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(*E*)-4'-Amino-3,4,5-trimethoxystilbene의 선택적인 합성 및 결정 구조

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A Highly Stereoselective Synthesis and Crystal Structure of (*E*)-4'-Amino-3,4,5-trimethoxystilbene

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요 약. 3,4,5-Trimethoxybenzaldehyde과 *p*-nitrotoluene을 출발물질로 하여 두 단계 반응으로 (*E*)-4'-amino-3,4,5-trimethoxystilbene을 합성할 수 있는 합성 방법을 개발하였으며, 이 화합물에 대한 결정 구조를 X-ray 회절분석법으로 결정하였다.
주제어: (*E*)-4'-amino-3,4,5-trimethoxystilbene, (*E*)-3,4,5-trimethoxy-4'-nitrostilbene, 입체 선택성, 결정 구조, 수소결합

ABSTRACT. A new and highly stereoselective synthesis of (*E*)-4'-amino-3,4,5-trimethoxystilbene was achieved by using 3,4,5-trimethoxybenzaldehyde and *p*-nitrotoluene as starting materials through condensation under solvent-free condition and followed by the reducing of nitro group with the system of $NH_2NH_2/FeCl_3/C$ in ethanol. The crystal structure of (*E*)-4'-amino-3,4,5-trimethoxystilbene was also determined by X-ray diffraction analysis.
Keywords: (*E*)-4'-amino-3,4,5-trimethoxystilbene, (*E*)-3,4,5-trimethoxy-4'-nitrostilbene, Stereoselectivity, Crystal structure, Hydrogen bond

INTRODUCTION

The polymethoxylated stilbenes are very useful building block for many applications in materials science and synthetic chemistry since *E*/*Z* isomerization, cyclization, cyclodimerization, and statistical C-C bond formations (polymerization, crosslinking) offer various reaction possibilities.[1] Interest in the drug synthesis and evaluation of polymethoxylated stilbenes as potential anticancer agents stems from the discovery of many such natural products as antimitotic and antileukemic agents.[2-6] Therefore, in order to obtain new analogues of polymethoxylated stilbenes with antitumor activity, previously we designed and synthesized a series of (*E*)-4'-alkyloylimino-3,4,5-trimethoxystilbene[7] from (*E*)-4'-amino-3,4,5-trimethoxystilbene (**1**) as a key starting material. In this process, starting compound **1** was synthesized from the condensation of 3,4,5-trimethoxybenzaldehyde and *p*-nitrotoluene in the presence of MeONa with low yield and following reduced reaction (total yield <28%).[8] Recently we found a new synthesis method of **1** and fortunately got single crystal of **1**. The present paper describes the synthesis method and the crystal structure features of compound **1**.

EXPERIMENTAL

General

All chemicals were of analytical reagent grade. The NMR spectra were recorded with a Bruker AVANCE300 spectrometer using TMS as internal standard. The IR spectra were recorded with a Nicolet 170SX FT-IR spectrometer using KBr pellets. Elemental analyses were performed on a VarioEL CHNS Elementar Analysensystem. The melting points were determined using a WRS-113 digital melting point instrument (the thermometer was not corrected).

Synthesis of (*E*)-3,4,5-trimethoxy-4'-nitrostilbene

1.96 g (10.0 mmol) 3,4,5-trimethoxybenzaldehyde, 1.37

g (10.0 mmol) *p*-nitrotoluene, 2.76 g (20.0 mmol) anhydrous K_2CO_3 and 1.0 mL PGE-400 were added to 50 mL flask and the mixture was heated to 100 ºC with magnetic stirring for 3 h. To the mixture was added water of 10.0 mL and filtered. After the filter cake was rinsed with H_2O (5 mL×3) and recrystallized with ethanol, 3,4,5-trimethoxy-4'-nitrostilbene of 2.40 g was obtained as pale yellow solid in 85% yield. M.p. 192-194 ºC; ^{1}H-NMR(300 MHz, $CDCl_3$) δ: 3.89(s, 3H, OCH_3), 3.93(s, 6H, $2OCH_3$), 6.77(s, 2H, 2,6-Ar-H), 7.07(d, 1H, *J*=16.2 Hz, -CH=CH-), 7.17(d, 1H, *J*=16.2 Hz, -CH=CH-), 7.64(d, 2H, 2',6'-Ar-H), 8.24 (d, 2H, 3',5'-Ar-H); ^{13}C-NMR(75 MHz, $CDCl_3$) δ: 56.2, 60.9, 104.4, 124.1, 125.7, 126.7, 131.8, 133.3, 139.2, 143.8, 146.7, 153.6; IR(KBr) ν: 3066, 2928, 2831, 1633, 1587, 1503, 1454, 1329, 1236, 1122, 980 cm^{-1}. Anal. Calcd. for $C_{17}H_{17}NO_5$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.77; H, 5.39; N, 4.43%.

