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An Ultimate Stereocontrol in Asymmetric Synthesis of Optically Pure Fully Aromatic Helicenes

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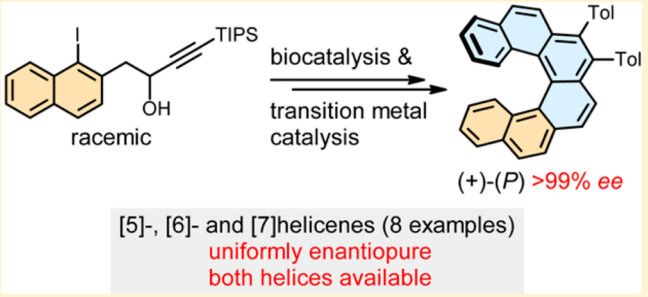
Supporting Information

ABSTRACT: The role of the helicity of small molecules in enantioselective catalysis, molecular recognition, self-assembly, material science, biology, and nanoscience is much less understood than that of point-, axial-, or planar-chiral molecules. To uncover the envisaged potential of helically chiral polyaromatics represented by iconic helicenes, their availability in an optically pure form through asymmetric synthesis is urgently needed. We provide a solution to this problem present since the birth of helicene chemistry in 1956 by developing a general synthetic methodology for the preparation of uniformly enantiopure fully aromatic [5]-, [6]-, and [7]helicenes and their functionalized derivatives. [2 + 2 + 2] Cycloisomerization of chiral triynes combined with asymmetric transformation of the first kind (ultimately controlled by the 1,3-allylic-type strain) is central to this endeavor. The point-to-helical chirality transfer utilizing a traceless chiral auxiliary features a remarkable resistance to diverse structural perturbations.



INTRODUCTION

An enormous attention has been paid to controlling the relative or absolute configuration at the stereogenic center(s), which are ubiquitous in natural products, biomolecules, and pharmaceuticals.[1] However, there are also other types of chirality such as axial, planar, or helical. While various approaches to optically pure axially chiral compounds (e.g., biaryls[2] or allenes[3]) and planar ones (e.g., ferrocenes[4] or cyclophanes[5]) have been developed, asymmetric synthesis of optically pure helically chiral molecules represented by iconic helicenes[6−12] is still far from perfection. These intramolecularly overcrowded molecules consisting of all-ortho-fused benzene rings such as [6]helicene **1** (Figure 1) have attracted increasing attention owing to their remarkable shape and unique chiroptical properties and the first astonishing applications to enantioselective organo- or transition-metal catalysis,[13−15] molecular recognition,[16] self-assembly,[17] nonlinear optical materials,[18] chiroptical materials,[19,20] surface science,[21−23] helicene transition-metal complexes,[24,25] chiral materials,[26,27] and other branches of chemistry.[28,29] Intriguingly, in all the cases described above except for two,[30,31] the enantiomerically pure helicenes were obtained by resolving corresponding racemates mostly by using expensive chiral columns for liquid chromatography. It creates an urgent need for the development of a practical asymmetric synthesis of helicenes in an optically pure form.

Indeed, various concepts have recently emerged such as enantioselective[32−36] or diastereoselective[31,37,38] alkyne [2 + 2 + 2] cycloisomerization, stereoconservative alkene metathesis,[39] asymmetric Diels−Alder reactions with sulfinyl quinones,[10] diastereoselective photocyclodehydrogenation of diaryl olefins,[14,40] enantioselective Fischer indole reaction,[41] and other reactions.[6−12] Despite the fact that promising levels of stereoselectivity were achieved, none of these methods could be considered general. However, a strong indication has recently been noticed that a stereocontrol stemming from 1,3-allylic-type strain[42] can successfully be applied to Co^{I}- or Ni^{0}-catalyzed [2 + 2 + 2] cycloisomerization of centrally chiral triynes to provide optically pure [5]-, [6]- and [7]helicene surrogates comprising two 2*H*-pyran rings.[43]

