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Communication

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Rhodium-Catalyzed Enantioselective Synthesis, Crystal Structures, and Photophysical Properties of Helically Chiral 1,1′-Bitriphenylenes

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Supporting Information

ABSTRACT: The highly enantioselective synthesis of helically chiral 1,1′-bitriphenylenes has been achieved via rhodium-catalyzed double [2 + 2 + 2] cycloaddition of biaryl-linked tetraynes with 1,4-diynes (up to 93% ee). Crystal structures and photophysical properties of these helically chiral 1,1′-bitriphenylenes have also been studied.

Triphenylene and fluorene derivatives have attracted much attention in materials chemistry because of their rigid, planar, conjugated structures.[1] For example, triphenylenes bearing long aliphatic side chains form discotic liquid crystals through self-assembly.[2] Oligo- or polyfluorene derivatives are employed in organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs).[3] On the other hand, helicenes have also attracted much attention as potential candidates for optical or electronic functional materials because of their unique helical chirality as well as rigid conjugated structures.[4] By combining these three types of fascinating π-conjugated structures, we designed new [7]helicenes, helically chiral 1,1′-bitriphenylenes, bearing both triphenylene and fluorene cores, as shown in Figure 1.[5] We anticipated that these new [7]helicenes could be synthesized via the double [2 + 2 + 2] cycloaddition of a biaryl-linked tetrayne with 1,4-diynes in an enantioselective manner.[6,7] In this paper, we disclose the catalytic enantioselective synthesis, crystal structures, and optical properties of helically chiral 1,1′-bitriphenylenes.

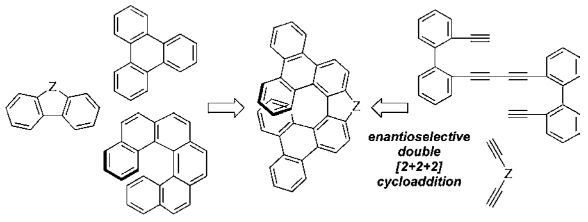

Figure 1. Our design of helically chiral 1,1′-bitriphenylenes.

Our research group has reported the enantioselective synthesis of helicene-like molecules via the double [2 + 2 + 2] cycloaddition of tetraynes with dialkynyl ketones catalyzed by a cationic rhodium(I)/axially chiral biaryl bisphosphine complex.[6f] Thus, we first screened various axially chiral biaryl bisphosphine ligands (Figure 2) for the rhodium(I)-catalyzed enantioselective double [2 + 2 + 2] cycloaddition of biaryl-linked tetrayne **1a** with dialkynyl ketone **2a**, leading to helically chiral 1,1′-bitriphenylene **3aa** (Table 1, entries 1−7). Pleasingly, the reactions of **1a** and **2a** proceeded at room temperature, and the use of (*S*)-xyl-Segphos as a ligand furnished **3aa** in good yield with the highest ee value (entry 5). Although the Deiters group previously reported a synthesis of triphenylenes via [2 + 2 + 2] cycloaddition of a biaryl-linked diyne with alkynes using a nickel catalyst, microwave heating was necessary.[8] The use of an axially chiral biaryl bisphosphine ligand is critical. The reaction using a chiral nonbiaryl bisphosphine ligand, (*R*,*R*)-Me-Duphos (Figure 2), resulted in a low yield and ee value (entry 8).

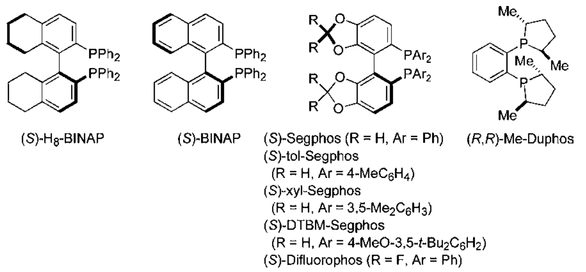

Figure 2. Structures of chiral bisphosphine ligands.

