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Thermolysis of 1-(Methylideneamino)-1*H*-pyrrole-2,3-diones. Synthesis of Pyrazolooxazines by [4+2]-Cycloaddition of Azomethine Imines to Alkenes

V. E. Zhulanov, M. V. Dmitriev, and A. N. Maslivets*

Perm State National Research University, ul. Bukireva 15, Perm, 614990 Russia
**e-mail: koh2@psu.ru*

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Abstract—Thermolysis of methyl 3-acyl-1-[(diphenylmethylidene)amino]-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates generates 4-acyl-1-(diphenylmethylidene)-3-(methoxycarbonyl)-1*H*-pyrazol-1-ium-5-olates which react with alkenes to give methyl 3-acyl-7,7-diphenyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylates. The product structure was confirmed by X-ray analysis.

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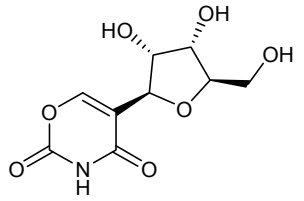
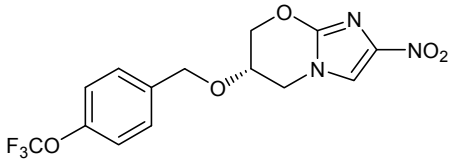
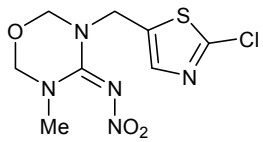
Oxazine and oxadiazine rings are structural fragments of many biologically active compounds. Examples are the natural antibiotic oxazinomycin active against Ehrlich ascite carcinoma [1], experimental antitubercular drug pretomanid (PA-824) [2], selective insecticide of the neonicotinoid series thiamethoxam which is low toxic for mammalians [3], non-benzodiazepine anxiolytic etifoxine which is superior to benzodiazepine analogs in efficiency [4], and anti-HIV drug efavirenz [5].

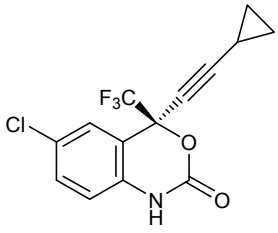
We previously proposed a convenient procedure for the synthesis of pyrazolo[5,1-*b*][1,3]oxazines via [4+2]-cycloaddition of butyl vinyl ether with 1,4-dipoles generated *in situ* from 1-[(diphenylmethylidene)-amino]-1*H*-pyrrole-2,3-diones [6]. With the goal of estimating the scope of this reaction, in the present work we used ethyl vinyl ether, styrene, and 3,4-dihydro-2*H*-pyran as dipolarophiles.

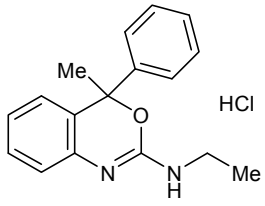
Methyl 4-aryl(alkyl)[2-(diphenylmethylidene)hydrazinyl]-4-oxobut-2-enoates **1a**–**1d** reacted with oxalyl chloride in anhydrous chloroform at 60–65°C for 90–100 min to give methyl 3-acyl-1-[(diphenylmethylidene)amino]-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates **2a**–**2d** which were reacted further without isolation. The reactions of pyrrolediones **2a**–**2d** with 3,4-dihydro-2*H*-pyran (**3**), ethyl vinyl ether (**4**), and styrene (**5**) at a ratio of 1:5 on heating in anhydrous *o*-xylene at 90–130°C for 10–90 min (until


