Scientific article
UDC 547.818.1
DOI: 10.52957/2782-1900-2026-7-2-93-101

SYNTHESIS OF IMIDES OF 4,6-DIPHENYL-3,4-DIHYDRO-2*H*-THIOPYRAN-2,3-DICARBOXYLIC ACID

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Keywords: *2H-thiopyrans, maleimides, anhydrides, anilines*

Abstract. *A new approach to the synthesis of imides of vicinal thiopyrandicarboxylic acids, based on the construction of the imide fragment via acylation of anilines with 4,6-diphenyl-3,4-dihydro-2H-thiopyran-2,3-dicarboxylic acid anhydride, has been developed. The proposed method successfully enhances known approaches associated with the formation of the thiopyran ring.*

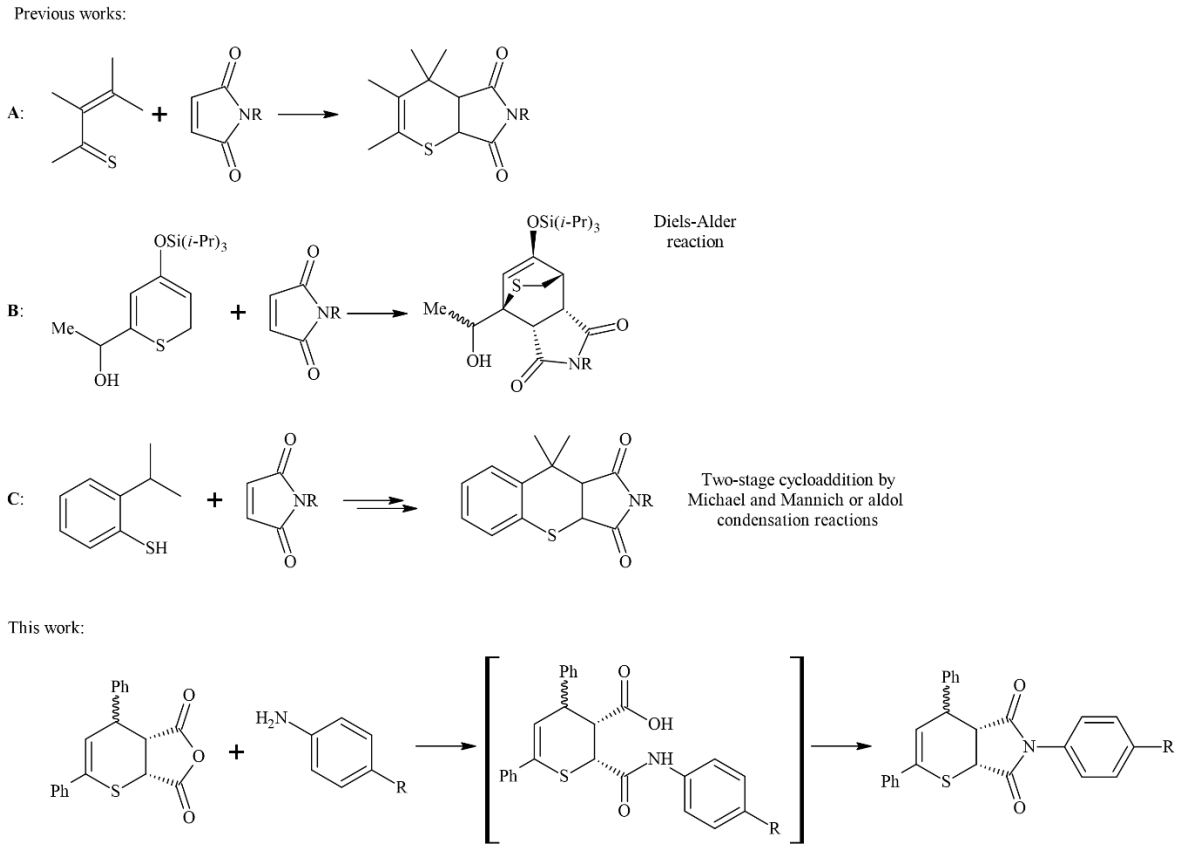
For citation:
Starostin M.V., Malinina A.V., Karpov D.S., Ovchinnikov K.L., Aldoshin A.S., Kolobov A.V. Synthesis of imides of 4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-2,3-dicarboxylic acid // From Chemistry towards Technology Step-by-Step. 2026. Vol. 7, Iss. 2. P. 93-101. URL: https://chemintech.ru/en/nauka/issue/7273/view

