Thermal transformation of cyclopropylazoarenes into the five-membered nitrogen-containing heterocycles

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Cyclopropylazoarenes containing methoxy groups in the aromatic ring give the corresponding *N*-arylpyrazolines on the reflux in *o*-dichlorobenzene or on $SnCl_2$ catalysis at 80 °C in good yields. The products can be smoothly oxidized into the corresponding pyrazoles. Thermolysis of cyclopropylazoarenes containing hydroxy groups in the aromatic ring proceeds more complicated. Thus in the case of resorcin azo derivative, strong resinification of the reaction mixture is observed and the corresponding *N*-arylpyrazoline is isolated only in ~40% yield. Under similar conditions, thermolysis of 1-cyclopropyl- and 1-(1-methylcyclopropyl)azo-2-naphthol proceeds otherwise and unexpectedly leads to naphtho[1,2-*d*]oxazole derivatives with degradation of the cyclopropane ring.

Key words: cyclopropylazoarenes, thermolysis, *N*-arylpyrazolines, *N*-arylpyrazoles, naphtho[1,2-*d*]oxazoles, heterocyclization.

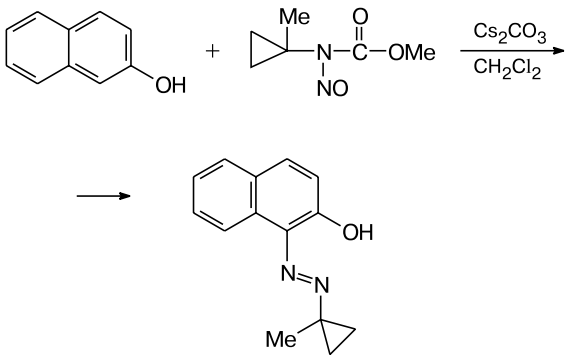
Owing to the last years research directed on a development of methods for the generation and trapping of cyclopropyldiazonium ion, it was shown that this intermediate can afford products of azo-coupling in preparative yields.[1,2] As a rule, *N*-cyclopropyl-*N*-nitrosourea serves as the source of cyclopropyldiazonium since its decomposition under action of bases in the presence of active azo components, CH-acids or hydroxy arenes, leads to cyclopropylhydrazones[1] or cyclopropylazoarenes,[2,3] respectively. It should be noted that cyclopropylazo compounds are the structural analogs of vinylcyclopropanes, the ability of which to give cyclopentenes under thermolysis is well known.[4] Similarly, cyclopropylazo compounds rearrange into *N*-substituted pyrazolines.[5—10] However, transformations of functionalized cyclopropylazo compounds are practically not studied due to low availability of these compounds. Development of convenient methods for the preparation of cyclopropylazoarenes gives a possibility, in particular, to study their thermal transformations and to use this methodology for the synthesis of substituted *N*-arylpyrazolines, pyrazoles, and, in some cases, fused 1,3-oxazoles.

As some literature data show, isomerization of cyclopropylazo compounds into pyrazolines proceeds under both the thermolysis[5—7] (140—200 °C) and photolysis[8,9] (254 or 366 nm). In addition, it was shown[10] that addition of $SnCl_2$ allows one to reduce temperature of the process to 80 °C and to obtain isomerization products in good yields.

We used readily available 4-cyclopropylazoresorcinol (**1a**),[11] 1-cyclopropylazo-2-naphthol (**2a**),[2] and 1-(1-methylcyclopropyl)azo-2-naphthol (**2c**), as well as their *O*-methylated derivatives, *viz.*, 1-cyclopropylazo-2,4-dimethoxybenzene (**1b**) and 1-cyclopropylazo-2-methoxynaphthalene (**2b**), as the subjects of our research.

Compound **2c** was obtained by the reaction of excess 2-naphthol with methyl *N*-nitroso-*N*-(1-methylcyclopropyl)carbamate[12] in the presence of Cs_2CO_3 as the base at room temperature (Scheme 1). The reaction is slow (9 days), but rather selective. According to the ^1H NMR spectra, denitrosation of starting methyl *N*-nitroso-*N*-(1-methylcyclopropyl)carbamate[12] and partial methylation of 2-naphthol at the hydroxy group occured as the side processes.

Scheme 1



2c (90%)

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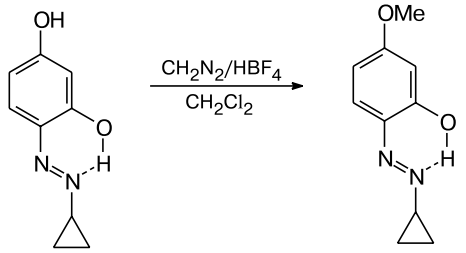
In the ^{1}H NMR spectrum of compound **2c**, the signal for the proton of the OH group is observed at δ 13.8, which is characteristic of the hydroxyl bound to the azo fragment by a hydrogen bond.[2,3] The signal for the methyl group appears as the singlet at δ 1.69, while the protons of the cyclopropane ring as two muliplets at δ 1.24 and 1.58, respectively.

Preparation of *O*-methylated derivatives **1b** and **2b** was a difficult problem since the hydroxy groups in compounds **1a** and **2a**, located in *ortho*-position to the azo fragment, form stable intramolecular hydrogen bond with the nitrogen atom[2,3] and, owing to this, can be hardly involved into chemical transformations. We tried several methods for the methylation of phenols suggested in the literature. It turned out that the use of MeI in CH_2Cl_2 in the presence of K_2CO_3 or the two-phase system NaOH—H_2O/CH_2Cl_2 in the presence of a phase-transfer catalyst did not give the desired methylation products in considerable yields. An etherial solution of diazomethane in the absence of a catalyst can not methylate compounds **1a** and **2a** either, whereas their interaction with CH_2N_2 in the presence of catalytic amount of $BF_3 \cdot Et_2O$ leads to the complex mixture of compounds.

Selective methylation of azoresorcinol **1a** has been successfully accomplished under action of diazomethane in the presence of HBF_4. In this case, the hydroxy group not involved into the formation of intramolecular hydrogen bond undergoes the methylation; 2-cyclopropylazo-5-methoxyphenol (**3**) is the reaction product, which was isolated in 63% yield (Scheme 2).

