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2-Bromo[6]helicene as a key intermediate for [6]helicene functionalization

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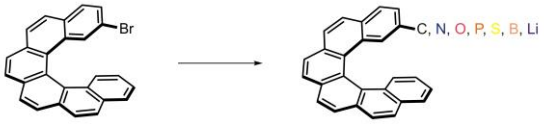


Abstract

The synthesis of 2-bromo[6]helicene was revised and improved up to 51% yield. Its reactivity was thoroughly investigated and a library of 17 different carbon, boron, nitrogen, phosphorus, oxygen and sulfur substituted derivatives was prepared. The racemization barrier for 2-bromo[6]helicene was determined and the usage of enantiomers in the synthesis of optically pure helicenes was rationalized. The three most energy-demanding reactions using enantiomerically pure 2-bromo[6]helicene were tested in order to confirm the predicted enantiomeric excess.

Introduction

Helicenes are a class of helically chiral compounds which possess a fully conjugated aromatic system[1]. Their highly delocalized π-electron system along with the inherent chirality predicts unique optical and electronic properties. Helicenes exhibit high values of specific rotation[2], strong circular dichroism[3], electroluminescence[4,5], circularly polarized luminescence[6,7], and non-linear optical properties[8–11]. Furthermore, helicenes have revealed semiconductive behavior[12,13]. All these properties predetermine their utilization in a wide range of applications in organic electronic devices[14–16]. These molecules have proved to be useful in asymmetric catalysis, both as ligands or as organocatalysts[17–19]. Helicenes can be also used as building blocks in functional polymers[20].

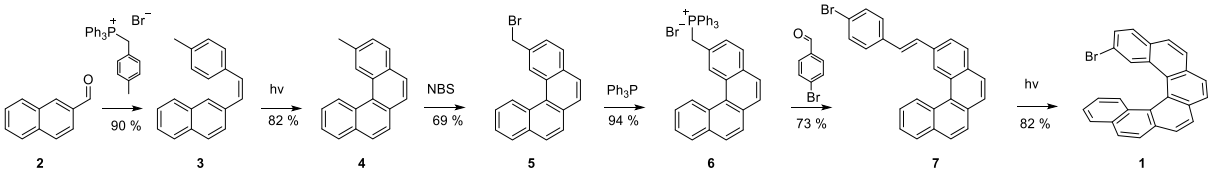
Generally, two methods can be employed for the synthesis of helicene-based molecules: a suitable substituent can be introduced to the molecule of a helicene precursor before the final cyclization step[21], or the appropriate helicene-based compound can be functionalized after cyclization[16,22]. Despite the fact that 2-bromo[6]helicene **1**, first described in 1972[23], offers plenty of possibilities for similar derivatization owing to the versatility of the bromine atom, it was scarcely used for further reactions in the past. There were only few exceptions, mainly focused on reverse preparation of unsubstituted [6]helicene in order to retain some specific properties of the original material. For example, this approach was employed in the crucial attribution of the dextrorotation to the (*P*)-helicene enantiomer[23]. Other synthetic utilizations of 2-bromo[6]helicene have not been found. Since the reactivity of **1** is somewhat different from other bromo-substituted aromatic compounds and the

availability of this compound is limited, the potential of this molecule in helicene chemistry remains unexploited.

In this article, we present a revised synthesis of this compound, featuring shorter and more efficient synthetic pathway when compared to the original synthesis[23]. Similarly to our previous study on 9-bromo[7]helicene[24], we present a coherent exploration of its reactivity, providing robust procedures for preparation of 17 different compounds. The emphasis is on high-yielding metal catalyzed cross-coupling reactions and microwave-assisted synthesis. Furthermore, the racemization barrier was determined and the synthesis of optically pure derivatives from 2-bromo[6]helicene enantiomers was rationalized.

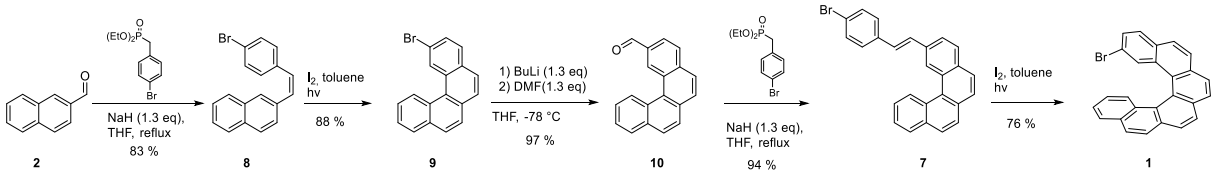
Results and discussion

The synthetic procedure for preparation of 2-bromo[6]helicene **1** was first published in 1972[23] and is shown in Scheme 1. The key reactions in the 6-step sequence are Wittig reactions, providing two stilbene-like precursors **3** and **7**, and the subsequent photocyclization taking place under irradiation by a medium-pressure mercury vapor lamp. However, there are two low-yielding reactions, which significantly decrease the overall yield of the synthesis to only 28 %. The first problematic step is a radical bromination of **4**, which provides the benzylic bromide **5** in 69 % yield, and the other is the second Wittig reaction of **6** with 73 % yield.



Scheme 1: Original synthesis of **1**.

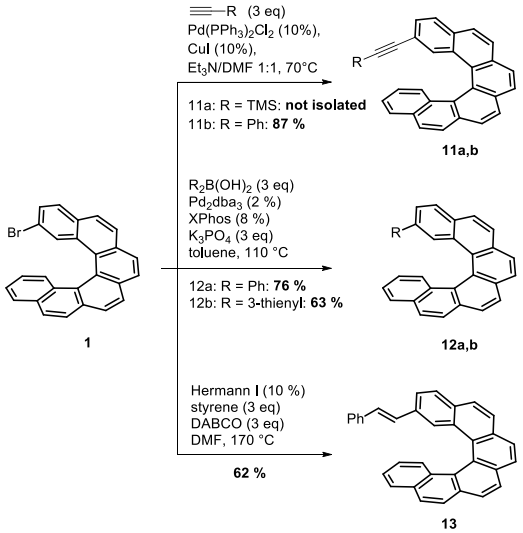
In order to avoid the low-yielding reaction steps, the original synthesis was revisited and several improvements were implemented (Scheme 2). The key benzo[*c*]phenanthrene precursor **5** containing a bromomethylene group was replaced by precursor **10** possessing a carbonyl group. This measure in fact reduced the number of reaction steps needed for 2-bromo[6]helicene **1** preparation by one. Furthermore, the Horner-Wadsworth-Emmons reaction employing easily prepared diethyl(4-bromobenzyl)phosphonate was utilized for both stilbene-forming steps instead of the Wittig reaction. Both photocyclization reactions were performed in a flow reactor, which greatly reduced the reaction time and solvent consumption of the process. All above-mentioned improvements increased the overall yield of the reaction sequence from the original 28 % up to 51 %.



Scheme 2: Improved synthesis of **1**.

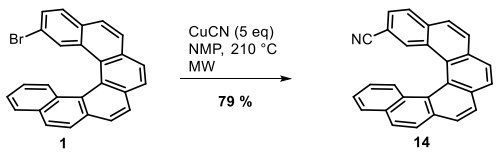
The optimization of 2-bromo[6]helicene **1** synthesis was followed by a rigorous screening of its reactivity, since the bromine atom unlocks the possibility of introducing a plethora of substituents

into position 2 of the helicene skeleton. The formation of C-C bonds via cross-coupling reactions represents one of the main areas of interest and therefore Sonogashira, Suzuki-Miyaura and Heck coupling reactions were tested (Scheme 3). The reaction of **1** with (trimethylsilyl)acetylene provided product **11a** in conversions only up to 20 %, while using phenylacetylene under the same conditions of Sonogashira coupling provided full conversion and product **11b** was isolated in 87 % yield. The low conversion in the first case can be attributed to the higher steric demands of trimethylsilyl in the proximity of a helicene moiety in comparison with a phenyl substituent. 2-Phenyl[6]helicene **12a** was formed in 76 % yield in Suzuki-Miyaura coupling in the presence of Pd_2dba_3, XPhos, K_3PO_4 and phenylboronic acid. A similar reaction conducted with heteroarylboronic acids can be used to introduce different heteroatoms to the molecule, e.g. reaction with 3-thienylboronic acid provides 2-(thien-3-yl)[6]helicene **12b** in 63 % yield. Moreover, 2-styryl[6]helicene **13** was prepared in 62 % yield when trans-bis(acetato)bis[o-(di-o-tolylphosphino)benzyl]dipalladium(II) known as Hermann I precatalyst in the presence of DABCO and styrene were used. The latter is particularly intriguing, as the stilbene-like product potentially allows for the extension of the helicene system via photocyclization as proposed by Martin[22].



Scheme 3: C-C couplings of **1**

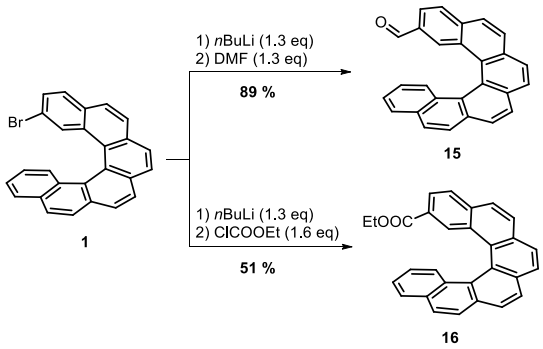
Rosemund-von Braun cyanation (Scheme 4) was chosen as another example of metal promoted process providing 2-cyano[6]helicene **14** (79 % yield), another readily transformable intermediate for further derivatization. This reaction was also performed in a microwave reactor, therefore the full conversion is achieved in less than 3 hours.



Scheme 4: Rosemund-von Braun reaction of **1**.

