

Supporting Information

Structural Studies on Bioactive Compounds. 40.¹ Synthesis and Biological Properties of Fluoro-, Methoxyl- and Amino-substituted 3-Phenyl-4*H*-1-benzopyran-4-ones and a Comparison of Their Antitumor Activities with Related 2-Phenylbenzothiazoles

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Contents of SI:

- Full characterization data for compounds **8b-k**, **12b-o**, **13b-g**, **14b-g**, additional references and microanalytical data (CHN) for new compounds.

8-Fluoro-3-iodo-4*H*-1-benzopyran-4-one (8b). Prepared according to Method C, in chloroform, from 3-dimethylamino-1-(3-fluoro-2-hydroxyphenyl)propenone (**7b**), as a white solid (78%), mp 102-103 °C; IR (KBr) 1640, 1615, 1562, 1488, 1452, 1434, 1359, 1311, 1264, 1217 cm⁻¹; δ_{H} (CDCl₃) 8.34 (1H, s, H-2), 8.02 (1H, dt, $J = 1.6, 8.0$, ArH), 7.51 (1H, td, $J = 1.6, 10.0$, ArH), 7.40 (1H, td, $J = 4.6, 8.0$, ArH); MS-CI (m/z): 291 ($M^+ + 1$). Anal. (C₉H₄FIO₂) C, H.

7-Fluoro-3-iodo-4*H*-1-benzopyran-4-one (8c). Prepared according to Method C, in chloroform, from 3-dimethylamino-1-(4-fluoro-2-hydroxyphenyl)propenone (**7c**), as a white solid (66%), mp 107-109 °C; IR (KBr) 1651, 1605, 1555, 1489, 1434, 1367, 1357, 1294, 1255, 1227 cm⁻¹; δ_{H} (CDCl₃) 8.25-8.31 (2H, m, ArH and H-2), 7.19 (2H, m, ArH); δ_{C} (CDCl₃) 179.9 (C=O), 166.1 (d, $J = 250$, C-F), 158.2 (CH), 157.5 (d, $J = 13.8$, C), 129.8 (d, $J = 10.5$, CH), 119.0 (C), 115.4 (d, $J = 22.5$, CH), 105.1 (d, $J = 25$, CH), 87.5 (C-I); MS-CI (m/z): 291 ($M^+ + 1$). Anal. (C₉H₄FIO₂) C, H.

6-Fluoro-3-iodo-4*H*-1-benzopyran-4-one (8d). Prepared according to Method C, in chloroform, from 3-dimethylamino-1-(5-fluoro-2-hydroxyphenyl)propenone (**7d**), as a white solid (85%), mp 120-122 °C; IR (KBr) 1644, 1623, 1564, 1552, 1473, 1444, 1361, 1303, 1241 cm⁻¹; δ_{H} (CDCl₃) 8.32 (1H, s, H-2), 7.90 (1H, m, H-5), 7.47 (2H, m, H-7, H-8); δ_{C} (CDCl₃) 173.1 (C=O), 158.5 (d, $J = 250$, C-F), 158.3 (CH), 152.8 (C), 123.5 (d, $J = 100$, CH), 123.2 (d, $J = 30$, C), 120.9 (d, $J = 30$, CH), 111.7 (d, $J = 100$, CH), 86.3 (C-I); MS-CI (m/z): 291 ($M^+ + 1$). Anal. (C₉H₄FIO₂) C, H.

7,8-Difluoro-3-iodo-4*H*-1-benzopyran-4-one (8e). Prepared according to Method C, in chloroform, from 3-dimethylamino-1-(3,4-difluoro-2-hydroxyphenyl)propenone (**7e**), as a white solid (63%), mp 135-137 °C; IR (KBr) 1649, 1562, 1512, 1458, 1364, 1316, 1279, 1213 cm⁻¹; δ_{H} (CDCl₃, ¹⁹F decoupled) 8.33 (1H, s, H-2), 8.03 (1H, d, $J = 8.5$, ArH), 7.29 (1H, d, $J = 8.5$, ArH); MS-CI (m/z): 309 ($M^+ + 1$). Anal. (C₉H₃F₂IO₂) C, H.

