SYNTHESIS OF COMPOUNDS WITH THE NOVEL 2,3,7-TRIAZAPHENALENE RING SYSTEM

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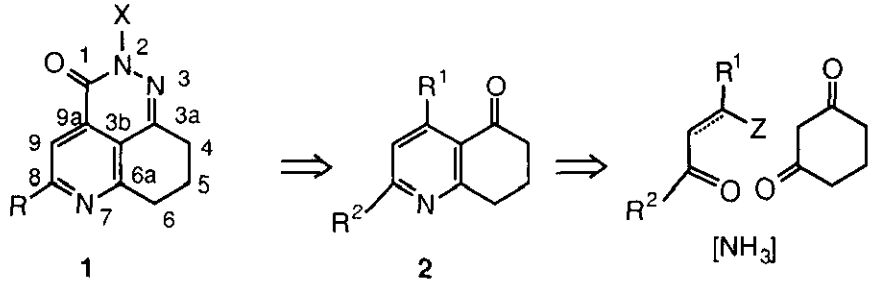
Abstract - The title compounds (**1a**) and (**1c-f**) were prepared from the new 5-oxo-5,6,7,8-tetrahydroquinolines (**2a**) and (**2c**,**d**), which were synthesized from cyclohexane-1,3-dione.

Introduction

In the course of the synthesis of some 5-oxo-5,6,7,8-tetrahydroquinolines (**2**) we became interested in their annulation to the 2,3,7-triazaphenalene ring system (cf. **1**) as a potential new pharmacophore.

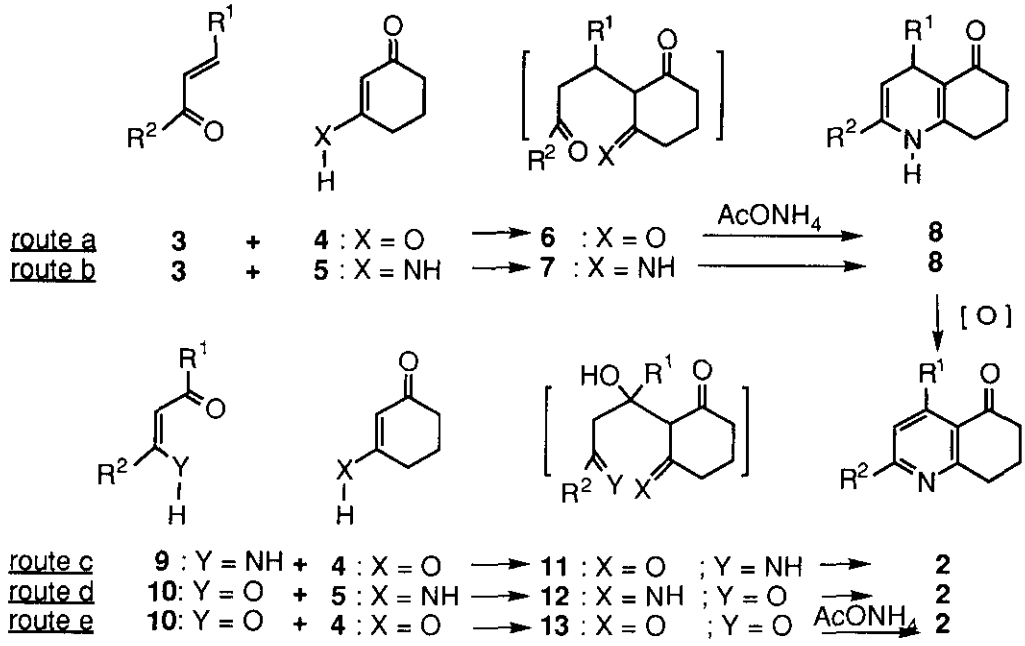


1 **2**

Scheme 1

For that purpose we prepared tetrahydroquinolines (**2**) in which R^1 was a carboxylic ester group, and further reacted them with hydrazines. *According to the syntheses of pyridines in the literature,*

tetrahydroquinolines (**2**) could formally be obtained *via* a "3 + 2 + N" cyclization among cyclohexane-1,3-dione, a suitable enone (Z = H) or β-diketone (Z = OH) equivalent, and ammonia (Scheme 1). Five possible routes were then considered (Scheme 2).



