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Conjugate Addition

# Highly Enantioselective Catalytic Conjugate Addition of N-Heterocycles to α,β-Unsaturated Ketones and Imides**

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Nitrogen-containing heterocycles and their derivatives have broad application in synthetic, materials, and biological chemistry, and as a result their synthesis and reactivity are subjects of considerable interest.[1] Generation of chiral N-heteroaromatic derivatives in optically active form is a challenging facet of this research area that has seen important, but somewhat uneven progress.[2] For example, neither stoichiometric nor catalytic asymmetric conjugate additions of nitrogen-centered nucleophiles based on N-heterocyclic structures has been developed, despite the impressive recent advances in the general area of 1,4-addition chemistry and the utility that the resulting products might hold.[3,4] Potential applications might include preparation of novel non-natural nucleosides (NNNs),[5] a class of compounds with a broad range of important biological applications.[6,7] Our group demonstrated recently that [(salen)Al] complexes efficiently catalyze the highly enantioselective conjugate addition of $HN_3$,[8a,e] HCN,[8b] electron-deficient nitrile derivatives,[8c,e] and oximes[8d] to α,β-unsaturated imides and ketones in the absence of added base. As each of these nucleophiles includes a relatively acidic X−H (X = N, C, O) bond ($pK_a$ 5–17), we hypothesized that heterocyclic compounds bearing similarly acidic N−H bonds might be suitable reaction partners in [(salen)Al]-catalyzed conjugate additions. Herein, we report the successful development of catalytic asymmetric conjugate additions of aromatic N-heterocycles to α,β-unsaturated carbonyl compounds. Both α,β-unsaturated imides and ketones undergo efficient and highly regio- and enantioselective additions with a variety of both fused and nonfused aromatic heterocyclic compounds. This methodology introduces a new, versatile synthetic method for the preparation of interesting chiral building blocks, including NNNs.

Purine, the structural core of the nucleobases in the most promising antiviral agents,[7a] was chosen as a model substrate. It contains a relatively acidic N−H bond ($pK_a$ 8.6) and is known to exist in two (N7-H and N9-H) tautomeric forms.[9a] The oxo-bridged dimeric catalyst **1**[8c] was found to promote the addition of purine to 3-hepten-2-one (**2b**) in the absence of external base. The reaction resulted in full conversion into

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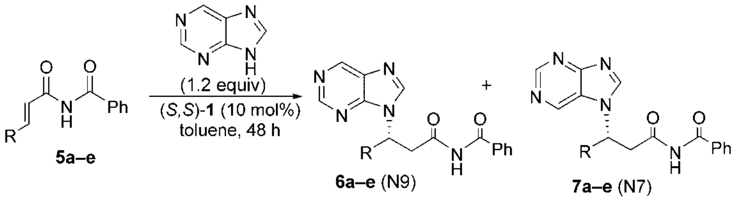
a mixture of the N9 and N7 regioisomers (**3b** and **4b**) within 36 h in THF. The products were obtained in a 3:1 ratio favoring the N9 derivative and with encouraging enantioselectivity (88% *ee*) in the major regioisomer. Optimization studies revealed that reactions carried out in nonpolar solvents led to increased regio- and enantioselectivity, consistent with observations made in other conjugate additions mediated by [Al–salen] catalysts.[8] Reactions carried out in toluene provided the best results, with product **3b** generated in excellent regioselectivity (**3b**/**4b** = 20:1, 80% yield of isolated **3b**) and with 95% *ee*. Generally good reactivity as well as high regio- and enantioselectivity were attained with α,β-unsaturated ketones bearing aliphatic β-substituents (Table 1).[10]

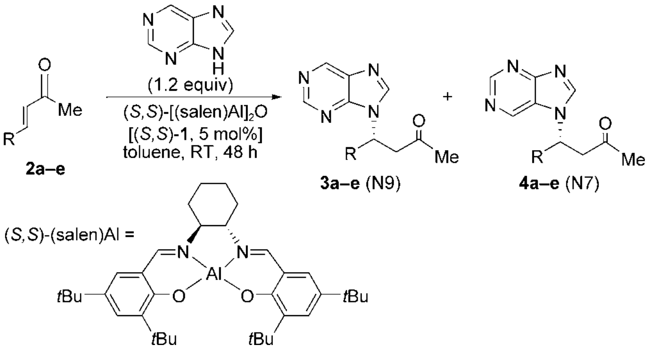
***Table 2:*** Conjugate addition of purine to imides **5a**–**e**.



