

# Synthesis of Long Oxahelicenes by Polycyclization in a Flow Reactor

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Dedicated to Professor Thomas J. Katz

**Abstract:** A series of oxahelicenes composed of ortho/meta-annulated benzene/pyridine and 2H-pyran rings were synthesized on the basis of the cobalt(I)-mediated (or rhodium(I)- or nickel(0)-mediated) double, triple, or quadruple [2+2+2] cycloisomerization of branched aromatic hexa-, nona-, or dodecynes, thus allowing the construction of 6, 9, or 12 rings in a single operation. The use of a flow reactor was found to be beneficial for the multicyclization reactions. The stereogenic centers present in some of the oligoynes steered the helical folding in such a way that the final oxa[9]-, [13]-, [17]- and [19]helicenes were obtained in both enantiomerically and diastereomerically pure form. Specifically, the oxa[19]helicenes beat the current record in the length of a helicene backbone. Single-molecule conductivity was studied by the mechanically controllable break-junction method with a pyridooxa[9]helicene.

Long helically chiral (hetero)[*n*]helicenes<sup>[1]</sup> ( $n \geq 11$ ) are both challenging synthetic targets and potentially useful materials for molecular (electro)mechanics,<sup>[2]</sup> (opto)electronics,<sup>[3]</sup> and chiroptics.<sup>[4]</sup> Although numerous methods for the preparation of helicenes, heterohelicenes, and their analogues have been developed, only the multiple photocyclodehydrogenation of diaryl olefins and the [2+2+2] cycloisomerization of alkynes have so far passed the tough test for synthetic methods that are suitable for the preparation of molecular screws containing more than eleven all-ortho condensed rings.<sup>[1]</sup>

The current record in helicene length is held by Mori et al., who recently accomplished the synthesis of the [16]helicene and its derivative **1** (Figure 1) by the use of a sextuple photocyclodehydrogenation to fold a cleverly designed single-strand arylene-vinylene precursor into a helix.<sup>[5]</sup> Even more carbocycles are present in [17]heliphene **2** (angular [9]phenylene) reported by Vollhardt and co-workers, whose landmark synthesis relied on the triple cobalt(I)-mediated [2+2+2] cycloisomerization of an aromatic nonayne.<sup>[6]</sup> The low yields of such multiple cyclizations (10 and 2–3.5 %, respectively) manifest, however, both the limits of the current synthetic methodologies and the structural complexity of the highest helicenes.<sup>[7]</sup> Not surprisingly, the lower homologues, such as the [15]- and [13]thia-helicene reported by Yamada et al.,<sup>[8]</sup> the [14]- and [12]helicene synthesized by Martin and Baes,<sup>[9]</sup> and the [13]helicene described by Martin et al.,<sup>[10]</sup> are also quite rare. Intriguingly, Werz and co-workers recently demonstrated the synthesis of a truncated [12]helicene analogue.<sup>[11]</sup> In contrast, successful and diverse approaches to [11]helicene and its analogues were

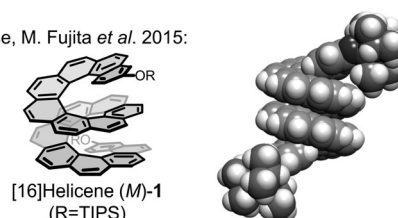
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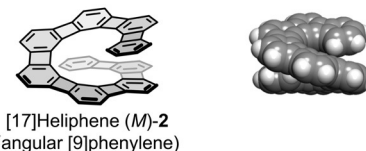
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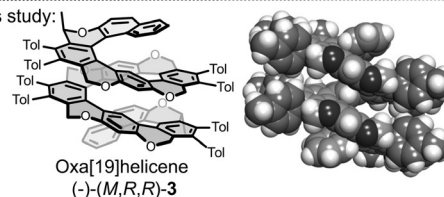
T. Murase, M. Fujita *et al.* 2015:



K. P. C. Vollhardt *et al.* 2002:



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**Figure 1.** The longest helicenes and their analogues synthesized to date. TIPS = triisopropylsilyl, Tol = *p*-tolyl.

