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Synthesis of some Schiff Bases of 3-Aroyl-6-aryl-4-hydroxy-2 *H*-pyran-2-ones

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Summary. The reaction of 3-aroyl-6-aryl-4-hydroxy-2 *H*-pyran-2-ones (*Ar* = *p*-tolyl, 1,1′-biphenyl-4-yl or thienyl) with aniline and substituted *o*-phenylenediamine (*R* = H, CH_3 or Cl) yields a series of new Schiff bases **2a – f** in 51 – 72% yield. Bromination of **1a** gave the 5-bromo derivative **1c**, while the compounds **1a**, **1b**, **2b**, **2e**, and **2f** were converted into 2,6-diaryl-4 *H*-pyran-4-ones **3a – c**. All products have been fully characterized.

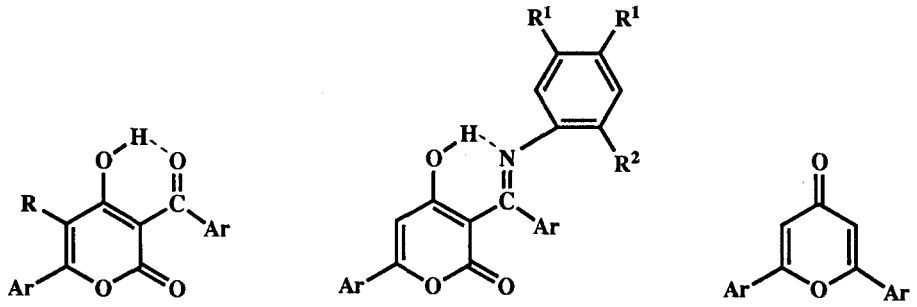
Keywords. Aniline; 3-Aroyl-6-aryl-4-hydroxy-2 *H*-pyran-2-ones; Schiff bases; Substituted *o*-phenylenediamines.

Synthese von Schiff'schen Basen von 3-Aroyl-6-aryl-4-hydroxy-2 *H*-pyran-2-onen

Zusammenfassung. Die Reaktion von 3-Aroyl-6-aryl-4-hydroxy-2 *H*-pyran-2-onen (*Ar* = *p*-Tolyl, 1,1′-Biphenyl-4-yl oder Thienyl) mit Anilin und substituierten *o*-Phenylendiaminen liefert neue Schiff'sche Basen **2a – f** in 51 – 72% Ausbeute. Bromierung von **1a** gab das 5-Bromderivate **1c**, während die Verbindungen **1a**, **1b**, **2b**, **2e** und **2f** in 2,6-Diaryl-4 *H*-pyran-4-onen **3a – c** übergeführt wurden. Alle Produkte wurden voll charakterisiert.

Introduction

During recent years we have maintained a strong interest in derivatives of 3-aroyl-6-aryl-4-hydroxy-2 *H*-pyran-2-ones with potential biological activity. Previous reports from our laboratories have described the effect of 4-hydroxy-3-(*p*-toluoyl)-6-(*p*-tolyl)-2 *H*-pyran-2-one (**1a**) and its 5-bromo derivative **1c** on bacteria, yeast and moulds. Compound **1c** significantly inhibited growth of all tested microorganisms especially growth and aflatoxin production of the aflatoxigenic mould *Aspergillus parasiticus* NRRL 2299 [1 – 3]. Continuing our investigation, we report now the synthesis of compounds **1a** and **1c** as well as the synthesis of some novel derivatives of 4-hydroxy-3-(*p*-toluoyl)-6-(*p*-tolyl)- (**1a**), 6-[(1,1′-biphenyl)-4-yl]-3-[1,1′-biphenyl)-4-ylcarbonyl]-4-hydroxy- (**1b**) and 4-hydroxy-3-(2-thenoyl)-5-(2-thienyl)-2 *H*-pyran-2-ones (**1d**) with bromine, aniline, *o*-phenylenediamine, 4,5-dichloro- and 4,5-dimethyl-*o*-phenylenediamine (Scheme 1).



1 **2** **3**

Scheme 1

Table 1.

