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Citation for final published version:

Giorgi, Pascal D., Miedziak, Peter John, Edwards, Jennifer Kelly, Hutchings, Graham John and Antoniotti, Sylvain 2017. Bicatalytic multistep reactions en route to the one-pot total synthesis of complex molecules: easy access to chromene and 1,2-dihydroquinoline derivatives from simple substrates. ChemCatChem 9 (1), pp. 70-75. 10.1002/cctc.201600925 filefile

Publishers page: http://dx.doi.org/10.1002/cctc.201600925
<http://dx.doi.org/10.1002/cctc.201600925>

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Bicatalytic multistep reactions en route to the one-pot total synthesis of complex molecules: easy access to chromene and 1,2-dihydroquinoline derivatives from simple substrates.


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1. General information

$^1$H NMR and $^{13}$C NMR spectra were recorded on a BRUCKER AC 200 (200 MHz). $^1$H NMR spectra are reported as follows: chemical shift in ppm ($\delta$) relative to the chemical shift of CDCl$_3$ at 7.26 ppm or TMS at 0 ppm. Integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), and coupling constants (Hz). $^{13}$C NMR spectra chemical shift are reported in ppm ($\delta$) relative to CDCl$_3$ at 77.16 ppm. Column chromatography was carried out on silica gel (spherical 15-30 µm, neutral, 63–200 µm, Geduran Si 60, Merck KGaA). GC-TCD analyses were carried out using a Shimadzu QP2010 plus gas chromatograph, under the following operationz conditions: vector gas, He; injector temperature, 250 °C; detector temperature, 210 °C at 60 mA; split ratio, 1/20; total flow, 22.5 ml min$^{-1}$; Phenomenex Zebron ZB5MS column, polydimethylsiloxane (10 m, inside diameter 0.10 mm, film thickness 0.10 µm); temperature program, 80–200 °C at 10 °C min$^{-1}$ and 200 °C for 8 min. GC/MS analyses were performed by using a Shimadzu QP2010 gas chromatograph (conditions: carrier gas, He; injector and detector temperatures, 250 °C; injected volume, 0.5 µL; split ratio, 1/100; pressure, 180 kPa; SLB-5ms capillary column (thickness: 0.25 mm, length: 30 m, inside diameter: 0.25 mm); temperature program, 60–315 °C at 10 °C min$^{-1}$, and 10 min at 315 °C) coupled to a mass selective detector. Mass spectra were obtained by electron ionisation at 70 eV, m/z 35–400, source temperature 250 °C; only the most abundant ions are given. High resolution mass spectrometry (HRMS) was performed at ERINI platform (Grasse, FRANCE) using a Waters APGC coupled with a Waters Xevo G2 QTOF spectrometer. Screening reactions were performed in a Carousel 12 Plus parallel synthesizer purchased from Radleys.

Materials. Dimethyl formamide (DMF), tetrahydrofuran (THF), toluene, ppyrrolidine, methanol (MeOH), Ethanol (EtOH), and cyclohexane (CHX) were dried and/or distilled according to conventional procedures. $^1$Na$_2$CO$_3$, K$_2$CO$_3$, NaOH, H$_2$SO$_4$, sodium hydride, tert-butyl hydroperoxide (TBHP), dimethyl sulfate, 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) and diisobutyl aluminium hydride were purchased (Aldrich) and used as received.
2. TEM Analysis of catalysts A-D / Screening reaction conditions

Schema a: TEM of catalyst A (Au NPs/TiO$_2$ - AUROlite$^\text{®}$).

Schema b: TEM of catalyst B (Au NPs/Al$_2$O$_3$ - AUROlite$^\text{®}$).

Schema c: TEM of catalyst C (Au NPs/TiO$_2$ - AUROlite$^\text{®}$).
[¥]: Transmission electron microscopy (TEM) was carried out using a Jeol 2100 with a LaB$_6$ filament operating at 200KV. Samples were prepared by dispersing the powder catalyst in ethanol and dropping the suspension onto a lacey carbon film over a 300 mesh copper grid.
3. Preparation of starting materials allylic alcohol (6a) and (7a)

