Organic Letters
Letter
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# Carbon Cationic Relay via Superelectrophiles: Synthesis of Spiro-diazafluorenes

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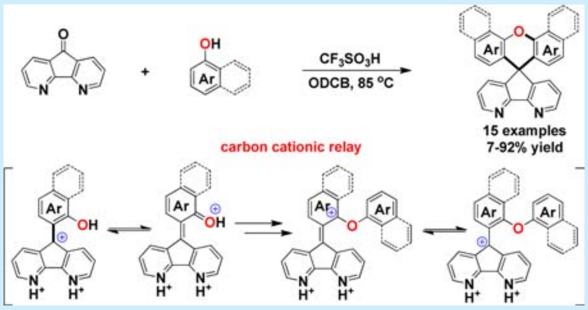
*Supporting Information*

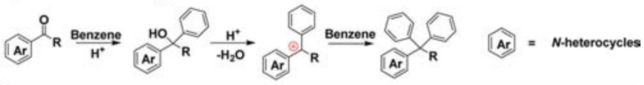
**ABSTRACT:** Superelectrophilic-initiated carbon cationic relay reactions of diazafluorenones with phenols were developed to provide strategically novel and atom-economic access to spirodiazafluorenes via tandem Friedel−Crafts reaction, nucleophilic addition, and intramolecular cyclization sequences. A range of spirodiazafluorenes that are difficult to synthesize with traditional protocols has been constructed successfully in middle to high yields using this method.



Since it was first exploited in the 1970s by Olah,[1] superelectrophilic chemistry has attracted growing attention due to its novel reaction pathways,[2] charge distributions, and conformational transformations.[3] Distinguished from common electrophilic reactions, highly charged organic intermediates in superelectrophilic reactions give rise to evidently enhancing reactivity because of charge−charge Coulombic repulsion.[4] These cations containing at least two positive charges stem from monocationic electrophiles with lone-pair or p-electrons able to coordinate with protons in superacid.[1b,4,5] Among them, *N*-heterocycles involving pyridine and imidazole usually participate in superelectrophilic Friedel−Crafts processes,[5a−c,6] which have been divided into two types according to the occurrence of carbon cationic charge ($C^+$) delocalization until now (Scheme 1a,[5a]b[5a−c]). One of the processes connected with $C^+$ migration is capable of rendering promising candidates for development of cationic relay chemistry, which is the counterpart of anion-relay chemistry.[7] However, these $C^+$ relay reactions have not yet been established on account of $C^+$ quenching for aromatization (Scheme 1b). As a result, some novel ideas such as discovery of rearrangement[7] or charge regeneration from heterolysis are raised to overcome above difficulty. Hence, developing superelectrophile-based $C^+$ relay reactions to easily create multifunctional building blocks such as *N*-heterocycle-based spiro-arenes is of great significance but still challengeable.

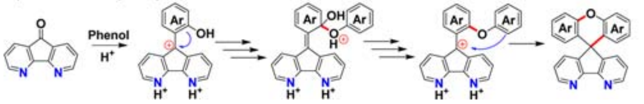
**Scheme 1. Superelectrophilic Friedel−Crafts Reactions**

1a):Previous work:No charge delocalization from ketone



1b):Previous work:Charge delocalization from alcohol

1c):Our work: Charge relay from diazafluorenone



With rigid π-conjugated orthogonal configuration, spirofluorenes (SFs) play a key role in organic/plastic electronics including OLEDs,[8] solar cells,[9] memory devices,[10] and others.[11] On that basis, spirodiazafluorenes (SDAFs) incorporating functions of diazafluorenes (DAFs) such as electron-acceptor, coordination ability, and C−N···H interactions will expand potential applications in chemistry and materials.[12] However, there are merely three kinds of SDAFs, as the synthetic method called Clarkson's route suffers from complicated steps and limited brominated sites.[12] In addition, DAFs characteristics cause SDAFs failure to be constructed in a simple protocol such as Xie and Huang's Friedel−Crafts reaction.[8f,13] Fortunately, inspired by transformation from DAFs to superelectrophiles participating in the process, we are likely to overcome this synthetic obstacle. DAF tertiary alcohol-based superelectrophilic precursors can be afforded via in situ formation of diazafluorenones and phenols. In addition, repetitive dehy-

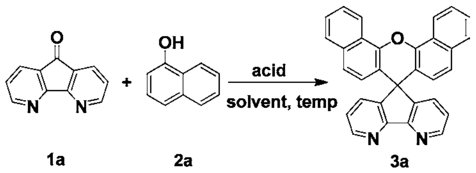
**Received:** August 30, 2016
**Published:** December 1, 2016

DOI: 10.1021/acs.orglett.6b02595
*Org. Lett.* 2016, 18, 6220−6223

dration guarantees the cationic-relay process. Toward this end, cationic-relay reactions are proposed to construct SDAFs, which not only provide a one-pot method superior to traditional routes but also realize $C^+$ relay in superelectrophilic chemistry (Scheme 1c). Therefore, in this work, we focus our attention on the synthesis of SDAFs where a $C^+$ relay process was taken advantage of in order to construct C–O and C–C bonds ingeniously.

