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Metal-Free Enantioselective Electrophilic Activation of Allenamides: Stereoselective Dearomatization of Indoles**

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Dedicated to Professor Pier Giorgio Cozzi on the occasion of his 50th birthday

Abstract: *The effective and unprecedented chiral BINOL phosphoric acid catalyzed (1–10 mol%) dearomatization of indoles through electrophilic activation of allenamides (ee up to 94%), is documented. Besides the synthesis of 3,3-disubstituted indolenine cores, a dearomatization/hydrogen transfer cascade sequence is also presented as a new synthetic shortcut toward highly enantiomerically enriched indolines.*

The hydrogen bond (HB) activation mode is recognized worldwide as one of the most powerful strategies in the field of metal-free asymmetric manipulation of heteroatom-based organic functional groups and anions.[1] On the contrary, the use of metal-free noncovalent interactions for the direct activation of carbon-based unsaturated π systems has rarely found solutions so far.

In this segment, a Brønsted acid (BA) assisted intramolecular hydroamination of isolated alkenes was reported by the group of Ackermann ($ee_{max} = 17\%$)[2a] and more recently by Toste and co-workers.[2b] In the latter case, the efficiency of chiral dithiophosphoric acids in promoting the enantioselective intramolecular nucleophilic addition to 1,2-/1,3-dienes was demonstrated. Additionally, chiral BAs were also reported catalyzing Friedel–Crafts-type alkylations of indoles by the groups of Terada[3a] and Zhou,[3b] employing electron-rich alkenes (i.e., enamides and enecarbamates) as precursors of the alkylating agents. Here, classic hydrogen-bond contacts between the chiral promoter and the nitrogen atom of the aldimino tautomer, were invoked in the enantiodiscriminating event of the catalytic process. Finally, Terada and co-workers reported on the suitability of BINOL-based phosphoric acids in delivering the enantioselective addition of azlactones to 3-vinylindoles (i.e., ene-type reaction).[3c]

To face the current growing demand for stereochemical manipulations of C–C π systems by metal-free activation, we envisaged bifunctional allenamides as a valuable organic platform to access chemical diversity.[4] This class of "electron-rich" π systems is receiving growing attention in asymmetric synthesis through metal-assisted electrophilic activation.[5] The coordination of chiral late-transition-metal (LTM) complexes to the allenyl framework "C=C=C" is known to deliver positively charged intermediates **A** that can smoothly undergo condensation with a variety of nucleophilic agents both at the α or γ position (Figure 1a). Amongst others, enantioselective cycloaddition reactions represent one of the most explored stereoselective transformations involving allenamides with the active participation of chiral gold complexes as promoters.[6]

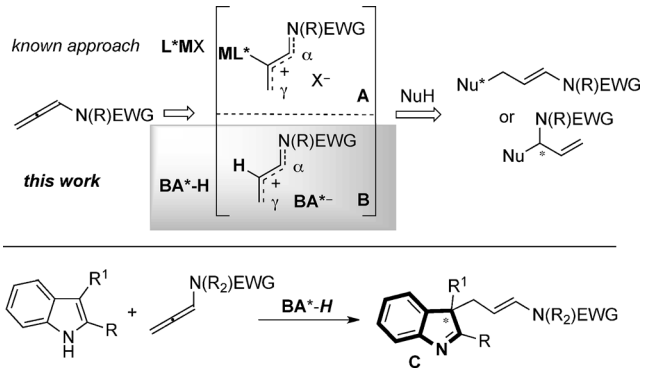

Figure 1. a) Conventional (metal) and "unconventional" (metal-free) electrophilic activation of allenamides in asymmetric synthesis. b) Enantioselective Brønsted acid catalyzed dearomatization of indoles with allenamides: the model reaction.

