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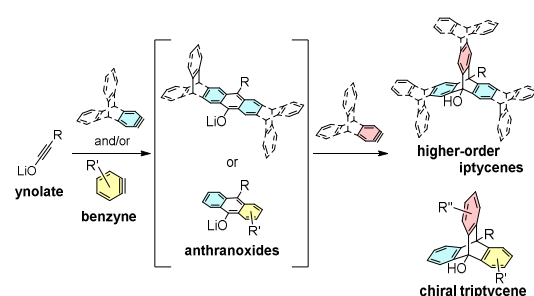


One-Pot Synthesis of Iptycenes and Dissymmetric Triptycenes Using Ynolate-Benzzyne Triple Cycloaddition

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Supporting Information Placeholder



ABSTRACT: Iptycenes such as noniptycenes, heptiptycenes, pentiptycenes as well as dissymmetric triptycenes having three different aryl groups have been synthesized in a one-pot manner using triple cycloaddition of ynolate with benzynes. The method consists of two-stages involving (1) *in-situ* formation of anthranoxides via double [2+2] cycloaddition of ynolate with benzynes and (2) a Diels-Alder reaction of anthranoxides with another benzyne. This method enables rapid access to higher order iptycenes and dissymmetric triptycenes, which have been conventionally synthesized in much longer steps.

Triptycene is a propeller-shaped aromatic compound in which three benzene rings are fused, and molecules containing this compound are called iptycenes.¹ The most notable feature of iptycenes, including triptycene, is the formation of cavities between benzene rings due to their rigid molecular framework.² This cavities has been utilized for molecular recognition and self-assembly to develop functional materials such as porous and functional polymers,³ molecular machines,⁴ host molecules,⁵ and organic thin layers.⁶

Higher-order iptycenes, which have more than seven benzene rings, are expected to exhibit higher functionality than conventionally used pentiptycenes and triptycenes. As the order of iptycenes increases, the total volume of the intramolecular cavities also increases,^{2,7} and a greater number of functional groups can be introduced in the expanded triptycene scaffold. These characteristics are believed to apply them into porous materials with controlled cavity properties and various optical materials by tuning the electronic properties of each benzene ring. Additionally, we recently succeeded in synthesizing acenes through the ring opening of the triptycene scaffold,⁸ demonstrating that higher-order iptycenes can serve as precursors for higher acenes.

Furthermore, another class of molecules with great potential is dissymmetric triptycenes bearing different substituents on their three blades.^{9,10} These are chiral molecules with a stereogenic bridgehead carbon and are expected to be useful for enantiomeric recognition by utilizing the cavity as a chiral environment, as well as for the development of chiral materials that

take advantage of chiral optical effects such as circularly polarized luminescence materials.¹¹

Although higher-order iptycenes and dissymmetric triptycenes represent valuable molecular architectures, their synthesis is hampered by common limitations. The triptycene framework is typically constructed via cycloaddition reactions of anthracene with benzoquinone or benzyne, but scaling these methods to larger frameworks or dissymmetric derivatives requires laborious, multi-step sequences. As a result, both higher-order and dissymmetric iptycenes suffer from poor synthetic accessibility. While the symmetric functionalization of all three blades of triptycene is well-documented,¹² introducing distinct functionalities selectively onto a single blade remains a significant challenge,¹³ particularly for larger iptycenes. An alternative strategy involves using dissymmetric anthracenes bearing different substituents on the terminal benzene rings prior to framework construction. However, such anthracenes require lengthy, step-intensive syntheses,¹⁴ making this approach impractical for general application. Thus, the lack of efficient, versatile methods that enable the direct synthesis of both higher-order iptycenes and dissymmetric triptycenes underscores a pressing need for new synthetic strategies.

