A New Synthesis of Bis-Enaminones via Acylation of Ketones

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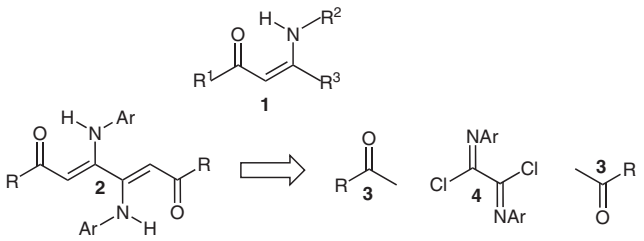
Dedicated to Prof. Branko Stanovnik, Ljubljana, on the occasion of his 70th birthday

Abstract: A short and efficient synthesis for a series of 1,6-diaryl-3,4-diarylaminohexa-2,4-diene-1,6-diones was developed. Based on the acylation-prototropism sequence during the reaction of various aryl methyl ketones with bis-imidoyl chlorides, the products were isolated in good yields. Substituted acetophenones, acetylthiophene, 3-acetylpyridine, and acetylferrocene can be integrated into this reaction as ketone component. Similarly, α-tetralone can be transformed with bis-electrophiles into the corresponding bis-enaminones. Treatment of 2-acetylpyridine with *N*,*N*′-bis(4-tolyl)ethanebis(imidoyl) dichloride yielded not only the expected bis-enaminone, but also a new quinolizine derivative which was structurally characterized by single crystal X-ray analysis. Analogously, pinacolone and cyclopropyl methyl ketone can readily be converted into bis-enaminones. Monoimidoyl chlorides showed the same reactivity, providing derivatives in high yields.

Key words: acylations, ketones, tautomerism, enaminones, bis-imidoyl chlorides

Enaminones **1** are versatile and readily obtainable building blocks and their chemistry has received considerable attention in recent years, mainly for the synthesis of heterocyclic compounds.[1] In contrast, data for bis-enaminones **2** (Figure 1) are quite rare. These bifunctional compounds might offer the possibility of synthesizing new and interesting bis-heterocycles. In addition, bis-enaminones **2** should be of interest for the preparation of dinuclear metal complexes. 1,6-Diaryl/alkyl-1,3,4,6-tetrones,[2] which are easily available by Claisen condensation of aryl/alkyl methyl ketones with diethyl oxalate, provide a synthetic entry via aminolysis reactions to compounds of type **2**. However, their aminolysis is only described with vicinal diamines such as *o*-phenylenediamine or 1,2-diaminocyclohexane and resulted in the formation of cyclic products of the piperazine type.[3]

Based on our previous experiences, another synthetic pathway to compounds of type **2** should consist in the acylation reaction of aryl methyl ketones **3** with bis-arylimidoyl chlorides **4** (Scheme 1). During the last decade, we demonstrated that the latter derivatives are excellent (and selective) bis-electrophiles that can be employed in a wide range as C_2-building blocks for heterocyclic as well as for carbocyclic compounds.[4] In many cases, during acylation of substrates with **4** a very fast prototropic shift takes place forming enamino substructures. Our aim was therefore to develop a short and efficient route to derivatives of type **2** exploiting this acylation–prototropism cascade.



Scheme 1

Generally, the bis-imidoyl chlorides **4** are available by chlorination of appropriate oxanilides **5** with phosphorus pentachloride in toluene.[4a] However, the favored way of obtaining oxanilides – the aminolysis of oxalyl chloride with substituted anilines[5] – has several disadvantages. Thus, an additional base (triethylamine) for the binding of HCl is necessary, which results in a mixture of oxanilides and amine hydrochloride. In the course of time-consuming purification steps and drying, the pure oxanilide is converted into **4** by treatment with PCl_5 in the final step. In addition, the oxanilides **5** were obtained as large crystals, which needed substantial longer chlorination times than in a fine disperse, amorphous state due to their insolubility. We have now optimized this process in the form of a two-step one-pot protocol for the preparation of the bis-electrophiles **4**. In the first step, the oxanilides **5** were prepared by the addition of oxalyl chloride (one equivalent) to aniline (two equivalents) in toluene without any additional base. Within a few minutes, a slurry of pure **5** in toluene was obtained, which was directly chlorinated (PCl_5) without further purification. After recrystallization, the bis-arylimidoyl chlorides **4a–c** were obtained in good yields (70–80%) as yellow crystals (Scheme 2). In order to achieve better solubility of the products, derivative **4d** was synthesized. It can be isolated by the same improved procedure as a viscous yellow oil.

Acetophenone (**3a**, R = Ph) reacts readily with the bis-electrophile **4b**. Under quite mild conditions (THF in the presence of *t*-BuOK at –30 °C), a single product (TLC)

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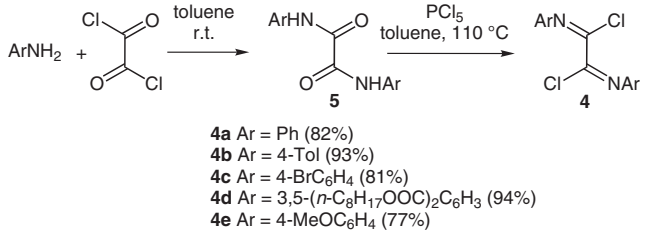
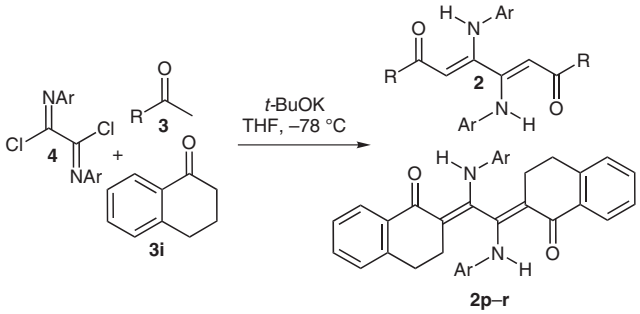


Scheme 2



Scheme 3

was isolated in high yields as yellow crystals and recrystallized from DMF. Due to the existence of intermolecular hydrogen bonds, the product is relatively insoluble in other common solvents. Elemental analysis (and MS data, see discussion below, Scheme 3) confirmed the presence of a 2:1 acylation product **2a**. Evidence for the high symmetry in this novel 1,6-diphenyl-3,4-ditolylaminohexa-2,4-diene-1,6-dione (**2a**) (Scheme 3) was provided by single sets of signals in its ^{1}H and ^{13}C NMR spectra. The NH protons of derivative **2a** showed resonance at 12.40 ppm, and the signals for the methine protons were observed at 2.24 ppm. In the ^{13}C NMR spectrum, the signal for the carbonyl carbons was observed at 189.9 ppm whereas the signal for the methine groups appeared at higher fields at 96.1 ppm.

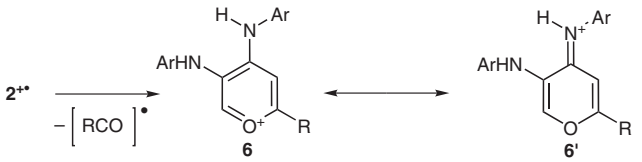
Employing the same procedure, the bis-imidoyl chlorides **4a–e** as well as the acetophenone derivatives **3b–d** were