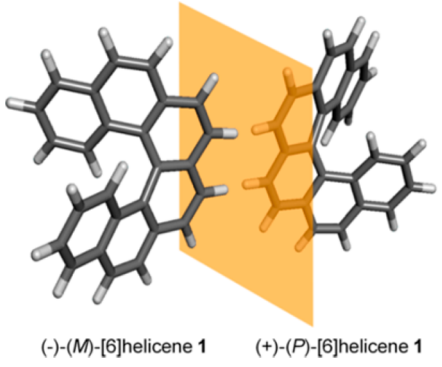


Figure 1. Molecular shape of (−)-(*M*)- and (+)-(*P*)-[6]helicene **1**. The prefix [6] stands for the number of all-ortho-fused benzene rings (the full name of **1** is hexahelicene).

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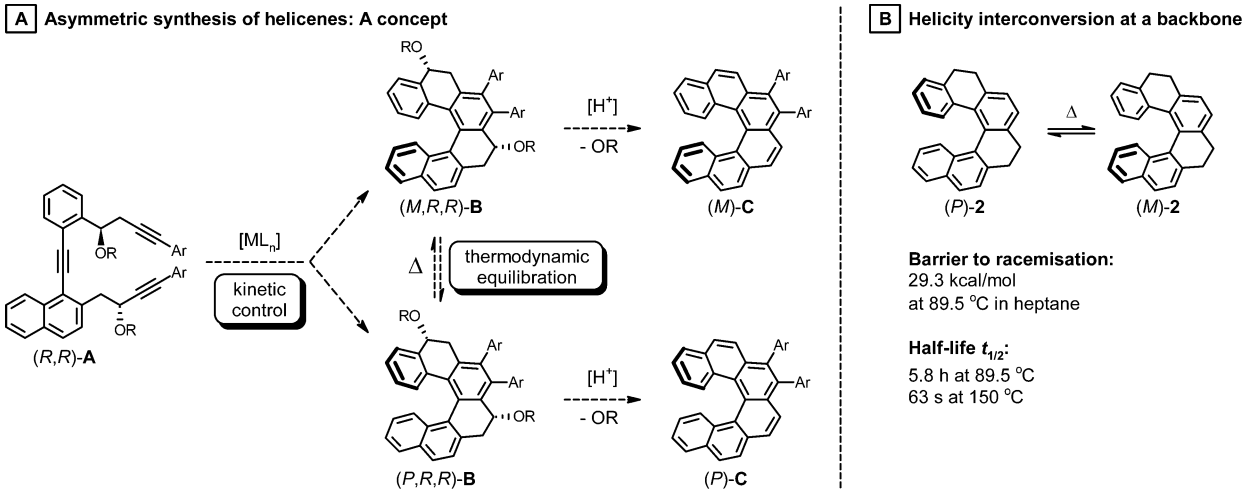
Scheme 1. A Concept of Asymmetric Synthesis of Helicenes[a]



[a]The overall stereochemical outcome of [2 + 2 + 2] cycloisomerization of (*R*,*R*)-**A** to form (*M*,*R*,*R*)-**B** or (*P*,*R*,*R*)-**B** diastereomers could be governed either by kinetic or thermodynamic factors. The barrier to racemization of the bare helical backbone **2** is high enough to allow for kinetic stereocontrol at ambient temperature and low enough to employ thermodynamic equilibration at high temperature; Ar = aryl, R = alkyl, acyl.

