One-Pot Preparation of (*NH*)-Phenanthridinones and Amide-Functionalized [7]Helicene-like Molecules from Biaryl Dicarboxylic Acids

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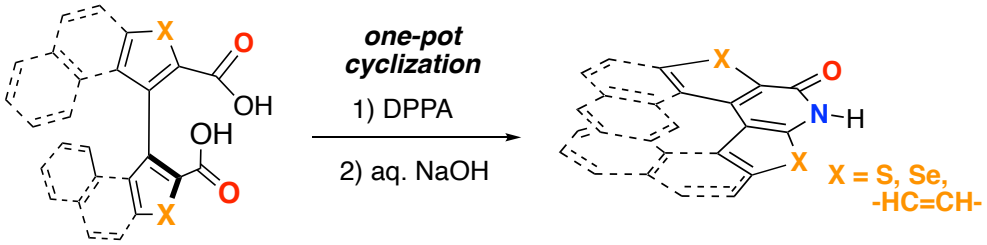
Supporting Information Placeholder



ABSTRACT: A one-pot transformation of biaryl dicarboxylic acids to (*NH*)-phenanthridinone derivatives based on a Curtius rearrangement and subsequent basic hydrolysis was developed. This method is also applicable for the preparation of optically active amide-functionalized [7]helicene-like molecules. Furthermore, aza[5]helicene derivatives with a phosphate moiety were isolated as a product of the Curtius rearrangement step in the case of substrates that bear chalcogen atoms. The stereostructures of these products, revealed by X-ray diffraction analysis, suggested that chalcogen-bonding and pnictogen-bonding interactions might contribute to their stabilization. The configurational stability of the helicene-like molecules and their chiroptical properties were further investigated.

INTRODUCTION

Phenanthridinones have attracted attention as a core molecular motif in bioactive natural products and as lead compounds for pharmaceutical development, because these derivatives exhibit varied biological activity (e.g., poly(ADP-ribose)polymerase-3)[1] as well as anti-viral activity.[2] Therefore, intensive synthetic efforts have been devoted to the synthesis of phenanthridinone derivatives. Although a number of synthetic strategies have afforded *N*-substituted phenanthridinones,[3] the development of synthetic methods that directly furnish (*NH*)-phenanthridinones (phenanthridinones without substitution at the amide group), which avoids additional operations to remove the *N*-substituent, would still be desirable.[4]

We have already reported the synthesis of phenanthridinones via the palladium-catalyzed coupling of 2-bromobenzamide derivatives (**1**) in the presence of phosphine ligand **2** (Scheme 1A).[5] This method was further extended for the construction of phenanthridinone derivative **5**, which bears an extended π-system, under phosphine-free coupling conditions.[6] Although these reactions are efficient, only *N*-protected phenanthridinone derivatives can be prepared.

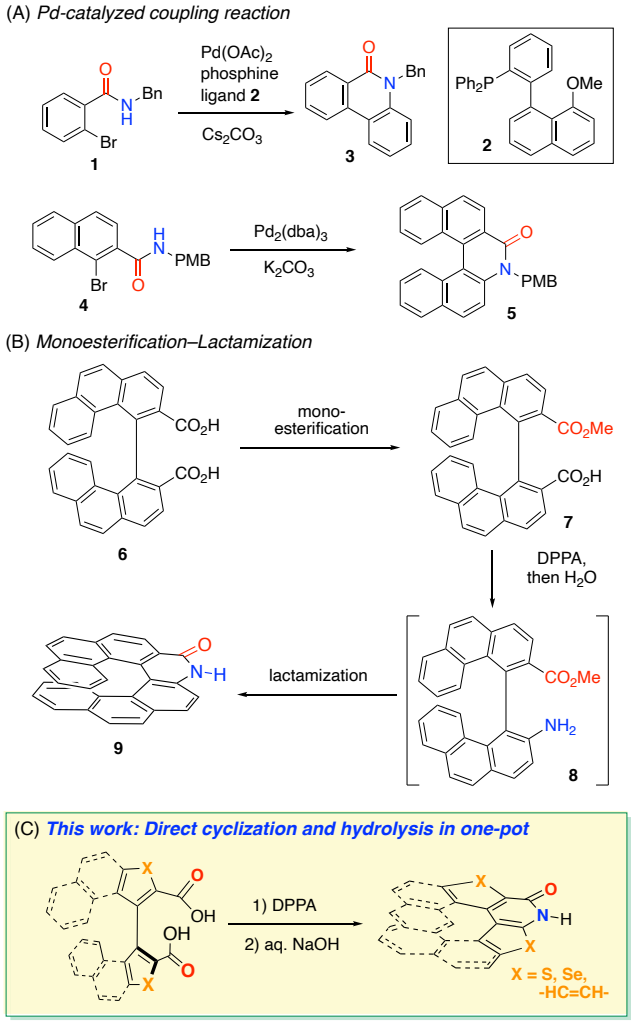
On the other hand, inspired by the [5]helicene-like structure of **5**, amide-functionalized [7]helicene-like molecule **9** was prepared via lactamization of *in-situ*-generated biphenanthrene δ-amino acid derivative **8** in racemic form (Scheme 1B).[7] This synthetic method is characterized by simple cyclization conditions without photo-cyclization of styrene-type substrates or transition-metal-catalyzed reactions, both of which are frequently employed as cyclization strategies to obtain helicenes and helicene-related derivatives. Although this lactamization to helicene-like molecules is convenient, the selective monoesterification of biphenanthryl dicarboxylic acid **6** to **7** is required to distinguish the carboxy groups prior to the key lactamization of **8**. A selective monoesterification procedure for biaryl dicarboxylic acids was developed by our group;[8] however, these conditions are not always be applicable, and are especially unsuitable for substrate **13** (Scheme 3), which bears sulfur atoms in the fused cyclic system.[9,10]

Functionalized helicenes and helicene-like molecules that contain sulfur and other heteroatoms in their conjugated π-

systems have received attention as unique chiral elements[11] for organic materials,[12] catalysts,[13] and bioactive compounds.[14] Therefore, a versatile synthetic method with high functional-group tolerance that provides access to optically active helicene and helicene-like molecules would be very attractive.

Herein, we describe the direct lactamization of biaryl dicarboxylic acids to (*NH*)-phenanthridinones and amide-functionalized [7]helicene-like molecules using a Curtius rearrangement followed by a basic hydrolysis, which does not require a monoesterification (Scheme 1C).[15] Moreover, the structural and spectral properties as well as the configurational stability of the amide-functionalized helicene-like molecules and their corresponding azahelicene phosphate derivatives are described.

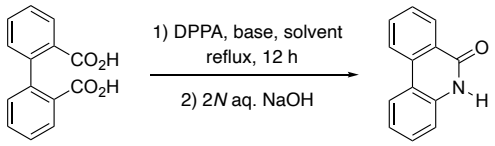
Scheme 1. Previous Work on Amide-functionalized Helicenes and our One-pot Strategy.



RESULTS AND DISCUSSION

Synthesis of phenanthridinone derivatives and amide-functionalized helicene-like molecules in a one-pot process. First, we applied the Curtius rearrangement conditions to diphenic acid (**10a**) (Table 1). After treatment of **10a** with diphenylphosphoryl azide (DPPA, 1.0 equiv.) and *N*,*N*-diisopropylethylamine (DIPEA, 2.0 equiv.) in toluene, all volatiles were removed from the mixture and the residue was treated with 2*N* aq. NaOH, which furnished lactamized phenanthridinone **11a** in 17% yield (Table 1, entry 1). To increase the yield, the reaction conditions were optimized.

Table 1. Optimization of the reaction conditions.



