

Supporting Information-I

Asymmetric Synthesis of Drug-like Spiro[chroman-3,3'-indolin]-2'-ones through Aminoal-catalysis

D. B. Ramachary,* M. Shiva Prasad, S. Vijaya Laxmi and R. Madhavachary

*Catalysis Laboratory, School of Chemistry, University of Hyderabad, Central University (P.O.),
Hyderabad 500 046, India*

ramsc@uohyd.ernet.in and ramchary.db@gmail.com

General Methods: The ^1H 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 ^1H 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 α ($\lambda = 0.71073 \text{ \AA}$) 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 α fine-focus sealed tube ($\lambda = 0.71073 \text{ \AA}$). 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_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

The enantiomeric excess (*ee*) of the *r*-M products was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H, Chiralcel OJ-H, Chiralpak AD-H, Chiralpak AS-H and Lux 5u Amylose-2, Lux 5u Cellulose-1, Lux 5u Cellulose-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. The substrates of 3-substituted oxindoles **2** were prepared from the corresponding isatins and oxindoles according to the procedures previously reported.¹ The substrates of *O*-hydroxy cinnamaldehydes **1** were prepared according to previous literature reports.²

General Experimental Procedures:

Procedure A: In an ordinary glass vial equipped with a magnetic stirring bar, a mixture of *R*-(+)-DPPOTMS **3** (19.6 mg, 0.06 mmol) and acetic acid **4b** (0.0034 mL, 0.06 mmol) in CHCl₃ (0.6 mL), was added 2-hydroxycinnamaldehyde **1a** (53 mg, 0.36 mmol) and allowed to stir for 10 min followed by addition of **2** (96 mg, 0.3 mmol). After stirring the reaction mixture for 12 h the reaction mixture was loaded on to silica gel column directly eluting with hexane/EtOAc (10:1 to 10:2).

Procedure B: In an ordinary glass vial equipped with a magnetic stirring bar, a mixture of *R*-(+)-DPPOTMS **3** (19.6 mg, 0.06 mmol) and acetic acid **4b** (0.0034 mL, 0.06 mmol) in CHCl₃ (0.6 mL), was added 2-hydroxycinnamaldehyde **1a** (53 mg, 0.36 mmol) and allowed to stir for 10 min followed by addition of **2** (96 mg, 0.3 mmol). After stirring the reaction mixture at 25 °C for 12 h, was added 1.0 mL CHCl₃ and Ph₃P=CHCO₂Et **6** (209 mg, 0.6 mmol). After stirring the reaction mixture for 2 h the reaction mixture was loaded on to silica gel column directly eluting with hexane/EtOAc (10:1 to 10:2).

Procedure C: In an ordinary glass vial equipped with a magnetic stirring bar, a mixture of *R*-(+)-DPPOTMS **3** (19.6 mg, 0.06 mmol) and acetic acid **4b** (0.0034 mL, 0.06 mmol) in CHCl₃ (0.6 mL), was added 2-hydroxycinnamaldehyde **1a** (53 mg, 0.36 mmol) and allowed to stir for

10 min followed by addition of **2a** (96 mg, 0.3 mmol). After stirring the reaction mixture at 25 °C for 12 h, was added 1.0 mL of CHCl₃, malononitrile (24 mg, 0.36 mmol) and Hantzsch ester **8** (84 mg, 0.36 mmol). After stirring the reaction mixture at 25 °C for 1 h, then reaction mixture was loaded on to silica gel column directly eluting with hexane/EtOAc (10:2 to 10:3).

Procedure D: In an oven dried round bottomed flask with *r*-M product **5aa** (150 mg, 0.3 mmol), was added methanol (1.0 mL), trimethyl orthoformate (63 mg, 0.6 mmol) and *p*-TSA.H₂O (6 mg, 0.03 mmol). After stirring the reaction mixture at 25 °C for 15 min 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 over (Na₂SO₄), filtered and concentrated. Pure chiral acetal product **10'aa** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate 10:1).

In an oven dried round bottomed flask a solution of above acetal product **10'aa** (70 mg, 0.136 mmol) and LiAlH₄ (52 mg, 1.36 mmol) in dry THF (3 mL) was stirred under N₂ atmosphere in an ice bath and allowed to slowly warm to room temperature followed by reflux at 70 °C for about 24 h, then the mixture was quenched with EtOAc (1 mL), MeOH (1 mL), H₂O (5 mL), and then extracted with EtOAc three times, dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10:1).

Procedure E: All racemic products 7aa–kp were prepared in 40-85% yield and 45-99% *de* through *r*-M reaction as shown below: In an ordinary glass vial equipped with a magnetic stirring bar, a mixture of (±)-DPPOTMS **3** (19.6 mg, 0.06 mmol) in CHCl₃ (0.6 mL) was added functionalized 2-hydroxycinnamaldehydes **1a-k** (0.36 mmol) and allowed to stir for 10 min followed by addition of **2a-p** (0.3 mmol). After stirring the reaction mixture at 25 °C for 7-12 h, was added 1.0 mL CHCl₃ and Ph₃P=CHCO₂Et **6** (209 mg, 0.6 mmol). After stirring the reaction mixture for 2 h the reaction mixture was loaded on to silica gel column directly eluting with hexane/EtOAc (10:1 to 10:2).

