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Synthesis of Substituted Helicenes by Ir-Catalyzed Annulative Coupling of Biarylcarboxylic Acid Chlorides with Alkynes

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Abstract

A series of substituted [4] and [5]helicenes were synthesized in moderate to good yields by an Ir-catalyzed annulative coupling of biarylcarboxylic acid chlorides with internal alkynes, which involves facile C-H bond cleavage and decarbonylation. The double annulative coupling of 1,1':5',1''-ternaphthalene-2,2''-dicarboxylic acid dichloride with 4-octyne was also accomplished to give rise to an S-shaped double helicene. Unexpectedly, a π -extended benzofluoranthene-merged [5]helicene was constructed through the annulative coupling and the successive C(aryl)-C(aryl) bond forming reaction when 1,1':4',1''-ternaphthalene-2,2''-dicarboxylic acid dichloride was employed as the substrate. The crystal structure and the optical properties of the latter unique product were also investigated.

Keywords: Helicene, C-H Bond Functionalization, Ir-Catalyzed Coupling

1. Introduction

Helicenes. which are screw-sense π -conjugated polyaromatic compounds, are receiving immense attention due to their potential utility as functional organic molecules.¹ The characteristic features of helicenes offer promising prospects for applications in asymmetric catalysis, supramolecular chemistry, liquid crystals, and organic devices.1a-1d Various synthetic approaches for the efficient construction of twisted conjugated aromatic systems have been actively investigated. As one such approach, the aromatic C-H bond activation reactions by transition-metal catalysts are promising due to their efficient and straightforward nature that allows access to a wide range of condensed aromatic compounds.² Meanwhile, there have only been few studies of helicene synthesis so far although they could render a number of approaches to carboand hetero-helicenes with asymmetrical blades.³ As part of our continuous efforts to uncover new approaches to helicene

synthesis, we previously reported the synthesis of azahelicene N-oxides by a Pd-catalyzed direct C-H annulation of the pendant Z-bromovinyl side chain (Scheme 1 (1)).^{3d} However, some drawbacks remain, including the need to introduce a Z-bromovinyl side chain and to activate a C-H bond by an electron-withdrawing N-oxide group. In order to synthesize multi-functionalized helicenes, it is crucial for the development of versatile methods to overcome such drawbacks.



Scheme 1. Helicene synthesis involving C-H bond cleavage.

In light of these results, we focused on the development of an Ir-catalyzed annulative coupling of biarylcarboxylic acid chlorides with alkynes in our quest for the efficient helicene synthesis (Scheme 1 (2)). This protocol features a unique process that involves two successive carbon-carbon bond formation steps accompanied by the elimination of carbon monoxide and hydrogen chloride via facile C-H bond cleavage, which would confer a high degree of flexibility in the design of helicene molecules.⁴ Consequently, we took on the task of synthesizing a series of [4] and [5]helicenes by using the above methodology. The results are reported herein.

2. Results and Discussion

In order to optimize the reaction conditions, we initially evaluated the performance of several phosphine ligands in the transformation of 1-phenyl-2-naphthoyl chloride (1) into corresponding benzophenanthrene derivative 2 using 4-octyne as the coupling partner (Table 1).

 Table 1. Ligand screening for Ir-catalyzed annulative coupling of 1-phenyl-2-naphthoyl chloride (1) with 4-octyne.



 Table 2.
 Substrate scope for Ir-catalyzed annulative coupling of 1-aryl-2-naphthoyl chloride 3 with alkynes 4.



In the first instance, **1** was reacted with 4-octyne for 18 h in refluxing xylene in the presence of $[IrCl(cod)]_2$ together with $P^tBu_3 \cdot HBF_4$, which was an optimal ligand in our previous study.⁴ Under these conditions, desired product **2** was furnished in 57% yield (entry 1). The major byproduct for this reaction was 1-phenyl-2-naphthoic acid (27%), which was formed by the hydrolysis of unreacted starting material **1**. For

