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PII: S0040-4020(19)30397-7

DOI: https://doi.org/10.1016/j.tet.2019.04.007

Reference: TET 30252

To appear in: *Tetrahedron*

Received Date: 11 January 2019

Revised Date: 31 March 2019

Accepted Date: 2 April 2019

Please cite this article as: Farat OK, Ananyev IV, Varenichenko SA, Tatarets AL, Markov VI, Vilsmeier-Haack reagent: An efficient reagent for the transformation of substituted 1,3-naphthoxazines into xanthene-type dyes, *Tetrahedron* (2019), doi: https://doi.org/10.1016/j.tet.2019.04.007.

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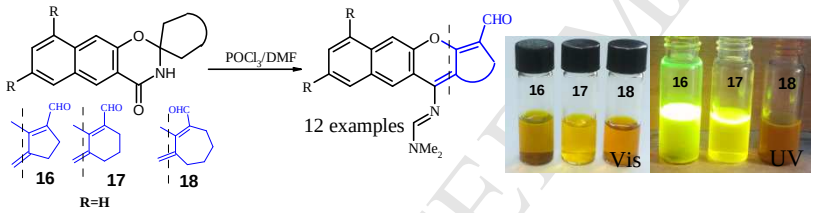

Vilsmeier-Haack reagent: an efficient reagent for the transformation of substituted 1,3-naphthoxazines into xanthene-type dyes

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Keywords: Vilsmeier–Haack reagent; rearrangement; heterocyclic dye; Stokes shift; crystal structure

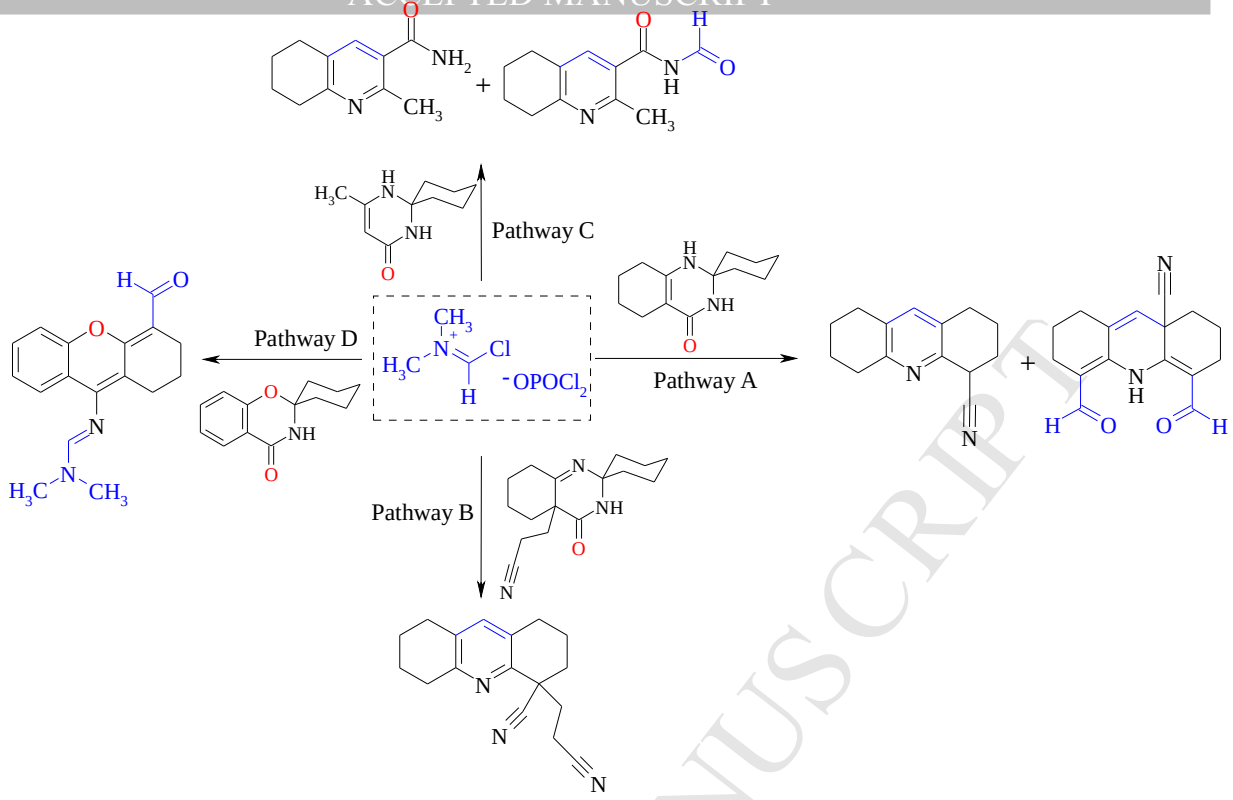
Abstract

Derivatives of 1,3-naphthoxazines containing from five to seven-membered spiro ring – under Vilsmeier–Haack reaction conditions are rearranged into novel xanthene-type compounds. All synthesized aminochromene derivatives fluoresce in organic solvents with extra large Stokes shifts (100–133 nm). It was found that compounds containing five-membered annulated aliphatic rings in methanol solution have the best spectral characteristics. These compounds have moderate quantum yields of 28.36–28.94%, and extra large Stokes shifts 106 and 115 nm.

Introduction

The importance of the Vilsmeier–Haack reagent in organic chemistry is unquestionable, not only for introduction of CHO group into the activated aromatic and heteroaromatic compounds, but also for various condensations, cyclizations and rearrangements (for example, see reviews[1–6]). In our previous works, it was shown that, under the action of this reagent, the substituted spiroquinazolones are rearranged into hydroacridine derivatives (Pathways A and B),[7,8] and the substituted spiropyrimidones – are converted into quinazolines (Pathway C).[9] It was also found that substituted 1,3-benzoxazines in the Vilsmeier-Haack reaction conditions are transformed into formylxanthene derivatives (Pathway D)[10,11] (**Scheme 1**). The reaction we discovered (Pathway D) allows obtaining novel functionally substituted fluorophores, capable of being used as low molecular weight building blocks for organic synthesis. These xanthene derivatives fluoresce in acetonitrile solution with large Stokes shifts and moderate fluorescence quantum yields. Introduction of formylxanthenes into Knoevenagel condensation and Schiff reaction gave dyes with high extinction coefficients.[12,13] Similar formylxanthene derivatives are used for the synthesis of near-infrared fluorescent dyes.[14–18]

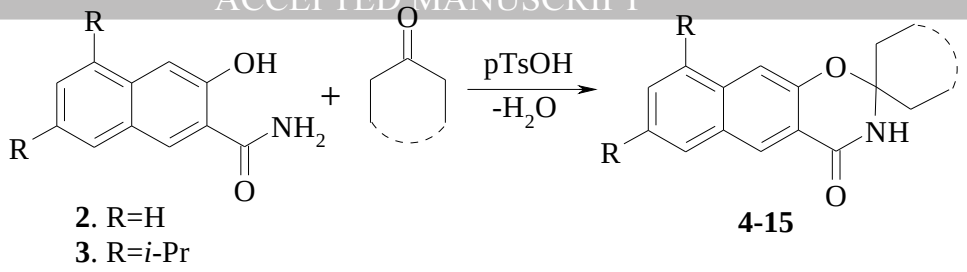
This article presents the rearrangement of substituted 1,3-naphthoxazines into xanthene-type compounds under the action of Vilsmeier-Haack reagent, as well as the investigation of the spectral properties of the novel compounds. The increase in the number of examples of newly discovered rearrangement is interesting not only from the point of view of obtaining new fluorophores, but also for expanding the synthetic arsenal of organic chemistry methods.



Scheme 1. Examples of the use of Vilsmeier–Haack reagent in our previous studies.

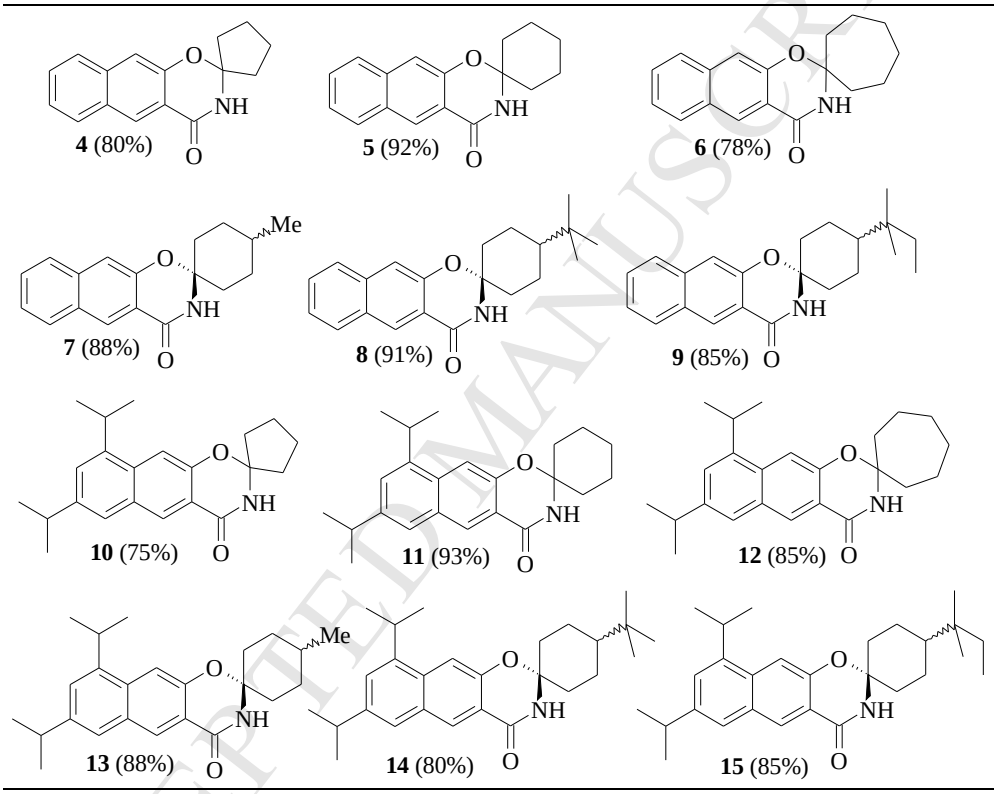
Synthesis and identification

The next step in our research was the synthesis and investigation of the reactivity of substituted 1,3-naphthoxazines under the conditions of the Vilsmeier-Haack reaction. Spiroderivatives **4–15** were obtained by the known method[10] — by the interaction of the corresponding amides with cyclic ketones under acid catalysis with the removal of formed reaction water (**Scheme 2**). The structures of the obtained compounds were determined by ^{1}H, ^{13}C NMR and FTIR spectroscopy, as well as mass spectrometry. Compounds **7–9** and **13–15** were found to form as a mixture of stereoisomers.

