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Synthesis of New Functionally Substituted Aryl- and Hetarylcarbamates Based on Ninhydrin

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Abstract—The condensation of methyl (ethyl) phenylcarbamates with ninhydrin in concentrated sulfuric acid gave dialkyl [1,3-dioxoindan-2,2-diyldi(4,1-phenylene)]biscarbamates. Treatment of the latter with hydrazine hydrate resulted in the transformation of the indandione fragment into phthalazinone. Ninhydrin reacted with methyl (hydroxyphenyl)carbamates in glacial acetic acid to produce dihydroxy derivative of oxotrihydroindeno[1,2-*b*][1]benzofuran possessing a carbamate group. Tandem reaction of ninhydrin with methyl (acetylphenyl)carbamates on heating in boiling glacial acetic acid, followed by addition of hydrazine hydrate in acetonitrile, afforded methyl (5-oxo-5*H*-indeno[1,2-*c*]pyridazin-3-yl)phenylcarbamates.

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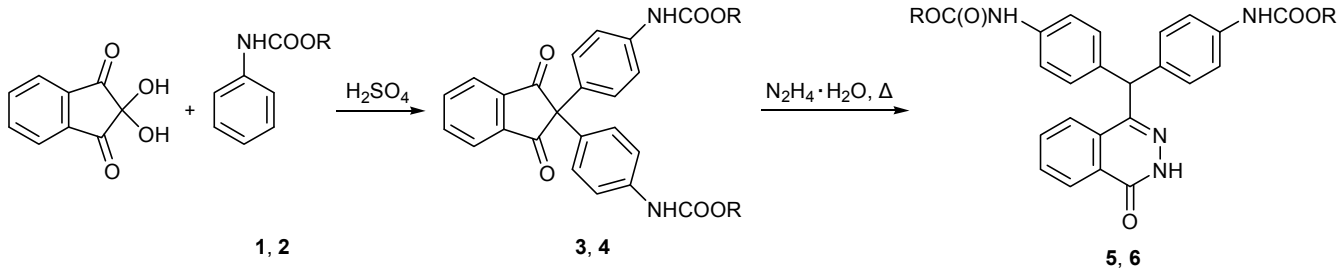
Ninhydrin [2,2-dihydroxy-1*H*-indene-1,3(2*H*)-dione] is an important intermediate product in the synthesis of various five-membered N,O,S-heterocyclic compounds, including pyrrole [1, 2], pyrrolidine, pyrrolizidine [3, 4], dihydropyrazole [5], imidazole, imidazolidine [6, 7], di- and tetrahydrofuran [8, 9], benzofuran [10], thiophene [11], oxazolidine [12], and thiazolidine derivatives [13]. These heterocycles can be obtained from ninhydrin via cycloaddition [3], cyclocondensation [5], Wittig [7], Pictet–Spengler [14], Baylis–Hillman [15], and other reactions [14]. Ninhydrin is frequently used in multicomponent reactions [4]. Reactions of ninhydrin leading to the formation of six-membered N,O,S-heterocycles are also known; in particular syntheses of pyridines, piperidines [14, 16], pyrimidines [17], piperazines, pyrazines [14, 18], quinoxalines [19], phthalazines [20], pyridazines [21], triazines [22], pyrans [23], oxazines [24], and other compounds [14] have been reported. Condensations of ninhydrin with some aromatic compounds were studied in [25]. However, we have found no published data on reactions of ninhydrin with alkyl phenylcarbamates **1** and **2**.

The condensation of ninhydrin with methyl and ethyl phenylcarbamates **1** and **2** in concentrated sulfuric acid at 25°C gave the corresponding *para*,*para*′-substituted bis-phenylcarbamates **3** and **4** in 94 and 97% yield with high regioselectivity (Scheme 1). The structure of **3** and **4** was confirmed by IR and ^{1}H NMR spectra. Their ^{1}H NMR spectra contained doublet signals from 8 aromatic protons in the regions δ 7.23–7.24 and 7.33–7.34 ppm. 1,3-Dioxo-2,3-dihydro-1*H*-indenes **3** and **4** containing phenylcarbamate fragments in the 2-position attract considerable interest as sub-

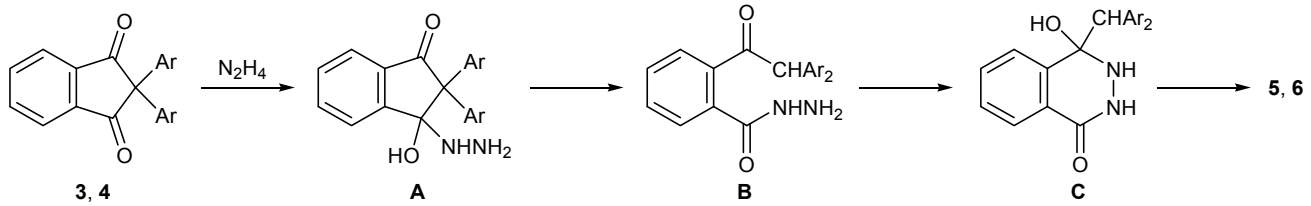
Scheme 1.



