Azido-1,2,5-oxadiazoles in reactions with 1,3-dicarbonyl compounds

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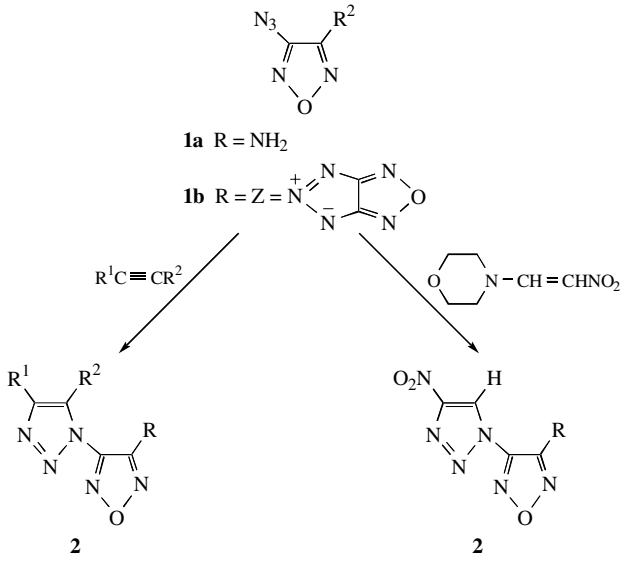
The 1,3-dipolar cycloaddition of azido-1,2,5-oxadiazoles (azidofurazans) to dicarbonyl compounds was studied, and a new procedure for the synthesis of 4-R-3-(4-R^1-5-R^2-1,2,3-triazol-1-yl)-1,2,5-oxadiazoles was proposed.

Previously, we found that the interaction of 3-azido-4-aminofurazan **1a** and 5-[4-azido-(1,2,5)-oxadiazol-3-yl]-5*H*-[1,2,3]-triazolo[4,5-*c*][1,2,5]oxadiazole **1b**, with substituted acetylenes[1] or morpholinonitroethylene[2] resulted in 1,3-dipolar cycloaddition products, (1,2,3-triazol-1-yl)furazans **2** (Scheme 1).

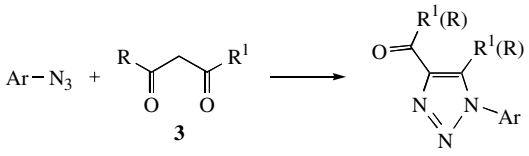


Scheme 1

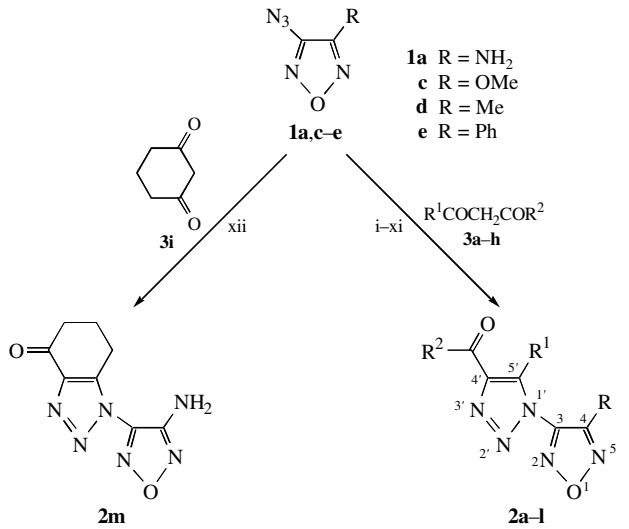
Triazolylfurazans **2**, whose derivatives exhibited various biological activities,[3,4] can be studied as potentially biologically active compounds. In this context, it seems reasonable to develop new preparative procedures for the synthesis of these compounds.

