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# Rhodium Catalyzed Enantioselective Synthesis of Highly Fluorescent and CPL Active Dispiroindeno[2,1-c]fluorenes

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Dedicated to Professor Tamotsu Takahashi on the occasion of his retirement

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**Abstract:** The enantioselective synthesis of chiral [7]-helical dispiroindeno[2,1-c]indeno[2,1-c]fluorenes (DSF-IFs) was achieved for the first time in good yields with high e.r. values (e.r. up to 99:1). The crucial step of the whole reaction sequence was enantioselective intramolecular [2+2+2] cycloaddition of tethered trienediols to indenofluorenediols that was catalyzed by a Rh/SEGPBOS<sup>®</sup> complex. Further transformations lead to the corresponding DSF-IFs. The prepared helically chiral DSF-IFs combine circularly polarized luminescence (CPL) activity ( $g_{lum} = \sim 10^{-3}$ ) with exceptionally high fluorescence quantum yields (up to  $\Phi_{lum} = 0.97$ ).

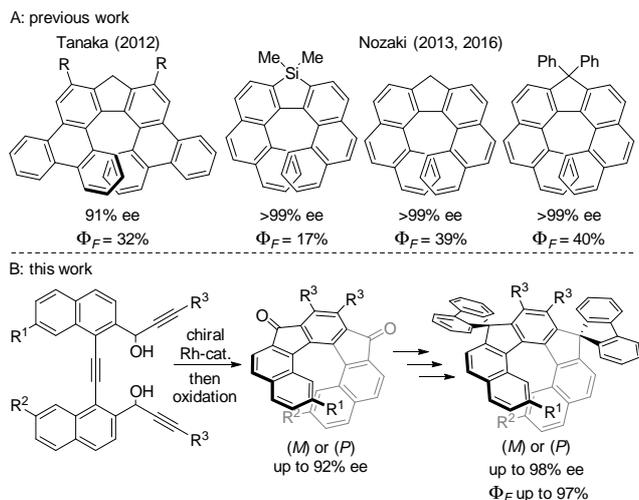
The growing interest in advanced materials based on chiral molecules emitting circularly polarized light (CPL)<sup>[1–3]</sup> originates from the increasing number of their potential applications in bioimaging,<sup>[4]</sup> 3D displays,<sup>[5,6]</sup> quantum computers,<sup>[7]</sup> CPL lasers,<sup>[8]</sup> OLED screens,<sup>[9,10]</sup> and sensors.<sup>[11,12]</sup> Overall efficiency of CPL active molecule is characterized by circular polarization luminosity  $\Lambda_{cpl}$  as defined by Mori<sup>[13,14]</sup> where all key parameters,  $f$  (oscillator strength),  $g_{lum}$  (luminescence dissymmetry factor) and  $\Phi_{lum}$  (emission quantum yield) are taken into account. In contrast to early studied lanthanide complexes based CPL active materials (high  $g_{lum}$ , lower  $\Phi_{lum}$ ), where the emission

wavelength is set by the electronically forbidden f-f transition centered on corresponding metal, the emission tunability of electronically allowed  $\pi-\pi^*$  transition of rigid aromatic systems (lower  $g_{lum}$ , high  $\Phi_{lum}$ ) by the elaboration of molecular skeleton put these small organic molecules (SOMs) to the center of current interest. Since there is not imminent correlation between those two values ( $g_{lum}$  can be improved without affecting  $\Phi_{lum}$ )<sup>[14]</sup> the SOMs holding high  $\Phi_{lum}$  stands for excellent starting points for development of truly efficient CPL active material and causes a development of new methods for their simple, modular and efficient preparation highly desirable.