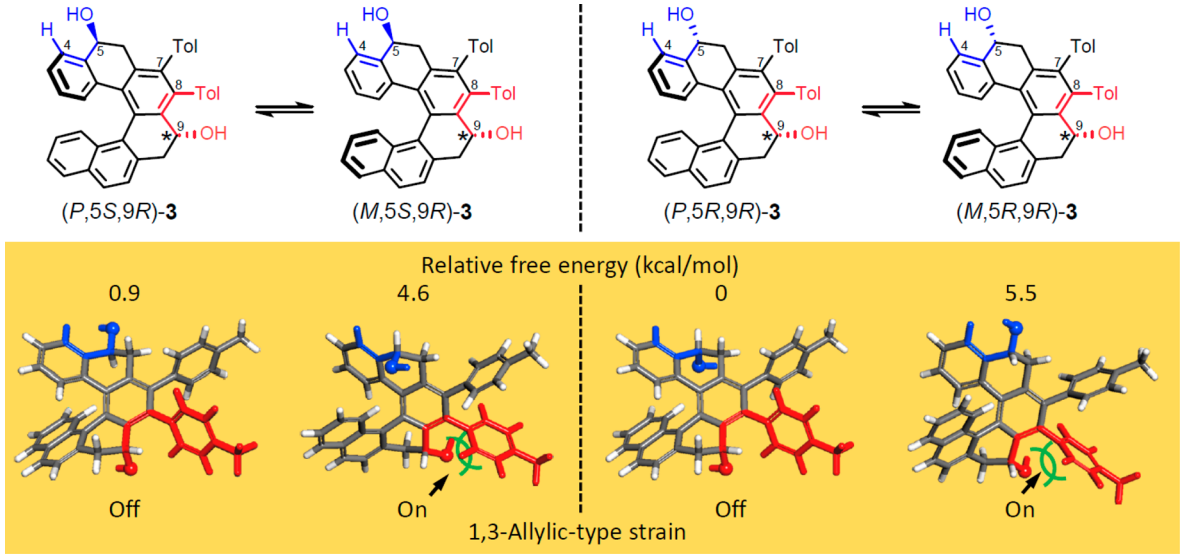


Figure 2. 1,3-Allylic-type strain in the diastereomeric [6]helicene precursors **3**. Each of the four diastereomers comprises two chiral centers placed in two different allylic-type subunits: A blue one (inducing no 1,3-allylic-type strain) and a red one (inducing possibly a 1,3-allylic-type strain); the absolute configuration of the 9-OH group is set arbitrarily (*R*) (marked by an asterisk). The helical backbone prefers conformations, which prevents the 1,3-allylic-type strain: The (*P*,5*S*,9*R*)- and (*P*,5*R*,9*R*)-**3** diastereomers of the same helicity should dominate. The free energies were calculated by DFT (b97d/cc-pVDZ, in THF); Tol = 4-methylphenyl.

Herein, we report on an ultimate stereocontrol through the 1,3-allylic-type strain in an asymmetric synthesis of archetypal fully aromatic [5]-, [6]-, and [7]helicenes to be uniformly obtained in enantiomer ratios of >99:<1. This study, which utilizes a biocatalytic approach to enantiopure building blocks and traceless chiral auxiliary strategy in asymmetric synthesis, provides a solution to a problem of helicene chemistry present since its birth in 1956 (M. S. Newman and D. Lednicer)[44] that was the lack of a general synthetic methodology for the preparation of diverse enantiopure helicenes.

RESULTS AND DISSCUSSION

Theoretical Basis of the Helicity Control. The transition-metal-catalyzed [2 + 2 + 2] cycloisomerization of a model enantiopure triyne (*R*,*R*)-**A** should deliver diastereomeric tetrahydrohelicenes (*M*,*R*,*R*)- and (*P*,*R*,*R*)-**B** that differ in helicity (Scheme 1). They could be produced in unequal amounts if stereodiscriminating kinetic or thermodynamic factors operate in the process. While the genuine kinetic stereocontrol assumes no equilibration between the diastereomeric products, their thermodynamic control requires their feasible interconversion. Actually, tetrahydro[6]helicene **2**,[33] a bare helical backbone in (*M*,*R*,*R*)- and (*P*,*R*,*R*)-**B**, perfectly fulfills such requirements: Its barrier to racemization of 29.3 kcal/mol is high enough to allow for kinetic stereocontrol at ambient temperature and low enough for thermodynamic equilibration at high temperature. Supposing one of the diastereomers **B** is formed preferentially, the oxygen functionalities might be subsequently removed as traceless chiral auxiliaries by acid-assisted elimination to form fully aromatic

