Microwave-assisted synthesis and antibacterial activity of novel chenodeoxycholic acid thiosemicarbazone derivatives

Liying Qiu, Zhichuan Shi, Qinggang Mei and Zhigang Zhao*

College of Chemistry and Environmental Protection Engineering, Southwest University for Nationalities, Chengdu 610041, P. R. China

A rapid and efficient method for the synthesis of novel chenodeoxycholic acid thiosemicarbazone derivatives under solvent-free conditions using microwave irradiation is reported. Ten novel compounds have been synthesised in good yields. Their structures were elucidated by ^{1}H NMR, IR, ESI-MS spectra and elemental analysis. Preliminary results showed that some of these compounds possess inhibitory effects against *S. typhimurium* and *E. coli.*

Keywords: thiosemicarbazone, microwave irradiation, antibacterial activity, chenodeoxycholic acid, solvent-free conditions

Thiosemicarbazones and their metal complexes have received considerable attention[1–3] in view of their various biological activities, variables bonding modes, and structural diversity. The structural diversity of thiosemicarbazones varies by condensation with different carbonyl compounds and by alkylation of different part of the thiosemicarbazide moiety. The biological activity and the medicinal properties of thiosemicarbazones depends upon the chemical nature of the moiety attached to the C=S carbon atom.[4,5] Compounds with thiosemicarbazone structure are known to possess tranquilising, anti-viral, analgesic, hypnotic, anti-tumour, anti-depressant, anti-bacterial, muscle relaxing, anti-fungal and anti-inflammatory properties.[6–9]

Recent developments in "green chemistry" can minimise the environmental harmfulness of classical reactions. One of the most popular approaches is the application of microwave techniques for organic synthesis. This technology can enhance the selectivity and improve product yields.[10–13] For this reason, the application of microwave irradiation under solvent-free conditions has gained popularity over the usual homogeneous and heterogeneous reactions.

As is evident from the literature, research has been carried out on steroidal thiosemicarbazone derivatives but no work has been done on chenodeoxycholic acid thiosemicarbazones and their screening against bacteria.[14,15] Recently, our research group has been working microwave solvent-free synthesis of thiosemicarbazone derivatives.[16,17] As a continuation of this work, we report good yields in the synthesis of novel chenodeoxycholic acid thiosemicarbazones under solvent-free conditions using neutral aluminum oxide as a mineral support. Some compounds were tested *in vitro* against bacteria such as *Staphylococcus pyogenes*, *Salmonella typhimurium* and *Escherichia coli*. The synthetic route is depicted in Scheme 1.

Results and discussion

The structures of the compounds **4a–j** were confirmed by IR, mass, ^{1}H NMR and elementary analysis. Their mass spectra showed the expected molecular ions in high intensity. The IR spectra of these compounds exhibited a characteristic strong absorption at 3174–3307 cm^{-1} due to N–H stretching vibration; The strong bands in the region 1699–1740 cm^{-1} indicated the absorption of C=O. Strong absorption bands falling within the range of 1521–1609 cm^{-1} and the range of 1229–1293 cm^{-1} were assigned to the C=N and C=S respectively. In the ^{1}H NMR spectra, the singlets between δ 8.54 and 9.42 ppm were assigned to the protons of the NH. A doublet signal due to the other NH proton was observed at 8.54–9.76 ppm. In addition, the singlet peaks at 1.26–1.29 ppm, 0.68–0.69 ppm and the double peaks at 0.92–0.94 ppm were the characteristic of steroidal structure. The singlets at 3.67 ppm were assigned to the protons of the $COOCH_3$.

In searching for the best conditions, we also carried out a series of experiments, varying the microwave irradiation power, time and different supporters. We used the synthesis of **4a** for example and we found that the highest yield was obtained when the time was 5.0 min at 450 W by using neutral aluminum oxide as the solid support.

As shown in Table 1, we carried out the synthetic comparison of **4a–j** between microwave irradiation in the solvent-free conditions and conventional heating. It was easy to see that microwave irradiation greatly decreased the reaction time from 360–480 min to 4.0–6.0 min. However, the yields also increased from 45–62% to 86–92%. Consequently, the use of microwave technology in conjunction with the use of solvent-free conditions allows expeditious and efficient procedures in this organic synthesis.

