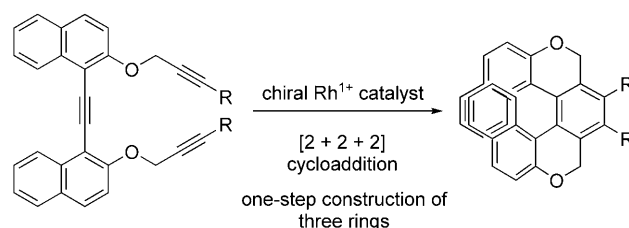


One-Step Construction of Five Successive Rings by Rhodium-Catalyzed Intermolecular Double [2+2+2] Cycloaddition: Enantioenriched [9]Helicene-Like Molecules**

Ken Tanaka,* Naohiro Fukawa, Takeshi Suda, and Keiichi Noguchi

Helicenes and helicene-like molecules have long attracted much attention because of their potential applications to optical or electronic functional materials.^[1] Therefore, flexible as well as convenient methods for their syntheses are highly desired for structural alterations and supply of sufficient quantities.^[2] The most frequently employed method for the synthesis of helicenes is the oxidative photocyclization of stilbene-type precursors, however this procedure cannot be conducted on a large scale because of the highly dilute reaction conditions.^[3] Several non-photochemical methods for the synthesis of [6]- and [7]helicenes and helicene-like molecules have been developed to date.^[4] As such, transition metal mediated intramolecular [2+2+2] cycloadditions of triynes are useful methods for the synthesis of [6]- and [7]helicene-like molecules through the formation of three successive rings.^[5,6] Stará and co-workers pioneered this strategy by using cobalt- or nickel-mediated or catalyzed [2+2+2] cycloadditions.^[5] Following this pioneering work, we recently reported a cationic rhodium(I)/chiral bisphosphine complex, which catalyzed the intramolecular [2+2+2] cycloadditions of 2-naphthol-linked triynes, leading to enantioenriched [7]helicene-like molecules (Scheme 1).^[6,7] Notably, non-photochemical methods that can furnish higher ordered ($\geq$ [8]) helicenes and helicene-like molecules are rare.^[8]

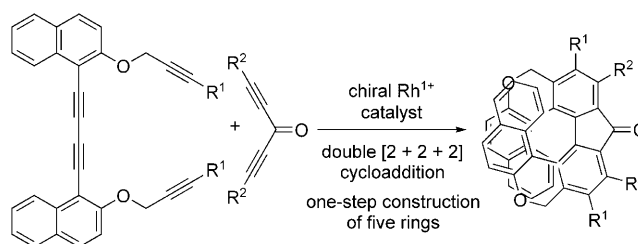
To access sterically more demanding [9]helicene-like molecules^[9] starting from commercially available 2-naphthol, we designed an intermolecular double [2+2+2] cycloaddition



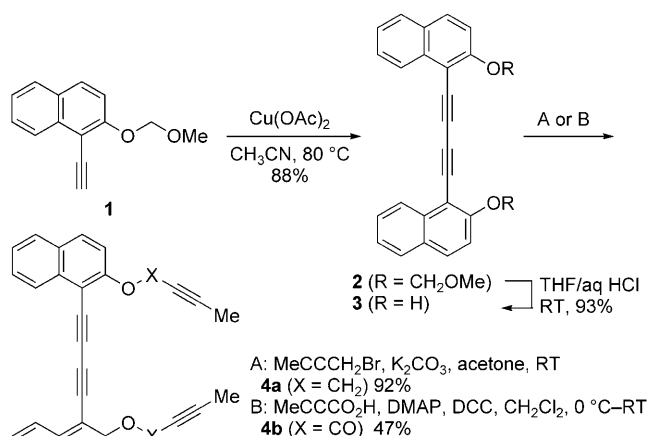
Scheme 1. Rhodium-catalyzed intramolecular [2+2+2] cycloaddition leading to enantioenriched [7]helicene-like molecules.

between a 2-naphthol-linked tetrayne and a dialkynylketone,^[10] which forms five successive rings (Scheme 2). This method would furnish various [9]helicene-like molecules, containing a densely substituted fluorenone core, by changing substituents of each cycloaddition partner.

The 2-naphthol-linked tetraynes **4** were readily prepared by a three-step sequence starting from a known terminal alkyne **1**^[7] as shown in Scheme 3. A copper-mediated



Scheme 2. Rhodium-catalyzed intermolecular double [2+2+2] cycloaddition leading to enantioenriched [9]helicene-like molecules.



