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## Accepted Article

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**Authors:** Yang Sun, Kais Dhbaibi, Hortense Lauwick, Claudia Lalli, Gregory Taupier, Yann Molard, rafael gramage-doria, Sylvie Dérien, Jeanne Crassous, and Mathieu Jérôme Achard

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## RESEARCH ARTICLE

# Asymmetric Ruthenium Catalysis Enables Fluorophores with Point Chirality Displaying CPL Properties

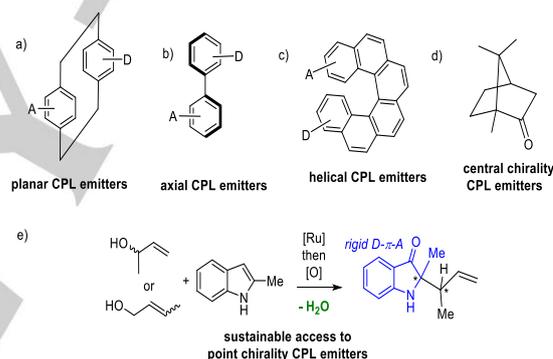
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Dedication ((optional))

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**Abstract:** A novel enantiopure  $\pi$ -allylruthenium(IV) precatalyst allowed the enantioselective and stereospecific allylations of indoles and gave access to indolin-3-ones containing vicinal stereogenic centers. Facile separation of diastereoisomers exhibiting opposite CPL activities in diverse solvents including water demonstrated the potential of these sustainable transformation and of the newly prepared molecules.

compounds have never been studied. Catalysts enabling regio-entanto- and stereo-selective alkylation from acyclic unactivated



**Figure 1.** overview of different classes of CPL emitters

## Introduction

Owing to their potential applications in material sciences by inducing circularly polarized luminescence (CPL), chiral organic emitters have recently attracted considerable attention.<sup>[1]</sup> While metal-based and lanthanides complexes have demonstrated strong interest in both generating strong CPL activity and efficient phosphorescence or long-lived emission for incorporation into CP-OLEDs,<sup>[2]</sup> fluorescent fully organic  $\pi$ -conjugated systems have shown wider variability and easier processability.<sup>[3]</sup> Most reports in the literature deal with axially, planar or helically chiral fluorophores (Figure 1).<sup>[1]</sup> Additionally, reports dealing with central chirality mainly arise from chiral pool scaffolds thus hampering access to both enantiomers.<sup>[4]</sup> While these simple molecules display moderate signals in their monomeric state, dimerization, immobilization, aggregation and other strategies allowed the enhancement of the CPL dissymmetry factor,  $g_{lum}$  through diverse mechanisms.<sup>[5]</sup> However, the synthesis of such chiral compounds usually necessitates multi-step methodologies and generates several types of wastes. Thus, alternative ecofriendly and straightforward approaches minimizing steps and wastes are highly desirable. Among the high-value added chemicals, indoxyl derivatives containing the indolin-3-one core structure and a quaternary stereogenic center at the 2-position are an attractive class of compounds with interesting tunable photophysical properties.<sup>[6]</sup> Owing to the presence of a rigid conjugated electron-donor acceptor fragment nearby the quaternary stereogenic center, several indolin-3-ones exhibit impressive photoemissive properties.<sup>[6a-g]</sup> However, chiroptical properties of such

allylic alcohols are so far unknown. The development of such systems would allow the access to pure indolin-3-one stereoisomers minimizing steps with water as the only side product of the overall reactions (Figure 1e). In this regard, transition metal-catalyzed allylations become a powerful strategy to access a broad variety of high value-added products and various transition metal complexes were developed to achieve regio- and enantio-selective allylation of indole derivatives at the C or the N positions.<sup>[7]</sup> Among them, reports dealing with iridium precatalysts dominate this field.<sup>[8-10]</sup> Even if these classes of catalysts have proven to activate branched allylic alcohols enantioselectively, the use of linear derivatives to date still require activated linear allylic substrates. Similarly, various palladium precatalysts were found to be able to activate allylic alcohols including enantio- and stereo-selective alkylations with regioselectivity in favor of the less hindered terminal allyl carbon.<sup>[11]</sup> Efficient rhodium-, nickel- or gold-based catalysts have provided interesting results for the alkylation of indole derivatives.<sup>[12-14]</sup> Since the pioneering discoveries of Watanabe and coworkers, ruthenium-based catalysts have emerged as promising complementary systems to perform regioselective allylic substitution in favor of the branched products and various

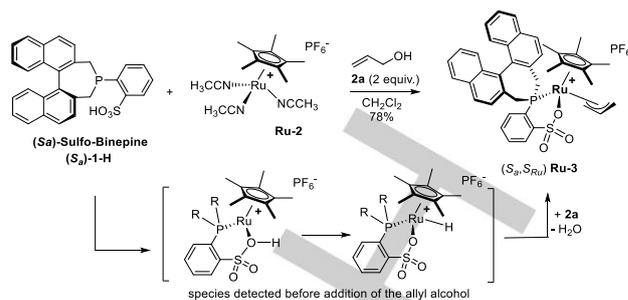
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enantioselective or stereospecific protocols have been reported from activated allylic derivatives.<sup>[15-18]</sup> Ruthenium precatalysts containing sulfonate or carboxylate moieties developed by Pregosin, Kitamura and us were found to activate allylic alcohols.<sup>[6e,15d,17,18]</sup> Despite our recently discovered allylation-oxidation sequence of branched 2,3-disubstituted indoles *via* a semi-pinacol rearrangement of the resulting hydroxyindolenines in the presence of a well-defined ruthenium(IV) allyl complex [Ru(Cp\*)(DPPBS)( $\eta^3$ -propenyl)][PF<sub>6</sub>]**Ru-3** bearing DiPhenylPhosphinoBenzene Sulfonate (DPPBS) ligand, an enantioselective version is yet to be reported.<sup>[6e]</sup>

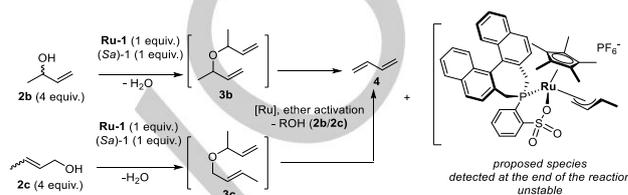
Herein, we describe a first report on the ruthenium-catalyzed activation of acyclic, either linear crotyl alcohol or branched but-3-en-2-ol, allowing the straightforward access to useful chiral indolin-3-one emitters *via* regio-, stereo- and enantioselective allylation reactions and their photophysical (absorption and emission) and chiroptical properties (Electronic Circular Dichroism – ECD and CPL activities). Interestingly, we examined how switching the nature of the allylic alcohol can generate the four different stereoisomers possessing two asymmetric carbons, and how stereoisomerism influences the chiroptical properties, both in organic solvents and in water.

