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Gas-phase thermolysis of 1-acylnaphtho[1,8-*de*][1,2,3]triazines. Interesting direct routes towards condensed naphtho[1,8-*de*] heterocyclic ring systems

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Abstract—FVP pyrolysis of 1-acylnaphtho[1,8-*de*][1,2,3]triazines at 500 °C and 10^{-2} Torr gave exclusively the corresponding 2-substituted naphtho[1,8-*de*][1,3]oxazines. The latter was also obtained by static pyrolysis but in lower yield along with the corresponding *N*-(naphthalen-1-yl)acylamides. The reaction was studied kinetically and mechanistically.

1. Introduction

In a previous publication[1] we reviewed the flash vacuum pyrolysis (FVP) of cinnolines, 1,2,3-benzotriazines and 1,2,4-benzotriazines, which have been shown to give direct and easy access to many interesting compounds, some of which are otherwise difficult to obtain. The primary step in the pyrolysis of these compounds involves mainly N_2 elimination, yielding the corresponding diradical intermediates. On the other hand, pyrolysis of thieno[3,2-*e*][1,2,4]triazines has been shown to follow in part the same initial step ($-N_2$), in addition to another important pathway leading to N–N cleavage followed by several rearrangements and/or fragmentation leading finally to interesting heterocyclic systems.[1]

In continuation of our recent interest in the pyrolytic behaviour of the above mentioned ring systems, we describe in the present work the pyrolytic behaviour of naphtho[1,8-*de*][1,2,3]triazine derivatives. Little attention has been directed towards such interesting chemistry. Thus, pyrolysis of 1-arylnaphtho[1,8-*de*][1,2,3]triazines **1** has been shown to give the corresponding 7*H*-benzo[*kl*]acridine derivatives **2**.[2] The 8-nitro derivative of **2** has been prepared in a very low yield from the corresponding triazine **1** (Ar=*o*-nitrophenyl) by heating with a large excess of $(EtO)_3P$ along with other products.[3] These two reactions resemble very much the pyrolytic behaviour of the substituted benzotriazoles **3**, which have been extensively used for the preparation of many interesting heterocyclic systems **4**.[4,5] Thus, derivatives of indole,[4,6] carbazole,[7] isomeric pyridoindoles,[7d,8] pyrido[1,2-*a*]benzimidazole,[8] benzimdazo[1,2-*a*]pyrimidine,[9] benzimdazo[1,2-*a*]pyridazine,[9] benzimidazo[2,1-*a*]isoquinoline,[10] benzimidazo[1,2-*b*]cinnoline,[4] benzimidazo[2,1-*b*]benzothiazole,[11] phenanthridine,[12] benzoxazole,[10,13] and quinolines[14] as well as other heterocyclic systems became readily available. Similarity of the pyrolytic behaviour of benzotriazole and naphtho[1,8-*de*][1,2,3]triazine derivatives lies in the fact that they both undergo elimination of N_2 followed by intramolecular cyclization with the appropriate substituent (Scheme 1). Thus, it is expected that pyrolysis of the appropriately substituted naphtho[1,8-*de*][1,2,3]triazine derivatives would open an important synthetic route to many condensed heterocyclic systems, condensed on the *peri* positions of the naphthalene ring. Some diradicals were generated from 1-alkylnaphtho[1,8-*de*][1,2,3]triazine derivatives and 1-acetylnaphtho[1,8-*de*][1,2,3]triazine by photolysis.[15] However, no intramolecular cyclization of these photolytically generated diradicals could be proved.[15]

In order to study the potential application of naphtho[1,8-*de*][1,2,3]triazine in pyrolytic synthesis we describe in the present work, the pyrolytic reactions of 1-acylnaphtho[1,8-*de*][1,2,3]triazines **6** together with kinetic and suggested mechanism for this pyrolytic reaction in comparison with the analogous benzotriazole derivatives.

Keywords: FVP; Naphtho[1,8-*de*][1,2,3]triazines; Naphtho[1,8-*de*][1,3]oxazines; Heterocycles.
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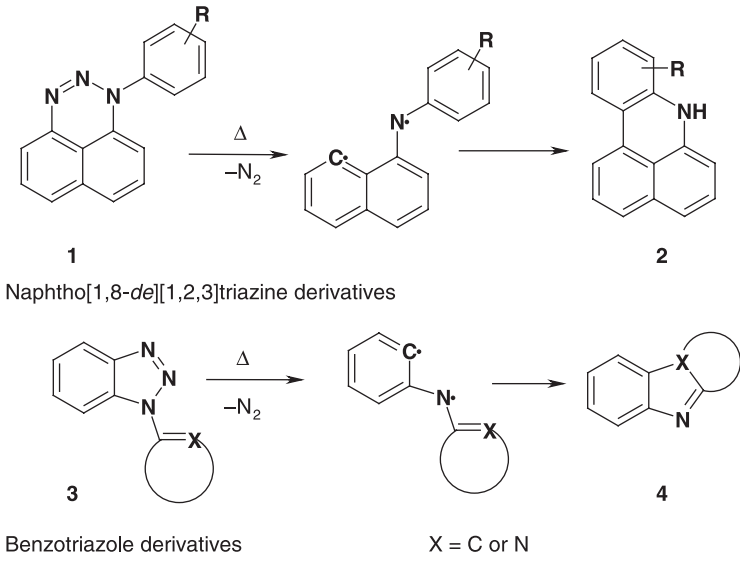


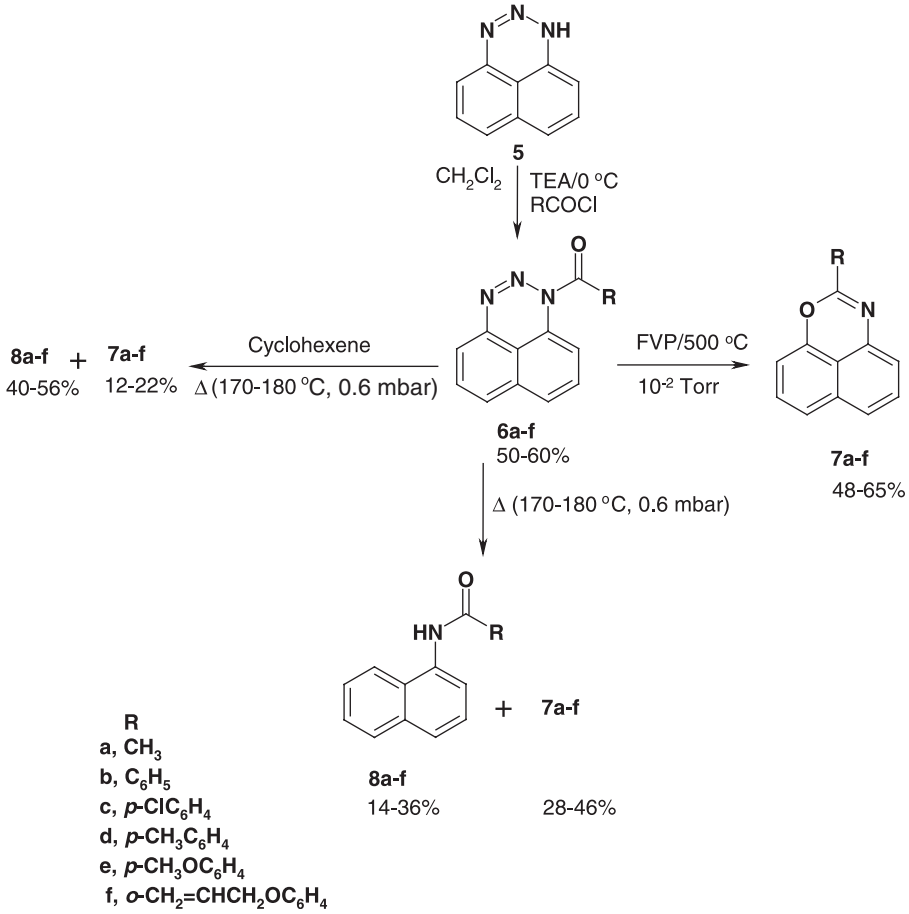
Scheme 1.

2. Results and discussion

2.1. Pyrolysate composition and reaction pathway

Literature shows that only the 1-acetyl derivative **6a** has been prepared in 32% yield by reacting **5** with NaH in dry ether followed by heating at reflux with acetyl chloride.[15] In the present investigation, we have been able to prepare the acyl derivatives **6a–f** (50–60% yields) upon treatment **5** in CH_2Cl_2 and triethylamine at 0 °C with the appropriate acid chloride. This acylation reaction has been found to give a lot of tarry materials and other minor by-products (Scheme 2).

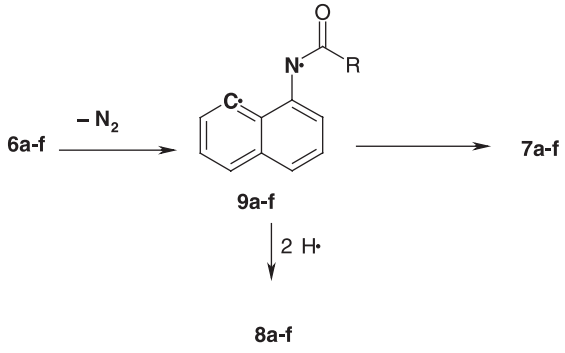
FVP of each of **6a–f** at 500 °C and 0.02 Torr gave the corresponding pure 2-substituted naphtho[1,8-de][1,3]-oxazines **7a–f** in 48–65% yields. On the other hand, gas



Scheme 2.

Table 1. Pyrolysis products of 1-acylnaphtho[1,8-*de*][1,2,3]triazines **6a–d**

Substrate	Pyrolysis products (% yields)	
6a	**7a**	**8a**
FVP	63	0
Static	28	14
Static (cyclohexene)	19	43
6b	**7b**	**8b**
FVP	56	0
Static	40	28
Static (cyclohexene)	12	52
6c	**7c**	**8c**
FVP	65	0
Static	43	29
Static (cyclohexene)	19	54
6d	**7d**	**8d**
FVP	61	0
Static	46	36
Static (cyclohexene)	18	56
6e	**7e**	**8e**
FVP	59	0
Static	39	15
Static (cyclohexene)	22	41
6f	**7f**	**8f**
FVP	48	0
Static	38	17
Static (cyclohexene)	14	40



Scheme 3.

phase pyrolysis of **6a–f** at 170–180 °C and 0.06 mbar gave a mixture of **7a–f** and *N*-(naphthalen-1-yl)acylamides **8a–f** in the percentage yields indicated in Table 1.

The pyrolysates were qualitatively and quantitatively determined by HPLC (Table 1) and by ^{1}H NMR spectroscopy.

Scheme 3 illustrates possible mechanistic routes explaining the formation of the products **7**, **8** obtained in the present pyrolytic study. The reaction starts by extrusion of N_2 to give the diradicals **9a–f**, which then undergo intramolecular cyclization to give the corresponding oxazines **7a–f**. The latter are the only observed product from FVP of **6a–f**. In the present study, attempts to investigate the possible intramolecular cycloaddition of the diradical **9** on C=C by using the *o*-allyloxybenzoyl derivative **6f** did not succeed, and we only obtained the normal reaction observed with the other derivatives **6a–e**. The formation of the acylamide derivatives **8** can be achieved by addition of hydrogen to the diradicals **9**, and this process seems to be appreciable in the static pyrolysis due to the longer reaction times and also as a result of charring of some of the materials, resulting in the availability of hydrogen in the reaction medium. This assumption was substantiated by the fact that repeating all static pyrolysis reaction in the presence of cyclohexene (good hydrogen source)[1] led to an increase in the percent yields of the corresponding derivatives **8**, and a decrease of the corresponding oxazines **7** as shown in Table 1.

2.2. Kinetic data and comparative molecular reactivity

The rates of gas-phase thermolysis of the 1-aroylnaphthotriazines **6b**,**c** and **6e**, were measured over the temperature range 347–428 K with an average range of 55 K per substrate, in order to ensure reliable activation parameters for the first-order gas-phase elimination process of these compounds.[16] The kinetic data is given in Table 2. Each rate constant recorded is an average from at least three independent evaluations of the rate at each reaction temperature, and are in agreement to within ±2% rate spread. The Arrhenius parameters were obtained from strictly linear correlations over >85% reaction. The Arrhenius parameters and rate constants (k/s^{-1}) calculated at 450 K for substrates **6b**,**c** and **6e** are summarized in Table 2. The rate data of related 1-acylbenzotriazoles has been reported in an earlier publication and are tabulated in Table 3.[17] The reaction mechanism (Scheme 3) and the kinetic data allow the following conclusions and structure/reactivity correlations to be made:

Table 2. Rate coeffecients (k/s^{-1}), Arrhenius parameters of 1-acylnaphtho[1,8-*de*][1,2,3]triazines **6b**,**c**,**e**

Compound	*T*/K	10^4 k/s^{-1}	log *A*/s^{-1}	E_a/kJ mol^{-1}	$k_{450\ K}/s^{-1}$
6b	389.25	0.966	7.727±0.69	88.767±5.48	3.508×10^{-3}
	409.25	3.343			
	418.85	4.885			
	428.85	13.01			
	448.55	32.95			
6c	374.15	0.458	8.164±0.28	90.779±2.21	5.641×10^{-3}
	383.85	0.883			
	403.45	3.127			
	413.25	7.564			
	433.15	21.07			
	443.35	40.72			
6e	374.25	0.597	9.143±0.33	96.972±2.50	1.046×10^{-3}
	393.85	2.565			
	413.45	11.70			
	423.40	20.18			

Table 3. k_{rel} of 1-acylnaphtho[1,8-*de*][1,2,3]triazines compared to the corresponding 1-acylbenzotriazoles (ArCOBT)

Ar	(**6b**,**c**,**e**) $k_{N450\ K}/s^{-1}$	ArCOBT $k_{BT450\ K}/s^{-1}$	$K_{rel}=k_N/k_{BT}$
C_6H_5	3.508×10^{-3}	2.543×10^{-3}	1.38
p-ClC_6H_5	5.641×10^{-3}	2.753×10^{-3}	1.94
p-$H_3COC_6H_5$	1.046×10^{-3}	8.243×10^{-4}	4.66

- The aroylbenzotriazoles are less reactive than aroylnapthotriazines. This structural effect could be rathionalized in terms of resonance stabilization extended by conjugation in naphthotriazine more than it does in benzotriazole.
- We have noted earlier[4] that the effect of substituents not conjugated to the benzotriazole radical centre of the benzotriazole biradical intermediate are moderate and that electron-withdrawing groups tend to increase the molecular reactivity of BT compounds while electron-donating groups have an opposite effect. This is also the case with the naphthotriazine substrates **6a–e** under study as evidenced by their rates of pyrolysis (Table 2).

3. Conclusions

The present study offers interesting routes towards many condensed heterocyclic systems condensed on the *peri* positions of the naphthalene ring, of which many derivatives exhibit interesting photo-emission properties. Of the compounds synthesized in the present work some interesting studies on the fluorescence spectra of a series of 1-aminonaphthalene derivatives,[18a] and naphtho[1,8-*de*][1,3]oxazine derivates were reported.[18b]

4. Experimental

All melting points are uncorrected. IR spectra were recorded in KBr disks using Perkin Elmer System 2000 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400, 400 MHz super-conducting NMR spectrometer. LCMS were measured using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalyses were performed on LECO CHNS-932 Elemental Analyzer.

4.1. Pyrolysis of 6a–f: general procedures

(A) Static pyrolysis of **6a–f**

Each substrate (0.2 g) was introduced in the reaction tube (1.5×12 cm Pyrex), cooled in liquid nitrogen, sealed under vacuum (0.06 mbar) and placed in the pyrolyser for 15 min at 170–180 °C, a temperature that is required for complete pyrolysis of the substrate as indicated by a preliminary HPLC study. The products were separated by column chromatography using Merck Al-silica gel $60F_{254}$, with EtOAc–petroleum ether (40/60) (1–10% of EtOAc) to give successively **7** followed by **8**.

(B) Static pyrolysis of **6a–f** *with cyclohexene*

Each substrate (0.2 g) and cyclohexene (0.1 g) were introduced in the reaction tube (1.5×12 cm Pyrex), cooled in liquid nitrogen, sealed under vacuum (0.06 mbar) and placed in the pyrolyser for 15 min at 170–180 °C. The products were separated by column chromatography using Merck Al-silica gel $60F_{254}$, with EtOAC–petroleum ether (40/60) (1–10% of EtOAc) to give successively **7** followed by **8**.

(C) Flash vacuum pyrolysis of **6a–d**

The apparatus used was similar to the one, which has been described in our recent publications.[1,7] The sample was volatilized from a tube in a Büchi Kugelrohr oven through a 30×2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to a temperature of 500 °C, the temperature being monitored by a Pt/Pt-13%Rh thermocouple situated at the centre of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2} Torr by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the cold trap and the pump. Under these conditions the contact time in the hot zone was estimated to be ≅10 ms. The different zones of the products collected in the U-shaped trap were analyzed by ^1H, ^{13}C NMR, IR and GC–MS. Relative and percent yields were determined from ^1H NMR.

4.2. Pyrolysis products

4.2.1. Naphtho[1,8-*de*][1,3]oxazine 7.

4.2.1.1. 2-Methylnaphtho[1,8-*de*][1,3]oxazine 7a. Colourless crystals from petroleum ether (40–60), mp 68–70 °C (lit.[19] mp 68 °C). LCMS *m*/*z*=184 (M+1). ^1H NMR ($CDCl_3$): δ 7.40 (d, 1H, *J*=8.4 Hz), 7.33 (m, 2H), 7.28 (d, 1H, *J*=8.0 Hz), 6.93 (d, 1H, *J*=7.0 Hz), 6.69 (d, 1H, *J*=7.8 Hz), 2.27 (s, 3H, CH_3).

4.2.1.2. 2-Phenylnaphtho[1,8-*de*][1,3]oxazine 7b. Colourless crystals from ethanol, mp 135–136 °C (lit.[20] mp 134 °C). LCMS *m*/*z*=246 (M+1). IR: 3053, 1638, 1597, 1373, 1315, 1253, 1092, 822, 764, 693. ^1H NMR ($CDCl_3$): δ 8.24 (d, 2H, *J*=7.8 Hz), 7.52 (m, 3H), 7.43 (t, 1H, *J*=8.0 Hz), 7.33 (m, 3H), 7.10 (dd, 1H, *J*=7.8, 1.2 Hz), 6.86 (dd, 1H, *J*=7.8, 1.2 Hz). ^{13}C NMR ($CDCl_3$): δ 155.3 (C), 149.9 (C), 137.9 (C), 134.3 (C), 131.8 (CH), 131.2 (C), 128.8 (CH), 128.4 (2CH), 127.8 (2CH), 122.6 (CH), 123.2 (CH), 120.9 (CH), 119.0 (C), 117.2 (CH), 106.2 (CH). Anal. Calcd for $C_{17}H_{11}NO$ (245.3): C 83.25; H 5.52; N 5.71. Found: C 83.20; H 4.95; N 5.62.

4.2.1.3. 2-(4-Chlorophenyl)naphtho[1,8-*de*][1,3]oxazine 7c. Pale yellow crystals from ethanol, mp 140–142 °C. LCMS *m*/*z*=280 (M+1), 282 (M+3). IR: 3060, 1638, 1590, 1487, 1374, 1252, 1091, 1015, 823, 768, 724.

^{1}H NMR ($CDCl_3$): δ 8.17 (dd, 2H, J=8.4, 1.7 Hz), 7.48 (dd, 2H, J=8.4, 1.7 Hz), 7.44 (d, 1H, J=8 Hz) 7.38 (m, 2H), 7.34 (t, 1H, J=8 Hz), 7.08 (dd, 1H, J=7.6, 1.0 Hz), 6.83 (dd, 1H, J=7.3, 1.0 Hz). ^{13}C NMR ($CDCl_3$): δ 154.4 (C), 149.7 (C), 138.1 (C), 137.6 (C), 134.3 (C), 129.7 (C), 129.1 (2CH), 128.8 (CH), 128.7 (2CH), 127.8 (CH), 123.5 (CH), 121.0 (CH), 118.9 (C), 117.3 (CH), 106.1 (CH). Anal. Calcd for $C_{17}H_{10}ClNO$ (279.7): C 73.00; H 3.60; N, 5.01. Found: C 73.02; H 3.55; N 5.00.

4.2.1.4. 2-(4-Methylphenyl)naphtho[1,8-*de*][1,3]oxazine 7d. Yellow crystals from ethanol, mp 158–160 °C. LCMS m/z=260 (M+1). IR: 3061, 2961, 2923, 2853, 1638, 1594, 1449, 1376, 1251, 1089, 816, 760. ^{1}H NMR ($CDCl_3$): δ 8.12 (d, 2H, J=8.2 Hz), 7.34 (m, 4H), 7.32 (d, 2H, J=8.1 Hz), 7.08 (dd, 1H, J=7.0, 1.0 Hz), 6.84 (dd, 1H, J=7.0, 1.0 Hz), 2.46 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 153.8 (C), 148.3 (C), 140.8 (C), 136.4 (C), 132.7 (C), 127.5 (2CH), 127.1 (CH), 126.8 (C), 126.1 (2CH), 126.0 (CH), 121.4 (CH), 119.2 (CH), 117.4 (C), 115.3 (CH), 104.4 (CH), 20.0 (CH_3). Anal. Calcd for $C_{18}H_{13}NO$ (259.3): C 83.38; H 5.05; N 5.40. Found: C 83.30; H 4.95; N 5.42.

4.2.1.5. 2-(4-Methoxyphenyl)naphtho[1,8-*de*][1,3]oxazine 7e. Yellow crystals from ethanol, mp 142–143 °C. LCMS m/z=276 (M+1). IR: 3060, 1638, 1594, 1499, 1376, 1251, 1089, 816, 760. ^{1}H NMR ($CDCl_3$): δ 8.19 (d, 2H, J=8.8 Hz), 7.42–7.30 (m, 4H), 7.08 (d, 1H, J=6.8 Hz), 7.01 (d, 2H, J=8.8 Hz), 6.83 (dd, 1H, J=7.0, 1.0 Hz), 3.91 (s, 3H). Anal. Calcd for $C_{18}H_{13}NO_2$ (275.3): C 78.53; H 4.72; N 5.09. Found: C 78.50; H 4.55; N 4.92.

4.2.1.6. 2-(2-Allyloxyphenyl)naphtho[1,8-*de*][1,3]oxazine 7f. Colourless crystals from ethanol, mp 98–100 °C. LCMS m/z=302 (M+1). IR: 3060, 2910, 2863, 1691, 1598, 1486, 1450, 1372, 1315, 977, 857, 765. ^{1}H NMR ($CDCl_3$): δ 8.34 (dd, 1H, J=6.8, 1.8 Hz), 7.66 (dd, 1H, J=7.6, 1.4 Hz), 7.53–7.42 (m, 6H), 7.09 (t, 1H, J=8.0 Hz), 6.95 (d, 1H, J=8.4 Hz), 5.90 (m, 1H), 5.29 (dd, 1H, J=17.2, 1.4 Hz), 5.09 (dd, 1H, J=10.4, 1.4 Hz), 4.61 (d, 2H, J=4.8 Hz). ^{13}C NMR ($CDCl_3$): δ 171.4 (C), 155.4 (C), 134.2 (C), 132.7 (C), 132.6 (*CH*=CH_2), 131.7 (CH), 129.0 (CH), 128.9 (C), 128.8 (CH), 128.5 (CH), 127.7 (CH), 126.2 (C), 122.4 (CH), 121.5 (CH), 120.8 (CH), 117.1 (=CH_2), 116.5 (C), 112.2 (CH), 109.9 (CH), 69.4 (CH_2). Anal. Calcd for $C_{20}H_{15}NO_2$ (301): C 79.73; H 4.98; N 4.6. Found: C 79.70; H 4.95; N 4.62.

4.2.2. *N*-[Naphthalen-1-yl]acylamides 8.

4.2.2.1. *N*-[Naphthalen-1-yl]acetamide 8a. Colourless crystals from petroleum ether (40–60), mp 157–158 °C (lit.[21a,b] mp 159–160 °C). LCMS m/z=186 (M+1). ^{1}H NMR (DMSO-d_6): δ 10.01 (br, 1H, NH), 8.00 (m, 2H), 7.74 (d, 1H, J=8 Hz), 7.68 (d, 1H, J=8 Hz, 7.52 (m, 2H), 7.46 (t, 1H, J=8 Hz), 2.17 (s, 3H, CH_3).

4.2.2.2. *N*-(Naphthalen-1-yl)benzamide 8b. Colourless crystals from ethanol, mp 167–168 °C (lit.[22] mp 164–165 °C). LCMS m/z=248 (M+1). ^{1}H NMR ($CDCl_3$): δ 8.22 (br, 1H, NH), 8.10 (d, 1H, J=7 Hz), 8.03 (d, 2H, J=7.2 Hz), 7.94 (m, 2H), 7.78 (d, 1H, J=8.2 Hz), 7.63 (t, 1H, J=7.2 Hz) 7.58 (m, 5H).

4.2.2.3. 4-Chloro-*N*-(naphthalen-1-yl)benzamide 8c. Colourless crystals from petroleum ether (80–100), mp 208–210 °C. LCMS m/z=282 (M+1), 284 (M+3). IR (KBr): 3193 (br), 3047, 1641, 1596, 1483, 1310, 1090, 845, 803, 771, 677. ^{1}H NMR (DMSO): δ 10.54 (br, 1H, NH), 8.11 (d, 2H, J=8.2 Hz), 7.96 (m, 2H), 7.88 (d, 1H, J=7.7 Hz), 7.65 (d, 2H, J=8.1 Hz), 7.57 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 166.3 (CO), 137.6 (C), 134.8 (C), 134.6 (C), 134.2 (C), 130.8 (2CH), 130.2 (C), 129.6 (2CH), 129.1 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH), 126.6 (CH), 125.0 (CH), 124.3 (CH). Anal. Calcd for $C_{17}H_{12}ClNO$ (281.7): C 72.47; H 4.29; N 4.97. Found: C 72.40; H 4.21; N 4.86.

4.2.2.4. 4-Methyl-*N*-(naphthalen-1-yl)benzamide 8d. Colourless crystals from ethanol, mp 170–172 °C (lit.[23] mp 171–173 °C). LCMS m/z=262 (M+1). ^{1}H NMR ($CDCl_3$): δ 8.22 (br s, 1H, NH), 8.06 (d, 1H, J=8.0 Hz), 7.91 (m, 4H), 7.77 (d, 1H, J=8.2 Hz), 7.56 (m, 3H), 7.36 (d, 2H, J=8.0 Hz), 2.47 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 164.6 (C=O), 140.9 (C), 132.5 (C), 130.8 (C), 130.3 (C), 127.9 (2CH), 127.2 (CH), 125.8 (C), 125.6 (2CH), 124.8 (CH), 124.4 (CH), 124.3 (CH), 124.2 (CH), 119.5 (CH), 119.0 (CH), 19.9 (CH_3). Anal. Calcd for $C_{18}H_{15}NO$ (361.3): C 82.73; H 5.79; N 5.36. Found: C 82.59; H 5.77; N 5.44.

4.2.2.5. 4-Methoxy-*N*-(naphthalen-1-yl)benzamide 8e. Colourless crystals from ethanol, mp 205–206 °C (lit.[24] mp 203–205 °C). LCMS m/z=278 (M+1). ^{1}H NMR ($CDCl_3$): δ 8.17 (br, 1H, NH), 8.04 (d, 1H, J=7.8 Hz), 7.98 (d, 2H, J=8.6 Hz), 7.92 (t, 2H, J=7.4 Hz), 7.76 (d, 1H, J=8.2 Hz), 7.55 (m, 3H), 7.03 (d, 2H, J=8.6 Hz), 3.92 (s, 3H, OCH_3).

4.2.2.6. 2-Allyloxy-*N*-(naphthalen-1-yl)benzamide 8f. Colorless crystals from MeOH/H_2O, mp 102–104 °C. LCMS=304 (M+1). IR (KBr): 3356, 3051, 1660, 1598, 1544, 1501, 1483, 1403, 1342, 1297, 1220, 994, 934, 746, 630. ^{1}H NMR ($CDCl_3$): δ 10.44 (br s, 1H, NH), 8.43 (dd, 1H, J=7.8, 1.4 Hz), 8.39 (d, 1H, J=7.6 Hz), 8.04 (d, 1H, J=8.8 Hz), 7.92 (d, 1H, J=6.4 Hz), 7.72 (d 1H, J=8.2 Hz), 7.58–7.52 (m, 4H), 7.21 (t, 1H, J=7.6 Hz), 7.12 (d, 1H, J=8.3 Hz), 6.25 (m, 1H), 5.58 (d, 1H, J=17.2 Hz), 5.46 (d, 1H, J=10.3 Hz), 4.89 (d, 2H, J=5.8 Hz). ^{13}C NMR ($CDCl_3$): δ 163.6 (C), 156.5 (C), 134.1 (C), 133.3 (CH), 132.9 (CH), 131.9 (CH), 128.8 (CH), 126.6 (C), 126.2 (CH), 125.9 (CH), 125.8 (C, CH), 124.9 (CH), 122.3 (C), 122.1 (CH), 121.0 (CH), 120.5 (=CH_2, Dept), 119.8 (CH), 112.7 (CH), 70.6 (CH_2). Anal. Calcd for $C_{20}H_{17}NO_2$ (303.3): C 79.19; H 5.65; N 4.62. Found: C 79.10; H 5.59; N 4.53.

4.2.3. Naphtho[1,8-*de*][1,2,3]triazine 5. To a cold (0 °C) solution of 1,8-diaminonaphthalene (1.58 g, 10 mmol) in aqueous acetic acid (50%, 30 mL) was added portionwise with stirring solid sodium nitrite (0.8 g, 11 mmol). Stirring was then continued for 5 h at 0 °C. The dark brown precipitate was collected and washed with water and then recrystallized from EtOH/H_2O to give reddish brown powder, yield 1.0 g (60%), mp 244–246 °C (dec.) (lit.[25] mp 230 °C, decomp.) LCMS m/z=170 (M+1). IR: 3500–2500 (br), 1642, 1593, 1464, 1356, 1333, 1281, 1184, 1158, 1121, 1086, 887, 815, 758. ^{1}H NMR (DMSO-d_6): δ 13.29 (s,

1H, NH), 7.26 (m, 2H), 7.13 (t, 1H, $J=8.0$ Hz), 7.03 (d, 1H, $J=8.4$ Hz), 6.89 (d, 1H, $J=8.2$ Hz), 6.13 (d, 1H, $J=7.2$ Hz). ^{13}C NMR (DMSO): δ 139.4 (C), 133.9 (C), 133.3 (C), 129.6 (CH), 129.4 (CH), 123.9 (CH), 118.7 (C), 118.6 (CH), 114.4 (CH), 99.0 (CH).

4.3. 1-Acylnaphtho[1,8-*de*][1,2,3]triazines 6a–f: general procedure

To a stirred cold (0 °C) suspension of **5** (1.69 g, 10 mmol) in dichloromethane (25 mL) was added TEA (1 mL) followed by dropwise addition of the appropriate acid chloride (12 mmol). After complete addition the reaction mixture was kept stirring at 0 °C for 2 h and then at room temperature overnight. After washing with sodium bicarbonate solution (10%, 100 mL) the organic layer was separated and dried with anhydrous sodium sulfate. The solvent was then evaporated in vacuo and the residue was crystallized to give the corresponding products **6a–f**.

4.3.1. 1-Acetylnaphtho[1,8-*de*][1,2,3]triazine 6a. Yield 1.3 g (61%.) Yellow crystals from petroleum ether (80–100), mp 98–100 °C (lit.[15] 97–98). LCMS $m/z=212$ (M+1). IR: 3063, 1707, 1628, 1430,1366, 1296, 1033, 944, 828, 771. ^{1}H NMR ($CDCl_3$): δ 8.22 (dd, 1H, $J=7.6$, 1.0 Hz), 7.63 (d, 1H, $J=8.4$ Hz), 7.54 (d, 1H, $J=7.0$ Hz), 7.48–7.38 (m, 3H), 2.72 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.6 (C=O), 134.3 (C), 132.7 (C), 128.8 (CH), 128.7 (C), 128.6 (CH), 127.7 (CH), 122.3 (CH), 121.6 (CH), 116.5 (C), 110.3 (CH), 24.7 (CH_3). Anal. Calcd for $C_{12}H_9N_3O$ (211.2): C 68.24; H 4.29; N 19.65. Found: C 68.31; H 4.21; N 19.55.

4.3.2. 1-Benzoylnaphtho[1,8-*de*][1,2,3]triazine 6b. Yield 1.6 (60%). Yellow crystals from EtOH/$CHCl_3$, mp 145–147 °C. LCMS $m/z=274$ (M+1). IR: 3058, 1689, 1632, 1578, 1524, 1484, 1446, 1410, 1339, 1307, 1255, 1174, 1037, 976, 858, 825, 764, 703. ^{1}H NMR ($CDCl_3$): δ 8.11 (d, 1H, $J=7.4$ Hz), 7.81 (d, 2H, $J=7.3$ Hz), 7.67 (d, 1H, $J=7.6$ Hz), 7.57 (t, 1H, $J=7.6$ Hz), 7.50–7.43 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 171.9 (C=O), 140.4 (C), 134.5 (C), 134.2 (C), 132.9 (C), 131.8 (CH), 139.9 (2CH), 128.8 (CH), 128.7 (CH), 128.1 (2CH), 127.8 (CH), 122.5 (CH), 121.5 (CH), 116.7 (C), 119.8 (CH). Anal. Calcd for $C_{17}H_{11}N_3O$ (273.3): C 74.71; H 4.06; N 15.38. Found: C 74.61; H 4.21; N 14.05.

4.3.3. 1-(4-Chlorobenzoyl)naphtho[1,8-*de*][1,2,3]triazine 6c. Yield 1.8 g (58%). Yellow crystals from petroleum ether (80–100), mp 150–152 °C. LCMS $m/z=308$ (M+1), 310 (M+3). IR: 3051, 1683, 1641, 1593, 1526, 1482, 1277, 1091, 1013, 846, 814, 756. ^{1}H NMR ($CDCl_3$): δ 8.11 (dd, 1H, $J=7.4$, 1.0 Hz), 7.76 (d, 2H, $J=7.8$ Hz), 7.66 (d, 1H, $J=7.2$ Hz), 7.54–7.43 (m, 6H). Anal. Calcd for $C_{17}H_{10}ClN_3O$ (307.7): C 66.35; H 3.28; N 13.65. Found: C 66.34; H 3.63; N 13.43.

4.3.4. 1-(4-Methylbenzoyl)naphtho[1,8-*de*][1,2,3]triazine 6d. Yield 1.6 g (56%). Yellow crystals EtOH, mp 170–172 °C. LCMS $m/z=288$ (M+1). IR: 3052, 2995, 2839, 1687, 1604, 1511, 1371, 1304, 1259, 1176, 1033, 976, 862, 825, 765. ^{1}H NMR ($CDCl_3$): δ 8.05 (dd, 1H, $J=7.2$, 1.2 Hz), 7.74 (d, 2H, $J=8.0$ Hz), 7.63 (dd, 1H, $J=7.2$, 1.0 Hz), 7.50–7.41 (m, 4H), 7.29 (d, 2H, $J=8$ Hz), 2.46 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 171.8 (C=O), 142.7 (C), 134.3 (C), 132.9 (C), 131.4 (C), 130.2 (2CH), 129.3 (C), 128.8 (2CH), 128.7 (CH), 128.5 (CH), 127.9 (CH), 122.3 (CH), 121.3 (CH), 116.8 (C), 109.5 (CH), 21.7 (CH_3). Anal. Calcd for $C_{18}H_{13}N_3O$ (287.3): C 75.25; H 4.56; N 14.62. Found: C 74.98; H 4.49; N 14.60.

4.3.5. 1-(4-Methoxybenzoyl)naphtho[1,8-*de*][1,2,3]triazine 6e. Yield 1.8 g (60%). Yellow crystals from EtOH, mp 158–160 °C. LCMS $m/z=304$ (M+1). IR: 3056, 2839, 1686, 1603, 1510, 1373, 1306, 1259, 1176, 1032, 976, 862, 840, 824, 759. ^{1}H NMR ($CDCl_3$): δ 7.95 (dd, 1H, $J=7.0$, 1.5 Hz), 7.86 (d, 2H, $J=8.8$ Hz), 7.62 (dd, 1H, $J=7.6$, 1.6 Hz), 7.49–7.39 (m, 4H), 6.98 (d, 2H, $J=8.8$ Hz), 3.91 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 171.0 (C=O), 162.9 (C), 134.5 (C), 133.0 (C), 132.7 (2CH), 129.4 (C), 128.7 (CH), 128.4 (CH), 127.9 (CH), 126.1 (C), 122.1 (CH), 121.0 (CH), 116.9 (C), 113.4 (2CH), 109.1 (CH), 55.5 (OCH_3). Anal. Calcd for $C_{18}H_{13}N_3O_2$ (303.3): C 71.28; H 4.32; N 13.85. Found: C 71.21; H 4.41; N 13.64.

4.3.6. 1-(2-Allyloxybenzoyl)naphtho[1,8-*de*][1,2,3]triazine 6f. Yield 1.6 g (50%). Yellow oil. LCMS $m/z=330$ (M+1). ^{1}H NMR ($CDCl_3$): δ 7.84 (dd, 1H, $J=7.6$, 1.6 Hz), 7.45 (dd, 1H, $J=8.0$, 1.6 Hz), 7.43 (d, 1H, $J=8.0$ Hz), 7.39–7.30 (m, 3H), 7.06 (t, 2H, $J=8.0$ Hz), 7.02 (d, 1H, $J=7.0$ Hz), 6.75 (d, 1H, $J=6.8$ Hz), 6.09 (m, 1H), 5.55 (dd, 1H, $J=15.6$, 1.4 Hz), 5.30 (dd, 1H, $J=10.8$, 1.4 Hz), 4.68 (m, 2H). Anal. Calcd for $C_{20}H_{15}N_3O_2$ (329): C 72.94; H 4.55; N 12.76. Found: C 72.83; H 4.41; N 12.68.

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