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# A novel method for the synthesis of 2-arylquinolin-4(1*H*)-ones

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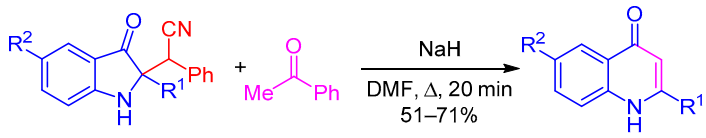



$R^1$ = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 3,4-$Me_2C_6H_3$; $R^2$ = H, Me, *i*-Pr

A simple one-pot method for the synthesis of 2-substituted quinolin-4(1*H*)-ones from synthetically accessible 2-(2-aryl(alkyl)-3-oxoindolin-2-yl)-2-phenylacetonitriles was developed.

**Keywords**: indolin-3-ones, quinolin-4(1*H*)-ones, cyclopropane, nucleophilic addition, ring expansion.

Quinolin-4(1*H*)-ones present a class of compounds that are first and foremost known for their wide spectrum of antibacterial activity. Drugs based on this structural fragment (Fig. 1) are actively used in human and veterinary medicine, especially in livestock and poultry farming.[1]

In addition to their wide range of antibacterial properties, other properties of natural and synthetic derivatives of quinolin-4(1*H*)-ones have been reported such as antiviral, antiparasitic, antifungal, and neuroprotective activity.[2–4] For example, the alkaloid graveoline of plant origin as well as a number of substituted 2-phenylquinolin-4(1*H*)-ones (Fig. 2) proved to be a promising anticancer agents,[5–7] acting on various stages (including apoptosis and autophagy) of the life of many human tumor cell lines. Data obtained from extensive biological activity studies[8–10] and structure–activity relationship studies[11] suggest that the antitumor activity of 2-phenylquinolin-4(1*H*)-ones is likely not related to a single position and arises from combinations of various substituents.

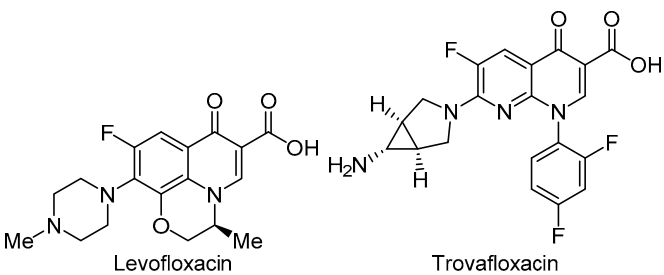



**Figure 1**. Fourth-generation fluoroquinolones.

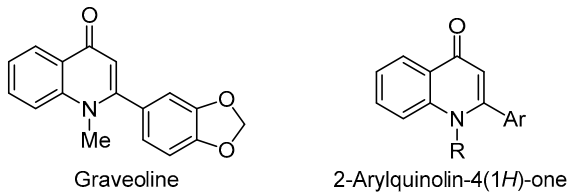


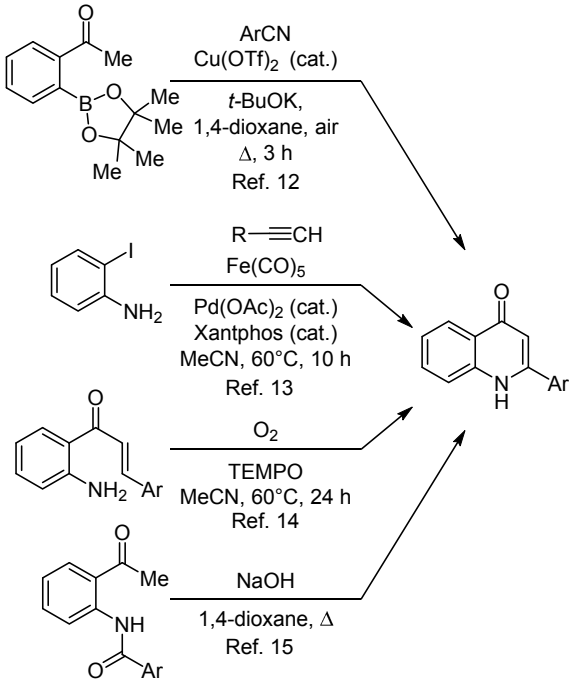

**Figure 2**. The structures of graveoline and 2-arylquinolin-4(1*H*)-one derivatives.

Considering the privileged position of these structures, the search for new methods for their synthesis is an urgent task for research. Several classical methods based on nucleophilic, metal-catalyzed, and oxidative cyclizations are known (Scheme 1).

