

# Rapid and Facile Synthesis of 4-Aryl-5-imino-3-phenyl-1*H*-naphtho[2,3-*f*]-1,2,4-triazepine-6,11-diones via the Reaction of Amidrazones with Dicyanonaphthoquinone

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One-pot syntheses of various 4-aryl-5-imino-3-phenyl-1*H*-naphtho[2,3-*f*]-1,2,4-triazepine-6,11-diones **5a–f** via reaction of amidrazones **1a–f** with 1,4-dioxo-1,4-dihydronaphthalene-2,3-dicarbonitrile (**4**) are reported.

**Key words:** Amidrazones, Dioxonaphthalene-dicarbonitrile and 1,2,4-Triazepines

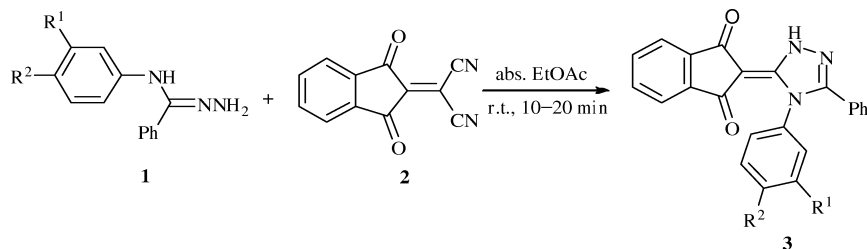
## Introduction

Amidrazone derivatives are considered an important class of amidines since they can be used in heterocyclic syntheses [1]. Amidines are used very often in pharmacological and medicinal applications [2–6]. Formamidines have attracted the interest of many research groups for their biological activity and pharmacological potential [7]. The ease of forming C–N and C=N bonds is reflected in their extensive use for the preparation of heterocycles. While the terminal nitrogen atom of the hydrazone moiety in amidrazones (C=N–NH<sub>2</sub>) is the most powerful nucleophilic center, the other two nitrogen atoms can also act as nucleophiles and thus complete cyclization processes. Amidrazones display fungistatic, bacteriostatic, and antimycotic activities [8a] and also function as herbicides [8b] and lipoxygenase-1 inhibitors [8c]. Recently, Aly *et al.* have demonstrated a very convenient one-step synthesis of 1,2,4-triazoles by the rapid reaction of amidrazones **1a–f** with 2-(1,3-dioxo-indan-2-ylidene)malononitrile (**2**) (Scheme 1) [9]. We have also investigated the reactions of amidines and their analogs

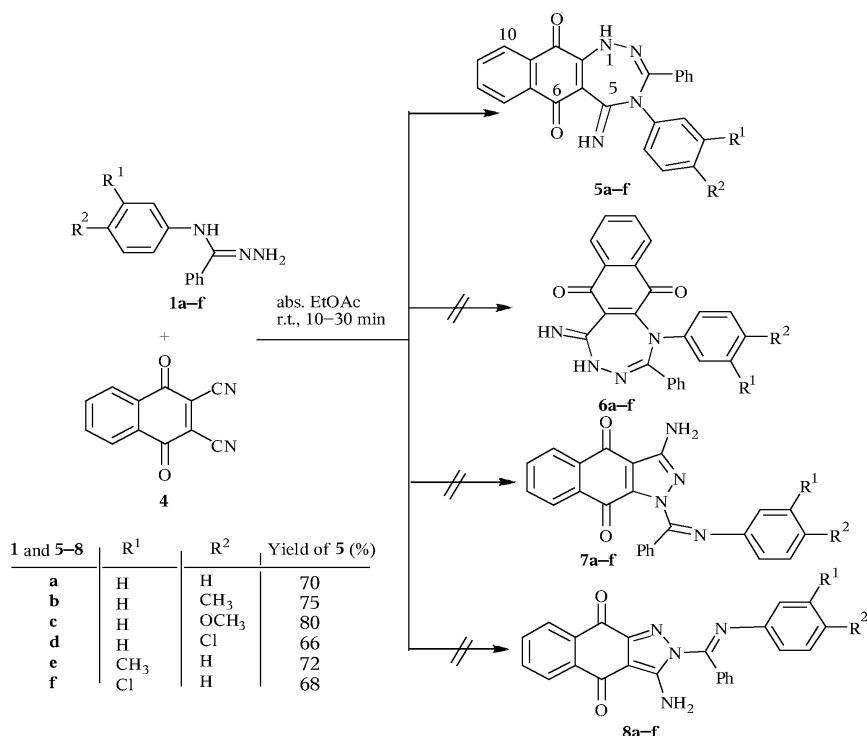
with  $\pi$ -acceptors; various five- and six-membered mono- and di-aza-heterocycles were obtained [10–12]. Previously, it was reported that the reaction of 1,2,4-triazino[5,6-*b*]indole-3-thione with 1,4-dioxo-1,4-dihydronaphthalene-2,3-dicarbonitrile gave the corresponding triazepinotriazino-indoles [13]. In this publication we investigate the reactions of amidrazones **1a–f** with 1,4-dioxo-1,4-dihydronaphthalene-2,3-dicarbonitrile (**4**) as a  $\pi$ -electron deficient acceptor aiming to obtain heterocyclic compounds, which might have prospective biological activities.