## Results and Discussion

We first focused on the synthesis of the  $\pi$ -allyl ruthenium(IV) precatalyst. After treatment of equimolar amount of our recently reported (Sa)-sulfo-binepine **1-H** with [Ru(Cp\*)(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub>**Ru-2** at room temperature, sharp multiple signals were observed in <sup>1</sup>H NMR.<sup>[19]</sup> A hydride signal located at -7.53 ppm (*J*<sub>PH</sub>=31 Hz) of a cationic hydridoruthenium(IV) species arising from the protonation-anionation of the ruthenium(II) center by the sulfonic acid moiety was observed.<sup>[11g,20]</sup> Chelate formation was evidenced by the modification of the diastereotopic proton signals for the two CH<sub>2</sub> moieties of the sulfobinepine ligand and by <sup>31</sup>P NMR (Figure S1). Interestingly, a broad signal located at no less than 25 ppm in <sup>1</sup>H NMR accounting for the ruthenium(II) precursor was also noticed (Scheme 1). Even if we suspect a tridentate  $\kappa^3$ -P,O,O coordination mode of the ligand or a dimer formation,<sup>[19]</sup> these formal 16e species undergoes rapid aggregation in less than 15 mins leading to the disappearance of the signals both in <sup>1</sup>H and <sup>31</sup>P NMR; THF signals arising from sulfo-binepine synthesis being only visible in <sup>1</sup>H NMR. Addition of allyl alcohol **2a** (2 equiv.) to this mixture led to the formation of a yellowish solution and reappearance of characteristic signals in NMR spectroscopy which upon concentration led to the precipitation of the expected stable allylruthenium(IV) complex [Ru(Cp\*)(1)( $\eta^3$ -propenyl)][PF<sub>6</sub>]**Ru-3** as only one diastereoisomer; diallylated ether along with other side products remaining in solution. In



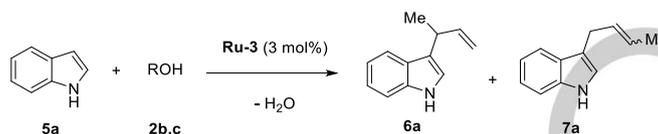
Scheme 1. Synthesis of the well-defined (Sa,SRu) **Ru-3** ruthenium(IV) complex.



Scheme 2. Monitoring the substoichiometric reaction with linear **2c** and branched **2b** allylic alcohols.

contrast, replacing allyl alcohol in the experiment described above by the addition of 4 equivalents of but-3-en-2-ol **2b** resulted in a complex mixture (Scheme 2). Formation of the dibranched diallylated ether **3b** was observed at room temperature <sup>1</sup>H NMR reaching around 50% conversion after one hour along with the formation a major ruthenium species located in <sup>31</sup>P NMR at 42.7 (s) ppm and traces of butadiene **4**.<sup>[21]</sup> Complete consumption of both ether **3b** and alcohol **2b** acting both as nucleophiles and allylic sources occurred after 16 hours to fully generate butadiene **4**.<sup>[22]</sup> All these reactions are proposed to be reversible but the low miscibility of water in CD<sub>2</sub>Cl<sub>2</sub> facilitates these processes.<sup>[21,22]</sup> An unstable allyl ruthenium(IV) was the only observable species located at 39 ppm in <sup>31</sup>P NMR with characteristic  $\pi$ -allyl signals in <sup>1</sup>H NMR in the same range as **Ru-3** and previously reported **Ru-1**. When the reaction was carried out in the presence of the linear crotyl alcohol **2c**, same  $\pi$ -allylruthenium species were observed along with butadiene at the end of the reaction during NMR analyses. However, these allylic species were only detected at the end of these reactions raising the question of the enantioselective outcomes in the presence of other nucleophiles.

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**Table 1.** Stereospecific versus enantioselective allylation of indole **5a**<sup>[a]</sup>

Entry	ROH	Solvent, T(°C)	er <sup>[b]</sup>	Absolute Configuration	ratio <b>6a/7a</b> <sup>[c]</sup>	conv.(yield) <sup>[d]</sup>
1	<b>2b</b> ( <i>rac.</i> )	CH <sub>2</sub> Cl <sub>2</sub> , (30°C)	50:50	-	97/3	100(90%)
2	<b>2b</b> ( <i>R</i> ) 87% ee	CH <sub>2</sub> Cl <sub>2</sub> , (30°C)	93:7	( <i>R</i> )	98/2	100(90%)
3 <sup>[e]</sup>	<b>2b</b> ( <i>R</i> ) 87% ee	CH <sub>2</sub> Cl <sub>2</sub> , (30°C)	93:7	( <i>R</i> )	99/1	100
4	<b>2c</b> ( <i>E/Z</i> : 93:7)	CH <sub>2</sub> Cl <sub>2</sub> , (30°C)	8:92	( <i>S</i> )	92/8	98(86%)
5	<b>2c</b> ( <i>E/Z</i> : 93:7)	CH <sub>2</sub> Cl <sub>2</sub> , (20°C)	9:91	( <i>S</i> )	92/8	88
6	<b>2c</b> ( <i>E/Z</i> : 93:7)	CH <sub>2</sub> Cl <sub>2</sub> , (40°C)	12:88	( <i>S</i> )	89/11	100
7	<b>2c</b> ( <i>E/Z</i> : 93:7)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> , (60°C)	14:85	( <i>S</i> )	86/14	90