6,8-Difluoro-3-iodo-4*H*-1-benzopyran-4-one (8f). Prepared according to Method C, in chloroform, from 3-dimethylamino-1-(3,5-difluoro-2-hydroxyphenyl)propenone (**7f**), as a white solid (41%), mp 93-95 °C; IR (KBr) 1656, 1630, 1618, 1563, 1488, 1470, 1447, 1380, 1314, 1283 cm⁻¹; δ_{H} (CDCl₃) 8.33 (1H, s, H-2), 7.70 (1H, m, ArH), 7.29 (1H, m, ArH); MS-EI (m/z): 308 (M^+). Anal. (C₉H₃F₂IO₂) C, H.

6,7-Difluoro-3-iodo-4*H*-1-benzopyran-4-one (8g). Prepared according to Method C, in chloroform, from 3-dimethylamino-1-(4,5-difluoro-2-hydroxyphenyl)propenone (**7g**), as a white solid (27%), mp 118-120 °C; IR (KBr) 1649, 1621, 1563, 1499, 1454, 1373, 1349, 1299, 1290, 1209 cm⁻¹; δ_{H} (CDCl₃) 8.29 (1H, s, H-2), 8.03 (1H, m, ArH), 7.33 (1H, m, ArH); MS-EI (m/z): 308 (M^+). Anal. (C₉H₃F₂IO₂) C, H.

3-Iodo-7-methoxy-4*H*-1-benzopyran-4-one (8h). Prepared according to Method C, in methanol, from 3-dimethylamino-1-(2-hydroxy-4-methoxyphenyl)propenone (**7h**), as a pale brown solid (59%), mp 103-105 °C; IR (KBr) 1638, 1608, 1586, 1545, 1464, 1435, 1384, 1350, 1266, 1218 cm⁻¹; δ_{H} (CDCl₃) 8.23 (1H, s, H-2), 8.16 (1H, d, $J = 9.0$, H-5), 7.01 (1H, dd, $J = 2.4, 9.0$, H-6), 6.85 (1H, d, $J = 2.4$, H-8), 3.92 (3H, s, OCH₃); MS-CI (m/z): 303 ($M^+ + 1$). Anal. (C₁₀H₇IO₃) C, H.

3-Iodo-6-methoxy-4*H*-1-benzopyran-4-one (8i). Prepared according to Method C, in methanol, from 3-dimethylamino-1-(2-hydroxy-5-methoxyphenyl)propenone (**7i**), as a pale brown solid (64%), mp 112-113 °C; IR (KBr) 1638, 1608, 1586, 1545, 1464, 1435, 1384, 1350, 1266, 1218 cm⁻¹; δ_H (CDCl₃) 8.29 (1H, s, H-2), 7.59 (1H, d, *J* = 3.0, H-5), 7.42 (1H, d, *J* = 9.0, H-8), 7.30 (1H, dd, *J* = 3.0, 9.0, H-7), 3.91 (3H, s, OCH₃); MS-CI (*m/z*): 303 (M⁺+1). Anal. (C₁₀H₇IO₃) C, H.

3-Iodo-5-methoxy-4*H*-1-benzopyran-4-one (8j). Prepared according to Method C, in methanol, from 3-dimethylamino-1-(2-hydroxy-6-methoxyphenyl)propenone (**7j**), as a pale brown solid (43%), mp 143-145 °C; IR (KBr) 1668, 1645, 1609, 1566, 1474, 1436, 1345, 1269 cm⁻¹; δ_H (CDCl₃) 8.10 (1H, s, H-2), 7.53 (1H, t, *J* = 8.0, H-7), 6.94 (1H, d, *J* = 8.0, ArH), 6.81 (1H, d, *J* = 8.0, ArH), 3.92 (3H, s, OCH₃); MS-CI (*m/z*): 303 (M⁺+1). Anal. (C₁₀H₇IO₃) C, H.

5,7-Dimethoxy-3-iodo-4*H*-1-benzopyran-4-one (8k).¹ Prepared according to Method C, in methanol, from 3-dimethylamino-1-(4,6-dimethoxy-2-hydroxyphenyl)propenone (**7k**), as a white solid (29%), mp 157-159 °C; δ_H (CDCl₃) 8.10 (1H, s, H-2), 6.43 (1H, d, *J* = 2.3, ArH), 6.38 (1H, d, *J* = 2.3, ArH), 3.92 (3H, s, OCH₃), 3.88 (3H, s, OCH₃).