In this context, helicenes,<sup>[15–19]</sup> heterohelicenes<sup>[19,20]</sup> and helical compounds<sup>[19,21–30]</sup> as representatives of SOMs have enjoyed a surge of interest as their twisted molecular structures and inherent helical chirality has been proven as a valuable structural motive for examining CPL properties.<sup>[31,32]</sup>

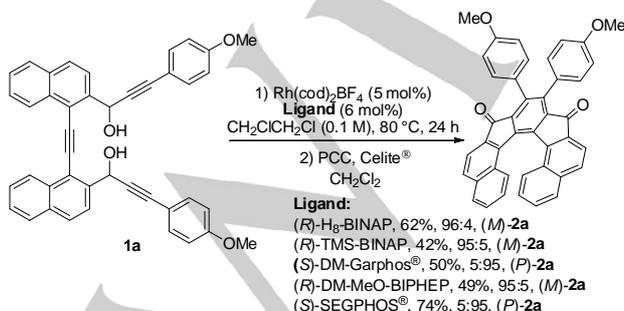
Recently, we have introduced a fast, simple, and modular approach to various compounds possessing fluorene scaffold<sup>[33–35]</sup>, and subsequently, we have combined this structural motive with the element of helicity in the preparation of highly fluorescent [5]- and [7]-helical indeno[2,1-c]fluorenes.<sup>[36]</sup> The expected configurational stability and superior fluorescence quantum yields of the later ones drive us to attempt

enantioselective synthesis<sup>[37–41]</sup> of these compounds and evaluate also their chiroptical properties (Scheme 1).



**Scheme 1.** Previously synthesized chiral helical fluorenes (the upper row) and our approach to new chiral helical dispiroindeno[2,1-c]fluorenes.

At the outset, we synthesized a set of various triynediols **1** according to our previously reported procedure (see the Supporting Information).<sup>[36]</sup> Triynediol **1a** was chosen as a representative substrate to study catalytic enantioselective cyclotrimerization under different conditions by using combinations of  $\text{Rh}(\text{cod})_2\text{BF}_4$  (5 mol%) and chiral phosphines (6 or 12 mol%) in  $\text{CH}_2\text{ClCH}_2\text{Cl}$  at 80 °C on 0.1 mmol scale (for details, see Table S1-3). The reaction proceeded with the full consumption of the starting material forming a mixture of diastereoisomeric diols were directly oxidized with PCC in  $\text{CH}_2\text{Cl}_2$  to diketone **2a** to obtain a product with the helical chirality element only. The oxidation proceeded without erosion of its ee value. The best results in terms of highest asymmetric induction were obtained with (*R*)- $\text{H}_8$ -BINAP (96:4 e.r.). Ligands such as (*R*)-TMS-BINAP, (*S*)-DM-Garphos<sup>®</sup>, (*R*)-DM-MeO-BIPHEP, and (*S*)-SEGPHOS<sup>®</sup> yielded **2a** with a nice enantiopurity of 95:5 e.r. (Scheme 2). The latter ligand, SEGPHOS<sup>®</sup> (*S* or *R*), was used for further experiments because of a good combination of high enantioselectivity and the product yield.



**Scheme 2.** Catalytic enantioselective cyclotrimerization and oxidation of **1a** to **2a**.

Next, we focused our attention on other factors such as temperature or catalyst loading to increase asymmetric induction in the [2+2+2] cyclotrimerization (see Table S4). We were pleased to notice that running the reaction at 60 °C, the desired product (*P*)-**2a** was obtained in 76% isolated yield, and the excellent enantiomeric ratio of 97:3. Below that temperature, the course of the reaction almost ceased. Similarly, the use of 1 mol% of the catalyst load did not provide the product in sufficient amounts.

