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SIMULTANEOUS FORMATION OF ANTIPARALLEL β-SHEET-LIKE AND TYPE II β-TURN-LIKE STRUCTURES BASED ON INTRODUCTION OF DIPEPTIDE CHAINS WITH HETEROCHIRAL SEQUENCE INTO FERROCENE SCAFFOLD

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Abstract – Simultaneous formation of antiparallel β-sheet-like and type II β-turn-like structures through the intramolecular hydrogen bonds was achieved by the symmetrical introduction of two dipeptide chains with heterochiral sequence (-L-Ala-D-Pro-4APy or -D-Ala-L-Pro-4APy) into the ferrocene scaffold as a central reverse-turn unit. X-Ray crystallographic analyses clarified the chirality-organized structures of the ferrocene-peptide bioconjugates, in which the helical chirality of the ferrocene unit was induced. The ferrocene-peptide bioconjugates exhibited an induced circular dichroism (ICD) based on the helical chirality at the absorbance region of the ferrocene moiety.

INTRODUCTION

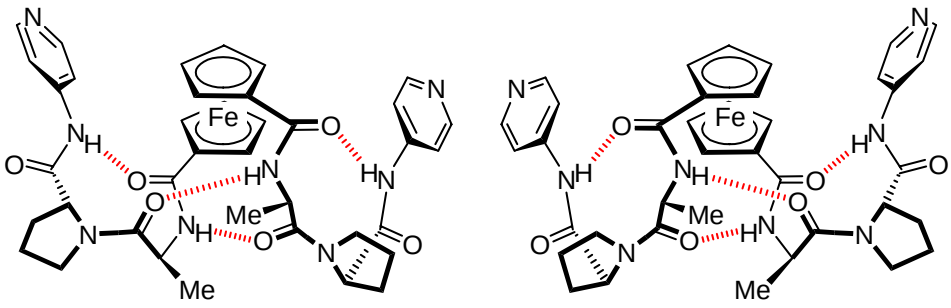
Architectural molecular assemblies in proteins are constructed to fulfill various functions. Turns are key structural elements in protein secondary structures. Considerable attention has been focused on in the design of β-turn[1-2] and γ-turn mimics.[2a, 2e-f, 3] Recently, the research field of bioorganometallic chemistry, which is a hybrid area between biochemistry and organometallic chemistry, has received extensive interest. Conjuction of organometallic compounds with biomolecules such as amino acids and peptides to design bioconjugates has undergone rapid development.[4] Ferrocenes are a reliable organometallic scaffold as a central reverse-turn unit because the inter-ring spacing of Cp is about 3.3 Å, which is appropriate for hydrogen bonding of the attached peptide strands. The introduction of peptides into the

ferrocene scaffold has been demonstrated to design ferrocene-peptide bioconjugates, which induce highly ordered structures of peptides, and to develop new biomaterials.[2g, 3e-f, 5-6] We herein report the symmetrical introduction of two dipeptide chains with heterochiral sequence (-L-Ala-D-Pro-4APy or -D-Ala-L-Pro-4APy) into the ferrocene scaffold as a central reverse-turn unit to induce the simultaneous formation of antiparallel β-sheet-like and type II β-turn-like structures through the intramolecular hydrogen bonds.

