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Dearomative Michael addition involving enals and 2-nitrobenzofurans realized under NHC-catalysis†

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In this manuscript, the first enantioselective dearomative Michael addition between α,β-unsaturated aldehydes and 2-nitrobenzofurans realized under N-heterocyclic carbene activation has been described. The reaction proceeds *via* addition of homoenolate to Michael acceptors leading to the formation of biologically important heterocycles with high yields and stereoselectivities. Their functionalization potential has been confirmed in selected, diastereoselective transformations.

The discovery of new synthetic approaches that allows for the transformation of aromatic systems in a highly selective fashion remains an exciting area of research.[1] As a consequence, reactions capable of disturbing the aromatic π-system have received considerable attention. Among different approaches to accomplish this task, catalytic asymmetric dearomatization (CADA) reactions of simple (hetero)aromatic compounds constitute a highly reliable tool for the assembly of enantiomerically enriched polycyclic molecules.[2] Many of these reactions are typically focused on the process of dearomatization of electron-rich (hetero)arenes based on their nucleophilic nature.[3] Introduction of an appropriate electron-withdrawing substituent in the structure of (hetero)arenes leads to reversal of their reactivity into electron-deficient systems acting as an electrophile susceptible to CADA.[4]

Recently, important applications of electron-poor nitro-substituted heteroarenes (such as 2- and 3-nitroindoles,[5] 2-nitrobenzofurans[6,7] or 2- and 3-nitrobenzothiophenes[8]) in dearomative transformations for the construction of fused-heterocycles have appeared in the literature. Due to the immense biological importance of the 2,3-disubstituted-2,3-dihydrobenzoheterocycle motif,[9] the development of new strategies for the construction of such chiral oxygen- or sulfur-containing scaffolds has received considerable attention from the organic and medicinal chemistry community. In recent years, 2-nitrobenzofurans and 2-nitrobenzothiophenes have been successfully used as C-2 synthons in various enantioselective dearomative reactions using both transition-metal catalysis[6,8a,8b] and organocatalysis.[7,8c] However, all of these transformations proceed in a cascade manner and utilize both the electrophilicity of the starting material and nucleophilicity of the initially formed adduct, thus leading to polycyclic frameworks, mainly (3 + 2)- or (4 + 2)-cycloadducts (Scheme 1, top).[6–8] On the other hand, 2-nitrobenzofurans are a class of promising reagents that undergo simple dearomative Michael additions (Scheme 1, top), with such an approach being still undeveloped.

A survey of the literature revealed only one example of this type of reactivity. In 2019, the Yuan group described the enantioselective reaction of 2-nitrobenzofurans with 3-pyrrolyl-oxindoles in the straightforward construction of chiral 2,3-dihydrobenzofurans (Scheme 1, center).[10] Given the lack of simple additions involving 2-nitrobenzofurans and our continuous research activity in catalytic asymmetric dearomative transformations,[11] we became interested in the development of the enantioselective CADA Michael reaction between electron-deficient 2-nitrobenzofurans **1** and α,β-unsaturated aldehydes **2**. Herein, we report the first organocatalytic dearomative Michael addition realized under NHC catalysis[12] leading to the formation of chiral 2,3-disubstituted-2,3-dihydrobenzo-heterocycles **3** (Scheme 1, bottom). The reaction was realized employing homoenolate chemistry that served as a powerful means for the redox functionalization of α,β-unsaturated aldehydes with nitroolefins constituting an important class of electrophiles employed (Scheme 1, center).[13]

The reaction between 2-nitrobenzofuran **1a** and *trans*-cinnamaldehyde **2a** was selected as a model transformation (Table 1). Initially, various readily available chiral NHC catalysts **4** were evaluated in THF at room temperature. It was found that