	R	*Ar*		R^1	R^2	*Ar*		*Ar*
1a,	H	*p*-tolyl	**2a**,	H	H	*p*-tolyl	**3a**,	*p*-tolyl
1b,	H	(1,1'-biphenyl)-4-yl	**2b**,	H	NH_2	*p*-tolyl	**3b**,	(1,1'-biphenyl)-4-yl
1c,	Br	*p*-tolyl	**2c**,	Cl	NH_2	*p*-tolyl	**3c**,	2-thienyl
			2d,	CH_3	NH_2	*p*-tolyl		
			2e,	H	NH_2	(1,1'-biphenyl)-4-yl		
			2f,	H	NH_2	2-thienyl		
			4,	H	$NH(COCH_3)$	*p*-tolyl		

Results and Discussion

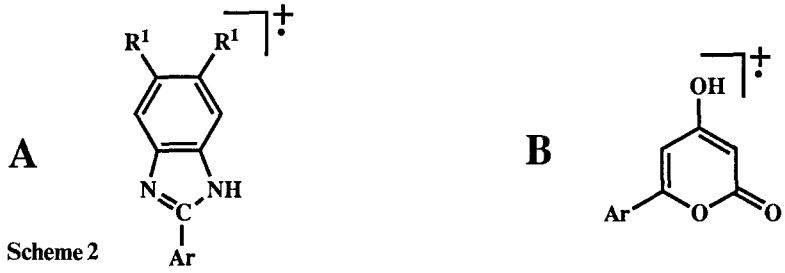
Compounds **1a** and **1b** were prepared by the oxidation of 1,6-diaryl-hexane-1,3,4,6-tetrones with lead tetraacetate in glacial acetic acid [4] in 77% and 54% yields, respectively; their chelated structure was established by reaction with metal ions [5].

The bromination of the compound **1a** in chloroform gave **1c** in fairly good yield (69%). The structure was particularly proved by loss of the ^{1}H-NMR-signal for H-5 in the 2*H*-pyran-2-one ring of **1a**.

Treatment of **1a** with aniline in hot ethanol afforded the Schiff base **2a** in 51% yield as the product of nucleophylic attack at the carbonyl group in the aroyl substituent at 3-position of the 2*H*-pyran-2-one ring. The ^{1}H-NMR spectra of **2a** revealed the hydroxyl proton at position 4 of the 2*H*-pyran-2-one ring.

By condensation of **1a**, **1b**, and **1d** with *o*-phenylenediamine, 3,4-dichloro- and 3,4-dimethyl-*o*-phenylenediamine the Schiff bases **2b**–**f** have been obtained by reacting only one amino group with the carbonyl group in the aroyl substituent of **1**. The benzimidazolines [6] or 1,5-benzodiazepines [7] were not obtained.

The IR spectra of **2b**–**f** compounds revealed evidence for the presence of the amino groups (3460–3220 cm^{-1}). Furthermore, the ^{1}H-NMR spectra showed signals for the NH_2 group ($\delta = 2.9-4.0$ ppm) and broad signals corresponding to the hydroxyl protons ($\delta = 15$ ppm). The mass spectra of **2b**–**e** exhibited characteristic fragmentations. The most characteristic ions observed were those of arylbenzimidazol **A** (base peak) and 6-aryl-4-hydroxy 2*H*-pyran-2-one **B** (Scheme 2).



Scheme 2

Refluxing the Schiff base **2b** in acetic acid for two hours gave 2 *H*-pyran-2-one, while heating of **2b**, **e** or **f** in a mixture of glacial acetic acid and concentrated hydrochloric acid (2 : 1) furnished 2,6-diaryl-4-pyran-4-ones **3a – c**. Their structures were proven by comparison with congeneric structures **3a** and **3b** derived from **1a** and **1b** [8].

Experimental Part

Melting points were determined on a Kofler microscope and are uncorrected. IR spectra were taken on a Perkin Elmer 257 spectrophotometer (KBr pellets). ^{1}H-NMR spectra were recorded on a Varian A-60 A and JEOL FX-900 spectrometers, mass spectra on a Varian CH-7 and CEC 21-110C spectrometers.