Synthesis of (*E*)-4'-amino-3,4,5-trimethoxystilbene (1)

(*E*)-3,4,5-Trimethoxy-4'-nitrostilbene of 3.15 g (10.0 mmol), activated carbon of 1.50 g and $FeCl_3 \cdot 6H_2O$ of 0.10 g were added to ethanol of 70.0 mL. The mixture was heated to reflux. 4.0 mL (47.0 mmol) hydrazine hydrate of 80% was dripped to the refluxing mixture. After refluxing for another 2 h, the result mixture was filtered. The filtrate was concentrated to 20 mL in vacuum. To residue was added H_2O of 20 mL and filtered, (*E*)-4'-amino-3,4,5-trimethoxystilbene of 2.59 g was obtained as white crystal in 91% yield. M.p. 140-142 ºC; ^{1}H-NMR(300 MHz, $CDCl_3$) δ: 3.86(s, 3H, $-OCH_3$), 3.90(s, 6H, 2-OCH_3), 6.69(d, 2H, 3',5'-Ar-H), 6.69(s, 2H, 2,6-Ar-H), 6.86(d, 1H, *J*=18.0 Hz, -CH=CH-), 6.90(d, 1H, *J*=18.0 Hz, -CH=CH-), 7.30(d, 2H, 2',6'-Ar-H); ^{13}C-NMR(75 MHz, $CDCl_3$) δ: 56.2, 60.9, 104.4, 124.1, 125.7, 126.7, 131.8, 133.3, 139.2, 143.8, 146.7, 153.6; IR IR(KBr) ν: 3430, 3353, 2936, 2832, 1634, 1578, 1508, 1454, 1234, 1119, 955(trans, CH=CH) cm^{-1}. Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.63; H, 6.55; N, 4.77%.

Crystal structure determination of 1

After recrystallization from acetone, white single crystals of **1** were obtained, which were suitable for X-ray diffraction analysis. X-ray diffraction data were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ=0.071073 nm) by using φ and ω scan technique. The structure has solved by a direct method with the SHELXS-97 program[9] and refined on F^2 by the full-matrix least-squares method with the SHELXL-97 program.[10] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added at calculated positions and refined using a riding model. The crystal used for the diffraction study showed no decomposition during data collection. The crystal data, experimental details, and refinement results are summarized in *Table* 1. Tables containing complete information on atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, anisotropic displacement parameters and hydrogen coordinates are available from the authors upon request.

***Table* 1.** Crystal data and structure refinement for **1**

Empirical formula	$C_{17}H_{19}NO_3$
Formula weight	285.33
Crystal size	0.28 × 0.20 × 0.13 mm^3
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	*a*=7.5400(9) Å, α= 90° *b*= 15.9876(19) Å, β=90° *c*=12.6546(15) Å, γ= 90°
Volume	*V*=1525.5(3) Å^3
Z	4
Calculated density	1.242 Mg/m^3
Absorption coefficient	0.085 mm^{-1}
F (000)	608
Theta range for data collection	2.05° to 25.04°
Limiting indices	-8*h*8, -19*k*16, -15*l*13
Reflections collected / unique	7206/2361 [*R*(int) = 0.0272]
Completeness to θ = 25.10	100.0%
Max. and min. transmission	0.9889 and 0.9763
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2361/1/194
Goodness-of-fit on F^2	0.987
Absorption correction	None
Final *R* indices[$I > 2\sigma(I)$]	*R*1 = 0.0522, *wR*2 = 0.0944
R indices (all data)	*R*1 = 0.1054, *wR*2 = 0.1176
Absolute structure parameter	2(2)
Extinction coefficient	0.0163(17)
Largest diff. peak and hole	0.174 and -0.162 e Å^{-3}