1, **2** **3**, **4** **5**, **6**

1, **3**, **5**, R = Me; **2**, **4**, **6**, R = Et.

Scheme 2.



3, **5**, Ar = 4-MeOC(O)NHC$_6$H$_4$; **4**, **6**, Ar = 4-EtOC(O)NHC$_6$H$_4$.

strates for subsequent heterocyclization. The condensation of **3** and **4** with hydrazine hydrate on heating for 15 min under reflux afforded phthalazinones **5** and **6** in 62 and 60% yield, respectively (Scheme 1). In the ^{1}H NMR spectra of **5** and **6**, the CH proton resonated as a singlet at δ 5.89–5.90 ppm, and the phthalazine NH signal was located in a weaker field (δ 10.80 ppm) than the carbamate NH signal (δ 9.85–9.87 ppm).

Presumably, the reaction involves initial nucleophilic addition of hydrazine to one carbonyl group of ninhydrin with the formation of tetrahedral intermediate **A**. Heterolytic dissociation of C–C bond in the five-membered ring of **A** gives intermediate **B** which undergoes intramolecular heterocyclization via nucleophilic attack of the amino group on the carbonyl group. Elimination of water molecule from intermediate **C** yields final phthalazine **5** or **6** (Scheme 2).

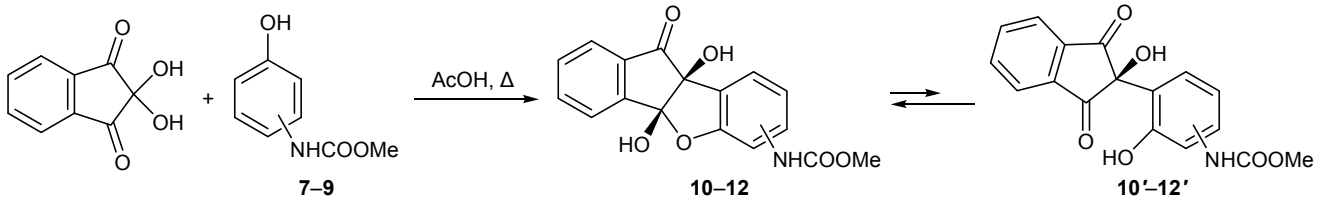
It is known that ninhydrin reacts with phenols to give benzofuran derivatives [26]. We reacted isomeric methyl (hydroxyphenyl)carbamates **7**–**9** with ninhydrin in boiling glacial acetic acid and obtained 63–65% of fused benzofuran derivatives **10**–**12** (Scheme 3). The structure of **10**–**12** was confirmed by IR and ^{1}H NMR spectra. The ^{1}H NMR spectrum of **12** in $CDCl_3$ displayed a triplet at δ 7.57 ppm, a multiplet at δ 7.76–7.80 ppm, and a doublet at δ 8.01 ppm due to four aromatic protons of the ninhydrin fragment, and protons of the two hydroxy groups resonated as two singlets at δ 3.93 and 4.75 ppm. According to spectral data, cyclic benzofuran structures **10**–**12** in solution exist in equilibrium with minor open isomers **10′**–**12′** [27].

With a view to further functionalization of compounds **10**–**12**, ninhydrin was brought into reaction with hydroxyphenylcarbamates **7**–**9** in boiling glacial acetic acid, followed by addition of urea. The products of this reaction were methyl *N*-[3(4,3)-(3,5-dioxo-2,5-dihydro-3*H*-imidazo[5,1-*a*]isoindol-1-yl)-2(3,4)-hydroxyphenyl]carbamates **13**–**15** (yield 67–72%; Scheme 4). The structure of **13**–**15** was confirmed by IR and ^{1}H NMR spectra, as well as by ^{13}C NMR spectrum of **15**. In the ^{1}H NMR spectra of **13**–**15**, NH proton of the imidazole fragment resonated as a broadened singlet at δ 10.64–10.65 ppm, whereas the carbamate NH signal appeared in a stronger field (δ 9.75–9.76 ppm). The ^{13}C NMR spectrum of **15** contained signals of aromatic carbons and carbon atoms of the carbamate group, two carbonyl carbon signals at δ_C 152.31 and 157.62 ppm, and a signal at δ_C 111.64 ppm due to the C^1 atom of the imidazole fragment.