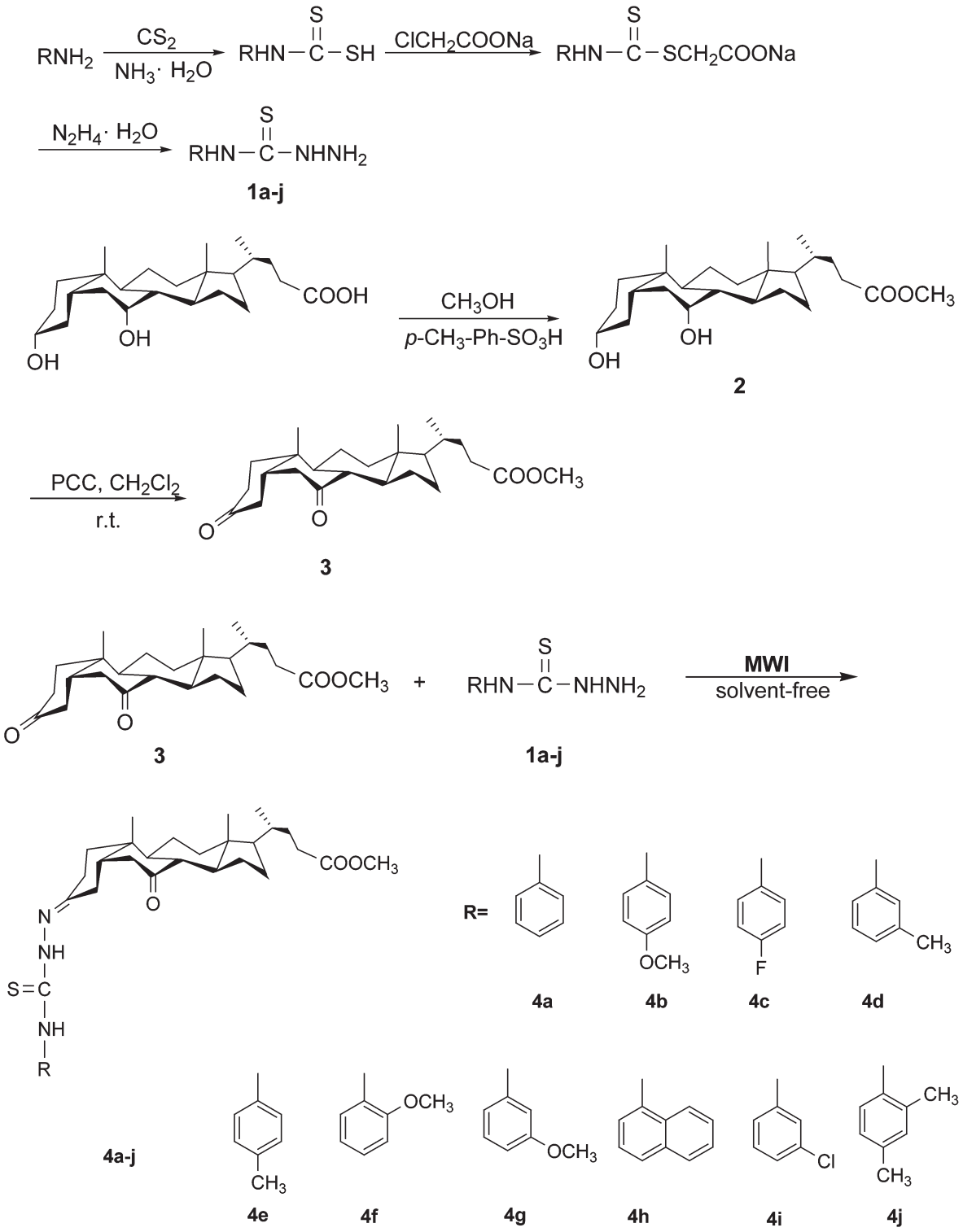
The *in vitro* antibacterial activities of compounds **4a–d** were examined using cultures of *S. pyogenes*, *S. typhimurium* and *E. coli*. Amoxicillin (30 μg) was used as the standard drug. The MIC was evaluated by the macro-dilution test using standard inoculums of 10^{-5} CFU mL^{-1}. Serial dilutions of the test compounds, previously dissolved in DMSO were prepared to final concentrations of 512, 256, 128, 64, 32, 16, 8, 4, 2 and 1 μg mL^{-1}. To each tube was added 100 μL of a 24 h old inoculum. The MIC which inhibits the visible growth after 18 h, was determined visually after incubation for 18 h, at 37°C. The results are presented in Table 2. These compounds have good inhibitory activity against *S. typhimuriun* and *E. coli*. More antibacterial experiments are under study.

