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# Decatungstate-Photocatalyzed Dearomative Hydroacylation of Indoles: Direct Synthesis of 2-Acylindolines

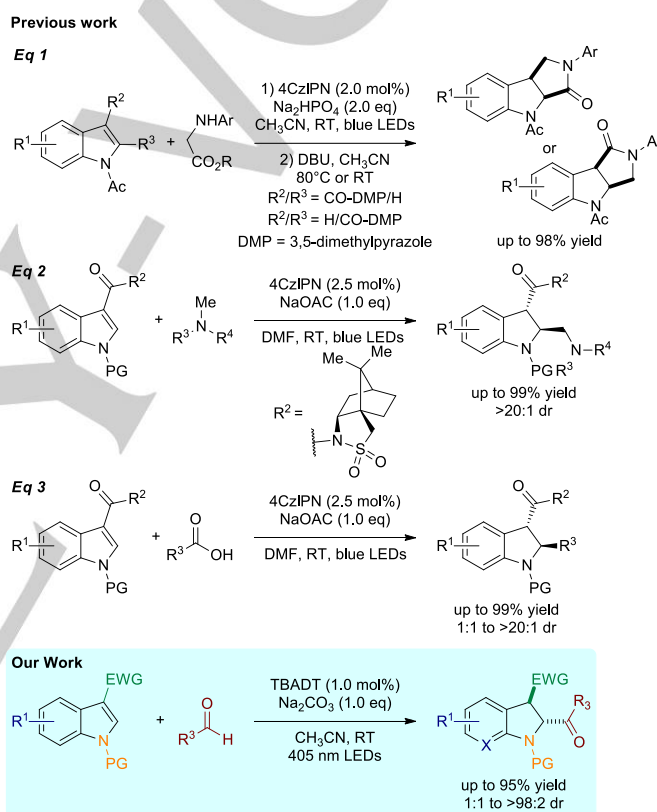
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**Abstract:** We report herein a convenient and scalable dearomative hydroacylation reaction of indoles. Employing readily available aldehydes as the acyl source and TBADT as an inexpensive direct HAT photocatalyst, a variety of indoles derivatives were converted into synthetically interesting 2-acylindolines in good to excellent yields as well as great diastereoselectivity under mild conditions. An asymmetric version of the reaction was successfully developed and an experimental mechanistic investigation was carried out in order to gain further insights on the assumed reaction pathway.

## Introduction

2-Acylindolines are frequently found in biologically active products as well as pharmaceuticals.<sup>[1]</sup> In addition, they can serve as valuable intermediates for the construction of naturally occurring alkaloids.<sup>[2]</sup> To the best of our knowledge, there are only few methods for their synthesis reported in literature, most of them requiring multiple steps.<sup>[2,3]</sup> Thus, the development of a novel route towards 2-acylindolines from simple, inexpensive and readily available starting materials still remains highly desirable. In this respect, dearomatization of indoles is an attractive tool to access indolines in a single step.<sup>[4]</sup> Notably, photochemical intermolecular hydro-functionalization of electron-deficient indoles have recently attracted great research interests,<sup>[5]</sup> enabling the syntheses of highly functionalized indolines. For example, in 2020, Zhang, You *et al.* developed an efficient organophotoredox-catalyzed hydroalkylative dearomatization of C2- and C3-substituted indoles using *N*-arylglycine derivatives as electron-rich radical precursors. Lactams were obtained in high yields and complete diastereoselectivity after DBU-mediated cyclization (Scheme 1, eq 1).<sup>[6]</sup> One year later, Wang *et al.* accomplished an elegant stereoselective hydroalkylation of electron-poor indoles bearing Oppolzer's camphorsultam auxiliary with tertiary amines leading to various enantioenriched indolines in good yields with excellent diastereoselectivities (Scheme 1, eq 2).<sup>[7a]</sup> Later the same year, the same group disclosed a diastereoselective dearomative hydro-functionalization of indoles through radical decarboxylation of a wide variety of aliphatic carboxylic acids (Scheme 1, eq 3).<sup>[7b]</sup> It is

worth noting however that all these examples relies on the same organic dye – 4CzIPN – letting room for further explorations involving ideally a robust and easy to handle photocatalyst. Hence, inspired by these works and based on our experience in photoredox processes,<sup>[8]</sup> we envisaged a new methodology for the preparation of the desired 2-acylindolines via a photocatalytic dearomative hydroacylation of indoles.