Introduction

The development of methods for the targeted synthesis and the study of the properties of heterocyclic compounds are the key directions of modern organic chemistry. Thiopyran derivatives serve as a striking example of such systems, as they possess a wide range of biological activities [1]. In addition to pharmaceutical applications, these compounds are in demand in the production of innovative materials: electrodes, dyes, fluorescent additives, and organic semiconductors [2]. Indeed, cyclic imides are widely sought after in medicinal chemistry, agrochemistry, and catalysis [3]. In this context, the development of efficient methods for the synthesis of imides of vicinal thiopyrandicarboxylic acids is of significant theoretical and applied importance.

Two main approaches to the synthesis of the heterocyclic structures under consideration are described in the literature [4]. The first method is based on the addition of maleimides to sulfur-containing substrates via the Diels–Alder reaction. In this approach, α,β-unsaturated thiocarbonyl compounds (Scheme 1, A) [5–13] or 2*H*-thiopyrans (Scheme 1, B) [14] are mainly used as dienes. The second method involves the sequential cycloaddition of thiophenols or thiophenolates to maleimides, proceeding as a cascade of Michael and Mannich reactions or aldol condensation (Scheme 1, C) [15–19].

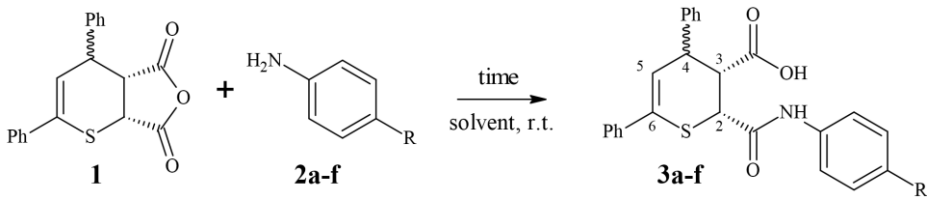
Thus, the most known methods for the synthesis of imides of 2*H*-thiopyrandicarboxylic acids are based on the cycloaddition of maleimides to various sulfur-containing substrates. At the same time, approaches to the preparation of thiopyran ring heterocycles based on the construction of the imide fragment itself are practically unknown. In this regard, the present work is devoted to the development of a new method for the synthesis of *N*-arylimides of 2*H*-thiopyrandicarboxylic acids based on the acylation of anilines with 4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-2,3-dicarboxylic acid anhydride followed by intramolecular cyclization of the obtained intermediates (Scheme 1).



Scheme 1

Main body

At the first stage of the work, we studied the acylation of a series of anilines **2a–f** with anhydride **1**, leading to the formation of the corresponding (2*R**,3*R**)-2-(arylcarbamoyl)-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-3-carboxylic acids **3a–f** (Scheme 2). Anhydride **1** was synthesized via the hetero-Diels–Alder reaction of (2*E*)-1,3-diphenylprop-2-ene-1-thione with maleic anhydride [7].



2, **3**: R = Me (**a**), H (**b**), OMe (**c**), NO_2 (**d**), Br (**e**), COOH (**f**)

Scheme 2

Using the reaction of anhydride **1** with *p*-toluidine **2a** as an example, we showed that for acylation of sufficiently nucleophilic substrates, the nature of the solvent does not significantly affect the reaction time or the yield of the target product (Table 1, experiments 1–3). Thus, in nonpolar toluene and dichloromethane, as well as in polar acetic acid, the processes were completed within 30 minutes, affording amic acid **3a** in 73–79% yield. The reaction also proceeded efficiently using aniline **2b**, *p*-methoxyaniline **2c**, and *p*-bromoaniline **2e** in dichloromethane: the target amic acids **3b**,**c**,**e** were obtained in 61–78% yield within 10–40 minutes at room temperature (Table 1, experiments 4, 5, 8).

