Enaminones in Heterocyclic Synthesis: a New Regioselective Synthesis of 2,3,6-Trisubstituted Pyridines, 6-Substituted-3-Aroylpyridines and 1,3,5-Triaroylbenzenes

Balkis Al-Saleh [a], Mervat Mohammed Abdelkhalik [b],
Afaf Mohammed Eltoukhy [b], and Mohammed Hilmy Elnagdi *[c]

[a] Department of Chemistry, Faculty of Science, University of Kuwait, P. O. Box 5969 Safat, 13060 Kuwait
[b] Department of Chemistry, Girls College for Arts, Science and Education, Ain Shams University, P. O. Box 11757 Heliopolis, Cairo, A. R. Egypt
[c] Department of Chemistry, Faculty of Science, Cairo University, Giza, A. R. Egypt
e-mail: Shelmy@access.com.eg
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1-Substituted-3-dimethylaminopropenones **1a-d** reacted with acetylacetone and with ethyl acetoacetate to yield regioselectively 2,3,6-trisubstituted pyridines. Refluxing **1a-d** in acetic acid/ammonium acetate resulted in the formation of 6-substituted-3-aroylpyridines, whereas refluxing in acetic acid alone afforded 1,3,5-triaroylbenzene.

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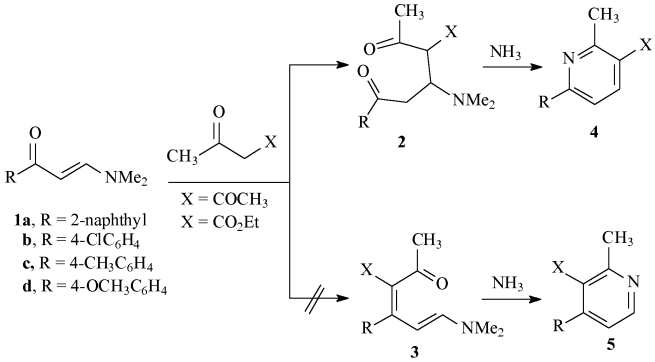
Enaminones are readily obtainable, versatile reagents and their chemistry has recently received considerable attention [1-3]. In conjunction with our interest in exploring the synthetic potential of 1-substituted-3-dimethylaminopropenones **1a-d** we report here efficient syntheses of 2,3,6-trisubstituted pyridines, 6-substituted-3-aroylpyridines and of 1,3,5-triaroylbenzenes utilizing **1a-d** as starting materials. 2,3,6-Trisubstituted pyridines have found extensive utility as pharmaceuticals, *e.g.*, 2,6-diamino-3-phenylazopyridine is used as antibacterial for urinary tract infection [4]. Synthetic approaches to pyridines are well documented [5,6]. Moreover, several 2,3,6-trisubstituted pyridines have previously been synthesized *via* reacting 1-substituted-3-dimethylaminopropanone hydrochlorides with β-aminovinyl ester [7] and 2-substituted-5-aroylpyridines have been obtained earlier *via* reacting hydroxymethyleneacetophenone with ammonia [8].

Compounds **1a,b** reacted readily with acetylacetone in refluxing acetic acid and in the presence of ammonium acetate to yield a product that may be formulated as **4a,b** or **5a,b.** Thus initial addition of active methylene moiety to the α,β-unsaturated double bond in **1** would yield the Michael adduct **2** that cyclizes in the presence of ammonium acetate into **4**. Alternately initial condensation of active methylene moiety with carbonyl function would yield **3** which in the presence of ammonium acetate cyclizes into **5**. Although it is generally accepted that carbanions initially add to the activated double bond in enones [9], it has been recently shown that the situation is different in the reaction of malononitrile with enaminones and products resulting from either initial addition across the activated double bond or at the carbonyl moiety has been isolated. The outcome of the reaction has been shown to depend on the applied reaction conditions [10,11]. Consequently conclusive structure elucidation for the structure of products of reacting **1** with acetylacetone seemed mandatory. Structure **4** could be established for the reaction product based on ^{1}H NMR spectra and NOE difference experiments. For example, the ^{1}H NMR spectra of compound **4a** revealed two singlets at δ = 2.65 and 2.92 ppm for the acetyl and methyl protons, along with two doublets at δ = 7.80 and 8.10 ppm J = 8.0 Hz for pyridine H-5 and H-4. Such coupling value is characteristic for pyridines H-3 and H-4 and much higher than that for H-2 and H-3 (4-6 Hz) [12]. Moreover, irradiating the signal at δ = 8.10 ppm enhanced the acetyl methyl signal at δ = 2.65 ppm and *vice versa* (Scheme 1).

