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Synthesis, Structure, and Photophysical/Chiroptical Properties of Benzopicene-Based π-Conjugated Molecules

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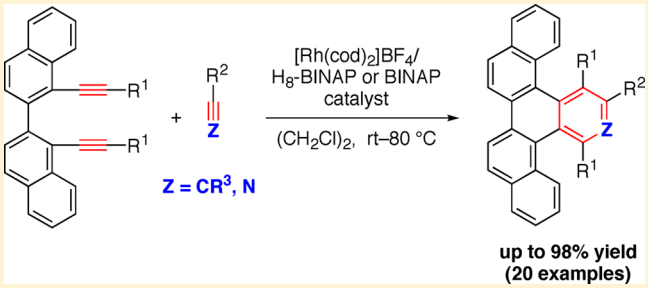
Supporting Information

ABSTRACT: The convenient synthesis of substituted benzopicenes and azabenzopicenes has been achieved by the cationic rhodium(I)/H_8–BINAP or BINAP complex-catalyzed [2+2+2] cycloaddition under mild conditions. This method was applied to the synthesis of benzopicene-based long ladder and helical molecules. The X-ray crystal structure analysis revealed that the benzopicene-based helical molecule is highly distorted and the average distance of overlapped rings is markedly shorter than that in the triphenylene-based helical molecule. Photophysical and chiroptical properties of these benzopicene and azabenzopicene derivatives have also been examined. With respect to photophysical properties, substituted benzopicenes and azabenzopicenes showed red shifts of absorption and emission maxima compared with the corresponding triphenylenes and azatriphenylenes. With respect to chiroptical properties, the CPL spectra of the benzopicene-based helical molecule showed two opposite peaks, and thus the value of the CPL was smaller than that of the triphenylene-based helical molecule presumably due to the presence of two chiral fluorophores.



INTRODUCTION

Polycyclic aromatic compounds have attracted much attention in materials chemistry because of their fascinating electrical and photophysical properties.[1] For the synthesis of these compounds, the transition-metal-mediated [2+2+2] cycloaddition is one of the most powerful methods.[2] For example, Müllen and co-workers reported the synthesis of hexabenzocoronenes by the cobalt-mediated [2+2+2] cycloaddition of diarylacetylenes followed by cyclodehydrogenation.[3] Takahashi and co-workers reported the synthesis of substituted pentacenes by the zirconium-mediated [2+2+2] cycloaddition of diynes with monoynes followed by aromatization.[4] Not only planar polycyclic aromatic compounds but also nonplanar ones could also be synthesized by the [2+2+2] cycloaddition. Stará, Starý, and co-workers reported the synthesis of helicene-like molecules[5] by the cobalt or nickel-mediated intramolecular [2+2+2] cycloaddition of triynes.[6] On the other hand, our research group reported the synthesis of substituted triphenylenes **A** and azatriphenylenes **B** by the rhodium-catalyzed [2+2+2] cycloaddition[7] of biphenyl-linked diynes with alkynes and nitriles (Scheme 1).[8] This method was successfully applied to the synthesis of triphenylene-based long ladder[8] and helical molecules **C**–**E** (Scheme 1).[9] These results prompted our investigation into the rhodium-catalyzed [2+2+2] cycloaddition of binaphthyl-linked diynes with alkynes and nitriles, leading to substituted benzopicenes and azabenzopicenes, synthesis[10,11] and properties[10a,f] of which have been reported in a limited number of examples.

In this paper, we disclose the rhodium-catalyzed synthesis of substituted benzopicenes and azabenzopicenes, and its application to the synthesis of benzopicene-based long ladder and helical molecules. Comparison of structures and photophysical/chiroptical properties between benzopicene- and triphenylene-based π-conjugated molecules is also disclosed.

RESULTS AND DISCUSSION

We first examined the synthesis of substituted benzopicenes and azabenzopicenes as shown in Scheme 2. Pleasingly, the reactions of binaphthyl-linked terminal diyne **1a** and electron-deficient unsymmetrical internal alkynes **2a**–**c** (1.1 equiv) proceeded at room temperature by using a cationic rhodium(I)/(*S*)-H_8–BINAP complex (10 mol %) as a catalyst to give the corresponding benzopicenes **3aa**–**c** in high yields. For highly electron-deficient internal alkyne **2d**, the use of excess **2d** (2 equiv) and (*S*)-BINAP instead of (*S*)-H_8–BINAP was necessary in order to suppress the undesired homo-[2+2+2] cycloaddition of **1a**. Electron-rich propargyl alcohols **2e**,**f** and propargyl ether **2g** were also suitable substrates for this process. Aliphatic alkynes **2h**,**i** could also be employed, but reactivity of internal alkyne **2h** was lower than that of terminal alkyne **2i**. With respect to diynes, electron-deficient binaphtyl-linked internal diyne **1b** reacted with electron rich internal alkyne

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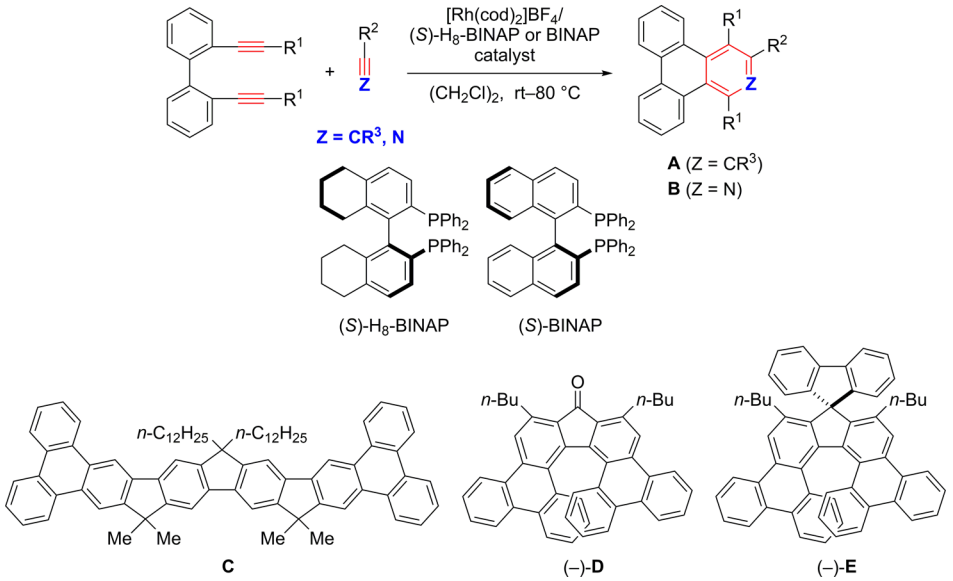
Scheme 1. Rhodium-Catalyzed [2+2+2] Cycloadditions of Bipheyl-Linked Diynes with Alkynes and Nitriles



2g to give the corresponding benzopicene **3bg** in excellent yield.

We next examined the substituted azabenzopicene synthesis as shown in Scheme 2. The reaction of terminal diyne **1a** and benzonitrile (**2j**) proceeded at room temperature by using the cationic rhodium(I)/(*S*)-BINAP complex (10 mol %) as a catalyst to give the corresponding azabenzopicene **3aj** in low yield. Interestingly, electron-deficient benzonitriles **2k,l** showed higher reactivity than **2j**, on the contrary, electron-rich benzonitriles **2m** showed lower reactivity than **2j**. Although elevated reaction temperature (80 °C) was required, the reactions of activated nitriles **2n,o** and **1a** proceeded to give the corresponding azabenzopicene **3an** and **3ao** in moderate yields. Internal diyne **1b** reacted with activated nitrile **2n** at room temperature to give the corresponding azabenzopicene **3bn** in moderate yield.

The present rhodium-catalyzed [2+2+2] cycloaddition of binaphthyl-linked diynes with alkynes was successfully applied to the synthesis of a benzopicene-based long ladder molecule (Scheme 3).[12,13] The reaction of diyne **1a** with fluorene-linked bispropargyl alcohol **4** in the presence of the cationic rhodium(I)/(*S*)-H_8–BINAP catalyst proceeded at room temperature to give fluorene-linked bibenzopicene **5** in moderate yield. Subsequent dehydration afforded benzopicene-based long ladder molecule **6** in high yield.

