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CONDENSED DIAZEPINES. SYNTHESIS OF 1-R-3,4-DIHYDRO-5*H*-BENZOTHIENO[2,3-*d*][1,2]DIAZEPIN-4-ONES

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Novel 1-R-3,4-dihydro-5H-benzothieno[2,3-d][1,2]diazepin-4-ones have been prepared by the cyclization of 2-acyl(aroyl)benzo[b]thiophene-3-acetic acids or 1-R-benzothieno[2,3-c]pyr-3-ones with hydrazine hydrate.

Keywords: 2-acyl(aroyl)benzo[*b*]thiophene-3-acetic acids, 1-aryl-3,4-dihydro-5*H*-benzothieno[2,3-*d*]-[1,2]diazepin-4-ones, hydrazine hydrate, cyclization.

1-Aryl-3,5-dihydro-4*H*-2,3-benzodiazepin-4-ones are actively studied in connection with their antispasmodic activity [1-4]. They are also of interest as starting materials in the synthesis of condensed triazolo- and tetrazolo-2,3-benzodiazepines [5-9].

Known routes for preparing 2,3-benzodiazepin-4-ones are based on the reaction of hydrazine with 2-aroyl(acetyl)-4,5-dimethoxyphenylacetic acids or their esters [10, 11]. Amongst heterocyclic analogs of 2,3-benzodiazepin-4-ones there are known only 3*H*-[1,2]diazepino[5,6-*b*]indoles and the 2,3-dihydro-2-oxo-1*H*-[1,2]diazepino[4,5-*b*]indoles and 1-aryl-3,4-dihydro-5*H*-benzofuro[2,3-*d*][1,2]diazepin-4-ones obtained by us [12-14].

In continuing our work on the synthesis of hetero analogs of 2,3-benzodiazepin-4-ones, we have studied the cyclization of 2-acyl(aroyl)benzo[*b*]thiophene-3-acetic acids, their methyl esters, and amides using hydrazine hydrate.

Under the same experimental conditions the reaction occurs differently for the 2-acetyl- (**1a**) and 2-propionyl-5-methylbenzo[*b*]thiophene-3-acetic acid (**1b**) with hydrazine hydrate in alcohol or the sodium salts of these acids in water with subsequent acidification by acetic acid. Acid **1a** gives the hydrazone **2**, while the reaction of acid **1b** with hydrazine leads to the azine **3**. Moreover, heating hydrazone **2** in acetic acid does not

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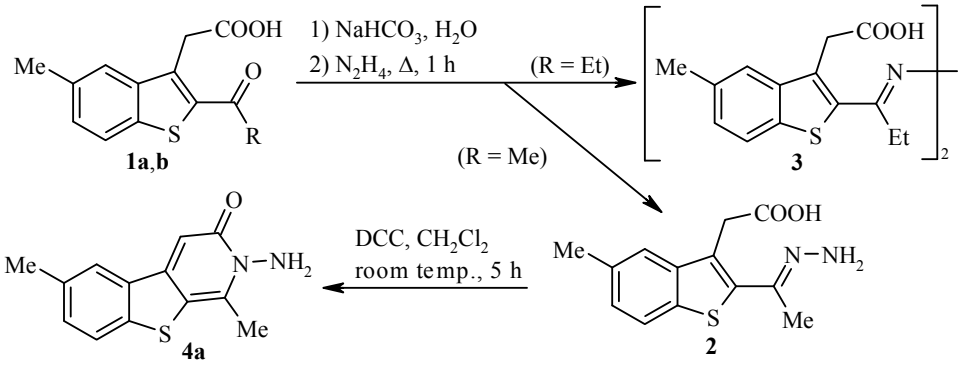
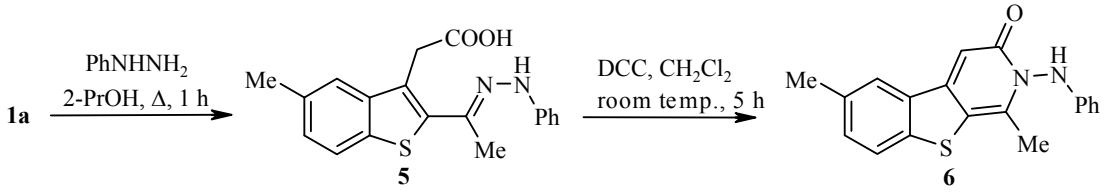
give the corresponding azine (as observed for benzo[*b*]furan and indole hydrazones having a similar structure [13, 15]). In the presence of dicyclohexylcarbodiimide (DCC), the hydrazone **2** cyclizes to 2-amino-1,6-dimethylbenzothieno[2,3-*c*]pyridin-3-one (**4a**).

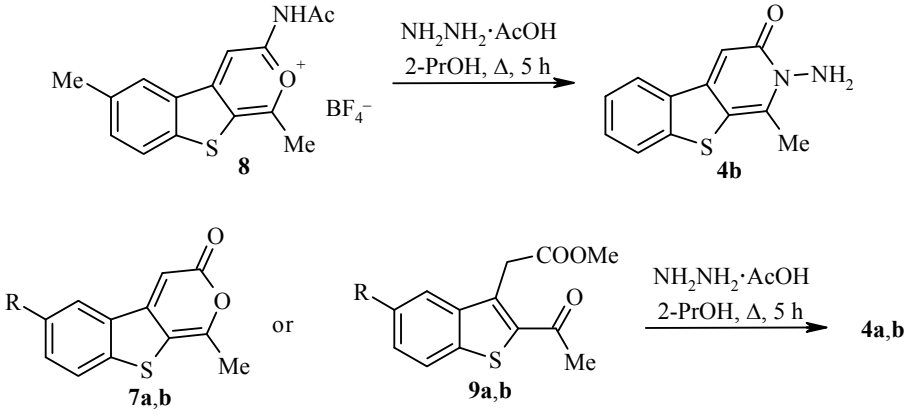


1 **a** R = Me, **b** R = Et

The cyclization of 2-acetyl-5-methylbenzo[*b*]thiophene-3-acetic acid phenylhydrazone (**5**) occurs similarly, in this case forming the 1,6-dimethyl-2-phenylaminobenzothieno[2,3-*c*]pyridin-3-one (**6**).



The 6-R-1-methylbenzothieno[2,3-*c*]pyr-3-ones **7a**,**b**, 3-acetylamino-1,6-dimethylbenzothieno-[2,3-*c*]pyrilium tetrafluoroborate (**8**), and 5-R-2-acetylbenzo[*b*]thiophene-3-acetic acid esters **9a**,**b** react with hydrazine acetate in 2-propanol to form the 2-amino derivatives **4a**,**b**.



