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Manganese-Catalyzed Asymmetric Oxidation of Methylene C−H of Spirocyclic Oxindoles and Dihydroquinolinones with Hydrogen Peroxide

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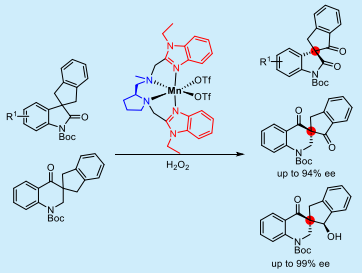
Supporting Information

ABSTRACT: A highly efficient strategy for the enantioselective oxidation of methylene C−H of spirocyclic oxindoles and dihydroquinolinones has been established, in which an earth-abundant manganese catalyst and hydrogen peroxide are used. Noteworthy, the manganese catalyst can be applied to the asymmetric hydroxylation of spirocyclic 2,3-dihydroquinolin-4-ones with 94−99% ee.



C−H bonds are ubiquitous structural units in readily available hydrocarbons as well as other organic molecules; thus, methods for direct transforming of C(sp^3)−H bonds into oxygen-containing compounds (e.g., alcohol, ketone) have been explored extensively.[1] Enantioselective oxidation of C(sp^3)−H bonds that can produce chiral alcohols or ketones directly, however, has proven to be a long-standing challenging goal.[2] Previous studies focused on the use of chiral metalloporphyrins and analogues. For example, the asymmetric hydroxylation of ethylbenzenes was first demonstrated by Groves and co-workers in 1989.[3] Over the past decades several further examples with Mn, Ru metalloporphyrins have been reported. Nevertheless, only moderate enantioselectivities were observed.[4] Alternatively, salen manganese complexes have also been studied in the asymmetric hydroxylation of benzylic C−H and oxidation of benzylic methylene group to chiral ketones, but these methods only provided poor substrate conversions and low to moderate enantioselectivities.[5] Notably, the Bach group has reported the first example of porphyrin Ru(II)-catalyzed asymmetric oxidation of spirocyclic oxindoles in good to excellent enantioselectivities with 2,6-dichloropyridine *N*-oxide as a terminal oxidant.[6] While this work offers a novel strategy for enantioselective preparation of valuable spirocyclic ketones via late-stage oxidation, this method requires further oxidative treatment with pyridinium chlorochromate (PCC) or Swern conditions for the oxidation of an intermediate alcohol to achieve a satisfactory yield. Considering the utility of this method, the development of a more efficient catalyst would be especially desirable.

The past several decades have witnessed the significant developments of biomimetic oxidation catalysis.[7,8] Our group has been engaging in the development of chiral bioinspired metal complex (e.g., Mn, Fe, with chiral N4 ligands) catalyzed asymmetric oxidation reactions with H_2O_2 as the terminal oxidant.[9] Very recently, we have reported a manganese catalyst system that catalyzes the asymmetric oxidation of the benzylic methylene C−H of spirocyclic compounds with high enantioselectivity.[10] More importantly, Costas and co-workers elegantly developed an enantioselective oxidation of aliphatic methylene C−H catalyzed by a similar N4 manganese catalyst using H_2O_2 as the oxidant (Scheme 1A).[11] Inspired by these successes, we envisioned that the catalytic system involving chiral manganese catalyst and H_2O_2 could be applicable to enantioselective oxidation of methylene C−H of prochiral spirocyclic oxindoles and other azaheterocycles (Scheme 1B). In view of the fact that the enantioselective hydroxylation of C(sp^3)−H remains challenging,[12] it would be more attractive to realize this reaction. Herein, we describe the asymmetric oxidation of the benzylic methylene C−H of spirocyclic oxindoles and quinolinones catalyzed by manganese complexes of N4 ligands, using aqueous H_2O_2 as the terminal oxidant. More importantly, this work also realizes the highly enantioselective hydroxylation of quinolinone precursors (up to 99% ee) (Scheme 1B).

Initially, the spirocyclic oxindole precursor **1a** was chosen as the model substrate. Our previous studies have demonstrated that small-molecule manganese complex **C1** is effective in enantioselective oxidation reactions.[10,11] Thus, Mn complex **C1** was selected as the catalyst to optimize the reaction conditions. We were pleased to observe that product **2a** was obtained in 34% yield and 89% ee in the presence of aqueous H_2O_2 and 1.0 mol % **C1** as the catalyst (Table 1, entry 1).

