Synthesis of 3,4-dihydro-2*H*-pyrrole 1-oxide based aldonitrones as potential spin trapping agents

Andrey I. Taratayko,[a,b]* Christina S. Becker,[a,b] Igor' A. Grigor'ev,[a] Yurii V. Gatilov,[a] Tatyana V. Rybalova,[a] and Vladimir A. Reznikov[a,b]

[a] *N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Akad. Lavrent'ev Ave. 9, 630090 Novosibirsk, Russia*
[b] *Novosibirsk State University, Pirogova Street 2, 630090 Novosibirsk, Russia*
E-mail: taratayk@nioch.nsc.ru

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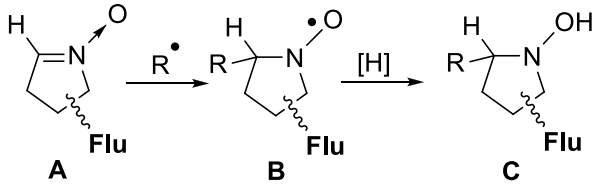
Abstract
Different synthetic approaches to fluorescent 3,4-dihydro-2*H*-pyrrole 1-oxide aldonitrones that are of potential interest as spin traps are discussed.

Keywords: Aldonitrones, spin traps, 3,4-dihydro-2*H*-pyrrole 1-oxide, fluorescence, organo-metallic compounds

Introduction

Aldonitrones based on pyrroline N-oxide derivatives (type **A**, scheme 1) are widely used as spin traps of short-living radicals in biological systems[1,2,3] that permits the determination of both the concentration and a structure of these radicals by the analysis of ESR of spin adducts of type **B** formed (scheme 1). This method possesses some obvious limitations. Different types of radicals react with nitrones with different rates,[4] and spin adducts formed have different lifetime and the main route of their transformation is bio-reduction to the hydroxylamines (type **C**, scheme 1). Thereby, the concentration of the spin adduct may be insufficient for the ESR spectrum registration and its interpretation. Furthermore, signals in spectra can broaden due to high solution viscosity or presence of dissolved oxygen, etc., hindering the interpretation of the spectra observed.



Scheme 1. The essence of spin trapping.

It is well known that the presence of both fluorescent fragment and nitroxide group in one molecule leads to significant decrease of quantum yield of fluorescence. This phenomenon was proposed to use in the systems where transformation "nitroxide – hydroxylamine" takes place (as a result of bio-reduction) for biochemical studies.[5] This phenomenon probably may be used for the detecting of short-living radicals in "inversed manner". In the case of conversion of diamagnetic spin trap into spin adduct – nitroxide the initial fluoresce quenching should be observe, that could provide the possibility of measurement of the radical concentration based on fluorescent quantum yield decrease.[6,7] This approach doesn't allow the determination of the nature of free radical, but seems to be prospective to increase the sensitivity in comparison to ESR method.

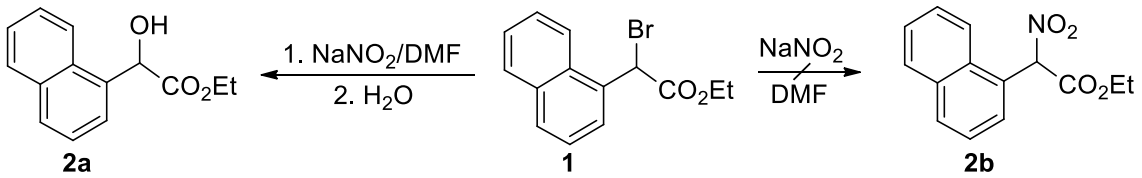
Thus, the aim of this work is the synthesis of aldonitrones (ketonitrones possess lower rates of free radicals capture[8]) based on 3,4-dihydro-2*H*-pyrrole 1-oxides containing fluorescent substituent. Noteworthy, that the presence of hydrophilic group is highly desirable in order to increase the solubility of spin trap in water phase that is very important particularly in biochemical investigations.

Results and Discussion

Different synthetic approaches were used to achieve the posed goal. They can be conditionally divided into two types. The first is the insertion of fluorescent moiety at the stage of heterocycle ring construction and the second is based on modifications of suitable heterocycle using reactivity of nitrone or other groups in a molecule.

The general method to synthesize the derivatives of 3,4-dihydro-2*H*-pyrrole 1-oxide is based on the condensation reaction of aliphatic nitro compounds with *α,β*-unsaturated carbonyl compounds followed by reductive cyclization of initially formed 1,4-nitroaldehydes or 1,4-nitroketones.[9,10]

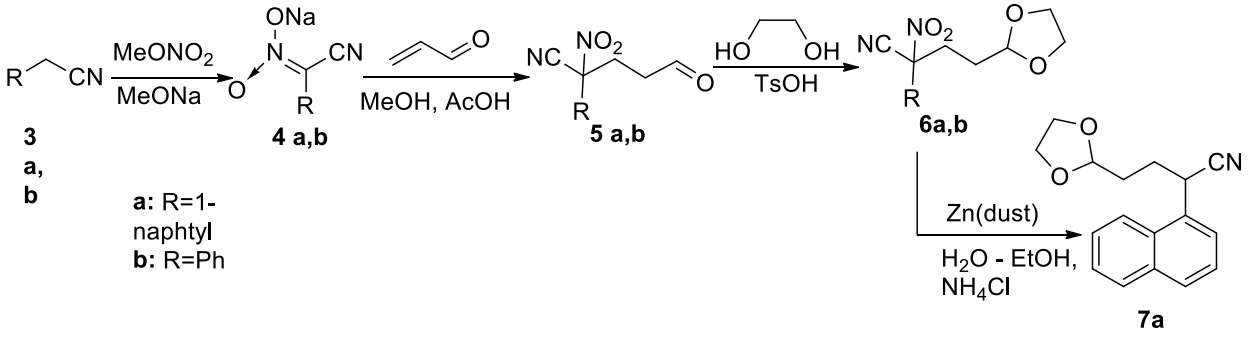
Starting **2b,** containing naphthalene-1-yl group as fluorescent moiety and ester group for further transformation into hydrophilic carboxyl group could be synthesized by reaction of ethyl 2-bromo-2-(naphthalene-1-yl)acetate with sodium nitrite in DMF in the presence of phloroglucinol similarly to that, described for ethyl 2-bromophenylacetate.[11] However in the case of **1** the main, if not the sole product of the reaction was ethyl 2-hydroxy-2-(naphthalene-1-yl)acetate **2a**, probably due to significant steric hindrance (Scheme 2).



2a **1** **2b**

Scheme 2. Reaction of bromide **1** with sodium nitrite.

An alternative approach for fluorescent nitrones synthesis could be the condensations of *aci*-nitro compounds salts bearing fluorescent fragment and cyano group as a precursor of hydrophilic moiety, with acrolein. Sodium salts **4a,b,** were synthesized by condensation of nitriles **3a,b** with methyl nitrate in the presence of sodium methylate (Scheme 3). Reaction of compounds **4a,b** with acrolein in the presence of double excess of acetic acid leads to compounds **5a,b**, but complete consumption of reagents wasn't observe. Increasing of the reaction time from 24 to 48 hours under similar conditions leads to products yield decrease (from 65% to 48% for **5a**) (Scheme 3). The structure of **5a** was proved by X-ray analysis (Figure 1).



Scheme 3. Synthesis and reduction of 1,4-nitroaldehyde **6**.

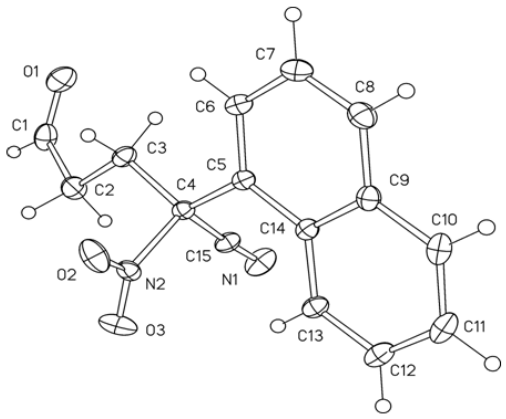
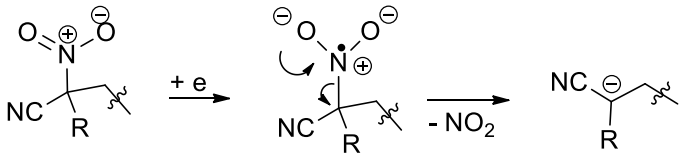


Figure 1. The molecular structure of **5a.**

Further reaction of **5a,b** with ethylene glycol in the presence of catalytic amount of TsOH gives 1,3-dioxolanes **6a,b**. Reduction of nitro group in **6a** by zinc dust in water-ethanol solution in the presence of NH_4Cl unexpectedly leads to 4-(1,3-dioxolan-2-yl)-2-(naphthalen-1-yl)butanenitrile 7**a** instead of the desired hydroxylamine. Probably, the reason of this transformation is the presence of electron withdrawing cyano group, that stabilize anion – product of elimination reaction of initially formed anion-radical – product of one-electron

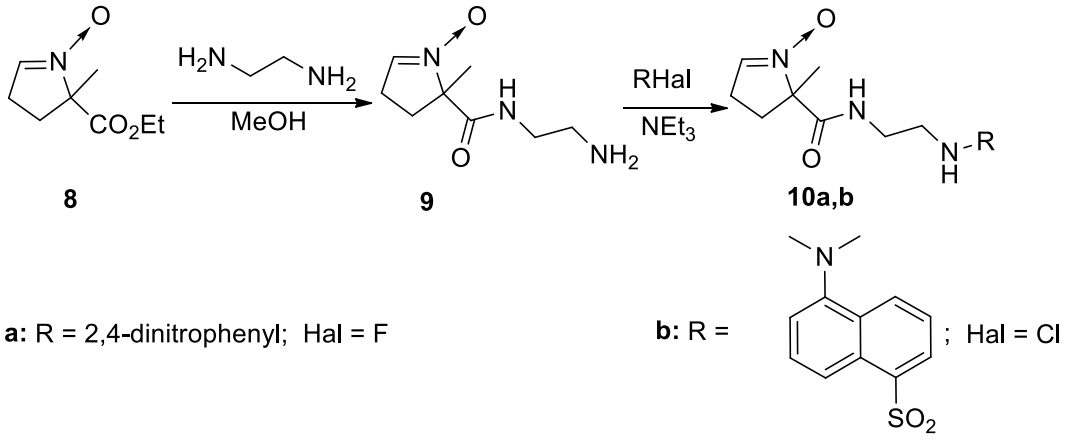
reduction. Hereby, in this case elimination of anion-radical is faster than its protonation (Scheme 4).



