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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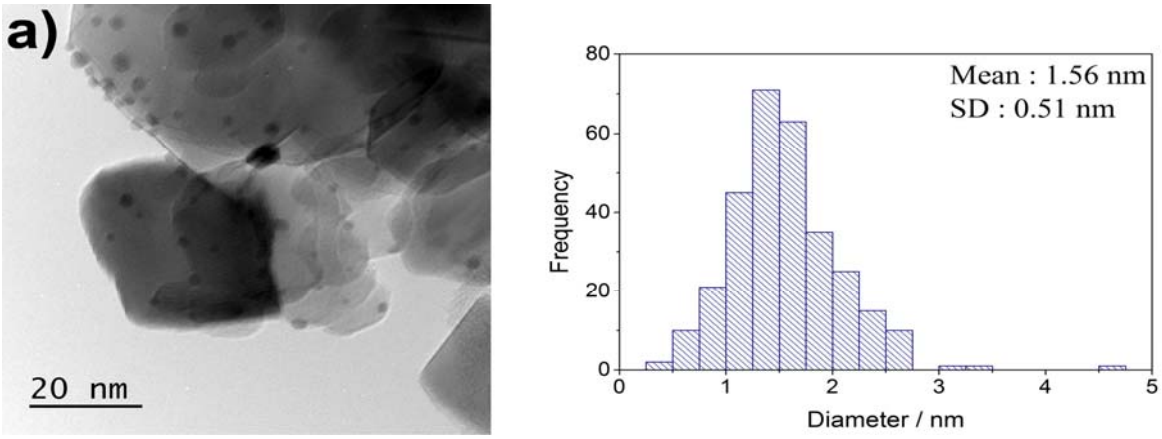
Supporting information

1. General information

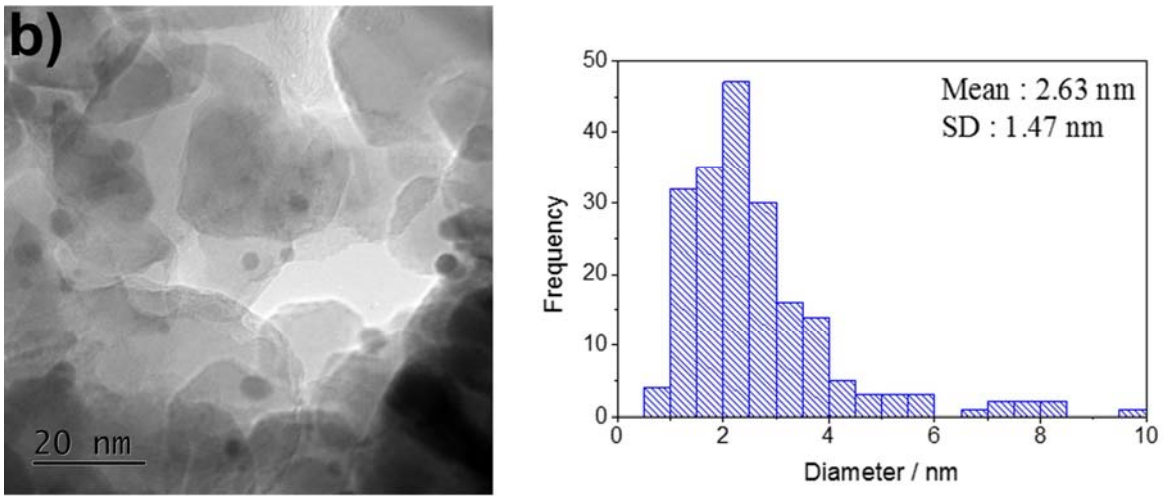
^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUCKER AC 200 (200 MHz). ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm or TMS at 0 ppm. Integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), and coupling constants (Hz). ^{13}C NMR spectra chemical shift are reported in ppm (δ) 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), tetrahydrofurane (THF), toluene, pyrrolidine, methanol (MeOH), Ethanol (EtOH), and cyclohexane (CHX) were dried and/or distilled according to conventional procedures.[1] Na_2CO_3, K_2CO_3, NaOH, H_2SO_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.

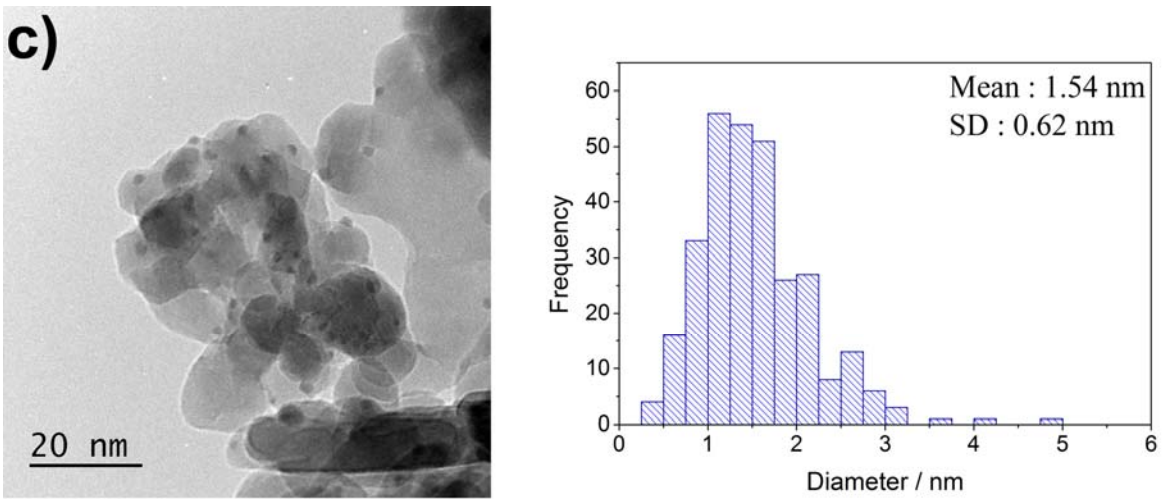
2. TEM Analysis of catalysts A-D / Screening reaction conditions



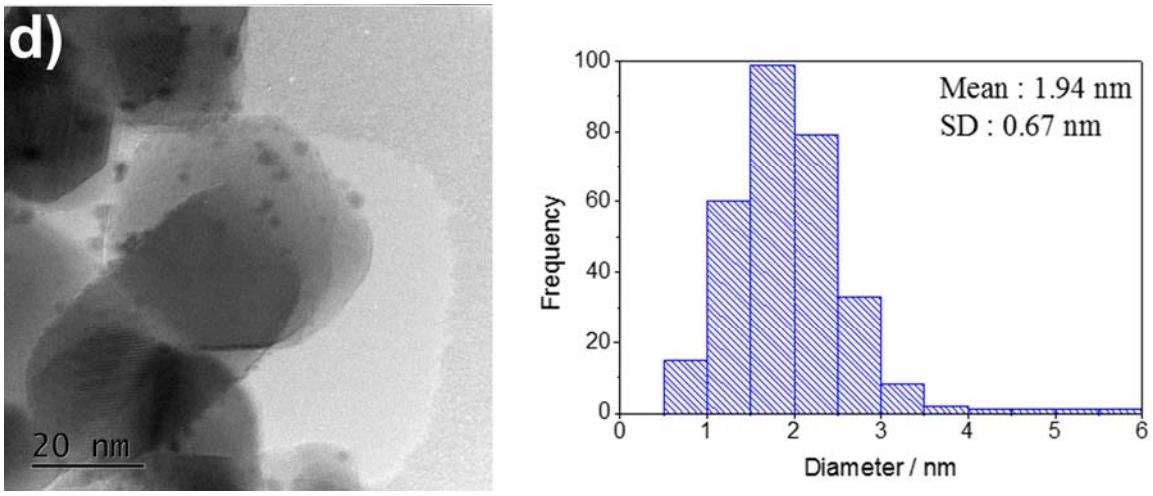
Schema a: TEM[¥] of catalyst A (Au NPs/TiO_2 - AUROlite®).



Schema b: TEM[¥] of catalyst B (Au NPs/Al_2O_3 - AUROlite®).



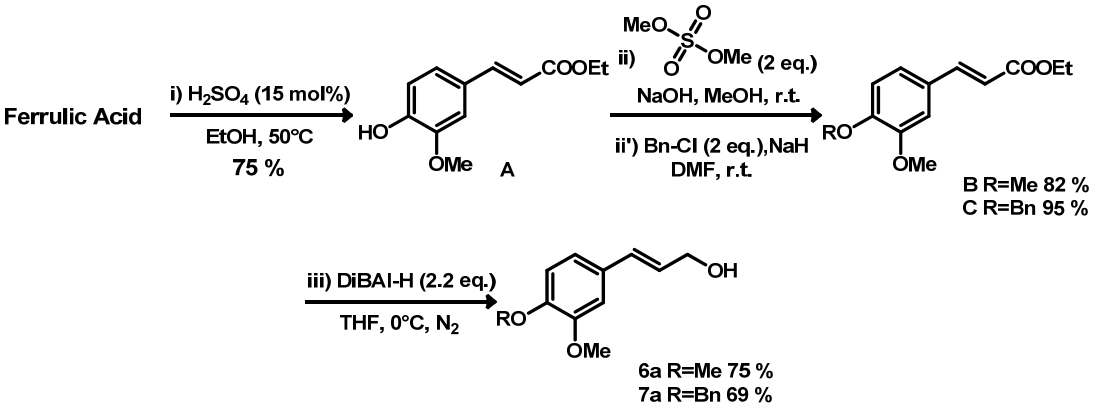
Schema c: TEM[¥] of catalyst C (Au NPs/ZnO - AUROlite®).

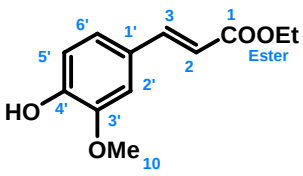


Schema d: TEM[¥] of catalyst D (Au NPs/TiO_2 – prepared by impregnation)

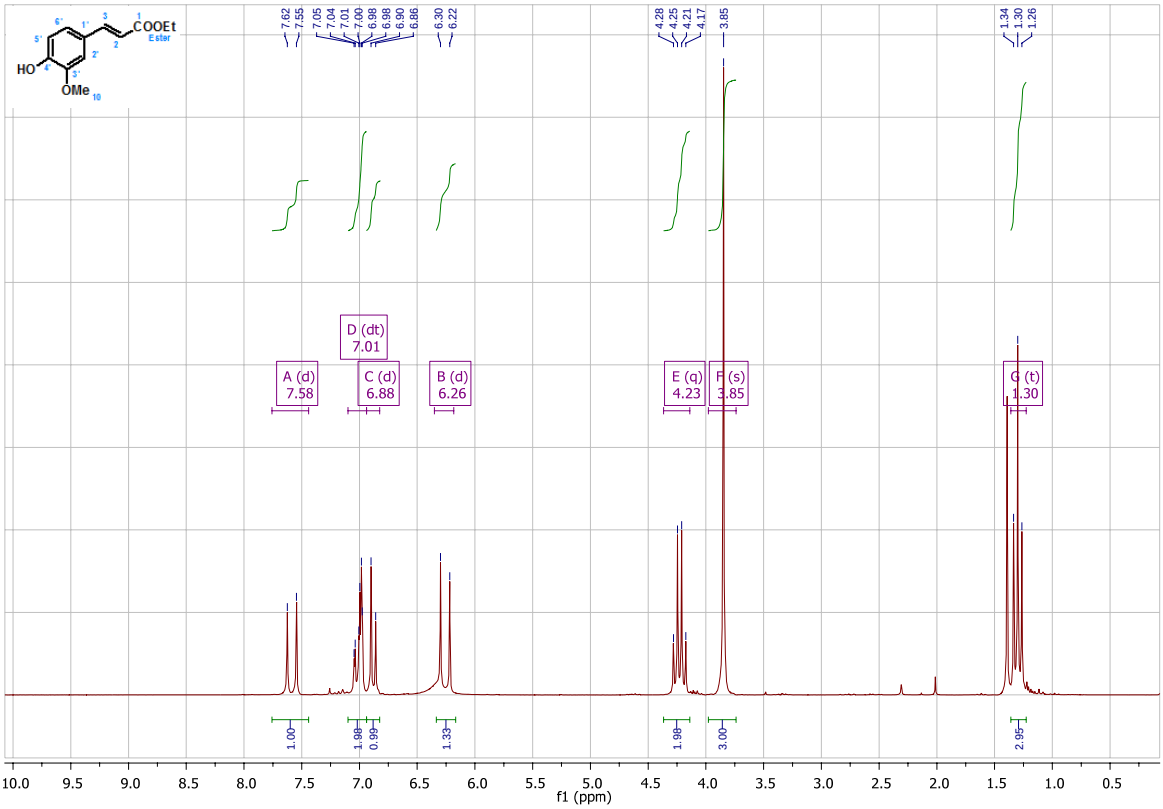
[¥]: Transmission electron microscopy (TEM) was carried out using a Jeol 2100 with a LaB_6 filament operating at 200KV. Samples were prepared by dispersing the powder catalyst in ethanol and dropping the suspension onto a lacey carbon film over a 300 mesh copper grid.

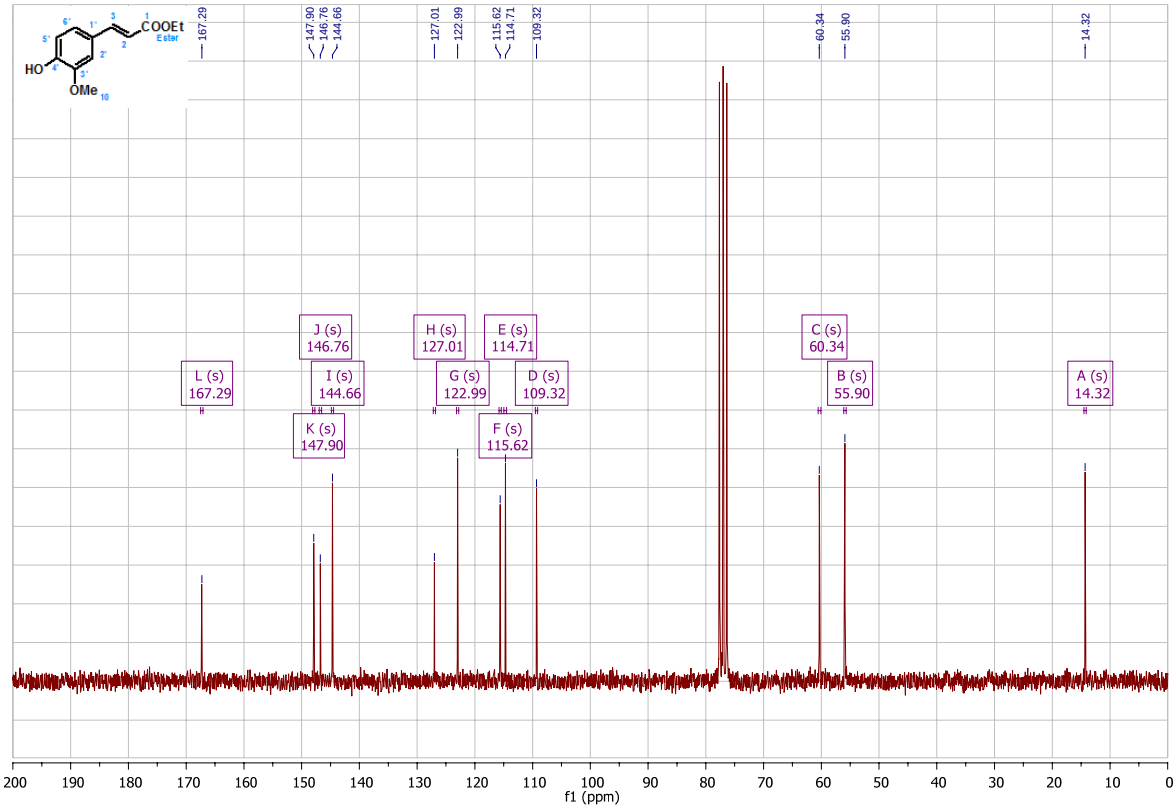
3. Preparation of starting materials allylic alcohol (6a) and (7a)

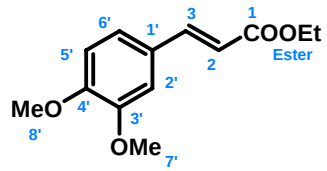




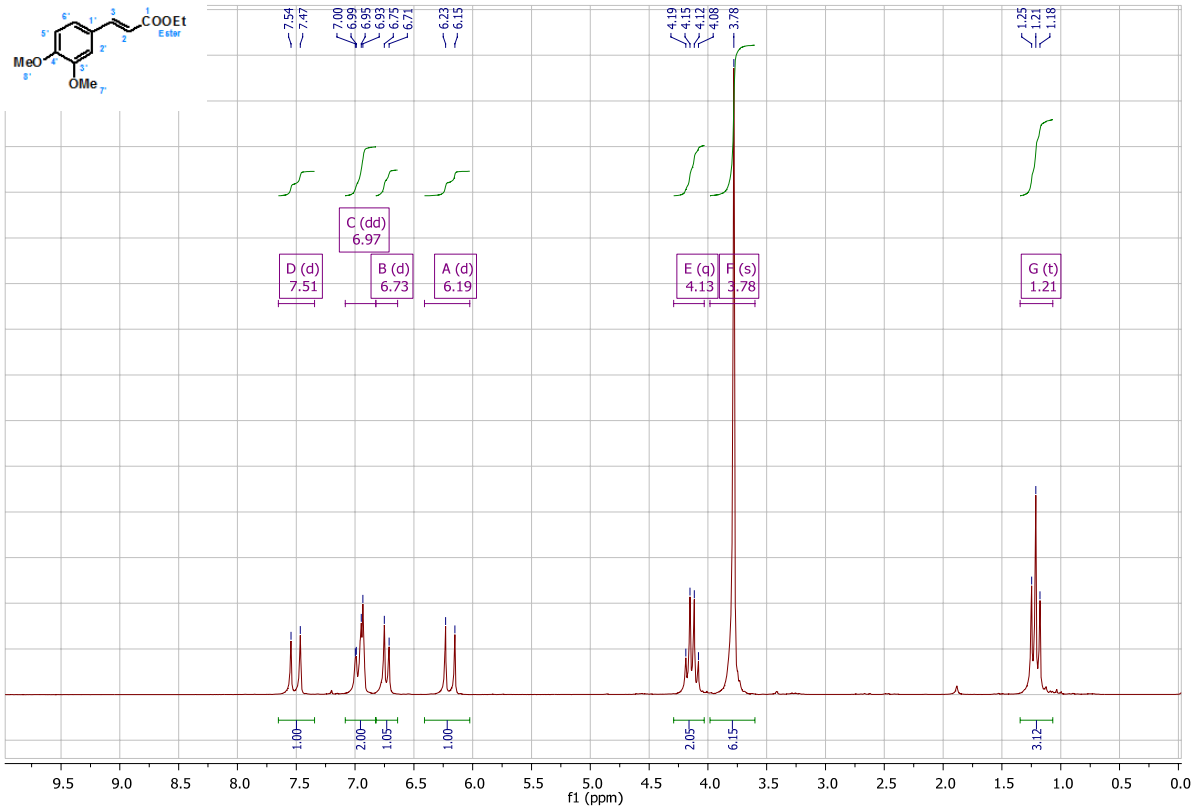
Ethyl (*E*)-3-(4-hydroxy-3-methoxyphenyl)propanoate (**A**). A 50 mL dried round-bottom flask equipped with a stir bar was cooled to 0 °C. Ferrulic acid (2.0 g, 1.0 equiv., 10.29 mmol) and anhydrous EtOH (25 mL, 0.41 M) were added, followed by dropwise addition of H_2SO_4 (414 µL, 1.5 equiv.). The mixture 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 $Na_2CO_{3(aq.)}$ 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 $MgSO_4$, 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: ^{1}H NMR** ($CDCl_3$, 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). **^{13}C NMR** (50 MHz, $CDCl_3$) 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).