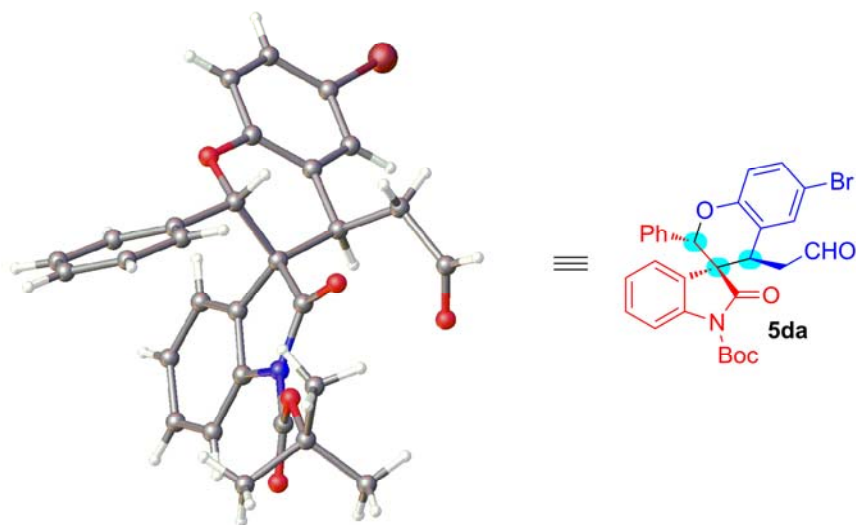
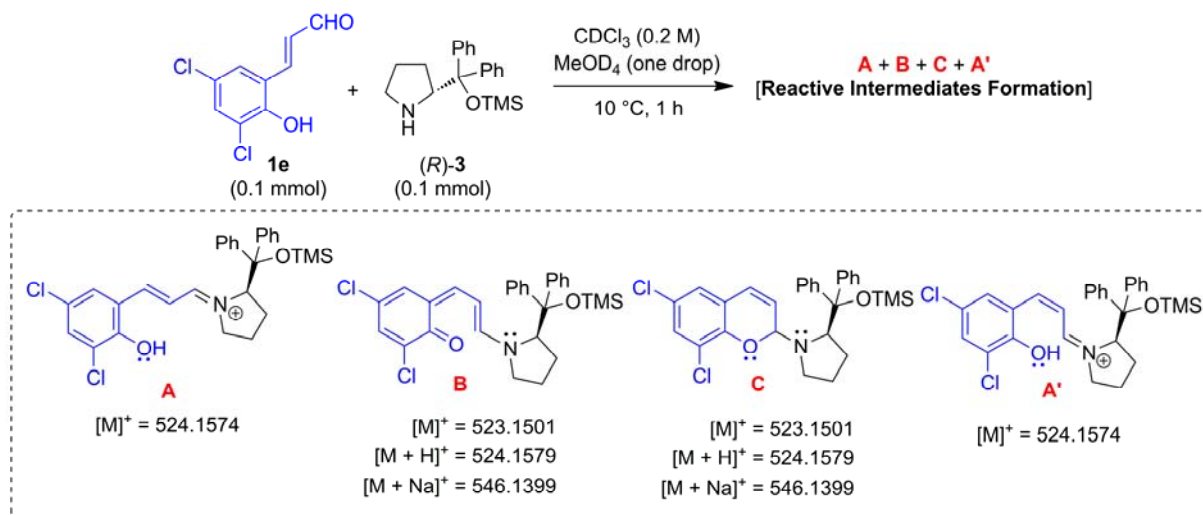
