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Article

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Catalytic Enantioselective Synthesis of Axially Chiral Polycyclic Aromatic Hydrocarbons (PAHs) via Regioselective C-C Bond Activation of Biphenylenes

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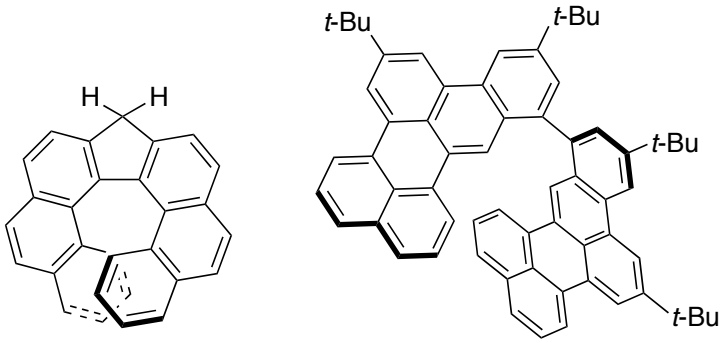
ABSTRACT:

Chiral polycyclic aromatic hydrocarbons (PAHs) are expected to have unusual physical properties due to their chirality and expanded π-conjugated system. Indeed, PAHs are promising compounds as chiral recognizers and organic semiconductors. Therefore, an efficient method for the synthesis of chiral PAHs is strongly desired. In contrast to helically chiral PAHs, there are only limited examples of enantioselective synthesis of axially chiral PAHs. Herein, we report the catalytic enantioselective synthesis of benzo[*b*]fluoranthene-based axially chiral PAHs in excellent yields and enantioselectivities (up to >99%, >99% ee) by regioselective cleavage of the sterically hindered C-C bond of biphenylenes. The consecutive cyclizations could provide polycyclic PAHs with two chiral axes. The obtained chiral PAHs have high ε values (up to $\varepsilon = 8.9\times10^4$), quantum yields (up to $\Phi = 0.67$) and circularly polarized luminescence (CPL) property ($|g_{lum}|$ = up to 3.5×10^{-3}).

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have attracted much attention because of their unique physical properties and they have been studied for possible applications as organic electronic materials.[1] Thus, PAHs have been recognized as synthetic targets for the development of new methodologies and as templates for the bottom-up synthesis of nanocarbons.[2] For example, Itami and co-workers established the annulative π-extension (APEX) reaction for the synthesis of fused aromatic hydrocarbons from simple aromatic compounds.[3] Recently, they further achieved living APEX polymerization to synthesize graphene nanoribbon from phenanthrene as a simple initiator.[4]

Chiral PAHs have the potential for use in new types of optical devices because they likely have circularly polarized luminescence (CPL) properties.[5] For instance, in 2016, Nozaki and co-workers reported [7]helicene-like compounds possessing a fluorene skeleton and those showed large *g* values (dissymmetry factor) for CPL (up to $|g_{lum}| = 3.0\times10^{-3}$).[6] In contrast, axially chiral PAHs also have relatively strong CPL: Hirose, Matsuda, and co-workers synthesized a 13,13'-bibenzo[*b*]perylenyl derivative, which had a high fluorescence yield ($\Phi = 0.64$) as well as a strong CPL ($|g_{lum}| = 5\times10^{-3}$).[7] However, in both cases, the enantioenriched molecules were prepared from racemic compounds by HPLC resolution using the chiral stationary phase column.



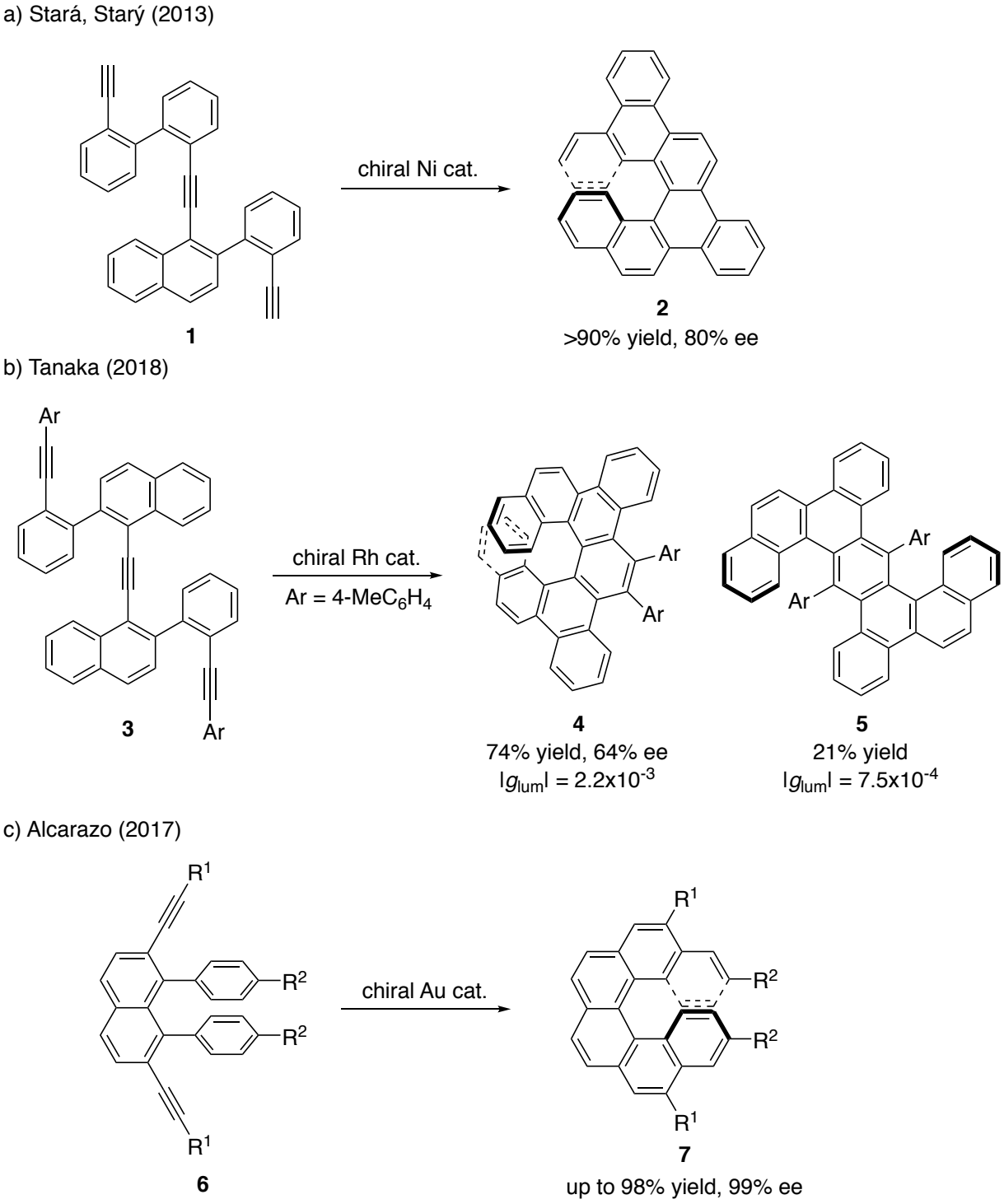
$\Phi = 0.39$, $|g_{lum}| = 3.0\text{x}10^{-3}$ Nozaki (2016)