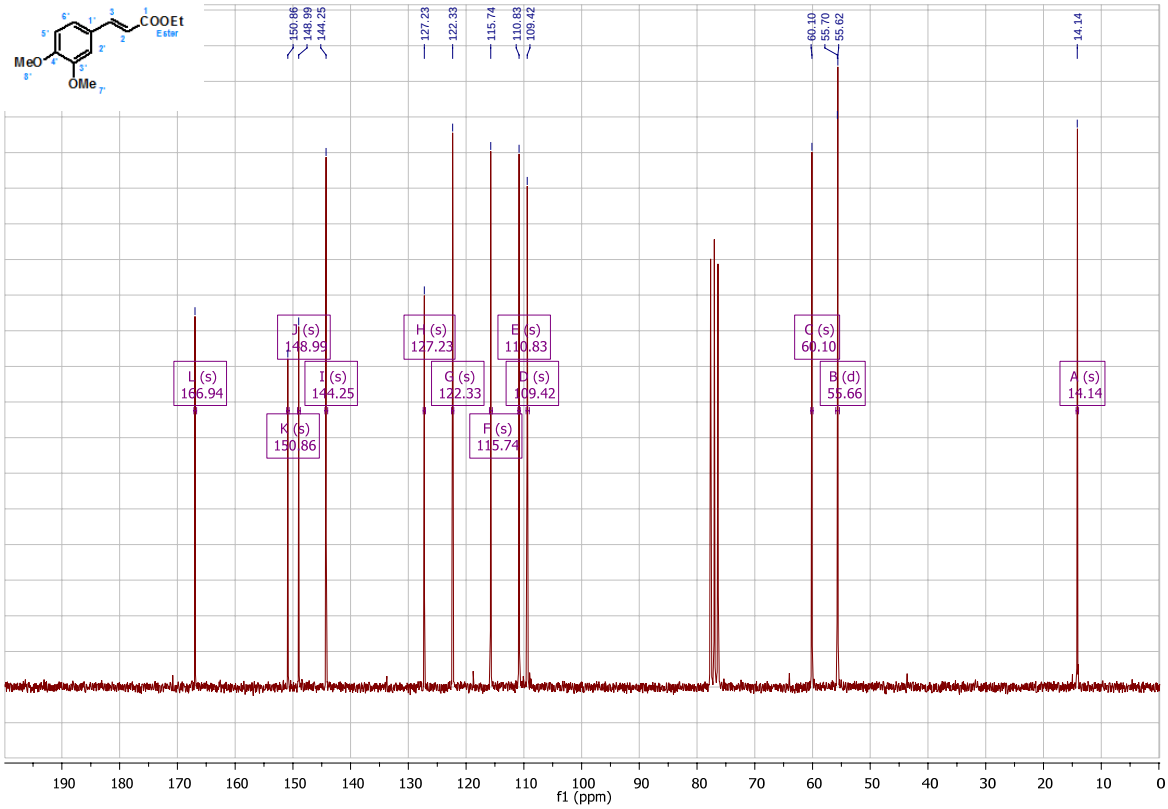

COOEt
Ester
HO
OMe
D (dt)
7.01
A (d)
7.58
C (d)
6.88
B (d)
6.26
E (q)
4.23
F (s)
3.85
G (t)
1.30
f1 (ppm)

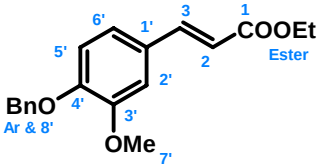

COOEt
Ester
HO
OMe
L (s)
167.29
J (s)
146.76
I (s)
144.66
K (s)
147.90
H (s)
127.01
G (s)
122.99
E (s)
114.71
D (s)
109.32
F (s)
115.62
C (s)
60.34
B (s)
55.90
A (s)
14.32
f1 (ppm)



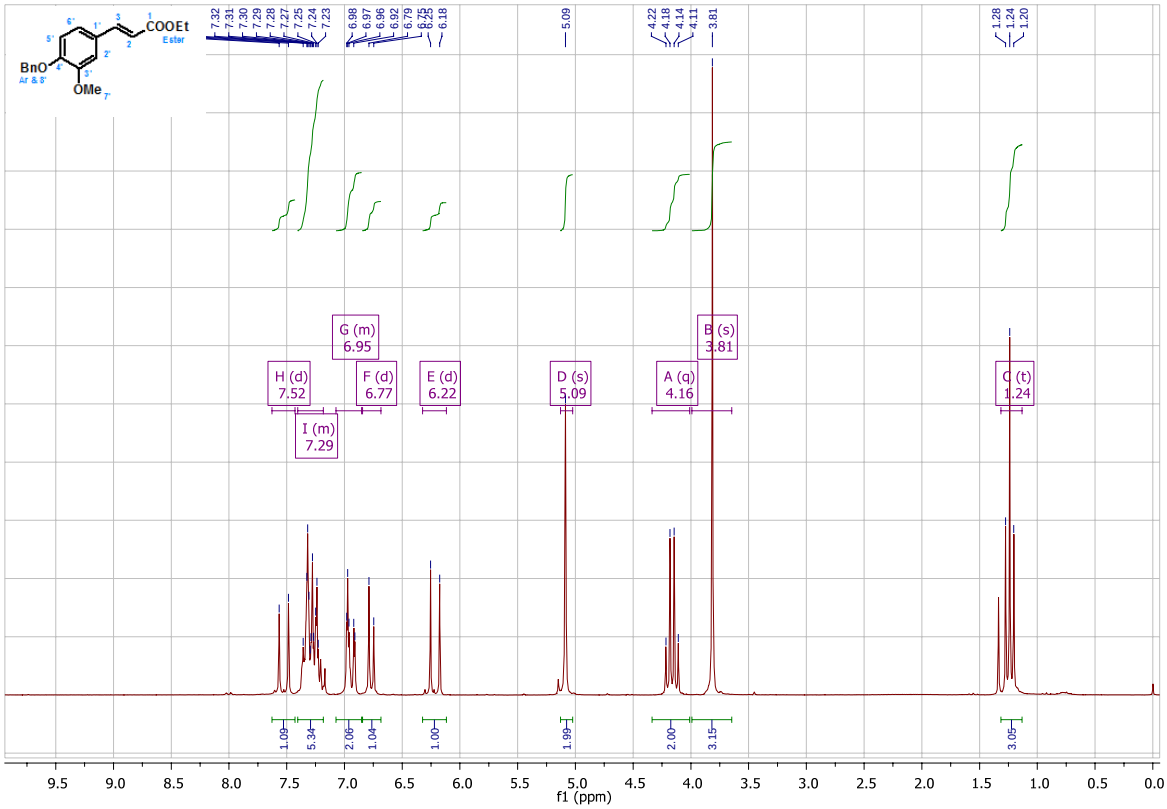
Ethyl (*E*)-3-(3,4-dimethoxyphenyl)propanoate (**B**). To 50 mL dried round-bottom flask equipped with a reflux condenser and a dropping funnel were introduced carefully, ethyl (E)-3-(4-hydroxy-3-methoxyphenyl)propanoate (850 mg, 3.82 mmol), sodium hydroxide (184 mg, 1.27 equiv., 4.84 mmol), anhydrous 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 $NH_4Cl_{(aq.)}$ solution (20 mL) and extracted with diethyl ether (3x30 mL). The pooled extracts were dried over $MgSO_4$, 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:** ^{1}**H NMR** (200 MHz, $CDCl_3$) 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).^{13}**C NMR** (50 MHz, $CDCl_3$) 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** (EI, 70 eV) m/z 236.0 (100), 191.0 (65), 164.1 (53).

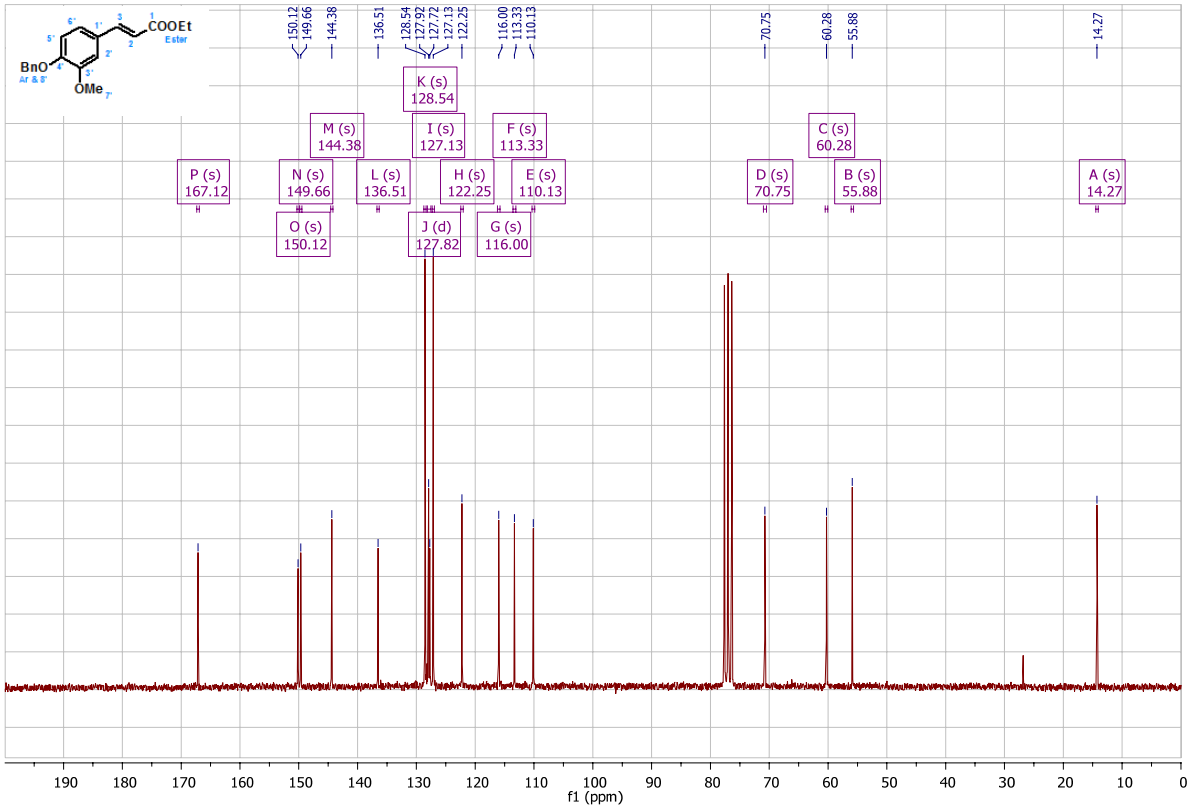






Ethyl (*E*)-3-(4-(benzyloxy)-3-methoxyphenyl)propanoate (**C**). To a 25 mL dried round-bottom flask at 0 °C, ethyl (E)-3-(4-hydroxy-3-methoxyphenyl)propanoate (500 mg, 1.60 mmol), sodium hydride (60 % oil dispersed) (70.4 mg, 1.76 mmol) and fresh distilled DMF (5 mL, 0.32 M) were added at once. The 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 $NH_4Cl_{(aq.)}$ solution (15 mL) at 0 °C, and the aqueous phase was extracted with DCM (3x10 mL), and pooled organic layers were dried over $MgSO_4$, 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:** **^{1}H NMR** (200 MHz, $CDCl_3$) 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). **^{13}C NMR** (50 MHz, $CDCl_3$) 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** (EI, 70 eV) m/z 91.0 (100), 312.1 (9), 92.1 (8). **HRMS** calcd for exact mass $C_{19}H_{20}O_4$ 312.1362, found 312.1361, Δ=0.1 ppm.


COOEt
Ester
BnO
Ar & 8'
OMe
7'
7.32
7.31
7.30
7.29
7.28
7.27
7.25
7.24
7.23
6.98
6.97
6.96
6.92
6.79
6.25
6.18
5.09
4.22
4.18
4.14
4.11
3.81
1.28
1.24
1.20
G (m)
6.95
B (s)
3.81
H (d)
7.52
F (d)
6.77
E (d)
6.22
D (s)
5.09
A (q)
4.16
C (t)
1.24
I (m)
7.29
1.09
5.34
2.06
1.04
1.00
1.99
2.00
3.15
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


COOEt
Ester
BnO
Ar & 8'
OMe
7'
150.12
149.66
144.38
136.51
128.54
127.92
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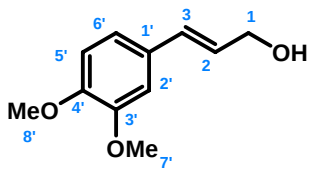
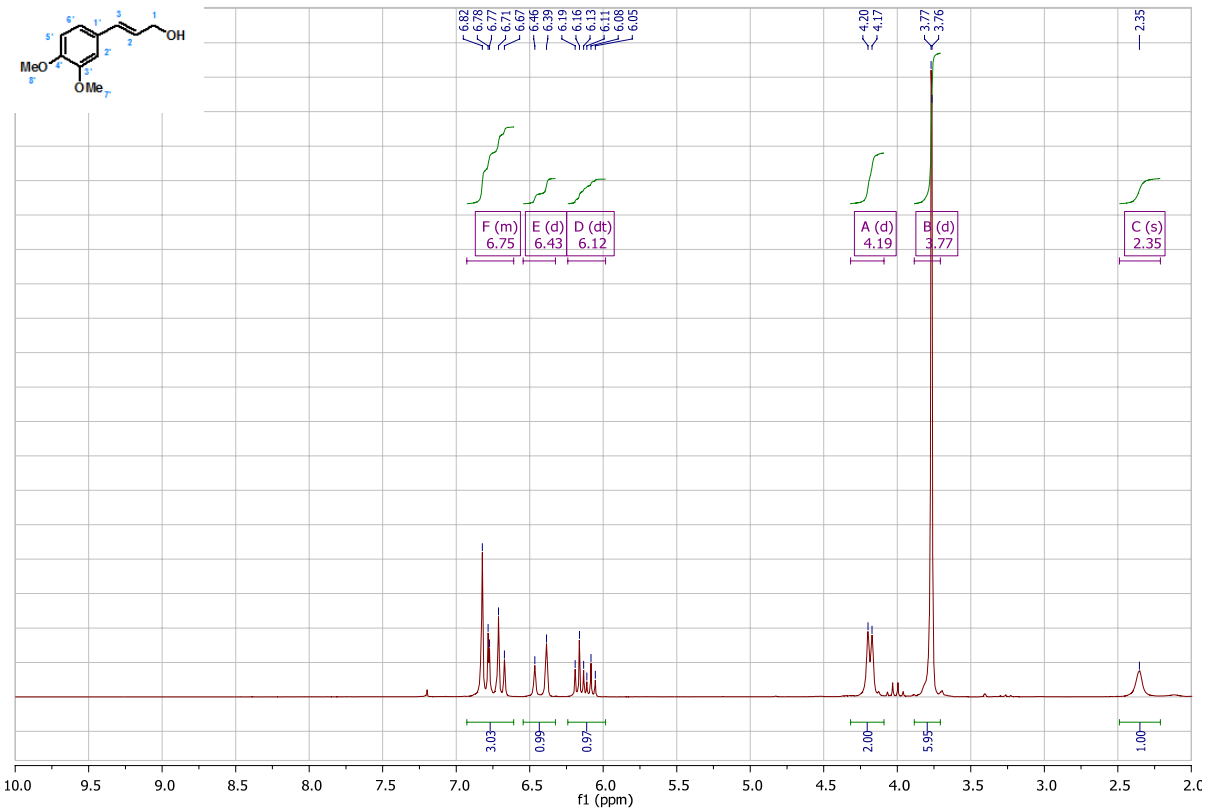
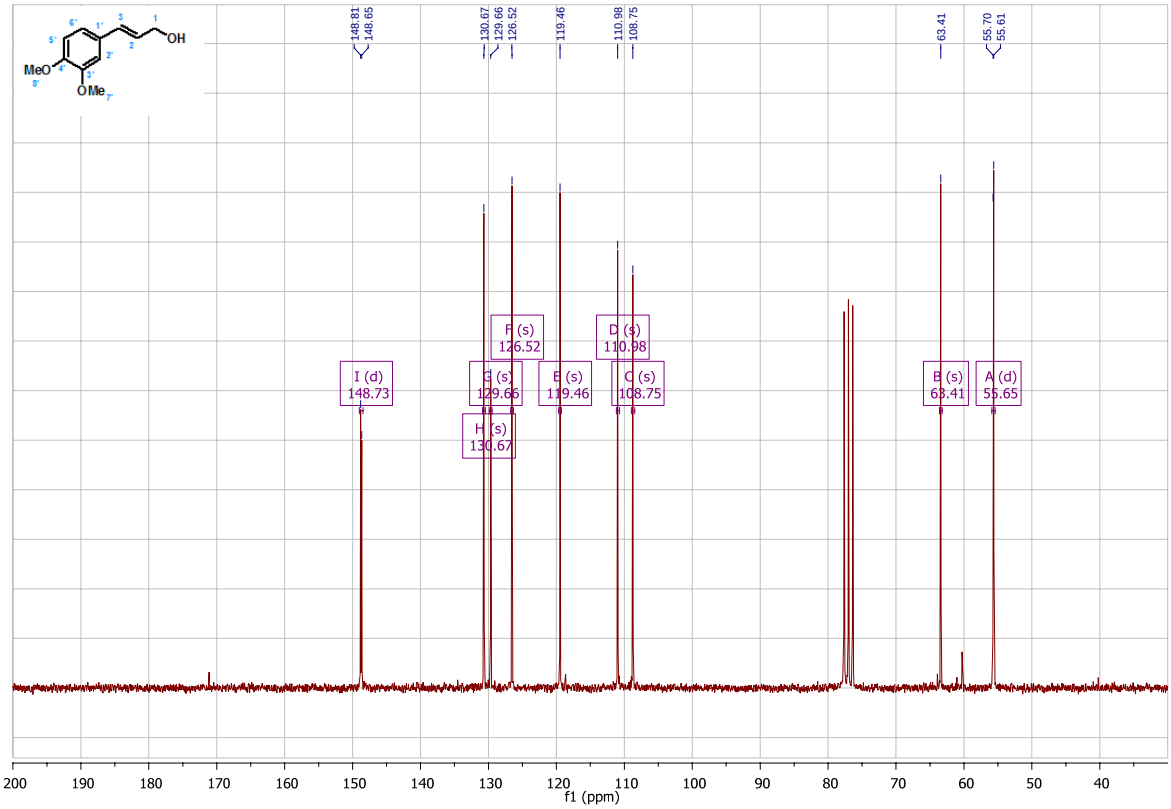
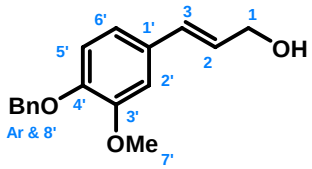
127.13
122.25
116.00
113.33
110.13
70.75
60.28
55.88
14.27
K (s)
128.54
M (s)
144.38
I (s)
127.13
F (s)
113.33
C (s)
60.28
P (s)
167.12
N (s)
149.66
L (s)
136.51
H (s)
122.25
E (s)
110.13
D (s)
70.75
B (s)
55.88
A (s)
14.27
O (s)
150.12
J (d)
127.82
G (s)
116.00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



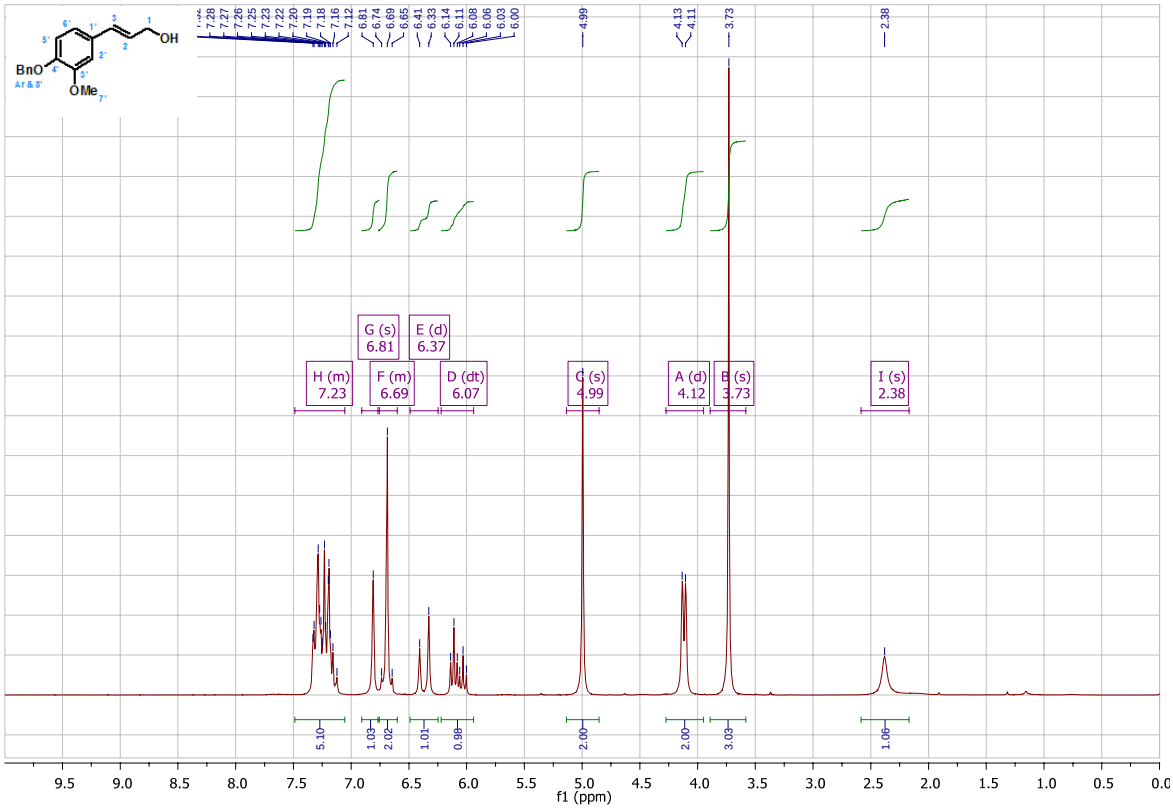
(*E*)-3-(3,4-dimethoxyphenyl)prop-2-en-1-ol (**6a**). To a 25 mL dried round-bottom flask at 0°C under nitrogen atmosphere containing ethyl (*E*)-3-(3,4-dimethoxyphenyl)propanoate (500 mg, 2.1 mmol), a diisobutylaluminium hydride solution (4.66 mL, 2.2 equiv., 4.66 mmol) was added dropwise in THF (6 mL). After stirring for 3 hours the reaction mixture was treated with saturated $NH_4Cl_{(aq.)}$ 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 $MgSO_4$, 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**): **^{1}H NMR** (200 MHz, $CDCl_3$) 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). **^{13}C NMR** (50 MHz, $CDCl_3$) 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** calcd for exact mass $C_{11}H_{14}O_3$ 194.0943, found 194.0950, Δ=0.7 ppm.