Oxazinomycin

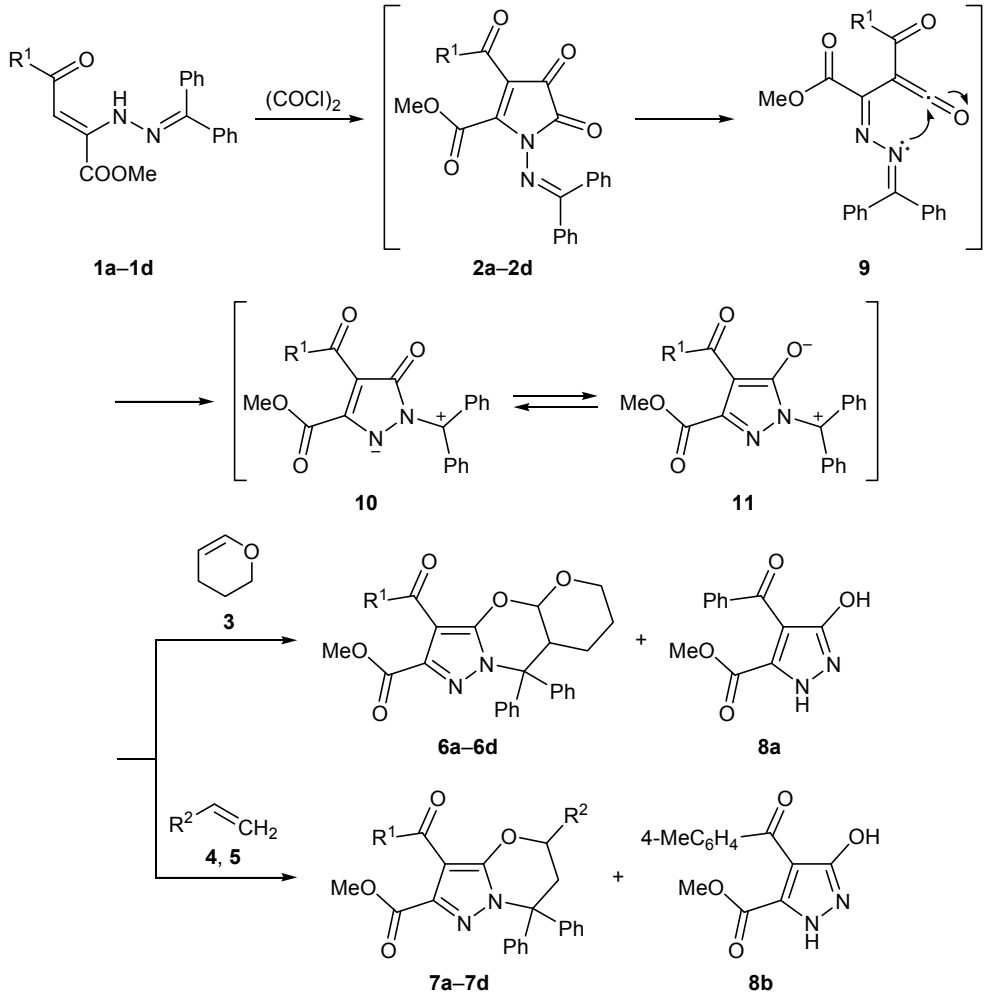

Pretomanid (PA-824)


Thiamethoxam


Efavirenz


Etifoxine

Scheme 1.



1, **2**, **6**, R^1 = Ph (**a**), C_6H_4Me-4 (**b**), C_6H_4Cl-4 (**c**), *t*-Bu (**d**); **4**, R^2 = OEt; **5**, R^2 = Ph; **7**, R^1 = C_6H_4Me-4, R^2 = OEt (**a**); R^1 = *t*-Bu, R^2 = OEt (**b**); R^1 = C_6H_4Me-4, R^2 = Ph (**c**); R^1 = C_6H_4Cl-4, R^2 = Ph (**d**).

disappearance of the dark violet color of azomethine imines generated by thermolysis) afforded methyl 3-acyl-9,9-diphenyl-4a,7,8,8a-tetrahydro-6*H*,9*H*-pyrano[3,2-*e*]pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylates **6a**–**6d** and methyl 3-acyl-7,7-diphenyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylates **7a**–**7d**. In some cases, methyl 4-acyl-3-hydroxy-1*H*-pyrazole-5-carboxylates **8a** and **8b** were isolated as minor products. The structure of compounds **6** and **8** was confirmed by X-ray analysis of **6c** and **8b**.

Compounds **6a**–**6d** and **7a**–**7d** are colorless crystalline solids readily soluble in DMSO, chloroform, and acetone and insoluble in alkanes and water.

