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From benzil arylimines to 2*H*-benzo-1,4-thiazines, benzothiazoles or indoles

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Abstract—A series of benzil monoarylimines (**1**) was treated with phosphorus pentasulfide in refluxing toluene or xylene. Thionation of **1** occurred readily to afford either 2*H*-benzo-1,4-thiazines (**2**) or indoles (**4**) *via* annulation reactions, depending strongly on the nature of the *meta* substituent of the arylamino group. Mechanisms for these rearrangements were proposed. Furthermore, subsequent oxidation of **2** provided benzothiazoles (**3**). All compounds were fully characterized by IR, MS, ^{13}C and ^{1}H NMR. © 2001 Elsevier Science Ltd. All rights reserved.

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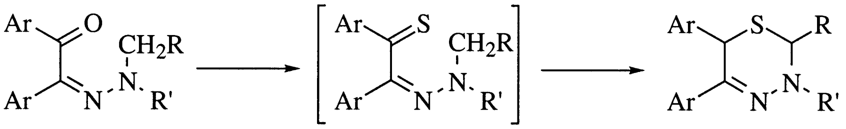
1. Introduction

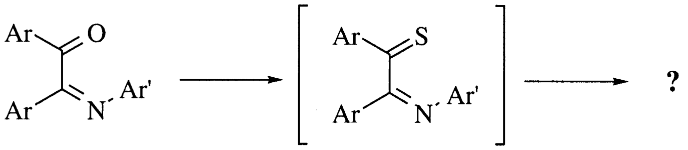
A number of polysubstituted polyheterocyclic compounds display significant pharmacological activities. Among those, benzo-1,4-thiazines,[1] benzothiazoles[2] or indoles[3] have been extensively investigated. For example, highly substituted indoles were recently tested for antiinflammatory, ulcerogenic and antispasmodic activities[4] whereas a methotrexate derivative bearing a benzothiazine moiety was successfully evaluated as an antirheumatic agent[1b]. Furthermore, 2-arylbenzothiazoles are currently confirmed as a novel class of potent and selective antitumor agents[5]. Therefore, it looks important to search for new methods to synthesize such compounds.

In the course of our ongoing studies on heterodienic synthons,[6] we have previously described that thionation of benzil monohydrazones led to 3,6-dihydro-2*H*-1,3,4-thiadiazines by rearrangement.[7] Obviously, the nucleophilic properties of sulfur were assumed to induce cyclization of the corresponding thiocarbonyl derivatives (Scheme 1).

These considerations in mind, we decided to extend this activation method to further 1-oxa-4-azadienes. On the other hand, we planned to develop a novel approach to build complex condensed heterocyclic compounds. α-Aryliminoketones were consequently thought to be suitable candidates for such investigations (Scheme 2).



Scheme 1.



Scheme 2.

Keywords: sulfuration; cyclization; benzothiazines; benzothiazoles; indoles.

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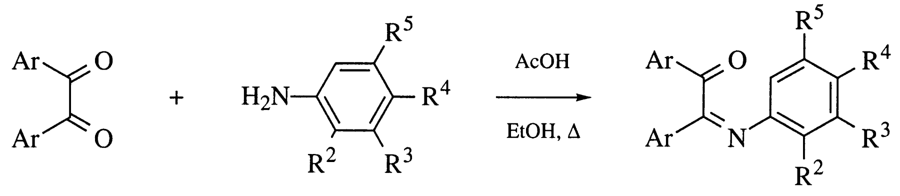


1

Scheme 3.

Table 1. Benzil arylimines **1**

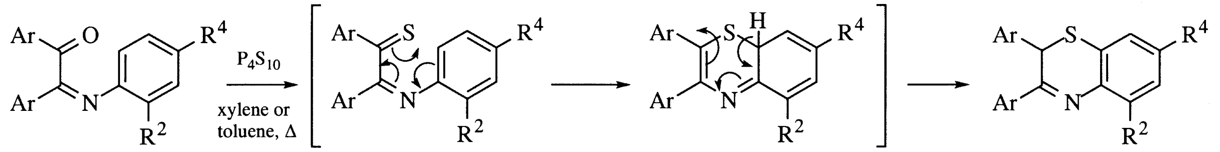
Compd	Ar	R^2	R^3	R^4	R^5	Yield (%)	mp (°C)[a] (Lit.)[Ref.]
1a	C_6H_5	H	H	Cl	H	68	101–103 (98–100)[9,10]
1b	C_6H_5	H	H	H	H	68	117–119 (104–106)[9,10]
1c	C_6H_5	H	H	CH_3	H	80	111–113 (110)[9,10]
1d	C_6H_5	H	OCH_3	H	H	68	86–87
1e	C_6H_5	H	H	OCH_3	H	68	115–118 (114–116)[9,10]
1f	C_6H_5	H	H	SCH_3	H	73	73–76
1g	C_6H_5	H	H	$N(CH_3)_2$	H	78	141–143 (134–136)[10]
1h	C_6H_5	OCH_3	H	OCH_3	H	66	105–106
1i	C_6H_5	H	OCH_3	OCH_3	H	66	87–89
1j	C_6H_5	H	OCH_3	OCH_3	OCH_3	69	yellow oil
1k	C_6H_5	H	H	$N(C_2H_5)_2$	H	71	120–121
1l	*p*-$CH_3OC_6H_4$	H	H	$N(CH_3)_2$	H	75	140–141
1m	*p*-$CH_3OC_6H_4$	H	H	$N(C_2H_5)_2$	H	62	170–171

[a] Compounds **1a–f**, **h**, **j**: yellow crystals, **1g**, **k**, **m**: red crystals, **1l**: orange crystals.

The aim of this paper is to report a part of our work directed to the preparation of benzil arylimines (**1**) substituted with dialkylamino, methoxy or methylsulfanyl groups in different positions on the ring and to the transformation of these compounds into interesting heterocycles via sulfuration reaction of their carbonyl group.

2. Results and discussion

The preparation of benzil monoarylimines (**1**) was accomplished according to a procedure developed in our laboratory[8] by condensation of benzil or *p*-methoxybenzil with one equivalent of an aromatic amine and acetic acid in boiling ethanol (Scheme 3). As the success of the reaction depends upon the nucleophilic properties of the arylamine, the presence of electron-withdrawing substituents in *ortho* or *para* position was to be excluded. Nevertheless, we were able to prepare in good yields a series of differently substituted starting materials, most of them bearing an electron-releasing group in *para* position (Table 1).