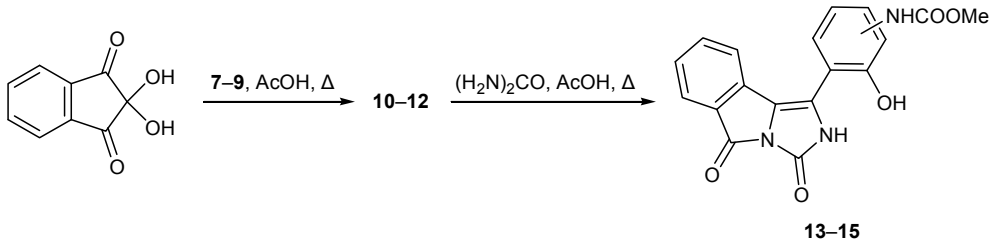
Scheme 5 illustrates a probable mechanism of this reaction. Nucleophilic attack of the urea amino group on the carbonyl carbon atom of **10′**–**12′** is accompanied by opening of the five-membered ring with formation of intermediate **A** which undergoes heterocyclization as a result of intramolecular nucleophilic attack of the NH nitrogen atom on the other carbonyl group. Intermediate **B** thus formed is converted to structure **C** via subsequent heterocyclization involving the NH_2 group and electrophilic carbon atom. Elimination of water molecule from **C** yields final compound **13**–**15**.

We also studied the condensation of ninhydrin with methyl (acetylphenyl)carbamates **16**–**18** on heating in boiling glacial acetic acid, followed by addition of hydrazine hydrate in acetonitrile. This reaction

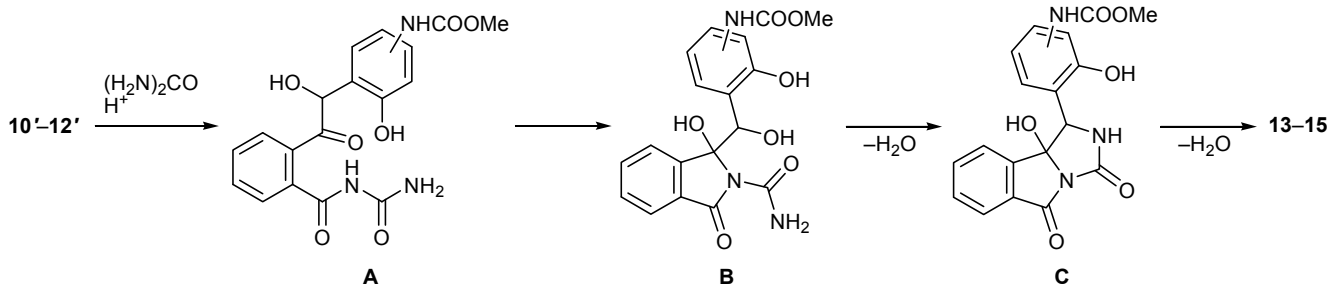
Scheme 3.



Scheme 4.



Scheme 5.



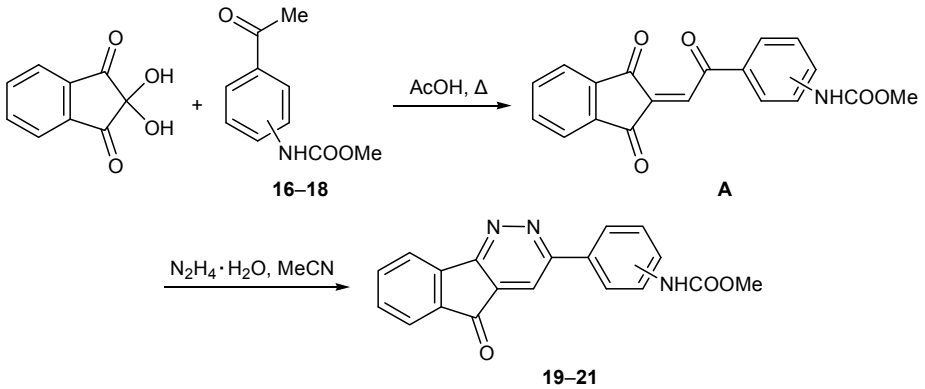
afforded indeno[1,2-*c*]pyridazines **19**–**21** in 85–89% yield Scheme 6). The ^{1}H NMR spectra of **19**–**21** showed signals from protons of the indene and phenylcarbamate fragments, as well as a signal at δ 7.74–7.81 ppm, which was assigned to the 4-H proton (pyridazine fragment); the position of the 4-H signal was consistent with the data for structurally related indeno[1,2-*c*]pyridazine derivatives [28]. The reaction is likely to involve aldolization–crotonization to give intermediate **A** which undergoes heterocyclization with hydrazine.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer at 500.13 MHz using tetramethylsilane as internal standard. The ^{13}C NMR spectrum of a solution of **15** in DMSO-d_6 was obtained on the same instrument at 126 MHz with complete decoupling from protons. The IR spectra were measured on an InfraLUM FT-02 spectrometer from samples prepared as KBr discs or thin films. The purity of the isolated compounds was checked by TLC on Silufol UV-254 plates; spots were visualized by treatment with iodine vapor.