It is well known that aromatic azides can form 1,2,3-triazoles by cycloaddition to not only acetylenes or activated olefins but also compounds containing active CH_2 groups, such as 1,3-dicarbonyl compounds **3**[5–11] (Scheme 2). The position of the RCO group depends on the reaction mechanism.[7,8,12,13] Triazoles are not always the only products of the above reaction. Amines, diazo compounds, *etc.*, can be formed depending on the nature of the azide and the carbonyl component and on reaction conditions.[5–7,12,14]

In this work, we examined the cycloaddition of azidofurazans to 1,3-dicarbonyl compounds (Schemes 3 and 4) in order to develop a new procedure for the synthesis of compounds **2**. We used azidofurazans **1a–e** containing the following substituents: amino (**1a**), methoxy (**1c**), methyl (**1d**), phenyl (**1e**) and oxapentaazapentalenyl (**1b**) groups. Acetylacetone **3a**, benzoylacetone **3b**, dibenzoylmethane **3c**, acetoacetic ester **3d**, benzoylacetic ester **3e**, their analogues **3f–h** and cyclic diketones **3i**,**j** were used as dicarbonyl compounds. The reactions with azide **1a** (Scheme 3, i–viii, xi) were studied most extensively. Solvents (EtOH, MeOH, H_2O and aqueous ethanol) and activating bases (Et_3N, MeONa, Na_2CO_3, K_2CO_3 and $MgCO_3$) were varied.



Scheme 2



2a R = NH_2, R^1 = R^2 = Me
b R = NH_2, R^1 = Me, R^2 = Ph
c R = NH_2, R^1 = Ph, R^2 = Me
d R = NH_2, R^1 = R^2 = Ph
e R = NH_2, R^1 = Me, R^2 = OEt
f R = NH_2, R^1 = Ph, R^2 = OEt
g R = NH_2, R^1 = Et, R^2 = OMe
h R = NH_2, R^1 = Pr, R^2 = OEt
i R = NH_2, R^1 = CH_2OMe, R^2 = OMe
j R = OMe, R^1 = R^2 = Me
k R = R^1 = R^2 = Me
l R = Ph, R^1 = R^2 = Me

3a R^1 = R^2 = Me
b R^1 = Me, R^2 = Ph
c R^1 = R^2 = Ph
d R^1 = Me, R^2 = OEt
e R^1 = Ph, R^2 = OEt
f R^1 = Et, R^2 = OMe
g R^1 = Pr, R^2 = OEt
h R^1 = CH_2OMe, R^2 = OMe

Scheme 3 *Reagents and conditions*: i, **1a**, **3a**, MeOH, $MgCO_3$, 8 h, H_2O (Et_3N, K_2CO_3, Na_2CO_3), 30 min, **2a**; ii, **1a**, **3b**, EtOH–H_2O 1:5, K_2CO_3, 30 min, **2b**, **2c**; iii, **1a**, **3c**, MeOH, $MgCO_3$, 8 h, **2d**; iv, **1a**, **3d**, H_2O, Et_3N (EtOH, K_2CO_3), 30 min (15 min), **2e**; v, **1a**, **3e**, EtOH, $MgCO_3$, **2h**, **2f**; vi, **1a**, **3f**, MeOH, $MgCO_3$, 8 h, K_2CO_3, 2 h, **2g**; vii, **1a**, **3g**, EtOH, $MgCO_3$, 10 h, **2h**; viii, **1a**, **3h**, EtOH, $MgCO_3$, 16 h, **2i**; ix, **1c**, **3a**, MeOH, $MgCO_3$, 10 h, **2j**; x, **1d**, **3a**, H_2O, K_2CO_3, 8 h, **2k**; xi, **1e**, **3a**, EtOH–H_2O 1:1, Et_3N, 10 h, **2l**; xii, **1a**, **3i**, EtOH, $MgCO_3$, 8 h, **2m**.

We found that the majority of the tested reactions resulted in cycloaddition products, triazolylfurazans **2a–m** (Scheme 3, i–xii), which were obtained in high yields.† We also found that, as distinct from published data, the amount of a base required for cycloaddition is lower that an equimolar amount by a factor of 2–10. Triazolylfurazans were successfully formed not only in the presence of Et_3N, which is frequently used for the activation of dicarbonyl compounds, but also under the action of alkali metal carbonates or $MgCO_3$. Sodium methylate was found to be inappropriate for the reaction with azide **1a**.

Water, which was not used previously in the reactions of azides with dicarbonyl compounds, and aqueous ethanol were found to

be most favourable for the preparation of triazolylfurazans based on azide **1a**. The reactions rapidly proceeded in aqueous media (within 30 min with azide **1a** or within a few hours with other azidofurazans) without heating, and almost pure cycloaddition products **2** were precipitated. Reactions in ethanol as a solvent were performed on boiling.

