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Efficiency of Second Harmonic Generation from Amino Acids, Peptides, and Polypeptides Carrying Polarizable Aromatic Groups

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The SHG efficiencies of optically active amino acids, their monomeric derivatives, linear and cyclic dipeptides, tripeptides, and polypeptides carrying polarizable groups were tested. Among the 91 samples, L-valine-*p*-nitroanilide (Val-NA) showed the largest SHG [9.2 × $I^{2\omega}$(urea)]. Val-NA was found to be phase-matchable and transparent down to 420 nm. Monopeptide and dipeptide derivatives of *p*-nitrophenylalanine also showed large SHG and were transparent down to 420 nm.

INTRODUCTION

New compounds which show large second harmonic generation (SHG) have been searched for by many workers.[1] Amino acids, peptides and polypeptides are potential SHG substances, because of their dissymmetric structure in the molecular level and in their molecular organizations. Rieckhoff and Peticolas[2] and, later, Delfino[3] reported the SHG efficiencies of amino acids, peptides, and proteins in the powdered state. They found, however, no larger SHG efficiency than that of urea; L- or D-valine showed the largest SHG [6.7 – 6.9 × $I^{2\omega}(\alpha\text{-}SiO_2)$ = ca. 0.1 × $I^{2\omega}$(urea), fundamental light = 1064 nm]. One of the reasons for the small SHG

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is that the natural amino acids examined by them had no highly polarizable side groups. Therefore, a possibility to observe high SHG efficiencies still remains if one attaches highly polarizable groups on the side chain and/or the main chain of amino acids or peptide derivatives. Indeed, it is well known that *N*-dinitrophenyl-L-alanine methyl ester [or more commonly named as methyl (3,4-dinitrophenyl)-2-aminopropanoate (MAP)] shows about 10 times as high SHG efficiency as urea in the powdered state.[4] The ethyl ester derivative has been found to show even higher SHG efficiency.[4]

In this study some artificial amino acids carrying polarizable substituents and peptides and polypeptides containing those amino acids were synthesized. Their SHG efficiencies in the powdered state were measured using a Nd-YAG laser as a fundamental light source.

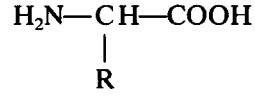
MEASUREMENTS

The SHG efficiency of powdered samples was measured according to the method of Kurtz and Perry.[5] The light source was a Nd-YAG Q-switched laser (pulse width = 12 ns, 1064 nm). The sample was held on a glass plate and the laser beam was introduced perpendicularly to the glass plate. The second-harmonic light (532 nm) was monitored with an angle of 45° from the incident beam. The SH light was passed through a grating monochrometer and detected by a photomultiplier tube. The intensity was directly read from the oscilloscope connected to the photomultiplier tube. The crystalline samples were ground and the component with a particle size of 125–200 μm was used for the measurement. The SHG efficiency was presented using the SHG intensity of powdered urea as a standard. The relative error of the SHG efficiency is about ±30%.

RESULTS AND DISCUSSION

SHG efficiency of amino acids and their monomeric derivatives

Table I lists the SHG efficiency of some natural and synthetic amino acids (1). No or very small SHG was observed



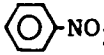
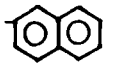
(1)

for most of the natural amino acids, as has been reported by Delfino.[3] However, synthetic amino acids carrying polarizable side groups, i.e., L- and D-γ-*p*-nitrophenylglutamine [Glu(NA)] and D-*p*-nitrophenylalanine (nitroPhe) showed stronger SHG than urea.

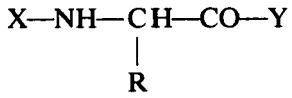
The SHG efficiencies of monomeric derivatives of natural and synthetic amino

TABLE I

SHG Efficiency of α-Amino Acids: $H_2N—CH(R)—COOH$

Materials	Size(μ)	SHG eff.(χUrea)	R
D-Ala	125-200	0.0	$-CH_3$
D-Asp	125-200	0.2	$-CH_2COOH$
L-Glu	125-200	0.0	$-(CH_2)_2COOH$
L-Glu(NA)•H_2O	125-200	3.3	$-(CH_2)_2CONH$  $-NO_2$
D-Glu(NA)•H_2O	125-200	3.1	
L-Ile	125-200	0.0	$-CH(CH_3)CH_2CH_3$
L-Phe	125-200	0.0	$-CH_2$ 
D-Phe	125-200	0.0	
L-nitroPhe	125-200	0.9	$-CH_2$  $-NO_2$
D-nitroPhe	125-200	1.2	
L-Thr	125-200	0.1	$-CH(OH)CH_3$
L-Val	125-200	0.2	$-CH(CH_3)_2$
L-2-napAla	125-200	0.0	$-CH_2$ 

acids (II) are listed in Table II.

