Asymmetric Catalysis

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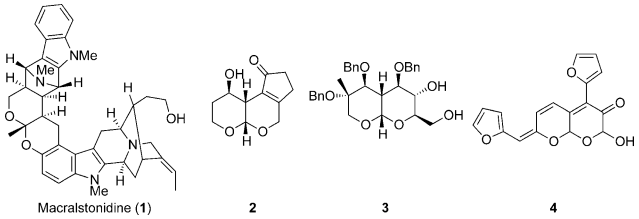
Diastereodivergent Catalysis Using Modularly Designed Organocatalysts: Synthesis of both *cis*- and *trans*-Fused Pyrano[2,3-*b*]pyrans

*Huicai Huang, Swapna Konda, and John C.-G. Zhao**

Abstract: *Both enantiomers of cis- and trans-fused 3,4,4a,8a-tetrahydro-2H,5H-pyrano[2,3-b]pyran-7-carboxylates have been obtained in high diastereoselectivities and enantioselectivities from the same starting materials using a tandem inverse-electron-demand hetero-Diels–Alder/oxa-Michael reaction catalyzed by modularly designed organocatalysts (MDOs). Diastereodivergence was achieved in these reactions through the direct control of the stereochemistry of the bridgehead atoms of the fused ring using new MDOs self-assembled from both enantiomers of proline and cinchona alkaloid thiourea derivatives.*

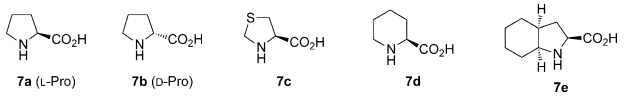


Scheme 1. Natural and synthetic products containing the pyrano[2,3-*b*]pyran moiety.

Significant advances have been made in the field of asymmetric catalysis by the organic community and they now allow routine access to numerous, chiral organic molecules in high enantiopurity.[1] Despite these advances, accessing all the possible stereoisomers with high stereocontrol remains a notable challenge.[2] Diastereodivergent catalysis,[2] which is aimed at generating different diastereomers from the same substrate(s) in a catalytic reaction, is the most direct and efficient method for obtaining multiple diastereomers.[3,4] Lately, the power of diastereodivergent catalysis has been clearly demonstrated in the synthesis of multiple stereoisomers of linear[3] and cyclic compounds[4] having multiple stereogenic centers. However, achieving diastereodivergence through the direct control of the stereochemistry of the bridgehead atoms of fused ring systems still remains a challenging task, and to our knowledge, there is no report of such a method.

The pyrano[2,3-*b*]pyran moiety can be found as a substructure in many natural and synthetic products, some of which exhibit interesting biological activities. A few examples are collected in Scheme 1. Macralstonidine (**1**) is one of many fused bis(indole) alkaloids isolated from the *Alstonia* species and has antimalarial activity.[5] The compound **2** is produced by a rare bacterial strain *Actinoalloteichus nanshanensis sp. Nov.*[6] The compound **3** is a key precursor for the synthesis of ansamycins,[7] whereas **4** has potent anticancer activities.[8] Because of their interesting biological activities and their relevance to natural products, several stereoselective methods have been developed for the synthesis of pyrano[2,3-*b*]pyran derivatives.[9] However, most of these methods lead to the formation of racemic *cis*-fused diastereomers only. Catalytic enantioselective syntheses of the *cis*-fused diastereomers are rare,[9c,d] and, to the best of our knowledge, no such method is available for the *trans*-fused diastereomers. Not surprisingly, there is no method that can achieve the catalytic enantio- and diastereodivergent synthesis of both *cis*- and *trans*-fused pyrano[2,3-*b*]pyrans. Previously we demonstrated[4b] that modularly designed organocatalysts (MDOs), which are self-assembled from amino acids and cinchona alkaloid derivatives in the reaction medium,[10] are able to achieve high enantio- and diastereodivergence in the synthesis of cyclohexane derivatives with four contiguous stereogenic centers. Herein we report that MDOs can also catalyze the enantio- and diastereodivergent synthesis of both enantiomers of *cis*- and *trans*-fused pyrano[2,3-*b*]pyran derivatives from the same substrates by a tandem hetero-Diels–Alder[10d,11]/oxa-Michael[12] reaction,[13] and diastereodivergence is achieved through the direct control of the stereochemistry of the bridgehead atoms of the fused rings.