7, **9** **a** R = H, **b** R = Me

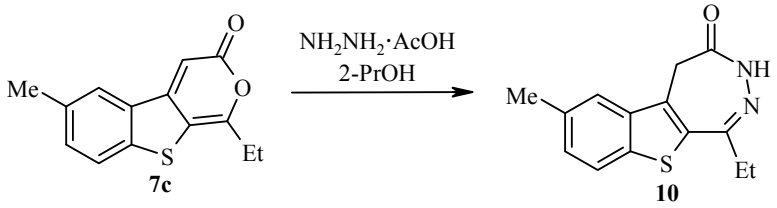
Treatment of 1-ethyl-6-methylbenzothieno[2,3-*c*]pyr-3-one (**7c**) with hydrazine acetate in 2-propanol unexpectedly gave the 1-ethyl-7-methylbenzothieno[2,3-*d*][1,2]diazepin-4-one (**10**).

TABLE 1. Physicochemical Characteristics of the Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %				Mp, °C	Yield, % (method)
		C	H	N	S		
1	2	3	4	5	6	7	8
1a	$C_{13}H_{12}O_3S$	62.76 / 62.88	4.75 / 4.84	—	13.01 / 12.91	173-174	94
1b	$C_{14}H_{14}O_3S$	64.24 / 64.10	5.44 / 5.38	—	12.34 / 12.22		95
2	$C_{13}H_{14}N_2O_2S$	59.41 / 59.52	5.45 / 5.38	10.59 / 10.68	12.31 / 12.22	150-151	83
3	$C_{28}H_{28}N_2O_4S_2$	64.69 / 64.59	5.50 / 5.42	5.47 / 5.38	12.39 / 12.32	179-180	90
4a	$C_{13}H_{12}N_2OS$	64.03 / 63.91	5.02 / 4.95	11.35 / 11.47	13.21 / 13.12	260-261	67 (A) 74 (B) 72 (C) 62 (D)
4b	$C_{12}H_{10}N_2OS$	62.72 / 62.59	4.31 / 4.38	12.22 / 12.16	13.83 / 13.92	252-253	63 (A) 74 (B) 72 (C)
5	$C_{19}H_{18}N_2O_2S$	67.52 / 67.43	5.28 / 5.36	8.15 / 8.28	9.39 / 9.47	186-187	75
6	$C_{19}H_{16}N_2OS$	71.10 / 71.22	5.10 / 5.03	8.82 / 8.74	9.93 / 10.01	234-235	63
7a	$C_{12}H_8O_2S$	66.53 / 66.65	3.65 / 3.73	—	14.43 / 14.83	206-207	92
7c	$C_{14}H_{12}O_2S$	68.70 / 68.83	4.90 / 4.95	—	13.19 / 13.12	118-120	93
8	$C_{14}H_{12}BF_4NO_2S$	48.65 / 48.72	3.43 / 3.50	4.11 / 4.06	9.21 / 9.29	200-201	48
9a	$C_{13}H_{12}O_3S$	62.73 / 62.88	4.81 / 4.87	—	12.84 / 12.91	118-120	78
9b	$C_{14}H_{14}O_3S$	63.97 / 64.10	5.43 / 5.38	—	12.29 / 12.22	105-106	85
10	$C_{14}H_{14}N_2OS$	65.21 / 65.09	5.40 / 5.46	10.92 / 10.84	12.33 / 12.41	189-190	64
11a	$C_{15}H_{19}N_3OS$	62.39 / 62.25	6.70 / 6.62	14.43 / 14.52	11.14 / 11.08	131-132	73
11b	$C_{17}H_{21}N_3O_2S$	61.49 / 61.61	6.48 / 6.39	12.54 / 12.68	9.58 / 9.67	124-125	75
12a	$C_{20}H_{21}N_3OS$	68.45 / 68.35	5.94 / 6.02	11.83 / 11.96	9.18 / 9.12	216-217	84
12b	$C_{20}H_{21}N_3O_2S$	65.48 / 65.37	5.82 / 5.76	11.32 / 11.43	8.83 / 8.73	190-192	82
13a	$C_{17}H_{10}O_2S$	73.45 / 73.36	3.54 / 3.62	—	11.64 / 11.52	216-217	65
13b	$C_{18}H_{12}O_2S$	73.82 / 73.95	4.19 / 4.14	—	11.08 / 10.97	205-207	70
13c	$C_{18}H_{12}O_3S$	70.01 / 70.11	3.99 / 3.92	—	10.31 / 10.40	204-205	72
13d	$C_{19}H_{14}O_4S$	67.31 / 67.44	4.25 / 4.17	—	9.60 / 9.48	203-204	85
13e	$C_{15}H_8O_2S_2$	63.22 / 63.36	2.79 / 2.84	—	22.66 / 22.55	170-172	54
14a	$C_{17}H_{12}O_3S$	69.02 / 68.90	4.13 / 4.08	—	10.94 / 10.82	149-150	55
14b	$C_{18}H_{14}O_3S$	69.80 / 69.66	4.60 / 4.55	—	10.25 / 10.33	158-159	77
14c	$C_{18}H_{14}O_4S$	66.13 / 66.24	4.39 / 4.32	—	9.93 / 9.82	151-152	82
14d	$C_{19}H_{16}O_5S$	64.15 / 64.03	4.59 / 4.53	—	9.11 / 9.00	174-175	88
14e	$C_{15}H_{10}O_3S_2$	59.46 / 59.58	3.39 / 3.33	—	21.32 / 21.21	184-185	85
14f	$C_{19}H_{16}O_3S$	70.47 / 70.35	4.92 / 4.97	—	9.98 / 9.88	194-195	94
14g	$C_{19}H_{16}O_4S$	66.92 / 67.04	4.79 / 4.74	—	9.54 / 9.42	164-165	82

TABLE 1 (continued)

1	2	3	4	5	6	7	8
15a	$C_{17}H_{12}N_2OS$	69.72 69.84	4.20 4.14	9.48 9.58	11.08 10.97	236-237	52 (A) 47 (B)
15b	$C_{18}H_{14}N_2OS$	70.69 70.56	4.56 4.61	9.22 9.14	10.56 10.47	222-224	40 (A) 84 (B) 48 (C)
15c	$C_{18}H_{14}N_2O_2S$	67.18 67.06	4.45 4.38	8.60 8.69	10.02 9.95	198-200	46 (A) 84 (B)
15d	$C_{19}H_{16}N_2O_3S$	64.68 64.76	4.51 4.58	8.02 7.95	9.18 9.10	203-205	44 (A) 45 (B)
15e	$C_{15}H_{10}N_2OS_2$	60.26 60.38	3.42 3.38	9.48 9.39	21.60 21.49	182-183	56 (A) 48 (B)
15f	$C_{19}H_{16}N_2OS$	71.33 71.22	5.10 5.03	8.66 8.74	10.09 10.01	269-270	51 (B) 32 (B)
15g	$C_{19}H_{16}N_2O_2S$	67.72 67.84	4.84 4.79	8.41 8.33	9.65 9.53	218-220	33 (B) 37 (C)
16a	$C_{19}H_{16}O_3S$	70.47 70.35	5.04 4.97	—	9.98 9.88	121-122	68
16b	$C_{20}H_{18}O_3S$	70.87 70.98	5.42 5.36	—	9.59 9.47	136-137	72
16c	$C_{20}H_{18}O_4S$	67.65 67.78	5.07 5.12	—	9.13 9.05	116-117	69



The structure of diazepinone **10** was proved by X-ray structural analysis (Fig. 1).

