$$\chi_{dimer} = N g^2 \mu_B^2 S(S+1)(1+u)/3kT \quad (1a)$$

$$u = \coth[JS(S+1)/kT] - kT/JS(S+1) \quad (1b)$$

$$\chi_M = \chi_{dimer}/[1 - \chi_{dimer}(2zJ'/Ng^2\mu_B^2)] \quad (1c)$$

The best fit for $\chi_M T$ versus T in the range of 9–300 K (solid line shown in Figure 3a) leads to the following parameters: $J/k = 71.18$ K, $J'/k = 0.58$ K, $g = 2.07$ and $R = 2.0 \times 10^{-2}$ ($R = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calcd}]^2/\Sigma[(\chi_M)_{obs}]^2$). The small positive J' value implies that the exchange interaction through the axial asymmetrical EE bridging azide is very weakly ferromagnetic. This is mainly because of the strict orthogonality of σ_x and π_z azide orbitals.[3b] The low temperature magnetic data (2–20 K) measured at different external fields between 200 Oe to 10 kOe indicate that the value of $\chi_M T$ increases greatly with decreasing magnetic field. This result suggest that the presence of field-saturation effects in addition to the possible weak inter-layer antiferromagnetic interaction may cause the decrease of $\chi_M T$ below 9 K.

Very recently, Monfort et al.[11] reported a 2D molecular material with Ni^{II} centers and azide units that shows metamagnetic behavior. Our work supplies the first 2D metal–azide bridged compounds with long-range ferromagnetic ordering properties. Details of further magnetic measurements can be found in the Supporting Information.

Experimental Section

A solution of $CuCl_2 \cdot 6H_2O$ (1 mmol) in methanol (10 mL) was added to a solution of NaN_3 (2 mmol) and the hydrobromide salt of benzylamine (1 mmol) in H_2O (25 mL). A Black-brown precipitate formed over several minutes. The solid was collected by filtration and washed with methanol and diethyl ether (yield ca. 75%). Elemental analysis calcd for $C_7H_9CuN_7$ (%): C 32.97, H 3.53, N 38.47, Cu, 24.93; found: C 32.78, H 3.70, N 38.56, Cu 25.00; IR: $\tilde{\nu}_{max} = 2094$, 2056 cm^{-1}(ν_{asym} N_3). Black needles suitable for single-crystal X-ray analysis were obtained by slow evaporation of the filtrate in air.

Received: April 17, 2000 [Z14999]

[1] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**.

[2] a) S. Sikorav, I. Bkouche-Waksman, O. Kahn, *Inorg. Chem.* **1984**, *23*, 490; b) O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin, Y. Jeannin, *Inorg. Chem.* **1983**, *22*, 2877; c) J. Comarmond, P. Plumere, J. M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn, I. Morgenstern-Badarau, *J. Am. Chem. Soc.* **1982**, *104*, 6330; d) R. Cortes, M. Karmele Urtiaga, L. Lezama, J. R. Larramendi, M. Isabel Arriortua, T. Rojo, *J. Chem. Soc. Dalton Trans.* **1993**, 3685; e) Y. Agnus, R. Louis, R. Weiss, *J. Am. Chem. Soc.* **1979**, 3381; f) M. Charlot, O. Kahn, M. Chaillet, C. Larrieu, *J. Am. Chem. Soc.* **1986**, *108*, 2574; g) K. D. Karlin, J. C. Hayes, J. P. Hutchinson, J. Zubieta, *J. Chem. Soc. Chem. Commun.* **1983**, 376; h) M. A. Aebersold, B. Gillon, O. Plantevin, L. Pardi, O. Kahn, P. Bergerat, I. Seggern, F. Tuczek, L. Ohrstrom, A. Grand, E. Lelievre-Berna, *J. Am. Chem. Soc.* **1998**, *120*, 5238.

[3] a) M. H. W. Lam, Y. Y. Tang, K. M. Fung, X. Z. You, W. T. Wong, *Chem. Commun.* **1997**, 957; b) J. C. Liu, D. G. Fu, J. Z. Zhuang, C. Y. Duan, X. Z. You, *J. Chem. Soc. Dalton Trans.* **1999**, 2337.

[4] S. S. Tandon, L. K. Thompson, D. O. Miller, *Chem. Commun.* **1995**, 1907.