On the other hand, upon switching to weakly nucleophilic *p*-nitroaniline **2d** and *p*-aminobenzoic acid **2f**, the acylation rate decreased significantly. In particular, when the reaction with *p*-nitroaniline **2d** was conducted in CH_2Cl_2 solution at room temperature for 30 days, the target amic acid **3d** was isolated in only 26% yield with incomplete conversion of the starting reagents (Table 1, experiment 6). However, replacing dichloromethane with glacial acetic acid made it possible to substantially reduce the reaction time (by more than 90 times) and increase the product yield to 57% (Table 1, experiment 7). Using analogous conditions for *p*-aminobenzoic acid **2f** afforded the corresponding amic acid **3f** in 86% yield (Table 1, experiment 8).

Table 1. Synthesis conditions for (2*R**,3*R**)-2-(arylcarbamoyl)-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-3-carboxylic acids **3a–f** from anhydride **1**

Experiment	Product code	R	Solvent	Reaction time [1], min	Yield is **3**, %.
1	**3a**	Me	PhMe	30	79
2			CH_2Cl_2	30	75
3			AcOH	20	73
4	**3b**	H	CH_2Cl_2	40	72
5	**3c**	OMe	CH_2Cl_2	10	61
6	**3d**	NO_2	CH_2Cl_2	43200[2]	26
7			AcOH	1020[2]	57
8	**3e**	Br	CH_2Cl_2	30	78
9	**3f**	COOH	AcOH	7200	86

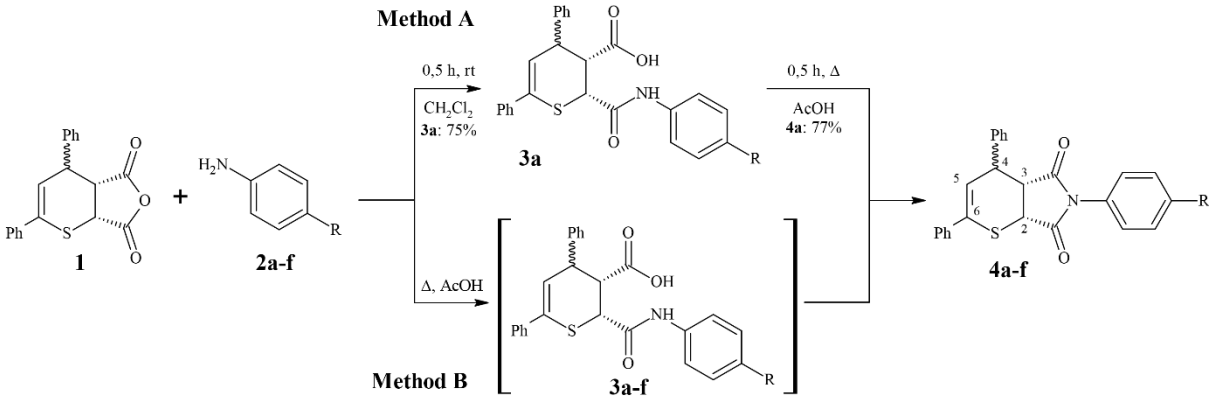
[1]The reaction time until complete conversion of the starting anhydride **1** (except for **3d**) was determined by TLC monitoring. Samples were taken every 10 min.

[2]The precipitate of amic acid **3d** was filtered off at incomplete conversion of **1**.

