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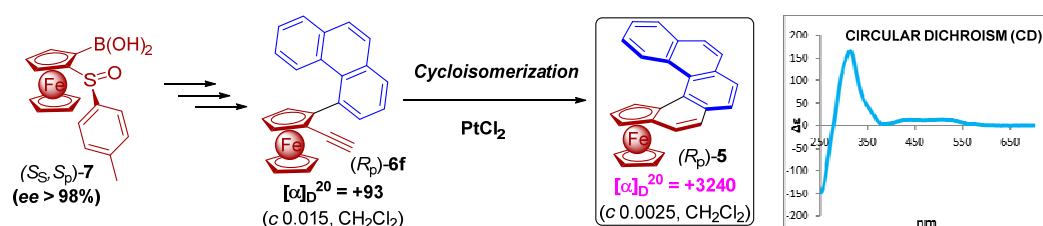
Asymmetric synthesis and chiroptical properties of enantiopure helical ferrocenes

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Supporting Information Placeholder



ABSTRACT: An enantiopure helical ferrocene (*R_p*)-**5** with five *ortho*-condensed aromatic rings was synthesized using a PtCl₂-catalyzed cycloisomerization of planar-chiral 2-ethynyl-1-(4-phenanthrenyl)ferrocene (*R_p*)-**6f**, prepared in 3 steps from known enantiopure sulfanyl ferrocenyl boronic acid (*S_S,S_p*)-**7**, as the source of planar chirality. This pentacyclic helical ferrocene showed a very high optical rotation value and strong CD signals.

The development of chiral molecules that show strong chiroptical properties may lead to new multifunctional molecular materials.¹ In this context, helicenes, polycyclic *ortho*-fused aromatic systems with twisted π backbones displaying helical chirality, exhibit unique properties, such as high values of optical rotation and intense circular dichroism response. Consequently, they have found interesting applications in asymmetric catalysis, supramolecular chemistry, liquid crystals, and organic electronic devices.²

On the other hand, planar-chiral ferrocenes have received great attention in view of their increasing importance in the fields of asymmetric catalysis, enantioselective synthesis, and materials science. They have been widely used as privileged scaffolds for the synthesis of efficient chiral ligands and catalysts playing an important role in asymmetric organic synthesis both in academia and industry. The design, synthesis and utilization of ferrocene-based chiral ligands have expanded rapidly over the last decades.³

During last years, organometallic helicenes in which a transition metal is included within the helical π -framework have emerged as highly promising candidates for optoelectronic applications, owing to the presence of the metal center.⁴ Coordination of the polycyclic aromatic molecules to metal atoms may alter the electronic density distribution and significantly change their properties. Thus, the switching of chiral metal-based systems has great potential,⁵ due to the possibility of reversibly modifying the molecule by changing the properties of the metal center (geometry, redox state).

Despite the great achievements performed up to date in this field, to the best of our knowledge, there are only a few examples of helical ferrocenes in which the central iron atom of the

ferrocene unit is bounded directly into the helicene framework through the *ortho*-annulation to several aromatic rings (Figure 1a-c).⁶⁻⁸ In all cases reported, the synthetic strategy was based on the initial formation of the helicene framework containing one or two cyclopentadienyl rings, followed by formation of the ferrocene unit. Thus, it is worth to mention the pioneering work of Katz,⁶ who in 1982 described the first synthesis of a racemic [7]-helicene with the ferrocene unit at the edge of its skeleton (Figure 1a).^{6a} Several years later, the enantiomerically enriched derivative was prepared through asymmetric synthesis exhibiting an intense absorption in the visible region and a strong signal in its circular dichroism (CD) spectra.^{6b} In 2007, Thiel reported the synthesis of a series of ferrocenes with the dibenzo[c,g]fluorenyl (Dbf) ligand, in which the ferrocene unit is situated at the middle of the [5]-helicene structure (Figure 1b),⁷ although racemization proceeded rapidly at room temperature in solution.^{7a} This problem was solved by Nozaki in 2017 by synthesizing an enantiopure [7]-helicene analogue (Figure 1c), with a high racemization barrier, through chiral HPLC resolution of the corresponding racemic derivative.⁸ This helical ferrocene showed large optical rotations and intense circular dichroism (CD) responses.

