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Full Paper

Enantioselective Photochemical Rearrangements of Spirooxindole Epoxides Catalyzed by a Chiral Bifunctional Xanthone

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The title compounds were shown to undergo an enantioselective photochemical rearrangement to 3-acylindolin-2-ones (16–33 % ee). A xanthone, which is tethered via an anellated oxazole to a chiral 1,5,7-trimethyl-3-azabicyclo[3.3.1]nonan-2-one scaffold, efficiently catalyzed this reaction at λ 366 nm, presumably by triplet sensitization. The observed enantioselectivity can be explained by hydrogen bonding of the oxindole substrate and the putative 1,3-diradical intermediate to the lactam part of the catalyst. Although one substrate enantiomer is processed with minor preference over the other, it was shown that the reaction is not stereospecific. Rather, the main reason for the observed selectivity is the enantioselective migration step.

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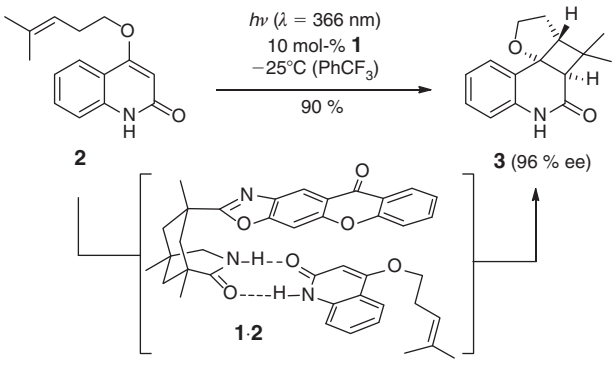
Introduction

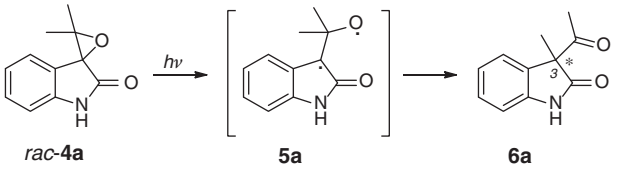
In recent years, there has been a rapidly growing interest in the enantioselective catalysis of photochemical reactions. Their fascinating architecture and their biological relevance make it desirable to obtain photoproducts in enantiomerically pure forms. Among the different approaches, which are employed to achieve this goal,[1] the development of chiral sensitizers has a long-standing history and has over the years resulted in several key contributions to enantioselective photocatalysis.[2] In our group, the chiral xanthone **1** (Scheme 1) has been developed from a previously reported chiral template[3] and it has turned out to be a remarkable catalyst for enantioselective [2+2] photocycloaddition reactions.[4] Its pivotal design element is a bicyclic lactam unit, which allows for pre-association of a given photochemical substrate and ensures a close proximity of the sensitizing unit and substrate chromophore.



Scheme 1. Enantioselective intramolecular [2+2] photocycloaddition of quinolone **2** mediated by catalyst **1** via a putative complex **1**·**2**.

Quinolone **2**, for example, which features a tethered olefin unit for intramolecular [2+2] photocycloaddition, was shown to form product **3** in the presence of 10 mol-% of catalyst **1** in high yield and with excellent enantioselectivity.[4c] The reaction likely proceeds via complex **1**·**2** in which the sensitization of the substrate is facilitated and the high enantioface differentiation is secured. At the chosen wavelength (λ 366 nm), direct excitation of substrate **2** is not feasible because the compound shows no significant absorption at this wavelength.

Apart from the success catalyst **1** has encountered in [2+2] photocycloaddition chemistry, the hydrogen bonding and sensitization approach should be applicable also to other photochemical reactions. Prerequisites for this approach are the presence of a two-point hydrogen bonding site, ideally a lactam unit, in the substrate and a suitable reaction, which can be initiated by triplet sensitization. Recent reports by the group of W. Zhang[5] have drawn our interest to the photochemical rearrangement of spirooxindole epoxides to 3-acylindolin-2-ones. Despite the fact that photochemical epoxide rearrangements have been extensively investigated in the past,[6,7] there has been very little evidence that transformations of this type could be initiated by triplet sensitization.[8] The Zhang group, however, noted a significant catalytic effect exerted by typical triplet sensitizers (acetone, benzophenone) in the above-mentioned spirooxindole epoxide rearrangement. Of particular interest was the observation that the *N*-unprotected spirooxindole *rac*-**4a** (Scheme 2) underwent the reaction and delivered the rearrangement product *rac*-**6a** in high yield.[5b] We speculated that the reaction would proceed via a prochiral triplet diradical such as **5a** and wondered whether it would be feasible to induce an enantioselective reaction course to chiral product **6a** with a defined stereogenic centre at carbon atom C-3.



Scheme 2. Putative mechanistic course of the photochemical spirooxindole epoxide rearrangement[5b] via the prochiral intermediate **5a**.

In this account, we provide full details on the synthesis of several *N*-unsubstituted spirooxindole epoxides, their benzophenone-mediated rearrangement to racemic products, and studies towards an enantioselective reaction course in the presence of chiral xanthone **1**. Mechanistic experiments were performed to elucidate the influence of the stereogenic centre in the starting material on the enantioselectivity of the photochemical rearrangement.

Results and Discussion

Synthesis of the Substrates

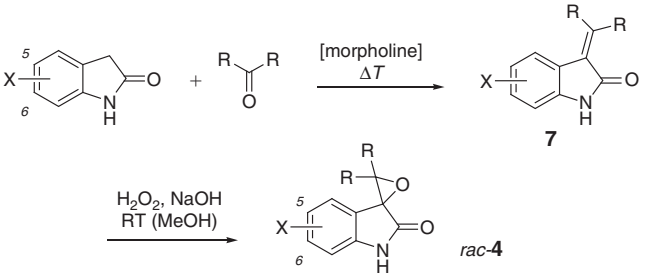
The synthesis of substrates *rac*-**4** (Table 1) followed known procedures. In the first step, the respective 1,3-dihydroindol-2-ones (indolin-2-ones, oxindoles) underwent a morpholine-catalyzed Knoevenagel-type condensation to 3-alkylidene-indolin-2-ones **7**.[5,9] The reactions were performed at reflux temperature in an excess of the respective ketone as the solvent. Yields were high for the acetone-derived products (entries 1, 5, 7–11), but turned out to be lower for the other dialkylketones (entries 2–4, 6). In the second step, the olefins were converted into the respective epoxides *rac*-**4** by treatment with hydrogen peroxide under basic conditions (Weitz–Scheffer epoxidation).[10] The epoxidation protocol was not further optimized and all reactions were performed at ambient temperature overnight (16 h). Yields were moderate to good in most instances. However, for two substrates (entries 5 and 10), consecutive reactions severely diminished the yield. As a result of this observation, the epoxidation of substrate **7k** was stopped after 7 h (entry 11), leading to a significant improved yield as compared with the reaction of the analogous 5-chloroindolin-2-one (substrate **7e**, entry 5).

A few additional substrates *rac*-**8**–*rac*-**10** (Fig. 1) were also considered to be useful, but were not prepared by the general protocol. Detailed procedures for their syntheses are provided in the Supplementary Material. Cyclopropane *rac*-**8** was available from 3-propylidene-indolin-2-one (*rac*-**7a**) by Corey–Chaykovsky methylenation with trimethylsulfoxonium iodide.[11] The epoxy ester *rac*-**9** was obtained as a mixture of separable diastereoisomers (diastereomeric ratio, dr = 67/33) from isatin by a Wittig reaction[12] with commercially available (carbethoxymethylene)triphenylphosphorane and subsequent Weitz–Scheffer epoxidation[10] in ethanol. The methyl-substituted epoxide *rac*-**10** (dr = 67/33) was accessible also from isatin by an aldol condensation procedure[13] and epoxidation of the resulting 3-ethylidene-indolin-2-one.

Racemic Reactions

Upon irradiation at λ 366 nm[14] in acetonitrile for 1 h at room temperature, most of the spirooxindole epoxides *rac*-**4** showed no conversion according to NMR monitoring. Indeed, UV-visible spectra of most compounds revealed that there is no absorption in this wavelength region (see Supplementary Material). Only the absorption spectra of the 5-methoxy- (*rac*-**4g**) and 5-methyl-substituted derivative (*rac*-**4h**) showed a slight overlap with the emission spectrum of the irradiation source. Minor amounts of the respective rearrangement products were identified in these cases (22 % and 18 %, respectively) after an irradiation time of 1 h.

Table 1. Preparation of spirooxindole epoxides *rac*-4 from the respective indolin-2-ones via 3-alkylidene-indolin-2-ones 7



Entry	X	R,R	Olefin	Yield[A] [%]	Epoxide	Yield[B] [%]
1	H	Me,Me	**7a**	99	*rac*-**4a**	88
2	H	Et,Et	**7b**	58	*rac*-**4b**	88
3	H	–$(CH_2)_4$–	**7c**	63	*rac*-**4c**	55
4	H	–$(CH_2)_5$–	**7d**	59	*rac*-**4d**	64
5	6-Cl	Me,Me	**7e**	95	*rac*-**4e**	48
6	6-Cl	Et,Et	**7f**	53	*rac*-**4f**	66
7	5-MeO	Me,Me	**7g**	97	*rac*-**4g**	78
8	5-Me	Me,Me	**7h**	63	*rac*-**4h**	61
9	5-CF_3	Me,Me	**7i**	95	*rac*-**4i**	99
10	5-Cl	Me,Me	**7j**	93	*rac*-**4j**	31
11	6-Br	Me,Me	**7k**	96	*rac*-**4k**	99[C]

[A]The condensation reaction was performed typically at a substrate concentration of $c = 0.1$ M and with morpholine (0.5 equiv.) in the respective ketone RCOR at reflux temperature for 16 h. The yield refers to isolated pure product after chromatographic purification.
[B]The epoxidation reaction was performed with NaOH (2.5 equiv.) and aqueous H_2O_2 solution (35 % v/v, 15 equiv.) in methanol ($c = 65$ mM) for 16 h. The yield refers to isolated pure product after chromatographic purification.
[C]The reaction time for the epoxidation was only 7 h.

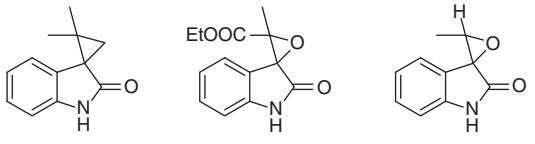
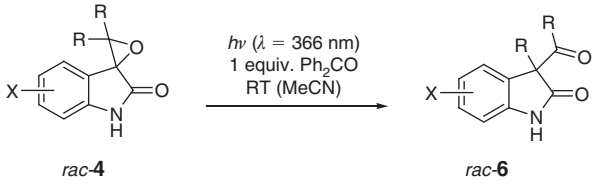


Fig. 1. Structure of spirooxindoles *rac*-**8**, *rac*-**9**, and *rac*-**10**.

