JOC The Journal of Organic Chemistry

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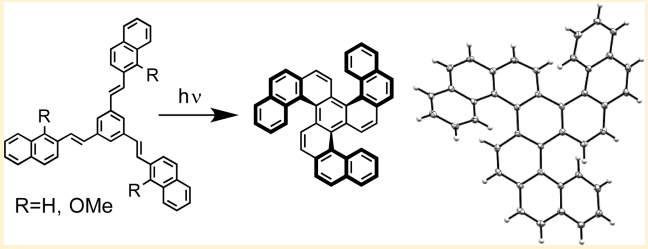
Synthesis of a Three-Bladed Propeller-Shaped Triple [5]Helicene

Hiromu Saito,[†] Akira Uchida,[†] and Soichiro Watanabe*[,†,‡]

[†]Department of Biomolecular Science, Faculty of Science, and [‡]Research Center for Materials with Integrated Properties, Toho University, Miyama 2-2-1, Funabashi, Chiba 274-8510, Japan

Supporting Information

ABSTRACT: Three-bladed propeller-shaped triple [5]-helicene was synthesized using eliminative and oxidative photocyclization reactions, which proceeded in 37 and 63% yields, respectively. Chromatographic purification gave a mixture of diastereomers, and the *PPM* and *PMM* isomers were gradually converted to the thermodynamically more stable *PPP* and *MMM* isomers at room temperature. The activation parameters for the racemization of the *PPP* and *MMM* isomers were determined, and the structure of the triple [5]helicene was determined by X-ray crystallographic analysis.



INTRODUCTION

Helicenes are a class of polycyclic aromatic hydrocarbons (PAHs) consisting of ortho-fused benzene rings or some other type of aromatic system.[1] Compounds belonging to this class are simply referred to as [*n*]helicenes, where the *n* denotes the number of successive ortho-fused aromatic rings. One of the most unique structural features of helicenes is their inherent helical chirality, which occurs in systems where *n* is greater than six.[2] Helicenes with a large *n* value and multihelicenes, where more than one of the aromatic rings is shared by more than two helicene units, represent attractive targets for organic synthesis. The synthesis of [16]helicene, the longest helicene synthesized to date, was recently reported.[3] For multihelicenes, several compounds have been reported containing two helicene moieties in the same molecule,[4−10] which are sometimes referred to as "double helicenes". A few "triple helicenes"[11−13] and "quadruple helicenes"[14] have also been reported, where three and four helicene moieties coexist in the same molecule, respectively.

The syntheses of double and triple helicenes reported to date generally rely on the cyclotrimerization of arynes.[6,7,11−13] Although oxidative photocyclization represents a powerful alternative for the synthesis of PAHs, including multihelicenes,[4,5] this method has been largely overlooked because it can potentially lead to the formation of undesired compounds. In particular, the synthesis of [5]helicene using an oxidative photocyclization reaction led to the formation of benzo[*ghi*]perylene as an unwanted overannulation product.[15−17] Although several improved methods have been devised to avoid the formation of overannulation products by introducing an appropriate functional group to the benzene ring,[18−20] these processes tend to make it increasingly difficult to synthesize the multihelicene precursor.

During the course of our recent study on the selective synthesis of the preferred isomers of PAHs by photocyclization,[21] we became interested in the synthesis of the triple [5]helicene **1** using a photocyclization strategy. Whereas the structural isomers **2**[11] and **3**[6] have been synthesized, compound **1** has not yet been reported in the literature (Figure 1). We were intrigued by this omission because compound **1** is a simple PAH that does not contain any vulnerable functional groups. We therefore hypothesized that the absence of compound **1** from the literature reflected the lack of an efficient synthetic method or a suitable precursor for preparing the target compound. Herein, we describe, for the first time, the synthesis of the three-bladed propeller-shaped triple [5]-helicene **1**.

Figure 1. Triple [5]helicene **1** and its structural isomers **2** and **3**. One of the [5]helicene units in each compound is shown in red.

RESULTS AND DISCUSSION

Compounds **2** and **3** were synthesized by the metal-catalyzed cyclotrimerization of arynes **4** and **5**, respectively. This approach is particularly attractive for compound **2** because it avoids the formation of structural isomers after the cyclotrimerization. Although the cyclotrimerization of **5** could potentially lead to the formation of two isomers **1** and **3**, compound **3** is the only product to have ever been reported for this reaction (Figure 2).