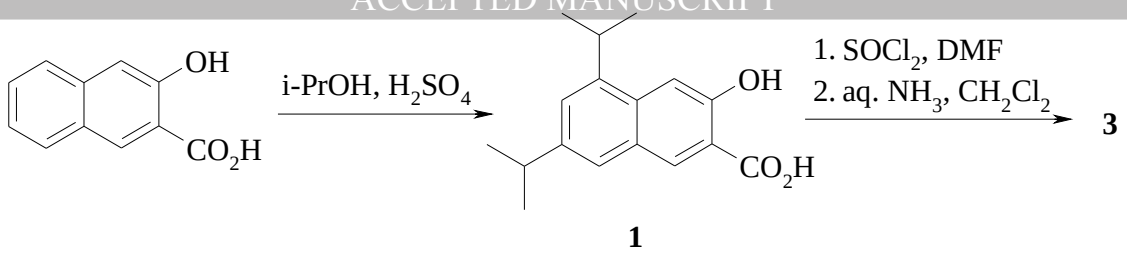


Scheme 2. Synthesis of substituted naphthoxazines

Table 1. Synthesized naphthoxazines (Structures and yields of substituted naphthoxazines obtained) *via* **Scheme 2**.



Amide **2** was obtained through the corresponding acid chloride[19] according to the method[20] and amide **3** was synthesized by alkylation of commercially available 3-hydroxy-2-naphthoic acid with isopropyl alcohol in concentrated sulfuric acid, followed by amidation (**Scheme 3**). Alternatively, amide **3** can also be obtained by alkylation of unsubstituted amide **2** under similar conditions.



Scheme 3. Synthesis of substituted 3-hydroxy-2-naphthoic acid **1**

The structure of acid **1** was confirmed by a complex of spectral analysis methods, including ^{1}H, ^{13}C NMR and FTIR spectroscopy, as well as mass spectrometry. To determine the exact structure of product **1** experiments of two-dimensional heteronuclear correlation of HSQC and HMBC were performed in addition. Some important ^{1}H-^{13}C HMBC correlations for compound **1** are presented on **Figure 1**. Full set of data of heteronuclear correlations is given in the Supplementary materials.

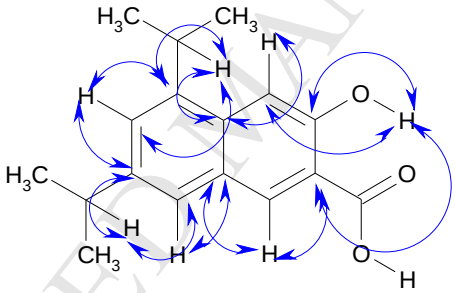
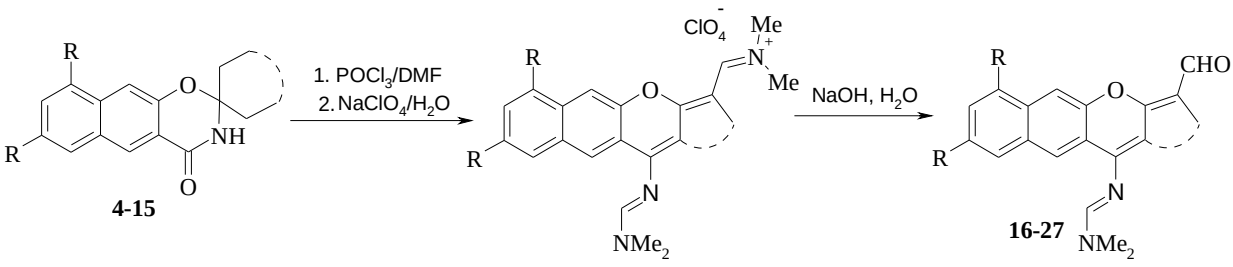


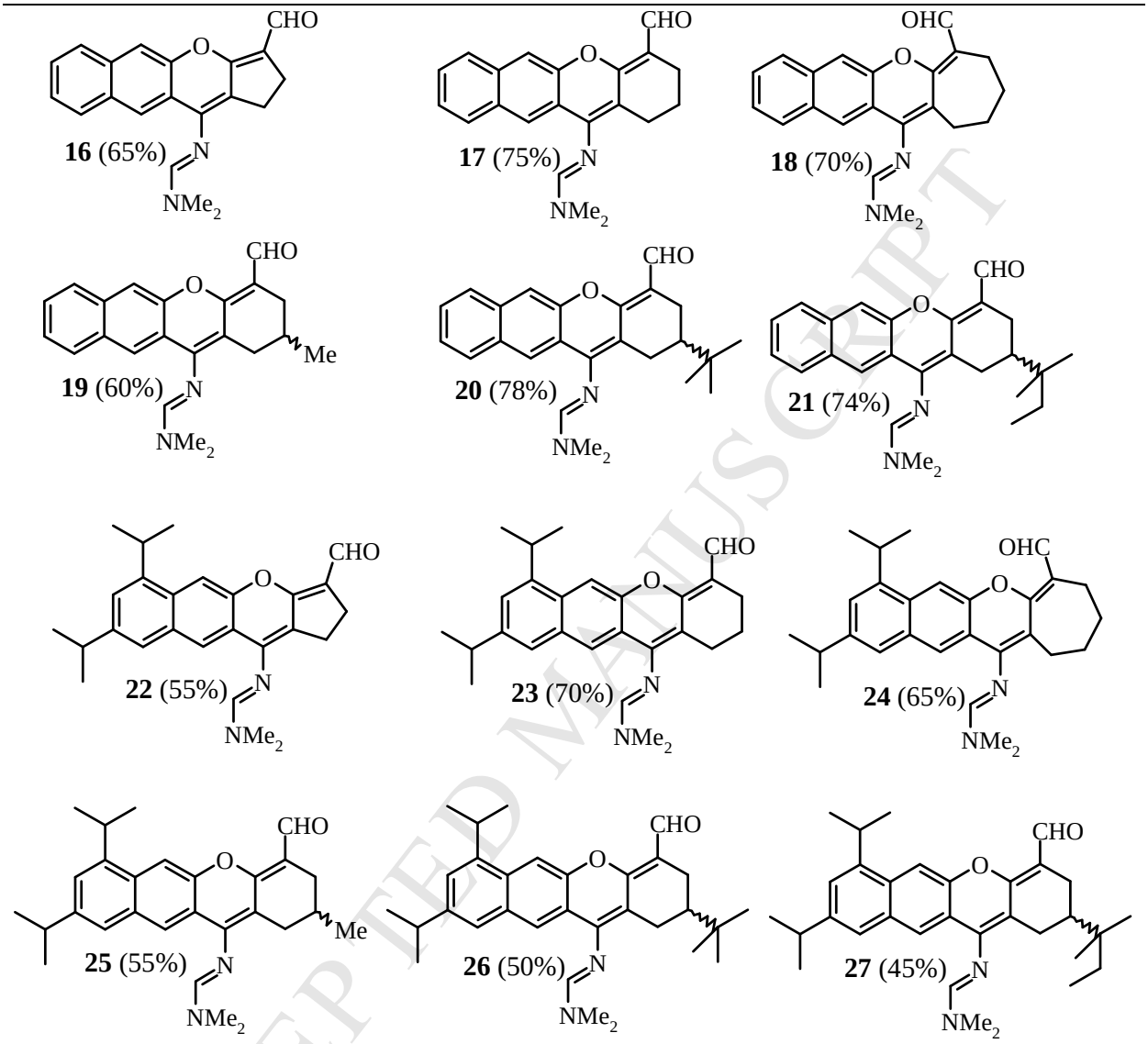
Figure 1. Some important ^{1}H-^{13}C HMBC correlations for acid **1**

The interaction of the spirans **4–15** with the Vilsmeier–Haack reagent at 80° C for 1.5 h yielded previously unknown xanthene derivatives **16–27**. The reaction products were isolated *via* the intermediate perchlorate salts, which were then introduced into the hydrolysis reaction. Compounds **7–9** and **13–15** were used for further reactions as a mixture of isomers.



Scheme 4. Synthesis of xanthene-type compounds

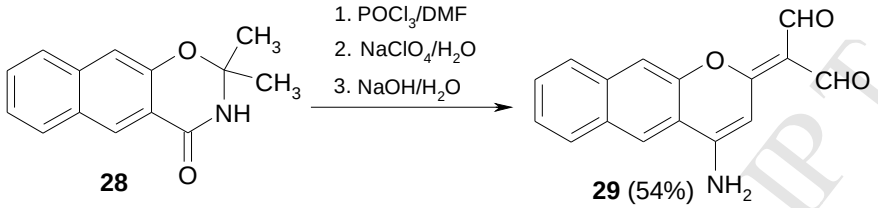
Table 2. Structures and synthetic yields of xanthene-type compounds obtained by the reactions of **Scheme 4**



The structures of the synthesized compounds were confirmed by ^{1}H NMR, ^{13}C NMR, FTIR spectroscopy and mass spectrometric data. In addition, X-ray diffraction analysis was performed for compounds **16–18**. The ^{1}H and ^{13}C NMR spectra of these compounds have a characteristic signal of the formyl group at ~10.3 ppm and ~187 ppm, respectively. An analysis of bond lengths of compounds **16–18** shows a significant elongation of carbonyl bonds up to 1.2388 (18)–1.2407 (14) Å compared with the average C=O bond length in aldehydes – 1.192 Å.[21] Signals at ~1630 cm^{-1} are observed in the IR spectra, corresponding to the signals from CHO groups conjugated with an electron-donating group, which position are

closer to amide carbonyl group than to aldehydes by the values of the wavenumber.

It is worth to mention that dimethyl substituted naphthoxazine **28** under the similar conditions gives diformyl derivative **29**.