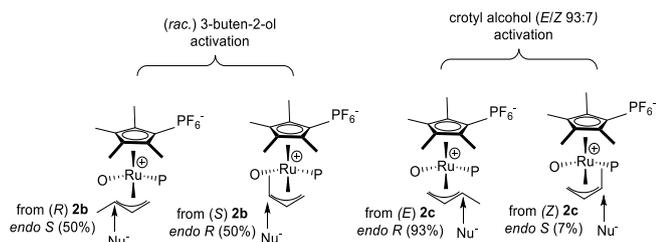
[a] Experimental conditions: all reactions were performed under an inert atmosphere of argon at indicated temperature and carried out with indole **5a** (0.4 mmol), allylic alcohols **2** (0.4 mmol), metallic precursor ( $S_{\text{a}}, S_{\text{Ru}}$ ) **Ru-3** (3 mol%) in a closed Schlenk tube in deaerated solvent (0.5 mL). [b] er of **6a** was determined by chiral HPLC analysis (Chiralcel OJ). [c] Determined by <sup>1</sup>H NMR of the crude reaction mixture. [d] Conversions were determined by GC and numbers in parentheses correspond to the isolated yield of the product **6a** after column chromatography. [e] reaction was carried out in the presence of the racemic **Ru-1** precatalyst.

Having established that both crotyl alcohol **2c** and methyl vinyl carbinol **2b** can be activated in the presence of the sulfonamide containing catalyst, we next attempted, the reactions of these alcohols in the presence of indole **5a** and the allylic ruthenium precatalyst **Ru-3** (Table 1). Treatment of indole **5a** with equimolar amount of the *rac.* but-3-en-2-ol **2b** in the presence of catalytic amount of the well-defined ruthenium **Ru-3** complex afforded the chiral allylated indole **6a** in isolated yield up to 90% (Table 1, entry 1). Traces of linear product **7a** was also detected in the crude reaction mixture by <sup>1</sup>H NMR reaching a Branched/Linear of compounds **6a/7a** ratio of 97:3. Chiral HPLC analysis demonstrated the formation of a racemic mixture. In contrast, treatment of the enantiomerically enriched(-),(*R*)-but-3-en-2-ol **2b** (87% ee) with indole gave the allylated indole **6a** with 93:7 e.r. (Table 1, entry 2).<sup>[23]</sup> The absolute configuration (*R*) was determined by comparison with previously reported data confirming a net retention of configuration.<sup>[10a,12]</sup> Noteworthy that the racemic chiral at ruthenium **Ru-1** complex led to similar results

confirming a stereospecific process (Table 1, entry 3).<sup>[16,24]</sup> In contrast, treatment of the crotyl alcohol **2c** (93:7 *E/Z* ratio) with indole **5** under similar reaction conditions gave the same product **6a** in 86% isolated yield. Regioselectivity was slightly eroded reaching a 92:8 **6a/7a** ratio. However, product **6a** was obtained with 8:92 e.r. in favor of the (*S*) enantiomer (Table 1, entry 4). Increasing reaction temperature, lowered concomitantly regio- and enantio-selectivities whereas reaction performed at room temperature lowered conversion (Table 1, entries 5,6,7). It is important to note that for these entries, the obtained enantiomeric ratios are similar to the obtained regioselectivities correlated to the *E/Z* ratio of the starting material **2c** indicating a selective approach toward the unsaturated enantiotopic faces and the absence of isomerization processes. Taken together, these results demonstrate that racemic and both enantiomers can be selectively obtained with the same enantiopure precatalyst ( $S_{\text{a}}, S_{\text{Ru}}$ )-**Ru-3** by simply varying the nature of the unactivated allylic alcohol. A fast nucleophilic attack prior to isomerization

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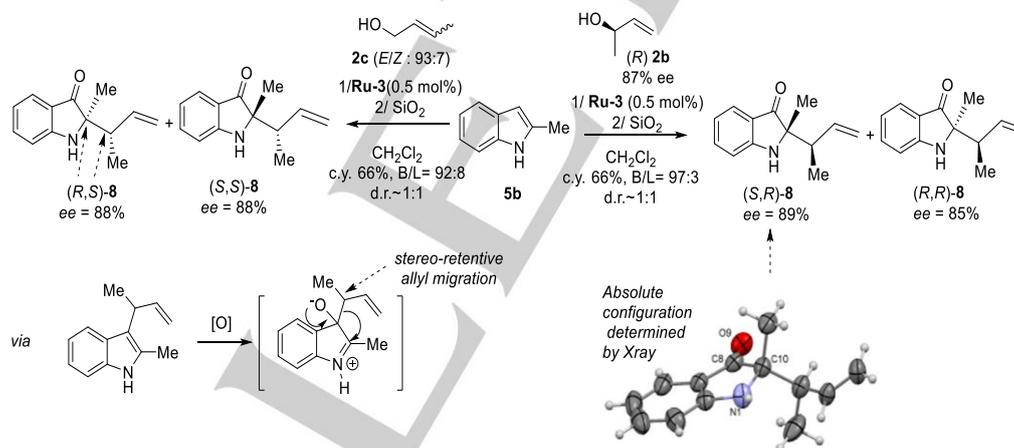
might account for these results and a putative model of activation is described in Figure 2. Reminiscent to the so-called “memory effect”,<sup>[24]</sup> if concerted activation of the alcohol occurs on the same side of the sulfonate moiety as previously suggested by Pregosin, Kitamura and us, the corresponding  $\pi$  allyl ruthenium species should be obtained.<sup>[6e,17]</sup> Owing to the longer Ru-C(allyl) bond length for the substituted terminal allyl carbon in the corresponding  $\pi$ -allyl ruthenium species featuring Cp\* ligand, a higher reactivity of this carbon center toward nucleophiles favors the branched selectivity.<sup>[17,18]</sup> Thus, a racemic mixture of the corresponding allylated species is expected. In contrast, starting from crotyl alcohol containing a mixture of *cis/trans* isomers (93% *trans*), an enantiomeric ratio close to 7:93 should be expected.



