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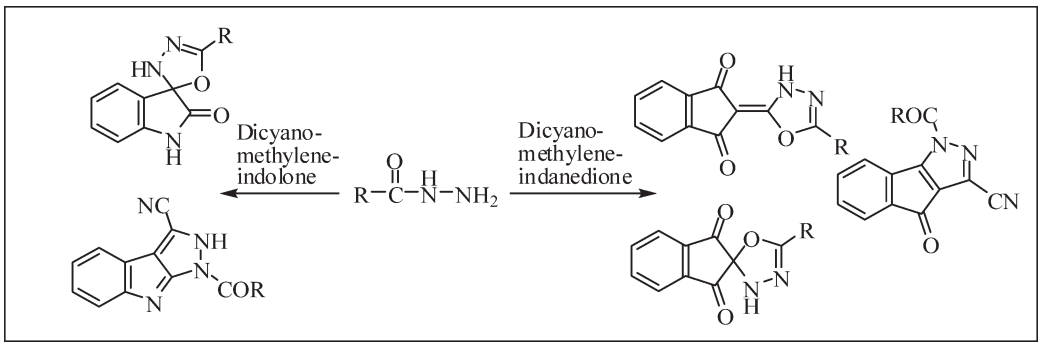

(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (**2**, in dimethylformamide solution), 3-(dicyanomethylene)-2-indolone (**3**, in ethanol/piperidine solution) act on substituted carbohydrazides **1a–e** forming the derivatives of oxadiazolylideneindene-1,3-diones **4a–e**, spiro(indene-2,2′-oxadiazole)-1,3-dione **5a–e**, cyloxoindenopyrazolecarbonitriles **6a–e**, spiro(indoline-3,2′-oxadiazol)-2-ones **11a–e**, and acylpyrazoloindoles **13a–e**. Rational for these conversions involving the nucleophilic addition on the dicyanomethylene carbon atom are presented.

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INTRODUCTION

In organic π-acceptors containing dicyanomethylene groups such as ethenetetracarbonitrile and (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (**2**), the nitrile groups can be substituted by the nucleophilic nitrogen atom of primary aromatic [1–3] and secondary aliphatic amines [4,5]. Tertiary aromatic amines (like *N*,*N*-dimethylaniline) are prone to attack to the C=C double bond of **2** with their *para*-position, followed by release of HCN [3,6–10]. By reaction of acceptor **2** with tertiary cyclic amines, one can generate the iminium ions and formation of the α-cyanated amines [11]. Additionally, the reaction of **2** with arylazoaminopyrazoles [12,13], 2-mercaptobenzazoles [14], thiocarbohydrazide, and thiocarbazones [15] as well as *N*-arylisoindolines [16] have been reported. Closely analogous 3-(dicyanomethylene)-2-indolone (**3**) [17] which is a ylidene malononitrile like **2** reacted with thiobarbituric acid [18], *S*,*S*- and *N*,*S*-acetals [19], cyclohexanedione [20], and another active methylene systems to give spiroheterocyclic compounds [21,22]. The reaction of *N*,*N*′-diarylacetamidines with **2** afforded indenoazepine-6-ones [23]. In contrast, spiro[2,3-dihydro-indol-3,4′-pyridino]-5′-carbonitriles were obtained from the reaction of *N*,*N*′-diarylacetamidines with **3** [23].

Recently, we have reported an efficient transformation of substituted acylhydrazinecarbothioamides with **2** and **3** into oxoindenopyrrolylidenehydrazide, thiazoloindolylidenehydrazide, and pyrroloindolylidenehyrazide derivatives [24].

These intriguing transformations led us to investigate the reaction of carbohydrazides **1a–e** bearing a selection of aromatic and heterocyclic substitutions with acceptor systems **2** and **3** (Fig. 1).

RESULTS AND DISCUSSION

Dimethylformamide solutions of **2** and substituted carbohydrazides **1a–e** in a molar ratio of 2:1 were stirred at room temperature for 48 h. Concentration of the reaction mixture yielded reddish brown crystals from 2-(5-substituted-1,3,4-oxadiazol-2(3*H*)-ylidene)-1*H*-indene-1,3-(2*H*)-diones **4a–e** (51–57%). The remaining soluble materials were subjected to preparative layer chromatography to give 5′-substituted spiro(indene-2,2′-[1,3,4]-oxadiazole)-1,3-dione **5a–e** (13–17%) and 1-acyl-4-oxo-indeno[1,2-*c*]pyrazole-3-carbonitriles **6a–e** (11–15%).

The structures of **4a–e** were delineated from their spectroscopic properties and gross compositions. The products **4a–e** resulted from **1a–e** were found to be

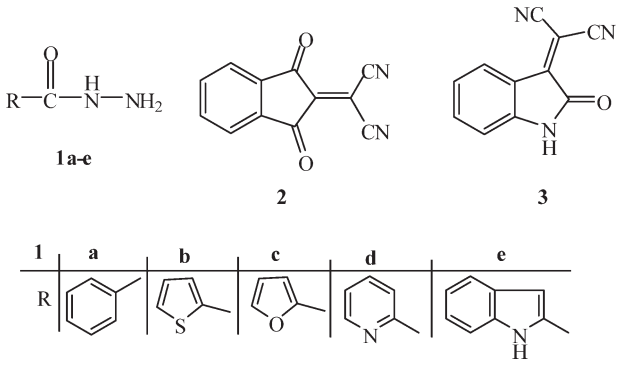
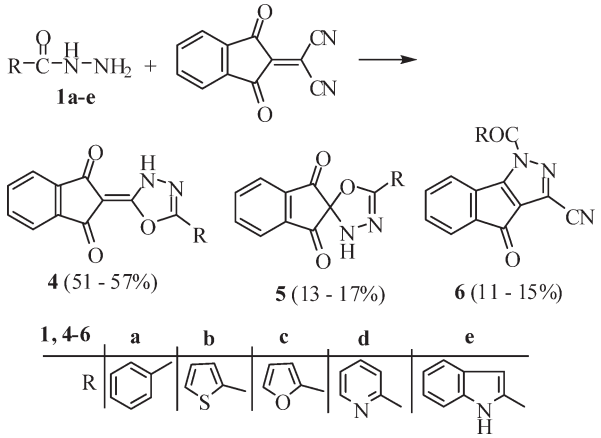