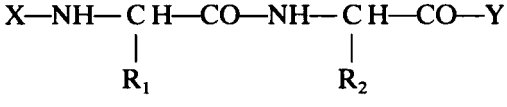


(2)

No SHG was observed from the derivatives of artificial amino acids carrying non-polar aromatic side groups, i.e., naphthyl, pyrenyl, and anthryl groups. Introduction of *p*-nitrophenyl groups in the side chain or at the amino or carboxyl group of amino acid is very effective to induce strong SHG. The *N*-dinitrophenyl (DNP) derivatives of ornithine and β-alanine show a little smaller SHG efficiency than MAP. However, DNP-nitroPhe showed only marginal SHG. DNP-Gly showed no SHG, but this cannot be accounted for solely in terms of the lack of chiral center, because DNP-β-Ala shows very intense SHG. It is especially noteworthy that *p*-nitrophenylanilides of valine and leucine showed comparable SHG to MAP (10 times stronger than urea).

SHG of linear and cyclic dipeptides

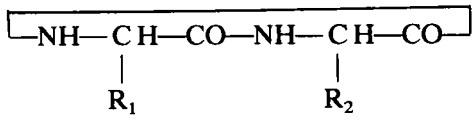
Since nitroPhe and its monomeric derivatives showed high SHG, its dipeptide derivatives (3) were synthesized and



(3)

tested for the SHG efficiency. The results are listed in Table III. In most cases the dipeptides show much smaller SHG than the amino acid or monomeric derivatives of nitroPhe. However, Boc-L-nitroPhe-D-nitroPhe and Boc-D-nitroPhe-L-nitro-Phe-OMe which are enantiomeric counterparts, showed SHG twice stronger than urea. The SHG efficiency is very sensitive to the stereoisomer of the constituent amino acid, as exemplified by the small SHG of the L–L and D–D derivatives.

The SHG of cyclic dipeptides (IV) was also tested.



(4)

Results are shown in Table IV. Since the two side groups of an L–L or D–D cyclic dipeptide locate on the same side of the dipeptide ring, they should have a non-centrosymmetric molecular structure. However, only very small SHG was observed for all cyclic dipeptides examined, including cyclo(L-nitro-Phe-L-nitroPhe). The small SHG may be accounted for in terms of the cancellation of the hyperpolarization in the crystalline state.

TABLE II

SHG Efficiency of α-Amino Acid Derivatives: X—NH—CH(R)—CO—Y

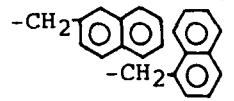
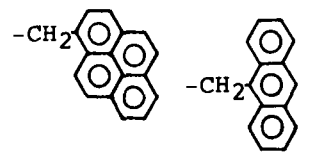
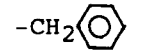
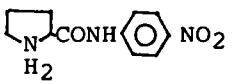
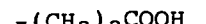
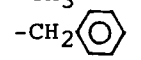
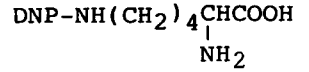
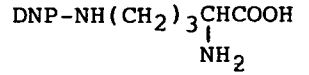
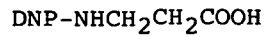
Materials	Size(μ)	SHG eff.(χUrea)	R
Boc-D-nitroPhe	125-200	<0.1	
Boc-D-nitroPhe-ONp	125-200	0.0	
Boc-L-nitroPhe-OMe	125-200	2.0	
Ac-D-nitroPhe	125-200	0.0	
Z-D-nitroPhe	125-200	0.0	
L-nitroPhe-OMe•HCl	125-200	0.6	
D-nitroPhe-OMe•HCl	125-200	0.7	
Boc-L-Glu(NA)	125-200	0.4	
L-2-napAla-OMe	125-200	0.0	
Ac-L-2-napAla-OEt	125-200	0.0	
Ac-L-1-napAla-OMe	125-200	0.0	
Z-D-1-pyrAla	125-200	0.0	
Ac-D-1-pyrAla-OMe	125-200	0.0	
Ac-9-antAla	125-200	0.0	
L-Ala-NA	125-200	0.3	$-CH_3$
L-Val-NA	125-200	9.2	$-CH(CH_3)_2$
L-Leu-NA	125-200	5.3	$-CH_2CH(CH_3)_2$