In summary, we have developed a highly efficient and eco-friendly method for the preparation of chenodeoxycholic acid thiosemicarbazones. The reaction was conducted in the presence of neutral aluminum oxide, without using solvent, and assisted by microwave irradiation. The present method has many advantages compared to the conventional method, including shorter reaction times, good product yields and fulfills green chemistry protocols. The importance of such work lies in the possibility that these new compounds might be more helpful in designing more potent antibacterial agents for biological and therapeutic use.

Experimental

Melting points were determined on a micro-melting point apparatus and the thermometer was uncorrected. IR spectra were obtained on 1700 PerkinElmer FTIR using KBr disks. ^{1}H NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were determined on FinniganLCQ^{DECA} instrument. Elemental analysis was performed on a Carlo-Erba-1106 auto-analyser. All reactions were performed in a commercial microwave reactor (XH-100A, 100–1000W, Beijing XiangHu Science and Technology Development Co. Ltd, Beijing, P.R. China). All the solvents were purified before use. Compound **2** were prepared by known procedure.[18]

* Correspondent. E-mail: zzg63129@yahoo.com.cn



Scheme 1 The synthetic route of the thiosemicarzones **4a–j**.

Preparation of substituted thiosemicarbazides **1a–j**;[19] *general procedure*

Carbon disuldfide was added dropwise (0.8 mL) to a solution of substituted amine (0.01 mol) in ethanol (10 mL) and concentrated aqueous ammonia (2 mL) was added The mixture was stirred at 15–20°C for 1–2 h to form a solid. Sodium chloroacetate (1.2 g) was added to the stirred mixture and then 85% hydrazine hydrate (1.2 mL) was added. Stirring continued at 60°C for 4 h to obtain a solid. The crude product was then recrystallised from ethanol to obtain each thiosemicarbazides **1a–j**. The melting points of thiosemicarbazides **1a–j** are shown in Table 3.

Synthesis of methyl 3,7-dioxocholan-24-oate (**3**)[20]

Pyridinium chlorochromate (PCC) (3.03 mmol) was added to a solution of compound **2** (0.25 g, 0.615 mmol) in dry CH_2Cl_2 (20 ml) at room temperature. The reaction was completed in 12 h. The solvent was removed under reduced pressure, and the crude product was purified by chromatography on silica gel using ethyl acetate to give white solid, yield 86%; m.p. 155–156°C (lit.[21] m.p. 154–156°C); $[\alpha]_D^{20} = -21.5$ (*c* 0.12, CH_2Cl_2); IR (KBr) (cm^{-1}): 2953, 2873, 1709, 1403, 1375, 1214, 1174, 1010, 966; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.67 (s, 3H, $COOCH_3$), 1.31 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 827 ($[2M+23]^+$, 100).

Table 1 Synthetic comparison of thiosemicarbzaones **4a–j** between solvent-free conditions under microwave irradiation and conventional heating

Compd	Conventional method		Microwave method		t_C/t_{MW}[a]
	t/min	Yield/%	t/min	Yield/%	
4a	400	57	5.0	87	80
4b	360	53	4.0	94	90
4c	420	62	5.5	86	76
4d	480	51	5.5	88	87
4e	360	52	4.0	90	90
4f	420	47	4.5	90	93
4g	420	55	5.0	89	84
4h	480	49	6.0	87	80
4i	360	45	5.5	89	65
4j	300	55	4.0	92	75

$t_{C,}$ Conventional method time; $t_{MW,}$ microwave method time.