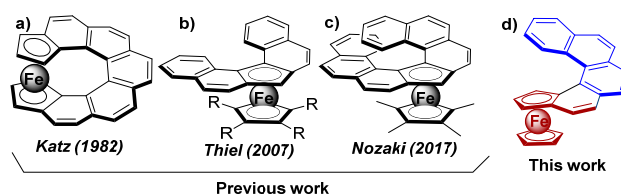


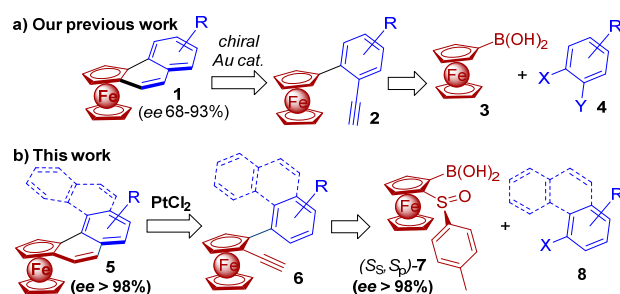
Figure 1. Helical ferrocenes synthesized up to date.

Herein, we report the asymmetric synthesis and chiroptical properties of an enantiopure [5]-helicene derivative with the ferrocene unit bounded at the end of the helical framework (Figure 1d) using a new strategy in which the helicenic structure is generated at the end of the synthetic sequence from previously formed enantiopure planar-chiral ferrocenes.

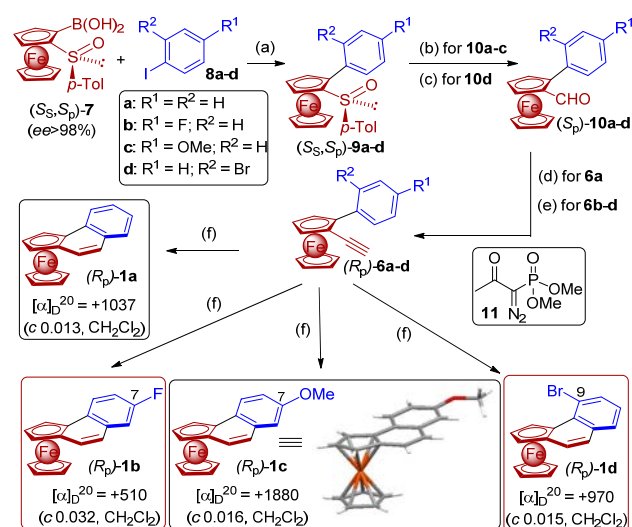
We have recently described an approach to planar-chiral tricyclic *ortho*-condensed aromatic ferrocenes **1**, in moderate to good optical purities (*ee* 68-93%), through the enantioselective cationic Au(I)-catalyzed cycloisomerization of *ortho*-alkynylaryl ferrocenes **2**, prepared in several steps starting from a Suzuki coupling of ferrocenyl boronic acid **3** and aryl halides **4** (Scheme 1a).⁹ In order to prepare new and more extended derivatives, such as the pentacyclic helical ferrocene **5** in enantiopure form, we designed a new synthetic approach based on the PtCl₂-catalyzed cycloisomerization¹⁰ of planar-chiral 2-ethynyl-1-(4-phenanthrenyl)ferrocene **6** (Scheme 1b). This compound would be obtained after several steps, starting from a Suzuki coupling between known enantiopure sulfinyl ferrocenyl boronic acid (*S_S,S_P*)-**7**, as the source of planar chirality, and 4-bromo phenanthrene **8** (R = H, X = Br). In comparison with the former approach (Scheme 1a), the synthetic strategy depicted in Scheme 1b would allow to synthesize higher homologues in enantiopure form, with the aim of studying their chiroptical properties. This would be a more versatile strategy since it is based on the use of more accessible mono or disubstituted aromatic halides **8** rather than the corresponding di- or trisubstituted derivatives **4**, for the initial Suzuki coupling.