In this direction, the well-known isolobal analogy often interconnecting [Au^{I}] species and the proton,[7] introduces also chiral σ acids (i.e., Brønsted acids; BAs) as effective promoting agents for the stereochemical manipulation of allenamides. Here, the realization of tight contact ion pairs between the chiral anion and the obtained α,β-unsaturated iminium species **B** (Figure 1a) could provide the ideal stereochemical environment to control the stereochemical pathway of the entire process. However, it should be mentioned that no examples of metal-free electrophilic activation of allenamides in enantioselective transformations have been reported so far.[8]

To verify the feasibility of this working hypothesis, we considered the challenging C3-site-selective intermolecular

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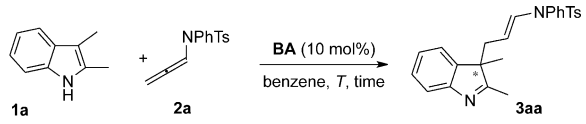
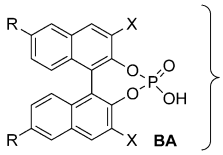
enantioselective dearomatization of N(H)-free indoles as the benchmark process.[9] The realization of this transformation would result in the direct synthesis of densely functionalized enantiomerically enriched 3,3-disubstituted indolenine cores featuring an all-carbon quaternary stereogenic center at the C3 position (**C**, Figure 1b).[10] This transformation has been a recent focus of our research program.[11] In particular, we recently reported on the key role of the gold counterion in controlling both reactivity and regioselectivity in the condensation of indoles with allenamides.[12] These findings inspired and supported the working hypothesis of the present enantioselective metal-free variant.

The condensation of 2,3-dimethylindole (**1a**) and readily available, moisture-tolerant *N*-phenyl-*N*-sulfonylallenamide (**2a**) was selected as the model transformation. A range of chiral BINOL-based phosphate catalysts (**I**–**VII**, 10 mol%) was screened at room temperature in anhydrous benzene as the reaction media (Table 1).[13]

Table 1: Optimization of the catalytic system.[a]





I: X = 3,5-$(CF_3)_2C_6H_3$, R = H
II: X = $SiPh_3$, R = H
III: X = 9-anthracenyl, R = H
IV: X = 2,4,6-$(iPr)_3C_6H_2$, R = H
V: X = 2-naphthyl, R = H
VI: X = 2,4,6-$(Cy)_3C_6H_2$, R = H
VII: X = 2,4,6-$(Cy)_3C_6H_2$, R = nC_8H_{17}

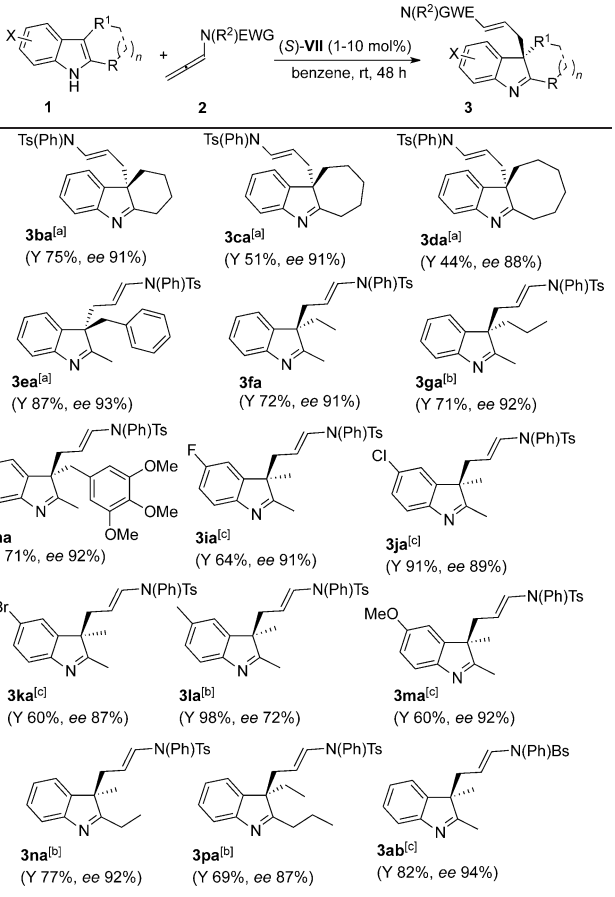
Entry	BA	*T* [°C]/*t* [h]	Yield [%] **3aa**[b]	*ee* [%] **3aa**[c]
1	(*R*)-**I**	25/16	53	28 (*S*)
2	(*R*)-**II**	25/16	61	8 (*S*)
3	(*R*)-**III**	25/16	92	72 (*S*)
4	(*R*)-**IV**	25/16	75	82 (*S*)
5	(*R*)-**V**	25/16	53	25 (*S*)
6	(*S*)-**VI**	25/16	88	84 (*R*)
7	(*R*)-**VII**	25/16	98	92 (*S*)
8[d]	(*R*)-**VII**	10/16	72	94 (*S*)
9[e]	(*R*)-**VII**	25/72	57	87 (*S*)
10[f]	(*R*)-**VII**	rt/16	95	85 (*S*)