[5] a) Z. N. Chen, H. X. Zhang, K. B. Yu, B. S. Kang, *Chem. Lett.* **1998**, 275; b) G. D. Munno, M. Julve, F. Lloret, J. Faus, M. Verdaguer, A. Caneschi, *Angew. Chem.* **1993**, *105*, 1122; Angew. *Chem. Int. Ed. Engl.* **1993**, *32*, 1046; c) L. K. Thompson, S. S. Tandon, F. Lloret, J. Cano, M. Julve, *Inorg. Chem.* **1997**, *36*, 3301; d) G. W. Bushnell, M. A. Khan, *Can. J. Chem.* **1974**, *52*, 3125; e) F. A. Mautner, M. A. S. Goher, *Polyhedron* **1994**, *13*, 2141; f) M. A. S. Goher, F. A. Mautner, *Polyhedron* **1998**, *17*, 1561.

[6] a) G. D. Munno, M. G. Lombardi, M. Julve, F. Lloret, J. Faus, *Inorg. Chim. Acta* **1998**, *282*, 82; b) Z. Shen, J. L. Zuo, Z. Yu, Y. Zhang, J. F. Bai, C. M. Che, H. K. Fun, J. J. Vittal, X. Z. You., *J. Chem. Soc. Dalton Trans.* **1999**, 3393; c) A. Escuer, R. Vicente, M. S. El Fallah, M. A. S. Goher, F. A. Mautner, *Inorg. Chem.* **1998**, *37*, 4466; d) T. C. W. Mak, M. A. S. Goher, *Inorg. Chim. Acta* **1986**, *115*, 17; e) F. A. Mautner, M. A. S. Goher, *Polyhedron* **1992**, *11*, 2537; f) F. A. Mautner, M. A. S. Goher, *Polyhedron* **1993**, *12*, 2823.

[7] a) Z. N. Chen, J. Qiu, Z. K. Wu, D. G. Fu, K. B. Yu, W. X. Tang, *J. Chem. Soc. Dalton Trans.* **1994**, 1923; b) A. Escuer, R. Vicente, M. A. S. Goher, F. A. Mautner, *Inorg. Chem.* **1998**, *37*, 782; c) G. De Munno, T. Poerio, G. Viau, M. Julve, F. Lloret, Y. Journaux, E. Riviere, *Chem. Commun.* **1996**, 2587; d) A. Escuer, R. Vicente, M. A. S. Goher, F. A. Mautner, *Inorg. Chem.* **1995**, *34*, 5707.

[8] A. Escuer, R. Vicente, M. A. S. Goher, F. A. Mautner, *Inorg. Chem.* **1997**, *36*, 3440.

[9] J. Ribas, M. Monfort, X. Solans, M. Drillon, *Inorg. Chem.* **1994**, *33*, 742.

[10] Crystal data ($C_7H_9CuN_7$): monoclinic, space group $P2_1/c$; $a = 13.664(1)$, $b = 5.4609(4)$, $c = 14.165(1)$ Å, $\beta = 96.395(1)^\circ$, $V = 1050.38(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.611$ g cm^{-3}, $\mu = 2.058$ mm^{-1}, $F(000) = 516$, $\lambda = 0.71073$ Å, $T = 293$ K; 7132 reflections were measured on a Siemens SMART CCD area detector diffractometer and yielded 2586 unique data ($2\Theta_{max} = 56.62^\circ$, $R_{int} = 0.0664$, semiempirical absorption corrections). The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELXTL. R(on F^2) = 0.0504, ωR(on F^2) = 0.0827, 136 parameters. Largest difference peak/hole 0.751/−0.730 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142222. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] M. Monfort, I. Resino, J. Ribas, H. Stoeckli-Evans, *Angew. Chem.* **2000**, *112*, 197; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 191.