Received: March 1, 2017

DOI: 10.1021/acs.joc.7b00486
J. Org. Chem. XXXX, XXX, XXX−XXX

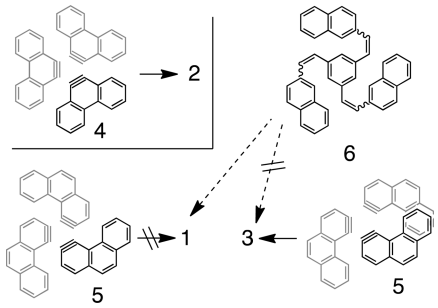


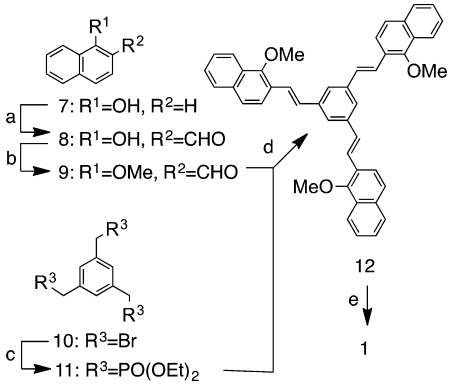
Figure 2. Plausible arrangements of arynes **4** and **5** for the cyclotrimerization reaction. Compound **6** is a promising precursor for the synthesis of triple [5]helicene **1** via a photocyclization reaction.

This is not surprising considering that the cyclotrimerization of an aryne derived from a naphthalene congener afforded two structural isomers, with the unsymmetrical compound, corresponding to **3**, being obtained as the major product.[11]

We considered that an oxidative photocyclization reaction could be used to provide facile access to compound **1**. We selected compound **6** as a suitable substrate to evaluate this hypothesis because the oxidative photocyclization of 1,3,5-tristyrylbenzene, a smaller analogue of compound **6**, has already been reported to give triple [4]helicene.[22] Prior to investigating the photocyclization reaction of compound **6**, we wanted to select a strategy that would avoid the possibility of an undesired overannulation reaction. We therefore selected an eliminative photocyclization reaction[23] to achieve the synthesis of compound **1** because this reaction can be conducted in the absence of an oxidant for the aromatization step.

The route that we used for the synthesis of triple [5]helicene **1** is shown in Scheme 1. The introduction of a formyl group at

Scheme 1. Synthesis of Triple [5]Helicene 1 (Eliminative Photocyclization)[a]

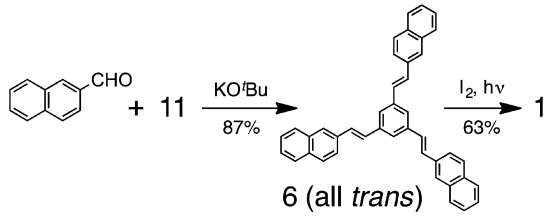


[a]Reagents and conditions: (a) $MgCl_2$, $(CH_2O)_n$, NEt_3, CH_3CN, 52%; (b) MeI, K_2CO_3, DMF, 91%; (c) $P(OEt)_3$, toluene, quant.; (d) KO^{t}Bu, THF, 48%; (e) H_2SO_4 (3 equiv), 450 W high-pressure mercury lamp, benzene, 37%.

the 2-position of 1-naphthol (**7**) gave compound **8**, which was converted to the corresponding methyl ether **9**. Triphosphonate **11** was prepared in quantitative yield by the Arbuzov reaction of 1,3,5-tri(bromomethyl)benzene (**10**) with triethyl phosphite. Precursor **12** was synthesized by the reaction of compound **9** with **11**, which was irradiated with a 450 W high-pressure mercury lamp in deoxygenated benzene for 6 h to afford triple [5]helicene **1** in 37% yield. The last step in this sequence involved three cyclization reactions in a same molecule, representing an average yield of 72% for each cyclization.

