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A CONVENIENT ONE-POT SYNTHESIS OF ARENE-CENTERED TRIS(THIAZOLINE) COMPOUNDS

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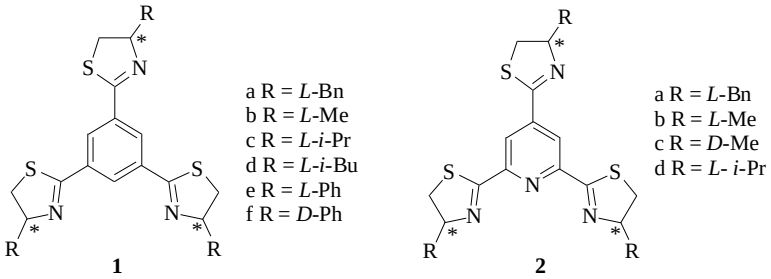
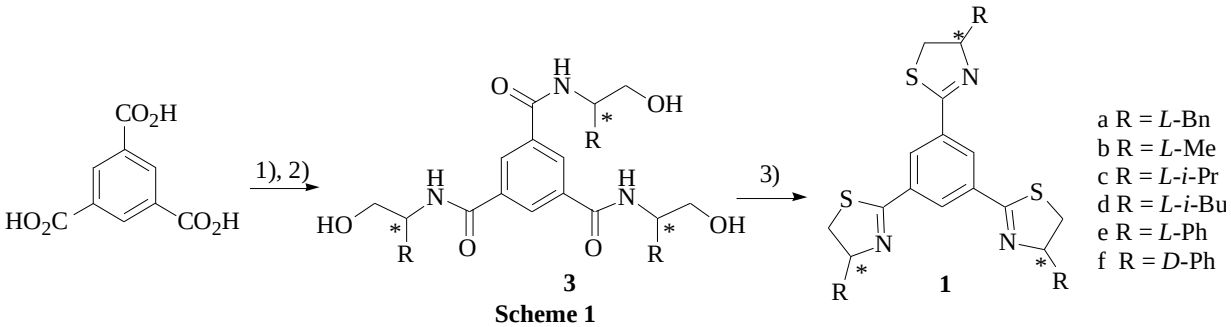
Abstract – A simple and practical one-pot synthesis of novel enantiopure tris(thiazoline) compounds was documented. The desired products were obtained in moderate to good yields through three steps from commercially available 1, 3, 5-benzenetricarboxylic acid or 2, 4, 6-pyridinetricarboxylic acid, and chiral amino alcohols. Only one column chromatographic purification was needed for the three steps.

Thiazoline rings have been found in a large number of biological active natural products, such as thiangazole,[1] curacin A,[2] and lissoclinamides.[3] Moreover, thiazoline compounds have been widely applied as food additives,[4] agrochemicals,[5] chiral ligands,[6] and so on. In view of the versatile properties of thiazoline compounds, their synthesis attracts the attention from many researchers. To date, many methods have been developed for the construction of thiazoline ring system. One major type of the methods is the condensation of 2-aminoethanethiol with carboxylic acids or their derivatives, such as nitriles, esters, and iminoesters.[7] Another type is the cyclization of β-hydroxythioamides.[8] Besides of the two types of methods, some other methods have also been developed with both advantages and deficients.[9] In recent years, direct cyclization of β-hydroxyamide has been employed as one convenient method for its simplicity and practicability. Some mono- and bis-thiazoline compounds have been synthesized with Lawesson reagent or phosphorus pentasulfide (P_2S_5) as reagent.[10] However, the generality of this method has not been comfirmed. Thus, our effort was focused on the development of efficient and general route towards arene-centered tris(thiazoline) compounds, analogue of arene-centered tris(oxazoline) compounds with versatile properties.[11] Herein, we would like to document the efficient one-pot preparation of tris(thiazoline) compounds **1** and **2** with potent applications in molecular

recognition and self-assembly.