By using the aldehyde **5a** and α-ketoester **6a** as model substrates, an extensive screening of the MDOs, formed in situ from the precatalysts, was conducted to assess their ability to catalyze the tandem reaction and to effect the desired diastereodivergence (see Table 1). Some of the representative catalyst modules are collected in Schemes 2 and 3 (for more details, see the Supporting Information). As the selected data in Table 1 show, when the MDO formed from L-proline (**7a**) and the quinidine thiourea **8a** was used as the catalyst in toluene at room temperature, the desired *cis*-fused pyrano-



Scheme 2. Most stereoselective reaction proline and proline-type catalysts.

[*] Dr. H. Huang, S. Konda, Prof. Dr. J. C.-G. Zhao
Department of Chemistry, University of Texas at San Antonio
One UTSA Circle, San Antonio, TX 78249-0698 (USA)
E-mail: cong.zhao@utsa.edu

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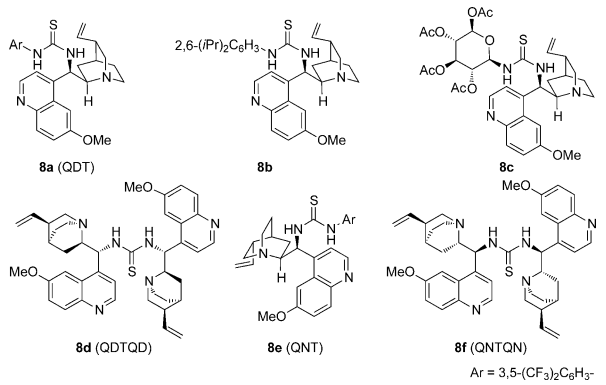
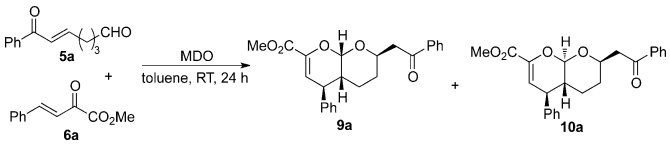


Scheme 3. Structures of selected catalysts.

Table 1: Optimization of the reaction conditions.[a]



Entry	Catalyst modules		Yield [%][b]	d.r. (**9a**/**10a**)[c]	*ee* [%][d]
1	**7a**	**8a**	89	92:8	99
2	**7b**	**8a**	65	48:52	n.d.[e]
3	**7c**	**8a**	25	91:9	97
4	**7d**	**8a**	48	92:8	93
5	**7e**	**8a**	82	92:8	97
6	**7a**	**8b**	52	52:48	92
7	**7a**	**8c**	75	39:61	58
8	**7a**	**8d**	64	10:90	96
9	**7a**	**8e**	63	45:55	n.d.[e]
10	**7e**	**8d**	85	13:87	94
11	**7b**	**8d**	43	30:70	8
12[f]	**7a**	**8a**	92	94:6	>99
13[f]	**7a**	**8d**	89	7:93	>99

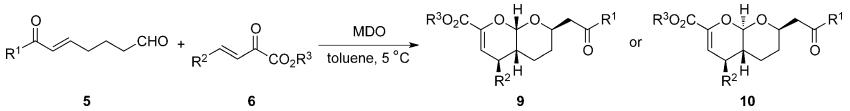
[a] Unless otherwise noted, all reactions were carried out with **5a** (0.10 mmol), **6a** (0.12 mmol), and the two catalyst modules (0.010 mol, 10 mol % each) in anhydrous toluene (0.5 mL) at RT for 24 h. [b] Combined yield of the isolated **9a** and **10a** after column chromatography. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined for the major diastereomer by HPLC analysis using a chiral stationary phase. [e] Not determined. [f] Carried out with **5a** (0.20 mmol), **6a** (0.24 mmol), and the two catalyst modules (0.020 mmol, 10 mol % each) at 5 °C in toluene (0.3 mL) for 24 h.

