Microwave assisted three-component coupling-addition-S_NAr (CASNAR) sequences to annelated 4*H*-thiopyran-4-ones

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Electronic Supplementary Information (ESI)

a) Experimental details for the synthesis of annelated 4*H*-thiochromen-4-ones 4, 7, 8, 9

General procedure for the synthesis of annelated 4*H*-thiochromen-4-ones 4, 7, 8, 9

In a 10 ml microwave-tube $PdCl_2(PPh_3)_2$ (15 mg, 0.02 mmol) and CuI (8 mg, 0.04 mmol) were dissolved in degassed THF (4 mL). Then, to this orange solution acid chloride **1** (1.25 mmol), alkyne **2** (1.00 mmol), and triethylamine (1.05 mmol) were added. The reaction mixture was stirred at room temp for 1 h. Finally, sodium sulfide nonahydrate (**3**) followed by ethanol (1 mL) were added to this suspension and the reaction mixture was heated at 90 °C in the microwave cavity for 90 min. After cooling to room temp, the solvent was removed under reduced pressure and the crude products were purified by silica gel flash column chromatography (hexane/ethyl acetate) to afford the analytically pure 4*H*-thiochromen-4-ones **4**, **7**, **8**, and **9** (for experimental details see Tables 7-9).

Table 1 One-pot three-component synthesis of 4*H*-thiochromen-4-ones **4**.

Entry	Aroyl chloride **1**	Alkyne **2**	$Na_2S \cdot 9\ H_2O$ (**3**)	Yield
1	198 mg (1.25 mmol) of **1a**	99 mg (1.00 mmol) of **2a**	360 mg (1.50 mmol)	63 mg (39%) of **4a**
2	198 mg (1.25 mmol) of **1a**	103 mg (1.00 mmol) of **2b**	360 mg (1.50 mmol)	149 mg (73%) of **4b**
3	198 mg (1.25 mmol) of **1a**	159 mg (1.00 mmol) of **2c**	360 mg (1.50 mmol)	219 mg (76%) of **4c**
4	198 mg (1.25 mmol) of **1a**	133 mg (1.00 mmol) of **2d**	360 mg (1.50 mmol)	206 mg (77%) of **4d**
5	198 mg (1.25 mmol) of **1a**	163 mg (1.00 mmol) of **2e**	360 mg (1.50 mmol)	218 mg (73%) of **4e**
6	198 mg (1.25 mmol) of **1a**	137 mg (1.00 mmol) of **2f**	360 mg (1.50 mmol)	141 mg (52%) of **4f**
7	198 mg (1.25 mmol) of **1a**	83 mg (1.00 mmol) of **2g**	360 mg (1.50 mmol)	129 mg (59%) of **4g**
8	198 mg (1.25 mmol) of **1a**	211 mg (1.00 mmol) of **2h**	360 mg (1.50 mmol)	218 mg (63%) of **4h**
9	198 mg (1.25 mmol) of **1a**	183 mg (1.00 mmol) of **2i**	360 mg (1.50 mmol)	162 mg (51%) of **4i**
10	262 mg (1.25 mmol) of **1c**	99 mg (1.00 mmol) of **2a**	360 mg (1.50 mmol)	68 mg (35%) of **4j**

11	262 mg (1.25 mmol) of **1c**	103 mg (1.00 mmol) of **2b**	360 mg (1.50 mmol)	165 mg (61%) of **4k**
12	262 mg (1.25 mmol) of **1c**	117 mg (1.00 mmol) of **2j**	360 mg (1.50 mmol)	136 mg (48%) of **4l**
13	262 mg (1.25 mmol) of **1c**	159 mg (1.00 mmol) of **2c**	360 mg (1.50 mmol)	136 mg (66%) of **4m**
14	262 mg (1.25 mmol) of **1c**	163 mg (1.00 mmol) of **2e**	360 mg (1.50 mmol)	193 mg (59%) of **4n**
15	262 mg (1.25 mmol) of **1c**	121 mg (1.00 mmol) of **2k**	360 mg (1.50 mmol)	135 mg (47%) of **4o**

4*H*-Thiochromen-4-one (4a)

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (d, ^{3}J = 10.5 Hz, 1 H), 7.53-7.56 (m, 1 H), 7.60-7.62 (m, 2 H), 7.82 (d, ^{3}J = 10.5 Hz, 1 H), 8.53-8.56 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 125.9 (CH), 126.7 (CH), 127.8 (CH), 128.7 (CH), 131.4 (CH), 133.3 (C_{quat}), 137.5 (C_{quat}), 137.8 (CH), 179.7 (C_{quat}). EI MS (R_f = 13.3 min, 70 eV, *m/z* (%)): 163 (10), 162 (M^+, 100), 136 (55), 134 (75), 108 (38), 89 (11), 82 (11), 69 (25), 67 (20), 63 (16), 58 (13), 50 (10). IR (KBr): $\tilde{\nu}$ = 1665 cm^{-1} (m), 1624 (s), 1586 (s), 1482 (w), 1437 (m), 1365 (m), 1295 (m), 1251 (m), 1157 (m), 1093 (w), 1041 (w), 957 (w), 824 (w), 793 (w), 755 (s), 714 (m), 599 (m), 557 (m). Anal. calcd. for C_9H_6OS (162.2): C 66.64, H 3.73; Found: C 66.54, H 3.96%.

2-Phenyl-4*H*-thiochromen-4-one (4b)

Yellow solid, mp. 116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (s, 1 H), 7.48-7.58 (m, 4 H), 7.62-7.71 (m, 4 H), 8.54-8.57 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.4 (CH), 126.5 (CH), 127.0 (2 CH), 127.8 (CH), 128.6 (CH), 129.3 (2 CH), 130.8 (CH), 130.9 (C_{quat}), 131.6 (CH), 136.6 (C_{quat}), 137.7 (C_{quat}), 153.1 (C_{quat}), 180.8 (C_{quat}). EI MS (R_f = 15.6 min, 70 eV, *m/z* (%)): 239 (18), 238 (M^+, 100), 211 (14), 210 (83), 165 (14), 136 (59), 108 (45), 105 (12), 92 (11), 82 (12), 69 (17). IR (KBr): $\tilde{\nu}$ = 2976 cm^{-1} (m), 1621 (s), 1589 (s), 1551 (m), 1490 (w), 1449 (w), 1435 (m), 1335 (s), 1241 (w), 1166 (w), 1133 (w), 1099 (s), 1050 (s), 880 (m), 864 (m), 799 (w), 761 (s), 733 (s), 697 (s), 666 (m), 583 (m). Anal. calcd. for $C_{20}H_{18}O_3S$ (338.4): C 75.60, H 4.23; Found: C 75.51, H 4.41%.

2-(4-^{t}Butylphenyl)-4*H*-thiochromen-4-one (4c)

Yellow solid, mp. 90 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (s, 9 H), 7.26 (s, 1 H), 7.52 (d, ^{3}J = 8.4 Hz, 2 H), 7.55-7.56 (m, 1 H), 7.59-7.68 (m, 4 H), 8.54-8.56 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.2 (3 CH_3), 34.9 (C_{quat}), 122.9 (CH), 126.3 (2 CH), 126.5 (CH), 126.6 (2 CH), 127.7 (CH), 128.6 (CH), 130.9 (C_{quat}), 131.5 (CH), 133.6 (C_{quat}), 137.7 (C_{quat}), 153.0 (C_{quat}), 154.5 (C_{quat}), 180.9 (C_{quat}). EI MS (R_f = 21.8 min, 70 eV, *m/z* (%)): 295 (11), 294 (M^+, 53), 280 (21), 279 (100), 251 (13), 140 (12), 137 (42), 126 (11), 115 (14), 111 (31), 109 (11), 108 (13). IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} (s), 2904 (w), 2868 (w), 1621 (s), 1544 (m), 1508 (m), 1461 (w), 1439 (s), 1406 (w), 1364 (w), 1333 (s), 1269 (m), 1201 (w), 1130 (m), 1102 (s), 1029 (m), 915 (w), 870 (w), 837 (s), 779 (s), 745 (s), 711 (m), 666 (m). Anal. calcd. for $C_{19}H_{18}OS \cdot 1/6\ CH_2Cl_2$ (294.4 + 14.2): C 74.60, H 5.99; Found: C 74.63, H 5.76%.

2-(4-Methoxyphenyl)-4*H*-thiochromen-4-one (4d)

Yellow solid, mp. 97 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 3 H), 7.01 (d, ^{3}J = 8.8 Hz, 2 H), 7.20 (s, 1 H), 7.54 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.3 Hz, 1 H), 7.61 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.3 Hz, 1 H), 7.64-7.67 (m, 3 H), 8.54 (dd, ^{3}J = 8.1 Hz, ^{4}J = 1.3 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5 (CH_3), 114.7 (2 CH), 122.2 (CH), 126.4 (CH), 127.6 (CH), 128.3 (2 CH), 128.5 (CH), 128.8 (C_{quat}), 130.9 (C_{quat}), 131.5 (CH), 137.6 (C_{quat}), 152.7 (C_{quat}), 161.9 (C_{quat}), 180.9 (C_{quat}). EI MS (R_f = 20.3 min, 70 eV, *m/z* (%)): 269 (19), 268 (M^+, 100), 267 (17), 240 (39), 225 (25), 197 (11), 136 (34), 132 (56), 120 (10), 117 (14), 108 (29), 89 (22), 69 (10), 63 (13). IR (KBr): $\tilde{\nu}$ = 1628 cm^{-1} (s), 1605 (s), 1551 (w), 1509 (s), 1438 (w), 1336 (m), 1311 (w), 1269 (s), 1246 (w), 1184 (m), 1130 (w), 1117 (w), 1103 (w), 1020 (m), 862 (w), 831 (s), 798 (m), 774 (m), 732 (m), 666 (w), 623 (w), 568 (w), 517 (m). Anal. calcd. for $C_{16}H_{12}O_2S$ (268.3): C 71.62, H 4.51; Found: C 71.66, H 4.21%.

