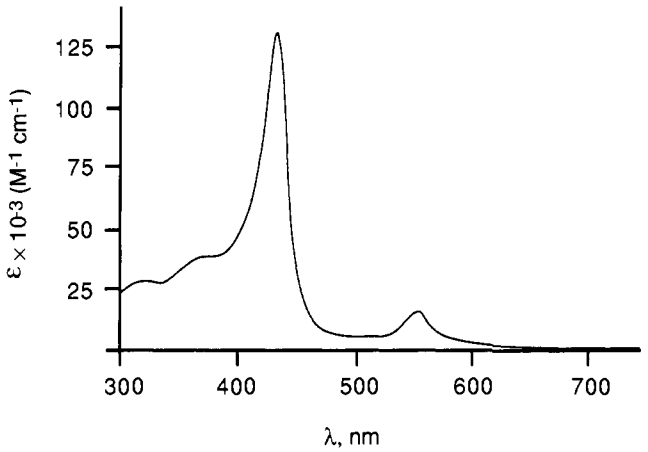
most high-spin (TPP)Fe^{III} complexes. However, this compares well with that seen for the high-spin peroxo Fe(III) complex (with side-on η^2:η^2 coordination), [(TPP)Fe(O_2^{2-})]$^-$, characterized by Valentine and co-workers;[11] the red shift of the Soret band has been attributed to the dinegative charge of the peroxo ligand.[11b]



(2) Complex **3** is EPR silent (77 K), consistent with the coupled integer-spin formulation. (3) In an infrared spectrum, **3** possesses a band at 855 cm^{-1} not seen in **1**, **2**, or other (F_8-TPP)Fe-X (X = Cl$^-$, OH$^-$) compounds. When **3** is prepared using $^{18}O_2$ (99%), the 855-cm^{-1} band largely disappears, and a greatly enhanced absorption is seen at ~780–790 cm^{-1}, where other bands already occur. Additional studies will be required to determine an assignment.[12] (4) The ^{1}H NMR spectrum of **3** (CD_3CN) indicates that only a single porphyrin species is present, exhibiting a pyrrole H-resonance at 65 ppm, split meta phenyl signals at 9.6 and 9.2 ppm, and a para phenyl absorption at 7.8 ppm. These observations are also consistent with a high-spin Fe(III) environment and are again comparable to [(TPP)Fe(O_2^{2-})]$^-$ (61, 9.2, and 7.2 ppm, respectively).[13] The pyrrole signal assignment in **3** was confirmed by ^{2}H NMR spectroscopy of the pyrrole deuteriated porphyrin. (5) The room temperature magnetic moment of **3** is 5.2 ± 0.2 μ_B (Evans method in CD_3CN), a value consistent with the suggestion that **3** is a coupled $S = {}^5/_2$ (i.e., heme) and $S = {}^1/_2$ (i.e., Cu(II)) system. Further temperature dependent magnetic studies are needed.

Additional chemical evidence for a peroxo group in [Fe^{III}-(O_2^{2-})-Cu^{II}](ClO_4) (**3**) comes from reactivity with CO_2 and SO_2 (Scheme I), reagents which are often used to react with metal–dioxygen complexes.[14-16] Carbon dioxide reacts with **3**, and a carbonato dinuclear complex [{(TMPA)Cu}$_2$(CO_3)]$^{2+}$[17] and (F_8-TPP)Fe-OH[18] were isolated after workup. Since [(TPP)-Fe-(O_2^{2-})]$^-$ is known to react with SO_2 to give sulfate,[16] a better test is the reaction of SO_2 with **3**. Here, exposure to SO_2, decomposition with HCl(aq), and addition of Ba^{2+} demonstrate that sulfate is indeed produced. The isolated gravimetrically determined yield is 50%; when the TPP analogue [(TPP)Fe-(O_2^{2-})-Cu(TMPA)]$^+$[9] is tested in this manner, a 70% yield can be obtained. Neither (F_8-TPP)Fe-OH nor [(TMPA)Cu(Cl)]$^+$ gives sulfate upon reaction with SO_2.

In conclusion, the reaction of O_2 with porphyrin-Fe(II) and Cu(I) complexes leads to dinuclear peroxo-bridged [Fe^{III}-(O_2^{2-})-Cu^{II}]$^+$ (**3**) species. A complete electronic/magnetic and structural description of **3** is underway. Spectroscopically detected intermediates involving heme a_3 and O_2 or reduced derivatives (e.g., peroxo or ferryl) have been implicated in *Cc*O action;[1] bridged Fe/Cu[1a,b,19] or discrete copper–dioxygen species[20] also may be involved. The results described here represent a conspicuous step toward developing systems which may aid in understanding O_2-reduction mechanism(s), structures, and protonation steps involving both (porphyrin)iron and copper ion.

