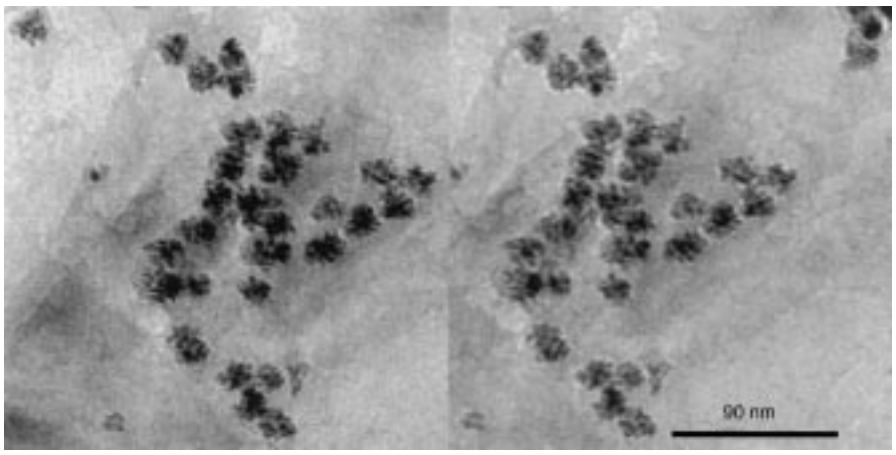

Figure 3. Stereoview of a TEM micrograph of ruthenium particles in a frozen solution of methanol/THF (10/90; cryomicroscopy technique).

the solvent composition, and 3) the influence of concentration, temperature, and excess cyclooctane—can be understood if one imagines the formation of a nanosized emulsion whose droplets act as nanoreactors. Methanol could be ordered around the particles by forming hydrogen-bonded networks with THF. These structures would be more stable when both solvents are present, since methanol is a good hydrogen-bond donor, and THF a good hydrogen-bond acceptor. The core of the droplets would be lipophilic, as can be deduced from the influence of as little as two equivalents of cyclooctane relative to ruthenium.

In conclusion, we have prepared novel ruthenium nanoparticles that are free of protective oxide or polymer layers, uncontaminated by ligands or impurities from the synthesis other than the solvent mixture, soluble in organic solvents, and controllable in size by means of the solvent composition. These highly porous particles are catalytically active and remain unchanged by the catalytic process.

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Broadening the Aldolase Catalytic Antibody Repertoire by Combining Reactive Immunization and Transition State Theory: New Enantio- and Diastereoselectivities**

Guofu Zhong, Richard A. Lerner,* and Carlos F. Barbas III*

The aldol reaction is a C–C bond forming reaction that is key to the practice of synthetic organic chemistry.[1] As a result of its utility intensive effort has been applied to the development of catalytic enantioselective variants of this reaction. Catalytic enantioselective aldol reactions are typically accomplished with preformed enolates and chiral transition metal catalysts[2a–e] or with natural aldolase enzymes.[2f–h] The enantioselectivity of transition metal catalyzed aldol reactions is readily reversed by exchange of the chiral ligand that directs the stereochemical course of the reaction. However, a general approach to the reversal of enantioselectivity is not available with enzymes. To address the problem of the de novo

[*] Prof. Dr. C. F. Barbas III, Prof. Dr. R. A. Lerner, Prof. Dr. G. Zhong
The Skaggs Institute for Chemical Biology and
The Department of Molecular Biology
The Scripps Research Institute
10550, North Torrey Pines Road, La Jolla, CA 92037 (USA)
Fax: (+1) 858-784-9098
E-mail: carlos@scripps.edu

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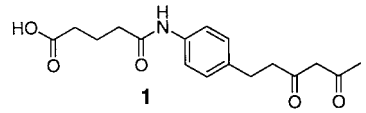
generation of aldolase enzymes, we developed the strategy of reactive immunization using β-diketone haptens to program into antibodies a chemical mechanism analogous to that used by nature's Class I aldolase enzymes.[3a] The chemistry of this class of enzymes is based on a unique chemically reactive lysine residue that is essential to the covalent mechanism of these catalysts.