Previously, our research group reported the enantioselective synthesis of 1,1′-bitriphenylene-based carbo-,[9] phospha-,[9] and sila[7]helicenes[14] by the rhodium-catalyzed double [2+2+2] cycloaddition of a biphenyl-linked tetrayne with carbonyl-, phosphorus-, and silicon-linked diynes.[15−18] In a similar way, the present [2+2+2] cycloaddition was applied to the enantioselective synthesis of benzopicene-based helical molecules (Scheme 4). The reactions of binaphtyl-linked tetrayne **7** and carbonyl-lineked diynes **8a,b** proceeded at room temperature in the presence of the cationic rhodium(I)/(*S*)-H_8–BINAP catalyst to give the corresponding benzopicene-based helical molecules **9a,b** with high ee values, although the product yields were low. Arylation of **9a** with 2-bromobiphenyl (**10**) followed by dehydration furnished spirofluorene **11** in good yield without racemization.

The X-ray crystal structure of racemic **9b** is shown in Figure 1. As shown in the top view, three rings were overlapped each other. As shown in the side view, picene moieties were highly distorted presumably due to large steric hindrance.[10d] The distances between three pairs of two overlapped rings were 3.488, 3.302, and 3.556 Å (average distance = 3.449 Å), respectively, from left side to right side. This average distance of overlapped rings in **9b** is markedly shorter than that in triphenylene-based helical molecule **D** (3.834 Å).[19]

Absorption and emission data of representative benzopicenes and azabenzopicenes are shown in Table 1, and Figures 2 and 3. Substituted benzopicenes and azabenzopicenes absorbed UV−vis light at around 280 and 310 nm,[10a] and showed maximum emission at around 410 nm. Thus, substituted benzopicenes and azabenzopicenes showed red shifts of absorption and emission maxima compared with the corresponding triphenylenes **A** and azatriphenylenes **B**.[8] Benzopicene-based long ladder and helical molecules **6** and **11** also showed significant red shifts of absorption and emission maxima compared with the corresponding triphenylene-based molecules **C**[8] and **E**.[9] With respect to fluorescence quantum yields, those of ethoxycarbonyl-substituted benzopicene **3ac** and 4-cyanophenyl-substituted azabenzopicene **3al** were around 20%, which are higher than the yields of the others.[20] The fluorescence quantum yield of benzopicene-based long ladder molecule **6** was very high in $CHCl_3$ (86%), which is comparable to that of triphenylene-based long ladder molecule **C** (88%).[8] However, the fluorescence quantum yield of benzopicene-based helical molecule **11** was lower than that of triphenylene-based helical molecule **E** (30%).[9] The fluorescence quantum yields of ladder molecules **6** and **C** and helical molecules **11** and **E** in the solid state were also determined, which revealed that those of the ladder molecules in the solid state are significant lower than in the solution state presumably due to the stacking of planar structures.

Finally, we examined the chiroptical properties of benzopicene-based helical molecule **11**. The optical rotation value of **11** was 322, which is smaller than that (684) of triphenylene-based helicene **E**.[9] The corresponding electronic circular dichroism (ECD) spectra of (+)-**11** (98% ee) and (−)-**11** (96% ee) in

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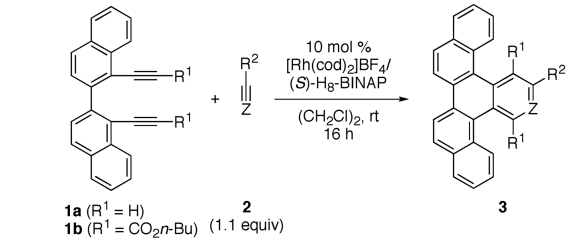
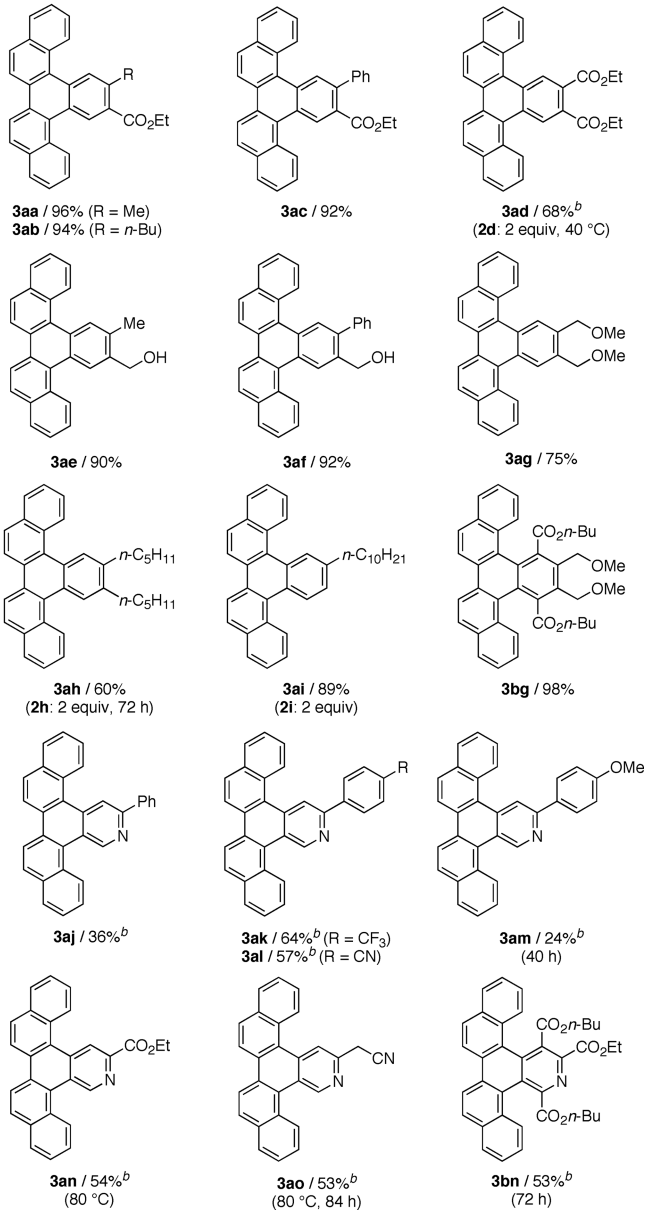
Scheme 2. Scope of Rhodium-Catalyzed [2+2+2] Cycloadditions of Binaphtyl-Linked Diynes with Alkynes and Nitriles[a,b]



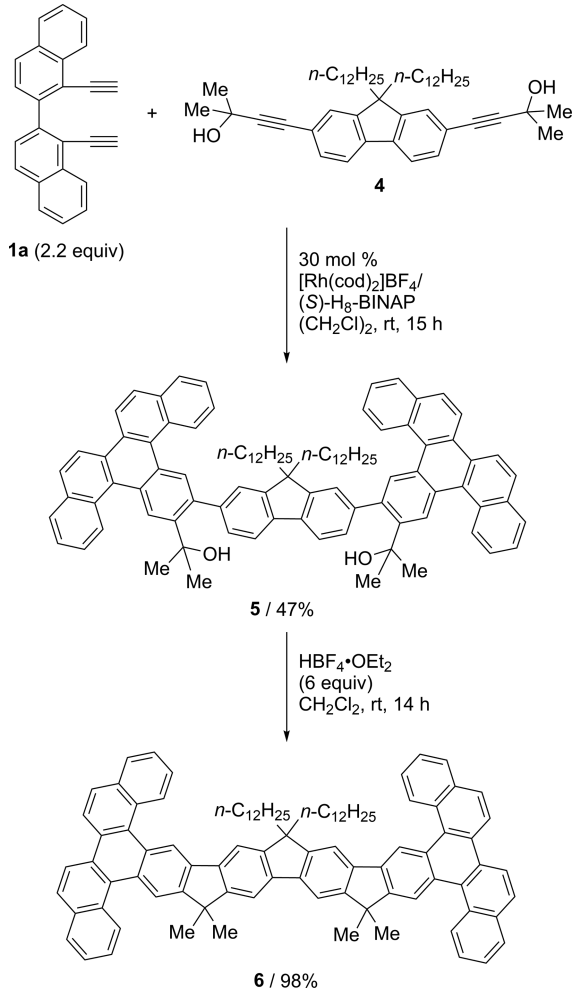
1a (R^1 = H)
1b (R^1 = CO_2n-Bu)
2 (1.1 equiv)
3



