Synthesis of dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-ones from 2-nitrobenzoic acids

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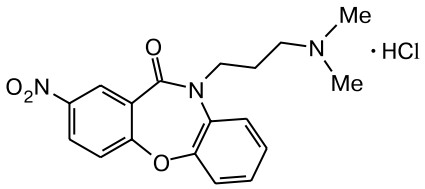
Base-catalyzed intramolecular nucleophilic substitution for the 2-nitro group in 2-hydroxyanilides of 2-nitrobenzoic acids gave dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-ones. In particular, 3-nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one was obtained from *N*-(2-hydroxyphenyl)-2,4-dinitrobenzamide. The nitro group in the product could also be replaced under the action of O- and S-nucleophiles.

Key words: benzamides, nitroarenes, dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-ones, nucleophilic substitution, heterocyclization.

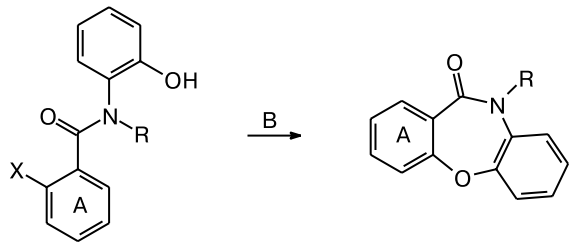
Proceeding further in our investigations into utilization of polynitroarenes,[1—4] we have paid attention to the possibility of obtaining benzooxazepines. Compounds of this class exhibit various kinds of biological activity.[5,6] In particular, 10-[3-(dimethylamino)propyl]-2-nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (Sintamil®) is known as an efficient antidepressant.[7,8]



Sintamil

It is known that dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-ones are obtained by intramolecular cyclization of 2-hydroxyanilides of some *ortho*-halobenzoic acids (X = Cl and F)[9—11] (usually in the presence of additional electron-withdrawing substituents in the ring A, Scheme 1).

Scheme 1



B is the base. X = Cl, F.

Recently,[12,13] we have found that intramolecular nucleophilic substitution for the nitro group in 2-hydroxyanilide of 2,4,6-trinitrobenzoic acid (X = NO_2) can also be used to obtain these compounds.

Here we show that such a cyclization can occur in 2-nitrobenzoic acid derivatives containing less than three nitro groups in the benzene ring. This allows one to extend the range of accessible oxazepinones. For instance, 2-hydroxyanilides of 2,4-dinitrobenzoic acid (**3**) (prepared from 2,4-dinitrobenzoyl chloride **1a** and 2-aminophenols **2**) underwent cyclization in hot DMF in the presence of K_2CO_3 to give 3-nitrodibenzooxazepinones **4** in high yields (Scheme 2).

Obviously, the presence of two nitro groups in compounds **3a—d** facilitates intramolecular replacement of one of them. Nevertheless, mononitro derivative **5** underwent an analogous transformation (though under more drastic conditions) to give unsubstituted dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one **6** in good yield (Scheme 3).

It is worth noting that the cyclization of 2-hydroxyanilide of 2-chlorobenzoic acid into compound **6** is incomplete even under more drastic conditions.[10]

N-Substituted oxazepinones **4** can be obtained not only by cyclization of the corresponding 2-hydroxyanilides **3** (see Scheme 2) but also by *N*-alkylation of compound **4a** (in this way, *N*-methyl derivative **4e** was synthesized (Scheme 4)).

The nitro group in compounds **4** can be replaced by nucleophiles to give products **7** (Scheme 5, Table 1). S-Nucleophiles (thiols and benzenethiols) reacted relatively easily (at 80 °C), while O-nucleophiles (phenols) remained inert below 150 °C, *i.e.*, the temperature at which the nitro group in benzanilide **5** is intramolecularly