Ethyl (E)-3-(4-hydroxy-3-methoxyphenyl)propanoate (A). A 50 mL dried round-bottom flask equipped with a stir bar was cooled to 0 °C. Ferrulic acid (2.0 g, 1.0 equiv., 10.29 mmol) and anhydrous EtOH (25 mL, 0.41 M) were added, followed by dropwise addition of H₂SO₄ (414 μL, 1.5 equiv.). The mixture was slowly warmed to 50 °C and stirred for 12 hours. After completion of the reaction monitored by TLC, the reaction was carefully quenched with saturated Na₂CO₃(aq) solution at 0 °C and DCM (30 mL) was added. The layers were separated and the aqueous phase was further extracted with DCM (3x30 mL). The organic extracts were dried over MgSO₄, filtered and evaporated under reduced pressure. The product was purified by silica gel chromatography using 10/90 EtOAc/CHX to 40/60 EtOAc/CHX gradient, affording desired compound as a white oil (75 %). Analytical data: ¹H NMR (CDCl₃, 200 MHz) δ (ppm) 7.59 (d, J=16 Hz, 1H), 7.00 (m, 2H), 6.88 (d, J=8 Hz, 1H), 6.36 (d, J=16 Hz, 1H), 4.23 (q, J=6 Hz, 2H), 3.85 (s, 3H), 1.30 (t, J=6 Hz, 3H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 167.3, 147.9, 146.8, 144.7, 127.0, 123.0, 115.6, 114.7, 109.3, 60.3, 55.9, 14.3. MS (EI, 70 eV) m/z 222.2 (100), 44.1 (87), 150.2 (83).
Ethyl (E)-3-(3,4-dimethoxyphenyl)propanoate (B). To 50 mL dried round-bottom flask equipped with a reflux condenser and a dropping funnel were introduced carefully, ethyl (E)-3-(4-hydroxy-3-methoxyphenyl)propanoate (850 mg, 3.82 mmol), sodium hydroxide (184 mg, 1.27 equiv., 4.84 mmol), anhydrous MeOH (20 mL, 0.19 M), and dimethyl sulfate (734 µL, 2 equiv., 7.68 mmol). The reaction mixture was then refluxed for 2 hours and after completion of the reaction monitored by TLC, the reaction mixture was cooled to room temperature, quenched with saturated NH₄Cl(aq.) solution (20 mL) and extracted with diethyl ether (3x30 mL). The pooled extracts were dried over MgSO₄, filtered and evaporated under reduced pressure. The product was purified by silica gel chromatography using 10/90 EtOAc/CHX to 40/60 EtOAc/CHX gradient, giving the corresponding compound as a yellow pale oil (82 %). Analytical data: ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.51 (d, J=16 Hz, 1H), 6.93-7.00 (m, 2H), 6.73 (d, J=8 Hz, 1H), 6.19 (d, J=16 Hz, 1H), 4.13 (q, J=6 Hz, 2H), 3.78 (s, 6H), 1.21 (t, J=8 Hz, 3H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 166.9, 150.9, 149.0, 144.3, 127.2, 122.3, 115.7, 110.8, 109.4, 60.1, 55.7, 55.6, 14.1. MS (El, 70 eV) m/z 236.0 (100), 191.0 (65), 164.1 (53).
Ethyl (E)-3-(4-(benzoyloxy)-3-methoxyphenyl)propanoate (C). To a 25 mL dried round-bottom flask at 0 °C, ethyl (E)-3-(4-hydroxy-3-methoxyphenyl)propanoate (500 mg, 1.60 mmol), sodium hydride (60 % oil dispersed) (70.4 mg, 1.76 mmol) and fresh distilled DMF (5 mL, 0.32 M) were added at once. The reaction mixture was slowly warmed to room temperature and stirred for 5 hours. After completion of the reaction monitored by TLC, the reaction was quenched with saturated NH₄Cl(aq.) solution (15 mL) at 0 °C, and the aqueous phase was extracted with DCM (3x10 mL), and pooled organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure, prior a purification via silica gel was carrying out using 0/100 Ether/PE to 20/80 Ether/PE gradient, affording the desired compound as a colorless oil (95%).

**Analytical data:** ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.53 (d, J=16 Hz, 1H), 7.23-7.36 (m, 5H), 6.91-6.98 (m, 2H), 6.77 (d, J=8 Hz, 1H), 6.24 (d, 1H), 5.09 (s, 2H), 4.17 (q, J=8 Hz, 2H), 3.82 (s, 3H), 1.24 (t, J=8 Hz, 3H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 167.1, 150.1, 149.7, 144.0, 136.5, 128.5, 127.9, 127.7, 127.1, 122.3, 116.0, 113.3, 110.1, 70.8, 60.3, 55.9, 14.3. MS (El, 70 eV) m/z 91.0 (100), 312.1 (9), 92.1 (8). HRMS calcd for exact mass C₁₉H₂₀O₄ 312.1362, found 312.1361, Δ=0.1 ppm.
(E)-3-(3,4-dimethoxyphenyl)prop-2-en-1-ol (6a). To a 25 mL dried round-bottom flask at 0°C under nitrogen atmosphere containing ethyl (E)-3-(3,4-dimethoxyphenyl)propanoate (500 mg, 2.1 mmol), a diisobutylaluminium hydride solution (4.66 mL, 2.2 equiv., 4.66 mmol) was added dropwise in THF (6 mL). After stirring for 3 hours the reaction mixture was treated with saturated NH₄Cl(aq.) solution (10 mL) and let stirred for 1 more hour. After completion of the reaction, monitored by TLC, the mixture was warmed to room temperature, extracted with EtOAc (3×5 mL) and the pooled organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure, prior a purification via silica gel was carrying out using 30/70 EtOAc/CHX to 40/60 EtOAc/CHX gradient, affording the desired compound as a colorless solid (75%).

