Supporting Information-I

A general approach to high-yielding asymmetric synthesis of chiral 3-alkyl-4-nitromethylchromans via cascade Barbas-Michael and acetalization reactions

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General Methods: The $^1$H NMR and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for $^1$H NMR and relative to the central CDCl$_3$ resonance ($\delta = 77.0$) for $^{13}$C NMR. In the $^{13}$C NMR spectra, the nature of the carbons (C, CH, CH$_2$ or CH$_3$) was determined by recording the DEPT-135 experiment, and is given in parentheses. The coupling constants $J$ are given in Hz. Column chromatography was performed using Acme’s silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-K$\alpha$ ($\lambda = 0.71073$ Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-K$\alpha$ fine-focus sealed tube ($\lambda = 0.71073$ Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by
irradiation with UV light and/or by treatment with a solution of p-anisaldehyde (23 mL), conc. H$_2$SO$_4$ (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

The enantiomeric excess (ee) of the BMA products was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H, Chiralcel OJ-H, Chiralpak AD-H, Chiralpak AS-H or Lux 5u Amylose-2 columns and hexane/2-propanol as the eluent. Retention times and solvent ratios are indicated in the respective entries.

**Materials:** All solvents and commercially available chemicals were used as received.

**General Experimental Procedures for the Cascade BMA Reactions:**

**Procedure A:** General procedure for amine-catalyzed asymmetric cascade BMA reaction of aldehydes 1 with 2-(2-nitrovinyl)phenols 2: In an ordinary glass vial equipped with a magnetic stirring bar, to a mixture of D-DPPOTMS 3e (0.1 mmol) and PhCO$_2$H 4a (0.1 mmol) in DCM (2.0 mL), was added propionaldehyde 1a (5.0 mmol, 10 equiv.) or aldehydes 1b-f (0.75 mmol, 1.5 equiv.) and of 2-(2-nitrovinyl)phenols 2a-j (0.5 mmol). After stirring the reaction mixture at 25 °C as shown in Tables 1-2, the crude reaction mixture was worked up with aqueous NH$_4$Cl solution and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na$_2$SO$_4$), filtered and concentrated. Pure chiral products 5/6 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure B:** General procedure for amino acid-catalyzed cascade BMA reaction of aldehydes 1 with 2-(2-nitrovinyl)phenols 2: In an ordinary glass vial equipped with a magnetic stirring bar, to DL-proline 3a (12 mg, 0.1 mmol) in DMSO (2.0 mL), was added propionaldehyde 1a (5.0 mmol, 10 equiv.) or aldehydes 1b-f (0.75 mmol, 1.5 equiv.) and of 2-(2-nitrovinyl)phenols 2a-j (0.5 mmol). After stirring the reaction mixture at 25 °C for 2-9 h, the crude reaction mixture was worked up with aqueous NH$_4$Cl solution and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na$_2$SO$_4$), filtered and concentrated. Pure achiral products (±)-5/6 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure C:** General procedure for the oxidation of cascade BMA products with PCC: In an oven dried round bottom flask, to the lactol 5/6 (0.3 mmol), added dry DCM (3.0 mL), NaOAc (0.9 mmol, 3 equiv.) and PCC (0.9 mmol, 3 equiv.). After stirring the reaction mixture at 0 °C for 0.5 h, it was brought to 25 °C and stirred for 1-2 h. The crude reaction mixture was passed through a pad of celite and
concentrated to dryness. Pure chiral products 7 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure D: General procedure for the oxidation of cascade BMA products with IBX:** In an oven dried round bottom flask, to the lactol 5/6 (0.3 mmol), added dry CHCl₃ (3.0 mL), and IBX (0.45 mmol, 1.5 equiv.). After stirring the reaction mixture at 65 °C for 15-24 h, it was brought to 25 °C and the crude reaction mixture was passed through a pad of celite and concentrated to dryness. Pure chiral products 7 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure E: General procedure for the reduction of cascade BMA products:** In an oven dried round bottom flask, to the lactol 5/6 (0.3 mmol), added dry MeOH (3.0 mL), and NaBH₄ (0.45 mmol, 1.5 equiv.). After stirring the reaction mixture at 0 °C for 0.5 h, it was brought to 25 °C and the crude reaction mixture was worked up with aqueous NH₄Cl solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure chiral product 9 was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure F: General procedure for the Brønsted acid-catalyzed acetalization of cascade BMA products:** In an ordinary glass vial equipped with a magnetic stirring bar, to a cascade BMA products 5/6 (0.3 mmol) was dissolved in dry MeOH (a) (3.0 mL) and cooled to 0 °C, and added p-TSA (19 mg, 20 mol%). The mixture was stirred at the same temperature for 30 min and then brought to room temperature and stirred for 3-5 h. The crude reaction mixture was worked up with aqueous NaHCO₃ solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure chiral products 5 and 6 were separated by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure G: Brønsted acid-catalyzed hydrolysis of cascade BMA products:** In an oven dried round bottom flask, to the lactol 5/6 (0.3 mmol), added dry toluene (3.0 mL), and p-TSA.H₂O (3.5 mg, 10 mol%). After heating reaction mixture to 110 °C for 1 h, it was brought to 25 °C and the crude reaction mixture was worked up with aqueous NaHCO₃ solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure chiral product 11 was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).
Procedure H: *Hydrogenation followed by protection of nitro products:* In an oven dried round bottom flask, was taken activated (10%) Pd/C (7 mg, 10 mol-%), with compound (−)-11aa (0.3 mmol) dissolved in dry MeOH (3.0 mL) and stirred under H₂ atmosphere at 25 °C for 4 or 14 h. The reaction mixture was passed through a pad of celite and concentrated to dryness. The crude mixture was taken in a dry oven dried round bottom flask in dry DCM (3.0 mL) and added successively dry triethylamine (60 µL, 0.4 mmol) and di-tert-butyl carbonate (86 mg, 0.4 mmol) at 0 °C. The resulting mixture was stirred at 25 °C for 2 h and then worked up with aqueous NH₄Cl and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure product (−)-12aa or (+)-13aa was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure I: *Synthesis of chiral chromane acetates via cascade W/OM reactions on BMA products:* In an oven dried round bottomed flask, to the lactol 5aa (253 mg, 1.0 mmol), added dry toluene (0.1 M) and methyl-(triphenylphosphorylidine)acetate (501mg, 1.5 mmol). This reaction mixture was refluxed at 110 °C for 4 h. After the reaction is completed, it is cooled to room temperature and pure products 14aa was obtained by column chromatography using EtOAc/hexane and isolated as liquid.

![Figure S1](image)

*Figure S1.* X-Ray crystal structure of chiral 8-methoxy-3-methyl-4-nitromethyl-chroman-2-one (7aa).
**Table S1:** Synthesis of achiral BMA products 5, 7 and 9

![Chemical structure](image)

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<th>Time (h)</th>
<th>Products 5/7/9</th>
<th>Products yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>de (%)&lt;sup&gt;ç&lt;/sup&gt;</th>
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<sup>a</sup> Reactions were carried out in DMSO (0.25 M) with 10 equiv. of 1a or 1.5 equiv. of 1b-f relative to the 2a-j (0.5 mmol) in the presence of 20-mol% of catalyst DL-3a. <sup>b</sup> Yield refers to the column purified product. <sup>c</sup> Ratio or de is based on HPLC analysis. <sup>d</sup> DL-DPPOTMS 3c (20 mol%) used as catalyst in DCM (0.25 M).
(3\text{S}, 4\text{R})-8-Methoxy-3-methyl-4-nitromethylchroman-2-ol (5\text{aa}): Prepared by following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = +20.06^\circ$ (c = 0.28 g/100 mL, CHCl$_3$); IR (Neat): $\nu_{\text{max}}$ 3659 (O-H), 2974, 1551 (NO$_2$), 1490, 1379, 1222, 1130, 976, 757, 658 and 632 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 1:1 ratio of isomers) $\delta$ 6.93-6.82 (4H, m), 6.64 (2H, br d, $J = 6.0$ Hz), 5.59 (1H, s), 5.50 (1H, s), 4.98-4.91 (2H, m), 4.74 (1H, dd, $J = 13.2$, 8.0 Hz), 4.60 (1H, dd, $J = 12.8$, 9.2 Hz), 4.23-4.16 (2H, m), 4.16-4.13 (1H, m), 3.86 (6H, s, OCH$_3$), 3.75-3.72 (1H, m), 2.45-2.42 (1H, m), 2.24-2.21 (1H, m), 1.25 (3H, d, $J = 7.2$ Hz), 0.98 (3H, d, $J = 7.2$ Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135, 1:1 ratio of isomers) $\delta$ 148.3 (2 x C), 140.1 (C), 140.0 (C), 122.8 (2 x C), 121.2 (CH), 121.0 (CH), 120.5 (CH), 117.9 (CH), 110.6 (CH), 110.5 (CH), 95.5 (CH), 94.8 (CH), 78.1 (CH$_2$), 76.2 (CH$_2$), 55.8 (2 x CH$_3$), 36.4 (CH), 33.4 (CH), 32.6 (CH), 32.2 (CH), 12.4 (CH$_3$), 11.1 (CH$_3$); LRMS m/z 254.20 (M + H$^+$), calcd for C$_{12}$H$_{15}$NO$_5$ 253.095; HRMS m/z 252.0889 (M$^-$H), calcd for C$_{12}$H$_{15}$NO$_5$H$^+$ 252.0872; Anal. calcd for C$_{12}$H$_{15}$NO$_5$ (253.095): C, 56.91; H, 5.97; N, 5.53. Found: C, 56.88; H, 6.02; N, 5.46%.

(3\text{S}, 4\text{R})-3-Methyl-4-nitromethylchroman-2-ol (5\text{ab}): Prepared by following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = +39.28^\circ$ (c = 0.31 g/100 mL, CHCl$_3$); IR (Neat): $\nu_{\text{max}}$ 3625 (O-H), 2973, 1551 (NO$_2$), 1453, 1379, 1222, 1027, 757, 674 and 648 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 1:1 ratio of isomers) $\delta$ 7.23-7.18 (2H, m), 7.01 (2H, d, $J = 7.6$ Hz), 6.97-6.89 (2H, m), 6.86 (2H, t, $J = 7.2$ Hz), 5.46 (1H, br s), 5.30 (1H, br s), 4.95-4.90 (2H, m), 4.74 (1H, dd, $J = 13.2$, 8.4 Hz), 4.59 (1H, dd, $J = 12.4$, 8.8 Hz), 4.14-4.12 (1H, m), 3.75-3.70 (1H, m), 3.62 (1H, d, $J = 2.8$ Hz), 3.50 (1H, br s), 2.44-2.40 (1H, m), 2.23-2.18 (1H, m), 1.22 (3H, d, $J = 7.2$ Hz), 0.97 (3H, d, $J = 6.8$ Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135, 1:1 ratio of isomers) $\delta$ 150.7 (C), 150.5 (C), 129.1 (CH), 128.8 (CH), 128.7 (CH), 126.2 (CH), 121.7 (C), 121.6 (CH), 121.5 (CH), 119.7 (C), 117.3 (CH), 117.3 (CH), 95.3 (CH), 94.6 (CH), 78.1 (CH$_2$), 76.1 (CH$_2$), 36.3 (CH), 33.4 (CH), 32.6 (CH), 32.3 (CH), 12.4 (CH$_3$), 11.0 (CH$_3$); LRMS m/z 223.80 (M + H$^+$), calcd for C$_{11}$H$_{13}$NO$_3$ 223.084; Anal. calcd for C$_{11}$H$_{13}$NO$_3$ (223.084): C, 59.19; H, 5.87; N, 6.27. Found: C, 59.25; H, 5.81; N, 6.21%.