In our original design the β-diketone functionality of hapten **1** was used as a reactive immunogen to trap a chemically reactive lysine residue in the active site of an



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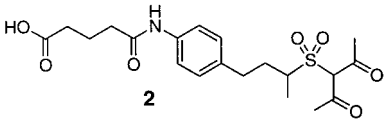

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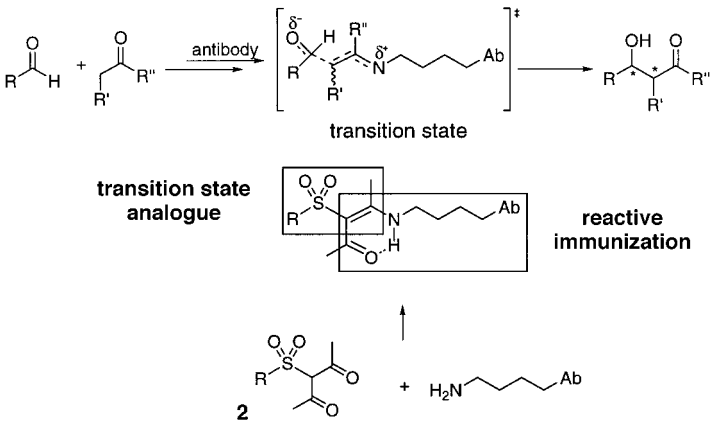
antibody. Covalent trapping was facilitated by intramolecular hydrogen bonding that stabilizes an enaminone in the active site of the antibody. The chemical mechanism leading up to the stabilized enaminone should match that of Class I aldolases over this portion of the reaction coordinate. Given the mechanistic symmetry around the transition state in which the C–C bond is formed, this approach allowed for the programming of this multi-step reaction mechanism into antibodies.[3a,d] The resulting efficient antibody catalysts ab38C2 (Aldrich) and ab33F12 have been shown to catalyze a broad array of enantioselective aldol and retro-aldol reactions.[3] Herein we present our efforts to increase the repertoire of catalysts for this reaction, in particular to search for antibodies with antipodal reactivity. In this search we tested the potential of a new hapten design concept to provide more efficient reaction programming.

Towards these goals, the β-diketo sulfone hapten **2** was designed and synthesized. A perceived limitation of our original hapten design (**1**) is that it does not address the tetrahedral geometry of the rate-determining transition state of the C–C bond forming step.[3a, 4] Hapten **2** addresses this limitation and contains features common to the transition state analogue approach that has been successful for so many reactions[5] and the β-diketone functionality key to the reactive immunization strategy. The tetrahedral geometry of the sulfone moiety in hapten **2** mimics the tetrahedral transition state of the C–C bond forming step and therefore should facilitate nucleophilic attack of the enaminone intermediate on the acceptor aldehyde (Scheme 1).

Mice were immunized with hapten **2** coupled to the carrier protein keyhole limpet hemocyanin (KLH) and 17 monoclonal antibodies were prepared and purified.[3a] All antibodies were first screened for their ability to covalently react with 2,4-pentanedione to form a stable enaminone.[3a] Nine antibodies, 85A2, 85C7, 92F9, 93F3, 84G3, 84G11, 84H9, 85H6, and 90G8, showed the characteristic enaminone absorption maximum at 316 nm after incubation with 2,4-pentanedione. All antibodies were then assayed with fluorescent and UV-active retro-aldol substrates (±)-**3**[6] and (±)-**4**, [3f] respectively. Catalysis was observed only with antibodies that had demonstrated enaminone formation with 2,4-pentanedione. A study of the ability of the antibodies to catalyze the aldol addition of acetone to 3-(4-acetamidophenyl)propanal (**12**) and 4-isobutyramidobenzaldehyde (**13**) identified the same catalysts. All antibody-catalyzed aldol and retro-aldol reactions followed Michaelis–Menten kinetics and were inhibited by the addition of a stoichiometric amount of 2,4-pentanedione. These results are consistent with a covalent catalytic mechanism in which a reactive amine is programmed in these antibodies.[3] The number of catalysts prepared using this hapten, 9 of 17, is significantly greater than our previous studies with hapten **1**, where only 2 of 20 antibodies were catalysts.[3a]