**Figure 2.** Putative model accounting for allylic alcohols activation from (*S<sub>a</sub>*, *S<sub>Ru</sub>*) **Ru-3** precatalyst and preferential nucleophile approach

In continuation, with the influence of chirality toward modification of properties, we next investigated the application of these transformations towards the straightforward access to chiral

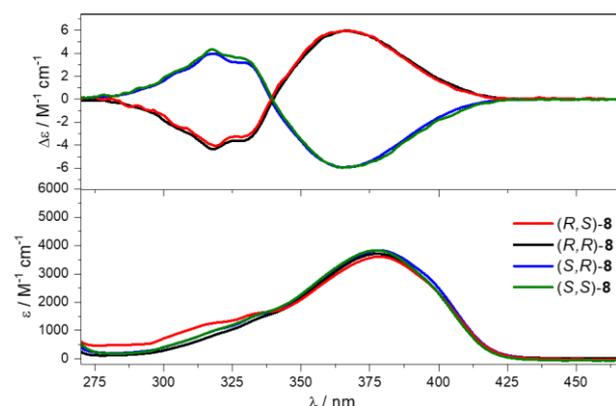
emitters. We thus applied these procedures to access to the four stereoisomers of indolin-3-ones with the same precatalyst (**S<sub>a</sub>**, **S<sub>Ru</sub>**)-**Ru-3**.<sup>[6e]</sup> 2-methylindole **5b** (4 mmol scale) was then tested in the presence of allylic alcohols **2** (Scheme 3). When using as low as 0.5% of precatalyst **Ru-3** loading, complete conversions were obtained during allylations from either crotyl alcohol **2c** or enriched(-), (*R*)-but-3-en-2-ol **2b** which was confirmed by GC analyses with branched/linear ratio of 92:8 and 97:3, respectively. Noteworthy, that at this reaction scale, water droplets deposit at the top of the Schlenk tube allowing roughly visual appreciation of the conversion by naked eyes. Since obtained 2,3-disubstituted indole intermediates are sensitive toward oxidation at position 3 of the indole nucleus and owing to the low steric hindrance of the methyl group at position 2, free rotation around the allylic fragment is expected allowing formation of both diastereoisomers arising from solid state oxidation.<sup>[6e]</sup> Thus, the resulted crude mixtures were then suspended in SiO<sub>2</sub> and stirred under an air atmosphere to afford after oxidation and semi pinacol rearrangement, the corresponding allylated indolin-3-ones **8**. Completion of the reactions were achieved after 24 hours affording 66% overall yields after purification. Owing to the presence of vicinal stereogenic centers, the diastereoisomers were easily separated by trivial purification by column chromatography affording the four distinct stereoisomers to further evaluate the influence of the stereogenic centers on their optical properties. Absolute configurations were unambiguously determined by X-ray analysis from the crystallization of (*S,R*)-**8**.<sup>[25]</sup>



**Scheme 3.** Access to the four stereoisomers of allylated indolin-3-one **8** and molecular structure of (*S,R*)-**8** (CCDC 2205725).

First, the optical and chiroptical properties were evaluated at the ground state by means of UV-vis absorption and ECD spectra. The absorption spectra of compounds (*R,S*)-**8**, (*S,S*)-**8**, (*S,R*)-**8** and (*R,R*)-**8**<sup>[26]</sup> recorded in dichloromethane solution at room temperature are depicted on Figure 3. All compounds display a broad band centered at 378 nm ( $\epsilon \sim 3800 \text{ M}^{-1} \text{ cm}^{-1}$ ) that can be attributed to an intramolecular charge-transfer (ICT) transition, in agreement with the previously reported optical behaviour of indolin-3-one analogues.<sup>[6e]</sup> In addition, small shoulders of moderate intensity ( $\epsilon \sim 650\text{-}1500 \text{ M}^{-1} \text{ cm}^{-1}$ ) are present around 300, 318 and 330 nm.

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**Figure 3.** UV-vis (bottom) and ECD (top) spectra of *(R,S)*-**8** (red)/*(S,S)*-**8** (green) and *(S,R)*-**8** (blue)/*(R,R)*-**8** (black) in dichloromethane solutions (298 K,  $C \sim 10^{-5}$  M).

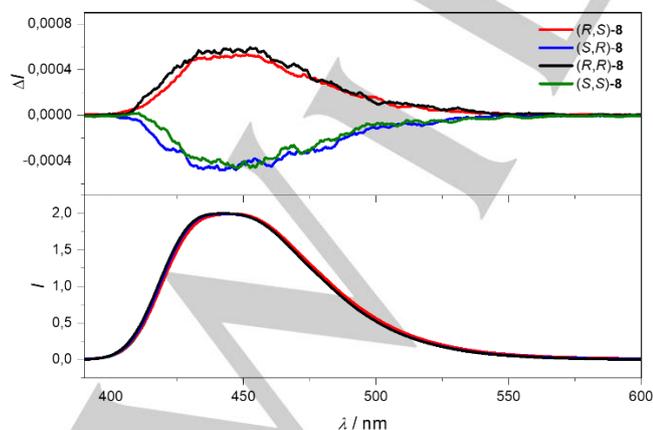
ECD spectra of each enantiomeric pair of compounds display mirror-image relationship. Furthermore, the two epimeric species generated during the reaction show chiroptical responses that are

similar in amplitude and opposite in signs, indicating that the response is mainly governed by the chiral cyclic scaffold and the configuration at the quaternary carbon stereocenter, with low contribution of the pendant chiral allyl chain. For instance, *(S,R)*-**8** exhibits first a positive ECD band at the higher energy ( $\Delta\epsilon = +4 \text{ M}^{-1} \text{ cm}^{-1}$  at 317 nm) with some visible vibronic structuration, and a second negative band at lower energy ( $\Delta\epsilon = -5.9 \text{ M}^{-1} \text{ cm}^{-1}$  at 365 nm). The absorption dissymmetry factor ( $g_{\text{abs}} = \Delta\epsilon/\epsilon$ ) spectra depicted on Figure S3 display almost perfect mirror-image

