I. General experimental

Proton (1H) and carbon (13C) NMR spectra were recorded on a Bruker DRX600 spectrometer operating at 150 MHz for carbon nuclei or a Bruker DRX400 spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei. Infrared spectra (ν max) were recorded on an Agilent Cary 630 FTIR Spectrometer. High resolution mass spectra (HRMS) (ESI) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration. Analytical chiral HPLC was performed with a Agilent Technologies 1260 HPLC using a RegisCell™ 5μm column (4.6 mm x 25 cm) obtained from Regis Technologies, Inc. with visualization at, 230, 220 or 210 nm. Flash column chromatography was performed on silica gel (Davisil LC60A, 40-63 μm silica media) using compressed air. Thin layer chromatography (TLC) was performed using aluminum-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F254 plates). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with potassium permanganate or vanillin stain followed by heating. Starting materials and reagents were purchased from Sigma-Aldrich, Oakwood, Combi-Blocks or Chemieliva and were used as supplied. Diethyl ether (Et2O) and tetrahydrofuran (THF) were dried over sodium benzphenone ketyl. Dichloromethane (CH2Cl2) was dried by passing over activated alumina. Toluene was dried by passing over activated 3 Å molecular sieves. DMF was dried by stirring with calcium hydride overnight then was filtered and distilled under reduced pressure, and stored over 3 Å molecular sieves. DMSO was dried by stirring over activated 3 Å molecular sieves overnight and then distilled under reduced pressure, and stored over 3 Å molecular sieves. Methanol was dried over and distilled from magnesium methoxide. Unless otherwise stated, all reactions were conducted in
flame-dried glassware under an atmosphere of nitrogen. Benzaldehyde **SI-1** was prepared according to literature procedures. NHC was prepared by first generating the carbene from the corresponding triazolium tetrafluoroborate salt, using equimolar potassium hexamethyldisilazide. The reaction mixture was then filtered in toluene and the filtrate concentrated. DA-cyclobutane **14a** was prepared according to literature procedures. Racemic β-lactone **13a** was prepared using IPr·HCl as the precatalyst and reacted at room temperature.

II. Synthesis of β–lactone **13a**

**\( (E)-3-(2,6-Dimethoxy-4-pentylphenyl)acrylic acid (15b) \)**

![Diagram](image)

Following a modified procedure of Ling, a 250 mL round bottom flask was charged with aldehyde **SI-1** (19.2 g, 81 mmol), malonic acid (16.9 g, 162 mmol), piperidine (6.5 mL), and pyridine (100 mL). The flask was sealed and heated to 100 °C for 16 h. After cooling to room temperature, the mixture was poured into ice cold water. Following acidification with concentrated HCl, the precipitate was washed with H2O (500 mL) and hexanes (500 mL) before being dried at 60 °C *in vacuo*. The title compound **15b** (18.7 g, 83%) was isolated as an off-white solid. \( R_f 0.1 \) (1:1, v/v hexanes : EtOAc); MP 180-182 °C IR \( \nu_{\text{max}} \) 2930, 2862, 2688, 1675, 1599, 1563, 1409 1201, 1121 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl3) \( \delta \) 8.23 (d, \( J = 16.2 \) Hz, 1H), 6.86 (d, \( J = 16.2 \) Hz, 1H), 6.38 (s, 2H), 3.88 (s, 6H), 2.61-2.57 (m, 2H), 1.67-1.60 (m, 2H), 1.38-1.31 (m, 4H), 0.91 (t, \( J = 7.0 \) Hz, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl3) \( \delta \) 174.3, 160.3, 148.0, 138.0, 118.5, 109.9, 104.0, 55.8, 37.1, 31.7, 31.0, 22.7, 14.2 ppm; HRMS (ESI) \( m/z \) Found: (M+H)+, C\(_{16}\)H\(_{22}\)O\(_4\), 279.1591, requires 279.1591.