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Scheme 1. Asymmetric Oxidation of Methylene C−H Catalyzed by N4 Manganese Complex Using H_2O_2

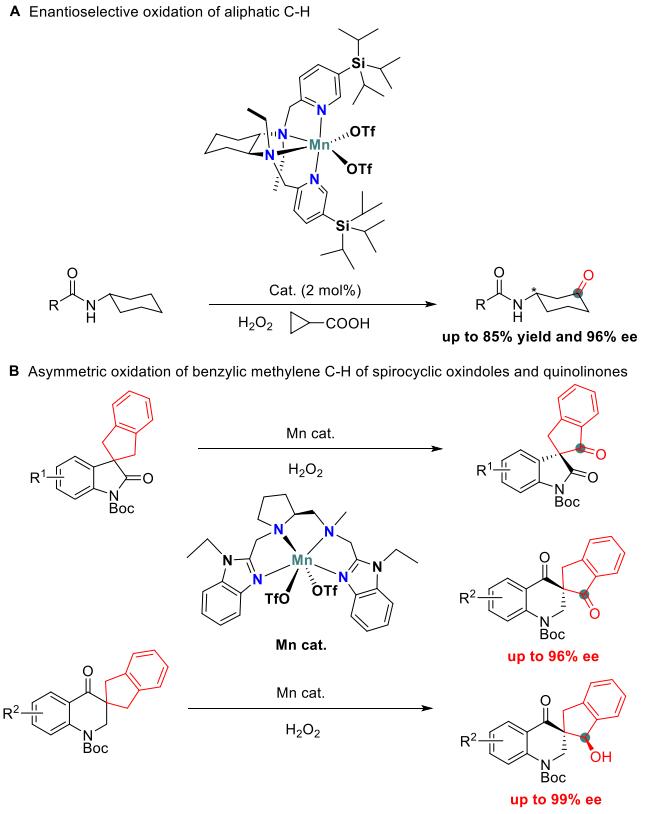
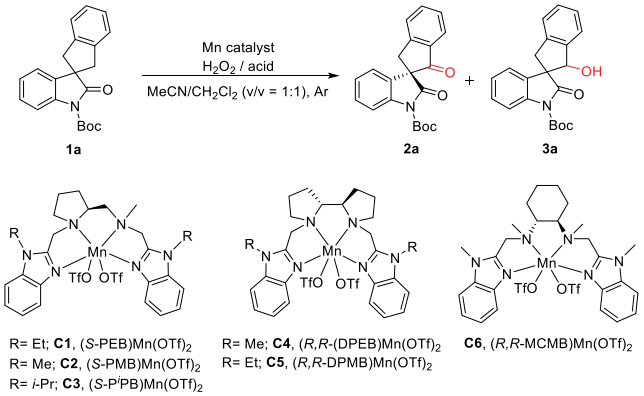


Table 1. Optimization of Asymmetric Oxidation Using Manganese Catalyst[a]



entry	Mn cat.	H_2O_2 (equiv)	acid additive	conv (%)	yield (**2a**) (%)[b]	ee (%)[c]
1[d]	**C1**	7	DMBA	64	34	89
2	**C1**	7	DMBA	80	63	91
3[e]	**C1**	7	DMBA	72	49	90
4	**C1**	5	DMBA	70	44	90
5	**C1**	3	DMBA	64	34	88
6[f]	**C1**	7	DMBA	82	60	91
7[g]	**C1**	7	AcOH	72	32	81
8[h]	**C1**	7	EHA	64	45	81
9	**C2**	7	DMBA	68	52	75
10	**C3**	7	DMBA	64	50	91
11	**C4**	7	DMBA	68	43	−79
12	**C5**	7	DMBA	83	62	−90
13	**C6**	7	DMBA	74	46	−84
14[i]	**C1**	7	DMBA	71	49	89