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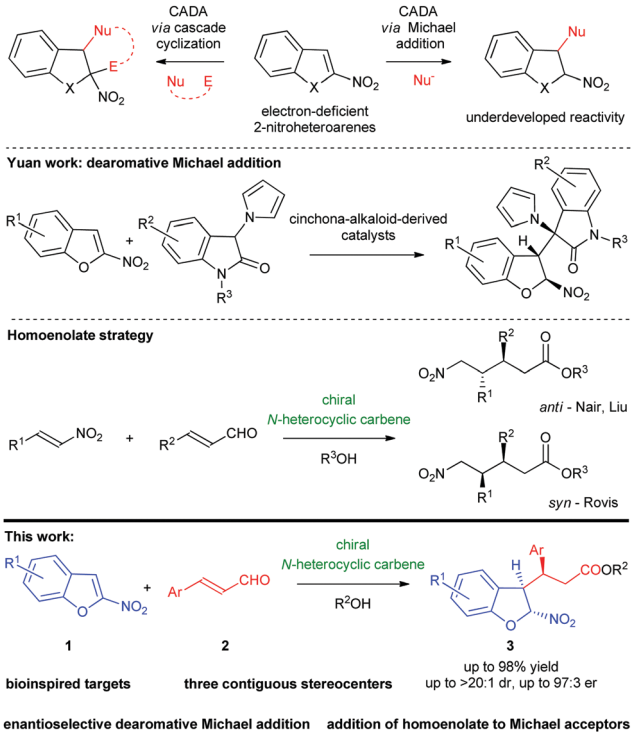
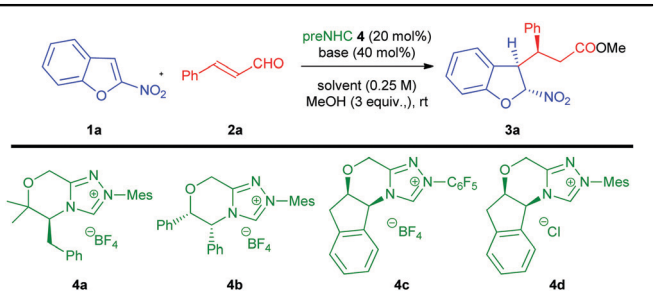


Scheme 1 Design of catalytic asymmetric dearomative reactions of 2-nitrobenzo-heteroarenes.

2-nitrobenzofuran **1a** was fully consumed when the reactions were carried out in the presence of the precatalysts **4a,b** and **d** using Cs_2CO_3 as a base, but **3a** was isolated with moderate yields (Table 1, entries 1–2, 4). Aminoindanol-based NHC precatalyst **4c** bearing a pentafluorophenyl group showed no catalytic activity in the reaction (Table 1, entry 3). Careful examination of ^{1}H NMR of the crude reaction mixtures indicated that methyl 3-phenylpropanoate was the by-product responsible for the low yields observed. Screening of bases did not lead to significant improvement of the results. However, both Cs_2CO_3 and triethylamine provided the best reaction outcomes (Table 1, compare entries 4, 7 *vs.* 5, 6). Subsequently, solvent screening revealed that diethyl ether was the best choice, yielding the desired product **3a** without erosion of the enantio- or diastereoselectivity, when reacting with TEA as a base and **4d** as a NHC-precatalyst (Table 1, compare entry 11 *vs.* 7–10). Lowering the reaction temperature to 5 °C led to a substantial increase of the yield with an excellent enantiomeric excess (Table 1, entry 12). It should be noted that under these conditions the formation of methyl 3-phenylpropanoate was not observed in the crude reaction mixture. The decrease of the temperature to −10 °C led to the drop of the diastereoselectivity of the process (Table 1, entry 13). When the catalyst loading **4d** was reduced (to 10 mol%), the addition still proceeded smoothly (Table, entry 14). Unfortunately, further reduction of the amount of catalyst (to 5 mol%) suppressed the reaction rate resulting in a lower yield (Table 1, entry 15). Finally, the conditions shown in Table 1, entry 14 were selected as the optimal conditions to investigate the generality of the process.