Table 1 Bis-enaminones of Type **2**

2	3	4	R	Ar	Mp (°C)[6]
2a	**3a**	**4b**	Ph	4-MeC_6H_4	232
2b	**3b**	**4b**	4-MeC_6H_4	4-MeC_6H_4	242
2c	**3a**	**4a**	Ph	Ph	218
2d	**3a**	**4b**	4-MeC_6H_4	Ph	240
2e	**3c**	**4b**	4-BrC_6H_4	4-MeC_6H_4	254
2f	**3d**	**4b**	4-MeOC_6H_4	4-MeC_6H_4	236
2g	**3d**	**4c**	4-MeOC_6H_4	4-BrC_6H_4	238
2h	**3b**	**4d**	4-MeC_6H_4	3,5(*n*-$C_8H_{17}OOC)_2C_6H_3$	oil
2i	**3e**	**4b**	2-thienyl	4-MeC_6H_4	256
2j	**3f**	**4b**	3-pyridyl	4-MeC_6H_4	223
2k	**3g**	**4b**	ferrocenyl	4-MeC_6H_4	dec.
2l	**3a**	**4c**	4-MeC_6H_4	4-BrC_6H_4	254
2m	**3h**	**4b**	2-pyridyl	4-MeC_6H_4	233
2n	**3h**	**4c**	2-pyridyl	4-BrC_6H_4	237
2o	**3d**	**4e**	4-MeOC_6H_4	4-MeOC_6H_4	196
2p	**3i**	**4a**	see text	Ph	198
2q	**3i**	**4b**	see text	4-MeC_6H_4	204
2r	**3i**	**4c**	see text	4-BrC_6H_4	246
2s	**3j**	**4a**	*t*-Bu	Ph	167
2t	**3j**	**4b**	*t*-Bu	4-MeC_6H_4	146
2u	**3k**	**4a**	*c*-Pr	Ph	186
2v	**3k**	**4b**	*c*-Pr	4-MeC_6H_4	181
2w	**3k**	**4e**	*c*-Pr	4-MeOC_6H_4	162

integrated into this reaction (Table 1). The derivatives **2b–g** were isolated as yellow crystalline compounds, which showed chemical properties similar to those of **2a**. The reaction of **4d** with 4-methylacetophenone (**3b**) resulted in the soluble derivative **2h**, caused by the existence of four lipophilic *n*-octyl ester substructures.

The mass spectra (EI) of derivatives **2** showed some interesting features: on the one hand, no $[M]^+$ peak was detected in any of the cases. However, at mild ionization conditions and application of relatively large probe amounts, a weak peak for the molecule ion was detected. On the other hand, the base peak measured in all cases was assigned to pyrylium ion **6** (Scheme 4), which resulted from the extrusion reaction of an acyl residue from $[M]^+$. As a result of two donor-acceptor chromophores in the molecule, compounds **2** formed dark yellow solutions (Table 1); for example **2b** absorbed in $CHCl_3$ at $\lambda_{max} = 396$ nm, (log $\varepsilon = 3.9$).



Scheme 4

Further structural details were obtained from a single crystal X-ray analysis of **2e**. The result of this analysis showed that **2e** is a monomer in the solid state (Figure 1). The bond lengths and angles were in the expected range; only the bonds between N1–C3/C4–N2 were somewhat shortened. Due to a strong hydrogen bridge between the NH groups and the oxygen atoms of the carbonyl groups, the *cis* configuration predominated in the solid state.

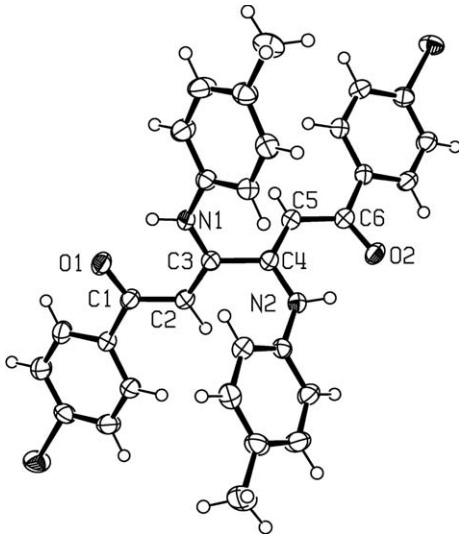


Figure 1 ORTEP plot (50% probability ellipsoids) of the solid state molecular structure of **2e**, selected bond lengths in Å: O1–C1 1.250(6), O2–C6 1.249(6), N1–C3 1.345(6), N2–C4 1.350(6), C1–C2 1.438(6), C2–C3 1.372(6), C3–C4 1.499(6), C4–C5 1.372(6), C5–C6 1.436(6).

Other methyl ketones such as 2-acetylthiophene (**3e**), 3-acetylpyridine (**3f**) and acetylferrocene (MeCOFc) **3g** reacted with **4b** under similar mild conditions to yield the corresponding 1,6-diaryl-3,4-ditolylaminohexa-2,4-diene-1,6-diones **2** (Table 1). Analogously, α-tetralone (**3i**) was transformed with bis-electrophiles **4** into the corresponding enaminones of types **2p–r** (Scheme 2), which in contrast to those of the acetophenone series are well soluble in most common solvents.

The presence of an additional electrophilic center in 2-acetylpyridine (**3h**) guaranteed the formation of a further product. Using TLC, not only the expected yellow hexa-2,4-diene-1,6-diones **2m**,**n** but also a red side product **7** was detected; both products were separated by column chromatography. After recrystallization, **7** was obtained as red, green shining crystals. Elemental analysis as well as MS data confirmed the presence of a 2:1 acylation product. However, the ^1H as well as the ^{13}C NMR spectra only showed complex sets of signals located mainly in the part of aromatic protons/carbons. The structure of **7** was established by single crystal X-ray analysis (Figure 2). Thus, compound **7** can be regarded as a derivative of 1*H*-1-oxoquinolizine (Scheme 5). The bond lengths and angles are in the expected range for this structure; only the bond N3–C3 was somewhat shortened. The solutions of **7** are dark red which could be interpreted as result of its cross-conjugated system. Compound **7** showed a broad and strong absorption between 450 and 550 nm in its UV/vis spectrum ($CHCl_3$), with a maximum at 515 nm (log $\varepsilon = 4.3$). Furthermore, **7** is electrochemically active and could be reduced reversibly. Employing square wave measurements, two peaks at –0.718 V and at –1.196 V can be ascribed as two different electron transfer steps. The quasi-reversibility of the reduction was confirmed by cyclovoltammetric measurements ($\Delta E^1_{RED,OX} = 0.122$ V, $\Delta E^2_{RED,OX} = 0.085$ V). The resulting semiquinone formation constant is relatively high ($K_{SEM} = 1.26 \times 10^8$).

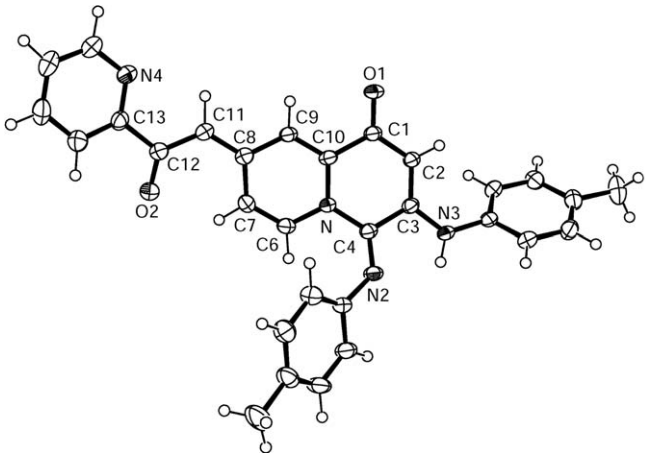
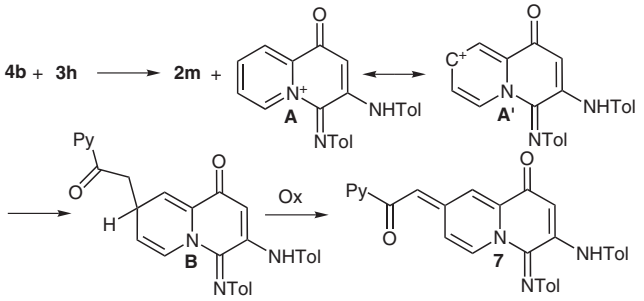


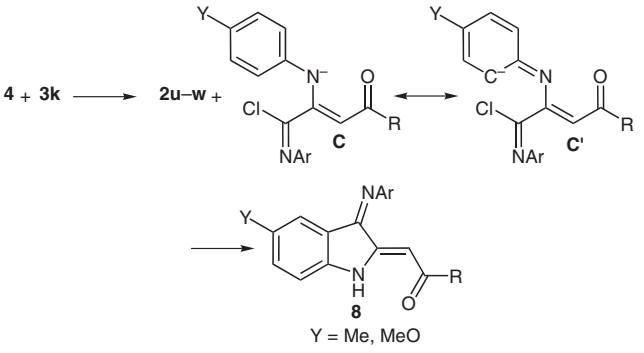
Figure 2 ORTEP plot (50% probability ellipsoids) of the solid state molecular structure of **7**, selected bond lengths in Å: O1–C1 1.237(2), O2–C12 1.235(2), N–C4 1.419(2), N–C6 1.388(3), N–C10 1.400(2), N2–C4 1.273(2), N3–C3 1.350(2), C1–C2 1.415(3), C2–C3 1.367(3), C3–C4 1.488(3), C6–C7 1.340(3), C7–C8 1.442(3), C8–C9 1.437(3), C9–C10 1.353(3), C1–C10 1.494(3), C8–C11 1.381(3), C11–C12 1.441(3).

