Synthesis of novel triazole derivatives of methyl 3-oxocholanate using microwave irradiation

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An efficient rapid method for the synthesis of new triazole derivatives derived from methyl 3-oxocholanate under microwave irradiation has been developed. These new compounds were characterised by ^{1}H NMR, IR, ESI-MS spectra and elemental analyses. Some of these triazoles were tested for antibacterial activity against *Staphylococcus aureus*, *Candida albicans* and *Escherichia coli*.

Keywords: 1,2,4-triazole, Schiff base, lithocholic acid, microwave irradiation

1,2,4-Triazole derivatives exhibit analgesic, anticancer, antimicrobial, anti-inflammatory, antioxidant, tumour inhibitory properties.[1–6] A number of drugs such as Ribavirin (antiviral agent), Rizatriptan (antimigraine agent), Alprazolam (anxiolytic agent), Fluconazole and Itraconazole (antifungal agents) possess a triazole nucleus. Furthermore, Schiff base derivatives of 1,2,4-triazoles and their reduction products have also been found to possess pharmacological activity.[7–13] Recently, steroidal building blocks have attracted the interest of research groups in many branches of science and technology, such as the medical and pharmacological fields, supramolecular chemistry and nanotechnology.[14–17]

Microwave-assisted organic synthesis is an important technique in green synthetic chemistry. It possesses useful attributes, such as ease of manipulation, enhanced reaction rates, clean reaction outcomes and high yields.[18–23]

To the best of our knowledge, no work has been published on the synthesis and physicochemical properties of triazole derivatives obtained from methyl 3-oxocholanate. In view of this, we now report a simple, efficient and rapid synthetic method for preparing steroidal triazoles based on methyl 3-oxocholanate by condensation of the steroidal ketone with the 4-amino-3-substituted-1H-1,2,4-triazole-5-thione under microwave irradiation. The synthetic route is depicted in Scheme 1.

Result and discussion

The structures of **7a–i** were established by their elemental analysis and spectroscopic data. The IR spectra of **4a–i** showed absorption bands at 3310–3250 cm^{-1} due to the NH_2 group, which were absent in the IR spectra of **7a–i**. The IR spectra of **6** had a strong characteristic absorption at 1712 attributed to the C=O which was not present in the spectra of compounds **7a–i**. There was strong characteristic absorption at 3208–3092 cm^{-1} due to the NH stretching vibration and absorption in the region 1740–1721 cm^{-1} assigned to the CO_2CH_3. The bands at 1633–1612 cm^{-1} indicated absorption due to a C=N. The strong absorption bands falling within the range 1322–1293 and 1104–1076 cm^{-1} were assigned to the C=S. The ^{1}H NMR(DMSO-d_6, 400 MHz) spectra of **4a–i** showed a broad signal in the region 6.20–5.79 ppm attributed to the NH_2 group which was not present in the spectra of compounds **7a–i**. The singlet peak at 14.17–13.91 ppm assigned to the NH. The protons of the ArH appeared at 8.06–7.08 ppm. The protons of the CO_2CH_3 group gave signals in the range 3.57 ppm. Three hydrogen doublets and singlets in the range 0.87, 0.85 and 0.61 ppm were assigned to 21-CH_3, 19-CH_3 and 18-CH_3, respectively. The ESI-MS spectra showed the expected molecular ions with high intensity.

As shown in Table 1, we carried out a comparison of the synthesis of **7a–i** between microwave and conventional methods. Compared to the conventional method, microwave heating greatly decreased the reaction time from 180–300 min to 4–8 min and decreased the solvent required from 10 mL to 2 mL. It was obvious that yields increased from 50–70% to 85–90%.

Compounds **7a, 7d**, **7i** were evaluated for their antibacterial activity against *S. aureus*, *C. albicans* and *E. coli* using an agar dilution method. Preliminary results indicated that these steroidal triazoles had a good inhibitory effect. Detailed investigations of the anti-bacterial activity of compounds **7a–i** are under way.