2-(3,4-Dimethoxyphenyl)-4*H*-thiochromen-4-one (4e)

Yellow solid, mp. 126 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.94 (s, 3 H), 3.96 (s, 3 H), 6.96 (d, ^{3}J = 8.4 Hz, 1 H), 7.19 (d, ^{4}J = 2.2 Hz, 1 H), 7.22 (s, 1 H), 7.31 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.2 Hz, 1 H), 7.54 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.3 Hz, 1 H), 7.61 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 6.8 Hz, ^{4}J = 1.3 Hz, 1 H), 7.63-7.67 (m, 1 H), 8.53 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.2 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.05 (CH_3), 56.06 (CH_3), 109.6 (CH), 111.3 (CH), 120.0 (CH), 122.3 (CH), 126.4 (CH), 127.7 (CH), 128.5 (CH), 129.1 (C_{quat}), 130.9 (C_{quat}), 131.5 (CH), 137.6 (C_{quat}), 149.5 (C_{quat}), 151.4 (C_{quat}), 152.9 (C_{quat}), 180.9 (C_{quat}). EI MS (R_f = 31.7 min, 70 eV, *m/z* (%)): 299 (19), 298 (M^+, 100), 255 (13), 162 (25), 137 (13), 136 (13), 135 (16), 119 (10), 108 (16), 91 (19), 75 (11), 65 (11). IR (KBr): $\tilde{\nu}$ = 1589 cm^{-1} (s),

1544 (w), 1510 (s), 1467 (m), 1440 (m), 1418 (m), 1320 (s), 1268 (s), 1248 (s), 1169 (m), 1144 (m), 1100 (w), 1021 (m), 850 (m), 806 (m), 785 (m), 766 (m), 684 (w), 630 (w), 581 (m). Anal. calcd. for $C_{17}H_{14}O_3S$ (298.4): C 68.44, H 4.73; Found: C 68.46, H 5.57%.

2-(4-Chlorophenyl)-4*H*-thiochromen-4-one (4f)

Yellow solid, mp. 154 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (s, 1 H), 7.49 (d, ^3J = 8.6 Hz, 2 H), 7.56 (ddd, ^3J = 8.2 Hz, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1 H), 7.61-7.68 (m, 4 H), 8.54-8.55 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.6 (CH), 126.5 (CH), 127.9 (CH), 128.2 (2 CH), 128.7 (CH), 129.6 (2 CH), 130.8 (C_{quat}), 131.8 (CH), 135.0 (C_{quat}), 137.1 (C_{quat}), 137.3 (C_{quat}), 151.6 (C_{quat}), 180.7 (C_{quat}). EI MS (R_f = 18.2 min, 70 eV, *m/z* (%)): 274 (^{37}Cl-M^+, 32), 273 (16), 272 (^{35}Cl-M^+, 79), 271 (16), 246 (35), 245 (12), 244 (78), 165 (12), 163 (11), 137 (12), 136 (100), 122 (15), 108 (68), 104 (24), 82 (17), 76 (11), 75 (12), 69 (27), 63 (15), 58 (12). IR (KBr): $\tilde{\nu}$ = 3017 cm^{-1} (w), 1632 (s), 1591 (m), 1552 (w), 1487 (w), 1439 (w), 1400 (w), 1329 (m), 1129 (w), 1104 (w), 1090 (w), 1011 (w), 901 (w), 830 (m), 778 (m), 733 (m). Anal. calcd. for $C_{15}H_9ClOS$ (272.8): C 66.05, H 3.33; Found: C 65.86, H 3.09%.

2-Butyl-4*H*-thiochromen-4-one (4g)

Yellow solid, mp. 36 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (t, ^3J = 7.4 Hz, 3 H), 1.41 (s, ^3J = 7.3 Hz, 2 H), 1.70 (q, ^3J = 7.6 Hz, 2 H), 2.66 (t, ^3J = 7.7 Hz, 2 H), 6.85 (s, 1 H), 7.46-7.51 (m, 1 H), 7.53-7.56 (m, 2 H), 8.46-8.50 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.6 (CH_3), 21.9 (CH_2), 31.8 (CH_2), 37.1 (CH_2), 124.1 (CH), 126.1 (CH), 127.4 (CH), 128.5 (CH), 130.9 (C_{quat}), 131.2 (CH), 137.7 (C_{quat}), 156.4 (C_{quat}), 180.6 (C_{quat}). EI MS (R_f = 12.7 min, 70 eV, *m/z* (%)): 218 (M^+, 24), 177 (12), 176 (100), 147 (13), 137 (12), 136 (71), 108 (17). IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} (m), 2935 (m), 2871 (w), 1624 (s), 1588 (s), 1551 (m), 1461 (m), 1438 (m), 1381 (w), 1321 (m), 1236 (w), 1136 (w), 1099 (m), 1079 (w), 1026 (w), 931 (w), 859 (m), 799 (m), 771 (m), 745 (m), 685 (w), 649 (w), 551 (w). Anal. calcd. for $C_{13}H_{14}OS$ (218.3): C 71.52, H 6.46; found: C 71.30, H 6.39%.

2-Ferrocenyl-4*H*-thiochromen-4-one (4h)

Deep red solid, mp. 174 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.19 (s, 5 H), 4.52 (t, ^3J = 1.9 Hz, 2 H), 4.81 (t, ^3J = 1.9 Hz, 2 H), 7.12 (s, 1 H), 7.49-7.53 (m, 1 H), 7.58-7.60 (m, 2 H), 8.50 (dd, ^3J = 8.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 67.4 (2 CH), 70.8 (5 CH), 71.1 (2 CH), 80.0 (C_{quat}), 119.8 (CH), 126.1 (CH), 127.4 (CH), 128.5 (CH), 131.2 (C_{quat}), 131.3 (CH), 137.4 (C_{quat}), 154.8 (C_{quat}), 180.2 (C_{quat}). EI MS (70 eV, *m/z* (%)): 348 (24), 346 (M^+,

66), 165 (13), 121 (53), 56 (100), 45 (14), 43 (47). IR (KBr): $\tilde{\nu}$ = 1609 cm^{-1} (s), 1563 (m), 1543 (m), 1438 (w), 1347 (w), 1321 (m), 1264 (w), 1133 (w), 1052 (w), 879 (w), 818 (w), 785 (w), 734 (m), 602 (w), 503 (m). Anal. calcd. for $C_{19}H_{14}FeOS$ (346.2): C 65.91, H 4.08; found: C 65.64, H 4.04%.

2-(6-Methoxynaphthalen-2-yl)-4*H*-thiochromen-4-one (4i)

Yellow solid, mp. 147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.93 (s, 3 H), 7.13 (d, ^4J = 1.9 Hz, 1 H), 7.20 (dd, ^3J = 8.9 Hz, ^4J = 1.9 Hz, 1 H), 7.33 (s, 1 H), 7.53 (d, ^3J = 7.5 Hz, 1 H), 7.58-7.63 (m, 2 H), 7.69 (d, ^3J = 8.6 Hz, 1 H), 7.79 (dd, ^3J = 8.7 Hz, ^4J = 2.7 Hz, 2 H), 8.08 (s, 1 H), 8.54 (d, ^3J = 8.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4 (CH_3), 105.6 (CH), 120.0 (CH), 122.9 (CH), 124.1 (CH), 126.4 (CH), 126.7 (CH), 127.6 (CH), 127.9 (CH), 128.4 (C_{quat}), 128.5 (CH), 130.2 (CH), 130.9 (C_{quat}), 131.3 (C_{quat}), 131.5 (CH), 135.7 (C_{quat}), 137.6 (C_{quat}), 153.0 (C_{quat}), 159.0 (C_{quat}), 180.8 (C_{quat}). EI MS (R_f = 53.3 min, 70 eV, *m/z* (%)): 319 (18), 318 (M^+, 100), 290 (16), 278 (13), 275 (25), 247 (22), 217 (12), 207 (59), 182 (41), 168 (13), 165 (13), 164 (14), 147 (13), 146 (15), 145 (17), 139 (27), 136 (21), 135 (17), 127 (13), 124 (19), 76 (17), 64 (14), 53 (21). IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (w), 2959 (w), 1615 (s), 1592 (s), 1543 (m), 1503 (w), 1481 (m), 1458 (w), 1438 (m), 1395 (m), 1348 (w), 1324 (m), 1268 (m), 1232 (m), 1185 (m), 1121 (w), 1101 (w), 1029 (m), 915 (w), 887 (w), 853 (m), 816 (w), 779 (w), 779 (w), 737 (w), 656 (w), 600 (w), 523 (m). Anal. calcd. for $C_{20}H_{14}O_2S$ (318.4): C 75.45, H 4.43; found: C 75.17, H 4.45%.

7-Chloro-4*H*-thiochromen-4-one (4j)

Yellow solid, mp. 106 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (d, ^3J = 10.5 Hz, 1 H), 7.48 (dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz, 1 H), 7.60 (d, ^3J = 2.0 Hz, 1 H), 7.78 (d, ^4J = 10.5 Hz, 1 H), 8.46 (d, ^3J = 8.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 125.9 (CH), 126.1 (CH), 128.5 (CH), 130.3 (2 CH), 130.6 (C_{quat}), 137.4 (CH), 138.2 (C_{quat}), 138.8 (C_{quat}), 178.9 (C_{quat}). EI MS (R_f = 15.1 min, 70 eV, *m/z* (%)): 198 (^{37}Cl-M^+, 37), 197 (11), 196 (^{35}Cl-M^+, 100), 170 (79), 168 (79), 142 (25), 133 (13), 107 (21), 89 (17), 85 (13), 84 (28), 75 (13), 74 (12), 69 (23), 66 (13), 63 (32), 62 (11). IR (KBr): $\tilde{\nu}$ = 1626 cm^{-1} (s), 1589 (s), 1460 (w), 1390 (m), 1353 (w), 1309 (w), 1159 (w), 1137 (w), 1105 (w), 860 (w), 827 (w), 802 (m), 727 (w), 525 (w). Anal. calcd. for C_9H_5ClOS (196.7): C 54.97, H 2.56; found: C 54.96, H 2.67%.