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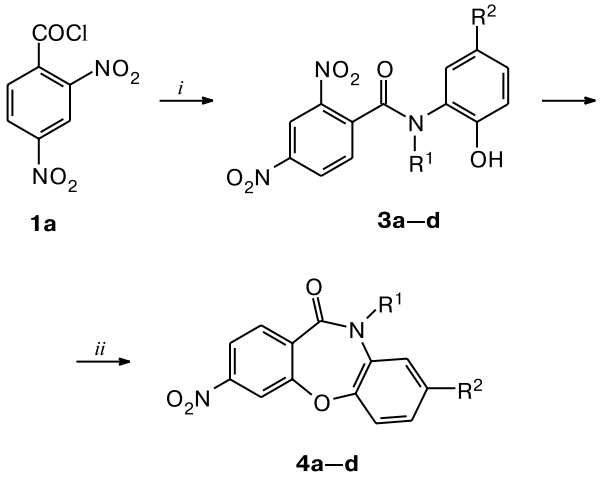
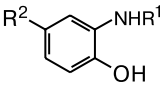
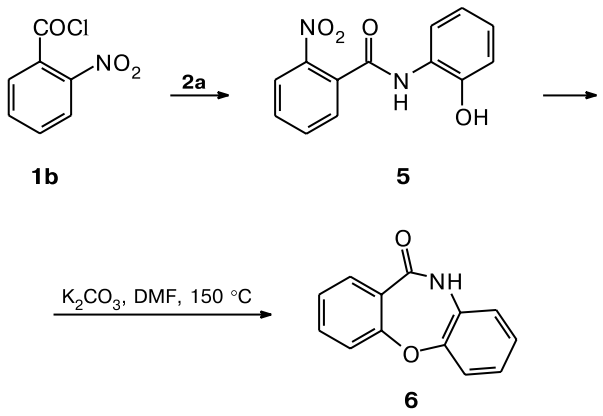
Scheme 2



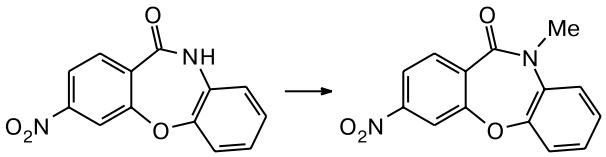
i.  (**2a—d**), *ii*. K_2CO_3, DMF, 120 °C.

	a	b	c	d
R^1	H	$PhCH_2$	4-$MeOC_6H_4CH_2$	H
R^2	H	H	H	Cl

Scheme 3



Scheme 4



Reagents and conditions: Me_2SO_4, NaOH, H_2O—acetone, 60 °C.

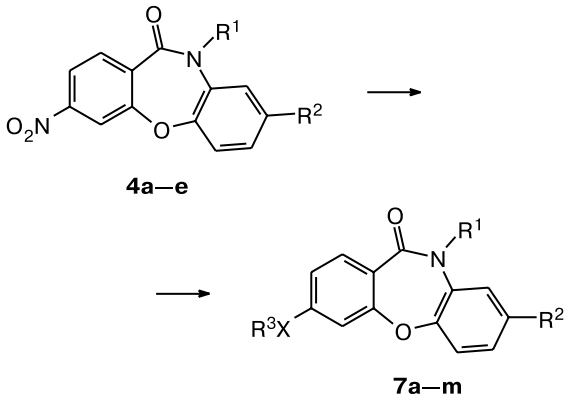
replaced by the aryloxide anion (see Scheme 3). The reaction allows various phenols to be employed; lower yields were obtained from phenols with *ortho*-substituents and those with electron-withdrawing groups (see Table 1; *cf.* compounds **7a,b** and **7c—e**).

It should be noted that *N*-substituted derivatives **4** reacted more rapidly than unsubstituted oxazepinone **4a** (*cf.* the reaction durations for **7a** and **7f,g**). Apparently, this is due to competitive proton abstraction from the amide N atom in compound **4a** (especially for O-nucleophiles, which are more basic than their S-analogs). In addition, the highly basic methoxide anion easily displaced the nitro group from *N*-methyl derivative **4e** but

Table 1. Reaction conditions and the yields of dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-ones **4a—d**, **6**, and **7**