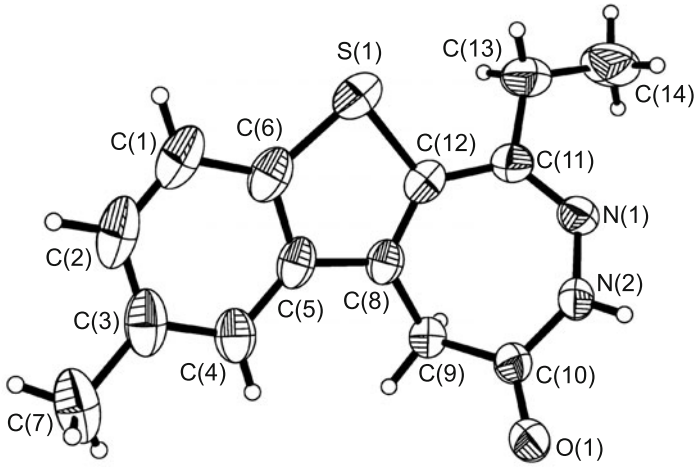
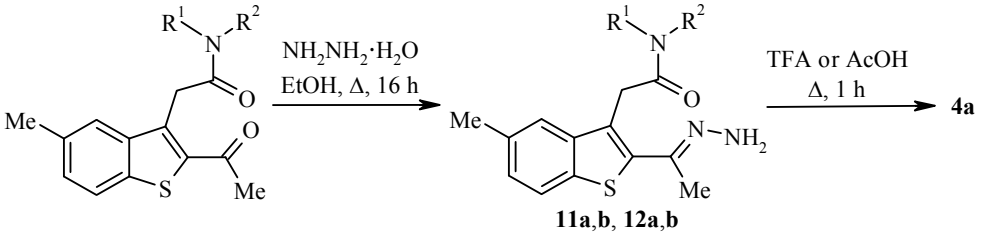


Fig. 1. Molecular structure of compound **10** with atoms represented by thermal vibration ellipsoids of 50% probability.

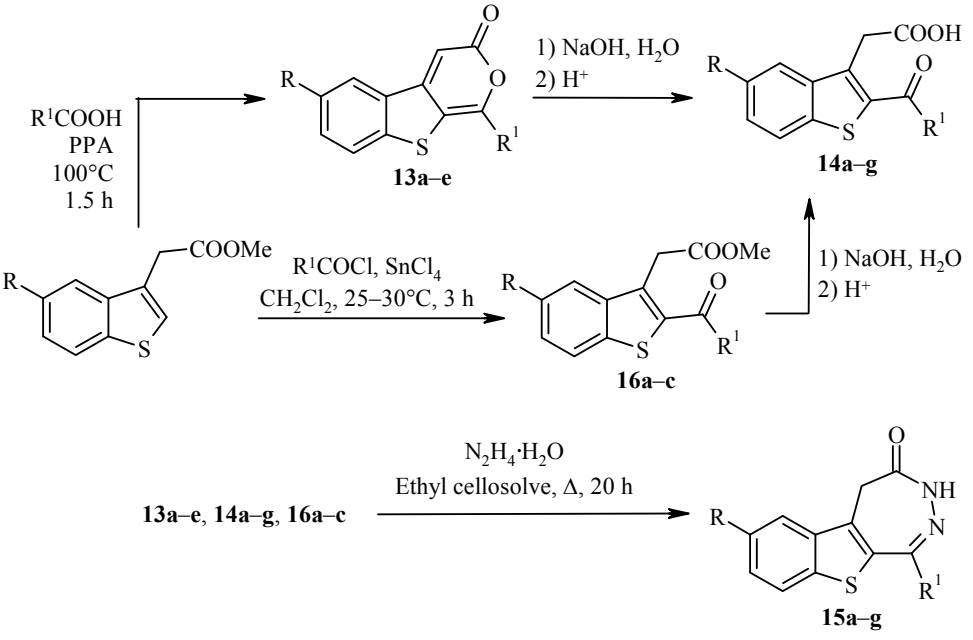
The diazepine ring has a "boat" conformation. The atoms C(10), N(1), and N(2) deviated from the mean square plane of the remaining ring atoms by 0.68, 1.45, and 1.18 Å, respectively. The ethyl group is coplanar with the C(11)–C(12) bond (dihedral angle C(14)–C(13)–C(11)–C(12) is -178.3(3)º). The molecules in the compound **10** crystal form chains along the (0 0 1) crystallographic direction as a result of the intermolecular hydrogen bonds N(2)–H(2B)···O(1)' (0.5+*x*, -0.5+*y*, -0.5+*z*): H···O 2.06 Å, N–H···O 172º).

The 2-acetylbenzo[b]thiophen-3-acetic acid dimethylamide and morpholide [16], and the 2-acetylbenzo[*b*]thiophene-3-acetic acid arylamides [15] react with hydrazine hydrate in alcohol under prolonged reflux to give only the corresponding hydrazones **11a**,**b** and **12a**,**b**. Hydrazinolysis of the amide groups in alcohol does not occur. Subsequent heating of hydrazones **11a**,**b** and **12a**,**b** in acetic or trifluoroacetic acid gives the 2-amino derivative **4a**.



11 a $R^1 = R^2 =$ Me; **b** $R^1+R^2 = (CH_2CH_2)_2O$; **12 a** $R^1 =$ H, $R^2 = 4\text{-MeC}_6H_4$; **b** $R^1 =$ H, $R^2 = 4\text{-MeOC}_6H_4$

The 1-aryl benzothieno[2,3-*c*]pyr-3-ones **13a-e**, prepared by acylation of benzo[*b*]thiophene-3-acetic acid esters using benzoic acids in PPA, are internal esters of the 2-aroylbenzo[*b*]thiophene-3-acetic acids **14a-e**. They can be used in the synthesis of diazepines analogously to benzofuran derivatives [14].



