An Efficient Synthesis of 2,3-Dihydro-1*H*-pyrimido[1,2-*a*]quinoxaline 6-Oxides

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Abstract : 5-Substituted 2,3-dihydro-1*H*-pyrimido[1,2-*a*]quinoxaline 6-oxides **1a**–**f** were synthesized by ring closure of *N*-acyl-*N*′-(*o*-nitroaryl)-1,3-propanediamines **2** with ethyl polyphosphate (PPE) or trimethylsilyl polyphosphate (PPSE) to the corresponding 2-substituted 1-(*o*-nitroaryl)-1,4,5,6-tetrahydropyrimidines **3**, followed by spontaneous heterocyclization. The method was extended to the synthesis of the homologous 6-aryl-1,2,3,4-tetrahydro-1,3-diazepino[1,2-*a*]quinoxaline 7-oxide (**1g**).

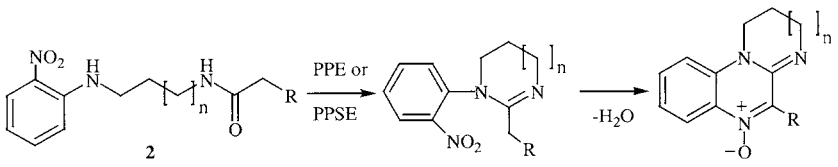
Key words: heterocycles, nitrogen, cyclizations, antibiotics, antitumor agents

2,3-Dihydro-1*H*-pyrimido[1,2-*a*]quinoxaline 6-oxides are of interest due to the biological activity shown by some of their derivatives. Some suitably substituted derivatives possess antineoplastic activity,[1] specially against hypoxic tumors. Other pyrimidoquinoxaline 6-oxides have been employed as antiamoebic[2] and antianaerobic agents.[3]

The reported synthetic procedure for 5-aryl-2,3-dihydro-1*H*-pyrimido[1,2-*a*]quinoxaline 6-oxides[2,3] involves a displacement-cyclization reaction of 2-benzyl-1,4,5,6-tetrahydropyrimidines with *o*-nitrohalobenzenes and leads in general to poor yields (30% or less) of the desired heterocycles. To our knowledge, no synthetic procedure has been reported for the preparation of 5-alkyl derivatives.

The present paper describes an improved approach to the synthesis of 5-aryl derivatives **1a**–**d** from easily available starting materials with high yields. 5-Arylalkyl and alkyl derivatives **1e**,**f**, respectively, were prepared by the same procedure. The procedure was extended to the synthesis of the homologous 1,2,3,4-tetrahydro-6-phenyl-1,3-diazepino[1,2-*a*]quinoxaline 7-oxide (**1g**), a condensed nitrogen heterocycle which, to our knowledge, has not been previously described in the literature.

The synthetic procedure for the 5-substituted 2,3-dihydro-1*H*-pyrimido[1,2-*a*]quinoxaline 6-oxides **1a**–**f** is displayed in Scheme 1. The starting materials, *N*-acyl-*N*′-(*o*-nitroaryl)trimethylenediamines **2** (n = 1), are easily synthesized by acylation of the corresponding *N*-(*o*-nitrophenyl)-1,3-propanediamines. Treatment of arylacetyl derivatives **2a**–**d** with ethyl polyphosphate (PPE) leads to unstable 2-benzyl-1-(*o*-nitrophenyl)-1,4,5,6-tetrahydropyrimidines **3a**–**d** which were detected by TLC but could not be isolated as pure compounds due to spontaneous in situ cyclization leading to *N*-oxides **1** (Table 1). Heterocyclization of intermediates **3a**–**d** was achieved in ca. 24 hours and was easily monitored by TLC.



