

2-Bromo-1-arylethyldenemalononitriles - Convenient Reagents for the Regioselective Synthesis of Fused Pyridines.

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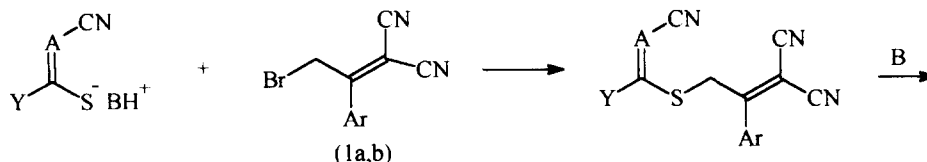
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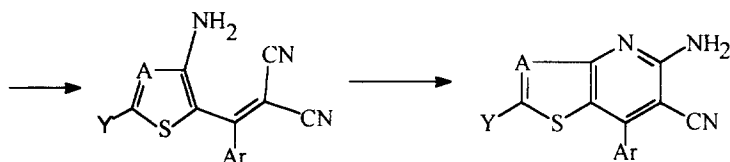
Abstract: 2-Bromo-1-arylethyldenemalononitriles react with conjugated thiolatocyanides to give products of regioselective S alkylation that can be subsequently involved in the Thorpe reaction. Resulting enaminonitriles form pyridine ring under base catalysis yielding thienodipyridines. According to this common scheme, functionally substituted thieno[3,2-*b*]pyridines, thiazolo[4,5-*b*]pyridines, thieno[3,2-*b*:4,5-*b'*]dipyridines, their hydrogenated analogues, and pyrido[2',3':4,5]thieno[2,3-*d*]pyrimidine were synthesized. © 1997 Elsevier Science Ltd.

Substituted thieno- and thiazolopyridines reveal different types of biological activity¹. The known methods of synthesis of these compounds involve several steps, characterizing with rigid conditions and low yields or require hardly accessible starting materials^{2,3}.

For the regioselective synthesis of thieno- or thiazolopyridines we propose 2-bromo-1-arylethyldenemalononitriles (1a,b) as convenient reagents. 2-Bromo-1-phenylethyldenemalononitrile (1a) were prepared for the first time in 1965⁴. Until now several papers concerning the synthetic applications of this reagent have been published. In one group of articles, it is used for cyclopropane synthesis, in others it appears as the reagent in the synthesis of pyrroles⁵⁻⁸. However, no reaction leading to thieno- or thiazolopyridines has been described.

We report now a new convenient method for the synthesis of fused 2-amino-3-cyanopyridines from functionally substituted enethiolatocyanides and 2-bromo-1-arylethyldenemalononitriles. Synthesis of the fused pyridines was performed according to the following scheme:



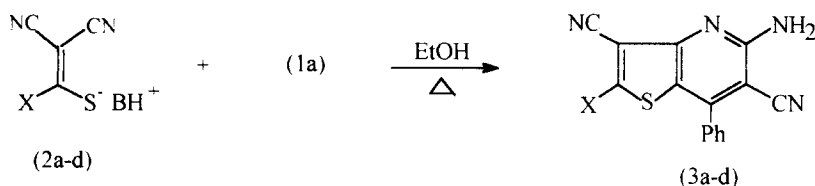


A=N, CR'

B = piperidine (here and later), 1a: Ar = Ph, b: Ar = 4-BrC₆H₄

Initially, regioselective alkylation of thiolate at the S atom with formation of an acyclic product takes place. The latter then undergoes a Thorpe cyclization yielding the aminothiophene or -thiazole ring. Resulting substituted thiophene or thiazole closes the pyridine ring under base catalysis.