## Results and Discussion

Herein we report on the reaction between amidrazones **1a–f** with 1,4-dioxo-1,4-dihydronaphthalene-2,3-dicarbonitrile (**4**). Scheme 2 outlines the reactions of **1a–f** with **4** in dry ethyl acetate under N<sub>2</sub> atmosphere. The reaction proceeded in a few minutes to yield, after chromatographic purification and recrystallization, compounds **5a–f** (66–80 %). We chose amidrazones **1a–f** having aryl groups with electron donating and withdrawing substituents on the benzene



Scheme 1. Reactions of amidrazones **1** with **2** yielding 1,2,4-triazoles **3** [9].



Scheme 2. Synthesis of new 4-aryl-5-amino-3-phenyl-naphtho-[2,3-*f*]-1*H*-triazepine-6,11-diones **5a-f**.

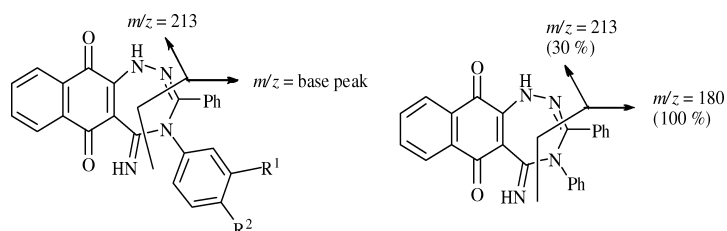


Fig. 1. Mass fragmentation patterns of compounds **5a-f** (left); example as in **5a** (right).

ring, in order to examine their effect on the course of the reaction. The structures of compounds **5a-f** were assigned using the usual spectroscopic tools such as IR, NMR (<sup>1</sup>H, <sup>13</sup>C) and mass spectra, in addition to elemental analyses. Compounds **5a-f** showed IR absorption peaks at  $\nu = 3450\text{--}3440$  (NH) and  $3348\text{--}3340$  cm<sup>-1</sup> (C=NH) along with broad bands at  $\nu = 1695\text{--}1680$  cm<sup>-1</sup> corresponding to the carbonyl groups. The mass spectra (EI mode) of compounds **5a-f** showed the molecular ions, although not as the base peaks. For example, the mass spectrum of **5a** showed a molecular ion at  $m/z = 392$  (18 %) (Fig. 1), and the elemental analysis confirmed the molecular formula as C<sub>24</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>. The mass spectral fragmentation patterns of **5a-f** (Fig. 1) are well in agreement with the assigned structures, but not with the regioisomeric structures **6a-f**, taking into consider-

ation that the fragmentation across the N–N and *N*-naphthoquinone bonds rarely occurs (Fig. 1).