Scheme 4. Supposed mechanism of **7a** formation.

Thus, we failed to insert the fluorescent fragment into a molecule that may be a precursor of desired heterocycle and the next step of our work was the attempts of introducing of fluorescent moiety using reactivity of functional groups already presented in suitable heterocycle.

We succeed to insert fluorescent moiety into the aldonitrone molecule with the use of 2-(ethoxycarbonyl)-2-methyl-3,4-dihydro-2*H*-pyrrole 1-oxide (EMPO)[1] **8** as starting material. Commercially available compound **8** nowadays is used as a spin trap that readily reacts with superoxide radical.[12] We found that reaction of **8** with excess of ethylenediamine (Scheme 5) gives aminoamide **9** and further reaction of **9** with 2,4-dinitrofluorobenzene or 5-(dimethylamino)naphthalene-1-sulfonyl chloride (dansyl chloride) in the presence of triethylamine yields **10a** and **10b** respectively.



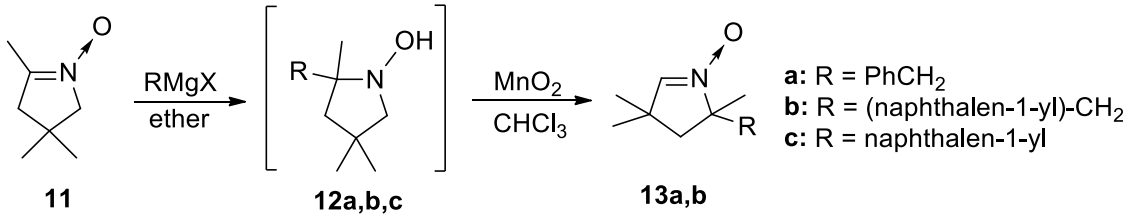
Scheme 5. Synthesis of **10a-b** from EMPO.

Nitrone **8** could be very promising precursor for fluorescent spin traps, since variation of fluorescent moiety on the last step of synthesis allows to produce spin traps with different physical and chemical properties. Limitations of this approach are high commercial value of **8** and its limited availability.

Another way of introduction of the fluorescent moiety is the synthetic sequence including reaction of nitrones with appropriate organometallic compounds followed by oxidation of

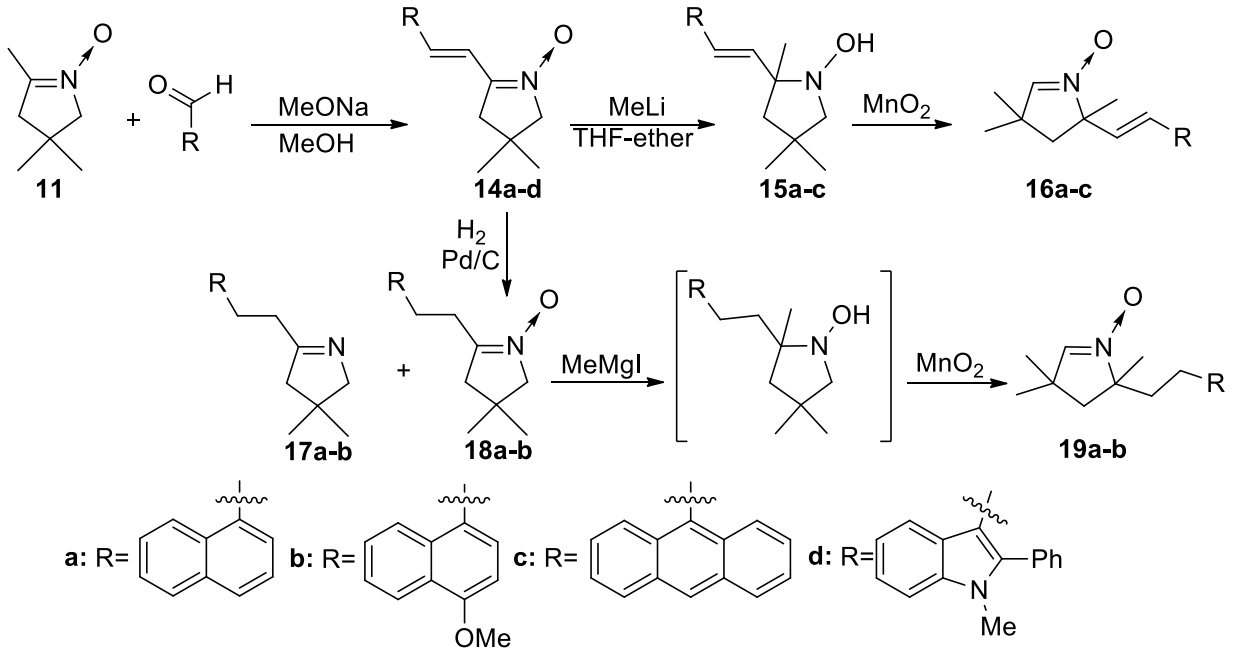
hydroxylamines formed into nitrones. This method was previously widely used in the synthesis of pyrrolidine (proxyl) nitroxides.[13,14]

Reaction of benzylmagnesium chloride as a model reagent with nitrone **11** leads to hydroxylamine **12a**, which was oxidized without purification by manganese dioxide into nitrone **13a** (Scheme 6). Similarly, nitrone **13b** was obtained by reaction of (naphthalen-1-ylmethyl)magnesium chloride with nitrone **11**. Addition of naphthalen-1-ylmagnesium bromide to nitrone **11** did not proceed probably due to steric hindrance. In this case cross-metallation of methyl group in the position 5 of heterocycle seems to proceed with further self-condensation products formation.[15]



Scheme 6. Synthesis of nitrones **13a-b.**

The last approach examined was based on the condensation of nitrone **11** with aldehydes[16] containing fluorescent moiety and further transformations of formed α,β-unsaturated nitrones (Scheme 7).



Scheme 7. Synthesis of nitrones **16a-c** and **19a-b**.

It was shown that nitrone **11** easily reacts with series of aromatic aldehydes with formation of **14**. It should be noted, that the resulting products possessed *trans*-configuration of double bond. Molecular structures of **14a** and **14d** are shown on the Figures 2 and 3 respectively. Further modification of nitrones **14** was carried out by two different ways.

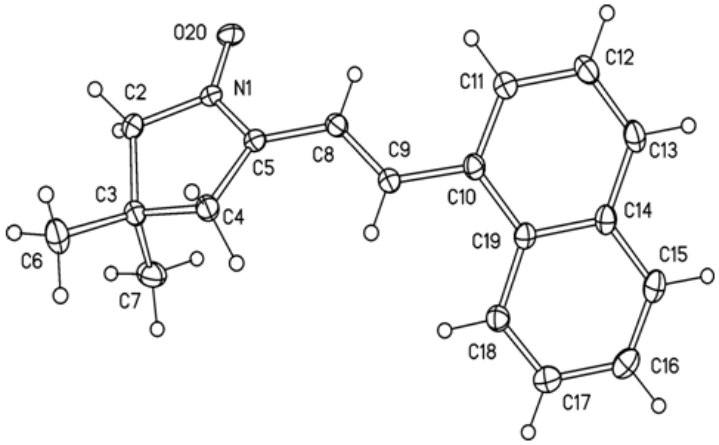


Figure 2. The molecular structure of **14a**.

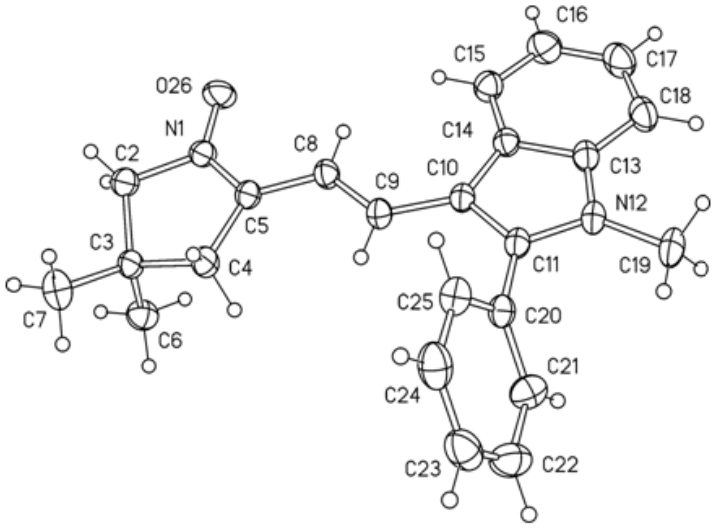


Figure 3. The molecular structure of **14d**.

When **14a-c** reacted with methyllithium in the THF – ether solution hydroxylamines **15a-c** were formed. They were oxidized without isolation in individual form into nitrones **16a-c**.

When **14a-b** were hydrogenated at atmospheric pressure in the presence of Pd/C catalyst, nitrones **18a-b** were formed along with pyrrolines **17a-b** as a by-products. Further treatment of

18a-b by methylmagnesium iodide followed by oxidation of formed hydroxylamines leads to aldonitrones **19a-b**.

Thus, nitrone **11** was shown to be a convenient precursor for the series fluorescent nitrones **16** and **19** possessed different absorption and emission maxima. An applicability of synthesized fluorescent nitrones as spin traps will be studied at an early day.

Experimental Section

General. All spectra and elemental analyses were carried out by the Chemical Service Center of the Novosibirsk Institute of Organic Chemistry. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-300 and AV-400 spectrometers; solvents were used as internal standards. IR spectra were recorded on Bruker IFS 66 spectrometer for KBr pellets (concentration 0.25%, pellet thickness 1 mm). Mass spectra were recorded on DFS (Thermo Electron) spectrometer and on Bruker micrOTOF-Q spectrometer in a direct input. GC-MS spectra were recorded on HP1800A (Hewlett-Packard) spectrometr. Fluorescence spectra were recorded on Cary Eclipse fluorimeter for 10^{-5}M solutions in chloroform. Melting points were measured in a sealed capillary. Silufol UV 254 and Merck Kieselgel 60 F254 plates were used for TLC monitoring. Chromatography was carried out using "Merck" silica gel (0.063–0.100 mm) for column chromatography.
The X-ray diffraction experiments for compounds **5a**, **14a**, **14d** were carried out on Bruker KAPPA APEX II diffractometer (graphite-monochromated Mo Kα radiation). Reflection intensities were corrected for absorption by SADABS program. The structures was solved by direct methods using the SHELXS-97 program[17] and refined by anisotropic (isotropic for all H atoms) full-matrix least-squares method against F^2 of all reflections using SHELX-97 program. The positions of the hydrogen were calculated geometrically and refined in riding model.
The obtained crystal structure was analyzed for short contacts between non-bonded atoms and hydrogen bonding (table 1) using the PLATON program.[18] Crystallographic data for the structures of compounds **5a**, **14a**, **14d** in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 917551 - 917553. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 122 3336033 or e-mail: deposit@ccdc.cam.ac.uk; internet: www.ccdc.cam.ac.uk).