It was envisaged that the overannulation reaction would be suppressed during the oxidative photocyclization because of the demanding steric congestion around each [5]helicene unit in **1**. This idea encouraged us to investigate the use of an oxidative photocyclization to obtain compound **1** because this shorter synthetic route would represent a considerable practical advantage. To confirm this possibility, we synthesized compound **6** in several short steps (Scheme 2).

Scheme 2. Synthesis of Triple [5]Helicene 1 (Oxidative Photocyclization)



Compound **11** was reacted with 2-naphthaldehyde to give **6** (all-*trans* form), which was irradiated with a 450 W high-pressure mercury lamp in the presence of iodine (0.1 equiv) to give compound **1** in 63% yield. This yield was better than that obtained via the eliminative photocyclization process, indicating that this new strategy effectively suppressed the overannulation reaction.

The structure of the compound **1** was determined by ^{1}H NMR, ^{13}C NMR, HRMS, and X-ray crystallographic analyses. Before analyzing these data, we considered the different isomers of compound **1**. The energy barrier for the racemization of the *P* and *M* isomers of the parent [5]helicene is too low to allow for the isolation of the individual isomers at room temperature.[24] In contrast, the different isomers of hexabenzotriphenylene **2** could be readily isolated because of the helicity of the [5]helicene unit. Considering the structural similarity of compounds **1** and **2**, it was envisaged that the individual isomers of compound **1** could also be isolated. Based on the helical chirality of the [5]helicene unit, we expected that compound **1** would exist as two diastereomers: *PPP* (or its enantiomer, *MMM*) and *PPM* (or its enantiomer, *PMM*), where one *P* or *M* indicates the helicity of one [5]helicene moiety (Figure 3).

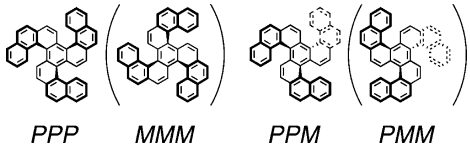


Figure 3. Diastereomers of triple [5]helicene **1** together with their enantiomers in parentheses.

To avoid the possibility of these compounds isomerizing during the purification process, we separated the oxidative photocyclization product without heating. The ^{1}H NMR spectra of the major and minor products were recorded after preparative HPLC purification. The main product gave eight different proton signals and was readily assigned as the *PPP* (or *MMM*) isomer. The ^{1}H NMR spectrum of the minor product

DOI: 10.1021/acs.joc.7b00486
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was much more complicated than that of the major product and also contained signals corresponding to the *PPP* (or *MMM*) isomer (Figures S1–S4). The ^{1}H NMR spectra of this sample gradually changed at room temperature to ultimately give a spectrum consistent with that of the *PPP* (or *MMM*) isomer (Figure 4). These results indicated that the minor product of the reaction was the *PPM* (or *PMM*) isomer.

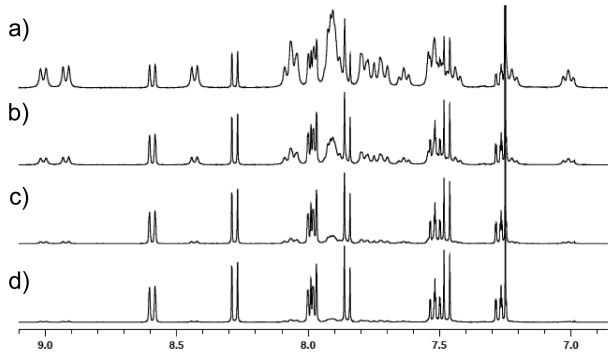

Figure 4. Changes in the ^{1}H NMR spectra of compound **1** during the isomerization of its *PPM* (*PMM*) isomer to the *PPP* (*MMM*) isomer. (a) Immediately after HPLC separation, after (b) 1 day, (c) 3.6 days, and (d) 6.6 days at room temperature.

Furthermore, the half-life for the isomerization of this product to the more thermodynamically stable *PPP* (or *MMM*) isomer was determined to 2.3 days (Figure S5). According to the ^{1}H NMR spectrum of the sample before HPLC separation, the ratio of the *PPP* (or *MMM*) and *PPM* (or *PMM*) isomers was approximately 2:1, indicating that more than 30% of the compound **1** obtained immediately after the reaction was the *PPM* (or *PMM*) isomer.