To address these challenges, we focused on the two synthetic methods for triptycene that we had previously reported, both of which rely on the generation of anthranoxides as a key intermediate. The first method involves the synthesis of C₃-

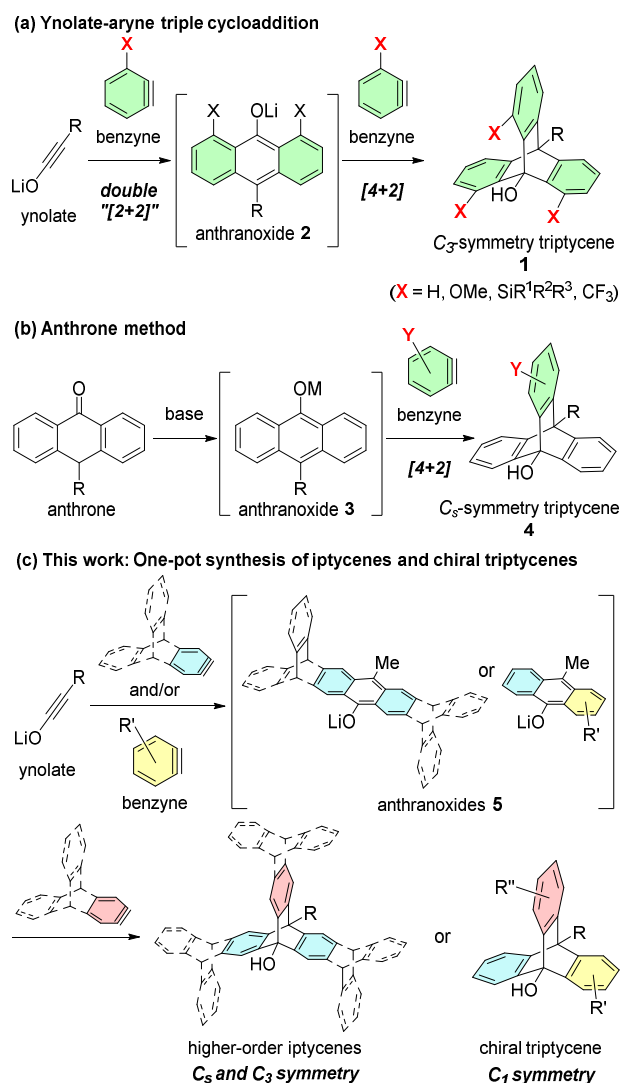
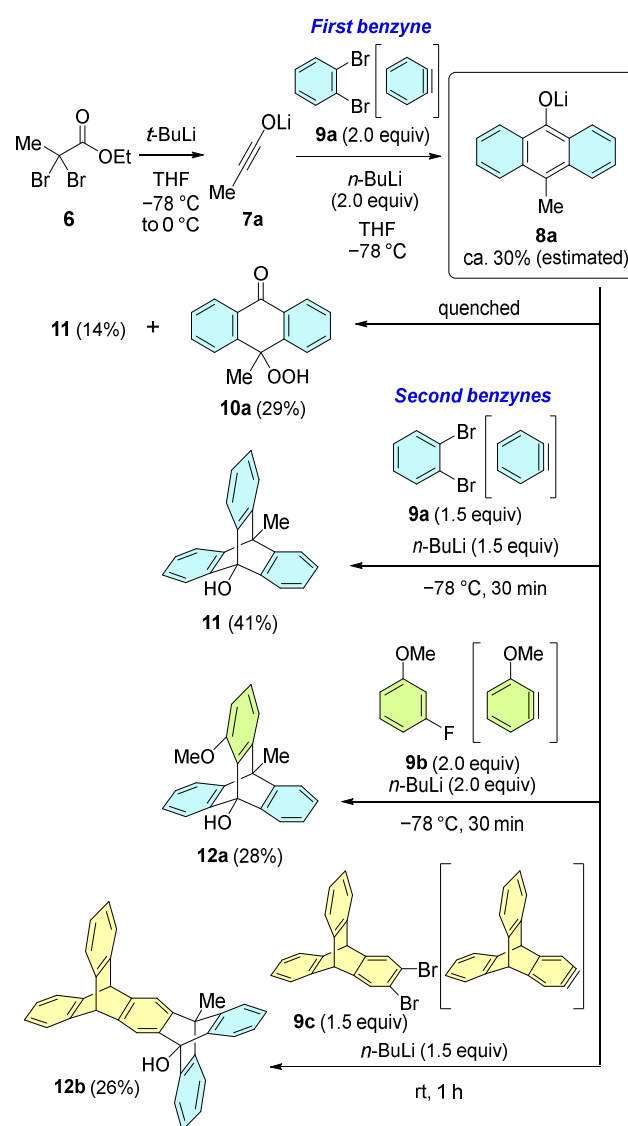


Figure 1. Our previous and current works.