The ^{1}H NMR spectra of **6a**–**6d** contained signals of aromatic protons and protons in the substituents thereon, a nine-proton singlet from the *tert*-butyl group (in **6d**), a three-proton singlet of the ester methoxy group (δ 3.70–3.93 ppm), signals of protons in the bridgehead positions (8a-H and 4a-H, δ 3.04–3.10 and 5.77–5.83 ppm, respectively), and methylene proton signals (6-H, 7-H, 8-H; δ 1.23–4.03 ppm). Compounds **7a**–**7d** showed in the ^{1}H NMR spectra signals from aromatic substituents, *tert*-butyl group in **7a** (9H), substituent on C^5, methoxycarbonyl group (3H, δ 3.57–3.80 ppm), 5-H (δ 5.20– 5.27 ppm), and C^6H_2 group (2H, δ 3.01–3.80 ppm).

According to the X-ray diffraction data, compound **6c** (Fig. 1) crystallized in centrosymmetric space group belonging to the triclinic crystal system. The pyrazole ring is planar within 0.005 Å, while the oxazine ring adopts a *half-chair* conformation with the C^5 and C^9 atoms deviating from the $O^1C^3N^2C^4$ plane by 0.638 and –0.116 Å, respectively. The pyran ring has a *chair* conformation. The six-membered heterocycles are *cis*-

fused, so that the H^5 and H^9 protons appear in a *gauche* orientation with respect to each other. The pyrazole ring plane forms with the $C^{10}C^{11}C^{12}C^{13}C^{14}C^{15}$ and $C^{16}C^{17}C^{18}C^{19}C^{20}C^{21}$ planes dihedral angles of 63.0 and 76.0°, respectively.

Compounds **8a** and **8b** are colorless crystalline solids readily soluble in DMSO, chloroform, and acetone and insoluble in alkanes and water. Their ^{1}H NMR spectra displayed signals from aromatic protons and substituents in the aromatic rings, singlets of the ester group (δ 3.50–3.60 ppm), and broadened singlets of the NH and OH protons (δ 10.35–10.63 and 13.16–13.20 ppm, respectively).

According to the X-ray diffraction data, compound **8b** (Fig. 2) crystallized in a centrosymmetric space group belonging to the moniclinic crystal system. The pyrazole ring is planar within 0.002 Å. Molecules **8b** in crystal are linked to each other through intermolecular hydrogen bonds N^2–$H^{2A}\cdots O^1$ [$O^1\cdots H^{2A}$ 1.95(2), N^2–H^{2A} 0.89(2), $N^2\cdots O^1$ 2.779(2) Å] and O^4–$H^{4A}\cdots N^1$ [O^4–H^{4A} 0.88(2), $N^1\cdots H^{4A}$ 1.86(2), $N^1\cdots O^4$ 2.731(2) Å].

Presumably, the formation of compounds **6a**–**6d** and **7a**–**7d** involves thermal decarbonylation of pyrrolediones **2** with generation of hydrazonoylketenes **9** which undergo intramolecular cyclization to azomethine imines **10**. The latter are capable of dimerizing in [3+3] or [4+4] mode provided that no other trapping reagent is present [6]. Alkenes as dipolarophiles react with azomethine imines **10** in the form of iminium enolates **11** according to the [4+2]-dipolar cycloaddition path. Compounds **8a** and **8b** were not target products; they were formed via addition of water to azomethine imines **10** with elimination of benzophenone molecule.

The described reaction is an example of synthesis of difficultly accessible substituted pyrazolo[5,1-*b*]-[1,3]oxazines and pyrano[3,2-*e*]pyrazolo[5,1-*b*][1,3]-oxazines with several functional substituents in the pyrazole and oxazine rings.

EXPERIMENTAL

The IR spectra were recorded in mineral oil on a Perkin Elmer Spectrum Two spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III HD 400 spectrometer at 400 and 100 MHz, respectively, using $CDCl_3$ as solvent and hexamethyldisiloxane as internal standard. The elemental analyses were obtained on a Vario Micro cube analyzer. The purity of the synthesized compounds was checked by TLC on Silica gel 60 F_{254} plates (Merck) using benzene–ethyl acetate (5:1) and ethyl acetate as eluent; spots were visualized by treatment with iodine vapor.

