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TRANSFORMATION OF 1,5-DIPHENYLPENTANE-1,3,5-TRIONE. THE SYNTHESIS OF SUBSTITUTED (4*H*)-PYRANONES, PYRIDIN-4(1*H*)-ONES AND 4*H*-PYRANO[3,2-*c*]PYRIDIN-4-ONES

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Abstract – 1,5-Diphenylpentane-1,3,5-trione (**1**) was transformed by the reaction either with *N*,*N*-dimethylformamide dimethyl acetal (DMFDMA) or *N*,*N*-dimethylacetamide dimethyl acetal (DMADMA) into (*N*,*N*-dimethylamino)-methylidene derivatives **2a,b** as intermediates. They were converted in the presence of silica gel into 5-benzoyl-2-phenylpyran-4-one (**3a**) and its 6-methyl derivative **3b**, while the corresponding 5-benzoyl- 2-phenylpyridin-4(1*H*)-one (**4**) was formed by the reaction with NH_4Cl. Compound **3b** gave the corresponding (*N*,*N*-dimethylamino)methylidene derivative **5** with DMFDMA, which was cyclized in aqueous ammonia into 2,5-diphenyl-4*H*-pyrano[3,2-*c*]pyridin-4-one (**7**). The reaction of **1** with excess of DMFDMA followed by reaction with ammonia or primary amines yielded 1-substituted 3,5-dibenzoylpyridin-4(1*H*)-ones (**9a-m**).

INTRODUCTION

Substituted pyridin-4(1*H*)-ones are key structural elements in medicinal chemistry and versatile intermediates in organic synthesis.[1] Many derivatives have been extensively investigated in connection with the preparation of various alkaloid skeletons.[2,3] Pyridin-4(1*H*)-ones have shown antibacterial,[4] antimalarial,[5] antineoplastic,[6] and other pharmacological activities.

Recently, one step synthesis of 3,5- dibenzoyl-2,6-diphenyl-4-pyrone from the reaction of dibenzoyl-methane with oxalyl chloride has been described,[7] while some other 4-pyranone derivatives have been prepared from α-oxoketene, generated *in situ* from 4-ethoxycarbonyl-5-phenyl-2,3-dihydrofuran-2,3-dione and dibenzoylmethane.[7] Condensation reaction of 4-pyranone derivatives with excess primary amines has provided a series of pyridin-4(1*H*)-one derivatives.[8]

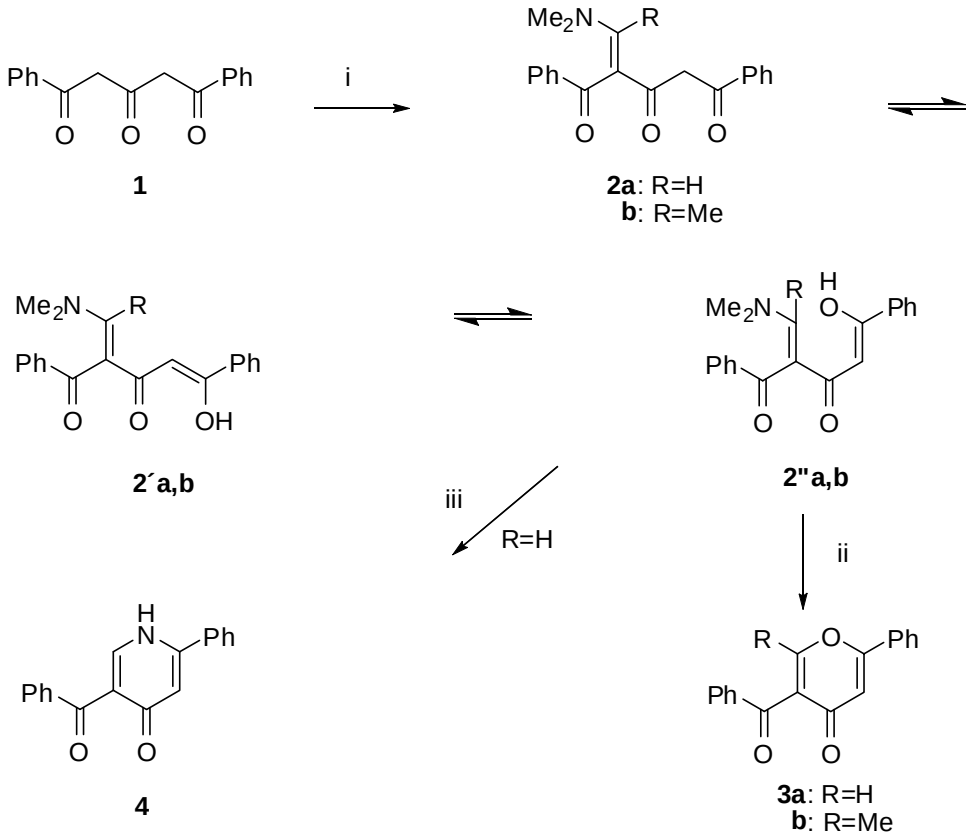
3-Dimethylaminopropenoates and the related enaminones have been demonstrated to be useful reagents in heterocyclic synthesis,[9-16] including preparation of some natural products and their analogs, such as aplysinopsins,[17-20] meridianines,[21,22] and dipodazines.[23,24] As part of our interest, we have recently reported an efficient method for the preparation and functionalization of highly substituted 1-aminopyrroline, 1-aminopyrrole, and oxazoline-pyrroline fused system from 1,2-diaza-1,3-butadines and 3-dimethylaminopropenoates.[25] Recently, dialkyl acetonedicarboxylates as compounds with two activated methylene groups have been used as starting compounds for preparation of mono and bis(dimethylamino)methylidene intermediates which have been further transformed into 1-substituted 4-oxo-1,4-dihydropyridine-3,5-dicarboxylates,[26] 2*H*-pyrazolo[4,3-*c*]pyridine-7-carboxylates,[27] hetero- aryl substituted pyrazoles,[28] heteroaryl substituted pyrimidines,[29] and pyrazolo[4,3-*d*][1,2]diazepine-8-carboxylates.[30,31] In this paper, we report transformations of 1,5-diphenylpentane-1,3,5-trione into substituted 5-benzoylpyran-4-one, 5-benzoylpyridin-4(1*H*)-one, 4*H*-pyrano[3,2-*c*]pyridin-4-one, and 1-substituted 3,5-dibenzoylpyridin-4(1*H*)-ones.