Most indicative was the presence of a characteristic fragmentation peak for **5a-c** and **5e,f** at  $m/z = 213$  (30–40 %) independent of the substitution pattern, together with a major fragment (the base peak for **5a-e**) corresponding to the two aryl groups plus the C–N connection between them (for **5a**,  $m/z = 180$ , Fig. 1). In the case of **5d** the peak at  $m/z = 213$  appeared as the base peak. Interestingly, molecular mechanics calculations (MM2) [14] of **5a**, as an example, indicated that the distance between the NH proton and the oxygen of the carbonyl group (C-11) amounts to  $\sim 2.2$  Å. However, the distance between the imino-NH proton and the oxygen of the other carbonyl group (C-6) is found at  $\sim 1.7$  Å enabling the formation of a hydrogen bond and consequently of a six-membered ring as

shown in Scheme 2. Accordingly, the imino-NH proton appeared more deshielded (*i. e.* in **5a**  $\delta = 5.80$  ppm) than expected (Experimental Section). The molecular mechanics calculations (MM2) [14] of the steric energies, as optimized by molecular mechanics for compounds **5a** and **6a**, showed that compound **5a** has a lower steric energy value ( $\Delta E = 35.65$  kcal/mol) than its isomer **6a** ( $\Delta E = 41.76$  kcal/mol). The  $^1\text{H}$  NMR spectrum of **5a** showed three double-doublets for the naphthalenone's phenyl protons at  $\delta = 7.90$  ( $J = 7.8$ , 1.2 Hz, 10-H), 7.85 ( $J = 7.8$ , 1.2 Hz, 7-H) and 7.70 ppm ( $J = 8.0$ , 1.2 Hz, 8-, 9-H). The  $^{13}\text{C}$  NMR signals observed of **5a** confirmed the proposed structure by the appearance of signals for C-3, -5 and the two carbonyl carbons (C-6 and -11) at  $\delta = 164.0$ , 162.0, 186.2 and 185.0 ppm, respectively. Conclusive evidence for the proposed structure of compounds **5a–d** was obtained from NOE experiments. For example, in **5a**, saturation of the *ortho*-protons of the phenyl group attached to C-4 caused enhancement to *ortho*-protons of the phenyl group attached to C-3 (Fig. 2). Furthermore, in **5d**, saturation of the signal at  $\delta = 6.50$  ppm, on the chlorophenyl ring, caused enhancement of the signals at  $\delta = 7.62$  ppm, for the unsubstituted phenyl. Direct one-bond attached hydrogen-carbon correlations were established by  $^1\text{H}$ ,  $^{13}\text{C}$ -COSY experiments (HETCOR). Besides, a correlation was found between the signals of C-5 and of the *ortho*-protons of the phenyl groups attached to N-4. This correlation would not be expected in structures of **6a–f**.

Additionally, the COSY C-H and H-H spectra of **5a–f** supported the proposed structures. The magnitude of the NOE depends upon the internuclear distance in space as  $1/r^6$ , where  $r$  is the internuclear separation [15]. In practical terms, NOEs are rarely seen between pairs of protons that are separated by more than about 4.5 Å. NOEs have been correlated with internuclear distances as follows: strong (1.8–2.9 Å), medium (1.8–3.7 Å) and weak (3.0–4.5 Å) [16]. For compounds **5a–f**, sharp to medium NOEs between the imino protons and the *ortho*-protons of the phenyl group attached to C-4 were observed, which consequently supported the proposed structures of compounds **5a–f**, whereas such effects should be absent in the alternative structures of **6**, **7**, and **8**.

Furthermore, the  $^1\text{H}$  NMR spectra ruled out that compounds **7a–f** and **8a–f** were obtained due to the absence of the expected broad singlet of the amino

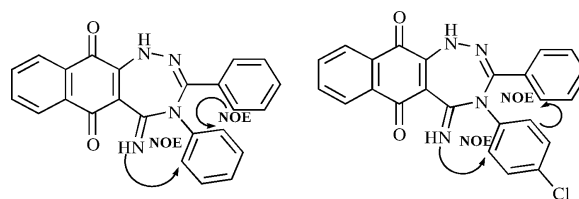


Fig. 2. NOE experiments in compounds **5a** and **5d**.

protons, and supported the proposal that the obtained products did not have the constitution of **7** and/or **8**. Instead, two distinctive proton signals were recorded, each for one proton arising from the imino-NH and the NH of the triazepine ring.