Analytical data (6a): ¹H NMR (200 MHz, CDCl₃) δ (ppm) 6.68-6.83 (m, 3H), 6.43 (d, J=16 Hz, 1H), 6.06-6.20 (m, 1H), 4.20 (d, J=6 Hz, 2H), 3.78 (d, 6H), 2.32 (b, 1H).

¹³C NMR (50 MHz, CDCl₃) δ (ppm) 148.8, 148.7, 130.7, 129.7, 126.5, 119.5, 111.0, 108.8, 63.4, 55.7, 26.7.

MS (EI, 70 eV) m/z 151.1 (100), 194.1 (59), 138.1 (57). HRMS calcld for exact mass C₁₁H₁₄O₃ 194.0943, found 194.0950, ∆=0.7 ppm.
To a 25 mL dried round-bottom flask at 0°C under nitrogen atmosphere containing ethyl \((E)-3-(4-(benzyloxy)-3-methoxyphenyl)propanoate\) (600 mg, 1.92 mmol), a diisobutylaluminium hydride solution (4.27 mL, 4.27 mmol, 2.2 equiv) was added dropwise in THF (5.5 mL). After stirring for 3 hours the reaction mixture treated was saturated \(\text{NH}_4\text{Cl}_{(aq)}\) solution (10 mL) and let stirred for 1 more hour. After completion of the reaction, monitored by TLC, the mixture was warmed to room temperature, extracted with EtOAc (3×5 mL) and pooled organic layers were dried over \(\text{MgSO}_4\), filtered and evaporated under reduced pressure, prior a purification via silica gel was carried out using 30/70 \(\text{EtOAc/CHX}\) to 40/60 \(\text{EtOAc/CHX}\) gradient, affording the desired compound as a colorless solid (69%).

**Analytical data:**

\(^1\text{H NMR} (200 \text{ MHz, CDCl}_3) \delta (ppm)\) 7.16-7.33 (m, 5H), 6.81 (s, 1H), 6.69 (s, 2H), 6.37 (d, \(J=16 \text{ Hz, 1H})\), 6.03-6.14 (m, 1H), 4.99 (s, 2H), 4.12 (d, \(J=6 \text{ Hz, 2H})\), 3.73 (s, 3H), 2.38 (b, 1H).

\(^{13}\text{C NMR} (50 \text{ MHz, CDCl}_3) \delta (ppm)\) 149.4, 147.8, 136.8, 130.6, 130.2, 128.3, 127.7, 127.1, 126.7, 119.3, 113.7, 109.4, 70.8, 63.3, 55.7.

**MS** (EI, 70 eV) \(m/z\) 91.1 (100), 43.9 (29), 270.1 (6).

**HRMS** calcd for exact mass \(\text{C}_{17}\text{H}_{18}\text{O}_3\) 270.1256, found 270.1257, \(\Delta=0.1 \text{ ppm}\).
4. Procedures for the cascade Oxidation / Hetero Michael / Aldolisation reaction.

**Method A:** To a dried reactor under O\textsubscript{2} atmosphere, catalyst B (0.08 mmol, 0.08 equiv.), tert-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous THF (2.0 mL, 0.5 M) and prenol (1 mmol, 1.0 equiv.) were added. The solution was stirred at 60 °C for 8 h. Salicylaldehyde (1.2 mmol, 1.2 equiv.) and TBD (0.3 mmol, 0.3 equiv.) and 3 Å molecular sieves (50 mg) were then added at once and the reaction mixture was stirred for 15 hours at room temperature. After completion of the reaction monitored by TLC, the reactor was quenched with NH\textsubscript{4}Cl (aq.) solution (5 mL) extract with DCM solution (3x5 mL) filtered through a celite pad further eluted with DCM (5 mL). The layers were separated and the residual organic phase was washed with brine further extracted with more DCM (3x5 mL), prior being concentrated in vacuo. The crude residue was then purified via silica-gel column chromatography using a 30-50% diethyl ether/petroleum ether gradient solvent, affording the corresponding chromene.