The synthetic route is illustrated in Scheme 1**.** The starting material benzenetricarboxylic acid was refluxed in $SOCl_2$ for 12 h, and the excess $SOCl_2$ was removed *in vacuo*. The crude triacyl chlorides were dissolved in CH_2Cl_2 and added dropwise to the solution of amino alcohols and Et_3N in CH_2Cl_2 at 0 °C. After being stirring for 4 h, the solvent was removed *in vacuo*, and the crude intermediate tris(β-hydroxyamides) were used in the cyclization step without further purification. The mixture of P_2S_5 with tris(β-hydroxyamides) was refluxed in toluene for 6~8 h in the presence of Et_3N. The desired tris(thiazoline) compounds were obtained in 58~82%.yield after purification, as listed in Table 1. During the whole synthetic course, only one column chromatographic purification was needed. The addition of Et_3N and high temperature were crucial, while refluxing only in toluene or Et_3N gave no product (Entries 2 and 3). Alternatively, pyridine can be used instead of toluene/Et_3N in this reaction, though the yield decreased significantly (Entry 4). The cheap reagent P_2S_5 was quite effective in the cyclization step. On the contrary, using Lawesson reagent[12] in the final step the tris(thiazoline) **1a** was only obtained in 20% yield. For different chiral amino alcohols, the corresponding tris(thiazoline) compounds was afforded in moderate to good yields (Entries 5~9). The structure of the novel tris(thiazoline) compounds were thoroughly characterized by spectroscopic methods. In addition, the single crystal of tris(thiazoline) **(*S*)-1e** was cultivated and detected by X-Ray crystal diffraction analysis, as illustrated in Figure 1.[13]



Scheme 1

1) $SOCl_2$ 2) amino alcohol, Et_3N, CH_2Cl_2 3) P_2S_5, Et_3N, toluene

Table 1. Synthesis of benzene-centered tris(thiazoline) compounds.

Entry	R	Reaction condition[a]	Refluxing time (h)	Yield [b] (%)
1	*L*-Bn	toluene/Et_3N	6	82
2	*L*-Bn	toluene	10	no reaction
3	*L*-Bn	Et_3N	10	no reaction
4	*L*-Bn	pyridine	6	60
5	*L*-Me	toluene/ Et_3 N	6	78
6	*L*-*i*-Pr	toluene/Et_3N	6	72
7	*L*-*i*-Bu	toluene/Et_3N	6	58
8	*L*-Ph	toluene/Et_3N	8	68
9	*D*-Ph	toluene/Et_3N	8	73

[a]All reactions were performed using P_2S_5 as cyclizing reagent.

[b]Isolated Yield by Column Chromatography.

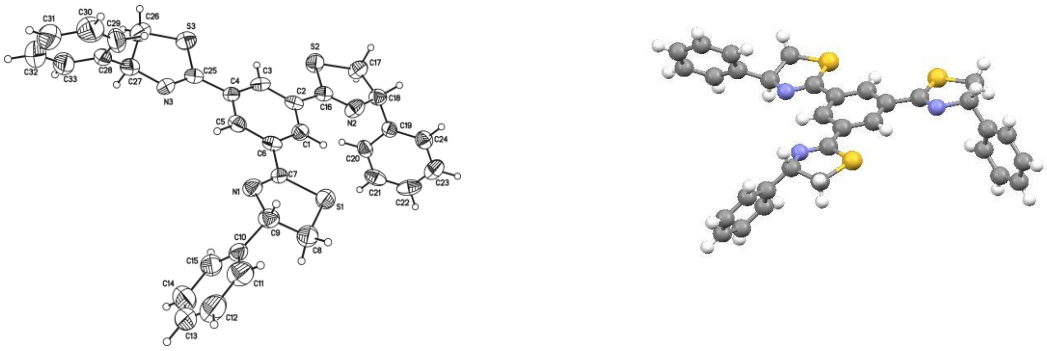
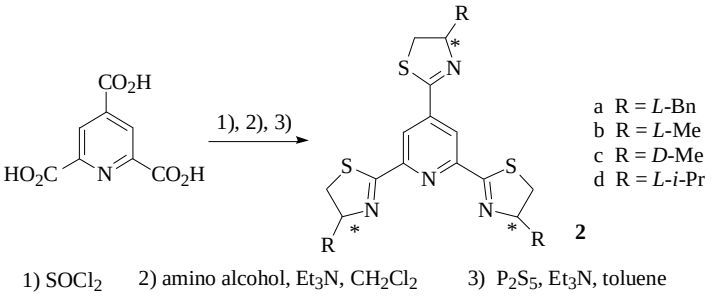