With optimized reaction conditions in hands, triynediols **1a-1i** were subjected to the enantioselective [2+2+2] cyclotrimerization/oxidation reaction sequence on 1 mmol scale (Scheme 3). First, the reactions of triynediols **1a-d** possessing EDG ( $\text{R}^2 = \text{OMe}$ ) and EWG ( $\text{R}^2 = \text{CF}_3, \text{Cl}$ ) on the aromatic rings were examined. In the case of the triynediol **1a**, the reaction was performed with (*S*)- and (*R*)-SEGPHOS<sup>®</sup> to give diones (*P*)- and (*M*)-**2a** in 70 and 53% isolated yields and good e.r.s of 8:92 and 93:7, respectively. When **1b** was engaged, compound (*P*)-**2b** was obtained with the excellent isolated yield of 88% and 9:91 e.r. The reactions of triynediols **1c** and **1d** bearing EWGs provided the corresponding products (*P*)-**2c** and (*P*)-**2d** in 80% and 57% isolated yield and e.r.s of 90:10 and 96:4, respectively. A generally good asymmetric induction of the aryl capped triynes is in accordance with the previously observed phenomenon for cyclotrimerization of triynes leading to helicenes.<sup>[15]</sup> As far as a synthesis of unsubstituted dione **2f** is concerned, two routes were examined. Pathway A started with cyclotrimerization of **1e** followed by desilylation of **2e**. Pathway B, the more straightforward one, started with cyclotrimerization of **1f**. Using pathway A, cyclotrimerization/oxidation of **1e** gave **2e**, which was without isolation subjected to desilylation, providing **2f** in a low yield of 20% and 69:31 e.r. The direct cyclotrimerization of **1f** (pathway B) gave rise to **2f** in a moderate yield of 43% and 61:39 e.r. Eventually, the methodology was applied to cyclotrimerization of **1g** bearing the *n*-propyl group. It furnished (*P*)-**2g** in a reasonable isolated yield of 65% and moderate enantioselectivity (e.r. 81:19). To expand the scope of the reaction, cyclotrimerization was also carried out with triynes **1h** and **1i** bearing one or two methoxy groups on the naphthalene moieties. Although the reaction proceeded as expected, it gave the desired products **2h** and **2i** in rather low 23 and 25% isolated yields and slight drop of enantioselectivity with e.r.s of 82:18 and 81:19, respectively. The lower yields could be accounted for by increased steric hindrance by the methoxy group(s) in the position(s) 2 or 2 and 15.

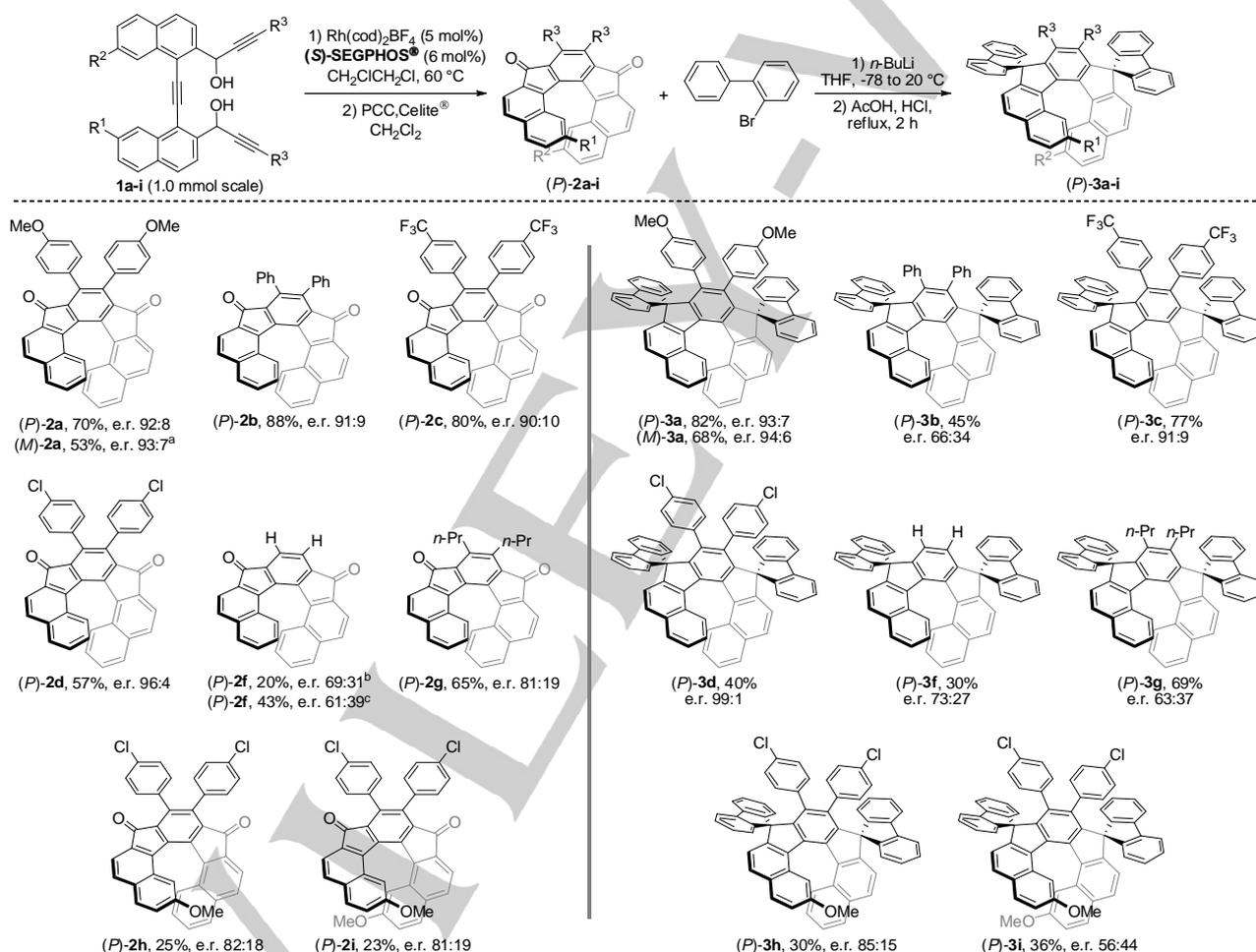
DFT calculation of energies of several tentative rhodacycloheptatrienes was carried out, to elucidate the origin of the *P* configuration, (see Supporting information, section XI). The calculation revealed that the most energetically favored intermediate is P0 (*P,S,R,S*<sub>ligand</sub>) which leads to the product with *P* helicity. The energy difference between diastereoisomers P0 and M0 (*M,S,R,S*<sub>ligand</sub>) that would lead to *M* helicity is 44 kJ·mol<sup>-1</sup>. Such an energy difference is sufficient to understand the preferential formation of the *P* configuration when using the (*S*)-ligand.