Acknowledgment. We are grateful for the support of the National Institutes of Health (GM 28962, K.D.K.) and National Science Foundation (NSF DMB9001530, B.H.H.).

Registry No. 1, 141981-26-2; **2**, 114581-82-7; **3**-(ClO_4), 141981-28-4; **3**-(PF_6), 141981-31-9; C *c* O, 9001-16-5; (TPP)Fe-pip$_2$, 17845-65-7; [(TPP)Fe-(O_2^{2-})Cu(TMPA)](ClO_4), 141981-30-8; [{(TMPA)-Cu}$_2$$CO_3$]$^{2+}$, 118458-34-7; SO_2, 7446-09-5; CO_2, 124-38-9; $BaSO_4$, 7727-43-7; O_2^{2-}, 14915-07-2.

Supplementary Material Available: Mössbauer spectra of **3**-ClO_4 (1 page). Ordering information is given on any current masthead page.

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Asymmetric Desymmetrization by Enantioselective Catalysis of Carbonyl–Ene Reaction: Remote Internal Asymmetric Induction

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"Asymmetric desymmetrization"[1] of a symmetrical and achiral molecule is a basic and potential methodology for asymmetric synthesis. While the ability of enzymes to transform differentially symmetrical, hence enantiotopic, functional groups is well known,[2] little exploration has been performed on a similar ability of nonenzymatic catalysts,[3] particularly for C–C bond formation.[4] Recently, we developed an asymmetric catalytic carbonyl–ene reaction with prochiral glyoxylate as an efficient method for asymmetric C–C bond formation.[5] The asymmetric catalytic reaction involving a prochiral ene component with planar sym-

Table I. Asymmetric Desymmetrization of **2**.

entry	molarity (**2** : **3**)	% yield[a]	*syn* (% ee) : *anti*
1	1.0 : 1.0	62 (27)	>99 (>99) : <1
2	1.0 : 2.0	57 (27)	>99 (>99) : <1

[a] Calculated value based on the recovery of **2**. Value in parenthesis refers to the isolated yield.

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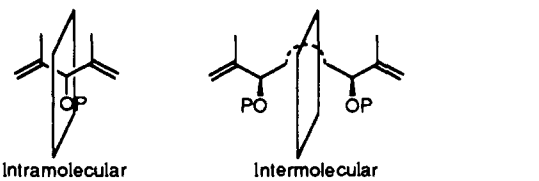
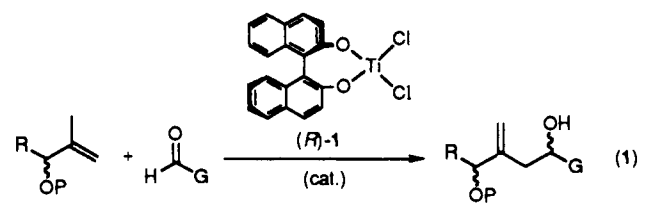
Table II. Kinetic Resolution of **7**.

entry	ene	molarity (**7** : **3**)	% yield[a]	*syn* (% ee) : *anti*	% recovery of **7** (% ee)	k_S/k_R
1	**7a**	1.0 : 2.0	74 (34)	>99 (99.5) : <1	54 (59.4)	690
2	**7a**	2.0 : 1.0	70 (28)	>99 (99.6) : <1	60 (37.8)	720
3	**7c**	1.0 : 2.0	48 (20)	>99 (96.2) : <1	59 (22.0)	64

[a] Calculated values based on the recovery of **7**. Value in parenthesis refers to the isolated yield.