The physicochemical characteristics of products **3a** and **3b** are similar to those obtained previously [20]. The structure of amic acids **3c–f** was confirmed by a combination of ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry (HRMS). Moreover, HPLC analysis of the reaction mixtures did not reveal the presence of any other by-products. This fact allows us to assert that, under the conditions studied, the reaction proceeds strictly regioselectively to form exclusively one regioisomer containing the carbamoyl group at the C(2) position.

When amic acids **3** are heated to reflux in glacial acetic acid, they undergo intramolecular cyclization to form *N*-arylimides of 2*H*-thiopyrandicarboxylic acids **4** (Scheme 3). Thus, imide **4a** was obtained from amic acid **3a** in 77% yield (Scheme 3, Method A). Furthermore, it seemed promising to synthesize the target imides as a *one-pot* process without isolation of the

intermediate amic acids **3** (Scheme 3, Method B). Therefore, by heating anhydride **1** with anilines **2a–f** in acetic acid for 0.5–5 h, the target imides **4a–f** were obtained in 40–65% yield over two steps (Table 2). The one-pot Method B provided a higher yield of product **4a** (65%) compared to two-step Method A (58% over two steps), while the purity of the target compound obtained by both methods proved to be comparable.



2, **3**, **4**: R = Me (**a**), H (**b**), OMe (**c**), NO_2 (**d**), Br (**e**), COOH (**f**)

According to Table 2, the reaction time depends significantly on the nature of the substituent R in the aromatic ring. Electron-donating substituents, as expected, increase the nucleophilicity of the nitrogen atom of the amide group, thereby accelerating the intramolecular acylation process. Electron-withdrawing groups, in contrast, reduce the nucleophilicity of the amide center and, as a consequence, lead to a decrease in the cyclization rate.

Table 2. Synthesis conditions for (4a*R**,7a*R**)-2,4-diphenyl-6-aryl-4a,7a-dihydrothiopyrano[2,3-c]pyrrole-5,7(4*H*,6*H*)-diones **4a–f** from anhydride **1** according to method B

Experiment	Product code	R	Reaction time, min	Yield is **4**, %.
1	**4a**	Me	60	65
2	**4b**	H	120	62
3	**4c**	OMe	30	61
4	**4d**	NO_2	300	45[1]
5	**4e**	Br	120	61
6	**4f**	COOH	300	40[1]

[1]The precipitate of imides **4d,f** was filtered off at incomplete conversion of **1**.

The physicochemical characteristics of compounds **4a–d** are similar to those described in the literature [7, 21]. In the cited sources, **4a–d** were obtained via the hetero-Diels–Alder reaction of (2*E*)-1,3-diphenylprop-2-ene-1-thione with the corresponding maleimides. The yields of **4a–d** under those conditions were 34–69%, which is comparable to our results. The structure of the newly synthesized imides **4e**,**f** was also confirmed by a combination of ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry (HRMS).

The main advantage of the developed method is the possibility of facile structural variation of the acylation products. This distinguishes it favorably from traditional approaches based on maleimides. This feature is of key importance for generating combinatorial libraries

intended for high-throughput screening in the search for new biologically active substances. At the same time, the yield and purity of the target heterocycles remain consistently high.

Thus, a new approach has been developed for the synthesis of (4a*R**,7a*R**)-2,4-diphenyl-6-aryl-4a,7a-dihydrothiopyrano[2,3-c]pyrrole-5,7(4*H*,6*H*)-diones **4a–f**, based on the regioselective acylation of a series of anilines **2a–f** with anhydride **1** followed by intramolecular cyclization of the resulting intermediates. Two alternative methods for implementing this approach are proposed: a classical two-step method (with isolation of the intermediate amic acids **3**) and a *one-pot* process without their isolation. As a result, *one-pot* method is more efficient and provides higher overall yields of the target heterocycles. The electronic nature of the substituent in the aromatic ring of the aniline has a decisive influence on the reaction rate at both stages of the process: electron-donating groups significantly accelerate both the intermolecular acylation of the anhydride and the subsequent intramolecular cyclization, whereas electron-withdrawing substituents substantially slow down these processes.

