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Synthesis of the 6-oxidopyrido[1,2-*a*]quinoxalinium derivatives from quinoxalin-2-one and aldehydes – new examples of domino reactions

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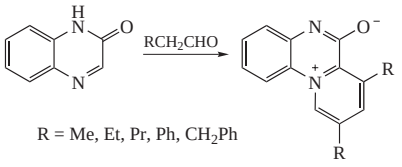
Quinoxalin-2-one reacts with aldehydes on heating in the presence of an acid to afford 6-oxidopyrido[1,2-*a*]quinoxalinium zwitter ions which on treatment with picric acid give picrates.

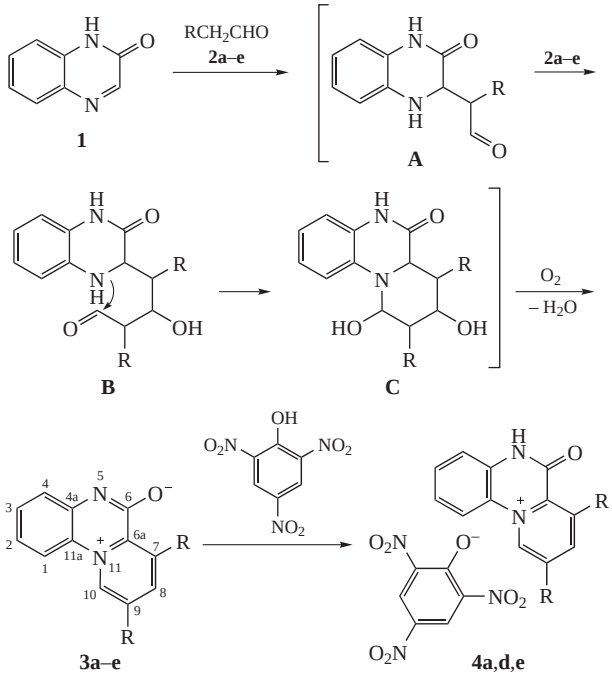


The reactions of quinoxalinium salts with acetylacetone and ethyl acetoacetate in the presence of bases (diethyl- and triethylamines) give 3a,4,9,9a-tetrahydro-*endo*-furo[2,3-*b*]quinoxalines.[1] Cyclization of 1,3-bis(silyl enol ethers) with quinoxaline leads to 6-alkylidene-2,3-benzo-1,4-diaza-7-oxabicyclo[4.3.0]non-2-enes.[2] Hydrogen substitution in the heterocyclic core of quinoxaline in its reactions with various C-nucleophiles under mild conditions in the presence of an acid gives C–C bonding products.[3] Recently, we reported the reactions of quinoxalin-2-one with β-diketones to furnish derivatives of a new tricyclic system, 6a,7-dihydro-5*H*-pyrido[1,2-*a*]quinoxaline-6,8-dione.[4]

In the course of work aimed at the functionalization of quinoxalines, we studied the reactions of quinoxalin-2-one with aldehydes under acidic catalysis conditions. We have found that quinoxalin-2-one **1** reacts with alkanals **2a**–**c** in the presence of an acid to yield 6-oxidopyrido[1,2-*a*]quinoxalinium derivatives **3a**–**c** (Scheme 1). The reactions of quinoxalone **1** with 3-phenylpropanal **2d** and phenylacetaldehyde **2e** occur in a similar way. However, in these cases, individual pyrido[1,2-*a*]quinoxalinium derivatives **4d**,**e** were isolated as salts with picric acid from non-purified semiproducts **3d**,**e**. Analogously, picrate **4a** was synthesized from individual derivative **3a** by the treatment with picric acid. The structures of synthesized pyridoquinoxalinium derivatives **3a**–**c** and **4a**,**d**,**e** were confirmed by ^{1}H, ^{13}C NMR spectra and 2D ^{1}H–^{13}C HSQC and HMBC experiments.†

Compounds **3** exist as zwitter ions, whereas compounds **4** are organic salts. ^{1}H NMR spectra of zwitter ions **3** contain chracteristic signals of H^8 and H^{10} protons of the pyridine ring at δ 8.1–8.3 and 9.7–9.8, respectively, and none of the signals for NH or OH protons. Signals of NH protons in the ^{1}H NMR spectra of salts **4** are observed in the region of δ 12.7–12.9. The integral intensity ratio of proton signals in pyridoquinoxalinium cations and picrate anions indicates that salts **4** contain the ions in equimolar ratio.

