

Efficient Synthesis of Cyclopropane-Fused Heterocycles with Bromoethylsulfonium Salt

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The 3-azabicyclo[3.1.0]hexane is a common motif in natural products.^[1–6] Furthermore this rigid framework represents a privileged class of pharmacologically active compounds, often showing enhanced binding affinities with their targets (Figure 1).^[7] These bicycles also represent conformationally restricted analogues of piperidines (e.g. trovafloxacin).^[8] When substituted with a carboxylic acid moiety, they resemble conformationally restricted analogues of glutamate, gamma-amino butyric acid (GABA) or α/β -proline analogues (Figure 2).^[9]

Numerous methods have been developed for the construction of azabicyclo[3.1.0]hexanes.^[10] These include the Kulinkovich/de Meijere reaction,^[11,12] cyclisation of tethered amines with metals (Pd,^[13] Ru,^[14] Rh,^[15] Ag^[16]), cyclisation of tethered cyclopropanes^[17] and the Simmons–Smith^[18]/Corey–Chaykovsky^[19]/sulfur ylide–Au^[20] cyclopropanations. These methods are usually only effective in the synthesis of one specific type of scaffold.

We were keen to develop a general strategy that could deliver 3-azabicyclo[3.1.0]hexanes with a range of functional groups in a range of positions. Our design plan for the synthesis of the scaffold was to effect a tandem process initiated by conjugate addition of an unsaturated amine **1** to vinyl sulfonium salt **2**, generated in situ from the stable and crystalline salt **3** (Scheme 1). The intermediate sulfur ylide **4** would undergo intramolecular addition to the Michael acceptor to give a sulfonium enolate **5**, which would ring-close to the cyclopropane **6**.

This tandem process is related to the previously described reactions that bear aldehydes or imines in place of Michael

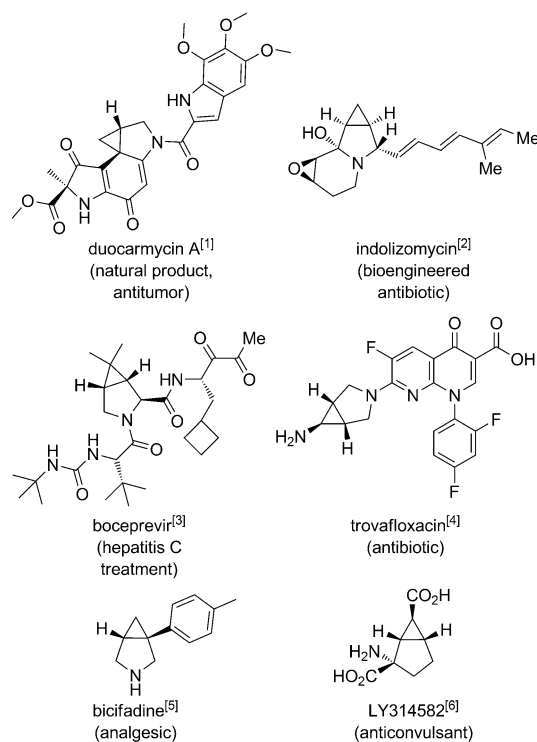


Figure 1. Selected examples of important bicyclo[3.1.0]hexanes.

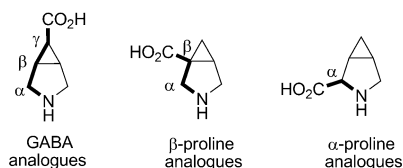
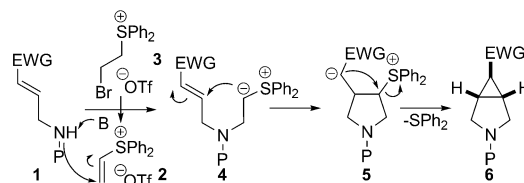


Figure 2. Conformationally restricted scaffolds discussed in this work.

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Scheme 1. Proposed mechanism of the reaction. B = base; EWG = electron-withdrawing group.

acceptors, giving fused bicyclic epoxides and aziridines, respectively.^[21,22] However, the more complex reaction with Michael acceptors (leading to products with additional stereogenic centres) has not been previously reported.^[23] The potential for a very rapid increase in molecular complexity from simple starting materials was an additional attractive feature of the chemistry. In this paper, we report the successful realisation of this strategy and the formation of azabicyclo[3.1.0]hexanes with surprisingly high diastereoselectivity.