the further improvement of yield, other phosphine ligands were also examined. Among them, JohnPhos was found to give a comparable yield to that using $P^{t}Bu_{3} \cdot HBF_{4}$, forming product 2 in 50% yield (entry 2). PCy3·HBF4 was also inferior to P^tBu₃·HBF₄ (entry 3). Therefore, P^tBu₃·HBF₄ was confirmed to be the ligand of choice for the substituted helicene synthesis. After the optimization studies, we adopted the conditions to the synthesis of other substituted [4] and [5]helicenes (Table 2). The substrates we prepared were as follows: 1-(*o*-tolyl)-2-naphthoyl chloride (3a),1-(o-methoxyphenyl)-2-naphthoyl chloride (**3b**), 1-naphthyl-2-naphthoyl chloride (3c), 1-(phenanthren-9-yl)-2-naphthoyl chloride (3d) and 1-(pyren-4-yl)-2-naphthoyl chloride (3e). These substrates were coupled with internal alkynes 4a-c for 18 h in refluxing xylene in the presence of [IrCl(cod)]₂/P^tBu₃·HBF₄ and a series of substituted [4] or [5]helicene derivatives 5 with symmetric and asymmetric blades were obtained in preparatively useful yields. In particular, π -extended helicenes 5ea-5ec, which have a pyrene-helicene hybrid structure, were obtained in reasonable yields. The hybrid core derivatives are known to exhibit unique physical properties.⁵ Meanwhile, multiple helicenes with plural helicities have attracted considerable attention and been developed actively in recent years as these compounds may have unique optoelectronic properties.^{6–11} Thus, we next examined double annulative coupling reactions for substrates with two carboxylic acid chloride functions, anticipating the generation of S- and W-shaped double helicenes (Figure 1).



S-Shaped Double Helicene



W-Shaped Double Helicene

Figure 1. Disconnection approach for the synthesis of S- and W-shaped double helicenes.



Scheme 2. Synthesis of S-shaped double helicene **7** by double Ir-catalyzed coupling.

Initially, we prepared 1,1':5',1''-ternaphthalene-2,2''-dicarboxylic acid dichloride (6) by cross-coupling and subsequent conventional transformations (see Supporting Information for details) and conducted the reaction with 4-octyne in the presence of 10 mol% of Ir catalyst under standard conditions. To our delight, the double coupling reaction proceeded to afford desired S-shaped double helicene 7 albeit in a low yield. Other by-products were also formed but could not be identified.



Scheme 3. Synthesis of 9 via successive C-H bond cleavage.

One of the possible reasons for the low yield may be the increased molecular distortion by the plural helicities. Next, expecting the formation of a W-shaped double helicene,

1,1':4',1''-ternaphthalene-2,2''-dicarboxylic acid dichloride (8) was prepared and subjected to the double annulative coupling as above. However, the desired W-shaped product could not In this case, benzo[*i*]fluoranthene-merged be obtained. helicene 9 was isolated in 8% yield instead (Scheme 3) and its bonding nature was confirmed by X-ray diffraction analysis (vide infra). A plausible reaction mechanism for the formation of 9 is illustrated in Scheme 4. The formation of 9 may be rationalized by two successive coupling processes involving a single Ir-catalyzed annulative coupling with alkyne (First Ir Cycle) and an Ir-catalyzed direct C(aryl)-C(aryl) coupling (Second Ir Cycle). Initially, acyliridium species A is formed and subsequent decarbonylation and C-H bond cleavage take place to give iridacycle intermediate \mathbf{B}^4 Insertion of the alkyne gives seven-membered iridacycle intermediate C and subsequent reductive elimination gives singly cyclized product 10. Then, thus-formed 10 enters the second Ir-catalyzed C-C bond formation process (Second Ir Cycle). Another acyl chloride unit reacts with the Ir catalyst



Scheme 4. Plausible reaction mechanism for the formation of 9.

to form acyl iridium **D** and to avoid steric repulsion between one of the *n*-propyl groups and the acyl iridium group, a rotation around the axis occurs to produce iridacycle intermediate E. Finally, reductive elimination gives product 9. Single crystals of 9 suitable for X-ray diffraction analysis were obtained as yellow prisms by room-temperature vapor diffusion of hexane into chloroform solution. The dihedral angle defined by the two least squares planes in the [5]helicene moiety was measured as 50.9°, which is within the typical range of those of [5]helicene derivatives,¹² whereas the benzo[*j*]fluoranthene moiety in 9 was found to be almost flat (Figure 2 (b)). The crystal packing of 9 showed that the Pand M-isomers of the [5]helicene moiety formed a pair of molecules via the intermolecular π - π stacking between the benzo[*j*]fluoranthene moieties, whose interplanar distance was calculated as 3.525 Å. In addition, CH-π interaction was observed between both edged aromatic rings of the benzo[*j*]fluoranthene and [5]helicene moieties with a distance of 2.776 Å (Figure 2 (c)).