In conclusion, we have developed a protocol for the synthesis of steroidal triazoles based on methyl 3-oxocholanate. The salient features of this protocol include the simple reaction set-up, less use of organic solvent, high yields of products, and short reaction time. These advantages should render the synthesis of steroidal triazoles faster, efficient and environmental friendly.

Experimental

Melting points were determined on a micro-melting point apparatus and the thermometer was uncorrected. IR spectra were obtained on 1700 Perkin-Elmer FTIR using KBr disks. ^{1}H NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using TMS as internal standard. Mass spectra were determined on a Finnigan LCQ^{DECA} instrument. Elemental analyses were performed on a Carlo-Erba-1106 autoanalyser. All reactions were performed in a commercial microwave reactor(XH-100A, 100-1000 W, Beijing Xianghu Science and Technology Development Co. Ltd, Beijing, P.R. China). Optical rotations were measured on a Wzz-2B polarimeter. All the solvents were purified before use.

Preparation of **5:**[24] Lithocholic acid (5 mmol), *p*-TsOH (1 mmol) and anhydrous methanol (50 mL) were added to a round-bottomed flask, and stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was dissolved with ethyl acetate (30 mL). The resultant solution was washed with

Table 1 Synthetic comparison of **7a–i** between the microwave and conventional methods

Compd.	Conventional method		Microwave method		t_c/t_w[a]
	Time/min	Yield/%	Time/min	Yield/%	
7a	180	70	4	90	45
7b	300	50	8	86	37
7c	300	55	8	85	37
7d	180	70	4	90	45
7e	250	65	5	87	50
7f	250	67	6	86	41
7g	250	66	7	85	35
7h	250	65	7	86	35
7i	300	55	8	85	37

t_c, Conventional method time; t_w, microwave method time.

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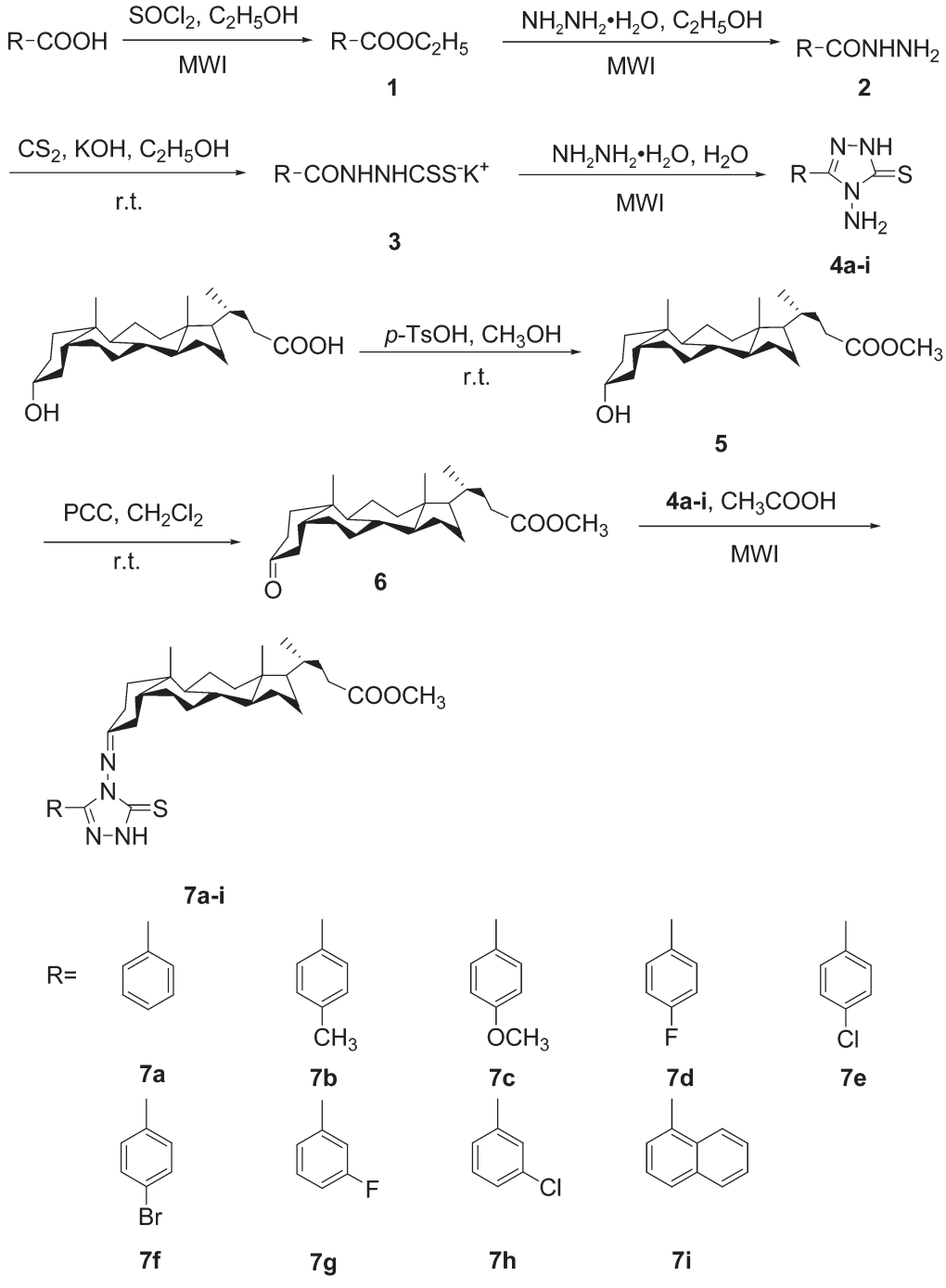