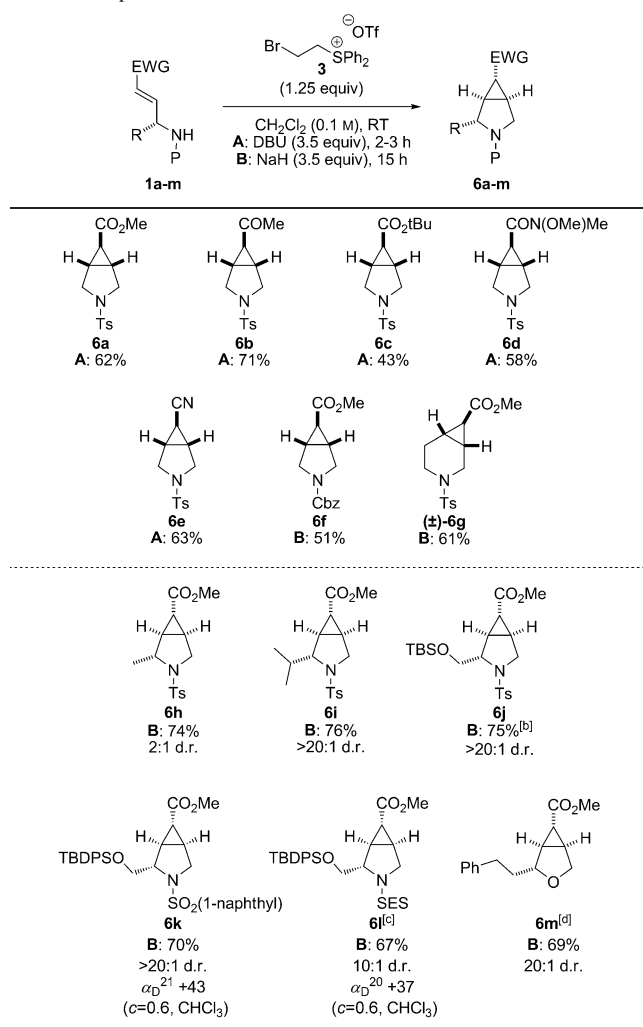
Our studies began with the preparation of a diverse array of allylic amines. The allylic amines **1a–g** were prepared in one step by using either cross-metathesis^[24] or Wittig chemistry. Similarly, **1h–j** were synthesized in two steps from commercially available, amino-acid derived methyl esters through a diisobutylaluminium hydride (DIBAL-H) reduction/Wittig reaction sequence. Allylic amines **1k**, and **1l** with the appropriate protecting groups required several steps,^[25] whilst **1m** was available in one step from reaction of dihydrocinnamaldehyde with a vinylchromium nucleophile (see Supporting Information for details).^[26]

The reaction of unsaturated amide **1a** with the stable and crystalline salt **3** was initially tested. After optimisation of the process (see Supporting Information for details), a set of conditions were established (method **A**) that led to moderate–high yields of the [3.1.0] bicycles with complete diastereoselectivity (Table 1).^[27] For example, unsaturated amide **1a** gave the cyclopropane **6a** in 62% yield as a single diastereomer. The Michael acceptors tested bore a range of electron-withdrawing groups, including Me and *t*Bu esters, ketones, amides and nitriles (**6a–e**). Furthermore, in the case of the unsubstituted allylic amide, the *N*-Cbz (Cbz = carbobenzyloxy) carbamate **1f**^[28] could also be employed in place of the tosyl protecting group leading to the pyrrolidine **6f**. The piperidine **6g** was also accessible using the same process and again was formed with complete diastereoselectivity.

The method was further extended to a range of α -substituted allylic amines (**1h–m**), although in this case NaH was found to be superior to 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; method **B**, Table 1). With a small substituent (Me, **1h**), the azabicyclo[3.1.0] hexane **6h** was formed with low diastereoselectivity but with larger substituents (**1i**, **1j**) the adducts (**6i**, **6j**) were formed with essentially complete diastereoselectivity. In terms of the *N*-protecting group, with α -substituted allylic amines, it was not possible to use the Cbz or *tert*-butoxycarbonyl (Boc) groups, but the more easily cleavable^[28] 1-naphthyl or 2-(trimethylsilyl)ethyl sulfonamides (**1k**, **1l**) worked well giving similarly high yields and diastereoselectivities. Interestingly, allylic alcohol **1m** could also be used and gave the tetrahydrofuran **6m**, again with high selectivity. The methodology readily lent itself to the preparation of enantioenriched products, as illustrated with **6k** and **6l**, since the α -substituted allylic amines are easily obtained from chiral amino acids (serine in this case).

