

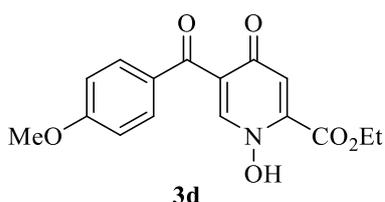
**Synthesis of ethyl 4-(isoxazol-4-yl)-2,4-dioxobutanoates
from ethyl 5-aryl-4-pyrone-2-carboxylates and hydroxylamine**

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Experimental

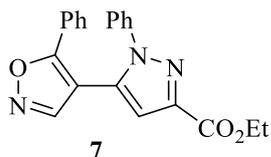
IR spectra were recorded on a PerkinElmer Spectrum BX-II instrument with ATR accessory. ^1H and ^{13}C NMR spectra were acquired on a Bruker Avance II spectrometer (400 and 100 MHz, respectively) in $\text{DMSO-}d_6$ or CDCl_3 , with TMS and residual solvent peaks as internal standard. Naphthalene ring protons were denoted as H Naph protons, pyrazole protons – H Pz, isoxazole protons – H Is. Elemental analysis was performed on a PE 2400 automated analyzer. Melting points were determined on an SMP30 apparatus.

Ethyl 1-hydroxy-5-(4-methoxybenzoyl)-4-oxo-1,4-dihydropyridine-2-carboxylate **3d**.



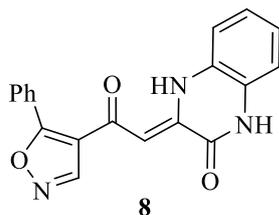
This compound along with **2d** was obtained from $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.124 g, 1.79 mmol, 2.3 equiv) and KOH (0.094 g, 1.68 mmol) (general procedure). Yield 0.038 g (16%), a yellow solid, mp 187–190 °C. ^1H NMR ($\text{DMSO-}d_6$) δ : 1.38 (t, 3H, Me, J 7.1 Hz), 3.86 (s, 3H, MeO), 4.38 (q, 2H, CH_2 , J 7.1 Hz), 6.59 (s, 1H, H-3), 6.94 (d, 2H, H-3, H-5 Ph, J 8.8 Hz), 7.74 (d, 1H, H-2, H-6 Ph, J 8.8 Hz), 7.99 (s, 1H, H-6), the OH proton was not observed due to broadening. IR (ATR, v/cm^{-1}): 3044, 1728, 1656, 1718, 1597, 1282, 1251, 853. Found (%): C, 58.47; H, 4.67; N, 4.49. Calc. for $\text{C}_{16}\text{H}_{15}\text{NO}_6\cdot 0.5\text{H}_2\text{O}$ (%): C, 58.89; H, 4.94; N, 4.29.

Ethyl 1-phenyl-5-(5-phenylisoxazol-4-yl)-1H-pyrazole-3-carboxylate 7.



A mixture of isoxazole **2a** (0.080 g, 0.28 mmol) and PhNHNH₂·HCl (0.049 g, 0.34 mmol) in 1 ml EtOH was refluxed for 1 h. The obtained solution was diluted with 3 ml water. The resulting residue was filtered off and recrystallized from hexane–toluene. Yield 0.072 g (72%), a yellow solid, mp 120–121 °C. ¹H NMR (DMSO-*d*₆) δ: 1.38 (t, 3H, Me, *J* 6.9 Hz), 4.35 (q, 2H, CH₂, *J* 6.9 Hz), 7.06 (s, 1H, =CH), 7.21–7.26 (m, 2H, Ph), 7.28–7.33 (m, 3H, Ph), 7.34–7.46 (m, 5H, Ph), 8.56 (s, 1H, =CH Is). IR (ATR, v/cm⁻¹): 3132, 2985, 17141597, 1518, 1338, 1216, 757. Found (%): C, 70.06; H, 4.81; N, 11.40. Calc. for C₂₁H₁₇N₃O₃ (%): C, 70.18; H, 4.77; N, 11.69.

(Z)-3-[2-Oxo-2-(5-phenylisoxazol-4-yl)ethylidene]-3,4-dihydroquinoxalin-2(1H)-one 8.



A mixture of isoxazole **2a** (0.080 g, 0.28 mmol) and *o*-phenylenediamine (0.036 g, 0.33 mmol) was refluxed in 1 ml EtOH for 30 min. The resulting precipitate was filtered off and washed with EtOH. Yield 0.076 g (81%), an orange solid, mp 245–247 °C. ¹H NMR (DMSO-*d*₆) δ: 6.48 (s, 1H, =CH), 7.03–7.21 (m, 4H), 7.33–7.43 (m, 1H), 7.47–7.64 (m, 1H), 8.04 (d, 2H, H-2, H-6 Ph, *J* 7.1 Hz), 8.97 (s, 1H, =CH Is), 11.19 (s, 1H, NH Qn), 13.49 (s, 1H, NH Qn). ¹³C NMR (DMSO-*d*₆) δ: 92.2, 115.3, 116.6, 117.7, 123.6, 123.8, 124.2, 126.67, 126.71, 128.1, 128.8, 131.3, 145.5, 151.3, 155.3, 168.7, 182.0. IR (ATR, v/cm⁻¹): 3232, 3065, 3005, 1694, 1553, 1209. Found (%): C, 67.46; H, 3.95; N, 12.32. Calc. for C₁₉H₁₃N₃O₃·0.33H₂O (%): C, 67.66; H, 4.08; N, 12.46.