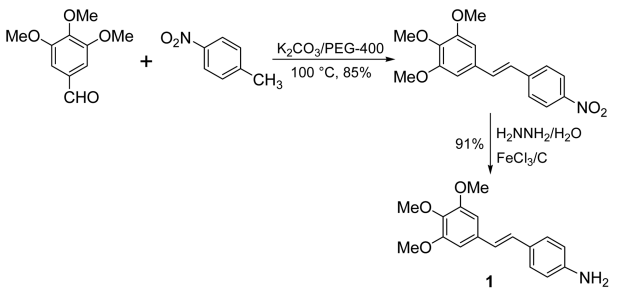
Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 710679 for compound **1**. Copies of this information can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Synthesis of (*E*)-4'-amino-3,4,5-trimethoxystilbene

To the best of our knowledge, a few literatures reported on the synthesis of compound **1**. Cushman's group, for the synthesis of an array of methoxylated stilbenes and related compounds as potential cytotoxic agents and their evaluation for the inhibition of tubulin polymerization, preparaed compound **1** by two steps.[11] First, through Wittig reaction of 3,4,5-trimethoxybenzyl triphenyl phosphonium bromide with *p*-nitrobenzaldehyde in the presence of sodium hydride in benzene under an argon atmosphere for 16 h gave the mixture of *cis*- and *trans*-3,4,5-trimethoxy-4'-nitrostilbene, followed by preparative thin layer chromatographic separation got the corresponding *trans*-3,4,5-trimethoxy-4'-nitrostilbene in 44% yield. Then the result compound was reduced with lithium aluminum hydride in THF to provide (*E*)-4'-amino-3,4,5-trimethoxystilbene in 82% yield. There are three drawbacks obviously in this course: phosphonium bromide, sodium hydride and lithium aluminum hydride are sensitive to moist or air, thus the reaction need in anhydrous condition and under an argon atmosphere; the low stereoselectivity of reaction gave a mixture of *cis*- and *trans*-3,4,5-trimethoxy-4'-nitrostilbene and a low reaction yield. To overcome these disadvantages, we attempted to find a new synthesis method for compound **1**. Initial synthesis of **1**, we refered to Zou's method for synthesis of pterostilbene,[12] the mixture of 10 mmol 3,4,5-trimethoxybenzaldehyde and 20 mmol *p*-nitrotoluene was refluxed in dry methanol in the presence of sodium methoxide for 48 h to give (*E*)-3,4,5-trimethoxy-4'-nitrostilbene in 39% yield. Basic substance, sodium methoxide, is necessary in this reaction. It despoils the proton of the methyl of *p*-nitrotoluene to yield nucleophilicity carbanion. The double bond is formed from the nucleophilic addition of the carbanion to carbonyl of 3,4,5-trimethoxybenzaldehyde and followed by dehydration. The result compound was reduced by hydrazine hydrate of 50% in ethanol in the presence of catalyst of $FeCl_3$ and activated carbon to give compound **1** in 71% yield. However, this process still need in anhydrous condition and longer time, and exhibited a low yield (total yield <28%).[8]

Some reactions can be achieved in high yield and shorter time by grinding under solvent free condition.[13] Therefore we grinded the mixture of 3,4,5-trimethoxybenzaldehyde, *p*-nitrotoluene and anhydrous K_2CO_3 to explore the solvent free synthesis of 3,4,5-trimethoxy-4'-nitrostilbene, but the result indicated the reaction did not occur, maybe because K_2CO_3 did not adequately touch with *p*-nitrotoluene to despoil the proton of the methyl in solid. Polyethylene glycols(PEGs) have been widely used as phase transfer catalyst in many organic reactions[14,15] owing to their stability, low cost, environment-friendly and easy availability. It is more effective that PEGs catalyze the reactions of K^+ or Na^+ salts participation.[16] Thus Cao's group used PEG-400 and K_2CO_3 as catalysts to explore Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate etc as active methylene compounds under solvent free condition, and got successfully an efficient synthesis method for mono-arylidene compounds.[17] In our exploration for the synthesis reaction of stilbene, namely diarylidene compound, when adding PEG-400 as a phase transfer catalyst to the mixture of 3,4,5-trimethoxybenzaldehyde, *p*-nitrotoluene and anhydrous K_2CO_3, after adequately grinding and depositing the mixture for 24 h, 3,4,5-trimethoxy-4'-nitrostilbene was found by tracking reaction with TLC. This result inspirited us to further explore this process. Considering *p*-nitrotoluene has a lower melting point at 54.5 °C, we want to know whether the condensation reaction of 3,4,5-trimethoxybenzaldehyde with *p*-nitrotoluene can be accelerated in the presence of anhydrous K_2CO_3 and PEG-400 when the mixture are heated up to melting point temperature of *p*-nitrotoluene, namely *p*-nitrotoluene being a reactant and a solvent. A good result was gotten when the mixture of 10.0 mmol 3,4,5-trimethoxybenzaldehyde, 10.0 mmol *p*-nitrotoluene, 20.0 mmol anhydrous K_2CO_3 and 1.0 mL PGE-400 was heated to 100 °C with magnetic stirring for 3 h. After adding water to mixture and filtrating, recrystallizing with ethanol, 3,4,5-trimethoxy-4'-nitrostilbene was obtained in 85% yield (see *Scheme* 1), *trans* isomer was obtained exclusively by this simple process without chromatographic separation, which was confirmed by its characteristic coupling constant in NMR spectrum for the olefinic protons of 16.2 Hz.[18] This method exhibited remarkable advantage compared with previous one. It is possible that this method



