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Brønsted Acid/Rhodium(II) Cooperative Catalytic Asymmetric Three-Component Aldol-Type Reaction for the Synthesis of 3-Amino Oxindoles

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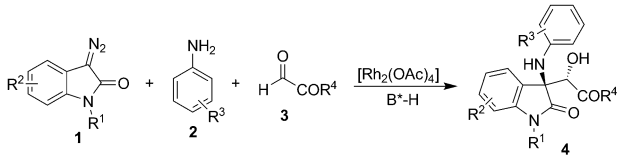
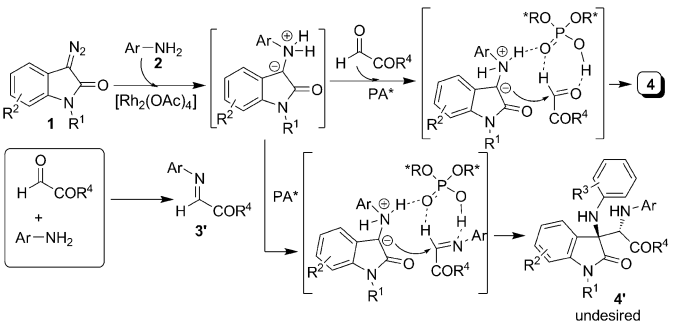
The prevalence of the 3,3′-disubstituted oxindole skeleton as a core structural element in a large family of natural products and biologically interesting molecules has attracted increasing attention from research groups worldwide to develop efficient and stereocontrolled methods of constructing quaternary stereogenic carbons of this type.[1–4] Of the known 3,3′-disubstituted oxindoles, those that contain an amine functionality at C3 have been found in many biologically active compounds[5] and, therefore, the stereoselective construction of structures of this type is of significant synthetic importance. The known procedures to construct 3-amino oxindoles have been established by using the asymmetric amination of 3-substituted oxindoles,[6] addition reaction to isatin imines,[7] and other methods.[8] Despite these elegant achievements, stereoselective multicomponent synthetic methods to access highly functionalized 3-amino-2-oxindole derivatives are still in great demand.

Previously, Hu and co-workers described a three-component aldol-type reaction of diazo esters and anilines with aryl aldehydes by using rhodium(II) acetate as a catalyst.[9] However, the resultant products were obtained in low diastereoselectivities. Moreover, an enantioselective version of this protocol has not been realized yet.[10] Hu and our group found that a combination of the rhodium complex with chiral phosphoric acids was able to effectively control the enantioselectivity of three-component Mannich-type reactions that involved diazo esters, alcohols, and imines.[11] Subsequently, Hu and co-workers successfully applied this strategy to other related transformations.[12] Zhou and co-workers identified the fact that binary catalysts of this type enable the amide and diazo esters to undergo a highly stereoselective N–H insertion reaction.[13] Terada and Toda demonstrated that the binary catalyst system was able to render a relay catalytic cascade carbonyl ylide formation and enantioselective reduction reaction.[14] However, such a combined catalyst has not yet been applied to the enantioselective three-component aldol-type reactions of diazo esters and anilines (or alcohols) with aldehydes. Herein, we report a highly enantioselective three-component reaction of 3-diazooxindoles and anilines with glyoxylates cooperatively catalyzed by a rhodium complex and chiral phosphoric acid, which gives highly functionalized 3-amino oxindoles with excellent enantioselectivities (Scheme 1).



Scheme 1. Brønsted acid/rhodium acetate cooperative catalytic asymmetric three-component aldol-type reaction for the synthesis of 3-amino oxindoles.

The reaction basically proceeds via a rhodium-catalyzed generation of ammonium ylides from 3-diazooxindoles (**1**) and anilines (**2**) followed by a chiral Brønsted acid-catalyzed enantioselective aldol-type reaction with glyoxylates to give optically active products **4**. In this reaction, the phosphoric acid presumably activates the formyl group of the glyoxylates through a hydrogen-bonding interaction,[15] and simultaneously the phosphoryl oxygen might be able to function as a Lewis base capable of forming an additional hydrogen bond with ammonium ylides to stabilize the transition state (Scheme 2).[2e,16] As such, the key point to control the stereoselectivity would be the chiral Brønsted acids. However, anilines are principally able to form imines **3′** with glyoxylates[17] and, therefore, the competitive Mannich reaction that gives undesired **4′** could occur under the catalysis of the



Scheme 2. The proposed pathway for the title reaction.