**Scheme 1.** Photocatalytic hydro-functionalization of indoles.

## Results and Discussion

In recent years, visible light-induced catalytic hydroacylation processes for the purpose of introducing carbonyl groups to  $\pi$ -systems enjoyed a lot of methodological developments.<sup>[9]</sup> Among them, hydrogen atom transfer (HAT) involving aldehydes as acyl radical sources under mild reaction conditions has become a strategy of choice.<sup>[9c-g,i,o-r,w]</sup> In particular, contrary to classical ruthenium- and iridium-photoactivable complexes, decatungstate anion ( $[W_{10}O_{32}]^{4-}$ ) – belonging to the family of polyoxometalate species (POMs) – does not require a cocatalyst to realize such hydrogen atom abstractions. In this context, Fagnoni *et al.*<sup>[10a-f]</sup> reported effective hydroacylations of electron-poor olefins using this affordable catalyst based on an Earth's crust abundant transition metal.<sup>[9c-g,10,11,12]</sup> Encouraged by these smooth protocols for the generation of acyl radicals, we supposed that a

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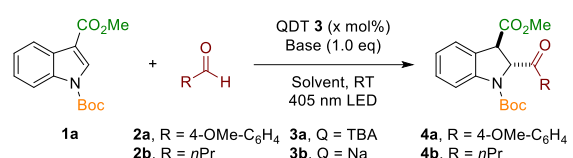
[‡] These authors contributed equally to this work;

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decatungstate anion photocatalyst could promote the hydroacylation of indoles to provide a direct access to 2-acylindolines.<sup>[13]</sup> To test our assumption, we initially investigated the reaction of *N*-Boc indole **1a** with 2.0 eq of *para*-anisaldehyde (**2a**) in the presence of tetrabutylammonium decatungstate (TBADT (**3a**), 5 mol%) under 405 nm light irradiation (Table 1, entry 1). Gratifyingly, the desired hydroacylated indoline **4a** was formed as a single *trans* diastereomer, albeit in relatively moderate yield due to competing aerobic oxidation of the aldehyde.<sup>[14]</sup> However, even under carefully deoxygenated conditions, the formation of carboxylic acid could not be completely suppressed. Since it can be deleterious to photocatalytic activity, some inorganic bases were added in the