The subsequent analysis of the *PPP* (or *MMM*) isomer of **1** by HPLC over a chiral column revealed that this product existed as a 1:1 mixture of enantiomers, corresponding to the *PPP* and *MMM* isomers. These enantiomers were separated and found to be stable at room temperature (Figure S6). A kinetic study of the thermal racemization process of one of these enantiomers in toluene was conducted by HPLC. The activation parameters for the racemization were determined to be $\Delta H^{\ddagger}$ = 27.0 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = −1.4 cal·mol^{-1}·K^{-1}, giving $\Delta G^{\ddagger}$ = 27.4 kcal·mol^{-1} at 25 °C (Figures S7 and S8). This $\Delta G^{\ddagger}$ value was comparable with the value reported for the conversion of C_2 to the corresponding D_3 symmetric isomer in compound **2**.[12] Although the $\Delta S^{\ddagger}$ value obtained for the racemization of compound **1** is smaller than those reported for [*n*]helicenes (*n* = 5–9),[25,26] it is not an unlikely value, considering that even positive values have been observed for the isomerization and racemization of quadruple helicenes.[14] It is possible that the loss of entropy in the transition states is very small because the stable conformations of some multihelicenes, including that of compound **1**, have little flexibility.

To clarify our understanding of these isomerization and racemization processes, we conducted density functional theory (DFT) calculations at B3LYP/6-31G* level to optimize the different isomers of compound **1**, as well as the transition state for the isomerization (Figure 5). The *PPP* (or *MMM*) isomer was calculated to be more stable than the *PPM* (or *PMM*) isomer by 3.0 kcal·mol^{-1}. The calculated $\Delta G^{\ddagger}$ value for racemization (29.5 kcal·mol^{-1}) was consistent with that value obtained in the kinetic study. The transition states for the

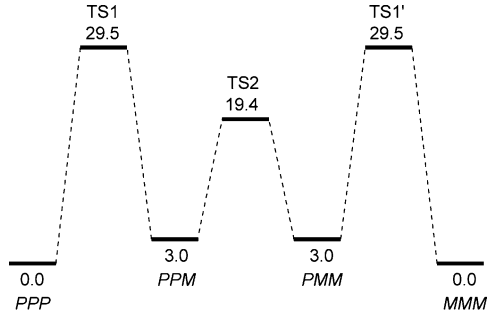

Figure 5. Energy profile for the isomerization of triple [5]helicene **1**, as estimated by DFT calculations.

conversion of *PPP* to *PPM* (TS1) and *PPM* to *PMM* (TS2) showed that the two benzene rings at both ends of the [5]helicene unit were oriented face-to-face, as is commonly seen in other helicene isomerization processes (Figure 6).[27,28]

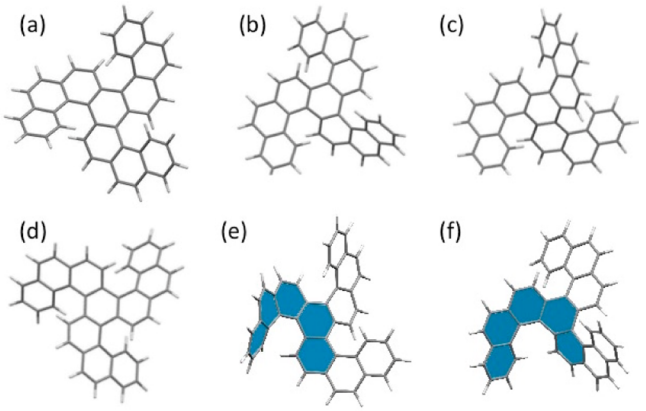

Figure 6. Optimized structures of compound **1** for (a) *PPP*, (b) *PPM*, (c) *PMM*, (d) *MMM*, (e) TS1, and (f) TS2.

