Supporting Information-I

Observation of Neighboring ortho-Hydroxyl Group Participation in Organocatalytic Asymmetric Sequential Michael-Lactonization Reactions: Synthesis of Highly Substituted Chiral Spirodihydrocoumarins

Dhevalapally B. Ramachary,* R. Madhavachary and M. Shiva Prasad

School of Chemistry, University of Hyderabad, Central University (P.O.), Hyderabad 500 046, India
ramsc@uohyd.ernet.in

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. \( \text{H}_2\text{SO}_4 \) (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

The enantiomeric excess (ee) of the sequential M-L 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.

**Preparation of \( \beta \)-keto esters:** \( \beta \)-keto ester \( 1a \) is commercially available and \( 1b, 1c \) and \( 1d \) were prepared according to literature procedures.\(^1\)\(^3\)


**General Experimental Procedures for the Sequential M-L Reactions:**

**Procedure A:** *General procedure for amine-catalyzed racemic Michael reaction of keto-esters 1 with 2-(2-nitrovinyl)phenols 2:* In an ordinary glass vial equipped with a magnetic stirring bar, to the 1:1 mixture of \( 3a/3d \) (each 5 mol\%) in DCM (1.0 mL), were added \( 1a \) (0.4 mmol, 1.33 equiv.) and 2-(2-nitrovinyl)phenols \( 2a-i \) (0.3 mmol). After stirring the reaction mixture at 25 °C as shown in Table S1, the crude reaction mixture was concentrated and pure racemic products \( 4/5 \) were obtained by quick filtration (silica gel, mixture of hexane/ethyl acetate).

**Procedure B:** *General procedure for quinine-NH-thiourea-catalyzed asymmetric Michael reaction of keto-esters 1 with 2-(2-nitrovinyl)phenols 2:* In an ordinary glass vial equipped with a magnetic stirring bar, to the \( 3f \) or \( 3h \) (10 mol\%) in DCM (1.0 mL), were added \( 1a-d \) (0.4 mmol, 1.33 equiv.) and 2-(2-nitrovinyl)phenols \( 2a-i \) (0.3 mmol). After stirring the reaction mixture at 25 °C as shown in Tables 1-2, the crude reaction mixture was concentrated and pure chiral products \( 4/5 \) were obtained by quick filtration (silica gel, mixture of hexane/ethyl acetate).

**Procedure C:** *General procedure for amine-/p-TSA-catalyzed racemic sequential Michael-lactonization reaction of keto-esters 1 with 2-(2-nitrovinyl)phenols 2:* In an ordinary glass vial equipped with a magnetic stirring bar, to the 1:1 mixture of \( 3a/3d \) (each 5 mol\%) in DCM (1.0 mL), were added \( 1a-c \) (0.4 mmol, 1.33 equiv.)

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mmol, 1.33 equiv.) and 2-(2-nitrovinyl)phenols 2a-i (0.3 mmol). After stirring the reaction mixture at 25 °C as shown in Tables S1, the crude reaction mixture was quickly filtered through silica gel, concentrated and taken into a oven dried round bottom flask equipped with a magnetic stirring bar, to this add dry DCE (4.0 mL) and p-TSA (0.03 mmol, 10 mol%). After stirring the reaction mixture at 80 °C for 3-4 h, the crude reaction mixture was worked up with aqueous NaHCO₃ solution and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure racemic products 6 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure D:** General procedure for quinine-NH-thiourea-/p-TSA-catalyzed asymmetric sequential Michael-lactonization reaction of keto-esters 1 with 2-(2-nitrovinyl)phenols 2: In an ordinary glass vial equipped with a magnetic stirring bar, to the 3f or 3h (10 mol%) in DCM (1.0 mL), were added 1a-c (0.4 mmol, 1.33 equiv.) and of 2-(2-nitrovinyl)phenols 2a-i (0.3 mmol). After stirring the reaction mixture at 25 °C as shown in Tables S1-2, the crude reaction mixture was filtered through silica gel, concentrated and taken into a oven dried round bottom flask equipped with a magnetic stirring bar, to this add dry DCE (4.0 mL) and p-TSA (0.03 mmol, 10 mol%). After stirring the reaction mixture at 80 °C for 4 h, the crude reaction mixture was worked up with aqueous NaHCO₃ solution and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure chiral products 6 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure E:** General procedure for quinine-NH-thiourea-/PCC-mediated asymmetric sequential Michael-oxidation reaction of keto-ester 1d with 2-(2-nitrovinyl)phenols 2: In an ordinary glass vial equipped with a magnetic stirring bar, to the 3f or 3h (10 mol%) in DCM (1.0 mL), were added 1d (0.4 mmol, 1.33 equiv.) and 2-(2-nitrovinyl)phenols 2a or 2d (0.3 mmol). After stirring the reaction mixture at 25 °C as shown in Table 2, the crude reaction mixture was filtered through silica gel, concentrated and taken into a oven dried round bottom flask equipped with a magnetic stirring bar, to this added dry DCE (3.0 mL), silica gel (3 equiv.) and PCC (0.9 mmol, 3 equiv.). After stirring the reaction mixture at room temperature for 24 h, the crude reaction mixture was passed through a pad of celite and concentrated to dryness. Pure chiral products 6da or 6dd were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure F:** Lewis acid-induced hydrolysis of cascade Michael products 4/5: In an oven dried round bottomed flask, to the compound 4aa/5aa (90 mg, 0.3 mmol), added dry DCM (0.1 M) under N₂ through syringe and BF₃·Et₂O (1.1 equiv.) at 0 °C. This reaction mixture was stirred for 1.5 h at same temperature, brought the reaction to room temperature and worked up with H₂O and the aqueous layer was extracted
with DCM (3 x 10 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure product 7aa was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure G: Protection of Michael products 4/5:** In a dry oven dried round bottom flask, to the compound 4aa/5aa (0.3 mmol) in dry DCM (3.0 mL) were added successively dry triethylamine (70 µL, 0.6 mmol) and acetyl chloride (0.6 mmol) at 0 °C. The resulting mixture was stirred at 25 °C for 12 h and then worked up with aqueous NH₄Cl and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure acetyl protected product 8aa was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Procedure H: Hydrogenation of protected Michael products 8:** The product 8aa was taken in an oven dried round bottom flask which contains activated 10% Pd/C (7 mg, 10 mol-%), and dry EtOAc (3.0 mL) were added and stirred under H₂ atmosphere at 25 °C for 24 h. The reaction mixture was passed through a pad of celite and concentrated to dryness. Pure product (+)-9aa was obtained by quick column chromatography (silica gel, mixture of hexane/ethyl acetate).

*Figure S1.* X-Ray crystal structure of chiral (1'S,4'R)-4-(nitromethyl)spiro[chroman-3,1'-cyclopentane]-2,2'-dione (6aa).
Table S1: Synthesis of racemic spirodihydrocoumarin products 6<sup>o-g</sup>

<table>
<thead>
<tr>
<th>Product</th>
<th>Reaction Conditions</th>
<th>Separation</th>
<th>Yield (%)</th>
<th>de (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-syn-6aa</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>75%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6ah</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>65%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6ac</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>70%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6ad</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>75%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6aa</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>65%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6af</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>70%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6ag</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>70%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6ah</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>75%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-4ai</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>90%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6bi</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>98%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6ca</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>50%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>rac-syn-6a (65%)</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>&gt;99%</td>
<td></td>
</tr>
<tr>
<td>rac-syn-6a (50%)</td>
<td>1a + 2 (1:1) (10 mol%) in DCM (0.3 M)</td>
<td>p-TSA (10 mol%) in DCE (0.075 M) at 80 °C</td>
<td>&gt;99%</td>
<td></td>
</tr>
</tbody>
</table>