7-Chloro-2-phenyl-4*H*-thiochromen-4-one (4k)

Yellow solid, mp. 120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (s, 1 H), 7.49-7.54 (m, 4 H), 7.66-7.69 (m, 3 H), 8.47 (d, ^{3}J = 8.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.5 (CH), 125.8 (CH), 126.9 (2 CH), 128.5 (CH), 129.3 (C_{quat}), 129.4 (2 CH), 130.2 (CH), 131.2 (CH), 136.2 (C_{quat}), 138.3 (C_{quat}), 139.0 (C_{quat}), 152.8 (C_{quat}), 180.0 (C_{quat}). EI MS (R_f = 23.2 min, 70 eV, *m/z* (%)): 274 (^{37}Cl-M^+, 38), 273 (20), 272 (^{35}Cl-M^+, 98), 271 (16), 246 (39), 245 (17), 244 (100), 208 (15), 172 (20), 170 (57), 165 (16), 144 (11), 142 (32), 123 (13), 122 (27), 107 (26), 104 (25), 75 (15), 69 (17), 63 (21). IR (KBr): $\tilde{\nu}$ = 1617 cm^{-1} (s), 1588 (s), 1491 (w), 1445 (w), 1390 (m), 1325 (m), 1253 (w), 1138 (w), 1105 (m), 895 (w), 859 (m), 824 (m), 771 (w), 751 (m), 735 (w), 691 (m), 667 (w), 611 (w), 579 (w), 552 (w). Anal. calcd. for $C_{15}H_9ClOS$ (272.8): C 66.05, H 3.33; found: C 65.96, H 3.40%.

7-Chloro-2-*p*-tolyl-4*H*-thiochromen-4-one (4l)

Yellow solid, mp. 133 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3 H), 7.20 (s, 1 H), 7.31 (d, ^{3}J = 8.1 Hz, 2 H), 7.49 (dd, ^{3}J = 8.7 Hz, ^{4}J = 1.9 Hz, 1 H), 7.57 (d, ^{3}J = 8.1 Hz, 2 H), 7.65 (d, ^{4}J = 1.9 Hz, 1 H), 8.46 (d, ^{3}J = 8.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.4 (CH_3), 123.0 (CH), 125.7 (CH), 126.8 (2 CH), 128.4 (CH), 129.3 (C_{quat}), 130.0 (2 CH), 130.2 (CH), 133.3 (C_{quat}), 138.2 (C_{quat}), 139.1 (C_{quat}), 141.6 (C_{quat}), 151.9 (C_{quat}), 180.1 (C_{quat}). EI MS (R_f = 25.6 min, 70 eV, *m/z* (%)): 288 (^{37}Cl-M^+, 40), 287 (24), 286 (^{35}Cl-M^+, 100), 285 (16), 260 (35), 259 (19), 258 (94), 257 (14), 223 (11), 221 (16), 172 (18), 170 (54), 142 (30), 129 (17), 116 (23), 115 (53), 112 (11), 111 (35), 107 (20), 89 (15), 69 (12), 63 (22). IR (KBr): $\tilde{\nu}$ = 1637 cm^{-1} (s), 1588 (s), 1561 (w), 1543 (w), 1509 (w), 1459 (w), 1384 (m), 1323 (s), 1308 (w), 1190 (w), 1144 (w), 1109 (w), 866 (w), 833 (m), 810 (s), 753 (w), 837 (w), 535 (w). Anal. calcd. for $C_{16}H_{11}ClOS$ (286.8): C 67.01, H 3.87; found: C 66.97, H 3.70%.

2-(4-^{t}Butylphenyl)-7-chloro-4*H*-thiochromen-4-one (4m)

Yellow solid, mp. 119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (s, 9 H), 7.23 (s, 1 H), 7.48 (dd, ^{3}J = 8.7 Hz, ^{4}J = 2.0 Hz, 1 H), 7.52 (d, ^{3}J = 8.5 Hz, 2 H), 7.62 (d, ^{3}J = 8.5 Hz, 2 H), 7.65 (d, ^{3}J = 2.0 Hz, 1 H), 8.46 (d, ^{3}J = 8.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.1 (3 CH_3), 34.9 (C_{quat}), 122.9 (CH), 125.7 (CH), 126.4 (2 CH), 126.6 (2 CH), 128.3 (CH), 129.3 (C_{quat}), 130.1 (CH), 133.2 (C_{quat}), 138.2 (C_{quat}), 139.1 (C_{quat}), 152.8 (C_{quat}), 154.7 (C_{quat}), 180.0 (C_{quat}). EI MS (R_f = 26.2 min, 70 eV, *m/z* (%)): 330 (^{37}Cl-$M^{+\cdot}$, 18), 328 (^{35}Cl-M^+, 45), 315 (38), 314 (19), 313 (100), 285 (10), 173 (11), 171 (31), 143 (14), 130 (15), 129 (37), 115 (18). IR (KBr): $\tilde{\nu}$ = 2967 cm^{-1} (m), 1612 (s), 1584 (s), 1537 (w), 1509 (w), 1460 (w), 1408 (w),

1385 (m), 1326 (m), 1313 (m), 1266 (w), 1203 (w), 1106 (m), 1052 (w), 881 (w), 830 (m), 756 (w), 715 (w), 687 (w), 659 (w), 631 (w), 591 (w), 535 (w). Anal. calcd. for $C_{19}H_{17}ClOS$ (290.7): C 61.97, H 2.77; found: C 62.20, H 2.68%.

7-Chloro-2-(3,4-dimethoxyphenyl)-4*H*-thiochromen-4-one (4n)

Yellow solid, mp. 202 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.95 (s, 3 H), 3.96 (s, 3 H), 6.97 (d, ^3J = 8.4 Hz, 1 H), 7.12 (d, ^4J = 1.8 Hz, 1 H), 7.19 (s, 1 H), 7.30 (dd, ^3J = 8.4 Hz, ^4J = 1.9 Hz, 1 H), 7.49 (dd, ^3J = 8.7 Hz, ^4J = 1.6 Hz, 1 H), 7.65 (d, ^4J = 1.6 Hz, 1 H), 8.46 (d, ^3J = 8.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.1 (2 CH_3), 109.5 (CH), 111.4 (CH), 120.0 (CH), 122.4 (CH), 125.7 (CH), 128.4 (CH), 128.7 (C_{quat}), 129.3 (C_{quat}), 130.2 (CH), 138.3 (C_{quat}), 139.0 (C_{quat}), 149.6 (C_{quat}), 151.6 (C_{quat}), 152.7 (C_{quat}), 180.1 (C_{quat}). EI MS (70 eV, *m/z* (%)): 335 (12), 334 (^{37}Cl-M$^+$, 21), 333 (52), 332 (^{35}Cl-M$^+$, 75), 226 (17), 218 (13), 173 (20), 172 (21), 171 (47), 170 (35), 162 (90), 147 (40), 144 (13), 142 (31), 119 (51), 110 (14), 108 (13), 107 (24), 101 (11), 91 (100), 89 (28), 77 (11), 76 (54), 69 (31), 65 (77), 63 (43), 55 (21), 53 (21), 51 (20), 50 (23), 45 (31), 44 (11), 43 (55), 41 (15), 39 (23). IR (KBr): $\tilde{\nu}$ = 1627 cm^{-1} (s), 1587 (s), 1520 (s), 1469 (w), 1444 (w), 1412 (w), 1383 (w), 1340 (m), 1315 (w), 1276 (s), 1233 (w), 1179 (m), 1147 (m), 1109 (w), 1046 (w), 1023 (m), 848 (m), 829 (w), 804 (w), 774 (w), 743 (w), 628 (w), 552 (w). Anal. calcd. for $C_{17}H_{13}ClO_3S \cdot 1/3\ C_4H_8O_2$ (328.9): C 69.39, H 5.21; found: C 69.41, H 5.32%.

7-Chloro-2-(4-fluorophenyl)-4*H*-thiochromen-4-one (4o)

Yellow solid, mp. 144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (s, 1 H), 7.21 (t, ^3J = 8.5 Hz, 2 H), 7.50 (dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz, 1 H), 7.65-7.68 (m, 3 H), 8.47 (d, ^3J = 8.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.0 (d, $^2J_{FC}$ = 22.1 Hz, 2 CH), 123.6 (CH), 125.8 (CH), 128.6 (CH), 128.9 (d, $^3J_{FC}$ = 8.7 Hz, 2 CH), 129.2 (C_{quat}), 130.3 (CH), 132.7 (d, $^4J_{FC}$ = 3.3 Hz, C_{quat}), 138.5 (C_{quat}), 138.8 (C_{quat}), 151.5 (C_{quat}), 164.4 (d, $^1J_{FC}$ = 253.1 Hz, C_{quat}), 179.9 (C_{quat}). EI MS (R_f = 17.0 min, 70 eV, *m/z* (%)): 292 (^{37}Cl-M$^+$, 35), 291 (21), 290 (^{35}Cl-M$^+$, 91), 289 (12), 264 (36), 263 (16), 262 (100), 226 (13), 183 (17), 172 (27), 170 (71), 144 (17), 142 (34), 132 (16), 131 (37), 120 (12), 113 (20), 107 (35), 75 (11), 69 (19), 63 (23). IR (KBr): $\tilde{\nu}$ = 1619 cm^{-1} (s), 1588 (m), 1506 (m), 1459 (w), 1390 (w), 1325 (w), 1243 (m), 1163 (w), 1140 (w), 1106 (m), 823 (m), 757 (w), 638 (w), 535 (w), 503 (w). Anal. calcd. for $C_{15}H_8ClFOS$ (290.7): C 61.97, H 2.77; found: C 62.20, H 2.68%.