1

2

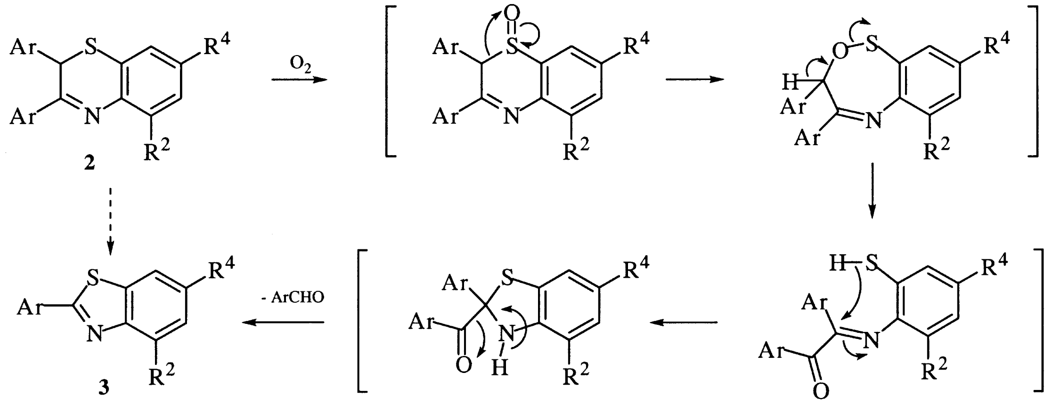
Scheme 4.

Table 2. 2*H*-Benzo-1,4-thiazines **2** and benzothiazoles **3**

Entry	Ar	R^2	R^4	Compd **2**		Compd **3**	
				Yield (%)	mp (°C)[a] (Lit.)[Ref.]	Yield[b] (%)	mp (°C)[a] (Lit.)[Ref.]
a	C_6H_5	H	Cl	35	120–122	–	–
b	C_6H_5	H	H	43	101–103 (100)[16]	67	111–112 (115–116)[17,18]
c	C_6H_5	H	CH_3	43	123–126	79	124–125 (124–126)[18]
e	C_6H_5	H	OCH_3	36	68–71	72	111–113 (114–115)[5b]
f	C_6H_5	H	SCH_3	41	115–118	71	112–114
g	C_6H_5	H	$N(CH_3)_2$	45	151–153	64	130–131 (134–135)[19]
h	C_6H_5	OCH_3	OCH_3	38	139–141	77	125–127
k	C_6H_5	H	$N(C_2H_5)_2$	36	137–140	59	112–113
l	*p*-$CH_3OC_6H_4$	H	$N(CH_3)_2$	38	89–92	67	142–144
m	*p*-$CH_3OC_6H_4$	H	$N(C_2H_5)_2$	38	114–116	73	113–115

[a] Compounds **2**, **3e–g**, **3k–m**: yellow crystals, compounds **3b**, **c**, **h**: white crystals.

[b] Yields based on starting compounds **2.**



Scheme 5.

Table 3. Indoles **4**

Compd	R^4	R^5	Yield (%)	mp (°C)[a] (Lit.)[Ref.]
4d	H	H	79	208–209 (203–204)[20]
4i	OCH_3	H	67	199–200
4j	OCH_3	OCH_3	71	219–220

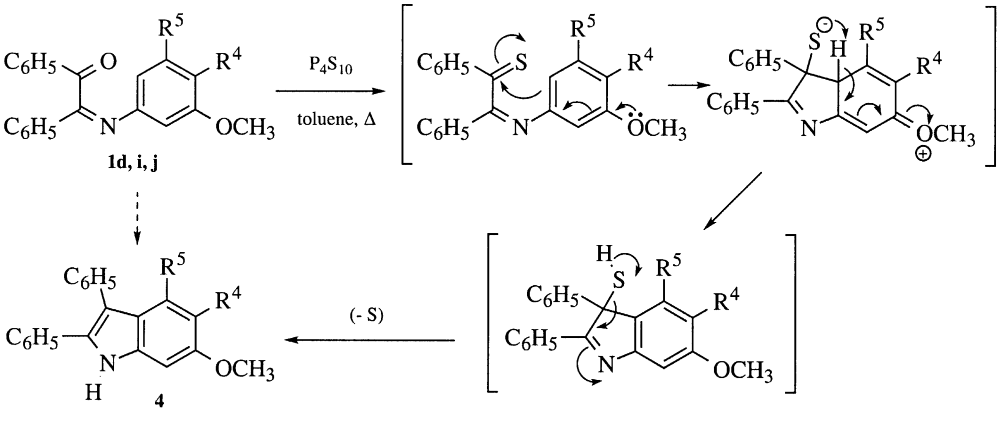
[a] Compounds **4**: white crystals.

Sulfuration of benzil phenylimine has already been investigated by Hafez et al. in the 1980s'. The use of Lawesson's reagent afforded 3,4,5-triphenyl-2-(4-methoxyphenyl)-1,3,2-thiazaphosphole as a sole product instead of the corresponding α-phenyliminothioketone.[11] However, in a following paper, phosphorus pentasulfide was reported to successfully thionate 1,2-diphenyl-2-phenyliminoethanone leading to 1,2-diphenyl-2-phenyliminoethanethione, the latter being described as a stable compound.[12]

In contrast with the above result, we were not able to isolate aryliminothioketones when reacting compounds **1** with phosphorus pentasulfide. In fact, if thionation probably occurred, the generation of the corresponding unstable thioxo derivatives systematically underwent intramolecular cyclization. Interestingly, a clear difference in reactivity was found depending on the position and nature of the substituents on the starting arylamine, inducing annulation to afford unexpectedly either 2*H*-benzo-1,4-thiazines and benzothiazoles or indoles.

In the cases of *para* or *para and ortho* substituted aromatic amines, the reaction furnished predominantly 2*H*-benzo-1,4-thiazines (**2**). We suggest the reaction to proceed through the carbonyl sulfuration, followed by an intramolecular [4+2] cyclization involving both the thiazadienic system and the aromatic ring, and achieved by a [1,5]-proton shift (Scheme 4).