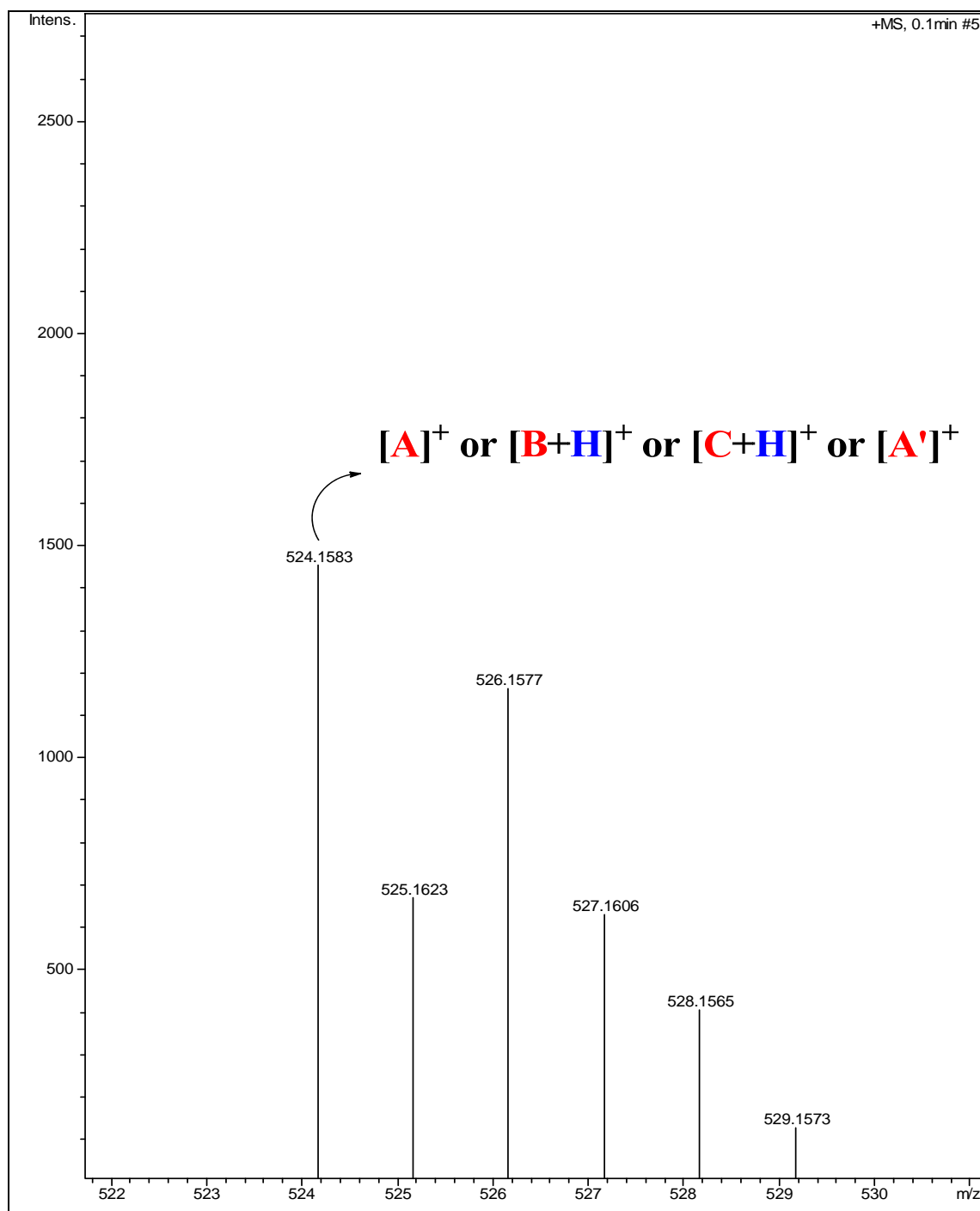
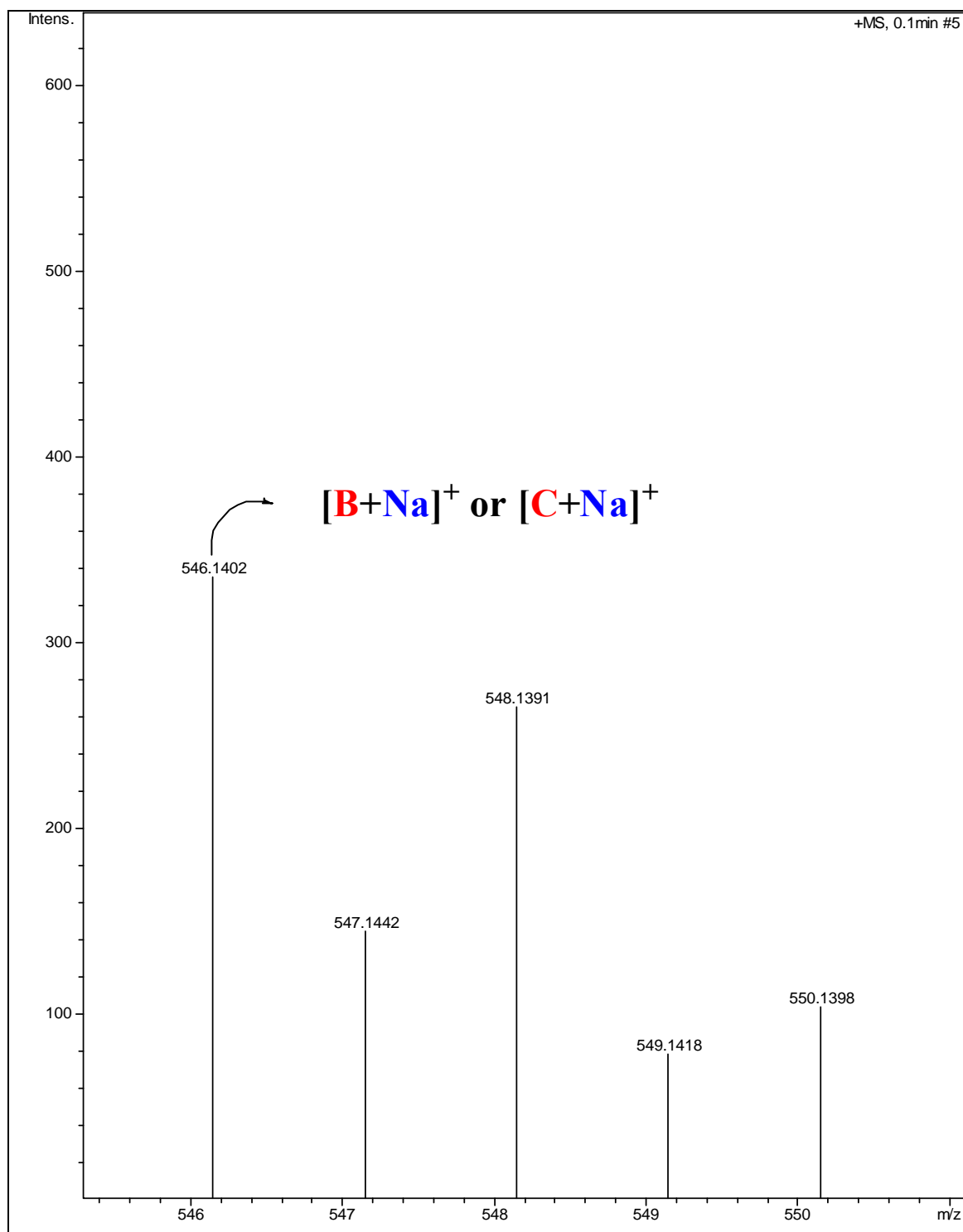