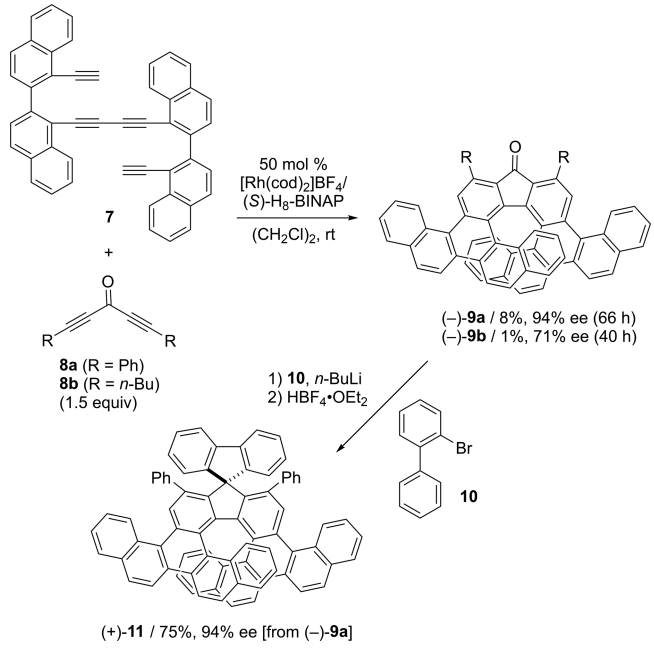
[a] $[Rh(cod)_2]BF_4$ (0.0050 mmol), (*S*)-H_8–BINAP (0.0050 mmol), **1** (0.050 mmol), **2** (0.055–0.10 mmol), and $(CH_2Cl)_2$ (2.0 mL) were used. The cited yields are of the isolated products. [b] (*S*)-BINAP was used instead of (*S*)-H_8–BINAP.

$CHCl_3$ is shown in Figure 4. It was found that these enantiomers show strong Cotton effects, which are mirror images. Furthermore, we attempted to measure circularly polarized luminescence (CPL) of (+)-**11** (Figure 4). The

Scheme 3. Synthesis of a Benzopicene-Based Long Ladder Molecule



Scheme 4. Enantioselective Synthesis of Benzopicene-Based Helical Molecules



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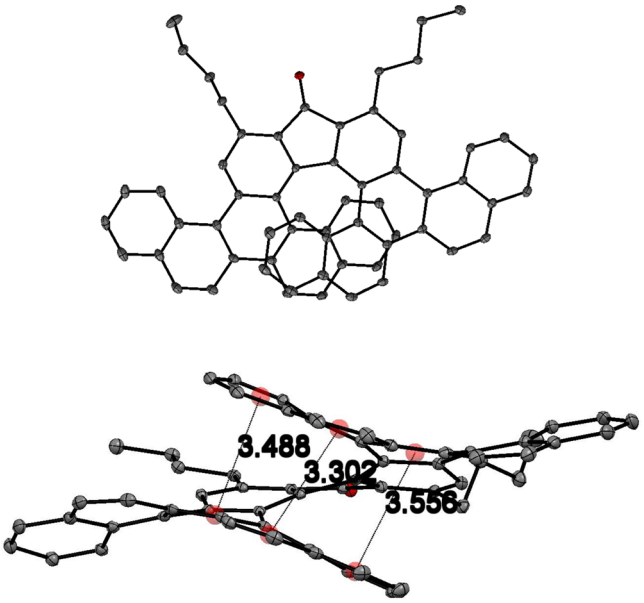

Figure 1. ORTEP diagrams of (±)-**9b** [top view (top) and side view (bottom)] with ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

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.[21] Interestingly, the CPL spectra showed two opposite peaks, the peak tops of which were 479.5 and 543.5 nm. The value of the CPL was $g_{lum} = -7 \times 10^{-4}$ at 543.5 nm, which is smaller than that (-3.2×10^{-2} at 449 nm) of triphenylene-based helicene (−)-**E**,[9,22,23] presumably due to the presence of two types of chiral fluorophores.[19]

CONCLUSION

In conclusion, we have achieved the convenient synthesis of substituted benzopicenes and azabenzopicenes by the cationic rhodium(I)/H_8–BINAP or BINAP complex-catalyzed [2+2+2] cycloaddition under mild conditions. This method was applied to the synthesis of benzopicene-based long ladder and helical molecules. The X-ray crystal structure analysis revealed that the benzopicene-based helical molecule is highly distorted and the

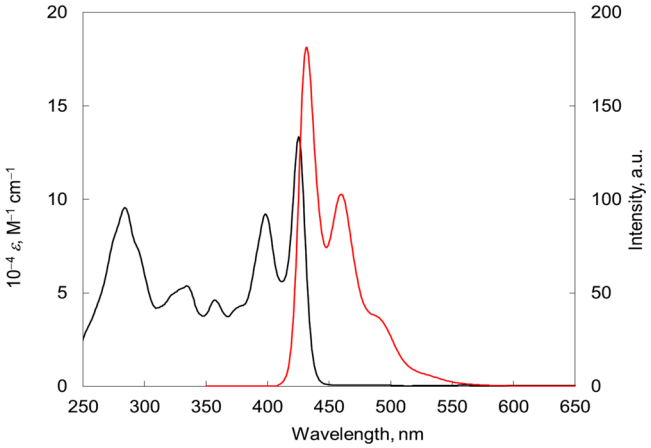

Figure 2. UV/vis absorption (black) and emission (red) spectra of **6** in $CHCl_3$ with excitation at 410 nm.

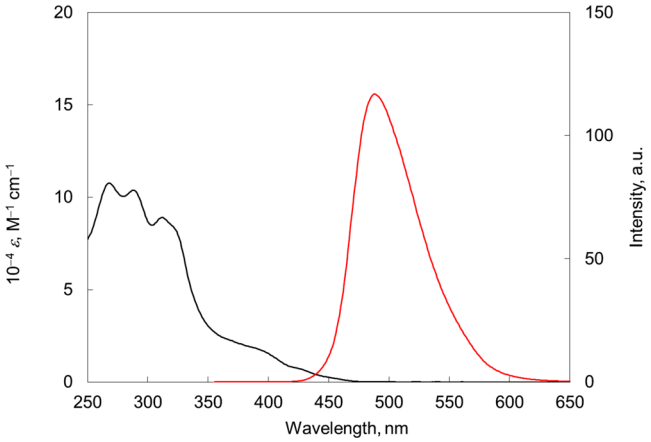

Figure 3. UV/vis absorption (black) and emission (red) spectra of **11** in $CHCl_3$ with excitation at 350 nm.

