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Reactions of 2*H*(4*H*)-chromenes with dinucleophiles: one-step synthesis of 2-(1*H*-(bi)pyrazol-3-yl)- and 2-(1,4(5)-(benzo)diazepin-4-yl)phenols

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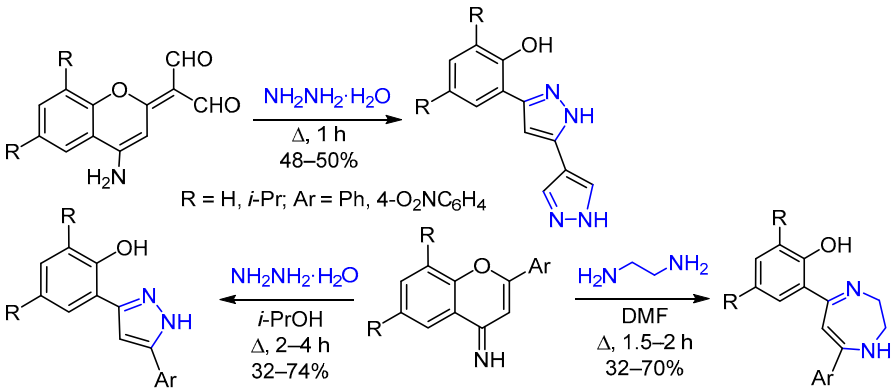


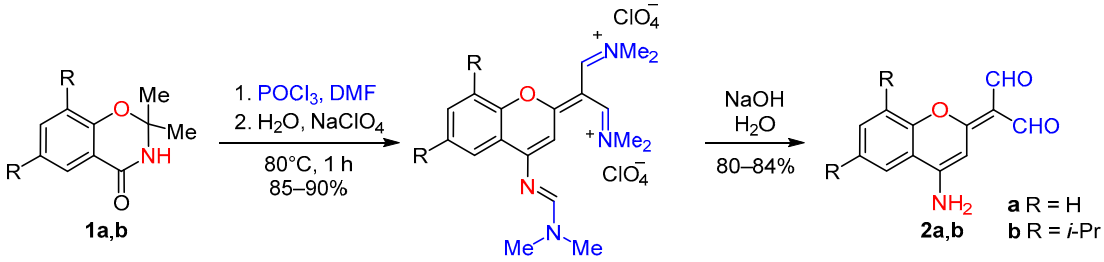
Novel derivatives of 2-(1*H*-(bi)pyrazol-3-yl)phenols and 2-(1,4(5)-(benzo)diazepin-4-yl)phenols were obtained in the reaction of (4-amino-2*H*-chromen-2-ylidene)malondialdehyde and 4*H*-chromen-4-imines with 1,2-, 1,3-, and 1,4-dinucleophiles proceeding as a cascade reaction initiated by the Michael reaction.

Keywords: chromenes, dipyrazoles, dinucleophiles, rearrangement, Vilsmeier–Haack reagent.

Currently, one of the most rapidly developing areas of modern organic chemistry is the transformation (recyclization) reactions of heterocyclic systems. These chemical transformations lead not only to the rapid formation of complex molecules, but also provide the possibility of their further modification. Chromene derivatives are very promising starting model compounds for the study of such transformations. Due to their high reactivity, various heterocyclic compounds may be formed.[1] The presence of several electrophilic centers in chromene derivatives makes it possible to study in detail the recyclization reactions with various nucleophilic reagents, resulting in *o*-hydroxyphenyl derivatives of pyrazoles and oxazoles,[2–6] pyrazines and quinoxalines,[7] as well as aminopyrimidines.[8,9] *o*-Hydroxyphenyl group is of interest as a structural fragment of a large number of biologically active compounds,[10–13] stabilizers of polymeric materials,[14,15] antioxidants, and analytical reagents for complexation with transition metal ions.[16]

Earlier,[17] we obtained from compounds **1a**,**b** polyfunctional diformyl derivatives of chromenes **2a**,**b** (Scheme 1), promising starting compounds for combinatorial chemistry due to the large number of possible functionalization options. They are also attractive due to their photophysical properties: in the solid state, derivatives of (4-amino-chromen-2-ylidene)malondialdehyde **2a**,**b** fluoresce in the red region of the spectrum with a Stokes shift of 47 and 67 nm (1230 and 1900 cm^{-1}), respectively.[18]

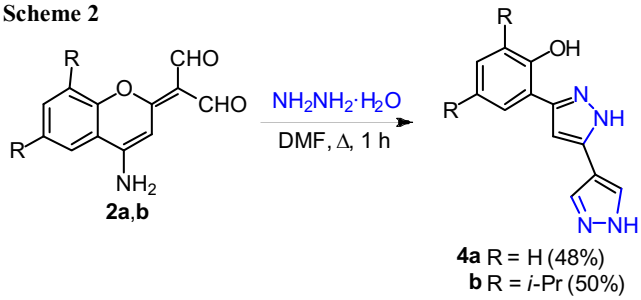
Scheme 1



In the reaction of compounds **2a**,**b** with hydrazine hydrate, the pyranyl ring is opened to form *o*-hydroxyphenyl derivatives, dipyrazoles **4a**,**b**, in 48–50% yields (Scheme 2).

Presumably, the reaction proceeds according to the mechanism of nucleophilic addition at the C-2 atom of chromenes **2a**,**b**, and compounds **4a**,**b** are formed as a result of the subsequent 5-*exo*-*trig* cyclization. Compound **4a** retains its ability to fluorescence in the solid state in the yellow-green region of the spectrum.