In order to research this relay reaction and optimize conditions, diazafluorenone (**1a**) and 1-naphthol (**2a**) were used as model reaction substrates (Table 1). First, several strong acids (10 equiv), determining the start of reaction, were investigated by using 1, 2-dichlorobenzene (ODCB) as the solvent at 100 °C (entries 1–3). This reaction proved recalcitrant when using $CH_3SO_3H$ or $H_2SO_4$ and mass starting materials remained. To our delight, superacid $CF_3SO_3H$ can afford **3a** in 40% yield and **1a** did not exist, but reducing the amount of $CF_3SO_3H$ substantially decreased the yield of **3a** (entry 4) and most **1a** was surplus as well, suggesting that an excess amount (10 equiv) of $CF_3SO_3H$ should be a crucial condition associated with superelectrophilic generation according to previous literatures.[5a] Second, the effect of temperature upon $CF_3SO_3H$ (10 equiv) and ODCB provided 25% (35 °C), 40% (60 and 100 °C), 50% (85 °C), and 8% (120 °C) yields respectively (entries 3, 5–8). High temperature led to product decomposition and low temperature prevented dehydration, both of which obviously lower the yield.[5a,b] Furthermore, ODCB was screened to be the most suitable solvent in comparison with other solvents such as DMSO, 1,4-dioxane, and DCE (entries 9–11). In addition, toluene can react with **1a**, which lies in 0 yield of **3a** (entry 12). Finally, the feeding amount of **2a** was reduced to 3.0 equiv with a similar yield (entry 13), indicating that decreasing yields, with less acid, are consistent with the formation of highly charged ions.

**Table 1. Cascades Forming SDAFs (3a): Optimization Using Diazafluorenone and 1-Naphthol**[a]

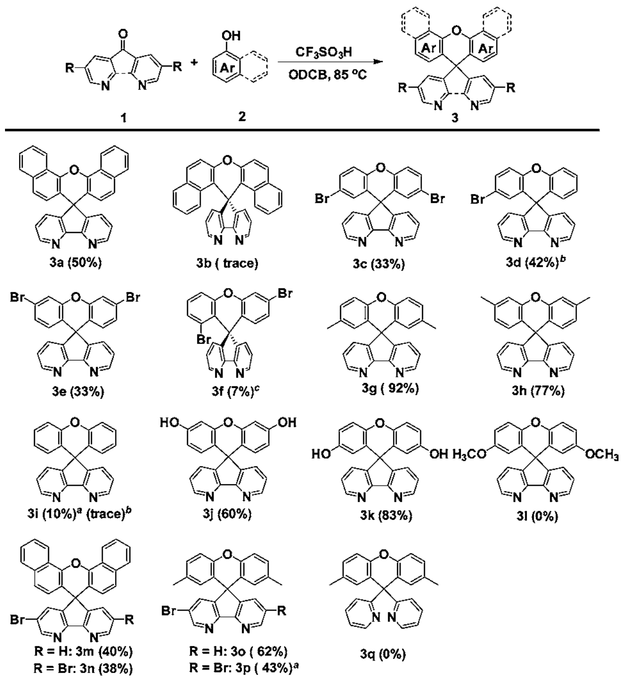


| entry | acid | temp (°C) | solvent | yield[b] (%) |
|---|---|---|---|---|
| 1 | $CH_3SO_3H$ | 100 | ODCB | trace |
| 2 | $H_2SO_4$ | 100 | ODCB | trace |
| 3 | $CF_3SO_3H$ | 100 | ODCB | 40 |
| 4 | $CF_3SO_3H$ | 85 | ODCB | trace[cd] |
| 5 | $CF_3SO_3H$ | 120 | ODCB | 8 |
| **6** | **$CF_3SO_3H$** | **85** | **ODCB** | **50** |
| 7 | $CF_3SO_3H$ | 60 | ODCB | 40 |
| 8 | $CF_3SO_3H$ | 35 | ODCB | 25 |
| 9 | $CF_3SO_3H$ | 85 | DMSO | trace |
| 10 | $CF_3SO_3H$ | 85 | dioxane | 0 |
| 11 | $CF_3SO_3H$ | 85 | DCE | 30 |
| 12 | $CF_3SO_3H$ | 85 | toluene | 0 |
| 13 | $CF_3SO_3H$ | 85 | ODCB | 45[e] |