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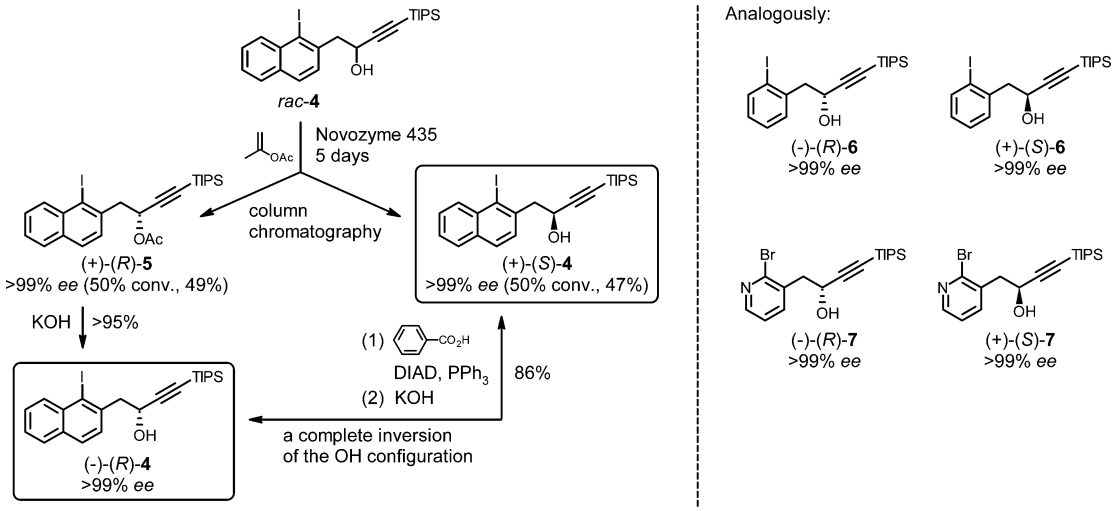
Scheme 2. Chemical/Biocatalytic Synthesis of the Key Enantiopure Building Blocks 4, 6, and 7[a]



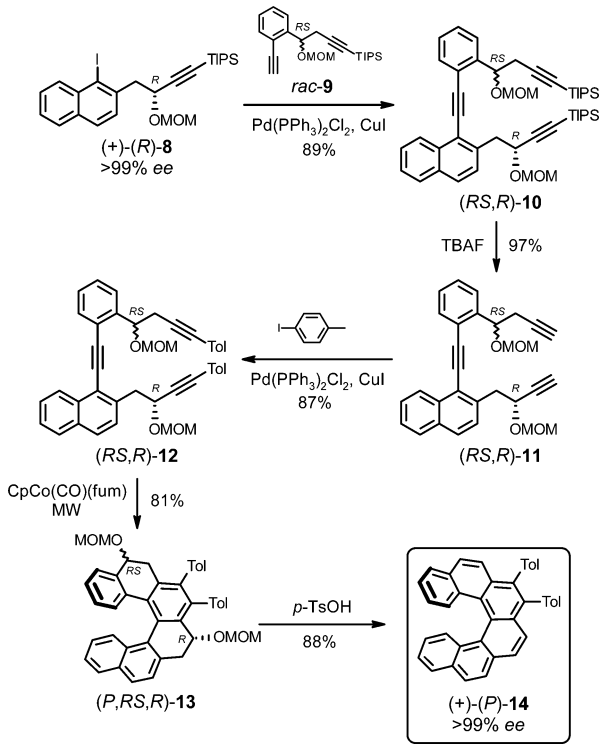
[a]Lipase-catalyzed transesterification was central to the kinetic resolution of the racemic secondary alcohols. The absolute configuration of the chiral building blocks was deduced backward from the helicity of the final fully aromatic helicenes. DIAD = diisopropyl azodicarboxylate, TIPS = triisopropylsilyl.