In the presence of benzophenone as a triplet sensitizer, all tested symmetrically substituted spirooxindole epoxides *rac*-**4a**–*rac*-**4i** delivered the expected 3-acylindolin-2-ones *rac*-**6** with high chemoselectivity (Table 2). An irradiation time of 1 h was sufficient for complete conversion in most cases and the yields for products *rac*-**6** varied between 81 % and 99 %. Only the epoxides with an additional spirocenter (entries 3, 4) at the epoxide ring showed reduced reactivity. The reaction of substrate *rac*-**4c** was complete after 4 h. Substrate *rac*-**4d** required 2.5 h (150 min) for its conversion to be complete.

When the benzophenone-mediated rearrangement was attempted with the other spirocyclic substrates *rac*-**8**–*rac*-**10** (Fig. 1), no conversion was observed even after prolonged irradiation. Though it can be argued that cyclopropane *rac*-**8**

Table 2. Benzophenone-mediated photochemical rearrangement of epoxides *rac*-4 to 3-acylindolin-2-ones *rac*-6



rac-**4** *rac*-**6**

Entry[A]	Substrate	X	R,R	Product	Yield[B] [%]
1	*rac*-**4a**	H	Me,Me	*rac*-**6a**	99
2	*rac*-**4b**	H	Et,Et	*rac*-**6b**	95
3	*rac*-**4c**	H	–$(CH_2)_4$–	*rac*-**6c**	81[C]
4	*rac*-**4d**	H	–$(CH_2)_5$–	*rac*-**6d**	85[D]
5	*rac*-**4e**	6-Cl	Me,Me	*rac*-**6e**	85
6	*rac*-**4f**	6-Cl	Et,Et	*rac*-**6f**	91
7	*rac*-**4g**	5-MeO	Me,Me	*rac*-**6g**	93[E]
8	*rac*-**4h**	5-Me	Me,Me	*rac*-**6h**	96[F]
9	*rac*-**4i**	5-CF_3	Me,Me	*rac*-**6i**	93
10	*rac*-**4j**	5-Cl	Me,Me	*rac*-**6j**	91
11	*rac*-**4k**	6-Br	Me,Me	*rac*-**6k**	93

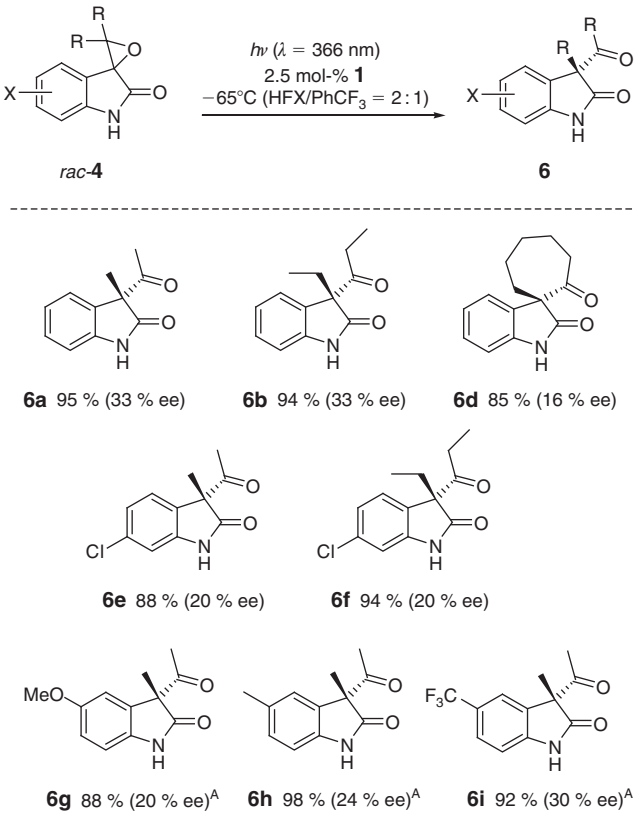
[A]All photochemical rearrangement reactions were conducted for 1 h at ambient temperature (air-cooled) in Duran tubes using a RPR-100 photochemical reactor with 16 fluorescent lamps (λ 366 nm)[4c] as the irradiation source and benzophenone (1 equiv.) as the sensitizer in dry, de-aerated acetonitrile ($c = 10$ mM).
[B]Yield of isolated product after chromatographic purification.
[C]The irradiation time was 4 h.
[D]The irradiation time was 150 min.
[E]The compound showed a non-catalyzed background reaction (22 % conversion after 1 h).
[F]The compound showed a non-catalyzed background reaction (18 % conversion after 1h).

contains no cleavable epoxide C–O bond, the fact that the other two epoxides showed no conversion is surprising. The separated diastereoisomers of epoxy ester *rac*-**10** were individually subjected to the irradiation conditions. There was no indication for epimerization, thus suggesting that the desired C–O bond cleavage did not proceed. In the case of substrate *rac*-**9**, the diastereomeric mixture (dr = 67/33) was used, the composition of which remained unchanged during the irradiation.

It has been reported that the photochemical ring-opening of spirooxindole epoxides can also be performed by a photoinduced electron transfer (PET) employing 2,4,6-triphenylpyrylium tetrafluoroborate as the catalyst.[5a] Under these conditions, it was feasible to trap the intermediate radical cation before any rearrangement by olefins. We attempted similar trapping experiments with various olefins under the benzophenone-mediated conditions. No trapping products were isolated. The observation supports the mechanistic hypothesis that benzophenone and related ketones operate in this reaction by triplet sensitization.

Enantioselective Catalysis

Encouraged by the effective rearrangement of substrates *rac*-**4** in the presence of benzophenone, we attempted enantioselective reactions employing chiral xanthone catalyst **1**. In order to achieve a maximum degree of association between the putative catalyst **1** and the substrates, the reaction temperature of the enantioselective rearrangement reactions was kept as low as possible. In an earlier work, we had shown that a 2 : 1 mixture of hexafluoro-1,3-xylene (HFX) and trifluorotoluene ($PhCF_3$) is a



Scheme 3. Enantioselective photochemical rearrangement of epoxides *rac*-**4** to 3-acylindolin-2-ones **6** catalyzed by chiral xanthone **1**. All photochemical rearrangement reactions were conducted at −65°C in Duran tubes using a RPR-100 photochemical reactor with 16 fluorescent lamps (λ 366 nm).[4c] Yields of isolated products were determined after chromatographic purification. The enantioselectivity was determined by chiral HPLC or chiral GLC analysis (see Supplementary Material). [A]5 mol-% of catalyst **1** was employed.

suitable reaction medium, in which triplet-sensitized reactions can be performed at temperatures as low as −65°C.[4e] The same solvent mixture was employed in the present set of reactions, and preliminary experiments were performed with 5 mol-% of the catalyst. With substrate *rac*-**4a**, the reaction was shown to be complete after 1.5 h, and it delivered product **6a** in a yield of 95 %. The product was dextrorotatory ($[\alpha]_D$ +68.9, *c* 1.0 in CH_2Cl_2) which readily allowed – based on the fact that the (*S*)-isomer is levorotatory[15] – its configuration assignment to the (*R*)-series. In addition, the HPLC elution order under comparable conditions (e.g. same chiral stationary phase) was identical to the reported elution order for the (*S*)- and (*R*)-enantiomers.[15] The enantiomeric excess in favour of compound **6a** was relatively low, however, and was determined to be 33 % ee by chiral HPLC and gas–liquid chromatography (GLC) analysis. It was shown that the same enantioselectivity could also be achieved with a catalyst loading of 2.5 mol-%. Most of the other reactions, which are summarized in Scheme 3, were performed under the latter conditions.

Full conversion for substrates *rac*-**4b** and *rac*-**4d** was achieved after 2.5 h, and products **6b** and **6d** were obtained in very high yields. The enantioselectivity for the propionyl-substituted indolin-2-one **6b** was equal to that recorded for its acetyl analogue (33 % ee). The cyclopentyl-derivative *rac*-**4c** did not react under the reaction conditions employed, and no cyclohexanone product **6c** was formed after prolonged

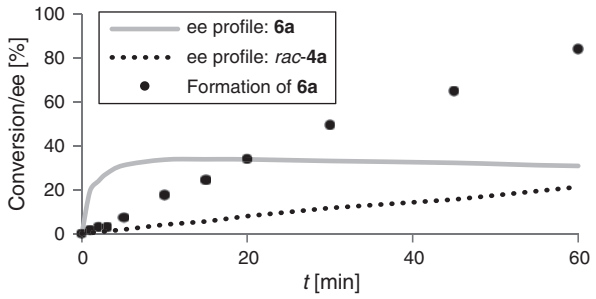


Fig. 2. Rate-to-ee profile for the reaction of *rac*-**4a** → **6a** in the presence of catalyst **1** (Table 3).

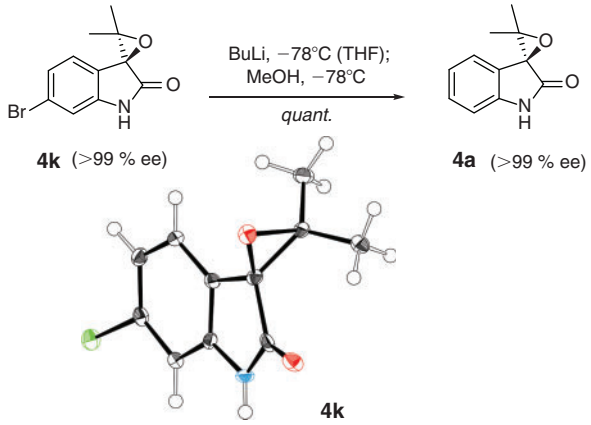
irradiation. The starting material was almost completely recovered. Its homologue *rac*-**4d** gave the expected cycloheptanone **6d** with low enantioselectivity (16 % ee). In the 6-chloro series, the dimethyl-substituted epoxide *rac*-**4e** and the respective diethyl-substituted substrate *rac*-**4f** resulted in the same enantioselectivity. In the former case, product **6e** was obtained with 88 % yield and 20 % ee. In the latter case, product **6f** was isolated with 94 % yield.