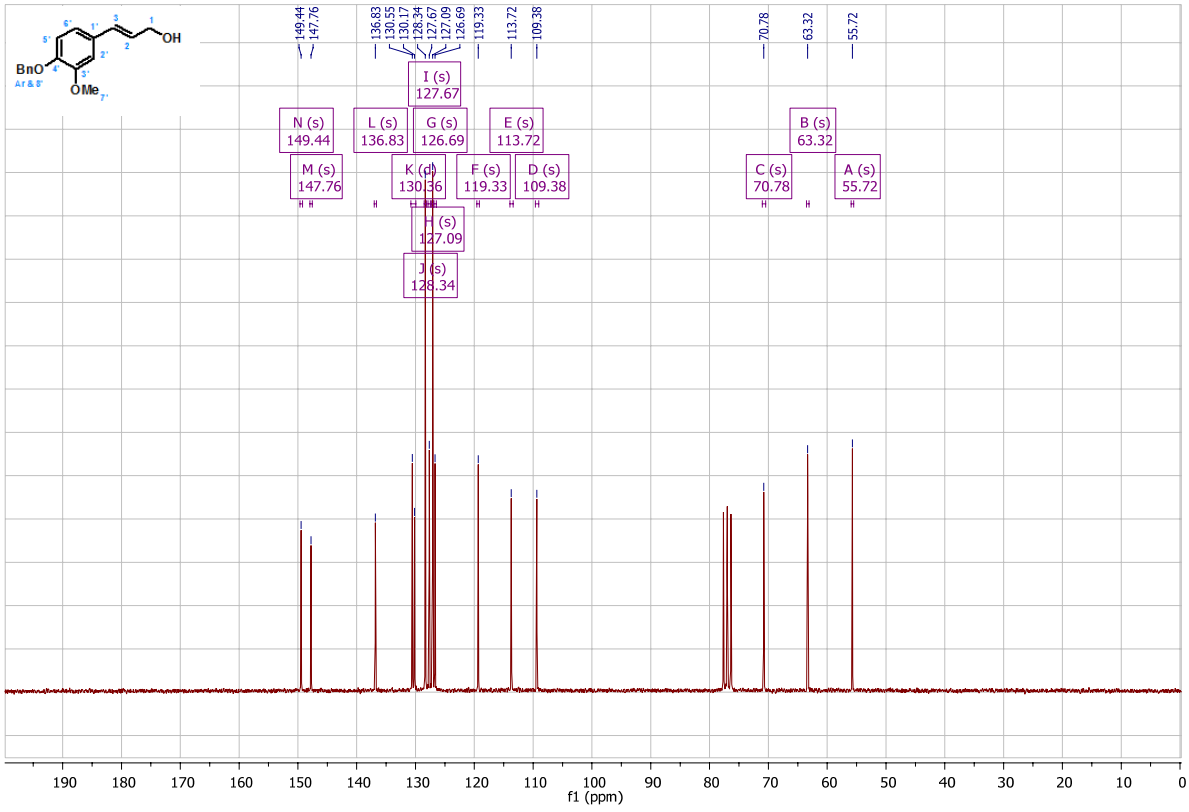






(*E*)-3-(4-(benzyloxy)-3-methoxyphenyl)prop-2-en-1-ol (**7a**). To a 25 mL dried round-bottom flask at 0°C under nitrogen atmosphere containing ethyl (*E*)-3-(4-(benzyloxy)-3-methoxyphenyl)propanoate (600 mg, 1.92 mmol), a diisobutylaluminium hydride solution (4.27 mL,4.27 mmol, 2.2 equiv) was added dropwise in THF (5.5 mL). After stirring for 3 hours the reaction mixture treated was saturated $NH_4Cl_{(aq.)}$ 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 $MgSO_4$, 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 (**69 %**). **Analytical data:** **^{1}H NMR** (200 MHz, $CDCl_3$) δ (ppm) 7.16-7.33 (m, 5H), 6.81 (s, 1H), 6.69 (s, 2H), 6.37 (d, *J*=16 Hz, 1H), 6.03-6.14 (m, 1H), 4.99 (s, 2H), 4.12 (d, *J*=6 Hz, 2H), 3.73 (s, 3H), 2.38 (b, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (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 $C_{17}H_{18}O_3$ 270.1256, found 270.1257, Δ=0.1 ppm.


BnO
OMe
OH
G (s) 6.81
E (d) 6.37
H (m) 7.23
F (m) 6.69
D (dt) 6.07
C (s) 4.99
A (d) 4.12
B (s) 3.73
I (s) 2.38
f1 (ppm)


BnO
OMe
OH
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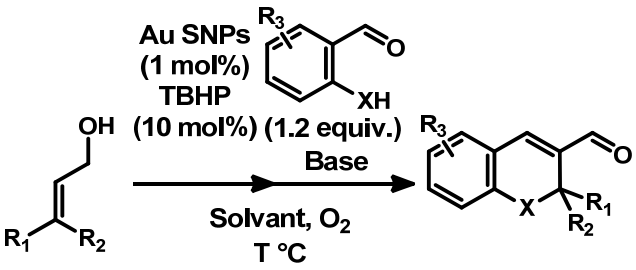
N (s) 149.44
L (s) 136.83
G (s) 126.69
E (s) 113.72
M (s) 147.76
K (d) 130.36
F (s) 119.33
D (s) 109.38
H (s) 127.09
J (s) 128.34
B (s) 63.32
C (s) 70.78
A (s) 55.72
f1 (ppm)

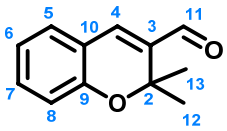
4. **Procedures for the cascade Oxidation / Hetero Michael / Aldolisation reaction.**



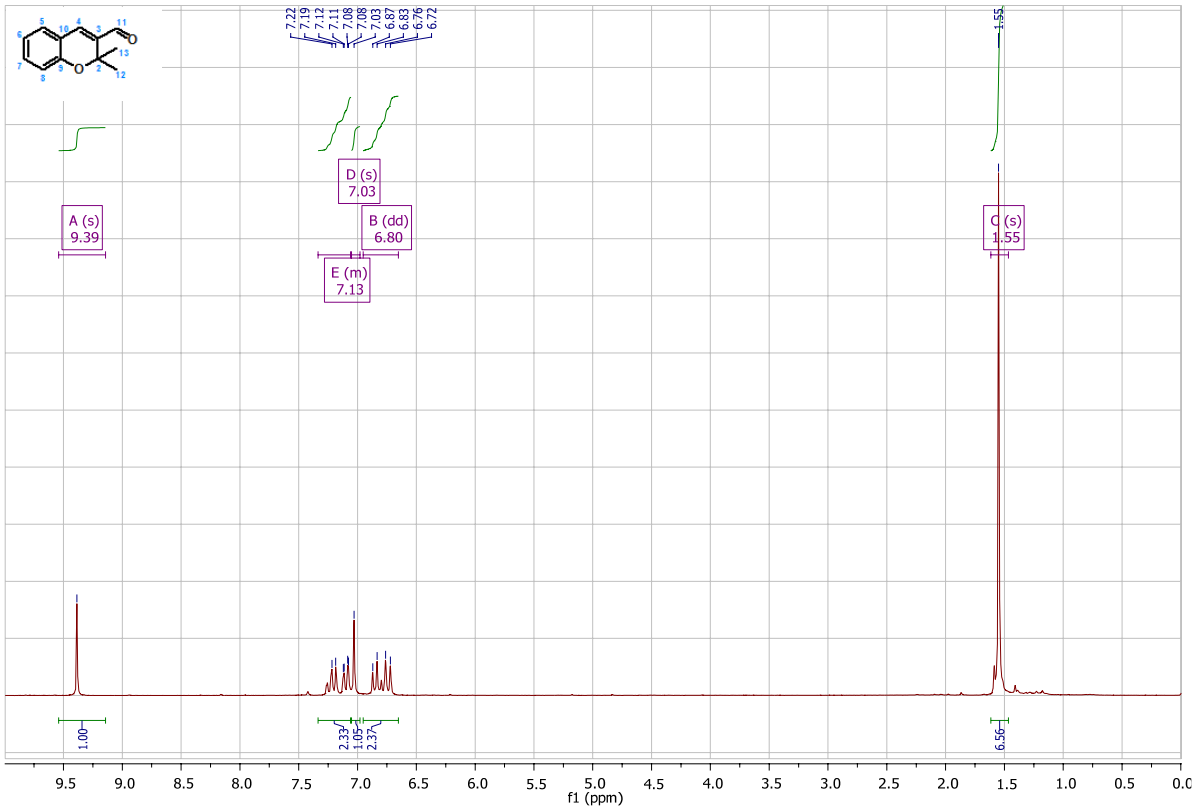
Method A: To a dried reactor under O_2 atmosphere, catalyst **B** (0.08 mmol, 0.08 equiv.), *tert*-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous THF (2.0 mL, 0.5 M) and prenol (1 mmol, 1.0 equiv.) were added. The solution was stirred at 60 °C for 8 h. Salicylaldehyde (1.2 mmol, 1.2 equiv.) 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 $NH_4Cl_{(aq.)}$ 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.

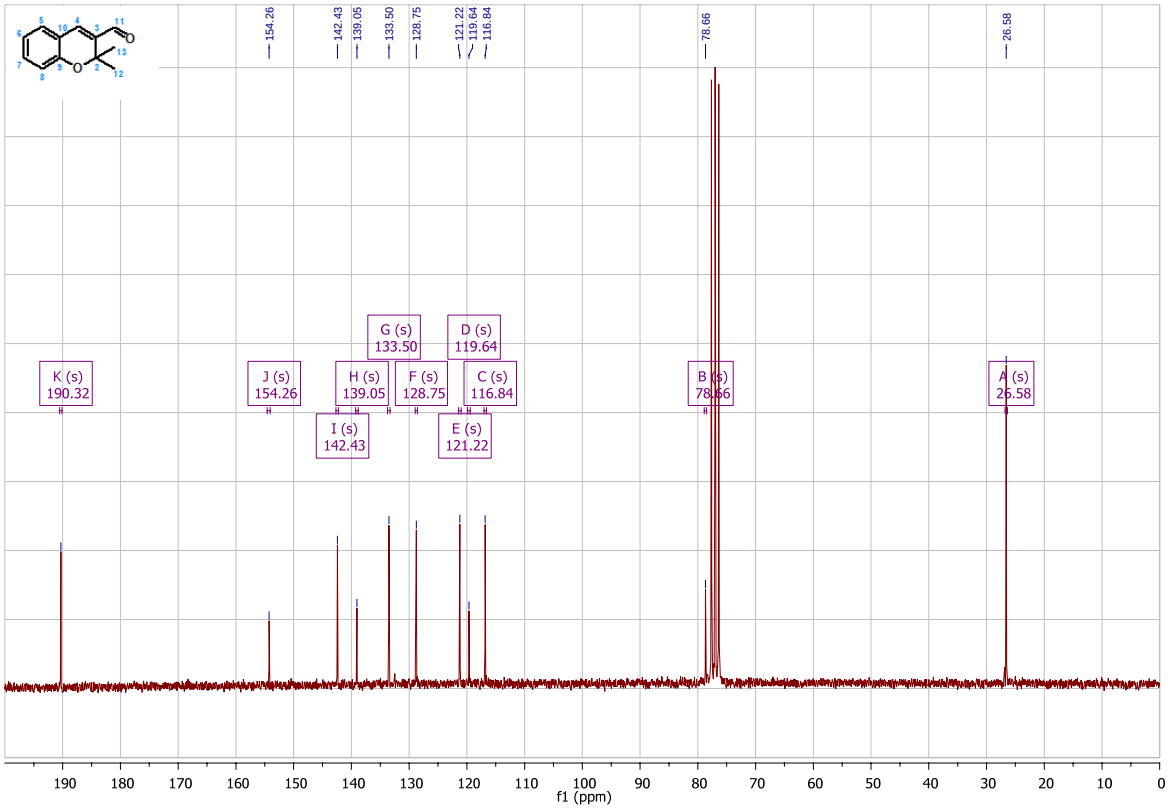
Method B: To a dried reactor under O_2 atmosphere, catalyst **B** (0.08 mmol, 0.08 equiv.), *tert*-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous toluene (2.0 mL, 0.5 M) and allylic alcohol (1 mmol, 1.0 equiv.) were added. The solution was stirred at 80 °C for 8 h. Salicylaldehyde (1.2 mmol, 1.2 equiv.) and K_2CO_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 $NH_4Cl_{(aq.)}$ 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.

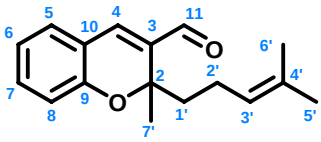
Method C: To a dried reactor under O_2 atmosphere, catalyst **B** (0.08 mmol, 0.08 mol%), *tert*-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous THF (2.0 mL, 0.5 M) and allylic alcohol (1 mmol, 1.0 equiv.) were added. The solution was stirred at 60 °C for 8 h. Salicylaldehyde (1.2 mmol, 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 eaction 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 $NH_4Cl_{(aq.)}$ solution (20 mL), extracted with DCM (3x10 mL) and concentrated in vacuo, prior a purification via silica-gel chromatography using 20-40% EtOAc/CHX gradient solvent, affording the corresponding 2*H*-chromene / dihydroquinoline.



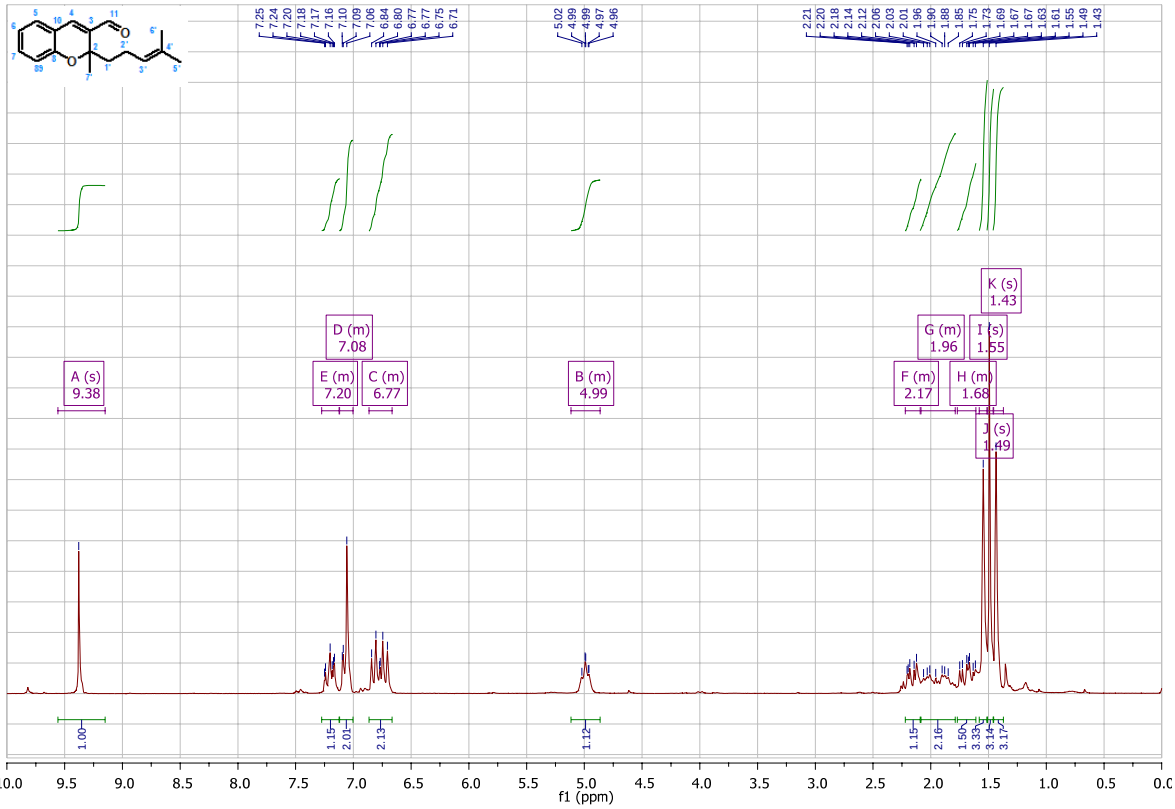
2,2-dimethyl-2*H*-chromene-3-carbaldehyde (**2c**). **Method A** was used to obtain **2c**. Prenol (102 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), anhydrous THF (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), TBD (14 mg, 10 mol%), 3Å MS (50 mg) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow dark oil (59). **Analytical data: ^{1}H NMR** (200 MHz, $CDCl_3$) 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). **^{13}C NMR** (50 MHz, $CDCl_3$) 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 $C_{12}H_{13}O_2$ $(M+H)^+$ 189.0916 found 189.0915 Δ=0.1 ppm.







2-methyl-2-(4-methylpent-3-enyl)-2*H*-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_2CO_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 (tb, 1H), 1.82-2.38 (m, 4H), 1.70 (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, CDCl3) 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.