In order to validate the approach depicted in Scheme 1b, we decided to prepare several enantiopure tricyclic *ortho*-condensed aromatic ferrocenes bearing substituents at different positions, starting with the synthesis of the unsubstituted derivative (*R_P*)-**1a** (Scheme 2). Thus, the Suzuki coupling between known *p*-tolylsulfinyl ferrocenyl boronic acid (*S_S,S_P*)-**7** (>98% *ee*)¹¹ and iodobenzene (**8a**), in the presence of PdCl₂(dppf) and NaOH,¹² afforded phenyl-substituted ferrocene (*S_S,S_P*)-**9a** in 79% yield. Next, the sulfoxide-lithium exchange on (*S_S,S_P*)-**9a** effected by *tert*-BuLi, followed by the addition of *N,N*-dimethylformamide (DMF) as formylating agent,¹³ yielded a 64% of 1-formyl-2-phenyl ferrocene (*S_P*)-**10a**. The subsequent transformation of the formyl group of (*S_P*)-**10a** into a triple bond was carried out using the two-step Corey-Fuchs procedure.¹⁴ Thus, reaction of (*S_P*)-**10a** with CBr₄ and PPh₃ afforded the corresponding dibromoalkene which, without purification, was treated with *n*-BuLi furnishing 2-ethynyl-1-phenyl ferrocene (*R_P*)-**6a**, in 60% yield. Finally, the PtCl₂-catalyzed cycloisomerization of (*R_P*)-**6a** in toluene at 100 °C gave enantiopure *ortho*-condensed aromatic tricyclic ferrocene (*R_P*)-**1a** in 92% yield {[α]_D²⁰ = +1037 (*c* 0.013, CH₂Cl₂)}.¹⁵

Scheme 1. Asymmetric synthetic approaches to *ortho*-condensed aromatic ferrocenes.



Scheme 2. Asymmetric synthesis of enantiopure tricyclic *ortho*-condensed aromatic ferrocenes (*R_P*)-1a-d**.**



Conditions: (a) PdCl₂(dppf), NaOH, toluene-H₂O, 110 °C, overnight, 51-91%. (b) *t*-BuLi, DMF, THF, -78 °C, 2 h, 64-81%. (c) PhLi, DMF, THF, -78 °C, 2 h, 73%. (d) i. CBr₄, PPh₃, CH₂Cl₂, 0 °C, 2 h; ii. *n*-BuLi, Et₂O/THF, -78 °C to rt, 2 h, 60%. (e) **11**, K₂CO₃, MeOH, rt, 48 h, 55-81%. (f) PtCl₂ (10%), toluene, 100 °C, 2-5 h, 82-95%.

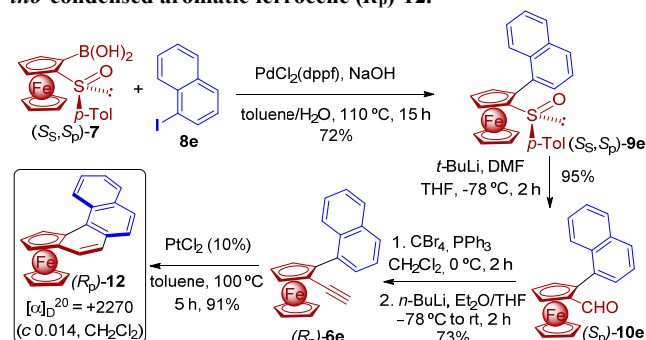
A similar synthetic sequence was applied for the synthesis of derivatives bearing electron-withdrawing (F) or electron-donating (OMe) substituents at C-7 position of the aromatic system (Scheme 2). Thus, the Suzuki coupling of (*S_S,S_P*)-**7** and *p*-fluoro iodobenzene (**8b**) gave rise to the aryl sulfoxide (*S_S,S_P*)-**9b** in 91% yield, which after sulfoxide-lithium exchange followed by formylation furnished aldehyde (*S_P*)-**10b**, in 79% yield. Although the Corey-Fuchs procedure worked well for the transformation of aldehyde (*S_P*)-**10b** into alkyne (*R_P*)-**6b**, we obtained better yield by applying the Seyferth-Gilbert homologation¹⁶ using the Ohira-Bestmann reagent **11**.¹⁷ Under these conditions, alkyne (*R_P*)-**6b** was isolated, after chromatographic purification, in 85% yield. The cycloisomerization of (*R_P*)-**6b** with PtCl₂ afforded enantiopure fluoro tricyclic ferrocene (*R_P*)-**1b** in 85% yield {[α]_D²⁰ = +510 (*c* 0.032, CH₂Cl₂)}.¹⁵