Table 1. Comparison of Photophysical Properties between Representative Benzopicenes/Azabenzopicenes and Triphenylenes/Azatriphenylenes[a]

compound	UV absorption λ_{max}/nm	fluorescence λ_{max}/nm (excitation wavelength/nm)	ϕ_F (excitation wavelength/nm)
3ac	281, 316	417, 436 (320)	0.196 (320)
3af	281, 313	408, 426 (320)	0.092 (310)
A (R^1 = H, R^2 = Ph, R^3 = CO_2Et)[b]	270	384 (270)	0.099 (270)
A (R^1 = H, R^2 = Ph, R^3 = CH_2OH)[b]	266	369 (270)	0.030 (270)
3aj	282, 308	413, 433 (320)	0.156 (320)
3ak	281, 321	411, 433 (320)	0.166 (320)
3al	280, 327	413, 435 (320)	0.208 (330)
3am	284, 309	420 (320)	0.150 (310)
3an	275, 322	408, 430 (320)	0.136 (320)
B (R^1 = H, R^2 = 4-NCC_6H_4)[b]	277	363, 381 (280)	0.306 (280)
B (R^1 = H, R^2 = 4-$MeOC_6H_4$)[b]	259, 279	377, 387 (280)	0.230 (280)
6	284, 398, 425	432, 460 (410)	0.855 (400), 0.058 (370)[d]
C[b]	260, 385, 407	412, 437 (410)	0.881 (400), 0.114 (300)[b,d]
11	268, 289, 312	488 (350)	0.180 (400), 0.069 (260)[d]
E[c]	262, 370, 400	449 (350)	0.296 (350), 0.121 (360)[d]

[a]Measured in $CHCl_3$ at 25 °C. UV-absorption: **3** (1×10^{-5} M), **6** (1×10^{-6} M), and **11** (4×10^{-6} M). fluorescence: **3** (1×10^{-6} M), **6** (1×10^{-6} M), and **11** (3×10^{-5} M). ϕ_F: **3** (1×10^{-6} M), **6** (1×10^{-6} M), and **11** (5×10^{-6} M). [b]Data of ref 8. [c]Data of ref 9. [d]In the solid state.

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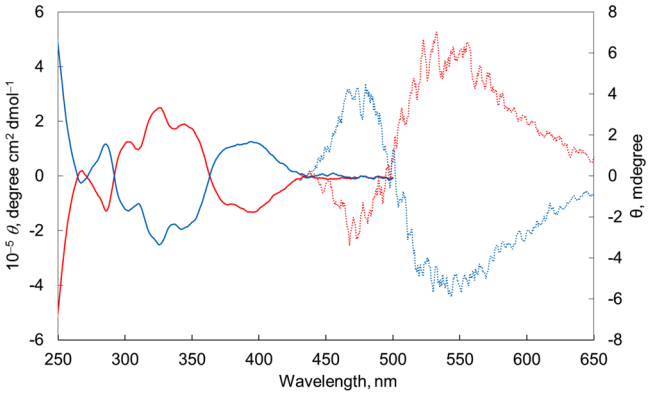

Figure 4. ECD (solid line) and CPL (dashed line) spectra of (+)-**11** (blue) and (−)-**11** (red) in $CHCl_3$.

average distance of overlapped rings is markedly shorter than that in the triphenylene-based helical molecule. Photophysical and chiroptical properties of these benzopicene and azabenzopicene derivatives have also been examined. With respect to photophysical properties, substituted benzopicenes and azabenzopicenes showed red shifts of absorption and emission maxima compared with the corresponding triphenylenes and azatriphenylenes. With respect to chiroptical properties, the CPL spectra of the benzopicene-based helical molecule showed two opposite peaks and the value of the CPL was smaller than that of the triphenylene-based helical molecule presumably due to the presence of two chiral fluorophores.

EXPERIMENTAL SECTION

General. Anhydrous CH_2Cl_2 was obtained from Aldrich (no. 27,099-7) or Wako (no. 041-32345) and used as received. Anhydrous $(CH_2Cl)_2$ (no. 28,450-5) was obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4 Å (Wako) prior to use. Diynes **4**,[24] **8a**,[25] and **8b**[26] were prepared according to the literatures. H_8−BINAP was obtained from Takasago International Corporation. ^1H and ^{13}C NMR data were recorded with ^{13}C operating frequencies of 100 and 150 MHz, respectively, at ambient temperature. HRMS data were obtained by an ESI-TOF or APCI-TOF mass spectrometry. All reactions were carried out under nitrogen or argon with magnetic stirring.

*1,1′-Diethynyl-2,2′-binaphthalene (**1a**).* To a solution of CBr_4 (879 mg, 2.65 mmol) in CH_2Cl_2 (25 mL) was added dropwise PPh_3 (1.39 g, 5.30 mmol) in CH_2Cl_2 (15 mL) at 0 °C, and the mixture was stirred for 15 min. To the resulting solution was added a solution of [2,2′-binaphthalene]-1,1′-dicarbaldehyde[27] (206 mg, 0.663 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 3 h. The mixture was concentrated, and *n*-hexane/Et_2O (4:1) was added to the mixture. The mixture was filtered and concentrated. The residue was purified by a silica gel column chromatography (eluent: *n*-hexane/$CHCl_3$ = 5:1) to give tetrabromide. To a solution of the tetrabromide in THF (10 mL) was added a solution of LDA at −78 °C, which was prepared from diisopropylamine (0.697 mL, 4.93 mmol) in THF (10 mL) and *n*-BuLi (3.18 mL, 4.93 mmol, 1.55 M in *n*-hexane) at 0 °C. The mixture was gradually warmed to −40 °C over 2 h. The reaction was quenched by water and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (eluent: *n*-hexane/EtOAc = 30:1) to give **1a** (164 mg, 0.541 mmol, 82% yield). Colorless solid; mp 144.2−146.1 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.50 (d, J = 4.2 Hz, 2H), 7.92 (d, J = 4.1 Hz, 4H), 7.68−7.53 (m, 6H), 3.33 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.1, 133.8, 132.4, 128.22, 128.20, 128.0, 127.2, 126.6, 118.7, 85.9, 80.5; HRMS (APCI) calcd for $C_{24}H_{15}$ $[M + H]^+$ 303.1168, found 303.1180.

*Dibutyl 3,3′-([2,2′-binaphthalene]-1,1′-diyl)dipropiolate (**1b**).* To a stirred solution of **1a** (121 mg, 0.400 mmol) in THF (5 mL) was added dropwise *n*-BuLi (0.57 mL, 0.88 mmol, 1.55 M in *n*-hexane) at −78 °C for 30 min. To the resulting solution was slowly added a solution of *n*-butyl chloroformate (0.20 mL, 1.6 mmol) in THF (1 mL) at −78 °C, and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (eluent: *n*-hexane/EtOAc = 20:1) to give **1b** (152 mg, 0.302 mmol, 76% yield). Pale yellow syrupy oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.46 (d, J = 4.2 Hz, 2H), 8.04 (d, J = 4.2 Hz, 2H), 7.94 (d, J = 4.0 Hz, 2H), 7.73−7.65 (m, 4H), 7.61 (ddd, J = 8.2, 7.0, 1.2 Hz, 2H), 4.07 (t, J = 6.6 Hz, 4H), 1.58−1.45 (m, 4H), 1.32−1.20 (m, 4H), 4.07 (t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.0, 144.0, 134.0, 132.5, 130.3, 128.4, 127.99, 127.96, 127.1, 126.3, 116.5, 89.0, 83.4, 65.8, 30.3, 19.0, 13.6; HRMS (ESI) calcd for $C_{34}H_{30}O_4Na$ $[M + Na]^+$ 525.2042, found 525.2038.

*Representative Procedure for Rh-Catalyzed [2+2+2] Cycloaddition (Table 1, **3aa**).* H_8−BINAP (3.2 mg, 0.0050 mmol) and $[Rh(cod)_2]BF_4$ (2.0 mg, 0.0050 mmol) were dissolved in CH_2Cl_2, and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting mixture was concentrated. To a solution of the residue and **2a** (0.055 mmol, 6.2 mg) in $(CH_2Cl)_2$ (1.1 mL) was added a solution of **1a** (15.1 mg, 0.0500 mmol) in $(CH_2Cl)_2$ (0.9 mL). The mixture was stirred at room temperature for 16 h. The resulting solution was concentrated and purified by a preparative thin layer chromatography (TLC, eluent: *n*-hexane/$CHCl_3$/toluene =3:3:1) to give **3aa** (20.0 mg, 0.0482 mmol, 96% yield).