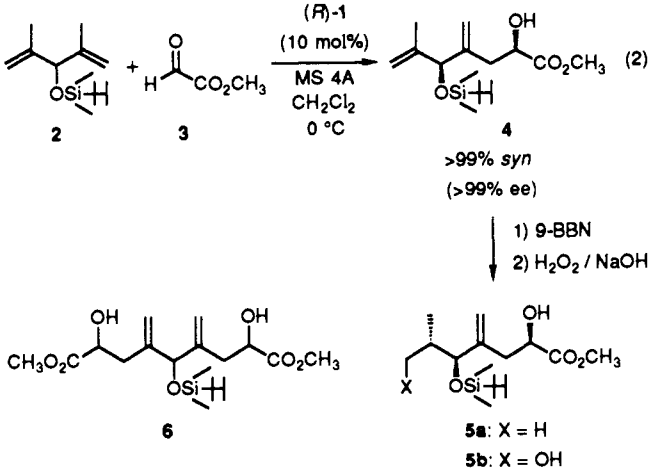
metry should lead to an access to remote internal asymmetric induction,[6] which is otherwise difficult to attain[7] (eq 1). Furthermore, the kinetic resolution[8] of racemic ene substrates might be recognized as an intermolecular desymmetrization. Disclosed herein are the remarkably high levels of remote asymmetric induction through asymmetric desymmetrization, kinetic resolution, and double asymmetric induction[9] by the asymmetric catalytic glyoxylate–ene reactions.





(1)

First we examined the glyoxylate–ene reaction with symmetrical bis-allylic silyl ethers (**2**) catalyzed by the chiral titanium complex (*R*)-**1** prepared from optically pure binaphthol (BINOL)[5] (eq 2). Thus, the (2*R*,5*S*)-syn product (**4**)[10,11] was obtained in more than 99% ee[12] along with >99% syn diastereoselectivity, irrespective of the aldehyde stoichiometry (Table I).[13] Further transformation of the desymmetrized product **4** by anti diastereofacial selective hydroboration[14] regioselectively gave the triol **5b** in 51% isolated yield.[15] Thus, these examples represent a rarely precedented asymmetric transformation based on asymmetric catalytic desymmetrization involving C–C bond formation.



(2)

Next, the kinetic resolution of racemic allylic alcohols (**7**) represents an example of remote relative asymmetric induction (eq 3).[6] The catalyst (*R*)-**1** provides the (2*R*,5*S*)-syn product (**5a**)[16] with >99% diastereoselectivity along with 99.5% ee[12] (Table II, entry 1). Furthermore, the starting alcohol **7a** was recovered with 59.4% ee (*R*). The high diastereoselectivity, coupled with the high % ee of the ene product (**5**), strongly suggests that the chiral catalyst (*R*)-**1** efficiently discriminates the two enantiomeric ene components **7** (k_S/k_R: ca. 700 for **7a**, 64 for **7c**).[17] In fact, the double asymmetric induction with (*R*)-**7c** using the catalyst (*S*)-**1** ("matched" catalytic system) provides the complete (>99%) 1,4-syn diastereoselectivity along with high chemical yield (71%)

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(10) Regioselective hydrogenation of **4** (H_2 (1 atm), Rh-C, EtOH) gave the (2*R*,5*S*)-syn product (**5a**), which was obtained independently by the reaction with (*S*)-valine-derived **7a** (eq 3).

(11) (2*R*,5*S*)-*syn*-**4**: $[\alpha]^{26}_D = -9.76°$ (*c* = 2.18, $CHCl_3$); ^1H NMR 1.57 (s, 3 H), 2.29 (dd, *J* = 14.9, 7.7 Hz, 1 H), 2.50 (dd, *J* = 14.9, 3.9 Hz, 1 H), 3.75 (s, 3 H), 4.35 (dd, *J* = 7.7, 3.9 Hz, 1 H), 4.47 (s, 1 H) ppm. *syn*- and *anti*-**4** were obtained in a ratio of 5:1 with 1 equiv of $SnCl_4$; *anti*-**4** ^1H NMR 3.76 (s, 3 H), 4.27–4.37 (m, 1 H), 4.52 (s, 1 H) ppm.

(12) The enantiomeric excess and absolute configuration of the 2-methoxy derivative was determined by LIS-NMR analysis using (+)-Eu(DPPM)$_3$ as described in ref 5c.

(13) We have obtained no double ene product **6** even with the use of more than 2 equiv of glyoxylate (**3**). The use of $SnCl_4$ gave, however, **6** in 91% isolated yield.

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(15) ^1H NMR 0.93 (d, *J* = 7.1 Hz, 3 H), 2.39 (dd, *J* = 16.1, 5.9 Hz, 1 H), 2.51 (dd, *J* = 16.1, 5.9 Hz, 1 H), 3.56 (dd, *J* = 10.9, 5.4 Hz, 1 H), 3.65 (dd, *J* = 10.9, 3.8 Hz, 1 H), 3.69 (s, 3 H), 5.00 and 5.11 (2s, 1.8 and 0.2 H) ppm.