Reaction of ethyl 2-bromo-2-(naphthalene-1-yl)acetate with sodium nitrite. To a stirred solution of sodium nitrtite (0.55 g, 7.99 mmol) and phloroglucinol (0.6 g, 4.74 mmol) in anhydrous DMF (7.5 mL) a solution of ethyl 2-bromo-2-(naphthalene-1-yl)acetate (1.3 g, 4.44 mmol) in anhydrous DMF (2 mL) was added. Dark solution was kept for 17 hours at room temperature and poured into 20 mL of ice-cold water. Resulted solution was extracted by ether (3 × 20 mL) and the combined extract was washed by 30 mL of saturated sodium hydrocarbonate solution, dried with $MgSO_4$ and concentrated *in vacuo*. According to GC-MS and ^{1}H NMR

analysis formation of ethyl 2-nitro-2-(naphthalene-1-yl)acetate didn't proceed. The main product of reaction was ethyl 2-hydroxy-2-(naphthalene-1-yl)acetate. In the ^{1}H NMR (300.13 MHz, $CDCl_3$) spectrum of the reaction mixture the following characteristic signals was observed: δ 1.12 (t, $J^3_{H,H}$ 7.2 Hz, 3H, C<u>H</u>$_3$CH$_2$), 3.67 (br.s, 1H, O<u>H</u>), 4.10 – 4.30 (m, 2H, CH$_3$C<u>H</u>$_2$), 5.79 (s, 1H, C<u>H</u>OH), 7.40 – 8.10 (m, 7H, arom). This signals correspond to spectrum of 2-hydroxy-2-(naphthalene-1-yl)acetate.[19]

Sodium cyano(naphthalen-1-yl)methyleneazinate (4a) was synthesized as described previously.[20] IR(ν_{max}, cm^{-1}): 2203 (C≡N), 1475 (NO_2Na), 1454, 1332, 1266, 1250, 1094, 947, 769. ^{1}H NMR (400.13 MHz, $(CD_3)_2SO$): δ 7.47 – 7.51 (m, 4H), 7.80 – 7.84 (m, 2H), 7.89 – 7.92 (m, 1H, arom.). ^{13}C NMR (100.61 MHz, $(CD_3)_2SO$): δ 121.6 (<u>C</u>N), 125.4, 125.56, 125.59, 126.0, 127.4, 127.8, 128.1, 130.5, 131.0, 133.4 (arom.), 166.9 (br. s., <u>C</u>=NO_2Na).

Sodium cyano(phenyl)methyleneazinate (4b) was obtained by the procedure described for **4a** from **3b** (2.46g, 21 mmol). Colorless crystals, yield 58%, 2.2 g; mp above 250 ºC; IR(ν_{max}, cm^{-1}): 2212, 1503, 1477 (NO_2Na), 1436, 1353, 1232, 751. ^{1}H NMR (300.13 MHz, $(CD_3)_2SO$): δ 6.96 – 7.03 (m, 1H), 7.22 – 7.30 (m, 1H), 7.77–7.82 (m, 2H, Ph). ^{13}C NMR (75.46, $(CD_3)_2SO$): δ 119.9 (<u>C</u>N), 122.9, 123.4, 127.9, 133.4 (Ph), 165.8 (br. s., <u>C</u>=NO_2Na).

2-(Naphthalen-1-yl)-2-nitro-5-oxopentanenitrile (5a). Glacial acetic acid (0.01 mL, 1.71 mmol) and acrolein (0.057 mL, 0.855 mmol) were added to a stirred solution of **4a** (0.20 g, 0.855 mmol) in anhydrous methanol (0.85 mL).Resulted solution was kept for 24 hours at 45 ºC. The solvent was removed on reduced pressure, the residue was diluted with water (2 mL) and extracted with chloroform (3 × 4 mL). Combined extract was dried with $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by chromatography with a mixture of $CHCl_3$ – MeOH (50:1) as eluent. Colorless crystals, yield 150 mg (65%), mp 106 – 108 ºC (from mixture hexane – ethylacetate 3:1, with decomposition); IR(ν_{max}, cm^{-1}): 2833, 2728, 1727 (C=O), 1576, 1349 (NO_2), 802, 776. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.79 – 2.89 (m, 1H, C<u>H</u>$_2$CHO), 3.04 – 3.13 (m, 1H, C<u>H</u>$_2$CHO), 3.22 – 3.27 (m, 1H, C<u>H</u>$_2$CH$_2$CHO), 7.54 – 7.67 (m, 3H), 7.82 – 7.85 (m, 1H), 7.93 – 7.97 (m, 1H), 8.02–8.07 (m, 2H, arom.), 9.85 (s, 1H, C<u>H</u>O). ^{13}C NMR (100.61MHz, $CDCl_3$): δ 30.3 (<u>C</u>H$_2$CHO), 39.4 (<u>C</u>H$_2$CH$_2$CHO), 89.1 (<u>C</u>(CN)(NO_2)), 114.7 (<u>C</u>N), 122.1, 124.9, 126.4, 126.8, 127.1, 128.7, 129.8, 130.0, 134.4 (arom.), 197.5 (<u>C</u>HO). Calcd. for $C_{15}H_{12}N_2O_3$ (268.08): C 67.16, H 4.51, N 10.44. Found: C 67.00, H 4.32, N 10.47.

Crystallographic data for comp **5a**: $C_{15}H_{12}N_2O_3$, M = 268.27, monoclinic, $P2_1/c$, a = 11.2063(8), b = 10.9032(7), c = 10.5235(7) Å, β = 91.050(2)°, V = 1285.6(2) Å^3, Z = 4, D_{calcd} = 1.386 g·cm^{-3}, μ(Mo-$K\alpha$) = 0.099 mm^{-1}, F(000) = 560, (θ 1.82 - 29.17°, completeness 99.8%), T 150(2) K, colorless prism, (0.56 × 0.16 × 0.15) mm^3, transmission 0.9615 – 0.9895, 25142 measured reflections in index range -15<=h<=15, -14<=k<=14, -14<=l<=13, 3472 independent (R_{int} = 0.0218), 203 parameters, 3055 observed [$I > 2\sigma(I)$], R_1 = 0.0410, wR_2 = 0.1274 (all data), GOOF 1.069, largest diff. peak and hole 0.321 and -0.209 e.A^{-3}. The atom positions of cyano and nitro groups are disordered due to enatiomers placement in the same position with ratio 85:15

2-Nitro-5-oxo-2-phenylpentanenitrile (5b) was synthesized according to the procedure described for **5a** from **4b** (0.16 g, 0.855 mmol). Pale yellow oil, yield 66%; IR(ν_{max}, cm^{-1}): 1726

(C=O), 1570, 1452 (NO_2), 1338, 640. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.69 – 2.73 (m, 2H, C<u>H</u>$_2$CHO), 2.82 – 2.90 (m, 1H, C<u>H</u>$_2$CH$_2$CHO), 3.06 – 3.14 (m, 1H, C<u>H</u>$_2$CH$_2$CHO), 7.44 – 7.51 (m, 3H), 7.65 – 7.68 (m, 2H, Ph), 9.73 (br. s, 1H, C<u>H</u>O). ^{13}C NMR (100.61MHz, $CDCl_3$): δ 30.5 (<u>C</u>H$_2$CH$_2$CHO), 39.0 (<u>C</u>H$_2$CHO), 91.3 (<u>C</u>(CN)NO$_2$), 114.1 (<u>C</u>N), 126.4, 129.8, 130.7, 131.8 (Ph), 197.6 (<u>C</u>HO Calcd. for $C_{11}H_{10}N_2O_3$ (218.07): C 60.55, H 4.62, N 12.84. Found: C 60.99, H 4.83, N 12.63.

4-(1,3-Dioxolan-2-yl)-2-(naphthalen-1-yl)-2-nitrobutanenitrile (6a). A mixture of **5a** (1.0 g, 3.63 mmol), ethylene glycol (0.24 mL, 4.37 mmol), TsOH (0.006 g, 0.034 mmol) and benzene (1.2 mL) was refluxed with Dean-Stark apparatus until the end of water separation (about 3.5 hours). Then the reaction mixture was diluted by benzene (5mL) and washed consequentially by sodium hydrocarbonate saturated solution (2 × 5 mL) and water (2 × 5mL). Combined organic extract was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by chromatography with a mixture of $CHCl_3$ – MeOH (30:1) as eluent. Colorless crystals, yield 0.71 g (61%,); mp 111 – 113 ºC (from mixture hexane – ethylacetate 4:1, with decomposition); IR(ν_{max}, cm^{-1}): 2961, 2888, 1571 (NO_2), 1147, 1027, 810, 781. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.92 – 2.04 (m, 1H, C<u>H</u>$_2$CH(O)O), 2.16 – 2.28 (m, 1H, C<u>H</u>$_2$CH(O)O), 3.00 – 3.07 (m, 2H, C<u>H</u>$_2$CH$_2$CH(O)O), 3.89 – 4.02 (m, 4H, OC<u>H</u>$_2$C<u>H</u>$_2$O), 5.05 (t, 1H, $J^3_{H,H}$ 4.0 Hz, OC<u>H</u>O), 7.50 – 7.66 (m, 3H), 7.82 – 7.85 (m, 1H), 7.91 – 7.95 (m, 1H), 7.99 – 8.03 (m, 1H), 8.08 – 8.13 (m, 1H, arom.). ^{13}C NMR (100.61MHz, $CDCl_3$): δ 29.1 (<u>C</u>H$_2$CH(O)O), 31.6 (<u>C</u>H$_2$CH$_2$CH(O)O), 65.11 (O<u>C</u>H$_2$CH$_2$O), 65.14 (O<u>C</u>H$_2$CH$_2$O), 89.4 (<u>C</u>(CN)(NO$_2$)), 102.2 (O<u>C</u>HO), 114.7 (<u>C</u>N), 122.0, 124.6, 126.5, 126.66, 126.72, 128.2, 129.7, 129.8, 132.8, 134.2 (arom.). Calcd. for $C_{17}H_{16}N_2O_4$ (312.32): C 65.38, H 5.16, N 8.97. Found: C 65.62, H 5.08, N 9.07.

