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Synthesis of Benzo[*b*]fluoranthenes and Spiroacridines from Fluorene-Derived Alkenes and *N*-Arylimines via a Tandem Reaction with Benzynes

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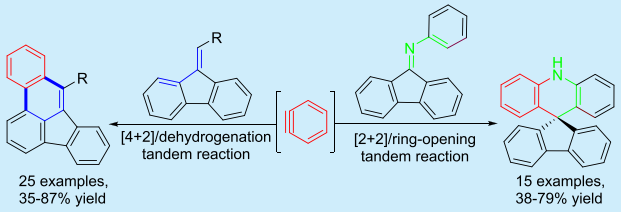
Supporting Information

ABSTRACT: Two tandem processes involving the cycloaddition of benzynes have been developed for the synthesis of polyaromatic hydrocarbons. Benzynes react with fluorene-derived alkenes through a tandem Diels−Alder reaction/dehydrogenation process to afford benzo[*b*]fluoranthenes in 35−87% yields. In addition, an unprecedented [2 + 2] cycloaddition/ring-opening sequence of benzynes and fluorene-derived *N*-arylimines provides facile access to spiroacridines in 38−79% yields.

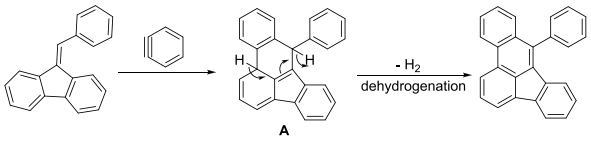


The past two decades have witnessed remarkable progress in benzyne chemistry.[1] As one of the most reactive organic species, benzyne has been used widely in synthetic chemistry, medicinal chemistry, and advanced functional materials. Owing to their distinct electronic properties, benzynes can serve as dienophiles in a series of pericyclic reactions,[2] insertion-cyclizaton,[3] and multicomponent coupling reactions.[4] In particular, the Diels−Alder reaction of benzynes[5] provides a powerful tool for the rapid construction of various carbocycles and heterocycles.

Both polycyclic aromatic hydrocarbons (PAH) and spiro-functionalized polycyclic aromatic hydrocarbons (SPAH) are important structural motifs found in many natural products and biologically active compounds.[6] In particular, owing to their unique photophysical and electrochemical properties, these versatile molecules have been utilized widely in optoelectronic materials.[7] Therefore, the development of efficient methods for the synthesis of PAHs and SPAHs is highly desirable. In 2007, Xie and Zhang[8] reported the synthesis of anthracene derivatives via a tandem reaction of imidazole and benzyne that involves a Diels−Alder reaction. In 2010, Guitián and co-workers[9] developed a domino Diels−Alder reaction of benzyne for the preparation of perylene derivatives. Subsequently, the same group[10] further reported that perylene operated as a diene to undergo a Diels−Alder reaction with benzyne. Following Pd-catalyzed trimerization, this afforded a 22-ring aromatic hydrocarbon. Recently, Biju and co-workers[11] reported an efficient Diels−Alder reaction between benzyne and styrenes for the construction of dihydropheanthrenes. Very recently, Peña and co-workers[12] developed a novel [4 + 2] cycloaddition/on-surface deoxygenation cascade process of benzynes, which provided facile access to decacene. In addition, Gidron and co-workers[13] reported an interesting sequential Diels−Alder reaction of benzynes and oligofurans to construct oligoarenes. Despite remarkable progress made in this research field, development of an efficient and straightforward method for the synthesis of PAHs and SPAHs via the cyclization of benzynes is still highly desirable.

With our continuing interest in benzyne chemistry[14] and spirofluorene chemistry,[15] we postulated that benzynes could undergo [4 + 2] cycloaddition with fluorene-derived alkenes to form intermediate **A**, the dehydrogenation of which would lead to the formation of benzo[*b*]fluoranthene (Scheme 1).