Scheme 2

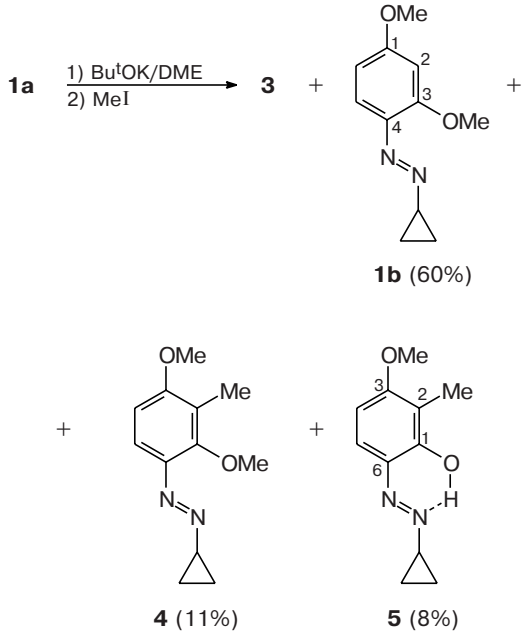


1a **3**

In the ^{1}H NMR spectrum of compoundя **3**, the signal for the proton of the OH group is observed at δ 12.2, which is characteristic of the hydroxyl bound to the azo fragment by a hydrogen bond. Earlier, we have shown[3] that hydroxy groups in *ortho*- and *para*-positions with respect to cyclopropylazo fragment appear in the ^{1}H NMR spectra at δ 11.7 and 5.6, respectively.

For the methylation of both hydroxy groups in compound **1a**, we developed a procedure according to which compound **1a** was first treated with Bu^{t}OK in dimethoxyethane and then, methyl iodide was added to the solution of the phenoxide obtained. This procedure allowed us to obtain dimethoxy derivative **1b** in no less than 60% yield. In this case, despite of the use of 3.3 equiv. of MeI per 1 mol of the substrate, the methylation of the OH group closer to the azo fragment is not yet complete, while the excess of methyl iodide partially methylates the aromatic ring in the forming methoxybenzenes **1b** and **3** to afford substituted toluenes **4** and **5** (Scheme 3). The reaction mixture was separated by column chromatography on SiO_2 using a mixture of toluene with methanol in the ratio 100 : 1 as the eluent to isolate compounds **1b** and **4** and a mixture of azophenols **3** and **5**, which then was separated in the system toluene—light petroleum, 1 : 3.

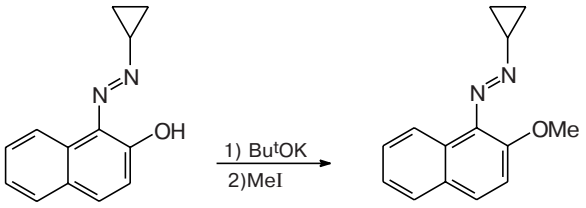
Scheme 3



In the ^{1}H NMR spectra of compounds **4** and **5**, the signals for the methyl groups resonate as the singlets at δ 2.19 and 2.09, respectively, whereas the protons of the aromatic ring as two doublets with the spin-spin coupling constant *ca.* 9 Hz, which is characteristic of this type of substitution. The structures of compounds obtained were also confirmed by the ^{13}C NMR spectra, mass spectrometry and elemental analysis data.

Methylation of naphthol **2a** under similar conditions proceeds more selectively and gives methoxy derivative **2b** in 72% yield (Scheme 4). The ^{1}H NMR spectrum of the compound obtained differs from that for starting naphthol in the absence of the upfield signal for the OH group and appearance of the singlet for the methoxy group at δ 3.94. The signals for other protons change insignificantly in comparison with **2a**. In the ^{13}C NMR spectrum, the signals for the C(2) and C(3) atoms undergo the largest shift: both are shifted by ~5 ppm downfield on passing from **2a** to **2b**.

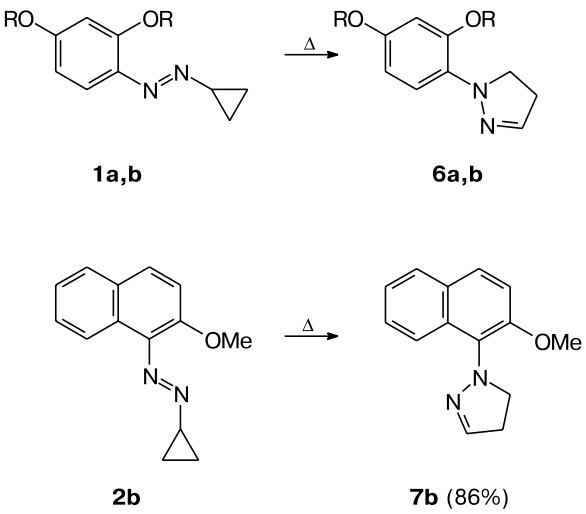
Scheme 4



2a **2b** (72%)

Thermolysis of cyclopropylazoarenes **1b** and **2b** in boiling xylene or *o*-dichlorobenzene showed that their rearrangement into pyrazolines begins at ~140 °C, however, proceeds yet too slow at this temperature, approximately by 10% for 6 h. Conducting the reaction in boiling *o*-dichlorobenzene under Ar for 6 h was more efficient: in this case, pyrazolines **6b** and **7b** (Scheme 5) were obtained in 84—86% yield as low-melting air-sensitive crystals.

Scheme 5



1a,b **6a,b**

2b **7b** (86%)

R = H (**a**), Me (**b**)

The ^{1}H NMR spectra of pyrazolines obtained are characterized by the signals for the protons of the heterocyclic fragment appearing as a narrow triplet at δ 6.9 for proton H(3), doublet of triplets at δ 2.9 for two protons H(4), and a triplet at δ 3.6 for the methylene protons H(5). In this case, the chemical shifts and the spin-spin coupling constants for the protons of the aromatic ring changes insignificantly on passing from the azo compounds to pyrazolines. To obtain satisfactory data of elemental analysis, pyrazolines **6b** and **7b**, because of their rather low stability, were additionally purified by preparative TLC directly before the analysis.

In contrast to the methoxy derivatives of azoarenes **1b** and **2b**, thermolysis of hydroxy derivatives **1a** and **2a** proceeds in a more complicated way. The reflux of azophenol **1a** in *o*-dichlorobenzene leads to a rather strong resinification of the reaction mixture, however, when the reaction was carried out for 1 h and when conversion of the starting azophenol is incomplete (~50%), the corresponding pyrazoline **6a** can be obtained (see Scheme 5), the yield of which with respect to the converted azophenol **1a** is ~41%. Attempts to obtain for pyrazoline **6a** satisfactory elemental analysis data were unsuccessful because of its low stability, but its structure was reliably confirmed by the mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy data (see Experimental).