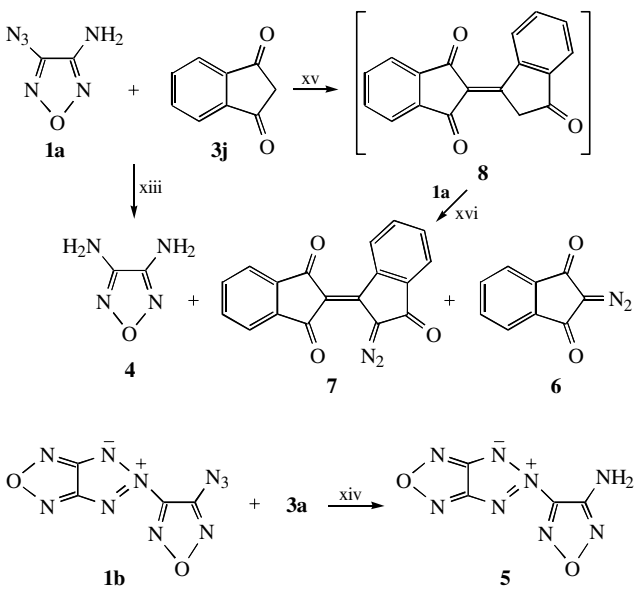
Under the specified conditions, azidofurazans reacted with 1,3-dicarbonyl compounds much more rapidly than with substituted acetylenes.

Reactions shown in Scheme 4 do not result in the synthesis of products **2**. The interaction of azide **1a** with indanedione **3k** (Scheme 4, xiii) or azide **1b** with acetylacetone (xiv) result in amine **4** or **5**, respectively. Amine **5**, which was described previously, was isolated in 83% yield and identified by TLC and ^{1}H and ^{13}C NMR spectra.

Along with amine **4**, 2-diazo-1,3-indanedione[16] **6** and diazobindone[16] **7** were formed in reaction xiii. Compounds **6** and **4** were identified by mass spectrometry (*m*/*z* 172 and 100 correspond to their molecular ions); amine **4** was also identified by chromatography. Diazobindone **7** (mp 208 °C[16]) was isolated in 75% yield. This compound is likely formed from indanedione self-condensation product **8** (Scheme 4), similarly to the reaction of indole with *p*-tosylazide in an alkaline medium.[16] This hypothesis was supported by control experiments (xv, xvi), which demonstrated that indanedione **3j** was converted into bindone **8** on boiling with $MgCO_3$ in ethanol. The reaction of bindone **8** with azide **1a** under the same conditions afforded diazobindone **7**. It is likely that reactions xiii and xiv occur as described previously.[7,14]

The structures of compounds **2a**–**m** were determined from the data of elemental analysis, IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry.‡

In the assignment of signals in the ^{13}C NMR spectra, we used a selective heteronuclear double resonance procedure and took into account the multiplicity of signals obtained in the measurement of ^{13}C–^{1}H spin–spin coupling constants (for compounds **2b**,**j**,**k**,**l**). Thus, for example, in the region 135–165 ppm, the spectrum of **2j** exhibited two quartets with J ^{13}C, ^{1}H 7.3 and 3.8 Hz, which were attributed to C-5′ and C-4, respectively, a narrower signal at 141.5 ppm, which was ascribed to C-3, and a broadened signal at 142.6 ppm, which was attributed to C-4′.



Scheme 4 *Reagents and conditions*: xiii, EtOH, $MgCO_3$, 5 min; xiv, EtOH, $MgCO_3$, 6 min.

† *General preparation procedure for triazoles* **2a**–**m**. A mixture of azide **1** and dicarbonyl compound **3** in water or aqueous ethanol was stirred in the presence of a catalyst at room temperature until vigorous precipitation. The precipitate was filtered off, washed with water and dried in air. The mixture of reactants was boiled in ethanol until the complete reaction of the azide. The reaction mixture was evaporated to dryness in a vacuum; the residue was washed with water and dried in air. In reactions with $MgCO_3$, a hot ethanolic solution was initially filtered from the inorganic salt and then evaporated to dryness; the residue was washed with water and dried in air.