10a **11a**

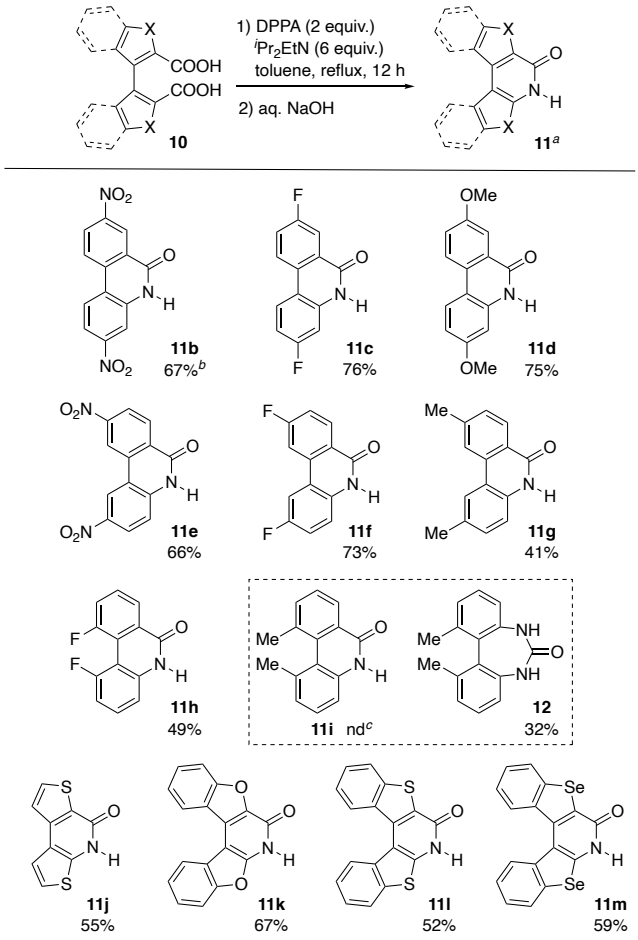
entry	DPPA (eq.)	base (eq.)	solvent	**11a** (%)[a]
1	1.0	$^{i}Pr_2EtN$ (2.0)	toluene	17
2	2.0	$^{i}Pr_2EtN$ (2.0)	toluene	72
3	3.0	$^{i}Pr_2EtN$ (2.0)	toluene	38
4	4.0	$^{i}Pr_2EtN$ (2.0)	toluene	26
5	2.0	$^{i}Pr_2EtN$ (4.0)	toluene	73
6	2.0	$^{i}Pr_2EtN$ (6.0)	toluene	80
7	2.0	Et_3N (6.0)	toluene	33
8	2.0	DBU (6.0)	toluene	50
9	2.0	$^{i}Pr_2EtN$ (6.0)	THF	27
10[b]	2.0	$^{i}Pr_2EtN$ (6.0)	toluene	79

[a]Isolated yield. [b]**10a** (2.0 g, 8.3 mmol) was used.

The results of the optimization showed that the amount of DPPA is important for this cyclization. When the amount of DPPA was increased to 2.0 equivalents, the yield increased dramatically to 72% (entry 2). However, further increasing the amount of DPPA to 3.0 or 4.0 equivalents decreased the yield to 38% and 26%, respectively (entries 3 and 4). After further surveying the effect of the number of equivalents of DIPEA, the optimal reaction conditions were established (2.0 equiv. of DPPA, 6.0 equiv. of DIPEA) to furnish **11a** in 80% yield (Entry 6). Changing the base to Et_3N or 1,8-diazabicyclo[5.4.0]undec-7ene (DBU), or the solvent to THF, did not improve the results (Entries 7–9). This reaction can also be successfully performed on the gram scale under the optimized conditions (entry 10).

With the optimized conditions in hand, biaryl substrates bearing a variety of substituents and heteroaromatic rings were tested (Scheme 2). In the case of substrates substituted at the 4,4′ and 5,5’ positions with nitro, fluorine, or methoxy substituents, the corresponding products (**11b**–**11f**) were obtained in good yield, albeit that methyl substituted **10g** provided only 41% yield. One case in which the expected product was not obtained was the reaction of **10i**, which bears methyl groups at the *ortho*-positions of the biaryl axis; here, the unexpected cyclic urea **12** was obtained instead of **11i**, although the reaction of **10h**, which contains fluorine atoms at the same positions, furnished **11h**. This could potentially be interpreted in terms of the steric repulsion between the methyl groups in the bay region during the cyclization toward **11i**. Substrates bearing heteroaromatic rings containing O, S, and Se were also tested and furnished the corresponding products (**11j**-**m**) in moderate to good yield.

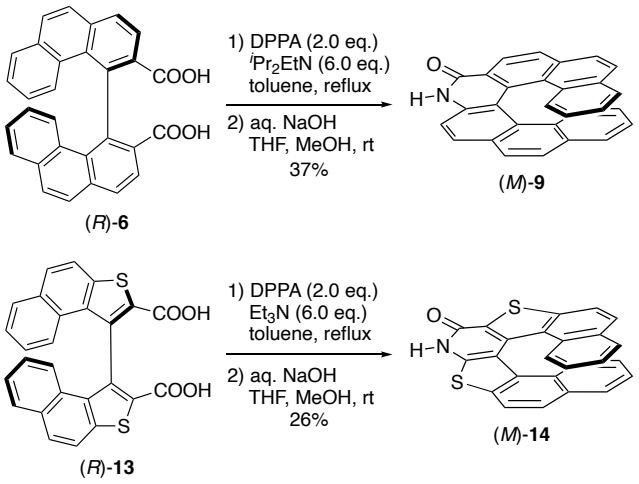
Scheme 2. Preparation of substituted phenanthridinone derivatives.



[a]Isolated yield. [b]Without hydrolysis. [c]nd: Not detected.

Although the result of the cyclization of **10i** suggested that this reaction is relatively sensitive to steric congestion, we moved on to examine the preparation of amide-functionalized helicenes, which exhibit a sufficiently high racemization barrier at ambient temperature (Scheme 3). Under the optimal conditions (Table 1, Entry 6), dicarboxylic acid (*R*)-**6** furnished the expected amide-functionalized [7]helicene (*M*)-**9** in optically pure form, albeit that the yield was not satisfactory. In the case of sulfur-containing (*R*)-**13**,[9] the chemical yield was slightly improved by employing Et_3N instead of DIPEA to give (*M*)-**14** in 26% yield (Scheme 3). During the cyclization, a decrease in the optical purity of the starting dicarboxylic acid (*R*)-**13** (>99% ee) was not observed, and (*M*)-**14** was obtained in >99% ee. As the optically active starting materials (*R*)-**6** and (*R*)-**13** can be readily prepared, this cyclization is promising for the preparation of optically active helicene-like molecules.

Scheme 3. Synthesis of optically active amide-functionalized helicenes.



During our investigation into the reactions of the substrates **10j**–**10m** and **13**, which bear chalcogen atoms, we isolated diphenyl *O*-phosphorus esters **15j**–**15m** and **16**, which containing a partial structure of DPPA in the initial DPPA treatment step prior to the addition of aqueous NaOH (Figure 1A). Compound **16** was readily hydrolyzed to furnish **14** through treatment with aqueous NaOH. This result suggests that these *O*-phosphorus esters are generated as an initial product under the Curtius reaction conditions prior to treatment with aqueous NaOH, albeit that the corresponding *O*-phosphorus esters were not detected in the reactions of dicarboxylic acids **10a**–**10h**, which do not contain chalcogen atoms.

The single-crystal X-ray diffraction analysis of **15l** and **15m** suggested that only chalcogen-atom-containing substrates furnish *O*-phosphorus esters as isolable compounds (Figures 1B and 1C). In **15l**, contacts were observed between sulfur and the carbonyl oxygen atoms (3.003(2) Å), as well as between phosphorus and the nitrogen atom of the amide substituent (2.928(3) Å), that are shorter than the sum of the van der Waals radii of S–O (3.32 Å) and P–N (3.35 Å). These short contacts were also found in **15m**, with a P–N distance of 2.968(2) Å and a Se–O distance of 3.102(2) Å, which are shorter than the sum of the van der Waals radii of Se–O (3.42 Å). These close contacts and the planar conformation of the N–C, C–O, and O–P bonds (ϕN,C–O,P = –7.3(4)° for **15l** and 5.4(3)° for **15m**) suggested chalcogen- and pnictogen-bonding interactions between the S–O, Se–O, and N–P atoms.[16,17] These additional non-covalent interactions could stabilize these phosphorus esters and thus render them isolable intermediates. Furthermore, these aza[5]helicene structures show helical chirality based on the twisted π-systems (ϕa,b–c,d: –15.9 ° for **15l** and ϕa,b–c,d: –16.4 ° for **15m**).