RESULTS AND DISCUSSION

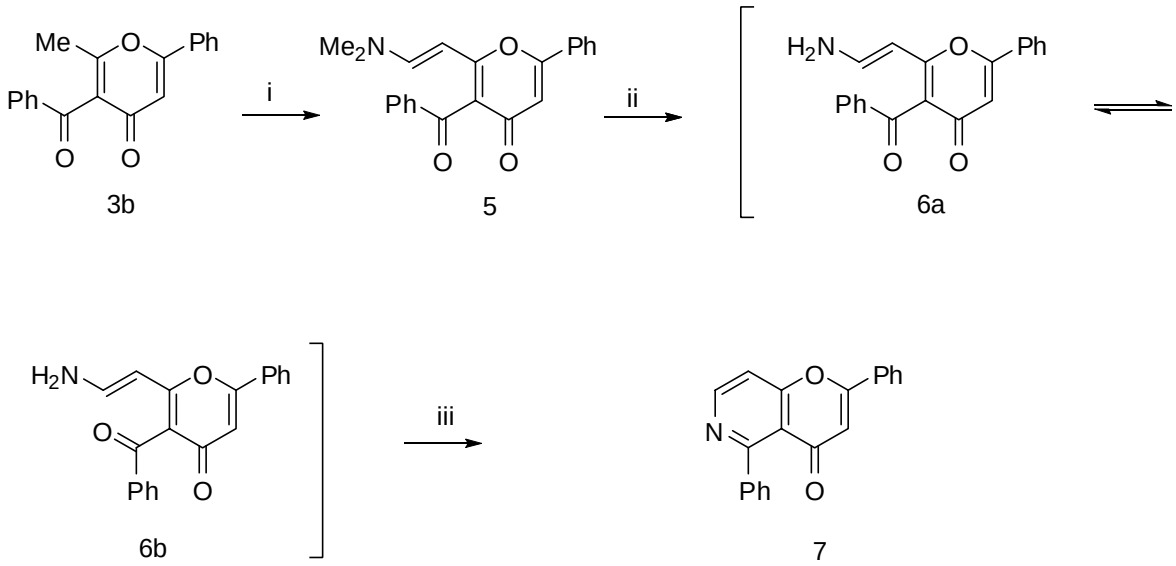
When 1,5-diphenylpentane-1,3,5-trione (**1**) was heated under reflux with an excess of *N*,*N*-dimethylformamide dimethyl acetal (DMFDMA) or *N*,*N*-dimethylacetamide dimethyl acetal (DMADMA) in *n*-propyl acetate for 1 hour, the corresponding crude (*N*,*N*-dimethylamino)-methylidene-1,5-diphenylpentane-1,3,5-trione (**2a**) and mono-(*N*,*N*-dimethylamino)ethylidene-1,5-diphenylpentane-1,3,5-trione (**2b**) were obtained. They were not isolated in pure form. When the reaction mixture obtained by evaporation of volatile components was purified by column chromatography over ($CHCl_3$:MeOH = 95:5, silica gel) the corresponding 5-benzoyl-2-phenyl-*4H*-pyran-4-one (**3a**) and its 6-methyl derivative **3b** were isolated in 33 % and 78 % yields. The cyclization occurred most probably in the presence of silicagel. Namely, when the crude reaction mixture, obtained by evaporation of volatile components, was treated with NH_4Cl in ethanol at room temperature for 5 h, the corresponding 5-benzoyl-2-phenylpyridin-4(1*H*)-one (**4**) was formed in 57 % yield (Scheme 1).

