Supplementary Information

Studies on the photochemical oxidation of *N,N*-diacyl-1,4-dihydropyrazine derivatives

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Preparation of *N,N*-diacyl-1,4-dihydropyrazine derivatives

1,4-diacetyl-1,4-dihydropyrazine (1a)^[1] white solid; mp 188-190 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.11 (s, 6H), 5.82-6.62 (m, 4H).

1,4-dibenzoyl-1,4-dihydropyrazine (1b)^[1] yellow solid; mp 195-197 °C; ¹H NMR (400 MHz, CDCl₃) δ 5.78-6.93 (m, 4H), 7.49-7.56 (m, 10H).

General procedure for the photooxygenation of *N,N*-diacyl-1,4-dihydropyrazines (1)

5 mmol of **1** was dissolved in 200 mL of acetone and poured into the photolysis unit. Photoirradiations were performed using a 450 W medium-pressure mercury lamp and monitored by TLC. After completion, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel using a mixed solvent of petroleum ether and ethyl acetate (10:1 v/v) to provide the main products (**2-4**).

1,1'-(2-hydroxy-3-methoxy-2,3-dihydropyrazine-1,4-diyl)diethanone (2a)

Colorless needles, mp 141-143 °C; ¹H NMR (400 MHz, CDCl₃): δ 6.44-6.63 (m, 1H, -OH), 6.08-6.42 (m, 2H, -CH=CH), 5.26-5.87 (m, 2H, -CH), 3.16-3.27 (m, 3H, -OCH₃), 2.14-2.22 (m, 6H, -COCH₃); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 169.7, 169.6, 168.3, 168.1, 167.8, 167.7, 109.5, 108.0, 107.9, 107.0, 106.7, 105.6, 104.5, 83.1, 82.9, 78.3, 78.0, 75.1, 74.7, 69.8, 69.3, 55.5, 55.4, 54.6, 21.9, 21.8, 21.7, 21.6, 21.3, 21.2, 21.1, 21.0; HRMS (ESI) calculated for C₉H₁₄N₂O₄ (M+Na⁺): 237.08513, found 237.08357. Single crystal X-ray diffraction of **2a** (Deposition number

CCDC-995230).

1,4-diacetyl-1,2,3,4-tetrahydropyrazine-2,3-diyl diacetate (3a)

Colorless needles, mp 150-152 °C; ^1H NMR (400 MHz, CDCl_3): δ 6.72-7.28 (m, 2H, -CH=CH), 6.07-6.69 (m, 2H, -CH), 2.30-2.32 (m, 6H, -OCOCH₃), 2.03-2.12 (m, 6H, -COCH₃); ^{13}C NMR (100 MHz, CDCl_3): δ 169.4, 169.1, 169.0, 168.0, 167.7, 108.2, 107.2, 106.6, 105.6, 73.9, 73.3, 70.3, 69.6, 21.2, 20.8, 20.7, 20.6; HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_6$ ($\text{M}+\text{Na}^+$): 307.09061, found 307.08990.

(2,3-dihydroxy-2,3-dihydropyrazine-1,4-diyl)bis(phenylmethanone) (4b)

Colorless needles, mp 174-175 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.54-7.63 (m, 10H, -ArH), 6.69-6.79 (m, 2H, -OH), 6.00-6.54 (m, 2H, -CH=CH), 5.01-5.89 (m, 2H, -CH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 168.3, 134.6, 131.1, 128.8, 128.3, 110.9, 108.0, 105.3, 77.3, 72.4; HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$ ($\text{M}+\text{Na}^+$): 347.10078, found 347.10043. Single crystal X-ray diffraction of **4b** (Deposition number CCDC-995229).

¹H NMR spectrum of the compound **1a** (400MHz, CDCl₃)

¹H NMR spectrum of the compound **1b** (400MHz, CDCl₃)

^1H NMR spectrum of the compound **2a** (400MHz, $\text{DMSO}-d_6$)

^{13}C NMR spectrum of the compound **2a** (100MHz, $\text{DMSO}-d_6$)

Variable-temperature ^1H NMR spectrum of **2a** in $\text{DMSO-}d_6$ (323 K)

Variable-temperature ^1H NMR spectrum of **2a** in $\text{DMSO-}d_6$ (353 K)

¹H NMR spectrum of the compound **3a** (400MHz, CDCl₃)

¹³C NMR spectrum of the compound **3a** (100MHz, CDCl₃)

H-H COSY spectrum of **3a** in CDCl_3

C-H COSY spectrum of **3a** in CDCl_3

Table 1. Crystal data of compound **2a** and **4b**

Crystal	2a	4b
Empirical formula	C ₉ H ₁₄ N ₂ O ₄	C ₁₈ H ₁₆ N ₂ O ₄
Formula weight	214.22	324.33
Temperature	113(2)K	113(2)K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Orthorhombic, Pna2(1)	Orthorhombic, Pna2(1)
Unit cell dimensions	$a = 6.5788(13)$ $b = 21.857(4)$ $c = 6.8898(14)$ $\alpha = 90.00^\circ$ $\beta = 99.00^\circ$ $\gamma = 90.00^\circ$	$a = 20.436(3)$ $b = 6.7450(4)$ $c = 11.3490(16)$ $\alpha = 90.00^\circ$ $\beta = 90.00^\circ$ $\gamma = 90.00^\circ$
Volume	990.7(3) Å ³	1564.4(4) Å ³
Z	4	4
Calculated density	1.436Mg m ⁻³	1.377Mg m ⁻³
Absorption coefficient	0.114 mm ⁻¹	0.099 mm ⁻¹
$F(000)$	456	680
Crystal size	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.12
θ Range for data collection	1.86 – 27.93°	1.99 – 27.90°
Index ranges	-8 ≤ h ≤ 8, -28 ≤ k ≤ 28, -8 ≤ l ≤ 9	-26 ≤ h ≤ 26, -8 ≤ k ≤ 8, -14 ≤ l ≤ 14
Reflections collected/unique	9060/2287 [$R_{\text{int}}=0.0464$]	15368/3675 [$R_{\text{int}}=0.0584$]
Data/restraints/parameters	2287/1/141	3675/3/224
Goodness-of-fit on F^2	1.048	1.085
R indices (all data)	$R^1 = 0.0401$, $wR^2 = 0.0712$	$R^1 = 0.0541$, $wR^2 = 0.1159$
Final R indices	$R^1 = 0.0332$, $wR^2 = 0.0687$	$R^1 = 0.0490$, $wR^2 = 0.1129$
Extinction coefficient	0.050(4)	0.0123(18)
Largest diff. peak and hole	0.216 and -0.184 e Å ⁻³	0.366 and -0.189 e Å ⁻³

Reference

1. Gottlieb, R.; Pfeleiderer, W. *Liebigs Ann. Chem.* **1981**, 1981, 1451-1456.