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(E)-3-(2,6-Dimethoxy-4-pentylphenyl)acryloyl fluoride (15a)

Following the procedure of Georg,\textsuperscript{7} to a suspension of α,β-unsaturated carboxylic acid 15b (8.4 g, 30 mmol) in CH₂Cl₂ (60 ml) at 0 °C was added diethylaminosulfur trifluoride (6.0 mL, 45 mmol). After stirring at 0 °C for 30 minutes, the reaction was quenched by slow addition of NaHCO₃ (200 ml of a saturated aqueous solution). The mixture was extracted with CH₂Cl₂ (3 x 50 ml), the organic phase dried (Na₂SO₄), concentrated under reduced pressure and the crude material purified via flash column chromatography. The title compound 15a (7.3 g, 83%) was isolated as an off-white solid. Rₚ 0.8 (10:3, v/v hexanes : EtOAc); MP 30-32°C IR ν max 2932, 2858, 1781, 1602, 1565, 1459, 1118, 1089 cm⁻¹ ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 16.2 Hz, 1H), 6.77 (dd, J = 16.2, 7.6 Hz, 1H), 6.39 (s, 2H), 3.89 (s, 6H), 2.62-2.58 (m, 2H), 1.67-1.60 (m, 2H), 1.38-1.30 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 159.8 (d, J = 334.4 Hz), 149.8, 142.6 (d, J = 7.4 Hz), 112.4 (d, J = 63.9 Hz), 112.0, 109.2, 104.0, 55.8, 37.1, 31.6, 30.8, 22.6, 14.1 ppm; HRMS (ESI) m/z Found: (M−H)−, C₁₆H₂₁FO₃, 279.1398, requires 279.1396.

Dimethyl (1R,2S,6S)-2-(2,6-dimethoxy-4-pentylphenyl)-8-oxo-7-oxabicyclo[4.2.0]octane-3,3-dicarboxylate (13a)

A two-neck flask equipped with a reflux condenser and septum was charged with donor-acceptor cyclobutane 14a (2.1 g, 10.7 mmol), α,β-unsaturated acyl fluoride 15a (3.0 g, 10.7 mmol), THF (85 ml) and DMF (10 ml). The solution was placed in an 80 °C oil bath, then a solution of NHC (0.58 g, 1.6 mmol) in THF (5 ml) was added. The septum was replaced with a stopper and the reaction mixture was stirred at 80 °C for 2 hours. The mixture was then allowed to cool to room temperature, before being concentrated under reduced pressure and the crude material purified via flash column chromatography. The title compound 13a (7.3 g, 45%) was isolated as a yellow oil and as a single diastereoisomer as observed by ¹H-NMR (>20:1 dr). Rₚ 0.3 (10:3, v/v hexanes : EtOAc); RegisCell™

\textsuperscript{7} Bappert, E.; Müller, P.; Fu, G. F. Chem. Commun. 2006, 2604.
5 μm, hexane : iPrOH 95:5, 1 ml/min, λ = 230 nm, fraction t₁ = 16.82 min (major enantiomer) and 20.30 min (minor enantiomer); er = 98:2 \[\alpha]_{D}^{25} = -129.8^\circ (c = 0.03 \text{ CHCl}_3); \text{ MP 95-97 }^\circ \text{C}; \text{ IR } \nu_{\text{max}} 2932, 1857, 1819, 1731, 1608, 1230, 1118 cm^{-1}; \text{ }^1\text{H NMR (400 MHz, CDCl}_3) \delta 6.30 (s, 1H); 6.29 (s, 1H) 5.14 (d, J = 1.1 Hz, 1H), 4.88-4.83 (m, 1H), 3.85 (dd, J = 6.9, 1.1 Hz, 1H), 3.77 (s, 6H), 3.75 (brs, 3H), 3.16 (s, 3H) 2.61-2.48 (m, 4H), 2.02-1.96 (m, 1H), 1.86-1.77 (m, 1H), 1.61-1.53 (m, 2H), 1.37-1.25 (m, 4H) 0.88 (t, J = 6.8 Hz, 3H) ppm; \text{ }^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 172.1(1), 172.0(7), 158.0, 157.7, 144.3, 115.3, 104.1(3), 104.0(5), 70.5, 57.5, 56.0, 55.1, 53.0, 52.9, 51.7, 36.6, 31.6, 31.1 29.3, 25.0, 24.7, 22.6, 14.2 ppm; HRMS (ESI) m/z Found: (M+H)^+ , C₂₄H₃₂O₈, 449.2170, requires 449.2167.