Scheme 1. Working Hypothesis



We first tested the Diels−Alder reaction of fluorene-derived alkene **1a** with 1.5 equiv of Kobayashi's reagent[16] **2a** and 4.5 equiv of CsF in acetonitrile at room temperature. Indeed, the desired PAH product **3a** was successfully obtained in 29% yield (Table 1, entry 1). When KF/18-crown-6 was substituted for CsF, only 18% yield was obtained (Table 1, entry 2). Other fluoride sources, such as TBAF, TMAF, and TBAT, only led to the generation of a trace amount of **3a** (Table 1, entries 3−5). The yield of the product increased to 39% when 3.0 equiv of benzyne precursor **2a** and 12.0 equiv of CsF were used (Table 1, entry 6). A brief screening of the reaction solvent showed that THF gave the greatest reaction yield (Table 1, entries 7−10). In separate attempts, raising the reaction temperature to 70 °C or lowering the reaction temperature to 0 °C did not

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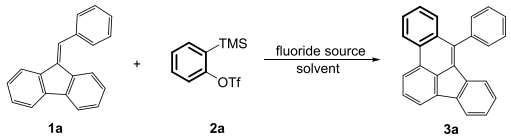
Table 1. Optimization of Reaction Conditions[a]



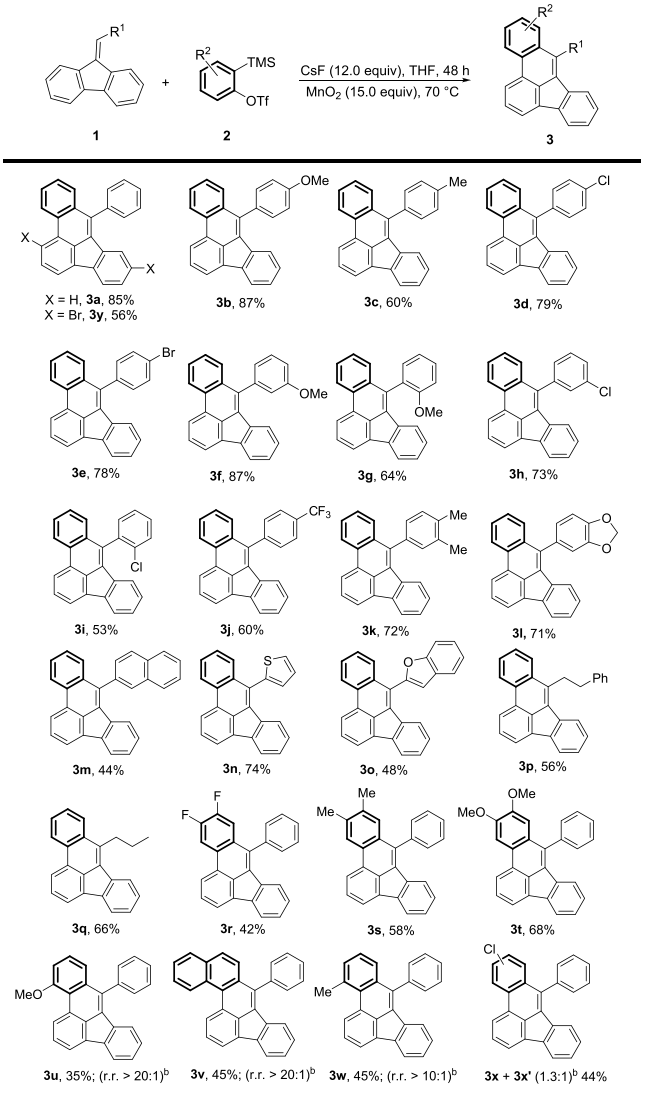
entry	solvent	additives	time (h)	temp (°C)	yield[b] (%)
1[c]	CH_3CN	CsF (4.5 equiv)	60	rt	29
2[c]	CH_3CN	KF+18-C-6 (4.5 equiv)	60	rt	18
3[c]	CH_3CN	TBAT (4.5 equiv)	30	rt	trace
4[c]	CH_3CN	TBAF (4.5 equiv)	60	rt	trace
5	CH_3CN	TMAF (4.5 equiv)	60	rt	trace
6	CH_3CN	CsF (12.0 equiv)	40	rt	39
7	DCM	CsF (12.0 equiv)	45	rt	trace
8	THF	CsF (12.0 equiv)	60	rt	45
9	toluene	CsF (12.0 equiv)	36	rt	trace
10	DMF	CsF (12.0 equiv)	70	rt	trace
11	THF	CsF (12.0 equiv)	40	70	23
12	THF	CsF (12.0 equiv)	136	0	44
13	THF	CsF (12.0 equiv), Cs_2CO_3 (1.0 equiv)	36	rt	37
14	THF	CsF (12.0 equiv), MnO_2 (15.0 equiv)	48	rt	38
15	THF	CsF (12.0 equiv), MnO_2 (15.0 equiv)	48	70	85
16	THF	CsF (12.0 equiv), DDQ (15.0 equiv)	48	70	trace
17	THF	CsF (12.0 equiv), Bu_4NI (15.0 equiv)	48	70	11
18	THF	CsF (12.0 equiv), $KHSO_5$ (15.0 equiv)	48	70	<10
19	THF	CsF (12.0 equiv), $KMnO_4$ (15.0 equiv)	48	70	<10
20	THF	CsF (12.0 equiv), $K_2Cr_2O_7$ (15.0 equiv)	48	70	12
21	THF	CsF (12.0 equiv), $K_2S_2O_8$ (15.0 equiv)	48	70	45
22	THF	CsF (12.0 equiv), $KClO_3$ (15.0 equiv)	48	70	10
23	THF	CsF (12.0 equiv), O_2	48	70	13
24	THF	CsF (12.0 equiv), MnO_2 (10.0 equiv)	48	70	58
25	THF	CsF (12.0 equiv), MnO_2 (20.0 equiv)	48	70	71