Scheme 1



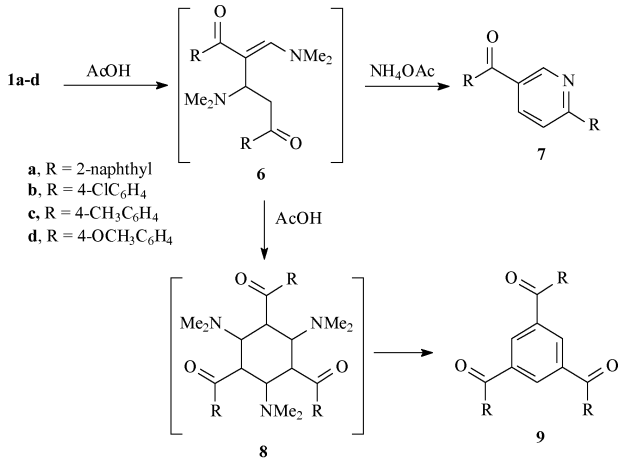
1a, R = 2-naphthyl
b, R = 4-ClC_6H_4
c, R = 4-$CH_3C_6H_4$
d, R = 4-$OCH_3C_6H_4$

2-5a, R = 2-naphthyl, X = $COCH_3$
b, R = 4-ClC_6H_4, X = $COCH_3$
c, R = 4-$CH_3C_6H_4$, X = $COCH_3$
d, R = 4-$OCH_3C_6H_4$, X = $COCH_3$
e, R = 2-naphthyl, X = CO_2Et
f, R = 4-ClC_6H_4, X = CO_2Et
g, R = 4-$CH_3C_6H_4$, X = CO_2Et
h, R = 4-$OCH_3C_6H_4$, X = CO_2Et

The reaction of **1c,d** was attempted with acetylacetone under the same reaction conditions did not afford the expected pyridines **4c,d**. However, products **7c,d** were obtained. These are assumed to be formed *via* initial addition of two molecules of **1c,d** yielding intermediate **6** that cyclises by action of ammonia into **7c,d** [7]. Compounds **7b,d** have been prepared earlier in the self-condensation

reaction of hydroxymethylenacetophenone in the presence of NH_3 [8]. Although, reactivity of C-2 in enaminones toward nitrogen electrophiles have recently been reported [13-15], to our knowledge only reaction of enaminones with 1,4-naphthoquinone has recently been reported [16]. In a trial to isolate intermediate **6**, compounds **1c,d** were refluxed in acetic acid alone, however under this condition the triaroylbenzene derivatives **9c,d** were the only isolable products. It is most likely that intermediate **6** reacted swiftly with a third molecule of **1c,d** yielding intermediate **8** that loses three molecules of dimethylamine yielding the final product **9c,d**. It is interesting to report here that the ^{1}H NMR spectra of this symmetrically trisubstituted benzene, taking compound **9c** as typical example, showed a singlet for 3 protons at δ = 8.45 ppm for the three benzene protons. This excluded completely the possibility of non-symmetrical substituted regioisomers for this reaction product (Scheme 2).

Scheme 2



Similar to the behavior of **1c,d** compounds **1a,b** afforded the pyridine derivatives **7a,b** on reflux in acetic acid and ammonium acetate, while **1a** afforded the triaroylbenzene **9a** on reflux in acetic acid (Scheme 2).