It must be pointed out that oxidation of **2** leading to benzothiazoles (**3**) by ring contraction is certainly involved during the workup procedure. Thus, the yields of **2** given in Table 2 are somewhat underestimated. Indeed, the resulting benzothiazines were found to be unstable when purified by column chromatography. However, once they have been isolated, stability of **2** must be emphasized. It is also noteworthy that the reaction can be completed at the benzothiazole stage by heating overnight the corresponding benzothiazines with silica without any solvent (Table 2). These results are not surprising since it is well known that exposing a 1,4-thiazine to oxidation leads easily to sulfoxides, which may then evolve towards thiazoles.[13] We suggest that oxidation of 2*H*-benzo-1,4-thiazines with oxygen provides benzoylthiazolines in the same way, which then undergo a ring contraction with concomitant



Scheme 6.

loss of benzaldehyde, giving rise to benzothiazoles (**3**) (Scheme 5). The latest mechanism step has already been proposed by Bayer et al.[14] Furthermore, a slightly different mechanism was recently reported by Puebla et al., who have successfully carried out the dehydrogenation of a 3,4-dihydro-2*H*-benzo-1,4-thiazine with DDQ in order to confirm its structure and observed the ring contraction of the resulting benzothiazolium salt under basic conditions.[15]

Conversely, in the presence of an initial aromatic amine bearing a *meta* methoxy group, the reaction occurred in the same conditions to provide unequivocally indoles (**4**) in high yields with total regioselectivity, as indicated in Table 3. Although the mechanistic details of this reaction remain unknown, we speculate that the benzil arylimine is also first converted to the α-aryliminothioketone. However, in this case, the electron-donating effect of the 3-methoxy substituent is strong enough to induce an intramolecular conjugate addition regiospecifically at the 6-position of the arylamine moiety rather than the [4+2] cyclization path, thus yielding to **4** through an electrophilic substitution followed by sulfur extrusion (Scheme 6). The indoles were unambiguously characterized by spectroscopic data. The ^{1}H NMR spectrum of **4i** showed two singlets at δ 6.91 and 7.09 due to the indolic protons and thus excluded the 4,5-dimethoxy structure.

So this last reaction allows to prepare a desulfurized compound via the thionation of the stable carbonyl starting material. Moreover our method offers a reliable alternative to previous indolization routes[20] such as Fischer cyclization, since it provides exclusively one regioisomer in high yields.

3. Conclusion

In summary, this study has shown powerfull new applications of 1-thia-4-azadienes, which have already provided an easy access to 1,4-thiazines, thiazoles, thiazolines and even to 1,3,4-thiadiazines.[2] Interestingly, the synthetic usefulness of this method is based on the possibility of synthesizing either 2*H*-benzo-1,4-thiazines and benzothiazoles or indoles by the opportune choice of the C-3 substituent on the initial arylamine. Further work exploiting the potential of this approach applied to polysubstituted heterocycles actually investigated in the laboratory will be reported very soon.

4. Experimental

4.1. General

All reagents were purchased from Acros Organics and Aldrich. The elemental analyses were performed by the C.N.R.S. Analysis Laboratory (Vernaison). Column chromatography was conducted on silica gel 60 (40–63 μm), available from E. Merck. Thin layer chromatography was performed on 0.5 mm×20 cm×20 cm E. Merck silica gel plate (60 F-254). Melting points measured using a Reichert microscope were uncorrected. The ^{13}C and ^{1}H NMR spectra were recorded at room temperature using a BRUKER AC 200 at 50 and 200 MHz, respectively. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane as internal standard. Mass spectra were determined with a Hewlett Packard 5989 spectrometer. The IR spectra were obtained using a BRUKER Vector 22 spectrometer.

All microanalyses were satisfactory (C ±0.3; H ±0.3; N ±0.3; S ±0.3).

4.2. Preparation of starting benzil monoarylimines 1

To a solution of benzil (5 mmol) and acetic acid (5 mmol) in ethanol (8 mL) was added the aromatic amine (5 mmol) (7.5 mmol for **1a**) at room temperature (for **1a**, the reaction was performed without acetic acid, but in toluene with 3 Å molecular sieves (2 g)). After stirring under reflux for 20 h, the solvent was removed. The mixture was then diluted with ethyl acetate, washed with a saturated solution of NH_4Cl, dried over $MgSO_4$ and evaporated under vacuum. The crude product was chromatographed (eluting with CH_2Cl_2 for **1g**, **k**, **l**, **m**; CH_2Cl_2/petroleum ether (4:1) for **1d**, **e**, **f**, **h**, **i**, **j**; CH_2Cl_2/petroleum ether (3:2) for **1a**, **b**, **c**), affording compounds **1**, which were crystallized from ethanol (except for **1j**, which was isolated as an oil).

Physical and analytical data are presented in Tables 1 and 4.

4.3. Sulfuration of benzil monoarylimines. Preparation of benzothiazines 2 and indoles 4

To a solution of benzil monoarylimine (**1**) (3 mmol) in xylene (**2a**, **b**, **c**, **e**, **f**, **h**) or toluene (**2g**, **k**, **l**, **m**, **4**) (30 mL) was added portionwise P_4S_{10} (0.9 mmol for **2a**, **b**, **c**, **f**, **g**, **h**; 1.2 mmol for **2e**, **k**, **l**, **m**; 0.6 mmol for **4**). The reaction mixture was refluxed for 24 h for **2** or 4 h for **4**. Then it was cooled, filtered through a short pad of celite and concentrated under reduced pressure. Purification by flash chromatography (using as eluant CH_2Cl_2 for **2g**, **h**, **k**, **l**, **m**; CH_2Cl_2/petroleum ether (4:1) for **2e**, **f**, **4**; CH_2Cl_2/petroleum ether (3:2) for **2a**, **b**, **c**) afforded compounds **2** and **4**, which were crystallized from ether (**2**) or ethanol (**4**).

Physical and analytical data are presented in Tables 3, 5 and 6.