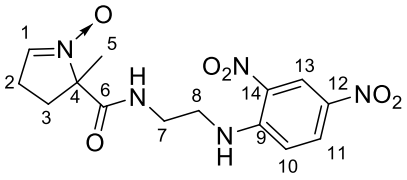
4-(1,3-Dioxolan-2-yl)-2-nitro-2-phenylbutanenitrile (6b) was synthesized according to the procedure described for **6a** from **5b** (0.81 g, 3.73 mmol). Pale yellow oil, yield 0.69 g (72%); IR(ν_{max}, cm^{-1}): 2959, 2890, 1570, 1338 (NO_2), 1138, 1028, 693. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.80–1.90 (m, 2H, C<u>H</u>$_2$CH(O)O), 2.61–2.72 (m, 1H, C<u>H</u>$_2$CH$_2$CHOO), 2.85–2.97 (m, 1H, C<u>H</u>$_2$CH$_2$CH(O)O), 3.82–3.95 (m, 4H, OC<u>H</u>$_2$C<u>H</u>$_2$O), 4.94 (t, 1H, $J^3_{H,H}$ 4.0 Hz, OC<u>H</u>O), 7.41–7.49 (m, 3H), 7.66–7.70 (m, 2H, Ph). ^{13}C NMR (75.46MHz, $CDCl_3$): δ 29.1 (<u>C</u>H$_2$CH$_2$CHO), 32.0 (<u>C</u>H$_2$CHO), 65.16 (O<u>C</u>H$_2$CH$_2$O), 65.19 (OCH$_2$<u>C</u>H$_2$O), 92.0 (<u>C</u>(CN)NO$_2$), 102.2 (O<u>C</u>HO), 114.3 (<u>C</u>N), 126.5, 129.6, 131.1, 131.5 (Ph). Calcd. for $C_{13}H_{14}N_2NaO_4$: *m/z* 285.0850 [M+Na]$^+$. Found: *m/z* 285.0846 [M+Na]$^+$.

4-(1,3-Dioxolan-2-yl)-2-(naphthalen-1-yl)butanenitrile (7a). To a cooled stirred mixture of **6a** (0.574 g, 1.84 mmol), NH_4Cl (0.108 g, 2.02 mmol), EtOH (6 mL) and water (6mL) zinc dust (0.499 g, 7.67 mmol) was added by small portion maintaining the temperature at 10 °C. After the addition of zinc, cooling was removed and mixture was vigorously stirred for 2 hours at room temperature. The precipitate was filtered off and washed with methanol (3 × 4 mL). The filtrate was concentrated *in vacuo* and the residue was diluted with water (5 mL) and extracted by chloroform (4 × 5 mL). Combined organic extract was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by chromatography with a mixture of

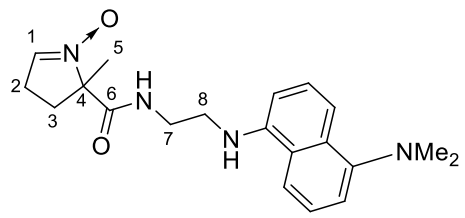
$CHCl_3$ – MeOH (40:1) as eluent. Pale yellow oil, yield 0.15 g (31%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.93–1.96 (m, 2H, C$\underline{H}_2$CHOO), 2.09 – 2.21 (m, 2H, C$\underline{H}_2$CH-arom.), 3.81 – 3.95 (m, 4H, OC$\underline{H}_2$C$\underline{H}_2$O), 4.69 (dd, 1H, $J^3_{H,H}$ 5.4 Hz, $J^3_{H,H}$ 9.3 Hz, C$\underline{H}$-arom.), 4.91 (t, 1H, $J^3_{H,H}$ 4.3 Hz, OC$\underline{H}$O), 7.43 – 7.58 (m, 3H), 7.66–7.69 (m, 1H), 7.79 – 7.83 (m, 1H), 7.86 – 7.89 (m, 1H), 7.91 – 7.95 (m, 1H, arom). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 28.9 (C$\underline{H}_2$CH(O)O), 31.0 (C$\underline{H}_2$CH-arom.), 34.1 (C$\underline{H}$–arom), 64.95 (OC$\underline{H}_2$CH$_2$O), 65.02 (OCH$_2$C$\underline{H}_2$O), 103.5 (OC$\underline{H}$O), 121.0 (C$\underline{N}$), 122.2, 125.48, 125.52, 126.1, 126.9, 129.0, 129.3, 130.0, 131.6, 134.0 (arom).

2-(2-Aminoethylcarbamoyl)-2-methyl-3,4-dihydro-2H-pyrrole 1-oxide 9. A solution of ethylenediamine (3.9 mL, 58 mmol) and 2-(ethoxycarbonyl)-2-methyl-3,4-dihydro-2H-pyrrole 1-oxide **8** (1g, 5.8 mmol) in methanol (2mL) was kept for 48 hours at room temperature and then concentrated *in vacuo*. The residue was purified by chromatography with a mixture of $CHCl_3$ – methanol – NEt_3 (30:10:1) as eluent. Pale yellow oil, yield 42%, 0.45 g; IR(ν_{max}, cm^{-1}): 3327 (N–H), 2936, 1660 (C=O), 1529, 752. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.63 (s, 3H, CH_3), 2.06 (dt, 2H, $J^3_{H,H}$ 7.9 Hz, $J^2_{H,H}$ 13.5 Hz, C$\underline{H}_2$C(CH$_3$)CO), 2.53 (dt, 2H, $J^3_{H,H}$ 7.9 Hz, $J^3_{H,H}$ 2.7 Hz, C$\underline{H}_2$CH=N), 2.75 (t, 2H, $J^3_{H,H}$ 6.2 Hz, C$\underline{H}_2$CH$_2$NH$_2$), 2.87 – 2.96 (m, 2H, N$\underline{H}_2$), 3.23 (q, 2H, $J^3_{H,H}$ 6.2 Hz, CH$_2$C$\underline{H}_2$NH$_2$), 6.92 (t,1H, $J^3_{H,H}$ 2.7 Hz, C$\underline{H}$=N), 8.56 (br. s, 1H, N$\underline{H}$). ^{13}C NMR (75.46MHz, $CDCl_3$): δ 24.1 (CH_3), 24.6 (C$\underline{H}_2$CH$_2$NH$_2$), 30.4 (CH$_2$C$\underline{H}_2$NH$_2$), 41.3 (N=CHC$\underline{H}_2$), 42.4 (C$\underline{H}_2$C(CH$_3$)CO), 78.6 (C$\underline{C}$(CH$_3$)CO), 137.1 (N=C$\underline{H}$), 170.9 (C=O). Calcd. for $C_8H_{15}N_3O_2$: *m/z* 185.1159 [M]$^+$. Found: *m/z* 185.1160 [M]$^+$.

2-(2-(2,4-Dinitrophenylamino)ethylcarbamoyl)-2-methyl-3,4-dihydro-2*H*-pyrrole 1-oxide 10a. A solution of 2,4-dinitrofluorobenzene (0.093 g, 0.5 mmol) and triethylamine (0.08 mL, 0.5 mmol) in anhydrous acetonitrile (2.5 mL) was added dropwise to a solution of **9** (0.1 g, 0.5 mmol) in anhydrous acetonitrile (10 mL). The reaction mixture was stirred for 1.5 hours at room temperature and then concentrated *in vacuo*. The residue was diluted with chloroform (10 mL) and washed with brine. Combined organic extract was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Product was purified by TLC on alumina with chloroform as eluent. Bright yellow oil, yield 0.097 g (55%); IR (ν_{max}, cm^{-1}): 3359 (N–H), 1676 (C=O), 1618, 1607(C=N), 1524 (NO_2), 1335 (NO_2). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.67 (s, 3H, CH_3), 2.15 (m, 1H, C(2)H$_2$), 2.60 (t, 2H, $J^3_{H,H}$ 6.9 Hz, C(3)H$_2$, 2.89 – 2.96 (m, 1H, C(2)H$_2$), 3.13 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$NH), 6.96 (br. s, 1H, C(1)$\underline{H}$), 7.03 (d, 1H, $J^3_{H,H}$ 9.5 Hz, H(10)), 8.25 (dd, 1H, $J^3_{H,H}$ 2.5 Hz, $J^3_{H,H}$ 9.5 Hz, H(11)), 8.70 (br. c,1H, C(9)–N$\underline{H}$), 8.95 (br. s,1H, CON$\underline{H}$), 9.08 (d, 1H, $J^3_{H,H}$ 2.5 Hz, H(13)). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 24.2 (C(8)), 24.7 (C(7)), 37.9 (C(3)), 43.1 (C(2)), 46.3 (C(5)), 78.5 (C(4)), 114.1 (C(10)), 124.3 (C(13)), 130.5 (C(11)), 130.8 (C(14)), 136.3 (C(12)), 137.8 (C(9)), 148.5 (C(1)), 172.1 (C(6)).



2-(2-(5-(Dimethylamino)naphthalene-1-sulfonamido)ethylcarbamoyl)-2-methyl-3,4-dihydro-2*H*-pyrrole 1-oxide 10b was synthesized according to the procedure described for **10a** from **9** (0.1 g, 0.5 mmol) and dansyl chloride (0.135 g, 0.5 mmol). Pale yellowish-green oil, yield 0.059 g (28%); IR(ν_{max}, cm^{-1}): 3396 (N–H), 2940, 2863, 1669 (C=O), 1542 (C=N), 1453, 1320



(S=O), 1144 (S=O), 792, 625, 570. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.55 (s, 3H, C$\underline{H}_3$), 2.01 (dt, 1H, $J^3_{H,H}$ 8.0 Hz, $J^2_{H,H}$ 13.4 Hz, C(3)$\underline{H}$), 2.50 (dt, 1H, $J^3_{H,H}$ 7.6 Hz, $J^2_{H,H}$ 2.7 Hz, C(2)$\underline{H}_2$), 2.79 – 2.90 (m, 1H, C(3)$\underline{H}$), 2.83 (s, 6H, N(C$\underline{H}_3$)$_2$), 3.00 (t, 2H, $J^3_{H,H}$ 6.0 Hz, C(8)$\underline{H}_2$), 3.30 (q, 2H, $J^3_{H,H}$ 6.0 Hz, C(7)$\underline{H}_2$), 6.69 (br. s, 1H, SO_2N$\underline{H}$), 7.04 (t, 1H, $J^3_{H,H}$ 2.7 Hz, C(1)$\underline{H}$), 7.11 (d, 1H, $J^3_{H,H}$ 7.5 Hz), 7.42–7.51 (m, 2H), 8.16 (dd, 1H, $J^3_{H,H}$ 7.3 Hz, $J^4_{H,H}$ 1.2 Hz), 8.27 (dt, 1H, $J^3_{H,H}$ 8.7 Hz, $J^4_{H,H}$ 0.9 Hz), 8.47 (dt, 1H, $J^3_{H,H}$ 8.5 Hz, $J^4_{H,H}$ 0.9 Hz, arom.), 8.54 (br. t, 1H, $J^3_{H,H}$ 5.8 Hz, CON$\underline{H}$). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 23. 6 (C(6)), 24.9 (C(2)), 30.5 (C(7)), 39.2 (C(3)), 43.1 (C(8)), 45.5 (N($\underline{C}$H$_3$)$_2$), 78.7 (C(4)), 115.2, 119.1, 123.3, 128.3, 129.4, 129.7, 130.0, 130.3, 135.1 (arom.), 138.8 (C(1)), 152.0 (arom.), 171.3 (C(5)). Calcd. for $C_{20}H_{26}N_4SO_4$: *m/z* 418.1669 $[M]^+$. Found: *m/z* 418.1664 $[M]^+$. Absorption maximum – 342 nm, emission maximum – 496 nm.