* Reactions were carried out in DCM (0.3 M) with 1.3 equiv. of 1a relative to the 2a-4 (0.3 mmol) in the presence of 10.5 mol% of catalyst 3a + 3d [1:1]. After one quick filtration, resulting products 4f-5b were treated with 10 mol% of p-TSA in DCE (0.075 M) for 24 h at 80 °C. Yield refers to the column purified product. ^ Ratio or de is based on HPLC analysis.  
  ^ 2-oxocyclohexanecarboxaldehyde 1d used as substrate and PCC mediated oxidation utilized for the cyclization reaction.
(S)-ethyl 1-[(R)-1-(2-hydroxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate \([(+)-4aa]\) and (3α,9R,9aS)-ethyl 3α-hydroxy-9-(nitromethyl)-1,2,3,3α,9,9a-hexahydrocyclopenta[b]chromene-9a-carboxylate \([(+)-5aa]\): Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid. \([α]_D^{25} = +20.3° \ (c = 0.42 \ g/100 \ mL, \ CHCl_3, >99.9\% \ ee)\). IR (Neat): \(ν_{max} 3449 \ (O-H), 2980, 2257, 1730 \ (C=O), 1726 \ (C=O), 1555 \ (NO_2), 1379 \ (NO_2), 1231, 1015, 860, 733 \ and \ 648 \ cm^{-1}; \) 1H NMR (CDCl3, 1:1 ratio of 4aa and 5aa) \(δ 7.24-7.20 \ (2H, m), 7.15-7.09 \ (2H, m), 7.00 \ (1H, t, \ J = 7.6 \ Hz), 6.93 \ (1H, d, \ J = 8.0 \ Hz), 6.88 \ (1H, t, \ J = 7.6 \ Hz), 6.81 \ (1H, d, \ J = 8.0 \ Hz), 6.61 \ (1H, br s, OH, phenolic-OH), 5.22 \ (1H, dd, \ J = 13.6, 4.0 \ Hz), 5.11 \ (1H, dd, \ J = 13.6, 10.0 \ Hz), 4.76 \ (1H, dd, \ J = 13.6, 6.4 \ Hz), 4.57 \ (1H, dd, \ J = 12.8, 5.6 \ Hz), 4.56 \ (1H, br s, tert-OH), 4.46-4.40 \ (2H, m), 4.31-4.17 \ (4H, m, 2 x OCH_2CH_3), 2.44-2.38 \ (2H, m), 2.29-2.22 \ (2H, m), 2.12-1.88 \ (6H, m), 1.82-1.71 \ (1H, m), 1.59-1.51 \ (1H, m), 1.33 \ (3H, t, \ J = 7.2 \ Hz, OCH_2CH_3), 1.27 \ (3H, t, \ J = 7.2 \ Hz, OCH_2CH_3); \) 13C NMR (CDCl3, DEPT-135, 1:1 ratio of 4aa and 5aa) \(δ 214.4 \ (C, C=O), 174.0 \ (C, O-C=O), 169.6 \ (C, O-C=O), 154.0 \ (C), 150.7 \ (C), 130.1 \ (CH), 129.4 \ (CH), 129.0 \ (CH), 126.3 \ (CH), 122.6 \ (C), 122.5 \ (CH), 121.1 \ (CH), 120.1 \ (C), 118.4 \ (CH), 117.3 \ (CH), 106.3 \ (C, O-C-OH), 77.4 \ (CH_2), 76.2 \ (CH_2), 63.1 \ (C), 62.6 \ (CH_2), 62.4 \ (CH_3), 56.4 \ (C), 39.8 \ (CH), 37.8 \ (CH_2), 36.7 \ (CH_2), 36.4 \ (CH), 31.7 \ (CH_2), 27.6 \ (CH_2), 19.3 \ (CH_2), 19.1 \ (CH_2), 13.9 \ (CH_3), 13.8 \ (CH_3); \) LRMS m/z 322.15 (M + H+), calcd for C_{16}H_{19}NO_6 321.1212; Anal. calcd for C_{16}H_{19}NO_6 (321.1212): C, 59.81; H, 5.96; N, 4.36. Found: C, 59.75; H, 5.89; N, 4.41%.

(R)-ethyl 1-[(S)-1-(2-hydroxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate \([−)-4aa]\) and (3αR,9S,9aR)-ethyl 3α-hydroxy-9-(nitromethyl)-1,2,3,3α,9,9a-hexahydrocyclopenta[b]chromene-9a-carboxylate \([−)-5aa]\): Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid; \([α]_D^{25} = −19.2° \ (c = 0.42 \ g/100 \ mL, \ CHCl_3, 98\% \ ee); \) IR (Neat): \(ν_{max} 3435 \ (O-H), 2966, 1720 \ (C=O), 1718 \ (C=O), 1552 \ (NO_2), 1455, 1375 \ (NO_2), 1226, 1051, 1014 \ and 755 \ cm^{-1}. \)
and 820 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 1:1 ratio of 4ab and 5ab) $\delta$ 7.05-6.98 (1H, m), 6.96-6.88 (2H, m), 6.87-6.82 (2H, m), 6.80-6.76 (1H, m), 6.46 (1H, br s, Ph-OH), 5.20 (1H, dd, $J = 13.8, 3.9$ Hz), 5.06 (1H, dd, $J = 13.7, 10.3$ Hz), 4.71 (1H, dd, $J = 14.0, 6.7$ Hz), 4.58 (1H, dd, $J = 14.0, 5.2$ Hz), 4.50 (1H, br s, tert-OH), 4.41 (2H, br t, $J = 6.2$ Hz), 4.29 (2H, q, $J = 6.8$ Hz, OCH$_2$CH$_3$), 4.22 (2H, q, $J = 6.8$ Hz, OCH$_2$CH$_3$), 4.50 (1H, br s, tert-OH), 4.41 (2H, br t, $J = 6.2$ Hz), 4.29 (2H, q, $J = 6.8$ Hz, OCH$_2$CH$_3$), 4.22 (2H, q, $J = 6.8$ Hz, OCH$_2$CH$_3$), 2.51-2.36 (2H, m), 2.33-2.23 (2H, m), 2.16-2.08 (1H, m), 2.06-1.98 (2H, m), 1.97-1.84 (2H, m), 1.82-1.71 (1H, m), 1.56-1.48 (1H, m), 1.33 (3H, t, $J = 7.1$ Hz, OCH$_2$C$_3$H$_7$), 1.28 (3H, t, $J = 7.1$ Hz, OCH$_2$C$_3$H$_7$), 0.91-0.83 (1H, m); $^{13}$C NMR (CDCl$_3$, DEPT-135, 1:1 ratio of 4ab and 5ab) $\delta$ 214.3 (C, C=O), 173.8 (C, O-C=O), 169.5 (C, O-C=O), 157.9 (C, d, $J = 239.7$ Hz, C-F), 156.9 (C, d, $J = 238.0$ Hz, C-F), 150.4 (C, d, $J = 2.2$ Hz), 146.7 (C, d, $J = 2.2$ Hz), 124.3 (C, d, $J = 7.1$ Hz), 119.6 (CH, d, $J = 8.2$ Hz), 118.4 (CH, d, $J = 8.1$ Hz), 116.0 (CH, d, $J = 18.1$ Hz), 115.8 (CH, d, $J = 18.2$ Hz), 113.0 (CH), 112.8 (CH), 106.7 (C, O-C=O), 77.0 (CH$_2$), 76.0 (CH$_2$), 62.9 (C), 62.7 (CH$_2$, OCH$_2$CH$_3$), 62.5 (CH$_2$, OCH$_2$CH$_3$), 56.3 (C), 39.2 (CH$_2$), 37.7 (CH$_2$), 36.7 (CH$_2$), 31.9 (CH$_2$), 27.7 (CH$_2$), 19.3 (CH$_2$), 19.1 (CH$_2$), 13.8 (CH$_3$). HRMS m/z 362.1016 (M + Na), calcd for C$_{16}$H$_{18}$FNO$_6$Na 362.1016; Anal. calcd for C$_{16}$H$_{18}$FNO$_6$ (339.1118): C, 56.63; H, 5.35; N, 4.13. Found: C, 56.71; H, 5.31; N, 4.19%.

(5S)-ethyl 1-[(R)-1-(5-chloro-2-hydroxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4ac) and (3aS,9R,9aS)-ethyl 7-chloro-3a-hydroxy-9-(nitromethyl)-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-9a-carboxylate (5ac):

Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid; $[\alpha]_D^{25} = -5.90^\circ$ (c = 1.00 g/100 mL, CHCl$_3$); IR (Neat): $\nu_{\text{max}}$ 3428 (O-H), 2982, 1742 (C=O), 1724 (C=O), 1554 (NO$_2$), 1379 (NO$_2$), 1231, 1169, 1018 and 820 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 1:1 ratio of 4ac and 5ac) $\delta$ 7.24 (1H, d, $J = 2.0$ Hz), 7.19 (1H, d, $J = 8.4$, 1.6 Hz), 7.11-7.08 (2H, m), 6.87 (1H, d, $J = 8.8$ Hz), 6.76 (1H, d, $J = 8.8$ Hz), 6.80-6.70 (1H, br s, Ph-OH), 5.22 (1H, dd, $J = 13.6, 4.0$ Hz), 5.06 (1H, dd, $J = 13.6, 10.4$ Hz), 4.72 (1H, dd, $J = 14.0, 6.4$ Hz), 4.58 (1H, dd, $J = 14.0, 5.6$ Hz), 4.53 (1H, br s, tert-OH), 4.40 (1H, t, $J = 6.0$ Hz), 4.38-4.30 (1H, m), 4.30-4.18 (4H, m, 2 x OCH$_2$CH$_3$), 2.50-2.38 (2H, m), 2.35-2.23 (2H, m), 2.19-2.10 (1H, m), 2.06-1.98 (3H, m), 1.95-1.85 (2H, m), 1.82-1.71 (1H, m), 1.55-1.47 (1H, m), 1.33 (3H, t, $J = 7.2$ Hz, OCH$_2$CH$_3$), 1.28 (3H, t, $J = 7.2$ Hz, OCH$_2$CH$_3$); $^{13}$C NMR (CDCl$_3$, DEPT-135, 1:1 ratio of 4ac and 5ac) $\delta$ 214.2 (C, C=O), 173.7 (C, O-C=O), 169.5 (C, O-C=O), 153.1 (C), 149.3 (C), 129.7 (CH), 129.4 (CH), 129.1 (CH), 127.3 (C), 126.3 (CH), 125.8 (C), 124.6 (C), 121.7 (C), 119.7 (CH), 118.5 (CH), 106.5 (C, O-C=O), 77.0 (CH$_2$), 75.9 (CH$_2$), 62.8 (C), 62.7 (CH$_2$), 62.5 (CH$_2$), 56.0 (C), 37.6 (CH$_2$), 36.5 (CH$_2$), 36.3 (2 x CH), 31.9 (CH$_2$), 27.5 (CH$_2$), 19.2 (CH$_2$), 18.9 (CH$_2$), 13.9 (CH$_3$), 13.8 (CH$_3$); HRMS m/z 3428 (O-H).
(S)-ethyl 1-[(R)-1-(5-bromo-2-hydroxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4ad) and (3aS,9R,9aS)-ethyl 7-bromo-3a-hydroxy-9-(nitromethyl)-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-9a-carboxylate (5ad):
Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid; \([\alpha]_D^{25} = -1.82^\circ \) (c = 0.71 g/100 mL, CHCl₃); IR (Neat): \(\nu_{\text{max}}\) 3447 (O-H), 2959, 1742 (C=O), 1721 (C=O), 1614, 1557 (NO₂), 1379 (NO₂), 1233, 1122, 1092, 937, 858 and 733 cm⁻¹; \(^1\)H NMR (CDCl₃, 1:1 ratio of 4ad and 5ad) \(\delta\) 7.37-7.31 (2H, m), 7.26-7.23 (2H, m), 6.82 (1H, d, \(J = 8.4 \) Hz), 6.73 (1H, d, \(J = 8.8 \) Hz), 5.21 (1H, dd, \(J = 14.0, 4.0 \) Hz), 5.05 (1H, dd, \(J = 14.0, 10.4 \) Hz), 4.73 (1H, dd, \(J = 14.0, 6.4 \) Hz), 4.58 (1H, dd, \(J = 14.4, 5.6 \) Hz), 4.41 (1H, br t, \(J = 5.6 \) Hz), 4.40-4.30 (1H, m), 4.27 (2H, q, \(J = 7.2 \) Hz), 4.22 (2H, q, \(J = 7.2 \) Hz, OCH₂CH₃), 2.48-2.39 (2H, m), 2.35-2.25 (2H, m), 2.20-2.11 (1H, m), 1.94-1.89 (2H, m), 1.80-1.77 (1H, m), 1.56-1.49 (1H, m), 1.34 (3H, t, \(J = 7.2 \) Hz, OCH₂CH₃), 1.29 (3H, t, \(J = 7.2 \) Hz, OCH₂CH₃); \(^1\)C NMR (CDCl₃, DEPT-135, 1:1 ratio of 4ad and 5ad) \(\delta\) 214.2 (C, C=O), 173.7 (C, O-C=O), 169.5 (C, O-C=O), 153.6 (C), 149.9 (C), 132.6 (CH), 132.3 (CH), 132.0 (CH), 129.2 (CH), 125.1 (C), 122.2 (C), 120.2 (CH), 119.1 (CH), 114.6 (C), 113.1 (C), 106.4 (C, O-C=O), 77.0 (CH₂), 75.9 (CH₂), 62.9 (CH₂), 62.8 (CH₂), 62.6 (C), 55.9 (C), 37.6 (CH₂), 36.5 (CH₂), 36.2 (2 x CH), 31.9 (CH₂), 27.5 (CH₂), 19.2 (CH₂), 18.9 (CH₂), 13.9 (CH₃), 13.8 (CH₃); HRMS m/z 422.0215 (M + Na), calcd for C₁₆H₁₈BrNO₆Na 422.0215; Anal. calcd for C₁₆H₁₈BrNO₆ (399.0317): C, 48.02; H, 4.53; N, 3.50. Found: C, 48.12; H, 4.49; N, 3.56%. 

(S)-ethyl 1-[(R)-1-(2-hydroxy-5-methylphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4ae) and (3aS,9R,9aS)-ethyl 3a-hydroxy-7-methyl-9-(nitromethyl)-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-9a-carboxylate (5ae):
Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid; \([\alpha]_D^{25} = -1.82^\circ \) (c = 0.71 g/100 mL, CHCl₃); IR (Neat): \(\nu_{\text{max}}\) 3434 (O-H), 2924, 1742 (C=O), 1724 (C=O), 1555 (NO₂), 1377 (NO₂), 1232, 1119, 1018 and 818 cm⁻¹; \(^1\)H NMR (CDCl₃, 1:1 ratio of 4ae and 5ae) \(\delta\) 7.03 (1H, br d, \(J = 8.0 \) Hz), 6.98 (1H, br s), 6.94 (1H, br d, \(J = 8.0 \) Hz), 6.90 (1H, br s), 6.84 (1H, d, \(J = 8.4 \) Hz), 6.72 (1H, d, \(J = 8.0 \) Hz), 6.25 (1H, br s, Ph-OH), 5.19 (1H, dd, \(J = 13.6, 4.4 \) Hz), 5.09 (1H, dd, \(J = 13.2, 10.0 \) Hz), 4.77 (1H, dd, \(J = 14.0, 6.8 \) Hz), 4.56 (1H, dd, \(J = 14.0, 5.6 \) Hz), 4.47 (1H, br s, tert-OH), 4.40 (2H, t,
J = 6.0 Hz), 4.34-4.25 (2H, m, OCH₂CH₃), 4.21 (2H, q, J = 6.8 Hz, OCH₂CH₃), 2.47-2.39 (2H, m), 2.33-2.22 (1H, m), 2.29 (3H, s, ArCH₃), 2.24 (3H, s, ArCH₃), 2.13-2.09 (2H, m), 2.01-1.94 (3H, m), 1.93-1.76 (3H, m), 1.59-1.52 (1H, m), 1.34 (3H, t, J = 7.2 Hz, OCH₂CH₃), 1.28 (3H, t, J = 7.2 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135, 1:1 ratio of 4af and 5af) δ 214.3 (C, C=O), 174.0 (C, O-C=O), 169.5 (C, O-C=O), 152.0 (C), 148.4 (C), 131.9 (C), 130.3 (C), 130.0 (CH), 129.6 (CH), 126.6 (2 x CH), 122.3 (C), 119.7 (C), 118.2 (CH), 117.3 (CH), 106.2 (C, O-C=O), 77.3 (CH₂), 76.1 (CH₂), 63.1 (C), 62.5 (CH₂), 62.3 (CH₂), 56.4 (C), 37.7 (CH₂), 36.7 (CH₂), 36.5 (2 x CH), 31.5 (CH₂), 27.6 (CH₂), 20.7 (CH₃, ArCH₃), 20.6 (CH₃, ArCH₃), 19.2 (CH₂), 19.0 (CH₂), 13.9 (CH₃, OCH₂CH₃), 13.8 (CH₃, OCH₂CH₃); HRMS m/z 358.1267 (M + Na), calcd for C₁₇H₂₁NO₆Na 358.1267; Anal. calcd for C₁₇H₂₁NO₆ (335.1369): C, 60.89; H, 6.31; N, 4.18. Found: C, 60.75; H, 6.38; N, 4.12%.

(S)-ethyl 1-[(R)-1-(2-hydroxy-5-methoxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4af) and (3aS,9R,9aS)-ethyl 3a-hydroxy-7-methoxy-9-(nitromethyl)-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-9a-carboxylate (5af):

Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid; [α]D²⁵ = -15.47° (c = 0.28 g/100 mL, CHCl₃); IR (Neat): ν max 3434 (O-H), 2961, 2484, 1742 (C=O), 1723 (C=O), 1557 (NO₂), 1377 (NO₂), 1231, 1180, 1020 and 818 cm⁻¹; ¹H NMR (CDCl₃, 1:1 ratio of 4af and 5af) δ 6.90 (1H, d, J = 8.8 Hz), 6.84-6.78 (3H, m), 6.73 (1H, dd, J = 8.8, 2.8 Hz), 6.66 (1H, d, J = 2.4 Hz), 5.75 (1H, br s, Ph-OH), 5.13 (1H, dd, J = 13.6, 4.4 Hz), 5.05 (1H, dd, J = 13.6, 10.0 Hz), 4.75 (1H, dd, J = 14.0, 6.8 Hz), 4.57 (1H, dd, J = 13.6, 5.6 Hz), 4.49-4.44 (1H, m, tert-OH), 4.39 (1H, t, J = 6.4 Hz), 4.35-4.32 (1H, m), 4.31-4.26 (2H, m, OCH₂CH₃), 4.25-4.19 (2H, m, OCH₂CH₃), 3.77 (3H, s, OCH₃), 3.75 (3H, s, OCH₃); HRMS m/z 374.1216 (M + Na), calcd for C₁₇H₂₁NO₇Na 374.1216; Anal. calcd for C₁₇H₂₁NO₇ (351.1318): C, 58.11; H, 6.02; N, 3.91%.
(S)-ethyl 1-[(R)-1-(2-hydroxy-4-methoxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4ag) and (3aS,9R,9aS)-ethyl 3a-hydroxy-6-methoxy-9-(nitromethyl)-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-9a-carboxylate (5ag):
Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid; 
\[\alpha]_D^{25} = -4.21^\circ \ (c = 0.43 \text{ g/100 mL}, \text{CHCl}_3); \] IR (Neat): \( \nu_{\text{max}} \)
O-H 3428, 2965, 2224, 1739 (C=O), 1723 (C=O), 1618, 1555 (NO2), 1379 (NO2), 1231, 1167, 1033, 839 and 733 cm\(^{-1}\); 1H NMR (CDCl3, 1:1 ratio of 4ag and 5ag) δ 7.11 (1H, d, \( J = 8.8 \) Hz), 7.00 (1H, dd, \( J = 8.4, 0.8 \) Hz), 6.59 (1H, dd, \( J = 8.8, 2.8 \) Hz), 6.50 (1H, d, \( J = 2.8 \) Hz), 6.46 (1H, dd, \( J = 8.8, 2.4 \) Hz), 6.40 (1H, d, \( J = 13.6, 4.8 \) Hz), 5.10 (1H, dd, \( J = 13.6, 4.8 \) Hz), 5.04 (1H, dd, \( J = 13.2, 10.0 \) Hz), 4.72 (1H, dd, \( J = 14.0, 6.4 \) Hz), 4.55 (1H, dd, \( J = 14.0, 5.6 \) Hz), 3.78 (3H, s, OC\(_2\)H\(_3\)), 3.74 (3H, s, OC\(_2\)H\(_3\)), 2.47-2.39 (2H, m), 2.31-2.25 (1H, m), 2.21-2.11 (2H, m), 1.92-1.73 (3H, m), 1.62-1.54 (1H, m), 1.34 (3H, t, \( J = 7.2 \) Hz, OCH\(_2\)CH\(_3\)), 1.28 (3H, t, \( J = 7.2 \) Hz, OCH\(_2\)CH\(_3\)); 13C NMR (CDCl3, DEPT-135, 1:1 ratio of 4ag and 5ag) δ 214.7 (C, C=O), 174.2 (C, O-C=O), 169.7 (C, O-C=O), 160.4 (C), 160.1 (C), 151.6 (C), 133.8 (CH), 127.1 (CH), 114.5 (C), 111.5 (C), 109.4 (CH), 107.1 (CH), 106.1 (C, O-C=O), 103.2 (CH), 103.1 (CH), 77.5 (CH2), 76.2 (CH2), 63.4 (C), 62.6 (CH2), 62.4 (CH2), 55.9 (C), 55.3 (CH3, OCH3), 55.2 (CH3, OCH3), 37.7 (CH2), 36.6 (CH2), 36.0 (2 x CH), 31.4 (CH2), 27.2 (CH2), 19.3 (CH2), 18.7 (CH2), 13.9 (CH3), 13.8 (CH3); HRMS m/z 374.1216 (M + Na), calcld for C\(_{17}\)H\(_{21}\)NO\(_7\)Na 374.1216; Anal. calcld for C\(_{17}\)H\(_{21}\)NO\(_7\) (351.1318): C, 58.11; H, 6.02; N, 3.99. Found: C, 58.23; H, 6.08; N, 4.05%.

(S)-ethyl 1-[(R)-1-(2,3-dihydroxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4ah) and (3aS,9R,9aS)-ethyl 3a,5-dihydroxy-9-(nitromethyl)-1,2,3,3a,9,9a-hexahydrocyclopenta[b]chromene-9a-carboxylate (5ah):
Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid; 
\[\alpha]_D^{25} = -15.47^\circ \ (c = 0.28 \text{ g/100 mL}, \text{CHCl}_3); \] IR (Neat): \( \nu_{\text{max}} \)
O-H 3447, 2982, 2564, 1740 (C=O), 1721 (C=O), 1620, 1595 (NO2), 1579 (NO2), 1231, 1165, 914, 831 and 737 cm\(^{-1}\); 1H NMR (CDCl3, 3:1 ratio of 4ah and 5ah) δ 6.95-6.85 (2H, m), 6.84-6.77 (2H, m), 6.71-6.63 (2H, m), 5.04 (1H, dd, \( J = 14.0, 5.2 \) Hz), 4.99 (1H, dd, \( J = 14.0, 10.0 \) Hz), 4.77 (1H, dd, \( J = 14.0, 6.8 \) Hz), 4.58-4.51 (2H, m), 4.43 (1H, t, \( J = 6.4 \) Hz), 4.37-4.27 (2H, m, OCH\(_2\)CH\(_3\)), 4.22 (2H, q, \( J = 7.6 \) Hz, OCH\(_2\)CH\(_3\)), 2.48-2.44 (3H, m), 2.32-2.27 (1H, m), 2.21-2.05 (3H, m), 2.02-1.91 (3H, m), 1.86-1.69 (1H, m), 1.60-1.51 (1H, m), 1.34 (3H, t, \( J = 7.2 \) Hz, OCH\(_2\)CH\(_3\)), 1.28 (3H, t, \( J = 7.2 \) Hz, OCH\(_2\)CH\(_3\)); 13C NMR
(CDCl₃, DEPT-135, 3:1 ratio of 4ah and 5ah) δ 215.7 (C, C=O), 173.8 (C, O-C=O), 169.5 (C, O-C=O), 146.0 (C), 145.7 (C), 142.1 (C), 137.8 (C), 123.1 (CH), 121.4 (CH), 120.8 (C), 117.1 (CH), 114.9 (2 x CH), 114.5 (CH), 107.3 (C, O-C=O), 77.0 (CH₂), 75.7 (CH₂), 63.8 (C), 62.7 (2 x CH₂), 56.9 (C), 39.2 (CH), 37.7 (CH₂), 36.8 (CH₂), 36.8 (CH), 30.8 (CH₂), 27.8 (CH₂), 19.4 (CH₂), 19.2 (CH₂), 13.8 (CH₃, OCH₂CH₃), 13.8 (CH₃, OCH₂CH₃); HRMS m/z 360.1109 (M + Na), calcd for C₁₆H₁⁹NO₇Na 360.1059; Anal. calcd for C₁₆H₁⁹NO₇ (337.1162): C, 56.97; H, 5.68; N, 4.15. Found: C, 56.85; H, 5.62; N, 4.19%.

(S)-ethyl 1-[(R)-1-(2-hydroxy-3-methoxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4ai):

Prepared following the procedure B 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 Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 0.5 mL/min, λ = 254 nm), tᵣ = 18.89 min (minor), tᵣ = 20.45 min (major). [α]D²⁵ = +4.8° (c = 0.42 g/100 mL, CHCl₃, 98% ee); IR (Neat): νmax 3450 (O-H), 2961, 1740 (C=O), 1725, 1555 (NO₂), 1379 (NO₂), 1283, 1081, and 1022 cm⁻¹; 1H NMR (CDCl₃) δ 6.90-6.88 (1H, m), 6.82-6.76 (2H, m), 5.94 (1H, br s, OH), 5.35 (1H, dd, J = 13.6, 3.6 Hz), 5.22 (1H, dd, J = 13.6, 10.4 Hz), 4.36 (1H, dd, J = 10.8, 4.0 Hz), 4.20 (2H, q, J = 7.2 Hz, OCH₂CH₃), 3.87 (3H, s, OCH₃), 2.40-2.32 (3H, m), 2.08-2.01 (2H, m), 1.95-1.89 (1H, m), 1.28 (3H, t, J = 7.2 Hz, OCH₂CH₃); 13C NMR (CDCl₃, DEPT-135) δ 213.0 (C, C=O), 169.3 (C, O-C=O), 146.4 (C), 144.3 (C), 121.8 (CH), 121.7 (C), 120.0 (CH), 76.2 (CH₂), 62.5 (C), 61.9 (CH₂, OCH₂CH₃), 55.9 (CH₂, OCH₂CH₃), 39.7 (CH), 37.9 (CH₂), 32.2 (CH₂), 19.2 (CH₂), 14.0 (CH₃, OCH₂CH₃); LRMS m/z 352.10 (M + H⁺), calcd for C₁₇H₂₁NO₇ 351.1318; Anal. calcd for C₁₇H₂₁NO₇ (351.1318): C, 58.11; H, 6.02; N, 3.99. Found: C, 58.23; H, 5.96; N, 4.07%.

(S)-isopropyl 1-[(R)-1-(2-hydroxy-3-methoxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4bi):

Prepared following the procedure B 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 Chiralcel OD-H column (hexane/2-propanol = 90:10, flow rate 0.5 mL/min, λ = 254 nm), tᵣ = 23.07 min (minor), tᵣ = 26.96 min (major). [α]D²⁵ = +5.6° (c = 0.143 g/100 mL, CHCl₃, 99% ee); IR (Neat): νmax 3468 (O-H), 2926, 1742 (C=O), 1723, 1615, 1555 (NO₂), 1377 (NO₂), 1254, 1101, and 1026 cm⁻¹; 1H NMR (CDCl₃) δ 6.92-6.88 (1H, m), 6.79-6.76 (2H, m), 5.99 (1H, br s, OH), 5.34 (1H, dd, J = 13.6, 3.6 Hz), 5.20 (1H, dd, J = 13.6, 10.8 Hz), 5.07-5.01 (1H, m, OCH(CH₃)₂), 4.36 (1H, dd, J = 10.8, 4.0 Hz), 3.84 (3H, s, OCH₃), 2.38-2.28 (3H, m), 2.07-1.97 (2H, m), 1.92-1.87 (1H, m), 1.25 (3H, d, J = 6.0 Hz, OCH(CH₃)₂), 1.22 (3H, d, J = 6.4 Hz, OCH(CH₃)₂); 1³C NMR (CDCl₃, DEPT-135) δ 213.1 (C, C=O), 212.2 (C, C=O), 19.4 (CH₂), 19.2 (CH₂), 14.0 (CH₃, OCH₂CH₃).
168.9 (C, O-C=O), 146.4 (C), 144.3 (C), 122.0 (C), 121.8 (CH), 120.0 (CH), 110.0 (CH), 76.3 (CH2),
69.8 (CH, OCH(CH3)2), 62.5 (C), 56.0 (CH3, OCH3), 39.6 (CH), 37.8 (CH2), 32.3 (CH2), 21.6 (CH3), 21.5
(CH3), 19.2 (CH2); LRMS m/z 366.15 (M + H+), calcd for C18H23NO7 365.1475; Anal. calcd for
C18H23NO7 (365.1475): C, 59.17; H, 6.34; N, 3.83. Found: C, 59.25; H, 6.41; N, 3.76%.