**Table 1.** Survey of Reaction Conditions for Photocatalyzed Dearomative Hydroacylation of Indoles<sup>[a]</sup>

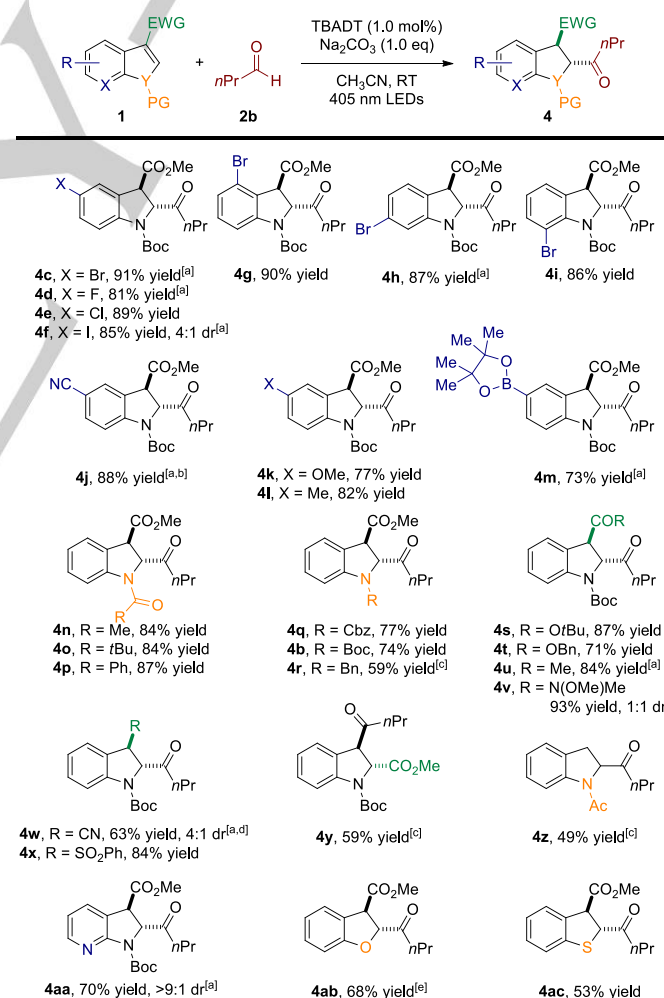


Entry	<b>3a</b> (x mol%)	Base	Solvent	<b>4</b> Yield [%] <sup>[b]</sup> (Yield [%] <sup>[c]</sup> )
1	5	-	CH <sub>3</sub> CN	66 [ <b>4a</b> ]
2	5	NaHCO <sub>3</sub>	CH <sub>3</sub> CN	66 [ <b>4a</b> ]
3	5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	72 [ <b>4a</b> ]
4	5	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	50 [ <b>4a</b> ]
5 <sup>[d]</sup>	5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	73 [ <b>4a</b> ]
6	5	Na <sub>2</sub> CO <sub>3</sub>	Acetone	70 [ <b>4a</b> ]
7	5	Na <sub>2</sub> CO <sub>3</sub>	THF	trace
8	5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (4:1)	trace
9	5	Na <sub>2</sub> CO <sub>3</sub>	Acetone/H <sub>2</sub> O (4:1)	51
10 <sup>[e]</sup>	5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	76 [ <b>4a</b> ]
11 <sup>[f]</sup>	5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	69 [ <b>4a</b> ]
12 <sup>[e,g,h]</sup>	2.5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	72 [ <b>4a</b> ], (70)
13 <sup>[e,g,i]</sup>	2.5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	72 [ <b>4a</b> ], (68)
14 <sup>[e,g,i]</sup>	1	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	78 [ <b>4a</b> ], (73)
15 <sup>[e,g]</sup>	1	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	78 [ <b>4b</b> ], (74)
16	0	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	x [ <b>4a</b> ]
17	0	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	0 [ <b>4b</b> ]
18 <sup>[j]</sup>	5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	x [ <b>4a</b> ]
19 <sup>[j]</sup>	5	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	0 [ <b>4b</b> ]

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol) and **3** (0.01 mmol, 5 mol%) in 2.0 mL of CH<sub>3</sub>CN under argon, for 24 h. [b] <sup>1</sup>H NMR yield to *trans*-isomer **4** determined using dibenzyl ether as external standard. In each case, the ratio of *trans/cis* stereoisomers was determined to be higher than 98:2 by <sup>1</sup>H NMR. *Trans*-relative configuration was determined by X-ray single crystal structure analysis of **4aw**. [c] Yields refer to chromatographically pure *trans*-isomer **4**. [d]

With NaDT (**3b**). [e] With 1.0 mL of CH<sub>3</sub>CN. [f] With 4.0 mL of CH<sub>3</sub>CN. [g] 8 h reaction time. [h] With 1.2 eq of **2a**. [i] With 1.2 eq of **1a**. [j] No light irradiation.