Comparison between the spectra of zwitter ion **3a** and picrate **4a** shows a considerable difference in the chemical shifts of the



a R = Me **d** R = Ph
b R = Et **e** R = CH_2Ph
c R = Pr

Scheme 1

† NMR spectra were recorded on Bruker AVANCE-500 and AVANCE-400 spectrometers. ^{1}H chemical shifts were measured relative to TMS as the internal standard; ^{13}C chemical shifts were measured relative to the DMSO-d_6 signal, δ_C 39.5, while the ^{15}N chemical shifts were measured relative to liquid ammonia as the external standard. The complete assignment of ^{1}H and ^{13}C signals was based on 2D ^{1}H–^{13}C HSQC and HMBC experiments. Mass spectra (EI) were obtained on a GCMS-QP2010 Ultra instrument (Shimadzu) at 70 eV energy, a source temperature of 200 °C, and an interface temperature of 150 °C. High resolution mass spectra were recorded on a 'maXis impact HD' ultra-high resolution quadrupole time-of-flight mass spectrometer (Bruker Daltonik GmbH) equipped with standard ESI and APCI sources. Solutions of samples in methanol were injected at a flow rate of 240 μl h^{-1} (ESI) or 420 μl h^{-1} (APCI) using a syringe pump, model 100 (KD Scientific Inc.). Ions were recorded in the

^{1}H and ^{13}C nuclei in pyridoquinoxalinium. In fact, the signals of the C^6, C^4, and C^{4a} atoms in picrate **4a** are considerably shifted upfield as compared with those of the zwitter ion **3a** (Δ_C 6.18, 8.37 and 13.88, respectively), whereas the signals of the other carbon atoms are shifted downfield. The greatest shifts are observed for the C^2, C^8, C^9, and C^{10} atoms (Δ_C 4.36, 4.02, 3.90, 4.52). We believe that this is explained by electron density redistribution and a shift of tautomeric equilibrium towards the keto form that predominates in picrates **4**.

This assumption is confirmed by the values of ^{15}N chemical shifts obtained from 2D ^{1}H–^{15}N HMBC experiments for compounds **3a**,**b** and **4a**,**e** (Figure 1). The chemical shifts of N^{11} nitrogen atoms are in the range of δ 208–210 for both zwitter ions **3** and picrates **4**, whereas the shifts of N^5 ones change by almost 100 ppm: from δ 238 in **3a**,**b** to δ 144 in **4a**,**e**.

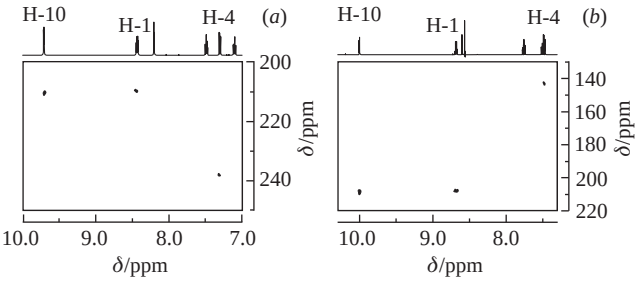


Figure 1 Fragments of the 2D ^{1}H–^{15}N HMBC spectra (500 MHz, DMSO-d_6) of compounds (*a*) **3a** and (*b*) **4a**.

The keto form in the crystals of salts **4a**,**d**,**e** is also confirmed by the presence of an absorption band of the C=O group at 1704, 1696 and 1694 cm^{-1}, respectively, in the IR spectra of these compounds. This absorption band is not observed in the IR spectra of products **3**.

The high resolution mass spectra (HRMS) of compounds **3a**, **4a** were recorded for the corresponding solutions in methanol, using electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). The ESI mass spectrum of zwitter ion **3a** contains peaks corresponding to $[M+H]^+$ protonated

mass range of 50–2200 Da with parameters based on the pre-installed Direct-Infusion method. Masses were calibrated by HPC method, based on signals from the G1969-85000 and G2432A calibration mixtures (Agilent Technologies). Mass spectra were processed using the Compass for oTOF series 1.7 software package (oTOF Control 3.4; Bruker Compass Data Analysis 4.2). IR spectra of the crystals of compounds **4a**,**d**,**e** were recorded on a Bruker Alpha (NPVO, ZnSe) IR spectrometer. Microanalyses were performed using a Perkin-Elmer 2400 Series II CHNS/O analyzer.