The reaction of pyranone **3b** with DMFDMA yielded compound **5**. In the last reaction step, compound **5** was converted into 2,5-diphenyl-4*H*-pyrano[3,2-*c*]pyridin-4-one (**7**) by cyclization of compound **5** in aqueous ammonia. When this reaction was performed in DMF at 80 °C, the dimethylamino group was substituted with the amino group and subsequently cyclized into the final product (Scheme 2).

The reaction of 1,5-diphenyl-1,3,5-pentanetrione (**1**) with excess of DMFDMA followed by addition of amines yielded 1-substituted 3,5-dibenzoyl-4-oxo-1,4-dihydropyridines (**2**). The reaction of 1,5-diphenyl-



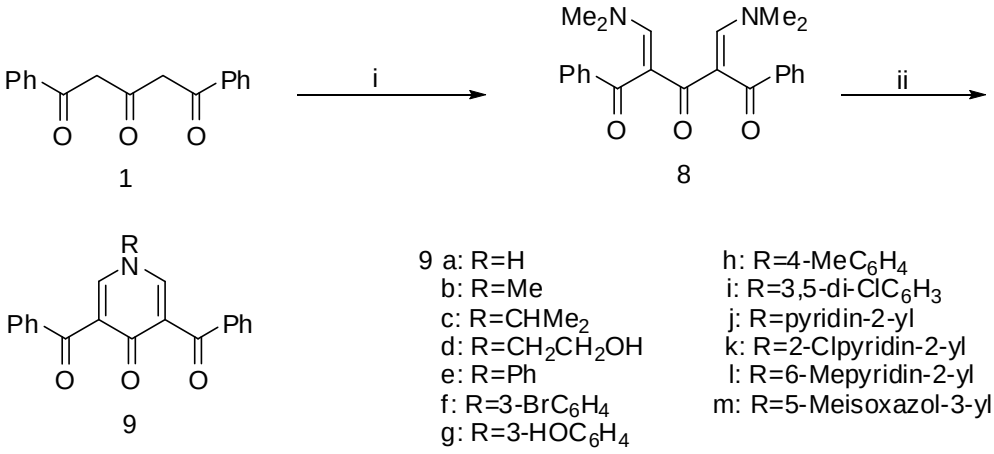
Scheme 1. Reagents and conditions: i for **2a:** DMFDMA, *n*-PrOAc, reflux; for **2b**: DMADMA, *n*-PrOAc, reflux; ii column chromatography, silica gel; iii NH_4Cl, EtOH, rt.



Scheme 2. i DMFDMA, *n*-PrOAc, reflux; ii DMF, NH_4OH (25% aq. solution); iii 80 ˚C, 19 h

1,3,5-pentanetrione (**1**) with excess of DMFDMA afforded bis(*N*,*N*-dimethylamino)methylidene derivatives **8**, which were, without purification, followed by addition of amines yielded 1-substituted

3,5-dibenzoylpyridin-4(1*H*)-ones (**9**). The reaction of 1,5-diphenyl-1,3,5-pentanetrione with DMFDMA was carried on in *n*-propyl acetate as a solvent at reflux temperature for 12 hours and the solvent was removed by distillation at reduced pressure. The oily residue was dissolved in another solvent and the cyclization with various amines to form 1-substituted 3,5-dibenzoyl 4-oxo-1,4-dihydropyridines (**2**) was performed at reflux temperature of the solvent, usually ethanol. This reaction was catalyzed by addition of catalytical amount of conc. HCl. (Scheme 3).