Asymmetric Conjugate Addition of Azide to α,β-Unsaturated Carbonyl Compounds Catalyzed by Simple Peptides**

Thomas E. Horstmann, David J. Guerin, and Scott J. Miller*

Stimulated by the efficiency exhibited by enzymes, chemists have sought not only to understand the mechanistic basis for enzymatic reactions, but also to reproduce and even surpass their capabilities. The complementary fields of enzymatic catalysis and transition metal based asymmetric catalysis have recorded many successes in the field of enantioselective reaction development. One question at the interface of these

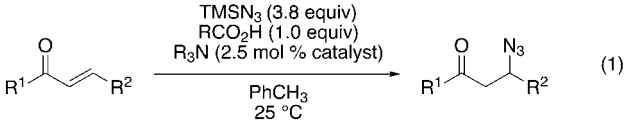
[*] Prof. S. J. Miller, T. E. Horstmann, D. J. Guerin
Department of Chemistry
Boston College
Chestnut Hill, MA 02467-3860 (USA)
Fax: (+1) 617-552-3620
E-mail: scott.miller.1@bc.edu

[**] This research was supported by the U.S. National Institutes of Health (GM-57595). We are also grateful to the U.S. National Science Foundation for generous support in the form of a CAREER Award (CHE-9874963). In addition, we thank DuPont, Eli Lilly, Glaxo-Wellcome, and the Merck Chemistry Council for research support. S.J.M. is a Fellow of the Alfred P. Sloan Foundation, a Cottrell Scholar of Research Corporation, and a Camille Dreyfus Teacher-Scholar.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

powerful areas is that of the basis for enantioselectivity when a small-molecule catalyst is composed entirely of peptidic structural elements. Answers to this question could provide indirect insight into the fundamental connection between peptide structure and function. Indeed, low-molecular-weight, metal-free peptides have recently been found to be excellent asymmetric catalysts for a number of organic transformations including the enantioselective Strecker reaction[1] and asymmetric acylation reactions.[2] Even proline itself (and simple derivatives thereof) has been used as an asymmetric catalyst for the direct asymmetric aldol reaction,[3] the Robinson annulation,[4] and very recently the Diels–Alder reaction.[5, 6] Herein, we report the application of small peptide catalysts to a fundamentally different asymmetric transformation, the enantioselective conjugate addition of azide ion to enoate derivatives.

We recently reported that simple tertiary amines catalyze the conjugate addition of azide ion to enoates under mild conditions [Eq. (1); $TMSN_3$ = trimethylsilyl azide].[7, 8] From

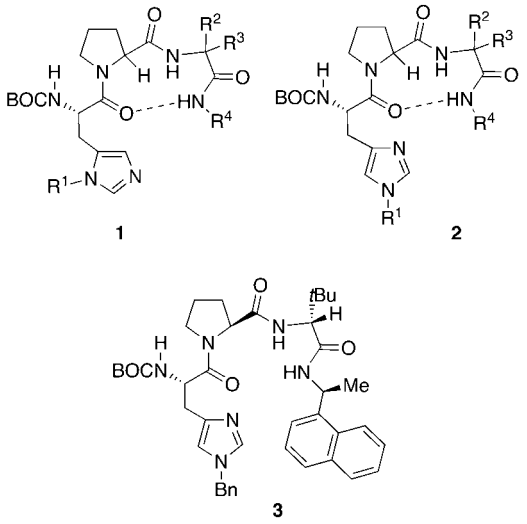


(1)

the point of view of synthesis, this reaction is significant in that the product, a β-azido carbonyl compound, may be converted into a β-amino acid. β-Amino acids are important targets for asymmetric synthesis as synthons,[9, 10] and also as monomers for the synthesis of "β-peptides", a biostable class of compounds currently under study for application as peptide-like drug molecules.[11] Documenting a highly significant advance in this area, Jacobsen and Myers recently disclosed an efficient asymmetric synthesis of β-azido imides employing chiral salen-type complexes of aluminum as catalysts for HN_3 addition (salen = *N*,*N*′-bis(salicylicidene)ethylenediamine dianion).[12] Described below is a fundamentally different approach to the problem in which metal-free catalysts (2.5 mol %) are used to deliver azide ion in an asymmetric fashion under mild conditions ($PhCH_3$, 25 °C).