4.4. Preparation of benzothiazoles 3

The benzothiazine (**2**) (1 mmol) was vigorously stirred at 100°C with silica (0.5 g) for 20 h. The mixture was cooled, then diluted with CH_2Cl_2 and chromatographed (using as eluent CH_2Cl_2 for **3b**, **c**, **e**, **f**, **h**; CH_2Cl_2/ethyl acetate (19:1) for **3g**, **k**, **l**, **m**). Compounds **3** were crystallized from ethanol.

Physical and analytical data are presented in Tables 3 and 7.

Acknowledgements

The authors wish to express their gratitude to the French Ministry of Education and CNRS for financial support.

Table 4. Physical data for benzil arylimines **1**

Compd	^{1}H RMN ($CDCl_3$) δ, ppm	^{13}C RMN ($CDCl_3$) δ, ppm	IR (KBr)[a] cm^{-1}	MS m/e (%)
1a	6.82, 7.09 (2d, *J*=8.5 Hz, 4 H-Ar), 7.32–7.55 (m, 6 H-Ar), 7.73–7.89 (m, 4 H-Ar)	122.0, 123.3, 128.9, 129.0, 129.1, 129.5, 132.1, 134.7 (14 CH-Ar), 130.2, 134.7, 135.0, 147.9 (4 C-Ar), 167.1 (C=N), 197.4 (C=O)	1664, 1624, 1477, 1192, 906, 836, 690, 666	321/319 (1/3, M$^{+\cdot}$), 217/215 (10/32), 216/214 (70/100), 113/111 (16/51), 77 (32), 75 (37), 51 (13)
1b	6.86–6.95 (m, 3H-Ar), 7.08–7.16 (m, 2 H-Ar), 7.27–7.52 (m, 6 H-Ar), 7.73–7.91 (m, 4 H-Ar)	120.6, 124.8, 128.3, 128.8, 129.0, 129.4, 131.8, 134.4 (15 CH-Ar), 134.9, 135.3, 149.4 (3 C-Ar), 166.4 (C=N), 197.8 (C=O)	1667, 1622, 1591, 1576, 695, 687	285 (4, M$^{+\cdot}$), 181 (22), 180 (100), 77 (53), 51 (22)
1c	2.17 (s, 3H, CH_3), 6.80, 6.93 (2d, *J*=8.1 Hz, 4H-Ar), 7.29–7.51 (m, 6 H-Ar), 7.75–7.89 (m, 4 H-Ar)	21.0 (CH_3), 120.7, 128.2, 128.9, 129.0, 129.4, 129.5, 131.7, 134.4 (14 CH-Ar), 134.5, 134.8, 135.5, 146.8 (4 C-Ar), 166.0 (C=N), 198.2 (C=O)	1664, 1619, 1575, 1446, 1226, 1193, 1169, 698	299 (6, M$^{+\cdot}$), 195 (37), 194 (100), 91 (55), 77 (18), 65 (43)
1d	3.65 (s, 3H, OCH_3), 6.44–6.49 (m, 3H-Ar), 7.01 (t, *J*=8.0 Hz, 1 H-Ar), 7.34–7.49 (m, 6H-Ar), 7.75–7.89 (m, 4H-Ar)	55.3 (OCH_3), 106.1, 111.1, 113.1 128.3, 129.1 129.5, 129.6, 131.9, 134.4 (14 CH-Ar), 135.0, 135.2, 150.6, 159.9 (4 C-Ar), 166.5 (C=N), 197.6 (C=O)	1601, 1577, 1140, 692	315 (2, M$^{+\cdot}$), 211 (15), 210 (100), 107 (10), 92 (20), 77 (30)
1e	3.68 (s, 3H, OCH_3), 6.66, 6.89 (2d, *J*=8.7 Hz, 4H-Ar), 7.26–7.51 (m, 6 H-Ar), 7.75–7.88 (m, 4 H-Ar)	55.2 (OCH_3), 113.9, 122.2, 127.9, 128.7, 128.8, 129.2, 131.4, 134.3 (14 CH-Ar), 134.5, 135.3, 142.3, 157.0 (4 C-Ar), 165.3 (C=N), 198.6 (C=O)	1669, 1501, 1289, 1240	315 (5, M$^{+\cdot}$), 211 (15), 210 (100), 92 (13), 77 (23)
1f	2.36 (s, 3H, SCH_3), 6.84, 7.04 (2d, *J*=8.7 Hz, 4H-Ar), 7.28–7.56 (m, 6 H-Ar), 7.72–8.00 (m, 4 H-Ar)	16.4 (SCH_3), 121.5, 127.4, 128.2, 129.0, 129.0, 129.2, 129.4, 130.1 (14 CH-Ar), 131.8, 134.6, 135.0, 146.8 (4 C-Ar), 166.3 (C=N), 198.0 (C=O)	1674, 1576, 1475, 1447, 1231, 1196, 826, 697, 691	331 (11, M$^{+\cdot}$), 227 (18), 226 (100), 77 (8)