Scheme 3. i DMFDMA, *n*-PrOAc, reflux; ii RNH_2, reflux

1-Substituted 3,5-dibenzoyl 4-oxo-1,4-dihydropyridines (**9**) are crystalline compounds and were isolated by crystallization directly from the reaction mixtures in height yields. It was proved successfully that 1,5-diphenyl-1,3,5-pentanetrione (**1**) is useful also for the other conversions with DMFDMA.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. The ^{1}H NMR spectra were obtained on a Bruker Avance DPX 300 (300 MHz) spectrometer in such solvent as DMSO-d_6 and $CDCl_3$ with TMS as the internal standard, MS spectra on an AutoSpecQ spectrometer, IR spectra on a Perkin-Elmer 1310 infrared spectrophotometer and elemental analyses for *C*, *H* and *N* on a Perkin-Elmer CHN Analyser 2400.

5-Benzoyl-2-phenyl-4*H*-pyranone (3a). To a solution of 1,5-diphenyl-1,3,5-pentanetrione (666 mg , 2,5 mmol) in *n*-propyl acetate (5 mL) was added DMFDMA (2 mL, 14,3 mmol) and the mixture was stirred at rt for 30 min. The reaction mixture was concentrated in vacuum. The residue was chromatographed on a column of silica gel. Elution with $CHCl_3$: MeOH (98 : 2). Yield 33.3 %; mp 174 - 176 ^{o}C (from EtOH). IR (KBr, cm^{-1}): 2981, 1735, 1686, 1641, 1580. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.16 (s, 1H, H_3), 7.50 – 7.77 (m, 6H, Ph), 7.82 – 8.10 (m, 4H, Ph), 8.66 (s, 1H, H_6). ^{13}C NMR (300 MHz, CF_3COOH)

δ: 14.1 (OCH_2CH_3), 14.4 (OCH_2CH_3) , 42.6, 47.9, 48.6, 59.9 (OCH_2CH_3), 60.7 (OCH_2CH_3), 101.1, 159.3, 167.4 (COOEt), 169.2 (COOEt), 189.6 (CO). *Anal.* Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.58; H, 4.07.

5-Benzoyl-6-methyl-2-phenyl-4*H*-pyranone (3b). To a suspension of 1,5-diphenylpentane-1,3,5- trione (532 mg, 2 mmol) in *n*-propyl acetate (5 mL) was added DMADMA (0.35 ml, 2,2 mmol) and the mixture was stirred at reflux temperature for 1 h. The reaction mixture was concentrated *in vacuo* and 2 mL of EtOH was added. The precipitated product was filtered. Yield 77.9 %; mp 151 - 153 °C (from EtOH). IR (KBr, cm^{-1}): 1649, 1618, 1400, 914, 691. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.29 (s, 3H, CH_3), 7.06 (s, 1H, H_3), 7.50 – 7.77 (m, 6H, Ph), 7.82 – 8.10 (m, 4H, Ph). ^{13}C NMR (300 MHz, CF_3COOH) δ: 17.9, 110.4, 125.86, 126.0, 129.0, 129.1, 129.1, 130.5, 131.7, 134.1, 136.2, 162.9, 163.8, 176.8, 193.6. *Anal.* Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86; N. Found: C, 78.92; H, 4.71.

5-Benzoyl-2-phenylpyridin-4(1*H*)-one (4). To a solution of 1,5-diphenyl-1,3,5-pentanetrione (1.33 g, 5 mmol) in *n*-propyl acetate (10 mL) was added DMFDMA (4 mL, 28.5 mmol) and the mixture was stirred at rt for 30 min. The reaction mixture was concentrated *in vacuo*. The residue was dissolved in EtOH (10 mL) and NH_4Cl (401 mg, 7.5 mmol) was added. The mixture was stirred at rt for 5 h, cooled and the precipitate was collected by filtration. Yield 57.3 %, mp 249 - 251 °C (from EtOH). IR (KBr, cm^{-1}): 2981, 1735, 1686, 1641, 1580. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.6 – 8.3 (m, 12H, Ph, $H_{3,6}$), 11.8 – 12.2 (broad s, 1H, N*H*). ^{13}C NMR (300 MHz, CF_3CO_2H) δ: 14.1 (OCH_2CH_3), 14.4 (OCH_2CH_3), 42.6, 47.9, 48.6, 59.9 (OCH_2CH_3), 60.7 (OCH_2CH_3), 101.1, 159.3, 167.4 (COOEt), 169.2 (COOEt), 189.6 (CO). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.77; H, 4.84; N, 5.14.