13–15 a–e R = H, **a** $R^1 =$ Ph, **b** $R^1 = 4\text{-MeC}_6H_4$, **c** $R^1 = 4\text{-MeOC}_6H_4$, **d** $R^1 = 3,4\text{-(MeO)}_2C_6H_3$,
e $R^1 =$ 2-thienyl; **f**,**g** R = Me, **f** $R^1 = 4\text{-MeC}_6H_4$, **g** $R^1 = 3\text{-MeOC}_6H_4$;
16 a R = H, $R^1 = 4\text{-MeC}_6H_4$; **b** R = Me, $R^1 = 4\text{-MeC}_6H_4$; **c** R = Me, $R^1 = 3\text{-MeOC}_6H_4$

Conversion of the 1-arylbenzothieno[2,3-*c*]pyrones **13a-e** to the corresponding 1-aryl-3,4-dihydro-5*H* benzothieno[2,3-*d*][1,2]diazepin-4-ones **15a-e** occurs upon prolonged refluxing with a fivefold excess of hydrazine hydrate in ethyl cellosolve in the presence of catalytic amounts of acetic acid (method A). The benzothieno[2,3-*d*][1,2]diazepin-4-ones **15a-g** can also be prepared under analogous conditions by cyclization of the 2-aroylbenzo[*b*]thiophene-3-acetic acids **14a-g** (method B) or their esters **16a-c** (method C). The yields of the diazepines **15a-g** are similar when using the different methods.

TABLE 2. ^{1}H NMR Spectra of the Compounds Synthesized

Compound	Chemical shifts, δ, ppm (*J*, Hz)
1	2
1a	2.51 (3H, s, 5-CH_3); 2.60 (3H, s, $COCH_3$); 4.18 (2H, s, $C\underline{H}_2COOH$); 7.34 (1H, d, *J* = 8.0, H-6); 7.70 (1H, s, H-4); 7.78 (1H, d, *J* = 8.0, H-7); 12.28 (1H, s, COOH)
1b	1.18 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 2.50 (3H, s, 5-CH_3); 2.95 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 4.17 (2H, s, $C\underline{H}_2COOH$); 7.32 (1H, d, *J* = 8.0, H-6); 7.68 (1H, s, H-4); 7.76 (1H, d, *J* = 8.0, H-7); 12.25 (1H, s, COOH)
2	2.21 (3H, s, CH_3C=N); 2.49 (3H, s, 5-CH_3); 3.89 (2H, s, $C\underline{H}_2COOH$); 6.65 (2H, s, NH_2); 7.13 (1H, d, *J* = 8.0, H-6); 7.50 (1H, s, H-4); 7.64 (1H, d, *J* = 8.0, H-7); 12.85 (1H, s, COOH)
3	1.22 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 2.51 (3H, s, 5-CH_3); 3.00 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 4.22 (2H, s, $C\underline{H}_2COOH$); 7.23 (1H, d, *J* = 8.0, H-6); 7.59 (1H, s, H-4); 7.73 (1H, d, *J* = 8.0, H-7); 12.25 (1H, s, COOH)
4a	2.46 (3H, s, 6-CH_3); 2.63 (3H, s, 1-CH_3); 6.45 (2H, s, NH_2); 7.09 (1H, s, H-4); 7.37 (1H, d, *J* = 8.0, H-7); 7.71 (1H, d, *J* = 8.0, H-8); 7.98 (1H, s, H-5)
4b	2.62 (3H, s, 1-CH_3); 6.43 (2H, s, NH_2); 7.21 (1H, s, H-4); 7.44 (1H, t, *J* = 8.0, H-7); 7.56 (1H, t, *J* = 8.0, H-6); 7.90 (1H, d, *J* = 8.0, H-8); 8.21 (1H, d, *J* = 8.0, H-5)
5	2.40 (3H, s, CH_3C=N); 2.50 (3H, s, 5-CH_3); 4.11 (2H, s, $C\underline{H}_2COOH$); 6.76 (1H, t, *J* = 8.0, H-4'); 7.14 (1H, d, *J* = 8.0, H-6); 7.19-7.25 (4H, m, H-2',3',5',6'); 7.48 (1H, s, H-4); 7.65 (1H, d, *J* = 8.0, H-7); 9.27 (1H, s, NH); 12.24 (1H, s, COOH)
6	2.58 (3H, s, 6-CH_3); 2.65 (3H, s, 1-CH_3); 6.62 (2H, d, *J* = 8.0, H-2',6'); 6.84 (1H, t, *J* = 8.0, H-4'); 7.17 (2H, t, *J* = 8.0, H-3',5'); 7.24 (1H, s, H-4); 7.47 (1H, d, *J* = 8.0, H-7); 7.96 (1H, d, *J* = 8.0, H-8); 8.09 (1H, s, H-5); 9.04 (1H, s, NH)
7a	2.40 (3H, s, 1-CH_3); 6.86 (1H, s, H-4); 7.39 (1H, t, *J* = 8.0, H-7); 7.59 (1H, t, *J* = 8.0, H-6); 7.77 (1H, d, *J* = 8.0, H-8); 8.16 (1H, d, *J* = 8.0, H-5)
7c	1.38 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 2.47 (3H, s, 5-CH_3); 2.71 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 6.71 (1H, s, H-4); 7.39 (1H, d, *J* = 8.0, H-7); 7.58 (1H, d, *J* = 8.0, H-8); 7.88 (1H, s, H-5)
8*	2.51 (3H, s, $NHCOC\underline{H}_3$); 3.13 (3H, s, 1-CH_3); 7.78 (1H, t, *J* = 8.0, H-7); 8.01 (1H, t, *J* = 8.0, H-6); 8.06 (1H, d, *J* = 8.0, H-8); 8.57 (1H, d, *J* = 8.0, H-5); 9.02 (1H, s, H-4); 10.55 (1H, s, NHCO)
9a	2.62 (3H, s, CH_3C=O); 3.67 (3H, s, OCH_3); 4.29 (2H, s, CH_2); 7.46 (1H, t, *J* = 8.0, H-6); 7.52 (1H, t, *J* = 8.0, H-5); 7.91 (2H, d, *J* = 8.0, H-4,7)
9b	2.51 (3H, s, 5-CH_3); 2.60 (3H, s, CH_3C=O); 3.65 (3H, s, OCH_3); 4.18 (2H, s, CH_2); 7.34 (1H, d, *J* = 8.0, H-6); 7.70 (1H, s, H-4); 7.78 (1H, d, *J* = 8.0, H-7)
10	1.26 (3H, t, *J* = 7.2, $C\underline{H}_3CH_2$); 2.53 (3H, s, 7-CH_3); 2.78 (2H, q, *J* = 7.2, $CH_3C\underline{H}_2$); 3.56 (2H, s, CH_2); 7.26 (1H, d, *J* = 8.0, H-8); 7.72 (1H, s, H-6); 7.73 (1H, d, *J* = 8.0, H-9); 10.71 (1H, s, NH)
11a	2.13 (3H, s, CH_3C=N); 2.45 (3H, s, 5-CH_3); 2.85 (3H, s) и 3.02 (3H, s, $N(CH_3)_2$); 4.02 (2H, s, CH_2); 6.36 (2H, s, NH_2); 6.95 (1H, d, *J* = 8.0, H-6); 7.17 (1H, s, H-4); 7.40 (1H, d, *J* = 8.0, H-7)
11b	2.06 (3H, s, CH_3C=N); 2.40 (3H, s, 5-CH_3); 3.36-3.52 (8H, m, $N(CH_2CH_2)_2O$); 4.01 (2H, s, CH_2); 6.77 (2H, s, NH_2); 7.02 (1H, d, *J* = 8.0, H-6); 7.31 (1H, s, H-4); 7.41 (1H, d, *J* = 8.0, H-7)
12a	2.23 (3H, s, CH_3C=N); 2.24 (3H, s, 4'-CH_3); 2.49 (3H, s, 5-CH_3); 3.92 (2H, s, CH_2); 6.79 (2H, s, NH_2); 6.98 (2H, d, *J* = 8.0, H-3',5'); 7.13 (1H, d, *J* = 8.0, H-6); 7.40 (2H, d, *J* = 8.0, H-2',6'); 7.63 (1H, d, *J* = 8.0, H-7); 7.73 (1H, s, H-4); 10.52 (1H, s, NH)
12b	2.25 (3H, s, CH_3C=N); 2.50 (3H, s, 5-CH_3); 3.71 (3H, s, 4'-OCH_3); 3.91 (2H, s, CH_2); 6.74 (2H, d, *J* = 8.0, H-3',5'); 6.79 (2H, s, NH_2); 7.13 (1H, d, *J* = 8.0, H-6); 7.45 (2H, d, *J* = 8.0, H-2',6'); 7.62 (1H, d, *J* = 8.0, H-7); 7.75 (1H, s, H-4); 10.45 (1H, s, NH)
13a	7.06 (1H, s, H-4); 7.44 (1H, t, *J* = 8.0, H-7); 7.54 (1H, t, *J* = 8.0, H-4'); 7.60 (2H, d, *J* = 8.0, H-3',5'); 7.62 (1H, t, *J* = 8.0, H-6); 7.73 (1H, d, *J* = 8.0, H-8); 7.96 (2H, d, *J* = 8.0, H-2',6'); 8.22 (1H, d, *J* = 8.0, H-5)
13b	2.45 (3H, s, 4'-CH_3); 7.05 (1H, s, H-4); 7.41 (2H, d, *J* = 8.0, H-3',5'); 7.44 (1H, t, *J* = 8.0, H-7); 7.62 (1H, t, *J* = 8.0, H-6); 7.77 (1H, d, *J* = 8.0, H-8); 7.83 (2H, d, *J* = 8.0, H-2',6'); 8.23 (1H, d, *J* = 8.0, H-5)
13c	3.90 (3H, s, 4'-OCH_3); 7.00 (1H, s, H-4); 7.14 (2H, d, *J* = 8.0, H-3',5'); 7.45 (1H, t, *J* = 8.0, H-7); 7.63 (1H, t, *J* = 8.0, H-6); 7.79 (1H, d, *J* = 8.0, H-8); 7.90 (2H, d, *J* = 8.0, H-2',6'); 8.24 (1H, d, *J* = 8.0, H-5)