Figure 1. Substituted carbohydrazides and some electron acceptors.

formed by reacting one molecule of **1a–e** and one molecule of **2** *via* loss two molecules of HCN. The molecular ions in their EI-mass spectra confirm the molecular masses and the gross compositions. Furthermore, the following common features of the fragmentation patterns lend support to the assigned structures: Loss of RCO giving rise to the ion $m/z = 185$ common in the spectra of all five compounds. The resulting fragment ions undergo loss of 28 a.m.u. (dinitrogen or CO group). The ir spectra show characteristic absorptions for NH group in range 3330 to 3355 and carbonyl absorption at 1705–1720 cm^{-1} as expected for indane-1,3-dione ring system. Strong bands around 1080–1095 have to be assigned to C—O—C group [25].

The ^{1}H NMR spectra show the presence of a broad signal for 1H at $\delta = 12.57$–12.64 ppm due to oxadiazole-NH, and additionally, the expected signals for R groups. In the ^{13}C NMR spectrum of **4b**, the carbonyl groups resonate at 187.34 ppm. Further peaks at 91.64 (indene-C-2) [16], 154.55 (oxadiazole-C-5), and 174.26 (oxadiazole-C-2) lend support to the structures assigned to **4a–e** (Scheme 1).

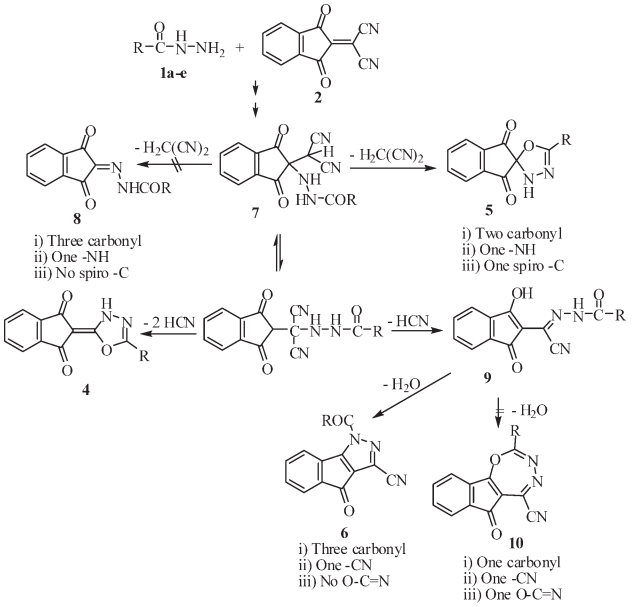
Scheme 1



Compounds **5a–e** show sharp absorptions characteristic of carbonyl group at 1725–1710, NH group at 3330–3315, C=N group at 1630–1620 cm^{-1}, as well as C—O—C group 1095–1080 cm^{-1}. The ^{1}H NMR spectrum (DMSO-d_6) of **5a** clearly shows the presence of oxadiazole-NH at ($\delta = 12.55$ ppm) and phenyl protons at ($\delta = 7.34$–8.12 ppm). The ^{13}C NMR of **5a** shows signals at $\delta = 103.67$ for (spiro-C-2,2′), 156.47 (C-5), and 187.42 (C-1,3), in addition to aryl carbons. The molecular formulae of compounds **5a–e** were supported by elemental analysis and mass spectra, which gave the expected molecular ion peaks. The alternative structure **8** (Scheme 2) based on the same elemental composition could be eliminated according to ir, ^{1}H NMR and ^{13}C NMR spectral data.

The results of combustion analysis and spectroscopic data suggested the presence of acyloxoindenopyrazole derivatives **6a–e** as one of the products from the reaction between **1a–e** and **2**. The gross formula, $C_{20}H_{10}N_4O_2$, **6e** was confirmed by the mass spectrum, which exhibited the molecular ion at m/z 338 (26%) and the fragmentation pattern at 312, 284, 144, 140, 104, 91, 77, and 65. The ir spectrum showed absorptions at 3365 (NH), 2220 (CN), and 1710, 1665 (CO). The ^{1}H NMR spectrum of **6e** displayed one broad singlet at 11.69 ppm for 1H (indole-NH) and another sharp singlet at 6.64 due to indole-CH in addition to the aromatic protons. In its ^{13}C NMR spectrum, C-3 and C-4 resonate at $\delta = 121.69$ and 189.31 ppm, respectively; further peaks are at $\delta = 99.91$ ppm (indole-CH), 105.06 (C-3a), 149.76 (C-8a), 167.72 acyl-CO, and cyano group at 118.11 ppm.

Scheme 2



Compound **10** (Scheme 2) could be ruled out, owing to the presence of acyl-CO signals in the ^{13}C NMR spectra. A rational for the formation of the products **4–6** is presented in scheme 2. The carbohydrazides **1a–e** and **2** give the neutral adduct **7**. Elimination of a molecule of malononitrile afforded compounds **5**, whereas elimination two molecules of HCN gave compounds **4**. Elimination one molecule of HCN from the adduct **7** afforded the intermediate **9** followed by elimination a molecule of H_2O to give oxoindenopyrazole derivatives **6**.

Reflux of one mole of **1a–e** with two equivalents of 3-(dicyanomethylene)-2-indolone (**3**) in ethanol/piperidine resulted in pink coloration of the solution, which later became yellowish brown. The residue remaining after concentration was subjected to preparative layer chromatography to give 5′-substituted-spiro[indoline-3,2′-1,3,4-oxadiazol]-2-one **11a–e** (64–71%) and 1-(substituted-2-carbonyl)-1,2-dihydro-pyrazolo[3,4-*b*]-indole-3-carbonitrile **13a–e** (21–26%) (Scheme 3).

