

Supplementary material to:

J-P. Li, P-Z. Zheng, J-G. Zhu, R-J. Liu and G-R. Qu, An expedient method for the synthesis of acylhydrazones under microwave irradiation in solvent-free medium, *S. Afr. J. Chem.*, 2006, **59**, 90–92.

Experimental

The experimental data for the known acylhydrazones are provided below. The reference numbers below correspond to the references in the main manuscript.

*1-[(2,4-Dichlorophenoxy)acetyl]-2-(2-hydroxybenzylidene)-hydrazine*²⁵ (**A1**). White crystals. M.p. 202–204°C, Lit²⁵: 191°C. Yield – 93%. IR (KBr): 3321 (NH), 3450 (OH), 1677 (C=O), 1481 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.81, 11.56 (2s, 1H, N-H), 10.93, 9.98 (2s, 1H, OH), 8.46, 8.28 (2s, 1H, CH=N), 7.69–6.81 (m, 7H, ArH), 5.25, 4.80 (2s, 2H, CH₂). Anal. calcd. for C₁₅H₁₂Cl₂N₂O₃: C, 53.12; H, 3.57; N, 8.26. Found: C, 53.28; H, 2.49; N, 8.29.

*1-[(4-Iodophenoxy)acetyl]-2-(2-hydroxybenzylidene)-hydrazine*²⁶ (**A2**). White crystals. M.p. 234–235°C, Yield – 95%. IR (KBr): 3302 (NH), 3467 (OH), 1679 (C=O), 1488 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.76, 11.50 (2s, 1H, N-H), 10.99, 9.99 (2s, 1H, OH), 8.52, 8.27 (2s, 1H, CH=N), 7.68–6.73 (m, 8H, ArH), 5.08, 4.66 (2s, 2H, CH₂). Anal. calcd. for C₁₅H₁₃IN₂O₃: C, 45.47; H, 3.31; N, 7.07. Found: C, 45.54; H, 3.49; N, 6.99.

*1-Phenoxyacetyl-2-(2-hydroxybenzylidene)-hydrazine*²⁷ (**A3**). White crystals. M.p. 180–181°C, Lit²⁷: 173–175°C. Yield – 95%. IR (KBr): 3328 (NH), 3457 (OH), 1678 (C=O), 1498 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.77, 11.49 (2s, 1H, N-H), 11.02, 10.01 (2s, 1H, OH), 8.54, 8.28 (2s, 1H, CH=N), 7.69–6.81 (m, 9H, ArH), 5.073, 4.660 (2s, 2H, CH₂). ¹³C NMR (100MHz, DMSO-d₆): δ 169.14, 164.65, 158.63, 158.16, 157.82, 156.84, 148.77, 141.88, 131.95, 131.63, 129.99, 129.84, 129.75, 126.96, 121.78, 121.18, 120.45, 119.85, 119.81, 119.06, 116.83, 116.57, 115.17, 114.92. Anal. calcd. for C₁₅H₁₄N₂O₃: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.74; H, 5.29; N, 10.30.

1-(1-Naphthylacetyl)-2-(2-hydroxybenzylidene)-hydrazine^{28,29} (**A4**). White crystals. M.p. 252–254°C, Yield – 93%. IR (KBr): 3300 (NH), 3462 (OH), 1668 (C=O), 1489 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.92, 11.40 (2s, 1H, N-H), 11.06, 10.05 (2s, 1H, OH), 8.42, 8.33 (2s, 1H, CH=N), 8.10–6.85 (m, 11H, ArH), 4.41, 4.04 (2s, 2H, CH₂). Anal. calcd. for C₁₉H₁₆N₂O₂: C, 74.98; H, 5.30; N, 9.20. Found: C, 75.11; H, 5.42; N, 9.02.

*1-Benzoyl-2-(2-hydroxybenzylidene)-hydrazine*³⁰ (**A5**). White crystals. M.p. 176–178°C, Lit³⁰: 163–164°C. Yield – 96%. IR (KBr): 3271 (NH), 3467 (OH), 1674 (C=O), 1488 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 12.09 (s, 1H, N-H), 22.29 (s, 1H, OH), 8.63 (s, 1H, CH=N), 7.93–6.88 (m, 9H, ArH). Anal. calcd. for C₁₄H₁₂N₂O₂: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.12; H, 5.21; N, 11.52.

*1-[(2,4-Dichlorophenoxy)acetyl]-2-benzylidene-hydrazine*³¹ (**B1**). White crystals. M.p. 196–198°C, Yield – 95%. IR(KBr): 3331(NH), 1685(C=O), 1483(C=N) cm⁻¹. ¹H NMR(400 MHz, DMSO-d₆): δ 11.64, 11.59 (2s, 1H, N-H), 8.24, 7.94(2s, 1H, CH=N), 7.69–7.04(m, 8H, ArH), 5.28, 4.78(2s, 2H, CH₂). Anal. calcd. for C₁₅H₁₂Cl₂N₂O₂: C, 55.75; H, 3.74; N, 8.67. Found: C, 55.58; H, 3.50; N, 8.89.