(3\text{S}, 4\text{R})-6-Fluoro-3-methyl-4-nitromethylchroman-2-ol (5\text{ac}): Prepared by following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = +43.46^\circ$ (c = 0.15 g/100 mL, CHCl$_3$); IR (Neat): $\nu_{\text{max}}$ 3626 (O-H), 2973, 1551 (NO$_2$), 1493, 1379, 1197, 982, 818, 663 and 616 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 1:1 ratio of isomers) $\delta$ 6.94-6.88 (2H, m), 6.85-6.79 (2H, m), 6.76-6.72 (2H, m), 5.45 (1H, s), 5.36 (1H, s), 4.92 (1H, dd, $J = 13.6$, 4.8 Hz), 4.88 (1H, dd, $J = 10.8$, 4.8 Hz), 4.73 (1H, dd, $J = 13.6$, 8.4 Hz), 4.60 (1H, dd, $J = 12.4$, 8.4 Hz), 4.11-4.08 (1H, m), 3.72-3.68 (1H, m), 3.39 (1H, t, $J = 6.8$ Hz).
(3S, 4R)-6-Chloro-3-methyl-4-nitromethylchroman-2-ol (5ad): Prepared by following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = +21.46^\circ$ (c = 0.28 g/100 mL, CHCl$_3$); IR (Neat): $\nu_{\text{max}}$ 3620 (O-H), 2975, 1551 (NO$_2$), 1494, 1380, 1198, 980, 817 and 664 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 1:1 ratio of isomers) $\delta$ 7.17-7.11 (2H, m), 7.00 (1H, s), 6.98 (1H, s), 6.82-6.77 (2H, m), 5.45 (1H, br s), 5.36 (1H, d, J = 2.8 Hz), 4.95-4.87 (2H, m), 4.70 (1H, dd, J = 13.6, 8.0 Hz), 4.59 (1H, dd, J = 12.4, 8.8 Hz), 4.09-4.05 (1H, m), 3.71-3.67 (1H, m), 2.40-2.35 (1H, m), 2.21-2.18 (1H, m), 1.21 (3H, d, J = 7.2 Hz), 0.95 (3H, d, J = 7.2 Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135, 1:1 ratio of isomers) $\delta$ 149.3 (C), 148.7 (C), 132.1 (CH), 131.8 (CH), 131.3 (CH), 129.0 (CH), 124.0 (C), 121.9 (C), 119.3 (2 x CH), 113.7 (C), 113.4 (C), 95.3 (CH), 94.7 (CH), 77.7 (CH$_2$), 75.7 (CH$_2$), 36.0 (CH), 33.2 (CH), 32.6 (CH), 32.0 (CH), 12.3 (CH$_3$), 10.9 (CH$_3$); LRMS m/z 256.20 (M - H$^+$), calcd for C$_{11}$H$_{12}$ClNO$_4$ 257.045; Anal. calcd for C$_{11}$H$_{12}$ClNO$_4$ (257.045): C, 51.27; H, 4.69; N, 5.44. Found: C, 51.35; H, 4.72; N, 5.39%.

(3S, 4R)-6-Bromo-3-methyl-4-nitromethylchroman-2-ol (cis-5ae): Prepared by following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = +17.36^\circ$ (c = 0.28 g/100 mL, CHCl$_3$); IR (Neat): $\nu_{\text{max}}$ 3595 (O-H), 2974, 1551 (NO$_2$), 1379, 1222, 976, 757, 658 and 632 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 1:1 ratio of isomers, major compound) $\delta$ 7.30-7.25 (2H, m), 7.14 (1H, br s), 7.11 (1H, br s), 6.75 (1H, d, J = 8.0 Hz), 6.74 (1H, d, J = 8.0 Hz), 5.45 (1H, s), 5.35 (1H, d, J = 2.8 Hz), 4.95-4.87 (2H, m), 4.71-4.66 (1H, m), 4.64-4.55 (1H, m), 4.09-4.04 (1H, m), 3.76 (1H, br s), 3.71-3.66 (1H, m), 3.62 (1H, br s), 2.39-2.36 (1H, m), 2.20-2.16 (1H, m), 1.20 (3H, d, J = 7.2 Hz), 0.94 (3H, d, J = 7.2 Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135, 1:1 ratio of isomers, major compound) $\delta$ 150.0 (C), 149.9 (C), 132.1 (CH), 131.8 (CH), 131.3 (CH), 129.0 (CH), 124.0 (C), 121.9 (C), 119.3 (2 x CH), 113.7 (C), 113.4 (C), 95.3 (CH), 94.7 (CH), 77.7 (CH$_2$), 75.7 (CH$_2$), 36.0 (CH), 33.2 (CH), 32.6 (CH), 32.0 (CH), 12.4 (CH$_3$), 11.0 (CH$_3$); LRMS m/z 300 (M), calcd for C$_{11}$H$_{12}$BrNO$_4$ 300.995; Anal. calcd for C$_{11}$H$_{12}$BrNO$_4$ (300.995): C, 43.73; H, 4.00; N, 4.64. Found: C, 43.85; H, 4.09; N, 4.61%.
(3S, 4R)-6,8-Dichloro-3-methyl-4-nitromethylchroman-2-ol (5af): Prepared by following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as solid. \([\alpha]_D^{25} = +11.24^\circ \ (c = 0.57 \text{ g/100 mL, CHCl}_3); \) IR (Neat): \(\nu_{\text{max}} 3620, 2975, 1551 \ (\text{NO}_2), 1494, 1380, 980, 664 \) and 640 \(\text{cm}^{-1}; \) \(^1\)H NMR (CDCl\(_3, 1:1 \) ratio of isomers) \(\delta 7.36-7.31 \ (2\text{H, m}), 6.96-6.93 \ (2\text{H, m}), 5.61 \ (1\text{H, t, } J = 2.8 \text{ Hz}), 5.52 \ (1\text{H, t, } J = 2.8 \text{ Hz}), 4.97-4.87 \ (2\text{H, m}), 4.14-4.09 \ (1\text{H, m}), 3.76 \ (2\text{H, d, } J = 3.2 \text{ Hz}); \) \(^1^3\)C NMR (CDCl\(_3, \) DEPT-135, 1:1 ratio of isomers) \(\delta 145.7 \ (\text{C}), 145.5 \ (\text{C}), 129.5 \ (\text{CH}), 129.2 \ (\text{CH}), 127.1 \ (\text{CH}), 126.2 \ (\text{C}), 126.0 \ (\text{C}), 124.8 \ (\text{CH}), 123.2 \ (\text{C}), 123.1 \ (\text{C}), 122.9 \ (\text{C}), 121.7 \ (\text{C}), 95.9 \ (\text{CH}), 95.1 \ (\text{CH}), 77.6 \ (\text{CH}_2), 75.6 \ (\text{CH}_2), 37.8 \ (\text{CH}), 36.2 \ (\text{CH}), 33.2 \ (\text{CH}), 32.1 \ (\text{CH}), 12.5 \ (\text{CH}_3), 11.0 \ (\text{CH}_3); \) LRMS m/z 290 (M–H\(^+\)), caledd for C\(_{11}\)H\(_{11}\)Cl\(_2\)NO\(_4\) 291.0065; Anal. caledd for C\(_{11}\)H\(_{11}\)Cl\(_2\)NO\(_4\) (291.0065): C, 45.23; H, 3.80; N, 4.79. Found: C, 45.31; H, 3.75; N, 4.85%.

(3S, 4R)-6-Methoxy-3-methyl-4-nitromethylchroman-2-ol (5ag): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as solid. \([\alpha]_D^{25} = +23.8^\circ \ (c = 0.33 \text{ g/100 mL, CHCl}_3); \) IR (Neat): \(\nu_{\text{max}} 3589, 2973, 1550 \ (\text{NO}_2), 1490, 1379, 1222, 1131, 977, 757 \) and 635 \(\text{cm}^{-1}; \) \(^1\)H NMR (CDCl\(_3, 1:1 \) ratio of isomers) \(\delta 6.80-6.78 \ (4\text{H, m}), 6.57-6.55 \ (2\text{H, m}), 5.42 \ (1\text{H, br s}), 5.33 \ (1\text{H, dd, } J = 13.2, 8.0 \text{ Hz}), 4.61 \ (1\text{H, dd, } J = 12.8, 8.8 \text{ Hz}), 4.10-4.05 \ (1\text{H, m}), 3.76 \ (3\text{H, s, OCH}_3), 3.74 \ (3\text{H, s, OCH}_3); \) \(^1^3\)C NMR (CDCl\(_3, \) DEPT-135, 1:1 ratio of isomers) \(\delta 154.2 \ (\text{C}), 153.9 \ (\text{C}), 144.6 \ (\text{C}), 144.4 \ (\text{C}), 122.3 \ (\text{C}), 120.5 \ (\text{C}), 118.0 \ (\text{CH}), 117.9 \ (\text{CH}), 115.5 \ (\text{CH}), 114.2 \ (\text{CH}), 112.9 \ (\text{CH}), 111.7 \ (\text{CH}), 95.3 \ (\text{CH}), 94.6 \ (\text{CH}), 78.1 \ (\text{CH}_2), 76.2 \ (\text{CH}_2), 55.7 \ (2 \text{x CH}_3), 36.7 \ (\text{CH}), 33.5 \ (\text{CH}), 32.5 \ (\text{CH}), 12.5 \ (\text{CH}_3), 11.2 \ (\text{CH}_3); \) LRMS m/z 252 (M–H\(^+\)), caledd for C\(_{12}\)H\(_{15}\)NO\(_5\) 253.0950; HRMS m/z 276.0851 (M + Na), caledd for C\(_{12}\)H\(_{15}\)NO\(_5\)Na 276.0848; Anal. caledd for C\(_{12}\)H\(_{15}\)NO\(_5\) (253.0950): C, 56.91; H, 5.97; N, 5.33. Found: C, 56.85; H, 5.91; N, 5.58%.

