Novel one pot synthesis of substituted 1,2,4-triazines

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Abstract
Substituted-1,2,4-triazines were conveniently prepared in one pot by the condensation of amides and 1,2-diketones in presence of base, followed by cyclisation with hydrazine hydrate.

Keywords: 1, 2, 4-Triazine, regioisomeric triazines, sodium tertiarybutoxide, hydrazine, diketone

Introduction

1,2,4-Triazines and their derivatives have been widely studied in terms of their synthetic methodologies and reactivity since some of these derivatives were reported to have promising biological activities.[1] The synthesis of 1,2,4-triazines and their derivatives are well documented[2] and their methods of preparation are manifold and varied. A survey of the literature revealed that 1,2-dicarbonyl compounds (aliphatic, aromatic and aromatic-aliphatic) are the most common reagents used for the synthesis of 1,2,4-triazines and their derivatives.[3] Laakso and coworkers,[4] as well as other groups,[5] reported the condensation of acylhydrazides with benzil in acetic acid containing ammonium acetate to give 5,6-diphenyl-1,2,4-triazines with various aromatic and heterocyclic groups attached at position 3. A similar method was also applied by Metze and his group[6] and also Hasselquist[7] using a variety of aliphatic and aromatic 1,2-diketones and aliphatic, aromatic, and heterocyclic acid hydrazides but with preliminary isolation of the 1,2-diketones monoacylhydrazones followed by ring closure with alcoholic ammonia under pressure to give substituted 1,2,4-triazines. Kumar and his group[8] reported the synthesis of 5,6-bisaryl-1,2,4-triazines which were also shown to have potent anticonvulsant activity.

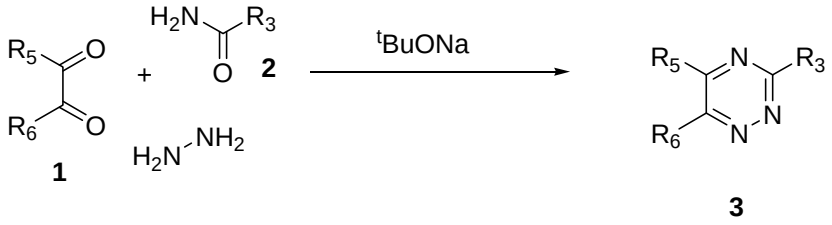
Results and Discussion

Recently, we have reported the synthesis of trisubstituted pyridazines by the condensation of 1,2-diketones with acetophenone in the presence of base, followed by cyclisation with hydrazine

hydrate.[9] Based on the same principle, we describe here the synthesis of 1,2,4-triazines starting from amides and 1,2-dicarbonyl compounds and hydrazine hydrate in the presence of base.

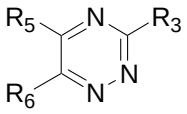
The novelty of the procedure lies in the fact that the whole reaction sequence is carried out by the stepwise addition of the reagents at the completion of each step without isolating the intermediates as they are formed. Thus, the one pot synthesis of the title compound was achieved via the N-(2-oxo-1,2-disubstituted-ethylidene)-amide intermediate, which was generated in situ by the condensation of amides with 1, 2-dicarbonyl compounds in presence of base. As reported earlier with unsymmetrical diketones,10 a mixture of two possible isomers11 is obtained. However there is predominance of one over the other. This is due to the difference in reactivity of the two carbonyl groups where the more electrophilic carbonyl is reacted first. With 1-phenyl-1, 2-propanedione, a mixture of regioisomeric triazines is obtained.12 Lee and coworkers13 have shown similar reactions where both 6,6'- and 6,5'-bis-1,2,4-triazinyls were obtained as major and minor products respectively.

In general, amides like formamide, acetamide and benzamide when condensed with aromatic 1,2-diketones formed a jelly mass, which is the condensed product. The condensed product can be cyclised to stable 1,2,4-substituted triazines by treatment with hydrazine hydrate. In all these cases solid products are obtained. The reaction was also carried out under microwave irradiation without using solvent. The results of the conventional process and the microwave irradiation process were compared which revealed that the latter process gave a comparatively higher yield in a shorter reaction time (Table 1).