Piperidinium 1-substituted-2,2-dicyanoethylene-1-thiolates (2a-c), obtained *in situ* from the corresponding sodium salts⁹, react with (1a) in ethanol at 50-60°C with formation of the thienopyridines (3a-c). Analogously, piperidinium 1-methylthio-2,2-dicyanoethylene-1-thiolate (2d), obtained *in situ* from 2,2-dicyanoethylene-1,1-dithiolate¹⁰ and methyl iodide followed by subsequent treatment by acetic acid and piperidine, yielded thienopyridine (3d):

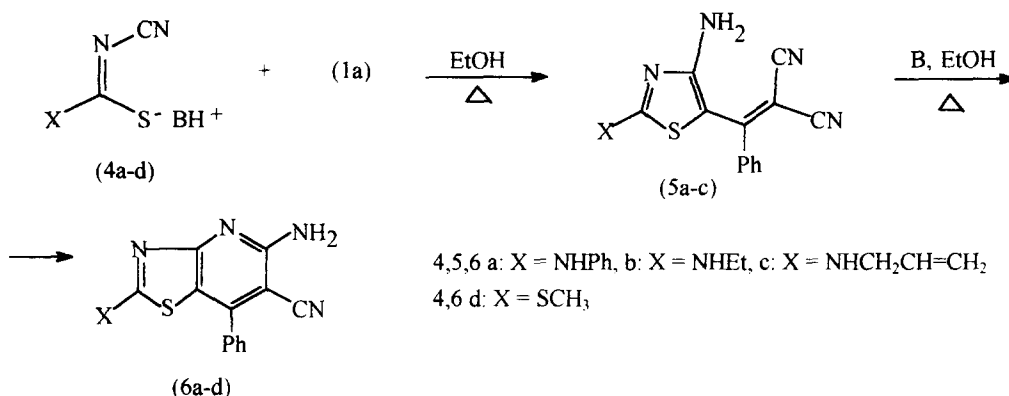


2,3 a: X = PhNH, b: X = EtNH, c: X = CH₂=CHCH₂NH, d: X = SMe

Attempted isolation of acyclic products and substituted thiophenes failed under these conditions.

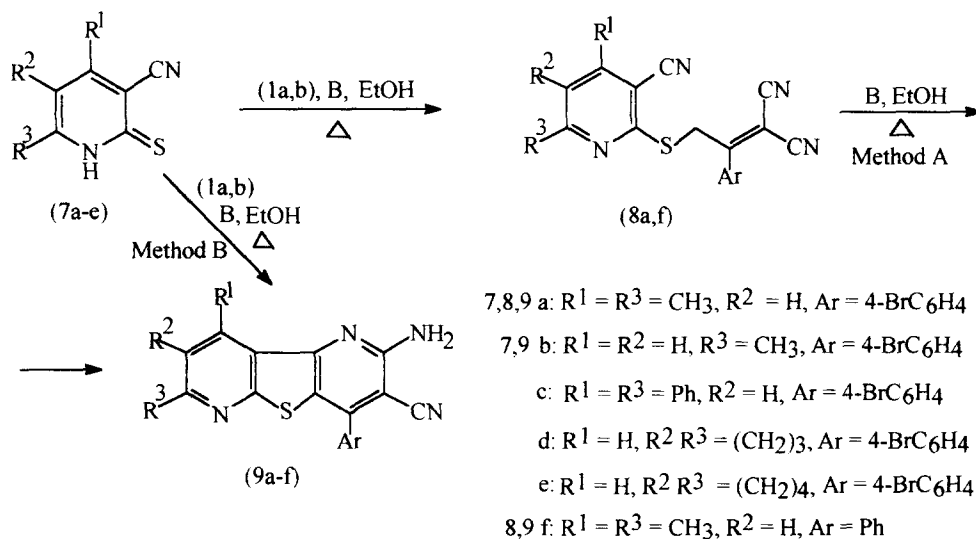
The piperidinium salts of N-substituted-N'-cyanothioureas (4a-c), obtained *in situ* from corresponding sodium salts¹¹, react with (1a) in ethanol at 50-60°C forming the substituted thiazoles (5a-c). Subsequent treatment of these compounds by a catalytic quantity of piperidine in ethanol under heating afford thiazolopyridine (6a-c).