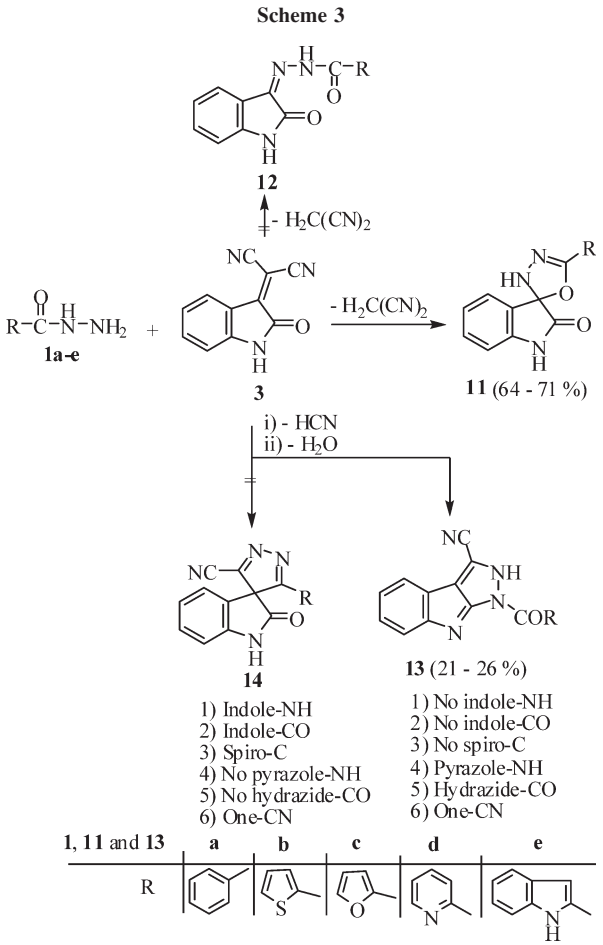
Compounds 11a–e. The EI-mass spectra of 11a–e are characterized by molecular ions of low intensity and loss of 28 a.m.u. (may be dinitrogen or carbonyl group) followed by loss of 144 a.m.u. from the molecular ion of 11e (probably indol-2-carbonyl). The ir spectrum showed absorption at 3325–3370 (NH's), 1720 (CO), 1090 (C-O-C). The ^1H NMR spectrum of 11e showed the presence of three broad signals with the ratio 1:1:1 centered at 9.81, 11.75, and 12.38 due to indolinone-NH, indole-NH, and oxadiazole -NH, respectively. Indole-CH resonate at 6.57 ppm in addition to the aromatic protons. Signals around 93.66 (spiro C-3 = C-2′), 101.96 (indole-CH), 154.84 (C-5′), and 177.90 (CO) in addition to the aromatic carbons.

The alternative structure **12** was ruled out based on mp, ir, ^1H NMR and ^{13}C NMR spectral data. It has been reported that **1a** and isatine were ball-milled at room temperature for 3 h to give **12a** [26] after drying at 0.01 bar at 80°C. Also, **12a** was obtained during the reaction of **1a** with isatine under reflux in MeOH [27].

Recently, it has been reported that under acetylating condition, isatine-3-acylhydrazones were transformed into selectively acylated derivatives and into the corresponding 3-acetyl-1,3,4-oxadiazolines [28].

Compounds 13a–e. Substituted carbonyl-1,2-dihydro-pyrazolo[3,4-*b*]indole-3-carbonitrile **13a–e** (21–26%), the ir spectrum of **13b** shown absorption bands characteristic of NH group at 3395 cm^{-1}, strong cyano group at 2215, and one carbonyl absorption at 1660 cm^{-1}. ^1H NMR spectrum of **13b** clearly supports the presence of broad signals centered at 11.98 ppm due to pyrazole-NH, aromatic, and thiophene protons were also observed. The ^{13}C NMR spectrum of **13b** exhibited a signal at δ = 169.64 for carbonyl group, 118.24 (CN), 102.36 (C-3a), and 148.66 (C-8a). Therefore, we will concentrate on the interplay between the formation of the products **13a–e** and alternative structure **14**. The a priori possible isomeric structures **14** were ruled out on the basis of ^1H NMR and ^{13}C NMR, which clearly support the presence of pyrazole-NH [29] and hydrazide-CO groups. Also, the spectral data showed the absence of indolone-CO, indolone-NH, and spiro-carbons [30].

Scheme 3



EXPERIMENTAL

Mps were determined with a Gallenkamp melting point apparatus and were uncorected. The ir spectra were recorded with a Shimadzu 408 instrument using potassium bromide pellets. Five hundred Megahertz ^1H and 125 MHz ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer. Chemical shifts are expressed as δ (ppm) with reference to tetramethylsilane as internal standard, br = broad, s =singlet, and m = multiplet. ^{13}C assignments (q = quaternary carbon atoms) were made with the aid DEPT 135/90 spectra. The mass spectra (70 eV, electron impact mode) were recorded on Varian MAT CH-7 instrument. Elemental analyses were carried out at the Microanalytical Center, Cairo University, Egypt. Preparative layer chromatography (PLC) was made using 48 cm × 20 cm glass plates covered with slurry

applied and air dried 1.0 mm thick layers of Merck silica gel Pf_{254}. Zones were detected by indicator fluorescence quenching upon 254 nm exposure, removed from plates, and extracted with cold acetone

Starting materials. Substituted carbohydrazides 1a–e were prepared according to published procedures [31–36], as were 2-thiophene carbo-hydrazide (1b), mp 135–137°C (lit. [31] 134–136°C); furan-2-carbohydrazide (1c), mp 77–79 (lit. [32] 78°C); 2-pyridine carbohydrazide (1d), mp 136–138°C (lit. [33] 137°C); indole-2-carbohydrazide (1e), mp 243–245°C (lit. [34–36] 246°C) and phenyl carbohydrazide (1a) (Aldrich) was used as received. 2-(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)pro-panedinitrile(dicyanomethyleneindane-1,3-dione) (2) was prepared according chatterjee [37], yellow crystals, mp 282–284°C with decomposition, black preheated to 260°C (lit. [37] 280–285°C with decomp.). 3-(Dicyanomethylene)-2-indolone (3) was prepared according to Fatiadi [17], brick-red needles, mp 235–236°C (lit. [17] 235–237°C).