28 **29** (54%)

The structure of the synthesized compound **29** was confirmed by ^{1}H NMR, ^{13}C NMR, FTIR spectroscopy and mass spectrometric data. The signals of the NH_2 protons in the ^{1}H NMR experiment in DMSO at 20 °C, give two singlet signals at 9.17 ppm and 8.95 ppm, which, along with the signals from the protons CHO at 9.95 ppm, indicates a strong conjugation between the amino and the formyl groups. Temperature increase in the ^{1}H NMR experiment to 60 °C leads to a coalescence of the signals of NH_2 group protons, appeared in the form of a broadened singlet at 9.00 ppm (See supplementary materials). The obtained data indicate that formally single bond C-N acquires the character of a partially double bond, which are in agreement with the previous data for similar compounds.[10]

The single crystal X-ray diffraction studies of compounds **16–18** (**Fig. 2–4**) revealed that the size of the aliphatic cycle affects both intra- and intermolecular structure peculiarities. In **16** the compact aliphatic ring exhibits a nearly flat conformation with maximal displacements of atoms from mean-squared plane being less than 0.037 Å. At the same time, the sofa and boat conformations are observed for the aliphatic cycles in **17** and **18**, respectively (**Fig. 5**). The latter, together with the different rigidity of cycles, results in a slight variation of bond length distribution. For instance, the C-C bond between aliphatic cycle and carbonyl group and the annulated C-C bonds lengthen (on ca. 0.02 Å) upon an increase of the aliphatic ring. The most pronounced difference is observed for the rotation of the dimethylamidine fragment with respect to the xanthene moiety. Namely, the C5-C6-N1-C18 torsion angle in **16** (**Fig. 2**) is equal to 41.8(2)°, while

its analogs in **17** and **18** correspond to the rotation in the opposite direction (290.5(2)° and 308.0(1)°, respectively). The absolute values of these angles are in line with our recent DFT studies[11] concerning the interplay between steric effects and dimethylamidine conjugation in similar systems. One should note that the dimethylamidine fragment rotation in **16–18** is evidently caused by the conformation of the aliphatic cycle. Namely, in **16** and **17** the methylene groups of the latter participate in the CH…π intermolecular contacts which bound molecules into centrosymmetric dimers. These dimers, in turn, are always additionally stabilized by CH…O interactions between the CH group of the dimethylamidine fragment and the carbonyl oxygen atom (**Fig. 6**). A similar situation is observed in **18** where above-mentioned methylene and CH groups form intermolecular contacts with the same oxygen atom (**Fig. 7**). The different rotation of the dimethylamidine fragment in the compounds **16–18** can be also explained by other effects of crystal packing. Namely, the dimethylamidine fragment in **16** participates in five shortened CH…O contacts with the carbonyl oxygen atom of three neighboring molecules (C…O distances 3.41–3.65Å, CHO angles 147–175° with normalized hydrogen atoms). In compounds **17** and **18** less directional and weaker CH…π and H…H contacts are also observed for the dimethylamidine fragment, while it forms a smaller number of CH…O contacts (one in **17** with the C…O distance equals 3.2 Å, two in **18** with the C…O distances equal 3.33 and 3.52 Å).

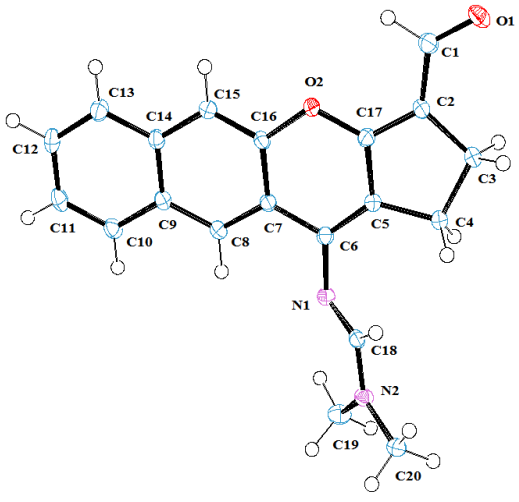


Figure 2. ORTEPs of the molecule **16** with thermal ellipsoids at 50% level for all non-hydrogen atoms.

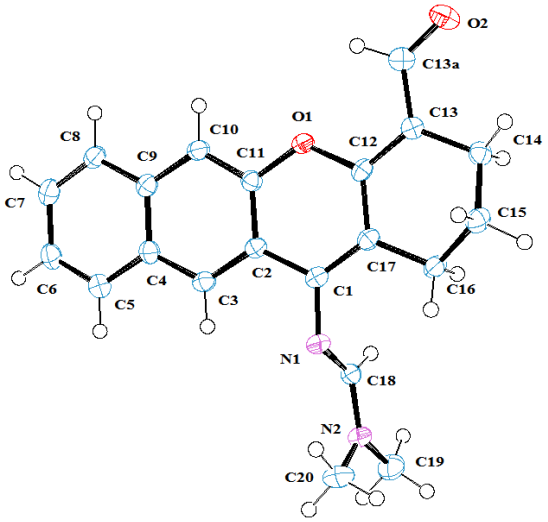


Figure 3. ORTEPs of the molecule **17** with thermal ellipsoids at 50% level for all non-hydrogen atoms.

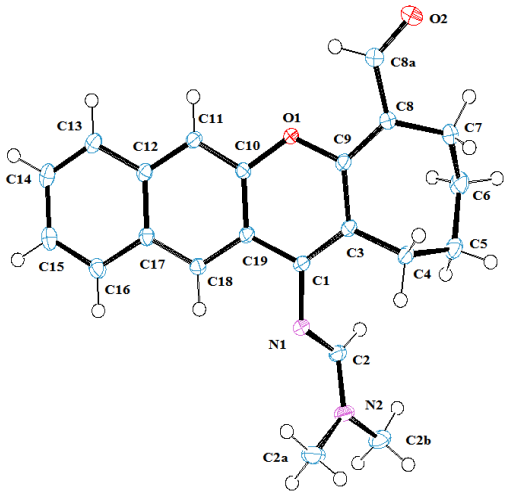


Figure 4. ORTEPs of the molecule **18** with thermal ellipsoids at 50% level for all non-hydrogen atoms.

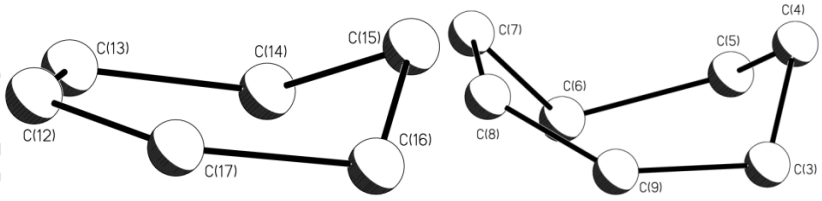


Figure 5. Conformations of aliphatic cycles in **17** (left) and **18** (right)

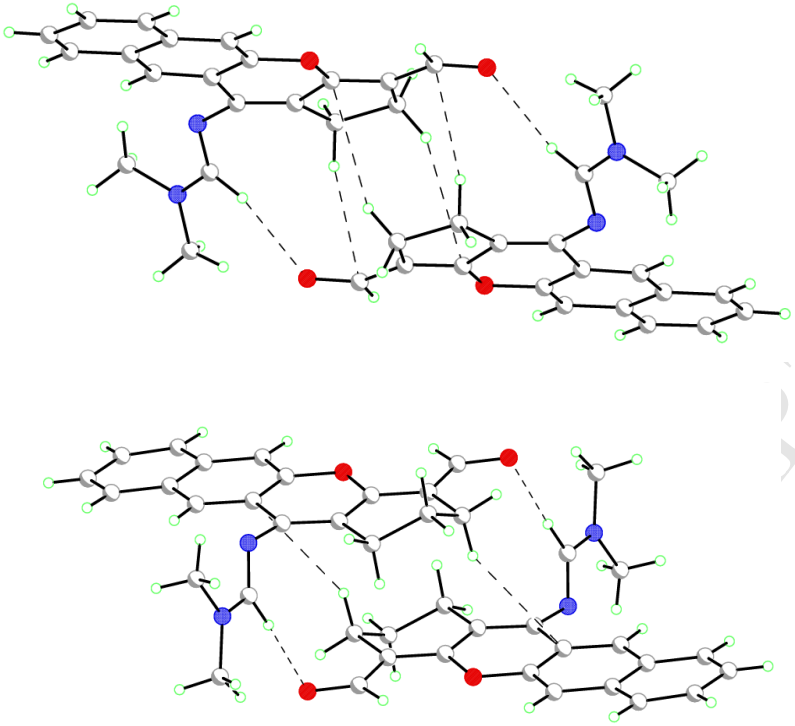


Figure 6. Centrosymmetric dimers of molecules **16** (top) and **17** (bottom) in crystal stabilized by CH…π and CH…O interactions (dashed lines).

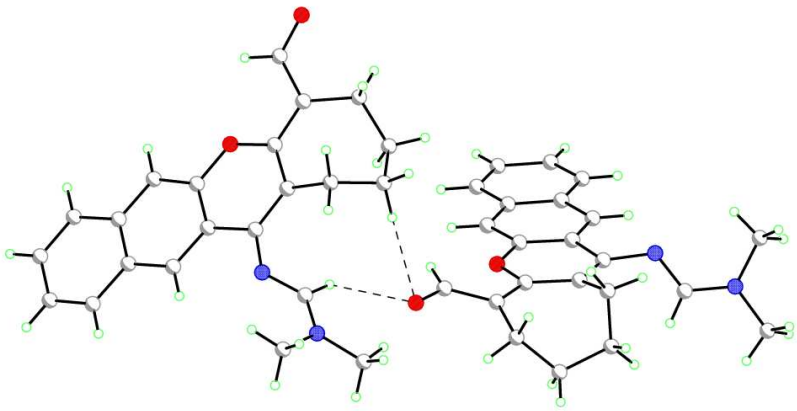


Figure 7. The dimer of molecules **18** in crystal stabilized by CH…O interactions of carbonyl oxygen atom with the aliphatic cycle and the dimethylamidine fragment (dashed lines).

Spectral properties

Absorption and emission properties of dyes **16–18** were obtained in five solvents of various polarities to evaluate the effect of the size of the annulated aliphatic cycles in xanthene-likes moiety of novel dyes. Normalized spectra of all these dyes are given in Supplementary materials. The spectra of compounds **16–18**

were recorded for $2.5 \cdot 10^{-5}$ mol/L solutions. The synthesized dyes **16–18** showed absorption and emission in the range of 424–435 nm and 524–529 nm respectively in solvents of varying polarities (**Table 3**), so the compounds **16–18** are characterized by sufficiently large Stokes shift of 4300–5590 cm^{-1} (**Table 3**). The size of the aliphatic cycle of the chromene moiety do not affect greatly the extinction coefficient or position of absorption and emission. It must be noted that the lowest extinction coefficients for these dyes are observed for solutions in toluene. The positions of the long-wavelength absorption bands and emission maxima of all compounds are almost independent of the physicochemical characteristics of the solvent, which indicates that the dipole moments of these compounds are not very large in the ground and excited states. At the same time, large Stokes shifts evidenced about significant redistribution of the electron density in molecules in the structurally and solvated-relaxed electronically excited state. The highest fluorescence quantum yields are observed for compound **16**, and the lowest ones – for compound **18** in all investigated solvents. Cyclopentene derivative **16** indicates more pronounced vibrational structure in emission spectra as compared to cyclohexene and cycloheptene derivatives **17** and **18**, respectively. It is evidenced that flattening of molecule **16** occurs in the excited state, while the vibrational motion of the more flexible cyclohexene and cycloheptene rings prevents flattening of the molecule. Motion of the more flexible cyclohexene (and even more for cycloheptene) moiety in the excited state also leads to an increase in nonradiative energy dissipation, and as a result, to a decrease in fluorescence quantum yields. So, the annulated five-membered aliphatic cycle in **16** is more rigid and makes the chromophoric system more planar, as compared to the six- and seven-membered aliphatic cycles in **17** and **18**. The more pronounced vibrational bands in the fluorescence spectra of **16** indicate the more rigid structure of this molecule in the excited state. The highest quantum yields for dyes **16–18** are observed in methanol solutions (**Table 3**). Just for these solutions the lowest Stokes shifts were noted that means methanol leads to less energy loss upon electron density redistribution in the excited state. Probably the reconfiguration of

the solvation shell upon relaxation with methanol in the excited state is less pronounced, resulting in stabilization of the excited state and an increase the fluorescence quantum yield. **Figure 8** shows the photographs of compounds **16–18** in methanol solutions under irradiation with visible and ultraviolet light (365 nm)

