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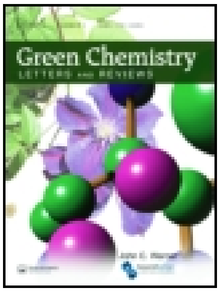

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Green technologies in organic synthesis: self-condensation of enamines, enaminones and enaminoesters under microwave irradiation in ionic liquid

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RESEARCH LETTER

Green technologies in organic synthesis: self-condensation of enamines, enaminones and enaminoesters under microwave irradiation in ionic liquid

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Utilizing green technologies as microwave (MW) irradiation and ionic liquids (ILs), we could produce 1,3,5-trisubstituted benzene **3**, **7**, **9**, and **14** by self-condensation of enamines **1**, enaminones **4**, **8,** and enaminoester **10**, respectively, in the presence of pyridinium chloride ([PyH]Cl) for short time. Also, we synthesized pyridine derivatives **17**, upon irradiating enaminones **4** in domestic MW oven for short time.

Keywords: green chemistry; ionic liquids; microwave irradiation; trisubstituted benzene; self-condensation; X-ray crystal structure determination

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Introduction

Adopting green methodologies for synthesis of polyfunctional aromatics and heteroaromatics is now receiving considerable attention (*1–3*). In the last decade, we were interested in exploring potentialities of enamines and we could already discover several novel synthesis of polyfunctional aromatics and heteroaromatics utilizing enamines as starting materials (*4–6*). Recently, we have been interested in adopting green methodologies to our synthetic approaches and we could efficiently adopt microwave (MW) irradiation as energy source for quite a number of our synthesis (*3,7–11*). In the present article, we report the utility of domestic MW as energy source and ionic liquid (IL) as solvent for self-condensation of enamines, reported recently from our laboratories via refluxing the enamines in acetic acid, in presence or absence of ammonium ion for several hours (*12–14*). We observed that with this technique, high boiling solvents evaporate producing some hazard. To avoid this complication we thought to adopt MW heating in IL trying to conduct the reactions of enamines and enaminones in a green way. ILs are one of several technologies used in green chemistry that aimed to reduce environmental harmful effect of chemicals like organovolatile solvent (*15*). Many of these solvents are known to upset our ecosystems by depleting the ozone layer and participating in the reactions that form tropospheric smog. In addition, some solvents are neurotoxins, may cause sterility, or may cause cancer. While continuous using of these solvents would not be acceptable from both an environmental and a health perspective, such operations are difficult to achieve, and alternative solvents are currently being sought to minimize the problems inherent in solvent release to the environment. ILs are believed to have minimum vapor pressure and have been observed to increase MW energy absorption (*16*). Therefore, several MW reactions have been already successfully conducted in ILs (*17*).

Results and discussion

The substituted enamines **1a–f**, enaminones **4a–j**, **8**, and enaminoesters **10a–c** were prepared and their structures were further investigated in the light of reported existence of **8** in *Z*-form (*18*). Contradicting all previous reports on structure of enaminones (*19–21*), now we confirm that this enaminone exists in *trans* form as indicated earlier by Al-Mousawi (*22*).

Previously, it has been reported that enamines **1a–c** gave only the open chain compounds **2a–c** upon treatment with AcOH (*23*). In our hands, heating enamines **1a–f** in [PyH]Cl afforded 1,3,5-trisubstituted benzene **3a,b** as the only reaction products (Scheme 1).

Enaminones **4a–j**, prepared by reacting methylketones with dimethyl formamid dimethyl acetal (*DMFDMA*) in MW oven (*24*), underwent self-condensation on heating at 110°C in [PyH]Cl, as an IL, for 20 min or irradiation at 400 watt, 105°C for 1 min in a modified domestic MW oven yielding

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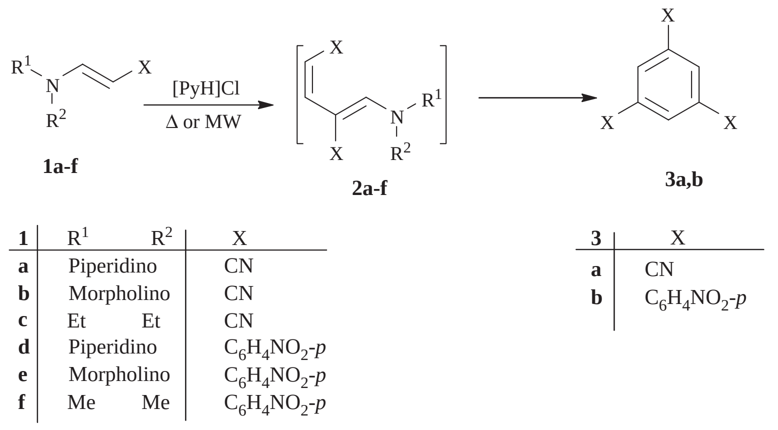