**Method B:** To a dried reactor under O\textsubscript{2} atmosphere, catalyst B (0.08 mmol, 0.08 equiv.), tert-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous toluene (2.0 mL, 0.5 M) and allylic alcohol (1 mmol, 1.0 equiv.) were added. The solution was stirred at 80 °C for 8 h. Salicylaldehyde (1.2 mmol, 1.2 equiv.) and K\textsubscript{2}CO\textsubscript{3} (1.2 mmol, 1.2 equiv.) in anhydrous MeOH (500 mL) were then added at once and the reaction mixture was stirred for 18 hours at rt. After completion of the reaction monitored by TLC, the reactor was cooled down to room temperature, quenched with NH\textsubscript{4}Cl (aq.) solution (50 mL) extract with DCM solution (3x10 mL) filtered through a celite pad further eluted with DCM (5 mL). The layers were separated and the residual organic phase was washed with brine further extracted with more DCM (3x5 mL), prior being concentrated in vacuo. The crude residue was then purified via silica-gel column chromatography using a 30-50% diethyl ether/petroleum ether gradient solvent, affording the corresponding chromene.

**Method C:** To a dried reactor under O\textsubscript{2} atmosphere, catalyst B (0.08 mmol, 0.08 mol%), tert-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous THF (2.0 mL, 0.5 M) and allylic alcohol (1 mmol, 1.0 equiv.) were added. The solution was stirred at 60 °C for 8 h. Salicylaldehyde (1.2 mmol, 1.2 equiv.), pyrrolidine (0.3 mmol, 0.3 equiv.) and 3 Å molecular sieves (50 mg) were then added at once and the reaction mixture was stirred for 15-21 hours at rt. After completion of the reaction monitored by TLC, the reaction mixture diluted with DCM (10 mL), filtered through a short celite pad and eluted with DCM (10 mL). The resulting organic crude mixture was treated with a saturated NH\textsubscript{4}Cl(aq.) solution (20 mL), extracted with DCM (3x10 mL) and concentrated in vacuo, prior a purification via silica-gel chromatography using 20-40% Et\textsubscript{2}OAc/CH\textsubscript{3}OH gradient solvent, affording the corresponding 2H-chromene / dihydroquinoline.
2,2-dimethyl-2H-chromene-3-carbaldehyde (2c). Method A was used to obtain 2c. Prenol (102 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), anhydrous THF (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), TBD (14 mg, 10 mol%), 3Å MS (50 mg) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow dark oil (59). **Analytical data:** ¹H NMR (200 MHz, CDCl₃) δ (ppm) 9.39 (s, 1H), 7.08-7.22 (m, 2H), 7.03 (s, 1H), 6.73-6.88 (m, 2H), 1.55 (s, 6H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 190.3, 154.3, 142.4, 139.1, 133.5, 128.8, 121.2, 119.6, 116.8, 78.6, 26.7. MS (EI, 70 eV) m/z 173.1 (100), 115.1 (57), 188.1 (4). **HRMS** calcd for exact mass C₁₂H₁₃O₂ (M+H)⁺ 189.0916 found 189.0915 Δ=0.1 ppm.
2-methyl-2-(4-methylpent-3-enyl)-2H-chromene-3-carbaldehyde (3c).