Similar to the behavior of **1a,b** with acetylacetone, compounds **1a-d** react with ethyl acetoacetate to yield the pyridine derivatives **4e-h**. Alternate isomeric structures **5e-h** were ruled out based on the ^{1}H NMR, which revealed pyridine protons with a coupling constant value $J \cong 8.2$ Hz, that is typical for pyridine H-3 and H-4 [12] (Scheme 1).

Compounds **4f-h** have also been obtained earlier from the reaction of 1-aroyl-3-dimethylaminopropanone hydrochloride or hydroxymethylenacetophenone derivatives with ethyl 3-aminocrotonate [7,17]. Some descriptions of **7** and **9** has been described in a recent communication [18]

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded in KBr with a Pye Unicam SP 1100 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-390 400 MHz spectrometer in [$^2H_6$] DMSO as solvent and TMS as internal standard; chemical shifts are reported in δ units (ppm). Mass spectra were measured on MS 30 and MS 9 (AEI), 70 eV. Microanalyses were performed on LECO CHNS-932. Microanalytical data were obtained from the Microanalytical Data Unit at Cairo University The authors are grateful to University of Kuwait R. A. for Analytical Facilities provided by SAF through project Sc 101. Compounds **1a-d** were prepared following published procedure [19].

3-Dimethylamino-1-naphthalen-2-yl-prop-2-en-1-one (**1a**).

This compound was obtained in 92% yield, 2.07 g; mp 106 °C; IR (KBr) ν_{max} = 3425 (NMe_2), 3054 (arom. CH), 1677 cm^{-1} (CO); MS (EI, 70 eV): *m/z* = 225 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ_H = 3.18 (s, 3H, NCH_3), 3.36 (s, 3H, NCH_3), 5.90 (d, 1H, *J* = 12.3 Hz, H-2), 7.33-7.55 (m, 2H, arom. H) 7.86-8.05 (m, 5H; 4H arom. H and 1H H-3), 8.49 (s, 1H, arom. H).

Anal. Calcd. for $C_{15}H_{15}NO$ (225.28): C, 79.97; H, 6.71; N, 6.22. Found: C, 80.20; H, 6.48; N 6.32.

1-(4-Chlorophenyl)-3-dimethylaminoprop-2-en-1-one (**1b**).

This compound was obtained in 90% yield, 1.90 g; mp 102 °C; IR (KBr) ν_{max} = 3440 (NMe_2), 3070 (arom. CH), 2970 (aliph. CH), 1646 (CO), 1600 cm^{-1} (arom. C=C); MS (EI, 70 eV): *m/z* = 209 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ_H = 2.95 (s, 3H, NCH_3), 3.14 (s, 3H, NCH_3), 5.78 (d, 1H, *J* = 12.3 Hz, H-2), 8.01 (d, 2H, *J* = 8.1 Hz, arom-H), 8.05-8.21 (m, 3H, arom-H and H-3); (209.5).

Anal. Calcd. for $C_{11}H_{12}NOCl$: C, 63.00; H, 5.72; N 6.68. Found C 63.06, H 5.70, N 6.65.

3-Dimethylamino-1-*p*-tolylprop-2-en-1-one (**1c**).

This compound was obtained in 92% yield, 1.73 g; mp 94 °C; IR (KBr) ν_{max} = 3434 (NMe_2), 3070 (arom. CH), 2970 (aliph. CH), 1644 (CO), 1600 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 189 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ_H = 2.40 (s, 3H, CH_3), 2.93 (s, 3H, NCH_3), 3.13 (s, 3H, NCH_3), 5.73 (d, 1H, *J* = 12.3 Hz, H-2), 7.22 (d, 2H, *J* = 8.0 Hz, arom-H), 7.79-7.83 (m, 3H, arom-H and H-3).

Anal.Calcd. for $C_{12}H_{15}NO$ (189.25): C, 76.15; H, 7.99; N, 7.40. Found: C, 76.15; H, 7.81; N, 7.59.

3-Dimethylamino-1-(4-methoxy-phenyl)-prop-2-en-1-one (**1d**).

