Synthetic Methods

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Catalytic Asymmetric Synthesis of 8-Oxabicyclooctanes by Intermolecular [5+2] Pyrylium Cycloadditions**

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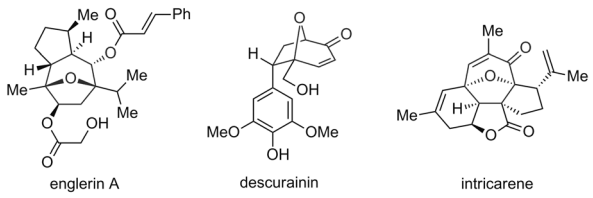
Abstract: *Highly enantioselective intermolecular [5+2] cycloadditions of pyrylium ion intermediates with electron-rich alkenes are promoted by a dual catalyst system composed of an achiral thiourea and a chiral primary aminothiourea. The observed enantioselectivity is highly dependent on the substitution pattern of the 5π component, and the basis for this effect is analyzed using experimental and computational evidence. The resultant 8-oxabicyclo[3.2.1]octane derivatives possess a scaffold common in natural products and medicinally active compounds and are also versatile chiral building blocks for further manipulations. Several stereoselective complexity-generating transformations of the 8-oxabicyclooctane products are presented.*

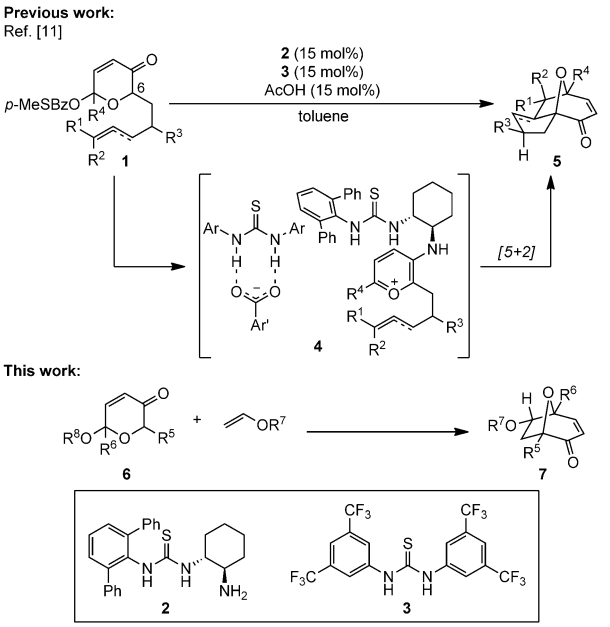
Chiral 8-oxabicyclo[3.2.1]octane architectures reside at the core of numerous natural products and biologically significant compounds (Scheme 1).[1,2] Heterocycles of this class have also proven to be valuable intermediates in the stereoselective synthesis of oxygenated seven-membered carbocycles[3]



Scheme 1. The 8-oxabicyclo[3.2.1]octane core in selected natural products.

and tetrahydrofuran derivatives.[4] Successful stereoselective approaches to the 8-oxabicyclo[3.2.1]octane framework have relied on transition-metal-catalyzed [3+2] cycloadditions,[5] [4+3] cycloadditions,[6] diastereoselective [5+2] cycloadditions,[7] and diastereoselective cascade cyclizations.[8]

The [5+2] cycloaddition of a pyrylium ylide precursor with a C_2 dipolarophile (e.g. **6** to **7**, Scheme 2) provides a concise approach to the 8-oxabicyclo[3.2.1]octane framework, while also embedding a reactive α,β-unsaturated ketone in the bicyclic core.[9,10] The products can thus be subjected to stereoselective elaboration to afford a diverse array of chiral structures in just one or two steps (see below). We reported recently that a dual catalyst system consisting of the chiral primary amine **2** and the achiral thiourea **3** catalyzes enantioselective intramolecular [5+2] cycloadditions of alkenylpyranones of structure **1** through the proposed intermediacy of thiourea-complexed aminopyrylium salts (**4**, Scheme 2).[11–13] While this method enables the preparation of a range of complex tricyclic products, the corresponding intermolecular reaction would provide more general access to 8-oxabicyclo[3.2.1]octane derivatives from simpler and more accessible starting materials.[14] However, initial efforts to effect intermolecular variants of these reactions proved unsuccessful (< 40% *ee*).[11] Here, we disclose that closer examination of this reaction manifold has revealed striking substrate structure-enantioselectivity effects and has led to the successful development of highly enantioselective intermolecular [5+2] cycloadditions.