Piperidinium cyanimino(methylthio)carbothiolate (4d), obtained *in situ* from sodium cyanimino-carbodithiolate¹² and methyl iodide followed by subsequent treatment with acetic acid and piperidine, reacts to yield thiazolopyridine (6d):

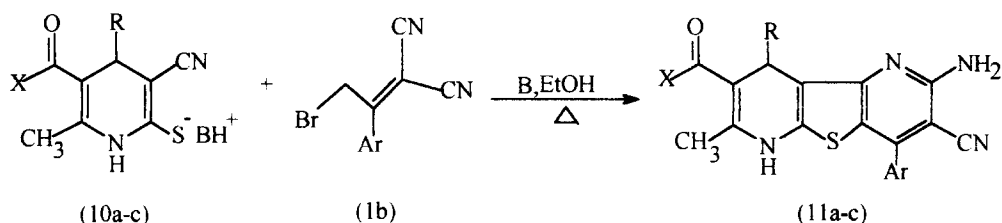


As in the case of the salts (2a-d), isolation of acyclic products failed. The possibility of isolation of thiazoles (5a-c) is connected apparently with reduced nucleophilic activity of NH₂ group in such compounds.

Piperidinium 3-cyanopyridine-2-thiolates, obtained *in situ* from pyridinethiones (7a-e) and piperidine, react with (1a,b) yielding S-alkylated products (8a,f). The possibility of isolation of acyclic products in this case may be explained by considerably lower electrophilicity of nitrile carbon atom than that in the cases described before. In the presence of excess of piperidine, the reaction proceeds further and leads to thienodipyridines (9a,f) (Method A), which were also prepared from starting pyridinethiones (7a,f) by the action of an excess of piperidine followed by addition of (1a,b) (Method B). Also a number of other thienodipyridines (9b-e) were obtained using method B:



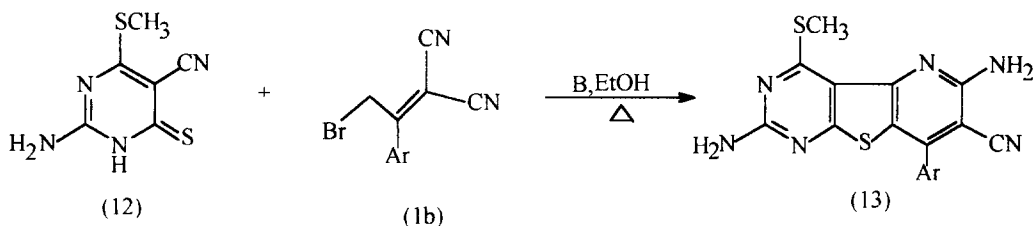
3-Cyano-1,4-dihydropyridine-2-thiolates (10a-c) react with (1b) in ethanol in the presence of a catalytic amount of piperidine with formation of dihydrothienodipyridines (11a-c). In this case stability of hydrogenated structure would allow synthesis of the new type of compounds, analogous to those that possess a cardiotonic activity.



Ar = 4-BrC₆H₄

a: R = 4-MeOC₆H₄, X = OEt; b: R = 2-O₂NC₆H₄, X = Me; c: R = 2-thienyl, X = OEt

3-Cyano-2(1H)-pyrimidinethione (12) reacts with 2-bromo-1-(4-bromophenyl)ethylidenemalononitrile (1b) according to the common scheme forming pyridothienopyrimidine (13), thus opening a way to the synthesis of different functionally-substituted fused pyrimidines.



Ar = 4-BrC₆H₄

Yields and characteristics of prepared compounds are presented in tables 1-3.

IR-Spectra are informative for the establishment of structures of prepared compounds. Thus, in the acyclic compounds (8a,f) two characteristic bands of CN-groups - at 2240-2234 cm⁻¹ (m., aromatic CN) and 2224-2220 cm⁻¹ (s., C(CN)₂) are observed. Spectra of the monocyclic compounds (5a-c) indicate presence of two bands of CN groups at 2150-2210 cm⁻¹. After the closure of the pyridine ring only one band remains. The chemical shifts of protons of NH₂-groups in ¹H NMR-spectra of thiazoles (5a-c) are also characteristic (wide singlet at 6.4-6.65 ppm with reduced intensity), while amino groups in all thieno-(thiazolo)pyridine fragments appear in stronger field up to 8.0 ppm. The NH Group in the spectra of hydrogenated thienodipyridines (11a-c) appear at 10.0-10.5 ppm. In ¹H NMR-spectrum of (13) NH₂ of pyrimidine ring appears at 7.51 ppm.