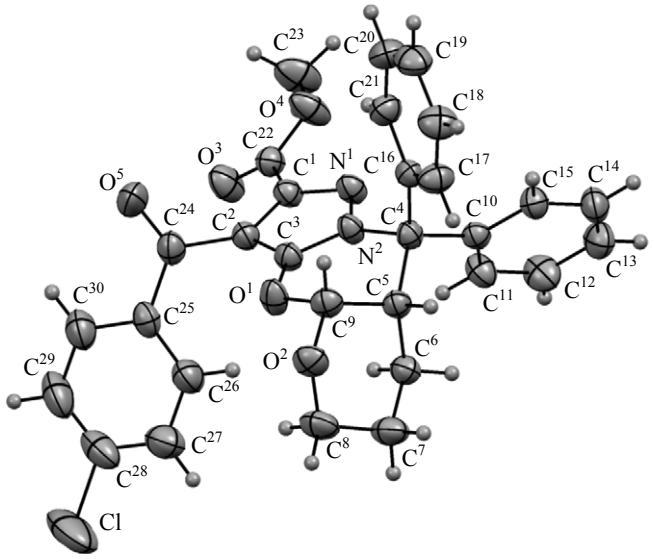


Fig. 1. Structure of the molecule of methyl (4a*S**,8a*R**)-3-(4-chlorobenzoyl)-9,9-diphenyl-4a,7,8,8a-tetrahydro-6*H*,9*H*-pyrano[3,2-*e*]pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (**6a**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

The X-ray diffraction data for compounds **6c** and **8b** were obtained on an Xcalibur R automated four-circle diffractometer (Agilent Technologies) according to standard procedure [MoK_α radiation, temperature 295(2) K, ω-scanning with a step of 1°] using CrysAlisPro software [7]. A correction for absorption

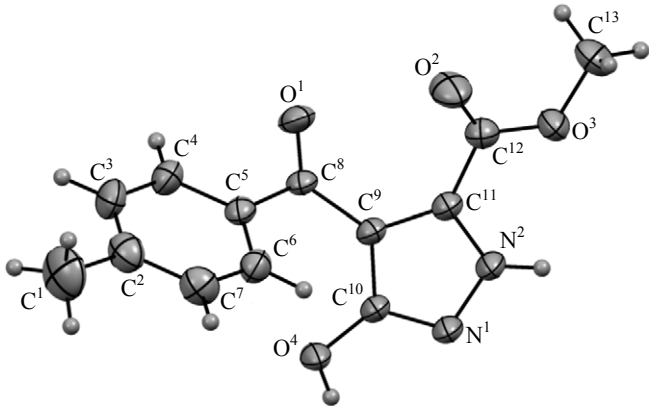


Fig. 2. Structure of the molecule of methyl 3-hydroxy-4-(4-methylbenzoyl)-1*H*-pyrazole-5-carboxylate (**8b**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

was applied empirically using SCALE3 ABSPACK algorithm [7]. The structures were solved by the direct method using SHELXS-97 and were refined against F^2 in anisotropic approximation for non-hydrogen atoms using SHELXL-97 [8]; hydrogen atoms were included in the refinement process according to the riding model in isotropic approximation with dependent thermal parameters.

The data for compound **6c** were acquired from a 0.5×0.3×0.2-mm fragment of a colorless single crystal. Triclinic crystal system, space group *P*–1; unit cell parameters: a = 7.3713(10), b = 10.3134 (12), c = 18.546(2) Å; α = 99.188(9), β = 99.071(10), γ = 110.235(12)°; Z = 2. Completeness 99.9% for θ < 26.00°. Final divergence factors: R_1 = 0.0557, wR_2 = 0.1294 [for 4226 reflections with $I > 2\sigma(I)$]; R_1 = 0.0807, wR_2 = 0.1468 (for all 5899 independent reflections, R_{int} = 0.0415); goodness of fit 1.045; Δρ = 0.235/–0.385 $\bar{e}$Å^{-3}.