Figure 1. The molecular structure of (*S*)-**1e** shown from different view

With the optimized reaction conditions in hand, we further investigated the synthesis of pyridine-centered tris(thiazoline) compounds starting from 2,4,6-pyridinetricarboxylic acid[14] (Scheme 2). The reaction results were listed in Table 2. Generally, the yields in these cases were lower than corresponding benzene-centered tris(thiazoline) compounds **1** (Entries 10~13). When R was phenyl, no expected tris(thiazoline) compound was obtained (Entries 14 and 15), but complex mixture indicated by TLC analysis. Similar result was obtained when purified tris(β-hydroxyamide) was used. Such a phenomenon can be attributed to the nucleophilic nitrogen atom in the pyridine unit, which may react with the intermediates in the ring-closing step.



Scheme 2

Table 2. Synthesis of pyridine-centered tris(thiazoline) compounds.

Entry	R	Reaction condition	Refluxing Time (h)	Yield (%)[a]
10	*L*-Bn	toluene/Et_3N	6	42
11	*L*-Me	toluene/Et_3N	8	30
12	*D*-Me	toluene/Et_3N	8	38
13	*L*-*i*-Pr	toluene/Et_3N	8	33
14	*L*-Ph	toluene/Et_3N	8	0
15	*L*-Ph	pyridine	12	0

[a]Isolated yield by Column Chromatography.

On the basis of our experimental results and relevant reports,[10, 12] we deduced that the simple reagent combination of P_2S_5 and Et_3N is not only suitable for the synthesis of mono- and bis(thiazoline) compounds, but also suitable for complex tris(thiazoline) compounds. The thiazolines with aryl or tertiary alkyl group at 2-position can be synthesized efficiently, while those with α-hydrogen at 2-position are not suitable target, an alternative route to those complex thiazoline compounds was developed by our group.[15] The mechanism of the cyclization step is not clear now, it is hypothesized that the carbonyl group is thionated, and the hydroxyl group is transformed to a leaving group by P_2S_5 before the intramolecular nucleophilic substitution is occurred.

In conclusion, two series of chiral tris(thiazoline) compounds with benzene and pyridine centers were synthesized in one pot through a continuous 3-step sequence with P_2S_5/Et_3N mediated cyclization of corresponding tris(β-hydroxyamides) as key step. The desired products can be obtained in moderate to good overall yields with only one column chromatographic purification. The mild condition and easy purification indicate the possibility of its application in large scale synthesis of fine chemicals. Although bis(thiazoline) with benzene and pyridine skeleton have been synthesized, this paper afford further extension for the synthesis of complex thiazoline compounds based on previous report.[16, 6d] The

application of the products in molecular recognition and self-assembly are under going in our laboratory.

EXPERIMENTAL

General. Melting points were measured on an XT-4 melting point apparatus without correction. NMR spectra were recorded on a Bruker Avance DPX300 spectrometer with tetramethylsilane as internal standard. Infrared spectra were obtained on a Nicolet AVATAR 330 FT-IR spectrometer. Optical rotations were measured on a Perkin–Elmer 341 LC polarimeter. Mass spectra were carried out using a VG Autospec instrument. Elemental analyses were carried out on an Elementar Vario EL instrument. Solvents were purified and dried following standard procedures.