Scheme 1. Mechanism of the antibody-catalyzed aldol reaction and reactive immunization with **2** for the generation of new aldolase antibodies.

In order to compare these antibodies with the commercially available aldolase antibody 38C2, several aldol and retro-aldol reactions were chosen for study. Antibodies 93F3 and 84G3 were characterized in detail in these studies.

Scope and synthetic utility: To begin to probe the synthetic scope and enantioselectivity of these antibodies, we studied their utility in the kinetic resolutions of β-hydroxyketones. Racemic aldols **3**–**7** were treated with ab93F3 or ab84G3 (0.2–0.4 mol %) in aqueous buffer as previously described for ab38C2.[3f] Analysis by high-performance liquid chromatography (HPLC) indicated that in each case the retro-aldolization reactions halted at approximately 50 % conversion, which showed that the antibody was highly enantioselective. The unconverted aldols were recovered and studied using chiral-phase HPLC. Comparison of the results with those of enantiomerically enriched standards[7] indicated that the catalyst was highly enantioselective and provided the recovered *S* aldols with *ee* values typically greater than 96 % (Table 1). Antibody 38C2 provides the corresponding *R* aldols by kinetic resolution, thus ab93F3 is its antipodal complement. The study with ab84G3 revealed an enantioselectivity similar to ab93F3.[8]

We then studied the catalysis of the synthetic reaction of acetone with four different aldehydes, **12**, **13**, 4-nitrobenzaldehyde (**14**), and 4-nitrocinnamaldehyde (**15**), to aldols **5** and **8**–**10** (Table 2). Chiral-phase HPLC analysis demonstrated that the enantioselectivities of ab93F3- and ab84G3-catalyzed aldol addition reactions are substrate dependant.

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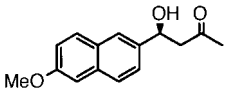
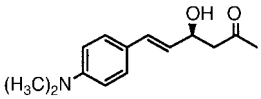
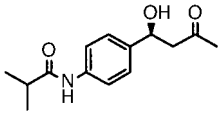
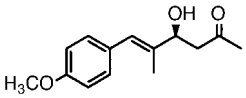
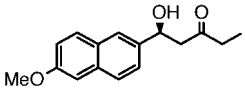
Table 1. Antibody-catalyzed kinetic resolutions by retro-aldolization.

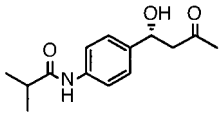
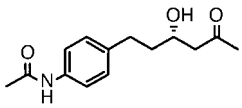
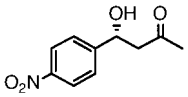
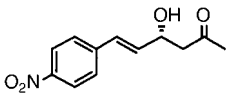
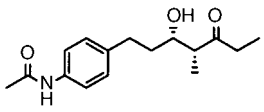
Product[a]		Conversion [%]	*ee* [%]
	(*S*)-**3**	50	99[a]
	(*S*)-**4**	50	97[a]
	(*S*)-**5**	52	> 99[a,b]
	(*S*)-**6**	50	96[a]
	(S)-**7**	50	> 99[b]

[a] Antibody 93F3 was used. Absolute configurations were assigned by comparing aldol products with those obtained from ab38C2 catalyzed reactions. [b] Antibody 84G3.