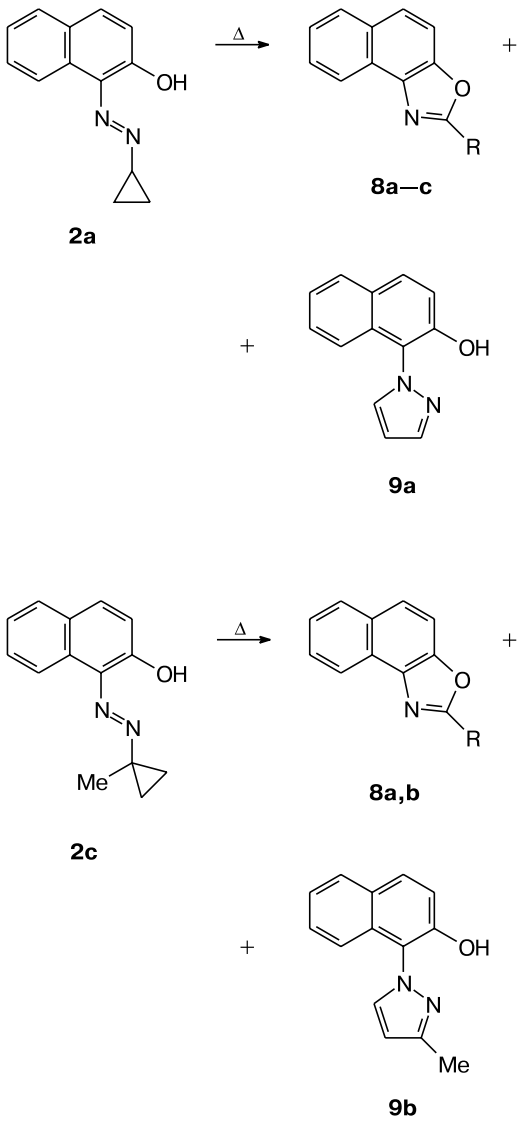
Under similar conditions, thermolysis of azonaphthol **2a** proceeds differently and, instead of expected pyrazoline, leads to naphtho[1,2-d]oxazole **8a**, its homologs **8b,c**, and 1-(2-hydroxynaphthyl)-1*H*-pyrazole (**9a**). When the reaction is carried out under argon their ratio is ~1 : 1 : 1 : 0.2 (73% total yield, Scheme 6). When the reaction is carried out in air, they are formed approximately in equal amounts. It can be noted that the presence of oxygen has insignificant influence on the course of the reaction and the composition of the products remains unchanged. When the reaction temperature is reduced to 160 °C, its rate decreases and naphthoxazoles **8a—c** practically are not formed. Compound **9a** is obtained as the only reaction product with partial resinification of starting azonaphthol **2a**.

Thermolysis of azonaphthol **2c** proceeds similarly and leads to oxazoles **8a** and **8b** and 3-methyl-1-(2-hydroxynaphthyl)-1*H*-pyrazole (**9b**) in the ratio ~6.5 : 1 : 3.5. Compound **2c** thermally is less stable than **2a**: ~3 h at 180 °C is needed for the complete conversion of **2c**, whereas for azonaphthol **2a** ~12 h is required. The compounds obtained were isolated in individual states by column chromatography on SiO_2.

The structures of naphthooxazoles **8a—c** were established on the bases of the ^{1}H and ^{13}C NMR spectra. It was found that the spectra of compounds **8a,b** completely agree with those described in the literature,[13] whereas the ^{1}H and ^{13}C NMR spectra for oxazole **8c** differ from those for **8b** by the absence of the signal for the methyl group at δ_H 2.75 or δ_C 14.7 and by the presence of two groups of signals characteristic of the ethyl substituent. In the ^{1}H NMR spectra of pyrazoles **9a,b**, the signals for the protons are in the aromatic region: δ_H 6.40—7.90. In the ^{1}H NMR spectrum of compound **9b**, the signal for the methyl group at δ_H 2.46 is also present, that is characteristic of the methyl group at the aromatic ring.

At present, we cannot give a reasonable scheme for the formation of naphthooxazole and its homologs because of improbability of elimination of the C_2H_5N, CH_3N, or NH fragments from the starting cyclopropylazoarene **2a**, which points out either the possibility of its bimolecular transformations or proceeding of oxidation-reduction processes.

Scheme 6

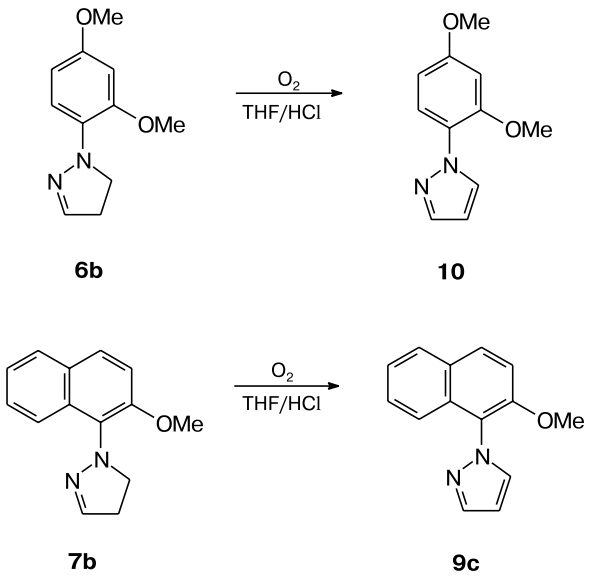


R = H (**a**), Me (**b**), Et (**c**)

Thermolysis of azo compounds **1a**,**b** and **2a**,**b** in boiling benzene in the presence of $SnCl_2$ according to the procedure described earlier[10] did not give a considerable advantage. It turned out that compounds **1a** and **2a** rapidly give insoluble precipitate, possibly, owing to the coordination of the free OH group with the tin atom, and further heating does not lead to any identifiable products. Under similar conditions, compounds **1b** and **2b** methylated at the hydroxyl give expected pyrazolines **6b** and **7b** in 65 and 63% yield, respectively (see Scheme 5), however, at 80 °C, the reaction is accompanied by a considerable resinification.

We supposed that the low yields of pyrazolines **6b** and **7b** in the case of catalytic version of the reaction can be caused by elimination of HCl owing to the partial hydrolysis of $SnCl_2$ during the reaction. After dissolution of the pyrazolines obtained in THF and addition of catalytic amount of hydrochloric acid, we found that under these conditions, pyrazoles **10** and **9c** are formed with rather good selectivity in 78 and 61% yield, respectively (Scheme 7). The atmospheric oxygen can play the role of oxidant in this reaction. In the absence of HCl, the oxidation is slower and nonselective.