Reactions of carbohydrazides 1a–e with (2). To a solution of **2** (416 mg, 2.0 mmol) in dry dimethylformamide (DMF) (15 mL), a solution of **1a–e** (1.0 mmol each) in 5 mL of DMF was added drop wise over 5 min at room temperature with stirring and admission of air for 3 h and left standing for 48 h at room temperature. Reddish brown crystals were precipitated, filtered, and washed with small amount of cold ethanol, which contains 2-(5-substituted-1,3,4-oxadiazol-2-(3*H*)-ylidene)-1*H*-indene-1,3-(2*H*)-diones (**4a–e**). The filtration was concentrated to dryness and dissolved in a few mL of acetone and subjected to PLC using toluene/ethyl acetate (2:1) to afford two zones. The fastest migrating fraction contained compounds **5a–e** and the slowest migrating zone contained **6a–e**.

2-(5-Phenyl-1,3,4-oxadiazol-2-(3*H*)-ylidene)-1*H*-indene-1,3-(2*H*)-dione (4a). This compound was obtained as reddish brown crystals (acetonitrile), mp 247–249°C; ir: NH 3340, CO 1710, C=N 1630, Aryl and C=C 1605, C—O—C 1085 cm^{-1}. ^1H NMR: δ 7.38–8.18 (m, 9H, Ar—H), 12.64 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 91.57 (indene-C-2), 126.31, 128.41, 129.67, 135.86, 138.17 (Ar—CH), 141.27, 143.67 (Ar—C), 154.67 (C-5), 174.34 (C-2), 187.38 (CO); ms: *m*/*z* 290 (M^+, 31), 185 (52), 153 (13), 105 (100), 104 (76), 77 (68), 65 (55). Anal. Calcd. for $C_{17}H_{10}N_2O_3$: C, 70.34; H, 3.47; N, 9.65. Found: C, 70.57; H, 3.39; N, 9.73.

2-(5-(Thiophen-2-yl)-1,3,4-oxadiazol-2-(3*H*)-ylidene)-1*H*-indene-1,3-(2*H*)-dione (4b). This compound was obtained as reddish brown crystals (acetonitrile), mp 270–272°C; ir: NH 3330, CO 1715, C=N 1625, Aryl and C=C 1600, C—O—C 1080; ^1H NMR: δ 7.19–8.16 (m, 7H, Ar—H and thiophene-H), 12.62 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 91.64 (indene-C-2), 126.14, 127.49, 129.57, 130.12, 135.66 (Ar—CH), 141.39, 144.15 (Ar—C), 154.55 (C-5), 174.26 (C-2), 187.34 (CO); ms *m*/*z*: 296 (M^+, 25), 185 (44), 111 (65), 104 (100), 76 (76), 65 (44). Anal. Calcd. for $C_{15}H_8N_2O_3S$: C, 60.80; H, 2.72; N, 9.45; S, 10.82. Found: C, 61.02; H, 2.86; N, 9.28; S, 11.03.

2-(5-(Furan-2-yl)-1,3,4-oxadiazol-2-(3*H*)-ylidene)-1*H*-indene-1,3-(2*H*)-dione (4c). This compound was obtained as reddish brown crystals (methanol), mp 228–230°C; ir: NH 3345, CO 1720, C=N 1620, Aryl and C=C 1605, C—O—C 1090; ^1H NMR: δ 7.14–8.21 (m, 7H, Ar—H and furan-H), 12.59 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 91.65 (indene-C-2), 126.03, 126.33, 127.41, 134.88 (Ar—CH and furan-CH), 140.97, 142.85, 143.66, 145.54 (Ar—C and furan-C-2, C-5), 155.12 (C-5), 174.16 (C-2), 187.83 (CO); ms *m*/*z*: 280 (M^+, 41), 185 (37), 104 (77), 95 (100), 76 (56), 65 (66). Anal. Calcd. for $C_{15}H_8N_2O_4$: C, 64.29; H, 2.88; N, 10.00. Found: C, 64.11; H, 3.04; N, 9.83.

2-(5-(Pyridine-2-yl)-1,3,4-oxadiazol-2-(3*H*)-ylidene)-1*H*-indene-1,3-(2*H*)-dione (4d). This compound was obtained as reddish brown crystals (methanol), mp 262–264°C; ir: NH 3355, CO 1705, C=N 1630, Aryl and C=C 1610, C—O—C 1095; ^1H NMR: δ 7.54–8.43 (m, 8H, Ar—H and pyridine-H), 12.57 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 91.48 (indene-C-2), 126.33, 126.84, 126.87, 136.33 (Ar—CH and pyridine-CH), 141.44, 143.59 (Ar—C), 147.14, 149.34 (pyridine-C-2, C-6), 155.12 (C-5), 174.32 (C-2), 187.66 (CO); ms *m*/*z*: 291 (M^+, 24), 185 (29), 106 (58), 104 (67), 76 (66), 65 (100). Anal. Calcd. for $C_{16}H_9N_3O_3$: C, 65.98; H, 3.11; N, 14.43. Found: C, 66.17; H, 2.98; N, 14.27.