Dimethyl [(1,3-dioxo-2,3-dihydro-1*H*-indene-2,2-diyl)di(4,1-phenylene)]biscarbamate (3). A mixture of 0.997 g (5.6 mmol) of ninhydrin, 1.69 g (11.2 mmol) of methyl phenylcarbamate (**1**), and 10 mL of concentrated sulfuric acid was stirred for 8 h at 25°C. The mixture was poured onto 10–20 g of ice and extracted with chloroform. The extract was washed twice with water (50 mL) and 10% aqueous sodium chloride and dried over anhydrous magnesium

Scheme 6.



16, **19**, 2-NHCOOMe; **17**, **20**, 3-NHCOOMe; **18**, **21**, 4-NHCOOMe.

sulfate, the solvent was distilled off, and the residue was recrystallized from chloroform. Yield 2.34 g (94%), colorless crystals, mp 109–110°C. IR spectrum, ν, cm^{-1}: 3310 (NH), 1715, 1700 (C=O), 1610, 1578, 1565 (C=C_{arom}). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.71 s (6H, OMe), 7.23 d (4H, H_{arom}, J = 8.7 Hz), 7.34 d (4H, H_{arom}, J = 8.7 Hz), 7.87–7.90 m (2H, H_{arom}), 8.06–8.09 m (2H, H_{arom}), 9.86 br.s (2H, NH). Found, %: C 67.41; H 4.54; N 6.10. $C_{25}H_{20}N_2O_6$. Calculated, %: C 67.57; H 4.51; N 6.31.

Diethyl [(1,3-dioxo-2,3-dihydro-1*H*-indene-2,2-diyl)di(4,1-phenylene)]biscarbamate (4) was synthesized in a similar way. Yield 2.56 g (97%), colorless crystals, mp 114–115°C. IR spectrum, ν, cm^{-1}: 3310 (NH), 1714, 1700 (C=O), 1610, 1575, 1560 (C=C_{arom}). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 t (6H, $CH_2C\mathbf{H}_3$, J = 7.1 Hz), 4.07 q (4H, OCH_2, J = 7.1 Hz), 7.24 d (4H, H_{arom}, J = 8.7 Hz), 7.33 d (4H, H_{arom}, J = 8.7 Hz), 7.86–7.89 m (2H, H_{arom}), 8.05–8.08 m (2H, H_{arom}), 9.87 br.s (2H, NH). Found, %: C 68.53; H 4.94; N 5.79. $C_{27}H_{24}N_2O_6$. Calculated, %: C 68.64; H 5.09; N 5.93.

Dimethyl [(4-oxo-3,4-dihydrophthalazin-1-yl)-methylenedi(4,1-phenylene)]biscarbamate (5). A mixture of 0.62 g (1.4 mmol) of bis-carbamate **3** and 10 mL of 99% hydrazine hydrate was refluxed for 15 min. The mixture was cooled and acidified with 6 N aqueous HCl to pH 6. The precipitate was filtered off and treated with chloroform, the solvent was removed, and the residue was recrystallized from chloroform–petroleum ether (1:2). Yield 0.39 g (62%), light yellow crystals, mp 167–169°C. IR spectrum, ν, cm^{-1}: 3308, 3174 (NH), 1710, 1658 (C=O), 1596, 1580 (C=C_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 s (6H, OMe), 5.89 s (1H, CH), 7.13 d (4H, H_{arom}, J = 8.6 Hz), 7.30 d (4H, H_{arom}, J = 8.6 Hz), 7.70–7.74 m (3H, H_{arom}), 8.44–8.46 m (1H, H_{arom}), 9.85 br.s (2H, N**H**CO_2Me), 10.80 br.s (1H, NNH). Found, %: C 65.64; H 4.54; N 12.12. $C_{25}H_{22}N_4O_5$. Calculated, %: C 65.50; H 4.80; N 12.23.