| Product | R | Yield [%][a] | **6**/**7**[b] | *ee* [%][c] |
|---|---|---|---|---|
| **6a** | Me[d] | 74 | 5:1 | 95 |
| **6b** | Pr[e] | 69 | 3:1 | 95 |
| **6c** | *i*Pr[e] | 64 | 10:1 | 98 |
| **6d** | $CH_2Ph$[e] | 63 | 3:1 | 96 |
| **6e** | $CH_2OTBS$[e] | 65 | 3:1 | 94 |

[a] Yield of isolated **6**, after chromatography, from reactions carried out on a 0.5-mmol scale. [b] Determined by $^1H$ NMR spectroscopy. [c] Determined by HPLC through commercial columns with chiral stationary phases (see Supporting Information). [d] The reaction was carried out at 23 °C. [e] The reaction was carried out at 65 °C. TBS = *tert*-butyldimethylsilyl.

***Table 1:*** Conjugate addition of purine to enones **2a**–**e**.



| Product | R | Yield [%][a] | **3**/**4**[b] | *ee* [%][c] |
|---|---|---|---|---|
| **3a** | Me | 78 | 14:1 | 90 |
| **3b** | Pr | 80 | 20:1 | 95 |
| **3c** | Bu | 76 | 17:1 | 93 |
| **3d** | *i*Pr | 86 | >99:1 | 91 |
| **3e** | $CH_2CH_2OBn$ | 74 | >99:1 | 93 |

[a] Yield of isolated **3**, after chromatography, from reactions carried out on a 0.5-mmol scale. [b] Determined by $^1H$ NMR spectroscopy. [c] Determined by HPLC through commercial columns with chiral stationary phases (see Supporting Information).

α,β-Unsaturated imides were also found to be useful substrates, although lower reaction rates were observed with these electrophiles. Thus, 10 mol% of catalyst **1** was required for the reaction of purine with crotyl imide **5a** to allow complete substrate conversion within 48 h (Table 2). More-hindered imides **5b**–**e** proved even less reactive; however, useful rates were achieved at slightly elevated temperatures with minimal compromise in enantioselectivity (products **6b**–**e**). Lower regioselectivities were obtained with imides than with the corresponding enones, but *N*9-alkylated products could still be isolated in pure form and in synthetically useful yields.

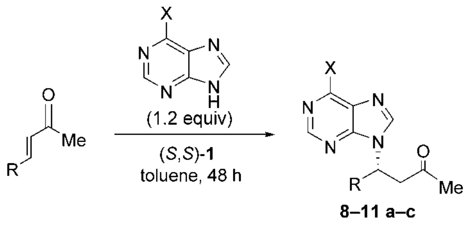
Substituted purines also proved to be interesting substrates in conjugate addition reactions catalyzed by **1**. Although adenine, the parent 6-amino derivative, displayed no reactivity, the *N*-Boc-protected analogue[11] underwent addition to 3-hepten-2-one in the presence of **1** (5 mol%) at 23 °C to afford **8a** in 58% yield with 82% *ee* after 48 h. In the specific case of *N*-Boc-adenine, incorporation of *tert*-butyl alcohol as an additive[12] led to significant rate accelerations and generally good results in additions of this nucleophile to enones bearing aliphatic β substituents (products **8a**–**c**, Table 3). Extremely high regioselectivity for *N*9-substituted products was observed in these [(salen)Al$^{III}$]-catalyzed reactions, in marked contrast to racemic 1,4-conjugate additions of adenine and related compounds catalyzed by Brønsted bases, which invariably afford mixtures of N9 and N7 regioisomers.[4b,d,e]

Other 6-substituted purine derivatives, such as 6-benzyloxypurine, 6-chloropurine, and 6-methylsulfanylpurine, displayed excellent reactivity and enantioselectivity in conjugate additions to α,β-unsaturated ketones (products **9**–**11**, Table 3). Again, exclusive formation of the N9 regioisomers was observed in all cases. The utilization of chloropurine in this method may prove especially noteworthy, as relatively facile nucleophilic substitution of chloride should enable preparation of a wide range of derivatives.[9a]

Reactions of α,β-unsaturated imides with 6-substituted purine derivatives proved substantially slower, although again useful results could be obtained at elevated reaction temperatures (Table 4).[13] The N9 adduct was generated exclusively in good yields and enantioselectivities. Thus, all conjugate additions of 6-substituted purine derivatives to α,β-unsaturated ketones and imides were found to afford the N9 regioisomers with very high selectivity.