2-(5-(1*H*-Indol-2-yl)-1,3,4-oxadiazol-2-(3*H*)-ylidene)-1*H*-indene-1,3-(2*H*)-dione (4e). This compound was obtained as reddish brown crystals (methanol), mp 291–293°C; ir: NH 3385–3340, CO 1720, C=N 1625, Aryl and C=C 1590, C—O—C 1095; ^1H NMR: δ 6.58 (s, 1H, indole-CH), 7.09–8.13 (m, 8H, Ar—H), 11.69 (br, 1H, indole-NH), 12.61 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 91.76 (indene-C-2), 102.12 (indole-CH), 125.23 (indole-C-2), 126.27, 127.96, 135.78, 138.26 (Ar—CH), 140.22, 141.38, 142.57, 143.81 (Ar—C), 155.06 (C-5), 174.47 (C-2), 187.71 (CO); ms *m*/*z*: 329 (M^+, 39), 225 (23), 185 (34), 144 (41), 104 (74), 91 (57), 76 (100), 65 (69). Anal. Calcd. for $C_{19}H_{11}N_3O_3$: C, 69.30; H, 3.37; N, 12.76. Found: C, 69.13; H, 3.25; N, 12.95.

5′-Phenyl-3′*H*-spiro(indene-2,2′-[1,3,4]oxadiazole)-1,3-dione (5a). This compound was obtained as yellow crystals (ethanol), mp 206–208°C; ir: NH 3325, CO 1715, C=N 1625, Ar—C=C 1595, C—O—C 1090; ^1H NMR: δ 7.34–8.12 (m, 9H, Ar—H), 12.55 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 103.67 (C-2,2′), 126.27, 126.56, 128.31, 129.26, 130.44 (Ar—CH), 132.84, 134.71 (Ar—C), 156.47 (C-5′), 187.42 (C-1,3); ms *m*/*z*: 278 (M^+, 34), 250 (49), 145 (67), 105 (89), 104 (59), 77 (100), 65 (71); Anal. Calcd. for $C_{16}H_{10}N_2O_3$: C, 69.06; H, 3.62; N, 10.07. Found: C, 68.84; H, 3.73; N, 9.88.

5′-(Thiophen-2-yl)-3′*H*-spiro(indene-2,2′-[1,3,4]oxadi-azole)-1,3-dione (5b). This compound was obtained as yellow crystals (ethanol), mp 227–228°C; ir: NH 3315, CO 1710, C=N 1620, Ar—C=C 1600, C—O—C 1080; ^1H NMR: δ 7.23–8.15 (m, 7H, Ar—H and thiophene-H), 12.51 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 103.69 (C-2,2′), 126.36, 126.72, 127.94, 128.66, 130.46 (Ar—CH and thiophene-CH), 132.82, 134.66 (Ar—C and thiophene-C), 156.39 (C-5′), 187.47 (C-1,3); ms *m*/*z*: 284 (M^+, 41), 256 (17), 145 (46), 111 (100), 104 (73), 77 (64), 65 (55); Anal. Calcd. for $C_{14}H_8N_2O_3S$: C, 59.15; H, 2.84; N, 9.85; S, 11.28. Found: C, 58.89; H, 2.92; N, 10.03; S, 11.05.

5′-(Furan-2-yl)-3′*H*-spiro(indene-2,2′-[1,3,4]oxadiazole)-1,3-dione (5c). This compound was obtained as yellow crystals (acetonitrile), mp 189–190°C; ir: NH 3320, CO 1710, C=N 1625, C—O—C 1100, 1080; ^1H NMR: δ 7.26–8.15 (m, 7H, Ar—H and furan-H), 12.54 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 103.71 (C-2,2′), 125.97, 126.43, 126.42, 130.34 (Ar—CH and furan-CH), 134.26 (Ar—C), 140.96, 141.88 (furan-C-2, C-5), 156.47 (C-5′), 187.55 (C-1,3); ms *m*/*z*: 268 (M^+, 33), 240 (21), 145 (28), 104 (67), 95 (81), 77 (100), 65 (49); Anal. Calcd. for $C_{14}H_8N_2O_4$: C, 62.69; H, 3.01; N, 10.44. Found: C, 62.46; H, 2.94; N, 10.67.

5′-(Pyridin-2-yl)-3′*H*-spiro(indene-2,2′-[1,3,4]oxadiazole)-1,3-dione (5d). This compound was obtained as orange crystals (acetonitrile), mp 214–216°C, ir: NH 3330, CO 1715, C=N 1630, C—O—C 1095; ^{1}H NMR: δ 7.28–8.46 (m, 8H, Ar—H and pyridine-H), 12.50 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 103.55 (C-2,2′), 126.11, 126.47, 126.96, 130.54, 132.16 (Ar—CH and pyridine-CH), 134.71 (Ar—C), 147.93, 148.67 (pyridine-C2, C6), 156.79 (C-5′), 187.56 (C-1,3); ms *m*/*z*: 279 (M^+, 51), 251 (26), 145 (55), 106 (67), 104 (89), 78 (100), 77 (92), 65 (41); Anal. Calcd. for $C_{15}H_9N_3O_3$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.71; H, 3.36; N, 14.87.

5′-(1*H*-Indol-2-yl)-3′*H*-spiro(indene-2,2′-[1,3,4]oxadi-azole)-1,3-dione (5e). This compound was obtained as orange crystals (methanol), mp 283–285°C; ir: 3380-NH 3325, CO 1710, C=N 1630, C—O—C 1095; ^{1}H NMR: δ 6.61 (s, 1H, indole-H), 7.19–8.22 (m, 8H, Ar—H), 11.71 (br, 1H, indole-NH), 12.53 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 99.76 (indole-CH), 103.42 (C-2,2′), 122.87 (indole-CH-2), 125.88, 126.29, 126.44, 127.63, 128.41, 130.55 (Ar—CH), 132.77, 133.52, 134.89 (Ar—C), 156.36 (C-5′), 187.64 (C-1,3); ms *m*/*z*: 317 (M^+, 18), 289 (26), 144 (57), 145 (37), 116 (29), 104 (76), 91 (89), 77 (100), 65 (71); Anal. Calcd. for $C_{18}H_{11}N_3O_3$: C, 68.14; H, 3.49; N, 13.24. Found: C, 67.88; H, 3.36; N, 13.45.