A (s) 9.38
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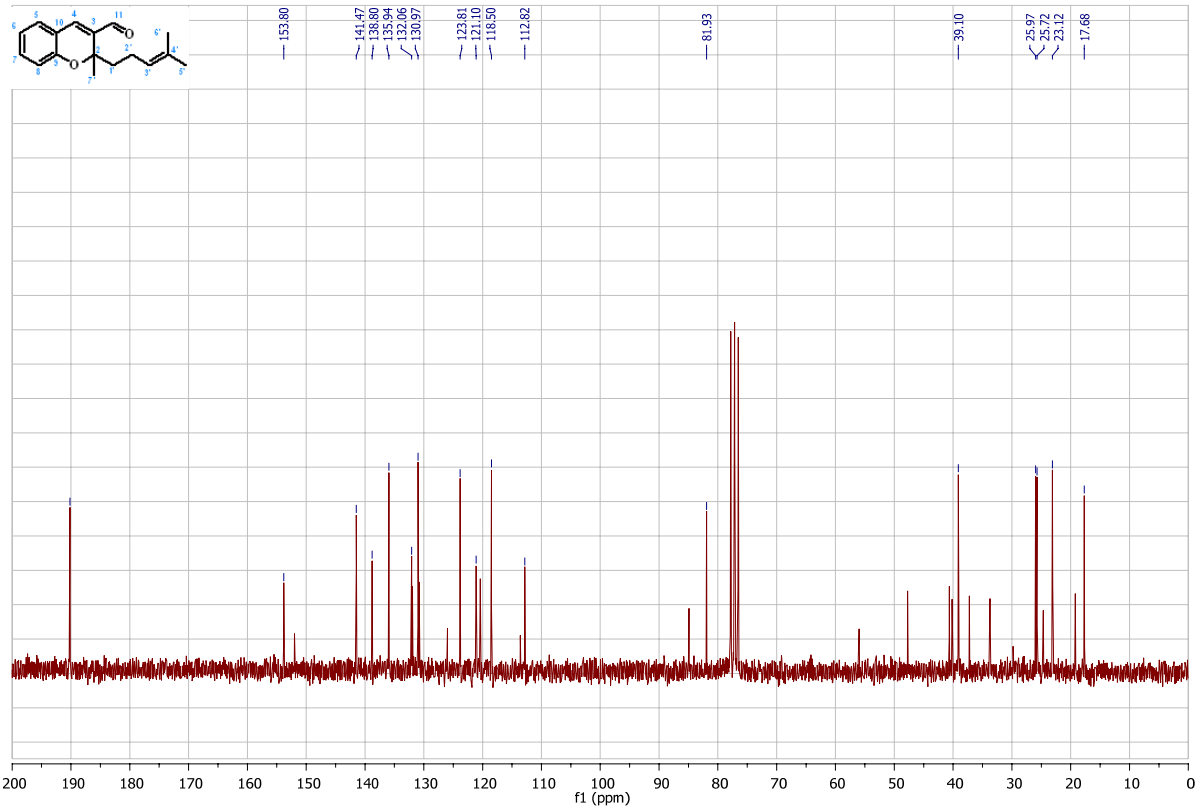
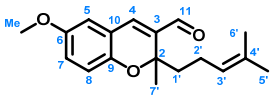
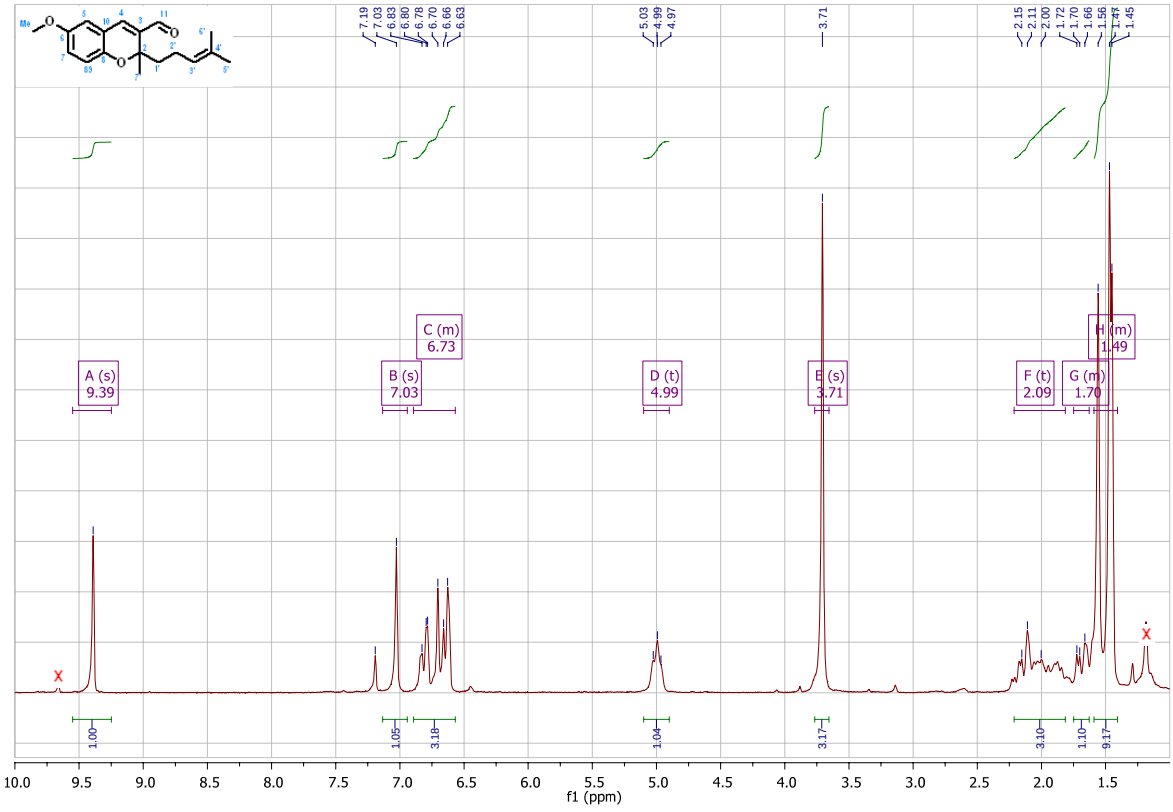
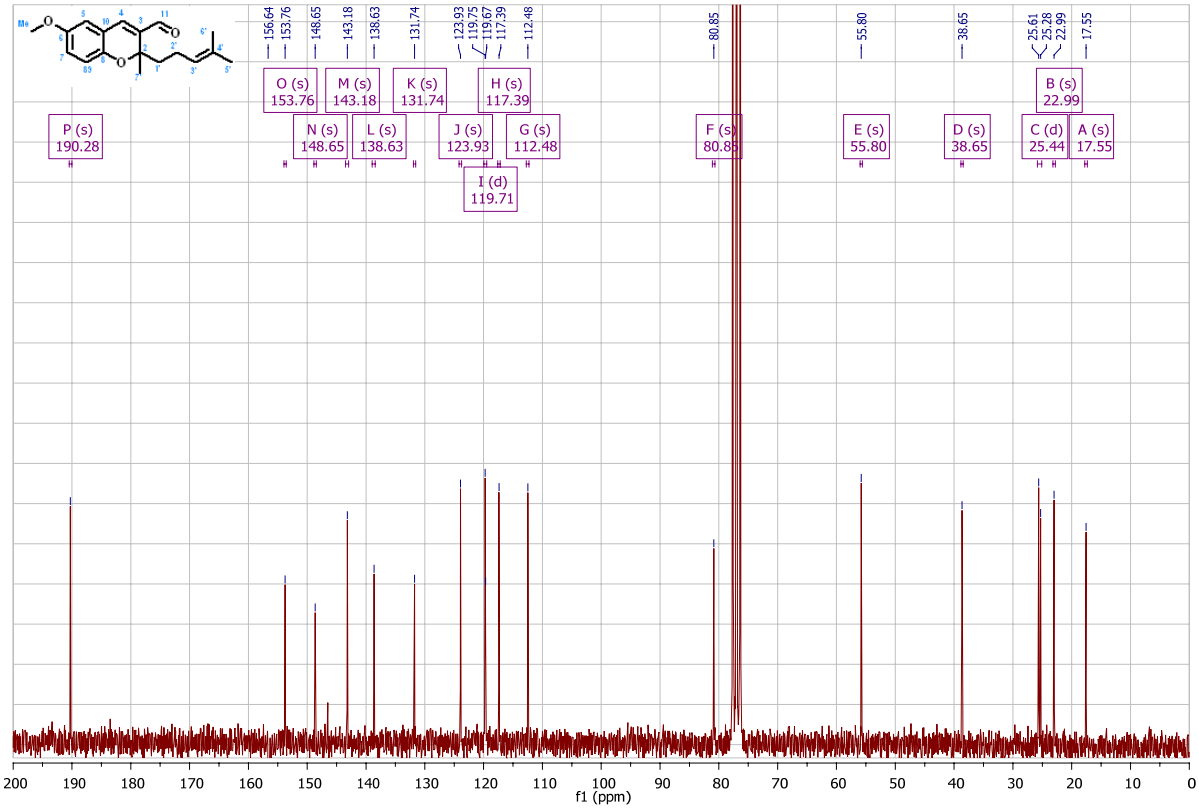
E (m) 7.20
C (m) 6.77
B (m) 4.99
K (s) 1.43
G (m) 1.96
I (s) 1.55
F (m) 2.17
H (m) 1.68
J (s) 1.49
f1 (ppm)

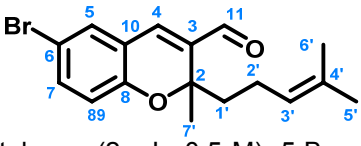

153.80
141.47
138.80
135.94
132.06
130.97
123.81
121.10
118.50
112.82
81.93
39.10
25.97
25.72
23.12
17.68
f1 (ppm)



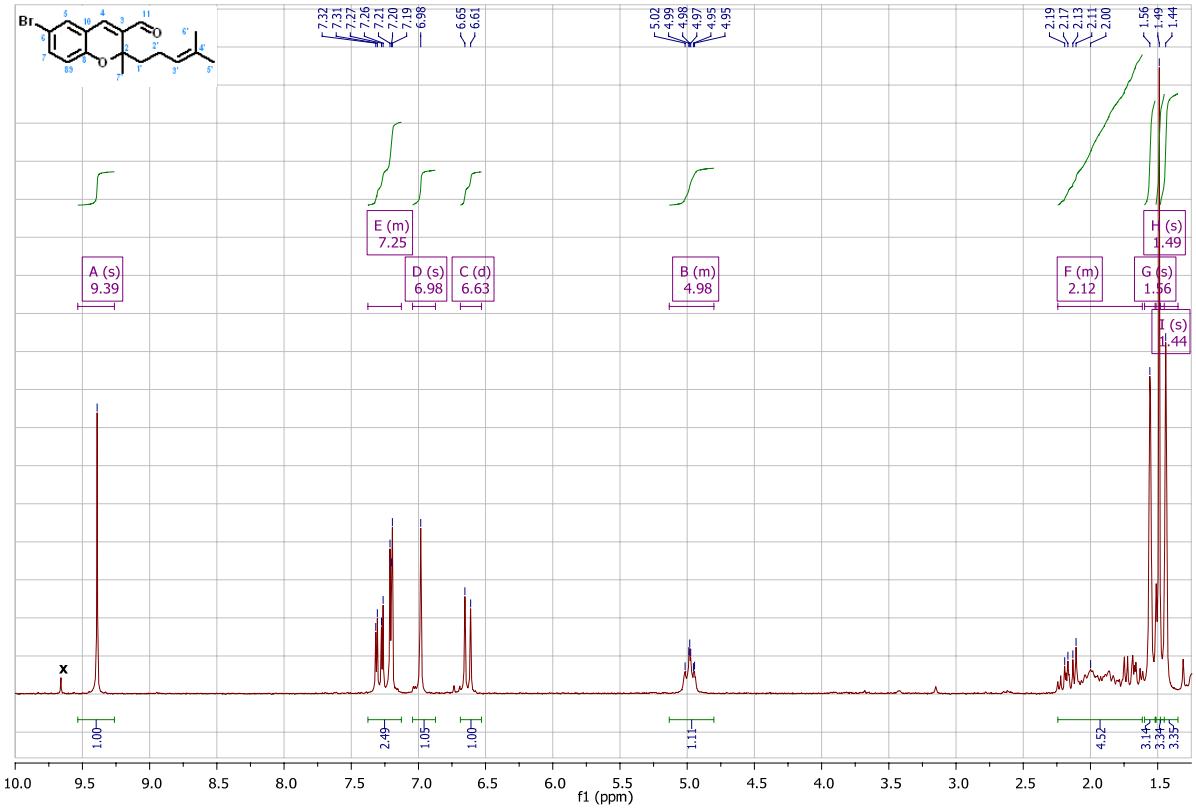
6-methoxy-2-methyl-2-(4-methylpent-3-enyl)-2*H*-chromene-3-carbaldehyde (**3e**). **Method B** was used to obtain **3e**. Nerol (181 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M), 2-hydroxy-5-methoxybenzaldehyde (150 µL, 1.2 equiv., 1.2 mmol), K_2CO_3 (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, $CDCl_3$) δ (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, $CDCl_3$) δ (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, Δ=3.5 ppm.

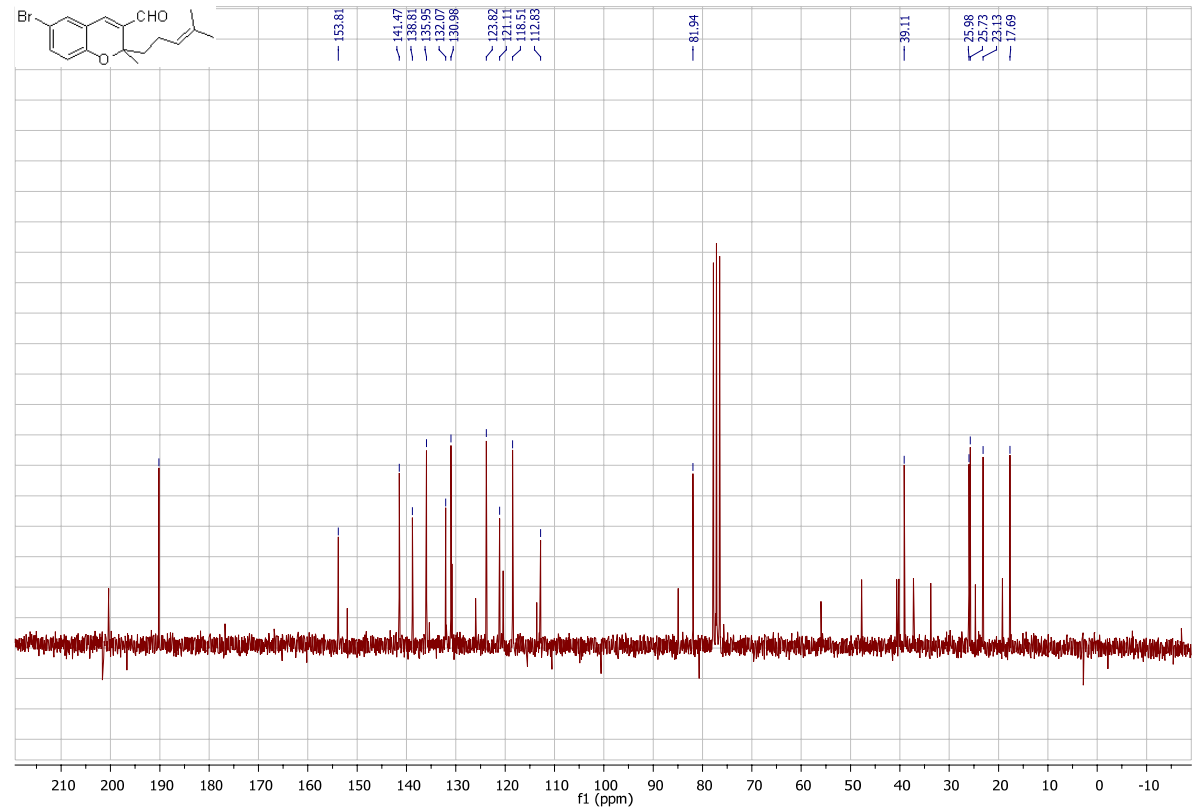






6-Bromo-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-chromene-3-carbaldehyde (**3g**). **Method B** was used to obtain **3g**. Nerol (181 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M), 5-Bromosalicylaldehyde (240 mg, 1.2 equiv., 1.2 mmol), K_2CO_3 (169 mg, 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^4=10 Hz, J^3=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)-chromane-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 $C_{17}H_{19}O_2Br$ 334.0568, found 334.0566, Δ=0.6 ppm.


Br
7.32
7.31
7.27
7.26
7.21
7.20
7.19
6.98
6.65
6.61
5.02
4.99
4.98
4.97
4.95
4.95
2.19
2.17
2.13
2.11
2.00
1.56
1.49
1.44
A (s) 9.39
E (m) 7.25
D (s) 6.98
C (d) 6.63
B (m) 4.98
F (m) 2.12
G (s) 1.56
H (s) 1.49
I (s) 1.44
x
1.00
2.49
1.05
1.00
1.11
4.52
3.14
3.34
3.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


Br
CHO
153.81
141.47
138.81
135.95
132.07
130.98
123.82
121.11
118.51
112.83
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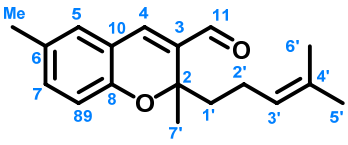
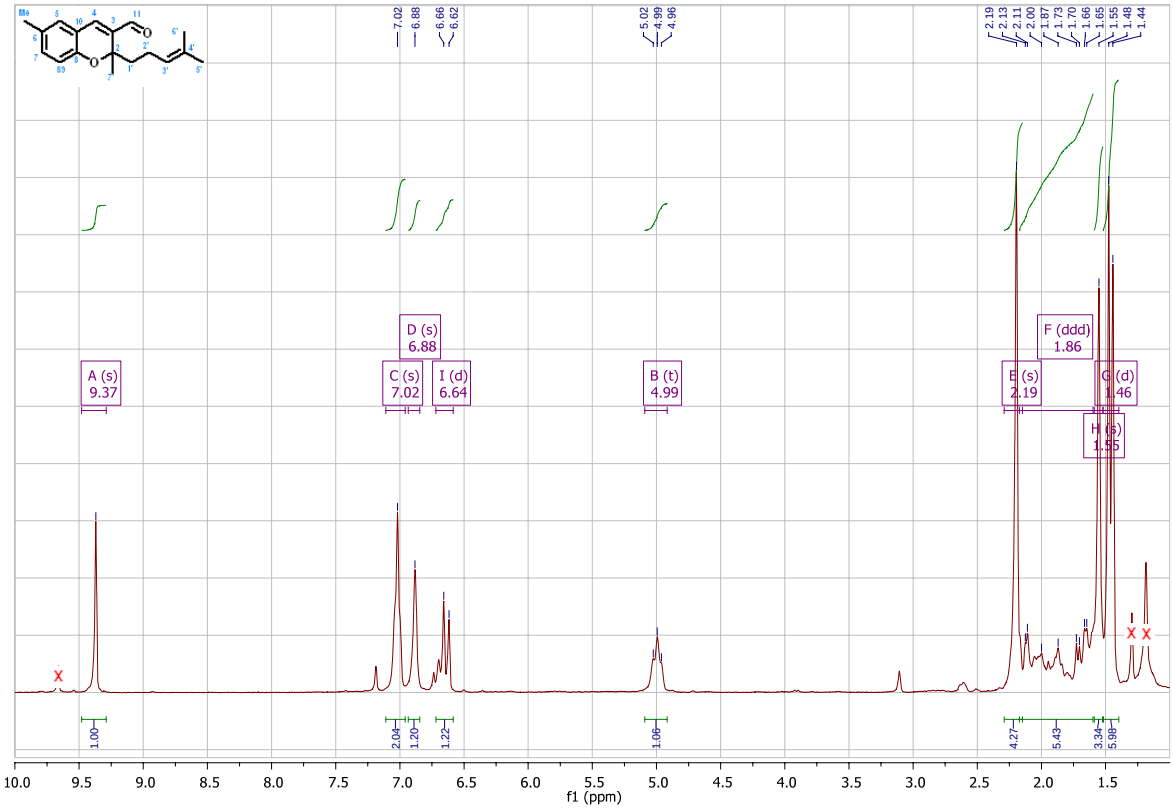
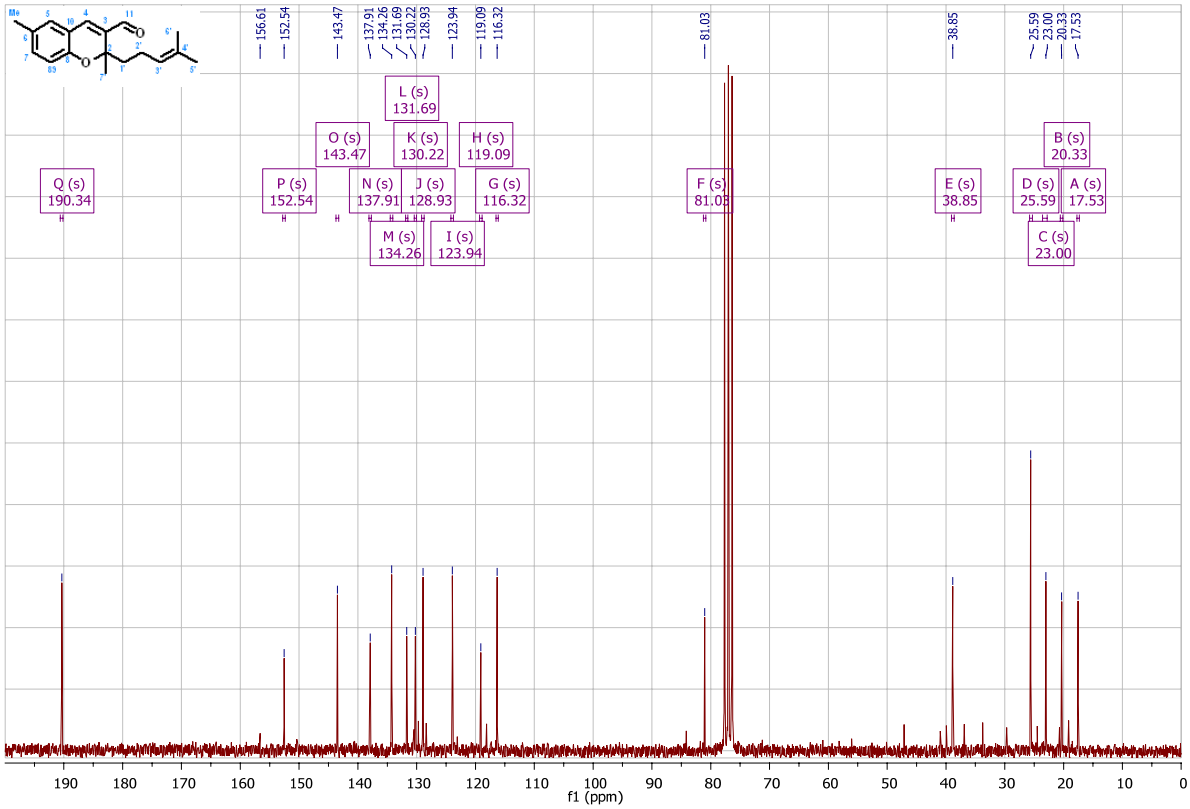
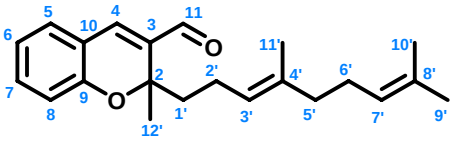
25.88
25.73
23.13
17.69
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



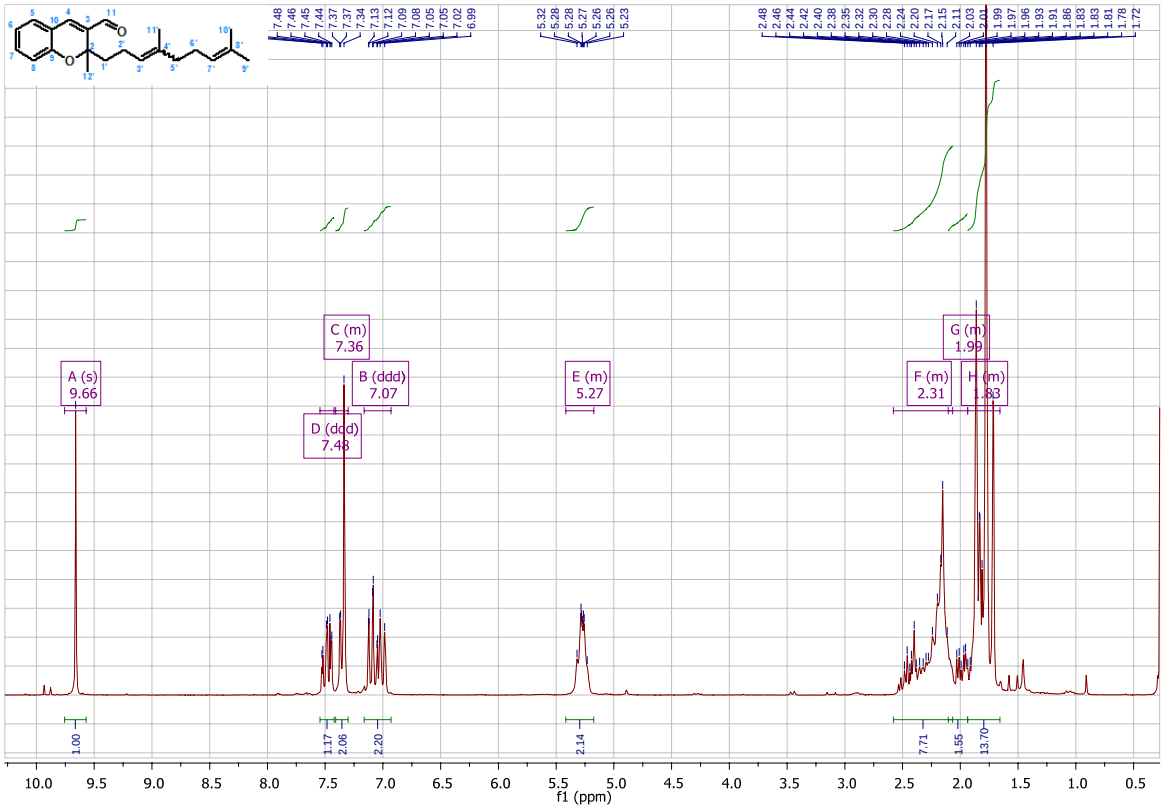
2,6-methyl-2-(4-methylpent-3-enyl)-2*H*-chromene-3-carbaldehyde (**3h**). **Method C** was used to obtain **3h**. Nerol (181 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M), 2-hydroxy-5-methylbenzldehyde (163 mg, 1.2 equiv., 1.2 mmol), K_2CO_3 (169 mg, 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).

