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Organocatalytic asymmetric nitrocyclopropanation of α,β-unsaturated aldehydes

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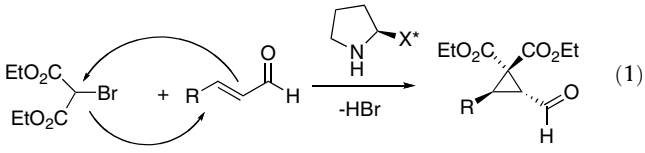
ABSTRACT

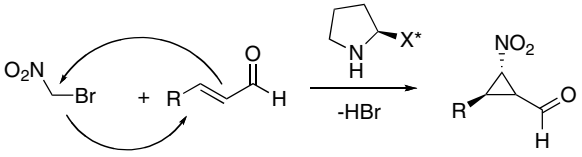
A novel organocatalytic highly enantioselective nitrocyclopropanation reaction of α,β-unsaturated aldehydes is presented. The 1-nitro-2-formylcyclopropane derivatives synthesized from this catalytic transformation were converted to the corresponding β-nitromethyl-acid esters, which are excellent precursors of GABA analogues such as Baclofen, by subsequent organocatalytic chemoselective ring-opening.

The cyclopropane motif is an important target for organic chemists and is also a constituent of several natural products and biologically active agents.[1] Moreover, cyclopropyl derivatives are attractive synthetic intermediates[2] and are employed as building blocks in complex molecule[3] and peptide synthesis.[4] Consequently, the importance of cyclopropyl derivatives has encouraged organic chemists to develop asymmetric methods for their synthesis.[5] High levels of asymmetric induction have been achieved involving metal catalyzed intermolecular cyclopropanations of electron rich olefins.[6] In pioneering work, Aggarwal,[7] Gaunt[8] and MacMillan[9] have employed either preformed or in situ generated ylides for the catalytic cyclopropanation of α,β-unsaturated ketones, amides, esters, nitriles, sulfones and aldehydes. Connon utilised cinchona alkaloids as catalysts for the cyclopropanation of nitroalkanes.[10] We recently developed an organocatalytic, highly enantioselective cyclopropanation of enals using chiral pyrrolidine derivatives as catalysts (Eq. 1).[11]



(1)

Nitro-substituted cyclopropanes are valuable synthons which can be converted to a variety of functionalities.[12,13] For example, a diastereoselective nitrocyclopropanation has been reported by Ballini et al.[14] Notably, Ley and co-workers reported the first organocatalytic nitrocyclopropanation of cyclohexanone using their proline tetrazole catalyst.[15] Inspired by this work and our own research on catalytic domino Michael/α-alkylation reactions,[11a,b,16] we envisioned that reaction between 2-bromonitromethane and α,β-unsaturated aldehydes would give the corresponding 1-nitrocyclopropanes (Eq. 2). Herein, we disclose the novel organocatalytic, highly enantioselective nitrocyclopropanation of α,β-unsaturated aldehydes and the formal asymmetric synthesis of important GABA (γ-amino butyric acid) analogues such as Baclofen.



(2)

In initial catalyst, organic base and solvent screens, we found that chiral amines **4**–**8** catalyzed the reaction between cinnamic aldehyde **1a** and 2-bromonitromethane **2a**, to give the corresponding 2-formyl-cyclopropanes **3a** and **3a′** (Table 1).[17]

The reactions catalyzed by (*S*)-proline **4** and diamine **5** furnished **3a** and **3a′** in good combined yields (1:1 and 3:1 ratio, respectively) but with modest ees. The reaction with 2-carboxylic acid dihydroindole **6** as the catalyst led to the formation of *ent*-**3a** and *ent*-**3a′** in 52% combined yield (1:1 ratio) with 91% and 86% ee, respectively, after 48 h reaction time (entry 3). Notably, after 3 h, using protected diphenylprolinol **8** as the catalyst, we were able to isolate 1-nitrocyclopropanes **3a** and **3a′** containing three contiguous stereocentres in 63% combined yield with 95% and 97% ee, respectively (entry 5). Thus, we decided to further optimize the organocatalytic nitrocyclopropanation of enals using chiral amine **8**[18] as the catalyst. The reaction was highly enantioselective in $CHCl_3$, CH_2Cl_2, toluene, Et_2O and CH_3CN. However, the diastereoselectivity decreased in CH_2Cl_2, Et_2O and CH_3CN where an additional minor diastereoisomer **3a″** was formed. The diastereo- and enantioselectivity of the reaction was also sensitive to the choice of organic base (entries 10–12). For example, the diastereoselectivity increased when morpholine was used instead of TEA as an additive but the enantioselectivity decreased. With these results in hand, we decided to use $CHCl_3$ as the solvent, TEA as a