General procedure for the synthesis of tris(thiazoline) 1a~f

The 1, 3, 5-benzenetricarboxylic acid (0.42 g, 2.0 mmol) was refluxed with $SOCl_2$ (3.0 mL) for 12 h, then the excess $SOCl_2$ was removed in *vacuo*. Benzene (5 mL) was added and the solvent was removed again to dryness to remove the trace amount of $SOCl_2$ and afford the triacyl trichloride. The triacyl trichloride in CH_2Cl_2 (20 mL) was added dropwise to a solution of amino alcohol (6.40 mmol) and Et_3N (4 mL, 28.9 mmol) in CH_2Cl_2 (20 mL) at 0 °C and stirred at rt for 4~6 h. The reaction mixture was evaporated to remove the solvent in vacuo, and toluene (20 mL) and Et_3N (6 mL, 43.4 mmol) were added to the crude trihydroxyl triamide, P_2S_5 (2.0 g, 9.0 mmol) was added under refluxing in 3 portions within 1 h, and the suspension was continued to reflux for another 6~8 h. After being cooled to room temperature, the solution was washed with H_2O (5 mL×2), dried over anhydrous Na_2SO_4 and concentrated to give the crude product. Column chromatographic purification on silica gel (40% ethyl acetate in petroleum ether) afforded the tris(thiazoline) compounds **1a~f.**

1, 3, 5-Tris[2-(4*S*)-4-benzyl-1, 3-thiazolin-2-yl]benzene (1a)

Pale oil, $[\alpha]_D^{25}$ -84.4 (*c* 0.15 in CH_2Cl_2). IR (cm^{-1}): 3025, 2923, 1610, 1584, 1494, 1189, 741, 699. ^1H NMR ($CDCl_3$): δ 8.37 (s, 3H, ArH), 7.29 (m, 15H, ArH), 5.00~4.91 (m, 3H, CHN=), 3.41~3.31 (m, 6H, CH_2S), 3.20 (dd, J = 6.90, 11.4 Hz, 3H), 2.84 (dd, J = 9.30, 13.5 Hz 3H). ^{13}C NMR ($CDCl_3$): δ 165.9, 138.3, 134.1, 130.4, 129.3, 128.5, 126.5, 78.8, 40.1, 37.6. MS: m/z 604 (M+1). *Anal.* Calcd for $C_{36}H_{33}N_3S_3$: C, 71.60; H, 5.53; N, 6.96. Found: C, 71.85; H, 5.41; N, 6.78.

1, 3, 5-Tris[2-(4*S*)-4-methyl-1, 3-thiazolin-2-yl]benzene (1b)

Mp 155~157 °C. $[\alpha]_D^{25}$ -64.0 (*c* 0.15 in CH_2Cl_2). IR (cm^{-1}): 2971, 2927, 1610, 1587, 1433, 1372, 1188, 923, 715. ^1H NMR ($CDCl_3$): δ 8.47 (s, 3H, ArH), 4.80~4.77 (m, CHN=, 3H), 3.57 (dd, J = 8.10, 10.50 Hz, 3H), 3.08 (dd, J = 8.10, 10.50 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 165.0, 134.1, 130.2, 73.1, 40.3, 20.3. MS:

m/z 376 (M+1). *Anal.* Calcd for $C_{18}H_{21}N_3S_3$: C, 57.58; H, 5.64; N, 11.19. Found: C, 57.85; H, 5.61; N, 11.28.

1, 3, 5-Tris[2-(4*S*)-4-*i*-propyl-1, 3-thiazolin-2-yl]benzene (1c)

Mp 159~161 °C. $[\alpha]_D^{25}$ -49.7 (*c* 0.10 in CH_2Cl_2). IR (cm^{-1}): 2958, 2870, 1613, 1588, 1384, 1366, 1192, 1019, 722. ^1H NMR ($CDCl_3$): δ 8.31 (s, 3H, ArH), 4.49~4.08 (m, 3H, CHN=), 3.43 (dd, *J* = 8.70, 11.1Hz 3H), 3.18 (dd, *J* = 9.6, 11.1 Hz, 3H), 2.14~2.08 (m, 3H, CH), 1.13 (d, *J* = 6.60 Hz, 9H), 1.02 (d, *J* = 6.60 Hz, 9H). ^{13}C NMR ($CDCl_3$): δ 164.8, 134.1, 130.2, 84.3, 35.7, 33.2, 19.8, 18.9. MS: m/z 460 (M+1). *Anal.* Calcd for $C_{27}H_{39}N_3S_3$: C, 62.70; H, 7.34; N, 9.14. Found: C, 62.85; H, 7.41; N, 9.05.