symmetric 1,8,13-trisubstituted triptycene **1** via triple cycloaddition of ynolate with substituted benzyne (Figure 1(a)).¹⁵ The key step in this reaction is the formation of an electron-rich anthracene intermediate, anthranoxide **2**, generated through the double [2+2] cycloaddition of ynolate with two benzyne. Due to its electron-rich nature, anthranoxide exhibits extremely high reactivity toward benzyne, and its polarized structure enables high regioselectivity in cycloaddition with substituted benzyne. Building on this approach, we developed a second method, in which anthranoxide **3** is prepared via deprotonation of anthrone, followed by cycloaddition with benzyne, affording C_3 -symmetric triptycene **4** (Figure 1(b)).¹⁶ This strategy was successfully applied to the systematic synthesis of higher-order iptycenes containing up to 13 aromatic rings, which is the longest-chain iptycene reported to date.⁷ Based on these two approaches, in this paper, we report the one-pot two-stage synthesis of C_3 - and C_3 -symmetric higher-order iptycenes, as well as dissymmetric triptycenes (Figure 1(c)).

In order to synthesize higher-order iptycenes and dissymmetric triptycenes using ynolate-benzyne triple cycloaddition, we focused on the *in situ* preparation of anthranoxide **8a** using methyl-substituted ynolate **7a**, prepared from α,α -dibromo

ester **6**,¹⁷ and unsubstituted benzyne (Scheme 1). Our previous DFT calculations suggested that while the first and second [2+2] cycloadditions proceed rapidly without an activation barrier, the third Diels-Alder (DA) reaction (the reaction between anthranoxide and benzyne) involves a small activation barrier.^{15a} This indicates that if these processes are controlled, the reaction could be halted at the anthranoxide intermediate. Thus, we carefully screened the reaction conditions and found that using 2 equivalents of 1,2-dibromobenzene (**9a**) at -78°C led to the *in situ* preparation of **8a**. After quenching the reaction, 10-hydroperoxy-10-methylanthrone (**10a**) was obtained in 29% yield along with 14% of triptycene **11**. Since anthranoxide **8a** is a highly electron-rich anthracene, oxidation by air during the work-up process provided hydroperoxide **10a**. Based on the yield of **10a**, we estimated that anthranoxide **8a** was formed *in situ* in about 30% yield. Based on this result, we devised a two-stage strategy: (1) *in situ* generation of anthranoxide from ynolate and first benzyne, followed by (2) a DA reaction between anthranoxide and second benzyne to construct triptycene



Scheme 1. Two-stage one-pot synthesis of triptycenes and pentyptycene using unsubstituted benzyne.

scaffold. Subsequently, anthranoxides **8a** generated *in situ* under above conditions were further subjected to the DA reaction with the second benzyne (Scheme 1). When using benzyne derived from 1,2-dibromobenzene (**9a**), the yield of the resulting triptycene **11** was 41%, which suggested the DA reaction occurred efficiently. Using 3-methoxybenzyne derived from precursor **9b** as the second benzyne, methoxytriptycene **12a** was obtained in 28% yield. In addition, the reaction with triptycene derived from 2,3-dibromotriptycene (**9c**) provided pentiptycene **12b** in 26% yield. These results clearly show that the two-stage method is useful for the synthesis of Cs-symmetric iptycenes using two different benzyne.

Based on the conditions developed above, another types of Cs-symmetry triptycenes were synthesized using 3-methoxybenzyne as the first benzyne (Table 1). Because dimethoxyanthranoxide **8b** is highly electron-rich, work-up process in air of this species resulted in giving multiple oxidized products including hydroperoxide **10b**, making it difficult to estimate the precise yield of **10b**. When unsubstituted benzyne derived from **9a** was used as the second benzyne, triptycene **13a** was obtained in 32% yield. The reactions using naphthalene, 1,3-dimethoxybenzyne, and triptycene as the second benzyne also yielded the corresponding triptycenes **13b,c** and pentiptycene **13d** in 36%, 15%, and 18% yields, respectively, achieving the facile synthesis of functionalized triptycenes.