Expanding this methodology further, we were able to utilise easily accessible aza-Morita–Baylis–Hillman adducts

Table 1. Scope of the transformation.^[a]



[a] All yields are isolated yields and diastereomeric ratio (d.r.) is determined by ^1H NMR spectroscopy of the crude material. [b] Yield of TBS deprotected product including an in situ deprotection with TBAF (5 equiv) added after 15 h. [c] Reaction at 0°C , if run at RT yield is 75% and d.r. is 7:1. [d] Minor traces of the other diastereoisomer are visible in the ^1H NMR spectrum. SES = 2-(trimethylsilyl)ethanesulfonyl, TBAF = tetrabutylammonium fluoride.

7a–c^[29] (one step from the acrylate), as the starting materials for the cyclisation. These reactions now led to the formation of β -proline-derived fused cyclopropanes **8a–c** (Table 2).^[30]

Whilst unsaturated esters **7a** and **7b** worked well, giving the corresponding adducts **8a** and **8b**, respectively, in high yields with very high diastereoselectivity, unsaturated ketone (**7c**) behaved differently. In this case the major product was the epoxy-annulation adduct **9**. Evidently, after 1,4-addition of the amide **7c** to the vinyl sulfonium salt **1**, the ylide intermediate reacts in a more favoured 6-*exo*-trig mode with the ketone moiety, rather than the desired 6-*endo*-trig mode with the alkene. Nevertheless, the pyrrolidine **8c** was formed with high diastereoselectivity as before. The methodology readily lends itself to asymmetric synthe-

Table 2. Reactivity of (aza)-Morita-Baylis-Hillman adducts.^[a]

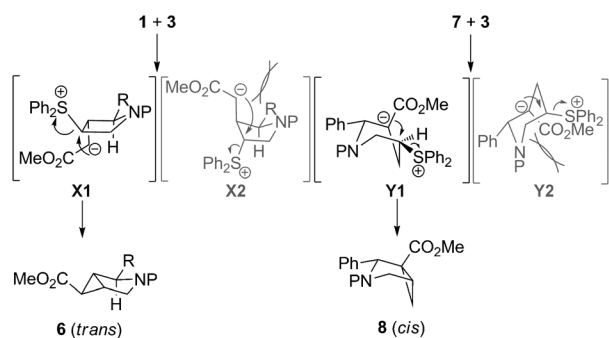
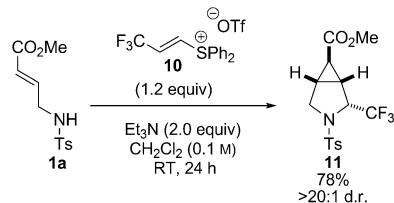
	$\text{Br-CH}_2\text{-CH}_2\text{-SPh}_2^{\oplus}\text{OTf}^-$ (3) (2.0 equiv) in 2 steps	
7a : X = OMe	(\pm)- 8a , 64%, >20:1 d.r.	
7b : X = <i>Or</i> Bu	(\pm)- 8b , 45%, >20:1 d.r.	
7a : X = OMe (82% <i>ee</i>)	(+)- 8a , 63%, >20:1 d.r.; 82% <i>ee</i> (>99% <i>ee</i> after recrystallization) ^[b]	
7c : X = Me		
	(\pm)- 8c (minor) 16% >20:1 d.r.	(\pm)- 9 (major) 76% 1:1 d.r.

[a] All yields are isolated yields and d.r. is determined by ¹H NMR spectroscopy of the crude. [b] The *ee* was determined by chiral supercritical-fluid chromatography (SFC), see the Supporting Information for full details.

sis, since the aza-Morita-Baylis-Hillman adducts **7a,b** are obtainable using asymmetric organocatalysis.^[31] This was illustrated by the use of (+)-**7a** (82% *ee*; *ee* = enantiomeric excess), which gave the [3.1.0] bicyclic (+)-**8a** without measurable racemization, which was increased to >99% *ee* after recrystallization.

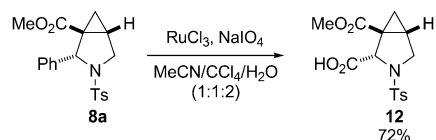
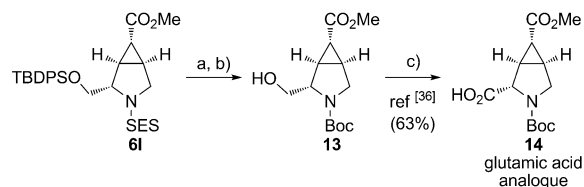
The relative stereochemistry of cyclopropanes **6g, 6i**, and **8a** were determined by X-ray analysis and related compounds were assigned by analogy (see the Supporting Information for details). It is believed that the steps prior to ring closure are reversible and that the selectivity is determined in the nonreversible ring-closure step that forms the cyclopropane. The origin of selectivity of the two classes of substrates **1** and **7** can be rationalised by considering the nonbonded steric interactions in the TSs for which the less hindered **X1** and **Y1** are favoured over **X2** and **Y2**, which subsequently leads to the preferred formation of *trans* (**6h-m**) and *cis* (**8a-c**) isomers (Scheme 2).