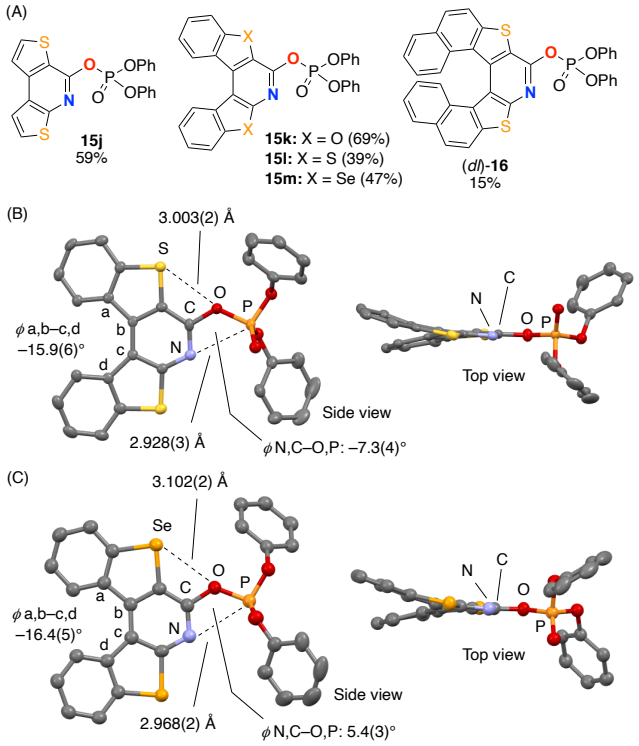
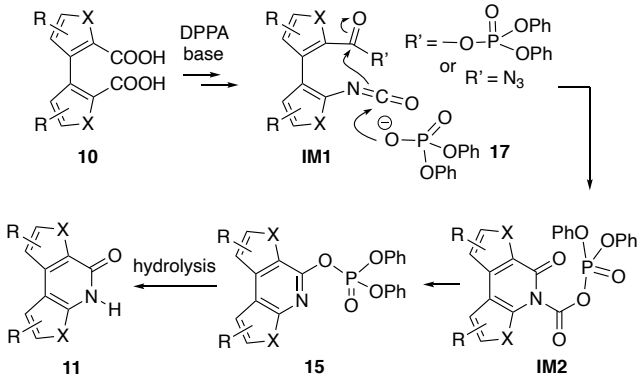


Figure 1. (A) Solid-state structures of the phosphorus esters of aza[5]helicene derivatives. (B) Crystal structure of **15l**. (C) Crystal structure of **15m**; all thermal ellipsoids at 50% probability.

Considering the generation of the phosphorus esters and the requirement for 2 equivalents of DPPA to obtain a reasonable yield of **11a** (Table 1, Entry 2), we would like to propose the reaction mechanism for the cyclization reaction shown in Scheme 4. After one of the carboxy groups of biaryl dicarboxylic acid **10** is converted into the isocyanate group in **IM1** via the Curtius rearrangement, this group might accept the phosphate anion **17** to give **IM2** through cyclization with the activated carbonyl group. The *N*→*O* rearrangement of the phosphate group of **IM2** would thus give **15**. Successive treatment with NaOH would then furnish phenanthridinone derivative **11**.

Scheme 4. Outline of the cyclization process.



Configurational stability and spectral properties of the amide-functionalized helicene-like molecules. We envisioned that amide-functionalized helicene-like molecules **9** and **14** could potentially serve as chiral functionalized molecules, provided that their racemization barriers are sufficiently high to ensure configurational stability. We have already confirmed via DFT calculations that **9** can be expected to exhibit a sufficiently high racemization barrier ($\Delta G^{\ddagger}$ = 41.4 kcal/mol) to be configurationally stable at ambient temperature.[7] In the present study, the racemization barrier of sulfur-functionalized **14** was determined to be 34.3 kcal/mol at 132 °C based on monitoring the decrease in enantiomeric excess in chlorobenzene under reflux conditions. These results suggested that **14** also exhibits sufficient configurational stability to serve as a chiral molecule, albeit that its racemization barrier is lower than that of **9**.

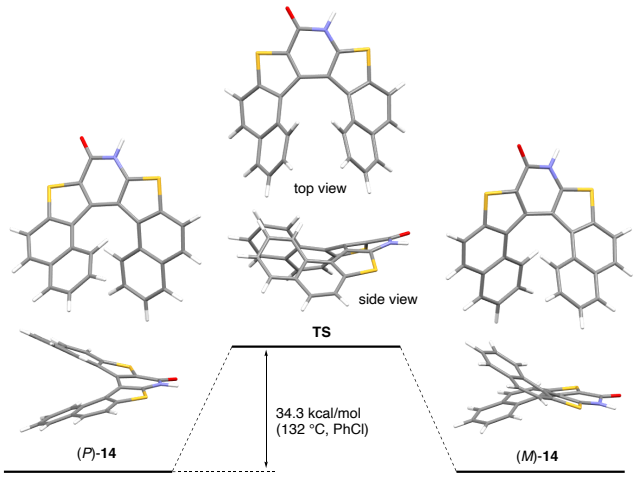


Figure 2. Racemization barrier and DFT-optimized ground-state and transition-state structures of **14** in the racemization process, calculated at the ωB97xd/6-311+G(d,p)//B3LYP/6-31G(d,p) level of theory..

The racemization process of **14** in chlorobenzene was also investigated using DFT calculations at the ωB97xd/6-311+G(d,p)//B3LYP/6-31G(d,p) level of theory.[18] The results of the calculations suggested that the racemization proceeds via a C_s-symmetric transition state (Figure 2).[19] Furthermore, we used DFT calculations to deduce the racemization barrier of sulfur-containing [5]helicene-like **11l** (3.4 kcal/mol), which is too low for **11l** to be configurationally stable at room temperature. In this case, the results of the calculations indicated that the racemization proceeds via a planar transition state (Figure 3). Interestingly, Se-containing [5]helicene-like **11m** showed a higher racemization barrier ($\Delta G^{\ddagger}$ = 7.2 kcal/mol) than **11l**.[20]

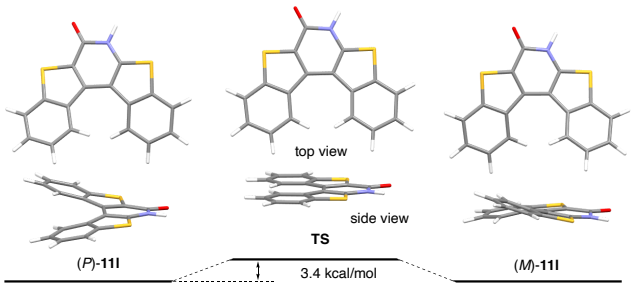


Figure 3. Racemization barrier and DFT-optimized ground-state and transition-state structures of **11l** during the racemization, calculated at the ωB97xd/6-311+G(d,p)//B3LYP/6-31G(d,p) level of theory.

The lower racemization barrier of **14** compared to that of **9** indicated that the replacement of the two benzene rings by two thiophene rings greatly decreases the helical stability. Sulfur-containing **14** showed a lower racemization barrier because the terminal rings of **14** are further apart from each other and the overlap area is smaller than that of **9** due to the introduction of thiophene rings instead of benzene rings (Figure 4).[11c] Thus, the steric interactions between the two terminal rings in **14** can be expected to be weaker than those in **9** during racemization.

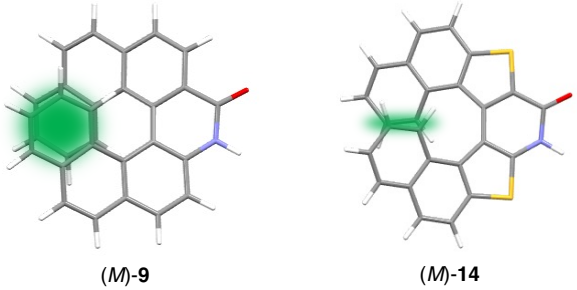


Figure 4. Comparison of the overlap area (green) in (*M*)-**9** and (*M*)-**14**.