*Ethyl 15-Methylbenzo[s]picene-14-carboxylate (**3aa**).* Colorless solid, mp 184.0−186.4 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.52 (s, 1H), 8.90 (d, J = 8.1 Hz, 2H), 8.73 (s, 1H), 8.53 (dd J = 8.9, 2.0, 2H), 8.05−7.93(m, 4H), 7.73−7.53 (m, 4H), 4.43 (q, J = 7.1 Hz, 2H), 2.80 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.7, 136.6, 133.6, 133.4, 132.4, 132.3, 131.2, 129.8, 129.6, 129.0, 128.6, 128.20, 128.19, 128.1, 127.9, 127.8, 127.7, 127.6, 127.3, 126.41, 126.38, 126.2, 126.1, 120.6, 120.5, 60.9, 22.2, 14.4; HRMS (ESI) calcd for $C_{30}H_{22}O_2Na$ $[M + Na]^+$ 437.1512, found 437.1513.

*Ethyl 15-Butylbenzo[s]picene-14-carboxylate (**3ab**).* Colorless solid, mp 184.6−185.5 °C, 21.6 mg (94%); ^1H NMR ($CDCl_3$, 400 MHz) δ 9.50 (s, 1H), 8.94 (d, J = 8.4 Hz, 2H), 8.76 (s, 1H), 8.55 (dd, J = 8.8, 4.9 Hz, 2H), 8.05−7.95 (m, 4H), 7.72−7.55 (m, 4H), 4.44 (q, J = 7.1 Hz, 2H), 3.18 (t, J = 7.7 Hz, 2H), 1.80−1.65 (m, 2H), 1.57−1.45 (m, 2H), 1.44 (q, J = 7.1 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 141.1, 133.6, 133.5, 132.5, 132.2, 130.7, 129.9, 129.6, 129.0, 128.6, 128.24, 128.23, 128.19, 128.1, 127.9, 127.8, 127.7, 127.3, 126.5, 126.41, 126.39, 126.2, 126.1, 120.7, 20.6, 60.9, 34.5, 34.1, 22.8, 14.4, 14.1; HRMS (ESI) calcd for $C_{33}H_{28}O_2Na$ $[M + Na]^+$ 479.1982, found 479.1980.

*Ethyl 15-Phenylbenzo[s]picene-14-carboxylate (**3ac**).* Colorless solid, mp 164.0−166.4 °C, 22.0 mg (92%); ^1H NMR ($CDCl_3$, 400 MHz) δ 9.47 (s, 1H), 8.99 (d, J = 8.4 Hz, 1H), 8.94 (d, J = 8.4 Hz, 1H), 8.92 (s, 1H), 8.56 (d, J = 9.0 Hz, 2H), 8.05−7.98 (m, 3H), 7.98 (d, J = 7.8, 1H), 7.72 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.67−7.53 (m, 3H), 7.51−7.33 (m, 5H), 4.18 (q, J = 7.1 Hz, 2H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 141.7, 139.4, 133.6, 133.4, 131.7, 131.6, 131.0, 129.8, 129.6, 129.0, 128.9, 128.77, 128.75, 128.7, 128.3, 128.23, 128.15, 128.1, 128.0, 127.14, 127.11, 126.72, 126.67, 126.3, 126.2, 120.6, 120.5, 61.1, 13.7; HRMS (ESI) calcd for $C_{35}H_{24}O_2Na$ $[M + Na]^+$ 499.1669, found 499.1676.

*Diethyl Benzo[s]picene-14,15-dicarboxylate (**3ad**).* After hydrogenation of the Rh catalyst, a $(CH_2Cl)_2$ solution of **1a** and **2d** was added dropwise to a $(CH_2Cl)_2$ solution of the Rh catalyst. Colorless solid, mp 176.2−177.5 °C, 16.2 mg (68%); ^1H NMR ($CDCl_3$, 400 MHz) δ 9.32 (s, 2H), 8.91 (d, J = 8.4 Hz, 2H), 8.59 (d, J = 8.9 Hz, 2H), 8.08 (d, J = 8.9 Hz, 2H), 8.04 (d, J = 7.9 Hz, 2H),7.73 (d, J = 8.3, 6.9, 1.4 Hz, 2H), 7.69−7.62 (m, 2H), 4.45 (q, J = 7.2 Hz, 4H), 1.42 (t,

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J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 133.5, 131.0, 130.5, 129.6, 129.2, 129.0, 128.9, 128.3, 128.0, 127.0, 126.7, 126.5, 120.5, 61.7, 14.2; HRMS (ESI) calcd for $C_{32}H_{24}O_4Na$ $[M + Na]^+$ 495.1567, found 495.1564.

*(15-Methylbenzo[s]picen-14-yl)methanol (**3ae**).* Colorless solid, mp 270 °C (dec.), 16.8 mg (90%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.00 (d, J = 8.4 Hz, 2H), 8.93 (s, 1H), 8.76 (s, 1H), 8.60 (dd, J = 9.0, 2.6 Hz, 2H), 8.07−7.96 (m, 4H), 7.72−7.57 (m, 4H), 4.31 (s, 2H), 2.60 (s, 3H), 1.68 (br, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.1, 134.4, 133.52, 133.48, 130.3, 129.9, 129.8, 129.7, 128.7, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.4, 127.0, 126.2, 126.1, 126.00, 125.97, 120.74, 120.70, 64.1, 19.2; HRMS (ESI) calcd for $C_{28}H_{20}O$ [M] 372.1509, found 372.1504.

*(15-Phenylbenzo[s]picen-14-yl)methanol (**3af**).* Colorless solid, mp 224.5−226.5 °C, 20.0 mg (92%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.12 (s, 1H), 9.06 (d, J = 8.2 Hz, 1H), 8.95 (d, J = 7.8 Hz, 1H), 8.87 (s, 1H), 8.61 (d, J = 8.8 Hz, 2H), 8.11−7.91 (m, 4H), 7.75−7.33 (m, 9H), 4.84 (s, 2H), 1.73 (br, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.7, 139.4, 136.3, 133.6, 133.5, 130.4, 129.82, 129.80, 129.7, 129.6, 129.4, 128.9, 128.5, 128.3, 128.21, 128.16, 128.15, 128.1, 128.0, 127.4, 127.22, 127.15, 126.43, 126.42, 126.1, 126.0, 120.69, 120.67, 63.7; HRMS (ESI) calcd for $C_{33}H_{22}ONa$ $[M + Na]^+$ 457.1563, found 457.1546.

*14,15-Bis(methoxymethyl)benzo[s]picene (**3ag**).* Colorless solid, mp 133.5−136.0 °C, 15.7 mg (75%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.0 (d, J = 8.4 Hz, 2H), 8.96 (s, 2H), 8.5 (d, J = 8.9 Hz, 2H), 8.04−7.98 (m, 4H), 7.68 (ddd, J = 8.3, 6.9, 1.4 Hz, 2H), 7.64−7.57 (m, 2H), 4.77 (s, 4H), 3.47 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.4, 133.5, 129.8, 129.7, 129.4, 128.3, 128.1, 127.9, 127.8, 127.2, 126.3, 126.0, 120.7, 72.7, 58.3; HRMS (ESI) calcd for $C_{30}H_{24}O_2Na$ $[M + Na]^+$ 439.1669, found 439.1658.

*14,15-Dipentylbenzo[s]picene (**3ah**).* Colorless solid, mp 107.4−108.8 °C, 14.1 mg (60%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.03 (d, J = 8.4 Hz, 2H), 8.73 (s, 2H), 8.61 (d, J = 9.0 Hz, 2H), 8.05−7.97 (m, 4H), 7.67 (ddd, J = 8.3, 6.9, 1.4 Hz, 2H), 7.61 (ddd, J = 8.0, 6.8, 1.2 Hz, 2H), 2.86 (t, J = 7.8 Hz, 4H), 1.82−1.71 (m, 4H), 1.56−1.38 (m, 8H), 0.96 (t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.4, 133.5, 129.9, 129.1, 128.5, 128.4, 128.1, 127.5, 127.4, 127.2, 125.9, 125.8, 120.8, 33.0, 32.0, 31.0, 22.7, 14.1; HRMS (ESI) calcd for $C_{36}H_{36}$ [M] 468.2817, found 468.2803.