The cyclopropanation-annulation reaction was further extended to include the medicinally important CF₃ group. Thus, reaction of **1a** with the CF₃-substituted vinyl sulfonium salt **10**^[32] gave the CF₃-substituted [3.1.0]pyrrolidine

Scheme 2. Model for diastereoselectivity in the formation of **6** and **8**.Scheme 3. Formation of **11** with β -CF₃ vinylsulfonium salt **10**.

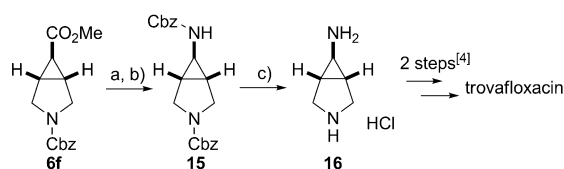
11,^[33] again with essentially complete diastereoselectivity^[21i] (Scheme 3).

The synthetic utility of the methodology is illustrated through a range of functional-group transformations of several of the [3.1.0]pyrrolidines. For example, oxidative cleavage of the Ph group^[34] in **8a** gave pyrrolidine **12**, which is both an α - and a β -amino acid derivative (Scheme 4).^[35] De-

Scheme 4. Oxidation to α,β -amino acid derivative **12**.Scheme 5. Deprotection and transformation of **6f**: a) CsF (5 equiv), DMF (0.1 M), 95 °C, 4 h then b) Boc₂O (1.2 equiv), NEt₃ (3 equiv), CH₂Cl₂, RT, 2 h, 62% over 2 steps; c) PDC (4 equiv), DMF (0.5 M), ref. [36], 63%. PDC = pyridinium dichromate.

protection and oxidation of **6f** gave the conformationally locked glutamic acid analogue **14** (Scheme 5).^[36]

Finally, pyrrolidine **6f** was converted into 6-amino-3-azabicyclo[3.1.0]hexan-3-ium chloride **16**, an intermediate used in the synthesis of trovafloxacin, a potent antibiotic.^[4] Thus, saponification of the ester **6f**, followed by the Schmidt reaction with diphenyl phosphoryl azide (DPPA) gave pyr-

Scheme 6. Formal synthesis of the trovafloxacin precursor **16**: a) aq. NaOH (1 M), THF, RT, 15 h then b) DPPA (1.1 equiv), NEt₃ (1.1 equiv), BnOH (5 equiv), PhMe (0.25 M), 90 °C, 1.5 h, 62% (0.3 g scale) over 2 steps; c) H₂ (1 atm), Pd/C (cat.), HCl in Et₂O (2 M, 3 equiv), MeOH, RT, 3 h, 99%.

rolidine **15**. Finally, hydrogenolysis gave amino pyrrolidine **16** in just a few synthetic steps (Scheme 6).

In conclusion we have developed a novel, efficient and versatile route for the formation of cyclopropane-fused heterocycles from easily available starting materials. In comparison to previous methods, this protocol enables the synthesis of a more diverse range of substituted and functionalized [3.1.0] scaffolds with very high diastereoselectivity. There is considerable interest in exploring this class of bioactive compounds, which should now be enabled by the methodology described herein.

Experimental Section

General: A stirred solution of amine or alcohol **1** (1.0 equiv) and diphenyl bromoethyl sulfonium salt **3** (1.25 equiv, commercially available) in anhydrous solvent (0.1 M) at room temperature under an inert atmosphere was treated with base (3.5 equiv) and stirred for the indicated time (until complete consumption of starting material was detected by HPLC or TLC analysis). The reaction mixture was then quenched with 10% aqueous citric acid solution (15 mL per mmol of **1**) and the aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL per mmol of **1**). The combined organic layers were washed with brine (30 mL per mmol of **1**), dried (MgSO₄) and concentrated in vacuo. The crude reaction mixture was purified by flash chromatography, eluting with either EtOAc/*n*-pentane or Et₂O/*n*-pentane to give the desired product.

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Keywords: amino acids • Baylis–Hillman reaction • cyclopropanes • heterocycles • sulfur ylides

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