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Supporting Information

A New Au-Catalyzed Domino Cyclization and Oxidative Coupling Reaction

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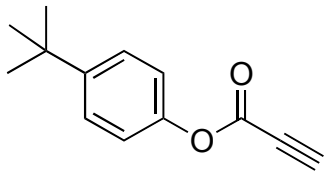
Experimental:

Phenylpropionic ester[1] as well as the water free solution of *tert*-butylhydroperoxide in cyclohexane[2] were prepared according to the literature.

General procedure for the preparation of Arylpropinoic esters:

The arylalcohole (1.00 eq.) and propionic acid (1.00–1.10 eq.) were dissolved in dichloromethane (1 ml/mmol), the mixture was cooled down to 0 °C, a solution of DCC (1.00 eq.) and DMAP (0.10 eq.), dissolved in dichloromethane (1 mL/mmol), was added drop wise, that the temperature of the reaction mixture remained under 5 °C. The mixture was stirred for 4 h. The precipitate was filtered off and the solution was washed with H_2O. The organic layers were combined, dried over Na_2SO_4 and the volatile parts were removed under reduced pressure. The product was purified by flash column chromatography.

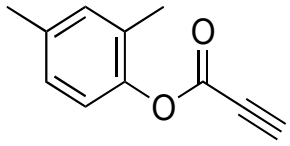
Synthesis of 4-*tert*-butylphenyl propiolate (**1a**):



According to the general procedure 4-*tert*-butylphenol (3.65 g, 24.3 mmol), propionic acid (1.5 mL, 24.3 mmol), DCC (5.01 g, 24.3 mmol) and DMAP (0.297 g, 2.43 mmol) were reacted in 40 mL DCM to give the title compound (3.84 g, 78%).
Mp = 41–43 °C.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41 (m, 2H), 7.06 (m, 2H), 3.06 (s, 1H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.15, 149.50, 147.43, 126.50, 120.51, 76.55 74.36, 34.54, 31.35.
IR: (ν/cm^{-1}) 3239, 2963, 2905, 2870, 2109, 1711, 1503, 1477, 1462, 1410, 1393, 1366, 1270, 1208, 1196, 1166, 1108, 1015, 917, 833, 809, 854, 732, 713.
MS: (EI, *m/z*) 202 (M+, 28%), 187 (100%).

The analytical data correspond to the literature[3].

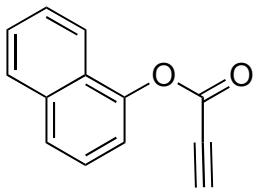
Synthesis of 2,4-dimethylphenyl propiolate (**1c**):



According to the general procedure 2,4-dimethylphenol (1.41 g, 11.6 mmol), propionic acid (0.75 mL, 12.2 mmol), DCC (2.39 g, 11.6 mmol) and DMAP (141 mg, 1.16 mmol) were reacted in 20 mL DCM to give the title compound (0.712 g, 35 %)

Mp = 51–53 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (s, 1H), 7.02 (d, 1H, *J* = 8.2), 6.94 (d, 1H, *J* = 8.2), 3.06 (s, 1H), 2.32 (s, 3H), 2.18 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.48, 146.61, 136.90, 132.39, 129.91, 128.05, 121.63, 76.98, 74.66, 21.26, 16.45.
IR: (ν/cm^{-1}) 3231, 3026, 2923, 2123, 1715, 1500, 1436, 1251, 1183, 1109, 1038, 952, 932, 907, 818, 749, 718.
MS: (EI, *m/z*) 174 (M^+, 97%), 122 (100%).

Synthesis of naphthalen-1-yl propiolate (**1d**):

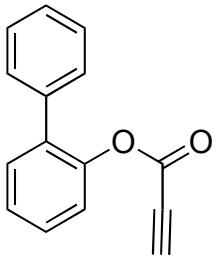


According to the general procedure 1-naphthol (1.67 g, 11.6 mmol), propionic acid (0.75 mL, 12.2 mmol), DCC (2.39 g, 11.6 mmol) and DMAP (141 mg, 1.16 mmol) were reacted in 20 mL DCM to give the title compound (1.27 g, 56 %).

Mp = 41–42 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (ddd, 2H, *J* = 3.3, 8.1, 10.5), 7.80 (d, 1H, *J* = 8.3), 7.56 (m, 2H), 7.49 (m, 1H), 7.33 (d, 1H, *J* = 7.5), 3.15 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.54, 146.11, 135.12, 128.53, 127.34, 127.29, 127.20, 126.66, 125.76, 121.41, 118.46, 77.71, 74.62.

IR: (ν/cm^{-1}) 3246, 3231, 3062, 2118, 1708, 1599, 1509, 1463, 1388, 1211, 1040, 1014, 918, 866, 787, 762, 716.
MS: (EI, *m/z*) 196 (M^+, 70%), 144 (100%).

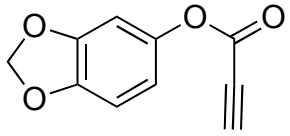
Synthesis of biphenyl-2-yl propiolate (**1e**):



According to the general procedure biphenyl-2-ol (1.97 g, 11.6 mmol), propionic acid (0.75 mL, 12.2 mmol), DCC (2.39 g, 11.6 mmol) and DMAP (141 mg, 1.16 mmol) were reacted in 20 mL DCM to give the title compound (1.11 g, 43 %).

Mp = 58–60 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 8H), 7.19 (dd, 1H, J = 1.5, 7.7), 2.94 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.29, 147.16, 137.25, 135.21, 131.57, 129.28, 129.08, 128.89, 128.16, 127.58, 122.87, 77.06, 74.44.
IR: (ν/cm^{-1}) 3266, 3081, 3059, 3032, 2128, 1723, 1479, 1451, 1431, 1195, 1175, 1156, 1109, 1071, 1048, 1010, 965, 918, 833, 782, 763, 735, 707, 694.
MS: (EI, *m/z*) 222 (M^+, 100%).

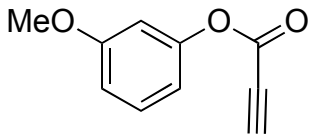
Synthesis of benzo[*d*][1,3]dioxol-5-yl propiolate (**1f**):



According to the general procedure benzo[*d*][1,3]dioxol-5-ol (1.60 g, 11.6 mmol), propionic acid (0.75 mL, 12.2 mmol), DCC (2.39 g, 11.6 mmol) and DMAP (141 mg, 1.16 mmol) were reacted in 20 mL DCM to give the title compound (1.06 g, 48 %).

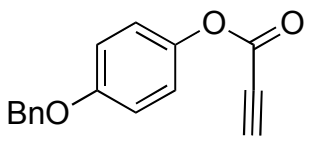
Mp = 80–82 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.78 (d, 1H, *J* = 8.4), 6.65 (d, 1H, *J* = 2.4), 6.59 (dd, 1H, *J* = 2.4, 8.4), 5.99 (s, 2H), 3.07 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ =151.22, 148.07, 145.89, 143.91, 113.72, 108.01, 103.31, 101.85, 76.91, 74.10.
IR: (ν/cm^{-1}) 3227, 2907, 2799, 2120, 1717, 1640, 1612, 1503, 1485, 1445, 1366, 1246, 1197, 1169, 1119, 1095, 1036, 947, 935, 925, 902, 844, 812, 781, 755, 722, 652.
MS: (EI, *m/z*) 190 (M^+, 49%), 138 (100%).

Synthesis of 3-methoxyphenyl propiolate (**1g**):



According to the general procedure 3-(methoxy)phenol (4.39 mL , 40.5 mmol), propionic acid (3.06 mL, 40.5 mmol), DCC (8.44 g, 40.5 mmol) and DMAP (500 mg, 4.05 mmol) were reacted in 80 mL DCM to give the title compound as an oil (5.13 g, 72 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (t, 1H, *J* = 8.2), 6.82 (ddd, 1H, *J* = 0.8, 2.3, 8.2), 6.75 (ddd, 1H, *J* = 0.8, 2.3, 8.2), 6.70 (t, 1H, *J* = 2.3), 3.80 (s, 3H), 3.08 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.52, 150.81, 150.61, 129.98, 113.33, 112.41, 107.21, 76.77, 74.19, 55.44.
IR: (ν/cm^{-1}) 3271, 3009, 2967, 2941, 2838, 2120, 1729, 1609, 1588, 1488, 1452, 1316, 1286, 1263, 1191, 1130, 1076, 1041, 997, 945, 906, 871, 840, 773, 748 685.
MS: (EI, *m/z*) 176 (M^+, 65%), 124 (100%).