(S)-ethyl 1-[(R)-2-nitro-1-phenylethyl]-2-oxocyclopentanecarboxylate (4aj): Prepared by procedure B
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
Chiralcel OD-H column (hexane/2-propanol = 90:10, flow rate 0.7 mL/min, λ = 254 nm), tR = 15.05 min (major), tR = 22.10 min (minor). [α]D 25 = +31.2° (c = 1.42
g/100 mL, CHCl3, 79% ee and 89% de); IR (Neat): νmax 2979, 1748 (C=O), 1721, 1552
(NO2), 1378 (NO2), 1225, 1147, and 752 cm⁻¹; 1H NMR (CDCl3, 89% de, major isomer)
δ 7.32-7.28 (3H, m), 7.27-7.24 (2H, m), 5.17 (1H, dd, J = 14.0, 4.0 Hz), 5.01 (1H, dd, J = 13.5, 11.0 Hz),
4.21 (2H, q, J = 8.0, 2.0 Hz, OCH2CH3), 4.07 (1H, dd, J = 11.5, 4.0 Hz), 2.40-2.31 (2H, m), 2.05-1.88
(3H, m), 1.84-1.77 (1H, m), 1.27 (3H, t, J = 7.0 Hz, OCH2CH3); 13C NMR (CDCl3, DEPT-135, 89% de,
major isomer) δ 212.3 (C, C=O), 169.3 (C, O-C=O), 135.4 (C), 129.3 (2 x CH), 128.8 (2 x CH), 128.2
(CH), 76.5 (CH2), 62.4 (C), 62.2 (CH2, OCH2CH3), 46.2 (CH), 37.9 (CH2), 31.2 (CH2), 19.3 (CH2), 13.9
(CH3, OCH2CH3); LRMS m/z 306.20 (M + H+), calcd for C16H19NO5 305.1263; Anal. calcd for
C16H19NO5 (305.1263): C, 62.85; H, 6.32; N, 4.51%.

Configuration assignment: The absolute stereochemistry of (+)-4aj was assigned as (S, R) by
correlation with other examples and also by comparison of the retention time of HPLC with the literature
data.4

Reference 4: (a) H. Y. Bae, S. Some, J. S. Oh, Y. S. Lee and C. E. Song, Chem. Commun., 2011, 47,

(S)-ethyl 1-[(R)-1-(3-hydroxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (4ak): Prepared by
procedure B 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
Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tR = 7.42 min (major), tR = 9.08 min (minor).
[α]D 25 = +26.1° (c = 1.35 g/100 mL, CHCl3, 78% ee and 73% de); IR (Neat): νmax 3343 (O-H), 2977,
1716 (C=O), 1552 (NO2), 1378 (NO2), 1228, 1147, 1023 908, 785 and 703 cm⁻¹; 1H NMR (CDCl3, 73%
(1'R,4'R)-6-bromo-2-hydroxy-4-(nitromethyl)spiro[chroman-3,1'-cyclohexan]-2'-one (5dd): Prepared by procedure B and purified by column chromatography using EtOAc/hexane and isolated as liquid. [$\alpha$]$_D^{25}$ = $-9.9^\circ$ (c = 0.38 g/100 mL, CHCl$_3$); IR (Neat): $\nu_{max}$ 3427 (O-H), 2952, 1705 (C=O), 1552 (NO$_2$), 1481, 1377 (NO$_2$), 1223, 1018 and 904 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 3:1 ratio of isomers, major isomer) $\delta$ 7.33 (1H, dd, $J$ = 8.8, 2.4 Hz), 7.18 (1H, d, $J$ = 2.0 Hz), 6.79 (1H, s, O-CH$_2$O), 5.62 (1H, d, $J$ = 8.8 Hz), 4.62 (1H, dd, $J$ = 14.4, 2.4 Hz), 4.10-4.08 (1H, m), 3.94 (1H, br s, OH), 2.69-2.51 (2H, m), 2.18-2.09 (1H, m), 1.93-1.83 (2H, m), 1.81-1.73 (3H, m); $^{13}$C NMR (CDCl$_3$, 3:1 ratio of isomers, major isomer) $\delta$ 212.8 (C, C=O), 148.1 (C), 132.6 (CH), 131.7 (CH), 122.7 (C), 119.4 (CH), 114.3 (C), 94.0 (CH, O-CH-O), 79.1 (CH$_2$), 53.0 (C), 40.1 (CH$_2$), 36.8 (CH), 34.8 (CH$_2$), 28.6 (CH$_2$), 20.4 (CH$_2$); LRMS m/z 370.15 (M + H$^+$), calc'd for C$_{15}$H$_{16}$BrNO$_5$ 369.0212; Anal. calc'd for C$_{15}$H$_{16}$BrNO$_5$ (369.0212): C, 48.67; H, 4.36; N, 3.78. Found: C, 48.56; H, 4.41; N, 3.73%.

(1'S,4'R)-4-(nitromethyl)spiro[chroman-3,1'-cyclopentane]-2,2'-dione (6aa): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 142-145 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_k$ = 20.99 min (major), $t_k$ = 26.44 min (minor). [$\alpha$]$_D^{25}$ = $-36.5^\circ$ (c = 0.34 g/100 mL, CHCl$_3$, >99.9% ee); IR (Neat): $\nu_{max}$ 2954, 1762 (C=O), 1726, 1666 (NO$_2$), 1366 (NO$_2$), 1171, 1016, 911, 811 and 754 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.42-7.38 (1H, m), 7.22-7.17 (2H, m), 7.15-7.13 (1H, m), 5.56 (1H, dd, $J$ = 10.8, 4.0 Hz), 4.42 (1H, dd, $J$ = 10.8, 8.0 Hz), 3.78 (1H, dd, $J$ = 8.0, 4.0 Hz), 2.73-2.67 (1H, m), 2.51-2.45 (1H, m), 2.22-2.19 (1H, m), 2.10-1.99 (3H, m); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 212.6 (C, C=O), 166.6 (C, O-C=O), 150.3 (C), 130.4 (CH), 128.8 (CH), 125.6 (CH), 120.6 (C), 117.2 (CH), 75.5 (CH$_2$), 54.9 (C), 41.6 (CH), 39.1 (CH$_2$), 35.7 (CH$_2$), 18.7 (CH$_2$); LRMS m/z 276.15 (M + H$^+$), calc'd for C$_{14}$H$_{13}$NO$_5$ 275.0794; Anal. calc'd for C$_{14}$H$_{13}$NO$_5$ (275.0794): C, 61.09; H, 4.76; N, 5.09. Found: C, 61.13; H, 4.68; N, 5.17%.
(1'R,4S)-4-(nitromethyl)spiro[chroman-3,1'-cyclopentane]-2,2'-dione (6aa): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 143-145 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), \( t_R = 20.52 \text{ min (minor)}, t_R = 25.46 \text{ min (major)} \). \([\alpha]_D^{25} = +28.7^\circ (c = 0.42 \text{ g/100 mL, CHCl}_3, 98\% \text{ ee})\); IR (Neat): \( \nu_{\max} 2962, 1758 (\text{C=O}), 1736, 1546 (\text{NO}_2), 1375 (\text{NO}_2), 1258, 1087, 1011 \text{ and 793 cm}^{-1}.\)