Experimental part

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 instrument at operating frequencies of 400 and 101 MHz, respectively. ^{1}H and ^{13}C chemical shifts are given relative to the residual solvent signal (δ_H = 2.50 and δ_C = 39.52 ppm for solutions in DMSO-d_6). High-resolution mass spectra were recorded on an Orbitrap QExactive Plus instrument (Thermo Scientific) under electrospray ionization conditions. Ion source parameters: drying gas pressure is 12, nebulizing gas and curtain gas flow rates are 4 and 1 arbitrary units, desolvation line temperature is 320 °C, needle voltage is 3.8 kV in positive ion detection mode and 3.2 kV in negative ion detection mode, S-lens RF voltage is 55 arb. units. Mass spectra were recorded in the m/z range of 100–2500 Da at a spectral resolution of 70,000. Thin-layer chromatography (TLC) was performed on Sorbfil PTSKh-P-V-UV plates (eluent: petroleum ether – ethyl acetate (1:1)). Melting points were determined on an Electrothermal IA 9300 Series apparatus. HPLC was performed on a Shimadzu Prominence LC-20A chromatograph with a photometric detector, λ_{max} 210 and 254 nm, Phenomenex Luna C18(2) column, 5 μm, 4.6 × 250 mm. Reagents and solvents (ECOS-1, Aldrich, Acros) are commercially available and were used without further purification. The synthesis method and physicochemical characteristics of compound **1** are described in [7].

General procedure for the synthesis of amic acids 3a–f. To a stirred solution of 1.00 g (3.1 mmol) of anhydride **1** in 6 mL of CH_2Cl_2 (AcOH for the synthesis of **3d**,**f**) at room temperature was added a solution of 3.4 mmol of the corresponding aniline **2a–f** in 4 mL of CH_2Cl_2 (AcOH for the synthesis of **3d**,**f**). The reaction mixture was stirred until the reaction was complete (monitored by TLC). The precipitated solid was filtered off, washed on the filter with cold CH_2Cl_2, and dried in vacuo.

(2*R,3*R**)-2-[(4-Methoxyphenyl)carbamoyl]-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-3-carboxylic acid (3c).** Yield is 0.84 g (61%), white powder, Tmelt. = 166-168 °C. ^{1}H NMR (DMSO-d_6, δ, ppm., *J*/Hz): 3.72 (s, 3H, OMe), 3.78 (dd, 1H, C(3)H, J_1 = 5.6, J_2 = 2.9), 4.17 (dd, 1H, C(4)H, *J* = 5.7, 2.6), 4.87 (d, 1H, C(2)H, *J* = 2.8), 6.26 (d, 1H, C(5)H, *J* = 2.5), 6.86 – 6.95 (m, 2H, ArH), 7.23 (t, 1H, *J* = 7.3, ArH), 7.30 – 7.38 (m, 3H, ArH), 7.38 – 7.44 (m,

4H, ArH), 7.46 – 7.51 (m, 2H, ArH), 7.56 – 7.62 (m, 2H, ArH), 10.20 (s, 1H, NH), 11.83 (s, 1H, COOH). ^{13}C NMR (DMSO-d_6, δ, ppm.): 44.30, 45.73, 50.58, 55.22, 113.96, 120.40, 121.11, 125.88, 126.60, 128.05, 128.25, 128.68, 131.90, 133.64, 139.35, 141.58, 155.51, 166.50, 169.38. Mass-spectrum (ESI), m/z (I_{rel} (%)): found 468.1244 $[M+Na]^+$ (93), calculated for $[C_{26}H_{23}NNaO_4S]^+$ 468.1240.

