

(十七) 4-Oxo-2,3,4,9-tetrahydrofuro[2,3-*b*]quinolin-3-one substituted phenyl hydrazone (241-246) 之合成

4-Oxo-2,3,4,9-tetrahydrofuro[2,3-*b*]quinolin-3-one 2*o*-chlorophenyl hydrazone (241)之合成

取化合物 27 (2.01g, 0.01mole)及 2-chlorophenylhydrazine (2.85g, 0.02mole)置於 30ml 絕對酒精中，加入 1ml 冰醋酸(glacial acetic acid)並迴流 6 小時再以減壓濃縮至乾。殘餘物溶於苯 (50ml) 中並用 2 % 稀鹽酸及水依次萃取，取苯層再以無水硫酸鎂乾燥並過濾後以減壓濃縮至乾。殘餘物以管柱層析法用溶媒 (chloroform)沖提，再以 95% 乙醇做再結晶得到化合物 241(1.38g, 42.3%)，mp：149-151。光譜數據如下：MS m/z : M^+ 324.9, $(M+2)^+$ 326.9; IR (KBr) cm^{-1} : 3334.1 ($C_3=N-NH-$), 1628.4 ($C_4=O$); UV λ_{max} nm (MeOH) (log ϵ): 306 (4.17); 1H -NMR (DMSO- d_6) δ : 5.29 (2H, s, H-2), 6.65 (1H, t, $J=7.8$ Hz, H-5'), 7.14 (2H, t, $J=8.4$ Hz, H-4'), 7.23-7.30 (2H, m, H-3', H-6'), 7.36 (1H, t, $J=7.0$ Hz, H-6), 7.47 (1H, d, $J=8.0$ Hz, H-8), 7.65 (1H, t, $J=8.4$ Hz, H-7), 8.16 (1H, d, $J=8.0$ Hz, H-5), 12.14 (1H, s, $C_3=N-NH-$); ^{13}C -NMR (DMSO- d_6) δ : 75.08 (C-2), 99.25 (C-3a), 112.76 (C-6'), 115.97 (C-2'), 118.29 (C-4a, C-4'), 124.02 (C-5'), 124.26 (C-8), 126.23 (C-6), 127.93 (C-5), 129.44 (C-2'), 132.69 (C-7), 137.48 (C-8a), 140.71 (C-1'), 142.40 (C-3), 168.72 (C-9a), 172.06 (C-4).

4-Oxo-2,3,4,9-tetrahydrofuro[2,3-*b*]quinolin-3-one 3*o*-chlorophenyl hydrazone (242)之合成

取化合物 27 (2.01g, 0.01mole)及 3-chlorophenylhydrazine (2.85g, 0.02mole)為原料，比照化合物 241 的合成法及處理步驟，得化合物 242(1.51g, 46.3%)，mp：143-145。光譜數據如下：MS m/z : M^+ 324.9, $(M+2)^+$ 326.9; IR (KBr) cm^{-1} : 3380.3 ($C_3=N-NH-$), 1649.9 ($C_4=O$); UV λ_{max} nm (MeOH) (log ϵ): 306 (3.91); 1H -NMR (DMSO- d_6) δ : 5.31 (2H, s, H-2), 6.64 (1H, d, $J=7.8$ Hz, H-4'), 6.78 (1H, d, $J=8.4$ Hz, H-6'), 6.91 (1H, s, H-2'), 7.16 (1H, t, $J=8.2$ Hz, H-5'), 7.39 (1H, t, $J=7.8$ Hz, H-6), 7.48 (1H, d, $J=8.2$ Hz, H-8), 7.67 (1H, t, $J=8.8$ Hz, H-7), 8.17 (1H, d, $J=8.0$ Hz, H-5), 12.35 (1H, s, $C_3=N-NH-$); ^{13}C -NMR (DMSO- d_6) δ : 74.83 (C-2), 99.35 (C-3a), 109.82 (C-2'), 110.03 (C-6'), 116.91 (C-4'), 118.20 (C-8), 123.83 (C-4a), 124.40 (C-6), 126.19 (C-5), 130.92 (C-5'), 132.77 (C-7), 134.18 (C-3'), 137.16 (C-8a), 140.27 (C-1'), 147.08 (C-3), 168.55 (C-9a), 171.96 (C-4).

4-Oxo-2,3,4,9-tetrahydrofuro[2,3-*b*]quinolin-3-one 4*o*-chlorophenyl hydrazone (243)之合成

取化合物 27 (2.01g, 0.01mole)及 4-chlorophenylhydrazine (2.85g, 0.02mole)為原料，比照化合物 241 的合成法及處理步驟，得化合物 243 (1.47g, 45.1%)，mp：135-137。光譜數據如下：MS m/z : M^+ 324.9, $(M+2)^+$ 327.0; IR (KBr) cm^{-1} : 3403.5 ($C_3=N-NH-$), 1628.4 ($C_4=O$); UV λ_{max} nm (MeOH) (log ϵ): 307 (4.39); 1H -NMR (DMSO- d_6) δ : 5.25 (2H, s, H-2), 6.88 (2H, d, $J=8.4$ Hz, H-2', H-6'), 7.17 (2H, d, $J=8.4$ Hz, H-3', H-5'), 7.35 (1H, t, $J=8.2$ Hz, H-6), 7.46 (1H, d, $J=8.2$ Hz, H-8), 7.64 (1H, t, $J=8.2$ Hz, H-7), 8.16 (1H, d, $J=8.2$ Hz, H-5), 12.33 (1H, s, $C_3=N-NH-$); ^{13}C -NMR (DMSO- d_6) δ : 74.84 (C-2), 99.46 (C-3a), 112.38 (C-2', C-6'),

118.30 (C-8), 120.67 (C-4'), 123.94 (C-4a), 124.44 (C-6), 126.22 (C-5), 129.15 (C-3', C-5'), 132.80 (C-7), 137.26 (C-8a), 139.63 (C-1'), 144.67 (C-3), 168.60 (C-9a), 171.94 (C-4).