Scheme 7



The ^1H NMR spectra of the products can definitely indicate aromatization of the heterocyclic ring, in which the signals for the protons of the pyrazole ring with characteristic chemical shifts and corresponding muliplicity appear, as well as the chemical shifts for three carbon atoms of this fragment in the ^{13}C NMR spectra at δ 106 (C(4)), 132 (C(5)), and 140 (C(3)), that corresponds to the expected chemical shifts for the *N*-aryl-substituted pyrazole ring.[14]

In conclusion, we showed that thermolysis of cyclopropylazoarenes containing OH or OMe groups in *ortho*-position to the azo fragment can lead to pyrazolines in high yield, the subsequent oxidation of which in a number of cases proceeds selectively and leads to pyrazoles. Thermolysis in boiling *o*-dichlorobenzene is preferable; though the use of $SnCl_2$ as the catalyst allows one to significantly decrease the temperature of the process, however, leads to a decrease in the yields of the target products, and can not be applied at all for the compounds with OH group. Thermolysis of 1-cyclopropylazonaphthol (**2a**) proceeds quite unexpectedly: it is accompanied by the fragmentation of the azocyclopropane fragment with the formation of naphtho[1,2-*d*]oxazole derivatives.

On the whole, the use of methoxy-substituted cyclopropylazoarenes is more preferable since their transfor-

mations during thermolysis proceed with higher yields, are more predictable, and the pyrazolines formed are more stable to air oxygen.

Experimental

^{1}H and ^{13}C spectra were recorded on a Bruker AM-300 spectrometer (300 and 75.5 MHz, respectively) for solutions in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct inlet). Silica gel 60 (0.040—0.063 mm, Merck) was used for chromatography. Azo compounds **1a** and **2a** and methyl *N*-(1-methylcyclopropyl)*N*-nitrosocarbamate were synthesized according to the procedures described earlier.[11,2,12] Solutions of CH_2N_2 and HBF_4 were prepared according to the known procedure.[15]

4-Cyclopropylazo-1-methoxybenzene. A solution of HBF_4 in Et_2O (0.1 mL, 0.008 mmol) and a solution of CH_2N_2 in CH_2Cl_2 (15 mL, 4.5 mmol) were added to a solution of 4-cyclopropylazophenol (50 mg, 0.3 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 3 h at room temperature, then, another portion of the HBF_4 solution (0.1 mL) was added followed by a portionwise addition of the CH_2N_2 solution in CH_2Cl_2 (40 mL, 12 mmol) for 1 h. After 2 h, the reaction was stopped, a few drops of acetic acid was added into the reaction mixture to decompose the excess CH_2N_2. The solution obtained was washed with saturated aqueous $NaHCO_3$ (2×20 mL) and NaCl (2×20 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by preparative TLC (SiO_2, eluent — benzene) collecting the yellow band with $R_f = 0.45$ to obtain 4-cyclopropylazo-1-methoxybenzene (18 mg, 36%) as yellow oil. Partial MS, m/z (I_{rel} (%)): 176 (81) $[M]^+$, 161 (100) $[M - Me]^+$, 121 (37) $[M - C_3H_5N]^+$, 107 (35) $[M - C_3H_5N_2]^+$. ^{1}H NMR ($CDCl_3$), δ: 1.21 and 1.46 (both m, 2 H each, CH_2CH_2); 3.66 (tt, 1 H, CH, J_{trans} = 3.6 Hz, J_{cis} = 7.1 Hz); 3.83 (s, 3 H, OMe); 6.92 (m, 2 H, H(2) + H(6)), 7.60 (m, 2 H, H(3) + H(5)). ^{13}C NMR, δ: 9.4 (CH_2CH_2); 50.4 (CH); 55.6 (OMe); 114.0 (C(2) + C(6)); 123.5 (C(3) + C(5)); 146.4 (C(4)); 161.0 (C(1)).

2-Cyclopropylazo-5-methoxyphenol (3). A solution of HBF_4 (0.3 mL, 0.025 mmol) was added to a solution of 4-cyclopropylazo-1,3-dihydroxybenzene (**1a**) (100 mg, 0.6 mmol) in CH_2Cl_2 (30 mL) with stirring followed by a portionwise addition of a CH_2N_2 solution (30 mL, 9 mmol) for 20 min. The reaction mixture was stirred for 1.5 h at room temperature, a few drops of acetic acid was added into the reaction mixture to decompose the excess CH_2N_2, the solution obtained was washed with saturated aq. $NaHCO_3$ (2×20 mL) and NaCl (2×20 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The residue was separated by column chromatography on SiO_2 (eluent — toluene) to obtain azo compound **3** (68 mg, 63%) as bright yellow crystals with m.p. 5—6 °C. The ^{1}H and ^{13}C NMR spectra correspond to those described earlier.[11]

Methylation of phenol 1a upon treatment with MeI. A solution of 4-(cyclopropylazo)resorcinol (**1**) (400 mg, 2.3 mmol) in DME (15 mL) was added to a solution of Bu^{t}OK (780 mg, 7.0 mmol) in DME (25 mL) with stirring. The suspension formed was stirred for 2 h at room temperature, then MeI (1.08 g, 7.6 mmol) was added and this was stirred for 3 days at 20 °C. After that, the reaction mixture was diluted with CH_2Cl_2, (40 mL), a precipitate formed was filtered off and washed with CH_2Cl_2 (10 mL). The filtrate was concentrated and the residue was separated by column chromatography on SiO_2 (eluent — toluene—methanol, 100 : 1) to obtain a mixture of compounds **3** and **5** (75 mg) as yellow oil, azo compound **4** (55 mg, 11%) as yellow oil with the purity of ~95%, and azo compound **1b** (276 mg, 60%) as yellowish orange needle-like crystals with m.p. 51—52 °C. The mixture of compounds **3** and **5** was repeatedly separated by column chromatography on SiO_2 (eluent — toluene—light petroleum (40—70), 1 : 3) to obtain azophenol **3** (32 mg, 7%), identical to the sample described earlier,[11] and azo compound **5** (36 mg, 8%) as yellow crystals with m.p. 55—56 °C.