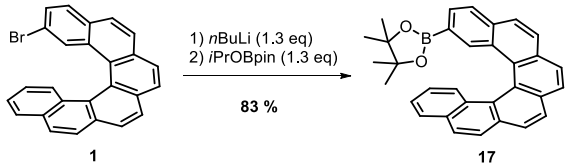
The cyano compound **14** can be used for preparation of various carbonyl group-containing derivatives, however it is more convenient to prepare these directly by the reaction of carbon

electrophiles with helicene nucleophile generated by alkyllithium. Reaction of DMF or ethyl chloroformate and acidic workup gives [6]helicene-2-yl carbaldehyde **15** or carboxylic acid ester **16,** respectively (Scheme 5). Yields of the reaction are highly dependent on the stability of the lithiated intermediate. When the lithiation is conducted at -78 °C for 30 minutes, carbaldehyde **15** is isolated in 54 % yield. Lowering the temperature to -98 °C in a N_2(l)/MeOH cooling bath leads to a slight increase in isolated yield (63 %). A significant improvement is achieved when the lithiation time is reduced to only 1 minute before the addition of DMF. This adjustment provided 89 % yield of product **15**. The remaining material can be recovered as unsubstituted [6]helicene.



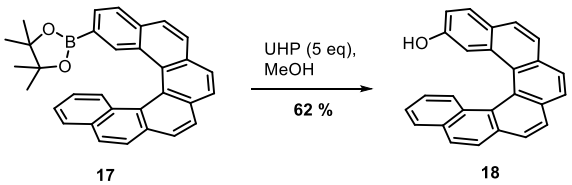
Scheme 5: Lithiation of **1** and reaction with carbon electrophiles.

Similarly, lithiated helicene can react with heteroatom electrophiles. Using the above-mentioned conditions for lithiation, helicene-2-yl pinacol boronate **17** can be prepared in 83 % yield (Scheme 6). The same compound can also be prepared by Pd-catalyzed borylation with bis(pinacolato)diboron, however only in 39% yield. This derivative can be used as a transmetallating agent in a Suzuki-Miyaura reaction.



Scheme 6: Lithiation of **1** and reaction with boron electrophile.

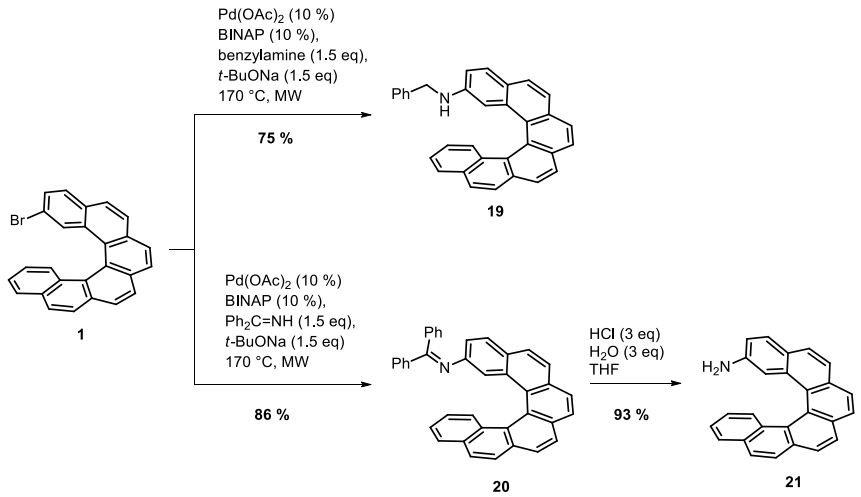
Hydroxyl groups are another in-demand functionalities. They can be obtained by *ipso*-oxidation of boronates using urea-hydrogen peroxide adduct (UHP) from precursor **17**[25]. Upon overnight stirring of the reaction mixture, it is possible to obtain 2-hydroxy[6]helicene **18** in 62 % yield (Scheme 7).



Scheme 7: 2-Hydroxy [6]helicene **18** synthesis via *ipso*-oxidation of boronate **17**.

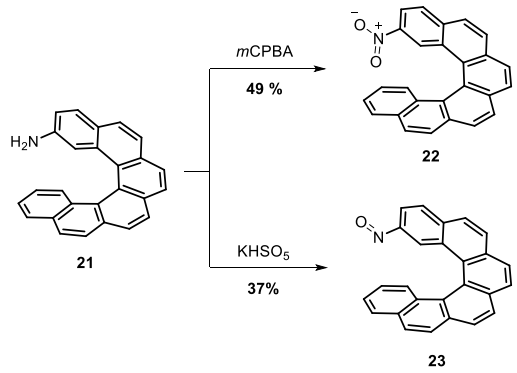
Buchwald-Hartwig amination is one of the most effective ways for preparation of aryl amines[26]. In our case, this palladium catalyzed process was used in reaction of **1** with benzylamine and benzophenone imine. The reactants accompanied by palladium acetate, BINAP and sodium *tert*-

butoxide afforded products in very good yields of 75 % (**19**) and 86 % (**20**) respectively (Scheme 8). Microwave irradiation reduced the time needed for full conversion to less than 2 hours. 2-Amino[6]helicene **21** was obtained after acidic hydrolysis of imine precursor **20** in 93 % yield.



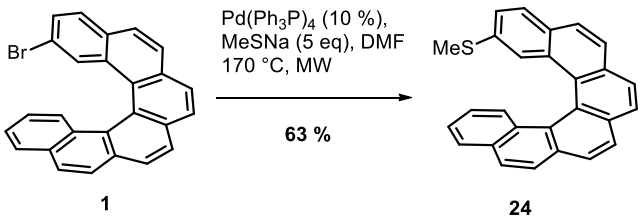
Scheme 8: Buchwald-Hartwig amination of **1**.

Other nitrogen-containing compounds can be prepared by different oxidation techniques. Aminohelicene **21** can be oxidized by excess of 3-chloroperbenzoic acid to a corresponding nitro compound **22** in 49 % yield after recrystallization. When the same substrate is treated with 20 equivalents of potassium peroxymonosulphate in a two-phase solvent system, 2-nitroso[6]helicene **23** can be isolated in 37 % yield (Scheme 9). Vigorous stirring of the reaction mixture is necessary to achieve a sufficient reaction rate and to avoid possible side reactions.



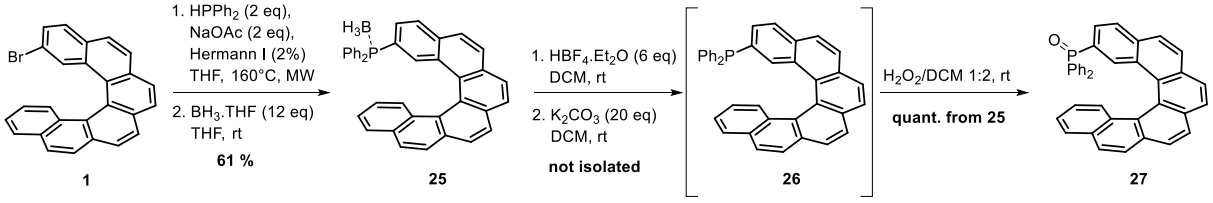
Scheme 9: Oxidation of **21**.

Sulfur-containing compounds are of great importance**,** especially in material and surface chemistry[27,28]. Similarly to our previously published protocol for this reaction on a different substrate[24], 2-(methylsulfanyl)[6]helicene **24** was synthesized in 63 % yield in the presence of $Pd(PPh_3)_4$ and sodium methanethiolate (Scheme 10).



Scheme 10: Introduction of sulfanyl group.

With regard to the possible use of helicenes in asymmetric catalysis, phosphino-helicene **25** was prepared according to the previously published methodology inspired by Kappe[29]. A coupling reaction of diphenylphosphine with 2-bromo[6]helicene **1** in a microwave reactor gave product **25** in 61% yield after borane protection. Protection by the formation of borane complex had to be used, due to the rapid oxidation of free phosphine **26** to the corresponding phosphine oxide **27**. Complex **25** is stable and can be easily deprotected to phosphine **26** by reaction with tetrafluoroboric acid[30]. Phosphine oxide **27** can be prepared quantitatively from phosphine complex **25** after deprotection and subsequent oxidation reaction with hydrogen peroxide in quantitative yield (Scheme 11).



Scheme 11: Preparation of helicenes **25** – **27** bearing different phosphorus functionalities.

All of the above-mentioned reactions were optimized for racemic starting material **1**. Regarding the reaction conditions for derivatization of 2-bromo[6]helicene **1**, some of these reactions can be easily applied also to individual 2-bromo[6]helicene enantiomers resulting in an optically pure functional molecule without significant loss of enantiomeric excess (*ee*). On the contrary, reactions performed above approximately 150°C are generally considered inappropriate for preparation of optically pure helicenes due to their tendency to racemize at elevated temperatures. Three of the described reactions were conducted at significantly elevated temperatures; namely the preparation of phosphanylhelicene **25** (160°C), the Buchwald-Hartwig amination providing aryl amine **19** (170°C), and the Rosemund-von Braun cyanation affording 2-cyano[6]helicene **14** (210°C). In order to judge the suitability of certain conditions for the enantioselective reaction and to predict the *ee* of the products reliably, the racemization barrier of **1** became a matter of interest.

The enantiomers (*M*)-**1** and (*P*)-**1** were isolated using a chiral HPLC and the racemization process was monitored at 185, 192, 202 and 212 °C, subsequently. The determined Gibbs free energy at 465 K (36.5 kcal/mol) was close to that reported for unsubstituted [6]helicene[31,32]. Based on rate constants obtained at different temperatures, a simple prediction of enantiomeric excess for any reaction conditions can be made. The solvent effect, racemization of products and other possible influences were omitted in the first approximation. The prediction was then confronted with the *ee* values obtained by enantioselective reactions. Phosphanylhelicene (*P*)-**25** was prepared with 99 %*ee* after 60 minutes at 160 °C compared to 99 %*ee*. 2-Benzylamino[6]helicene (*P*)-**19** was obtained with 96 %*ee* after 120 minutes at 170 °C compared to the calculated 96 %*ee*, which is in excellent agreement with the prediction. Contrary to the predicted 24 %*ee*, the preparation of 2-cyano[6]helicene (*M*)-**14** provided only 1 %*ee* after 60 minutes at 210 °C. The collected data clearly indicate that a reaction conducted for several hours at a temperature up to 160 °C can be used for derivatization of (*P*)-**1** or (*M*)-**1** without a significant decrease in helicene enantiopurity (see SI for details).