The formation of bicyclic **7** can be rationalized by the following mechanism: initial attack of the enolate of **3h** at **4** resulted in the intermediate **A**. A second enolate then attacks the 4-position (**A′**) of the pyridine ring forming intermediate **B**, which finally was oxidized to yield **7** (Scheme 5).



Scheme 5

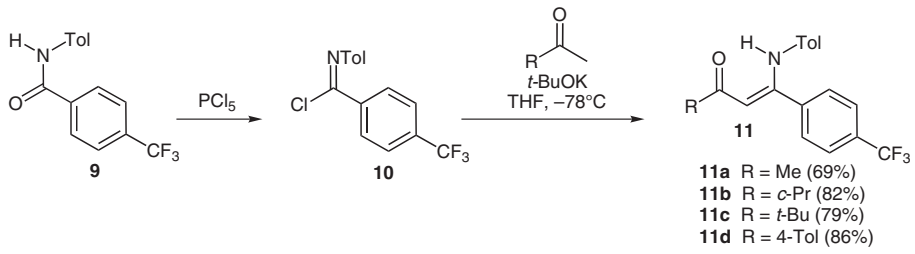
The synthetic concept presented here is not only restricted to aryl methyl ketones. In a smooth reaction, pinacolone (**3j**) and cyclopropyl methyl ketone (**3k**) were converted into 1,6-dialkyl-3,4-diarylaminohexa-2,4-diene-1,6-diones of type **2**. These new bis-enaminones were isolated as yellow, well soluble crystalline compounds (Table 1). Whereas in the case of ketone **3j**, only traces of a red byproduct (derivatives of isatine) were detected, the use of **3k** allowed the isolation of compounds **8b**,**c** as red crystals. Elemental analysis and MS data confirmed the presence of 1:1 cyclization products **8b**,**c** (Scheme 6). In the ^{1}H NMR spectrum of **8b**, a singlet at 2.4 ppm indicated an intramolecular acylation reaction within the diimino substructure. Dark red **8** was easily deprotonated with *t*-BuOK under the formation of turquoise solutions of delocalized anions, the neutral form being regenerated upon treatment with acids. Generally, these derivatives showed the characteristic chemical behavior of isatines which were already prepared earlier starting from **4**.[7] Their formation can be explained by intramolecular *ortho*-attack of the firstly formed acylation product **C′**, followed by proton shift and rearomatization (Scheme 6). The ^{1}H as well as the ^{13}C NMR spectra of **8** displayed complex sets of signals due to dynamic interconversion processes of *E*/*Z* forms.



Scheme 6

Finally, we tested the synthetic concept on 'simple' imidoyl chlorides. For this reason, the imidoyl chloride **10** was synthesized from benzanilide **9**. Recently, this concept was successfully applied for the synthesis of β-bromodifluoromethyl β-enaminoketones,[8a] as well as for a short way to quinolones starting from acetophenones and trifluoroacetimidoyl chlorides.[8b] In both cases sodium hydride had been used as the base. We substituted this base by the cheaper and easier to handle *t*-BuOK. Thus, 4-methylacetophenone (**3b**) reacted under similar mild conditions as described above readily with **10** yielding only a single product (TLC), which was isolated in high yield as yellow crystals. Elemental analysis and MS data confirmed the presence of a 1:1 acylation product **11d**. In its ^{1}H NMR, characteristic signals for the NH proton at 12.79 ppm, and the methine proton at 6.03 ppm were detected. The ^{13}C NMR signals at 189.9 ppm (C=O) and at 86.9 ppm (CH=) gave further evidence for the structure of an enaminone. Analogously, pinacolone (**3j**), cyclopropyl methyl ketone (**3k**) and acetone (**3l**) could successfully be transformed into the corresponding enaminone **11** (Scheme 7).

Based on the acylation reaction of aryl methyl ketones **3** with bis-imidoyl chlorides **4**, a short and efficient synthesis for a series of 1,6-diaryl-3,4-diarylaminohexa-2,4-diene-1,6-diones **2** was developed. The products **2** were isolated as yellow crystalline compounds in high yields. The chemical nature of the starting ketone can be varied in a wide range from substituted acetophenones to acetylthiophene (**3e**), 3-acetylpyridine (**3f**) and acetylferrocene **3g**. As a cyclic version of acetophenones, α-tetralone (**3i**) was successfully transformed with **4** into the corresponding enaminones of type **2**. Whereas most ketones gave only one main product, the use of 2-acetylpyridine (**3h**) additionally yielded the quinolizine derivative



Scheme 7

7. Its formation can easily be explained due to the existence of the electrophilic γ-carbon in the acylated pyridine ring. The synthetic concept is not only restricted to aryl methyl ketones. Pinacolone (**3j**) as well as cyclopropyl methyl ketone (**3k**) were readily converted into enaminones **2**. Monoimidoyl chlorides such as **10** showed the same reactivity. The reaction is exemplified with four different ketones giving the corresponding products **11** in high yields.

The reagents described in the following section were purchased from commercial sources and were used directly unless otherwise stated in the text. All solvents were of reagent grade and were dried according to common practice and were distilled prior to use. The *N*,*N*′-bis-(4-methoxyphenyl)oxaldiimidoyl chloride (**4e**) was synthesized according to literature.[4a] Reactions were monitored by TLC, carried out on 0.2 mm Merck silica gel plates (60 F_{254}). The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 250 and 400 spectrometers; shifts are relative to the signals of the solvent. Melting points were measured with a Galen III apparatus (Boëtius system) or with the Kofler apparatus and are uncorrected.

Bis-imidoyl Chlorides 4; General Procedure
To a solution of the corresponding aniline (0.5 mol) in toluene (400 mL) was added oxalyl chloride (33.0 g, 0.26 mol) over 10 min. A slurry of **5** was formed, and the mixture was stirred for 20 min at r.t. To the slurry PCl_5 (105 g, 0.505 mol) was added. The mixture was refluxed until no further HCl evolved. The dark yellow mixture was concentrated in vacuo to dryness and the crude product was recrystallized from toluene–*n*-heptane.

Bis-imidoyl Chloride 4a
Yield: 82%; yellow crystals; mp 115 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.53–7.44 (m, 4 H), 7.33–7.27 (m, 2 H), 7.16–7.13 (m, 4 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 145.8, 138.7, 129.0, 127.0, 120.4.

Bis-imidoyl Chloride 4b
Yield: 93%; yellow crystals; mp 111 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8 Hz, 4 H), 6.99 (d, *J* = 8 Hz, 4 H), 2.30 (s, 6 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 143.0, 137.8, 136.8, 129.5, 120.9, 21.1.

Bis-imidoyl Chloride 4c
Yield: 81%; yellow crystals; mp 191 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8 Hz, 4 H), 7.02 (d, *J* = 8 Hz, 4 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 144.4, 139.1, 132.2, 122.3, 120.4.

Oxanilide 5d
Yield: 89%; white crystals; mp 184 °C (toluene–*n*-heptane).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.51 (s, 2 H, NH), 8.53 (s, 6 H), 4.37 (t, *J* = 7 Hz, 8 H, OCH_2), 1.81–0.86 (m, 60 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 165.1 (C=O), 157.4, 136.5, 132.2, 127.6, 124.6, 65.9 (OCH_2), 31.8, 29.2, 28.6, 26.0, 22.6, 14.1.

MS (EI): *m*/*z* (%) = 864 (1, [M^+]), 405 (30), 293 (40), 43 (80, [$C_7H_7^+$]).

Anal. Calcd for $C_{50}H_{76}N_2O_{10}$: C, 69.41; H, 8.85; N, 3.24. Found: C, 69.34; H, 8.87; N, 3.10.

