

Enantiotopos-Selective C–H Oxygenation Catalyzed by a Supramolecular Ruthenium Complex**

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Abstract: Spirocyclic oxindoles undergo an enantioselective oxygenation reaction (nine examples; *e.r.* up to 97:3) upon catalysis by a chiral ruthenium porphyrin complex (1 mol %). The catalyst exhibits a lactam ring, which is responsible for substrate association through hydrogen bonds, and an active ruthenium center, which is in a defined spatial relationship to the oxygenation substrate. DFT calculations illustrate the perfect alignment of the active site with the reactive C–H bond and suggest—in line with the kinetic isotope effect—an oxygen rebound mechanism for the reaction.

The area of enantioselective catalysis has evolved considerably over the past few decades enabling the synthesis of a large number of structurally diverse and biologically active compounds in high enantiopurity.^[1] However, despite considerable advances, there are still transformations that biological systems can routinely achieve that are problematic for man-made catalysts. For example, monooxygenase enzymes such as cytochrome P450 are known to be able to oxidize relatively inert aliphatic C–H bonds into more fundamentally useful C–OH or carbonyl functional groups in a highly regio- and stereoselective manner.^[2] Since the C–H bond is the most abundant linkage in nature, the development of an oxidation process that exhibits enzyme-like selectivity^[3] would be extremely valuable. Given that the active site of enzymes such as cytochrome P450 is composed of an iron metalloporphyrin structure, several chiral catalysts based on this

system have been developed. One early example of this was described by Groves and Viski, who designed an iron metalloporphyrin catalyst to achieve an asymmetric C–H oxygenation reaction. This approach successfully converted several hydrocarbon substrates into the corresponding secondary alcohols in good enantiomeric ratios (*e.r.* up to 86:14).^[4] Further research by the groups of Che,^[5] Groves,^[6] Simonneaux^[7] as well as others^[8] has resulted in the development of manganese and ruthenium metalloporphyrins as alternative systems with which this reaction could be achieved, albeit with moderate levels of enantioselectivity.^[9]

In a recent research program we have started to design chiral metalloporphyrin-based catalysts for enantioselective oxidation reactions.^[10] When applying them to C–H oxygenation^[11,12] substrates, the overoxidation of secondary alcohols to the respective ketones was an issue, which was difficult to overcome. Although the differentiation of enantiotopic hydrogen atoms in compound **1** (Figure 1), for example,

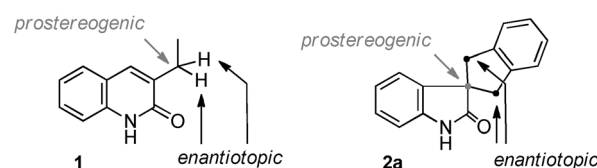


Figure 1. Enantiotopic hydrogen atoms in substrate **1** and enantiotopic methylene groups in substrate **2a**.

leads to a stereogenic center, this center is destroyed in a subsequent oxidation step. We therefore searched for substrates in which the stereogenic center would be retained upon oxidation of a primarily formed secondary alcohol.^[13] Spirocyclic oxindoles,^[14] such as **2a**, were found to be suited for this purpose and we herein report our preliminary results toward their enantioselective reactions. By employing a supramolecular^[15] ruthenium catalyst we could achieve a selectivity of up to 97:3 in favor of one of the two enantiotopic methylene groups.

In previous work,^[10] catalyst **3** (Figure 2) had been used for the enantioselective epoxidation of 3-alkenylquinolones

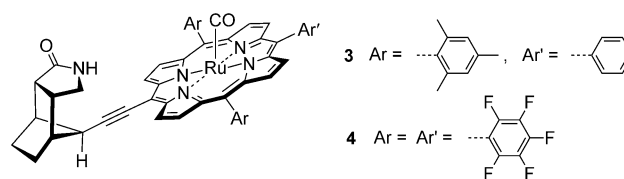


Figure 2. Structure of ruthenium porphyrin catalysts **3** and **4**.