An increased catalyst loading (5 mol-%) did not show any improvement in chemo- or enantioselectivity for the reaction *rac*-**4e** → **6e**. In contrast, higher catalyst loadings were required to achieve full conversion for substrates *rac*-**4 g** into *rac*-**4i**. Conversion was incomplete after 4 h using a catalyst loading of 2.5 mol-%, whereas the reactions went to completion with 5 mol-% catalyst within 1.5 h. Yields were high (88–98 %), but enantioselectivities varied between 20–30 % ee. In all cases, products **6b** and **6d**–**6i** were dextrorotatory, indicating that the major enantiomer was formed with the same absolute configuration as that observed for the reaction *rac*-**4a** → **6a**. The potential substrates *rac*-**4i** and *rac*-**4j** (Table 2) turned out to be poorly soluble in the non-polar solvent mixture even at ambient temperature and enantioselective reactions could consequently not be performed.

Origin of Stereoselectivity

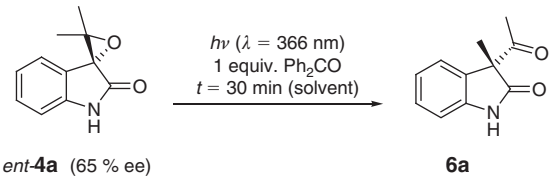
A rate profile of the reaction *rac*-**4a** → **6a** (see Fig. 2 and Supplementary Material) in the presence of catalyst **1** (Scheme 3) was correlated with the ee values of the substrate and the product (GLC analysis). It showed that the product ee increased within a few minutes (10 % conversion) to a value of ~35 % and remained essentially unchanged with ongoing reaction. The substrate, however, underwent a steady increase in ee while the reaction progressed. An ee of 4 % was recorded at 10 % conversion and the maximum ee was found to be 25 % shortly before complete conversion.

The absolute configuration of the product was known (see above), whereas the absolute configuration of the substrate enantiomers **4a** and *ent*-**4a** had to be determined. To this end, the racemic 6-bromosubstituted spirooxindole epoxide *rac*-**4k** was separated into its enantiomers by semi-preparative chiral HPLC. The absolute configuration of enantiomer **4k** was found by anomalous X-ray diffraction to be the (*S*)-configuration at the spiro centre (Scheme 4). Conversion of enantiomerically pure compound **4k** into the parent spirooxindole epoxide **4a** was achieved by bromine–lithium exchange and subsequent methanolysis. Based on this dataset, it was possible to assign the (*S*)-configuration to epoxide **4a** and the (*R*)-configuration to its enantiomer *ent*-**4a**. The enantiomer, which was enriched in the photochemical reaction *rac*-**4a** → **6a**, turned out to be compound **4a**.



Scheme 4. Crystal structure of enantiopure 6-bromoindolone epoxide **4k** and its transformation into enantiopure epoxide **4a**.

Table 3. Benzophenone-mediated photochemical rearrangement of epoxides *rac*-4 to 3-acylindolin-2-ones *rac*-6

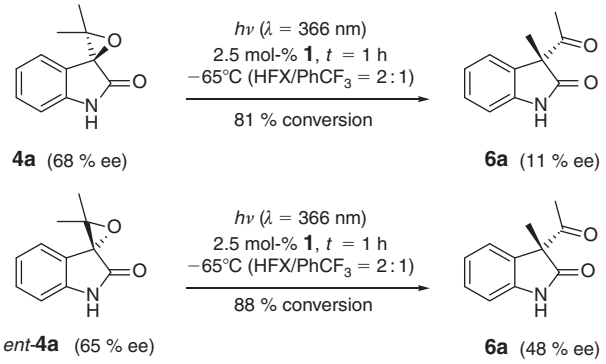


Entry[A]	*T* [°C]	Solvent	Conversion [%][B]	ee [%][C]
1	−40	MeCN	100	4
2	−40	HFX/PhCF$_3$ = 2 : 1	100	12
3	−65	HFX/PhCF$_3$ = 2 : 1	86	16

[A]All photochemical rearrangement reactions were conducted for 30 min at the given temperature *T* in Duran tubes using a RPR-100 photochemical reactor with 16 fluorescent lamps (λ 366 nm)[4c] as the irradiation source and benzophenone (1 equiv.) as the sensitizer.
[B]The conversion was determined by GLC analysis.
[C]Parameter ee was determined by chiral HPLC and chiral GLC analysis.

Although complete separation of enantiomers **4a** and *ent*-**4a** was not feasible by semi-preparative chiral HPLC (and the production of this material via bromine–lithium exchange was too tedious), it was possible to obtain enriched enantiomers for further studies. In a first set of experiments, the spirooxindole epoxide *ent*-**4a** was subjected to the conditions of the benzophenone-mediated rearrangement (Table 3). In the absence of any further source of chirality, the reaction in acetonitrile at −40°C delivered the rearranged product with a low, but detectable ee of 4 % (entry 1). Conversion was quantitative after 30 min. In the solvent mixture of HFX and trifluorotoluene (entries 2 and 3), the enantioselectivity was higher, but the reaction remained incomplete at −65°C after 30 min. The recorded enantioselectivities were 12 % ee at −40°C (entry 2) and 16 % ee at −65°C (entry 3). Clearly, the reaction is by no means stereospecific. However, it is likely that there is a chiral memory effect[16] favouring a formal inversion at the stereogenic spiro centre in a putative 1,3-diradical.

The rate-to-ee profile of the reaction *rac*-**4a** → **6a** and the results of the benzophenone-mediated rearrangement



Scheme 5. Photochemical rearrangement of epoxides **4a** and *ent*-**4a** to 3-acylindolin-2-one **6a** catalyzed by chiral xanthone **1**.

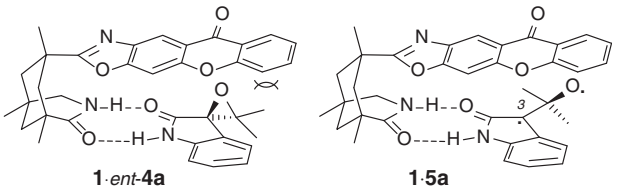


Fig. 3. Putative complexes of catalyst **1** with substrate *ent*-**4a** and with intermediate **5a**.

reactions (Table 3) suggest that catalyst **1** preferably processes enantiomer *ent*-**4a** and enhances the intrinsic preference of this enantiomer to deliver the rearrangement product **6a**. If this was true, it would be expected that the reaction of substrate *ent*-**4a** should occur with higher enantioselectivity than the reaction of the racemic substrate *rac*-**4a**, whereas the reaction of substrate **4a** should be less enantioselective (matched or mismatched pairs). This hypothesis was probed by subjecting the enantio-enriched epoxides **4a** and *ent*-**4a** to the reaction conditions of the enantioselective rearrangement reaction (Scheme 5). Indeed, it was found that both reactions delivered predominantly the same enantiomer **6a**, but the enantioselectivity was much higher (48 % ee) in the latter than in the former case (11 % ee). Furthermore, substrate *ent*-**4a** was processed with a higher rate (88 % conversion after 1 h versus 81 % conversion for **4a**). A rate-to-ee profile for both reactions (see Supplementary Material) showed that the ee of substrate **4a** decreased slowly and was still relatively high (~40 % ee) at almost complete conversion, whereas the ee of substrate *ent*-**4a** decreased more rapidly.

Based on the stereochemical results, it appears reasonable to assume that binding of *ent*-**4a** to catalyst **1** is favoured over binding of substrate **4a**. As depicted in Fig. 3, the steric interaction of the epoxide oxygen atom with the xanthone unit in complex **1**·*ent*-**4a** should be less severe than the related interaction of the two geminal methyl groups at the epoxide core with the xanthone in the diastereomeric complex **1**·**4a** (not shown). This assumption is in line with the fact that *ent*-**4a** is more readily processed than its enantiomer and that there is a kinetic resolution in favour of **4a**. The further fate of the substrates after triplet sensitization has mechanistically not been elucidated. However, based on the hypothesis that a 1,3-diradical **5a** is formed, it would be understandable that migration of the methyl group occurs preferentially from the respective *Si* face because the top face (*Re* face) of the radical centre at carbon atom C-3 is shielded by the xanthone in complex **1**·**5a**.

In earlier studies,[4b,c] we have shown that the lifetime of reaction intermediates is decisive for enantioface differentiation in complexes of catalyst **1**. If the lifetime is long and/or if the association of the intermediate to the catalyst is weak, the dissociation of the intermediate from the catalyst competes with the enantioselective reaction course within the complex. Owing to the fact that even enantio-enriched substrate *ent*-**4a** did not deliver product **6a** with high enantioselectivity (Scheme 5), it appears likely that this scenario applies to the present reaction, i.e. dissociation of **5a** from complex **1**·**5a** is more rapid than migration. For quinolones, such as compound **2**, the dissociation rate constant was estimated to be in the order of 10^7–10^8 s^{-1}. Considering a similar rate for the dissociation of complex **1**·**5a**, the rate of migration would need to be below this value. Although rates for the specific 1,2-migration **5a** → **6a** are – to the best of our knowledge – not known, the rate constant for a photochemical methyl 1,2-migration has been determined as 10^5 s^{-1}.[17] Along this line of arguments, the relatively slow migration might account for the limited success of the reaction regarding an enantioselective reaction course. While a PET mechanism cannot be completely ruled out for the xanthone-catalyzed reaction, it is unlikely that the intermediate radical cation formed from spiroindole epoxide would readily dissociate from the xanthone radical anion. Indeed, this complex should be more stable and should allow for higher enantioselectivities.

Conclusion

In summary, the rearrangement of spirooxindole epoxides to 3-acyl-3-alkylindolin-2-ones was shown to be a high-yielding reaction if performed in the presence of a suitable triplet sensitizer at long wavelength (λ 366 nm). The required substrates were readily accessible from commercially available starting materials in good yields. The reaction could be performed enantioselectively (up to 33 % ee) in the presence of a chiral xanthone catalyst, which features a lactam hydrogen bonding site for substrate association. Although the results demonstrate that the concept of enantioselective triplet sensitization is viable, the enantioselectivity of the reaction remained disappointing when compared with [2+2] photocycloaddition reactions with lactam substrates. It is assumed that the rearrangement step, which follows the sensitized generation of the intermediate, is relatively slow and occurs for large fractions of the intermediates after dissociation from the chiral catalyst.

Experimental

General Methods

Photochemical experiments were performed in flame-dried glassware under positive pressure of argon in Duran tubes (diameter = 1.2 cm for racemic reactions and diameter = 1.0 cm for catalytic reactions) in an RPR-100 photochemical reactor (Southern New England Ultra Violet Co., Branford, CT, USA) using fluorescent lamps with an emission maximum at λ 366 nm (Black light blue, 8 W, Philips Lighting). The solvent mixture ($HXF/PhCF_3 = 2:1$) was freshly prepared before low-temperature reaction. Prior to irradiation, the reaction mixture was degassed by purging with argon in an ultrasonicating bath for 15 min. For further general information see Ref. [18] and the Supplementary Material. NMR assignments were based on the nomenclature for the respective products as given below for three representative compounds (Fig. 4).

