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Asymmetric Michael Addition of 1-Acetylindolin-3-ones to β-Nitrostyrenes Catalyzed by Bifunctional Thioureas: A Simple Access to 2-Functionalized Indoles

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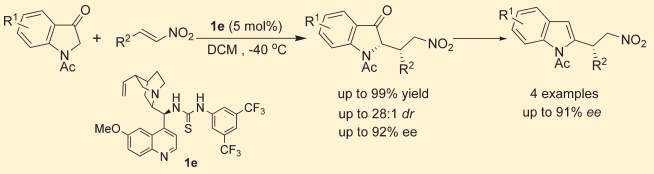
Supporting Information

ABSTRACT: The first asymmetric Michael addition of 1-acetylindolin-3-ones to β-nitrostyrenes has been developed. 2-Substituted indolin-3-one derivatives were obtained with excellent yields (up to 99%) and good stereoselectivities (up to 28:1 dr and 92% ee), which could be transformed into 2-functionalized indoles easily without racemization. This achievement might further contribute to the chemistry and pharmacology of indole-related compounds.



The catalytic asymmetric Michael addition is one of the most important approaches to carbon−carbon bond formation in asymmetric synthesis. Remarkable progress has been made in the organocatalytic version of this reaction in recent years.[1,2] Many chemists in the world continue to investigate new substrates, catalysts, and catalytic systems. Indole is a common building unit, and its interesting chemical properties have inspired chemists to design and synthesize a variety of its derivatives. Since its discovery in 1866, more than 80000 papers related to indole chemistry have been published.[3]

Because of the reactive difference between the 2- and 3-positions of indole, much more successful examples have been applied to the formation of 3-substituted indoles than to the formation of 2-substituted indoles.[4] Thus, the preparation of 2-substituted indoles, particularly optically active ones, is still a challenge.[5] Although You et al. and Wang et al. have reported organocatalyzed asymmetric Friedel−Crafts reactions of 4,7-dihydroindoles to provide 2-substituted indole derivatives after subsequent oxidation, these reactions were limited by substrate scope and harsh reaction conditions.[6] Recently, the Takenaka group has also reported an efficient approach to C2-alkylated indole derivatives with the asymmetric conjugate addition of 4,7-dihydroindoles to β-nitrostyrenes catalyzed by 2-aminopyridinium ions.[7] Indolin-3-ones, a class of important building blocks, are used in total synthesis frequently.[8] However, compared to 2-oxindoles,[9] the application of indolin-3-ones as nucleophiles is limited.[10] Herein, we report the first highly enantio- and diastereoselective addition of 1-acetylindolin-3-ones to nitroolefins catalyzed by thioureas and its application to the synthesis of 2-functionalized indoles.

We initially investigated the reaction of 1-acetylindolin-3-one **2a** with *trans*-β-nitrostyrene **3a** in the presence of readily available diarylprolinol trimethylsilyl ether **1a** (20%) in DCM. The Michael addition proceeded slowly to afford desired product **4a** in 44% yield almost without stereoselectivity (Table 1, entry 1). (*S*)-1-(2-Pyrrolidinylmethyl)pyrrolidine **1b**,[11] thiourea−primary amine catalyst **1c**, and thiourea−secondary amine catalyst **1d** also gave almost racemic product.

To our delight, thiourea−cyclic tertiary amine catalysts (**1e** and **1f**) provided good yields, diastereoselectivities, and enantioselectivities.[12] The best outcome was obtained with bifunctional catalyst **1e** derivated from quinine (Table 1, entry 5).

The screening of different organic solvents with 5% catalyst **1e** was carried out. The reaction proceeded faster in chlorinated solvents (Table 2, entries 1 and 3). In polar solvents such as EtOH and THF, the reaction occurred in high yields but lower enantioselectivities (Table 2, entries 4 and 5). When the reaction temperature was dropped to −40 °C in DCM, the best result was obtained with 99% yield, 12:1 dr, and 91% ee (Table 2, entry 8). Increasing the catalyst loading to 10% did not show any beneficial effect to the diastereo- and enantioselectivity (Table 2, entry 9).