RESULTS AND DISCUSSION

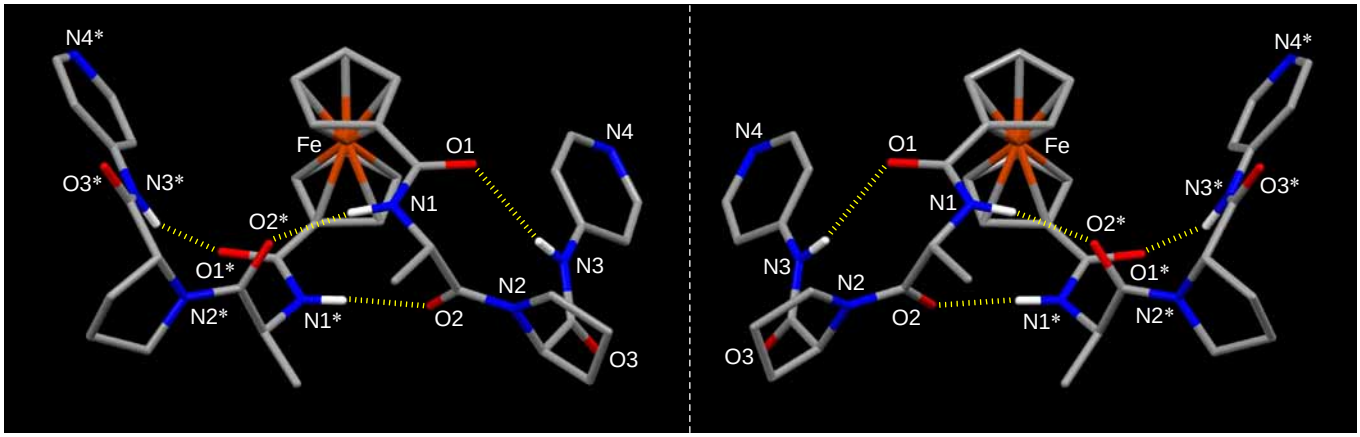
The dipeptide chain with heterochiral sequence such as L-Pro-D-Ala has been reported to enforce a reverse-turn conformation.[7] The alanylproline heterochiral sequence was focused on as a dipeptide chain based on a hydrogen bonding alanyl moiety and a sterically constrained proline as a well-known turn inducer in proteins. The ferrocene-peptide bioconjugates **1** and **2** were prepared by the reaction of 1,1'-bis(chlorocarbonyl)ferrocene and the corresponding dipeptide derivatives (Figure 1). The single-crystal X-ray structure determination (Tables 1-3) of **1** revealed the *P* helical arrangement of the ferrocene unit, which was induced by the chirality organization through the formation of interchain antiparallel β-sheet-like hydrogen bonding between NH (Ala) and CO (Ala of another chain) of each dipeptide chain (N(1) • • • O(2*), 2.906(2) Å; N(1*) • • • O(2), 3.041(2) Å), as depicted in Figure 2a. The most impressive feature of the structure is that the NH adjacent to the pyridyl moiety participates in the intrachain hydrogen bonding with CO adjacent to the ferrocene unit of the same peptide chain (N(3) • • • O(1), 3.283(3) Å; N(3*) • • • O(1*), 3.289(3) Å) to nucleate a β-turn-like structure in each dipeptide chain. The torsion angles ϕ_2 (ϕ_2 = -66.1(3)° and ϕ_2* = -66.7(3)°), ψ_2 (ψ_2 = 144.5(2)° and ψ_2* = 146.4(3)°), ϕ_3 (ϕ_3 = 84.1(3)° and ϕ_3* = 82.4(3)°), and ψ_3 (ψ_3 = -3.3(3)° and ψ_3* = -2.1(3)°) of **1** indicated a type II β-turn-like structure similar to an ideal type II β-turn (ϕ_2 = -60°, ψ_2 = 120°, ϕ_3 = 80°, and ψ_3 = 0°) (Table 3). The symmetrical introduction of the alanylproline heterochiral sequence as a dipeptide chain into the ferrocene scaffold was found to induce not only the simultaneous formation of antiparallel β-sheet-like and type II β-turn-like structures through the intramolecular hydrogen bonds, but also the helical chirality of the ferrocene unit, wherein the ferrocene scaffold acts as a central reverse-turn.

As is apparent from Figure 2b, the *M* helical arrangement of the ferrocene unit is formed in the molecular structure of **2** composed of the dipeptide chains (-D-Ala-L-Pro-4APy), which is in a good mirror image relationship with **1**, indicating that **1** and **2** are the conformational enantiomers. The opposite values of the torsion angles of **2** (ϕ_2 (ϕ_2 = 65.7(4)° and ϕ_2* = 67.1(4)°), ψ_2 (ψ_2 = -144.4(3)° and ψ_2* = -146.4(3)°), ϕ_3 (ϕ_3 = -83.6(4)° and ϕ_3* = -82.2(4)°), and ψ_3 (ψ_3 = 3.4(5)° and ψ_3* = 1.7(4)°)) were observed as compared with those of **1**.



Fc(-L-Ala-D-Pro-4APy)$_2$ **1** Fc(-D-Ala-L-Pro-4APy)$_2$ **2**

Figure 1. Ferrocenes bearing the dipeptide chains with heterochiral sequence (-L-Ala-D-Pro-4APy or -L-Ala-D-Pro-4APy).