Table 3. UV-Vis absorption and emission properties[a] of compounds **16–18** in different solvents

Solvent	Solvent polarity, E_T^N [c]	Compound	$\lambda_{Abs\text{-}max}$ (nm)	$\lambda_{Em\text{-}max}$ (nm)	$\varepsilon_{max}x10^4$ (M^{-1} cm^{-1})	λ_{Ex}(nm)	Φ_F[b], %	Stokes shift, nm/cm^{-1}
PhMe	0.099	**16**	424	540	1.27	424	1.89	116/5070
		17	425	555	1.85	425	1.87	130/5510
		18	424	524	1.89	424	0.14	100/4500
CH_2Cl_2	0.309	**16**	426	550	2.43	426	12.77	124/5290
		17	430	550	2.31	430	3.74	120/5070
		18	426	550	2.58	426	0.10	124/5290
MeOH	0.762	**16**	435	535	2.85	435	28.94	100/4300
		17	435	550	2.52	435	7.21	115/4810
		18	430	550	2.15	430	0.07	120/5070
MeCN	0.460	**16**	424	530	2.62	424	16.52	106/4720
		17	430	555	2.31	430	2.95	125/5210
		18	425	555	2.20	425	0.04	130/5510
DMF	0.386	**16**	427	548	2.80	427	24.42	121/5170
		17	430	559	2.24	430	4.90	129/5590
		18	426	559	2.44	426	0.07	133/5590

[a]Absorption ($\lambda_{Abs\text{-}max}$), emission ($\lambda_{Em\text{-}max}$), excitation (λ_{Ex}) maxima and extinction coefficients (ε_{max}) were determined.
[b]Quantum yields (Φ_F) determined at 20 °C using quinine in 0.1 M H_2SO_4 (Φ_F=0.55) as the standard.[22] The quantum yields are corrected for the refractive indices of solvents and inner-filter effects.
[c]Normalized values of solvent polarity were taken from[23]

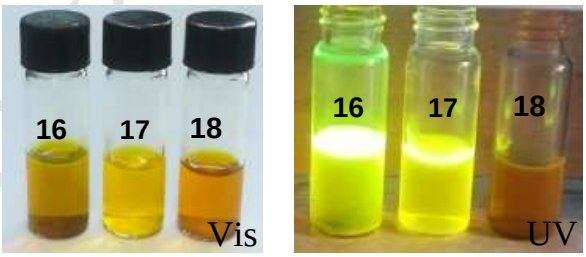


Figure 8. Methanol solutions of compounds **16–18** upon irradiation with visible and UV light (365 nm)

Absorption and emission spectra of compounds **19–27** were recorded in methanol for $2.5 \cdot 10^{-5}$ mol/L solutions. The normalized absorption as well as emission spectra for all nine compounds are presented in Supplementary materials. Photophysical parameters such as molar extinction coefficients, Stokes shifts, fluorescence quantum yields of compounds **19–27** in methanol solution were

evaluated and represented in **Table 4**. It was shown that the introduction of alkyl groups into the aromatic and aliphatic part of dyes **19–27** does not significantly affect the absorption and emission maxima, as well as the Stokes shift and the fluorescence quantum yield. At the same time, a decrease in the extinction coefficient for compounds **19–27** compared with dyes **16–18** should be noted.

Table 4. UV-Vis absorption and emission properties[a] of compounds **19–27** in MeOH

Compound	$\lambda_{Abs\text{-}max}$ (nm)	$\lambda_{Em\text{-}max}$ (nm)	$\varepsilon_{max}x10^4$ (M^{-1} cm^{-1})	λ_{Ex}(nm)	Φ_F[b], %	Stokes shift, nm/cm^{-1}
19	428	555	1.92	428	8.14	127/5350
20	430	555	1.87	430	6.52	125/5240
21	430	555	1.57	430	6.11	125/5240
22	432	538	2.02	432	28.36	106/4560
23	435	556	1.14	435	7.33	121/5000
24	429	553	1.23	429	0.05	124/5230
25	433	556	1.68	433	8.22	123/5110
26	429	558	1.33	429	6.22	129/5390
27	430	558	1.14	430	6.14	128/5330

[a]Absorption ($\lambda_{Abs\text{-}max}$), emission ($\lambda_{Em\text{-}max}$), excitation (λ_{Ex}) maxima and extinction coefficients (ε_{max}) were determined.
[b]Quantum yields (Φ_F) determined at 20 °C using quinine in 0.1 M H_2SO_4 (Φ_F=0.55) as the standard.[22] The quantum yields are corrected for the refractive indices of solvents and inner-filter effects.

Conclusion

In this work, we have synthesized and studied the spectral properties in different solvents of aminochromene derivatives containing formylated, partially hydrogenated five, six and seven-membered cycles. It was shown that 1,3-naphthoxazines which contained five-, six- or seven-membered spiro rings are rearranged into novel xanthene-type compounds during Vilsmeier–Haack reagent. All synthesized aminochromene derivatives fluoresce in organic solvents with extra large Stokes shifts (100–133 nm). It was found that compounds containing five-membered annulated saturated rings in methanol solution have the best spectral characteristics. These compounds have moderate quantum yields of 28.36–28.94%, and extra large Stokes shifts 106 and 115 nm. The obtained compounds are highly functionalized and could serve as low-molecular-weight building blocks for organic synthesis and as organic fluorophores.

Experimental section

Unless otherwise stated, all reagents of analytical grade were purchased from commercial suppliers and used without any further purification. The ^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker Avance II 400 spectrometer (400.13 MHz and 100.62 MHz for ^{1}H and ^{13}C, respectively) or Bruker Avance 600 spectrometer (600.13 MHz and 150.91 MHz for ^{1}H and ^{13}C, respectively) in DMSO-d_6 or $CDCl_3$ using residual solvent peak (δ 2.50 ppm and 7.26 ppm; 39.50 ppm and 77.16 ppm for ^{1}H and ^{13}C, respectively) as a reference. The ^{1}H and ^{13}C NMR spectra for compounds **13, 14** and **15** are presented for the predominant isomer. The FTIR spectra were recorded in KBr pellets using a Varian 640 FT–IR spectrometer. The UV−vis spectra were measured by a Hitachi U-1900 spectrophotometer using quartz cuvette with optical path length 10 mm, the baseline was corrected relative to the solvent absorption. Excitation and emission luminescence spectra were collected using Hitachi F-7000 spectrofluorometer for solutions in different solvents placed in a standart quartz cuvette with an optical path length 10 mm, 90° geometry. The EI mass spectra were recorded on Kratos MS 30 with direct injection of the sample to the ionization chamber at temperature of 250 °C with 70 eV ionizing electrons. The FAB mass spectra were recorded on a VG7070 spectrometer. Desorption of the ions from the solution of the samples in meta-nitrobenzyl alcohol was realized with a beam of argon atoms with energy 8 keV. Elemental analysis was performed on a LECO CHN-900 instrument. Melting points were carried out using an Electrothermal 9100 Digital Melting Point apparatus and were uncorrected. The control of reactions and the purity of the obtained compounds were monitored by TLC on Merck Silica gel 60 F-254 plates with 10:1, v/v $CHCl_3$/MeOH as eluent.

Synthesis

*3-Hydroxy-5,7-diisopropyl-2-naphthoic acid (**1**)*

3 mL (0.04 mol) of *i*-PrOH was slowly added to 8 mL of conc. H_2SO_4 with stirring and ice-cooling. Then 2.82 g (0.015 mol) of 3-hydroxy-2-naphthoic acid was added to the obtained solution and heated at 80° C for 1.5 h. Reaction mixture was

left for 12 h at room temperature, poured onto ice, the acid **1** was filtered off, dried and crystallized from n-hexane. The yield is 3.10 g (76%), mp 162–164 °C. FTIR (KBr pellets, ν, cm^{-1}): 3302 (O-H), 3059, 2960–2872, 1660 (C=O). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 11.07 (1H, br s, OH), 9.98 (1H, s, OH), 8.60 (1H, s, 1-H Ar), 7.60 (1H, s, 4-H Ar), 7.53 (1H, s, 8-H Ar), 7.40 (1H, s, 6-H Ar), 3.56–3.63 (1H, m, *CH*$(CH_3)_2$), 3.01–3.07 (1H, m, *CH*$(CH_3)_2$), 1.41 (6H, d, ^{3}J=6.9 Hz, CH(*CH*$_3)_2$), 1.36 (6H, d, ^{3}J=6.9 Hz, CH(*CH*$_3)_2$). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 175.1, 155.9, 144.4, 143.3, 135.8, 134.5, 128.2, 126.1, 123.6, 112.4, 108.4, 34.2, 28.9, 23.9, 23.4. Mass spectrum (EI), *m/z* (I_{rel}, %): 272 $[M]^+$ (56). Found, %: C 75.11; H 7.57. $C_{17}H_{20}O_3$. Calculated, %: C 74.97; H 7.40.

*3-Hydroxy-2-naphthamide (**2**)*

To a suspension of 3-hydroxy-2-naphthoic acid (5 g, 0.027 mol) in 225 mL CH_2Cl_2 were added a few drops of DMF and 3.65 mL (0.05 mol) of $SOCl_2$. The mixture was refluxed with stirring for 1 h. Then the solvent was evaporated on a rotary evaporator to dryness. The obtained acid chloride was dissolved in 60 ml of CH_2Cl_2, and the resulting solution was slowly added dropwise with vigorous stirring to a mixture of concentrated NH_4OH (50 mL) and CH_2Cl_2 (30 mL). The mixture was vigorously stirred at room temperature for 24 h and then acidified to a pH 3 with 10% HCl. The precipitate formed was filtered off, washed with sodium carbonate solution, water and dried in air. Yield: 3.58 g (72%), mp 216–218 °C (lit.[20] mp 216–217 °C). FTIR (KBr pellets, ν, cm^{-1}): 3464 (O-H), 3344 (as NH_2), 3228 (sy NH_2), 3051, 2924–2852, 1645 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 12.53 (1H, br s, OH), 8.66 (1H, br s) and 8.08 (1H, br s, NH_2), 8.57 (1H, s, 1-H Ar), 7.82 (1H, d, ^{3}J=8.1 Hz, 8-H Ar), 7.73 (1H, d, ^{3}J=8.3 Hz, 5-H Ar), 7.49 (1H, t, ^{3}J=7.6 Hz, 6-H Ar), 7.32–7.35 (1H, m, 7-H Ar), 7.27 (1H, s, 4-H Ar). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 171.4, 156.5, 136.4, 129.9, 128.8, 128.4, 126.5, 125.8, 123.6, 117.4, 110.8.