reaction media and a slight yield increase was observed with Na<sub>2</sub>CO<sub>3</sub> (entry 3). Changing decatungstate counter ion from tetrabutylammonium to sodium had almost no effect on the reaction (entry 5). In this context, we decided to continue our optimization study by keeping TBADT as photocatalyst. Although, the subsequent solvent screening – limited by solubility issues for the catalyst – did not offer further improvement (entries 6 to 9), the presence of water was deleterious to the reactions. Higher concentration enabled modest yield amelioration (entry 10). Pleasingly, decreasing the catalyst loading to 2.5 mol% while reducing the amount of aldehyde to 1.2 equivalent only resulted in a moderate erosion of the yield (entry 12). Conversely, introducing a slight excess of **1a** led to a comparable result (entry 13). It was even possible to further reduce the catalytic loading to reach 1 mol% without observing a significant impact on the yield (entry 14). Finally, to check that these reaction conditions could be expanded to aliphatic aldehydes, we performed the reaction with butyraldehyde and, to our delight, the desired product **4b** was obtained in 74% yield as a single diastereomer (entry 15).



**Scheme 2.** Indoles scope of the synthesis of acylindolines **4**. Reaction conditions: **1** (0.2 mmol), **2b** (0.4 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.2 mmol) and **3a** (1 mol%) in 2.0 mL of CH<sub>3</sub>CN under argon and 405 nm irradiation for 24 h. Yields are based on isolated pure product after column chromatography. *Trans* relative configuration was assumed by analogy with **4aw**. [a] In acetone. [b] With 0.22

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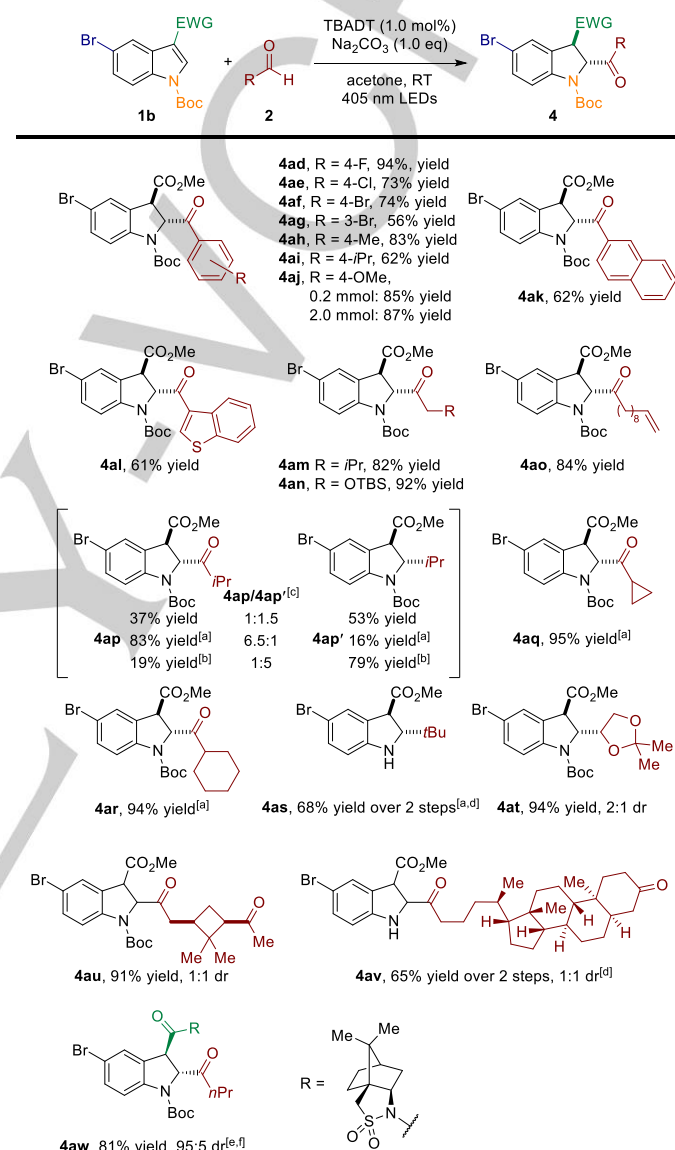
mmol of **2b**. [c] With 0.8 mmol of **2b** and 2.5 mol% of **3a** for 48 h. [d] With 0.21 mmol of **2b**. [e] At 0.15 mmol scale.

