Solvent-free one-pot efficient and highly regioselective access to functionalized thiazolopyridones from α -enolic dithioesters

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Dedicated to Professor (Dr.) J. S. Yadav on the occasion of his 65th birthday

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Abstract

An operationally simple, highly convergent and straightforward synthesis of diverse thiazolopyridones has been achieved *via* three-component domino coupling (3CDC) of α -enolic dithioesters, cysteamine and dialkyl acetylenedicarboxylates under solvent-free conditions. The approach is carbon-economic and relies on sequential cyclic *N,S*-acetal formation/Michael addition/*N*-cyclization cascade forming consecutive C-C, C-N and C-S bonds in one-pot.

Keywords: Thiazolopyridones, α -enolic dithioesters, domino coupling, cascade reactions, solvent-free conditions

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Introduction

The key goal in modern organic synthesis is to design and develop new synthetic strategies for the rapid generation of function-oriented molecules by improving resource efficiency that provides maximum structural diversity and complexity with step, atom, and cost economy. Cascade processes that incorporate multiple bond-forming events in one-pot have come into play, and are of paramount interest in organic synthesis.¹⁻⁴ The synthesis of heterocycles has always been a key aspect, and increasingly attracted the synthetic pursuit of chemists. They are vital part of new drug discovery and indispensable materials in the implementation of any industrial evolution.⁵⁻⁷

Among the fused *N,S*-heterocyclic frameworks, thiazolopyridones are versatile privileged scaffolds present in many biologically important products and pharmaceuticals. They exhibit activities like DNA gyrase B inhibitors^{8,9} and antibacterial agents.^{10,11} Furthermore,

thiazolopyridones have also been utilized in the synthesis of natural-product-like heterocycles.¹² Thiazolo ring-fused 2-pyridones have proven to be highly interesting scaffolds for the development of biologically active compounds particularly introducing a variety of substituents in the 2-pyridone part of the heterocycles.¹³ Further, thiazolofused 2-pyridones have been halogenated with complete regioselectivity to synthesize 6-bromo-8-iodo-substituted bicyclic 2-pyridones in gram scale.¹⁴ Recently, a selective intramolecular 5-*exo*-dig or 6-*endo*-dig cyclization enroute to 2-furanone or 2-pyrone containing tricyclic scaffolds have been developed.¹⁵ An efficient method to synthesize a novel rigid tricyclic peptidomimetic scaffold through ring-closure of amino-functionalized bicyclic 2-pyridones has been discovered.¹⁶

Among available reports for the synthesis of benzothiazolopyridones,¹⁷⁻²⁰ most of them suffer from significant limitations such as harsh reaction conditions, expensive catalysts / reagents, prolonged reaction times, multistep syntheses and poor availability of starting materials. In combination, the above facts prompted us to develop a new straightforward and widely applicable approach for the synthesis of thiazolopyridones. The carbon-sulfur and carbon-nitrogen bond formations constitute a very important class of reactions in biological processes. In view of the spectacular role of domino reaction in chemical transformations, we are interested in developing metal-free and solvent-free multicomponent reactions to construct complex molecules from readily available simple precursors in a single operation. α -Enolic dithioesters are valuable synthetic targets due to their versatile reactivity as powerful intermediates toward the synthesis of various heterocycles.²¹⁻²⁵ Solvent-free MCRs of α -enolic dithioesters are particularly intriguing and have attracted remarkable interest. In continuation of our research interests regarding the synthetic utility of α -enolic dithioesters,²⁶⁻³¹ particularly aimed at exploring one-pot solvent-free synthetic protocols,³²⁻³⁸ we report herein an operationally simple and expedient one-pot synthesis of thiazolopyridones under metal-free and solvent-free conditions *via* one-pot multicomponent domino reaction (MDR) involving a sequence of cyclic *N,S*-acetal formation/Michael addition/N-cyclization cascade in good to excellent yield (Scheme 1).

Scheme 1. Synthesis of thiazolopyridones **4**.