‡ All new compounds exhibited satisfactory elemental analysis data. The ^{13}C and ^{1}H NMR spectra of compounds **2a**–**m** were measured on a Bruker AM-300 spectrometer (75.5 MHz for ^{13}C and 300 MHz for ^{1}H) in a Fourier transform pulse mode as solutions in [$^2H_6$]DMSO ($\delta_{^{13}C}$ 39.5, $\delta_{^1H}$ 2.5) or $CDCl_3$ ($\delta_{^{13}C}$ 77.1, $\delta_{^1H}$ 7.27). The IR spectra were recorded on a Specord M80 instrument in KBr pellets. The TLC monitoring was performed using Silufol UV-254 plates (Czech Republic).

2a (i) yield 81–93%, mp 145 °C (MeOH); R_f 0.55 (PhH–EtOAc, 3:1). IR (KBr, ν_{max}/cm^{-1}): 3430, 3340 (NH_2), 3020 (Me), 1710 (C=O), 1650, 1610, 1580, 1560, 1530, 1480, 1415, 1370, 1310, 1270, 1240, 1205, 1120, 1060, 1025, 1000, 980, 960, 930. ^{1}H NMR ($CDCl_3$) δ: 2.48 (s, 3H, Me), 2.61 (s, 3H, COMe), 4.46 (s, 2H, NH_2). ^{13}C NMR ([$^2H_6$]DMSO) δ: 192.9 (C=O), 152.4 (C-4), 142.7 (C-3), 142.3 (C-4′), 140.2 (C-5′), 27.8 (COMe), 9.6 (Me). MS, *m*/*z* (%): 208 (M^+, 50), 193 (M^+ – Me, 23), 180 ($M^+ - N_2$, 5), 165 (M^+ – COMe, 24), 150 (18), 149 (45), 138 (42), 123 (60), 108 (79), 53 (100).

2b (ii) yield 91%, mp 176–177 °C (MeOH); R_f 0.63 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}), 3480, 3384 (NH_2), 3064, 1656 , 1632, 1584, 1560, 1532, 1448, 1404, 1360, 1312, 1248, 1184, 1144, 1092, 1056, 976, 912, 864, 736. ^{1}H NMR ([$^2H_6$]DMSO) δ: 2,75 (s, 3H, Me), 6.60 (s, 2H, NH_2), 7.58 (t, 2H, *m*-H-Ph, J 7.9 Hz), 7.70 (t, 1H, *p*-H-Ph, J 7.9 Hz), 8.24 (d, 2H, *o*-H-Ph, J 7.9 Hz). ^{13}C NMR ([$^2H_6$]DMSO) δ: 186.2 (C=O), 152.4 (C-4), 142.2 (C-3), 142.5 (C-4′), 142.4 (C-5′), 136.7 ($C_{i\text{-Ph}}$), 133.2 ($C_{p\text{-Ph}}$), 130.0 ($C_{o\text{-Ph}}$), 128.3 ($C_{m\text{-Ph}}$), 9.9 (Me). MS, *m*/*z* (%): 270 (M^+, 5), 242 ($M^+ - N_2$, 5), 241 ($M^+ - NH_2$, 15), 212 ($M^+ - N_2$ – NO, 10), 185 (14), 157 (10), 115 (28), 105 (M^+ – PhCO, 100), 77 (66).

2c (ii) yield 5%, mp 150 °C (MeOH); R_f 0.32 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}): 3416, 3320, 1696, 1636, 1592, 1544, 1484, 1448, 1432, 1408, 1372, 1352, 1312, 1248, 1200, 1104, 1024, 984, 952, 872, 768, 744. ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.65 (s, 3H, Me), 6.64 (s, 2H, NH_2), 7.44 (m, 5H, Ph). ^{13}C NMR ([$^2H_6$]DMSO) δ: 192.1 (C=O), 153.6 [(C-4)-NH_2], 143.1 (C-4′), 142.5 (C-3), 141.9 (C-5′), 131.1 ($C_{p\text{-Ph}}$), 130.1 ($C_{o\text{-Ph}}$), 128.8 ($C_{m\text{-Ph}}$), 124.2 ($C_{i\text{-Ph}}$), 28.5 (CO–*Me*). MS, *m*/*z* (%): 270 (M^+, 5), 255 (M^+ – Me, 1), 227 (M^+ – COMe, 1), 212 ($M^+ - N_2$ – NO, 10), 200 ($M^+ - N_2$–H_2N–C=N–, 4), 143 (18), 128 (15), 77 (Ph, 8), 43 (COMe, 100).

