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Synthesis of Spirocyclic Diarylfluorenes by One-Pot Twofold S_NAr Reactions of Diaryl Sulfones with Diarylmethanes

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Supporting Information

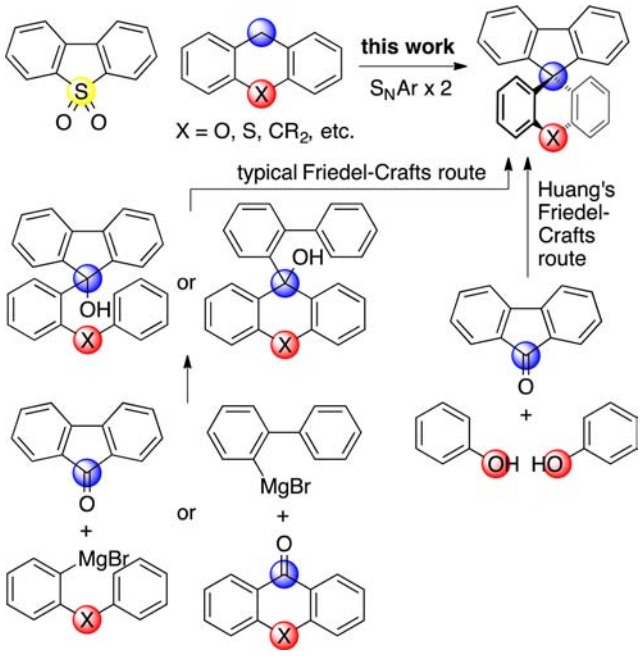
ABSTRACT: Treatment of dibenzothiophene dioxides with cyclic diarylmethanes in the presence of $KN(SiMe_3)_2$ results in the formation of fluorene-based spirocyclic tetraarylmethanes in a single operation. The transformation would proceed via an intermolecular S_NAr reaction of the dioxides with cyclic diarylmethylpotassium followed by intramolecular S_NAr cyclization. This straightforward strategy provides a wide range of spirocyclic diarylfluorenes including unusual ones that are otherwise difficult to synthesize.

Spirocyclic bifluorene cores have attracted recent attention in the fields of molecular tectonics,[1] chiral molecular recognition,[2] and molecular electronics[3] including low-molecular-weight light emitting materials[4] and macromolecular ones.[5] The bifluorene system is comprised of two conformationally fixed and well-conjugated biphenyl units, which leads to interesting photophysical and electrochemical properties such as high fluorescence quantum yields as well as chemical robustness favorable for long-lived organic materials. Additionally, its perpendicular framework results in its high solubility, which is advantageous for easy material processing.

Taking advantage of these fascinating properties of the bifluorene core, some research groups are interested in other spirocyclic 9,9-diarylfluorenes such as fluorene−xanthene,[6] −thioxanthene,[7] and −dihydroanthracene[6b,8] hybrids. Due to the different ring sizes and/or the presence of a heteroatom, these molecules show intriguing properties that are better than or different from those of bifluorene-based analogues. Among them, fluorene−xanthene hybrids have been well investigated not only because they show fascinating properties but also because they are readily available through Friedel−Crafts cyclization reactions under harsh acidic conditions,[6,9] especially through Huang's one-pot condensation method (Scheme 1).[6o,10] Much less attention has been paid to spirocyclic fluorene−thioxanthene and −dihydroanthracene analogs, mainly owing to the lack of efficient synthetic routes.[6b,7,8,9b] It is thus of great importance to develop convenient and efficient synthetic routes to these coveted spirocyclic 9,9-diarylfluorenes.[11] From a wider viewpoint, it is also interesting to invent a new approach to tetraarylmethanes, a simple yet synthetically challenging entity, without resorting to Friedel−Crafts reactions.[12]

Recently, our group has been interested in developing "aromatic metamorphosis", which represents a transformation of one aromatic system to another one through partial disassembly of the starting aromatic ring.[13−16] Among our work, the aromatic metamorphosis of dibenzothiophenes to carbazoles[13b] consists of two steps: (1) oxidation into the corresponding sulfones and (2) transition-metal-free twofold S_NAr reactions with aniline.[17−19] This carbazole synthesis is

Scheme 1. Approaches to Spirocyclic 9,9-Diarylfluorenes



advantageous since one naturally does not suffer from residual transition metal impurities that could adversely affect the device performances of the final products.

We thus envisioned that this S_NAr-based strategy is applicable to the efficient synthesis of spirocyclic 9,9-diarylfluorenes in a single operation, which is disclosed herein. To the best of our knowledge, this is the first base-mediated strategy for the synthesis of bispirocyclic tetraarylmethanes.

