[5C + 1S] Annulation: A Facile and Efficient Synthetic Route toward Functionalized 2,3-Dihydrothiopyran-4-ones

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2-(Benzo[d][1,3]dioxol-5-yl)-5-benzoyl-6-ethylthio-2,3-dihydrothiopyran-4-one

(**2b**): Yellowish semisolid; ^1H NMR (500 MHz, CDCl_3) δ = 1.26 (t, J = 7.5 Hz, 3H), 2.93-3.04 (m, 3H), 3.19 (dd, J = 14.0, 16.5 Hz, 1H), 4.74 (dd, J = 3.5, 14.0 Hz, 1H), 6.02 (s, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.92 (s, 1H), 7.44-7.47 (m, 2H), 7.55-7.58 (m, 1H), 7.88 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ = 194.66, 190.82, 160.48, 148.15, 148.00, 136.72, 134.26, 131.63, 131.32, 129.39, 129.34, 122.22, 108.98, 108.67, 101.90, 44.62, 44.03, 40.48, 27.33, 15.37. IR (KBr, cm^{-1}) 1670, 1637, 1489, 1444, 1296, 1251, 1035, 926, 813.

5-Benzoyl-2-(4-chlorophenyl)-6-ethylthio-2,3-dihydrothiopyran-4-one (2c): mp:

127-129 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ = 1.26 (t, J = 7.5 Hz, 3H), 2.93-3.05 (m, 3H), 3.23 (dd, J = 13.5, 16.5 Hz, 1H), 4.80 (dd, J = 3.0, 13.5 Hz, 1H), 7.38-7.46 (m, 6H), 7.55-7.58 (m, 1H), 7.85 (dd, J = 1.0, 8.0 Hz, 2H). IR (KBr, cm^{-1}) 1669, 1636, 1491, 1296, 1232, 1091, 856. HRMS-ESI (m/z): $[\text{M} + \text{K}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{ClO}_2\text{S}_2\text{K}$, 426.9990; found 426.9987.

5-Benzoyl-2-(2-chlorophenyl)-6-ethylthio-2,3-dihydrothiopyran-4-one (2d): White

semisolid; ^1H NMR (500 MHz, CDCl_3) δ = 1.26 (t, J = 7.5 Hz, 3H), 2.93-3.07 (m, 3H), 3.25 (dd, J = 13.0, 16.5 Hz, 1H), 5.03 (dd, J = 3.0, 13.0 Hz, 1H), 7.32-7.39 (m, 2H), 7.45-7.48 (m, 3H), 7.53-7.59 (m, 2H), 7.90 (d, J = 7.5 Hz, 2H). IR (KBr, cm^{-1}) 1660, 1643, 1534, 1313, 1290, 1091, 832.

5-Benzoyl-6-ethylthio-2-(pyridin-3-yl)-2,3-dihydrothiopyran-4-one (2e): mp:

115-117 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ = 1.25 (t, J = 7.5 Hz, 3H), 2.93-3.06 (m, 3H), 3.26 (dd, J = 13.5, 16.5 Hz, 1H), 4.84 (dd, J = 2.0, 13.5 Hz, 1H), 7.37-7.40 (m,

1H), 7.43-7.46 (m, 2H), 7.55-7.58 (m, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 2H), 8.65 (d, $J = 4.5$ Hz, 1H), 8.73 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) $\delta =$ 194.39, 189.34, 161.28, 150.53, 149.51, 136.79, 135.30, 133.92, 132.89, 131.87, 129.40, 128.97, 124.14, 44.56, 43.94, 27.93, 14.90. IR (KBr, cm^{-1}) 1673, 1631, 1498, 1297, 1232, 860, 814, 684. HRMS-ESI (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_2\text{S}_2\text{Na}$, 378.0593; found 378.0557.

(E)-5-benzoyl-6-ethylthio-2-styryl-2,3-dihydrothiopyran-4-one (2f): Yellowish semisolid; ^1H NMR (500 MHz, CDCl_3) $\delta =$ 1.27 (t, $J = 7.5$ Hz, 3H), 2.99-3.05 (m, 4H), 4.42-4.44 (m, 1H), 6.30 (dd, $J = 7.0, 16.0$ Hz, 1H), 6.75 (d, $J = 16.0$ Hz, 1H), 7.31-7.39 (m, 5H), 7.43 (d, $J = 7.5$ Hz, 2H), 7.51-7.54 (m, 1H), 7.87 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) $\delta =$ 194.14, 189.21, 160.45, 136.46, 135.20, 134.36, 133.24, 131.51, 128.93, 128.55, 128.43, 128.38, 126.48, 124.16, 44.66, 42.92, 27.40, 14.45.

5-Benzoyl-6-methylthio-2-(4-chlorophenyl)-2,3-dihydrothiopyran-4-one (2g): mp: 101-103 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) $\delta =$ 2.46 (s, 3H), 2.30 (dd, $J = 3.0, 16.5$ Hz, 1H), 3.22 (dd, $J = 9.0, 16.5$ Hz, 1H), 4.80 (dd, $J = 3.0, 9.0$ Hz, 1H), 7.37-7.47 (m, 6H), 7.55-7.59 (m, 1H), 7.85 (d, $J = 7.5$ Hz, 2H).