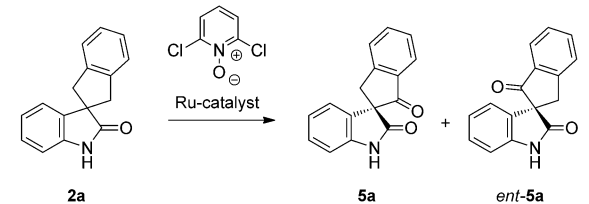
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Table 1: Selected optimization conditions for the enantioselective oxidation **2a**→**5a**.



Entry ^[a]	Ru-cat. [mol %]	Solvent	Temp. [°C]	Conv. ^[b] [%]	e.r. ^[c]
1	3 (1.0)	CH ₂ Cl ₂	50	45	65:35
2	4 (1.0)	CH ₂ Cl ₂	50	60	95:5
3	4 (1.0)	CH ₂ Cl ₂	35	39	97:3
4	4 (1.0)	CH ₂ Cl ₂	65	68	92:8
5	4 (1.0)	CHCl ₃	50	42	95:5
6	4 (1.0)	DCE ^[d]	50	49	92:8
7	4 (0.2)	CH ₂ Cl ₂	50	34	96:4
8	4 (2.0)	CH ₂ Cl ₂	50	60	94:6
9 ^[e]	4 (1.0)	CH ₂ Cl ₂	50	39	98:2

[a] Reaction conditions: **2a** (1.0 equiv, $c = 26$ mM), 2,6-dichloropyridine *N*-oxide (2.2 equiv), $t = 20$ h. [b] Conversion as determined by GC analysis. [c] Enantiomeric ratio (**5a**/*ent*-**5a**) as determined by HPLC analysis on a chiral stationary phase following column chromatography. [d] 1,2-Dichloroethane. [e] Dropwise addition of substrate **2a** over 2 h using a syringe pump.

(e.r. up to 99:1) and it was therefore chosen as a starting point for the present investigation. In the first instance, substrate **2a** was treated with **3** (1 mol %) in CH₂Cl₂ at 50 °C with 2,6-dichloropyridine *N*-oxide as an external oxidant^[16] (Table 1, entry 1). To our delight, these conditions resulted in the desired C–H oxygenation, albeit with moderate substrate conversion (45 %) and enantiotopos-selectivity (e.r. = 65:35) for ketone **5a**. Further tuning the properties of the catalyst^[17] by polyhalogenation of the *meso* aryl positions led eventually to the synthesis of catalyst **4** (see the Supporting Information, SI). Such an approach is known to a) increase the stability of the porphyrin complex to oxidative degradation^[18] and b) create a more electrophilic metal–oxo entity.^[19] This modification resulted in not only better conversion (60 %), but dramatically improved the observed e.r. to 95:5 in favor of ketone **5a** (entry 2).

Control experiments by either omitting catalyst **4** or 2,6-dichloropyridine *N*-oxide revealed no reaction (see SI). Whilst the conversion could be increased at higher temperature, this was found to lead to a slight deterioration in e.r. (entry 4). The enantioselectivity could be increased at lower temperature (entry 3) or with a lower catalyst loading (entry 7), although this time at the expense of conversion. Other chlorinated solvents were suitable (entries 5 and 6) but did not show any benefit compared to dichloromethane, neither did an increased catalyst loading (entry 8). The best e.r. (98:2) was obtained following a dropwise addition of substrate **2a** to a mixture of catalyst **4** and 2,6-dichloropyridine *N*-oxide at 50 °C (entry 9). However, in this case the conversion of substrate **2a** was inferior (39 %) to that obtained in entry 2. Attempts to formally improve the yield by making the oxidant the limiting reagent were not undertaken. Instead, the conditions described in entry 2 of Table 1