2-Benzyl-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide 13a. To a solution of benzylmagnesium chloride, prepared from magnesium (0.236 g, 9.84 mmol) and benzyl chloride (1.43 g, 9.50 mmol) in anhydrous ether (11mL), a solution of 3,3,5-trimethyl-3,4-dihydro-2H-pyrrole 1-oxide **11** (1.0 g, 7.87 mmol) in anhydrous ether (1.5 mL) was added. The reaction mixture was stirred for 0.7 hours at room temperature and the excess of Grignard reagent was decomposed by addition of saturated ammonium chloride solution (10 mL). Ether solution was separated and water layer was extracted with ether (5 × 20 mL). Combined organic phases were dried with $MgSO_4$ and a solvent was removed under reduced pressure. The residue was dissolved in chloroform (30 mL) and manganese dioxide (0.5 g) was added. The resulting mixture was stirred for 3.5 hours at room temperature, manganese dioxide was filtered off and washed with chloroform (40 mL). The filtrate was concentrated *in vacuo*, and the residue was purified by chromatography with a mixture of chloroform – methanol (50:1) as eluent. Pale yellow crystals, yield 1.1 g (64%); mp 82 – 84 ºC (from hexane); IR (ν_{max}, cm^{-1}): 2958, 1581 (C=N), 1450, 1243, 1172, 1156, 821, 765, 723, 707, 601. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.28 (s, 3H, C$\underline{H}_3$), 1.01 (s, 3H, C$\underline{H}_3$), 1.48 (s, 3H, C$\underline{H}_3$), 1.80 (dd, AB-system, 2H, $J^2_{H,H}$ 13.4 Hz, C(CH$_3$)$_2$C$\underline{H}_2$), 2.89 (dd, 2H, AB-system, $J^2_{H,H}$ 13.8 Hz, PhC$\underline{H}_2$), 6.42 (s, 1H, N=C$\underline{H}$), 7.09–7.20 (m, 5H, Ph). ^{13}C NMR (100.61MHz, $CDCl_3$): δ 26.8 ($\underline{C}$H$_3$), 27.9 ($\underline{C}$H$_3$), 29.3 ($\underline{C}$H$_3$), 37.7 ($\underline{C}$(CH$_3$)$_2$), 43.2 (Ph$\underline{C}$H$_2$), 43.6 ($\underline{C}$H$_2$C(CH$_3$)$_2$), 78.1 ($\underline{C}$(CH$_3$)CH$_2$Ph), 126.9, 128.3, 130.3, 136.3 (Ph), 142.1 ($\underline{C}$H=N). Calcd. for $C_{14}H_{19}NO$: *m/z* 217.1461 $[M]^+$. Found: *m/z* 217.1462 $[M]^+$.

2,4,4-Trimethyl-2-(naphthalen-1-ylmethyl)-3,4-dihydro-2*H*-pyrrole 1-oxide 13b was synthesized according to the procedure described for **13a** from magnesium (0.236 g, 9.84 mmol), 1-chloromethylnaphthalene (1.76 g, 9.50 mmol) and **11** (1.0 g, 7.87 mmol). White powder, yield 1.26 g (60%); mp 79 – 82 ºC (from hexane); IR (ν_{max}, cm^{-1}): 3026, 2966, 1581 (C=N), 1453, 1262, 1169, 811, 787, 605. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.02 (s, 3H, C$\underline{H}_3$), 0.95 (s, 3H, C$\underline{H}_3$), 1.60 (s, 3H, C$\underline{H}_3$), 1.75 (dd, AB-system, 2H, $J^2_{H,H}$ 13.4 Hz, C(CH$_3$)$_2$C$\underline{H}_2$), 3.47 (dd, AB-system, 2H, $J^2_{H,H}$ 14.4 Hz, arom–C$\underline{H}_2$), 6.46 (s, 1H, N=C$\underline{H}$), 7.30 – 7.39 (m, 2H), 7.41 – 7.46 (m, 2H), 7.66 (d, 1H, $J^3_{H,H}$ 8.1 Hz), 7.74 (d, 1H, $J^3_{H,H}$ 8.1 Hz), 7.98 (d, 1H, $J^3_{H,H}$ 8.5 Hz, arom.). ^{13}C

NMR (100.61 MHz, $CDCl_3$): δ 26.7 ($\underline{C}H_3$), 28.4 ($\underline{C}H_3$), 29.2 ($\underline{C}H_3$), 37.8 (Napht-$\underline{C}H_2$), 37.8 ($\underline{C}(CH_3)_2$), 43.8 ($\underline{C}H_2C(CH_3)_2$), 79.0 ($\underline{C}(CH_3)CH_2$–Napht), 123.7, 125.3, 125.6, 126.1, 127.6, 128.5, 128.8, 132.8, 132.9, 133.7 (Napht.),142.0 ($\underline{C}H$=N). Calcd. for $C_{18}H_{21}NO$: *m/z* 267.1618 $[M]^+$. Found: *m/z* 267.1619 $[M]^+$. Absorption maximum – 283 nm, emission maximum – 337 nm.

(E)-3,3-Dimethyl-5-(2-(naphthalen-1-yl)vinyl)-3,4-dihydro-2*H*-pyrrole 1-oxide 14a. To a stirring solution of sodium methylate (0.85 g, 15.75 mmol) in anhydrous methanol (7.5 mL) compound **11** (1.0 g, 7.87 mmol) and 1-naphthaldehyde (1.84 g, 11.81 mmol) were added. Resulting mixture was refluxed for 3.5 hours and cooled. The reaction mixture was diluted with water (10 mL) and extracted with chloroform (3 × 20 mL). Combined organic extract was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by chromatography with a mixture of chloroform - methanol (50:1) as eluent. Pale yellow crystals, yield 1.69 g (81%); mp 113 – 115 ºC (from mixture hexane – ethyl acetate 5:1); IR (ν_{max}, cm^{-1}): 2955, 1539 (C=N), 1406, 1285, 1260, 1224, 1162, 981, 798, 781, 661. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.26 (s, 6H, $C(C\underline{H}_3)_2$), 2.81 (s, 2H, $C\underline{H}_2C(CH_3)_2$), 3.85 (s, 2H, N=C–$C\underline{H}_2$), 7.42 – 7.53 (m, 4H, Napht and Napht–$C\underline{H}$=CH), 7.64 (d, 1H, $J^3_{H,H}$ 16.3 Hz, Napht–HC=$C\underline{H}$), 7.78 – 7.86 (m, 3H Napht), 8.09 (d, 1H, $J^3_{H,H}$ 8.4 Hz, Napht). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 28.3 ($C(\underline{C}H_3)_2$), 32.9 ($\underline{C}(CH_3)_2$), 43.7 (N=C–$\underline{C}H_2$), 75.3 ($\underline{C}H_2C(CH_3)_2$), 118.4 (Napht–HC=$\underline{C}$H), 123.0, 124.5, 125.8, 126.1, 126.6, 128.9, 129.6, 131.4 (Napht), 132.8 (Napht–H$\underline{C}$=CH), 133.0, 133.8 (Napht), 143.9 ($\underline{C}$=N). Calcd. for $C_{18}H_{19}NO$: *m/z* 265.1461 $[M]^+$. Found: *m/z* 265.1463 $[M]^+$. Absorption maximum – 301 nm, emission maximum – 366 nm.

Crystallographic data for comp **14a.** $C_{18}H_{19}NO$, M = 265.34, orthorhombic, $P2_12_12_1$, a = 6.3974(2), b = 11.7839(5), c = 19.2374(8) Å, V = 1450.2(1) Å^3, Z = 4, D_{calcd} = 1.215 g·cm^{-3}, μ(Mo-$K\alpha$) = 0.075 mm^{-1}, F(000) = 568, (θ 2.03 – 27.89°, completeness 100%), T 200(2) K, colorless plate, (1.00 × 0.60 × 0.20) mm^3, transmission 0.9026 □ 0.9103, 30333 measured reflections in index range -8<=h<=7, -15<=k<=15, -25<=l<=25, 3473 independent (R_{int} = 0.0452), 183 parameters, 3255 observed [I> 2σ(I)], R_1 = 0.0314, wR_2 = 0.1085 (all data), GOOF 1.153, largest diff. peak and hole 0.205 and -0.234 e.A^{-3}.

(E)-5-(2-(4-Methoxynaphthalen-1-yl)vinyl)-3,3-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide 14b was synthesized according to the procedure described for **14a** from 4-methoxy-1-naphthaldehyde (2.2 g, 11.81 mmol) and **11** (1.0 g, 7.87 mmol). Yellow crystals, yield 2.00 g (86%); mp 154 ºC (from mixture hexane – ethyl acetate 4:1); IR (ν_{max}, cm^{-1}): 2955, 1578 (C=N), 1545, 1463, 1402, 1373, 1281, 1229, 1096, 963, 766. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.24 (s, 6H, $C(C\underline{H}_3)_2$), 2.77 (s, 2H, $C\underline{H}_2C$=N), 3.83 (s, 2H,$C\underline{H}_2N$=C), 3.97 (s, 3H, $C\underline{H}_3O$), 6.79 (d, 1H, $J^3_{H,H}$ 8.2 Hz, arom.), 7.39 (d, 1H, $J^3_{H,H}$ 16.2 Hz, arom–CH=$C\underline{H}$), 7.43 – 7.488 (m, 1H, arom.), 7.50 – 7.56 (m, 2H, arom. and arom-$C\underline{H}$=CH), 7.81 (d, 1H, $J^3_{H,H}$ 8.2 Hz, arom.), 8.01 – 8.05 (m, 1H), 8.25 – 8.28 (m, 1H, arom). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 28.3 ($C(\underline{C}H_3)_2$), 32.9 ($\underline{C}(CH_3)_2$), 43.6 ($\underline{C}H_2C$=N), 55.7 ($\underline{C}H_3O$), 75.1 ($\underline{C}H_2N$=C), 104.1, 116.1, 122.6 (arom), 122.8 ($\underline{C}$H=CH–arom), 125.2 (arom), 125.4 (CH=$\underline{C}$H–arom), 125.6, 127.1, 132.0, 132.8 (arom), 144.3

(C=N), 156.6 (arom). Calcd. for $C_{19}H_{21}NO_2$ (295.16): C 77.26, H 7.17, N 4.74. Found: C 77.32, H 6.97, N 4.68. Absorption maximum – 324 nm, emission maximum – 413 nm.