1-Benzoyl-4-oxo-1,4-dihydroindeno[1,2-*c*]pyrazole-3-carbonitrile (6a). This compound was obtained as pale yellow crystals (acetonitrile), mp 273–275°C; ir: Ar—CH 3090, CN 2215, CO (1720, 1660), C=N 1620, Ar—C=C 1590; ^{1}H NMR: δ 7.31–8.21 (m, 9H, Ar—H); ^{13}C NMR: δ 105.12 (C-3a), 118.12 (CN), 121.75 (C-3), 126.76, 126.94, 127.85, 129.22, 130.12, 130.41 (Ar—CH), 132.18, 134.71 (Ar—C), 149.53 (C-8b), 167.54 (CO), 189.27 (C-4); ms *m*/*z*: 299 (M^+, 26), 273 (16), 245 (41), 140 (61), 105 (100), 104 (74), 77 (56), 65 (64); Anal. Calcd. for $C_{18}H_9N_3O_2$: C, 72.24; H, 3.03; N, 14.04. Found: C, 72.39; H, 2.89; N, 13.83.

4-Oxo-1-(thiophene-2-carbonyl)-1,4-dihydroindeno[1,2-*c*]pyrazole-3-carbonitrile (6b). This compound was obtained as pale yellow crystals (ethanol), mp 296–298°C; ir: Ar—CH 3105, CN 2220, CO (1715, 1665), C=N 1620, Ar—C=C 1590; ^{1}H NMR: δ 7.22–8.16 (m, 7H, Ar—H and thiophene-H); ^{13}C NMR: δ 104.96 (C-3a), 118.19 (CN), 121.71 (C-3), 126.75, 128.45, 129.97, 130.26, 130.54 (Ar—CH and thiophene-CH), 132.28 (Ar—C), 139.26 (thiophene-C), 149.67 (C-8b), 167.49 (CO), 189.34 (C-4); ms *m*/*z*: 305 (M^+, 22), 279 (19), 251 (46), 140 (41), 111 (100), 104 (83), 77 (69), 65 (59); Anal. Calcd. for $C_{16}H_7N_3O_2S$: C, 62.94; H, 2.31; N, 13.76; S, 10.50. Found: C, 63.19; H, 2.43; N, 13.54; S, 10.68.

1-(Furan-2-carbonyl)-4-oxo-1,4-dihydroindeno[1,2-*c*]-pyrazole-3-carbonitrile (6c). This compound was obtained as pale yellow crystals (ethanol), mp 265–267°C; ir: Ar—CH 3085, CN 2210, CO (1715, 1660), C=N 1615, Ar—C=C 1585, C—O—C 1085; ^{1}H NMR: δ 7.31–8.15 (m, 7H, Ar—H and furan-H); ^{13}C NMR: δ 105.09 (C-3a), 118.22 (CN), 121.68 (C-3), 125.94, 126.35, 128.90, 130.56 (Ar—C and furan-C), 141.18, 142.26 (furan-C-2, C-5), 149.74 (C-8b), 167.61 (CO), 189.28 (C-4); ms: *m*/*z* 289 (M^+, 39), 253 (22), 225 (32), 130 (29), 104 (74), 95 (81), 77 (100), 65 (61); $C_{16}H_7N_3O_3$: C, 66.44; H, 2.44; N, 14.53. Found: C, 66.27; H, 2.57; N, 14.71.

4-Oxo-1-picolinoyl-1,4-dihydroindeno[1,2-*c*]pyrazole-3-carbonitrile (6d). This compound was obtained as yellow crystals (acetonitrile), mp 284–286°C; ir: Ar—CH 3115, CN 2215, CO (1715, 1665), C=N 1620, Ar—C=C 1590; ^{1}H NMR: δ 7.28–8.49 (m, 8H, Ar—H and pyridine-H); ^{13}C NMR: δ 104.92 (C-3a), 118.12 (CN), 121.74 (C-3), 126.32, 126.53, 127.19, 127.44, 130.47, 132.22 (Ar—CH and pyridine-CH), 134.65 (Ar—C), 148.11, 148.72 (pyridine-C-2, C6), 149.79 (C-8b), 167.70 (CO), 189.29 (C-4); ms: *m*/*z* 300 (M^+, 28), 274 (9), 246 (19), 140 (38), 106 (100), 104 (91), 77 (83), 65 (54). Anal. Calcd. for $C_{17}H_8N_4O_2$: C, 68.00; H, 2.69; N, 18.66. Found: C, 67.78; H, 2.78; N, 18.83.

1-(1*H*-Indole-2-carbonyl)-4-oxo-1,4-dihydroindeno[1,2-*c*]pyrazole-3-carbonitrile (6e). This compound was obtained as yellow crystals (methanol), mp 311–313°C; ir: NH 3365, CN 2220, CO (1710, 1665), C=N 1625, Ar—C=C 1595; ^{1}H NMR: δ 6.64 (s, 1H, indole-H), 7.28–8.19 (m, 8H, Ar—H), 11.69 (br, 1H, indole-NH); ^{13}C NMR: δ 99.91 (indole-CH), 105.06 (C-3a), 118.19 (CN), 121.69 (C-3), 126.12, 126.22, 126.45, 126.86, 127.61, 128.22, 130.51 (Ar—CH), 132.69, 134.18, 134.87, 135.29 (Ar—C), 149.76 (C-8b), 167.72 (CO), 189.31 (C-4); ms: *m*/*z* 338 (M^+, 27), 312 (21), 284 (46), 144 (87), 140 (51), 104 (79), 91 (100), 77 (82), 65 (43); Anal. Calcd. for $C_{20}H_{10}N_4O_2$: C, 71.00; H, 2.98; N, 16.56. Found: C, 70.83; H, 3.11; N, 16.77.