Scheme 1

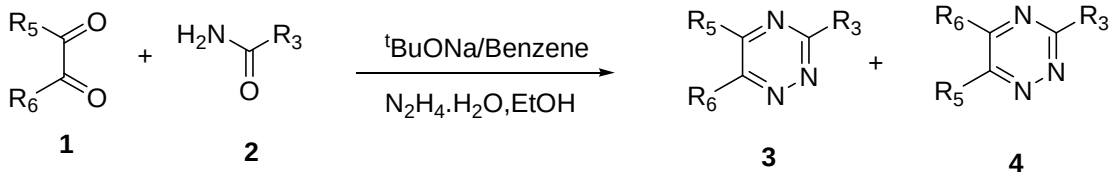
Table 1. Preparation of 3, 5, 6-trisubstituted 1, 2, 4-triazines



3 (a-r)

Entry	Prod-ucts	R_3	R_5	R_6	Time		Yields%		Mpt (^oC)
					Conv (Hrs)	MWI (Sec)	Conv	MWI	
1	**3a**	H	C_6H_5	C_6H_5	3	180	56	60	112
2	**3b**	CH_3	C_6H_5	C_6H_5	4	240	78	80	91
3	**3c**	C_6H_5	C_6H_5	C_6H_5	4	240	61	67	174
4	**3d**	H	4-$OMeC_6H_4$	C_6H_5	5	300	64	67	167
5	**3e**	CH_3	4-$OMeC_6H_4$	C_6H_5	6	360	57	62	135
6	**3f**	C_6H_5	4-$OMeC_6H_4$	C_6H_5	5	300	65	70	152
7	**3g**	H	4-ClC_6H_4	C_6H_5	3	180	60	68	118
8	**3h**	CH_3	4-ClC_6H_4	C_6H_5	4	240	61	67	120
9	**3i**	C_6H_5	4-ClC_6H_4	C_6H_5	5	300	72	77	108
10	**3j**	H	Furyl	Furyl	5	300	57	63	127
11	**3k**	CH_3	Furyl	Furyl	6	360	61	69	143
12	**3l**	C_6H_5	Furyl	Furyl	5	300	58	65	162
13	**3m**	H	CH_3	CH_3	5	300	41	52	46
14	**3n**	CH_3	CH_3	CH_3	6	360	42	50	94-96
15	**3o**	C_6H_5	CH_3	CH_3	5	300	37	43	79-80
16	**3p**	H	pyridyl	Pyridyl	6	360	43	49	87-90
17	**3q**	CH_3	pyridyl	Pyridyl	5	300	45	42	115-117
18	**3r**	C_6H_5	Pyridyl	pyridyl	5	300	51	61	163-164

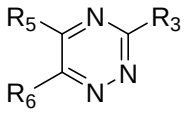
CONV = Conventional heating procedure
MWI = Microwave irradiation



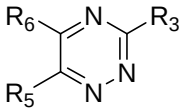
1 **2** **3** **4**

Scheme 2

Table 2. Preparation of Regioisomeric di- and tri-substituted 1, 2, 4-triazines



3(s-v)



4(s-v)

Products	R_5	R_6	R_3	Yields%	M.Pt(°C)
3s	CH_3	C_6H_5	H	25	89-90
4s	C_6H_5	CH_3	H	13	91-93
3t	CH_3	C_6H_5	C_6H_5	27	113-115
4t	C_6H_5	CH_3	C_6H_5	15	110-112
3u	H	4-MeC_6H_4	C_6H_5	29	128-130
4u	4-MeC_6H_4	H	C_6H_5	12	118-121
3v	C_6H_5	4-$Me_2NC_6H_4$	H	33	170-172
4v	4-$Me_2NC_6H_4$	C_6H_5	H	17	165-167

Experimental Section

General Procedures. Melting points were determined in open capillary tubes with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a BOMEM DA-8 FT-IR instrument and the frequencies are expressed in cm^{-1}. NMR spectra (90 MHz) were recorded on a Varian EM-390 spectrometer and high-resolution ^1H and ^{13}C NMR (300 MHz) spectra were recorded on a Bruker ACF-300 spectrometer using $CDCl_3$ as the solvent. Chemical shifts are reported in ppm downfield from internal tetramethylsilane and are given on the □ scale. Mass spectral data were obtained with a JEOL D-300 (EI) mass spectrometer. Elemental analyses were carried out on a Heraeus CHN-O-Rapid analyzer. All compounds give satisfactory elemental analyses within $\pm$ 0.5 % of the theoretical values. All reactions were monitored by TLC using glass plates coated with silica gel (ACME) containing 13% $CaSO_4$ as binder and developed in an iodine chamber or under UVGL-15 mineral light 254 lamp (in the case of HF254 silica gel coated plates). Column chromatographic separations were carried out using ACME silica gel (60-120 mesh).