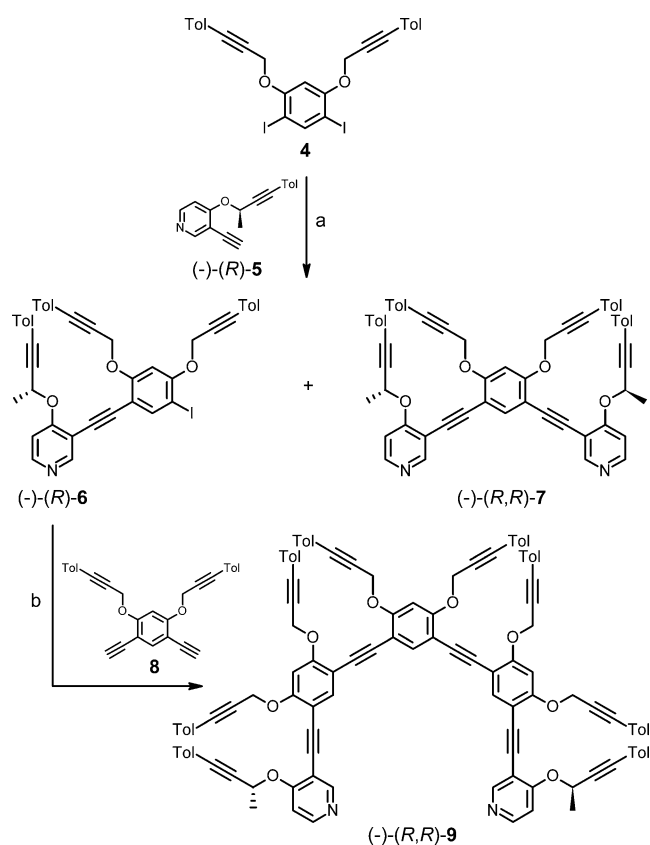
reported by Martin and Baes,<sup>[9]</sup> Wynberg et al.,<sup>[12]</sup> Rajca and co-workers,<sup>[13]</sup> Tanaka and co-workers,<sup>[14]</sup> Werz and co-workers,<sup>[11]</sup> and us.<sup>[15]</sup> Although the asymmetric synthesis of long (hetero)[*n*]helicenes ( $n \geq 11$ ) has been attempted rarely,<sup>[16]</sup> recent results are truly encouraging: We demonstrated the diastereoselective cobalt(I)-mediated double [2+2+2] cycloisomerization of a centrally chiral hexayne to generate the *ortho/meta*-fused [11]helicene analogue with d.r. 90:10.<sup>[15]</sup> Analogously, Tanaka and co-workers used the rhodium(I)-catalyzed enantioselective double [2+2+2] cycloisomerization of an achiral hexayne to obtain the all-*ortho*-fused oxa[11]helicene with 91% *ee*.<sup>[14]</sup>

Herein, we report the synthesis of a series of oxahelicenes in both racemic and enantiomerically pure form by the multiple [2+2+2] cycloisomerization of branched aromatic oligoynes. This approach produced the longest helicene analogues prepared so far, such as (–)-(M,R,R)-**3** (Figure 1). We also initiated studies on the single-molecule conductivity of helicenes by employing the mechanically controllable break-junction method.

On the basis of the principles of the stepwise assembly of oligo(*m*-phenyleneethynylene)s, studied extensively by Moore and co-workers as foldamers,<sup>[17]</sup> we attempted the preparation of the oxahelicene precursors **7** and **9–14** (achiral or enantiomerically pure; Table 1). The synthesis of (–)-(R,R)-**9** exemplifies the approach to the key arylene–ethynylene short monodispersed oligomers (Scheme 1; for the preparation of **7** and **9–14**, see the Supporting Information). The Sonogashira monocoupling of diiodide **4** with alkyne (–)-(R)-**5** (1.5 equiv) led to the desymmetrized iodide (–)-(R)-**6** as the main product (56%), accompanied by the symmetrical hexayne (–)-(R,R)-**7** (25%) resulting from double coupling. After their separation by liquid chromatography, the iodide (–)-(R)-**6** was subjected to a final coupling reaction with diyne **8** to provide the target nonayne (–)-(R,R)-**9** in satisfactory yield.