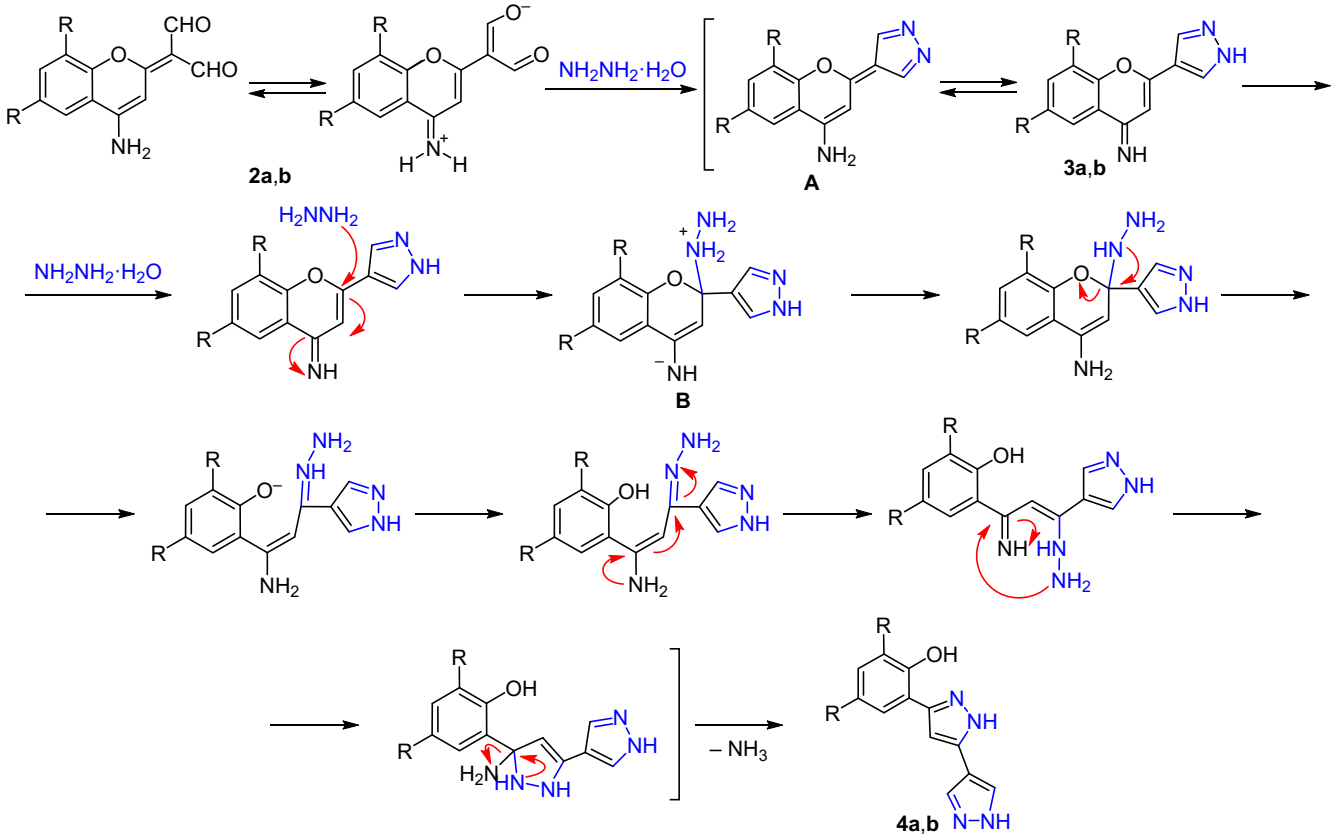
Scheme 2



In the literature, only two examples of the preparation of such dipyrazoles can been found: the reaction of 4*H*,4'*H*-3,3-bischromene-4,4'-dione derivatives with hydrazine[19] and the treatment of 3-(3-aryl-3-oxopropenyl)chromen-4-ones with hydrazine with their subsequent oxidation to dipyrazoles.[20]

We have proposed a possible route for this reaction (Scheme 3). An analysis of the bond lengths of compound **2a**[17] shows a significant redistribution of the electron density in the molecule from the amino group to the malondialdehyde group. Thus, carbonyl bonds are lengthened to 1.226(3)–1.241(3) Å compared to the average C=O bond length in aldehydes of 1.192 Å and the C(9)–N(1) bond, at 1.316(3)–1.320(3) Å, is slightly shortened compared with the average value for C(sp^2)–NH_2 bonds (1.336 Å).[21] Despite the significantly reduced electrophilicity of the carbon atoms of the carbonyl groups compared to the carbon atoms of an aldehyde group which is not conjugated with an electron-donating substituent, in the first stage, the cyclic intermediate **A** is formed, for

Scheme 3



which prototropic tautomerism is possible. The presence of an activated double bond in the chromene ring allows intermediates **3a**,**b** to be regarded as Michael acceptors. This is followed by the addition of the hydrazine molecule at the double bond with the formation of the unstable Michael adduct **B**, which stabilizes by cleavage of the chromene ring and subsequent cyclization to dipyrazoles **4a**,**b**.

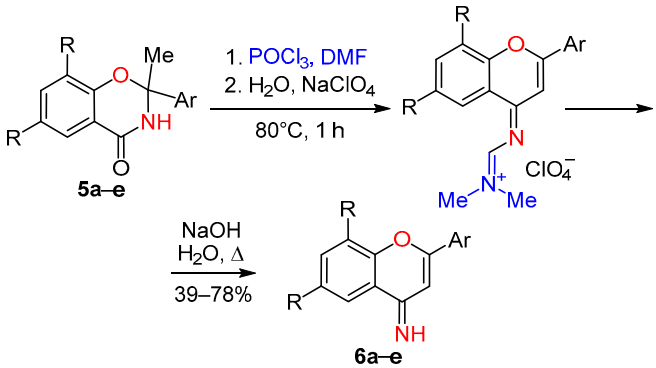
^{1}H NMR spectra of compounds **4a**,**b** contain the characteristic singlet signals of the protons of NH groups in the 13.07–13.33 ppm range and the signal of the proton of the hydroxyl group in the 10.98–11.20 ppm range. In the ^{13}C NMR spectra of compounds **4a**,**b**, the signals of the carbon atoms of the pyrazole rings as well as the carbon atom bonded to the OH group are recorded. Vibrations of the OH and NH groups in the IR spectrum of compound **4a** correspond to intense absorption bands at 3418 and 2292–3252 cm^{-1}.

In order to expand the number of examples of an effective method for the synthesis of pyrazole derivatives, we obtained new model compounds, imines **6a**–**e** (Scheme 4), which possess an activated double bond. Despite the availability of literature data on the recyclization of chromones by the action of nucleophilic reagents, it is necessary to emphasize the lack of information on the reactivity of 4*H*-chromen-4-imines under these conditions. Considering the different electronegativity of oxygen and nitrogen atoms, it was necessary to establish whether the replacement of the C=O group in the chromone ring by the C=NH group in the chromene ring would influence the course of the reaction.

Synthesis of imine derivatives **6b**–**e** illustrates the general nature of the new multistage cascade reaction, namely, rearrangement of geminal 1,3-benzoxazines **5b**–**e** by the action of the Vilsmeier–Haack reagent, which has previously been described in one example.[17] Compounds **5a**–**e** were prepared according to a published method.[23]

The characteristic signal of the 3-CH proton of chromene products **6a**–**e** appears at 6.91–7.45 ppm.

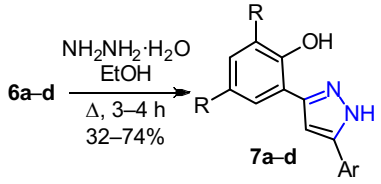
Scheme 4



a R = H, Ar = Ph; **b** R = H, Ar = 4-$O_2NC_6H_4$; **c** R = *i*-Pr, Ar = Ph; **d** R = *i*-Pr, Ar = 4-$O_2NC_6H_4$; **e** R = H, Ar = 4-BrC_6H_4

The expected substituted (1*H*-pyrazol-3-yl)phenols **7a**–**d** (Scheme 5) were obtained in the reaction of imines **6a**–**d** with hydrazine hydrate. The structure of compounds **7a**–**d**, confirmed by a collection of spectral data, suggests that the nature of this reaction is very close to the recyclization of benzopyrans **2a**,**b**.

Scheme 5



a R = H, Ar = Ph
b R = H, Ar = 4-$O_2NC_6H_4$
c R = *i*-Pr, Ar = Ph
d R = *i*-Pr, Ar = 4-$O_2NC_6H_4$

To establish the most preferred localization of NH protons in dipyrazoles **4a**,**b** and pyrazoles **7a**–**d**, we investigated the tautomeric properties of compounds **4a**, **7a**,**b** (Fig. 1) by quantum-chemical calculations using the MP2/6-311+G(d,p) approximation (Table 1).