The optical rotation of (*M*)-**9** and (*M*)-**14** in DMSO are relatively high ($[\alpha]_D^{18}$ = +1954.5 for (*M*)-**9** and $[\alpha]_D^{19}$ = –1869.4 for (*M*)-**14**), even though they are smaller than that of (*M*)-carbo[7]helicene ($[\alpha]_D^{25}$ = +5577).[21]

Finally, the CD spectra of **9** and **14** were measured in THF (Figure 5). The spectrum of (*M*)-**9** showed a positive Cotton effect from 290 nm to 400 nm, a negative Cotton effect from 240 nm to 290 nm, and a positive Cotton effect at wavelengths smaller than 240 nm (red line). The spectrum of (*P*)-**9** showed a CD spectrum (blue line) that was the exact mirror image of the spectrum of the (*M*)-isomer. The CD spectrum of (*M*)-**14** showed a negative Cotton effect from 320 nm to 360 nm, a large negative Cotton effect from 250 nm to 290 nm, and a large positive Cotton effect from 210 nm to 250 nm (orange line). The spectrum of (*P*)-**16** showed opposite Cotton effects (green line). These CD spectra thus clearly show that the enantiomers of **9** and **14** were prepared using the developed one-pot processes (Scheme 3).

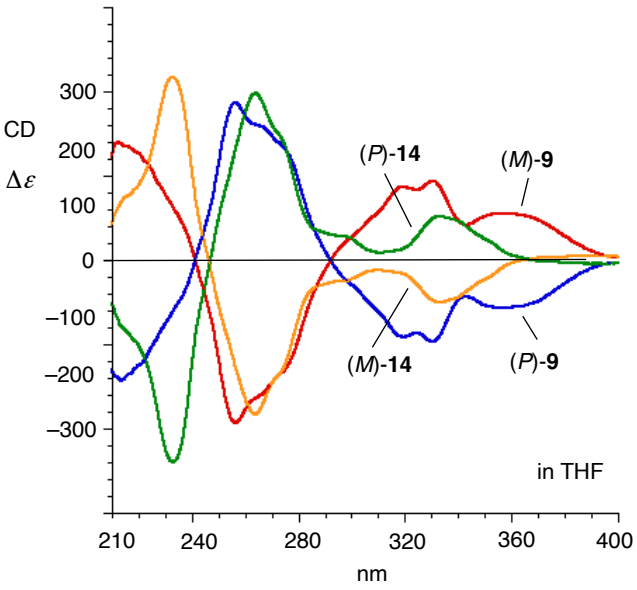


Figure 5. CD spectra of the enantiomers of **9** and **14** in THF.

CONCLUSION

In this study, a one-pot cyclization process was developed that provides (*NH*)-phenanthridinone derivatives from biaryl dicarboxylic acids. This method was also extended to the preparation of optically active amide-functionalized [7]helicene-like molecules. In the case of chalcogen-containing substrates, the phosphorus esters of the aza[5]helicene derivatives were isolated during the Curtius rearrangement step. The racemization barriers of the amide-functionalized [7]helicene-like molecules revealed that these molecules are configurationally stable at ambient temperature.

Further investigations into the reaction mechanism of this one-pot process and applications of these conditions to unsymmetrically substituted biaryl dicarboxylic acids are currently in progress in our laboratory.

EXPERIMENTAL

General Information. Uncorrected melting points were measured using a Yanagimoto micro melting point apparatus or a Büchi Melting Point M-565. NMR spectra were obtained with a JEOL ECX-400 PKT, a JEOL ECA-600, a Bruker UltraShield 300, or a Bruker Ascend 500 spectrometer. Chemical shifts are given in units of ppm (^{1}H NMR in $CDCl_3$: tetramethylsilane as the internal standard at 0 ppm; ^{13}C NMR in $CDCl_3$: $CDCl_3$ as the internal standard at 77.16 ppm; ^{31}P NMR in $CDCl_3$: H_3PO_4 as the internal standard at 0 ppm; ^{1}H NMR in acetone-d_6: acetone as the internal standard at 2.05 ppm; ^{13}C NMR in acetone-d_6: acetone as an internal standard at 29.84 ppm and 206.26 ppm; ^{1}H NMR in methanol-d_4: methanol as the internal standard at 3.31 ppm; ^{13}C NMR in methanol-d_4: methanol-d_4 as the internal standard at 49.00 ppm; ^{1}H NMR in DMSO-d_6: DMSO as the internal standard at 2.50 ppm; ^{13}C NMR in DMSO-d_6: DMSO as the internal standard at 39.52 ppm). Spin–spin coupling constants are given in units of Hz. IR spectra were recorded on a JASCO FT-IR 4200 or a JASCO FT-IR 4600 spectrometer.

Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JEOL GCmate II (for EI), a JEOL MStation JMS-700 spectrometer (for FAB), on a Bruker Daltonics Impact HD-KC or a Shimadzu LCMS-IT-TOF (for ESI). The specific rotation was measured with a JASCO P-2200 polarimeter. UV/Vis spectra were recorded with a JASCO V-550 UV/Vis spectrophotometer. CD spectra were recorded with a JASCO J-720W spectropolarimeter.

Column chromatography on silica gel was carried out using silica gel 60 N (spherical, neutral, 63–210 μm, Kanto Chemical Co., Inc.). TLC analyses and preparative TLC (PTLC) analyses were performed on commercial glass plates bearing a 0.25 mm layer or 0.5 mm layer of Merck Kiesel-gel 60 F_{254}, respectively. Analytical HPLC was carried out with a JASCO PU-2089 Plus instrument equipped with a Daicel CHIRALPAK IC (4.6 mm × 250 mm), CHIRALPAK OD-H (4.6 mm × 250 mm), or CHIRALPAK AD-H (4.6 mm × 250 mm) and a JASCO UV-2075 Plus UV/Vis detector (detection: 254 nm). Preparative HPLC was run with a JASCO PU-2086 Plus instrument equipped with a COSMOSIL 5SL-II (20 mm × 250 mm) and a JASCO UV-2075 Plus UV/Vis detector (detection: 254 nm).

All chemical reagents were obtained from common commercial sources and used as received.

Optimized Conditions for the Synthesis of Phenanthridinone 11a (Table 1, entry 6). To a solution of diphenic acid **10a** (242 mg, 1.0 mmol, 1.0 equiv.) in toluene (10 mL), DPPA (430 μL, 2.0 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.0 mmol, 6.0 equiv.) were added at rt. After refluxing for 12 h under an Ar atmosphere, the reaction mixture was concentrated *in vacuo*; the thus obtained residue was dissolved in THF/MeOH/2*N* aq. NaOH (1:1:1, 60 mL) and stirred at rt for 12 h. The reaction mixture was extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Finally the obtained residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 3:2) to afford phenanthridinone **11a** (156 mg, 80%).

Gram-scale Synthesis of 11a (Table 1, entry 10). To a solution of diphenic acid **10a** (2.00 g, 8.26 mmol, 1.0 equiv.) in toluene (60 mL), DPPA (3.55 mL, 16.5 mmol, 2.0 equiv.) and DIPEA (8.63 mL, 49.5 mmol, 6.0 equiv.) were added at rt. After refluxing for 12 h under an Ar atmosphere, the reaction mixture was concentrated *in vacuo*; the thus obtained residue was dissolved in THF/MeOH/2*N* aq. NaOH (1:1:1, 120 mL) and stirred at rt for 12 h. The reaction mixture was extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was washed with $CHCl_3$/*n*-hexane (1:1), and further purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 1:1) to afford phenanthridinone **11a** (1.28 g, 79%).