For ultimate establishment of the structures of thienodipyridines 9 and thiazolopyridines 6 the X-ray analysis of compounds (9f)¹³ and (6c)¹⁴ were run.

Thus, we have found a new common regioselective method for the synthesis of functionally substituted aminothieno(thiazolo)pyridines using enethiolatnitriles and 2-bromo-1-arylethylidene-malononitriles.

EXPERIMENTAL

IR-Spectra were recorded in tablets of KBr on Specord-M80, ^1H and ^{13}C NMR-spectra - on Bruker WM250 (250 MHz) in DMSO- D_6 solution. Elemental analysis was obtained on Perkin-Elmer C,H,N-analyser (obtained data were in agreement with calculated). Yields and characteristics of obtained compounds are presented in the tables 1-3.

Starting materials were prepared by described methods: (1a,b)⁸, (7a-e)^{15,16}, (10a-c)¹⁷, (12)¹⁸ respectively.

2-Amino-6-(substituted amino)-7-phenylthieno[3,2-b]pyridine-3,6-dicarbonitriles(3a-c)

To a solution of 2 mmol of sodium 1-(substituted amino)-2,2-dicyanoethylene-1-thiolate in 15 ml of ethanol a 2 mmol of acetic acid and then after 2 min 2mmol of piperidine were added. The resulting mixture was heated to 50°C and then 2 mmol of 2-bromo-1-phenylethylidenemalononitrile (1a) was added. Precipitated product was filtered off, washed with ethanol and dried in the air.

4-Amino-2-(substituted amino)-5-(2,2-dicyano-1-phenylethenyl)thiazoles (5a-c)

To a solution of 2 mmol of sodium salt of N-substituted-N'-cyanothiourea in 10 ml of ethanol a 2 mmol of acetic acid and then after 2 min 2mmol of piperidine were added. The resulting mixture was heated to 50°C and then 2 mmol of 2-bromo-1-phenylethylidenemalononitrile (1a) was added. Precipitated product was filtered off, washed with small amount of ethanol and dried in the air.

5-Amino-2-(substituted amino)-7-phenylthiazolo[4,5-b]pyridine-6-carbonitriles (6a-c)

Solution of 2 mmol of 4-amino-5-(2,2-dicyano-1-phenyl)-2-(substituted amino)thiazole (5a-c) in 30 ml of ethanol was heated to 50°C and 2-3 drops of piperidine were added. Solution was boiled till the beginning of precipitate formation. Then the resulting mixture was allowed to stand for 30 min. Precipitated product was filtered off, washed with ethanol and dried in the air.

5-Amino-2-methylthio-7-phenylthieno[3,2-b]pyridine-3,6-dicarbonitrile (3d)

To a solution of 2 mmol of sodium 2,2-dicyanoethylene-1,1-dithiolate in 15 ml of ethanol a 2 mmol of methyl iodide was added and mixture was allowed to stand for 0.5h. After that 2 mmol of acetic acid, 2 mmol of piperidine and 2 mmol of (1a) were added consecutively and the mixture was heated to 50°C. Precipitated product was filtered off, washed with ethanol and dried in the air.

5-Amino-2-methylthio-7-phenylthiazolo[4,5-*b*]pyridine-6-carbonitrile (6d)

was synthesised as for 5-amino-2-methylthio-7-phenylthieno[3,2-*b*]pyridine-3,6-dicarbonitrile (3d), sodium cyaniminocarbodithiolate being used instead of sodium 2,2-dicyanoethylene-1,1-dithiolate.