Scheme 2. Enantioselective [5+2] cycloadditions. Bz = benzoyl.

The racemic pyranone **8a** (Scheme 3), which is superficially analogous to pyranone substrates **1** identified as optimal for the intramolecular reaction,[11] was examined initially as a model substrate for the study of the intermolecular cycloaddition. Treatment of **8a** with a series of

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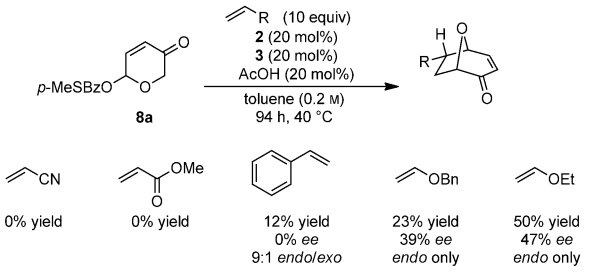
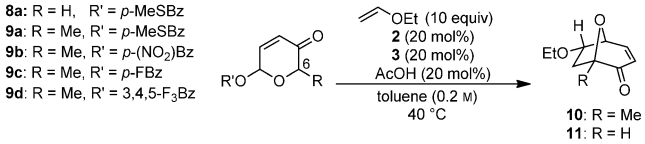


Scheme 3. Screen of 2π components.

terminal alkenes under the dual catalyst conditions developed in the original study revealed that the electronic properties of the 2π component had a strong effect on reactivity.[15] Electron-deficient olefins such as acrylonitrile and methyl acrylate were completely inert; styrene displayed measurable but low reactivity to afford racemic product; electron-rich olefins such as benzyl vinyl ether and ethyl vinyl ether underwent cycloaddition with higher conversions and encouraging enantioselectivity. The observation that a nucleophilic 2π reactant is required in the catalytic reaction is consistent with a mechanism involving a cationic, electron-poor aminopyrylium intermediate analogous to **4** (Scheme 2) rather than an ambiphilic, zwitterionic oxidopyrylium intermediate.[9f,g]

It proved possible to affect the enantioselectivity of the intermolecular cycloaddition reaction to a remarkable degree through relatively subtle modifications to the structure of the pyrylium precursor. All substrates shown to undergo intramolecular [5+2] cycloadditions with high enantioselectivity in the original study possessed a linkage to the 2π component through the 6-position of the pyranone (**1**, Scheme 2).[11] The possibility that the presence of a 6-substituent might affect the enantioselectivity in the intermolecular reaction was evaluated by comparing the reaction of **8a** with that of methylated pyranone **9a** (Table 1, entries 1 and 2).[15] The dramatic improvement in the enantioselectivity observed with methylated derivative **9a** suggests a critical role of that substituent in controlling the transition-structure geometry in the catalytic reaction (see below).

Table 1: Reaction optimization.[a]



Entry	Substrate	*t* [h]	Yield[b] [%]	*ee*[c] [%]
1	**8a**	48	53	47
2	**9a**	48	55	90
3	**9b**	48	63	94
4	**9c**	48	65	93
5	**9d**	48	73	92
6[d]	**9d**	72	75	96

[a] Reactions were performed on a 0.07 mmol scale. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Determined by HPLC using commercial columns with chiral stationary phases. [d] 5 equiv ethyl vinyl ether, room temperature.