(3S, 4R)-7-Methoxy-3-methyl-4-nitromethylchroman-2-ol (5ah): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. \([\alpha]_D^{25} = +42.18^\circ \ (c = 0.43 \text{ g/100 mL, CHCl}_3); \) IR (Neat): \(\nu_{\text{max}} 3625 \ (\text{O-H}), 2973, 1551 \ (\text{NO}_2), 1453, 1379, 1222, 1027, 757, 674 \) and 617 \(\text{cm}^{-1}; \) \(^1\)H NMR (CDCl\(_3, 1:1 \) ratio of isomers) \(\delta 6.91 \ (2\text{H, d, } J = 8.8 \text{ Hz}), 6.55-6.50 \ (2\text{H, m}), 6.45 \ (1\text{H, d, } J = 2.4 \text{ Hz}), 6.42 \ (1\text{H, d, } J = 2.4 \text{ Hz}), 5.46 \ (1\text{H, br s}), 5.36 \ (1\text{H, d, } J = 2.8 \text{ Hz}), 4.89 \ (2\text{H, td, } J = 11.2, 6.0 \text{ Hz}), 4.75 \ (1\text{H, dd, } J = 13.2, 8.4 \text{ Hz}), 4.59 \ (1\text{H, dd, } J = 12.4, 8.8 \text{ Hz}), 4.07-4.03 \ (1\text{H, m}), 3.79 \ (3\text{H, s, OCH}_3), 3.78 \ (3\text{H, s, OCH}_3), 3.70-3.66 \ (1\text{H, m}), 3.44-3.35 \ (2\text{H, m}), 2.43-2.40 \ (1\text{H, m}), 2.23-
2.20 (1H, m), 1.23 (3H, d, J = 7.2 Hz), 0.99 (3H, d, J = 7.2 Hz); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135, 1:1 ratio of isomers) δ 160.3 (C), 160.1 (C), 151.8 (C), 151.5 (C), 129.3 (CH), 126.9 (CH), 114.0 (C), 111.9 (C), 108.1 (CH), 108.0 (CH), 102.5 (CH), 102.3 (CH), 95.5 (CH), 94.7 (CH), 78.3 (CH\(_2\)), 76.3 (CH\(_2\)), 55.3 (2 x OCH\(_3\)), 35.9 (CH), 33.6 (CH), 32.53 (CH), 32.47 (CH), 12.5 (CH\(_3\)), 11.1 (CH\(_3\)); LRMS m/z 251.90 (M - H\(^+\)), calcd for C\(_{12}\)H\(_{15}\)NO\(_5\) 253.0954; Anal. calcd for C\(_{12}\)H\(_{15}\)NO\(_5\) (253.0954): C, 56.91; H, 5.97; N, 5.53. Found: C, 56.85; H, 5.92; N, 5.49%.

(3\(S\), 4\(R\))-3,6-Dimethyl-4-nitromethylchroman-2-ol (5ai): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. \([\alpha]_D^{25} = +20.56^\circ\) (c = 0.28 g/100 mL, CHCl\(_3\)); IR (Neat): \(\nu_{\text{max}}\) 3620 (O-H), 2975, 1551 (NO\(_2\)), 1494, 1380, 1198, 980, 817, 664 and 615 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 1:1 ratio of isomers) δ 7.04-7.01 (2H, m), 6.83 (2H, br s), 6.79 (1H, d, J = 6.4 Hz), 6.77 (1H, d, J = 6.4 Hz), 5.46 (1H, br s), 5.36 (1H, br s), 4.98-4.93 (2H, m), 4.75 (1H, dd, J = 13.2, 7.6 Hz), 4.62 (1H, dd, J = 12.4, 8.8 Hz), 4.12-4.07 (1H, m), 3.73-3.69 (1H, m), 3.40-3.35 (2H, m), 2.45-2.38 (1H, m), 2.29 (3H, s, ArCH\(_3\)), 2.27 (3H, s, ArCH\(_3\)), 2.24-2.18 (1H, m), 1.24 (3H, d, J = 7.2 Hz), 0.99 (3H, d, J = 7.2 Hz); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135, 1:1 ratio of isomers) δ 148.4 (C), 148.3 (C), 131.0 (C), 130.9 (C), 129.8 (CH), 129.5 (CH), 128.9 (CH), 126.5 (CH), 121.4 (C), 119.4 (C), 117.2 (CH), 117.1 (CH), 95.3 (CH), 94.7 (CH), 78.2 (CH\(_2\)), 76.2 (CH\(_2\)), 36.3 (CH), 33.5 (CH), 32.8 (CH), 32.4 (CH), 20.7 (CH\(_3\)), 20.5 (CH\(_3\)), 12.5 (CH\(_3\)), 11.1 (CH\(_3\)); LRMS m/z 238.55 (M + H\(^+\)), calcd for C\(_{12}\)H\(_{15}\)NO\(_4\) 237.100; Anal. calcd for C\(_{12}\)H\(_{15}\)NO\(_4\) (237.100): C, 60.75; H, 6.37; N, 5.90. Found: C, 60.81; H, 6.32; N, 5.86%.

(3\(S\), 4\(R\))-3-Methyl-4-nitromethylchroman-2,8-diol (5aj): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. \([\alpha]_D^{25} = +33.2^\circ\) (c = 0.14 g/100 mL, CHCl\(_3\)); IR (Neat): \(\nu_{\text{max}}\) 3625 (O-H), 2973, 1551 (NO\(_2\)), 1453, 1379, 1222, 1027, 979, 757, 674 and 617 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 1:1 ratio of isomers) δ 6.86-6.76 (4H, m), 6.55-6.53 (2H, m), 6.09 (2H, br s), 5.48 (1H, d, J = 2.0 Hz), 5.38 (1H, d, J = 3.2 Hz), 4.88 (2H, ddd, J = 12.8, 6.4, 3.6 Hz), 4.73 (1H, dd, J = 13.2, 8.0 Hz), 4.58 (1H, dd, J = 12.8, 8.8 Hz), 4.07-4.02 (1H, m), 3.74-3.69 (1H, m), 2.40-2.35 (1H, m), 2.20-2.18 (1H, m), 1.19 (3H, d, J = 7.2 Hz), 0.94 (3H, d, J = 6.8 Hz); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135, 1:1 ratio of isomers) δ 144.8 (2 x C), 138.2 (2 x C), 122.1 (C), 121.6 (CH), 121.4 (CH), 120.2 (C), 119.5 (CH), 117.3 (CH), 114.4 (2 x CH), 95.6 (CH), 94.9 (CH), 77.8 (CH\(_2\)), 75.9 (CH\(_3\)), 36.2 (CH), 33.6 (CH), 32.9 (CH), 32.7 (CH), 12.1 (CH\(_3\)), 11.1 (CH\(_3\)); LRMS m/z 240.15 (M + H\(^+\)), calcd for C\(_{11}\)H\(_{13}\)NO\(_5\) 239.0794; Anal. calcd for C\(_{11}\)H\(_{13}\)NO\(_5\) (239.0794): C, 55.23; H, 5.48; N, 5.86. Found: C, 55.16; H, 5.45; N, 5.92%.
(3S, 4R)-3-Ethyl-8-methoxy-4-nitromethylchroman-2-ol (5ba): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 105 °C; [α]D25 = +39.13° (c = 0.30 g/100 mL, CHCl3); IR (Neat): νmax 3626, 2975, 1551 (NO2), 1493, 1379, 1197, 1083, 818, 663 and 616 cm⁻¹; ¹H NMR (CDCl3) δ 6.90-6.79 (2H, m), 6.62-6.59 (1H, m), 5.10 (1H, br s), 4.87-4.76 (2H, m), 3.82 (3H, s, OCH3), 3.78-3.74 (1H, m), 2.16-2.14 (1H, m), 1.76-1.59 (2H, m), 1.09 (3H, t, J = 7.6 Hz); ¹³C NMR (CDCl3, DEPT-135) δ 147.9 (C), 139.8 (C), 123.0 (C), 120.7 (CH), 120.6 (CH), 110.4 (CH), 93.4 (CH), 78.1 (CH2), 55.4 (CH3), 40.3 (CH), 34.4 (CH), 20.7 (CH2), 11.2 (CH3); LRMS m/z 268.30 (M+H+), calcd for C13H17NO5 267.1107; Anal. calcd for C13H17NO5 (267.1107): C, 58.42; H, 6.41; N, 5.24. Found: C, 58.31; H, 6.44; N, 5.28%.

(3S, 4R)-3-Benzyl-8-methoxy-4-nitromethylchroman-2-ol (5ca): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 95 °C; [α]D25 = +14.07° (c = 0.23 g/100 mL, CHCl3); IR (Neat): νmax 3462 (O-H), 2973, 1551 (NO2), 1494, 1379, 1198, 981, 817 and 634 cm⁻¹; ¹H NMR (CDCl3) δ 7.34-7.13 (5H, m), 6.89-6.75 (2H, m), 6.63 (1H, t, J = 8.0 Hz), 5.55 (1H, s), 5.17-4.97 (2H, m), 4.91-4.86 (1H, m), 4.24-4.21 (1H, m), 3.80 (3H, s), 3.75-3.73 (1H, m), 3.01-2.91 (1H, m); ¹³C NMR (CDCl3, DEPT-135) δ 147.9 (C), 139.7 (C), 137.9 (C), 128.6 (5 x CH), 126.6 (CH), 122.9 (C), 121.0 (CH), 110.6 (CH), 92.9 (CH), 78.1 (CH2), 55.5 (CH3), 40.5 (CH), 34.7 (CH), 34.0 (CH2); LRMS m/z 330.55 (M+H+), calcd for C18H19NO5 329.126; HRMS m/z 352.1168 (M+Na), calcd for C18H19NO5Na 352.1161; Anal. calcd for C18H19NO5 (329.126): C, 65.64; H, 5.81; N, 4.25. Found: C, 65.58; H, 5.81; N, 4.29%.

(3S, 4R)-3-Benzyl-8-methoxy-4-nitromethylchroman-2-ol (5da): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid. [α]D25 = +17.37° (c = 0.48 g/100 mL, CHCl3); IR (Neat): νmax 3462 (O-H), 2978, 1548 (NO2), 1482, 1380, 1264, 1085, 982, 733 and 634 cm⁻¹; ¹H NMR (CDCl3, 2:1 ratio of isomers) δ 7.38-7.33 (10H, m), 6.95-6.88 (2H, m), 6.82-6.66 (4H, m), 5.74-5.71 (2H, m), 4.85-4.57 (8H, m), 4.16-4.12 (2H, m), 3.89-3.87 (2H, m), 3.80 (6H, s, OCH3); ¹³C NMR (CDCl3, DEPT-135, 2:1 ratio of isomers) δ 148.6 (C), 148.4 (C), 148.3 (2 x C), 140.5 (C), 140.3 (C), 140.1 (C), 139.6 (C), 137.4 (C), 137.3 (2 x C), 137.1 (C), 128.7-127.99 (20 x CH), 121.9 (2 x CH), 121.7 (CH), 121.6 (CH), 121.4 (2 x CH), 121.1 (CH), 120.9 (CH), 120.2 (2 x C), 119.3 (2 x C), 118.6 (2 x CH), 118.6 (CH), 111.0 (CH), 110.7 (2 x CH), 92.6 (CH), 91.1 (CH), 90.7 (CH), 89.6 (CH), 77.4 (CH2), 77.2 (CH2), 75.1 (CH2), 74.9 (CH2), 73.5 (CH), 72.7 (CH), 72.67 (CH2), 72.64 (CH),
72.38 (CH₂), 71.96 (CH₂), 71.92 (CH), 71.5 (CH₂), 55.74 (3 x CH₃), 55.70 (CH₃), 36.4 (CH), 36.1 (CH), 35.7 (CH), 34.4 (CH); LRMS m/z 344.00 (M − H⁺), calcd for C₁₈H₁₉NO₆ 345.11; HRMS m/z 368.1103 (M + Na), calcd for C₁₈H₁₉NO₆Na 368.1110; Anal. calcd for C₁₈H₁₉NO₆ (345.11): C, 62.60; H, 5.55; N, 4.06. Found: C, 62.48; H, 5.49; N, 4.12%.