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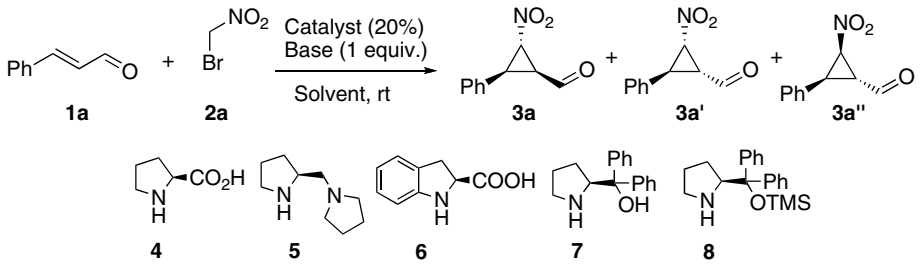
Table 1
Screening of the enantioselective reaction between **1a** and **2a**[a]



Entry	Catalyst	Base	Solvent	Time (h)	Yield[b] (%)	Dr[c] (**3a**:**3a′**:**3a″**)	ee[d] (%) (**3a**:**3a′**)
1	**4**	TEA	$CHCl_3$	1	59	1:1:0	25:25
2	**5**	TEA	$CHCl_3$	2	69	3:1:0	25:25
3	**6**	TEA	$CHCl_3$	48	52	1:1:0	−91:−86
4	**7**	TEA	$CHCl_3$	24	Trace	n.d.	n.d.
5	**8**	TEA	$CHCl_3$	3	63	1:1:0	95:97
6	**8**	TEA	CH_2Cl_2	6	61	4:2:1	91:93
7	**8**	TEA	Toluene	3	59	1:1:0	95:95
8	**8**	TEA	CH_3CN	8	58	3:2:1	92:96
9	**8**	TEA	Et_2O	8	35	1:1:1	78:87
10	**8**	Morpholine	$CHCl_3$	2	69	3:1:0	51:54
11	**8**	Piperazine	$CHCl_3$	3	46	1:1:0	21:22
12	**8**	Lutidine	$CHCl_3$	6	59	1:1:0	95:95

[a] Experimental conditions: To a mixture of **1a** (0.30 mmol), chiral pyrrolidine (20 mol %) and base (0.25 mmol) in 1.0 mL of solvent was added 2-bromonitromethane **2a** (0.25 mmol) and the reaction mixture was stirred under the conditions shown in the Table.
[b] Isolated combined yield of pure compounds **3**.
[c] Diastereoisomeric ratio as determined by ^{1}H NMR.
[d] Enantiomeric excess determined by chiral-phase HPLC analysis. n.d. = not determined.

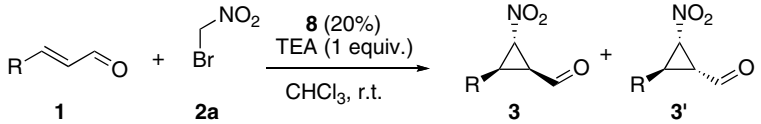
proton sponge and chiral amine **8** as the catalyst for the reactions between various enals **1** and 2-bromonitromethane **2a** (Table 2).[17]

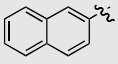
The chiral amine **8** catalyzed reactions were highly chemo- and enantioselective (91–99% ee) and gave the corresponding 1-nitro-2-formyl-cyclopropanes **3** in moderate to high yields. Of the four possible diastereoisomers only two were formed in ratios ranging from 1:1 to 3:1. Based on the importance of GABA (γ-amino butyric acid) analogues such as Baclofen,[19] we decided to investigate the possibility of chemoselective ring-opening of the 1-nitro-2-formyl-cyclopropane derivatives **3** using heterocyclic carbene catalysis (Scheme 1).[11a,b,20]