Bis-imidoyl Chloride 4d
Yield: 94%; yellow oil.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.99 (s, 2 H), 7.95 (s, 4 H), 4.37 (t, *J* = 7 Hz, 8 H, OCH_2), 1.81–0.86 (m, 60 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 165.1 (C=O), 146.0, 132.2, 132.1, 126.0, 125.3, 65.8 (OCH_2), 31.8, 29.2, 28.6, 26.0, 22.6, 14.0.

MS (EI): *m*/*z* (%) = 902 (2, [M^+]), 450 (10), 320 (10), 69 (80), 43 (100).

1,6-Diaryl/alkyl-3,4-diarylaminohexa-2,4-diene-1,6-diones 2; General Procedure
A solution of the corresponding aryl/alkyl ketone **3** (12 mmol) in anhyd THF (50 mL) was cooled down to –30 °C and *t*-BuOK (2.7 g, 24 mmol) was added. To the solution was added the corresponding bis-arylimidoyl chloride **4** (6 mmol). The deep red mixture was stirred at 10 °C for 30 min. The mixture was acidified by addition of HCl to pH 7 and then diluted with H_2O (500 mL). The yellow precipitate was collected by filtration, washed with Et_2O (20 mL) and dried. Recrystallization from DMF gave pure derivatives of type **2**. The following purification was employed for **2h**, **2k**, **2m**–**w**: The crude product was dissolved in $CHCl_3$ (100 mL) and the solution was dried (Na_2SO_4) and filtered over a short column of SiO_2. After removing the solvent in vacuo, the product was purified by column chromatography on silica gel ($CHCl_3$–*n*-heptane) or by recrystallization from $CHCl_3$–*n*-heptane (Table 1).

1,6-Diphenyl-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2a)
Yield: 83%; yellow crystals; mp 232 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.40 (s, 2 H, NH), 8.00 (m, 4 H, CH_{phenyl}), 7.57 (m, 4 H, CH_{phenyl}), 7.51 (m, 2 H, CH_{phenyl}), 7.03 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 6.81 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 6.41 (s, 2 H, =CH), 2.24 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 189.9 (C=O), 154.5, 139.3, 135.9, 134.8, 132.8, 129.8, 129.0, 127.8, 122.0, 96.1, 20.8.

Anal. Calcd for $C_{32}H_{28}N_2O_2$: C, 81.33; H, 5.97; N, 5.93. Found: C, 81.12; H, 5.95; N, 5.97.

1,6-Ditolyl-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2b)
Yield: 91%; yellow crystals; mp 242 °C.

IR (ATR): 3025, 2921, 1585, 1550, 1512, 1465, 1253, 1049, 772, 689 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.45 (s, 2 H, NH), 7.89 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 7.30 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 7.01 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 6.79 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 6.41 (s, 2 H, =CH), 2.37 (s, 6 H, CH_3), 2.20 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 189.7 (C=O), 162.5 (C-1), 154.3, 136.7, 136.0, 134.6, 129.8, 129.6, 127.9, 121.8, 96.0 (CH), 21.5, 20.8.

MS (EI): *m*/*z* (%) = 500 (1, [M^+]), 482 (5, [M – H_2O^+]), 381 (90), 119 (100, [$C_8H_7O^+$]).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 396 nm (3.9).

Anal. Calcd for $C_{34}H_{32}N_2O_2$: C, 81.57; H, 6.44; N, 5.66. Found: C, 81.28; H, 6.68; N, 5.73.

1,6-Diphenyl-3,4-diphenylaminohexa-2,4-diene-1,6-dione (2c)
Yield: 85%; yellow crystals; mp 218 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.44 (s, 2 H, NH), 8.03–6.89 (m, 20 H, CH_{phenyl}), 6.48 (s, 2 H, =CH).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 190.2 (C=O), 154.2 (C-1), 139.3, 138.4, 132.4, 129.8, 129.3, 127.8, 125.3, 121.9, 96.7 (CH).

Anal. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 80.95; H, 5.48; N, 6.37.

1,6-Ditolyl-3,4-diphenylaminohexa-2,4-diene-1,6-dione (2d)
Yield: 87%; yellow crystals; mp 240 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.43 (s, 2 H, NH), 7.91 (d, J = 8 Hz, 4 H, CH_{arom}), 7.37–6.88 (m, 14 H, CH_{arom}), 6.43 (s, 2 H, =CH), 2.39 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 190.0 (C=O), 153.9 (C-1), 142.7, 138.5, 136.7, 129.8, 129.6, 129.3, 127.9, 121.8, 96.6, 21.5.

Anal. Calcd for $C_{32}H_{28}N_2O_2$: C, 81.33; H, 5.97; N, 5.93. Found: C, 81.38; H, 6.96; N, 5.88.

1,6-Bis(4-bromophenyl)-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2e)
Yield: 90%; yellow crystals; mp 254 °C.

IR (ATR): 3024, 2923, 1583, 1560, 1513, 1461, 1249, 1070, 1005, 778 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.43 (s, 2 H, NH), 7.97 (d, J = 8 Hz, 4 H, CH_{arom}), 7.70 (d, J = 8 Hz, 4 H, CH_{arom}), 7.00 (d, J = 8 Hz, 4 H, CH_{arom}), 6.73 (d, J = 8 Hz, 4 H, CH_{tolyl}), 6.47 (s, 2 H, =CH), 2.21 (s, 6 H, CH_3).

MS (EI): m/z (%) = 632 (2), 630 (5), 628 (2, [M$^+$]), 447 (50), 445 (100), 315 (10), 183 (50).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 400 nm (3.7).

Anal. Calcd for $C_{34}H_{26}Br_2N_2O_2$: C, 60.97; H, 4.16; Br, 25.35; N, 4.44. Found: C, 61.00; H, 4.16; Br, 25.01; N, 4.08.

1,6-Bis(4-methoxyphenyl)-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2f)
Yield: 83%; yellow crystals; mp 236 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.44 (s, 2 H, NH), 8.01 (d, J = 8 Hz, 4 H, CH_{arom}), 7.02 (d, J = 8 Hz, 4 H, CH_{arom}), 6.98 (d, J = 8 Hz, 4 H, CH_{arom}), 6.74 (d, J = 8 Hz, 4 H, CH_{tolyl}), 6.40 (s, 2 H, =CH), 3.83 (s, 6 H, OCH_3), 2.20 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 188.8 (C=O), 162.8, 153.9, 135.9, 134.3, 131.7, 130.0, 129.7, 121.6, 114.3, 95.6, 55.9 (OCH_3), 20.8 (CH_3).

MS (EI): m/z (%) = 532 (1, [M$^+$]), 514 (10, [M – H_2O^+]), 397 (100), 135 (100, [$C_8H_7O_2^+$]).

Anal. Calcd for $C_{34}H_{32}N_2O_4$: C, 78.67; H, 6.06; N, 5.26. Found: C, 78.40; H, 5.94; N, 5.22.

1,6-Bis(4-methoxyphenyl)-3,4-bis(4-bromophenylamino)hexa-2,4-diene-1,6-dione (2g)
Yield: 86%; yellow crystals; mp 238 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.23 (s, 2 H, NH), 8.03 (d, J = 8 Hz, 4 H, CH_{arom}), 7.36 (d, J = 8 Hz, 4 H, CH_{arom}), 7.04 (d, J = 8 Hz, 4 H, CH_{arom}), 6.81 (d, J = 8 Hz, 4 H, CH_{arom}), 6.51 (s, 2 H, =CH), 3.86 (s, 6 H, OCH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 189.4 (C=O), 163.2 (C-1), 152.8, 138.0, 132.1, 131.8, 130.2, 123.6, 117.1, 114.5, 97.5 (CH), 56.0 (OCH_3).

MS (EI): m/z (%) = 664 (1), 662 (2), 660 (1, [M$^+$]), 646 (2), 644 (5), 642 (2, [M – H_2O^+]), 529 (50), 527 (100), 625 (50, [M – $C_8H_7O_2^+$]), 173 (70), 135 (90, [$C_8H_7O_2^+$]).

Anal. Calcd for $C_{32}H_{26}Br_2N_2O_4$: C, 58.03; H, 3.96; N, 4.23. Found: C, 58.02; H, 3.92; N, 4.18.