However, the presented methods are limited by low tolerance to functional groups and, in some cases, by the need to use transition metal salt complexes. In this work, we propose a simple one-pot method for the synthesis of 2-aryl(alkyl)quinolin-4(1*H*)-ones by treating synthetically readily accessible 2-(2-aryl(alkyl)-3-oxoindolin-2-yl)-2-phenylacetonitriles **4**, obtained by the spirocyclization reaction of indoles **1** with β-nitrostyrenes **2** in an acidic medium[16,17] *via* intermediate spiroadducts **3**, with a catalytic amount of base (Scheme 2).

Some years earlier, we described a series of transformations of these 2-(2-aryl(alkyl)-3-oxoindolin-2-yl)-2-phenylacetonitriles **4** into various heterocycles **5**–**9** by the action of reducing agents,[18] aza-binucleophiles,[19,20] O-nucleophiles[21] (Scheme 3).

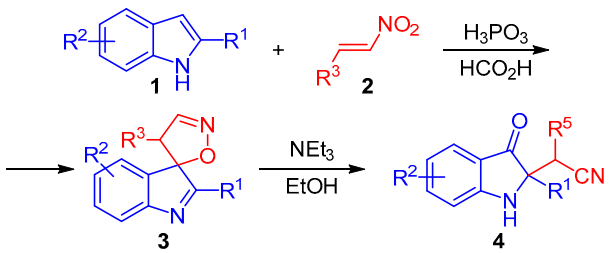
**Scheme 1**



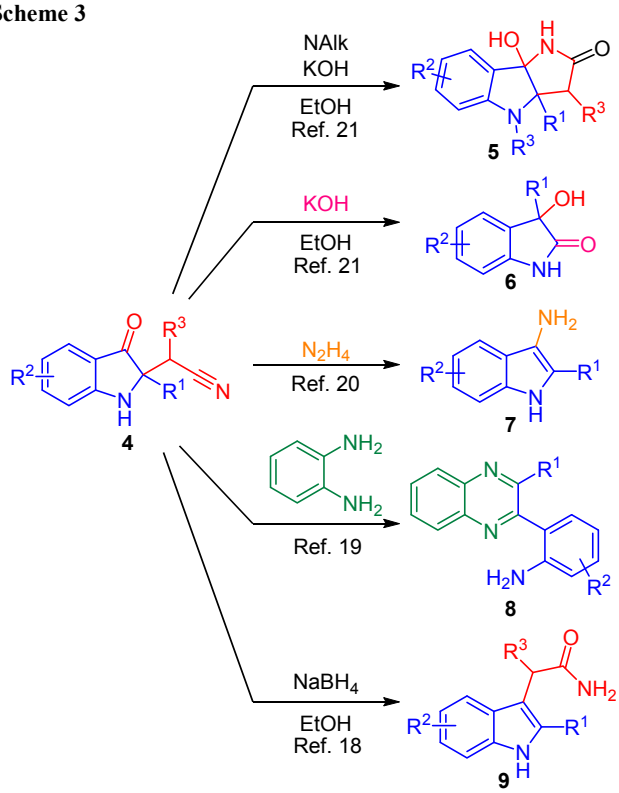

Previously, we also demonstrated an original rearrangement[22] of *N*-alkyl-2-(2-aryl-3-oxoindolin-2-yl)-2-phenylacetonitriles **4** into 2,3-diaryl-substituted quinolin-4(1*H*)-ones **10**. This transformation proceeds *via* deprotonation of the methylene proton CH followed by attack at the carbonyl group with the formation of a cyclopropane intermediate, the opening of which leads to the expansion of the pyrrole ring into the pyridin-4(1*H*)-one ring (Scheme 4).