1	R^1	R^2	X
a	Piperidino		CN
b	Morpholino		CN
c	Et	Et	CN
d	Piperidino		$C_6H_4NO_2$-*p*
e	Morpholino		$C_6H_4NO_2$-*p*
f	Me	Me	$C_6H_4NO_2$-*p*

3	X
a	CN
b	$C_6H_4NO_2$-*p*

Scheme 1. Synthesis of 1,3,5-trisubstituted benzene **3a,b**.

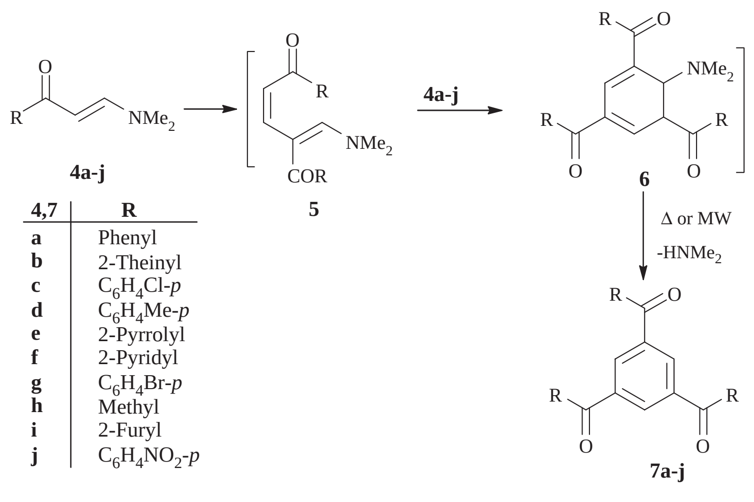
1,3,5-trisubstituted benzene **7a–j** (Scheme 2) in high yield (Table 1).

From Table 1 one can see that there is an improvement in rates and yields of reactions under both conventional heating and MW in IL, compared with classical condition in reported literature (*12*).

We believe that **4a–j** is initially converted to the open chain intermediate **5** that then adds further one molecule of **4a–j** to yield the intermediate **6** that is aromatized, under these reaction conditions, to the final isolable products **7a–j**. Similarly, compound **8** afforded **9** under the same reaction conditions (Scheme 3). The structure of **9** was established for the reaction product on the basis of its elemental analysis and spectral data (MS, IR, ^{1}H NMR; see Section "Experimental"). Finally, the structure of **9** was unambiguously confirmed by X-ray crystallography (Figure 1).[1]

In the same way, enaminoesters **10a–c** underwent self-condensation to yield triethylbenzene-1,3,5-tricarboxylat **14**. The formation of **14** is assumed to proceed via self-condensation of **10** to yield the intermediate **11** which reacts with another molecule of **10** to give another intermediate **12** which then loses two molecules of secondary amines (piperidine, morpholine, or diethylamine) to give the final product **14** (Scheme 4). Alternatively, compound **14** may be formed through [2+2+2] cycloaddition of **10** to give the intermediate **13** which undergoes aromatization by lose three molecules of secondary amines, under the reaction conditions, to give **14**.

Heating enaminones **4a,b,d,e,g** with excess of ammonium acetate, as an IL, at 110°C for 20 min or irradiating under MW for 1 min at 400 watt, 105°C yielded the 2-aryl (or heteroaryl)-5-aroyl (or hetroaroyl)-pyridines **17a–e**. The formation of **17a–e** may take place through an initial self-condensation of **4**, via loss one molecule of dimethylamine, to yield the intermediate **15** which reacts directly with ammonium ion to give a further enamine intermediate **16**. The



4,7	R
a	Phenyl
b	2-Theinyl
c	C_6H_4Cl-*p*
d	C_6H_4Me-*p*
e	2-Pyrrolyl
f	2-Pyridyl
g	C_6H_4Br-*p*
h	Methyl
i	2-Furyl
j	$C_6H_4NO_2$-*p*

Scheme 2. Synthesis of 1,3,5-triaroyl benzene **7a-j**.