(1'S,4R)-6-fluoro-4-(nitromethyl)spiro[chroman-3,1'-cyclopentane]-2,2'-dione (6ab): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 125-127 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), \( t_R = 23.46 \text{ min (major)}, t_R = 33.42 \text{ min (minor)} \). \([\alpha]_D^{25} = –22.8^\circ (c = 0.63 \text{ g/100 mL, CHCl}_3, 88\% \text{ ee})\); IR (Neat): \( \nu_{\max} 2953, 1762 (\text{C=O}), 1725, 1552 (\text{NO}_2), 1366 (\text{NO}_2), 1191, 1016, 981 \text{ and 754 cm}^{-1}; 1H NMR (CDCl}_3) \delta 7.12-7.10 (2H, m), 6.96 (1H, br dd, \( J = 7.6, 2.0 \text{ Hz} \)), 5.58 (1H, dd, \( J = 13.6, 4.8 \text{ Hz} \)), 4.42 (1H, dd, \( J = 13.6, 10.0 \text{ Hz} \)), 3.77 (1H, dd, \( J = 10.0, 4.8 \text{ Hz} \)), 2.74-2.67 (1H, m), 2.54-2.44 (1H, m), 2.22-2.18 (1H, m), 2.12-1.99 (3H, m); 13C NMR (CDCl}_3, DEPT-135) \delta 212.1 (C, C=O), 166.1 (C, O-C=O), 159.3 (C, d, \( J = 245.6 \text{ Hz} \)), 146.4 (C, d, \( J = 3.1 \text{ Hz} \)), 122.3 (C, d, \( J = 8.0 \text{ Hz} \)), 118.7 (CH, d, \( J = 8.3 \text{ Hz} \)), 117.2 (CH, d, \( J = 23.4 \text{ Hz} \)), 115.7 (CH, d, \( J = 24.5 \text{ Hz} \)), 75.0 (CH}_2), 54.4 (C), 41.5 (CH), 39.0 (CH}_2), 35.6 (CH}_2), 18.6 (CH}_2); LRMS m/z 294.25 (M + H\(^+\)), calcd for C\(_{14}\)H\(_{12}\)FNO\(_5\) 293.0700; Anal. calcd for C\(_{14}\)H\(_{12}\)FNO\(_5\) (293.0700): C, 57.34; H, 4.12; N, 4.78. Found: C, 57.25; H, 4.19; N, 4.71%.

(1'S,4R)-6-chloro-4-(nitromethyl)spiro[chroman-3,1'-cyclopentane]-2,2'-dione (6ac): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 116-118 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), \( t_R = 24.85 \text{ min (major)}, t_R = 34.65 \text{ min (minor)} \). \([\alpha]_D^{25} = –12.1^\circ (c = 0.28 \text{ g/100 mL, CHCl}_3, 87\% \text{ ee})\); IR (Neat): \( \nu_{\max} 2957, 1767 (\text{C=O}), 1742, 1549 (\text{NO}_2), 1375 (\text{NO}_2), 1292, 1134, 826 \text{ and 660 cm}^{-1}; 1H NMR (CDCl}_3) \delta 7.37 (1H, dd, \( J = 8.4, 2.4 \text{ Hz} \)), 7.22 (1H, d, \( J = 2.4 \text{ Hz} \)), 7.09 (1H, d, \( J = 8.8 \text{ Hz} \)), 5.57 (1H, dd, \( J = 14.0, 4.8 \text{ Hz} \)), 4.42 (1H, dd, \( J = 14.0, 10.0 \text{ Hz} \)), 3.76 (1H, dd, \( J = 10.0, 4.8 \text{ Hz} \)), 2.74-2.67 (1H, m), 2.54-2.44 (1H, m), 2.22-2.17 (1H, m), 2.10-1.98 (3H, m); 13C NMR (CDCl}_3, DEPT-135) \delta 212.0 (C, C=O), 158.9 (C, O-C=O), 148.9 (C), 130.8 (C), 130.6 (CH), 128.7 (CH), 122.3 (C), 118.6 (CH), 75.0 (CH}_2), 54.5 (C), 41.4 (CH), 39.0 (CH}_2), 35.7 (CH}_2), 18.7 (CH}_2); LRMS m/z 310.00 (M + H\(^+\)), calcd for C\(_{14}\)H\(_{12}\)ClNO\(_5\) \(_2\)N\(_2\)O\(_5\) \(_2\)}
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309.0404: Anal. calcd for C₁₄H₁₂ClNO₅ (309.0404): C, 54.29; H, 3.91; N, 4.52. Found: C, 54.19; H, 3.96; N, 4.48%.

(1’S,4R)-6-bromo-4-(nitromethyl)spiro[chroman-3,1’-cyclopentane]-2,2’-dione (6ad): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 120-122 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 27.45 min (major), tᵣ = 38.37 min (minor). [α]D²⁵ = +14.0° (c = 0.27 g/100 mL, CHCl₃, >99.9% ee); IR (Neat): ν max 2921, 1759 (C=O), 1734, 1547 (NO₂), 1380 (NO₂), 1342, 1221, 1145, 941, 785 and 761 cm -1; ¹H NMR (CDCl₃) δ 7.52 (1H, dd, J = 8.8, 2.4 Hz), 7.37 (1H, d, J = 2.4 Hz), 7.03 (1H, d, J = 8.4 Hz), 5.54 (1H, dd, J = 14.0, 4.8 Hz), 4.42 (1H, dd, J = 14.0, 9.6 Hz), 3.76 (1H, dd, J = 9.6, 4.8 Hz), 2.75-2.67 (1H, m), 2.54-2.44 (1H, m), 2.22-2.17 (1H, m), 2.11-1.97 (3H, m); ¹³C NMR (CDCl₃, DEPT-135) δ 211.9 (C, C=O), 165.8 (C, O-C=O), 149.4 (C), 133.5 (CH), 131.5 (CH), 122.7 (C), 118.9 (CH), 118.2 (C), 74.9 (CH₂), 54.4 (C), 41.2 (CH), 39.0 (CH₂), 35.7 (CH₂), 18.7 (CH₃); LRMS m/z 353.20 (M + H +), calcd for C₁₄H₁₂BrNO₅ 352.9899; calcd for C₁₄H₁₂BrNO₅ (352.9899): C, 47.48; H, 3.42; N, 3.95. Found: C, 47.56; H, 3.37; N, 3.89%.

(1’R,4S)-6-bromo-4-(nitromethyl)spiro[chroman-3,1’-cyclopentane]-2,2’-dione (6ad): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 118-119 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 28.22 min (minor), tᵣ = 38.36 min (major). [α]D²⁵ = –12.9° (c = 0.28 g/100 mL, CHCl₃, 96% ee); IR (Neat): ν max 2924, 1761 (C=O), 1729, 1551 (NO₂), 1455, 1376 (NO₂), 1336, 1223, 1180, 1031 and 756 cm -1.

(1’S,4R)-6-methyl-4-(nitromethyl)spiro[chroman-3,1’-cyclopentane]-2,2’-dione (6ae): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 130-133 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 22.10 min (minor). [α]D²⁵ = –18.3° (c = 0.28 g/100 mL, CHCl₃, 96% ee); IR (Neat): ν max 2921, 1758 (C=O), 1735, 1550 (NO₂), 1379 (NO₂), 1221, 1145, 897 and 760 cm -1; ¹H NMR (CDCl₃) δ 7.17 (1H, d, J = 8.0 Hz), 7.01 (1H, d, J = 8.0 Hz), 6.98 (1H, br s), 5.54 (1H, dd, J = 13.6, 4.8 Hz), 4.40 (1H, dd, J = 13.2, 10.0 Hz), 3.73 (1H, dd, J = 9.6, 4.8 Hz), 2.72-2.65 (1H, m), 2.52-2.43 (1H, m), 2.33 (3H, s, CH₃), 2.21-2.17 (1H, m), 2.10-1.97 (3H, m); ¹³C NMR (CDCl₃, DEPT-135) δ 212.6 (C, C=O),
166.7 (C, O=C=O), 148.2 (C), 135.5 (C), 130.9 (CH), 129.0 (CH), 120.2 (C), 116.9 (CH), 75.5 (CH_2), 54.9 (C), 41.6 (CH), 39.1 (CH_2), 35.7 (CH_3), 20.7 (CH_3), 18.7 (CH_2); LRMS m/z 290.05 (M + H^+), calcd for C_{15}H_{15}NO_5 289.0950; Anal. calcd for C_{15}H_{15}NO_5 (289.0950): C, 62.28; H, 5.23; N, 4.84. Found: C, 62.35; H, 5.28; N, 4.79%.

(1'R,4S)-6-methyl-4-(nitromethyl)spiro[chroman-3,1'-cyclopentane]-2,2'-dione (6ae): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 126-128 °C; The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 15.72 min (minor), t_R = 19.32 min (major). [α]_D^{25} = +26.0° (c = 0.42 g/100 mL, CHCl_3, 99% ee); IR (Neat): \( \nu_{\text{max}} \) 2962, 1759 (C=O), 1736, 1546 (NO_2), 1375 (NO_2), 1258, 1086, 1011 and 793 cm^{-1}.

(1'S,4R)-6-methoxy-4-(nitromethyl)spiro[chroman-3,1'-cyclopentane]-2,2'-dione (6af): Prepared by procedure D 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 Chiralcel OD-H column (hexane/2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 23.94 min (major), t_R = 32.88 min (minor). [α]_D^{25} = -35.2° (c = 0.30 g/100 mL, CHCl_3, 84% ee); IR (Neat): \( \nu_{\text{max}} \) 2924, 1762 (C=O), 1733, 1546 (NO_2), 1375 (NO_2), 1258, 1086, 1011 and 793 cm^{-1}; 1H NMR (CDCl_3) \( \delta \) 7.06 (1H, d, J = 9.2 Hz), 6.89 (1H, dd, J = 9.2, 3.2 Hz), 6.71 (1H, d, J = 2.8 Hz), 5.55 (1H, dd, J = 13.6, 4.8 Hz), 4.41 (1H, dd, J = 13.6, 10.0 Hz), 3.79 (3H, s, OCH_3), 3.73 (1H, dd, J = 10.0, 4.8 Hz), 2.72-2.65 (1H, m), 2.52-2.45 (1H, m), 2.22-2.18 (1H, m), 2.10-1.98 (3H, m); 13C NMR (CDCl_3, DEPT-135) \( \delta \) 212.6 (C, C=O), 166.7 (C, O=C=O), 156.8 (C), 144.0 (C), 121.5 (C), 118.0 (CH), 115.4 (CH), 113.7 (CH), 75.4 (CH_3), 55.7 (CH_3, OCH_3), 54.8 (C), 41.8 (CH), 39.1 (CH_3), 35.6 (CH_3), 18.7 (CH_2); LRMS m/z 306.15 (M + H^+), calcd for C_{15}H_{15}NO_6 305.0899; Anal. calcd for C_{15}H_{15}NO_6 (305.0899): C, 59.01; H, 4.95; N, 4.59. Found: C, 59.11; H, 5.03; N, 4.52%.

