Novel and Efficient Synthesis of 2-Aminooxazoles from Pyrimidin-2(1*H*)-one

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Abstract: Stepwise conversion of pyrimidin-2(1*H*)-one to 2-amino-5-aryloxazoles via oxazolo[3,2-*a*]pyrimidinium salts is reported. The sequence involves, (i) regioselective N-alkylation of pyrimidone by phenacyl bromides, (ii) cyclization of obtained 1-(2-aryl-2-oxoethyl)pyrimidin-2(1*H*)-ones into oxazolo[3,2-*a*]pyrimidinium salts under the action of fuming sulfuric (or triflic) acid, and (iii) reaction of the obtained salts with hydrazine leading to 2-amino-5-aryloxazoles.

Key words: fused ring systems, ring closure, ring opening, oxazoles, protecting groups

In our previous investigation[1] we described a simple route to 5-aryloxazoles **IVa** bearing a ω-aminodienyl residue by ring opening of bicyclic oxazolo[3,2-*a*]pyridinium salts **IIIa** (Scheme 1), which in turn can easily be obtained from 2-pyridone **Ia** via *N*-phenacyl-2-pyridones **IIa**. The overall simplicity of this methodology to obtain a substituted five-membered azole (like **IVa**) from a six-membered azine **Ia** via bridgehead azolo-azine **IIIa** (rarely used in heterocyclic synthesis) stimulated our interest to expand this strategy to the related family of pyrimidine derivatives. The retrosynthetic sequence of the suggested conversions is shown on Scheme 2.

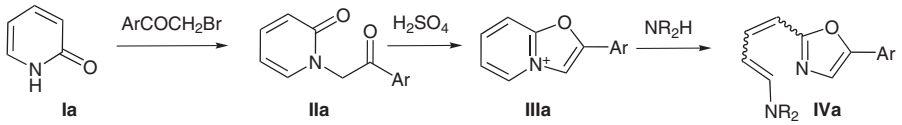
One would expect that similar transformations starting from pyrimidin-2(1*H*)-one (**1**, 2-pyrimidone) and involving *N*-phenacyl derivatives **IIb** and oxazolo[3,2-*a*]pyrimidinium salts **IIIb** may lead to unstable oxazolyl-substituted aza-dienes **IVb**, which, therefore, could be precursors of 2-aminooxazoles **V**. In this communication we confirm this idea and report our first successful preparation of 5-aryl-2-aminoxazoles **V** starting from pyrimidone **1**. The overall sequence shown in Scheme 2 has never been realized, although some related reactions have been briefly discussed in the literature.

N-Phenacylation of Pyrimidin-2(1*H*)-one (1)

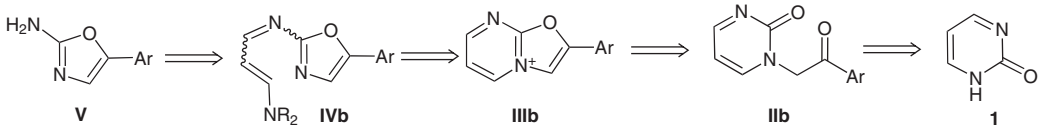
The reaction of 2-pyrimidone **1** and its derivatives with α-halogenocarbonyl compounds is poorly investigated in the literature. There are only two examples of phenacylation in the 2-pyrimidone series, namely for 5-chloro-4-phenyl-2-pyrimidone[2] and the sterically hindered 4,6-dimethyl-2-pyrimidone.[3] Regarding the parent pyrimidone **1** only reactions with diethylacetal of bromoacetaldehyde[4] and chloroacetic acid derivatives[5] have been studied. In all these cases exclusive formation of the *N*-alkyl isomer was observed. Several 4-aryl-*N*-phenacyl-2-pyrimidones were prepared from α-aminoketones by an alternative strategy, not involving the alkylation step.[6]

Earlier examined alkylation reactions were carried out in bipolar aprotic solvents with pyrimidone alkali salts. We studied phenacylation of **1** in two different ways: using K_2CO_3 as the base (Method A) and starting from the initially prepared sodium salt of **1** (Method B). Various phenacyl bromides have been used (Scheme 3, Table 1), and in all cases the *N*-phenacyl derivatives **2a**–**h** were the only products obtained in high yields.

In the IR spectra of **2a**–**h** two types of bands for CO group were observed, one for N–C=O fragment of pyrimidone (~1660 cm^{-1}) and another one for carbonyl group (~1700 cm^{-1}), thus clearly confirming selective N-alkylation. (Evidently, in the case of O-phenacylation one would ex-



Scheme 1



Scheme 2

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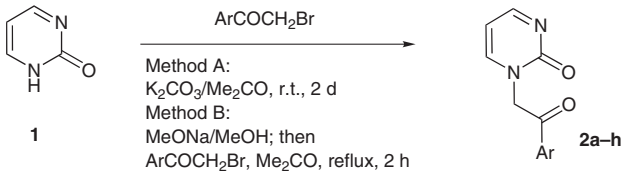


Scheme 3

Table 1 *N*-Phenacyl-2-pyrimidones **2a**–**h** Prepared

Compound	Ar	Method	Yield (%)
2a	4-ClC_6H_4	A	90
2b	4-BrC_6H_4	A	95
2c	2,4-$Cl_2C_6H_3$	B	60
2d	4-$NO_2C_6H_4$	B	65
2e	3-$NO_2C_6H_4$	B	63
2f	Ph	A	79
2g	4-MeC_6H_4	A	81
2h	4-$MeOC_6H_4$	A	70

pect no amide frequencies.) The structure of compound **2a** (and the regioselectivity of alkylation) was confirmed by single crystal X-ray analysis (Figure 1).