Table 1. Comparing yield of **7a–j** using thermal and microwave irradiation in the presence of IL.

		Yield		Time (min)		
Compound number	R	Δ	μw	Δ	μw	Literature yield
7a	phenyl	86	91	20	1	79$^{(12)}$
7b	2-thienyl	88	97	20	1	85$^{(12)}$
7c	C_6H_4Cl-*p*	100	100	20	1	–
7d	C_6H_4Me-*p*	99	100	20	1	–
7e	2-pyrrolyl	70	100	20	1	–
7f	2-pyridyl	72	100	20	1	89$^{(12)}$
7g	C_6H_4Br-*p*	94	95	20	1	–
7h	methyl	60	70	20	1	65$^{(12)}$
7i	2-furyl	64	87	20	1	87$^{(12)}$
7j	$C_6H_4NO_2$-*p*	100	100	20	1	–

latter undergoes intramolecular cyclocondensation, via loss one molecule of water, to give the final products **17a–e** (Scheme 5).

Temperature measured during exposure in MW experiment which confirms the rate augmentation during MW heating. Temperature measurement is performed for all reactions with thermocouple sensors, which show sufficient accuracy for the presented reactions used to monitor the temperature inside the vessel; it was found that ≈105–110°C, to ensure reproducibility.

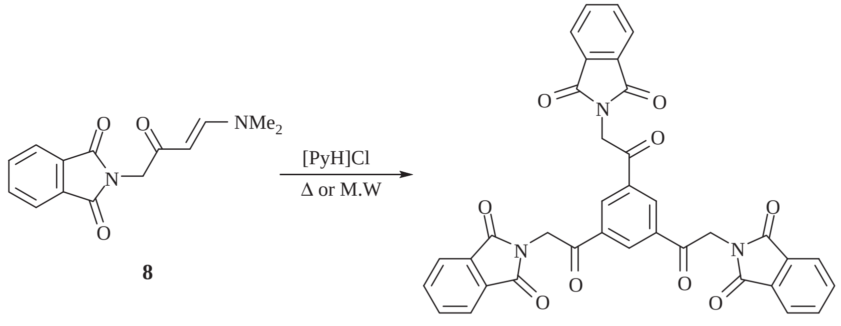
Experimental

All melting points were measured on a Gallenkamp electrothermal melting point apparatus and are uncorrected. The IR absorption spectra were measured on a Nicolet Magna 520FT IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated dimethylsulfoxide [DMSO] or deutrated chloroform ($CDCl_3$) at 200 MHz on a Varian Gemini NMR spectrometer and a Bruker DPX 400 MHz spectrometer using tetramethylsilane (TMS) as an internal reference. Mass spectra were performed on a Shimadzu GCMS-QP 1000 EX mass spectrometer at 70 eV. X-ray crystallography was carried out on a Kappa CCD Enraf Nonius FR 590 diffractometer, National Research Center, Dokki, Cairo, Egypt. MW irradiation was carried out using the commercial MW oven (SGO 1000 W), with a thermocouple used to monitor the temperature inside the vessel and it was found that ≈105–110°C. Elemental analyses were performed on Perkin Elmer 2400 CHN elemental analyzer flowchart. Elemental analyses (C, H, N, S) were conducted using the Elemental Analyser XBO and results were found to be within ±0.2% of the calculated values.

General procedure for the preparation of compounds 3a,b

Method I (Δ)

A mixture of pyridinium chloride ([PyH]Cl; 0.4 mol) and enamines **1a–f** (0.1 mol) was heated at 110°C for 30–60 min and was allowed to cool to room temperature. Then, it was treated with ethanol. The solid product so formed was collected by filtration, dried, and recrystallized from ethanol.



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9

Scheme 3. Synthesis of 2,2′,2′′-(2,2′,2′′-(Benzene-1,3,5-triyl)tris(2-oxoethane-2,1-diyl))triisoindoline-1,3-dione **9**.