1,6-Ditolyl-3,4-bis(3,5-dicarboxyoctylphenylamino)hexa-2,4-diene-1,6-dione (2h)
Yield: 63%; yellow oil.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 12.36 (s, 2 H, NH), 7.94 (d, J = 8 Hz, 4 H, CH_{arom}), 7.52 (s, 4 H, CH_{arom}), 7.31 (d, J = 8 Hz, 4 H, CH_{arom}), 7.26 (s, 2 H, CH_{arom}), 6.54 (s, 2 H, =CH), 4.19 (t, J = 7 Hz, 8 H, CO_2CH_2), 2.45 (s, 6 H, CH_3), 1.62–0.86 (m, 60 H, CH_2).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 190.7 (C=O), 164.7 (C=O), 153.0, 143.1, 138.4, 136.1, 131.7, 129.3, 127.7, 127.0, 126.5, 97.2, 65.6 (OCH_2), 31.8, 29.1, 28.6, 28.4, 25.8, 22.6, 21.6 (Ar*C*H_3), 14.1 (CH_3).

MS (EI): m/z (%) = 1096 (1, [M$^+$]), 1012 (10), 978 (100), 405 (30), 119 (60, [$C_7H_7^+$]).

MS (ESI, MeOH–$CHCl_3$): m/z = 1119 (100%, [M + Na$^+$]).

Anal. Calcd for $C_{68}H_{92}N_2O_{10}$: C, 74.42; H, 8.45; N, 2.55. Found: C, 74.01; H, 8.29; N, 2.45.

1,6-Bis(2-thienyl)-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2i)
Yield: 81%; yellow crystals; mp 256 °C.

IR (ATR): 3076, 3020, 2917, 1590, 1553, 1512, 1461, 1409, 1304, 1260, 1064, 789, 766, 719 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.04 (s, 2 H, NH), 8.01 (d, J = 4 Hz, 2 H, $CH_{thienyl}$), 7.90 (d, J = 4 Hz, 2 H, $CH_{thienyl}$), 7.19 (m, 2 H, $CH_{thienyl}$), 6.99 (d, J = 8 Hz, 4 H, CH_{tolyl}), 6.74 (d, J = 8 Hz, 4 H, CH_{tolyl}), 6.38 (s, 2 H, =CH), 2.21 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 183.1 (C=O), 153.8, 146.4, 135.8, 134.6, 133.5, 130.9, 129.8, 129.0, 121.8, 96.1, 20.8 (CH_3).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 403 nm (4.1).

Anal. Calcd for $C_{28}H_{24}N_2O_2S_2$: C, 69.35; H, 4.99; N, 5.78; S, 13.23. Found: C, 69.08; H, 5.03; N, 5.97; S, 13.09.

1,6-Bis(3-pyridyl)-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2j)
Yield: 82%; yellow crystals; mp 223 °C.

IR (ATR): 3025, 2917, 1584, 1547, 1515, 1462, 1258, 1016, 780, 685 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.42 (s, 2 H, NH), 9.20 (s, 2 H, $CH_{pyridyl}$), 8.74 (m, 2 H, $CH_{pyridyl}$), 8.36 (m, 2 H, $CH_{pyridyl}$), 7.53 (m, 2 H, $CH_{pyridyl}$), 7.03 (d, J = 8 Hz, 4 H, CH_{tolyl}), 6.81 (d, J = 8 Hz, 4 H, CH_{tolyl}), 6.52 (s, 2 H, =CH), 2.25 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 188.3 (C=O), 154.9, 152.8, 149.1, 135.5, 135.3, 135.1, 134.3, 129.8, 124.1, 122.2, 96.3 (CH), 20.8 (CH_3).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 397 nm (4.5).

Anal. Calcd for $C_{30}H_{26}N_4O_2$: C, 75.93; H, 5.52; N, 11.81. Found: C, 75.93; H, 5.53; N, 11.85.

1,6-Diferrocenyl-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2k)
Yield: 91%; red crystals; mp >250 °C (dec.)

IR (ATR): 3078, 2917, 2859, 1603, 1559, 1519, 1475, 1264, 1094, 816, 798 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): δ = 12.21 (s, 2 H, NH), 6.99 (d, J = 8 Hz, 4 H, CH_{tolyl}), 6.88 (d, J = 8 Hz, 4 H, CH_{tolyl}), 5.70 (s, 2 H, =CH), 4.79 (s, 4 H, C_5H_5), 4.47 (s, 4 H, C_5H_5), 4.16 (s, 10 H, C_5H_5), 2.25 (s, 6 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 194.5 (C=O), 152.1, 136.1, 134.1, 129.4, 121.3, 96.8 (CH), 81.6 (1-C_5H_5), 71.7 (C_5H_5), 69.9 (C_5H_5), 68.7 (C_5H_5), 20.8.

MS (EI): *m/z* (%) = 690 (20), 689 (30), 688 (80), 687 (30, [M^+]), 583 (20), 475 (100), 228 (20).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 389 (4.5), 487 nm (3.8).

Anal. Calcd for $C_{40}H_{36}Fe_2N_2O_2$: C, 69.79; H, 5.27; N, 3.83. Found: C, 69.35; H, 5.15; N, 3.83.

1,6-Ditolyl-3,4-bis(4-bromophenylamino)hexa-2,4-diene-1,6-dione (2l)
Yield: 82%; yellow crystals; mp 254 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.24 (s, 2 H, NH), 7.94 (d, *J* = 8 Hz, 4 H, CH_{arom}), 7.37 (d, *J* = 8 Hz, 4 H, CH_{arom}), 7.32 (d, *J* = 8 Hz, 4 H, CH_{arom}), 6.83 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 6.52 (s, 2 H, =CH), 2.39 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 189.5 (C=O), 162.3, 153.3, 136.9, 136.1, 132.2, 129.7, 128.1, 127.9, 123.7, 97.6, 21.5.

MS (EI): *m/z* (%) = 632 (1), 630 (3), 628 (1, [M^+]), 614 (5), 612 (10), 610 (5, [M – H_2O^+]), 513 (50), 511 (100), 509 (50, [M – $C_8H_7O^+$]), 173 (90), 119 (95, [$C_8H_7O^+$]).

Anal. Calcd for $C_{32}H_{26}Br_2N_2O_2$: C, 60.97; H, 4.16; N, 4.44. Found: C, 60.90; H, 4.17; N, 4.47.

1,6-Bis(2-pyridyl)-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2m)
Yield: 69%; yellow crystals; mp 233 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.39 (s, 2 H, NH), 8.71–6.62 (m, 16 H, CH_{arom}), 6.07 (s, 2 H, =CH), 2.24 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 188.5 (C=O), 154.9, 149.5, 138.1, 138.0, 136.8, 135.5, 133.7, 129.8, 123.5, 122.9, 94.9, 21.0.

MS (EI): *m/z* (%) = 474 (60, [M^+]), 368 (100), 354 (60), 91 (50, [$C_7H_7^+$]), 78 (80).

Anal. Calcd for $C_{30}H_{26}N_4O_2$: C, 75.93; H, 5.52; N, 11.81. Found: C, 75.57; H, 5.48; N, 11.72.

Quinolizine Derivative 7
Yield: 8%; red crystals; mp 193 °C.

IR (ATR): 3245, 2994, 1584, 1515, 1275, 1244, 1071, 1073, 812, 795 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.66 (m, 1 H, =CH), 8.11–7.78 (m, 4 H, CH_{arom}), 7.41–7.11 (m, 9 H, CH_{arom}), 6.84 (d, *J* = 8 Hz, 2 H, =CH), 6.25 (s, 1 H, =CH), 2.38 (s, 6 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 188.5 (C=O), 175.1 (C=O), 156.1, 148.5, 154.9, 148.5, 142.9, 136.8, 136.5, 135.4, 135.1, 134.3, 130.9, 130.6, 130.3, 129.4, 125.8, 123.8, 122.0, 119.8, 119.5, 112.4, 109.1, 100.6, 21.0.

MS (FAB, NBA): *m/z* (%) = 473 (40, [M + H^+]), 356 (20), 241 (60).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 444 (4.2), 516 nm (4.3).

Anal. Calcd for $C_{30}H_{24}N_4O_2$: C, 76.25; H, 5.12; N, 11.86. Found: C, 75.99; H, 5.07; N, 11.65.