For the preparation of MeO-substituted derivative (*R_P*)-**1c** from boronic acid (*S_S,S_P*)-**7** and *p*-methoxy iodobenzene (**8c**), we used the same experimental conditions that for (*R_P*)-**1b**, via sulfoxide (*S_S,S_P*)-**9c** (51%), aldehyde (*S_P*)-**10c** (81%) and alkyne (*R_P*)-**6c** (61%), whose PtCl₂-catalyzed cycloisomerization gave rise to enantiopure (*R_P*)-**1c** in 82% yield {[α]_D²⁰ = +1880 (*c* 0.016, CH₂Cl₂)}.¹⁵ The absolute configuration of (*R_P*)-**1c**, as well as the planar disposition of their three aromatic rings, was confirmed by X-ray diffraction (see SI).

Finally, we were also interested in the synthesis of a derivative bearing a bulky bromine at the most hindered C-9 position of the aromatic framework, (*R_P*)-**1d** (Scheme 2). Thus, the Suzuki coupling of (*S_S,S_P*)-**7** and *o*-bromo iodo benzene (**8d**) afforded bromoaromatic sulfoxide (*S_S,S_P*)-**9d** in 67% yield.^{11a} The selective sulfoxide-lithium exchange of (*S_S,S_P*)-**9d** was effected in this case by an inverse addition using PhLi,¹⁸ followed by formylation with DMF, affording aldehyde (*S_P*)-**10d**, in 73% yield. Finally, the Seyferth-Gilbert homologation of (*S_P*)-**10d**, followed by PtCl₂-catalyzed cycloisomerization of alkyne (*R_P*)-**6d** (55%), allowed us to obtain enantiopure tricyclic ferrocene (*R_P*)-**1d** in 95% yield {[α]_D²⁰ = +970 (*c* 0.015, CH₂Cl₂)}.¹⁵

Having demonstrated the scope of the Pt-catalyzed cycloisomerization process for the synthesis of differently substituted enantiopure tricyclic aromatic ferrocenes **1a-d**, we were interested in extending the methodology to the construction of a planar-chiral tetracyclic aromatic ferrocene such as (*R_p*)-**12**, using the four-step sequence depicted in Scheme 3. Thus, the Suzuki coupling of (*S_S,S_p*)-**7** with 1-iodonaphthalene (**8e**) gave rise to the aryl sulfoxide (*S_S,S_p*)-**9e** in 72% yield,¹² which after sulfoxide-lithium exchange followed by formylation furnished aldehyde (*S_p*)-**10e**, in 95% yield. The reaction of (*S_p*)-**10e** with CBr₄ and PPh₃ followed by treatment of the dibromoalkene intermediate with *n*-BuLi afforded alkyne (*R_p*)-**6e**, in 73% yield. Finally, the cycloisomerization of (*R_p*)-**6e** with PtCl₂ (10%) gave rise to enantiopure helical tetracyclic ferrocene (*R_p*)-**12** in 92% yield [$[\alpha]_D^{20} = +2270$ (*c* 0.014, CH₂Cl₂)].¹⁵

Scheme 3. Asymmetric synthesis of enantiopure tetracyclic *ortho*-condensed aromatic ferrocene (*R_p*)-12**.**



The circular dichroism (CD) spectra of enantiopure tricyclic *ortho*-condensed aromatic ferrocenes (*R_p*)-**1a-d** and tetracyclic derivative (*R_p*)-**12** are shown in Figure 2.