1, 3, 5-Tris[2-(4*S*)-iso-butyl-1, 3-thiazolin-2-yl]benzene (1d)

Pale oil, $[\alpha]_D^{25}$ -55.4 (*c* 0.10 in CH_2Cl_2). IR (cm^{-1}): 2954, 2868, 1612, 1587, 1433, 1384, 1366, 1186, 718. ^1H NMR ($CDCl_3$): δ 8.30 (s, 3H, ArH), 4.75~4.65 (m, 3H, CHN=), 3.52 (dd, *J* = 8.10, 10.8 Hz, 3H, CH_2S), 3.08 (dd, *J* = 8.1, 10.8 Hz, 3H, CH_2S), 1.94~1.80 (m, 6H, CH_2), 1.53~1.44 (m, 3H, CH), 1.01 (d, *J* = 6.60 Hz, 9H), 1.00(d, *J* = 6.60 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 164.8, 134.2, 130.2, 44.1, 38.9, 25.8, 22.9, 22.5. MS: m/z; 502 (M+1). *Anal.* Calcd for $C_{27}H_{39}N_3S_3$: C, 64.62; H, 7.83; N, 8.37. Found: C, 64.82; H, 7.60; N, 8.28.

1, 3, 5-Tris[2-(4*S*)-4-phenyl-1, 3-thiazolin-2-yl]benzene (1e)

Mp 139~140 °C. $[\alpha]_D^{25}$ -80.8 (*c* 0.15 in CH_2Cl_2). IR (cm^{-1}) : 3026, 1610, 1580, 1492, 1179, 738, 697. ^1H NMR ($CDCl_3$): δ 8.55 (s, 3H), 7.42~7.25 (m, 15H, ArH), 5.73 (t, *J* = 9.0 Hz, 3H, CHN=), 3.86 (dd, *J* = 8.7, 11.40 Hz, 3H), 3.37 (dd, *J* = 9.30, 11.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 167.1, 141.7, 134.1, 130.9, 128.7, 127.7, 126.6, 80.9, 41.4. MS: m/z 562 (M+1). *Anal.* Calcd for $C_{33}H_{27}N_3S_3$: C, 70.55; H, 4.84; N, 9.14. Found: C, 70.43; H, 5.11; N, 9.02.

1, 3, 5-Tris[2-(4*R*)-4-phenyl-1, 3-thiazolin-2-yl]benzene (1f)

Mp 139~140 °C. $[\alpha]_D^{25}$ +81.4 (*c* 0.15 in CH_2Cl_2). IR (cm^{-1}): 3029, 1610, 1580, 1492, 1179, 737, 697. ^1H NMR ($CDCl_3$): δ 8.55 (s, 3H), 7.36 (m, 15H), 5.73 (t, 3H), 3.86 (dd, 3H), 3.37 (dd, 3H). ^{13}C NMR ($CDCl_3$): δ 167.1, 141.7, 134.1, 130.9, 128.7, 127.7, 126.6, 80.9, 41.4. MS: m/z 562 (M+1). *Anal.* Calcd for $C_{33}H_{27}N_3S_3$: C, 70.55; H, 4.84; N, 9.14. Found: C, 70.65; H, 4.98; N, 9.00.

General procedure for the synthesis of tris(thiazoline) 2a~d

The 2, 4, 6-pyridinetricarboxylic acid (0.422 g, 2.0 mmol) was refluxed with $SOCl_2$ (3.0 mL) for 8 h, then the excess $SOCl_2$ was removed in vacuo. Benzene (5 mL) was added and the solvent was removed again

to dryness to remove the trace amount of $SOCl_2$ and afforded the triacyl trichloride. The triacyl trichloride in CH_2Cl_2 (20 mL) was added dropwise to a solution of amino alcohol (6.40 mmol) and Et_3N (4 mL, 28.9 mmol) in CH_2Cl_2 (20 mL) at 0 °C and stirred at rt for 4~6 h. The reaction mixture was evaporated to remove the solvent in *vacuo,* and toluene (20 mL) and Et_3N (6 mL, 43.4 mmol) were added to the crude trihydroxyl triamide, P_2S_5 (2.0 g, 9.0 mmol) was added under refluxing in three portions within 1 h, and the suspension was continued to reflux for another 6~8 h. After being cooled to rt, the solution was washed with H_2O (5 mL×2), dried over anhydrous Na_2SO_4 and concentrated to give the crude product. Column chromatographic purification on silica gel (50% EtOAc in petroleum ether) afforded the tris(thiazoline) compounds **2a~d.**

2, 4, 6-Tris[2-(4*S*)-4-benzyl-1, 3-thiazolin-2-yl]pyridine (2a)

Mp 152~154 °C. $[\alpha]_D^{25}$ -76.4 (*c* 0.10 in CH_2Cl_2). MS: m/z 605(M+1); IR (cm^{-1}): 3026, 2937, 1601, 1494, 1185, 722, 700; ^{1}H NMR ($CDCl_3$): δ 8.53 (s, 2 H, ArH), 7.63~7.25 (m, 15 H, ArH), 5.08~4.93 (m, 3 H, CHN=), 3.45~3.30 (m, 6 H, CH_2S), 3.16~3.10 (m, 3 H, CH_2Ph), 2.84 (m, 3 H, CH_2Ph). ^{13}C NMR ($CDCl_3$): δ 168.9, 165.0, 151.3, 141.9, 138.3, 138.0, 129.7, 129.3, 128.6, 128.5, 126.6, 126.5, 121.3, 79.5, 79.0, 40.3, 40.9, 37.8, 36.2. *Anal.* Calcd for $C_{35}H_{327}N_4S_3$: C, 69.50; H, 5.33; N, 9.26. Found: C, 69.63; H, 5.21; N, 9.21.

2, 4, 6-Tris[2-(4*S*)-4-methyl-1, 3-thiazolin-2-yl]pyridine (2b)

Mp 162~163 °C. $[\alpha]_D^{25}$ -42.6 (*c* 0.10 in CH_2Cl_2). IR (cm^{-1}): 2967, 2925, 1603, 1450, 1374, 1183, 1025, 923, 715. ^{1}H NMR ($CDCl_3$): δ 8.47(s, 2H), 4.90~4.77 (m, 3H), 3.63~3.47 (m, 3H), 3.14~2.98 (m, 3H), 1.46 (t, *J* = 6.6 Hz, 9H). ^{13}C NMR ($CDCl_3$): δ 168.0, 164.0, 151.3, 141.9, 121.2, 73.7, 73.2, 40.4, 38.8, 20.5, 20.2. MS: m/z 377 (M+1). *Anal.* Calcd for $C_{17}H_{20}N_4S_3$: C, 54.22; H, 3.50; N, 14.88. Found: C, 54.29; H, 3.61; N, 14.94.

2, 4, 6-Tris[2-(4*R*)-4-methyl-1, 3-thiazolin-2-yl]pyridine (2c)

Mp 162~163 °C. $[\alpha]_D^{25}$ +44.1 (*c* 0.10 in CH_2Cl_2). IR (cm^{-1}): 2966, 2926, 1603, 1552, 1185 1022, 923, 713; ^{1}H NMR ($CDCl_3$): δ 8.48 (s, 2H), 4.91~4.77 (m, 3H, CHN=), 3.63~3.48 (m, 3H, CH_2S), 3.14~2.98 (m, 3H, CH_2S), 1.46 (t, *J* = 6.6 Hz, 9H). ^{13}C NMR ($CDCl_3$): *δ* 168.0, 164.0, 151.3, 141.9, 121.2, 73.7, 73.2, 40.4, 38.8, 20.5, 20.2. *Anal.* Calcd for $C_{17}H_{20}N_4S_3$: C, 54.22; H, 3.50; N, 14.88. Found: C, 54.37; H, 3.57; N, 14.80.

2, 4, 6-Tris[2-(4*S*)-4-iso-propyl-1, 3-thiazolin-2-yl] pyridine (2d)

Mp 132~134 °C. $[\alpha]_D^{25}$ -48.2 (*c* 0.10 in CH_2Cl_2). IR (cm^{-1}): 2958, 2870, 1609, 1552, 1175, 1018, 932,

723. ^{1}H NMR ($CDCl_3$): δ 8.47 (s, 2H, ArH), 4.59~4.47 (m, 3H, CHN=), 3.50~3.37 (m, 3H, CH_2), 3.25~3.08 (m, 3H, CH_2), 2.16~2.09 (m, 3H, CH), 1.13~1.01 (m, 18 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 168.0, 164.0, 151.2, 141.8, 121.1, 84.9, 84.5, 35.7, 34.1, 33.4, 33.2, 19.7, 18.9. MS: m/z 461(M+1). *Anal.* Calcd for $C_{23}H_{32}N_4S_3$: C, 59.96; H, 7.00; N, 12.16. Found: C, 59.83; H, 7.16; N, 12.21.

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REFERENCES AND NOTES

1. (a) R. Jansen, B. Kunze, H. Reichenbach, E. Jurkiewicz, G. Hunsmann, and G. Höfle, *Liebigs Ann. Chem.*, 1992, 357; (b) R. Jansen, D. Schomburg, and G. Höfle, *Liebigs Ann. Chem.*, 1993, 701.
2. (a) J. D. White, T.-S. Kim, and M. Nambu, *J. Am. Chem. Soc.*, 1995, **117**, 5612; (b) P. Wipf, J. T. Reeves, R. Balachandran, and B. W. Day, *J. Med. Chem.*, 2002, **45**, 1901.
3. G. Pattenden and J. P. Michael, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1.
4. (a) G. MacLeod and J. Ames, *J. Food Sci.*, 1987, **52**, 42; (b) A. Adams and N. De Kimpe, *Chem. Rev.*, 2006, **106**, 2299.
5. (a) R. Caujolle, J. D. Favrot, P. R. Loiseau, M. Payard, H. Amarouch, H. Lazrek, M. D. Linas, J. P. Seguela, and P. M. Loiseau, *Pharm. Acta Helv.*,1991, **66**, 237; (b) B. George and E. P. Papadopoulos, *J. Org. Chem.*, 1977, **42**, 441.
6. (a) M. Irnak, T. Lehnert, and M. M. K. Boysen, *Tetrahedon Lett.*, 2007, **48**, 7890; (b) S. F. Lu, D. M. Du, J. X. Xu, and S. W. Zhang, *J. Am. Chem. Soc.*, 2006, **128**, 7418; (c) I. Abrunhosa, L. Delain-Bioton, A. C. Gaumont, M. Gulea, and S. Masson, *Tetrahedron*, 2004, **60**, 9263; (d) I. Abrunhosa, M. Gulea, J. Levillain, and S. Masson, *Tetrahedron: Asymmetry*, 2001, **12**, 2851.
7. (a) H. Vorbrüggen and K. Krolikiewicz, *Tetrahedron*, 1993, **49**, 9353; (b) C. A. Busacca, Y. Dong, and E. M. Spinelli, *Tetrahedron Lett.*, 1996, **37**, 2935; (c) M. North and G. Pattenden, *Tetrahedron*, 1990, **46**, 8267; (d) C. D. J. Boden, G. Pattenden, and T. Ye, *Synlett*, 1995, 417; (e) S. Singh, S. J. Rao, and M. W. Pennington, *J. Org. Chem.*, 2004, **69**, 4551; (f) A. R. Katritzky, C.-M. Cai, K. Suzuki, and S. K. Singh, *J. Org. Chem.*, 2004, **69**, 811; (g) T.-S. Kim, Y.-J. Lee, B.-S. Jeong, H.-g. Park, and S.-s. Jew, *J. Org. Chem.*, 2006, **71**, 8276.
8. (a) P. Wipf and C. P. Miller, *Tetrahedron Lett.*, 1992, **33**, 6267; (b) L. Pierre, G. Pierre, and L. Jean-Paul, *Synlett*, 1995, 171; (c) P. Wipf, C. P. Miller, S. Venkatraman, and P. C. Fritch, *Tetrahedron Lett.*, 1995, **36**, 6395; (d) M. Z. Hoemann, K. A. Agrios, and J. Aubé, *Tetrahedron*, 1997, **53**, 11087; (e) S. G. Mahler, G. L. Serra, D. Antonow, and E. Manta, *Tetrahedron Lett.*, 2002, **42**,

8143; (f) J. Levillain, G. Dubant, I. Abrunhosa, M. Gulea, and A.-C. Gaumont, *Chem. Commun.*, 2003, 2914; (g) F. Yokokawa, T. Asano, T. Okino, W. H. Gerwick, and T. Shioiri, *Tetrahedron*, 2004, **60**, 6859; (h) S. Wagner, D. Schumann, U. Linne, U. Koert, and M. A. Marahiel, *J. Am. Chem. Soc.*, 2006, **128**, 10513.