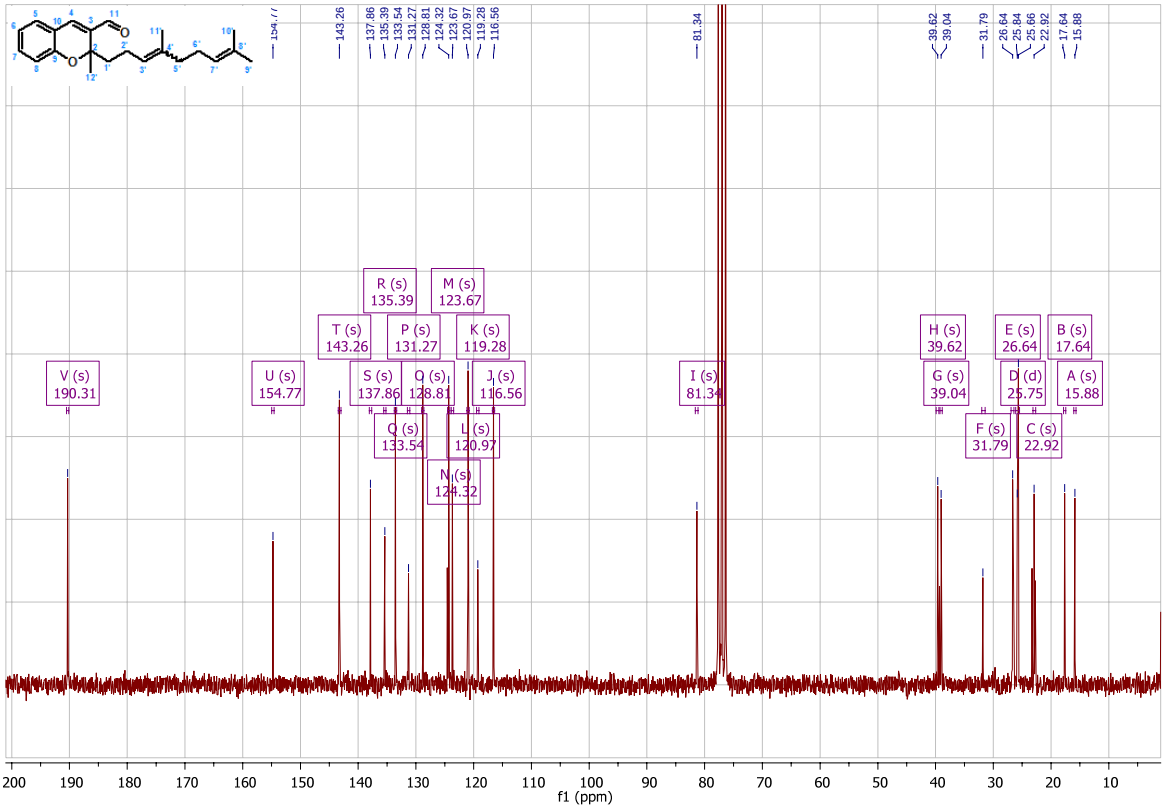


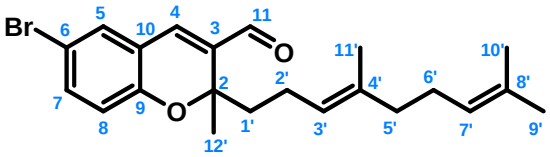




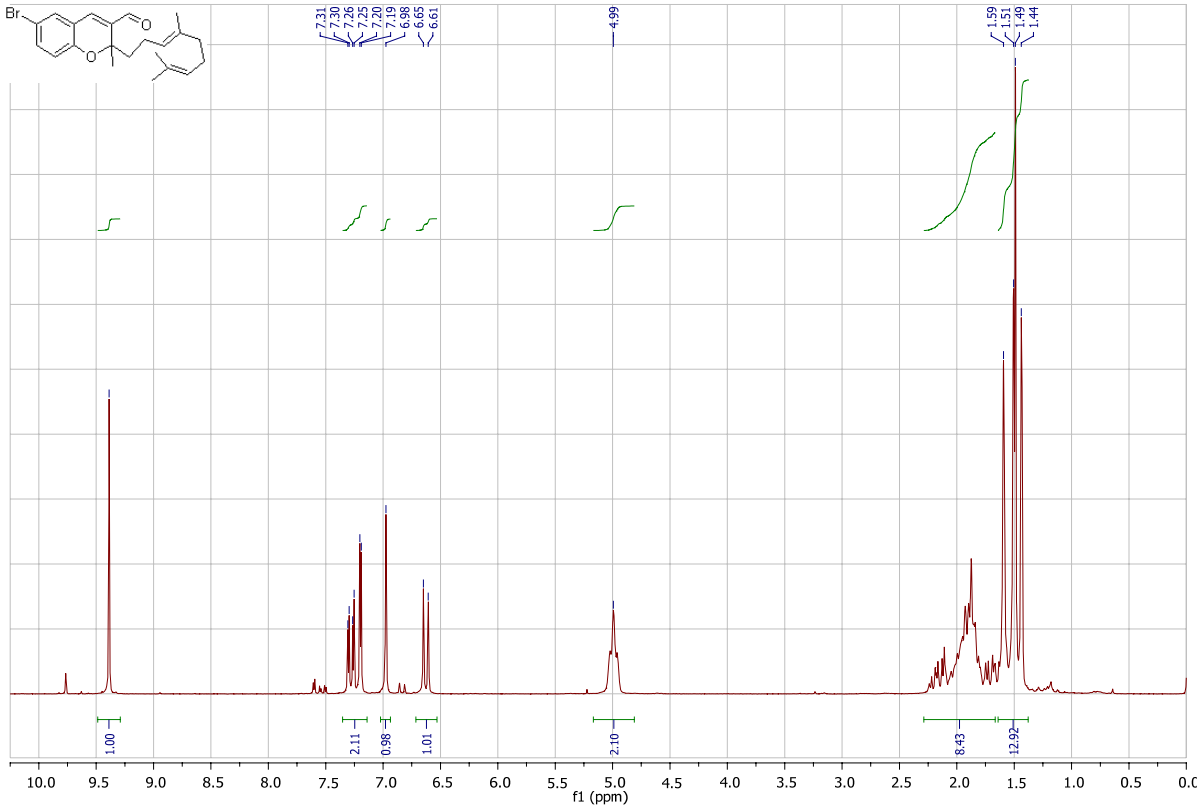
2-(4,8-dimethylnona-3,7-dienyl)-2-methyl-2*H*-chromene-3-carbaldehyde (**4c**). **Method B** was used to obtain **4c**. *Trans,trans* farnesol (250 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), anhydrous toluene (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), K_2CO_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 (**58%**). **Analytical data:** **^{1}H NMR** (200 MHz, $CDCl_3$) 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). **^{13}C NMR** (50 MHz, $CDCl_3$) 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 $C_{22}H_{28}O_2$ 324.2089 found 324.2078 Δ=1.1 ppm.

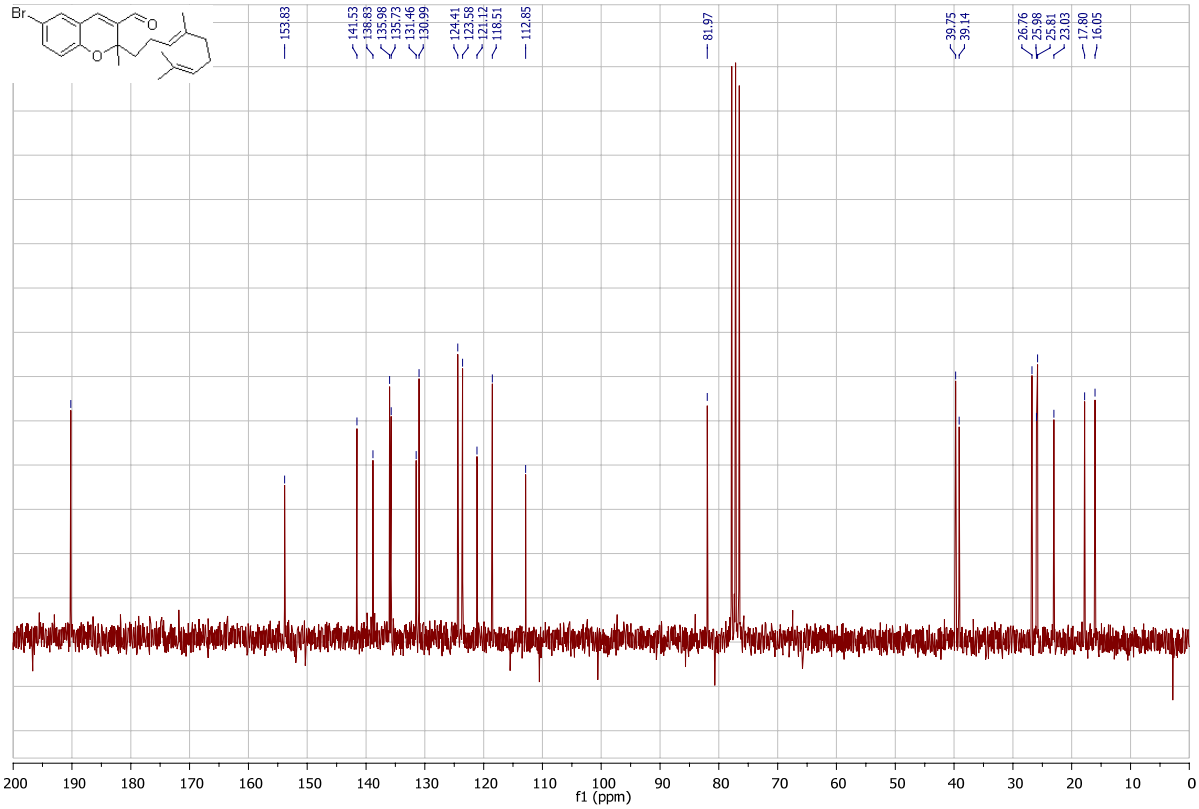

A (s)
9.66
C (m)
7.36
B (ddd)
7.07
D (ddd)
7.48
E (m)
5.27
G (m)
1.99
F (m)
2.31
H (m)
1.83
f1 (ppm)

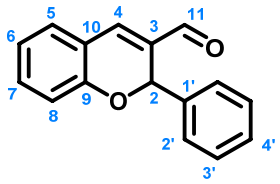

V (s)
190.31
U (s)
154.77
R (s)
135.39
M (s)
123.67
T (s)
143.26
P (s)
131.27
K (s)
119.28
S (s)
137.86
Q (s)
128.81
J (s)
116.56
O (s)
133.54
L (s)
120.97
N (s)
124.32
I (s)
81.34
H (s)
39.62
G (s)
39.04
E (s)
26.64
D (d)
25.75
B (s)
17.64
A (s)
15.88
F (s)
31.79
C (s)
22.92
f1 (ppm)



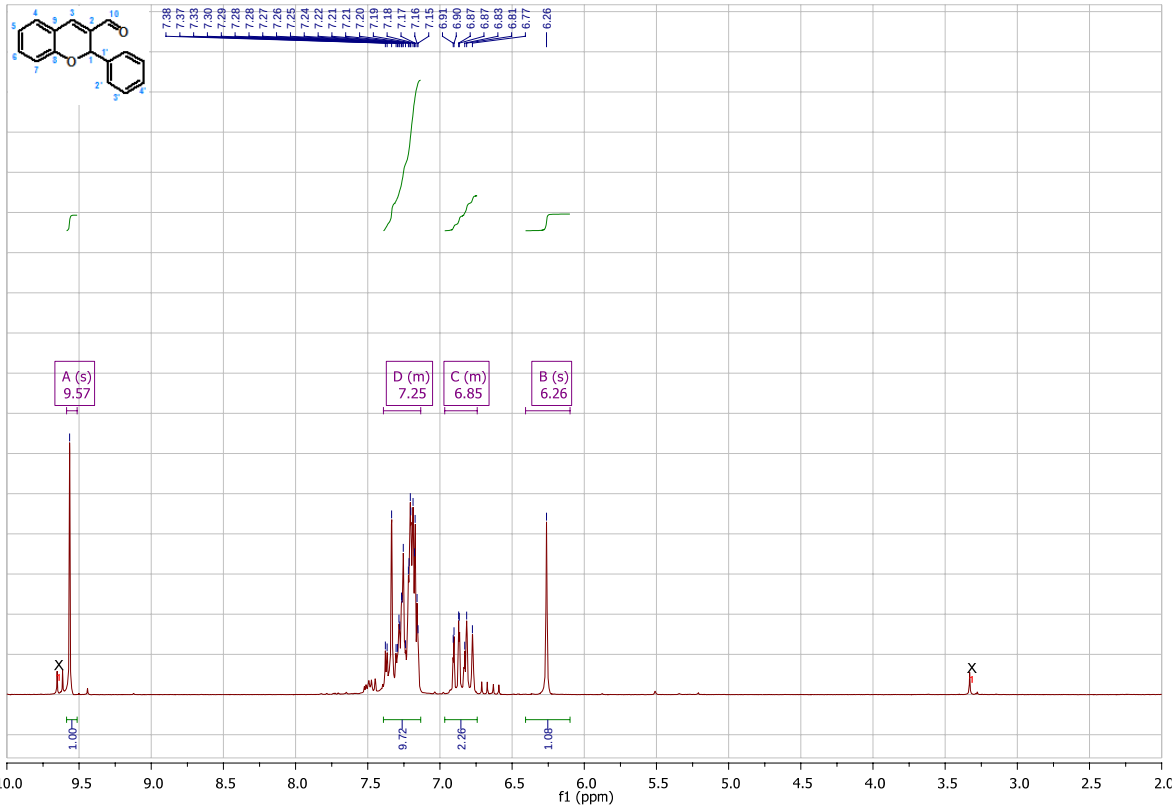
6-Bromo-2-(4,8-dimethylnona-3,7-dienyl)-2-methyl-2*H*-chromene-3-carbaldehyde (**4g**). **Method B** was used to obtain **4g**. *Trans,trans* farnesol (250 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), anhydrous toluene (2 mL, 0.5 M), 5-bromosalicylaldehyde (241 mg, 1.2 equiv., 1.2 mmol), K_2CO_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: ^{1}H 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). **^{13}C 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).

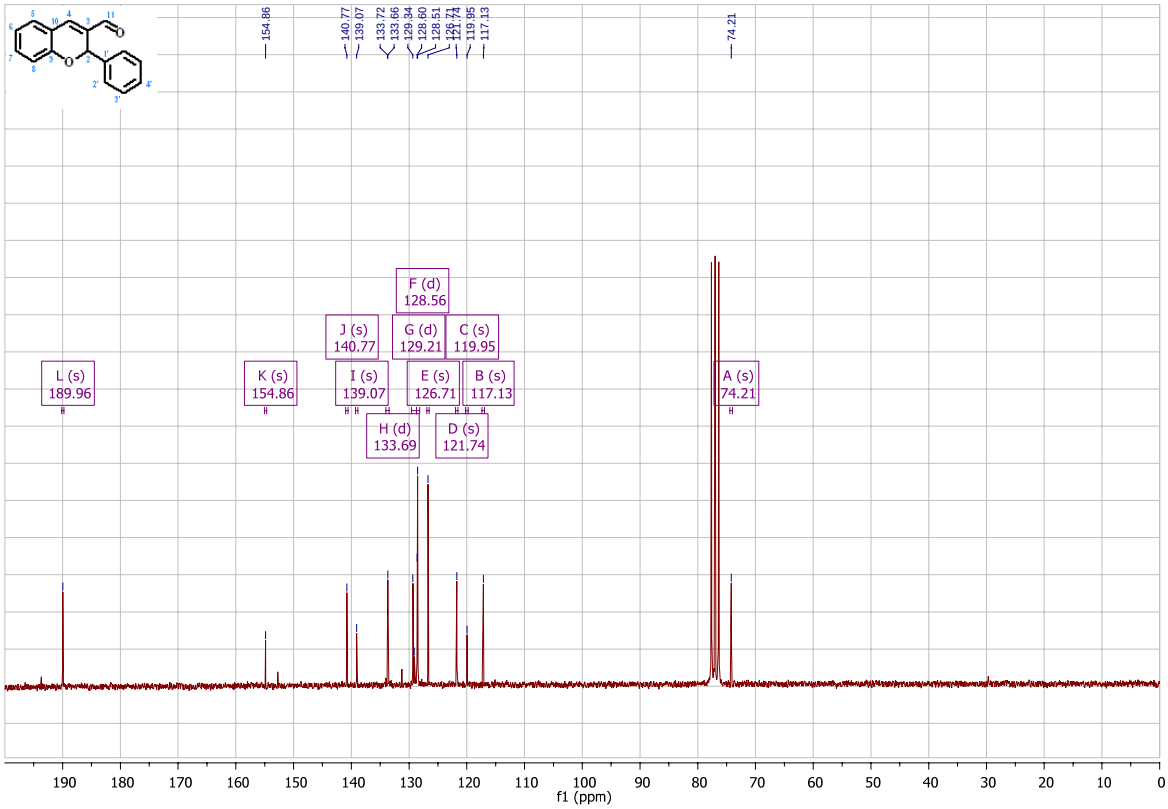


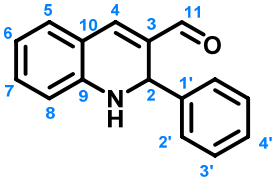




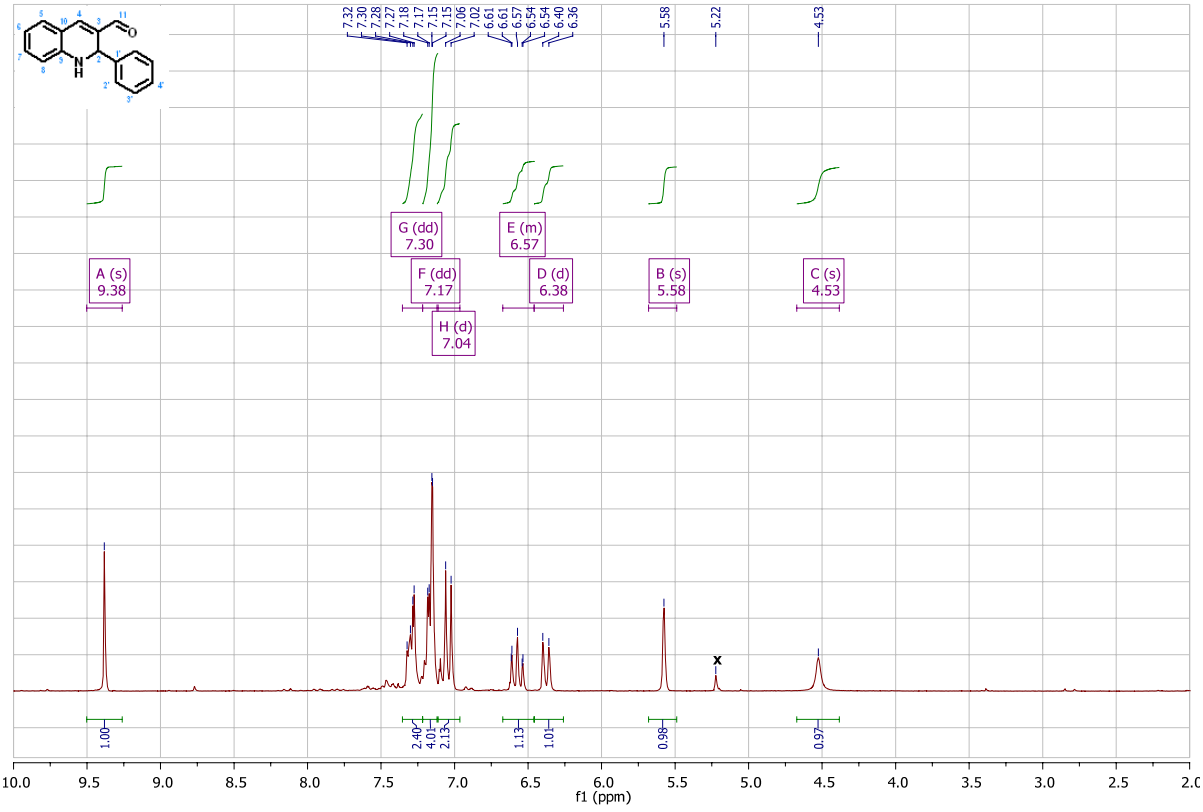
2-Phenyl-2*H*-chromene-3-carbaldehyde (**5c**). **Method C** was used to obtain **5c**. Cinnamyl alcohol **5a** (134 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 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, $CDCl_3$) δ (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, $CDCl_3$) δ (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).