Other fused aromatic heterocyclic compounds also proved useful as substrates in this conjugate-addition chemistry. Benzotriazole bears a relatively acidic N−H bond (p$K_a$ 8.6) and exists in solution in two tautomeric forms (N1-H and N2-H).[9b] This nucleophile underwent reaction with various α,β-unsaturated ketones, resulting in two regionisomeric products (N1 and N2), each generated in high

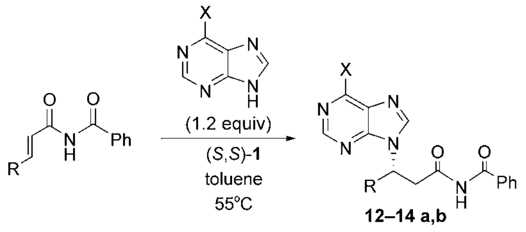
*Table 3:* Conjugate addition of 6-substituted purines to α,β-unsaturated enones.



| Product | X | R | Yield [%][a] | *ee* [%][b] |
|---|---|---|---|---|
| **8a** | | Pr | 67 | 95 |
| **8b** | NHBoc[c] | *i*Pr | 60 | 98 |
| **8c** | | $CH_2CH_2OBn$ | 61 | 99 |
| **9a** | | Pr | 93 | 97 |
| **9b** | OBn[d] | *i*Pr | 89 | 96 |
| **9c** | | $CH_2CH_2OBn$ | 75 | 95 |
| **10a** | | Pr | 95 | 91 |
| **10b** | Cl[e] | *i*Pr | 85 | 93.5 |
| **10c** | | $CH_2CH_2OBn$ | 82 | 96 |
| **11a** | | Pr | 91 | 97 |
| **11b** | SMe[e] | *i*Pr | 88 | 98 |
| **11c** | | $CH_2CH_2OBn$ | 79 | 96 |

[a] Yield of isolated product, after chromatography, from reactions carried out on a 0.5-mmol scale. [b] Determined by HPLC through commercial columns with chiral stationary phases (see Supporting Information). [c] The reaction was carried out with **1** (10 mol%) and *tert*-butyl alcohol (0.6 equiv) at 0°C. [d] The reaction was carried out with **1** (10 mol%) at 23°C. [e] The reaction was carried out with **1** (5 mol%) at 23°C. Bn = benzyl, Boc = *tert*-butoxycarbonyl.

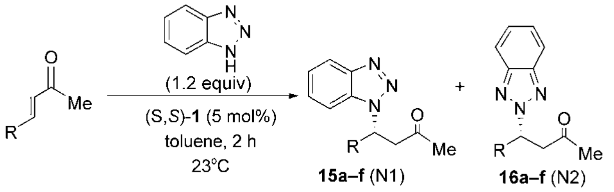
*Table 4:* Conjugate addition of 6-substituted purines to α,β-unsaturated imides.



| Product | X | R | *t* [h] | Yield [%][a] | *ee* [%][b] |
|---|---|---|---|---|---|
| **12a** | OBn[c] | Me | 48 | 81 | 91 |
| **12b** | | $CH_2OTBS$ | 48 | 77 | 95 |
| **13a** | Cl[d] | Me | 18 | 92 | 97 |
| **13b** | | $CH_2OTBS$ | 24 | 93 | 97 |
| **14a** | SMe[d] | Me | 48 | 90 | 95.5 |
| **14b** | | $CH_2OTBS$ | 48 | 79 | 96.5 |

[a] Yield of isolated product, after chromatography, from reactions carried out on a 0.5-mmol scale. [b] Determined by HPLC through commercial columns with chiral stationary phases (see Supporting Information). [c] The reaction was carried out with **1** (10 mol%). [d] The reaction was carried out with **1** (5 mol%).

*Table 5:* Conjugate addition of benzotriazole to enones **2a**–**f**.



| Product | R | Yield [%][a]<br>**15** | **15**/**16**[b] | *ee* [%][c]<br>**15** | *ee* [%][c]<br>**16** |
|---|---|---|---|---|---|
| **a** | Me | 72 | 3:1 | 92 | 92 |
| **b** | Pr | 75 | 3:1 | 94 | 98 |
| **c** | *i*Pr | 67 | 3:1 | 98 | 98 |
| **d** | $CH_2CH_2OBn$ | 65 | 2.6:1 | 91 | 93 |
| **e** | Ph[d] | 53 | 2:1 | 90 | 88 |
| **f**[e] | *p*-BrPh | 60 | 2.5:1 | 70 (98)[f] | – |