General procedure for the synthesis of di-and tri-substituted-1, 2, 4-triazines

A. Conventional method

To a well stirred solution of sodium tertiary-butoxide (0.01 moles) in dry benzene, or THF at room temperature, a solution of 0.01 moles of amide (formamide, acetamide and benzamide) in benzene was added, followed by the addition of the 1,2-diketone (biacetyl, benzil, p-methoxy

benzil, furil, pyridil) (0.01 moles). A solid, jelly-like mass is formed immediately due to the formation of the but-2-ene-1,4-dicarbonyl system. 10 ml of EtOH was added to dissolve the solid mass. Hydrazine hydrate was then added and the reaction mixture was further stirred at room temperature. After the reaction was completed (monitored by TLC), the product was extracted with benzene, dried over anhydrous Na_2SO_4 and the solvent distilled off. After keeping in the fridge for four hours or more, a crystalline solid is formed which was purified by repeated recrystallisation from EtOH or by column chromatography using hexane as the eluent.

B. Microwave method

A mixture of diketone (1 mmol), amide (1 mmol), hydrazine hydrate (1.5 mmol) and sodium tertiary-butoxide (1 g) is ground thoroughly and irradiated in a microwave oven at 450 W for about 3 to 6 minutes at an interval of 30 seconds. During the irradiation, the solid melts and a sticky crude product is formed upon cooling. It is washed repeatedly with H_2O and then with hexane and finally dissolved in boiling EtOH, which afford crystalline solid upon cooling. It is further purified by repeated recrystalliztion (EtOH) or by column chromatography to give the pure products in good to excellent yield.

All the products were characterised by melting point, NMR, IR, mass spectra and CHN analysis.

Preparation of regioisomeric 1, 2, 4-triazines

To a stirred solution of sodium tertiary-butoxide (0.01 moles) in benzene, amide (Benzamide and formamide) is added, followed by 1, 2-dicarbonyl compound (0.01 moles). Stirring is continued when a jelly-like liquid is formed. 10 ml of EtOH is added to dissolve the jelly reaction mixture. Then 2 ml of hydrazine hydrate is added and the solution heated at reflux for 2.5 hours. Evaporation of the solvent under reduced pressure affords a reddish brown liquid, which is poured into H_2O and extracted with CH_2Cl_2 (3 x 100 mL), washed with $NaHCO_3$ solution and dried with Na_2SO_4. Evaporation of the solvent under reduced pressure affords reddish brown oil which contained the regioisomeric triazines. Column chromatography on silica gel and elution with 1:1 CH_2Cl_2/hexanes affords an initial fraction, **3(s-v)** in about 24-33% yield as solid products. Further elution with the same solvent affords the second fraction, **4(s-v)** in about 13-17% yield (Table-II).

5,6-Diphenyl-1,2,4-triazine (3a). Yield 56%; mp: 112°C; ^{1}H NMR: 7.25-7.94 (m, 10H), 9.60 (s, 1H); ^{13}C NMR: 125.0, 126.4, 127.2, 127.9, 129.4, 130.1, 131.2, 136.1, 155.8, 157.0, 161.2; Mass: 233 (M^+); IR (cm^{-1}): ν_{max} 3060, 1620, 1585, 1485, 1440, 1405; Anal. Calcd. for $C_{15}H_{11}N_3$: C, 77.25; H, 4.72; N, 18.02; Found: C, 77.41; H, 4.86; N, 17.87.