(a) (b)

Figure 2. Molecular structures of (a) **1** and (b) **2**.

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{38}H_{42}N_8O_6Fe$	$C_{38}H_{42}N_8O_6Fe$
formula weight	762.65	762.65
crystal system	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)
a, Å	12.0174(6)	12.0550(3)
b, Å	12.5942(5)	12.6006(3)
c, Å	12.5089(6)	12.5507(1)
β, deg	104.942(2)	105.077(2)
V, Å^3	1829.2(1)	1840.84(6)
Z	2	2
D_{calcd}, g cm^{-3}	1.385	1.376
μ(Mo Kα), cm^{-1}	4.70	4.67
T, °C	4.0	23.0
λ(Mo Kα), Å	0.71069	0.71069
$R1$ [a]	0.042	0.048
$wR2$ [b]	0.122	0.128

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Hydrogen Bonds for **1** and **2**

crystal	type [a]	donor	acceptor	D • • • A (Å)	D–H • • • A (°)
1	inter	N(1)	O(2*)	2.906(2)	168(2)
	inter	N(1*)	O(2)	3.041(2)	174(2)
	intra	N(3)	O(1)	3.283(3)	157(2)
	intra	N(3*)	O(1*)	3.289(3)	150(2)
2	inter	N(1)	O(2*)	2.908(3)	168(3)
	inter	N(1*)	O(2)	3.046(3)	171(2)
	intra	N(3)	O(1)	3.296(4)	156(3)
	intra	N(3*)	O(1*)	3.293(4)	150(2)

[a] inter: interchain, intra: intrachain.

Table 3. Torsion Angles (deg) for **1** and **2**

	angle [a]	**1**	**2**
ϕ_2	C(6)-N(1)-C(7a)-C(8)	-66.1(3)	65.7(4)
ψ_2	N(1)-C(7a)-C(8)-N(2)	144.5(2)	-144.4(3)
ω_2	C(7a)-C(8)-N(2)-C(9a)	177.7(2)	-177.9(3)
ϕ_3	C(8)-N(2)-C(9a)-C(10)	84.1(3)	-83.6(4)
ψ_3	N(2)-C(9a)-C(10)-N(3)	-3.3(3)	3.4(5)
ϕ_2*	C(6*)-N(1*)-C(7a*)-C(8*)	-66.7(3)	67.1(4)
ψ_2*	N(1*)-C(7a*)-C(8*)-N(2*)	146.4(3)	-146.4(3)
ω_2*	C(7a*)-C(8*)-N(2*)-C(9a*)	-178.9(3)	178.9(3)
ϕ_3*	C(8*)-N(2*)-C(9a*)-C(10*)	82.4(3)	-82.2(4)
ψ_3*	N(2*)-C(9a*)-C(10*)-N(3*)	-2.1(3)	1.7(4)

[a] Symbol used for torsion angles in peptides (IUPAC–IUB Commission on Biochemical Nomenclature).

Table 4. Selected Spectroscopic Data for **1** and **2**

		^{1}H NMR N-H (ppm) [a]		FT-IR ν_{N-H} (cm^{-1}) [a]
		$CDCl_3$	$CDCl_3$/DMSO-d_6 (9:1)	CH_2Cl_2
1	Ala N-H	8.67	8.69	3308
	Py N-H	8.99	9.01	
2	Ala N-H	8.67	8.69	3308
	Py N-H	8.99	9.01	

[a] 1.0 x 10^{-2} M.