**Method B** was used to obtain 3c. Nerol (181 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), anhydrous toluene (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), K$_2$CO$_3$ (169 mg, 1.2 equiv.), MeOH (500 mL) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow brown oil (60 %). **Analytical data:** $^1$H NMR (200 MHz, CDCl$_3$) δ (ppm) 9.58 (s, 1H), 7.37-7.44 (m, 1H), 7.28 (s, 2H), 6.91-7.04 (m, 2H), 5.19 (t, J=12 Hz, 9H). $^{13}$C NMR (50 MHz, CDCl$_3$) (contaminated with small amounts of the corresponding 4-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-chromane-3-carbaldehyde formed after purification) δ (ppm) 13C NMR (50 MHz, CDCl$_3$) δ 190.2, 153.8, 141.5, 138.8, 135.9, 132.1, 131.0, 123.8, 121.1, 118.5, 112.8, 81.9, 39.1, 26.0, 25.7, 23.1, 17.7. **MS** (EI, 70 eV) m/z 173.1 (100), 174.1 (37), 256.1 (4). **HRMS** calcd for exact mass C$_{17}$H$_{20}$O$_2$ 256.1463 found 256.1464 Δ=0.1 ppm.
6-methoxy-2-methyl-2-(4-methylpent-3-enyl)-2H-chromene-3-carbaldehyde (3e). Method B was used to obtain 3e. Nerol (181 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M), 2-hydroxy-5-methoxybenzaldehyde (150 µL, 1.2 equiv., 1.2 mmol), K$_2$CO$_3$ (169 mg, 1.2 equiv.), MeOH (500 mL) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow dark oil (60 %). Analytical data: $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ (ppm) 9.39 (s, 1H), 7.03 (s, 1H), 6.63-6.70 (m, 3H), 5.01 (tb, 1H), 3.71 (s, 3H), 1.70-2.17 (m, 4H), 1.56 (s, 3H), 1.47 (s, 3H), 1.45 (s, 3H). $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ (ppm) 190.3, 153.8, 148.7, 143.2, 138.6, 131.7, 123.9, 119.8, 119.7, 117.4, 112.5, 80.9, 55.8, 38.7, 25.6, 25.3, 23.0, 17.6. MS (EI, 70 eV) m/z 207.1 (100), 286.0 (49), 138.1 (44). HRMS calcd for exact mass C$_{18}$H$_{22}$O$_3$ 286.1569, found 286.1579, $\Delta$=3.5 ppm.
6-Bromo-2-methyl-2-(4-methylpent-3-en-1-yl)-2H-chromene-3-carbaldehyde (3g). Method B was used to obtain 3g. Nerol (181 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M), 5-Bromosalicylaldehyde (240 mg, 1.2 equiv., 1.2 mmol), K$_2$CO$_3$ (169 mg, 1.2 equiv.), MeOH (500 mL) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow-brown oil (65%). Analytical data: $^1$H NMR (200 MHz, CDCl$_3$) δ (ppm) 9.39 (s, 1H), 7.27-7.32 (dd, $^J_3$=10 Hz, $^J_4$=2 Hz, 1H), 7.26 (s, 1H), 6.98(s, 1H), 6.63 (d, $^J_3$=8 Hz, 1H), 4.98 (tb, 1H), 1.69-2.13 (m, 4H), 1.56 (s, 3H), 1.49 (s, 3H), 1.44 (s, 3H). $^{13}$C NMR (50 MHz, CDCl$_3$) (contaminated with small amounts of the corresponding 6-bromo-4-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-chromene-3-carbaldehyde formed after purification) δ (ppm) 190.2, 153.8, 141.5, 138.8, 135.9, 132.1, 131.0, 123.8, 121.1, 118.5, 112.8, 81.9, 39.1, 26.0, 25.7, 23.1, 17.7. HRMS calcd for exact mass C$_{17}$H$_{19}$O$_2$Br 334.0568, found 334.0566, Δ=0.6 ppm.
2,6-methyl-2-(4-methylpent-3-enyl)-2H-chromene-3-carbaldehyde (3h). Method C was used to obtain 3h. Nerol (181 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M), 2-hydroxy-5-methylbenzaldehyde (163 mg, 1.2 equiv., 1.2 mmol), K$_2$CO$_3$ (169 mg, 1.2 equiv.), MeOH (500 mL) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow pale solid (38 %). Analytical data: $^1$H NMR (200 MHz, CDCl$_3$) δ (ppm) 9.58 (s, 1H), 7.37-7.44 (m, 1H), 7.28 (s, 2H), 6.91-7.04 (m, 2H), 5.19 (tb, 1H), 1.82-2.38 (m, 4H), 1.70 (t, J=12 Hz, 9H). $^{13}$C NMR (50 MHz, CDCl$_3$) δ (ppm) 190.3, 156.6, 152.5, 143.8, 137.9, 134.3, 131.7, 130.2, 128.9, 123.9, 119.1, 116.3, 81.0, 38.9, 25.6, 23.0, 20.3, 17.5. MS (EI, 70 eV) m/z 207.1 (100), 270.1 (59), 149.2 (56).