Table 1 NHC-catalyzed dearomative Michael addition with enals and 2-nitrobenzofurans – optimization studies[a]



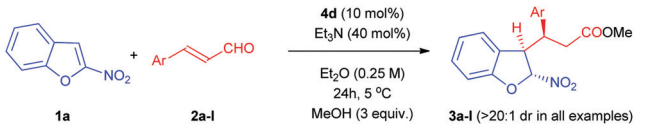
	Solvent (preNHC)	Base	Conv. (yield)[b] [%]	dr[c]	er[d]
1	THF (**4a**)	Cs_2CO_3	>95 (60)	>20:1	90:10
2	THF (**4b**)	Cs_2CO_3	>95 (62)	>20:1	15:85
3	THF (**4c**)	Cs_2CO_3	<5	n.d	n.d
4	THF (**4d**)	Cs_2CO_3	>95 (66)	>20:1	92.8
5	THF (**4d**)	K_2CO_3	>95 (60)	>20:1	90:10
6	THF (**4d**)	DIPEA	>95 (54)	>20:1	92:8
7	THF (**4d**)	TEA	>95 (60)	9:1	92:8
8	DCE (**4d**)	Cs_2CO_3	<5	n.d	n.d
9	1,4-Dioxane (**4d**)	Cs_2CO_3	<5	n.d	n.d
10	Et_2O (**4d**)	Cs_2CO_3	>95 (43)	>20:1	97:3
11	Et_2O (**4d**)	TEA	>95 (76)	>20:1	96:4
12[e]	Et_2O (**4d**)	TEA	>95 (93)	>20:1	96.5:3.5
13[f]	Et_2O (**4d**)	TEA	>95 (74)	16:1	96:4
14[eg]	Et_2O (**4d**)	TEA	>95 (92)	>20:1	96.5:3.5
15[eh]	Et_2O (**4d**)	TEA	>95 (74)	>20:1	96.5:3.5
16[ehi]	Et_2O (**4d**)	TEA	>95 (84)	>20:1	96.5:3.5

[a] Reactions performed on a 0.05 mmol scale using **1a** (1.0 equiv.), **2a** (1.5 equiv.) and the preNHC catalyst **4** (20 mol%) in 0.2 mL of the solvent for 24 h at rt. [b] Determined by ^{1}H NMR of the crude reaction mixture. In parentheses, the yield of isolated product **3a** after column chromatography is given. [c] Determined by ^{1}H NMR of the crude reaction mixture. [d] Determined by chiral HPLC. [e] The reaction was performed at 5 °C. [f] The reaction was performed at −10 °C. [g] The reaction was performed using **4d** (10 mol%). [h] The reaction was performed using **4d** (5 mol%). [i] The reaction was performed on a 1 mmol scale for 48 h. DCE – 1,2-dichloroethane.

Importantly, the reaction proved to be easily scalable with comparable results obtained on a 20-fold higher scale using only 5 mol% of the precatalyst **4d** (Table 1, entry 16).

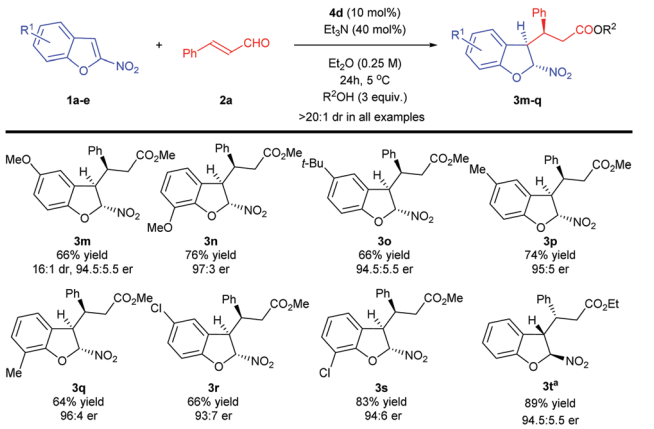
Under the optimized reaction conditions, the scope and limitations of the reaction were carefully explored (Table 2 and Scheme 2). As shown in Table 2, the dearomative Michael reaction was applicable to a wide range of α,β-unsaturated aldehydes **2a–l**, affording corresponding products **3a–l** in high yields and high diastereo- and enantioselectivity. It was found that the reactivity and stereoselectivity were almost unaffected by the incorporation of various electron-donating substituents at different positions of the aromatic ring in *trans*-cinnamaldehydes **2b–e** (Table 2, products **3b–e**). Aldehydes **2f–h** with electron-withdrawing substituents in different positions (2-Cl, 3-F and 4-Cl) on the aromatic ring were also all suitable substrates for this reaction, resulting in the formation of the corresponding products **3f–h** in high yield and stereoselectivity. Notably, in the case of aldehyde **2i**, the reaction proceeded smoothly with 2-nitrobenzofuran **1a**, but the desired product **3i** was obtained with diminished enantiocontrol. Also *trans*-cinnamaldehydes **2j** and **2k** with a double substitution