a : R^1, $R^2 = CO_2Me$
b : R^1, R^2 = Me
c : $R^1 = CO_2Me$; R^2 = Me
d : $R^1 = CO_2Et$; R^2 = *p* - (Cl)Ph

Scheme 2

In routes a and b, which are related to the Doebner-Miller synthesis of quinolines, Michael addition of **4** or **5** onto enone (**3**) gives intermediate (**6**) or (**7**), respectively, which cyclizes to dihydropyridine (**8**) with (route a) or without (route b) ammonium acetate. In both cases a further oxidation of **8** gives the pyridine (**2**). Most examples of such previous approaches in the syntheses of pyridines[2] have been reported as divergent routes along attempted Nenitzescu syntheses of indoles and one ester (**2**, $R^1 = CO_2Me$; R^2 = t-Bu) has been prepared[3] by this method.

In routes c and d the use of an enamino ketone (**9**) or of a β-diketone (**10**) in place of an enone avoids the last oxidation step: aldolisation to intermediates (**11**) or (**12**) allows the further cyclization and subsequent aromatization to give **2**. By the route e, ammonium acetate and intermediate (**13**) also lead to **2**. The same approaches, related to the Friedländer synthesis of quinolines,[4] have been used in the syntheses of simple pyridines.[5] The only difference between the routes c and d is that the amino appendage is first fixed onto either of the two reactants.

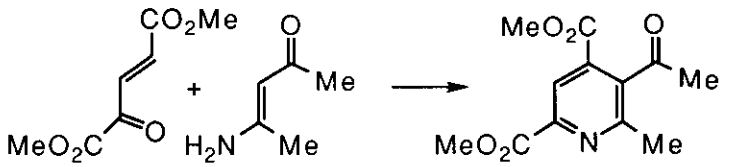
Results

• Route a

Heating dimethyl 2-oxoglutaconate (**3a**) with cyclohexane-1,3-dione (**4**) and ammonium acetate in acetic acid under an argon atmosphere allowed isolation of the dihydropyridine (**8a**) in 30 % yield. Chromatography of the reaction mixture on a silica gel column resulted in oxidation of **8a** to **2a**, which was isolated in 16 % yield from **3a**. Otherwise, oxidation of **8a** to **2a** was conveniently performed (80%) with t-BuOCl.

• Route b

Replacement of **4** by **5** and the absence of ammonium acetate improved the procedure: pyridine (**2a**) was directly obtained in 46 % yield. As a further illustration of this route, the highly substituted pyridine (**14**) was obtained (85 %) from **3a** and enaminone (**9b**) (Scheme 3).



3a **9b** **14**

Scheme 3

• Route c

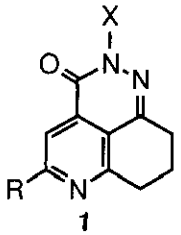
Considering enaminone (**9b**) as the "left part" of the pyridine ring, it was reacted (Scheme 2) with cyclohexane-1,3-dione (**4**) to yield the new dimethyltetrahydroquinoline (**2b**) (53 %).

• Route d

Reaction of enaminone (**5**) with acylpyruvates (**10a**, **10c** and **10d**) gave the corresponding bicyclic pyridinecarboxylates (**2a** (70 %), **2c** (54 %), and **2d** (46 %)).

• Route e

Exposure of **10c** and **10d** to diketone (**4**) and ammonium acetate led to **2c** and **2d** in the same yield as that of the route d (55% and 45%, respectively).



1

	R	X
a	CO_2Me	H
c	Me	H
d	*p*-(Cl)Ph	H
e	Me	Ph
f	Me	2,4-$(NO_2)_2$-Ph

Treatment of 5-oxo-5,6,7,8-tetrahydroquinolines (**2a**, **2c** and **2d**) with hydrazine smoothly generated the novel 2,4,5,6-tetrahydro-2,3,7-triazaphenalene ring system, yielding (**1a** (95 %), **1c** (53 %), and **1d** (90 %)).