Table 2 MIC (μg mL^{-1}) of thiosemicarbzaones and positive Amoxicillin control

Compd	*S. pyogenes*	*S. typhimurium*	*E. coli*
4a	256	128	64
4b	128	64	64
4c	128	32	32
4d	256	64	64
Amoxicillin	32	32	32

Table 3 The melting points of substituted thiosemicarbazides **1a–j**

Product	Formula	M.p./°C	Lit M.p./°C
1a	$C_7H_9N_3S$	137–138	136–138[22]
1b	$C_8H_{11}N_3OS$	150–151	152[23]
1c	$C_7H_8FN_3S$	154–155	153[24]
1d	$C_8H_{11}N_3S$	93–94	92[25]
1e	$C_8H_{11}N_3S$	136–137	137[26]
1f	$C_8H_{11}N_3OS$	158–159	159[27]
1g	$C_8H_{11}N_3OS$	159–160	161[28]
1h	$C_{11}H_{11}N_3S$	136–137	138–139[27]
1i	$C_7H_8ClN_3S$	126–127	126–127[29]
1j	$C_9H_{13}N_3S$	134–135	135[30]

Preparation of thiosemicarbazones **4a–j**; *general procedure*

Conventional method: Steroidal ketones (**3**) (0.1 g, 0.26 mmol) and substituted thiosemicarbazides (**1a–j**) (0.26 mmol) were dissolved in 10 mL ethanol. After completely dissolving the substrates, two drops of acetic acid were added. The mixture was stirred for 5–8 h at 80°C. After cooling the products were filtered and recrystallised from ethanol in 45–62% yields.

Microwave irradiation method: Steroidal ketones (**3**) (0.1 g, 0.26 mmol), substituted thiosemicarbazides (**1a–j**) (0.26 mmol) and neutral aluminium oxide (0.3 g) were put in a porcelain mortar, and concentrated acetic acid (two drops) was added. After grinding, the mixture was put in a round-bottom flask (25 mL) and placed in a microwave oven. It was irradiated for 4.0–6.0 min at 400–600 W. The reaction mixture was cooled to room temperature and dissolved in DMSO and filtered. The filtrate was added to water and the product was formed. The product was recrystallised from ethanol in 86–94% yields. The physical and spectra data of the compounds **4a–j** are as follows.

4a: White solid, yield 87%, m.p. 99–100 °C, $[\alpha]_D^{20} = -81.70$ (*c* 0.10, CH_2Cl_2); IR (KBr)(cm^{-1}): 3259, 2948, 2870, 1739, 1701, 1598, 1536, 1485, 1440, 1264, 1174, 1037, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.25 (s, 1H, NH), 8.62 (d, 1H, *J* = 8.0 Hz, NH), 7.64 (d, 2H, *J* = 8.0 Hz, ArH), 7.37 (t, 2H, *J* = 7.6 Hz , ArH), 7.22 (t, 1H, *J* = 7.2 Hz, ArH), 3.66 (s, 3H, $COOCH_3$), 1.26 (s, 3H, 19-CH_3), 0.92 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.68 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1103 ($[2M+1]^+$, 100). Ana1. Calcd for $C_{32}H_{45}N_3O_3S$: C, 69.65; H, 8.22; N, 7.62. Found: C, 69.60; H, 8.18; N, 7.58%.

4b: White solid, yield 94%, m.p. 164–165°C, $[\alpha]_D^{20} = -100.80$ (*c* 0.10, CH_2Cl_2); IR (KBr) (cm^{-1}): 3286, 3174, 2951, 2875, 1721, 1594, 1547, 1516, 1244, 1177, 1033, 833; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.07 (s, 1H, NH), 8.58 (d, 1H, *J* = 7.2 Hz, NH), 7.46 (d, 2H, *J* = 8.8 Hz, ArH), 6.91 (d, 2H, *J* = 7.6 Hz, ArH), 3.81 (s, 3H, Ar-OCH_3), 3.67 (s, 3H, $COOCH_3$), 1.27 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 604 ($[M+23]^+$, 100). Ana1. Calcd for $C_{33}H_{47}N_3O_4S$: C, 68.12; H, 8.14; N, 7.22. Found: C, 68.04; H, 8.12; N, 7.18%.

