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Diastereodivergent Asymmetric 1,4-Addition of Oxindoles to Nitroolefins by Using Polyfunctional Nickel-Hydrogen-Bond-Azolium Catalysts**

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Abstract: *Diastereodivergency is a challenge for catalytic asymmetric synthesis. For many reaction types, the generation of one diastereomer is inherently preferred, while the other diastereomers are not directly accessible with high efficiency and require circuitous synthetic approaches. Overwriting the inherent preference by means of a catalyst requires control over the spatial positions of both reaction partners. We report a novel polyfunctional catalyst type in which a Ni^{II}-bis(phenoxyimine) unit, free hydroxy groups, and an axially chiral bisimidazolium entity participate in the stereocontrol of the direct 1,4-addition of oxindoles to nitroolefins. Both epimers of the 1,4-adduct are accessible in excess on demand by changes to the ligand constitution and configuration. As the products have been reported to be valuable precursors to indole alkaloids, this method should allow access to their epimeric derivatives.*

Chiral compounds with a nonsymmetric constitution featuring n stereocenters can, in principal, exist as 2^n different stereoisomers, that is, 2^{n-1} enantiomeric pairs of diastereomers.[1] For many reaction types, the formation of one of these diastereomers is inherently preferred,[2] while efficient direct access to the other diastereomers (here called "unnatural" diastereomers) very often represents an unsolved problem. The number of catalytic asymmetric methods for diastereodivergent access to all possible diastereomers is, in general, still quite small.[3] Catalytic systems capable of switching the diastereoselectivity outcome on demand require special strategies, which are different from more traditional catalyst designs to overcome the inherent stereochemical preferences. The development of such catalysts is an important task, because both the absolute and relative configurations have an impact on the properties of a compound, for example, in terms of its physiological activity.[4]

Here we describe a modular polyfunctional catalyst concept which allows enantioselective access to both possible sets of diastereomers in the direct 1,4-addition of oxindoles to nitroolefins. This reaction type has been intensively studied in the last few years[5] because chiral oxindoles are both ubiquitous in nature and the products represent valuable building blocks for alkaloid syntheses.[6] Despite the growing number of reported methods for the direct 1,4-addition of 3-alkyl oxindoles to nitroolefins, all of them have in common that product diastereomers with identical relative configuration are formed in excess,[5] while no efficient route is currently known for the epimeric product series.

We created a polyfunctional catalyst design featuring a Ni^{II}-bis(phenoxyimine) unit equipped with free OH groups and an axially chiral bisimidazolium moiety as a chiral linker (Figure 1). We anticipated that cooperative catalysis might

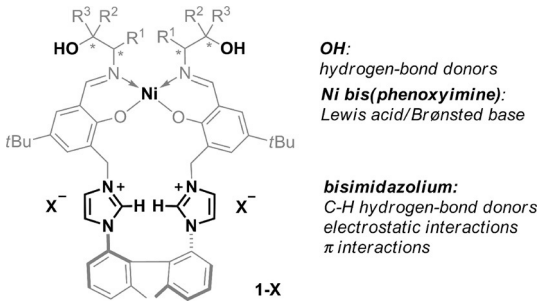

Figure 1. General design of the polyfunctional catalysts **1-X**.

create new opportunities for a diastereodivergent bond-forming process,[7] because the simultaneous interaction of both substrates with the different activating groups of a polyfunctional catalyst should allow both reactants to be preorganized in a defined manner in space during the stereoselectivity-determining step. While the Ni^{II}-bis(phenoxyimine) entity in **1-X** (X^- indicates the counterion) might serve as a Lewis acid/Brønsted base to trigger the oxindole enolization, the nitroolefin might be activated simultaneously by hydrogen bonds.[8] The bisimidazolium linker might also allow for electrostatic and/or π interactions.[9] The interplay of different chirality elements within the catalyst should provide additional handles for control of the relative spatial positions of both substrates in the reactive catalyst species.