The effect of the amounts of **2a** and the catalyst was then examined. Increasing the amount of **2a** improved the yield of **3aa** (Table 2, entry 2 vs 1). The catalyst loading could be reduced to 10 mol % without erosion of the product ee value, although the product yield decreased (entry 2 vs 3). Thus, the scope of the rhodium-catalyzed enantioselective [2 + 2 + 2] cycloaddition of biaryl-linked tetraynes **1** with dialkynyl ketones **2** was examined. Not only dihexynyl ketone **2a** but also didodecynyl ketone **2b** and phenyl-, chloro-, and benzyloxy-substituted dipentynyl ketones **2c−e** could participate in this reaction when the cationic rhodium(I)/(*S*)-xyl-Segphos catalyst was used (entries 4−7). With respect to tetraynes, not only **1a** but also

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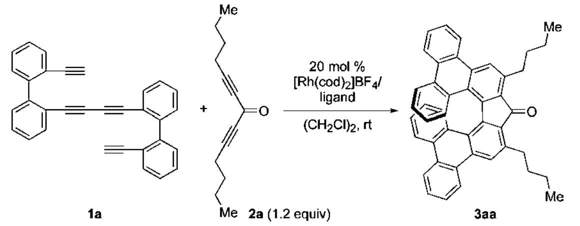
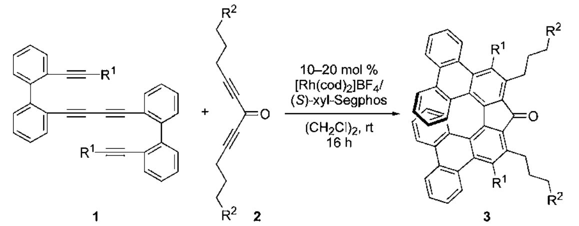
Table 1. Screening of Ligands for the Rh-Catalyzed Enantioselective Double [2 + 2 + 2] Cycloaddition of **1a** with **2a**[a]



entry	ligand	time (h)	yield (%)[b]	ee (%)
1	(*S*)-H$_8$-BINAP	16	72	39
2	(*S*)-BINAP	16	73	67
3	(*S*)-Segphos	16	67	74
4	(*S*)-tol-Segphos	16	68	57
5	(*S*)-xyl-Segphos	16	63	91
6	(*S*)-DTBM-Segphos	91	17	75
7	(*S*)-Difluorophos	16	71	86
8	(*R,R*)-Me-Duphos	16	22	52

[a] [Rh(cod)$_2$]BF$_4$ (0.010 mmol), ligand (0.010 mmol), **1a** (0.050 mmol), **2a** (0.060 mmol), and (CH$_2$Cl)$_2$ (2.0 mL) were used. [b] Isolated yields.

Table 2. Enantioselective Synthesis of Helical 1,1′-Bitriphenylenes **3** via Rh-Catalyzed Double [2 + 2 + 2] Cycloaddition[a]



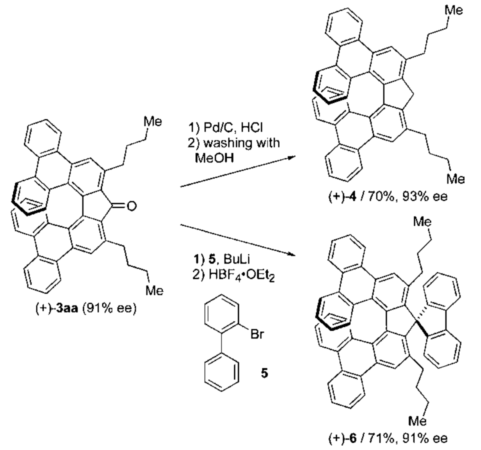
entry	**1** (R^1)	**2** (R^2, equiv)	catalyst (mol %)	**3**	yield (%)[b]	ee (%)
1	**1a** (H)	**2a** (Me, 2)	20	(+)-**3aa**	63	91
2	**1a** (H)	**2a** (Me, 2)	20	(+)-**3aa**	67	91
3[c]	**1a** (H)	**2a** (Me, 2)	10	(+)-**3aa**	59	91
4	**1a** (H)	**2b** [(CH$_2$)$_6$CH$_3$, 2]	20	(+)-**3ab**	62	92
5	**1a** (H)	**2c** (Ph, 2)	20	(+)-**3ac**	60	91
6	**1a** (H)	**2d** (Cl, 2)	20	(+)-(*P*)-**3ad**	59	93
7	**1a** (H)	**2e** (OBn, 1.2)	20	(+)-**3ae**	49	91
8[d,e]	**1b** (CO$_2$*n*-Bu)	**2a** (Me, 1.2)	20	(+)-**3ba**	74	66
9[c,d,f]	**1b** (CO$_2$*n*-Bu)	**2a** (Me, 1.2)	10	(+)-**3ba**	73	65
10[d]	**1b** (CO$_2$*n*-Bu)	**2d** (Cl, 1.2)	20	(+)-**3bd**	73	53