(E)-5-(2-(Anthracen-9-yl)vinyl)-3,3-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide 14c was synthesized according to the procedure described for **14a** from anthracene-9-carbaldehyde (2.43 g, 11.81 mmol) and **11** (1.0 g, 7.87 mmol). Orange crystals, yield 1.81 g (73%); mp 191 ºC (from ethyl acetate); IR (ν_{max}, cm^{-1}): 3043, 2959, 1540 (C=N), 1444, 1284, 1272, 1230, 1213, 1174, 1160, 891, 850, 739. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.33 (s, 6H, C(CH_3)$_2$), 2.92 (s, 2H, CH_2C=N), 3.93 (s, 2H, CH_2N=C), 7.32 (d, 1H, $J^3_{H,H}$ 16.7 Hz, arom–CH=CH), 7.41–7.48 (m, 4H, arom.), 7.76 (d, 1H, $J^3_{H,H}$ 16.7 Hz, arom–CH=CH), 7.93–7.97 (m, 2H.), 8.20–8.24 (m, 2H), 8.36 (s, 1H, arom.). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 28.5 (C(CH_3)$_2$), 33.0 (C(CH_3)$_2$), 43.8 (CH_2C=N), 75.4 (CH_2N=C), 124.7 (arom–CH=CH), 125.5 (4C), 126.2 (2C), 128.0, 128.9 (2C), 129.4 (2C), 130.6, 131.4 (2C, arom.), 133.6 (arom–CH=CH), 144.2 (C=N). Calcd. for $C_{22}H_{21}NO$ (295.16): C 83.78, H 6.71, N 4.44. Found: C 83.42, H 6.66, N 4.58. Absorption maximum – 371 nm, emission maximum – 447 nm.

(E)-3,3-Dimethyl-5-(2-(1-methyl-2-phenyl-1*H*-indol-3-yl)vinyl)-3,4-dihydro-2*H*-pyrrole 1-oxide 14d was synthesized according to the procedure described for **14a** from 1-methyl-2-phenyl-1H-indole-3-carbaldehyde (2.78 g, 11.81 mmol) and **11** (1.0 g, 7.87 mmol). Yellow crystals, yield 0.70 g (26%); mp 212 – 215 ºC (from mixture hexane – ethyl acetate 5:1 with decomposition); IR (ν_{max}, cm^{-1}): 2925, 1606 (C=N), 1549, 1470, 1440, 1384, 1281, 1227, 1157, 1069, 957, 822, 739, 698. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.16 (s, 6H, C(CH_3)$_2$), 2.49 (s, 2H, CH_2C=N), 3.56 (s, 3H, NCH_3), 3.76 (s, 2H, CH_2N=C), 6.78 (d, 1H, $J^3_{H,H}$ 16.7 Hz, CH=CH–C=N), 7.24 – 7.29 (m, 2H), 7.30 – 7.32 (m, 1H, arom), 7.34 – 7.38 (m, 3H, arom and CH=CH–C=N), 7.42 – 7.52 (m, 3H), 8.15 – 8.19 (m, 1H, arom). ^{13}C NMR (75.47MHz, $CDCl_3$): δ 28.3 (C(CH_3)$_2$), 38.5 (C(CH_3)$_2$), 43.1 (CH_2C=N), 74.7 (CH_2N=C), 109.9, 111.9, 112.4, 121.4, 121.6, 123.1, 125.2, 128.6 (2C, arom), 129.0 (CH=CH-C=N), 130.5, 130.9 (2C, arom.), 131.0 (CH=CH–C=N), 138.0, 143.4 (arom.), 145.3 (C=N). Calcd. for $C_{23}H_{24}N_2O$: *m/z* 344.1883 $[M]^+$. Found: *m/z* 344.1880 $[M]^+$. Absorption maximum – 256 nm, emission maximum – 383 nm.

Crystallographic data for comp **14d.** $C_{23}H_{24}N_2O$, M = 344.44, orthorhombic, *P*bca, a = 15.4643(6), b = 14.2594(6), c = 17.2945(8) Å, V = 3813.6(3) Å^3, Z = 8, D_{calcd} = 1.200 g·cm^{-3}, μ(Mo-$K\alpha$) = 0.074 mm^{-1}, F(000) = 1472, (θ 2.27 – 27.53°, completeness 99.5%), T 296(2) K, yellow pyramid, (0.80 × 0.60 × 0.60) mm^3, transmission 0.8912 – 0.9103, 71876 measured reflections in index range -20<=h<=20, -18<=k<=18, -22<=l<=22, 4379 independent (R_{int} = 0.0412), 238 parameters, 3480 observed [I> 2σ(I)], R_1 = 0.0494, wR_2 = 0.1415 (all data), GOOF 1.052, largest diff. peak and hole 0.205 and -0.234 e.A^{-3}.

The naphthyl fragment in the molecule of compounds **5a** and **14a** is planar within ±0.013(1) and ±0.027(1) with bond lengths equal within the experimental errors and being close to average statistical values[21]. The indole fragment in the molecule of compound **14d** is planar within ±0.008(1) Å. The parameters of intramolecular hydrogen bond C13–H…N2 of **5a** are H…N 2.59, C…N 3.075(4) Å, C–H…N 112° (Wan der Waals radius sums are[22] H…O 2.68, C…O 3.35, H…N 2.74 and C…N 3.41 Å). Supramolecular structure of **5a** crystal can be described as

π(C9÷C14)…π(C9÷C14)-stacking dimmers (with inter-plane and inter-centroid distances being equal to 3.3698(5) and 3.5389(7) Å respectively) combined into layers being parallel to (*b*,*c*) plane by C12–H…π(C5C6C7C8C9C14) interactoin (with distances from H to cycle plain and center equal to 2.98 and 3.10 Å) and C3–H…O3 interactions (with H…O 2.30, C…O 3.141(2) Å and C–H…O 142°)

Torsion angle C8=C9–C10–C11 of **14d** equaling to 33.7(2)° indicates decreasing of C8=C9 bond conjugation with naphthyl fragment which leads to lengthening of C9–C10 bond to 1.474(2) Å in comparison with 1.445(2) for the same bond of **14d** (torsion angle C8=C9–C10–C11 is 179.4(1)°). The dihydropyrrole cycle in molecules of the compounds **14a** and **14d** adopts the envelope conformation with a puckering angle equal 25.8(1) and 25.5(2)°. The conjugation of double bonds N1=C5 of dihydropyrrole cicle and double bonds C8=C9 in both compounds are indicated by values of C5–C8 and C5=N1 bond lengths (1.437(2) and 1.431(2) Å for the first bond, 1.316(2) and 1.312(2) Å for the second one), the torsion angle N1=C5–C8=C9 is –165.0(1)° for **14a** and 178.0(1)° for **14d.** Moreover, the averaged length of unconjugated C5=N1 bond on the set of 21 compound structures with 3,4-dihydropyrroline 1-oxide fragment from CSDB[23] equals to1.289(5) Å. Angle between indole and phenyl fragment planes for **14d** is 61.7(1)°. The nitroxyl group of both compounds forms a big number of intermolecular hydrogen bonds (table 1) characterizing together with C–H π interactions cryctal structure of compounds **14a** and **14d**. C6–H π(C10C11C12C13C14C19) interaction of compound **14a** is described by distances from hydrogen atom to plain and center of cycle equaling to 2.89 and 2.98 Å, C2–H π(C10÷C14), C4–H π(C13÷C18), C6–H… π(C20÷C25), interactions of compounds **14d** have distances from atom H to the plains 2.87, 2.93, 2.82 Å and to the centers of cycles – 2.95, 2.95, 2.87Å**.**

(*E*)-2,4,4-Trimethyl-2-(2-(naphthalen-1-yl)vinyl)pyrrolidin-1-ol 15a. To a stirred solution of methyllithium, prepared from lithium (0.143 g, 20. 4 mmol) and methyl iodide (0.63 g, 10.2 mmol) in anhydrous ether (9 mL), a solution of **14a** (0.9 g, 3.4 mmol) in anhydrous THF (3 mL) was added. The resulting mixture was stirred for 2 hours at room temperature. The excess of methyllithium was decomposed by addition of water (10 mL). Ether solution was separated and water layer was extracted with chloroform (3 × 20 mL). Combined organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The product was precipitated by addition of ether to residue, filtered off and dried. White powder, yield 0.85 g (89%); IR (ν_{max}, cm^{-1}): 3227 (OH), 2964, 2925, 2854, 1445, 1169, 1082, 980, 792, 779. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.13 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.45 (s, 3H, C<u>H</u>$_3$), 1.84 (dd, AB-system, 2H, $J^2_{H,H}$ 13.0 Hz, C<u>H</u>$_2$C(CH$_3$)$_2$), 3.00 (s, 2H, C<u>H</u>$_2$NOH), 6.54 (d, 2H, $J^3_{H,H}$ 15.4 Hz, Napht-CH=C<u>H</u>), 7.22 (d, 2H, $J^3_{H,H}$ 15.4 Hz, Napht–C<u>H</u>=CH), 7.37 – 7.51 (m, 4H, Napht. and N–O<u>H</u>), 7.60 (d, 1H, $J^3_{H,H}$ 6.1 Hz), 7.73 (d, 1H, $J^3_{H,H}$ 7.6 Hz), 7.82 (d, 1H, $J^3_{H,H}$ 6.9 Hz), 8.09 (d, 1H, $J^3_{H,H}$ 7.3 Hz, Napht.). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 30.9 (C(<u>C</u>H$_3$)$_2$), 31.1 (<u>C</u>H$_3$), 33.2 (<u>C</u>(CH$_3$)$_2$), 50.9 (<u>C</u>H$_2$C(CH$_3$)$_2$), 68.5 (<u>C</u>H$_2$NOH), 69.1 (<u>C</u>CH$_3$), 123.9, 124.0, 125.8 (2C), 126.0 (Napht.), 126.2 (Napht -CH=<u>C</u>H), 127.7, 128.6, 131.4, 133.7, 135.4 (Napht), 138.4 (Napht–<u>C</u>H=CH). Calcd. for $C_{19}H_{23}NO$: *m/z* 281.1774 $[M]^+$. Found: *m/z* 281.1773 $[M]^+$.