The data for compound **8b** were acquired from a 0.4×0.3×0.25-mm fragment of a colorless single crystal. Monoclinic crystal system, space group $P2_1/n$; unit cell parameters: a = 10.979(2), b = 10.5429(19), c = 11.632(3) Å; β = 111.30(3)°; Z = 4. Completeness 99.8% for θ < 26.00°. Final divergence factors: R_1 = 0.0498, wR_2 = 0.1260 [for 2327 reflections with $I > 2\sigma(I)$]; R_1 = 0.0640, wR_2 = 0.1379 (for all 2936 independent reflections, R_{int} = 0.0386); goodness of fit 1.067; Δρ = 0.204/–0.356 $\bar{e}$Å^{-3}.

The CIF files containing complete crystallographic data sets were deposited to the Cambridge Crystallographic Data Centre [CCDC entry nos. 1544136 (**6c**) and 1544137 (**8b**)] and are available at *www.ccdc.cam.ac.uk*.

Methyl (4a*S,8a*R**)-3-benzoyl-9,9-diphenyl-4a,7,8,8a-tetrahydro-6*H*,9*H*-pyrano[3,2-*e*]pyrazolo-[5,1-*b*][1,3]oxazine-2-carboxylate (6a) and methyl 4-benzoyl-3-hydroxy-1*H*-pyrazole-5-carboxylate (8a).** Oxalyl chloride, 1.0 mmol, was added to a solution of 1.0 mmol of compound **1a** in 5 mL of anhydrous chloroform. The mixture was refluxed for 90 min with stirring, 5 mL of anhydrous *o*-xylene was added, and chloroform was distilled off by raising the temperature to 130°C. The mixture was refluxed for 10 min at 130–140°C, 5.0 mmol of 3,4-dihydro-2*H*-pyran was added, and the mixture was refluxed for 90 min more. It was then cooled and evaporated under reduced pressure, and the residue was recrystallized. Yield of **6a** 23%, mp 175–177°C (from acetone). IR spectrum, ν, cm^{-1}: 1724, 1655, 1640, 1566. ^{1}H NMR spectrum, δ, ppm: 1.31 d.d (1H, J = 12.3, 4.0 Hz), 1.57–1.73 m (1H), 1.73–1.85 m (2H, CH_2), 3.10 d.d.d (1H, OCHC**H**, J = 12.0, 3.9, 2.1 Hz), 3.71 s (3H, MeO), 3.79 d (1H, OCH_2, J = 11.3 Hz), 3.86–4.00 m (1H, OCH_2), 5.83 s (1H, OCH), 7.05–7.16 m (2H, H_{arom}), 7.29–7.70 m (11H, H_{arom}), 7.86–7.96 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 24.7, 41.5, 52.2 (MeO), 61.5, 71.8, 97.1, 104.0, 127.2 (2C), 127.9 (2C), 128.0, 128.3 (2C), 128.6, 128.8 (2C), 129.1 (2C), 129.3 (2C), 132.7, 138.8, 138.9, 141.4, 142.8, 151.8, 162.6 (MeO**C**O), 188.1 (Ar**C**O). Found, %: C 72.77; H 5.27; N 5.63. $C_{30}H_{26}N_2O_5$. Calculated, %: C 72.86; H 5.30; N 5.66.

The mother liquor was concentrated, and the residue was dried. Yield of **8a** 12%, mp 205–206°C (from toluene). IR spectrum, ν, cm^{-1}: 3250, 1750, 1720, 1670. ^{1}H NMR spectrum, δ, ppm: 3.50 s (3H, MeO), 7.49 t (2H, H_{arom}, J = 7.6 Hz), 7.61 t (1H, H_{arom}, J = 7.2 Hz), 7.61 d (2H, H_{arom}, J = 5.8 Hz), 10.63 s (1H, NH), 13.16 s (1H, OH). Found, %: C 58.36; H 4.05; N 11.35. $C_{12}H_{10}N_2O_4$. Calculated, %: C 58.54; H 4.09; N 11.38.