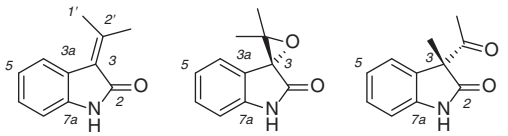


Fig. 4. Numbering used for representative compounds.

Representative Procedures

Knoevenagel-Type Condensation of 2-Oxoindoles with Symmetric Ketones (RP 1)

3-(Propan-2-yliden)indolin-2-one (**7a**): A solution of indolin-2-one (500 mg, 3.76 mmol, 1.0 equiv.) in acetone (15 mL, 0.25 M) was heated in the presence of catalytic amounts of morpholine (164 µL, 164 mg, 1.88 mmol, 0.5 equiv.) for 16 h at reflux temperature. After complete consumption of the indolin-2-one (determined by thin layer chromatography (TLC)) all volatiles were removed under vacuum. Column chromatography (column diameter = 5 cm, 30 g silica, v/v (P/EA) = 6 : 4 → 1 : 1) afforded the title compound (650 mg, 3.75 mmol, 99 %) as a yellow solid. Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (*virt.*). R_F 0.70 (P/EA = 3 : 7; UV). δ_H ($CDCl_3$, 250 MHz, 300 K) 7.96 (1H, br s, NH), 7.52 (1H, br d, ^3J 7.7, H-4), 7.19 (1H, *virt.* td, $^3J \approx {}^3J$ 7.7, ^4J 1.2, H-6), 7.01 (1H, *virt.* td, $^3J \approx {}^3J$ 7.7, ^4J 1.2, H-5), 6.85 (1H, ddd, ^3J 7.7, ^4J 1.2, ^5J 0.6, H-7), 2.62 (3H, s, H-3′), 2.39 (3H, s, H-1′). δ_C ($CDCl_3$, 63 MHz, 300 K) 169.5 (s, C-2), 155.7 (s, C-2′), 139.3 (s, C-7a), 127.7 (d, C-6), 124.6 (s, C-3), 123.9 (d, C-5), 123.0 (s, C-3a), 121.8 (d, C-4), 109.3 (d, C-7), 25.4 (q, C-1′), 23.3 (q, C-3′). The NMR data match the values reported in the literature.[9]

Weitz–Scheffer Epoxidation of Olefins (RP 2)

3′,3′-Dimethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4a**): Freshly powdered NaOH (329 mg, 8.23 mmol, 2.5 equiv.) was dissolved in methanol (50 mL, 65 mM based on olefin). Subsequently, olefin **7a** (570 mg, 3.29 mmol, 1.0 equiv.) and aqueous H_2O_2 solution (35 %, 4.33 mL, 4.80 g, 49.4 mmol, 15 equiv.) were added, and the mixture was stirred for 16 h, after which TLC indicated full conversion of the starting material. The excess of H_2O_2 was quenched with catalytic amounts of MnO_2 and after the gas evolution had ceased most of the methanol was evaporated under vacuum. The liquid residue was dissolved in water (65 mL), and saturated aqueous NH_4Cl solution (65 mL) was added. The combined aqueous layers were extracted with CH_2Cl_2 (3 × 65 mL) and the combined organic layers were dried over Na_2SO_4. After filtration, the organic solvents were evaporated under vacuum. Column chromatography (column diameter = 5 cm, 30 g silica, P/EA = 6 : 4 → 1 : 1) afforded the title compound (545 mg, 2.88 mmol, 88 %) as a colourless solid. R_F 0.87 (v/v (P/EA) = 3 : 7; UV). $[\alpha]_D^{RT}$ +70.9 (*c* 1.0 in CH_2Cl_2, 100 % ee, **4a**) (RT = room temperature); $[\alpha]_D^{RT}$ −71.8 (*c* 1.0 in CH_2Cl_2, 100 % ee, *ent*-**4a**). λ_{max}/nm (CH_3CN, 1.0 mM) (ε/M^{-1} cm^{-1}) 301 (1380). 251 (5200). δ_H ($CDCl_3$, 250 MHz, 300 K) 8.00 (1H, br s, NH), 7.30 (1H, *virt.* td, $^3J \approx {}^3J$ 7.7, ^4J 1.3, H-6), 7.20 (1H, br d, ^3J 7.6, H-4), 7.05 (1H, *virt.* td, $^3J \approx {}^3J$ 7.6, ^4J 1.0, H-5), 6.93 (1H, *virt.* dt, ^3J 7.7, $^4J \approx {}^4J$ 0.7, H-7), 1.76 (3H, s, CH_3), 1.63 (3H, s, CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 175.0 (s, C-2), 142.1 (s, C-7a), 129.8 (d, C-6), 125.1 (d, C-4), 123.9 (s, C-3a), 122.4 (d, C-5), 110.5 (d, C-7), 74.1 (s, C–O), 67.1 (s, C-3), 21.1 (q, CH_3), 18.7 (q, CH_3). The spectroscopic data match the values reported in the literature.[9] **Chiral HPLC:** (AS-H, ^{n}hexane/^{i}PrOH = 70 : 30, 1 mL min^{-1}, λ 210 nm and 254 nm); t_R 15.3 min (**4a**), t_R 38.4 min (*ent*-**4a**). **Chiral GLC:** t_R 36.0 min (**4a**), t_R 36.1 min (*ent*-**4a**) [60°C (1 min), 5°C min^{-1} → 160°C (10 min), 15°C min^{-1} → 220°C (20 min)].

Benzophenone-Sensitized Rearrangements (RP 3)

3-Acetyl-3-methylindolin-2-one (*rac*-**6a**)**:** A solution of spirooxindole epoxide **4a** (18.9 mg, 100 µmol, 1.0 equiv.) and benzophenone (18.2 mg, 100 µmol, 1.0 equiv.) in dry acetonitrile (10 mL, 10 mM) was irradiated at room temperature at λ 366 nm for 1 h. Evaporation of the solvent and column chromatography (column diameter = 2.5 cm, 10 g silica, P/EA = 8 : 2 → 6 : 4) afforded the title compound (18.8 mg, 99.4 µmol, 99 %) as a colourless solid. For analytical data, see next section.

Enantioselective Catalytic Rearrangements (RP 4)

(*R*)-3-Acetyl-3-methylindolin-2-one (**6a**)**:** A solution of spirooxindole epoxide **4a** (18.9 mg, 100 µmol, 1.0 equiv.) containing xanthone catalyst **1** (1.04 mg, 2.50 µmol, 2.5 mol-%) in HFX/$PhCF_3$ (2 : 1, 10 mL, 10 mM) was irradiated at −65°C at λ 366 nm for 90 min. The reaction mixture was directly subjected to column chromatography (column diameter = 2.5 cm, 10 g silica, P/EA = 8 : 2 → 6 : 4) without evaporation of the solvent. The title compound (18.0 mg, 94.9 µmol, 95 %, 33 % ee) was obtained as a colourless solid. R_F 0.65 (P/EE = 1 : 1; UV). $[\alpha]_D^{RT}$ +68.9 (*c* 1.0 in CH_2Cl_2, 33 % *ee*). δ_H ($CDCl_3$, 250 MHz, 300 K) 9.20 (1H, s, NH), 7.31 (1H, *virt.* td, $^3J \approx {}^3J$ 7.6, ^4J 1.6, H-6), 7.17–6.99 (3H, m, H-4/H-5/H-7), 2.05 (3H, s, $COCH_3$), 1.61 (3H, s, CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 200.9 (s, CO), 178.7 (s, C-2), 141.1 (s, C-7a), 130.1 (s, C-3a), 129.3 (d, C-6), 123.9 (d, C-4), 123.4 (d, C-5), 110.6 (d, C-7), 62.8 (s, C-3), 26.1 (q, $COCH_3$), 19.0 (q, CH_3). **Chiral HPLC**: (AS-H, ^{n}hexane/^{i}PrOH = 70 : 30, 1 mL min^{-1}, λ 210 nm and 254 nm); t_R 10.1 min (**6a**), t_R 13.8 min (*ent*-**6a**). **Chiral GLC:** t_R 34.7 min (**6a**), t_R 34.9 min (*ent*-**6a**) [60°C (1 min), 5°C min^{-1} → 160°C (10 min), 15°C min^{-1} → 220°C (20 min)]. The sign of the optical rotation and the spectroscopic data match the values reported in the literature.[15]

3-(Pentan-3-ylidene)indolin-2-one (**7b**): Prepared from 2-oxindole according to RP 1 on a 2.96 mmol scale. The *title compound* (650 mg, 1.75 mmol, 59 %) was obtained as a yellow solid. R_F 0.73 (P/EA = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3167br (NH), 3139w, 2970m, 2935w, 1663s (C=O), 1613s, 1446s, 1337vs, 1221s, 851br. δ_H ($CDCl_3$, 300 MHz, 300 K) 7.78 (1H, br s, NH), 7.48 (1H, br d, ^3J 7.7, H-4), 7.18 (1H, *virt.* td, $^3J \approx {}^3J$ 7.7, ^4J 1.2, H-6), 7.01 (1H, *virt.* td, $^3J \approx {}^3J$ 7.7, ^4J 1.2, H-5), 6.84 (1H, ddd, ^3J 7.8, ^4J 1.2, ^5J 0.6, H-7), 3.04 (2H, q, ^3J 7.6, H-4′), 2.69 (2H, q, ^3J 7.6, H-2′), 1.26 (3H, t, ^3J 7.6, H-5′), 1.19 (3H, t, ^3J 7.6, H-1′). δ_C ($CDCl_3$, 75 MHz, 300 K) 169.8 (s, C-2), 167.4 (s, C-3′), 139.8 (s, C-7a), 127.7 (d, C-6), 123.7 (s, C-3), 123.6 (d, C-4), 121.9 (s, C-3a), 121.8 (d, C-5), 109.6 (d, C-7), 28.9 (t, C-2′), 27.0 (t, C-4′), 12.8 (q, C-1′), 11.6 (q, C-5′). *m*/*z* (HRMS ESI) 202.1225; $[M + H]^+$ ($C_{13}H_{15}NO$) requires 202.1225. HRMS = high-resolution mass spectrometry; ESI = electrospray ionization.

6-Chloro-3-(propan-2-ylidene)indolin-2-one (**7e**): Prepared from 6-chloro-2-oxindole according to RP 1 on a 1.79 mmol scale. The *title compound* (352 mg, 1.70 mmol, 95 %) was obtained as a red solid. R_F 0.68 (P/EA = 1 : 1; UV).