Results and Discussion

To the best of our knowledge, no report on the synthesis of thiazolopyridones utilizing α -enolic dithioesters is known to date. To optimize the reaction condition for the synthesis of thiazolopyridones, methyl 3-hydroxy-3-phenyl-prop-2-enedithioate (**1a**), cysteamine (**2**) and diethyl acetylenedicarboxylate (**3a**) were taken as model substrates. We performed the model

reaction under varying conditions, and the results are listed in Table 1. In an initial study, **1a** upon treatment with **2** gave cyclic *N,S*-acetal, which has been isolated and fully characterized.³⁹ Subsequent treatment of *N,S*-acetal **A** with **3a** in refluxing methanol afforded the desired thiazolopyridone **4a** in 85% yield within 4 h. Next to check the influence of solvents, we screened various solvents such as polar protic, low boiling polar aprotic and high boiling polar aprotic solvents (Table 1, entries 2-8). The high boiling polar aprotic solvents displayed better results (Table 1, entries 6 and 7). In one attempt, we tried the reaction under sonication at 40 °C by adding 2 drops of ethanol for homogenization of reaction mixture. Work up of the reaction afforded the desired product in 85% yield within 3 h. Finally, we performed the model reaction under solvent-free conditions at 110 °C. Satisfyingly, the reaction completed within 10 min consuming the reactants completely and furnished the desired product in 63% yield (Table 1, entry 10). In order to make the reaction milder, we reduced the temperature after formation of cyclic *N,S*-acetal to 90 °C, when the desired product was obtained in 87% yield within 30 min (Table 1, entry 11). Further lowering in temperature could not improve the result (Table 1, entry 12). Thus, the best reaction conditions for the formation of **4a** was found to be **1a** (1 mmol), **2** (1 mmol), **3a** (1 mmol), at 90 °C under solvent-free condition (Table 1, entry 11).

Table 1. Optimization studies for the synthesis of thiazolopyridone^a **4a**

Entry	Solvent	Temp (°C)	Time (h)	Yield ^b (%)
1	Methanol	Reflux	4.0	85
2	Ethanol	Reflux	3.5	80
3	DCM	Reflux	4.5	70
4	Chloroform	Reflux	4.0	72
5	Acetonitrile	Reflux	5.0	75
6	DMF	110	1.5	80
7	DMSO	110	1.0	80
8	Water	100	24	trace
9	Ethanol, 2 drops	40 (sonication)	3.0	85
10	none	110	10 min	63
11	none	90	30 min	87
12	none	80	1.0	70

^a All reactions were performed with **1a** (1 mmol), **2** (1 mmol), and **3a** (1 mmol); ^b Isolated pure yields.

Experiments probing the scope and generality of this protocol under optimized conditions are summarized in Table 2. A broad range of α -enolic dithioesters **1**, bearing R^1 as aryl, hetaryl, and extended aromatic groups, were tolerated well. Dialkyl acetylenedicarboxylates **3** bearing both methyl and ethyl as R^2 could be employed to afford thiazolopyridones **4** in good to excellent yields. All reactions proceeded smoothly and afforded the corresponding product **4** in high yield. A range of α -enolic dithioesters bearing R^1 as aryl groups with electron-donating substituents were well tolerated, and gave considerably higher yields than those with electron-withdrawing group (**4c-f** vs. **4g**). Moreover, halogen substitution on the R^1 of dithioester did not disturb the reactivity, and the corresponding products were formed in high yields (**4h, i**). Importantly, dithioester **1** bearing a heteroaromatic moiety at R^1 was also compatibly providing high yield of the product (**4j-l**). After successful utilization of aromatic dithioesters, we next extended our study to various extended aromatics such as 1-naphthyl R^1 substituent, which was also tolerated well and furnished the product (**4m**) in good yield.