Under optimized reaction conditions, a wide range of nitroolefins **3** and 1-acetylindolin-3-ones **2** were investigated in this asymmetric Michael addition reaction. The results are summarized in Table 3. In most cases, excellent yields and good dr and ee values were obtained for the desired products.[13] Structural variation of nitroolefins could be tolerated (Table 3). The electron-withdrawing (Table 3, entries 4−10), electron-donating (Table3, entries 2 and 3), and neutral (Table 3, entry 1) systems could participate in the reactions. And the electronic nature of the aromatic ring of nitroolefin had limited influence on the stereochemical outcome. 2-Furyl-substituted nitroolefin **3k** was also well tolerated under the optimized reaction conditions (97% yield, 11:1 dr and 89% ee; Table 3, entry 11). Unfortunately,

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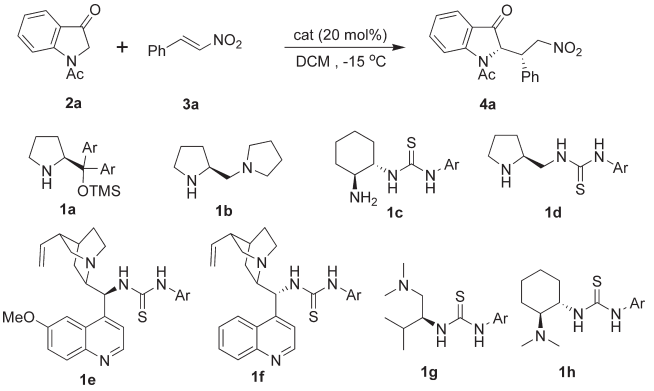
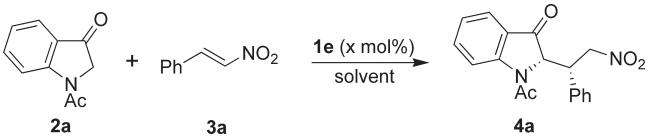
Table 1. Screening of the Catalysts



entry[a]	1	time (h)	yield (%)	dr[b]	ee[c] (%)
1	**1a**	24	44	5:1	−7
2	**1b**	24	91	2.1:1	−6
3	**1c**	24	83	2.2:1	13
4	**1d**	24	99	2:1	8
5	**1e**	1	96	9:1	88
6	**1f**	1	94	8:1	−84
7	**1g**	2	76	8:1	−78
8	**1h**	2	62	2.2:1	−77

[a] Unless otherwise noted, reactions were carried out with **2a** (0.2 mmol), **3a** (0.3 mmol), and catalyst **1** (20%) in 0.4 mL DCM at −15 °C. [b] Determined by ^{1}H NMR spectroscopic analysis of the crude product mixture. [c] Determined by chiral HPLC analysis. Ar = 3,5-$(CF_3)_2C_6H_3$

Table 2. Optimization of the Reaction Conditions

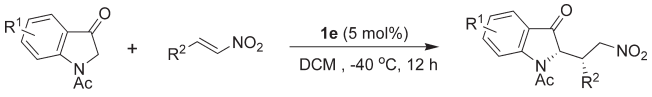


entry[a]	**1e** (mol %)	solvent	T (°C)	time (h)	yield (%)	dr[b]	ee[c] (%)
1	5	DCM	−15	3	91	10:1	84
2	5	toluene	−15	8	92	6:1	88
3	5	$CHCl_3$	−15	3	88	6:1	85
4	5	THF	−15	24	98	10:1	73
5	5	EtOH	−15	24	99	5:1	35
6	5	toluene	−40	24	97	9:1	90
7	5	$CHCl_3$	−40	10	92	8:1	84
8	5	DCM	−40	12	99	12:1	91
9	10	DCM	−40	6	97	10:1	91