III. Synthesis of normethyl-(−)-Δ⁹-THC (18)

**Methyl (1R,2R)-2',6'-dimethoxy-4'-pentyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-carboxylate (trans-19)**

A solution of β-lactone 13a (0.96 g, 2.1 mmol), LiCl (0.36 g, 8.6 mmol) and H₂O (77 µL, 4.3 mmol) in DMSO (8 mL) was heated to 170 °C for 16 hours. The mixture was cooled to rt, H₂O (10 mL) added and the mixture extracted with EtOAc (3 x 15 mL). The organic phase was washed with brine (1 x 20 ml), dried (MgSO₄), concentrated under reduced pressure and the crude material passed through a silica plug (2:10, v/v hexanes : EtOAc). The crude residue was dissolved in a freshly prepared solution of NaOMe (10 mL, 1 M, 10 mmol) and heated to 65 °C for 3 d. The mixture was cooled to rt, neutralized with HCl (0.1 M) and extracted with Et₂O (3 x 3 mL). The organic phase was washed with H₂O (2 x 10 mL), dried (Na₂SO₄), concentrated under reduced pressure and the crude material purified via flash column chromatography to afford the title compound trans-19 in 54% yield. Rf 0.3 (20:1, v/v hexanes : EtOAc); IR \nu_{\text{max}} 2933, 2836, 1731, 1590, 1472, 1243, 1103 cm^{-1}; \text{ }^1\text{H NMR (400 MHz, CDCl}_3) \delta 6.35 (s, 2H), 5.71-5.65 (m, 1H), 5.47 (d, J = 9.9 Hz, 1H), 4.28 (brd, J = 9.9 Hz, 1H), 3.76 (s, 6H), 3.47 (s, 3H), 3.25-3.19 (m, 1H), 2.50-2.53 (m, 2H), 2.23-2.11 (m, 2H), 2.10-1.98 (m, 1H), 1.94-1.83 (m, 1H), 1.65-1.58 (m, 2H), 1.38-1.27 (m, 4H) 0.91 (t, J = 6.6 Hz, 3H) ppm; \text{ }^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 176.7, 158.8, 142.9, 130.9, 123.9, 116.8, 104.9, 56.0, 51.2, 43.7, 36.6, 34.8, 31.8, 31.1, 26.9, 24.6, 22.7, 14.2 ppm; HRMS (ESI) m/z Found: (M+H)^+ , C₂₄H₃₂O₈, 449.2216, requires 449.2217.
(6aR,10aR)-6,6-Dimethyl-3-pentyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-1-ol (normethyl-(-)-Δ⁹-THC (18))

Following the procedure of Carreira,⁸ to a solution of trans-19 (88 mg, 0.25 mmol) in Et₂O (2 mL) was added MeMgI (0.84 mL, 3.75 M in Et₂O, 2.5 mmol) dropwise. The mixture was stirred for 16 h at rt before the solvent was removed under reduced pressure. The residue was heated to 160 °C under reduced pressure (150 mbar) for 1 h before it was cooled to room temperature, diluted with Et₂O (3 mL) and quenched with NH₄Cl (3 mL of saturated aqueous solution). The mixture was extracted with Et₂O (3 x 3 ml), the organic phase dried (Na₂SO₄) and concentrated under reduced pressure. The crude residue was taken up in CH₂Cl₂ (2 mL), and ZnBr₂ (86 mg, 0.4 mmol) and MgSO₄ (120 mg, 1 mmol) were added. The mixture was stirred for 4 h at rt before the reaction was quenched by the addition of NH₄Cl (3 mL of saturated aqueous solution). The mixture was extracted with CH₂Cl₂ (3 x 2 mL), the organic phase dried (Na₂SO₄), concentrated under reduced pressure and the crude material purified via flash column chromatography to afford the title compound 18 in 62% yield. 

IR νmax 3405, 2928, 2859, 1703, 1621, 1578, 1425, 1046 cm⁻¹  = –56.3° (c = 0.03, CHCl₃) ¹H NMR (400 MHz, CDCl₃) δ 6.62 (dq, J = 10.0, 2.1 Hz 1H), 6.28 (d, J = 1.5 Hz, 1H), 6.13 (d, J = 1.5 Hz, 1H), 5.66 (dq, J = 10.0, 3.2 Hz 1H), 4.77 (s, 1H) 3.26 (d, J = 11.0, Hz, 1H), 2.45-2.42 (m, 2H), 2.31-2.19 (m, 2H), 1.96-1.88 (m, 1H), 1.79-1.73 (m, 1H), 1.60-1.52 (m, 2H), 1.43-1.40 (m, 1H), 1.42 (s, 3H) 1.34-1.26 (m, 4H), 1.10 (s, 3H), 0.88 (t, J = 7.0 Hz, 3H) ppm ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 154.3, 143.0, 129.9, 126.9, 110.2, 108.9, 107.7, 77.5, 45.6, 35.6, 33.8, 31.7, 30.8, 27.6, 26.6, 25.0, 22.7, 19.5, 14.2 ppm HRMS (ESI) m/z Found: (M+H)⁺, C₂₀H₂₆O₂, 301.2159, requires 301.2162.