The UV/vis spectrum of compound **1** in chloroform showed an absorption maximum at 352 nm with an extension coefficient of 8.3 × 10^4 M^{-1}·cm^{-1}. The fluorescence spectrum of compound **1** showed an emission maximum at 469 nm with an excitation wavelength of 352 nm (Figure 7) and a

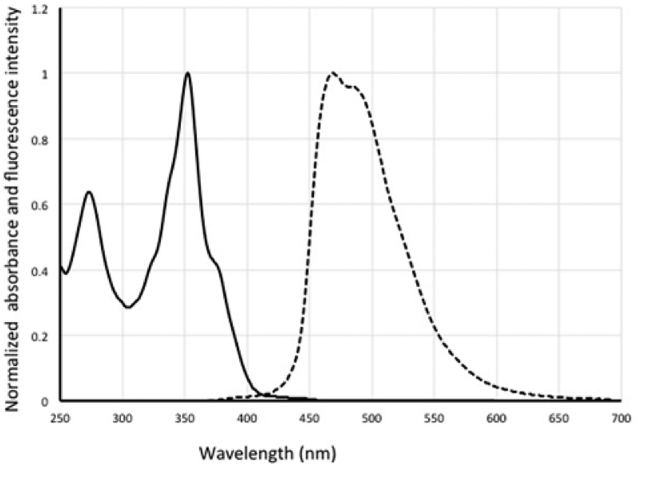

Figure 7. UV/vis (solid line) and fluorescence spectra (λ_{ex} 352 nm, dotted line) of triple [5]helicene **1** in chloroform.

DOI: 10.1021/acs.joc.7b00486
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fluorescence quantum yield of 0.026. The fluorescence lifetime was 5.2 ns with an excitation wavelength of 400 nm (Figure S9). The absorption and emission maxima were longer than those for [5]helicene[29] and similar to those for double [5]helicene[9] and hexabenzotriphenylene **2**,[30] which have the same number of benzene rings.

The unique C_3-symmetrical structure of compound **1** influences the electronic distribution of the HOMO and LUMO. DFT calculations suggest that both the HOMO and the LUMO of compound **1** are doubly degenerate and are mainly located in the central region of the molecule (Figure 8).

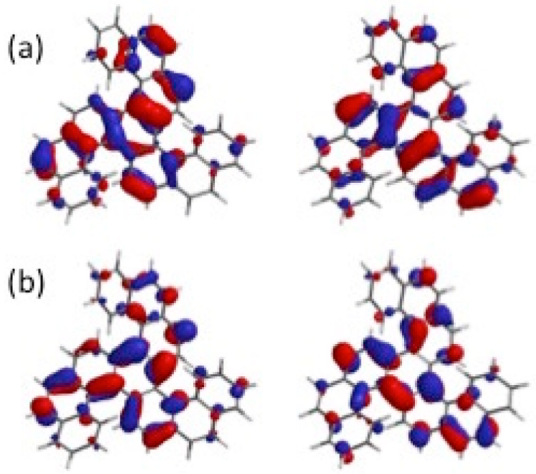

Figure 8. Electronic distributions of the HOMO (a) and LUMO (b) of compound **1** (*PPP* isomer) calculated with the DFT method (B3LYP/6-31G*).

This result is in sharp contrast to the parent [5]helicene, in which both the HOMO and LUMO are delocalized throughout the whole molecule.[29] The calculated HOMO and LUMO energy levels for compound **1** were −5.29 and −1.60 eV, respectively. The former is higher than that for the parent [5]helicene (−5.49 eV), and the latter is lower than that obtained for [5]helicene (−1.29 eV) at the same level of theory, which suggests that the HOMO−LUMO energy gap in compound **1** is reduced compared with that in [5]helicene. This estimation is consistent with the red shift in the UV and fluorescence spectra of compound **1** compared with those of [5]helicene.

The circular dichroism (CD) spectrum of the second of the two fractions eluted by HPLC (96% ee) exhibited a positive Cotton effect in the region of 330−390 nm ($\Delta\varepsilon$ 347 nm, 88 $M^{-1}\cdot cm^{-1}$) as well as a negative Cotton effect below 330 nm ($\Delta\varepsilon$ 281 nm, 342 $M^{-1}\cdot cm^{-1}$).

The CD spectrum of the first fraction (93% ee) was the mirror opposite of that of the second fraction (Figure 9). Because the spectral characteristics of the second enantiomer were similar to those of the *P*-helicenes,[31] the enantiomers in the first and second fractions were tentatively assigned to the *MMM* and *PPP* isomers, respectively.