Reaction of quinoxalin-2-one **1** *with aldehydes* **2a**–**e**. A mixture of quinoxalone **1** (0.5 mmol) and the corresponding aldehyde **2** (1.0 mmol) in acetic acid (2 ml) was heated in a sealed vessel at 110 °C for 75–80 h. The solvent was evaporated *in vacuo*. The solid residue was treated with 30% aqueous ethanol (5 ml), and the resulting suspension was filtered to remove impurities. The filtrate was treated with concentrated ammonia solution to adjust pH to 8–9 and kept at room temperature for 2.5–3 h. The resulting precipitate of product **3** was filtered and washed with cold water (2 ml).

*7,9-Dimethylpyrido[1,2-*a*]quinoxalin-11-ium-6-olate* **3a**. Yield 50–55%, mp 223–224 °C. ^{1}H NMR (500.1 MHz, DMSO-d_6) δ: 2.56 (s, 3H, C^{9}Me), 2.98 (s, 3H, C^{7}Me), 7.10 (ddd, 1H, H^2, *J* 8.6, 7.0, 1.6 Hz), 7.30 (dd, 1H, H^4, *J* 8.2, 1.6 Hz), 7.49 (ddd, 1H, H^3, *J* 8.2, 7.0, 1.2 Hz), 8.20 (s, 1H, H^8), 8.43 (d, 1H, H^1, *J* 8.6 Hz), 9.70 (s, 1H, H^{10}). ^{13}C NMR (125.7 MHz, DMSO-d_6) δ: 17.79 (C^9*Me*), 23.47 (C^7*Me*), 117.44 (C^1), 119.77 (C^2), 121.61 (C^{11a}), 125.71 (C^4), 130.62 (C^3), 130.85 (C^{10}), 133.17 (C^{6a}), 136.02 (C^9), 139.34 (C^7), 144.99 (C^8), 145.24 (C^{4a}), 161.39 (C^6). ^{15}N NMR (50.7 MHz, DMSO-d_6) δ: 210.3 (N^{11}), 238.4 (N^5). MS (EI), *m*/*z* (%): 225 (28) $[M+1]^+$, 224 (72) $[M]^+$, 197 (16), 196 (100), 195 (52), 181 (27), 180 (6). HRMS (ESI), *m*/*z*: +225.1023 $[M]^+$ (calc. for $[C_{14}H_{13}N_2O]^+$, *m*/*z:* 225.1022); –223.0873 $[M]^-$ (calc. for $[C_{14}H_{11}N_2O]^-$, *m*/*z:* 223.0877). Found (%): C, 74.95; H, 5.36; N, 12.51. Calc. for $C_{14}H_{12}N_2O$ (%): C, 74.98; H, 5.39; N, 12.49.

*7,9-Diethylpyrido[1,2-*a*]quinoxalin-11-ium-6-olate* **3b**. Yield 30–35%, mp 128–129 °C. ^{1}H NMR (500.1 MHz, DMSO-d_6) δ: 1.28 (t, 3H, H$^{2'}$, *J* 7.3 Hz), 1.34 (t, 3H, H$^{2''}$, *J* 7.6 Hz), 2.93 (q, 2H, H$^{1''}$, *J* 7.6 Hz), 3.55 (q, 2H, H$^{1'}$, *J* 7.3 Hz), 7.11 (ddd, 1H, H^2, *J* 8.7, 7.0, 1.5 Hz), 7.32 (dd, 1H, H^4, *J* 8.2, 1.5 Hz), 7.50 (t, 1H, H^3, *J* 7.6 Hz), 8.31 (s, 1H, H^8), 8.48 (d, 1H, H^1, *J* 8.7 Hz), 9.71 (s, 1H, H^{10}). ^{13}C NMR (125.7 MHz, DMSO-d_6) δ: 14.78 (C$^{2''}$), 16.35 (C$^{2'}$), 25.16 (C$^{1''}$), 28.30 (C$^{1'}$), 117.61 (C^1), 119.75 (C^2), 121.72 (C^{11a}), 125.71 (C^4), 130.59 (C^3, C^{10}), 133.00 (C^{6a}), 141.87 (C^9), 143.04 (C^8), 145.10 (C^{4a}), 145.48 (C^7), 160.73 (C^6). ^{15}N NMR (50.7 MHz, DMSO-d_6) δ: 210.4 (N^{11}), 238.9 (N^5). MS (EI), *m*/*z* (%): 253 (31) $[M+1]^+$, 252 (100) $[M]^+$, 251 (90), 236 (13), 235 (21), 224 (26), 223 (63), 208 (13), 196 (24), 195 (13), 181 (21). Found (%): C, 76.13; H, 6.42; N, 11.07. Calc. for $C_{16}H_{16}N_2O$ (%): C, 76.16; H, 6.39; N, 11.10.