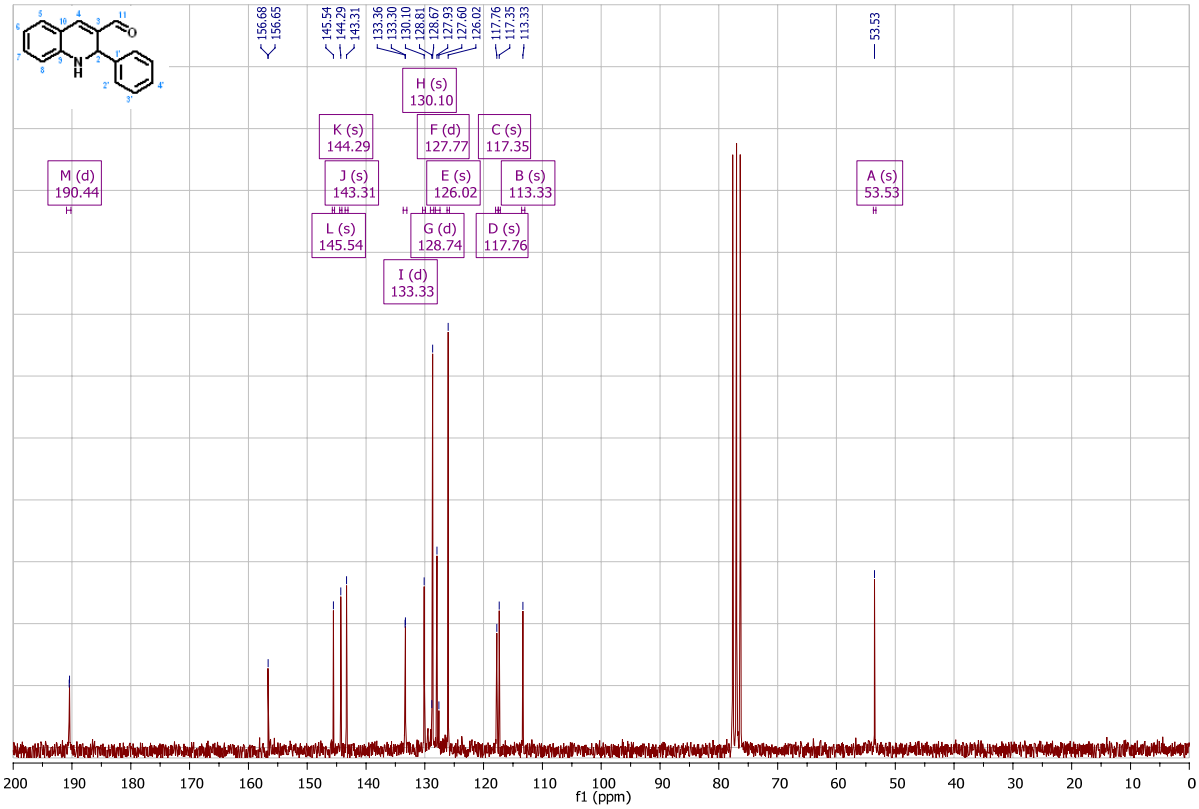

A (s)
9.57
D (m)
7.25
C (m)
6.85
B (s)
6.26
X
X
1.00
9.72
2.26
1.08
f1 (ppm)

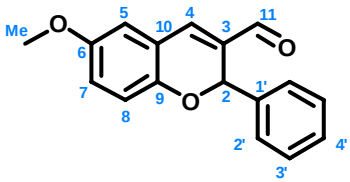

F (d)
128.56
J (s)
140.77
G (d)
129.21
C (s)
119.95
L (s)
189.96
K (s)
154.86
I (s)
139.07
E (s)
126.71
B (s)
117.13
H (d)
133.69
D (s)
121.74
A (s)
74.21
f1 (ppm)



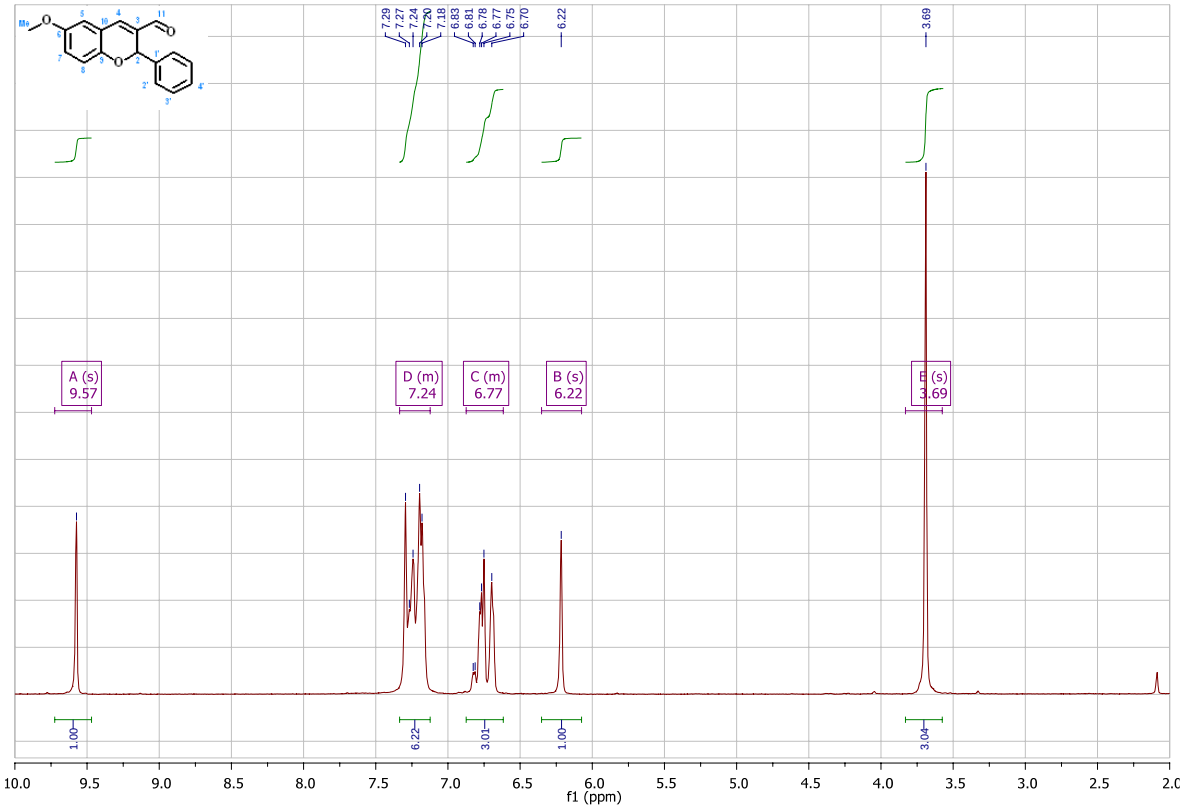
2-Phenyl-1,2-dihydroquinoline-3-carbaldehyde (**5d**). **Method C** was used to obtain **5d**. Cinnamyl alcohol (134 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), 2-aminobenzaldehyde (145.2 mg, 1.2 equiv., 1.2 mmol), pyrollidine (37.8 µL, 30 mol%), 3Å MS (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, $CDCl_3$) δ (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, $CDCl_3$) δ (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 Δ=0.3 ppm.

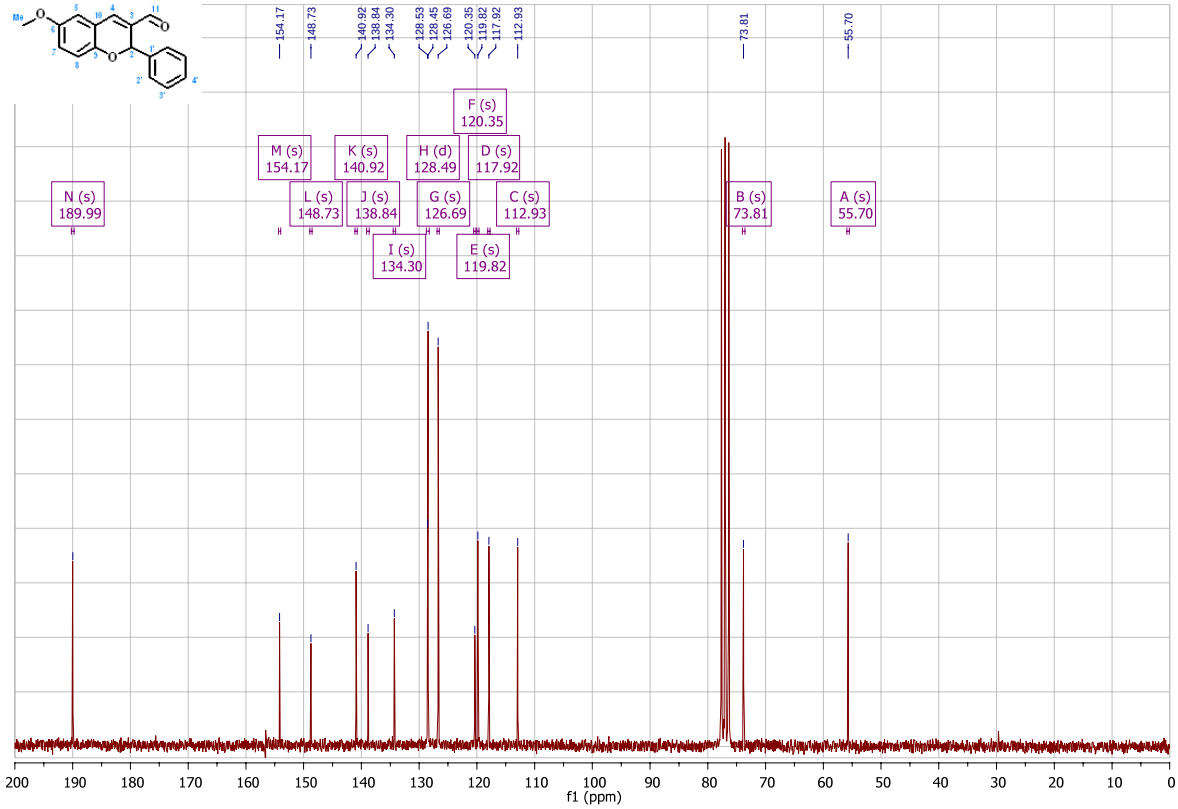


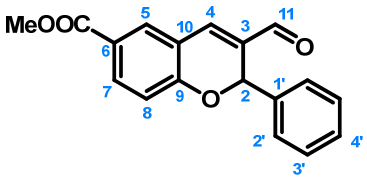




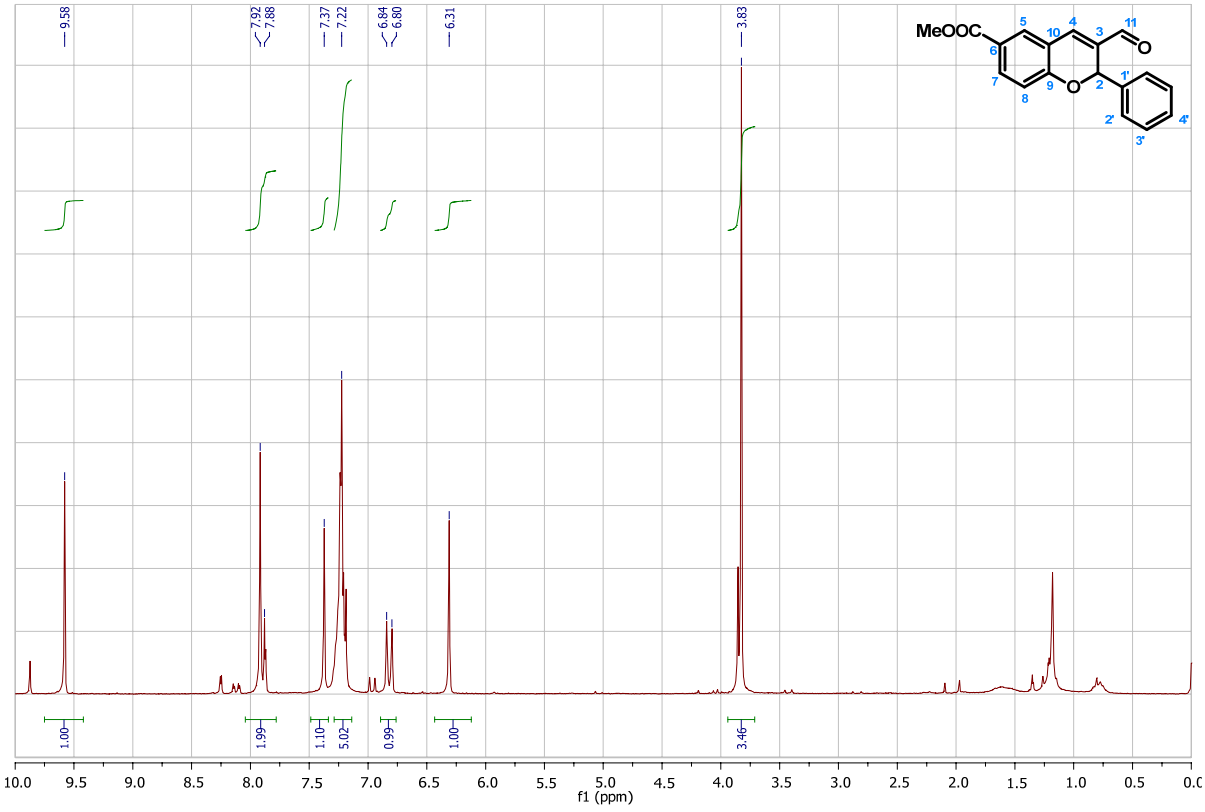
6-Methoxy-2-phenyl-2*H*-chromene-3-carbaldehyde (**5e**). **Method C** was used to obtain **5e**. Cinnamyl alcohol (134 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2mL, 0.5 M), 2-hydroxy-5-methoxybenzaldehyde (150 µL, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 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.

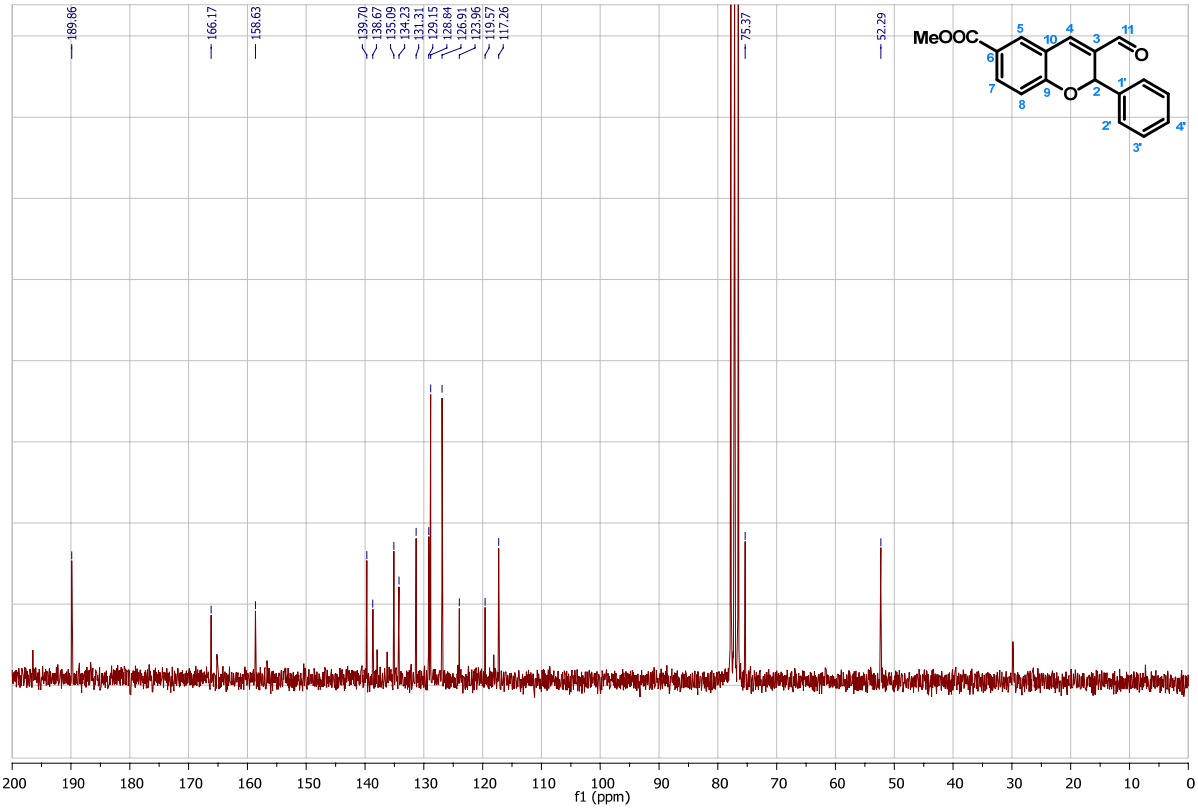

A (s) 9.57
D (m) 7.24
C (m) 6.77
B (s) 6.22
E (s) 3.69
f1 (ppm)

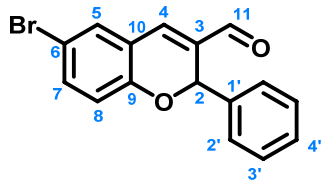

N (s) 189.99
M (s) 154.17
L (s) 148.73
K (s) 140.92
J (s) 138.84
I (s) 134.30
H (d) 128.49
G (s) 126.69
F (s) 120.35
E (s) 119.82
D (s) 117.92
C (s) 112.93
B (s) 73.81
A (s) 55.70
f1 (ppm)



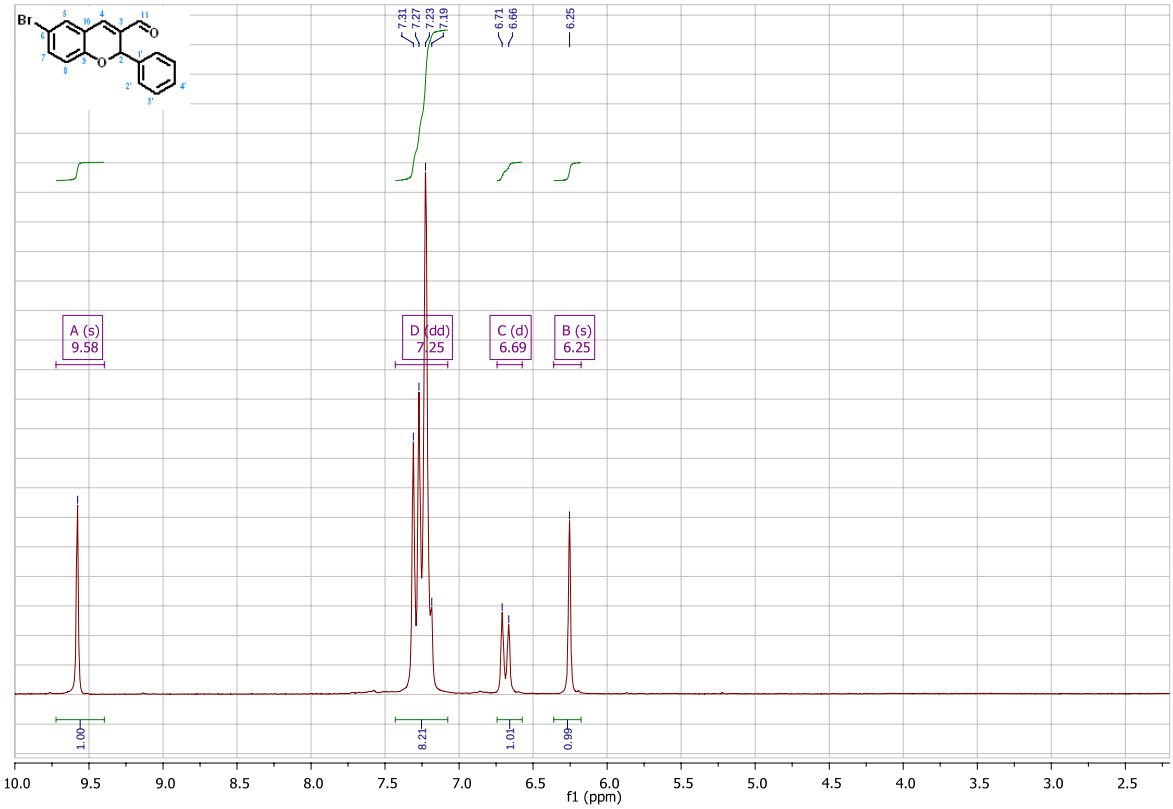
6-(Carboxymethyl)-2-phenyl-2*H*-chromene-3-carbaldehyde (**5f**). **Method C** was used to obtain **5f** with cinnamyl alcohol (134 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), methyl 3-formyl-4-hydroxybenzoate (240 mg, 1.2 equiv., 1.2 mmol), pyrrolidine (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, $CDCl_3$) δ (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, $CDCl_3$) δ (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).