ν_{max} (ATR)/cm^{-1} 3256br (NH), 3094w, 2920w, 2850w, 1704vs (C=O), 1616s, 1485w, 1330m, 1256m, 1221m, 751s, 696vs. δ_H ($CDCl_3$, 400 MHz, 300 K) 8.74 (1H, br s, NH), 7.40 (1H, d, ^3J 8.3, H-4), 6.97 (1H, dd, ^3J 8.3, ^4J 2.0, H-5), 6.88 (1H, d, ^4J 2.0, H-7), 2.61 (3H, s, H-3′), 2.35 (3H, s, H-1′). δ_C ($CDCl_3$, 101 MHz, 300 K) 169.8 (s, C-2), 156.7 (s, C-2′), 140.5 (s, C-7a), 133.3 (s, C-6), 124.5 (d, C-4), 123.0 (s, C-3a), 122.4 (s, C-3), 121.6 (d, C-5) 110.0 (d, C-7), 25.5 (q, C-1′), 23.4 (q, C-3′). *m/z* (HRMS ESI) 208.0523; $[M + H]^+$ ($C_{11}H_{11}{}^{35}ClNO$) requires 208.0524. *m/z* (HRMS ESI) 210.0494; $[M + H]^+$ ($C_{11}H_{11}{}^{37}ClNO$) requires 210.0494.

6-Chloro-3-(pentan-3-ylidene)indolin-2-one (**7f**): Prepared from 6-chloro-2-oxindole according to RP 1 on a 2.39 mmol scale. The *title compound* (301 mg, 1.28 mmol, 45 %) was obtained as a red solid. R_F 0.66 (P/EA = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3217br (NH), 3104w, 2890w, 2850w, 1709vs (C=O), 1626m, 1450 w, 1330m, 1256m, 1221m. δ_H ($CDCl_3$, 250 MHz, 300 K) 7.87 (1H, s, NH), 7.38 (1H, d, ^3J 8.3, H-4), 6.98 (1H, dd, ^3J 8.3, ^4J 2.0, H-5), 6.85 (1H, d, ^4J 2.0, H-7), 3.03 (2H, q, ^3J 7.5, H-2′), 2.66 (2H, q, ^3J 7.6, H-4′), 1.25 (3H, t, ^3J 7.5, H-1′), 1.18 (3H, t, ^3J 7.5, H-5′). δ_C ($CDCl_3$, 63 MHz, 300 K) 169.1 (s, C-2), 168.2 (s, C-3′), 140.6 (s, C-7a), 133.3 (s, C-6), 124.5 (d, C-4), 122.3 (s, C-3), 121.8 (d, C-5), 121.0 (s, C-3a), 109.8 (d, C-7), 28.9 (t, C-2′), 27.1 (t, C-4′), 12.7 (q, C-1′), 11.6 (q, C-5′). *m/z* (HRMS ESI) 236.0838; $[M + H]^+$ ($C_{13}H_{14}{}^{35}ClNO$) requires 236.0837. *m/z* (HRMS ESI) 238.0807; $[M + H]^+$ ($C_{13}H_{14}{}^{37}ClNO$) requires 238.0807.

5-Methoxy-3-(propan-2-ylidene)indolin-2-one (**7g**): Prepared from 5-methoxy-2-oxindole according to RP 1 on a 938 µmol scale. The *title compound* (176 mg, 866 µmol, 92 %) was obtained as a yellow solid. R_F 0.45 (P/EA = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3150w, 3030w, 2938w, 2836w, 1694vs (C=O), 1619s, 1594w, 1479s, 1305m, 1203w. δ_H ($CDCl_3$, 250 MHz, 300 K) 8.07 (1H, s, NH), 7.14 (1H, d, ^4J 1.6, H-4), 6.78–6.72 (2H, m, H-6/H-7), 3.81 (3H, s, OCH_3), 2.62 (3H, s, H-3′), 2.36 (3H, s, H-1′). δ_C ($CDCl_3$, 63 MHz, 300 K) 169.8 (s, C-2), 156.0 (s, C-3′), 155.2 (s, C-5), 133.4 (s, C-7a), 125.6 (s, C-3a), 123.4 (s, C-3), 111.9 (d, C-4), 111.8 (d, C-6), 109.3 (d, C-7), 56.1 (q, OCH_3), 25.3 (q, C-1′), 23.3 (q, C-3′). *m/z* (HRMS ESI) 204.1019; $[M + H)]^+$ ($C_{12}H_{13}NO_2$) requires 204.1019.

5-Methyl-3-(propan-2-ylidene)indolin-2-one (**7h**): Prepared from 5-methyl-2-oxindole according to RP 1 on a 924 µmol scale. The *title compound* (110 mg, 587 µmol, 63 %) was obtained as an orange solid. R_F 0.67 (P/EA = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3167br (NH), 3148w, 3025m, 2913w, 2858w, 1698vs (C=O), 1614s, 1480vs, 1316m, 1249m, 1211m. δ_H ($CDCl_3$, 250 MHz, 300 K) 8.12 (1H, br s, NH), 7.34 (1H, br s, H-4), 7.01 (1H, br d, ^3J 7.8, H-6), 6.77 (1H, d, ^3J 7.8, H-7), 2.61 (3H, s, CH_3), 2.39 (3H, s, H-3′), 2.36 (s, 3H, H-1′). δ_C ($CDCl_3$, 63 MHz, 300 K) 169.5 (s, C-2), 156.2 (s, C-3′), 136.7 (s, C-7a), 131.0 (s, C-5), 128.0 (d, C-6), 124.5 (s, C-4), 124.4 (d, C-3), 122.9 (s, C-3a), 109.1 (d, C-7), 25.4 (q, CH_3), 23.3 (q, C-1′), 21.4 (q, C-3′). *m/z* (HRMS ESI) 188.1070; $[M + H]^+$ ($C_{12}H_{13}NO$) requires 188.1017.

5-Trifluoromethyl-3-(propan-2-ylidene)indolin-2-one (**7i**): Prepared from 5-trifluoromethyl-2-oxindole according to RP 1 on a 1.00 mmol scale. The *title compound* (230 mg, 953 µmol, 95 %) was obtained as a yellow solid. R_F 0.75 (P/EA = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3164w, 3122w, 3037w, 2924w, 2882w, 1704vs (C=O), 1616s, 1480vs, 1334s, 1305s, 1105s (C–F). δ_H ($CDCl_3$, 250 MHz, 296 K) 8.64 (1H, br s, NH), 7.72 (1H, br s, H-4), 7.47 (1H, br d, ^3J 8.2, H-6), 6.95 (1H, d, ^3J 8.2, H-7), 2.65 (3H, s, H-3′), 2.43 (3H, s, H-1′). δ_C ($CDCl_3$, 75 MHz, 295 K) 169.5 (s, C-2), 158.7 (s, C-2′), 142.0 (s, C-7a), 125.1 (dq, $^3J_{CF}$ 3.9, C-6), 124.6 (s, C-3), 124.2 (q, $^2J_{CF}$ 32.1, C-5), 122.7 (q, ^1J 291, CF_3), 122.1 (s, C-3a), 120.6 (dq, $^3J_{CF}$ 4.1, C-4), 109.2 (d, C-7), 25.6 (q, C-1′), 23.6 (q, C-3′). *m/z* (HRMS ESI) 242.0786; $[M + H]^+$ requires 242.0787.

5-Chloro-3-(propan-2-ylidene)indolin-2-one (**7j**): Prepared from 5-chloro-2-oxindole according to RP 1 on a 1.82 mmol scale. The *title compound* (350 mg, 1.69 mmol, 93 %) was obtained as a yellow solid. R_F 0.50 (P/EA = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3250br (NH), 3082w, 2915w, 2844w, 1702vs (C=O), 1606s, 1481w, 1322m, 1211m, 745m. δ_H ($CDCl_3$, 400 MHz, 300 K) 8.56 (1H, br s, NH), 7.47 (1H, d, ^4J 2.0, H-4), 7.16 (1H, dd, ^3J 8.3, ^4J 2.0, H-6), 6.80 (1H, d, ^3J 8.3, H-7), 2.62 (3H, s, H-3′), 2.37 (3H, s, H-1′). δ_C ($CDCl_3$, 101 MHz, 300 K) 169.6 (s, C-2), 157.9 (s, C-2′), 138.0 (s, C-7a), 127.1 (d, C-6), 126.4 (s, C-5), 125.9 (s, C-3), 124.0 (d, C-4), 122.7 (s, C-3a), 110.3 (s, C-7), 25.6 (q, C-1′), 23.6 (q, C-3′). *m/z* (HRMS ESI) 208.0523; $[M + H]^+$ ($C_{11}H_{11}{}^{35}ClNO$) requires 208.0524. *m/z* (HRMS ESI) 210.0494; $[M + H]^+$ ($C_{11}H_{11}{}^{37}ClNO$) requires 210.0494.

6-Bromo-3-(propan-2-ylidene)indolin-2-one (**7k**): Prepared from 6-bromo-2-oxindole according to RP 1 on a 773 µmol scale. The *title compound* (187 mg, 742 µmol, 96 %) was obtained as a yellow solid. R_F 0.73 (P/EE = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3259br (NH), 2920w, 2854w, 1704vs (C=O), 1609m, 1482w, 1447m, 1337m, 1214m. δ_H ($CDCl_3$, 400 MHz, 300 K) 8.43 (1H, br s, NH), 7.22 (1H, d, ^3J 8.3, H-4), 7.13 (1H, dd, ^3J 8.3, ^4J 1.9, H-5), 7.03 (1H, d, ^4J 1.9, H-7), 2.60 (3H, s, H-3′), 2.35 (3H, s, H-1′). δ_C ($CDCl_3$, 101 MHz, 300 K) 169.12 (s, C-2), 156.9 (s, C-2′), 140.4 (s, C-7a), 124.9 (d, C-4), 124.6 (d, C-5), 123.5 (s, C-3a), 122.3 (s, C-3), 121.2 (d, C-4), 112.6 (d, C-7), 25.5 (q, C-1′), 23.4 (q, C-3′). *m/z* (HRMS ESI) 252.0017; $[M + H]^+$ ($C_{11}H_{10}{}^{79}BrNO$) requires 252.0019. *m/z* (HRMS ESI) 253.9997; $[M + H]^+$ ($C_{11}H_{10}{}^{81}BrNO$) requires 253.9998.