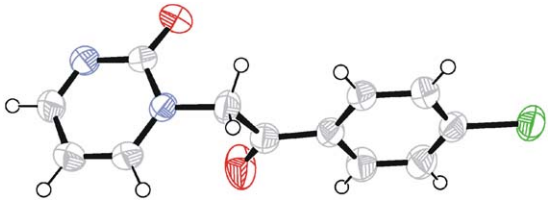
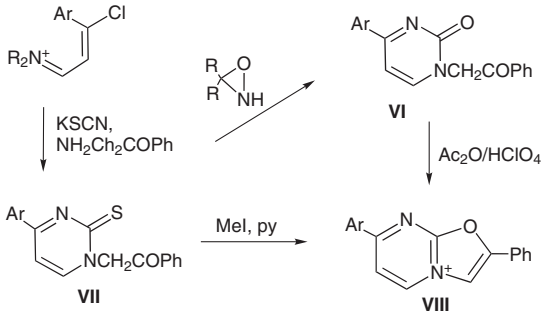


Figure 1 X-ray crystal structure of the compound **2a**

Cyclization of *N*-Phenacyl-2-pyrimidones 2 to Oxazolo[3,2-*a*]pyrimidinium Salts 3

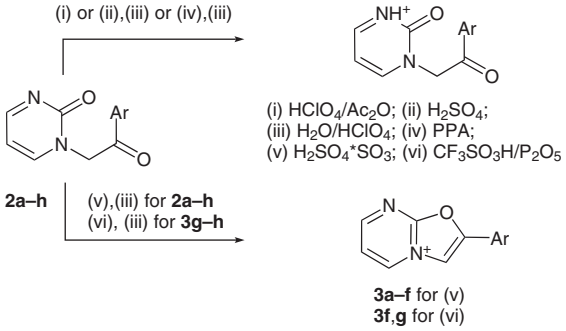
Aromatic oxazolo[3,2-*a*]pyrimidinium cation with bridgehead nitrogen atom could be prepared by two different ways, either from oxazole or from pyrimidine, and both strategies have been realized. The first approach is illustrated by condensation of 4,5-disubstituted 2-aminooxazoles with acetylacetone[7] leading to 5,7-dimethyloxazolo[3,2-*a*]pyrimidinium salts. The alternative way (Scheme 4) involved cyclization of hardly available *N*-phenacyl-2-pyrimidones **VI** (by using somewhat unsafe combination of Ac_2O and $HClO_4$) or their thione precursors **VII**, leading to 2,7-diaryl-substututed salts **VIII**.[6,8]

We have tried to perform the cyclization of *N*-phenacyl-2-pyrimidones **2** using the above protocol[6] in a mixture of Ac_2O and $HClO_4$. The isolated crystalline substances,



Scheme 4

however, were not the desired bicyclic salts. In the ^1H NMR spectra of the products the singlet of NCH_2-group remained unchanged, and the general downfield shift of all peaks confirmed that the products were protonated starting materials **2** (Scheme 5). Bradsher had reported[9] that sulfuric acid could be a suitable dehydration agent for analogous cyclization in the pyridone series (**IIa** to **IIIa**). However, our attempts to use H_2SO_4 or PPA for cyclization of pyrimidones **2** also led to the salts of starting compounds.



Scheme 5

Nevertheless, fuming sulfuric acid (20–30 mass% of SO_3) turned out to be the reagent of choice, and its use resulted in the formation of the desired salts **3a**–**e** (Scheme 5) in excellent yields (Table 2, Method A).

Table 2 2-Aryloxazolo[3,2-*a*]pyrimidinium Perchlorates **3a**–**g** Prepared

Compound	Ar	Method	Yield (%)
3a	4-ClC_6H_4	A	90
3b	4-BrC_6H_4	A	85
3c	2,4-$Cl_2C_6H_3$	A	83
3d	4-$NO_2C_6H_4$	A	80
3e	3-$NO_2C_6H_4$	A	87
3f	Ph	A	55
3f	Ph	B	79
3g	4-MeC_6H_4	B	75

The salts **3** could be easily isolated as perchlorates. The singlet of CH_2 group at 5.4 ppm (initially observed in parent *N*-phenacyl-2-pyrimidones) disappeared in the ^1H NMR spectra of the salts **3**, and new downfield singlet of formed oxazole ring appeared at 9.24–9.59 ppm. Respectively, in the ^{13}C spectra the signal for the methylene group observed for phenacyl derivatives **2** (at ~55 ppm) is changed to aromatic oxazole signal (at 110–115 ppm) for **3**. Final confirmation of the structural change followed from X-ray structure analysis of the crystal of compound **3b** (Figure 2).

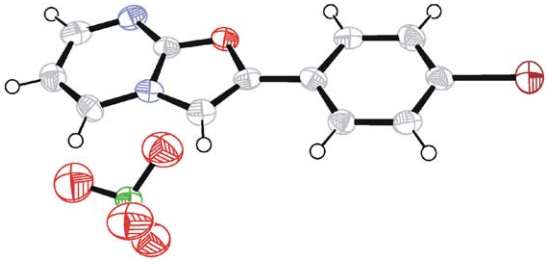


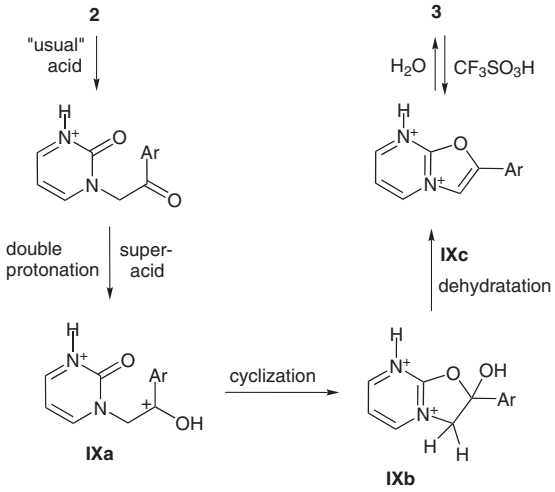
Figure 2 X-ray crystal structure of the compound **3b**

In the case of N-phenacyl-2-pyrimidones **2g**,**h** with donor groups (4-Me or 4-MeO) in the benzene ring, the obtained products were insoluble in most solvents and had high melting points, so it was difficult to prove their structures. We suppose that in these cases SO_3 caused sulfonation of the benzene ring. (Analogous sulfonation was observed during the attempts to prepare oxazolopyridinium salts from electron rich phenacyl pyridones in sulfuric acid,[9] that is even a weaker sulfonation media than oleum.) In the case of *N*-phenacyl derivative **2f** (unsubstituted at benzene ring) partial sulfonation was also observed, however, decrease of temperature and using DMSO for purification has allowed us to obtain 2-phenyl derivative **3f** pure.