$\Phi = 0.64$, $|g_{lum}| = 5\text{x}10^{-3}$ Hirose and Matsuda (2016)

Figure 1. Selected examples of chiral PAHs

For further studies of chiral PAHs, the catalytic enantioselective synthesis of chiral carbohelicenes have been developed. The most well-established method for the preparation of enantioenriched benzenoid helicene is transition-metal-catalyzed [2+2+2] cycloaddition.[8] In 2013, Stará, Starý, and co-workers synthesized chiral dibenzo[6]helicenes **2** from triyne **1** via nickel-catalyzed enantioselective [2+2+2] cycloaddition (Scheme 1, **a**).[8a] In 2018, Tanaka and co-workers reported the rhodium-catalyzed enantioselective synthesis of dibenzo[7]helicenes **4** via [2+2+2] cycloaddition and of twisted anthracene **5** via [2+1+2+1] cycloaddition from tetrayne **3** (Scheme 1, **b**).[8e] In particular, the dibenzo[7]helicenes **4**

showed relatively strong CPL property ($|g_{lum}| = 2.2\times10^{-3}$). Cycloisomerization was also used for the synthesis of helically chiral helicenes. In 2017, Alcarazo and co-workers achieved an enantioselective synthesis of [6]carbohelicene **7** from diyne **6** by using a chiral gold catalyst (Scheme 1, **c**).[9] Contrastingly, there are no examples of the enantioselective construction of PAHs possessing a biaryl system without any heteroatom as far as we know. While there are several approaches for the asymmetric synthesis of axially chiral biaryl compounds such as binaphthyl, a heteroatom such as oxygen, nitrogen or sulfur is usually required.[10]

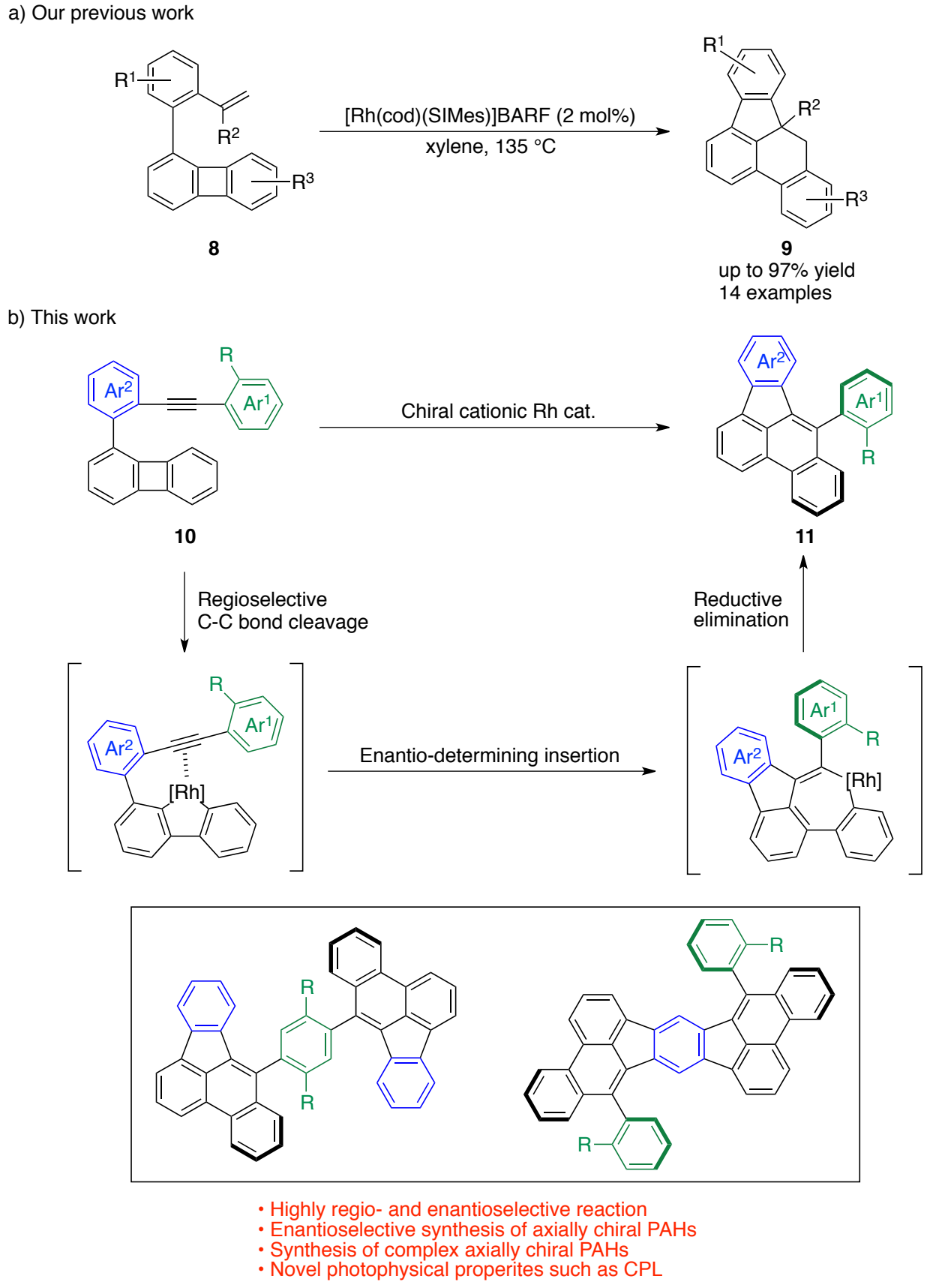


Scheme 1. Successful examples for enantioselective synthesis of helically chiral PAHs