Conclusion

2-bromo[6]helicene **1** was shown to be a suitable starting material for synthesis of functional molecules based on a [6]helicene skeleton. The method of 2-bromo[6]helicene **1** preparation was revised and improved, bringing the overall yield up to 51 % over 5 steps. Its reactivity was investigated and a library of 17 different carbon, boron, nitrogen, phosphorus, oxygen and sulfur substituted derivatives bearing a [6]helicene-2-yl moiety was synthesized including 13 previously unknown [6]helicene derivatives. Thermodynamic data for the racemization barrier of 2-bromo[6]helicene **1** were determined. The effect of reaction conditions on racemization in reactions using pure enantiomer was rationalized. Three of the most energetically demanding reactions were performed with pure enantiomer **1** providing enantiomeric excesses of the products close to the predicted values. Therefore, the individual enantiomers of 2-bromo[6]helicene **1** can also be utilized in the synthesis of optically pure [6]helicene derivatives opening further applications of these molecules in various fields of chemistry and material science.

Experimental Section

^{1}H, $^{13}C\{^{1}H\}$, ^{19}F, ^{31}P and $^{31}P\{^{1}H\}$, ^{11}B and $^{11}B\{^{1}H\}$ spectra were recorded using Bruker Avance 400 and Varian Inova 500 MHz instruments. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, $CFCl_3$ and ext. H_3PO_4 and 15 % $BF_3.OEt_2$ or referenced to residuals of $CDCl_3$ (δ = 7.26 ppm and δ = 77.00 ppm, respectively); CD_2Cl_2 (δ = 5.30 ppm and 54.00 ppm respectively) and CD_3CN (δ = 1.94 ppm and 118.69 ppm respectively). The coupling constants J are given in Hz. For the correct assignment of both the ^{1}H and ^{13}C NMR spectra of key compounds, COSY, HSQC, and HMBC experiments were performed. Electron impact (EI) mass spectra were measured at an ionizing voltage of 70 eV in a positive mode and the *m/z* values are given along with their relative intensities (%). For exact mass measurement, the spectra were internally calibrated using Na-formate or APCI-TOF tuning mix. ESI and APCI high-resolution mass spectra were measured in positive mode using a micrOTOF QIII mass spectrometer (Bruker) and were determined by software Compass Data Analysis. Infrared spectroscopy spectra were determined on a Nicolet 6700 in chloroform. TLC was performed on Silica gel 60 F_{254}- or 60 RP-18 F_{254} aluminum sheets and compounds were visualized by UV light (254 and 366 nm) or PMA solution. Column chromatography was performed on an HPFC Biotage SP1 or Isolera One system with pre-packed flash silica gel or C_{18} columns. The standard Schlenk technique was used for all reactions; cannula filtration technique was used for filtrations under inert atmosphere. Microwave experiments were performed on an Anton Paar Monowave 300 equipped with simultaneous temperature measurement with IR and a fiber optic sensor. Commercially available reagent-grade materials were used as received. Diethyl 4-bromobenzylphosphonate[33] and Herrmann I precatalyst (trans-bis(acetato)bis[o-(di-o-tolylphosphino)benzyl]dipalladium(II))[34] were prepared according to published procedures. Solvents were degassed by five freeze-pump-thaw cycles. Tetrahydrofuran and toluene were freshly distilled from sodium/benzophenone under an atmosphere of argon. The *ee* values were determined by integration of UV traces (255 nm) of HPLC chromatograms (at Varian ProStar 230 SDA + ProStar 330 PDA detector (200 – 400 nm). The HPLC analyses were performed on Kromasil Cellucoat (Akzo Nobel) column (250 x 4.6 mm, 10 μm) using *n*-heptane/2-propanol (99.65:0.35 for **1**, 99.25:0.75 for **14**, 98.75:1.25 for **19** and 99.5:0.5 for **25**) as mobile phase at a flow rate of 2 mL/min (approx. 102 atm at 28 °C). Specific rotations were measured at 589 nm in chloroform at 20 °C on JASCO P-2000 Polarimeter and are given in deg cm^3 g^{-1} dm^{-1} as an average value from 50 measurements. All melting points are uncorrected and were taken on Kofler melting point apparatus with microscope.

2-(4-Bromostyryl)naphtalene (**8**). A round bottom flask was charged with sodium hydride (60% in mineral oil, 0.27 g, 6.7 mmol, 1.05 eq) under Ar and dry THF (50 mL) was added. Into the suspension, diethyl 4-bromobenzylphosphonate (2.06 g, 6.7 mmol, 1.05 eq) was added dropwise and stirred for 10 minutes. 2-Napthaldehyde (1 g, 6.4 mmol, 1 eq) was dissolved in dry THF (30 mL) and added dropwise. The mixture was heated up to 50 °C and stirred overnight. Reaction was quenched with water (100 mL) and THF was evaporated. The suspension was filtered, collected precipitate was dissolved in dichloromethane, dried over magnesium sulfate and evaporated. The residue was then filtered through a pad of silicagel, eluting with petroleum ether. Volatiles were removed to yield 2-(4-bromostyryl)naphthalene **8** (1.65 g, 83%) in the form of white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.79 (m, 4H), 7.73 (dd, J_1 = 8.7 Hz, J_2 = 1.7 Hz, 1H), 7.53–7.40 (m, 6H), 7.27 (d, J = 16.3 Hz,

1H), 7.16 (d, J = 16.3 Hz, 1H). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{18}H_{14}Br$ 309.0273; found 309.0278. Spectra are in accordance with known literature[35].

2-Bromobenzo[c]phenantrene (**9**). 2-(4-Bromostyryl)napthalene **8** (4 g, 13 mmol, 1 eq) was dissolved in 4 L of toluene and iodine (300 mg, 1.18 mmol, 15 mol%) was added into the mixture. The mixture was pumped through flow photoreactor (300 m of capillary (ID = 2 mm), 6 x 400 W medium pressure mercury discharge lamps, 50 mL/min). After the reaction, the mixture was washed through a column with a layer of sodium thiosulfate (50 g) and a layer of silicagel (30 g). The solvents were evaporated and crude product recrystallized from methanol, yielding 2-bromobenzo[*c*]phenantrene **9** as a white solid (2.43 g, 61%). The rest of the reaction mixture was purified by column chromatography with 30:1 hexane/ethylacetate, yielding an additional 1.07 g (27%) of white powder. The combined yield of the reaction was 3.50 g of 2-bromobenzo[*c*]phenantrene **9** (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.29 (d, J = 1.8 Hz, 1 H), 9.05 (d, J = 8.5 Hz, 1H), 8.03 (dd, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.86–7.85 (m, 2H), 7.82 (d, J = 8.5 Hz, 1H), 7.74 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.5 Hz, 1H), 7.71 (dd, J_1 = 6.7 Hz, J_2 = 1.9 Hz, 1H), 7.66 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.2 Hz, 1H). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{18}H_{12}Br$ 307.0116; found 307.0115. Spectra are in accordance with known literature[36].

Benzo[c]phenantrene-2-carbaldehyde (**10**). 2-Bromobenzo[*c*]phenantrene **9** (6.26 g, 20.4 mmol, 1 eq) was dissolved in dry tetrahydrofurane (150 mL) under Ar atmosphere and cooled down to -78 °C. *n*BuLi (2.5M, 10.6 mL, 26.5 mmol, 1.3 eq) was added dropwise and the mixture was stirred for an hour. Afterwards, *N,N*-dimethylformamide (4 mL, 51.7 mmol, 2.53 eq) was added and the reaction was stirred for additional 1 hour. Excessive *n*BuLi was quenched by MeOH (10 mL), reaction mixture was extracted with dichloromethane (3x100 mL), and combined organic layers were dried over magnesium sulfate, filtered and solvents evaporated. Crystallization from DCM/MeOH gave 5.07 g (97 %) of white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.29 (s, 1H), 9.60 (s, 1H), 9.08 (d, J = 8.4 Hz, 1H), 8.16–8.09 (m, 2H), 8.08 (dd, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 1H), 8.02–7.94 (m, 3H), 7.87 (d, J = 8.5 Hz, 1H), 7.78 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.5 Hz, 1H), 7.70 (ddd, J_1 = 7.0 Hz, J_2 = 7.0 Hz, J_3 = 1.2 Hz, 1H). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{19}H_{13}O$ 257.0961; found 257.0959. Spectra are in accordance with known literature[37].

2-(4-Bromostyryl)benzo[c]phenantrene (**7**). A Round bottom flask was charged with sodium hydride (40%, 0.71 g, 17.8 mmol, 1.01 eq) under Ar atmosphere and dry THF (100 mL) was added. Into the suspension, diethyl (4-bromobenzyl)phosphonate (5.4 g, 17.6 mmol) was added dropwise and stirred for 10 minutes. Benzo[c]phenantrene-2-carbaldehyde **10** (3.5 g, 13.7 mmol) was dissolved in dry THF (70 mL) and added dropwise. The mixture was heated up to 50 °C and stirred overnight. The reaction was quenched with water (100 mL) and THF was evaporated. The mixture was filtered; precipitate was dissolved in dichloromethane, dried over $MgSO_4$ and filtered through the silicapad. DCM was evaporated and residual volatiles removed by high vacuum, yielding 2-(4-bromostyryl)benzo[*c*]phenantrene **7** (5.25 g, 94 %) as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (d, J = 8.2 Hz, 2H), 8.05 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.94–7.79 (m, 5H), 7.77–7.71 (m, 1H), 7.69–7.63 (m, 1H), 7.54–7.46 (m, 4H), 7.37 (d, J = 16.3 Hz, 1H), 7.22 (d, J = 16.3 Hz, 1H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ 136.3, 134.8, 133.5, 133.2, 131.8 (2C), 131.3, 130.6, 130.3, 130.0, 129.0, 128.6, 128.0 (2C), 127.8, 127.7, 127.6, 127.33, 127.32, 127.10, 127.04, 126.9, 126.3, 125.9, 123.1, 121.4. IR ($CHCl_3$, ν cm^{-1}): 1627, 1326, 985, 962, 827, 607, 411. EI MS: 408 (100 %, M^+), 328 (46 %), 313 (22 %), 300 (17 %), 226 (20 %), 164 (39 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{26}H_{18}Br$ 409.0586; found 409.0580.