Scheme 3. Syntheses of tetraynes **4a** and **4b**. DMAP = 4-dimethylaminopyridine, DCC = dicyclohexylcarbodiimide.

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homocoupling of **1** and subsequent treatment with aqueous HCl furnished the 2-naphthol-substituted 1,3-diyne **3**. Etherification of **3** with 1-bromo-2-butyne gave the ether-linked tetrayne **4a**. Ester-linked tetrayne **4b** was also prepared by esterification of **3** with 2-butyric acid.

Upon obtaining tetraynes **4a** and **4b**, we first investigated an intermolecular double [2+2+2] cycloaddition of the ether-linked tetrayne **4a** with dialkynylketone **5a** in the presence of cationic rhodium(I) complexes and various bis(phosphine) ligands (Figure 1). The study revealed that the use of

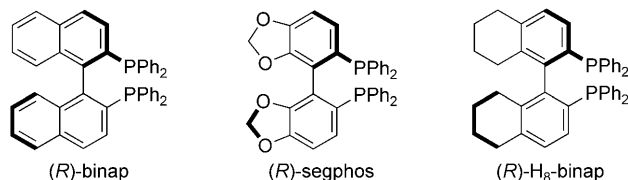
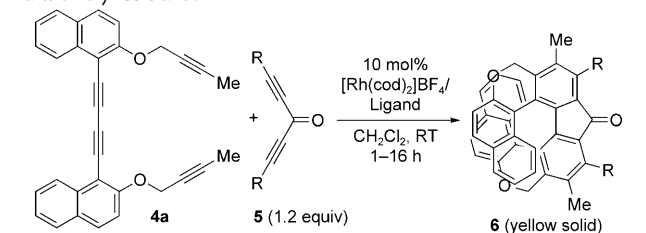


Figure 1. Structures of axially chiral biaryl bisphosphine ligands.

10 mol % of a [Rh(cod)₂]BF₄/(R)-segphos (cod = cycloocta-1,5-diene) complex at room temperature furnished the expected fluorenone-containing [9]helicene-like molecule **6aa** as a yellow solid in 56 % yield upon isolation and

Table 1: Rhodium-catalyzed double [2+2+2] cycloadditions of tetrayne **4a** with diynes **5a–d**.



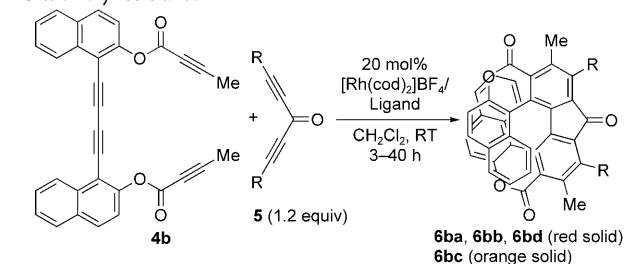
Entry	5 (R)	Ligand	6	Yield [%] ^[a] (ee [%])
1 ^[b]	5a (Me)	(R)-segphos	(P)-(+)- 6aa	56 (47)
2	5b (nBu)	(R)-segphos	(+)- 6ab	40 (39)
3	5c (Ph)	(R)-H ₈ -binap	(-)- 6ac	53 (18)
4 ^[c]	5d (CH ₂ OMe)	(R)-segphos	(+)- 6ad	26 (26)
5 ^[c]	5d (CH ₂ OMe)	(R)-H ₈ -binap	(-)- 6ad	56 (10)

[a] Yield of isolated product. [b] **5a**: 2 equiv. [c] Catalyst: 20 mol %.

47 % ee (Table 1, entry 1). In addition to **5a**, *n*-butyl- (Table 1, entry 2), phenyl- (Table 1, entry 3), and methoxymethyl substituted diethynylketones (Table 1, entries 4 and 5) participated in this reaction at room temperature by employing a cationic rhodium(I)/(R)-segphos or (R)-H₈-binap complex (10–20 mol %) as the catalyst.

Next, an intermolecular double [2+2+2] cycloaddition of ester-linked tetrayne **4b** with **5a** was also investigated, revealing that the use of 20 mol % of a [Rh(cod)₂]BF₄/(R)-binap complex at room temperature furnished the expected fluorenone-containing [9]helicene-like molecule **6ba** as a red solid in 42 % yield and 26 % ee (Table 2, entry 1). The reactions of **4b** with *n*-butyl- (Table 2, entry 2) and phenyl-substituted diethynylketones (Table 2, entry 3) also pro-

Table 2: Rhodium-catalyzed double [2+2+2] cycloadditions of tetrayne **4b** with diynes **5a–d**.