*Phenanthridin-6(5H)-one (**11a**).* ^{1}H and ^{13}C NMR spectra of the obtained **11a** were identical to the literature data.[22]

Substrate Scope for the One-pot Cyclization. *3,8-Dinitrophenanthridin-6(5H)-one (**11b**).*[1] To a solution of 4,4'-dinitro-[1,1'-biphenyl]-2,2'-dicarboxylic acid (**10b**)[23] (332 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 μL, 2.00 mol, 2.0 equiv.) and DIPEA (1.05 mL, 6.00 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*.* The resulting residue was washed with $CHCl_3$/MeOH (19:1) to obtain **11b** (190 mg, 67%). *The corresponding *O*-phosphorus ester was not detected in the ^{1}H NMR spectrum of the residue. Yellow solid; M.p. > 300 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.28 (brs, 1H), 8.89 (d, J = 2.4 Hz, 1H), 8.76 (d, J = 9.0 Hz, 1H), 8.70–8.52 (m, 2H), 8.11 (d, J = 2.1 Hz, 1H), 8.01 (dd, J = 8.8, 2.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.5, 148.4, 147.5, 137.9, 137.6, 127.2, 126.9, 126.4, 126.2, 122.7, 121.3, 116.7, 111.4; IR (neat) 3371, 3084, 2960, 2877, 1679, 1615, 1519, 1348, 846, 735, 452 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{13}H_8N_3O_5$ $(M+H)^+$ 286.0458, found 286.0456.

*3,8-Difluorophenanthridin-6(5H)-one (**11c**).* To a solution of 4,4'-difluoro-[1,1'-biphenyl]-2,2'-dicarboxylic acid (**10c**) (278 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 μL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.0 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. The resulting residue was dissolved in THF/MeOH/2*N* aq. NaOH (1:1:1, 60 mL) and stirred at rt for 12 h. The reaction mixture was extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was washed with $CHCl_3$ to furnish **11c** (175 mg, 76%). Colorless amorphous solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.90 (brs, 1H), 8.52 (dd, J = 9.0, 5.1 Hz, 1H), 8.46–8.34 (m, 1H), 7.92 (dd, J = 9.3, 2.9 Hz, 1H), 7.72 (td, J = 8.7, 2.9 Hz, 1H), 7.16–7.04 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.3 (d, J = 244 Hz), 161.4 (d, J = 245 Hz), 160.1 (d, J = 3.8 Hz), 137.6 (d, J = 11 Hz), 130.6 (d, J = 2.5 Hz), 126.9 (d, J = 7.5 Hz), 125.9 (d, J = 1.3 Hz), 125.8 (d, J = 3.8 Hz), 121.2 (d, J = 24 Hz), 114.0 (d, J = 2.5 Hz), 112.5 (d, J = 21 Hz), 110.1 (d, J = 23 Hz), 102.1 (d, J = 25 Hz); IR (neat) 2969, 2885, 1690, 1670, 1627, 1487, 1260, 1169, 870, 795, 524, 468 cm^{-1}; HRMS (EI) m/z calcd. for $C_{13}H_7F_2NO$ $(M)^+$ 231.0496, found 231.0496.

*3,8-Dimethoxyphenanthridin-6(5H)-one (**11d**).* To a solution of 4,4'-dimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylic acid (**10d**)[24] (52.3 mg, 0.173 mmol, 1.0 equiv.) in toluene (8 mL), DPPA (76 μL, 0.346 mmol, 2.0 equiv.) and DIPEA (185 μL, 1.04 mmol, 6.0 equiv.) were added at rt. After refluxing for 12 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (2:1:1, 8 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 1:1) to afford **11d** (33 mg, 75%). Colorless amorphous solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.60 (br s, 1H), 8.32 (d, J = 8.9 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 2.9 Hz, 1H), 7.40 (dd, J = 8.9, 2.9 Hz, 1H), 6.90–6.79 (m, 2H), 3.89 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.9, 159.5, 158.2, 136.9, 128.1, 125.7, 124.1, 124.0, 121.8, 111.3, 110.1, 108.5, 99.5, 55.4, 55.3; IR (neat) 2835, 1658, 1612, 1485, 1365, 1265, 1196, 1169, 1045, 799, 777 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{13}NO_3$ $(M)^+$ 255.0895, found 255.0895.

*2,9-Dinitrophenanthridin-6(5H)-one (**11e**).* To a solution of 5,5′-dinitro-[1,1′-biphenyl]-2,2′-dicarboxylic acid (**10e**) (332 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 μL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.00 mL, 5.74 mmol, 5.75 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq.

NaOH (1:1:1, 60 mL) was stirred at rt for 5 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was washed with $CHCl_3$/*n*-hexane (1:1) to obtain **11e** (188 mg, 66%). Yellow solid; M.p. >300 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.43 (br s, 1H), 9.48–9.11 (m, 2H), 8.61–8.20 (m, 3H), 7.43 (d, J = 8.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.8, 150.6, 142.4, 141.8, 134.3, 134.2, 129.8, 125.6, 123.0, 120.6, 119.1, 117.3, 116.7; IR (neat) 3100, 2889, 2857, 1666, 1615, 1531, 1335, 1148, 846, 786, 559 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{13}H_8N_3O_5$ $(M+H)^+$ 286.0458, found 286.0458.

*2,9-Difluorophenanthridin-6(5H)-one (**11f**).* To a solution of 5,5'-difluoro-[1,1'-biphenyl]-2,2'-dicarboxylic acid (**10f**) (278 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 µL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.00 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (1:1:1, 60 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was washed with $CHCl_3$ to obtain **11f** (168 mg, 73%). Colorless amorphous solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.75 (br s, 1H), 8.41–8.29 (m, 2H), 8.25 (dd, J = 10.4, 2.5 Hz, 1H), 7.49 (dt, J = 8.6, 2.4 Hz, 1H), 7.44–7.30 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.0 (d, J = 249 Hz), 159.9, 157.7 (d, J = 236 Hz), 136.4 (dd, J = 10, 2.5 Hz), 133.6 (d, J = 1.3 Hz), 130.9 (d, J = 10 Hz), 122.7 (d, J = 1.3 Hz), 118.2 (dd, J = 8.1, 2.5 Hz), 118.0 (d, J = 18 Hz), 117.8 (d, J = 2.5 Hz), 116.6 (d, J = 24 Hz), 109.7 (d, J = 24 Hz), 109.3 (d, J = 24 Hz); IR (neat) 3428, 3175, 3143, 3040, 2997, 2861, 1686, 1610, 1507, 1443, 1367, 1208, 866, 818, 671, 587 cm^{-1}; HRMS (EI) m/z calcd. for $C_{13}H_7F_2NO$ $(M)^+$ 231.0496, found 231.0497.

*2,9-Dimethylphenanthridin-6(5H)-one (**11g**).* To a solution of 5,5'-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylic acid (**10g**) (270 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 µL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.00 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (1:1:1, 60 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 7:3 to 1:1), and washed with $CHCl_3$/*n*-hexane (1:2) to obtain **11g** (93 mg, 41%). Colorless solid; M.p. 269–270 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.50 (br s, 1H), 8.30 (s, 1H), 8.23–8.13 (m, 2H), 7.49–7.38 (m, 1H), 7.34–7.19 (m, 2H), 2.52 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.7, 142.9, 134.6, 134.2, 131.1, 130.5, 129.0, 127.5, 123.5, 123.0, 122.5, 117.4, 116.0, 21.5, 20.7; IR (neat) 2856, 1658, 1613, 1364, 827, 778, 687, 659, 624, 530, 445 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{13}NO$ $(M)^+$ 223.0997, found 223.0998.

*1,10-Difluorophenanthridin-6(5H)-one (**11h**).* To a solution of 6,6'-difluoro-[1,1'-biphenyl]-2,2'-dicarboxylic acid (**10h**) (278 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 µL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.00 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (1 : 1 : 1, 60 mL) was stirred at rt. for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 7:3 to AcOEt only), and washed with $CHCl_3$/*n*-hexane (1:1) to obtain **11h** (113 mg, 49%). Colorless solid; M.p. >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.96 (br s, 1H), 8.26–8.15 (m, 1H), 7.78–7.68 (m, 2H), 7.59–7.51 (m, 1H), 7.23 (dd, J = 8.2, 1.2 Hz, 1H), 7.14–7.05 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.6 (d, J = 1.4 Hz), 160.3–156.6 (m, 2*C*) 138.6 (dd, J = 4.8, 2.3 Hz), 131.1 (dd, J = 7.6, 4.1 Hz), 129.8 (dd, J = 6.6, 3.8 Hz), 128.7, 123.6, 120.6 (dd, J = 17.7, 7.8 Hz), 118.9 (dd, J = 10.1, 2.0 Hz), 111.9, 109.7 (dd, J = 16.3, 8.9 Hz), 103.2 (dd, J = 10.7, 4.3 Hz); IR (neat) 3044, 3008, 2873, 1683, 1618, 1559, 1380, 1268, 791, 731, 516, 492 cm^{-1}; HRMS (APCI) m/z calcd. for $C_{13}H_8F_2NO$ $(M+H)^+$ 232.0568, found 232.0570.

