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Letter

Cross-Dehydrogenative Cyclization–Dimerization Cascade Sequence for the Synthesis of Symmetrical 3,3′-Bisoxindoles

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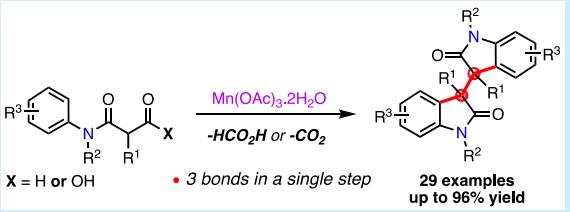
ABSTRACT: The synthesis of symmetrical 3,3′-bisoxindoles from simple acyclic β-oxoanilides is reported. The described method forges three new C–C bonds in a single step via a sequential $Mn(OAc)_3{\cdot}2H_2O$ mediated oxidative radical cyclization-fragmentation–dimerization process. The scope of this reaction is demonstrated in the preparation of a variety of 3,3′-bisoxindoles, as well as its application toward the formal synthesis of the Calycanthaceae alkaloid, (±)-folicanthine.



Bisoxindoles represent a particularly exciting class of compounds for synthetic organic chemists. Not only do they possess interesting biological activities,[1] but they serve as important synthetic intermediates in the construction of complex natural products.[2] Specifically, they are perfectly poised to forge the contiguous quaternary stereogenic centers found in cyclotryptamine alkaloids (Figure 1),[3,4] which themselves have significant biological profiles.

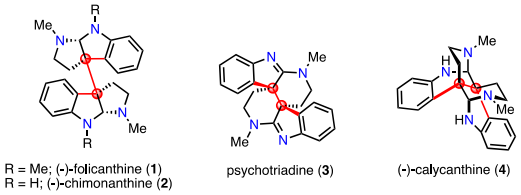


Figure 1. Cyclotryptamine alkaloids.

An obvious disconnection in visualizing the formation of the quaternary bisoxindole framework identifies the strategy of simply combining two oxindole derived fragments together. Therefore, it is not surprising that the overwhelming majority of reports toward the synthesis of bisoxindoles utilize this approach, namely, additions to isatin derivates[5] and the direct dimerization of oxindole intermediates (Figure 2a),[6] promoted either chemically or photochemically. Other methods involving already cyclic starting materials include C3/C3′ functionalization of monosubstituted bisoxindoles,[7] as well as the functionalization of 3-indolyl-oxindoles.[8] By contrast, methods for the synthesis of bisoxindoles from acyclic precursors are rare and typically involve a double cyclization protocol starting from bis-anilides (Figure 2b).[9] Rarer still are methodologies that construct the bisoxindole framework from simple monomeric anilides through a sequential cyclization-dimerization process; the only such report is by Zhang who made use of a copper-catalyzed arylation–dimerization sequence as the key

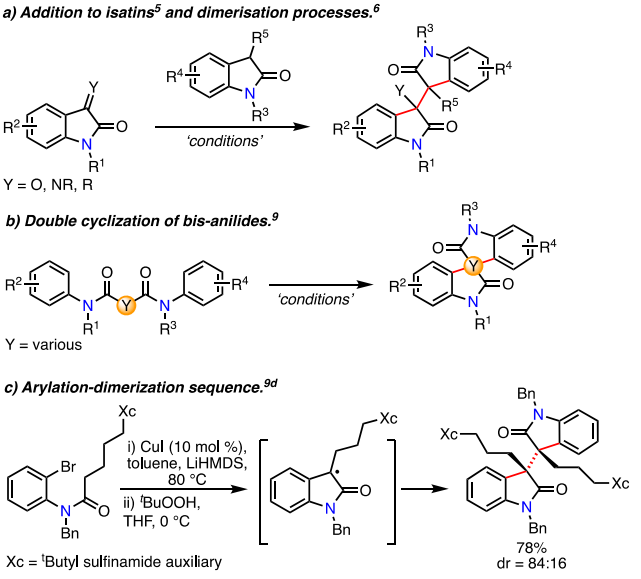


Figure 2. (a–c) Previously reported approaches for the synthesis of bisoxindoles.

step toward the total synthesis of various cyclotryptamine alkaloids (Figure 2c).[9d] Herein, we report a one-step oxidative cross-dehydrogenative cyclization–fragmentation–dimerization sequence for the synthesis of symmetrical bisoxindoles (Figure 3), with the key cyclization step proceeding via a formal $C(sp^2)$–H/$C(sp^3)$–H activation, and its application

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toward the synthesis of the Calycanthaceae alkaloid, (±)-folicanthine.