[2,3-*b*]pyran **9a** was obtained in 89% yield, 92:8 d.r., and 99% *ee* after 24 hours (entry 1). In contrast, when either **7a** or **8a** was used alone as the catalyst under similar reaction conditions, no reaction was observed. These results clearly indicate that the observed catalytic activity is a cooperative action of both modules. When D-proline (**7b**) and **8a** were used to form the MDO, formation of a substantial amount of the *trans*-fused product **10a** was observed. However, **10a** is not predominant in the product mixture (entry 2). The product **9a** was also obtained with similar d.r. and *ee* values when the amino acids **7c**, **7d**, and **7e** were used together with **8a** to form the MDOs (entries 3–5). However, the yields were lower. In contrast, the MDOs formed from **8a** and *trans*-4-hydroxy-L-proline and several primary amino acids were not effective at all (see the Supporting Information). Thus, these screenings identified **7a** and **8a** as good modules for obtaining **9a**. Next, additional cinchona alkaloid modules were screened with the best amino acid module **7a**. Good results were also obtained with a cinchonine-derived thiourea, however, quinidine-derived squaramides, guanidine, and sulfonamide, the Takemoto thiourea, and a quinidine-derived 6′ thiourea all proved to be poor stereocontrol modules since they all led to inferior results in the product d.r. and *ee* values (see the Supporting Information). Nevertheless, when quinidine-derived thioureas with a more bulky substituent on the thiourea moiety, such as **8b** and **8c**, were used with **7a** to form the MDOs, we noticed that the formation of the *trans*-fused **10a** increased (entries 6 and 7). These results hint that the steric factor on the thiourea moiety might be important for the formation of **10a**. To verify this, a very bulky **8d** was synthesized[14] and used in the reaction with **7a**. Gratifyingly, **10a** was indeed obtained with a high d.r. value (90:10) and a high *ee* value (entry 8). In contrast, the MDO formed from **7a** and the quinine thiourea **8e** yielded poor results (entry 9). With **8d**, the best choice for the formation of **10a**, a brief evaluation of some additional amino acids were conducted. While slightly inferior results were obtained with **7e** (entry 10), very poor results were obtained with **7b** (entry 11). Thus, our extensive screening identified the best MDO for obtaining **9a** is **7a**/**8a** (entry 1), while the best MDO for obtaining **10a** is **7a**/**8d** (entry 8).

Then the reaction conditions were further optimized (for more details, see Table S2 in the Supporting Information). Under the optimized reaction conditions, **9a** was obtained in 92% yield as essentially a single enantiomer with a high diastereoselectivity using the MDO **7a**/**8a** (Table 1, entry 12). Similar results for **10a** were also obtained with the MDO of **7a**/**8d** under these optimized reaction conditions (entry 13).

The scope of this diastereodivergent tandem reaction was established by screening more substrates under the optimized reaction conditions. The results are summarized in Table 2. As the results in the table show, **9a** may be obtained by using **7a**/**8a** (entry 1), and the enantiomer of **9a** may also be obtained with excellent d.r. and *ee* values by employing the pseudo-enantiomeric **7b**/**8e** (entry 2). The effects of the ester were first evaluated, and it was found that the diastereoselectivity dropped with the increase of the size of the ester group (entries 1, 3, and 4). Nonetheless, both electron-withdrawing (entries 5–8) and electron-donating (entries 9 and 10) groups at the *para*-position of the phenyl ring of **6** have only minimal influence on the reactivity and stereochemical outcome of this reaction. This reaction is also not sensitive towards the position of the substituent on the phenyl ring (entries 11 and 12 versus 7). Excellent results were also obtained for the product of a γ-alkyl-substituted α-ketoester (**9l**; entry 13). Similarly, the *para*-substituent on the phenyl ring of **5** has almost no influence on the reactivity and stereoselectivity (entries 14–16). The 7-alkyl-substituted 7-oxohept-5-enal also gave the expected product **9p** in high yield as well as with high d.r. and *ee* values (entry 17). Very similar results were also obtained for the *trans*-fused **10** by using the MDOs of **7a**/**8d** or its pseudoenantiomer **7b**/**8f** (entries 18–34).These results hint that these two different MDOs (**7a**/**8a** and **7a**/**8d**) are catalyzing the reactions in a similar manner.