3-(4-Bromophenyl)-4*H*-1-benzopyran-4-one (12b).² Prepared (20%), from **8a** and 4-chlorophenylboronic acid by General Method D, as a white solid, mp 182-184 °C; IR (KBr) 1635, 1465, 1373, 1352, 1288 cm⁻¹; δ_H (CDCl₃) 8.32 (1H, dd, *J* = 2.0, 8.0, ArH), 8.05 (1H, s, H-2), 7.69 (2H, m, ArH), 7.54 (4H, m, ArH), 7.35 (1H, m, ArH); MS-CI (*m/z*): 301/303 (M⁺ +1).

3-(3-Nitrophenyl)-4*H*-1-benzopyran-4-one (12c). Prepared (50%), from **8a** and 3-nitrophenylboronic acid by General Method D, as an orange/brown solid, mp 194-196 °C (lit. 194-196 °C³); IR (KBr) 1645, 1615, 1568, 1524, 1510, 1464, 1433, 1351, 1292, 1229 cm⁻¹; δ_H (CDCl₃) 8.46 (1H, t, *J* = 2.0, H-2'), 8.34 (1H, dd, *J* = 1.4, 8.0, ArH), 8.27 (1H, m, ArH), 8.16 (1H, s, H-2), 8.00 (1H, dt, *J* = 1.6, 8.0, ArH), 7.76 (1H, td, *J* = 1.7, 7.0, ArH), 7.65 (1H, t, *J* = 8.0, ArH), 7.51 (2H, m, ArH); MS-CI (*m/z*): 268 (M⁺ +1).

3-(3-Methoxyphenyl)-4*H*-1-benzopyran-4-one (12d).⁴ Prepared (95%), from **8a** and 3-methoxyphenylboronic acid by General Method D, as a white solid, mp 78-79 °C; IR (KBr) 1639, 1616, 1606, 1577, 1567, 1484, 1462, 1434, 1382, 1357, 1316, 1291, 1248, 1220 cm⁻¹; δ_H (CDCl₃) 8.33 (1H, dd, *J* = 1.6, 8.0, ArH), 8.04 (1H, s, H-2), 7.70 (1H, td, *J* = 1.6, 8.0, ArH), 7.41 (3H, m, ArH), 7.15 (2H, m, ArH), 6.95 (1H, m, ArH), 3.85 (3H, s, OCH₃); MS-CI (*m/z*): 253 (M⁺ +1).

3-(4-Methoxyphenyl)-4*H*-1-benzopyran-4-one (12e). Prepared (99%), from **8a** and 4-methoxyphenylboronic acid by General Method D, as a white solid, mp 138-139 °C (lit. 141-142 °C²); IR (KBr) 1639, 1616, 1606, 1577, 1567, 1484, 1462, 1434, 1382, 1357, 1316, 1291, 1248, 1220 cm⁻¹; δ_H (CDCl₃) 8.33 (1H, dd, *J* = 1.6, 8.0, ArH), 8.04 (1H, s, H-2), 7.70 (1H, td, *J* = 1.6, 8.0, ArH), 7.41 (3H, m, ArH), 7.15 (2H, m, ArH), 6.95 (1H, m, ArH), 3.85 (3H, s, OCH₃); MS-CI (*m/z*): 253 (M⁺ +1).

3-(3,4-Dimethoxyphenyl)-4*H*-1-benzopyran-4-one (12f). Prepared (76%), from **8a** and 3,4-dimethoxyphenylboronic acid by General Method D, as a white solid, mp 136-138 °C; IR (KBr) 1639, 1617, 1607, 1577, 1568, 1515, 1463, 1409, 1375, 1315, 1272, 1253, 1208 cm⁻¹; δ_H (CDCl₃) 8.33 (1H, dd, *J* = 1.8, 8.0, ArH), 8.04 (1H, s, H-2), 7.71 (1H, m, ArH), 7.47 (2H, m, ArH), 7.23 (1H, d, *J* = 2.0, ArH), 7.08 (1H, dd, *J* = 2.0, 8.3, ArH), 6.95 (1H, d, *J* = 8.3, H-2'), 3.95 (3H, s, OCH₃), 3.93 (3H, s, OCH₃); MS-CI (*m/z*): 283 (M⁺ +1); Anal. (C₁₇H₁₄O₄) C, H.