Table 2. Scope of substrate for the synthesis of thiazolopyridones^a **4**

Product	R^1	R^2	Time (min)	Yield ^b (%)
4a	Ph	Et	30	87
4b	Ph	Me	40	80
4c	4-MeC ₆ H ₄	Et	30	92
4d	4-MeOC ₆ H ₄	Et	45	82
4e	3-MeOC ₆ H ₄	Me	45	85
4f	1,3-benzodioxol-5-yl	Me	35	90
4g	4-F ₃ CC ₆ H ₄	Me	55	75
4h	2-ClC ₆ H ₄	Et	50	75
4i	2-ClC ₆ H ₄	Me	45	70
4j	2-furyl	Et	40	80
4k	2-thienyl	Et	50	73
4l	2-thienyl	Me	45	70
4m	1-naphthyl	Et	60	85

^a All reactions were performed with **1**, **2**, and **3** (1 mmol of each); ^b Isolated pure yields.

The structures of all the synthesized thiazolopyridone derivatives **4** were deduced by their satisfactory spectral (¹H, ¹³C NMR and mass) studies and explicitly established by the single

crystal X-ray diffraction analysis (see the ESI) of one representative compound, **4a** (CCDC-947810) (Figure 1).

Figure1. ORTEP diagram of **4a**.

By taking our entire experimental outcomes into consideration, a plausible reaction mechanism accounting for the formation of compound **4** is outlined in Scheme 2. The first step is believed to be the formation of cyclic *N,S*-acetal **A** by the reaction of α -enolic dithioester **1** with cysteamine **2**. The cyclic *N,S*-acetal **A** has been isolated and fully characterized.³⁹ Next, conjugate addition of *N,S*-acetal **A** to dialkyl acetylenedicarboxylate **3** gave an intermediate **B**, which rapidly undergoes intramolecular regioselective *N*-cyclization to furnish the desired bicyclic thiazolopyridone **4**. During the course of our investigation, we could not observe the formation of pyrrolothiazolone **5** even in a trace.

Scheme 2. Plausible mechanism for the formation of thiazolopyridones **4**.

Conclusions

In summary, we have developed an operationally simple and straightforward one-pot multicomponent reaction involving dithioesters, cysteamine and dialkyl acetylenedicarboxylate under metal-free and solvent-free conditions for the first time. The reaction resulted in a convenient synthesis of diverse highly functionalized thiazolopyridones in high yields from

acyclic precursors. This convergent and highly regioselective approach exhibits an unusually high multiple C-C, C-N and C-S bond forming efficiency utilizing all the reactants efficiently in structure, cost, and step economies. It is noteworthy that the reaction tolerates a broad range of functional groups. Significantly, the presence of keto-group and ester groups makes these compounds excellent entrants as precursors for further synthetic renovations. We hope this clean and green MCC protocol may be of immense value for both synthetic and medicinal chemists.

Experimental Section

The commercially available starting materials were used as received without further purification. α -Enolic dithioesters **1** were prepared by the reported procedure.²¹ ^1H and ^{13}C NMR spectra were recorded on NMR spectrometers operating at 300 and 75 MHz, respectively. Chemical shifts (δ) are given in parts per million (ppm) using the residual solvent peaks as reference relative to TMS. J values are given in Hz.

General procedure for the synthesis of thiazolopyridones (4). A round bottom flask was charged with the appropriate α -enolic dithioesters **1** (1 mmol), cysteamine **2** (1 mmol) and placed in a pre-heated oil bath at 110 °C. The reaction mixture was heated for 15 min until formation of the cyclic N,S-acetal (monitored by TLC) was complete, then the temperature was reduced to 90 °C and dialkyl acetylenedicarboxylate **3** (1 mmol) was added. The reaction mixture was stirred for the stipulated time (see Table 2). After completion of the reaction (TLC), the reaction was quenched with water and the solution was extracted with DCM followed by washing with brine. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The resultant reaction mixture was purified by column chromatography using silica gel as stationary phase and ethyl acetate-hexane (3:7) as eluent to afford the analytically pure product **4**.