[a] Reaction conditions: 0.2 mmol of **2a**, 0.3 mmol of **3a** in 0.4 mL of solvent. [b] Determined by ^{1}H NMR spectroscopic analysis of the crude product mixture. [c] Determined by chiral HPLC analysis.

cyclohexyl-substituted nitroolefin **3l** (Table 3, entry 12) took no reaction under the optimized reaction conditions. When the reaction temperature was raised to 16 °C, the reaction proceeded well in the presence of 20% **1e** to give the product in 96% yield, 1.3:1 dr, and 67% ee. Substituted 1-acetylindolin-3-ones were also well tolerated (Table 3, entries 13 −16).[14] With this protocol, highly enantioenriched 2-substituted 1-acetylindolin-3-ones could be easily obtained.

Table 3. Catalytic Asymmetric Michael Addition of 1-Acetylindolin-3-ones to Nitroolefins



entry[a]	R^1	R^2	yield (%)	dr[b]	ee[c] (%)
1	H	Ph	99 (**4a**)	12:1	91
2	H	4-MeC_6H_4	90 (**4b**)	13:1	88
3	H	2-$MeOC_6H_4$	96 (**4c**)	26:1	91
4	H	2-BrC_6H_4	92 (**4d**)	4:1	87
5	H	3-BrC_6H_4	75 (**4e**)	10:1	80
6[d]	H	4-BrC_6H_4	97 (**4f**)	28:1	86
7	H	3-$NO_2C_6H_4$	94 (**4g**)	12:1	78
8	H	2-ClC_6H_4	98 (**4h**)	18:1	90
9	H	3-ClC_6H_4	95 (**4i**)	15:1	89
10	H	4-ClC_6H_4	91 (**4j**)	18:1	90
11	H	2-furyl	97 (**4k**)	11:1	89
12[e]	H	cyclohexyl	96 (**4l**)	1.3:1	67 (80[f])
13	5-Me	Ph	93 (**4m**)	8:1	91
14	4-Br	Ph	91 (**4n**)	13:1	92
15	5-Br	Ph	89(**4o**)	12:1	92
16	6-COOMe	Ph	80(**4p**)	11:1	85

[a] Unless otherwise noted, the reactions were carried out with **2** (0.2 mmol), **3** (0.3 mmol), and catalyst **1e** (5%) in 0.4 mL of DCM at −40 °C. [b] Determined by ^{1}H NMR spectroscopic analysis of the crude product mixture. [c] Determined by chiral HPLC analysis. [d] The reaction needed 24 h to complete. [e] The reaction was performed at 16 °C for 36 h, and 20% **1e** was used. [f] The ee value of the minor diastereomer.

Table 4. Synthesis of 2-Substituted Indole Derivatives

entry[a]	4	yield (%)	ee[b] (%)
1	**4a** (Ph)	57 (**5a**)	91
2	**4c** (2-$MeOC_6H_4$)	55 (**5c**)	90
3	**4f** (4-BrC_6H_4)	61 (**5f**)	86
4	**4i** (3-ClC_6H_4)	54 (**5i**)	88

[a] Reaction conditions: see the Supporting Information for details. [b] Determined by chiral HPLC analysis; see the Supporting Information.

In order to apply this reaction in the synthesis of 2-substituted indole derivatives, 2-substituted 1-acetylindolin-3-ones **4** were reduced with $NaBH_4$ in MeOH followed by dehydration in the presence of *p*-TSA at 80 °C. Fortunately, although one stereogenic center was destroyed, the desired 2-substituted indoles **5** were obtained in moderate yields and good enantioselectivities. This transformation provided a convenient access to 2-substituted indoles.

To determine the absolute configuration of the asymmetric Michael adduct, a single crystal of compound **4f** bearing a bromine atom was obtained for X-ray crystallographic analysis.[15] As shown in Figure 1, the newly formed stereogenic centers in **4f** were confirmed as *S*,*S*.