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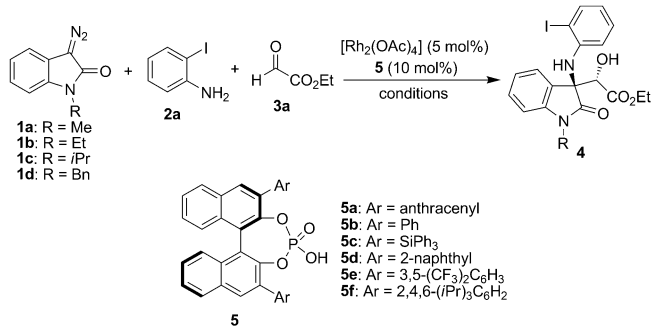
Brønsted acid, as reported previously.[11] Thus, the chemoselectivity is another challenge in addition to control of the stereoselectivity (Scheme 2).

The validation of the hypothesis started with a reaction of *N*-methyl-3-diazo oxindole **1a** with 2-iodoaniline **2a** and ethyl glyoxylate **3a** in dichloromethane by using rhodium acetate (2 mol%) and binol-based phosphoric acid **5a** (10 mol%) as the combined catalyst. As we expected, the reaction indeed proceeded to give desired product **4aa** in 74% yield, but the stereoselectivity turned out to be unsatisfactory and the minor diastereomer was obtained in higher enantioselectivity (Table 1, entry 1). It is worth mentioning

Table 1. Optimization of reaction conditions.[a]



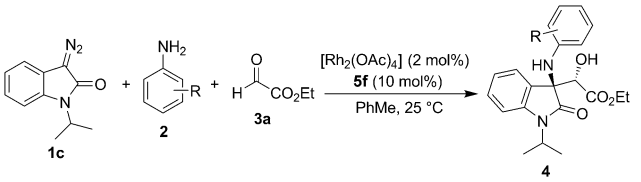
Entry	5	1	Solvent	4	Yield [%][b]	d.r.[c]	*ee* [%][d]
1	**5a**	**1a**	CH_2Cl_2	**4aa**	74	1.6:1	34 (80)
2	**5b**	**1a**	CH_2Cl_2	**4aa**	82	2.5:1	35 (62)
3	**5c**	**1a**	CH_2Cl_2	**4aa**	88	1.5:1	68 (45)
4	**5d**	**1a**	CH_2Cl_2	**4aa**	72	1.9:1	21 (83)
5	**5e**	**1a**	CH_2Cl_2	**4aa**	86	1.7:1	16 (37)
6	**5f**	**1a**	CH_2Cl_2	**4aa**	77	3.5:1	73 (62)
7	**5f**	**1a**	$CHCl_3$	**4aa**	60	3.8:1	66 (42)
8	**5f**	**1a**	CCl_4	**4aa**	60	4.0:1	75 (70)
9	**5f**	**1a**	PhF	**4aa**	65	4.0:1	73 (57)
10	**5f**	**1a**	PhCl	**4aa**	62	3.8:1	71 (35)
11	**5f**	**1a**	PhMe	**4aa**	62	4.2:1	82 (51)
12[e]	**5f**	**1a**	PhMe	**4aa**	76	4.5:1	82 (53)
13[f]	**5f**	**1a**	PhMe	**4aa**	70	4.5:1	82 (50)
14[e]	**5f**	**1b**	PhMe	**4ba**	80	5.5:1	77 (0)
15[e]	**5f**	**1c**	PhMe	**4ca**	92	10:1	85 (55)
16[e]	**5f**	**1d**	PhMe	**4da**	65	5.0:1	74 (50)
17[e,g]	**5f**	**1c**	PhMe	**4ca**	trace	–	–

[a] Unless indicated otherwise, the reaction was carried out by addition of **1** (0.15 mmol) and **2a** (0.15 mol) in solvent (1 mL) to a mixture of $[Rh_2(OAc)_4]$ (2 mol%), **3a** (1.5 mmol), and **5** (10 mol%) in solvent (1.0 mL) at 25°C for 1 h. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy of the crude product. [d] Major (minor) diastereomer, determined by using HPLC. [e] The ratio of **1/2a/3a** was 1:1:5. [f] The ratio of **1/2a/3a** was 1:1:2. [g] At 0°C.