With the optimized conditions in hand, the scope of the dearomative hydroacylation between butyraldehyde and selected indoles was examined first (Scheme 2). It was found that indoles substituted by electron-withdrawing (CN, F, Br, I, Cl) and electron-donating (Me and MeO) groups at the 4-, 5-, 6- and 7-positions were appropriate substrates providing the corresponding *trans*-indolines **4c** to **4l** in high yields (77 to 91% yield). To our delight,

indole bearing pinacol boronic ester which can be used subsequently in metal-catalyzed couplings, is well tolerated. Various protecting groups on the nitrogen atom of indoles such as benzylcarbamate, acetate, pivaloate or benzoate were all suitable (**4n** to **4r**). Even the electron-rich *N*-benzyl group-protected indole, which was unreactive in a previously reported likewise dearomatization,<sup>[7b]</sup> gave the desired indoline **4r** in good yield when an excess of aldehyde (4.0 eq) was used. Several electron-deficient functional groups at the C3-position (including ketone, sulfone, cyanide and amide) of indole proved to be compatible in the process affording the corresponding product **4b** and **4s** to **4x** in good yield. However, lower diastereoselectivities were obtained with indoles containing either a cyano or Weinreb amide functionality. It is noteworthy that 2-ester substituted indoles led to 3-acylindole **4y** which is appealing in view of natural products preparation.<sup>[15]</sup> Remarkably, this dearomatization condition was even applicable to the more electron-rich unsubstituted *N*-acylindole, furnishing indoline **4z** in decent yield. Additionally, the reaction scope was broadened to other (hetero)arenes such as 7-azaindole, benzo[*b*]thiophene and benzofuran and the resulting dearomatized products **4aa**, **4ab** and **4ac** were formed in good yields with moderate to excellent diastereoselectivities (from 9:1 to >98:2 dr).

Next, the scope of aldehydes in reaction with *N*-Boc indole **1b** was assessed (Scheme 3). Due to the limited solubility of this partner in acetonitrile, this solvent was replaced by acetone which was proved equally good in the optimization study. A wide range of electron-rich and electron-poor aromatic aldehydes gave indolines **4ad-4aj** in moderate to high yields with excellent diastereoselectivities. 2-Naphthaldehyde and benzo[*b*]thiophene-3-carboxaldehyde were also suitable to synthesize the desired adducts **4ak** and **4al** in high yields. Then, a series of functionalized aliphatic aldehydes were tested. Linear aldehydes with a terminal olefin or silyl ether functional group efficiently provided the desired indolines **4an** and **4ao** respectively. In contrast,  $\alpha$ -branched aldehydes such as iso-propionaldehyde resulted in a mixture of acylated **4ap** and alkylated product **4ap'** (1:1.5), due to the competitive decarbonylation. As reported by other groups,<sup>[9c-g,10a,f,11,16]</sup> we were pleased to isolate acylated product in better yield (83%) when the reaction was performed at lower temperature (1.5 °C). Under this condition, use of cyclic aldehydes (cyclopropanal and cyclohexanal) led to the desired acylated indolines **4aq** and **4ar** as the single product. However, the alkylated products **4as** and **4at** were exclusively formed with pivalaldehyde and *D*-glyceraldehyde acetal. In the first case, only a partial conversion was observed (indoline/indole 4.5:1 according to the <sup>1</sup>H NMR of the crude mixture) the resulting product could not be easily separated from remaining starting material but this isolation issue was easily circumvented after an

acidic deprotection of the Boc protecting group. Notably, hydroacylation of indoles derived from natural products proceeded efficiently (**4au** and **4av**), providing thus a powerful synthetic tool for late-stage modification.<sup>[17]</sup> In addition, we investigated an asymmetric version of our methodology using an Oppolzer's camphorsultam indole derivative.<sup>[7]</sup> When subjected to the optimized reaction conditions, it afforded **4aw** in 81% yield and 95:5 dr.