4-Hydroxy-3-(p-toluoyl)-6-(p-tolyl)-2 H-pyran-2-one (**1a**)

To a stirred solution of 1,6-di(*p*-tolyl)-hexane-1,3,4,6-tetrone [9] (10 g, 0.031 mol) in glacial acetic acid (250 ml), lead tetraacetate (27.6 g, 0.062 mol) was added in small portions over a period of 2 h and the reaction mixture was stirred for further 6 h. Two recrystallizations from acetic acid gave pale yellow needles. Yield 7.62 g (79%), m. p. 194 – 195°C, lit. m. p. 194 – 195°C [10]. IR: 1 735 (pyron CO), 1 620 (chelat. C = O), 1 595 ($C_3 = C_4$), 1 540 ($C_5 = C_6$), 1 445, 1 410 sh (phenyl C = C), 1 365 (CH_3), 1 290, 1 240, 1 210, 1 180 (C-O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 2.40$ (s, 6 H, CH_3), 6.58 (s, 1 H, H_5), 7.26 (s, 4 H, phenyl), 7.83 (d, $J = 8$ Hz, 4 H, phenyl), 15.97 (broad s, 1 H, OH). MS(EI): *m*/e (%) = 320 (7), 119 (100), 91 (82). $C_{20}H_{16}O_4$ (320.328): calcd. C 74.99, H 5.03; found C 75.05, H 5.06.

6-[(1,1'-Biphenyl)-4-yl]-3-[(1,1'-biphenyl)-4-ylcarbonyl]-4-hydroxy-2 H-pyran-2-one (**1b**)

1,6-bis[1,1'-biphenyl)-4-yl]-hexane-1,3,4,6-tetrone [9] (50 g, 0.112 mol) and lead tetraacetate (124 g, 0.280 mol) were reacting in the same way as described for the preparation of **1a** at 50 – 65°C for 8 h. Yield 26.8 g (54%) of pale yellow crystals from dioxane, m. p. 253.5 – 255°C. IR: 1 725 (pyron CO), 1 618 (chelat. C = O), 1 585 ($C_3 = C_4$), 1 520 ($C_5 = C_6$), 1 475, 1 440, 1 420, 1 395 (phenyl C = C), 1 280, 1 263, 1 215, 1 180 (C-O) cm^{-1}. ^{1}H-NMR (*DMSO-d*$_6$): $\delta = 6.95$ (s, 1 H, H_5), 7.45 (d, $J = 6$ Hz, 6 H, phenyl), 7.83 (m, 12 H, phenyl), 14.98 (broad s, 1 H, OH). MS(EI): *m*/e (%) = 444 (100), 181 (61), 153 (18). $C_{30}H_{20}O_4$ (444.46): calcd. C 81.06, H 4.53; found C 80.90, H 4.91.

5-Bromo-4-hydroxy-3-(p-toluoyl)-6-(p-tolyl)-2 H-pyran-2-one (**1c**)

A magnetically stirred solution of **1a** (0.64 g, 0.002 mol) in chloroform (20 ml) was treated with bromine (0.32 g, 0.002 mol) and the resulting mixture was heated to reflux for 1 h. The solvent was removed under reduced pressure and the residue recrystallized from methanol and ethanol/chloroform giving a white product. Yield 0.554 g (69%), m. p. 236 – 237°C. IR: 1 735 (pyron CO), 1 612 (chelat. CO), 1 590 ($C_3 = C_4$), 1 530, 1 502 ($C_5 = C_6$), 1 445, 1 380 sh (phenyl C = C), 1 340 (CH_3), 1 290, 1 270, 1 210, 1 185 (C-O), 625 (C-Br) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 2.40$ (s, 6 H, CH_3), 7.29 (s, 4 H, phenyl),

7.78 (d, $J=8$ Hz, 4 H, phenyl), 17.53 (broad s, 1 H, OH). MS(EI): *m/e* (%) = 399 (9.63), 319 (100), 119 (52), 91 (44). $C_{20}H_{15}O_4Br$ (399.224): calcd. C 60.16, H 3.78, Br 20.07; found C 60.10, H 4.03, Br 20.22.

4-Hydroxy-3-[phenylimino-(p-toluoyl)]-6-(p-tolyl)-2 H-pyran-2-one (**2 a**)