1,6-Bis(2-pyridyl)-3,4-bis(4-bromophenyl)aminohexa-2,4-diene-1,6-dione (2n)
Yield: 74%; yellow crystals; mp 237 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 343 K): δ = 12.35 (s, 2 H, NH), 8.65–6.83 (m, 16 H, CH_{arom}), 6.66 (s, 2 H, =CH).

^{13}C NMR (100 MHz, DMSO-d_6, 343 K): δ = 189.6 (C=O), 154.2, 148.9, 140.2, 137.1, 137.0, 134.8, 132.2, 131.8, 127.0, 112.5, 96.3.

Anal. Calcd for $C_{28}H_{20}Br_2N_4O_2$: C, 55.65; H, 3.34; N, 9.27. Found: C, 55.66; H, 3.32; N, 9.13.

1,6-Bis(4-methoxyphenyl)-3,4-bis(4-methoxyphenyl)aminohexa-2,4-diene-1,6-dione (2o)
Yield: 89%; yellow crystals; mp 196 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 12.40 (s, 2 H, NH), 7.99 (d, *J* = 8 Hz, 4 H, CH_{arom}), 6.98 (d, *J* = 8 Hz, 4 H, CH_{arom}), 6.72 (d, *J* = 8 Hz, 4 H, CH_{arom}), 6.65 (d, *J* = 8 Hz, 4 H, CH_{arom}), 6.29 (s, 2 H, =CH), 3.90 (s, 6 H, OCH_3), 3.76 (s, 6 H, OCH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 189.1 (C=O), 162.6, 157.0, 154.7, 132.1, 131.3, 129.3, 123.3, 114.4, 113.8, 94.7, 55.44 (OCH_3), 55.36 (OCH_3).

Anal. Calcd for $C_{34}H_{32}N_2O_6$: C, 72.33; H, 5.71; N, 4.96. Found: C, 72.54; H, 5.62; N, 4.81.

Bis[1-(anilinomethylene)-2-oxotetrahydronaphthalene] (2p)
Yield: 83%; yellow crystals; mp 198 °C.

^{1}H NMR (250 MHz, acetone-d_6): δ = 13.70 (s, 2 H, NH), 8.00–7.97 (m, 2 H, =CH), 7.41–7.12 (m, 16 H, CH_{arom}), 2.72–2.43 (m, 8 H, CH_2).

^{13}C NMR (63 MHz, acetone-d_6): δ = 187.6 (C=O), 148.1, 142.5, 138.6, 134.7, 132.6, 132.0, 128.3, 127.3, 127.0, 122.9, 117.0, 104.2, 28.5, 25.3.

MS (EI): *m/z* (%) = 496 (80, [M^+]), 403 (90), 376 (90), 351 (90), 248 (80), 230 (80), 115 (90), 77 (100, [$C_6H_5^+$]).

Anal. Calcd for $C_{34}H_{28}N_2O_2$: C, 82.23; H, 5.68; N, 5.64. Found: C, 82.22; H, 5.81; N, 5.64.

Bis[1-(4-tolylaminomethylene)-2-oxotetrahydronaphthalene] (2q)
Yield: 90%; yellow crystals; mp 204 °C.

IR (ATR): 3026, 2969, 2836, 1585, 1555, 1513, 1454, 1299, 1233, 1161, 807, 736 cm^{-1}.

^{1}H NMR (250 MHz, DMSO-d_6): δ = 13.56 (s, 2 H, NH), 7.88 (m, 2 H, CH_{arom}), 7.41–7.32 (m, 4 H, CH_{arom}), 7.19 (m, 2 H, CH_{arom}), 7.08 (m, 8 H, CH_{tolyl}), 2.75–2.60 (m, 4 H, CH_2), 2.45–2.25 (m, 4 H, CH_2), 2.18 (s, 6 H, CH_3).

^{13}C NMR (63 MHz, DMSO-d_6): δ = 186.9 (C=O), 149.6, 142.2, 136.5, 134.8, 134.4, 132.6, 130.3, 128.2, 127.2, 126.7, 120.8, 102.4, 28.4, 25.0, 20.7.

MS (EI): *m/z* (%) = 524 (10, [M^+]), 418 (90), 262 (100), 91 (80, [$C_7H_7^+$]).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 416 nm (4.2).

Anal. Calcd for $C_{36}H_{32}N_2O_2$: C, 82.41; H, 6.15; N, 5.34. Found: C, 82.26; H, 6.15; N, 5.39.

Bis[1-(4-bromophenylaminomethylene)-2-oxotetrahydronaphthalene] (2r)
Yield: 76%; yellow crystals; mp 246 °C.

^{1}H NMR (250 MHz, DMSO-d_6): δ = 13.37 (s, 2 H, NH), 7.94 (m, 2 H, CH_{arom}), 7.63–7.40 (m, 4 H, CH_{arom}), 7.38–7.35 (m, 4 H, CH_{arom}), 7.24 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.11 (d, *J* = 8 Hz, 4 H, CH_{arom}), 2.78–2.72 (m, 2 H, CH_2), 2.63–2.50 (m, 6 H, CH_2).

^{13}C NMR (63 MHz, DMSO-d_6): δ = 187.6 (C=O), 148.1 (C-1), 142.5, 138.6, 134.7, 132.6, 132.0, 128.3, 127.3, 127.0, 122.9, 117.0, 104.2, 28.5, 25.3.

MS (EI): *m/z* (%) = 656 (5), 654 (10), 652 (5, [M^+]), 482 (100), 326 (100).

Anal. Calcd for $C_{34}H_{26}Br_2N_2O_2$: C, 62.40; H, 4.00; N, 4.28. Found: C, 62.26; H, 4.02; N, 4.51.

1,6-Di(*tert*-butyl)-3,4-diphenylaminohexa-2,4-diene-1,6-dione (2s)
Yield: 83%; yellow crystals; mp 167 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 12.00 (s, 2 H, NH), 7.12–6.95 (m, 6 H, CH_{arom}), 6.78–6.75 (m, 4 H, CH_{arom}), 5.60 (s, 2 H, =CH), 1.16 (s, 18 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 206.8 (C=O), 153.1, 138.3, 128.6, 124.4, 121.4, 95.1, 42.5, 27.3 (CH_3).

MS (EI): *m*/*z* (%) = 404 (1, [M$^+$]), 319 (100), 263 (40), 77 (15), 57 (25).

Anal. Calcd for $C_{26}H_{32}N_2O_2$: C, 77.19; H, 7.97; N, 6.92. Found: C, 77.10; H, 8.03; N, 6.89.

1,6-Di(*tert*-butyl)-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2t)
Yield: 87%; yellow crystals; mp 146 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 11.98 (s, 2 H, NH), 6.90 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 6.67 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 5.55 (s, 2 H, =CH), 2.25 (s, 6 H, ArC*H*$_3$), 1.15 (s, 18 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 206.6 (C=O), 153.6, 135.8, 134.1, 129.2, 121.5, 94.6, 42.3, 27.4 [C(*C*H$_3$)$_3$], 20.8 (Ar*C*H$_3$).

MS (EI): *m*/*z* = 433 (1, [M + H$^+$]), 347 (80, [$C_{23}H_{27}N_2O^+$]), 291 (20), 216 (10), 174 (10), 91 (15), 57 (100).

Anal. Calcd for $C_{28}H_{36}N_2O_2$: C, 77.74; H, 8.39; N, 6.48. Found: C, 77.53; H, 8.56; N, 6.36.

1,6-Di(cyclopropyl)-3,4-diphenylaminohexa-2,4-diene-1,6-dione (2u)
Yield: 78%; yellow crystals; mp 186 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 11.82 (s, 2 H, NH), 7.44–6.64 (m, 10 H, CH_{phenyl}), 5.74 (s, 2 H, =CH), 1.94–1.84 (m, 2 H, $CH_{c\text{-}Pr}$), 1.09–0.90 (m, 8 H, CH_2).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 200.1 (C=O), 151.6, 138.1, 128.6, 124.3, 121.3, 99.1 (CH), 21.2, 10.4.

MS (EI): *m*/*z* (%) = 372 (1, [M$^+$]), 303 (100), 186 (20, [M$^+$/2]).

Anal. Calcd for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found C, 77.12; H, 6.77; N, 7.53.