[a] Unless otherwise noted, **1a** (1 mmol) and **2a** (5 mmol) with $CF_3SO_3H$ (10 mmol) in ODCB (2.5 mL) were stirred at 85 °C. [b] Isolated yield. [c] With 3 equiv of $CF_3SO_3H$. [d] With 6 equiv of $CF_3SO_3H$. [e] With 3 equiv of **2a**.

To extend the scope of the method to the synthesis of SDAFs, the reaction of several diazafluorenones and phenols was evaluated under the optimized conditions (Table 1, entry 6), and different substituent groups on phenols were examined (Scheme 2). Compared with 1-naphthol, 2-naphthol was not compatible with this route. 4-Bromophenol led to the corresponding spiro-products **3c** in 33% yields, with the byproducts **3d** and **3i** being obtained in 42% yield and a trace amount, respectively, as well. What's more, the yield of **3d** will increase at the cost of lowering the yield of **3c** if the reaction time is prolonged. 3-Bromophenol and **1a** were reacted to achieve the desired product **3e** isolated in 33% yield and byproduct **3f** (in 7% yield) with a strange asymmetric structure where one bromine atom seemed to migrate from the 3′ site to the 1′ site on the xanthene. In fact, a couple of isomerides (**3e** and **3f**) were obtained because one bromine atom rotates with the rotary benzene and forms two kinds of conformations after construction of the ether bond. *p*-Cresol and *m*-cresol afforded spiro-products **3g** and **3h** in 92% and 77% yields, respectively. Hydroquinone and resorcinol were adapted to result in **3j** and **3k** in moderate yields. Nevertheless, 4-methoxyphenol (**3l**) and phenol (**3i**) were not tolerated, affording the desired products in 0–10% yields, respectively. The above results suggested that it is essential to enhance the yields of spiro-adducts by driving **1a** to attack the *o*-position of phenols induced by electronic or steric effects. On the other hand, the scope of diazafluorenones was examined roughly. Bromo-derived diazafluorenones were proved to be less effective, as manifested by reserving spiro-products (**3m–p**) in low to moderate yields. Also, when di(pyridin-2-yl)methanone was subjected to above identical

**Scheme 2. Synthetic Method of SDAFs via One-Pot Cascade Reaction**[a]



[a] Reaction conditions: **1** (1 mmol) and **2** (5 mmol) with $CF_3SO_3H$ acid (10 mmol) in 1, 2-dichlorobenzene (2 mL) were stirred at 85 °C. Isolated yield. [b] The byproduct in the reaction of **1a** with 4-bromophenol. [c] The byproduct in the reaction of **1a** with 3-bromophenol.

DOI: 10.1021/acs.orglett.6b02595
Org. Lett. 2016, 18, 6220–6223

conditions, no desired product was obtained owing to its special electronic effects, which are responsible for the inhibition of the $C^+$ relay process.[5c]

$^1H$ and $^{13}C$ NMR and HRMS were exerted to precisely demonstrate the molecular structure of SDAFs (in Supporting Information). It is very interesting to observe the single-crystal structure of **3f** in terms of spiro-structure and noncovalent force (Figure 1).[14] In this structure, the dihedral angle between DAF and xanthene plane is 90.521°, exhibiting an approximately perpendicular geometric configuration. In addition, the dihedral angle on the xanthene moiety is 174.163°, which is not an absolute plane. Apart from the spiro-skeleton, intermolecular interactions are depicted by taking measurement of the distance between molecules. For **3f**, two kinds of weak forces control its crystal involving N···Br and C−N···H force in the distance of 2.951 and 2.621 Å, respectively. Furthermore, the C−N···H force can also be observed unambiguously in the $^1H$ NMR spectrum (Supporting Information).