Scheme 1 The synthetic route to the triazole derivatives **7a–i**.

$NaHCO_3$ (3 × 30 mL), saturated salt water (3 × 30 mL), and then dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the resulting crude product was purified by column chromatography on silica gel using $V(CH_2Cl_2)$: $V(CH_3COOCH_2CH_3)$= 10:1 as eluant to give 2.16 g. White solid, yield 94%, m.p. 126–127 °C, $[\alpha]_D^{20}$ + 34.7 (*c* 0.90, CH_2Cl_2)[lit.[25] 125–127 °C $[\alpha]_D^{20}$ + 29°]; IR (cm^{-1}): 3522, 2933, 1717, 1100; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.66 (s, 3H, CO_2CH_3), 3.63–3.59 (m, 1H, 3β-H), 0.96 (s, 3H, 19-CH_3), 0.87 (d, *J* = 6.4 Hz, 3H, 21-CH_3), 0.64 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 803 ($[2M+23]^+$, 100). Anal. Calcd for $C_{25}H_{42}O_3$: C, 76.87; H, 10.84. Found: C, 76.70; H, 10.90%.

Preparation of **6:**[25,26] Pyridinium chlorochromate (PCC) (6 mmol) was added to the solution of methyl 3α-hydroxycholan-24-oate (**1**) (4 mmol) in anhydrous CH_2Cl_2 (40 mL) and the reaction mixture was stirred at room temperature. The reaction was completed in 12 h, and the solution was poured onto a silica gel column and eluted with ethyl acetate. White solid, yield 87%; m.p. 115–117 °C, $[\alpha]_D^{20}$ + 190.0 (*c* 0.10, CH_2Cl_2))[lit.[27] 119–120 °C $[\alpha]_D^{20}$ + 32°]; IR (cm^{-1}): 2933, 1737, 1712, 1175; ^1H NMR (DMSO-d_6, 400 MHz) δ: 3.58 (s, 3H, CO_2CH_3), 0.97 (s, 3H, 19-CH_3), 0.88 (d, *J* = 6.4 Hz, 3H, 21-CH_3), 0.65 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 799 ($[2M+23]^+$, 100). Anal. Calcd for $C_{25}H_{40}O_3$: C, 77.27; H, 10.38. Found: C, 77.10; H, 10.40%.

Preparation of **4a–i:**[28] Substituted acid was esterified with ethanol in the presence of $SOCl_2$ under microwave irradiation. The ester was refluxed with hydrazine hydrate in ethanol to obtain the carbohydrazide. The carbohydrazide on reaction with carbon disulfide in ethanolic potassium hydroxide yielded the corresponding dithiocarbazinate in good yield which was directly used for the next step without further purification. The triazole was synthesised by refluxing dithiocarbazinate with hydrazine hydrate and water. The crude product was then recrystallised from ethanol to give a pure sample. (Table 2).