Synthesis of 4-(benzyloxy)phenyl propiolate (**1h**):

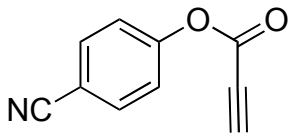


According to the general procedure 4-(benzyloxy)phenol (2.32 g, 11.6 mmol), propionic acid (0.75 mL, 12.2 mmol), DCC (2.39 g, 11.6 mmol) and DMAP (141 mg, 1.16 mmol) were reacted in 20 mL DCM to give the title compound (0.975 g, 33 %).

Mp = 62–63 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 5H), 7.07 (m, 2H), 6.98 (m, 2H), 5.06 (s, 2H), 3.06 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.40, 151.78, 143.88, 137.05, 129.08, 128.54, 127.90, 122.52, 115.99, 77.14, 74.74, 70.85.
IR: (ν/cm^{-1}) 3232, 3223, 3073, 2933, 2875, 2122, 1720, 1711, 1594, 1501, 1464, 1453, 1384, 1245, 1204, 1174, 1101, 1017, 1008, 906, 835, 823, 740, 693.
MS: (EI, *m/z*) 252 (M^{+}, 11%), 91 (100%).

The analytical data correspond to the literature[Error! Bookmark not defined.].

Synthesis of 4-cyanophenyl propiolate (**1i**):

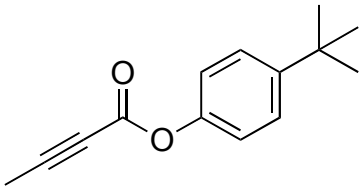


According to the general procedure 4-hydroxybenzonitrile (1.28 g, 11.6 mmol), propionic acid (0.75 mL, 12.2 mmol), DCC (2.39 g, 11.6 mmol) and DMAP (141 mg, 1.16 mmol) were reacted in 20 mL DCM to give the title compound (0.164 g, 8.3 %).

Mp = 128–130 ºC (decomposition).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dt, 2H, *J* = 8.8, 2.2), 7.31 (dt, 2H, *J* = 8.8, 2.2), 3.15 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.23, 150.21, 134.29, 122.88, 118.34, 111.10, 78.34, 74.03;
IR: (ν/cm^{-1}) 3232, 3104, 2238, 2121, 1725, 1604, 1497, 1412, 1214, 1205, 1189, 1183, 1165, 1102, 1022, 913, 851, 822, 757, 731, 702.
MS: (EI, *m/z*) 171 (M^{+}, 17%), 53 (100%).

The analytical data correspond to the literature[1].

Synthesis of 4-*tert*-butylphenyl but-2-ynoate (**1j**):



According to the general procedure 4-*tert*-butylphenol (0.710 g, 4.73 mmol), 2-butynoic acid (0.400 g, 4.76 mmol), DCC (1.03 g, 4.99 mmol) and DMAP (58.2 mg, 0.476 mmol) were reacted in 8 mL DCM to give the title compound (0.808 g, 79 %).

Mp = 67–68ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, 2H, *J* = 8.8), 7.05 (d, 2H, *J* = 8.8), 2.06 (s, 3H), 1.32 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.59, 149.57, 148.13, 126.85, 121.12, 88.27, 72.63, 34.95, 31.81, 4.39.
IR: (ν/cm^{-1}) 2968, 2935, 2924, 2909, 2869, 2293, 2233, 1717, 1501, 1362, 1250, 1202, 1167, 1109, 1042, 1017, 946, 879, 814, 742, 724.
MS: (EI, *m/z*) 216 (M^+, 11%), 135 (100%).

The analytical data correspond to the literature[3].

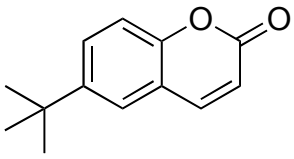
General procedure for the domino cyclization oxidative coupling reaction:

$HAuCl_4$ (0.05 eq.) was suspended in dry 1,2-dichloroethane. A 80% solution of *tert*-butylhydroperoxide (5.00 eq.) in cyclohexane was added and the arylpropionicester (1.00 eq.) was dissolved in the solution. The mixture was heated to 60 °C and was stirred for 24h. If a precipitate was formed, it was filtered off and re-crystallized. The excess peroxide was reduced with $Na_2S_2O_3$ (10% aq. solution). The mixture was diluted with dichloromethane and washed with H_2O. The organic layers were dried over Na_2SO_4 and the volatile parts were removed under reduced pressure. The product was purified by flash column chromatography.

Synthesis 6-*tert*-butyl-2*H*-chromen-2-one (**2a**) and 6,6'-di-*tert*-butyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3a**):

According to the general procedure 4-*tert*-butylphenyl propiolate (100 mg, 0.494 mmol), $HAuCl_4$ (8.4 mg, 0.0247 mmol), and *tert*-butyl peroxide (278 mg, 80% in cyclohexane, 2.47 mmol) were reacted in 10 mL DCE to yield 6-*tert*-butyl-2*H*-chromen-2-one (32.0 mg, 32%) and 6,6'-di-*tert*-butyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (54.7 mg, 55%).

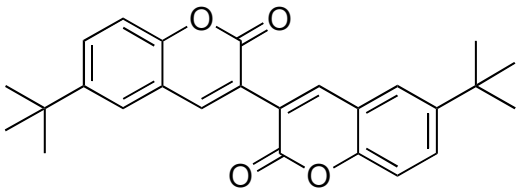
6-Tert-*butyl-2*H-*chromen-2-one (**2a**):*



Mp = 59–61 °C.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, 1H, *J* = 9.5), 7.58 (dd, 1H, *J* = 2.4, 8.7), 7.44 (d, 1H, *J* = 2.4), 7.27 (d, 1H, *J* = 8.7), 6.40 (d, 1H, *J* = 9.5), 1.35 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.13, 152.04, 147.54, 143.85, 129.48, 124.09, 118.24, 116.42, 116.39, 34.51, 31.32.
IR: (ν/cm^{-1}) 3077, 3043, 2951, 2907, 2870, 1721, 1606, 1574, 1488, 1464, 1450, 1395, 1378, 1361, 1263, 1215, 1183, 1141, 1119, 1087, 936, 911, 885, 839, 817, 735, 700, 652.
MS: (EI, *m/z*) 202 (M^+, 21%), 187 (100%).

The analytical data correspond with the literature[4].

6,6'-Di-tert-*butyl-2*H,*2'*H-*3,3'-bichromene-2,2'-dione (**3a**):*



Mp = >250 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 2H), 7.62 (dd, 2H, *J* = 2.3, 8.7), 7.58 (d, 2H, *J* = 2.3), 7.31 (d, 2H, *J* = 8.7), 1.37 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.91, 151.75, 148.30, 144.56, 130.50, 125.58, 120.16, 118.97, 116.33, 35.04, 31.77.

IR: (ν/cm^{-1}) 3049, 2961, 2903, 2867, 1761, 1704, 1608, 1572, 1498, 1458, 1365, 1330, 1272, 1235, 1203, 1173, 1132, 1090, 1073, 1001, 930, 825, 820, 780, 764, 744, 712, 664, 623.

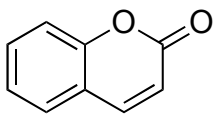
MS: (EI, *m/z*) 402 (M^+, 58%), 387 (100%).

UV λ_{max} ($CHCl_3$) nm (log ε): 361 (4.45).

Synthesis 2*H*-chromen-2-one (**2b**) and 2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3b**):

According to the general procedure phenyl propiolate (100 mg, 0.684 mmol), $HAuCl_4$ (11.6 mg, 0.0342 mmol), and *tert*-butyl peroxide (0.384 g, 80% in cyclohexane, 3.42 mmol) were reacted in 10 mL DCE to yield coumarin (39.7 mg, 40%) and 2*H*,2'*H*-3,3'-bichromene-2,2'-dione (26.9 mg, 27%).