Attempts at the multiple [2+2+2] cycloisomerization of the model oligoynes started with a comparison of the efficiency of various metal complexes in the cyclization of the readily accessible hexayne **10** (stoichiometric or superstoichiometric amounts of  $ML_n$  were used to guarantee complete conversion). Although [Ni(cod)<sub>2</sub>] (in a Schlenk flask) and [Cp\*Rh(CH<sub>2</sub>=CH<sub>2</sub>)<sub>2</sub>] (in a microwave reactor) exhibited slightly better performance than [CpCo(CO)<sub>2</sub>]/PPh<sub>3</sub> (in a Schlenk flask under irradiation with visible light) or [Rh<sub>2</sub>(CH<sub>2</sub>=CH<sub>2</sub>)<sub>4</sub>Cl<sub>2</sub>] (in a microwave reactor) in providing oxa[9]helicene *rac*-**15** (Table 1, entry 1), [CpCo(CO)<sub>2</sub>] (in a flow reactor) outperformed [Ni(cod)<sub>2</sub>]/PPh<sub>3</sub> (in a Schlenk flask) in promoting the cyclization of enantiomerically pure (–)-(R,R)-**7** into oxa[9]helicene (–)-(M,R,R)-**16** as a single diastereomer (entry 2).

Accordingly, subsequent multiple [2+2+2] cycloisomerization reactions were preformed in the presence of [CpCo(CO)<sub>2</sub>] in a flow reactor. The other metal complexes mentioned above were ineffective in cyclizations of the longer oligoynes. Thus, the achiral naphthyl-derived hexayne **11** was converted into [11]helicene *rac*-**17** (entry 3), and the enantiomerically pure pyridine-derived nonayne (–)-(R,R)-**12** delivered the diastereomerically pure pyridooxa-

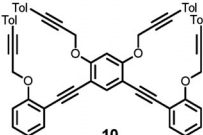
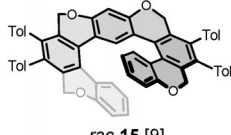
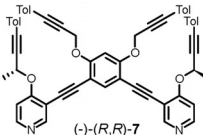
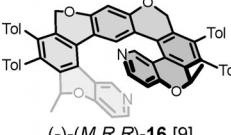
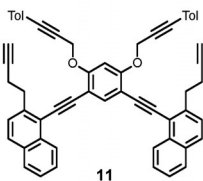
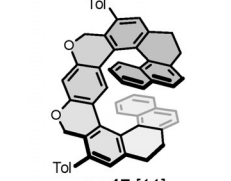
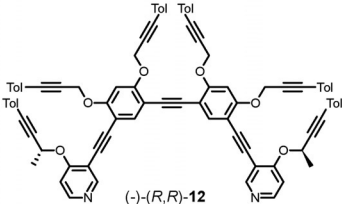
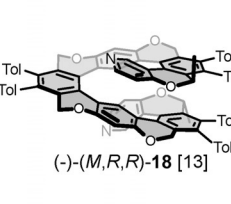
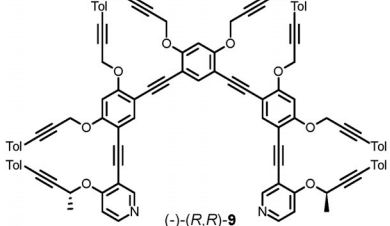
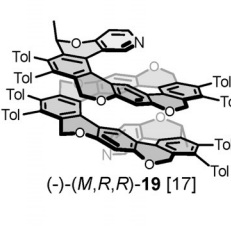
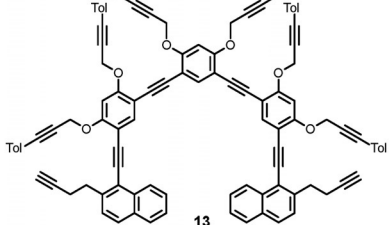
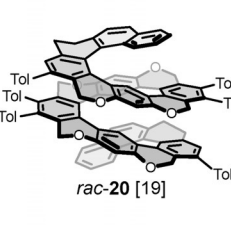
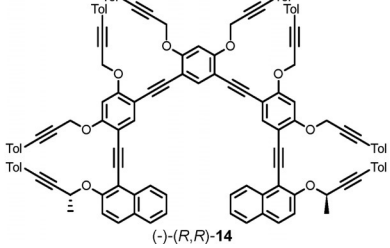
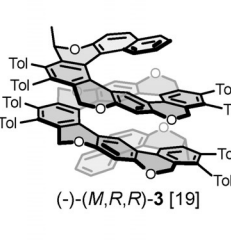