5-Benzoyl-6-[2-(*N*,*N*-dimethylamino)ethenyl]-2-phenyl-4*H*-pyranone (5). To a suspension of 1,5-diphenyl-1,3,5-pentanetrione (532 mg, 2 mmol) in *n*-propyl acetate (5 mL) was added DMADMA (0.35 mL, 2,2 mmol) and the mixture was stirred at reflux temperature for 1 h. Then 1,4 mL (10 mmol) DMFDMA was added and the mixture was stirred additionally at reflux temperature for 16 h. The reaction mixture was cooled and the precipitated product was collected by filtration. Yield 68.0 %; mp 233 - 241 °C (from EtOH). IR (KBr, cm^{-1}): 3061, 1675, 1639, 1584, 1542, 1387. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.50 – 3.00 (broad s, 3H, $N(CH_3)$), 2.80 – 3.40 (broad s, 3H, $N(CH_3)$), 4.75 (d, 1H, $CH{=}CHNMe_2$, J = 12.6 Hz (*trans*)), 6.75 (s, 1H, H_3), 7.45 – 7.67 (m, 6H, Ph), 7.66 (d, 1H: $CH{=}CHNMe_2$, J = 12.6 Hz (*trans*)), 7.77 – 7.83 (m, 2H, Ph), 7.90 - 8.06 (m, 2H, Ph). ^{13}C NMR (300 MHz, CF_3CO_2H) δ: 83.7, 109.3, 114.8, 125.9,

128.6, 128.8, 129.1, 131.0, 131.1, 133.1, 137.7, 148.4, 160.1, 164.1, 176.0, 195.2. *Anal.* Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.54; N, 4.06. Found: C, 76.40; H, 5.63; N, 3.93.

2,5-Diphenyl-4*H*-pyrano[3,2-*c*]pyridin-4-one (7). To a solution of 345 mg (1 mmol) of 5-benzoyl-6-[2-(dimethylamino)ethenyl]-2-phenyl-4*H*-pyranone (**5**) in DMF (5 mL) was added 0.15 mL 25 % NH_4OH (2.0 mmol) and one drop of conc. HCl and the mixture was stirred at 80 °C for19 h. The reaction mixture was cooled and the precipitated product was collected by filtration. Yield 45.8 %; mp 195 - 197 °C (from EtOH). IR (KBr, cm^{-1}): 3060, 1660, 1651, 1359, 690. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.06 (s, 1H, H_3), 7.36 – 7.77 (m, 8H, Ph), 7.78 (d, 1H, H_7), J = 6.0 Hz), 8.10 – 8.15 (m, 2H, Ph), 8.82 (d, 1H, H_8), J = 6.0 Hz) ^{13}C NMR (300 MHz, CF_3COOH) δ: 109.8, 112.3, 116.8, 126.3, 127.1, 128.1, 129.2, 129.3, 130.4, 132.0, 140.3, 151.5, 160.4, 161.1, 162.4, 176.1. *Anal.* Calcd for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.31; H, 4.23; N, 4.42.

General procedure for preparation of 1-substituted 3,5-dibenzoylpyridin-4(1*H*)-ones (9a-m)

The suspension of 1,5-diphenyl-1,3,5-pentanetrione (532 mg, 2 mmol) in *n*-propyl acetate (5 mL) was stirred at reflux temperature for several h. The reaction mixture was concentrated *in vacuo* and the residue was dissolved in EtOH (5 mL). Then 2.4 mmol of the corresponding amine and one drop of conc. HCl were added and the mixture was stirred at reflux temperature to complete the reaction. The mixture was then cooled and the precipitated product was collected by filtration. In this manner, the following compounds were prepared:

3,5-Dibenzoylpyridin-4(1*H*)-one (9a). This compound was prepared using ammonia refluxing for 2 h. Yield 48 %; mp 331-332 °C (from EtOH). IR (KBr, cm^{-1}): 3422, 1667, 1633, 1538, 1267, 593. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.48 (m, 4H, $H_{3,5}$ (Ph)), 7.59 (m, 2H, H_4 (Ph)), 7.78 (m, 4H, $H_{2,6}$ (Ph)), 8.09 (s, 2H, $H_{2,6}$), 11,50 – 12.50 (broad s, 1H, N*H*). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 128.28, 129.02, 129.88, 132.90, 137.12, 140.03, 173.46, 194.22. *Anal.* Calcd for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62. Found: C, 75.53; H, 4.28; N, 4.91.

