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Reversal of the sense of enantioselectivity between 1- and 2-aza[6]helicenes used as chiral inducers of asymmetric autocatalysis†

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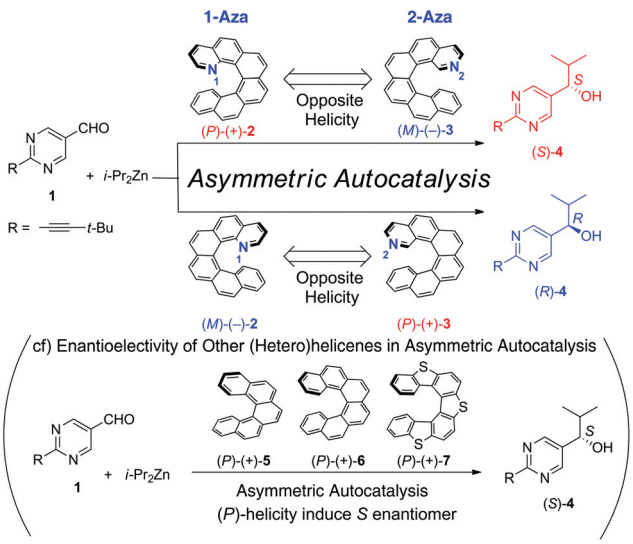
Reversal of the sense of enantioselectivity was observed between 1-aza[6]helicene 2 and 2-aza[6]helicene 3 employed as chiral inducers of asymmetric autocatalysis of pyrimidyl alkanol. In the presence of (*P*)-(+)-1-aza[6]helicene 2, the reaction of pyrimidine-5-carbaldehyde 1 with diisopropylzinc afforded, in conjunction with asymmetric autocatalysis, (*S*)-pyrimidyl alkanol 4 with high ee. Surprisingly, the reaction in the presence of (*P*)-(+)-2-aza[6] helicene 3 gave the opposite enantiomer of (*R*)-alkanol 4 with high ee. In the same manner, (*M*)-(−)-2 and (*M*)-(−)-3 afforded (*R*)- and (*S*)-alkanol 4, respectively. The sense of enantioselectivity is controlled not only by the helicity of the azahelicene derivatives but also by the position of the nitrogen atom.

Enormous progress has been achieved in the absolute stereochemistry control of enantioselective catalytic organic reactions within the last few decades. Although various types of chirality inducers have systematically been explored, small helical organocatalysts or metal complexes bearing helical ligands have rarely been used in enantioselective catalysis until recently.[1] Stimulated by a successful development of diverse synthetic methodologies for the preparation of functionalized (hetero)helicenes in a racemic or enantiopure form,[2,3] their application to enantioselective catalysis has nowadays been attracting considerable attention and this field of chiroscience is rapidly expanding. Within the last few years, new helicene-derived chiral inducers have been prepared and their high efficiency in chirality transfer (or reactivity) in diverse fields of catalysis was demonstrated by Cauteruccio *et al.*,[4] Cauteruccio, Benaglia *et al.*,[5] Licandro, Hashmi *et al.*,[6] Marinetti, Voituriez *et al.*,[7] Suemune, Usui *et al.*,[8] Tsujihara, Kawano *et al.*[9] and Stará, Starý *et al.*[10] However, to the best of our knowledge, only a few studies on azahelicenes (or their simple derivatives) in enantioselective catalysis have so far been carried out by Carbery *et al.*,[11] Stará, Starý *et al.*[12] and Takenaka *et al.*[13]

In the realm of enantioselective catalysis, the Soai reaction[14–16] possesses a prominent position as it exhibits a unique chirality amplification through the asymmetric autocatalysis. Chirality inducers of a fascinating diversity (ranging from circularly polarized light[17] to isotopically chiral compounds[18] and chiral inorganic materials[19]) were found to control effectively the absolute configuration of enantiopure or highly enantioenriched 5-pyrimidyl alkanol as the product of diisopropylzinc addition to the corresponding pyrimidine-5-carbaldehyde. Intriguingly, the influence of helically chiral (hetero)helicenes on the stereochemical outcome of this reaction has already been examined to find a high level of chirality transfer (Scheme 1).[20] Regardless of the absence/presence of



Scheme 1 Reversal of enantioselectivity by the positions of the nitrogen atoms of 1- and 2-aza[6]helicenes.