Further improvement in both the enantioselectivity and the yield of the cycloaddition reaction was achieved through electronic tuning of the leaving group on the pyranone. While the *p*-thiomethylbenzoate leaving group had been identified as optimal in the intramolecular reaction, electron-deficient analogues **9b–d** were found to be advantageous in the intermolecular manifold (entries 3–5).[16] In particular, 3,4,5-trifluorobenzoate derivative **9d** provided the best balance of reactivity and enantioselectivity, and further improvement in the *ee* values could be achieved by carrying out the reaction at ambient temperature and decreasing the amount of ethyl vinyl ether from 10 to 5 equivalents relative to pyranone (entry 6).

Having thus established viable parameters for effecting highly enantioselective intermolecular [5+2] cycloadditions of a pyrylium ion precursor, an investigation of the reaction substrate scope was carried out (Table 2).[17] Pyranones bearing longer alkyl chains at the 6-position also undergo cycloaddition with ethyl vinyl ether with high enantioselectivity (entry 2); however β-branching in the side chain has a deleterious effect on reactivity (entries 3 and 4). Cycloadducts bearing siloxymethylene groups could be accessed in

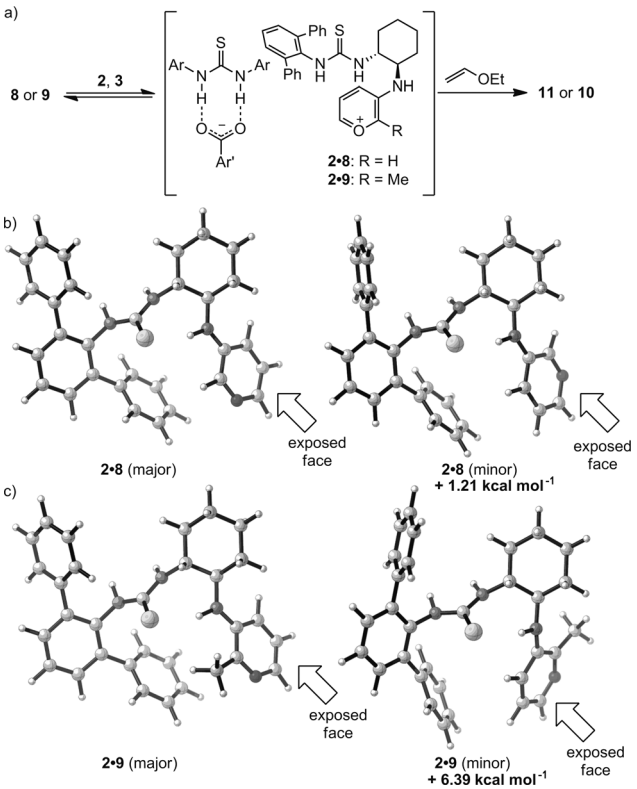


Figure 1. a) Formation of intermediate aminopyrylium. b,c) Lowest energy calculated structures (B3LYP/6-31G(d)) of the aminopyrylium ions **2·8** and **2·9**. In both cases, the major conformer has the face of the aminopyrylium ion that leads to the major observed enantiomer of cycloadduct exposed, while the other face is shielded. The difference in energy between the major and minor conformers is substantially higher for **2·9**, however, and that is a potential explanation for the higher enantioselectivities obtained in cycloadditions of **9**. (b) and (c) were generated using CYLview.[25]

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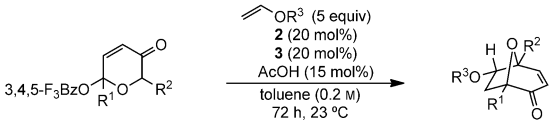
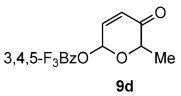
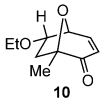
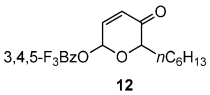
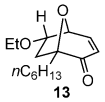
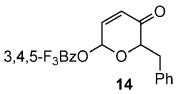
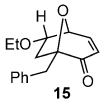
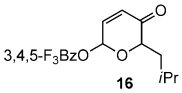
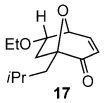
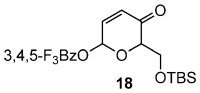
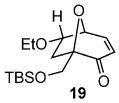
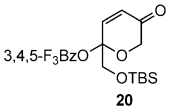
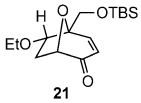
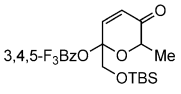
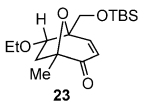
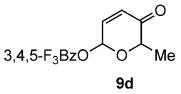
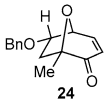
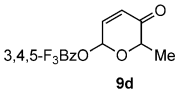
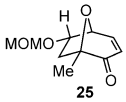
Table 2: Substrate scope.[a]