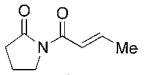
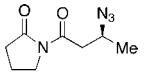
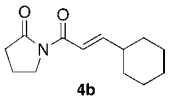
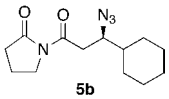
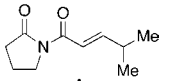
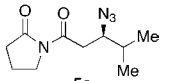
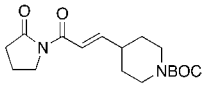
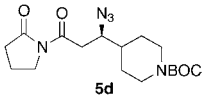
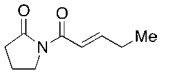
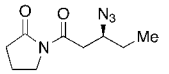
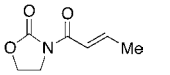
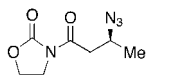
Previous studies from our laboratory have shown that peptide β-turns represent suitable templates for the development of asymmetric catalysts for acylation reactions. While catalysts such as peptide **1** (with the imidazole nitrogen atom proximal to the amino acid side chain alkylated, the "π-nitrogen") are active for the conjugate addition, none of the peptides we studied in this class afford products with appreciable enantiomeric excess. In contrast, catalysts with the "τ-nitrogen" alkylated (e.g., **2**), are not only active, but they also yield products that exhibit significant enantiomeric excess. Of the catalysts we screened, peptide **3** has emerged as particularly promising.

As shown in Table 1, screening a variety of substrates in the reaction with chiral catalyst **3** (2.5 mol %) resulted in the identification of pyrrolidinone-derived imides **4** as suitable substrates for further study. Crotonate-derived substrate **4a** is converted to **5a** (3.8 equiv $TMSN_3$, 1.0 equiv *t*BuCOOH/$PhCH_3$, 25 °C) within 24 h in 97 % yield, and the product



1 2 3

Table 1. Substrate scope for β-azidation employing catalyst **3**.[a]

Entry	Substrate	Product	Yield [%][b]	*ee* [%][c]
1	 **4a**	 **5a**	97	63
2	 **4b**	 **5b**	79	85
3	 **4c**	 **5c**	84	82
4	 **4d**	 **5d**	85	71
5	 **4e**	 **5e**	91	71
6	 **6**	 **7**	85	45

[a] All reactions conducted according to the optimized conditions. See Supporting Information for details. [b] Yield of isolated product after silica gel chromatography. [c] Determined by chiral HPLC. Reported *ee* values are the average of five runs. See Supporting Information for details.

exhibits an *ee* of 63 % (Table 1, entry 1). Substrates that possess a γ-branch on the acrylate moiety exhibit more enantioselective reactions. Cyclohexyl-substituted acrylate **4b** undergoes efficient conversion to azide **5b** with 85 % *ee* (79 % yield, Table 1, entry 2). Similarly, isopropyl-substituted acrylate **4c** participates in an efficient asymmetric azidation, undergoing transformation to **5c** in 82 % *ee* (84 % yield, Table 1, entry 3). Piperidine derivative **4d** undergoes conversion to azide **5d** in 71 % *ee*, and 85 % yield (Table 1, entry 4). *n*-Pentenoic acid derivative **4e** participates in the reaction, affording product **5e** with 71 % *ee* (91 % yield, Table 1, entry 5). Notably, simple ester substrates such as ethyl

  0044-8249/00/11220-3782 $ 17.50+.50/0 *Angew. Chem.* **2000**, *112*, Nr. 20

crotonate are inert under the reaction conditions. The more conventional oxazolidinone **6** is somewhat less reactive than **4a**, and the product **7** shows also a reduced level of enantiomeric excess in comparison to product **5a** (85% yield, 45% *ee*, Table 1, entry 6).

Examination of a variety of other peptides reveals that, as in our studies of asymmetric acyl transfer, subtle changes in the β-turn structure have a substantial impact on reaction efficiency. Catalysts **8**–**11** provide representative results (Table 2). In general, all peptides containing the N-terminal

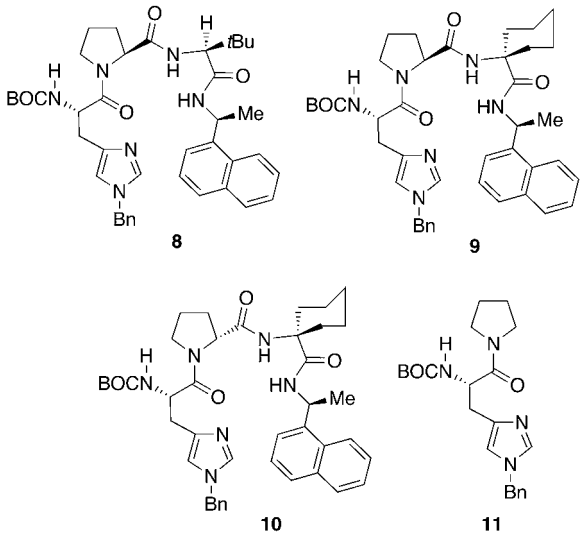


Table 2. Screen of selected catalysts for β-azidation of substrate **4a**.

