the literature, a rational reaction mechanism is proposed in Scheme 4.[3-12] First, photoexcitation of $[Ru(bpy)_3]^{2+}$ by light irradiation generates the excited state $*[Ru(bpy)_3]^{2+}$, and it is then oxidizes to $[Ru(bpy)_3]^{3+}$ by $ArN_2^+BF_4^-$ (Ar = *p*-$NO_2C_6H_4$), thereby leading to a radical Ar• *via* a single-electron-transfer (SET) process.[13] Subsequently, the radical Ar• adds onto the C=C bond of **1a** to give intermediate **A**. Then the intermediate **A** is transformed into intermediate **B** *via* a dearomative cyclization process. In the presence of Ru(III) species, the intermediate **B** is then oxidized to the carbocation **C** , along with the Ru(III) species simultaneously reducing to its initial state Ru(II) species. Finally, the carbocation **C** reacts with H_2O

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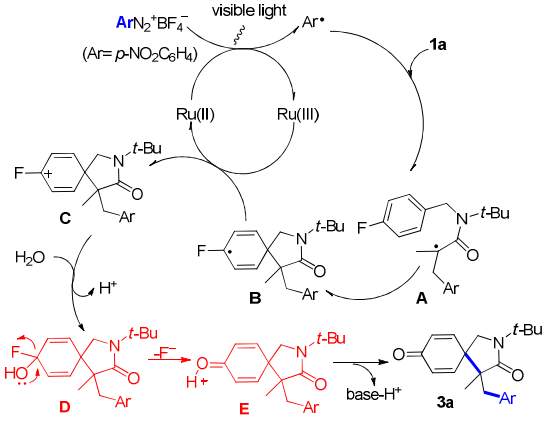
to yield cation **E** *via* the cleavage of C-F bond.[12] Finally, the intermediate **E** is transformed to desired **3a** with the abstraction of hydrogen atom under the aid of base.

Scheme 4 Proposed mechanism for the formation of **3a**



Conclusions

In summary, we have disclosed a visible-light-induced dearomative Meerwein cyclization of *N*-(*p*/*o*-fluorobenzyl)acrylamide *via* C-F bond cleavage applying water as the oxygen source for the first time. The spirocyclization reactions exhibit excellent compatibility with a wide scope of *N*-(fluorobenzyl)acrylamide and aryldiazonium salts, allowing for rapid construction of various azaspirocyclic cyclohexadienones under mild conditions (e.g., room temperature). The use of readily available aryldiazonium salts as aryl radical source, and environment-friendly water as the external oxygen source, in combination with clean and atomic-economy Ru-based photoredox catalysis, make this protocol high attractive for organic and medicinal practitioner, therein providing a valuable complementary entry to 2-azaspiro[4.5]deca-6,9-diene-3,8-diones.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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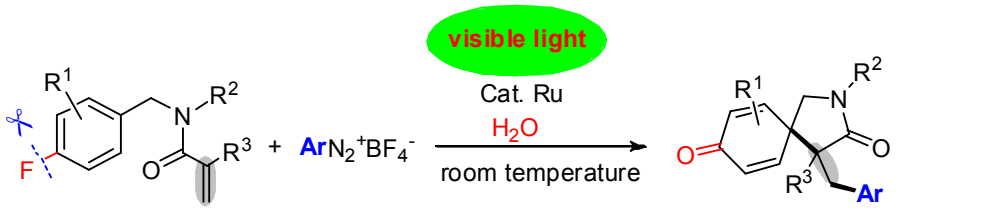

28 examples, up to 87% yields

- water as the terminal oxidant or oxygen source
- highly efficient C-F bond activation
- atomic-economy photoredox catalysis
- mild reaction conditions and broad substrate scope