[a]Standard conditions: **1a** (0.10 mmol), **2a** (0.30 mmol), solvent: 2.0 mL. MnO_2 (commercial manganese dioxide was calcined in a muffle furnace under air at 200 °C for 5 h with a heating rate of 5 °C/min). [b]Isolated yield. [c]**1a** (0.10 mmol), **2a** (0.15 mmol).

improve the reaction yield (Table 1, entries 11 and 12), and the addition of a base or an oxidant had no apparent effect (Table 1, entries 13 and 14). However, to our great delight, on the addition of 15.0 equiv of MnO_2, the reaction proceeded efficiently in THF at 70 °C, affording **3a** in 85% yield (Table 1, entry 15). Encouraged by this success, other common organic and inorganic oxidants were subsequently evaluated for the cycloaddition. Unfortunately, only $K_2S_2O_8$ promoted the reaction, whereas other oxidants proved to be inefficient (Table 1, entries 16–23). Surprisingly, both increasing and reducing the amount of MnO_2 lowered the yield of **3a** (Table 1, entries 24 and 25).

Having evaluated the optimal reaction conditions, we then explored the substrate scope of this reaction (Scheme 2). Both electron-donating- and electron-withdrawing-group-substituted alkenes participated in the cycloaddition well, producing the

Scheme 2. Synthesis of Benzo[*b*]fluoranthene[a]



[a]General conditions: **1** (0.10 mmol), **2** (0.30 mmol), CsF (1.20 mmol), MnO_2 (1.50 mmol), anhydrous tetrahydrofuran (2.0 mL), 70 °C, and 48 h. The yields reported are isolated yields. [b]Regioisometric ratio (r.r.) was determined by ^1H NMR analysis.

corresponding PAH products in high yields (Scheme 2, **3a**–**3e**). The electronic properties and substitution positions of the substituents had no apparent impact on the reaction yield (Scheme 2, **3f**–**3l**). Bulky naphthyl-derived alkene **1m** underwent the cycloaddition in moderate yield (Scheme 2, **3m**). In addition, the heteroaryl-derived dienes[17] coupled with benzyne smoothly to afford **3n** and **3o** in 74 and 48% yields, respectively (Scheme 2, **3n**–**3o**). Notably, alkyl-substituted alkenes were competent substrates for the reaction, producing the corresponding products in good yields (Scheme 2, **3p**–**3q**). Symmetrical benzynes with electron-withdrawing or electron-donating substituents efficiently coupled with a fluorene-derived alkene to provide the desired products in moderate to good yields (Scheme 2, **3r**–**3t**). Unsymmetrical 3-methoxybenzyne, α,β-naphthalene, and 3-methylbenzyne performed the cycloaddition well to furnish the corresponding PAHs with excellent regioselectivity (Scheme 2, **3u**–**3w**). When unsymmetrical 4-chlorobenzyne was employed for the reaction, two regioisomers were obtained as an inseparable

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mixture with 44% overall yield (Scheme 2, **3x**/**3x′**). The 2,7-dibromofluorene-derived alkene reacted with benzyne to afford dibromo-substituted benzo[*b*]fluoranthene **3y** in 56% yield (Scheme 2, **3y**).

The structure of **3a** was unambiguously confirmed by single crystal X-ray analysis (Figure 1). (See the back matter of this paper for relevant CCDC codes).