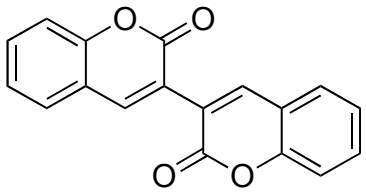
*Coumarin (**2b**):*



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, 1H, *J* = 9.5), 7.50 (m, 2H), 7.28 (m, 2H), 6.40 (d, 1H, *J* = 9.5).

The compound was identified by comparison with a commercial sample (Lancaster).

*2*H,*2'*H-*3,3'-Bichromene-2,2'-dione (**3b**):*



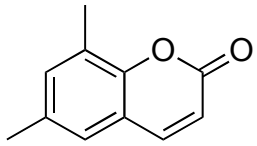
Mp = >250 °C.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 2H), 7.65 (m, 4H), 7.40 (m, 4H).
IR: (ν/cm^{-1}) 3080, 2924, 2853, 1720, 1607, 1563, 1488, 1447, 1346, 1248, 1187, 1153, 1129, 1120, 928, 909, 746.
MS: (EI, *m/z*) 290 (M^+, 90%), 262 (100%).

The analytical data correspond to the literature[5].

Synthesis of 6,8-dimethyl-2*H*-chromen-2-one (**2c**) and 6,6',8,8'-tetramethyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3c**):

According to the general procedure 2,4-dimethylphenyl propiolate (120 mg, 0.69 mmol), $HAuCl_4$ (11.7 mg, 0.035 mmol) and *tert*-butyl peroxide (233 mg, 80% in cyclohexane, 2.17 mmol) were reacted in 10 mL DCE to yield 6,8-dimethyl-2*H*-chromen-2-one (23.3 mg, 19 %) and 6,6',8,8'-tetramethyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (33 mg, 28 %).

*6,8-Dimethyl-2*H*-chromen-2-one (**2c**):*

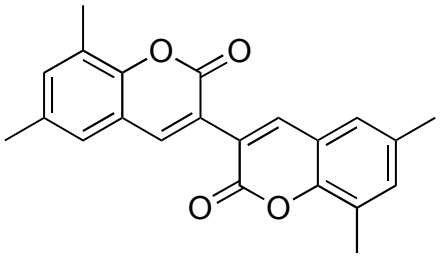


Mp = 71–73 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, 1H, *J* = 9.5), 7.20 (s, 1H), 7.10 (s, 1H), 6.38 (d, 1H, *J* = 9.5), 2.42 (s, 3H), 2.36 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.75, 150.95, 144.20, 134.72, 133.99, 126.39, 125.77, 118.77, 116.63, 21.08, 15.76.
IR: (ν/cm^{-1}) 3105, 3034, 2956, 2919, 2855, 1695, 1607, 1584, 1428, 1379, 1254, 1245, 1160, 1114, 1057, 914, 862, 826, 759.

MS: (EI, *m/z*) 174 (M^+, 100%).

The analytical data correspond to the literature[6].

*6,6′,8,8′-Tetramethyl-2*H*,2*′H*-3,3′-bichromene-2,2′-dione (**3c**):*

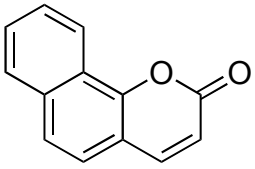


Mp = >250 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 2H), 7.22 (s, 4H), 2.45 (s, 6H), 2.38 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.91, 150.32, 144.25, 135.16, 134.25, 126.64, 125.87, 120.41, 119.09, 21.14, 15.70.
IR: (ν/cm^{-1}) 2958, 2924, 2863, 1695, 1607, 1577, 1447, 1350, 1334, 1289, 1247, 1164, 1135, 1041, 1082, 925, 856, 835, 771, 739.
MS: (EI, *m/z*) 346 (M^+, 100%).

Synthesis of 2*H*-benzo[*h*]chromen-2-one (**2d**) and 2*H*,2′*H*-3,3′-bibenzo[*h*]chromene-2,2′-dione (**3d**):

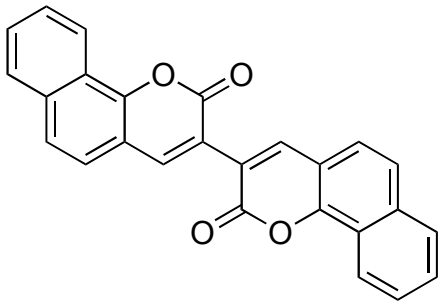
According to the general procedure naphthalen-1-yl propiolate (120 mg, 0.612 mmol), $HAuCl_4$ (10.4 mg, 0.0306 mmol) and *tert*-butyl peroxide (207 mg, 80% in cyclohexane, 1.84 mmol) were reacted in 10 mL DCE to yield 2*H*-benzo[*h*]chromen-2-one (15.2 mg, 13 %) and 2*H*,2′*H*-3,3′-bibenzo[*h*]chromene-2,2′-dione (80.0 mg, 67 %).

*2*H*-Benzo[*h*]chromen-2-one (**2d**):*



Mp = 100–102 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.81 (m, 2H), 7.63 (m, 3H), 7.42 (d, 1H, *J* = 8.5), 6.49 (d, 1H, *J* = 9.5).
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.36, 151.71, 144.62, 135.24, 129.13, 128.22, 127.60, 124.86, 123.99, 123.46, 122.70, 116.33, 114.67.
IR: (ν/cm^{-1}) 3069, 2997, 2957, 2924, 2853, 1707, 1634, 1597, 1558, 1502, 1466, 1435, 1402, 1379, 13401277, 1223, 1209, 1171, 1146, 1117, 1032, 1007, 906, 849, 743, 694.
MS: (EI, *m/z*) 196 (M^+, 91%), 168 (100%).

*2*H*,2'*H*-3,3'-Bibenzo[*h*]chromene-2,2'-dione (**3d**):*

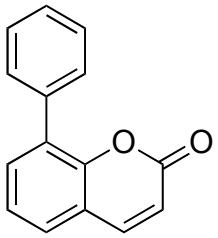


Mp = >250 ºC.
^{1}H NMR (400 MHz, $C_2D_2Cl_4$): 8.79 (s, 2H), 8.60 (m, 2H), 7.95 (m, 2H), 7.78 (d, 2H, *J* = 8.4), 7.72 (m, 4H), 7.63 (d, 2H, *J* = 8.6).
^{13}C NMR (150 MHz, $C_2D_2Cl_4$): δ 160.18, 150.70, 144.11, 135.13, 129.24, 128.18, 127.58, 125.01, 124.40, 122.69, 122.36, 119.85, 114.78.
IR: (ν/cm^{-1}) 3112, 3070, 1669, 1631, 1589, 1555, 1496, 1469, 1377, 1344, 1307, 1282, 1231, 1204, 1147, 1111, 1045, 1015, 942, 910, 870, 835, 811, 798, 784, 754, 708.
MS: (EI, *m/z*) 390 (M^+, 100%).

Synthesis of 8-phenyl-2*H*-chromen-2-one (**2e**) and 8,8'-diphenyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3e**):

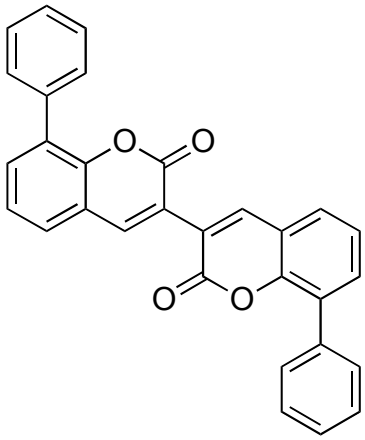
According to the general procedure biphenyl-2-yl propiolate (144 mg, 0.650 mmol), $HAuCl_4$ (11.0 mg, 0.0325 mmol) and *tert*-butyl peroxide (220 mg, 80% in cyclohexane, 1.84 mmol) were reacted in 10 mL DCE to yield starting material (17.8 mg, 12 %), 8-phenyl-2*H*-chromen-2-one (26.0 mg, 18 %) and 8,8'-diphenyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (53.4 mg, 37 %).