2-Cyclopropyl-1-(2,4-dimethoxyphenyl)diazene (1b). Found (%): C, 64.27; H, 7.04; N, 13.51. $C_{11}H_{14}N_2O_2$. Calculated (%): C, 64.06; H, 6.84; N, 13.58. Partial MS, m/z (I_{rel} (%)): 206 (80) $[M]^+$, 191 (41) $[M - Me]^+$, 164 (43), 150 (23), 136 (42), 122 (53), 107 (45), 39 (100). ^{1}H NMR ($CDCl_3$), δ: 1.21 and 1.47 (both m, 2 H each, CH_2CH_2); 3.75 (tt, 1 H, CH, J_{trans} = 3.4 Hz, J_{cis} = 7.1 Hz); 3.82 and 3.96 (both s, 3 H each, 2 OMe); 6.44 (dd, 1 H, H(5), ^4J = 2.5 Hz, ^3J = 8.9 Hz); 6.54 (d, 1 H, H(3), ^4J = 2.5 Hz); 7.37 (d, 1 H, H(6), ^3J = 8.9 Hz). ^{13}C NMR, δ: 9.5 (CH_2CH_2); 51.1 (CH); 55.5 and 56.0 (2 OMe); 98.7 (C(3)); 104.9 (C(5)); 118.1 (C(6)); 135.7 (C(1)); 156.7 and 162.3 (C(2) + C(4)).

2-Cyclopropyl-1-(2,4-dimethoxy-3-methylphenyl)diazene (4). Partial MS, m/z (I_{rel} (%)): 220 (81) $[M]^+$, 205 (73) $[M - Me]^+$, 190 (25) $[M - C_2H_6]^+$, 178 (58) $[M - C_3H_6]^+$, 39 (100). ^{1}H NMR ($CDCl_3$), δ: 1.21 and 1.47 (both m, 2 H each, CH_2CH_2); 2.19 (s, 3 H, Me); 3.77 (tt, 1 H, CH, J_{trans} = 3.4 Hz, J_{cis} = 7.1 Hz); 3.83 and 3.93 (both s, 3 H each, 2 OMe); 6.59 (d, 1 H, H(5), ^3J = 9.0 Hz); 7.24 (d, 1 H, H(6), ^3J = 9.0 Hz). ^{13}C NMR, δ: 8.8 (Me); 9.5 (CH_2CH_2); 50.8 (CH)); 55.7 and 62.8 (2 OMe); 105.7 (C(5)); 114.8 (C(6)); 120.1 (C(3)); 139.6 (C(1)); 156.0 and 159.9 (C(2) + C(4)).

6-Cyclopropylazo-3-methoxy-2-methylphenol (5). Found (%): C, 64.19; H, 6.74; N, 13.77. $C_{11}H_{14}N_2O_2$. Calculated (%): C, 64.06; H, 6.84; N, 13.58. Partial MS, m/z (I_{rel} (%)): 206 (98) $[M]^+$, 164 (100) $[M - C_3H_6]^+$, 108 (72), 39 (88). ^{1}H NMR ($CDCl_3$), δ: 1.25 and 1.36 (both m, 2 H each, CH_2CH_2); 2.09 (s, 3 H, Me); 3.77 (tt, 1 H, CH, J_{trans} = 3.9 Hz, J_{cis} = 6.7 Hz); 3.88 (s, 3 H, OMe); 6.55 (d, 1 H, H(5), ^3J = 8.8 Hz); 7.55 (d, 1 H, H(6), ^3J = 8.8 Hz); 12.43 (br.s, 1 H, OH). ^{13}C NMR, δ: 7.6 (Me); 10.0 (CH_2CH_2); 48.3 (CH); 55.8 (OMe); 102.0 (C(4)); 113.5 (C(2)); 130.0 (C(5)); 131.8 (C(6)); 152.2 (C(3)); 160.2 (C(1)).

1-(2,4-Dihydroxyphenyl)-4,5-dihydro-1*H*-pyrazole (6a). A solution of azo compound **1a** (50 mg, 0.3 mmol) in anhydrous *o*-dichlorobenzene (4 mL) was refluxed for 1 h under Ar with stirring, a precipitate formed was filtered off. The filtrate was concentrated *in vacuo* at 0.1 Torr. The residue, containing according to the ^{1}H NMR spectra compounds **1a** and **6a**, was separated by preparative TLC on SiO_2 (eluent — toluene—ethyl acetate, 5 : 1) collecting the yellow band with $R_f = 0.5$ for **1a** and $R_f = 0.3$ for **6a**. The starting azo compound **1a** (18 mg) and pyrazoline **6a** (13 mg, 41%) as yellow powder, rapidly liquifying in air were isolated. Partial MS, m/z (I_{rel} (%)): 178 (67) $[M]^+$, 150 (15) $[M - N_2]^+$, 136 (73) $[M - C_3H_6]^+$, 41 (56), 38 (100). ^{1}H NMR ($CDCl_3$), δ: 2.86 (dt, 2 H, H(4), ^3J = 1.9 Hz, ^3J = 10.2 Hz); 3.63 (t, 2 H, H(5), ^3J = 10.2 Hz); 5.40 (br.s, 1 H, OH); 6.32 (dd, 1 H, H(5′), ^4J = 2.7 Hz, ^3J = 8.6 Hz); 6.41 (d, 1 H, H(6′), ^3J = 8.6 Hz); 6.49 (d, 1 H, H(3′), ^4J = 2.7 Hz); 6.81 (t, 1 H, H(3), ^3J = 1.9 Hz); 9.92 (br.s, 1 H, OH). ^{13}C NMR, δ: 32.1 (C(4)); 48.9 (C(5)); 104.8 (C(3′)); 106.1 (C(5′)); 114.1 (C(6′)); 127.3 (C(1′)); 139.8 (C(3)); 147.9 and 150.9 (C(2′) + C(4′)).

1-(2,4-Dimethoxyphenyl)-4,5-dihydro-1*H*-pyrazole (6b). ***A***. Anhydrous $SnCl_2$ (11 mg, 0.06 mmol) was added to a solution of azo compound **1b** (83 mg, 0.4 mmol) in benzene (20 mL) and the mixture was refluxed for 6 h with stirring under argon. A black precipitate formed was filtered off, the filtrate was concentrated, the residue was purified by preparative TLC on SiO_2 (eluent — toluene—methanol, 20 : 1) collecting the band with R_f = 0.5 to obtain pyrazoline **6b** (54 mg, 65%) as colorless crystals with m.p. 28—30 °C.