To the solution of **1 a** (0.32 g, 0.001 mol) in ethanol (80 ml) aniline (0.1 g, 0.001 mol) was added. The solution was heated under stirring and refluxing for 4 h, and the precipitate separated by filtration. After heating for 1 h under reflux in ethanol (40 ml), pale yellow crystals were obtained. Yield 0.202 g (51%), m. p. 222–222.5°C. IR: 1730 (pyron CO), 1612 (H-bonded C=N), 1570 ($C_3=C_4$), 1540 ($C_5=C_6$), 1462, 1442, 1408 (phenyl C=C), 1370 (CH_3), 1334 (C-N), 1290, 1248, 1219, 1180 (C-O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta=2.34$ (s, 1 H, H_5), 6.86 (d, $J=5$ Hz, 2 H, phenyl), 7.13 (s, 9 H, phenyl), 7.69 (d, $J=8$ Hz, 2 H, phenyl), 15.78 (broad s, 1 H, OH). MS(EI): *m/e* (%) = 395 (24), 194 (22), 77 (100). $C_{26}H_{21}NO_3$ (395.436): calcd. C 78.96, H 5.35, N 3.54; found C 79.02, H 5.35, N 3.54.

General Procedure for the Reaction of 4-Hydroxy-3-(p-toluoyl)-6-(p-tolyl)-2 H-pyran-2-one (**1 a**) *with o-Phenylenediamine, 3,4-Dichloro-, and 3,4-Dimethyl-o-phenylenediamine*

To a stirred and boiling solution of **1 a** (0.320 g, 0.001 mol) in ethanol (30 ml) a solution of *o*-phenylenediamine (R^1 = H, Cl or CH_3) (0.0012 mol) in ethanol (30 ml) was added. After refluxing for 2 h, the mixture was left overnight in a refrigerator. The precipitate was filtered off, washed with ethanol and recrystallized from chloroform/ethanol (1 : 2) giving **2 b**, **2 c**, and **2 d**.

3-[2-Aminophenylimino(p-toluoyl)]-4-hydroxy-6-(p-tolyl)-2 H-pyran-2-one (**2 b**)

This compound was obtained as orange-yellow crystalline. Yield 0.296 g (72%), m. p. 214–215°C. IR: 3460, 3360 (N-H of NH_2), 3230 (NH_2), 1710–1690 (pyron CO), 1632 (C=N), 1615, 1605 (C-N), 1570 ($C_3=C_4$), 1540 ($C_5=C_6$), 1455, 1410 (phenyl C=C), 1370 (CH_3), 1335, 1312 (C-N), 1285, 1255, 1190 (C-O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta=2.31$ (s, 6 H, CH_3), 2.91 (broad s, 2 H, NH_2), 6.45 (s, 1 H, H_5), 6.71 (s, 2 H, phenyl), 7.11 (s, 8 H, phenyl), 7.69 (d, $J=8$ Hz, 2 H, phenyl), 15.26 (broad s, 1 H, OH). MS(EI): *m/e* (%) = 410 (2), 208 (100), 202 (10). $C_{26}H_{22}N_2O_3$ (410.452): calcd. C 76.08, H 5.40, N 6.83; found C 76.21, H 5.25, N 6.85.

3-[2-Amino-4,5-dichlorophenylimino(p-toluoyl)]-4-hydroxy-6-(p-tolyl)-2 H-pyran-2-one (**2 c**)

This compound was obtained as green-yellow crystalline. Yield 0.278 g (58%), m. p. 204–205°C. IR: 3400, 3330 (N-H of NH_2), 3220 (NH_2), 1715 (pyron CO), 1630 (C=N), 1615 (C-N), 1570 ($C_3=C_4$), 1520 ($C_5=C_6$), 1450, 1435 (phenyl C=C), 1363 (CH_3), 1332, 1310 (C-N), 1260, 1240, 1182 (C-O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta=2.35$ (s, 6 H, CH_3), 4.01 (broad s, 2 H, NH_2), 6.45 (s, 1 H, H_5), 6.76 (s, 2 H, phenyl), 7.13 (s, 8 H, phenyl), 7.68 (d, $J=8$ Hz, 2 H, phenyl), 15.42 (broad s, 1 H, OH). MS(EI): *m/e* (%) = 480/478 (4.6/3.1), 278/276 (100/69), 202 (46). $C_{26}H_{20}N_2O_3Cl_2$ (479.342): calcd. C 65.14, H 4.21, N 5.85; found C 65.37, H 4.39, N 5.67.