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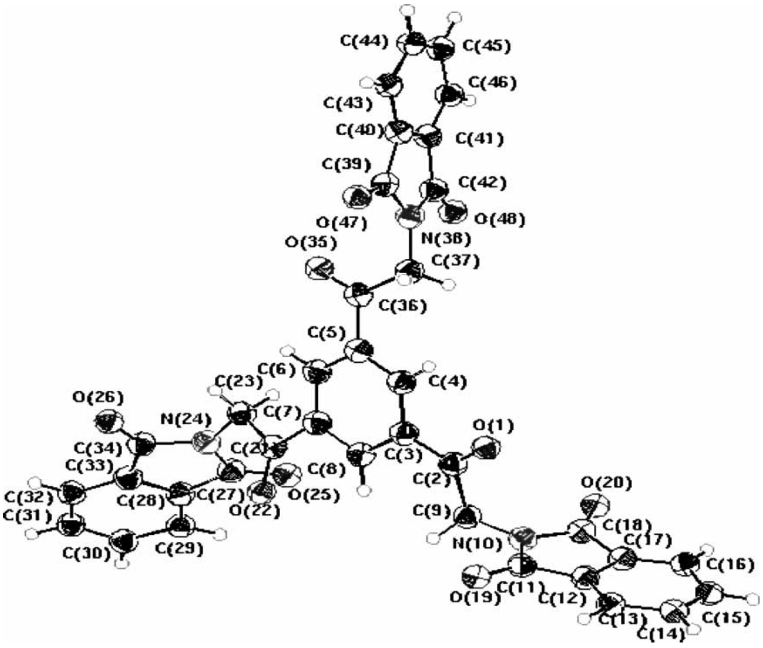


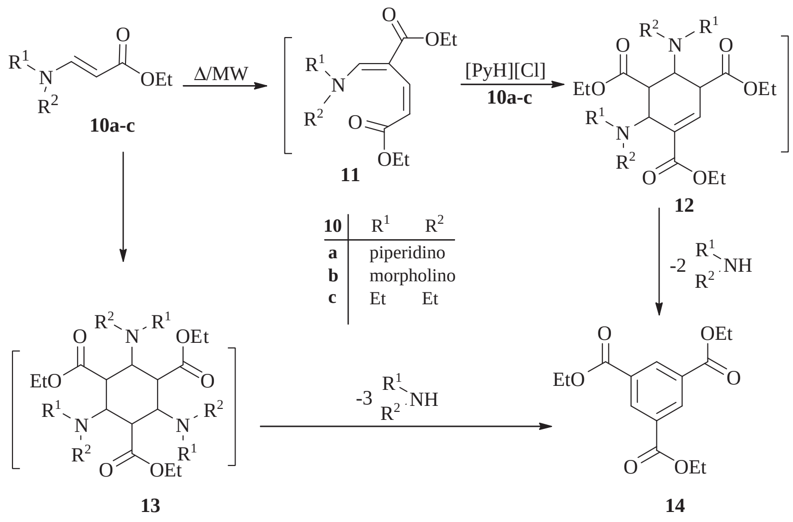
Figure 1. Molecular structure of **9** with atoms labeling scheme.

Method II (MW)

A mixture of [PyH]Cl (0.4 mol) and enamines **1a–f** (0.1 mol) was placed in the MW oven and irradiated at 400 watt, 105°C for 1–3 min. After cooling to room temperature, it was treated with ethanol. The solid product so formed was collected by filtration, dried, and recrystallized from ethanol.

*Compound (**3a**, $C_9H_3N_3$).* [55% (Method I), 67% (Method II)] as a brown powder; mp > 300°C (from EtOH); $\nu_{\max/}$(KBr)cm^{-1} 3095 (aromatic CH), 2212 (CN); *m/z* (EI) 153 (M$^+$, 43%). (Found: C, 70.55; H, 2.03; N, 27.43. $C_9H_3N_3$ Calculated: C, 70.59; H, 1.97; N, 27.44%)

*Compound (**3b**, $C_{24}H_{15}N_3O_6$).* [60% (Method I), 77% (Method II)] as a brown powder; mp > 300°C; $\nu_{\max/}$(KBr)cm^{-1} 3089 (aromatic CH), 1510, 1341 (NO_2); *m/z* (EI) 441 (M$^+$, 100%); δ_H(400 MHz; DMSO-d$_6$) 7.68 (3 H, s, Ar-H), 8.10 (6 H, d, *J* 8, ArH), 8.58 (6 H, d, *J* 8, ArH). (Found: C, 65.39; H, 3.51; N, 9.63. $C_{24}H_{15}N_3O_6$ Calculated: C, 65.31; H, 3.43; N, 9.52%)



10	R¹	R²
a	piperidino	
b	morpholino	
c	Et	Et

Scheme 4. Synthesis of triethyl benzene-1,3,5-tricarboxylate **14**.