B. A solution of azo compound **1b** (120 mg, 0.6 mmol) in anhydrous *o*-dichlorobenzene (15 mL) was refluxed for 6 h under Ar with stirring, then the solvent was evaporated *in vacuo* at 0.1 Torr. The residue was dissolved in benzene (1 mL), light petroleum (10 mL) was added, a precipitate formed was removed, the filtrate was concentrated, and the residue was purified by column chromatography on SiO_2 (eluent — toluene—methanol, 25 : 1) to obtain pyrazoline **6b** (101 mg, 84%). Found (%): C, 64.32; H, 7.07; N, 13.98. $C_{11}H_{14}N_2O_2$. Calculated (%): C, 64.06; H, 6.84; N, 13.58. Partial MS, *m/z* (I_{rel} (%)): 206 (100) $[M]^+$, 191 (45) $[M - Me]^+$, 164 (40). ^{1}H NMR ($CDCl_3$), δ: 2.86 (dt, 2 H, C(4)H_2, ^3J = 1.7 Hz, ^3J = 9.8 Hz); 3.56 (t, 2 H, C(5)H_2, ^3J = 9.8 Hz); 3.80 and 3.87 (both s, 3 H each, 2 OMe); 6.45 (dd, 1 H, H(5′), ^4J = 2.6 Hz, ^3J = 8.6 Hz); 6.51 (d, 1 H, H(3′), ^4J = 2.6 Hz); 6.92 (t, 1 H, H(3), ^3J = 1.7 Hz); 7.20 (d, 1 H, H(6′), ^3J = 8.6 Hz). ^{13}C NMR, δ: 34.5 (C(4)); 52.6 (C(5)); 55.6 (2 OMe); 99.6 (C(3′)); 103.9 (C(5′)); 120.4 (C(6′)); 132.3 (C(1′)); 143.2 (C(3)); 152.0 and 156.9 (C(2′) + C(4′)).

1-(2,4-Dimethoxyphenyl)-1*H*-pyrazole (10). A solution of HCl in tetrahydrofuran ((1 mL, 0.4 mmol) prepared by mixing 36% aq. HCl (1.25 g) with tetrahydrofuran (30 mL)) was added to a solution of pyrazoline **6b** (40 mg, 0.2 mmol) in THF (10 mL) and this was stirred for 4 h at room temperature in air. After that, anhydrous K_2CO_3 (200 mg) was added to the reaction mixture, which was stirred for another 30 min. A precipitate of salts formed was filtered off and the solvent was removed *in vacuo*. The residue was separated by column chromatography on SiO_2 (eluent — toluene—methanol, 40 : 1) to obtain pyrazole **10** (31 mg, 78%) as colorless oil with the purity of ~95%. Partial MS, *m/z* (I_{rel} (%)): 204 (100) $[M]^+$, 175 (28) $[M - H - N_2]^+$, 159 (42). ^{1}H NMR ($CDCl_3$), δ: 3.83 and 3.85 (both s, 3 H each, 2 OMe); 6.40 (br.t, 1 H, H(4), ^3J = 2.1 Hz); 6.56 (dd, 1 H, H(5′), ^4J = 2.6 Hz, ^3J = 8.3 Hz); 6.58 (d, 1 H, H(5), ^3J = 2.2 Hz); 7.53 (d, 1 H, H(6′), ^3J = 8.3 Hz); 7.69 (d, 1 H, H(3), ^3J = 1.9 Hz); 7.86 (d, 1 H, H(3′), ^4J = 2.6 Hz). ^{13}C NMR, δ: 55.7 and 56.0 (2 OMe); 99.7 (C(3′)); 104.6 and 105.9 (C(4) + C(5′)); 123.6 (C(1′)); 126.5 (C(6′)); 131.5 (C(5)); 139.8 (C(3)); 153.0 and 159.9 (C(2′) + C(4′)).

1-Cyclopropylazo-2-methoxynaphthalene (2b). A solution of 1-(cyclopropylazo)-2-naphthol (**2a**) (300 mg, 1.4 mmol) in DME (5 mL) was added to a solution of Bu^{t}OK (225 mg, 2.0 mmol) in DME (10 mL) with stirring. A suspension formed was stirred for 1 h at 20 °C, then MeI (355 mg, 2.5 mmol) was added and this was stirred for 3 days. After that, CH_2Cl_2 (20 mL) was added to the reaction mixture, a precipitate formed was filtered off and washed with CH_2Cl_2 (5 mL). The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on SiO_2 (eluent — benzene—methanol, 60 : 1) to obtain 1-(cyclopropylazo)-2-methoxynaphthalene (**2b**) (230 mg, 72%) as yellow oil. Found (%): C, 74.53; H, 6.55; N, 12.29. $C_{14}H_{14}N_2O$. Calculated (%): C, 74.31; H, 6.24; N, 12.38. Partial MS, *m/z* (I_{rel} (%)): 226 (100) $[M]^+$, 211 (68) $[M - Me]^+$, 142 (54), 115 (45). ^{1}H NMR ($CDCl_3$), δ: 1.33 and 1.64 (both m, 2 H each, CH_2CH_2); 3.89 (s, 3 H, OMe); 3.95 (tt, 1 H, CH, J_{trans} = 3.3 Hz, J_{cis} = 7.1 Hz); 7.28 (d, 1 H, H(3), ^3J = 9.1 Hz); 7.33 (ddd, 1 H, H(6), ^4J = 1.3 Hz, ^3J = 6.8 Hz, ^3J = 8.1 Hz); 7.43 (ddd, 1 H, H(7), ^4J = 1.4 Hz, ^3J = 6.8 Hz, ^3J = 8.4 Hz); 7.73 (br.d, 1 H, H(4), ^3J = 9.1 Hz); 7.75 (br.d, 1 H, H(5), ^3J = 8.1 Hz); 7.96 (br.d, 1 H, H(8), ^3J = 8.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 10.0 (CH_2CH_2); 52.1 (CH); 57.1 (OMe); 114.3 (C(3)); 122.3 (C(8)); 124.0 (C(6)); 127.1 (C(7)); 127.2 (C(9)); 127.8 (C(5)); 129.0 (C(4)); 129.1 (C(10)); 136.2 (C(1)); 147.5 (C(2)).