Figure S1. Crystal structure of functionalized spiro[chroman-3,3'-indolin]-2'-one (**5da**).

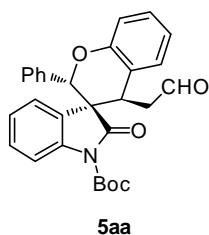
Figure S2: HRMS experiment see the formation of catalytic species of animals.







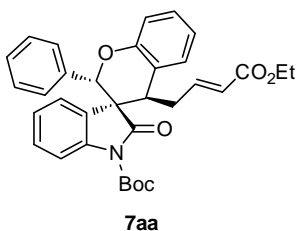
(2*S*,3*S*,4*R*)-tert-butyl-2'-oxo-4-(2-oxoethyl)-2-phenylspiro[chroman-3,3'-indoline]-1'-



5aa

carboxylate (5aa): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as white gummy solid. $[\alpha]_D^{25} = +4.71^\circ$ ($c = 1.0$ g/100 mL, CHCl_3); IR (Neat): ν_{max} 2978, 1786, 1736, 1726, 1481, 1248, 1149, 1056, 841 and 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 9.81 (1H, br s), 7.57-7.54 (1H, m), 7.32-7.22 (2H, m), 7.20-7.15 (2H, m), 7.11-7.02 (4H, m), 7.00-6.92 (3H, m), 6.84 (1H, d, $J = 7.6$ Hz), 5.37 (1H, s), 4.14 (1H, dd, $J = 18.8, 10.0$ Hz), 3.91 (1H, d, $J = 9.2$ Hz), 2.79 (1H, dd, $J = 18.8, 2.8$ Hz), 1.50 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (CDCl_3 , DEPT-135) δ 198.9 (CH, CHO), 174.7 (C, N-C=O), 154.2 (C, NCO₂), 148.1 (C), 139.0 (C), 134.7 (C), 129.9 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 127.8 (2 x CH), 127.7 (C), 127.5 (2 x CH), 124.7 (CH), 124.3 (CH), 123.4 (C), 122.1 (CH), 117.0 (CH), 114.5 (CH), 84.1 (C), 77.4 (CH), 52.6 (C), 49.4 (CH₂), 37.1 (CH), 27.8 (3 x CH₃); HRMS m/z 470.1967 (M+H), calcd for $\text{C}_{29}\text{H}_{27}\text{NO}_5\text{H}$ 470.1967.

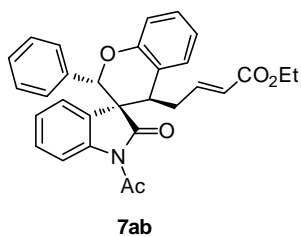
(2*S*,3*S*,4*R*)-tert-butyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-2'-oxo-2-phenylspiro[chroman-



7aa

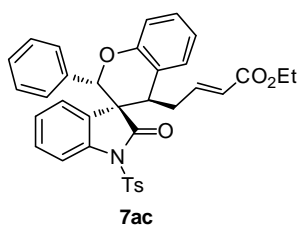
3,3'-indoline]-1'-carboxylate (7aa): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2 column (hexane/2-propanol = 98:2, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 38.0$ min (major), $t_R = 43.0$ min (minor). $[\alpha]_D^{25} = -34.2^\circ$ ($c = 0.19$ g/100 mL, CHCl_3 , 99% *ee*); IR (Neat): ν_{max} 2981, 1790, 1755, 1717, 1493, 1250, 1200, 1148, 1044, 841 and 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (1H, d, $J = 8.4$ Hz), 7.33-7.29 (1H, m), 7.22-7.06 (6H, m), 7.03-6.92 (5H, m), 6.68 (1H, d, $J = 7.6$ Hz), 5.85 (1H, d, $J = 15.6$ Hz), 5.58 (1H, s), 4.17 (2H, q, $J = 7.2$ Hz), 3.46 (1H, br td, $J = 14.8, 5.2$ Hz), 3.13 (1H, t, $J = 6.4$ Hz), 2.85 (1H, br td, $J = 14.4, 8.0$ Hz), 1.54 (9H, s), 1.27 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.8 (C, N-C=O), 166.3 (C, O-C=O), 154.1 (C, N-CO₂), 148.4 (C), 146.5 (CH), 138.9 (C), 135.3 (C), 130.6 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 127.9 (2 x CH), 127.8 (C), 127.6 (2 x CH), 125.0 (CH), 124.3 (CH), 123.6 (CH), 122.0 (C), 121.4 (CH), 117.0 (CH), 114.3 (CH), 84.3 (C), 77.4 (CH), 60.2 (CH₂), 53.7 (C), 43.1 (CH), 36.4 (CH₂), 28.0 (3 x CH₃), 14.3 (CH₃); HRMS m/z 562.2208 (M + Na), calcd for $\text{C}_{33}\text{H}_{33}\text{NO}_6\text{Na}$ 562.2206.