4c: White solid, yield 86%, m.p. 115–116°C, $[\alpha]_D^{20} = -78.37$ (*c* 0.10, CH_2Cl_2); IR (KBr) (cm^{-1}): 3293, 2950, 2871, 1738, 1710, 1609, 1521, 1258, 1186, 1053, 835; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.15 (s, 1H, NH), 8.75 (d, 1H, *J* = 7.2 Hz, NH), 7.56 (t, 2H, *J* = 8.0 Hz , ArH), 7.07 (t, 2H, *J* = 8.4 Hz, ArH), 3.67 (s, 3H, $COOCH_3$), 1.27 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 570 ($[M+1]^+$, 100). Ana1. Calcd for $C_{32}H_{44}FN_3O_3S$: C, 67.46; H, 7.78; N, 7.37. Found: C, 67.43; H, 7.75; N, 7.34%.

4d: White solid, yield 88%, m.p. 131–132 °C, $[\alpha]_D^{20} = -73.37$ (*c* 0.10, CH_2Cl_2); IR (KBr) (cm^{-1}): 3300, 3180, 2950, 2869, 1737, 1711, 1591, 1550, 1492, 1437, 1379, 1274, 1200, 1160, 1097, 1048, 787; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.19 (s, 1H, NH), 8.54 (d, 1H, *J* = 8.4 Hz, NH), 7.45 (t, 2H, *J* = 5.6 Hz, ArH), 7.26 (t, 1H, *J* = 6.4 Hz, ArH), 7.03 (d, 1H, *J* = 7.6 Hz, ArH), 3.67 (s, 3H, $COOCH_3$), 2.37 (s, 3H, $ArCH_3$), 1.27 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1131 ($[2M+1]^+$, 100). Ana1. Calcd for $C_{33}H_{47}N_3O_3S$: C, 70.05; H, 8.37; N, 7.43. Found: C, 70.02; H, 8.36; N, 7.40%.

4e: White solid, yield 90%, m.p. 151–152°C, $[\alpha]_D^{20} = -123.78$ (*c* 0.10, CH_2Cl_2); IR (KBr) (cm^{-1}): 3282, 3220, 2951, 2870, 1737, 1708, 1591, 1546, 1481, 1439, 1269, 1176, 1045, 819; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.15 (s, 1H, NH), 8.59 (d, 1H, *J* = 7.2 Hz, NH), 7.48 (d, 2H, *J* = 8.0 Hz, ArH), 7.18 (t, 2H, *J* = 8.0 Hz, ArH), 3.67 (s, 3H, $COOCH_3$), 2.35 (s, 3H, $ArCH_3$), 1.27 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1131 ($[2M+1]^+$, 100). Ana1. Calcd for $C_{33}H_{47}N_3O_3S$: C, 70.05; H, 8.37; N, 7.43. Found: C, 69.99; H, 8.35; N, 7.40%.

4f: White solid, yield 90%, m.p. 179–180 °C, $[\alpha]_D^{20} = -93.58$ (*c* 0.10, CH_2Cl_2); IR (KBr) (cm^{-1}): 3256, 2947, 1740, 1702, 1598, 1542, 1463, 1377, 1287, 1229, 1176, 1031, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.76 (d, 1H, *J* = 9.6 Hz, NH), 8.69 (t, 1H, *J* = 8.4 Hz and *J* = 8.0 Hz, ArH), 8.54 (s, 1H, NH), 7.13 (t, 1H, *J* = 8.0 Hz, ArH), 6.99 (t, 1H, *J* = 8.0 Hz, ArH), 6.91 (d, 1H, *J* = 8.0 Hz, ArH), 3.88 (s, 3H, $COOCH_3$), 3.67 (s, 3H, $COOCH_3$), 1.27 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 604 ($[M+23]^+$, 100). Ana1. Calcd for $C_{33}H_{47}N_3O_4S$: C, 68.12; H, 8.14; N, 7.22. Found: C, 68.07; H, 8.13; N, 7.20%.

4g: White solid, yield 89%, m.p. 151–152°C, $[\alpha]_D^{20} = -129.50$ (*c* 0.10, CH_2Cl_2); IR (KBr)(cm^{-1}): 3288, 2948, 2873, 1733, 1711, 1598, 1547, 1458, 1431, 1293, 1161, 1038, 779; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.26 (s, 1H, NH), 8.57 (d, 1H, *J* = 8.8 Hz, NH), 7.46 (d, 1H, *J* = 7.6 Hz, ArH), 7.28–7.24 (m, 1H, ArH), 7.12 (d, 1H, *J* = 7.6 Hz, ArH), 6.76 (d, 1H, *J* = 8.0 Hz, ArH), 3.82 (s, 3H, Ar-OCH_3), 3.67 (s, 3H, $COOCH_3$), 1.27 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 604 ($[M+23]^+$, 100). Ana1. Calcd for $C_{33}H_{47}N_3O_4S$: C, 68.12; H, 8.14; N, 7.22. Found: C, 68.10; H, 8.13; N, 7.20%.

4h: White solid, yield 87%, m.p. 118–119°C, $[\alpha]_D^{20} = -83.37$ (*c* 0.10, CH_2Cl_2); IR (KBr) (cm^{-1}): 3307, 2946, 2871, 1735, 1708, 1596, 1505, 1470, 1380, 1268, 1199, 1166, 1093, 1019, 775; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.42 (s, 1H, NH), 8.75 (d, 1H, *J* = 9.2 Hz, NH), 7.93–7.85 (m, 3H, ArH), 7.82 (d, 1H, *J* = 8.0 Hz, ArH), 7.55–7.51 (m, 3H, ArH), 3.67 (s, 3H, $COOCH_3$), 1.29 (s, 3H, 19-CH_3), 0.94 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.70 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1225 ($[2M+23]^+$, 100). Ana1. Calcd for $C_{36}H_{47}N_3O_3S$: C, 71.84; H, 7.87; N, 6.98. Found: C, 71.82; H, 7.85; N, 6.94%.

4i: White solid, yield 89%, m.p. 141–142°C, $[\alpha]_D^{20} = -79.50$ (*c* 0.10, CH_2Cl_2); IR (KBr) (cm^{-1}): 3270, 2933, 2860, 1734, 1699, 1592, 1521, 1486, 1378, 1269, 1172, 1055, 713; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.11 (s, 1H, NH), 8.59 (d, 1H, *J* = 6.8 Hz, NH), 7.45 (t, 1H, *J* = 4.8 Hz and *J* = 4.8 Hz, ArH), 7.26 (d, 1H, *J* = 6.8 Hz, ArH), 7.03 (d, 1H, *J* = 7.2 Hz, ArH), 6.86 (d, 1H, *J* = 8.0 Hz, ArH), 3.82 (s, 3H, Ar-OCH_3), 3.67 (s, 3H, $COOCH_3$), 1.27 (s, 3H, 19-CH_3), 0.93 (d, 3H, *J* = 6.0 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 586 ($[M+1]^+$, 100). Ana1. Calcd for $C_{32}H_{44}ClN_3O_3S$: C, 65.56; H, 7.57; N, 7.17. Found: C, 65.44; H, 7.53; N, 7.15%.

4j: White solid, yield 92%, m.p. 175–176 ℃, $[\alpha]_D^{20} = -40.78$ (*c* 0.10, CH_2Cl_2); IR (KBr) (cm^{-1}): 3281, 3196, 2952, 2870, 1739, 1711, 1593, 1549, 1491, 1442, 1272, 1230, 1172, 1044, 823; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (d, 1H, *J* = 8.4 Hz, NH), 8.66 (s, 1H, NH), 7.43 (t, 1H, *J* = 7.6 Hz, ArH), 7.06 (s, 1H, ArH), 7.04 (s, 1H, ArH), 3.67 (s, 3H, $COOCH_3$), 2.32 (s, 3H, $ArCH_3$), 2.26 (s, 3H, $ArCH_3$), 1.27 (s, 3H, 19-CH_3), 0.94 (d, 3H, *J* = 6.4 Hz, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 580 ($[M+1]^+$, 100). Ana1. Calcd for $C_{34}H_{49}N_3O_3S$: C, 70.43; H, 8.52; N, 7.25. Found: C, 70.37; H, 8.50; N, 7.23%.

We thank the Special Financial Project of Central Chinese University (No. 11NZYQN05) and the Science and Technology Bureau of Sichuan Province (No. 2011JY0035) for financial support.

Received 26 June 2011; accepted 14 July 2011
Paper 1100763 doi: 10.3184/174751911X13129090186347
Published online: 29 August 2011

References

1 T.S. Lobana, S. Khanna, G. Hundal, R.J. Bucher and A. Catineiras, *Polyhedron*, 2009, **28**, 3899.
2 J.S. Casas, M.S.G. Tasende and J. Sordo, *Coord. Chem. Rev.*, 2000, **209**, 197.
3 A.M. Vijesh, A.M. Isloor, V. Prabhu, S. Ahmad and S. Malladi, *Eur. J. Med. Chem.*, 2010, **45**, 5460.
4 D. Mishra, S. Naskar, M.G.B. Drew and S.K. Chattopadhyay, *Inorg. Chim. Acta*, 2006, **359**, 585.
5 B. Prathima, Y.S. Rao, S.A. Reddy, Y.P. Reddy and A.V. Reddy, *Spectrochim. Acta, A*, 2010, **77**, 248.
6 B. Yang, S.S. Zhang and H.X. Li, *Chem. Res. Chinese Univ.*, 2006, **22**, 738.
7 H. Beraldo and D. Gambino, *Mini Rev. Med. Chem.*, 2004, **4**, 31.
8 S. Singh, F. Athar, M.R. Maurya and A. Azam, *Eur. J. Med. Chem.*, 2006, **41**, 592.
9 S. Singh, F. Athar and A. Azam, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 5424.
10 H. Naeimi and L. Moradi, *Catal. Commum.*, 2006, **7**, 1067.
11 V. Pollshettiwar and S.V. Rajender, *Acc. Chem. Res.*, 208, **41**, 629.
12 E. Ramesh and R. Raghunathan, *Tetrahedron Lett.*, 2008, **49**, 1812.
13 C.O. Kappe, *Angew. Chem. Int. Ed.*, 2004, **43**, 6250.
14 K.H. Reddy, P.S. Reddy and P.R. Babu, *J. Inorg. Biochem.*, 1999, **77**, 169.
15 P.B. Savage, *Eur. J. Org. Chem.*, 2002, **5**, 759.
16 Z.C. Shi, Z.G. Zhao, X.L. Liu and Y. Chen, *Chin. Chem. Lett.*, 2011, **22**, 405.
17 Z.G. Zhao, X.L. Liu, L.L. Liu and G.H. Li, *J. Chem. Res.*, 2010, **34**, 455.
18 Z.G. Zhao, P.Y. Zhang, Z.X. Yang and S.H. Chen, *Chin. J. Org. Chem.* (in Chinese), 2005, **25**, 679.
19 C.Y. Liu, G.W. Ying, J. Qian, Z. Li and A.H. Yu, *Chem. Reag.* (in Chinese), 2003, **25**, 160.
20 J.G. Cui, L.L. Huang, Y.M. Huang and J.C. Fan, *Chin. J. Org. Chem.* (in Chinese), 2009, **29**, 971.
21 Z.Q. Wang, H.Q. Que, L.Z. Jiang and W.S. Zhou, *Chin. J. Org. Chem.* (in Chinese), 1989, **9**, 83.
22 S.K. Chawla, *Polyhedron.*, 2006, **25**, 627.
23 R. Stanislav, *Collect. Czech. Chem. Commun.*, 1986, **5**, 1692.
24 A.K. Parekh, *Indian J. Chem., Sect. B*, 2006, **45**, 1072.
25 A. Mohammad, *Acta Pharma. Sci.*, 2008, **50**, 23.
26 R.W. Bost and W.F. Smith, *J. Am. Chem. Soc.*, 1931, **53**, 652.
27 M. Tisler, *Croat. Chem. Acta*, 1965, **28**, 147.
28 K. Joseph, *DE 832891* 1952.
29 A.J. Cowper, *J. Indian. Chem. Soc.*, 1981, **58**, 1087.
30 A. Mohammad, *Orient. J. Chem.*, 2006, **22**, 57.