Similarly, reaction of **2c** with phenylhydrazine gave compound (**1e**) (30 %), while difficulties were encountered in the purification step. Dinitrophenylhydrazine derivative (**1f**) was more efficiently prepared (77 %) through nucleophilic aromatic substitution of 1-fluoro-2,4-dinitrobenzene with **1c**. It is interesting to note that some derivatives of these 1-oxo-2,4,5,6-tetrahydro-2,3,7-triazaphenalenes showed platelet aggregation inhibition activity.[6]

Experimental

Ir spectra (ν, cm^{-1}) were recorded on a Beckman Acculab spectrophotometer; uv spectra were recorded on a Varian 634 spectrophotometer; ^1H- and ^{13}C-Nmr spectra were measured on a Bruker AC 300 apparatus at 300 MHz and 75 MHz, respectively. High resolution electronic impact mass spectra (E = 70 eV) were obtained on a JEOL JMS D-300 spectrometer; Merck Kieselgel 60 PF_{254} was used for thin layer chromatography and Kieselgel 60 for column chromatography. Melting points were uncorrected. Compounds (**3a**, **5** and **9b**) were prepared by the procedures described by Corey,[7] Zymalkowski and Rimek[8] and Büchi,[9] respectively. Compounds (**10a**) and (**10c**) were prepared as described.[10,11] **10d**[12] was prepared according to Zdenek's procedure.[10]

2,4-Bismethoxycarbonyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline (8a) (route a).

A solution of 1,3-cyclohexanedione (0.40 g, 3.57 mmol) in methanol (5 ml) was added to a solution of NaOH (0.142 g, 3.55 mmol) in 10 ml of methanol. Then dimethyl 2-oxoglutaconate (0.55 g, 3.57 mmol) in methanol (5 ml) was added and the solution was stirred for 45 min. Ammonium acetate (1.4 g, 18 mmol) and acetic acid (5 ml) were added. The solution was refluxed for 3 h, then concentrated. The residue was mixed with water and extracted with ether. The organic layer was washed with saturated $NaHCO_3$ and brine. Purification of the crude product (*) (tlc) gave **8a**, as brownish solid (0.28 g, 30%). Uv (MeOH): 210, 234, 340, 394 nm. Ir: 3340, 2980, 2940, 2880, 1730, 1720, 1690, 1600, 1580, 1250, 830 cm^{-1}. ^1H-Nmr ($CDCl_3$) δ: 6.71 (s, 1H), 6.05 (d, J= 7 Hz, 1H), 4.46 (d, J= 7 Hz, 1H), 3.85 (s, 3H), 2.55-2.90 (m, 4H), 2.08 (m, 2H). ^{13}C-Nmr δ: 195.6, 172.3, 162.5, 152.7, 127.8, 110.7, 104.0, 52.6, 52.2, 39.0, 36.3, 27.6, 21.0. HReims: 265.0910 (calculated for $C_{13}H_{15}NO_5$: 265.0950). Ms (m/z): 265 (M^+, 2%), 220 (67 %), 206 (100%).

2,4-Bismethoxycarbonyl-5-oxo-5,6,7,8-tetrahydroquinoline (2a) by oxidation of 8a with t-BuOCl.

To a solution of **8a** (0.12 g, 0.45 mmol) in 20 ml of methanol, t-BuOCl (0.064 g, 50 μL, 0.585 mmol) was added at 10°C under stirring. After 10 min, the solution was diluted with water (30 ml) and the mixture was extracted with $CHCl_3$. The organic layer was washed with water and dried over $MgSO_4$. After concentration, the residue was purified by tlc (eluent: AcOEt) to give **2a** (90 mg, 80%) as pale yellow cristals after crystallisation from ether. mp: 115-116°C (ether). Uv (MeOH): 225, 242, 291 nm. Ir: 1740, 1720, 1700, 1590 cm^{-1}. ^1H-Nmr ($CDCl_3$) δ: 8.01 (s, 1H), 4.06 (s, 3H), 4.00 (s, 3H), 3.30 (t, J= 7 Hz, 2H), 2.78 (t, J= 7 Hz, 2H), 2.25 (q, J= 7 Hz, 2H). ^{13}C-Nmr δ: 196.0, 168.1, 168.0, 164.6, 164.2, 142.9, 126.6, 121.4, 53.3, 53.2, 38.5, 32.7, 21.2. HReims: 263.0759 (calculated for $C_{13}H_{13}NO_5$: 263.0792). Ms (m/z): 263 ($M^{+\cdot}$, 9%), 205 (25%), 177 (100%). Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 58.89; H, 5.03; N, 5.15.