Ethyl 8-benzoyl-5-oxo-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4a). White solid (0.223 g, 87 %); mp 160-162 °C. ^1H NMR (300 MHz, CDCl_3): δ 7.65 (d, J 6.9 Hz, 2H), 7.53 (t, J 7.2 Hz, 1H), 7.43 (t, J 7.2 Hz, 2H), 6.63 (s, 1H), 4.56 (t, J 7.8 Hz, 2H), 3.66 (q, J 7.2 Hz, 2H), 3.37 (t, J 7.5 Hz, 2H), 0.98 (t, J 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 191.9, 165.1, 160.4, 156.9, 143.8, 138.2, 132.5, 128.5, 128.3, 115.9, 110.5, 62.0, 50.6, 28.1, 13.3. IR (KBr, cm^{-1}): 3048, 2983, 1720, 1673, 1634, 1485, 1270, 1063. HRMS (ESI^+): calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4\text{S}$ [$\text{M}+\text{H}^+$], 330.0795; found, 330.0807.

Methyl 8-benzoyl-5-oxo-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4b). White solid (0.252 g, 80 %); mp 190-192 °C. ^1H NMR (300 MHz, CDCl_3): δ 7.62 (d, J 7.2 Hz, 2H), 7.51 (d, J 7.2 Hz, 1H), 7.46-7.41 (m, 2H), 6.61 (s, 1H), 4.56 (t, J 7.8 Hz, 2H), 3.37 (t, J 7.8 Hz, 2H), 3.23 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 192.0, 169.1, 165.7, 160.4, 157.2, 143.6, 138.4, 132.5, 128.6, 128.2, 116.0, 110.6, 52.3, 50.7, 28.2. HRMS (ESI^+): calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_4\text{S}$ [$\text{M}+\text{H}^+$], 316.0638; found, 316.0655.

Ethyl 8-(4-methylbenzoyl)-5-oxo-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4c). White solid (0.315 g, 92 %); mp 152-153 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.56 (d, *J* 7.8 Hz, 2H), 7.22 (d, *J* 7.5 Hz, 2H), 6.62 (s, 1H), 4.55 (t, *J* 7.5 Hz, 2H), 3.70 (q, *J* 6.9 Hz, 2H), 3.36 (t, *J* 7.5 Hz, 2H), 2.39 (s, 3H), 0.99 (t, *J* 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 191.7, 165.2, 160.5, 156.2, 143.8, 143.5, 135.5, 129.2, 128.5, 116.0, 115.9, 110.9, 62.0, 50.6, 28.2, 21.5, 13.3. HRMS (ESI⁺): calcd for C₁₈H₁₇NO₄S [M+H⁺], 344.0951; found, 344.0973.

Ethyl 8-(4-methoxybenzoyl)-5-oxo-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4d). Brown solid (0.294 g, 82 %); mp 108-110 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.65 (d, *J* 8.1 Hz, 2H), 6.91 (d, *J* 8.1 Hz, 2H), 6.64 (s, 1H), 4.54 (t, *J* 7.2 Hz, 2H), 3.85-3.77 (m, 5H), 3.37 (t, *J* 7.2 Hz, 2H), 1.01 (t, *J* 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 190.7, 165.1, 163.2, 160.4, 155.5, 143.6, 130.6, 115.8, 115.7, 113.6, 111.6, 61.9, 55.3, 50.6, 28.2, 13.2. HRMS (ESI⁺): calcd for C₁₈H₁₇NO₅S [M+H⁺], 360.0900; found, 360.0915.

Methyl 8-(3-methoxybenzoyl)-5-oxo-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4e). Brown solid (0.293 g, 85 %); mp 110-112 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.35-7.26 (m, 1H), 7.19-7.05 (m, 3H), 6.61 (s, 1H), 4.57 (t, *J* 7.5 Hz, 2H), 3.84 (s, 3H), 3.38 (t, *J* 7.5 Hz, 2H), 3.28 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 191.5, 165.5, 160.3, 159.6, 157.3, 143.5, 139.4, 129.5, 120.6, 119.2, 115.8, 115.7, 112.2, 110.5, 55.2, 52.2, 50.6, 28.1. HRMS (ESI⁺): calcd for C₁₇H₁₅NO₅S [M+H⁺], 346.0744; found, 346.0760.