(2*R,3*R**)-2-[(4-Nitrophenyl)carbamoyl]-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-3-carboxylic acid (3d).** Yield is 0.86 g (53 %), white powder, Tmelt. = 185-187 °C. ^{1}H NMR (DMSO-d_6, δ, ppm., *J*/Hz): 3.88 (dd, 1H, C(3)H, *J* = 5.6, 2.9), 4.20 (dd, 1H, C(4)H, J_1 = 5.5, J_2 = 2.6), 5.02 (d, 1H, C(2)H, *J* = 2.8), 6.32 (d, 1H, C(5)H, *J* = 2.5), 7.25 (t, 1H, *J* = 7.3), 7.31 – 7.48 (m, 7 H), 7.57 – 7.64 (m, 2 H), 7.78 – 7.96 (m, 2 H), 8.19 – 8.36 (m, 2 H), 10.98 (s, 1 H, CONH), 11.98 (s, 1 H, COOH). ^{13}C NMR (DMSO-d6, δ, ppm): 44.16, 45.70, 50.92, 119.10, 120.56, 125.12, 126.61, 128.05, 128.33, 128.70, 133.20, 139.22, 141.44, 142.48, 144.97, 168.06, 169.20. Mass-spectrum (ESI), m/z (I_{rel} (%)): found 483.0989 $[M+Na]^+$ (100), calculated for $[C_{25}H_{20}N_2NaO_5S]$ 483.0985.

(2*R,3*R**)-2-[(4-Bromphenyl)carbamoyl]-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-3-carboxylic acid (3e).** Yield is 0.89 g (58 %), white powder, Tmelt. = 197-198 °C. ^{1}H NMR (DMSO-d_6, δ, ppm, *J*/Hz): 3.81 (dd, 1H, C(3)H, J_1 = 5.6, J_2 = 2.9), 4.18 (dd, 1H, C(4)H, J_1 = 5.6, J_2 = 2.6), 4.92 (d, 1H, C(2)H, *J* = 2.9), 6.28 (d, 1H, C(5)H, *J* = 2.5), 7.19 – 7.28 (m, 1H, ArH), 7.30 – 7.38 (m, 3H, ArH), 7.38– 7.46 (m, 4H, ArH), 7.47 – 7.54 (m, 2H, ArH), 7.58 (m, 4H, ArH, J_1 = 7.1, J_2 = 6.1, J_3 = 1.6), 10.49 (s, 1H, NH), 11.89 (s, 1H, COOH). ^{13}C NMR (DMSO-d_6, δ, ppm): 44.22, 45.64, 50.72, 115.26, 120.45, 121.31, 121.41, 125.89, 126.62, 128.06, 128.29, 128.68, 131.70, 133.46, 138.12, 139.28, 141.49, 167.18, 169.26. Mass-spectrum (ESI), m/z (I_{rel} (%)): found 516.0237 $[M+Na]^+$ (97), calculated for $[C_{25}H_{20}BrNNaO_3S]$ 516.0239.

(2*R,3*R**)-2-[(4-Carboxyphenyl)carbamoyl]-4,6-diphenyl-3,4-dihydro-2*H*-thiopyran-3-carboxylic acid (3f).** Yield is 1.23 g (86 %), white powder, Tmelt. = 207-208 °C. (DMSO-d_6, δ, ppm., *J*/Hz): 3.83 (dd, 1H, C(3)H, J_1 = 5.6, J_2 = 2.9), 4.18 (dd, 1H, C(4)H, J_1 = 5.6, J_2 = 2.6), 4.95 (d, 1H, C(2)H, *J* = 2.8), 6.29 (d, 1H, C(5)H, *J* = 2.5), 7.20 – 7.26 (m, 1H, ArH), 7.30 – 7.38 (m, 3H, ArH), 7.38– 7.45 (m, 4H, ArH), 7.54 – 7.63 (m, 2H, ArH), 7.68 – 7.75 (m, 2H, ArH), 7.88 – 7.97 (m, 2H), 10.66 (s, 1H, NH), 12.32 (s, 2H, 2COOH). ^{13}C NMR (DMSO-d_6, δ, ppm): 44.20, 45.71, 50.87, 118.68, 120.50, 125.48, 125.90, 126.60, 128.05, 128.30, 128.69, 130.52, 133.36, 139.27, 141.50, 142.86, 166.93, 167.54, 169.26. Mass-spectrum (ESI), m/z (I_{rel} (%)): found 482.1034 $[M+Na]^+$ (100), calculated for $[C_{26}H_{21}NNaO_5S]$ 482.1033.