Higher-order iptycenes were then synthesized using triptycene as the first benzyne (Table 2). As a result of optimization on the reaction conditions, treatment of methyl substituted ynone **7a** with triptycene derived from 3 equivalents of precursor **9c** at $-100\text{ }^{\circ}\text{C}$ (condition A) provided hydroperoxide **10c** in 13% yield, which suggested estimated yield of anthranoxide **8c**. Subsequently, reaction of anthranoxide **8c** with 3-methoxybenzyne at room temperature yielded almost no desired products, probably because the steric bulkiness of anthranoxide **10c** inhibited the cycloaddition. Therefore, the reaction between **8c** and 3-methoxybenzyne was carried out at an elevated temperature (condition A), affording heptiptycene **14a** in 11% yield.

The structure assignment and regioselectivity are supported by the downfield shift of the OH proton ($\delta > 6\text{ ppm}$) in the ^1H NMR spectrum, indicating intramolecular hydrogen bonding. Similar shifts were also observed in the following examples. Under the condition A, the reactions using 4-fluoro-3-methoxybenzyne, 1,5-dimethoxybenzyne, 1,6-dimethoxybenzyne, and 2,3-naphthalene as the second aryne provided the corresponding heptiptycenes **14b-e** in 14%, 10%, 4%, and 14%, respectively. Furthermore, the cycloaddition of **8c** with triptycene yielded noniptycene **15a** in 7% yield. By further optimizing the reaction conditions, it was found that the reaction of ynone **7a** with 1.1 equivalents of triptycene precursor **9c** at $-78\text{ }^{\circ}\text{C}$ in the first stage (condition B) enhanced the generation of anthranoxide **8c** (yield of hydroperoxide **10c** increased to 20%), thus improving the yield of noniptycene **15a** to 18%. Under the condition B, the yield of methoxyheptiptycene **14a** through the reaction with 3-methoxybenzyne also increased to 19%. Additionally, when butyl substituted ynone **7b** was treated with 2.0 equivalents of triptycene precursor **9c** (condition C, yield of hydroperoxide **10d** was 12%), butyl substituted heptiptycene **14f** and noniptycene **15b** were obtained in 16% and 14%, respectively. It is worth noting that while Hart reported the first synthesis of noniptycene in eight steps in total yield of 9%,¹⁸ our method provided noniptycenes in significantly higher yields in a one-pot manner. This synthesis is also superior in that it allows the introduction of functional groups essential for the application of iptycenes.

Encouraged by the successful one-pot synthesis of various triptycenes and higher-order iptycenes using two different benzyne, we next examined the more challenging case of employing three different benzyne to construct a dissymmetric chiral triptycene bearing three distinct aryl groups. Methyl substituted ynone **7a** was treated with a mixture of 3-methoxybenzyne and unsubstituted benzyne derived respectively from precursors **9a,b** to *in situ* prepare the anthranoxide intermediate, which was then reacted with 1,5-dimethoxybenzyne generated