**Scheme 1.** Synthetic route to (–)-(R,R)-**7** and (–)-(R,R)-**9**, oligoyne precursors of the corresponding long oxahelicenes: a) (–)-(R)-**5** (1.5 equiv), [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (5 mol%), CuI (10 mol%), *i*Pr<sub>2</sub>NH, benzene (3:1), room temperature, 2 h, 56% for (–)-(R)-**6**, 25% for (–)-(R,R)-**7**; b) **8** (1.1 equiv), [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (5 mol%), CuI (10 mol%), *i*Pr<sub>2</sub>NH, toluene (2:1), room temperature, 16 h, 36%. Tol = *p*-tolyl.

[13]helicene (–)-(M,R,R)-**18** (entry 4). The successful triple [2+2+2] cycloisomerization of the latter oligoyne prompted us to attempt the quadruple cyclization of dodecaynes to close 12 rings in a single operation. Indeed, the enantiomerically pure pyridine-derived dodecayne (–)-(R,R)-**9** furnished the diastereomerically pure pyridooxa[17]helicene compound (–)-(M,R,R)-**19** (entry 5). Importantly, the achiral naphthyl-derived dodecayne **13** underwent the desired multiple cyclization to give the oxa[19]helicene *rac*-**20** (entry 6). Finally, the enantiomerically pure naphthyl-derived dodecayne (–)-(R,R)-**14** was successfully converted into the diastereomerically pure oxa[19]helicene (–)-(M,R,R)-**3** (entry 7).

The preparative yields of the cyclized products were 18–53%, thus indicating a loose correlation between the yield and the length of the helix (the average yield per [2+2+2] cycloisomerization reaction was calculated to be 63–83%). Importantly, the use of the high-temperature high-pressure flow reactor was a key to this success; in the case of multiple cyclization reactions of the longest oligoynes, the yield surpassed that observed upon microwave or conventional heating. This positive effect of the flow reactor might be attributed to efficient heat transfer and therefore the short reaction time (8–16 min), which resulted in reduced intermediate/product deterioration. The asymmetric synthesis of

**Table 1:** Multiple [2+2+2] cycloisomerization of oligoynes **7** and **9–14** into the corresponding long oxahelicenes **3** and **15–20**.

Entry	Starting oligoyne	ML <sub>n</sub> /Ligand (equiv.)	Cond. <sup>[a]</sup>	Helicene product <sup>[b],[c]</sup>	Yield [%] <sup>[d]</sup>
1		Ni(cod) <sub>2</sub> (2.0) CpCo(CO) <sub>2</sub> (2.0)/PPh <sub>3</sub> (4.0) Cp*Rh(CH <sub>2</sub> =CH <sub>2</sub> ) <sub>2</sub> (1.0) Rh <sub>2</sub> (CH <sub>2</sub> =CH <sub>2</sub> ) <sub>4</sub> Cl <sub>2</sub> (1.0)	A		51
			B		41
			C		50
			C		40
2		Ni(cod) <sub>2</sub> (0.5)/PPh <sub>3</sub> (1.0) CpCo(CO) <sub>2</sub> (0.6)	A		43
			D		53
3		CpCo(CO) <sub>2</sub> (2.0)	D		50
4		CpCo(CO) <sub>2</sub> (0.9)	D		35
5		CpCo(CO) <sub>2</sub> (1.2)	D		18
6		CpCo(CO) <sub>2</sub> (2.0)	D		47
7		CpCo(CO) <sub>2</sub> (2.0)	D		20

[a] Reaction conditions A: THF, room temperature, 1–16 h; B: decane, 140 °C, 30 min, irradiation with a halogen lamp; C: THF, 140 °C, 15 min, microwave reactor; D: THF, 250 °C, 8–16 min, flow reactor. [b] In the case of racemates, only the *M* enantiomer is shown for clarity. [c] The number of *ortho/meta* condensed rings is given in square brackets. [d] Yield of the isolated product. cod = 1,5-cyclooctadiene, Cp\* = 1,2,3,4,5-pentamethylcyclopentadienyl.