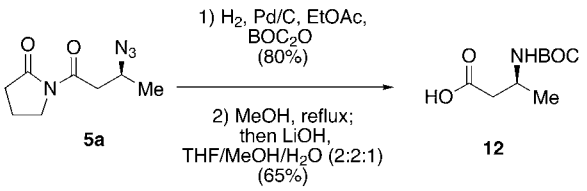
Entry	Catalyst	Conversion [%] [a]	*ee* [%] [b]
1	**3**	100	63
2	**8**	74	14
3	**9**	82	63
4	**10**	75	−21
5	**11**	72	no Selectivity

[a] Determined by 400 MHz ^{1}H NMR spectroscopy. [b] Determined by chiral HPLC. See Supporting Information for details.

τ-(benzyl)-histidine residue were found to be catalytically active. Systematic variation of the residues revealed that in the $i+2$ position, D-*t*Leu was found to give rise to a more selective catalyst than L-*t*Leu. As stated above, for the crotonyl-substituted substrate **4a**, catalyst **3** affords the product with quantitative conversion and 63% *ee* (Table 2, entry 1). However, when catalyst **8** is employed (identical to **3** except for the exchange of L-*t*Leu in place of the D-*t*Leu), the product is obtained in only 14% *ee* (74% conversion, Table 2, entry 2). The effect of the proline stereogenic center was ascertained by comparing the performance of peptides **9** and **10**, with a spirocyclic amino acid in the $i+2$ position. In the case of catalyst **9**, with L-Pro in the $i+1$ position, the product is obtained in 63% *ee* (82% conversion, Table 2, entry 3). However, with D-Pro in this position (catalyst **10**, Table 2, entry 4), the product is delivered with only 21% *ee*. Notably, this diastereomeric catalyst afforded opposite enantioselectivity in the conjugate addition. Control peptide **11**, devoid of any secondary structure, resulted in nonselective reactions under all conditions employed (Table 2, entry 5).

The mechanistic basis for the reaction selectivities is under investigation. Certainly, the conformation of the peptide catalyst plays a role in dictating the enantioselectivity of a given catalyst, and studies to determine the reactive conformations are underway.[13] In addition, "nonlinear" effects have achieved an important status in asymmetric catalysis as a tool for elucidating kinetically significant noncovalent interactions among chiral catalysts. We thus carried out a study to probe for such effects in reactions catalyzed by **3**. Indeed, a linear increase in product ee is observed with a linear increase in the *ee* value of the catalyst at the optimized dilution for the reaction conditions ($R^2 = 0.98$).[14] While the interpretation of such probes for nonlinear behavior is a matter of some discussion,[15] the results are consistent with the catalyst behaving in a monomeric form during the stereochemistry-determining step.

To demonstrate that the pyrrolidinone-derived products of these reactions are readily converted to the corresponding protected β-amino acid synthons, we carried out the following sequence [Eq. (2)]. Product **5a** was subjected to catalytic hydrogenation (Pd/C, EtOAc) in the presence of BOC_2O (80% yield; BOC = butoxycarbonyl). The resulting protected amine was then hydrolyzed by employing a two-step sequence that affords the N-BOC amino acid **12** in 65% yield.



In summary, we have shown that simple β-turn peptides armed with a τ-(benzyl)-His residue are enantioselective catalysts for the azidation of β-substituted acrylate derivatives. As in our previous studies of asymmetric acyl transfer, there appears to be a close connection between amino acid sequence in the peptides and the enantioselectivities that are observed. Future studies will involve a combination of catalyst screening and mechanistic studies targeted at improved catalyst selectivities and also a detailed understanding of how these systems work.