2-(2-Aryl-3,3-dicyano-2-propen-1-ylthio)-4,6-dimethylpyridine-3-carbonitriles (8a,f)

To a solution of 2 mmol of pyridinethione (7a) in 15 ml of ethanol 1.9 mmol of piperidine was added. The resulting mixture was heated to 50°C and then 2 mmol of 2-bromo-1-arylethylidenemalononitrile (1a,b) was added. Precipitated product was filtered off, washed with ethanol and dried in the air.

(8a) ¹³C NMR spectrum, ppm: 19.60 (4-CH₃), 23.94 (6-CH₃), 34.87(CH₂), 86.17(C(CN)₂), 104.8(C3), 112.64 and 112.88(side chain CN), 114.58(3-CN), 121.31(C5), 125.73 (C_p-Ar), 130.21(C_m-Ar), 131.39 (C_o-Ar), 132.78(C_i-Ar), 152.88(C4), 158.39(C2), 161.83(C6), 174.61 (C=C(CN)₂)

(8f) ¹³C NMR spectrum, ppm: 19.60 (4-CH₃), 23.88 (6-CH₃), 34.96(CH₂), 86.60(C(CN)₂), 104.8(C3), 112.86 and 113.10(side chain CN), 114.61(3-CN), 121.27(C5), 128.16 (C_m-Ar), 128.83(C_o-Ar), 132.02 (C_p-Ar), 133.63(C_i-Ar), 152.86(C4), 158.54(C2), 161.83(C6), 175.79 (C=C(CN)₂)

2-Amino-4-aryl-3-thieno[2,3-*b*:4,5-*b'*]dipyridine-3-carbonitriles (9a-f)

Method A. To the solution of (8a,f) in boiling ethanol 2-3 drops of piperidine were added. Precipitated product was filtered off, washed with ethanol and dried in the air.

Method B. To a solution of 2 mmol of pyridinethione (7a-e) in 15 ml of ethanol 2.1 mmol of piperidine was added. The resulting mixture was heated to 50°C and then 2 mmol of 2-bromo-1-arylethylidenemalononitrile (1a,b) was added. Precipitated product was filtered off, washed with ethanol and dried in the air.

2-Amino-4-aryl-6,9-dihydrothieno[2,3-*b*:4,5-*b'*]dipyridine-3-carbonitriles (11a-c)

To a solution of 5 mmol of piperidinium salt (7a) in 20 ml of ethanol 5.1 mmol of (1b) was added. The resulting mixture was heated at 40°C during 10 min and then the resulting mixture was allowed to stand for 30 min. Precipitated product was filtered off, washed with ethanol and dried in the air.

8-(4-Bromophenyl)-2,6-diamino-4-methylthiopyrido[3',2':4,5]thieno[3,2-*d*]pyrimidine-7-carbonitrile (13)

was synthesised as for 2-amino-4-arylthieno[2,3-*b*:4,5-*b'*]dipyridine-3-carbonitriles (9a-f) (method B), 3-Cyano-2(1H)-pyrimidinethione (12) being used instead of pyridinethiones (7a-e).

Acknowledgement: This work was supported by Russian Fundamental Research Found (Grant No. 94-03-08823a)

Table 1. Thienopyridines (3),thiazoles (5) and thiazolopyridines (6)