A characteristic feature of the structure of compounds **4a**, **7a**,**b** is the nonplanar mutual arrangement of rings, which is consistent with the X-ray diffraction data of similar compounds.[24,25] The dihedral angle between pyrazole rings (as well as pyrazole and phenyl (nitroaryl)) varies within 38.4–52.0° for N(2)–H tautomers and 25.2–30.3° for N(1)–H forms. The dihedral angle between the phenol and pyrazole rings is significantly smaller (15.9–21.0°), which can be explained by the formation of O–H···N or O···H–N hydrogen bonds with a length of 1.82–1.83 Å and 2.11 Å, respectively. The high strength of the O–H···N bond increases the stability of the N(2)–H tautomers for all studied compounds. The position of the proton in the second pyrazole ring of compound **4a** has practically no effect on the energy of the compound. It should be noted that, unlike pyrazoles **4a**, **7a**, for which the occupancy of the N(2)–H forms exceeds 99%, there is a significant occupancy of the tautomeric N(1)–H form (20%) in the case of nitroaryl derivative **7b**. This is due to the electron-withdrawing effect of the nitro group, as a result of which the basicity of the N(1) atom in the N(2)–H tautomer decreases (and, as a result, the energy of the O–H···N hydrogen bond decreases), and the acidity of the N(1)-H group increases in the corresponding tautomer, which leads to an increase in the energy of the O···H–N hydrogen bond as compared to compounds **4a** and **7a**. This is experimentally confirmed by the ^{1}H NMR spectrum of compound **7b**, where, unlike the spectra of compounds **4a** and **7a**, the signals of the protons of the OH and NH groups are not observed due to deuterium exchange with the solvent.

We found that when benzopyran **2a** reacts with *o*-phenylenediamine under the conditions of acid catalysis, benzodiazepine **8** is formed (Scheme 6). Unlike the parent compound, fluorescence is not observed for compound **8**.

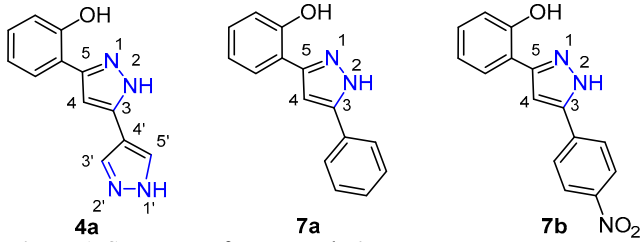
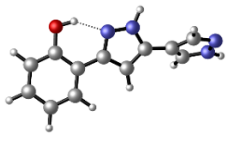
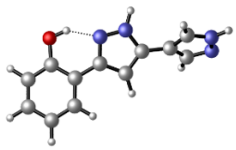
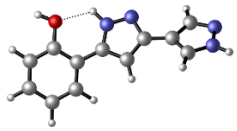
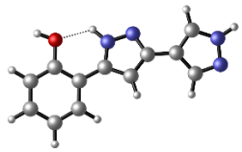
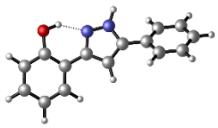
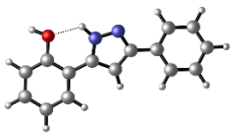
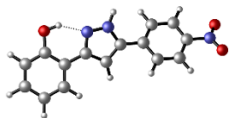
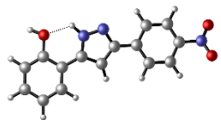


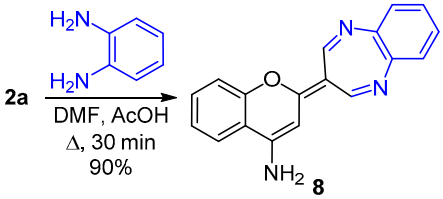
Figure 1. Structures of compounds **4a**, **7a**,**b**.

Table 1. Quantum-chemical data of the localization of the proton of the NH group in dipyrazole **4a** and pyrazoles **7a**,**b**

Parameter	Compound			
	4a			
				
ΔG_{rel}, kJ/mol	0.00	0.63	12.75	12.56
Occupancy, %	55.95	43.38	0.32	0.35
α*, deg	20.2	19.8	15.9	20.0
β**, deg	48.9	52.0	30.3	27.5
Hydrogen bond length, Å	1.820	1.820	2.110	2.110
	7a		**7b**	
				
ΔG_{rel}, kJ/mol	0.00	14.71	0.00	3.43
Occupancy, %	99.74	0.26	79.97	20.03
α*, deg	19.0	19.7	21.0	20.2
γ***, deg	40.9	29.3	38.4	25.2
Hydrogen bond length, Å	1.820	2.110	1.830	2.110

* The angle between hydroxyphenyl and pyrazole rings.
** The angle between pyrazole rings.
*** The angle between pyrazole and phenyl (nitroaryl) rings.

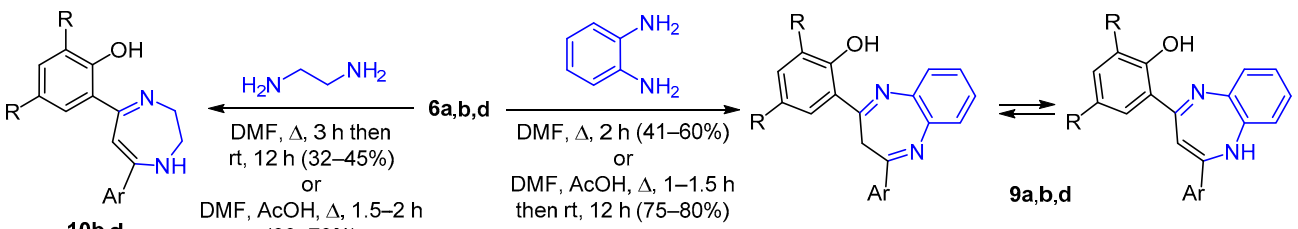
Scheme 6



In the reaction with 1,4-dinucleophiles, *o*-phenylenediamine and ethylenediamine, imines **6a**,**b**,**d** form recyclization products *o*-hydroxyphenylbenzodiazepines **9a**,**b**,**d** and **10b**,**d** (Scheme 7). The reaction was carried out by heating under reflux in DMF for 1–3 h; when AcOH was present in catalytic amounts, the product yields somewhat increased. Benzodiazepine **9a** exhibits the ability to fluorescence in the solid state in the yellow-green region of the spectrum.

The structure of compound **9b** was proven by X-ray structural analysis (Fig. 2). In the solid state, the molecules of compound **9b** are linked by weak intermolecular hydrogen bonds of the C–H···π type. The seven-membered ring of the heterocycle is in the "bath" conformation. The C(1), C(6), and C(8) atoms deviate from the RMS plane of the rest of the heterocyclic ring atoms by 0.55 Å in molecule A and by 0.63 and 0.77 Å in molecule B. The *p*-nitrophenyl and *o*-hydroxylphenyl substituents are somewhat noncoplanar with the endocyclic double bonds N(1)=C(9) and N(2)=C(7) (torsion angles N(1)–C(9)–C(16)–C(21) equal 15(1)° in molecule A and 9(1)° in molecule B; angles N(2)–C(7)–C(10)–C(11) equal 2(1)° in molecule A and 4(1)° in molecule B), which is a consequence of significant steric repulsion between atoms of the aromatic rings and atoms of the heterocyclic ring (shortened intramolecular contacts H(21a)···N (1a) 2.45 Å, H(17a)···C(8a) 2.73 Å, H(17a)···H(8ab) 2.07 Å, H(8ab)···C(17a) 2.65 Å, H(15a)···C(8a) 2.66 Å, H(8ab)···C(15a) 2.61 Å, H (8ab)···H(15a) 2.02 Å in molecule A and H(21b)···N(1b) 2.44 Å, H(17b)···C(8b) 2.73 Å, H(17b)···H(8bb) 2.06 Å, H(8bb)···C (17b) 2.63 Å, H(15b)···C(8b) 2.68 Å, H(8bb)···C(15b) 2.62 Å, H(8bb)···H(15b) 2.03 Å in molecule B with the sum of van der

Scheme 7



a R = H. Ar = Ph: **b** R = H. Ar = 4-$O_2NC_6H_4$: **d** R = *i*-Pr. Ar = 4-$O_2NC_6H_4$

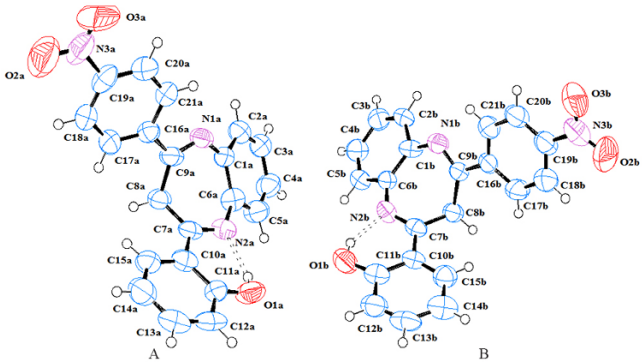


Figure 2. Molecular structure of compound **9b** with atoms represented as thermal vibration ellipsoids with 50% probability. The intramolecular hydrogen bonds OH···N are denoted by dashed lines.