A library of the helical diones **2** was converted into dispiroindeno[2,1-c]fluorenes **3** (Scheme 3) by using the known two-steps procedure involving addition of *ortho*-lithiobiphenyl to carbonyl groups followed by Friedel-Crafts cyclization under acidic conditions.<sup>[42,43]</sup> First, both enantiomers of the diketone (*P*)- and (*M*)-**2a** were transformed into the dispiro-compound (*P*)-

and (*M*)-**3a** in 82 and 68% isolated yields. It is worthy to notice that this two-step reaction proceeded without erosion of its enantiopurity. Also, a simple dissolution of isolated (*M*)-**3a** and (*P*)-**3a** in  $\text{CH}_2\text{Cl}_2$  followed by addition of MeOH resulted in precipitation of the helical indenofluorenes with  $\geq 97:3$  e.r.s. Then, three other dispiro-compounds (*P*)-**3b-d** were synthesized with moderate to good yields of 45, 77, and 40%, respectively. Concerning the non-substituted dispiro-compound (*P*)-**3f**, it was isolated in only 30% of yield. The low yields can be explained by its low solubility and with it associated problems during purification. Finally, the helicene-like compound possessing a long alkyl chain (*P*)-**3g** was also isolated in a good yield of 69%. In an analogical manner were prepared dispiro-compounds (*P*)-**3h,i** in 30, and 36% isolated yields, respectively. However, enantiopurity of the isolated dispirobismethoxy derivative **3i** was unexpectedly low (e.r. 56:44), even though the cyclotrimerization proceeded with good asymmetric induction (e.r. 81:19). Carrying

out the spirocyclization under several conditions revealed that the enantiomeric ratio has changed depending on the isolation method. Moreover, during column chromatography on silica gel various fractions have different enantiomeric ratios. We assume that the observed "loss" of enantiopurity could be associated with aggregations during separation owing to its generally low solubility. A similar phenomenon has been observed previously in other cases (for a discussion, see Supporting Information, section V).<sup>[44,45]</sup>

As far as racemization barriers are concerned, comparable values for dione **2a** and dispiroindenofluorene **3a** were revealed (135.8 and 136.0  $\text{kJ}\cdot\text{mol}^{-1}$  respectively) (see Supporting Information, Section VI). Those values are rather closer to that of [6]helicene (149.0  $\text{kJ}\cdot\text{mol}^{-1}$ )<sup>[46]</sup> than to [5]helicene (100.8  $\text{kJ}\cdot\text{mol}^{-1}$ ).<sup>[47]</sup>



**Scheme 3.** Scope of the enantioselective [2+2+2] cyclotrimerization of trienediols **1a-i** to **2a-i** and synthesis of dispiroindenofluorenes **3**. <sup>a</sup>(*R*)-SEGPHOS<sup>®</sup> was used. <sup>b</sup>Starting from **1e**. <sup>c</sup>Starting from **1f**.