TABLE 2 (continued)

1	2
13d	3.87 (3H, s, 3'-OCH_3); 3.89 (3H, s, 4'-OCH_3); 7.09 (1H, s, H-4); 7.19 (1H, d, *J* = 8.0, H-5'); 7.35 (1H, s, H-6'); 7.39 (1H, s, H-2'); 7.51 (1H, t, *J* = 8.0, H-7); 7.65 (1H, t, *J* = 8.0, H-6); 7.87 (1H, d, *J* = 8.0, H-8); 8.29 (1H, d, *J* = 8.0, H-5)
13e	6.96 (1H, s, H-4); 7.30 (1H, t, *J* = 4.0, H-4'); 7.44 (1H, t, *J* = 8.0, H-7); 7.62 (1H, t, *J* = 8.0, H-6); 7.73 (1H, d, *J* = 4.0, H-5'); 7.77 (1H, d, *J* = 8.0, H-8); 7.84 (1H, d, *J* = 4.0, H-3'); 8.19 (1H, d, *J* = 8.0, H-5)
14a	4.06 (2H, s, CH_2); 7.48-7.66 (5H, m, H-5,6,3',4',5'); 7.84-7.97 (4H, m, H-4,7,2',6'); 12.25 (1H, s, COOH)
14b	2.44 (3H, s, 4'-CH_3); 4.03 (2H, s, CH_2); 7.29 (2H, d, *J* = 8.0, H-3',5'); 7.43-7.50 (2H, m, H-5,6); 7.76 (2H, d, *J* = 8.0, H-2',6'); 7.87-7.91 (2H, m, H-4,7); 12.21 (1H, s, COOH)
14c	3.87 (3H, s, 4'-OCH_3); 3.98 (2H, s, CH_2); 6.98 (2H, d, *J* = 8.0, H-3',5'); 7.42-7.49 (2H, m, H-5,6); 7.86 (2H, d, *J* = 8.0, H-2',6'); 7.87-7.90 (2H, m, H-4,7); 12.21 (1H, s, COOH)
14d	3.83 (3H, s, 3'-OCH_3); 3.87 (3H, s, 4'-OCH_3); 4.00 (2H, s, CH_2); 7.01 (1H, d, *J* = 8.0, H-5'); 7.34 (1H, d, *J* = 8.0, H-6'); 7.39 (1H, s, H-2'); 7.45-7.55 (2H, m, H-5,6); 7.87-7.99 (2H, m, H-4,7); 12.33 (1H, s, COOH)
14e	3.00 (COOH in exchange with H_2O); 4.12 (2H, s, CH_2); 7.21 (1H, t, *J* = 4.0, H-4'); 7.45-7.52 (2H, m, H-5,6); 7.86 (1H, d, *J* = 4.0, H-5'); 7.91 (1H, d, *J* = 8.0, H-7); 7.94 (1H, d, *J* = 8.0, H-4); 8.00 (1H, d, *J* = 4.0, H-3')
14f	2.45 (3H, s, 4'-CH_3); 2.51 (3H, s, 5-CH_3); 3.00 (COOH in exchange with H_2O); 4.00 (2H, s, CH_2); 7.28 (2H, d, *J* = 8.0, H-3',5'); 7.31 (1H, d, *J* = 8.0, H-6); 7.67 (1H, s, H-4); 7.75 (2H, d, *J* = 8.0, H-2',6'); 7.75 (1H, d, *J* = 8.0, H-7)
14g	2.52 (3H, s, 5-CH_3); 3.85 (3H, s, 3'-OCH_3); 4.02 (2H, s, CH_2); 7.15 (1H, d, *J* = 8.0, H-4'); 7.32 (2H, m, H-2',6); 7.41 (2H, m, H-5',6'); 7.70 (1H, s, H-4); 7.78 (1H, d, *J* = 8.0, H-7); 12.22 (1H, s, COOH)
15a	3.75 (2H, s, CH_2); 7.42-7.47 (4H, m, H-8,3',4',5'); 7.49 (1H, t, *J* = 8.0, H-7); 7.78 (2H, d, *J* = 8.0, H-2',6'); 7.85 (1H, d, *J* = 8.0, H-9); 8.02 (1H, d, *J* = 8.0, H-6); 11.22 (1H, s, NH)
15b	2.41 (3H, s, 4'-CH_3); 3.73 (2H, s, CH_2); 7.21 (2H, d, *J* = 8.0, H-3',5'); 7.45 (1H, t, *J* = 8.0, H-8); 7.49 (1H, t, *J* = 8.0, H-7); 7.66 (2H, d, *J* = 8.0, H-2',6'); 7.85 (1H, t, *J* = 8.0, H-9); 8.01 (1H, d, *J* = 8.0, H-6); 11.12 (1H, s, NH)
15c	3.72 (2H, s, CH_2); 3.84 (3H, s, 4'-OCH_3); 6.92 (2H, d, *J* = 8.0, H-3',5'); 7.45 (1H, t, *J* = 8.0, H-8); 7.48 (1H, t, *J* = 8.0, H-7); 7.71 (2H, d, *J* = 8.0, H-2',6'); 7.85 (1H, t, *J* = 8.0, H-9); 8.00 (1H, d, *J* = 8.0, H-6); 11.04 (1H, s, NH)
15d	3.74 (2H, s, CH_2); 3.84 (3H, s, 3'-OCH_3); 3.87 (3H, s, 4'-OCH_3); 6.91 (1H, d, *J* = 8.0, H-5'); 7.31 (1H, d, *J* = 8.0, H-6'); 7.37 (1H, s, H-2'); 7.47 (1H, t, *J* = 8.0, H-8); 7.50 (1H, t, *J* = 8.0, H-7); 7.88 (1H, d, *J* = 8.0, H-9); 8.03 (1H, d, *J* = 8.0, H-6); 11.06 (1H, s, NH)