3-[2-Amino-4,5-dimethylphenylimino(p-toluoyl)]-4-hydroxy-6-(p-tolyl)-2 H-pyran-2-one (**2 d**)

This compound was obtained as orange-yellow crystalline. Yield 0.262 g (58%), m.p. 188–190°C. IR: 3400, 3330 (N-H of NH_2), 3240 (NH_2), 1710 (pyron CO), 1632 (C=N), 1615 (C-N), 1570 ($C_3=C_4$), 1530 ($C_5=C_6$), 1445, 1410 (phenyl C=C), 1365 (CH_3), 1335, 1310 (C-N), 1270, 1250, 1182 (C-O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta=1.87$ (s, 6 H, CH_3), 2.29 (s, 6 H, CH_3), 3.73 (broad s, 2 H, NH_2), 6.26 (s, 1 H, H_5), 6.41 (s, 2 H, phenyl), 7.11 (s, 6 H, phenyl), 7.66 (d, $J=8$ Hz, 2 H, phenyl), 15.10 (broad s, 1 H, OH), MS(EI): *m/e* (%) = 438 (27), 236 (100), 202 (21). $C_{28}H_{26}N_2O_3$ (440.504): calcd. C 76.69, H 5.98, N 6.39; found C 76.48, H 6.20, N 6.59.

3-[2-Aminophenylimino(1,1'-biphenyl)-4-ylcarbonyl]-6-[(1,1'-biphenyl)-4-yl]-4-hydroxy-2H-pyran-2-one (**2e**)

To a solution of **1b** (0.446 g, 0.001 mol) in butanol a solution of *o*-phenylenediamine (0.278 g, 0.002 mol) in ethanol (10 ml) was added and refluxed for 1 h. The precipitate was filtered off and recrystallized from dioxane to give pale orange crystals. Yield 0.381 g (71%), m.p. 225–226°C. IR: 3420, 3380 (N-H of NH_2), 3220 (NH_2), 1715 (pyron CO), 1620 (C=N), 1610 (C-N), 1555 ($C_3=C_4$), 1530 ($C_5=C_6$), 1480, 1449, 1405, 1320 (phenyl C=C), 1340, 1320 (C-N), 1282, 1240, 1188 (C-O) cm^{-1}. ^{1}H-NMR (*DMSO-d_6*): $\delta=3.56$ (s, 2H, NH_2), 6.35 (s, 1H, H_5), 7.37 (m, 4H, phenyl), 7.46 (m, 18H, phenyl), 15.00 (broad s, 1H, OH). $C_{36}H_{26}N_2O_3$ (534.584): calcd. C 80.88, H 4.90, N 5.24; found C 80.65, H 5.13, N 5.39.

3-[(2-Aminophenylimino)-2-thenoyl)]-4-hydroxy-6-(2-thienyl)-2H-pyran-2-one (**2f**)

This compound was obtained from 4-hydroxy-3-(2-thenoyl)-5-(2-thienyl)-2*H*-pyran-2-one [11] (0.304 g, 0.001 mol) as orange crystalline in the same way as described for the preparation of **2e**. Yield 0.199 g (51%), m.p. 230–231°C. IR: 3425, 3340 (N-H of NH_2), 1720 (pyron CO), 1625 (C=N), 1570–1460 (C=C pyron and thienyl), 1440, 1400 (C=C phenyl), 1360, 1335, 1305 (C-N), 1250 (thienyl), 1230, 1215, 1180 (C-O), 1040, 1020 (thienyl). ^{1}H-NMR ($CDCl_3$): $\delta=3.88$ (s, 2H, NH_2), 6.33 (s, 1H, H_5), 6.73 (m, 3H, thienyl), 7.13 (m, 4H, phenyl), 7.62 (m, 3H, thienyl), 15.01 (broad s, 1H, OH). $C_{20}H_{14}N_2O_3S_2$ (394.46): calcd. C 60.92, H 3.55, N 7.10; found C 60.85, H 3.79, N 7.01.

2,6-Di(p-tolyl)-4H-pyran-4-one (**3a**)

A. Method from **1a**

A solution of **1a** (3.52 g, 0.011 mol) in a mixture of glac. acetic acid (160 ml) and conc. hydrochloric acid (80 ml) was refluxed for 23 h. To a stirred cold solution water (120 ml) was gradually added and the precipitate filtered off. Recrystallization from ethanol afforded a white crystalline product. Yield 1.98 g (65%), m.p. 179.5–181°C, lit. m.p. 178–180°C [12].