*1,11-Dimethyl-5,7-dihydro-6H-dibenzo[d,f][1,3]diazepin-6-one (**12**).* To a solution of 6,6'-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylic acid (**10i**) (270 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 µL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.00 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the residue in THF/MeOH/2*N* aq. NaOH (1:1:1, 60 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 7:3 to AcOEt only), and washed with $CHCl_3$/*n*-hexane (1:1) to obtain the urea **12** (76 mg, 32%). For substrate **10i**, the corresponding (*NH*)-phenanthridinone **11i** was not detected. Colorless amorphous solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.58 (br s, 2H), 7.19 (t, J = 7.7 Hz, 2H), 7.06–7.00 (m, 2H), 6.96 (dd, J = 8.0, 1.3 Hz, 2H), 2.07 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5, 142.5, 137.0, 128.2, 127.5, 125.4, 118.3, 19.5; IR (neat) 3240, 3143, 3025, 2925, 1929, 1690, 1567, 1427, 1380, 874, 798, 687 cm^{-1}; HRMS (APCI) m/z calcd. for $C_{15}H_{15}N_2O$ $(M+H)^+$ 239.1179, found 239.1181.

*Dithieno[2,3-b:3',2'-d]pyridin-5(4H)-one (**11j**).* To a solution of [3,3'-bithiophene]-2,2'-dicarboxylic acid (**10j**) (254 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 µL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.00 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (1:1:1, 60 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 3:2 to 1:1), and washed with $CHCl_3$/*n*-hexane (1 : 9) to obtain **11j** (114 mg, 55%). Pale yellow amorphous solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.58 (br s, 1H), 8.15 (d, J = 5.2 Hz, 1H), 7.78 (d, J = 5.1 Hz, 1H), 7.56 (d, J = 5.6 Hz, 1H), 7.28 (d, J = 5.6 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.9, 142.3, 141.3, 134.7, 126.8, 123.4, 121.0, 117.41, 117.35; IR (neat) 2781,

1621, 1180, 1112, 883, 845, 714, 643, 580, 453 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_9H_5NOS_2$ $(M)^+$ 206.9813, found 206.9815.

*Bis(benzofuro)[2,3-b:3',2'-d]pyridin-7(6H)-one (**11k**).* To a solution of [3,3'-bibenzofuran]-2,2'-dicarboxylic acid (**10k**) (58 mg, 0.18 mmol, 1.0 equiv.) in toluene (5 mL), DPPA (77 µL, 0.36 mmol, 2.0 equiv.) and DIPEA (188 µL, 1.08 mmol, 6.0 equiv.) were added at rt. After refluxing for 12 h under an Ar atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (2:1:1, 16 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 1:1 and then $CHCl_3$) and then washed with $CHCl_3$/*n*-hexane (1:1) to obtain **11k** (33 mg, 67%). Colorless solid; M.p. >300 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.62 (d, J = 7.8 Hz, 1H), 8.45–8.37 (m, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.81–7.75 (m, 2H), 7.65–7.59 (m, 1H), 7.56–7.47 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 156.6, 152.9, 151.9, 130.02, 129.98, 124.10, 124.05, 123.8, 122.9, 122.3, 121.6, 121.5, 112.9, 111.7 (three carbon signals were overlapped); IR (neat) 3435, 3029, 2590, 1655, 1599, 1451, 1180, 1053, 750, 499 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{10}NO_3$ $(M+H)^+$ 276.0655, found 276.0654.

*Benzo[4,5]thieno[2,3-b]benzo[4,5]thieno[3,2-d]pyridin-7(6H)-one (**11l**).* To a solution of [3,3'-bibenzo[*b*]thiophene]-2,2'-dicarboxylic acid (**10l**)[25] (354 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 µL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.00 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (1:1:1, 60 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was washed with $CHCl_3$ to obtain **11l** (158 mg, 52%). Pale yellow solid; M.p. >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.21 (br s, 1H), 8.91–8.78 (m, 1H), 8.58 (d, J = 8.2 Hz, 1H), 8.30–8.19 (m, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.75–7.62 (m, 2H), 7.57 (t, J = 7.7 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.1, 141.5, 137.2, 134.5, 133.3, 133.2, 128.0, 126.3, 125.2, 125.0, 124.3, 124.2, 123.5, 123.0 (three carbon signals overlapped); IR (neat) 2657, 1635, 1453, 1120, 903, 748, 718, 615, 575, 410 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{17}H_9NOS_2$ $(M)^+$ 307.0126, found 307.0125.

*Benzo[4,5]selenopheno[2,3-b]benzo[4,5]selenopheno[3,2-d]pyridin-7(6H)-one (**11m**).* To a solution of [3,3′-bibenzo[b]selenophene]-2,2′-dicarboxylic acid (**10m**) (448 mg, 1.00 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (430 µL, 2.00 mmol, 2.0 equiv.) and DIPEA (1.05 mL, 6.00 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (1:1:1, 30 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 7:3 to 3:2), and washed with $CHCl_3$ to obtain **11m** (237 mg, 59%). Yellow solid; M.p. >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.90 (br s, 1H), 8.71–8.64 (m, 1H), 8.36 (d, J = 8.2 Hz, 1H), 8.33–8.29 (m, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.61–7.54 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.2, 142.6, 140.9, 137.2, 135.5, 135.0, 127.9, 127.8, 127.5, 126.7, 124.8, 124.6, 124.3 (four carbon signals were overlapped); IR (neat) 3431, 2833, 1651, 1523, 1443, 1113, 750, 711, 603, 535, 428 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{17}H_9NOSe_2$ $(M)^+$ 402.9014, found 402.9019.

Preparation of *O*-Phosphate Derivatives. *Dithieno[2,3-b:3',2'-d]pyridin-5-yl diphenyl phosphate (**15j**).* To a solution of [3,3′-bithiophene]-2,2′-dicarboxylic acid (**10j**) (300 mg, 1.18 mmol, 1.0 equiv.) in toluene (25 mL), DPPA (507 µL, 2.36 mmol, 2.0 equiv.) and DIPEA (1.23 mL, 7.08 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was quenched with 2*N* aq. HCl and extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 3:2) to afford **15j** (306 mg, 59%). Pale yellow solid; M.p. 138–139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 5.3 Hz, 1H), 7.65 (dd, J = 5.3, 0.5 Hz, 1H), 7.55 (d, J = 5.9 Hz, 1H), 7.51 (d, J = 5.9 Hz, 1H), 7.46–7.34 (m, 8H), 7.28–7.20 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (d, J = 0.8 Hz), 150.9 (d, J = 7.5 Hz), 149.2 (d, J = 6.8 Hz), 143.8 (d, J = 0.8 Hz), 133.2, 129.9 (d, J = 0.8 Hz), 126.3, 125.81 (d, J = 1.5 Hz), 125.76, 122.1, 121.8 (d, J = 9.8 Hz), 120.7 (d, J = 5.3 Hz), 119.4; ^{31}P NMR (200 MHz, $CDCl_3$) δ –18.7; IR (neat) 1584, 1481, 1311, 1179, 1154, 1065, 942, 737, 687, 507 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{21}H_{14}NO_4PS_2$ $(M)^+$ 439.0102, found 439.0099.

*Bis(benzofuro)[2,3-b:3',2'-d]pyridin-7-yl diphenyl phosphate (**15k**).* To a solution of [3,3′-bibenzofuran]-2,2′-dicarboxylic acid (**10k**) (100 mg, 0.31 mmol, 1.0 equiv.) in toluene (20 mL), DPPA (133 µL, 0.62 mmol, 2.0 equiv.) and DIPEA (324 µL, 1.86 mmol, 6.0 equiv.) were added at rt. After refluxing for 15 h under a N_2 atmosphere, the reaction mixture was quenched with 2*N* aq. HCl and extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 4:1 to 3:1) to afford **15k** (109 mg, 69%). Pale yellow solid; M.p. 163–164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (dt, J = 7.9, 1.0 Hz, 1H), 8.24 (dd, J = 7.7, 1.3 Hz, 1H), 7.73–7.60 (m, 3H), 7.60–7.34 (m, 11H), 7.30–7.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 155.4 (d, J = 0.8 Hz), 155.1, 150.8 (d, J = 7.5 Hz), 139.3 (d, J = 6.8 Hz), 138.2 (d, J = 7.5 Hz), 130.7, 130.3, 130.0 (d, J = 0.8 Hz), 127.9, 125.9 (d, J = 1.5 Hz), 124.1 (d, J = 0.8 Hz), 123.8, 122.6, 122.3 (d, J = 2.3 Hz), 120.7 (d, J = 5.3 Hz), 113.1, 112.5, 108.6 (two carbon signals overlapped); ^{31}P NMR (200 MHz, $CDCl_3$) δ –18.3; IR (neat) 1640, 1597, 1485, 1450, 1395, 1310, 1184, 1048, 939, 741, 519 cm^{-1}; HRMS (EI) m/z calcd. for $C_{29}H_{18}NO_6P$ $(M)^+$ 507.0872, found 507.0873.

*Benzo[4,5]thieno[2,3-b]benzo[4,5]thieno[3,2-d]pyridin-7-yl diphenyl phosphate (**15l**).* To a solution of [3,3'-bibenzo[*b*]thiophene]-2,2'-dicarboxylic acid (**10l**)[25] (400 mg, 1.13 mmol, 1.0 equiv.) in toluene (40 mL), DPPA (485 µL, 2.26 mmol, 2.0 equiv.) and DIPEA (1.17 mL, 6.77 mmol, 6.0 equiv.) were added at rt. After refluxing for 16.5 h under a N_2 atmosphere, the reaction mixture was quenched with 2*N* aq. HCl and extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in*

vacuo. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 9:1 to 4:1) to afford **15l** (235 mg, 39%). **15l** was further purified by recrystallization from AcOEt. Colorless solid; M.p. 155–156 °C; The chemical shifts of the ^{1}H NMR signals depend on the concentration: ^{1}H NMR (500 MHz, $CDCl_3$, 0.005 M) δ 9.09 (d, J = 8.1 Hz, 1H), 8.91 (d, J = 7.8 Hz, 1H), 8.05–7.95 (m, 2H), 7.71–7.52 (m, 4H), 7.47–7.40 (m, 7H), 7.30–7.21 (m, 3H); ^{1}H NMR (500 MHz, $CDCl_3$, 0.1 M) δ 8.94 (d, J = 8.2 Hz, 1H), 8.80–8.75 (m, 1H), 7.95–7.85 (m, 2H), 7.60–7.55 (m, 1H), 7.54–7.38 (m, 11H), 7.29–7.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 0.1 M) δ 155.4, 150.8 (d, J = 7.5 Hz), 150.3 (d, J = 6.8 Hz), 141.7, 141.2, 138.0, 134.0, 132.5, 130.0 (d, J = 0.8 Hz), 129.0, 126.6, 126.2, 125.9 (d, J = 1.5 Hz), 124.9, 124.6, 124.4, 123.7, 123.4, 123.1, 121.6 (d, J = 9.0 Hz), 120.8 (d, J = 4.5 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ –18.7; IR (neat) 1588, 1525, 1487, 1342, 1300, 1181, 1161, 936, 751, 687 cm^{-1}; HRMS (EI) *m/z* calcd. for $C_{29}H_{18}NO_4PS_2$ $(M)^+$ 539.0415, found 539.0411. Crystallographic data for **15l** (recrystallized from AcOEt): $C_{29}H_{18}NO_{18}PS_2$, M = 539.53, monoclinic, $P2_1$, a = 7.58210(10), b = 30.1544(7) Å, c = 10.5015(2) Å, α = 90°, β = 95.411(2)°, γ = 90°, V = 2399.65(8) Å^3, Z = 4, ρ_{calcd} = 1.493 g cm^{-3}, T = 103 K, 43732 reflections measured, 4708 unique. The final R_1 and wR were 0.0626 and 0.1297 (all data). The X-ray data for **15l** have been deposited at the Cambridge Crystallographic Data Center under reference number CCDC 2111093.

*Benzo[4,5]selenopheno[2,3-b]benzo[4,5]selenopheno[3,2-d]pyridin-7-yl diphenyl phosphate (**15m**).* To a solution of [3,3′-bibenzo[b]selenophene]-2,2′-dicarboxylic acid (**10m**) (428 mg, 0.96 mmol, 1.0 equiv.) in toluene (60 mL), DPPA (411 µL, 1.91 mmol, 2.0 equiv.) and DIPEA (998 µL, 5.73 mmol, 6.0 equiv.) were added at rt. After refluxing for 18 h under a N_2 atmosphere, the reaction mixture was quenched with 2*N* aq. HCl and extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 4:1 to 7:3) to afford **15m** (286 mg, 47%). **15m** was further purified by recrystallization from AcOEt/*n*-hexane. Pale yellow solid; M.p. 149–150 °C; The chemical shifts of the ^{1}H NMR signals depend on the concentration: ^{1}H NMR (500 MHz, $CDCl_3$, 0.005 M) δ 8.98 (d, J = 7.9 Hz, 1H), 8.78 (d, J = 7.9 Hz, 1H), 8.05–7.94 (m, 2H), 7.60–7.37 (m, 11H), 7.31–7.21 (m, 3H); ^{1}H NMR (500 MHz, $CDCl_3$, 0.1 M) δ 8.89 (d, J = 8.0 Hz, 1H), 8.70 (dd, J = 7.1, 2.1 Hz, 1H), 7.98–7.87 (m, 2H), 7.52–7.34 (m, 12H), 7.30–7.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 0.1 M) δ 157.9 (d, J = 0.8 Hz), 151.8 (d, J = 6.8 Hz), 150.9 (d, J = 7.5 Hz), 145.0 (d, J = 0.6 Hz), 142.0, 139.0, 136.5, 134.9, 130.0 (d, J = 1.5 Hz), 129.1, 127.7, 127.6, 126.9, 126.8, 126.7, 126.4, 125.9 (d, J = 1.5 Hz), 124.4, 124.3, 121.7 (d, J = 5.3 Hz), 120.7 (d, J = 4.5 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ –18.7; IR (neat) 1487, 1341, 1300, 1276, 1177, 962, 930, 755, 687, 522 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{29}H_{18}NaNO_4PSe_2$ $(M+Na)^+$ 657.9202, found 657.9217. Crystallographic data of **15m** (recrystallized from AcOEt/*n*-hexane): $C_{29}H_{18}NO_{18}PSe_2$, M = 633.33, monoclinic, $P2_1/n$, a = 8.34950(10) Å, b = 18.8577(2) Å, c = 15.9730(2) Å, α = 90°, β = 103.7580(10)°, γ = 90°, V = 2442.83(5) Å^3, Z = 4, ρ_{calcd} = 1.722 g cm^{-3}, T = 103 K, 44328 reflections measured, 4794 unique. The final R_1 and wR were 0.0568 and 0.1351 (all data). The X-ray data for **15m** have been deposited at the Cambridge Crystallographic Data Center under reference number CCDC 2111039.

*Naphtho[1′,2′:4,5]thieno[2,3-b]naphtho[1′,2′:4,5]thieno[3,2-d]pyridin-9-yl diphenyl phosphate ((dl)-**16**).* To a solution of [1,1′-binaphtho[2,1-b]thiophene]-2,2′-dicarboxylic acid ((*dl*)-**13**)[9] (114 mg, 0.25 mmol, 1.0 equiv.) in toluene (10 mL), DPPA (108 µL, 0.5 mmol, 2.0 equiv.) and Et_3N (192 µL, 1.5 mmol, 6.0 equiv.) were added at rt. After refluxing for 4 h under a N_2 atmosphere, the reaction mixture was quenched with 2*N* aq. HCl and extracted with AcOEt. The organic layer was separated, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 4:1 to 3:1) to afford (*dl*)-**16** (24 mg, 15%). Yellow solid; M.p. 126–127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 8.6 Hz, 1H), 8.05–8.00 (m, 2H), 7.98 (d, J = 8.6 Hz, 1H), 7.91–7.87 (m, 2H), 7.56–7.49 (m, 4H), 7.49–7.42 (m, 4H), 7.32–7.13 (m, 6H), 6.48–6.38 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 150.9 (d, J = 7.5 Hz), 149.7 (d, J = 6.0 Hz), 141.2, 140.2, 136.0, 130.9, 130.8 (d, J = 4.5 Hz), 130.6, 130.5 (d, J = 6.0 Hz), 130.0, 129.0, 128.1 (d, J = 17 Hz), 127.9, 127.0, 126.6, 125.9, 125.6, 125.1, 124.8, 124.2, 122.5, 121.8 (d, J = 9.0 Hz), 120.8 (d, J = 4.5 Hz), 120.5 (d, J = 11 Hz) (four carbon signals overlapped); IR (neat) 3057, 2969, 2328, 2164, 1487, 1308, 1184, 1073, 961, 942, 802, 679, 516 cm^{-1}; HRMS (EI) m/z calcd. for $C_{37}H_{22}NO_4PS_2$ $(M)^+$ 639.0728, found 639.0741.

Synthesis of Optically Active Amide-functionalized [7]Helicene-like Molecule 9. *(M)-Dinaphtho[1,2-a:2′,1′-k]phenanthridine-10(9H)-one ((M)-**9**).* To a solution of (*R*)-[4,4'-biphenanthrene]-3,3'-dicarboxylic acid ((*R*)-**6**) (1.5 mg, 3.4 µmol, 1.0 equiv.) in toluene (1 mL), DPPA (1.5 µL, 6.8 µmol, 2.0 equiv.) and DIPEA (3.6 µL, 20 µmol, 6.0 equiv.) were added at rt. After refluxing for 12 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (2:1:1, 2 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with 1*N* aq. HCl, sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was further purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 3:1) to afford (*M*)-**9** (0.50 mg, 37%). The enantiomeric excess of (*M*)-**9** was determined by HPLC analysis (for details, see the Supporting Information); column: CHIRALPAK AD-H (4.6 mm × 250 mm); eluent: *n*-hexane:isopropyl alcohol (IPA) = 9:1; flow rate: 1.0 mL/min; retention time: 10.7 min (for (*M*)-**9**) and 13.3 min (for (*P*)-**9**); UV detection: 254 nm. Yellow solid; M.p. >300 °C; $[\alpha]_D^{18}$ = +1954.5 (*c* 0.2, DMSO, >99% ee); CD (THF) λ_{ext} ($\Delta\varepsilon$): 356 (55.01), 330 (93.66), 319 (87.21), 256 (–193.38), 212 (139.71) nm; UV (THF) λ_{max} (logε): 310sh (4.26), 263 (4.64), 225sh (4.97) nm.

(*P*)-**9** was also prepared in 38% yield from (*S*)-**6** using the same procedure. CD (THF) λ_{ext} ($\Delta\varepsilon$): 356 (–56.64), 330 (–96.89), 319 (–90.88), 256 (186.7), 213 (–142.84) nm.

^{1}H and ^{13}C NMR spectra of the obtained (*M*)-**9** and (*P*)-**9** were identical to the literature data for racemic **9**.[7a] ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.23 (br s, 1H), 8.43 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.76–7.69 (m, 3H), 7.49 (d, J = 8.7 Hz, 1H), 7.42 (d, J = 7.3 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 8.7 Hz, 1H), 6.99–6.92 (m, 2H), 6.84 (d, J = 8.2 Hz, 1H), 6.40–6.30 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.9, 136.8, 134.6, 132.5, 132.3, 132.0, 131.1, 129.8, 129.5, 129.1, 128.8, 128.7, 128.3, 127.5, 127.44, 127.39, 126.7, 126.4, 126.3, 126.24,

126.19, 125.9, 124.2, 124.10, 124.06, 123.4, 116.8, 111.9 (one carbon signal overlapped).

Synthesis of Optically Active Amide-functionalized [7]Helicene-like Molecule 14. *(M)-Naphtho[1',2':4,5]thieno[2,3-b]naphtho[1',2':4,5]thieno[3,2-d]pyridine-9(8H)-one ((M)-**14**).* To a solution of (*R*)-[1,1'-binaphtho[2,1-*b*]thiophene]-2,2'-dicarboxylic acid ((*R*)-**13**)[9] (114 mg, 0.25 mmol, 1.0 equiv.) in toluene (10 mL), DPPA (108 μL, 0.50 mmol, 2.0 equiv.) and Et_3N (209 μL, 1.50 mmol, 6.0 equiv.) were added at rt. After refluxing for 12 h under a N_2 atmosphere, the reaction mixture was concentrated *in vacuo*. Then, a solution of the resulting residue in THF/MeOH/2*N* aq. NaOH (2:1:1, 20 mL) was stirred at rt for 12 h, and the reaction mixture was extracted with AcOEt. The organic layer was separated, washed with sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was further purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 3:2 to 2:3) to afford (*M*)-**14** (27 mg, 26%). The enantiomeric excess of (*M*)-**14** was determined by HPLC analysis (for details, see the Supporting Information); column: CHIRALPAK IC (4.6 mm × 250 mm); eluent: *n*-hexane:IPA = 9:1; flow rate: 1.0 mL/min; retention time: 23.3 min (for (*P*)-**14**) and 36.6 min (for (*M*)-**14**); UV detection: 254 nm. Yellow solid; M.p. >300 °C; $[\alpha]_D^{19}$ = –1869.5 (*c* 0.5, DMSO, >99% ee); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (d, J = 8.7 Hz, 1H), 8.21–8.14 (m, 2H), 8.02–7.98 (m, 1H), 7.97–7.91 (m, 2H), 7.39–7.34 (m, 1H), 7.28–7.21 (m, 2H), 7.20–7.15 (m, 1H), 6.51–6.45 (m, 1H), 6.43–6.37 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.0, 140.9, 137.1, 131.0, 130.8, 130.6, 130.1, 130.0, 129.6, 128.9, 127.9, 127.8, 126.0, 125.7, 125.5, 125.4, 125.0, 124.3, 123.4, 121.2, 120.7 (four carbon signals overlapped); IR (neat) 3048, 2924, 1647, 1515, 1440, 1360, 1225, 1137, 608 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{25}H_{14}NOS_2$ $(M+H)^+$ 408.0511, found 408.0510; CD (THF) λ_{ext} ($\Delta\varepsilon$): 333 (–50.16), 330 (93.66), 264 (–182.89), 234 (217.18) nm; UV (THF) λ_{max} (logε): 318 (4.25), 230sh (4.97) nm.

(*P*)-**14** was also prepared from (*S*)-**13** by the same procedure in 24% yield. CD (THF) λ_{ext} ($\Delta\varepsilon$): 333 (52.04), 330 (93.66), 264 (187.93) 234 (–236.91) nm.

Hydrolysis of (*dl*)-16 to (*dl*)-14. A solution of (*dl*)-**16** (24 mg, 37.5 μmol) in THF/MeOH/2*N* aq. NaOH (2:1:1, 4 mL) was stirred at rt for 12 h. Then, the reaction mixture was extracted with AcOEt (5 mL × 3). The organic layers were combined and washed with 1*N* aq. HCl, sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was further purified by column chromatography (SiO_2, *n*-hexane:AcOEt = 3:1 to 1:1) to afford (*dl*)-**14** (15 mg, quant.).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, spectroscopic data for all new compounds, and HPLC data (PDF).

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Notes

This paper is dedicated to the memory of the late Prof. Toshiyuki Kan, who passed away July 24, 2021.

ACKNOWLEDGMENT

This work was financially supported by a Grant-in-Aid for Scientific Research (B) (18H02554).

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