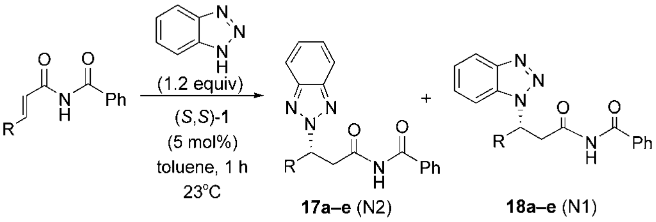
[a] Yield of isolated product **15**, after chromatography, from reactions carried out on a 0.5-mmol scale. [b] Determined by $^1H$ NMR spectroscopy. [c] Determined by HPLC through commercial columns with chiral stationary phases (see Supporting Information). [d] Reaction time: 48 h. [e] Absolute configuration determined by X-ray crystallography (Supporting Information). [f] Number in parentheses is the *ee* value after recrystallization.

enantioselectivity (Table 5). Additions to β-aryl substituted enones also proceeded with high enantioselectivity, although prolonged reaction times were needed to obtain useful yields (**15e**,**f** and **16e**,**f**). X-ray crystallographic analysis of product **15f** served to confirm that the absolute stereochemistry of the products was consistent with that seen in all previous [(salen)-Al]-catalyzed conjugate addition reactions.[8,14]

Reactions of benzotriazole with α,β-unsaturated imides also led efficiently to mixtures of N1 and N2 adducts, although the major regioisomeric products were reversed in comparison to those obtained in enone additions (Table 6). Again, both regioisomers were generated with high enantioselectivity, and aliphatic as well as aromatic β-substituted α,β-unsaturated imides were useful substrates.

The scope of useful nucleophiles is not limited to fused aromatic heterocyclic compounds, and any heterocycle that bears appropriately acidic N–H groups may be suitable substrates in these [(salen)Al]-catalyzed conjugate addition

*Table 6:* Conjugate addition of benzotriazole to α,β-unsaturated imides.



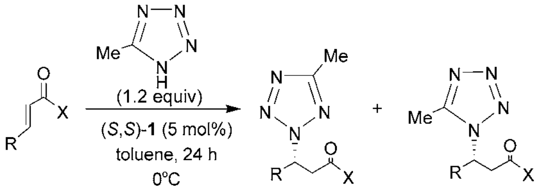
| Product | R | Yield [%][a]<br>**17** | **17**/**18**[b] | *ee* [%][c]<br>**17** | *ee* [%][c]<br>**18** |
|---|---|---|---|---|---|
| **a** | Pr | 69 | 3:1 | 99 | 98 |
| **b** | *i*Pr | 65 | 2.5:1 | >99 | >99 |
| **c** | $CH_2Ph$ | 67 | 2:1 | 96 | 96 |
| **d** | $CH_2OBn$ | 64 | 2:1 | 99 | 98 |
| **e** | Ph | 55 | 1.4:1 | 99 | 95 |

[a] Yield of isolated product, after chromatography, from reactions carried out on a 0.5-mmol scale. [b] Determined by $^1H$ NMR spectroscopy. [c] Determined by HPLC through commercial columns with chiral stationary phases (see Supporting Information).

reactions. We were particularly interested in 1,2,3-triazole (p$K_a$ 9.3) and tetrazole (p$K_a$ 4.76), as these ring frameworks have found increasingly important applications in materials and pharmaceutical sciences.[9b,c] Substituted triazole derivates may be accessed efficiently by sequential catalytic asymmetric conjugate addition of $HN_3$ to α,β-unsaturated carbonyl compounds[8a,e] followed by [2+3] cycloaddition with alkynes catalyzed by $CuSO_4$.[8e,15] However, the analogous route to substituted tetrazoles is less straightforward owing to the fact that intermolecular 1,3-dipolar cycloaddition of organic azides and nitriles remains a difficult transformation that is limited in scope.[16] Therefore, we explored the direct synthesis of substituted tetrazoles by 1,4-conjugate addition of tetrazole to α,β-unsaturated carbonyl compounds.

Tetrazole itself proved not to be a competent substrate in the [(salen)Al]-catalyzed reactions, promoting instead precipitation of the aluminum complex as an intractable polymer. We assumed that tetrazole was acting as a polycoordinating ligand to form oligomeric $Al^{III}$ species,[17] and examined more sterically encumbered, substituted tetrazoles in the reaction. Gratifyingly, 5-methyl tetrazole displayed the desired reactivity with both α,β-unsaturated ketones and imides. Mixtures of 1,5- and 2,5- substituted regioisomers were formed with high enantioselectivity under the optimal reaction conditions (Table 7).