Table 2: Substrate scope of the MDO-catalyzed diastereodivergent tandem hetero-Diels–Alder/oxa-Michael reaction.[a]



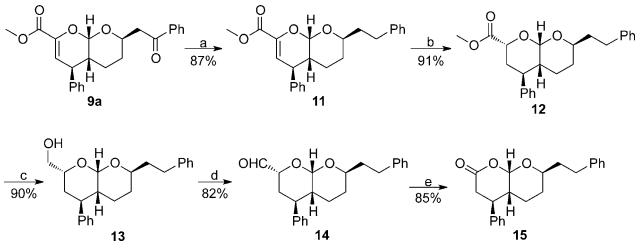
5 6 9 10

Entry	R^1	R^2	R^3	MDO	*t* [h]	Major product	Yield [%][b]	d.r.[c]	*ee* [%][d]
1	Ph	Ph	Me	**7a/8a**	24	**9a**	92	94:6	>99
2	Ph	Ph	Me	**7b/8e**	24	*ent*-**9a**	87	94:6	>99
3	Ph	Ph	Et	**7a/8a**	24	**9b**	91	90:10	>99
4	Ph	Ph	*i*Pr	**7a/8a**	24	**9c**	89	88:12	>99
5	Ph	4-FC_6H_4	Me	**7a/8a**	24	**9d**	90	93:7	>99
6	Ph	4-ClC_6H_4	Me	**7a/8a**	28	**9e**	92	92:8	97
7	Ph	4-BrC_6H_4	Me	**7a/8a**	24	**9f**	91	94:6	99
8	Ph	4-$CF_3C_6H_4$	Me	**7a/8a**	24	**9g**	93	94:6	99
9	Ph	4-MeC_6H_4	Me	**7a/8a**	24	**9h**	88	93:7	>99
10	Ph	4-$MeOC_6H_4$	Me	**7a/8a**	24	**9i**	85	93:7	>99
11	Ph	2-BrC_6H_4	Me	**7a/8a**	28	**9j**	93	99:1	>99
12	Ph	3-BrC_6H_4	Me	**7a/8a**	28	**9k**	88	92:8	>99
13	Ph	*n*-C_5H_{11}	Et	**7a/8a**	72	**9l**	74	90:10	>96
14	4-ClC_6H_4	3-BrC_6H_4	Me	**7a/8a**	24	**9m**	93	95:5	>99
15	4-BrC_6H_4	4-BrC_6H_4	Me	**7a/8a**	24	**9n**	92	94:6	>99
16	4-$MeOC_6H_4$	4-BrC_6H_4	Me	**7a/8a**	24	**9o**	92	93:7	99
17	*t*Bu	Ph	Me	**7a/8a**	48	**9p**	78	91:9	>99
18	Ph	Ph	Me	**7a/8d**	24	**10a**	89	93:7	>99
19	Ph	Ph	Me	**7b/8f**	24	*ent*-**10a**	85	94:6	>99
20	Ph	Ph	Et	**7a/8d**	24	**10b**	92	90:10	>99
21	Ph	Ph	*i*Pr	**7a/8d**	24	**10c**	91	88:12	99
22	Ph	4-FC_6H_4	Me	**7a/8d**	24	**10d**	91	92:8	>99
23	Ph	4-ClC_6H_4	Me	**7a/8d**	26	**10e**	95	96:4	>99
24	Ph	4-BrC_6H_4	Me	**7a/8d**	24	**10f**	88	93:7	99
25	Ph	4-$CF_3C_6H_4$	Me	**7a/8d**	24	**10g**	89	93:7	>99
26	Ph	4-MeC_6H_4	Me	**7a/8d**	48	**10h**	82	92:8	98
27	Ph	4-$MeOC_6H_4$	Me	**7a/8d**	48	**10i**	83	92:8	97
28	Ph	2-BrC_6H_4	Me	**7a/8d**	28	**10j**	90	98:2	94
29	Ph	3-BrC_6H_4	Me	**7a/8d**	28	**10k**	90	92:8	99
30	Ph	*n*-C_5H_{11}	Et	**7a/8d**	72	**10l**	70	89:11	98
31	4-ClC_6H_4	3-BrC_6H_4	Me	**7a/8d**	24	**10m**	91	94:6	98
32	4-BrC_6H_4	4-BrC_6H_4	Me	**7a/8d**	24	**10n**	90	93:7	>99
33	4-$MeOC_6H_4$	4-BrC_6H_4	Me	**7a/8d**	24	**10o**	87	93:7	99
34[e]	*t*Bu	Ph	Me	**7a/8d**	72	**10p**	81	92:8	>99