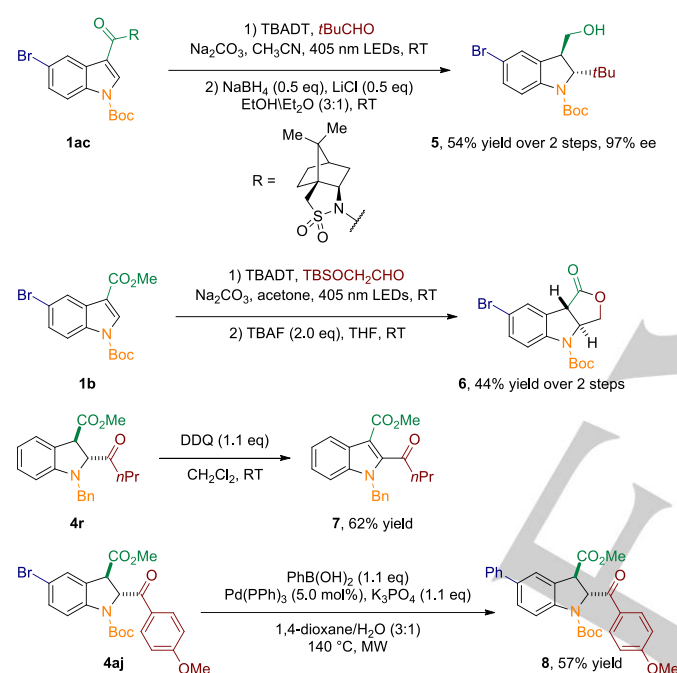
**Scheme 3.** Aldehydes scope of the synthesis of acylindolines **4**. Reaction conditions: **1** (0.2 mmol), **2b** (0.4 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.2 mmol) and **3a** (1 mol%) in 2.0 mL of acetone under argon and 405 nm irradiation for 24 h. Yields are based on isolated pure product after column chromatography. *Trans* relative configuration from **4ad** to **4as** was assumed by analogy with **4aw** [a] at 1.5 °C. [b] With 2.5 mol% of **3a** at reflux. [c] <sup>1</sup>H NMR ratio of the crude mixture. [d] Subsequent Boc deprotection: TFA (3.0 mmol) in 2.0 mL of 1,2-DCE. [e] At 0.16 mmol scale. [f] *Trans* absolute configuration was determined by X-ray single crystal structure analysis

Additionally, this substrate was diastereoselectively alkylated with pivalaldehyde. Conversion was partial (indoline/indole 3:1 <sup>1</sup>H NMR ratio) but the intermediate was directly engaged in a Lewis-acid mediated reduction with NaBH<sub>4</sub> to cleave the chiral auxiliary and obtain alcohol **5** in good yield with 97% ee (Scheme 4). To illustrate the robustness of our process, the reaction was

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performed up to 2.0 mmol and the corresponding acylated indoline **4ak** was isolated with maintained yield and diastereoselectivity (Scheme 3).

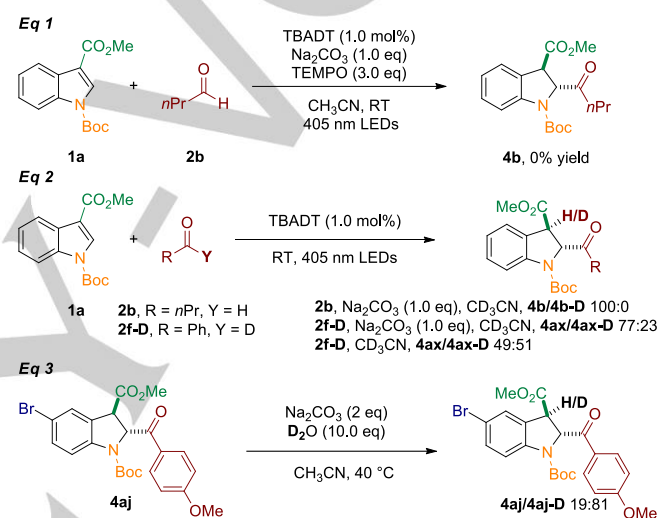
The synthetic utility of this strategy was further demonstrated by a series of successful transformations of indolines **4** (Scheme 4). Inspired by the decarbonylation of  $\beta$ -oxygenated acyl radical, we imagined the alkylation of indole **1b** by 2-((*tert*-butyldimethylsilyl)oxy)acetaldehyde followed by subsequent silylether cleavage affording tetrahydro-1-*H*-furo[3,4-*b*]indol-1-one **6**, a structural motif in diverse natural products, in 44% yield over two steps. Moreover, after DDQ oxidation,<sup>[19]</sup> indoline **4s** was smoothly converted into 2-acylated indole **7**,<sup>[13b]</sup> an important substructure found in natural products.<sup>[20]</sup> Eventually, the Suzuki–Miyaura cross-coupling of **4aj** with phenyl boronic acid under microwave condition, led to the corresponding indoline in 57% yield and with no change of the diastereoselectivity.