***Scheme* 1.** Synthesis of (*E*)-4'-amino-3,4,5-trimethoxystilbene.

will be applied extensively to stereoselective synthesis of other stilbene compounds. Subsequently, (*E*)-3,4,5-trimethoxy-4'-nitrostilbene was reduced with hydrazine hydrate of 80% in the presence of catalyst of $FeCl_3$ and activated carbon in ethanol to give compound **1** in 91% yield without isomerization of *trans* double bond. This course for synthesis of **1** avoided completely anhydrous condition and using noxious organic solvent.

Crystal structure of (*E*)-4'-amino-3,4,5-trimethoxystilbene

Fig. 1 shows the molecular structure of **1** from X-ray crystallographically determining, while the crystal data and selected parameters are summarized in *Table* 1 and

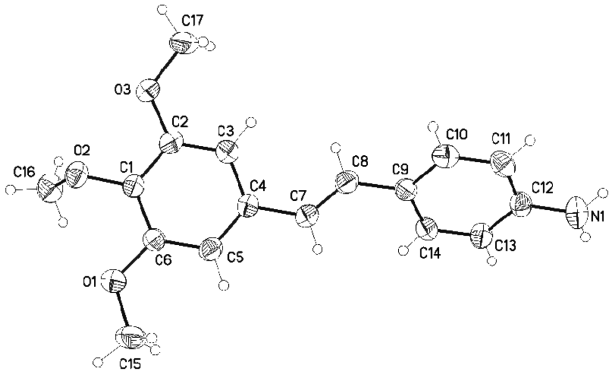


***Fig*. 1.** Molecular structure of **1**.

***Table* 2.** Selected bond lengths [Å] and torsion angles [deg] for **1**

N(1)-C(12)	1.390(5)	O(1)-C(6)	1.377(5)
O(1)-C(15)	1.430(4)	O(2)-C(1)	1.383(5)
O(2)-C(16)	1.437(5)	O(3)-C(2)	1.377(4)
O(3)-C(17)	1.440(4)	C(1)-C(6)	1.376(5)
C(1)-C(2)	1.388(5)	C(2)-C(3)	1.372(5)
C(3)-C(4)	1.403(6)	C(4)-C(5)	1.384(5)
C(4)-C(7)	1.464(6)	C(5)-C(6)	1.381(5)
C(7)-C(8)	1.316(5)	C(8)-C(9)	1.458(5)
C(9)-C(14)	1.384(5)	C(9)-C(10)	1.392(5)
C(10)-C(11)	1.375(5)	C(11)-C(12)	1.374(6)
C(12)-C(13)	1.390(6)	C(13)-C(14)	1.365(5)
C(16)-O(2)-C(1)-C(2)		110.1(4)	
C(17)-O(3)-C(2)-C(3)		-11.1(6)	
O(2)-C(1)-C(2)-C(3)		176.2(4)	
C(6)-C(1)-C(2)-O(3)		-179.0(4)	
C(2)-C(1)-C(6)-O(1)		176.5(4)	
C(15)-O(1)-C(6)-C(5)		14.5(7)	
C(3)-C(4)-C(7)-C(8)		24.3(7)	
C(4)-C(7)-C(8)-C(9)		-178.3(4)	
C(7)-C(8)-C(9)-C(14)		16.6(7)	
N(1)-C(12)-C(13)-C(14)		178.5(4)	