Diethyl [(4-oxo-3,4-dihydrophthalazin-1-yl)-methylenedi(4,1-phenylene)]biscarbamate (6) was synthesized in a similar way from 0.644 g (1.4 mmol) of compound **4**. Yield 0.4 g (60%), light yellow crystals, mp 155–158°C (from chloroform–petroleum ether, 1:2). IR spectrum, ν, cm^{-1}: 3310, 3190 (NH), 1710, 1659 (C=O), 1595, 1577 (C=C_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.25 t (6H, $CH_2C\mathbf{H}_3$, J = 7.0 Hz), 4.17 q (4H, OCH_2, J = 7.0 Hz), 5.90 s (1H, CH), 7.13 d (4H, H_{arom}, J = 8.6 Hz), 7.29 d (4H, H_{arom}, J = 8.6 Hz), 7.70–7.74 m (3H, H_{arom}), 8.45–8.47 m (1H, H_{arom}, J = 8.1 Hz), 9.87 br.s (2H, N**H**CO_2Me), 10.80 br.s (1H, NNH). Found, %: C 66.48; H 4.98; N 11.39. $C_{27}H_{26}N_4O_5$. Calculated, %: C 66.67; H 5.35; N 11.52.

Methyl (4b,9b-dihydroxy-10-oxo-9b,10-dihydro-4b*H*-indeno[1,2-*b*][1]benzofuran-6-yl)carbamate (10). A mixture of 0.356 g (2 mmol) of ninhydrin and 0.334 g (2 mmol) of carbamate **7** in 5 mL of glacial acetic acid was refluxed for 3 h. The mixture was cooled and poured onto 50 g of ice, and the precipitate was filtered off, washed with water (50 mL), dried in air, and purified by recrystallization from chloroform–hexane (1:2). Yield 0.39 g (60%), colorless crystals, mp 135–138°C. IR spectrum, ν, cm^{-1}: 3556, 3310 (OH, NH), 1710, 1675 (C=O), 1610, 1590, 1575 (C=C_{arom}). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.71 s (3H, OCH_3), 3.94 s (1H, OH), 4.75 s (1H, OH), 6.78 d (1H, H_{arom}, J = 7.6 Hz), 7.21 t (1H, H_{arom}, J = 7.6 Hz), 7.57 t (1H, H_{arom}, J = 7.1 Hz), 7.76–7.80 m (2H, H_{arom}), 8.01 d (1H, H_{arom}, J = 6.9 Hz), 8.14 d (1H, H_{arom}, J = 7.9 Hz), 9.89 br.s (1H, NH). Found, %: C 62.23; H 3.84; N 3.96. $C_{17}H_{13}NO_6$. Calculated, %: C 62.39; H 3.98; N 4.28.

Compounds **11** and **12** were synthesized in a similar way.

Methyl (4b,9b-dihydroxy-10-oxo-9b,10-dihydro-4b*H*-indeno[1,2-*b*][1]benzofuran-7-yl)carbamate (11). Yield 0.41 g (63%), colorless crystals, mp 152–154°C. IR spectrum, ν, cm^{-1}: 3560, 3310 (OH, NH), 1710, 1686 (C=O), 1610, 1595, 1577 (C=C_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 s (3H, OCH_3), 3.95 s (1H, OH), 4.76 s (1H, OH), 6.78 d (1H, H_{arom}, J = 7.9 Hz), 7.22 d (1H, H_{arom}, J = 7.9 Hz), 7.48 s (1H, H_{arom}), 7.57 t (1H, H_{arom}, J = 7.1 Hz), 7.76–7.80 m (2H, H_{arom}), 8.01 d (1H, H_{arom}, J = 6.9 Hz), 9.87 br.s (1H, NH). Found, %: C 62.14; H 4.03; N 4.16. $C_{17}H_{13}NO_6$. Calculated, %: C 62.39; H 3.98; N 4.28.