Aldols (*R*)-**5**, (*R*)-**9**, and (*R*)-**10** are provided in essentially enantiomerically pure form with either catalyst, while a moderate enantioselectivity is obtained in the synthesis of (*S*)-**8** (69% *ee* with ab93F3 (Table 2) or 54% with ab84G3). The *ee* values obtained with these catalysts are quite similar to those obtained with ab38C2, however, the enantioselectivity is reversed.

To examine the diastereoselectivity of ab93F3, we studied the reaction of 3-pentanone to give aldol **11**. In this case ab93F3 provided *syn*-**11** as the major product. The antibody 93F3 exhibited diastereo- and enantioselectivities that differ from that obtained with ab38C2. Antibody 93F3 provides **11** with 90% *de* (*syn*-α-isomer) and 90% *ee*, while ab38C2 provides **11** with 62% *de* (*anti*-isomer) and 59% *ee*.

Table 2. Antibody 93F3 catalyzed aldol reactions.

Product[a]		*ee* [%]
	(*R*)-**5**	> 99%
	(*S*)-**8**	69%
	(*R*)-**9**	95%
	(*R*)-**10**	98%
	(*S,R*)-**11**	90% (*syn*:*anti* = 95:5)

[a] Absolute configurations assigned by asymmetric synthesis of the aldols.[7]

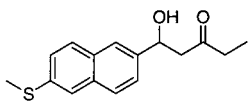
To further characterize the scope of reactions catalyzed by these antibodies, we have studied a variety of ketones as aldol donor substrates in the reaction with aldehyde **14**. Preliminary results indicate that in addition to acetone and 3-pentanone, seven ketones: 2-butanone, 3-methyl-2-butanone, 2-pentanone, cyclopentanone, cyclohexanone, hydroxyacetone, and fluoroacetone, are substrates. Thus these antibodies share the characteristic broad scope we observed previously with ab38C2.

Kinetic studies: The results of kinetic studies of three retro-aldol reactions and one aldol addition reaction are provided (Table 3). The catalytic proficiency[9] of ab93F3 and ab84G3 exceeds that of ab38C2 in most of the cases studied (see Supporting Information for more examples). A threefold increase in the catalytic proficiency is observed in the aldol reaction of 3-pentanone with **12** that provides (*S,R*)-**11**. The overall trend towards increased efficiency is consistent with the notion that the inclusion of transition state analogy into the hapten design results in increased catalytic efficiency. This effect is particularly evident with substrate **7** where a 10^3-fold increase in proficiency over ab38C2 is observed. On the basis of the success of this substrate we synthesized analogue **16**.

Table 3. Kinetic parameters for antibody-catalyzed aldol and retro-aldol reactions.

Substrate	Antibody	k_{cat}[a,b] [min^{-1}]	K_m [a,b] [μM]	k_{cat}/k_{uncat}[c]	$(k_{cat}/K_m)/k_{uncat}$[d]
(±)-**3**	93F3	2.65	15	2.7×10^6	1.8×10^{11}
	84G3	3.5	23	3.6×10^6	1.6×10^{11}
	38C2[6]	1.0	14	1.0×10^6	7.1×10^{10}
(±)-**7**	93F3	43.3	6.5	4.9×10^7	7.4×10^{12}
	84G3	46.8	10.3	5.2×10^7	5.0×10^{12}
	38C2	0.053	29.5	5.8×10^4	2.0×10^9
(*R*)-**16**	93F3	69.6	2.6	1.9×10^8	7.4×10^{13}
	84G3	81.4	4.2	2.3×10^8	5.4×10^{13}
12 & acetone	93F3	33×10^{-3}	34	1.5×10^5	4.4×10^9
	84G3	27×10^{-3}	29	1.2×10^5	4.1×10^9
	38C2[3a]	6.7×10^{-3}	17	2.9×10^4	1.7×10^9

[a] Conditions: The data for (±)-**7** and (*R*)-**16** were collected using phosphate buffer at pH 7.7, others were studied in phosphate buffered saline (PBS) at pH 7.4. [b] Per antibody active site. k_{cat} and K_m were obtained by fitting experimental data to nonlinear regression analysis using Grafit software. [c] Aldol reaction rate constants in units of M. [d] Retro-aldol reaction rate constants in units of M^{-1}.