To synthesize enantioenriched axially chiral PAHs, we developed a strategy involving the more-hindered site-selective cleavage of a biphenylene skeleton. While biphenylene is an antiaromatic hydrocarbon, which exhibits enormous strain at central 4-membered ring, transition metal complexes readily cleave the strained C-C bond to provide dibenzometallacyclopentadiene complexes as useful C-4 units for the construction of various ring systems.[11] We previously reported the regioselective cleavage

of the sterically more hindered C-C bond of biphenylenes **8** and subsequent intramolecular cyclization with alkene in the presence of a Rh catalyst.[12] In this reaction, the alkene moiety acted as both a directing group and a reaction site to form dihydrobenzo[*b*]fluoranthenes **9**. Since catalytic and regioselective activation of a sterically hindered C-C bond is still rare, it seems that this methodology has the potential to form complex PAHs. Moreover, we previously reported the enantioselective intermolecular cyclization of biphenylene and *ortho*-substituted aryl alkynes for the synthesis of axially chiral phenanthrene derivatives.[13]

Against this background, we assumed that, if an enantioselective cyclization of biphenylene **10** proceeds with regioselective cleavage of a sterically hindered C-C bond assisted by the coordination of an alkyne moiety, an axially chiral benzo[*b*]fluoranthene derivative **11** could be obtained via an enantiodetermining insertion of an alkyne moiety to a Rh-C bond, and enantioselective synthesis of unique axially chiral PAHs can be realized. In this study, we achieved a Rh-catalyzed enantioselective synthesis of benzo[*b*]fluoranthene-based chiral PAHs in excellent yields with excellent enantioselectivities. In addition, we also obtained various poly-conjugated axially chiral PAHs by consecutive cyclizations.

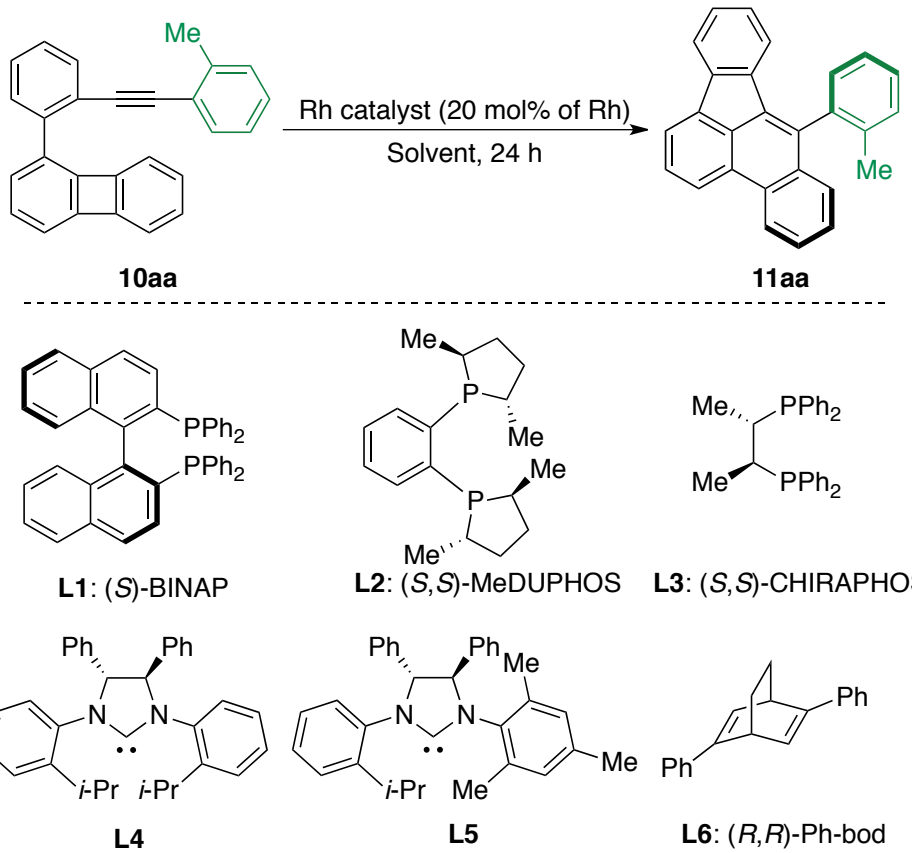


Scheme 2. Our previous work and the concept of this work

Discussion

We chose a biphenylene derivative **10aa** as a model substrate and screened various cationic chiral Rh catalysts (Table 1).[14] When chiral diphosphine ligands **L1-3** were used, the desired product **11aa** was obtained in high yield, albeit with poor enantioselectivity (Entries 1-3). In the case of chiral *N*-heterocyclic carbenes (NHC) ligands **L4** and **L5**, enantioselectivities were moderate or low (Entries 4, 5). We supposed that stronger *trans* effect of alkyne moieties increased the distance between chiral moiety and substrate.[15] As a result, enantiocontrol of the reaction became more difficult. Therefore, we tried chiral diene ligand **L6**, and chiral product **11aa** was obtained with the highest ee of 78% (Entry 6). Screening of the solvent at 135 °C (bath temperature) revealed that cyclopentyl methyl ether (CPME) was the best choice with regard to both yield and ee (Entries 6-9). The prepared $[RhCl(\mathbf{L6})]_2$ gave the same results as the catalyst prepared *in situ* (Entries 9 and 10). The reaction temperature was crucial for the enantioselectivity and we achieved almost quantitative yield with excellent enantioselectivity at 80 °C (Entries 10-12). The comparable result was obtained also in chlorobenzene at 80 °C (Entry 13). We assumed that racemization proceeded at the high temperature. We measured that the rate constant of racemization for **11aa** at 160 °C (433 K) is 8.99×10^{-6} s^{-1} and calculated that the flipping energy of the axial chirality ($\Delta G^{\ddagger}$) is 35.7 kcal/mol according to the Eyring equation. This result means that the half-life of **11aa** at 80 °C (353 K) is 18 years and that it hardly racemizes at the temperature.[16] The reaction could be conducted by the ten times scale without loss of yield and ee (Entry 14). The amount of catalyst could be reduced to 5 mol% of Rh with a slight decrease of yield and ee (Entry 15). We further investigated the present reaction using the conditions in entry 12.