TABLE II (*continued*)

L-Phe-NA	125-200	<0.1	
L-Pro-NA	125-200	0.1	
L-Glu-NA	125-200	0.5	
DNP-Gly	125-200	0.0	
DNP-L-Ala	125-200	0.8	
DNP-L-Phe	125-200	1.0	
DNP-D-nitroPhe	125-200	0.1	
DNP-L-Lys•HCl	125-200	1.3	
DNP-L-Orn•HCl	125-200	4.7	
DNP-β-Ala	125-200	6.7	

X: Boc-
Ac- 
Z- 
DNP- 

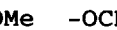
Y: -OMe
-OEt 
-ONp
-NA 

TABLE III

SHG Efficiency of Linear Dipeptides: X-NHCH(R_1)CONHCH(R_2)CO—Y

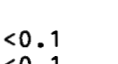
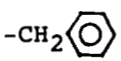
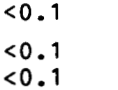
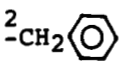
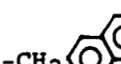
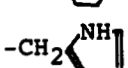
Materials	Size(μ)	SHG eff.(χUrea)	R_1	R_2
Boc-L-Ala-L-nitroPhe-OMe	125-200	0.5	$-CH_3$	$-CH_2$-Ph-NO_2
Boc-D-Ala-L-nitroPhe-OMe	125-200	0.2		
Boc-L-dmaPhe-L-nitroPhe-OMe	125-200	<0.1	$-CH_2$-Ph-$N(CH_3)_2$	
Boc-L-dmaPhe-D-nitroPhe-OMe	125-200	<0.1		
Boc-L-Val-L-nitroPhe-OMe	125-200	<0.1	$-CH(CH_3)_2$	
Boc-D-nitroPhe-Aib-OMe	125-200	<0.1		
Boc-Aib-L-nitroPhe-OMe	125-200	0.0		
Z-L-Ala-L-nitroPhe-OMe	125-200	1.0		
L-Val-L-nitroPhe-OMe·HCl	125-200	0.0		
Boc-nitroPhe-nitroPhe-OMe				
L L	125-200	0.2	$-CH_2$-Ph-NO_2	$-CH_2$-Ph-NO_2
D D	125-200	0.2		
L D	125-200	1.4		
D L	125-200	2.0		
Ac-D-nitroPhe-L-nitroPhe-OMe	125-200	0.0		
L-nitroPhe-L-nitroPhe-OMe·HCl	125-200	0.5		
D-nitroPhe-L-nitroPhe-OMe·HCl	125-200	<0.1		
L-Val-L-Ala-NA	125-200	0.1	$-CH(CH_3)_2$	$-CH_3$

X: Boc- $(CH_3)_3COCO-$
Z- Ph-CH_2OCO-
Ac- CH_3CO-

Y: -OMe $-OCH_3$
-NA $-NH$-Ph-NO_2

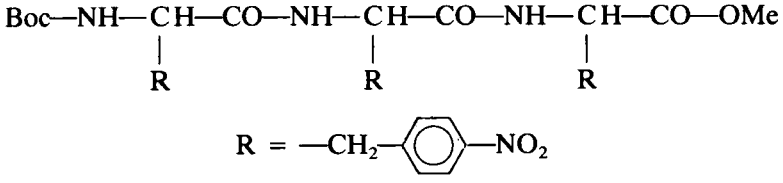
TABLE IV

SHG Efficiency of Cyclic Dipeptides: $\boxed{\text{—NHCH(R}_1\text{)CONHCH(R}_2\text{)CO—}}$