*14-Decylbenzo[s]picene (**3ai**).* Pale yellow syrupy oil, 20.9 mg (89%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.00 (d, J = 8.2 Hz, 1H), 8.99 (d, J = 8.2 Hz, 1H), 8.85 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 1.3 Hz, 1H), 8.58 (dd, J = 9.0, 3.3 Hz, 2H), 8.04−7.93 (m, 4H), 7.69−7.55 (m, 4H), 7.45 (dd, J = 8.4, 1.7 Hz, 1H), 2.84 (d, J = 7.6 Hz, 2H), 1.81−1.70 (m, 2H), 1.48−1.18 (m, 14H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 133.51, 133.49, 130.3, 129.9, 129.8, 129.1, 128.42, 128.37, 128.34, 128.13, 128.09, 127.8, 127.6, 127.5, 127.4, 127.34, 127.32, 127.0, 126.00, 125.97, 125.90, 125.86, 120.74, 120.70, 36.3, 31.9, 31.6, 29.7, 29.6, 29.4, 29.4, 22.7, 14.1; HRMS (ESI) calcd for $C_{36}H_{36}$ [M] 468.2812, found 468.2804.

*Dibutyl 14,15-bis(methoxymethyl)benzo[s]picene-13,16-dicarboxylate (**3bg**).* After hydrogenation of the Rh catalyst, a $(CH_2Cl)_2$ solution of **1b** and **2g** was added dropwise to a $(CH_2Cl)_2$ solution of the Rh catalyst. Yellow amorphous, 30.4 mg (98%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (d, J = 8.8 Hz, 2H), 8.36−8.27 (m, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.94−7.87 (m, 2H), 7.57−7.47 (m, 4H), 5.06 (d, J = 10.6 Hz, 2H), 4.77 (d, J = 10.7 Hz, 2H), 3.55 (dt, J = 10.6, 6.3 Hz, 2H), 3.43 (s, 6H), 2.82 (br, 2H), 1.08−0.81 (m, 8H), 0.72 (d, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 135.9, 135.3, 132.0, 130.5, 129.3, 128.8, 128.74, 128.67, 126.8, 126.6, 126.1, 125.7, 119.7, 67.6, 65.1, 58.6, 29.8, 18.8, 13.6; HRMS (ESI) calcd for $C_{40}H_{40}O_6Na$ $[M + Na]^+$ 639.2717, found 639.2701.

*15-Phenyldinaphtho[1,2-f:2′,1′-h]isoquinoline (**3aj**).* Colorless solid, mp 278.7−280.2 °C, 7.2 mg (36%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.24 (s, 1H), 9.17 (s, 1H), 9.01 (t, J = 8.7 Hz, 2H), 8.62 (d, J = 8.8 Hz, 1H), 8.61 (d, J = 8.7 Hz, 1H), 8.20 (d, J = 7.3 Hz, 2H), 8.16−8.01 (m, 4H), 7.82−7.61 (m, 4H), 7.55 (t, J = 7.3 Hz, 2H), 7.46 (t, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.0, 151.8, 139.7, 135.1, 133.7, 133.5, 130.1, 129.8, 129.1, 128.9, 128.8, 128.6, 128.55, 128.52, 128.34, 128.28, 127.6, 127.1, 126.8, 126.7, 126.5, 126.1, 125.5, 124.0, 120.7, 120.6, 117.4; HRMS (ESI) calcd for $C_{31}H_{20}N$ $[M + H]^+$ 406.1590, found 406.1577.

*15-[4-(Trifluoromethyl)phenyl]dinaphtho[1,2-f:2′,1′-h]isoquinoline (**3ak**).* Colorless solid, mp 264.1−265.6 °C, 15.1 mg (64%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.2 (s, 1H), 9.17 (s, 1H), 8.96 (d, J = 8.0 Hz, 2H), 8.68−8.57 (m, 2H), 8.29 (d, J = 8.0 Hz, 2H), 8.18−8.03 (m, 4H), 7.83−7.65 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.9, 151.2, 142.9, 134.9, 133.7, 133.5, 130.6 (q, $2J_{C-F}$ = 32 Hz), 130.2, 130.0, 129.7, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 127.4, 127.19, 127.16, 127.0, 126.8, 126.6, 125.8 (q, $3J_{C-F}$ = 4 Hz), 125.3, 124.4, 124.3 (q, $1J_{C-F}$ = 270 Hz), 120.6, 120.5, 117.9; HRMS (ESI) calcd for $C_{32}H_{19}F_3N$ $[M + H]^+$ 474.1464, found 474.1446.

*4-(Dinaphtho[1,2-f:2′,1′-h]isoquinolin-15-yl)benzonitrile (**3al**).* Colorless solid, mp >300 °C, 12.3 mg (57%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.17 (s, 1H), 9.11 (s, 1H), 8.95−8.85 (m, 2H), 8.594 (d, J = 8.9 Hz, 1H), 8.586 (d, J = 8.9 Hz, 1H), 8.25 (d, J = 8.2 Hz, 2H), 8.17−8.02 (m, 4H), 7.85−7.63 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 150.4, 143.7, 134.8, 133.6, 133.5, 132.7, 130.2, 130.1, 129.6, 129.00, 128.95, 128.7, 128.4, 127.4, 127.3, 127.2, 127.0, 126.8, 126.7, 125.7, 125.2, 124.6, 120.6, 120.5, 119.0, 118.1, 112.1; HRMS (ESI) calcd for $C_{32}H_{19}N_2$ $[M + H]^+$ 431.1543, found 431.1537.

*15-(4-Methoxyphenyl)dinaphtho[1,2-f:2′,1′-h]isoquinoline (**3am**).* Pale yellow solid, mp 237.8−238.6 °C, 5.2 mg (24%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.2 (s, 1H), 9.10 (s, 1H), 9.06−8.95 (m, 2H), 8.67−8.56 (m, 2H), 8.20−8.02 (m, 6H), 7.81−7.62 (m, 4H), 7.08 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.5, 152.8, 151.6, 135.1, 133.7, 133.5, 132.3, 130.1, 129.9, 129.7, 129.1, 128.6, 128.5, 128.33, 128.31, 128.26, 128.2, 127.6, 127.0, 126.8, 126.6, 126.4, 126.2, 125.5, 123.6, 120.7, 120.6, 116.4, 114.3, 55.4; HRMS (ESI) calcd for $C_{32}H_{22}NO$ $[M + H]^+$ 436.1701, found 436.1691.

*Ethyl Dinaphtho[1,2-f:2′,1′-h]isoquinoline-15-carboxylate (**3an**).* Colorless solid, mp 226.3−228.6 °C, 10.8 mg (54%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.26 (s, 1H), 9.64 (s, 1H), 8.98−8.86 (m, 2H), 8.61 (d, J = 8.8 Hz, 2H), 8.17−8.09 (m, 2H), 8.06 (d, J = 7.9 Hz, 2H), 7.83−7.63 (m, 4H), 4.59 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9; 151.9, 143.4, 134.2, 133.5, 133.4, 130.4, 130.2, 129.7, 129.51, 129.47, 129.0, 128.5, 128.4, 127.7, 127.5, 127.2, 127.0, 126.8, 126.7, 125.4, 125.3, 123.6, 120.5, 120.4, 62.0, 14.5; HRMS (ESI) calcd for $C_{28}H_{19}NNaO_2$ $[M + Na]^+$ 424.1313, found 424.1298.

*2-(Dinaphtho[1,2-f:2′,1′-h]isoquinolin-15-yl)acetonitrile (**3ao**).* Pale brown solid, mp 241.4−242.6 °C, 9.8 mg (53%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.10 (s, 1H), 8.89 (d, J = 8.1 Hz, 2H), 8.85 (s, 1H), 8.61 (d, J = 8.9 Hz, 2H), 8.18−8.02 (m, 4H), 7.83−7.63 (m, 4H), 4.16 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.2, 145.9, 135.1, 133.6, 133.4, 130.34, 130.28, 129.5, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 127.4, 127.3, 127.1, 126.81, 126.76, 125.5, 124.7, 124.3, 120.5, 119.3, 117.3, 26.8; HRMS (ESI) calcd for $C_{27}H_{17}N_2$ $[M + H]^+$ 369.1392, found 369.1386.