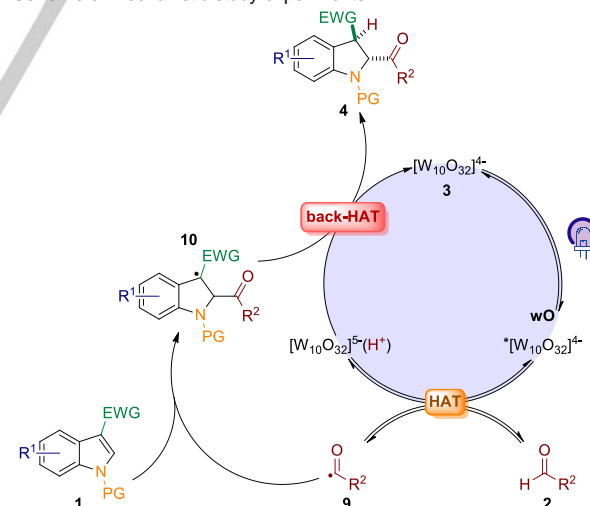
**Scheme 4.** Synthetic transformations of indolines **4**.

To gain further insight into the mechanism of our hydroacylation, we performed some control experiments. Both light stimulation and TBADT photocatalyst are essential for the formation of product (Table 1, entries 16–19). In addition, no reaction took place in the presence of radical scavengers like 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, 3.0 eq) thereby indicating that a radical pathway is involved (Scheme 5, eq 1). A light on/off switch experiment revealed that the transformation required continuous irradiation to proceed (see the Supporting Information). To complete this study, deuteration and H/D exchange experiments were carried out. Firstly, no D incorporation of the cyclized product **4b** was detected when deuterated acetonitrile was employed in presence of  $\text{Na}_2\text{CO}_3$ . In contrast, the addition of deuterated benzaldehyde led to 23% D incorporation in **4ax**. However, when the same reaction was performed in absence of base, deuterium incorporation increased to reach 51%. This result probably indicates a scrambling of the deuterium incorporation due to a base-mediated enolization of indoline **4** (Scheme 5, eq 2) traces of water being the hypothesized proton source. It was

supported by a direct H/D exchange reaction **4aj** with  $\text{D}_2\text{O}$  in acetonitrile in presence of a base (Scheme 5, eq 3). Moreover, the absence of deuterium incorporation when  $\text{CD}_3\text{CN}$  was used indicates that there is no H/D exchange between the solvent and the product (see the Supporting Information). On the basis of the above results and previous reports,<sup>[9c–f,10,11]</sup> a possible mechanism is proposed in Scheme 6. Upon irradiation at 405 nm, decatungstate anion ( $[\text{W}_{10}\text{O}_{32}]^{4-}$ , **3**) is sensitized to an excited triplet state ( $^*[\text{W}_{10}\text{O}_{32}]^{4-}$ , **wO**), which can abstract a hydrogen from aldehyde **2** to generate  $[\text{W}_{10}\text{O}_{32}]^{5-}(\text{H}^+)$  and acyl radical intermediate **9**.<sup>[10a–f,11d]</sup> This resulting nucleophilic species can subsequently undergo a regioselective addition to electron-deficient indole **1** leading to C2-acylated radical **10**. The catalytic cycle eventually finishes with the transfer of both a proton and an electron from  $[\text{W}_{10}\text{O}_{32}]^{5-}(\text{H}^+)$  in a back-HAT like step to form *trans*-indoline product **4**.<sup>[9c]</sup>