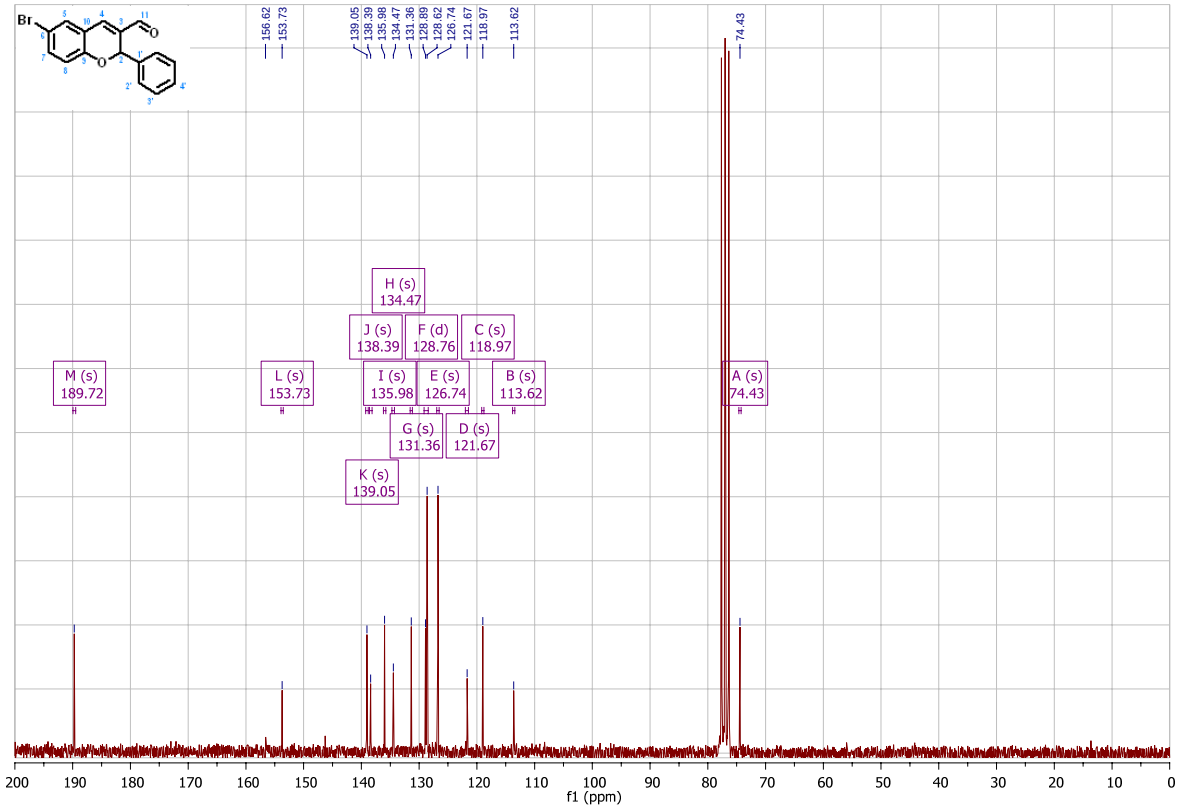


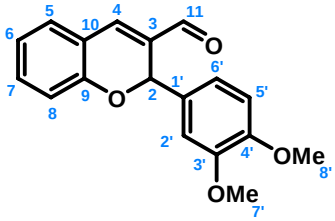




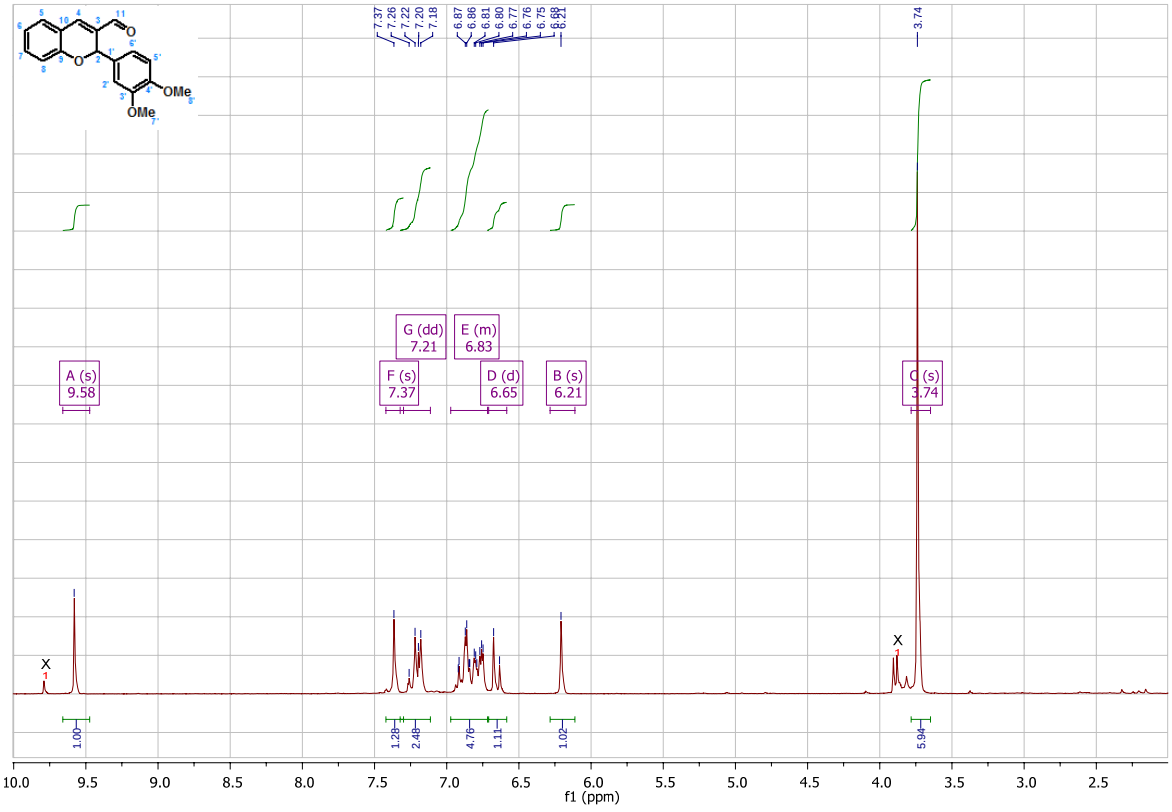
6-Bromo-2-phenyl-2*H*-chromene-3-carbaldehyde (**5g**). **Method C** was used to obtain **5g** with cinnamyl alcohol (134 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), 5-bromosalicylaldehyde (240 mg, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 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.

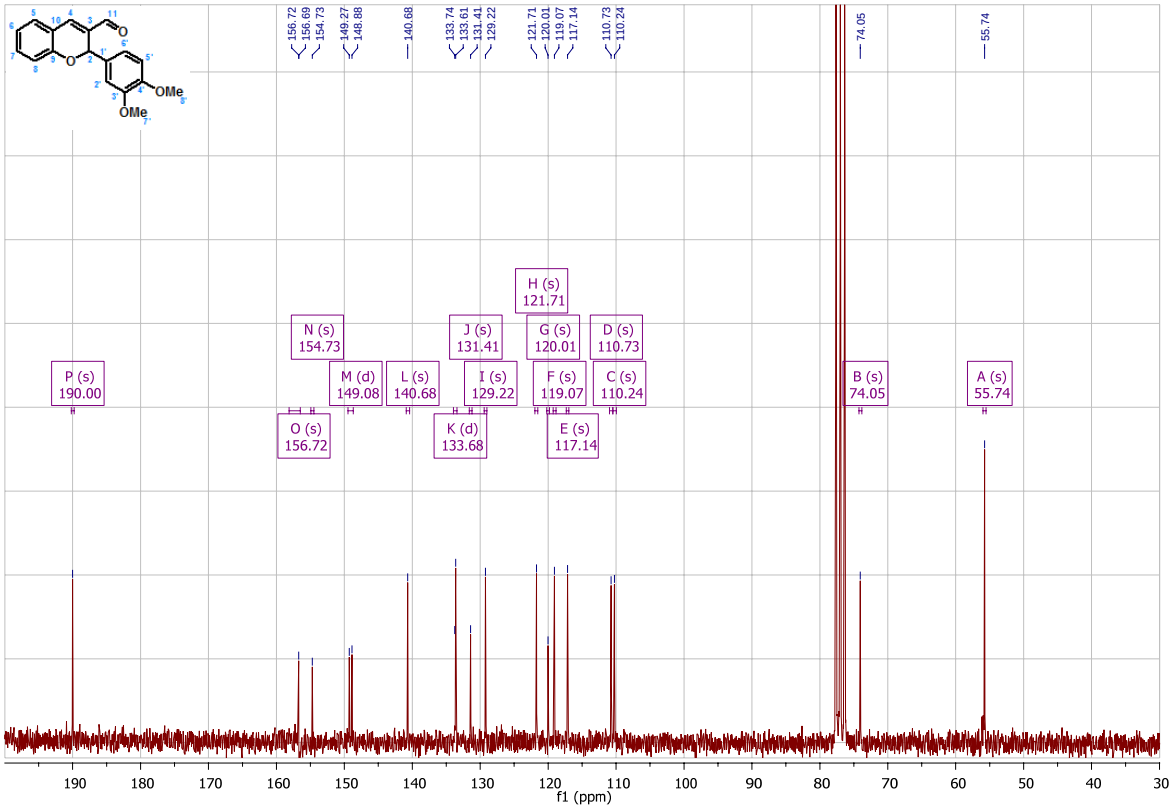

A (s)
9.58
D (dd)
7.25
C (d)
6.69
B (s)
6.25
f1 (ppm)

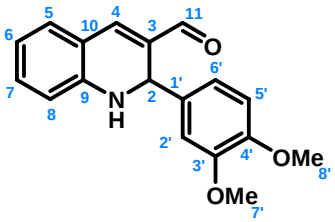

H (s)
134.47
J (s)
138.39
F (d)
128.76
C (s)
118.97
M (s)
189.72
L (s)
153.73
I (s)
135.98
E (s)
126.74
B (s)
113.62
A (s)
74.43
G (s)
131.36
D (s)
121.67
K (s)
139.05
f1 (ppm)



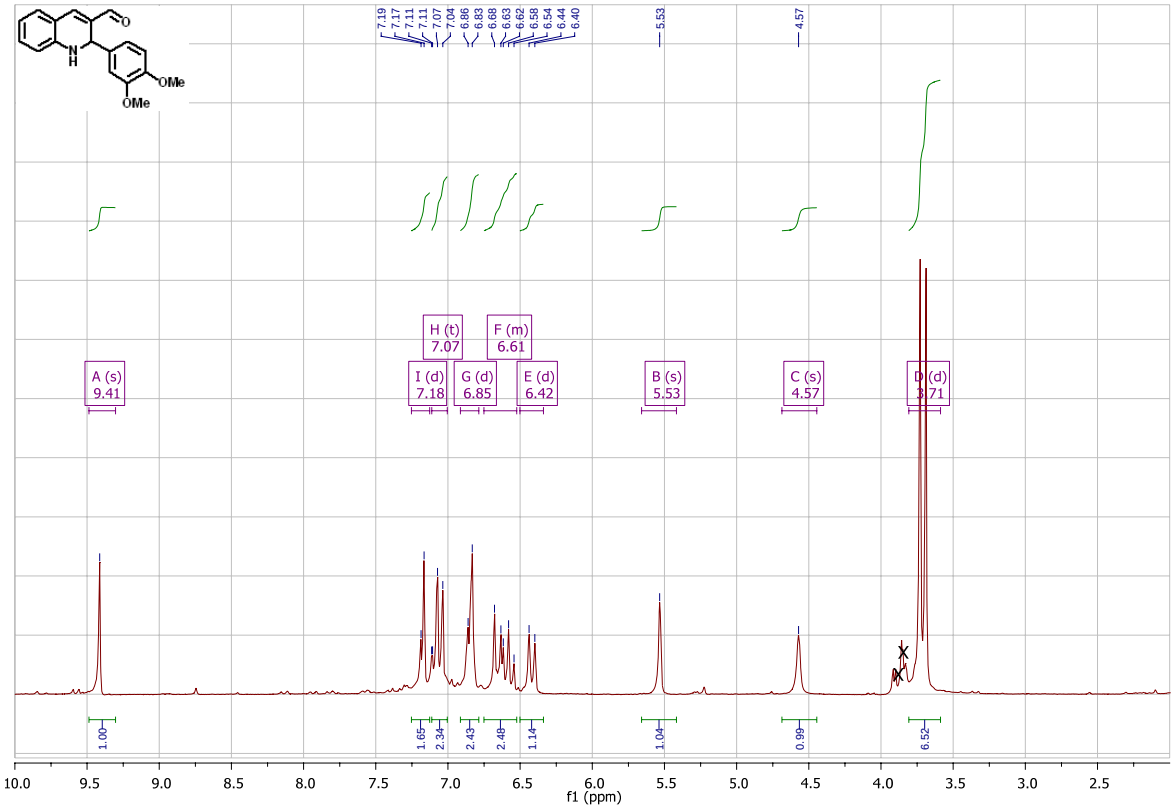
2-(3,4-dimethoxyphenyl)-2*H*-chromene-3-carbaldehyde (**6c**). **Method C** was used to obtain **6c**. **6a** (196 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2mL, 0.5 M), salicyladehyde (124 µL, 1.2 equiv., 1.2 mmol), pyrrolidine (37.8 µL, 30 mol%), 3Å MS (50 mg) 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** (EI, 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.

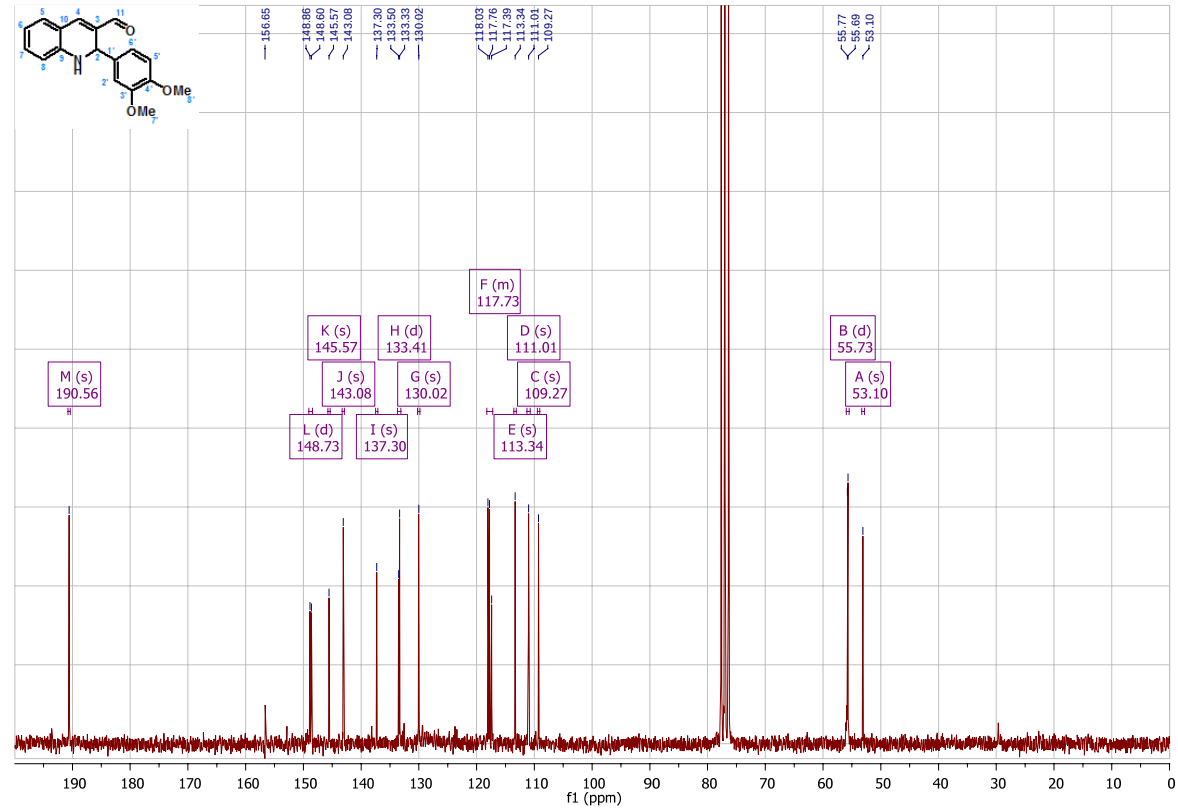


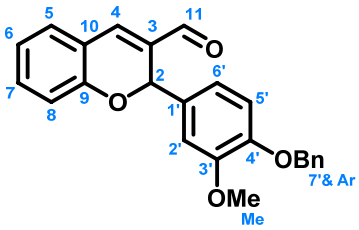




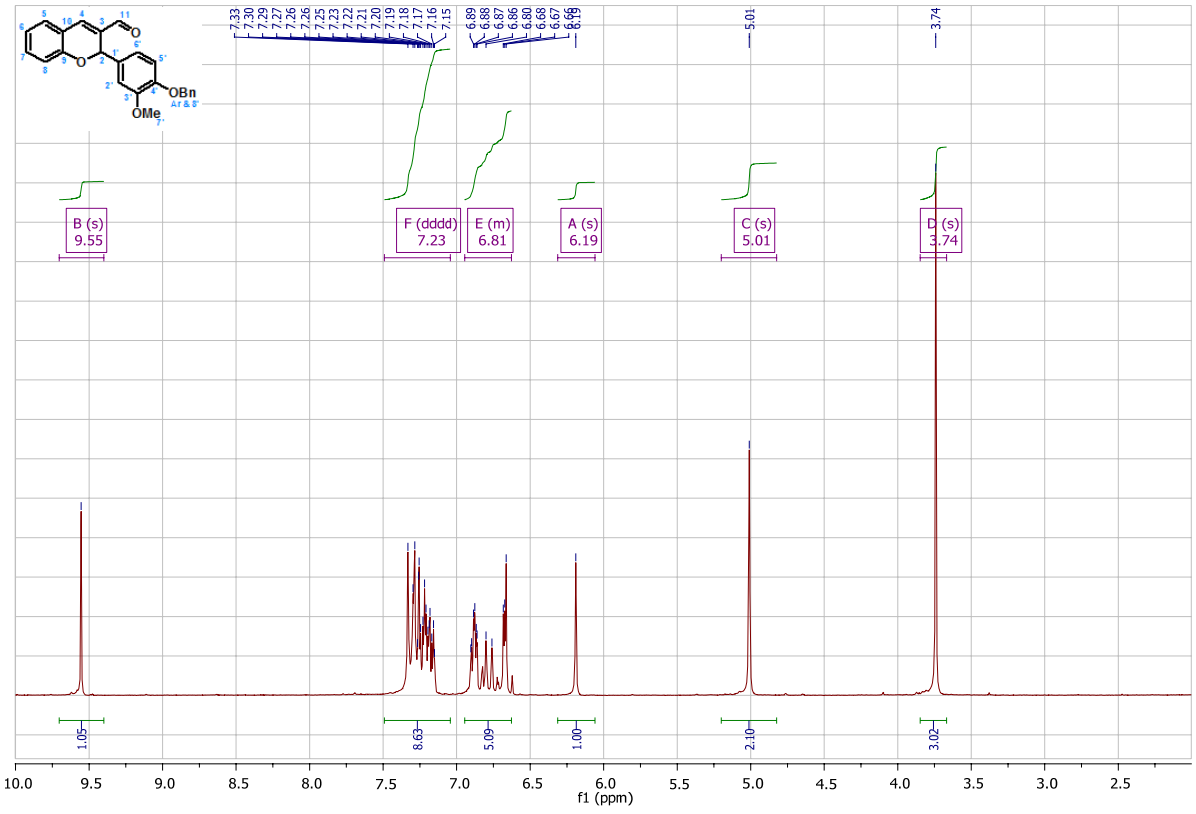
2-(3,4-dimethoxyphenyl)-1,2-dihydroquinoline-3-carbaldehyde (**6d**). **Method C** was used to obtain **6d**. **6a** (196 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), 2-aminobenzaldehyde (145.2 mg, 1.2 equiv., 1.2 mmol), pyrollidine (37.8 µL, 30 mol%), 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.