*3-Hydroxy-5,7-diisopropyl-2-naphthamide (**3**)*

Amide **3** was obtained by procedure similar to compound **2**. Yield 70%, yellow powder, mp 144–146°C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3413 (O-H), 3356 (as NH_2), 3199 (sy NH_2), 3034, 2960–2870, 1649 (C=O). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 11.60 (1H, br s, OH), 8.00 (1H, s, Ar), 7.55 (1H, s, Ar), 7.40 (1H, s, Ar), 7.32 (1H, s, Ar), 6.62 (1H, br s) and 6.31 (1H, br s, NH_2), 3.51–3.58 (1H, m, *CH*(CH_3)$_2$), 2.95–3.01 (1H, m, *CH*(CH_3)$_2$), 1.37 (6H, d, ^3J=6.9 Hz, CH(*CH*$_3$)$_2$), 1.31 (6H, d, ^3J=6.9 Hz, CH(*CH*$_3$)$_2$). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 172.8, 156.4, 144.2, 143.2, 134.5, 128.8, 127.7, 125.0, 122.8, 115.1, 108.9, 34.1, 28.9, 23.9, 23.4. Mass spectrum (EI), *m/z* (I_{rel}, %): 271 $[M]^+$ (60). Found, %: C 75.40; H 7.89; N 5.23. $C_{17}H_{21}NO_2$. Calculated, %: C 75.25; H 7.80; N 5.16.

*Synthesis of Spirans **4–15** (General method)*

A mixture of the corresponding salicylamide (0.010 mol), ketone (0.012 mol) and p-TsOH×H_2O (0.03 mol) in toluene (45 mL) was refluxed for 8 h with continuous removal of water with a Dean–Stark trap. A solvent was evaporated to dryness under reduced pressure, the solid residue was washed with 5% aq. NaOH solution and filtered off.

*Spiro[cyclopentane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**4**)*

Yield 80%, yellow powder, mp 220–222°C (DMF) (lit.[24] mp 221–222 °C). FTIR (KBr pellets, ν, cm^{-1}): 3186 (N-H), 3066, 2958–2873, 1684 (C=O), 1633. ^{1}H NMR (600 MHz, $CDCl_3$/DMSO-d_6, ppm): δ = 8.77 (1H, s, NH), 8.36 (1H, s, Ar), 7.82 (1H, d, ^3J=8.1 Hz, Ar), 7.68 (1H, d, ^3J=8.2 Hz, Ar), 7.44 (1H, t, ^3J=7.1 Hz, Ar), 7.32 (1H, d, ^3J=7.1 Hz, Ar), 7.23 (1H, s, Ar), 2.07–2.12 (2H, m), 1.70–1.86 (6H, m). ^{13}C NMR (151 MHz, $CDCl_3$/DMSO-d_6, ppm): δ = 162.0, 151.8, 136.1, 128.7, 128.3, 127.9, 126.1, 124.2, 118.7, 111.9, 96.9, 37.5, 22.2.

*Spiro[cyclohexane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**5**)*

Yield 92%, yellow powder, mp 232–234°C (DMF) (lit.[24] mp 233–234 °C). FTIR (KBr pellets, ν, cm^{-1}): 3178 (N-H), 3062, 2940–2848, 1685 (C=O), 1635. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 8.90 (1H, s, NH), 8.43 (1H, s, Ar), 8.02 (1H, d, ^3J=8.2 Hz, Ar), 7.84 (1H, d, ^3J=8.2 Hz, Ar), 7.55 (1H, t, ^3J=7.0 Hz, Ar), 7.45 (1H, s, Ar), 7.42 (1H, d, ^3J=7.1 Hz, Ar), 1.96–2.02 (2H, m), 1.56–1.66 (7H, m), 1.20–1.26 (1H, m). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 161.0, 151.3, 136.4, 129.3, 128.5, 128.4, 128.3, 126.6, 124.7, 119.1, 112.1, 87.4, 35.8, 24.2, 21.5.

*Spiro[cycloheptane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**6**)*

Yield 78%, yellow powder, mp 273–274 °C (DMF). FTIR (KBr pellets, ν, cm^{-1}): 3174 (N-H), 3062, 2931–2854, 1670 (C=O), 1633. ^{1}H NMR (600 MHz, DMSO-d_6, ppm): δ = 8.93 (1H, s, NH), 8.41 (1H, s, Ar), 8.01 (1H, d, ^3J=7.9 Hz, Ar), 7.82 (1H, d, ^3J=8.0 Hz, Ar), 7.54 (1H, t, ^3J=7.1 Hz, Ar), 7.39–7.42 (2H, m, Ar), 2.08–2.13 (2H, m), 1.91–1.97 (2H, m), 1.44–1.86 (8H, m). ^{13}C NMR (151 MHz, DMSO-d_6, ppm): δ = 160.9, 151.5, 136.4, 129.3, 128.5, 128.4, 128.3, 126.5, 124.7, 118.9, 112.1, 91.6, 39.7, 28.4, 20.9. Mass spectrum (EI), *m/z* (I_{rel}, %): 281 $[M]^+$ (28). Found, %: C 76.94; H 6.92; N 5.05. $C_{18}H_{19}NO_2$. Calculated, %: C 76.84; H 6.81; N 4.98.

*4-Methylspiro[cyclohexane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**7**)*

Yield 88%, yellow powder, mp 250–260 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3178 (N-H), 3064, 2943–2864, 1676 (C=O), 1635. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 8.52 (1H, s, Ar), 7.88–7.90 (1H, m, Ar), 7.85 (0.64H, s, NH), 7.71–7.74 (1H, m, Ar), 7.60 (0.26H, s, NH), 7.45–7.52 (1H, m, Ar), 7.34–7.42 (1.80H, m, Ar), 7.30 (0.20H, s, Ar), 2.27–2.30 (2H, m), 2.14–2.16 (0.50H, m), 1.31–1.85 (6.50H, m), 0.95–1.01 (3H, m). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 162.3, 150.7, 136.1, 128.6, 128.5, 128.1, 127.6, 125.8, 123.9, 117.4, 111.8, 86.4, 35.3, 30.2, 29.4, 21.0. Mass spectrum (EI), *m/z* (I_{rel}, %): 281 $[M]^+$ (35). Found, %: C 76.97; H 6.91; N 5.09. $C_{18}H_{19}NO_2$. Calculated, %: C 76.84; H 6.81; N 4.98.

*4-tert-Butylspiro[cyclohexane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**8**)*

Yield 91%, yellow powder, mp 250–256 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3186 (N-H), 3066, 2956–2866, 1682 (C=O), 1635. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.02 (0.24H, br s, NH), 8.78 (0.76H, br s, NH), 8.43 (1H, s, Ar), 8.01 (1H, d, ^3J=8.2 Hz, Ar), 7.85 (0.73H, d, ^3J=8.2 Hz, Ar), 7.81 (0.27H, d, ^3J=8.4 Hz, Ar), 7.54 (1H, t, ^3J=7.4 Hz, Ar), 7.38–7.43 (2H, m, Ar), 2.07–2.20 (2.50H, m), 1.57–1.64 (4H, m), 1.39–1.45 (2.50H, m), 0.87 (9H, s). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 161.6, 161.5, 152.2, 151.6, 136.7, 129.6, 128.9, 128.8, 128.7, 127.0, 126.9, 125.1, 125.0, 119.5, 112.5, 112.3, 88.5, 87.4, 46.7, 46.3, 36.8, 36.3, 32.5, 32.4, 27.9, 27.8, 27.4, 22.8, 22.6. Mass spectrum (EI), *m/z* (I_{rel}, %): 323 $[M]^+$ (48). Found, %: C 78.12; H 7.91; N 4.45. $C_{21}H_{25}NO_2$. Calculated, %: C 77.98; H 7.79; N 4.33.

*4-(1,1-Dimethylpropyl)spiro[cyclohexane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**9**)*

Yield 85%, yellow powder, mp 225–231 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3176 (N-H), 3060, 2960–2868, 1685 (C=O), 1635. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 8.54 (1H, s, Ar), 7.95 (0.78H, br s, NH), 7.90 (1H, d,^3J=7.6 Hz, Ar), 7.73–7.75 (1.22H, m, Ar, NH), 7.52 (1H, t, ^3J=6.4 Hz, Ar), 7.40 (1H, t, ^3J=6.6 Hz, Ar), 7.36 (0.78H, s, Ar), 7.31 (0.22H, s, Ar), 2.27–2.36 (2H, m), 1.55–1.64 (5.50H, m), 1.23–1.32 (3.50H, m), 0.78–0.89 (9H, m). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 162.4, 150.7, 136.1, 128.6, 128.5, 158.1, 127.6, 125.8, 123.9, 117.8, 111.8, 42.9, 25.9, 33.8, 31.8, 23.4, 21.7, 21.5, 7.3. Mass spectrum (EI), *m/z* (I_{rel}, %): 337 $[M]^+$ (43). Found, %: C 78.45; H 8.11; N 4.21. $C_{22}H_{27}NO_2$. Calculated, %: C 78.30; H 8.06; N 4.15.

*7',9'-Diisopropylspiro[cyclopentane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**10**)*

Yield 75%, yellow powder, mp 112–115 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3198 (N-H), 3066, 2960–2872, 1682 (C=O), 1631. ^{1}H NMR (600 MHz, $CDCl_3$,

ppm): δ = 8.49 (1H. s, Ar), 7.57 (1H, s, Ar), 7.54 (2H, br s, Ar, NH), 7.38 (1H, s, Ar), 3.56–3.64 (1H, m, *CH*(CH_3)$_2$), 3.02–3.08 (1H, m, *CH*(CH_3)$_2$), 1.83–1.92 (8H, m, 4CH_2), 1.41 (6H, d, ^3J=6.8 Hz, CH(*CH_3*)$_2$), 1.34 (6H, d, ^3J=6.8 Hz, CH(*CH_3*)$_2$). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 162.9, 150.9, 144.1, 142.6, 132.9, 129.1, 129.0, 123.8, 122.8, 116.9, 107.8, 96.4, 37.6, 33.3, 28.0, 22.9, 22.5, 22.0. Mass spectrum (EI), *m/z* (I_{rel}, %): 337 $[M]^+$ (56). Found, %: C 78.50; H 8.16; N 4.28. $C_{22}H_{27}NO_2$. Calculated, %: C 78.30; H 8.06; N 4.15.

7',9'-Diisopropylspiro[cyclohexane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one ***(11)***

Yield 93%, yellow powder, mp 188–190 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3182 (N-H), 3064, 2958–2864, 1676 (C=O), 1633. ^{1}H NMR (600 MHz, DMSO-d_6, ppm): δ = 8.81 (1H, s, NH), 8.34 (1H, s, Ar), 7.67 (1H, s, Ar), 7.52 (1H, s, Ar), 7.38 (1H, s, Ar), 3.56–3.62 (1H, m, *CH*(CH_3)$_2$), 2.97–3.05 (1H, m, *CH*(CH_3)$_2$), 1.99–2.02 (2H, m), 1.58–1.65 (7H, m), 1.32 (6H, d, ^3J=6.7 Hz, CH(*CH_3*)$_2$), 1.27 (6H, d, ^3J=6.9 Hz, CH(*CH_3*)$_2$), 1.25 (1H, m). ^{13}C NMR (151 MHz, DMSO-d_6,ppm): δ = 161.0, 150.8, 144.1, 142.8, 132.8, 129.2, 128.7, 124.0, 123.3, 118.4, 107.8, 87.2, 35.8, 33.5, 28.2, 24.2, 23.7, 23.2, 21.5. Mass spectrum (EI), *m/z* (I_{rel}, %): 351 $[M]^+$ (96). Found, %: C 78.66; H 8.36; N 4.04. $C_{23}H_{29}NO_2$. Calculated, %: C 78.60; H 8.32; N 3.98.