In order to avoid the sulfonation problem, we have tried to perform cyclization of SO_3-sensitive compounds **2f**–**h** in a mixture of triflic acid and P_2O_5 (Scheme 5). In this case the desired salts **3f**,**g** were obtained in good yields (Table 2, Method B), whereas the compound **2h** decomposed completely.

Cyclization Mechanism

The formation of fused oxazoles **3** from **2** resembles closure of *N*-acyl-α-aminocarbonyl compounds to oxazoles (known as Robinson–Gabriel cyclization in the case of monocycles). The influence of the nature of acid on the results of the cyclization of **2** to **3** may bring some light to the mechanism of this conversion. Clearly, the oxygen in the bicycles **3** originates from the amide group in pyrimidones **2**; this mechanism was proved by isotope label for monocyclic case,[10] and there is no evidence for its change in the case of bicyclic analogs. Therefore, protonation of the ketone oxygen in phenacyl derivatives **2** is required. However, 2-pyrimidones **2** have the concurrent basic center – the second nitrogen atom in the ring. As we have seen, use of H_2SO_4, PPA or $HClO_4$–Ac_2O systems led only to the salts of **2**, whereas the use of stronger acids (super acids) like H_2SO_4–SO_3 or CF_3SO_3H resulted in successful cyclization. This may indicate that the real cyclization mechanism requires somewhat unusual assumption on the formation of dications **IX** as the reaction intermediates (Scheme 6).



Scheme 6

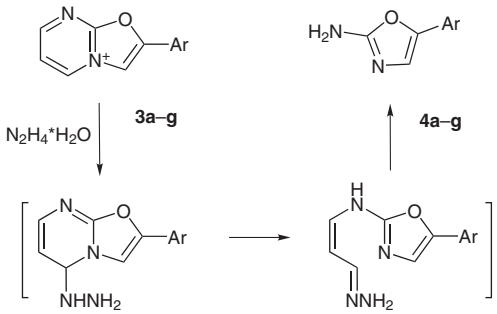
As an indirect proof of this hypothesis, one could consider the changes in the color of reaction mixtures: usual acids caused no changes, whereas super acids brought to solutions bright (yellow to red) colors. The same colors appeared when the final solid perchlorates **3** were dissolved in triflic acid.

Conversion of Oxazolo[3,2-*a*]pyrimidinium Salts 3 to 2-Amino-5-aryloxazoles 4

Although the structures of the type **3** are known for decades, there are no examples of their reactions with nucleophiles. We found that in reactions with hydrazine bicyclic salts **3a**–**g** underwent selective cleavage of the pyrimidine fragment leading with excellent yields to 2-amino-5-aryloxazoles **4a**–**g** (Scheme 7, Table 3). Although hydrazinolysis of structurally related oxazolopyridinium salt **IIIa** led to the cleavage and transformation of oxazole part,[11] in the case of the salts **3** there is no evidence for ambident properties of the bicycle.

Melting points and ^1H NMR spectral data of the aminooxazoles **4a**,**b**,**d**,**f**,**g** correspond to literature data, and for previously unknown compound **4c**,**e** we obtained satisfactory data of elementary analysis. Structure of most oxazoles **4** was confirmed by ^{13}C NMR spectra and mass spectra (which are absent in the literature), and the structure **4b** was proved by X-ray analysis (Figure 3).

Derivatives of 2-aminoxazole possess various types of biological activities; the parent scaffold is present in some



Scheme 7

Table 3 2-Amino-5-aryloxazoles Prepared

Compound	Ar	Yield (%)
4a	4-ClC_6H_4	95
4b	4-BrC_6H_4	96
4c	2,4-$Cl_2C_6H_3$	88
4d	4-$NO_2C_6H_4$	93
4e	3-$NO_2C_6H_4$	88
4f	Ph	90
4g	4-MeC_6H_4	82

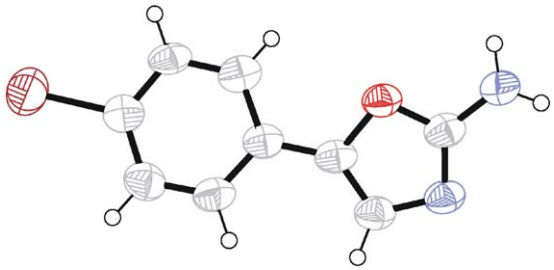
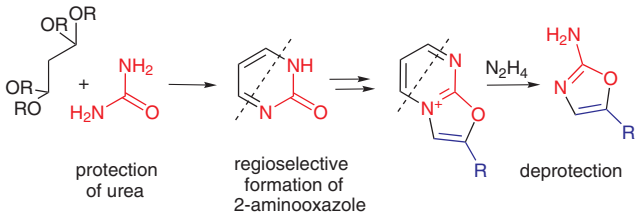


Figure 3 X-ray crystal structure of the compound **4b**

common drugs: antiseptic sulfamoxole and sulfaguanole, anti-asthmatic isamoxole, hypotensive azepexole, and anti-inflammatory ditazole. Many simple *N*-acyl- and *N*-alkyl derivatives of this family display anti-inflammatory[12] and antiviral[13] activities, and very recently N-substituted 2-aminoxazoles have been found as a novel class of VEGFR2 kinase inhibitors.[14] Therefore, development of flexible routes to this family remains an actual task. It should be mentioned that common methods leading to 2-aminooxazoles are frequently multistep reactions that require complicated reagents or the processes are accompanied by side reactions. The 'handbook' strategy to 2-aminooxazoles – reaction of cyanamide with α-hydroxycarbonyl compounds[15] – is difficult to apply for the synthesis of 5-aryl substituted 2-aminooxazoles **4**, since the starting materials would be poorly available α-hydroxy derivatives of phenylacetic aldehyde. Another old strategy is cyclocondensation of urea with α-halogencarbonyl compounds;[16] this process is complicated by concurrent formation of imidazolones.[15b] Again, for the synthesis of compounds **4** it would be necessary to start from hardly available 2-halogen derivatives of arylacetic aldehydes.