(*E*)-2,4,4-Trimethyl-2-(2-(naphthalen-1-yl)vinyl)-3,4-dihydro-2*H*-pyrrole 1-oxide 16a. Manganese dioxide (100 mg) was added to a stirred solution of **15a** (0.08 g, 0.28 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for 0.5 hours, then manganese dioxide was filtered off and washed with chloroform (10 mL). Filtrate was concentrated *in vacuo*, product was purified by preparative TLC on alumina with chloroform as eluent. Colorless crystals, yield 0.065 g (82%); mp 134 - 136 ºC (from mixture hexane – ethyl acetate 4:1); IR (ν_{max}, cm^{-1}): 3043, 2960, 1580 (C=N), 1242, 1163, 959, 802, 791. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.26 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.74 (s, 3H, C<u>H</u>$_3$), 2.28 (dd, AB-system, 2H, $J^2_{H,H}$ 13.2 Hz, C<u>H</u>$_2$), 6.45 (d, 1H, $J^3_{H,H}$ 16.0 Hz, Napht–CH=C<u>H</u>), 6.77 (s, 1H, C<u>H</u>=N), 7.33–7.51 (m, 4H, Napht and Napht–C<u>H</u>=CH), 7.74 (d, 1H $J^3_{H,H}$ 8.1 Hz), 7.78 – 7.83 (m, 1H), 8.02 – 8.07 (m, 1H, Napht.). ^{13}C NMR (75.47MHz, $CDCl_3$): δ 26.4 (C<u>H</u>$_3$), 28.0 (C(<u>C</u>H$_3$)$_2$), 28.5 (C(<u>C</u>H$_3$)$_2$), 38.8 (<u>C</u>(CH$_3$)$_2$), 48.8 (<u>C</u>H$_2$), 78.4 (CH=N–<u>C</u>), 123.8, 124.2, 125.6, 125.9), 126.2 (Napht.), 127.3 (Napht-CH=<u>C</u>H), 128.3, 128.6, 131.3, 133.6, 134.1 (Napht.), 134.9 (Napht–<u>C</u>H=CH), 141.3 (<u>C</u>H=N). Calcd. for $C_{19}H_{21}NO$: *m/z* 279.1618 $[M]^+$. Found: *m/z* 279.1614 $[M]^+$. Absorption maximum – 300 nm, emission maximum – 359 nm.

(*E*)-2-(2-(4-Methoxynaphthalen-1-yl)vinyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide 16b. To a stirred solution of methyllithium, prepared from lithium (0.200 g, 28. 47 mmol) and methyl iodide (0.89 g, 14.24 mmol) in anhydrous ether (10 mL)) a solution of compound **14b** (1.4 g, 4.75 mmol) in anhydrous THF (15 mL) was added dropwise. A resulted mixture was stirred for 2 hours at room temperature, then an excess of methyllithium was decomposed by addition of water (10 mL). Ether solution was separated and water layer was extracted with chloroform (4 × 20 mL). Combined organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue was dissolved in chloroform (30 mL) and manganese dioxide (0.2 g) was added. The resulting mixture was stirred for 1 hour at room temperature, then manganese dioxide was filtered off and washed with chloroform (40 mL). Filtrate was concentrated *in vacuo*, and the product was purified by chromatography with a mixture of chloroform – methanol (50:1) as eluent. Pale yellow crystals, yield 1.17 g (80%); mp 116 ºC (from mixture hexane – ethyl acetate 5:1); IR (ν_{max}, cm^{-1}): 2964, 1575 (C=N), 1462, 1388, 1271, 1244, 1164, 1095, 821, 766. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.25 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.73 (s, 3H, C<u>H</u>$_3$), 2.27 (dd, AB-system, 2H, $J^2_{H,H}$ 13.3 Hz, C(CH$_3$)$_2$C<u>H</u>$_2$), 3.96 (s, 3H, C<u>H</u>$_3$O), 6.37 (d, 1H, $J^3_{H,H}$ 15.9 Hz, C<u>H</u>=CH–arom), 6.74 (d, 1H, $J^3_{H,H}$ 8.2 Hz, arom), 6.76 (s, 1H, C<u>H</u>=N), 7.27 (d, 1H, $J^3_{H,H}$ 15.9 Hz, CH=C<u>H</u>–arom), 7.41 – 7.53 (m, 3H), 7.96 – 8.01 (m, 1H), 8.23 – 8.27 (m, 1H, arom.). ^{13}C NMR (75.47MHz, $CDCl_3$): δ 26.5 (C(C<u>H</u>$_3$)$_2$), 28.1 (C(<u>C</u>H$_3$)$_2$), 28.5 (<u>C</u>H$_3$CCH=CH), 38.8 (<u>C</u>(CH$_3$)$_2$), 48.8 (<u>C</u>H$_2$), 55.6 (<u>C</u>H$_3$O), 78.5 (CH$_3$<u>C</u>CH=CH), 103.8, 122.5, 123.5, 124.4, 125.2, 125.5, 126.5, 126.7 (arom.), 127.2 (<u>C</u>H=CH-arom), 132.1 (arom), 132.9 (CH=<u>C</u>H-arom), 141.3 (<u>C</u>H=N), 155.6 (arom). Calcd. for $C_{20}H_{23}NO_2$ (309.40): C 77.64, H 7.49, N 4.53. Found: C 77.20, H 7.51, N 4.58. Absorption maximum – 318 nm, emission maximum – 387 nm.

(*E*)-2-(2-(Anthracen-9-yl)vinyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide 16c was synthesized according to the procedure, described for **16b** from **14c** (1.40g, 4.75 mmol). Yellow

crystals, yield 0.78 g (50%); mp 135 – 137 ºC (with decomposition); IR (ν_{max}, cm^{-1}): 3022, 2963, 2866, 1574 (C=N), 1455, 1441, 1350, 1267, 1244, 1158, 992, 894, 738, 608. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.32 (s, 6H, C(C$\underline{H}_3$)$_2$), 1.89 (s, 3H, C$\underline{H}_3$), 2.35 (dd, AB-system, 2H, $J^2_{H,H}$ 13.3 Hz, C(CH$_3$)$_2$C$\underline{H}_2$), 6.22 (d, 1H, $J^3_{H,H}$ 16.4 Hz, C$\underline{H}$=CH–arom), 6.99 (C$\underline{H}$=N), 7.38–7.48 (m, 5H, arom and C$\underline{H}$=CH–arom), 7.93 – 7.97 (m, 2H), 8.20 – 8.24 (m, 2H), 8.34 (s, 1H, arom.). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 25.6 (C(C$\underline{H}_3$)$_2$), 28.0 (C(C$\underline{H}_3$)$_2$), 28.3 ($\underline{C}$H$_3$CCH=CH), 39.0 ($\underline{C}$(CH$_3$)$_2$), 48.7 ($\underline{C}$H$_2$), 78.2 (CH$_3\underline{C}$CH=CH), 125.0 (2C), 125.5 (2C), 126.5 (arom.), 126.7 ($\underline{C}$H=CH–arom), 128.4, 129.3 (2C), 131.1, 131.2 (2C), 139.5 (CH=$\underline{C}$H–arom), 143.2 ($\underline{C}$H=N). Calcd. for $C_{23}H_{23}NO$: *m/z* 329.1772 $[M]^+$. Found: *m/z* 329.1774 $[M]^+$. Absorption maximum – 372 nm, emission maximum – 435 nm.

Hydrogenation of compounds **14a-b** (7.55 mmol) was carried out in methanol (20mL) in the presence of Pd/C (5% Pd) as catalyst at atmospheric pressure for 4 hours. The catalyst was filtered off, washed with methanol (40 mL) and the filtrate was concentrated *in vacuo*, products were isolated by chromatography with a mixture of ethyl acetate – methanol (1:1) as eluent. Compounds **17a-b** and **18a-b** were eluted sequentially.

3,3-Dimethyl-5-(2-(naphthalen-1-yl)ethyl)-3,4-dihydro-2*H*-pyrrole 17a. Yellow oil, yield 0.19 g (10%); IR (ν_{max}, cm^{-1}): 2953, 2928, 2864, 1639 (C=N), 1462, 1428, 798, 780. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.08 (s, 6H, C(C$\underline{H}_3$)$_2$), 2.31 (t, 2H, $J^4_{H,H}$ 1.7 Hz, (CH$_3$)$_2$CC$\underline{H}_2$C=N), 2.67–2.74 (m, 2H, C$\underline{H}_2$–CH$_2$–Napht), 3.35–3.42 (m, 2H, CH$_2$–C$\underline{H}_2$–Napht), 3.59 (m, 2H, (CH$_3$)$_2$C–C$\underline{H}_2$–N=C), 7.33–7.41 (m, 2H), 7.43–7.54 (m, 2H), 7.69–7.73 (m, 1H), 7.82–7.86 (m, 1H), 8.04–8.08 (m, 1H, Napht). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 28.1 (C($\underline{C}$H$_3$)$_2$), 29.5 ($\underline{C}$H$_2$C=N), 35.1 (CH$_2\underline{C}$H$_2$–Napht), 38.4 ($\underline{C}$(CH$_3$)$_2$), 52.7 ($\underline{C}$H$_2$CH$_2$–Napht 74.3 ($\underline{C}$H$_2$–N=C), 123.7, 125.5, 125.6, 125.8, 126.0, 126.9, 128.8, 131.8, 133.9, 137.7 (Napht), 177.3 ($\underline{C}$=N). Calcd. for $C_{18}H_{21}N$: *m/z* 251.1669 $[M]^+$. Found: *m/z* 250.1588 $[M-1]^+$.

3,3-Dimethyl-5-(2-(naphthalen-1-yl)ethyl)-3,4-dihydro-2*H*-pyrrole 1-oxide 18a. Pale yellow oil, yield 1.61 g (80%); IR (ν_{max}, cm^{-1}): 2958, 1625, 1597 (C=N), 1431,1319, 1249, 1167, 800, 754. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.94 (s, 6H, C(C$\underline{H}_3$)$_2$), 2.11 (s, 2H, C$\underline{H}_2$C=N), 2.87 (t, 2H, $J^3_{H,H}$ 7.5 Hz, C$\underline{H}_2$CH$_2$–Napht), 3.27 (t, 2H, $J^3_{H,H}$ 7.5 Hz, CH$_2$C$\underline{H}_2$–Napht), 3.72 (s, 2H, C=N(O)–C$\underline{H}_2$), 7.28–7.33(m, 2H), 7.39–7.44 (m, 1H), 7.45–7.50 (m, 1H), 7.63–7.67 (m, 1H), 7.78 (d, 1H, $J^3_{H,H}$ 8.1 Hz), 8.01 (d, 1H, $J^3_{H,H}$ 8.4 Hz, Napht). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 27.3 (CH$_2$–$\underline{C}$H$_2$–Napht), 27.6 ($\underline{C}$H$_2$C=N), 28.1 (C($\underline{C}$H$_3$)$_2$), 32.3 ($\underline{C}$(CH$_3$)$_2$), 46.9 ($\underline{C}$H$_2$CH$_2$–Napht), 74.2 (C=N–$\underline{C}$H$_2$), 123.5, 125.6, 125.7, 125.9, 126.3, 127.2, 128.8, 131.8, 133.8, 136.3 (Napht), 151.3 ($\underline{C}$=N). Calcd. for $C_{18}H_{21}NO$: *m/z* 267.1618 $[M]^+$. Found: *m/z* 267.1615 $[M]^+$. Absorption maximum – 283 nm, emission maximum – 337 nm.