2 3 1

Compounds **1-3**	n	R	Yield (%)
a	1	C_6H_5	91
b	1	*p*-ClC_6H_4	86
c	1	*p*-$NO_2C_6H_4$	78
d	1	*p*-$CH_3OC_6H_4$	85
e	1	$CH_2C_6H_5$	49
f	1	CH_3	48
g	2	*p*-ClC_6H_4	25

Scheme 1

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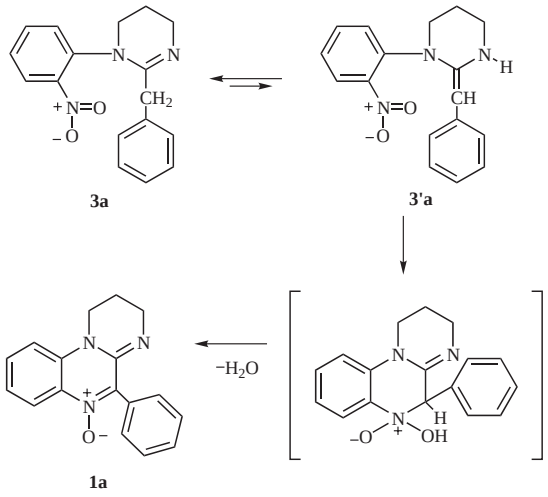
From a mechanistic point of view, it can be considered that the reaction results from an initial nucleophilic attack of the benzylic carbon of the amidine **3** (or its tautomeric form **3′**) on the nitro group, followed by proton transfer and dehydration (Scheme 2). A similar mechanism was proposed by Strauss[4] for the reaction of phenylacetamidine with *o*-halonitrobenzenes leading to quinoxaline *N*-oxides.



Scheme 2

Application of our procedure to alkanoyl derivatives **2e**,**f** leads to the corresponding *N*-oxides **1e**,**f** (Table 1). Treatment of such precursors with trimethylsilyl polyphosphate (PPSE)[5] afforded the corresponding 1,4,5,6-tetrahydropyrimidines **3e**,**f**, which were isolated and characterized spectroscopically (^{1}H NMR and mass spectrometry). In contrast to 2-arylmethyl derivatives **3a**–**d**, disappearance of the amidines in this case takes several days for completion. The observed difference in heterocyclization rates can be related to the lower acidity of the methylene group adjacent to the amidine moiety in compounds **3e**,**f** when compared to the 2-benzyl derivatives **3a**–**d**. The requirement of a relatively acidic α-methylene was also pointed out by Strauss[4] to account for the lack of reactivity of propionamidine towards 2,4-dinitrofluorobenzene. Due to the low heterocyclization rates of compounds **3e**,**f**, conversion to the corresponding *N*-oxides is accompanied to some extent by amidine hydrolysis. This collateral reaction regenerates the corresponding amino amides **2e**,**f**, thus diminishing reaction yields. In fact, when *N*-acetyl-*N′*-(*o*-nitrophenyl)-1,3-propanediamine (**2**, n = 1, R = H) was treated with PPSE in order to obtain