(3S, 4R)-8-Methoxy-4-nitromethyl-3-propylchroman-2-ol (5ea): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid.  
\[ [\alpha]_D^{25} = +19.9^\circ (c = 0.58 \text{ g/100 mL, CHCl}_3); \]  
IR (Neat): ν max 3459 (OH), 2965, 1549 (NO₂), 1484, 1379, 1264, 1205, 983, 733 and 634 cm⁻¹; ¹H NMR (CDCl₃, 4:1 ratio of isomers, major isomer) δ 6.85-6.80 (2H, m), 6.62 (1H, d, J = 7.2 Hz), 5.66 (1H, s), 4.87-4.76 (2H, m), 4.15-4.09 (1H, m), 3.85 (3H, s), 3.76-3.72 (1H, m), 2.29-2.27 (1H, m), 1.67-1.58 (2H, m), 1.56-1.47 (2H, m), 1.00 (3H, t, J = 7.2 Hz); ¹³C NMR (CDCl₃, DEPT-135, 4:1 ratio of isomers, major isomer) δ 148.2 (C), 139.8 (C), 123.0 (C), 120.9 (CH), 120.7 (CH), 110.6 (CH), 93.7 (CH), 78.3 (CH₂), 55.7 (CH₃), 38.3 (CH), 34.8 (CH), 29.9 (CH₂), 20.4 (CH₂), 14.1 (CH₃); LRMS m/z 282.20 (M + H⁺), calcd for C₁₄H₁₉NO₅ 281.1263; Anal. calcd for C₁₄H₁₉NO₅ (281.1263): C, 59.78; H, 6.81; N, 4.98. Found: C, 59.68; H, 6.85; N, 4.91%.

(3S, 4R)-3-Butyl-8-methoxy-4-nitromethylchroman-2-ol (5fa): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as liquid.  
\[ [\alpha]_D^{25} = +18.05^\circ (c = 0.23 \text{ g/100 mL, CHCl}_3); \]  
IR (Neat): ν max 3459 (O-H), 2965, 1549 (NO₂), 1484, 1379, 1264, 1085, 983, 733 and 634 cm⁻¹; ¹H NMR (CDCl₃, 4:1 ratio of isomers, major isomer) δ 7.01-6.78 (2H, m), 6.64-6.62 (1H, m), 5.68 (1H, s), 4.89-4.80 (1H, m), 4.72 (1H, dd, J = 10.4, 4.4 Hz), 4.65 (1H, dd, J = 10.0, 6.0 Hz), 3.85 (3H, s, OCH₃), 3.76 (1H, m), 2.23 (1H, m), 1.80-1.20 (6H, m), 0.96 (3H, t, J = 6.0 Hz); ¹³C NMR (CDCl₃, DEPT-135, 4:1 ratio of isomers, major isomer) δ 148.0 (C), 139.8 (C), 123.2 (C), 120.7 (CH), 120.6 (CH), 110.5 (CH), 93.7 (CH), 78.2 (CH₂), 55.5 (CH₃), 38.5 (CH), 34.7 (CH), 28.8 (CH₂), 27.4 (CH₂), 22.6 (CH₂), 13.8 (CH₃); LRMS m/z 296.20 (M + H⁺), calcd for C₁₅H₂₁NO₅ 295.142; Anal. calcd for C₁₅H₂₁NO₅ (295.142): C, 59.78; H, 6.81; N, 4.98. Found: C, 59.68; H, 6.85; N, 4.91%.

(3S, 4R)-8-Methoxy-3-methyl-4-nitromethylchroman-2-one (7aa): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 99 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 60:40, flow rate 1.0 mL/min, λ = 254 nm), tR = 34.20 min (major), tR = 50.21 min (minor).  
\[ [\alpha]_D^{25} = +97.4^\circ (c = 0.2 \text{ g/100 mL, CHCl}_3, 99\% \text{ ee}); \]  
IR (Neat): ν max 2973, 1760 (C=O), 1552 (NO₂), 1455, 1379, 1273, 1025, 839, 756, 663 and 635 cm⁻¹; ¹H NMR (CDCl₃) δ 7.08 (1H, t, J = 8.0 Hz), 7.01-6.78 (2H, m), 6.64-6.62 (1H, m), 5.68 (1H, s), 4.89-4.80 (1H, m), 4.72 (1H, dd, J = 10.4, 4.4 Hz), 4.65 (1H, dd, J = 10.0, 6.0 Hz), 3.85 (3H, s, OCH₃), 3.76 (1H, m), 2.23 (1H, m), 1.80-1.20 (6H, m), 0.96 (3H, t, J = 6.0 Hz); ¹³C NMR (CDCl₃, DEPT-135, 4:1 ratio of isomers, major isomer) δ 148.0 (C), 139.8 (C), 123.2 (C), 120.7 (CH), 120.6 (CH), 110.5 (CH), 93.7 (CH), 78.2 (CH₂), 55.5 (CH₃), 38.5 (CH), 34.7 (CH), 28.8 (CH₂), 27.4 (CH₂), 22.6 (CH₂), 13.8 (CH₃); LRMS m/z 296.20 (M + H⁺), calcd for C₁₅H₂₁NO₅ 295.142; Anal. calcd for C₁₅H₂₁NO₅ (295.142): C, 61.00; H, 7.17; N, 4.74. Found: C, 60.15; H, 7.12; N, 4.71%.
6.95 (1H, d, J = 7.2 Hz), 6.74 (1H, d, J = 7.2 Hz), 4.65 (1H, dd, J = 12.4, 3.2 Hz), 4.34 (1H, dd, J = 12.4, 9.6 Hz), 3.90 (3H, s, OCH₃), 3.82 (1H, quintet, J = 5.2 Hz), 3.13 (1H, quintet, J = 6.8 Hz), 1.42 (3H, d, J = 7.2 Hz); 13C NMR (CDCl₃, DEPT-135) δ 168.7 (C, O-C=O), 147.9 (C), 140.2 (C), 125.1 (C), 123.6 (CH), 119.2 (CH), 112.7 (CH), 75.5 (CH₂), 56.1 (CH₃), 39.7 (CH), 36.6 (CH), 12.2 (CH₃); LRMS m/z 252.05 (M + H⁺), calcd for C₁₂H₁₃NO₅ 251.0794; HRMS m/z 252.0873 (M + H⁺), calcd for C₁₂H₁₃NO₅H⁺ 252.0872; Anal. calcd for C₁₂H₁₃NO₅ (251.0794): C, 57.37; H, 5.22; N, 5.58. Found: C, 57.45; H, 5.18; N, 5.62%.

(3S, 4R)-6-Chloro-3-methyl-4-nitromethylchroman-2-one (7ad): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 133 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 75:25, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 30.46 min (minor), tᵣ = 36.24 min (major). [α]D₂⁵ = +20.0° (c = 0.1 g/100 mL, CHCl₃, >99% ee); IR (Neat): νmax 2975, 1763 (C=O), 1552 (NO₂), 1455, 1380, 1274, 1155, 1025, 824, 661 and 635 cm⁻¹; ¹H NMR (CDCl₃) δ 7.31 (1H, d, J = 8.4 Hz), 7.18 (1H, s), 7.04 (1H, d, J = 8.4 Hz), 4.66 (1H, dd, J = 13.2, 5.2 Hz), 4.35 (1H, dd, J = 12.4, 9.6 Hz), 3.82-3.77 (1H, m), 1.40 (3H, d, J = 6.8 Hz); 13C NMR (CDCl₃, DEPT-135) δ 168.6 (C), 149.5 (C), 130.2 (CH), 130.1 (C), 127.9 (CH), 124.1 (C), 118.8 (CH), 79.9 (CH₂), 39.0 (CH), 36.4 (CH), 12.0 (CH₃); LRMS m/z 256.00 (M + H⁺), calcd for C₁₁H₁₀ClNO₄ 255.0298; HRMS m/z 254.0180 (M – H⁺), calcd for C₁₁H₁₀ClNO₄⁻ 254.0220; Anal. calcd for C₁₁H₁₀ClNO₄ (255.0298): C, 51.68; H, 3.94; N, 5.48. Found: C, 51.75; H, 3.91; N, 5.42%.

(3S, 4R)-6,8-Dichloro-3-methyl-4-nitromethylchroman-2-one (7af): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 178 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 55.73 min (minor), tᵣ = 67.06 min (major). [α]D₂⁵ = +87.78° (c = 0.11 g/100 mL, CHCl₃, >99% ee); IR (Neat): νmax 2976, 1760 (C=O), 1552 (NO₂), 1450, 1380, 1274, 1154, 1025, 827, 662, 640 and 616 cm⁻¹; ¹H NMR (CDCl₃) δ 7.44 (1H, s), 7.10 (1H, s), 4.67 (1H, dd, J = 12.8, 4.8 Hz), 4.35 (1H, dd, J = 13.2, 10.0 Hz), 3.86-3.80 (1H, m), 3.12 (1H, quintet, J = 6.8 Hz), 1.44 (3H, d, J = 7.2 Hz); 13C NMR (CDCl₃, DEPT-135) δ 167.4 (C, O-C=O), 145.9 (C), 130.7 (CH), 130.1 (C), 126.4 (CH), 125.4 (C), 123.5 (C), 74.7 (CH₂), 39.4 (CH), 36.4 (CH), 12.0 (CH₃); LRMS m/z 289.95 (M + H⁺), calcd for C₁₁H₁₀Cl₂NO₄ 288.9909; HRMS m/z 287.9822 (M – H⁺), calcd for C₁₁H₁₀Cl₂NO₄-H⁺ 287.9831; Anal. calcd for C₁₁H₁₀Cl₂NO₄ (288.9909): C, 51.68; H, 3.94; N, 4.83. Found: C, 45.61; H, 3.18; N, 4.79%.
(3S, 4R)-6-Methoxy-3-methyl-4-nitromethylchroman-2-one (7ag): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 80 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), tR = 48.54 min (minor), tR = 57.97 min (major). [α]D25 = +44.88° (c = 0.11 g/100 mL, CHCl3, 99.7% ee); IR (Neat): νmax 2973, 1758 (C=O), 1552 (NO2), 1455, 1379, 1273, 1025, 839, 756, 663 and 635 cm−1; 1H NMR (CDCl3) δ 7.03 (1H, d, J = 9.2 Hz), 6.86 (1H, dd, J = 9.2, 3.2 Hz), 6.68 (1H, d, J = 3.2 Hz), 4.65 (1H, dd, J = 12.8, 5.2 Hz), 4.34 (1H, dd, J = 12.8, 10.0 Hz), 3.81-3.76 (1H, m), 3.78 (3H, s, OCH3), 3.13-3.06 (1H, m), 1.40 (3H, d, J = 7.2 Hz); 13C NMR (CDCl3, DEPT-135) δ 169.5 (C, O-C=O), 156.5 (C), 144.8 (C), 123.4 (C), 118.3 (CH), 115.3 (CH), 112.9 (CH), 75.4 (CH2), 55.8 (CH3), 39.6 (CH), 36.7 (CH), 12.2 (CH3); LRMS m/z 252.00 (M + H+), calcd for C12H13NO5 251.0794; HRMS m/z 252.0870 (M + H+), calcd for C12H13NO5H+ 252.0872; Anal. calcd for C12H13NO5 (251.0794): C, 57.37; H, 5.22; N, 5.58. Found: C, 57.45; H, 5.26; N, 5.51%.