**Table 2.** Photophysical data for compounds *(R,S)*-**8**, *(S,S)*-**8**, *(S,R)*-**8** and *(R,R)*-**8** in  $\text{CH}_2\text{Cl}_2$ .<sup>[a]</sup>

Compounds	$\epsilon_{\text{max}} (\text{M}^{-1} \text{ cm}^{-1}), (\lambda \text{ (nm)})$	$\lambda_{\text{em}} (\text{nm})$	$\Phi_f$	$[\alpha]_D^{23}$	$g_{\text{abs}} (\lambda, \text{nm})$	$g_{\text{lum}} (\lambda, \text{nm})$	$g_{\text{lum}}/g_{\text{abs}}$	ee (%) <sup>b</sup>
<i>(R,S)</i> - <b>8</b>	3603 (379)	443	0.38 ( $\text{CH}_2\text{Cl}_2$ ),	+ 250 (c 0.24)	$4.6 \times 10^{-3}$ (316); $2.1 \times 10^{-3}$ (360)	$5.1 \times 10^{-4}$ (443)	0.21	88
<i>(S,S)</i> - <b>8</b>	3800 (379)	443	0.35 ( $\text{CH}_2\text{Cl}_2$ )	- 160 (c 0.24)	$5.2 \times 10^{-3}$ (316); $1.9 \times 10^{-3}$ (360)	$4.3 \times 10^{-4}$ (443)	0.22	88
<i>(S,R)</i> - <b>8</b>	3820 (379)	442	0.41 ( $\text{CH}_2\text{Cl}_2$ ), 0.43 (DMF), 0.21 (toluene), 0.28 (THF), 0.45 ( $\text{C}_2\text{H}_5\text{OH}$ ), 0.58 ( $\text{H}_2\text{O}$ )	- 298 (c 0.004)	$4.3 \times 10^{-3}$ (316); $1.9 \times 10^{-3}$ (360)	$4.8 \times 10^{-4}$ (442)	0.25	89
<i>(R,R)</i> - <b>8</b>	3700 (379)	442	0.32 ( $\text{CH}_2\text{Cl}_2$ )	+ 173 (c 0.004)	$5.3 \times 10^{-3}$ (316); $1.9 \times 10^{-3}$ (360)	$5.5 \times 10^{-4}$ (442)	0.28	85

[a] Unless otherwise stated, the concentration is  $\sim 10^{-5} \text{ mol L}^{-1}$  and  $\lambda_{\text{exc}} = 375 \text{ nm}$ . <sup>b</sup> ee of compounds **8** were determined by chiral HPLC analysis (Chiralcel ODH)



**Figure 4.** CPL (top) and normalized fluorescence (bottom) spectra of *(S,S)*-**8** (green), *(R,S)*-**8** (red), *(S,R)*-**8** (blue) and *(R,R)*-**8** (black) in dichloromethane solutions ( $\lambda_{\text{ex}} = 375 \text{ nm}$ ).

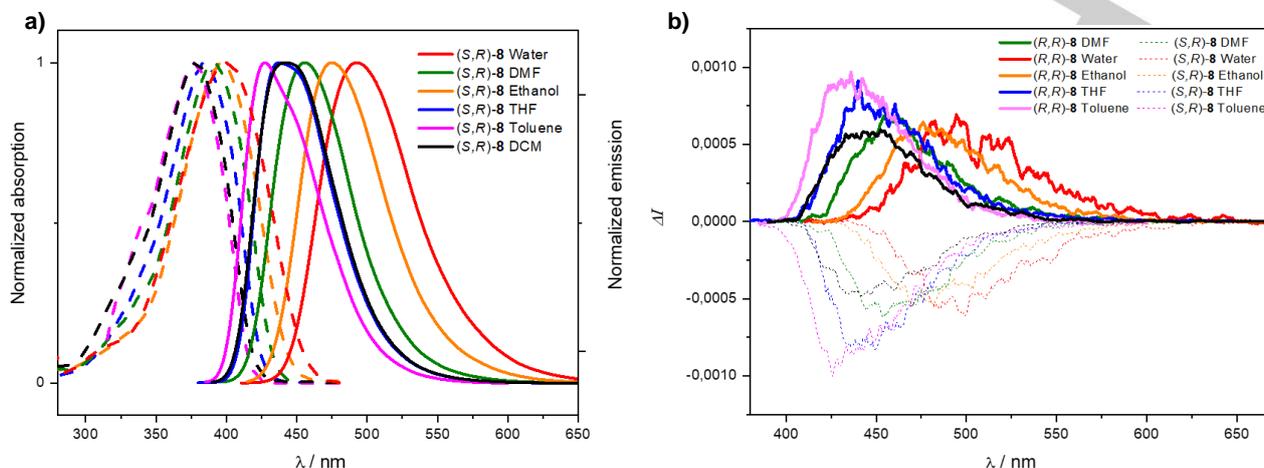
relationship for each enantiomeric pair *(R,S)*-**8**/*(S,R)*-**8** and *(S,S)*-**8**/*(R,R)*-**8** and values around  $1.9\text{--}5.3 \times 10^{-3}$ . It should be noticed that optical rotation values, registered for all four stereoisomers and summarized in the Table 2, enable to distinguish between the two different diastereomers (within the measurement errors), with the *(R,S)*-**8** [*(S,R)*-**8**] displaying higher values compared to *(R,R)*-**8** [*(S,S)*-**8**], but with the sign being governed by the cyclic chiral scaffold.