| Com- pound | Molecular formula | mp, °C | IR-spectrum, ν , cm^{-1} | ^1H NMR-spectrum, ppm, (J, Hz) | Yield, % |
|---------------|--|-------------|--|---|-------------|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 3a | $\text{C}_{21}\text{H}_{13}\text{N}_5\text{S}$ | 260- 262 | 3445,3341,3316, 3197(NH); 2217 (CN);1635,1600, 1533 | 6.91(s.,2H, NH_2), 7.21(m.,1H, p- HNHPh), 7.38(m.,4H, o- HNHPh and m- HNHPh), 7.55(s.,5H, 4-Ph); 10.46(br.s., 1H, NHR) | 72 |
| 3b | $\text{C}_{17}\text{H}_{13}\text{N}_5\text{S}$ | 287- 289 | 3458,3275,3184, 2978(NH); 2210 (CN);1632,1588, 1575,1543,1522 | 1.19(t., J=7, 3H, CH_3), 3.31(q., J=7, 2H, CH_2), 6.88(s., 2H, NH_2), 7.59(s., 5H, Ph); 8.97(s., 1H, NHR) | 81 |
| 3c | $\text{C}_{18}\text{H}_{13}\text{N}_5\text{S}$ | 275- 277 | 3460,3340,3303, 3159(NH); 2211 (CN);1634,1549, 1527 | 3.92(d., 2H, $-\text{CH}_2-$); 5.10-5.28(m., 2H, $=\text{CH}_2$), 5.82 (m., 1H, $-\text{CH}=\text{}$), 6.87(s., 2H, NH_2), 7.55(s., 5H, Ph); 9.27(s., 1H, NHR) | 85 |
| 3d | $\text{C}_{16}\text{H}_{10}\text{N}_4\text{S}_2$ | 286- 288 | 3460, 3312,3170 (NH);2238, 2215 (CN);1681,1545, 1538, 1367 | 2.76(s., 3H, CH_3), 7.23(s., 2H, NH_2); 7.61(s., 5H, Ph) | 88 |
| 5a | $\text{C}_{19}\text{H}_{13}\text{N}_5\text{S}$ | 1 | 3466,3359,3278, 3083(NH); 2212, 2198 (CN);1621, 1601, 1560,1536 | 6.43(br.s., $\sim 1\text{H}$, NH_2) ² , 7.05-7.69(m., 10H, NHPh and 4-Ph), 11.25(s.,1H, NHR) | 93 |
| 5b | $\text{C}_{15}\text{H}_{13}\text{N}_5\text{S}$ | 1 | 3453,3300,3244, 3118,3042 (NH); 2213, 2196(CN); 1641, 1587 | 1.17(t., J=7, 3H, CH_3), 3.40(q., J=7, 2H, CH_2), 6.60(br.s., $\sim 1\text{H}$, NH_2) ² , 7.30-7.63(m., 5H, Ph), 9.31(s., 1H, NHR) | 96 |
| 5c | $\text{C}_{16}\text{H}_{13}\text{N}_5\text{S}$ | 1 | 3448,3297,3160, 3119(NH); 2210, 2191 (CN);1636, 1576, 1457 | 4.01(d., 2H, $-\text{CH}_2-$); 5.20(m., 2H, $=\text{CH}_2$), 5.87 (m., 1H, $-\text{CH}=\text{}$), 6.62(br.s., $\sim 1\text{H}$, NH_2) ² , 7.35-7.62(m.,5H, Ph), 9.48 (s.,1H, NHR) | 96 |
| 6a | $\text{C}_{19}\text{H}_{13}\text{N}_5\text{S}$ | 310- 311 | 3422, 3284,3180 (NH);2212(CN); 1611,1599,1540, 1502 | 6.78(s., 2H, NH_2), 7.00-7.80 (m., 10H, NHPh and 4-Ph), 10.96(s., 1H, NHR) | 59 |
| 6b | $\text{C}_{15}\text{H}_{13}\text{N}_5\text{S}$ | 294- 295 | 3493,3352,3170, 2972(NH); 2220 (CN);1609,1553, 1523, 1449 | 1.20(t., J=7, 3H, CH_3), 3.40(q., J=7, 2H, CH_2), 6.28(s.,2H, NH_2), 7.50-7.59 (m.,5H, Ph), 8.58(s.,1H, NHR) | 67 |

Table 1. Continuation

| 1 | 2 | 3 | 4 | 5 | 6 |
|----|---|-------------|--|--|----|
| 6c | C ₁₆ H ₁₃ N ₃ S | 236- 238 | 3461, 3295, 3103 (NH); 2217(CN); 1642, 1595, 1580, 1523 | 4.01(d., 2H, -CH ₂ -); 5.17(m., 2H, =CH ₂), 5.87 (m., 1H, -CH=), 6.63 (s., 2H, NH ₂), 7.55(s., 5H, Ph), 8.95 (s., 1H, NHR) | 70 |
| 6d | C ₁₄ H ₁₀ N ₄ S ₂ | 216- 218 | 3481, 3272, 3140 (NH); 2210(CN); 1632, 1553, 1531, 1496 | 2.78(s., 3H, CH ₃), 6.79(s., 2H, NH ₂), 7.54-7.66(m., 5H, Ph) | 74 |

¹ Under heating undergoes cyclization with the formation of bicyclic product. The melting point observed is equal to corresponding thiazolopyridine's one.

² The reduced integral is probably due to H-D exchange.

Table 2. Hydrogenated thienodipyridines (11)

| Compound | Molecular formula | mp, °C | IR-spectrum, ν , cm ⁻¹ | H ¹ NMR-spectrum, ppm, (J, Hz) | Yield, % |
|----------|--|-------------|---|--|----------|
| 11a | C ₂₈ H ₂₃ Br N ₄ O ₃ S | 208- 209 | 3460, 3322(NH), 2210(CN), 1690 (C=O), 1608(C=N) | 1.20(t., 3H, J=7, CH ₂ CH ₃), 2.40(s., 3H, 7-CH ₃), 3.69(s., 3H, OCH ₃), 4.05(q., 2H, J=7, CH ₂ CH ₃), 5.32(s., 1H, 9-H), 6.70(s., 2H, 2-NH ₂), 6.76 and 7.27 (AA'BB', 4H, H-9 _{Ar}), 7.56 and 7.82 (AA'BB', 4H, H-4 _{Ar}), 10.21(s., 1H, 6- NH) | 82 |
| 11b | C ₂₆ H ₁₈ Br N ₅ O ₃ S | 210- 212 | 3480, 3380(NH), 2210 (CN), 1645 (C=O), 1604(C=N), 1533(NO ₂) | 2.15(s., 3H, 7-CH ₃), 2.37(s., 3H, COCH ₃), 6.01 (s., 2H, 2-NH ₂), 6.34 (s., 1H, 9-H), 7.37(d.-d., 1H, J ₁ =8.4, J ₂ =6.7, J ₃ =2.1, 4'-H 9 _{Ar}), 7.50 and 7.75(AA'BB', 4H, 4 _{Ar}), 7.54-7.69(m., 2H, 5'.6'-H 9 _{Ar}), 7.85(d.-d., 1H, J ₁ =8.4, J ₂ =1, 3'-H 9 _{Ar}), 13.5(br.s., 1H, 6-NH) | 41 |
| 11c | C ₂₅ H ₁₉ Br N ₄ O ₂ S ₂ | 270 | 3450, 3290(NH), 2210(CN), 1680 (C=O), 1620(C=N) | 1.20(t., 3H, J=7, CH ₂ CH ₃), 2.38(s., 3H, 7-CH ₃), 4.09(q., 2H, J=7, CH ₂ CH ₃), 5.65(s., 1H, 9-H), 6.78(s., 2H, 2-NH ₂), 6.83(m., 2H, 3', 4'-H 9-thienyl), 7.19(d., 1H, J=5, 5'-H 9-thienyl), 7.56 and 7.80 (AA'BB', 4H, 4 _{Ar}), 10.33(s., 1H, 6-NH) | 55 |

Table 3. Pyridines (8), thienodipyridines (9), and pyridothienopyrimidine (13)