2d (iii) yield 73%, mp 145 °C (EtOH); R_f 0.68 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}): 3460, 3340, 3250, 1670, 1640, 1610, 1570, 1490, 1460, 1420, 1390, 1340, 1310, 1290, 1260, 1230, 1180, 1110, 1080, 1040, 1020, 990, 920, 860, 850, 810, 780, 750, 700. ^{1}H NMR ([$^2H_6$]DMSO) δ: 6.72 (s, 2H, NH_2), 7.44 (s, 5H, Ph), 7.54 (t, 2H, Ph), 7.68 (t, 1H, Ph), 8.10 (d, 2H, Ph). ^{13}C NMR ([$^2H_6$]DMSO) δ: 186.0 (C=O), 153.4 (C-4), 143.4 (C-4′), 142.9 (C-5′), 142.4 (C-3), 136.7 ($C_{i\text{-COPh}}$), 133.5 ($C_{p\text{-COPh}}$), 130.6 ($C_{p\text{-Ph}}$), 130.2 ($C_{o\text{-COPh}}$), 129.8 ($C_{o\text{-Ph}}$), 128.5 ($C_{m\text{-Ph}}$), 128.4 ($C_{m\text{-COPh}}$), 124.2 ($C_{i\text{-Ph}}$).

2e (iv) yield 81% (91%), mp 121–122 °C (PhH); R_f 0.53 (PhH–EtOAc, 3:1). IR (KBr, ν_{max}/cm^{-1}): 3440, 3340 (NH_2), 3010 (CH), 1750 (C=O), 1640, 1590, 1480, 1450, 1420, 1390, 1360, 1320, 1240, 1220, 1150, 1120, 1060, 1020, 1000, 980, 870, 850. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.34 (t, 3H, Me, J 5.8 Hz), 2.63 (s, 3H, *Me*CH_2), 4.46 (q, 2H, CH_2, J 7.1 Hz), 6.65 (s, 2H, NH_2). ^{13}C NMR ([$^2H_6$]DMSO) δ: 160.5 (C=O), 152.4 (C-4), 142.4 (C-5′), 141.7 (C-3), 136.3 (C-4′), 61.0 (OCH_2), 14.1 (CH_2*Me*), 9.7 (Me).

2f (v) yield 82%, mp 138–139 °C (MeOH); R_f 0.39 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}): 3470, 3420, 3350 (NH_2), 3010, 1750, 1740 (C=O), 1650, 1590, 1560, 1490, 1455, 1430, 1390, 1360, 1320, 1290, 1260, 1230, 1220, 1150, 1125, 1040, 1010, 990, 874, 870, 770, 700. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.16 (t, 3H, Me, J 7.5 Hz), 4.25 (q, 2H, CH_2, J 8.3 Hz), 6.67 (s, 2H, NH_2), 7.50 (m, 5H, Ph). ^{13}C NMR ([$^2H_6$]DMSO) δ: 159.7 (C=O), 153.3 (C-4), 143.4 (C-5′), 142.2 (C-3), 136.4 (C-4′), 130.6 ($C_{p\text{-Ph}}$), 129.9 ($C_{o\text{-Ph}}$), 128,3 ($C_{m\text{-Ph}}$), 123.9 ($C_{i\text{-Ph}}$), 60.9 (OCH_2), 13.8 (Me). MS, *m*/*z* (%): 300 (M^+, 15), 270 (M^+ – NO, 5), 242 ($M^+ - NO - N_2$, 4), 215 (M^+ – C – $COOCH_2$Me, 25), 145 (100).

2g (vi) yield 83% (76%), mp 157 °C (MeOH); R_f 0.32 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}): 3720, 3408, 3320, 3256, 3216, 2984, 2952, 2888, 2848, 2168, 1720,1644, 1600, 1564, 1452, 1424, 1368, 1328, 1304, 1288, 1236, 1216, 1132, 1068, 1016, 988, 952, 864, 816, 792, 736, 712, 696, 656. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.14 (t, 3H, Me, J 8.9 Hz), 3.07 (q, 2H, CH_2, J 8.9 Hz), 3.92 (s, 3H, OMe), 6.67 (s, 2H, NH_2). ^{13}C NMR ([$^2H_6$]DMSO) δ: 160.7 (C=O), 152.5 (C-4), 146.6 (C-5′), 142.1 (C-3), 135.5 (C-4′), 52.0 (OMe), 16.9 (CH_2), 12.5 (Me).