Table 2, respectively. The bond lengths and angles in molecule **1** are closely similar to that of stilbene itself and its derivatives.[19-21] The C(4)-C(7) and C(8)-C(9) bonds [1.464 (6) and 1.458 (5) Å, respectively] are relatively short compared with a normal single bond of 1.54 Å,[22] this indicate the resonance and partial double bond character of C(4)-C(7) and C(8)-C(9). The structure data shows compound **1** has an anomalously short olefinic bond of 1.316 (5) Å, compared to the normal conjugated olefinic bond of 1.38 Å.[22] This antifact was attributed to two factors: orientational disorder and dynamical disorder due to torsional vibration of the C-phenyl bonds in a direction perpendicular to the molecular plane.[23,24] The dihedral angel of C(4)-C(7)-C(8)-C(9)[-178.3(4)°] indicate that C(4)-C(7)-C(8)-C(9) are nearly coplane resulting from sp^2 hybridization of C(7) and C(8), but two benze ring are not coplane and the two planes of benze rings form a interplanar angel of 45.11°. This indicate that partial double bond character of C(4)-C(7) and C(8)-C(9) may permit two benze rings to slightly twist in the axeses of C(4)-C(7) and C(8)-C(9), respectively. In molecule of **1**, the carbon atoms of methoxy groups are almost coplane with the aromatic rings, except the carbon atom of O(2) methoxy group, which twists to avoid steric hindrance with the neighbouring O(1) and O(3) methoxy groups, with the torsion of C(16)-O(2)-C(1)-C(2)[110.1(4)°].

As showing in *Fig*. 2, molecules of **1** interact via N—H···O(3) hydrogen bonds (0.860, 2.388, 3.031Å; ∠NHO 131.96°), forming infinite zigzag chains along the c axis. Two C-H···π interactions of C(15)-H(15)---Cg1@ (2.788 Å, Cg1@ presents the center of ring C(9)—C(14) in molecule@) and C(17)-H(17)---Cg1$ (3.621Å, Cg1$ presents the center of ring C(9)—C(14) in molecule $) assemble the title compound **1** to three dimension networks.

CONCLUSIONS

A new and efficient synthesis method of (*E*)-4'-amino-3,4,5-trimethoxystilbene was achieved using 3,4,5-trimethoxybenzaldehyde and *p*-nitrotoluene as starting materials in presence of anhydrous K_2CO_3 and PEG-400, through condensation under solvent-free condition and subsequently reducing of nitro group by the system of $NH_2NH_2/FeCl_3/C$ in ethanol. This method avoided completely anhydrous condition and using noxious organic solvent, and exhibited high stereoselectivity, higher total yield in 77% and shorter reaction time. Meanwhile, the crystal structure of (*E*)-4'-amino-3,4,5-trimethoxystilbene was determined by X-ray diffraction analysis.

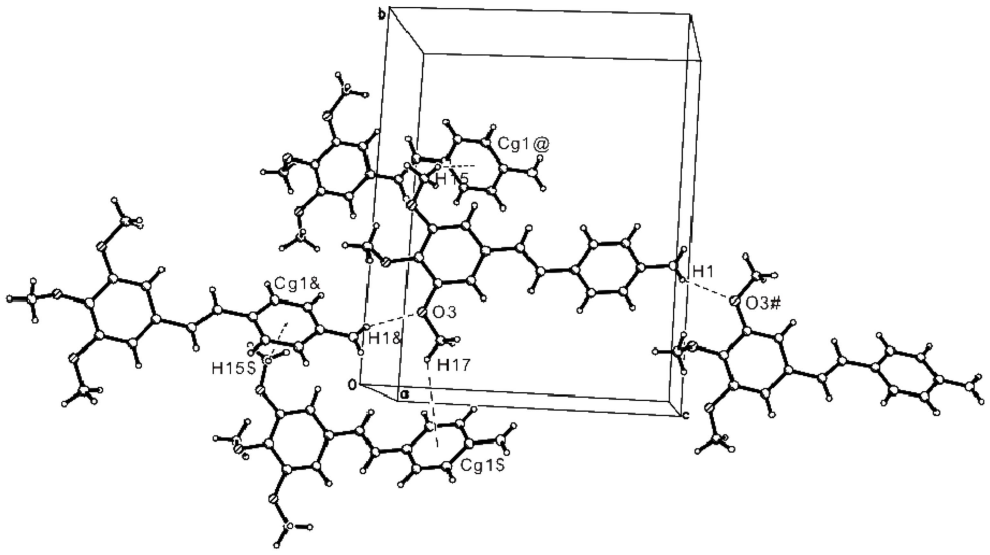


***Fig.* 2.** Intermolecular interactions in the crystal of **1**. Symmetry codes: (@) 1-x, 1-y, -1/2+z; (#) 1/2+x, 1/2-y, 1+z; ($) 1/2-x, -1/2+y, -1/2+z; (&) -1/2+x, 1/2-y, -1+z.