(3S, 4R)-7-Methoxy-3-methyl-4-nitromethylchroman-2-one (7ah): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 80 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tR = 43.47 min (major), tR = 53.07 min (minor). [α]D25 = +115.16° (c = 0.14 g/100 mL, CHCl3, 99% ee); IR (Neat): νmax 2973, 1763 (C=O), 1552 (NO2), 1448 (C), 123.4 (C), 118.3 (CH), 115.3 (CH), 112.9 (CH), 75.4 (CH2), 55.8 (CH3), 39.6 (CH), 36.7 (CH), 12.2 (CH3); LRMS m/z 252.00 (M + H+), calcd for C12H13NO5 251.0794; HRMS m/z 252.0870 (M + H+), calcd for C12H13NO5H+ 252.0872; Anal. calcd for C12H13NO5 (251.0794): C, 57.37; H, 5.22; N, 5.58. Found: C, 57.45; H, 5.26; N, 5.51%.

(3S, 4R)-3,6-Dimethyl-4-nitromethylchroman-2-one (7ai): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 110 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), tR = 43.47 min (major), tR = 53.07 min (minor). [α]D25 = +63.27° (c = 0.15 g/100 mL, CHCl3, 99.6% ee); IR (Neat): νmax 2974, 1763 (C=O), 1552 (NO2), 1455,
1379, 1025, 825, 784, 662 and 636 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.13 (1H, d, $J$ = 8.0 Hz), 6.98 (1H, d, $J$ = 8.4 Hz), 6.95 (1H, s), 4.64 (1H, dd, $J$ = 12.4, 4.8 Hz), 4.33 (1H, dd, $J$ = 12.4, 9.6 Hz), 3.79-3.74 (1H, m), 3.09 (1H, quintet, $J$ = 6.4 Hz), 2.30 (3H, s, ArCH$_3$), 1.39 (3H, d, $J$ = 7.2 Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 169.5 (C, O-C=O), 148.8 (C), 134.7 (C), 130.6 (CH), 128.2 (CH), 122.2 (C), 117.1 (CH), 75.5 (CH$_2$), 39.3 (CH), 36.8 (CH), 20.7 (CH$_3$), 12.1 (CH$_3$); LRMS m/z 236.05 (M + H$^+$), calcd for C$_{12}$H$_{13}$NO$_4$ 235.0845; HRMS m/z 234.0764 (M – H$^+$), calcd for C$_{12}$H$_{13}$NO$_4$-H$^+$ 234.0767; Anal. calcd for C$_{12}$H$_{13}$NO$_4$ (235.0845): C, 61.27; H, 5.57; N, 5.95. Found: C, 61.32; H, 5.53; N, 5.89%.

(3$S$, 4$R$)-3-Ethyl-8-methoxy-4-nitromethylchroman-2-one (cis-7ba): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as oily liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Lux 5u Amylose-2 column (hexane/2-propanol = 75:25, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_R$ = 17.43 min (major), $t_R$ = 22.23 min (minor) [for cis-7ba]; $t_R$ = 13.28 min (major), $t_R$ = 14.86 min (minor) [for trans-7ba]. $[\alpha]_D^{25} = +36.59$° ($c = 0.41$ g/100 mL, CHCl$_3$, >99.9% ee); IR (Neat): $\nu_{\text{max}}$ 2976, 1760 (C=O), 1552 (NO$_2$), 1455, 1380, 1274, 1154, 1025, 827, 662, 640 and 616 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.06 (1H, t, $J$ = 8.0 Hz), 6.94 (1H, d, $J$ = 8.4 Hz), 6.73 (1H, d, $J$ = 8.0 Hz), 4.58 (1H, dd, $J$ = 12.4, 4.8 Hz), 4.30 (1H, dd, $J$ = 12.0, 10.8 Hz), 3.92-3.91 (1H, m), 3.89 (3H, s, OCH$_3$), 2.85-2.77 (1H, m), 2.16-2.07 (1H, m), 1.59-1.50 (1H, m), 1.13 (3H, t, $J$ = 7.6 Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 168.2 (C, O-C=O), 147.8 (C), 140.0 (C), 125.0 (CH), 123.7 (C), 119.2 (CH), 112.6 (CH), 55.0 (CH$_3$), 43.2 (CH), 37.6 (CH), 19.9 (CH$_2$), 11.9 (CH$_3$); LRMS m/z 266.20 (M + H$^+$), calcd for C$_{13}$H$_{15}$NO$_5$ 265.0950; HRMS m/z 264.0870 (M – H$^+$), calcd for C$_{13}$H$_{15}$NO$_5$-H$^+$ 264.0872; Anal. calcd for C$_{13}$H$_{15}$NO$_5$ (265.0950): C, 58.86; H, 5.70; N, 5.28. Found: C, 58.79; H, 5.75; N, 5.22%.

(3$S$, 4$R$)-3-Benzyl-8-methoxy-4-nitromethylchroman-2-one (7ca): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 128 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_R$ = 24.94 min (minor), $t_R$ = 34.75 min (major). $[\alpha]_D^{25} = +16.55$° ($c = 0.28$ g/100 mL, CHCl$_3$, 99.3% ee); IR (Neat): $\nu_{\text{max}}$ 3112, 2975, 1763 (C=O), 1552 (NO$_2$), 1455, 1380, 1211, 1117, 1025, 824, 663 and 631 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.37 (2H, br t, $J$ = 7.6 Hz), 7.30 (1H, br d, $J$ = 7.6 Hz), 7.28 (2H, br d, $J$ = 7.6 Hz), 7.02 (1H, t, $J$ = 7.6 Hz), 6.92 (1H, dd, $J$ = 8.4, 1.2 Hz), 6.61 (1H, dd, $J$ = 7.6, 1.2 Hz), 4.74 (1H, dd, $J$ = 12.0, 4.4 Hz), 4.37 (1H, dd, $J$ = 12.4, 10.8 Hz), 3.87 (3H, s), 3.55-3.50 (1H, m), 3.52 (1H, dd, $J$= 14.8, 5.6 Hz), 3.29-3.24 (1H, m), 2.77 (1H, dd, $J$ = 14.8, 9.6 Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 168.0 (C, O-
C=O), 147.9 (C), 140.1 (C), 137.1 (C), 129.1 (2 x CH), 128.7 (2 x CH), 127.3 (CH), 125.1 (CH), 123.8 (C), 119.4 (CH), 112.7 (CH), 75.3 (CH₂), 56.1 (CH₃), 43.4 (CH), 36.9 (CH), 32.4 (CH₂); LRMS m/z 328.25 (M + H⁺), calcd for C₁₈H₁₇NO₅ 327.1107; HRMS m/z 326.1022 (M – H⁺), calcd for C₁₈H₁₇NO₅-H⁺ 326.1029; Anal. calcd for C₁₈H₁₇NO₅ (325.1107): C, 66.05; H, 5.23; N, 4.28. Found: C, 66.15; H, 5.17; N, 4.32%.

(3S, 4R)-3-Benzylxy-8-methoxy-4-nitromethylchroman-2-one (cis-7da): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as oily liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 49.12 min (major), tᵣ = 65.82 min (minor) [for cis-7da]; tᵣ = 57.41 min (minor), tᵣ = 105.14 min (major) [for trans-7da]. [α]D²⁵ = +14.13° (c = 0.07 g/100 mL, CHCl₃, 87% ee); IR (Neat): νmax 3112, 2975, 1763 (C=O), 1552 (NO₂), 1455, 1380, 1153, 1025, 824, 663 and 631 cm⁻¹; ¹H NMR (CDCl₃) δ 7.38-7.32 (5H, m), 7.06 (1H, t, J = 7.6 Hz), 6.92 (1H, d, J = 8.0 Hz), 6.72 (1H, d, J = 7.6 Hz), 5.07-5.04 (1H, m), 4.89 (1H, dd, J = 12.8, 4.8 Hz), 4.75 (1H, d, J = 9.6 Hz), 4.44-4.39 (1H, m), 4.05 (1H, m), 3.95-3.85 (1H, m), 3.87 (3H, s); ¹³C NMR (CDCl₃, DEPT-135) δ 165.7 (C), 147.6 (C), 139.2 (C), 136.2 (C), 128.6 (2 x CH), 128.4 (CH), 128.1 (2 x CH), 125.4 (CH), 121.0 (C), 119.8 (CH), 112.8 (CH), 74.9 (CH₂), 73.2 (CH₂), 71.4 (CH), 56.0 (CH₃), 39.9 (CH); LRMS m/z 344.15 (M + H⁺), calcd for C₁₈H₁₇NO₆ 343.1056; Anal. calcd for C₁₈H₁₇NO₆ (343.1056): C, 62.97; H, 4.99; N, 4.08. Found: C, 62.85; H, 5.03; N, 4.12%.

(3S, 4R)-8-Methoxy-4-nitromethyl-3-propylchroman-2-one (7ea): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 76-78 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 92:8, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 42.45 min (minor), tᵣ = 58.37 min (major). [α]D²⁵ = +27.56° (c = 0.14 g/100 mL, CHCl₃, 99% ee); IR (Neat): νmax 3112, 2973, 1762, 1552 (NO₂), 1455, 1379, 1273, 1025, 839, 756, 663 and 635 cm⁻¹; ¹H NMR (CDCl₃) δ 7.06 (1H, t, J = 7.6 Hz), 4.59 (1H, dd, J = 12.4, 4.8 Hz), 4.30 (1H, t, J = 11.2 Hz), 3.89 (3H, s), 3.86-3.83 (1H, m), 2.94-2.86 (1H, m), 2.00 (1H, m), 1.66-1.43 (3H, m), 0.99 (3H, t, J = 6.8 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 168.3 (C, O-C=O), 147.8 (C), 140.0 (C), 125.0 (CH), 123.8 (C), 119.2 (CH), 112.6 (CH), 75.4 (CH₂), 56.0 (CH₃), 41.2 (CH), 37.9 (CH), 28.7 (CH₂), 20.5 (CH₂), 13.8 (CH₃); LRMS m/z 279.90 (M + H⁺), calcd for C₁₄H₁₇NO₅ 279.1107; HRMS m/z 280.1179 (M + H⁺), calcd for
C₁₄H₁₇NO₅H⁺ 280.1185; Anal. calcd for C₁₄H₁₇NO₅ (279.1107): C, 60.21; H, 6.14; N, 5.02. Found: C, 60.28; H, 6.09; N, 5.11%.