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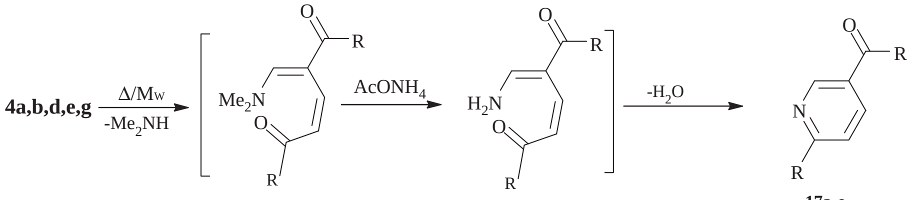

15 **16** **17a-e**

17	R
a	phenyl
b	2-thienyl
c	C_6H_4Me-*p*
d	2-pyrrolyl
e	C_6H_4Br-*p*

Scheme 5. Synthesis of 2-aryl-5-aroylpyridines **17a-e**.

General procedure for the preparation of 1,3,5-Trisubstituted benzene 7a–j

Method I (Δ)

A mixture of [PyH]Cl (0.4 mol) and enaminones **4a–j** (0.1 mol) was heated at 110°C for 20 min and was allowed to cool to room temperature. Then, it was treated with a mixture of ethanol/dioxane (3:1). The solid product so formed was collected by filtration, dried, and recrystallized from dioxane.

Method II (MW)

A mixture of [PyH]Cl (0.4 mol) and enaminones **4a–j** (0.1 mol) was placed in the MW oven and irradiated at 400 Watt, 105°C for 1 min The reaction mixture left to cool to room temperature and then treated with a mixture of ethanol/dioxane (3:1). The solid product so formed was collected by filtration, dried, and recrystallized from dioxane.

*(5-(3-Chlorobenzoyl)-1,3-phenylene)bis((4-chlorophenyl)methanone) (**7c**, $C_{27}H_{15}Cl_3O_3$).* Mp 184–186°C; $\nu_{max/}$(KBr)cm^{-1} 3082 (aromatic CH), 1667 (C=O); *m*/*z* (EI) 492 (M$^+$ +1, 14%); δ_H(400 MHz; DMSO-d$_6$) 7.65 (6 H, d, *J* 8, ArH), 7.86 (6 H, d, *J* 8, ArH), 8.23 (3 H, s, Ar-H); δ_C(400 MHz; DMSO-d$_6$) 129.46, 132.34, 135.36, 138.90 (C_6H_4-Cl-*p*), 134.31, 137.81 (C_6H_3-CO), 193.80(*C*=O). (Found: C, 65.70; H, 3.00. $C_{27}H_{15}Cl_3O_3$ Calculated: C, 65.68; H, 3.06%.)

*(5-(3-Methylbenzoyl)-1,3-phenylene)bis(p-tolylmethanone) (**7d**, $C_{30}H_{24}O_3$).* Mp 131–133°C; $\nu_{max/}$(KBr)cm^{-1} 3035 (aromatic CH), 2925 (aliphatic CH), 1663 (C=O); *m*/*z* (EI) 432 (M$^+$, 9%); δ_H(400 MHz; DMSO-d$_6$) 2.40 (9 H, s, 3C*H*$_3$), 7.38 (6 H, d, *J* 8, ArH), 7.74 (6 H, d, *J* 8, ArH), 8.20 (3 H, s, Ar-H); δ_C(400 MHz; DMSO-d$_6$) 21.77 (3 × *C*H$_3$), 129.87, 130.64, 133.93, 144.46 (C_6H_4-CH$_3$-*p*), 134.08, 138.23 (C_6H_3-CO), 194.48 (*C*=O). (Found: C, 83.40; H, 5.81. Calculated: C, 83.31; H, 5.59%.)