Methyl (4b,9b-dihydroxy-10-oxo-9b,10-dihydro-4b*H*-indeno[1,2-*b*][1]benzofuran-8-yl)carbamate (12). Yield 0.42 g (65%), colorless crystals, mp 133–135°C. IR spectrum, ν, cm^{-1}: 3580, 3310 (OH, NH), 1710, 1680 (C=O), 1610, 1595, 1577 (C=C_{arom}). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.71 s (3H, OCH_3), 3.93 s (1H, OH), 4.75 s (1H, OH), 7.49 d (1H, H_{arom}, J = 8.3 Hz), 7.53 s (1H, H_{arom}), 7.57 t (1H, H_{arom}, J = 7.1 Hz), 7.73 d (1H, H_{arom}, J = 8.3 Hz), 7.76–7.80 m (2H, H_{arom}), 8.01 d (1H, H_{arom}, J = 6.9 Hz), 9.87 br.s (1H, NH). Found, %: C 62.21; H 3.95; N 4.20. $C_{17}H_{13}NO_6$. Calculated, %: C 62.39; H 3.98; N 4.28.

Methyl [3-(3,5-dioxo-2,5-dihydro-3*H*-imidazo-[5,1-*a*]isoindol-1-yl)-2-hydroxyphenyl]carbamate (13). A mixture of 0.356 g (2 mmol) of ninhydrin and 0.334 g (2 mmol) of carbamate **7** in 6 mL of glacial acetic acid was refluxed for 5 h. The mixture was cooled to room temperature, 0.25 g (4.4 mmol) of urea was added, and the mixture was refluxed for 2.5 h. The mixture was cooled and poured into ice water, and the precipitate was filtered off, washed with water (25 mL), dried in air, and purified by recrystallization from petroleum ether–ethyl acetate (2:1). Yield 0.51 g (72%), yellow crystals, mp 168–170°C. IR spectrum, ν, cm^{-1}: 3360–3310 (OH, NH), 1721, 1710 (C=O), 1608, 1575, 1560 (C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 s (3H, OMe), 4.17 s (1H, OH), 7.27 t (1H, H_{arom}, J = 8.0 Hz), 7.44–7.52 m (3H, H_{arom}), 7.96 d (1H, H_{arom}, J = 7.7 Hz), 8.31 d (1H, H_{arom}, J = 8.0 Hz), 8.37 d (1H, H_{arom}, J = 7.7 Hz), 9.75 br.s (1H, N**H**CO_2Me), 10.65 s (1H, N^2H). Found, %: C 61.39; H 3.64; N 11.85. $C_{18}H_{13}N_3O_5$. Calculated, %: C 61.54; H 3.70; N 11.97.

Compounds **14** and **15** were synthesized in a similar way.

Methyl [4-(3,5-dioxo-2,5-dihydro-3*H*-imidazo-[5,1-*a*]isoindol-1-yl)-3-hydroxyphenyl]carbamate (14) was synthesized from 0.356 g (2 mmol) of ninhydrin, 0.334 g (2 mmol) of methyl (3-hydroxyphenyl)carbamate (**8**), and 0.25 g (4.4 mmol) of urea in 6 mL of glacial acetic acid. Yield 0.48 g (69%), yellow crystals, mp 183–185°C. IR spectrum, ν, cm^{-1}: 3340–3310 (OH, NH), 1720, 1710 (C=O), 1610, 1575, 1560 (C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 s (3H, OMe), 4.71 s (1H, OH), 7.18–7.24 m (2H, H_{arom}), 7.49–7.54 m (2H, H_{arom}), 7.67 d (1H, H_{arom}, J = 7.9 Hz), 7.92 d (1H, H_{arom}, J = 7.7 Hz), 8.41 d (1H, H_{arom}, J = 7.7 Hz), 9.75 br.s (1H, N**H**CO_2Me), 10.64 br.s (1H, N^2H). Found, %: C 61.47; H 3.58; N 11.74. $C_{18}H_{13}N_3O_5$. Calculated, %: C 61.54; H 3.70; N 11.97.

