Supporting Information
for DOI: 10.1055/s-0028-1083537
© Georg Thieme Verlag KG Stuttgart · New York 2008
Supporting Information

Novel extensions of the tert-amino effect:
Formation of phenanthridines and diarene-fused azocines from ortho-ortho'-functionalized biaryls

Ágnes Polonka-Bálint, a Caterina Saraceno, a Krisztina Ludányi, b
Attila Bényei, c Péter Mátyus* a

a Department of Organic Chemistry, b Department of Pharmacy, Semmelweis University,
Hőgyes Endre u. 7., 1092 Budapest, Hungary
Fax: +36(1)2170851; E-mail: peter.matyus@szerves.sote.hu

c Institute of Physical Chemistry, University of Debrecen, Egyetem tér 1., 4010 Debrecen,
Hungary

Contents

General Methods S2
Experimental Details and Spectroscopic Data S2-S17
Table of Characteristic NMR Data S17
References S18
General Methods

All reagents and solvents were purchased from commercial sources and used without further purification. Melting points were determined on a Büchi-540 capillary melting points apparatus and are uncorrected. The $^1$H and $^{13}$C NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO-$d_6$), chloroform (CDCl$_3$) or methanol (MeOD) solution at 25 °C using a Varian Mercury Plus spectrometer at frequency of 400 MHz and 100 MHz, respectively and reported in ppm. For structure elucidation, one-dimensional $^1$H, $^{13}$C, DEPT, two-dimensional $^1$H, $^1$H-COSY, $^1$H, $^{13}$C-HSQC, $^1$H, $^{13}$C-HMBC measurements were run. Chemical shifts are given on the $\delta$-scale with references to TMS (for deuterated chloroform solutions) or to that of the solvent (MeOD: 3.31 and 49.0 ppm, DMSO-$d_6$: 2.50 and 39.5 ppm, $^1$H and $^{13}$C NMR shifts respectively). For NMR and X-ray assignment data an arbitrary numbering was applied for each compound. Mass spectra utilizing fast atom bombardment (FAB) ionization were recorded on a VG-ZAB-2SEQ spectrometer. The IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer in KBr pellets. Elemental analyses were measured on a Carlo Erba 1012 apparatus. The microwave assisted reactions were carried out in a CEM-Discover MW system. TLC on silica gel plates was used to check product purity and monitor the reactions. For column chromatography purification, Kieselgel 60 (Merck, 0.040-0.063 mm) was used. The structures of all compounds were consistent with their analytical and spectroscopic data.

Single crystals were grown by very slow evaporation of hexane (7b), hexane-ethylacetate (13a) or methanol (16c, 19a, 23a) solutions. Data were collected using Enraf Nonius MACH3 (7b, 16c, 23a) or Rigaku R-axis Rapid (3a) or Bruker APEX (19a) diffractometer, Mo Kα or Cu Kα radiation. The structure were routinely solved using the SIR-92 software$^1$ and refined on $F^2$ using SHELX-97 program$^2$, publication material was prepared with the WINGX-97 suite.$^3$ Anisotropic refinement of non hydrogen atoms. Hydrogen atoms were placed into geometric positions except OH hydrogen atoms at solvate methanol in 23a, orientation of methyl groups were refined using a riding model. Additional crystallographic information is provided in the deposited CIF.

Compounds 6a and 6b were prepared by a modified literature process$^4$. Compounds 7c$^5$, 9$^6$ and 11a-c$^7$ were synthesized according to the literature procedure.

Experimental Details and Spectroscopic Data

Synthesis of 1-(2-bromophenyl)pyrrolidine (6a) and 1-(2-bromophenyl)piperidine (6b)

2-Bromoaniline (5) (8.601 g, 50 mmol) was dissolved in toluene (60 mL) and the solution was stirred at room temperature. Subsequently, 1,4-dibromobutane (19.432 g, 90 mmol for 6a) or 1,5-dibromopentane (20.695 g, 90 mmol for 6b) and N-ethyl-N-isopropylpropan-2-amine (15.509 g, 120 mmol)
were added. The mixture was stirred and heated at 120 °C. After 15 h the reaction was complete as monitored by TLC (eluent: chloroform) and the mixture was cooled to room temperature. The crystalline salt was filtered off, washed with toluene (3×50 mL), and the liquid phase was evaporated. The brown oily residue was distilled under reduced pressure to give 1-(2-bromophenyl)pyrrolidine (6a, 80%, bp 102 °C/3 mmHg, lit.: 100 °C/0.8 mmHg) or 1-(2-bromophenyl)piperidine (6b, 81%, bp 118 °C/3 mmHg, lit.: 110-111 °C/0.2 mmHg) as pale yellow oils. NMR spectra were consistent with the literature data.4

**General procedure for Suzuki cross-coupling reaction (7a,b, 12a-c)**

The *ortho*-halogen compound (6a,b, 11a-c) (10 mmol) was dissolved in dimethoxyethane (15 mL), and Pd(PPh₃)₄ (577.8 mg, 0.50 mmol,) was added to the solution at room temperature under argon flow. After stirring the mixture at room temperature for 10 min, 2-formylphenylboronic acid (2.249 g, 15 mmol,) and aq 2N Na₂CO₃ solution (10.6 mL) were added and the reaction mixture was refluxed at 110 °C (oil temperature). When the reaction was complete (monitored by TLC, eluent: *n*-hexane - ethyl acetate 4:1 for 7a,b; chloroform – acetone 9:1 for 12a-c), the reaction mixture was cooled and poured onto ice (100 g). The solution was filtered on Celite and washed with ethyl acetate (100 mL). The aqueous phase was extracted with ethyl acetate (7a,b) or chloroform (12a-c) (3×40 mL). The combined organic layers were washed with water (1×20 mL), dried over MgSO₄, evaporated under reduced pressure. The oily residue was purified by flash column chromatography on silica gel (eluent: *n*-hexane - ethyl acetate 15:1 for 7a; *n*-hexane - ethyl acetate 9:1 for 7b; diisopropyl ether – acetone 8:1 for 12a-c).

**2’-Pyrrolidin-1-ylbiphenyl-2-carbaldehyde (7a)**

90%; yellow oil, after storing at -20 °C for two weeks there were obtained yellow crystals; mp 40-41 °C. IR: νₘₐₓ = 3054, 2968, 2924, 2852, 1688, 1594, 756 cm⁻¹. ¹H NMR (CDCl₃): 9.69 (d, J = 0.8 Hz, 1H, H-18), 7.92 (dd, J = 7.9, 1.4 Hz, 1H, H-16), 7.62 (ddd, J = 7.7, 7.3, 1.4 Hz, 1H, H-14), 7.46-7.39 (m, 2H, H-13,15), 7.30 (ddd, J = 8.2, 7.4, 1.7 Hz, 1H, H-8), 7.21 (ddd, J = 7.4, 1.7, 0.3 Hz, 1H, H-10), 6.96 (td, J = 7.4, 1.0 Hz, 1H, H-9), 6.93 (dd, J = 8.2, 1.0 Hz, 1H, H-7), 2.76 (m, 4H, H-2,5), 1.66 (m, 4H, H-3,4). ¹³C NMR (CDCl₃): 193.1 (C-18), 149.3 (C-6), 145.9 (C-12), 134.5 (C-14), 134.1 (C-17), 132.6 (C-10), 131.2 (C-13), 129.7 (C-8), 128.0 (C-15), 127.8 (C-11), 127.2 (C-16), 120.5 (C-9), 116.0 (C-7), 50.9 (C-2,5), 25.5 (C-3,4). Anal. calcd for C₁₇H₁₇NO (251.32): C, 81.24; H, 6.82; N, 5.57. Found: C, 81.22; H, 6.93; N, 5.53.
2'-Piperidin-1-ylbiphenyl-2-carbaldehyde (7b)

\[
\begin{align*}
\text{CHO} \quad \text{O}
\end{align*}
\]