The variation of the yields of products **5a–f** depended on the type of substituents in the aromatic ring in **1a–f**. The presence of electron donating substituents such as methyl and methoxy groups increased the product yields. Since the reaction of amidrazones **1a–f** and **4** can be described as a reaction between donor and acceptor, an increase of the donating ability would, of course, increase the yields of the obtained products.

Mechanistically, the reaction of **4** with **1a–f** is ascribed to addition of the hydrazono-NH<sub>2</sub> of **1** to the C-2 of quinone **4**, followed by elimination of HCN. Subsequently, there is another nucleophilic attack by the azomethine group on the remaining cyano group. Based on the fact that the amidrazone moiety can exist in a tautomeric form which enables **1** to have binucleophilic reactivity arising from the presence of an NHNH<sub>2</sub> group, one could also expect the formation of naphthopyrazoles **7a–f** (Scheme 2). However, this suggestion is excluded by the spectroscopic data discussed above. It is important to mention that bis-acetylenic ketones were used for the efficient (88–91 %) one-pot synthesis of triazepines [17]. The synthetic potential and biological activity of benzotriazepines are the subjects of intense investigations in medicinal chemistry. The area of biological interest of this family of compounds have been extended recently to various diseases such as cancer [18], viral infections (HIV) [19] and cardiovascular disorders [20,21]. In this lead a great number of publications have reported on 1,3,5-benzotriazepines [22–26], but little work has been carried out on 1,2,4-benzotriazepines [27,28]. Therefore, our method is considered as a convenient procedure to synthesize 1,2,4-triazepine derivatives. The advantages are the reasonable yields, and the ease with which the reaction can be carried out as a one-pot procedure.

## Experimental Section

All melting points were recorded on a Gallenkamp apparatus.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra (Bruker AM 400,  $^1\text{H}$ : 400.13 MHz,  $^{13}\text{C}$ : 100.6 MHz) were obtained from  $\text{CDCl}_3$  solutions; the chemical shifts are given relative to the internal standard TMS. For preparative thin layer chromatography (PLC), glass plates (20 × 48 cm) were covered with a slurry of silica gel (Merck PF<sub>254</sub>) and air dried. The solvents stated were employed for development. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm UV light. Elemental analyses were carried out in the Microanalysis Center of the Institut für Anorganische Chemie, Technische Universität Braunschweig. Mass spectroscopy was performed with a Finnigan Mat 8430 spectrometer at 70 eV in EI mode at the Institute of Organic Chemistry, TU Braunschweig. IR spectra were obtained on a Shimadzu 470 spectrophotometer using potassium bromide pellets.

### Starting materials

Amidrazones **1a–f** were prepared according to reference [1]. 1,4-Dioxo-1,4-dihydro-naphthalene-2,3-dicarbonitrile (**4**) was prepared from 2,3-dichloro-1,4-naphthoquinone (obtained from Merck) according to Budni [29].

### Reaction of **1a–f** with 1,4-dioxo-1,4-dihydronaphthalene-2,3-dicarbonitrile (**4**)

#### General procedure

A 250 mL two-necked bottom flask was flame-dried under  $\text{N}_2$  and then cooled to r. t. To this flask was added a solution of **1a–f** (1 mmol) in absolute ethyl acetate (100 mL), followed by **4** (0.208 g 1 mmol). The reaction mixture was stirred at r. t. for 10–30 min until the starting materials were consumed (as monitored by TLC). The solvent was removed under vacuum and the residue was separated by PLC (silica gel, toluene : ethyl acetate = 5 : 2). The obtained products **5a–f** were recrystallized from the stated solvents.