Table 2 One-pot three-component synthesis of 4*H*-thiopyrano[2,3-b]pyridin-4-ones **7**.

Entry	Aroyl chloride **1**	Alkyne **2**	$Na_2S \cdot 9\ H_2O$ (**3**)	Yield
1	220 mg (1.25 mmol) of **1d**	99 mg (1.00 mmol) of **2a**	360 mg (1.50 mmol)	101 mg (62%) of **7a**
2	220 mg (1.25 mmol) of **1d**	103 mg (1.00 mmol) of **2b**	360 mg (1.50 mmol)	132 mg (55%) of **7b**
3	220 mg (1.25 mmol) of **1d**	117 mg (1.00 mmol) of **2j**	360 mg (1.50 mmol)	58 mg (23%) of **7c**
4	220 mg (1.25 mmol) of **1d**	159 mg (1.00 mmol) of **2j**	360 mg (1.50 mmol)	45 mg (15%) of **7d**
5	220 mg (1.25 mmol) of **1d**	137 mg (1.00 mmol) of **2f**	360 mg (1.50 mmol)	85 mg (31%) of **7e**
6	220 mg (1.25 mmol) of **1d**	211 mg (1.00 mmol) of **2h**	360 mg (1.50 mmol)	67 mg (19%) of **7f**
7	220 mg (1.25 mmol) of **1d**	83 mg (1.00 mmol) of **2g**	360 mg (1.50 mmol)	36 mg (17%) of **7g**
8	220 mg (1.25 mmol) of **1d**	67 mg (1.00 mmol) of **2l**	360 mg (1.50 mmol)	107 mg (53%) of **7h**

4*H*-Thiopyrano[2,3-b]pyridin-4-one (7a)

Yellow solid, mp. 135 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04 (d, ^3J = 10.6 Hz, 1 H), 7.50 (dd, ^3J = 8.1 Hz, ^3J = 4.5 Hz, 1 H), 7.93 (d, ^3J = 10.6 Hz, 1 H), 8.77 (dd, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 1 H), 8.80 (dd, ^3J = 4.5 Hz, ^4J = 1.8 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.0 (CH), 126.1 (CH), 129.7 (C_{quat}), 136.9 (CH), 139.5 (CH), 152.7 (CH), 158.8 (C_{quat}), 180.6 (C_{quat}). EI MS (70 eV, *m/z* (%)): 164 (11), 163 (M^+, 100), 137 (18), 135 (28), 109 (11). IR (KBr): $\tilde{\nu}$ = 1625 cm^{-1} (s), 1579 (m), 1509 (w), 1450 (w), 1398 (s), 1366 (m), 1305 (w), 1265 (w), 1157 (w), 1072 (w), 842 (w), 791 (m), 717 (w), 670 (w). Anal. calcd. for C_8H_5NOS (163.2): C 58.88, H 3.09, N 8.58; found: C 58.81, H 3.18, N 8.45%.

2-Phenyl-4*H*-thiopyrano[2,3-b]pyridin-4-one (7b)

Yellow solid, mp. 110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (s, 1 H), 7.42-7.48 (m, 4 H), 7.63-7.65 (m, 2 H), 8.70 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1 H), 8.75 (d, ^3J = 3.2 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 122.9 (CH), 123.6 (CH), 127.0 (2 CH), 128.1 (C_{quat}),129.4

(2 CH), 131.1 (CH), 136.3 (C_{quat}), 136.7 (CH), 152.8 (CH), 154.8 (C_{quat}), 159.1 (C_{quat}), 181.3 (C_{quat}). EI MS (R_f = 15.4 min, 70 eV, *m/z* (%)): 240 (18), 239 (M^+, 100), 238 (20), 211 (65), 210 (19), 137 (15), 109 (28), 105 (13), 102 (15), 84 (14), 82 (17), 51 (13). IR (KBr): $\tilde{\nu}$ = 1636 cm^{-1} (s), 1579 (s), 1544 (w), 1450 (w), 1401 (m), 1339 (m), 1130 (w), 877 (w), 818 (w), 758 (m), 688 (m). Anal. calcd. for $C_{14}H_9NOS \cdot 1/3\ H_2O$ (239.3 + 6.0): C 68.55, H 3.97, N 5.71; found: C 68.21, H 3.77, N 5.52%.

2-*p*-Tolyl-4*H*-thiopyrano[2,3-b]pyridin-4-one (7c)

Yellow solid, mp. 142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.45 (s, 3 H), 7.27 (s, 1 H), 7.34 (d, ^3J = 7.9 Hz, 2 H), 7.51 (dd, ^3J = 8.7 Hz, ^4J = 4.5 Hz, 1 H), 7.62 (d, ^3J = 8.2 Hz, 2 H), 8.77 (dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz, 1 H), 8.79 (dd, ^3J = 4.5 Hz, ^4J = 1.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.4 (CH_3), 122.85 (CH), 122.92 (CH), 126.8 (2 CH), 128.1 (C_{quat}), 130.1 (2 CH), 133.4 (C_{quat}), 136.7 (CH), 141.8 (C_{quat}), 152.7 (CH), 156.0 (C_{quat}), 160.8 (C_{quat}), 181.4 (C_{quat}). EI MS (R_f = 16.8 min, 70 eV, *m/z* (%)): 253 (M^+, 100), 252 (17), 225 (60), 224 (23), 116 (20), 115 (42), 112 (11), 109 (17), 99 (10), 82 (11). IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1} (w), 1621 (s), 1577 (s), 1507 (w), 1451 (w), 1402 (s), 1336 (s), 1268 (w), 1236 (w), 1220 (w), 1190 (w), 1131 (m), 1080 (w), 1042 (w), 910 (w), 869 (w), 814 (s), 754 (w), 736 (w), 687 (w), 638 (w), 581 (w), 552 (w). Anal. calcd. for $C_{15}H_{11}NOS$ (253.3): C 71.11, H 4.38, N 5.53; found: C 70.79, H 4.47, N 5.42%.

2-(4-^{t}Butylphenyl)-4*H*-thiopyrano[2,3-b]pyridin-4-one (7d)

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (s, 9 H), 7.26 (s, 1 H), 7.49 (dd, ^3J = 8.0 Hz, ^3J = 4.5 Hz, 1 H), 7.54 (d, ^3J = 8.6 Hz, 2 H), 7.66 (d, ^3J = 8.6 Hz, 2 H), 8.76 (dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz, 1 H), 8.80 (dd, ^3J = 4.5 Hz, ^4J = 1.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.1 (3 CH), 34.9 (C_{quat}), 122.8 (CH), 122.9 (CH), 126.4 (2 CH), 126.7 (2 CH), 128.1 (C_{quat}), 133.3 (C_{quat}), 136.7 (CH), 152.7 (CH), 154.7 (C_{quat}), 154.8 (C_{quat}), 159.1 (C_{quat}), 181.4 (C_{quat}). EI MS (R_f = 21.2 min, 70 eV, *m/z* (%)): 295 (M^+, 39), 281 (19), 280 (100), 252 (16), 140 (10), 138 (37), 115 (18), 112 (35), 110 (12). IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} (m), 2866 (m), 1618 (s), 1584 (s), 1543 (w), 1509 (m), 1460 (m), 1402 (m), 1348 (m), 1268 (m), 1204 (w), 1135 (m), 1110 (m), 865 (w), 832 (m), 809 (m), 751 (m), 683 (w), 586 (w), 529 (w). Anal. calcd. for $C_{18}H_{17}NOS \cdot 1/3\ CHCl_3$ (295.4 + 39.8): C 65.69, H 5.21, N 4.18; found: C 65.43, H 5.25, N 3.78%.

2-(4-Chlorophenyl)-4*H*-thiopyrano[2,3-b]pyridin-4-one (7e)

Yellow solid, mp. 197 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (s, 1 H), 7.49-7.52 (m, 3 H), 7.64 (d, ^{3}J = 8.5 Hz, 2 H), 8.75 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.7 Hz, 1 H), 8.80 (dd, ^{3}J = 4.1 Hz, ^{4}J = 1.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.1 (CH), 123.6 (CH), 128.0 (C_{quat}), 128.2 (2 CH), 129.7 (2 CH), 134.7 (C_{quat}), 136.8 (CH), 137.5 (C_{quat}), 152.9 (CH), 153.3 (C_{quat}), 158.7 (C_{quat}), 181.2 (C_{quat}). EI MS (R_f = 17.8 min, 70 eV, *m/z* (%)): 275 (^{37}Cl-M^+, 46), 274 (23), 273 (^{35}Cl-M^+, 100), 247 (27), 246 (16), 245 (64), 244 (11), 210 (13), 209 (13), 207 (16), 139 (10), 137 (31), 136 (20), 123 (11), 109 (47), 105 (20), 101 (11), 91 (15), 83 (16), 82 (32), 77 (14), 75 (17), 51 (13). IR (KBr): $\tilde{\nu}$ = 1631 cm^{-1} (s), 1581 (s), 1489 (m), 1452 (w), 1402 (s), 1336 (m), 1272 (w), 1240 (m), 1218 (w), 1130 (w), 1095 (w), 1012 (w), 913 (w), 882 (w), 830 (m), 809 (m), 747 (m), 714 (w), 679 (w), 632 (w), 579 (w), 505 (w). Anal. calcd. for $C_{14}H_8ClNOS$ (273.7): C 61.43, H 2.95, N 5.12; found: C 61.22, H 3.08, N 4.89%.