68%; orange crystals; mp 101-103 °C. IR: \(\nu_{\text{max}} = 3058, 2946, 2754, 1690, 1594, 762 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\)): 9.63 (d, \(J = 0.8 \text{ Hz}, 1\text{H, H-19}\)), 7.98 (dd, \(J = 7.8, 1.4 \text{ Hz}, 1\text{H, H-17}\)), 7.66 (td, \(J = 7.5, 1.5 \text{ Hz}, 1\text{H, H-15}\)), 7.45 (tm, \(J = 7.5 \text{ Hz}, 1\text{H, H-16}\)), 7.41-7.30 (m, 3H, H-9,11,14), 7.16 (td, \(J = 7.5, 1.2 \text{ Hz}, 1\text{H, H-10}\)), 7.05 (dd, \(J = 8.0, 1.0 \text{ Hz}, 1\text{H, H-8}\)), 2.80-2.50 (m, 4H, H-2,6), 1.45-1.15 (m, 6H, H-3,4,5). \(^{13}\)C NMR (CDCl\(_3\)): 193.0 (C-19), 152.7 (C-7), 143.7 (C-13), 134.6 (C-15), 133.7 (C-18), 132.7 (C-12), 131.7 (C-11), 131.0 (C-14), 130.3 (C-9), 128.1 (C-16), 127.1 (C-17), 124.1 (C-10), 119.2 (C-8), 53.1 (C-2,6), 25.9 (C-3,5), 24.6 (C-4). Anal. calcd for C\(_{18}\)H\(_{19}\)NO (265.35): C, 81.47; H, 7.22; N, 5.28. Found: C, 81.73; H, 7.31; N, 5.19.

2-(2-Methyl-3-oxo-5-pyrrolidin-1-yl-2,3-dihydropyridazin-4-yl)benzaldehyde (12a)

\[
\begin{align*}
\text{CHO} \quad \text{O}
\end{align*}
\]

After purification by column chromatography the product was recrystallized from a mixture of ethyl acetate - n-hexane (2.3:1).

65%; yellow crystals; mp 140-141 °C. IR: \(\nu_{\text{max}} = 3066, 2962, 2766, 1694, 1608, 776 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\)): 9.96 (d, \(J = 0.7 \text{ Hz}, 1\text{H, H-18}\)), 7.95 (dm, \(J = 7.7 \text{ Hz}, 1\text{H, H-16}\)), 7.68 (s, 1H, H-7), 7.56 (td, \(J = 7.7 \text{ Hz}, 1\text{H, H-14}\)), 7.45 (tm, \(J = 7.7 \text{ Hz}, 1\text{H, H-15}\)), 7.29 (dm, \(J = 7.7 \text{ Hz}, 1\text{H, H-13}\)), 3.73 (s, 3H, NCH\(_3\)), 3.13-2.92 (m, 4H, H-2,5), 1.90-1.67 (m, 4H, H-3,4). \(^{13}\)C NMR (CDCl\(_3\)): 192.9 (C-18), 161.7 (C-10), 146.0 (C-6), 139.1 (C-12), 136.3 (C-17), 133.5 (C-14), 133.4 (C-13), 129.8 (C-7), 128.8 (C-15), 128.2 (C-16), 109.1 (C-11), 51.1 (C-2,5), 40.4 (NCH\(_3\)), 26.1 (C-3,4). Anal. calcd for C\(_{16}\)H\(_{19}\)NO\(_2\) (283.33): C, 67.83; H, 6.05; N, 14.83. Found: C, 67.73; H, 6.12; N, 14.86.

2-(2-Methyl-3-oxo-5-piperidin-1-yl-2,3-dihydropyridazin-4-yl)benzaldehyde (12b)

\[
\begin{align*}
\text{CHO} \quad \text{O}
\end{align*}
\]

After purification by column chromatography the product was recrystallized from a mixture of ethyl acetate - n-hexane (2.3:1).
61%; yellow crystals; mp 134-135 °C. IR: \( \nu_{\text{max}} = 3070, 2942, 2758, 1692, 1624, 1584, 784 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 9.84 (s, 1H, H-19), 7.98 (dm, \( J = 7.8 \text{ Hz} \), 1H, H-17), 7.72 (s, 1H, H-8), 7.64 (tm, \( J = 7.8 \text{ Hz} \), 1H, H-14), 3.75 (s, 3H, NCH\(_3\)), 3.04-2.84 (m, 4H, H-2,6), 1.58-1.29 (m, 6H, H-3,4,5). \(^{13}\)C NMR (CDCl\(_3\)): 192.1 (C-19), 161.3 (C-11), 150.5 (C-7), 137.6 (C-13), 134.3 (C-15), 134.2 (C-18), 131.9 (C-8), 131.7 (C-14), 128.9 (C-16), 128.5 (C-17), 116.6 (C-12), 50.8 (C-2,6), 40.6 (NCH\(_3\)), 25.9 (C-3,5), 24.2 (C-4). Anal. calcd for C\(_{17}\)H\(_{19}\)N\(_3\)O\(_2\) (297.35): C, 68.67; H, 6.44; N, 14.13. Found: C, 68.65; H, 6.89; N, 14.07.

2-[5-(Dimethylamino)-2-methyl-3-oxo-2,3-dihydropyridazin-4-yl]benzaldehyde (12c)

After purification by column chromatography the product was recrystallized from a mixture of ethyl acetate - n-hexane (2.3:1).

68%; yellow crystals; mp 153-154 °C. IR: \( \nu_{\text{max}} = 3058, 2742, 1698, 1608, 1590, 758 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 9.90 (d, \( J = 0.7 \text{ Hz} \), 1H, H-16), 7.96 (dm, \( J = 7.6 \text{ Hz} \), 1H, H-14), 7.74 (s, 1H, H-5), 7.60 (tm, \( J = 7.6 \text{ Hz} \), 1H, H-13), 7.31 (dm, \( J = 7.6 \text{ Hz} \), 1H, H-11), 3.73 (s, 3H, NCH\(_3\)), 2.69 (s, 6H, H-2,3). \(^{13}\)C NMR (CDCl\(_3\)): 192.3 (C-16), 161.4 (C-8), 149.5 (C-4), 138.5 (C-10), 135.4 (C-15), 134.1 (C-12), 132.3 (C-11), 130.5 (C-5), 128.9 (C-13), 128.7 (C-14), 112.6 (C-9), 42.3 (C-2,3), 40.5 (NCH\(_3\)). Anal. calcd for C\(_{14}\)H\(_{15}\)N\(_3\)O\(_2\) (257.29): C, 65.35; H, 5.88; N, 16.33. Found: C, 65.27; H, 5.90; N, 16.29.

General procedure for Knoevenagel condensations (13a-c, 14b, 15a,c, 16a-c, 17a-c, 18a-c)

A mixture of the aldehyde (7a,b, 12a-c) (4 mmol), dry ethanol (15 mL), malononitrile (264.2 mg, 4 mmol for 13a-c, 17a-c), or 1H-indene-1,3(2H)-dione (584.6 mg, 4 mmol for 14b, 15a,c); or a mixture of 1,4-dioxane (15 mL) and 1H-indene-1,3(2H)-dione (584.6 mg, 4 mmol for 18a-c), or N,N-dimethyl barbituric acid (624.6 mg, 4 mmol for 16a-c) was stirred at room temperature for 24-48 h. For 17a-c, 18a-c pyridazinones few drops of piperidine were also added to the solution. The reaction was monitored by TLC (eluent: n-hexane - ethyl acetate 4:1 for 13a-c, 14b, 15a,c, 16a-c; chloroform - acetone 9:1 for 17a-c, 18a-c). (Working-up procedure and purification, see below.)