Compounds **6b**–**6d** were synthesized in a similar way.

Methyl (4a*S,8a*R**)-3-(4-methylbenzoyl)-9,9-diphenyl-4a,7,8,8a-tetrahydro-6*H*,9*H*-pyrano[3,2-*e*]-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (6b).** Yield 26%, mp 246–248°C (from acetone). IR spectrum, ν, cm^{-1}: 1724, 1650, 1606, 1566. ^{1}H NMR spectrum, δ, ppm: 1.23–1.37 m (1H), 1.59–1.80 m (3H, CH_2), 2.47 s (3H, Me), 3.10 d (1H, OCHC**H**, J = 10.4 Hz), 3.74 s (3H, MeO), 3.80 d (1H, J = 9.4 Hz), 3.89–4.03 m (1H, OCH_2), 5.81 s (1H, OCH), 7.15–7.07 m (2H, H_{arom}), 7.25–7.54 m (8H, H_{arom}), 7.66 d (2H, H_{arom}, J = 7.6 Hz), 7.82 d (2H, H_{arom}, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 21.8, 24.8, 41.5, 52.2 (MeO), 61.6, 71.9, 97.0, 104.2, 127.2 (2C), 127.9 (2C), 128.0, 128.6, 128.9 (2C), 129.0 (2C), 129.1 (2C), 129.6 (2C), 136.3, 138.9, 141.4, 142.7, 143.6, 151.5, 162.6 (MeO**C**O), 187.8 (Ar**C**O). Found, %: C 73.17; H 5.53; N 5.48. $C_{31}H_{28}N_2O_5$. Calculated, %: C 73.21; H 5.55; N 5.51.

Methyl (4a*S,8a*R**)-3-(4-chlorobenzoyl)-9,9-diphenyl-4a,7,8,8a-tetrahydro-6*H*,9*H*-pyrano[3,2-*e*]-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (6c).** Yield 25%, mp 261–263°C (from acetone). IR spectrum, ν, cm^{-1}: 1722, 1656, 1586, 1565. ^{1}H NMR spectrum, δ, ppm: 1.23 d.d (1H, J = 8.8, 5.2 Hz), 1.50–1.66 m (1H, CH_2), 1.67–1.80 m (2H, CH_2), 3.04 d.d.d (1H, OCHC**H**, J = 12.3, 4.0, 2.1 Hz), 3.70 s (3H,

MeO), 3.72–3.79 m (1H, OCH_2), 3.80–3.92 m (1H, OCH_2), 5.77 s (1H, OCH), 6.95–7.12 m (2H, H_{arom}), 7.23–7.32 m (3H, H_{arom}), 7.33–7.49 m (5H, H_{arom}), 7.56–7.63 m (2H, H_{arom}), 7.71–7.89 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 24.7, 41.4, 52.3 (MeO), 61.6, 71.9, 97.3, 103.7, 127.2 (2C), 127.9 (2C), 128.0, 128.7 (3C), 128.8 (2C), 129.2 (2C), 130.8 (2C), 137.2, 138.8, 139.2, 141.3, 142.7, 151.8, 162.5 (MeO**C**O), 186.8 (Ar**C**O). Found, %: C 68.07; H 4.73; N 5.26. $C_{30}H_{25}ClN_2O_5$. Calculated, %: C 68.12; H 4.76; N 5.30.