Methyl 8-(1,3-benzodioxol-5-ylcarbonyl)-5-oxo-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4f). Yellow solid (0.323 g, 90 %); mp 145-147 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.22 (s, 1H), 7.12 (d, *J* 7.8 Hz, 1H), 6.79 (d, *J* 8.1 Hz, 1H), 6.61 (s, 1H), 6.04 (s, 2H), 4.54 (t, *J* 7.8 Hz, 2H), 3.44 (s, 3H), 3.37 (t, *J* 7.5 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 190.3, 165.4, 160.3, 155.6, 151.4, 148.1, 143.2, 132.5, 124.6, 115.87, 115.81, 110.8, 107.9, 107.6, 101.8, 52.4, 50.6, 28.2. HRMS (ESI⁺): calcd for C₁₇H₁₃NO₆S [M+H⁺], 360.0536; found, 360.0551.

Methyl 5-oxo-8-[4-(trifluoromethyl)benzoyl]-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4g). Light yellow solid (0.287 g, 75 %); mp 196-197 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.74-7.68 (m, 4H), 6.62 (s, 1H), 4.58 (t, *J* 7.8 Hz, 2H), 3.40 (t, *J* 7.8 Hz, 2H), 3.26 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 190.6, 165.3, 160.1, 158.1, 143.1, 141.3, 133.5 (q, *J* 32.7 Hz 1C), 128.3, 125.4 (q, *J* 3.75 Hz, 1C), 121.5, 116.1, 109.7, 52.3, 50.6, 28.1. IR (KBr, cm⁻¹): 2952, 1715, 1670, 1640, 1445, 1337, 1274, 1123, 1107, 1072. HRMS (ESI⁺): calcd for C₁₇H₁₂F₃NO₄S [M+H⁺], 384.0512; found, 384.0527.

Ethyl 8-(2-chlorobenzoyl)-5-oxo-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4h). Brown solid (0.272 g, 75 %); mp 183-185 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.44-7.28 (m, 4H), 6.43 (s, 1H), 4.55 (t, *J* 7.8 Hz, 2H), 3.71 (q, *J* 7.2 Hz, 2H), 3.37 (t, *J* 7.8 Hz, 2H), 1.11 (t, *J* 7.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 189.3, 165.5, 160.3, 159.6, 144.7, 137.6, 132.5, 131.9, 130.5, 130.0, 126.5, 115.5, 115.4, 62.1, 50.5, 28.1, 13.6. IR (KBr, cm⁻¹): 2978, 1730, 1669, 1620, 1479, 1262. HRMS (ESI⁺): calcd for C₁₇H₁₄ClNO₄S [M+H⁺], 364.0405; found, 364.0418.

Methyl 8-(2-chlorobenzoyl)-5-oxo-2,3-dihydro-5H-thiazolo[3,2-a]pyridine-7-carboxylate (4i). Brown solid (0.244 g, 70 %); mp 181-183 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.43-7.30 (m, 4H), 6.43 (s, 1H), 4.55 (t, *J* 7.5 Hz, 2H), 3.36-3.28 (m, 5H). ¹³C NMR (75 MHz, CDCl₃):

δ 189.2, 165.9, 160.1, 159.8, 144.1, 137.6, 132.3, 131.8, 130.5, 129.7, 126.5, 115.5, 115.3, 110.6, 52.4, 50.4, 28.0. HRMS (ESI⁺): calcd for C₁₆H₁₂ClNO₄S [M+H⁺], 350.0248; found, 350.0262.