Spirooxindole Epoxides

3′,3′-Diethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4b**): Prepared from **7b** according to RP 2 on a 1.68 mmol scale. The *title compound* (323 mg, 1.49 mmol, 88 %) was obtained as a colourless solid. R_F 0.50 (P/EE = 8 : 2; UV). ν_{max} (ATR)/cm^{-1} 3280br (NH) 2932w, 2859w, 1741vs (C=O), 1621m, 1467s, 1203s, 1114m, 749s, 696vs. λ_{max}/nm (CH_3CN, 1.0 mM) (ε/M^{-1} cm^{-1}) 301 (1380), 251 (5200). δ_H ($CDCl_3$, 250 MHz, 300 K) 8.34 (1H, br s, NH), 7.30 (1H, *virt*. td, $^3J \approx {}^3J$ 7.7, ^4J 1.3, H-6), 7.20 (1H, br d, ^3J 7.5, H-4), 7.04 (1H, *virt*. td, $^3J \approx {}^3J$ 7.6, ^4J 1.0, H-5), 6.93 (1H, br d, ^3J 7.7, H-7), 2.29 (1H, dq, ^2J 14.8, ^3J 7.5, C*H*H), 2.10 (1H, dq, ^2J 14.8, ^3J 7.5, C*H*H), 2.03 (1H, dq, ^2J 15.1, ^3J 7.6, CH*H*), 1.82 (1H, dq, ^2J 15.1, ^3J 7.6, CH*H*), 1.03 (3H, t, ^3J 7.5, CH_3), 1.01 (3H, t, ^3J 7.6, CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 175.5 (s, C-2), 142.1 (s, C-7a), 129.6 (d, C-6), 124.9 (d, C-5), 124.1 (s, C-3a), 122.3 (d, C-4), 110.6 (d, C-7), 74.6 (s, C–O), 65.5 (s, C-3), 22.9 (t, CH_2), 22.8 (t, CH_2), 9.92 (q, CH_3), 9.46 (q, CH_3). *m/z* (HRMS ESI) 218.1175; $[M + H]^+$ ($C_{13}H_{15}NO_2$) requires 218.1176.

6-Chloro-3′,3′-dimethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4e**): Prepared from **7e** according to RP 2 on a 1.66 mmol scale. The *title compound* (180 mg, 805 µmol, 48 %) was obtained as a colourless solid. R_F 0.80 (P/EE = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3128br (NH), 2966w, 2935w, 1712vs (C=O), 1618s, 1455m, 1334w, 1217w, 924w, 660w. λ_{max}/nm (CH_3CN, 1.0 mM) (ε/M^{-1} cm^{-1}) 301 (1810), 254 (5500). δ_H ($CDCl_3$, 360 MHz, 297 K) 8.14 (1H, br s, NH), 7.12 (1H, *virt.* dt, ^3J 8.1,

$^5J \approx {}^6J$ 0.6, H-4), 7.05 (1H, dd, ^3J 8.1, ^4J 1.8, H-5), 6.97 (1H, dd, ^4J 1.8, ^5J 0.5, H-7), 1.77 (3H, d, ^6J 0.5, CH_3), 1.62 (3H, d, ^6J 0.5, CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 174.68 (s, C-2), 143.1 (s, C-7a), 135.7 (s, C-6), 126.0 (d, C-5), 122.4 (d, C-4), 122.4 (s, C-3a), 111.2 (d, C-7), 67.4 (s, C–O), 64.7 (s, C-3), 21.1 (q, CH_3), 18.7 (q, CH_3). *m/z* (HRMS ESI) 224.0473; $[M + H]^+$ ($C_{11}H_{10}{}^{35}ClNO_2$) requires 224.0473. *m/z* (HRMS ESI) 226.0444; $[M + H]^+$ ($C_{11}H_{10}{}^{37}ClNO_2$) requires 226.0443.

6-Chloro-3′,3′-diethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4f**): Prepared from **7f** according to RP 2 on a 1.25 mmol scale. The *title compound* (207 mg, 822 µmol, 65 %) was obtained as a colourless solid. R_F 0.81 (P/EE = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3128br (NH), 2968w, 2930w, 1708vs (C=O), 1619s, 1460m, 1334w, 1220w, 919w, 661w. λ_{max}/nm (CH_3CN, 1.0 mM) ($\varepsilon/M^{-1}\,cm^{-1}$) 301 (1800), 254 (5520). δ_H ($CDCl_3$, 250 MHz, 300 K) 8.03 (1H, br s, NH), 7.11 (1H, d, ^3J 8.1, H-4), 7.02 (1H, dd, ^3J 8.1, ^4J 1.8, H-5), 6.94 (1H, d, ^4J 1.8, H-7), 2.27 (1H, dq, ^2J 15.0, ^3J 7.4, C*H*H), 2.07 (1H, dq, ^2J 14.4, ^3J 7.5, C*H*H), 1.98 (1H, dq, ^2J 15.0, ^3J 7.4, CH*H*), 1.78 (1H, dq, ^2J 14.4, ^3J 7.5, CH*H*), 1.02 (3H, t, ^3J 7.4, CH_3), 1.00 (3H, t, ^3J 7.5, CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 174.9 (s, C-2), 143.0 (s, C-7a), 135.5 (s, C-6), 125.8 (d, C-5), 122.5 (s, C-3a), 122.4 (d, C-4), 111.1 (d, C-7), 74.9 (s, C–O), 65.2 (s, C-3), 23.1 (t, CH_2), 20.8 (t, CH_2), 9.87 (q, CH_3). 9.47 (q, CH_3). *m/z* (HRMS ESI) 252.0785; $[M + H]^+$ ($C_{13}H_{14}{}^{35}ClNO_2$) requires 252.0786. *m/z* (HRMS ESI) 254.0756; $[M + H]^+$ ($C_{13}H_{14}{}^{37}ClNO_2$) requires 254.0765.

5-Methoxy-3′,3′-dimethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4g**): Prepared from **7g** according to RP 2 on a 836 µmol scale. The *title compound* (142 mg, 650 µmol, 78 %) was obtained as a colourless solid. R_F 0.64 (P/EE = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3276br (NH), 3019w, 2966w, 2931w, 1725s, 1685vs (C=O), 1483m, 1437w, 1208w, 1027w, 825w, 755w. λ_{max}/nm (CH_3CN, 1.0 mM) ($\varepsilon/M^{-1}\,cm^{-1}$) 323 (1780), 261 (6814). δ_H ($CDCl_3$, 400 MHz, 300 K) 8.48 (1H, br s, NH), 6.87–6.81 (2H, m, H6/H-7), 6.79 (1H, br d, ^4J 2.0, H-4), 3.78 (3H, s, OCH_3), 1.77 (3H, s, CH_3), 1.62 (3H, s, CH_3). δ_C ($CDCl_3$, 101 MHz, 300 K) 175.4 (s, C-2), 155.6 (s, C-5), 135.5 (s, C-7a), 125.2 (s, C-3a), 114.3 (d, C-4), 112.5 (d, C-6), 111.0 (d, C-7), 67.1 (s, C–O), 65.5 (s, C-3), 56.0 (q, OCH_3), 21.0 (q, CH_3), 18.8 (q, CH_3). *m/z* (HRMS ESI) 220.0968; $[M + H]^+$ ($C_{12}H_{13}NO_3$) requires 220.0968.

5-Methyl-3′,3′-dimethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4h**): Prepared from **7h** according to RP 2 on a 561 µmol scale. The *title compound* (68.8 mg, 343 µmol, 61 %) was obtained as a colourless solid. R_F 0.71 (P/EE = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3308br (NH), 2966w, 2919w, 2850w, 1731s, 1704vs (C=O), 1622m, 1487m, 1375w, 1156m, 755w, 710w. λ_{max}/nm (CH_3CN, 1.0 mM) ($\varepsilon/M^{-1}\,cm^{-1}$) 309 (1490), 253 (6190). δ_H ($CDCl_3$, 250 MHz, 300 K) 8.12 (1H, br s, NH), 7.10 (1H, dd, ^3J 7.9, ^4J 0.8, H-6), 7.00 (1H, br s, H-4), 6.82 (1H, d, ^3J 7.9, H-7), 2.33 (3H, s, C5–CH_3), 1.76 (3H, s, CH_3), 1.62 (3H, s, CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 175.2 (s, C-2), 139.7 (s, C-7a), 131.9 (s, C-5), 130.5 (d, C-4), 125.9 (d, C-6), 124.0 (d, C-3a), 110.3 (d, C-7), 67.0 (s, C–O), 65.2 (s, C-3), 21.3 (q, C5–*C*H_3), 21.1 (q, CH_3), 18.8 (q, CH_3). *m/z* (HRMS ESI) 204.1019; $[M + H]^+$ ($C_{12}H_{13}NO_2$) requires 204.1019.

5-Trifluoromethyl-3′,3′-dimethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4i**): Prepared from **7i** according to RP 2 on a 829 µmol scale. The *title compound* (213 mg, 829 µmol, >99 %) was obtained as a colourless solid. R_F 0.75 (P/EE = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3051br (NH), 2896w, 2864w, 1719vs (C=O), 1626s, 1332m, 1298m, 1105vs, 1056m, 749w. λ_{max}/nm (CH_3CN, 1.0 mM) ($\varepsilon/M^{-1}\,cm^{-1}$) 297 (1540), 254 (7500). δ_H ($CDCl_3$, 400 MHz, 298 K) 8.76 (1H, br s, NH), 7.60 (1H, dd, ^3J 8.2, ^4J 0.8, H-6), 7.42 (1H, d, ^4J 0.8, H-4), 7.06 (1H, d, ^3J 8.2, H-7), 1.78 (3H, s, CH_3), 1.65 (3H, s, CH_3). δ_C ($CDCl_3$,101 MHz, 300 K) 175.2 (s, C-2), 145.1 (s, C-7a), 127.4 (dq, $^3J_{CF}$ 3.7, C-4), 125.0 (s, C-3a), 124.9 (q, $^2J_{CF}$ 35.9, C-5), 124.1 (q, $^1J_{CF}$ 282, CF_3), 122.1 (dq, $^3J_{CF}$ 3.5, C-6), 110.6 (d, C-7), 67.8 (s, C-O), 64.8 (s, C-3), 21.4 (q, CH_3), 18.7 (q, CH_3). *m/z* (HRMS ESI) 258.0736; $[M + H]^+$ ($C_{12}H_{10}F_3NO_2$) requires 258.0736.