The are only few alternative methodologies to prepare 2-amino-5-aryloxazoles: Curtius rearrangement of oxazolyl-2-carboxylic acids hydrazides,[17] multistep synthesis starting from *N*-(tosylmethyl)-*N*′-tritylcarbodiimide,[18] and condensation of α-bromoketones with *N*-cyanourea.[19] Hence the strategy proposed in this communication, involving simple sequence with high yields and requiring cheap materials, may serve as a competitive complementary route to the class of compounds **4**.

Closer inspection of the suggested strategy may clarify, that actual use of 2-pyrimidone as the source of NCO fragment of 2-aminoxazole is nothing else but applying the idea of protecting group. Indeed, reaction of urea with α-bromoketones proceeds in a complex manner without clear regioselectivity (in contrast to thiourea). Pyrimidone may be considered as a sort of 'protected' urea that may be selectively N-phenacylated. Here the protecting group is the fragment of malonaldehyde, which is safely removed by hydrazinolysis at the final step. The role of malonaldehyde as protecting group is not only envisaged: in fact, most common way to obtain 2-pyrimidone is the condensation of urea with malonaldehyde derivatives. Hence, the overall sequence of 'protection and deprotection' of urea in the synthesis of 2-aminoxazoles can be described as shown in Scheme 8.



Scheme 8

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on AM 400 Bruker spectrometer for ^{1}H at 360 MHz and for ^{13}C at 90 or 100 MHz. Chemical shifts are reported in ppm referenced to residual protons in the deuterated solvent. IR spectra were obtained on UR-20 spectrometer in Nujol. Mass spectra were determined on Kratos MS-30 mass spectrometer (EI 70 eV). TLC was performed with Silufol UV-254 (Merck). The experimental intensities of diffraction reflections for single crystals of compounds **2a**,[20] **3b**,[21] and **4b**[22] were measured on a CAD4 automated diffractometer (MoKα radiation, graphite monochromator, ω scan mode) at r.t. All subsequent calculations were carried out with the SHELX97 program package.

2-Pyrimidone hydrochloride was prepared by reaction of urea with malonaldehyde bis(dimethyl acetal) (1,1,3,3-tetramethoxypropane) by a method described in the literature[20] [yield: 71%; yellow solid; mp 203–207 °C; (Lit.[23] mp 210 °C)].

1-(2-Aryl-2-oxoethyl)pyrimidin-2(1*H*)-ones 2a,b,f–h; 1-[(2-(4-Chlorophenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2a); Typical Procedure; Method A

K_2CO_3 (55.2 g, 0.4 mol) was added under stirring to a suspension of 2-pyrimidone hydrochloride (26.5 g, 0.2 mol) in anhyd acetone

(500 mL). A solution of 4-chlorophenacyl bromide (23.3 g, 0.1 mol) in acetone (100 mL) was added, and the mixture was stirred for 2 days at r.t. Acetone was evaporated in vacuum, and the residue was washed with H_2O, then with EtOAc. The product was isolated by suction and recrystallized from MeCN to afford **2a**; yield: 22.3 g (90%).

1-(2-Aryl-2-oxoethyl)pyrimidin-2(1*H*)-ones 2c–e; 1-[(2-(2,4-Dichlorophenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2c); Typical Procedure; Method B

2-Pyrimidone hydrochloride (26.5 g, 0.2 mol) was added to a freshly prepared solution of NaOMe obtained by reaction of Na (9.2 g, 0.4 mol) with absolute MeOH (400 mL). The mixture was stirred for 30 min, and MeOH was evaporated under reduced pressure. The residue was suspended in anhyd acetone (400 mL), and a solution of 2,4-dichlorophenacyl bromide (26.8 g, 0.1 mol) in acetone (200 mL) was added with stirring. The mixture was refluxed for 2 h and treated as described in Method A to give **2c**; yield: 17.0 g (60%).

1-[(2-(4-Chlorophenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2a)

Yield: 90%; white solid; mp 230–231 °C; R_f = 0.15 ($CHCl_3$–MeOH, 10:1).

IR (Nujol): 1695, 1615 cm^{-1}.

^1H NMR (360 MHz, DMSO-d_6): δ = 5.48 (s, 2 H, CH_2), 6.51 (m, 1 H, H-5), 7.68 (m, 2 H, Ar-H, BB′), 8.07 (m, 2 H, Ar-H, AA′), 8.13 (m, 1 H, H-4), 8.62 (m, 1 H, H-6).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 56.1 (CH_2), 103.8 (C-5), 129.1 (C-3′, Ar), 129.8 (C-2′, Ar), 133.0 (C-1′, Ar), 139.0 (C-4′, Ar), 150.5 [C-4 (6)], 155.5 (C-2), 166.7 [C-6 (4)], 191.6 (C=O).

Anal. Calcd for $C_{12}H_9ClN_2O_2$: C, 57.96; H, 3.65; N, 11.27. Found: C, 57.67; H, 3.41; N, 11.29.

1-[(2-(4-Bromophenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2b)

Yield: 95%; white solid; mp 237–239 °C; R_f = 0.15 ($CHCl_3$–MeOH, 10:1).

IR (Nujol): 1700, 1660 cm^{-1}.

^1H NMR (360 MHz, DMSO-d_6): δ = 5.43 (s, 2 H, CH_2), 6.41 (m, 1 H, H-5), 7.72 (m, 2 H, Ar-H, BB′), 7.99 (m, 2 H, Ar-H, AA′), 8.08 (m, 1 H, H-4), 8.57 (m, 1 H, H-6).

Anal. Calcd for $C_{12}H_9BrN_2O_2$: C, 49.17; H, 3.09; N, 9.56. Found: C, 48.75; H, 2.89; N, 9.36.

1-[(2-(2,4-Dichlorophenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2c)

Yield: 60%; white solid; mp 205–207 °C; R_f = 0.15 ($CHCl_3$–MeOH, 10:1).

IR (Nujol): 1710, 1680 cm^{-1}.

^1H NMR (360 MHz, DMSO-d_6): δ = 5.27 (s, 2 H, CH_2), 6.42 (m, 1 H, H-5), 7.51 (d, $J_{5',6'}$ = 8.2 Hz, 1 H, H-5′-Ar), 7.57 (s, 1 H, H-3′-Ar), 7.91 (d, $J_{6',5'}$ = 8.2 Hz, 1 H, H-6′-Ar), 8.19 (m, 1 H, H-4), 8.57 (m, 1 H, H-6).