| Compound | Molecular formula | mp, °C | IR-spectrum, ν , cm^{-1} | ^1H NMR-spectrum, ppm (J, Hz) | Yield, % |
|----------|--|---------|---|---|----------|
| 8a | $\text{C}_{19}\text{H}_{13}\text{BrN}_4\text{S}$ | 137-138 | 2240(3-CN), 2224 (side chain CN), 1627, 1582, 1548 | 2.37 (s., 3H, 4-CH ₃), 2.57 (s., 3H, 6-CH ₃), 4.90 (s., 2H, CH ₂), 7.15 (s., 1H, H5), 7.48 and 7.76 (AA'BB', 4H, H _{Ar}) | 57 |
| 8f | $\text{C}_{19}\text{H}_{14}\text{N}_4\text{S}$ | 139-140 | 2234(3-CN), 2220 (side chain CN), 1593, 1445 | 2.35 (s., 3H, 4-CH ₃), 2.54 (s., 3H, 6-CH ₃), 4.90 (s., 2H, CH ₂), 7.14 (s., 1H, H5), 7.48-7.60 (m., 5H, H _{Ar}) | 64 |
| 9a | $\text{C}_{19}\text{H}_{13}\text{BrN}_4\text{S}$ | 319-320 | 3484, 3368(NH); 2225(CN); 1627, 1548, 1490 | 2.57 (s., 3H, 7-CH ₃), 2.94 (s., 3H, 9-CH ₃), 7.0 (s., 2H, 2-NH ₂), 7.24 (s., 1H, H8), 7.64 and 7.85 (AA'BB', 4H, H _{Ar}) | 95 |
| 9b | $\text{C}_{18}\text{H}_{11}\text{BrN}_4\text{S}$ | 254-256 | 3485, 3380(NH); 2220(CN); 1640, 1531, 1492 | 2.62 (s., 3H, 7-CH ₃), 7.13 (s., 2H, 2-NH ₂), 7.43 (d., J=8, 1H, H8), 8.36 (d., J=8, 1H, H9), 7.65 and 7.86 (AA'BB', 4H, H _{Ar}) | 72 |
| 9c | $\text{C}_{29}\text{H}_{17}\text{BrN}_4\text{S}$ | 271-272 | 3425, 3304, 3208 (NH); 2222(CN); 1632, 1568, 1522, 1500 | 7.0 - 7.60 (m., 6H, H _{p-Ph} and H _{m-Ph}), 7.50 - 7.60 (m., 4H, H _{o-Ph}), 7.67 and 7.86 (AA'BB', 4H, H _{3-Ar}), 7.95 (s., 2H, 2-NH ₂), 8.02 (s., 1H, H8) | 57 |
| 9d | $\text{C}_{20}\text{H}_{13}\text{BrN}_4\text{S}$ | 305-307 | 3480, 3380, 3350, (NH); 2220(CN); 1616, 1548, 1480 | 2.13 (t., 2H, R ² -R ³), 3.07 (m., 4H., R ² -R ³), 7.11 (s., 2H, 2-NH ₂), 7.67 and 7.86 (AA'BB', 4H, H _{Ar}), 8.28 (s., 1H., H8), | 84 |
| 9e | $\text{C}_{21}\text{H}_{15}\text{BrN}_4\text{S}$ | 308-310 | 3484, 3380(NH); 2222(CN); 1615, 1546, 1492 | 1.75 - 1.95 (m., 4H, R ² -R ³), 2.90 - 3.05 (m., 4H., R ² -R ³), 7.12 (s., 2H, 2-NH ₂), 7.67 and 7.86 (AA'BB', 4H, H _{Ar}), 8.18 (s., 1H., H8), | 87 |
| 9f | $\text{C}_{19}\text{H}_{14}\text{N}_4\text{S}$ | 289-290 | 3517, 3408(NH); 2218(CN); 1620, 1505, 1438 | 2.55 (s., 3H, 7-CH ₃), 2.94 (s., 3H, 9-CH ₃), 6.98 (s., 2H, 2-NH ₂), 7.22 (s., 1H, H8), 7.58-7.70 (m., 5H, H _{Ph}) | 94 |
| 13 | $\text{C}_{17}\text{H}_{11}\text{BrN}_6\text{S}_2$ | >300 | 3465, 3380, 3286, 3160(NH), 2215 (CN), 1620, 1531, 1490 | 2.51 (s., 3H, SCH ₃), 6.90 (s., 2H, 2-NH ₂), 7.41 (s., 2H, 7-NH ₂), 7.59 and 7.82 (4H, AA'BB', H _{Ar}) | 80 |

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