2h (vii) yield 87%, mp 69–70 °C (EtOH–H_2O, 1:1); R_f 0.48 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}): 3460, 3340, 3260, 3220, 3000, 2950, 2920, 1740, 1720, 1640, 1600, 1580, 1480, 1460, 1410,1390, 1380, 1340, 1310, 1290, 1240, 1220, 1190, 1130, 1120, 1090, 1030, 1020, 990, 950, 910,

A comparison between chemical shifts in the ^{13}C NMR spectra of **2a**,**j** ([$^2H_6$]DMSO) and **2k**,**l** ($CDCl_3$) suggests that a substituent at the 4-position has almost no effect on the chemical shift of a triazole ring (< ±0.3 ppm). The structures of compounds **2b** and **2c** were unambiguously derived from ^{13}C NMR spectra based on the difference between the chemical shifts of carbonyl groups in acetyl (192 ppm) and benzoyl (186 ppm) units, which is consistent with the chemical shift of carbonyl in the structures containing analogous groups (**2a**, **2j**–**l** and **2d**, respectively).

Note that the chemical shifts of $^{13}C_i$ in a phenyl ring at a double bond (~124 ppm) (**2c**,**d**,**f**) and in a benzoyl moiety (~136 ppm) (**2b**,**d**) are significantly different.

References

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2 L. V. Batog, V. Yu. Rozhkov, Yu. A. Strelenko, O. V. Lebedev and L. I. Khmel'nitskii, *Khim. Geterotsikl. Soedin*., 2000, 406 [*Chem. Heterocycl. Compd*. (*Engl. Transl.*), 2000, **36**, 343].

870, 850, 830, 790, 775, 730, 710. ^1H NMR ([$^2H_6$]acetone) δ: 0.98 (t, 3H, *Me*CH_2O, *J* 7.0 Hz), 1.40 (t, 3H, Me, *J* 7.0 Hz), 1.72 (m, 2H, CH_2–C*H*$_2$Me, *J* 7.0 Hz), 3.26 [t, 2H, C(5′)-CH_2, *J* 7.0 Hz], 4.44 (q, 2H, Me–C*H*$_2$O, *J* 7.0 Hz), 6.20 (s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ: 160.6 (C=O), 150.9 (C-4), 144.9 (C-5′), 142.2 (C-3), 137.1 (C-4′), 61.6 (OCH_2), 25.6 [C(5′)-*C*H$_2$], 21.8 [C(5′)-CH$_2$-*C*H$_2$].

2i (viii) yield 94%, mp 126–127 °C (EtOH); R_f 0.37 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}): 3460, 3250 (NH_2), 3010, 2960, 2940, 2910, 2890, 2850, 2830 (Alk), 1720 (C=O), 1640, 1590, 1570, 1480, 1460, 1390, 1360, 1290, 1250, 1220, 1200, 1140, 1110, 1090, 1050, 1000, 980, 950, 830, 800, 780. ^1H NMR ([$^2H_6$]DMSO) δ: 3.20 (s, 3H, MeO), 3.94 (s, 3H, COOMe), 4.92 (s, 2H, CH_2), 6.62 (s, 2H, NH_2). ^{13}C NMR ([$^2H_6$]DMSO) δ: 160.4 (C=O), 152.8 (C-4), 142.7 (C-3), 141.2 (C-5′), 136.7 (C-4′), 61.6 (CH_2), 58.3 (OMe), 52.3 (COOMe).

2j (ix) yield 61%, mp 97–98 °C (MeOH); R_f 0.63 (PhH–EtOAc, 3:1); IR (KBr, ν_{max}/cm^{-1}): 3000, 2944 (Me), 1692 (C=O), 1600, 1576, 1556, 1452, 1424, 1392, 1368, 1304, 1232, 1104, 1056, 1024, 992, 976, 952, 920, 868, 720, 688, 656. ^1H NMR ([$^2H_6$]DMSO) δ: 2.53 (s, 3H, Me), 2.54 (s, 3H, COMe), 4.40 (s, 3H, OMe). ^{13}C NMR ([$^2H_6$]DMSO) δ: 192.5 (C=O, $^2J_{CH}$ 6.3 Hz), 160.4 (C-4, $^3J_{CH}$ 3.8 Hz), 142.6 (C-4′), 141.5 (C-3), 140.0 (C-5′, $^2J_{CH}$ 7.3 Hz), 60.3 (OMe, $^1J_{CH}$ 149.5 Hz), 27.6 (COMe, $^1J_{CH}$ 132.3 Hz), 9.1 (Me, $^1J_{CH}$ 132.4 Hz). MS, *m*/*z* (%): 223 (M^+, 3), 208 (M^+ – Me, 1), 195 (M^+ – N_2, 1), 180 (M^+ – COMe, 1), 43 (COMe, 100).