2-Bromo[6]helicene (**1**). 2-(4-Bromostyryl)benzo[*c*]phenantrene **7** (2 g, 4.9 mmol, 1 eq) was dissolved in 4 L of toluene and iodine (200 mg, 1.58 mmol) was added. The mixture was pumped through flow photoreactor (300 m of capillary (ID = 2 mm), 6 x 400 W medium pressure mercury discharge lamps, 50 mL/min). After the reaction, the mixture was washed trough the column with a layer of sodium thiosulfate (50 g) and a layer of silicagel (30 g). Solvents were evaporated and crude product recrystallized from DCM/MeOH to yield 1.51 g (76 %) of yellow powder. Mp = 253–254 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–7.94 (m, 7H), 7.90–7.85 (m, 2H), 7.74 (d, J = 1.7 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1 H), 7.56 (d, J_1 = 8.6 Hz, 1H), 7.34–7.28 (m, 2 H), 6.74 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.3 Hz, 1H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ 133.1, 132.2, 131.6, 131.5, 131.0, 130.5, 130.2, 129.6, 128.9, 128.5, 128.1, 127.8, 127.6, 127.5, 127.5, 127.3, 127.08, 127.07, 126.9, 126.8, 126.7, 126.2, 125.9, 124.7, 123.9, 119.1. IR ($CHCl_3$, ν cm^{-1}): 3050, 1603, 1519, 1509, 1472, 1437, 1375, 1192, 1143, 1079, 1043, 1035, 961, 909, 867, 848, 824, 686, 621, 571, 480, 427. EI MS: 408 (87 %, $M^{\cdot+}$), 406 (82 %), 326 (94 %), 300 (100 %), 162 (43 %). HRMS (ESI/QTOF) *m/z* $[M]^+$ Calcd for $C_{26}H_{15}Br$ 409.0413; found 409.0417. Chiral separation: t_R = 6.17 min ((-)-**1**), 13.27 min ((+)-**1**). Specific rotation of dextrorotatory (+)-**1** and levorotatory (-)-**1** were measured in $CHCl_3$ $[\alpha]_D^{20}$ = +3494 ± 4° (c 0.0534) and $[\alpha]_D^{20}$ = −3456 ± 6° (c 0.0622). Mp = 282–284 °C ((+)-**1**), Mp = 281–283 °C ((-)-**1**).

2-(2-trimethylsilylethyn-1-yl)[6]helicene (**11a**). Compound **11a** was prepared according to the procedure described in **11b**. Due to the low conversion (GC-MS), product was not isolated. **EI MS:** 424 (100 %, $M^{+\cdot}$), 409 (13 %), 351 (42%), 337 (26 %), 324 (14 %), 300 (15 %), 207 (19 %).

2-(Phenylethynyl)[6]helicene (**11b**). 2-Bromo[6]helicene **1** (100 mg, 0.25 mmol, 1 eq) tetrakis(triphenyl)palladium (17 mg, 0.02 mmol) and copper (I) iodide (4 mg, 0.02 mmol) were dissolved in dimethylformamide (2 mL) and trimethylamine (2 mL) under argon atmosphere. Phenylacetylene (82 μL, 0.75 mmol, 3 eq) was added into the reaction. The reaction mixture was

stirred under Ar atmosphere at 70°C overnight. After the reaction an aqueous solution of ammonium chloride (20 mL, 25% V/V aqueous solution) was added and the product was extracted with ethyl acetate (20 mL). The organic layer was washed with HCl (20 mL, 10% V/V aqueous solution) and brine (20 mL, saturated solution). Then, the organic layer was dried over magnesium sulfate, filtered, and the solvent was evaporated at the reduced pressure. Flash-chromatography (petroleum ether / ethyl acetate 30:1) gave 2-(phenylethynyl)[6]helicene **11b** (91 mg, 87%) as a yellow powder. Mp = 65–66 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07–7.93 (m, 7H), 7.89 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.81–7.76 (m, 2H), 7.59 (d, J = 8.5 Hz, 1H), 7.35–7.29 (m, 6H), 7.28–7.25 (m, 1H), 6.74 (ddd, J_1 = 6.8 Hz, J_2 = 6.8 Hz, J_3 = 1.0 Hz, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 133.2, 132.13, 132.11, 131.5, 131.42, 131.41 (2C), 131.2, 129.7, 129.3, 128.2 (2C), 127.91, 127.90, 127.8, 127.7, 127.6, 127.5, 127.42, 127.40 (2C), 127.34, 127.30, 127.13, 127.12, 126.9, 126.2, 125.9, 124.7, 124.0, 123.5, 119.4, 89.4, 88.5. IR ($CHCl_3$, ν cm^{-1}): 3086, 2205, 1598, 1571, 1490, 1443, 1156, 1070, 1037, 691, 623, 524. EI MS: 428 (100 %, $M^{+\cdot}$), 427 (85 %), 425 (15 %), 424 (37 %), 411 (24 %), 337 (34 %), 206 (38 %). HRMS (APCI/QTOF) *m/z* $[M]^+$ Calcd for $C_{34}H_{20}$ 428.1559; found 428.1554.

2-Phenyl[6]helicene (**12a**). 2-Bromo[6]helicene **1** (50 mg, 0.123 mmol, 1 eq), $Pd_2dba_3.CHCl_3$ (2.6 mg, 2.5 µmol, 2 mol%), XPhos (4.7 mg, 9.8 µmol, 8 mol%), phenyl boronic acid (37.3 mg, 0.246 mmol, 2 eq) and K_3PO_4 (52 mg, 0.246 mmol, 2 eq) were added to a pre-dried Schlenk flask, which was subsequently secured. Dry toluene (5 mL) was then added and the reaction mixture was heated at 90 °C for 3 h under Ar atmosphere and then cooled to room temperature. The crude reaction mixture was filtered through a short pad of silica gel, eluting with toluene (100 mL). Crude product was recrystallized from a DCM/MeOH mixture to give 2-phenyl[6]helicene **12a** (37.7 mg, 76%) as a pale yellow powder in satisfactory purity. Mp = 206–208 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–7.93 (m, 9H), 7.93–7.85 (m, 2H), 7.77 (d, J = 8.5 Hz, 1H), 7.49 (dd, J_1 = 8.2 Hz, J_2 = 1.8 Hz, 1H), 7.24 (ddd, J_1 = 7.0 Hz, J_2 = 7.0 Hz, J_3 = 1.0 Hz, 1H), 7.22–7.14 (m, 3H), 6.80 - 6.72 (m, 3H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 141.0, 137.9, 133.2, 132.4, 131.6, 131.4, 130.9, 130.1, 129.8, 128.2, 128.12, 128.08 (3C), 127.6, 127.58, 127.56, 127.47, 127.34, 127.31, 127.23 (2C), 127.03, 126.99, 126.73, 126.68 (2C), 126.3, 126.1, 124.92, 124.86, 124.1. IR ($CHCl_3$, ν cm^{-1}): 3083 1602, 1575, 1493, 1140, 1333, 1192, 1075, 1035, 990, 699, 624. EI MS: 404 (100 %, M^+), 387 (10 %) 374 (9 %), 327 (23 %), 313 (9 %), 300 (37 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{32}H_{21}$ 405.1638; found 405.1632.

3-([6]Helicen-2-yl)thiophene (**12b**). A Schlenk flask was charged with 2-bromo[6]helicene **1** (50 mg, 0,123 mmol, 1 eq), $Pd_2(dba)_3.CHCl_3$ (2.5 mg, 2.5 µmol, 2 mol%), XPhos (dicyclohexyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine) (2.3 mg, 4.9 µmol, 4 mol%), (thiophen-3-yl)boronic acid (47.1 mg, 0.368 mmol, 3 eq) and K_3PO_4 (313 mg, 1.473 mmol, 12 eq). The mixture was heated at 90 °C for 3 h in dry toluene (10 mL) under Ar atmosphere and then cooled to room temperature. The crude reaction mixture was filtered through a short pad of silica gel, eluting with toluene (100 mL). Crude product was recrystallized from DCM/MeOH mixture to give 3-([6]Helicen-2-yl)thiophene **12b** (31.5 mg, 63%) as a pale yellow powder in a satisfactory purity. Mp = 206–207 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–7.97 (m, 6H), 7.95 (d, J = 1.5 Hz, 1H), 7.92 (s, 2H), 7.86–7.81 (m, 2H), 7.74 (d, J = 8.6 Hz, 1H), 7.46 (dd, J_1 = 8.2, J_2 = 1.7 Hz, 1H), 7.21 (ddd, J_1 = 7.0 Hz, J_2 = 7.0 Hz, J_3 = 1.0 Hz, 1H), 7.14 (dd, J_1 = 4.9 Hz, J_2 = 3.0 Hz, 1H), 6.75 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.3 Hz, 1H), 6.68 (dd, J_1 = 2.9 Hz, J_2 = 1.3 Hz, 1H), 6.61 (dd, J_1 = 5.0 Hz, J_2 = 1.3 Hz, 1H). ^{13}C NMR {^{1}H}

(126MHz, $CDCl_3$): δ 142.2, 133.2, 132.4, 132.1, 131.6, 131.4, 130.8, 130.1, 129.8, 128.07, 128.06, 128.05, 127.60, 127.58, 127.56, 127.42, 127.35, 127.25, 127.0 (2C), 126.7, 126.3, 126.10, 126.08, 125.8, 125.4, 124.9, 124.4, 124.1, 120.0 ppm. IR ($CHCl_3$, ν cm^{-1}): 3050, 1540, 1405, 1250, 1085, 1033, 848, 830, 684, 657. EI MS: 410 (100 %, M^+), 350 (12 %), 324 (14 %), 313 (10 %), 300 (33 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{30}H_{19}S$ 411.1202; found 411.1205.