*7,9-Dipropylpyrido[1,2-*a*]quinoxalin-11-ium-6-olate* **3c**. Yield 30–35%, mp 138–139 °C. ^{1}H NMR (400.1 MHz, DMSO-d_6) δ: 1.01 (t, 6H, H$^{3'}$, H$^{3''}$, *J* 7.3 Hz), 1.66–1.83 (m, 4H, H$^{2'}$, H$^{2''}$), 2.90 and 3.52 (both m, 2H, H$^{2'}$, H$^{2''}$), 7.08 (ddd, 1H, H^2, *J* 8.7, 7.0, 1.5 Hz), 7.32 (dd, 1H, H^4, *J* 8.3, 1.5 Hz), 7.47 (dd, 1H, H^3, *J* 8.3, 7.0 Hz), 8.16 (d, 1H, H^8, *J* 1.3 Hz), 8.45 (d, 1H, H^1, *J* 8.7 Hz), 9.71 (d, 1H, H^{10}, *J* 1.3 Hz). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 13.27, 13.79 (C$^{3'}$, C$^{3''}$), 23.35, 24.60 (C$^{2'}$, C$^{2''}$), 33.51, 36.68 (C$^{1'}$, C$^{1''}$), 117.41 (C^1), 119.67 (C^2), 121.58 (C^{11a}), 125.36 (C^4), 130.38 (C^3), 130.83 (C^{10}), 133.03 (C^{6a}), 140.16 (C^9), 143.71 (C^8), 143.87 (C^7), 144.66 (C^{4a}), 160.36 (C^6). MS (EI), *m*/*z* (%): 281 (14) $[M+1]^+$, 280 (28) $[M]^+$, 265 (100), 263 (21), 252 (7), 236 (11), 235 (7), 224 (6), 181 (9). Found (%): C, 77.08; H, 7.23; N, 9.97. Calc. for $C_{18}H_{20}N_2O$ (%): C, 77.11; H, 7.19; N, 9.99.

*7,9-Dimethyl-6-oxo-5,6-dihydropyrido[1,2-*a*]quinoxalin-11-ium 2,4,6-trinitrophenoxide* **4a**. A mixture of compound **3a** (0.015 g, 0.066 mmol) and picric acid (0.016 g, 0.070 mmol) was dissolved with heating in anhydrous ethanol (8 ml). The resulting solution was kept at room temperature for 2.5–3 h. The precipitate was filtered to give 0.015 g (50%) of compound **4a**, mp 248–249 °C. ^{1}H NMR (500.1 MHz, DMSO-d_6) δ: 2.67 (s, 3H, C^{9}Me), 2.97 (s, 3H, C^{7}Me), 7.50 (ddd, 1H, H^2, *J* 8.8, 7.3, 1.5 Hz), 7.48 (ddd, 1H, H^4, *J* 8.2, 1.5 Hz), 7.76 (ddd, 1H, H^3, *J* 8.2, 7.3, 0.7 Hz), 8.56 (s, 2H, H$^3_{pic}$), 8.60 (br. s, 1H, H^8), 8.68 (d, 1H, H^1, *J* 8.8 Hz), 10.01 (br. s, 1H, H^{10}), 12.76 (br. s, 1H, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6) δ: 18.03 (C^9*Me*), 22.60 (C^7*Me*), 117.34 (C^4), 118.91 (C^1), 122.93 (C^{11a}), 124.08 (C$^4_{pic}$), 124.13 (C^2), 125.15 (C$^3_{pic}$), 131.36 (C^{4a}), 132.50 (C^3), 135.23 (C^{6a}), 135.37 (C^{10}), 139.92 (C^9), 141.48 (C^7), 141.79 (C$^2_{pic}$), 149.01 (C^8), 155.21 (C^6), 160.75 (C$^1_{pic}$). ^{15}N NMR (50.7 MHz, DMSO-d_6) δ: 143.6 (N^5), 208.1 (N^{11}), 367.3 (C^{2}NO$_2$), 371.2 (C^{4}NO$_2$). MS (EI), *m*/*z* (%): 229 (70), 226 (23), 225 (45), 224 (16), 196 (55), 195 (54). HRMS (ESI), *m*/*z*: –227.9897 (calc. for picrate anion $[C_6H_2N_3O_7]^-$, *m*/*z*: 227.9898). Found (%): C, 53.02; H, 3.36; N, 15.42. Calc. for $C_{20}H_{15}N_5O_8$ (%): C, 52.99; H, 3.33; N, 15.45.