Microwave preparation of **7a–i**: In a round-bottomed flask, methyl 3-oxocholan-24-oate (1 mmol) was dissolved in 2 mL glacial acetic acid and then 4-amino-3-substituted-1H-1,2,4-triazole-5-thione

Table 2 The melting point of triazole **4a–i**

Compd.	Formula	M.p./ ºC	Lit m.p./ ºC
4a	$C_8H_8N_4S$	202–204	203–204[29]
4b	$C_9H_{10}N_4S$	201–203	201[28]
4c	$C_9H_{10}N_4OS$	199–200	201[29]
4d	$C_8H_7N_4FS$	206–207	208[28]
4e	$C_8H_7N_4ClS$	211–212	210–212[28]
4f	$C_8H_7N_4BrS$	203–204	205–206[28]
4g	$C_8H_7N_4FS$	218–220	220[28]
4h	$C_8H_7N_4ClS$	211–213	215–217[28]
4i	$C_{12}H_{10}N_4S$	204–205	206[30]

(1 mmol) was added. The round-bottomed flask was placed in the microwave oven and irradiated for 4-8 min in 300 W. The reaction was monitored by TLC. Then the reaction mixture was cooled to room temperature and the required solid was precipitated out. It was filtered, washed thoroughly with anhydrous ethanol, and dried under vacuum. The crude product was recrystallised from ethanol to give a pure sample.

Methyl 3-(3-phenyl-5-thioxo-1H-1,2,4-triazol-4-ylimino)cholanate (**7a**): White solid, yield 90%, m.p. 201–203 °C, $[\alpha]_D^{20}$ – 26.7 (*c* 0.34, CH_2Cl_2); IR (cm^{-1}): 3108, 2931, 1723, 1633, 1499, 1449, 1380, 1319, 1169, 1076, 758, 694; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.03 (s, 1H, NH), 7.72–7.70 (m, 2H, ArH), 7.54 (s, 3H, ArH), 3.57 (s, 3H, CO_2CH_3), 0.87 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.85 (s, 3H, 19-CH_3), 0.61 (s, 3H, 18-CH_3). ESI-MS *m/z* (%): 1147 ($[2M+23]^+$, 100). Anal. Calcd for $C_{33}H_{46}N_4O_2S$: C, 70.42; H, 8.24; N, 9.95. Found: C, 70.34; H, 8.27; N, 9.91%.

Methyl 3-(3-(4-methyphenyl)-5-thioxo-1H-1,2,4-triazol-4-ylimino) cholanate (**7b**): White solid, yield 86%, m.p. 191–193 °C, $[\alpha]_D^{20}$ – 79.0 (*c* 0.23, CH_2Cl_2); IR (cm^{-1}): 3093, 2929, 1740, 1622, 1512, 1440, 1380, 1294, 1170, 1101, 825; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 13.97 (s, 1H, NH), 7.61 (t, *J* = 8.0 Hz, 2H, ArH), 7.34 (t, *J* = 7.2 Hz, 2H, ArH), 3.57 (s, 3H, CO_2CH_3), 2.36 (s, 3H, Ar-CH_3), 0.87 (d, *J* = 6.0 Hz, 3H, 21-CH_3), 0.85 (s, 3H, 19-CH_3), 0.61(s, 3H, 18-CH_3). ESI-MS *m/z* (%): 1175 ($[2M+23]^+$, 100). Anal. Calcd for $C_{34}H_{48}N_4O_2S$: C, 70.78; H, 8.39; N, 9.71. Found: C, 70.89; H, 8.40; N, 9.68%.