(E)-ethyl-4-((2S,3S,4R)-1'-acetyl-2'-oxo-2-phenylspiro[chroman-3,3'-indolin]-4-yl)but-2-



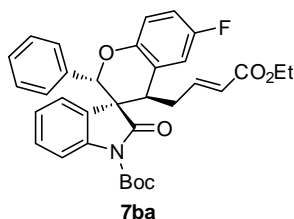
enoate (7ab): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white gummy solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2 column (hexane/2-propanol = 98:2, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 33.47$ min (major), $t_R = 55.41$ min (minor). $[\alpha]_D^{25} = -36.0^\circ$ ($c = 0.31$ g/100 mL, CHCl_3 , 84% *ee*); IR (Neat): ν_{max} 3030, 2980, 1753, 1725, 1649, 1479, 1309, 980, 761 and 701 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.02 (1H, d, $J = 8.4$ Hz), 7.36-7.18 (3H, m), 7.14-7.09 (4H, m), 7.07-7.00 (5H, m), 6.77 (1H, dd, $J = 8.0, 2.0$ Hz), 5.87 (1H, td, $J = 14.4, 1.2$ Hz), 5.56 (1H, s), 4.19 (2H, q, $J = 7.2$ Hz), 3.45 (1H, dtd, $J = 14.8, 6.4, 1.2$ Hz), 3.21 (1H, t, $J = 6.4$ Hz), 2.85 (1H, dtd, $J = 14.8, 6.4, 1.2$ Hz), 2.48 (3H, s, CH_3CO), 1.29 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 176.3 (C, N-C=O), 170.3 (C, N-C=O), 166.2 (C, O-C=O), 154.1 (C), 146.5 (CH), 139.2 (C), 135.0 (C), 130.5 (CH), 128.9 (3 x CH), 128.0 (C), 127.9 (2 x CH), 127.7 (2 x CH), 125.2 (CH), 124.8 (CH), 123.5 (CH), 122.0 (C), 121.6 (CH), 117.0 (CH), 115.9 (CH), 77.4 (CH), 60.3 (CH_2), 53.7 (C), 43.4 (CH), 36.6 (CH_2), 26.7 (CH_3), 14.3 (CH_3); HRMS m/z 504.1787 (M+Na), calcd for $\text{C}_{30}\text{H}_{27}\text{NO}_5\text{Na}$ 504.1787.

(E)-ethyl-4-((2S,3S,4R)-2'-oxo-2-phenyl-1'-tosylspiro[chroman-3,3'-indolin]-4-yl)but-2-



enoate (7ac): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow gummy solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R = 20.84$ min (major), $t_R = 36.36$ min (minor). $[\alpha]_D^{25} = -109.56^\circ$ ($c = 0.20$ g/100 mL, CHCl_3 , 96% *ee*); IR (Neat): ν_{max} 2926, 1753, 1720, 1484, 1386, 1188, 1150, 958 and 744 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.70 (3H, br d, $J = 8.4$ Hz), 7.33-7.24 (5H, m), 7.08-7.00 (5H, m), 6.85 (2H, t, $J = 7.6$ Hz), 6.72 (2H, d, $J = 8.0$ Hz), 6.69-6.64 (1H, m), 5.30 (1H, d, $J = 15.6$ Hz), 5.25 (1H, s), 4.13 (2H, q, $J = 7.2$ Hz), 4.02 (1H, t, $J = 6.0$ Hz), 2.45 (3H, s, ArCH_3), 2.29-2.21 (1H, m), 2.05-1.97 (1H, m), 1.27 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 175.0 (C, N-C=O), 165.7 (C, O-C=O), 154.3 (C), 145.4 (C), 144.9 (CH), 139.7 (C), 134.9 (C), 134.2 (C), 129.7 (2 x CH),

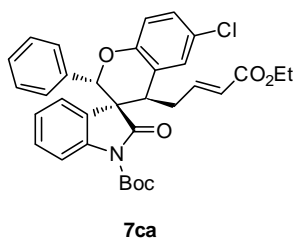
129.4 (CH), 128.4 (2 x CH), 127.8 (2 x CH), 127.6 (3 x CH), 127.0 (2 x CH), 126.5 (CH), 124.6 (CH), 124.4 (C), 122.7 (C), 122.7 (CH), 122.1 (CH), 117.0 (CH), 113.2 (CH), 81.8 (CH), 60.2 (CH₂), 55.5 (C), 42.0 (CH), 33.5 (CH₂), 21.7 (CH₃), 14.2 (CH₃); HRMS m/z 616.1770 (M+Na), calcd for C₃₅H₃₁NO₆SNa 616.1770.



(2S,3S,4R)-tert-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-6-fluoro-2'-oxo-2-phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7ba):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white solid with M.P. 51°C. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2 column (hexane/2-propanol = 95:5, flow rate 0.5 mL/min, λ = 254 nm), t_R = 15.89 min (major), t_R = 24.74 min (minor). $[\alpha]_D^{25} = -22.97^\circ$ ($c = 0.58$ g/100 mL, CHCl₃, 91% *ee*); IR (Neat): ν_{\max} 2981, 1790, 1752, 1717, 1493, 1347, 1287, 1250, 1148, 1044, 842 and 749 cm⁻¹; ¹H NMR (CDCl₃) δ 7.55 (1H, d, $J = 8.0$ Hz), 7.35-6.95 (10H, m), 6.80 (1H, d, $J = 8.4$ Hz), 6.70 (1H, d, $J = 7.6$ Hz), 5.86 (1H, d, $J = 15.6$ Hz), 5.52 (1H, s), 4.17 (2H, q, $J = 6.8$ Hz), 3.41 (1H, br td, $J = 14.8, 5.2$ Hz), 3.11 (1H, t, $J = 6.0$ Hz), 2.85 (1H, br td, $J = 14.4, 8.0$ Hz), 1.53 (9H, s), 1.27 (3H, t, $J = 6.8$ Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 173.5 (C, N-C=O), 166.1 (C, O-C=O), 157.0 (C, d, $J = 239.1$ Hz, C-F), 150.1 (C, N-CO₂), 148.4 (C), 145.8 (CH), 138.9 (C), 135.0 (C), 128.9 (CH), 128.6 (CH), 127.8 (2 x CH), 127.6 (2 x CH), 127.5 (C), 124.9 (CH), 124.4 (CH), 124.0 (CH), 123.3 (C, d, $J = 7.0$ Hz), 118.1 (CH, d, $J = 7.8$ Hz), 116.2 (CH, d, $J = 22.2$ Hz), 116.0 (CH, d, $J = 22.5$ Hz), 114.4 (CH), 84.4 (C), 77.7 (CH), 60.3 (CH₂), 53.4 (C), 43.1 (CH), 36.2 (CH₂), 27.9 (3 x CH₃), 14.2 (CH₃); HRMS m/z 580.2110 (M+Na), calcd for C₃₃H₃₂FNO₆Na 580.2112.