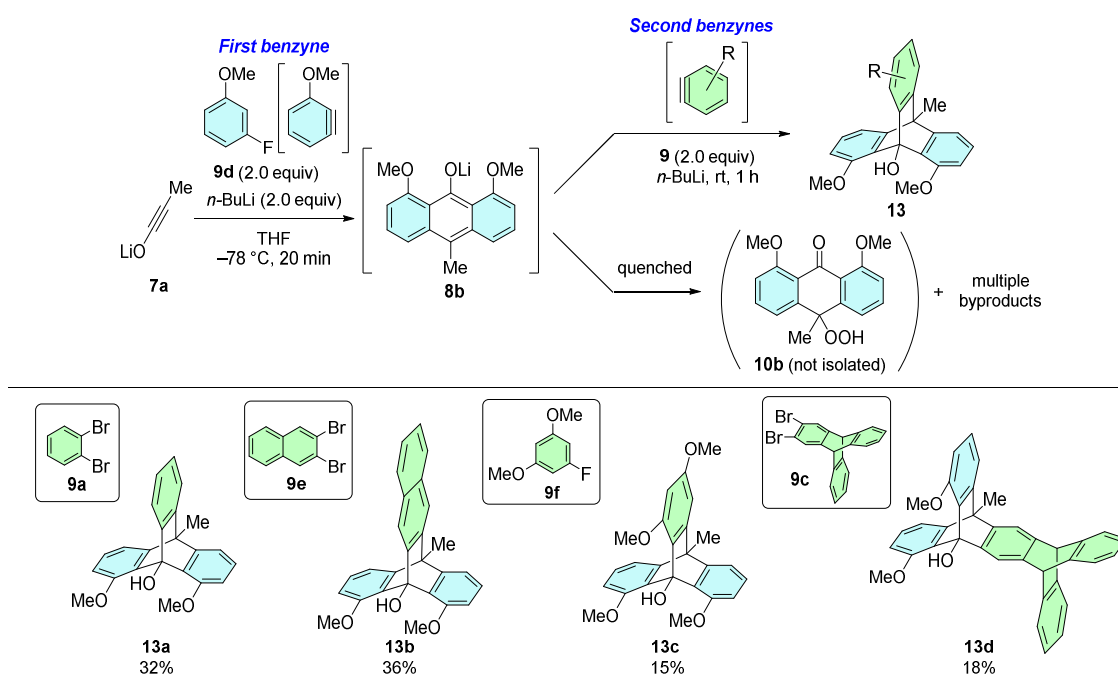


Table 1. One-pot synthesis of triptycenes and pentiptycene using 3-methoxybenzyne.

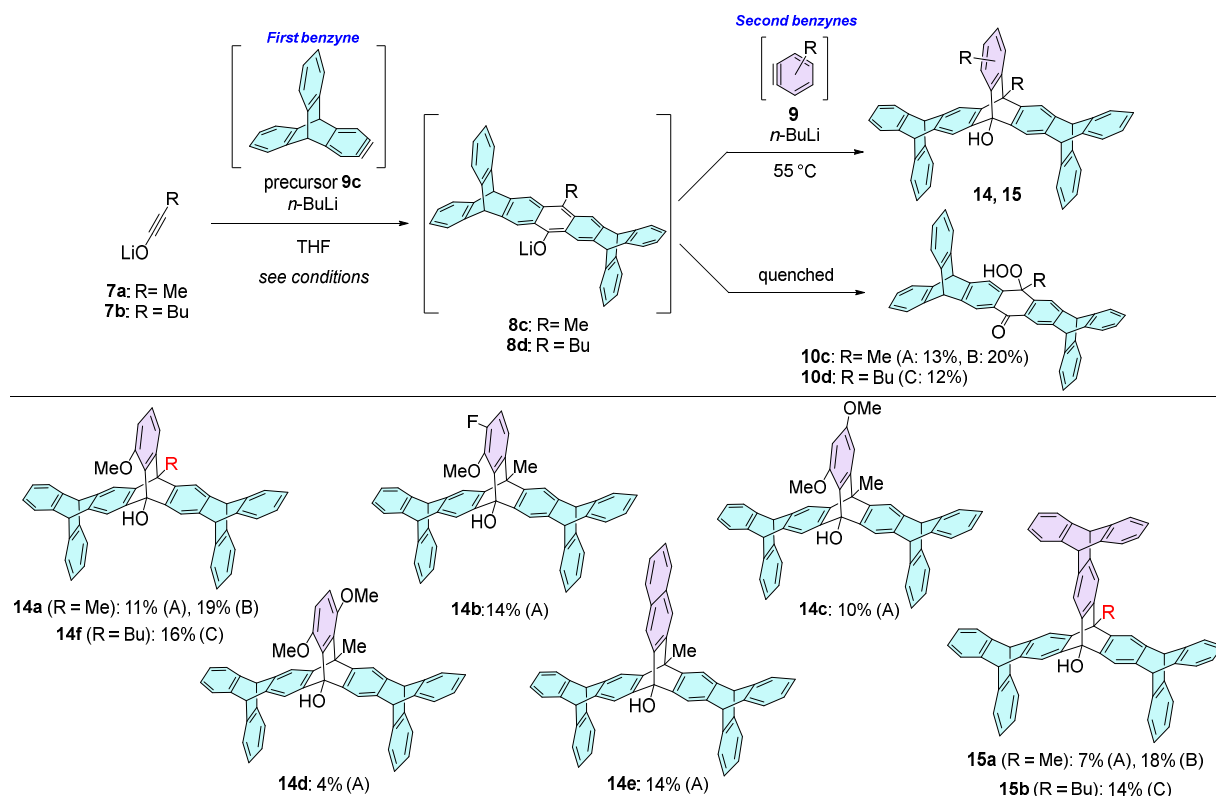
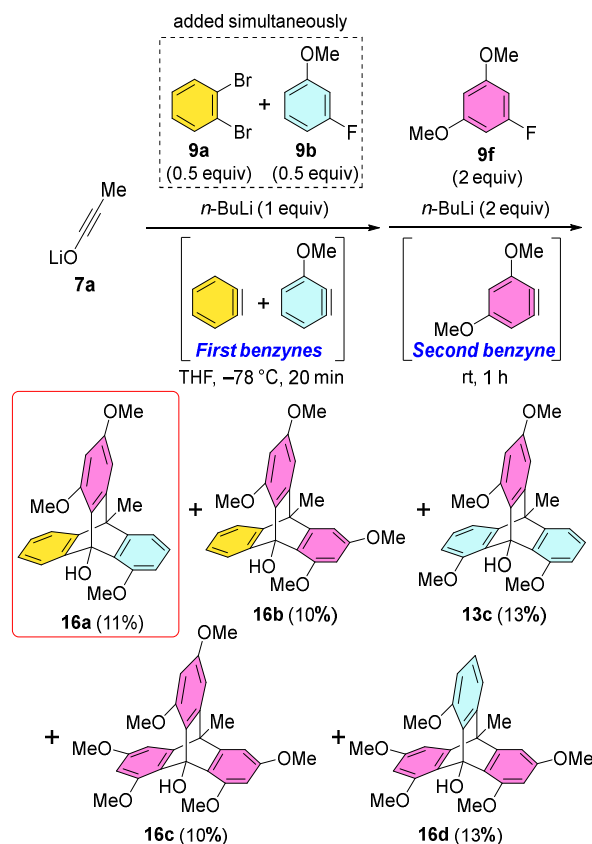