Despite the efficacy of the rearrangement, it had a big drawback – the need to introduce an *N*-alkyl substituent, which required not only an additional synthetic alkylation step, but also significantly reduced the combined yield. It was also not applicable if quinolin-4(1*H*)-one with unsubstituted position 1 was the target. We assumed that replacing the benzyl cyanide fragment in the molecule of the starting cyano ketone **4a** with another one containing mobile CH protons would allow a similar rearrangement to occur leading to quinolones **10** substituted at position 3 with electron-withdrawing groups. Considering the tendency of 2-(2-aryl-3-oxoindolin-2-yl)-2-phenylacetonitriles **4** to lose the benzyl cyanide fragment in a basic medium, we attempted to add acetophenone (**12**) to 3*H*-indol-3-one **11** formed in this process followed by cascade cyclization of the α-carbonyl carbon of 1,4-diketone **13** at the C-3 atom of indolone (Scheme 5). The reaction was carried out in anhydrous DMF; NaH was chosen as the base since it had shown success in our previous work.[22]

**Scheme 2**



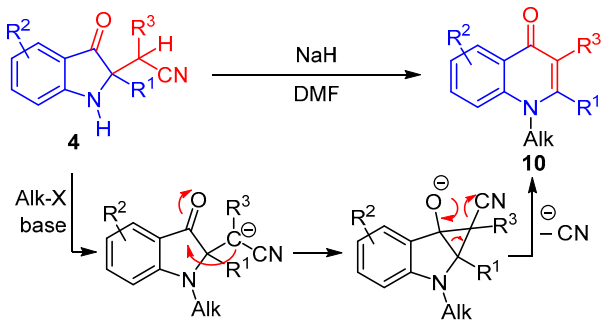

**Scheme 3**



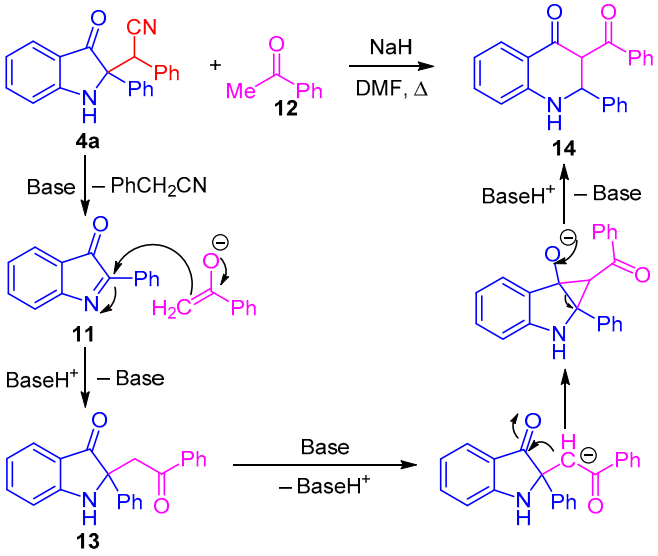

However, instead of the expected 3-benzoyl-2-phenyl-2,3-dihydroquinolin-4(1*H*)-one (**14**), 2-phenylquinolin-4(1*H*)-one (**16**) was the sole product detected in the reaction mixture. The probable mechanism of its formation is the retro-Claisen cleavage typical of 1,3-diketones leading to 2-phenyl-2,3-dihydroquinolin-4(1*H*)-one (**15**), the further oxidation of which in air led to 2-phenylquinolin-4(1*H*)-one (**16a**) (Scheme 6).

In the course of optimizing the reaction conditions, we attempted to preserve the benzoyl moiety by oxidizing 3-benzoyl-2-phenyl-2,3-dihydroquinolin-4(1*H*)-one (**14**) to the corresponding 3-benzoyl-2-phenyl-2,3-quinolin-4(1*H*)-one. $I_2$, $MnO_2$, and DDQ were tried as oxidizing agents; however, these attempts did not lead to the expected result but to a decrease in the yield of 2-phenylquinolin-4(1*H*)-one (**16a**) or to complete resinification of the reaction