2-(4,8-dimethylnona-3,7-dienyl)-2-methyl-2H-chromene-3-carbaldehyde (4c). Method B was used to obtain 4c. *Trans,trans* farnesol (250 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), anhydrous toluene (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), K₂CO₃ (169 mg, 1.2 equiv.), MeOH (500 mL) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow-brown oil (58%). **Analytical data:** ¹H NMR (200 MHz, CDCl₃) δ (ppm) 9.66 (s, 1H), 7.39-7.47 (m, 1H), 7.23 (m, 2H), 6.93-7.07 (m, 2H), 5.27 (qb, 2H), 2.10-2.48 (m, 7H), 1.76-1.78 (m, 5H), 1.72 (s, 6H), 1.40 (s, 3H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 190.3, 154.8, 143.3, 143.3, 137.9, 135.4, 133.5, 131.3, 128.8, 124.3, 123.7, 121.0, 119.3, 116.6, 81.3, 39.6, 39.0, 31.8, 26.6, 25.8, 22.9, 17.6, 15.9. **MS** (EI, 70 eV) m/z 173.1 (100), 174.1 (57), 324.1 (4). **HRMS** calcd for exact mass C₂₂H₂₈O₂ 324.2089 found 324.2078 Δ=1.1 ppm.
6-Bromo-2-(4,8-dimethylnona-3,7-dienyl)-2-methyl-2H-chromene-3-carbaldehyde (4g). Method B was used to obtain 4g. *Trans,trans* farnesol (250 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), anhydrous toluene (2 mL, 0.5 M), 5-bromosalicyaldehyde (241 mg, 1.2 equiv., 1.2 mmol), K$_2$CO$_3$ (169 mg, 1.2 equiv.), MeOH (500 mL) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow oil (64%). **Analytical data:** ¹H NMR (200 MHz, CDCl$_3$) δ (ppm) 9.39 (s, 1H), 7.28 (dd, J=2.4 Hz, J=8.6 Hz, 1H), 7.20 (d, J=2.44 Hz, 1H), 6.98 (s, 1H), 6.63 (d, J=8.6 Hz, 1H), 4.99 (m, 2H), 2.30-1.65 (m, 8H), 1.59 (s, 3H), 1.51 (s, 3H), 1.49 (s, 3H), 1.44 (s, 3H). ¹³C NMR (50 MHz, CDCl$_3$) δ (ppm) 190.2, 153.8, 141.5, 138.8, 136.0, 135.7, 131.5, 131.0, 124.4, 123.58, 121.1, 118.5, 112.8, 82.0, 39.7, 39.1, 26.8, 26.0, 25.8, 23.0, 17.8, 16.0. MS (EI, 70 eV) m/z 404(2), 402(2), 254(24), 253(38), 252(25), 251(36), 144(12), 115(18), 69(80), 53(11), 41(100).
Method C was used to obtain 5c. Cinnamyl alcohol 5a (134 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) at 60 °C under an oxygen atmosphere, yielded the desired compound as a yellow dark oil (90 %). **Analytical data: **\(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) (ppm) 9.57 (s, 1H), 7.15-7.38 (m, 8H), 6.77-6.91 (m, 2H), 6.26 (s, 1H). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) (ppm) 189.9, 154.7, 140.8, 139.1, 133.7, 133.7, 129.3, 128.6, 128.5, 126.7, 121.7, 120.0, 117.1, 74.2. **MS** (EI, 70 eV) m/z 207.1 (100), 236.0 (59), 178.1 (44).
2-Phenyl-1,2-dihydroquinoline-3-carbaldehyde (5d). **Method C** was used to obtain 5d. Cinnamyl alcohol (134 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), 2-aminobenzaldehyde (145.2 mg, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) at 60 °C under an oxygen atmosphere, yielded the desired compound as a red crystal (93 %). **Analytical data:** \(^{1}H\) NMR (200 MHz, CDCl\(_3\)) \(\delta\) (ppm) 9.38 (s, 1H), 7.02-7.32 (m, 8H), 6.57 (t, 1H), 6.38 (d, 1H), 5.58 (s, 1H), 4.53 (sb, 1H). \(^{13}C\) NMR (50 MHz, CDCl\(_3\)) \(\delta\) (ppm) 190.9, 145.5, 144.3, 143.3, 133.4, 130.1, 128.8, 127.9, 127.6, 126.0, 117.8, 117.4, 113.3, 53.5. **MS** (EI, 70 eV) m/z 234.1 (100), 103.1 (63), 235.1 (61). **HRMS** calcd for exact mass C\(_{16}\)H\(_{13}\)NO (M+H)\(^+\) 235.0997 found 235.0994 \(\Delta=0.3\) ppm.
Method C was used to obtain 5e. Cinnamyl alcohol (134 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2mL, 0.5 M), 2-hydroxy-5-methoxybenzaldehyde (150 µL, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) at 60 °C under an oxygen atmosphere, yielded the desired compound as a yellow pale solid (72 %). Analytical data: $^1$H NMR (200 MHz, CDCl$_3$) δ (ppm) 9.57 (s, 1H), 7.18-7.29 (m, 6H), 6.70-6.78 (m, 2H), 6.22 (s, 1H), 3.69 (s, 3H). $^{13}$C NMR (50 MHz, CDCl$_3$) δ (ppm) 190.0, 154.2, 148.7, 140.9, 138.8, 134.3, 128.5, 128.5, 126.7, 120.4, 119.8, 117.9, 112.9, 73.8, 55.7. MS (EI, 70 eV) m/z 266.0 (100), 237.5 (43), 40.8 (22). HRMS calcd for exact mass C$_{17}$H$_{14}$O$_3$ 266.0943, found 266.0946, Δ=1.1 ppm.
6-(Carboxymethyl)-2-phenyl-2H-chromene-3-carbaldehyde (5f).