3,5-Dibenzoyl-1-methylpyridin-4(1*H*)-one (9b). This compound was prepared using methylamine in EtOH at rt for 1 h. Yield 73 %; mp 215-217 °C (from EtOH). IR (KBr, cm^{-1}): 3060, 1660, 1650, 1586, 1178. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.80 (s, 3H: CH_3), 7.48 (m, 4H, $H_{3,5}$ (Ph)), 7.59 (m, 2H, H_4 (Ph)), 7.78 (m, 4H, $H_{2,6}$ (Ph)), 8.16 (s, 2H, $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 43.49, 128.31, 129.05,

129.99, 133.01, 137.03, 144.01, 172.42, 193.90. *Anal.* Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.75; H, 4.81; N, 4.45.

3,5-Dibenzoyl-1-isopropylpyridin-4(1*H*)-one (9c). This compound was prepared using isopropylamine in EtOH refluxing for 5 h. Yield 38 %; mp 252-254 °C (from EtOH). IR (KBr, cm^{-1}): 3083, 1662, 1582, 1172. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.46 (d, 6H, CH_3, J = 6.6 Hz), 4.48 (q, 1H: CH, J = 6.6 Hz), 7.50 (m, 4H, $H_{3,5}$ (Ph)), 7.59 (m, 2H, H_4 (Ph)), 7.80 (m, 4H; $H_{2,6}$ (Ph)), 8.29 (s, 2H, $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 21.9, 58.6, 128.3, 129.1, 130.4, 133.0, 137.0, 140.7, 172.8, 194.0. *Anal.* Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.54; N, 4.06. Found: C, 76.76; H, 5.48; N, 4.31.

3,5-Dibenzoyl-1-(2-hydroxyethyl)pyridin-4(1*H*)-one (9d). This compound was prepared using 2-ethanolamine in EtOH refluxing for 3h. Yield 53 %; mp 205-207 °C (from *i*-PrOH). IR (KBr, cm^{-1}): 3382, 3052, 1665, 990. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.73 (m, 2H, NC$\underline{H}_2$), 4.11 (m, 2H: C$\underline{H}_2$OH), 5.15 (t, 1H: O$\underline{H}$, J = 5.4 Hz), 7.50 (m, 4H: 2 × $H_{3,5}$ (Ph)), 7.60 (m, 2H: 2 × H_4 (Ph)), 7.80 (m, 4H: 2 × $H_{2,6}$ (Ph)), 8.16 (s, 2H: $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6): δ 58.6, 60.0, 128.3, 129.1, 129.8, 133.0, 137.1, 143.6, 172.7, 193.9. *Anal.* Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.99; H, 5.02; N, 3.80.

3,5-Dibenzoyl-1-phenyl-pyridin-4(1*H*)-one (9e). This compound was prepared using aniline in EtOH refluxing for 15 h. Yield 61 %; mp 226-228 °C (from EtOH). IR (KBr, cm^{-1}): 3056, 1667, 1644, 1589, 1244. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.40 – 7.80 (m, 9H, Ph), 7.72 (m, 2H , H_4 (Ph)), 7.88 (m, 4H; $H_{2,6}$ (Ph)), 8.42 (s, 2H; $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 123.3, 128.4, 128.6, 129.3, 129.9, 130.5, 133.2, 136.9, 141.5, 142.2, 172.9, 193.4. *Anal.* Calcd for $C_{25}H_{17}NO_3$: C, 79.14; H, 4.52; N, 3.69. Found: C, 79.42; H, 4.36; N, 3.61.

1-(3-Bromophenyl)-3,5-dibenzoylpyridin-4(1*H*)-one (9f). This compound was prepared using 3-bromoaniline in EtOH refluxing for 5 h. Yield 63 %; mp 236-239 °C (from EtOH). IR (KBr, cm^{-1}): 1670, 1642, 1590, 1529, 1243. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.40 – 7.80 (m, 9H, Ph), 7.85 – 7.91 (m, 4H, (Ph)), 8.05 (m, 1H, Ph), 8.45 (s, 2H, $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 122.2, 122.6, 126.5, 128.4, 129.3, 130.4, 131.4, 131.6, 133.3, 136.8, 141.3, 143.3, 173.0, 193.3. *Anal.* Calcd for $C_{25}H_{16}BrNO_3$: C, 65.52; H, 3.52; N, 3.06. Found: C, 65.80; H, 3.49; N, 2.68.