[(2’-Pyrrolidin-1-ylbiphenyl-2-yl)methylidene]malononitrile (13a)
The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (eluent: dichloromethane - n-hexane 9:1).

95%; red powder; mp 84-85 °C. IR: \( \nu_{\text{max}} = 3058, 3026, 2838, 2224, 1652, 1584, 762 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 8.14 (dm, \( J = 8.1 \text{ Hz} \), 1H, H-16), 7.64 (tm, \( J = 7.5 \text{ Hz} \), 1H, H-14), 7.58 (s, 1H, H-18), 7.52 (dm, \( J = 7.5 \text{ Hz} \), 1H, H-13), 7.47 (ddm, \( J = 7.5, 8.1 \text{ Hz} \), 1H, H-15), 7.33 (ddd, \( J = 8.2, 7.2, 1.7 \text{ Hz} \), 1H, H-8), 7.10 (dm, \( J = 8.1 \text{ Hz} \), 1H, H-10), 6.98-6.91 (m, 2H, H-7,9), 2.84 -2.70 (m, 4H, H-2,5), 1.86-1.62 (m, 4H, H-3,4).

\(^{13}\)C NMR (CDCl\(_3\)): 162.4 (C-18), 149.1 (C-6), 145.9 (C-12), 134.7 (C-14), 132.8 (C-10), 131.5 (C-13), 130.4 (C-8), 129.9 (C-17), 128.5 (C-16), 128.3 (C-15), 127.6 (C-11), 120.3 (C-9), 116.1 (C-7), 114.3 and 113.0 (C-20,21), 81.9 (C-19), 51.0 (C-2,5), 25.8 (C-3,4). Anal. calcd for C\(_{20}\)H\(_{17}\)N\(_3\) (299.37): C, 80.24; H, 5.72; N, 14.04. Found: C, 80.32; H, 5.66; N, 14.01. HRMS: Calcd for (C\(_{20}\)H\(_{17}\)N\(_3\)+H\(^+\)): 300.1501. Found: 300.1489.

The precipitate was filtered off and washed with cold ethanol.

68%; yellow powder; mp 133 °C. IR: \( \nu_{\text{max}} = 3056, 2936, 2790, 2222, 1584, 764 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 8.26 (dm, \( J = 7.9 \text{ Hz} \), 1H, H-17), 7.69 (td, \( J = 7.6, 1.2 \text{ Hz} \), 1H, H-15), 7.60 (s, 1H, H-19), 7.50 (ddd, \( J = 7.8, 7.6 \text{ Hz} \), 1H, H-16), 7.46 (dm, \( J = 7.6 \text{ Hz} \), 1H, H-14), 7.40 (ddd, \( J = 8.0, 7.2, 2.0 \text{ Hz} \), 1H, H-9), 7.18 (dd, \( J = 7.6, 2.0 \text{ Hz} \), 1H, H-11), 7.14 (ddd, \( J = 7.2, 7.2, 1.1 \text{ Hz} \), 1H, H-10), 7.09 (dd, \( J = 8.0, 1.1 \text{ Hz} \), 1H, H-8), 2.78-2.70 (m, 2H, H-2 or H-6), 2.68-2.58 (m, 2H, H-2 or H-6), 1.47-1.30 (m, 6H, H-3,4,5). \(^{13}\)C NMR (CDCl\(_3\)): 163.1 (C-19), 152.6 (C-7), 144.6 (C-13), 135.1 (C-15), 133.0 (C-12), 132.2 (C-11), 131.6 (C-14), 130.9 (C-9), 129.3 (C-18), 128.5 (C-16), 128.4 (C-17), 123.9 (C-10), 119.6 (C-8), 115.0 and 113.7 (C-21,22), 81.5 (C-20), 53.1 (C-2,6), 26.5 (C-3,5), 24.5 (C-4). Anal. calcd for C\(_{21}\)H\(_{19}\)N\(_3\) (313.40): C, 80.48; H, 6.11; N, 13.41. Found: C, 80.47; H, 6.10; N, 13.39. HRMS: Calcd for (C\(_{21}\)H\(_{19}\)N\(_3\)+H\(^+\)): 314.1657. Found: 314.1643.

The precipitate was filtered off and washed with cold ethanol.

84%; white crystals; mp 96-97 °C. IR: \( \nu_{\text{max}} = 2948, 2170, 2124, 1450, 766 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 8.18 (dm, \( J = 8.0 \text{ Hz} \), 1H, H-14), 7.68 (tm, \( J = 7.6 \text{ Hz} \), 1H, H-12), 7.57 (s, 1H, H-16), 7.54-7.45 (m, 2H, H-
11, 13), 7.40 (ddd, J = 8.1, 7.3, 1.8 Hz, 1H, H-6), 7.21 (dd, J = 7.6, 1.8 Hz, 1H, H-8), 7.12 (ddd, J = 7.6, 7.3, 1.2 Hz, 1H, H-7), 7.07 (dd, J = 8.1, 1.2 Hz, 1H, H-5), 2.45 (s, 6H, H-2,3). 13C NMR (CDCl3): 162.8 (C-16), 151.8 (C-4), 144.1 (C-10), 134.9 (C-12), 132.4 (C-8), 131.7 (C-9), 131.4 (C-13), 130.9 (C-6), 129.4 (C-15), 128.8 (C-14), 128.5 (C-11), 123.4 (C-7), 119.1 (C-5), 114.9 and 113.5 (C-18,19), 80.4 (C-17), 43.0 (C-2,3).


2-{[2’-(Piperidin-1-yl)biphenyl-2-yl]methylidene}indane-1,3-dione (14b)

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (eluent: toluene - ethyl acetate 20:1). After the purification by flash column chromatography the residue was recrystallized from ethyl acetate. 36%; orange crystals; mp 144 °C. IR: \( \nu_{\text{max}} = 3058, 2938, 1722, 1680, 1584, 768, 732 \) cm\(^{-1}\). 1H NMR (CDCl3): 8.81 (dm, J = 7.7 Hz, 1H, H-17), 8.03-7.88 (br m, 2H, H-23,26), 7.82 (s, 1H, H-19), 7.80-7.74 (m, 2H, H-24,25), 7.61 (td, J = 7.6, 1.3 Hz, 1H, H-15), 7.50-7.43 (m, 2H, H-14,16), 7.36 (dd, J = 8.0, 7.3, 1.7 Hz, 1H, H-9), 7.23 (dd, J = 7.3, 1.7 Hz, 1H, H-11), 7.11 (td, J = 7.3, 1.1 Hz, 1H, H-10), 7.07 (dd, J = 8.0, 1.1 Hz, 1H, H-8), 2.82-2.68 (m, 2H, H-2 or H-6), 2.68-2.54 (m, 2H, H-2 or H-6), 1.32-1.01 (m, 6H, H-3,4,5). 13C NMR (CDCl3): 191.7 and 189.9 (C-21,28), 152.6 (C-7), 148.3 (C-19), 145.5 (C-13), 135.6 (C-24,25), 134.4 (C-12), 133.7 (C-15), 133.2 (C-17), 132.4 (C-11), 130.9 (C-18), 130.8 (C-14), 130.2 (C-9), 127.6 (C-16), 127.1 (C-20), 123.7 (C-23,26), 123.6 (C-10), 119.4 (C-8), 53.1 (C-2,6), 26.2 (C-3,4,5). HRMS: Calcd for (C27H23NO2+H\(^{+}\)): 394.1807. Found: 394.1791.