Method C was used to obtain 5f with cinnamyl alcohol (134 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), methyl 3-formyl-4-hydroxybenzoate (240 mg, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) at 60 °C under an oxygen atmosphere, yielded the desired compound as an orange solid (52 %).

Analytical data: $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ (ppm) 9.58 (s, 1H), 7.90 (m, 2H), 7.37 (s, 1H), 7.30-7.10 (m, 5H), 6.82 (d, $J$=9 Hz, 1H), 6.31 (s, 1H), 3.83 (s, 3H). $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ (ppm) 189.9, 166.2, 158.6, 139.7, 138.7, 135.1, 134.2, 131.3, 129.1, 128.8, 126.9, 124.0, 119.6, 117.3, 75.4, 52.3. MS (EI, 70 eV) m/z 265.0 (100), 294.0 (49), 178.0 (32), 293.0 (25).
6-Bromo-2-phenyl-2H-chromene-3-carbaldehyde (5g). **Method C** was used to obtain 5g with cinnamyl alcohol (134 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), 5-bromosalicylaldehyde (240 mg, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) at 60 °C under an oxygen atmosphere, yielded the desired compound as an orange solid (52%). **Analytical data:** $^1$H NMR (200 MHz, CDCl$_3$) δ (ppm) 9.58 (s, 1H), 7.15-7.31 (m, 8H), 6.77 (d, $J$=10 Hz, 1H), 6.25 (s, 1H). $^{13}$C NMR (50 MHz, CDCl$_3$) δ (ppm) 189.7, 153.7, 139.1, 138.4, 136.0, 134.5, 131.4, 128.8, 126.7, 121.7, 119.0, 113.6, 74.4. MS (EI, 70 eV) m/z 285.1 (100), 287.1 (99), 314.0 (55). HRMS calcd for exact mass C$_{16}$H$_{11}$BrO$_2$ 313.9942, found 313.9940, Δ=0.6 ppm.
2-(3,4-dimethoxyphenyl)-2H-chromene-3-carboxaldehyde (6c). **Method C** was used to obtain 6c. 6a (196 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) at 60 °C under an oxygen atmosphere, yielded the desired compound as a yellow oil (86%). **Analytical data:** $^1$H NMR (200 MHz, CDCl$_3$) δ (ppm) 9.58 (s, 1H), 7.37 (s, 1H), 7.20 (d, J=8 Hz, 2H), 6.68-6.87 (m, 5H), 6.21 (s, 1H), 3.74 (s, 6H). $^{13}$C NMR (50 MHz, CDCl$_3$) δ (ppm) 190.0, 156.7, 154.7, 149.3, 148.9, 140.7, 133.8, 133.6, 131.4, 129.2, 121.7, 120.0, 119.1, 117.2, 110.7, 110.2, 74.1, 55.7. **MS** (El, 70 eV) m/z 267.1 (100), 296.1 (33), 268.1 (13). **HRMS** calcd for exact mass C$_{18}$H$_{16}$O$_4$ 296.1049, found 296.1051, Δ=0.2 ppm.
2-(3,4-dimethoxyphenyl)-1,2-dihydroquinoline-3-carbaldehyde (6d).

Method C was used to obtain 6d. 6a (196 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), 2-aminobenzaldehyde (145.2 mg, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) at 60 °C under an oxygen atmosphere, yielded the desired compound as a dark red solid (79 %). Analytical data: $^1$H NMR (200 MHz, CDCl$_3$) δ (ppm) 9.41 (s, 1H), 7.16 (s, 1H), 7.03-7.07 (m, 2H), 6.84 (m, 2H), 6.54-6.86 (m, 2H), 6.42 (d, $J$=4 Hz, 1H), 5.54 (d, $J$=2 Hz, 1H), 4.56 (b, 1H), 3.73 (s, 3H), 3.69 (s, 3H). $^{13}$C NMR (50 MHz, CDCl$_3$) δ (ppm) 190.6, 148.9, 148.6, 145.6, 143.1, 137.3, 133.5, 133.3, 130.0, 118.0, 117.8, 117.4, 113.3, 111.0, 109.3, 55.8, 55.7, 53.1. MS (EI, 70 eV) m/z 293.1 (100), 158.0 (62), 295.1 (20). HRMS calcd for exact mass C$_{18}$H$_{17}$NO$_3$ 295.1208, found 295.1206, Δ=0.7 ppm.
2-(4-(benzyloxy)-3-methoxyphenyl)-2H-chromene-3-carbaldehyde (7c). General procedure method C was used to obtain 7c. 7a (270 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) at 60 °C over oxygen atmosphere, yield the desired compound as a yellow dark solid (91 %). Analytical data (3h): ¹H NMR (200 MHz, CDCl₃) δ (ppm) 9.55 (s, 1H), 7.15-7.33 (m, 8H), 6.66-6.88 (m, 5H), 6.19 (s, 1H), 5.01 (s, 2H), 3.74 (s, 3H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 190.0, 154.8, 149.47, 148.5, 140.7, 137.0, 133.7, 133.6, 132.0, 129.2, 128.5, 127.8, 127.1, 121.7, 120.0, 119.0, 117.1, 113.3, 110.8, 74.0, 70.8, 55.9. Mass spectrum (EI, 70 eV) m/z (% relative intensity) 91.1 (100), 207 (39), 372 (10).
5. Procedure D for the synthesis of dihydroquinoline 5d in one-pot from simple precursors.