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heteroatoms and the length of the backbone, the use of the (*P*)-(+) enantiomers of [5]helicene **5**, [6]helicene **6** or tetrathia [7]helicenes **7** in catalytic amounts resulted uniformly in the formation of (*S*)-(−)-**4**. Complementarily, the respective (*M*)-(−) helicene enantiomers induced the opposite chirality of (*R*)-(+)-**4**. Although different mechanisms of the chirality transfer were proposed (a noncovalent interaction between the helical hydrocarbons **5** or **6** and pyrimidine-5-carbaldehyde **1** to form a chiral aldehyde complex[20a] or, alternatively, coordination of diisopropylzinc to sulfur atoms of thiahelicenes **7** to generate a chiral active zinc species[20b]), a pivotal role of the helicity of the chirality inducer in the enantioselective reaction was experimentally demonstrated. Interestingly, the enantioselective addition of diethylzinc to benzaldehyde and its derivatives under catalysis by (*P*,*P*)-(+)-bis[5]helicenediol was pioneered by Katz *et al.*[21] They observed the good ee's and predominant formation of (*S*)-(−)-1-phenylpropanol (and its *o*-chloro, *p*-chloro and *p*-methoxy derivatives of the same absolute configuration) in agreement with the aforementioned results by Soai *et al.* Thus, as so far found, the use of (*P*)-helicene as the chirality inducer in the asymmetric addition of dialkylzinc to (hetero) aromatic aldehydes leads generally to the (*S*)-configuration of the corresponding (hetero)aryl alkanol while (*M*)-helicene favors the formation of (*R*)-(hetero)aryl alkanol.

Herein, we report on the use of the enantioenriched (*P*)-(+)/(*M*)-(−)-1-aza[6]helicene **2**[22] and 2-aza[6]helicene **3**[22] (Scheme 1) as chirality inducers in the enantioselective addition of diisopropylzinc (i-Pr_2Zn) to pyrimidine-5-carbaldehyde **1** to demonstrate that the absolute configuration of the resulting pyrimidyl alkanol **4** is controlled not only by the helicity of the azahelicene derivatives but also the position of the nitrogen atom in them.

Both 1-aza[6]helicene **2** and 2-aza[6]helicene **3** were synthesized in the racemic form by employing [2 + 2 + 2] cycloisomerization of triynes to form their helical backbone.[22] Optically pure (*M*) and (*P*) enantiomers were obtained by resolution of the corresponding racemates by co-crystallization with (+)-*O*,*O*′-dibenzoyl-*d*-tartaric acid or HPLC on a Chiralcel OD-H column (heptane/2-propanol 3 : 1). The helicity of the resolved enantiomers was unequivocally assigned by comparing their ECD spectra with that of (*P*)-(+)-[6]helicene[23] whose helicity is known.[24] Furthermore, the absolute helicities of both 1- and 2-aza[6]helicene were confirmed by single crystal X-ray diffraction analysis of enantiopure crystals with a Cu Kα X-ray source.‡

The results of asymmetric autocatalysis initiated by enantioenriched 1-aza[6]helicenes **2** or 2-aza[6]helicenes **3** are summarized in Table 1.§ When pyrimidine-5-carbaldehyde **1** was reacted with i-Pr_2Zn using (*P*)-(+)-1-aza[6]helicene **2** with >99% ee as the chiral inducer, (*S*)-(−)-pyrimidyl alkanol **4** with 99% ee was obtained (Table 1, entry 1). On the other hand, the presence of (*M*)-(−)-**2** with 99% ee gave the opposite enantiomer of (*R*)-(+)-alkanol **4** with 97% ee (entry 2). The ee of the products was amplified over >99.5% by additional rounds of asymmetric autocatalysis cycles.[14b] The correlation between the absolute configurations of 1-aza[6]helicene **2** and the alkanol **4** is