*13,16-Dibutyl 15-ethyl dinaphtho[1,2-f:2′,1′-h]isoquinoline-13,15,16-tricarboxylate (**3bn**).* Yellow amorphous, 16.1 mg (53%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62−8.48 (m, 2H), 8.41 (d, J = 8.0 Hz, 1H), 8.35−8.27 (m, 1H), 8.17 (t, J = 9.0 Hz, 2H), 8.04−7.95 (m, 2H), 7.69−7.54 (m, 4H), 4.59−4.40 (m, 2H), 3.75 (br, 2H), 3.25 (br, 2H), 1.45 (t, J = 7.2 Hz, 3H), 1.22−0.86 (m, 8H), 0.83−0.68 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.0, 166.7, 153.1, 147.2, 133.4, 132.2, 131.9, 131.4, 131.2, 130.99, 130.97, 130.2, 129.8, 127.8, 127.6, 127.4, 127.1, 127.0, 126.8, 126.7, 126.0, 124.3, 123.4, 119.8, 11.7, 66.1, 62.5, 29.81, 29.78, 18.9, 18.8, 14.1, 13.65, 13.6; HRMS (ESI) calcd for $C_{38}H_{35}O_6NNa$ $[M + Na]^+$ 624.2362, found 624.2350.

*2,2′-[(9,9-Didodecyl-9H-fluorene-2,7-diyl)bis(benzo[s]picene-15,14-diyl)]bis(propan-2-ol) (**5**).* H_8−BINAP (5.7 mg, 0.0090 mmol) and $[Rh(cod)_2]BF_4$ (3.7 mg, 0.0090 mmol) were dissolved in CH_2Cl_2, and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 50 min, the resulting mixture was concentrated. To a solution of the residue and **4** (20.0 mg, 0.0300 mmol) in $(CH_2Cl)_2$ (0.8 mL) was added a solution of **1a** (20.0 mg, 0.0660

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mmol) in $(CH_2Cl)_2$ (1.2 mL). The mixture was stirred at room temperature for 15 h. The resulting solution was concentrated and purified by a preparative TLC (eluent: *n*-hexane/CH_2Cl_2 = 1:3) to give **5** (17.8 mg, 0.0140 mmol, 47% yield). Pale yellow solid, mp 130 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.36 (s, 2H), 9.11 (d, J = 8.4 Hz, 2H), 9.04−8.96 (m, 2H), 8.80 (s, 2H), 8.66 (dd, J = 9.1, 2.8 Hz, 2H), 8.13−7.95 (m, 8H), 7.82 (d, J = 7.6 Hz, 2H), 7.78−7.70 (m, 2H), 7.69−7.62 (m, 2H), 7.58−7.44 (m, 8H), 2.14−1.92 (m, 6H), 1.65 (s, 12H), 1.31−1.00 (m, 36H), 0.90−0.72 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 144.6, 142.7, 139.9, 138.9, 133.6, 133.5, 132.5, 129.9, 129.8, 129.2, 128.7, 128.3, 128.21, 128.18, 128.1, 128.0, 127.9, 127.5, 126.8, 126.7, 126.4, 126.2, 126.1, 126.0, 124.7, 120.79, 120.76, 119.3, 74.4, 55.4, 40.6, 32.7, 31.9, 30.3, 29.7, 29.64, 29.62, 29.56, 29.3, 24.2, 22.7, 14.1, 1.0; HRMS (ESI) calcd for $C_{95}H_{98}O_2Na$ $[M + Na]^+$ 1293.7459, found 1293.7457.

Ladder Molecule 6. Tetrafluoroboric acid diethyl ether complex (5.3 μL, 6.3 mg, 0.039 mmol) was added to a stirred solution of **5** (8.2 mg, 0.0064 mmol) in CH_2Cl_2 (3 mL), and the mixture was stirred at room temperature for 14 h. The resulting solution was concentrated and purified by a preparative TLC (eluent: *n*-hexane/CH_2Cl_2 = 10:1) to give **6** (7.8 mg, 0.0063 mmol, 98% yield). Yellow solid, mp 155 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.31 (s, 2H), 9.26 (d, J = 8.4 Hz, 2H), 9.08 (d, J = 8.4 Hz, 2H), 9.00 (s, 2H), 8.69−8.61 (m, 4H), 8.13−8.01 (m, 8H), 7.90 (s, 2H), 7.86−7.80 (m, 4H), 7.77−7.60 (m, 6H), 2.22−2.10 (m, 4H), 1.75 (s, 12H), 1.20−0.99 (m, 36H), 0.82−0.71 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.8, 152.5, 151.1, 141.5, 138.6, 138.2, 133.7, 130.15, 130.07, 130.05, 129.8, 128.6, 128.4, 128.3, 128.24, 128.21, 128.15, 127.60, 127.58, 127.5, 127.4, 126.2 126.1, 126.0, 125.9, 122.9, 120.8, 119.7, 114.7, 113.8, 54.8, 46.8, 41.0, 31.8, 30.1, 29.63, 29.58, 29.57, 29.52, 29.4, 29.2, 28.0, 23.9, 22.6, 14.0; HRMS (APCI) calcd for $C_{95}H_{95}$ $[M + H]^+$ 1235.7428, found 1235.7411.

Tetrayne 7. To a stirred solution of **1a** (1.98 g, 6.56 mmol) in THF (114 mL) was added EtMgBr (2.51 mL, 7.54 mmol, 3.0 M in Et_2O) at 0 °C, and the resulting mixture was stirred at room temperature for 1 h. To the solution was added a solution of (3-cyanopropyl)-dimethylchlorosilane (1.23 mL, 1.22 g, 7.54 mmol) in THF (21 mL), and the resulting mixture was stirred at room temperature for 17 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (eluent: *n*-hexane/EtOAc = 20:1−10:1) to give 4-(((1′-ethynyl-[2,2′-binaphthalen]-1-yl)ethynyl)dimethylsilyl)-butanenitrile (1.32 g, 3.09 mmol, 47% yield). Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 7.98−7.86 (m, 4H), 7.70−7.50 (m, 6H), 3.32 (s, 1H), 1.81 (br, 2H), 1.24−1.11 (m, 2H), 0.53−0.41 (m, 2H), 0.06 (br, 6H).

To a stirred solution of 4-(((1′-ethynyl-[2,2′-binaphthalen]-1-yl)ethynyl)dimethylsilyl)butanenitrile (1.66 g, 0.387 mmol) in pyridine (16 mL) was added CuCl (23 mg, 0.23 mmol), and the mixture was stirred under bubbling air at 40 °C for 2.5 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. To a solution of the residue in MeOH (5 mL) and THF (5 mL) was added a solution of K_2CO_3 (268 mg, 1.94 mmol) in water (2.5 mL). The mixture was stirred at room temperature for 5 h. The reaction mixture was concentrated and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (eluent: *n*-hexane/CH_2Cl_2 = 4:1) to give 7 (105 mg, 0.175 mmol, 90% yield). Yellow solid; mp 200 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.50 (d, J = 8.4 Hz, 2H), 8.36−8.27 (m, 2H), 7.94−7.83 (m, 6H), 7.76 (d, J = 8.5 Hz, 2H), 7.70−7.50 (m, 12H), 3.31 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9, 142.6, 134.2, 133.9, 132.5, 132.4, 128.4, 128.23, 128.16, 127.4, 127.2, 126.73, 126.66, 126.6, 118.63, 118.55, 86.1, 82.6, 80.8, 80.6; HRMS (APCI) calcd for $C_{48}H_{27}$ $[M + H]^+$ 603.2107, found 603.2105.