**Table 7:** Conjugate addition of 5-methyltetrazole to α,β-unsaturated ketones and imides.



2,5-product
**19a–c:** X=Me
**21a,b:** X=NHCOPh

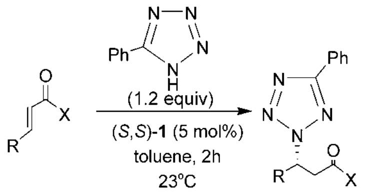
1,5-product
**20a–c:** X=Me
**22a,b:** X=NHCOPh

| Products | R | Yield [%][a] 2,5-product | Yield [%][a] 1,5-product | *ee* [%][b] 2,5-product | *ee* [%][b] 1,5-product |
|---|---|---|---|---|---|
| **19a**, **20a** | Pr | 42 | 40 | 94 | 94.5 |
| **19b**, **20b** | *i*Pr | 64 | 27 | 95 | 96 |
| **19c**, **20c** | $CH_2CH_2OBn$ | 63 | 30 | 87.5 | 87 |
| **21a**, **22a** | $CH_3$ | 61 | 35 | 93 | 92 |
| **21b**, **22b** | $CH_2OTBS$ | 56 | 35 | 96 | 94.5 |

[a] Yield of isolated pure regioisomer, after chromatography, from reactions carried out on a 0.5-mmol scale. [b] Determined by HPLC through commercial columns with chiral stationary phases (see Supporting Information).

When 5-phenyl tetrazole was used as a nucleophile, the 2,5-substituted regioisomer was obtained as the *only product* in high yield and enantioselectivity (Table 8). Similarly high reactivity and enantioselectivity and exclusive regioselectivity were attained in the reactions of tetrazole with unsaturated imides. The electronic effect of tetrazole *C*-aryl substituents in promoting nucleophilic reactions at N2 is precedented.[9c]

**Table 8:** Conjugate addition of 5-phenyltetrazole to α,β-unsaturated ketones and imides.

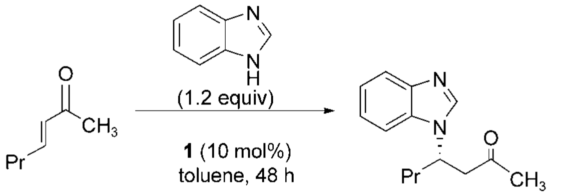


**23a–c:** X=$CH_3$
**24a,b:** X=NHCOPh

| Product | R | Yield [%][a] | *ee* [%][b] |
|---|---|---|---|
| **23a** | Pr | 94 | 99 |
| **23b** | *i*Pr | 93 | 95.5 |
| **23c** | $CH_2CH_2OBn$ | 90 | 94 |
| **24a** | $CH_3$ | 93 | 95.5 |
| **24b** | $CH_2OTBS$ | 94 | 97 |

[a] Yield of isolated product, after chromatography, from reactions carried out on a 0.5-mmol scale. [b] Determined by HPLC through commercial columns with chiral stationary phases (see Supporting Information).

Although this methodology is mostly applicable to relatively acidic heterocycles of p$K_a$(N-H) < 10, useful reactivity could be achieved for less-acidic compounds. For example, benzimidazole (p$K_a$ 12.75) underwent reaction with 3-hepten-2-one at 23 °C to afford 1,4-addition product **25** in 20 % yield with 90 % *ee* after 48 h (Scheme 1). The reactivity was improved by carrying out the reaction at 60 °C for 2 days (yield of isolated product is 73 %), although this was accompanied by a significant decrease in enantioselectivity (81 % *ee*).



**25**

23°C: 20% yield, 90% *ee*
60°C: 73% yield, 81% *ee*

**Scheme 1.** 1,4-Addition of benzimidazole (p$K_a$ 12.75) to 3-hepten-2-one.

In summary, catalytic asymmetric conjugate addition of N–H- containing heterocycles to α,β-unsaturated ketones and imides has been developed successfully. A wide range of fused and nonfused heterocyclic compounds are useful substrates, generally demonstrating good reactivity and enantioselectivity. This methodology opens a new entry to the synthesis of non-natural nucleosides. Mechanistic studies of these reactions are underway.

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**Keywords:** aluminum · asymmetric catalysis · heterocycles · nucleobases · synthetic methods

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