6-Fluoro-3-(4-methoxyphenyl)-4H-1-benzopyran-4-one (12g). Prepared (93%), from **8d** and 4-methoxyphenylboronic acid by General Method D, as a white solid, mp 181-183 °C; IR (KBr) 1637, 1568, 1517, 1484, 1466, 1446, 1367, 1292, 1272, 1255, 1220 cm⁻¹; δ_{H} (CDCl₃) 8.02 (1H, s, H-2), 7.96 (1H, dd, $J = 2.8, 8.3$, ArH), 7.46 (4H, m, ArH), 7.00 (2H, d, $J = 9.0$, H-3', H-5'), 3.86 (3H, s, OCH₃); MS-CI (m/z): 271 (M⁺+1); Anal. (C₁₆H₁₁FO₃) C, H.

6-Fluoro-3-(3,4-dimethoxyphenyl)-4H-1-benzopyran-4-one (12h). Prepared (79%), from **8d** and 3,4-dimethoxyphenylboronic acid by General Method D, as a white solid, mp 152-154 °C; IR (KBr) 1651, 1609, 1589, 1576, 1524, 1447, 1453, 1414, 1378, 1326, 1293, 1271, 1231 cm⁻¹; δ_{H} (CDCl₃) 8.05 (1H, s, H-2), 7.96 (1H, dd, $J = 3.0, 8.5$, H-5), 7.47 (2H, m, H-7, H-8), 7.21 (1H, d, $J = 2.0$, H-2'), 7.08 (1H, dd, $J = 2.0, 8.3$, H-6'), 6.95 (1H, d, $J = 8.3$, H-5'), 3.95 (3H, s, OCH₃), 3.93 (3H, s, OCH₃); MS-CI (m/z): 301 (M⁺+1); Anal. (C₁₇H₁₃FO₄) C, H.

6-Fluoro-3-(3,4-methylenedioxyphenyl)-4H-1-benzopyran-4-one (12i). Prepared (36%), from **8d** and 3,4-methylenedioxyphenylboronic acid by General Method D, as a white solid, mp 221-223 °C; IR (KBr) 1638, 1625, 1609, 1578, 1496, 1483, 1440, 1380, 1334, 1284, 1258, 1237 cm⁻¹; δ_{H} (CDCl₃) 8.01 (1H, s, H-2), 7.96 (1H, dd, $J = 2.6, 8.3$, ArH), 7.46 (3H, m, ArH), 7.11 (1H, d, $J = 1.8$, H-2'), 6.99 (1H, dd, $J = 1.8, 8.0$, H-6'), 6.90 (1H, d, $J = 8.0$, H-5'), 6.01 (2H, s, CH₂); MS-EI (m/z): 284 (M⁺); Acc. Mass (EI+) m/z 284.0493 (calc. mass for C₁₆H₉FO₄ 284.0485).

7-Fluoro-3-(4-methoxyphenyl)-4H-1-benzopyran-4-one (12j). Prepared (96%), from **8c** and 4-methoxyphenylboronic acid by General Method D, as a white solid, mp 171-173 °C; IR (KBr) 1644, 1517, 1497, 1446, 1371, 1296, 1253 cm⁻¹; δ_{H} (CDCl₃) 8.34 (1H, m, H-5), 7.98 (1H, s, H-2), 7.51 (2H, d, $J = 7.5$, H-2', H-6'), 7.18 (2H, m, H-6, H-8), 7.00 (2H, d, $J = 7.5$, H-3', H-5'), 3.86 (3H, s, OCH₃); MS-CI (m/z): 271 (M⁺+1); Anal. (C₁₆H₁₁FO₃) C, H.

7-Fluoro-3-(3,4-dimethoxyphenyl)-4H-1-benzopyran-4-one (12k). Prepared (67%), from **8c** and 3,4-dimethoxyphenylboronic acid by General Method D, as a white solid, mp 165-167 °C; IR (KBr) 1642, 1616, 1518, 1465, 1441, 1413, 1383, 1359, 1320, 1253, 1207 cm⁻¹; δ_{H} (CDCl₃) 8.34 (1H, dd, $J = 6.5, 9.8$, ArH), 8.01 (1H, s, H-2), 7.18 (3H, m, ArH), 7.07 (1H, dd, $J = 2.0, 8.5$, ArH), 6.95 (1H, d, $J = 8.0$, H-5'), 3.94 (3H, s, OCH₃), 3.93 (3H, s, OCH₃); MS-CI (m/z): 301 (M⁺+1); Anal. (C₁₇H₁₃FO₄) C, H.