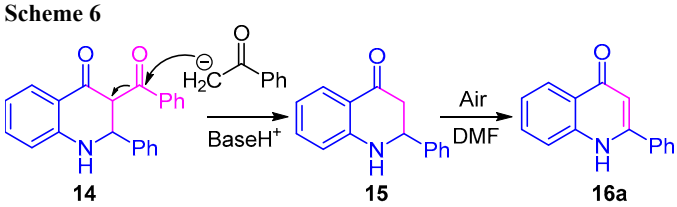
**Scheme 4**



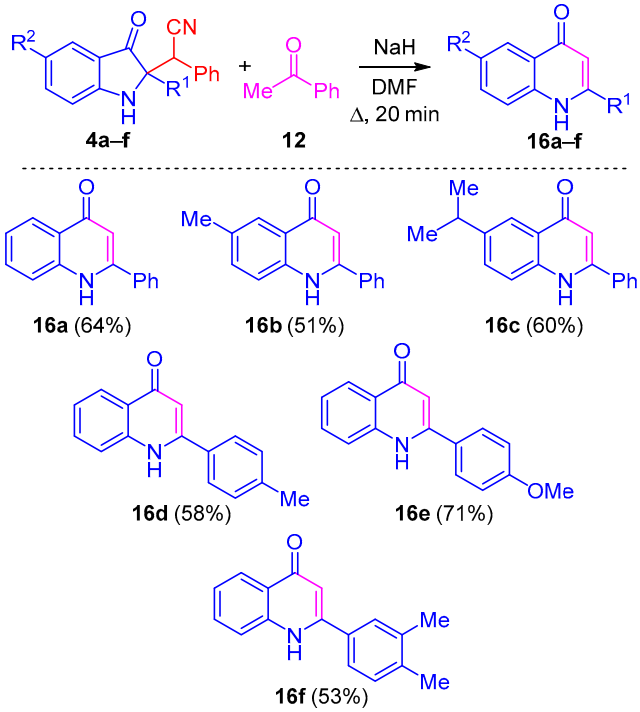
**Scheme 5**




**Scheme 6**




**Scheme 7**




mixture. Attempts to lower the reaction temperature and replace the base and solvent (Table 1) also failed. In solvents with low boiling points, low conversion of 1,4-diketone **13** was observed, indicating that intramolecular cyclization to form the cyclopropane intermediate requires a temperature close to the boiling point of DMF (153°C).

Having established the optimal conditions, we synthesized a number of 2-arylquinolin-4(1*H*)-ones **16a–f** in good yields (Scheme 7). It was found that the introduction of electron-donating substituents into the structure of the starting 2-(2-aryl-3-oxoindolin-2-yl)-2-phenylacetonitrile did not have a significant effect on either the reaction rate or yields.

To conclude, the presented work demonstrates a new method for the synthesis of 2-arylquinolin-4(1*H*)-ones, based on an original rearrangement of phenacyl-substituted indoxyls generated *in situ* from cyanobenzyl indoxyls. This method has extended the application of the methodology for the functionalization of cyclic acylimines to 3*H*-indol-3-ones, paving the way for the expansion of the 3-indolone ring to a 4-pyridone ring, which leads to the formation of structures of interest for further study of biological activity.

**Table 1**. Optimization of reaction conditions for the preparation of 3-benzoyl-2-phenyl-2,3-dihydroquinolin-4(1*H*)-one (**14**)

| Base | Temperature, °C | Solvent | Yield, % |
|---|---|---|---|
| **NaH** | **Reflux** | **DMF** | **64** |
| $Cs_2CO_3$ | Reflux | DMF | 49 |
| $Cs_2CO_3$ | Reflux | DMSO | 40 |
| $K_2CO_3$ | Reflux | EtOH | 10 |
| NaH | 100 | DMF | 15 |
| NaH | Reflux | 1,4-Dioxane | 19 |

## Experimental

IR spectra were registered on a Shimadzu IRAffinity-1S Fourier transform spectrometer with the ATR accessory with samples in thin-film cells. $^1$H and $^{13}$C NMR spectra were acquired on a Bruker Avance III HD spectrometer (400 and 101 MHz, respectively) in DMSO-$d_6$, with the residual solvent signals (2.50 ppm for $^1$H nuclei and 39.5 ppm for $^{13}$C nuclei) serving as internal standard. High-resolution mass spectra were recorded on a Bruker Maxis Impact spectrometer using a direct injection system, electrospray ionization, $HCO_2Na$–$HCO_2H$ calibrant. The progress of the reactions was monitored by TLC on ALUGRAM® Xtra SIL G UV 254 plates, eluent EtOAc–hexane, 1:2, visualization in UV light. The resulting compounds were purified on Macherey-Nagel 60 silica gel (0.04–0.063 mm). Melting points were determined on a Stuart SMP30 instrument.

The starting 2-(2-aryl-3-oxoindolin-2-yl)-2-phenylacetonitriles **4a–f** were obtained according to previously described methods.[16,17] The remaining compounds were acquired from commercial sources and were used without additional purification.