[6]helicene (*M*)- or (*P*)-**C** conserving the stereochemical outcome of the cyclization/equilibration step. The computational prediction of stereoselectivity in a transition-metal-catalyzed reaction controlled by kinetic factors requires a detailed description of the mechanism, and therefore, it is all but trivial. In the case of the thermodynamic control, however, a difference in free energies of the interconverting stereoisomers can directly be correlated with the stereoselectivity of the process and, most importantly, easily computed.

Under conditions allowing postcyclization thermodynamic equilibration, the expected stereocontrol could stem from the 1,3-allylic-type strain[42] that might be imposed on some of the four model diastereomers (*P*,5*S*,9*R*)-, (*P*,5*R*,9*R*)-, (*M*,5*S*,9*R*)-, and (*M*,5*R*,9*R*)-**3** (Figure 2). By keeping the absolute configuration of 9-OH arbitrarily (*R*), there are two pairs of diastereomers that differ only in helicity, which is supposed to invert through a purely conformational process: (*P*,5*S*,9*R*)-**3** ⇌ (*M*,5*S*,9*R*)-**3** and (*P*,5*R*,9*R*)-**3** ⇌ (*M*,5*R*,9*R*)-**3**. Density functional theory (DFT) calculations revealed that both low-energy diastereomers (*P*,5*S*,9*R*)- and (*P*,5*R*,9*R*)-**3a** have (*P*) helicity, while both high-energy diastereomers (*M*,5*S*,9*R*)- and (*M*,5*R*,9*R*)-**3** have (*M*) helicity. Moreover, the free energy differences between the interconverting diastereomers are 3.7 and 5.5 kcal/mol which should ensure an overall 99.9:0.1 predominance of (*P*) helices over (*M*) ones under thermodynamic equilibration (reachable within 1 min or less at temperatures over 150 °C). Under such circumstances, the population of conformers (*M*,5*S*,9*R*)- and (*M*,5*R*,9*R*)-**3**, where the 1,3-allylic-type strain is "on" (there is steric repulsion between the pseudoequatorial 9-OH group and 8-tolyl one, both lying in the same plane), would be reduced. Thus, the only absolute configuration of the 9-OH group should determine the helicity of the backbone, while the 5-OH group should be stereochemically innocent.

Controlling Helicity: Proof of Principle. In order to carry out asymmetric synthesis of key tetrahydrohelicenes such as (*M*,5*R*,9*S*)/(*M*,5*S*,9*S*)-**3** to get the (*M*)-[6]helicene derivative or (*P*,5*S*,9*R*)/(*P*,5*R*,9*R*)-**3** to get the (*P*)-[6]helicene derivative, the enantiopure building blocks (−)-(*R*)- and (+)-(*S*)- **4** first had to be prepared (Scheme 2). Starting from commercially available 1-bromo-2-(methoxymethyl)naphthalene or 1-bromonaphthalene-2-carbaldehyde, we took advantage of biocatalysis to resolve the racemic secondary alcohol **4** by kinetically controlled transesterification with isopropenyl acetate.

Scheme 3. Asymmetric Synthesis of the Enantiopure (+)-(*P*)-[6]Helicene 14[a]



[a]A key step of the synthesis is Co^{I}-catalyzed [2 + 2 + 2] cycloisomerization of (*R*,*R*)- and (*S*,*R*)-**12** (1:1) to receive (*P*,*R*,*R*)- and (*P*,*S*,*R*)-**13** (1:1). Acid-promoted elimination of the methoxymethoxy groups leads to enantiopure (+)-(*P*)-**14** (>99% ee); Cp = cyclopentadienyl, fum = dimethyl fumarate, MOM = methoxymethyl, MW = microwave reactor, TBAF = tetrabutylammonium fluoride, TIPS = triisopropylsilyl, Tol = 4-methylphenyl, Ts = 4-methylphenyl sulfonyl.