(1'S,4R)-7-methoxy-4-(nitromethyl)spiro[chroman-3,1'-cyclopentane]-2,2'-dione (6ag): Prepared by procedure D 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 = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 13.50 min (major), t_R = 17.75 min (minor). [α]_D^{25} = -41.1° (c = 0.29 g/100 mL, CHCl_3, 90% ee); IR (Neat): \( \nu_{\text{max}} \) 2953, 1764 (C=O), 1737, 1545 (NO_2), 1386 (NO_2), 1222, 1140, 893 and 816 cm^{-1}; 1H NMR (CDCl_3) \( \delta \) 7.08 (1H, d, J = 8.4 Hz), 6.69 (1H, dd, J = 8.4, 2.8 Hz), 6.66 (1H, d, J = 2.8 Hz) 5.46 (1H, dd, J = 13.2, 4.8 Hz), 4.39 (1H, dd, J = 13.6, 10.0 Hz).
Hz), 3.81 (3H, s, OCH₃), 3.71 (1H, dd, J = 10.0, 5.2 Hz), 2.71-2.63 (1H, m), 2.52-2.43 (1H, m), 2.22-2.18 (1H, m), 2.09-1.99 (3H, m); 13C NMR (CDCl₃, DEPT-135) δ 212.6 (C, C=O), 166.5 (C, O-C=O), 161.1 (C), 151.1 (C), 129.3 (CH), 112.2 (C), 111.3 (CH), 102.9 (CH), 75.8 (CH₂), 55.6 (CH₃, OCH₃), 55.2 (C), 41.0 (CH₂), 39.1 (CH₂), 35.7 (CH₂), 18.7 (CH₂); LRMS m/z 306.15 (M + H⁺), calcd for C₁₅H₁₅NO₆ 305.0899; Anal. calcd for C₁₅H₁₅NO₆ (305.0899): C, 59.01; H, 4.95; N, 4.59. Found: C, 59.11; H, 4.92; N, 4.51%.

(1′R,4S)-8-hydroxy-4-(nitromethyl)spiro[chroman-3,1′-cyclopentane]-2,2′-dione (6ah): Prepared by procedure D 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 Chiralcel OD-H column (hexane/2-propanol = 90:10, flow rate 0.5 mL/min, λ = 254 nm), tᵣ = 66.89 min (minor), tᵣ = 76.20 min (major). [α]D²⁵ = +15.4° (c = 0.143 g/100 mL, CHCl₃, 76% ee); IR (Neat): νmax 3419 (O-H), 2961, 1763 (C=O), 1736, 1555 (NO₂), 1480, 1342 (NO₂), 1262, 1033, and 734 cm⁻¹; 1H NMR (CDCl₃) δ 7.08-7.00 (2H, m), 6.73 (1H, dd, J = 7.2, 1.6 Hz), 6.00 (1H, br s, OH), 5.46 (1H, dd, J = 13.6, 5.2 Hz), 4.44 (1H, dd, J = 13.6, 9.2 Hz), 3.80 (1H, dd, J = 9.6, 5.2 Hz), 2.72-2.65 (1H, m), 2.56-2.47 (1H, m), 2.26-2.22 (1H, m), 2.12-2.04 (3H, m); 13C NMR (CDCl₃, DEPT-135) δ 212.3 (C, C=O), 165.8 (C, O-C=O), 143.8 (C), 137.7 (C), 126.1 (CH), 121.0 (C), 119.7 (CH), 117.5 (CH), 75.4 (CH₂), 55.0 (C), 41.6 (CH), 39.1 (CH₂), 35.8 (CH₂), 18.8 (CH₂); LRMS m/z 292.10 (M + H⁺), calcd for C₁₄H₁₃NO₆ 291.0743; Anal. calcd for C₁₄H₁₃NO₆ (291.0743): C, 57.73; H, 4.50; N, 4.81. Found: C, 57.62; H, 4.58; N, 4.76%.

(2′S,4R)-4-(nitromethyl)-3′,4′-dihydro-1′H-spiro[chroman-3,2′-naphthalene]-1′,2-dione (6ca): Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 167-169°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 = 18.96 min (major), tᵣ = 26.08 min (minor). [α]D²⁵ = −193.4° (c = 0.057 g/100 mL, CHCl₃, >99.9% ee); IR (Neat): νmax 2921, 1756 (C=O), 1734, 1550 (NO₂), 1456, 1377 (NO₂), 1221, 1146, and 759 cm⁻¹; 1H NMR (CDCl₃) δ 8.11 (1H, d, J = 8.0 Hz), 7.55 (1H, t, J = 7.2 Hz), 7.43-7.38 (2H, m), 7.26-7.20 (2H, m), 7.22-7.10 (2H, m), 5.56 (1H, dd, J = 13.5, 5.0 Hz), 4.51 (1H, dd, J = 13.5, 10.0 Hz), 4.02 (1H, dd, J = 9.5, 5.0 Hz), 2.98 (2H, t, J = 6.0 Hz), 2.34 (1H, td, J = 14.0, 5.0 Hz), 2.12 (1H, td, J = 14.5, 7.0 Hz); 13C NMR (CDCl₃, DEPT-135) δ 193.3 (C, C=O), 165.8 (C, O-C=O), 150.2 (C), 142.1 (C), 134.5 (CH), 132.2 (C), 130.4 (CH), 129.1 (CH), 128.6 (CH), 128.5 (CH), 127.5 (CH), 125.8 (CH), 120.8 (C), 117.1 (CH), 77.3 (CH₂), 53.7 (C), 41.3 (CH), 30.9 (CH₂), 25.4 (CH₂); LRMS m/z 338.25 (M + H⁺),
calcd for C_{19}H_{15}NO_{5} 337.0950; Anal. calcd for C_{19}H_{15}NO_{5} (337.0950): C, 67.65; H, 4.48; N, 4.15. Found: C, 67.56; H, 4.52; N, 4.21%.

\((2'R,4S)-4-(\text{nitromethyl})-3',4'-\text{dihydro}-1'H-\text{spiro}[\text{chroman-3,2'-naphthalene}]-1',2'-\text{dione}\) (6ca):
Prepared by procedure D and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 172-173 °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), \(t_R = 19.19\) min (minor), \(t_R = 26.06\) min (major). \([\alpha]_D^{25} = +157.3^\circ\) (c = 0.25 g/100 mL, CHCl\(_3\), 97% ee); IR (Neat): \(\nu_{\text{max}} 2924, 1759\) (C=O), 1734, 1547 (\(\text{NO}_2\)), 1493, 1375 (\(\text{NO}_2\)), 1257, 1011, and 815 cm\(^{-1}\).

\((1'S,4R)-4-(\text{nitromethyl})\text{spiro}[\text{chroman-3,1'-cyclohexane}]-2,2'-\text{dione}\) (6da):
Prepared by procedure E and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 142-145 °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, \(\lambda = 254\) nm), \(t_R = 17.04\) min (major), \(t_R = 19.30\) min (minor). \([\alpha]_D^{25} = -43.7^\circ\) (c = 0.128 g/100 mL, CHCl\(_3\), 99% ee); IR (Neat): \(\nu_{\text{max}} 2931, 1759\) (C=O), 1710, 1512 (\(\text{NO}_2\)), 1370 (\(\text{NO}_2\)), 1244, 1036, 811 and 767 cm\(^{-1}\); \(1H\) NMR (CDCl\(_3\)) \(\delta 7.37\) (1H, t, \(J = 7.6\) Hz), 7.22 (1H, d, \(J = 7.2\) Hz), 7.15 (1H, t, \(J = 7.6\) Hz), 7.10 (1H, d, \(J = 8.0\) Hz), 5.41 (1H, dd, \(J = 12.8, 4.0\) Hz), 4.21 (1H, dd, \(J = 12.4, 10.4\) Hz), 3.90 (1H, dd, \(J = 10.4, 4.0\) Hz), 3.39-3.31 (1H, m), 2.62-2.58 (1H, m), 2.17-2.14 (2H, m), 1.75-1.67 (3H, m), 1.50 (1H, td, \(J = 12.0, 3.6\) Hz); \(13C\) NMR (CDCl\(_3\), DEPT-135) \(\delta 206.9\) (C, O-C=O), 166.1 (C, O-C=O), 150.0 (CH), 129.2 (CH), 125.6 (CH), 121.4 (C), 116.5 (CH), 76.7 (CH\(_2\)), 56.3 (C), 41.8 (CH\(_2\)), 41.77 (CH\(_2\)), 36.3 (CH\(_2\)), 27.7 (CH\(_2\)), 21.9 (CH\(_2\)); LRMS m/z 290.05 (M + H\(^+\)), calcd for C\(_{15}\)H\(_{15}\)NO\(_5\) 289.0950; Anal. calcd for C\(_{15}\)H\(_{15}\)NO\(_5\) (289.0950): C, 62.28; H, 5.23; N, 4.84. Found: C, 62.14; H, 5.27; N, 4.75%.