[a] All reactions were performed in dry benzene under nitrogen conditions (**1a**/**2a**/**BA** = 2:1:0.1, unless otherwise specified). [b] Determined after flash chromatography. [c] Determined with chiral HPLC. Absolute configuration in brackets. [d] At 10°C. [e] 1 mol% of catalyst was used. [f] With activated 5 Å molecular sieves.

From the data collected in Table 1 several conclusions can be drawn. Firstly, the reaction outcome generally shows a regiochemical preference for the nucleophilic C3 attack by indole on the γ position of the allenamide, with respect to the N1 analogues, even in the presence of nitrogen-free substrate **1a**. Secondly, the screening of differently decorated chiral BINOL phosphoric acids led to important conclusions about the impact of the BA structure on the course of the stereochemical reaction. In particular, (*S*)-C_8-TCyP (**VII**) performed exceptionally in the model reaction, providing the indolenine **3aa** in quantitative yield and 92% *ee* (entry 7).[14] The enantiomeric excess could also be slightly increased up to 94% by reducing the temperature to 10°C (entry 8), but no significant changes were recorded in the presence of molecular sieves (entry 10). Last but not least, the efficiency of the present metal-free stereoselective electrophilic activation of allenamides was further emphasized by the synthetically acceptable performance of **VII** when utilized at a loading of 1 mol% (*ee* 87%, entry 9).

The scope of the catalytic methodology was investigated by subjecting a range of 2,3-disubstituted indoles (**1b**–**p**) to dearomatization under the optimized catalytic conditions (**VII** = 1–10 mol%, benzene, 16/72 h, rt). The chemical and stereochemical outcomes are summarized in Table 2.

Table 2: Scope of the enantioselective protocol.



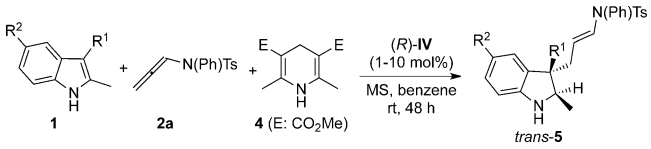
[a] (*R*)-**VII** was used. [b] Catalyst loading 5 mol%, time 72 h. [c] Catalyst loading 1 mol%, time 72 h. Ts = *p*-toluenesulfonyl, Bs = benzenesulfonyl, Y = yield.

Remarkably, all the substrates underwent the dearomatization process with high degrees of stereoselectivity. In particular, indoles carrying cyclic C(2,3)-fused substituents (**1b**–**d**) performed efficiently, leading to the desired indolenines **3ba**–**3da** in moderate to good yields and excellent enantiomeric excess up to 93%. Saturated aliphatic as well as benzylic organic residues at the C3-position of the indole (**1e**–**h**) also provided high stereodifferentiation (*ee* 87–93%). Similar conclusions can be drawn for C2-Et- and C2-*n*Pr-substituted indoles **1n**–**p**, which provided the corresponding dearomat-

ized compounds in acceptable yields (69–77%) and *ee* (87–92%). Subsequently, the tolerance of the organocatalytic approach toward substituents at the indolyl periphery was verified. A range of differently C5-substituted indoles (**1i–m**) was treated with allenamide **2a** in the presence of **VII**. To our delight, synthetically acceptable levels of stereoinduction were achieved with *ee* up to 92% in the case of 5-F and 5-MeO indole derivatives. Finally, variations on the allenamide units were also investigated (see the Supporting Information, SI), highlighting arylsulfonyl groups as the best electron-withdrawing group (EWG; yield 82%, *ee* 94% with 1 mol% of **VII**).[15]