1,6-Di(cyclopropyl)-3,4-ditolylaminohexa-2,4-diene-1,6-dione (2v)
Yield: 72%; yellow crystals; mp 181 °C.

IR (ATR): 3316, 3002, 2919, 1592, 1563, 1514, 1464, 1383, 1242, 1123, 1025, 801 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 11.80 (s, 2 H, NH), 7.20 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 6.86 (d, *J* = 8 Hz, 4 H, CH_{tolyl}), 5.67 (s, 2 H, =CH), 2.24 (s, 6 H, ArC*H*$_3$), 1.91–1.81 (m, 2 H, $CH_{c\text{-}Pr}$), 1.07–0.88 (m, 8 H, CH_2).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 199.8 (C=O), 152.0, 135.6, 134.1, 129.1, 121.3, 98.6 (CH), 21.1, 20.8, 10.2.

MS (EI): *m*/*z* (%) = 400 (1, [M$^+$]), 357 (10), 307 (100), 200 (40, [M$^+$/2]).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 369 nm (4.3).

Anal. Calcd for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99. Found: C, 77.70; H, 7.14; N, 6.95.

1-Cyclopropyl-2-(5-methyl-3-tolyliminoindoline-2-ylidene)ethanone (8b)
Yield: 5%; red crystals; mp 152 °C.

IR (ATR): 3344, 3304, 3011, 2922, 1653, 1605, 1570, 1409, 1364, 1183, 1111, 914, 824 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ (major isomer) = 10.33 (s, 1 H, NH), 7.57–6.70 (m, 7 H, CH_{arom}), 6.44 (s, 1 H, =CH), 2.41 (s, 3 H, CH_3), 2.04 (s, 3 H, ArC*H*$_3$), 1.71–1.62 (m, 1 H, $CH_{cyclopropyl}$), 1.13–0.91 (m, 4 H, CH_2).

^{13}C NMR (63 MHz, $CDCl_3$): δ (major isomer) = 201.4 (C=O), 159.9, 149.4, 148.3, 147.5, 134.3, 130.7, 129.9, 129.7, 126.9, 119.8, 118.2, 117.6, 110.7, 94.7, 21.9, 20.8, 10.6.

MS (EI): *m*/*z* = 316 (80, [M$^+$]), 247 (100), 231 (40), 91 (30, [$C_7H_7^+$]).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 487 nm (4.0).

Anal. Calcd for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.48; H, 6.56; N, 8.82.

1,6-Di(Cyclopropyl)-3,4-bis(4-methoxyphenyl)aminohexa-2,4-diene-1,6-dione (2w)
Yield: 67%; yellow crystals; mp 162 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 11.75 (s, 2 H, NH), 6.60 (m, 8 H, CH_{tolyl}), 5.69 (s, 2 H, =CH), 3.74 (s, 6 H, OCH_3), 1.91–1.84 (m, 2 H, $CH_{c\text{-}Pr}$), 0.91–0.87 (m, 8 H, CH_2).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 199.7 (C=O), 156.8, 152.4, 131.4, 123.0, 113.8, 98.3, 55.4 (OCH_3), 21.1, 10.1.

MS (EI): *m*/*z* (%) = 432 (1, [M$^+$]), 416 (1), 363 (100), 216 (40, [M$^+$/2]).

Anal. Calcd for $C_{26}H_{28}N_2O_4$: C, 72.20; H, 6.53; N, 6.48. Found: C, 72.15; H, 6.53; N, 6.36.

1-Cyclopropyl-2-(5-methyl-3-tolyliminoindoline-2-ylidene)ethanone (8c)
Yield: 7%; red crystals; mp 146 °C.

IR (ATR): 3348, 3290, 3007, 2933, 1651, 1606, 1567, 1473, 1367, 1285, 1184, 1113, 1026, 808 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ (major isomer) = 10.29 (s, 1 H, NH), 7.74–6.33 (m, 7 H, CH_{arom}), 5.99 (s, 1 H, =CH), 3.93 (s, 3 H), 3.49 (s, 3 H), 1.70–1.65 (m, 1 H, $CH_{c\text{-}Pr}$), 1.12–0.85 (m, 4 H, CH_2).

^{13}C NMR (63 MHz, $CDCl_3$): δ (major isomer) = 201.2 (C=O), 157.3, 154.1, 149.7, 143.8, 124.2, 122.5, 121.2, 120.0 117.9, 114.3, 113.3, 111.4, 94.6, 55.6, 55.5, 21.8, 10.6.

MS (EI): *m*/*z* (%) = 348 (10, [M$^+$]), 255 (40), 134 (80), 122 (100).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 514 nm (3.8).

Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.11; H, 5.83; N, 8.28.

***N*-Tolyl-4-trifluoromethylbenzamide (9)**
To a solution of 4-toluidine (10.8 g, 101 mmol) in toluene (100 mL) and Et_3N (10.2 g, 101 mmol) was added 4-trifluoromethylbenzoyl chloride (21.4 g, 102 mmol) over 10 min. The mixture was stirred for 20 min at r.t. and the solvent was removed in vacuo. The precipitate was treated with H_2O, collected by filtration, and dried over $CaCl_2$. The crude product was recrystallized from $CHCl_3$–*n*-heptane to yield pure **9**; yield: 73%; white crystals; mp 238 °C.

^{1}H NMR (250 MHz, DMSO-d_6): δ = 10.37 (s, 1 H, NH), 8.12 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.89 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.64 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.16 (d, *J* = 8 Hz, 2 H, CH_{arom}), 2.27 (s, 3 H, CH_3).

^{13}C NMR (63 MHz, DMSO-d_6): δ = 164.6, 139.3, 136.7, 133.5, 133.1 (q, ^2J = 32 Hz, CF_3), 129.5, 128.9, 125.7 (q, ^3J = 4 Hz), 123.1 (q, ^1J = 273 Hz), 120.9, 21.0 (Ar*C*H$_3$).

MS (EI): *m*/*z* (%) = 279 (5, [M$^+$]), 173 (70), 145 (100, [$C_7H_5F_3^+$]), 77 (50).

Anal. Calcd for $C_{15}H_{12}F_3NO$: C, 64.51; H, 4.33; N, 5.02. Found: C, 64.37; H, 4.52; N, 5.00.

N-Tolyl-4-trifluoromethylbenzimidoyl Chloride (10)

Compound **9** (10.0 g, 36 mmol) was suspended in toluene (50 mL) and PCl_5 (7.7 g, 37 mmol) was added. The mixture was heated under reflux until no further HCl evolved. After removal of the solvent in vacuo, the crude product was recrystallized from *n*-heptane; yield: 93%; white crystals; mp 107 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.74 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.25 (d, *J* = 8 Hz, 2 H, CH_{arom}), 6.99 (d, *J* = 8 Hz, 2 H, CH_{arom}), 2.40 (s, 3 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 144.4, 141.0, 138.9, 135.4, 133.4 (q, ^2J = 32 Hz), 129.7, 129.5, 125.4 (q, ^3J = 4 Hz), 123.7 (q, ^1J = 273 Hz, CF_3), 120.6, 21.0 (CH_3).

MS (EI): *m*/*z* (%) = 299 (109), 297 (20, [M^+]), 262 (90), 91 (100, [$C_7H_7^+$]).

Anal. Calcd for $C_{15}H_{11}ClF_3N$: C, 60.52; H, 3.72; N, 4.70. Found: C, 60.40; H, 3.79; N, 4.83.

1-Aryl/alkyl-3-tolylamino-3-(4-trifluoromethylphenyl)prop-2-ene-1-ones 11; General Procedure

A solution of the corresponding aryl/alkyl ketone **3** (8 mmol) in anhyd THF (30 mL) was cooled down to –30 °C and *t*-BuOK (1.8 g, 16 mmol) was added. To this mixture was added **10** (2.4 g, 8 mmol). The deep red mixture was stirred at 10 °C for 30 min. The mixture was acidified to pH 7 and the solvent was removed in vacuo. The yellow residue was dissolved in $CHCl_3$ (100 mL) and the solution was dried (Na_2SO_4), and filtered over a short column of SiO_2. After removal of the solvent, the crude product was purified by column chromatography on silica gel ($CHCl_3$–*n*-heptane) or alternatively, was purified by recrystallization from $CHCl_3$–*n*-heptane.