1-Oxo-2-(6H-5λλλλ-spiro[phenanthridin-5,1’-pyrrolidin]-5-ylium-6-yl)-1H-indene-3-olate (15a)

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (toluene – ethanol - aq 25% NH3 solution 5:1:0.1). 30%; brown crystals; mp 63-65 °C. IR: \( \nu_{\text{max}} = 3022, 2958, 1686, 1654, 1558, 724 \) cm\(^{-1}\). 1H NMR (CDCl3): 7.92 (dm, J = 7.8 Hz, 1H, H-16), 7.73-7.61 (m, 4H, H-10,13,23,24), 7.57-7.47 (m, 3H, H-14,22,25), 7.44-7.31 (m, 3H, H-8,9,15), 7.17 (dm, J = 7.7 Hz, 1H, H-7), 6.66 (s, 1H, H-18), 3.90-3.30 (br m, 4H, H-2,5), 2.10-1.78 (br m, 4H, H-3,4). 13C NMR (CDCl3): 192.0 (C-20,27), 144.3 (C-6), 140.6 (C-21,26), 137.3 (C-
2-(5,5-Dimethyl-5,6-dihydrophenanthridinium-6-yl)-1-oxo-1H-indene-3-olate (15c)

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate – acetone - isopropanol 4:4:1).

18%; yellow crystals; mp 210-213 °C. IR: $\nu_{\text{max}}$ = 3034, 2928, 1614, 1564, 764, 752 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 7.96 (dd, $J = 7.8, 1.4$ Hz, 1H, H-8), 7.82 (dm, $J = 7.8$ Hz, 1H, H-11), 7.64 (dm, $J = 7.8$ Hz, 1H, H-14), 7.61 (tm, $J = 7.8$ Hz, 1H, H-7), 7.57-7.47 (m, 5H, H-5,6,12,21,22), 6.07 (s, 1H, H-16), 3.30 (s, 6H, H-2,3).

$^{13}$C NMR (CDCl$_3$): 143.4 (C-4), 131.8 (C-10), 131.7 (C-20,23), 131.0 (C-14), 131.0 (C-7), 130.6 (C-13), 130.5 (C-12), 130.4 (C-15), 130.1 (C-9), 130.1 (C-6), 128.0 (C-8), 124.4 (C-11), 119.9 (C-21,22), 119.1 (C-5), 95.8 (C-17), 81.5 (C-16), 50.3 (C-2,3). HRMS: Calcd for (C$_{24}$H$_{21}$NO$_2$+H$^+$): 380.1650. Found: 380.1634.

1,3-Dimethyl-2,6-dioxo-5-(6H-5λ$^5$-spiro[phenanthridin-5,1'-pyrrolidin]-5-ylium-6-yl)-1,2,3,6-tetrahydropyrimidine-4-olate (16a)

The solvent was evaporated, and the oily residue was treated with n-hexane - isopropanol 7:1 to afford pale-pink crystals.

83%; mp 140-143 °C. IR: $\nu_{\text{max}}$ = 3038, 2954, 1682, 1626, 762, 728 cm$^{-1}$. $^1$H NMR (MeOD): 8.09 (dd, $J = 7.7, 1.2$ Hz, 1H, H-10), 7.98 (d, $J = 7.9$ Hz, 1H, H-13), 7.63 (td, $J = 7.7, 0.9$ Hz, 1H, H-9), 7.56 (dm, $J = 8.3$ Hz, 1H, H-7), 7.50-7.41 (m, 2H, H-8,14), 7.37 (td, $J = 7.6, 1.1$ Hz, 1H, H-15), 7.29 (dm, $J = 7.6$ Hz, 1H, H-16), 6.29 (s, 1H, H-18), 4.14-3.91 (m, 4H, H-2,5), 3.29 (s, 3H, NCH$_3$), 2.93 (s, 3H, NCH$_3$), 2.27-2.13 (m, 4H, H-3,4). $^{13}$C NMR (MeOD): 167.3 and 164.1 (C-20,24), 154.7 (C-22), 141.5 (C-6), 133.8 (C-17), 132.8 (C-12), 132.0 (C-11), 131.4 (C-9), 130.1 (C-15), 129.7 and 129.5 (C-8,14), 128.5 (C-16), 127.8 (C-10), 124.0 (C-13), 120.9 (C-7), 84.1 (C-19), 76.6 (C-18), 64.1 (C-2,5), 28.6 and 27.6 (2xNCH$_3$), 23.7 (C-3,4). HRMS: Calcd for (C$_{23}$H$_{23}$N$_3$O$_3$+H$^+$): 390.1818. Found: 390.1795.
1,3-Dimethyl-2,6-dioxo-5-(6H-5λ5-spiro[phenanthridin-5,1’-piperidin]-5-ylium-6-yl)-1,2,3,6-
tetrahydropyrimidine-4-olate (16b)

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (ethyl acetate – acetone - isopropanol 4:4:1). After purification by flash column chromatography the residue was washed with n-hexane and then diethyl ether.

36%; white crystals; mp 63-64 °C. IR: $\nu_{\text{max}}$ = 3060, 2938, 1674, 1622, 1584, 948, 750 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 7.64 (dd, $J$ = 7.7, 1.1 Hz, 1H, H-14), 7.62-7.55 (m, 2H, H-11,17), 7.49 (s, 1H, H-19), 7.46 (td, $J$ = 7.7 1.4 Hz, 1H, H-15), 7.41-7.29 (m, 4H, H-8,9,10,16), 3.50-3.15 (br m, 4H, H-2,6), 3.32 (s, 3H, NCH$_3$), 3.12 (s, 3H, NCH$_3$), 1.78-1.60 (br m, 4H, H-3,5), 1.60-1.50 (br m, 2H, H-4). $^{13}$C NMR (CDCl$_3$): 164.7 and 162.2 (C-21,25), 153.1 (C-23), 146.8 (C-7), 137.1 (C-13), 133.0 (C-12), 132.0 (C-18), 130.8 (C-15), 130.3 (C-11), 129.5 (C-17), 129.4 (C-9), 128.7 (C-16), 127.1 (C-10), 126.6 (C-14), 120.1 (C-8), 119.5 (C-19), 98.4 (C-20), 56.3 (C-2,6), 29.1 and 28.5 (2×NCH$_3$), 24.6 (C-3,5), 23.6 (C-4). HRMS: Calcd for (C$_{24}$H$_{26}$N$_3$O$_3$+H$^+$): 404.1974. Found: 404.1951.

5-(5,5-Dimethyl-5,6-dihydrophenanthridinium-6-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-
tetrahydropyrimidine-4-olate (16c)

The precipitate was filtered off and washed with cold ethanol.

75%; white crystals; mp 224-226 °C. IR: $\nu_{\text{max}}$ = 3062, 2902, 1672, 1600, 788 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 7.98 (dd, $J$ = 7.9, 1.5 Hz, 1H, H-8), 7.83 (d, $J$ = 7.6 Hz, 1H, H-11), 7.62 (tm, $J$ = 7.6 Hz, 1H, H-7), 7.58 (dd, $J$ = 8.4, 1.0 Hz, 1H, H-5), 7.52-7.40 (m, 4H, H-6,12,13,14), 6.48 (s, 1H, H-16), 3.41 (s, 6H, H-2,3), 3.37 (s, 3H, NCH$_3$), 3.29 (s, 3H, NCH$_3$). $^{13}$C NMR (CDCl$_3$): 166.9 and 163.9 (C-18,22), 154.3 (C-20), 143.6 (C-4), 131.4 (C-7), 130.7 (C-10,15), 130.5, 130.3, 130.0 and 129.8 (C-6,12,13,14), 129.9 (C-9), 127.6 (C-8), 123.7 (C-11), 118.4 (C-5), 79.6 (C-16), 78.6 (C-17), 51.1 (C-2,3), 28.8 and 28.1 (2×NCH$_3$). HRMS: Caled for (C$_{21}$H$_{25}$N$_3$O$_3$+H$^+$): 364.1661. Found: 364.1639.
[2-(2-Methyl-3-oxo-5-pyrrolidin-1-yl-2,3-dihydropyridazin-4-yl)benzylidene]malononitrile (17a)