(3S, 4R)-3-Butyl-8-methoxy-4-nitromethylchroman-2-one (7fa): Prepared following the procedure D and purified by column chromatography using EtOAc/hexane and isolated as oily liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 70:30, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 14.47 min (minor), tᵣ = 18.73 min (major). [α]D²⁵ = +12.14° (c = 0.15 g/100 mL, CHCl₃, 90% ee); IR (Neat): νmax 2976, 1763 (C=O), 1552 (NO₂), 1456, 1379, 1273, 1024, 840, 823, 754, and 625 cm⁻¹; ¹H NMR (CDCl₃) δ 7.07 (1H, t, J = 8.0 Hz), 6.94 (1H, d, J = 7.6 Hz), 6.72 (1H, d, J = 7.6 Hz), 4.69 (1H, dd, J = 12.4, 4.8 Hz), 4.30 (1H, t, J = 10.8 Hz), 3.90 (3H, s), 3.90-3.80 (1H, m), 0.95 (3H, t, J = 7.2 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 168.3 (C, O-C=O), 147.8 (C), 140.1 (C), 125.0 (CH), 123.8 (C), 119.3 (CH), 112.7 (CH), 75.5 (CH₂), 56.1 (CH₃), 41.5 (CH), 37.9 (CH), 29.4 (CH₂), 26.3 (CH₂), 22.4 (CH₃), 13.8 (CH₃); LRMS m/z 294.00 (M + H⁺), calcd for C₁₅H₁₉NO₅ 293.1263; HRMS m/z 294.1340 (M + H⁺), calcd for C₁₅H₁₉NO₅H⁺ 294.1341; Anal. calcd for C₁₅H₁₉NO₅ (293.1263): C, 61.42; H, 6.53; N, 4.78. Found: C, 61.48; H, 6.57; N, 4.71%.

(1R, 2S)-2-(3-Hydroxy-2-methyl-1-nitromethylpropyl)phenol (9ab): Prepared following the procedure E and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 68 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ, = 254 nm), tᵣ = 7.53 min (minor), tᵣ = 9.57 min (major). [α]D²⁵ = +21.4° (c = 0.28 g/100 mL, EtOH, 89% ee); IR (Neat): νmax 3373 (O–H), 2975, 1552 (NO₂), 1456, 1379, 1273, 1024, 840, 823, 754, and 625 cm⁻¹; ¹H NMR (CDCl₃) δ 7.13 (1H, t, J = 7.2 Hz), 6.99 (1H, d, J = 7.2 Hz), 6.87 (1H, t, J = 7.2 Hz), 6.86 (1H, d, J = 8.0 Hz), 4.86-4.76 (2H, m), 4.29-4.24 (1H, m), 3.50 (1H, dd, J = 11.2, 4.0 Hz), 3.11 (1H, t, J = 10.8 Hz), 2.24 (1H, br s, OH), 2.17-2.15 (1H, m), 0.77 (3H, d, J = 6.8 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 154.8 (C), 128.8 (CH), 128.6 (CH), 122.2 (C), 120.4 (CH), 116.4 (CH), 77.9 (CH₂), 65.3 (CH₂), 37.1 (CH), 36.7 (CH), 11.5 (CH₃); LRMS m/z 226.20 (M + H⁺), calcd for C₁₁H₁₅NO₄ 225.1001; HRMS m/z 224.0926 (M + H⁺), calcd for C₁₁H₁₅NO₄-H⁺ 224.0926; Anal. calcd for C₁₁H₁₅NO₄ (225.1001): C, 58.66; H, 6.71; N, 6.22. Found: C, 58.55; H, 6.76; N, 6.18%.

(1R, 2S)-4-Fluoro-2-(3-hydroxy-2-methyl-1-nitromethylpropyl)phenol (9ac): Prepared following the procedure E and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 103 °C; The enantiomeric excess (ee) was determined by chiral
stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 16.24 min (minor), t_R = 24.02 min (major). [α]_D^{25} = +12.6° (c = 0.3 g/100 mL, CHCl₃, 89% ee); IR (Neat): ν_max 3379 (O-H), 2974, 1553 (NO₂), 1450, 1379, 1273, 1025, 840, 821, 708, 637 and 602 cm⁻¹; ¹H NMR (CD₃OD) δ 6.86 (1H, dd, J = 10.4, 3.2 Hz), 6.82 (1H, dd, J = 8.4, 3.2 Hz), 6.77 (1H, dd, J = 8.4, 4.8 Hz), 5.05-4.94 (2H, m), 4.64 (1H, br s), 3.80-3.74 (1H, m), 3.53 (2H, d, J = 5.6 Hz), 2.22-2.12 (1H, m), 0.83 (3H, d, J = 6.8 Hz); ¹³C NMR (CD₃OD, DEPT-135) δ 156.2 (C, d, J = 234.1 Hz), 151.6 (C), 126.2 (C, d, J = 6.5 Hz), 116.0 (CH), 115.8 (CH, d, J = 17.7 Hz), 113.8 (CH, d, J = 22.7 Hz), 77.1 (CH₂), 64.8 (CH₂), 36.9 (CH), 13.8 (CH₃); LRMS m/z 243.90 (M + H⁺), calcd for C₁₁H₁₄FNO₄ 243.0907; HRMS m/z 242.0833 (M – H +), calcd for C₁₁H₁₄FNO₄ – H⁺ 242.0829; Anal. calcd for C₁₁H₁₄FNO₄ (243.0907): C, 54.32; H, 5.80; N, 5.76. Found: C, 54.42; H, 5.86; N, 5.71%.

(1R, 2S)-4-Chloro-2-(3-hydroxy-2-methyl-1-nitromethylpropyl)phenol (9ad): Prepared following the procedure E and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 135 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate 0.8 mL/min, λ = 254 nm), t_R = 21.43 min (minor), t_R = 33.11 min (major). [α]_D^{25} = +13.73° (c = 0.31 g/100 mL, EtOH, 96.8% ee); IR (Neat): ν_max 3377 (O-H), 2975, 151.6 (C), 126.2 (C, d, J = 6.5 Hz), 116.0 (CH), 115.8 (CH, d, J = 17.7 Hz), 113.8 (CH, d, J = 22.7 Hz), 77.1 (CH₂), 64.8 (CH₂), 36.9 (CH), 13.8 (CH₃); LRMS m/z 260.20 (M + H⁺), calcd for C₁₁H₁₄ClNO₄ 259.0611; HRMS m/z 258.0530 (M – H +), calcd for C₁₁H₁₄ClNO₄ – H⁺ 258.0533; Anal. calcd for C₁₁H₁₄ClNO₄ (259.0611): C, 50.88; H, 5.43; N, 5.39. Found: C, 50.75; H, 5.49; N, 5.34%.

(1R, 2S)-4-Bromo-2-(3-hydroxy-2-methyl-1-nitromethylpropyl)phenol (9ae): Prepared following the procedure E and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 160 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 88:12, flow rate 1.0 mL/min, λ = 254 nm), t_R = 12.86 min (minor), t_R = 18.96 min (major). [α]_D^{25} = +12.7° (c = 0.3 g/100 mL, EtOH, 89.5% ee); IR (Neat): ν_max 3367 (O-H), 2972, 1515 (NO₂), 1449, 1379, 1274, 1025, 820, 657 and 632 cm⁻¹; ¹H NMR (CD₃OD) δ 7.22 (1H, s), 7.20 (1H, d, J = 4.0 Hz), 6.73 (1H, d, J = 8.0 Hz), 5.55-4.94 (2H, m), 3.72-3.68 (1H, m), 3.54 (2H, d, J = 4.0 Hz), 2.21-
2.14 (1H, m), 0.82 (3H, d, \( J = 8.0 \) Hz); \(^{13}\)C NMR (CD\(_3\)OD, DEPT-135) \( \delta \) 154.9 (C), 132.4 (CH), 130.6 (CH), 127.4 (C), 117.0 (CH), 110.7 (C), 77.0 (CH\(_2\)), 64.7 (CH\(_2\)), 42.4 (CH), 36.8 (CH), 14.1 (CH\(_3\)); LRMS m/z 302.50 (M – H\(^+\)), calcd for C\(_{11}\)H\(_{14}\)BrNO\(_4\) 303.0106; HRMS m/z 302.0028 (M – H\(^+\)), calcd for C\(_{11}\)H\(_{14}\)BrNO\(_4\) – H\(^+\) 302.0028; Anal. calcd for C\(_{11}\)H\(_{14}\)BrNO\(_4\) (303.0106): C, 43.44; H, 4.64; N, 4.61. Found: C, 43.51; H, 4.68; N, 4.65%.

(1R, 2S)-3-(3-Hydroxy-2-methyl-1-nitromethylpropyl)benzene-1,2-diol (9aj): Prepared following the procedure E and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 92:8, flow rate 1.0 mL/min, \( \lambda \) = 254 nm), \( t_R \) = 46.98 min (minor), \( t_R \) = 51.19 min (major). [\( \alpha \)]\(_D\)\(^{25} \) = -17.6° (c = 0.11 g/100 mL, CHCl\(_3\), >99% ee); IR (Neat): \( \nu \)\(_{\text{max}}\) 3589 (O-H), 2973, 1550 (NO\(_2\)), 1490, 1379, 1222, 1131, 1042, 757 and 635 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\(_3\)) \( \delta \) 6.79-6.71 (2H, m), 6.51 (1H, dd, \( J = 6.4, 1.2 \) Hz), 4.78 (2H, d, \( J = 7.6 \) Hz), 4.22 (1H, m), 3.54 (1H, dd, \( J = 11.2, 4.0 \) Hz), 3.06 (1H, t, \( J = 10.4 \) Hz), 2.14 (1H, m), 0.77 (3H, d, \( J = 6.8 \) Hz); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \( \delta \) 145.5 (C), 142.7 (C), 122.4 (C), 120.9 (CH), 119.5 (CH), 114.2 (CH), 77.6 (CH\(_2\)), 65.5 (CH\(_2\)), 36.5 (CH), 36.2 (CH), 10.9 (CH\(_3\)); LRMS m/z 242.05 (M + H\(^+\)), calcd for C\(_{11}\)H\(_{15}\)NO\(_5\) 241.0950; HRMS m/z 240.0870 (M – H\(^+\)), calcd for C\(_{11}\)H\(_{15}\)NO\(_5\) – H\(^+\) 240.0872; Anal. calcd for C\(_{11}\)H\(_{15}\)NO\(_5\) (241.0950): C, 54.77; H, 6.27; N, 5.81. Found: C, 54.61; H, 6.32; N, 5.75%.