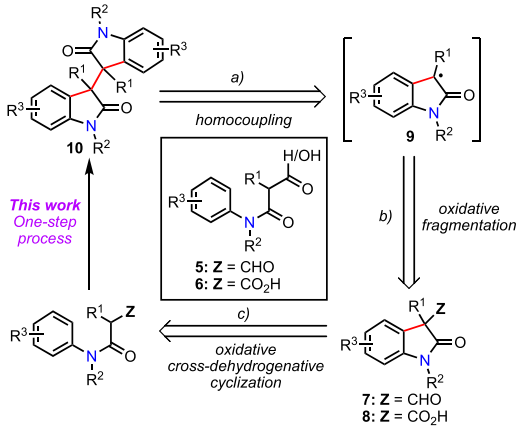


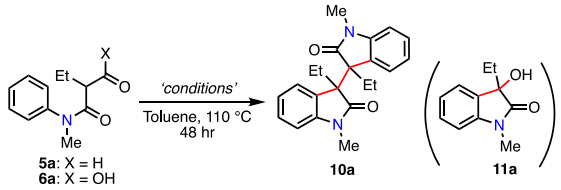
Figure 3. Our approach for the one-step synthesis of bisoxindoles from acyclic precursors.

In conceptualizing our one-step strategy, we identified three key disconnections (Figure 3). Namely, the formation of the desired bisoxindole **10** from the homocoupling of methine radical **9** (Figure 3a), generated in turn via a homolytic fragmentation of a suitable oxindole **7**/**8** (Figure 3b), that could be obtained using an oxidative cross-dehydrogenative cyclization reaction (Figure 3c). The cross-dehydrogenative cyclization[10] and the homocoupling steps[6] are well-established as independent transformations in the literature and therefore the only consideration remaining was selecting an appropriate group **Z** (Figure 3), as a delayed radical precursor—stable enough to promote the oxidative cross-dehydrogenative cyclization, but labile enough to afford radical intermediate **9** in the subsequent step of the cascade sequence. This led us to identify oxoanilides **5** and **6** (where **Z** = formyl (**5**) and carboxylic acid (**6**)), respectively, Figure 3), as key starting materials since both cross-dehydrogenative cyclizations of related oxoanilides,[10] as well as oxidative deformylation[11,12] and decarboxylation[13] processes, have been reported in the literature. Furthermore, we considered the relative stability of starting materials **5** and **6**, and by extension accessing the related oxindoles **7** and **8**, to be more attractive throughout the entire envisage cascade, when compared to other functional groups for the homolytic generation of radical **9**.[14] It is noteworthy to mention that aldehydes **5** are remarkably stable—up to 6 months refrigerated and up to 1 week of bench storage—and their syntheses are often shorter than the related acid **6** (see the Supporting Information).

Table 1 shows selected results of our optimization studies using oxoanilides **5a** and **6a** as model substrates (see Table S1 in the Supporting Information for full data). We initially set out to develop a metal-catalyzed process as either via a deformylative or decarboxylative strategy and using air as the terminal oxidant to regenerate the active catalyst[15] for each requisite oxidation step.