Table 2 NHC-catalyzed dearomative Michael addition with enals and 2-nitrobenzofurans – α,β-unsaturated aldehyde **2** scope



Entry	3 (2)	Ar	Yield [%]	er
1	**3a** (**2a**)	Ph	92	96.5 : 3.5
2	**3b** (**2b**)	2-MeOC$_6$H$_4$	98	93 : 7
3	**3c** (**2c**)	3-MeOC$_6$H$_4$	74	94.5 : 5.5
4	**3d** (**2d**)	4-MeOC$_6$H$_4$	79	96.5 : 3.5
5[a]	**3e** (**2e**)	4-MeC$_6$H$_4$	78	94.5 : 5.5
6[a]	**3f** (**2f**)	2-ClC$_6$H$_4$	74	94.5 : 5.5
7	**3g** (**2g**)	3-FC$_6$H$_4$	83	95 : 5
8	**3h** (**2h**)	4-ClC$_6$H$_4$	77	95 : 5
9	**3i** (**2i**)	4-NO$_2$C$_6$H$_4$	74	85 : 15
10[a]	**3j** (**2j**)	2-Naphthyl	69	80.5 : 19.5
11	**3k** (**2k**)	2,4-ClC$_6$H$_3$	71	94 : 6
12	**3l** (**2l**)	2-Furyl	87	94.5 : 5.5

[a] In the reaction, *ent*-**4d** was used as the catalyst and the opposite enantiomer was formed.



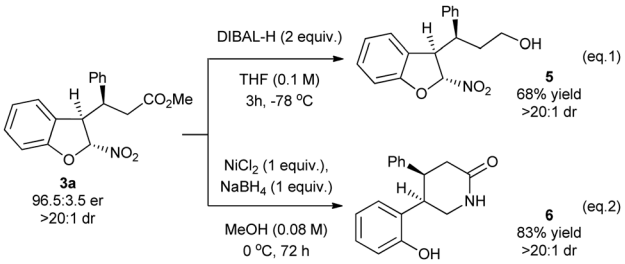
Scheme 2 NHC-catalyzed dearomative Michael addition with enals and 2-nitrobenzofurans–2-nitrobenzofuran **1** scope. [a] In the reaction, *ent*-**4d** was used as the catalyst and the opposite enantiomer was formed.

pattern gave access to the corresponding products **3j** and **3k** in moderate to high enantioselectivity. Finally, the reactivity and stereoselectivity were hardly affected by the incorporation of a heteroaromatic ring in **2l**, as **3l** was obtained effectively.

Further exploration of the substrate scope was focused on the utilization of various 2-nitrobenzofurans **1b–h** (Scheme 2).

The dearomative Michael reaction was compatible with C5 and C7-substituted acceptors **1** containing groups of different electronic properties, providing products **3m–s** in good to high yields and with excellent stereoselection.