The chiroptical properties of these compounds were also examined at the excited state and the unpolarized and circularly polarized luminescence spectra were recorded first in  $\text{CH}_2\text{Cl}_2$  (Figure 4). All the compounds display non-structured emission spectra in the blue region with a maximum around 443–442 nm with mirror-image CPL signals and emission dissymmetry factor ( $g_{\text{lum}} = 2\Delta I/I$ ) values between  $4.3 \times 10^{-4}$  and  $5.3 \times 10^{-4}$  (see detailed values on Table 2), with positive signals for *(R,S)*-**8**/*(R,R)*-**8** and negative ones for *(S,S)*-**8**/*(S,R)*-**8** demonstrating that the simple separation of a set of diastereoisomers allows a rapid overview of the opposite CPL activities. Solvent dependence in fluorescence (Figure 5a) and CPL (Figure 5b) was

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also investigated for diastereoisomers (*S,R*)-**8** and (*R,R*)-**8** and a remarkable bathochromic shift was obtained moving from blue fluorescence in toluene ( $\lambda_{\max} = 427$  nm) to green fluorescence in water ( $\lambda_{\max} = 492$  nm), with the red shift nicely following the

solvent polarity. The positive solvatochromism was accompanied with a decrease of the CPL activities going from nonpolar to polar environment. This behaviour



**Figure 5.** a) Normalized emission (solid line) and absorption (dashed line) spectra of (*S,R*)-**8** in toluene (Magenta), THF (Blue), DCM (black), DMF (green), ethanol (orange) and water (red). b) CPL spectra of (*R,R*)-**8** (solid lines) and (*S,R*)-**8** (dashed lines) in toluene (Magenta), THF (Blue), DCM (black), DMF (green), ethanol (orange) and water (red) (298K,  $C \sim 10^{-5}$  M).

could be predictable and one can speculate a diminished response for  $g_{lum}$  in polar solvent due to the strengthening of the electric dipole transition moment.<sup>[27,28]</sup> Indeed, the emission dissymmetry factors show a higher response in toluene and THF solvents with a  $g_{lum}$  of  $8.8 \times 10^{-4}$  at 427 nm and  $7.2 \times 10^{-4}$  at 437 nm, respectively, for (*S,R*)-**8**, conversely the CPL show an almost two-fold decrease in DCM [ $g_{lum}$ ] =  $4.8 \times 10^{-4}$ . In contrast, absolute quantum yields follow the opposite trend showing a higher response in water and DCM solvents. Interestingly, these chiral chromophores are CPL active in water ( $g_{lum} = 6.6 \times 10^{-4}$ ); small organic molecules that show CPL responses in water are scarce and could be considered as interesting building blocks for biologically relevant applications that require aqueous solubility.<sup>[29-32]</sup> On the other hand, CPL stimuli-responsive materials are of great interest due to their possible incorporation in security technologies and their potential application as smart CPL sensors.<sup>[33-37]</sup>

## Conclusion

In conclusion, we have synthesized an enantiopure  $\pi$ -allylruthenium(IV) precatalyst **Ru-3** allowing the enantioselective and stereospecific allylations of indole by switching the nature (branched versus linear) of the acyclic allylic alcohols generating water as the only side product of the reaction. Extension of this transformation was applied to the one-pot two-steps preparation of the four indolin-3-one stereoisomers. This novel methodology enabled straightforward preparation of enantiomerically enriched indolin-3-ones possessing two asymmetric carbons, whose chiroptical properties are governed by the chiral cyclic scaffold rather than the chiral chain. By this method, we could show that the simple separation of enantioenriched diastereoisomers with central chirality are able to display opposite significant CPL activity, with dissymmetry factors up to  $8.8 \times 10^{-4}$  in toluene solvent and appealing solvatochromism. We believe that this

methodology expands the access to still rare chiral fluorophores in water.

## Experimental section

### Preparation of the [Ru(Cp\*)(1)( $\eta^3$ -propenyl)][PF<sub>6</sub>] complex (**S<sub>a</sub>**, **S<sub>Ru</sub>**)-**Ru-3**

(*S<sub>a</sub>*)-Sulfo-binepine<sup>[19]</sup> **1-H** (0.054 g, 0.115 mmol) and [Ru(Cp\*)(MeCN)<sub>3</sub>][PF<sub>6</sub>] **Ru-1** (0.058 g, 0.115 mmol), were added to a 15 mL Schlenk tube. The Schlenk tube was evacuated and filled with argon three times followed by the addition of deaerated dichloromethane (2 mL). The resulted orange homogeneous solution was stirred for 15 min. Allyl alcohol **2a** (15  $\mu$ L  $\sim$  2 eq.) was added and the solution immediately turned yellow. After stirring for additional 14 h, concentration afforded a pale-yellow precipitate. Removal of the solution and washing with dry, degassed *n*-hexane led to a yellow powder (0.082 g, 78%); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.22 (ddd,  $J = 7.9, 4.3, 1.3$  Hz, 1H), 8.13 (d,  $J = 8.1$  Hz, 1H), 8.06 (d,  $J = 8.3$  Hz, 1H), 7.85 (d,  $J = 8.2$  Hz, 1H), 7.71 (t,  $J = 7.7$  Hz, 1H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.52-7.45 (m, 3H), 7.36-7.28 (m, 3H), 7.23 (d,  $J = 8.7$  Hz, 1H), 7.20 (d,  $J = 8.6$  Hz, 1H), 6.95 (t,  $J = 8.4$  Hz, 1H), 6.63 (dd,  $J = 8.4, 1.3$  Hz, 1H), 5.32-5.28 (m, 1H, CH allyl), 4.70 (dd,  $J = 13.5, 4.9$  Hz, 1H, CH<sub>2</sub> binepine), 4.10 (d,  $J = 7.1$  Hz, 1H, CH<sub>2</sub> allyl), 4.04 (dd,  $J = 16.8, 14.1$  Hz, 1H, CH<sub>2</sub> binepine), 3.86-3.80 (m, 1H, CH<sub>2</sub> allyl), 3.60 (d,  $J = 10.9, 2.9$  Hz, 1H, CH<sub>2</sub> allyl), 3.38 (d,  $J = 14.0$  Hz, 1H, CH<sub>2</sub> binepine), 3.24 (dd,  $J = 13.5, 5.2$  Hz, 1H, CH<sub>2</sub> binepine), 1.61-1.58 (m, 1H, CH<sub>2</sub> allyl), 1.61 (d,  $J = 1.8$  Hz, 15H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  145.8 (d,  $J_{p-c} = 10.2$  Hz, C<sub>q</sub>), 136.3 (d,  $J_{p-c} = 3.0$  Hz, C<sub>q</sub>), 134.2 (d,  $J_{p-c} = 2.3$  Hz, C<sub>q</sub>), 133.7 (d,  $J_{p-c} = 2.4$  Hz, C<sub>q</sub>), 133.5 (d,  $J_{p-c} = 3.4$  Hz, C<sub>q</sub>), 133.4 (d,  $J_{p-c} = 2.4$  Hz, CH), 133.1 (d,  $J_{p-c} = 2.3$  Hz, C<sub>q</sub>), 131.1 (s, CH), 131.0 (d,  $J_{p-c} = 6.4$  Hz, CH), 130.7 (d,  $J_{p-c} = 7.0$  Hz, CH), 130.6 (s, CH), 129.6 (d,  $J_{p-c} = 13$  Hz, C<sub>q</sub>), 129.4 (d,  $J_{p-c} = 13$  Hz, C<sub>q</sub>).