8-Fluoro-3-(3,4-dimethoxyphenyl)-4H-1-benzopyran-4-one (12l). Prepared (42%), from **8b** and 3,4-dimethoxyphenylboronic acid by General Method D, as a white solid, mp 146-148 °C; IR (KBr) 1645, 1622, 1608, 1582, 1575, 1521, 1488, 1456, 1439, 1412, 1377, 1355, 1331 cm⁻¹; δ_{H} (CDCl₃) 8.06 (2H, m, ArH and H-2), 7.41 (2H, m, ArH), 7.19 (1H, d, $J = 2.0$, H-2'), 7.06 (1H, dd, $J = 2.0, 8.3$, H-6'), 6.94 (1H, d, $J = 8.3$, H-5'), 3.93 (3H, s, OCH₃), 3.92 (3H, s, OCH₃); MS-EI (m/z): 300 (M⁺); Acc. Mass (EI+) m/z 300.0791 (calc. mass for C₁₇H₁₃FO₄ 300.0798).

6,7-Difluoro-3-(3,4-dimethoxyphenyl)-4H-1-benzopyran-4-one (12m). Prepared (27%), from **8g** and 3,4-dimethoxyphenylboronic acid by General Method D, as a white solid, mp 169-171 °C; IR (KBr) 1647, 1627, 1613, 1586, 1519, 1507, 1493, 1458, 1447, 1417, 1380, 1321, 1264, 1217, 1199 cm⁻¹; δ_{H} (CDCl₃) 8.06 (1H, m, ArH), 8.02 (1H, s, H-2), 7.31 (1H, m, ArH), 7.18 (1H, d, $J = 2.0$, H-2'), 7.06 (1H, dd, $J = 2.0, 8.3$, H-6'), 6.95 (1H, d, $J = 8.3$, H-5'), 3.94 (3H, s, OCH₃), 3.93 (3H, s, OCH₃); MS-CI (m/z): 319 (M⁺+1); Anal. (C₁₇H₁₂F₂O₄) C, H.

6,8-Difluoro-3-(3,4-dimethoxyphenyl)-4H-1-benzopyran-4-one (12n). Prepared (72%), from **8f** and 3,4-dimethoxyphenylboronic acid by General Method D, as a white solid, mp 178-180 °C; IR (KBr) 1657, 1631, 1580, 1523, 1477, 1446, 1412,

1385, 1336, 1299, 1268, 1219 cm^{-1} ; δ_{H} (CDCl_3) 8.07 (1H, s, H-2), 7.76 (1H, m, ArH), 7.27 (1H, m, ArH), 7.18 (1H, d, $J = 2.0$, H-2'), 7.07 (1H, dd, $J = 2.0$, 8.5, H-6'), 6.96 (1H, d, $J = 8.5$, H-5'), 3.94 (3H, s, OCH_3), 3.93 (3H, s, OCH_3); MS-CI (m/z): 319 ($\text{M}^+ + 1$); Anal. ($\text{C}_{17}\text{H}_{12}\text{F}_2\text{O}_4$) C, H.

7,8-Difluoro-3-(3,4-dimethoxyphenyl)-4H-1-benzopyran-4-one (12o). Prepared (52%), from **8e** and 3,4-dimethoxyphenylboronic acid by General Method D, as a white solid, mp 181-183 $^{\circ}\text{C}$; IR (KBr) 1614, 1589, 1576, 1518, 1468, 1459, 1451, 1377, 1356, 1318, 1295, 1274, 1255, 1226 cm^{-1} ; δ_{H} (CDCl_3 , ^{19}F decoupled) 8.08 (1H, d, $J = 9.1$, ArH), 8.06 (1H, s, H-2), 7.27 (1H, d, $J = 9.1$, ArH), 7.18 (1H, d, $J = 2.0$, H-2'), 7.07 (1H, dd, $J = 2.0$, 8.3, H-6'), 6.96 (1H, d, $J = 8.3$, H-5'), 3.94 (3H, s, OCH_3), 3.93 (3H, s, OCH_3); MS-CI (m/z): 319 ($\text{M}^+ + 1$); Anal. ($\text{C}_{17}\text{H}_{12}\text{F}_2\text{O}_4$) C, H.