Finally, different alcohols, such as ethanol, butanol and sterically hindered *tert*-butanol were tested. To our delight, ethanol worked well to give **3t** in high yield with excellent enantiomeric ratio. Attempts to use other alcohols resulted in suppression of the reactivity (< 5% conversion, products not shown). Similarly, when 2-nitrobenzothiophene, 2-nitroindole,

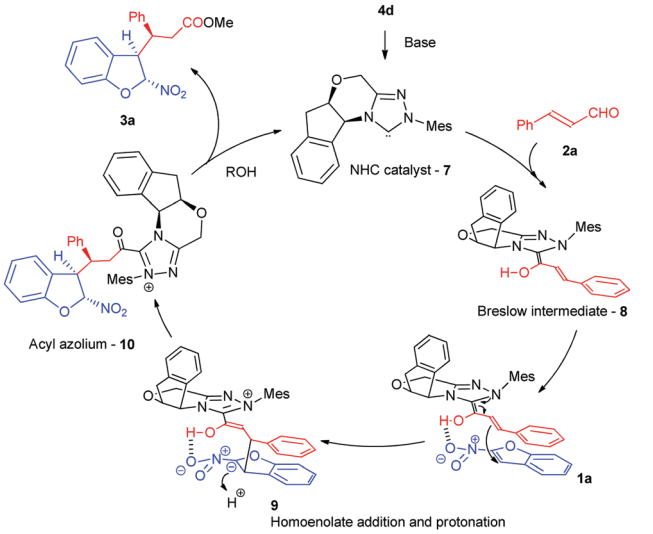


Scheme 3 Diastereoselective transformations of **3a**.

3-nitroindole and 3-nitrobenzofuran were used, no reaction was observed.

The usefulness of the obtained adducts was demonstrated in selected transformations (Scheme 3). Firstly, the treatment of the optically pure adduct **3a** with diisobutylaluminum hydride in THF led to chemoselective reduction of the ester group to give an alcohol **5** in 68% yield without erosion of the diastereoselectivity (Scheme 3, eq. 1). Product **3a** was also transformed into the δ-lactam **6** *via* a cascade reaction with sodium borohydride in the presence of nickel chloride in MeOH. Initially, the reduction of the nitro group and lactamization occurred. Subsequently, the reaction involving opening of the dihydrobenzofuran ring and reduction provided **6** as a single diastereoisomer (Scheme 3, eq. 2).

The absolute configuration of the products was unequivocally confirmed by the single crystal X-ray analysis of **3j** (for details, see the ESI†).[14] The stereochemistry of other products was assigned by analogy. Based on the configurational assignments, a possible mechanism of this dearomative Michael reaction was proposed (Scheme 4). It was initiated through the addition of an *in situ* generated NHC **7** to the α,β-unsaturated aldehyde **2a** to give the corresponding Breslow intermediate **8**. The Michael acceptor **1a** was activated and oriented in space through the H-bonding interaction between



Scheme 4 NHC-catalyzed dearomative Michael addition with enals and 2-nitrobenzofurans – mechanistic considerations.

the hydroxyl group of **8** and the nitro group in **1a**. Simultaneously, π-stacking between the phenyl ring of **8** and aromatic ring of **1a** and the steric effect of the chiral motif of the NHC catalyst favored the *Re*-face attack of the C3-position of 2-nitrobenzofuran by homoenolate **8** in a stereoselective manner. With the formation of adduct **9** accomplished, its protonation and subsequent tautomerization to acyl azolium **10** took place. The esterification of **9** in the presence of a nucleophile furnished the final adduct **3a** with (C2*R*, C3*R*, C10*S*) configuration.

In summary, we have successfully developed the first catalytic asymmetric dearomative transformation between 2-nitrobenzofurans and α,β-unsaturated aldehydes catalyzed by N-heterocyclic carbenes. This process proceeds through the addition of a homoenolate to 2-nitrobenzofurans leading to enantioenriched heterocycles with three contiguous stereocenters with high efficiency and stereoselectivity. The presented work constitutes the unique application of NHC catalysis in the transformation of electron-poor 2-nitrobenzofurans. Further exploration of the catalytic asymmetric dearomatization of electron-deficient heteroarenes is currently underway.

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Conflicts of interest

There are no conflicts to declare.

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14 CCDC 2105519 contains the supplementary crystallographic data for this paper†.