Waals radii[26] H···N 2.67 Å, H···C 2.87 Å, H···H 2.34 Å). It can be assumed that the weaker rotation of the *o*-hydroxyphenyl substituent is due to the formation of an intramolecular O(1)–H···N(2) hydrogen bond (H···N 1.84 Å, angle O–H···N 144° in molecule A and H···N 1.84 Å, angle O–H···N 146° in molecule B).

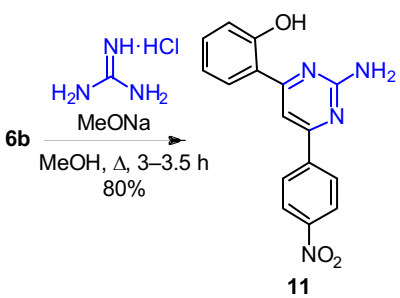
A notable feature of the spectral data of diazepins **9a**,**b** is the predominance of the diimine (3*H*) form in the presence of a couple of drops of CF_3CO_2H, while for compound **9d**, the enamine (1*H*) form is observed in DMSO-d_6.

As a result of the reaction of imine **6b** with the 1,3-dinucleophile guanidine, aminopyrimidine **11** was obtained in good yield (Scheme 8). The reaction was carried out by refluxing in MeOH in the presence of an equimolar amount of MeONa, since guanidine was used as the hydrochloride.

In the ^{1}H NMR spectrum of aminopyrimidine **11**, the signal of the OH group proton is at 13.75 ppm. The characteristic signal of the pyrimidine ring has a chemical shift of 7.96 ppm, and the signals of the amino group protons are at 6.94 ppm. The vibrations of the amino group in the IR spectrum correspond to an intense absorption band at 3358 cm^{-1}. At 3428 cm^{-1}, the absorption band of the OH group can be found. In the ^{13}C NMR spectrum, the characteristic signals of the carbon atoms of the chromene and pyrimidine rings resonate in the downfield region of the spectrum.

To conclude, an effective one-step method for the synthesis of previously unknown 2-(1*H*-(bi)pyrazol-3-yl)-phenols, 2-(1,4(5)-(benzo)diazepin-4-yl)phenols, and pyrimidin-4-ylphenol by the reaction of 2*H*(4*H*)-chromenes with 1,2-, 1,3-, and 1,4-dinucleophiles is presented in this work. Replacing the C=O group with the C=NH group in the chromene ring reduces the reactivity with respect to dinucleophilic reagents compared to chromones, but the reaction proceeds in a similar way. This recyclization can be widely used in the synthesis of *o*-hydroxyphenyl derivatives of heterocyclic compounds.

Scheme 8



Experimental

IR spectra were registered on a PerkinElmer One FT-IR spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance II 400 spectrometer (400 and 100 MHz, respectively) in DMSO-d_6 or DMSO-d_6–CF_3CO_2D, 10:1 (compounds **8**, **9a**,**b**), with TMS as internal standard. Mass spectra (FAB ionization) were registered on a VG-7070 spectrometer. Ion desorption from *m*-nitrobenzyl alcohol was done by a beam of argon atoms with an energy of 8 keV. Mass spectra (EI ionization, 70 eV) for compounds **4a** and **8** were recorded on a Varian 1200L apparatus with direct sample injection at 250°C ionization chamber temperature. Elemental analysis was performed on a LECO CHN-900 Elemental analyzer. Melting points were determined on an Electrothermal 9100 Digital apparatus. Monitoring of the reaction progress and assessment of the purity of synthesized compounds was done by TLC on Silica gel 60 F_{254} (Merck) plates, eluent $CHCl_3$–*i*-PrOH, 10:1, visualization in the iodine chamber.

Compounds **2a** and **6a** were synthesized following a published method.[17]

Synthesis of bipyrazoles 4a,b (General method). Dialdehyde **2a**,**b** (1.2 g, 5.6 mmol) was dissolved in DMF (10 ml). Hydrazine hydrate (0.54 ml, 11.1 mmol) was added to the solution, and the mixture heated under reflux for 1 h. After cooling, the solution was poured into H_2O (20 ml), the formed precipitate was filtered off and recrystallized from methanol.

2-(1'*H*,2*H*-3,4'-Bipyrazol-5-yl)phenol (4a). Yield 0.61 g (48%), light-yellow powder, mp 260–261°C. IR spectrum, ν, cm^{-1}: 3418 (OH), 3252 (NH), 2922 (NH). ^{1}H NMR spectrum, δ, ppm: 13.33 (1H, s, NH); 13.13 (1H, s, NH); 10.98 (1H, s, OH); 8.16 (1H, br. s, H Ar); 7.92 (1H, br. s, H Ar); 7.70–7.68 (1H, m, H Ar); 7.17–7.15 (1H, m, H Ar); 7.00 (1H, s, H Ar); 6.89–6.87 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 155.3; 151.1; 136.9; 136.5; 128.7; 126.5; 119.1; 118.3; 117.6; 116.3; 110.2; 98.4. Mass spectrum, *m*/*z* (I_{rel}, %): 226 $[M]^+$ (100). Found, %: C 63.76; H 4.58; N 24.67. $C_{12}H_{10}N_4O$. Calculated, %: C 63.71; H 4.46; N 24.76.

2-(1'*H*,2*H*-3,4'-Bipyrazol-5-yl)-4,6-diisopropylphenol (4b). Yield 0.86 g (50%), light-beige powder, mp 254–255°C. ^{1}H NMR spectrum, δ, ppm: 13.26 (1H, s, NH); 13.07 (1H, s, NH); 11.20 (1H, s, OH); 8.17 (1H, s, H Ar); 7.95 (1H, s, H Ar); 7.36 (1H, s, H Ar); 7.01–6.98 (2H, m, H Ar); 3.28–3.26 (1H, m, C<u>H</u>$(CH_3)_2$); 2.86–2.85 (1H, m, C<u>H</u>$(CH_3)_2$); 1.22–1.20 (12H, m, CH_3). ^{13}C NMR spectrum, δ, ppm: 152.1; 150.9; 138.6; 136.9; 134.8; 126.3; 123.5; 121.4 (2C); 115.9; 110.4; 98.3; 33.2; 26.7; 24.5; 22.7. Mass spectrum, *m*/*z* (I_{rel}, %): 311 $[M+H]^+$ (100). Found, %:

C 69.58; H 7.09; N 18.12. $C_{18}H_{22}N_4O$. Calculated, %: C 69.65; H 7.14; N 18.05.