(2S, 3S, 4R)-2-Methoxy-3-methyl-4-nitromethylchroman (trans-5aba): Prepared following the procedure F and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 80 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 98:2, flow rate 0.5 mL/min, \( \lambda \) = 254 nm), \( t_R \) = 15.12 min (minor), \( t_R \) = 18.80 min (major). [\( \alpha \)]\(_D\)\(^{25} \) = -23.60° (c = 0.44 g/100 mL, CHCl\(_3\), 98% ee); IR (Neat): \( \nu \)\(_{\text{max}}\) 2974, 1551 (NO\(_2\)), 1494, 1380, 1198, 982, 913, 818 and 635 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\(_3\)) \( \delta \) 7.20 (1H, t, \( J = 7.2 \) Hz), 7.00 (1H, d, \( J = 6.8 \) Hz), 6.91 (1H, t, \( J = 6.8 \) Hz), 6.89 (1H, d, \( J = 8.0 \) Hz), 4.95 (1H, br s), 4.87 (1H, dd, \( J = 13.2, 5.2 \) Hz), 4.62 (1H, dd, \( J = 13.2, 7.6 \) Hz), 3.07-3.68 (1H, m), 3.48 (3H, s), 2.47-1.44 (1H, m), 1.20 (3H, d, \( J = 7.2 \) Hz); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \( \delta \) 150.6 (C), 129.0 (CH), 128.8 (CH), 122.2 (C), 121.3 (CH), 117.5 (CH), 101.2 (CH), 78.2 (CH\(_2\)), 56.2 (CH\(_3\)), 36.5 (CH), 33.3 (CH), 12.7 (CH\(_3\)); LRMS m/z 236.60 (M – H\(^+\)), calcd for C\(_{12}\)H\(_{13}\)NO\(_3\) 237.1001; HRMS m/z 236.60 (M – H\(^+\)), calcd for C\(_{12}\)H\(_{13}\)NO\(_3\) – H\(^+\) 236.60; Anal. calcd for C\(_{12}\)H\(_{13}\)NO\(_3\) (237.1001): C, 54.77; H, 6.27; N, 5.81. Found: C, 60.85; H, 6.32; N, 5.85%.

(2R, 3S, 4R)-2-Methoxy-3-methyl-4-nitromethylchroman (cis-5aba): Prepared following the
procedure F and purified by column chromatography using EtOAc/hexane and isolated as oily liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 98:02, flow rate 1.0 mL/min, λ = 254 nm), t_R = 20.56 min (minor), t_R = 24.70 min (major). [α]_D^{25} = +86.90° (c = 0.14 g/100 mL, CHCl_3, >99% ee); IR (Neat): ν max 2974, 1551 (NO_2), 1494, 1380, 1198, 982, 913, 818 and 635 cm⁻¹; ¹H NMR (CDCl_3) δ 7.23-7.19 (1H, m), 7.00-6.90 (3H, m), 4.95 (1H, dd, J = 12.4, 6.4 Hz), 4.88 (1H, br s), 4.57 (1H, dd, J = 12.8, 9.2 Hz), 4.08-4.06 (1H, m), 3.49 (3H, s), 2.21-2.20 (1H, m), 0.97 (3H, d, J = 6.8 Hz); ¹³C NMR (CDCl_3, DEPT-135) δ 150.9 (C), 128.8 (CH), 126.0 (CH), 121.6 (CH), 120.0 (C), 117.6 (CH), 101.9 (CH), 76.1 (CH_2), 55.8 (CH_3), 33.0 (CH), 31.8 (CH), 10.9 (CH_3); LRMS m/z 236.50 (M - H+), calcd for C_12H_15NO_4 237.1001; Anal. calcd for C_12H_15NO_4 (237.1001): C, 60.75; H, 6.37; N, 5.90. Found: C, 60.80; H, 6.35; N, 5.88%.

(2S, 3S, 4R)-6-Chloro-2-methoxy-3-methyl-4-nitromethylchroman (trans-5ada): Prepared following the procedure F and purified by column chromatography using EtOAc/hexane and isolated as oily liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 98:02, flow rate 0.5 mL/min, λ = 254 nm), t_R = 18.46 min (minor), t_R = 23.32 min (major). [α]_D^{25} = −45.4° (c = 0.28 g/100 mL, CHCl_3, 80.71% ee); IR (Neat): ν max 2973, 1551 (NO_2), 1494, 1429, 1379, 1198, 982, 913, 817 and 634 cm⁻¹; ¹H NMR (CDCl_3) δ 7.15 (1H, d, J = 8.8 Hz), 7.01 (1H, s), 6.83 (1H, d, J = 8.8 Hz), 4.92 (1H, br s), 4.89 (1H, dd, J = 13.6, 4.4 Hz), 4.59 (1H, dd, J = 13.6, 7.6 Hz), 3.67-3.65 (1H, m), 3.47 (3H, s), 2.41 (1H, m), 1.19 (3H, d, J = 7.2 Hz); ¹³C NMR (CDCl_3, DEPT-135) δ 149.3 (C), 129.2 (CH), 128.4 (CH), 126.2 (C), 123.9 (C), 118.9 (CH), 101.3 (CH), 77.9 (CH_2), 56.3 (CH_3), 36.2 (CH), 33.2 (CH), 12.6 (CH_3); LRMS m/z 272.30 (M + H+), calcd for C_{12}H_{14}ClNO_4 271.0611; HRMS m/z 270.0533 (M – H+), calcd for C_{12}H_{14}ClNO_4-H 270.0533; Anal. calcd for C_{12}H_{14}ClNO_4 (271.0611): C, 53.05; H, 5.19; N, 5.16. Found: C, 53.12; H, 5.23; N, 5.13%.

(2R, 3S, 4R)-6-Chloro-2-methoxy-3-methyl-4-nitromethylchroman (cis-5ada): Prepared following the procedure F and purified by column chromatography using EtOAc/hexane and isolated as oily liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 99:1, flow rate 0.5 mL/min, λ = 254 nm), t_R = 36.79 min (major), t_R = 43.02 min (minor). [α]_D^{25} = +28.08° (c = 0.1 g/100 mL, CHCl_3, 88.92% ee); IR (Neat): ν max 2978, 1551 (NO_2), 1494, 1429, 1379, 1198, 982, 913, 817 and 634 cm⁻¹; ¹H NMR (CDCl_3) δ 7.18-7.15 (1H, m), 6.98 (1H, s), 6.85 (1H, d, J = 8.4 Hz), 4.93-4.87 (2H, m), 4.57 (1H, dd, J = 12.4, 9.2 Hz), 4.07-4.02 (1H, m), 3.48 (3H, s), 2.20-2.19 (1H, m), 0.94 (3H, d, J = 7.2 Hz); ¹³C NMR (CDCl_3, DEPT-135) δ 149.5 (C), 128.8 (CH), 126.4 (C), 126.0 (CH), 121.7 (C), 118.9 (CH), 101.9 (CH), 75.7 (CH_2), 55.8 (CH_3), 32.9 (CH), 31.5 (CH), 23.7 (CH_3); LRMS m/z 272.30 (M + H+), calcd for C_{12}H_{14}ClNO_4 271.0611; HRMS m/z 270.0533 (M – H+), calcd for C_{12}H_{14}ClNO_4-H 270.0533; Anal. calcd for C_{12}H_{14}ClNO_4 (271.0611): C, 53.05; H, 5.19; N, 5.16. Found: C, 53.12; H, 5.23; N, 5.13%.
10.8 (CH₃); LRMS m/z 272.30 (M + H⁺), calcd for C₁₂H₁₄NO₄ 271.0611; Anal. calcd for C₁₂H₁₄NO₄ (271.0611): C, 53.05; H, 5.19; N, 5.16. Found: C, 53.15; H, 5.22; N, 5.09%.

(4R)-8-Methoxy-3-methyl-4-nitromethyl-4H-chromene (11aa): Prepared following the procedure G and purified by column chromatography using EtOAc/hexane and isolated as white solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 45.41 min (minor), tᵣ = 61.92 min (major). [α]D⁰ = −62.74 (c = 0.28 g/100 mL, CHCl₃, 99% ee); IR (Neat): ν max 1619 (C=C), 1584, 1544, 1484, 1266, 1213, 1125, 1102, 774, 733, 646 and 622 cm⁻¹; ¹H NMR (CDCl₃) δ 7.01 (1H, t, J = 8.0 Hz), 6.84 (1H, d, J = 8.4 Hz), 6.69 (1H, d, J = 8.0 Hz), 6.65 (1H, s), 4.56 (1H, dd, J = 12.0, 4.8 Hz), 4.44 (1H, dd, J = 11.6, 7.2 Hz), 4.14 (1H, t, J = 6.8 Hz), 3.89 (3H, s), 1.79 (3H, s); ¹³C NMR (CDCl₃, DEPT-135) δ 147.9 (C), 140.9 (C), 138.7 (CH), 123.6 (CH), 119.8 (C), 119.5 (CH), 110.7 (CH), 107.6 (C), 79.6 (CH₂), 56.0 (CH₃), 38.8 (CH), 16.0 (CH₃); LRMS m/z 235.90 (M + H⁺), calcd for C₁₂H₁₃NO₄ 235.0845; Anal. calcd for C₁₂H₁₃NO₄ (235.0845): C, 61.27; H, 5.57; N, 5.95. Found: C, 61.33; H, 5.52; N, 6.07%.

tert-Butyl (4R)-(8-Methoxy-3-methyl-4H-chromen-4-ylmethyl)carbamate (12aa): Prepared following the procedure H and purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 13.85 min (major), tᵣ = 16.0 min (minor). [α]D⁰ = −20.06° (c = 0.1 g/100 mL, CHCl₃, 80.9% ee); IR (Neat): ν max 2975, 1710 (C=O), 1485, 1266, 1171, 780, 737, and 622 cm⁻¹; ¹H NMR (CDCl₃) δ 6.98 (1H, t, J = 8.0 Hz), 6.77 (1H, d, J = 8.0 Hz), 6.73 (1H, d, J = 7.6 Hz), 6.60 (1H, s), 4.45 (1H, br s), 3.88 (3H, s), 3.47-3.46 (1H, m), 3.41-3.39 (2H, m), 1.74 (3H, s), 1.37 (9H, s); ¹³C NMR (CDCl₃, DEPT-135) δ 156.0 (C), 147.6 (C), 141.3 (C), 137.3 (CH), 123.0 (CH), 121.9 (C), 120.2 (CH), 109.7 (CH), 109.5 (C), 79.2 (CH₂), 55.9 (CH₃), 44.1 (CH₂), 39.2 (CH), 28.2 (3 x CH₃), 16.1 (CH₃); LRMS m/z 303.95 (M - H⁺), calcd for C₁₇H₂₃NO₄ 305.1627; Anal. calcd for C₁₇H₂₃NO₄ (305.1627): C, 66.27; H, 5.57; N, 5.95. Found: C, 66.33; H, 5.52; N, 6.07%.