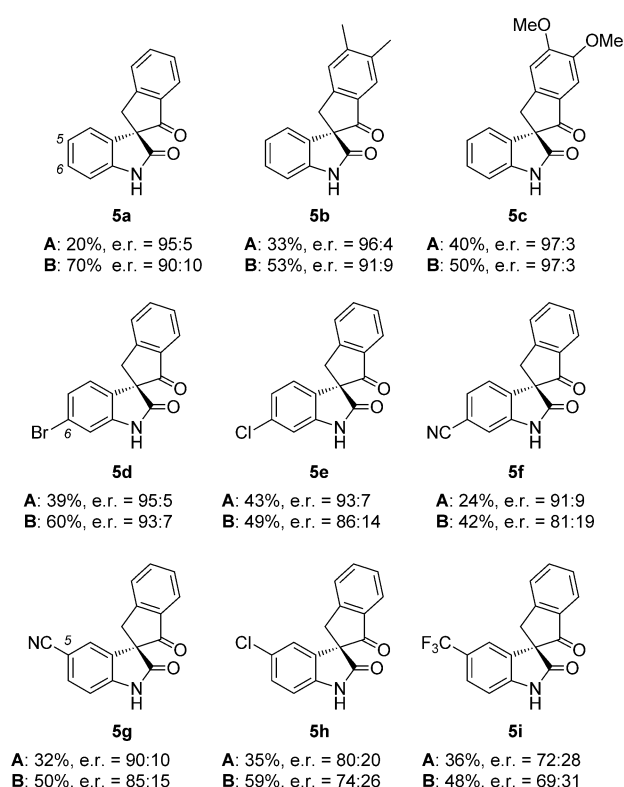


Figure 3. Products **5** obtained by enantioselective ruthenium-catalyzed oxidation of various spirocyclic oxindoles **2**. Method A: substrate (1.0 equiv), catalyst **4** (1 mol %), 2,6-dichloropyridine *N*-oxide (2.2 equiv), CH₂Cl₂, 50 °C, 20 h. Method B: Yield and e.r. following submission of the crude material (from step A) to either Swern or PCC oxidation conditions (see SI).

were selected for further work since they gave the best balance between conversion (60 %) and e.r. (95:5).

Despite the relatively high conversion of **2a** under the optimized conditions, the desired ketone **5a** was only isolated in a yield of 20 % (Figure 3). It quickly became evident that the discrepancy between conversion and yield was due to the fact that the intermediate alcohol was not completely oxidized under the reaction conditions and it was therefore desirable to further improve the yield through a second oxidation step. To this end, the crude reaction mixture obtained from the C–H activation process was submitted directly to a number of different oxidation conditions (see SI). The most challenging part of these studies was to find an oxidation reaction, which would not lead to a significant decrease of the e.r. due to a retro-aldol process (see below). The best results obtained involved the submission of the crude material to either pyridinium chlorochromate (PCC)^[20] or Swern conditions.^[21] Both provided the ketone product in a much improved yield of 70 % and with a high e.r. of 90:10. Submission of the oxindole substrate (**2a**) directly to the oxidation conditions led to no detectable quantity of ketone by ¹H NMR spectroscopy or gas chromatography (GC).

The effect of different substituents on the enantioselectivity was studied in a first set of experiments with spirocyclic oxindoles bearing methyl or methoxy substitution on the indane aromatic ring (Figure 3). Pleasingly, both of these

substrates were readily processed, providing ketones **5b** and **5c** in excellent e.r. (96:4 and 97:3, respectively) following C–H oxygenation. Importantly, in the case of the methoxy-substituted substrate, secondary oxidation under Swern conditions resulted in an identical e.r. (97:3) to that recorded for the initial enantiotopos-selective C–H oxygenation process. Subsequently, we assessed the influence of substituents at the C5 and C6 positions of the oxindole ring system (oxindole numbering, see Figure 3). Substitution at the C6 position by Br, Cl, and CN (**5d**, **5e**, and **5f**, respectively) gratifyingly also led to high enantiomeric ratios (91:9 to 95:5), which increased slightly in the order CN<Cl<Br. The e.r. following the second oxidation step was found to decrease more significantly as the electron-withdrawing capacity of the substituent increased (CN>Cl>Br). The use of substrates that were differentially substituted at the C5 position led to considerable differences in enantioselectivity. Whilst CN substitution again resulted in high e.r. (90:10), the introduction of Cl and CF₃ gave lower selectivity (80:20 and 72:28).