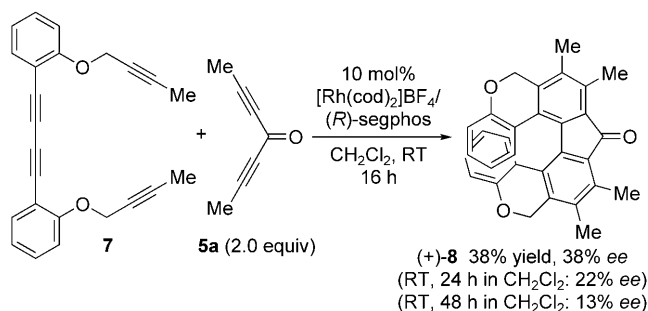


Entry	5 (R)	Ligand	6	Yield [%] ^[a] (ee [%])
1	5a (Me)	(R)-binap	(P)-(+)- 6ba	42 (26)
2	5b (nBu)	(R)-H ₈ -binap	(-)- 6bb	58 (32)
3	5c (Ph)	(R)-segphos	(-)- 6bc	61 (31)
4 ^[b]	5d (CH ₂ OMe)	(R)-segphos	(+)- 6bd	32 (60)

[a] Yield of isolated product. [b] Catalyst: 40 mol %. Solvent: (CH₂Cl)₂. Temperature: 40 °C.

ceeded by employing the cationic rhodium(I)/(R)-H₈-binap or (R)-segphos complex (20 mol %) as the catalyst. Although a high loading of the cationic rhodium(I)/(R)-segphos complex was required, the reaction of **4b** and methoxymethyl-substituted diethynylketone **5d** proceeded to yield the corresponding [9]helicene-like molecule **6bd** with the highest ee value (Table 2, entry 4).

As expected, fluorenone-containing [9]helicene-like molecules **6**, possessing large overlapping rings, did not undergo racemization at room temperature in CH₂Cl₂. In contrast, fluorenone-containing [7]helicene-like molecule **8**, which was prepared from phenol-linked tetrayne **7** and dialkynylketone **5a**, underwent gradual racemization under the same conditions (Scheme 4).



Scheme 4. Synthesis and racemization of fluorenone-containing [7]helicene-like molecule **8**.

The enantiopure crystal of (P)-(+)-**6aa** was readily prepared by recrystallization (Figure 2).^[11] The pseudohelical axes of [9]helicene-like molecules are nearly parallel to the *a*-axis (ca. 16.5°). The molecules that are related by the crystallographic 2₁-axes along the *c*-axis are packed almost parallel to the *bc*-plane. Adjacent molecular layers along the *a*-axis are related by the other 2₁-axes along the *b*-axis. Therefore, the helically chiral molecules are stacked in a partially overlapped fashion along the *a*-axis.

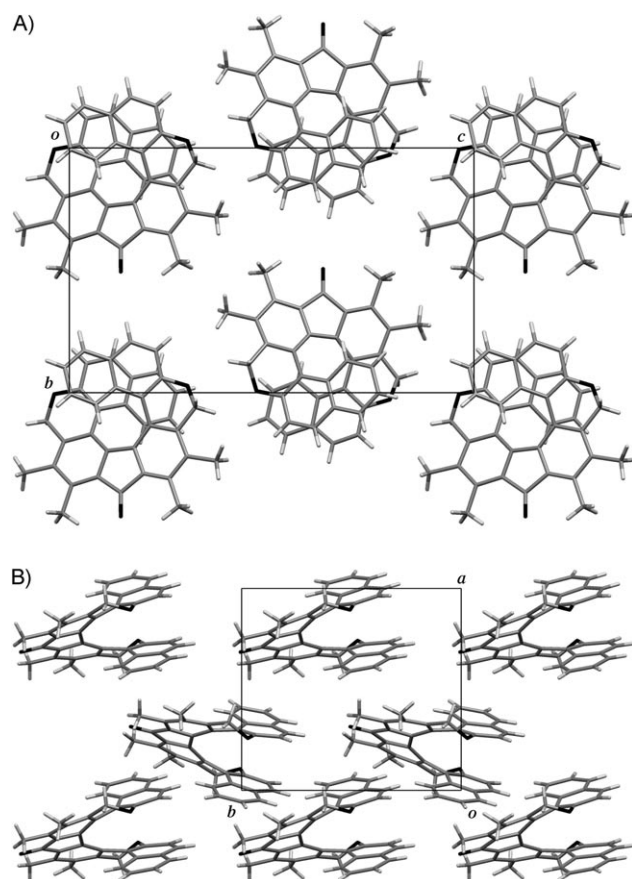


Figure 2. Packing structure of enantiopure (P)-(+)-**6aa**. A) *a*-projection view, B) *c*-projection view.