7',9'-Diisopropylspiro[cycloheptane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one ***(12)***

Yield 85%, yellow powder, mp 97–100 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3192 (N-H), 3066, 2960–2866, 1678 (C=O), 1631. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 8.47 (1H. s, Ar), 7.56 (1H, s, Ar), 7.54 (2H, br s, Ar, NH), 7.37 (1H, s, Ar), 3.58–3.66 (1H, m, *CH*(CH_3)$_2$), 3.02–3.06 (1H, m, *CH*(CH_3)$_2$), 2.27–2.31 (2H, m), 1.98–2.02 (2H, m), 1.68–1.76 (6H, m), 1.50–1.56 (2H, m), 1.41 (6H, d, ^3J=6.9 Hz, CH(*CH_3*)$_2$), 1.34 (6H, d, ^3J=6.9 Hz, CH(*CH_3*)$_2$). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 162.1, 150.4, 143.9, 142.5, 133.0, 128.8, 123.7, 122.8, 116.8, 112.3,

107.7, 90.9, 43.0, 39.4, 33.2, 27.7, 22.9, 22.5, 20.5. Mass spectrum (EI), *m/z* (I_{rel}, %): 365 $[M]^+$ (41). Found, %: C 79.03; H 8.68; N 3.90. $C_{24}H_{31}NO_2$. Calculated, %: C 78.87; H 8.55; N 3.83.

*7',9'-Diisopropyl-4-methylspiro[cyclohexane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**13**)*

Yield 88%, yellow powder, mp 247–254 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3170 (N-H), 3062, 2956–2870, 1678 (C=O), 1633. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 8.49 (1H, s, Ar), 7.58 (2H, s, Ar), 7.46 (1H, br s, Ar, NH), 7.37 (1H, s, Ar), 3.60–3.66 (1H, m, *CH*$(CH_3)_2$), 3.02–3.06 (1H, m, *CH*$(CH_3)_2$), 2.28–2.32 (3H, m), 1.46–1.68 (6H, m), 1.43 (6H, d, ^3J=6.8 Hz, CH(*CH*$_3)_2$), 1.35 (6H, d, ^3J=6.9 Hz, CH(*CH*$_3)_2$), 1.00–1.03 (3H, m, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 162.4, 150.2, 144.0, 142.6, 132.9, 129.0, 124.9, 123.7, 122.8, 117.0, 107.8, 86.4, 35.3, 33.3, 30.3, 29.4, 28.0, 23.0, 22.6, 21.0. Mass spectrum (EI), *m/z* (I_{rel}, %): 365 $[M]^+$ (47). Found, %: C 79.04; H 8.64; N 3.87. $C_{24}H_{31}NO_2$. Calculated, %: C 78.87; H 8.55; N 3.83.

*7',9'-Diisopropyl-4-tert-butylspiro[cyclohexane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**14**)*

Yield 80%, yellow powder, mp 130–136 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3199 (N-H), 3070, 2960–2870, 1678 (C=O), 1631. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.47 (1H, s, Ar), 7.76 (1H, br s, NH), 7.55 (1H, s, Ar), 7.54 (1H, s, Ar), 7.37 (1H, s, Ar), 3.58–3.64 (1H, m, *CH*$(CH_3)_2$), 3.02–3.06 (1H, m, *CH*$(CH_3)_2$), 2.28–2.32 (3H, m), 1.46–1.68 (6H, m), 1.43 (6H, d, ^3J=6.8 Hz, CH(*CH*$_3)_2$), 1.35 (6H, d, ^3J=6.9 Hz, CH(*CH*$_3)_2$), 0.91 (9H, s, t-Bu). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 162.6, 150.0, 144.1, 142.7, 132.9, 128.8, 128.7, 124.7, 122.8, 117.0, 107.8, 86.4, 35.3, 33.3, 30.3, 29.4, 28.0, 26.7, 23.0, 22.6, 21.0. Mass spectrum (EI), *m/z* (I_{rel}, %): 407 $[M]^+$ (52). Found, %: C 79.84; H 9.28; N 3.56. $C_{27}H_{37}NO_2$. Calculated, %: C 79.56; H 9.15; N 3.44.

*7',9'-Diisopropyl-4-(1,1-dimethylpropyl)spiro[cyclohexane-1,2'-naphtho[2,3-e][1,3]oxazin]-4'(3'H)-one (**15**)*

Yield 85%, yellow powder, mp 105–115 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 3190 (N-H), 3068, 2960–2872, 1680 (C=O), 1631. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.48 (1H. s, Ar), 7.76 (1H, br s, NH), 7.56 (1H, s, Ar), 7.54 (1H, s, Ar), 7.37 (1H, s, Ar), 3.59–3.64 (1H, m, *CH*$(CH_3)_2$), 3.02–3.06 (1H, m, *CH*$(CH_3)_2$), 2.28–2.32 (3H, m), 1.46–1.68 (8H, m), 1.43 (6H, d, ^3J=6.8 Hz, CH(*CH*$_3$)$_2$), 1.35 (6H, d, ^3J=6.9 Hz, CH(*CH*$_3$)$_2$), 0.91 (6H, m), 0.82–0.84 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 163.0, 151.2, 144.9, 143.5, 132.7, 128.6, 128.3, 124.2, 123.2, 117.0, 107.8, 86.4, 35.3, 33.3, 30.3, 29.4, 28.2, 26.4, 23.1, 22.7, 22.5, 21.0, 8.2. Mass spectrum (EI), *m/z* (I_{rel},%): 421 $[M]^+$ (46). Found, %: C 79.95; H 9.48; N 3.42. $C_{27}H_{37}NO_2$. Calculated, %: C 79.77; H 9.32; N 3.32.

*Synthesis of compounds **16–27** (General Method)*

Compound **4** (2.53 g, 0.01 mol) was added to the Vilsmeier reagent prepared from $POCl_3$ (2.75 mL, 0.03 mol) and DMF (4.61 mL, 0.06 mol) with ice cooling. The reaction mixture was stirred and heated on a water bath at 80 °C for 1.5 h. Then the reaction mixture was cooled to 10 °C and treated with an ice-cold 15% aq. solution of $NaClO_4$ (10 mL). The precipitate of the organic salt was filtered off, dried and washed with toluene. The organic salt was dissolved in hot DMF (5 mL). To the obtained solution, an aqueous 15 % NaOH solution (1.5 mL) was added and the mixture was stirred vigorously at 60–75 °C for 5 min. The precipitated solid of compound **16** was filtered off. If no solid was formed, the solution was cooled to room temperature and water was added to crystallize the product.

Similarly to **16** compounds **17–27** and **29** were obtained.

*N'-(3-Formyl-1,2-dihydrobenzo[g]cyclopenta[b]chromen-11-yl)-N,N-dimethylimidoformamide (**16**)*

Yield 65%, yellow powder, mp 215–216 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 1626 (CHO). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.90 (1H, s, CHO), 8.23

(1H, s), 8.13 (1H, s, Ar), 7.95 (1H, d, ^3J=8.2 Hz, Ar), 7.87 (1H, d, ^3J=7.7 Hz, Ar), 7.69 (1H, s, Ar), 7.50 (1H, t, ^3J=7.3 Hz, Ar), 7.44 (1H, t, ^3J=7.5 Hz, Ar), 3.11 (6H, s, NMe_2), 2.84–2.87 (2H, m, CH_2), 2.55–2.58 (2H, m, CH_2). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.01 (1H, s, CHO), 7.82 (1H, d, ^3J=8.2 Hz, Ar), 7.76 (1H, s, Ar), 7.75 (1H, d, ^3J=8.2 Hz, Ar), 7.51 (1H, s, Ar), 7.45 (1H, t, ^3J=7.2 Hz, Ar), 7.39 (1H, t, ^3J=7.6 Hz, Ar), 3.18 (3H, s, Me), 3.10 (3H, s, Me), 2.81–2.84 (2H, m, CH_2), 2.73–2.76 (2H, m, CH_2). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 182.6, 165.5, 153.3, 149.6, 133.0, 129.7, 127.4, 126.2, 126.1, 126.0, 124.3, 122.3, 121.7, 120.0, 114.2, 110.6, 39.6, 33.5, 23.0, 22.6. Mass spectrum (FAB), *m/z* (I_{rel}, %): 319 $[M+H]^+$ (28). Found, %: C 75.60; H 5.75; N 8.87. $C_{20}H_{18}N_2O_2$. Calculated, %: C 75.45; H 5.70; N 8.80.

*N'-(4-Formyl-2,3-dihydro-1H-benzo[b]xanthen-12-yl)-N,N-dimethylimidoformamide (**17**)*

Yield 75%, yellow powder, mp 195–196 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 1636 (CHO). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.25 (1H, s, CHO), 8.05 (1H, s), 7.95 (1H, d, ^3J=8.1 Hz, Ar), 7.84 (1H, d, ^3J=8.2 Hz, Ar), 7.76 (1H, s, Ar), 7.66 (1H, s, Ar), 7.50 (1H, t, ^3J=7.0 Hz, Ar), 7.41 (1H, t, ^3J=7.0 Hz, Ar), 3.09 (3H, s, Me), 3.08 (3H, s, Me), 2.54 (2H, t, ^3J=6.1 Hz, CH_2), 2.31 (2H, t, ^3J=5.9 Hz, CH_2), 1.56–1.62 (2H, m, CH_2). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.35 (1H, s, CHO), 7.92 (1H, s, Ar), 7.80 (1H, d, ^3J=8.2 Hz, Ar), 7.72 (1H, d, ^3J=8.2 Hz, Ar), 7.42–7.75 (3H, m, Ar), 7.35 (1H, t, ^3J=7.0 Hz, Ar), 3.17 (3H, s, Me), 3.08 (3H, s, Me), 2.56 (2H, t, ^3J=6.1 Hz, CH_2), 2.45 (2H, t, ^3J=6.0 Hz, CH_2), 1.66–1.70 (2H, m, CH_2). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 187.3, 162.5, 153.8, 149.9, 146.3, 134.4, 130.2, 128.4, 127.2, 126.9, 124.9, 123.6, 121.8, 113.6, 112.4, 110.8, 40.4, 34.5, 25.6, 21.5, 20.9. Mass spectrum (EI), *m/z* (I_{rel}, %): 332 $[M]^+$ (67). Found, %: C 75.98; H 6.12; N 8.49. $C_{21}H_{20}N_2O_2$. Calculated, %: C 75.88; H 6.06; N 8.43.