The absolute configuration for the major enantiomer **5b** (from the reaction of substrate **2b**) was assessed by comparison of measured and calculated chiroptical data (see SI). It was shown that the mode of catalyst action relies on substrate association by two hydrogen bonds.^[22,23] If instead of substrate **2a** its *N*-methylated derivative was employed there was no oxidation reaction to be observed. Remarkably, the *N*-methylated derivative of catalyst **4** was incompetent in performing the oxidation of substrate **2a**, with no reaction observed and starting material **2a** re-isolated (see SI).

Mechanistically, it seems safe to assume that compound **4** is a precatalyst, which is oxidized by 2,6-dichloropyridine *N*-oxide to a ruthenium oxo complex.^[9] With this in mind, we attempted to rationalize the experimental results using DFT calculations. Although several attempts to locate the transition state for a concerted C–H oxygenation yielded no result, we could identify the transition state for a C–H abstraction postulating a Ru^V intermediate^[28] (Figure 4). With

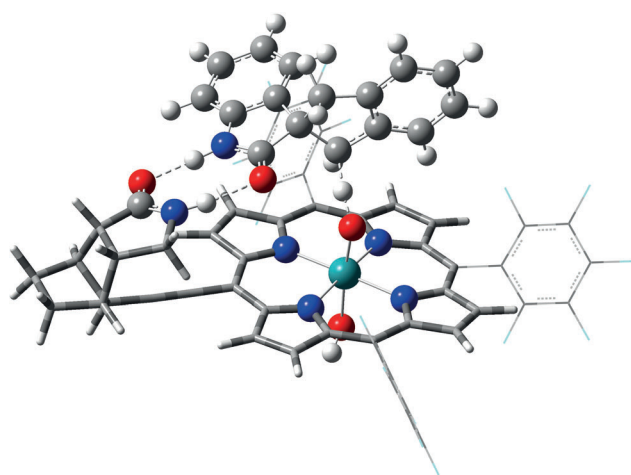


Figure 4. Favored transition state for the reaction **2a**→**5a** as calculated by DFT methods (M06L functional with SDD basis set and pseudopotential for ruthenium,^[24] 6-31G(d) for all other atoms).^[25] All calculations (see SI) were performed on the untruncated doublet complexes, employing Gaussian09^[26] with D3 dispersion correction by Grimme.^[27]

substrate **2a**, the Gibbs free energy barrier for this process was computed to be approximately 14 kcal mol^{−1}. Two hydrogen bonds are formed between catalyst and substrate (with C=O–NH distances of 1.76 Å for C=O_{catalyst}–HN_{substrate} and 1.92 Å for NH_{catalyst}–O=C_{substrate}). The hydrogen abstraction is associated with bond distances of O–H = 1.16 Å and H–C = 1.37 Å (O–H–C angle: 167°). The suggested transition state is in line with the absolute configuration determined for products **5**. Similar computational results were obtained for calculations performed with substrate **2c** (see SI). It is evident that substituents at the indane aromatic ring do not sterically interfere with the catalyst, which is in line with the high e.r. observed for products **5b** and **5c**. Further inspection reveals that the C5 position of the spirocyclic oxindole is in close proximity to one of the polyfluorinated *meso* aryl groups of the catalyst. As a result, we believe that as the steric bulk of the C5 substituent (substrates **2g–i**) increases there is a significant interaction with this aryl group, thereby leading to a destabilization of the transition state and lowering of the e.r. The extent to which the repulsion is detrimental correlates roughly with the size of the substituent (see above). The C6 position is evidently spatially located away from this group and thus avoids such interactions. Indeed, substrates **2d–f** reacted with enantioselectivities comparable to substrate **2a**.