1g	2.83 (s, 6H, $N(CH_3)_2$), 6.50, 6.93 (2d, *J*=8.9 Hz, 4H-Ar), 7.25–7.50 (m, 6 H-Ar), 7.76–7.89 (m, 4 H-Ar)	40.5 ($N(CH_3)_2$), 112.4, 122.9, 127.7 128.6, 128.8, 129.2, 130.8, 134.1 (14 CH-Ar), 134.5, 135.9, 138.4, 148.4 (4 C-Ar), 162.9 (C=N), 199.8 (C=O)	1666, 1511, 820, 700, 690	328 (13, M$^{+\cdot}$), 224 (16), 223 (100), 105 (7), 77 (11)
1h	3.65, 3.68 (2s, 6H, 2 OCH_3), 6.23 (d, *J*=9.4 Hz, 1H-Ar), 6.26 (s, 1H-Ar), 6.68 (d, *J*=9.4 Hz, 1H-Ar), 7.25–7.50 (m, 6 H-Ar), 7.79–7.89 (m, 4 H-Ar)	55.4 (2 OCH_3), 99.3, 103.6, 121.5, 128.3, 128.6, 128.8, 129.1, 131.5, 134.2 (13 CH-Ar), 132.4, 134.7, 135.5, 151.4, 158.3 (5 C-Ar), 166.5 (C=N), 197.9 (C=O)	1666, 1608, 1599, 1499, 1209, 1190, 1157, 1129	345 (6, M$^{+\cdot}$), 241 (16), 240 (100), 210 (8), 77 (7)
1i	3.72, 3.75 (2s, 6H, 2 OCH_3), 6.50 (dd, *J*=8.4 Hz, *J*=2.3 Hz, 1 H-Ar), 6.55 (d, *J*=2.3 Hz, 1 H-Ar), 6.63 (d, *J*=8.4 Hz, 1 H-Ar), 7.29–7.53 (m, 1H-Ar), 7.74–7.80 (m, 4H-Ar)	55.8, 56.0 (2 OCH_3), 105.7, 111.2, 113.0, 128.1, 128.9, 129.0, 129.3, 131.6, 134.4 (13 CH-Ar), 134.8, 135.4, 142.8, 146.6, 148.9 (5 C-Ar), 165.8 (C=N), 198.8 (C=O)	1668, 1507, 1258, 1237, 1134, 1022	345 (6, M$^{+\cdot}$), 241 (16), 240 (100), 122 (12), 79 (17), 77 (18), 51 (11)
1j	3.66 (s, 6H, 2 OCH_3), 3.70 (s, 3H, OCH_3), 6.16 (s, 2 H-Ar), 7.31–7.55 (m, 6H-Ar), 7.76–7.90 (m, 4H-Ar)	55.8 (2 OCH_3), 60.7 (OCH_3), 98.5, 128.0, 128.7, 129.1, 131.6, 134.2 (12 CH-Ar), 134.9, 135.0, 145.1, 153.0 (6 C-Ar), 166.4 (C=N), 198.1 (C=O)	1671, 1583, 1502, 1448, 1222, 1177, 1119, 1007, 690	375 (22, M$^{+\cdot}$), 271 (20), 270 (100), 109 (12), 105 (48), 81 (13), 77 (69), 66 (15), 51 (23)
1k	1.05 (t, *J*=7.1 Hz, 6H, 2 CH_3), 3.23 (q, *J*=7.1 Hz, 4H, 2 NCH_2), 6.45, 6.94 (2d, *J*=9.0 Hz, 4H-Ar), 7.30–7.51 (m, 6 H-Ar), 7.78–7.85 (m, 4 H-Ar)	12.5 (2 CH_3), 44.4 (2 NCH_2), 111.9, 123.5, 127.7 128.6, 128.8, 129.3, 130.7, 134.0 (14 CH-Ar), 134.8, 136.1, 137.5, 146.0 (4 C-Ar), 162.1 (C=N), 200.2 (C=O)	1663, 1612, 1511, 1269, 1207, 818, 697, 682	356 (18, M$^{+\cdot}$), 252 (18), 251 (100), 77 (12)
1l	2.82 (s, 6H, $N(CH_3)_2$), 3.77, 3.81 (2s, 6H, 2 OCH_3), 6.51, 6.93 (2d, *J*=8.9 Hz, 4H-Ar), 6.79, 7.76 (2d, *J*=8.8 Hz, 4H-Ar), 6.89, 7.80 (2d, *J*=8.9 Hz, 4H-Ar)	40.7 ($N(CH_3)_2$), 55.5, 55.6 (2 OCH_3), 112.7, 114.1, 114.2 122.9, 129.6, 131.9 (12 CH-Ar), 128.0, 129.0, 139.1, 148.3, 161.9, 164.3 (6 C-Ar), 163.0 (C=N), 198.2 (C=O)	1601, 1599, 1515, 1259, 1173	388 (7, M$^{+\cdot}$), 254 (18), 253 (100), 169 (10), 149 (14), 105 (10), 77 (17)
1m	1.06 (t, *J*=7.1 Hz, 6H, 2 CH_3), 3.24 (q, *J*=7.1 Hz, 4H, 2 NCH_2), 3.79, 3.82 (2s, 6H, 2 OCH_3), 6.46, 6.92 (2d, *J*=9.0 Hz, 4H-Ar), 6.80, 7.78 (2d, *J*=9.0 Hz, 4H-Ar), 6.89, 7.78 (2d, *J*=8.9 Hz, 4H-Ar)	12.6 (2 CH_3), 44.5 (2 NCH_2), 55.4, 55.5 (2 OCH_3), 112.2, 114.1, 114.2 123.4, 129.5, 131.9 (12 CH-Ar), 128.1, 129.2, 138.1, 145.8, 161.8, 164.3 (6 C-Ar), 162.2 (C=N), 198.6 (C=O)	1594, 1515, 1268, 1174, 1161	416 (14, M$^{+\cdot}$), 282 (20), 281 (100), 237 (7), 133 (8)