Synthesis of 1,3-benzoxazines 5a–e (General method). A solution of the corresponding salicylamide (10 mmol), ketone (12 mmol), and *p*-TsOH (5 mmol) in PhMe (70 ml) was heated under reflux for 4–6 h with azeotropic removal of water using the Deen–Stark adaptor. The reaction mixture was cooled to 10°C and stirred at this temperature for 1 h. The formed precipitate was filtered off, washed with PhMe (10 ml) followed by *i*-PrOH (10 ml), and dried at 50°C. The solid was mixed with 5% aqueous NaOH, filtered, and recrystallized from MeOH.

2-Methyl-2-phenyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one (5a). Yield 2.19 g (92%), white powder, mp 229–230°C (mp 227–228°C[27]). Spectral characteristics match literature data.[27]

2-Methyl-2-(4-nitrophenyl)-2,3-dihydro-4*H*-1,3-benzoxazin-4-one (5b). Yield 1.85 g (65%), white powder, mp 195–197°C. IR spectrum, ν, cm^{-1}: 3184 (NH), 3075 (CH Ar), 1680 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 9.58 (1H, s, NH); 8.15 (2H, d, ^3J = 8.8, H-3,5 Ar); 7.71 (2H, d, ^3J = 8.8, H-2,6 Ar); 7.61 (1H, d, ^3J = 7.7, H-5); 7.44 (1H, t, ^3J = 8.0, H-7); 7.10 (1H, d, ^3J = 8.0, H-8); 6.98 (1H, t, ^3J = 7.3, H-6); 1.81 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 161.6; 155.5; 151.1; 147.3; 134.8; 127.2; 127.1; 123.7; 122.4; 117.9; 117.3; 88.9; 29.6. Mass spectrum, *m*/*z* (I_{rel}, %): 285 $[M+H]^+$ (100). Found, %: C 63.43; H 4.34; N 9.79. $C_{15}H_{12}N_2O_4$. Calculated, %: C 63.38; H 4.26; N 9.85.

2-Methyl-2-phenyl-6,8-di(propan-2-yl)-2,3-dihydro-4*H*-1,3-benzoxazin-4-one (5c). Yield 2.43 g (75%), white powder, mp 205–207°C. IR spectrum, ν, cm^{-1}: 3174 (NH), 3060 (CH Ar), 2965 (CH), 1679 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 9.27 (1H, s, NH); 7.45–7.43 (2H, m, H Ph); 7.34–7.31 (3H, m, H Ph); 7.22–7.20 (2H, m, H-5,7); 3.40 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 2.76 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 1.80 (3H, s, CH_3); 1.20 (6H, d, ^3J = 6.8, CH$(C\underline{H}_3)_2$); 1.10 (6H, d, ^3J = 6.8, CH$(C\underline{H}_3)_2$). ^{13}C NMR spectrum, δ, ppm: 162.4; 150.5; 143.9; 141.2; 135.8; 129.3; 128.2; 128.1; 125.3; 121.4; 117.4; 88.8; 32.7; 30.3; 25.5; 23.8; 23.4; 22.6. Mass spectrum, *m*/*z* (I_{rel}, %): 324 $[M+H]^+$ (100). Found, %: C 77.84; H 7.86; N 4.27. $C_{21}H_{25}NO_2$. Calculated, %: C 77.98; H 7.79; N 4.33.

2-Methyl-2-(4-nitrophenyl)-6,8-di(propan-2-yl)-2,3-dihydro-4*H*-1,3-benzoxazin-4-one (5d). Yield 2.94 g (80%), beige powder, mp 218–220°C. IR spectrum, ν, cm^{-1}: 3184 (NH), 3078 (CH Ar), 2961 (CH), 1679 (C=O), 1524 (*as* NO_2), 1348 (*sym* NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 9.53 (1H, s, NH); 8.20 (2H, d, *J* = 8.3, H-3,5 Ar); 7.70 (2H, d, *J* = 8.7, H-2,6 Ar); 7.34 (1H, s, H-7); 7.25 (1H, s, H-5); 3.24 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 2.76 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 1.82 (3H, s, CH_3); 1.18 (6H, d, ^3J = 6.8, CH$(C\underline{H}_3)_2$); 1.07 (6H, d, ^3J = 6.8, CH$(C\underline{H}_3)_2$). ^{13}C NMR spectrum, δ, ppm: 162.1; 151.1; 150.2; 147.3; 141.7; 135.9; 129.5; 126.8; 123.6; 121.6; 117.3; 88.5; 32.7; 29.7; 25.5; 23.7; 22.5. Mass spectrum, *m*/*z* (I_{rel}, %): 369 $[M+H]^+$ (100). Found, %: C 68.37; H 6.46; N 7.67. $C_{21}H_{24}N_2O_4$ Calculated, %: C 68.46; H 6.57; N 7.60.

2-(4-Bromophenyl)-2-methyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one (5e). Yield 1.27 g (40%), white powder, mp 216–218°C. IR spectrum, ν, cm^{-1}: 3181 (NH), 3075 (CH Ar), 2912 (CH), 1679 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 9.47 (1H, s, NH); 7.61 (1H, d, ^3J = 7.3, H Ar); 7.50 (2H, d, ^3J = 8.3, H-3,5 Ar); 7.43 (1H, t, ^3J = 7.8, H Ar); 7.38 (2H, d, *J* = 8.3, H-2,6 Ar); 7.05 (1H, d, ^3J = 7.8, H Ar); 6.97 (1H, t, ^3J = 7.3, H Ar); 1.77 (1H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 161.7; 155.5; 143.2; 134.5; 131.2; 127.8; 127.0; 122.0; 121.4; 117.9; 117.1; 88.9; 29.9. Mass spectrum, *m*/*z* (I_{rel}, %): 318 $[M(^{81}Br)+H]^+$ (94), 320 $[M(^{79}Br)+H]^+$ (100). Found, %: C 56.74; H 3.86; N 4.33. $C_{15}H_{12}BrNO_2$. Calculated, %: C 56.63; H 3.80; N 4.40.

Synthesis of imines 6a–e (General method). The Vilsmeier–Haack reagent was prepared by mixing $POCl_3$ (0.9 ml, 9.6 mmol) and DMF (2.3 ml, 30 mmol) in ice bath. The corresponding oxazine **5a**–**e** (5 mmol) was added to the prepared reagent solution. The reaction mixture was heated in water bath at 80°C for 1 h, then cooled to 10°C, and 15% aqueous $NaClO_4$ (10 ml) added. The precipitate of the corresponding salt was filtered, dried, and purified by boiling with PhMe. The prepared perchlorate was dissolved in MeOH (5 ml) and treated with 15% aqueous NaOH (1.5 ml). The mixture was boiled for a few minutes, then cooled to room temperature, and diluted with H_2O (3–4 ml). The precipitate was filtered off, washed with H_2O, and the prepared imines **6a**–**e** purified by recrystallization from MeCN.

2-Phenyl-4*H*-chromen-4-imine (6a). Yield 0.86 g (78%), white powder, mp 70–72°C (mp 68–70°C[17]). Spectral characteristics match literature data.[17]

2-(4-Nitrophenyl)-4*H*-chromen-4-imine (6b). Yield 0.72 g (54%), yellow powder, mp 203–205°C. IR spectrum, ν, cm^{-1}: 3079 (CH Ar), 1524 (*as* NO_2), 1345 (*sym* NO_2). ^1H NMR spectrum, δ, ppm: 8.33–8.31 (4H, m, H Ar); 8.23–8.22 (1H, m, NH); 8.06–8.04 (1H, m, H Ar); 7.85–7.83 (1H, m, H Ar); 7.77–7.76 (1H, m, H Ar); 7.50–7.48 (1H, m, H Ar); 7.14 (1H, s, 3-CH). ^{13}C NMR spectrum, δ, ppm: 159.8; 159.3; 155.3; 148.7; 136.7; 134.1; 127.3; 125.3; 124.4; 123.5; 118.1; 108.8. Mass spectrum, *m*/*z* (I_{rel}, %): 267 $[M+H]^+$ (100). Found, %: C 67.76; H 3.69; N 10.59. $C_{15}H_{10}N_2O_3$. Calculated, %: C 67.67; H 3.79; N 10.52.