Single crystals of compound **1** were obtained as a DCM solvate following the crystallization of this material from dichloromethane (CCDC 1499672) (Figure 10). The unit cell of these crystals consisted of two *PPP* isomers and two *MMM* isomers. Compound **1** was grossly distorted as a consequence of steric hindrance in the fjord regions. The C1···C38, C10···C15, and C24···C29 distances were determined to be 2.911(2),

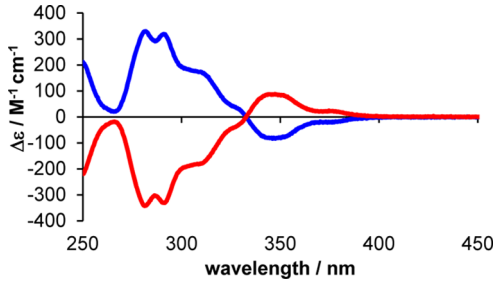

Figure 9. CD spectra in chloroform of the first (blue) and second (red) enantiomers of compound **1** to be eluted by HPLC.

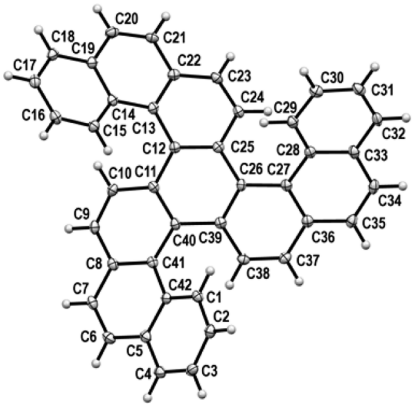

Figure 10. Crystal structure of **1** with 50% ellipsoids. The solvated dichloromethane molecule has been omitted for clarity.

2.930(3), and 2.939(3) Å, respectively, and the torsional angles of the C11−C12−C13−C14, C25−C26−C27−C28, and C39−C40−C41−C42 bonds were 34.8(3), 34.5(3), and 33.6(3)°, respectively. The central benzene ring in **1** adopted a flattened chair form. The ring itself consisted of alternating bond lengths with shorter lengths of 1.409(2), 1.412(2), and 1.408(2) Å for the C11−C40, C12−C25, and C26−C39 bonds and longer lengths of 1.458(2), 1.459(2), and 1.458(2) Å for the C11−C12, C25−C26, and C39−C40 bonds, respectively. Although compounds with chiral C_3 symmetry are expected to have potential use in several applications, such as asymmetric catalysis, molecular recognition, and the construction of nanoarchitectures, these compounds are not yet very popular.[32] Chiral C_3-symmetric triple [5]helicene **1** is therefore a promising candidate for new applications in these fields.

CONCLUSION

In conclusion, we have successfully synthesized the three-bladed propeller-shaped triple [5]helicene **1** using eliminative and oxidative photocyclization strategies. The yields for these cyclization reactions were acceptable considering that they both required three steps to assemble the fully cyclized product. It is noteworthy that the current triple oxidative photocyclization reaction did not suffer from undesired overannulation, representing a considerable improvement over the result observed for the synthesis of the parent [5]helicene under the same reaction conditions. The isomerization and racemization steps were analyzed kinetically to reveal their activation parameters. The structure of compound **1** was unambiguously determined by X-ray crystallographic analysis.

DOI: 10.1021/acs.joc.7b00486
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EXPERIMENTAL SECTION

General Methods. A 450 W high-pressure mercury lamp UM-452 (USHIO) was used for the photoreactions. Melting points were determined on a Yanaco micro melting point apparatus. All of the melting points were reported uncorrected. Preparative gel permeation chromatography was performed by LC-9201 (Japan Analytical Industry) using JAIGEL 1H+2H columns with $CHCl_3$ as a solvent. ^1H, ^{13}C, and ^{31}P NMR spectra were measured in $CDCl_3$ using a Bruker Avance 300 or 400 spectrometer with tetramethylsilane as an internal standard. UV−vis spectra were recorded on a HITACHI U-3010 spectrophotometer. Fluorescence emission spectra were measured on a HORIBA Spex Fluorolog 3 spectrometer. Absolute fluorescence quantum yield values were determined using a Hamamatsu Photonics C11347 Absolute PL quantum yield spectrometer (Quantaurus-QY). Fluorescence lifetime measurements were performed with a streak camera (C11200, Hamamatsu) as reported previously.[33] Circular dichroism spectra were measured using a JASCO J820 system. For the chiral separation and kinetic study, HPLC was conducted on a JASCO HPLC system equipped with a DAICEL CHIRALPAK IE column (4.6 × 250 mm) using a mixture of chloroform and hexane (1:1 v/v) as the eluent. High-resolution mass spectra were recorded on a Thermo Fisher Exactive with Orbitrap mass analyzer at the Center for Analytical Instrumentation, Chiba University, Japan.