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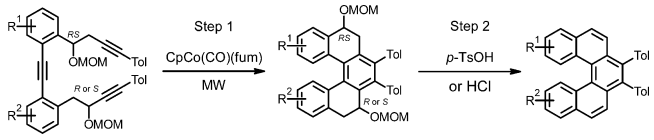
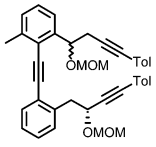
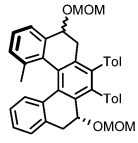
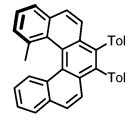
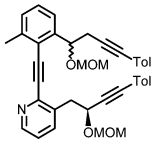
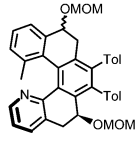
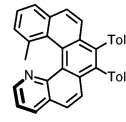
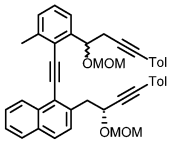
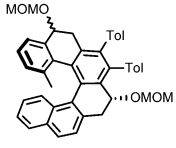
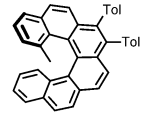
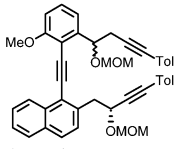
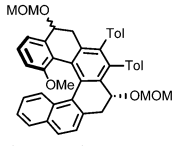
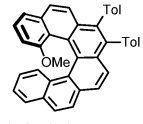
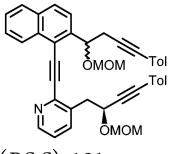
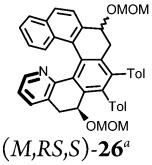
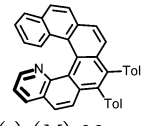
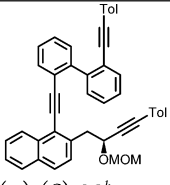
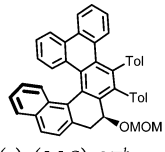
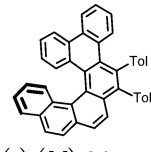
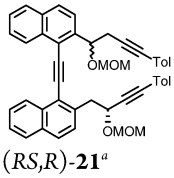
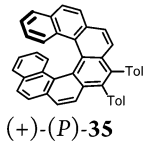
Table 1. Asymmetric Synthesis of the Enantiopure [5]-, [6]-, and [7]helicene 29−35



Entry	Triyne	Step 1 cond.[c]	Tetrahydro-helicene	Yield (%)[d]	Step 2 cond.[e]	Helicene	Yield (%)[d]	*Ee* (%)[f]
1	 (*RS*,*R*)-**15**[a]	A 180 °C 20 min	 (*P*,*RS*,*R*)-**22**[a]	86	B 45 °C 3 d	 (+)-(*P*)-**29**	75	>99
2	 (*RS*,*S*)-**16**[a]	A 150 °C 10 min	 (*M*,*RS*,*S*)-**23**[a]	92	B 45 °C 24 h	 (-)-(*M*)-**30**	67	>99
3	 (*RS*,*R*)-**17**[a]	A 180 °C 20 min	 (*P*,*RS*,*R*)-**24**[a]	77	B 45 °C 2 d	 (+)-(*P*)-**31**	88	>99
4	 (*RS*,*R*)-**18**[a]	A 180 °C 30 min	 (*P*,*RS*,*R*)-**25**[a]	80	C 45 °C 16 h	 (+)-(*P*)-**32**	67	>99
5	 (*RS*,*S*)-**19**[a]	A 150 °C 15 min	 (*M*,*RS*,*S*)-**26**[a]	89	B 45 °C 24 h	 (-)-(*M*)-**33**	74	>99
6	 (+)-(*S*)-**20**[b]	A 180 °C 15 min	 (-)-(*M*,*S*)-**27**[b]	73	B 45 °C 16 h	 (-)-(*M*)-**34**	92	>99
7	 (*RS*,*R*)-**21**[a]	A 170 °C 10 min	 (*P*,*RS*,*R*)-**28**[a]	74	B 45 °C 16 h	 (+)-(*P*)-**35**	69	>99

