Supporting Information

Efficient one-pot synthesis of 2,2-dimethyl-2*H*-chromenes via Pd(II)-catalyzed coupling and SiO₂-promoted condensation of *o*-halophenols with 2-methyl-3-buten-2-ol

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General

Chemical reagents were purchased from Aldrich, Acros and Merck and were used as received. Pressure tube was purchased from Ace Glassware (USA). NMR spectra were obtained using a Jeol ECA 400 (400 MHz) NMR spectrometer with TMS as the internal standard. All measurements were accomplished in solution in DMSO-*d*₆ or CDCl₃. Chemical shifts are reported in parts per million relative to CDCl₃ or TMS. Data for ¹H NMR are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants. All ¹³C NMR spectra were recorded with complete proton decoupling. Analytical thin layer chromatography (TLC) was carried out on Merck pre-coated aluminium silica gel sheets (Kieselgel 60 F₂₅₄). All products were purified by silica gel column chromatography using a hexane/EtOAc/chloroform eluent. All target compounds were characterized by ¹H NMR, ¹³C NMR and high resolution mass spectrographic (ESI) analyses. Compound **4a** (CAS registration number 2513-25-9), **4c** (CAS registration number 60986-49-4), **4d** (CAS registration number 30414-95-0), **4e** (CAS registration number 162335-02-6), **4i** (CAS registration number 157495-19-7) were known.

General procedure for the synthesis of 2,2-dimethyl-2*H*-chromenes.

A mixture of *o*-halophenol (1 equiv.), Pd(OAc)₂ (10 mol%), K₂CO₃ (3 equiv.), and 2-methyl-3-buten-2-ol (10 equiv.) in DMF (1 mL per mmol) in a pressure tube was heated to 140 °C for 6 ~ 8 h. The reaction was monitored by TLC until the starting material was completely consumed. Then, silica gel (20 equiv.) was added to the reaction mixture, followed by heating at 140 °C for another 4 ~ 16 h to give the desired 2,2-dimethyl-2*H*-chromenes.

8-chloro-2,2-dimethyl-2H-chromene-6-carbaldehyde (4f)

^1H NMR (400 MHz, CDCl_3): δ 9.79 (1H, s, CHO), 7.81 (1H, s, phenyl-H), 7.62 (1H, s, phenyl-H), 6.57 (1H, d, $J = 9.8$ Hz, -CH=), 5.95 (1H, d, $J = 10.1$ Hz, -CH=), 1.46 (6H, s, 2 x Me); ^{13}C NMR (100 MHz, CDCl_3): δ 190.5, 153.1, 132.5, 131.3, 130.1, 125.8, 122.5, 120.7, 120.6, 79.5, 28.1; HRMS calcd for $\text{C}_{12}\text{H}_{12}\text{ClO}_2$ $[\text{M}+\text{H}]^+ = 223.0518$. Found: 223.0512

methyl 2,2-dimethyl-2H-chromene-8-carboxylate (4g)

^1H NMR (400 MHz, CDCl_3): δ 7.47 (1H, dd, $J = 1.8, 7.9$ Hz, phenyl-H), 7.25 (1H, dd, $J = 1.8, 7.3$ Hz, phenyl-H), 6.89 (1H, t, $J = 7.6$ Hz, phenyl-H), 6.44 (1H, d, $J = 9.8$ Hz, -CH=), 5.83 (1H, d, $J = 10.1$ Hz, -CH=), 3.77 (3H, OMe), 1.38 (6H, s, 2 x Me); ^{13}C NMR (100 MHz, CDCl_3): δ 165.7, 152.0, 131.7, 130.0, 122.2, 121.5, 120.1, 119.2, 76.8, 51.7, 27.5; HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+ = 219.1022$. Found: 219.1021.

methyl-5,7-dimethoxy-2,2-dimethyl-2H-chromene-8-carboxylate (4h)

^1H NMR (400 MHz, CDCl_3): δ 6.48 (1H, d, $J = 9.8$ Hz, -CH=), 6.27 (1H, s, phenyl-H), 5.57 (1H, d, $J = 10.4$ Hz, -CH=), 3.84, 3.78, 3.72 (3H each, s, OMe), 1.30 (6H, s, 2 x Me); ^{13}C NMR (100 MHz, CDCl_3): δ 165.5, 157.3, 156.2, 150.9, 127.1, 115.8, 105.4, 103.2, 88.6, 76.4, 55.8, 51.7, 27.1; HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{O}_5$ $[\text{M}+\text{H}]^+ = 279.1224$. Found: 279.1223.

(*E*)-3-(2,4-dimethoxyphenyl)-1-(5-methoxy-2,2-dimethyl-2*H*-chromen-8-yl)prop-2-en-1-one (4j)

¹H NMR (400 MHz, CDCl₃): δ 7.72 (1H, d, *J* = 16.0 Hz, H_β), 7.56 (1H, d, *J* = 9.16 Hz, H_{5'}), 7.52-7.47 (2H, overlap, H_α, H_{6'}), 6.65 (1H, d, *J* = 9.16 Hz, H₆), 6.60-6.56 (3H, overlap, CH, H₃, H₅), 5.73 (1H, d, *J* = 10.1 Hz, -CH=), 3.83, 3.81, 3.80 (3H each, s, OMe), 1.40 (6H, s, 2 x Me); ¹³C NMR (100 MHz, CDCl₃): δ 189.7, 163.2, 160.3, 158.2, 153.0, 137.1, 131.6, 130.4, 129.9, 125.2, 122.0, 116.6, 110.3, 106.8, 104.6, 99.1, 77.2, 56.5, 56.3, 56.0, 27.9. HRMS calcd for C₂₃H₂₅O₅ [M+H]⁺ = 381.1703. Found: 381.1706.

^1H NMR 4f

^{13}C NMR 4f

^1H NMR 4g

^{13}C NMR 4g

^1H NMR 4h

^{13}C NMR 4h

^1H NMR 4j

^{13}C NMR 4j