2-Styryl[6]helicene (**13**). A pre-dried microwave vial was charged with 2-bromo[6]helicene **1** (50 mg, 0.1228 mmol, 1 eq), Herrmann I catalyst (11.5 mg, 0.0123 mmol, 10 mol%), DABCO (27.5 mg, 0.246 mmol, 2 eq), styrene (25.5 mg, 0.246 mmol, 2 eq) and DMF (4 mL). The reaction mixture was bubbled through with argon and reacted in a microwave reactor for 90 minutes at 150 °C. After the conversion was complete, solvent was removed from the reaction and the residue was dissolved in dichloromethane (20 mL) and washed with brine (3 x 25 mL) and water (25 mL). The organic phase was dried over $MgSO_4$, evaporated and consequently purified by flash chromatography using reverse-phase silica gel and acetonitrile as a mobile phase to give 2-styryl[6]helicene **13** as a pale yellow amorphous solid (32.6 mg, 62 % yield). The *cis*-**13** : *trans*-**13** ratio was estimated from ^{1}H NMR spectrum (approx. 1:5). *trans*-**13**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (m, 4H), 8.02 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.89 (s, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.82 (m, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.33 (m, 5H), 7.23 (m, 1H), 7.21 (ddd, J_1 = 6.8 Hz, J_2 = 6.8 Hz, J_3 = 1.1 Hz, 1H), 6.74 (ddd, J_1 = 6.8 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 6.24 (d, J = 16.0 Hz, 1H). *trans*-**13**: ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 137.4, 134.0, 133.2, 132.1, 131.6, 131.3, 131.3, 129.80, 129.75, 128.5 (2C), 128.21, 128.20, 128.0, 127.9, 127.8, 127.6, 127.54, 127.47, 127.38, 127.33, 127.31, 127.2, 127.01, 127.00, 126.5, 126.23 (2C), 126.20, 126.0, 125.6, 124.7, 124.5, 124.1. *cis*-**13**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (m, 4H), 7.99 (m, 1H), 7.94 (s, 2H), 7.83 (m, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.53 (d, J = 0.8 Hz, 1H), 7.28 (ddd, J_1 = 7.0 Hz, J_2 = 7.0 Hz, J_3 = 1.3 Hz, 1H), 7.14 (m, 3H), 7.04 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 1H), 6.95 (m, 2H), 6.81 (ddd, J_1 = 6.9 Hz, J_2 = 4.9 Hz, J_3 = 1.4 Hz, 1H), 6.29 (d, J = 12.1 Hz, 1H), 5.84 (d, J = 12.1 Hz, 1H). *cis*-**13**: ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 137.1, 134.0, 133.1, 131.9, 131.4, 131.3, 130.8, 130.03, 129.97, 129.87, 129.7, 129.0, 128.9 (2C), 128.5, 127.89 (2C), 127.88, 127.81, 127.78, 127.6, 127.54, 127.51, 127.22, 127.19, 126.89, 126.87, 126.85, 126.81, 126.2 (2C), 125.8, 124.5, 124.0. IR ($CHCl_3$, v cm^{-1}): 3058, 1621, 1600, 1571, 1489, 1447, 1412 (*cis*), 1290, 1177, 1157,1001, 960 (*trans*), 842, 719 (*trans*), 701, 637, 438. EI MS: 430 (100 %), 350 (6 %), 337 (29 %), 326 (21 %), 313 (9 %), 300 (29 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{34}H_{23}$ 431.1794; found 431.1792.

2-Cyano[6]helicene (**14**). 2-Bromo[6]helicene **1** (50 mg, 0.12 mmol, 1 eq) and copper (I) cyanide (55 mg, 0.62 mmol, 5 eq) were dissolved in *N*-methyl-2-pyrrolidone (2 mL) under Ar atmosphere. The reaction was heated in a microwave reactor to 210 °C for 3 hours. After the reaction an aqueous solution of ammonium chloride (20 mL, 25% V/V aqueous solution) was added and the product was extracted with ethyl acetate (2 x 20 mL). Combined organic layers were washed with brine (20 mL, saturated solution), dried over $MgSO_4$, filtered**,** and the solvent was evaporated at the reduced pressure. A recrystallization from DCM/MeOH (1:1) mixture gave 2-cyano[6]helicene **14** (34 mg, 79%) as a light brown powder. The same protocol for synthesis of (*M*)-**14** was used. The reaction ((*M*)-**1,** 10 mg, 0.025 mmol, 1 eq) was conducted at 210 °C for one hour. Crude reaction mixture was analyzed on chiral HPLC (1 %*ee* of (*M*)-**14**). Mp = 269 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d,

J = 1.9 Hz, 1H), 8.08 (d, J = 2.3 Hz, 1H), 8.04 (d, J = 1.1 Hz, 2H), 8.01–7.90 (m, 6H), 7.88 (d, J = 8.2 Hz, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.36 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H), 7.28 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.1 Hz, 1H), 6.69 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 133.41, 133.40, 133.4, 132.2, 131.8, 131.6, 129.7, 129.2, 129.0, 128.6, 128.5, 127.24, 128.22, 128.1, 127.24, 127.22, 127.19, 127.02, 126.98, 126.96, 126.5, 126.2, 126.0, 124.8, 123.7, 118.8, 107.7. IR ($CHCl_3$, ν cm^{-1}): 2229, 555. EI MS: 353 (100 %, $M^{+\cdot}$), 349 (15 %), 325 (26 %), 300 (22 %), 176 (12 %), 161 (13 %), 207 (95 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{27}H_{16}N$ 354.1277; found 354.1272. Chiral separation: t_R = 9.14 min ((-)-**14**), 23.91 min ((+)-**14**).

[6]helicene-2-yl carbaldehyde (**15**). 2-Bromo[6]helicene **1** (100 mg, 0.246 mmol, 1 eq) was placed in a pre-dried flask and secured. Anhydrous THF (10 mL) was added and the reaction mixture was cooled to -78 °C in a dry ice/ethanol bath. *n*-Butyl lithium (2.5M in THF, 128 µl, 0.320 mmol, 1.3 eq) was added dropwise and the reaction mixture was stirred for 1 min at the same temperature, before the addition of anhydrous DMF (23.3 mg, 0.3194 mmol, 1.3 eq). The reaction was stirred for 30 min and then removed from the bath and allowed to warm to room temperature. The reaction mixture was then quenched with diluted HCl (0.5 mL, 10% V/V aqueous solution) and evaporated to dryness. Residue was dissolved in DCM (20 mL) and washed with brine (2 x 20 mL, saturated solution) and water (20 mL). Combined organic phases were then dried over $MgSO_4$, evaporated, and the residue purified using column chromatography with petroleum ether / ethyl acetate 8:1. [6]Helicene-2-yl carbaldehyde **15** was obtained as a beige amorphous solid (77.8 mg, 89 % yield). Mp = 238–240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, J = 0.7 Hz, 1H), 8.12–7.92 (m, 9H), 7.90 (d, J = 8.3 Hz, 1H), 7.81 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.70 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 1H), 7.52–7.48 (m, 1H), 7.17 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.2 Hz, 1H), 6.65 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$): δ 191.9, 135.2, 135.0, 133.4, 132.7, 131.9, 131.6, 131.5, 129.7, 129.3, 129.2, 128.6, 128.2, 128.1, 127.84, 127.79, 127.75, 127.69, 127.5, 127.4, 127.2, 127.1, 126.3, 125.8, 124.8, 123.8, 122.1. IR ($CHCl_3$, ν cm^{-1}): 2813, 2762, 2726, 1690, 1398. EI MS: 356 (100 %, M^+), 337 (23 %), 327 (50 %), 313 (10 %), 300 (66 %), 162 (28 %), 150 (13 %). HRMS (ESI/QTOF) *m/z* $[M]^+$ Calcd for $C_{27}H_{17}O$ 356.1197; found 356.1192.

Ethyl 2-[6]helicenoate (**16**). 2-Bromo[6]helicene **1** (100 mg, 0.256 mmol, 1 eq) was dissolved in tetrahydrofuran (10 mL) under Ar atmosphere. The reaction was cooled to -78°C and *n*-BuLi (2.5 M in THF, 128 µL, 0.32 mmol, 1.3 eq) was added to the reaction. The reaction mixture was stirred at the same temperature for 1 minute and ethyl chloroformate (38 µL, 0,40 mmol, 1.6 eq) in THF (2 mL) was added to the reaction. The reaction mixture was warmed to room temperature and ammonium chloride (1 mL, 25% V/V aqueous solution) was added**,** and the product was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with brine (2 x 20 mL, saturated solution) and water (20 mL). The organic layer was dried over $MgSO_4$, filtered**,** and the solvent was evaporated at the reduced pressure. Flash-chromatography (petroleum ether/ethyl acetate 20:1) and recrystallization from DCM/MeOH 1:1 gave ethyl 2-[6]helicenoate **16** (50 mg, 51%) as a pale brown powder. Mp = 160–163°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.08–7.91 (m, 8H), 7.88–7.81 (m, 2H), 7.78 (d, J = 7.9 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H), 7.19 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.1 Hz, 1H), 6.66 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.3 Hz, 1H), 4.15–4.07 (m, 1H), 4.01–3.92 (m, 1H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 166.3, 134.2, 133.3, 132.3, 131.5, 131.4, 130.4, 129.4, 129.0, 128.7, 128.4, 128.1, 127.9, 127.7, 127.6 (2C), 127.5, 127.4, 127.30, 127.1, 126.9, 126.2, 126.1, 125.7, 125.3, 124.6, 124.0, 60.3, 14.1. IR ($CHCl_3$, ν cm^{-1}): 2979, 2929, 2875, 2855, 1708, 1476, 1465, 1405, 1303, 1277, 1260, 1121, 1109, 1046, 1022, 960. EI MS: 400

(100 %, $M^{+\cdot}$), 353 (7 %), 327 (63 %), 300 (51 %), 162 (16 %), 150 (9 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{29}H_{21}O_2$ 401.1536; found 401.1530.