IV. Synthesis of (-)-Δ8-THC (12)

**Dimethyl (1S,4S,5S,6R)-5-(2,6-dimethoxy-4-pentylphenyl)-3-oxo-2-oxabicyclo[2.2.2]octane-4,6-dicarboxylate (21)**

To a solution of β-lactone 13a (2.2 g, 5 mmol) in MeOH (20 mL) was added K₂CO₃ (1.4 g, 10 mmol) in one portion. The mixture was stirred at rt for 2 h before the solvent removed under reduced pressure. H₂O (20 mL) was added and the mixture was extracted with EtOAc (3 x 15 ml). The organic phase was dried, concentrated under reduced pressure and the crude material purified via flash column chromatography. The title compound 21 (2.0 g, 91%) was isolated as a yellow oil and as a single diastereomer as observed by 1H-NMR; Rᵥ 0.4 (5:2, v/v hexanes : EtOAc) IR ν max 2933, 2854, 1759, 1735, 1577, 1455, 1237, 1125 cm⁻¹; ¹H NMR (400MHz, CDCl₃) δ 6.35 (s, 2H), 5.16 (d, J = 3.4 Hz, 1H), 5.03 (d, J = 7.4 Hz, 1H), 3.81 (s, 6H), 3.68 (s, 3H), 3.60 (d, J = 7.4 Hz, 1H), 3.56 (s, 3H), 2.80 (ddd, J = 14.3, 11.2, 5.3 Hz, 1H), 2.55-2.51 (m, 2H) ppm; 2.19-1.98 (m, 3H), 1.63-1.56 (m, 2H), 1.37-1.28 (m, 4H), 0.90 (t, J = 6.6 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 172.3, 169.5, 159.1, 110.0, 104.8, 78.1, 54.3, 52.5, 52.2, 45.5, 36.6, 33.7, 31.8, 31.0, 26.0, 22.7, 22.2, 14.2 ppm; HRMS (ESI) m/z Found: (M+H)+, C₂₄H₃₂O₈, 449.2168, requires 449.2170.

**Methyl (1S,2R)-2-(2,6-dimethoxy-4-pentylphenyl)-4-oxocyclohexane-1-carboxylate and methyl (1R,2R)-2-(2,6-dimethoxy-4-pentylphenyl)-4-oxocyclohexane-1-carboxylate (cis-17 and trans-17)**

To a suspension of the β-lactone 13 (2.2 g, 5 mmol) in MeOH (20 mL) at 0 °C was added KCN (0.32 g, 5 mmol) in one portion. The mixture was stirred at this temperature until consumption of the starting material (monitored carefully by TLC) after which ice cold H₂O (30 mL) was added immediately. The mixture was extracted with EtOAc (3 x 30 ml), the organic phase dried (Na₂SO₄) and concentrated under reduced pressure. The crude residue was dissolved in EtOAc (20 mL), IBX (10 mmol) added and the suspension heated under reflux for 16 h. The suspension was cooled to rt, filtered through a pad of
Celite and the solvent removed under reduced pressure. The crude residue was dissolved in DMSO (10 mL), LiCl (10 mmol) and H₂O (7.5 mmol) were added, and the vessel sealed and heated to 170 °C for 2 h. The mixture was cooled to rt, H₂O (20 mL) added and the mixture extracted with EtOAc (3 x 20 mL). The organic phase was washed with brine (1 x 20 ml), dried (MgSO₄), concentrated under reduced pressure and the crude material purified via flash column chromatography. The title compound 17 (0.58 g, 32%) was isolated as a yellow oil as a separable mixture of diastereomers as observed by ¹H-NMR (3:2 cis/trans).

**cis-isomer** Rₜ 0.4 (5:2, v/v hexanes : EtOAc); IR νmax 2931, 2857, 1732, 1709, 1579, 1226, 1119 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.33 (s, 2H), 4.19-4.15, (m, 1H), 3.69 (s, 6H), 3.54 (s, 3H), 3.01 (dd, J = 16.3, 6.8 Hz, 1H), 2.32-2.14 (m, 2H), 1.90-1.83 (m, 1H), 1.64-1.57 (m, 2H), 1.37-1.30 (m, 4H) 0.90 (t, J = 7.0 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 209.1, 174.6, 158.5, 143.8, 113.7, 104.2, 54.9, 51.3, 45.0, 43.9, 39.2, 36.6, 34.2, 31.8, 31.1, 25.3, 22.7, 14.2 ppm; HRMS (ESI) m/z Found: (M+H)+, C₂₁H₃₀O₅, 363.2163, requires 363.2166.