2-Ferrocenyl-4*H*-thiopyrano[2,3-b]pyridin-4-one (7f)

Red solid, mp. 100 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.21 (s, 5 H), 4.56-4.57 (m, 2 H), 4.82-4.83 (m, 2 H), 7.11 (s, 1 H), 7.45 (dd, ^{3}J = 8.0 Hz, ^{4}J = 4.5 Hz, 1 H), 8.70 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.6 Hz, 1 H), 8.75 (dd, ^{3}J = 4.5 Hz, ^{4}J = 1.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 67.5 (2 CH), 70.9 (5 CH), 71.5 (2 CH), 79.5 (C_{quat}), 119.5 (CH), 122.6 (CH), 128.4 (C_{quat}), 136.5 (CH), 152.4 (CH), 156.8 (C_{quat}), 158.8 (C_{quat}), 180.5 (C_{quat}). EI MS (70 eV, *m/z* (%)): 348 (24), 347 (M^+, 100), 71 (9), 43 (47). IR (KBr): 1617 cm^{-1} (s), 1566 (s), 1543 (s), 1446 (w), 1397 (m), 1345 (m), 1320 (m), 1258 (m), 1131 (m), 1105 (w), 1035 (w), 815 (m), 749 (w), 727 (w), 678 (w). Anal. calcd. for $C_{22}H_{15}NOS_2 \cdot 1/7\ CH_2Cl_2$ (347.2 + 12.1): C 60.64, H 3.73, N 3.60; found: C 60.86, H 3.95, N 3.39%.

2-Butyl-4*H*-thiopyrano[2,3-b]pyridin-4-one (7g)

Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 (t, ^{3}J = 7.4 Hz, 3 H), 1.43 (s, ^{3}J = 7.4 Hz, 2 H), 1.74 (q, ^{3}J = 7.6 Hz, 2 H), 2.72 (t, ^{3}J = 7.7 Hz, 2 H), 6.88 (s, 1 H), 7.45 (dd, ^{3}J = 8.1 Hz, ^{3}J = 4.5 Hz, 1 H), 8.71 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.9 Hz, 1 H), 8.75 (dd, ^{3}J = 4.5 Hz, ^{4}J = 1.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.7 (CH_3), 22.0 (CH_2), 31.7 (CH_2), 37.3 (CH_2), 122.6 (CH), 124.2 (CH), 128.0 (C_{quat}), 136.7 (CH), 152.4 (CH), 158.4 (C_{quat}), 159.0 (C_{quat}), 181.1 (C_{quat}). EI MS (R_f = 17.5 min, 70 eV, *m/z* (%)): 219 (M^+, 17), 178 (11), 177 (100), 149 (40), 148 (11), 137 (21). IR (Film): $\tilde{\nu}$ = 2958 cm^{-1} (s), 2932 (s), 2872 (s), 1634 (s), 1582 (s), 1449 (m), 1398 (s), 1337 (s), 1269 (m), 1222 (w), 1140 (m), 1127 (m), 1068 (w), 1040 (w), 863

(m), 817 (m), 754 (m), 687 (m), 648 (w), 586 (w), 517 (w). Anal. calcd. for $C_{12}H_{13}NOS$ (219.3): C 65.72, H 5.97, N 6.39; found: C 65.54, H 6.03, N 6.28%.

2-Cyclopropyl-4*H*-thiopyrano[2,3-b]pyridin-4-one (7h)

Yellow solid, mp. 91 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.06-1.09 (m, 2 H), 1.17-1.21 (m, 2 H), 1.98-2.03 (m, 1 H), 6.78 (s, 1 H), 7.43 (dd, ^3J = 8.1 Hz, ^4J = 4.5 Hz, 1 H), 8.68 (dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz, 1 H), 8.73 (dd, ^3J = 4.5 Hz, ^4J = 1.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.6 (2 CH_2), 18.0 (CH), 121.0 (CH), 122.6 (CH), 128.3 (C_{quat}), 136.6 (CH), 152.4 (CH), 158.6 (C_{quat}), 160.9 (C_{quat}), 180.8 (C_{quat}). EI MS (R_f = 12.5 min, 70 eV, *m/z* (%)): 204 (14), 203 (M^+, 100), 202 (27), 188 (13), 175 (15), 174 (57), 173 (11), 170 (21), 148 (22), 138 (17), 137 (16), 110 (11), 109 (29), 83 (14), 82 (19), 77 (14), 75 (14), 69 (12), 65 (10), 51 (11). IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1} (s), 1617 (s), 1581 (m), 1430 (m), 1400 (s), 1332 (m), 1090 (s), 1049 (s), 881 (m), 811 (w), 755 (w), 685 (w). Anal. calcd. for $C_{11}H_9NOS$ (203.3): C 65.00, H 4.46, N 6.89; found: C 64.72, H 4.46, N 6.73%.

Table 3 One-pot three-component synthesis of 2-chloro-4*H*-thieno[2,3-b]thiopyran-4-ones **8** and 7*H*-benzo-[b]thieno[3,2-b]thiopyran-7-ones **9**.

Entry	Aroyl chloride **1**	Alkyne **2**	$Na_2S \cdot 9\ H_2O$ (**3**)	Yield
1	202 mg (0.94 mmol) of **1e**	77 mg (0.75 mmol) of **2b**	260 mg (1.13 mmol)	82 mg (40%) of **8a**
2	202 mg (0.94 mmol) of **1e**	119 mg (0.75 mmol) of **2c**	260 mg (1.13 mmol)	158 mg (63%) of **8b**
3	202 mg (0.94 mmol) of **1e**	122 mg (0.75 mmol) of **2e**	260 mg (1.13 mmol)	128 mg (51%) of **8c**
4	202 mg (0.94 mmol) of **1e**	62 mg (0.75 mmol) of **2g**	260 mg (1.13 mmol)	70 mg (36%) of **8d**
5	217 mg (0.94 mmol) of **1f**	77 mg (0.75 mmol) of **2b**	260 mg (1.13 mmol)	102 mg (46%) of **9a**
6	217 mg (0.94 mmol) of **1f**	119 mg (0.75 mmol) of **2c**	260 mg (1.13 mmol)	108 mg (41%) of **9b**
7	217 mg (0.94 mmol) of **1f**	122 mg (0.75 mmol) of **2k**	260 mg (1.13 mmol)	63 mg (27%) of **9c**
8	217 mg (0.94 mmol) of **1f**	62 mg (0.75 mmol) of **2l**	260 mg (1.13 mmol)	62 mg (32%) of **9d**

2-Chloro-6-phenyl-4*H*-thieno[2,3-b]thiopyran-4-one (8a)

Brown solid, mp. 167 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (s, 1 H), 7.49-7.54 (m, 3 H), 7.59-7.62 (m, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.2 (CH), 125.0 (CH), 127.0 (2 CH), 129.4 (2 CH), 131.0 (CH), 131.2 (C_{quat}), 135.9 (CH), 137.2 (CH), 142.6 (C_{quat}), 151.6 (C_{quat}), 175.7 (C_{quat}). EI MS (R_f = 17.3 min, 70 eV, *m/z* (%)): 280 (^{37}Cl-M^+, 41), 279 (31), 278 (^{35}Cl-M^+, 96), 277 (44), 250 (27), 207 (11), 178 (55), 176 (100), 150 (16), 148 (39), 125 (14), 113 (12), 102 (17), 77 (11), 76 (13), 69 (64), 51 (11). IR (KBr): $\tilde{\nu}$ = 1610 cm^{-1} (s), 1508 (w), 1489 (w), 1426 (s), 1405 (m), 1290 (w), 1259 (w), 1241 (m), 1162 (w), 1058 (w), 1003 (w), 901 (w), 868 (w), 855 (m), 773 (m), 726 (w), 696 (m), 677 (w), 613 (w), 577 (w), 524 (w). Anal. calcd. for $C_{13}H_7ClOS_2$ (278.8): C 56.01, H 2.53; found: C 56.06, H 2.81%.

6-(4-^{t}Butylphenyl)-2-chloro-4*H*-thieno[2,3-b]thiopyran-4-one (8b)

Brown solid, mp. 157 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (s, 9 H), 7.16 (s, 1 H), 7.51 (d, ^{3}J = 8.8 Hz, 2 H), 7.55 (d, ^{3}J = 8.8 Hz, 2 H), 7.57 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.1 (3 CH_3), 34.9 (C_{quat}), 124.1 (CH), 124.4 (CH), 126.4 (2 CH), 126.6 (2 CH), 131.0 (C_{quat}), 133.0 (C_{quat}), 137.2 (C_{quat}), 142.6 (C_{quat}), 151.5 (C_{quat}), 154.6 (C_{quat}), 175.7 (C_{quat}). EI MS (R_f = 32.0 min, 70 eV, *m/z* (%)): 336 (^{37}Cl-M^+, 32), 335 (12), 334 (^{35}Cl-M^+, 62), 321 (40), 320 (19), 319 (100), 290 (11), 263 (16), 207 (11), 179 (13), 178 (13), 177 (25), 176 (20), 148 (18), 147 (15), 146 (27), 128 (15), 127 (11), 115 (27), 69 (19). IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} (w), 1607 (s), 1508 (w), 1436 (w), 1414 (w), 1361 (w), 1271 (w), 1240 (w), 1114 (w), 1001 (w), 902 (w), 879 (w), 849 (w), 822 (w), 714 (w), 663 (w), 587 (w), 522 (w). Anal. calcd. for $C_{17}H_{15}ClOS_2$ (334.9): C 60.97, H 4.51; found: C 60.80, H 4.60%.

2-Chloro-6-(3,4-dimethoxyphenyl)-4*H*-thieno[2,3-b]thiopyran-4-one (8c)

Brown solid, mp. 148 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.94 (s, 3 H), 3.95 (s, 3 H), 6.95 (d, ^{3}J = 8.4 Hz, 1 H), 7.10 (d, ^{3}J = 2.0 Hz, 1 H), 7.15 (s, 1 H), 7.21 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.0 Hz, 1 H), 7.58 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.1 (2 CH), 109.6 (CH), 111.4 (CH), 120.0 (CH), 123.9 (CH), 124.2 (CH), 128.5 (C_{quat}), 131.0 (C_{quat}), 137.2 (CH), 142.5 (CH), 149.6 (C_{quat}), 151.49 (C_{quat}), 151.54 (C_{quat}), 175.8 (C_{quat}). EI MS (R_f = 30.5 min, 70 eV, *m/z* (%)): 341 (11), 340 (^{37}Cl-M^+, 36), 339 (18), 338 (^{35}Cl-M^+, 100), 337 (22), 307 (14), 232 (12), 163 (11), 162 (85), 155 (12), 148 (19), 147 (30), 176 (20), 119 (11), 101 (12), 91 (38), 89 (13), 76 (14), 69 (24), 65 (14), 63 (14). IR (KBr): $\tilde{\nu}$ = 1611 cm^{-1} (s), 1518 (s), 1437 (m), 1418 (w), 1336 (w), 1271 (s), 1236 (m), 1171 (w), 1147 (m), 1023 (m), 903 (w), 857 (w), 797 (w),

768 (w), 727 (w), 700 (w), 596 (w), 519 (w). Anal. calcd. for $C_{15}H_{11}ClO_3S_2$ (338.83): C 53.17, H 3.27; found: C 53.20, H 3.45%.