*N'-(7-Formyl-8,9,10,11-tetrahydrobenzo[g]cyclohepta[b]chromen-12-yl)-N,N-dimethylimidoformamide (**18**)*

Yield 70%, yellow powder, mp 180–183 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 1642 (CHO). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.39 (1H, s, CHO), 7.92 (1H, s), 7.79 (1H, d, ^{3}J=8.2 Hz, Ar), 7.71 (1H, d,^{3}J=8.2 Hz, Ar), 7.42 (1H, t, ^{3}J=7.4 Hz, Ar), 7.39 (2H, s, Ar), 7.34 (1H, t, ^{3}J=7.5 Hz, Ar), 3.17 (3H, s, Me), 3.09 (3H, s, Me), 2.63–2.66 (4H, m, $2CH_2$), 1.76–1.82 (4H, m, $2CH_2$). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 185.5, 166.5, 153.6, 150.0, 149.8, 134.6, 130.0, 128.5, 127.2, 126.9, 124.8, 123.9, 121.6, 117.9, 117.0, 110.5, 40.4, 34.6, 28.1, 26.1, 25.8, 20.0. Mass spectrum (EI), *m/z* (I_{rel}, %): 346 $[M]^+$ (77). Found, %: C 76.40; H 6.52; N 8.18. $C_{22}H_{22}N_2O_2$. Calculated, %: C 76.28; H 6.40; N 8.09.

*N'-(4-Formyl-2-methyl-2,3-dihydro-1H-benzo[b]xanthen-12-yl)-N,N-dimethylimidoformamide (**19**)*

Yield 60%, yellow powder, mp 217–220 °C (DMF). FTIR (KBr pellets, ν, cm^{-1}): 1639 (CHO). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.34 (1H, s, CHO), 7.92 (1H, s), 7.81 (1H, d, ^{3}J=8.1 Hz, Ar), 7.72 (1H, d, ^{3}J=8.2 Hz, Ar), 7.41–7.46 (3H, m, Ar), 7.36 (1H, t, ^{3}J=7.1 Hz, Ar), 3.19 (3H, s, Me), 3.10 (3H, s, Me), 2.70–2.77 (2H, m, CH_2), 2.02 (1H, dd, *J*=15.6 Hz, *J*=11.2 Hz), 1.90 (1H, dd, *J*=16.2 Hz, *J*=10.2 Hz), 1.70–1.77 (1H, m, CH), 1.06 (3H, d, ^{3}J=6.5 Hz, Me). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 187.3, 162.4, 153.7, 149.8, 145.6, 134.4, 130.1, 128.4, 127.2, 126.9, 124.9, 123.6, 121.7, 113.4, 111.7, 110.8, 40.4, 34.5, 33.5, 29.4, 27.0, 21.2. Mass spectrum (EI), *m/z* (I_{rel}, %): 346 $[M]^+$ (81). Found, %: C 76.43; H 6.54; N 8.18. $C_{22}H_{22}N_2O_2$. Calculated, %: C 76.28; H 6.40; N 8.09.

*N'-(2-tert-Butyl-4-formyl-2,3-dihydro-1H-benzo[b]xanthen-12-yl)-N,N-dimethylimidoformamide (**20**)*

Yield 78%, yellow powder, mp 215–217 °C (DMF). FTIR (KBr pellets, ν, cm^{-1}): 1635 (CHO). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.36 (1H, s, CHO), 7.91 (1H, s), 7.81 (1H, d, ^{3}J=8.3 Hz, Ar), 7.74 (1H, d, ^{3}J=8.1 Hz, Ar), 7.43–7.46 (3H, m, Ar), 7.35–7.39 (1H, m, Ar), 3.20 (3H, s, Me), 3.11 (3H, s, Me), 2.92 (1H, d, *J*=15.2 Hz), 2.82 (1H, d, *J*=15.9 Hz), 1.90–1.99 (2H, m, CH_2), 1.66–1.73 (1H, m,

CH), 0.97 (9H, s, t-Bu). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 187.5, 162.4, 153.8, 149.9, 146.3, 134.4, 130.1, 128.4, 127.2, 126.9, 124.9, 123.5, 121.8, 114.7, 112.5, 110.9, 46.7, 40.4, 34.6, 32.4, 27.5, 26.5, 22.7. Mass spectrum (EI), *m/z* (I_{rel}, %): 388 $[M]^+$ (86). Found, %: C 77.45; H 7.36; N 7.29. $C_{25}H_{28}N_2O_2$. Calculated, %: C 77.29; H 7.26; N 7.21.

*N'-[2-(1,1-Dimethylpropyl)-4-formyl-2,3-dihydro-1H-benzo[b]xanthen-12-yl]-N,N-dimethylimidoformamide (**21**)*

Yield 74%, yellow powder, mp 190–193 °C (DMF). FTIR (KBr pellets, ν, cm^{-1}): 1635 (CHO). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.35 (1H, s, CHO), 7.91 (1H, s), 7.81 (1H, d, ^3J=8.1 Hz, Ar), 7.73 (1H, d, ^3J=8.2 Hz, Ar), 7.41–7.46 (3H, m, Ar), 7.37 (1H, t, ^3J=7.4 Hz, Ar), 3.19 (3H, s, Me), 3.11 (3H, s, Me), 2.83–2.88 (1H, m), 2.73–2.78 (1H, m), 1.91–1.98 (2H, m, CH_2), 1.26–1.45 (3H, m), 0.89 (6H, s), 0.83 (3H, t, ^3J=7.5 Hz). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 187.4, 162.4, 153.8, 149.8, 146.4, 134.3, 130.1, 128.4, 127.2, 126.9, 124.9, 123.5, 121.8, 114.7, 112.6, 110.9, 40.4, 39.7, 34.7, 32.7, 26.0, 24.2, 24.1, 22.3, 8.3. Mass spectrum (EI), *m/z* (I_{rel}, %): 402 $[M]^+$ (75). Found, %: C 77.73; H 7.62; N 7.06. $C_{26}H_{30}N_2O_2$. Calculated, %: C 77.58; H 7.51; N 6.96.

*N'-(3-Formyl-6,8-diisopropyl-1,2-dihydrobenzo[g]cyclopenta[b]chromen-11-yl)-N,N-dimethylimidoformamide (**22**)*

Yield 55%, yellow powder, mp 235–238 °C (*i*-PrOH). FTIR (KBr pellets, ν, cm^{-1}): 1626 (CHO). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.02 (1H, s, CHO), 8.07 (1H, s), 7.76 (1H, s, Ar), 7.69 (1H, s, Ar), 7.53 (1H, s, Ar), 7.36 (1H, s, Ar), 3.57–3.66 (1H, m, $CH(CH_3)_2$), 3.20 (3H, s), 3.11 (3H, s), 3.02–3.04 (1H, m, $CH(CH_3)_2$), 2.83–2.87 (2H, m, CH_2), 2.55–2.58 (2H, m, CH_2), 1.34 (6H, d, ^3J=6.8 Hz, $CH(CH_3)_2$), 1.28 (6H, d, ^3J=6.9 Hz, $CH(CH_3)_2$). Mass spectrum (EI), *m/z* (I_{rel}, %): 402 $[M]^+$ (83). Found, %: C 77.71; H 7.58; N 7.03. $C_{26}H_{30}N_2O_2$. Calculated, %: C 77.58; H 7.51; N 6.96.

*N'-(4-Formyl-7,9-diisopropyl-2,3-dihydro-1H-benzo[b]xanthen-12-yl)-N,N-dimethylimidoformamide (**23**)*

Yield 70%, yellow powder, mp 218–220 °C (MeOH). FTIR (KBr pellets, ν, cm^{-1}): 1627 (CHO). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.32 (1H, s, CHO), 8.01 (1H, s), 7.82 (1H, s, Ar), 7.77 (1H, s, Ar), 7.62 (1H, s, Ar), 7.33 (1H, s, Ar), 3.61–3.66 (1H, m, *CH*(CH_3)$_2$), 3.09 (3H, s, Me), 3.08 (3H, s, Me), 2.97–3.04 (1H, m, *CH*(CH_3)$_2$), 2.57 (2H, t, ^3J=6.0 Hz, CH_2), 2.32 (2H, t, ^3J=5.7 Hz, CH_2), 1.56–1.62 (2H, m, CH_2), 1.34 (6H, d, ^3J=6.8 Hz, CH(*CH_3*)$_2$), 1.28 (6H, d, ^3J=6.9 Hz, CH(*CH_3*)$_2$). ^{13}C NMR (400 MHz, DMSO-d_6/CF_3CO_2D, ppm): δ = 187.3, 159.3, 157.3, 148.9, 146.1, 144.2, 131.6, 131.5, 131.1, 126.3, 124.7, 124.5, 123.1, 118.9, 116.5, 107.7, 44.1, 37.8, 34.2, 28.9, 25.6, 24.0, 23.6, 21.4, 20.2. Mass spectrum (FAB), *m/z* (I_{rel}, %): 417 $[M+H]^+$ (100). Found, %: C 76.03; H 7.80; N 6.76. $C_{27}H_{32}N_2O_2$. Calculated, %: C 77.85; H 7.74; N 6.72.

*N'-(7-Formyl-2,4-diisopropyl-8,9,10,11-tetrahydrobenzo[g]cyclohepta[b]chromen-12-yl)-N,N-dimethylimidoformamide (**24**)*

Yield 65%, yellow powder, mp 121–124 °C (MeOH). FTIR (KBr pellets, ν, cm^{-1}): 1635 (CHO). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 10.44 (1H, s, CHO), 7.88 (1H, s), 7.66 (1H, s, Ar), 7.48 (1H, s, Ar), 7.41 (1H, s, Ar), 7.29 (1H, s, Ar), 3.61–3.66 (1H, m, *CH*(CH_3)$_2$), 3.20 (3H, s, Me), 3.10 (3H, s, Me), 3.02–3.06 (1H, m, *CH*(CH_3)$_2$), 2.63–2.66 (4H, m, $2CH_2$), 1.76–1.82 (4H, m, $2CH_2$), 1.43 (6H, d, ^3J=6.8 Hz, CH(*CH_3*)$_2$), 1.35 (6H, d, ^3J=6.9 Hz, CH(*CH_3*)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 187.1, 162.6, 153.4, 149.4, 145.5, 144.9, 143.6, 131.0, 130.6, 124.0, 123.1, 122.5, 121.0, 113.4, 111.5, 107.0, 40.4, 34.5, 34.2, 33.5, 29.6, 29.3, 27.5, 24.0, 23.6, 22.9. Mass spectrum (EI), *m/z* (I_{rel}, %): 430 $[M]^+$ (73). Found, %: C 78.33; H 8.09; N 6.61. $C_{28}H_{34}N_2O_2$. Calculated, %: C 78.10; H 7.96; N 6.51.