1-(2-Methoxy-1-naphthyl)-4,5-dihydro-1*H*-pyrazole (7b) was obtained similarly to pyrazoline **6b** (method ***B***) from azo compound **2b** (90 mg, 0.4 mmol). After purification of the product by column chromatography on SiO_2 (eluent — toluene—methanol, 80 : 1) pyrazoline **7b** (77 mg, 86%) was obtained as colorless crystals rapidly oxidizing in air, m.p. 57—59 °C. Partial MS, *m/z* (I_{rel} (%)): 226 (100) $[M]^+$, 211 (52) $[M - Me]^+$, 115 (64). ^{1}H NMR ($CDCl_3$), δ: 2.93 (dt, 2 H, H(4), ^3J = 1.7 Hz, ^3J = 10.2 Hz); 3.66 (t, 2 H, H(5), ^3J = 10.2 Hz); 3.89 (s, 3 H, OMe); 6.87 (t, 1 H, H(3), ^3J = 1.7 Hz); 7.26 (d, 1 H, H(3′), ^3J = 9.1 Hz); 7.33 (ddd, 1 H, H(6′), ^4J = 1.2 Hz, ^3J = 6.9 Hz, ^3J = 8.0 Hz); 7.45 (ddd, 1 H, H(7′), ^4J = 1.3 Hz, ^3J = 6.9 Hz, ^3J = 8.5 Hz); 7.74 (br.d, 1 H, H(4′), ^3J = 9.1 Hz); 7.76 (br.d, 1 H, H(5′), J = 8.0 Hz); 8.27 (br.d, 1 H, H(8′), J = 8.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 34.5 (C(4)); 51.5 (C(5)); 56.6 (OMe); 113.5 (C(9′)); 114.6 (C(3′)); 123.2 (C(8′)); 123.8 (C(6′)); 126.4 (C(7′)); 127.7 (C(5′)); 128.2 (C(4′)); 129.4 and 133.2 (C(1′) and C(10′)); 140.3 (C(3)); 154.1 (C(2′)).

1-(2-Methoxy-1-naphthyl)-1*H*-pyrazole (9c) was obtained similarly to pyrazole **10** from pyrazoline **7b** (33 mg, 0.15 mmol). After purification of the product by column chromatography on SiO_2 (eluent — benzene—ethyl acetate, 20 : 1) pyrazole **9c** (20 mg, 61%) was obtained as colorless crystals, m.p. 75—76 °C. Found (%): C, 74.59; H, 5.76; N, 12.75. $C_{14}H_{12}N_2O$. Calculated (%): C, 74.98; H, 5.39; N, 12.49. Partial MS, *m/z* (I_{rel} (%)): 224 (42) $[M]^+$, 97 (73) $[M - C_3H_5N_2 - C_2H_4]^+$, 57 (100). ^{1}H NMR ($CDCl_3$), δ: 3.87 (s, 3 H, OMe); 6.55 (dd, 1 H, H(4), ^3J = 1.9 Hz, ^3J = 2.3 Hz); 7.23 (m, 1 H, H(8′)); 7.36 (ddd, 1 H, H(6′), ^4J = 1.5 Hz, ^3J = 6.8 Hz, ^3J = 8.3 Hz); 7.37 (d, 1 H, H(3′), ^3J = 9.1 Hz); 7.43 (ddd, 1 H, H(7′), ^4J = 1.5 Hz, ^3J = 6.8 Hz, ^3J = 8.3 Hz); 7.66 (dd, 1 H, H(5), ^4J = 0.7 Hz, ^3J = 2.3 Hz); 7.82 (m, 1 H, H(5′)); 7.87 (dd, 1 H, H(3), ^4J = 0.7 Hz, ^3J = 1.9 Hz); 7.94 (br.d, 1 H, H(4′), ^3J = 9.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 56.9 (OMe); 106.0 (C(4)); 110.0 (C(9′)); 113.6 (C(3′)); 122.1 (C(8′)); 124.4 (C(6′)); 127.7 (C(5′)); 127.8 (C(7′)); 128.8 and 132.3 (C(1′) and C(10′)); 130.7 (C(4′)); 133.0 (C(5)); 140.6 (C(3)); 152.6 (C(2′)).

Compounds 8a, 8b, and 8c. A solution of azo compound **2a** (200 mg, 0.9 mmol) in anhydrous *o*-dichlorobenzene (15 mL) was refluxed for 12 h under Ar, then the solvent was evaporated *in vacuo* at 0.1 Torr and the residue was separated by column chromatography on SiO_2 (eluent — toluene—AcOEt, 50 : 1) to obtain naphtho[1,2-*d*]oxazole (**8a**) (40 mg, 25%) as colorless crystals with m.p. 60—61 °C (data in Ref. 13: m.p. 61—63 °C), 2-methylnaphtho[1,2-*d*]oxazole (**8b**) (40 mg, 23%), and 2-ethylnaphtho[1,2-*d*]oxazole (**8c**) (45 mg, 25%) as colorless oils. ^{1}H and ^{13}C spectra of oxazoles **8a**,**b** agree with those described earlier.[13]

2-Ethylnaphtho[1,2-*d*]oxazole (8c). Partial MS, *m/z* (I_{rel} (%)): 197 (100) $[M]^+$, 182 (74) $[M - Me]^+$. ^{1}H NMR ($CDCl_3$), δ: 1.51 (t, 3 H, Me, ^3J = 7.6 Hz); 3.09 (q, 2 H, CH_2,

^3J = 7.6 Hz); 7.52 (ddd, 1 H, H(8), ^4J = 1.3 Hz, ^3J = 6.9 Hz, ^3J = 8.2 Hz); 7.64 (ddd, 1 H, H(7), ^4J = 1.4 Hz, ^3J = 6.9 Hz, ^3J = 8.2 Hz); 7.66 (d, 1 H, H(4), ^3J = 9.0 Hz); 7.76 (br.d, 1 H, H(5), ^3J = 9.0 Hz); 7.96 (br.d, 1 H, H(6), ^3J = 8.2 Hz); 8.48 (br.d, 1 H, H(9), ^3J = 8.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 11.5 (Me); 22.5 (CH_2); 110.7 (C(4)); 122.0 (C(9)); 125.1 (C(8)); 125.3 (C(5)); 126.3 (C(13)); 126.9 (C(7)); 128.5 (C(6)); 131.0 (C(10)); 136.4 (C(11)); 148.0 (C(12)); 167.3 (C(2)).