4,4,5,5-tetramethyl-2-([6]helicene-2-yl)-1,3,2-dioxaborolane (**17**). *Method A:* 2-Bromo[6]helicene **1** (100 mg, 0.256 mmol, 1 eq) was dissolved in tetrahydrofuran (10 mL) under Ar atmosphere. The reaction was cooled to -78°C and *n*-BuLi (128 µL, 0.32 mmol, 1.3 eq) was added into the reaction. The reaction mixture was stirred at the same temperature for 1 minute and *iso*-propoxyboronate pinacol ester (65.1 µL, 0.3194 mmol, 1.3 eq) was added. The reaction was slowly allowed to warm up to room temperature and stirred for an additional 60 min. The reaction was quenched with diluted HCl (0.5 mL, 10% V/V aqueous solution) and evaporated to dryness. The residuum was dissolved in dichloromethane (30 mL) and washed with water (3 x 30 mL). The organic phase was dried over $MgSO_4$, evaporated**,** and the crude product was further purified by means of column chromatography on silica gel with petroleum ether/ethyl acetate 8:1 as a mobile phase. Boronate **17** was obtained as a pale yellow amorphous solid (92.6 mg, 83 %). *Method B*: 2-Bromo[6]helicene **1** (50 mg, 0.1228 mmol, 1 eq), $PdCl_2$ (2.2 mg, 0,0123 mmol, 10 mol%), 1,1′-ferrocenediyl-bis(diphenylphosphine) (6.8 mg, 0.01228 mmol, 10 mol%), bis(pinacolato)diboron (46.8 mg, 0.1843 mmol, 1.5 eq), and sodium acetate (20.1 mg, 0.2457 mmol, 2 eq) were charged in a pre-dried microwave vial before DMF (3 mL) was added. The vial was reacted in a microwave reactor at 160 °C for 2 hours. Afterwards, the solvent was removed *in vacuo* and the residue chromatographed on silica gel with petroleum ether/ethylacetate 8:1 as a mobile phase. Boronate **17** was obtained as a pale yellow amorphous solid (21.5 mg, 39 %). Mp = 232–233 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 8.03–7.87 (m, 8H), 7.80 (d, J = 7.9 Hz, 1H), 7.75 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.57 (dd, J_1 = 7.9 Hz, J_2 = 1.1 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.17 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.2 Hz, 1H), 6.62 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$): δ 135.9, 133.5, 133.1, 132.1, 131.3, 131.1, 130.1, 129.7, 128.8, 128.21, 128.19, 127.69, 127.66, 127.58 (2C), 127.4, 127.3, 127.0, 126.8, 126.7, 126.5, 126.2, 125.2, 124.4, 124.1, 83.3 (2C), 24.9(2C), 24.3 (2C). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. IR ($CHCl_3$, ν cm^{-1}): 1481, 1406, 1395, 1380, 1369, 1330, 1167, 1143 1097, 963, 851. EI MS: 454 (100 %, M^+), 353 (21 %), 339 (8 %), 326 (40 %), 313 (11 %), 300 (27 %). HRMS (ESI/QTOF) *m/z* $[M]^+$ Calcd for $C_{32}H_{27}BO_2$ 454.2104; found 454.2146.

2-Hydroxy[6]helicene (**18**). 4,4,5,5-tetramethyl-2-([6]helicene-2-yl)-1,3,2-dioxaborolane **17** (100 mg, 0.2202 mmol, 1 eq) was dissolved in 25 mL of methanol before urea-hydrogen peroxide adduct (UHP) (103.5 mg, 1.101, 5 eq) was added in two parts over 5 minutes. The reaction was stirred until full conversion (indicated by TLC analysis). The solvent was then evaporated, the residue dissolved in ethylacetate (40 mL) and washed with brine (2 x 30 mL) and water (30 mL). After drying over $MgSO_4$ and evaporation of the organic phase, the crude product was recrystallized from DCM/MeOH to give **18** as a pale yellow powder (46.9 mg, 62 %). Mp = 238–240 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05–7.77 (m, 9H), 7.75 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.29 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.1 Hz, 1H), 6.93 (d, J = 2.6 Hz, 1H), 6.84 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H), 6.76 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1H), 4.38 (bs, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 153.1, 132.9, 131.8, 131.5, 131.3, 131.2, 130.0, 129.4, 127.64, 127.61, 127.5, 127.37, 127.34, 127.2, 127.00, 126.98, 126.96, 126.95, 126.8, 126.4, 125.9, 124.8, 124.2, 123.8, 116.0, 111.5. IR ($CHCl_3$, ν cm^{-1}):

3591, 1172. EI MS: 344 (100 %, M^+), 327 (33 %), 313 (24 %), 287 (11 %), 207 (14 %), 162 (23 %), 150 (16 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{26}H_{17}O$ 345.1274; found 345.1278.

2-(Benzylamino)[6]helicene (**19**). A pre-dried microwave vial was charged with 2-bromo[6]helicene **1** (200 mg, 0.4914 mmol, 1 eq), $Pd(OAc)_2$ (11.0 mg, 0.0491 mmol, 10 mol%), BINAP (30.5 mg, 0.0491 mmol, 10 mol%), *t*BuOK (82.5 mg, 0.7371 mmol, 1.5 eq) and benzylamine (80.4 µL, 0.7371 mmol, 1.5 eq). Dry toluene (18 mL) was added, argon was bubbled through the reaction mixture for 10 min before the vial was sealed. The reaction was performed in a microwave reactor at 170 °C for 2 h. After the reaction was complete, the solvent was removed and the residue was chromatographed on silica gel using petroleum ether/ethyl acetate 5:1 as a mobile phase. Product **19** was obtained as a yellow solid (159 mg, 75 %). The same protocol for synthesis of (*M*)-**19** was used. The reaction ((*M*)-**1,** 10 mg, 0.025 mmol, 1 eq) was conducted at 170 °C for 2 hours. Crude reaction mixture was analyzed on chiral HPLC (96 %*ee* of (*M*)-**19**). Mp = 152–154 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–7.90 (m, 7H), 7.87–7.80 (m, 2H), 7.73 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.38 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.1 Hz, 1H), 7.31–7.20 (m, 3H), 7.07–7.02 (m, 2H), 6.85 (ddd, J_1 = 6.8 Hz, J_2 = 6.8 Hz, J_3 = 1.4 Hz, 1H), 6.80 (d, J = 1.9 Hz, 1H), 6.64 (dd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, 1H), 3.44–3.33 (m, 2H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 145.4, 138.9, 132.9, 132.1, 131.5, 131.4, 131.1, 130.5, 128.6, 128.3 (2C), 127.7 (2C), 127.6 (3C), 127.50, 127.3, 127.11, 127.05, 126.95, 126.89, 126.59, 126.57 (2C), 125.7, 125.2, 124.6, 124.4, 122.1, 115.8, 107.6, 47.5. IR ($CHCl_3$, ν cm^{-1}): 3448, 1622, 1602, 1581, 1530, 1495, 1454, 1298, 1188, 1144, 1071, 1029, 984, 895, 831 700, 624, 469. EI MS: 433 (100 %, M^+), 340 (23 %), 326 (33 %), 313 (13 %), 300 (34 %), 207 (11 %), 162 (11 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{33}H_{24}N$ 434.1903; found 434.1901. Chiral separation: t_R = 18.22 min ((-)-**19**), 31.92 min ((+)-**19**).

N-(helicene-2-yl)-1,1-diphenylmethanimine (**20**). A pre-dried microwave vial was charged with 2-bromo[6]helicene **1** (500 mg, 1.228 mmol, 1 eq), $Pd(OAc)_2$ (27.5 mg, 0.123 mmol, 10 mol%), BINAP (76.4 mg, 0.1228 mmol, 10 mol%), *t*BuOK (206 mg, 1.842 mmol, 1.5 eq) and benzophenone imine (308 µL, 1.842 mmol, 1.5 eq). Dry toluene (18 mL) was added, argon was bubbled through the reaction mixture for 10 min before the vial was sealed. The reaction was performed in a microwave reactor at 170 °C for 2 h. After the reaction was complete, the cooled reaction mixture was filtered through a pad of silica gel, eluting with toluene. Solvent was evaporated *in vacuo* and the crude product was then recrystallized from DCM/MeOH mixture to give **20** as yellow powder (535 mg, 86 %). Mp = 273–275 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98–7.74 (m, 10H), 7.53–7.46 (m, 3H), 7.45–7.38 (m, 2H), 7.36–7.30 (m, 3H), 7.21-7.08 (m, 3H), 6.91 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4, 1H), 6.58–6.56 (m, 2H), 6.42 (dd, J_1 = 8.4 Hz, J_2 = 1.9 Hz, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 167.1, 147.8, 139.9, 135.8, 132.9, 131.9, 131.5, 131.4, 131.0, 130.4, 130.06, 129.96 (2C), 129.3 (2C), 128.40, 128.37, 128.04, 127.96 (2C), 127.91, 127.86, 127.77, 127.76, 127.75, 127.70 (2C), 127.6, 127.14, 127.06, 126.74, 126.72, 126.3, 125.6, 125.0, 124.7, 124.1, 121.5, 120.2. IR ($CHCl_3$, ν cm^{-1}): 1664, 1595, 1495, 1448, 1333, 1291, 1191, 1177, 1156, 1029, 981, 846, 624, 462, 406. EI MS: 507 (100 %, M^+), 415 (10 %), 341 (10 %), 326 (24 %), 300 (34 %), 281 (21 %), 207 (59 %), 73 (16 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{39}H_{26}N$ 508.2059; found 508.2051.

2-Amino[6]helicene (**21**). Iminohelicene **20** (429 mg, 0.848 mmol, 1 eq) was dissolved in dry THF (30 mL), water (45.7 µL, 2.543 mmol, 3 eq) and HCl (423 µL, 3 eq, 6M solution in isopropanol) was then added. The color of the reaction mixture turned red immediately after the addition of the HCl

only to fade to yellow in a few minutes while grey precipitate started to form. After the completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure and the crude product was triturated in Et_2O (30 mL) for 30 min. The solids were filtered off, suspended in EtOAc (200 mL) and washed with saturated Na_2CO_3 (3 x 100 mL). The combined organic phases were dried over $MgSO_4$, evaporated**,** and dried in **a** vacuum to afford 2-amino[6]helicene **21** as a dark yellow amorphous solid (270.4 mg, 93 %). Mp = 211–214 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–7.87 (m, 6H), 7.85–7.78 (m, 2H), 7.75–7.69 (m, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.31 (ddd, J_1 = 7.0 Hz, J_2 = 7.0 Hz, J_3 = 1.1, 1H), 6.82 (d, J = 2.1 Hz, 1H), 6.78 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4, 1H), 6.69 (dd, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 143.8, 132.8, 132.0, 131.6, 131.3, 131.1, 130.2, 128.8, 127.8, 127.7, 127.5, 127.4, 127.2, 127.1, 127.0, 126.8, 126.70, 126.67, 126.3, 125.78, 125.76, 124.6, 124.4, 122.6, 116.2, 111.7. IR ($CHCl_3$, ν cm^{-1}): 3485, 3367, 1627. EI MS: 343 (100 %, M^+), 326 (19 %), 313 (10 %), 300 (33 %), 281 (29 %), 207 (73 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{26}H_{18}N$ 344.1441; found 344.1439.