Table 1. Screening of reaction conditions[a]



Entry	Rh Catalyst	Solvent	Bath Temperature / °C	Yield / %	Ee / %
1[b]	$[Rh(cod)_2]$BARF + **L1**	Xylene	135	81	-18
2[b]	$[Rh(cod)_2]$BARF + **L2**	Xylene	135	>99	-2
3[b]	$[Rh(cod)_2]$BARF + **L3**	Xylene	135	86	0
4[b]	[RhCl(cod)(**L4**)]+NaBARF	Xylene	135	87	-42
5[b]	[RhCl(cod)(**L5**)]+NaBARF	Xylene	135	58	-4
6	$[RhCl(coe)_2]_2$+2 **L6**+2 NaBARF	Xylene	135	77	78
7	$[RhCl(coe)_2]_2$+2 **L6**+2 NaBARF	PhCl	135	>99	80
8	$[RhCl(coe)_2]_2$+2 **L6**+2 NaBARF	Dioxane	135	68	76
9	$[RhCl(coe)_2]_2$+2 **L6**+2 NaBARF	CPME	135	>99	88
10	$[RhCl(\mathbf{L6})]_2$+ 2 NaBARF	CPME	135	>99	88
11	$[RhCl(\mathbf{L6})]_2$+ 2 NaBARF	CPME	100	99	96
12	$[RhCl(\mathbf{L6})]_2$+ 2 NaBARF	CPME	80	99	97
13	$[RhCl(\mathbf{L6})]_2$+ 2 NaBARF	PhCl	80	>99	97
14[c]	$[RhCl(\mathbf{L6})]_2$+ 2 NaBARF	CPME	80	>99	97
15[d]	$[RhCl(\mathbf{L6})]_2$+ 2 NaBARF	CPME	80	94	96

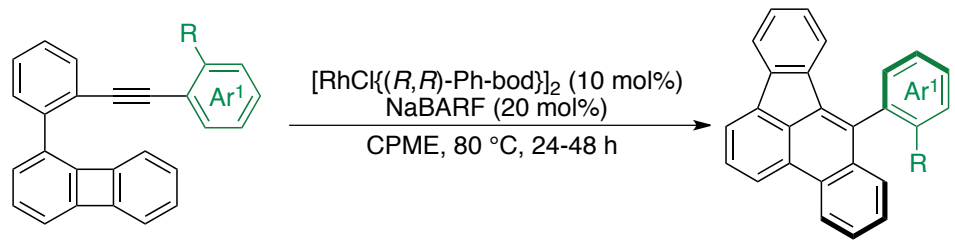
[a] The reaction was conducted in a sealed Schlenk tube: **10aa** (0.05 mmol), Rh catalyst (0.01 mmol of Rh), solvent (0.5 mL). [b] **10aa** (0.10 mmol), Rh catalyst (0.01 mmol of Rh), solvent (0.5 mL). [c] **10aa**

(0.50 mmol), Rh catalyst (0.1 mmol of Rh), solvent (5.0 mL). [d] The reaction was conducted in the presence of Rh catalyst (5 mol%) for 48 h. BARF = tetrakis[(3,5-trifluoromethyl)phenyl]borate

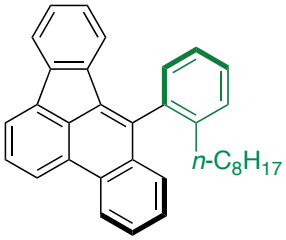
Next, we screened various substrates **10** which have different functional groups at the *ortho* position of the phenyl ring (Table 2). Although the reaction proceeded smoothly to give **11ba**, which has a longer alkyl chain, in excellent yield with excellent enantioselectivity, an alkoxy group had a negative effect on enantioselectivity (**11ca**) and the ee was moderate in both CPME and chlorobenzene. This was most likely because dissociation of the chiral diene was caused by the coordination of an oxygen atom to the metal center. 2-Biphenyl and 1-naphthyl groups could be used as substituents on the alkyne terminus (**11da**, **11ea**). When electron-withdrawing groups were attached to the *ortho* position of the phenyl ring (**11fa-ha**), the reactions also proceeded with high yields and ees. In particular, in the reaction of CF_3-substituted substrate **10fa**, chlorobenzene (98% ee) gave higher ee than CPME (85% ee). Based on the results of X-ray single-crystal analysis of **11ha**, the absolute configuration was assigned to be *R* isomer.[17,18] For the synthesis of complex PAHs, we synthesized pyrene-substituted substrates **10ia** and **10ja**, and pyrene-benzo[*b*]fluoranthene biaryl compounds **11ia** and **11ja** were obtained in excellent yields and ees. Overall, this reaction proceeded smoothly with various kinds of *ortho*-substituted aryl groups on the alkyne terminus.

Furthermore, we checked the effects of substituents on the *ortho*-phenylene-tether (Table 3). A methoxy group as an electron-donating group and a halogen atom as an electron-withdrawing group could be installed at all positions on the *ortho*-phenylene-tether (**11ab-ai**) with high yields and ees. Regarding the reaction of **10ae**, **10af**, and **10ai**, chlorobenzene was used as a solvent. We next examined naphthalene-tethered compounds. When 1-alkynyl-2-biphenylene-substituted substrate **10aj** was used, dibenzo[*b*,*l*]fluoranthene **11aj** was obtained in moderate yield with high enantioselectivity, but 30% of inseparable starting material **10aj** remained. The starting material was completely consumed in chlorobenzene along with a slight decrease of ee. In the case of the 2,3-naphthylene-tethered compound **10ak**, the reaction proceeded smoothly and gave dibenzo[*b*,*k*]fluoranthene **11ak**. Thiophene-tethered compound **10al** was also suitable for this reaction to give **11al** in excellent yield with excellent enantioselectivity.