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (eluent: chloroform - acetone 99:1). 87%; yellow foam; mp 67-68 °C. IR: \( \nu_{\text{max}} = 2950, 2870, 2226, 1590, 756 \text{ cm}^{-1} \). \(^1\)H NMR (DMSO-\(d_6\)): 8.26 (s, 1H, H-18), 8.03 (dm, \( J = 7.7 \text{ Hz} \), 1H, H-16), 7.89 (s, 1H, H-7), 7.62 (tm, \( J = 7.7 \text{ Hz} \), 1H, H-14), 7.54 (tm, \( J = 7.7 \text{ Hz} \), 1H, H-15), 7.30 (dm, \( J = 7.7 \text{ Hz} \), 1H, H-13), 3.56 (s, 3H, NCH\(_3\)), 3.02-2.87 (m, 4H, H-2,5), 1.85-1.53 (m, 4H, H-3,4). \(^{13}\)C NMR (DMSO-\(d_6\)): 162.4 (C-18), 159.6 (C-10), 145.2 (C-6), 138.6 (C-12), 127.7 (C-13), 132.4 (C-14), 132.1 (C-17), 129.9 (C-7), 127.9 (C-15), 127.1 (C-16), 114.1 and 113.1 (C-20,21), 106.9 (C-11), 82.2 (C-19), 50.1 (C-2,5), 39.5 (NCH\(_3\)), 24.9 (C-3,4). HRMS: Calcd for (C\(_{19}\)H\(_{17}\)N\(_5\)O+H\(^+\)) : 332.1511. Found: 332.1499.

[2-(2-Methyl-3-oxo-5-piperidin-1-yl-2,3-dihydropyridazin-4-yl)benzylidene]malononitrile (17b)

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (eluent: chloroform - acetone 99:1). 84%; yellow foam; mp 154-156 °C. IR: \( \nu_{\text{max}} = 2938, 2850, 2226, 1628, 758 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 8.25 (dm, \( J = 8.0 \text{ Hz} \), 1H, H-17), 7.73 (s, 1H, H-8), 7.70 (s, 1H, H-19), 7.65 (tm, \( J = 7.8 \text{ Hz} \), 1H, H-15), 7.50 (ddm, \( J = 8.0, 7.8 \text{ Hz} \), 1H, H-16), 7.44 (dm, \( J = 7.8 \text{ Hz} \), 1H, H-14), 3.75 (s, 3H, NCH\(_3\)), 3.00-2.85 (m, 4H, H-2,6), 1.58-1.34 (m, 6H, H-3,4,5). \(^{13}\)C NMR (CDCl\(_3\)) : 160.9 (C-19), 160.8 (C-11), 150.8 (C-7), 138.5 (C-13), 134.7 (C-15), 132.5 (C-14), 131.7 (C-8), 130.4 (C-18), 129.5 (C-16), 129.1 (C-17), 115.5 (C-12), 114.5 and 113.1 (C-21,22), 84.0 (C-20), 50.8 (C-2,6), 40.8 (NCH\(_3\)), 26.3 (C-3,5), 24.3 (C-4). HRMS: Calcd for (C\(_{20}\)H\(_{19}\)N\(_5\)O+H\(^+\)) : 346.1668. Found: 346.1652.
The precipitate was filtered off and washed with cold ethanol.
96%; yellow crystals; mp 199-202 °C. IR: \( \nu_{\text{max}} = 3056, 3024, 2970, 2922, 2226, 1590, 750 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 8.22 (dm, \( J = 8.0 \text{ Hz}, 1\text{H}, \text{H-14} \)), 7.76 (s, 1H, H-16), 7.74 (s, 1H, H-5), 7.61 (tm, \( J = 7.7 \text{ Hz}, 1\text{H}, \text{H-12} \)), 7.50 (ddm, \( J = 8.0, 7.7 \text{ Hz}, 1\text{H}, \text{H-13} \)), 7.38 (dm, \( J = 7.7 \text{ Hz}, 1\text{H}, \text{H-11} \)), 3.74 (s, 3H, NCH\(_3\)), 2.68 (s, 6H, H-2,3). \(^{13}\)C NMR (CDCl\(_3\)): 161.0 (C-16), 160.7 (C-8), 149.9 (C-4), 138.9 (C-10), 134.2 (C-12), 132.9 (C-11), 131.6 (C-15), 130.3 (C-5), 129.4 (C-13), 128.9 (C-14), 114.1 és 113.1 (C-18,19), 111.8 (C-9), 84.2 (C-17), 42.3 (C-2,3), 40.6 (NCH\(_3\)). HRMS: Calcd for (C\(_{17}\)H\(_{15}\)N\(_5\)O\(_+\)H\(_+\)): 306.1355. Found: 306.1345.

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (chloroform - ethyl acetate 4:3).
63%; yellow foam; mp 211 °C. IR: \( \nu_{\text{max}} = 3060, 2862, 1686, 1612, 1584, 858, 742 \text{ cm}^{-1} \). \(^1\)H NMR (DMSO-d\(_6\)): 8.62 (dm, \( J = 7.9 \text{ Hz}, 1\text{H}, \text{H-16} \)), 8.02-7.93 (m, 4H, H-22,23,24,25), 7.86 (s, 1H, H-7), 7.65 (s, 1H, H-18), 7.55 (td, \( J = 7.6, 1.4 \text{ Hz}, 1\text{H}, \text{H-14} \)), 7.48 (tm, \( J = 7.6, 1.4 \text{ Hz}, 1\text{H}, \text{H-15} \)), 7.33 (dd, \( J = 7.6, 1.4 \text{ Hz}, 1\text{H}, \text{H-13} \)), 3.57 (s, 3H, NCH\(_3\)), 2.96-2.83 (m, 4H, H-2,5), 1.68-1.46 (m, 4H, H-3,4). \(^{13}\)C NMR (DMSO-d\(_6\)): 189.5 and 188.2 (C-20,27), 159.6 (C-10), 145.2 (C-6), 144.4 (C-18), 141.8 and 139.4 (C-21,26), 139.6 (C-12), 135.9 (C-23,24), 132.6 (C-17), 132.3 (C-13), 131.4 (C-14), 131.3 (C-16), 129.7 (C-7), 129.0 (C-19), 127.1 (C-15), 123.0 (C-22,25), 108.0 (C-11), 50.2 (C-2,5), 39.1 (NCH\(_3\)), 26.1 (C-3,4). HRMS: Calcd for (C\(_{25}\)H\(_{21}\)N\(_3\)O\(_3\)H\(_+\)): 412.1661. Found: 412.1647.
2-{2-[2-Methyl-3-oxo-5-(piperidin-1-yl)-2,3-dihydropyridazin-4-yl]benzylidene}indane-1,3-dione (18b)

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (eluent: chloroform).

65%; yellow foam; mp 85 °C. IR: ν_{max} = 3064, 2928, 1686, 1620, 1584, 740 cm^{-1}. ^1H NMR (CDCl₃): 8.93-8.88 (m, 1H, H-17), 8.04-7.99 (m, 1H, H-24 or 25), 7.99-7.94 (m, 1H, H-24 or 25), 7.85-7.79 (m, 2H, H-23,26), 7.81 (s, 1H, H-19), 7.70 (s, 1H, H-8), 7.61 (td, J = 7.5, 1.3 Hz, 1H, H-15), 7.52-7.46 (m, 2H, H-14,16), 3.76 (s, 3H, NCH₃), 2.97-2.75 (m, 4H, H-2,6), 1.41-1.16 (m, 6H, H-3,4,5). ^13C NMR (CDCl₃): 191.0 and 189.4 (C-21,28), 161.4 (C-11), 150.6 (C-7), 147.1 (C-19), 143.2 and 140.7 (C-22,27), 139.6 (C-13), 136.0 and 135.8 (C-23,26), 133.5 (C-15), 133.2 (C-17), 132.1 (C-14), 132.0 (C-8), 131.3 (C-18), 129.3 (C-20), 128.6 (C-16), 124.1 and 123.9 (C-24,25), 117.3 (C-12), 50.5 (C-2,6), 40.7 (NCH₃), 26.2 (C-3,5), 24.4 (C-4). HRMS: Calcd for (C_{26}H_{23}N_{3}O_{3}+H^+): 426.1817. Found: 426.1802.