To our delight, the ring-opening worked well for nitrocyclopropanes **3a** and **3e** giving the corresponding 3-nitromethyl acid esters **9** in high yields and ees. For example, 3-nitromethyl acid ester **9e** was isolated in 85% yield and 92% ee.[21] Comparison with the literature revealed that the absolute configuration at C-3 of **9e** was (*S*) ($[\alpha]_D^{25}$ −4.4 (*c* 0.5, $CHCl_3$)), lit. (*R*-**9e**, $[\alpha]_D^{25}$ 4.0 (*c* 1.0, $CHCl_3$)[19a]). Moreover, by employing our newly developed one-pot combination of amine and heterocyclic carbene catalysis (AHCC), it was possible to prepare directly 3-nitromethyl acid esters **9** starting from the enals **1** and nitromethane **2a**.[11b]

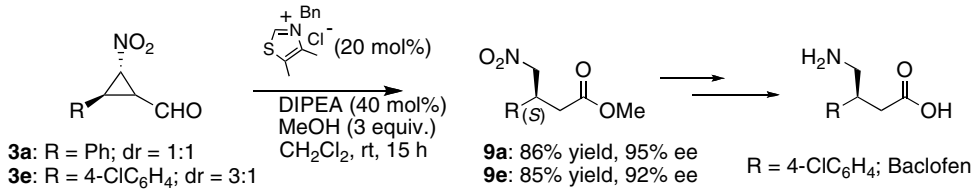
The relative stereochemistry of the different diastereoisomers **3** was confirmed by NOE experiments on diastereoisomers **3a**, **3a′** and **3a″**, respectively, and from the coupling constants of the ring-protons.The experiments revealed that the phenyl- and 2-formyl-groups of **3a** have a cis-relationship and the nitro group was trans to these two groups. In the case of 1-nitrocyclopropane **3a′**, the relative configuration between the phenyl group and the 2-formyl group was trans and the nitro group was cis to the 2-formyl group.

Table 2
Direct organocatalytic asymmetric nitrocyclopropanation of α,β-unsaturated aldehydes **1**[a]

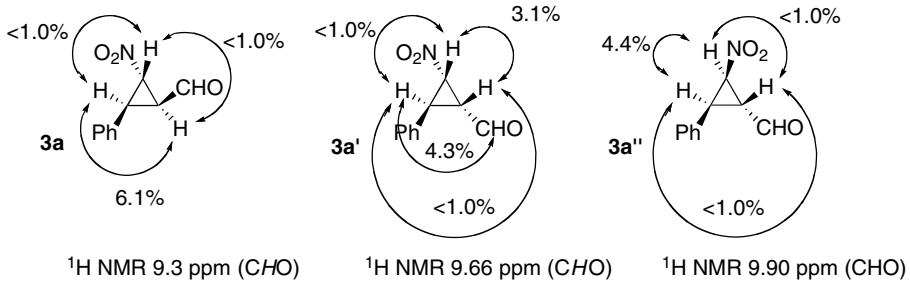


Entry	R	Time (h)	Products	Yield[b] (%)	Dr[c] (**3**:**3′**)	ee[d] (%) (**3**:**3′**)
1	Ph	3	**3a**:**3a′**	63	1:1	95:95
2	4-BrC_6H_4	2	**3b**:**3b′**	35 (95)[e]	3:1	95:n.d.
3	*n*-Pr	1	**3c**:**3c′**	42	1:1	91:92
4		1	**3d**:**3d′**	56	3:2	98:99
5	4-ClC_6H_4	2	**3e**:**3e′**	29 (94)[e]	3:1	92:n.d.