*8-Phenyl-2*H*-chromen-2-one (**2e**):*



mp = 127–129 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, 1H, *J* = 9.5), 7.60 (dd, 3H, *J* = 4.3, 9.9), 7.47 (m, 3H), 7.38 (m, 2H), 6.45 (d, 1H, *J* = 9.5).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.92, 151.29, 144.24, 136.00, 133.54, 130.78, 129.94, 128.92, 128.44, 127.62, 124.82, 119.68, 117.09.
IR: (ν/cm^{-1}) 3073, 2921, 2851, 1717, 1603, 1498, 1449, 1435, 1405, 1258, 1237, 1191, 1129, 1095, 1069, 1028, 916, 833, 762, 752, 711.
MS: (EI, *m/z*) 222 (M^+, 100%).

*8,8'-Diphenyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3e**):*

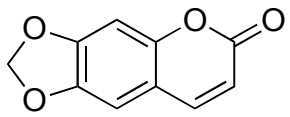


mp = >250 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 2H), 7.63 (dd, 6H, *J* = 4.7, 10.9), 7.59 (m, 2H), 7.51 (t, 4H, *J* = 7.5), 7.41 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.16, 150.68, 144.42, 135.89, 133.94, 130.31, 129.94, 128.98, 128.64, 128.52, 125.13, 120.41, 120.00.
IR: (ν/cm^{-1}) 3000, 2969, 1701, 1604, 1515, 1467, 1446, 1322, 1272, 1242, 1205, 1182, 1156, 1137, 1096, 1000, 989, 952, 845, 797, 739.
MS: (EI, *m/z*) 442 (M^+, 100%).

Synthesis 6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (**2f**) and 6*H*,6'*H*-7,7'-bi[1,3]dioxolo[4,5-*g*]chromene-6,6'-dione (**3f**):

According to the general procedure 3-methoxyphenyl propiolate (112 mg, 0.589 mmol), $HAuCl_4$ (10.0 mg, 0,0295 mmol), and *tert*-butyl peroxide (332 mg, 80% in cyclohexane, 2.95 mmol) were reacted in 10 mL DCE to yield 6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (33.6 mg, 30%) and 6*H*,6'*H*-7,7'-bi[1,3]dioxolo[4,5-*g*]chromene-6,6'-dione (55.7 mg, 50%).

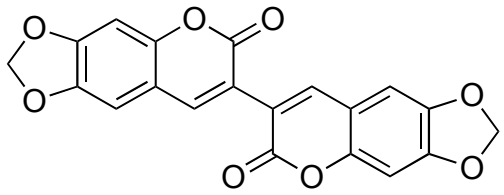
*6*H-*[1,3]Dioxolo[4,5*-g*]chromen-6-one (**2f**):*



Mp = 225–227 °C.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, 1H, *J* = 9.5), 6.83 (s, 2H), 6.28 (d, 1H, *J* = 9.5), 6.07 (s, 2H).
IR: (ν/cm^{-1}) 3080, 3057, 2992, 2918, 1702, 1683, 1623, 1580, 1489, 1451, 1418, 1397, 1385, 1269, 1256, 1224, 1186, 1163, 1112, 939, 921, 879, 751, 731.
MS: (EI, *m/z*) 190 (M^+, 100%).

The analytical data correspond to the literature[7,8].

*6*H,*6'*H-*7,7'-Bi[1,3]dioxolo[4,5*-g*]chromene-6,6'-dione (**3f**):*



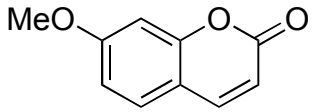
The dicoumarin was obtained as inseparable mixture with oxidized byproducts. The product showed the characteristic singulett for the dimer at 8.48 ppm in ^{1}H NMR and was identified by:

MS: (EI, *m/z*) 378 (M^+, 100%).

Synthesis 7-methoxy-2*H*-chromen-2-one (**2g**) and 7,7'-dimethoxy-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3g**):

According to the general procedure 3-methoxyphenyl propiolate (107 mg, 0.607 mmol), $HAuCl_4$ (10.3 mg, 0.0304 mmol), and *tert*-butyl peroxide (342 mg, 80% in cyclohexane, 3.04 mmol) were reacted in 10 mL DCE to yield 7-methoxy-2*H*-chromen-2-one (24.6 mg, 23%) and 7,7'-dimethoxy-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (42.5 mg, 40%).

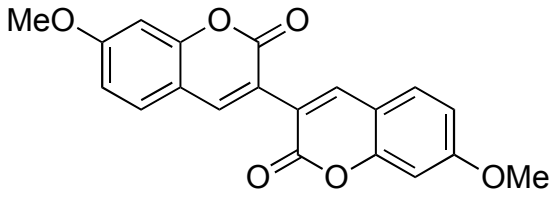
*7-Methoxy-2*H*-chromen-2-one (**2g**):*



Mp = 102–104 °C.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, 1H, *J* = 9.5), 7.36 (d, 1H, *J* = 8.5), 6.83 (dd, 1H, *J* = 2.4, 8.5), 6.80 (d, 1H, *J* = 2.4), 6.24 (d, 1H, *J* = 9.5), 3.86 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.78, 161.16, 155.86, 143.38, 128.71, 113.04, 112.55, 112.49, 100.80, 55.74.
IR: (ν/cm^{-1}) 3086, 3054, 3022, 2934, 2849, 1703, 1611, 1585, 1505, 1464, 1451, 1439, 1423, 1353, 1282, 1231, 1205, 1155, 1123, 1099, 1024, 981, 892, 825, 793, 704.
MS: (EI, *m/z*) 176 (M^+, 100%).

The analytical data correspond to the literature[7,8,9].

*7,7'-Dimethoxy-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3g**):*



Mp = >250 °C.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 2H), 7.49 (d, 2H, *J* = 8.6), 6.89 (dd, 2H, *J* = 2.4, 8.6), 6.85 (d, 2H, *J* = 2.4), 3.90 (s, 6H).

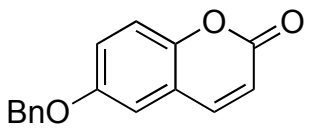
^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ = 160.27, 154.92, 142.94, 129.59, 117.11, 112.95, 112.61, 108.09, 100.26, 55.92.
IR: (ν/cm^{-1}) 3079, 3002, 2954, 2844, 1717, 1616, 1505, 1462, 1451, 1436, 1358, 1281, 1229, 1195, 1168, 1122, 1021, 982, 936, 923, 913, 822, 781, 763, 714.
MS: (EI, *m/z*) 350 (M^+, 100%).

The analytical data correspond to the literature[10].

Synthesis of 6-(benzyloxy)-2H-chromen-2-one (**2h**) and 6,6'-bis(benzyloxy)-2H,2'H-3,3'-bichromene-2,2'-dione (**3h**):

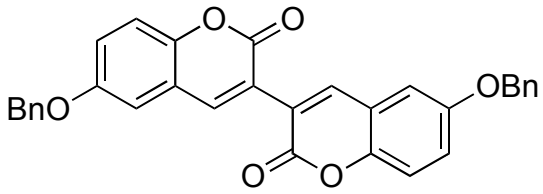
According to the general procedure 4-(benzyloxy)phenyl propiolate (164 mg, 0.650 mmol), $HAuCl_4$ (11.0 mg, 0.0325 mmol) and *tert*-butyl peroxide (220 mg, 80% in cyclohexane, 1.84 mmol) were reacted in 10 mL DCE to yield 6-(benzyloxy)-2H-chromen-2-one (13.7 mg, 8.3 %) and 6,6'-bis(benzyloxy)-2H,2'H-3,3'-bichromene-2,2'-dione (56.0 mg, 34 %).

*6-(Benzyloxy)-2*H*-chromen-2-one (**2h**):*



mp = 120–122 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, 1H, *J* = 9.6), 7.39 (m, 4H), 7.27 (d, 2H, *J* = 9.2), 7.18 (dd, 1H, *J* = 2.8, 9.2), 6.99 (d, 1H, *J* = 2.8), 6.42 (d, 1H, *J* = 9.6), 5.10 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.37, 155.60, 149.02, 143.60, 136.70, 129.15, 128.69, 127.87, 120.62, 119.61, 118.37, 117.54, 111.79, 71.14.
IR: (ν/cm^{-1}) 3089, 3050, 2932, 2871, 1702, 1566, 1491, 1444, 1382, 1270, 1191, 1167, 1107, 1016, 919, 882, 838, 816, 762, 751, 710, 696.
MS: (EI, *m/z*) 252 (M^+, 13%), 91 (100%).