2-{2-[5-(Dimethylamino)-2-methyl-3-oxo-2,3-dihydropyridazin-4-yl]benzylidene}-1H-indene-1,3(2H)-dione (18c)

The solvent was evaporated in vacuo, and the oily residue was purified by flash column chromatography on silica gel (eluent: chloroform).

63%; yellow foam; mp 80 °C. IR: ν_{max} = 3060, 2924, 2860, 1686, 1614, 1588, 740 cm^{-1}. ^1H NMR (CDCl₃): 8.78-8.73 (m, 1H, H-14), 8.04-7.95 (m, 2H, H-20,23), 7.84-7.80 (m, 2H, H-21,22), 7.78 (s, 1H, H-16), 7.69 (s, 1H, H-5), 7.59-7.54 (m, 1H, H-12), 7.51-7.44 (m, 2H, H-11,13), 3.75 (s, 3H, NCH₃), 2.58 (s, 6H, H-2,3). ^13C NMR (CDCl₃): 190.9 and 189.5 (C-18,25), 161.3 (C-8), 149.8 (C-4), 146.6 (C-16), 143.1 and 140.7 (C-19,24), 139.7 (C-10), 136.1 and 135.9 (C-21,22), 133.2 (C-14), 132.9 (C-12), 132.5 (C-11), 132.4 (C-15), 130.6 (C-5), 129.5 (C-17), 128.3 (C-13), 124.0 and 123.9 (C-20,23), 113.2 (C-9), 41.9 (C-2,3), 40.6 (NCH₃). HRMS: Calcd for (C_{26}H_{23}N_{3}O_{3}+H^+): 386.1504. Found: 386.1503.
Synthesis of azocine derivatives (19a,c, 20a, 21a)

The vinyl or zwitterionic compound (1 mmol) was dissolved in dry dimethyl sulphoxide (5 mL) and the reaction mixture was heated at 110 °C for 8 h (19a) or 30 min (20a, 21a) or at 160 °C for 72 h (19c) under argon atmosphere. When the reaction was complete (monitored by TLC, eluent: dichloromethane - n-hexane 1:1 for 19a; ethyl acetate for 19c, 20a, 21a), the mixture was cooled. The solvent was evaporated in a lyophilizator under reduced pressure. The solid residue was purified by flash column chromatography (eluent: dichloromethane - n-hexane 1:1 for 19a,c; ethyl acetate for 20a; toluene – ethanol - aq 25% NH$_3$ solution 20:1:0.1 for 21a).

6,7,8,8a-Tetrahydrodibenzo[e,g]pyrrolo[1,2-a]azocine-9,9(10H)-dicarbonitrile (19a)

![Chemical structure of 19a]

94%; white crystals; mp 168-169 °C. IR: $\nu_{\text{max}}$ = 3058, 2950, 2862, 2246, 1592, 754 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 7.49-7.35 (m, 3H, H-13,14,15), 7.34-7.24 (m, 2H, H-8,16), 7.01 (dd, $J = 7.6, 1.7$ Hz, 1H, H-10), 6.87-6.78 (m, 2H, H-7,9), 4.27 (dd, $J = 8.1, 2.6$ Hz, 1H, H-2), 3.98-3.88 (m, 1H, H-5), 3.64 (d, $J = 13.4$ Hz, 1H, H-18), 3.49-3.38 (m, 1H, H-5), 2.60-2.43 (m, 1H, H-4), 2.08-1.93 (m, 1H, H-4), 2.37-2.13 (m, 2H, H-3). $^{13}$C NMR (CDCl$_3$): 146.2 (C-6), 144.8 (C-12), 136.2 (C-10), 131.5 (C-13), 130.2 (C-16), 130.0 (C-14), 129.9 (C-8), 129.6 (C-17), 128.6 (C-15), 125.2 (C-11), 119.1 (C-9), 116.6 and 114.9 (C-20,21), 116.2 (C-7), 61.8 (C-2), 53.3 (C-5), 40.9 (C-19), 40.1 (C-18), 30.8 (C-3), 22.7 (C-4). Anal. calcd for C$_{20}$H$_{16}$N$_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.12; H, 5.68; N, 13.97. HRMS: Calcd for (C$_{20}$H$_{17}$N$_3$H$^+$): 300.1501. Found: 300.1490.

5-Methyl-5,8-dihydrodibenzo[b,d]azocine-7,7(6H)-dicarbonitrile (19c)

![Chemical structure of 19c]

23%; yellow crystals; mp 147-148 °C. IR: $\nu_{\text{max}}$ = 3062, 2950, 2246, 1596, 1494, 752 cm$^{-1}$. $^1$H NMR (CDCl$_3$): 7.46-7.30 (m, 5H, H-6,11,12,13,14), 7.11 (dd, $J = 7.6, 1.8$ Hz, 1H, H-8), 6.96 (ddd, $J = 7.6, 7.2, 1.2$ Hz, 1H, H-7), 6.92 (dm, $J = 8.5$ Hz, 1H, H-5), 4.11 (d, $J = 15.1$ Hz, 1H, H-2), 3.59 (dd, $J = 15.1, 0.9$ Hz, 1H, H-2), 3.42 (d, $J = 13.4$ Hz, 1H, H-16), 3.36 (d, $J = 13.4$ Hz, 1H, H-16), 3.18 (s, 3H, H-3). $^{13}$C NMR (CDCl$_3$): 147.4 (C-4), 144.4 (C-10), 135.9 (C-8), 131.5 (C-11), 131.0 (C-14), 130.2 (C-6), 130.0 (C-12), 129.9 (C-15), 128.6 (C-13), 127.6 (C-9), 120.8 (C-7), 116.8 (C-5), 116.4 and 114.2 (C-18,19), 58.8 (C-2), 44.5 (C-3), 39.2 (C-16), 35.5 (C-17). HRMS: Calcd for (C$_{18}$H$_{15}$N$_3$H$^+$): 274.1344. Found: 274.1335.
6,7,8a-Tetrahydro-10H-spiro[dibenzo[e,g]pyrrolo[1,2-a]azocin-9,2'-indene]-1',3'-dione (20a)