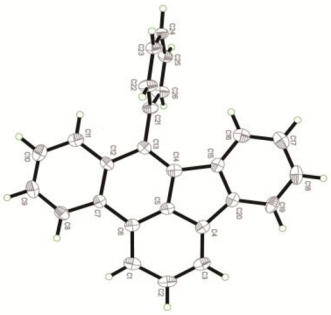
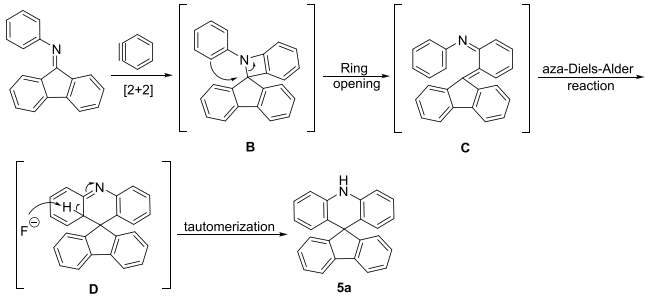


Figure 1. Single crystal X-ray structure for **3a**.

Benzynes can undergo aza-Diels–Alder reactions or [2 + 2] cycloadditions with imines and 2-aza-dienes.[18] In order to further demonstrate the application of our method, the cycloaddition between fluorene-derived *N*-aryl imines and benzynes was next investigated (Scheme 3). To our surprise,

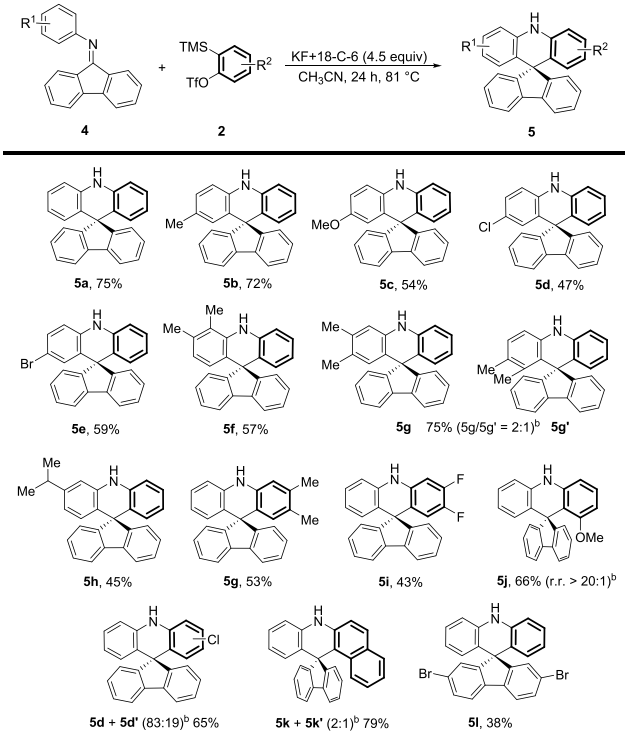
Scheme 3. Reaction Mechanism



neither [4 + 2] or [2 + 2] cycloaddition products were observed, and an unexpected spiroacridine **5a** was obtained as the major product. We postulated that benzyne undergoes [2 + 2] cycloaddition with imine **4a** to generate an azetidine intermediate **B**. The high ring strain of the four-membered ring then enables a fast intramolecular ring-opening reaction through the nucleophilic attack of the *N-ortho* position of the *N*-aryl ring and forms a quinomethide imine intermediate **C**. The subsequent intramolecular aza-Diels–Alder reaction of **C** leads to the formation of **D**, and afterward, the fluoride anion assisted tautomerization to produce spiroacridine **5a** (Scheme 3).

After a brief screening of different reaction parameters,[19] including the fluoride source, solvent, temperature, and molar ratio of reactants, the optimal reaction conditions were evaluated as 1.5 equiv of benzyne precursor **2** and 4.5 equiv of KF/18-crown-6 at 81 °C in acetonitrile. The generality of the reaction was then examined under the optimized reaction conditions. As shown in Scheme 4, fluorene-derived imines with both electron-donating and electron-withdrawing substituents on the *N*-aryl ring afforded the corresponding products in moderate to good yields (Scheme 4, **5b**–**5e**).

Scheme 4. Synthesis of Spiroacridines[a]



[a]General conditions: **4** (0.10 mmol), **2** (0.15 mmol), KF + 18-C-6 (0.45 mmol), anhydrous acetonitrile (2.0 mL), 81 °C, and 24 h. The yields reported are isolated yields. [b]Regioisometric ratio (r.r.) was determined by ^{1}H NMR analysis.