2-Nitro[6]helicene (**22**). 2-Amino[6]helicene **21** (50 mg, 0.145 mmol, 1 eq) and 3-chloroperbenozoic acid (72 mg, 0.436 mmol, 3 eq) was dissolved in dichloromethane (15 mL) and stirred for an hour. A complete consumption of starting material was observed by TLC. The reaction mixture was then washed with saturated brine (2 x 15 mL) and water (15 mL). The organic phase was dried over $MgSO_4$ and solvents were evaporated. The crude product was purified by column chromatography with petroleum ether : ethylacetate 8 : 1 as a mobile phase. The crude product was recrystallized from DCM/MeOH to give 2-nitro[6]helicene **22** (27 mg, 49%) as a dark yellow powder. Mp = 239–241 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, J = 1.8 Hz, 1H), 8.16–8.10 (m, 2H), 8.09–7.95 (m, 7H), 7.91 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.23–7.19 (m, 1H), 6.70–6.66 (m, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 144.3, 134.7, 133.4, 132.6, 132.0, 131.7, 130.5, 129.2, 128.8, 128.67, 128.61, 128.4 (2C), 128.3, 128.2, 127.3, 127.2, 126.97, 126.96, 126.8, 126.2, 125.8, 124.7, 124.4, 123.8, 119.0. IR ($CHCl_3$, ν cm^{-1}): 1515, 1508, 1339. EI MS: 373 (18 %), 357 (100 %), 340 (44 %), 326 (61 %), 313 (21 %), 300 (12 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{26}H_{16}NO_2$ 374.1176; found 374.1178.

2-Nitroso[6]helicene (**23**). 2-amino[6]helicene **21** (50 mg, 0.14 mmol, 1 eq) was dissolved in a minimum amount of dichloromethane (3 mL) and potassium peroxymonosulfate (443 mg, 2.91 mmol, 20 eq) in water (3 mL) was added. The two-phase mixture was stirred vigorously until the complete consumption of starting material was observed by TLC. The reaction mixture was then diluted with dichloromethane (20 mL) and washed with water (3 x 20 mL). The organic phase was then dried with $MgSO_4$ and consequently evaporated. Crude product was purified by column chromatography with petroleum ether : ethylacetate 8:1. After evaporation, 2-nitroso[6]helicene **23** was obtained (19 mg, 37 %) as a yellow amorphous solid. Mp = 215–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (d, J = 1.5 Hz, 1H), 8.21–7.90 (m, 8 H), 7.79–7.72(m, 2H), 7.60 (dm, J = 8.5 Hz, 1H), 7.08 (ddd, J_1 = 7.1 Hz, J_2 = 7.1 Hz, J_3 = 1.2, 1H), 6.83 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 6.64 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4, 1H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ 163.2, 135.9, 135.3, 133.6, 132.3, 132.0, 131.8, 131.3, 130.2, 129.4, 129.2, 128.7, 128.5, 128.3, 128.2, 128.1, 127.8, 127.6, 127.10, 127.06, 127.01, 126.2, 125.7, 124.7, 124.0, 108.3. IR ($CHCl_3$, ν cm^{-1}): 1453. EI MS: 358 (22 %, M^+), 341 (100 %), 326 (63 %), 314 (16 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{26}H_{16}NO$ 358.1226; found 358.1223.

2-(Methylsulphanyl)[6]helicene (**24**). A pre-dried microwave vial was charged with 2-bromo[6]helicene **1** (100 mg, 0.246 mmol, 1 eq), sodium methanethiolate (86.0 mg, 1.228 mmol, 5 eq) and $Pd(PPh_3)_4$ (29.6 mg, 0.027 mmol, 10 mol%) in 5 mL of dry DMF. Argon was bubbled through the reaction mixture for 10 min, after which the vial was placed in a microwave initiator and reacted at 170 °C for 30 min. Solvent was then removed and the residue was dissolved in DCM (20 mL) and washed with brine (2 x 20 mL, saturated aqueous solution) and water (20 mL). The organic phase was dried over $MgSO_4$, drying agent was filtered off and the solvent was removed under reduced pressure. Crude product was chromatographed on reverse-phase silica gel using MeCN/H_2O 95:5 as a mobile phase to yield 2-(methylsulphanyl)[6]helicene **24** as a pale yellow amorphous solid (57.9 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–7.82 (m, 9H), 7.71 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.46 (s, 1H), 7.31–7.26 (m, 1H), 7.13 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 6.77–6.73 (m, 1H), 1.65 (s, 3H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 135.4, 133.2, 132.0, 131.7, 131.3, 130.4, 129.8, 129.5, 127.9, 127.8, 127.7, 127.57, 127.52, 127.46, 127.3, 127.2, 127.14, 127.08, 127.0, 126.5, 126.0, 125.5, 125.3, 124.9, 124.0, 123.8, 14.8. IR ($CHCl_3$, ν cm^{-1}): 2855, 1438, 1318. EI MS: 374 (100 %, M^+), 326 (54 %), 300, (34 %), 162 (30 %). HRMS (ESI/QTOF) *m/z* $[M]^+$ Calcd for $C_{27}H_{18}S$ 374.1219; found 374.1232.

Borane 2-(diphenylphosphanyl)[6]helicene complex (**25**). 2-Bromo[6]helicene **1** (50 mg, 0.123 mmol, 1 eq), diphenylphosphine (47 µL, 0.246 mmol, 2 eq), sodium acetate (21 mg, 0.246 mmol, 2 eq) and Herrmann I (5 mg, 6.1 µmol, 5 mol%) were dissolved in THF (2 mL) under Ar atmosphere. The reaction was heated in a microwave reactor to 160 °C for 30 minutes. The reaction mixture was cooled to room temperature and 1M borane-tetrahydrofuran complex solution in THF (1.4 mL, 1.4 mmol, 12 eq) was added dropwise. The reaction mixture was stirred under Ar atmosphere at room temperature overnight. The solvent was removed at reduced pressure and the crude product was dissolved in dichloromethane and filtered through a short silica gel column and eluted with dichloromethane (50 mL). Borane 2-(diphenylphosphanyl)[6]helicene complex **25** (39 mg, 61%) was obtained after recrystallization from dichloromethane/methanol as a yellow powder. The same protocol for synthesis of (*M*)-**25** was used. The reaction ((*M*)-**1,** 10 mg, 0.025 mmol, 1 eq) was conducted at 160 °C for one hour. Crude reaction mixture was analyzed on chiral HPLC 99 %*ee* of (*M*)-**25**). Mp = 222–223 °C. ^{1}H NMR {^{31}P} (500 MHz, $CDCl_3$): δ 8.08 (bd, J = 13.3 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H), 8.00 (bd, J = 8.1 Hz, 1H), 7.97–7.87 (m, 5H), 7.84 (bd, J = 8.6 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.54 (d, J = 8.5 Hz 1H), 7.44–7.37 (m, 3H), 7.32–7.25 (m, 4H), 7.17 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.0, 1H), 7.11–7.04 (m, 4H), 6.73 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.3, 1H), 1.10–0.40 (bs, 3H). ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$): δ -38.35 (s). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 133.6 (d, $J_{P\text{-}C}$ = 11.3 Hz), 133.3, 133.1 (d, $J_{P\text{-}C}$ = 9.7 Hz, 2C), 132.9 (d, $J_{P\text{-}C}$ = 9.6 Hz, 2C), 132.6 (d, $J_{P\text{-}C}$ = 2.3 Hz), 132.3, 131.4, 131.3 (d, $J_{P\text{-}C}$ = 0.6 Hz), 130.7 (d, $J_{P\text{-}C}$ = 2.5 Hz), 130.6 (d, $J_{P\text{-}C}$ = 2.5 Hz), 130.1 (d, $J_{P\text{-}C}$ = 11.7 Hz), 129.3 (d, $J_{P\text{-}C}$ = 57.8 Hz), 129.0, 128.7, 128.6 (d, $J_{P\text{-}C}$ = 9.8 Hz), 128.57 (d, $J_{P\text{-}C}$ = 58.1 Hz), 128.55 (d, $J_{P\text{-}C}$ = 1.7 Hz, 2C), 128.50 (d, $J_{P\text{-}C}$ = 0.5 Hz), 128.47 (d, $J_{P\text{-}C}$ = 1.7 Hz, 2C), 128.2 (d, $J_{P\text{-}C}$ = 10.4 Hz) 128.05, 128.02, 127.96, 127.6, 127.5, 127.4, 127.2 (d, $J_{P\text{-}C}$ = 0.8 Hz), 126.8, 126.5, 126.2, 125.6, 125.3 (d, $J_{P\text{-}C}$ = 58.8 Hz) , 124.5, 123.7. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ 20.43 (bs). IR ($CHCl_3$, ν cm^{-1}): 2387, 2346, 1587, 1486, 1438, 1106, 1060, 1029, 1000, 914, 826, 693, 578. HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{38}H_{26}P$ 513.1766; found 513.1767. Chiral separation: t_R = 23.21 min ((-)-**23**), 28.99 min ((+)-**23**).