15e	3.74 (2H, s, CH_2); 7.09 (1H, t, *J* = 4.0, H-4'); 7.49-7.54 (3H, m, H-7,8,5'); 7.62 (1H, d, *J* = 4.0, H-3'); 7.92 (1H, d, *J* = 8.0, H-9); 8.03 (1H, d, *J* = 8.0, H-6); 11.16 (1H, s, NH)
15f	2.42 (3H, s, 4'-CH_3); 2.54 (3H, s, 7-CH_3); 3.73 (2H, s, CH_2); 7.24 (2H, d, *J* = 8.0, H-3',5'); 7.31 (1H, d, *J* = 8.0, H-8); 7.66 (2H, d, *J* = 8.0, H-2',6'); 7.77 (1H, d, *J* = 8.0, H-9); 7.83 (1H, s, H-6); 11.18 (1H, s, NH)
15g	2.55 (3H, s, 7-CH_3); 3.72 (2H, s, CH_2); 3.84 (3H, s, 3'-OCH_3); 6.97 (1H, d, *J* = 8.0, H-4'); 7.27-7.34 (4H, m, H-8,2',5',6'); 7.72 (1H, d, *J* = 8.0, H-9); 7.80 (1H, s, H-6); 11.13 (1H, s, NH)
16a	2.47 (3H, s, 4'-CH_3); 3.63 (3H, s, OCH_3); 4.13 (2H, s, CH_2); 7.32 (2H, d, *J* = 8.0, H-3',5'); 7.46-7.53 (2H, m, H-5,6); 7.78 (2H, d, *J* = 8.0, H-2',6'); 7.89-7.93 (2H, m, H-4,7)
16b	2.46 (3H, s, 4'-CH_3); 2.52 (3H, s, 5-CH_3); 3.63 (3H, s, OCH_3); 4.10 (2H, s, CH_2); 7.28 (1H, d, *J* = 8.0, H-3',5'); 7.32 (1H, d, *J* = 8.0, H-6); 7.64 (1H, s, H-4); 7.74-7.78 (2H, m, H-7,2',6')
16c	2.56 (3H, s, 5-CH_3); 3.68 (3H, s, OCH_3); 3.90 (3H, s, 3'-OCH_3); 4.16 (2H, s, CH_2); 7.20 (1H, d, *J* = 8.0, H-4'); 7.36 (1H, s, H-2'); 7.39 (1H, d, *J* = 8.0, H-6); 7.45 (2H, m, H-5',6'); 7.73 (1H, s, H-4); 7.84 (1H, d, *J* = 8.0, H-7)

*Spectrum recorded in $CDCl_3$–CF_3COOH.

TABLE 3. Mass Spectra of Compounds **4b**, **10**, **15a-g**

Compound	*m/z* (I_{rel}, %)*
4b	230 $[M]^+$ (100), 214 (13), 201 (69), 185 (38), 171 (19), 160 (38), 145 (20), 127 (15), 115 (52), 101 (34), 93 (19), 74 (22), 69 (37), 63 (20), 57 (10), 51 (19), 45 (37), 39 (20)
10	259 (12), 258 $[M]^+$ (100), 242 (11), 229 (27), 216 (18), 214 (5), 201 (7), 186 (6), 115 (5), 44 (5)
15a	292 $[M]^+$ (100), 263 (65), 250 (15), 234 (27), 189 (9), 132 (12), 117 (12), 89 (7), 77 (13), 63 (7), 51 (11), 39 (8)
15b	308 (6), 307 (22), 306 $[M]^+$ (100), 305 (27), 278 (14), 277 (63), 264 (12), 263 (8), 249 (6), 247 (5), 235 (10), 234 (20), 202 (5), 145 (5), 139 (8), 138 (9), 131 (9), 123 (5), 117 (10), 104 (5), 102 (5), 101 (5), 91 (8), 78 (6), 69 (5), 45 (5)
15c	324 (5), 323 (18), 322 $[M]^+$ (100), 321 (17), 320 (6), 294 (11), 293 (58), 292 (8), 280 (8), 279 (9), 265 (11), 264 (6), 250 (7), 235 (5), 234 (9), 222 (9), 221 (23), 189 (6), 161 (5), 147 (8), 146 (5), 111 (5), 110 (8), 45 (8)
15d	354 (7), 353 (22), 352 $[M]^+$ (100), 351 (9), 324 (7), 323 (38), 309 (7), 295 (6), 221 (9), 208 (7), 162 (9), 161 (6), 104 (8)
15e	300 (8), 299 (19), 298 $[M]^+$ (100), 297 (5), 283 (6), 271 (6), 270 (13), 269 (64), 268 (6), 256 (7), 255 (12), 254 (8), 241 (11), 240 (15), 208 (6), 135 (7), 120 (13), 45 (8), 44 (8)
15f	320 $[M]^+$ (100), 291 (54), 278 (13), 248 (9), 145 (10), 131 (8), 129 (8), 91 (7)
15g	338 (7), 337 (30), 336 $[M]^+$ (100), 335 (17), 308 (10), 307 (48), 294 (10), 293 (7), 264 (5), 235 (5), 154 (6), 45 (5)