6-Fluoro-3-(trimethylstannyl)-4H-1-benzopyran-4-one (13b). Prepared (90%), from **8d** by General Method E, as a white crystalline solid, mp 118-120 $^{\circ}\text{C}$; IR (KBr) 1619, 1598, 1564, 1553, 1474, 1449, 1377, 1311 cm^{-1} ; δ_{H} (CDCl_3) 7.78 (1H, m, ArH), 7.61 (1H, s, H-2), 7.40 (2H, m, ArH), 0.36 (9H, s, SnMe_3); MS-CI (m/z): 313 ($\text{M}^+ - \text{CH}_2$); Anal. ($\text{C}_{12}\text{H}_{13}\text{FO}_2\text{Sn}$) C, H.

7-Fluoro-3-(trimethylstannyl)-4H-1-benzopyran-4-one (13c). Prepared (80%), from **8c** by General Method E, as a white crystalline solid, mp 106-108 $^{\circ}\text{C}$; IR (KBr) 1618, 1559, 1492, 1441, 1375, 1304, 1264, 1229, 1158 cm^{-1} ; δ_{H} (CDCl_3) 8.16 (1H, m, ArH), 7.57 (1H, s, H-2), 7.10 (2H, m, ArH), 0.35 (9H, s, SnMe_3); MS-CI (m/z): 313 ($\text{M}^+ - \text{CH}_2$); Anal. ($\text{C}_{12}\text{H}_{13}\text{FO}_2\text{Sn}$) C, H.

6-Methoxy-3-(trimethylstannyl)-4H-1-benzopyran-4-one (13d). Prepared (73%), from **8i** by General Method E, as a white crystalline solid, mp 83-85 $^{\circ}\text{C}$; IR (KBr) 1607, 1588, 1572, 1557, 1483, 1445, 1372, 1331, 1318, 1268 cm^{-1} ; δ_{H} (CDCl_3) 7.52 (2H, m, ArH and H-2), 7.22 (2H, m, ArH), 3.80 (3H, s, OCH_3), 0.27 (9H, s, SnMe_3); MS-CI (m/z): 341 ($\text{M}^+ + 2$), 339 (M^+); Anal. ($\text{C}_{13}\text{H}_{16}\text{O}_3\text{Sn}$) C, H.

7-Methoxy-3-(trimethylstannyl)-4H-1-benzopyran-4-one (13e). Prepared (38%), from **8h** by General Method E, as a white crystalline solid, mp 87-89 $^{\circ}\text{C}$; IR (KBr) 1638, 1608, 1586, 1545, 1464, 1435, 1384, 1350, 1266, 1218 cm^{-1} ; δ_{H} (CDCl_3) 7.52 (2H, m, H-8 and H-2), 6.97 (1H, dd, $J = 1.0$, 8.0, H-6), 6.79 (1H, d, $J = 8.0$, H-5), 3.98 (3H, s, OCH_3), 0.32 (9H, s, SnMe_3); MS-CI (m/z): 341 ($\text{M}^+ + 2$), 339 (M^+); Anal. ($\text{C}_{13}\text{H}_{16}\text{O}_3\text{Sn}$) C, H.

6,7-Difluoro-3-(trimethylstannyl)-4H-1-benzopyran-4-one (13f). Prepared (77%), from **8g** by General Method E, as a white crystalline solid, mp 171-173 $^{\circ}\text{C}$; IR (KBr) 1635, 1617, 1561, 1495, 1451, 1380, 1289, 1197 cm^{-1} ; δ_{H} (CDCl_3) 7.92 (1H, m, ArH), 7.59 (1H, s, H-2), 7.27 (1H, m, ArH), 0.37 (9H, s, SnMe_3); MS-CI (m/z): 331 ($\text{M}^+ - \text{CH}_2$); Anal. ($\text{C}_{12}\text{H}_{12}\text{F}_2\text{O}_2\text{Sn}$) C, H.