98%; yellow crystals; mp 100-115 °C. IR: \( \nu_{\text{max}} = 3058, 2854, 1736, 1702, 1626, 1594, 760 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 8.02-7.94 (m, 2H, H-22,25), 7.90-7.82 (m, 2H, H-23,24), 7.49 (dd, \( J = 7.6, 1.4 \text{ Hz} \), 1H, H-13), 7.40 (td, \( J = 7.5, 1.5 \text{ Hz} \), 1H, H-14), 7.35-7.26 (m, 2H, H-8,15), 7.04 (dd, \( J = 7.5, 1.4 \text{ Hz} \), 1H, H-16), 7.00 (dd, \( J = 7.8, 1.8 \text{ Hz} \), 1H, H-10), 6.81 (dm, \( J = 8.6 \text{ Hz} \), 1H, H-7), 6.75 (td, \( J = 7.4 \text{ Hz} \), 1H, H-9), 4.45 (dd, \( J = 7.7, 2.6 \text{ Hz} \), 1H, H-2), 3.73-3.64 (m, 1H, H-5\(_x\)), 3.55 (d, \( J = 13.6 \text{ Hz} \), 1H, H-18\(_x\)), 3.35-3.27 (m, 1H, H-5\(_y\)), 2.73 (d, \( J = 13.6 \text{ Hz} \), 1H, H-18\(_y\)), 2.09-1.96 (m, 1H, H-3\(_x\)), 1.52-1.42 (m, 1H, H-3\(_y\)), 1.87-1.73 (m, 1H, H-4\(_x\)), 1.72-1.59 (m, 1H, H-4\(_y\)). \(^{13}\)C NMR (CDCl\(_3\)): 204.3 and 201.2 (C-20,27), 146.8 (C-6), 145.2 (C-12), 142.9 and 142.6 (C-21,26), 136.4 (C-23,24), 135.9 (C-10), 133.7 (C-17), 131.2 (C-13,16), 129.4 and 126.7 (C-8,15), 128.4 (C-14), 125.9 (C-11), 123.5 (C-22,25), 117.1 (C-9), 115.1 (C-7), 61.1 (C-2), 56.4 (C-19), 51.8 (C-5), 37.5 (C-18), 30.4 (C-3), 23.3 (C-4). HRMS: Calcd for (C\(_{26}\)H\(_{21}\)NO\(_2\)): 379.1572. Found: 379.1549.

After purification by column flash chromatography, the oily residue was treated with \( n \)-hexane to obtain white crystals. 28%; white crystals; mp 135-138 °C. IR: \( \nu_{\text{max}} = 3060, 2956, 1682, 1594, 752 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): 7.46 (dd, \( J = 7.7, 1.3 \text{ Hz} \), 1H, H-13), 7.40 (td, \( J = 7.7, 1.3 \text{ Hz} \), 1H, H-14), 7.33-7.22 (m, 2H, H-8,15), 6.96 (dm, \( J = 7.7 \text{ Hz} \), 1H, H-16), 6.93 (dd, \( J = 7.6, 1.7 \text{ Hz} \), 1H, H-10), 6.78 (dm, \( J = 8.5 \text{ Hz} \), 1H, H-7), 6.74 (tm, \( J = 7.6 \text{ Hz} \), 1H, H-9), 4.51 (dd, \( J = 7.8, 4.3 \text{ Hz} \), 1H, H-2), 3.75 (d, \( J = 13.6 \text{ Hz} \), 1H, H-18\(_x\)), 3.72-3.63 (m, 1H, H-5\(_y\)), 3.38-3.29 (m, 1H, H-5\(_y\)), 3.34 (s, 3H, NCH\(_3\)), 3.32 (s, 3H, NCH\(_3\)) 2.89 (d, \( J = 13.6 \text{ Hz} \), 1H, H-18\(_y\)), 2.09-1.96 (m, 1H, H-3\(_y\)), 1.52-1.42 (m, 1H, H-3\(_y\)), 1.87-1.73 (m, 1H, H-4\(_y\)), 1.72-1.59 (m, 1H, H-4\(_y\)). \(^{13}\)C NMR (CDCl\(_3\)): 170.9 and 169.5 (C-20,24), 152.0 (C-22), 146.6 (C-6), 145.1 (C-12), 135.5 (C-10), 132.9 (C-17), 131.7 (C-16), 131.1 (C-13), 129.5 (C-8), 128.8 (C-14), 126.6 (C-15), 126.3 (C-11), 117.5 (C-9), 115.9 (C-7), 63.0 (C-2), 55.0 (C-19), 52.9 (C-5), 41.6 (C-18), 31.2 (C-3), 29.6 and 29.1 (2\( \times \)NCH\(_3\)), 23.2 (C-4). HRMS: Calcd for (C\(_{26}\)H\(_{23}\)N\(_3\)O\(_3\)+H\(^+\)): 390.1818. Found: 390.1797.

1',3'-Dimethyl-6,7,8a-tetrahydro-2'H,10H-spiro[dibenzo[e,g]pyrrolo[1,2-a]azocin-9,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione (21a)
Microwave assisted ring closure reaction of 13a

\[(2\text{-Pyrrolidin-1-ylbiphenyl-2-yl)methylidene}]malononitrile (13a) (500.0 mg, 1.67 mmol) was weighed into a microwave tube (10 mL) and heated at 100 °C for 30 min in a microwave apparatus (300 W). When the reaction was complete as monitored by TLC (eluent: dichloromethane), the mixture was cooled and purified by flash column chromatography on silica gel (eluent: n-hexane - ethyl acetate 5:1). Two products were obtained: 6,7,8,8a-tetrahydrodibenzo[e,g]pyrrolo[1,2-a]azocin-9,9(10H)-dicarbonitrile (19a, 23%) and phenanthridine (22, 35%).

Phenanthridine (22)

35%; beige crystals; mp 105 °C. The NMR spectra are consistent with the literature data. HRMS: Calcd for (C_{13}H_{9}N+H^+): 180.0813. Found: 180.0804.

Synthesis of 23a, 24a, 25, 26 pyridazinones

The vinyl compound (1.70 mmol) was dissolved in dry dimethyl sulphoxide (7 mL) and the solution was heated at 160 °C under argon atmosphere (6 h for 18a; 24 h for 17a; 48 h for 17b, 18b, 18c; 96 h for 17c). When the reaction was complete (monitored by TLC, eluent: ethyl acetate), the mixture was cooled, then the solvent was evaporated under reduced pressure in a liophilizator. The solid residue was purified by flash column chromatography on silica gel (eluent: toluene - acetone 9:1 for 23a, 24a; toluene - acetone 15:1 for 25, 26).

2-Methyl-1-oxo-2,6,7,8,8a,10-hexahydropyridazino[4,5-a]pyrrolo[1,2-c][3]benzazocine-9,9(1H)-dicarbonitrile (23a)

The product was recrystallized from isopropanol.

38%; white crystals; mp 250 °C. IR: \(\nu_{\text{max}} = 2950, 2908, 2862, 2246, 1592, 754 \text{ cm}^{-1}\). \(^{1}H\) NMR (CDCl\(_3\)): 7.68 (s, 1H, H-7), 7.64-7.58 (m, 1H, H-13), 7.48-7.34 (m, 3H, H-14, 15, 16), 4.21 (dd, \(J = 7.9, 3.5 \text{ Hz}\), 1H, H-2), 4.07-3.95 (m, 1H, H-5\(_{x}\)), 3.72 (s, 3H, NCH\(_3\)), 3.69-3.59 (m, 1H, H-5\(_{y}\)), 3.54 (d, \(J = 12.9 \text{ Hz}\), 1H, H-18\(_{x}\)), 3.47 (d, \(J = 12.9 \text{ Hz}\), 1H, H-18\(_{y}\)), 2.58-2.41 (m, 1H, H-4\(_{x}\)), 2.38-2.18 (m, 2H, H-3), 2.12-1.97 (m, 1H, H-4\(_{y}\)). \(^{13}C\) NMR (CDCl\(_3\)): 161.4 (C-10), 144.9 (C-6), 135.0 (C-12), 133.7 (C-13), 130.6 (C-16), 130.0 (C-7), 129.9 (C-15), 129.3 (C-17), 129.0 (C-14), 115.9 and 114.1 (C-20, 21), 112.7 (C-11), 61.1 (C-2), 53.2 (C-
S16

5), 40.9 (NCH₃), 40.3 (C-18), 40.2 (C-19), 30.4 (C-3), 23.0 (C-4). HRMS: Calcd for (C₁₉H₁₇N₃O+H⁺): 332.1511. Found: 332.1499.