Materials	Size(μ)	SHG eff.(χUrea)	R_1	R_2
cyclo(L-Phe-L-Phe)	125-200	0.0		
cyclo(nitroPhe-nitroPhe)				
L L	UG	<0.1		
D D	UG	<0.1		
D L	UG	<0.1		
cyclo(L-dmaPhe-L-nitroPhe)	UG	<0.1		
(L-dmaPhe-D-nitroPhe)	UG	<0.1		
cyclo(D-nitroPhe-Aib)	UG	0.0		
cyclo(L-1-napAla-L-1-napAla)	UG	0.0		
cyclo(D-1-pyrAla-D-1-pyrAla)	UG	0.0		
cyclo(Gly-L-His)	125-200	0.0	-H	
cyclo(L-Ala-L-His)	125-200	<0.1	$-CH_3$	
(D-Ala-L-His)	125-200	<0.1		
cyclo(L-Leu-L-His)	125-200	0.0	$-CH_2CH(CH_3)_2$	
(D-Leu-L-His)	125-200	0.0		
cyclo(L-Nle-L-His)	125-200	0.0	$-CH_2(CH_2)_2CH_3$	
(D-Nle-L-His)	125-200	0.0		
cyclo(L-Phe-L-His)	125-200	0.0		
(D-Phe-L-His)	125-200	0.0		
cyclo(L-Val-L-His)	125-200	0.1	$-CH(CH_3)_2$	
(D-Val-L-His)	125-200	0.1		

Tripeptides and polypeptides

Since the dipeptide of nitroPhe showed strong SHG, four tripeptides of nitroPhe (5) with L–D–L, L–D–D, L–L–D, and D–D–D



(5)

sequences were prepared. However, none of the four showed higher SHG than $0.1 \times I^{2\omega}$(urea). No SHG was detected also in such aromatic substituted polypeptides as poly(L-alanine), poly(L-phenylalanine), poly(D-nitrophenylalanine), poly(γ-benzyl L-glutamate), poly(*S*-benzyl-L-cysteine), poly(*N*-benzyl-L-histidine), poly(L-tryptophan), poly(L-tyrosine), and poly(O-benzyloxycarbonyl L-tyrosine). The molecular conformations of those polypeptides were found to be α-helix from infrared spectroscopy, except for poly(*S*-benzyl-L-cysteine), which is in a β-form. It was again shown that the noncentrosymmetric molecular structure did not necessarily induce strong SHG. Although the powder samples of the polypeptides did not show measurable SHG, a possibility still remains to observe an efficient SHG if a highly oriented polymer film were prepared and tested by a light waveguide technique.

The survey to find effective SHG substances from 91 amino acid derivatives including polypeptides, gave the following potential compounds which showed higher SHG than urea; L- or *D*-nitroPhe (0.9–1.2), L- or *D*-Glu(NA) · H_2O (3.3–3.1), Boc-L-nitroPhe-OMe (2.0), L-Val-NA (9.2), L-Leu-NA (5.3), DNP-L-Phe (1.0), DNP-L-Lys HCl (1.3), DNP-L-Orn HCl (4.7), DNP-β-Ala (6.7), *Z*-L-Ala-L-nitroPhe-OMe (1.0), Boc-L-nitroPhe-D-nitroPhe-OMe or its D–L isomer (1.4–2.0).

Phase matching

Phase matching is another important property for SHG materials to be used in practice. The phase matching ability is most easily judged from the particle size dependence of the SHG efficiency of powdered sample.[5] An SHG intensity ($I^{2\omega}$) of phase-matchable substance increases initially by increasing the average particle diameter up to about 5 times the coherent length. The efficiency remains almost constant for larger particle sizes. In contrast, the SHG intensity of non-phase-matchable substance shows a peak at the point where the average diameter of the particle coincides with the coherent length and it drops sharply with a further increase of the particle size. Figure 1 exemplifies the particle-size dependence of the SHG intensity from L-Val-NA powder which showed the largest SHG efficiency. The initial increase and the later flat region strongly suggests the phase-matchable nature of this substance. Similar particle-size dependence was observed for L-Leu-NA, Boc-D-nitroPhe-L-nitroPhe-OMe indicating the phase-matchable nature of these substances.

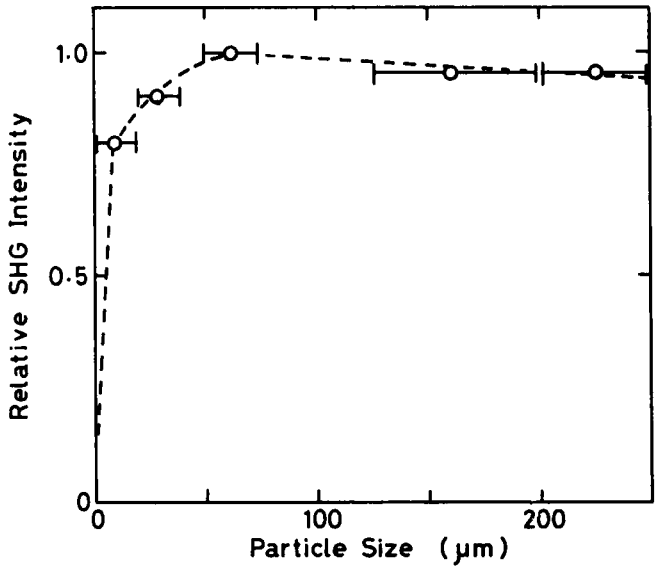


FIGURE 1 Dependence of SHG intensity on average particle diameter for L-Val-NA powders.