(2S,3S,4R)-tert-butyl-6-chloro-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-2'-oxo-2-

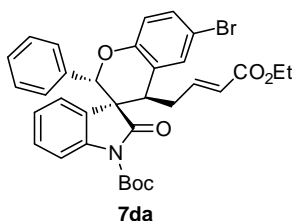


phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7ca): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column

(hexane/2-propanol = 98:2, flow rate 0.5 mL/min, λ = 254 nm), t_R = 20.50 min (major), t_R = 24.70 min (minor). $[\alpha]_D^{25} = -29.7^\circ$ ($c = 0.35$ g/100 mL, CHCl₃, 96% *ee*); IR (Neat): ν_{\max} 2980,

1784, 1758, 1722, 1652, 1605, 1479, 1350, 1250, 1150 and 753 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (1H, d, $J = 8.4$ Hz), 7.30-7.16 (3H, m), 7.11-7.07 (3H, m), 7.03-6.95 (5H, m), 6.69 (1H, d, $J = 7.2$ Hz), 5.86 (1H, d, $J = 16.0$ Hz), 5.53 (1H, s), 4.18 (2H, q, $J = 7.2$ Hz), 3.34 (1H, dtd, $J = 14.0, 6.8, 1.2$ Hz), 3.11 (1H, t, $J = 6.4$ Hz), 2.85 (1H, br td, $J = 14.8, 8.0$ Hz), 1.53 (9H, s), 1.28 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.4 (C, N-C=O), 166.1 (C, O-C=O), 152.7 (N-CO₂), 148.3 (C), 145.7 (CH), 138.9 (C), 134.8 (C), 129.9 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 127.8 (2 x CH), 127.7 (2 x CH), 127.4 (C), 126.1 (C), 124.9 (CH), 124.4 (CH), 124.1 (CH), 123.7 (C), 118.4 (CH), 114.5 (CH), 84.5 (C), 77.7 (CH), 60.3 (CH₂), 53.3 (C), 42.9 (CH), 36.2 (CH₂), 28.0 (3 x CH₃), 14.3 (CH₃); HRMS m/z 596.1818 (M + Na), calcd for C₃₃H₃₂ClNO₆Na 596.1816.

(2S,3S,4R)-tert-butyl-6-bromo-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-2'-oxo-2-



7da

phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7da): Prepared

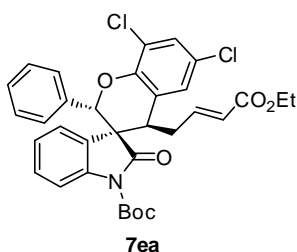
by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale brown solid with M.P. 54°C.

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), $t_R = 22.52$ min (major), $t_R = 28.0$ min (minor). $[\alpha]_D^{25} = -18.8^\circ$ ($c = 0.19$ g/100 mL, CHCl_3 , 92% *ee*); IR (Neat): ν_{max} 2981, 1789, 1749, 1719, 1498, 1346, 1277, 1251, 1149, 1104, 1045, 816 and 751 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (1H, d, $J = 8.0$ Hz), 7.40 (1H, dd, $J = 8.8, 2.4$ Hz), 7.24-7.15 (3H, m), 7.08 (2H, t, $J = 8$ Hz), 6.99-6.92 (5H, m), 6.69 (1H, d, $J = 7.6$ Hz), 5.86 (1H, d, $J = 15.6$ Hz), 5.52 (1H, s), 4.18 (2H, q, $J = 7.2$ Hz), 3.39 (1H, br td, $J = 14.4, 5.6$ Hz), 3.10 (1H, t, $J = 6.0$ Hz), 2.84 (1H, br td, $J = 14.4, 7.6$ Hz), 1.53 (9H, s), 1.28 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.3 (C, N-C=O), 166.0 (C, O-C=O), 153.2 (C, N-CO₂), 148.2 (C), 145.5 (CH), 138.8 (C), 134.7 (C), 132.8 (CH), 131.7 (CH), 128.8 (CH), 128.6 (CH), 127.7 (2 x CH), 127.5 (2 x CH), 127.2 (C), 124.8 (CH), 124.3 (CH), 124.1 (C), 124.0 (CH), 118.7 (CH), 114.4 (CH), 113.3 (C), 84.4 (C), 77.6 (CH), 60.2 (CH₂), 53.2 (C), 42.7 (CH), 36.2 (CH₂), 27.8 (3 x CH₃), 14.2 (CH₃); HRMS m/z 640.1310 (M + Na), calcd for C₃₃H₃₂BrNO₆Na 640.1311.