(*) When the reaction mixture was purified by column chromatography ($CHCl_3$-MeOH 99:1 as eluent), **2a** was isolated (16 %) from a complex mixture of coloured products.

Synthesis of 2,4-Bismethoxycarbonyl-5-oxo-5,6,7,8-tetrahydroquinoline (2a) by condensation of 3-aminocyclohex-2-en-1-one and dimethyl 2-oxoglutaconate (route b).

A mixture of dimethyl 2-oxoglutaconate (1.72 g, 10 mmol) and 3-aminocyclohex-2-en-1-one (1.16 g, 10 mmol) was heated for 3 h in acetic acid (20 ml). The solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (*eluent*: $CHCl_3$-MeOH 99:1) *to give* **2a** (1.1 g, 46%). *mp*: 115-116°C.

Synthesis of 2,4-Bismethoxycarbonyl-5-oxo-5,6,7,8-tetrahydroquinoline (2a) by condensation of 3-aminocyclohex-2-en-1-one and dimethyl 2,4-dioxoglutarate (route d).

A mixture of dimethyl 2,4-dioxoglutarate (0.55 g, 3.5 mmol) and 3-aminocyclohex-2-en-1-one (0.39 g, 3.5 mmol) was refluxed in acetic acid (20 ml) for 20 h. Acetic acid was evaporated under reduced pressure and the resulting oil was column chromatographed (eluent: $CHCl_3$-MeOH 99:1), to give **2a** (0.64 g, 70%). mp: 115-116°C.

5-Acetyl-2,4-dimethoxycarbonyl-6-methylpyridine (14) (route b).

A solution of 4-aminopent-3-en-2-one (0.24 g, 2.42 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a solution of dimethyl 2-oxoglutaconate (0.542 g, 3.14 mmol) in CH_2Cl_2 (10 ml). The solution was stirred at room temperature for 4 h, then acidified with gaseous HCl and stirred for 10 h. After concentration, the residue was dissolved in CH_2Cl_2, washed with a saturated $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$ and concentrated. The product was triturated with ether to give **14** (0.520 g, 85%) as pale yellow crystals. mp: 108-109°C (ether). Uv (MeOH): 210, 291 nm. *Ir: 3050, 2970, 1730, 1700, 1560 cm*$^{-1}$. ^{1}H-Nmr (*$CDCl_3$*) *δ: 8.40* (s, 1H), 4.02 (s, 1H), 3.90 (s, 3H), 2.61 (s, 3H), 2.50 (s, 3H). ^{13}C-Nmr δ: 201.3, 164.4, 164.3, 155.0, 147.9, 140.2, 135.0, 122.1, 53.0, 31.1, 22.2 ppm. HReims: 251.0759 (calculated for $C_{12}H_{13}NO_5$: 251.0794). Ms (m/z): 251 (M^+, 3%), 236 (100%), 221 (23%), 193 (50%). Anal. Calcd for $C_{12}H_{13}NO_5$: C, 57.36; H, 5.21; N, 5.58. Found: C, 57.44; H, 5.02; N, 5.63.

2,4-Dimethyl-5-oxo-5,6,7,8-tetrahydroquinoline (2b) (route c).