tert-Butyl-(3S, 4R)-(8-Methoxy-3-methyl-chroman-4-ylmethyl)carbamate (13aa) and tert-Butyl-(3R, 4R)-(8-Methoxy-3-methyl-chroman-4-ylmethyl)carbamate (trans-13aa): Prepared following the procedure H and purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) of cis-13aa and trans-13aa was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 17.66 min (major), tᵣ = 27.78 min (minor).
min (minor); \( t_R = 23.82 \text{ min (major), } t_R = 30.35 \text{ min (minor).} \) \( [\alpha]_D^{25} = +59.33^\circ (c = 0.14 \text{ g/100 mL, CHCl}_3, 93\% \text{ ee}); \) IR (Neat): \( \nu_{\text{max}} \) 2962, 1712 (C=O), 1484, 1263, 830, 681, and 634 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 1:1 ratio of isomers) \( \delta \) 6.86-6.80 (2H, m), 6.76-6.70 (4H, m), 4.58 (2H, br s), 4.21-4.18 (2H, m), 3.86 (6H, s), 3.49-3.67 (4H, m), 2.98 (1H, br s), 2.62 (1H, br s), 2.30 (1H, br s), 2.04 (1H, br s), 1.44 (9H, s), 1.43 (9H, s), 1.08 (3H, d, \( J = 5.6 \text{ Hz} \)), 1.06 (3H, d, \( J = 6.4 \text{ Hz} \)); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135, 1:1 ratio of isomers) \( \delta \) 156.1 (C), 155.7 (C), 148.3 (2 x C), 144.2 (C), 143.4 (C), 123.8 (C), 122.6 (C), 121.3 (CH), 121.1 (CH), 120.1 (CH), 119.6 (CH), 109.6 (CH), 109.3 (CH), 82.0 (C), 79.4 (C), 69.2 (CH2), 68.6 (CH2), 55.8 (2 x CH3), 44.6 (CH3), 41.6 (CH2), 41.5 (CH), 38.3 (CH), 29.0 (CH), 28.4 (3 x CH3), 28.33 (3 x CH3), 28.2 (CH), 16.8 (CH3), 12.9 (CH3); LRMS m/z 306.30 (M - H +), calcd for C\(_{17}\)H\(_{25}\)NO\(_4\) 307.1784; Anal. calcd for C\(_{17}\)H\(_{25}\)NO\(_4\) (307.1784): C, 66.43; H, 8.20; N, 4.56. Found: C, 66.25; H, 8.16; N, 4.61%.

(4R)-3-Methyl-4-nitromethyl-4'H-chromene (11ab): Prepared following the procedure G and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp: 78 °C. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, \( \lambda = 254 \text{ nm} \)), \( t_R = 14.54 \text{ min (minor), } t_R = 15.62 \text{ min (major).} \) \( [\alpha]_D^{25} = -114.94^\circ (c = 0.143 \text{ g/100 mL, CHCl}_3, 94\% \text{ ee}); \) IR (Neat): \( \nu_{\text{max}} \) 1619 (C=C), 1544, 1484, 1382, 1266, 1234, 1213, 1125, 774, 733, 646 and 622 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 7.27-7.21 (1H, m), 7.11-7.04 (2H, m), 6.97 (1H, d, \( J = 8.0 \text{ Hz} \)), 6.56 (1H, br s), 4.57 (1H, dd, \( J = 11.6, 4.8 \text{ Hz} \)), 4.46 (1H, dd, \( J = 11.6, 7.2 \text{ Hz} \)), 4.13 (1H, br t, \( J = 6.4 \text{ Hz} \)), 1.78 (3H, s); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135) \( \delta \) 151.2 (C), 138.7 (CH), 128.7 (CH), 128.1 (CH), 123.8 (CH), 119.0 (C), 116.6 (CH), 107.4 (C), 79.6 (CH), 38.8 (CH), 16.0 (CH2); LRMS m/z 206.00 (M + H +), calcd for C\(_{11}\)H\(_{11}\)NO\(_3\) 205.0739; Anal. calcd for C\(_{11}\)H\(_{11}\)NO\(_3\) (205.0739): C, 64.38; H, 5.40; N, 6.83. Found: C, 64.29; H, 5.45; N, 6.79%.

tert-Butyl-(3S, 4R)-(3-methyl-chroman-4-ylmethyl)carbamate (cis-13ab) and tert-Butyl-(3R, 4R)-(3-methyl-chroman-4-ylmethyl)carbamate (trans-13ab): Prepared following the procedure H and purified by column chromatography using EtOAc/hexane and isolated as liquid. \( [\alpha]_D^{25} = +45.17^\circ (c = 0.071 \text{ g/100 mL, CHCl}_3, 94\% \text{ ee}); \) IR (Neat): \( \nu_{\text{max}} \) 3477, 1708 (C=O), 1358, 1259, 1062, 979, 755, and 644 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 1.6:1 ratio of isomers) \( \delta \) 7.15-7.10 (4H, m), 6.89 (2H, t, \( J = 7.2 \text{ Hz} \)), 6.82 (1H, d, \( J = 7.6 \text{ Hz} \)), 4.63 (2H, br s), 4.15 (1H, d, \( J = 10.8 \text{ Hz} \)), 4.10 (1H, dd, \( J = 10.8, 3.2 \text{ Hz} \)), 3.95 (1H, t, \( J = 10.4 \text{ Hz} \)), 3.87 (1H, dd, \( J = 10.8, 5.2 \text{ Hz} \)), 3.47-3.40 (2H, m), 3.37-3.32 (2H, m), 2.98 (1H, br s), 2.62 (1H, br s), 2.31 (1H, br s), 2.04 (1H, br s), 1.46 (9H, s, 3 x CH3), 1.44 (9H, s, 3 x CH3), 1.08 (3H, d, \( J = 6.8 \text{ Hz} \), CHCH\(_2\)), 1.07 (3H, d, \( J = 6.8 \text{ Hz} \), CHCH\(_2\)); \(^{13}\)C NMR (CDCl\(_3\), DEPT-135, 1.6:1 ratio of isomers) \( \delta \) 156.1 (C), 155.8 (C), 154.7 (C), 154.0 (C), 129.7 (CH), 129.3 (CH), 128.0 (CH), 127.7 (CH)
(CH), 123.2 (C), 121.9 (C), 120.6 (CH), 120.1 (CH), 116.9 (CH), 116.7 (CH), 79.4 (2 x C), 68.9 (CH2), 68.1 (CH2), 44.7 (2 x CH2), 41.6 (2 x CH), 38.4 (CH), 29.2 (CH), 28.3 (6 x CH3), 16.8 (CH3), 12.9 (CH3); LRMS m/z 278.00 (M + H+), calcd for C16H23NO3 277.1678; Anal. calcd for C16H23NO3 (277.1678): C, 69.29; H, 8.36; N, 5.05. Found: C, 69.15; H, 8.29; N, 5.12%.

**Methyl (2R, 3S, 4R)-(8-methoxy-3-methyl-4-nitromethyl-chroman-2-yl)acetate (cis-14aa):** Prepared by following the procedure I and purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = +51.01^\circ$ (c = 0.385 g/100 mL, CHCl3); IR (Neat): νmax 2953, 1738, 1554 (NO2), 1437, 1379, 1265, 1059, 951, 825, 783 and 700 cm−1; 1H NMR (CDCl3) δ 6.88 (1H, t, J = 8.0 Hz), 6.78 (1H, d, J = 7.2 Hz), 6.73 (1H, d, J = 8.0 Hz), 4.64 (2H, d, J = 7.6 Hz), 4.47 (1H, t, J = 6.8 Hz), 3.83 (3H, s, OCH3), 3.74 (3H, s, OCH3), 3.43 (1H, t, J = 7.6 Hz), 3.02 (1H, dd, J = 15.6, 6.8 Hz), 2.70 (1H, dd, J = 16.0, 6.8 Hz), 2.02 (1H, q, J = 6.8 Hz), 0.99 (3H, d, J = 6.8 Hz); 13C NMR (CDCl3, DEPT-135) δ 170.6 (C), 148.3 (C), 144.0 (C), 121.6 (CH), 121.0 (CH), 118.5 (C), 110.8 (CH), 80.5 (CH2), 70.5 (CH), 56.0 (CH3, OCH3), 51.9 (CH3, OCH3), 41.2 (CH), 37.2 (CH2), 30.2 (CH), 12.2 (CH3); LRMS m/z 308.00 (M - H+), calcd for C15H19NO6 309.12; Anal. calcd for C15H19NO6 (309.12): C, 58.25; H, 6.19; N, 4.53. Found: C, 58.32; H, 6.23; N, 4.46%.

**Methyl (2S, 3S, 4R)-(8-methoxy-3-methyl-4-nitromethyl-chroman-2-yl)acetate (trans-14aa):** Prepared by following the procedure I and purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25} = +28.94^\circ$ (c = 0.471 g/100 mL, CHCl3); IR (Neat): νmax 2953, 2596, 1732, 1554 (NO2), 1483, 1265, 1084, 906, 733 and 692 cm−1; 1H NMR (CDCl3, 2:1 ratio of isomers, major isomer) δ 6.95-6.72 (3H, m), 4.63 (2H, d, J = 6.8 Hz), 4.47 (1H, q, J = 6.4 Hz), 3.81 (3H, s, OCH3), 3.72 (3H, s, OCH3), 3.80-3.72 (1H, m), 2.80-2.71 (2H, m), 2.21-2.18 (1H, m), 1.07 (3H, d, J = 7.2 Hz, CH3CH2); 13C NMR (CDCl3, DEPT-135, 2:1 ratio of isomers, major isomer) δ 170.7 (C), 148.6 (C), 142.3 (C), 120.6 (CH), 119.4 (CH), 116.6 (C), 111.2 (CH), 79.4 (CH2), 74.6 (CH), 56.0 (CH3, OCH3), 51.9 (CH3, OCH3), 38.3 (CH), 36.4 (CH2), 32.4 (CH), 12.1 (CH3); LRMS m/z 308.00 (M - H+), calcd for C15H19NO6 309.12; Anal. calcd for C15H19NO6 (309.12): C, 58.25; H, 6.19; N, 4.53. Found: C, 58.19; H, 6.17; N, 4.58%.

**Datablock: dbr15a (Compound (−)-7aa):**
**Bond precision:**  
C-C = 0.0054 Å  
Wavelength=1.54184 Å

**Cell:**  
a=5.6366(2)  
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**Temperature:** 293 K

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**Correction method:** MULTI-SCAN

**Data completeness:** 1.59/0.95  
**Theta (max):** 61.220

**R(reflections):** 0.0920 (1669)  
**wR2(reflections):** 0.2354 (1782)
Datablock dbr15a (Compound (−)-7aa) - ellipsoid plot