* Peaks reported with intensities greater than 5% that of the base peak.

Hence, we have shown that the route of heterocyclization of 2-acyl(aroyl)benzo[*b*]thiophene-3-acetic acids with hydrazine hydrate depends on the substituents in the acyl fragment, and the reaction requires an acid catalyst. The 2-acetylbenzo[*b*]thiophene-3-acetic acid derivatives do not give cyclic products upon treatment with hydrazine hydrate, yielding only the corresponding hydrazones, treatment of which with organic acids leads to formation of six-membered structures – 2-amino-1,6-dimethylbenzothieno[2,3-*c*]pyridin-3-ones, while aryl substituents favour the production of 5*H*-benzothieno[2,3-*d*][1,2]diazepin-4-ones.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker DRX-400 instrument (400 MHz) using DMSO-d_6 with TMS as internal standard. EI mass spectra were recorded on an MX-1321 mass spectrometer with ionization energy 70 eV, ionization chamber temperature 220ºC, and direct sample injection. Elemental analysis was performed on a Vario MICRO cube CHN analyzer, while sulfur was determined by titration as sulfate anion after combustion in oxygen. Melting points were determined on a Boetius hot stage apparatus. The properties of the products synthesized are given in Tables 1-3.

2-Acetyl-5-methylbenzo[*b*]thiophene-3-acetic Acid (1a) and 5-Methyl-2-propionylbenzo[*b*]thiophene-3-acetic Acid (1b) (General Method). Compound **7b**,**c** (0.010 mol) was added to 30 ml of an aqueous solution containing NaOH (1.0 g, 0.025 mol) and heated to complete dissolution. The solution was cooled and acidified with formic acid. The precipitate formed was filtered off, washed with water, dried, and recrystallized from 2-PrOH.

2-Acetyl-5-methylbenzo[*b*]thiophene-3-acetic Acid Hydrazone (2). A. Compound **1a** (2.48 g, 0.01 mol) was dissolved in 5% aqueous $NaHCO_3$ solution (30 ml), and hydrazine hydrate (2.5 g, 0.05 mol) was added. The mixture was refluxed for 1 h, cooled, and acidified to pH < 7 using acetic acid. The precipitate was filtered off and recrystallized from 2-PrOH.

B. Compound **1a** (2.48 g, 0.01 mol) was dissolved in EtOH (30 ml), and hydrazine hydrate (2.5 g, 0.05 mol) was added. The mixture was refluxed for 1 h, ethanol (20 ml) was distilled off, water (20 ml) was added, and the product was acidified to pH < 7 using acetic acid. The precipitate formed was filtered off and recrystallized from 2-PrOH.

5-Methyl-2-propionylbenzo[*b*]thiophene-3-acetic Acid Azine (3). Obtained similarly to compound **2** (method A) from compound **1b** and recrystallized from aqueous DMSO.

2-Amino-1,6-dimethylbenzothieno[2,3-*c*]pyridin-3(2*H*)-one (4a). A. Dicyclohexylcarbodiimide (0.72 g, 3.5 mmol) was added to a solution of the hydrazone **2** (0.73 g, 3.0 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred for 5 h and the precipitated dicyclohexylurea was filtered off and washed with CH_2Cl_2. The filtrate was evaporated *in vacuo* and recrystallized from MeOH.

B. The corresponding 2-acetylbenzo[b]thiophene-3-acetic acid amide hydrazone **11a**,**b**, **12a**,**b** [16] (1 g) was dissolved in AcOH (20 ml) (in the case of compounds **11a**,**b**) or trifluoroacetic acid (20 ml) (for compounds **12a**,**b**) and refluxed for 1 h. The mixture was cooled, diluted with water (50 ml), and the reaction mixture was neutralized by the addition of aqueous ammonia solution to pH > 7. The precipitate formed was filtered off, washed with water, and recrystallized from MeOH

C. Hydrazine acetate (4.50 g, 0.05 mol) was added to a solution of compound **7b** (2.30 g, 0.01 mol) in 2-PrOH (30 ml), and the reaction mixture was refluxed for 5 h. The target product precipitated during the reaction. The mixture was cooled, the precipitate was filtered off, washed with 2-PrOH and water, and recrystallized from MeOH.

D. Obtained similarly from methyl 2-acetyl-5-methylbenzo[*b*]thiophene-3-acetate (**9b**).

2-Amino-1-methylbenzothieno[2,3-*c*]pyridin-3(2*H*)-one (4b). A. Hydrazine acetate (4.50 g, 0.05 mol) was added to a suspension of the pyrilium tetrafluoroborate **8** (3.45 g, 0.01 mol) in 2-PrOH (30 ml), and the reaction mixture was refluxed for 5 h. The target product precipitated during the reaction. The mixture was cooled, the precipitate was filtered off, washed with 2-PrOH and water, and recrystallized from MeOH.

B. Obtained similarly from 1-methylbenzothieno[2,3-*c*]pyr-3-one (**7a**).

C. Obtained similarly from methyl 2-acetylbenzo[*b*]thiophene-3-acetate (**9a**).

2-Acetyl-5-methylbenzo[*b*]thiophene-3-acetic Acid Phenylhydrazone (5). Phenylhydrazine (1.62 g, 0.015 mol) was added to a solution of compound **1a** (2.48 g, 0.01 mol) in 2-PrOH, and the reaction mixture was refluxed for 1 h. The reaction mixture was cooled, and the precipitate formed was filtered off, washed with cold 2-PrOH, and recrystallized from MeOH.