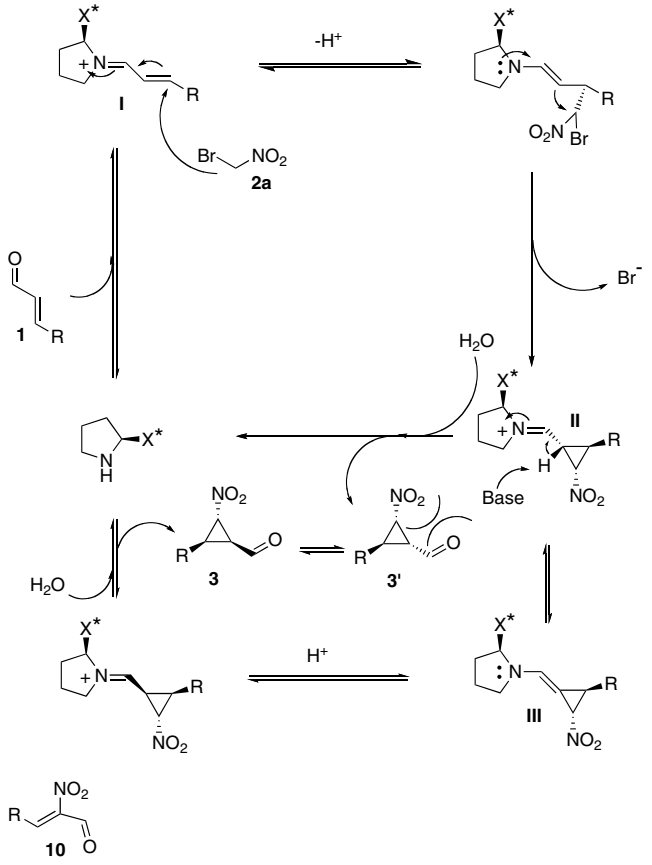
[a] Experimental conditions: To a mixture of enal **1** (0.30 mmol), catalyst **8** (20 mol %) and TEA (0.25 mmol) in $CHCl_3$ (1.0 mL) was added 2-bromonitromethane **2a** (0.25 mmol) and the reaction mixture was stirred under the conditions shown in the Table.
[b] Isolated combined yield of pure compounds **3**.
[c] Diastereoisomeric ratio as determined by ^{1}H NMR.
[d] Enantiomeric excess determined by chiral-phase HPLC analysis.
[e] Yield based on recovered starting material **1**. n.d. = not determined.



Scheme 1. Organocatalytic ring-opening of 1-nitrocyclopropanes **3a** and **3e**.



Based on the absolute and relative configuration of nitrocyclopropane derivatives **3**, we propose the following mechanism to account for the organocatalytic nitrocyclopropanation reaction of enals **1**. Accordingly, efficient shielding of the *Si*-face (*Re* when R = Aryl) of the chiral iminium intermediate **I** by the bulky aryl groups of chiral pyrrolidine **8** leads to stereoselective *Re*-facial nucleophilic conjugate addition by the 2-bromonitromethane **2a** (Scheme 2). Next, the generated chiral enamine intermediate undergoes intramolecular 3-*exo*-*tert* nucleophilic attack to form the cyclopropane ring. The intramolecular ring-closure pushes the equilibrium forward and makes this step irreversible. This is the same type of mechanism that occurs during the organocatalytic asymmetric epoxidation,[22a,b] aziridination[23] and cyclopropanation of enals.[11] Hydrolysis of iminium intermediate **II** releases the catalyst and gives the corresponding 2-formyl cyclopropane **3′**. Due to steric repulsion between the nitro-group and the catalyst of iminium complex **II** or the nitro- and 2-formyl-groups of **3′**, epimerization occurs via intermediate **III** and diastereoisomer **3** is formed. Moreover, we also observed that enal **10** could be formed via intermediate **III** and subsequent ring-opening under certain reaction conditions.[11] In the case of (*S*)-2-carboxylic acid dihydroindole **6** catalysis, the bromomalonate **2** approached the opposite face of the iminium intermediate to give cyclopropanes *ent*-**3**.



Scheme 2. Proposed reaction mechanism.