### 3,4-Diphenyl-5-imino-1*H*-naphtho[2,3-*f*]-1,2,4-triazepine-6,11-dione (**5a**)

Yellow crystals (0.38 g, 70 %);  $R_f$  = 0.4 ( $\text{CH}_2\text{Cl}_2$ ), m. p. 230 °C (ethyl acetate). – UV ( $\text{CH}_3\text{CN}$ ):  $\lambda$  (lg  $\epsilon$ ) = 460 (4.10). – IR (KBr):  $\nu$  = 3450, 3340 (m,  $\text{NH}_2$ , =NH), 3100–3095 (m, Ar-CH), 1690–1680 (s, CO), 1610 (s, C=N), 1590 (C=C)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 7.90 (dd,  $J$  = 7.8, 1.2 Hz, 1 H, 10-H), 7.85 (dd,  $J$  = 7.8, 1.2 Hz, 1 H, 7-H), 7.70 (dd,  $J$  = 8.0, 1.2 Hz, 2 H, 8-, 9-H), 7.53–7.50 (m, 2 H, Ph-H), 7.33–7.30 (m, 2 H, Ph-H), 7.10 (s, 1 H,  $\text{NH}^1$ ), 7.02–7.00 (m, 1 H, Ph-H), 6.89–6.86 (m, 2 H, Ph-H), 6.63–6.60 (m, 2 H, Ph-H), 6.58–6.56 (m, 1 H, Ph-H), 5.80 (s, 1 H, N-NH). –  $^{13}\text{C}$  NMR (100.6 MHz,

$\text{CDCl}_3$ ):  $\delta$  = 186.2 (C-6), 185.0 (C-11), 164.0 (C-3), 162.0 (C-5), 155.8 (C-5a), 139.0 (N-C-Ph), 136.8 (C-10a), 135.6 (C-6a), 132.2 (CH-10), 132.0 (CH-7), 131.2 (CH-8, -9), 131.6 (C-Ph), 129.8 (2 *ortho*-CH-Ph), 128.4 (2 *meta*-CH-Ph), 127.2 (*para*-CH-Ph), 126.8 (2 *ortho*-CH-Ph), 126.4 (2 *meta*-CH-Ph), 125.0 (*para*-CH-Ph), 122.6 (C-11a). – MS (EI, 70 eV):  $m/z$  (%) = 392 (18)  $[\text{M}]^+$ , 315 (22), 238 (32), 213 (30), 196 (12), 180 (100), 119 (22), 105 (30), 91 (18), 77 (33), 51 (20). –  $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_2$  (392.420): calcd. C 73.46, H 4.11, N 14.28; found C 73.53, H 4.09, N 14.34.

### 5-Imino-4-(4-methylphenyl)-3-phenyl-1*H*-naphtho-[2,3-*f*]-1,2,4-triazepine-6,11-dione (**5b**)

Yellow crystals (0.30 g, 75 %);  $R_f$  = 0.35 ( $\text{CH}_2\text{Cl}_2$ ), m. p. 210 °C (ethanol). – UV ( $\text{CH}_3\text{CN}$ ):  $\lambda$  (lg  $\epsilon$ ) = 465 (4.12). – IR (KBr):  $\nu$  = 3446, 3345 (m,  $\text{NH}_2$ , =NH), 3070–3080 (m, Ar-CH), 2980–2860 (m, aliph. CH), 1692–1682 (s, CO), 1612 (s, C=N), 1594 (C=C)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 7.96 (dd,  $J$  = 8.0, 1.2 Hz, 1 H, 10-H), 7.88 (dd,  $J$  = 8.0, 1.2 Hz, 1 H, 7-H), 7.74 (dd,  $J$  = 8.0, 1.2 Hz, 2 H, 8-, 9-H), 7.55–7.53 (m, 2 H, Ph-H), 7.33–7.30 (m, 2 H, Ph-H), 7.15 (s, 1 H,  $\text{NH}^1$ ), 7.02–6.90 (m, 3 H, Ph-H), 6.66 (dd,  $J$  = 8.0, 1.2 Hz, 2 H,  $\text{CH}_3\text{Ph-H}$ ), 5.86 (s, 1 H, imino-NH), 2.30 (s, 3 H,  $\text{CH}_3$ ). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 186.0 (C-6), 185.2 (C-11), 163.8 (C-3), 162.2 (C-5), 154.8 (C-5a), 139.4 (N-C-Ph), 136.6 (C-10a), 135.8 (C-6a), 133.0 (CH-10), 132.6 (Ph-C- $\text{CH}_3$ ), 131.8 (CH-7), 131.4 (CH-8, -9), 130.6 (C-Ph), 130.2 (2 CH-Ph $\text{CH}_3$ ), 129.6 (2 *ortho*-CH-Ph), 128.6 (2 *meta*-CH-Ph), 128.0 (2 CH-Ph $\text{CH}_3$ ), 126.9 (*para*-CH-Ph), 122.8 (C-11a), 34.2 ( $\text{CH}_3$ ). – MS (EI, 70 eV):  $m/z$  (%) = 406 (26)  $[\text{M}]^+$ , 390 (24), 312 (20), 236 (28), 213 (40), 193 (100), 119 (20), 105 (34), 91 (20), 77 (36), 51 (22). –  $\text{C}_{25}\text{H}_{18}\text{N}_4\text{O}_2$  (406.450): calcd. C 73.88, H 4.46, N 13.78; found C 73.63, H 4.40, N 13.65.

### 5-Imino-4-(4-methoxyphenyl)-3-phenyl-1*H*-naphtho-[2,3-*f*]-1,2,4-triazepine-6,11-dione (**5c**)

Yellow crystals (0.32 g, 80 %);  $R_f$  = 0.35 ( $\text{CH}_2\text{Cl}_2$ ), m. p. 182 °C (ethanol). – UV ( $\text{CH}_3\text{CN}$ ):  $\lambda$  (lg  $\epsilon$ ) = 472 (4.18). – IR (KBr):  $\nu$  = 3442, 3342 (m,  $\text{NH}_2$ , =NH), 3112–3090 (m, Ar-CH), 2989–2850 (m, aliph. CH), 1695–1682 (s, CO), 1620 (s, C=N), 1596 (C=C)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 7.90 (dd,  $J$  = 8.0, 1.2 Hz, 1 H, 10-H), 7.82 (dd,  $J$  = 8.0, 1.2 Hz, 1 H, 7-H), 7.72 (dd,  $J$  = 8.0, 1.2 Hz, 2 H, 8-, 9-H), 7.60 (dd,  $J$  = 8.0, 1.2 Hz, 2 H,  $\text{OCH}_3\text{Ph-H}$ ), 7.50–7.47 (m, 2 H, Ph-H), 7.35–7.30 (m, 3 H, Ph-H), 6.90 (dd,  $J$  = 8.0, 1.2 Hz, 2 H,  $\text{OCH}_3\text{Ph-H}$ ), 7.15 (s, 1 H,  $\text{NH}^1$ ), 5.88 (s, 1 H, imino-NH), 3.90 (s, 3 H,  $\text{OCH}_3$ ). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 186.2 (C-6), 185.0 (C-11), 163.2 (C-3), 162.0 (C-5), 154.6 (C-5a), 150.8 (Ph-C- $\text{OCH}_3$ ), 139.0 (N-C-Ph), 136.4 (C-10a), 136.2 (2 CH-

PhOCH<sub>3</sub>), 135.6 (C-6a), 133.6 (CH-10), 131.5 (CH-7), 131.4 (CH-8, -9), 130.8 (C-Ph), 130.0 (2 CH-PhOCH<sub>3</sub>), 129.2 (2 *ortho*-CH-Ph), 128.2 (2 *meta*-CH-Ph), 126.9 (*para*-CH-Ph), 122.6 (C-11a), 53.2 (OCH<sub>3</sub>). – MS (EI, 70 eV): *m/z* (%) = 422 (24) [M]<sup>+</sup>, 406 (16), 390 (20), 236 (24), 227 (34), 213 (38), 209 (100), 180 (24), 105 (30), 91 (22), 77 (40), 51 (20). – C<sub>25</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub> (422.450): calcd. C 71.08, H 4.29, N 13.26; found C 71.20, H 4.20, N 13.34.