Methyl3-(3-(4-methoxyphenyl)-5-thioxo-1H-1,2,4-triazol-4-ylimino) cholanate (**7c**): White solid, yield 85%, m.p. 198–200 °C, $[\alpha]_D^{20}$ – 33.3 (*c* 0.41, CH_2Cl_2); IR (cm^{-1}): 3111, 2936, 1738, 1612, 1512, 1431, 1385, 1305, 1175, 1076, 840, 799; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 13.91 (s, 1H, NH), 7.67 (t, *J* = 8.4 Hz, 2H, ArH), 7.08 (t, *J* = 9.2 Hz, 2H, ArH), 3.81 (s, 3H, Ar-OCH_3), 3.57 (s, 3H, CO_2CH_3), 0.87 (d, *J* = 6.4 Hz, 3H, 21-CH_3), 0.85 (s, 3H, 19-CH_3), 0.61 (s, 3H, 18-CH_3). ESI-MS *m/z* (%): 593 ($[M+1]^+$, 100). Anal. Calcd for $C_{34}H_{48}N_4O_3S$: C, 68.88; H, 8.16; N, 9.45. Found: C, 68.98; H, 8.17; N, 9.43%.

Methyl 3-(3-(4-fluorophenyl)-5-thioxo-1H-1,2,4-triazol-4-ylimino) cholanate (**7d**): Yellow solid, yield 90%, m.p. 201–203 °C, $[\alpha]_D^{20}$ – 16.8 (*c* 0.27, CH_2Cl_2); IR (cm^{-1}): 3099, 2931, 1727, 1631, 1507, 1448, 1382, 1315, 1162, 1099, 847; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.04 (s, 1H, NH), 7.79–7.76 (m, 2H, ArH), 7.43–7.37 (m, 2H, ArH), 3.57 (s, 3H, CO_2CH_3), 0.87 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.85 (s, 3H, 19-CH_3), 0.61 (s, 3H, 18-CH_3). ESI-MS *m/z* (%): 581 ($[M+1]^+$, 100). Anal. Calcd for $C_{33}H_{45}FN_4O_2S$: C, 68.24; H, 7.81; N, 9.65. Found: C, 68.38; H, 7.78; N, 9.62%.

Methyl 3-(3-(4-chlorophenyl)-5-thioxo-1H-1,2,4-triazol-4-ylimino) cholanate (**7e**): Yellow solid, yield 87%, m.p. 183–185 °C, $[\alpha]_D^{20}$ – 67.2 (*c* 1.15, CH_2Cl_2); IR (cm^{-1}): 3095, 2929, 1728, 1629, 1497, 1449, 1381, 1310, 1170, 1095, 835; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.09 (s, 1H, NH), 7.76 (t, *J* = 8.4 Hz, 2H, ArH), 7.65–7.59 (m, 2H, ArH), 3.57 (s, 3H, CO_2CH_3), 0.87 (d, *J* = 6.4 Hz, 3H, 21-CH_3), 0.85 (s, 3H, 19-CH_3), 0.61 (s, 3H, 18-CH_3). ESI-MS *m/z* (%): 597 ($[M+1]^+$, 100). Anal. Calcd for $C_{33}H_{45}ClN_4O_2S$: C, 66.36; H, 7.59; N, 9.38. Found: C, 66.47; H, 7.61; N, 9.36%.

Methyl 3-(3-(4-bromophenyl)-5-thioxo-1H-1,2,4-triazol-4-ylimino) cholanate (**7f**): Yellow solid, yield 86%, m.p. 197–199 °C, $[\alpha]_D^{20}$ – 11.1 (*c* 0.82, CH_2Cl_2); IR (cm^{-1}): 3092, 2928, 1740, 1622, 1500, 1438, 1379, 1293, 1169, 1070, 832; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.10 (s, 1H, NH), 7.77–7.66 (m, 4H, ArH), 3.57 (s, 3H, CO_2CH_3), 0.87 (d, *J* = 6.4 Hz, 3H, 21-CH_3), 0.85 (s, 3H, 19-CH_3), 0.61 (s, 3H, 18-CH_3). ESI-MS *m/z* (%): 643 ($[M+1]^+$, 100). Anal. Calcd for $C_{33}H_{45}BrN_4O_2S$: C, 61.77; H, 7.07; N, 8.73. Found: C, 61.70; H, 7.09; N, 8.75%.