Methyl (4a*S,8a*R**)-3-(2,2-dimethylpropanoyl)-9,9-diphenyl-4a,7,8,8a-tetrahydro-6*H*,9*H*-pyrano[3,2-*e*]pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (6d).** Yield 26%, mp 191–92°C (from acetone). IR spectrum, ν, cm^{-1}: 1728, 1697, 1662, 1545. ^1H NMR spectrum, δ, ppm: 1.35 s (9H, Me_3C), 1.56–1.69 m (2H), 1.74–1.85 m (2H), 3.08 d.d.d (1H, OCHC**H**, *J* = 12.4, 3.9, 2.1 Hz), 3.84–3.91 m (1H), 3.93 s (3H, MeO), 3.95–4.03 m (1H), 5.81 s (1H, OCH), 7.05–7.12 m (2H, H_{arom}), 7.29–7.39 m (4H, H_{arom}), 7.40–7.47 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.8, 24.8, 26.6 (3C), 41.7, 44.8, 52.3 (MeO), 61.7, 71.8, 97.0, 104.8, 127.1 (2C), 127.9 (2C), 128.0, 128.1, 128.2, 128.3, 128.5, 128.9 (2C), 129.1 (2C), 129.6, 163.0 (MeO**C**O), 204.0 (Me_3C**C**O). Found, %: C 70.73; H 6.60; N 5.85. $C_{28}H_{30}N_2O_5$. Calculated, %: C 70.87; H 6.73; N 5.90.

Methyl 5-ethoxy-3-(4-methylbenzoyl)-7,7-diphenyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (7a) and methyl 3-hydroxy-4-(4-methylbenzoyl)-1*H*-pyrazole-5-carboxylate (8b). Oxalyl chloride, 1.0 mmol, was added to a solution of 1.0 mmol of compound **1b** in 5 mL of anhydrous chloroform. The mixture was refluxed for 10 min with stirring, 5 mL of anhydrous *o*-xylene was added, and chloroform was distilled off by raising the temperature to 130. The mixture was refluxed for 10 min at 130–140°C and cooled to 90–100°C, 5.0 mmol of ethyl vinyl ether was added, and the mixture was heated for 15 min more. The resulting solution was cooled and evaporated under reduced pressure. Yield of **7a** 26%, mp 180–183°C (from acetone). IR spectrum, ν, cm^{-1}: 1740, 1634, 1607, 1550. ^1H NMR spectrum, δ, ppm: 1.06 t (3H, *J* = 6.8 Hz), 2.39 s (3H, Me), 3.00–3.13 m (2H, CHC$\mathbf{H}_2$), 3.39–3.51 m (1H, OCH_2), 3.57 s (3H, MeO), 3.67–3.80 m (1H, OCH_2), 5.21 d (1H, C**H**CH_2, *J* = 6.8 Hz), 7.13 d (2H, H_{arom}, *J* = 6.5 Hz), 7.18–7.28 m (4H, H_{arom}), 7.28–7.44 m (6H, H_{arom}), 7.74 d (2H, H_{arom}, *J* = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.9, 21.8, 42.1, 52.1 (MeO), 65.7, 68.3, 99.6, 104.3, 127.2 (2C), 128.3 (2C), 128.4 (2C), 128.6 (2C), 128.9 (2C), 129.0 (2C), 129.5 (2C), 136.6, 141.0, 142.0, 142.9, 143.2, 151.6, 162.6 (MeO**C**O), 188.2 (Ar**C**O). Found, %: C 72.49; H 5.65; N 5.61. $C_{30}H_{28}N_2O_5$. Calculated, %: C 72.56; H 5.68; N 5.64.

The mother liquor obtained after recrystallization of **7a** from acetone was concentrated, and the residue was recrystallized from toluene. Yield of **8b** 15%, mp 210–212°C (from toluene). IR spectrum, ν, cm^{-1}: 3250, 1770, 1670, 1620. ^1H NMR spectrum, δ, ppm: 2.40 s (3H, Me), 3.60 s (3H, MeO), 7.26 d (2H, H_{arom}, *J* = 8.0 Hz), 7.60 d (2H, H_{arom}, *J* = 8.0 Hz), 10.35 s (1H, NH), 13.20 s (1H, OH). Found, %: C 59.82; H 4.51; N 10.73. $C_{13}H_{12}N_2O_4$. Calculated, %: C 60.00; H 4.65; N 10.76.

Compounds **7b**–**7d** were synthesized in a similar way.