Cut-off wavelength

The transparency to the second harmonic light is also an important property for an SHG material. The second harmonic wavelength is 532 nm in the present experiment where an Nd-YAG laser is used as a fundamental light source. However, SHG materials should be transparent down to about 400 nm when a semiconductor laser will be used as a light source. The transmittance spectra of some SHG substances in highly concentrated solutions are compared in Figure 2. Dinitrophenyl derivatives, including MAP, shows a cut-off wavelength at about 500 nm. The mononitro derivatives, including amino acid–NA and nitroPhe derivatives, are transparent down to about 420 nm, suggesting the superiority of the mononitro compounds for SHG materials when the SHG material was used with semiconductor lasers.

Conclusion

Among 91 amino acid derivatives, L-Val-NA was found to show the highest SHG [$9.2 \times I^{2\omega}$(urea)]. This substance is phase-matchable and transparent down to 420 nm. Among the peptide compounds, the dipeptide of *p*-nitroPhe showed a stronger SHG than urea and was transparent down to 420 nm.

Materials

The amino acids listed in Table I are available from Sigma Chemical Co. (P.O. Box 14508, St. Louis, USA) The monomeric derivatives of nitroPhe listed in Table II were synthesized in this laboratory. All linear and cyclic dipeptides listed in Tables III and IV and all tripeptides were newly synthesized in this study or in the

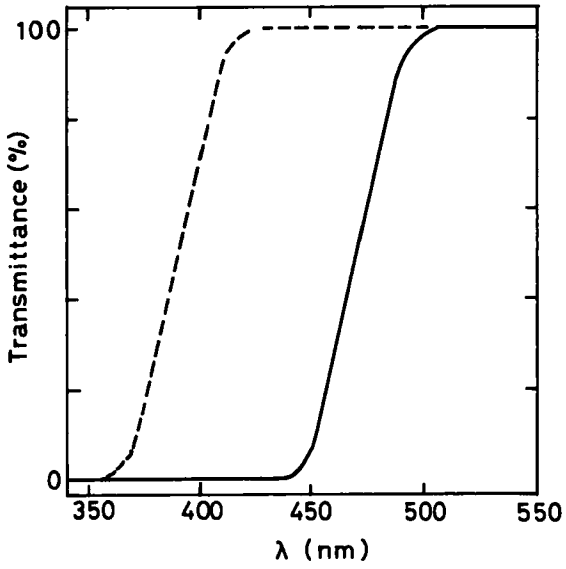


FIGURE 2 Transmittance of concentrated solutions of amino acids, amino acid *p*-nitroanilides, *N*-(2,4-dinitrophenyl)amino acids, and Boc-(nitroPhe)$_2$-OMe. Concentration = 0.1 mol/L. (——): DNP—β—Ala, DNP-L-Orn, and DNP-Lys in methanol; (---): nitroPhe in 2*N* HCl, Glu(NA), Val-NA, Leu-NA, and Glu-NA in methanol, and Boc-(nitroPhe)$_2$-OMe in DMF.

previous studies.[6-10] All polypeptides except for poly(nitroPhe) were purchased from Sigma. In the following, the synthetic methods of some nitroPhe and DNP derivatives which showed strong SHG are described.

Boc-L-nitroPhe. L-NitroPhe (0.5 g) was dissolved in dioxane/water (7/3) mixture (5 mL) and di-*t*-butyldicarbonate (Boc_2O) 0.53 g and aqueous $NaHCO_3$ solution (0.28 g/3 mL) were added simultaneously under cooling by ice. The mixture was stirred for 30 min at the ice temperature and stirred further at room temperature for 12 h. The pH of the reaction mixture was lowered with $KHSO_4$ to about 2 and the product was extracted with ethyl acetate. The extract was washed with saturated NaCl solution and dried with Na_2SO_4. The solvent was evaporated and hexane was added to the oil that remained. White crystal which appeared after standing the mixture in refrigerator was collected and recrystallized from ethanol. Yield 0.5 g, mp. 122–124°C.