In the event, using a 50 mol % catalyst loading of $Mn(OAc)_3{\cdot}2H_2O$ (~17 mol % per oxidation step) produced the desired bisoxindole **10a** in 53% and 37% yield, from the corresponding aldehyde (**5a**) and acid (**6a**), respectively, together with a 32% and 11% yield of hydroxyoxindole **11a**, respectively (Table 1, entries 1 and 2). It quickly became clear

Table 1. Selected Optimization Results of the One-Step Cyclization-Dimerization Cascade Sequence



entry	X = H/OH	oxidant	equiv	yield of **10a**[a] (%)	yield of **11a** (%)
1[b]	H	$Mn(OAc)_3{\cdot}2H_2O$	0.50	53	32
2[b]	OH	$Mn(OAc)_3{\cdot}2H_2O$	0.50	37	11
3[c,d]	H	$Mn(OAc)_3{\cdot}2H_2O$	3.0	92	–
4[c,e]	OH	$Mn(OAc)_3{\cdot}2H_2O$	3.0	81	–

[a]Isolated yields as an ~1:1 mixture of separable meso:(±)-D,L-diastereomers. [b]Under air. [c]Under argon. [d]ACN as the solvent, reflux. [e]THF as the solvent (vigorous reflux).

that the interception of methine radical **9a** (Figure 3) by O_2 under the aerobic conditions in the formation of **11a**, rather than the desired homocoupling, was a significant competing process. Gratifyingly, switching to an anaerobic system and using a stoichiometric amount of oxidant, albeit 1 equiv per requisite oxidation step, ultimately (and following solvent optimization; Table S2 in the Supporting Information), produced the ideal set of conditions for both aldehyde **5a** and carboxylic acid **6a**, affording **10a** in 92% and 81% yield, respectively (Table 1, entries 3 and 4). With these conditions in hand, we explored the substrate scope of the cascade sequence utilizing both starting materials (Scheme 1), paying attention to any distinct advantages between the deformylative (**5**) and decarboxylative (**6**) strategies.

Various alkyl groups (R^1) were well-tolerated, producing bisoxindoles **10a**–**10h** in yields of 56%–93%. Modification of the protecting group (R^2) on the aniline afforded the *N*-benzyl protected bisoxindole **10i** in yields of 90% and 91%, from the corresponding aldehyde and carboxylic acid, respectively. Variation of the substituents around the aromatic ring (R^3) utilizing halides, electron-withdrawing, and electron-releasing groups, afforded **10j**–**10q** in 70%–96% yield as well as disubstituted bisoxindoles **10r**–**10s** in 59%–95% yield. All things considered, these two strategies, namely, via a deformylative or decarboxylative fragmentation, appear largely complementary. A specific point of difference encountered during the course of our work, however, was found in the synthesis of bisoxindole **10t**, which was produced in 65% yield from acid **6t**. Conversely, **10t** could not be accessed via the corresponding aldehyde **5t** as its synthesis via our prescribed formylation failed.

The proposed mechanism of the reaction, using the formation of **10a** as a representative example, is shown in Scheme 2 (see Supporting Information for full details). The oxidative cross-dehydrogenative cyclization step likely proceeds in accordance with current mechanistic thinking, involving conversion to oxindoles **7a**/**8a**, from **5a**/**6a**, respectively, via two sequential oxidative single electron transfer (SET) processes.[10] Following deprotonation of **8a** to the corresponding carboxylate anion, a third oxidative SET process generates methine radical **9a** with concomitant loss of