[a] Except for **1j**: film.

Table 5. Physical data for 2*H*-benzo-1,4-thiazines **2**

Compd	^{1}H RMN ($CDCl_3$) δ, ppm	^{13}C RMN ($CDCl_3$) δ, ppm	IR (KBr) cm^{-1}	MS m/e (%)
2a	5.25 (s, 1H, CH), 7.13–7.26 (m, 7 H-Ar), 7.37–7.46 (m, 3 H-Ar), 7.50 (d, J=8.9 Hz, 1 H-Ar), 7.92–8.01 (m, 2 H-Ar)	38.9 (CH), 127.0, 127.3, 127.4, 127.7, 128.2, 128.9, 129.0, 129.3, 131.2 (13 CH-Ar), 121.7, 132.7, 137.3, 138.0, 141.6 (5 C-Ar), 157.5 (C=N)	1594, 1449, 1446, 726, 693, 688	337/335 (30/78, $M^{+\cdot}$), 336/334 (53/100), 260/258 (6/15), 178 (14), 165 (10)
2b	5.24 (s, 1H, CH), 7.10 (t, J=7.5 Hz, 1 H-Ar), 7.16–7.24 (m, 7 H-Ar), 7.42–7.44 (m, 3 H-Ar), 7.59 (d, J=7.9 Hz, 1 H-Ar), 7.97–8.00 (m, 2 H-Ar)	34.4 (CH), 123.4, 125.4, 126.6, 127.8, 128.6, 129.2, 129.2, 130.1, 130.4 (14 CH-Ar), 121.8, 131.2, 133.8, 135.2 (4 C-Ar), 154.2 (C=N)	–	301 (83, $M^{+\cdot}$), 300 (100), 224 (19), 223 (10), 197 (12), 178 (12), 165 (23), 121 (13), 77 (11)
2c	2.26 (s, 3H, CH_3), 5.20 (s, 1H, CH), 7.03 (s, 1 H-Ar), 7.05 (d, J=7.9 Hz, 1 H-Ar), 7.16–7.21 (m, 5 H-Ar), 7.40–7.41 (m, 3 H-Ar), 7.46 (d, J=7.9 Hz, 1 H-Ar), 7.95–7.97 (m, 2 H-Ar)	21.3 (CH_3), 39.3 (CH), 127.4, 127.6, 127.8, 128.0, 128.1, 128.2, 128.8, 128.9, 130.7 (13 CH-Ar), 119.3, 137.6, 138.1, 138.5, 141.0 (5 C-Ar), 156.2 (C=N)	1606, 1446, 817, 764, 724, 693, 690	315 (74, $M^{+\cdot}$), 314 (100), 238 (18), 178 (12), 165 (13)
2e	3.75 (s, 3H, OCH_3), 5.20 (s, 1H, CH), 6.70 (d, J=2.8 Hz, 1 H-Ar), 6.78 (dd, J=8.7 Hz, J=2.8 Hz, 1 H-Ar), 7.19–7.25 (m, 5 H-Ar), 7.39–7.42 (m, 3 H-Ar), 7.51 (d, J=8.7 Hz, 1 H-Ar), 7.92–7.97 (m, 2 H-Ar)	39.3 (CH), 55.6 (OCH_3), 112.0, 113.3, 127.4, 128.0, 128.8, 128.9, 129.7, 130.5 (13 CH-Ar), 121.0, 137.3, 138.2, 138.5, 158.7 (5 C-Ar), 154.7 (C=N)	1679, 1603, 1226, 1211, 826, 684	331 (68, $M^{+\cdot}$), 330 (100), 254 (11)
2f	2.44 (s, 3H, SCH_3), 5.24 (s, 1H, CH), 7.03 (d, J=2.1 Hz, 1 H-Ar), 7.09 (dd, J=8.3 Hz, J=2.1 Hz, 1 H-Ar), 7.11–7.19 (m, 5 H-Ar), 7.39–7.45 (m, 3 H-Ar), 7.49 (d, J=8.3 Hz, 1 H-Ar), 7.93–8.00 (m, 2 H-Ar)	15.7 (SCH_3), 39.2 (CH), 124.5, 124.7, 127.4, 127.6, 128.1, 128.6, 128.8, 129.0, 130.81 (13 CH-Ar), 120.7, 137.8, 138.1, 138.3, 140.5 (5 C-Ar), 156.2 (C=N)	1681, 1477, 1049, 1035, 824, 758, 683	347 (88, $M^{+\cdot}$), 346 (100), 331 (12), 270 (18), 184 (10), 178 (13), 122 (29), 121 (19)
2g	2.92 (s, 6H, $N(CH_3)_2$), 5.17 (s, 1H, CH), 6.43 (d, J=2.8 Hz, 1 H-Ar), 6.58 (dd, J=8.7 Hz, J=2.8 Hz, 1 H-Ar), 7.15–7.24 (m, 5 H-Ar), 7.35–7.39 (m, 3 H-Ar), 7.45 (d, J=8.7 Hz, 1 H-Ar), 7.89–7.94 (m, 2 H-Ar)	39.9 (CH), 40.4 ($N(CH_3)_2$), 110.0, 110.9, 127.1, 127.4, 127.8, 128.7, 128.9, 129.8, 129.9 (13 CH-Ar), 120.7, 133.9, 138.9, 139.0, 149.7 (5 C-Ar), 152.1 (C=N)	1607, 1576, 1551, 1442, 1368	344 (100, $M^{+\cdot}$), 343 (93), 267 (18)
2h	3.74, 3.94 (2s, 6H, 2 OCH_3), 5.22 (s, 1H, CH), 6.31 (d, J=2.4 Hz, 1 H-Ar), 6.34 (d, J=2.4 Hz, 1 H-Ar), 7.14–7.29 (m, 5 H-Ar), 7.34–7.44 (m, 3 H-Ar), 7.91–8.00 (m, 2 H-Ar)	39.0 (CH), 55.6, 56.4 (2 OCH_3), 98.0, 102.7, 127.4, 127.6, 127.9, 128.7, 128.8, 130.3 (12 CH-Ar), 122.0, 127.8, 137.9, 138.8, 152.7, 159.2 (6 C-Ar), 156.7 (C=N)	1597, 1558, 1313, 1150, 1060, 695	361 (100, $M^{+\cdot}$), 360 (77), 346 (15), 284 (7), 270 (40)
2k	1.13 (t, J=7.1 Hz, 6H, 2 CH_3), 3.30 (q, J=7.1 Hz, 4H, 2 NCH_2), 5.16 (s, 1H, CH), 6.37 (d, J=2.9 Hz, 1 H-Ar), 6.54 (dd, J=9.0 Hz, J=2.9 Hz, 1 H-Ar), 7.17–7.29 (m, 5 H-Ar), 7.33–7.40 (m, 3 H-Ar), 7.54 (d, J=9.0 Hz, 1 H-Ar), 7.88–7.93 (m, 2 H-Ar)	12.7 (2 CH_3), 39.9 (CH), 44.4 (2 NCH_2), 109.0, 110.1, 126.9, 127.3, 127.6, 128.5, 128.8, 129.7, 130.0 (13 CH-Ar), 120.8, 133.0, 138.9, 139.1, 147.2 (5 C-Ar), 151.1 (C=N)	1608, 1493, 1352, 1197, 695	372 (100, $M^{+\cdot}$), 371 (75), 358 (16), 357 (60), 328 (10), 327 (18)
2l	2.89 (s, 6H, $N(CH_3)_2$), 3.66, 3.79 (2s, 6H, 2 OCH_3), 5.12 (s, 1H, CH), 6.43 (d, J=2.5 Hz, 1 H-Ar), 6.57 (dd, J=8.9 Hz, J=2.5 Hz, 1 H-Ar), 6.68, 7.12 (2d, J=8.5 Hz, 4 H-Ar), 6.88, 7.88 (2d, J=8.7 Hz, 4 H-Ar), 7.42 (d, J=8.9 Hz, 1 H-Ar)	39.2 (CH), 40.5 ($N(CH_3)_2$), 55.2, 55.5 (2 OCH_3), 110.2, 110.9, 114.0, 114.3, 128.5, 128.7, 129.4 (11 CH-Ar), 120.5, 130.9, 131.5, 134.0, 149.4, 159.1, 161.1 (7 C-Ar), 152.1 (C=N)	1604, 1509, 1254, 1172, 834	404 (100, $M^{+\cdot}$), 403 (57), 389 (29)
2m	1.13 (t, J=6.9 Hz, 6H, 2 CH_3), 3.30 (q, J=6.9 Hz, 4H, 2 NCH_2), 3.70, 3.81 (2s, 6H, 2 OCH_3), 5.11 (s, 1H, CH), 6.38 (d, J=2.1 Hz, 1 H-Ar), 6.54 (dd, J=8.8 Hz, J=2.1 Hz, 1 H-Ar), 6.71, 7.14 (2d, J=8.5 Hz, 4 H-Ar), 6.88, 7.86 (2d, J=8.8 Hz, 4 H-Ar), 7.39 (d, J=8.8 Hz, 1 H-Ar)	12.8 (2 CH_3), 39.4 (CH), 44.4 (2 NCH_2), 55.2, 55.5 (2 OCH_3), 109.3, 110.2, 114.0, 114.2, 128.6, 129.7 (11 CH-Ar), 120.7, 131.1, 131.6, 133.2, 147.0, 159.1, 161.0 (7 C-Ar), 151.2 (C=N)	1599, 1508, 1259, 830, 783	432 (100, $M^{+\cdot}$), 431 (54), 418 (27), 417 (96), 373 (10), 227 (10), 216 (13), 208 (14), 132 (12)