5-(2-(4-Methoxynaphthalen-1-yl)ethyl)-3,3-dimethyl-3,4-dihydro-2*H*-pyrrole 17b. Yellow oil, yield 0.254 g (12%); IR (ν_{max}, cm^{-1}): 2955, 2932, 2866, 1640 (C=N), 1588, 1464, 1391, 1274, 1246, 1094, 766. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.05 (s, 6H, C(C$\underline{H}_3$)$_2$), 2.30 (t, 2H, $J^4_{H,H}$ 1.5 Hz, (CH$_3$)$_2$CC$\underline{H}_2$C=N), 2.69–2.74 (m, 2H, C$\underline{H}_2$–CH$_2$–arom), 3.24 – 3.29 (m, 2H, CH$_2$C$\underline{H}_2$–arom), 3.58 (q, 2H, $J^4_{H,H}$ 1.5 Hz, (CH$_3$)$_2$C–C$\underline{H}_2$–N=C), 3.93 (s, 3H, C$\underline{H}_3$O), 6.69 (d,

1H, $J^3_{H,H}$ 7.9 Hz), 7.22 (d, 1H, $J^3_{H,H}$ 7.9 Hz), 7.43 – 7.47 (m, 1H), 7.49 – 7.54 (m, 1H), 7.96 (d, 1H, $J^3_{H,H}$ 8.4 Hz), 8.28 – 8.31 (m, 1H, arom.). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 27.9 ($C(\underline{C}H_3)_2$), 29.1 ($\underline{C}H_2C$=N), 34.8 ($CH_2\underline{C}H_2$–arom), 38.1 ($\underline{C}(CH_3)_2$), 52.6 ($\underline{C}H_2CH_2$–arom), 55.4 ($\underline{C}H_3O$), 72.9 ($\underline{C}H_2$–N=C), 103.4, 122.7, 123.4, 124.9, 125.6, 126.0, 126.5, 129.0, 132.5, 154.4 (arom), 179.4 ($\underline{C}$=N). Calcd. for $C_{19}H_{23}NO$: *m/z* 281.1774 $[M]^+$. Found: *m/z* 281.1772 $[M]^+$.

5-(2-(4-Methoxynaphthalen-1-yl)ethyl)-3,3-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide 18b. Pale yellow oil, yield 1.86 g (83%); IR (ν_{max}, cm^{-1}): 2959, 1708 (C=N), 1588, 1464, 1393, 1373, 1273, 1248, 1226, 1161, 1093, 767. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.93 (s, 6H, $C(C\underline{H}_3)_2$), 2.08 (s 2H, $(CH_3)_2CC\underline{H}_2C$=N), 2.79 (t, 2H, $J^3_{H,H}$ 7.6 Hz, $C\underline{H}_2$–CH_2–arom), 3.19 (t, 2H, $J^3_{H,H}$ 7.6 Hz, CH_2–$C\underline{H}_2$–arom), 3.66 (s, 2H, $(CH_3)_2C$–$C\underline{H}_2$–N=C), 3.86 (s, 3H, $C\underline{H}_3O$), 6.63 (d, 1H, $J^3_{H,H}$ 7.8 Hz), 7.15 (d, 1H, $J^3_{H,H}$ 7.8 Hz), 7.36 – 7.41 (m, 1H), 7.44 – 7.49 (m, 1H), 7.94 (d, 1H, $J^3_{H,H}$ 8.5 Hz,), 8.20 – 8.24 (m, 1H, arom.). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 26.8 (CH_2–$C\underline{H}_2$–arom), 27.7 ($\underline{C}H_2C$=N), 27.9 ($C(\underline{C}H_3)_2$), 32.2 ($\underline{C}(CH_3)_2$), 46.9 ($C\underline{H}_2CH_2$–arom), 55.3 ($\underline{C}H_3O$), 74.3 (C=N–$\underline{C}H_2$), 103.2, 122.5, 123.2, 124.8, 125.6, 125.7, 126.5, 128.0, 132.4 (arom), 149.8 ($\underline{C}$=N), 154.4 (arom). Calcd. for $C_{19}H_{23}NO_2$: *m/z* 297.1773 $[M]^+$. Found: *m/z* 297.1772 $[M]^+$. Absorption maximum – 302 nm, emission maximum – 357 nm.

2,4,4-Trimethyl-2-(2-(naphthalen-1-yl)ethyl)-3,4-dihydro-2*H*-pyrrole 1-oxide 19a. To a stirred solution of methylmagnesium iodide, prepared from magnesium (0.510 g, 21.2 mmol) and methyl iodide (1.31 mL, 21.0 mmol) in anhydrous ether (15 mL), a solution of **18a** (1.4 g, 5.24 mmol) in anhydrous ether (5 mL) was added. Reaction mixture was stirred for 2 hours at room temperature, the excess of Grignard reagent was decomposed by addition of saturated ammonium chloride solution (15 mL). Ether solution was separated and water layer was extracted with ether (4 × 20 mL). Combined organic extract were dried with $MgSO_4$, the solvent was removed under reduced pressure. The residue was dissolved in chloroform (30 mL), manganese dioxide (0.2 g) was added and the resulting mixture was stirred for 1 hour at room temperature. Then manganese dioxide was filtered off and washed with chloroform (40 mL). The filtrate was concentrated *in vacuo*, compound **19a** was purified by chromatography with a mixture of chloroform – methanol (50:1) as eluent. Colorless crystals, yield 0.9 g (61%); mp 111 – 112 ºC (from mixture hexane - ethylacetate 5:1); IR (ν_{max}, cm^{-1}): 2963, 1577 (C=N), 1459, 1264, 1237, 1170, 800, 781, 729. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.26 (s, 3H, $C(C\underline{H}_3)_2$), 1.28 (s, 3H, $C(C\underline{H}_3)_2$), 1.54 (s, 3H, $C\underline{H}_3$), 1.92–2.00 (m, 2H, $C\underline{H}_2CH_2$–Napht), 2.24–2.30 (m, 2H, $C\underline{H}_2CH_2$–Napht), 3.01–3.06 (m, 2H, $(CH_3)_2CC\underline{H}_2$), 6.73 (s, 1H, $C\underline{H}$=N), 7.30 – 7.37 (m, 2H), 7.42 – 7.46 (m, 1H), 7.49 – 7.53 (m, 1H,), 7.68 (d, 1H, $J^3_{H,H}$ 7.8 Hz), 7.79 – 7.82 (m, 1H), 8.10 (d, 1H, $J^3_{H,H}$ 8.5 Hz, Napht). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 27.1 (CH_2–$\underline{C}H_2$–arom), 27.7 ($\underline{C}H_2C(CH_3)_2$), 28.6 ($C(\underline{C}H_3)_2$), 29.1 ($C(\underline{C}H_3)_2$), 38.1 ($\underline{C}(CH_3)_2$), 39.8 ($\underline{C}H_3$), 45.8 ($\underline{C}H_2$–$CH_2$-Napht), 77.3 (C=N–$\underline{C}(CH_3)CH_2$), 123.8, 125.6 (2C), 126.1, 126.2, 127.0, 128.8, 131.9, 133.9, 137.4 (Napht), 141.2 ($\underline{C}$H=N). Calcd. for $C_{18}H_{21}NO$: *m/z* 281.1774 $[M]^+$. Found: *m/z* 281.1771 $[M]^+$. Absorption maximum – 284 nm, emission maximum – 337 nm.

2-(2-(4-Methoxynaphthalen-1-yl)ethyl)-2,4,4-trimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide 19b was synthesized according to the procedure described for **19a** from **18b** (1.56 g, 5.24 mmol).

Colorless crystals, yield 1.21 g (74%); mp 144 – 146 ºC (from mixture hexane – ethyl acetate 4:1); IR (ν_{max}, cm^{-1}): 2965, 2927, 1589 (C=N), 1464, 1393, 1268, 1250, 1161, 1090, 822, 775. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.26 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.28 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.53 (s, 3H, C$\underline{H}_3$), 1.93 – 2.02 (m, 2H, C$\underline{H}_2$CH$_2$–arom), 2.21 – 2.29 (m, 2H, C$\underline{H}_2$CH$_2$–arom), 2.92 – 2.99 (m, 2H, (CH$_3$)$_2$CC$\underline{H}_2$), 3.94 (s, 3H, C$\underline{H}_3$O), 6.69 (d, 1H, $J^3_{H,H}$ 7.8 Hz, arom.), 6.79 (s, 1H, C$\underline{H}$=N), 7.21 (d, 1H, $J^3_{H,H}$ 7.8 Hz), 7.41–7.47 (m, 1H), 7.50–7.56 (m, 1H), 8.00 (d, 1H, $J^3_{H,H}$ 8.3 Hz), 8.25 – 8.29 (m, 1H, arom). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 27.0 (CH$_2$–$\underline{C}$H$_2$–arom), 27.2 ($\underline{C}$H$_2$C(CH$_3$)$_2$), 28.5 (C($\underline{C}$H$_3$)$_2$), 29.0 (C($\underline{C}$H$_3$)$_2$), 38.3 ($\underline{C}$(CH$_3$)$_2$), 39.9 ($\underline{C}$H$_3$), 45.8 ($\underline{C}$H$_2$–CH$_2$–arom), 55.5 ($\underline{C}$H$_3$O), 77.5 (C=N–$\underline{C}$(CH$_3$)CH$_2$), 103.5, 122.6, 123.6, 125.0, 125.8, 126.0, 126.7, 129.2, 132.6 (arom), 142.1 ($\underline{C}$H=N), 154.4 (arom.). Calcd. for $C_{20}H_{25}NO_2$: *m/z* 311.1876 $[M]^+$. Found: *m/z* 311.1889 $[M]^+$. Absorption maximum – 301 nm, emission maximum – 358 nm.

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