*Benzene-1,3,5-triyltris((1H-pyrrol-2-yl)methanone) (**7e**, $C_{21}H_{15}N_3O_3$).* Mp 256–258°C; $\nu_{max/}$(KBr)cm^{-1} 3287 (NH), 3050 (aromatic CH), 1669 (C=O); *m*/*z* (EI) 357 (M$^+$, 31%); δ_H(400 MHz; DMSO-d$_6$) 6.31 (3 H, t, *J* 2.2, 3 × pyrrolyl H-4), 6.94 (3 H, d, *J* 2.2, 3 × pyrrolyl H-3), 7.29 (3 H, d, *J* 2.2, 3 × pyrrolyl H-5), 8.36 (3 H, s, Ar-H), 12.22 (3 H, s, pyrrole N*H*); δ_C(400 MHz; DMSO-d$_6$) 111.25, 120.39, 127.78, 130.75 (pyrrole carbons), 131.80, 139.42 (C_6H_3-CO), 182.69 (3*C*=O). (Found: C, 70.66; H, 4.26; N, 11.66. $C_{21}H_{15}N_3O_3$ Calculated: C, 70.58; H, 4.23; N, 11.76%.)

*Benzene-1,3,5-triyltris((4-bromophenyl)methanone) (**7g**, $C_{27}H_{15}Br_3O_3$).* Mp 205–207°C; $\nu_{max/}$(KBr)cm^{-1} 3065 (aromatic CH), 1665 (C=O); *m*/*z* (EI) 626 (M$^+$, 13%); ^{1}H δ_H(400 MHz; DMSO-d$_6$) 7.62-7.68 (12 H, m, ArH), 8.31 (3 H, s, Ar-H); δ_C(400 MHz; DMSO-d$_6$) 128.82, 131.58, 132.18, 135.02 (C_6H_4-Br-*p*), 133.98, 138.10 (C_6H_3-CO), 193.64 (*C*=O). (Found: C, 51.76; H, 2.32. $C_{27}H_{15}Br_3O_3$ Calculated: C, 51.71; H, 2.41%.)

*Benzene-1,3,5-triyltris((4-nitrophenyl)methanone) (**7j**, $C_{27}H_{15}N_3O_9$).* Mp 196–198°C; $\nu_{max/}$(KBr)cm^{-1} 3086 (aromatic CH), 1665 (C=O), 1526, 1337 (NO$_2$); *m*/*z* (EI) 525 (M$^+$, 12%); δ_H(400 MHz; DMSO-d$_6$) 7.99 (6 H, d, *J* 8, ArH), 8.31 (6 H, d, *J* 8, ArH), 8.42 (3 H, s, Ar-H); δ_C(400 MHz; DMSO-d$_6$) 123.93, 130.87, 140,98, 150.56 (C_6H_4-NO$_2$-*p*), 134.62, 137.74 (C_6H_3-CO), 196.34 (*C*=O). (Found: C, 61.81; H, 2.79; N, 8.12. Calculated: C, 61.72; H, 2.88; N, 8.00%.)

General procedure for the preparation of 2,2′,2″-(2,2′,2″-(Benzene-1,3,5-triyl)tris(2-oxoethane-2,1-diyl))triisoindoline-1,3-dione 9

Method I (Δ)

A mixture of [PyH]Cl (0.4 mol) and enaminone **8** (0.1 mol) was heated at 110°C for 20 min After cooling to room temperature, the reaction mixture was treated with ethanol. The solid product so

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formed was collected by filtration, dried, and recrystallized from ethanol.

Method II (MW)

A mixture of [PyH]Cl (0.4 mol) and enaminone **8** (0.1 mol) was placed in the MW oven and irradiated at 400 watt, 105°C for 0.5 min. After cooling to room temperature, it was treated with ethanol. The solid product so formed was collected by filtration, dried, and recrystallized from ethanol to give compound **9** as pale yellow crystals.

*2,2′,2″-(2,2′,2″-(Benzene-1,3,5-triyl)tris(2-oxoethane-2,1-diyl))triisoindoline-1,3-dione (**9**, $C_{36}H_{21}N_3O_9$).* [89% (Method I), 98% (Method II)] as a brown powder; mp 295–297°C; $\nu_{max/}$(KBr)cm^{-1} 3070 (aromatic CH), 1774 (C = O), 1704 (C = O); *m/z* (EI) 639 (M^+, 7%); δ_H(400 MHz; DMSO-d$_6$) 5.56 (6 H, s, 3CH$_2$), 7.91-7.97 (12 H, m, phthalimide-H), 8.99 (3 H, t, *J* 8, Ar-H). (Found: C, 67.55; H, 3.49; N, 6.50. $C_{36}H_{21}N_3O_9$ Calculated: C, 67.61; H, 3.31; N, 6.57%.)