3,5-Dibenzoyl-1-(3-hydroxyphenyl)pyridin-4(1*H*)-one (9g). This compound was prepared using 3-hydroxyaniline in EtOH refluxing for 5 h. Yield 57 %; mp 280-282 °C (from MeCN). IR (KBr, cm^{-1}): 3283, 1669, 1606, 1521, 1202. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.90 (ddd, 1H, H_6 or H_4 (Ar), J_1 = 8.1 Hz, J_2 = 2.4 Hz, J_3 = 2.1 Hz), 7.05 (dd, 1H, H_2 (Ar), J_1 = 2.4 Hz, J_2 = 2.4 Hz), 7.09 (ddd, 1H, H_6 or H_4 (Ar), J_1 = 8.1 Hz, J_2 = 2.4 Hz, J_3 = 2.1Hz), 7.37 (dd, 1H, H_5 (Ar), J_1 = 8.1 Hz, J_2 = 8.1Hz), 7.50 (m, 4H, $H_{3,5}$ (Ph)), 7.60 (m, 2H, H_4 (Ph)), 7.87 (m, 4H, $H_{2,6}$ (Ph)), 8.36 (s, 2H, $H_{2,6}$), 10.09 (broad s, 1H, OH). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 110.3, 113.6, 115.7, 128.4, 129.3, 130.4, 130.8, 133.2, 136.9, 141.4, 143.3, 158.5, 172.9, 193.4. *Anal.* Calcd for $C_{25}H_{17}NO_4$: C, 75.94; H, 4.33; N, 3.54. Found: C, 76.45; H, 4.45; N, 3.24.

3,5-Dibenzoyl-1-(4-methylphenyl)pyridin-4(1*H*)-one (9h). This compound was prepared using *p*-toluidine in EtOH refluxing for 2 h. Yield 56 %; mp 245-246 °C (from EtOH). IR (KBr, cm^{-1}): 1667, 1643, 1590, 1244, 694. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.38 (s, 3H: CH_3), 7.37 (d, 2H, Ar), 7.50 (m, 4H; $H_{3,5}$ (Ph)), 7.60 (m, 4H; H_4 (Ph), Ar), 7.87 (m, 4H, $H_{2,6}$ (Ph)), 8.37 (s, 2H, $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 20.5, 123.0, 128.4, 129.2, 130.2, 130.5, 133.2, 136.9, 138.3, 139.9, 141.5, 172.81, 193.4. *Anal.* Calcd for $C_{26}H_{19}NO_3$: C, 79.37; H, 4.87; N, 3.56. Found: C, 79.79; H, 4.75; N, 3.65.

3,5-Dibenzoyl-1-(3,4-dichlorophenyl)pyridin-4(1*H*)-one (9i). This compound was prepared using 3,4-dichloroaniline in EtOH refluxing for 2 h. Yield 62 %; mp 245-247 °C (from MeCN). IR (KBr, cm^{-1}): 1641, 1597, 1525, 1236. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.52 (m, 4H, $H_{3,5}$ (Ph)), 7.64 (m, 2H, H_4 (Ph)), 7.75 (dd, 1H, H_6 (Ar), J_1 = 8.7 Hz, J_2 = 2,7 Hz), 7.87 (m, 5H, $H_{2,6}$ (Ph), H_5 (Ar)), 8.15 (d, 1H, H_2 (Ar), J_2 = 2.7 Hz), 8.45 (s, 2H, $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 123.9, 125.9, 128.4, 129.2, 130.4, 131.2, 131.4, 132.0, 133.3, 136.8, 141.3, 141.6, 173.0, 193.3. *Anal.* Calcd for $C_{25}H_{15}Cl_2NO_3$: C, 66.98; H, 3.37; N, 3.12. Found: C, 67.46; H, 3.23; N, 2.92.