The solid-state structures of [7]helicene-like compounds **3d** (Figure 1), **3f**, and **2a** were determined by X-ray crystallographic analysis. The sums of five dihedral angles, which should reflect the degree of molecular twist, is 70.1° for **3d** and 70.6° for **3f**. These values are smaller than those of the

related [7]helicene-like compounds with only one 5-membered ring<sup>[48,49]</sup>, indicating a lesser lead for helix axial advance.

Figure 2 shows the UV/Vis absorption and fluorescence spectra of indenofluorenes **3** in dichloromethane (see also Figures S9 and S10), and the spectral data are summarized in

Table 1. As in our previous study,<sup>[36]</sup> the substituents at 8 and 9 positions do not alter absorption properties. The spectra differ perceptibly only in molar attenuation coefficients with characteristic absorption bands at about 314, 335, 373, and the lowest energy absorption around 392 nm. The presence of methoxy group(s) in **3h** and **3i** also does not significantly change the absorption properties. The lowest energy absorption has been previously assigned<sup>[36]</sup> to  $\pi-\pi^*$  transition contributed exclusively from HOMO/LUMO pair, both distributed merely over the helical core.

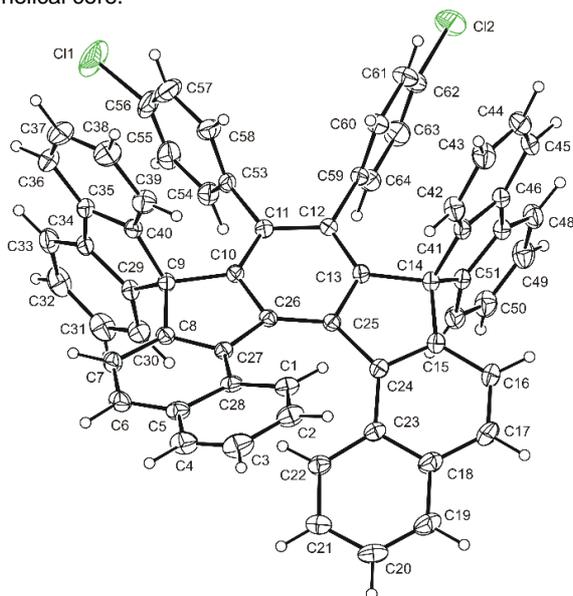


Figure 1. The ORTEP plot of **3d**. Ellipsoids are shown with 30% probability.

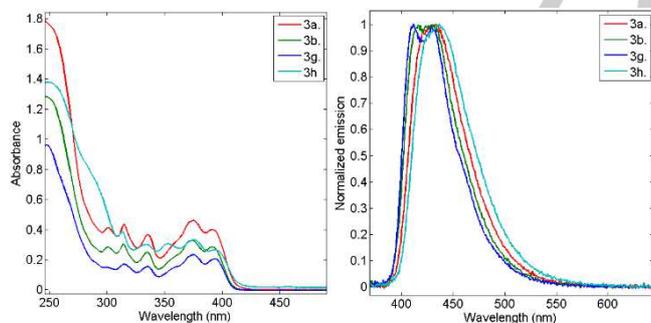


Figure 2. UV/Vis absorption (left) and normalized emission spectra (right) of **3a**, **3b**, **3g** and **3h** recorded in  $\text{CH}_2\text{Cl}_2$  (for **3c**, **3d**, **3f** and **3i** see Figures S7 and S8).