*6,6'-Bis(benzyloxy)-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3h**):*



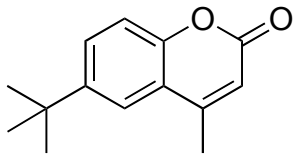
The dicoumarin was obtained as inseparable mixture with oxidized byproducts. The product showed characteristic singulett for the dimer ~ 8.5 ppm in ^{1}H NMR and was identified by:

MS: (EI, *m/z*) 502 (M^+, 3.8%), 91 (100%).

Synthesis of 6-*tert*-butyl-4-methyl-2*H*-chromen-2-one (**2j**) and 6,6'-di-*tert*-butyl-4,4'-dimethyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3j**):

According to the general procedure 4-*tert*-butylphenyl but-2-ynoate (141 mg, 0.650 mmol), $HAuCl_4$ (11.0 mg, 0.0325 mmol) and *tert*-butyl peroxide (220 mg, 80% in cyclohexane, 1.84 mmol) were reacted in 10 mL DCE to yield starting material (43.8 mg, 31 %), 6-*tert*-butyl-4-methyl-2*H*-chromen-2-one (29.5 mg, 21 %) and 6,6'-di-*tert*-butyl-4,4'-dimethyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (20.4 mg, 15 %).

6-Tert-*Butyl-4-methyl-2*H*-chromen-2-one (**2j**):*

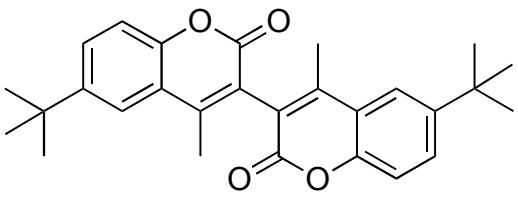


mp = 110–112 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, 1H, *J* = 2.3, 8.8), 7.55 (d, 1H, *J* = 2.3), 7.27 (d, 1H, *J* = 8.8), 6.28 (q, 1H, , *J* = 1.3), 2.46 (d, 3H, *J* = 1.3), 1.36 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.53, 153.06, 151.94, 147.64, 129.84, 120.97, 119.69, 117.07, 115.36, 35.09, 31.83, 19.12.
IR: (ν/cm^{-1}) 3074, 3053, 2961, 2943, 2912, 2831, 1701, 1605, 1566, 1491, 1470, 1450, 1435, 1387, 1279, 1259, 1186, 1167, 1045, 937, 916, 885, 845, 804, 752.

MS: (EI, *m/z*) 216 (M^+, 20%), 201 (100%).

The analytical data correspond to the literature[11].

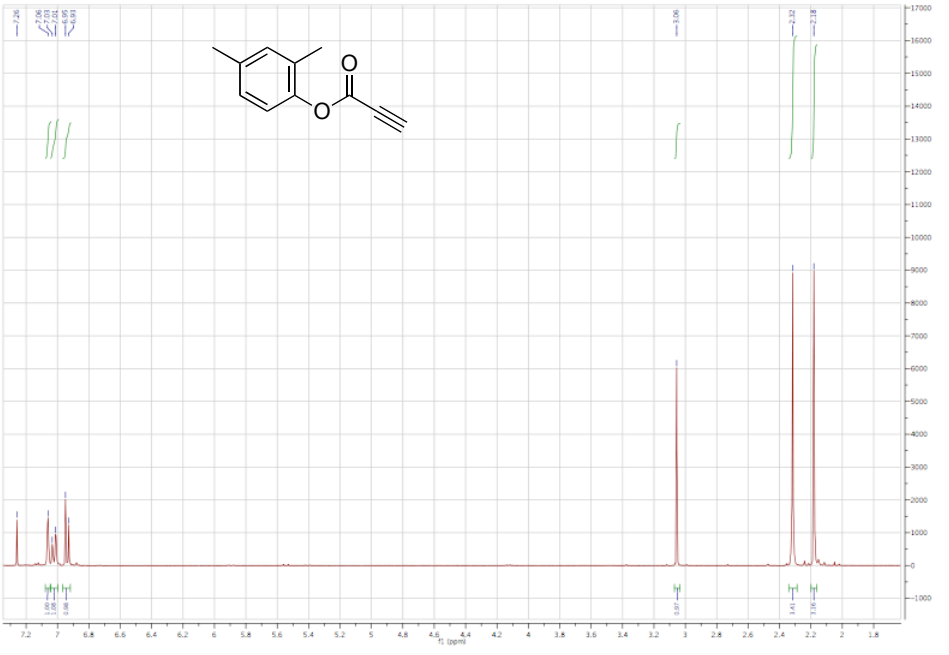
6,6′-Di-tert-*butyl-4,4′-dimethyl-2*H,*2′*H-*3,3′-bichromene-2,2′-dione* (***3j***)*:*



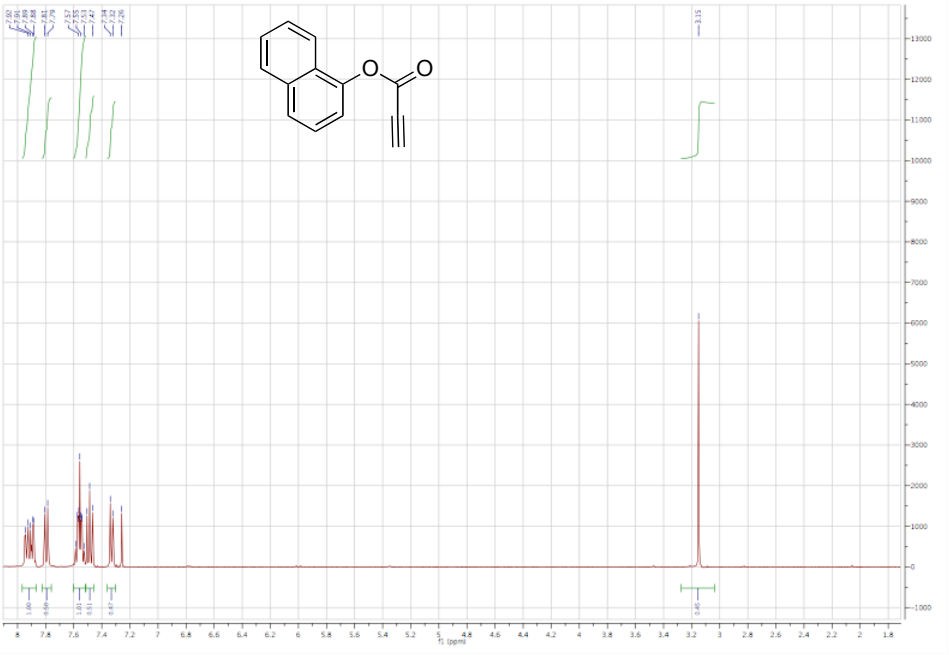
mp = 226–228 ºC.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 2H, *J* = 2.2), 7.63 (dd, 2H, *J* = 2.2, 8.6), 7.33 (d, 2H, *J* = 8.6), 2.37 (s, 6H), 1.38 (s, 19H).
^{13}H NMR (100 MHz, $CDCl_3$): δ 160.18, 152.07, 151.51, 147.83, 130.08, 121.68, 120.84, 119.62, 116.99, 35.16, 31.84, 16.80.
IR: (ν/cm^{-1}) 2959, 2928, 2870, 1704, 1609, 1601, 1560, 1495, 1460, 1433, 1418, 1364, 1342, 1310, 1256, 1180, 1150, 1109, 1074, 1024, 943, 908, 881, 843, 824, 797, 771, 698.
MS: (EI, *m/z*) 430 (M^+, 7.6%), 415 (100%).