(16) (2*R*,5*S*)-*syn*-**5a**: $[\alpha]^{26}_D = -6.65°$ (*c* = 1.24, $CHCl_3$); ^1H NMR 2.26 (dd, *J* = 15.8, 8.4 Hz, 1 H), 2.63 (dd, *J* = 15.8, 3.5 Hz, 1 H), 3.77 (s, 3 H), 4.38 (dd, *J* = 8.4, 3.5 Hz, 1 H), 5.06 (s, 2 H) ppm. *syn*- and *anti*-**5a** were obtained in a ratio of 1:2 with the use of $SnCl_4$; *anti*-**5a**: ^1H NMR 2.38 (dd, *J* = 15.4, 8.9 Hz, 1 H), 2.53 (dd, *J* = 15.4, 3.3 Hz, 1 H), 3.78 (s, 3 H), 4.33 (dd, *J* = 8.9, 3.3 Hz, 1 H), 5.02 (br s, 1 H), 5.06 (br s, 1 H) ppm.

Table III. Double Asymmetric Induction with **7** and **1**.

entry	ene	catalyst	% yield[a]	*syn* : *anti*
1	(*S*)-**7a**	(*R*)-**1**	96 (70)	>99 : <1
2	(*R*)-**7c**	(*S*)-**1**	71 (50)	>99 : <1
3	(*R*)-**7c**	(*R*)-**1**	33 (19)	50 : 50

[a] Calculated value based on the recovery of **7**. Value in parenthesis refers to the isolated yield.

(Table III, entry 2). In contrast, the reaction of (*R*)-**7c** using (*R*)-**1** ("mismatched" catalytic system) affords the diastereomeric mixture (syn/anti = 1/1) in low yield (33%) (entry 3). Furthermore, these results clearly show that the alkoxy group acts as a controlling element not only for stereo- but also for regiocontrol.[18]

In summary, we have demonstrated that the chiral titanium complex catalyzed glyoxylate–ene reactions involving prochiral and chiral ene components provide remarkably high levels of remote asymmetric induction through asymmetric desymmetrization and chiral recognition during the C–C bond formations.

Acknowledgment. The authors are grateful to Professor Takeshi Nakai for his continuous encouragement and useful discussions. The authors are also grateful to Professor Thomas R. Hoye for his comments and useful discussions. This research was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan, the Asahi-Kasei Award in Synthetic Organic Chemistry, Japan, and the Iwaki Scholarship Foundation.

Supplementary Material Available: Typical experimental procedures for the kinetic resolution and physical data of the ene products (**4** and **5**) and recovered **7** (3 pages). Ordering information is given on any current masthead page.

(17) This number is obtained from the following equation: $\ln [(1-c)(1-ee_{recov})]/\ln [(1-c)(1+ee_{recov})]$, $c = ee_{recov}/(ee_{recov} + ee_{prod})$, $0 < c$, $ee < 1$ where c is the fraction of consumption of racemate. Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. See also: Wang, Y.-F.; Chen, C.-S.; Girdaukas, G.; Sih, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 3695.

(18) It is rather surprising that only one regioisomer was obtained, in sharp contrast to the low-to-moderate level of regioselectivity in the competitive case of methyl vs methylene or methine hydrogen shift.[5c] For the controlling effect of alkoxy groups of (homo)allylic ethers in the regio- and stereochemistries of carbonyl–ene reactions, see: Mikami, K.; Shimizu, M.; Nakai, T. *J. Org. Chem.* **1991**, *56*, 2952.