[a] [Rh(cod)$_2$]BF$_4$ (0.010 mmol), (*S*)-xyl-Segphos (0.010 mmol), **1** (0.050 mmol), **2** (0.060–0.10 mmol), and (CH$_2$Cl)$_2$ (2.0 mL) were used. [b] Isolated yields. [c] [Rh(cod)$_2$]BF$_4$ (0.0050 mmol) and (*S*)-xyl-Segphos (0.0050 mmol) were used. [d] Ligand: (*S*)-Difluorophos. [e] For 40 h. [f] For 72 h.

electron-deficient tetrayne **1b** reacted with dialkynyl ketones **2a** and **2d** in the presence of the cationic rhodium(I)/(*S*)-Difluorophos complex (10–20 mol %) to give the corresponding helicenes **3ba** and **3bd** in high yields, although the ee values were moderate (entries 8–10).

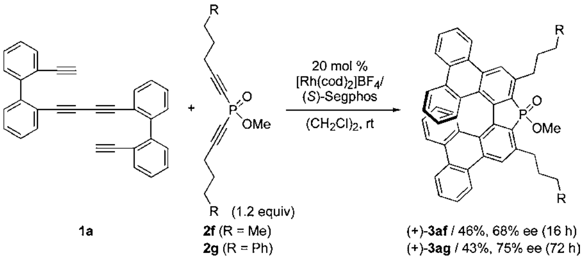
Fluorenone **3aa** was readily derivatized into fluorene derivatives without erosion of its ee value (Scheme 1). Hydrogenation of **3aa** in the presence of Pd/C and HCl furnished fluorene **4** in good yield. Arylation of **3aa** with 2-bromobiphenyl (**5**) followed by dehydration[9] furnished spirofluorene **6** in good yield.

Scheme 1.



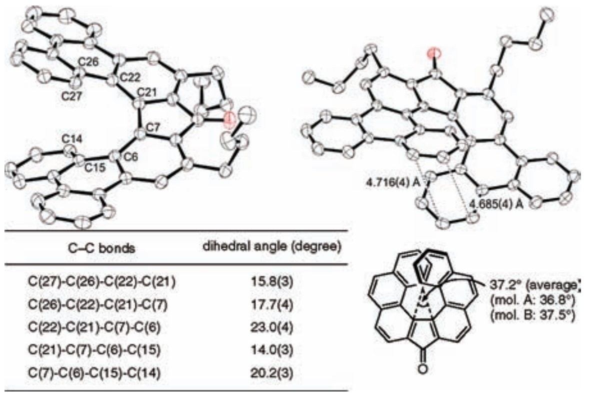
Our research group recently reported the enantioselective synthesis of helically chiral phosphafluorenes via [2 + 2 + 2] cycloaddition of tetraynes with dialkynyl phosphine oxides catalyzed by a cationic rhodium(I)/axially chiral biaryl bisphosphine complex.[6h,10] Thus, we next examined the enantioselective [2 + 2 + 2] cycloaddition of **1a** with dialkynyl phosphine oxides **2f** and **2g** in the presence of the cationic rhodium(I)/axially chiral biaryl bisphosphine complex. Pleasingly, these reactions proceeded at room temperature using (*S*)-Segphos as a ligand, giving the desired helicenes **3af** and **3ag** in moderate yields with good ee values (Scheme 2).

Scheme 2.