Figure 2. X-ray crystallography of **9** (a: Front View, b: Side View, c: Crystal Packing).

Although π embedded in a [5]helicene moiety, such as pyrene,⁵ corranulene,¹³ and others,¹⁴ were well investigated, to the best our knowledge, the reported fluoranthene–[5]helicene hybrid derivative is only benzo[*j*]indeno[1,2,3-*hi*]chrysene (**11**)^{15,16} (see ref 15 for the structure of **11**). As **9** showed a green emission in CHCl₃ solution (Figure 3, (a)) and a yellow emission in powder form (Figure 3, (b)), we investigated its photophysical properties (Figure 4).



Figure 3. Photographs of (a) green emission in $CHCl_3$ solution and (b) yellow emission in powder of 9 excited at 365 nm.



Figure 4. UV-vis absorption in $CHCl_3$ solution (blue line), fluorescence in $CHCl_3$ solution (green line), and fluorescence in powder form (orange line) of **9**.

The UV-vis spectrum of 9 in CHCl₃ showed complicated absorptions with λ_{max} of 318, 356, and 402 nm and a shoulder at 432 nm. The longest absorption (432 nm) was significantly red-shifted compared to those of [5]helicene (350 nm)^{5d} and benzo[*j*]fluoranthene (365 nm),¹⁷ which should be ascribed to the extended π -conjugation. Time-dependent (TD) DFT calculations at B3LYP/6-311+G(2d,p)/B3LYP/6-31G(d) level of theory revealed that this absorption is assignable to the HOMO-LUMO transition ($\lambda_{calc} = 460.8 \text{ nm}, f = 0.180$). The HOMO (-5.26 eV) is delocalized over the whole molecule, whereas the LUMO (-1.97 eV) is mainly delocalized over the benzo[*i*]fluoranthene moiety together with some contribution of the [5]helicene moiety (Figure S1). The fluorescence spectrum of 9 in CHCl₃ solution is a mirror image of the longer wavelength region of the UV-vis spectrum (370-460 nm) (Figure 4), the maxima of which ($\lambda_{max} = 484$ and 510 nm) are also red-shifted compared to those of [5]helicene (375 nm)^{5d} and benzo[*j*]fluoranthene (468 nm).¹⁷ The fluorescence spectrum of 9 in powder form ($\lambda_{max} = 560$ nm) is broad and red-shifted compared to that in solution, which may be

explained by the paring nature of two molecules as found in the X-ray diffraction analysis. The quantum yield ($\Phi_{\rm f}$) of **9** in CHCl₃ solution is 0.16, which is higher than that of [5]helicene ($\Phi_{\rm f} = 0.04$)¹⁸ and benzo[*j*]fluoranthene ($\Phi_{\rm f} = 0.07$).¹⁹ The observed lifetime ($\tau_{\rm s}$) is 7.6 ns, which is shorter than that of [5]helicene ($\tau_{\rm s} = 25.5$ ns)¹⁸ and comparable to that of benzo[*j*]fluoranthene ($\tau_{\rm s} = 8.0$ ns).¹⁹ The quantum yield and the observed lifetime of **9** in powder form are 0.073 and 12–13 ns, respectively.²⁰

3. Conclusion

We have succeeded in constructing a series of substituted [4] and [5]helicenes by the Ir-catalyzed annulative coupling of biarylcarboxylic acid chlorides with internal alkynes in moderate to good yields. This protocol enabled us to integrate three different components into a framework, thereby delivering multi-functionalized helicenes. We also succeeded in synthesizing S-shaped double helicene 7. During the course of this work, we unexpectedly synthesized benzofluoranthene-merged helicene 9, which showed unique optical properties.

4. Experimental

Typical Procedure for Reactions of 3 with 4 in Table 2. The carboxylic acid chlorides **3** were prepared by the procedure described in Supporting Information. To the crude mixture of acid chloride **3** was added $[IrCl(cod)]_2$, 'Bu₃P·HBF₄, and *p*-xylene (0.2 M). After the addition of alkyne (5 equiv.), the reaction mixture was stirred at 160 °C (bath temperature) for 18 h. The volatiles were removed under reduced pressure at room temperature. The residue was chromatographed on silica gel with eluent (hexane/EtOAc or hexane/CHCl₃) to give **5**.

Supporting Information

Detailed experimental procedures, spectroscopic data for the products, theoretical studies, and crystallographic data for **9** are described. This material is available on http://dx.doi.org/xxxxx/bcsj.20180081.

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