\((1'S,4R)-6\)-bromo-4-(\text{nitromethyl})\text{spiro}[\text{chroman-3,1'-cyclohexane}]-2,2'-\text{dione}\) (6dd):
Prepared by procedure E and purified by column chromatography using EtOAc/hexane and isolated as white solid. Mp 120 °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, \(\lambda = 254\) nm), \(t_R = 25.34\) min (major), \(t_R = 30.76\) min (minor). \([\alpha]_D^{25} = -4.2^\circ\) (c = 0.21 g/100 mL, CHCl\(_3\), 79% ee); IR (Neat): \(\nu_{\text{max}} 2918, 1764\) (C=O), 1718, 1552 (NO\(_2\)), 1380 (NO\(_2\)), 1242, 1029 and 822 cm\(^{-1}\); \(1H\) NMR (CDCl\(_3\)) \(\delta 7.49\) (1H, dd, \(J = 8.4, 2.0\) Hz), 7.38 (1H, d, \(J = 2.4\) Hz), 7.00 (1H, d, \(J = 8.8\) Hz), 5.37 (1H, dd, \(J = 13.2, 4.4\) Hz), 4.22 (1H, dd, \(J = 13.2, 10.4\) Hz), 3.87 (1H, dd, \(J = 10.4, 4.0\) Hz), 3.38-3.29 (1H, m), 2.62-2.58 (1H, m), 2.20-2.11 (2H, m), 1.77-1.60 (3H, m), 1.52 (1H, td, \(J = 13.6, 3.6\) Hz); \(13C\) NMR (CDCl\(_3\), DEPT-135) \(\delta 206.5\) (C,
C=O), 165.4 (C, O-C=O), 149.2 (C), 133.2 (CH), 131.9 (CH), 123.7 (C), 118.2 (C), 118.2 (CH), 76.3
(CH2), 56.0 (C), 41.7 (CH2), 41.4 (CH), 36.4 (CH2), 27.7 (CH2), 21.9 (CH2); LRMS m/z 368.10 (M + H+),
Found: C, 48.85; H, 3.76; N, 3.85%.

(9R,9aS)-ethyl 9-(nitromethyl)-1,2,9,9a-tetrahydrocyclopenta[b]chromene-9a-carboxylate (7aa):
Prepared following the procedure F 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 = 90:10, flow rate 0.5 mL/min, λ = 254 nm), tR = 12.26 min (major), tR =
13.12 min (minor). [α]D 25 = –142.5° (c = 0.085 g/100 mL, CHCl3, 60% ee and >99% de);
IR (Neat): νmax 2926, 1736 (C=O), 1678, 1557 (NO2), 1375 (NO2), 1246, 862, 804 and 756 cm–1; 1H NMR
(CDCl3) δ 7.22 (1H, dt, J = 8.8, 1.6 Hz), 7.08 (1H, dd, J = 7.2, 1.2 Hz), 6.96-6.91 (2H, m), 5.37 (1H, t, J = 2.4 Hz,
olefinic-H), 4.68 (1H, dd, J = 11.2, 4.4 Hz), 4.32-4.23 (2H, m), 4.04-3.98 (2H, m, OCH2CH3), 2.56-2.47
(1H, m), 2.39-2.28 (2H, m), 2.13-2.07 (1H, m), 0.99 (3H, t, J = 6.8 Hz, OCH2C2H5); 13C NMR (CDCl3,
DEPT-135) δ 172.4 (C, O-C=O), 152.1 (C), 148.7 (C), 129.9 (CH), 129.8 (CH), 122.7 (CH), 120.6 (C),
116.7 (CH), 105.7 (CH), 77.8 (CH2), 61.6 (CH2, OCH2CH3), 54.6 (C), 40.5 (CH), 30.0 (CH2), 25.9 (CH2),
13.8 (CH3, OCH2CH3); LRMS m/z 304.15 (M + H+), calcd for C16H17NO5 303.1107; Anal. calcd for
C16H17NO5 (303.1107): C, 63.36; H, 5.65; N, 4.62. Found: C, 63.18; H, 5.71; N, 4.56%.

(R)-ethyl 1-[(S)-1-(2-acetoxyphenyl)-2-nitroethyl]-2-oxocyclopentanecarboxylate (8aa):
Prepared following the procedure G and purified by column chromatography using
EtOAc/hexane and isolated as liquid; [α]D 25 = –16.7° (c = 1.32 g/100 mL, CHCl3, 98% ee);
IR (Neat): νmax 2931, 1764 (C=O), 1726, 1551 (NO2), 1381 (NO2), 1211, 1014, and
915 cm–1; 1H NMR (CDCl3) δ 7.49 (1H, d, J = 6.4 Hz), 7.32 (1H, t, J = 5.6 Hz), 7.22
(1H, t, J = 6.0 Hz), 7.14 (1H, d, J = 6.4 Hz), 5.34 (1H, dd, J = 11.2, 2.8 Hz), 4.95 (1H,
 dd, J = 11.2, 7.6 Hz), 4.33 (1H, dd, J = 7.6, 3.2 Hz), 4.21 (2H, q, J = 6.0 Hz, OCH2CH3), 2.50-2.40 (2H,
m), 2.38 (3H, s, O=C=CH3), 2.33-2.23 (1H, m), 2.00-1.94 (2H, m), 1.92-1.86 (1H, m), 1.27 (3H, t, J = 6.0 Hz,
OCH2CH3); 13C NMR (CDCl3, DEPT-135) δ 212.4 (C, C=O), 169.6 (C, O-C=O), 168.9 (C, O=C=O),
149.2 (C), 129.0 (CH), 128.8 (CH), 128.7 (C), 126.4 (CH), 123.3 (CH), 77.0 (CH2), 62.2 (C), 62.18 (CH2,
OCH2CH3), 38.1 (CH), 37.6 (CH2), 32.6 (CH3), 21.1 (CH2), 19.2 (CH2), 13.9 (CH3, OCH2CH3); LRMS
m/z 364.40 (M + H+), calcd for C18H17NO7 363.1318; Anal. calcd for C18H17NO7 (363.1318): C, 59.50; H,
5.83; N, 3.85. Found: C, 59.41; H, 5.87; N, 3.79%.
(3S,3aR)-ethyl 3-(2-acetoxyphenyl)-2,3a,4,5,6-hexahydrocyclopenta[b]pyrrole-3a-carboxylate (9aa): Prepared following the procedure H and purified by column chromatography using EtOAc/hexane and isolated as oil; $[\alpha]_D^{25} = +160.2^\circ$ ($c = 1.21 \text{ g/100 mL}, \text{CHCl}_3$, 98% ee); IR (Neat): $\nu_{\text{max}}$ 2930, 1761 (C=O), 1736, 1655 (NO$_2$), 1493, 1370 (NO$_2$), 1207, 1017, 912, 812 and 756 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.30 (1H, t, $J = 8.0$ Hz), 7.26 (1H, d, $J = 8.4$ Hz), 7.18 (1H, t, $J = 7.6$ Hz), 7.11 (1H, d, $J = 8.0$ Hz), 5.19 (1H, t, $J = 12.0$ Hz), 4.24 (1H, dd, $J = 12.4$, 8.8 Hz), 4.05 (1H, dd, $J = 10.8$, 8.4 Hz), 3.83 (2H, q, $J = 7.2$ Hz, OCH$_2$CH$_3$), 2.76-2.61 (2H, m), 2.33 (3H, s, O=CCH$_3$), 2.27-2.16 (1H, m), 2.14-1.99 (2H, m), 1.71-1.63 (1H, m), 0.97 (3H, t, $J = 7.2$ Hz, OCH$_2$CH$_3$); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 169.3 (C, O-C=O), 168.6 (C, O-C=O), 154.1 (C), 149.3 (C), 129.0 (CH), 127.1 (CH), 126.3 (C), 125.8 (CH), 122.9 (CH), 69.8 (CH$_2$), 67.8 (C), 61.7 (CH$_2$, OCH$_2$CH$_3$), 45.4 (CH), 35.3 (CH$_2$), 26.5 (CH$_2$), 21.9 (CH$_2$), 21.2 (CH$_3$, O=CCH$_3$), 13.7 (CH$_3$, OCH$_2$CH$_3$); LRMS m/z 316.10 (M + H$^+$), calcd for C$_{18}$H$_{21}$NO$_4$ 315.1471; Anal. calcd for C$_{18}$H$_{21}$NO$_4$ (315.1471): C, 68.55; H, 6.71; N, 4.44. Found: C, 68.46; H, 6.67; N, 4.51%.
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