6-Butyl-2-chloro-4*H*-thieno[2,3-b]thiopyran-4-one (8d)

Brown solid, mp. 38 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (t, ^3J = 7.4 Hz, 3 H), 1.40 (se, ^3J = 7.4 Hz, 2 H), 1.69 (q, ^3J = 7.6 Hz, 2 H), 2.69 (t, ^3J = 7.6 Hz, 2 H), 6.81 (s, 1 H), 7.53 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.6 (CH_3), 21.9 (CH_2), 32.1 (CH_2), 36.8 (CH_2), 124.1 (CH), 152.4 (CH), 130.7 (C_{quat}), 137.2 (C_{quat}), 142.2 (C_{quat}), 154.2 (C_{quat}), 175.7 (C_{quat}). EI MS (R_f = 19.1 min, 70 eV, *m/z* (%)): 260 (^{37}Cl-M^+, 27), 259 (10), 258 (^{35}Cl-M^+, 61), 218 (43), 217 (12), 216 (100), 188 (17), 187 (11), 178 (27), 177 (13), 176 (61), 148 (22), 69 (40). IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} (m), 2868 (w), 1612 (s), 1509 (w), 1459 (w), 1434 (m), 1408 (m), 1237 (m), 1059 (w), 861 (m), 789 (w), 726 (w), 693 (w), 669 (w), 522 (w). Anal. calcd. for $C_{11}H_{11}ClOS_2 \cdot 1/4\ C_3H_6O$ (258.8 + 14.5): C 51.64, H 4.61; found: C 51.95, H 4.43%.

6-Phenyl-4*H*-benzothieno[2,3-b]thiopyran-4-one (9a)

Beige solid, mp. 157 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (s, 1 H), 7.49-7.53 (m, 4 H), 7.55-7.59 (m, 1 H), 7.68-7.70 (m, 2 H), 7.96-7.98 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 122.4 (CH), 132.7 (CH), 124.6 (CH), 125.2 (CH), 127.2 (2 CH), 128.6 (CH), 129.4 (2 CH), 130.8 (CH), 135.3 (C_{quat}), 136.1 (C_{quat}), 136.3 (C_{quat}), 137.3 (C_{quat}), 140.7 (C_{quat}), 152.1 (C_{quat}), 176.9 (C_{quat}). EI MS (70 eV, *m/z* (%)): 296 (12), 295 (20), 294 (M^+, 100), 266 (33), 192 (13), 164 (18), 133 (20), 120 (21), 40 (56). IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (s), 1593 (s), 1544 (m), 1528 (w), 1499 (m), 1443 (m), 1345 (m), 1300 (m), 1242 (w), 1085 (m), 1052 (m), 951 (m), 864 (m), 753 (s), 727 (m), 684 (s), 578 (s). Anal. calcd. for $C_{17}H_{10}OS_2 \cdot 1/8\ CH_2Cl_2$ (294.4 + 10.6): C 67.44, H 3.49; found: C 67.49, H 3.79%.

6-(4-^{t}Butylphenyl)-4*H*-benzothieno[2,3-b]thiopyran-4-one (9b)

Beige solid, mp. 173 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (s, 9 H), 7.29 (s, 1 H), 7.47-7.50 (m, 1 H), 7.52-7.57 (m, 3 H), 7.63 (d, ^3J = 8.5 Hz, 2 H), 7.95 (t, ^3J = 8.7 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.1 (3 CH_3), 34.9 (C_{quat}), 122.4 (CH), 123.6 (CH), 124.0 (CH), 125.2 (CH), 126.4 (2 CH), 126.8 (2 CH), 128.5 (CH), 133.3 (C_{quat}), 135.3 (C_{quat}), 136.1 (C_{quat}), 137.2 (C_{quat}), 140.6 (C_{quat}), 152.1 (C_{quat}), 154.4 (C_{quat}), 176.9 (C_{quat}). EI MS (70 eV, *m/z* (%)): 350 (M^+, 13), 294 (27), 293 (21), 279 (44), 280 (11), 267 (15), 232 (15), 197 (15), 195 (45), 185 (11), 183 (14), 167 (54), 150 (12), 149 (100), 113 (15), 71 (20), 70 (20), 57 (31), 57 (31), 55 (11), 44 (10), 43 (34), 41 (11), 40 (79). IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1} (w), 1598 (s), 1498 (m),

1431 (m), 1353 (m), 1304 (m), 1111 (w), 1084 (m), 1052 (m), 1025 (w), 949 (w), 868 (w), 755 (s), 128 (m), 696 (w), 585 (m), 538 (w). Anal. calcd. for $C_{21}H_{18}OS_2$ (350.5): C 71.96, H 5.18; found: C 70.95, H 5.37%.

6-(4-Fluor0phenyl)-4*H*-benzothieno[2,3-b]thiopyran-4-one (9c)

Beige solid, mp. 205 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21-7.25 (m, 2 H), 7.27 (s, 1 H), 7.54 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.0 Hz, 1 H), 7.60 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.0 Hz, 1 H), 7.70 (d, ^3J = 8.9 Hz, 1 H), 7.71 (d, ^3J = 8.9 Hz, 1 H), 7.99-8.01 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 116.6 (CH), 116.8 (CH), 122.6 (CH), 123.9 (CH), 124.8 (CH), 125.5 (CH), 128.8 (CH), 129.3 (CH), 129.4 (CH), 132.6 (C_{quat}), 135.2 (C_{quat}), 136.2 (C_{quat}), 140.9 (C_{quat}), 151.0 (C_{quat}), 163.4 (C_{quat}), 176.9 (C_{quat}). EI MS (70 eV, *m/z* (%)): 314 (12), 313 (23), 312 (M^+, 100), 284 (31), 195 (23), 192 (14), 167 (13), 164 (17), 149 (24), 120 (16), 57 (12), 44 (14), 43 (18), 40 (62). IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1} (s), 1560 (s), 1486 (m), 1458 (m), 1399 (m), 1304 (w), 1217 (m), 1171 (w), 1105 (m), 1091 (s), 1054 (w), 1030 (w), 1011 (m), 963 (w), 892 (w), 821 (s), 783 (m), 756 (s), 730 (w), 545 (w), 521 (w). Anal. calcd. for $C_{17}H_9FOS_2$ (312.4): C 64.36, H 2.90; found: C 64.16, H 3.18%.

6-Cyclopropyl-4*H*-benzothieno[2,3-b]thiopyran-4-one (9d)

Beige solid, mp. 145 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04-1.08 (m, 2 H), 1.19-1.23 (m, 2 H), 2.07-2.12 (m, 1 H), 6.86 (s, 1 H), 7.48-7.52 (m, 1 H), 7.54-7.57 (m, 1 H), 7.91 (d, ^3J = 8.0 Hz, 1 H), 7.96 (d, ^3J = 8.1 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.5 (2 CH_2), 17.6 (CH), 122.3 (CH), 122.4 (CH), 123.7 (CH), 125.1 (CH), 128.4 (CH), 134.5 (C_{quat}), 136.1 (C_{quat}), 137.2 (C_{quat}), 140.6 (C_{quat}), 157.5 (C_{quat}), 176.8 (C_{quat}). EI MS (70 eV, *m/z* (%)): 260 (11), 259 (17), 258 (M^+, 100), 257 (12), 230 (11), 229 (12), 203 (11), 192 (15), 164 (14), 120 (10). IR (KBr): $\tilde{\nu}$ = 1597 cm^{-1} (s), 1498 (w), 1435 (w), 1368 (w), 1311 (w), 1163 (w), 1082 (w), 1049 (w), 999 (w), 871 (w), 847 (w), 757 (w), 727 (w). Anal. calcd. for $C_{14}H_{10}OS_2$ (258.4): C 65.08, H 3.90; found: C 65.15, H 3.90%.

b) X-Ray coordinates

X-Ray coordinates of **4i**

Center Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	**S1**	**1.0545**	**3.9186**	**9.0231**
2	**O1**	**2.5212**	**0.4226**	**11.2706**
3	**O2**	**5.9411**	**3.0370**	**1.5845**
4	**C1**	**2.2794**	**2.7769**	**8.5617**
5	**C2**	**2.6285**	**1.7354**	**9.3560**
6	**H21**	**3.2884**	**1.1706**	**9.0238**
7	**C3**	**2.0989**	**1.3980**	**10.6557**
8	**C4**	**1.0255**	**2.2362**	**11.2335**
9	**C5**	**0.5155**	**3.3597**	**10.5839**
10	**C6**	**-0.5231**	**4.0911**	**11.1607**
11	**H61**	**-0.8587**	**4.8396**	**10.7226**
12	**C7**	**-1.0485**	**3.7188**	**12.3572**
13	**H71**	**-1.7452**	**4.2085**	**12.7309**
14	**C8**	**-0.5484**	**2.6119**	**13.0205**
15	**H81**	**-0.9040**	**2.3613**	**13.8425**
16	**C9**	**0.4681**	**1.8886**	**12.4659**
17	**H91**	**0.7972**	**1.1466**	**12.9197**
18	**C10**	**2.8742**	**3.0565**	**7.2301**
19	**C11**	**3.7707**	**2.1858**	**6.6523**
20	**H111**	**4.0125**	**1.4152**	**7.1136**
21	**C12**	**4.3309**	**2.4266**	**5.3873**
22	**C13**	**3.9665**	**3.5987**	**4.6669**
23	**C14**	**3.0644**	**4.4871**	**5.2784**
24	**H141**	**2.8219**	**5.2666**	**4.8329**
25	**C15**	**2.5391**	**4.2332**	**6.5044**
26	**H151**	**1.9457**	**4.8435**	**6.8790**
27	**C16**	**5.2447**	**1.5329**	**4.7741**
28	**H161**	**5.5101**	**0.7687**	**5.2329**
29	**C17**	**5.7366**	**1.7650**	**3.5439**
30	**H171**	**6.3274**	**1.1560**	**3.1633**
31	**C18**	**5.3651**	**2.9284**	**2.8188**
32	**C19**	**4.5005**	**3.8268**	**3.3732**
33	**H191**	**4.2605**	**4.5912**	**2.9010**
34	**C20**	**5.5632**	**4.1591**	**0.7913**
35	**H201**	**6.0219**	**4.1243**	**-0.0513**