*7,9-Diphenyl-6-oxo-5,6-dihydropyrido[1,2-*a*]quinoxalin-11-ium 2,4,6-trinitrophenoxide* **4d**. A mixture of compound **1** (0.073 g, 0.5 mmol) and phenylacetaldehyde (0.120 g, 1.0 mmol) in acetic acid (2 ml) was heated in a sealed vessel at 110 °C for 70 h. The mixture was concentrated to dryness *in vacuo*. The precipitate was suspended in 70% ethanol (5 ml) and treated with concentrated aqueous ammonia to adjust pH to 8–9. The precipitate that formed was filtered off and washed with chloroform (4–5 ml). The resulting semiproduct was dissolved in ethanol (50 ml) and filtered. Picric acid (0.115 g, 0.5 mmol) was added to the filtrate. The mixture was heated until dissolution and cooled to room temperature. The precipitate formed was filtered off to give 0.059 g (24%) of compound **4d**, mp 137–138 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.48–7.51 (m, 3H, H$^{3'}$, H$^{4'}$), 7.52–7.57 (m, 2H, H^2, H^4), 7.58–7.61 (m, 2H, H$^{2'}$), 7.65–7.69 (m, 3H, H$^{3''}$, H$^{4''}$), 7.82 (t, 1H, H^3, *J* 7.7 Hz), 8.21 (dd, 2H, H$^{2''}$, *J* 7.7, 2.0 Hz), 8.58 (s, 2H, H$^3_{pic}$), 8.91 (d, H^8, *J* 1.7 Hz), 9.03 (d, 1H, H^1, *J* 8.7 Hz), 10.25 (d, 1H, H^{10}, *J* 1.7 Hz), 12.72 (br. s, 1H, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6) δ: 117.38 (C^4), 120.10 (C^1), 123.28 (C^{11a}), 123.98 (C^2), 124.06 (C$^4_{pic}$), 125.10 (C$^3_{pic}$), 127.70 (C$^{3'}$), 128.24 (C$^{4'}$), 128.68 (C$^{2'}$), 128.76 (C$^{2''}$), 129.33 (C$^{3''}$), 130.76 (C$^{4''}$), 131.74 (C^{4a}), 132.49 (C$^{1''}$), 132.73 (C^3), 134.50 (C^{10}), 135.61 (C^{6a}), 138.12 (C$^{1'}$), 140.01 (C^9), 141.81 (C$^2_{pic}$), 143.57 (C^7), 144.82 (C^8), 153.49 (C^6), 160.73 (C$^1_{pic}$). MS (EI), *m*/*z* (%): 350 (31), 349 (74), 348 (41), 347 (69), 321 (21), 320 (64), 319 (100), 318 (11), 317 (12), 304 (19), 229 (13). Found (%): C, 62.36; H, 3.34; N, 12.15. Calc. for $C_{30}H_{19}N_5O_8$ (%): C, 62.39; H, 3.32; N, 12.13.

molecules, while its ESI mass spectrum recorded in the negative ion detection mode shows a distinct peak of moderate intensity corresponding to the deprotonated molecule, $[M-H]^-$.