Table 1 Asymmetric autocatalysis initiated by enantioenriched 1-aza[6]helicene **2** and 2-aza[6]helicene **3**

	1-Aza[6]helicene **2**[a] or 2-aza[6]helicene **3**[b]		Pyrimidyl alkanol **4**		
Entry		ee [%]	Yield [%]	ee[c] [%]	Config.
1	(*P*)-(+)-**2**	>99	89	99 (99.5)[d]	*S*
2	(*M*)-(−)-**2**	>99	89	97 (99.5)[d]	*R*
3	(*P*)-(+)-**2**	>99	85	77	*S*
4	(*M*)-(−)-**2**	>99	90	92	*R*
5	(*P*)-(+)-**2**	33	91	99	*S*
6	(*M*)-(−)-**2**	30	94	96	*R*
7	(*P*)-(+)-**3**	>99	88	93	*R*
8	(*M*)-(−)-**3**	>99	84	97	*S*
9	(*P*)-(+)-**3**	>99	72	91	*R*
10	(*M*)-(−)-**3**	>99	87	89	*S*
11	(*P*)-(+)-**3**	>99	73	91	*R*
12	(*M*)-(−)-**3**	>99	74	93	*S*

[a] Reaction conditions: molar ratio **1** : **2** : i-Pr_2Zn = 1 : 0.4 : 6.7 in toluene 0 °C, additional aldehyde **1** (6.7 equiv. and 26.7 equiv.) and i-Pr_2Zn (20 equiv. and 53.3 equiv.) were added stepwise. [b] Molar ratio reaction conditions: **1** : **3** : i-Pr_2Zn = 1 : 0.2 : 6.7 in toluene 0 °C, additional aldehyde **1** (6.7 equiv. and 26.7 equiv.) and i-Pr_2Zn (20 equiv. and 53.3 equiv.) were added stepwise. [c] The ee value was determined by HPLC. [d] After additional rounds of asymmetric autocatalysis.[14b]

reproducible (entries 3 and 4). Even when the chiral initiators of (*P*)-(+)- and (*M*)-(−)-**2** of a low enantioenrichment (33% ee and 30% ee, respectively) were employed, the same correlation of absolute configurations was manifested by the formation of (*S*)-(−)- and (*R*)-(+)-alkanol **4** with 99% and 96% ee, respectively. This selectivity of the chiral 1-aza[6]helicene **2** as a chiral inducer of asymmetric autocatalysis, *i.e.*, (*P*)-(+)-**2** affords (*S*)-(−)-alkanol **4**, is constant with the stereocontrol by (*P*)-(+)-[5]helicene **5**, (*P*)-(+)-[6]helicene **6** and (*P*)-(+)-thia[7]helicene **7** affording also (*S*)-(−)-alkanol **4**.

Unexpected results, however, were obtained when 2-aza[6]helicene **3** was used as the chiral inducer. In the presence of (*P*)-(+)-**3**, (*R*)-(+)-alkanol **4** with 93% ee was formed instead of (*S*)-(−)-**4** (entry 7). The opposite enantiomer (*M*)-(−)-**3** gave (*S*)-(−)-**4** with 97% ee (entry 8) and, as shown in entries 9–12, these intriguing opposite enantioselectivity correlations were reproducible. Although the actual mechanism of the chirality transfer by helicenes in asymmetric autocatalysis is not clear so far, this enantioselectivity reversal induced by 2-aza[6]helicene **3** in contrast to other helicenes might be caused by the presence of an accessible coordinative nitrogen atom. As expected from the structure of **3**, the steric hindrance around the 2-position of [6]helicene is much smaller than that around the 1-position. Furthermore, from the result of an X-ray crystallography analysis, 2-aza[6]helicene **3** has the larger helicity pitch than 1-aza[6]helicene **2** due to the steric repulsion between the C–H units in the 1- and 16-positions.[22] ‡ Accordingly, 2-aza[6]helicene **3** is proposed to be coordinated to alkyl zinc. It is worth noting that an interaction between the pyrimidine ring and zinc reagent was already considered to play a key role in the mechanism of the asymmetric autocatalysis reaction.[25]