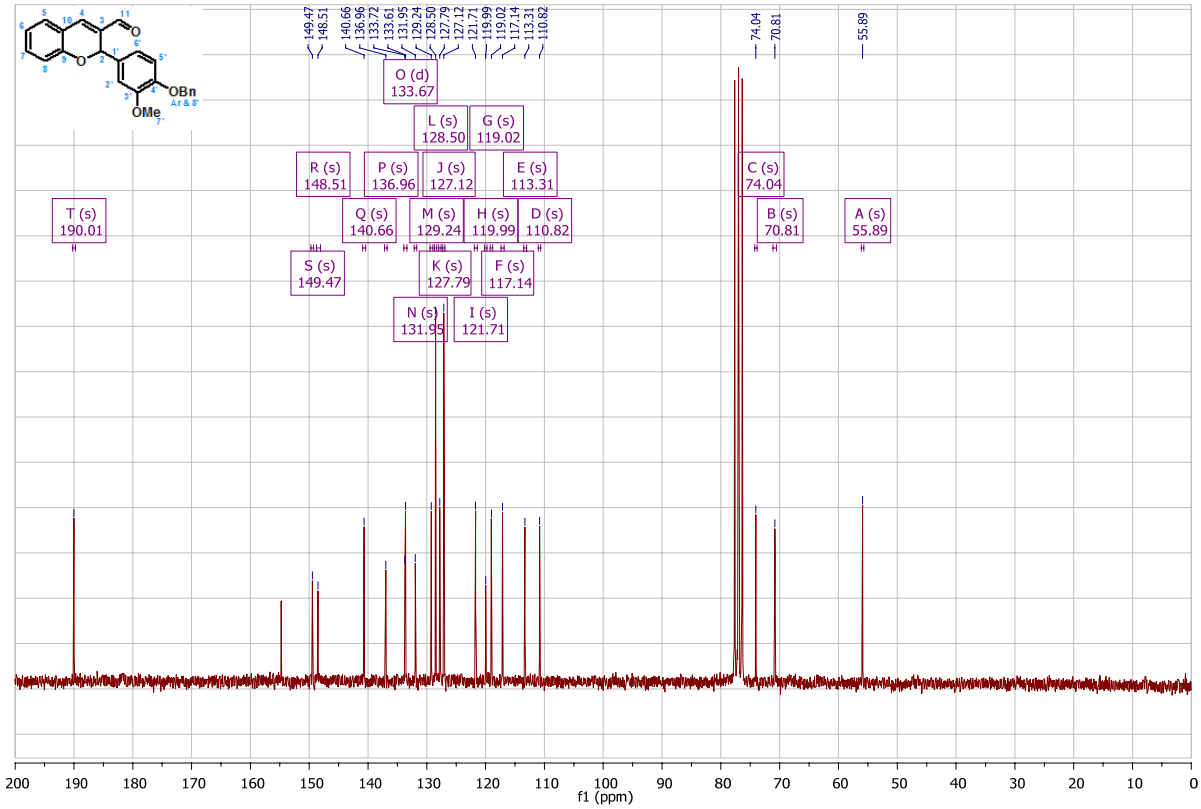

OMe
OMe
7.19
7.17
7.11
7.11
7.07
7.04
6.86
6.83
6.68
6.63
6.62
6.58
6.54
6.44
6.40
5.53
4.57
H (t)
7.07
F (m)
6.61
A (s)
9.41
I (d)
7.18
G (d)
6.85
E (d)
6.42
B (s)
5.53
C (s)
4.57
D (d)
3.71
1.00
1.65
2.34
2.43
2.48
1.14
1.04
0.99
6.52
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)


OMe
OMe
156.65
148.86
148.60
145.57
143.08
137.30
133.50
133.33
130.02
118.03
117.76
117.39
113.34
111.01
109.27
55.77
55.69
53.10
F (m)
117.73
K (s)
145.57
H (d)
133.41
D (s)
111.01
B (d)
55.73
M (s)
190.56
J (s)
143.08
G (s)
130.02
C (s)
109.27
A (s)
53.10
L (d)
148.73
I (s)
137.30
E (s)
113.34
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

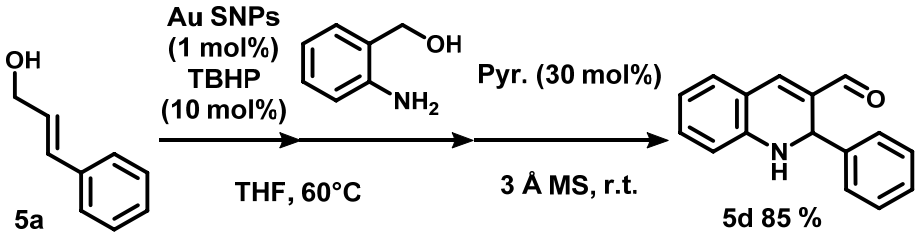


2-(4-(benzyloxy)-3-methoxyphenyl)-2*H*-chromene-3-carbaldehyde (**7c**). General procedure **method C** was used to obtain **7c**. **7a** (270 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M), salicylaldehyde (124 µL, 1.2 equiv., 1.2 mmol), pyrollidine (37.8 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):** **^{1}H NMR** (200 MHz, $CDCl_3$) 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). **^{13}C NMR** (50 MHz, $CDCl_3$) 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.**

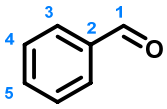


Method D: To a dried reactor under O_2 atmosphere, catalyst **B** (0.08 mmol, 0.08 equiv.), *tert*-butyl hydroperoxide solution (0.1 mmol, 0.1 equiv.), anhydrous THF (2.0 mL, 0.5 M) and **5a** cinnamyl alcohol (1 mmol, 1.0 equiv.) were added. The solution was stirred at 60 °C for 8 h. 2-Aminobenzyl alcohol (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 for 15 hours at rt. After completion of the reaction monitored by TLC, the reactor was quenched with $NH_4Cl_{(aq.)}$ 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**.

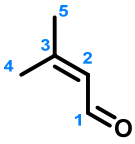
6. Procedure E for the oxidation of alcohols over supported gold nanoparticles Au SNPs/M_xO_y.

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 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.

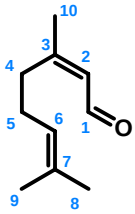
These products were characterized by comparison with authentic samples or literature data.



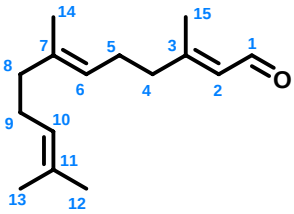
Benzaldehyde (**1b**). **Method D** was used to obtain **1b**. Benzyl alcohol (108 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow liquid (**87 %**).



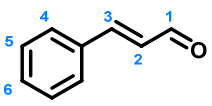
Prenal (**2b**). **Method E** was used to obtain **2b**. Prenol (102 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow liquid (**68%**).



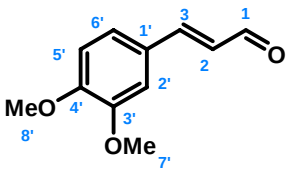
Neral (**3b**). **Method E** was used to obtain **3b**. Nerol (181 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow pale oil (**67%**).



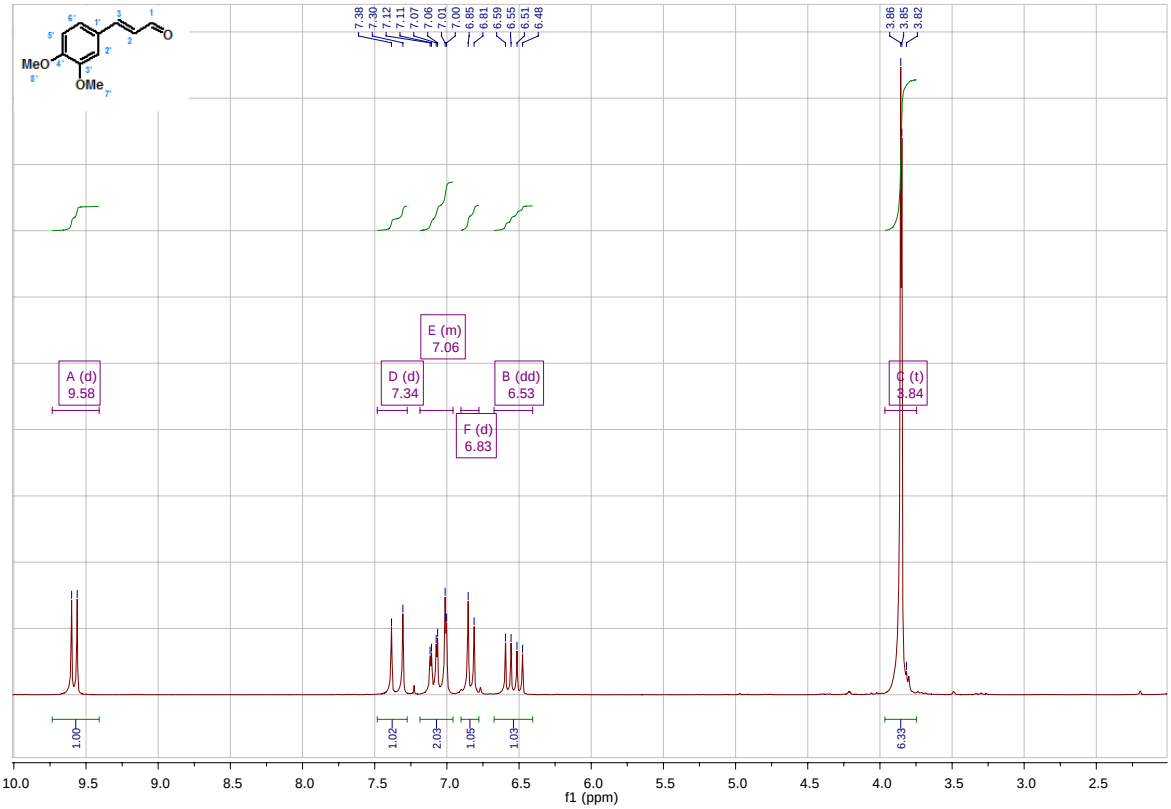
Farnesal (**4b**). **Method E** was used to obtain **4b**. *Trans,trans* farnesol (250 µL, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), toluene (2 mL, 0.5 M) at 80 °C under an oxygen atmosphere, yielded the desired compound as a yellow pale oil (**68%**).

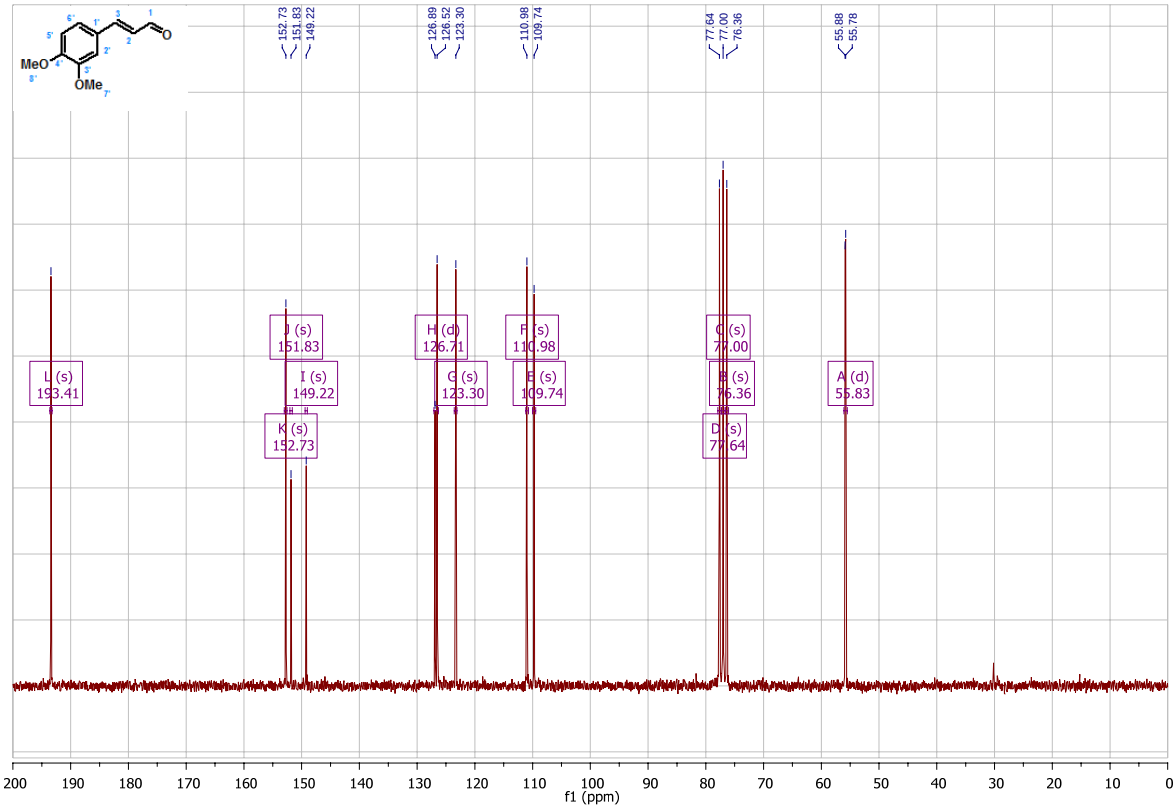


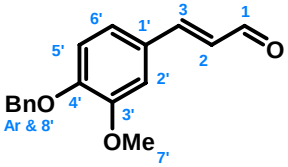
Cinnamaldehyde (**5b**). **Method E** was used to obtain **5b**. Cinnamyl alcohol **5a** (134 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2mL, 0.5 M) at 60 °C under an oxygen atmosphere, yielded the desired compound as a yellow orange liquid (**99%**).



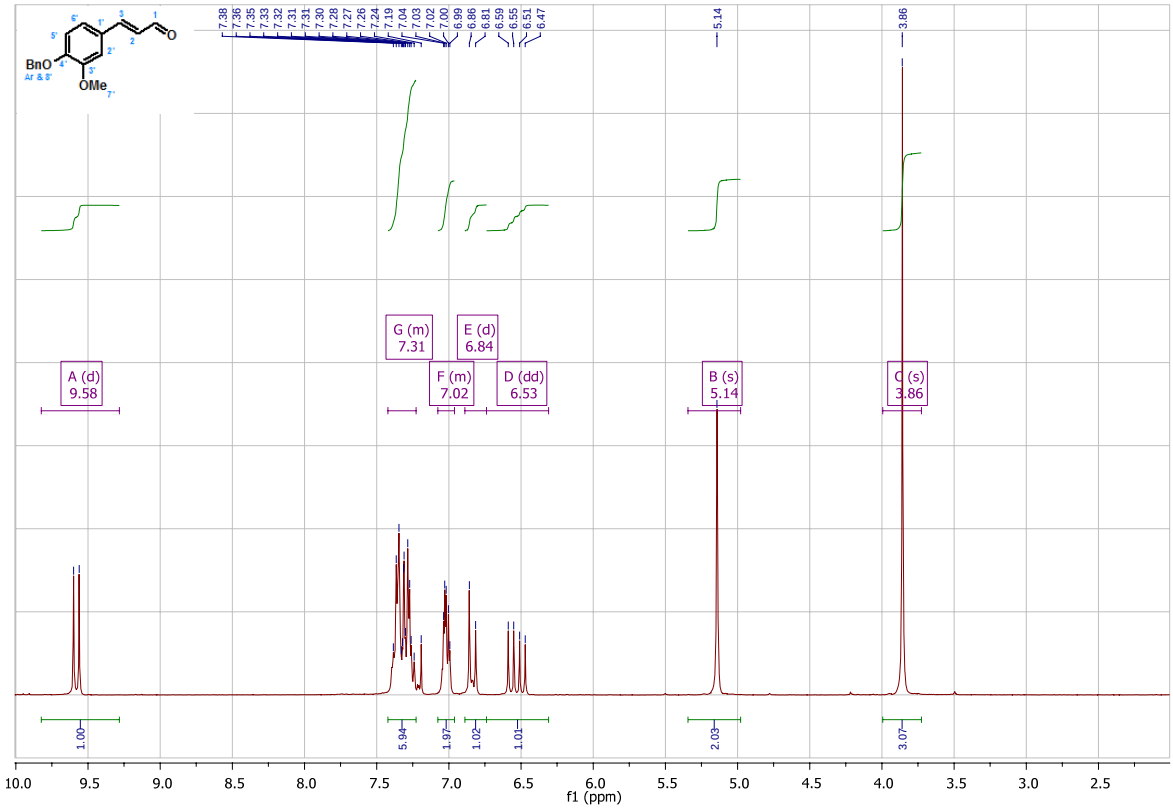
3-(3,4-Dimethoxyphenyl)-prop-2-enal (**6b**). **Method E** was used to obtain **6b**. **6a** (196 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M) at 60 °C under an oxygen atmosphere, yielded the desired compound as a pale yellow solid (**95%**). **Analytical data:** **^{1}H NMR** (200 MHz, $CDCl_3$) 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 NMR** (50 MHz, $CDCl_3$) 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).

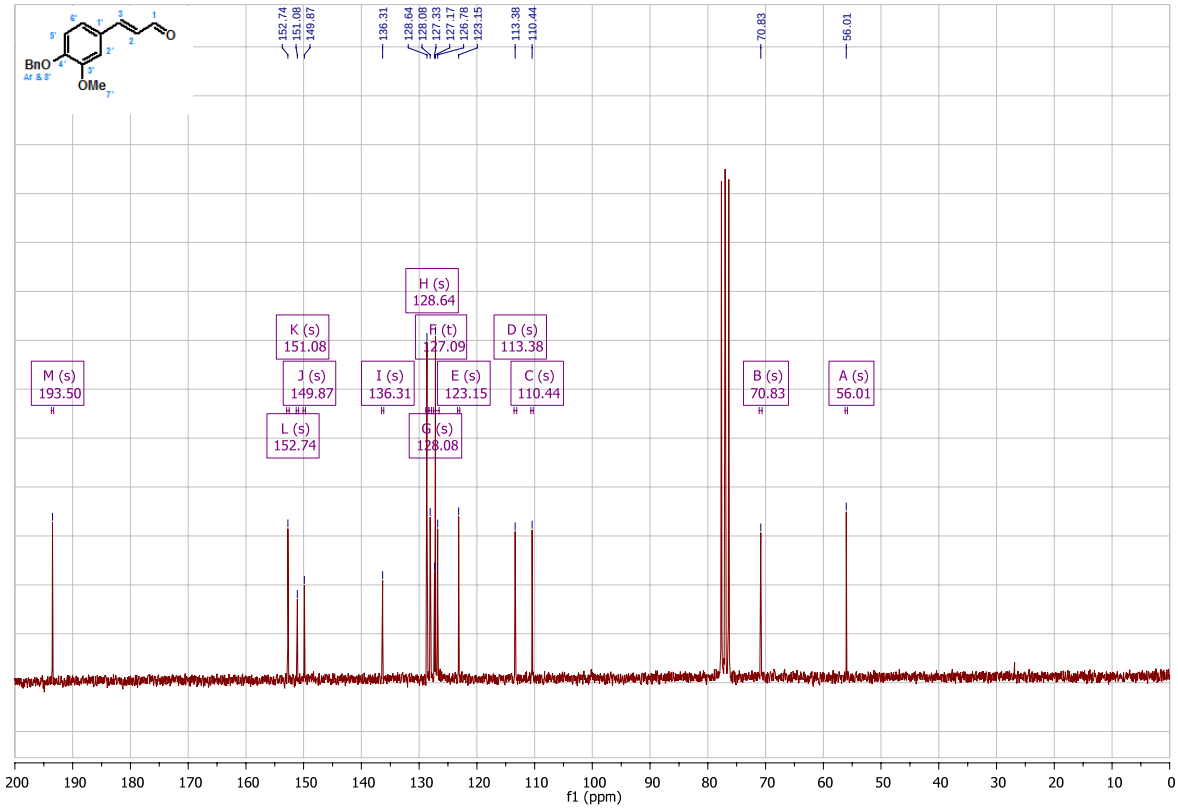






3-(4-(benzyloxy)-3-methoxyphenyl)-prop-2-enal (**7b**). **Method E** was used to obtain **7b**. **7a** (270 mg, 1 mmol), catalyst **B** (158.4 mg, 0.8 mol%), TBHP (18.2 µL, 10 mol%), THF (2 mL, 0.5 M) at 60 °C under an oxygen atmosphere, yielded the desired compound as a pale yellow oil (**93%**). **Analytical data:** **^{1}H NMR** (200 MHz, $CDCl_3$) 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). **^{13}C NMR** (50 MHz, $CDCl_3$) 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** (EI, 70 eV) m/z 91.1 (100), 65.0 (9), 268.1 (6). **HRMS** calcd for exact mass $C_{17}H_{16}O_3$ 268.1099 found 268.1097.


BnO
OMe
A (d) 9.58
G (m) 7.31
E (d) 6.84
F (m) 7.02
D (dd) 6.53
B (s) 5.14
C (s) 3.86
f1 (ppm)


BnO
OMe
M (s) 193.50
K (s) 151.08
J (s) 149.87
L (s) 152.74
I (s) 136.31
H (s) 128.64
F (t) 127.09
G (s) 128.08
E (s) 123.15
D (s) 113.38
C (s) 110.44
B (s) 70.83
A (s) 56.01
f1 (ppm)