9. (a) F. S. Han, H. Osajima, M. Cheung, H. Tokuyama, and T. Fukuyama, *Chem. Eur. J.*, 2007, **13**, 3026; (b) A. Manaka, T. Ishii, K. Takahashi, and M. Sato, *Tetrahedron Lett.*, 2005, **46**, 419; (c) S. L.You, H. Razavi, and J. W. Kelly, *Angew. Chem. Int. Ed.*, 2003, **42**, 83; (d) X. Fernaadez, R. Fellous, and E. Duñach, *Tetrahedron Lett.*, 2000, **41**, 3381; (e) L. Gauzy, Y. L. Merrer, and J. C. Depezay, *Tetrahedron Lett.*, 1999, **40**, 3705.
10. (a) Sh. F. Lu, D. M. Du, Shi. W. Zhang, and J. X. Xu, *Tetrahedron: Asymmetry*, 2004, **15**, 3433; (b) A. Tárraga, P. Molina, D. Curiel, and D. Bautista, *Tetrahedron: Asymmetry*, 2002, **13**, 1621.
11. (a) S.-G. Kim, K.-H. Kim, Y.-K. Kim, S.-K. Shin, and K.-H. Ann, *J. Am. Chem. Soc.*, 2003, **125**, 13819; (b) S. -G. Kim, K. -H. Kim, J. Jung, S. K. Shin, and K. H. Ann, *J. Am. Chem. Soc.*, 2002, **124**, 591; (c) H. J. Kim, D. Moon, M. S. Lah, and J. I. Hong, *Angew. Chem., Int. Ed.*, 2002, **41**, 3174; (d) S. G. Kim, and K. H. Ahn, *Chem. Eur. J.*, 2000, **6**, 3399; (e) H. J. Kim, Y. H. Kim, and J. I. Hong, *Tetrahedron Lett.*, 2001, **42**, 5049.
12. (a) Y. Kodama, M. Ori, and T. Nishio, *Helv. Chim. Acta*, 2005, **88**, 187; (b) T. Nishio, *J. Org. Chem.*, 1997, **62**, 1106.
13. Intensity data for the title complex were collected at 293(2)K on a Rigaku AFC6S diffractometerr. Crystallographic data: $C_{33}H_{27}N_3S_3$, M = 561.76, monoclinic, space group C_2, a = 30.595(6) Å, b = 6.0296(12)Å, c = 19.425(4) Å, α = 90.00°, β = 126.86 (3)°, γ = 90.00°, V = 2867.0(10)Å^3, Z = 4, D = 1.301 g.cm^{-3}; MoKα (λ = 0.71073 Å), T = 293(2)K, μ = 0.286 mm^{-1}, crystal size (mm) 0.50×0.18.×0.18. Area detector data collected on a Rigaku AFC6S diffractometer. A total of 6187 reflections were collected (2.10< θ <25.03). Structure solution by direct method (SHELXS-97), refinement by full-matrix least-squares using all reflections, R_1 = 0.0793, wR_2 = 0.0812, GOF = 0.913. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-701494. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
14. L. Syper, K. Lkog, and J. Mlochowskki, *Tetrahedron*, 1980, **36**, 123.
15. X.-M. Cheng, Zh.-B. Zheng, N. Li, Zh.-H. Qin, and B. Fu, *Tetrahedron: Asymmetry*, 2008, **19,** 2159.
16. T. Nishio, Y. Kodama, and Y. Tsurum, *Phosphorus, Sulfur and Silicon and Related Elements*, 2005, **180** (5-6), 1449.