7,8-Difluoro-3-(trimethylstannyl)-4H-1-benzopyran-4-one (13g). Prepared (66%), from **8e** by General Method E, as a white crystalline solid, mp 176-178 $^{\circ}\text{C}$; IR (KBr) 1642, 1630, 1560, 1512, 1455, 1380, 1329, 1279, 1222, 1209 cm^{-1} ; δ_{H} (CDCl_3) 7.90 (1H, m, ArH), 7.61 (1H, s, H-2), 7.20 (1H, m, ArH), 0.36 (9H, s, SnMe_3); MS-CI (m/z): 331 ($\text{M}^+ - \text{CH}_2$); Anal. ($\text{C}_{12}\text{H}_{12}\text{F}_2\text{O}_2\text{Sn}$) C, H.

6-Fluoro-3-(4-nitrophenyl)-4H-1-benzopyran-4-one (14b). Prepared (53%), from **13b** by General Method F, as an orange solid, mp 235-237 $^{\circ}\text{C}$; IR (KBr) 1640, 1601, 1516, 1479, 1350, 1273 cm^{-1} ; δ_{H} (CDCl_3) 8.33 (2H, d, $J = 8.5$, H-3', H-5'), 8.15 (1H, s, H-2), 7.97 (1H, m, ArH), 7.80 (2H, d, $J = 8.5$, H-2', H-6'), 7.51 (2H, m, ArH); MS-EI (m/z): 285 (M^+); Anal. ($\text{C}_{15}\text{H}_8\text{FNO}_4$) C, H, N.

7-Fluoro-3-(4-nitrophenyl)-4H-1-benzopyran-4-one (14c). Prepared (46%), from **13c** by General Method F, as an orange solid, mp 222-225 $^{\circ}\text{C}$; IR (KBr) 1665,

1624, 1598, 1516, 1442, 1347, 1250 cm^{-1} ; δ_{H} (CDCl_3) 8.35 (3H, m, ArH), 8.12 (1H, s, H-2), 7.79 (2H, d, $J = 9.0$, H-2', H-6'), 7.22 (2H, m, ArH); MS-EI (m/z): 285 (M^+); Anal. ($\text{C}_{15}\text{H}_8\text{FNO}_4$) C, H, N.

6-Methoxy-3-(4-nitrophenyl)-4H-1-benzopyran-4-one (14d).⁵ Prepared (26%), from **13d** by General Method F, as an orange solid, mp 229-231 $^{\circ}\text{C}$; δ_{H} (CDCl_3) 8.30 (2H, d, $J = 9.0$, H-3', H-5'), 8.11 (1H, s, H-2), 7.77 (2H, d, $J = 9.0$, H-2', H-6'), 7.67 (1H, m, ArH), 7.47 (1H, m, ArH), 7.36 (1H, m, ArH), 3.92 (3H, s, OCH_3); MS-CI (m/z): 298 ($\text{M}^+ + 1$).

7-Methoxy-3-(4-nitrophenyl)-4H-1-benzopyran-4-one (14e).⁶ Prepared (23%), from **13e** by General Method F, as an orange solid, mp 241-243 $^{\circ}\text{C}$; δ_{H} (CDCl_3) 8.27 (2H, d, $J = 9.0$, H-3', H-5'), 7.97 (1H, s, H-2), 7.77 (2H, d, $J = 9.0$, H-2', H-6'), 7.62 (1H, m, ArH), 7.08 (1H, m, ArH), 6.88 (1H, m, ArH), 4.00 (3H, s, OCH_3); MS-CI (m/z): 298 ($\text{M}^+ + 1$).

Attempted Synthesis of 6,7-Difluoro- (14f) and 7,8-Difluoro-3-(4-nitrophenyl)-4H-1-benzopyran-4-one (14g). Stille coupling between **13f** (0.25 g, 0.72 mmol) and 4-iodonitrobenzene (0.164 g, 0.66 mmol) according to Method E furnished 6,7-difluoro-4H-1-benzopyran-4-one (**15a**) (0.036 g, 0.20 mmol, 30%); δ_{H} (CDCl_3) 7.30 (1H, m, ArH), 7.20 (1H, d, $J = 10.0$, C=CH), 6.63 (1H, m, ArH), 6.36 (1H, d, $J = 10.0$, C=CH); MS-CI (m/z): 183 ($\text{M}^+ + 1$). Similarly prepared (0.18 mmol, 25%), from **13g** (0.25 g, 0.72 mmol) was 7,8-difluoro-4H-1-benzopyran-4-one (**15b**); δ_{H} (CDCl_3) 7.38 (1H, m, ArH), 7.19 (1H, d, $J = 10.0$, C=CH), 6.71 (1H, m, ArH), 6.35 (1H, d, $J = 10.0$, C=CH); MS-CI (m/z): 183 ($\text{M}^+ + 1$).