**Synthesis of 2-arylquinolin-4(1*H*)-ones 16a–e** (General method). 2-(2-Aryl-3-oxoindolin-2-yl)-2-phenylacetonitrile **4a–f** (1.0 mmol), acetophenone (**12**) (1.1 mmol, 132 mg), and DMF (2 ml) were charged into a 5-ml round-bottom flask equipped with a magnetic stir bar and a reflux condenser. NaH (60% dispersion in mineral oil; 80 mg, 2 mmol) was added to the reaction mixture in small portions while stirring at room temperature. After the addition of NaH was completed, the mixture was heated to

reflux and maintained at this temperature for 20 min. After cooling, the mixture was poured into $H_2O$ and acidified with a small amount of aqueous HCl. The resulting mixture was then extracted with EtOAc (3×25 ml), the combined organics were washed with saturated aqueous NaCl, and dried over $Na_2SO_4$. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica gel (eluent: EtOAc–hexane, 3:1).

**2-Phenylquinolin-4(1*H*)-one (16a)**. Yield 141 mg (64%), beige powder, mp 239–240°C (mp 240–242°C[23]), $R_f$ 0.17 (EtOAc–hexane, 4:1). IR spectrum, ν, $cm^{-1}$: 845, 1139, 1264, 1354, 1508, 1536, 1644, 2827, 2975, 3070. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 6.35 (1H, s, H Ar); 7.34 (1H, t, *J* = 7.4, H Ar); 7.56–7.60 (3H, m, H Ar); 7.65–7.70 (1H, m, H Ar); 7.78 (1H, d, *J* = 8.3, H Ar); 7.81–7.85 (2H, m, H Ar); 8.11 (1H, d, *J* = 8.0, H Ar); 11.77 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 107.4; 118.8; 123.4; 124.8; 124.9; 127.5 (2C); 129.1 (2C); 130.6; 131.9; 134.3; 140.6; 150.1; 177.1 (C=O). Found, *m*/*z*: 222.0910 $[M+H]^+$. $C_{15}H_{12}NO$. Calculated, *m*/*z*: 222.0913.

**6-Methyl-2-phenylquinolin-4(1*H*)-one (16b)**. Yield 120 mg (51%), pale-yellow powder, mp 290–291°C (mp 287–289°C[24]), $R_f$ 0.22 (EtOAc–hexane, 4:1). IR spectrum, ν, $cm^{-1}$: 1503, 1540, 1657, 1731, 1742, 1917, 2929. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.42 (3H, s, $CH_3$); 6.30 (1H, s, H Ar); 7.50 (1H, dd, *J* = 8.5, *J* = 1.8, H Ar); 7.56–7.60 (3H, m, H Ar); 7.67 (1H, d, *J* = 8.4, H Ar); 7.80–7.85 (2H, m, H Ar); 7.89 (1H, s, H Ar); 11.68 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 20.8 ($CH_3$); 107.1; 118.7; 124.0; 124.6; 127.4 (2C); 129.1 (2C); 130.4; 132.6; 133.3; 134.3; 138.6; 149.6; 176.8 (C=O). Found, *m*/*z*: 236.1070 $[M+H]^+$. $C_{16}H_{14}NO$. Calculated, *m*/*z*: 236.1070.

**6-Isopropyl-2-phenylquinolin-4(1*H*)-one (16c)**. Yield 158 mg (60%), white powder, mp 278–279°C, $R_f$ 0.28 (EtOAc–hexane, 4:1). IR spectrum, ν, $cm^{-1}$: 832, 1141, 1256, 1496, 1542, 1579, 1593, 1638, 2968. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.24 (6H, d, *J* = 6.4, $2CH_3$); 2.95–3.05 (1H, m, CH); 6.34 (1H, s, H Ar); 7.57 (4H, s, H Ar); 7.72 (1H, d, *J* = 7.9, H Ar); 7.83 (2H, s, H Ar); 7.95 (1H, s, H Ar); 11.74 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 23.9 ($2CH_3$); 33.2 (CH); 107.0; 118.9; 121.1; 124.8; 127.4 (2C); 129.0 (2C); 130.4; 131.0; 134.3; 139.0; 143.5; 149.7; 177.0 (C=O). Found, *m*/*z*: 264.1384 $[M+H]^+$. $C_{18}H_{18}NO$. Calculated, *m*/*z*: 264.1383.