[a]A 1:1 mixture of enantiopure diastereomers. [b]Enantiopure. [c]A: CpCo(CO)(fum) (0.5 equiv), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (10 mg/1 mL of a solution), THF, microwave reactor. [d]Isolated. [e]B: *p*-Toluenesulfonic acid (10.0 equiv), toluene; C: HCl (aqueous, 10 equiv), acetonitrile. [f]Enantiomer ratios uniformly >99:<1, determined by HPLC on a chiral column (Chiralpak IA or IC); MOM = methoxymethyl, MW = microwave reactor, Tol = 4-methylphenyl.

Novozyme 435 was highly substrate specific so that enzymatic acetylation of (−)-(*R*)-**4** to (+)-(*R*)-**5** could be led to completion without practically any overreaction, as (+)-(*S*)-**4** reacted significantly slower. Naturally, the lipase was available in a single

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enantiomeric form, but a smooth mutual interconversion of (−)-(*R*)- and (+)-(*S*)-**4** by the Mitsunobu reaction followed by ester hydrolysis makes this approach highly versatile to transform all *rac*-**4** to either desired enantiomer in >99% ee. Using the same methodology, (−)-(*R*)-**6**, **7** and (+)-(*S*)-**6**, **7** were synthesized, all in an optically pure form (>99% ee).

The synthesis of the chiral building blocks could be done on a multigram scale including the enzymatic kinetic resolution (in 12 g batches in the case of *rac*-**4**) that underscores its practicality.

To assemble the helicene backbone (Scheme 3), the enantiopure naphthyl iodide (+)-(*R*)-**8** having its hydroxy group protected through methoxymethyl ether was cross-coupled with the racemic phenyl acetylene *rac*-**9** under Sonogashira reaction conditions to form a 1:1 diastereomeric mixture of triynes (*R*,*R*)- and (*S*,*R*)-**10**. As theoretically analyzed and discussed above, the configuration at the stereogenic center in the benzylic position of triyne **10** should not influence the stereochemical outcome of the planned cyclization to a tetrahydro[6]helicene derivative, and therefore, we could disregard its configuration and further work with a mixture of diastereomers. Since the presence of the triisopropylsilyl groups rendered the triynes **10** unreactive toward [2 + 2 + 2] cycloisomerization, we displaced them by tolyl groups through the successive desilylation upon treatment with tetrabutylammonium fluoride and a Sonogashira coupling of the deprotected triynes (*R*,*R*)- and (*S*,*R*)-**11** with 4-iodotoluene to obtain the target triynes (*R*,*R*)- and (*S*,*R*)-**12**. The key step of the synthesis was microwave-assisted Co^{I}-catalyzed [2 + 2 + 2] cycloisomerization of triynes to receive a 1:1 diastereomeric mixture of tetrahydro[6]helicene derivatives (*P*,*R*,*R*)- and (*P*,*S*,*R*)-**13** possessing uniform helicity. Finally, we pursued *p*-toluenesulfonic acid-mediated elimination of both the methoxymethoxy groups to fully aromatize the backbone and, most importantly, to receive the enantiopure tolylated (+)-(*P*)-[6]helicene **14**.