Received: June 5, 2000 [Z15220]

[1] a) M. S. Sigman, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 4901–4902; b) M. S. Iyer, K. M. Gigstad, N. D. Namdev, M. Lipton, *J. Am. Chem. Soc.* **1996**, *118*, 4910–4911.
[2] a) S. J. Miller, G. T. Copeland, N. Papaioannou, T. E. Horstmann, E. M. Ruel, *J. Am. Chem. Soc.* **1998**, *120*, 1629–1630; b) G. T. Copeland, E. R. Jarvo, S. J. Miller, *J. Org. Chem.* **1998**, *63*, 6784–6785; c) E. R. Jarvo, G. T. Copeland, N. Papaioannou, P. J. Bonitatebus, Jr., S. J. Miller, *J. Am. Chem. Soc.* **1999**, *121*, 11638–11643.
[3] B. List, R. A. Lerner, C. F. Barbas III, *J. Am. Chem. Soc.* **2000**, *122*, 2395–2396.
[4] C. Agami, C. Puchot, H. Sevestre, *Tetrahedron Lett.* **1986**, 1501–1504.
[5] K. A. Ahrendt, C. J. Borths, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2000**, *122*, 4243–4244.

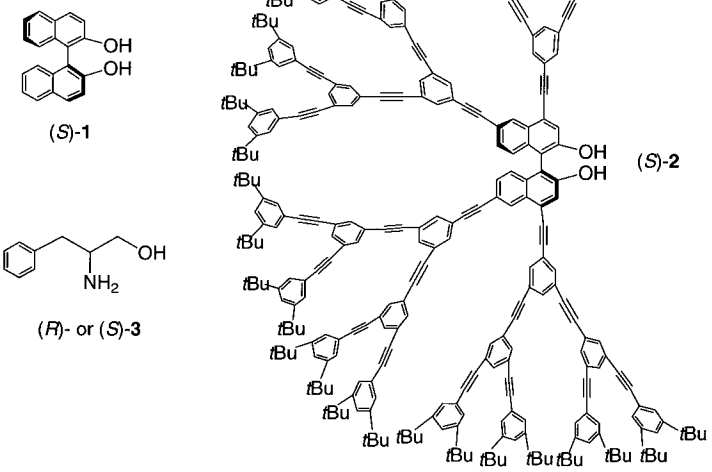
[6] For other representative metal-free asymmetric catalysts that do not employ peptides, see: a) Y. Iwabuchi, M. Nakatani, N. Yokoyama, S. Hatakeyama, *J. Am. Chem. Soc.* **1999**, *121*, 10219 – 10220; b) E. J. Corey, M. J. Grogan, *Org. Lett.* **1999**, *1*, 157 – 160; c) H. Hemstra, H. Wynberg, *J. Am. Chem. Soc.* **1981**, *103*, 417 – 430. For examples involving peptide-based catalysts, see: d) K. Tanaka, A. Mori, S. Inoue, *J. Org. Chem.* **1990**, *55*, 181 – 185; e) S. Itsuno, M. Sakakura, K. Ito, *J. Org. Chem.* **1990**, *55*, 6047 – 6049.
[7] D. J. Guerin, T. E. Horstmann, S. J. Miller, *Org. Lett.* **1999**, *1*, 1107 – 1109.
[8] See also: a) P. Lakshmipathi, A. V. Rama Rao, *Tetrahedron Lett.* **1997**, *38*, 2551 – 2552; b) B. Y. Chung, Y. S. Park, I. S. Cho, B. C. Hyun, *Bull. Korean Chem. Soc.* **1988**, *9*, 269 – 270.
[9] a) *Enantioselective Synthesis of β-Amino Acids* (Ed.: E. Juaristi), Wiley-VCH, New York, **1997**; b) D. C. Cole, *Tetrahedron* **1994**, *50*, 9517 – 9582.
[10] For noteworthy recent advances, see: a) S. Kobayashi, S. Nagayama, *J. Am. Chem. Soc.* **1997**, *119*, 10049 – 10053; b) D. Ferraris, B. Young, T. Dudding, T. Lectka, *J. Am. Chem. Soc.* **1998**, *120*, 4548 – 4549; c) M. P. Sibi, J. J. Shay, M. Liu, C. P. Jasperse, *J. Am. Chem. Soc.* **1998**, *120*, 6615 – 6616; d) B. J. Kim, Y. S. Park, P. Beak, *J. Org. Chem.* **1999**, *64*, 1705 – 1708; e) D. A. Evans, L. D. Wu, J. J. M. Wiener, J. S. Johnson, D. H. B. Ripin, J. S. Tedrow, *J. Org. Chem.* **1999**, *64*, 6411 – 6417; f) T. P. Tang, J. A. Ellman, *J. Org. Chem.* **1999**, *64*, 12 – 13.
[11] For representative studies in the field, see: a) D. H. Appella, J. J. Barchi, S. R. Durrell, S. H. Gellman, *J. Am. Chem. Soc.* **1999**, *121*, 2309 – 2310; b) K. Gademan, M. Ernst, D. Hoyer, D. Seebach, *Angew. Chem.* **1999**, *111*, 1302 – 1304; *Angew. Chem. Int. Ed.* **1999**, *38*, 1223 – 1226.
[12] J. K. Myers, E. N. Jacobsen, *J. Am. Chem. Soc.* **1999**, *121*, 8959 – 8960.
[13] For example, we have recently reported that β-turns with τ-(benzyl)-His in the N-terminal position can adopt Asx-Pro turnlike structures. See: J. T. Blank, D. J. Guerin, S. J. Miller, *Org. Lett.* **2000**, *2*, 1247 – 1249.
[14] The plot documenting the absence of a nonlinear effect may be found in the Supporting Information.
[15] a) D. G. Blackmond, *Acc. Chem. Res.* **2000**, 33, 402 – 411; b) H. B. Kagan, T. O. Luukas in *Comprehensive Asymmetric Catalysis, Vol. 1* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), **1999**, pp. 101 – 118.