*(−)-8,10-Diphenyl-9H-fluoreno[3,4-s:5,6-s′]dipicen-9-one [(−)-**9a**].* (*S*)-H_8−BINAP (15.8 mg, 0.0250 mmol) and $[Rh(cod)_2]BF_4$ (10.2 mg, 0.0250 mmol) were dissolved in CH_2Cl_2, and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting mixture was concentrated. To a solution of the residue and **8a** (17.3 mg, 0.0750 mmol) in $(CH_2Cl)_2$ (2 mL) was added a solution of 7 (30.1 mg, 0.0500 mmol) in $(CH_2Cl)_2$ (4 mL). The mixture was stirred at room temperature for 66 h. The resulting solution was concentrated and purified by a preparative TLC (eluent: *n*-hexane/CH_2Cl_2 = 2:1) to give (−)-**9a** (3.2 mg, 0.038 mmol, 8% yield, 94% ee). Orange solid, mp >300 °C; $[\alpha]^{25}_D$ − 3954° (*c* 0.10, $CHCl_3$, 95% ee); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.87 (s, 2H), 8.84 (d, J = 8.4 Hz, 2H), 8.27 (d, J = 8.9 Hz, 2H), 8.04−7.94 (m, 6H), 7.93−7.86 (m, 4H), 7.71 (d, J = 8.8 Hz, 2H), 7.65 (ddd, J = 8.3, 6.9, 1.4 Hz, 2H), 7.60−7.40 (m, 10H), 7.22 (d, J = 8.4 Hz, 2H), 6.67−6.61 (m, 2H), 6.29−6.23 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.7, 138.7, 137.9, 134.0, 13.7, 131.8, 131.1, 130.8, 130.6, 130.09, 129.99, 129.5, 128.8, 128.50, 128.48, 128.4, 128.2, 128.12, 128.09, 127.9, 126.5, 126.4, 126.3, 125.8, 125.5, 124.9, 124.3, 124.0, 120.5, 119.4; HRMS (APCI) calcd for $C_{65}H_{37}O$ $[M + H]^+$ 833.2839, found 833.2823; CHIRALPAK IF-3, *n*-hexane/CH_2Cl_2 = 75:25, 1.0 mL/min, retention times: 15.8 min (major isomer) and 28.9 min (minor isomer).

*(−)-8,10-Dibutyl-9H-fluoreno[3,4-s:5,6-s′]dipicen-9-one [(−)-**9b**].* (*S*)-H_8−BINAP (15.8 mg, 0.0250 mmol) and $[Rh(cod)_2]BF_4$ (10.2 mg, 0.0250 mmol) were dissolved in CH_2Cl_2, and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting mixture was concentrated. To a solution of the residue in $(CH_2Cl)_2$ (0.4 mL) was added a solution of 7 (30.1 mg, 0.0500 mmol) and **8b** (14.3 mg, 0.0750 mmol) in $(CH_2Cl)_2$ (2.6 mL). The mixture was stirred at room temperature for 40 h. The resulting solution was concentrated and purified by a preparative TLC (eluent: *n*-hexane/$CHCl_3$/toluene = 4:4:1) to give (−)-**9b** (0.38 mg, 0.00048 mmol, 1% yield, 71% ee). Orange solid, mp 95.0−98.1 °C; $[\alpha]^{25}_D$ − 923° (*c* 0.040, $CHCl_3$, 65% ee); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.76 (d, J = 5.5 Hz, 2H), 8.73 (s, 2H), 8.24 (d, J = 5.8 Hz, 2H), 8.01 (d, J = 5.1 Hz, 2H), 7.94−7.91 (m, 4H), 7.69−7.62 (m, 4H), 7.59 (t, J = 4.7 Hz, 2H), 7.50 (d, J = 5.3 Hz, 2H), 7.05 (d, J = 5.6 Hz, 2H), 6.64 (t, J = 4.7 Hz, 2H), 6.20−6.15 (m, 2H), 3.74−3.66 (m, 2H), 3.56−3.48 (m, 2H), 2.07−1.98 (m, 4H), 1.68 (sextet, J = 5.0 Hz, 4H), 1.12 (t, J = 5.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 150.6, 139.3, 133.9, 133.7, 131.7 130.8, 130.7, 130.13, 130.08, 128.9, 128.73, 128.67, 128.4, 128.1. 128.0, 127.9, 126.4, 126.2, 126.1, 125.6, 125.4, 125.2, 124.2, 123.5, 120.6 119.3, 33.2, 31.6, 22.9, 14.3; HRMS (APCI) calcd for $C_{61}H_{45}O$ $[M + H]^+$ 793.3465, found 793.3465; CHIRALPAK IF-3, *n*-hexane/CH_2Cl_2 = 82:18, 1.0 mL/min, retention times: 17.9 min (major isomer) and 24.4 min (minor isomer). Racemic crystals of (±)-**9b**, obtained by recrystallization from CH_2Cl_2/*n*-hexane at room temperature, were subjected to the X-ray crystallographic analysis.[19]

(+)-8′,10′-Diphenylspiro[fluorene-9,9′-fluoreno[3,4-s:5,6-s′]-dipicene] [(+)-11]. *n*-BuLi (0.19 mL, 0.31 mmol, 1.64 mol/L in *n*-hexane) was added dropwise to a stirred solution of 2-bromobiphenyl **10** (146 mg, 0.624 mmol) in THF (1 mL) at −78 °C, and the resulting mixture was stirred for 20 min. To the solution was added a solution of (−)-**9a** (5.2 mg, 0.0062 mmol, 95% ee) in THF (2 mL) at −78 °C, and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a preparative TLC (eluent: *n*-hexane/CH_2Cl_2/toluene =1:1) to give fluorenyl alcohol [9-([1,1′-biphenyl]-2-yl)-8,10-diphenyl-9*H*-fluoreno-[3,4-*s*:5,6-*s*′]dipicen-9-ol]. To a stirred solution of thus obtained fluorenyl alcohol in CH_2Cl_2 (2 mL) was added tetrafluoroboric acid diethyl ether complex (34 μL, 0.25 mmol), and the mixture was stirred at room temperature for 13 h. The resulting solution was concentrated and purified by a preparative TLC (eluent: *n*-hexane/$CHCl_3$ = 2:1) to give impure (+)-**11**. This impure (+)-**11** was washed with a small amount of methanol and *n*-hexane to give analytically pure (+)-**11** (4.5 mg, 0.0047 mmol, 75% yield, 94% ee). Yellow solid, mp 260 °C (dec.); $[\alpha]^{25}_D$ + 322° (*c* 0.045, $CHCl_3$, 94% ee); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (d, J = 8.1 Hz, 2H), 8.64 (s, 2H), 8.36 (d, J = 9.0 Hz,

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2H), 8.12 (d, J = 9.0 Hz, 2H), 8.00−7.89 (m, 4H), 7.73 (d, J = 8.8 Hz, 2H), 7.60−7.51 (m, 4H), 7.50−7.39 (m, 4H), 7.20−7.08 (m, 6H), 7.02−6.90 (m, 4H), 6.72 (t, J = 7.7 Hz, 4H), 6.61 (ddd, J = 7.8 Hz, 2H), 6.32 (d, J = 7.2 Hz, 4H), 6.26 (ddd, J = 8.3, 7.0, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.1, 143.6, 143.4, 142.5, 139.0, 137.2, 133.5, 131.7, 129.8, 129.62, 129.61, 129.3, 129.1, 128.9, 128.8, 128.6, 127.9, 127.8, 127.4, 127.1, 127.0, 126.9, 126.7, 126.4, 126.3, 125.9, 125.5, 125.4, 125.3, 125.2, 124.1, 123.8, 123.5, 120.9, 120.2, 119.8, 66.1; HRMS (ESI) calcd for $C_{77}H_{44}$ [M] 968.3443, found 968.3438; CHIRALPAK IF-3, n-hexane/CH_2Cl_2 = 80:20, 1.0 mL/min, retention times: 10.4 min (major isomer) and 20.5 min (minor isomer).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02757.

Crystal data for (±)-**9b**, chiral HPLC charts, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

X-ray crystallographic information file for (±)-**9b** (CIF)

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Notes

The authors declare no competing financial interest.

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