In summary, we have reported a simple, highly enantioselective catalytic nitrocyclopropanation reaction of unmodified enals, which gives the corresponding 1-nitro-2-formylcyclopropanes in 91–99% ee. This is the first example of a highly enantioselective organocatalytic nitrocyclopropanation of α,β-unsaturated aldehydes. Examples of the 1-nitro-2-formylcyclopropane products were converted to the corresponding β-nitromethyl-esters (>92% ee), which are excellent precursors of GABA analogues such as Baclofen, by organocatalytic chemoselective ring-opening.

Acknowledgements

We gratefully acknowledge the Swedish National Research Council, Carl-Trygger Foundation and the Swedish Governmental Agency for Innovation Systems (VINNOVA) for financial support.

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17. Typical experimental procedure for the organocatalytic nitrocyclopropanation: To a stirred solution of catalyst **8** (0.05 mmol, 20 mol %), α,β-unsaturated aldehyde **1** (0.30 mmol, 1.2 equiv) and Et_3N (0.25 mmol, 1.0 equiv) in $CHCl_3$ (1.0 mL) was added bromonitromethane **2a** (0.25 mmol, 1.0 equiv). The reaction mixture was stirred vigorously at room temperature for the reported time. Next, the crude product was purified by silica gel chromatography (pentane/EtOAc-mixtures) to give the corresponding nitrocyclopropane derivatives **3**.
Compound **3a**: Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.29 (d, J = 3.2 Hz, 1H), 7.32–7.24 (m, 5H), 5.31 (dd, J = 3.6 Hz, 4.8Hz, 1H), 3.85 (dd, J = 4.8 Hz, 11.2 Hz, 1H), 3.42 (dt, J = 3.6 Hz, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 193.1, 129.4, 129.2, 129.0, 128.7, 62.6, 38.7, 36.4. HRMS (ESI): calcd for $[M+Na]^+$ ($C_{10}H_9NO_3$) requires m/z 214.0475, found, 214.0482. The enantiomeric excess was determined by HPLC using an OD-H column (*n*-hexane/*i*-PrOH = 90:10, λ = 230 nm), 1.0 mL/min; t_R = major enantiomer 23.5 min, minor enantiomer 26.9 min. $[\alpha]_D^{23}$ −51.9 (c = 1.0, $CHCl_3$) (for a diastereomeric mixture **3a**/**3a**′ of 3:1).
Compound **3a**′: Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (d, J = 5.2 Hz, 1H), 7.37–7.24 (m, 5H), 4.81 (dd, J = 4.8 Hz, 8.4 Hz, 1H), 4.00 (dd, J = 4.8 Hz, 7.6 Hz, 1H), 2.70 (dt, J = 4.8 Hz, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 193.4, 130.4, 129.2, 129.0, 128.8, 39.4, 32.7, 29.8. HRMS (ESI): calcd for $[M+Na]^+$ ($C_{10}H_9NO_3$) requires m/z 214.0475, found 214.0482. The enantiomeric excess was determined by HPLC using an OD-H column (*n*-hexane/*i*-PrOH = 90:10, λ = 230 nm), 1.0 mL/min; t_R = major enantiomer 37.1 min, minor enantiomer 39.5 min.
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21. Methyl (*S*)-3-(4-chlorophenyl)-4-nitrobutanoate **9e**: $[\alpha]_D^{25}$ −4.4 (c 0.5, $CHCl_3$); (lit. for the (*R*) enantiomer: $[\alpha]_D^{25}$ +4.0 (c 1.0, $CHCl_3$)[19a]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.28 (m, 2H), 7.19–7.16 (m, 2H), 4.72 (dd, J = 5.1, 12.8 Hz, 1H), 4.61 (dd, J = 8.0, 12.8 Hz, 1H), 3.99–3.95 (m, 1H), 3.64 (s, 3H), 2.75 (dd, J = 4.0, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9. 136.9, 134.1, 129.5, 128.9, 79.3, 52.2, 39.7, 37.5; The enantiomeric excess was determined by HPLC with an ODH column (*n*-hexane/*i*-PrOH = 85:15, λ = 205 nm), 0.5 mL/min; t_R = minor enantiomer 25.8 min, major enantiomer 39.8 min. HRMS(ESI) the exact mass calculated for $[M+Na]^+$ ($C_{11}H_{12}ClO_4NNa$) requires m/z 280.0347, found m/z 280.0341.
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