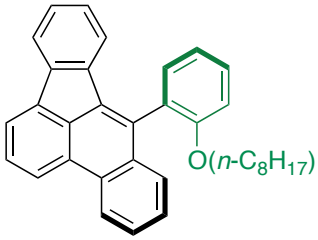
Table 2. Screening of the *ortho*-substituents on phenyl ring[a]



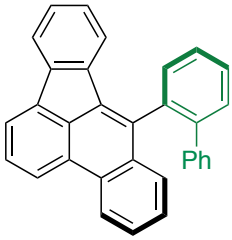
10 **11**



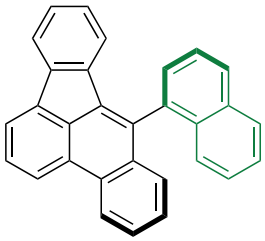
11ba
93%, 97% ee



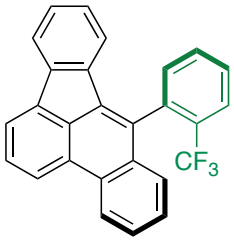
11ca
>99%, 68% ee
>99%, 64% ee[b]



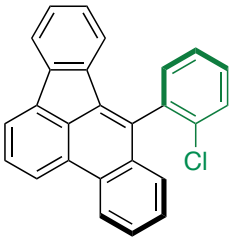
11da
>99%, 98% ee



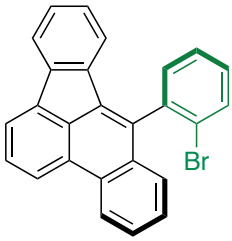
11ea
91%, 93% ee



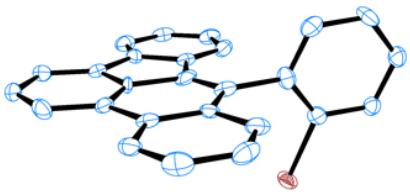
11fa[b]
89%, 98% ee



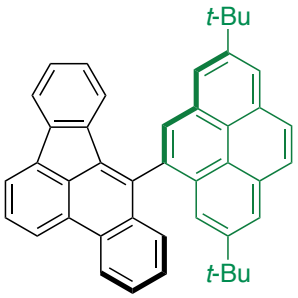
11ga
91%, 94% ee



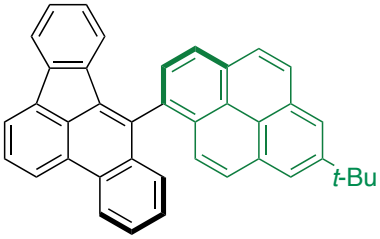
11ha
96%, 92% ee



X-ray structure of **11ha**[17]
(Thermal ellipsoids shown
at 50% probability)



11ia
>99%, 98% ee

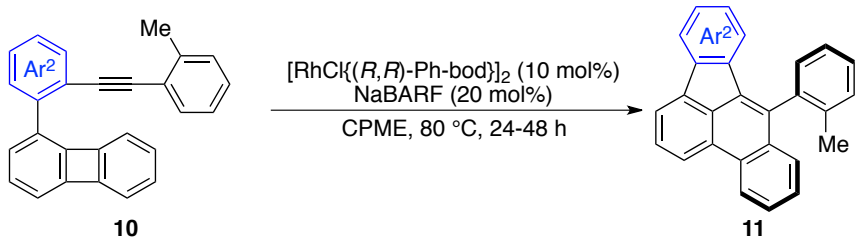


11ja
>99%, 99% ee

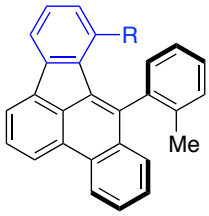
[a] **10** (0.05 mmol), [RhCl{(*R*,*R*)-Ph-bod}]$_2$ (0.005 mmol), NaBARF (0.01 mmol), CPME (0.5 mL).

[b] The reaction was conducted in chlorobenzene.

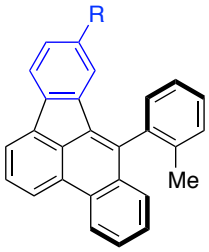
Table 3. Screening of *ortho*-phenylene tethers[a]



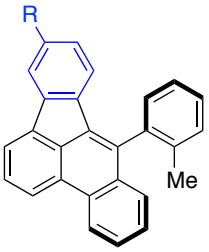
10 **11**



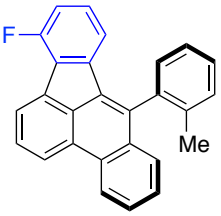
11ab (R = OMe); 82%, 93% ee
11ac (R = F); >99%, 94% ee[b]



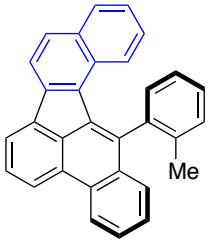
11ad (R = OMe); 61%, 97% ee
11ae (R = F); >99%, 98% ee[c]
11af (R = Cl); 92%, 91% ee[c]



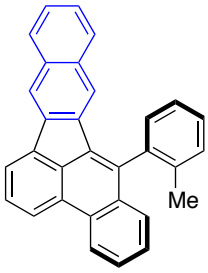
11ag (R = OMe); 88%, 97% ee
11ah (R = F); 79%, 93% ee



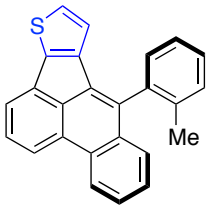
11ai; 98%, 97% ee[c]



11aj; 53%, 84% ee (**10aj**; 30%)
94%, 78% ee[c]



