Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

An Asymmetric Dehydrogenative Diels−Alder Reaction for the Synthesis of Chiral Tetrahydrocarbazole Derivatives

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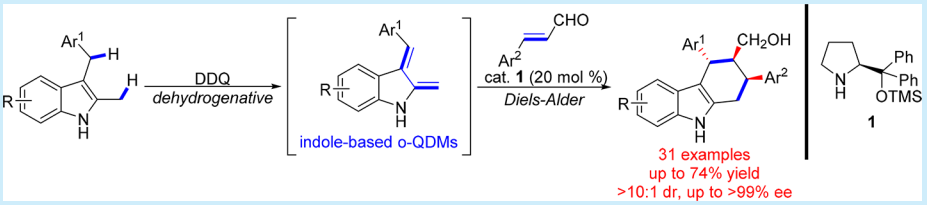
Supporting Information



ABSTRACT: An asymmetric dehydrogenative Diels−Alder reaction of 2-methyl-3-phenylmethylindoles and α,β-unsaturated aldehydes has been established. The successful in situ generation of the indole *ortho*-quinodimethane intermediate and the iminium activation of enals are the keys to success, providing various tetrahydrocarbazole derivatives with up to >99% ee.

The direct functionalization of C−H bonds represents a powerful strategy for the synthesis of structurally complex molecules from commonly available precursors.[1] The cross-dehydrogenative coupling (CDC) of two C−H bonds provides a new perspective on efficient C−C bond formation.[2] Particularly, the dehydrogenative generation of diverse dienes for a Diels−Alder reaction has emerged as a unique protocol for one-step construction of six-membered carbocycles.[3] In 2011, White et al. reported a Pd-catalyzed allylic C−H dehydrogenative oxidation of terminal olefins to generate dienes, which were then trapped by maleimides.[4] Later, Porco et al. employed Pt/C-cyclopentene or DDQ to oxidize allylbenzene derivatives. Diels−Alder reaction of the resulting diene and an enone enabled the total synthesis of Brosimones A and B.[5] Very recently, the Antonchick group successfully expanded the scope of diene precursors to simple alkyl arenes. A variety of electron-deficient alkenes were used as the dienophiles in this Diels−Alder reaction.[6]

Tetrahydrocarbazole containing multiple stereogenic centers, as a privileged structural motif, is widely distributed in naturally occurring indole alkaloids and synthetic pharmaceuticals, which exhibit various significant bioactivities (Figure 1B).[7,8] Despite progress toward the synthesis of tetrahydrocarbazole derivatives, novel and more efficient strategies are still needed to improve the structural diversity, especially in the fields of organic and medicinal chemistry. Dehydrogenative Diels−Alder reaction has also been applied to tetrahydrocarbazole synthesis. Zhang et al. discovered an indole-2,3-quinodimethane[9,10] pathway for DDQ-promoted Diels−Alder reaction of 2-methyl-3-arylmethylindoles and dienophiles (Figure 1A).[9] 3-Ethyl indoles were also amenable to a dehydrogenative Diels−Alder reaction in a similar manner, although further aromatization dominated in this whole process.[11] With our

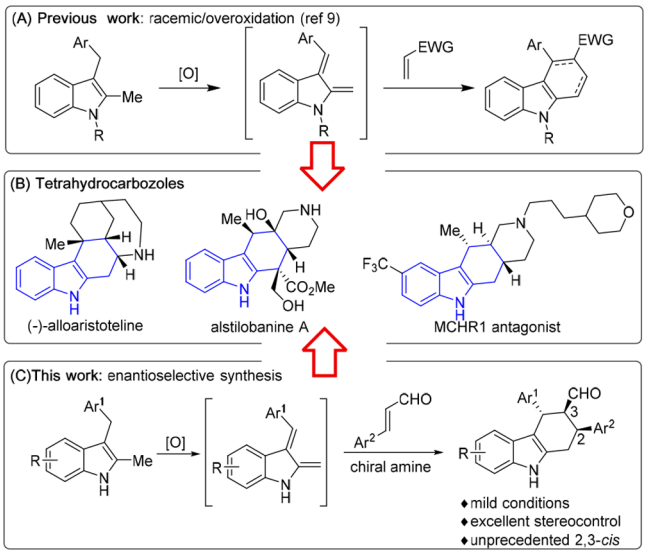


Figure 1. Oxidative dehydrogenative Diels−Alder reactions of indole compounds for synthesis of tetrahydrocarbazoles. EWG = electron-withdrawing group.

continued interest in asymmetric oxidative C−H functionalization, we anticipated developing an enantioselective version of this reaction. To the best of our knowledge, there is no precedent describing an oxidative construction of the chiral tetrahydrocarbazoles, probably due to (1) compatibility issues between oxidants and chiral catalysts[12] and (2) undesired overoxidation. Herein, we report the first asymmetric

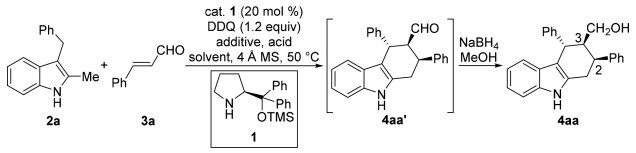
Received: October 18, 2017

DOI: 10.1021/acs.orglett.7b03251
Org. Lett. XXXX, XXX, XXX−XXX

dehydrogenative Diels–Alder reaction of 2-methyl-3-arylmethylindoles and α,β-unsaturated aldehydes (Figure 1C). In this reaction, the classical LUMO-lowering activation of α, β-unsaturated aldehydes by a secondary chiral amine catalyst[13] was able to deliver excellent stereocontrol, affording optically active tetrahydrocarbazoles bearing three contiguous chiral centers.

As the beginning of this work, we evaluated the model reaction of 3-benzyl-2-methyl-1*H*-indole **2a** with cinnamaldehyde **3a**, in the presence of 4 Å MS, using DDQ (2,3-dichloro-5,6-dicyanohydroquinone) as the oxidant and α,α-diphenylprolinoltrimethylsilyl ether[14] **1**/benzoic acid as the catalysis system (Table 1). Gratifyingly, the reaction in $CHCl_3$, at 50 °C,

Table 1. Optimization of the Reaction Conditions[a]



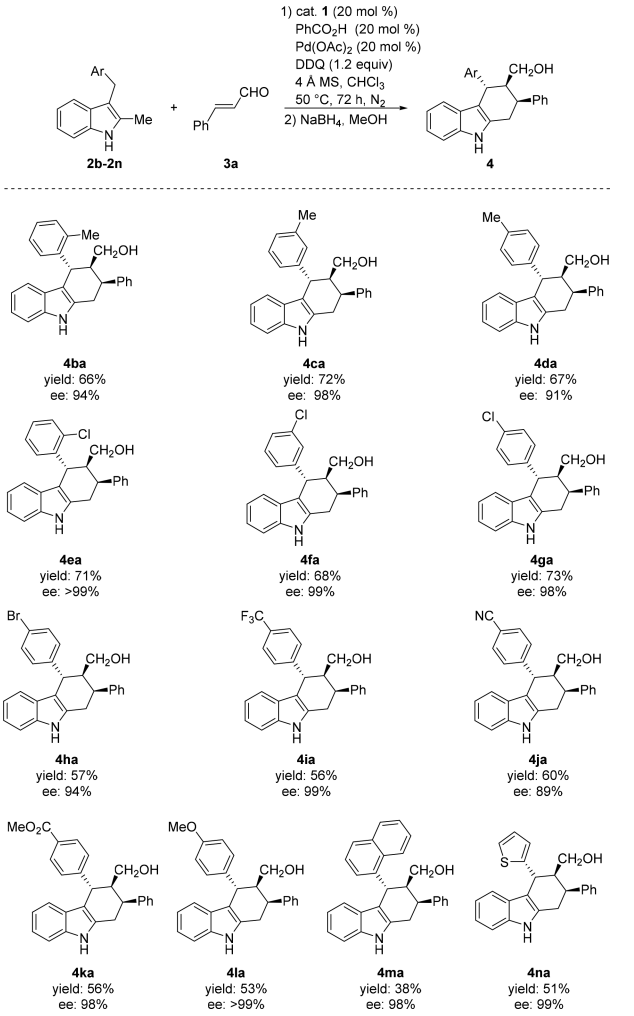
entry	additive	acid	solvent	yield[b](%)	dr[c]	ee[d]
1	-	$PhCO_2H$	$CHCl_3$	57	3:1	99
2	-	$(PhO)_2P(O)OH$	$CHCl_3$	12	3.4:1	n.d.
3	-	AcOH	$CHCl_3$	35	1.4:1	91
4	-	TFA	$CHCl_3$	23	7:1	99
5	-	$PhCO_2H$	$ClCH_2CH_2Cl$	41	2.9:1	99
6	-	$PhCO_2H$	THF	33	1:1	98
7	-	$PhCO_2H$	toluene	29	2:1	99
8	-	$PhCO_2H$	DMSO	-		
9	$CuCl_2$	$PhCO_2H$	$CHCl_3$	50	>10:1	89
10	$NiCl_2$	$PhCO_2H$	$CHCl_3$	63	>10:1	91
11	$Pd(OAc)_2$	$PhCO_2H$	$CHCl_3$	70	>10:1	98
12[e]	$Pd(OAc)_2$	$PhCO_2H$	$CHCl_3$	74	>10:1	99

[a]Unless indicated otherwise, the reaction of **2a** (0.15 mmol), **3a** (0.3 mmol), acid (0.03 mmol), catalyst **1** (0.03 mmol), DDQ (0.18 mmol), and 4 Å MS (50 mg) was carried out in solvent (1.0 mL) at 50 °C for 72 h. n.d. = not determined. [b]Isolated yields of **4aa** for two steps. [c]Determined by ^1H NMR spectroscopic analysis. [d]Determined by HPLC analysis. [e]The reaction was carried out under a N_2 atmosphere.

gave very promising results. After reduction with $NaBH_4$ in MeOH, a 3:1 dr was observed and the major diastereomer **4aa** was isolated in 57% yield with 99% ee along with a minor amount of the oxidative byproduct of 3-benzoyl-2-methyl-1*H*-indole (entry 1). Varying the Brønsted acids generally led to diminished yields (entries 2–4). It is noteworthy that a stronger Brønsted acid improved the diastereoselectivity (entries 2, 4 vs 1). Investigation of solvents, including 1,2-dichloroethane (DCE), tetrahydrofuran (THF), toluene, and DMSO, suggested that $CHCl_3$ was still the best (entries 5–8 vs 1). With the goal of improving the diastereoselectivity, we continued to evaluate the effect of additional additives. A catalytic amount of transition-metal salts indeed improved the result (entries 9–12). For example, the addition of 20 mol % $CuCl_2$ or $NiCl_2$ would give >10:1 dr, however, at the cost of lower enantioselectivities (entries 9–10). In the case of $Pd(OAc)_2$, positive effects on both the yield and diastereoselectivity were observed (70% yield, dr >10:1) without erosion of the enantioselectivity (entry 11). Finally, the reaction under a N_2 atmosphere provided **4aa** in 74% isolated yield, with >10:1 dr and 99% ee (entry 12). The structure and absolute configuration of product **4aa** were assigned by X-ray analysis (see Supporting Information), disclosing an unusual 2,3-*cis* favored Diels–Alder reaction of indole-2,3-quinodimethanes.[11c–f,h,i]

With the optimal conditions in hand, the generality of 2-methyl-3-arylmethylindoles **2** was then investigated. In most cases, substrates with electron-donating or -withdrawing substitutions (**2b–2n**) were amenable to this reaction, delivering the corresponding tetrahydrocarbazoles **4ba–4na** in moderate yields (38%–73%), with excellent diastereoselectivities (all dr >10:1) and enantioselectivities (up to >99% ee) (Scheme 1). The reaction of substrate **2j** bearing a cyano group

Scheme 1. Scope of 2-Methyl-3-arylmethylindoles[a]



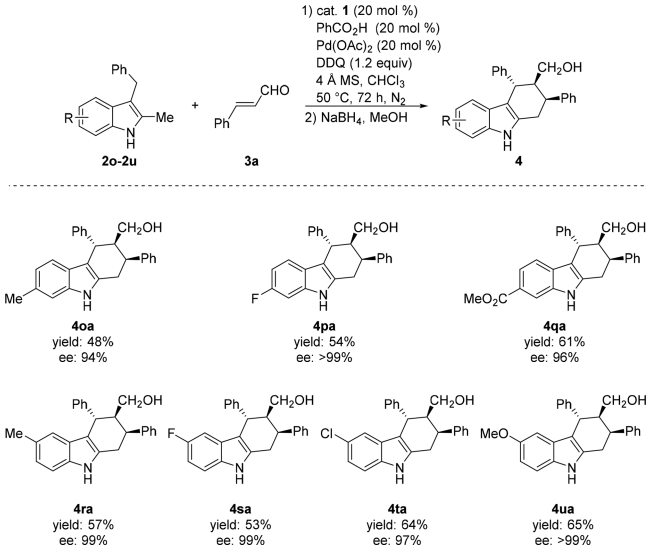
[a]Reaction conditions: **2b–2n** (0.15 mmol), **3a** (0.3 mmol), benzoic acid (0.03 mmol), catalyst **1** (0.03 mmol), $Pd(OAc)_2$ (0.03 mmol), DDQ (0.18 mmol), 4 Å MS (50 mg) in $CHCl_3$ (1.0 mL) under N_2 at 50 °C for 72 h. dr >10:1.

at the *para*-position of the phenyl ring gave product **4ja** with slightly lower 89% ee. 1-Naphthyl-substituted 3-indolemethane also provided product **4ma** with excellent enantioselectivity (98% ee), albeit in low yield. Moreover, 2-thienyl substituted substrate **2n** was tolerated in this reaction, affording **4na** in moderate yield with 99% ee.

Substituents on the indole ring were also well tolerated (Scheme 2). Regardless of the position and electronic character of the substituents, reactions proceeded smoothly under the optimal conditions, furnishing chiral tetrahydrocarbazoles **4oa–**

DOI: 10.1021/acs.orglett.7b03251
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 2. Scope of Substituted 2-Methyl-3-phenylmethylindoles[a]

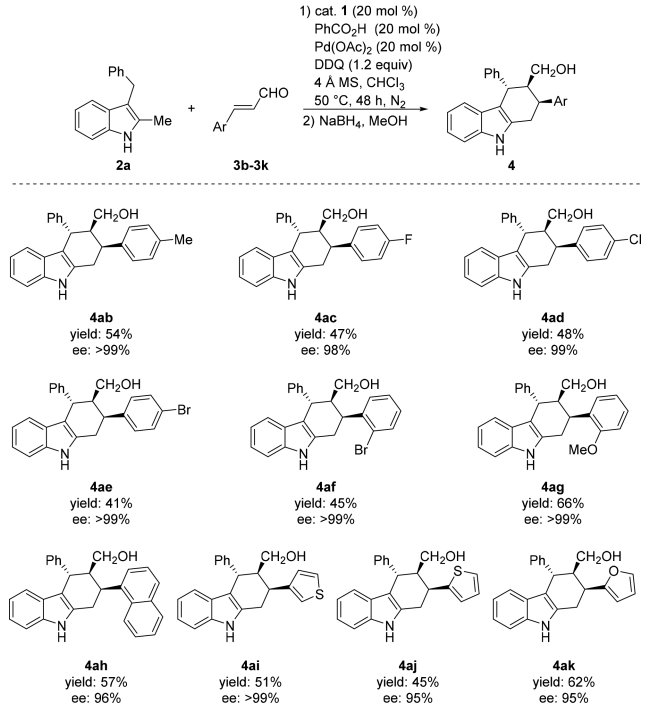


[a]Reaction conditions: **2o**−**2u** (0.15 mmol), **3a** (0.3 mmol), benzoic acid (0.03 mmol), catalyst **1** (0.03 mmol), $Pd(OAc)_2$ (0.03 mmol), DDQ (0.18 mmol), 4 Å MS (50 mg) in $CHCl_3$ (1.0 mL) under N_2 at 50 °C for 72 h. dr >10:1.

4ua in moderate yields (48−65%), with excellent diastereoselectivities (>10:1) and enantioselectivities (94−99% ee).

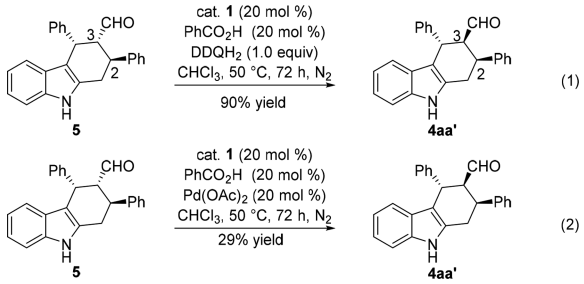
An array of α,β-unsaturated aldehydes with mono-β-aryl or heteroaryl substitutions was examined (Scheme 3). The substituents on the phenyl ring of the cinnamaldehyde had no substantial differences in the stereoselectivities and afforded the corresponding products **4ab**−**4ag** in 41−66% yield, with 98% to >99% ee. Moreover, a β-(1-naphthyl) substituted enal substrate gave the product **4ah** in 57% yield and with 96% ee. Compared to the β-(2-thienyl) substituted enal **3j**, β-(3-thienyl) substituted compound **3i** furnished the product in higher yield and enantioselectivity. Notably, the furan ring of substrate **3k** was compatible with the oxidant and delivered the product **4ak** in 62% yield, with 95% ee.

Scheme 3. Scope of α,β-Unsaturated Aldehydes[a]



[a]Reaction conditions: **2a** (0.15 mmol), **3b**−**3k** (0.3 mmol), benzoic acid (0.03 mmol), catalyst **1** (0.03 mmol), $Pd(OAc)_2$ (0.03 mmol), DDQ (0.18 mmol), 4 Å MS (50 mg) in $CHCl_3$ (1.0 mL) under N_2 at 50 °C for 72 h. dr >10:1.

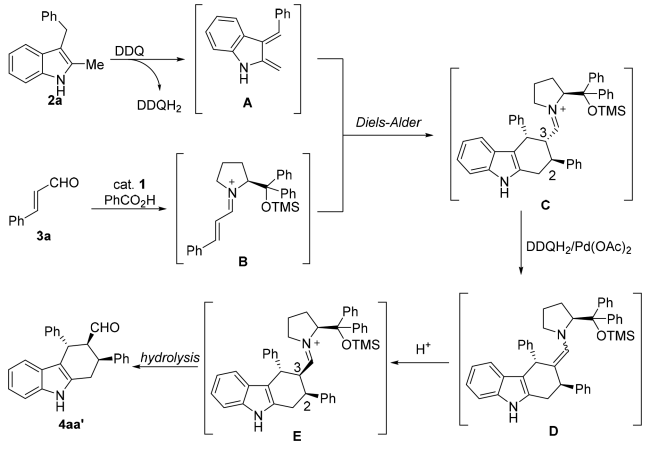
In order to fully understand the reaction process for the generation of the unusual 2,3-*cis* product, two control experiments were performed. In the above oxidation reaction system, $DDQH_2$ (2,3-dichloro-5,6-dicyanohydroquinone)[9] was finally produced as a byproduct which might promote the configuration transformation. Therefore, when the 2,3-*trans* aldehyde **5**[11e] was treated with $DDQH_2$ (1.0 equiv) in the presence of cat. **1** and $PhCO_2H$, the 2,3-*cis* product could be obtained in 90% yield (eq 1). Moreover, the additive $Pd(OAc)_2$



(20 mol %) played a similar role in this transformation and the aldehyde **5** converted to the product **4aa′** (29% yield) partly (eq 2). These facts clearly demonstrated that the unusual 2,3-*cis* product was produced from 2,3-*trans* aldehydes in the presence of $DDQH_2$ and $Pd(OAc)_2$.

To account for the stereochemical outcome of the reaction, we propose a plausible mechanism (Scheme 4). First, the

Scheme 4. Proposed Mechanism



indole *ortho*-quinodimethane intermediate **A** is formed from **2a** under the assistance of DDQ which leads to $DDQH_2$. Iminium ion **B** is generated from the aldehyde **3a** in the presence of cat. **1** and $PhCO_2H$. Then, the Diels−Alder reaction of intermediates **A** and **B** proceeds smoothly and provides the cycloadduct intermediate **C**. $DDQH_2$ and $Pd(OAc)_2$ promote the epimerization of the 3-position of the tetrahydrocarbazole unit and gives the 2,3-*cis* intermediate **E** via chiral enamine **D**.

DOI: 10.1021/acs.orglett.7b03251
Org. Lett. XXXX, XXX, XXX−XXX

Finally, upon hydrolysis and release of the catalyst **1**, iminium ion **E** furnishes 2,3-*cis* **4aa′**.

In conclusion, we have developed a novel asymmetric dehydrogenative Diels−Alder reaction between 2-methyl-3-phenylmethylindoles and α,β-unsaturated aldehydes. The combination of DDQ-promoted generation of the key indole-2,3-quinodimethane intermediate and the iminium activation of enals provided direct access to chiral tetrahydrocarbazole derivatives, along with excellent levels of diastereo- and enantioselectivity. Importantly, this protocol provides a step-economical strategy for synthesis of valuable chiral compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03251.

General and characterization data, ^{1}H and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 1569813 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.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the National Natural Science Foundation of China (NNSFC) (Grant 21672049) and Hefei University of Technology. We sincerely thank Dr. Dian-Feng Chen (Columbia University, US) for helpful discussions.

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