1-Hydroxy-2-naphthaldehyde (8). The title compound was synthesized by a previously reported method, and NMR data of the product matched those reported in the literature.[34]

1-Methoxy-2-naphthaldehyde (9). A solution of **8** (853.4 mg, 4.96 mmol) and potassium carbonate (1.03 g, 7.42 mmol) in DMF (10 mL) was treated with iodomethane (0.46 mL, 7.4 mmol) under an atmosphere of argon, and the resulting mixture was stirred for 15 h at room temperature. The mixture was then diluted with 1 M HCl (150 mL) and extracted with diethyl ether. The organic layer was washed with brine, dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel eluting with hexane and ethyl acetate (1:1 v/v) to afford **9** as an orange solid (833.9 mg, 4.49 mmol, 91%). The NMR data for this product matched those reported in the literature.[35]

9: ^1H NMR (300 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.25 (d, J = 7.8 Hz, 1H), 7.89−7.85 (m, 2H), 7.67−7.56 (m, 3H), 4.15 (s, 3H).

1,3,5-Tris(diethoxyphosphomethyl)benzene (11). The title compound was synthesized by a previously reported method, and NMR data of the product matched those reported in the literature.[36]

1,3,5-Tris((*E*)-2-(1-methoxynaphthalene-2-yl)vinyl)benzene (12). To a solution of potassium *tert*-butoxide (639.7 mg, 5.70 mmol) in THF (7 mL) was added a solution of **9** (349.2 mg, 1.88 mmol) and **11** (299.6 mg, 0.57 mmol) in THF (7 mL) at 0 °C under an atmosphere of argon, and the resulting mixture was stirred for 30 min. The reaction was then warmed to room temperature and stirred for 10 h. The reaction mixture was diluted with water (140 mL) and extracted with dichloromethane. The organic layer was washed with brine, dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by preparative HPLC to afford **12** (170.2 mg, 0.27 mmol, 48%) as a pale yellow solid.

12: mp 182.0−183.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 8.1 Hz, 3H), 7.85 (d, J = 8.7 Hz, 6H), 7.77 (d, J = 16.5 Hz, 3H), 7.76 (s, 3H), 7.67 (d, J = 8.7 Hz, 3H), 7.57−7.46 (m, 6H), 7.35 (d, J = 16.5 Hz, 3H), 4.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9(s), 138.6(s), 134.6(s), 129.5(d), 128.4(s), 128.1(d), 126.4(d), 126.3(d), 125.8(s), 124.5(d), 124.3(d), 123.7(d), 123.6(d), 122.5(d), 62.8(q); HRMS (ESI) m/z calcd for $C_{45}H_{37}O_3^+$ 625.2737 $[M + H]^+$; found 625.2742.

1,3,5-Tris((*E*)-2-(naphthalene-2-yl)vinyl)benzene (6). To a solution of potassium *tert*-butoxide (646.1 mg, 5.76 mmol) in THF (5 mL) was added a solution of 2-naphthaldehyde (297.8 mg, 1.91 mmol) and **11** (304.2 mg, 0.58 mmol) in THF (10 mL) at 0 °C under an atmosphere of argon, and the resulting mixture was warmed to room temperature and stirred for 15 h. The reaction mixture was diluted with water (30 mL) to give a precipitate, which was filtered and dried in vacuo to afford **6** (268.4 mg, 0.50 mmol, 87%) as a white solid.

6: mp 262.5−264.0 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 3H), 7.89−7.80 (m, 12H), 7.69 (s, 3H), 7.51−7.46 (m, 6H), 7.43 (d, J = 16.2 Hz, 3H), 7.32 (d, J = 16.2 Hz, 3H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2(d), 134.7(d), 133.7(s), 133.2(s), 129.5(d), 128.7(d), 128.4(d), 128.1(d), 127.8(d), 126.9(d), 126.4(d), 126.0(s), 124.1(s), 123.5(d); HRMS (APCI) m/z calcd for $C_{42}H_{31}^+$ 535.2420 $[M + H]^+$; found 535.2418.