^{1}H NMR-Spectra:

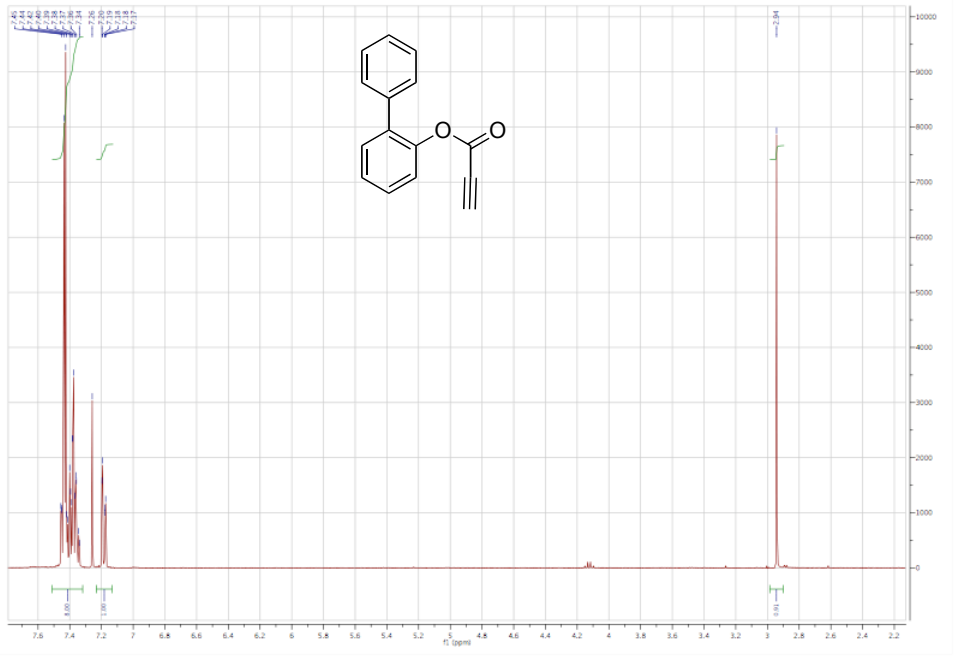
2,4-Dimethylphenyl propiolate (**1c**):



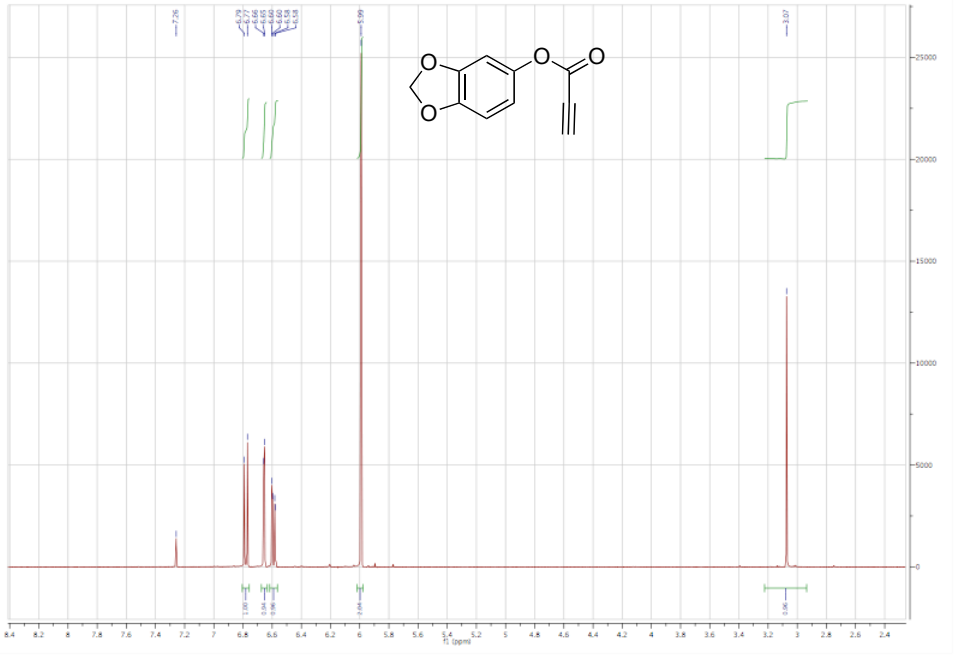
Naphthalen-1-yl propiolate (**1d**):



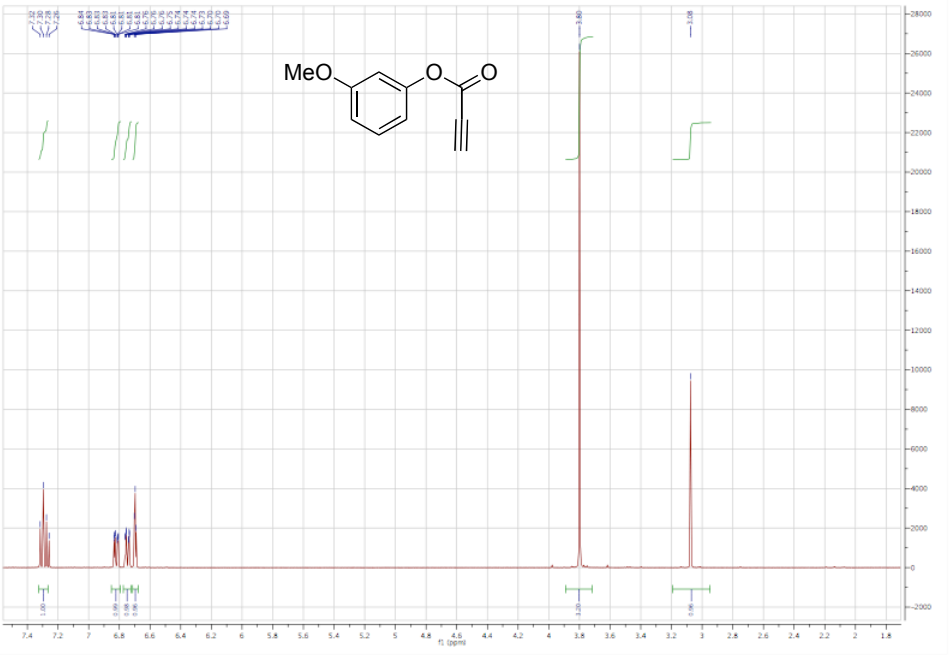
Biphenyl-2-yl propiolate (**1e**):



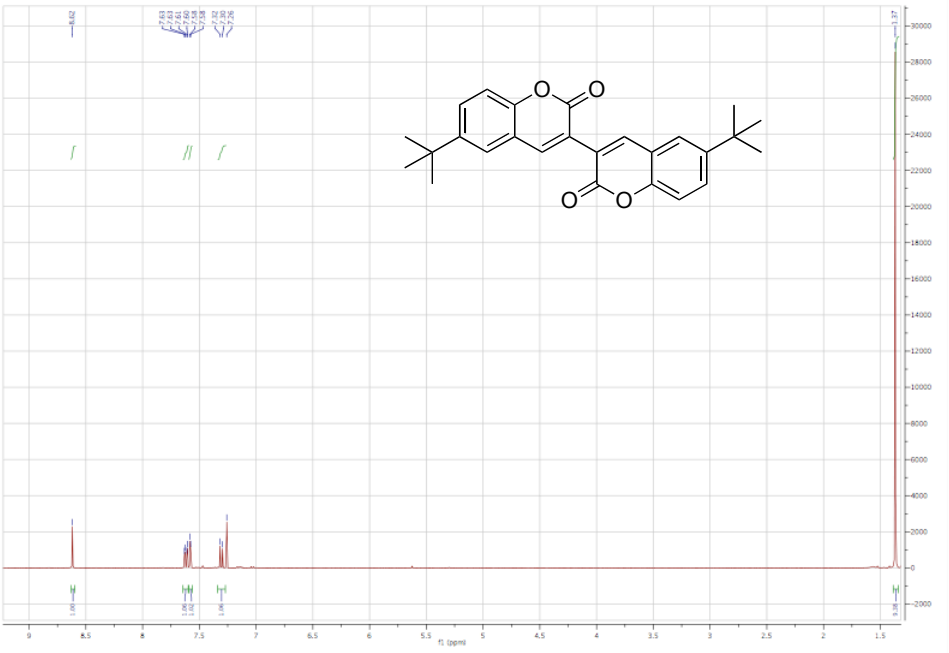
Benzo[*d*][1,3]dioxol-5-yl propiolate (**1f**):