This compound was obtained in 85% yield, 1.74 g (85%); M. p. 100 °C. IR (KBr) ν_{max} = 3430 (NMe_2), 3060 (arom. CH), 2980 (aliph. CH), 1674 (CO), 1600 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 205 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ_H = 2.56 (s, 3H, CH_3), 2.94 (s, 3H, NCH_3), 3.87 (s, 3H, NCH_3), 5.72 (d, 1H, *J* = 12.3 Hz, H-2), 6.93 (d, 2H, *J* = 7.5 Hz, arom-H), 7.79 (d, 1H, *J* = 12.3 Hz, H-3), 7.93 (d, 1H, *J* = 7.5 Hz, arom. H).

Anal. Calcd. for $C_{12}H_{15}NO_2$ (205.25): C, 70.22; H, 7.37; N, 6.82. Found: C, 69.98; H, 7.08; N, 6.80.

General Procedure for the Preparation of the Pyridine Derivatives **4a,b**.

To a solution of each of the enaminone **1a-d** (10 mmol) and ammonium acetate (1 g) in acetic acid (10 ml), acetylacetone (1.2 g, 12 mmol) was added. The reaction mixture was heated under reflux for 1 hour. The solvent was evaporated in vacuum; the residual solid was crystallized from dioxane.

1-(2-Methyl-6-naphthalen-2-yl-pyridin-3yl)ethanone (**4a**).

This compound was obtained in 82% yield, 2.14 g; mp 112 °C; IR (KBr) ν_{max} = 3050 (arom. CH), 2990 (aliph. CH), 1678 (CO),

1600 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 261 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ_H = 2.65 (s, 3H, $COCH_3$), 2.92 (s, 3H, CH_3), 7.53-7.57 (m, 2H, naphthyl-H), 7.80 (d, 1H, *J* = 8.0 Hz, pyridyl H-5), 7.88-7.92 (m, 1H; naphthyl-H), 7.96-8.02 (m, 2H, naphthyl-H), 8.10 (d, 1H, *J* = 8.0 Hz, pyridyl H-4), 8.21 (d, 1H, *J* = 8.5 Hz, naphthyl-H), 8.58 (s, 1H, naphthyl-H); ^{13}C NMR ($CDCl_3$): δ_C = 200.39 (CO), 159.14, 138.47,136.06, 134.40, 133.81, 131.06, 129.31, 129.18, 128.99, 128.12, 127.52, 127.34, 126.85, 124.94, 117.93, 29.78, 25.85.

Anal. Calcd. for $C_{18}H_{15}NO$ (261.31): C, 82.73; H, 5.79; N, 5.36. Found: C, 82.66; H, 5.63; N, 5.42.

1-[6-(4-Chlorophenyl)-2-methylpyridin-3-yl]ethanone (**4b**).

This compound was obtained in 80% yield, 1.96 g; mp 109 °C; IR (KBr) ν_{max} = 3068 (arom. CH), 2990 (aliph. CH), 1677 (CO), 1600 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 245 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ_H = 2.63 (s, 3H, $COCH_3$), 2.85 (s, 3H, CH_3), 7.45 (d, 2H, *J* = 8.0 Hz, phenyl-H), 7.63 (d, 1H, *J* = 8.0 Hz, pyridyl H-5), 8.02 (d, 2H, *J* = 8.0 Hz, phenyl-H), 8.06 (d, 1H, *J* = 8.0 Hz, pyridyl H-4).

Anal. Calcd. for $C_{14}H_{12}NOCl$ (245.7): C, 68.43; H, 4.92; N, 5.70. Found: C, 68.38; H, 4.59; N, 5.61.

General Procedure for the Preparation of the Pyridine Derivatives **4e-h**.

To a solution of each of the enaminones **1a-d** (10 mmol) and ammonium acetate (1 g) in acetic acid (10 ml), ethyl acetoacetate (1.56 g, 12 mmol) was added. The reaction mixture was heated under reflux for 1 hour. The solvent was evaporated under vacuum, and the residual solid was crystallized from dioxane.

