Supporting Information

Reaction of α -Oxoketene-*N,S*-arylaminoacetals with Vilsmeier Reagents: An Efficient Route to Highly Functionalized Quinolines and Their Benzo/Hetero- Fused Analogs

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Characterization data for compounds **1b-g**, and **1l**.

3-(3-Methoxyanilino)-3-methylthio-1-(2-bromophenyl)prop-2-en-1-one (1b). Yield 80% (3.03 g). Low melting solid, R_f 0.50 (8:2 hexane-EtOAc); IR (DCM): 2929, 1556, 1473, 1287 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.33 (s, 3H, SCH_3), 3.77 (s, 3H, OCH_3), 5.49 (s, 1H, CH), 6.77 (dd, $J = 8.4, 2.8$ Hz, 1H, ArH), 6.86 (t, $J = 2.4$ Hz, 1H, ArH), 6.91 (dd, $J = 7.6, 1.6$ Hz, 1H, ArH), 7.17 (dt, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.24 (t, $J = 7.6$ Hz, 1H, ArH), 7.31 (t, $J = 8.0$ Hz, 1H, ArH), 7.47 (dd, $J = 7.6, 1.2$ Hz, 1H, ArH), 7.56 (d, $J = 8.0$ Hz, 1H, ArH), 13.17 (brs, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): 14.6, 55.2, 92.34, 110.5, 112.35, 117.2, 119.3, 127.1, 129.1, 129.6, 130.1, 133.2, 138.8, 142.9, 159.9, 167.7, 187.5.

3-(3,4-Dimethoxyanilino)-3-methylthio-1-phenylprop-2-en-1-one (1c). Yield 85% (2.79 g). Pale yellow solid (CHCl_3 -hexane), mp 135-136 $^\circ\text{C}$; R_f 0.50 (8:2 hexane-EtOAc); IR (KBr): 1540, 1453, 1316 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.44 (s, 3H, SCH_3), 3.88 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 5.86 (brs, 1H, CH), 6.84 (d, $J = 2.0$ Hz, 1H, ArH), 6.86 (s, 1H, ArH), 6.90 (dd, $J = 8.2, 2.4$ Hz, 1H, ArH), 7.42-7.47 (m, 3H, ArH), 7.91 (dd, $J = 7.6, 2.0$ Hz, 2H, ArH), 13.36 (brs, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): 14.7, 55.8, 55.9, 88.0, 109.5, 110.8, 117.9, 126.9, 128.3, 130.8, 131.0, 140.2, 147.7, 149.0, 168.4, 185.9.

3-(3,4-Dimethoxyanilino)-3-methylthio-1-(2-bromophenyl)prop-2-en-1-one (1d). Yield 84% (3.43 g). Yellow solid (CHCl_3 -hexane), mp 112-113 $^\circ\text{C}$; R_f 0.44 (8.5:1.5 hexane-EtOAc); IR(KBr): 1555, 1465, 1232 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.33 (s, 3H, SCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 5.45 (brs, 1H, CH), 6.82-6.84 (m,

2H, ArH), 6.89 (dd, $J = 8.52, 2.2$ Hz, 1H, ArH), 7.2 (dt, $J = 7.58, 1.2$ Hz, 1H, ArH), 7.32 (dt, $J = 7.46, 1.0$ Hz, 1H, ArH), 7.47 (dd, $J = 7.58, 1.48$ Hz, 1H, ArH), 7.58 (dd, $J = 8.06$ Hz, 1H, ArH), 12.97 (brs, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): 14.7, 55.9, 60.0, 56.0, 91.8, 109.6, 110.8, 118.1, 119.4, 127.2, 129.1, 130.1, 133.3, 143.2, 147.9, 149.1, 168.8, 187.5.

3-(2,5-Dimethoxyanilino)-3-methylthio-1-phenylprop-2-en-1-one (1e). Yield 81% (2.67 g). Yellow solid (CHCl_3 -hexane), mp 85-86 °C; R_f 0.51 (8.5:1.5 hexane-EtOAc); IR(KBr): 1554, 1457, 1265 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.44 (s, 3H, SCH_3), 3.76 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.86 (brs, 1H, CH), 6.70 (dd, $J = 8.92, 2.92$ Hz, 1H, ArH), 6.85 (d, $J = 8.76$ Hz, 1H, ArH), 7.09 (d, $J = 2.92$ Hz, 1H, ArH), 7.39-7.44 (m, 3H, ArH), 7.9 (dd, $J = 6.84, 1.44$ Hz, 2H, ArH), 13.3 (brs, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): 14.9, 55.8, 56.42, 89.28, 111.2, 111.8, 112.1, 127.1, 128.0, 128.2, 130.8, 140.3, 146.9, 153.0, 166.9, 186.1.

3-(3-Fluoroanilino)-3-methylthio-1-phenylprop-2-en-1-one (1f). Yield 80% (2.29 g). Red viscous liquid; R_f 0.55 (9:1 hexane-EtOAc); IR (DCM): 3055, 1558, 1467, 1264 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.33 (s, 3H, SCH_3), 5.87 (s, 1H, CH), 6.86 (t, $J = 7.77$ Hz, 1H, ArH), 7.06 (dd, $J = 9.88, 2.2$ Hz, 2H, ArH), 7.20-7.26 (m, 1H, ArH), 7.36-7.42 (m, 3H, ArH), 7.90 (dd, $J = 7.44, 1.48$ Hz, 2H, ArH), 13.69 (brs, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): 14.3, 89.0, 111.3, 112.4, 119.9, 126.7, 128.0, 129.9, 130.8, 139.5, 161.1, 163.6, 166.4, 185.7.

3-Anilino-3-methylthio-1-phenylprop-2-en-1-one (1g). Yield 80% (2.15 g). Yellow low melting solid; R_f 0.45 (9:1 hexane-EtOAc); IR (DCM): 3057, 1553, 1467, 736 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.42 (s, 3H, SCH_3), 5.88 (brs, 1H, CH), 7.22-7.26 (m, 1H, ArH), 7.31-7.38 (m, 4H, ArH), 7.42-7.47 (m, 3H, ArH), 7.91 (dd, $J = 7.68, 2.2$ Hz, 2H, ArH), 13.53 (brs, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): 14.7, 88.4, 125.2, 126.4, 127.0, 128.3, 129.0, 130.9, 138.1, 140.1, 167.6, 186.1.

1-Bis(methoxy)-4-(3,4-dimethoxyanilino)-4-(methylthio)-3-buten-2-one (1l). Yield 78% (2.55 g). Deep red viscous liquid; R_f 0.40 (3:2 hexane-EtOAc); IR (DCM): 2949, 2837, 1554, 1471 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.38 (s, 3H, SCH_3), 3.44 (s, 6H, OCH_3), 3.87 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.65 (s, 1H, CH), 5.57 (s, 1H, CH), 6.78 (s, 1H, ArH), 6.84 (d, $J = 1.24$ Hz, 2H, ArH), 12.92 (brs, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): 14.6, 54.1, 55.8, 55.9, 86.8, 103.8, 109.5, 110.7, 118.0, 130.6, 147.9, 149.0, 170.2, 187.7.