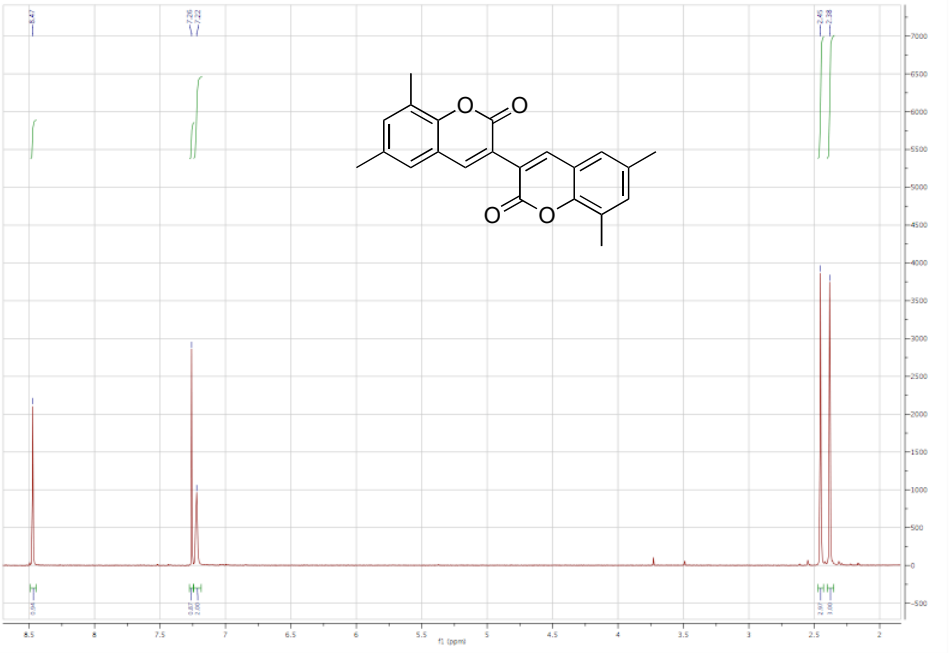
3-Methoxyphenyl propiolate (**1g**):



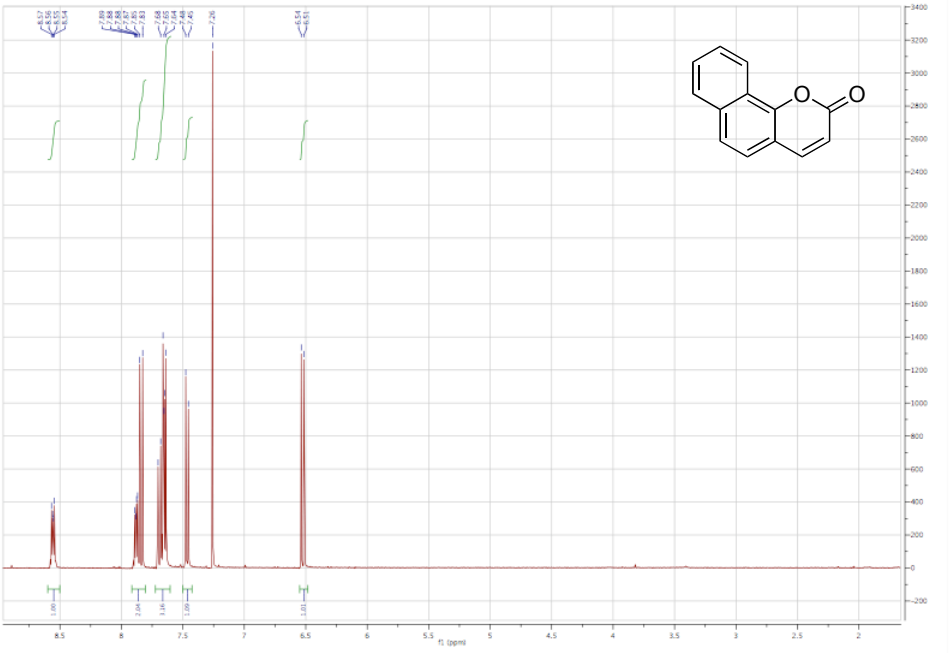
6,6'-Di-*tert*-butyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3a**):



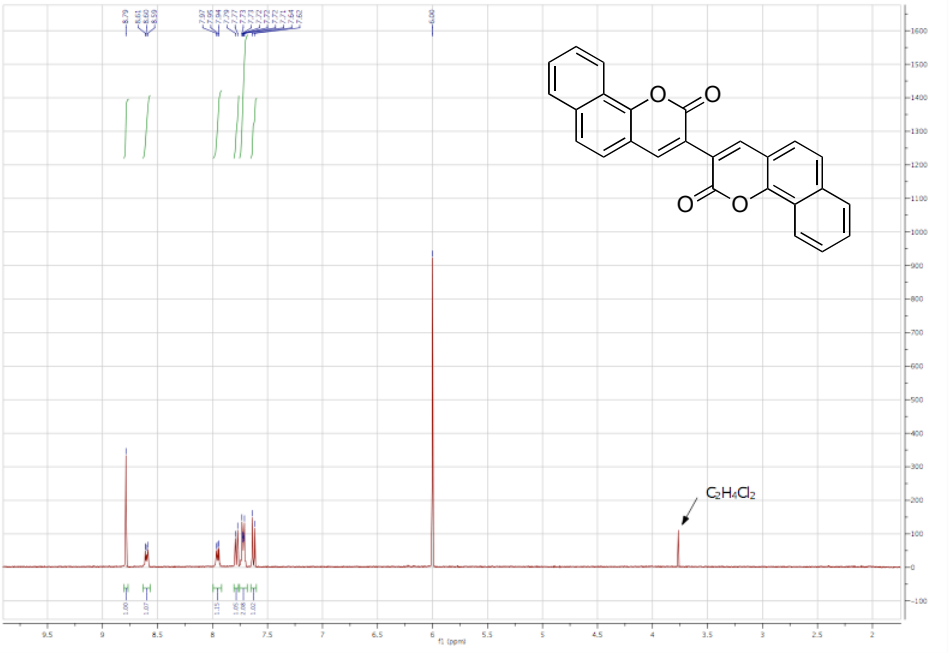
6,6',8,8'-Tetramethyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3c**):



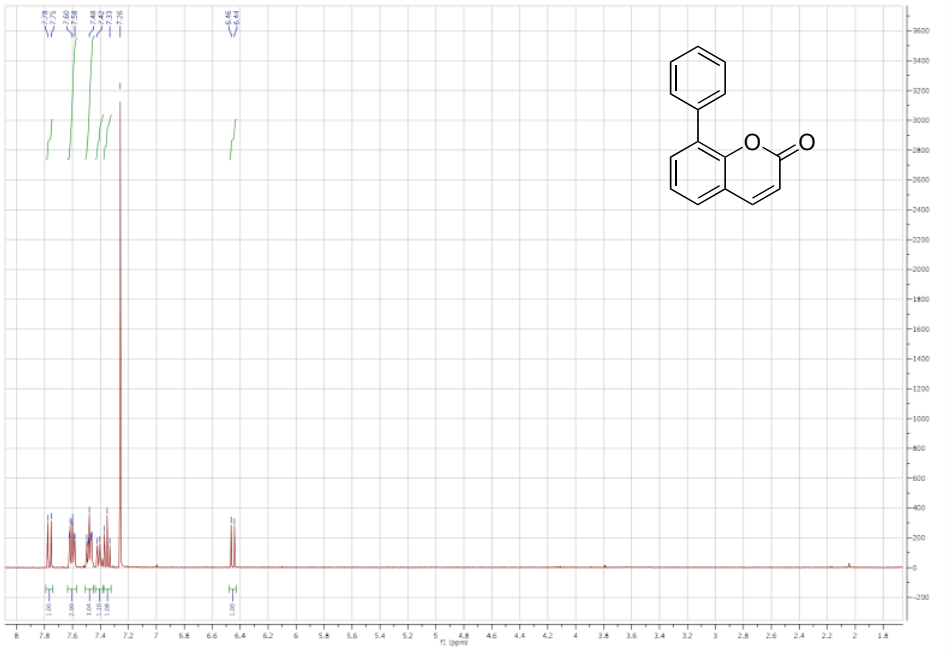
2*H*-Benzo[*h*]chromen-2-one (**2d**):