General procedure for the preparation of Triethyl benzene-1,3,5-tricarboxylate 14

Method I (Δ)

A mixture of [PyH]Cl (0.4 mol) and enaminoester **10a–c** (0.1 mol) was heated at 110°C for 30 min and was allowed to cool to room temperature. Then, it was treated with ethanol. The solid product so formed was collected by filtration, dried, and recrystallized from ethanol.

Method II (MW)

A mixture of [PyH]Cl (0.4 mol) and enaminoester **10a–c** (0.1 mol) was placed in the MW oven and irradiated at 400 watt, 105°C for 0.5 min. After cooling to room temperature, it was treated with ethanol. The solid product so formed was collected by filtration, dried, and recrystallized from ethanol, to give compound **14** as orange crystal.

*Triethyl benzene-1,3,5-tricarboxylate (**14**, $C_{15}H_{18}N_6$).* [55% (Method I), 83% (Method II)] as pale yellow; mp 127–129°C; $\nu_{max/}$(KBr)cm^{-1} 3099 (aromatic CH), 2994 (aliphatic CH), 1715 (CO ester); *m/z* (EI) 294 (M^+, 100%); δ_H(400 MHz; DMSO-d$_6$) 1.44 (9 H, t, *J* 6, 3 × C*H*$_3$), 4.45 (6 H, q, *J* 6, 3 × C*H*$_2$), 8.84 (3 H, s, Ar-H); δ_C(400 MHz; DMSO-d$_6$) 14.13 (3 × *C*H$_3$), 61.72 (3 × *C*H$_2$), 131.49, 135.30 (*C*$_6$H$_3$-CO), 165.09 (C$_6$H$_3$-*C*O). (Found: C, 61.29; H, 6.14. $C_{15}H_{18}N_6$ Calculated: C, 61.22; H, 6.16%.)

General procedure for the preparation of 2-Aryl-5-aroylpyridines 17a–e

Method I (Δ)

A mixture of ammonium acetate (0.4 mol) and enaminones **4a,b,d,e,g** (0.1 mol) was heated at 110°C in an oil bath for 20 min and was allowed to cool to room temperature. Then, it was treated with ethanol. The solid product so formed was collected by filtration, dried, and recrystallized from ethanol.

Method II (MW)

A mixture of ammonium acetate (0.4 mol) and enaminones **4a,b,d,e,g** (0.1 mol) was placed in the MW oven and irradiated at 400 watt, 105°C for 1 min. After cooling to room temperature, it was treated with ethanol. The solid product so formed was collected by filtration, dried, and recrystallized from ethanol.

*Phenyl(6-phenylpyridin-3-yl)methanone (**17a**, $C_{18}H_{13}NO$).* [50% (Method I), 65% (Method II)] as a yellow crystal; mp 120–122°C; $\nu_{max/}$(KBr)cm^{-1} 3080 (aromatic CH), 1662 (C = O); *m/z* (EI) 259 (M^+, 86%); δ_H(400 MHz; DMSO-d$_6$) 7.20-8.01 (12 H, m, 10 × Ar-H + 2b × pyridine-H); 9.03 (1 H, s, pyridine H-6); δ_C(400 MHz; DMSO-d$_6$) 123.65, 137,79 (*C*$_6$H$_5$), 123.87, 131.99 (CO*C*$_6$H$_5$), 135.01, 135.29, 167.90, 170.01 (pyridyl carbons), 189.99 (*C* = O). (Found: C, 83.24; H, 5.15; N, 5.48. Calculated: C, 83.37; H, 5.05; N, 5.40%.)

*Thiophen-2-yl(6-(thiophen-2-yl)pyridin-3-yl)methanone (**17b**, $C_{14}H_9NOS_2$).* [54% (Method I), 74% (Method II)] as a black powder; mp 128–129°C; $\nu_{max/}$(KBr)cm^{-1} 3071 (aromatic CH), 1660 (C = O); *m/z* (EI) 271 (M^+, 100%); δ_H(400 MHz; DMSO-d$_6$) 7.13 (1 H, t, *J* 4, C$_4$*H*$_3$S H-4), 7.32 (1 H, t, *J* 4, COC$_4$*H*$_3$S H-4), 7.22 (1 H, d, *J* 4, C$_4$*H*$_3$S H-3), 7.35 (1 H, d, *J* 4, C$_4$*H*$_3$S H-5), 7.71 (1 H, d, *J* 4, COC$_4$*H*$_3$S H-3), 7.77 (1 H, d, *J* 4, COC$_4$*H*$_3$S H-5), 8.11 (1 H, d, pyridine, H-3), 8.19 (1 H, d, pyridine H-4), 8.99 (1 H, s, pyridine H-6). (Found: C, 61.85; H, 3.34; N, 5.09. $C_{14}H_9NOS_2$ Calculated: C, 61.97; H, 3.34; N, 5.16%.)