Table 2. One-pot synthesis of heptiptycenes and noniptycenes. Conditions (A) 2,3-dibromotriptycene (**9c**, 3.0 equiv), $n\text{-BuLi}$ (3.0 equiv), $-100\text{ }^{\circ}\text{C}$, Condition (B) 2,3-dibromotriptycene (**9c**, 1.1 equiv), $n\text{-BuLi}$ (2.0 equiv), $-78\text{ }^{\circ}\text{C}$, Condition (C) 2,3-dibromotriptycene (**9c**, 2.0 equiv), $n\text{-BuLi}$ (2.0 equiv), $-78\text{ }^{\circ}\text{C}$.

from precursor **9f** (Scheme 2). Multiple triptycenes **16a-d** and **13c** were produced, but the desired dissymmetric triptycene **16a** was successfully isolated in 11% yield. Furthermore, enantiomers of **16a** were separated by HPLC on a chiral column (see supporting information). Although several methods to synthesize dissymmetric triptycenes have been reported, all of them requires cumbersome multi-step processes based on cycloaddition reactions of dissymmetric anthracenes with benzyne/benzoquinone and on desymmetrization of triptycenes. In contrast, the present method provided the dissymmetric triptycene with three different aryl groups in a one-pot fashion, providing a significant advantage as a convenient method.

In conclusion, we have achieved one-pot synthesis of C_s - and C_3 -symmetry triptycenes, pentiptycenes, heptiptycenes and noniptycenes as well as dissymmetric triptycene based on the two-stage strategy involving (1) *in-situ* formation of anthranoxides from ynone and the first benzyne and (2) DA reaction of the anthranoxides with the second benzyne. The yields of *in-situ* generated anthranoxides were estimated by isolated yields of the corresponding 10-hydroperoxyanthrone. Comparing the estimated yields of anthranoxides with those of the isolated iptycenes, the DA reaction at the second stage was suggested to proceed with good efficiency, which demonstrates significantly high reactivity of anthranoxides. It is noted that the one-pot method enabled rapid access to higher-order iptycenes such as heptiptycene and noniptycene as well as dissymmetric triptycene, which have been conventionally synthesized in much longer steps. We are currently studying further application of ynone-benzyne triple cycloaddition to rapid and efficient synthesis of larger and more functionalized iptycenes.



Scheme 2. One-pot synthesis of dissymmetric triptycene.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this paper are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General information, experimental procedures, characterization data, X-ray crystallographic data, and NMR spectra (PDF)

Accession Codes

Deposition Numbers 2450415 and 2450449 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformations-zentrum Karlsruhe Access Structures service.

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Author Contributions

All authors have given approval to the final version of the manuscript.

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