B. Method from **2b**

A solution of **2b** (0.102 g, 0.00025 mol) in a mixture of glac. acetic acid (16 ml) and conc. hydrochloric acid (8 ml) was treated in the same way as described in Method A. Yield 0.060 g (75%) of **3a**, m.p. 179.5–181°C. IR: 1640, 1610 (pyron CO), 1505, 1415 (C=C), 1382 (CH_3), 1283, 1260, 1190 (C-O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta=2.39$ (s, 6H, CH_3), 6.69 (s, 2H, H_3, H_5), 7.32 (d, $J=8.3$ Hz, 4H, phenyl), 7.63 (d, $J=8$ Hz, 4H, phenyl). MS(EI): *m*/e (%)=276 (54), 248 (100), 91 (18). $C_{19}H_{16}O_2$ (276.318): calcd. C 82.58, H 5.83; found C 82.82, H 5.83.

2,6-Di[(1,1'-biphenyl)-4-yl]-4H-pyran-4-one (**3b**)

A. Method from **1b**

A solution of **1b** (5 g, 0.0112 mol) in a mixture of glac. acetic acid (1000 ml) and conc. hydrochloric acid (500 ml) was refluxed for 96 h. Water (120 ml) was added and the precipitate recrystallized from toluene, affording a white crystalline product. Yield 2.1 g (47%), m.p. 250–251°C.

B. Method from **2e**

A solution of **2e** (0.114 g, 0.0003 mol) in a mixture of glac. acetic acid (20 ml) and conc. hydrochloric acid (10 ml) was refluxed for 42 h. Yield 0.045 g (53%), m.p. 250–251°C. IR: 1635, 1610 (pyron CO), 1550, 1485, 1410, 1380 (C=C), 1285, 1250, 1120 (C-O) cm^{-1}. ^{1}H-NMR (*DMSO-d_6*): $\delta=7.08$ (s, 2H, H_3, H_5), 7.48 (d, $J=5.86$ Hz, 8H, phenyl), 7.85 (dd, $J=8.3$ Hz, 10H, phenyl). MS(EI): *m*/e (%)=400 (68), 372 (100), 153 (11). $C_{29}H_{20}O_2$ (400.39): calcd. C 86.98, H 5.03; found C 87.10, H 5.16.

2,6-Di(2-thienyl)-4 H-pyran-4-one (**3 c**)

A mixture of **2 f** (0.197 g, 0.0005 mol) in glac. acetic acid (100 ml) and conc. hydrochloric acid (50 ml) was refluxed for 10 h, poured into water (300 ml) and evaporated to dryness in vacuo. The dry residue was recrystallized from chloroform/ethanol affording white-pale rosy crystals. Yield 0.72 g (55%), m. p. 163 – 164°C [12] IR: 1 62O (pyron CO), 1 563, 1 400, 1 370, 1 325 (C=C), 1 240, 1 225, 1 205 (C-O), 1 045, 1 035 (thienyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 6.59$ (s, 2 H, H_3 and H_5), 7.86 (t, 3 H, thienyl), 7.78 (t, 3 H, thienyl). $C_{13}H_8O_2S_2$ (260.33): calcd. C 59.97, H 3.10, S 24.63; found C 60.01, H 2.99, S 24.37.

N-Acetyl Derivative
3-[2-Acetylaminophenylimino(p-toluoyl)]-4-hydroxy-6-(p-tolyl)-2 H-pyran-2-one (**4**)

2 b (0.180 g, 0.00044 mol) in acetic anhydride (2 ml) was refluxed for 1 h and the yellow crystalls washed with ether and recrystallized from chloroform. Yield 0.168 g, (84%), m. p. 260 – 261°C. IR: 3 230 (NH), 1 720 sh, 1 670 (pyron CO), 1 620 (C=N), 1 605 (C-N), 1 580 – 1 470 (C=C pyran), 1 450 (C=C phenyl), 1 380 – 1 320 (CH_3, C-N), 1 280, 1 250, 1 190 (C-O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 2.12$ (t, 9 H, CH_3), 6.53 (s, 1 H, H_5), 6.96 (m, 8 H, phenyl), 7.56 (d, $J = 7.81$ Hz, phenyl), 7.91 (d, $J = 7.81$ Hz, 2 H, phenyl), 8.50 (s, 1 H, NH), 15.09 (broad s, 1 H, OH). $C_{28}H_{24}N_2O_4$ (452.49): calcd. C 74.32, H 5.35, N 6.19; found C 74.15, H 5.39, N 6.16.

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