[a] Unless otherwise noted, all reactions were carried out with **5** (0.20 mmol), **6** (0.24 mmol), and the two catalyst modules (0.020 mmol, 10 mol% each) in anhydrous toluene (0.3 mL) at 5 °C. [b] Combined yield of the isolated **9** and **10** after column chromatography. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined for the major diastereomer by HPLC analyses using a chiral stationary phase. [e] Carried out at 5 °C for 24 h, then RT for 48 h.

The absolute stereochemistry of the major diastereomers formed in this reaction were determined by the X-ray crystallographic analyses of **9m** and **10e** (see the Supporting Information).[15] Additionally, a series of control experiments to verify that a dynamic kinetic resolution (DKR) pathway is operable in this reaction are provided in the Supporting Information. Results of our control experiments indicate that there is a DKR when the reaction is catalyzed by either **8a** or **7a**/**8a** and that the diastereodivergence is achieved through the DKR.

The synthesized pyrano[2,3-*b*]pyrans can be readily derivatized to serve as useful building blocks in organic synthesis. For example, **9a** may be reduced to the compound **12** in a high yield in a diastereoselective manner (Scheme 4). The new stereogenic center in **12** was assigned according to a 2D-NOESY experiment (see the Supporting Information). The compound **12** may be further converted into the hexahydro-2*H*,5*H*-pyrano[2,3-*b*]pyran-2-one derivative **15** in a good overall yield. The lactone **15** contains the core functionality similar to building blocks used by the groups of Fukuyama[16a] and Mead[16b] in their synthetic work towards vinblastine and diarylheptanoids, respectively.



Scheme 4. Transformations of the tandem reaction product **9a**. Reaction conditions: a) $BF_3{\cdot}Et_2O$, Et_3SiH, CH_2Cl_2, RT, 1.5 h. b) 10% Pd/C, MeOH, 40 °C, 48 h. c) $LiAlH_4$, Et_2O, RT, 24 h. d) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C. e) *p*-anisidine, O_2, toluene, 50 °C, 24 h. DMSO = dimethylsulfoxide.

In summary, we have developed a highly enantio- and diastereodivergent synthesis of 3,4,4a,8a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]pyran-7-carboxylates catalyzed by novel MDOs. After optimization, both enantiomers of the *cis*- and *trans*-fused pyrano[2,3-*b*]pyran derivatives may be obtained in excellent yields, diastereomeric ratios (up to 98:2), and *ee* values (up to > 99 % *ee*) from the same substrates.

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Keywords: asymmetric catalysis · heterocycles · organocatalysis · self-assembly · synthetic methods

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