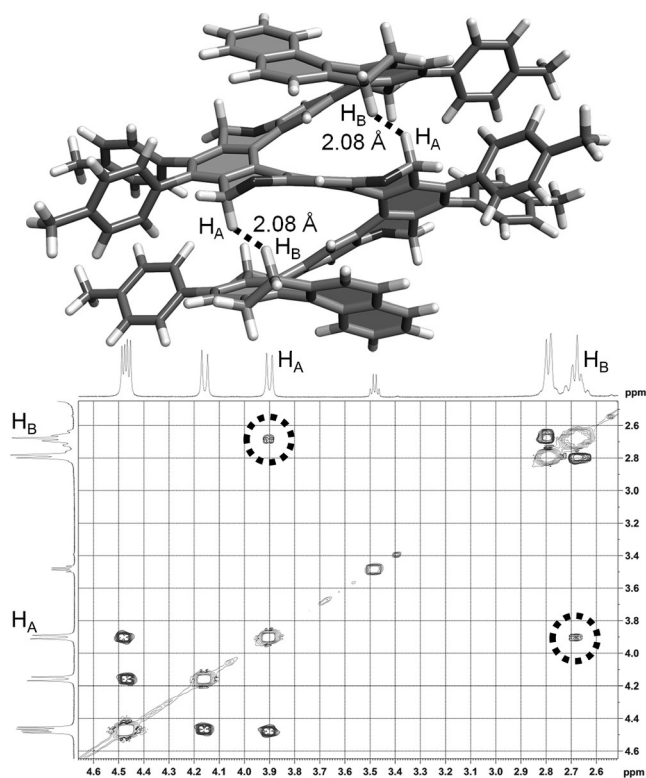
oxa[*n*]helicenes (–)-(*M,R,R*)-**3**, **16**, **18**, and **19** (*n* = 9, 13, 17, and 19), which is unprecedented in the family of long [*n*]helicenes (*n* > 11), benefited from both the commercial

availability of (*R*)- and (*S*)-but-3-yn-2-ol as the key chiral building block and the powerful stereocontrol induced by 1,3-allylic-type strain<sup>[18,19]</sup> in the folding of the enantiomerically

pure oligoyne precursors into the diastereomerically pure helices.

Despite our efforts to obtain material suitable for X-ray crystallographic analysis, the well-soluble helical products **3** and **15–20** bearing up to eight tolyl groups provided crystals of insufficient quality. Therefore, we inferred their helical structure from the electronic circular dichroism (ECD) and  $^1\text{H}$  NMR spectra, which confirmed the  $C_2$  symmetry of the cyclized products. For example, the folding of the centrally chiral dodecayne  $(-)-(R,R)$ -**9** into the corresponding oxa[17]helicene  $(-)-(M,R,R)$ -**19** led to a dramatic change in the ECD spectrum (see the Supporting Information). The helical product gave rise to new strong bands in the ECD spectrum, as a helically chiral chromophore was formed. The negative dichroism associated with the longest-wavelength band at 389 nm pointed to *M* helicity of the molecule, as already observed in the CD spectra of nonracemic helicenes<sup>[20]</sup> and their congeners.<sup>[19b,21]</sup> Moreover, the helical arrangement of the longest [19]helicenes  $(-)-(M,R,R)$ -**3** and *rac*-**20** was unequivocally confirmed by detailed analysis of their  $^1\text{H}$ - $^1\text{H}$  ROESY NMR spectra. As exemplified for *rac*-**20** (Figure 2), the spatial proximity (2.08 Å) of pseudoaxial hydrogen atoms of the innermost methylene units to the pseudoaxial a single diastereomer of the outermost methylene units (17 bonds apart) led to a through-space correlation between these atoms and a clearly visible cross-peak in the ROESY spectrum.