5-Chloro-3′,3′-dimethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4j**): Prepared from **7j** according to RP 2 on a 1.69 mol scale. The *title compound* (119 mg, 532 µmol, 31 %) was obtained as a colourless solid. R_F 0.55 (P/EE = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3127br (NH), 2966w, 2934w, 1712vs (C=O), 1688s, 1618m, 1189w, 1126w, 1070w, 903w, 772w. λ_{max}/nm (CH_3CN, 1.0 mM) ($\varepsilon/M^{-1}\,cm^{-1}$) 312 (1510), 255 (7790). δ_H ($CDCl_3$, 400 MHz, 298 K) 8.23 (1H, br s, NH), 7.28 (1H, dd, ^3J 8.4, ^4J 2.1, H-6), 7.16 (1H, d, ^4J 2.1, H-4), 6.87 (1H, d, ^3J 8.4, H-7), 1.76 (3H, s, CH_3), 1.62 (3H, s, CH_3). δ_C ($CDCl_3$, 101 MHz, 300 K) 174.7 (s, C-2), 140.6 (s, C-7a), 129.7 (d, C-6), 127.9 (s, C-5), 125.7 (s, 3a), 125.4 (d, C-4), 111.5 (d, C-7), 67.6 (s, C–O), 64.9 (s, C-3), 21.2 (q, CH_3), 18.7 (q, CH_3). *m/z* (HRMS ESI) 224.0472; $[M + H]^+$ ($C_{11}H_{10}{}^{35}ClNO_2$) requires 224.0473. *m/z* (HRMS ESI) 226.0443; $[M + H]^+$ ($C_{11}H_{10}{}^{37}ClNO_2$) requires 226.0443.

6-Bromo-3′,3′-dimethylspiro[indolin-3,2′-oxiran]-2-one (*rac*-**4k**): Prepared from **7k** according to RP 2 on a 595 µmol scale. The *title compound* (160 mg, 595 µmol, >99 %) was obtained as a colourless solid. R_F 0.75 (P/EE = 1 : 1; UV). $[\alpha]_D^{RT}$ +81.0 (*c* 1.0 in CH_2Cl_2, 100 % ee, **4k**); $[\alpha]_D^{RT}$ −79.9 (*c* 1.0 in CH_2Cl_2, 100 % ee, *ent*-**4k**). ν_{max} (ATR)/cm^{-1} 3253br (NH), 2935w, 1728vs (C=O), 1713vs, 1607s, 1479m, 1448w, 1356w, 1191w, 911w, 688s. λ_{max}/nm (CH_3CN, 1.0 mM) ($\varepsilon/M^{-1}\,cm^{-1}$) 301 (1830), 252 plateau (5540). δ_H ($CDCl_3$, 400 MHz, 298 K) 8.20 (1H, br s, NH), 7.19 (1H, dd, ^3J 8.1, ^4J 1.7, H-5), 7.11 (1H, d, ^4J 1.7, H-7), 7.04 (1H, d, ^3J 8.1, H-4), 1.75 (3H, s, CH_3), 1.60 (3H, s, CH_3). δ_C ($CDCl_3$, 101 MHz, 300 K) 174.8 (s, C-2), 143.2 (s, C-7a), 126.3 (d, C-5), 125.3 (d, C-4), 123.3 (s, C-3a), 122.9 (s, C-6), 114.0 (d, C-7), 67.4 (s, C–O), 64.8 (s, C-3), 21.1 (q, CH_3), 18.7 (q, CH_3). **Chiral HPLC:** (AS-H, ^{n}hexane/^{i}PrOH = 70 : 30, 1 mL min^{-1}, λ 210 nm and 254 nm); t_R 12.1 min (**4k**), t_R 24.2 min (*ent*-**4k**). *m/z* (HRMS ESI) 267.9968; $[M + H]^+$ ($C_{11}H_{10}{}^{79}BrNO_2$) requires 267.9967. *m/z* (HRMS ESI) 269.9947; $[M + H]^+$ ($C_{11}H_{10}{}^{81}BrNO_2$) requires 269.9947.

3-Acylindolin-2-ones

(*R*)-3-Ethyl-3-propionylindolin-2-one (**6b**): Prepared from *rac*-**4b** according to RP 4 on a 100 µmol scale. The *title compound* (19.8 mg, 91.1 µmol, 91 %, 33 % ee) was obtained as a colourless solid. R_F 0.58 (P/EA = 1 : 1; UV). $[\alpha]_D^{RT}$ +16.3 (*c* 1.0 in CH_2Cl_2, 33 % ee). ν_{max} (ATR)/cm^{-1} 3228br (NH), 2983w, 2929w, 1700vs (C=O), 1690vs (C=O), 1610m, 1312m, 1212m, 1197m. δ_H ($CDCl_3$, 250 MHz, 300 K) 9.11 (1H, br s, NH), 7.28 (1H, *virt*. td, $^3J \approx {}^3J$ 7.6, ^4J 1.6, H-6), 7.14 (1H, dd, ^3J 7.5, ^4J 1.5, H-4) 7.06 (1H, *virt*. td, $^3J \approx {}^3J$ 7.4, ^4J 1.0, H-5) 6.98 (1H, d, ^3J 7.7, H-7), 2.55 (1H, dq, ^2J 18.4, ^3J 7.2, COC*H*H), 2.34–2.17 (3H, m, COCH*H*/C3–CH_2), 0.95 (3H, t, ^3J 7.2, $COCH_2CH_3$), 0.67 (3H, t, ^3J 7.4, C3–CH_2CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 204.2 (s, CO), 178.0 (s, C-2), 141.8 (s, C-7a), 129.1 (d, C-6), 128.4 (s, C-3a), 124.2 (d, C-5), 123.2 (d, C-4), 110.3 (d, C-7), 67.7 (s, C-3), 32.6 (t, $COCH_2$), 26.8 (t, C3–CH_2), 8.21 (q, $COCH_2CH_3$), 7.75 (q, C3–CH_2CH_3). *m/z* (HRMS ESI) 218.1174; $[M + H]^+$ ($C_{13}H_{15}NO_2$) requires 218.1176. **Chiral**

GLC: t_R 83.1 min (**6b**), t_R 83.9 min (*ent*-**6b**) [60°C (1 min), 1.5°C min^{-1} → 220°C (10 min)].

(*R*)-Spiro[cycloheptane-1,3′-indolin]-2,2′-dione (**6d**): Prepared from *rac*-**4d** according to RP 4 on a 100 µmol scale. The *title compound* (20.4 mg, 93.8 µmol, 85 %, 16 % ee) was obtained as a colourless solid. R_F 0.55 (P/EA = 1 : 1; UV). $[\alpha]_D^{RT}$ +1.4 (*c* 1.0 in CH_2Cl_2, 16 % ee). δ_H ($CDCl_3$, 250 MHz, 300 K) 8.40 (1H, br s, NH), 7.28–7.18 (2H, m, H-4/H-6), 7.04 (1H, *virt*. td, $^3J \approx {}^3J$ 7.4, ^4J 1.4, H-5) 6.90 (1H, dd, ^3J 7.7, ^4J 1.4, H-7), 3.01 (1H, ddd, ^2J 11.2, ^3J 8.3, ^3J 2.4, COC*H*H), 2.76 (1H, ddd, ^2J 11.2, ^3J 7.7, ^3J 3.3, COCH*H*), 2.42–2.30 (1H, m, C3–C*H*H), 2.21–1.98 (2H, m, C3–CH*H*/CH_2), 1.94–1.69 (5H, m, CH_2). δ_C ($CDCl_3$, 63 MHz, 300 K) 207.4 (s, CO), 177.6 (s, C-2), 140.7 (s, C-7a), 131.3 (s, C-3a), 128.8 (d, C-6), 123.9 (d, C-5), 122.7 (d, C-4), 110.3 (d, C-7), 66.0 (s, C-3), 42.5 (t, CO*C*H_2), 34.8 (t, C3–*C*H_2), 31.0 (t, CH_2), 26.8 (t, CH_2), 25.4 (t, CH_2). **Chiral HPLC:** (OJ-H, ^{n}hexane/^{i}PrOH = 70 : 30, 1 mL min^{-1}, λ 210 nm and 254 nm); t_R 8.7 min (**6d**), t_R 17.4 min (*ent*-**6d**). The NMR data match the values reported in literature.[5b]

(*R*)-3-Acetyl-6-chloro-3-methylindolin-2-one (**6e**): Prepared from *rac*-**4e** according to RP 4 on a 100 µmol scale. The *title compound* (19.9 mg, 89.0 µmol, 89 %, 20 % ee) was obtained as a colourless solid. R_F 0.58 (P/EE = 1 : 1; UV). $[\alpha]_D^{RT}$ +14.6 (*c* 1.0 in CH_2Cl_2, 20 % ee). ν_{max} (ATR)/cm^{-1} 3245br (NH), 2980w, 2929w, 1715vs (C=O), 1704vs (C=O), 1612s, 1483m, 1448m, 1190m, 1074w, 810w, 695w. δ_H ($CDCl_3$, 250 MHz, 300 K) 9.04 (1H, br s, NH), 7.13–6.98 (3H, m, H-4/H-5/H-6), 2.07 (3H, s, $COCH_3$), 1.60 (3H, s, CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 200.1 (s, CO), 178.2 (s, C-2), 141.9 (s, C-7a), 135.0 (s, C-6), 124.8 (d, C-4), 123.3 (d, C-5), 122.4 (s, C-3a), 111.0 (d, C-7), 62.1 (s, C-3), 26.0 (q, CO*C*H_3), 19.1 (q, CH_3). *m*/*z* (HRMS ESI) 224.0471; $[M + H]^+$ ($C_{11}H_{10}{}^{35}ClNO_2$) requires 224.0473. **Chiral GLC:** t_R 95.3 min (**6e**), t_R 95.8 min (*ent*-**6e**) [60°C (1 min), 1.5°C min^{-1} → 220°C (10 min)].

(*R*)-6-Chloro-3-ethyl-3-propionylindolin-2-one (**6f**): Prepared from *rac*-**4f** according to RP 4 on a 100 µmol scale. The *title compound* (23.6 mg, 93.7 µmol, 94 %, 20 % ee) was obtained as a colourless solid. R_F 0.73 (P/EE = 1 : 1; UV). $[\alpha]_D^{RT}$ +29.3 (*c* 1.0 in CH_2Cl_2, 20 % ee). ν_{max} (ATR)/cm^{-1} 3243br (NH), 2985w, 2934w, 1719vs (C=O), 1700vs (C=O), 1605s, 1481m, 1447m, 1195m, 1070w, 811w, 694w. δ_H ($CDCl_3$, 250 MHz, 300 K) 8.85 (1H, br s, NH), 7.13–7.04 (2H, m, H-4/H-5), 7.03–6.96 (1H, m, H-7), 2.58 (1H, dq, ^2J 18.5, ^3J 7.2, COC*H*H), 2.40–2.14 (3H, m, COCH*H*/C3–CH_2), 0.97 (3H, t, ^3J 7.2, $COCH_2CH_3$), 0.68 (3H, t, ^3J 7.2, C3–CH_2CH_3). δ_C ($CDCl_3$, 63 MHz, 300 K) 200.6 (s, CO), 177.7 (s, C-2), 142.6 (s, C-7a), 134.9 (s, C-6), 126.7 (s, C-3a), 125.4 (d, C-4), 125.3 (d, C-5), 110.9 (d, C-7), 67.2 (s, C-3), 32.7 (t, CO*C*H_2), 27.2 (t, C3–*C*H_2), 8.2 (q, $COCH_2CH_3$), 7.7 (q, C3–CH_2CH_3). *m*/*z* (HRMS ESI) 252.0784; $[M + H]^+$ ($C_{13}H_{14}{}^{35}ClNO_2$) requires 252.0786. *m*/*z* (HRMS ESI) 254.0754; $[M + H]^+$ ($C_{13}H_{14}{}^{37}ClNO_2$) requires 254.0756. **Chiral GLC:** t_R 98.6 min (**6f**), t_R 99.2 min (*ent*-**6f**) [60°C (1 min), 1.5°C min^{-1} → 220°C (10 min)].