5,6-Diphenyl-3-methyl-1,2,4-triazine (3b). Yield 78%; mp: 91°C; ^{1}H NMR: 2.42 (s, 3H), 7.24-7.51 (m, 7H), 7.80-8.11 (m, 3H); ^{13}C NMR: 21.4, 124.8, 126.9, 128.7, 128.9, 129.0, 129.2, 129.7, 130.1, 136.9, 156.4, 157.6, 159.9; Mass: 247 (M^+); IR (cm^{-1}): ν_{max} 3061, 2921, 1577, 1488, 1445, 1393; Anal. Calcd. for $C_{16}H_{13}N_3$: C, 77.73; H, 5.26; N, 17.00, Found: C, 77.84; H, 5.15; N, 16.83;

3,5,6-Triphenyl-1,2,4-triazine (3c). Yield 61%; mp: 144°C; ^{1}H NMR: 7.31-7.50 (m, 12H), 7.80 (s, 1H), 8.11-8.13 (m, 2H); ^{13}C NMR: 124.5, 128.1, 128.3, 128.8, 129.0, 129.2, 129.9,

131.2, 134.5, 136.2, 136.5, 136.9, 156.5, 158.4, 162.1; Mass: 309(M^+); IR (cm^{-1}): ν_{max} 2978, 1672, 1477, 1414; Anal. Calcd. for $C_{21}H_{15}N_3$: C, 81.55; H, 4.85; N, 13.59; Found: C, 81.43; H 4.63; N, 13.50.

5-Anisyl-6-phenyl-1,2,4-triazine (3d). Yield 64%; mp: 167°C; ^{1}H NMR: 3.83 (s, 3H), 7.24-8.03 (m, 9H), 9.55 (s, 1H); ^{13}C NMR: 50.8, 124.3, 126.9, 127.3, 128.7, 129.3, 131.2, 134.3, 135.8 153.4, 156.1, 161.8; IR (cm^{-1}): ν_{max} 3023, 2961, 1608, 1568, 1480; Mass: 263(M^+); Anal. Calcd. for $C_{16}H_{13}N_3O$: C, 73.00; H, 4.94; N, 15.96; Found: C, 72.90; H, 4.85; N, 16.00.

5-Anisyl-3-methyl-6-phenyl-1,2,4-triazine (3e). Yield 58%; mp: 135°C; ^{1}H NMR: 2.60 (s, 3H), 3.85 (s, 3H), 7.3-8.0 (m, 9H); ^{13}C NMR: 28.0, 50.3, 125.3, 127.0, 127.9, 128.7, 129.4, 131.1, 131.3,136.1, 138.1, 154.3, 158.1, 160.2; IR (cm^{-1}): ν_{max} 3041, 2930, 1625, 1560, 1482, 1431; Mass: 277(M^+); Anal. Calcd. for $C_{17}H_{15}N_3O$: C, 73.64; H, 5.41; N, 15.16; Found: C, 73.84; H, 5.33; N, 15.00.

6-Anisyl-3,5-diphenyl-1,2,4-triazine (3f). Yield 65%; mp: 152°C; ^{1}H NMR: 3.84 (s, 3H), 7.31-7.80 (m, 12H), 8.10-8.25 (m, 2H); ^{13}C NMR: 50.5, 125.7, 126.0, 126.4, 127.0, 127.8, 128.6,129.3, 129.7, 130.4, 131.0, 132.4, 135.7, 155.1, 156.4, 160.3; IR (cm^{-1}): ν_{max} 3061, 2941, 1618, 1570, 1480; Mass: 339 (M^+); Anal. Calcd. for $C_{22}H_{17}N_3O$, C, 77.87; H, 5.01; N, 12.38; Found: C, 77.70; H, 4.89; N, 12.10.

6-(*p*-Chlorophenyl)-5-phenyl-1,2,4-triazine (3g). Yield 60%; mp: 118°C; ^{1}H NMR: 7.3-8.0 (m, 9H), 9.72 (s, 1H); ^{13}C NMR: 125.6, 126.0, 127.5, 128.2, 129.7, 132.7, 134.0, 135.6, 154.3, 156.1,162.0; IR (cm^{-1}): ν_{max} 3040, 1610, 1568,1460,1405; Mass: 267(M^+); Anal. Calcd. for $C_{15}H_{10}N_3Cl$: C 67.28, H 3.73, N 15.70; Found: C, 67.12; H, 3.84; N, 15.61.