Table 6. Physical data for benzothiazoles **3**

Compd	^{1}H RMN ($CDCl_3$) δ, ppm	^{13}C RMN ($CDCl_3$) δ, ppm	IR (KBr) cm^{-1}	MS m/e (%)
3b	7.37 (td, J=7.6 Hz, J=1.2 Hz, 1 H-Ar), 7.46–7.50 (m, 4 H-Ar), 7.88 (ddd, J=8.1 Hz, J=1.2 Hz, J=0.6 Hz, 1 H-Ar), 8.06–8.11 (m, 3 H-Ar)	121.8, 123.4, 125.3, 126.5, 127.7, 129.2, 131.1 (9 CH-Ar), 133.8, 135.2, 154.3 (3 C-Ar), 168.2 (C=N)	1479, 963, 767, 687	212 (15, (M+1)$^{+\cdot}$), 211 (100, M$^{+\cdot}$), 108 (23), 69 (16)
3c	2.49 (s, 3H, CH_3), 7.29 (dd, J=8.2 Hz, J=1.2 Hz, 1 H-Ar), 7.45–7.49 (m, 3 H-Ar), 7.68 (m, 1 H-Ar), 7.94 (d, J=8.2 Hz, 1 H-Ar), 8.04–8.09 (m, 2 H-Ar)	21.5 (CH_3), 121.3, 122.7, 127.4, 127.9, 128.9, 130.7 (8 CH-Ar), 133.7, 135.2, 135.3, 152.2 (4 C-Ar), 167.0 (C=N)	1480, 816, 768, 690	226 (28, (M+1)$^{+\cdot}$), 225 (100, M$^{+\cdot}$), 122 (26), 121 (40), 112 (13), 78 (16), 77 (23)
3e	3.85 (s, 3H, OCH_3), 7.07 (dd, J=8.9 Hz, J=2.6 Hz, 1 H-Ar), 7.31 (d, J=2.6 Hz, 1 H-Ar), 7.42–7.50 (m, 3 H-Ar), 7.94 (d, J=8.9 Hz, 1 H-Ar), 8.00–8.04 (m, 2 H-Ar)	55.9 (OCH_3), 104.2, 115.8, 123.8, 127.3, 129.1, 130.7 (8 CH-Ar), 133.9, 136.5, 148.8, 157.9 (4 C-Ar), 165.7 (C=N)	1483, 1265, 1226, 829	242 (26, (M+1)$^{+\cdot}$), 241 (100, M$^{+\cdot}$), 227 (13), 226 (84), 198 (34), 95 (31)
3f	2.55 (s, 3H, SCH_3), 7.38 (dd, J=8.6 Hz, J=1.9 Hz, 1 H-Ar), 7.43–7.50 (m, 3 H-Ar) 7.73 (d, J=1.9 Hz, 1 H-Ar), 7.94 (d, J=8.6 Hz, 1 H-Ar), 8.00–8.08 (m, 2 H-Ar)	16.8 (SCH_3), 119.1, 123.4, 126.1, 127.6, 129.2, 131.1 (8 CH-Ar), 133.7, 136.1, 136.3, 152.3 (4 C-Ar), 167.3 (C=N)	1478, 1259, 812, 758, 684	258 (29, (M+1)$^{+\cdot}$), 257 (100, M$^{+\cdot}$), 243 (11), 242 (72), 139 (18), 95 (15)
3g	3.02 (s, 6H, $N(CH_3)_2$), 6.96 (dd, J=9.1 Hz, J=2.5 Hz, 1 H-Ar), 7.11 (d, J=2.5 Hz, 1 H-Ar), 7.43–7.50 (m, 3 H-Ar), 7.90 (d, J=9.1 Hz, 1 H-Ar), 8.00–8.04 (m, 2 H-Ar)	41.0 ($N(CH_3)_2$), 103.0, 113.5, 123.3, 127.1, 128.9, 130.1 (8 CH-Ar), 134.2, 137.3, 146.2, 148.9 (4 C-Ar), 163.1 (C=N)	1604, 1593, 1574, 1507, 1440, 1354, 956, 687	255 (27, (M+1)$^{+\cdot}$), 254 (100, M$^{+\cdot}$), 253 (56), 239 (13), 238 (15)
3h	3.86, 4.03 (2s, 6H, 2 OCH_3), 6.54 (d, J=1.8 Hz, 1 H-Ar), 6.91 (d, J=1.8 Hz, 1 H-Ar) 7.41–7.44 (m, 3 H-Ar), 8.04–8.08 (m, 2 H-Ar)	55.9, 56.2 (2 OCH_3), 95.3, 98.1, 127.4, 128.9, 130.4 (7 CH-Ar), 133.8, 137.6, 139.5, 154.0, 159.1 (5 C-Ar), 164.2 (C=N)	1574, 1271, 1212, 1151	272 (29, (M+1)$^{+\cdot}$), 271 (100, M$^{+\cdot}$), 270 (74), 242 (52), 241 (28), 228 (11), 227 (11), 226 (14), 213 (12), 121 (26), 82 (11), 69 (10)
3k	1.22 (t, J=7.1 Hz, 6H, 2 CH_3), 3.43 (q, J=7.1 Hz, 4H, 2 NCH_2), 6.90 (dd, J=9.0 Hz, J=2.2 Hz, 1 H-Ar), 7.06 (d, J=2.2 Hz, 1 H-Ar) 7.37–7.52 (m, 3 H-Ar), 7.86 (d, J=9.0 Hz, 1 H-Ar), 7.96–8.08 (m, 2 H-Ar)	12.7 (2 CH_3), 45.1 (2 NCH_2), 102.3, 113.1, 123.7, 127.2, 129.1, 130.1 (8 CH-Ar), 134.3, 137.7, 145.7, 146.4 (4 C-Ar), 162.6 (C=N)	1592, 1543, 1509, 1468, 1354, 1273	283 (11, (M+1)$^{+\cdot}$), 282 (45, M$^{+\cdot}$), 268 (18), 267 (100), 239 (24), 238 (17), 211 (15), 210 (13)
3l	3.03 (s, 6H, $N(CH_3)_2$), 3.85 (s, 3H, OCH_3), 7.04 (dd, J=9.0 Hz, J=2.4 Hz, 1 H-Ar), 7.30 (d, J=2.4 Hz, 1 H-Ar), 7.89 (d, J=9.0 Hz, 1 H-Ar), 6.96, 7.95 (2d, J=8.9 Hz, 4 H-Ar)	41.4 ($N(CH_3)_2$), 55.6 (OCH_3), 103.6, 113.6, 114.4, 123.0, 128.7 (7 CH-Ar), 127.1, 131.9, 137.1, 146.6, 148.5 (5 C-Ar), 161.4 (C=N)	1607, 1483, 1251, 1174	285 (27, (M+1)$^{+\cdot}$), 284 (100, M$^{+\cdot}$), 283 (17), 270 (10), 269 (50), 241 (10), 142 (17)
3m	1.20 (t, J=7.1 Hz, 6H, 2 CH_3), 3.41 (q, J=7.1 Hz, 4H, 2 NCH_2), 3.85 (s, 3H, OCH_3), 6.88 (dd, J=9.0 Hz, J=2.5 Hz, 1 H-Ar), 7.05 (d, J=2.5 Hz, 1 H-Ar), 7.82 (d, J=9.0 Hz, 1 H-Ar), 6.96, 7.94 (2d, J=8.7 Hz, 4 H-Ar)	12.5 (2 CH_3), 45.3 (2 NCH_2), 55.6 (OCH_3), 103.8, 113.8, 114.4, 123.3, 128.7 (7 CH-Ar), 127.1, 131.9, 137.4, 145.6, 146.0 (5 C-Ar), 161.5 (C=N)	1608, 1465, 1252, 1170	313 (16, (M+1)$^{+\cdot}$), 312 (58, M$^{+\cdot}$), 298 (21), 297 (100), 269 (15), 268 (21), 253 (10), 135 (33)