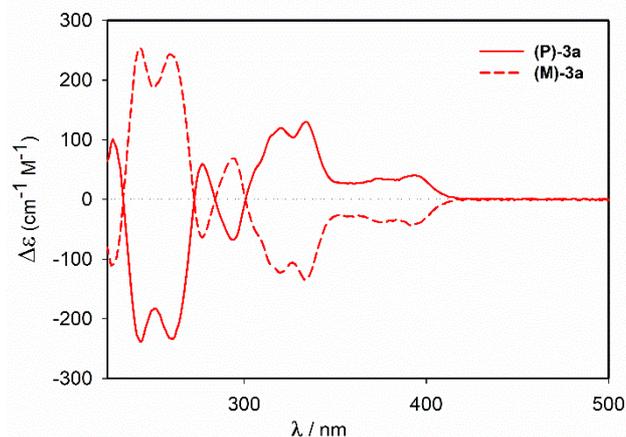
Table 1. Selected photo-physical properties data of **3a-d** and **3f-i** in  $\text{CH}_2\text{Cl}_2$ .

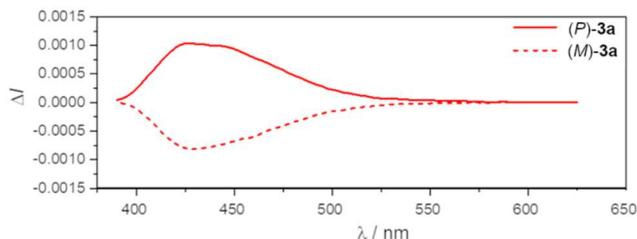
<b>3</b>	$\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon/10^4 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$ )	$\lambda_{\text{em}}/\text{nm}$	$\Phi_s^{[a]}$
<b>3a</b>	301 (4.11), 314 (4.32), 335 (3.67), 374 (4.60), 391 (3.99)	431	0.85
<b>3b</b>	301 (2.84), 314 (3.04), 335 (2.49), 374 (3.27), 391 (2.84)	417, 430	0.87
<b>3c</b>	301(3.87), 314 (4.16), 335 (3.77), 371 (4.57), 391 (4.00)	415, 430	0.78
<b>3d</b>	301 (2.86), 314 (3.06), 335 (2.71), 373 (3.22), 391 (2.76)	415, 429	0.75

<b>3f</b>	299 (1.71), 312 (2.06), 333 (1.27), 370 (2.45), 388 (2.10)	409, 423	0.87
<b>3g</b>	314 (1.70), 335 (1.54), 374 (2.32), 393 (2.05)	412, 428	0.86
<b>3h</b>	313 (3.83), 334 (3.02), 352 (3.06), 375 (3.33), 395 (2.65)	437	0.97
<b>3i</b>	312 (2.44), 352 (2.01), 368 (1.78), 393 (0.98)	433	0.82

[a] Absolute quantum yields ( $10^{-6} \text{ M}$  in  $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{exc}} = 350 \text{ nm}$ ).

Finally, the chiroptical properties of **3** were subjected to a preliminary evaluation. Organic helicenes are known to be good chiral fluorophores emitting CPL with emission dissymmetry factors  $g_{\text{lum}}$  of the order  $10^{-3}$ - $10^{-2}$ .<sup>[32,50]</sup> Conventional fully carbon based helicenes such as carbo[6]helicene usually display  $g_{\text{lum}}$  values around  $10^{-3}$ <sup>[51]</sup> and low quantum yields around 2-3 % (due to the efficient spin-orbit coupling in helical  $\pi$ -systems which deactivate radiative emission). As expected, the incorporation of two fused spiro units within the helical scaffold enables to increase the non-polarized emission performances with fluorescence absolute quantum yields in the range of 0.75-0.97 (Table 1). Those values belong to the highest among the configurationally stable helicenes and helical compounds. The CPL activity of enantioenriched (*P*)-**3a** and (*M*)-**3a** were measured as a representative example in  $\text{CH}_2\text{Cl}_2$  (Figure 4). The dissymmetry factors  $g_{\text{lum}}$  were found around  $-0.8 \times 10^{-3}$  for (*M*)-**3a** enantiomer (1:99 e.r.) and  $+1 \times 10^{-3}$  for (*P*)-**3a** enantiomer (97:3 e.r.) at the maximum emission wavelength (within the CPL instrument measurement error, average value  $|g_{\text{lum}}| = \pm 0.9 \times 10^{-3}$ , see the  $g_{\text{lum}}$  spectra in Supporting Information, section X). Those values are prevailing for SOMs and are in agreement with the absorption dissymmetry factor  $g_{\text{abs}}$  both in magnitude ( $\pm 1 \times 10^{-3}$  at 390 nm) and in signs (positive of (*P*)) and vice-versa, see the mirror-image CD curves for (*P*) and (*M*)-**3a** enantiomers (Figure 3). These results suggest small structural changes between ground and excited states and marginal vibrational effects.<sup>[52]</sup> For comparison, heptahelicenic fluorenyl structures have been synthesized by Tanaka and coworkers and displayed  $g_{\text{lum}}$  values as high as  $\pm 3 \times 10^{-2}$  but in this case the helicene was more  $\pi$ -conjugated thanks to the presence of additional fused rings.<sup>[26]</sup> In fact, the CPL activity in such helical fluorenyl derivatives is strongly structure-dependent since values of  $\pm 3 \times 10^{-3}$  have been obtained by Nozaki et al.<sup>[49,53]</sup>