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$c=6.7$  Hz, C<sub>q</sub>), 129.3 (d,  $J_{P-C}=2.2$  Hz, CH), 129.1 (d,  $J_{P-C}=1.0$  Hz, CH), 129.0 (d,  $J_{P-C}=1.4$  Hz, CH), 127.8 (d,  $J_{P-C}=4.1$  Hz, CH), 127.8 (s, CH), 127.5 (d,  $J_{P-C}=5.0$  Hz, CH), 127.4 (d,  $J_{P-C}=8.1$  Hz, CH), 127.3 (s, CH), 127.2 (s, CH), 126.9 (d,  $J_{P-C}=1.3$  Hz, CH), 124.3 (s, C<sub>q</sub>), 123.9 (s, C<sub>q</sub>), 109.7 (d,  $J_{P-C}=1.0$  Hz, C<sub>q</sub>, C<sub>5</sub>Me<sub>5</sub>), 96.6 (s, CH, allyl), 79.1 (d,  $J_{P-C}=3.3$  Hz, CH<sub>2</sub>, allyl), 52.6 (d,  $J_{P-C}=4.5$  Hz, CH<sub>2</sub>, allyl), 28.6 (d,  $J_{P-C}=28.5$  Hz, CH<sub>2</sub>, binepine), 28.5 (d,  $J_{P-C}=22.3$  Hz, CH<sub>2</sub>, binepine), 10.3 (s, CH<sub>3</sub>, C<sub>5</sub>Me<sub>5</sub>); <sup>31</sup>P NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  36.2 (s), -144.5 (hept,  $J=705$  Hz); HRMS calcd for [M-PF<sub>6</sub>]<sup>+</sup> C<sub>41</sub>H<sub>40</sub>O<sub>3</sub>PSRu 745.14738, found : 745.1474 (0 ppm).

**Stereospecific allylation of indole 5a:** In a Schlenk tube under an inert atmosphere of argon, indole **5a** (47 mg, 0.4 mmol, 1 eq.), dichloromethane (1 mL) and (-)-(*R*)-but-3-en-2-ol **2b** (87% ee) (34  $\mu$ L, 0.4 mmol, 1 eq.) were successively added and the resulting solution was stirred for five minutes. Ruthenium precatalyst **Ru-3** (10 mg, 3 mol%) was added and the Schlenk was immediately heated at 30°C for 16 hours. Then, the reaction was cooled to room temperature, monitored by GC analysis and stopped. The reaction mixture was filtrated on silica gel with pentane/diethyl ether eluant (2:3) in order to eliminate the catalyst affording allylated indole **6a** as colorless oil with branched/linear selectivity ~ 98:2 (90% yield).

**Enantioselective allylation of indole 5a:** In a Schlenk tube under an inert atmosphere of argon, indole **5a** (47 mg, 0.4 mmol, 1 eq.), dichloromethane (1 mL) and crotyl alcohol (93% (*E*)) **2c** (34  $\mu$ L, 0.4 mmol, 1 eq.) were successively added and the resulting solution was stirred for five minutes. Ruthenium precatalyst **Ru-3** (10 mg, 3 mol%) was added and the Schlenk was immediately heated at 30°C for 16 hours. Then, the reaction was cooled to room temperature, monitored by GC analysis and stopped. The reaction mixture was filtrated on silica gel with pentane/diethyl ether eluant (2:3) in order to eliminate the catalyst affording allylated indole as colorless oil with branched/linear selectivity ~ 92:8 (86% yield).

**3-(but-3-en-2-yl)-1H-indole 6a:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (brs, 1H), 7.66 (d,  $J=7.9$  Hz, 1H), 7.36 (dt,  $J=8.1, 0.9$  Hz, 1H), 7.19 (ddd,  $J=8.1, 6.9, 1.2$  Hz, 1H), 7.11 (ddd,  $J=8.0, 7.0, 1.1$  Hz, 1H), 6.98 (d,  $J=2.0$  Hz, 1H), 6.09 (ddd,  $J=17.0, 10.2, 6.7$  Hz, 1H), 5.14 (dt,  $J=17.2, 1.6$  Hz, 1H), 5.04 (dt,  $J=10.2, 1.5$  Hz, 1H), 3.78 (p,  $J=6.9$  Hz, 1H), 1.48 (d,  $J=7.0$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  143.4, 136.7, 126.9, 122.1, 120.5, 120.4, 119.7, 119.3, 112.8, 111.2, 35.0, 20.3. NMR analyses of 3-(but-3-en-2-yl)-1H-indole are in agreement with previously reported data.<sup>[17a]</sup>  
**(S)-3-(but-3-en-2-yl)-1H-indole(S)-6a from 2c** (93% (*E*)): Enantiomeric excess was determined by HPLC with Chiralcel OJ column (95:5 *n*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); tr (minor) = 37.49 min, tr (major) = 41.05 min, 8:92 er, 84% ee. Absolute configuration was attributed by comparison of the optical rotation with previously reported data.<sup>[10a,12]</sup>  
**(R)-3-(but-3-en-2-yl)-1H-indole (R)-6a from (R)-2b** (87% ee) : Enantiomeric excess was determined by HPLC with Chiralcel OJ column (95:5 *n*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); tr (major) = 37.11 min, tr (minor) = 42.76 min, 93.5:6.5 er, 87% ee. Absolute configuration was attributed by comparison of the optical rotation in chloroform with previously reported data.<sup>[10a,12]</sup>