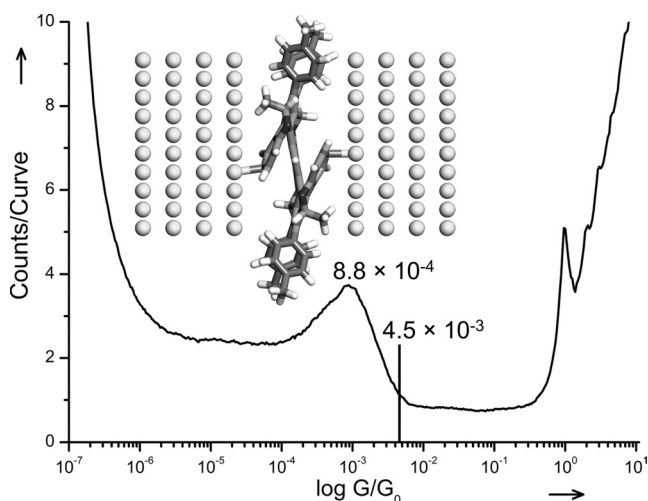
The availability of the series of oxa[9]-, [13]-, and [17]helicenes  $(-)-(M,R,R)$ -**16**, **18** and **19** terminated with pyridine units as suitable anchoring groups encouraged us to



**Figure 2.** Part of the  $^1\text{H}$ - $^1\text{H}$  ROESY NMR spectrum of *rac*-**20** showing a through-space correlation between protons from adjacent backbone loops. The molecular structure was optimized by the DFT (B3LYP/cc-pVDZ) method with the GD3 dispersion correction in vacuo.

study single-molecule conductivity by using the mechanically controllable break-junction method (MCBJ).<sup>[22]</sup> Helicenes are unique multichannel systems combining a chiral  $\pi$ -conjugated pathway with an achiral  $\pi$ - $\pi$  stacked pathway in a single molecule<sup>[23]</sup> and may express, among other phenomena, symmetry breaking in charge/spin transport.<sup>[24]</sup> In a pilot study, we measured by the MCBJ method the single-molecule conductance of pyridooxa[9]helicene  $(-)-(M,R,R)$ -**16** repeatedly sandwiched between gold nanoelectrodes. The 1D conductance histogram revealed the presence of a conductance peak corresponding to the single-molecule junction (Figure 3; for a 2D histogram, see the Supporting Information). Its maximum was found at  $8.8 \times 10^{-4} \text{ G/G}_0$  in relation to the calculated value of  $4.5 \times 10^{-3} \text{ G/G}_0$  (ATK, QuantumWise). The diffuse character of the peak was attributed to the superposition of a variable gold electrode geometry and the attachment configuration of the molecule. The conductance value reflects the presence of a cross-conjugated part of the molecule (a *meta*-substituted central benzene unit), which is expected to diminish the probability of tunneling along the  $\pi$ -conjugated pathway owing to the destructive interference effect.<sup>[25]</sup> A detailed study focused on the transport properties of helicenes will be reported separately.

In summary, we have developed a synthetic route to the longest oxahelicenes prepared to date, comprising up to 19 *ortho/meta*-fused benzene/2*H*-pyran rings in their helical backbone. The use of a flow reactor in the key step, the final multiple cobalt(I)-mediated alkyne [2+2+2] cycloisomerization to form up to 12 C–C bonds and 12 rings in a single operation, was found to be advantageous for the efficient folding of the branched aromatic oligoynes into oxa[9]-, [11]-, [13]-, [17]- and [19]helicenes in reasonable preparative yields (18–53%). Furthermore, the introduction of stereogenic



**Figure 3.** Single-molecule conductance of  $(-)-(M,R,R)$ -**16**, as measured by the MCBJ method (graph) and calculated by DFT (vertical mark). The experimental 1D conductance histogram was constructed from 10544 individual opening conductance traces indicating the presence of a molecule (70% of all curves; 2% bin size; measured in mesitylene at room temperature under argon). A theoretical model (DFT/PBE/SZP, DZP) of the Au(111)–single molecule–Au(111) junction used in the conductance calculations (NEGF, Landauer formalism, ATK) is shown in the inset.



centers of known absolute configuration into the oligoyne precursors resulted in complete stereoselectivity in the cyclization step to provide the inherently chiral products in enantio- and diastereomerically pure form. Finally, we have shown that the single-molecule conductivity of such complex  $\pi$ -electron systems equipped with anchoring pyrido groups can be investigated by means of the mechanically controllable break-junction method. Further studies in this direction are in progress.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** asymmetric synthesis · chirality · conducting materials · helical structures · heterocycles

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