36	**H202**	**5.7978**	**4.9690**	**1.2502**
37	**H203**	**4.6153**	**4.1398**	**0.6406**

X-Ray coordinates of **7h**

Center Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	**S1**	**5.6990**	**-3.8420**	**3.7276**
2	**O1**	**4.1406**	**-2.6522**	**-0.2152**
3	**N1**	**6.2114**	**-1.3423**	**3.8689**
4	**C1**	**5.0643**	**-4.8276**	**2.4673**
5	**C2**	**4.6467**	**-4.3581**	**1.3007**
6	**H21**	**4.3234**	**-4.9861**	**0.6958**
7	**C3**	**4.6364**	**-2.9880**	**0.8633**
8	**C4**	**5.2538**	**-1.9834**	**1.7424**
9	**C5**	**5.7125**	**-2.2512**	**3.0222**
10	**C6**	**5.4050**	**-0.6778**	**1.3038**
11	**H61**	**5.1463**	**-0.4454**	**0.4413**
12	**C7**	**5.9267**	**0.2568**	**2.1248**
13	**H71**	**6.0350**	**1.1335**	**1.8339**
14	**C8**	**6.2955**	**-0.1065**	**3.3974**
15	**H81**	**6.6242**	**0.5550**	**3.9625**
16	**C9**	**5.0691**	**-6.2583**	**2.8487**
17	**H91**	**5.3708**	**-6.4483**	**3.7616**
18	**C10**	**5.4197**	**-7.2833**	**1.8385**
19	**H101**	**5.6091**	**-6.9812**	**0.9364**
20	**H102**	**5.9448**	**-8.0444**	**2.1317**
21	**C11**	**4.0389**	**-7.1862**	**2.3127**
22	**H111**	**3.7127**	**-7.8864**	**2.8994**
23	**H112**	**3.3769**	**-6.8230**	**1.7038**
24	**S2**	**1.8164**	**-2.3763**	**3.8081**
25	**O2**	**0.0095**	**-2.2568**	**-0.1929**
26	**N2**	**1.3167**	**-4.8526**	**3.5632**
27	**C12**	**1.5508**	**-1.0316**	**2.7886**
28	**C13**	**1.0086**	**-1.1052**	**1.5902**
29	**H131**	**0.9238**	**-0.3044**	**1.1250**
30	**C14**	**0.5325**	**-2.2881**	**0.9202**
31	**C15**	**0.6842**	**-3.5811**	**1.6225**
32	**C16**	**1.2022**	**-3.7066**	**2.8714**

33	**C17**	**0.2671**	**-4.7529**	**0.9971**
34	**H171**	**-0.0830**	**-4.7278**	**0.1359**
35	**C18**	**0.3792**	**-5.9490**	**1.6686**
36	**H181**	**0.1072**	**-6.7449**	**1.2718**
37	**C19**	**0.8944**	**-5.9398**	**2.9193**
38	**H191**	**0.9587**	**-6.7544**	**3.3635**
39	**C20**	**2.0204**	**0.2311**	**3.4905**
40	**H201**	**2.4143**	**0.0483**	**4.3691**
41	**C21**	**1.3901**	**1.4297**	**3.4428**
42	**H211**	**0.6202**	**1.5111**	**2.8584**
43	**H212**	**1.3332**	**1.9421**	**4.2644**
44	**C22**	**2.6003**	**1.3011**	**2.8684**
45	**H221**	**3.3556**	**1.7238**	**3.3062**
46	**H222**	**2.6421**	**1.2925**	**1.8994**

c) Molecular modelling coordinates

Molecular modelling coordinates (B3LYP/6-311G++) of 2-phenyl-4H-thiochromen-4-one

Center Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	**C**	**-4.605199**	**-0.092666**	**0.000274**
2	**C**	**-3.631663**	**0.888308**	**0.112613**
3	**C**	**-2.259948**	**0.565330**	**0.062118**
4	**C**	**-1.900542**	**-0.781669**	**-0.104197**
5	**C**	**-2.880249**	**-1.778201**	**-0.217136**
6	**C**	**-4.225941**	**-1.433767**	**-0.165220**
7	**C**	**-1.281989**	**1.671920**	**0.196883**
8	**C**	**0.763318**	**0.200818**	**0.031206**
9	**C**	**0.146672**	**1.393338**	**0.191628**
10	**O**	**-1.679493**	**2.859974**	**0.333563**
11	**S**	**-0.164034**	**-1.348640**	**-0.217612**
12	**C**	**2.232368**	**0.031316**	**0.014937**
13	**C**	**2.853255**	**-1.067447**	**0.637483**
14	**C**	**3.040121**	**0.989632**	**-0.626158**
15	**C**	**4.242158**	**-1.194566**	**0.630014**
16	**C**	**4.428130**	**0.857952**	**-0.631393**
17	**C**	**5.034406**	**-0.233453**	**-0.002958**
18	**H**	**-5.652230**	**0.173832**	**0.040258**
19	**H**	**-3.885836**	**1.930216**	**0.242262**
20	**H**	**-2.586169**	**-2.810996**	**-0.345326**
21	**H**	**-4.977826**	**-2.206323**	**-0.252972**
22	**H**	**0.758683**	**2.270182**	**0.359565**
23	**H**	**2.250460**	**-1.806458**	**1.146219**
24	**H**	**2.575324**	**1.821407**	**-1.136610**
25	**H**	**4.703848**	**-2.039977**	**1.121870**
26	**H**	**5.033717**	**1.600585**	**-1.132977**
27	**H**	**6.111138**	**-0.335084**	**-0.009533**

Molecular modelling coordinates (B3LYP/6-311G++) of 2-(4-methoxyphenyl)-4H-thiochromen-4-one

Center Number	Atom	Coordinates (Angstroms)		
		X	Y	Z

1	**C**	**5.404481**	**-0.050581**	**0.055910**
2	**C**	**4.422267**	**0.919434**	**-0.075918**
3	**C**	**3.053613**	**0.582071**	**-0.044815**
4	**C**	**2.705928**	**-0.767692**	**0.122253**
5	**C**	**3.694277**	**-1.753347**	**0.253893**
6	**C**	**5.037008**	**-1.394922**	**0.221142**
7	**C**	**2.065527**	**1.677020**	**-0.203185**
8	**C**	**0.031115**	**0.185085**	**-0.069027**
9	**C**	**0.642050**	**1.382031**	**-0.230540**
10	**O**	**2.453959**	**2.869192**	**-0.336684**
11	**S**	**0.973858**	**-1.350872**	**0.218383**
12	**C**	**-1.432009**	**0.000084**	**-0.076061**
13	**C**	**-2.037792**	**-1.137867**	**-0.651372**
14	**C**	**-2.267922**	**0.975944**	**0.492652**
15	**C**	**-3.417328**	**-1.281218**	**-0.669255**
16	**C**	**-3.656283**	**0.840269**	**0.480381**
17	**C**	**-4.234051**	**-0.292251**	**-0.104358**
18	**C**	**-6.521720**	**0.448299**	**0.377817**
19	**O**	**-5.598726**	**-0.531868**	**-0.171918**
20	**H**	**6.449137**	**0.227014**	**0.030904**
21	**H**	**4.666961**	**1.963472**	**-0.206779**
22	**H**	**3.409072**	**-2.788698**	**0.381606**
23	**H**	**5.795600**	**-2.159136**	**0.323417**
24	**H**	**0.026184**	**2.250269**	**-0.426685**
25	**H**	**-1.422614**	**-1.899996**	**-1.108257**
26	**H**	**-1.828842**	**1.840081**	**0.971070**
27	**H**	**-3.888480**	**-2.142798**	**-1.118672**
28	**H**	**-4.265643**	**1.607310**	**0.933620**
29	**H**	**-7.508840**	**0.038459**	**0.194480**
30	**H**	**-6.369118**	**0.574848**	**1.451555**
31	**H**	**-6.421957**	**1.410381**	**-0.128677**

Molecular modelling coordinates (B3LYP/6-311G++) of 4-(4-oxo-4H-thiochromen-2-yl)benzonitrile

Center Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	**C**	**-5.234525**	**-0.173778**	**-0.000642**
2	**C**	**-4.283917**	**0.829285**	**0.112221**