*5-Imino-4-(4-chlorophenyl)-3-phenyl-1H-naphtho-[2,3-f]-1,2,4-triazepine-6,11-dione (5d)*

Yellow crystals (0.28 g, 66 %); *R*<sub>f</sub> = 0.45 (CH<sub>2</sub>Cl<sub>2</sub>), m. p. 190 °C (acetonitrile). – UV (CH<sub>3</sub>CN): λ (lg ε) = 438 (4.04). – IR (KBr): ν = 3444, 3340 (m, NH<sub>2</sub>, =NH), 3100–3050 (m, Ar-CH), 1692–1680 (s, CO), 1608 (s, C=N), 1590 (C=C) cm<sup>-1</sup>. – <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, TMS): δ = 7.96 (dd, *J* = 7.8, 1.0 Hz, 1 H, 10-H), 7.80 (dd, *J* = 7.8, 1.0 Hz, 1 H, 7-H), 7.62 (dd, *J* = 7.9, 1.1 Hz, 2 H, 8-, 9-H), 7.65–7.62 (m, 2 H, Ph-H), 7.28–7.25 (m, 2 H, Ph-H), 7.15 (s, 1 H, NH<sup>1</sup>), 6.98–6.95 (m, 1 H, Ph-H), 6.60 (dd, *J* = 8.0, 1.2 Hz, 2 H, ClPh-H), 6.50 (dd, *J* = 8.0, 1.2 Hz, 2 H, ClPh-H), 5.90 (s, 1 H, imino-NH). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 185.8 (C-6), 185.6 (C-11), 164.4 (C-3), 162.4 (C-5), 155.4 (C-5a), 138.4 (N-C-Ph), 136.6 (C-10a), 136.0 (C-6a), 132.8 (CH-10), 132.4 (CH-7), 131.2 (C-Ph), 131.0 (CH-8, -9), 129.0 (2 *ortho*-CH-Ph), 127.8 (2 *meta*-CH-Ph), 127.0 (*para*-CH-Ph), 126.2 (2 ClPh-CH), 124.0 (Cl-Ph-C), 122.6 (2 ClPh-CH), 120.4 (C-11a). – MS (EI, 70 eV): *m/z* (%) = 427 (10) [M]<sup>+</sup>, 426 (26), [M]<sup>+</sup>, 390 (22), 238 (26), 236 (24), 216 (22), 214 (35), 213 (100), 180 (28), 105 (34), 91 (20), 77 (34), 51 (24). – C<sub>24</sub>H<sub>15</sub>ClN<sub>4</sub>O<sub>2</sub> (426.870): calcd. C 67.53, H 3.54, Cl 8.31, N 13.13; found C 67.30, H 3.50, Cl 8.20, N 13.14.

*5-Imino-4-(3-methylphenyl)-3-phenyl-1H-naphtho-[2,3-f]-1,2,4-triazepine-6,11-dione (5e)*

Pale yellow crystals (0.24 g, 72 %); *R*<sub>f</sub> = 0.22 (CH<sub>2</sub>Cl<sub>2</sub>), m. p. 240 °C (ethanol). – UV (CH<sub>3</sub>CN): λ (lg ε) = 430 (4.00). – IR (KBr): ν = 3448, 3348 (m, NH<sub>2</sub>, =NH), 3108–3090 (m, Ar-CH), 2970–2820 (m, aliph. CH), 1692–1682