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REFERENCES

1. Soomro, S. A.; Schulz, A.; Meier, H. *Tetrahedron* **2006**, *62*, 8089.
2. Pinney, K. G.; Mejia M. P.; Villalobos, V. M.; Rosenquist, B. E.Pettit, G. R. Verdier-Pinard, P.; Hamel, E. *Bioorg. Med. Chem.* **2000**, *8*, 2417.
3. Bai, R.; Petit, G. R.; Hamel, E. *Biochem. Pharmacol*. **1990**, *39*, 1941.
4. Pettit, G. R.; Singh, S. B.; Cragg, G. M. *J. Org. Chem*. **1985**, *50*, 3404.
5. Pettit, G. R.; Singh, S. B.; Schmidt, J. M.; Nivin, M. L.; Hamel, E.; Lin, C. M. *J. Nat. Prod*. **1988**, *51*, 517.
6. Chang, J. Y.; Yang, M. F.; Chang, C. Y.; Chen, C. M.; Kuo, C. C.; Liou, J. P. *J. Med. Chem*. **2006**, *49*, 6412.
7. Zhang, X. Q.; Gu, H. M.; Xu, H. J.; Fu, H.; Li, B. L.; Guo, J.; Lai, Y. T.; Wang, W. *China Patent* 100861805, 2006.
8. Du, J.; Zhang, X. Q.; Guo, J.; Gu, H. M; Xu, H. J.; Li, B. L. *Huaxue Yanjiu Yu Yingyong* **2009**, *21*(1), 120.
9. Sheldrick, G. M. *SHELXS-97*. Program for the Solution of Crystal Structures. University of Göttingen, Germany, 1997.
10. Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
11. Cushman, M.; Nagarathnam, D.; Gopal, D.; Chakraborti, A. K.; Lin, C. M.; Hamel, E. *J. Med. Chem*. **1991**, *34*, 2579.
12. Zou, S.; Zhang, X. J.; Lin, H. Z. *China Patent* 101118854, 2003.
13. Li, B. L.; Zhang, Z. G.; Wang, W.; Li, J.; Wang, C. W. *Z. Naturforsch. B* **2008**, *63b*, 77.
14. Brem, G.; Lowpy, A.; Sansonlet, J. *Isr. J. Chem.* **1985**, *26*, 291.
15. Timko, J. M.; Moore, S. S.; Walba, D. M.; Hiberty, P.C.; Cram, D. J. *J. Am. Chem. Soc*. **1977**, *99*, 4207.
16. Wang, M. L.; Chang, K. R. *Ind. Eng. Chem. Res*. **1990**, *29*(1), 40.
17. Cao, Y. Q.; Dai, Z.; Zhang, R.; Chen, B. H. *Synth. Commun.* **2004**, *34*, 2965.
18. Silverstein, R. M.; Baeeler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley & Sons: New York, 1981, pp 264-265.
19. Bernstein, J.; Mirsky, K. *Acta Cryst. A* **1978**, *34*, 161.
20. Zhang, J.; Chen, S. F.; Klausmeyer, K. K.; Kane, R. R. *Acta Cryst. C* **2003**, *59*, 381.
21. Gordon, G. C.; Charles, R. E.; Robert, A.G.; Hilary, A. J. *Tetrahedron Lett*. **2006**, *47*, 2245.
22. Chen, X. M.; Cai, J. W. *Single-Crystal Structure Analysis Principles and Practices*, Science Press: Beijing, 2004, p 101.
23. Ogawa, K.; Sano, T.; Yoshimura, S.; Takeuchi, Y.; Toriumi, K. *J. Am. Chem. Soc*. **1992**, *114*, 1041.
24. Harada, J.; Ogawa, K. *J. Am. Chem. Soc*. **2001**, *123*, 10884.