Ethyl 2-Methyl-6-naphthalen-2-yl-nicotinate (**4e**).

This compound was obtained in 89% yield, 2.60 g; mp 92 °C; IR (KBr) ν_{max} = 3080 (arom. CH), 2924 (aliph. CH), 1715 (CO), 1596 cm^{-1} (arom. C=C); MS (EI, 70 eV): *m/z* = 291 [M$^+$]; ^{1}H NMR (DMSO): δ_H = 1.46 (t, 3H, *J* = 7.2 Hz, OCH_2CH_3), 2.99 (s, 3H, CH_3), 4.44 (q, 2H, *J* = 7.5 Hz, OCH_2CH_3), 7.52-7.57 (m, 2H, naphthyl-H), 7.80 (d, 2H, *J* = 8.16 Hz, pyridyl H-5), 7.88-7.92 (m, 1H, naphthyl-H), 7.96-8.00 (m, 2H, naphthyl-H), 8.22 (d, 1H, *J* = 8.2 Hz, naphthyl-H), 8.33 (d, 1H, *J* = 8.2 Hz, pyridyl H-4), 8.58 (s, 1H, naphthyl-H).

Anal. Calcd. for $C_{19}H_{17}NO_2$ (291.33): C, 78.33; H, 5.88; N, 4.81. Found: C, 78.45; H, 5.93; N, 5.07.

Ethyl 6-(4-Chlorophenyl)-2-methylnicotinate (**4f**).

This compound was obtained in 84% yield, 2.32 g; mp 76 °C; IR (KBr) ν_{max} = 3090 (arom. CH), 2979 (aliph. CH), 1724 (CO), 1607 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 275 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ_H = 1.44 (t, 3H, *J* = 6 Hz, OCH_2CH_3), 2.93 (s, 3H, CH_3), 4.42 (q, 2H, *J* = 6 Hz, OCH_2CH_3), 7.47 (d, 2H, *J* = 8.0 Hz, phenyl-H), 7.62 (d, 1H, *J* = 8.0 Hz, pyridyl H-5), 8.03 (d, 2H, *J* = 8.0 Hz, phenyl-H), 8.29 (d, 1H, *J* = 8.0 Hz, pyridyl H-4).

Anal. Calcd. for $C_{15}H_{14}NO_2Cl$ (275.76): C, 65.27; H, 5.07; N, 5.07. Found: C, 65.21; H, 4.98; N, 5.23.

Ethyl 2-Methyl-6-*p*-tolylmethylnicotinate **(4g**).

This compound was obtained in 82% yield, 2.09 g; mp 55 °C (lit. [17] mp 54 °C); IR (KBr) ν_{max} = 3090 (arom.CH), 2989 (aliph. CH), 1711 (CO), 1600 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 255 [M$^+$]; ^{1}H NMR (DMSO): δ_H = 1.31 (t, 3H, *J* = 7.5 Hz, OCH_2CH_3), 2.34 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 4.29 (q, 2H, *J* = 7.5 Hz, OCH_2CH_3), 7.28 (d, 2H, *J* = 8.2 Hz, phenyl-H), 7.81 (d, 1H, *J* = 8.2 Hz, pyridyl H-5), 8.01 (d, 2H, *J* = 8.2 Hz, phenyl-H), 8.16 (d, 1H, *J* = 8.2 Hz, pyridyl H-4).

Anal. Calcd. for $C_{16}H_{17}NO_2$ (255.30): C, 75.27; H, 6.71; N, 5.49. Found: C, 75.06; H, 6.74; N, 5.76.

Ethyl 6-(4-Methoxyphenyl)-2-methylnicotinate (**4h**).

This compound was obtained in 78% yield, 2.11 g; mp 67 °C (lit. [7] mp 68-69 °C; IR (KBr) ν_{max} = 3070 (arom. CH), 2993 (aliph. CH), 1712 (CO), 1590 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 271 [M$^+$]; ^{1}H NMR (DMSO): δ_H = 1.32 (t, 3H, *J* = 7.5 Hz, OCH_2CH_3), 2.76 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 4.30 (q, 2H, *J* = 7.5 Hz, OCH_2CH_3), 7.04 (d, 2H, *J* = 7.3 Hz, arom.H), 7.81 (d, 1H, *J* = 8.10 Hz, pyridyl H-5), 8.10 (d, 2H, *J* = 7.3 Hz, arom.H), 8.16 (d, 1H, *J* = 8.11 Hz, pyridyl H-4).

