Published in final edited form as:

European J Org Chem. 2018 October 24; 2018(39): 5397–5405. doi:10.1002/ejoc.201800922.

Enantiomerically Pure 5,13-Dicyano-9-oxa[7]helicene: Synthesis and Study

Riddhi Gupta^[a], Trevor A. Cabrer^[b], Gilles Muller^[b], and Ashutosh V. Bedekar^[a]

^[a]Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390 002, INDIA

^[b]Department of Chemistry, San José State University, One Washington Square, San José, California 95192-0101, USA

Abstract

Optically pure dicyano oxa[7]helicenes and helicene-like molecules have been prepared and investigated for their optical behavior. The isomers of the intermediate 4,4'-biphen-anthrene-3,3'-diol were resolved by physically separating their 1-menthyl carbonate derivatives. In this work a mild method was developed to cleave ArOMe in presence of a cyano group. The optical rotation of atropisomeric diol, helicenes-like compounds and the oxa[7]helicenes was observed to be in increasing order, while the molecules also showed good response to circularly polarized luminescence.

Keywords

Helicenes; Atropisomers; Photophysical properties; Luminescence

Introduction

Helically shaped molecules have fascinated the organic chemists as they pose exciting challenges for their synthesis as well as structural aspects. This class of compounds are known to exhibit unique properties associated with extended conjugation and show chirality due to the shape created, resulting from the internal twist. The developments in the field of helical molecules is well summarized in many reviews published recently.^[1] Although the earlier explorations were focused on carbohelicenes, recently more interesting properties have been observed for the heterohelicenes containing one or more hetero-atoms. Compounds with the rigid shape and twisted π -condensed ring systems, with the presence of different functionalities, tunable planarity are potential candidates for the study of their distinct photophysical and chiroptical properties. Several types of helical systems have been investigated with diverse photophysical properties such as luminescence,^[2] circularly polarized luminescence,^[3] fluorescence,^[4] circular dichroism,^[1a,5] etc., and the optical properties are discussed in few reviews.^[1h,6] The helical compounds have also been used in asymmetric catalysis, self-assembly and biomolecular recognition.^[7] Polycyclic aromatic compounds fused with oxygen containing rings, such as furans, are expected to possess high HOMO levels^[8] and are used in electronic devices such as organic light-emitting diodes and

organic field-effect transistors.^[9] Some of these kind of compounds have also been prepared and studied for their photophysical properties.^[10]

Due to some interesting properties we have been involved in the synthesis and study of different types of aza[*n*]helicenes.^[11] The oxygen analogues, oxa[*n*]helicenes have also been subject of active research and several reports on their synthesis and study are available.^[12] In continuation of our work in this area^[13] we have undertaken the present work to synthesize optically pure dicyano oxa[7]helicenes **1**, its helicenes like analogue **2** and discuss the findings of their response to circularly polarized luminescence (CPL) and optical rotation.

In our earlier efforts^[14] we have explored the conformational aspects of oxa[5]helicenes, where two naphthalene units were attached to furan moiety. We have concluded that the energy barrier for the isomerization of the conformations of oxa[5]helicenes is quite low for practical separation of the enantiomers. Hence, to provide sufficient steric bulk to prepare stable helical isomers we need to introduce additional aromatic rings, or make oxa[7]helicenes. In the present approach we intend to introduce cyano functionality in order to broaden the scope of the study as it is known to influence photophysical response by changing the energy levels of the orbitals^[15a] or in some cases directs the crucial supramolecular interactions leading to spontaneous resolution of helical molecules.^[15b] Based on these aspects we have designed the present helicenes **1** and helicenes-like molecule **2** and present their synthesis and study of photophysical properties. In these compounds we propose to replace the naphthalene unit by phenanthrene and introduce cyano groups symmetrically situated in the moiety. The latter class of helicene-like compounds diarylated [*d,f*][1,3]dioxepine analogues have been subject of similar study by our group and by others.^[16]

Results and Discussion

The target compound **1** is basically a diarylfuran derivative, which can be accessed by acid catalyzed dehydration of corresponding dihydroxy compound^[17] or by palladium mediated cyclization of its activated analogue.^[18] The required 9,9'-dicyano-4,4'-biphenanthryl-3,3'-diol **8** can be prepared by oxidative coupling of **7**. Based on this retrosynthetic strategy we began our synthesis by accessing stilbene derivative **5** as a single, *Z* isomer by Knoevenagel condensation of anisaldehyde **3** and benzyl cyanide **4** (Scheme 1). The photo induced

oxidative cyclization^[19] of **5** gave us the phenanthrene derivative **6** in good conversion. Both the acid sensitive functional groups survived during the reaction, confirmed by usual spectroscopic analysis. In the next part we needed to cleave the methyl ether to access phenol **7**. It was assumed that the usual stronger conditions such as BBr₃ or HBr/AcOH may damage the cyano group. The literature revealed a few methods of selectively cleaving aryl methyl ethers under milder conditions in presence of acid sensitive groups.^[20,21] However, our initial attempts to follow some of these protocols for converting **6** to phenol **7**, resulted in decomposition. Use of sodium iodide^[21] to cleave methyl ethers of phenol was investigated with some success, but the use of lithium bromide gave us clean reaction, although considerable unreacted **6** was recovered (Table 1, entry 1). Addition of phase-transfer catalyst^[20a] with bromide anion marginally affected the cleavage reaction (entry 2). Lower amount of LiBr or conducting reaction at lesser temperature resulted in poor conversion. The use of weakly acidic condition may help the promotion of the ether cleavage; hence reaction was performed with addition of solid materials like Montmorillonite K10 or Molecular Sieves. The presence of these additives considerably improved the cleavage reaction, where the desired product **7** was obtained in clean conversion, while the solid catalysts may be recovered and reused for further applications. Characterization of the product **7** clearly indicated that the acid labile cyano group remains unaffected during this reaction condition, even though the reaction temperature was a bit high.

Having established a practical method to access adequate quantities of 9-cyano-3-hydroxy phenanthrene **7**, the focus was shifted to its homocoupling method. There are few reports on the oxidative coupling of 3-hydroxy phenanthrene to the corresponding 3,3'-dihydroxy-4,4'-biphenanthryl,^[22] analogous to synthesis of BINOL from β -naphthol. The oxidative coupling reaction is known to proceed with copper or vanadium based homogeneous catalysts. Accordingly, we subjected the oxidative coupling of **7** in presence of Cu-TMEDA, prepared from Cu^ICl and tetramethylethylenediamine, in methanol at ambient conditions to afford the single regioisomer of ($\pm$)-**8** in medium yield (Scheme 2). Attempts to perform acid catalyzed dehydration reaction on this diol with *p*TsA, conc. H₂SO₄ and solid acidic catalysts like Montmorillonite K10 resulted in either no reaction or formation of decomposed material. Hence, we resorted to the other method of palladium catalytic cyclization^[18a] after due activation of the diol. Hence, **8** was converted to its mono nonafluoro sulfonate **9** by the known procedure and subjected to cyclization with palladium acetate-xantphos catalyst system. The cyclized product, the desired target 5,13-dicyano-9-oxa[7]helicenes **1** was isolated in moderate yield. The structure was established by usual spectral analysis, particularly typical shifts in ¹H NMR signals. Hydrogen attached to C1 and C17 fall underneath the last aromatic rings and are observed at much shielded region at 6.47 δ .