Ethyl 8-(furan-2-ylcarbonyl)-5-oxo-2,3-dihydro-5H-thiazolo[3,2-*a*]pyridine-7-carboxylate (4j). Brown solid (0.255 g, 80 %); mp 120-122 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.52 (s, 1H), 7.16 (d, *J* 3.6 Hz, 1H), 6.74 (s, 1H), 6.54 (s, 1H), 4.55 (t, *J* 7.8 Hz, 2H), 3.98 (q, *J* 7.2 Hz, 2H), 3.35 (t, *J* 7.8 Hz, 2H), 1.08 (t, *J* 7.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 178.7, 165.1, 160.4, 156.7, 152.6, 145.9, 145.8, 143.0, 117.2, 116.6, 116.5, 112.6, 112.5, 110.0, 62.1, 50.6, 28.1, 13.4. IR (KBr, cm⁻¹): 2984, 1723, 1665, 1631, 1458, 1425, 1257. HRMS (ESI⁺): calcd for C₁₅H₁₃NO₅S [M+H⁺], 320.0587; found, 320.0600.

Ethyl 5-oxo-8-(thiophen-2-ylcarbonyl)-2,3-dihydro-5H-thiazolo[3,2-*a*]pyridine-7-carboxylate (4k). Brown solid (0.259 g, 73 %); mp 130-132 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.66 (d, 5.1 Hz, 1H), 7.35 (d, *J* 3 Hz, 1H), 7.08-7.05 (m, 1H), 6.69 (s, 1H), 4.56 (t, *J* 7.5 Hz, 2H), 3.88 (q, *J* 6.9 Hz, 2H), 3.39 (t, *J* 7.2 Hz, 2H), 1.04 (t, *J* 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 183.8, 165.0, 160.3, 155.4, 144.1, 143.0, 133.9, 132.4, 127.7, 116.4, 116.3, 110.8, 62.1, 50.7, 28.3, 13.3. HRMS (ESI⁺): calcd for C₁₅H₁₃NO₄S₂ [M+H⁺], 336.0359; found, 336.0374.

Methyl 5-oxo-8-(thiophene-2-carbonyl)-2,3-dihydro-5H-thiazolo[3,2-*a*]pyridine-7-carboxylate (4l). White solid (0.224 g, 70 %); mp 129-131 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.66 (d, *J* 4.8 Hz, 1H), 7.32 (d, *J* 3.3 Hz, 1H), 7.07 (t, *J* 4.5 Hz, 1H), 6.67 (s, 1H), 4.56 (t, *J* 7.5 Hz, 2H), 3.44-3.37 (m, 7H). ¹³C NMR (75 MHz, CDCl₃): δ 183.9, 165.6, 160.4, 155.7, 144.0, 142.8, 133.8, 132.2, 127.7, 116.5, 116.4, 110.9, 52.5, 50.8, 28.3. IR (KBr, cm⁻¹): 2925, 1715, 1658, 1630, 1497, 1441, 1415, 1270. HRMS (ESI⁺): calcd for C₁₄H₁₁NO₄S₂ [M+H⁺], 322.0202; found, 322.0215.

Ethyl 8-(1-naphthoyl)-5-oxo-2,3-dihydro-5H-thiazolo[3,2-*a*]pyridine-7-carboxylate (4m). White solid (0.322 g, 85 %); mp 218-220 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.45 (d, *J* 8.1 Hz, 1H), 7.95-7.85 (m, 2H), 7.63-7.54 (m, 2H), 7.42 (s, 2H), 6.49 (s, 1H), 4.56 (t, *J* 7.2 Hz, 2H), 3.36 (t, *J* 8.1 Hz, 2H), 3.22 (s, 2H), 0.68 (t, *J* 7.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 192.3, 165.6, 160.4, 158.8, 145.0, 135.7, 133.8, 132.3, 130.5, 128.2, 127.8, 126.7, 125.8, 124.0, 115.5, 115.4, 61.8, 50.5, 28.1, 13.0. HRMS (ESI⁺): calcd for C₂₁H₁₇NO₄S [M+Na⁺], 402.0770; found, 402.0778.

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