A chirality-organized structure in solution was investigated by ^{1}H NMR, FT-IR, and CD analyses. The selected spectroscopic data for **1** and **2** were listed in Table 4. In the ^{1}H NMR spectrum of **1** in $CDCl_3$ (1.0 x 10^{-2} M), only one kind of the resonances of the Ala N-H and the NH adjacent to the pyridyl moiety were detected at a lower field (8.67 and 8.99 ppm). The N-H resonances of **1** were not perturbed by the addition of aliquots of DMSO-d_6 to $CDCl_3$ ($CDCl_3$/DMSO-d_6 (9:1): 8.69 and 9.01 ppm). These results indicate that the ferrocene **1** forms the symmetrical intramolecular hydrogen bonds even in solution. The FT-IR spectrum of **1** in CH_2Cl_2 (1.0 x 10^{-2} M) showed only one hydrogen bonded N-H stretch at 3308 cm^{-1}, which also supports the hydrogen bonding in **1**. In the CD spectrum of the ferrocene **1**, an induced circular dichroism (ICD) was observed at the absorbance region of the ferrocene moiety, indicating the *P*-helical chirality of the ferrocene moiety (Figure 3). Furthermore, the ferrocene **2** exhibited a mirror-imaged negative CD signal based on the *M*-helical chirality of the ferrocene moiety at the absorbance region of the ferrocene moiety. The chirality-organized structure via intramolecular hydrogen bondings is likely to be present in solution. Cp protons at the β position of the ferrocene moiety of **1** and **2** (4.06-4.04 and 3.07-3.06 ppm) were observed in a higher field in the ^{1}H NMR probably due to the ring-current effect of the pyridine π-ring, suggesting a type II β-turn-like structure as observed in the crystal structures. Proton magnetic resonance nuclear Overhauser effect (NOE) of **2** in $CDCl_3$ at 25 °C also provided a diagnostic evidence for this structure. Irradiation of the Cp proton at the β position enhanced the pyridyl protons (Figure 4). Irradiation of the Cp proton at the α position also enhanced the Ala NH, the NH adjacent to the pyridyl moiety, and the pyridyl protons (Figure 5). A type II β-turn-like structure was found to be formed in solution.

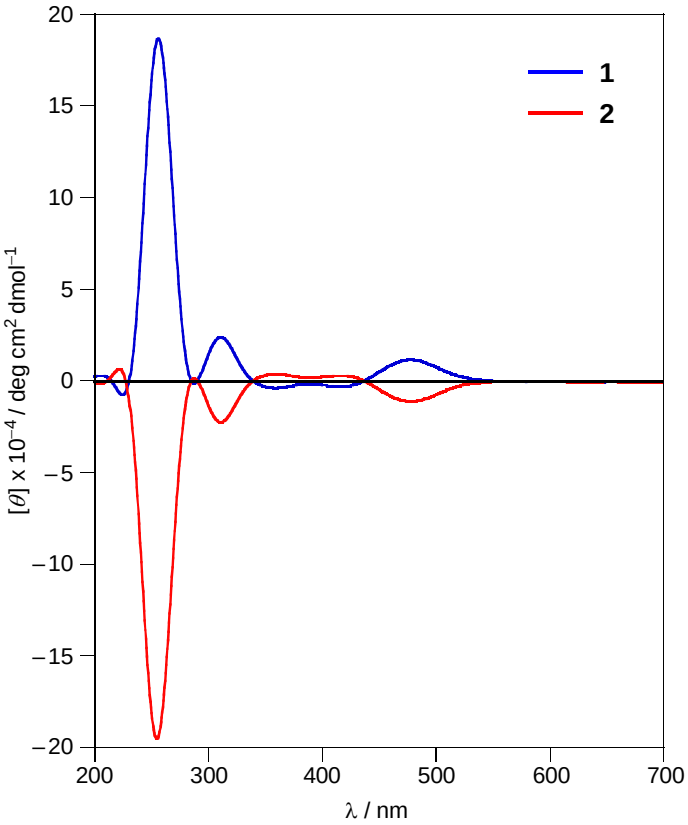


Figure 3. CD spectra of **1** and **2** in CH_2Cl_2 (1.0×10^{-4} M).

