indicate that the average difference in standard length between fish of ranks 2 and 3 was 10.1 mm (Fig. 2a). The coefficients of the growth analysis indicate that individuals of rank 3 that were experimentally elevated to rank 2 had the same growth rate as control individuals (rank 3) when their standard length was 10.8 mm greater than that of controls (Fig. 2b). The similarity of these two estimates shows that the size difference that is found between individuals adjacent in rank would be restored after the disappearance of intermediate individuals.

These findings show that there are well-defined size differences between individuals adjacent in rank within groups of *A. percula*, and that these are maintained by the precise regulation of subordinate growth. The maintenance of size differences may resolve evolutionary conflict over group membership, because subordinates do not become a threat to their dominants. The results indicate that the growth rate and the size adopted by any group-living organism could be a strategic response to its social environment.

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Hydrogen bonding

Single enantiomers from a chiral-alcohol catalyst

Hydrogen bonding acts as a ubiquitous glue to sustain the intricate architecture and functionality of proteins, nucleic acids and many supramolecular assemblies[1,2], but this weak interaction is seldom used as a force for promoting chemical reactions[3–5]. Here we show that a simple chiral alcohol uses hydrogen bonding to catalyse an important family of cycloaddition reactions of a diene with various aldehydes — moreover, this reaction is highly enantioselective, generating only one of the mirror-image forms of each dihydropyran product. This type of catalysis mimics the action of enzymes and antibodies, and is unlike traditional, metal-based catalysts used in organic chemistry[6].

Important biological molecules such as DNA and proteins, and therefore many pharmaceutical drugs, are chiral — that is, they are not superimposable on their mirror image (the pair of asymmetric molecules are known as enantiomers), so any chemical reaction that can selectively synthesize one enantiomeric form of a chiral compound is potentially very useful.

Candidate catalysts for such reactions are generally based on Lewis-acid metals[6]. On the basis of our discovery that hetero-Diels–Alder (HDA) reactions[7] between unactivated ketones and 1-amino-3-siloxy diene (compound **1**) are accelerated in protic solvents, we investigated the use of chiral alcohols for the asymmetric catalysis of these cycloadditions[8]. Of the possible alcohols that could be used for the HDA reaction between diene **1** and benzaldehyde, the TADDOL (α,α,α′,α′-tetraaryl-1,3-dioxolan-4,5-dimethanol) class of chiral alcohols, which are known to complex with carbonyl groups, was considered promising[9].

Figure 1 shows the scheme of the HDA reaction in the presence of this chiral alcohol. A solution of 0.1 mmol (*R,R*)-1-naphthyl TADDOL (**2**) and benzaldehyde (1.0 mmol) in toluene at −78 °C was treated with diene **1** (0.5 mmol) and stirred, causing a smooth HDA reaction to take place. Analysis of the reaction mixture by ^{1}H NMR indicated that the cycloadduct had been formed as a single diastereomer (**3**, where R is C_6H_5), tentatively assigned as *endo*. On treatment with acetyl chloride (1.0 mmol), the cycloadduct was converted to dihydropyrone (**4**, 70% overall yield).

Analysis of the product by high-performance liquid chromatography revealed that the *S*-enantiomer had been produced preferentially over the *R*-enantiomer (>99:1). The reaction is considerably accelerated by TADDOL (**2**): in its absence, there was no reaction under otherwise identical conditions. Moreover, the monomethyl and dimethylether derivatives of **2** were poor catalysts, indicating that the hydrogen-bonding capability of **2** is crucial for the catalytic function.

This metal-free asymmetric catalysis, which does not involve a covalent connection between the catalyst and the reactant[10], can be used for cycloadditions between **1** and a range of aldehydes with different R-groups (Fig. 1). Aromatic aldehydes were particularly effective as dienophiles in these HDA reactions. The resultant dihydropyrone products (see **4a–f** in supplementary information) were also consistently obtained with high enantiomer ratios. Aldehydes with aliphatic (**4g**) and α,β-unsaturated (**4h**) R-groups could be used successfully in these reactions.

Our results show that hydrogen bonding by a simple chiral alcohol to a carbonyl group can accomplish what has previously been considered to be in the domain of enzymes, catalytic antibodies and chiral metal-based Lewis acids. These studies indicate the broad potential for hydrogen-bond catalysis in asymmetric synthesis.

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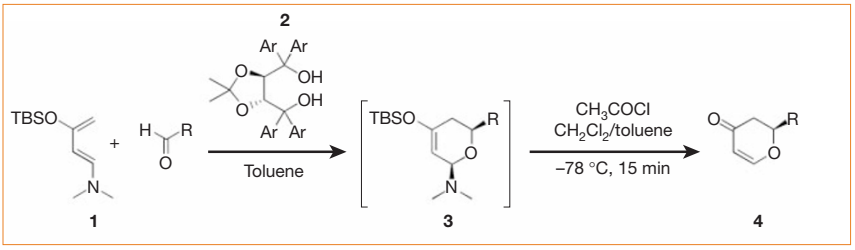

Figure 1 Asymmetric hetero-Diels–Alder reaction of diene **1** with aldehydes to produce dihydropyrones (**4**). The reaction is catalysed by hydrogen bonding and yields specific enantiomeric molecules (see supplementary information for eight examples of products — molecules **4a–h** — bearing different R-groups). TBS, *tert*-butyldimethylsilyl derivative; Ar, 1-naphthyl group. The experimental procedure involved adding diene (**1**, 0.5 mmol) to a solution of TADDOL (**2**, 0.1 mmol) and the aldehyde (1.0 mmol) in toluene (0.5 ml) cooled to −40 °C (−78 °C for **4a**, **4c** and **4f**). The mixture was stirred for 24 h at −40 °C (48 h for **4a**, **4c** and **4f**) and then diluted with CH_2Cl_2 (2.0 ml). Acetyl chloride (1.0 mmol) was added dropwise at −78 °C, and the mixture was stirred for a further 15 min and then separated by chromatography on silica gel (yields 52–97%; enantiomer ratio 96:4→99:1).