It is worth noting that cyclizing (*R*,*RS*)-**12** in the presence of $Ni(cod)_2/PPh_3$ at room temperature (under kinetic stereocontrol) led, after separating chromatographically the pairs of (*P*,*RS*,*R*)- and (*M*,*RS*,*R*)-**13** diastereomers and their following aromatization, to (+)-(*P*)- and (−)-(*M*)-[6]helicene **14** in a 63:37 ratio (for detail, see Supporting Information).

Asymmetric Synthesis of [5]-, [6]-, and [7]Helicene Derivatives. A successful demonstration of the proof of principle prompted us to apply the newly developed methodology also to the asymmetric synthesis of a series of [5]-, [6]-, and [7]helicene derivatives. Utilizing the enantiopure chiral building blocks (−)-(*R*)-**4**, (+)-(*S*)-**4**, (−)-(*R*)-**6**, and (+)-(*S*)-**7** (Scheme 2), we prepared a series of (*RS*,*R*)- or (*RS*,*S*)-triynes **15**-**21** as precursors of diverse helicenes, heterohelicenes and functionalized helicenes (Table 1). One we had these triynes in the form of 1:1 diastereomeric mixtures (absolute configuration of only one of their two stereogenic centers was controlled), they were subjected to [2 + 2 + 2] cycloisomerization under conditions where postcyclization thermal equilibration of the helical backbone was expected. Indeed, upon treatment with CpCo(CO)(fum)[45] in a microwave reactor, we obtained the corresponding tetrahydrohelicene derivatives **22**−**28** in good to high yields. Importantly, the ^{1}H NMR spectra of isolated products indicated in all cases the formation of only two diastereomers in accord with both the computational prediction and the outcome of the pilot cyclization (cf. Scheme 3). Furthermore, in the presence of acid, all the oxygenated tetrahydrohelicenes **22**−**28** underwent aromatization smoothly by eliminating the methoxymethoxy groups that had already fulfilled their roles either as a chiral auxiliary or a stereochemically innocent but synthetically important moiety. Significantly, all fully aromatic helicenes **29**−**35** were found to be enantiopure as checked by HPLC analysis on a chiral column. It is worth noting that we prepared the products **14** and **29**−**35** also in a racemic form (by a racemic synthesis or through thermal racemization of enantiopure products) to verify the separation of the enantiomer. Thus, we demonstrated a complete point-to-helical chirality transfer[31] in the series of configurationally stable [5]-, [6]-, and [7]helicene molecules regardless of their length (Table 1, entries 1 and 2 vs 3−6 vs 7), the presence of an embedded pyridine unit (entries 2 and 5), the attachment of Me or MeO substituents (entries 1−4), or an annulated benzene ring (entry 6). Such a remarkable independence of stereocontrol toward diverse structural perturbations stems from the fact that chirality transfer is controlled by a small but well-defined part of a molecule, leaving the rest highly unrestricted to structural changes.

■ CONCLUSIONS

We have developed a general methodology for the preparation of uniformly enantiopure fully aromatic [5]-, [6]-, and [7]helicenes through asymmetric synthesis. This approach is based on a tandem of [2 + 2 + 2] cycloisomerization of centrally chiral triynes and postcyclization thermodynamic equilibration of diastereomeric tetrahydrohelicene derivatives being ultimately controlled by the 1,3-allylic-type strain. The point-to-helical chirality transfer utilizing a traceless chiral auxiliary features a remarkable independence from the diverse structural perturbations allowing for the preparation of both parent and functionalized helicenes in enantiomer ratios of >99:<1. Thus, we have provided a solution to a problem of helicene chemistry present since its birth in 1956 that has been a limited access to iconic helical aromatics in an optically pure form through asymmetric synthesis. We believe that our achievements will stimulate further interest in enantiopure helicenes and their wider exploitation in various fields of science.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectroscopic data for the new compounds, determination of the barriers to racemization/epimerization, chiral HPLC analyses of the racemic and enantiopure helicenes, helicity assignment of the enantiopure helicenes, and ^{1}H and ^{13}C NMR spectra of the new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b02794.

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Notes

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