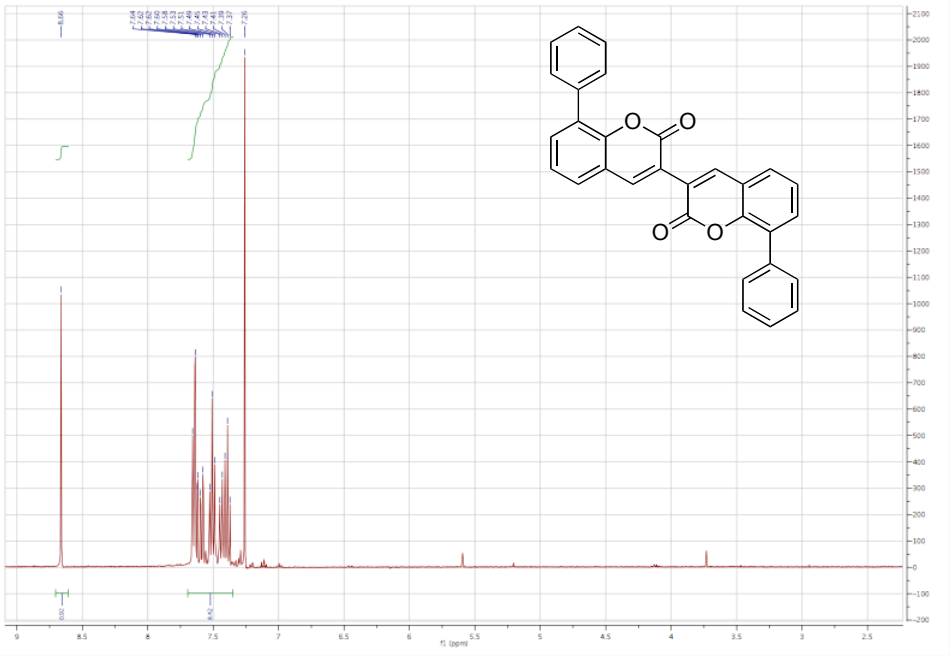
2*H*,2'*H*-3,3'-Bibenzo[*h*]chromene-2,2'-dione (**3d**) (in $C_2D_2Cl_4$):



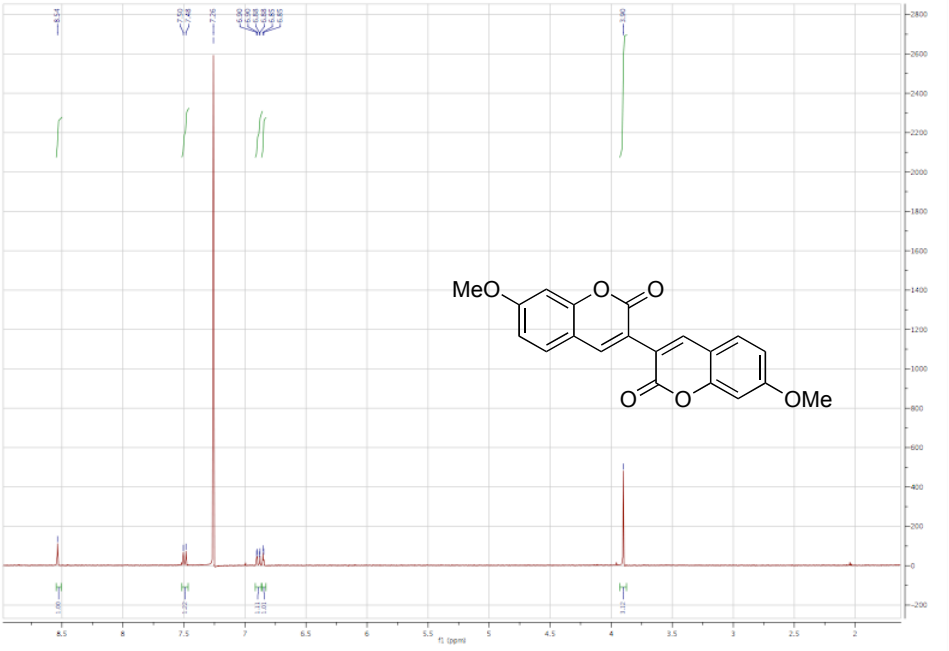
8-Phenyl-2*H*-chromen-2-one (**2e**):



8,8'-Diphenyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3e**):

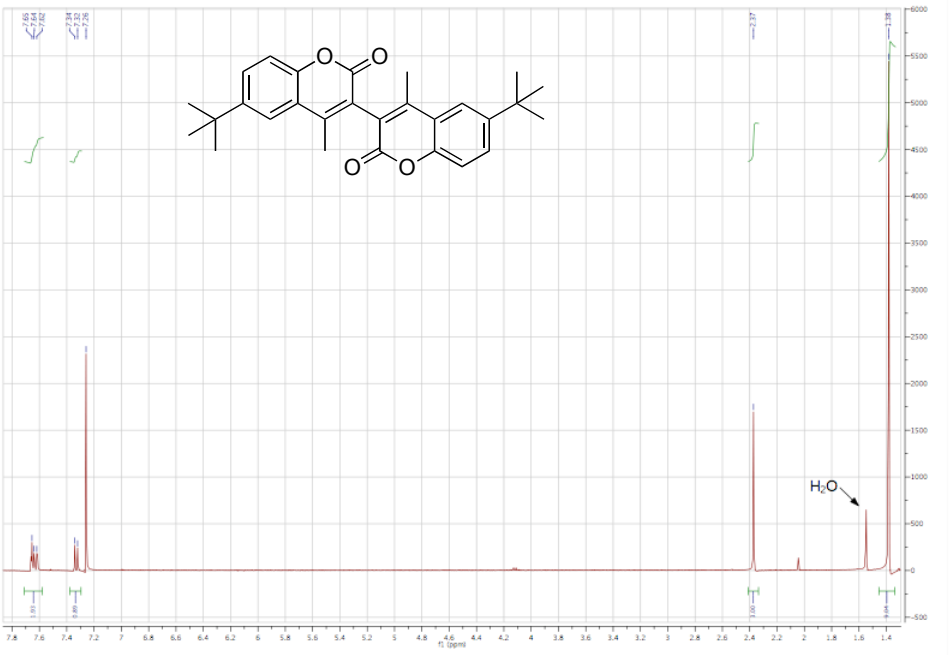


7,7'-Dimethoxy-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3g**):



6-(Benzyloxy)-2*H*-chromen-2-one (**2h**):

6,6'-Di-*tert*-butyl-4,4'-dimethyl-2*H*,2'*H*-3,3'-bichromene-2,2'-dione (**3j**):



[1] E. Bialecka-Florjanczyk, *Synth. Comm.* **2000**, *30*, 4417.

[2] H. Appel, F. Diem (Peroxid-Chemie GmbH), US 5488177, **1996**.

[3] C. Jia, D. Piao, T. Kitamura, Y. Fujiwara, *J. Org. Chem.* **2000**, *65*, 7516.

[4] Z. Shi, C. He, *J. Org. Chem.* **2004**, *69*, 3669.

[5] L. L. Woods, S. M. Shamma, *J. Chem. Eng. Data* **1970**, *15*, 355.

[6] Y. Liao, S. Hendrata, S. Y. Bae, B. Wang, *Chem. Pharm. Bull.* **2000**, *48*, 1138.

[7] B. M. Trost, F. D. Toste, K. Greenman, *J. Am. Chem. Soc.* **2003**, *125*, 4518.

[8] M. Kotani, K. Yamamoto, J. Oyamada, Y. Fujiwara and T. Kitamura, *Synthesis* **2000**, 1466.

[9] T. Kitamura, K. Yamamoto, K. Kotani, J. Oyamada and Y. Fujiwara, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1889.

[10] S. S. Lele, M. G. Patel, S. Sethna, *J. Chem. Soc.*, **1961**, 969.

[11] C. G. Jia,. D. G. Piao, J. Z. Oyamada, W. J. Lu, T. Kitamura, Y Fujiwara, *Science* **2000**, *287*, 1992.