Anal. Calcd for $C_{12}H_8Cl_2N_2O_2$: C, 50.91; H, 2.85; N, 9.89. Found: C, 50.74; H, 2.83; N, 9.75.

1-[(2-(4-Nitrophenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2d)

Yield: 65%; pale yellow solid; mp 215–217 °C; R_f = 0.15 ($CHCl_3$–MeOH, 10:1).

IR (Nujol): 1695, 1655 cm^{-1}.

^1H NMR (360 MHz, DMSO-d_6): δ = 5.55 (s, 2 H, CH_2), 6.54 (m, 1 H, H-5), 8.16 (m, 1 H, H-4), 8.28 (m, 2 H, Ar-H, BB′), 8.41 (m, 2 H, Ar-H, AA′), 8.65 (m, 1 H, H-6).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 56.6 (CH_2), 103.9 (C-5), 124.1 (C-3′, Ar), 129.5 (C-2′, Ar), 138.9 (C-1′, Ar), 150.4 (C-4′, Ar), 150.5 [C-4 (6)], 155.5 (C-2), 166.9 [C-6 (4)], 192.0 (C=O).

Anal. Calcd for $C_{12}H_9N_3O_4$: C, 55.60; H, 3.50; N, 16.21. Found: C, 55.69; H, 3.39; N, 16.49.

1-[(2-(3-Nitrophenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2e)

Yield: 63%; white solid; mp 162–164 °C; R_f = 0.15 ($CHCl_3$–MeOH, 10:1).

IR (Nujol): 1710, 1670 cm^{-1}.

^1H NMR (360 MHz, DMSO-d_6): δ = 5.55 (s, 2 H, CH_2), 6.45 (m, 1 H, H-5), 7.86 (m, 1 H, H-5′-Ar), 8.12 (m, 1 H, H-4), 8.48 (m, 2 H, H-4′-Ar, H-6′-Ar), 8.59 (m, 1 H, H-6), 8.76 (m, 1 H, H-2′-Ar).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 56.5 (CH_2), 103.9 (C-5), 122.3 (C-2′, Ar), 128.2 (C-4′, Ar), 130.8 (C-5′, Ar), 134.1 (C-6′, Ar), 135.6 (C-1′, Ar), 148.1 (C-3′, Ar), 150.4 [C-4 (6)], 155.5 (C-2), 166.9 [C-6 (4)], 191.4 (C=O).

Anal. Calcd for $C_{12}H_9N_3O_4$: C, 55.60; H, 3.50; N, 16.21. Found: C, 55.58; H, 3.42; N, 16.19.

1-(2-Oxo-2-phenylethyl)pyrimidin-2(1*H*)-one (2f)

Yield: 79%; white solid; mp 184–186 °C; R_f = 0.15 ($CHCl_3$–MeOH, 10:1).

IR (Nujol): 1710, 1650 cm^{-1}.

^1H NMR (360 MHz, DMSO-d_6): δ = 5.50 (s, 2 H, CH_2), 6.51 (m, 1 H, H-5), 7.60 (m, 2 H, H-3′-Ar), 7.73 (m, 1 H, H-4′-Ar), 8.06 (m, 2 H, H-2′-Ar), 8.15 (m, 1 H, H-4), 8.63 (m, 1 H, H-6).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 56.2 (CH_2), 103.7 (C-5), 127.9 (C-2′, Ar), 128.9 (C-3′, Ar), 134.1 (C-4′, Ar), 134.3 (C-1′, Ar), 150.6 [C-4 (6)], 155.5 (C-2), 166.7 [C-6 (4)], 192.4 (C=O).

Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 66.99; H, 4.86; N, 13.24.

1-[(2-(4-Methylphenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2g)

Yield: 81%; white solid; mp 197–199 °C; R_f = 0.15 ($CHCl_3$–MeOH, 10:1).

IR (Nujol): 1690, 1660 cm^{-1}.

^1H NMR (360 MHz, DMSO-d_6): δ = 3.29 (s, 3 H, CH_3), 5.45 (s, 2 H, CH_2), 6.50 (m, 1 H, H-5), 7.40 (m, 2 H, Ar-H, BB′), 7.95 (m, 2 H, Ar-H, AA′), 8.14 (m, 1 H, H-4), 8.62 (m, 1 H, H-6).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 21.2 (CH_3), 56.0 (CH_2), 103.6 (C-5), 128.0 (C-2′, Ar), 129.4 (C-3′, Ar), 131.9 (C-1′, Ar), 144.6 (C-4′, Ar), 150.6 [C-4 (6)], 155.5 (C-2), 166.6 [C-6 (4)], 191.9 (C=O).

Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.65; H, 5.49; N, 12.38.

1-[(2-(4-Methoxyphenyl)-2-oxoethyl]pyrimidin-2(1*H*)-one (2h)

Yield: 70%; white solid; mp 173–175 °C; R_f = 0.15 ($CHCl_3$–MeOH, 10:1).

IR (Nujol): 1700, 1640 cm^{-1}.

^1H NMR (360 MHz, DMSO-d_6): δ = 3.90 (s, 3 H, OCH_3), 5.40 (s, 2 H, CH_2), 6.41 (m, 1 H, H-5), 7.05 (m, 2 H, Ar-H, BB′), 8.01 (m, 2 H, Ar-H, AA′), 8.08 (m, 1 H, H-4), 8.56 (m, 1 H, H-6).

Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.88; H, 4.88; N, 11.56.

Attempted Cyclization of 2a

$HClO_4$ (0.3 mL) was carefully added under good cooling to Ac_2O (10 mL). Pyrimidone **2a** (0.746 g, 0.003 mol) was added, the colorless mixture was stirred for 30 min, and then kept for 24 h at r.t. The obtained precipitate was filtered, dried and recrystallized from

EtOH to afford the perchlorate of **2a**; yield: 1.00 g (96%); white solid; mp 325–327 °C.