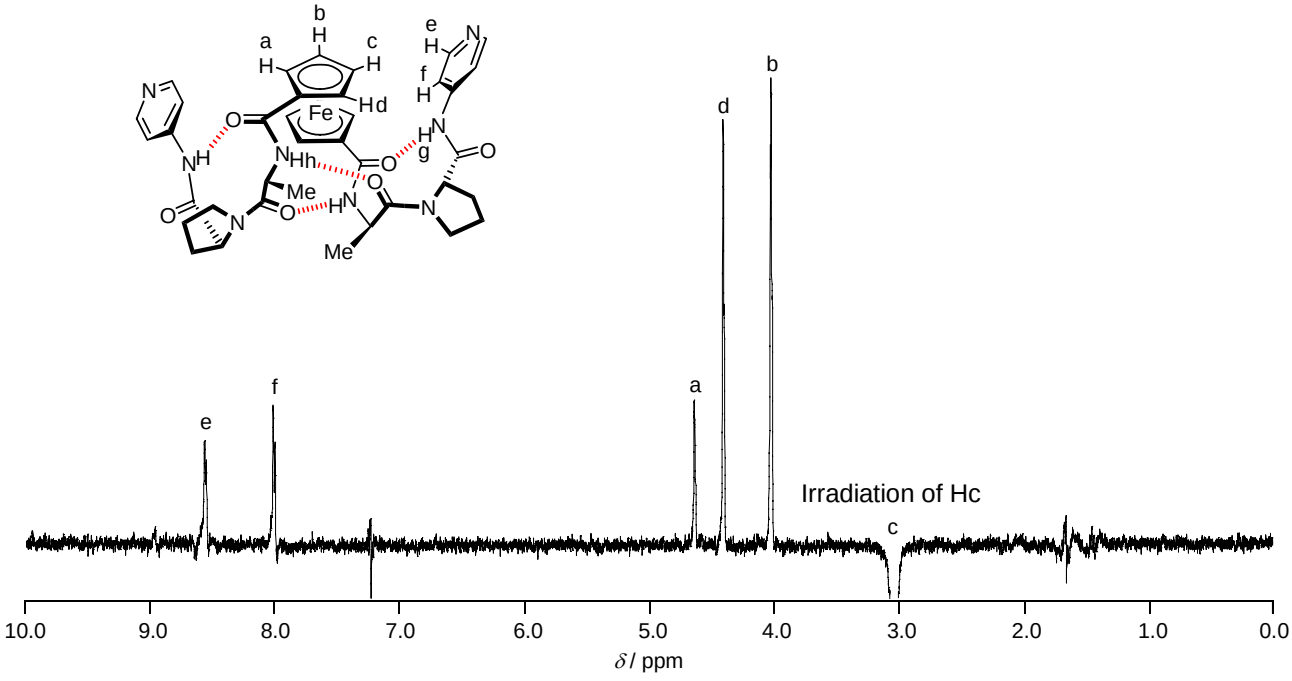


Figure 4. 400 MHz ^{1}H NMR difference NOE experiment performed at 25 °C with 2 second irradiation of a freeze-pump-thaw degassed 1.0×10^{-2} M solution of **2** in $CDCl_3$.