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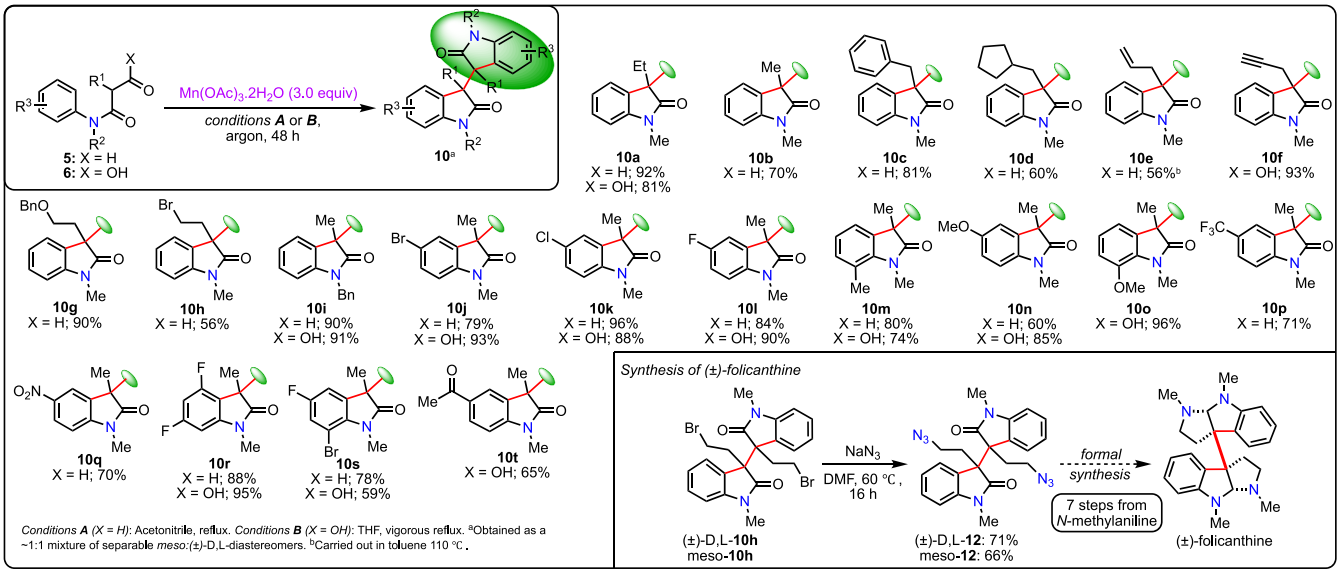
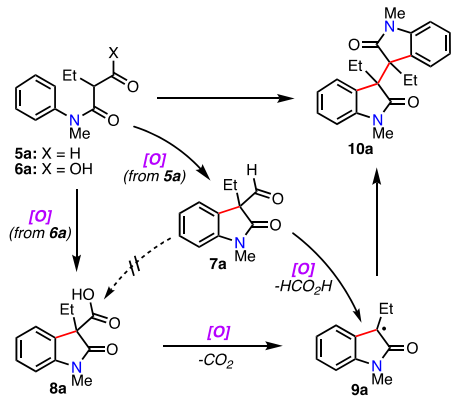
Scheme 1. Substrate Scope and Application to the Synthesis of (±)-Folicanthine



Scheme 2. Proposed Mechanism



CO_2,[14] which subsequently homocouples to afford bisoxindole **10a**. The mechanism for the generation of radical **9a** from **7a** is envisaged to proceed in accordance known deformylation processes mediated by polynuclear metal complexes.[11] We had considered an alternative pathway occurring via oxidation of aldehyde **7a** to carboxylic acid **8a**, followed by subsequent generation of radical **9a**. In this scenario, however, an additional oxidation step would be required and would imply a maximum theoretical yield of 75% over the cascade sequence (with 3 equiv of oxidant). As our yields obtained were generally above this threshold, it would suggest that this pathway is unlikely, but we cannot rule this out in all cases.

TEMPO trapping experiments with both **5a** and **6a** failed to produce any of the desired dimer **10a** (see Scheme S1 in the Supporting Information). In the case of acid **6a**, ketoamide **15a** was the major product isolated in 45% yield, while **5a** afforded ketoamide **15a** in 33% yield together with hydroxyoxinolde **11a** in 19% yield — overall supporting our proposed cascade sequence.

To further demonstrate the synthetic utility of this reaction, bisoxindole (±)-D,L-**10h** was easily converted into azide (±)-D,L-**12** in 71% yield (after recrystallization), which is a key intermediate in Ghosh's total synthesis of the Calycanthaceae alkaloid (±)-folicanthine,[5b] and thus completed the formal synthesis in only seven steps, starting from *N*-methylaniline (Scheme 1). Meso-**10h** was also suitable for this transformation, producing meso-**12** in 66% yield (after recrystallization), which can similarly be envisaged toward the total synthesis of meso-folicanthine.

In summary, we have developed a $Mn(OAc)_3{\cdot}2H_2O$ mediated one-step synthesis of symmetric bisoxindoles enabled by an oxidative cross-dehydrogenative cyclization−dimerization cascade sequence through the use of aldehydes and carboxylic acids as delayed radical precursors. The utility of this reaction was demonstrated by the synthesis of a diverse library of bisoxindoles as well as its application to the formal synthesis of (±)-folicanthine.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01799.

Experimental procedures and compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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