Reaction of carbohydrazides 1a–e with 3. Carbohydrazides **1a–e** (1.0 mmol) were dissolved in 20 mL absolute ethanol with two drops of pipridine and added to the indolone **3** (1 mmol) in 25 mL absolute ethanol, the mixture was heated under reflux for 5 h (for runs **1a–c** with **3**), and 7 h (for runs **1d**,**e** with **3**), cooled to room temperature. Concentrated and subjected to PLC using toluene/ethyl acetate (4:1) to give numerous colored zones, the two intense of which were removed and extracted. The fastest migrating one contained substituted spiro(indoline-3,2′-[1,3,4]oxadiazol)-2-one **11a–e**, the second zone contained substituted carbonylpyrazolo[3,4-*b*]indole-3-carbonitrile **13a–e**. Extraction of the zones with acetone and crystallized.

5′-Phenyl-3′*H*-spiro(indoline-3,2′-[1,2,4]oxadiazol)-2-one (11a). This compound was obtained as yellow crystals (ethanol), mp 231–233°C; ir: NH's 3310–3380, CO 1710, C=N 1620, Ar and C=C 1600, C—O—C 1085; ^{1}H NMR: δ 7.22–7.82 (m, 9H, Ar—H), 9.89 (br, 1H, indolone-NH), 12.56 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 93.74 (C-3 = C-2′), 126.54, 127.17, 127.94, 128.76, 131.24, 132.16 (Ar—CH), 135.33, 138.19, 142.55 (Ar—C), 154.85 (C-5′), 177.98 (CO); ms: *m*/*z* 265 (M^+, 36), 237 (17), 132 (56), 119 (68), 105 (74), 91 (82), 77 (100), 65 (42); Anal. Calcd. for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found: C, 68.16; H, 4.02; N, 16.05.

5′-(Thiophen-2-yl)-3′*H*-spiro(indoline-3,2′-[1,2,4]oxadi-azol)-2-one (11b). This compound was obtained as yellow crystals (acetonitril), mp 259–261°C; ir: NH's 3330–3375, CO 1720, C=N 1625, Ar and C=C 1590, C—O—C 1080; ^{1}H NMR: δ 7.11–7.74 (m, 7H, Ar—H and thiophene-H), 9.93 (br, 1H, indolone-NH), 12.46 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 93.65 (C-3 = C-2′), 126.17, 127.37, 127.88, 129.17, 130.17, 131.44 (Ar—CH and thiophene-CH), 132.16, 137.95, 142.35 (Ar—C and thiophene-C), 155.12 (C-5′), 178.09 (CO); ms: *m*/*z* 271 (M^+, 37), 139 (42), 119 (25), 111 (100), 91 (63), 77 (87), 65 (56); Anal. Calcd. for $C_{13}H_9N_3O_2S$: C, 57.55; H, 3.34; N, 15.49; S, 11.82. Found: C, 57.77; H, 3.21; N, 15.26; S, 12.06.

5′-(Furan-2-yl)-3′*H*-spiro(indoline-3,2′-[1,2,4]oxadiazol)-2-one (11c). This compound was obtained as pale yellow crystals (ethanol), mp 218–219°C; ir: NH's 3315–3380, CO 1715,

C=N 1620, Ar and C=C 1595, C—O—C 1085; ^{1}H NMR: δ 7.08–7.69 (m, 7H, Ar—H and furan-H), 9.90 (br, 1H, indolone-NH), 12.48 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 93.68 (C-3 = C-2′), 125.87, 126.82, 128.76, 129.97, 130.18 (Ar—CH and furan-CH), 132.76, 141.55, 141.96, 144.12 (Ar—C and furan-C-2, C-5), 155.29 (C-5′), 177.84 (CO); ms *m*/*z* 255 (M^+, 27), 227 (23), 142 (19), 119 (26), 85 (69), 91 (82), 77 (100), 65 (44); Anal. Calcd. for $C_{13}H_9N_3O_3$: C, 61.18; H, 3.55; N, 16.46. Found: C, 60.94; H, 3.64; N, 16.65.

5′-(Pyridin-2-yl)-3′*H*-spiro(indoline-3,2′-[1,2,4]oxadiazol)-2-one (11d). This compound was obtained as yellow crystals (acetonitril), mp 236–235°C; ir: NH's 3325–3380, CO 1725, C=N 1630, Ar and C=C 1600, C—O—C 1080; ^{1}H NMR: δ 7.24–8.46 (m, 8H, Ar—H and pyridine-H), 9.86 (br, 1H, indolone-NH), 12.49 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 93.75 (C-3 = C-2′), 126.26, 126.53, 127.79, 128.88, 130.16, 130.35 (Ar—CH and pyridine-CH), 132.19, 141.76 (Ar—C), 147.23, 148.89 (pyridine-C-2, C-6), 155.28 (C-5′), 178.05 (CO); ms: *m*/*z* 266 (M^+, 22), 160 (36), 132 (28), 119 (41), 106 (100), 91 (57), 77 (83), 65 (61); Anal. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 62.92; H, 3.91; N, 20.88.

5′-(1H-Indol-2-yl)-3′*H*-spiro(indoline-3,2′-[1,2,4]oxadi-azol)-2-one (11e). This compound was obtained as orange crystals (methanol), mp 187–188°C; ir: NH's 3290–3370, CO 1720, C=N 1630, Ar and C=C 1605, C—O—C 1090; ^{1}H NMR: δ 6.57 (indole-CH), 7.02–7.74 (m, 8H, Ar—H), 9.81 (br, 1H, indolone-NH), 11.75 (br, 1H, indole-NH), 12.55 (br, 1H, oxadiazole-NH); ^{13}C NMR: δ 93.66 (C-3 = C-2′), 101.96 (indole-CH), 126.26, 127.53, 128.82, 129.96, 130.31, 130.45 (Ar—CH), 132.26, 135.26, 138.92, 141.22, 142.11 (Ar—C and indole-C-2), 154.89 (C-5′), 177.90 (CO); ms: *m*/*z* 304 (M^+, 33), 276 (31), 144 (28), 132 (26), 119 (54), 91 (100), 77 (67), 65 (41); Anal. Calcd. for $C_{17}H_{12}N_4O_2$: C, 67.10; H, 3.97; N, 18.41. Found: C, 66.87; H, 4.12; N, 18.18.