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Microanalytical Data for New Compounds

Compound	Formula	% Found (required)		
		Carbon	Hydrogen	Nitrogen
6e	C ₈ H ₆ F ₂ O ₂	56.0 (55.8)	3.6 (3.5)	-
7c	C ₁₁ H ₁₂ FNO ₂	63.2 (63.2)	5.7 (5.8)	6.5 (6.7)
7d	C ₁₁ H ₁₂ FNO ₂	63.3 (63.2)	5.7 (5.8)	6.6 (6.7)
7e	C ₁₁ H ₁₁ F ₂ NO ₂	58.2 (58.2)	4.7 (4.9)	6.0 (6.2)
8a	C ₉ H ₅ IO ₂	39.7 (39.7)	1.7 (1.9)	-
8b	C ₉ H ₄ FIO ₂	37.4 (37.3)	1.3 (1.4)	-
8c	C ₉ H ₄ FIO ₂	37.3 (37.3)	1.4 (1.4)	-
8d	C ₉ H ₄ FIO ₂	37.3 (37.3)	1.5 (1.4)	-
8e	C ₉ H ₃ F ₂ IO ₂	35.2 (35.1)	0.9 (1.0)	-
8f	C ₉ H ₃ F ₂ IO ₂	35.1 (35.1)	0.9 (1.0)	-
8g	C ₉ H ₃ F ₂ IO ₂	35.2 (35.1)	0.9 (1.0)	-
8h	C ₁₀ H ₇ IO ₃	39.5 (39.8)	2.3 (2.3)	-
8i	C ₁₀ H ₇ IO ₃	39.9 (39.8)	2.3 (2.3)	-
8j	C ₁₀ H ₇ IO ₃	39.7 (39.8)	2.2 (2.3)	-
12f	C ₁₇ H ₁₄ O ₄	71.9 (72.3)	5.0 (5.0)	-
12g	C ₁₆ H ₁₁ FO ₃	70.9 (71.1)	4.0 (4.1)	-
12h	C ₁₇ H ₁₃ FO ₄	67.8 (68.0)	4.4 (4.4)	-
12j	C ₁₆ H ₁₁ FO ₃	71.0 (71.1)	4.1 (4.1)	-
12k	C ₁₇ H ₁₃ FO ₄	67.7 (68.0)	4.4 (4.4)	-
12m	C ₁₇ H ₁₂ F ₂ O ₄	64.0 (64.2)	3.7 (3.8)	-
12n	C ₁₇ H ₁₂ F ₂ O ₄	63.8 (64.2)	3.8 (3.8)	-
12o	C ₁₇ H ₁₂ F ₂ O ₄	63.9 (64.2)	3.7 (3.8)	-
13a	C ₁₂ H ₁₄ O ₂ Sn	46.5 (46.7)	4.7 (4.6)	-
13b	C ₁₂ H ₁₃ FO ₂ Sn	44.3 (44.1)	3.9 (4.0)	-
13c	C ₁₂ H ₁₃ FO ₂ Sn	44.0 (44.1)	3.9 (4.0)	-
13d	C ₁₃ H ₁₆ O ₃ Sn	46.0 (46.1)	4.8 (4.8)	-
13e	C ₁₃ H ₁₆ O ₃ Sn	46.1 (46.1)	4.8 (4.8)	-
13f	C ₁₂ H ₁₂ F ₂ O ₂ Sn	41.7 (41.8)	3.5 (3.5)	-
13g	C ₁₂ H ₁₂ F ₂ O ₂ Sn	41.8 (41.8)	3.5 (3.5)	-
14b	C ₁₅ H ₈ FNO ₄	63.1 (63.2)	2.9 (2.8)	4.6 (4.9)
14c	C ₁₅ H ₈ FNO ₄	63.4 (63.2)	2.9 (2.8)	4.9 (4.9)
16a	C ₁₅ H ₁₁ NO ₂	76.0 (75.9)	4.9 (4.7)	5.6 (5.4)