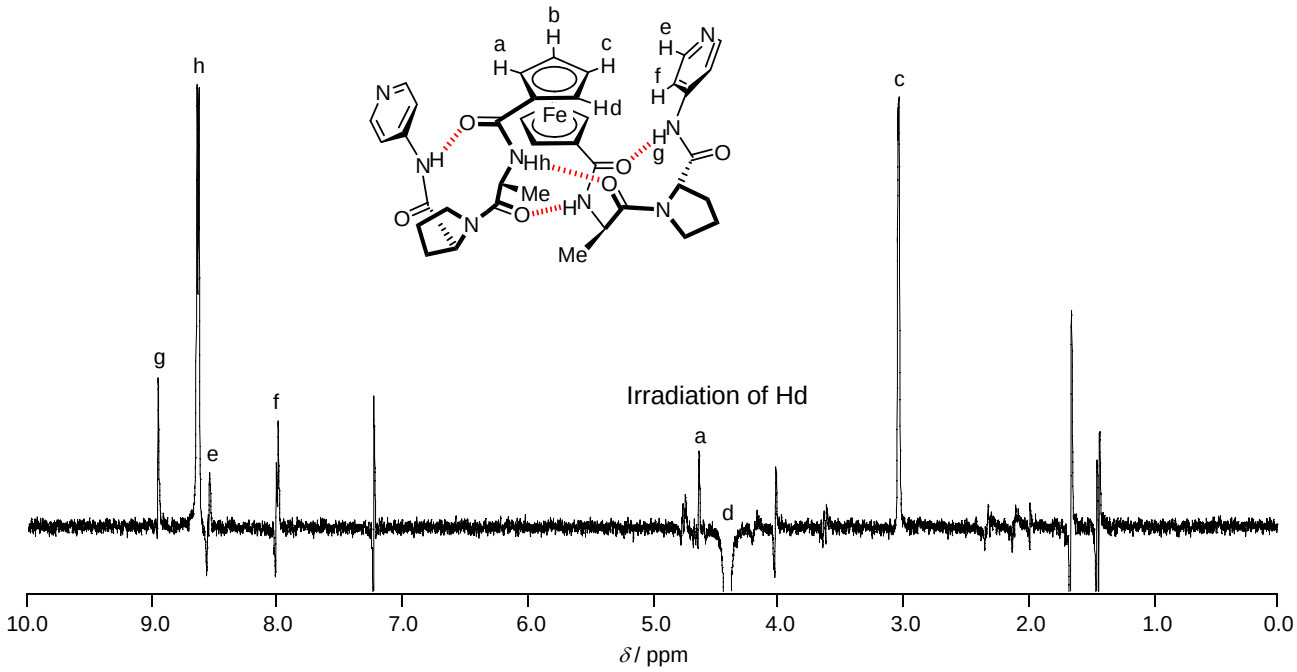


Figure 5. 400 MHz ^{1}H NMR difference NOE experiment performed at 25 °C with 2 second irradiation of a freeze-pump-thaw degassed 1.0 x 10^{-2} M solution of **2** in $CDCl_3$.

CONCLUSION

In conclusion, the ferrocene-peptide bioconjugates have been designed to form the chirality-organized structures in both solid and solution states. The symmetrical introduction of two minimum-sized dipeptide chains with heterochiral sequence (-L-Ala-D-Pro-4APy or -D-Ala-L-Pro-4APy) into the ferrocene scaffold as a central reverse-turn unit was found to induce the simultaneous formation of antiparallel β-sheet-like and type II β-turn-like structures through the intramolecular hydrogen bonds, in which the helical chirality of the ferrocene moiety was induced. The utilization of the virtue of hydrogen bond's directionality and specificity of the minimum-sized peptide chains possessing chiral centers and hydrogen bonding sites is considered to be a useful approach to artificial highly-ordered systems. The introduced C-terminal amido pyridyl moiety is envisioned to serve as a binding site for metal complexation.

EXPERIMENTAL

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480 Plus

spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECP 400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-700 mass spectrometer. Dipeptide derivatives were prepared according to the reported method by the coupling of Boc-Ala-Pro-OH with 4-aminopyridine using EDCI (T. Moriuchi, K. Yoshida, and T. Hirao, *Organometallics*, 2001, **20**, 3101.). 1,1'-Bis(chlorocarbonyl)ferrocene was prepared according to the literature method (F. W. Knobloch and W. H. Rauscher, *J. Polymer Sci.*, 1961, **54**, 651.).

General Procedure for the Synthesis of Ferrocenes 1 and 2 Bearing Two Heterochiral Dipeptide Chains.

To a stirred solution of Boc-Ala-Pro-4APy (725 mg, 2.0 mmol) in MeOH (16 mL) was added 30 mL of 1.0 M HCl/Et_2O solution under argon at rt, and the mixture was stirred at rt for 10 h. The solvent was removed in vacuo and the resulting residue was washed three times with anhydrous Et_2O to give H-Ala-Pro-4APy hydrochloric acid salt. To a stirred mixture of the thus-obtained H-Ala-Pro-4APy hydrochloric acid salt, 4-dimethylaminopyridine (12.0 mg, 0.098 mmol) and triethylamine (1.4 mL, 10 mmol) in CH_2Cl_2 (35 mL) was dropwise added the solution of 1,1'-bis(chlorocarbonyl)ferrocene (373 mg, 1.2 mmol) in CH_2Cl_2 (30 mL) under argon at 0 °C. The mixture was stirred at 0 °C for 1 h and then at rt for 20 h. The resulting mixture was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was chromatographed on alumina column eluting with EtOAc. The ferrocene **1** or **2** was isolated by recrystallization from CH_2Cl_2-hexane.