Table 1 Compounds **1a**–**g** Prepared

Product[a]	Mp (°C)	MS (*m*/*z*, M^{+})	Yield (%)	^{1}H NMR ($CDCl_3$/TMS)[b] δ, *J* (Hz)
1a	209–210 (EtOH)	277	91	8.37 (dd, 1 H_{arom}, J_1 = 8.2, J_2 = 1.5), 7.40–7.59 (m, 6 H_{arom}), 7.16 (dt, 1 H_{arom}, J_1 = 8.2, J_2 = 1.0), 7.07 (d, 1 H_{arom}, *J* = 8.2), 3.88 (t, 2 H, *J* = 6.2, CH_2N), 3.58 (t, 2 H, *J* = 5.4, CH_2N), 2.02–2.06 (m, 2 H, $CH_2CH_2CH_2$)
1b	231–233 (EtOH)	311, 313	86	8.36 (dd, 1 H_{arom}, J_1 = 7.8, J_2 = 1.5), 7.57 (dd, 2 H_{arom}, J_1 = 8.8, J_2 = 2.1), 7.51 (dt, 1 H_{arom}, J_1 = 8.5, J_2 = 1.5), 7.44 (dd, 2 H_{arom}, J_1 = 8.8, J_2 = 2.1), 7.15–7.20 (m, 1_{arom} H), 7.07 (d, 1 H_{arom}, *J* = 8.5), 3.88 (t, 2 H, *J* = 6.2, CH_2N), 3.58 (t, 2 H, *J* = 5.5, CH_2N), 2.00–2.08 (m, 2 H,$CH_2CH_2CH_2$)
1c	206–208 (EtOH)	322	78	8.30–8.36 (m, 3 H_{arom}), 7.80 (dd, 2 H_{arom}, J_1 = 6.9, J_2 = 2.0), 7.55 (dt, 1 H_{arom}, J_1 = 7.2, J_2 = 1.5), 7.20 (dt, 1 H_{arom}, J_1 = 8.4, J_2 = 1.0), 7.11 (d, 1 H_{arom}, *J* = 8.4), 3.91 (t, 2 H, *J* = 6.2, CH_2N), 3.57 (t, 2 H, *J* = 5.5, CH_2N), 2.05–2.09 (m, 2 H, $CH_2CH_2CH_2$)
1d	184–186 (EtOH)	307	85	8.38 (dd, 1 H_{arom}, J_1 = 8.2, J_2 = 1.5), 7.61 (d, 2 H_{arom}, *J* = 9.0), 7.49 (dt, 1 H_{arom}, J_1 = 7.8, J_2 = 1.5), 7.14–7.19 (m, 1 H_{arom}), 7.06 (d, 1 H_{arom}, *J* = 7.8), 6.98 (d, 2 H_{arom}, *J* = 9.0), 3.88 (t, 2 H, *J* = 5.5, CH_2N), 3.83 (s, 3 H, CH_3O), 3.60 (t, 2 H, *J* = 5.5, CH_2N), 2.01–2.09 (m, 2 H, $CH_2CH_2CH_2$)
1e	149–150 (EtOH)	291	49	8.31 (dd, 1 H_{arom}, J_1 = 6.9, J_2 = 1.5), 7.54 (d, 2 H_{arom}, *J* = 8.0), 7.43 (dt, 1 H_{arom}, J_1 = 7.0, J_2 = 1.5), 7.11–7.28 (m, 4 H_{arom}), 6.99 (d, 1 H_{arom}, *J* = 8.2), 4.43 (s, 2 H, $CH_2C_6H_5$), 3.83 (t, 2 H, *J* = 6.2, CH_2N), 3.70 (t, 2 H, *J* = 4.9, CH_2N), 2.05–2.11 (m, 2 H,$CH_2CH_2CH_2$)
1f	179–180 (EtOH)	215	48	8.35 (dd, 1 H_{arom}, J_1 = 8.2, J_2 = 1.5), 7.45 (dt, 1 H_{arom}, J_1 = 7.8, J_2 = 1.5), 7.13–7.19 (m, 1 H_{arom}), 7.03 (d, 1 H_{arom}, *J* = 7.8), 3.84 (t, 2 H, *J* = 6.2, CH_2N), 3.65 (t, 2 H, *J* = 5.5, CH_2N), 2.54 (s, 3 H, CH_3), 2.02–2.06 (m, 2 H, $CH_2CH_2CH_2$)
1g	oil	325, 327	25	8.30 (dd, 1 H_{arom}, J_1 = 8.3, J_2 = 1.3), 7.67 (dd, 2 H_{arom}, J_1 = 8.3, J_2 = 1.7), 7.51–7.54 (m, 1 H_{arom}), 7.45 (dd, 2 H_{arom}, J_1 = 8.3, J_2 = 1.7), 7.16 (t, 1 H_{arom}, *J* = 8.2), 7.08 (d, 1 H_{arom}, *J* = 8.2), 4.08 (t, *J* = 5.6, CH_2N), 3.87 (t, 2 H, *J* = 5.7, CH_2N), 2.18–2.21 (m, 2 H, $CH_2CH_2CH_2CH_2$), 2.01–2.04 (m, 2 H, $CH_2CH_2CH_2CH_2$)

[a] Satisfactory microanalyses obtained: C ±0.07, H ±0.06, N ±0.08.
[b] Recorded at 300 MHz, 25 °C.

the 5-unsubstituted pyrimidinoquinoxaline *N*-oxide (**1**, n = 1, R = H), the intermediate amidine (**3**, n = 1, R = H), regenerated the acyl derivative on standing.