**Scheme 5.** Mechanistic study experiments.



**Scheme 6.** Activation model and possible reaction mechanism.

## Conclusion

In conclusion, we have established an efficient diastereoselective photocatalytic dearomative hydroacylation for the synthesis of a variety of *trans*-2-acylindolines using only 1 mol% of inexpensive TBADT photocatalyst. The reaction

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accommodates a wide range of functionalized indoles, and both aromatic and aliphatic aldehydes were successfully employed, although deacylated products were produced with  $\alpha$ -branched aldehydes. This could be partially tuned by conducting the reaction at modulating temperature. In addition, we have developed an efficient synthesis of optically active 2-acylindolines using an indole bearing Oppolzer's camphorsultam chiral auxiliary. The procedure showcases an atom-economic and environmentally friendly method to dearomatize indoles in excellent yields and diastereoselectivities.

## Experimental Section

**General procedure for the photocatalytic dearomative hydroacylation of indoles:** Sodium carbonate (1.0 eq., 0.2 mmol) was charged in a Schlenk tube and the vessel was flame-dried under vacuum then backfilled with argon. TBADT (1.0 mol%, 0.002 mmol) was then charged, followed by the indole derivative (1.0 eq., 0.2 mmol). The Schlenk tube was purged under vacuum then backfilled again with argon 3 times after which the aldehyde (2.0 eq., 0.4 mmol) and distilled solvent (1.0 mL, 0.2 M) was added. The tube was capped with an unpierced septum and the reagents (except  $\text{Na}_2\text{CO}_3$ ) were solubilized. The reaction mixture was degassed by freeze-pump-thaw using 3 cycles, the last one ending with an argon backfilling. The mixture was irradiated for 24 h at 405 nm under a vigorous stirring. At the end of the reaction, the Schlenk tube was opened to air and a saturated aqueous solution of  $\text{NaHCO}_3$  was added. The mixture was diluted with distilled water and  $\text{CH}_2\text{Cl}_2$  and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$ . Combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography using a gradient of petroleum ether and AcOEt to afford the pure indoline.

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**Keywords:** Photocatalysis • Dearomatisation • Hydroacylation • Indole • Decatungstate

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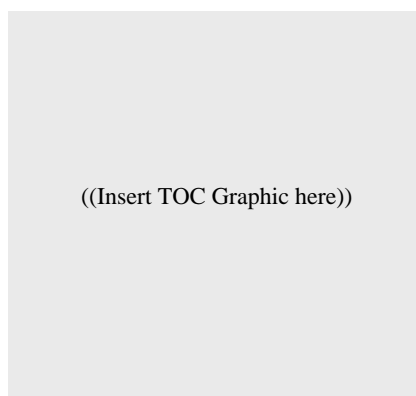
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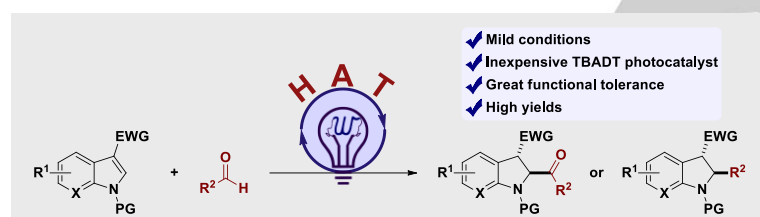
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“A POM out of the blue”. Decatungstate anion photocatalyzed a mild dearomatisation of indoles to access 2-acylindolines via direct hydrogen atom transfer under purple-light irradiation.

Thomas Varlet, Damien Bouchet, Elsa Van Elslande, and Géraldine Masson\*

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