*1-[(4-Iodophenoxy)acetyl]-2-benzylidene-hydrazine*²⁶ (**B2**). White crystals. M.p. 214–215°C, Yield – 91%. IR (KBr): 3298 (NH), 1685

(C=O), 1487 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.58, 11.53 (2s, 1H, N-H), 8.29, 7.98 (2s, 1H, CH=N), 7.69–6.75 (m, 9H, ArH), 5.12, 4.63 (2s, 2H, CH₂). Anal. calcd. for C₁₅H₁₃IN₂O₂: C, 47.39; H, 3.45; N, 7.37. Found: C, 47.58; H, 3.53; N, 7.20.

*1-Phenoxyacetyl-2-benzylidene-hydrazine*³² (**B3**). White crystals. M.p. 161–162°C, Lit³²: 142°C. Yield – 94%. IR (KBr): 3331 (NH), 1683 (C=O), 1497 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.56, 11.53 (2s, 1H, N-H), 8.32, 7.99 (2s, 1H, CH=N), 7.69–6.89 (m, 10H, ArH), 5.11, 4.63 (2s, 2H, CH₂). Anal. calcd. for C₁₅H₁₄N₂O₂: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.65; H, 5.42; N, 11.49.

1-(1-Naphthylacetyl)-2-benzylidene-hydrazine^{28,29} (**B4**). White crystals. M.p. 220–221°C, Yield – 91%. IR (KBr): 3290 (NH), 1670 (C=O), 1390 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.70, 11.44 (2s, 1H, N-H), 8.23, 8.03 (2s, 1H, CH=N), 7.68–7.39 (m, 11H, ArH), 4.44, 4.02 (2s, 2H, CH₂). Anal. calcd. for C₁₉H₁₆N₂O: C, 79.14; H, 5.59; N, 9.72. Found: C, 79.18; H, 5.68; N, 9.65.

*1-Benzoyl-2-benzylidene-hydrazine*³³ (**B5**). White crystals. M.p. 216–218°C, Lit³³: 210–212°C. Yield – 95%. IR (KBr): 3201 (NH), 1642 (C=O), 1488 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.84 (s, 1H, N-H), 8.46 (s, 1H, CH=N), 7.92–7.39 (m, 10H, ArH). Anal. calcd. for C₁₄H₁₂N₂O: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.67; H, 5.18; N, 12.57.

*1-[(2,4-Dichlorophenoxy)acetyl]-2-furaldehyde-hydrazine*³¹ (**C1**). White crystals. M.p. 176–178°C, Yield – 94%. IR (KBr): 3225 (NH), 1683 (C=O), 1485 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.58, 11.53 (2s, 1H, N-H), 8.12, 7.87 (2s, 1H, CH=N), 7.80–6.59 (m, 6H, ArH), 5.18, 4.75 (2s, 2H, CH₂). Anal. calcd. for C₁₃H₁₀Cl₂N₂O₃: C, 49.86; H, 3.22; N, 8.95. Found: C, 49.98; H, 3.40; N, 8.69.

*1-Phenoxyacetyl-2-furaldehyde-hydrazine*³⁴ (**C3**). White crystals. M.p. 139–141°C, Yield – 93%. IR (KBr): 3317 (NH), 1684 (C=O), 1497 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.50, 11.48 (2s, 1H, N-H), 8.21, 7.87 (2s, 1H, CH=N), 7.81–6.59 (m, 8H, ArH), 5.02, 4.61 (2s, 2H, CH₂). Anal. calcd. for C₁₃H₁₂N₂O₃: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.78; H, 5.11; N, 11.39.

*1-Benzoyl-2-furaldehyde-hydrazine*³⁵ (**C5**). Yellow crystals. M.p. 188–190°C, Yield – 94%. IR (KBr): 3247 (NH), 1645 (C=O), 1495 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.76 (s, 1H, N-H), 8.32 (s, 1H, CH=N), 7.88–6.61 (m, 8H, ArH). Anal. calcd. for C₁₂H₁₀N₂O₃: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.11; H, 4.50; N, 13.19.

*1-Phenoxyacetyl-2-cinnamylidene-hydrazine*³⁶ (**D3**). White crystals. M.p. 180–182°C, Lit³⁶: 167°C. Yield – 92%. IR (KBr): 3329 (NH), 1683 (C=O), 1498 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.46, 11.43 (2s, 1H, N-H), 8.09, 8.07 (2s, 1H, CH=N), 7.82, 7.80 (d, ArCH, 1H J=9.2Hz), 7.59–7.57 (m, 1H, =CH) 7.37–6.86 (m, 10H, ArH), 4.99, 4.61 (2s, 2H, CH₂). Anal. calcd. for C₁₇H₁₆N₂O₂: C, 72.84; H, 5.75; N, 9.99. Found: C, 39.98; H, 2.50; N, 10.49.

*1-Benzoyl-2-cinnamylidene-hydrazine*³⁷ (**D5**). White crystals. M.p. 201–203°C, Yield – 93%. IR (KBr): 3271 (NH), 1648 (C=O), 1491 (C=N) cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 11.71 (s, 1H, N-H),

8.23, 8.21 (d, 1H, CH=N, $J=7.2\text{Hz}$), 7.88, 7.87 (d, ArCH, 1H, $J=7.2\text{Hz}$), 7.61–7.48 (m, 1H, =CH) 7.56–7.00 (m, 10H, ArH). Anal. calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.87; H, 5.50; N, 11.34.