3-Methyl-6-(*p*-chlorophenyl)-5-phenyl-1,2,4-triazine (3h). Yield 61%; mp: 120°C; ^{1}H NMR: 2.68 (s, 1H), (m, 9H); ^{13}C NMR: 29.8, 125.9, 127.0, 127.9, 128.6, 130.8, 131.8, 133.0, 134.7, 154.0, 155.6, 162.1; IR (cm^{-1}): ν_{max} 3050, 2940, 1622, 1591, 1505, 1450; Mass: 281 (M^+); Anal. Calcd. for $C_{16}H_{12}N_3Cl$: C, 68.20; H, 4.26; N, 14.92; Found: C, 68.45; H, 4.30; N, 14.81.

3,5-Diphenyl-6-(*p*-chlorophenyl)-1,2,4-triazine (3i). Yield 72%; mp: 108°C; ^{1}H NMR: 7.29-7.96 (m, 12H), 8.07-8.22 (m, 2H); ^{13}C NMR: 125.3, 126.5, 127.2, 127.6, 128.0, 128.6, 129.0, 129.7, 131.8, 132.1, 133.2, 134.1, 155.4, 157.0, 161.9; IR (cm^{-1}): ν_{max} 3045, 1630, 1592, 1500, 1470; Mass: 343(M^+) Anal. Calcd. for $C_{21}H_{14}N_3Cl$: C, 73.36; H, 4.07; N, 12.22; Found: C, 73.44; H, 4.20; N, 12.12.

5,6-Difuryl-1,2,4-triazine (3j). Yield 57%; mp: 95°C; ^{1}H NMR: 6.24-6.61 (m, 6H), 9.71 (s, 1H); ^{13}C NMR: 112.1, 113.3, 116.1, 120.0, 124.3, 154.1, 158.0, 160.3 IR (cm^{-1}): ν_{max} 2978, 1624, 1477, 1415, 1074; Mass: 213(M^+), Anal. Calcd. for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.28; N, 19.72; Found: C, 62.08; H, 3.20; N, 19.50.

5,6-Difuryl-3-methyl-1,2,4-triazine (3k). Yield 61%; mp: 143°C; ^{1}H NMR: 2.61 (s, 3H), 6.26-8.05 (m, 6H); ^{13}C NMR: 27.9, 112.1, 112.6, 113.0, 114.3, 116.7, 120.6, 124.0, 125.3, 154.1, 158.9, 160.0; IR (cm^{-1}): ν_{max} 3002, 2924, 1620, 1495, 1415, 1033, Mass: 227(M^+), Anal. Calcd. for $C_{12}H_9N_3O_2$: C, 63.43, H, 3.96, N, 18.50, Found: C, 63.57; H, 3.84; N, 18.38.

5,6-Difuryl-3-phenyl-1,2,4-triazine (3l). Yield 58%; mp: 162°C; ^{1}HNMR: 6.25-6.75 (m, 6H), 7.71-8.01 (m, 5H); ^{13}C R: 112.0, 112.8, 113.6, 114.3, 115.0, 115.7, 117.1, 120.6, 129.0,

130.1, 132.6, 134.3, 153.6, 154.1, 161.2; IR (cm^{-1}): ν_{max} 3010, 1631, 1505, 1430, 1035; Mass: 289 (M^+); Anal. Calcd. for $C_{17}H_{11}N_3O_2$: C, 70.58, H, 3.80, N, 14.53; Found: C, 70.74; H, 3.71; N, 14.62.

5,6-Dimethyl-1,2,4-triazine (3m). Yield: 45%; mp: 46°C; ^{1}H NMR: □ 2.37 (s, 3H), 2.41 (s, 3H), 9.75 (s, 1H); ^{13}C NMR: □ 19.9, 21.3, 156.9, 159.9, 160.2. IR (cm^{-1}): ν_{max} 2931, 2919, 1511, 1483, Anal. Calcd. for $C_5H_7N_3$, C, 55.04; H, 6.42; N, 38.53; Found: C, 55.10; H, 6.45; N, 38.42.