^{1}H NMR (360 MHz, DMSO-d_6): δ = 5.73 (s, 2 H, CH_2), 6.98 (m, 1 H, H-5), 7.59 (m, 2 H, Ar-H, BB′), 8.09 (m, 2 H, Ar-H, AA′), 8.86 (m, 1 H, H-4), 8.91 (m, 1 H, H-6).

Anal. Calcd for $C_{12}H_{10}Cl_2N_2O_6$: C, 45.80; H, 3.52; N, 8.90. Found: C, 45.69; H, 3.43; N, 8.80.

Treatment of **2a** with concd H_2SO_4 and PPA led to the same perchlorate. In the case of $TiCl_4$ or $POCl_3$ no identifiable products were isolated.

2-Aryloxazolo[3,2-*a*]pyrimidinium Perchlorates 3a–f; 2-(4-Chlorophenyl)oxazolo[3,2-*a*]pyrimidinium Perchlorate (3a); Typical Procedure; Method A

Dried 4-chlorohenacylpyrimidone (**2a**; 4.28 g, 0.02 mol) was carefully added to a stirred mixture of fuming H_2SO_4 [32 mL; prepared by mixing of H_2SO_4 (25 mL, d = 1.84) and commercial (60 mass% of SO_3) fuming H_2SO_4 (17 mL, 34 g)]. [For **2c–e** fuming sulfuric acid (40 mL) with 30 mass% of SO_3 was used for mixing]. The temperature was kept in the range –5 to 0 °C. The mixture (orange to red) was stirred below 0 °C until the compound **2a** completely dissolved and then kept for 5 h under r.t. (For **2c** the mixture was kept for 24 h, and for **2d**,**e**, 72 h at r.t.). After that the mixture was carefully poured into crushed ice (500 g). Then $HClO_4$ (10 mL, 65%) was added. The product was isolated by suction filtration, washed with H_2O, then with EtOH and Et_2O, and dried in vacuum over P_2O_5 to afford **3a**; yield: 5.23 g (79%); white solid; mp 268–270 °C.

^{1}H NMR (360 MHz, DMSO-d_6): δ = 7.64 (m, 2 H, Ar-H, BB′), 8.06 (m, 2 H, Ar-H, AA′), 8.14 (dd, $J_{6,7}$ = 4.5 Hz, $J_{6,5}$ = 6.3 Hz, 1 H, H-6), 9.31 (s, 1 H, H-3), 9.34 (dd, $J_{7,6}$ = 4.5 Hz, $J_{7,5}$ = 1.7 Hz, 1 H, H-7), 9.66 (dd, $J_{5,6}$ = 6.3 Hz, $J_{5,7}$ = 1.7 Hz, 1 H, H-5).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 111.8 (C-3), 118.6 (C-6), 122.6 (C-1′, Ar), 127.7 (C-2′, Ar), 130.1 (C-3′, Ar), 137.1 (C-4′, Ar), 142.4 [C-7 (5)], 150.8 (C-2), 153.2 (C-9), 162.6 [C-5 (7)].

Anal. Calcd for $C_{12}H_8Cl_2N_2O_5$: C, 43.53; H, 2.44; N, 8.46. Found: C, 43.33; H, 2.40; N, 8.53.

2-(4-Bromophenyl)oxazolo[3,2-*a*]pyrimidinium Perchlorate (3b)

Yield: 85%; white solid; mp 279–281 °C.

^{1}H NMR (360 MHz, DMSO-d_6): δ = 7.81 (m, 2 H, Ar-H, BB′), 8.02 (m, 2 H, Ar-H, AA′), 8.14 (dd, $J_{6,7}$ = 4.6 Hz, $J_{6,5}$ = 6.3 Hz, 1 H, H-6), 9.31 (s, 1 H, H-3), 9.36 (dd, $J_{7,6}$ = 4.6 Hz, $J_{7,5}$ = 1.8 Hz, 1 H, H-7), 9.68 (dd, $J_{5,6}$ = 6.3 Hz, $J_{5,7}$ = 1.8 Hz, 1 H, H-5).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 111.8 (C-3), 118.5 (C-6), 122.9 (C-1′, Ar), 125.9 (C-4′, Ar), 127.8 (C-2′, Ar), 132.8 (C-3′, Ar), 142.3 [C-7 (5)], 150.8 (C-2), 153.2 (C-9), 162.6 [C-5 (7)].

Anal. Calcd for $C_{12}H_8Br_2N_2O_5$: C, 38.38; H, 2.15; N, 7.46. Found: C, 38.24; H, 1.99; N, 7.46.

2-(2,4-Dichlorophenyl)oxazolo[3,2-*a*]pyrimidinium Perchlorate (3c)

Yield: 83%; white solid; mp 315–317 °C.

^{1}H NMR (360 MHz, DMSO-d_6): δ = 7.69 (dd, $J_{5',6}$ = 8.9 Hz, $J_{5',3'}$ = 1.8 Hz, 1 H, H-5′-Ar), 7.82 (d, $J_{3',5'}$ = 1.8 Hz, 1 H, H-3′-Ar), 8.16 (m, 2 H, H-5-Ar + H-6′-Ar), 9.41 (dd, $J_{7,6}$ = 4.4 Hz, $J_{7,5}$ = 1.8 Hz, 1 H, H-7), 9.45 (s, 1 H, H-3), 9.61 (dd, $J_{5,6}$ = 6.2 Hz, $J_{5,7}$ = 1.8 Hz, 1 H, H-5).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 115.2 (C-3), 118.8 (C-6), 121.4 (C-1′, Ar), 128.9 (C-3′, Ar), 130.7 (C-6′, Ar), 131.0 (C-5′, Ar), 132.2 (C-2′, Ar), 137.4 (C-4′, Ar), 142.4 [C-7 (5)], 147.2 (C-2), 152.8 (C-9), 163.6 [C-5 (7)].

Anal. Calcd for $C_{12}H_7Cl_3N_2O_5$: C, 39.43; H, 1.93; N, 7.66. Found: C, 39.14; H, 1.91; N, 7.75.

2-(4-Nitrophenyl)oxazolo[3,2-*a*]pyrimidinium Perchlorate (3d)

Yield: 80%; pale yellow solid; mp 271–273 °C.