Starting reagent	R^1	R^2	R^3X	*t*/h	*T*/°C	Product	Yield (%)
3a	H	H	—	1	120	**4a**	94
3b	$PhCH_2$	H	—	1	120	**4b**	93
3c	4-$CH_3OC_6H_4CH_2$	H	—	1	120	**4c**	88
3d	H	Cl	—	1	120	**4d**	85
5	H	H	—	1.5	150	**6**	61
4a	H	H	PhO	2	150	**7a**	83
4a	H	H	3-MeC_6H_4O	2	150	**7b**	88
4a	H	H	2-$MeOC_6H_4O$	2	150	**7c**	46
4a	H	H	4-ClC_6H_4O	2	150	**7d**	38
4a	H	H	4-BrC_6H_4O	2	150	**7e**	32
4b	$PhCH_2$	H	PhO	1	150	**7f**	91
4e	Me	H	PhO	0.75	150	**7g**	92
4e	Me	H	MeO	1	150	**7h**	66
4d	H	Cl	PhO	2	150	**7i**	88
4d	H	Cl	3-MeC_6H_4O	2	150	**7j**	86
4a	H	H	PhS	1	80	**7k**	73
4a	H	H	4-MeC_6H_4S	1	80	**7l**	51
4a	H	H	Bu^nS	1	80	**7m**	67

Scheme 5



Reagents and conditions: R^3XH (X = O or S), K_2CO_3, DMF, 80—150 °C.

not from compound **4a** (the conversion of the latter did not exceed 50% nor was the corresponding substitution product isolated in the individual state because of the formation of unidentified by-products).

Thus, the developed approach allows easy transformations of mono- and dinitrobenzoic acids into various dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one derivatives.

Experimental

^{1}H NMR spectra were recorded on Bruker AM-300 and Bruker DRX-500 instruments (300.13 and 500.13 MHz, respectively) in DMSO-d_6. Mass spectra were recorded on a Kratos MS-30 instrument. The course of the reactions was monitored by TLC on Silufol plates with hexane—ethyl acetate (3 : 1) as an eluent. *N*-Benzyl-2-hydroxyaniline **2b** was prepared according to a known procedure.[14]

***N*-(4-Methoxybenzyl)-2-hydroxyaniline (2c).** A solution of 2-aminophenol (2.0 g, 18.4 mmol) and 4-methoxybenzaldehyde (2.5 g, 18.4 mmol) in methanol (4 mL) was stirred for 10 min and cooled. The precipitate of the Schiff base that formed was filtered off and washed with MeOH (1 mL). Then the Schiff base was suspended in MeOH (10 mL) and $NaBH_4$ (3.5 g, 92 mmol) was added in portions with vigorous stirring. The pH value of the reaction was maintained at a level of 8—9 by adding AcOH. The precipitate that formed was filtered off, washed with MeOH (1 mL), and dried. The yield was 2.91 g (69%), m.p. 121 °C (MeOH). Found (%): C, 73.67; H, 6.41; N, 6.23. $C_{14}H_{15}NO_2$. Calculated (%): C, 73.34; H, 6.59; N, 6.11. ^{1}H NMR, δ: 3.71 (s, 3 H, OMe); 4.20 (d, 2 H, *J* = 7.5 Hz); 5.02 (br.s, 1 H, NH); 6.40 (m, 2 H); 6.56 (t, 1 H, *J* = 8.1 Hz); 6.65 (d, 1 H, *J* = 8.1 Hz); 6.87, 7.27 (both d, 2 H each, *J* = 8.2 Hz); 9.13 (br.s, 1 H, OH).

***o*-Nitrobenzanilides 3a—d and 5 (general procedure).** Triethylamine (2.65 g, 26 mmol) was added for 1 h to a stirred suspension of acid chloride **1a,b** (25 mmol) and an appropriate aminophenol **2a—d** (25 mmol) in boiling dry benzene (150 mL). The reaction mixture was heated with stirring for an additional 3 h. The precipitate that formed was filtered off, washed with hot benzene (3×30 mL) and hot water (3×200 mL), and dried.