The synthesis of **1-Cl** is readily accomplished in three steps (Scheme 1) starting from the axially chiral bisimidazole **2**[10] and benzyl chloride **3**,[11] which were applied to a double S_N2-alkylation to provide **4**.[10,12] A subsequent diimine generation using enantiopure β-aminoalcohols followed by coordination to Ni^{II} provided the complexes **1-Cl** in very high overall yields.[13]

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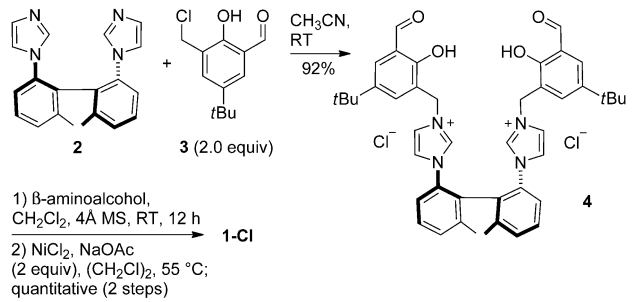


Scheme 1. Synthesis of the catalysts **1-Cl**.

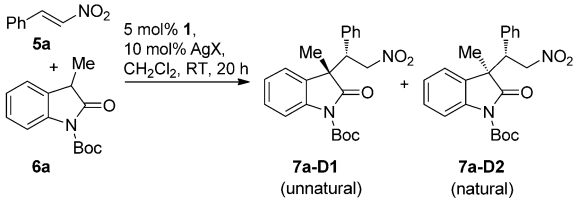
The complexes **1-Cl** were then investigated in the direct 1,4-addition of oxindole **6a** to 2-nitrostyrene (**5a**) in CH_2Cl_2 at room temperature in the presence of 5 mol% **1-Cl** (Table 1). Various iminoalcohol motifs were surveyed, which differed in their configurations and residues R^1–R^3.

Proof of principle was established with the (1*R*,2*S*)- and the (1*S*,2*R*)-norephedrine-derived complexes **1b-Cl** and **1c-Cl**, respectively. Whereas **1b-Cl** primarily produced the natural diastereomer D2 of **7a** (Table 1, entry 5), the unnatural epimer D1 was generated in excess with **1c-Cl** (Table 1, entry 9).[14] Improved diastereoselectivity favoring D1 was noted with **1a-Cl** derived from (1*S*,2*R*)-1,2-diphenyl-2-aminoethanol (Table 1, entry 1). Different silver salts were surveyed for a chloride exchange with **1a-Cl** and **1b-Cl**. Anions with low Lewis/Brønsted basicity such as BF_4^- further improved the stereoselectivities of both catalysts (Table 1, entries 2 and 6). Very similar data were obtained for $X^- =$ triflate and PF_6^- (not shown). In contrast, carboxylate counterions led to decreased stereoselectivities (Table 1, entries 3, 4, 7, and 8).

Catalysts with different iminoalcohol motifs were examined to understand the influence of the individual chirality elements. The catalysts **1d-Cl** and **1e-Cl** derived from (*R*)- and (*S*)-1-phenyl-2-aminoethanol, respectively, containing one stereocenter at the 1-position of the iminoalcohol side chains both favored D2 (Table 1, entries 10 and 11) and only **1d-Cl** formed D2 with good diastereo- and enantioselectivity. Catalysts **1f-Cl** and **1g-Cl** derived from (*R*)- and (*S*)-phenylglycinol, respectively, also both favored D2 (Table 1, entries 12 and 13). Enantioselectivity was poor with **1g-Cl**. Similar data were obtained with **1h-Cl** derived from 1*S*,2*S*-configured 1,2-diphenyl-2-aminoethanol (Table 1, entry 14). These results show that both stereocenters in the 1*S*,2*R*-configured iminoalcohol motifs in **1a-Cl** and **1c-Cl** are necessary for a switch to the unnatural diastereomer. It is also noteworthy that all the catalysts reported in Table 1 generated the same major enantiomers for D1 and D2. This indicates that the axially chiral bisimidazolium backbone plays the dominant role with regard to the enantiocontrol in a matched/mismatched system.

Various control systems were studied to learn more about the impact of the imidazolium linker (Table 2). The flexibility of the axially chiral bisimidazolium appears to be important for the observed diastereodivergency, because control experiments using bisimidazolium catalysts **8** and **8′** that feature a more rigid cyclohexane-1,2-diyl backbone always provided D2 in excess, irrespective of the iminoalcohol residues. Both

Table 1: Catalyst screening.