(2*S*,3*S*,4*R*)-tert-butyl-6,8-dichloro-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-2'-oxo-2-

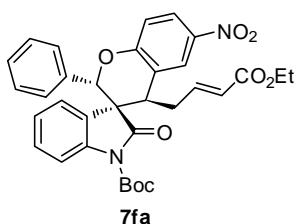
phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7ea): Prepared by following the



procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white gummy solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 95:5, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 15.55$ min (major), $t_R = 19.4$ min

(minor). $[\alpha]_D^{25} = +6.8^\circ$ ($c = 0.38$ g/100 mL, CHCl_3 , 81% *ee*); IR (Neat): ν_{max} 3068, 2975, 2899, 1764, 1726, 1644, 1479, 1463, 1353, 1156, 1046, and 866 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (1H, d, $J = 8.0$ Hz), 7.43 (1H, d, $J = 2.4$ Hz), 7.27-7.15 (2H, m), 7.10 (2H, t, $J = 7.6$ Hz), 7.03-6.88 (5H, m), 6.54 (1H, d, $J = 7.6$ Hz), 5.85 (1H, d, $J = 15.6$ Hz), 5.66 (1H, s), 4.18 (2H, q, $J = 7.2$ Hz), 3.44 (1H, br td, $J = 14.8, 5.2$ Hz), 3.10 (1H, t, $J = 6.8$ Hz), 2.80 (1H, br td, $J = 14.4, 8.0$ Hz), 1.55 (9H, s), 1.28 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.2 (C, N-C=O), 166.0 (C, O-C=O), 148.6 (C, N-CO₂), 148.3 (C), 145.1 (CH), 138.8 (C), 134.4 (C), 129.3 (CH), 129.1 (CH), 128.7 (CH), 128.5 (CH), 127.7 (4 x CH), 126.9 (C), 125.7 (C), 124.9 (C), 124.7 (CH), 124.5 (CH), 124.4 (CH), 122.7 (C), 114.6 (CH), 84.7 (C), 78.4 (CH), 60.4 (CH₂), 53.3 (C), 43.2 (CH), 35.8 (CH₂), 28.0 (3 x CH₃), 14.2 (CH₃); HRMS m/z 630.1426 (M +Na), calcd for C₃₃H₃₁Cl₂NO₆Na 630.1426.

(2*S*,3*S*,4*R*)-tert-butyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-6-nitro-2'-oxo-2-

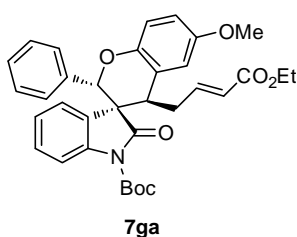


phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7fa): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow solid with M.P. is 56°C. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-

propanol = 97:3, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R = 13.50$ min (minor), $t_R = 15.68$ min (major). $[\alpha]_D^{25} = +6.48^\circ$ ($c = 0.74$ g/100 mL, CHCl_3 , 28% *ee*); IR (Neat): ν_{max} 2986, 2920, 2844, 1764, 1726, 1655, 1583, 1518, 1479, 1348, 1145 and 1107 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.23 (1H, dd, $J = 9.2, 2.8$ Hz), 8.06 (1H, d, $J = 2.8$ Hz), 7.59 (1H, d, $J = 8.4$ Hz), 7.24-7.17 (3H, m), 7.13 (2H, t, $J = 8.0$ Hz), 6.97 (2H, d, $J = 7.2$ Hz), 6.95 (2H, m), 6.53 (1H, d, $J = 7.6$ Hz), 5.83 (1H, d, $J = 15.6$ Hz), 5.65 (1H, s), 4.17 (2H, q, $J = 7.2$ Hz), 3.40 (1H, br td, $J = 14.0, 5.2$ Hz),

3.24 (1H, br t, $J = 7.2$ Hz), 2.85 (1H, br td, $J = 14.8, 8$ Hz), 1.55 (9H, s), 1.27 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 172.9 (C, N-C=O), 165.8 (C, O-C=O), 159.4 (C, N-CO₂), 148.2 (C), 144.5 (CH), 141.6 (C), 139.0 (C), 134.1 (C), 129.3 (CH), 129.0 (CH), 127.8 (4 x CH), 126.7 (C), 126.6 (CH), 124.9 (CH), 124.8 (CH), 124.5 (CH), 124.4 (CH), 122.8 (C), 117.7 (CH), 114.8 (CH), 84.8 (C), 78.6 (CH), 60.5 (CH₂), 53.0 (C), 42.6 (CH), 35.8 (CH₂), 28.0 (3 x CH₃), 14.2 (CH₃); HRMS m/z 607.2057 (M + Na), calcd for C₃₃H₃₂N₂O₈Na 607.2057.