Anal. Calcd. for $C_{16}H_{17}NO_3$ (271.30): C, 70.83; H, 6.32; N, 5.16. Found: C, 70.86; H, 6.17; N, 4.97.

General Procedure for the Preparation of the Pyridine Derivatives **7**.

A stirred suspension of acetic acid (10 ml) and ammonium acetate (1 g), was treated with each of the enaminone **1a-d** (10 mmol). The reaction mixture was heated under reflux for 1 hour after which it was cooled to room temperature. The precipitate, which formed, was collected by filtration and successively crystallized from dioxane.

Naphthalen-2-yl-(6-naphthalen-2-yl-pyridin-3-yl)methanone (**7a**).

This compound was obtained in 85% yield, 3.05 g; mp 145 °C; IR (KBr) ν_{max} = 3055 (arom. CH), 1651 (CO), 1600 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 359 [M$^+$]; ^{1}H NMR (DMSO): δ_H = 7.56-7.66 (m, 4H, arom. H), 7.97-8.17 (m, 8H, arom. H), 8.33-8.82 (m, 4H, arom. H), 9.10 (s, 1H, pyridyl H-2).

Anal. Calcd. for $C_{26}H_{17}NO$ (359.40): C, 86.88; H, 4.77; N, 3.90. Found: C, 86.67; H, 4.73; N, 4.03.

(4-Chlorophenyl)-[6-(4-chlorophenyl)pyridin-3-yl]methanone (**7b**).

This compound was obtained in 81% yield, 2.65g; mp 191 °C (lit. [8] mp 190 °C); IR (KBr) ν_{max} = 3055 (arom. CH), 1600 (arom.C=C), 1640 cm^{-1} (CO); MS (EI, 70 eV): *m/z* = 328 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ_H = 7.48 (d, 4H, *J* = 8.0 Hz, arom. H), 7.84 (d, 2H, *J* = 8.0 Hz, arom-H), 7.77 (d, 1H, *J* = 8.3 Hz, pyridyl H-5), 8.02 (d, 2H, *J* = 8.0 Hz, arom-H), 8.24 (d, 1H, *J* = 8.3 Hz, pyridyl H-4), 9.08 (s, 1H, pyridyl H-2).

Anal. Calcd. for $C_{18}H_{11}NOCl_2$ (328.2): C, 65.87; H, 3.38; N, 4.27. Found: C, 65.72; H, 3.19; N, 4.27.

p-Tolyl-(6-*p*-tolylpyridin-3-yl)methanone (**7c**).

This compound was obtained in 78% yield,2.23 g; mp 184 °C; IR (KBr) ν_{max} = 3100 (arom. CH), 2916 (aliph. CH), 1643 (CO), 1603 cm^{-1} (arom.C=C); MS (EI, 70 eV): *m/z* = 287 [M$^+$]; ^{1}H NMR ($CDCl_3$) δ_H = 2.45 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 7.34 (d, 4H, *J* = 8.1 Hz, arom. H), 7.79 (d, 2H, *J* = 8.1 Hz, arom-H), 7.87 (d, 1H, *J* = 8.3 Hz, pyridyl H-5), 8.01 (d, 2H, *J* = 8.1 Hz, arom-H), 8.20 (d, 1H, *J* = 8.3 Hz, pyridyl H-4), 9.06 (s, 1H, pyridyl H-2).

Anal. Calcd. for $C_{20}H_{17}NO$ (287.34): C, 83.59; H, 5.96; N, 4.88. Found: C, 83.67; H, 5.73; N, 5.04.

(4-Methoxyphenyl)-[6-(4-methoxyphenyl)pyridin-3-yl]-methanone (**7d**).