^{1}H NMR (360 MHz, DMSO-d_6): δ = 8.17 (dd, $J_{6,7}$ = 4.5 Hz, $J_{6,5}$ = 6.3 Hz, 1 H, H-6), 7.36 (m, 2 H, Ar-H, BB′), 8.46 (m, 2 H, Ar-H, AA′), 9.41 (dd, $J_{7,6}$ = 4.5 Hz, $J_{7,5}$ = 1.8 Hz, 1 H, H-7), 9.50 (s, 1 H, H-3), 9.73 (dd, $J_{5,6}$ = 6.3 Hz, $J_{5,7}$ = 1.8 Hz, 1 H, H-5).

Anal. Calcd for $C_{12}H_8ClN_3O_7$: C, 42.18; H, 2.36; N, 12.30. Found: C, 42.36; H, 2.48; N, 12.43.

2-(3-Nitrophenyl)oxazolo[3,2-*a*]pyrimidinium Perchlorate (3e)

Yield: 87%; white solid; mp 248–250 °C.

^{1}H NMR (360 MHz, CF_3CO_2D): δ = 8.66 (m, 1 H, H-3′-Ar), 8.83 (m, 1 H, H-6), 9.13 (m, 1 H, H-2′-Ar), 9.32 (m, 1 H, H-4′-Ar), 9.67 (m, 2 H, H-3-Ar + H-5′-Ar), 10.13 (m, 1 H, H-7), 10.19 (m, 1 H, H-5).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 113.3 (C-3), 118.6 (C-6), 120.7 (C-2′, Ar), 125.2 (C-1′, Ar), 126.5 (C-6′, Ar), 131.6 (C-4′, Ar), 131.8 (C-5′, Ar), 142.7 [C-7 (5)], 148.6 (C-3′, Ar), 149.6 (C-2), 153.3 (C-9), 163.3 [C-5 (7)].

Anal. Calcd for $C_{12}H_8ClN_3O_7$: C, 42.18; H, 2.36; N, 12.30. Found: C, 42.25; H, 2.22; N, 12.36.

2-Phenyloxazolo[3,2-*a*]pyrimidinium Perchlorate (3f)

Method A: To the precipitate, obtained after cyclization and addition of H_2O and $HClO_4$, was added DMSO (50 mL), the mixture was thoroughly suspended, and the insoluble part was filtered off. The filtrate was partially evaporated in vacuum and diluted with Et_2O (50 mL). The precipitate was filtered, washed with Et_2O and EtOH, and dried in vacuum over P_2O_5 to afford the **3f**; yield: 55%; white solid; mp 261–263 °C.

^{1}H NMR (360 MHz, CF_3CO_2D): δ = 8.84 (m, 3 H, H-6-Ar + H-3′-Ar), 9.19 (m, 3 H, H-2′,4′-Ar), 9.81 (s, 1 H, H-3), 10.49 (m, 1 H, H-7), 10.56 (m, 1 H, H-5).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 111.2 (C-3), 118.4 (C-6), 123.6 (C-1′, Ar), 125.9 (C-2′, Ar), 129.8 (C-3′, Ar), 132.3 (C-4′, Ar), 142.2 [C-7 (5)], 151.8 (C-2), 153.2 (C-9), 162.4 [C-5 (7)].

Anal. Calcd for $C_{12}H_9ClN_2O_5$: C, 48.58; H, 3.06; N, 9.44. Found: C, 48.65; H, 2.91; N, 9.38.

Method B: *N*-Phenacyl-2-pyrimidone **2f** (0.37 g, 0.0016 mol) was mixed with P_2O_5 (0.65 g, 0.0046 mol) and freshly distilled triflic acid (5 mL) was added to the mixture. The dark-red mixture obtained was refluxed for 3 h at 85–90 °C. The mixture was cooled and carefully poured into crushed ice (100 g). $HClO_4$ (3 mL) was added, and the precipitate was filtered, washed with H_2O, EtOH and Et_2O, and dried in vacuum over P_2O_5 to afford the **3f**; yield: 0.375 g (79%); white solid; mp 261–263 °C, identical to the sample obtained by Method A.

^{1}H NMR (360 MHz, DMSO-d_6): δ = 7.69 (m, 3 H, H-6-Ar + H-3′-Ar), 8.11 (m, 3 H, H-2′,4′-Ar), 9.28 (s, 1 H, H-3), 9.40 (m, 1 H, H-7), 9.67 (m, 1 H, H-5).

2-(4-Methylphenyl)oxazolo[3,2-a]pyrimidinium Perchlorate (3g)

Method B; yield 75%; white solid; mp 239–241 °C.

^{1}H NMR (360 MHz, DMSO-d_6): δ = 7.50 (m, 2 H, Ar-H, BB′), 7.98 (m, 2 H, Ar-H, AA′), 8.13 (m, 1 H, H-6), 9.20 (s, 1 H, H-3), 9.37 (m, 1 H, H-7), 9.64 (m, 1 H, H-5).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 21.2 (CH_3), 110.5 (C-3), 118.4 (C-6), 120.9 (C-1′, Ar), 125.8 (C-2′, Ar), 130.4 (C-3′, Ar), 142.1 [C-7 (5)], 142.8 (C-4′, Ar), 152.0 (C-2), 153.1 (C-9), 162.0 [C-5 (7)].

Anal. Calcd for $C_{13}H_{11}ClN_2O_5$: C, 50.26; H, 3.57; N, 11.41. Found: C, 50.40; H, 3.41; N, 11.32.

2-Amino-5-aryloxazoles 4a–g; 5-(4-Chlorophenyl)-1,3-oxazol-2-amine (4a); Typical Procedure

Perchlorate **3a** (3.3 g, 0.01 mol)) was suspended in anhyd MeCN (50 mL), and hydrazine hydrate (5 mL) was added with stirring. The mixture turned orange, and was refluxed for 20 min (until decolorization). The solution was cooled to r.t. and poured into cold H_2O (100 mL). The product was isolated by suction filtration and recrystallized from EtOH to afford **4a**; yield: 1.65 g (95%); white solid; mp 220–221 °C (Lit.[18a] mp 220–222 °C); R_f = 0.4 ($CHCl_3$–MeOH, 10:1).