**2-(4-Methylphenyl)quinolin-4(1*H*)-one (16d)**. Yield 136 mg (58%), beige powder, mp 263–264°C (mp 260–261°C[23]), $R_f$ 0.17 (EtOAc–hexane, 4:1). IR spectrum, ν, $cm^{-1}$: 811, 1020, 1143, 1249, 1443, 1470, 1498, 1539, 1578, 1593, 1632, 2802, 2894, 3063. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.40 (3H, s, $CH_3$); 6.33 (1H, s, H Ar); 7.33 (1H, t, *J* = 7.3, H Ar); 7.39 (2H, d, *J* = 8.0, H Ar); 7.64–7.69 (1H, m, H Ar); 7.74 (2H, d, *J* = 8.1, H Ar); 7.77 (1H, d, *J* = 8.4, H Ar); 8.09 (1H, dd, *J* = 8.1, *J* = 1.2, H Ar); 11.67 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 21.0 ($CH_3$); 107.0; 118.7; 123.3; 124.8; 124.9; 127.3 (2C); 129.6 (2C); 131.3; 131.8; 140.4; 140.6; 150.0; 177.0 (C=O). Found, *m*/*z*: 236.1072 $[M+H]^+$. $C_{16}H_{14}NO$. Calculated, *m*/*z*: 236.1070.

**2-(4-Methoxyphenyl)quinolin-4(1*H*)-one (16e)**. Yield 178 mg (71%), grey powder, mp 284–285°C (mp 288–290°C[23]), $R_f$ 0.14 (EtOAc–hexane, 4:1). IR spectrum, ν, $cm^{-1}$: 1025, 1249, 1539, 1574, 1615, 1650, 1689, 1872, 2855, 2918. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 3.84 (3H, s, $OCH_3$); 6.31 (1H, s, H Ar); 7.13 (2H, d, *J* = 8.9, H Ar); 7.32 (1H, t, *J* = 7.3, H Ar); 7.63–7.67 (1H, m, H Ar); 7.77 (1H, d, *J* = 8.3, H Ar); 7.81 (2H, d, *J* = 8.7, H Ar); 8.08 (1H, dd, *J* = 8.1, *J* = 1.3, H Ar); 11.62 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 55.5 ($OCH_3$); 106.5; 114.4 (2C); 118.7; 123.2; 124.7; 124.8; 126.3; 128.9; 131.7 (2C); 140.5; 149.7; 161.1; 176.9 (C=O). Found, *m*/*z*: 252.1015 $[M+H]^+$. $C_{16}H_{14}NO_2$. Calculated, *m*/*z*: 252.1019.

**2-(3,4-Dimethylphenyl)quinolin-4(1*H*)-one (16f)**. Yield 132 mg (53%), brown powder, mp 233–234°C (mp 229–231°C[23]), $R_f$ 0.25 (EtOAc–hexane, 4:1). IR spectrum, ν, $cm^{-1}$: 1021, 1140, 1258, 1360, 1435, 1470, 1495, 1544, 1583, 1597, 1634, 2855, 2918, 3258. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (3H, s, $CH_3$); 2.33 (3H, s, $CH_3$); 6.32 (1H, s, H Ar); 7.33 (2H, t, *J* = 7.3, H Ar); 7.56 (1H, d, *J* = 7.8, H Ar); 7.63 (1H, s, H Ar); 7.64–7.69 (1H, m, H Ar); 7.77 (1H, d, *J* = 8.3, H Ar); 8.09 (1H, dd, *J* = 8.1, *J* = 1.2, H Ar); 11.65 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 19.4 ($CH_3$); 19.5 ($CH_3$); 106.9; 118.7; 123.2; 124.8; 124.9 (2C); 128.2; 130.1; 131.6; 131.8; 137.1; 139.2; 140.6; 150.1; 177.0 (C=O). Found, *m*/*z*: 250.1225 $[M+H]^+$. $C_{17}H_{16}NO$. Calculated, *m*/*z*: 250.1226.

Supplementary information file containing $^1$H and $^{13}$C NMR and high-resolution mass spectra of compounds **16a–f** is available at the journal website http://link.springer.com/journal/10593.

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