This compound was obtained in 75% yield, 2.39 g; mp 186 °C (lit. [8] mp 188 °C); IR (KBr) ν_{max} = 3100 (arom. CH), 2993

(aliph. CH), 1607 (arom.C=C), 1675 cm^{-1} (CO); MS (EI, 70 eV): *m/z* = 319 [M^+]; ^1H NMR ($CDCl_3$): δ_H = 3.80 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 7.08 (d, 4H, *J* = 7.8 Hz, arom. H), 7.79 (d, 2H, *J* = 7.8 Hz, arom-H), 7.83 (d, 1H, *J* = 8.3 Hz, pyridyl H-5), 8.10 (d, 2H, *J* = 7.8 Hz, arom-H), 8.25 (d, 1H, *J* = 8.3 Hz, pyridyl H-4), 9.11 (s, 1H, pyridyl H-2).

Anal. Calcd. for $C_{20}H_{17}NO_3$ (319.36): C, 75.22; H, 5.37; N, 4.39. Found: C, 75.28; H, 5.12; N, 4.40.

General Procedure for the Preparation of **9a,c,d**.

Each of compound **1a,c,d** (10 mmol) was refluxed in acetic acid (20 ml) for 2 hours after which it was cooled to room temperature. The precipitate, which formed, was collected by filtration and successively crystallized from ethanol/dioxane (3:1 v/v).

1,3,5-Tri-2-naphthoylbenzene (**9a**).

This compound was obtained in 90% yield, 4.87 g; mp 225 °C; IR (KBr) ν_{max} = 3047 (arom. CH), 1651 (CO), 1608 cm^{-1} (arom. C=C); MS (EI, 70 eV): *m/z* = 540 [M^+]; ^1H NMR (DMSO): δ_H = 7.63-7.71 (m, 6H, naphthyl-H), 8.00 (t, 6H, *J* = 8.0 Hz, naphthyl-H), 8.10 (d, 3H, *J* = 8.8 Hz, naphthyl-H), 8.22 (d, 3H, *J* = 8.8 Hz, naphthyl-H), 8.45 (s, 3H, phenyl-H), 8.59 (s, 3H, naphthyl-H).

Anal. Calcd. for $C_{39}H_{24}O_3$ (540.58): C, 86.65; H, 4.48. Found: C, 86.43; H, 4.44.

1,3,5-Tri-*p*-toluoylbenzene (**9c**).

This compound was obtained in 90% yield, 3.88 g; mp 156 °C; IR (KBr) ν_{max} = 3060 (arom. CH), 2956 (aliph. CH), 1645 cm^{-1} (CO), 1602 (arom. C=C); MS (EI, 70 eV): *m/z* = 432 [M^+]; ^1H NMR (DMSO) δ_H = 2.42 (s, 9H, 3 CH_3), 7.20 (d, 6H, *J* = 8.0 Hz, arom. H), 7.82 (d, 6H, *J* = 8.0 Hz, arom. H), 8.45 (s, 3H, phenyl-H).

Anal. Calcd. for $C_{30}H_{24}O_3$ (432.52): C, 83.31; H, 5.59. Found: C, 83.36; H, 5.42.

1,3,5-Tri-4-methoxybenzoylbenzene (**9d**).

This compound was obtained in 88% yield, 4.22 g; mp 177 °C; IR (KBr) ν_{max} = 3054 (arom. CH), 2956 (aliph. CH), 1676 cm^{-1} (CO), 1609 (arom. C=C); MS (EI, 70 eV): *m/z* = 480 [M^+]; ^1H NMR (DMSO): δ_H = 3.90 (s, 9H, 3OCH_3), 7.06 (d, 6H, *J* = 7.8 Hz, arom. H), 8.01 (d, 6H, *J* = 7.8 Hz, arom. H), 8.48 (s, 3H, phenyl-H).

Anal. Calcd. for $C_{30}H_{24}O_6$ (480.52): C, 74.99; H, 5.03. Found: C, 75.12; H, 5.02.

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