2-(4-Chlorophenyl)-5-(4-ethoxybenzoyl)-6-ethylthio-2,3-dihydrothiopyran-4-one (2h): mp: 158-159 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) $\delta =$ 1.25 (t, $J = 7.5$ Hz, 3H), 1.44 (t, $J = 7.5$ Hz, 3H), 2.92-3.04 (m, 3H), 3.22 (dd, $J = 13.5, 16.5$ Hz, 1H), 4.10 (q, $J = 7.5$ Hz, 2H), 4.77 (dd, $J = 2.5, 13.5$ Hz, 1H), 6.91 (d, $J = 9.0$ Hz, 2H), 7.37-7.42 (m,

4H), 7.82 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) $\delta = 192.44, 189.17, 163.25, 160.00, 135.09, 134.54, 131.65, 131.40, 129.23, 129.11, 128.83, 127.87, 114.12, 63.55, 45.90, 43.85, 27.34, 14.46, 14.41$.

5-(4-Chlorobenzoyl)-2-(4-chlorophenyl)-6-ethylthio-2,3-dihydrothiopyran-4-one

(2i): mp: 152-155 °C; ^1H NMR (500 MHz, CDCl_3) $\delta = 1.27$ (t, $J = 7.5$ Hz, 3H), 2.97-3.04 (s, 3H), 3.23 (dd, $J = 13.5, 16.5$ Hz, 1H), 4.79 (dd, $J = 3.0, 13.5$ Hz, 1H), 7.38-7.43 (m, 6H), 7.78 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) $\delta = 192.07, 188.41, 161.22, 138.97, 134.15, 134.01, 129.83, 129.51, 128.46, 128.03, 45.29, 43.03, 26.62, 13.59$. IR (KBr, cm^{-1}) 1683, 1670, 1584, 1491, 1311, 1091, 1013, 856.

6-ethylthio-2-(*p*-tolyl)-2,3-dihydrothiopyran-4-one (2j): mp: 58-60 °C; ^1H NMR (500 MHz, CDCl_3) $\delta = 1.36$ (t, $J = 7.5$ Hz, 3H), 2.36 (s, 3H), 2.92 (dd, $J = 3.0, 16.5$ Hz, 1H), 2.94-3.06 (m, 2H), 3.10 (dd, $J = 14.5, 16.5$ Hz, 1H), 4.66 (dd, $J = 3.0, 14.5$ Hz, 1H), 6.26 (s, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H). IR (KBr, cm^{-1}) 2933, 1652, 1523, 1456, 1261.

2-(Benzo[d][1,3]dioxol-5-yl)-6-ethylthio-2,3-dihydrothiopyran-4-one (2k):

Semisolid; ^1H NMR (500 MHz, CDCl_3) $\delta = 1.36$ (t, $J = 7.5$ Hz, 3H), 2.90 (dd, $J = 3.0, 16.5$ Hz, 1H), 2.93-3.06 (m, 3H), 4.60 (dd, $J = 3.0, 14.0$ Hz, 1H), 5.98 (s, 2H), 6.25 (s, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.86 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) $\delta = 190.93, 162.22, 147.08, 146.88, 129.86, 120.28, 116.82, 107.59, 106.81, 100.42, 46.67, 44.05, 26.13, 12.78$. IR (KBr, cm^{-1}) 1647, 1544, 1481, 1399, 1326, 1207, 1090, 861.

2-(4-Chlorophenyl)-6-ethylthio-2,3-dihydrothiopyran-4-one (2l): mp: 81-84 °C; ¹H NMR (500 MHz, CDCl₃) δ = 1.35 (t, *J* = 7.5 Hz, 3H), 2.92 (dd, *J* = 2.5, 16.0 Hz, 1H), 2.93-3.03 (m, 2H), 3.06 (dd, *J* = 14.0, 16.0 Hz, 1H), 4.65 (dd, *J* = 2.5, 14.0 Hz, 1H), 6.25 (s, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H). IR (KBr, cm⁻¹) 1642, 1520, 1263, 1088, 828. HRMS-ESI (*m/z*): [2M + Na]⁺ calcd for [2C₁₃H₁₃ClOS₂ + Na] 591.0085; found 591.0117.

5-Benzoyl-2-(4-chlorophenyl)-6-ethylamino-2,3-dihydrothiopyran-4-one (3cb): mp: 150-151 °C; ¹H NMR (500 MHz, CDCl₃) δ = 1.36 (t, *J* = 7.0 Hz, 3H), 2.89 (dd, *J* = 10.5, 14.5 Hz, 1H), 3.44-3.49 (m, 2H), 3.56 (dd, *J* = 3.5, 14.5 Hz, 1H), 4.08 (dd, *J* = 3.5, 10.5 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.39-7.42 (m, 2H), 7.46-7.49 (m, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 10.96 (br s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ = 191.56, 182.10, 138.21, 135.24, 131.95, 130.12, 129.90, 129.53, 128.29, 127.30, 127.19, 126.48, 103.26, 54.87, 40.07, 37.13, 13.30. IR (KBr, cm⁻¹) 3215, 1669, 1590, 1490, 1414, 1357, 1297, 1092, 1014, 808, 768. ES-MS: (*m/z*): 372.3 [M + 1]⁺.