(*R*)-3-Acetyl-5-methoxy-3-methylindolin-2-one (**6g**): Prepared from *rac*-**4g** according to RP 4 on a 80.0 µmol scale with 5 mol-% of catalyst **1**. The *title compound* (15.5 mg, 70.7 µmol, 88 %, 20 % ee) was obtained as a colourless solid. R_F 0.31 (P/EE = 1 : 1; UV). $[\alpha]_D^{RT}$ +37.2 (*c* 1.0 in $CDCl_3$, 20 % ee). ν_{max} (ATR)/cm^{-1} 3248br (NH), 2988w, 2935w, 1780vs (C=O), 1740vs (C=O), 1601w, 1499s, 1438m, 1299m, 1204s, 1028w, 811w. δ_H ($CDCl_3$, 400 MHz, 300 K) 8.60 (1H, br s, NH), 6.90 (1H, d, ^3J 8.5, H-7), 6.82 (1H, dd, ^3J 8.5, ^4J 2.4, H-6), 6.73 (1H, d, ^4J 2.4, H-4), 3.77 (3H, s, OCH_3), 2.05 (3H, s, $COCH_3$), 1.59 (3H, s, CH_3). δ_C ($CDCl_3$, 100 MHz, 300 K) 200.9 (s, CO), 178.2 (s, C-2), 156.5 (s, C-5), 134.2 (s, C-7a), 131.5 (s, C-3a), 114.3 (d, C-6), 110.9 (d, C-7), 110.6 (d, C-4), 63.1 (s, C-3), 56.0 (q, OCH_3), 26.1 (q, CO*C*H_3), 19.1 (q, CH_3). *m*/*z* (HRMS ESI) 220.0967; $[M + H]^+$ ($C_{12}H_{13}NO_3$) requires 220.0968. **Chiral GLC:** t_R 37.7 min (**6g**), t_R 37.9 min (*ent*-**6g**) [60°C (1 min), 5°C min^{-1} → 160°C (10 min), 15°C min^{-1} → 220°C (20 min)].

(*R*)-3-Acetyl-3,5-dimethylindolin-2-one (**6h**): Prepared from *rac*-**4h** according to RP 4 on a 80.0 µmol scale with 5 mol-% of catalyst **1**. The *title compound* (16.0 mg, 78.8 µmol, 98 %, 24 % ee) was obtained as a colourless solid. R_F 0.54 (P/EE = 1 : 1; UV). $[\alpha]_D^{RT}$ +50.6 (*c* 1.0 in $CDCl_3$, 24 % ee). ν_{max} (ATR)/cm^{-1} 3252br (NH), 2983w, 2930w, 1724vs (C=O), 1702vs (C=O), 1622w, 1491m, 1355w, 1199w, 815w. δ_H ($CDCl_3$, 400 MHz, 300 K) 8.58 (1H, br s, NH), 7.08 (1H, br d, ^3J 7.9, H-6), 6.95 (1H, br s, H-4), 6.87 (1H, br d, ^3J 7.9, H-7), 2.31 (3H, s, C5–CH_3), 2.04 (3H, s, $COCH_3$), 1.59 (3H, s, CH_3). δ_C ($CDCl_3$, 101 MHz, 300 K) 201.0 (s, CO), 178.3 (s, C-2), 138.5 (s, C-7a), 133.1 (s, C-5), 130.3 (s, C-3a), 129.6 (d, C-6), 124.6 (d, C-4), 110.1 (d, C-7), 62.7 (s, C-3), 26.1 (q, C5–*C*H_3), 21.2 (q, CO*C*H_3), 19.0 (q, CH_3). *m*/*z* (HRMS ESI) 204.1018; $[M + H]^+$ ($C_{12}H_{13}NO_2$) requires 204.1019. **Chiral GLC:** t_R 35.4 min (**6h**), t_R 35.7 min (*ent*-**6h**) [60°C (1 min), 5°C min^{-1} → 160°C (10 min), 15°C min^{-1} → 220°C (20 min)].

(*R*)-3-Acetyl-3-methyl-5-(trifluoromethyl)indolin-2-one (**6i**): Prepared from *rac*-**4i** according to RP 4 on a 80.0 µmol scale with 5 mol-% of catalyst **1**. The *title compound* (18.9 mg, 73.4 µmol, 92 %, 30 % ee) was obtained as a colourless solid. R_F 0.39 (P/EE = 1 : 1; UV). $[\alpha]_D^{RT}$ +38.9 (*c* 1.0 in $CDCl_3$, 30 % ee). ν_{max} (ATR)/cm^{-1} 3252br (NH), 2931w, 2867w, 1731vs (C=O), 1125vs (C=O), 1626m, 1496w, 1360vs, 1162m, 1117s, 826w. δ_H ($CDCl_3$, 500 MHz, 300 K) 8.53 (1H, br s, NH), 7.59 (1H, dd, ^3J 8.3, ^4J 1.0, H-6), 7.42 (1H, br s, H-4), 7.08 (1H, d, ^4J 8.3, H-7), 2.11 (3H, s, $COCH_3$), 1.65 (3H, s, CH_3). δ_C ($CDCl_3$, 126 MHz, 300 K) 199.9 (s, CO), 177.7 (s, C-2), 143.7 (s, C-7a), 130.6 (s, C-3a), 127.1 (dq, $^3J_{CF}$ 4.0, C-4). 125.9 (q, $^2J_{CF}$ 32.9, C-5), 124.1 (q, $^1J_{CF}$ 271, CF_3), 121.4 (dq, $^3J_{CF}$ 3.8, C-6), 110.3 (d, C-7), 62.3 (s, C-3), 26.4 (q, CO*C*H_3), 19.5 (q, CH_3). *m*/*z* (HRMS ESI) 258.0735; $[M + H]^+$ ($C_{12}H_{10}F_3NO_2$) requires 258.0736. **Chiral GLC:** t_R 35.2 min (**6i**), 35.4 min (*ent*-**6i**) [60°C (1 min), 5°C min^{-1} → 160°C (10 min), 15°C min^{-1} → 220°C (20 min)].

rac-**3-Acetyl-5-chloro-3-methylindolin-2-one** (*rac*-**6j**)**:** Prepared from *rac*-**4j** according to RP 3 on a 100 µmol scale. The *title compound* (20.4 mg, 91.2 µmol, 91 %) was obtained as a colourless solid. R_F 0.69 (P/EA = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3240br (NH), 2922w, 1719vs (C=O), 171vs (C=O), 1614m, 1481m, 1281w, 1130w, 901w, 675w. δ_H ($CDCl_3$, 400 MHz, 300 K) 9.04 (1H, br s, NH), 7.27 (1H, dd, ^3J 8.3, ^4J 2.1, H-6), 7.14 (1H, d, ^4J 2.1, H-4), 6.94 (1H, d, ^3J 8.3, H-7), 2.09 (3H, s, $COCH_3$), 1.61 (3H, s, CH_3). δ_C ($CDCl_3$, 101 MHz, 300 K) 200.1 (s, CO), 178.1 (s, C-2), 139.5 (s, C-7a), 131.8 (s, C-5), 129.3 (d, C-6), 128.8 (s, C-3a), 124.6 (d, C-4), 111.5 (d, C-7), 62.8 (s, C-3), 26.2 (q, CO*C*H_3), 19.3 (q, CH_3). *m*/*z* (HRMS ESI) 224.0473; $[M + H]^+$ ($C_{11}H_{10}{}^{35}ClNO_2$) requires 224.0473. *m*/*z* (HRMS ESI) 226.0442; $[M + H]^+$ ($C_{11}H_{10}{}^{37}ClNO_2$) requires 226.0443.

rac-**3-Acetyl-6-bromo-3-methylindolin-2-one** (*rac*-**6k**)**:** Prepared from *rac*-**4k** according to RP 3 on a 100 µmol scale. The *title compound* (24.9 mg, 92.8 µmol, 93 %) was obtained as a colourless solid. R_F 0.65 (P/EA = 1 : 1; UV). ν_{max} (ATR)/cm^{-1} 3253br (NH), 2935w, 1728vs (C=O), 1713vs (C=O), 1607m, 1479m, 1448w, 1321w, 1130w, 911w, 688w. δ_H ($CDCl_3$, 500 MHz, 300 K) 8.31 (1H, br s, NH), 7.22 (1H, dd, ^3J 8.0, ^4J 1.7, H-5), 7.15 (1H, d, ^4J 1.7, H-7), 7.02 (1H, d, ^3J 8.0, H-4), 2.07

(3H, s, $COCH_3$), 1.59 (3H, s, CH_3). δ_C ($CDCl_3$, 126 MHz, 300 K) 200.2 (s, CO), 177.6 (s, C-2), 142.0 (s, C-7a), 129.0 (s, C-3a), 126.4 (d, C-5), 125.4 (d, C-4), 122.9 (s, C-6), 113.8 (d, C-7), 62.2 (s, C-3), 26.2 (q, $COCH_3$), 19.2 (q, CH_3). *m/z* (HRMS ESI) 267.9967; $[M + H]^+$ ($C_{11}H_{10}{}^{79}BrNO_2$) requires 267.9968. *m/z* (HRMS ESI) 269.9948; $[M + H]^+$ ($C_{11}H_{10}{}^{81}BrNO_2$) requires 269.9947.

*Single-Crystal X-Ray Absolute Structure Determination of Compound **4k***

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1400715. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44(0) 1223–336–033; email: deposit@ccdc.cam.ac.uk.

Supplementary Material

Experimental procedures for compounds *rac*-**8**, *rac*-**9**, and *rac*-**10**, ^1H and ^{13}C NMR spectra of new compounds, GLC and HPLC traces, and UV-visible spectra are available on the Journal's website.

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