**trans-isomer** Rₜ 0.3 (10:3, v/v hexanes : EtOAc); IR νmax 2931, 2857, 1735, 1713, 1580, 1454, 1120 cm⁻¹; [α]D²⁵⁻ = -190.5 ° (c = 0.05 CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.34 (s, 2H), 4.00 (ddd, J = 11.8, 11.0, 5.0 Hz, 1H), 3.79 (s, 6H), 3.51 (td, J = 11.0, 3.7 Hz, 1H) 3.44 (s, 3H), 3.00 (dd, J = 14.5, 11.8 Hz, 1H), 2.55-2.51 (m, 2H), 2.48-2.37 (m, 3H), 2.25-2.24 (m, 1H), 1.63-1.56 (m, 2H), 1.37-1.29 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 210.4, 175.1, 158.4, 143.6, 114.9, 104.7, 55.8, 51.5, 44.9, 44.2, 39.9, 36.6, 35.8, 31.8, 31.1, 28.3, 22.7, 14.2 ppm; HRMS (ESI) m/z Found: (M+H)+, C₂₁H₃₀O₅, 363.2161, requires 363.2166.

**Methyl (1R,2R)-2-(2,6-dimethoxy-4-pentylphenyl)-4-oxocyclohexane-1-carboxylate (trans-17)**

Following a modification of the procedure of Trost,⁹ a solution of cis-17 (181 mg, 0.5 mmol) in freshly prepared NaOMe (2.5 mL, 1 M, 2.5 mmol) was heated to 50 °C for 16 h. The mixture was cooled to rt, neutralized with HCl (0.1 M) and the mixture extracted with Et₂O (3 x 3 mL). The organic phase was washed with H₂O (2 x 10 mL), dried (Na₂SO₄), concentrated under reduced pressure and the crude material purified via flash column chromatography afford trans-17 in 83% yield.

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(-)-Δ8-Tetrahydrocannabinol (12)

Following a modified procedure of Carreira,8 to a solution of trans-17 (36 mg, 0.1 mmol) in Et2O (1 mL) was added MeMgI (0.33 mL, 3.0 M in Et2O, 1 mmol) dropwise. The yellow suspension was stirred for 16 h at rt before the solvent was removed under reduced pressure. The residue was heated to 160 °C under reduced pressure (150 mbar) for 1 h before it was cooled to room temperature, diluted with Et2O (3 mL) and quenched with NH4Cl (3 mL of saturated aqueous solution). The mixture was extracted with Et2O (3 x 3 ml), the organic phase dried (Na2SO4) and concentrated under reduced pressure. The crude residue was dissolved in CH2Cl2 (2 mL), and ZnBr2 (113 mg, 0.5 mmol) and MgSO4 (120 mg, 1 mmol) were added. The flask was sealed and heated to reflux for 30 h before the reaction was quenched by the addition of NH4Cl (3 mL of saturated aqueous solution). The mixture was extracted with CH2Cl2 (3 x 2 mL), the organic phase dried (Na2SO4), concentrated under reduced pressure and the crude material purified via flash column chromatography. The title compound 12 (14 mg, 40%) was isolated as a yellow oil. \([\alpha]D^{25}_{D} = -220.3° (c = 0.05, \text{CHCl}_3); \) lit.10 \([\alpha]D^{25}_{D} = -232.3° (c = 0.96, \text{CHCl}_3); \) Rf 0.5 (10:1, v/v hexanes : EtOAc); IR νmax 3443, 2957, 2929, 2857, 1624, 1579, 1426, 1183, 1033 cm⁻¹ 1H NMR (400 MHz, CDCl3) δ 6.28 (s, 1H), 6.11 (s, 1H), 5.43, (d, \(J = 4.1 \text{ Hz, 1H}), 4.70, (s, 1H), 3.21-3.17, (m, 1H), 2.73-2.67 (m, 1H), 2.46-2.42 (m, 2H), 2.16-2.10 (m, 1H), 1.89-1.75, (m, 3 H), 1.70 (s, 3H), 1.61-1.53 (m, 2H), 1.38 (s, 3H), 1.35-1.26 (m, 4H), 1.11 (s, 3H), 0.89 (t, \(J = 6.8 \text{ Hz, 3H}) \) ppm; 13C NMR (100 MHz, CDCl3) δ 155.0, 154.9, 142.9, 134.9, 119.5, 110.7, 110.3, 107.8, 76.8, 45.1, 36.2, 35.6, 31.7(4), 31.7(3), 30.7, 28.1, 27.7, 23.6, 22.7, 18.7, 14.2 ppm; HRMS (ESI) m/z Found: (M+H)+, C21H30O2, 314.2315, requires 314.2319.