Entry	Substrate	R^3	Product	Yield [%]	*ee*[b] [%]
1[c,f]	 **9d**	Et	 **10**	69	96
2	 **12**	Et	 **13**	59	90
3[c]	 **14**	Et	 **15**	22	88
4	 **16**	Et	 **17**	26	67
5	 **18**	Et	 **19**	64	86
6[c,d]	 **20**	Et	 **21**	95	64
7	 **22**	Et	 **23**	75	89
8[c]	 **9d**	Bn	 **24**	88	89
9[e]	 **9d**	MOM	 **25**	54	91

[a] Reactions were performed on a 0.2 mmol scale. Yields of isolated products after chromatography on silica gel. For details on substrate synthesis, see the Supporting Information. [b] Determined by HPLC using commercial columns with chiral stationary phases. [c] 15 mol% **2** + 15 mol% **3**. [d] 96 h at 0°C. [e] 10 equiv vinyl ether. [f] The absolute configuration of a derivative of **10** was determined by X-ray crystallography (see the Supporting Information), and that of all other products was assigned by analogy. MOM = methoxymethyl, TBS = *tert*-butyldimethylsilyl, Bn = benzyl.

moderate-to-good enantioselectivity under the catalytic conditions (entries 5–7). Products of this type have found extensive synthetic applications.[3a,d,7a,e,f] Benzyl vinyl ether (entry 8) and (methoxymethoxy)ethene (entry 9) were also used successfully as 2π components in the cycloaddition reaction, thereby affording products with readily cleavable ethers. However, styrene derivatives remain poorly reactive in reactions with **9d**, with the resultant cycloadducts formed with very low (< 15%) *ee* values. Enamines and polysubstituted vinyl ethers also proved to be poor substrates, the former undergoing hydrolysis under the reaction conditions and the latter exhibiting very low reactivity.[15]

We sought to elucidate the basis for the significant difference in enantioselectivity between the reactions of pyranones **8** and **9** (e.g. Table 1, entries 1 and 2) as a possible path toward gleaning insight into the mechanism of stereoinduction in these reactions. The formation of the adduct **2·9** (Figure 1a) was confirmed by mass spectrometric analysis of a reaction mixture sampled prior to addition of the vinyl ether component.[15] The lowest energy structures of the two aminopyrylium ions **2·8** and **2·9** were located computationally (Figure 1b,c left).[18] Rotation about the $C(sp^2)$–N bond in each structure and reoptimization then yielded ground-state structures in which the opposite face of the aminopyrilium ion is exposed (Figure 1b,c right).[19] In the minor conformer of **2·9**, a steric interaction between the methyl substituent and the catalyst's cyclohexyl backbone causes a significant distortion and energetic penalty (> 6 kcal mol^{-1} relative to the major conformer). That steric interaction is absent if the methyl group is omitted (Figure 1c), resulting in a much smaller energy difference between the conformations of **2·8**. We propose that the methyl substituent in **9** thus enforces a dominant reactive conformation of the aminopyrilium ion adduct, which results in a more highly enantioselective cycladdition pathway.