Table 7. Physical data for indoles **4**

Compd	^{1}H RMN δ, ppm[a]	^{13}C RMN δ, ppm[a]	IR (KBr) cm^{-1}	MS m/e (%)
4d	3.82 (s, 3H, OCH_3), 6.75 (dd, J=8.9 Hz, J=2.3 Hz, 1 H-Ar), 7.00 (d, J=2.3 Hz, 1 H-Ar), 7.18–7.51 (m, 11 H-Ar), 10.40 (br s, 1H, NH)	55.7 (OCH_3), 95.2, 110.9, 120.5, 126.9, 127.9, 128.8, 129.3, 129.3, 130.8 (13 CH-Ar), 115.0, 124.0 (2 C=C), 133.8, 134.0, 136.7, 138.2, 157.8 (5 C-Ar)	3338, 1260, 1196, 1158, 1122, 697	299 (100, M$^{+\cdot}$), 285 (14), 284 (68), 257 (10), 254 (11)
4i	3.87, 3.91 (2s, 6H, 2 OCH_3), 6.91, 7.09 (2s, 2 H-Ar), 7.25–7.45 (m, 10 H-Ar), 8.14 (br s, 1H, NH)	56.3, 56.6 (2 OCH_3), 94.6, 101.5, 126.3, 127.3, 127.9, 128.7, 128.8, 130.2 (12 CH-Ar), 115.1, 121.9 (2 C=C), 130.6, 132.9, 133.1, 136.6, 145.8, 147.7 (6 C-Ar)	3407, 1491, 1474, 1465, 1338, 1244, 1193, 1145, 702, 699	329 (100, M$^{+\cdot}$), 315 (11), 314 (49), 286 (20), 148 (11), 120 (10)
4j	3.30, 3.69, 3.83 (3s, 9H, 3 OCH_3), 6.77 (s, 1 H-Ar), 7.18–7.34 (m, 10 H-Ar), 11.36 (br s, 1H, NH)	56.9, 60.5, 60.8 (3 OCH_3), 90.4, 126.0, 126.7, 127.4, 127.6, 128.2, 130.9 (11 CH-Ar), 113.2, 115.4 (2 C=C), 132.5, 132.6, 133.0, 136.2, 136.4, 146.3, 150.6 (7 C-Ar)	3363, 1498, 1293, 1106, 696	359 (100, M$^{+\cdot}$), 345 (10), 344 (37), 301 (21), 286 (21), 230 (17), 164 (18)

[a] Spectra were recorded in Acetone d6 for **4d**, $CDCl_3$ for **4i**, DMSO d6 for **4j**.

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