Method D: To a dried reactor under O<sub>2</sub> atmosphere, catalyst B (0.08 mmol, 0.08 equiv.), tert-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous THF (2.0 mL, 0.5 M) and 5a cinnamyl alcohol (1 mmol, 1.0 equiv.) were added. The solution was stirred at 60 °C for 8 h. 2-Aminobenzyl alcohol (1.0 mmol, 1 equiv.) was added to the reaction mixture and let stirred for 8 more hours. Pyrrolidine (0.3 mmol, 30 mol%) and 3 Å molecular sieves (50 mg) were then added at once and the reaction mixture was stirred at 60 °C for 15 hours at rt. After completion of the reaction monitored by TLC, the reactor was quenched with NH<sub>4</sub>Cl (aq.) solution (5 mL) extract with DCM solution (3x5 mL) filtered through a celite pad further eluted with DCM (5 mL). The layers were separated and the residual organic phase was washed with brine further extracted with more DCM (3x5 mL), prior being concentrated in vacuo. The crude residue was then purified via silica-gel column chromatography using a 10-40% diethyl ether/petroleum ether gradient solvent, affording the corresponding dihydroquinoline 5d.
6. **Procedure E** for the oxidation of alcohols over supported gold nanoparticles Au SNPs/M$_x$O$_y$.

**Method E**: To a dried schlenk under O$_2$ atmosphere, catalyst (0.08 mmol, 0.08 equiv.), tert-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous solvent (2.0 mL, 0.5 M) and allylic alcohol (1 mmol, 1.0 equiv.) were added. The solution was kept under a vigorous stirring for 8 h. After completion of the reaction monitored by TLC or GC/TCD UV detector, DCM was added (10 mL) and the mixture filtered through a celite pad, further eluted with DCM (5 mL). The organic phase was then washed with brine further extracted with more DCM (3x5 mL), prior being concentrated in vacuo. The crude residue was then purified via silica-gel column chromatography using a 10-50% diethyl ether/petroleum ether gradient solvent, affording us the corresponding aldehyde in general excellent to quantitative yields.

These products were characterized by comparison with authentic samples or literature data.

Benzaldehyde (1b). **Method D** was used to obtain 1b. Benzyl alcohol (108 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow liquid (87%).

Prenal (2b). **Method E** was used to obtain 2b. Prenol (102 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow liquid (68%).

Neral (3b). **Method E** was used to obtain 3b. Nerol (181 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow pale oil (67%).

Farnesal (4b). **Method E** was used to obtain 4b. Trans,trans farnesol (250 µL, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow pale oil (68%).

Cinnamaldehyde (5b). **Method E** was used to obtain 5b. Cinnamyl alcohol 5a (134 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2mL, 0.5 M) at 60 °C under an oxygen atmosphere, yielded the desired compound as a yellow orange liquid (99%).
3-(3,4-Dimethoxyphenyl)-prop-2-enal (6b). **Method E** was used to obtain 6b. 6a (196 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M) at 60 °C under an oxygen atmosphere, yielded the desired compound as a pale yellow solid (95%). **Analytical data:** \[^1H\text{NMR}\] (200 MHz, CDCl\textsubscript{3}) δ (ppm) 9.58 (d, \(J^3=4\) Hz, 1H), 7.34 (d, \(J^3=16\) Hz, 1H), 7.06-7.11 (m, 2H), 6.82 (d, \(J^3=8\) Hz, 1H), 6.47-6.58 (m, 1H), 3.85 (s, 6H). \[^{13}C\text{NMR}\] (50 MHz, CDCl\textsubscript{3}) δ (ppm) 193.4, 152.7, 151.8, 149.2, 126.9, 126.5, 123.3, 111.0, 109.7, 55.9, 55.8. **MS** (EI, 70 eV) m/z 161.1 (100), 192.1 (86), 77.0 (57).
3-(4-(benzyloxy)-3-methoxyphenyl)-prop-2-enal (7b). Method E was used to obtain 7b. 7a (270 mg, 1 mmol), catalyst B (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M) at 60 °C under an oxygen atmosphere, yielded the desired compound as a pale yellow oil (93%). **Analytical data:** ¹H NMR (200 MHz, CDCl₃) δ (ppm) 9.58 (d, J=6 Hz, 1H), 7.19-7.38 (m, 6H), 6.99-7.04 (m, 2H), 6.83 (d, J=8 Hz, 1H), 6.47-6.58 (m, 1H), 5.14 (s, 2H), 3.85 (s, 3H). ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 193.5, 152.7, 151.1, 149.9, 136.3, 128.6, 128.1, 127.3, 127.2, 126.8, 123.2, 113.4, 110.4, 70.8, 56.0. **MS** (El, 70 eV) m/z 91.1 (100), 65.0 (9), 268.1 (6). **HRMS** calcd for exact mass C₁₇H₁₉O₃ 268.1099 found 268.1097.