4-Aminopent-3-en-2-one (3.0 g, 30 mmol), ammonium acetate (6.0 g, 78 mmol) and 1,3-cyclohexanedione (3.0 g, 27 mmol) were refluxed in acetic acid (20 ml) for 12 h. After cooling, the solvent was evaporated. The solution was treated according to the classical work-up. The crude *product was purified by column chromatography* (*eluent*: $CHCl_3$-MeOH 99:1) to yield **2b** (2.47 g, 53%). mp: 50°C (ether). Uv (MeOH): 208, 240, 335 nm. Ir: 1675, 1585, 1545 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 6.82 (s, 1H), 3.03 (t, J= 7 Hz, 2H), 2.58 (t, J= 7 Hz, 2H), 2.52 (s, 3H), 2.43 (s, 3H), 2.04 (q, J= 7 Hz, 2H). ^{13}C-Nmr δ: 199.4, 164.1, 161.1, 142.3, 125.2, 124.6, 40.2, 24.3, 22.3, 21.4. HReims: 175.0985 (calculated for $C_{11}H_{13}NO$: 175.0995). Ms (m/z): 175 ($M^{+\cdot}$, 70%), 147 (10%), 120 (20%), 104 (15%).

4-Methoxycarbonyl-2-methyl-5-oxo-5,6,7,8-tetrahydroquinoline (2c) (route e).
A mixture of methyl acetylpyruvate (1.9 g, 13 mmol), 1,3-cyclohexanedione (1.3 g, 12 mmol) and ammonium acetate (2.5 g, 35 mmol) was refluxed in acetic acid (100 ml) for 20 h. The acetic acid was evaporated under reduced pressure and the resulting oil was filtered on silicagel (eluent: $CHCl_3$). Compound (**2c**), as pale yellow cristals, was obtained by crystallisation from methanol (1.44 g, 55%). mp: 83-84°C (MeOH). Uv (MeOH): 241, 289 nm. Ir: 1740, 1680 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 7.05 (s, 1H), 3.96 (s, 3H), 3.14 (t, J= 7 Hz, 2H), 2.70 (t, J= 7 Hz, 2H), 2.61 (s, 3H), 2.18 (q, J= 7 Hz, 2H). ^{13}C-Nmr δ: 196.5, 169.0, 164.0, 163.5, 141.7, 122.2, 119.7, 52.9, 38.4, 32.7, 21.5. HReims: 219.0879 (calculated for $C_{12}H_{13}NO_3$: 219.0894). Ms (m/z): 219 ($M^{+\cdot}$, 2%), 191 (7%), 161 (8%), 133 (100%). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.97; N, 6.39. Found: C, 65.38; H, 6.22; N, 6.08.
Compound (**2c**) was obtained by the route d, starting from methyl acetylpyruvate (1.44 g, 10 mmol) and from 3-aminocyclohex-2-en-1-one (1.11 g, 10 mmol) in refluxing acetic acid (50 ml) (*cf.* **2a**, route e) in 54% yield (1.18 g).

2-(4-Chlorophenyl)-4-ethoxycarbonyl-5-oxo-5,6,7,8-tetrahydroquinoline (2d).
It was obtained (*cf.* **2c**, route e) starting from ethyl 4-chlorobenzoylpyruvate (1.45 g, 6 mmol), 1,3-cyclohexanedione (0.67 g, 6 mmol) and ammonium acetate (1.0 g, 13 mmol), in 45% yield (0.88 g). mp: 151-154°C (MeOH). Uv (MeOH): 222, 271, 310 nm. Ir: 1725, 1680, 1540 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 8.03 (d, J= 7 Hz, 1H), 7.60 (s, 1H), 7.45 (d, J= 7 Hz, 1H), 4.48 (q, J= 7 Hz, 2H), 3.20 (t, J= 7 Hz, 2H), 2.75 (t, J= 7 Hz, 2H), 2.20 (q, J= 7 Hz, 2H), 1.42 (t, J= 7 Hz, 3H). ^{13}C-Nmr δ: 196.3, 168.8, 164.5, 159.2, 143.0, 136.8, 135.9, 129.1, 122.9, 128.9, 116.5, 62.2, 38.5, 33.0, 21.5, 13.9. HReims: 329.0884 (calculated for $C_{18}H_{16}{}^{35}ClNO_3$: 329.0819). Ms (m/z): 329 (M^+, 6%), 302 (100%), 231 (25%). Anal. Calcd for $C_{18}H_{16}NO_3Cl$: C, 65.55; H, 4.89; N, 4.25. Found: C, 65.49; H, 4.96; N, 4.21.
Compound (**2d**) was also obtained by the route d (*cf.* **2c**), starting from ethyl 4-chlorobenzoylpyruvate (2.42 g, 10 mmol) and 3-aminocyclohex-2-en-1-one (1.11 g, 10 mmol) in 46% yield (1.48 g).