6,8-Diisopropyl-2-phenyl-4*H*-chromen-4-imine (6c). Yield 1.04 g (68%), yellow powder, mp 210–212°C. IR spectrum, ν, cm^{-1}: 3170 (NH), 2968 (CH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 10.46 (1H, s, NH); 8.22 (1H, s, H-7); 8.11–8.10 (2H, m, H Ph); 7.90 (1H, s, H-5); 7.72–7.70 (3H, m, H Ph); 7.45 (1H, s, 3-CH); 3.73 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 3.09 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 1.39 (6H, d, ^3J = 6.8, CH$(C\underline{H}_3)_2$); 1.30 (6H, d, ^3J = 6.8, CH$(C\underline{H}_3)_2$). ^{13}C NMR spectrum, δ, ppm: 163.7; 161.2; 150.4; 147.7; 138.4; 133.3; 132.9; 129.8; 129.6; 126.8; 118.4; 113.8; 98.9; 33.6; 27.0; 23.7; 22.4. Mass spectrum, *m*/*z* (I_{rel}, %): 306 $[M+H]^+$ (100). Found, %: C 82.67; H 7.50; N 4.65. $C_{21}H_{23}NO$. Calculated, %: C 82.58; H 7.59; N 4.59.

6,8-Diisopropyl-2-(4-nitrophenyl)-4*H*-chromen-4-imine (6d). Yield 0.82 g (47%), light-brown powder, mp 214–216°C. IR spectrum, ν, cm^{-1}: 3272 (NH), 2924–2961 (CH), 1521 (*as* NO_2), 1344 (*sym* NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): signal of the NH group proton not observed

due to deuterium exchange with solvent; 8.35 (1H, d, *J* = 8.3, H-3,5 Ar); 8.13 (1H, d, *J* = 8.3, H-2,6 Ar); 7.87 (1H, s, H-7); 7.41 (1H, s, H-5); 7.03 (1H, s, 3-CH); 3.57 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 2.97 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 1.32 (6H, d, ^3J = 6.8, CH(C<u>H</u>$_3)_2$); 1.25 (6H, d, ^3J = 6.8, CH(C<u>H</u>$_3)_2$). ^{13}C NMR spectrum, δ, ppm: 158.7; 151.4; 148.3; 147.9; 144.7; 138.0; 136.6; 127.4; 126.2; 123.9; 120.5; 118.3; 107.3; 33.2; 26.8; 23.8; 22.5. Mass spectrum, *m*/*z* (I_{rel}, %): 351 $[M+H]^+$ (100). Found, %: C 71.92; H 6.39; N 7.90. $C_{21}H_{22}N_2O_3$. Calculated, %: C 71.98; H 6.33; N 7.99.

2-(4-Bromophenyl)-4*H*-chromen-4-imine (6e). Yield 0.58 g (39%), yellow powder, mp 125–127°C. IR spectrum, ν, cm^{-1}: 3181 (NH), 3079 (CH Ar). ^{1}H NMR spectrum, δ, ppm: 8.16–8.14 (1H, m, H Ar); 7.88–7.86 (2H, m, H-3,5 Ar); 7.76–7.74 (2H, m, H-2,6 Ar); 7.63–7.61 (1H, m, H Ar); 7.52–7.50 (1H, m, H Ar); 7.38–7.36 (1H, m, H Ar); 6.91 (1H, s, 3-CH). ^{13}C NMR spectrum, δ, ppm: 158.4; 153.3; 152.8; 132.4; 131.9; 130.9; 127.3; 124.9; 124.1; 124.0; 120.9; 117.9; 105.3. Mass spectrum, *m*/*z* (I_{rel}, %): 302 $[M(^{81}Br)+H]^+$ (96), 300 $[M\ (^{79}Br)+H]^+$ (100). Found, %: C 60.16; H 3.49; N 4.59. $C_{15}H_{10}BrNO$. Calculated, %: C 60.02; H 3.36; N 4.67.

Synthesis of pyrazoles 7a–d (General method). Hydrazine hydrate (0.8 ml, 16 mmol) was added dropwise to a solution of the corresponding imine **6a**–**d** (4 mmol) in absolute EtOH (10 ml). The reaction mixture was heated under reflux for 3–4 h. The solution after cooling was poured into H_2O (20 ml), the formed precipitate was filtered off, washed with H_2O, and pyrazoles **7a**–**d** recrystallized from MeCN.

2-(4-Phenyl-1*H*-pyrazol-3-yl)phenol (7a). Yield 0.30 g (32%), light-yellow powder, mp 114–116°C (mp 120–122°C[28]). ^{1}H NMR spectrum, δ, ppm: 13.67 (1H, br. s, NH); 10.95 (1H, br. s, OH); 7.84–7.77 (4H, m, H Ar); 7.47–7.19 (4H, m, H Ar); 6.97–6.91 (3H, m, H Ar, H pyrazole). ^{13}C NMR spectrum, δ, ppm: 155.2; 151.2; 143.2; 129.9; 128.9; 126.9; 125.3; 125.0; 119.2; 116.9; 116.4; 99.9. Mass spectrum, *m*/*z* (I_{rel}, %): 237 $[M+H]^+$ (100). Found, %: C 76.14; H 5.08; N 11.95. $C_{15}H_{12}N_2O$. Calculated, %: C 76.25; H 5.12; N 11.86.

2-[5-(4-Nitrophenyl)-1*H*-pyrazol-3-yl]phenol (7b). Yield 0.71 g (63%), yellow powder, mp 218–220°C (mp 230–232°C[29]). IR spectrum, ν, cm^{-1}: 3350 (OH), 3187 (NH), 1521 (*as* NO_2), 1334 (*sym* NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): signals of the NH and OH group protons not observed due to deuterium exchange with solvent; 8.29 (2H, d, ^3J = 8.3, H-3,5 Ar); 8.11 (2H, d, *J* = 8.3, H-2,6 Ar); 7.71 (1H, d, ^3J = 6.8, H Ar); 7.38 (1H, s, H pyrazole); 7.20 (1H, t, ^3J = 7.8, H Ar); 6.99 (1H, d, ^3J = 7.8, H Ar); 6.91 (1H, t, ^3J = 6.8, H Ar). ^{13}C NMR spectrum, δ, ppm: 154.4; 150.8; 146.3; 129.3; 129.2; 127.3; 125.8; 124.1; 119.3; 116.4; 116.1; 102.4. Mass spectrum, *m*/*z* (I_{rel}, %): 282 $[M+H]^+$ (100). Found, %: C 64.17; H 3.87; N 14.89. $C_{15}H_{11}N_3O_3$. Calculated, %: C 64.05; H 3.94; N 14.94.