that the undesired Mannich reaction was not observed (**4′** in Scheme 2), presumably because the aldol-type reaction is faster than the corresponding Mannich side-reaction. A survey of chiral phosphoric acids identified (*R*)-TRIP (**5f**; TRIP = 3,3′-bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate) as a promising co-organocatalyst in terms of the diastereo- and enantioselectivity (Table 1, entries 2–6). Solvent screening revealed that nonpolar solvents are seemingly the reaction media of choice (Table 1, entries 7–11). In particular, toluene provided the best results (Table 1, entry 11). Increasing the stoichiometry of ethyl glyoxylate considerably improved the yields and maintained the stereoselectivity (Table 1, entries 12 and 13). Variation of the *N*-substituent of 3-diazo oxindoles **1** led to obvious influences on the reaction (Table 1, entries 14–17). Of these substrates, *N*-isopropyl-3-diazo oxindole **1c** gave the highest stereoselectivity (Table 1, entry 15). Lastly, the reaction was completely inhibited upon lowering the reaction temperature to 0°C (Table 1, entry 17).

Under the optimized conditions, the generality of the reaction towards anilines was investigated first (Table 2). A variety of substituents on the aniline could be tolerated. Ba-

Table 2. The generality of the reaction towards anilines.[a]



Entry	2, R	4	Yield [%][b]	d.r.[c]	*ee* [%][d]
1	**2b**, 2-Br	**4cb**	99	11:1	80
2	**2c**, 2-Cl	**4cc**	98	11:1	82
3	**2d**, 2-CN	**4cd**	91	16:1	91
4	**2e**, 2-CO_2Me	**4ce**	85	13:1	93
5	**2f**, 2-COPh	**4cf**	63	10:1	90
6	**2g**, 2-COMe	**4cg**	92	22:1	97
7	**2h**, 2-CO_2Me, 4-Br	**4ch**	95	38:1	99
8	**2i**, 2-CO_2Me, 4-Cl	**4ci**	88	27:1	98
9	**2j**, 2,5-$(CO_2Me)_2$	**4cj**	89	23:1	99
10	**2k**, 2-COMe, 4-Me	**4ck**	74	19:1	99
11	**2l**, 2-COMe, 4-Br	**4cl**	96	31:1	98
12	**2m**, 2-COMe, 4-Cl	**4cm**	87	22:1	90
13	**2n**, 2-COMe, 4-F	**4cn**	81	38:1	97
14	**2o**, 2-COMe, 3-F	**4co**	85	23:1	99
15	**2p**, 2-COMe, 5-F	**4cp**	88	21:1	95
16	**2q**, 2-COMe, 4,5-F_2	**4cq**	90	16:1	98
17	**2r**, 3-NO_2	**4cr**	63	3:1	38 (2)
18	**2s**, 4-NO_2	**4cs**	77	5:1	13 (0)

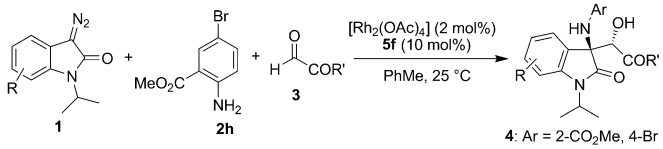
[a] Reaction conditions: A mixture of **1c** (0.15 mmol) and **2** (0.15 mol) in toluene (1 mL) was added to a mixture of $[Rh_2(OAc)_4]$ (2 mol%), **3a** (0.75 mmol), and **5f** (10 mol%) in toluene (1 mL) at 25°C for 1 h. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy of the crude product. [d] The major diastereomer was determined by using HPLC.

sically, the presence of an electron-withdrawing group on the aniline provided high enantioselectivity. For example, in monosubstituted anilines, higher enantioselectivities were observed for species with an electron-withdrawing group at the 2-position (Table 2, entries 1–6). Disubstituted anilines also participated in the three-component reaction in high yields that ranged from 74 to 96% and with excellent stereoselectivities of up to 38:1 d.r. and 99% *ee* (Table 2, entries 7–15). The reaction conditions were also amenable to trisubstituted anilines, which gave high conversion rates with excellent stereoselectivity, as exemplified by the reaction with **2q** (Table 2, entry 16). Anilines bearing either a *meta*- or a *para*- substituent also underwent a consecutive transfor-

mation to afford 3-amino-2-oxindole derivatives in moderate yields, but the enantioselectivities were much lower, which indicates that the stereoselectivity depends greatly on the substituent position on the aniline (Table 2, entries 17 and 18). The configuration of **4ca** was assigned by using X-ray analysis (see the Supporting Information).