Methyl 3-(2,2-dimethylpropanoyl)-5-ethoxy-7,7-diphenyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]-oxazine-2-carboxylate (7b). Yield 32%, mp 133–135°C (from acetone). IR spectrum, ν, cm^{-1}: 1737, 1697, 1656, 1539. ^1H NMR spectrum, δ, ppm: 1.18 t (3H, C$\mathbf{H}_3$CH$_2$, *J* = 7.1 Hz), 1.28 s (9H, Me_3C), 3.01–3.07 m (2H, CHC$\mathbf{H}_2$), 3.44–3.62 m (1H, CH_2O), 3.80 s (3H, MeO), 3.82–3.96 m (1H, CH_2O), 5.20 d.d (1H, C**H**CH_2, *J* = 10.6, 2.6 Hz), 7.04–7.11 m (2H, H_{arom}), 7.15–7.45 m (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 15.0, 26.6 (3C, $\mathbf{Me}_3$C), 42.3, 44.8, 52.2 (MeO), 65.8, 68.3, 99.8, 105.0, 127.1 (2C), 128.3 (2C), 128.6 (2C), 129.0 (2C), 129.3 (2C), 134.1, 141.1, 142.0, 147.9, 162.9 (MeO**C**O), 204.4 (Me_3C**C**O). Found, %: C 70.02; H 6.51; N 6.01. $C_{27}H_{30}N_2O_5$. Calculated, %: C 70.11; H 6.54; N 6.06.

Methyl 3-(4-methylbenzoyl)-5,7,7-triphenyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (7c). The mixture was refluxed for 10 min at 130–140°C, 5.0 mmol of styrene was added, and the mixture was heated for 60 min more. The solution was cooled and evaporated under reduced pressure. Yield 21%, mp 214–216°C (from acetone). IR spectrum, ν, cm^{-1}: 1731, 1640, 1605, 1550. ^1H NMR spectrum, δ, ppm: 2.46 s (3H, Me), 3.12 d.d (1H, CHC$\mathbf{H}_2$, *J* = 14.8, 10.7 Hz), 3.18 d.d (1H, CHC$\mathbf{H}_2$, *J* = 14.8, 2.7 Hz), 3.64 s (3H, MeO), 5.27 d.d (1H, C**H**CH_2, *J* = 10.6, 2.6 Hz), 7.26–7.56 m (19H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.8 (Me), 45.0, 52.0 (MeO), 69.2, 76.4, 104.2, 125.7 (2C), 127.2 (2C), 128.4 (2C), 128.5 (2C), 128.7 (2C), 128.8 (2C), 128.9, 129.0 (2C), 129.2 (2C), 129.5 (2C), 136.6, 137.7, 141.4, 141.9, 142.7,

143.3, 152.7, 162.6 (MeO**C**O), 188.2 (Ar**C**O). Found, %: C 77.09; H 5.21; N 5.26. $C_{34}H_{28}N_2O_4$. Calculated, %: C 77.25; H 5.34; N 5.30.

Methyl 3-(4-chlorobenzoyl)-5,7,7-triphenyl-6,7-dihydro-5*H*-pyrazolo[5,1-*b*][1,3]oxazine-2-carboxylate (7d). Yield 40%, mp 198–200°C (from acetone). IR spectrum, ν, cm^{-1}: 1737, 1636, 1587, 1546. ^1H NMR spectrum, δ, ppm: 3.09 d.d (1H, CHC**H**$_2$, J = 14.8, 10.8 Hz), 3.16 d.d (1H, CHC**H**$_2$, J = 14.8, 2.6 Hz), 3.61 s (3H, MeO), 5.21 d.d (1H, C**H**CH$_2$, J = 10.8, 2.4 Hz), 7.18–7.50 m (17H, H_{arom}), 7.77–7.84 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 44.8, 52.2 (MeO), 69,3, 76.7, 103.8, 125.7 (2C), 127.2 (2C), 128.5 (2C), 128.6 (2C), 128.7 (4C), 128.9 (2C), 129.0, 129.2 (2C), 130.7 (2C), 137.4, 137.5, 138.9, 141.3, 141.8, 142.7, 153.0, 162.5 (MeO**C**O), 187.1 (Ar**C**O). Found, %: C 72.11; H 4.46; N 5.06. $C_{33}H_{25}ClN_2O_4$. Calculated, %: C 72.19; H 4.59; N 5.10.

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