3,5-Dibenzoyl-1-(2-pyridyl)pyridin-4(1*H*)-one (9j). This compound was prepared using 2-aminopyridine in EtOH refluxing for 3 h. Yield 42 %; mp 216-218 °C (from EtOH). IR (KBr, cm^{-1}): 1644, 1592, 1245, 961. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.52 (m, 5H, $H_{3,5}$ (Ph), H_5 (Het)), 7.64 (m, 2H, H_4 (Ph)), 7.87 (m, 4H, $H_{2,6}$ (Ph)), 8.01 (broad d, 1H, H_3 (Het), J = 8.4 Hz), 8.11 (ddd, 1H, H_4 (Het), J_1 = 8.4 Hz, J_2 = 7.5 Hz,), 8.61 (ddd, 1H, H_6 (Het), J_1 = 4.8 Hz, J_2 = 1.8 Hz, J_3 = 0.6 Hz), 8.89 (s, 2H, $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 114.5, 123.6, 128.5, 129.2, 130.2, 133.3, 136.8 138.5, 140.3, 148.7, 151.0, 173.7, 193.4. *Anal.* Calcd for $C_{24}H_{16}N_2O_3$: C, 75.78; H, 4.24; N, 7.36. Found: C, 75.87; H, 4.11; N, 7.30.

1-(2-Chloro-3-pyridyl)-3,5-dibenzoylpyridin-4(1*H*)-one (9k). This compound was prepared using 3-amino-2-chloropyyridine in EtOH refluxing for 5 h. Yield 34%; mp 251-253 °C (from MeCN). IR (KBr, cm^{-1}): 1636, 1596, 1415, 1272. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.53 (m, 4H, $H_{3,5}$ (Ph)), 7.63 (m, 2H, H_4 (Ph)), 7.70 (dd, 1H, H_5 (Het), J_1 = 7.8 Hz, J_2 = 4.8 Hz), 7.86 (m, 4H, $H_{2,6}$ (Ph)), 8.38 (s, 2H, $H_{2,6}$), 8.38 (dd, 1H, H_4 (Het), J_1 = 7.8 Hz, J_2 = 1.8 Hz), 8.60 (dd, 1H, H_6 (Het), J_1 = 4.8 Hz, J_2 = 1.8 Hz). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 124.4, 128.5, 129.2, 130.1, 133.4, 136.4, 136.7, 138.0, 142.9, 146.5, 150.6, 172.9, 193.0. *Anal.* Calcd for $C_{24}H_{15}ClN_2O_3$: C, 69.49; H, 3.64; N, 6.75. Found: C, 69.57; H, 3.69; N, 7.00.

3,5-Dibenzoyl-1-(6-methyl-2-pyridyl)pyridin-4(1*H*)-one (9l). This compound was prepared using 2-amino-6-methylpyridine in EtOH refluxing for 3 h. yield 48 %; mp 244-246 °C (from EtOH/MeCN). IR (KBr, cm^{-1}): 1644, 1585, 1439, 1297. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.56 (s, 3H: CH_3), 7.40 (d, 1H H_5 (Het), J = 7.8 Hz), 7.51 (m, 4H, $H_{3,5}$ (Ph)), 7.63 (m, 2H, H_4 (Ph)), 7.79 (d, 1H, H_3 (Het), J = 8.4 Hz), 7.86 (m, 4H, $H_{2,6}$ (Ph)), 7.99 (dd, 1H, H_4 (Het), J_1 = 8.4 Hz, J_2 = 7.8 Hz), 8.86 (s, 2H, $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6): δ 23.7, 111.3, 122.9, 128.4, 129.2, 130.2, 133.3, 136.8, 138.4, 140.4, 150.35, 158.0, 173.7, 193.5. *Anal.* Calcd for $C_{25}H_{18}N_2O_3$:C, 76.13; H, 4.60; N, 7.10. Found: C, 76.30; H, 4.72; N, 7.35.

3,5-Dibenzoyl-1-(5-methyl-3-isoxazolyl)pyridin-4(1*H*)-one (9m). This compound was prepared using 3-amino-5-methylisooxazole in EtOH refluxing for 3 h. Yield 38 %; mp 218-222 °C (from *i*-PrOH/MeCN). IR (KBr, cm^{-1}): 3324, 3166, 1741, 1716, 1662, 1335. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.50 (s, 3H, CH_3), 7.07 (s, 1H, H_4 (Het)), 7.51 (m, 4H, $H_{3,5}$ (Ph)), 7.63 (m, 2H, H_4 (Ph)), 7.89 (m, 4H, $H_{2,6}$ (Ph)), 8.58 (s, 2H, $H_{2,6}$). ^{13}C NMR (300 MHz, DMSO-d_6) δ: 12.5, 95.3, 128.5, 129.3, 130.6, 133.5, 136.6, 138.1, 160.6, 173.3, 192.8. *Anal.* Calcd for $C_{23}H_{16}N_2O_4$: C, 71.87; H, 4.20; N, 7.29. Found: C, 72.09; H, 4.28; N, 7.18.

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