For imine **4f**, there is only one *N-ortho* position on the *N*-aryl ring that can undergo nucleophilic attack at the azetidine ring. Therefore, spiroacridine **5f** was furnished as the only product (Scheme 4, **5f**). On the other hand, imine **4g** has two *N-ortho* positions on the *N*-aryl ring, so the formation of inseparable regioisomers **5g** and **5g′** in a 2:1 ratio was achieved with 75% overall yield (Scheme 4, **5g** and **5g′**). Owing to the steric hindrance of the bulky isopropyl group, **5h** was afforded as the only regioisomer in 45% yield when imine **4h** was employed for the reaction (Scheme 4, **5h**). Dimethyl- and difluoro-substituted symmetrical benzynes provided the corresponding spiroacridines in moderate yields (Scheme 4, **5g**–**5i**). Once again, the use of the unsymmetrical 3-methoxybenzyne led to complete regioselectivity and yielded **5j** as the sole product (Scheme 4, **5j**). Unsymmetrical 4-chlorobenzyne and *α*,*β*-naphthlene underwent the reaction to afford the corresponding products in 65 and 79% yield, respectively with moderate regioselectivity (Scheme 4, **5d**/**5d′** and **5k**/**5k′**). In both cases, the major regioisomer could be isolated by column chromatography. Dibromo-substituted imine **4l** was also employed for the cascade process, and the desired product **5l** was isolated in 38% yield (Scheme 4, **5l**).

The structure of **5b** was also confirmed by X-ray crystallographic analysis (Figure 2). (See the back matter of this paper for relevant CCDC codes).

In order to shed light on the reaction mechanism, several other imines were prepared and tested for the tandem reaction with benzyne (Scheme 5). Both of the *N-ortho* positions of the *N*-aryl ring in substrate **4m**, derived from mesidine, are blocked by methyl groups, and no desired spiroacridine was detected (Scheme 5, eq 1). Fluorene-derived *N*-alkyl imine **4n**

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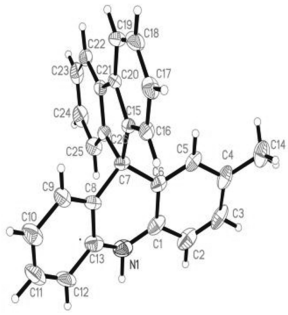
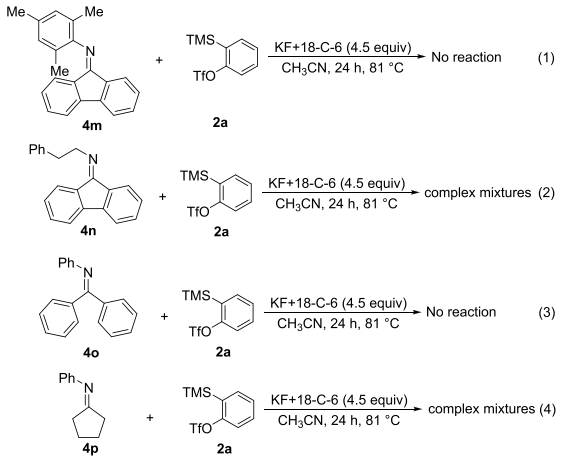


Figure 2. Single crystal X-ray structure for **5b**.

Scheme 5. Investigation of Different Imine Substrates



has no *N*-aryl group and therefore cannot undergo the tandem reaction (Scheme 5, eq 2). In contrast to fluorene-derived *N*-aryl imines, benzophenone-derived imine **4o** and cyclopentanone-derived imine **4p** gave no desired product (Scheme 5, eqs 3, 4). This result indicates that the nature of the fluorene structure palys a crucial role to the success of the tandem reactions.

In conclusion, we have developed an efficient and straightforward method for the synthesis of benzo[*b*]-fluoranthenes via a tandem Diels–Alder reaction/dehydrogenation of benzynes and fluorene-derived alkenes. We have also described a novel protocol for the preparation of spiroacridines that proceeds via a [2 + 2] cycloaddition/ring-opening sequence. This strategy provides a powerful tool for the construction of valuable polyaromatic skeletons. Further studies on a broader substrate scope and the application of this strategy are currently 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.9b00659.

Experimental details and spectroscopic data (PDF)

Accession Codes

CCDC 1891551, 1891561, and 1908380–1908382 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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