The extraordinary efficiency of the BINOL-based phosphoric acid C_8-TCYP (**VII**) in the regio- and stereoselective dearomatization of indoles offered the unique opportunity to extend the methodology to the preparation of enantiomerically enriched 3,3-disubstituted indolines[16] by transfer hydrogenation of the newly formed imine moiety of **3**.[17] In this direction, we envisioned a Brønsted acid catalyzed one-pot dearomatization/hydrogenation transfer sequence through a three-component reaction of the indole, the allenamide, and a Hantzsch ester (HE) **4**.[18] Remarkably, commercially available (*R*)-TRIP (**IV**) demonstrated exceptional efficiency in the proposed approach, leading to densely functionalized *trans*-C2/C3 indolines (**5**) in moderate yield (44–72%) and with excellent stereoinduction (Table 3). In particular, both

Table 3: Enantioselective dearomatization/hydrogen transfer cascade reaction.[a]

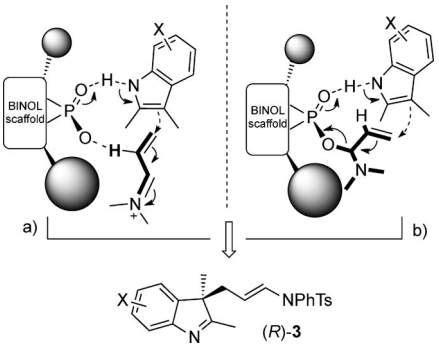


Entry	R^1/R^2 (**1**)	Yield [%][b] *trans* + *cis*	d.r.[c] *trans*/*cis*	*ee* [%][d] *trans*/*cis*
1	Me/H (**1a**)	51	19:1	98/82
2	Et/H (**1f**)	49	15:1	99/33
3	Me/Cl (**1j**)	72	11:1	95/70
4	Me/Br (**1k**)	60	10:1	95/82
5	Me/Me (**1l**)	44	12:1	94/n.d.

[a] All the reactions were performed under inert conditions using nitrogen gas (**1**:**2a**:HE:BA = 2:1:2:0.1, unless otherwise specified). [b] Determined after flash chromatography. [c] Determined on the reaction crude. [d] Determined with chiral HPLC. n.d. not determined.

EWGs and electron-donating groups (EDGs) located at the benzenoid ring of the indole were adequately supported by the protocol, leading to very high diastereomeric ratios (d.r. up to 19:1) as well as enantiomeric excesses (*ee* up to 99%).

Mechanistically, the selective protonation of the allenamide **2** at the β position by the **BA-H** would provide the necessary electrophilic activation of the electron-rich π system, delivering a transient α,β-unsaturated iminium intermediate **B** (Figure 1a). Subsequent Michael-type addition with the indole would result in the final product **3** (Scheme 1a). The basic site located at the phosphoryl oxygen atom



Scheme 1. Possible activation modes: noncovalent (a), and covalent (b) BA–allenamide interactions.

could also "regulate" the enantiodiscriminating step of the process by controlling the approaching trajectory of the heterocycle through hydrogen bond interaction (acid/base dual function catalysis).[19] The bifunctional catalysis could also account for the observed regiospecific C3 versus N1 functionalization of the indole. Differently, a covalent interaction between the catalyst and the π system, resulting from the hydrophosphorylation of the activated allenamide (i.e., an S_N2'-type mechanism, Scheme 1b) cannot be ruled out at the present.[2b,20]

Both hypothetical approaching trajectories depicted in Scheme 1 justify the overall stereochemistry recorded in the final product that was determined to be *R* by single-crystal X-ray analysis of indolenine **3ka** (see SI).[21]

In conclusion, an unprecedented electrophilic metal-free activation of allenamides is documented in the enantioselective intermolecular dearomatization of indoles. Chiral BINOL-based Brønsted acids (*S*)-C_8-TCYP and commercially available (*R*)-TRIP provide access to a library of 3,3-disubstituted indolines as well as indolenines in enantiomerically enriched form. Attempts to extend the present protocol to different organocatalyzed enantioselective manipulations of allenamides are currently under way in our laboratories.

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[21] CCDC 1009468 (**3ka**) 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.