In order to explore the applicability of the method to the synthesis of novel amidinoquinoxalines, *N*-(*p*-chlorophenyl)acetyl-*N*′-(*o*-nitroaryl)-1,4-diaminobutane (**2g**) was treated with PPE, yielding the corresponding 1,2-disubstituted-1,3-diazepine **3g**. Heterocyclization of amidine **3g** in chloroform for 36 hours afforded the corresponding *N*-oxide **1g** in modest yields (Table 1).

Melting points were taken on a Büchi capillary apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer with $CDCl_3$ as the solvent. Standard concentration of the samples was 20 mg/mL. Chemical shifts are reported in ppm (δ) relative to TMS as an internal standard. MS (EI) were recorded with a GC-MS Shimadzu QP-1000 spectrometer operating at 20 eV. TLC analyses were carried out on silica gel 60 F_{254} sheets. Column chromatography was performed on silica gel 60 (0.063–0.200 mm). Flash chromatography was performed on silica gel 60 (0.040–0.063 mm), with typically 30–50 g of stationary phase per gram of substance. Reagents, solvents and starting materials were purchased from standard sources and purified according to literature procedures.

N-(*o*-Nitrophenyl)-1,3-propanediamine[6] and *N*-(*o*-nitrophenyl)-1,4-butanediamine[7] were described in the literature.

N-Acyl-*N*′-(*o*-nitrophenyl)-1,*n*-(alkane)diamines 2; General Procedure

The acyl chloride (10 mmol) was added to a $CHCl_3$ solution of the corresponding *N*-(*o*-nitrophenyl)-1,*n*-diamine (10 mmol), followed by aq 4% NaOH (10 mL). The mixture was shaken for 15 min, after which the organic layer was separated, washed with H_2O, dried (Na_2SO_4) and filtered. The solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel using mixtures of $CHCl_3$–EtOAc as eluent.

N-(*o*-Nitrophenyl)-*N*′-phenylacetyl-1,3-propanediamine (2a)

Yield: 79%; mp 79–81 °C (EtOH–H_2O).

^{1}H NMR: δ = 8.15 (dd, 1 H_{arom}, J_1 = 8.7, J_2 = 1.6 Hz), 8.03 (br s, 1 H, NHCO), 7.40–7.43 (m, 1 H_{arom}), 7.23–7.40 (m, 5 H_{arom}), 6.75 (d, 1 H_{arom}, J = 8.1 Hz), 6.63 (dt, 1 H_{arom}, J_1 = 8.7, J_2 = 1.2 Hz), 5.57 (br s, 1 H, N*H*Ar), 3.59 (s, 2 H, CH_2CO), 3.35 (q, 2 H, J = 6.9 Hz, CH_2N), 3.27 (q, 2 H, J = 6.9 Hz, CH_2N), 1.85 (pent, 2 H, J = 6.9 Hz, $CH_2CH_2CH_2$).

MS: m/z = 313 (M^{+}).

Anal. Calcd for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.20; H, 6.15; N, 13.37.

N-(*p*-Chlorophenylacetyl)-*N*′-(*o*-nitrophenyl)-1,3-propanediamine (2b)

Yield: 99%; mp 107–109 °C (EtOH–H_2O).

^{1}H NMR: δ = 8.16 (dd, 1 H_{arom}, J_1 = 8.6, J_2 = 1.5 Hz), 8.04 (br s, 1 H, NHCO), 7.40–7.47 (m, 1 H_{arom}), 7.31 (dd, 2 H_{arom}, J_1 = 6.4, J_2 = 2.0 Hz), 7.19 (dd, 2 H_{arom}, J_1 = 6.4, J_2 = 2.0 Hz), 6.77 (d, 1 H_{arom}, J = 8.7 Hz), 6.65 (dt, 1 H_{arom}, J_1 = 8.6, J_2 = 1.3 Hz), 5.52 (br s, 1 H, N*H*Ar), 3.55 (s, 2 H, CH_2CO), 3.38 (q, 2 H, J = 6.7 Hz, CH_2N), 3.29 (t, 2 H, J = 6.7 Hz, CH_2N), 1.88 (pent, 2 H, J = 6.7 Hz, $CH_2CH_2CH_2$).

MS: m/z = 347/349 (M^{+}).

Anal. Calcd for $C_{17}H_{18}ClN_3O_3$: C, 58.71; H, 5.22; Cl, 10.19; N, 12.08. Found: C, 58.74; H, 5.25; Cl, 10.11; N, 12.02.

N-(*p*-Nitrophenylacetyl)-*N*′-(*o*-nitrophenyl)-1,3-propanediamine (2c)

Yield: 71%; mp 128–129 °C (MeOH–H_2O).

^{1}H NMR: δ = 8.13–8.19 (m, 3 H_{arom}), 8.06 (br s, 1 H, NHCO), 7.40–7.43 (m, 1 H_{arom}), 7.45 (d, 2 H_{arom}, J = 8.7 Hz), 6.78 (d, 1 H_{arom}, J = 8.7 Hz), 6.65 (t, 1 H_{arom}, J = 8.2 Hz), 5.80 (br s, 1 H, N*H*Ar), 3.66 (s, 2 H, CH_2CO), 3.42 (q, 2 H, J = 6.4 Hz, CH_2N), 3.30–3.36 (m, 2 H, CH_2N), 1.88–1.97 (m, 2 H, $CH_2CH_2CH_2$).

MS: m/z = 358 (M^{+}).

Anal. Calcd for $C_{17}H_{18}N_4O_5$: C, 56.98; H, 5.06; N, 15.63. Found: C, 56.92; H, 5.10; N, 15.58.

N-(*p*-Methoxyphenylacetyl)-*N*′-(*o*-nitrophenyl)-1,3-propanediamine (2d)

Yield: 70%; mp 92–94 °C (EtOH–H_2O).

^{1}H NMR: δ = 8.16 (dd, 1 H_{arom}, J_1 = 8.5, J_2 = 1.5 Hz), 8.03 (br s, 1 H, NHCO), 7.39–7.44 (m, 1 H_{arom}), 7.16 (dd, 2 H_{arom}, J_1 = 6.6, J_2 = 2.1 Hz), 6.87 (dd, 2 H_{arom}, J_1 = 6.6, J_2 = 2.1 Hz,), 6.76 (d, 1 H_{arom}, J = 8.7 Hz), 6.62–6.67 (m, 1 H_{arom}), 5.54 (br s, 1 H, N*H*Ar), 3.80 (s, 3 H, OCH_3), 3.53 (s, 2 H, CH_2CO), 3.36 (q, 2 H, J = 6.7 Hz, CH_2N), 3.28 (q, 2 H, J = 6.9 Hz, CH_2N), 1.81–1.90 (m, 2 H, $CH_2CH_2CH_2$).

MS: m/z = 343 (M^{+}).

Anal. Calcd for $C_{18}H_{21}N_3O_4$: C, 62.96; H, 6.16; N, 12.24. Found: C, 63.00; H, 6.19; N, 12.17.

N-(*o*-Nitrophenyl)-*N*′-(3-phenylpropionyl)-1,3-propanediamine (2e)

Yield: 65%; mp 98–99 °C (EtOH–H_2O).

^{1}H NMR: δ = 8.16 (dd, 1 H_{arom}, J_1 = 8.6, J_2 = 1.5 Hz), 8.02 (br s, 1 H, NHCO), 7.40–7.45 (m, 1 H_{arom}), 7.15–7.29 (m, 5 H_{arom}), 6.78 (d, 1 H_{arom}, J = 7.9 Hz), 6.62–6.67 (m, 1 H_{arom}), 5.55 (br s, 1 H, N*H*Ar), 3.35 (q, 2 H, J = 6.5 Hz, CH_2N), 3.20 (q, 2 H, J = 6.9 Hz, CH_2N), 2.97 (t, 2 H, J = 7.6 Hz, $CH_2C_6H_5$), 2.49 (t, 2 H, J = 7.6 Hz, CH_2CO), 1.81–1.85 (m, 2 H, $CH_2CH_2CH_2$).

MS: m/z = 327 (M^{+}).

Anal. Calcd for $C_{18}H_{21}N_3O_3$: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.10; H, 6.15; N, 12.78.

N-(*o*-Nitrophenyl)-*N*′-propionyl-1,3-propanediamine (2f)

Yield: 83%; mp 63–65 °C (EtOH–H_2O).

^{1}H NMR: δ = 8.17 (dd, 1 H_{arom}, J_1 = 8.6, J_2 = 1.5 Hz), 8.09 (br s, 1 H, NHCO), 7.44 (dt, 1 H_{arom}, J_1 = 7.8, J_2 = 1.5 Hz), 6.84 (d, 1 H_{arom}, J = 8.3 Hz), 6.63–6.68 (m, 1 H_{arom}), 5.61 (br s, 1 H, N*H*Ar), 3.33–3.45 (m, 4 H, CH_2N), 2.23 (q, 2 H, J = 7.5 Hz, CH_2CH_3), 1.92–1.97 (m, 2 H, $CH_2CH_2CH_2$), 1.16 (t, 3 H, J = 7.5 Hz, CH_2CH_3).

MS: m/z = 251 (M^{+}).

Anal. Calcd for $C_{12}H_{17}N_3O_3$: C, 57.36; H, 6.82; N, 16.72. Found: C, 57.42; H, 6.87; N, 16.68.

N-(*p*-Chlorophenylacetyl)-*N*′-(*o*-nitrophenyl)-1,4-butanediamine (2g)

Yield: 92%; mp 106–108 °C (EtOH–H_2O).

^{1}H NMR: δ = 8.16 (dd, 1 H_{arom}, J_1 = 8.6, J_2 = 1.5 Hz), 8.03 (br s, 1 H, NHCO), 7.40–7.43 (m, 1 H_{arom}), 7.35 (dd, 2 H_{arom}, J_1 = 6.4, J_2 = 2.0 Hz), 7.30 (dd, 2 H, J_1 = 6.4, J_2 = 2.0 Hz), 6.78 (d, 1 H_{arom},

J = 8.7 Hz), 6.68 (dt, 1 H_{arom}, J_1 = 8.6, J_2 = 1.3 Hz), 5.49 (br s, 1 H, N*H*Ar), 3.52 (s, 2 H, CH_2CO), 3.41 (q, 2 H, J = 6.9 Hz, CH_2N), 3.28 (q, 2 H, J = 6.9 Hz, CH_2N), 1.55–1.74 (m, 4 H).

MS: m/z = 361 ($M^{+\cdot}$).

5-Aryl-2,3-dihydro-1*H*-pyrimido[1,2-*a*]quinoxaline 6-Oxides 1a–d; General Procedure

A mixture of the corresponding diamine **2a**–**d** (0.5 g) and PPE[8] (10 mL) was refluxed for 5 h. After cooling, the mixture was extracted with H_2O (5 × 10 mL). The resulting aqueous acidic solutions were pooled, filtered, made alkaline (pH 12) with NaOH, and was extracted with $CHCl_3$ (3 × 20 mL). The organic phases were combined, washed with H_2O, dried (Na_2SO_4) and filtered. The $CHCl_3$ solution was left at r.t. until the disappearance of intermediate **3** as monitored by TLC (silica gel, $CHCl_3$–MeOH, 9:1) (ca. 24 h). The solvent was removed in vacuo and the crude product was purified by column chromatography (silica gel, $CHCl_3$–MeOH, 10:0 → 9:1) (Table. 1).