2k (x) yield 82%, mp 63–64 °C (MeOH); R_f 0.62 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}): 3740, 3370, 3015, 2320, 2170, 1690, 1590, 1530, 1420, 1390, 1370, 1300, 1230, 1100, 1070, 1025, 980, 950, 890, 705. ^1H NMR ($CDCl_3$) δ: 2.73 (s, 3H, Me), 2.77 (s, 3H, Me), 2.90 (s, 3H, Me). ^{13}C NMR ($CDCl_3$) δ: 193.4 (C=O, $^2J_{CH}$ 6.3 Hz), 149.7 (C-3), 147.7 (C-4, $^2J_{CH}$ 6.3 Hz), 143.6 (C-4′), 139.8 (C-5′, $^2J_{CH}$ 6.3 Hz), 28.1 (COMe, $^1J_{CH}$ 128.4 Hz), 10.4 (Me, $^2J_{CH}$ 132.6 Hz), 9.8 (Me, $^1J_{CH}$ 132.6 Hz). MS, *m*/*z* (%): 207 (M^+, 7), 192 (M^+ – Me, 1), 179 (M^+ – N_2, 1), 149 (M^+ – – N_2 – NO, 6), 43 (MeCO, 100).

2l (xi) yield 76%, mp 82 °C (MeOH); R_f 0.62 (PhH–EtOAc, 5:1). IR (KBr, ν_{max}/cm^{-1}): 3720, 3370, 2930, 2350, 2310, 2170, 1690, 1610, 1560, 1540, 1490, 1460, 1410, 1360, 1310, 1290, 1240, 1120, 1080, 1000, 980, 950, 910, 870, 860, 780, 740, 700. ^1H NMR ($CDCl_3$) δ: 2.61 (s, 3H, Me), 2.78 (s, 3H, Me), 7.50 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ: 193.4 (C=O, $^2J_{CH}$ 6.6 Hz), 151.4 (C-4), 147.8 (C-3), 143.6 (C-4′), 140.3 (C-5′, $^2J_{CH}$ 6.1 Hz), 131.7 ($C_{p\text{-Ph}}$), 128.2 ($C_{o\text{-Ph}}$), 123.0 (C-5′), 27.9 (COMe, $^1J_{CH}$ 128.6 Hz), 9.5 (Me, $^1J_{CH}$ 132.4 Hz). MS, *m*/*z* (%): 269 (M^+, 6), 254 (M^+ – Me, 1), 241 (M^+ – N_2, 1), 226 (M^+ – COMe, 1), 43 (MeCO, 100).

2m (xii) yield 75%, mp 224–225 °C (MeOH); R_f 0.37 (PhH–EtOAc, 3:1). IR (KBr, ν_{max}/cm^{-1}): 3420, 3320, 3250, 3210 (NH_2), 2970, 2920, 2890 (Alk), 1710 (C=O), 1640, 1590, 1580, 1560, 1470, 1430, 1410, 1290, 1250, 1190, 1100, 1090, 1080, 1050, 1030, 1020, 990, 900, 860, 730. ^1H NMR ([$^2H_6$]DMSO) δ: 2.20 (m, 2H, CH_2, *J* 7.2 Hz), 2.62 (t, 2H, CH_2, *J* 7.2 Hz), 3.20 (t, 2H, CH_2, *J* 7.2 Hz) 6.68 (s, 2H, NH_2). ^{13}C NMR ([$^2H_6$]DMSO) δ: 190.0 (C=O), 151.6 (C-4), 149.7 (C-4′), 141.5 (C-5′), 142.4 (C-3), 37.9 (CO*C*H$_2$), 20.9 [(C-5′)-*C*H$_2$], 22.1 (CO-CH$_2$-*C*H$_2$). MS, *m*/*z* (%): 220 (M^+, 11), 136 (6), 135 (92), 65 (100).

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