**Procedure for the one-pot allylation-oxidation sequence from 2-methylindole 5b :** In a Schlenk tube under an inert atmosphere of argon, 2-methylindole **5b** (500 mg, 3.8 mmol, 1 eq.), dichloromethane (6 mL) and allylic alcohols **2** (3.8 mmol, 1 eq.) were successively added and the resulting solution was stirred for five minutes. Ruthenium precatalyst **Ru-3** (17 mg, 0.5 mol%) was added and the Schlenk was immediately heated at 30°C for 16 hours. After cooling, completion of the allylation step was monitored by GC chromatography indicating conversion > 95%. Then the resulting solution was transferred in a flask containing SiO<sub>2</sub> (8 g) and CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The resulting mixture was concentrated using a rotary evaporator to give a white solid. The reaction mixture was placed in air under stirring at 60°C for two hours and at room temperature for additional 16 hrs. Complete conversion were observed by GC and NMR analyses with branched/linear selectivity > 97:3 from **2b** and branched/linear selectivity of 92:8 from **2c**. Purification by silica gel column chromatography (pet. ether: Et<sub>2</sub>O = 7 : 3) allowed the separation of the two diastereoisomers (66% overall yield); HRMS calcd for [M+Na]<sup>+</sup> C<sub>13</sub>H<sub>15</sub>NONa 224.10458, found : 224.1048.

**(S)-2-((R)-but-3-en-2-yl)-2-methylindolin-3-one (S,R)-8 from (R)-2b** (87% ee) : Yellow solid; er= 5.5:94.5; [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -298 (c 0.004, CH<sub>2</sub>Cl<sub>2</sub>) <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.54 (dt,  $J=7.7, 1.0$  Hz, 1H), 7.44 (ddd,  $J=8.3, 7.1, 1.4$  Hz, 1H), 6.89 (dt,  $J=8.3, 0.8$  Hz, 1H), 6.79 (ddd,  $J=7.8, 7.0, 0.8$  Hz, 1H), 5.93-5.79 (m, 1H), 5.21-5.17 (m, 1H), 5.16-5.12 (m, 1H), 4.70 (brs, 1H), 2.65-2.41 (m, 1H), 1.26 (s, 3H), 0.80 (d,  $J=6.7$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  205.3, 161.4, 139.4, 137.5, 124.8, 121.5, 119.0, 117.3, 112.9, 69.2, 45.0, 22.9, 14.4. Enantiomeric excess was determined by HPLC with Chiralcel ODH column (99:1 *n*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); tr (minor) = 15.5 min, tr (major) = 18.7 min, 89% ee.

**(R)-2-((S)-but-3-en-2-yl)-2-methylindolin-3-one (R,S)-8 from 2c** (93% (*E*)): Yellow solid; er= 93.7:6.3; [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +250 (c 0.24, CH<sub>2</sub>Cl<sub>2</sub>). Enantiomeric excess was determined by HPLC with Chiralcel ODH column (99:1 *n*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); tr (major) = 15.0 min, tr (minor) = 19.2 min, 88% ee.

**(R)-2-((R)-but-3-en-2-yl)-2-methylindolin-3-one (R,R)-8 from (R)-2b** (87% ee) : Yellow oil; er= 7.7:92.3; [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +173 (c 0.004, CH<sub>2</sub>Cl<sub>2</sub>) <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.51 (d,  $J=7.7$  Hz, 1H), 7.43 (ddd,  $J=8.3, 7.0, 1.4$  Hz, 1H), 6.86 (d,  $J=8.3$  Hz, 1H), 6.81-6.77 (m, 1H), 5.68 (ddd,  $J=17.1, 10.3, 8.4$  Hz, 1H), 5.02 (ddd,  $J=17.2, 1.9, 1.0$  Hz, 1H), 4.92 (dd,  $J=10.3, 1.9$  Hz, 1H), 4.67 (brs, 1H), 2.47 (p,  $J=7.2$  Hz, 1H), 1.26 (s, 3H), 1.11 (d,  $J=6.9$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  205.0, 160.9, 139.4, 137.4, 124.8, 121.3, 119.0, 116.4, 112.9, 69.1, 45.1, 21.3, 14.9. Enantiomeric excess was determined by HPLC with Chiralcel ODH column (99:1 *n*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); tr (major) = 16.7 min, tr (minor) = 20.7 min, 85% ee.

**(S)-2-((S)-but-3-en-2-yl)-2-methylindolin-3-one (S,S)-8 from 2c** (93% (*E*)): Yellow oil, er= 94.9:5.1, containing ~ 6% of racemic 2-(but-2-en-1-yl)-2-methylindolin-3-one side product, [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -160 (c 0.24, CH<sub>2</sub>Cl<sub>2</sub>). Enantiomeric excess was determined by HPLC with Chiralcel ODH column (99:1 *n*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); tr (minor) = 17.5 min, tr (major) = 21.2 min, 88% ee.

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**Keywords:** chirality • enantioselectivity • stereoselectivity • fluorescence • CPL

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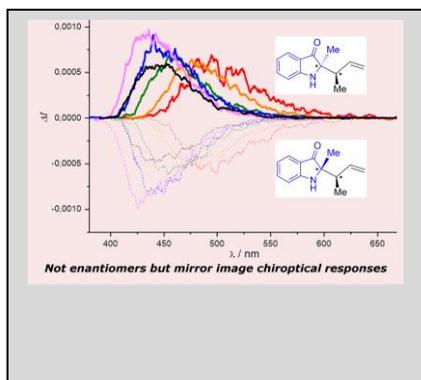
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## RESEARCH ARTICLE

## Entry for the Table of Contents

Through the use of a well-defined enantiopure  $\pi$ -allylic ruthenium(IV) precatalyst, facile access to enantioenriched indolin-3-one emitters was achieved. Facile separation of diastereoisomers demonstrated mirror image chiroptical responses



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