2,4-Diisopropyl-6-(5-phenyl-1*H*-pyrazol-3-yl)phenol (7c). Yield 0.95 g (74%), white powder, mp 190–192°C. IR spectrum, ν, cm^{-1}: 3367 (OH), 3347 (NH), 2954 (CH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): signals of the NH and OH group protons not observed due to deuterium exchange with solvent; 7.88 (2H, d, *J* = 8.3, H-5,7); 7.50–7.48 (3H, m, H Ph); 7.41–7.39 (2H, m, H Ph); 6.99 (1H, s, H Ph); 3.33–3.32 (1H, m, C<u>H</u>$(CH_3)_2$, signal overlaps with H_2O signal); 2.86 (1H, sept, ^3J = 6.8, C<u>H</u>$(CH_3)_2$); 1.22 (12H, d, ^3J = 6.8, 2CH(C<u>H</u>$_3)_2$). ^{13}C NMR spectrum, δ, ppm: 152.4; 150.8; 143.0; 138.6; 134.7; 128.9; 128.7; 128.5; 125.4; 123.5; 121.4; 115.7; 99.4; 33.1; 26.6; 24.3; 22.5. Mass spectrum, *m*/*z* (I_{rel}, %): 321 $[M+H]^+$ (100). Found, %: C 78.65; H 7.62; N 8.81. $C_{21}H_{24}N_2O$. Calculated, %: C 78.71; H 7.55; N 8.74.

2,4-Diisopropyl-6-[5-(4-nitrophenyl)-1*H*-pyrazol-3-yl]-phenol (7d). Yield 0.98 g (67%), white powder, mp 198–200°C. ^{1}H NMR spectrum, δ, ppm: 14.00 (1H, s, NH); 10.96 (1H, s, OH); 8.37–8.35 (2H, m, H-3,5 Ar); 8.14–8.12 (2H, m, H-2,6 Ar); 7.68 (1H, s, H-3); 7.49 (1H, s, H-5); 7.01 (1H, s, H pyrazole); 3.33 (1H, m, C<u>H</u>$(CH_3)_2$, signal overlaps with H_2O signal); 2.86–2.84 (1H, m, C<u>H</u>$(CH_3)_2$); 1.22–1.20 (12 H, m, CH(C<u>H</u>$_3)_2$). ^{13}C NMR spectrum, δ, ppm: 150.4; 146.7; 138.9; 135.0; 126.2; 124.3; 123.8; 121.6; 115.5; 101.9; 33.0; 26.5; 24.2; 22.6. Mass spectrum, *m*/*z* (I_{rel}, %): 366 $[M+H]^+$ (85), 365$[M]^+$ (100). Found, %: C 69.07; H 6.29; N 11.43. $C_{21}H_{23}N_3O_3$. Calculated, %: C 69.02; H 6.34; N 11.50.

2-(3*H*-1,5-Benzodiazepin-3-ylidene)-2*H*-chromen-4-amine (8). Dialdehyde **2a** (1 g, 4.65 mmol) and *o*-phenylenediamine (1 g, 9.26 mmol) were dissolved in DMF (15 ml), and a few drops of AcOH added. The reaction mixture was heated under reflux for 30 min, whereupon colored precipitate formed. The precipitated benzodiazepine was filtered off and recrystallized from DMF. Yield 1.20 g (90%), red powder, mp >300°C. ^{1}H NMR spectrum, δ, ppm: 9.60 (2H, br. s, NH_2); 8.64 (2H, s, 2CH=N); 8.14–8.12 (1H, m, H Ar); 7.89–7.87 (2H, m, H Ar); 7.47–7.45 (3H, m, H Ar); 7.11–7.09 (2H, m, H Ar); 6.95 (1H, s, 3-CH). Mass spectrum, *m*/*z* (I_{rel}, %): 287 $[M]^+$ (1), 44 (100). Found, %: C 75.37; H 4.53; N 14.57. $C_{18}H_{13}N_3O$. Calculated, %: C 75.25; H 4.56; N 14.63.

^{13}C NMR spectrum for compound **8** could not be recorded due to low solubility in DMSO-d_6, CF_3CO_2D, $CDCl_3$.

Synthesis of 1,5-benzodiazepines 9a,**b**,**d** (General procedure). Method I. A solution of the corresponding imine **6a**,**b**,**d** (1.5 mmol) and *o*-phenylenediamine (1.85 mmol) in DMF (3 ml) was heated under reflux for 2 h. After cooling to room temperature, a precipitate formed, which was filtered off and recrystallized.

Method II. AcOH (0.1 ml) was added to a solution of imine **6a**,**b**,**d** (4.42 mmol) and *o*-penylenediamine (9.7 mmol) in DMF (5 ml). The reaction mixture was heated under reflux for 1–1.5 h and kept at room temperature for 12 h. The formed precipitate was filtered off and recrystallized.

2-(4-Phenyl-1*H*-1,5-benzodiazepin-2-yl)phenol (9a). Yield 0.28 g (60%, method I), 1.03 g (75%, method II), yellow powder, mp 186–188°C (mp 108–110°C[26]). ^{1}H NMR spectrum, δ, ppm: 8.19–8.12 (4H, m, H Ar); 7.58–7.56 (2H, m, H Ar); 7.51–7.48 (3H, m, H Ar); 7.43–7.38 (2H, m, H Ar); 6.91–6.89 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 161.5; 159.2; 155.1; 141.1; 136.7; 135.7; 133.8; 131.2; 129.6; 128.7 128.6; 127.5; 126.3; 125.8; 118.7;

117.6; 33.0. Mass spectrum, *m/z* (I_{rel}, %): 313 $[M+H]^+$ (100). Found, %: C 80.97; H 5.29; N 8.63. $C_{21}H_{16}N_2O$. Calculated, %: C 80.75; H 5.16; N 8.97.

2-[2-(4-Nitrophenyl)-1*H*-1,5-benzodiazepin-4-yl]-phenol (9b). Yield 0.25 g (47%, method I), 1.26 g (80%, method II), yellow crystals, mp 260–262°C (mp 123–125°C[30]). IR spectrum, ν, cm^{-1}: 3358 (OH), 1551 (*as* NO_2), 1344 (*sym* NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.43 (2H, d, ^3J = 8.3, H-3,5 Ar); 8.30 (2H, d, ^3J = 8.3, H-2,6 Ar); 8.14–8.12 (1H, m, H Ar); 7.61–7.59 (2H, m, H Ar); 7.49–7.47 (2H, m, H Ar); 7.41–7.39 (1H, m, Ar); 6.93–6.91 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 175.1; 171.3; 156.9; 150.5; 141.1; 137.3; 135.8; 134.7; 130.3; 129.8; 125.6; 123.9; 121.7; 119.7; 117.5; 111.1; signal of the carbon of the CH_2 overlaps with DMSO-d_6 signal. Mass spectrum, *m/z* (I_{rel}, %): 358 $[M+H]^+$ (100). Found, %: C 70.67; H 4.29; N 11.53. $C_{21}H_{15}N_3O_3$. Calculated, %: C 70.58; H 4.23; N 11.76.

2,4-Diisopropyl-6-[2-(4-nitrophenyl)-1*H*-1,5-benzodiazepin-4-yl]phenol (9d). Yield 0.27 g (41%, method I), 1.46 g (75%, method II), red powder, mp 205–207°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.33 (2H, d, ^3J = 8.3, H-3,5 Ar); 8.07 (1H, s, H-5 Ar); 7.99 (2H, d, ^3J = 8.3, H-2,6 Ar); 7.47 (1H, s, H-7 Ar); 6.87–6.85 (1H, m, H Ar); 6.81–6.79 (1H, m, H Ar); 6.76–6.70 (2H, m, H Ar); 6.60– 6.58 (1H, m, H Ar); 4.66 (1H, s, CH); 3.62–3.60 (1H, m, C<u>H</u>$(CH_3)_2$); 3.04–3.02 (1H, m, C<u>H</u>$(CH_3)_2$); 1.34 (6H, d, ^3J = 6.8, CH(C<u>H</u>$_3)_2$); 1.27 (6H, d, ^3J = 6.8, CH(C<u>H</u>$_3)_2$). ^{13}C NMR spectrum, δ, ppm: 154.2; 150.7; 149.1; 148.2; 145.2; 140.7; 138.1; 136.7; 135.4; 127.4; 126.6; 124.3; 124.2; 121.7; 119.2; 118.8; 116.2; 114.5; 99.7; 33.3; 26.8; 23.9; 22.6. Mass spectrum, *m/z* (I_{rel}, %): 442 $[M+H]^+$ (81), 441 $[M]^+$ (100). Found, %: C 73.37; H 6.29; N 9.43. $C_{27}H_{27}N_3O_3$. Calculated, %: C 73.45; H 6.16; N 9.52.