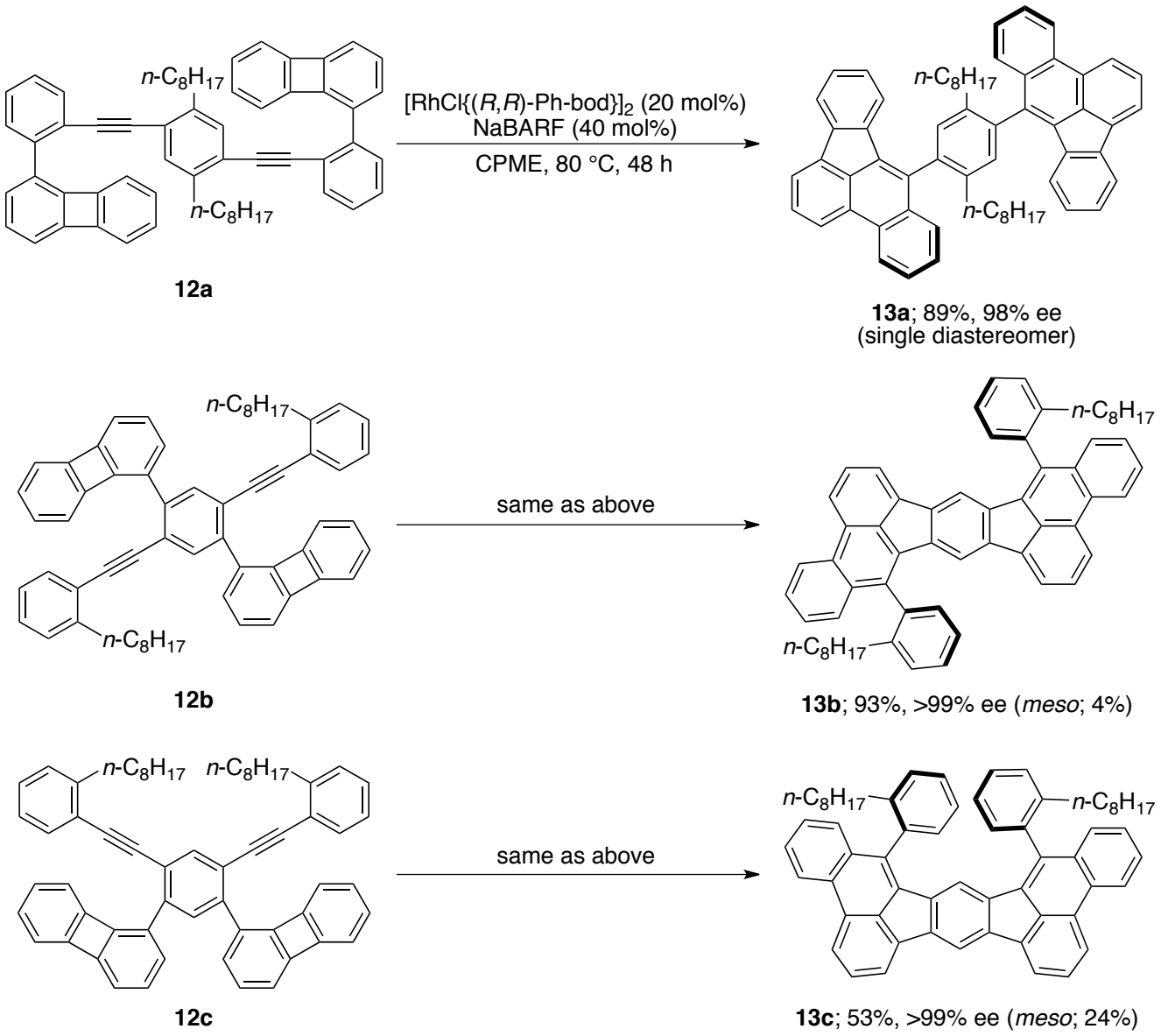
11ak; 98%, 91% ee



11al; 98%, 97% ee

[a] **10** (0.05 mmol), [RhCl{(*R*, *R*)-Ph-bod}]$_2$ (0.005 mmol), NaBARF (0.01 mmol), CPME (0.5 mL)
[b] The reaction was conducted at 100 °C. [c] The reaction was conducted in chlorobenzene.

To synthesize more complex PAHs, we used various substrates with two alkyne moieties and two biphenylene skeletons, and undertook consecutive cyclizations (Scheme 3). When **12a** was used, only *para*-phenylene-tethered chiral bis(benzo[*b*]fluoranthene) **13a** as an optically active diastereomer was obtained in high yield with excellent enantioselectivity. Next, we synthesized regioisomers **12b** and **12c**, where two alkyne moieties and two biphenylene skeletons were installed to the core benzene ring. When *para*-dialkynyl *para*-biphenylenyl compound **12b** was used, chiral nonacyclic compound **13b** was isolated in 93% yield with >99% ee, along with a slight amount of separable *meso* product (4%). Starting from *meta*-dialkynyl *meta*-biphenylenyl **12c**, compound **13c** was afforded in moderate yield with excellent enantioselectivity. In this case, separable *meso* product (24%) was also obtained probably due to a steric effect around the symmetrical axes.



Scheme 3. Consecutive cyclizations for complex axially chiral PAHs

Finally, we measured the photophysical properties of some of the synthesized PAHs.[19] The UV/Vis absorption spectra measured in DCM are shown in Figure 2. The benzo[*b*]fluoranthene skeleton itself has a relatively high ε value in the visible-light region. The spectra of **11ia** and **11ja** were red-shifted compared to those of 2-*tert*-butylpyrene and 2,7-di-*tert*-butylpyrene. Moreover, the spectra of **11ia** and **11ja** were slightly shifted compared to that of **11ba**. These observations can be explained in terms of internal interaction between the pyrene ring and benzo[*b*]fluoranthene skeleton. Regarding polycyclic products **13**, the UV spectrum of **13a** was almost the same as that of **11ba**, but the ε value of **13a** was higher than that of **11ba**. Compared to the spectrum of a benzo[*b*]fluoranthene unit, the spectra of nonacyclic aromatic hydrocarbons **13b** and **13c** were shifted to a longer wavelength side. In addition, **13b** had a higher ε value than **13c** and other benzo[*b*]fluoranthene derivatives.