1-(2-Hydroxy-1-naphthyl)-1*H*-pyrazole (9a). A solution of azo compound **2a** (45 mg, 0.22 mmol) in anhydrous *o*-dichlorobenzene (4 mL) was stirred for 10 h under Ar at 160 °C, then the solvent was evaporated *in vacuo* at 0.1 Torr and the residue was separated by preparative TLC on SiO_2 (eluent — ether — benzene, 1 : 1.5) collecting the yellow band with R_f = 0.90 (the starting compound **2a**) and colorless band with R_f = 0.53 (the product) to obtain azo compound **2a** (20 mg, 45%) and pyrazole **9a** (10 mg, 40%) as reddish oil. ^{1}H NMR ($CDCl_3$), δ: 6.63 (dd, 1 H, H(4), J_1 = 2.4 Hz, J_2 = 1.9 Hz); 7.29 (d, 1 H, H(3′), J = 8.9 Hz); 7.37 (ddd, 1 H, H(7′), J_1 = 8.0 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz); 7.47 (ddd, 1 H, H(6′), J_1 = 8.4 Hz, J_2 = 6.8 Hz, J_3 = 1.4 Hz); 7.72 (br.dd, 1 H, H(5′), J_1 = 8.4 Hz. J_2 = 1.2 Hz); 7.78 (br.d, 1 H, H(4′), J = 8.9 Hz); 7.83 (dd, 1 H, H(8′), J_1 = 8.0 Hz, J_2 = 1.4 Hz); 7.89 (d, 1 H, J = 1.8 Hz) and 7.91 (d, 1 H, J = 2.4 Hz) (H(3) and H(5)); 8.70 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 107.1 (C(4)); 119.0 (C(3′)); 119.5 (C(9′)); 120.9 (C(8′)); 123.9 (C(6′)); 127.6 (C(5′)); 128.5 (C(7′)); 127.9 and 129.0 (C(1′) and C(10′)); 139.9 (C(4′)); 132.9 (C(5)); 141.2 (C(3)); 149.0 (C(2′)).

1-[(1-Methylcyclopropyl)azo]-2-naphthol (2c). 2-Naphthol (64 mg, 0.32 mmol) and Cs_2CO_3 (521 mg, 1.6 mmol) were added to a solution of methyl *N*-nitroso-*N*-(1-methylcyclopropyl)carbamate (50 mg, 0.32 mmol) in CH_2Cl_2 (5 mL) and this was stirred for 90 h at room temperature. After that, another portions of 2-naphthol (60 mg, 0.3 mmol) and Cs_2CO_3 (380 mg, 1.17 mmol) were added to the reaction mixture and it was stirred for another 120 h until the signals of starting methyl *N*-nitroso-*N*-(1-methylcyclopropyl)carbamate disappear from the ^{1}H NMR spectrum of the reaction mixture. The solution was filtered, a precipitate formed was washed with $CHCl_3$ (3S5 mL), the combined filtrates were concentrated *in vacuo* and the residue was separated by column chromatography on SiO_2 (eluent — benzene—light petroleum (40—70), 1 : 2) collecting a bright yellow band to obtain azonaphthol **2c** (65 mg, 90%) as bright yellow needle-like crystals with m.p. 60—61 °C. Found (%): C, 74.35; H, 6.53; N, 12.22. $C_{14}H_{14}N_2O$. Calculated (%): C, 74.31; H, 6.24; N, 12.38. Partial MS, m/z (I_{rel} (%)): 226 (27) $[M]^+$, 211 (2) $[M - Me]^+$, 184 (23), 170 (30), 156 (52), 143 (24), 129 (98), 115 (77), 57 (100). ^{1}H NMR ($CDCl_3$), δ: 1.24 and 1.58 (both m, 2 H each, CH_2CH_2); 1.69 (s, 3 H, Me); 7.10 (br.d, 1 H, H(3), J = 9.0 Hz); 7.38 (ddd, 1 H, H(6), J_1 = 8.1 Hz, J_2 = 6.9 Hz, J_3 = 1.2 Hz); 7.55 (ddd, 1 H, H(7), J_1 = 8.3 Hz, J_2 = 6.9 Hz, J_3 = 1.3 Hz); 7.73 (br.d, 1 H, H(5), J = 8.1 Hz); 7.74 (br.d, 1 H, H(4), J = 9.0 Hz); 8.71 (br.d, 1 H, H(8), J = 8.3 Hz); 13.79 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 18.8 (CH_2); 19.2 (Me); 51.4 (C); 120.2 (C(3)); 121.7 (C(8)); 124.1 (C(6)); 127.6 (C(7)); 128.0 (C(5)); 127.8 and 128.2 (C(9) and C(10)); 132.8 (C(1)); 133.5 (C(4)); 152.7 (C(2)).

3-Methyl-1-(2-hydroxy-1-naphthyl)-1*H*-pyrazole (9b). A solution of azo compound **2c** (45 mg, 0.20 mmol) in anhydrous *o*-dichlorobenzene (5 mL) was refluxed for 3.5 h under Ar, then the solvent was evaporated *in vacuo* at 0.1 Torr. The residue was separated by preparative TLC on SiO_2 (eluent — benzene—AcOEt, 10 : 1) collecting colorless bands with R_f = 0.41 (**8b**), R_f = 0.49 (**8a**), and a red band with R_f = 0.36 (**9b**) to obtain naphtho[1,2-*d*]oxazole (**8a**) (11 mg, 33%) as colorless crystals, m.p. 60—61 °C, 2-methylnaphtho[1,2-*d*]oxazole (**8b**) (4 mg, 11%) as colorless oil, and pyrazole **9b** (11 mg, 25%) as red oil. The ^{1}H and ^{13}C NMR spectra of oxazoles **8a**,**b** agree with those described earlier.[13] **Compound 9b.** Partial MS, m/z (I_{rel} (%)): 224 (100) $[M]^+$, 207 (10) $[M-OH]^+$, 195 (97), 154 (31), 128 (29), 77 (53), 42 (65). ^{1}H NMR ($CDCl_3$), δ: 2.46 (s, 3 H, Me); 6.40 (d, 1 H, H(4), J = 2.3 Hz); 7.30 (d, 1 H, H(3′), J = 8.9 Hz); 7.37 (ddd, 1 H, H(6′), J_1 = 8.1 Hz, J_2 = 6.8 Hz, J_3 = 1.3 Hz); 7.48 (ddd, 1 H, H(7′), J_1 = 8.6 Hz, J_2 = 6.8 Hz, J_3 = 1.4 Hz); 7.77 (dd, 1 H, H(8′), J_1 = 8.6 Hz, J_2 = 1.3 Hz); 7.81 (br.d, 1 H, H(4′), J = 8.9 Hz); 7.82 (d, 1 H, H(5), J = 2.3 Hz); 7.83 (br.dd, 1 H, H(5′), J_1 = 8.1 Hz, J_2 = 1.4 Hz); 9.00 (br.s, 1 H. OH). ^{13}C NMR ($CDCl_3$), δ: 13.8 (Me); 106.9 (C(4)); 119.0 (C(3′)); 121.0 (C(4′)); 123.8 (C(6′)); 127.2, 128.3, 129.1 and 129.2 (C(3), C(1′), C(9′) and C(10′)); 127.4 (C(7′)); 128.5 (C(5′)); 129.4 (C(8′)); 133.6 (C(5)); 148.8 (C(2′)).

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