Synthesis of 1,4-diazepines 10b,d (General procedure). Method I. Imine **6b**,**d** (1.5 mmol) was dissolved in DMF (5 ml), and ethylenediamine (7.5 mmol) added. The reaction mixture was heated under reflux for 3 h. Then it was cooled to room temperature, poured into H_2O (20 ml), and kept for 12 h. The precipitate was filtered off and purified by recrystallization from MeCN.

Method II. AcOH (0.5 ml) was added to a solution of imine **6b**,**d** (4.42 mmol) and ethylenediamine (7.5 mmol) in DMF (5 ml), and the solution was heated under reflux for 1.5–2 h. The reaction mixture was poured into H_2O (25 ml), the precipitate was filtered off and recrystallized from MeCN.

2-[7-(4-Nitrophenyl)-2,3-dihydro-1*H*-1,4-diazepin-5-yl]-phenol (10b). Yield 0.15 g (32%, method I), 0.95 g (70%, method II), red crystals, mp 223–225°C. IR spectrum, ν, cm^{-1}: 3220 (OH), 3082 (NH), 1594 (*as* NO_2), 1341 (*sym* NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.30 (2H, d, ^3J = 8.7, H-3,5 Ar); 7.92 (2H, d, ^3J = 8.7, H-2,6 Ar); 7.64 (1H, d, ^3J = 8.7, H Ar); 7.11 (1H, t, ^3J = 7.8, H Ar); 6.61 (1H, d, ^3J = 7.8, H Ar); 6.46 (1H, t, ^3J = 7.8, H Ar); 5.67 (1H, s, H Ar), 3.91–3.89 (2H, m, CH_2); 3.59–3.57 (2H, m, CH_2). ^{13}C NMR spectrum, δ, ppm: 169.0; 168.1; 155.8; 148.3; 144.9; 132.2; 129.1; 127.8; 123.7; 120.6; 117.3; 113.7; 87.8; 50.4; 49.0. Mass spectrum, *m/z* (I_{rel}, %): 310 $[M+H]^+$ (100). Found, %: C 66.11; H 4.78; N 13.63. $C_{17}H_{15}N_3O_3$. Calculated, %: C 66.01; H 4.89; N 13.58.

2,4-Diisopropyl-6-[5-(4-nitrophenyl)-2,3-dihydro-1*H*-1,4-diazepin-7-yl]phenol (10d). Yield 0.27 g (45%, method I), 1.04 g (60%, method II), red crystals, mp 120–122°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.31 (2H, d, ^3J = 8.7, H-3,5 Ar); 7.89 (2H, d, ^3J = 8.7, H-2,6 Ar); 7.26 (1H, s, H-5 Ar); 6.99 (1H, s, H-3 Ar); 5.65 (1H, s, H Ar); 3.92–3.90 (2H, m, CH_2); 3.56–3.54 (2H, m, CH_2); 2.76–2.74 (1H, m, C<u>H</u>$(CH_3)_2$); 2.50 (1H, m, C<u>H</u>$(CH_3)_2$, signal overlaps with DMSO-d_6 signal); 1.15–1.12 (12H, m, 2CH(C<u>H</u>$_3)_2$)). ^{13}C NMR spectrum, δ, ppm: 168.4; 163.3; 154.9; 148.0; 145.0; 137.4; 132.9; 128.9; 125.8; 123.6; 121.9; 116.1; 88.5; 50.9; 49.0; 26.4; 25.6; 24.3; 22.5. Mass spectrum, *m/z* (I_{rel}, %): 394 $[M+H]^+$ (100). Found, %: C 70.33; H 6.78; N 10.76. $C_{23}H_{27}N_3O_3$. Calculated, %: C 70.21; H 6.92; N 10.68.

2-[2-Amino-6-(4-nitrophenyl)pyrimidin-4-yl]phenol (11). A solution of imine **6b** (3.4 mmol) and guanidine hydrochloride (6.8 mmol) in MeOH (10 ml) was added to alcohol solution of MeONa (6.8 mmol), and the mixture was heated under reflux for 3–3.5 h. The reaction mixture was cooled to room temperature and poured into ice water (20 ml). The precipitate was filtered off, dried, and recrystallized from MeOH. Yield 0.84 g (80%), light-yellow powder, mp 260–262°C. IR spectrum, ν, cm^{-1}: 3428 (OH), 3358 (NH_2), 1551 (*as* NO_2), 1344 (*sym* NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 13.75 (1H, s, OH); 8.50 (2H, d, ^3J = 8.3, H-3,5 Ar); 8.37 (2H, d, ^3J = 8.3, H-2,6 Ar); 8.26–8.24 (1H, m, H Ar); 7.96 (1H, s, H Py); 7.39–7.36 (3H, m, H Ar); 6.49 (2H, s, NH_2). ^{13}C NMR spectrum, δ, ppm: 165.8; 162.8; 161.3; 160.3; 148.6; 142.9; 132.8; 128.3; 128.1; 123.6; 118.8; 118.0; 117.3; 101.0. Mass spectrum, *m/z* (I_{rel}, %): 309 $[M+H]^+$ (96), 308 $[M]^+$ (100). Found, %: C 62.27; H 3.99; N 18.28. $C_{16}H_{12}N_4O_3$. Calculated, %: C 62.33; H 3.92; N 18.17.

X-ray structural analysis of compound 9b was performed on an X-calibur diffractometer (MoKα beam, CCD detector, graphite monochromator, ω-scan, $2\theta_{max}$ 50°). Crystals are rhombic ($C_{21}H_{15}N_3O_3$, *M* 357.36) at 20°C: *a* 19.476(4), *b* 4.8402(7), *c* 35.120(4) Å; *V* 3310.6(9) $Å^3$; *Z* 8; spatial symmetry group $Pna2_1$; d_{calc} 1.434 g/cm^3, μ(MoKα) 0.098 mm^{-1}, *F*(000) 1488. A total of 18304 reflections were collected (5778 of which were independent, R_{int} 0.110). The structure was solved with the direct method using the SHELXTL program set.[31,32] H atom positions were found from difference electron density synthesis and were refined according to the "rider" model with U_{iso} = 1.2U_{eq} of a non-hydrogen atom bonded with the hydrogen atom. Positions of the hydrogen atoms of the hydroxyl groups were refined in the isotropic approximation. The structure was refined against F^2 by the least-squares technique in the full-matrix anisotropic approximation for non-hydrogen atoms up to wR_2 0.227 over 5758 reflections (R_1 0.083 over 2791 reflections with $F > 4\sigma(F)$, *S* 0.940). Crystallographic data was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1856644).

The Supporting information file containing IR, ^1H, ^{13}C NMR, and mass spectra of the synthesized compounds is available at the journal website at http://link.springer.com/journal/10593.

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