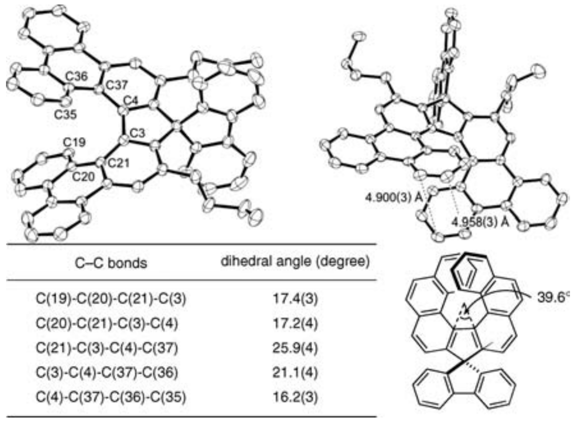
In our previous reports, racemization of a benzopyrano-fused helical fluorenone occurred in CH$_2$Cl$_2$ solution at room temperature[6f] while that of benzopyrano-fused helical phosphafluorenes did not occur under the same conditions, presumably because of the longer length of the C–P bond relative to the C–C bond.[6h] Similarly, racemization of fluorenone **3aa** occurred in (CH$_2$Cl)$_2$ solution at 80 °C (from 91% ee to 65% ee over 24 h), while no racemization of phosphafluorene **3af** was observed under the same conditions.[13] Very recently, Nakano, Nozaki, and co-workers[11] synthesized λ^5-phospha[7]helicenes via the double cross-coupling reaction. They also observed the high tolerance of the λ^5-phospha[7]helicenes toward racemization. Interestingly, the racemization of fluorene **4** in (CH$_2$Cl)$_2$ solution at 80 °C was slower (from 93% ee to 81% ee over 24 h) than that of fluorenone **3aa**, and no racemization of spirofluorene **6** was observed.[13]

To elucidate the higher tolerance of spirofluorene **6** than fluorenone **3aa** toward racemization, the crystal structures of **6** and **3aa** were compared, as shown in Figures 3 and 4. The sums of the five dihedral angles derived from the seven C–C bonds are 90.7° for **3aa** and 97.8° for **6**.[12] In addition, the larger angle



C–C bonds	dihedral angle (degree)
C(27)-C(26)-C(22)-C(21)	15.8(3)
C(26)-C(22)-C(21)-C(7)	17.7(4)
C(22)-C(21)-C(7)-C(6)	23.0(4)
C(21)-C(7)-C(6)-C(15)	14.0(3)
C(7)-C(6)-C(15)-C(14)	20.2(3)

Figure 3. Crystal structure analysis of enantiopure (+)-**3aa** with ellipsoids at 30% probability. The sum of the five dihedral angles is 90.7°.



C–C bonds	dihedral angle (degree)
C(19)-C(20)-C(21)-C(3)	17.4(3)
C(20)-C(21)-C(3)-C(4)	17.2(4)
C(21)-C(3)-C(4)-C(37)	25.9(4)
C(3)-C(4)-C(37)-C(36)	21.1(4)
C(4)-C(37)-C(36)-C(35)	16.2(3)

Figure 4. Crystal structure analysis of enantiopure (+)-**6** with ellipsoids at 30% probability. The sum of the five dihedral angles is 97.8°.

between the two formal C═C double bonds of the annelated cyclopentadiene fragment (Figures 3 and 4) in **6** (39.6°) relative to **3aa** [37.2° (average)] induces a larger overlap of the two terminal benzene rings in **6** than in **3aa**, resulting in a larger steric repulsion.[13,14] Indeed, the distances between two terminal benzene rings are 4.716 and 4.685 Å for **3aa** and 4.900 and 4.958 Å for **6**. These larger distortions of **6** account for the higher tolerance toward racemization. The absolute configuration of helicene (+)-**3ad** possessing two chlorine atoms was determined to be *P* by the anomalous dispersion method.[15]

Absorption and emission data for representative helically chiral 1,1′-bitriphenylenes **3aa**, **4**, **6**, and **3af** are shown in Table 3.

Table 3. Photophysical Properties of (+)-3aa, (+)-4, (+)-6, and (+)-3af[a]

compound	absorption λ_{max} (nm)[b]	fluorescence λ_{max} (nm)[c,d]	ϕ_F[c,d]	$[\alpha]_D^{25}$[e]
(+)-**3aa**	292, 361	572	0.021	1397
(+)-**4**	261, 364, 388	428	0.320	1087
(+)-**6**	262, 370, 400	449	0.296	684
(+)-**3af**	273, 370, 388	487	0.218	1230

[a] Measured in $CHCl_3$ at 25 °C. [b] 2×10^{-5} M. [c] 3×10^{-5} M. [d] Excited at 350 nm. [e] Values were calculated as 100% ee.

Fluorenone **3aa** and phosphafluorene **3af** showed large red shifts of the absorption and emission maxima compared with fluorenes **4** and **6**. Fluorenes **4** and **6** showed higher quantum yields (32.0% and 29.6%, respectively) in $CHCl_3$ solution than phosphafluorene **3af**, and that of fluorenone **3aa** was the lowest (2.1%) among the four helicenes.[16] Optical rotation values of these helicenes were also measured. Interestingly, the optical rotation value, which was calculated as 100% ee, was significantly smaller for spirofluorene **6** than for **3aa**, **4**, and **3af**.