2'-Methyl-2',6',7',8',8a',10'-hexahydro-1'H-spiro[inden-2,9'-pyridazino[4,5-a]pyrrolo[1,2-c][3]benzazocine]-1,1',3-trione (24a)

67%; yellow crystals; mp 257-259 °C. IR: v_max = 3060, 2930, 1700, 1590, 848, 756 cm⁻¹. ¹H NMR (DMSO-d₆): 8.08-7.99 (m, 4H, H-22,23,24,25), 7.86 (s, 1H, H-7), 7.45-7.39 (m, 1H, H-13), 7.30-7.21 (m, 2H, H-14,15), 7.12-7.07 (m, 1H, H-16), 4.18 (dd, J = 8.0, 2.8 Hz, 1H, H-2), 3.70-3.60 (m, 1H, H-5ₓ), 3.57 (s, 3H, NCH₃), 3.54-3.45 (m, 1H, H-5ᵧ), 3.14 (d, J = 13.6 Hz, 1H, H-18ₓ), 2.99 (d, J = 13.6 Hz, 1H, H-18ᵧ), 1.84-1.60 (m, 2H, H-3ₓ,4ₓ), 1.43-1.29 (m, 1H, H-4ᵧ), 1.21-1.11 (m, 1H, H-3ᵧ). ¹³C NMR (DMSO-d₆): 202.8 and 199.1 (C-20,27), 156.0 (C-10), 143.9 (C-6), 141.5 and 141.0 (C-21,26), 136.7 and 136.4 (C-23,24), 134.9 (C-12), 133.0 (C-17), 132.4 (C-13), 130.8 (C-16), 130.0 (C-7), 126.4 (C-15), 125.9 (C-14), 123.5 and 122.9 (C-22,25), 109.5 (C-11), 59.3 (C-2), 53.7 (C-19), 51.0 (C-5), 39.4 (NCH₃), 35.8 (C-18), 28.3 (C-3), 22.2 (C-4). HRMS: Calcd for (C₂₅H₂₁N₃O₃+H⁺): 412.1661. Found: 412.1648.

2-Methylpyridazino[4,5-c]isoquinolin-1(2Η)-one (25)

orange crystals; mp 133 °C. The NMR spectra are consistent with the literature data.⁹ HRMS: Calcd for (C₁₂H₉N₃O+H⁺): 212.0824. Found: 212.0815.

2-Methyl-1-oxo-1,2-dihydrobenzo[f]phenalazine-5-carbonitrile (26)

17b → 25 (30%) + 26 (14%)
yellow crystals; mp 181-182 °C. IR: $\nu_{\text{max}} = 3416, 2922, 2854, 2226, 1642, 754 \text{ cm}^{-1}$. $^1$H NMR (CDCl$_3$): 9.98 (dm, $J = 8.6$ Hz, 1H, H-9), 9.05 (s, 1H, H-14), 8.46 (s, 1H, H-3), 8.23 (dm, $J = 8.0$ Hz, 1H, H-12), 8.01 (ddm, $J = 8.6, 8.0$ Hz, 1H, H-10), 7.92 (tm, $J = 8.0$ Hz, 1H, H-11), 3.86 (s, 3H, NCH$_3$). $^{13}$C NMR (CDCl$_3$): 158.5 (C-6), 142.3 (C-14), 133.0 (C-3), 132.2 (C-10), 132.1 (C-13), 130.4 (C-8), 129.8 (C-12), 129.6 (C-11), 127.9 (C-2), 127.5 (C-9), 122.3 (C-7), 116.0 (CN), 104.9 (C-1), 40.4 (NCH$_3$). HRMS: Calcd for (C$_{14}$H$_9$N$_3$O$^+$$H^+$): 236.0824. Found: 236.0813.

Table of Characteristic NMR Data

**Vinyl derivatives (13, 14, 17, 18)**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_H$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13a</td>
<td>CDCl$_3$ 7.58</td>
</tr>
<tr>
<td>13b</td>
<td>CDCl$_3$ 7.60</td>
</tr>
<tr>
<td>13c</td>
<td>CDCl$_3$ 7.57</td>
</tr>
<tr>
<td>14b</td>
<td>CDCl$_3$ 7.82</td>
</tr>
<tr>
<td>17a</td>
<td>DMSO-$d_6$ 8.26</td>
</tr>
<tr>
<td>17b</td>
<td>CDCl$_3$ 7.70</td>
</tr>
<tr>
<td>17c</td>
<td>CDCl$_3$ 7.76</td>
</tr>
<tr>
<td>18a</td>
<td>DMSO-$d_6$ 7.65</td>
</tr>
<tr>
<td>18b</td>
<td>CDCl$_3$ 7.81</td>
</tr>
<tr>
<td>18c</td>
<td>CDCl$_3$ 7.78</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_C$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13a</td>
<td>CDCl$_3$ 162.4</td>
</tr>
<tr>
<td>13b</td>
<td>CDCl$_3$ 163.1</td>
</tr>
<tr>
<td>13c</td>
<td>CDCl$_3$ 162.8</td>
</tr>
<tr>
<td>14b</td>
<td>CDCl$_3$ 148.3</td>
</tr>
<tr>
<td>17a</td>
<td>DMSO-$d_6$ 162.4</td>
</tr>
<tr>
<td>17b</td>
<td>CDCl$_3$ 160.9</td>
</tr>
<tr>
<td>17c</td>
<td>CDCl$_3$ 161.0</td>
</tr>
<tr>
<td>18a</td>
<td>DMSO-$d_6$ 144.4</td>
</tr>
<tr>
<td>18b</td>
<td>CDCl$_3$ 147.1</td>
</tr>
<tr>
<td>18c</td>
<td>CDCl$_3$ 146.6</td>
</tr>
</tbody>
</table>

**6-Membered ring systems (15, 16)**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_H$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15a</td>
<td>CDCl$_3$ 6.66</td>
</tr>
<tr>
<td>15c</td>
<td>CDCl$_3$ 6.07</td>
</tr>
<tr>
<td>16a</td>
<td>MeOD 6.29</td>
</tr>
<tr>
<td>16b</td>
<td>CDCl$_3$ 7.49</td>
</tr>
<tr>
<td>16c</td>
<td>CDCl$_3$ 6.48</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_C$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15a</td>
<td>CDCl$_3$ 102.6</td>
</tr>
<tr>
<td>15c</td>
<td>CDCl$_3$ 81.5</td>
</tr>
<tr>
<td>16a</td>
<td>MeOD 76.6</td>
</tr>
<tr>
<td>16b</td>
<td>CDCl$_3$ 119.5</td>
</tr>
<tr>
<td>16c</td>
<td>CDCl$_3$ 79.6</td>
</tr>
</tbody>
</table>

**8-Membered ring systems (19-21, 23, 24)**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_H$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19a</td>
<td>CDCl$_3$ 3.64 and 3.38</td>
</tr>
<tr>
<td>19c</td>
<td>CDCl$_3$ 3.42 and 3.36</td>
</tr>
<tr>
<td>20a</td>
<td>CDCl$_3$ 3.55 and 2.73</td>
</tr>
<tr>
<td>21a</td>
<td>CDCl$_3$ 3.75 and 2.89</td>
</tr>
<tr>
<td>23a</td>
<td>CDCl$_3$ 3.54 and 3.47</td>
</tr>
<tr>
<td>24a</td>
<td>DMSO-$d_6$ 3.14 and 2.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_C$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19a</td>
<td>CDCl$_3$ 40.1</td>
</tr>
<tr>
<td>19c</td>
<td>CDCl$_3$ 39.2</td>
</tr>
<tr>
<td>20a</td>
<td>CDCl$_3$ 37.5</td>
</tr>
<tr>
<td>21a</td>
<td>CDCl$_3$ 41.6</td>
</tr>
<tr>
<td>23a</td>
<td>CDCl$_3$ 40.3</td>
</tr>
<tr>
<td>24a</td>
<td>DMSO-$d_6$ 35.8</td>
</tr>
</tbody>
</table>

Solvent $\delta_C$ (ppm)
References: