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# One-Pot Synthesis of 3,4-Dihydro-2*H*-pyrido[1,2-*a*][1,3,5]triazin-2-one Derivatives from *N*-(2'-pyridinyl)benzoylacetamide and Nitrosobenzenes

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**Abstract:** A convenient way leading to fused pyrido[1,2-*a*][1,3,5]triazine-2-ones is described. It consists in a one-pot, two-step reaction of *N*-(2'-pyridinyl)benzoylacetamide with nitrosobenzenes. On the other hand, *N*-(2'-pyridinyl)acetoacetamide provides a C-2 condensation/addition product in the reaction with nitrosobenzene. Reactivity of *N*-(2'-pyridinyl)benzoylthioacetamide and *N*-(2'-pyridinyl)acetothioacetamide with nitrosobenzene was also investigated; they undergo oxidative heterocyclization leading to [1,2,4]thiadiazolo[2,3-*a*]pyridine derivatives.

**Key words:** amides, heterocycles, pyridotriazines, thiadiazolopyridines, cycloadditions

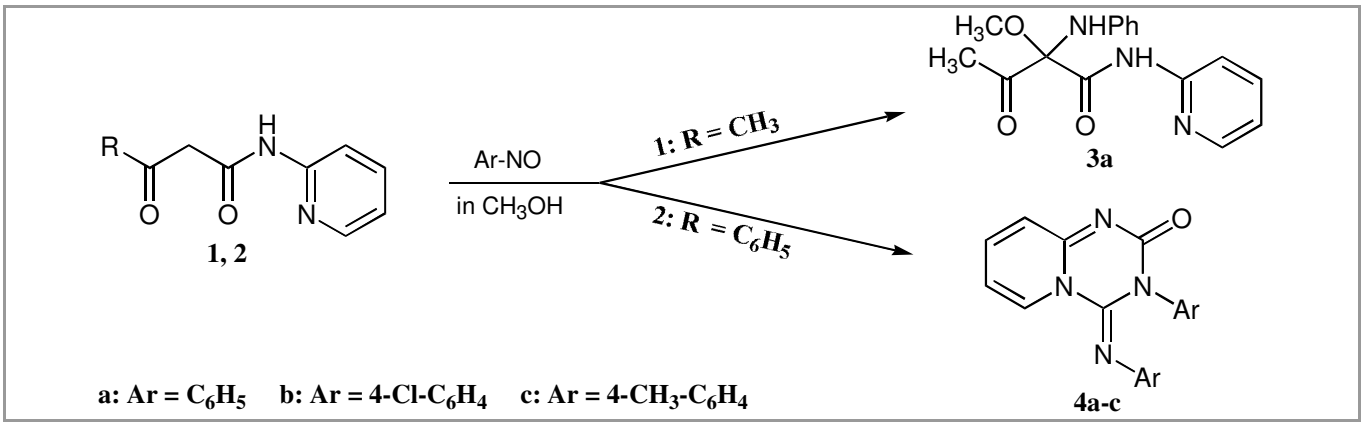
The interest in the pyrido[1,2-*a*][1,3,5]triazine system arises from its wide biological activity,[1,2] which comes from its antagonistic effect upon 5–$HT_2$ and 5–$HT_{2a}$ serotonine receptors. Such influence can result in: mediating coronary blood flow,[1a] decreasing mean arterial blood pressure,[1b] and the antithrombotic effect[1c] in mammals. Other disorders, for whose prophylactic or therapeutic treatment pyrido[1,2-*a*][1,3,5]triazine derivatives can be used, are those involving airway constriction in human or animals: asthma, emphysema, chronic bronchitis, chronic obstructive pulmonary disease,[2] and various psychotic conditions including schizophrenia, depression, anorectic or bulimic eating disorders, and anxiety in humans.[2c]

Since 1952, when a possible approach to this system was mentioned for the first time,[3a] several general methods of synthesis of pyrido[1,2-*a*][1,3,5]triazines have been invented, mostly leading to their oxo derivatives.

Cyclodimerization of iso(thio)cyanates leads to pyrido[1,2-*a*][1,3,5]triazine-2,4-di(thi)ones.[3b–d] The other ways include: reaction of isocyanates[4a] or active esters of imidodicarbonic[4b] or carbonic[4c] acid with 2-aminopyridine or other amidines and cyclisation of (thio)urea derivatives[3a] or their reaction with isothiocyanate.[4d] Pyrido[1,2-*a*][1,3,5]triazine-4-ones can be obtained from urea derivatives,[5a,b] e.g. by their cyclisation,[5a] or reaction of aryl isocyanate and unsymmetrical carbodiimide containing 2'-pyridine ring.[5c,d] There are only a few examples of syntheses of pyrido[1,2-*a*][1,3,5]triazine-2-(thi)ones.[3d,6]

It has recently been shown[7–10] that *N*-phenyl-2-methoxy-2-phenylaminoacetothioacetamide, which was obtained as the product of the reaction of *N*-phenylacetothioacetamide and nitrosobenzene in methanol, is a compound of particular interest. This compound has got capacity to react as bielectrophilic system on C2 in various ways, depending on reagents and reaction conditions, and usually leading to heterocyclic systems by new rearrangements.[7,8] These results encouraged us to undertake a study on reactivity of *N*-(2'-pyridinyl)acetoacetamide **1** and *N*-(2'-pyridinyl) benzoylacetamide **2** with nitrosobenzenes. Products of such type of reaction had proven useful as good building blocks for constructing various heterocyclic systems.[7,8]

*N*-(2'-pyridinyl)acetoacetamide **1** furnished expected product **3a,** in contrast to the reaction of *N*-(2'-pyridinyl)benzoylacetamide **2** with nitrosobenzenes. This reaction unexpectedly afforded pyrido[1,2-*a*][1,3,5]triazin-2-ones **4a-c** (Scheme 1).




**Scheme 1**

The structure of compounds **4a-c** could not be completely elucidated by IR, $^{1}$H NMR, $^{13}$C NMR and MS analyses, therefore it was established by X-ray analysis.[11] A perspective view of the molecule of **4a** with the crystallographic numbering scheme of non-hydrogen atoms is shown in Figure 1.

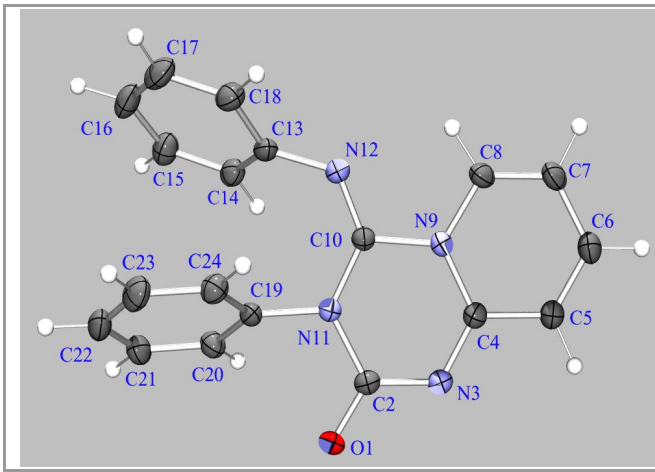
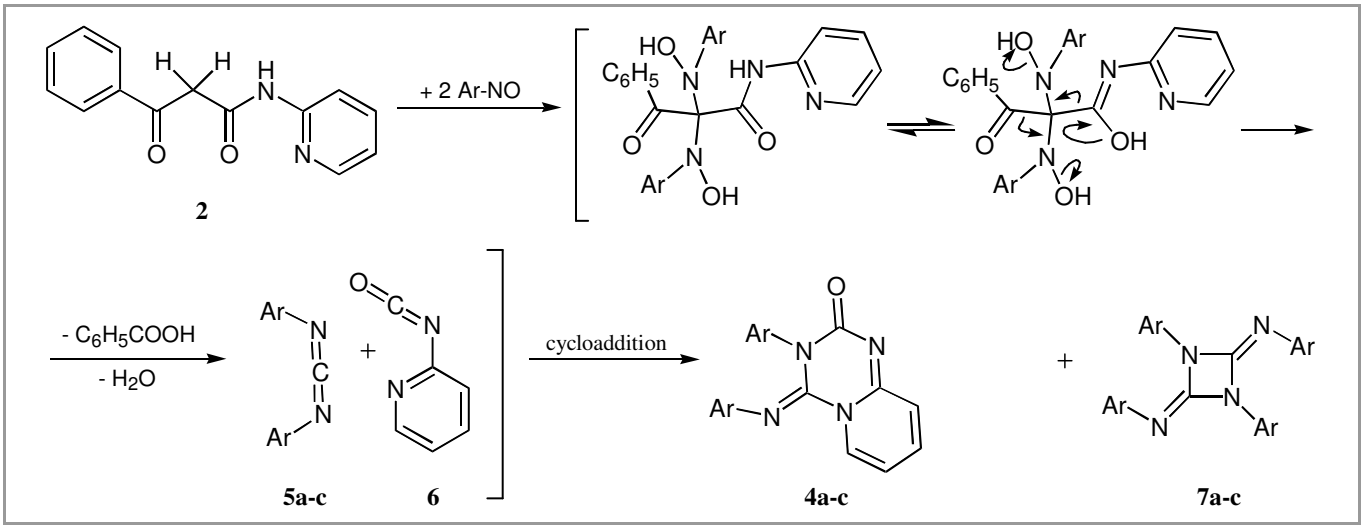



**Figure 1**

The packing in the crystal structure is dominated by van der Waals interactions with only intramolecular close contacts involving the C8, H108 and N12, and C20, H120 and O1 atoms (Figure 1). These interactions are fairy strong, with D-A distances equal to 264.9(3)Å and 294.0(3)Å, respectively, and rather angular (D-H...A angles equal 104(2)º and 84(2)º). Rather than affect the packing, these intramolecular interactions tend to stabilise the molecule's conformation. In fact, the molecular geometry is rather characteristic, because, in good approximation, all atoms lie in three planes: two planes passing through the phenyl moieties and the third one defined by the remaining atoms. Least-squares planes involving the phenyl rings are inclined to each other at an angle of 27.06(8)º, whereas they form angles of about 66° with the plane defined by the heterorings.

It is noteworthy that using 2 equiv. of the corresponding nitrosobenzene in reaction with **2** significantly increases yields of products **4a-c**. This fact suggests an simultaneous attack of two molecules of nitrosobenzene on C2 of **2**, with following splitting of C1–C2 and C2–C3 bonds. This results in forming corresponding carbodiimides **5a-c** and 2'-pyridinylisocyanate **6** (Scheme 2).



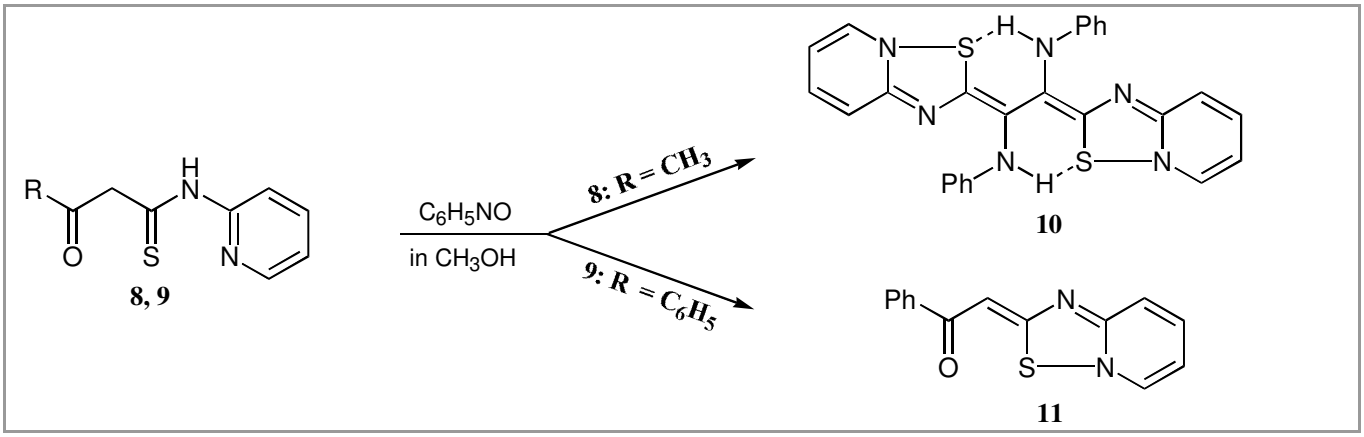

**Scheme 2**

Highly reactive intermediate symmetrical carbodiimides **5a-c** spontaneously react with 2'-pyridinylisocyanate **6**, formed *in situ*, via [4π+2π] heterocycloaddition between the N=C–N=C moiety of **6** as 4π component and the C=N moiety of **5a-c** as 2π component to yield pyrido[1,2-*a*][1,3,5]triazin-2-one derivatives **4a-c** as major products. At the same time dimerisation of carbodiimide occurs, leading to four-membered ring of 1,3-diazetine. The corresponding 1,3-diaryl-2,4-diarylimino-1,3-diazetines **7a-c** were isolated by chromatography of reaction mixtures remaining after separating the main products **4a-c** which did not need purification. Another fact that confirms the proposed [4π+2π] cycloaddition mechanism is (4*Z*) configuration of compounds **4a-c**.

Previously reported methods[5c,d] using [4π+2π] heterocycloaddition lead mostly to pyrido [1,2-*a*][1,3,5]triazin-4-ones, because the pyridine ring was a part of carbodiimide, not isocyanate.

Under the same conditions *N*-(2'-pyridinyl)acetothioacetamide **8** and *N*-(2'-pyridinyl)benzoylthioacetamide **9** underwent oxidative cyclization by the treatment with nitrosobenzene. Oxidative ring closure of **8** takes place between the nitrogen atom of the pyridine ring and the sulphur atom of the thioamide moiety forming a 1,2,4-thiadiazolo[2,3-*a*]pyridine derivative **10** with elimination of the acetyl fragment. In this case, however, using of 2 equiv. of nitrosobenzene did not increase the yield. The structure of compound **10** was established on the base of IR, $^{13}$C NMR, $^{1}$H NMR, and MS analyses and micro-

analysis. On the other hand *N*-(2'-pyridinyl)benzoylthioacetamide **9** gave known 1-phenyl-2-(2*H*-[1,2,4]thiadiazolo[2,3-*a*]pyridin-2-ylidene)ethanone **11**[12a] (Scheme 3). Such oxidation is a common way of obtaining [1,2,4]thiadiazolo[2,3-*a*]pyridine derivatives[13a,b,c] which constitute a new family of potassium channel openers,[13b] and exhibit excellent endothelin receptor antagonistic activity.[13d] They are also a subject of theoretical research.[13c,e]




**Scheme 3**

In conclusion, we have demonstrated a convenient one-pot preparation of (4*Z*)-3-phenyl-4-(phenylimino)-3,4-dihydro-2*H*-pyrido[1,2-*a*][1,3,5]triazin-2-ones **4a-c** starting from simple, cheap and easily available *N*-(2'-pyridinyl)benzoylacetamide and variously substituted nitrosobenzenes which work as oxidizing reagents. It is an experimentally straightforward and particularly suitable way for obtaining pure and easily isolable new examples of the pyrido[1,2-*a*][1,3,5]triazin-2-one system. It should be stressed that, in contrast to many known ways leading to 4-oxo and 2,4-dioxo derivatives of pyrido[1,2-*a*][1,3,5]triazine, there are only a few examples of syntheses of pyrido[1,2-*a*][1,3,5]-triazine-2-one derivatives.[6]

Physical data: Mps were determined on an electrothermal IA9000 digital mp apparatus and are uncorrected. IR spectra were obtained on a Bruker IFS 48 spectrometer. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker AMX 500 NMR spectrometer at r.t. Chemical shifts are given in ppm. Yields are given for pure products.

4-Chloronitrosobenzene and 4-methylnitrosobenzene were prepared according to the known procedure.[14]

**_N_-(2'-pyridinyl)acetoacetamide 1**

A solution of ethyl acetylacetate (17.3 mL, 0.1 mol) in xylene (70 mL) was warmed up to boil. To the boiling mixture 2-aminopyridine (9.4 g, 0.1 mol) was added in portions during 1 h, and the liberated EtOH was distilled. Then 20 mL of xylene were distilled. Cooling the mixture at 0 °C yielded the product, which was separated under reduced pressure.

Yield 80%, colorless needles; mp 113–114 °C. (Lit.[12e] mp 111–112 °C).

**_N_-(2'-pyridinyl)benzoylacetamide 2**

**2** was prepared in an analogous way as **1**, starting from ethyl benzoylacetate.

Yield 73%; colorless needles; mp 114–115 °C. (Lit.[12e] mp 113–114 °C).

**_N_-(2'-pyridinyl)-2-methoxy-2-phenylaminoacetoacetamide 3**

To a stirred solution of **1** (1.78 g, 0.01 mol) in MeOH (20 mL), nitrosobenzene (1.07 g, 0.01 mol) and solid NaOH (0.02 g) (as a catalyst) were added and the mixture was stirred overnight. The product was filtered off under reduced pressure.

Yield: 1.80 g (60%); white powder; mp 152–153 °C.

IR (KBr) = 3363, 3108, 1683 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 11.75 (s, 1 H, CONH), 8.20–7.01 (m, 9 H, CH ar.), 4.74 (s, 1 H, NH), 3.46 (s, 3 H, $OCH_3$), 2.44 (s, 3 H, $CH_3$).

$^{13}$C NMR ($CDCl_3$): δ = 204.2 ($\underline{C}OCH_3$), 168.2 (CONH), 148.1, 138.4, 129.2, 128.9, 124.8, 123.5, 121.3, 120.7, 114.6 (9 C ar.), 92.8 (C-2), 50.7 ($OCH_3$), 22.6 ($CH_3$).

MS (EI): *m/z* (%) = 225 (12, $M^+$–Ph), 121 (97, 2-PyNHCO), 93 (84, 2-PyNH), 77 (100, Ph).

Anal. Calcd for $C_{16}H_{17}N_3O_3$: C, 64.20; H, 5.72; N, 14.04. Found: C, 64.55; H, 5.50; N, 13.77.

**(4*Z*)-3-aryl-4-(arylimino)-3,4-dihydro-2*H*-pyrido[1,2-*a*][1,3,5] triazin-2-ones 4; General Procedure**

Compound **2** (0.48 g, 2 mmol) was dissolved in methanol (20 mL) at 40 °C and one drop of 25% water solution of NaOH (as a catalyst) were added. To the stirred solution, the corresponding nitrosobenzene was added (4 mmol) in several portions during 5 mins. The nitrosobenzene dissolved readily in the solution, which changed its color from green to orange-brown. The product was separated under reduced pressure after 2 h.

**(4*Z*)-3-phenyl-4-(phenylimino)-3,4-dihydro-2*H*-pyrido[1,2-*a*][1,3,5]triazin-2-one 4a**
Yield 0.33 g (52%); orange plates; mp 231–232 °C.

IR (KBr): 1703, 1648, 1553 $cm^{-1}$.

$^1H$ NMR (DMSO-$d_6$): δ = 8.88 (ddd, 1 H, *J* = 7.3, 1.5, 0.8 Hz), 7.85 (ddd, 1 H, *J* = 9.0, 6.8, 1.9 Hz), 7.09–7.06 (m, 3 H), 7.01–6.96 (m, 3 H), 6.93 (ddd, 1 H, *J* = 7.0, 6.8, 1.5 Hz), 6.82 (t, 2 H, *J* = 7.8 Hz), 6.60 (tt, 1 H, *J* = 7.3, 1.1 Hz), 6.40 (dd, 2 H, *J* = 8.5, 1.0 Hz).

$^{13}C$ NMR (DMSO-$d_6$): δ = 155.3, 143.9, 141.4, 136.1, 135.3, 130.1, 129.7, 127.7, 127.5, 127.2, 122.9, 121.1, 120.5, 112.5.

MS (EI): *m/z* (%) = 314 (2, $M^+$), 222 (35, $M^+$ – PhN), 194 (100, retro Diels-Alder reaction fragment (RDA)), 120 (4, RDA).

Anal. Calcd for $C_{19}H_{14}N_4O$: C, 72.60; H, 4.49; N, 17.82. Found: C, 72.48; H, 4.46; N, 17.74.

**(4*Z*)-3-(4-chlorophenyl)-4-[(chlorophenyl)imino]-3,4-dihydro-2*H*-pyrido[1,2-*a*][1,3,5]triazin-2-one 4b**
Yield: 0.31 g (40%); yellow-orange plates; mp 230–232 °C.

IR (KBr): 1721, 1663, 1550 $cm^{-1}$.

$^1H$ NMR (DMSO-$d_6$): δ = 8.87 (d, 1 H, *J* = 7.0 Hz), 7.86 (ddd, 1 H, *J* = 9.0, 7.0, 1.5 Hz), 7.14–7.08 (m, 5 H), 6.94 (td, 1 H, *J* = 7.0, 1.5 Hz), 6.90 (d, 2 H, *J* = 8.5 Hz), 6.44 (d, 2 H, *J* = 8.5 Hz).

$^{13}C$ NMR (DMSO-$d_6$): δ = 154.6, 152.4, 143.7, 141.6, 135.9, 135.0, 132.2, 131.7, 130.1, 127.9, 127.4, 125.3, 122.9, 122.4, 112.7.

MS (EI): *m/z* (%) = 382 (81, $M^+$), 262 (14, RDA), 120 (11, RDA).

Anal. Calcd for $C_{19}H_{12}Cl_2N_4O$: C, 59.55; H, 3.16; N, 14.62. Found: C, 59.39; H, 2.94; N, 14.50.

**(4*Z*)-3-(4-methylphenyl)-4-[(methylphenyl)imino]-3,4-dihydro-2*H*-pyrido[1,2-*a*][1,3,5]triazin-2-one 4c**
Yield: 0.33 g (48%); light orange plates; mp 228–229 °C.

IR (KBr) = 1704, 1647, 1556 $cm^{-1}$.

$^1H$ NMR (DMSO-$d_6$): δ = 8.86 (d, 1 H, *J* = 7.5 Hz), 7.83 (t, 1 H, *J* = 7.8 Hz), 7.05 (d, 1 H, *J* = 9.0 Hz), 6.91 (t, 1 H, *J* = 7.5 Hz), 6.89 (d, 2 H, *J* = 8.5 Hz), 6.77 (d, 2 H, *J* = 8.0 Hz), 6.62 (d, 2 H, *J* = 7.5 Hz), 6.24 (d, 2 H, *J* = 8.0 Hz), 2.12 (s, 3 H), 2.09 (s, 3 H).

$^{13}C$ NMR (DMSO-$d_6$): δ = 154.6, 142.2, 141.3, 136.5, 133.6, 130.1, 129.6, 129.3, 128.1, 127.8, 122.8, 120.3, 112.3, 30.6, 30.5.

MS (ESi): *m/z* = 343 ($M^+$), 223 (RDA).

Anal. Calcd for $C_{19}H_{18}N_4O$: C, 73.67; H, 5.30; N, 16.36. Found: C, 73.63; H, 5.38; N, 16.57.

***N*-[1,3-diaryl-4-(arylimino)-1,3-diazetidin-2-ylidene]-*N*-phenylamines 7; General Procedure**
The filtrate after separating **4** was evaporated. The brownish residue was chromatographed ($SiO_2$/$CHCl_3$). The first fraction gave the product.

***N*-[1,3-diphenyl-4-(phenylimino)-1,3-diazetidin-2-ylidene]-*N*-phenylamine 7a**
Yield 22%; pale yellow needles; mp 162–163 °C. (Lit.[15] mp 165–166 °C).

$^1H$ NMR and $^{13}C$ NMR analyses agree with known data for **7a**.[15]

***N*-{1,3-bis(4-chlorophenyl)-4-[(4-chlorophenyl)imino]-1,3-diazetidin-2-ylidene}-*N*-(4-chlorophenyl)amine 7b**
Yield 30%; pale yellow needles; mp 155–156 °C.

$^1H$ NMR ($CDCl_3$): δ = 8.24 (d, 4 H, *J* = 9.0 Hz), 8.15 (d, 4 H, *J* = 8.5 Hz) 7.47 (d, 4 H, *J* = 9.0 Hz), 7.44 (d, 4 H, *J* = 8.5 Hz).

$^{13}C$ NMR ($CDCl_3$): δ = 142.2, 138.1, 135.2, 129.0, 129.0, 127.0, 123.7.

***N*-{1,3-bis(4-methylphenyl)-4-[(4-methylphenyl)imino]-1,3-diazetidin-2-ylidene}-*N*-(4-methylphenyl)amine 7c**
Yield 30%; pale yellow needles; mp 152–153 °C.

$^1H$ NMR ($CDCl_3$): δ = 8.18 (d, 4 H, *J* = 8.5 Hz), 8.11 (d, 4 H, *J* = 8.5 Hz) 7.29 (d, 4 H, *J* = 8.5 Hz), 7.28 (d, 4 H, *J* = 8.5 Hz), 2.44 (s, 6 H, 2 $CH_3$), 2.42 (s, 3 H, 2 $CH_3$).

$^{13}C$ NMR ($CDCl_3$): δ = 141.9, 141.9, 140.0, 129.3, 129.3, 125.6, 122.2, 21.5, 21.3.

***N*-(2'-pyridinyl)acetothioacetamide 8 and *N*-(2'-pyridinyl) benzoylthioacetamide 9**
Compounds **8** and **9** was prepared according to the known procedure.[12a–d]

***N*-(2'-pyridinyl)acetothioacetamide 8**
Yield 42%; light yellow needles; mp 84–86 °C (Lit.[12a] mp 83.5–84 °C).

***N*-(2'-pyridinyl)benzoylthioacetamide 9**
Yield 35%; yellow needles; mp 90–91 °C (Lit.[12a] mp 91–92 °C).

***N,N'*-diphenyl-1,2-bis-[1,2,4]thiadiazolo[2,3-*a*]pyridin-2-ylidene-ethane-1,2-diamine 10**
To a stirred solution of **5** (0.29 g, 1.5 mmol) in MeOH (5 mL) nitrosobenzene (0.16 g, 1.5 mmol) and one drop of 25% water solution of NaOH (as a catalyst) were added. The product was filtered off under reduced pressure after 2 h.

Yield 39%; white powder; mp 234–235 °C (dec.).

IR (KBr) = 3348, 3317, 1629, 1600, 1564, 1546, 1496 $cm^{-1}$.

$^1H$ NMR (DMSO-$d_6$): δ = 8.67 (s, 2 H, 2 NH), 7.86 (dt, 2 H, *J* = 7.0, 1.0 Hz), 7.71 (dt, 2 H, *J* = 9.0, 1.0 Hz), 7.41 (ddd, 2 H, *J* = 9.0, 7.0, 1.0 Hz), 7.09 (d, 4 H, *J* = 8.0 Hz), 7.00 (td, 2 H, *J* = 7.0, 1.0 Hz), 6.73 (tt, 2 H, *J* = 7.2, 1.0 Hz), 6.45 (dt, 4 H, *J* = 7.5, 1.0 Hz).

$^{13}C$ NMR (DMSO-$d_6$): δ = 144.8, 141.9, 132.2, 129.2, 125.9, 125.5, 123.5, 119.0, 117.1, 113.6, 113.0.

MS (EI): *m/z* (%) = 238 [100, (1/2$M^+$–2H)], 137 [29, $C_6H_4N_2S$ (thiadiazolopyridine moiety)+1].

Anal. Calcd for $C_{26}H_{20}N_6S_2$: C, 64.98; H, 4.19; N, 17.49. Found: C, 64.76; H, 4.18; N, 17.39.

**1-phenyl-2-(2*H*-[1,2,4]thiadiazolo[2,3-*a*]pyridin-2-ylidene)ethanone 11**

To a stirred solution of **6** (0.51 g, 2 mmol) in MeOH (30 mL) nitrosobenzene (0.21g, 2 mmol) was added. After 2 h the product was filtered off under reduced pressure and recrystallized from cyclohexane.

Yield 54%; pale yellow needles; mp 229–231 °C. (Lit.[12a] mp 228–229 °C.

IR (KBr), $^1$H NMR,$^{13}$C NMR and MS (EI) analyses and Anal. Calcd for $C_{14}H_{10}N_2OS$ agree with the known data for **11**.[12a]

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(11) Compound **4a** with formula $C_{19}H_{14}N_4O$ crystallises in the monoclinic system, space group $P2_1/c$, with unit cell parameters a=1558.71(5), b=1331.37(3), c=727.70(2) Å, β=83.728(1)°, V=1.50108(7)x10$^9$ pm$^3$, Z=4. The X-ray diffraction data were collected on a KappaCCD (Bruker-Nonius) single-crystal diffractometer using MoKα radiation (55 kV, 30 mA). A total of 11584 reflections were collected and merged to give 3004 independent reflections (R(int) = 0.051) on a single-crystal sample (size 0.3x0.2x0.15 mm). The structure was solved in space group $P2_1/c$ by direct methods using the SHELXS86 program and refined by full-matrix least-squares method with SHELXL97. The differential Fourier map of electron density was featureless with no chemically significant peaks. All hydrogen atoms were located on a difference Fourier map of electron density. Final R indices for I>2σ(I) were equal to R1 = 0.055, wR2 = 0.109, and R1 = 0.0856, wR2 = 0.1240 for all data. The final difference Fourier map of electron density was featureless with the largest peak and hole at 1.7x10$^{-7}$ and -1.5x10$^{-7}$ e.pm$^{-3}$, respectively. The structural data have been deposited at the Cambridge Crystallographic Data Centre under the reference number CCDC .....

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**One-Pot Synthesis of 3,4-Dihydro-2*H*-pyrido[1,2-*a*][1,3,5]triazin-2-one Derivatives from *N*-(2'-pyridinyl) benzoylacetamide and Nitrosobenzenes**

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