**Figure 3.** ECD spectra of heptahelicenic derivatives (*P*)- and (*M*)-**3a** in CH<sub>2</sub>Cl<sub>2</sub>.**Figure 4.** CPL spectra of heptahelicenic derivatives (*P*)- and (*M*)-**3a** in CH<sub>2</sub>Cl<sub>2</sub>.

In conclusion, we introduce a highly enantioselective [2+2+2]-cyclootrimerization approach for a straightforward synthesis of helically chiral dispiroindeno[2,1-c]fluorenes by intramolecular cyclization of triynediols under mild reaction conditions. The best catalytic system turned out to be the Rh(I)/Segphos® system that enabled the reaction to proceed with high enantioselectivity (up to 92% ee) and high conversion to the product (up to 88% yield). The cyclootrimerization products were easily converted into the corresponding chiral [7]-helical dispiroindeno[2,1-c]fluorenes, a hitherto unreported class of highly emissive and CPL active chiral compounds. Their crystal structure analysis revealed a large overlap and distortion of the two terminal benzene rings, which account for the high tolerance of this “helicene” toward racemization. We anticipate this modular synthetic approach will be particularly useful for the theory-based, rationally designed targeted syntheses of further configurationally stable and commonly highly emissive indenofluorene derivatives with improved chiroptical properties whose preparation is currently undertaken.

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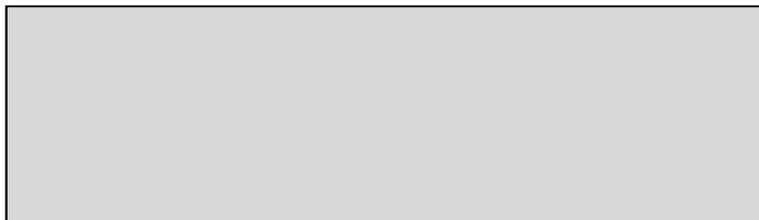
This work was supported by Czech Science Foundation (grant No. 18-17823S). LF and JC thank the Ministère de l'Éducation Nationale, de la Recherche et de la Technologie (MENRT), the Centre National de la Recherche Scientifique (CNRS) and Rennes Métropole.

**Keywords:** catalysis • CPL • enantioselective cyclootrimerization • helical compounds • indenofluorene

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**Entry for the Table of Contents**

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Enantioselective synthesis of configurationally stable [7]-helical dispiroindihydro[2,1-c]indeno[1,2-b]fluorenes (DSF-IFs) was accomplished with high e.r. values (up to 99:1) by using intramolecular [2+2+2] cycloaddition of tethered triynediols catalyzed by Rh(I)/SEGPHOS®. The chiral DSF-IFs had exceptionally high fluorescence ( $\Phi_{\text{lum}}$  up to 0.97) and circularly polarized luminescence (CPL) activity of  $g_{\text{lum}} = \sim 10^{-3}$ .

Institute and/or researcher Twitter usernames: **((optional))**