Despite significant structural differences between aniline and xanthene (**2a**), dibenzo[*b*,*d*]thiophene 5,5-dioxide (**1a**) reacted

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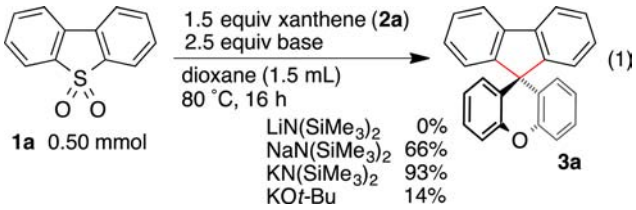
with **2a** by means of $KN(SiMe_3)_2$ similarly to afford the corresponding spiro[fluorene-9,9′-xanthene] (**3a**) in 93% yield (eq 1). $NaN(SiMe_3)_2$ was inferior to $KN(SiMe_3)_2$, yielding **3a** in



only 66% yield. Notably, the reaction did not proceed with $LiN(SiMe_3)_2$. Other potassium bases such as K_2CO_3, K_3PO_4, and KOAc were totally ineffective, whereas KO*t*-Bu promoted the reaction, albeit sluggishly.

With the optimized conditions in hand, the scope of cyclic diarylmethanes was examined in the reaction of **1a** (Figure 1).

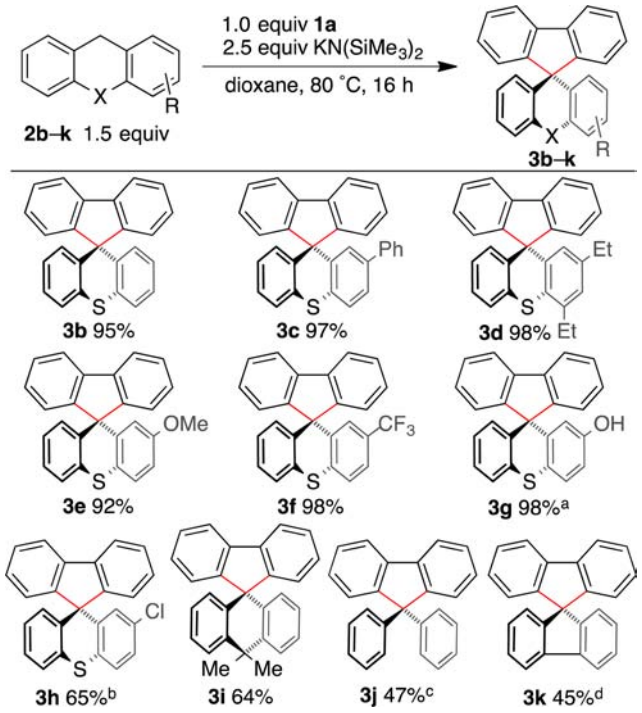
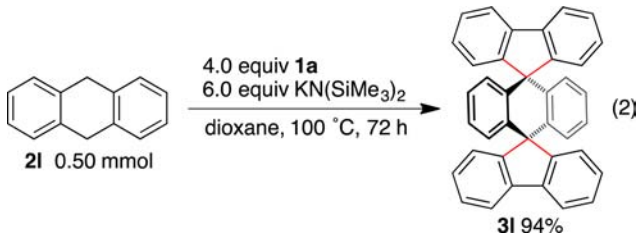


Figure 1. Scope with respect to cyclic diarylmethanes. [a] 3.5 equiv $KN(SiMe_3)_2$. [b] 2.0 equiv $KN(SiMe_3)_2$. **3b** was concommtantly formed in 27% yield. [c] At 120 °C. [d] Under microwave at 150 °C for 12 h.

Thioxanthene (**2b**) also reacted to afford spiro[fluorene-9,9′-thioxanthene] (**3b**) in 95% yield.[20] Commercially available 2-substituted thioxanthenes **2c–f** participated in the reaction regardless of the electronic nature of the substituent.[21] With the aid of one extra equivalent of $KN(SiMe_3)_2$, unprotected 2-hydroxythioxanthene (**2g**) was converted smoothly. The chloro group in 2-chlorothioxanthene (**2h**) partly survived to obtain **3h** in 65% yield, along with dechlorinated **3b** as a byproduct in 27% yield. 9,9-Dimethyl-9,10-dihydroanthracene (**2i**) bearing no heteroatom also reacted with **1a** to furnish **3i** in 64% yield. Unfortunately, acyclic diphenylmethane (**2j**) as well as fluorene (**2k**) reacted sluggishly, affording the corresponding products **3j** and **3k** in moderate yields even with higher temperatures. Interestingly, 9,10-dihydroanthracene (**2l**) reacted with 4 equiv of **1a** via a quadruple C–C bond-forming event to furnish **3l** in 94% yield (eq 2).