(s, CO), 1610 (s, C=N), 1596 (C=C) cm<sup>-1</sup>. – <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, TMS): δ = 7.90 (dd, *J* = 8.0, 1.2 Hz, 1 H, 10-H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 1 H, 7-H), 7.70 (dd, *J* = 8.0, 1.2 Hz, 2 H, 8-, 9-H), 7.40–7.28 (m, 4 H, Ph-H), 7.12 (s, 1 H, NH<sup>1</sup>), 7.02–6.80 (m, 5 H, Ph-H), 5.98 (s, 1 H, imino-NH), 2.28 (s, 3 H, CH<sub>3</sub>). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 186.2 (C-6), 185.0 (C-11), 163.6 (C-3), 162.0 (C-5), 154.4 (C-5a), 139.2 (N-C-Ph), 136.4 (C-10a), 135.6 (C-6a), 133.4 (CH-10), 132.8 (Ph-C-CH<sub>3</sub>), 132.0 (CH-7), 131.2 (CH-8, -9), 130.8 (C-Ph), 130.6, 129.4, 128.8, 128.4, 128.0, 127.6, 127.4 (CH-Ph), 126.6 (*para*-CH-Ph), 122.4 (C-11a), 33.6 (CH<sub>3</sub>). – MS (EI, 70 eV): *m/z* (%) = 406 (24) [M]<sup>+</sup>, 390 (20), 312 (18), 236 (24), 213 (40), 193 (100), 118 (24), 105 (32), 91 (22), 77 (34), 51 (20). – C<sub>25</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> (406.450): calcd. C 73.88, H 4.46, N 13.78; found C 73.70, H 4.40, N 13.60.

*5-Imino-4-(3-chlorophenyl)-3-phenyl-1H-naphtho-[2,3-f]-1,2,4-triazepine-6,11-dione (5f)*

Pale yellow crystals (0.27 g, 68 %); *R*<sub>f</sub> = 0.26 (CH<sub>2</sub>Cl<sub>2</sub>), m. p. 194 °C (ethyl acetate). – UV (CH<sub>3</sub>CN): λ (lg ε) = 412 (3.95). – IR (KBr): ν = 3440, 3346 (m, NH<sub>2</sub>, =NH), 3090–3020 (m, Ar-CH), 1692–1680 (s, CO), 1610 (s, C=N), 1590 (C=C) cm<sup>-1</sup>. – <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, TMS): δ = 7.86 (dd, *J* = 8.0, 1.2 Hz, 1 H, 10-H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 1 H, 7-H), 7.60 (dd, *J* = 7.9, 1.1 Hz, 2 H, 8-, 9-H), 7.65–7.34 (m, 4 H, Ph-H), 7.10 (s, 1 H, NH<sup>1</sup>), 6.90 (d, *J* = 1.2 Hz, 1 H, *ortho*-ClPh-H), 6.54–6.48 (m, 4 H, ClPh-H), 5.74 (s, 1 H, imino-NH). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 185.0 (C-6), 183.2 (C-11), 163.2 (C-3), 162.0 (C-5), 154.2 (C-5a), 138.0 (N-C-Ph), 136.2 (C-10a), 135.2 (C-6a), 132.0 (CH-10), 131.8 (CH-7), 131.0 (CH-8, -9), 130.8 (C-Ph), 129.2 (2 *ortho*-CH-Ph), 128.2 (2 *meta*-CH-Ph), 126.9 (*para*-CH-Ph), 126.0, 125.6, 125.0 (3 ClPh-CH), 124.0 (Cl-Ph-C), 122.6 (ClPh-CH), 122.6 (C-11a). – MS (EI, 70 eV): *m/z* (%) = 427 (10) [M]<sup>+</sup>, 426 (22) [M]<sup>+</sup>, 390 (22), 238 (26), 236 (24), 216 (22), 214 (35), 213 (32), 180 (18), 105 (34), 91 (20), 77 (34), 51 (24). – C<sub>24</sub>H<sub>15</sub>ClN<sub>4</sub>O<sub>2</sub> (426.870): calcd. C 67.53, H 3.54, Cl 8.31, N 13.13; found C 67.34, H 3.52, Cl 8.22, N 13.20.

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