The First Dendrimer-Based Enantioselective Fluorescent Sensor for the Recognition of Chiral Amino Alcohols**

Vincent J. Pugh, Qiao-Sheng Hu, and Lin Pu*

The development of fluorescence-based molecular sensors has received broad attention in research in recent years.[1–3] The use of fluorescence spectroscopic methods for molecular recognition has many advantages: fluorescence provides many more signaling modes for substrate detection, such as quenching, fluorescence enhancement, excimers, exciplexes, and lifetimes, than electronic absorption. The high sensitivity of fluorescence techniques requires the use of only very small amounts of sensor molecules. Fluorescence spectrometers are also of low cost and widely available. Fluorescence sensors can be further applied to continuous monitoring and remote sensing by using optical fibers. A large number of fluorescent sensors have been designed for applications in the detection of metal ions, phosphates, and neutral molecules.[1–3] Recently, a fluorescent sensor has also been used in the combinatorial search for catalysts.[4a] If such fluorescent sensors could be made enantioselective, they would allow a rapid analysis of the enantiomeric composition of thousands of chiral molecules generated by the combinatorial synthesis. This process would greatly facilitate the combinatorial discovery of asymmetric catalysts or reagents since the current chromatographic analysis of enantiomers is inherently a slow process. An enzyme-catalyzed release of fluorophores has been used in the search for catalytic antibodies for the enantioselective hydrolysis of acetates.[4b] Chiral discrimination by luminescence has also been studied in the past two decades.[5–9] These studies involve a variety of luminescent materials including inorganic complexes,[5] organic molecules,[6–8] and enzymes.[9] Enantioselective responses have been observed when chiral luminophores are treated with chiral quenchers or enhancers. The relationship between the fluorescence properties of the sensors and the enantiomeric purity of the substrates have been established in a few cases.[5b, 6g, 7, 9b]

Recently, we carried out a program to incorporate chiral dendrimers[10] into enantioselective fluorescent sensors as a real-time technique to quantitatively or semi-quantitatively determine the enantiomeric composition of chiral molecules. Properly designed dendritic materials have been found to show efficient migration of energy from the dendrons or periphery groups to the more conjugated units or core, which has led to greatly enhanced fluorescence intensity.[11–17] The strong fluorescence signals of such dendrimers should be very useful in the development of fluorescent sensors. Based on the structure of chiral 1,1′-bi-2-naphthol ((*S*)-**1**)[18] and the den-



[*] Prof. Dr. L. Pu, Dr. V. J. Pugh, Dr. Q.-S. Hu
Department of Chemistry
University of Virginia
Charlottesville, VA 22901
E-mail: lp6n@virginia.edu

[**] The support of this work by the National Institute of Health (1R01GM58454) is gratefully acknowledged. We also thank the partial support from the donors of the Petroleum Research Fund—administered by the American Chemical Society.

  0044-8249/00/11220-3784 $ 17.50+.50/0