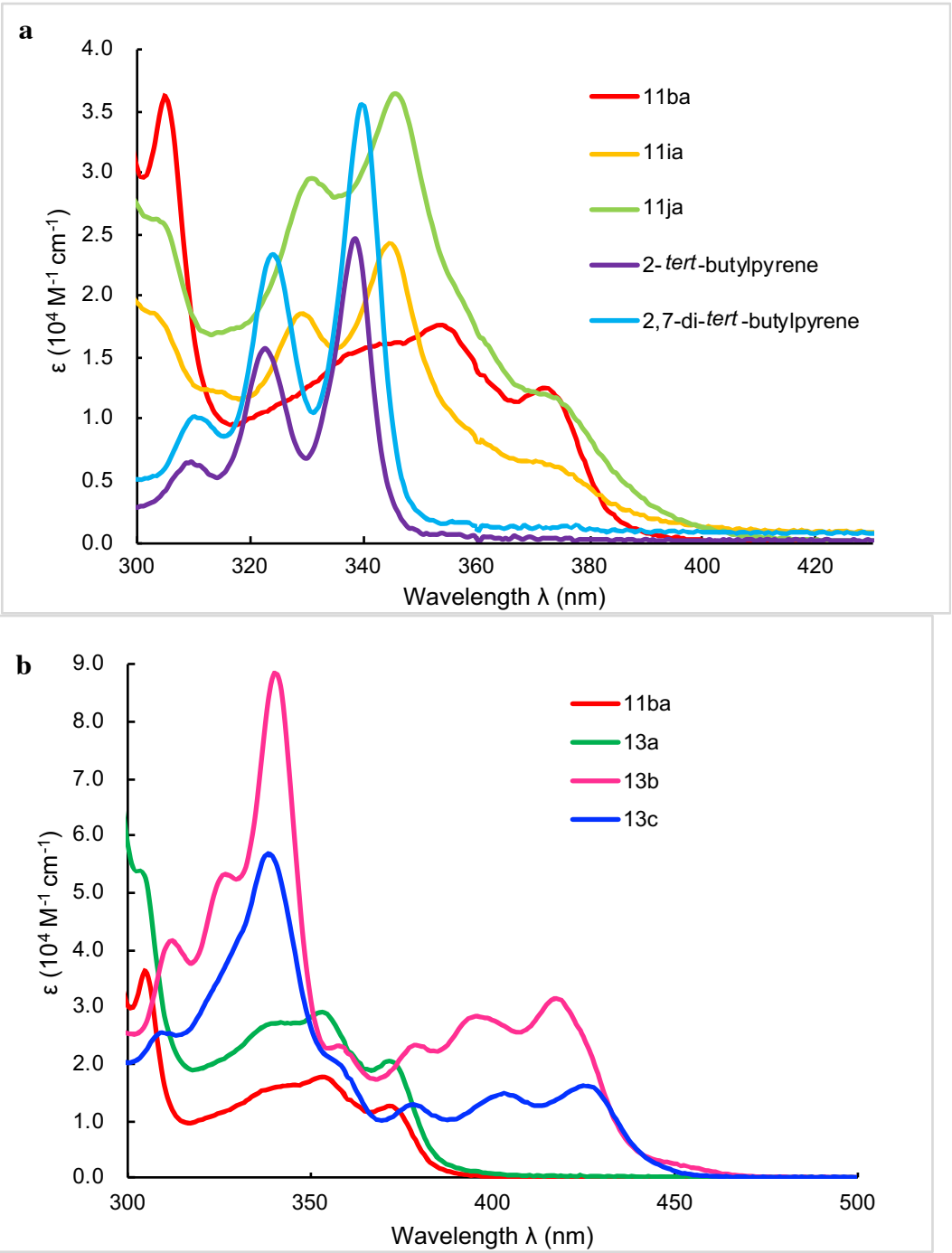


Figure 2. **a**, UV/Vis spectra of **11** and related compounds (**11ba**; 1.0×10^{-5} M, **11ia**; 1.0×10^{-5} M, **11ja**; 1.0×10^{-5} M, 2-*tert*-butylpyrene; 1.0×10^{-5} M, 2,7-di-*tert*-butylpyrene; 1.0×10^{-5} M). **b**, UV/Vis spectra of **11ba** and **13** (**11ba**; 1.0×10^{-5} M, **13a**; 1.0×10^{-5} M, **13b**; 1.0×10^{-5} M, **13c**; 1.0×10^{-5} M).

The fluorescence spectra and quantum yields of selected products were also measured (Figure 3). Interestingly, the shape of the fluorescence spectrum of **11ia** was almost the same as that of **11ja**. Furthermore, these spectra were shifted to a longer wavelength compared to that of **11ba**. This result probably suggested that internal energy was transferred from excited pyrene to the benzo[*b*]fluoranthene

skeleton. Compound **11ia** showed the same level of quantum yield as **11ba** (Φ = 0.29 and 0.27, respectively). Although pyrene derivatives **11ia** showed low quantum yields due to a loose bolt effect,[20] **11ja** had a relatively high quantum yield (Φ = 0.67). Compound **13a** had almost the same photophysical properties as **11ba**. The Stokes shifts of **13b** and **13c** (9064 cm^{-1} (1.12 eV) and 8774 cm^{-1} (1.09 eV), respectively) were significantly larger than that of **13a** (88 nm), which can be recognized that they are derived from the structural change of fused benzo[*b*]fluoranthene skeleton in the excited state. The quantum yields of both **13b** and **13c** were relatively high (Φ = 0.43 and 0.53, respectively).[21] Moreover, we measured CPL spectra of **11ja**, **13b**, and **13c** in 1.0×10^{-5} M DCM solution. As a result, pyrene-substituted **11ja** had a stronger CPL property ($|g_{lum}| = 3.5\times10^{-3}$) than π-extended compounds **13b** ($|g_{lum}| = 6.4\times10^{-4}$), and **13c** ($|g_{lum}| = 3.1\times10^{-4}$).