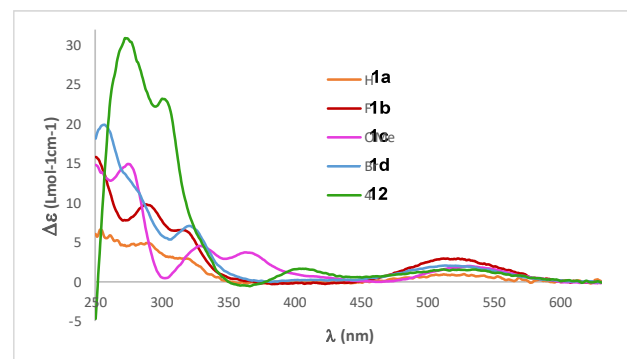


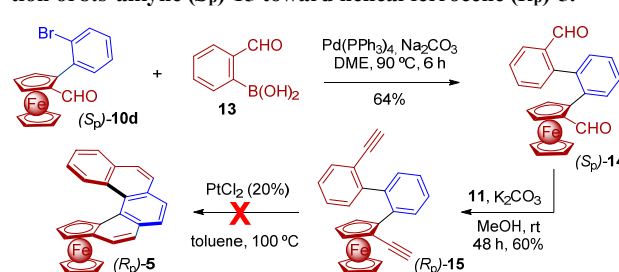
Figure 2. CD spectra of enantiopure tricyclic ferrocenes (*R_p*)-1a-d** and tetracyclic derivative (*R_p*)-**12**.**

As can be seen, all derivatives showed four positive bands, three of them between 250 and 400 nm and a red-shifted one centered at 520 nm, which could be attributed to an intramolecular charge-transfer transition between the planar-chiral ferrocenyl donor and the conjugated extended aromatic system, acting as acceptor.¹⁹ The unsubstituted tricyclic derivative (*R_p*)-**1a** presented the lower chiroptical response with a maximum near 250 nm ($\Delta\epsilon = +6.4$). The two derivatives (*R_p*)-**1b-c**, substituted at C-7 with F and OMe groups, showed a ca. three-fold ($\Delta\epsilon = +16$) intensity for that band, whereas compound (*R_p*)-**1d**, with a bulky bromo substituent at the most hindered C-9 position, presented the highest chiroptical response ($\Delta\epsilon = +21$) with respect to the other three planar tricyclic aromatic ferrocenes (*R_p*)-**1a-c**,

suggesting an incipient distortion of the planarity of the helical aromatic framework. This assumption was corroborated for the tetracyclic helical derivative (*R_p*)-**12** which showed a maximum at 277 nm ($\Delta\epsilon = +30.4$) with a five-fold intensity with respect to that presented by the unsubstituted planar tricyclic compound (*R_p*)-**1a**.

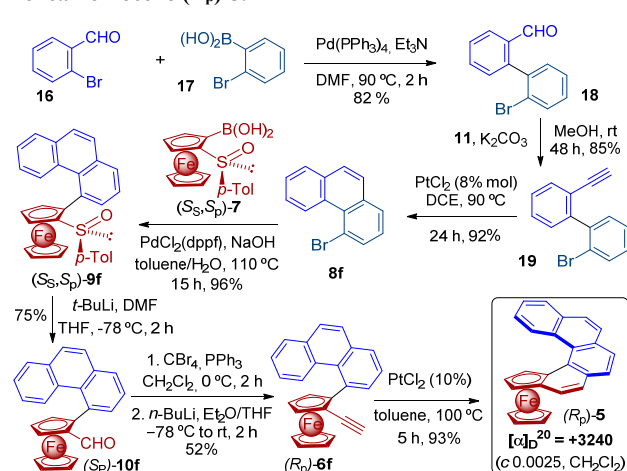
Once synthesized four enantiopure tricyclic aromatic ferrocenes (*R_p*)-**1a-d** and one tetracyclic derivative (*R_p*)-**12** and studied their chiroptical properties, we decided to address the main goal of this research, the asymmetric synthesis of enantiopure pentacyclic helical ferrocene (*R_p*)-**5**. Initially, we attempted a more convergent strategy featuring a double PtCl₂-catalyzed cycloisomerization of *bis*-alkyne (*S_p*)-**15** (Scheme 4). This derivative was prepared in two steps from the Suzuki coupling between bromoaromatic ferrocene (*S_p*)-**10**, obtained as depicted in Scheme 2, and boronic acid **13** followed by the Seyferth-Gilbert homologation of the *bis*-aldehyde (*S_p*)-**14**. Unfortunately, the treatment of *bis*-alkyne (*R_p*)-**15** with PtCl₂ (20%), under the standard conditions, led to a complex mixture of reaction.