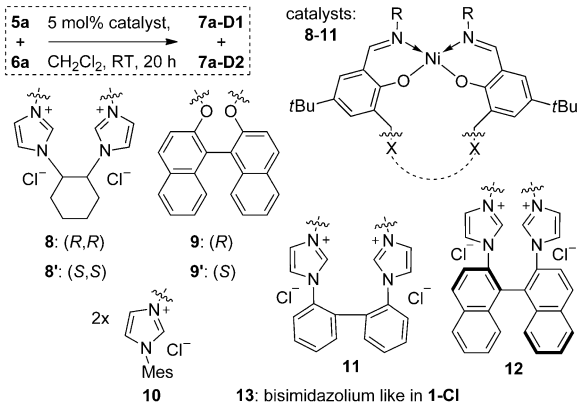


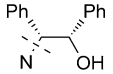
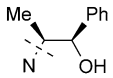
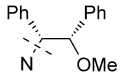
Entry	1-X	Yield 7a [%][a]	D1/D2[b]	*ee* D1 [%][c]	*ee* D2 [%][c]
1	**1a-Cl**[d]	>99	73:27	86	31
2	**1a-BF_4**	>99	79:21	97	62
3	**1a-$O_2CC_3F_7$**	63	63:37	67	30
4	**1a-OAc**	>99	46:54	38	14
5	**1b-Cl**[d]	>99	20:80	64	87
6	**1b-BF_4**	>99	17:83	69	91
7	**1b-$O_2CC_3F_7$**	68	15:85	11	61
8	**1b-OAc**	>99	30:70	14	47
9	**1c-Cl**[d]	>99	65:35	86	32
10	**1d-Cl**[d]	>99	16:84	40	86
11	**1e-Cl**[d]	>99	43:57	51	39
12	**1f-Cl**[d]	>99	24:76	61	72
13	**1g-Cl**[d]	>99	34:66	21	11
14	**1h-Cl**[d]	>99	40:60	25	13

[a] Yield of **7a** determined by ^{1}H NMR spectroscopy using an internal standard. [b] Diastereomeric ratio of **7a** determined by ^{1}H NMR spectroscopic analysis of the crude product. [c] Enantiomeric excess of **7a** determined by HPLC. [d] No Ag salt was used.

diastereomers were produced with poor to low enantioselectivity (Table 2, entries 1, 2, and 8). Similar results were obtained for catalysts **9** and **9'** with axially chiral, yet neutral (*R*)- and (*S*)-1,1'-bi-2-naphthol (BINOL) based linkers (Table 2, entries 3, 4, and 9). These results suggest that the bisimidazolium actively participates in the stereocontrol. Moreover, the control experiments with catalysts **10** (Mes = mesityl) featuring two independent imidazolium-containing phenoxyimine moieties (Table 2, entries 5 and 10) confirm that the axially chiral linker is an important factor for the observed switch in diastereoselectivity for catalysts **1a** and **1c**, as catalysts **10** both generate the natural diastereomer D2. It is also remarkable that catalysts **1a** and **10a** display enantiodivergency and generate D2 with the opposite absolute configuration. Similar phenomena were observed with the use of catalysts **11a** and **11b** (Table 2, entries 6 and 11), which have been prepared from an optically inactive biphenylbisimidazole. The natural diastereomer D2 was also formed in

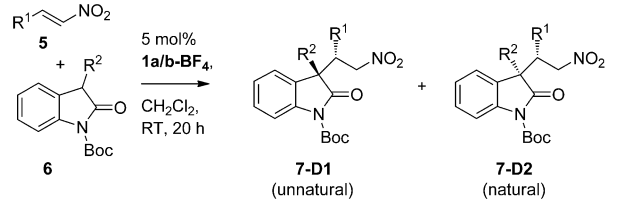
Table 2: Study of different control systems.



Entry	Catalyst	R	Yield [%][a]	D1/D2[b]	*ee* D1 [%][c]	*ee* D2 [%][c]
1	**8a**		>99	36:64	−9	3
2	**8′a**		60	26:74	7	−18
3	**9a**		>99	15:85	21	−30
4	**9′a**		>99	18:82	0	−25
5	**10a**		>99	14:86	16	−79
6	**11a**		>99	28:72	27	−70
7	**12a**		>99	69:31	86	45
8	**8b**		>99	32:68	−41	40
9	**9b**		>99	15:85	16	54
10	**10b**		>99	15:85	−15	69
11	**11b**		>99	24:76	−27	79
12	**12b**		>99	14:86	71	89
13	**13**		68	36:64	−20	2

[a–c] See Table 1. A minus sign for *ee* values indicates that the antipode to the depicted enantiomer was formed in excess.

Table 3: Diastereodivergency for different substrates.