Methyl [3-(3,5-dioxo-2,5-dihydro-3*H*-imidazo-[5,1-*a*]isoindol-1-yl)-4-hydroxyphenyl]carbamate (15) was synthesized from 0.356 g (2 mmol) of ninhydrin, 0.334 g (2 mmol) of carbamate **9**, and 0.25 g (4.4 mmol) of urea in 6 mL of glacial acetic acid. Yield 0.48 g (67%), yellow crystals, mp 232–235°C. IR spectrum, ν, cm^{-1}: 3330–3310 (OH, NH), 1720, 1710 (C=O), 1612, 1578, 1565 (C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 s (3H, OMe), 4.70 s (1H, OH), 7.17–7.23 m (2H, H_{arom}), 7.51–7.53 m (2H, H_{arom}), 7.67 d (1H, H_{arom}, J = 7.9 Hz), 8.11 d (1H, H_{arom}, J = 7.7 Hz), 8.46 d (1H, H_{arom}, J = 7.7 Hz), 9.76 br.s (1H, N**H**CO_2Me), 10.65 br.s (1H, N^2H). ^{13}C NMR spectrum, δ_C, ppm: 52.56 (OMe), 111.64 (C^1); 113.72, 116.35, 117.81, 122.22, 124.34, 126.40, 127.36, 127.62, 128.51, 129.42, 131.33, 144.74 (C_{arom}); 152.31 (C^3), 155.85 (NH**C**O_2Me), 157.62 (C^5). Found, %: C 61.20; H 3.65; N 12.04. $C_{18}H_{13}N_3O_5$. Calculated, %: C 61.54; H 3.70; N 11.97.

Methyl [2-(5-oxo-5*H*-indeno[1,2-*c*]pyridazin-3-yl)phenyl]carbamate (19). A mixture of 0.69 g (5 mmol) of ninhydrin and 0.965 g (5 mmol) of carbamate **16** in 10 mL of glacial acetic acid was refluxed for 4 h. The mixture was cooled and diluted with 30 mL of acetonitrile, 0.37 mL (7.5 mmol) of 98% hydrazine hydrate was added, and the mixture was stirred for 2 h at room temperature on a magnetic stirrer. The yellow precipitate was filtered off and recrystallized from chloroform–petroleum ether (1:3). Yield 1.41 g (85%), light yellow crystals, mp 213–215°C. IR spectrum, ν, cm^{-1}: 3315 (NH), 1718, 1705 (C=O), 1628, 1602, 1576, 1560 (C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 s (3H, OMe), 6.98 t (1H, H_{arom}, J = 7.3 Hz), 7.42–7.45 m (1H, H_{arom}), 7.50–7.58 m (2H, H_{arom}), 7.67 d (1H, H_{arom}, J = 7.3 Hz), 7.80 s (1H, 4-H), 7.83 d (1H, H_{arom}, J = 7.4 Hz), 7.93 d (1H, H_{arom}, J = 7.3 Hz), 8.40 d (1H, H_{arom}, J = 7.3 Hz), 9.87 br.s (1H, NH). Found, %: C 69.01; H 3.87; N 12.49. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.93; N 12.69.

Compounds **20** and **21** were synthesized in a similar way.

Methyl [3-(5-oxo-5*H*-indeno[1,2-*c*]pyridazin-3-yl)phenyl]carbamate (20) was synthesized from 0.965 g (5 mmol) of carbamate **17**. Yield 1.44 g (87%), light yellow crystals, mp 219–221°C. IR spectrum, ν, cm^{-1}: 3300 (NH), 1718, 1705 (C=O), 1615, 1583 (C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 s (3H, OMe), 7.51–7.68 m (5H, H_{arom}), 7.74 s (1H, 4-H), 7.80 d (1H, H_{arom}, J = 7.2 Hz), 8.32 d (1H, H_{arom}, J = 7.9 Hz), 8.79 s (1H, H_{arom}), 9.84 br.s (1H, NH). Found, %: C 69.00; H 3.85; N 12.51. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.93; N 12.69.

Methyl [4-(5-oxo-5*H*-indeno[1,2-*s*]pyridazin-3-yl)phenyl]carbamate (21) was synthesized from 0.965 g (5 mmol) of carbamate **18**. Yield 1.47 g (89%), light yellow crystals, mp 257–259°C. IR spectrum, ν, cm^{-1}: 3301 (NH), 1724 (C=O), 1602, 1564 (C=C_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 s (3H, OMe), 7.16 d (2H, H_{arom}, J = 8.5 Hz), 7.51–7.59 m (2H, H_{arom}), 7.68 d (1H, H_{arom}, J = 7.3 Hz), 7.78 d (1H, H_{arom}, J = 7.4 Hz), 7.81 s (1H, 4-H), 8.42 d (2H, H_{arom}, J = 8.5 Hz), 9.85 br.s (1H, NH). Found, %: C 68.76;

H 3.90; N 12.37. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.93; N 12.69.