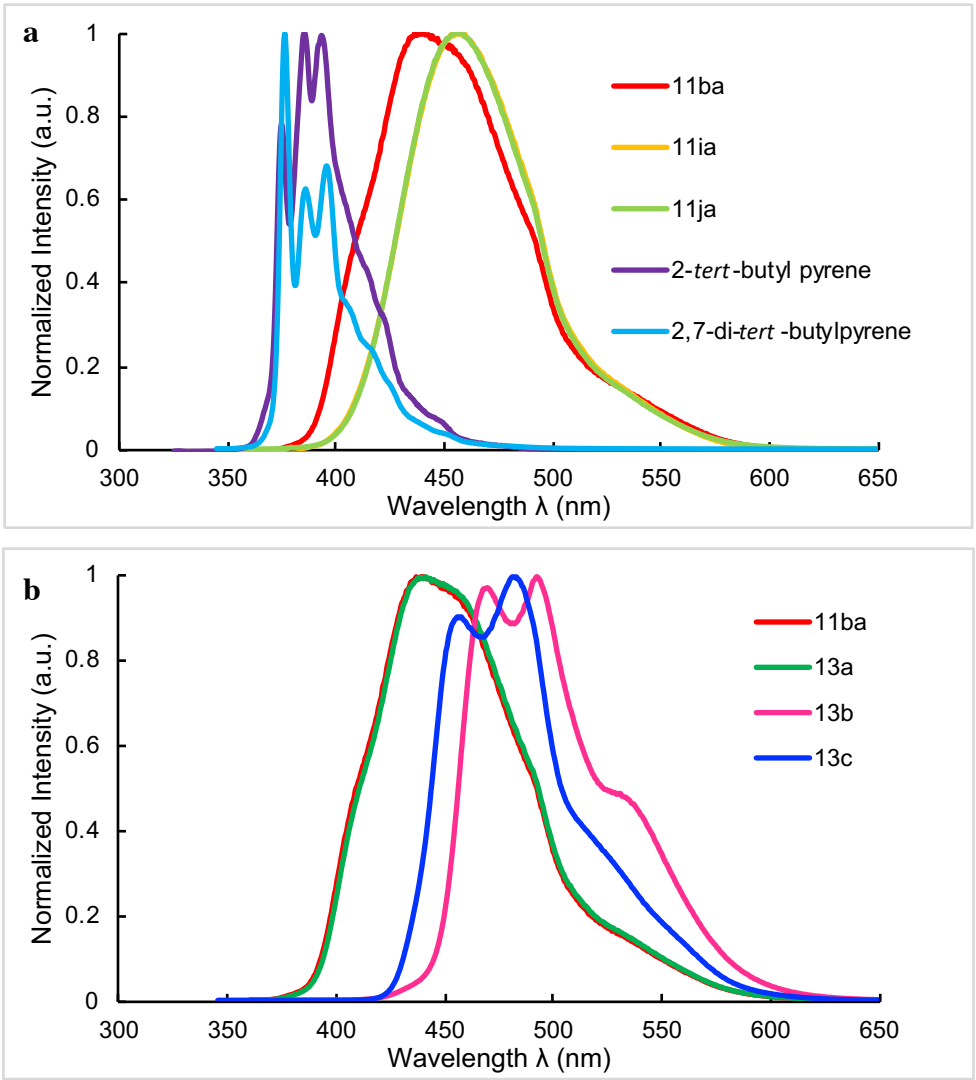


Figure 3. a, Fluorescence spectra of **11** and related compounds (concentration (excitation wavelength): **11ba**; 1.0×10^{-5} M (353.0 nm), **11ia**; 1.0×10^{-5} M (344.5 nm), **11ja**; 1.0×10^{-5} M (345.0 nm), 2-*tert*-butylpyrene; 1.0×10^{-5} M (322.5 nm), 2,7-di-*tert*-butylpyrene; 1.0×10^{-5} M (339.5 nm)) **b**,

Fluorescence spectra of **11ba** and **13** (concentration (excitation wavelength): **13a**; 1.0×10^{-5} M (353.0 nm), **13b**; 1.0×10^{-5} M (340.5 nm), **13c**; 1.0×10^{-5} M (338.5 nm))

Table 4. Quantum yields of selected compounds[a]

Compound	Φ	Compound	Φ
11ba	0.27	2,7-Di-*tert*-butylpyrene[22]	0.12
11ia	0.29	**13a**	0.28
11ja	0.67	**13b**	0.43
2-*tert*-Butylpyrene	0.082	**13c**	0.53

[a] Excitation wavelength (concentration) **11ba**; 353.0 nm (3.4×10^{-5} M), **11ia**; 344.5 nm (2.2×10^{-5} M), **11ja**; 345.0 nm (8.2×10^{-6} M), 2-*tert*-butylpyrene; 322.5 nm (2.8×10^{-5} M), 2,7-di-*tert*-butylpyrene; 339.5 nm (1.3×10^{-5} M), **13a**; 353.0 nm (1.9×10^{-5} M), **13b**; 340.5 nm (5.5×10^{-6} M), **13c**; 338.5 nm (7.5×10^{-6} M).

Conclusion

We have achieved a catalytic enantioselective synthesis of axially chiral PAHs via regioselective cleavage of biphenylenes. Axially chiral benzo[*b*]fluoranthene derivatives were obtained in excellent yields and ees with broad functional group tolerance. Moreover, PAHs which have two axial chiralities could be synthesized by consecutive cyclizations with high diastereoselectivity. Some of the obtained PAHs have photophysical properties such as strong UV absorption, fluorescence and CPL. Further investigations on the synthesis of highly complex PAHs with chirality and the application of fluoranthene derivatives are ongoing in our laboratory.

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Experimental Section

General procedure for a Rh-catalyzed enantioselective reaction

[RhCl{(*R*,*R*)-Ph-bod}]$_2$ (0.005 mmol, 10 mol%), NaBARF (0.01 mmol, 20 mol%) and substrates **10** (0.05 mmol, 1.0 equiv) were placed in a sealed Schlenk tube, which was then evacuated and backfilled with argon (×3). To the reaction vessel was added dehydrated CPME (0.5 mL, prepared by argon bubbling for 30 sec). The solution was then stirred at 80 °C (bath temperature) for 24-48 h. The reaction mixture was cooled to room temperature and the solvent was evaporated to dryness. The obtained crude products were purified by preparative thin-layer chromatography (PTLC) to give products **11**.

Data Availability

Crystallographic data for **11ha** has been deposited at the Cambridge Crystallographic Data Center with the code CCDC 1961208. All other data including experimental detail, characterization data for new compounds and photophysical properties are available on the Supporting Information.

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(16) See the Supporting Information for the experimental and calculated data in details (S10-11).

(17) Single crystal of **11ha** for X-ray analysis was obtained as a co-crystal with hexane. For the clarity, hexane was omitted from the figure in Table 2. CCDC 1961208 contains the supplementary crystallographic data of **11ha**.

(18) As a representative example, we simulated the CD spectra of (*R*)-**11ja** and it was in good agreement with that of measured CD spectra of the major enantiomer of **11ja**. Thus, we showed all cycloadducts in *R*-form. See Supporting Information in details (S16).

(19) CD spectra of **11ba, 11ia, 11ja,** and **13** were shown in the Supporting Information.

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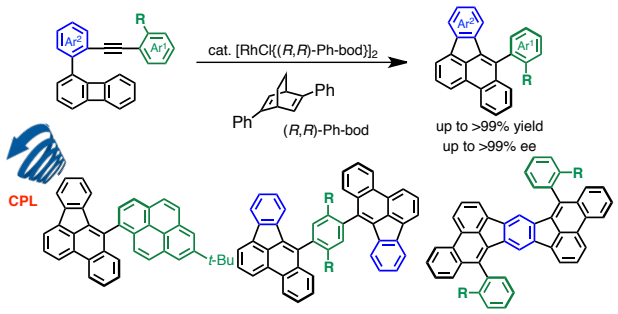
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(R,R)-Ph-bod
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