Entry	**1-BF$_4$**	**7**	R^1	R^2	Yield [%][b]	D1/D2[c]	*ee* [%][d]
1	**1a-BF$_4$**	**7a**	Ph	Me	96 (>99)	79:21	97
2	**1b-BF$_4$**				>99 (>99)	10:90	94
3	**1a-BF$_4$**	**7b**	4-Me-C_6H_4	Me	>99 (>99)	77:23	92
4	**1b-BF$_4$**				89 (91)	13:87	91
5	**1a-BF$_4$**	**7c**	4-MeO-C_6H_4	Me	97 (>99)	78:22	88
6	**1b-BF$_4$**				95 (98)	27:73	89
7	**1a-BF$_4$**	**7d**	4-Br-C_6H_4	Me	82 (97)	72:28	93
8	**1b-BF$_4$**				66 (90)	11:89	88
9	**1a-BF$_4$**	**7e**	2-Cl-C_6H_4	Me	72 (93)	94:6	95
10	**1b-BF$_4$**				60 (81)	34:66	94
11	**1a-BF$_4$**	**7f**	4-O_2N-C_6H_4	Me	93 (93)	76:24	95
12	**1b-BF$_4$**				83 (83)	12:88	85
13	**1a-BF$_4$**	**7g**	3-O_2N-C_6H_4	Me	90 (93)	80:20	97
14	**1b-BF$_4$**				66 (75)	15:85	90
15	**1a-BF$_4$**	**7h**	2-furyl	Me	96 (>99)	80:20	96
16	**1b-BF$_4$**				91 (93)	12:88	89
17[e]	**1a-BF$_4$**	**7i**	*i*Pr	Me	42 (42)	70:30	74
18[e]	**1b-BF$_4$**				77 (77)	17:83	90
19	**1a-BF$_4$**	**7j**	Ph	Et	80 (80)	60:40	95
20	**1b-BF$_4$**				95 (96)	13:87	57

[a] All reactions with **1b-BF$_4$** were carried out in the presence of 10 mol% HOAc. [b] Yield of isolated product **7** (in brackets, yield determined by ^{1}H NMR spectroscopy using an internal standard). [c] Diastereomeric ratio determined by ^{1}H NMR spectroscopic analysis of the crude product. [d] Enantiomeric excess of the major diastereomer determined by HPLC. [e] Reaction in 1,2-dichloroethane at 80°C.

excess with these two catalysts. The importance of an axially chiral bisimidazolium linker is further supported by the results obtained with catalysts **12a** and **12b**, which feature an *R*-configured [1,1′-binaphthalene]-2,2′-diamine (BINAM) based backbone. Catalysts **12a** and **12b** show similar stereoselectivity trends as their counterparts **1a** and **1b**. Complex **12a** thus also allows for the preferred formation of the unnatural diastereomer D1 with good enantioselectivity, whereas **12b** forms mainly D2 with good enantioselectivity (Table 2, entries 7 and 12).

Control experiments with catalyst **13**, in which the OH groups of **1a-Cl** are protected as methyl ethers (Table 2, entry 13), revealed that, in contrast to the use of **1a-Cl**, product **7a-D2** is formed in excess. The reactivity is also much lower in this case, thus indicating that activation by hydrogen bonding through the OH groups is an important factor.

To probe the generality of the diastereodivergency **1a-BF$_4$** and **1b-BF$_4$** were applied to various substrate combinations (Table 3). Since we found that the reactions catalyzed by **1b-BF$_4$** showed a somewhat higher stereoselectivity in the presence of catalytic amounts of HOAc (not shown above), all entries in Table 3 with this catalyst were carried out with HOAc, while **1a-BF$_4$** performed better in the absence of HOAc. A switch of the dominant diastereomer was observed in all investigated examples.

Similar reactivity as well as diastereo- and enantioselectivity to those with model substrate **5a** were observed for nitroolefins **5** equipped with σ and π donors (Table 3, entries 3 and 4 and 5 and 6, respectively) on aromatic residues R^1. Nitroolefins with σ and π acceptors on R^1 were also well tolerated and provided high enantioselectivities (Table 3, entries 7–14). The highest preference for the unnatural diastereomer D1 was found for an *ortho*-substituted Michael acceptor (Table 3, entry 9).