L-NitroPhe-OMe HCl. L-NitroPhe (0.5 g) was dissolved in 3*N* HCl in MeOH (10 mL) and stirred for 5 h at room temperature. The methanol and the HCl were removed by evaporation. Addition of methanol/ether (3/7) mixture gave white crystals, which were recrystallized from the methanol/ether mixture. Yield 0.47 g, mp. 203–206°C.

Boc-L-nitroPhe-OMe. L-NitroPhe-OMe HCl (2.6 g) was suspended in water (5 mL). Then, aqueous $NaHCO_3$ solution (2.52 g/10 mL) and dioxane (20 mL) were added to dissolve the hydrochloride. To the solution, Boc_2O (2.4 g) was added dropwise under cooling by ice and stirred for 30 min at room temperature. The

suspension obtained was neutralized with citric acid to pH = 4, and the precipitate was collected and washed with water. Yield 2.5 g, mp. 92–94°C. Elemental analysis: Calcd. for $C_{15}H_{20}N_2O_6$; C, 55.55%; H, 6.22%; N, 8.64%. Found; C, 55.71%; H, 6.21%; N, 8.64%.

DNP-L-nitroPhe. L-NitroPhe (0.5 g) and $NaHCO_3$ (0.785 g) were added to water (12 mL) and 2,4-dinitrofluorobenzene in ethanol (0.78 g/20 mL) was added dropwise under stirring at room temperature over 3 h. The ethanol was removed by evaporation and water was added. After adjusting the pH of the solution to 2 by HCl, the product was extracted with ethyl acetate, washed with NaCl solution and dried with $MgSO_4$. The solvent was evaporated and methanol/water (6/4) mixture (30 mL) was added to the oil. Crystals which appeared after storing the mixture in a refrigerator for 2 days were recrystallized from methanol. Yield 0.61 g, mp. 198–200°C.

Boc-D-Ala-L-nitroPhe-OMe. Boc-D-Ala (0.276 g) and L-nitro-Phe-OMe (0.38 g) were dissolved in dimethylformamide (DMF) (5 mL) and triethylamine (TEA) (0.147 g), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (water-soluble carbodiimide, WSC) (0.31 g), and 1-hydroxybenzotriazole hydrate (HOBt) (0.22 g) were added as a DMF (4 mL) solution under ice cooling. The mixture was stirred for 2 h at the ice temperature and further for 24 h at room temperature. The mixture was diluted with ethyl acetate and washed with 10% aqueous citric acid solution, 4% $NaHCO_3$ solution, and water. The mixture was dried on Na_2SO_4 and evaporated. Crude crystals obtained were recrystallized from ethyl acetate/hexane. Yield 0.36 g, mp. 121–124°C. Elemental analysis: calcd. for $C_{18}H_{25}N_3O_7$: C, 54.68%; H, 6.37%; N, 10.63%. Found: C, 54.57%; H, 6.32%; N, 10.71%. Boc-L-Ala-L-nitroPhe-OMe was also synthesized by the same procedure, mp. 139–141°C.

Boc--nitroPhe--nitroPhe-OMe. Boc-D-nitroPhe (0.2 g) and L-nitroPhe-OMe HCl (0.17 g) were dissolved in DMF (5 mL) and TEA (0.084 mL), WSC (0.136 g), and HOBt (0.096 g) were added as a DMF (3 mL) solution under ice cooling. Stirring at ice temperature was continued for 2 h and further for 24 h at room temperature. Ethyl acetate was added to the mixture and the solution was washed with 10% citric acid, saturated NaCl solution, 3% $NaHCO_3$ solution, and saturated NaCl solution in this order, and then dried with $MgSO_4$. The oil obtained after evaporation of the solvent was crystallized by the addition of hexane/ether (7/3) mixture. The crude product was recrystallized from ethyl acetate/hexane. Yield 0.28 g, mp. 196–198°C. Elemental analysis: Calcd. for $C_{24}H_{28}N_4O_9$: C, 55.81%; H, 5.46%; N, 10.85%. Found: C, 55.64%; H, 5.41%; N, 10.93%. The L–L–L–D, and D–D isomers were also synthesized by the same procedures.

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