V. Synthesis of (-)-Δ⁹-THC (1)

(-)-Δ⁹-Tetrahydrocannabinol (1)

Following a modified procedure of Petrzilka, dry hydrogen chloride was bubbled through a solution of Δ⁸-THC (12) (14 mg, 0.044 mmol) and ZnCl₂ (2.7 mg, 0.031 mmol) in CH₂Cl₂ (2 mL) for 2 h. Ice water (3 mL) was added, and the mixture extracted with CH₂Cl₂ (3 x 3 mL) before the organic phase was dried (Na₂SO₄) and concentrated under reduced pressure. The crude residue was taken up in toluene (2 mL) and a solution of potassium tert-amylate (0.7 mL, 0.5 M) added. The mixture was heated to 65 °C for 1 h before ice cold water (3 mL) was added. The mixture was extracted with EtOAc (3 x 3 mL), the organic phase dried (Na₂SO₄), concentrated under reduced pressure, and the crude material purified via flash column chromatography. The title compound 1 (12.5 mg, 89%) was isolated as a yellow oil. [α]D²⁵ = −112.0° (c = 0.01, CHCl₃); lit. [α]D²⁵ = −152.3° (c = 0.79, CHCl₃); Rf 0.5 (10:1, v/v hexanes : EtOAc); IR νmax 3391, 2957, 2928, 2858, 1624, 1578, 1426, 1184, 1035 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.31-6.29 (m, 1H), 6.27 (d, J = 1.5 Hz, 1H), 6.14 (d, J = 1.5 Hz, 1H), 4.68 (s, 1H) 3.20 (d, J = 10.9, Hz, 1H), 2.45-2.42 (m, 2H), 2.18-2.15 (m, 2H), 1.93-1.89 (m, 1H), 1.71-1.67 (m, 4H), 1.58-1.53 (m, 2H), 1.45-1.37 (m, 1H), 1.41 (s, 3H) 1.33-1.27 (m, 4H), 1.09 (s, 3H), 0.88 (s, J = 6.8 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 154.9, 154.3, 143.0, 134.6, 123.9, 110.3, 109.2, 107.7, 77.3, 46.0, 35.6, 33.7, 31.7, 31.3, 30.8, 27.7, 25.2, 23.5, 22.7, 19.4, 14.2 ppm; HRMS (ESI) m/z Found: (M+H)⁺, C₂₁H₃₀O₂, 314.2314, requires 314.2319.

VI. NMR spectra and HPLC traces

\((E)-3-(2,6\text{-Dimethoxy-4-pentylphenyl})\text{acrylic acid (15b)}\)
(E)-3-(2,6-Dimethoxy-4-pentylphenyl)acryloyl fluoride (15a)
Dimethyl (1R,2S,6S)-2-(2,6-dimethoxy-4-pentylphenyl)-8oxo-7oxabicyclo[4.2.0]octane-3,3-dicarboxylate (13a)
(1R,2R)-2',6'-Dimethoxy-4'-pentyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-carboxylate

(trans-19)
(6aR,10aR)-6,6-Dimethyl-3-pentyl-6a,7,8,10a-tetrahydro-6H-benzo[c]chromen-1-ol

(18)
Dimethyl (1S,4R,5S,6R)-5-(2,6-dimethoxy-4-pentylphenyl)-3-oxo-2-oxabicyclo[2.2.2]octane-4,6-dicarboxylate (21)
Methyl (1S,2R)-2-(2,6-dimethoxy-4-pentylphenyl)-4-oxocyclohexane-1-carboxylate

(cis-17)
Methyl (1R,2R)-2-(2,6-dimethoxy-4-pentylphenyl)-4-oxocyclohexane-1-carboxylate
(trans-17)
(−)-Δ9-Tetrahydrocannabinol (1)