Next, we investigated the scope of dibenzothiophene dioxides (Figure 2). Because our strategy does not rely on a Friedel–

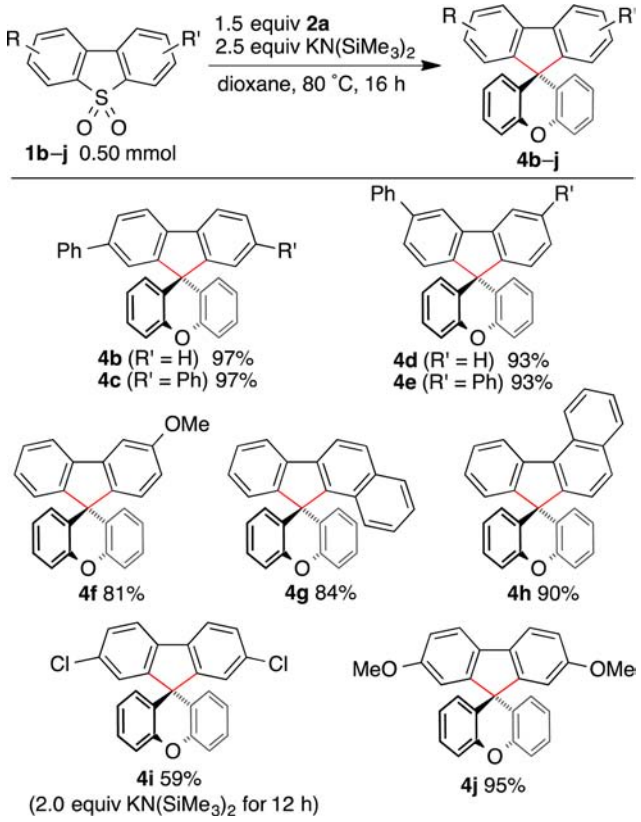


Figure 2. Scope of dibenzothiophene dioxides.

Crafts cyclization that would lack regioselectivity,[6] the synthesis of **4d–g** naturally proceeded with retention of the original substitution patterns of sulfones **1d–g**. Similar to the synthesis of **3h**, partial hydrodechlorination of **1i** and **4i** unfortunately occurred. Electron-donating methoxy groups did not show any detrimental effects to afford **4j** almost quantitatively.

Our synthetic strategy is totally different from conventional Grignard/Friedel–Crafts-based approaches, and one can synthesize spirocyclic diarylfluorenes that had been previously difficult to access. Benzothiophene-fused xanthene **2m** smoothly underwent reaction with **1a** to furnish **3m** in excellent yield (Scheme 2). Furthermore, oxidation of **3m** to sulfone **5** followed by another S_NAr reaction with **2a** delivered the novel bispirocyclic derivative **6** in 86% yield.

Taking advantage of the unique reactivity of benzothiophene dioxide (**7**) as a dienophile in the Diels–Alder reaction with isobenzofuran **8**, we were able to prepare π-conjugated benzonaphthothiophene dioxide **1k** easily (Scheme 3).[22] Despite the steric hindrance around the sulfur atom of **1k**, sterically congested spirocyclic compound **4k** was isolated in high yield.

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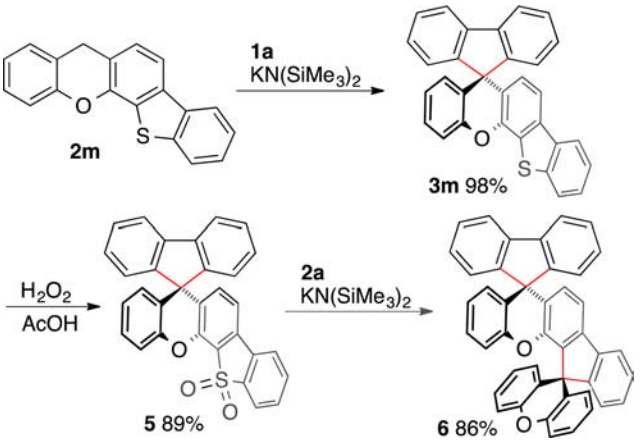
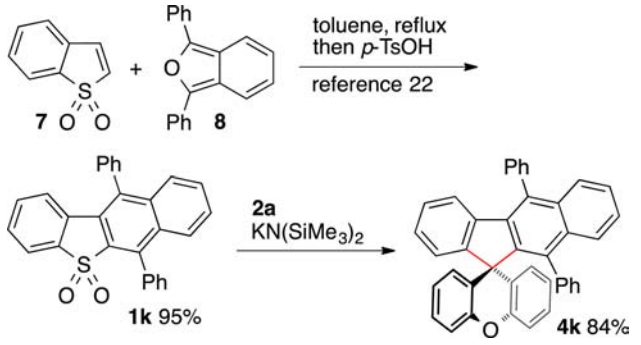
Scheme 2. Synthesis of Bispirocyclic Compound 6