Methyl 3-(3-(3-fluorophenyl)-5-thioxo-1H-1,2,4-triazol-4-ylimino) cholanate (**7g**): Yellow solid, yield 85%, m.p. 176–178 °C, $[\alpha]_D^{20}$ – 102.2 (*c* 0.62, CH_2Cl_2); IR (cm^{-1}): 3103, 2931, 1721, 1629, 1494, 1438, 1375, 1318, 1169, 1104, 789, 694; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.14 (s, 1H, NH), 7.70 (t, *J* = 4.4 Hz, 1H, ArH), 7.39 (t, *J* = 8.0 Hz, 2H, ArH), 7.20 (t, *J* = 13.2 Hz, 1H, ArH), 3.57 (s, 3H, CO_2CH_3), 0.86 (brs, 6H, 21-CH_3, 19-CH_3), 0.61 (s, 3H, 18-CH_3). ESI-MS *m/z* (%): 1183 ($[2M+23]^+$, 100). Anal. Calcd for $C_{33}H_{45}FN_4O_2S$: C, 68.24; H, 7.81 N, 9.65. Found: C, 68.32; H, 7.83; N, 9.63%.

Methyl 3-(3-(3-chlorophenyl)-5-thioxo-1H-1,2,4-triazol-4-ylimino) cholanate (**7h**): Yellow solid, yield 86%, m.p. 171–173 °C, $[\alpha]_D^{20}$ – 120.4 (*c* 0.61, CH_2Cl_2); IR (cm^{-1}): 3102, 2931, 1720, 1630, 1494, 1437, 1376, 1322, 1169, 1104, 785, 694; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.13 (s, 1H, NH), 7.73–7.70 (m, 2H, ArH), 7.58 (t, *J* = 6.8 Hz, 2H, ArH), 3.57 (s, 3H, CO_2CH_3), 0.86 (brs, 6H, 21-CH_3, 19-CH_3), 0.62 (s, 3H, 18-CH_3). ESI-MS *m/z* (%): 597 ($[M+1]^+$, 100). Anal. Calcd for $C_{33}H_{45}ClN_4O_2S$: C, 66.36; H, 7.59; N, 9.38. Found: C, 66.47; H, 7.56; N, 9.40%.

Methyl 3-(3-(naphthalen-1-yl)-5-thioxo-1H-1,2,4-triazol-4-ylimino) cholanate (**7i**): White solid, yield 85%, m.p. 168–170 °C, $[\alpha]_D^{20}$ – 62.7 (*c* 0.29, CH_2Cl_2); IR (cm^{-1}): 3208, 2934, 1723, 1631, 1480, 1450, 1376, 1298, 1172, 1103, 807, 781; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 14.17 (s, 1H, NH), 8.17 (d, *J* = 8.0 Hz, 1H, ArH), 8.07 (d, *J* = 8.0 Hz, 1H, ArH), 7.90 (d, *J* = 7.2 Hz, 1H, ArH), 7.68–7.62(m, 4H, ArH), 3.57 (s, 3H, CO_2CH_3), 0.86 (brs, 6H, 21-CH_3, 19-CH_3), 0.57 (s, 3H, 18-CH_3). ESI-MS *m/z* (%): 613 ($[M+1]^+$, 100). Anal. Calcd for $C_{37}H_{48}N_4O_2S$: C, 72.51; H, 7.89; N, 9.14. Found: C, 72.59; H, 7.92; N, 9.12%.

Conventional preparation of compounds **7a–i:** In a round-bottomed flask, methyl 3-oxo-cholan-24-oate (1 mmol) was dissolved in 10 mL glacial acetic acid and then 4-amino-3-substituted-1H-1,2,4-triazole-5-thione (1 mmol) was added. The reaction solution was heated under reflux for 180–300 min. The reaction was monitored by TLC. The mixture was cooled to room temperature and then the solvent was removed under reduced pressure and the required solid was precipitated out. It was filtered, washed thoroughly with anhydrous ethanol, and dried under vacuum. The crude product was recrystallized from ethanol to give a pure sample.

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