The catalyst systems can also be applied to nitroolefins carrying heterocycles, such as furyl, and alkyl chains, such as *i*Pr (Table 1, entries 15–18). Although the results for the latter substrates using **1a-BF$_4$** were inferior in terms of reactivity and stereoselectivity to those obtained with **1b-BF$_4$**, the

number of examples for alkyl-substituted nitroalkenes is, in general, small and α-branched alkyl residues have, to our knowledge, not yet been described.[5c,e] In addition, $R^2 = Et$ was also tolerated (Table 3, entries 19 and 20). Although D2 was formed with only a moderate *ee* value in that case (Table 3, entry 20), D1 was still formed with high enantioselectivity (Table 3, entry 19).

The observed diastereodivergency might be explained by a mechanism in which the Ni centers, OH groups, and the bisimidazolium moieties cooperate (Figure 2). A control

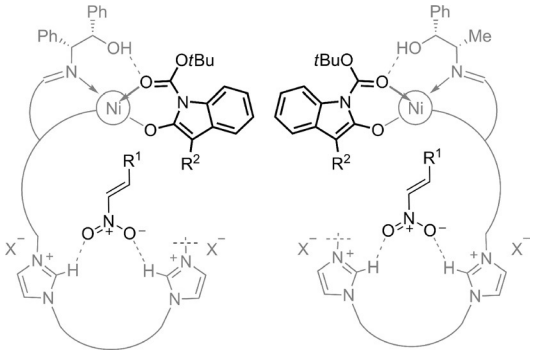


Figure 2. Simplified working model: whereas the preferred spatial orientation of the nitroolefin is mainly determined by the axially chiral bisimidazolium linker and thus similar for catalysts **1a** (left) and **1b** (right), the reactive orientation of the nucleophile depends on the iminoalcohol side chain (only the iminoalcohol moiety involved in a hydrogen bond with the substrate is shown for simplicity).

experiment with an *N*-methyloxindole resulted in no 1,4-adduct. We thus suggest a scenario in which oxindole enolization is triggered by bidentate coordination of the carbonyl group to Ni^{II}. As shown above, changes within the iminoalcohol side arms have an influence on the preferred configuration of the stereocenter at the oxindole. The orientation of the oxindole in the C–C bond-forming transition state might thus be dictated by the iminoalcohol moieties, whereas the preferred configuration of the generated stereocenter in the nitroalkane chain is always identical when using the R_a-configured bisimidazolium linker. For that reason, we suggest that the nitroolefin is activated by hydrogen bonds/electrostatic interactions with the bisimidazolium groups,[15] whereas the free hydroxy groups might be important to control the reactive conformation of the oxindole-Ni^{II} adduct (Figure 2). It should be noted that the iminoalcohol side chains can be symmetrically inequivalent after substrate coordination. The flexibility of an axially chiral bisimidazolium linker might be beneficial to readily adopt the optimal positions of both reacting centers.

In conclusion, we have developed a polyfunctional, readily available novel catalyst type which is capable of overwriting the inherent diastereoselectivity in direct 1,4-additions of oxindoles to nitroolefins to give rise to the epimeric product series, which was previously not accessible. Crucial for the switch in diastereoselectivity is the interplay of a Lewis acid, free hydroxy groups, and an axially chiral bisimidazolium linker in combination with the appropriate arrangement of the different chirality elements. The axially chiral bisimidazolium determines the configuration of the stereocenter generated at the nitroolefin, while the constitution as well as the relative and absolute configuration of the iminoalcohol side arms mainly control the stereocenter generated at the oxindole. The application of related polyfunctional catalysts to other reaction types is currently in progress.

Keywords: axial chirality · cooperative catalysis · hydrogen bonds · imidazolium · oxindoles

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[13] The structure of paramagnetic **1-Cl** is supported by ESI-MS, IR and UV/Vis spectroscopy as well as microanalyses. Moreover, deuteration experiments confirm that Ni-NHC (NHC = N-heterocyclic carbine) complexes have not been generated, because treatment of **1-Cl** with PPh_3 in the presence of 2 equiv of ^{2}H-OAc in CH_2Cl_2 regenerated the ligand with no deuterium incorporation in the bisimidazolium part, as determined by ^{1}H NMR spectroscopy.

[14] The absolute configuration of **7a-D1** was determined by X-ray crystal-structure analysis. CCDC 1054807 contains the supplementary crystallographic data. These data are provided free of charge by The Cambridge Crystallographic Data Centre. The absolute configuration of **7a-D2** was assigned by comparison to the literature data (see Ref. [5]).

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