5-Alkyl-2,3-dihydro-1*H*-pyrimido[1,2-*a*]quinoxaline 6-Oxides 1e,f; General Procedure

A mixture of the corresponding diamine **2e**,**f** (0.5 g) and a CH_2Cl_2 solution of PPSE[9] (10 mL) was refluxed for 5 h. After cooling, the mixture was extracted with H_2O (5 × 10 mL). The resulting acid solutions were pooled, filtered, made alkaline (pH 9) with $NaHCO_3$, and extracted with $CHCl_3$ (3 × 20 mL). The organic phases were combined, washed with H_2O, dried (Na_2SO_4) and filtered. After removal of the solvent in vacuo, the residual crude products were purified by column chromatography (silica gel, CH_2Cl_2–isopropylamine, 100:1→20:1), yielding compounds **3e**,**f** (vide infra). A $CHCl_3$ solution of the corresponding amidine was left at r.t. until disappearance of the starting material as monitored by TLC (silica gel, $CHCl_3$–MeOH, 9:1) (ca. 4 and 7 days for compounds **1e** and **1f**, respectively). The solvent was then removed in vacuo and the crude product was purified by column chromatography (silica gel, $CHCl_3$–MeOH, 10:0 → 9:1) (Table 1).

1-(*o*-Nitrophenyl)-2-(2-phenylethyl)-1,4,5,6-tetrahydropyrimidine (3e)

Yield: 73%; mp 68–70 °C (CH_2Cl_2–cyclohexane).

^{1}H NMR: δ = 7.90 (dd, 1 H_{arom}, J_1 = 8.2, J_2 = 1.5 Hz), 7.57 (t, 1 H_{arom}, J = 7.7 Hz), 7.42 (t, 1 H_{arom}, J = 7.7 Hz), 7.12–7.21 (m, 4 H_{arom}), 6.96–6.99 (m, 2 H_{arom}), 3.63 (t, 2 H, J = 6.6 Hz, CH_2N), 3.53 (t, 2 H, J = 5.5 Hz, CH_2N), 2.71–2.80 (m, 4 H, $CH_2CH_2C_6H_5$), 1.99–2.07 (m, 2 H, $CH_2CH_2CH_2$).

MS: m/z = 309 ($M^{+\cdot}$).

Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58. Found: C, 69.81; H, 6.24; N, 13.50.

2-Ethyl-1-(*o*-nitrophenyl)-1,4,5,6-tetrahydropyrimidine (3f)

Yield: 75%; oil.

^{1}H NMR: δ = 7.93 (dd, 1 H_{arom}, J_1 = 8.0, J_2 = 1.6 Hz), 7.63 (dt, 1 H_{arom}, J_1 = 7.7, J_2 = 1.6 Hz), 7.45–7.49 (m, 1 H_{arom}), 7.36 (d, 1 H_{arom}, J_1 = 7.7 Hz), 3.46–3.50 (m, 4 H, CH_2N), 2.02 (q, 2 H, J = 7.3 Hz, CH_2CH_3), 1.89 (pent, 2 H, J = 6.1 Hz, $CH_2CH_2CH_2$), 1.02 (t, 3 H, J = 7.3 Hz, CH_2CH_3).

MS: m/z = 233 ($M^{+\cdot}$).

Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.84; H, 6.52; N, 17.94.

6-(*p*-Chlorophenyl-1,2,3,4-tetrahydro-1,3-diazepino[1,2-*a*]-quinoxaline 7-Oxide (1g)

The same procedure as for compounds **1a**–**d** was used. Reaction time with PPE was 30 h. The intermediate **3g** disappeared in ca. 36 h.Yield, physical and spectral data of compound **1g** are given in Table 1.

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