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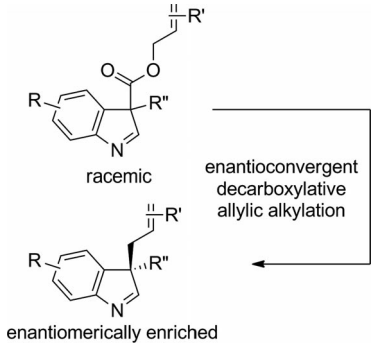
SHORT COMMUNICATION

Enantioconvergent Transformations

The enantioconvergent conversion of racemic allyl indolenin-3-carboxylates into enantiomerically enriched C3-quaternary indolenines is reported. A Pd-catalyzed decarboxylative allylic alkylation reaction is employed for both stereoablation and enantioselective formation of the quaternary carbon center.



Keywords: Enantioconvergent reactions / Palladium / Chirality / Allylic compounds / Boranes

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Catalytic Enantioconvergent Decarboxylative Allylic Alkylation of Allyl Indolenin-3-carboxylates

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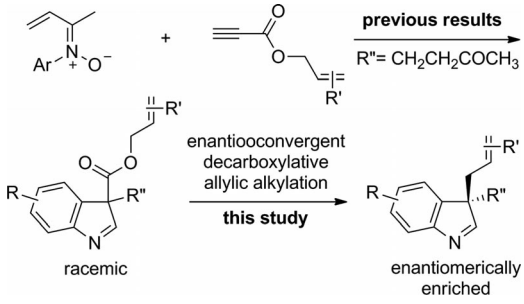
Keywords: Enantioconvergent reactions / Palladium / Chirality / Allylic compounds / Boranes

A catalytic enantioconvergent process has been developed for the conversion of racemic allyl indolenin-3-carboxylates into enantiomerically enriched C3-quaternary indolenines. A Pd-catalyzed decarboxylative allylic alkylation reaction was employed for both stereoablation of the racemic allyl indolenin-3-carboxylates and enantioselective formation of the quaternary carbon center.

Introduction

Enantioconvergent reactions are remarkable processes in which enantiomerically enriched products are produced from racemic starting materials through dynamic kinetic resolution (DKR),[1] dynamic kinetic asymmetric transformation (DYKAT),[2] or direct enantioconvergent transformation (DET).[3] These reactions allow enantioselective synthesis of useful chiral building blocks if the racemic starting materials are readily available. We recently developed approaches for the rapid synthesis of diversely substituted C3-quaternary indolenin-3-carboxylates.[4] Although our efforts for developing enantioselective variants of these reactions have been unsuccessful, we identified that the racemic compounds underwent facile decarboxylation upon saponification of their C3 esters to give the corresponding 3-substituted indoles. On the basis of these preliminary findings, we envisioned a DYKAT process through catalytic enantioselective decarboxylative allylic alkylation to convert these readily available allyl indolenin-3-carboxylates into enantiomerically enriched C3-quaternary indolenines (Scheme 1), which are valuable building blocks for the synthesis of complex indole alkaloids.[5] Significant challenges were anticipated for such a process, as a myriad of side reactions could potentially derail the envisioned process, such as the difficulty of the C3-quaternary allyl ester to undergo oxidative addition with Pd^0 and the ensuing decarboxylation reaction, inadequate π nucleophilicity of the initially formed indoles for reaction with the π–allyl complexes to generate the C3 quaternary center in the dearomatizing process,[6] competing N1- and C2-allylation reactions, and so on. Further, despite a number of reports on the intramolecular C3 alkylation of indoles to give spiroindolenines and on cascade reactions involving C3 alkylation accompanied by spontaneous cyclization of the indolenine intermediates to give the thermodynamically favorable pyrroloindolines or hexahydrocarbazoles,[7] dearomatizing allylic alkylation of 3-substituted indoles to give C3-quaternary indolenines is challenging and has only been rarely explored until recently.[8] Herein, we report the results of our study, which culminated in an enantioconvergent process for the synthesis of C3-quaternary indolenines through deracemization of the quaternary stereocenter of allyl indolenin-3-carboxylates.



Scheme 1. Enantioconvergent decarboxylative allylic alkylation of allyl indolenin-3-carboxylates.

Results and Discussion

Our foray into developing such a process started by testing its feasibility by using common Pd catalyzed allylic alkylation systems with **1a** as a model substrate (Table 1).[9] Following the precedent of Rawal and co-workers for the intermolecular decarboxylative allylic alkylation of indoles,[8b] we treated **1a** with $Pd_2(dba)_3$/(2-furyl)$_3$P (dba = dibenzylideneacetone) in CH_2Cl_2. Although decarboxylation product **3a** was isolated as the major product (56% yield), we were pleased to find that desired 3-allyl-3-alkyl-

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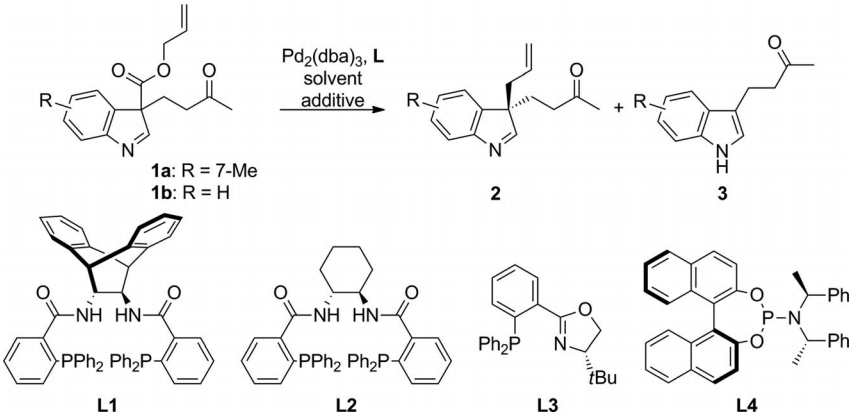
Table 1. Optimization of the reaction conditions.[a]



Entry	1	L	Additive	Solvent	T [°C]	% Yield **2**/**3**	% *ee* **2**[b]
1	**1a**	(2-furyl)$_3$P	none	CH_2Cl_2	23	34:56	n.a.
2	**1a**	(2-furyl)$_3$P	AcOH	CH_2Cl_2	23	0:85	n.a.
3	**1a**	(2-furyl)$_3$P	MeOH	CH_2Cl_2	23	30:70	n.a.
4	**1a**	(2-furyl)$_3$P	CuI	CH_2Cl_2	23	92:0	n.a.
5	**1b**	**L1**	none	CH_2Cl_2	23	0:37	n.a.
6	**1b**	**L1**	CuI	CH_2Cl_2	23	0:0	n.a.
7	**1b**	**L1**	Et_3B	CH_2Cl_2	23	62:16	49
8	**1b**	**L1**	$C_{12}H_{17}BO_2$	CH_2Cl_2	23	0:21	n.a.
9	**1b**	**L1**	hexyl-9-BBN	CH_2Cl_2	0	44:20	55
10	**1b**	**L1**	hexyl-9-BBN	toluene	0	48:14	56
11	**1b**	**L1**	hexyl-9-BBN	$(CHCl_2)_2$	0	44:23	64
12	**1b**	**L1**	hexyl-9-BBN	dioxane	0	48:19	48
13	**1b**	**L1**	hexyl-9-BBN	THF	0	43:20	65
14	**1b**	**L1**	hexyl-9-BBN	THF	–20	35:12	n.d.
15	**1b**	**L2**	hexyl-9-BBN	THF	0	44:21	57
16	**1b**	**L3**	hexyl-9-BBN	THF	0	0:13	n.d.
17	**1b**	**L1**	Ph_3B	THF	0	33:14	n.d.
18	**1b**	**L1**	$(F_6C_5)_3B$	THF	0	0:0	n.d.
19[c]	**1b**	**L1**	hexyl-9-BBN	THF	0	80:0	77

[a] Unless noted otherwise, the following conditions were used for the reactions: $Pd_2(dba)_3$ (2.5 mol-%), ligand (7.5 mol-%), and R_3B (0.5 equiv.) when applicable. [b] n.a.: not applicable, n.d.: not determined. [c] $Pd_2(dba)_3$ (2.3 mol-%), **L1** (11.25 mol-%), and hexyl-9-BBN (1.05 equiv.).

indolenine **2a** was also formed (34% yield; Table 1, entry 1). The efficiency of the reaction could be fine-tuned with additives. For example, whereas only decarboxylation product **3a** was formed when HOAc was used as an additive (Table 1, entry 2), the reaction proceeded essentially quantitatively to convert **1a** into **2a** and **3a** in 30 and 70% yield, respectively, in the presence of MeOH (Table 1, entry 3). The highest reaction efficiency was achieved when CuI was used as the additive; **3a** was formed in 92% yield and only a trace amount of **3b** was generated (Table 1, entry 4).[10]

Having established the feasibility of the reaction, we turned to chiral catalytic systems to develop an enantioconvergent variant of the transformation. Initial experiments with the use of $Pd_2(dba)_3$ and Trost ligand (*R*,*R*)-**L1** and **1b** as the substrate proved to be ineffective, as only decarboxylation product **3b** was formed, together with the recovered starting material (Table 1, entry 5). Surprisingly, the addition of CuI as the additive to the reaction led to complete recovery of the starting material (Table 1, entry 6). Being aware of the positive influence of trialkylboranes in Pd-catalyzed intermolecular allylation and benzylation reactions of indoles,[8a,11] we tested triethylborane (0.5 equiv.) as the reaction additive. Indeed, this led to the formation of **2b** in 62% yield with 49% *ee* (Table 1, entry 7). Encouraged by this result, we also tested *n*-hexylcatecholborane and *n*-hexyl-9-BBN (BBN = borabicyclo[3.3.1]nonane) for their effects. Whereas only decarboxylation product **3b** was formed when *n*-hexylcatecholborane was used (Table 1, entry 8), the addition of hexyl-9-BBN led to the formation of **2b** in 44% yield with 55% *ee* (Table 1, entry 9). Subsequent testing with Ph_3B and $(C_6F_5)_3B$ for reaction additive showed that they were not as effective (Table 1, entries 17 and 18). Further screening of the reaction conditions revealed THF to be the solvent of choice at 0 °C (Table 1, entries 13, 15, and 16) whereas low conversion was observed when the reaction was conducted at –20 °C (Table 1, entry 14). Trost ligand **L2** also catalyzed this Pd-catalyzed enantioconvergent transformation with slightly reduced enantioselectivity (Table 1, entry 15). Somewhat surprisingly, other common catalytic systems, such as $Pd_2(dba)_3$–**L3** (Table 1, entry 16) and $[Ir(cod)Cl]_2$–**L4** (not shown, cod = 1,5-cyclooctadiene), were found to be ineffective. Finally,

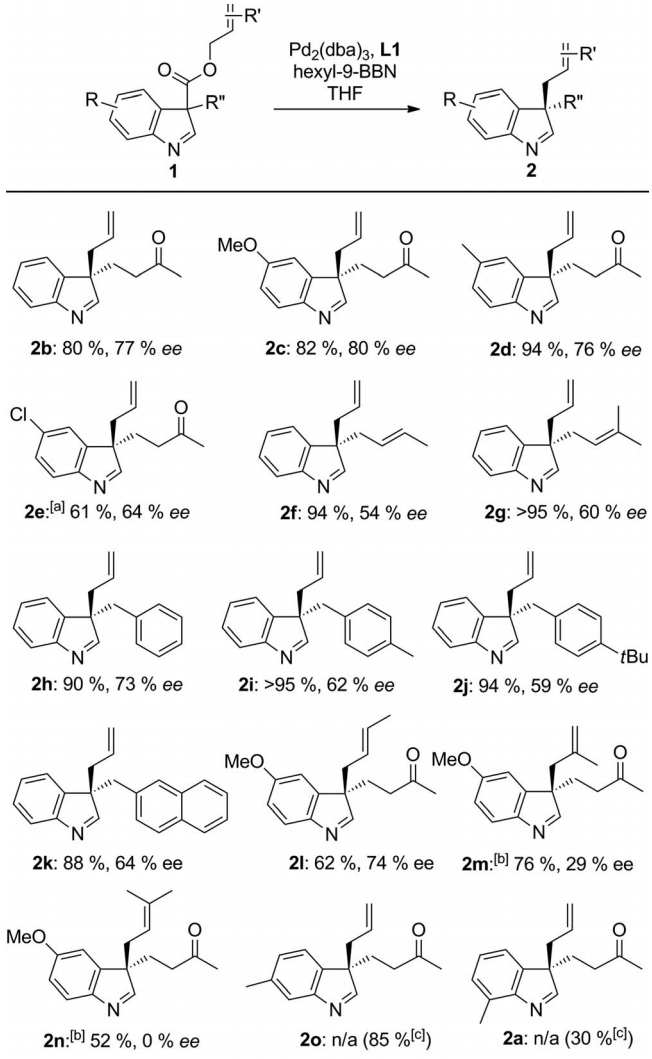
we were pleased to find that formation of decarboxylation product **3b** could be suppressed if a stoichiometric amount of hexyl-9-BBN (1.05 equiv.) was used, and the enantioselectivity could be improved to 77%*ee* if 11 mol-% of **L1** was employed (Table 1, entry 19).[12] The absolute stereochemical configuration of **2b** was assigned as shown by comparing its optical rotation with that of the literature value.[8a]

This enantioconvergent process appeared to be general and gave good yields for most of the substrates that we tested. Substitution at the C5 position was well tolerated. For example, 5-methoxy- and 5-methyl-substituted substrates underwent the decarboxylative allylic alkylation to give the corresponding products (i.e., **2c** and **2d**) in high yields (82 and 94%) with *ee* values (80 and 76%) similar to that of **2b** (Table 2). An electron-withdrawing chloride at the C5 position was also compatible even though the yield (61%) and *ee* (64%) of the product (i.e., **2e**) were somewhat reduced. Allyl indolenine-3-carboxylates with 3-allyl or 3-benzyl substitution gave uniformly high yields (>90%) upon decarboxylative allylic alkylation even though varying *ee* values were observed. For example, whereas prenyl-substituted indolenine **2g** was formed in 60%*ee* upon decarboxylative allylic alkylation, crotyl-substituted indolenine **2f** was formed with slightly lower enantioselectivity of 54%*ee*. Similarly, various benzyl-substituted C3-quaternary indolenines (i.e., **2h** to **2k**) were obtained with 59–73%*ee* upon reaction of the corresponding allyl indolenin-3-carboxylates. We were pleased to observe that **2l** was formed in 62% yield with 74%*ee* from the corresponding crotyl indolenin-3-carboxylate. An elevated reaction temperature (40 °C) was necessary for the reaction of the less-reactive methallyl ester to give **2m** in 76% yield with a low *ee* of 29%. Only racemic indolenine **2n** was formed in 52% yield when the corresponding prenyl ester was subjected to the reaction at elevated temperature. Methyl substitution at the C6 and C7 positions was found to be incompatible with the reaction, as only the decarboxylation products (i.e., **3a** and **3o**) were formed.

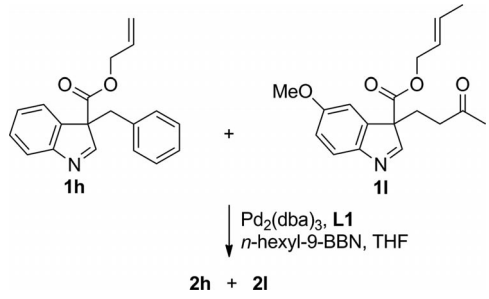
As part of the study and to gain insight into the mechanistic details of the reaction, a crossover experiment was carried out in which a 1:1 mixture of **1h/1l** was subjected to the decarboxylative allylic alkylation reaction conditions (Scheme 2). Only **2h** and **2l** were formed, and this indicates that the reactive species that were formed from each of the substrates remained closely associated during the process and recombined to give the products.

Our experimental findings suggest that the trialkylborane participates in the reaction both as a Lewis acid to facilitate decarboxylative elimination of the C3 esters and as part of a strongly π-nucleophilic *N*-indolyltrialkylborate species for dearomatizing C3-allylic alkylation to form the quaternary carbon center. A proposed reaction mechanism that accounts for these effects is depicted in Scheme 3.[13] First, N–B coordination of indolenine (**1**) and trialkylborane forms electron-deficient 3*H*-indolium intermediate **A**. This leads to activation of the allyl ester towards oxidative addition of Pd^0 and facilitates decarboxylation of the resulting C3 carboxylate to give tightly associated ion pair **B**.[14] Subsequent C3 allylation of the solvent-caged *N*-indolyltrialkylborate and the chiral cationic Pd–π–allyl complex gives **C**, which dissociates to form enantiomerically enriched C3-quaternary indolenine **2**. Formation of the electron-rich *N*-indolyltrialkylborate species leads to increased π-nucleo-

Table 2. Substrate scope.

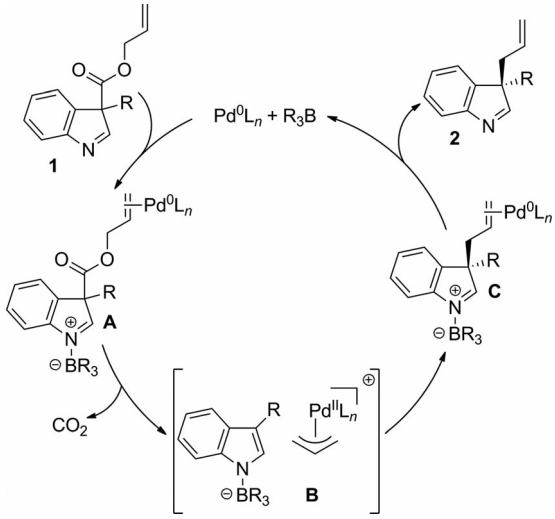


[a] Reaction carried out at room temperature. [b] Reaction carried out at 40–45 °C. [c] Yield of the decarboxylation product.