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REFERENCES

1. Black, D. St.C., Bowyer, M.C., Condie, G.C., Craig, D.C., and Kumar, N., *Tetrahedron*, 1994, vol. 50, p. 10983.
2. Rostami-Charati, F., Hossaini, Z., Khalilzadeh, M.A., and Jafaryan, H., *J. Heterocycl. Chem*., 2012, vol. 49, p. 217.
3. Bhaskar, G., Arun, Y., Balachandran, C., Saikumar, C., and Perumal, P.T., *Eur. J. Med. Chem*., 2012, vol. 51, p. 79.
4. Velikorodov, A.V. and Stepkina, N.N., *Russ. J. Org. Chem*., 2016, vol. 52, p. 1788.
5. Yavari, I., Seyfi, S., and Skoulika, S., *Helv. Chim. Acta*, 2012, vol. 95, p. 278.
6. Uma Devi, T., Priya, S., Selvanayagam, S., Ravikumar, K., and Anitha, K., *Spectrochim. Acta, Part A*, 2012, vol. 97, p. 1063.
7. Azizian, J., Karimi, A.R., Soleimani, E., Mohammadi, A.A., and Mohammadizadeh, M.R., *Heteroatom Chem*., 2006, vol. 17, p. 277.
8. Yavari, I., Adib, M., and Sayahi, M.H., *Tetrahedron Lett*., 2002, vol. 43, p. 2927.
9. Yavari, I., Arab-Salmanabadi, S., and Aminkhani, A., *J. Iran. Chem. Soc*., 2012, vol. 9, p. 503.
10. Malpani, Y., Achary, R., Kim, S.Y., Jeong, H.C., Kim, P., Han, S.B., Kim, M., Lee, C.-K., Kim, J.N., and Jung, Y.-C., *Eur. J. Med. Chem*., 2013, vol. 62, p. 534.
11. Harrison, W.T.A., Morrison, B.J., and Musgrave, O.C., *Tetrahedron*, 2004, vol. 60, p. 9255.
12. Mohammadizadeh, M.R. and Firoozi, N., *Tetrahedron Lett*., 2010, vol. 51, p. 2467.
13. Kuhn, R. and Hammer, I., *Chem. Ber*., 1951, vol. 84, p. 91.
14. Mohammadi Ziarani, G., Lashgari, N., Azimian, F., Kruger, H.G., and Gholamzadeh, P., *Arkivoc*, 2015, part (vi), p. 1.
15. Ramesh, E., Kathiresan, M., and Raghunathan, R., *Tetrahedron Lett*., 2007, vol. 48, p. 1835.
16. Kiruthika, S.E., Vidhya Lakshmi, N., Banu, B.R., and Perumal, P.T., *Tetrahedron Lett*., 2011, vol. 52, p. 6508.
17. Meshram, G., Wagh, P., Deshpande, S., and Amratlal, V., *Lett. Org. Chem*., 2013, vol. 10, p. 445.
18. Katritzky, A.R., Fan, W.-Q., Szajda, M., Li, Q.-L., and Kaster, K.S., *J. Heterocycl. Chem*., 1988, vol. 25, p. 591.
19. Aly, A.A., *J. Chem. Res*., 2011, vol. 35, p. 205.
20. Kundu, S.K., Pramanik, A., and Patra, A., *Synlett*, 2002, p. 823.
21. Abdel-Latif, E., Kaupp, G., and Metwally, M.A., *J. Chem. Res*., 2005, p. 187.
22. Ammar, Y.A., El-Sehrawi, H.M., El-Zahabi, H.S.A., Shawer, T.Z., and Ismail, M.M.F., *Pharma Chem*., 2012, vol. 4, p. 2140.
23. Kumar, V., Bell, M.R., Wetzel, J.R., Herrmann, J.L., McGarry, R., Schane, H.P., Winneker, R.C., Snyder, B.W., and Anzalone, A.J., *J. Med. Chem*., 1993, vol. 36, p. 3278.
24. Yavari, I., Hossani, Z., Sabbaghan, M., and Ghazanfarpour-Darjani, M., *Monatsh. Chem*., 2007, vol. 138, p. 677.
25. Klumpp, D.A., Fredrick, S., Lau, S., Jin, K.K., Bau, R., Surya Prakash, G.A., and Olah, G.A., *J. Org. Chem*., 1999, vol. 64, p. 5152.
26. Das, S., Fröhlich, R., and Pramanik, A., *Org. Lett*., 2006, vol. 8, p. 4263.
27. Na, J.E., GowriSankar, S., Lee, S., and Kim, J.N., *Bull. Korean Chem. Soc*., 2004, vol. 25, p. 569.
28. Kneubühler, S., Testa, B., Carta, V., Altomare, C., and Carotti, A., *Helv. Chim. Acta*, 1993, vol. 76, p. 1956.