3,5,6-Trimethyl-1,2,4-triazine (3n). Yield: 52%; mp 95°C; ^{1}H NMR: □ 2.35-2.40 (m, 6H), 2.42 (s, 3H), ^{13}C NMR: □ 20.1, 20.6, , 21.4, 157.1, 158.9, 161.3. IR (cm^{-1}): ν_{max} 2925, 2911, 1520, 1495, Anal. Calcd. for $C_6H_9N_3$, C, 58.53; H, 7.31; N, 34.14; Found: C, 58.55; H, 7.34; N, 34.00

3-Phenyl-5,6-dimethyl-1,2,4-triazine (3o). Yield: 48%; mp: 80°C; ^{1}H NMR: □ 2.34-2.39 (m, 6H), 7.76-7.81 (m, 5H), ^{13}C NMR: □ 20.3, 21.1 , 126.1, 128.0, 128.8, 129.4, 130.1, 158.0, 159.4, 162.1. IR (cm^{-1}): ν_{max} 3020, 2918, 1610, 1508, 1494,. Anal. Calcd. for $C_{11}H_{11}N_3$, C, 71.35; H, 5.94; N, 22.70; Found: C, 71.48; H, 5.90; N, 22.62.

5,6-Dipyridyl-1,2,4-triazine (3p). Yield: 44%; mp: 121-123°C; ^{1}H NMR □ 8.9-9.38 (m, 4H), 9.51-9.63 (m, 4H), 9.73 (s, 1H); ^{13}C NMR: □ 158.0, 158.7, 159.8, 160.0, 161.0, 161.5, 162.8, 163.0, 163.8, 164.0, 164.9, 165.4, 166.3, IR (cm^{-1}): ν_{max} 1605, 1508, 1495, 1410. Anal. Calcd. for $C_{13}H_9N_5$, C, 66.38; H, 3.82; N, 29.78; Found: C, 66.45; H, 3.89; N, 29.69.

3-Methyl-5,6-dipyridyl-1,2,4-triazine (3q). Yield: 49%; mp: 127°C; ^{1}H NMR: □ 2.32 (s, 3H), 9.01-9.45 (m, 4H), 9.49-9.60 (m, 4H), 9.73 (s, 1H); ^{13}C NMR: □ 160.3, 160.9, 161.1, 161.5, 162.2, 162.9, 164.0, 164.7, 165.1, IR (cm^{-1}): ν_{max} 1612, 1501, 1485, 1413 Anal. Calcd. for $C_{14}H_{11}N_5$, C, 67.46; H, 4.41; N, 28.11; Found: C, 67.37; H, 4.50; N, 28.20.

3-Phenyl-5,6-dipyridyl-1,2,4-triazine (3r). Yield: 55%; mp: 163°C; ^{1}H NMR: □ 8.31-8.68 (m,5H), 8.95-9.37 (m, 4H), 9.41-9.56 (m, 4H), ^{13}C NMR: □ 131.6, 134.1, 137.0, 141.1, 157.4, 158.0, 158.5, 159.2, 159.8, 160.0, 161.0, 161.9, 164.0, 164.7, 165.7, 166.0, 166.4; IR (cm^{-1}): ν_{max} 3040, 1620, 1504, 1490; Anal. Calcd. for $C_{19}H_{13}N_5$, C, 73.31; H, 4.18; N, 22.50; Found: C, 73.24; H, 4.11; N, 22.41.

5-Methyl-6-phenyl-1,2,4-triazine (3s). Yield: 25%; mp: 89-90°C; ^{1}H NMR: □ 2.64 (s, 3H), 7.64-8.16 (m, 5H), 9.80 (s,1H); ^{13}C NMR: □□□□ 124.6, 125.2, 129.0, 131.4, 133.6, 135.4, 158.0, 159.2, 161.5; IR (cm^{-1}): ν_{max} 3046, 1610, 1590, 1480, 1455; Mass: 171(M^+) Anal. Calcd. for $C_{10}H_9N_3$: C, 70.17; H, 5.26; N, 24.56; Found: C, 70.22; H, 5.29; N, 24.67.

5-Phenyl-6-methyl-1,2,4-triazine (4s). Yield: 13%; mp: 91-93°C; ^{1}H NMR: □ 2.70 (s, 3H), 7.71-8.20 (m, 5H); 9.81 (s,1H); ^{13}C NMR: □ 29.8, 124.2, 125.0, 128.8, 130.9, 133.4, 135.0, 158.7, 159.8, 162.0; IR (cm^{-1}): ν_{max} 3041, 1605, 1595, 1500, 1495; Mass: 171(M^+) Anal. Calcd. for $C_{10}H_9N_3$: C, 70.17; H, 5.26; N, 24.56; Found: C, 70.27; H, 5.34; N, 24.62.

3,6-Diphenyl-5-methyl-1,2,4-triazine (3t). Yield: 27%; mp: 113-115°C; ^{1}H NMR: □ 2.65 (s, 3H), 7.70 - 8.30 (m, 10H); ^{13}C NMR: □ 27.0, 124.8, 128.2, 128.6, 130.1, 131.1, 134.0, 135.7, 137.0, 157.6, 158.4, 162.4; IR (cm^{-1}): ν_{max} 3050, 1605, 1590, 1510, 1450; Mass: 247(M^+) Anal. Calcd. for $C_{16}H_{13}N_3$: C, 77.73; H, 5.26; N, 17.00; Found: C, 77.85; H, 5.40; N, 17.09.

3,5-Diphenyl-6-methyl-1,2,4-triazine (4t). Yield: 15%; mp: 110-112°C; ^{1}H NMR: □ 2.78 (s, 3H); 7.80 - 8.43 (m, 10H); ^{13}C NMR: □ 29.2, 124.5, 127.9, 128.3, 129.6, 130.8, 133.8, 135.6,

136.3, 156.8, 158.0, 162.2; IR (cm^{-1}): ν_{max} 3054, 1602, 1595, 1505, 1480; Mass: 247(M^+) Anal. Calcd. for $C_{16}H_{13}N_3$: C, 77.73; H, 5.26; N, 17.00; Found: C, 77.80; H, 5.46; N, 17.15.

6-(*p*-Methylphenyl)-3-phenyl-1,2,4-triazine (3u). Yield: 29%; mp: 128-130°C; ^{1}H NMR: δ 2.65 (s, 3H), 7.13-8.09 (m, 9H), 8.72(s, 1H); ^{13}C NMR: δ 29.0, 125.8, 129.2, 131.6, 133.1, 136.1, 138.0, 139.7, 112.0, 157.6, 159.4, 160.4; IR (cm^{-1}): ν_{max} 3030, 1605, 1595, 1457; Mass: 247(M^+) Anal. Calcd. for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99; Found: C, 77.72; H, 5.29; N, 17.03.

5-(*p*-Methylphenyl)-3-phenyl-1,2,4-triazine (4u). Yield: 12%; mp: 118-121°C; ^{1}H NMR: δ 2.65 (s,3H), 7.78-8.50 (m, 9H), 9.24(s, 1H); ^{13}C NMR: δ 28.0, 125.8, 129.2, 131.6, 133.1, 136.1, 138.0, 139.7, 112.0, 157.6, 159.4, 160.4; IR (cm^{-1}): ν_{max} 3035, 1615, 1590, 1450; Mass: 247(M^+) Anal. Calcd. for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99; Found: C, 77.73; H, 5.35; N, 17.02.

6-*p*-(*N,N*-Dimethylamino)phenyl-5-phenyl-1,2,4-triazine (3v). Yield: 33%; mp: 170-172°C; ^{1}H NMR: δ 2.80 (s, 6H), 7.37-8.23 (m, 9H), 9.70(s, 1H); ^{13}C NMR: δ 40.3, 122.8, 123.2, 127.2, 131.1, 137.1, 139.0, 141.7, 150.0, 155.8, 158.5, 159.0; IR (cm^{-1}): ν_{max} 3049, 1623, 1545, 1555; Mass: 276(M^+) Anal. Calcd. for $C_{17}H_{16}N_4$: C, 73.89; H, 5.84; N, 20.27; Found: C, 73.87; H, 5.83; N, 20.25.

5-*p*-(*N,N*-Dimethylamino)phenyl-6-phenyl-1,2,4-triazine(4v). Yield: 17%; mp: 139-141°C; ^{1}H NMR: δ 2.82 (s, 6H), 7.01-8.13 (m, 9H)), 9.85(s, 1H); ^{13}C NMR: δ 39.3, 120.8, 122.2, 126.2, 133.1, 136.1, 138.0, 139.7, 112.0, 155.8, 158.5, 159.0; IR (cm^{-1}): ν_{max} 3043, 1611, 1584; Mass: 276(M^+) Anal. Calcd. for $C_{17}H_{16}N$: C, 73.89; H, 5.84; N, 20.27; Found: C, 73.88; H, 5.86; N, 20.29.

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