[a]Reaction conditions: substrate **1a** (0.2 mmol), manganese catalyst (2.0 mol %), and 2,2-dimethylbutanoic acid (DMBA, 14.0 equiv) were dissolved in 1.0 mL of CH_2Cl_2 at 0 °C under an Ar atmosphere, and then H_2O_2 (30% aqueous solution diluted in 1.0 mL of MeCN) was added dropwise over 2 h using a syringe pump and stirred for additional 2 h. [b]Isolated yield of **2a**. [c]Determined by HPLC analysis on a Chiralcel AD-H column. [d]1.0 mol % of manganese catalyst **C1** as catalyst, and a 23% yield of alcohol **3a** was isolated. [e]DMBA (7.0 equiv) was used. [f]The reaction was performed at −20 °C. [g]AcOH (14.0 equiv) was used instead of DMBA. [h]2-Ethylhexanoic acid (EHA, 14.0 equiv) was used instead of DMBA. [i]Reaction was performed under air.

Further screening of reaction conditions, a catalytic system consisting of Mn catalyst **C1** (2.0 mol %), 2,2-dimethylbutanoic acid (DMBA, 14.0 equiv), and an oxidant (H_2O_2, 7.0 equiv), was found to promote the oxidation reaction at 0 °C, affording the product **2a** in satisfactory yield (63%) and 91% ee (Table 1, entries 2, 4, and 5). Lowering the temperature from 0 °C to −20 °C did not increase the yield and enantioselectivity (Table 2, entry 6). As previously reported, the reactivity and enantioselectivity of an epoxidation reaction promoted by metal complexes of N4 ligands are affected significantly by the carboxylic acid additives.[13] In the present reaction, the enantioselectivity decreased clearly when acetic acid or 2-ethylhexanoic acid was used as an additive instead of DMBA (Table 1, entries 7 and 8). In addition, replacement of manganese catalyst **C1** with other manganese complexes led to lower yields and enantioselectivities; only manganese complex **C5** provided a comparable result to that of **C1** (Table 1, entries 9−13). Reaction under air provides a lower yield (Table 1, entry 14).

With the optimized reaction conditions in hand, we then studied the scope of this asymmetric oxidation reaction (Scheme 2). In general, a variety of spirocyclic oxindoles bearing both electron-donating and -withdrawing groups at the oxindole ring were suitable for the reaction, providing the corresponding ketones **2a**−**2h** in good enantioselectivities (77−91% ee) and yields (45−67%). The reactions of spirocyclic substrates containing methoxy substitution on the Indane aromatic ring proceeded smoothly to afford the desired chiral ketones **2i**−**2k** in good yields (53−57%) with moderate enantioselectivities (55−69% ee). For the substrate **2l** bearing a pivaloyl group on the nitrogen instead of the *N*-Boc protecting group, it also reacted well with good enantioselectivity. But for the substrate without a protecting group on the nitrogen, nearly no reaction took place (see SI, substrate **1m**). The absolute configuration of **2c** was confirmed by comparison with the reported optical rotation after deprotection of the *N*-Boc group of **2c**.[6]

To further demonstrate the synthetic utility of our method catalyzed by the small-molecule manganese catalyst, we then examined the spirocyclic compounds based on 2,3-dihydroquinolin-4(1*H*)-ones, which are ubiquitous scaffolds of pharmaceuticals and natural products.[14] To our delight, spirocyclic precursor **4a** could be transformed into the desired *β*,*β*′-diketones with good to excellent enantioselectivity smoothly (Scheme 3, 94% ee). In particular, alcohol **6a** was isolated with a 26% yield and 97% ee (Scheme 3), despite racemization of the spiro alcohol generated from spirocyclic oxindole that would occur easily via a retro-aldol cleavage demonstrated previously by Bach and co-workers.[6] In light of the greater significance of enantioselective hydroxylation of C−