The structure of ($\pm$)-**1** was further confirmed by single-crystal X-ray analysis (Figure 1).^[23] The molecule shows stable helical conformation, separated on chiral phase HPLC columns at ambient conditions, which is also reflected in observed dihedral angle of 39.64° seen in the X-ray structure. As expected for the helical compounds, the carbon-carbon bond lengths of outside portion were lower than the normal aromatic system while the inside ones were

found to be slightly elongated, see supporting information for the details. Comparing the crystal structures, of **1** with oxa[7]helicenes^[18a] along with the CH- π and π - π interaction, indicated an additional C-N $\cdots$ H-Ar interaction (2.74 Å). The sum of five dihedral angles on the inner helical rim was reduced by 2.1° in case of oxa[7]helicenes (78.9°), to 76.8° in **1**. The angle between the planes passing through the two terminal rings in oxa[7]helicene is reported to be 33.63°, whereas it was found to be 39.64° in **1**.

As already mentioned the other class of helicene-like compounds diarylated [*d,f*] [1,3]dioxepine analogues are also subject of the present study. Thus, the diol **8** was subjected to ether formation with diiodomethane and Cs₂CO₃ as base. The dioxepine derivative **2** was obtained as single compound in good yield and isolated for characterization (Scheme 3). Efforts to grow good quality crystals of ($\pm$)-**2** for single-crystal X-ray analysis failed.

The other objective is to access optically pure isomers of **1** and **2** and to study optical and chiroptical properties of individual enantiomer. Separating the enantiomers of axially chiral samples of ($\pm$)-**8** is a challenging task. Converting helical enantiomers to diastereomers by attaching chiral auxiliary, making it suitable for physical separation and then regenerating the optically pure compounds is one of the standard protocols. Attaching (-)-menthyl chloroformate to hydroxyl group to make such separable diastereomers is often employed for resolution of chiral molecules.^[24] The racemic diol **8** was subjected to the bis-carbonate formation with (-)-menthyl chloroformate to obtain the diastereomeric mixture of **10** (Scheme 4). The purified mixture was subjected to crystallization in several solvents and the mixture of chloroform (30 %) in hexane was found suitable for this purpose. The crystals were separated and the ¹H NMR analysis indicated them to be of a single diastereomer of bis-carbonate of (-)-menthyl derivative (> 99 % *de*).

The single-crystal X-ray analysis^[23] of the solid compound obtained clearly established the stereochemistry of the chiral axis to be “*S*” of the carbonate (Figure 2). Solvent molecules were also seen trapped in the unit cell (not shown in the Figure), which was identified to be crystallized in P 2₁ 2₁ 2₁ space group.

The soluble portion after the crystals were separated contains the other diastereomer in 96 % diastereomeric excess as confirmed by ¹H NMR analysis.

The optically pure (*S*)-**10** was then subjected to alkaline hydrolysis to generate chirally enriched diol (*S*)-**8** (Scheme 5). Under the hydrolysis condition there appears to be no loss of optical purity of the atropisomeric diol, as confirmed by HPLC analysis on chiral phase column. Identical treatment was given to the solid obtained from the filtrate containing enriched (*R*)-**10** to regenerate (*R*)-**8**. Optically pure (*S*)-**8** was converted to (*P*)-**1** by step wise procedure as described earlier, while also converted to methylene bridge containing helicenes-like (*Sa*)-**2**. The other set of isomers, (*M*)-**1** and (*Ra*)-**2** were prepared from similar procedure from (*R*)-**8** (Figure 3).

Optical properties of compounds **1** and **2** were studied by UV/Vis and fluorescence spectroscopy (Table 2). The observed values of absorption and emission bands and the Stokes shift were in the expected range for such types of helical compounds.^[25] Helicene-

like compound **2** showed marginal red shift in the emission spectra (18 nm) and higher Stokes shift. The lower value of the emission maxima in helicenes is probably attributed to more facile intersystem crossing in such molecules.^[25b]

One of the important properties of optically pure helical compounds is their high optical rotation ($[\alpha]_D$) and molecular optical rotation ($[\phi]_D$). Moreover the helical materials are studied as isotropic planar chiral waveguides as universal chiral sensors.^[26] However, the primary requirement for making such sensory devices is to access materials which can show high degree of specific optical rotation. It is known that chiral compounds with chiral center or chiral axis tend to have much lower optical rotations, which tend to change to higher value when converted to helicenes-like molecules, while show further enhanced rotation when converted to helical compounds with continuous delocalization of electrons and high conjugation.^[16] The comparison of the present set of compounds also indicate to the similar observation (Table 3). Both the isomers of chirally pure sample of **8** showed much less rotation, which changed considerably when converted to helicenes-like compounds **2**. When the helical compound was synthesized, there was considerable increase in the value of optical rotation as well as molecular rotation. The sample of (*S*)-**8** with OR of +157 and molecular OR of +685 was converted to (*P*)-**1**, the values changed to +790 and +3306, respectively.

A considerable difference was found on comparing the physical properties of oxa[7]helicenes^[18a] with our 5,13-dicyano-9-oxa[7]helicene **1**. We found that there was an increase in the melting point and a decrease of solubility in organic solvents. There is also a considerable change in the specific optical rotation value which was reported to be +1430° (*c* = 0.10, CHCl₃) for (*P*)-oxa[7]helicene and +790° (*c* = 0.10, DMSO) for (*P*)-**1**. Also a Bathochromic shift of 10 nm was observed in the UV/Vis spectra, λ_{max} for oxa[7]helicene is reported to be around 313 nm whereas for **1** it shifted to 323 nm.

The separated isomers of **1** and **2** were further analyzed by circular dichroism (Figure 4), where two opposite bisignate couplets, were observed. The (*P*) isomer of helical compound **1** shows more pronounced positive signal (Figure 4b) as compared the (*P*) isomer of helicenes like compound **2** (Figure 4a), which is a typical observation for optically pure helicenes.^[16b,27]

The CPL activity was another useful chiroptical property to consider for the synthesized optically pure dicyano oxa[7]helicenes **1** and its helicenes-like analogue **2**. It allows to further investigate the influence of the helical-like structure of the compounds of interests on the chiroptical properties. The CPL spectra measured for the two sets of enantiomers (*P*)-/*(M)*-**1** and (*P*)-/*(M)*-**2** in DMSO solutions at 295 K are shown in Figure 5. Both sets of enantiomers, (*P*)-/*(M)*-**1** and (*P*)-/*(M)*-**2**, showed a somewhat mirror-like CPL signal with opposite g_{lum} values around the emission maximum (+0.003/−0.002 and +0.005/−0.002, respectively). These small values are in the typical range of g_{lum} values for most chiral organic molecules.^[28] However, these results confirm that the solutions of **1** and **2** in DMSO exhibit active CPL signals, and also that the emitted light is polarized in opposite directions for the two enantiomeric forms for each set of these helicenes-like structures. It is worth noting that **1** and **2** give a relatively similar CPL response, which is in accordance with the

slight structural differences between these two compounds resulting delocalization of electrons in helicenes **1** or helicenes-like compounds in **2**. One can conclude from the CPL results (i.e. similar g_{lum} values with a slightly larger value for **2**) that the structural changes are not sufficient to significantly influence in a different manner the chiroptical properties of these two compounds (at least from a CPL standpoint). This is in agreement with the well-established fact that the CPL activity is mainly dependent on the structural properties of the chiral compounds of interest.^[28]

Conclusions

Dicyano-substituted derivatives of oxa[7]helicenes and helicenes-like compounds have been prepared. During the synthesis, a mild and effective method is also developed to cleave aryl methyl ether, in presence of acid sensitive cyano group. The enantiomers of these compounds were accessed by making physically separable diastereomers of phenolic intermediate, by attaching (*l*)-menthyl chloroformate. The separated enantiomers were characterized by optical rotation, fluorescence and CD spectroscopy and circularly polarized luminescence. Both sets of enantiomers, (*P*)-/(*M*)-**1** and (*P*)-/(*M*)-**2**, showed a mirror-like CPL signal with opposite g_{lum} values around the emission maximum, which correspond to the typical range of similar chiral molecules.

Experimental Section

Reagents were purchased from Sigma–Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited, etc., and were used without further purification. All the glassware was flame dried before the experiment. All solvents used were stored on oven dried molecular sieves (4 Å). Thin Layer Chromatography was performed on Merck 60 F254 Aluminium coated plates. The spots were visualized under UV light or with iodine vapour. All the compounds were purified by column chromatography using SRL silica gel (60–120 mesh). ¹H and ¹³C NMR spectra are recorded on a 400 MHz Bruker Avance 400 spectrometer (100 MHz for ¹³C) with CDCl₃ as a solvent (unless specified) and TMS as an internal standard. Signal multiplicity is denoted as singlet (s), broad singlet (bs), doublet (d), doublet of doublet (dd), triplet (t), doublet of triplet (dt), quartet (q) and multiplet (m). Mass spectra were recorded on a Thermo-Fischer DSQ II GC–MS instrument. IR spectra were recorded on a Perkin–Elmer FTIR RXI spectrometer as KBr pallets or neat in the case of liquids. UV/Vis spectra were recorded on Perkin–Elmer Lambda-35. Fluorescence spectra were recorded on a JASCO FP-6300 spectrofluorometer. Specific optical rotations were measured on JACSO P-2000 polarimeter. Melting points were recorded in Thiele’s tube using paraffin oil and are uncorrected.

3-(4-Methoxyphenyl)-2-phenylacrylonitrile [5]:

A mixture of benzyl cyanide **4** (1.17 g; 10 mmol), finely ground solid KOH (0.65 g; 10 mmol) and 4-methoxybenzaldehyde **3** (0.68 g; 10 mmol) in methanol (30 mL) was stirred at room temperature for 6 hours. The resultant reaction mixture was concentrated under reduced pressure, poured into water and extracted using ethyl acetate (3×50 mL). The combined organic layer was dried with sodium sulfate and concentrated to give crude **5** as pale-yellow solid (2.23 g, 96 %); Melting Point: 96 °C (Lit.^[29] 93–95 °C); which is

recrystallized from ethyl acetate/petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ = 3.87 (s, 3 H), 6.99 (d, J = 8.8 Hz, 2 H), 7.37–7.41 (m, 1 H), 7.44 (d, J = 7.6 Hz, 2 H), 7.48 (s, 1 H), 7.67 (d, J = 7.6 Hz, 2 H), 7.91 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 55.5, 108.5, 114.4 (2 C), 118.6, 125.8 (2 C), 126.5, 128.8, 129.1 (2 C), 131.2 (2 C), 134.8, 141.9, 161.4 ppm. MS (DIP-EI): m/z (%) = 235 (21) $[\text{M}^+]$, 234 (17), 190 (100), 165 (91), 164 (57), 139 (25). IR (KBr): $\tilde{\nu}$ = 3013, 2844, 2207, 1596, 1507, 1448, 1304, 1250, 1179, 1026, 905, 828, 756, 693, 533 cm^{-1} .

3-Methoxyphenanthrene-9-carbonitrile [6]:

A solution of **5** (0.1 g, 0.42 mmol) and iodine (0.12 g, 0.47 mmol) in toluene (425 mL) and tetrahydrofuran (1.7 mL, 21.3 mmol, 50 equiv.) was irradiated in a standard immersion well photoreactor with 250W high pressure mercury vapor lamp for 24 hours. The reaction mixture was then washed with aqueous sodium thiosulfate and dried with anhydrous sodium sulfate. The concentrated mixture was purified on silica gel column using ethyl acetate and petroleum ether (1:4) to afford **6** as pale-yellow solid (0.093 g, 94 %); Melting Point: 118 °C (Lit:^[30] 116–118 °C). ^1H NMR (400 MHz, CDCl_3): δ = 4.07 (s, 3 H), 7.325 (dd, J = 8.8, 2.4 Hz, 1 H), 7.75–7.79 (m, 2 H), 7.87 (d, J = 8.8 Hz, 1 H), 8.035 (d, J = 2.0 Hz, 1 H), 8.21 (s, 1 H), 8.29–8.32 (m, 1 H), 8.63–8.66 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 55.6, 104.1, 106.6, 117.9, 118.4, 123.1, 124.5, 126.1, 127.7, 128.2, 129.3, 129.4, 131.2, 133.6, 135.5, 160.9 ppm. MS (DIP-EI): m/z (%) = 233 (100) $[\text{M}^+]$, 232 (61), 190 (39), 189 (77), 166 (14), 81 (38), 69 (40), 57 (27). IR (KBr): $\tilde{\nu}$ = 3022, 2966, 2935, 2845, 2217, 1618, 1503, 1453, 1372, 1232, 1144, 1030, 897, 835, 816, 721, 620, 565, 490, 427 cm^{-1} .

3-Hydroxyphenanthrene-9-carbonitrile [7]:

To a round-bottomed flask, was added **6** (0.5 g, 2.15 mmol), lithium bromide (0.37 g, 4.30 mmol) in dimethylformamide (30 mL). To this solution was added 4 Å molecular sieves (100 % w/w) and stirred at room temperature for 15 min, followed by heating in an oil bath to 180 °C for 22 h. The reaction mixture was then cooled to room temperature and filtered to remove molecular sieves. Water was added to the reaction mixture and it was allowed to stir till solution becomes clear. It was extracted using ethyl acetate (3×50 mL). The combined organic layer was dried with sodium sulfate and concentrated under reduced pressure. The concentrated mixture was purified on silica gel column using ethyl acetate and petroleum ether (2:3) to afford **7** as pale-yellow solid (0.39 g, 85 %); Melting Point: > 220 °C. ^1H NMR (400 MHz, CDCl_3): δ = 5.91 (s, 1 H), 7.265 (dd, J = 8.8, 2.0 Hz, 1 H), 7.73–7.79 (m, 2 H), 7.87 (d, J = 8.8 Hz, 1 H), 8.055 (d, J = 2.0 Hz, 1 H), 8.22 (s, 1 H), 8.28–8.32 (m, 1 H), 8.58–8.62 (m, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 107.2, 117.9, 118.3, 123.2, 124.6, 126.1, 127.8, 128.4, 129.2, 129.3, 131.6, 133.9, 135.4, 157.1 ppm. MS (DIPEI): m/z (%) = 219 (59) $[\text{M}^+]$, 218 (100), 201 (23), 190 (49), 165 (16), 163 (21). IR (KBr): $\tilde{\nu}$ = 3404, 2217, 1628, 1575, 1507, 1450, 1342, 1245, 1203, 899, 856, 810, 753, 621, 564 cm^{-1} .

3,3'-Dihydroxy-[4,4'-biphenanthrene]-9,9'-dicarbonitrile [(±)8]:

In a 50 mL round-bottomed flask, a mixture of 3-hydroxyphenanthrene-9-carbonitrile **7** (0.2 g, 0.9 mmol), $\text{CuCl}(\text{OH})[(\text{Me}_2\text{N})_2\text{CH}_2\text{CH}_2(\text{NMe}_2)_2]$ (0.21 g, 0.9 mmol) in methanol (25 mL) was placed and was sonicated for 10 min. The reaction mixture was stirred at room

temperature for 4.5 h under oxygen atmosphere (1 atm). The reaction mixture was concentrated to remove methanol and 1 *M* aqueous HCl was added. The resulting mixture was extracted with ethyl acetate (3×40 mL). The organic layer was dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. Purification of the crude residue by silica gel column chromatography with petroleum ether/ethyl acetate (1:1) as an eluent gave the ***rac*-8** as a colorless solid (0.11 g, 55 %); Melting Point: > 220 °C. Chiral HPLC was performed on Chiralpak OD-H in 30 % Isopropanol/hexane, at a flowrate of 1 mL/min and UV 254 nm, *t_R* 10.4 and 15.8 min. ¹H NMR (400 MHz, [D₆]DMSO): δ = 7.03–7.07 (m, 1 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 7.54–7.58 (m, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 8.11 (d, *J* = 8.8 Hz, 1 H), 8.17 (d, *J* = 8.8 Hz, 1 H), 8.71 (s, 1 H), 10.01 (br. s, 1 H) ppm. ¹³C NMR (100 MHz, [D₆]DMSO): δ = 104.9, 118.7, 118.9, 122.2, 125.5 (2 C), 125.8, 127.3, 128.4, 129.9, 130.8, 132.4, 132.8, 137.9, 157.3 ppm. MS (DIP-EI): *m/z* (%) = 436 (70) [M⁺], 435 (100), 367 (27), 313 (33), 312 (56), 220 (30), 218 (20). IR (KBr): $\tilde{\nu}$ = 3355, 2926, 2221, 1600, 1569, 1493, 1443, 1395, 1250, 1222, 1084, 898, 762, 661, 629, 569 cm⁻¹. HRMS (ESI) *m/z* calcd. for C₃₀H₁₆N₂O₂Na [M + Na] 459.1104, found 459.1109.

9,9'-Dicyano-(4,4'-biphenanthrene)-3,3'-diyl(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexylbiscarbonate [(±)10]:

To a solution of (±)-**8** (0.20 g, 0.45 mmol) and triethylamine (0.16 mL, 1.15 mmol) in dichloromethane was added (1*R*,2*S*,5*R*)-(–)-menthyl chloroformate (0.22 mL, 1.01 mmol) drop wise at 0 °C under N₂ atmosphere. After completion of the reaction (tlc), the reaction mixture was poured in ice cold water. The aqueous layer was extracted with dichloromethane (2×50 mL), the extracts were combined, and the organic layer was dried with Na₂SO₄ and evaporated to obtain a crude solid. The crude product was purified by column chromatography over silica gel using petroleum ether/ethyl acetate as eluent (13:1) furnishing a pale-yellow solid (0.30 g, 80 %).

(*S*)-9,9'-Dicyano-(4,4'-biphenanthrene)-3,3'-diyl-bis[(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl]biscarbonate [(*S*)-10]:

Melting Point: > 220 °C. [α]_D = +48 (*c* = 1.0, CHCl₃, 99 % *ee*). ¹H NMR (400 MHz, CDCl₃): δ = 0.36–0.45 (m, 1 H), 0.585 (d, *J* = 6.8 Hz, 3 H), 0.70–0.74 (m, 1 H), 0.78 (d, *J* = 7.2 Hz, 3 H), 0.80–0.84 (m, 1 H), 0.88 (d, *J* = 6.4 Hz, 3 H), 1.04–1.23 (m, 3 H), 1.45–1.58 (m, 3 H), 4.02 (dt, *J* = 10.8, 4.4 Hz, 1 H), 7.14–7.16 (m, 1 H), 7.61–7.65 (m, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 8.18 (d, *J* = 8.8 Hz, 1 H), 8.325 (dd, *J* = 8.0, 0.8 Hz, 1 H), 8.44 (s, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.2, 20.6, 21.9, 23.1, 25.7, 31.1, 33.8, 39.5, 46.2, 79.3, 110.4, 117.6, 123.6, 126.1, 126.3, 127.3, 127.9, 128.6, 129.2, 129.9, 130.1, 131.6, 132.1, 135.7, 149.2, 151.6 ppm. IR (KBr): $\tilde{\nu}$ = 2956, 2926, 2869, 2223, 1750, 1597, 1491, 1453, 1370, 1270, 1231, 1086, 1030, 954, 759 cm⁻¹. HRMS (ESI) *m/z* calcd. for C₅₂H₅₂N₂O₆Na [M + Na] 823.3718, found 823.3708.

(*R*)-9,9'-Dicyano-(4,4'-biphenanthrene)-3,3'-diyl-bis[(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl]biscarbonate [(*R*)-10]:

Melting Point: 98 °C. [α]_D = –175 (*c* = 1.0, CHCl₃, 96 % *ee*). ¹H NMR (400 MHz, CDCl₃): δ = 0.16 (d, *J* = 7.2 Hz, 3 H), 0.60 (d, *J* = 7.2 Hz, 3 H), 0.70–0.84 (m, 1 H), 0.865 (d, *J* = 6.4

Hz, 3 H), 0.96–0.99 (m, 1 H), 1.04–1.09 (m, 1 H), 1.27–1.28 (m, 2 H), 1.44–1.62 (m, 3 H), 1.72–1.75 (m, 1 H), 4.07 (dt, $J = 11.2, 4.4$ Hz, 1 H), 7.01–7.05 (m, 1 H), 7.51–7.55 (m, 1 H), 7.77 (d, $J = 8.8$ Hz, 1 H), 7.78 (d, $J = 8.4$ Hz, 1 H), 8.215 (d, $J = 8.8$ Hz, 1 H), 8.245 (dd, $J = 8.0, 0.8$ Hz, 1 H), 8.42 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 15.9, 20.3, 21.9, 23.2, 23.9, 25.9, 31.2, 33.8, 46.3, 79.4, 110.5, 117.6, 123.5, 126.1, 126.2, 127.3, 127.8, 128.4, 129.5, 129.8, 129.9, 131.7, 131.8, 135.5, 149.7, 151.9$ ppm.

Regeneration of Chiral Diol [(*S*)-8]:

To solution of KOH (0.042 g, 0.75 mmol) in degassed methanol (20 mL), 0.5 g of (*S*)-10 (0.63 mmol) was added and the mixture was allowed to stir at room temperature for 4 h after which no starting material remained (TLC). The mixture was concentrated and to it was added 20 mL of water. The aqueous layer was separated and acidified with 6 M HCl, producing a white precipitate that was extracted with ethyl acetate (2×30 mL). The ether layer was dried with Na_2SO_4 , filtered off and the solvent evaporated in vacuo to give (*S*)-8 as white solid (0.27 g, 86 %) (*S*)-8 [α]_D = +157 ($c = 0.1$, DMSO, 99 % ee).

Similar hydrolysis treatment of (*R*)-10 gave (*R*)-8 [α]_D = −150 ($c = 0.1$, DMSO, 96 % ee).

9,9'-Dicyano -3'-hydroxy-[4,4'-biphenanthren]-3-yl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate [(±)-9]:

A mixture of (±)-8 (0.1 g, 2.3 mmol) and triethylamine (0.035 mL, 2.5 mmol) in CH_2Cl_2 (10 mL) was placed in a round-bottomed flask. To this solution was slowly added nonafluorobutanesulfonyl fluoride (0.045 mL, 2.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 6 h and then concentrated to remove CH_2Cl_2 . The resulting mixture was extracted with ethyl acetate (40 mL×3). The organic layer was dried with anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. Purification of the crude residue by silica gel column chromatography with petroleum ether/ethyl acetate (70:30) as an eluent gave (±)9 as a pale yellow solid (0.14 g, 86 %); Melting Point: 106 °C; (*S*)-9 [α]_D = +59 ($c = 1.0$, CHCl_3 , 99 % ee); (*R*)-9 [α]_D = −56 ($c = 1.0$, CHCl_3 , 96 % ee). ^1H NMR (400 MHz, CDCl_3): $\delta = 5.61$ (br. s, 1 H), 7.04–7.08 (m, 1 H), 7.20–7.25 (m, 1 H), 7.39 (d, $J = 8.8$ Hz, 1 H), 7.57–7.61 (m, 1 H), 7.68–7.72 (m, 1 H), 7.77 (dd, $J = 8.8$ Hz, 1.2 H, 2 H), 8.12 (d, $J = 8.4$ Hz, 1 H), 8.28 (d, $J = 8.8$ Hz, 1 H), 8.32 (dd, $J = 8.4, 1.2$ Hz, 1 H), 8.37–8.40 (m, 2 H); 8.38 (s, 1 H), 8.48 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 107.9, 112.2, 117.2, 117.9, 118.1, 118.5, 121.9, 125.3, 125.4, 126.4, 126.6$ (2 C), 127.4, 128.2, 128.7, 129.3, 129.7, 129.9, 130.0, 130.5, 130.6, 131.0, 132.3, 132.6, 132.8, 133.3, 135.4, 136.1, 147.9, 154.7 ppm. MS (DIPEI): m/z (%) = 734 (39) [M^+]; 590 (39), 577 (43), 433 (55), 406 (100), 392 (56), 379 (69), 378 (95). IR (KBr): $\tilde{\nu} = 3334, 3076, 2226, 1663, 1607, 1574, 1526, 1498, 1423, 1351, 1239, 1035, 1009, 907, 792, 734, 693, 530, 488$ cm^{-1} . HRMS (ESI) m/z calcd. for $\text{C}_{34}\text{H}_{15}\text{N}_2\text{O}_4\text{F}_9\text{SNa}$ [$\text{M} + \text{Na}$] 741.0501, found 741.0502.

Diphenanthro[3,4-b:4',3'-d]furan-5,13-dicarbonitrile [(±)1]:

A mixture of (±)-9 (0.17 g, 0.23 mmol), $\text{Pd}(\text{OAc})_2$ (2.6 mg, 0.012 mmol), xantphos (27 mg, 0.046 mmol), anhydrous Cs_2CO_3 (0.16 g, 0.46 mmol) in xylene (10 mL) was placed in a 50 mL round-bottomed flask and degassed by sonicating for 10 min. The reaction mixture was stirred at 60 °C for 4 h under nitrogen atmosphere. The reaction mixture was cooled down to

ambient temperature and was then diluted with toluene (10 mL). The resulting mixture was washed with water, extracted with toluene, dried with anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (90:10) as an eluent to give (**±**)**1** as a pale-yellow solid (50 mg, 52 %). Melting Point: > 220 °C; (**P**)-**1** [α]_D = +790 (*c* = 0.1, DMSO, 99 % *ee*); (**M**)-**1** [α]_D = -755 (*c* = 0.1, DMSO, 96 % *ee*). ¹H NMR (400 MHz, [D₆]DMSO): δ = 6.45–6.48 (m, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.50–7.54 (m, 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 8.48 (d, *J* = 8.8 Hz, 1 H), 8.55 (d, *J* = 8.8 Hz, 1 H), 9.03 (s, 1 H) ppm. MS (DIP-ESI): *m/z* (%) = 418 (45) [M⁺], 410 (59), 312 (100), 256 (64), 236 (72), 199 (63), 155 (73), 140 (53). IR (KBr): $\tilde{\nu}$ = 2220, 1584, 1519, 1486, 1446, 1347, 1320, 1271, 1225, 1106, 922, 898, 772, 644 cm⁻¹. HRMS (ESI) *m/z* calcd. for C₃₀H₁₄N₂ONa [M + Na] 441.0998, found 441.0995.

Diphenanthro[3,4-d:4',3'-f][1,3]dioxepine-5,15-dicarbonitrile [(**±**)**2**]:

A solution of (**±**)-**8** (0.10 g, 0.23 mmol) and anhydrous Cs₂CO₃ (0.29 g, 1.15 mmol) in dry DMF (5 mL), CH₂I₂ (0.028 mL, 0.34 mmol) was added and the mixture was stirred for 6 h at room temperature under nitrogen atmosphere. After the completion of the reaction (tlc) the reaction mixture was poured in ice cold water. The aqueous layer was extracted with ethyl acetate (3×50 mL), dried with Na₂SO₄ and concentrated under reduced pressure to obtained crude solid. The crude product was purified by column chromatography over silica gel using petroleum ether/ethyl acetate as eluent (80:20) furnishing (**±**)-**2** as white solid (0.09 g, 88 %). Melting Point: > 220 °C; (**S**)-**2** [α]_D = +543 (*c* = 0.1, DMSO, 99 % *ee*); (**R**)-**2** [α]_D = -515 (*c* = 0.1, DMSO, 96 % *ee*). ¹H NMR (400 MHz, CDCl₃): δ = 5.89 (s, 1 H), 6.58–6.59 (m, 2 H), 7.19–7.23 (m, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 8.24 (s, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 102.1, 109.1, 117.6, 122.2, 124.9, 125.8, 126.1, 127.9, 128.9, 129.0, 129.1 (2 C), 131.8, 131.9, 135.0, 153.5 ppm. MS (DIP-ESI): *m/z* (%) = 448 (100) [M⁺], 447 (41), 368 (99), 313 (50), 236 (81), 152 (62), 111 (80). IR (KBr): $\tilde{\nu}$ = 3061, 2922, 2853, 2226, 1586, 1519, 1494, 1444, 1391, 1320, 1270, 1198, 1018, 973, 895, 767, 642, 554, 448 cm⁻¹. HRMS (TOF MS EI+) *m/z* calcd. for C₃₁H₁₆N₄O₂ [M] 448.1212, found 448.1207.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We are grateful to University Grants Commission (UGC), New Delhi [No. 42-279/2013 (SR)] and Science and Engineering Research Board (SERB), New Delhi [No. EMR/2016/006245] for the financial assistance to this work. We also thank Department of Science and Technology, New Delhi for the PURSE project under which the X-ray Diffraction Machine has been acquired at the Faculty of Science, MS University of Baroda. G. M. acknowledges the NIH Minority Biomedical Research Support (grant 1 SC3 GM089589-08) and the Henry Dreyfus Teacher-Scholar Award for financial supports.

References

- [1]. a)Grimme S, Harren J, Sobanski A, Vögtle F, Eur. J. Org. Chem 1998, 1491–1509;b)Urbano A, Angew. Chem. Int. Ed 2003, 42, 3986–3989; Angew. Chem. 2003, 115, 4116–4119;c)Collins SK,

- Vachon MP, Org. Biomol. Chem 2006, 4, 2518–2524; [PubMed: 16791312] d)Rajca A, Miyasaki M, in Functional Organic Materials (Eds.: Muller TJJ, Bunz UHF), Wiley-VCH, Weinheim, 2007, p. 547;e)Shen Y, Chen C-F, Chem. Rev 2012, 112, 1463–1535; [PubMed: 22017405] f)Gingras M, Chem. Soc. Rev 2013, 42, 968–1006; [PubMed: 23151799] g)Gingras M, Félix G, Peresutti R, Chem. Soc. Rev 2013, 42, 1007–1050; [PubMed: 23151610] h)Gingras M, Chem. Soc. Rev 2013, 42, 1051–1095; [PubMed: 23151680] i)Chen C-F, Shen Y, in Helicene chemistry: from synthesis to applications, Springer 2017.
- [2]. a)Oyama H, Nakano K, Harada T, Kuroda R, Naito M, Nobusawa K, Nozaki K, Org. Lett 2013, 15, 2104–2107; [PubMed: 23587064] b)Hua W, Liu Z, Duan L, Dong G, Qiu Y, Zhang B, Cui D, Tao X, Cheng N, Liu Y, RSC Adv. 2015, 5, 75–84.
- [3]. a)Field JE, Muller G, Richl JP, Venkataraman D, J. Am. Chem. Soc 2003, 125, 11808–11809; [PubMed: 14505389] b)Sawada Y, Furumi S, Takai A, Takeuchi A, Takeuchi M, Noguchi K, Tanaka K, J. Am. Chem. Soc 2012, 134, 4080–4083; [PubMed: 22335235] c)Yang T, Da Costa RC, Fuchter MJ, Campbell AJ, Nat. Photonics 2013, 7, 634–638;d)Shyam Sundar M, Talele HR, Mande HM, Bedekar AV, Tovar RC, Muller G, Tetrahedron Lett. 2014, 55, 1760–1764; [PubMed: 24707063] e)Nakamura K, Furumi S, Takeuchi M, Shibuya T, Tanaka K, J. Am. Chem. Soc 2014, 136, 5555–5558; [PubMed: 24670158] f)Morisaki Y, Gon M, Sasamori T, Tokitoh N, Chujo Y, J. Am. Chem. Soc 2014, 136, 3350–3353; [PubMed: 24527728] g)Brandt JR, Wang X, Yang Y, Campbell AJ, Fuchter MJ, J. Am. Chem. Soc 2016, 138, 9743–9746. [PubMed: 27434383]
- [4]. a)Morrison DJ, Trefz TK, Piers WE, McDonald R, Parvez M, J. Org. Chem 2005, 70, 5309–5312; [PubMed: 15960537] b)Wang ZY, Todd EK, Meng XS, Gao JP, J. Am. Chem. Soc 2005, 127, 11552–11553; [PubMed: 16104702] c)Rajapakse A, Gates KS, J. Org. Chem 2012, 77, 3531–3537; [PubMed: 22417220] d)Li M, Niu Y, Zhu X, Peng Q, Lu H-Y, Xia A, Chen C-F, Chem. Commun 2014, 50, 2993–2995;e)Li M, Yao W, Chen J-D, Lu H-Y, Zhao Y, Chen C-F, J. Mater. Chem. C 2014, 2, 8373–8380;f)Yamamoto Y, Sakai H, Yuasa J, Araki Y, Wada T, Sakanoue T, Takenobu T, Kawai T, Hasobe T, Chem. Eur. J 2016, 22, 4263–4273. [PubMed: 26863928]
- [5]. a)Nuckolls C, Katz TJ, Castellanos L, J. Am. Chem. Soc 1996, 118, 3767–3768;b)Nuckolls C, Katz TJ, J. Am. Chem. Soc 1998, 120, 9541–9544;c)Verbiest S, Van Elshocht M, Kauranen L, Hellemans J, Snauwaert C, Nuckolls C, Katz TJ, Persoons A, Science 1998, 282, 913–915; [PubMed: 9794754] d)Hassey R, Swain EJ, Hammer NI, Venkataraman D, Barnes MD, Science 2006, 314, 1437–1439; [PubMed: 17082419] e)Hassey R, McCarthy KD, Basak ESD, Venkataraman D, Barnes MD, Chirality 2008, 20, 1039–1046; [PubMed: 18512254] f)Kaseyama T, Furumi S, Zhang X, Tanaka K, Takeuchi M, Angew. Chem. Int. Ed 2011, 50, 3684–3687; Angew. Chem. 2011, 123, 3768–3771;g)Roose J, Achermann S, Dumele O, Diederich F, Eur. J. Org. Chem 2013, 3223–3231;h)Richardson RD, Baud MGJ, Weston CE, Rzepa HS, Kuimova MK, Fuchter MJ, Chem. Sci 2015, 6, 3853–3862. [PubMed: 29218156]
- [6]. Bosson J, Gouin J, Lacour J, Chem. Soc. Rev 2014, 43, 2824–2840. [PubMed: 24500211]
- [7]. a)Murguly E, McDonald R, Branda N, Org. Lett 2000, 2, 3169–3172; [PubMed: 11009373] b)Honzawa S, Okubo H, Anzai S, Yamaguchi M, Tsumoto K, Kumagai, Bioorg. Med. Chem 2002, 10, 3213–3218; [PubMed: 12150866] c)Xu Y, Zhang Y, Sugiyama H, Umano T, Osuga H, Tanaka K, J. Am. Chem. Soc 2004, 126, 6566–6567; [PubMed: 15161280] d)Shcherbina MA, Zeng X-B, Tadjiev T, Ungar C, Eichhorn SH, Philips KES, Katz TJ, Angew. Chem. Int. Ed 2009, 48, 7837–7840; Angew. Chem. 2009, 121, 7977–7980;e)Crittall MR, Rzepa H, Carbery DR, Org. Lett 2011, 13, 1250–1253; [PubMed: 21302969] f)Takenaka N, Sarangthem RS, Captain B, Angew. Chem. Int. Ed 2008, 47, 9708–9710; Angew. Chem. 2008, 120, 9854–9856;g)Aillard P, Voiturez A, Marinetti A, Dalton Trans. 2014, 43, 15263–15278; [PubMed: 25181754] h)Shen C, He X, Toupet L, Norel L, Rigaut S, Crassous J, Organometallics 2018, 37, 697–705;i)Petdum A, Panchan W, Swanglap P, Sirirak J, Sooksimuang T, Wanichacheva N, Sens. Actuators B 2018, 259, 862–870.
- [8]. a)Bunz UHF, Angew. Chem. Int. Ed 2010, 49, 5037–5040; Angew. Chem. 2010, 122, 5159–5162;b)Horner KE, Karadakov PB, J. Org. Chem 2013, 78, 8037–8043. [PubMed: 23879676]
- [9]. a)Tsuiji H, Mitsui C, Ilies L, Sato Y, Nakamura E, J. Am. Chem. Soc 2007, 129, 11902–11903; [PubMed: 17850088] b)Mitsui C, Soeda J, Miwa K, Tsuiji H, Takeya J, Nakamura E, J. Am. Chem. Soc 2012, 134, 5448–5451; [PubMed: 22413837] c)Nakano M, Niimi K, Miyazaki E, Osaka I, Takimiya K, J. Org. Chem 2012, 77, 8099–8111. [PubMed: 22889196]

- [10]. a) Mitsudo K, Harada J, Tanaka Y, Mandai H, Nishioka C, Tanaka H, Wakamiya A, Murata Y, Suga S, *J. Org. Chem* 2013, 78, 2763–2768; [PubMed: 23438033] b) Nakahara K, Mitsui C, Okamoto T, Yamagishi M, Miwa K, Sato H, Yamano A, Uemura T, Takeya J, *Chem. Lett* 2013, 42, 654–656; c) Nakanishi K, Sasamori T, Kuramochi K, Tohitoh N, Kawabata T, Tsubaki K, *J. Org. Chem* 2014, 79, 2625–2631; [PubMed: 24564354] d) Nakanishi K, Fukatsu D, Takaishi K, Tsuji T, Uenaka K, Kuramochi K, Kawabata T, Tsubaki K, *J. Am. Chem. Soc* 2014, 136, 7101–7109. [PubMed: 24738696]
- [11]. a) Upadhyay GM, Talele HR, Sahoo S, Bedekar AV, *Tetrahedron Lett.* 2014, 55, 5394–5399; b) Upadhyay GM, Bedekar AV, *Tetrahedron* 2015, 71, 5644–5649; c) Rajan B, Bedekar AV, *Synlett* 2017, 28, 2262–2266.
- [12]. a) Tomuschat P, Kröner L, Steckham E, Nieger M, Dötz KH, *Chem. Eur. J* 1999, 5, 700–707; b) Karikomi M, Yamada M, Ogawa Y, Houjou H, Seki K, Hiratani K, Haga K, Ueyehara T, *Tetrahedron Lett.* 2005, 46, 5867–5869; c) Salim M, Akutsu A, Kimura T, Minabe M, Karikomi M, *Tetrahedron Lett.* 2011, 52, 4518–4520; d) Salim M, Ubukata H, Kimura T, Karikomi M, *Tetrahedron Lett.* 2011, 52, 6591–6593; e) Karikomi M, Toda M, Sasaki Y, Shibuya M, Yamada K, Kimura T, Minabe M, Hiratani K, *Tetrahedron Lett.* 2014, 55, 7099–7101; f) Hasan M, Pandey AD, Khose VN, Mirgane NA, Karnik AV, *Eur. J. Org. Chem* 2015, 3702–3712; g) Matsuno T, Koyama Y, Hiroto S, Kumar J, Kawai T, Shinokubo H, *Chem. Commun* 2015, 51, 4607–4610; h) Sako M, Takeuchi Y, Tsujihara T, Kodaera J, Kawano T, Takizawa S, Sasai H, *J. Am. Chem. Soc* 2016, 138, 11481–11484; [PubMed: 27574874] i) Hasan M, Khose VN, Pandey AD, Borovkov V, Karnik AV, *Org. Lett* 2016, 18, 440–443. [PubMed: 26785298]
- [13]. Shyam Sundar M, Bedekar AV, *Org. Lett* 2015, 17, 5808–5811. [PubMed: 26571302]
- [14]. Shyam Sundar M, Sahoo S, Bedekar AV, *Tetrahedron: Asymmetry* 2016, 27, 777–781.
- [15]. a) Ito N, Hirose T, Matsuda K, *Org. Lett* 2014, 16, 2502–2505; [PubMed: 24749957] b) Stöhr M, Boz S, Schär M, Nguyen M-T, Pignedoli CA, Passerone D, Bernard Schweizer W, Thilgen C, Jung TA, Diederich F, *Angew. Chem. Int. Ed* 2011, 50, 9982–9986; *Angew. Chem.* 2011, 123, 10158–10162.
- [16]. Helicene like compounds: Jierry L, Harthong S, Aronica C, Mulatier J-C, Guy L, Guy S, *Org. Lett* 2012, 14, 288–291; [PubMed: 22176157] Talele HR, Sahoo S, Bedekar AV, *Org. Lett* 2012, 14, 3166–3169; [PubMed: 22671695] Bensalah-Ledoux A, Pitrat D, Reynaldo T, Srebro-Hooper M, Moore B, Autschbach J, Crassous J, Guy S, Guy L, *Chem. Eur. J* 2016, 22, 3333–3346; [PubMed: 26797752] Shyam Sundar M, Bedekar AV, *RSC Adv.* 2016, 6, 46258–46269.
- [17]. a) Yamato T, Hideshima C, Surya Prakash GK, Olah GA, *J. Org. Chem* 1991, 56, 3192–3194; b) Arienti A, Bigi F, Maggi R, Moggi P, Rastelli M, Sartori G, Trere A, *J. Chem. Soc., Perkin Trans 1* 1997, 1391–1395; c) Cui Y, Ngo HL, Lin B, *Inorg. Chem* 2002, 41, 1033; [PubMed: 11874332] d) Areephong J, Ruangsupapichart N, Thongpanchang T, *Tetrahedron Lett.* 2004, 45, 3067–3070.
- [18]. a) Nakano K, Hidehira Y, Takahashi K, Hiyama T, Nozaki K, *Angew. Chem. Int. Ed* 2005, 44, 7136–7138; *Angew. Chem.* 2005, 117, 7298–7300; b) Schneider JF, Nieger M, Nättinen K, Dötz KH, *Synthesis* 2005, 1109–1124; c) Wang B, Li M, Xu S, Song H, Wang B, *Synthesis* 2007, 1304–1308; d) Irie R, Tanoue A, Urakawa S, Imahori T, Igawa K, Matsumoto T, Tomooka K, Kikuta S, Uchida T, Katsuki T, *Chem. Lett* 2011, 40, 1343–1345.
- [19]. Talele HR, Gohil MJ, Bedekar AV, *Bull. Chem. Soc. Jpn* 2009, 82, 1182–1186.
- [20]. a) Brooks PR, Wirtz MC, Vetelino MG, Rescek DM, Woodworth GF, Morgan BP, Coe JW, *J. Org. Chem* 1999, 64, 9719–9721; b) Kuo LH, Ke DS, Lin CD, Jwo SS, Chang WH, *US20040024239*, 2004; c) Magano J, Chen MH, Clark JD, Nussbaumer T, *J. Org. Chem* 2006, 71, 7103–7105. [PubMed: 16930076]
- [21]. Olah GA, Husain A, Gupta BGB, Narang SC, *Angew. Chem. Int. Ed* 1981, 20, 690; *Angew. Chem.* 1981, 93, 705–706.
- [22]. a) Feringa B, Wynberg H, *Tetrahedron Lett.* 1977, 18, 4447–4450; b) Yamamoto K, Noda K, Okamoto Y, *J. Chem. Soc., Chem. Commun* 1985, 1065–1066; c) Noji M, Nakajima M, Koga K, *Tetrahedron Lett.* 1994, 35, 7983–7984; d) Terrasson V, Roy M, Moutard S, Lafontaine M-P, Pèpe G, Félix G, Gingras M, *RSC Adv.* 2014, 4, 32412–32414; e) Takizawa S, Kodaera J, Yoshida Y, Sako M, Breukers S, Enders D, Sasai H, *Tetrahedron* 2014, 70, 1786–1793.

- [23]. [CCDC 1527971](#) [for (±)-1] and [1816361](#) [for (S)-10] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from [The Cambridge Crystallographic Data Centre](#).
- [24]. a)Fabbri D, Delogu G, Lucchi OD, J. Org. Chem 1995, 60, 6599–6601;b)Kolotuchin SV, Meyers AI, J. Org. Chem 1999, 64, 7921–7928;c)Yudin AK, Martyn LJP, Pandiaraju S, Zheng J, Lough A, Org. Lett 2000, 2, 41–44; [PubMed: 10814241] d)Li Z, Liang X, Wu F, Wan B, Tetrahedron: Asymmetry 2004, 15, 665–669;e)Oertling H, Reckziegel A, Surburg H, Bertram H-J, Chem. Rev 2007, 107, 2136–2164. [PubMed: 17488063]
- [25]. a)Murayama K, Oike Y, Furumi S, Takeuchi M, Noguchi K, Tanaka K, Eur. J. Org. Chem 2015, 1409–1414;b)Oyama H, Akiyama M, Nakano K, Naito M, Nobusawa K, Nozaki K, Org. Lett 2016, 18, 3654–3657. [PubMed: 27400646]
- [26]. a)Engheta N, Pelet P, Opt. Lett 1989, 14, 593–601; [PubMed: 19752907] b)Guy S, Bensal-Ledoux A, Stoita-Crisan A, PIER B 2010, 24, 155–172.
- [27]. Blackmore PR, Kilner C, Milicevic SD, J. Org. Chem 2006, 71, 8212–8218. [PubMed: 17025314]
- [28]. a)Muller G, in Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials, First Edition (Ed.: de Bettencourt-Dias A), John Wiley & Sons, Inc.: Chichester, United Kingdom, 2014, Chapter 3, pp. 77–124;b)Sanchez-Carnerero EM, Agarrabeita AR, Moreno F, Maroto BL, Muller G, Ortiz MJ, de la Moya S, Chem. Eur. J 2015, 21, 13488–13500; [PubMed: 26136234] c)Riehl JP, Muller G, in Comprehensive Chiroptical Spectroscopy, First Edition (Eds.: Berova N, Polavarapu PL, Nakanishi K, Woody RW), John Wiley & Sons, Inc.: Hoboken, New Jersey, 2012, Vol. 1: Instrumentation, Methodologies, and Theoretical Simulations, Chapter 3, pp. 65–90.
- [29]. Raouafi S, Aloui F, Raouafi A, Hassine BB, C. R. Chim 2017, 20, 697–703.
- [30]. Zhang T, Huang X, Wu L, Eur. J. Org. Chem 2012, 3507–3519.

Figure 1.
ORTEP diagram of **1**.

Figure 2.
ORTEP of (S)-10.

Figure 3.
List of optically pure helicenes **1** & helicenes-like compounds **2** prepared.

Figure 4.

Circular Dichroism spectra of resolved helicene like (a) (Black Line) (*S*)-2 and (Red Line) (*R*)-2 at a concentration of 1.0×10^{-5} mol in chloroform at 25 °C; helicene (b) (Red Line) (*P*)-1 and (Black Line) (*M*)-1 at a concentration of 2.1×10^{-4} mol in DMSO at 25 °C.

Figure 5.

CPL (upper curve) and total luminescence (lower curve) spectra of (P)/(M)-1 (left) and (P)/(M)-2 (right) in 3.2 mM AR grade DMSO at 295 K, upon excitation at 367/388 and 388/395 nm, respectively [black for (P) and red for (M)].

Scheme 1.
Synthesis of 6-cyano-2-hydroxy phenanthrene (**7**).

Scheme 2.
Synthesis of oxa[7]helicenes **1**.

Scheme 4.

Separation of isomers of **8** by making diastereomer **10**.

Scheme 5. Regeneration of chiral **8** and synthesis of chiral **1** and **2**.

Table 1.Conditions studied for cleavage of methoxy group of **6**.^[a]

No	Additive	7 (% Y)	6 (% Y)
1	-	37	63
2	TBAB (0.1 equiv.)	51	49
3	Mont-K10 (40 % w/w)	73	25
4	Mont-K10 (100 % w/w)	82	16
5	4A MS (40 % w/w)	65	32
6	4A MS (100 % w/w)	85	12

^[a]LiBr (2 equiv.), DMF, 180 °C, 24 h.

Table 2.Photophysical properties of **1** and **2**.

Compound	λ_{abs} [nm]	λ_{ems} [nm]	Stokes Shift [nm]
1	323	421	98
2	310	439	129

Table 3.Chiroptical properties of isomers of **8**, **2** and **1**.

	(<i>R</i>)- 8	(<i>S</i>)- 8	(<i>R_a</i>)- 2	(<i>S_a</i>)- 2	(<i>M</i>)- 1	(<i>P</i>)- 1
$[\alpha]^{[a]}$	-150	+157	-515	+543	-755	+790
$[\phi]^{[b]}$	-655	+685	-2310	+2433	-3160	+3306

 $^{[a]}$ Specific optical rotation, $c = 0.1$, in DMSO. $^{[b]}$ Molecular optical rotation; (*R*)-**8**, (*R_a*)-**2** and (*M*)-**1** = 96 % *ee*; (*S*)-**8**, (*S_a*)-**2** and (*P*)-**1** = 99 % *ee*.