Scheme 2. A crossover experiment.

philicity for the dearomatizing C3 allylation reactions. Consistent with this hypothesis, only the decarboxylation product (i.e., **3a**) was formed when **1a** was subjected to the reaction conditions, likely due to impeded N–B coordination as a result of 7-Me substitution, which prevented formation of the nucleophilic *N*-indolyltrialkylborate species.[15]



Scheme 3. A proposed reaction mechanism.

Conclusions

We developed an enantioconvergent process for the conversion of racemic allyl indolenin-3-carboxylates into enantiomerically enriched C3-quaternary indolenines. This transformation employs a Pd-catalyzed decarboxylative allylic alkylation for both stereoablation and dearomatizing enantioselective alkylation to give the C3 quaternary center. Both the nucleophile and the electrophile are derived from the allyl indolenin-3-carboxylate under Pd catalysis. The trialkylborane was found to be an essential additive to the reaction. We attribute this trialkylborane effect to its ability to participate both as a Lewis acid to facilitate the decarboxylation process and as part of a strongly π-nucleophilic *N*-indolylborate species for dearomatizing the allylic alkylation to form the C3 quaternary centers. Studies to further explore the synthetic utility of these borate species are in progress.

Experimental Section

Borane Generation: A flame-dried, 3 mL conical flask was placed under an atmosphere of nitrogen and charged with a solution of 9-BBN (0.5 M in THF, 0.63 mL, 0.315 mmol). This solution was then diluted with THF (0.63 mL) and 1-hexene (93 μL, 0.75 mmol) was added. The reaction was stirred at room temperature for 4 h.

Enantioconvergent Decarboxylative Allylic Alkylation: A flame-dried, 10 mL flask was charged with $Pd_2(dba)_3$ (4.0 mg, 0.004 mmol) and (*R*,*R*)-ANDEN-phenyl Trost ligand **L1** (17.4 mg, 0.0214 mmol). The contents of the flask were placed under a nitrogen atmosphere and THF (4.4 mL) was added and stirred for 10 min at room temperature. The solution was cooled to 0 °C and cannulated to a flask containing (±)-allyl indolenin-3-carboxylate (0.19 mmol) under a nitrogen atmosphere at 0 °C. The reaction was stirred for 2 min at 0 °C and the aforementioned borane solution (0.8 mL) was added. The reaction was sealed with Parafilm® and stirred at 0 °C for 16 h.

Workup Procedure A: The reaction was quenched with the addition of a saturated aqueous solution of $NaHCO_3$ (3 mL), and the mixture was vigorously stirred for 2 h. The mixture was then diluted with water (5 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was dried (Na_2SO_4), filtered, and concentrated.

Workup Procedure B: The reaction was quenched with the addition of 2 N NaOH (2 mL) and diluted with EtOAc (3 mL). The mixture was then vigorously stirred for 2 h before it was diluted with water (5 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was dried (Na_2SO_4), filtered, and concentrated.

Workup Procedure C: Ethanolamine (35 μL, 0.57 mmol) was added to the reaction mixture, and the solution was stirred vigorously for 2 h. The resulting mixture was filtered, and the filtrate was washed with EtOAc (15 mL). The combined organic phase was washed with a saturated aqueous solution of Na_2CO_3 (5 mL) and brine (5 mL) before it was dried with Na_2SO_4, filtered, and concentrated.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures and characterization data, including ^{1}H NMR, ^{13}C NMR, and HRMS spectra and chiral HPLC traces for new compounds.

Acknowledgments

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[10] The effect of CuI appears to be specific to **1a**, as no reaction was observed when unsubstituted allyl indolenin-3-carboxylate (**1b**) was treated under the same reaction conditions.

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[12] See the Supporting Information for a list of the conditions that were tested.

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[14] An alternative pathway for Lewis acidic activation through O–B coordination of the trialkylborane and the carbonyl group of **2** is less likely because of the sterically congested environment.

[15] It is unclear why C6-methyl-substituted indolenine (i.e., **2o**) also failed to form under the reaction conditions.

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