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Since in antibody-based resolutions of aldols the unprocessed enantiomer can be inhibitory to the processing of the enantiomer that is the substrate for the antibody[3h], we isolated (*R*)-**16** using chiral-phase HPLC. A study of the kinetics of retro-aldolization of (*R*)-**16** by ab84G3 revealed that it was processed by the antibody extremely rapidly with a $k_{cat} = 1.4\ s^{-1}$. A study of the uncatalyzed reaction revealed that (*R*)-**16** was not more chemically reactive than the corresponding methoxy derivative **7**, and that the antibody provides a rate enhancement k_{cat}/k_{uncat} of 2.3×10^8. The catalytic proficiency[9] of ab84G3 for the retro-aldolization of aldol (*R*)-**16** is

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approximately 1000-fold higher than that reported for any other catalytic antibody.[3f, 10] The catalytic efficiency of the antibody for this substrate, $3.3 \times 10^5\ s^{-1}\,M^{-1}$, compares favorably with the efficiency of natural muscle aldolase, $4.9 \times 10^4\ s^{-1}\,M^{-1}$, in the retro-aldolization of its substrate fructose-1,6-bisphosphate.[11]

In conclusion, we have demonstrated that combining transition state analogy and reactive immunization design into a single hapten can result in increases both in the output of catalysts from the immune system as well as their efficiency. This strategy resulted in the characterization of the most proficient antibody catalysts prepared to date. Antibodies 93F3 and 84G3 catalyze a wide array of aldol reactions with *ee* values exceeding 95% in most of the cases studied. A new stereogenic center is formed when acetone is the aldol donor substrate by attack on the *re*-face of the aldehyde, which provides the antipodal complement of ab38C2 in aldol reactions. Both aldol enantiomers may be accessed through aldol and retro-aldol reactions. These catalysts should provide access to a wide variety of enantiomerically enriched synthons with application to natural product syntheses.

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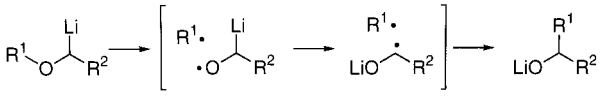
Enantioselective [1,2] Wittig Rearrangement Using an External Chiral Ligand**

Katsuhiko Tomooka,* Kyoko Yamamoto, and Takeshi Nakai*

Since its discovery by Wittig and Löhmann in 1942,[1] the reaction of α-lithiated ethers, now known as the [1,2] Wittig rearrangement, has attracted much interest from both mechanistic and synthetic points of view.[2] This type of carbanion rearrangement is recognized to proceed by means of the radical dissociation – recombination mechanism [Eq. (1)].[2, 3]



(1)

Despite its long history, however, no enantioselective versions of the Wittig rearrangement have been developed yet. Clearly, the radical character provides a great challenge. We now disclose the first enantioselective Wittig rearrangement which relies upon an asymmetric lithiation protocol[4] in which (*S*,*S*)-bis(dihydrooxazol) **3** serves as an external chiral ligand[5, 6] [Eq. (2)]. The most striking feature is that the

[*] Prof. Dr. K. Tomooka, K. Yamamoto, Prof. Dr. T. Nakai
Department of Applied Chemistry
Graduate School of Science and Engineering
Tokyo Institute of Technology
Meguro-ku, Tokyo 152-8552 (Japan)
Fax: (+81) 3-5734-3931
E-mail: ktomooka@o.cc.titech.ac.jp
takeshi@o.cc.titech.ac.jp

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