3	**C**	**-2.905154**	**0.537390**	**0.062266**
4	**C**	**-2.515941**	**-0.801379**	**-0.104137**
5	**C**	**-3.471715**	**-1.820077**	**-0.218487**
6	**C**	**-4.824904**	**-1.505753**	**-0.166692**
7	**C**	**-1.953231**	**1.665076**	**0.196537**
8	**C**	**0.123009**	**0.239290**	**0.028750**
9	**C**	**-0.516636**	**1.418985**	**C 0.187798**
10	**O**	**-2.373186**	**2.844274**	**0.332997**
11	**S**	**-0.766480**	**-1.331191**	**-0.214224**
12	**C**	**1.596088**	**0.106006**	**0.015081**
13	**C**	**2.242494**	**-0.981063**	**0.632014**
14	**C**	**2.383201**	**1.086230**	**-0.618333**
15	**C**	**3.629511**	**-1.079969**	**0.630272**
16	**C**	**3.770193**	**0.993176**	**-0.624004**
17	**C**	**4.408518**	**-0.092479**	**0.002130**
18	**C**	**5.835763**	**-0.193322**	**-0.003951**
19	**N**	**7.000488**	**-0.275921**	**-0.008565**
20	**H**	**-6.287230**	**0.068729**	**0.039164**
21	**H**	**-4.562576**	**1.864896**	**0.241650**
22	**H**	**-3.154790**	**-2.845927**	**-0.347235**
23	**H**	**-5.558934**	**-2.295043**	**-0.254967**
24	**H**	**0.074156**	**2.310910**	**0.352841**
25	**H**	**1.658571**	**1.738624**	**-1.134169**
26	**H**	**1.902735**	**1.910360**	**-1.125379**
27	**H**	**4.114376**	**-1.914153**	**1.116479**
28	**H**	**4.362922**	**1.749455**	**-1.118089**

Molecular modelling coordinates (B3LYP/6-311G++) of 2-phenyl-4H-chromen-4-one

Center Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	**C**	**-4.337824**	**-0.692169**	**0.002239**
2	**C**	**-3.628239**	**0.501598**	**-0.000136**
3	**C**	**-2.222990**	**0.494203**	**-0.000614**
4	**C**	**-1.563626**	**-0.741527**	**0.001658**
5	**C**	**-2.259792**	**-1.951270**	**0.004122**
6	**C**	**-3.650286**	**-1.919157**	**0.004316**
7	**C**	**-1.436257**	**1.741920**	**-0.003769**
8	**C**	**0.601447**	**0.345396**	**-0.000688**

9	**C**	**0.004508**	**1.564969**	**-0.003610**
10	**O**	**-1.976728**	**2.877557**	**-0.006612**
11	**C**	**2.044359**	**0.053471**	**-0.000181**
12	**C**	**2.500718**	**-1.277552**	**-0.009359**
13	**C**	**2.994279**	**1.093083**	**0.009751**
14	**C**	**3.866928**	**-1.557506**	**-0.009128**
15	**C**	**4.357237**	**0.807525**	**0.009829**
16	**C**	**4.800427**	**-0.518866**	**0.000273**
17	**O**	**-0.167517**	**-0.817828**	**0.001871**
18	**H**	**-5.418775**	**-0.681223**	**0.002477**
19	**H**	**-4.123770**	**1.461938**	**-0.001780**
20	**H**	**-1.708912**	**-2.880082**	**0.005944**
21	**H**	**-4.203880**	**-2.848133**	**0.006306**
22	**H**	**0.595742**	**2.466010**	**-0.006508**
23	**H**	**1.781189**	**-2.080626**	**-0.016571**
24	**H**	**2.673894**	**2.124911**	**0.018173**
25	**H**	**4.200915**	**-2.586247**	**-0.016394**
26	**H**	**5.072579**	**1.618575**	**0.017654**
27	**H**	**5.859645**	**-0.737669**	**0.000419**

Molecular modelling coordinates (B3LYP/6-311G++) of 2-(4-methoxyphenyl)-4H-chromen-4-one

Center Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	**C**	**-5.146972**	**-0.744221**	**0.045091**
2	**C**	**-4.457549**	**0.460620**	**0.000510**
3	**C**	**-3.052523**	**0.476995**	**-0.007008**
4	**C**	**-2.372323**	**-0.746614**	**0.030844**
5	**C**	**-3.047859**	**-1.967234**	**0.076046**
6	**C**	**-4.438745**	**-1.958731**	**0.082869**
7	**C**	**-2.287443**	**1.738180**	**-0.057885**
8	**C**	**-0.226050**	**0.377150**	**-0.017413**
9	**C**	**-0.845762**	**1.586204**	**-0.065906**
10	**O**	**-2.850597**	**2.862980**	**-0.096484**
11	**C**	**1.216448**	**0.110489**	**-0.013650**
12	**C**	**1.706030**	**-1.205613**	**-0.157243**
13	**C**	**2.148676**	**1.151880**	**0.131364**
14	**C**	**3.068630**	**-1.462000**	**-0.164242**

15	**C**	**3.519713**	**0.903171**	**0.125622**
16	**C**	**3.983259**	**-0.409646**	**-0.024759**
17	**C**	**6.341460**	**0.256465**	**0.090862**
18	**O**	**5.321408**	**-0.771514**	**-0.044749**
19	**O**	**-0.974959**	**-0.799351**	**0.028487**
20	**H**	**-6.227990**	**-0.751454**	**0.050916**
21	**H**	**-4.968774**	**1.412238**	**-0.030049**
22	**H**	**-2.481001**	**-2.885943**	**0.106062**
23	**H**	**-4.976468**	**-2.896372**	**0.118079**
24	**H**	**-0.269005**	**2.495093**	**-0.123481**
25	**H**	**1.006154**	**-2.018954**	**-0.265255**
26	**H**	**1.810807**	**2.169997**	**0.261771**
27	**H**	**3.452714**	**-2.465059**	**-0.277014**
28	**H**	**4.206425**	**1.727413**	**0.243382**
29	**H**	**7.284862**	**-0.275758**	**0.039187**
30	**H**	**6.281894**	**0.980781**	**-0.723908**
31	**H**	**6.259631**	**0.768535**	**1.051669**

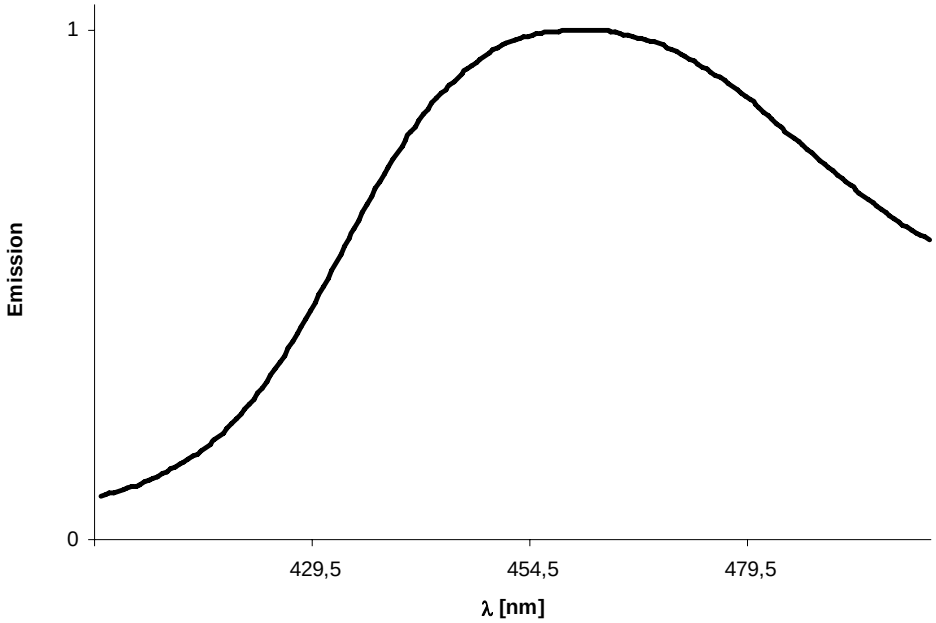
Molecular modelling coordinates (B3LYP/6-311G++) of 4-(4-oxo-4H-chromen-2-yl)benzonitrile

Center Number	Atom	Coordinates (Angstroms)		
		X	Y	Z
1	**C**	**-4.941227**	**-0.883341**	**0.000257**
2	**C**	**-4.301080**	**0.348836**	**-0.000281**
3	**C**	**-2.897487**	**0.420761**	**-0.000129**
4	**C**	**-2.169496**	**-0.776084**	**0.000577**
5	**C**	**-2.795037**	**-2.023327**	**0.001026**
6	**C**	**-4.185157**	**-2.069412**	**0.000876**
7	**C**	**-2.184174**	**1.710768**	**-0.000878**
8	**C**	**-0.071462**	**0.432839**	**0.000047**
9	**C**	**-0.733073**	**1.617076**	**-0.000856**
10	**O**	**-2.784198**	**2.814663**	**-0.001527**
11	**C**	**1.385847**	**0.223622**	**0.000219**
12	**C**	**1.915735**	**-1.079721**	**-0.001998**
13	**C**	**2.277102**	**1.313654**	**0.002356**
14	**C**	**3.290277**	**-1.289165**	**-0.002133**
15	**C**	**3.650512**	**1.110268**	**0.002241**
16	**C**	**4.173670**	**-0.196226**	**-0.000009**

17	**C**	**5.588297**	**-0.408003**	**-0.000178**
18	**N**	**6.743164**	**-0.581100**	**-0.000258**
19	**O**	**-0.769539**	**-0.772313**	**0.000764**
20	**H**	**-6.020901**	**-0.934004**	**0.000158**
21	**H**	**-4.850649**	**1.279232**	**-0.000803**
22	**H**	**-2.193227**	**-2.919903**	**0.001521**
23	**H**	**-4.685347**	**-3.028038**	**0.001226**
24	**H**	**-0.195822**	**2.551461**	**-0.001733**
25	**H**	**1.243117**	**-1.921963**	**-0.003645**
26	**H**	**1.902488**	**2.326405**	**0.004292**
27	**H**	**3.685057**	**-2.294911**	**-0.003884**
28	**H**	**4.323552**	**1.955353**	**0.003945**

d) Fluorescence spectrum of 4e-H^+

Normalized fluorescence spectrum of **4e-H^+**



Recorded in CH_2Cl_2, T = 298 K, excitation wavelength 440 nm, $\lambda_{max,\,em}$ = 460 nm, *Stokes* shift = 900 cm^{-1}