1: yield 42%; mp 167-169 °C (decomp); IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3308, 3052, 2984, 1694, 1644, 1621, 1589, 1537, 1508, 1278 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 1.0 x 10^{-2} M) δ 8.99 (s, 2H), 8.67 (d, 2H, J = 6.2 Hz), 8.59 (d, 4H, J = 6.5 Hz), 8.04 (d, 4H, J = 6.5 Hz), 4.79 (dd, 2H, J = 8.3, 3.3 Hz), 4.72-4.65 (m, 4H), 4.44-4.43 (m, 2H), 4.24-4.19 (m, 2H), 4.06-4.04 (m, 2H), 3.69-3.62 (m, 2H), 3.07-3.06 (m, 2H), 2.41-2.27 (m, 4H), 2.17-2.09 (m, 4H), 1.46 (d, 6H, J = 7.3 Hz); FAB-MS *m/z* 762 (M^+).

2: yield 52%; mp 167-169 °C (decomp); IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3308, 3052, 2984, 1694, 1644, 1621, 1589, 1537, 1508, 1278 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 1.0 x 10^{-2} M) δ 8.99 (s, 2H), 8.67 (d, 2H, J = 6.2 Hz), 8.59 (d, 4H, J = 6.5 Hz), 8.04 (d, 4H, J = 6.5 Hz), 4.79 (dd, 2H, J = 8.3, 3.3 Hz), 4.72-4.65 (m, 4H), 4.44-4.43 (m, 2H), 4.24-4.19 (m, 2H), 4.06-4.04 (m, 2H), 3.69-3.62 (m, 2H), 3.07-3.06 (m, 2H), 2.41-2.27 (m, 4H), 2.17-2.09 (m, 4H), 1.46 (d, 6H, J = 7.3 Hz); FAB-MS *m/z* 762 (M^+).

CD Measurements.

CD spectra were recorded using a JASCO J-720 spectropolarimeter in an deaerated CH_2Cl_2 solution with the concentration 1.0 x 10^{-4} M for **1** and **2** under argon at 25 °C.

Proton Magnetic Resonance Nuclear Overhauser Effect Measurements.

A sample was prepared under argon. Nuclear Overhauser effect experiments were performed with 2 second irradiation of a freeze-pump-thaw degassed 1.0 x 10^{-2} M solution in $CDCl_3$. The 400 MHz ^1H NMR spectra were recorded at 25 °C. Nuclear Overhauser enhancements were obtained by saturation of the desired resonance.

X-Ray Structure Analysis.

All measurements for **1** and **2** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The structures of **1** and **2** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-682409 for **1** and CCDC-682410 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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REFERENCES

1. For reviews on turn mimetics, see: (a) J. P. Schneider and J. W. Kelly, *Chem. Rev.*, 1995, **95**, 2169. (b) K. D. Stigers, M. J. Soth, and J. S. Nowick, *Curr. Opin. Chem. Biol.*, 1999, **3**, 714.
2. For references after 2002, see: (a) E. N. Prabhakaran, I. N. Rao, A. Boruah, and J. Iqbal, *J. Org. Chem.*, 2002, **67**, 8247. (b) J. M. Langenhan, I. A. Guzei, and S. H. Gellman, *Angew. Chem. Int. Ed.*, 2003, **42**, 2402. (c) K. S. Rotondi and L. M. Gierasch, *Biochemistry*, 2003, **42**, 7976. (d) G. M. Grotenbreg, M. S. M. Timmer, A. L. Llamas-Saiz, M. Verdoes, G. A. van der Marel, M. J. van Raaij, H. S. Overkleeft, and M. Overhand, *J. Am. Chem. Soc.*, 2004, **126**, 3444. (e) A. Trabocchi, D. Potenza, and A. Guarna, *Eur. J. Org. Chem.*, 2004, 4621. (f) R. L. Beyer, H. N. Hoang, T. G. Appleton, and D. P. Fairlie, *J. Am. Chem. Soc.*, 2004, **126**, 15096. (g) T. Moriuchi, T. Nagai, and T.

Hirao, *Org. Lett.*, 2005, **7**, 5265.