Vinylogous Polypeptides: An Alternative Peptide Backbone

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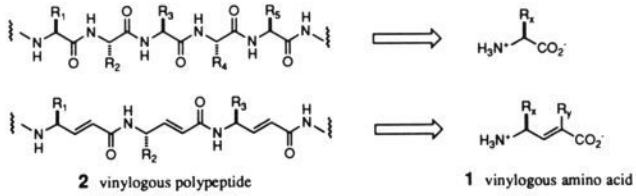
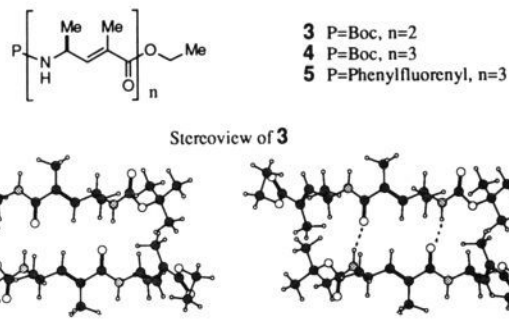
Despite the bewildering array of tertiary structures exhibited by polypeptide chains (i.e., proteins), it is remarkable that only two types of ordered secondary structures are observed: helices and sheets. An important early advance in protein chemistry was the successful prediction of these structural elements.[1] We have attempted to analyze the secondary and tertiary structure of polypeptide chains of building blocks not based on amino acids, but on derivatives of amino acids. The preparation of such materials is hoped to yield new classes of protein-like substances with alternative backbones. The initial system we chose to study consists of repeating units of extended amino acids that have an (*E*)-ethenyl unit inserted between the carbonyl carbon and Cα (vinylogous amino acids, **1**[2]). We now report the synthesis[3] and conformational analysis of vinylogous polypeptides **2** and the observation of their novel secondary structures by a combination



2 vinylogous polypeptide **1** vinylogous amino acid

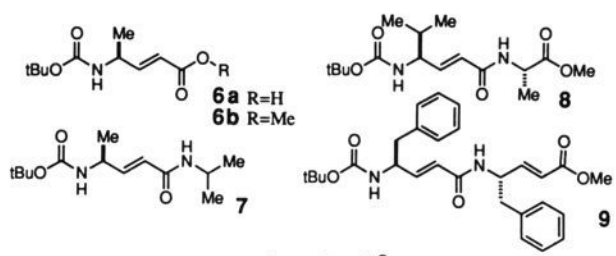
Figure 1. Comparison of polypeptides and vinylogous polypeptides.



3 P=Boc, n=2
4 P=Boc, n=3
5 P=Phenylfluorenyl, n=3

Stereoview of **3**

Figure 2. Vinylogous polypeptides can adopt artiparallel sheet secondary structure.



6a R=H
6b R=Me
8
7
9

Stereoview of **9**

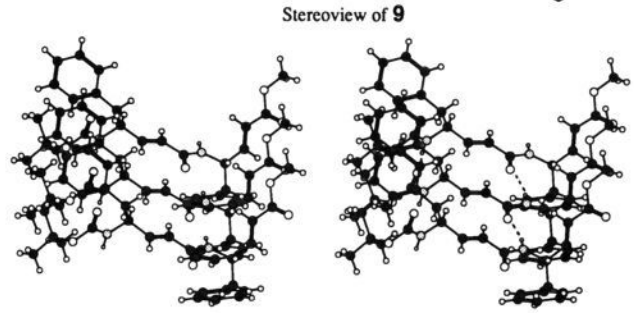


Figure 3. Vinylogous polypeptides can adopt parallel sheet secondary structure.

(2) Note that vinylogous polypeptides do not contain peptide isosteres (ref 2a); they have hydrogen-bonding donor and acceptor groups spaced in a way that is distinct from polypeptides or polypeptides that contain isosteric replacement of the peptide moiety. Vinylogous polypeptides are conceptually related to hexose-DNA (ref 2b), in that a systematic structural alteration has been provided to the repeating unit. (a) Goodman, M.; Chorev, M. *Acc. Chem. Res.* **1979**, *12*, 1–7. (b) Eschenmoser, A. *Nachr. Chem., Tech. Lab.* **1991**, *39* (7/8), 795.

(3) *N*-Boc amino acids were converted to their aldehydes via their Weinreb methoxamides (ref 3a–c) (HN(Me)OMe, DCC, CH_2Cl_2, 78–99%; $LiAlH_4$, THF, 84–94%). Homologations were performed with $Ph_3P{=}CHCO_2Me$ (CH_2Cl_2, 69–89% from Weinreb methoxamide) or $Ph_3P{=}CMeCO_2Et$ (CH_2Cl_2, 86–92% from Weinreb methoxamide). Amide couplings were achieved by treatment of amine (TFA, CH_2Cl_2 or 3 N HCl, MeOH) and carboxylic acid (LiOH, MeOH:H_2O = 3:1) components (1:1) with either DCC (1.05 equiv)/HOBT (1.05 equiv) or BOP (1.20 equiv) in CH_2Cl_2 (58–92%). (a) Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815–3818. (b) Fehrentz, J.; Castro, B. *Synthesis* **1983**, 676–678. (c) Lubell, W. D.; Rapoport, H. *J. Am. Chem. Soc.* **1987**, *109*, 236–239.

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