Scheme 4. Attempt of a double PtCl₂-catalyzed cycloisomerization of *bis*-alkyne (*S_p*)-15** toward helical ferrocene (*R_p*)-**5**.**



Then, we turned our attention to the previous strategy used for the synthesis of tricyclic and tetracyclic derivatives shown in Schemes 2 and 3. To achieve this goal, it was necessary to synthesize intermediate 4-bromophenanthrene (**8f**) (Scheme 5), which was prepared in a short three-step sequence avoiding other lengthy synthetic routes or inefficient photochemical procedures described in the literature.²⁰ Thus, the Suzuki coupling between 2-bromobenzaldehyde (**16**) and 2-bromophenyl boronic acid (**17**) afforded, in 82% yield,²¹ biaryl **18** which, after Seyferth-Gilbert homologation, followed by PtCl₂-catalyzed cycloisomerization of alkyne **19** (85%), allowed us to obtain 4-bromophenanthrene (**8f**), in 92% yield.

Scheme 5. Asymmetric synthesis of enantiopure pentacyclic helical ferrocene (*R_p*)-5**.**



Then, the Suzuki coupling of **8f** with (*S_S*,*S_P*)-**7** gave the aryl sulfoxide (*S_S*,*S_P*)-**9f** in 96% yield, which after sulfoxide-lithium exchange followed by formylation furnished aldehyde (*S_P*)-**10f**, in 75% yield. The reaction of (*S_P*)-**10f** with CBr₄ and PPh₃ followed by treatment of the dibromoalkene intermediate with *n*-BuLi afforded alkyne (*R_P*)-**6f**, in 52% yield. Finally, the cycloisomerization of (*R_P*)-**6f** with PtCl₂ (10%) led to enantiopure helical ferrocene (*R_P*)-**5**, in 93% yield, showing a very high optical rotation value $\{[\alpha]^{20}_D = +3240$ (*c* 0.0025, CH₂Cl₂) $\}$.¹⁵

The CD spectrum of enantiopure pentacyclic helical ferrocene (*R_P*)-**5** is shown in Figure 3, together with those of tricyclic and tetracyclic derivatives, (*R_P*)-**1a** and (*R_P*)-**12** for comparison. As can be seen, the pentacyclic helical ferrocene (*R_P*)-**5** showed a very intense circular dichroism response with a band at 317 nm ($\Delta\epsilon = +160$) with a five-fold intensity with respect to that presented by the tetracyclic helical derivative (*R_P*)-**12** and near thirty-fold intensity related to the unsubstituted planar tricyclic compound (*R_P*)-**1a**.²² This strong CD signal could be attributed to the presence of additional helical chirality in (*R_P*)-**12** due to a high distortion of the planarity by the presence of five *ortho*-condensed aromatic rings,

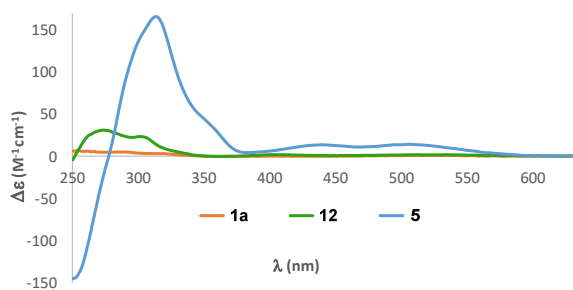


Figure 3. CD spectra of enantiopure tricyclic ferrocene (*R_P*)-**1a**, tetracyclic (*R_P*)-**12** and pentacyclic (*R_P*)-**5**.

In summary, we have described the enantioselective synthesis of planar-chiral enantiopure ferrocenes, with three, four and five *ortho*-condensed aromatic rings. The helicenic structure was generated at the end of the synthetic sequence featuring a PtCl₂-catalyzed cycloisomerization process of suitable planar-chiral ferrocenes previously formed from enantiopure (*S_S*,*S_P*)-*p*-tolylsulfinyl ferrocenyl boronic acid, as the source of planar chirality. The study of their chiroptical properties evidenced a very high optical value and a huge intensity of the CD signals for the pentacyclic derivative (*R_P*)-**5**, showing additional helical chirality, as a result of a high distortion of the planarity provoking a significant transfer of chirality from the planar-chiral ferrocene moiety to the helical *ortho*-condensed aromatic system.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, characterization data, copies of ¹H- and ¹³C-NMR spectra, and X-ray data for (*R_P*)-**1c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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