8-Methoxycarbonyl-1-oxo-2,4,5,6-tetrahydro-2,3,7-triazaphenalene (1a).
A solution of **2a** (790 mg, 3 mmol) and 98 % hydrazine monohydrate (165 mg, 0.16 ml, 3.3 mmol) in MeOH (20 ml) was kept at 25°C for 20 min. Then the solvent was evaporated and the residue was chromatographed on silicagel (eluent: $CHCl_3$-MeOH 98:2) to give 830 mg (95%) of **1a**. mp: 234°C (MeOH-ether). Uv (MeOH): 208, 220 (sh), 310, 325 nm. Ir: 1740, 1680 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 10.45 (br s, 1H), 8.85 (s, 1H), 4.11 (s, 3H), 3.35 (t, J= 7 Hz, 2H), 3.02 (t, J= 7 Hz, 2H), 2.25 (quintuplet, J= 7 Hz, 2H). ^{13}C-Nmr δ: 164.6, 161.8, 159.1, 148.1, 146.6, 133.7, 123.3, 119.2, 53.3, 32.6, 29.4, 22.4. HReims: 245.0781 (calculated for $C_{12}H_{11}N_3O_3$: 245.0799). Ms (m/z): 245 (M^+, 10%), 177 (100%). Anal. Calcd for $C_{12}H_{11}N_3O_3$: C, 58.77; H, 4.52; N, 17.13. Found: C, 58.31; H, 4.61; N, 16.68.

8-Methyl-1-oxo-2,4,5,6-tetrahydro-2,3,7-triazaphenalene (1c).
A solution of **2c** (208 mg, 0.95 mmol) and 98 % hydrazine monohydrate (62 mg, 60 µl, 1.24 mmol) in MeOH (5 ml) gave, under the same conditions as above, 102 mg of **1c** (53%), as pale yellow cristals. mp: 225-226°C (MeOH). Uv (MeOH): 206, 280, 325 nm. Ir: 1670 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 11.20 (br s, 1H), 7.91 (s, 1H), 3.21 (t, J= 7 Hz, 2H), 2.95 (t, J= 7 Hz, 2H), 2.75 (s, 3H), 2.21 (quintuplet, J= 7 Hz, 2H). ^{13}C-Nmr δ: 160.5, 160.3, 159.7, 146.2, 133.3, 119.1, 115.7, 32.1, 29.3, 22.7, 22.5. HReims: 201.0867 (calculated for $C_{11}H_{11}N_3O$: 201.0902). Ms (m/z): 201 ($M^{+\cdot}$, 100%), 200 (40%), 144 (5%). Anal. Calcd for $C_{11}H_{11}N_3O$: C, 65.66; H, 5.51; N, 20.88. Found: C, 65.26; H, 5.43; N, 20.62.

8-(4-Chlorophenyl)-1-oxo-2,4,5,6-tetrahydro-2,3,7-triazaphenalene (1d).
A solution of **2d** (500 mg, 1.52 mmol) and 98 % hydrazine monohydrate (78 mg, 76 µl, 1.56 mmol) in a mixture of methanol (5 ml) and CH_2Cl_2 (5 ml) was refluxed for 2.5 h; **1d** slowly crystallised from the mixture (402 mg, 90%). mp: 285-286°C (MeOH). Uv (MeOH): 208, 220 (sh), 248, 310, 335 nm. Ir: 1670 cm^{-1}. ^{1}H-Nmr (DMSO-d_6) δ: 11.45 (br s, 1H), 8.37 (s, 1H), 8.22 (d, J= 5 Hz, 2H), 7.57 (d, J= 5 Hz, 2H), 3.18 (t, J= 7 Hz, 2H), 2.89 (t, J= 7 Hz, 2H), 2.12 (quintuplet, J= 7 Hz, 2H). HReims: 297.0635 (calculated for $C_{16}H_{12}{}^{35}ClN_3O$: 297.0668). Ms (m/z): 299 (35%), 297 (100%), 206 (10%), 204 (35%). Anal. Calcd for $C_{16}H_{12}N_3OCl$: C, 64.54; H, 4.06; N, 14.11. Found: C, 64.44; H, 4.04; N, 13.80.