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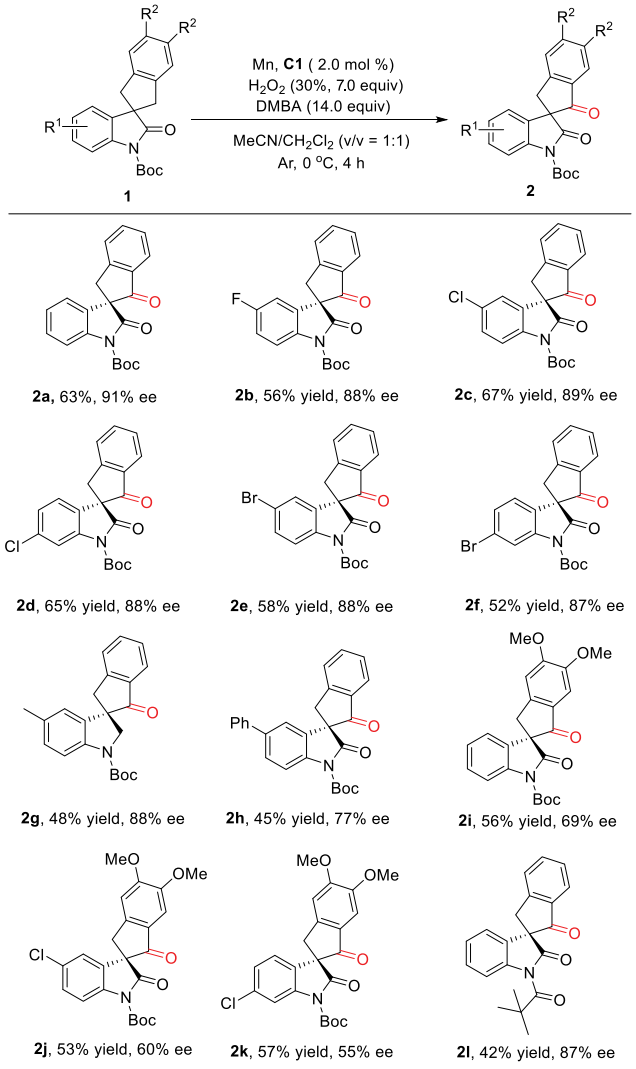
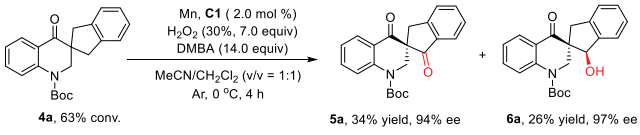
Scheme 2. Substrate Scope of Asymmetric Oxidation of Spirocyclic Oxindoles[a]



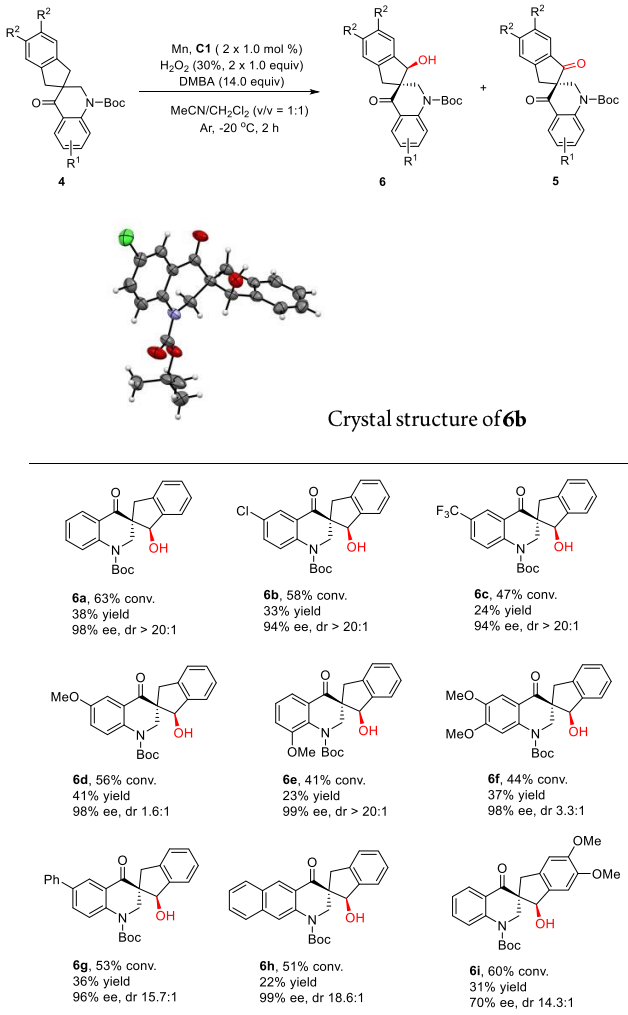
[a]Reaction conditions: substrate **1** (0.2 mmol), manganese catalyst **C1** (2.0 mol %), and 2,2-dimethylbutanoic acid (DMBA, 14.0 equiv) were dissolved in 1.0 mL of CH_2Cl_2 at 0 °C under an Ar atmosphere, and then H_2O_2 (7.o equiv, 30% aqueous solution diluted in 1.0 mL of MeCN) was added dropwise over 2 h using a syringe pump and stirred for additional 2 h; isolated yield.