1-Benzoyl-1,2-dihydropyrazolo[3,4-*b*]indole-3-carbonitrile (13a). This compound was obtained as pale yellow crystals (methanol), mp 279–281°C; ir: NH 3410, CN 2210, CO 1665, C=N 1625, Ar and C=C 1590; ^{1}H NMR: δ 7.34–7.96 (m, 9H, Ar—H), 11.96 (br, 1H, pyrazole-NH); ^{13}C NMR: δ 101.86 (C-3a), 118.16 (CN), 126.37, 126.89, 128.85, 129.71, 130.16, 130.97, 132.12 (Ar—CH and C-3), 136.33, 138.91, 141.74, 142.23 (Ar—C), 150.33 (C-8a), 169.44 (CO); ms: *m*/*z* 286 (M^+, 54), 181 (37), 154 (42), 126 (18), 105 (62), 91 (75), 77 (100), 65 (64); Anal. Calcd. for $C_{17}H_{10}N_4O$: C, 71.32; H, 3.52; N, 19.57. Found: C, 71.55; H, 3.39; N, 19.35.

1-(Thiophene-2-carbonyl)-1,2-dihydropyrazolo[3,4-*b*]-indole-3-carbonitrile (13b). This compound was obtained as pale yellow crystals (acetonitrile), mp 295–297°C; ir: NH 3395, CN 2215, CO 1660, C=N 1630, Ar and C=C 1600; ^{1}H NMR: δ 7.23–7.90 (m, 7H, Ar—H and thiophene-H), 11.98 (br, 1H, pyrazole-NH); ^{13}C NMR: δ 102.05 (C-3a), 118.24 (CN), 126.56, 126.84, 128.33, 129.61, 130.23, 130.85, 132.26 (Ar—CH, thiophene-CH and C-3), 135.89, 142.33, 146.13 (Ar—C and thiophene-C-2), 149.98 (C-8a), 169.64 (CO); ms: *m*/*z* 292 (M^+, 28), 181 (12), 153 (31), 126 (24), 111 (100), 91 (47), 77 (63), 65 (55); Anal. Calcd. for $C_{15}H_8N_4OS$: C, 61.63; H, 2.76; N, 19.17; S, 11.16. Found: C, 61.84; H, 2.63; N, 18.91; S, 10.97.

1-(Furan-2-carbonyl)-1,2-dihydropyrazolo[3,4-*b*]indole-3-carbonitrile (13c). This compound was obtained as pale yellow crystals (ethanol), mp 261–263°C; ir: NH 3390, CN 2220, CO 1665, C=N 1625, Ar and C=C 1585, C—O—C 1090; ^{1}H NMR: δ 7.31–7.96 (m, 7H, Ar—H and furan-H), 11.95 (br, 1H, pyrazole-NH); ^{13}C NMR: δ 101.93 (C-3a), 117.97 (CN), 126.44, 128.57, 129.64, 130.26, 130.86, 132.42 (Ar—CH, furan-CH and C-3), 135.57, 141.84, 145.33, 147.87 (Ar—C and furan-C-2, C-5), 150.14 (C-8a), 169.36 (CO); ms: *m*/*z* 276 (M^+, 39), 181 (23), 154 (33), 126 (18), 95 (84), 91 (100), 77 (67), 65 (52); Anal. Calcd. for $C_{15}H_8N_4O_2$: C, 65.22; H, 2.92; N, 20.28. Found: C, 65.41; H, 3.05; N, 20.07.

1-Picolinyl-1,2-dihydropyrazolo[3,4-*b*]indole-3-carbonitrile (13d). This compound was obtained as yellow crystals (acetonitrile), mp 290–292°C; ir: NH 3405, CN 2220, CO 1655, C=N 1630, Ar and C=C 1610; ^{1}H NMR: δ 7.33–8.41 (m, 8H, Ar—H and pyridine-H), 11.93 (br, 1H, pyrazole-NH); ^{13}C NMR: δ 102.12 (C-3a), 118.27 (CN), 126.45, 127.44, 128.55, 129.79, 130.16, 131.26, 132.19 (Ar—CH, pyridine-CH and C-3), 135.76, 141.88 (Ar—C), 148.92, 150.12, 151.64 (pyridine-C-2, C-6 and C-8a), 169.77 (CO); ms: *m*/*z* 287 (M^+, 43), 181 (18), 154 (25), 126 (13), 106 (75), 91 (100), 77 (83), 65 (66); Anal. Calcd. for $C_{16}H_9N_5O$: C, 66.89; H, 3.16; N, 24.38. Found: C, 67.04; H, 3.02; N, 24.21.

1-(1*H*-Indole-2-carbonyl-1,2-dihydropyrazolo[3,4-*b*]indole-3-carbonitrile (13e). This compound was obtained as yellow crystals (methanol), mp 304–306°C; ir: NH's 3290–3415, CN 2215, CO 1660, Ar and C=C 1595; ^{1}H NMR: δ 6.62 (s, 1H, indole-H), 7.18–7.88 (m, 8H, Ar—H), 11.71 (br, 1H, indole-NH), 11.97 (br, 1H, pyrazole-NH); ^{13}C NMR: δ 101.94 (C-3a), 118.29 (CN), 123.87 (indole-CH), 126.37, 126.94, 128.54, 129.17, 130.29, 131.47, 132.31 (Ar—CH and C-3), 135.29, 138.77, 139.27, 140.81, 142.16 (Ar—C and indole-C-2), 149.93 (C-8a), 169.65 (CO); ms: *m*/*z* 325 (M^+, 46), 181 (27), 154 (28), 144 (86), 91 (92), 77 (100), 65 (55); Anal. Calcd. for $C_{19}H_{11}N_5O$: C, 70.15; H, 3.41; N, 21.53. Found: C, 69.93; H, 3.55; N, 21.31.

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