3. For references after 1996, see: (a) T. P. Curran, N. M. Chandler, R. J. Kennedy, and M. T. Keaney, *Tetrahedron Lett.*, 1996, **37**, 1933. (b) J. M. Travins and F. A. Etzkorn, *J. Org. Chem.*, 1997, **62**, 8387. (c) A. Trabocchi, E. G. Occhiato, D. Potenza, and A. Guarna, *J. Org. Chem.*, 2002, **67**, 7483. (d) D. Yang, J. Qu, W. Li, D.-P. Wang, Y. Ren, and Y.-D. Wu, *J. Am. Chem. Soc.*, 2003, **125**, 14452. (e) T. Moriuchi, T. Nagai, and T. Hirao, *Org. Lett.*, 2006, **8**, 31. (f) T. Moriuchi, T. Fujiwara, and T. Hirao, *J. Organomet. Chem.*, 2007, **692**, 1353.
4. (a) G. Jaouen, A. Vessiéres, and I. S. Butler, *Acc. Chem. Res.*, 1993, **26**, 361. (b) R. Severin, R. Bergs, and W. Beck, *Angew. Chem. Int. Ed.*, 1998, **37**, 1634. (c) *J. Organomet. Chem., Bioorganometallic Chemistry* (ed. G. Jaouen), 1999, **589**, 1-126.
5. (a) R. S. Herrick, R. M. Jarret, T. P. Curran, D. R. Dragoli, M. B. Flaherty, S. E. Lindyberg, R. A. Slate, and L. C. Thornton, *Tetrahedron Lett.*, 1996, **37**, 5289. (b) W. Bauer, K. Polborn, and W. Beck, *J. Organomet. Chem.*, 1999, **579**, 269. (c) H.-B. Kraatz, D. M. Leek, A. Houmam, G. D. Enright, J. Lusztyk, and D. D. M. Wayner, *J. Organomet. Chem.*, 1999, **589**, 38. (d) I. Bediako-Amoa, R. Silerova, and H.-B. Kraatz, *Chem. Commun.*, 2002, 2430. (e) D. R. van Staveren, T. Weyhermüller, and N. Metzler-Nolte, *Dalton Trans.*, 2003, 210. (f) S. I. Kirin, D. Wissenbach, and N. Metzler-Nolte, *New J. Chem.*, 2005, **29**, 1168. (g) K. Heinze and M. Beckmann, *Eur. J. Inorg. Chem.*, 2005, 3450. (h) S. Chowdhury, D. A. R. Sanders, G. Schatte, and H.-B. Kraatz, *Angew. Chem. Int. Ed.*, 2006, **45**, 751. (i) L. Barišić, M. Čakić, K. A. Mahmoud, Y.-n. Liu, H.-B. Kraatz, H. Pritzkow, S. I. Kirin, N. Metzler-Nolte, and V. Rapić, *Chem. Eur. J.*, 2006, **12**, 4965. (j) S. Chowdhury, G. Schatte, and H.-B. Kraatz, *Angew. Chem. Int. Ed.*, 2006, **45**, 6882. (k) K. A. Mahmoud and H.-B. Kraatz, *Chem. Eur. J.*, 2007, **13**, 5885. (l) X. de Hatten, Z. Cournia, I. Huc, J. C. Smith, and N. Metzler-Nolte, *Chem. Eur. J.*, 2007, **13**, 8139.
6. (a) A. Nomoto, T. Moriuchi, S. Yamazaki, A. Ogawa, and T. Hirao, *Chem. Commun.*, 1998, 1963. (b) T. Moriuchi, A. Nomoto, K. Yoshida, and T. Hirao, *J. Organomet. Chem.*, 1999, **589**, 50. (c) T. Moriuchi, A. Nomoto, K. Yoshida, A. Ogawa, and T. Hirao, *J. Am. Chem. Soc.*, 2001, **123**, 68. (d) T. Moriuchi, A. Nomoto, K. Yoshida, and T. Hirao, *Organometallics*, 2001, **20**, 1008. (e) T. Moriuchi, K. Yoshida, and T. Hirao, *Organometallics*, 2001, **20**, 3101. (f) T. Moriuchi, K. Yoshida, and T. Hirao, *J. Organomet. Chem.*, 2001, **637-639**, 75. (g) T. Moriuchi, K. Yoshida, and T. Hirao, *J. Organomet. Chem.*, 2003, **668**, 31. (h) T. Moriuchi, K. Yoshida, and T. Hirao, *Org. Lett.*, 2003, **5**, 4285.
7. D. S. Kemp and B. R. Bowen, *Tetrahedron Lett.*, 1988, **29**, 5081.