Finally, we conducted circularly polarized luminescence (CPL) measurements (differential emission of right circularly polarized light vs left circularly polarized light in chiral molecular systems[17]) on **4** (93% ee) and **6** (91% ee) in chloroform. Figure 5 shows the corresponding circular dichroism (CD), CPL, UV–vis absorption, and fluorescence spectra of **4**. Compounds **4** and **6** exhibited CPL activities, as the CPL spectra of (+)-(*P*) and (−)-(*M*) helicenes are mirror images. The degree of CPL is given by the luminescence dissymmetry ratio, which is defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the luminescence intensities of left and right circularly polarized light, respectively. The values were $g_{lum} = -0.030$ at 428 nm for (−)-(*M*)-**4** and $g_{lum} = -0.032$ at 449 nm for (−)-(*M*)-**6**[15] in chloroform, which are comparable to those for our recently reported phthalhydrazide-functionalized [7]helicene-like molecule[18] ($g_{lum} = -0.035$ at 476 nm for the assembly state and −0.021 for the molecularly dispersed state) and significantly larger than those for helically chiral molecules reported to date.[19]

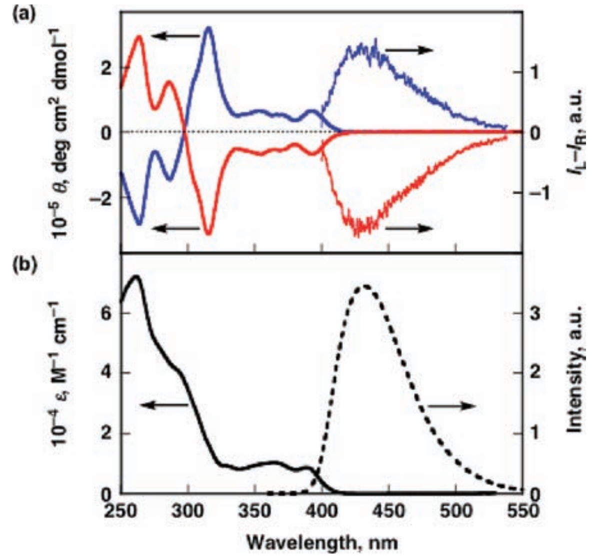


Figure 5. (a) CD and CPL spectra of (+)-(*P*)-**4** (blue line) and (−)-(*M*)-**4** (red line) at 2×10^{-5} M (10 mm path length) in $CHCl_3$ at 25 °C. (b) UV–vis and fluorescence spectra of (+)-(*P*)-**4** in $CHCl_3$ at 25 °C. The excitation wavelengths for fluorescence and CPL measurements were 350 and 375 nm, respectively.

In conclusion, we have achieved the highly enantioselective synthesis of helically chiral 1,1′-bitriphenylenes via rhodium-catalyzed double [2 + 2 + 2] cycloaddition. The present method realized the highest level of enantioselectivity in the synthesis of helicenes reported to date. Crystal structure analysis of the [7]helicene containing the spirofluorene moiety revealed a large overlap and distortion of the two terminal benzene rings, which account for the high tolerance of this helicene toward racemization. The CPL properties of [7]helicenes containing the fluorene or spirofluorene moiety are significantly larger than those of helicene derivatives reported to date. Future work will focus on further functionalization of these helicenes to enhance their chiroptical properties[20,21] and application of this methodology to the synthesis of various heteroatom-bridged helically chiral 1,1′-bitriphenylenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, compound characterization data, and X-ray crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) Nakano, Nozaki, and co-workers[11] reported that the sums of the five dihedral angles of oxa-, aza-, and thia[7]helicenes were 79−88°. On the other hand, that of λ^5-phospha[7]helicene was 95−100°.

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(14) In addition, the shorter distance between the centroids of the two terminal benzene rings in **6** (0.31 Å) than in **3aa** (0.96 Å) also explains the larger overlap of the two terminal benzene rings in **6** than in **3aa**. See the Supporting Information for details.

(15) See the Supporting Information.

(16) The fluorescence quantum yields for hexahelicene and triphenylene are 0.041 and 0.066; helically chiral 1,1′-bitriphenylenes **3aa**, **4**, and **6** exhibit higher fluorescence quantum yields. See: Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; Taylor & Francis: Boca Raton, FL, 2006.

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