*N'-(4-Formyl-7,9-diisopropyl-2-methyl-2,3-dihydro-1H-benzo[b]xanthen-12-yl)-N,N-dimethylimidoformamide (**25**)*

Yield 55%, yellow powder, mp 191–194 °C (MeOH). FTIR (KBr pellets, ν, cm^{-1}): 1630 (CHO). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.40 (1H, s, CHO), 7.88 (1H, s), 7.70 (1H, s, Ar), 7.49 (1H, s, Ar), 7.42 (1H, s, Ar), 7.31 (1H, s, Ar), 3.61–3.66 (1H, m, *CH*(CH_3)$_2$), 3.20 (3H, s, Me), 3.10 (3H, s, Me), 3.02–3.06 (1H, m, *CH*(CH_3)$_2$), 2.74–2.80 (2H, m, CH_2), 2.05 (1H, dd, *J*=15.3 Hz, *J*=11.3 Hz), 1.93 (1H, dd, *J*=15.9 Hz, *J*=10.3 Hz), 1.70–1.77 (1H, m, CH), 1.43 (6H, d, ^{3}*J*=6.8 Hz, CH(*CH*$_3$)$_2$), 1.35 (6H, d, ^{3}*J*=6.9 Hz, CH(*CH*$_3$)$_2$), 1.08 (3H, d, ^{3}*J*=6.5 Hz, Me). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 187.3, 162.8, 153.6, 149.6, 145.8, 145.0, 143.8, 131.2, 130.9, 124.0, 123.4, 122.6, 121.0, 113.4, 111.5, 107.0, 40.4, 34.5, 34.3, 33.5, 29.5, 29.0, 27.1, 24.0, 23.6, 21.3. Mass spectrum (EI), *m/z* (I_{rel}, %): 430 $[M]^+$ (81). Found, %: C 78.26; H 8.05; N 6.58. $C_{28}H_{34}N_2O_2$. Calculated, %: C 78.10; H 7.96; N 6.51.

*N'-(2-tert-Butyl-4-formyl-7,9-diisopropyl-2,3-dihydro-1H-benzo[b]xanthen-12-yl)-N,N-dimethylimidoformamide (**26**)*

Yield 50%, yellow powder, mp 139–142 °C (MeOH). FTIR (KBr pellets, ν, cm^{-1}): 1633 (CHO). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.38 (1H, s, CHO), 7.85 (1H, s), 7.70 (1H, s, Ar), 7.48 (1H, s, Ar), 7.42 (1H, s, Ar), 7.30 (1H, s, Ar), 3.60–3.66 (1H, m, *CH*(CH_3)$_2$), 3.20 (3H, s, Me), 3.10 (3H, s, Me), 3.00–3.05 (1H, m, *CH*(CH_3)$_2$), 2.92–2.95 (1H, m), 2.81–2.85 (1H, m), 1.92–1.99 (3H, m), 1.43 (6H, d, ^{3}*J*=6.8 Hz, CH(*CH*$_3$)$_2$), 1.35 (6H, d, ^{3}*J*=6.9 Hz, CH(*CH*$_3$)$_2$), 0.95 (9H, s, t-Bu). Mass spectrum (EI), *m/z* (I_{rel}, %): 472 $[M]^+$ (74). Found, %: C 78.90; H 8.68; N 6.03. $C_{31}H_{40}N_2O_2$. Calculated, %: C 78.77; H 8.53; N 5.93.

*N'-(2-(1,1-Dimethylpropyl)-4-formyl-7,9-diisopropyl-2,3-dihydro-1H-benzo[b]xanthen-12-yl)-N,N-dimethylimidoformamide (**27**)*

Yield 45%, yellow powder, mp 126–129 °C (MeOH). FTIR (KBr pellets, ν, cm^{-1}): 1634 (CHO). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 10.39 (1H, s, CHO), 7.85 (1H, s), 7.70 (1H, s, Ar), 7.48 (1H, s, Ar), 7.42 (1H, s, Ar), 7.30 (1H, s, Ar), 3.60–3.66 (1H, m, *CH*(CH_3)$_2$), 3.19 (3H, s, Me), 3.09 (3H, s, Me), 3.00–3.05 (1H, m,

CH(CH_3)$_2$), 2.87–2.90 (1H, m), 2.76–2.81 (1H, m), 1.94–1.98 (2H, m), 1.54–1.58 (1H, m), 1.43 (6H, d, ^3J=6.8 Hz, CH(*CH*$_3$)$_2$), 1.35 (6H, d, ^3J=6.9 Hz, CH(*CH*$_3$)$_2$), 0.90 (6H, s), 0.85 (3H, d, ^3J=6.5 Hz, CH_2). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ = 186.7, 162.2, 153.0, 149.0, 145.9, 144.4, 143.2, 130.6, 129.3, 123.3, 122.0, 120.4, 120.0, 113.4, 111.5, 107.0, 40.4, 34.5, 34.3, 33.5, 29.5, 29.0, 27.1, 26.2, 24.0, 22.0, 23.6, 21.3, 7.7. Mass spectrum (EI), *m/z* (I_{rel}, %): 486 $[M]^+$ (79). Found, %: C 79.23; H 8.88; N 5.90. $C_{31}H_{40}N_2O_2$. Calculated, %: C 78.97; H 8.70; N 5.76.

*2,2-Dimethyl-2,3-dihydro-4H-naphtho[2,3-e][1,3]oxazin-4-one (**28**)*

Compound **28** was obtained by the known procedure.[24] Yield 62%, white powder, mp 220–222 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 8.91 (1H, s, NH), 8.44 (1H, s, Ar), 8.03 (1H, d, ^3J=8.2 Hz, Ar), 7.83 (1H, d, ^3J=8.3 Hz, Ar), 7.55 (1H, t, ^3J=7.5 Hz, Ar), 7.40–7.44 (2H, m, Ar), 1.56 (6H, s, 2Me).

*(4-Amino-2H-benzo[g]chromen-2-ylidene)malonaldehyde (**29**)*

Yield 54%, yellow powder, mp 232–234 °C (MeOH). FTIR (KBr pellets, ν, cm^{-1}): 3307 (NH_2), 3032, 2923–2865, 1649 (C=O), 1574. ^{1}H NMR (400 MHz, 20 °C, DMSO-d_6, ppm): δ = 9.95 (2H, s, CHO), 9.17 (1H, s) and 8.95 (1H, s, NH_2), 8.84 (1H, s, Ar), 8.15 (1H, s, Ar), 8.04 (1H, d, ^3J=8.3 Hz, Ar), 7.98 (1H, d, ^3J=8.4 Hz, Ar), 7.79 (1H, s, Ar), 7.68 (1H, t, ^3J=7.0 Hz, Ar), 7.59 (1H, t, ^3J=8.0 Hz, Ar). ^{1}H NMR (400 MHz, 60 °C, DMSO-d_6, ppm): δ = 9.95 (2H, s, CHO), 9.00 (2H, br s, NH_2), 8.85 (1H, s, Ar), 8.14 (1H, s, Ar), 8.04 (1H, d, ^3J=8.3 Hz, Ar), 7.99 (1H, d, ^3J=8.4 Hz, Ar), 7.79 (1H, s, Ar), 7.68 (1H, t, ^3J=7.0 Hz, Ar), 7.59 (1H, t, ^3J=8.0 Hz, Ar).^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 186.1, 167.9, 156.3, 148.7, 135.2, 129.5, 129.0, 128.6, 127.2, 126.4, 124.1, 114.3, 114.0, 107.4, 90.8. Mass spectrum (FAB), *m/z* (I_{rel}, %): 266 $[M+H]^+$ (14). Found, %: C 72.51; H 4.25; N 5.34. $C_{16}H_{11}NO_3$. Calculated, %: C 72.45; H 4.18; N 5.28.

X-ray diffraction study

Crystals of **16** ($C_{20}H_{18}N_2O_2$, Mr = 318.36) are monoclinic, space group $P2_1/c$, at 120K: a = 11.7875(6) Å, b = 6.1475(3) Å, c = 21.3522(11) Å, β = 96.5170(10)°, V = 1537.26(13) $Å^3$, Z = 4, d_{calc}= 1.376 g/cm^{-3}, μ(MoKa) = 0.090 mm^{-1}, F(000) = 672. Intensities of 19768 reflections were measured with a Bruker APEX 2 Duo diffractometer (CCD detector) [l(MoKa) = 0.71073Å, ω-scans, 2q<60°] and 4484 independent reflections [R_{int}=0.0592] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The H(C) atom positions were calculated, these atoms were refined in the isotropic approximation within the riding model. For **16**, the refinement converged to wR_2 = 0.1348 and GOF = 1.028 for all independent reflections (R_1 = 0.0487 was calculated against F for 3088 observed reflections with I>2s(I)). Crystal data were deposited at Cambridge Crystal Database, deposition number CCDC 1874393.

Crystals of **17** ($C_{21}H_{20}N_2O_2$, Mr = 332.39) are monoclinic, space group $P2_1/c$, at 120K: a = 15.755(2) Å, b = 9.0624(13) Å, c = 12.5984(19) Å, β = 107.711(4)°, V = 1713.6(4) $Å^3$, Z = 4, d_{calc}= 1.288 g/cm^{-3}, μ(MoKa) = 0.084 mm^{-1}, F(000) = 704. Intensities of 14127 reflections were measured with a Bruker APEX 2 Duo diffractometer (CCD detector) [l(MoKa) = 0.71073Å, ω-scans, 2q<61°] and 5069 independent reflections [R_{int}=0.0559] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The H(C) atom positions were calculated, these atoms were refined in the isotropic approximation within the riding model. For **17**, the refinement converged to wR_2 = 0.1432 and GOF = 0.986 for all independent reflections (R_1 = 0.0553 was calculated against F for 3048 observed reflections with I>2s(I)). Crystal data were deposited at Cambridge Crystal Database, deposition number CCDC 1874392.

Crystals of **18** ($C_{22}H_{22}N_2O_2$, Mr = 346.41) are monoclinic, space group $P2_1/n$, at 120K: a = 8.1416(4) Å, b = 16.8250(8) Å, c = 13.0219(6) Å, β = 93.2860(10)°, V

= 1780.84(15) Å^3, Z = 4, d_{calc}= 1.292 g/cm^{-3}, μ(MoKa) = 0.083 mm^{-1}, F(000) = 736. Intensities of 23554 reflections were measured with a Bruker APEX 2 Duo diffractometer (CCD detector) [l(MoKa) = 0.71073Å, ω-scans, 2q<60°] and 5202 independent reflections [R_{int}=0.0306] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The H(C) atom positions were calculated, these atoms were refined in the isotropic approximation within the riding model. For **18**, the refinement converged to wR_2 = 0.1267 and GOF = 1.024 for all independent reflections (R_1 = 0.0440 was calculated against F for 4127 observed reflections with I>2s(I)). Crystal data were deposited at Cambridge Crystal Database, deposition number CCDC 1874394. All crystallography calculations were performed using the SHELX software.[25,26]

Acknowledgments

Authors are grateful to Dr. Borisova N. E. for NMR studies. The NMR measurements were supported by the Laboratory of Magnetic Tomography and Spectroscopy of Chemical Department of Moscow State University. I. V. Ananyev is grateful to the Russian Science Foundation (Project # 18-73-10131) for the support of X-ray diffraction studies. A. L. Tatarets is grateful to the NAS of Ukraine (project # 0117U001281).

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