*p-Tolyl(6-p-tolylpyridin-3-yl)methanone (**17c**, $C_{20}H_{17}NO$).* [62% (Method I), 75% (Method II)] as an orange crystal; mp 116–118°C; $\nu_{max/}$(KBr)cm^{-1} 3090 (aromatic CH), 2915 (aliphatic CH), 1667 (C = O); *m/z* (EI) 287 (M^+, 86%); δ_H(400 MHz; DMSO-d$_6$) 7.23 (2 H, d, *J* 8, ArH), 7.40 (2 H, d, *J* 8, ArH), 7.71 (2 H, d, *J* 8, ArH), 7.79 (2 H, d, *J* 8, ArH), 8.09-8.13 (2 H, m, pyridine H-3 and H-4), 8.93 (1 H, s, pyridine H-6); δ_C(400 MHz; DMSO-d$_6$) 21.55 (2 × *C*H$_3$), 127.48, 129.27, 132.22, 134.50 (*C*$_6$H$_4$-CH$_3$-*p*), 129.29, 130.11, 141.20 (CO*C*$_6$H$_4$-CH$_3$-*p*), 120.11, 138.07,

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154.53, 161.09 (pyridine carbons), 186.01 ($C=O$). (Found: C, 83.68; H, 5.83; N, 4.82. $C_{20}H_{17}NO$ Calculated: C, 83.59; H, 5.96; N, 4.87%.)

*(6-(1H-Pyrrol-2-yl)pyridin-3-yl)(1H-pyrrol-2-yl)methanone (**17d**, $C_{14}H_{11}N_3O$).* [50% (Method I), 66% (Method II)] as a brown powder; mp 133–134°C; $\nu_{max/}$(KBr)cm^{-1} 3086 (aromatic CH), 1670 ($C=O$) 3353 (NH); *m/z* (EI) 237 (M^+, 22%); δ_H(400 MHz; DMSO-d_6) 6.38 (1 H, t, *J* 2.2, pyrrole H-4), 6.41 (1 H, t, *J* 2.2, pyrrole H-4), 6.75 (1 H, d, *J* 2.2, pyrrole H-3), 7.15 (1 H, d, *J* 2.2, pyrrole H-3), 7.22 (1 H, d, *J* 2.2, pyrrole H-5), 7.47 (1 H, d, *J* 2.2, pyrrole H-5), 7.62 (1 H, d, *J* 8, pyridine H-3), 8.58 (1 H, d, *J* 8, pyridine H-4), 9.10 (1 H, s, pyridine H-6), 11.22 (2 H, s, pyrrole NH). (Found: C, 70.93; H, 4.56; N, 17.64. $C_{14}H_{11}N_3O$ Calculated: C, 70.87; H, 4.67; N, 17.71%.)

*(4-Bromophenyl)(6-(4-bromophenyl)pyridin-3-yl)methanone (**17e**, $C_{18}H_{11}Br_2NO$).* [55% (Method I), 77% (Method II)] as an orange crystal; mp 192–194°C; $\nu_{max/}$(KBr)cm^{-1} 3095 (aromatic CH), 1668 ($C=O$); *m/z* (EI) 417 (M^+, 45%); δ_H(400 MHz; DMSO-d_6) 7.44 (2 H, d, *J* 8, ArH), 7.62 (2 H, d, *J* 8, ArH), 7.76 (2 H, d, *J* 8, ArH), 7.83 (2 H, d, *J* 8, ArH), 7.97 (1 H, d, pyridine H-3), 8.18 (1 H, d, *J* 8, pyridine H-4), 8.98 (1 H, s, pyridine H-6). (Found: C, 51.96; H, 2.63; N, 3.45. $C_{18}H_{11}Br_2NO$ Calculated: C, 51.83; H, 2.66; N, 3.36%.)

Note

1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary puplications No. CCDC 686291. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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