Scheme 3. Asymmetric Oxidation of Methylene Group in Spirocyclic 2,3-Dihydroquinolin-4-one



H bonds, the reaction condtions for the asymmetric oxidation of **4a** were examined carefully (detail see Table S1). The alcohol **6a** was isolated as the major product in 38% yield with the addition of catalyst **C1** (1.0 mol %) and H_2O_2 (1.0 equiv) twice over a period of 2 h at −20 °C. In this case, the ketone **5a** was isolated only in 15% yield and 96% ee (see SI, Table S1). This result indicates that the ketone product is produced by the oxidation of the corresponding chiral alcohol. We then explored the substrate scope with the optimized conditions. The substrates containing substituted groups on the phenyl ring of 2,3-dihydroquinolin-4(1*H*)-one could be tolerated to afford the corresponding alcohol as major products in 22−41% yields with 94−99% ee (Scheme 4). The absolute configuration was confirmed by the determination of the crystal structure of **6b** (CCDC 1875664), and other alcohol products as well as *β*,*β*′-diketone **5a** were assigned analogously.

Scheme 4. Substrate Scope of Asymmetric Oxidation of Spirocyclic 2,3-Dihydroquinolin-4(1*H*)-ones[a]



[a]Reaction conditions: substrate **4** (0.2 mmol), manganese catalyst **C1** (1.0 mol %), and 2,2-dimethylbutanoic acid (DMBA, 14.0 equiv) were dissolved in 1.0 mL of CH_2Cl_2 at −20 °C under an Ar atmosphere, and H_2O_2 (1.0 equiv, 30% aqueous solution diluted in 0.5 mL of MeCN) was added dropwise over 30 min and stirred for additional 30 min; afterward, **C1** (1.0 mol %) was added to the reaction again, and a second addition of H_2O_2 (1.0 equiv) was performed in the same manner; total reaction time of 2 h; isolated yield.

It is believed that the methylene oxidation catalyzed by the manganese catalyst may occur via an alcohol intermediate.[6,10,15] In Bach's work, a PCC or Swern oxidation following C−H oxidation greatly improved the yield of the corresponding chiral ketone, indicating that the chiral Ru catalyst induced enantioselective oxidation of C−H to firstly generate a chiral alcohol.[6] According to the system based on the manganese complex of the N4 ligand, H_2O_2, and carboxylic acid, a Mn(V)-

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oxo species bearing a carboxylate moiety has been supported experimentally and theoretically; then it serves as the oxidizing intermediate via H-atom abstraction and following oxygen rebound to provide an alcohol product.[13a,16] Afterward, the alcohol product is oxidized by a carboxylate Mn(V)-oxo species to produce the desired ketone product.

In summary, we have developed a manganese-catalyzed protocol that allows for the enantioselective oxidation of methylene C−H in oxindoles or 2,3-dihydroquinolin-4-ones to ketones. It is noteworthy that the same manganese catalyst has been successfully applied to the asymmetric hydroxylation of spirocyclic 2,3-dihydroquinolin-4-ones with 70−99% ee. Overall, the current reaction is more environmentally friendly due to the involvement of the manganese complex as the catalyst and aqueous hydrogen peroxide as the terminal oxidant. Further applications of manganese-catalyzed enantioselective oxidation of unactivated C−H and mechanistic studies are currently ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03652.

Syntheses of the spirocyclic substrates (**1a−1l** and **4a−4h**); general procedure for the asymmetric oxidation of **1a−1l** and **4a−4h** catalyzed by manganese complex **C1** and analyses of the products (**2a−2l** and **6a−6h**) (PDF)

Accession Codes

CCDC 1875664 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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