The formation of pyrido[1,2-*a*]quinoxaline tricyclic system can be represented as a result of sequential stages (see Scheme 1): (1) attack of the C=N bond in quinoxalin-2-one by the α-carbon atom of the aldehyde alkyl group to give intermediate **A**; (2) addition of a second aldehyde molecule by the CH-active center to the C=O group of **A** to produce intermediate **B**; (3) intramolecular addition–cyclization in the intermediate **B** to form intermediate **C**; (4) dehydration and oxidation of intermediate **C** with atmospheric oxygen to give the final tricyclic product **3**. Note that derivatives of the pyrido[1,2-*a*]quinoxalinium heterocyclic system were previously obtained by reactions of 2-carboxy-4,5-diphenylpyrylium perchlorates with *o*-phenylenediamine.[5,6] To our knowledge, the annulation of the six-membered ring to quinoxalin-2-one in the reaction with two equivalents of aldehyde observed in this study is the first example of a domino reaction[7] to result in compounds based on a pyrido[1,2-*a*]quinoxalinium frame.

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*7,9-Dibenzyl-6-oxo-5,6-dihydropyrido[1,2-*a*]quinoxalin-11-ium 2,4,6-trinitrophenoxide* **4e**. A mixture of compound **1** (0.073 g, 0.5 mmol) and 3-phenylpropanal (0.134 g, 1.0 mmol) in acetic acid (2 ml) was heated in a sealed vessel at 110 °C for 70 h. The reaction mixture was concentrated to dryness *in vacuo*. The precipitate was suspended in 70% aqueous ethanol (7 ml) and treated with concentrated aqueous ammonia to bring pH to 8–9. The resulting precipitate was filtered off and dried in air. The thus obtained semiproduct (0.125–0.130 g) was dissolved in dichloromethane (20 ml) and filtered. Picric acid (0.229 g, 1.0 mmol) was added to the filtrate and the mixture was heated until complete dissolution. Salt **4e** was precipitated with diethyl ether from the resulting solution. The precipitate was filtered to give 0.080 g (26%) of compound **4e**, mp 159–160 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 4.39 (s, 2H, C^9CH_2), 4.92 (s, 2H, C^7CH_2), 7.17–7.21 (m, 3H, $H^{2'}$, $H^{4'}$), 7.23–7.28 (m, 3H, $H^{3'}$, $H^{4''}$), 7.31–7.38 (m, 4H, $H^{2''}$, $H^{3''}$), 7.50 (dd, 1H, H^4, *J* 8.2, 1.4 Hz), 7.56 (ddd, 1H, H^2, *J* 8.8, 7.2, 1.4 Hz), 7.79 (ddd, 1H, H^3, *J* 8.2, 7.2, 0.8 Hz), 8.58 (s, 2H, H^3_{pic}), 8.60 (d, 1H, H^8, *J* 1.4 Hz), 8.76 (d, 1H, H^1, *J* 8.8 Hz), 10.24 (d, 1H, H^{10}, *J* 1.4 Hz), 12.81 (br. s, 1H, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6) δ: 37.14 (C^9CH_2), 38.52 (C^7CH_2), 117.34 (C^4), 119.05 (C^1), 123.40 (C^{11a}), 124.10 (C^4_{pic}), 124.27 (C^2), 125.16 (C^3_{pic}), 126.27 ($C^{4'}$), 126.90 ($C^{4''}$), 128.31 ($C^{3'}$), 128.79 ($C^{3''}$), 128.85 ($C^{2'}$, $C^{2''}$), 131.31 (C^{4a}), 132.62 (C^3), 136.01 (C^{6a}), 136.11 (C^{10}), 138.41 ($C^{1''}$), 138.99 ($C^{1'}$), 141.82 (C^2_{pic}), 142.93 (C^9), 143.94 (C^7), 148.78 (C^8), 154.71 (C^6), 160.77 (C^1_{pic}). ^{15}N NMR (50.7 MHz, DMSO-d_6) δ: 143.9 (N^5), 209.4 (N^{11}), 367.1 (C^2NO_2), 371.0 (C^4NO_2). MS (EI), *m*/*z* (%): 378 (24), 377 (37), 376 (4), 313 (12), 301 (10), 229 (74), 199 (91). Found (%): C, 63.49; H, 3.87; N, 11.53. Calc. for $C_{32}H_{23}N_5O_8$ (%): C, 63.47; H, 3.83; N, 11.56.