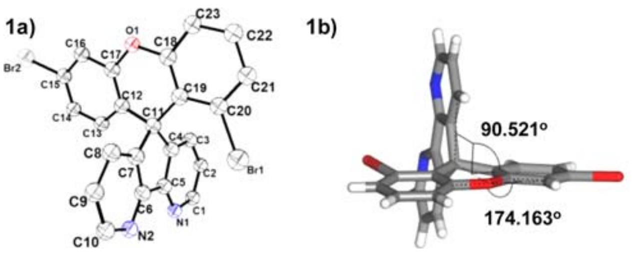
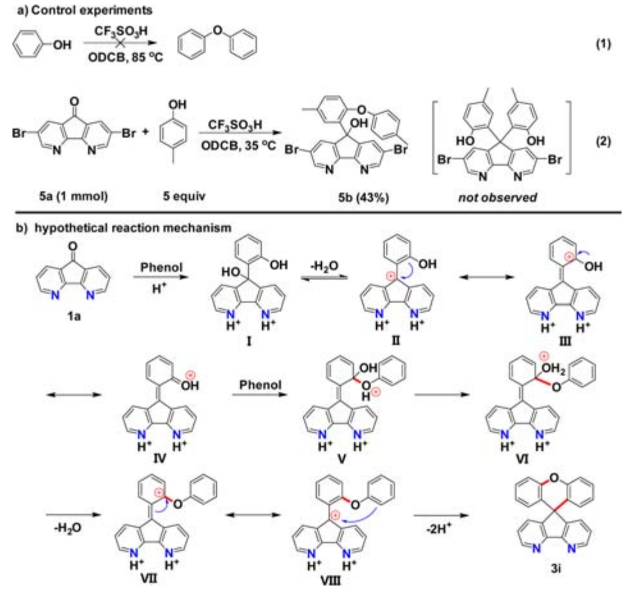


**Figure 1.** X-ray crystal structure of **3f**.

To further study the cationic relay reaction pathway, control experiments were performed (Scheme 3a). One experiment showed that no corresponding oxydibenzene was observed in the reaction of phenol under the same conditions, with substrate phenol recovered quantitatively (eq 1). On the contrary, the other experiment actually showed that the reactions of **5a** and *p*-cresol at 35 °C gave the corresponding DAF-derived tertiary alcohol **5b** (eq 2). The results indicated that (i) it is extremely difficult to intermolecularly build up an ether bond via two phenolic hydroxyl groups except for special activity and (ii) ether bond formation is involved in the mechanism as the key step. Furthermore, DAF-derived superelectrophiles should play an important role in which positive charge delocalization to phenol evidently enhances its reactivity, making it possible to construct an intermolecular C−O bond.

**Scheme 3. Control Experiments (a) and Hypothetical Reaction Mechanism (b, 3i Used as an Example)**



On the basis of all of the results described above, a possible mechanism for the cascade transformation into SDAFs (**3i** as an example) is proposed as depicted in Scheme 3b. An acid-induced intermolecular Friedel−Crafts reaction of **1a** and phenol takes place first, giving the key tertiary alcohol **I**. Then dehydration of **I** furnishes tertiary carbenium ion **II** and its resonance structure, hydroxycarbonium ion **III** and oxonium ion **IV**. Next, a nucleophilic addition between oxonium ion **IV** and phenol occurs to afford intermediate **V**, followed by the formation of a new carbon cation **VI** via the loss of one molecule of water. Finally, the carbenium ion transfer of **VII** leads to the formation of tertiary carbenium ion **VIII**, which undergoes intramolecular Friedel−Crafts cyclization and then removal of the proton to furnish the product **3i**. In the cascade reactions of cations, tandem C−C, C−O, and C−C bonds were established successfully.

In summary, we have successfully overcome the difficulties associated with the one-pot cascade reaction of spirodiazafluorenes starting from diazafluorenones and different phenols. In this tandem process, cationic charge relay realized by dehydration between phenols and DAFs novelly builds up C−O and C−C bond in order, whose process is on the precondition of repulsive interaction in a superelectrophilic system. Further optoelectrical application of spirodiazafluorenes prepared via this method is underway in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02595.

Experimental details and characterization of new compounds involving $^1H$ NMR and $^{13}C$ NMR spectra (PDF)

Crystallographic data for **3f** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The project was supported by the National Natural Science Funds for Excellent Young Scholars (21322402), National Natural Science Foundation of China (U1301243, 21274064, 21144004, 61177029, 20974046, 51273092, 61136003), Doctoral Fund of Ministry of Education of China (20133223110007), Natural Science Foundation of Jiangsu

Province (BK20150832, BM2012010), and Synergetic Innovation Center for Organic Electronics and Information Displays, NUPTSF (NY214176). The project was also funded by the excellent science and technology innovation team of Jiangsu Higher Education Institutions (2013).

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(14) CCDC 1471424 (**3f**) contains the supplementary crystallographic data for this paper. See the Supporting Information.