^{1}H NMR (360 MHz, DMSO-d_6): δ = 6.57 (br s, 2 H, NH_2), 7.01 (s, 1 H, H-4), 7.26 (m, 2 H, Ar-H, BB′), 7.41 (m, 2 H, Ar-H, AA′).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 123.4 (C-2′, Ar), 123.9 (C-4), 127.5 (C-1′, Ar), 128.8 (C-3′, Ar), 130.2 (C-4′, Ar), 142.0 (C-5), 161,5 (C-2).

MS (EI, 70 eV): *m*/*z* (%) = 138 (100), 194 (76).

5-(4-Bromophenyl)-1,3-oxazol-2-amine (4b)

Yield: 96%; white solid; mp 220–221 °C (Lit [19b] mp 220–222 °C); R_f = 0.4 ($CHCl_3$–MeOH, 10:1).

^{1}H NMR (360 MHz, DMSO-d_6): δ = 6.61 (br s, 2 H, NH_2), 7.04 (s, 1 H, H-4), 7.35 (m, 2 H, Ar-H, BB′), 7.44 (m, 2 H, Ar-H, AA′).

MS (EI, 70 eV): *m*/*z* (%) = 183 (100), 238 (100).

5-(2,4-Dichlorophenyl)-1,3-oxazol-2-amine (4c)

Yield: 88%; white solid; mp 202–204 °C; R_f = 0.4 ($CHCl_3$–MeOH, 10:1).

^{1}H NMR (360 MHz, DMSO-d_6): δ = 6.24 (br s, 2 H, NH_2), 7.23 (dd, $J_{5',6'}$ = 8.6 Hz, $J_{5',3'}$ = 2 Hz, 1 H, H-5′-Ar), 7.35 (s, 1 H, H-4), 7.38 (d, $J_{3',5'}$ = 2 Hz, 1 H, H-3′-Ar), 7.58 (d, $J_{6',5'}$ = 8.6 Hz, 1 H, H-6′-Ar).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 125.9 (C-1′, Ar), 126.3 (C-6′, Ar), 127.7 (C-4), 128.2 (C-2′, Ar), 128.7 (C-5′, Ar), 129.8 (C-3′, Ar), 130.4 (C-4′, Ar), 138.8 (C-5), 161.5 (C-2).

MS (EI, 70 eV): *m*/*z* (%) = 173 (64), 228 (100).

Anal. Calcd for $C_9H_6Cl_2N_2O$: C, 47.19; H, 2.64; N, 12.23. Found: C, 47.22; H, 2.68; N, 12.37.

5-(4-Nitrophenyl)-1,3-oxazol-2-amine (4d)

Yield: 93%; orange solid; mp 235–237 (Lit.[18a] 235–237 °C); R_f = 0.4 ($CHCl_3$–MeOH, 10:1).

^{1}H NMR (360 MHz, DMSO-d_6): δ = 6.99 (br s, 2 H, NH_2), 7.39 (s, 1 H, H-4), 7.60 (m, 2 H, Ar-H, BB′), 8.16 (m, 2 H, Ar-H, AA′).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 121.9 (C-2′, Ar), 124.6 (C-3′, Ar), 128.9 (C-4), 134.6 (C-1′, Ar), 141.5 (C-5), 144.5 (C-4′, Ar), 162.9 (C-2).

MS (EI, 70 eV): *m*/*z* (%) = 175 (47), 205 (100).

5-(3-Nitrophenyl)-1,3-oxazol-2-amine (4e)

Yield: 88%; orange solid; mp 201–203 °C; R_f = 0.4 ($CHCl_3$–MeOH, 10:1).

^{1}H NMR (360 MHz, DMSO-d_6): δ = 6.81 (br s, 2 H, NH_2), 7.27 (s, 1 H, H-4), 7.53 (m, 1 H, H-5′-Ar), 7.83 (m, 1 H, H-6′-Ar), 7.95 (m, 1 H, H-4′-Ar), 8.21 (m, 1 H, H-2′-Ar).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 115.7 (C-2′, Ar), 120.3 (C-4′, Ar), 126.1 (C-4), 127.8 (C-6′, Ar), 130.2 (C-1′, Ar), 130.5 (C-5′, Ar), 141.0 (C-5), 148.4 (C-3′, Ar), 162.1 (C-2).

MS (EI, 70 eV): *m*/*z* (%) = 175 (17), 205 (100).

Anal. Calcd for $C_9H_7N_3O_3$: C, 52.69; H, 3.44; N, 20.48. Found: C, 52.72; H, 3.32; N, 20.37.

5-Phenyl-1,3-oxazol-2-amine (4f)

Yield: 90%; white solid; mp 215–216 °C (Lit.[19b] mp 215–216 °C); R_f = 0.4 ($CHCl_3$–MeOH, 10:1).

^{1}H NMR (360 MHz, DMSO-d_6): δ = 6.48 (br s, 2 H, NH_2), 6.96 (s, 1 H, H-4), 7.12 (m, 1 H, H-4′-Ar), 7.30 (m, 2 H, H-3′-Ar), 7.42 (m, 2 H, H-2′-Ar).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 121.9 (C-2′, Ar), 123.0 (C-4), 126.2 (C-1′, Ar), 128.7 (C-4′, Ar), 128.8 (C-3′, Ar), 143.1 (C-5), 161.4 (C-2).

MS (EI, 70 eV): *m*/*z* (%) = 105 (70), 160 (100).

5-(4-Methylphenyl)-1,3-oxazol-2-amine (4g)

Yield: 82%; white solid; mp 218–220 (Lit.[18a] mp 218–220 °C); R_f = 0.4 ($CHCl_3$–MeOH, 10:1).

^{1}H NMR (360 MHz, DMSO-d_6): δ = 6.74 (br s, 2 H, NH_2), 7.09 (s, 1 H, H-4), 7.17 (m, 2 H, Ar-H, BB′), 7.32 (m, 2 H, Ar-H, AA′).

^{13}C NMR (90 MHz, DMSO-d_6): δ = 21.1 (CH_3), 121.9 (C-2′, Ar), 122.0 (C-4), 126.0 (C-1′, Ar), 129.3 (C-3′, Ar), 135.5 (C-4′, Ar), 143.2 (C-5), 161.0 (C-2).

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