The enantiopure acetone solvate crystals of (P)-(+)-**6ba** was also readily prepared by recrystallization (Figure 3).^[11] The pseudohelical axes of **6ba** are almost parallel to the *c*-axis (ca. 3.9°). The molecules that are related by crystallographic two-fold axes along the *b*-axis form a columnar structure. In this column, the fluorenone parts of the **6ba** molecules are stacked along the *c*-axis. In addition, intermolecular stacking between naphthalene rings was observed with an average ring separation of 3.415(2) Å.

Photophysical properties of helicene-like molecules **6** and **8** were briefly examined as shown in Table 3. As expected, highly conjugated ester-linked [9]helicene-like molecules **6ba–d** (Table 3, entries 5–8), containing two α -pyrone rings, exhibit larger optical rotation values than ether-linked [9]helicene-like molecules **6aa–d** (Table 3, entries 1–4). Interestingly, ether-linked [7]- and [9]helicene-like molecules **8** and **6aa** exhibit very close optical rotation values (Table 3, entries 1 and 9). In general, when the compounds possess two α -pyrone rings (Table 3, entries 5–8), bathochromic shifts in emission were observed when compared to **6aa–d** (Table 3, entries 1–4).

In conclusion, we have achieved the flexible and convenient syntheses of enantioenriched fluorenone-containing [9]helicene-like molecules by rhodium-catalyzed intermolecular double [2+2+2] cycloadditions. Their unique crystal structures and photophysical properties have also been

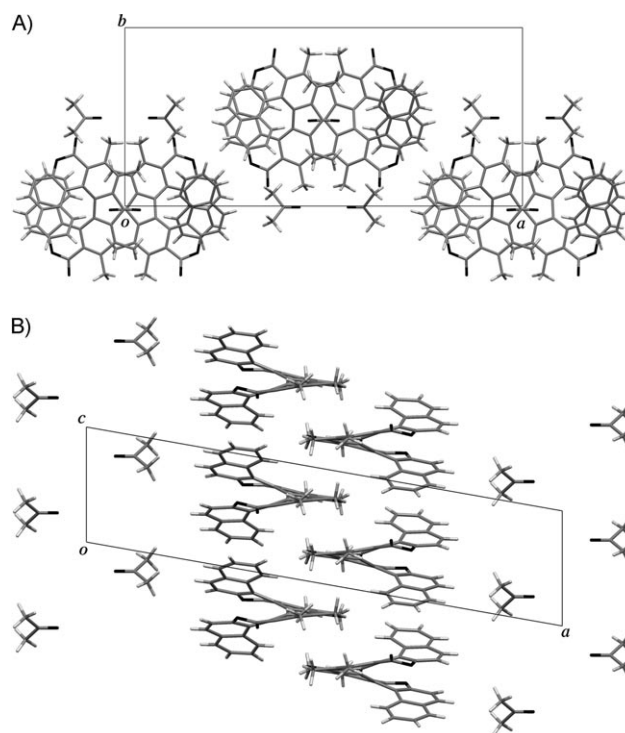


Figure 3. Packing structure of enantiopure (P)-(+)-**6ba**. A) *c*-projection view, B) *b*-projection view.

Table 3: Photophysical data of helicene-like molecule **6** and **8**.^[a]

Entry	Compound	$[\alpha]_D^{25[b]}$	UV Absorption $\lambda_{\max}$ [nm] ^[c]	Emission $\lambda_{\max}$ [nm]
1	(+)- 6aa	1250	356	556
2	(+)- 6ab	1499	357	554
3	(-)- 6ac	1151	377	420, 444
4	(+)- 6ad	1585	379	561
5	(+)- 6ba	2050	313	580
6	(-)- 6bb	1752	376	578
7	(-)- 6bc	1605	341	423, 572
8	(+)- 6bd	2033	381	472, 575
9	(+)- 8	1245	349	559

[a] Measured in CHCl₃. [b] Values are calculated as 100% ee. [c] Only the longest absorption maximum wavelengths are given.

determined. Future studies will focus on expanding the substrate scope including [11]helicene-like molecules and developing new materials by additional functionalization of these new helically chiral molecules.

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