8-Methyl-1-oxo-2-phenyl-2,4,5,6-tetrahydro-2,3,7-triazaphenalene (1e).
A solution of **1c** (100 mg, 0.49 mmol) and phenylhydrazine hydrochloride (72 mg, 0.50 mmol) in acetic acid (3 ml) was heated for 2.5 h under argon atmosphere. The mixture was diluted with CH_2Cl_2 (100 ml), neutralized ($NaHCO_3$) and washed with water. The organic phase was dried ($MgSO_4$), evaporated and purified by tlc (eluent: $CHCl_3$), to give **1e** (40 mg, 30%). mp: 234°C (MeOH, ether). Uv (MeOH): 210, 234, 332 nm. Ir: 1680, 1590 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 7.90 (s, 1H), 7.63 (d, J= 6 Hz, 2H), 7.48 (t, J= 6 Hz, 2H), 7.38 (t, J= 6 Hz, 1H), 3.20 (t, J= 7 Hz, 2H), 2.98 (t, J= 7 Hz, 2H), 2.75 (s, 1H), 2.25 (quintuplet, J= 7 Hz, 2H). ^{13}C-Nmr δ: 160.6, 160.5, 158.3, 145.6, 141.7, 134.0, 128.9, 127.9, 125.6, 116.6, 116.5, 32.4, 29.7, 22.8. HReims: 277.1205 (calculated for $C_{17}H_{15}N_3O$: 277.1213). Ms (m/z): 277 ($M^{+\cdot}$, 100%), 270 (60%), 133 (65%). Anal. Calcd for $C_{17}H_{15}N_3O$: C, 73.62; H, 5.45; N, 15.15. Found: C, 73.38; H, 5.63; N, 15.38.

2-(2,4-Dinitrophenyl)-8-methyl-1-oxo-2,4,5,6-tetrahydro-2,3,7-triazaphenalene (1f).
A suspension of **1c** (1.07 g, 5.32 mmol), 1,3-dinitro-4-fluorobenzene (1.75 g, 9.4 mmol), CsF (5.8 g, 38 mmol) and $BnMe_3NF$ (0.1 g, 0.7 mmol) in anhydrous THF (100 ml) was refluxed for 12 h. The coloured mixture was treated with activated carbon, then diluted with CH_2Cl_2 (250 ml) and washed with water. The organic phase was dried over $MgSO_4$, evaporated and purified by column chromatography (eluent: $CHCl_3$), to give **1f** (1.40 g, 77%), as reddish-yellow cristals. mp: 175-177°C (MeOH-ether). Uv (MeOH): 215, 285, 350 nm. Ir: 1680, 1590, 1540, 1345 cm^{-1}. ^{1}H-Nmr

($CDCl_3$) δ: 8.82 (d, J= 2 Hz, 1H), 8.56 (dd, J_1= 8, J_2= 2 Hz, 1H), 8.01 (d, J= 8 Hz, 1H), 7.87 (s, 1H), 3.24 (t, J= 7 Hz, 2H), 3.02 (t, J= 7 Hz, 2H), 2.77 (s, 3H), 2.29 (quintuplet, J= 7 Hz, 2H). ^{13}C-Nmr δ: 161.6, 160.6, 157.8, 147.9, 146.1, 144.5, 139.0, 132.3, 130.3, 127.5, 120.1, 117.9, 31.9, 29.2, 24.7, 22.2. HReims: 367.0900 (calculated for $C_{17}H_{13}N_5O_5$: 367.0916). Ms (m/z): 367 ($M^{+\cdot}$, 10%), 321 (45%), 215 (65%), 187 (100%), 184 (40%), 158 (40%). Anal. Calcd for $C_{17}H_{13}N_5O_5$: C, 55.59; H, 3.57; N, 19.07. Found: C, 55.87; H, 3.56; N, 18.64.

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