On the basis of the observed reactivity and experimental results of the Michael addition reactions, we propose that the reaction proceeds via a dual activation model. As shown in Figure 2, a thiourea moiety of the catalyst **1e** interacts through

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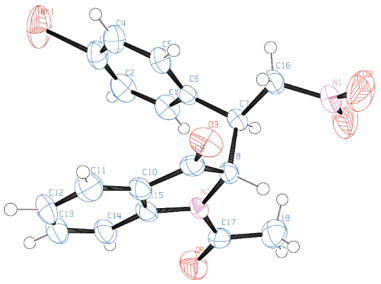

Figure 1. X-ray crystal structure of **4f**.

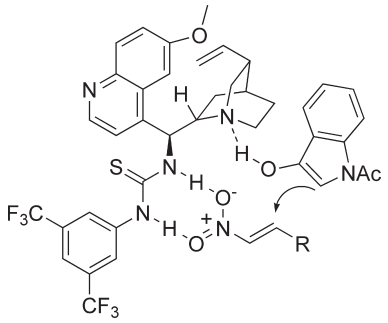

Figure 2. Proposed transition state model in the Micheal addition.

hydrogen bonding with a nitro group of the nitroalkene and enhances their electrophilicity while the tertiary amine deprotonates an acidic proton of 1-acetylindolin-3-one, generating a ternary complex. This proposed dual activation model might be responsible for the stereochemical outcome of the Michael adducts.

In conclusion, we have developed a bifunctional thiourea−tertiary amine-catalyzed asymmetric Michael addition of 1-acetylindolin-3-ones to β-nitrostyrenes in excellent yields and high diastereo- and enantioselectivities. The corresponding products could be subsequently converted to 2-functionalized indoles without loss of enantioselectivities. Further investigation and application of this methodology are ongoing.

EXPERIMENTAL SECTION

Representative Procedure for the Michael Addition of 1-Acetylindolin-3-one to β-Nitrostyrene (Table 3, Entry 1). To a solution of 1-acetylindolin-3-one **2a** (35 mg, 0.2 mmol, 1.0 equiv) and thiourea catalyst **1e** (6 mg, 0.01 mmol, 0.05 equiv) in freshly distilled DCM (0.4 mL) at −40 °C was added *trans*-β-nitrostyrene **3a** (45 mg, 0.3 mmol, 1.5 equiv). The resulting solution was stirred at −40 °C for 12 h. The reaction was quenched with saturated aqueous ammonium chloride solution. The aqueous layer was separated and extracted with ethyl acetate (3 times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography (PE/EA = 2:1) to afford 64 mg (99% yield) of **4a** (91% ee) and its minor diastereomer as a colorless oil (12:1 dr). Analytical data for **4a**: $[\alpha]_D^{20} = -59$ (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (s, 1H), 7.51−7.44 (m, 2H), 7.07−7.00 (m, 6H), 5.62 (dd, *J* = 6.0, 14.0 Hz, 1H), 5.32 (dd, *J* = 8.0, 14.0 Hz, 1H), 4.94 (d, *J* = 4.0 Hz, 1H), 4.39 (s, 1H), 2.52 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.0, 168.7, 136.9, 133.0, 128.2, 128.0, 127.9, 127.8, 124.7, 123.7, 122.7, 73.8, 65.5, 43.8, 24.0; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{20}N_3O_4$ $[M + NH_4]^+$:342.1448, found 342.1444. The enantiomeric excess was determined by HPLC with an AS-H column. (*n*-hexane/*i*-PrOH = 80:20), 1.0 mL/min; minor enantiomer, t_R = 31.9 min, major enantiomer, t_R = 41.0 min.

ASSOCIATED CONTENT

Supporting Information. Experimental details, spectral data for the products, and X-ray crystallographic data (CIF file of **4f**: CCDC 787026). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) CCDC 787026 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.