***N*-(2-Hydroxyphenyl)-2-nitrobenzamide (5).[15]** The yield was 83%, m.p. 199—202 °C.

***N*-(2-Hydroxyphenyl)-2,4-dinitrobenzamide (3a).** The yield was 92%, m.p. 192—194 °C (EtOH). Found (%): C, 51.27; H, 2.92; N, 14.02. $C_{13}H_9N_3O_6$. Calculated (%): C, 51.49; H, 2.99; N, 13.86. ^{1}H NMR, δ: 6.84 (t, 1 H, *J* = 8.1 Hz); 6.91 (d, 1 H, *J* = 8.2 Hz); 7.03 (t, 1 H, *J* = 8.2 Hz); 7.86 (d, 1 H, *J* = 8.1 Hz); 8.05, 8.64 (both d, 1 H each, *J* = 8.0 Hz); 8.82 (s, 1 H); 9.72, 10.10 (both br.s, 1 H each; NH and OH).

***N*-Benzyl-*N*-(2-hydroxyphenyl)-2,4-dinitrobenzamide (3b).** The yield was 81%, m.p. 172—174 °C (MeOH). Found (%): C, 60.69; H, 4.00; N, 10.97. $C_{20}H_{15}N_3O_6$. Calculated (%): C, 61.07; H, 3.84; N, 10.68. ^{1}H NMR, δ: 4.42, 5.52 (both d, 1 H each, *J* = 14.2 Hz); 6.43 (t, 1 H, *J* = 8.2 Hz); 6.65, 6.80 (both d, 1 H each, *J* = 8.2 Hz); 6.97 (t, 1 H, *J* = 8.2 Hz); 7.25—7.35 (m, 5 H); 7.71, 8.41 (both d, 1 H each, *J* = 7.9 Hz); 8.62 (s, 1 H); 10.28 (br.s, 1 H, NH).

***N*-(2-Hydroxyphenyl)-*N*-(4-methoxybenzyl)-2,4-dinitrobenzamide (3c).** The yield was 79%, m.p. 114—117 °C (benzene). The product crystallized as a 0.5 C_6H_6 solvate. Found (%): C, 62.02; H, 4.55; N, 8.81. $C_{21}H_{17}N_3O_7 \cdot 0.5\ C_6H_6$. Calculated (%): C, 62.34; H, 4.36; N, 9.09. ^{1}H NMR, δ: 3.72 (s, 3 H); 4.32, 5.47 (both d, 1 H each, *J* = 14.1 Hz); 6.43 (t, 1 H, *J* = 8.1 Hz); 6.60, 6.79 (both d, 1 H each, *J* = 8.2 Hz); 6.86 (d, 2 H, *J* = 8.2 Hz); 6.97 (t, 1 H, *J* = 8.1 Hz); 7.20 (d, 2 H, *J* = 8.2 Hz); 7.36 (s, 3 H, C_6H_6); 7.70, 8.41 (both d, 1 H each, *J* = 7.9 Hz); 8.60 (s, 1 H); 10.18 (br.s, 1 H, NH).

***N*-(5-Chloro-2-hydroxyphenyl)-2,4-dinitrobenzamide (3d).** The yield was 81%, m.p. 189—191 °C (EtOH). Found (%): C, 45.88; H, 2.25; N, 12.78; Cl, 10.66. $C_{13}H_8ClN_3O_6$. Calculated (%): C, 46.24; H, 2.39; N, 12.44; Cl, 10.50. ^{1}H NMR, δ: 6.91 (d, 1 H, *J* = 7.9 Hz); 7.07 (dd, 1 H, *J* = 7.9 Hz, *J* = 2.0 Hz); 8.00 (m, 2 H); 8.63 (dd, 1 H, *J* = 7.9 Hz, *J* = 2.0 Hz); 8.81 (d, 1 H, *J* = 2.0 Hz); 10.2 (br.s, 2 H, NH and OH).

Cyclization of *o*-nitrobenzanilides 3a—d and 5. Synthesis of dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-ones 4a—d and 6 (general procedure). A stirred suspension of 2-nitrobenzanilide (**3a—d** or **5**) (15.0 mmol) and calcined K_2CO_3 (3.1 g, 22.5 mmol) in dry DMF (30 mL) was heated on an oil bath. The reaction temperatures and durations are specified in Table 1. The reaction mixture was cooled, poured into water (400 mL), and acidified to pH 6. The precipitate that formed was filtered off, washed with hot water (5×100 mL) and MeOH (2×10 mL), and dried.

Dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (6).[16] The yield was 61%, m.p. 207—209 °C. ^{1}H NMR, δ: 7.10—7.20, 7.34 (both m, 3 H each); 7.60 (t, 1 H, *J* = 8.0 Hz), 7.78 (d, 1 H, *J* = 8.0 Hz); 10.52 (s, 1 H, NH).

3-Nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (4a).[10] The yield was 94%, m.p. 285—287 °C. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 256 $[M]^+$ (100), 210 (42), 182 (41), 154 (25). ^{1}H NMR, δ: 7.15—7.25 (m, 3 H); 7.48 (d, 1 H, *J* = 8.0 Hz); 8.04, 8.13 (both d, 1 H each, *J* = 8.1 Hz); 8.22 (s, 1 H); 10.78 (s, 1 H, NH).

10-Benzyl-3-nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (4b). The yield was 93%, m.p. 141—143 °C (benzene). Found (%): C, 69.04; H, 3.99; N, 8.37. $C_{20}H_{14}N_2O_4$. Calculated (%): C, 69.36; H, 4.07; N, 8.09. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 346 $[M]^+$ (29), 91 (100). ^{1}H NMR, δ: 5.40 (s, 2 H); 7.20—7.35 (m, 7 H); 7.51, 7.54 (both d, 1 H each, *J* = 8.2 Hz); 8.03, 8.13 (both d, 1 H each, *J* = 7.9 Hz); 8.25 (s, 1 H).

10-(4-Methoxybenzyl)-3-nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (4c). The yield was 88%, m.p. 64—66 °C (benzene). Found (%): C, 66.84; H, 4.40; N, 7.68. $C_{21}H_{16}N_2O_5$. Calculated (%): C, 67.02; H, 4.28; N, 7.44. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 376 $[M]^+$ (16), 121 (100). ^{1}H NMR, δ: 3.70 (s, 3 H); 5.32 (s, 2 H); 6.85 (d, 2 H, *J* = 8.2 Hz); 7.18—7.26 (m, 4 H); 7.48, 7.56 (both d, 1 H each, *J* = 8.1 Hz); 8.02, 8.13 (both d, 1 H each, *J* = 7.9 Hz); 8.22 (s, 1 H).

8-Chloro-3-nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (4d). The yield was 85%, sublimed at 200 °C (benzene). Found (%): C, 53.50; H, 2.40; N, 10.01; Cl, 11.96. $C_{13}H_7ClN_2O_4$. Calculated (%): C, 53.72; H, 2.43; N, 9.64; Cl, 12.20. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 292 $[M]^+$ (26), 290 $[M]^+$ (100), 255 (56), 75 (32). ^{1}H NMR, δ: 7.23 (m, 2 H); 7.52 (d, 1 H, *J* = 8.1 Hz); 8.03 (d, 1 H, *J* = 8.2 Hz); 8.15 (dd, 1 H, *J* = 7.9 Hz, *J* = 2.0 Hz); 8.27 (d, 1 H, *J* = 2.0 Hz); 10.93 (br.s, 1 H, NH).

10-Methyl-3-nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (4e). Dimethyl sulfate (1.51 g, 11.7 mmol) was added to a stirred suspension of 3-nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (**4a**) (1.54 g, 6 mmol) and NaOH (0.47 g, 11.7 mmol) in a mixture of acetone (7 mL) and water (7 mL). The reaction mixture was stirred at 60 °C for 1 h. The precipitate was filtered off, washed with water (50 mL), and dried. The yield was 1.38 g (85%), m.p. 138—141 °C (benzene). Found (%): C, 62.47; H, 3.61; N, 10.29. $C_{14}H_{10}N_2O_4$. Calculated (%): C, 62.22; H, 3.73; N, 10.37. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 270 $[M]^+$ (100), 253 (22), 226 (21), 196 (39), 167 (27). ^{1}H NMR, δ: 3.53 (s, 3 H, Me); 7.30, 7.54 (both m, 2 H each); 8.01 (d, 1 H, *J* = 8.1 Hz); 8.12 (dd, 1 H, *J* = 8.1 Hz, *J* = 2.1 Hz); 8.24 (d, 1 H, *J* = 2.1 Hz).

3-Substituted dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-ones (7a—m) (general procedure). A stirred suspension of 3-nitrodibenzooxazepinone **4a**—**e** (6.0 mmol), an appropriate nucleophile R^3XH (6.45 mmol) (see Table 1), and dry K_2CO_3 (1.24 g, 9.0 mmol) in dry DMF (10 mL) was heated on an oil bath. The reaction temperatures and durations are specified in Table 1. The reaction mixture was cooled, poured into water (100 mL), and acidified to pH 6. The precipitate that formed was filtered off, washed with hot water (5×50 mL), and dried. Products were crystallized from benzene. In the synthesis of compound **7h**, MeONa was used instead of MeOH and K_2CO_3; the product was purified by flash chromatography on silica gel with hexane—ethyl acetate (5 : 1) as an eluent.

3-Phenoxydibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7a) was obtained from compound **4a** and phenol. The yield was 83%, m.p. 213—215 °C. Found (%): C, 75.46; H, 4.48; N, 4.57. $C_{19}H_{13}NO_3$. Calculated (%): C, 75.24; H, 4.32; N, 4.62. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 303 $[M]^+$ (100), 275 (14), 154 (13), 87 (20). ^{1}H NMR, δ: 6.85 (m, 2 H); 7.10 (m, 1 H); 7.17 (m, 4 H); 7.27 (m, 2 H); 7.46 (t, 2 H, *J* = 7.9 Hz); 7.79 (d, 1 H, *J* = 8.1 Hz); 10.35 (br.s, 1 H, NH).

3-(3-Methylphenoxy)dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7b) was obtained analogously from *m*-cresol. The yield was 88%, m.p. 183—186 °C. Found (%): C, 75.53; H, 4.89; N, 4.32. $C_{20}H_{15}NO_3$. Calculated (%): C, 75.70; H, 4.76; N, 4.41. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 317 $[M]^+$ (100), 316 (32), 170 (26), 65 (87), 63 (70). ^{1}H NMR, δ: 2.31 (s, 3 H, Me); 6.85 (m, 2 H); 6.92 (d, 1 H, *J* = 8.0 Hz); 6.96 (s, 1 H); 7.06—7.12 (m, 2 H); 7.17 (m, 2 H); 7.28 (d, 1 H, *J* = 8.2 Hz); 7.33 (t, 1 H, *J* = 8.0 Hz); 7.78 (d, 1 H, *J* = 8.0 Hz); 10.29 (br.s, 1 H, NH).

3-(2-Methoxyphenoxy)dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7c) was obtained analogously from guaiacol. The yield was 46%, m.p. 181—182 °C. Found (%): C, 72.38; H, 4.29; N, 4.28. $C_{20}H_{15}NO_4$. Calculated (%): C, 72.06; H, 4.54; N, 4.20. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 333 $[M]^+$ (49), 127 (40), 77 (77), 63 (100), 52 (94). ^{1}H NMR, δ: 3.72 (s, 3 H, Me); 6.71 (m, 2 H); 7.04 (t, 1 H, *J* = 7.9 Hz); 7.10 (m, 1 H); 7.16 (m, 3 H); 7.24 (d, 1 H, *J* = 8.5 Hz); 7.28 (m, 2 H); 7.73 (d, 1 H, *J* = 8.1 Hz); 10.29 (br.s, 1 H, NH).

3-(4-Chlorophenoxy)dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7d) was obtained analogously from 4-chlorophenol. The yield was 38%, m.p. 227—230 °C. Found (%): C, 67.72; H, 3.68; Cl, 10.57; N, 4.09. $C_{19}H_{12}ClNO_3$. Calculated (%): C, 67.56; H, 3.58; Cl, 10.50; N, 4.15. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 339 $[M]^+$ (37), 337 $[M]^+$ (100), 73 (30), 56 (44). ^{1}H NMR, δ: 6.89 (d, 1 H, *J* = 8.2 Hz); 6.93 (s, 1 H); 7.12 (m, 1 H); 7.18 (m, 4 H); 7.31 (d, 1 H, *J* = 8.0 Hz); 7.50 (d, 2 H, *J* = 8.4 Hz); 7.78 (d, 1 H, *J* = 8.2 Hz); 10.39 (br.s, 1 H, NH).

3-(4-Bromophenoxy)dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7e) was obtained analogously from 4-bromophenol. The yield was 32%, m.p. 240—243 °C. Found (%): C, 59.62; H, 3.04; Br, 20.79; N, 3.66. $C_{19}H_{12}BrNO_3$. Calculated (%): C, 59.71; H, 3.16; Br, 20.91; N, 3.66. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 383 $[M]^+$ (98), 381 $[M]^+$ (100), 101 (11), 56 (41). ^{1}H NMR, δ: 6.90 (d, 1 H, *J* = 8.2 Hz); 6.94 (s, 1 H); 7.12 (m, 3 H); 7.18 (m, 2 H); 7.31 (d, 1 H, *J* = 8.0 Hz); 7.63 (d, 2 H, *J* = 8.4 Hz); 7.78 (d, 1 H, *J* = 8.4 Hz); 10.39 (br.s, 1 H, NH).

10-Benzyl-3-phenoxydibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7f) was obtained from compound **4b** and phenol. The yield was 91%, m.p. 72—75 °C. Found (%): C, 79.52; H, 4.94; N, 3.62. $C_{26}H_{19}NO_3$. Calculated (%): C, 79.37; H, 4.87; N, 3.56. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 393 $[M]^+$ (60), 302 (21), 91 (100). ^{1}H NMR, δ: 5.34 (s, 2 H); 6.87 (d, 1 H, *J* = 8.2 Hz); 6.93 (d, 1 H, *J* = 2.5 Hz); 7.12—7.22 (m, 5 H); 7.24—7.35 (m, 6 H); 7.46 (m, 3 H); 7.77 (d, 1 H, *J* = 8.4 Hz).

10-Methyl-3-phenoxydibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7g) was obtained from compound **4e** and phenol. The yield was 92%, m.p. 59—61 °C. Found (%): C, 75.51; H, 4.59; N, 4.52. $C_{20}H_{15}NO_3$. Calculated (%): C, 75.70; H, 4.76; N, 4.41. ^{1}H NMR, δ: 3.46 (s, 3 H, Me); 6.84 (dd, 1 H, *J* = 8.0 Hz, *J* = 2.2 Hz); 6.92 (d, 1 H, *J* = 2.0 Hz); 7.15 (d, 2 H, *J* = 8.0 Hz); 7.22 (t, 1 H, *J* = 8.2 Hz); 7.29 (m, 2 H); 7.37 (d, 1 H, *J* = 8.0 Hz); 7.45 (m, 3 H); 7.75 (d, 1 H, *J* = 8.0 Hz).

3-Methoxy-10-methyldibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7h) was obtained from compound **4e** and MeONa. The yield was 66%, a light yellow oil which slowly solidified. Found (%): C, 70.32; H, 5.02; N, 5.56. $C_{15}H_{13}NO_3$. Calculated (%): C, 70.58; H, 5.13; N, 5.49. ^{1}H NMR, δ: 3.47 (s, 3 H, NMe); 3.84 (s, 3 H, OMe); 6.88 (d, 1 H, *J* = 8.2 Hz); 6.92 (s, 1 H); 7.26, 7.42 (both m, 2 H each); 7.69 (d, 1 H, *J* = 8.0 Hz).

8-Chloro-3-phenoxydibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7i) was obtained from compound **4d** and phenol. The yield was 88%, sublimed at 163—165 °C. Found (%): C, 67.82; H, 3.67; Cl, 10.59; N, 4.10. $C_{19}H_{12}ClNO_3$. Calculated (%): C, 67.56; H, 3.58; Cl, 10.50; N, 4.15. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 339 $[M]^+$ (34), 338 (29), 337 $[M]^+$ (100), 302 (46). ^{1}H NMR, δ: 6.87 (dd, 1 H, *J* = 8.4 Hz, *J* = 3.0 Hz); 6.92 (d, 1 H, *J* = 3.0 Hz); 7.16—7.20 (m, 4 H); 7.27 (t, 1 H, *J* = 8.0 Hz); 7.36 (d, 1 H, *J* = 8.4 Hz); 7.47 (t, 2 H, *J* = 8.0 Hz); 7.78 (d, 1 H, *J* = 8.4 Hz); 10.52 (br.s, 1 H, NH).

8-Chloro-3-(3-methylphenoxy)dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7j) was obtained from compound **4d** and *m*-cresol. The yield was 86%, sublimed at 166—168 °C. Found (%): C, 68.07; H, 3.89; Cl, 10.18; N, 3.87. $C_{20}H_{14}ClNO_3$. Calculated (%): C, 68.28; H, 4.01; Cl, 10.08; N, 3.98. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 353 $[M]^+$ (36), 351 $[M]^+$ (100), 316 (78), 65 (31), 63 (34). ^{1}H NMR, δ: 2.32 (s, 3 H, Me); 6.86 (dd, 1 H, *J* = 8.2 Hz, *J* = 2.2 Hz); 6.90 (d, 1 H, *J* = 2.2 Hz); 6.94 (d, 1 H, *J* = 8.0 Hz); 6.98 (s, 1 H); 7.08 (d, 1 H, *J* = 8.0 Hz); 7.17 (dd, 1 H, *J* = 8.4 Hz, *J* = 2.5 Hz); 7.19 (d, 1 H, *J* = 2.5 Hz); 7.36 (m, 2 H); 7.77 (d, 1 H, *J* = 8.2 Hz); 10.50 (br.s, 1 H, NH).

3-(Phenylsulfanyl)dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7k) was obtained from compound **4a** and benzenethiol. The yield was 73%, m.p. 182—185 °C. Found (%): C, 71.38; H, 4.21; N, 4.47; S, 10.09. $C_{19}H_{13}NO_2S$. Calculated (%): C, 71.45; H, 4.10; N, 4.39; S 10.04. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 319 $[M]^+$ (100), 318 (45), 291 (11). ^{1}H NMR, δ: 7.03 (d, 1 H, *J* = 8.0 Hz); 7.10—7.25 (m, 4 H); 7.27 (d, 1 H, *J* = 8.2 Hz); 7.50 (m, 5 H); 7.70 (d, 1 H, *J* = 8.2 Hz); 10.45 (br.s, 1 H, NH).

3-[(4-Methylphenyl)sulfanyl]dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7l) was obtained from compound **4a** and 4-methylbenzenethiol. The yield was 51%, m.p. 196—197 °C. Found (%): C, 72.28; H, 4.26; N, 4.28; S, 9.56. $C_{20}H_{15}NO_2S$. Calculated (%): C, 72.05; H, 4.53; N, 4.20; S, 9.62. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 333 $[M]^+$ (100), 305 (10), 154 (10). ^{1}H NMR, δ: 2.39 (s, 3 H, Me); 6.93 (d, 1 H, *J* = 8.1 Hz); 6.97 (s, 1 H); 7.01 (t, 1 H, *J* = 8.2 Hz); 7.07 (t, 1 H, *J* = 8.1 Hz); 7.12 (m, 2 H); 7.25, 7.39 (both d, 2 H each, *J* = 8.0 Hz); 7.64 (d, 1 H, *J* = 8.0 Hz); 10.37 (br.s, 1 H, NH).

3-(Butylsulfanyl)dibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (7m) was obtained from compound **4a** and butanethiol. The yield was 67%, m.p. 158—161 °C. Found (%): C, 68.48; H, 5.83; N, 4.57; S, 10.84. $C_{17}H_{17}NO_2S$. Calculated (%): C, 68.20; H, 5.72; N, 4.68; S, 10.71. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 299 $[M]^+$ (100), 243 (92), 215 (20). ^{1}H NMR, δ: 0.90 (t, 3 H, Me, *J* = 7.4 Hz); 1.44, 1.61 (both m, 2 H each, CH_2); 3.07 (t, 2 H, CH_2S, *J* = 7.4 Hz); 7.12 (m, 1 H); 7.17 (m, 3 H); 7.22 (s, 1 H); 7.33, 7.68 (both d, 1 H each, *J* = 8.0 Hz); 10.32 (br.s, 1 H, NH).

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