(2-[6]helicenyl)diphenylphosphine oxide (**27**). Borane 2-(diphenylphosphanyl)[6]helicene complex **25** (50 mg, 0.097 mmol, 1 eq) was dissolved in dichloromethane (2 mL). Then diethyl ether-tetrafluoroboric acid complex (78 µL, 0.582 mmol, 6 eq) was added dropwise. The reaction mixture was stirred for 15 min at room temperature and then potassium carbonate (263 mg, 1.94 mmol, 20 eq) was added and the reaction mixture was stirred at the same temperature for another 15 min. Inorganic salts were filtered off and aqueous solution of hydrogen peroxide (1 mL, 30 % wt.) was added into the reaction. Reaction mixture was stirred overnight. After the reaction the crude mixture was extracted with dichloromethane (20 mL). The organic layer was washed with water (2 x 20 mL) and was dried over $MgSO_4$, filtered**,** and the solvent was evaporated at the reduced pressure. The reaction mixture gave (2-[6]helicenyl)diphenylphosphine oxide **27** (47 mg, 94%) as a yellow powder. Mp = 285–287 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 8.6 Hz, 1H), 8.01–7.89 (m, 7H), 7.85 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.70 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 1H), 7.61 (ddd, J_1 = 8.2 Hz, J_2 = 8.2 Hz, J_3 = 1.5, 1H), 7.57 (dm, J = 8.6 Hz, 1H), 7.51–7.46 (m, 1H), 7.41–7.37 (m, 1H), 7.37–7.31 (m, 2H), 7.29–7.23 (m, 3H), 7.13–7.04 (m, 4H), 6.77 (ddd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 133.3, 133.2 (d, $J_{P\text{-}C}$ = 2.6 Hz), 132.58 (d, $J_{P\text{-}C}$ = 104.1 Hz), 132.55 (d, $J_{P\text{-}C}$ = 11.8 Hz), 132.21, 132.0 (d, $J_{P\text{-}C}$ = 10.1 Hz, 2C), 131.74 (d, $J_{P\text{-}C}$ = 9.9 Hz, 2C), 131.74 (d, $J_{P\text{-}C}$ = 104.2 Hz), 131.46, 131.46 (d, $J_{P\text{-}C}$ = 2.8 Hz), 131.36 (d, $J_{P\text{-}C}$ = 1.0 Hz), 131.32 (d, $J_{P\text{-}C}$ = 2.7 Hz), 129.6 (d, $J_{P\text{-}C}$ = 13.7 Hz), 129.1, 128.8 (d, $J_{P\text{-}C}$ = 105.4 Hz), 128.6, 128.42, 128.29 (d, $J_{P\text{-}C}$ = 12.2 Hz, 2C), 128.28 (d, $J_{P\text{-}C}$ = 12.1 Hz), 128.23 (d, $J_{P\text{-}C}$ = 12.2 Hz, 2C), 128.20, 128.18, 128.07, 127.9, 127.7, 127.5 (d, $J_{P\text{-}C}$ = 7.5 Hz), 127.4 (d, $J_{P\text{-}C}$ = 9.6 Hz), 127.3 (d, $J_{P\text{-}C}$ = 1.1 Hz), 126.9, 126.6, 126.3, 125.7, 124.8, 123.7. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ 29.39 (s) ppm. IR ($CHCl_3$, ν cm^{-1}): 1589, 1482, 1438, 1250, 1172, 1028, 1001, 694. EI MS: 528 (8 %, $M^{+\cdot}$), 527 (17 %), 281 (17 %), 280 (30 %), 253 (10 %), 252 (10 %), 209 (15 %), 208 (29 %), 207 (96 %), 206 (100 %). HRMS (ESI/QTOF) *m/z* $[M + H]^+$ Calcd for $C_{38}H_{26}PO$ 529.1715; found 529.1712.

Racemization of 2-Bromo[6]helicene 1. Enantiomerically pure (*M*)-**1** (2.0 mg) was dissolved in hexadecane (2 mL) in a capped (PP-cap and rubber/PTFE septa) vial equipped with **a** stirring bar. The vial was wrapped into aluminum foil and heated to a constant temperature (458, 465, 475 or 487 K) using a hot plate magnetic stirrer with Pt1000 probe and stirred Wood's metal bath. The temperature was cross-checked using an external mercury-in-glass thermometer with 0.5 °C accuracy. The increasing concentration of (*P*)-**1** was monitored by chiral HPLC (Kromasil Cellucoat® column) in the course of time (for details see SI).

Supporting Information

Thermodynamic data, ^{1}H and ^{13}C NMR spectra, HPLC chromatograms.

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Note

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References

(1) Gingras, M. *Chem. Soc. Rev.* **2013**, *42* (3), 1051–1095.
(2) Moradpour, A.; Kagan, H.; Baes, M.; Morren, G.; Martin, R. H. *Tetrahedron* **1975**, *31* (17), 2139–2143.
(3) Jančařík, A.; Rybáček, J.; Cocq, K.; Chocholoušová, J. V.; Vacek, J.; Pohl, R.; Bednárová, L.; Fiedler, P.; Císařová, I.; Stará, I. G.; Starý, I. *Angew. Chemie - Int. Ed.* **2013**, *52* (38), 9970–9975.
(4) Morrison, D. J.; Trefz, T. K.; Piers, W. E.; McDonald, R.; Parvez, M. *J. Org. Chem.* **2005**, *70* (13), 5309–5312.
(5) Ooyama, Y.; Ito, G.; Fukuoka, H.; Nagano, T.; Kagawa, Y.; Imae, I.; Komaguchi, K.; Harima, Y. *Tetrahedron* **2010**, *66* (36), 7268–7271.
(6) Field, J. E.; Muller, G.; Riehl, J. P.; Venkataraman, D. *J. Am. Chem. Soc.* **2003**, *125* (39), 11808–11809.
(7) Tang, Y.; Cook, T. A.; Cohen, A. E. *J. Phys. Chem. A* **2009**, *113* (22), 6213–6216.
(8) Verbiest, T.; Van Elshocht, S.; Persoons, A.; Nuckolls, C.; Phillips, K. E.; Katz, T. J. *Langmuir* **2001**, *17* (16), 4685–4687.
(9) Van Elshocht, S.; Verbiest, T.; de Schaetzen, G.; Hellemans, L.; Phillips, K. E. S.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Chem. Phys. Lett.* **2000**, *323* (3–4), 340–344.
(10) Verbiest, T. *Science* **1998**, *282* (5390), 913–915.
(11) Bossi, A.; Licandro, E.; Maiorana, S.; Rigamonti, C.; Righetto, S.; Richard Stephenson, G.; Spassova, M.; Botek, E.; Champagne, B. *J. Phys. Chem. C* **2008**, *112* (21), 7900–7907.
(12) Hatakeyama, T.; Hashimoto, S.; Oba, T.; Nakamura, M. *J. Am. Chem. Soc.* **2012**, *134* (48), 19600–19603.
(13) Yang, Y.; Da Costa, R. C.; Fuchter, M. J.; Campbell, A. J. *Nat. Photonics* **2013**, *7* (8), 634–638.
(14) Sahasithiwat, S.; Mophuang, T.; Menbangpung, L.; Kamtonwong, S.; Sooksimuang, T. *Synth. Met.* **2010**, *160*, 1148–1152.
(15) Shi, L.; Liu, Z.; Dong, G.; Duan, L.; Qiu, Y.; Jia, J.; Guo, W.; Zhao, D.; Cui, D.; Tao, X. *Chem. - A Eur. J.* **2012**, *18* (26), 8092–8099.
(16) Storch, J.; Zadny, J.; Strasak, T.; Kubala, M.; Sykora, J.; Dusek, M.; Cirkva, V.; Matejka, P.; Krbal, M.; Vacek, J. *Chem. - A Eur. J.* **2015**, *21* (6), 2343–2347.
(17) Verbiest, T.; Sioncke, S.; Persoons, A.; Vyklický, L.; Katz, T. J. *Angew. Chemie - Int. Ed.* **2002**, *41* (20), 3882–3884.
(18) Reetz, M. T.; Beuttenm̈ller, E. W.; Goddard, R. *Tetrahedron Lett.* **1997**, *38* (18), 3211–3214.
(19) Dreher, S. D.; Katz, T. J.; Lam, K.; Rheingold, A. L. **2000**, No. c, 815–822.
(20) Hrbac, J.; Storch, J.; Halouzka, V.; Cirkva, V.; Matejka, P.; Vacek, J. *RSC Adv.* **2014**, *4* (86), 46102–46105.
(21) Anger, E.; Srebro, M.; Vanthuyne, N.; Toupet, L.; Rigaut, S.; Roussel, C.; Autschbach, J.; Crassous, J.; Réau, R. *J. Am. Chem. Soc.* **2012**, *134* (38), 15628–15631.
(22) Martin, R. H.; Libert, V. *J. Chem. Res. Miniprint* **1980**, *4*, 1940–1950.
(23) Lightner, D. A.; Hefelfinger, D. T.; Powers, T. W.; Frank, G. W.; Trueblood, K. N. *J. Am. Chem. Soc.* **1972**, *94* (10), 3492–3497.
(24) Žádný, J.; Velíšek, P.; Jakubec, M.; Sýkora, J.; Církva, V.; Storch, J. *Tetrahedron* **2013**, *69* (30), 6213–6218.
(25) Gupta, S.; Chaudhary, P.; Srivastava, V.; Kandasamy, J. *Tetrahedron Lett.* **2016**, *57* (23), 2506–2510.
(26) Abaev, V. T.; Serdyuk, O. V. *Russ. Chem. Rev.* **2008**, *77* (2), 177–192.
(27) Lowe, A. B. *Polym. (United Kingdom)* **2014**, *55* (22), 5517–5549.
(28) Pensa, E.; Cortés, E.; Corthey, G.; Carro, P.; Vericat, C.; Fonticelli, M. H.; Benítez, G.;

Rubert, A. A.; Salvarezza, R. C. *Acc. Chem. Res.* **2012**, *45* (8), 1183–1192.
(29) Stadler, A.; Kappe, C. O. *Org. Lett.* **2002**, *4* (20), 3541–3543.
(30) McKinstry, L.; Livinghouse, T. *Tetrahedron* **1995**, *51* (28), 7655–7666.
(31) Ravat, P.; Hinkelmann, R.; Steinebrunner, D.; Prescimone, A.; Bodoky, I.; Juríček, M. *Org. Lett.* **2017**, *19* (14), 3707–3710.
(32) Martin, R. H.; Marchant, M. J. *Tetrahedron Lett.* **1972**, *35*, 3707–3708.
(33) Urbani, M.; Ohkubo, K.; Islam, D. M. S.; Fukuzumi, S.; Langa, F. *Chem. - A Eur. J.* **2012**, *18* (24), 7473–7485.
(34) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C. -P; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chemie Int. Ed. English* **1995**, *34* (17), 1844–1848.
(35) Luo, T.; Zhang, R.; Zhang, W.; Shen, X.; Umemoto, T.; Hu, J. *Org. Lett.* **2014**, *16* (3), 888–891.
(36) Talele, H.; Av, B. *Arch. Org. Chem.* **2011**, *2011* (9), 15–37.
(37) Mehta, G.; Panda, G. *Tetrahedron Lett.* **1997**, *38* (12), 2145–2148.