4-Tolylamino-4-(4-trifluoromethylphenyl)but-3-ene-2-one (11a)

Yield: 69%; yellow crystals; mp 42–46 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 13.08 (s, 1 H, NH), 8.00 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.68 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.19 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.08 (d, *J* = 8 Hz, 2 H, CH_{arom}), 5.86 (s, 1 H, =CH), 2.37 (s, 3 H, ArCH_3), 2.13 (s, 3 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 186.6 (C=O), 163.7, 143.3, 136.2, 135.6, 132.2 (q, ^2J = 32 Hz, CF_3), 129.8, 127.3, 125.3, 124.0 (q, ^1J = 273 Hz), 124.9, 93.9, 20.9, 20.3.

MS (EI): *m*/*z* (%) = 319 (60, [M^+]), 173 (50), 146 (100).

Anal. Calcd for $C_{18}H_{16}F_3NO$: C, 67.70; H, 5.05; N, 4.39. Found: C, 67.35; H, 5.01; N, 4.48.

1-Cyclopropyl-3-tolylamino-3-(4-trifluoromethylphenyl)prop-2-ene-1-one (11b)

Yield: 82%; yellow crystals; mp 125 °C.

IR (ATR): 3013, 2945, 2923, 2858, 1604, 1565, 1519, 1322, 1275, 1163, 1121, 1108, 1060, 851, 775 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 12.19 (s, 1 H, NH), 7.56 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.46 (d, *J* = 8 Hz, 2 H, CH_{arom}), 6.90 (d, *J* = 8 Hz, 2 H, CH_{arom}), 6.57 (d, *J* = 8 Hz, 2 H, CH_{arom}), 5.51 (s, 1 H, =CH), 2.22 (s, 3 H, ArCH_3), 1.91–1.81 (m, 1 H, $CH_{c\text{-}Pr}$), 1.13–0.87 (m, 4 H, CH_2).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 199.4 (C=O), 157.1, 139.5, 136.6, 133.8, 131.2 (q, ^2J = 32 Hz), 129.4, 128.7, 125.4 (q, ^3J = 4 Hz), 123.8 (q, ^1J = 273 Hz, CF_3), 123.6, 100.4 (CH), 21.0 (ArCH_3), 20.7, 10.0.

MS (EI): *m*/*z* (%) = 345 (70, [M^+]), 344 (30, [M – H^+]), 304 (70), 276 (100), 69 (40, [$C_4H_5O^+$]).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 361 nm (4.2).

Anal. Calcd for $C_{20}H_{18}F_3NO$: C, 69.56; H, 5.25; N, 4.06. Found: C, 69.55; H, 5.16; N, 4.06.

1-*tert*-Butyl-3-tolylamino-3-(4-trifluoromethylphenyl)prop-2-ene-1-one (11c)

Yield: 79%; yellow crystals; mp 114 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 12.36 (s, 1 H, NH), 7.56 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.44 (d, *J* = 8 Hz, 2 H, CH_{arom}), 6.90 (d, *J* = 8 Hz, 2 H, CH_{arom}), 6.58 (d, *J* = 8 Hz, 2 H, CH_{arom}), 5.52 (s, 1 H, =CH), 2.22 (s, 3 H, ArCH_3), 1.23 (s, 9 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 206.2 (C=O), 158.8, 139.9, 136.6, 133.8, 131.4 (q, ^2J = 32 Hz), 129.4, 128.7, 125.4, 123.1 (q, ^1J = 273 Hz, CF_3), 123.0, 96.0, 42.4, 27.6, 20.7 (ArCH_3).

MS (EI): *m*/*z* (%) = 361 (5, [M^+]), 304 (100, [$C_{17}H_{13}F_3NO^+$]), 41 (20, [$C_4H_5O^+$]).

Anal. Calcd for $C_{21}H_{22}F_3NO$: C, 69.79; H, 6.14; N, 3.88. Found: C, 69.61; H, 5.80; N, 3.74.

1-Tolyl-3-tolylamino-3-(4-trifluoromethylphenyl)prop-2-ene-1-one (11d)

Yield: 86%; yellow crystals; mp 105–106 °C.

IR (ATR): 3032, 2922, 1596, 1561, 1512, 1320, 1163, 1123, 1048, 861, 773 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 12.79 (s, 1 H, NH), 7.88 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.60 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.51 (d, *J* = 8 Hz, 2 H, CH_{arom}), 7.25 (d, *J* = 8 Hz, 2 H, CH_{arom}), 6.95 (d, *J* = 8 Hz, 2 H, CH_{arom}), 6.66 (d, *J* = 8 Hz, 2 H, CH_{arom}), 6.03 (s, 1 H, =CH), 2.42 (s, 3 H, ArCH_3), 2.25 (s, 3 H, ArCH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 189.6 (C=O), 159.6, 142.0, 139.8, 137.0, 136.5, 134.2, 131.4 (q, ^2J = 32 Hz), 129.5, 129.1, 128.8, 127.3, 125.5 (q, ^3J = 4 Hz), 123.8 (q, ^1J = 273 Hz, CF_3), 123.3, 96.9 (CH), 21.5 (ArCH_3), 20.8 (ArCH_3).

MS (EI): *m*/*z* (%) = 395 (40, [M^+]), 394 (40, [M – H^+]), 276 (100), 119 (100, [$C_8H_7O^+$]).

UV/vis ($CHCl_3$): λ_{max} (log ε) = 386 nm (4.3).

Anal. Calcd for $C_{24}H_{20}F_3NO$: C, 72.90; H, 5.10; N, 3.54. Found: C, 72.65; H, 5.13; N, 3.58.

Crystal Structure Determination of 2e and 7

The intensity data for the compound were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[9] The structure was solved by direct methods (SHELXS)[10] and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97).[11] For the amine groups on N1, N2, the methine groups on C2, C5 of **2e** and all hydrogen atoms of **7** without the methyl groups were located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically.[11] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.[12]

Crystal Data for 2e

$C_{32}H_{26}Br_2N_2O_2$, Mr = 630.37 $gmol^{-1}$, yellow prism, size 0.05 × 0.05 × 0.05 mm^3, monoclinic, space group C2/c, *a* = 21.4503(6), *b* = 12.0702(5), *c* = 21.6890(9) Å, β = 105.919(3)°, *V* = 5400.1(4) $Å^3$, *T* = –90 °C, *Z* = 8, ρ_{calcd} = 1.551 gcm^{-3}, μ (Mo-K_α) = 30.35 cm^{-1}, *F*(000) = 2544, 17887 reflections in *h*(–27/23), *k*(–15/15), *l*(–23/28), measured in the range 1.95° ≤ Θ ≤ 27.47°, completeness Θ_{max} = 99.4%, 6141 independent reflections, R_{int} = 0.066, 4205 reflections with $F_o > 4\sigma(F_o)$, 361 parameters, 0

restraints, $R1_{obs} = 0.0598$, $wR2_{obs} = 0.1458$, $R1_{all} = 0.0967$, $wR^2_{all} = 0.1645$, GOOF = 1.065, largest difference peak and hole: 1.980/–0.721 e Å^{-3}.

Crystal Data for 7

$C_{30}H_{24}N_4O_2$, Mr = 472.53 gmol^{-1}, red prism, size 0.04 ´ 0.04 ´ 0.04 mm^3, orthorhombic, space group Pbca, $a = 16.8170(6)$, $b = 14.9217(5)$, $c = 19.3258(6)$ Å, $V = 4849.6(3)$ Å^3, $T = –90$ °C, $Z = 8$, $\rho_{calcd} = 1.294$ gcm^{-3}, μ (Mo-K$_\alpha$) = 0.83 cm^{-1}, $F(000) = 1984$, 31431 reflections in h(–21/17), k(–19/19), l(–23/25), measured in the range $2.11° \le \Theta \le 27.48°$, completeness $\Theta_{max} = 99.9\%$, 5549 independent reflections, $R_{int} = 0.0994$, 3449 reflections with $F_o > 4\sigma(F_o)$, 399 parameters, 0 restraints, $R1_{obs} = 0.0535$, $wR2_{obs} = 0.1131$, $R1_{all} = 0.1069$, $wR^2_{all} = 0.1374$, GOOF = 0.950, largest difference peak and hole: 0.267/–0.204 e Å^{-3}.

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