Conclusions

In conclusion, we have demonstrated the asymmetric autocatalysis of pyrimidyl alkanol **4** with chiral 1- and 2-aza[6]helicenes **2** and **3**. The absolute stereochemistry of the alkanol product can be controlled by the helicity of the used azahelicenes. Furthermore, we have confirmed the helicity of the enantiopure 1-aza[6]helicene **2** and 2-aza[6]helicene **3** by ECD spectra and X-ray single crystal analysis. We have found that the correlation between the helicity and enantioselectivity in asymmetric autocatalysis depends not only on the helicity of the chirality inducer but also on the position of the nitrogen atom. The mechanism of the chirality transfer remains still unclear but this unusual stereoselectivity reversal represents an interesting phenomenon that might be applied to asymmetric autocatalysis.

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‡X-ray diffraction analysis was performed using a Rigaku R-AXIS RAPID II imaging plate system with a Cu rotating anode X-ray source. The Flack parameter was determined by using the Parsons quotients method (Parsons, Flack and Wagner, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2013, **69**, 249–259) with SH. Due to the obtained crystal size and quality, the deviation of Flack parameters is slightly high (−0.1(4) for (*M*)-(−)-**2** and 0.1(4) for (*P*)-(+)-**3**). However, considering the good accordance of the ECD spectrum with other helicene derivatives we conclude that the assignment of the absolute structure is unequivocal. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1521682 for (*M*)-(−)-**2** and CCDC 1521681 for (*P*)-(+)-**3**.

§Typical experimental procedure (Table 1, entry 1): 1-Aza[6]helicene (*P*)-(+)-**2** (1.97 mg, 6.0×10^{-3} mmol, 0.4 equiv.) and pyrimidine-5-carbaldehyde **1** (2.8 mg, 0.015 mmol, 1 equiv.) were dissolved in 0.025 mL of toluene under an argon atmosphere. Then, diisopropylzinc in toluene (1.0 M, 0.10 mL, 0.10 mmol, 6.7 equiv.) was added dropwise over 2 h at 0 °C. After stirring overnight at 0 °C, one-pot scale up of asymmetric autocatalysis was performed by adding toluene (0.1 mL) and 1 M diisopropylzinc toluene solution (0.3 mL, 0.3 mmol) followed by the dropwise addition of aldehyde **1** (18.8 mg, 0.1 mmol) in toluene (0.5 mL) over 2 h. After 2 h stirring, the additional scale up of asymmetric autocatalysis was performed in the same way with toluene (3.5 mL), 1 M diisopropylzinc (0.8 mL, 0.8 mmol), and aldehyde **1** (75.3 mg, 0.4 mmol) in toluene (2 mL). The reaction mixture was stirred overnight, and the reaction was quenched using a mixture of sat. aq. NH_4Cl and 30% aq. NH_3 (2/1, v/v, 10 mL). The resulting mixture was extracted with AcOEt (3×). The combined organic layers were dried over anhydrous Na_2SO_4 and the volatiles were removed under reduced pressure. Purification of the residue using silica gel column chromatography (eluent: hexane/EtOAc = 2/1) gave (*S*)-(−)-5-pyrimidyl **4** (106.1 mg, 89% yield) with 99% ee. The ee value was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralpak IB: 4.6 mm × 250 mm, 254 nm UV detector, RT, 5% 2-propanol in hexane, 1.0 mL min^{-1}, retention time: 10.3 min for (*S*)-(−)-**4** and 14.1 min for (*R*)-(+)-**4**).

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