Triple [5]Helicene (Benzo[*c*]naphtho[2,1-*l*]phenanthro[3,4-*g*]chrysene, 1) by an Eliminative Photocyclization. To a solution of **12** (95.0 mg, 0.15 mmol) in deoxygenated benzene (150 mL) was added a 1 M solution of H_2SO_4 in *tert*-butylalcohol (0.45 mL, 0.45 mmol) at room temperature under an atmosphere of argon, and the resulting mixture was irradiated with UV light for 6 h. The reaction was then concentrated under reduced pressure to give a residue, which was dissolved in dichloromethane. The insoluble material was removed by filtration, and the filtrate was washed with brine, dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel eluting with a mixture of hexane and dichloromethane (4:1 v/v) to afford **1** as a yellow solid (29.7 mg, 0.056 mmol, 37%).

1: mp >300 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, J = 8.2 Hz, 3H), 8.28 (d, J = 8.8 Hz, 3H), 7.98 (dd, J = 8.2 Hz, 1.4 Hz, 3H), 7.97 (d, J = 8.5 Hz, 3H), 7.84 (d, J = 8.4 Hz, 3H), 7.54 (dt, J = 8.2 Hz, 0.7 Hz, 3H), 7.46 (d, J = 8.8 Hz, 3H), 7.26 (dt, J = 8.2 Hz, 1.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.6(s), 132.1(s), 131.79(s), 131.77(s), 129.6(d), 129.4(d), 128.1(d), 127.8(d), 127.2(s), 127.1(s), 126.2(d), 125.9(d), 125.5(d), 124.4(d); HRMS (APCI) m/z calcd for $C_{42}H_{25}^+$ 529.1951 $[M + H]^+$; found 529.1937.

Triple [5]Helicene (Benzo[*c*]naphtho[2,1-*l*]phenanthro[3,4-*g*]chrysene, 1) Oxidative Photocyclization. To a solution of compound **6** (99.7 mg, 0.186 mmol) in toluene (500 mL) was added a 37 mM solution of iodine in toluene (0.5 mL, 0.019 mmol), and the resulting mixture was irradiated with UV light for 2 h. The reaction mixture was evaporated under reduced pressure, and the residue was purified by column chromatography over silica gel eluting with a mixture of hexane and dichloromethane (5:1 to 4:1 v/v). The material was further purified by preparative HPLC to afford **1** as a yellow solid (61.6 mg, 0.117 mmol, 63%). Preparative HPLC separation afforded two fractions. The major fraction only contained the *PPP* and *MMM* isomers (51.5 mg), whereas the minor isomer contained approximately 80% of the *PPM* and *PMM* isomers and 20% of the *PPP* and *MMM* isomers (total 10.1 mg). These results indicated that the compound **1** material obtained after HPLC separation was 87% *PPP* (or *MMM*) isomer and 13% *PPM* (or *PMM*) isomer.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00486.

X-ray data for compound **1** (CIF)

^1H NMR spectra of all compounds and ^{13}C NMR of a new compound, chiral separation and kinetic study, fluorescence lifetime measurements, computational study, and method for crystal structure determination of compound **1** (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: soichiro@biomol.sci.toho-u.ac.jp.

ORCID

Soichiro Watanabe: 0000-0002-1227-3079

Notes

The authors declare no competing financial interest.

DOI: 10.1021/acs.joc.7b00486
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■ ACKNOWLEDGMENTS

The authors are grateful to Japan Analytical Industry and DAICEL Corporation for HPLC analysis of compound **1**. The authors thank Associate Professor Haruko Hosoi (Toho University) for the fluorescence lifetime measurements. This work was supported by MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2012-2016 (Grant S1201034). This work was also supported by Faculty of Science Grant-in-Aid for Scientific Research from Toho University (2015).

■ DEDICATION

This work is dedicated to Prof. Renji Okazaki on the occasion of his 80th birthday.

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DOI: 10.1021/acs.joc.7b00486
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