4-Oxo-2,3,4,9-tetrahydrofuro[2,3-*b*]quinolin-3-one 2,4-dichlorophenyl-hydrazone (244)之合成

取化合物 **27** (2.01g, 0.01mole) 及 2,4-dichlorophenylhydrazine (3.54g, 0.02mole) 為原料, 比照化合物 **241** 的合成法及處理步驟, 得化合物 **244** (1.68g, 46.7%), mp: 260-261。光譜數據如下: MS *m/z*: M^+ 358.8, $(M+2)^+$ 361.0; IR (KBr) cm^{-1} : 3380.3 ($\text{C}_3=\text{N}-\text{NH}-$), 1628.4 ($\text{C}_4=\text{O}$); UV λ_{max} nm (MeOH) ($\log \epsilon$): 307 (4.43); $^1\text{H-NMR}$ (DMSO- d_6) δ : 5.29 (2H, s, H-2), 7.17 (1H, dd, $J=8.8, 2.2$ Hz, H-5'), 7.25 (1H, d, $J=8.8$ Hz, H-6'), 7.32-7.40 (2H, m, H-6, H-3'), 7.48 (1H, t, $J=8.4$ Hz, H-8), 7.67 (1H, td, $J=7.2, 2.4$ Hz, H-7), 8.13 (1H, dd, $J=8.0, 1.2$ Hz, H-5), 12.29 (1H, s, $\text{C}_3=\text{N}-\text{NH}-$); $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 75.12 (C-2), 99.21 (C-3a), 113.64 (C-6'), 116.31 (C-2'), 118.20 (C-8), 120.67 (C-4'), 123.86 (C-4a), 124.37 (C-6), 126.23 (C-5), 127.96 (C-5'), 128.60 (C-3'), 132.82 (C-7), 137.31 (C-8a), 141.49 (C-1'), 141.63 (C-3), 168.69 (C-9a), 172.17 (C-4).

4-Oxo-2,3,4,9-tetrahydrofuro[2,3-*b*]quinolin-3-one 3,4-dichlorophenyl hydrazone (245)之合成

取化合物 **27** (2.01g, 0.01mole) 及 3,4-dichlorophenylhydrazine (3.54g, 0.02mole) 為原料, 比照化合物 **241** 的合成法及處理步驟, 得化合物 **245** (1.43g, 39.7%), mp: 195-197。光譜數據如下: MS *m/z*: M^+ 358.9, $(M+2)^+$ 361.0; IR (KBr) cm^{-1} : 3395.3 ($\text{C}_3=\text{N}-\text{NH}-$), 1613.0 ($\text{C}_4=\text{O}$); UV λ_{max} nm (MeOH) ($\log \epsilon$): 306 (4.33); $^1\text{H-NMR}$ (DMSO- d_6) δ : 5.29 (2H, s, H-2), 6.80 (1H, dd, $J=8.8, 2.6$ Hz, H-6'), 7.03 (1H, d, $J=2.6$ Hz, H-2'), 7.32-7.49 (3H, m, H-6, H-8, H-5'), 7.65-7.69 (1H, m, H-7), 8.16 (1H, dd, $J=8.2, 1.4$ Hz, H-5), 12.45 (1H, s, $\text{C}_3=\text{N}-\text{NH}-$); $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 74.83 (C-2), 99.35 (C-3a), 100.12 (C-6'), 111.50 (C-2'), 117.99 (C-4'), 118.32 (C-8), 123.78 (C-3'), 124.51 (C-4a), 126.21 (C-6), 131.14 (C-5), 131.89 (C-5'), 132.93 (C-7), 137.29 (C-8a), 141.25 (C-1'), 145.60 (C-3), 168.68 (C-9a), 172.03 (C-4).

4-Oxo-2,3,4,9-tetrahydrofuro[2,3-*b*]quinolin-3-one 2,4,6-trichlorophenyl hydrazone (246)之合成

取化合物 **27** (2.01g, 0.01mole) 及 2,4,6-trichlorophenylhydrazine (4.23g, 0.02mole) 為原料, 比照化合物 **241** 的合成法及處理步驟, 得化合物 **246** (1.79g, 45.3%), mp: 190-191。光譜數據如下: MS *m/z*: M^+ 393.2, $(M+2)^+$ 395.1; IR (KBr) cm^{-1} : 3400.1 ($\text{C}_3=\text{N}-\text{NH}-$), 1620.7 ($\text{C}_4=\text{O}$); UV λ_{max} nm (MeOH) ($\log \epsilon$): 306 (4.36); $^1\text{H-NMR}$ (DMSO- d_6) δ : 5.22 (2H, s, H-2), 7.36 (1H, t, $J=7.6$ Hz, H-6), 7.44-7.49 (3H, m, H-8, H-3', H-5'), 7.67 (1H, t, $J=7.6$ Hz, H-7), 8.13 (1H, d, $J=8.0$ Hz, H-5), 11.66 (1H, s, $\text{C}_3=\text{N}-\text{NH}-$); $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 74.89 (C-2), 99.22 (C-3a), 118.23 (C-8), 123.96 (C-4a), 124.33 (C-6), 124.90 (C-4'), 125.71 (C-2', C-6'), 126.20 (C-5), 128.94 (C-3', C-5'), 132.76 (C-7), 137.35 (C-8a), 138.85 (C-1'), 140.48 (C-3), 168.69 (C-9a), 171.89 (C-4).