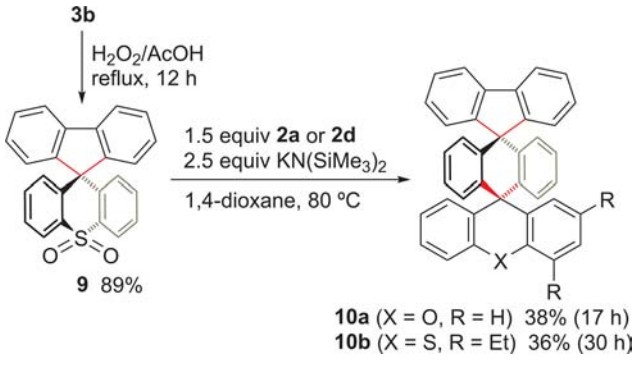


Scheme 3. Diels–Alder-Based π-Extension Followed by Twofold S_NAr Reaction



To showcase the high synthetic performance of our S_NAr-based spirocycle formation, we envisioned preparing linearly bispirocyclic compounds such as **10** through repetitive spirocycle formation (Scheme 4). Oxidation of **3b** that was obtained by our

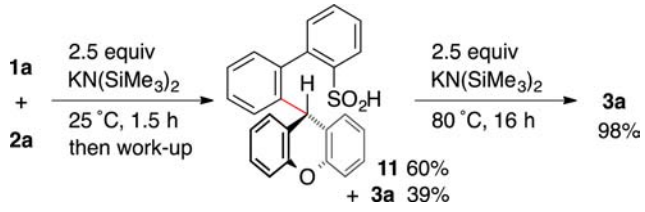
Scheme 4. Synthesis of Linearly Bispirocyclic Hexaarylenes



S_NAr-based strategy (Figure 1) afforded **9** in high yield. Although six-membered cyclic sulfone **9** proved to be inferior in reactivity to five-membered dibenzothiophene dioxides **1**, desired bispirocyclic compounds **10a** and **10b**[21] were formed in 38% and 36% yields, respectively.

We propose a reaction mechanism in analogy with our previous carbazole synthesis via sequential inter-/intramolecular S_NAr reactions.[13b] Indeed, upon treatment of **1a** with **2a** in the presence of $KN(SiMe_3)_2$ at a lower temperature of 25 °C, intermediary sulfinic acid **11** was isolated in 60% yield, along with spirocycle **3a** in 39% yield (Scheme 5). Subsequently, **11** was exposed to $KN(SiMe_3)_2$ at a higher temperature (80 °C) to yield **3a** in 98% yield.[23]

Scheme 5. Elucidation of Mechanism



In conclusion, we have invented a one-pot, practical strategy to prepare spirocyclic tetraarylmethanes, especially spirocyclic 9,9-diarylfluorenes. The twofold S_NAr reactions of dibenzothiophene dioxides with cyclic diarylmethanes proceed with the aid of $KN(SiMe_3)_2$, hence offering an approach complementary to the conventional Friedel–Crafts cyclization under acidic conditions. Our synthetic approach is unique to allow the synthesis of unusual spirocyclic compounds that are otherwise difficult to achieve. Current efforts are directed toward exploring new π-conjugated materials through our twofold S_NAr strategy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03384.

Experimental details, characterization data, NMR spectra of the products (PDF)
Crystallographic data for **3f** (CIF)
Crystallographic data for **10b** (CIF)

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Notes

The authors declare no competing financial interest.

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(20) An attempt to use 9,10-dihydroacridine resulted in the formation of a mixture of unidentified products showing a complex ^{1}H NMR spectrum in DMSO-d_6.

(21) X-ray crystallographic analysis unambiguously revealed the structures of **3f** and **10b**. For details, see Supporting Information.

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(23) The elimination of elusive and high-energy K_2SO_2 is unlikely. At this moment we speculate that trimethylsilylation of the SO_2^- unit with $HN(SiMe_3)_2$ generated in situ would afford **11′**, which should undergo a smoother S_NAr reaction.

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