1-[(2,4-Dichlorophenoxy)acetyl]-2-[(3-methoxy-4-hydroxy)benzylidene]-hydrazine³¹ (**E1**). White crystals. M.p. 192–194°C, Yield – 93%. IR (KBr): 3204 (NH), 3333, 3399 (OH), 1667 (C=O), 1482 (C=N) cm^{-1} . ¹H NMR (400 MHz, DMSO- d_6): δ 11.47, 11.38 (2s, 1H, N-H), 9.51, 9.46 (2s, 1H, OH), 8.10, 7.86 (2s, 1H, CH=N), 7.58–6.77 (m, 6H, ArH), 5.26, 4.74 (2s, 2H, CH₂), 3.78 (s, 3H, CH₃). Anal. calcd. for $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_4$: C, 52.05; H, 3.82; N, 7.59. Found: C, 52.18; H, 3.97; N, 7.38.

1-(1-Naphthylacetyl)-2-[(3-methoxy-4-hydroxy)benzylidene]-hydrazine³⁸ (**E4**). White crystals. M.p. 201–202°C, Yield – 91%. IR (KBr): 3236 (NH), 3504, 3435 (OH), 1671 (C=O), 1510 (C=N) cm^{-1} . ¹H NMR (400 MHz, DMSO- d_6): δ 11.50, 11.27 (2s, 1H, N-H), 9.47, 9.44 (2s, 1H, OH), 8.10, 7.89 (2s, 1H, CH=N), 8.08–6.78 (m, 8H, ArH), 4.41, 3.99 (2s, 2H, CH₂), 3.76, 3.73 (2s, 3H, CH₃). Anal. calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 71.98; H, 5.50; N, 8.19.

1-[(2,4-Dichlorophenoxy)acetyl]-2-(3-nitrobenzylidene)-hydrazine³⁹ (**F1**). White crystals. M.p. 224–226°C, Lit³⁹: 202–204°C. Yield – 89%. IR (KBr): 3327 (NH), 1679 (C=O), 1480 (C=N) cm^{-1} . ¹H NMR

(400 MHz, DMSO- d_6): δ 11.86 (s, 1H, N-H), 8.49, 8.48 (2s, 1H, CH=N), 8.36–7.06 (m, 7H, ArH), 5.34, 4.82 (2s, 2H, CH₂). Anal. calcd. for $\text{C}_{15}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_4$: C, 48.93; H, 3.01; N, 11.41. Found: C, 49.08; H, 2.90; N, 11.49.

1-[(2,4-Dichlorophenoxy)acetyl]-2-(4-chlorobenzylidene)-hydrazine²⁵ (**G1**). White crystals. M.p. 193–196°C, Lit²⁵: 185–186°C. Yield – 94%. IR (KBr): 3338 (NH), 1683 (C=O), 1487 (C=N) cm^{-1} . ¹H NMR (400 MHz, DMSO- d_6): δ 11.69, 11.65 (s, 1H, N-H), 8.23, 7.97 (2s, 1H, CH=N), 7.72–7.04 (m, 7H, ArH), 5.28, 4.78 (2s, 2H, CH₂). Anal. calcd. for $\text{C}_{15}\text{H}_{11}\text{Cl}_3\text{N}_2\text{O}_2$: C, 50.38; H, 3.10; N, 7.83. Found: C, 50.47; H, 3.23; N, 7.59.

1-Phenoxyacetyl-2-(3-chlorobenzylidene)-hydrazine¹ (**G3**). White crystals. M.p. 184–186°C, Yield – 95%. IR (KBr): 3306 (NH), 1683 (C=O), 1498 (C=N) cm^{-1} . ¹H NMR (400 MHz, DMSO- d_6): δ 11.61 (s, 1H, N-H), 8.31, 7.98 (2s, 1H, CH=N), 7.72–6.89 (m, 9H, ArH), 5.12, 4.64 (2s, 2H, CH₂). Anal. calcd. for $\text{C}_{15}\text{H}_{13}\text{ClN}_2\text{O}_2$: C, 62.40; H, 4.54; N, 9.70. Found: C, 62.31; H, 4.50; N, 9.89.

1-Benzoyl-2-(3-chlorobenzylidene)-hydrazine⁴⁰ (**G5**). White crystals. M.p. 182–184°C, Lit⁴⁰: 176–177°C. Yield – 96%. IR (KBr): 3290 (NH), 1669 (C=O), 1487 (C=N) cm^{-1} . ¹H NMR (400 MHz, DMSO- d_6): δ 11.89 (s, 1H, N-H), 8.43 (s, 1H, CH=N), 7.90–7.49 (m, 9H, ArH). Anal. calcd. for $\text{C}_{14}\text{H}_{11}\text{ClN}_2\text{O}$: C, 65.00; H, 4.29; N, 10.83. Found: C, 65.13; H, 4.40; N, 10.69.