General procedure for the synthesis of imides 4a–f (one-pot method). A mixture of 0.50 g (1.55 mmol) of anhydride **1** and 1.71 mmol of the corresponding aniline **2a–f** in 5 mL of glacial AcOH was heated to reflux until the reaction was complete (monitored by TLC). The reaction mixture was then cooled to room temperature. The precipitated solid was filtered off, washed on the filter with cold AcOH, then with a small amount of cold *i*-PrOH, and dried in vacuo.

(4a*R,7a*R**)-2,4-diphenyl-6-(4-bromophenyl)-4a,7a-dihydrothiopyrano[2,3-c]pyrrole-5,7(4*H*,6*H*)-dione 4e**. Yield is 0.45 g (61%), white powder, Tmelt. = 226-228 °C. ^{1}H NMR (DMSO-d_6, δ, ppm, *J*/Hz): 3.98 (t, 1H, C(4)H, *J* = 5.3), 4.15 (dd, 1H, C(3)H, J_1 = 9.0, J_2 = 4.9), 4.82 (d, 1H, C(2)H, *J* = 8.9), 6.91 – 7.09 (m, 3H,), 7.26 – 7.32 (m, 1H), 7.33 – 7.44 (m, 5H),

7.53 – 7.68 (m, 6H). ^{13}C NMR (DMSO-d6, δ, ppm): 45.81, 45.86, 51.65, 121.49, 126.64, 126.85, 128.16, 128.42, 128.75, 128.80, 129.17, 131.18, 132.04, 137.81, 137.86, 138.92, 174.19, 174.41. Mass-spectrum (ESI), m/z: found 498.0140 $[M+Na]^+$ (73), calculated for $C_{25}H_{18}BrNNaO_2S$ 498.0134.

4-[(4a*R,7a*R**)-2,4-diphenyl-5,7-dioxo-4a,5,7,7a-tetrahydrothiopyrano[2,3-c]pyrrol-6(4*H*)-yl]benzoic acid 4f**. Yield is 0.55 g (40%), white powder, T.melt. = 238-240 °C. ^{1}H NMR (DMSO-d6, δ, ppm, *J*/Hz): 3.99 (t, 1H, C(4)H, J = 5.3), 4.19 (dd, 1H, C(3)H, J_1 = 9.0, J_2 = 5.0), 4.84 (d, 1H, C(2)H, J = 8.9), 7.02 (d, 1H, C(5)H, J = 5.5), 7.14 – 7.22 (m, 2H, ArH), 7.29 (t, 1H, J = 7.3, ArH), 7.33 – 7.47 (m, 5H, ArH), 7.61 (dd, 4H, J_1 = 12.7, J_2 = 8.0, ArH), 7.92 – 8.05 (m, 2H, ArH), 13.13 (s, 1H, COOH). ^{13}C NMR (DMSO -d6, δ, ppm): 45.86, 51.69, 126.66, 126.72, 126.86, 128.18, 128.43, 128.81, 129.17, 129.98, 130.65, 135.67, 137.81, 137.87, 138.93, 166.55, 174.20, 174.41. Mass-spectrum (ESI), m/z: found 464.0931 $[M+Na]^+$ (100), calculated for $C_{26}H_{19}NNaO_4S$ 464.0927.

Funding

The NMR analyses were conducted within the framework of a state assignment of Lomonosov Moscow State University, registration number AAAA-A21-121012290046-4.

Conflict of interest

The authors declare no conflict of interest in financial or any other sphere.

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Received 09.04.2026
Approved after reviewing 05.05.2026
Accepted 28.05.2026