The optimized reaction conditions were next applied to 3-diazo oxindoles with different substituents at the benzene ring (Table 3). In general, 3-diazo oxindoles with either elec-

Table 3. The generality of the reaction towards 3-diazo oxindoles.[a]



Entry	**1**, R	**3**, R′	**4**	Yield [%][b]	d.r.[c]	*ee* [%][d]
1	**1e**, 4-Cl	**3a**, OEt	**4eh**	50	8:1	99
2	**1f**, 5-F	**3a**, OEt	**4fh**	95	13:1	87
3	**1g**, 5-Me	**3a**, OEt	**4gh**	81	34:1	98
4	**1h**, 5-OMe	**3a**, OEt	**4hh**	86	21:1	96
5	**1i**, 6-Br	**3a**, OEt	**4ih**	88	24:1	91
6	**1j**, 7-Br	**3a**, OEt	**4jh**	92	17:1	91
7	**1a**	**3b**, Me	**4kh**	69	>20:1	97
8	**1a**	**3c**, Ph	**4lh**	78	16:1	82

[a] Reaction conditions: A mixture of **1** (0.15 mmol) and **2h** (0.15 mol) in toluene (1 mL) was added to a mixture of $[Rh_2(OAc)_4]$ (2 mol%), **3** (0.75 mmol), and **5f** (10 mol%) in toluene (1 mL) at 25°C for 1 h. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy of the crude product. [d] The major diastereomer was determined by using HPLC.

tron-donating or -withdrawing groups underwent the three-component reaction smoothly to give the desired products in excellent enantioselectivities of up to 99% *ee*. Seemingly, the position of the substituent has little effect on the enantioselectivity. Thus, the three-component reaction involving either 6-bromo- or 7-bromo-3-diazo oxindole (**1i** or **1j**) proceeded cleanly to give the desired product with identical *ee* values (Table 3, entry 5 vs. 6). Moreover, the other glyoxylate analogues[18] were also able to participate in the reaction to give the desired products with high diastereo- and enantioselectivities (Table 3, entries 7 and 8).

In summary, we have realized a highly stereoselective three-component aldol-type reaction of 3-diazo oxindoles and anilines with glyoxylates by using rhodium/chiral Brønsted acid cooperative catalysis. In this reaction, the ammonium ylide generated from diazo esters and anilines catalyzed by rhodium acetate acts as an active nucleophile to participate in an enantioselective aldol-type reaction with glyoxylates under the catalysis of the chiral phosphoric acid. The protocol provides a straightforward and efficient route to access highly functionalized and structurally diverse 3-amino oxindoles in high optical purity. More importantly, these findings offer a platform for the rhodium/chiral phosphoric acid binary catalyst that could be applied to realize enantioselective versions of other aldol-type transformations that involve either ammonium or oxonium ylide intermediates formed from diazo carbonyls.

Experimental Section

Typical experimental procedure for the catalytic asymmetric synthesis of 3-amino oxindoles: A mixture of $[Rh_2(OAc)_4]$ (0.003 mmol), phosphoric acid **5f** (0.015 mmol), and **3** (0.75 mmol) was suspended in toluene (1 mL) at 25°C and stirred for 10 min, then **1** (0.15 mmol) and **2** (0.15 mmol) in toluene (1 mL) was added by syringe over 1 h. The reaction mixture was stirred at this temperature until the reaction was complete (monitored by TLC, 10–24 h). The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 3:1) to give product **4**. The diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude product and the enantiomeric excess was determined by HPLC by using a chiral column.

Acknowledgements

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Keywords: aldol reaction · asymmetric catalysis · Brønsted acid · cooperative effects · indoles

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[10] After completion of this work and during the preparation of this manuscript, an elegant finding by Che and co-workers that describes enantioselective coupling reactions of α-diazophosphonates, anilines, and electron-deficient aldehydes catalyzed by chiral dirhodium carboxylate was published online, see: C. Y. Zhou, J. C. Wang, J. Wei, Z. J. Xu, Z. Guo, K. H. Low, C. M. Che, *Angew. Chem.* **2012**, *124*, 11538; *Angew. Chem. Int. Ed.* **2012**, *51*, 11376.

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[18] The desired product could not be isolated when *p*-nitrobenzaldehyde was used as a substrate.

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