The 8-oxabicyclooctane cycloadducts possess several functional group handles for potential elaboration (Scheme 4). The synthesis of **10** was carried out successfully on 0.70 g batches of starting material under the conditions described in Table 2 to give cycloadduct in 69% yield and 96% *ee*. Products resulting from conjugate addition (**26**), epoxidation (**27**),[20] Diels–Alder reaction (**28**),[21] or Luche reduction (**29**) and subsequent acylation (**30**) were all generated as single diastereomers within detection limits. The cycloadduct **10** can also be subjected to hydrogenation to another key intermediate, saturated ketone **31**.[22] This heterocycle undergoes Grignard addition stereoselectively to afford tertiary alcohol **32**. Tosylhydrazone **33**, which is primed to undergo Shapiro or Bamford–Stevens reactions, can also be readily synthesized from intermediate **31**. Finally, σ-bond insertion of cyclohexyne yields an unusual 9,6-fused ring system (**34**) in a single step.[23]

The oxygen bridge of the 8-oxabicyclo-[3.2.1]octane framework can also be cleaved reductively. In the case of iodide **36**, this results in formation of an interesting seven-membered product possessing an exocyclic enone (Scheme 5).[24] As in all of the previous examples, the product was generated as a single diastereomer and without compromise of the optical purity of the initial cycloadduct.

In summary, the catalytic, asymmetric, intermolecular [5+2] pyrylium cycloadditions developed in this study provide

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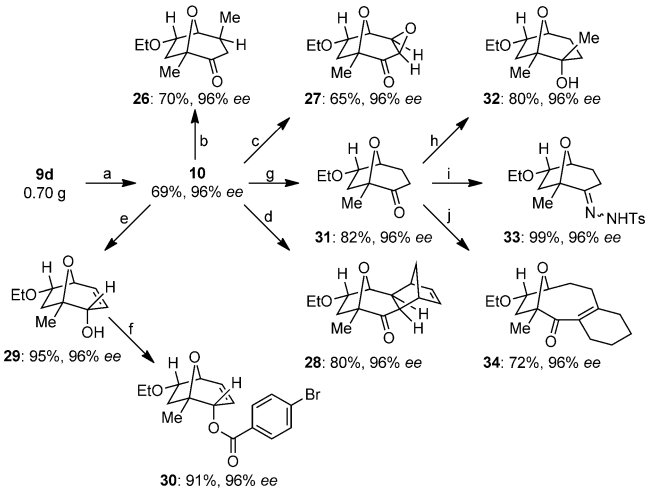
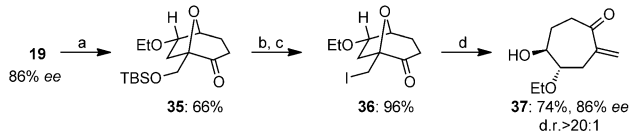


Scheme 4. Derivatization reactions. Reaction conditions: a) **2** (15 mol%), **3** (15 mol%), AcOH (15 mol%), ethyl vinyl ether, toluene; b) Me_2CuLi, Et_2O; c) *t*BuOOH, $NaHCO_3$, H_2O, MeOH; d) cyclopentadiene, $ZnCl_2$, C_6H_6; e) $CeCl_3{\cdot}7H_2O$, $NaBH_4$, MeOH; f) *p*-BrBzOH, DMAP, pyr., CH_2Cl_2; g) SiH_2Ph_2, $ZnCl_2$ (10 mol%), $[Pd(PPh_3)_4]$ (2 mol%), $CHCl_3$; h) MeMgI, Et_2O; i) H_2NNHTs, THF, H_2O; j) cyclohexenylphenyl iodonium tetrafluoroborate, $KOCEt_3$, THF. All products are isolated in d.r. > 20:1. DMAP = 4-dimethylaminopyridine, pyr. = pyridine, Ts = toluene-4-sulfonyl.



Scheme 5. Stereocontrolled preparation of cycloheptanone **37**. Reaction conditions: a) SiH_2Ph_2, $ZnCl_2$ (10 mol%), $[Pd(PPh_3)_4]$ (2 mol%), $CHCl_3$; b) AcOH, HCl, THF, H_2O; c) I_2, PPh_3, imidazole, C_6H_6; d) Zn, MeOH.

multifunctional chiral building blocks that are immediate precursors to a wide range of compound classes. Studies into the mechanism of catalyst cooperativity, as well as extension of the principle into other transformations, are the focus of continuing efforts in this laboratory.

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