After the C–H abstraction step, a fast rebound process leads to the transfer of the hydroxy group to the substrate. Although this process could be observed computationally, its barrier seems to be very low, and the consequent transition state could therefore not be located. A rough computational estimation of the primary kinetic isotope effect (KIE) associated with the C–H abstraction (neglecting tunneling effects) yielded a value of 6.4 (see SI). To validate this approximation, an intermolecular competition experiment (one-pot, 1:1 mixture) was conducted between spirocyclic oxindole **2a** and its deuterated analogue *d*₄-**2a** (Figure 5). A primary KIE of 6.1 was obtained, which was in excellent

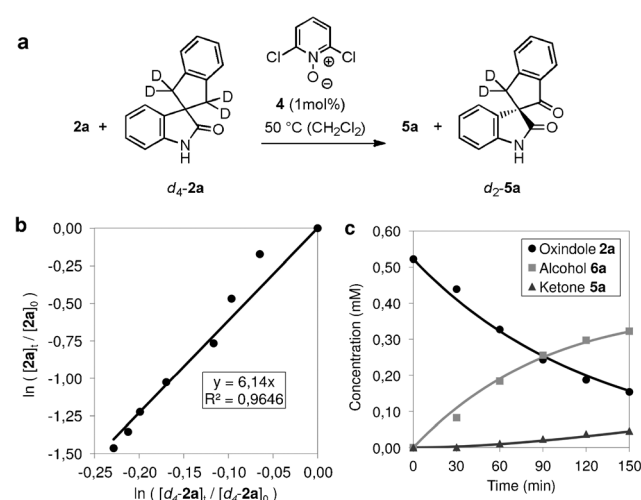
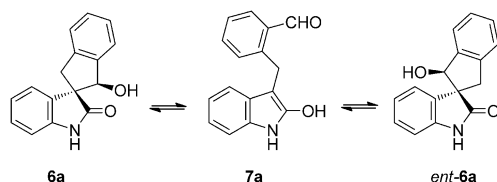


Figure 5. Measurement of the primary kinetic isotope effect (KIE): a) Intermolecular competition experiment between **2a** and *d*₄-**2a**. b) Determination of the KIE value from the line of best fit. c) Reaction profile for compounds **2a** (●) and **5a** (▲) and the calculated amount of intermediary formed alcohol **6a** (■).

agreement with the calculated value of 6.4. The high KIE value provides further evidence to suggest that C–H abstraction is the selectivity-determining step for this reaction.^[29] In the same experiment the formation of ketone **5a** and the change of the concentrations of the redox pair oxidant/reduced form were also measured. It was shown that the conversion of **2a** and the formation of alcohol **6a** and ketone **5a** follow the rate laws of a consecutive reaction **2a** → **6a** → **5a** with an expected sigmoid progression for the formation of ketone **5a**.

Mechanistically, the oxidation of the initially formed secondary alcohols **6** to the ketones **5** is suggested to occur through a two-electron process by alcohol coordination to the oxidant.^[30] There was no evidence that a kinetic resolution was involved in this process. Rather it was shown at least for one example (**2c** → **5c**) that the e.r. does not change in the subsequent oxidation step. For the other cases the loss in e.r. seems to be associated with a retro-aldol cleavage as depicted for alcohol **6a** in Scheme 1, which involves an achiral



Scheme 1. Racemization of alcohol **6a** via intermediate **7a**.

intermediate **7a**. Indeed the instability of alcohols related to **6a** has been reported earlier.^[31] In the present work, a reduced derivative of **7a** was isolated when subjecting ketone **5a** to reducing conditions (see SI). It appears as if the ring opening was favored by electron-withdrawing groups at the oxindole ring.

In summary, we have shown that supramolecular ruthenium complex **4** can be used to oxygenate spirocyclic oxindoles in a highly enantioselective fashion at low catalyst loading. Evidence was collected that the catalyst operates by simultaneously binding the substrate through hydrogen bonds at one site and performing the desired oxygenation reaction at another site. This enzyme-like mode of action ensures high selectivity but is also associated with a certain degree of substrate specificity. Still, a modular assembly with spatially remote sites for coordination and reaction seems a viable concept for chiral catalyst design in C–H activation chemistry.

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