1,6-Dimethyl-2-phenylaminobenzothieno[2,3-*c*]pyridin-3(2H)-one (6). Obtained by cyclization of phenylhydrazone **5** by a method analogous to method A for preparing compound **4a**. Recrystallized from 2-PrOH.

1-Methylbenzothieno[2,3-*c*]pyr-3-one (7a), 1,6-dimethylbenzothieno[2,3-*c*]pyr-3-one (7b), and 1-ethyl-6-methylbenzothieno[2,3-*c*]pyr-3-one (7c) were prepared by acylation of benzo[*b*]thiophene-3-acetic acid and 5-methylbenzo[*b*]thiophene-3-acetic acid using acetic and propionic anhydrides in the presence of $BF_3 \cdot Et_2O$ *via* the method reported in [17].

3-Acetylamino-1,6-dimethylbenzothieno[2,3-*c*]pyrilium Tetrafluoroborate (8) were prepared by acylation of benzothiophene-3-acetonitrile with acetic anhydride in the presence of $BF_3 \cdot Et_2O$, using the method reported in [18].

Methyl 2-acetylbenzo[*b*]thiophene-3-acetate (9a) and methyl 2-acetyl-5-methylbenzo[*b*]thiophene-3-acetate (9b) were prepared by esterification of the corresponding acids, using the method reported in [19].

1-Ethyl-7-methylbenzothieno[2,3-*d*][1,2]diazepin-4-one (10). Hydrazine acetate (4.50 g, 0.05 mol) was added to a solution of compound **7c** (2.44 g, 0.01 mol) in 2-PrOH (30 ml), and the reaction mixture was refluxed for 5 h. The reaction mixture was evaporated to half volume and diluted with water (20 ml). The precipitate formed was filtered off, washed with water, and recrystallized from 2-PrOH.

Hydrazones of the 2-Acetyl-5-methylbenzo[*b*]thiophene-3-acetic Acid Dimethylamide (11a) and 2-Acetyl-5-methylbenzo[*b*]thiophene-3-acetic Acid Morpholide (11b) (General Method). Hydrazine hydrate (5 ml) was added to a solution of the corresponding 2-acetyl-5-methylbenzo[*b*]thiophene-3-acetic acid amides [16] (0.01 mol) in 2-PrOH (50 ml), and the reaction mixture was refluxed for 3 h. The reaction mixture was cooled, and water (50 ml) was added. The precipitate was filtered off, washed with water, and recrystallized from 2-PrOH.

Hydrazones of 2-Acetyl-5-methylbenzo[*b*]thiophene-3-acetic Acid 4-Methylphenylamide (12a) and 2-Acetyl-5-methylbenzo[*b*]thiophene-3-acetic Acid 4-Methoxyphenylamide (12b) (General Method). Prepared similarly from the corresponding 4-methylphenyl- and 4-methoxyphenylamides of 2-acetyl-5-methylbenzo[*b*]thiophene-3-acetic acid [15].

1-Arylbenzothieno[2,3-*c*]pyr-3-ones 13a-e (General Method). Methyl benzothiophene-3-acetate (6.1 g, 0.03 mol) and the corresponding benzoic acid (0.05 mol) were added to polyphosphoric acid (prepared from 85% H_3PO_4 (22 ml) and P_2O_5 (44 g)). The mixture was stirred at 100ºC for 1.5 h. The reaction mixture was poured into water (400 ml), and K_2CO_3 was added until weakly alkaline (pH 9). The precipitate was filtered off and recrystallized from MeOH.

2-Aroylbenzo[*b*]thiophene-3-acetic Acids 14a-g (General Method). Compounds **13a-e** (0.010 mol) were added to an aqueous solution (30 ml) containing NaOH (1.0 g, 0.025 mol) and heated until full dissolution. The solution was cooled and acidified with formic acid. The precipitated compounds **14a-e** were filtered off, washed with water, dried, and recrystallized from 2-PrOH.

Compounds **14b**,**f**,**g** were prepared similarly from esters **16a-c**.

1-Aryl-3,4-dihydro-5*H*-benzothieno[2,3-*d*][1,2]diazepin-4-ones 15a-g (General Method). A. A solution of the corresponding 1-arylbenzothieno[2,3-*c*]pyrone **13a-e** (1 mmol) in ethyl cellosolve (10 ml) was refluxed for 20 h with hydrazine hydrate (5 mmol) in the presence of catalytic amounts (3-4 drops) of AcOH. The reaction mixture was diluted with water. The precipitated compounds **15a-e** were filtered off, washed with water, and recrystallized from 2-PrOH.

B. Compounds **15a-g** were prepared similarly from the 2-aroylbenzo[*b*]thiophene-3-acetic acids **14a-g**.

C. Compounds **15b**,**f**,**g** were prepared similarly from the 2-aroylbenzo[*b*]thiophene-3-acetic acid esters **16a-c**.

Methyl 2-aroylbenzo[*b*]thiophene-3-acetates 16a-c (General Method). A solution of methyl benzo[*b*]thiophene-3-acetate (1.10 g, 5.0 mmol) in CH_2Cl_2 (5 ml) was added to an acylating mixture prepared from $SnCl_4$ (1.70 g, 6.5 mmol) and the corresponding aroyl chloride (6.0 mmol) in dry CH_2Cl_2 (10 ml). The mixture was stirred at 25-30ºC for 3 h. The reaction mixture was poured into a mixture of ice (40 g) and HCl (7 ml) and extracted with CH_2Cl_2. The extract was washed with a dilute solution of $NaHCO_3$, water, dried over Na_2SO_4, and evaporated. The residue was recrystallized from 2-PrOH.

X-Ray Structural Analysis of Compound 10. Crystals of compound **10** ($C_{14}H_{14}N_2OS$, *M* 258.33) are tetragonal. At 293 K: *a* 19.1490(4), *b* 19.1490(4), *c* 7.3447(3) Å, *V* 2693.19(14) Å^3, *Z* 8; space group *P*-42$_1$*c*, d_{calc} 1.274 g/cm^3; μMoKα 0.230 mm^{-1}, *F*(000) 1088. The unit cell parameters and intensities of 12880 reflections (3882 independent, R_{int} 0.026) were measured on an Xcalibur-3 diffractometer (MoKα radiation, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ 60º). The structure was solved by the direct method using the SHELXTL software package [20]. The positions of the hydrogen atoms were solved from electron density difference synthesis and refined isotropically. The structure was refined by F^2 full-matrix least-squares analysis in the anisotropic approximation for non-hydrogen atoms to wR_2 0.102 for 3834 reflections (R_1 0.045 for 3069 reflections with $F > 4\sigma(F)$, *S* 1.026). The final atomic coordinates, geometric parameters of the molecule, and crystallographic data have been placed in the Cambridge Crystallographic Data Center as deposit CCDC 851691.

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