(2S,3S,4R)-tert-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2'-oxo-2-phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7ga): Prepared by following the

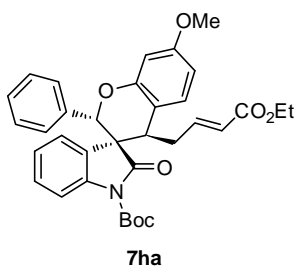


7ga

procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow gummy solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-1 column (hexane/2-propanol = 98:2, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 22.61$ min (major), t_R

= 27.55 min (minor). $[\alpha]_D^{25} = -18.4^\circ$ ($c = 1.0$ g/100 mL, CHCl_3 , 93% *ee*); IR (Neat): ν_{max} 2981, 1788, 1733, 1716, 1606, 1497, 1345, 1208, 1148, 1036, 839 and 749 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.54 (1H, d, $J = 8.0$ Hz), 7.23-7.15 (2H, m), 7.10-6.97 (7H, m), 6.89 (1H, br dd, $J = 9.2, 2.8$ Hz), 6.77-6.74 (1H, m), 6.57 (1H, d, $J = 3.2$ Hz), 5.87 (1H, d, $J = 15.6$ Hz), 5.52 (1H, s), 4.17 (2H, q, $J = 7.2$ Hz), 3.77 (3H, s, OCH₃), 3.49-3.42 (1H, m), 3.10 (1H, dd, $J = 11.2, 6.0$ Hz), 2.87 (1H, br td, $J = 14.8, 8.4$ Hz), 1.53 (9H, s), 1.27 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.8 (C, N-C=O), 166.3 (C, O-C=O), 153.7 (C, N-CO₂), 148.4 (C), 148.0 (C), 146.6 (CH), 138.8 (C), 135.3 (C), 128.7 (CH), 128.5 (CH), 127.9 (2 x CH), 127.8 (C), 127.6 (2 x CH), 125.1 (CH), 124.4 (CH), 123.6 (CH), 122.3 (C), 117.8 (CH), 115.7 (CH), 114.3 (CH), 114.2 (CH), 84.3 (C), 77.4 (CH), 60.2 (CH₂), 55.6 (CH₃, OCH₃), 53.7 (C), 43.4 (CH), 36.4 (CH₂), 28.0 (3 x CH₃), 14.3 (CH₃); HRMS m/z 592.2312 (M + Na), calcd for C₃₄H₃₅NO₇Na 592.2312.

(2S,3S,4R)-tert-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-7-methoxy-2'-oxo-2-

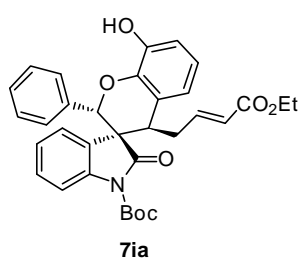


7ha

phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7ha): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as yellow viscous liquid; The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol =

98:2, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 20.67$ min (major), $t_R = 44.54$ min (minor). $[\alpha]_D^{25} = -13.2^\circ$ ($c = 0.38$ g/100 mL, CHCl_3 , >99.9% *ee*); IR (Neat): ν_{max} 2922, 1790, 1732, 1717, 1471, 1286, 1149, 1043, 841 and 752 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.54 (1H, d, $J = 8.4$ Hz), 7.23-7.15 (2H, m), 7.11-7.06 (2H, m), 7.0-6.94 (5H, m), 6.71 (1H, dd, $J = 7.6, 0.8$ Hz), 6.62-6.58 (2H, m), 5.85 (1H, d, $J = 15.6$ Hz), 5.56 (1H, s), 4.17 (2H, q, $J = 7.2$ Hz), 3.84 (3H, s, OCH_3), 3.39 (1H, br dtd, $J = 14.4, 8.4, 1.6$ Hz), 3.08 (1H, dd, $J = 7.6, 5.2$ Hz), 2.82 (1H, br td, $J = 14.4, 8.4$ Hz), 1.53 (9H, s), 1.27 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.8 (C, N-C=O), 166.4 (C, O-C=O), 160.0 (C, N-CO_2), 154.9 (C), 148.4 (C), 146.6 (CH), 138.9 (C), 135.2 (C), 131.2 (CH), 128.7 (CH), 128.5 (CH), 127.9 (2 x CH), 127.8 (C), 127.6 (2 x CH), 125.1 (CH), 124.3 (CH), 123.6 (CH), 114.3 (CH), 114.0 (C), 108.6 (CH), 101.3 (CH), 84.4 (C), 77.5 (CH), 60.2 (CH_2), 55.4 (CH_3 , OCH_3), 53.8 (C), 42.6 (CH), 36.5 (CH_2), 28.0 (3 x CH_3), 14.3 (CH_3); HRMS m/z 592.2312 ($\text{M} + \text{Na}$), calcd for $\text{C}_{34}\text{H}_{35}\text{NO}_7\text{Na}$ 592.2312.

(2S,3S,4R)-tert-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-8-hydroxy-2'-oxo-2-

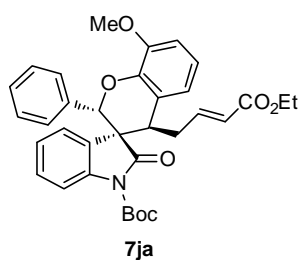


7ia

phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7ia): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as yellow viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-1 column (hexane/2-propanol = 97:3, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 35.82$ min (major), $t_R =$

44.28 min (minor). $[\alpha]_D^{25} = -21.0^\circ$ ($c = 0.71$ g/100 mL, CHCl_3 , 98% *ee*); IR (Neat): ν_{max} 3438, 2918, 1790, 1733, 1711, 1471, 1286, 1149, 1042, 841 and 752 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.50 (1H, d, $J = 8.0$ Hz), 7.27-7.17 (3H, m), 7.10-7.05 (3H, m), 7.00-6.93 (4H, m), 6.87 (2H, d, $J = 7.6$ Hz), 5.68 (1H, s, *OH*), 5.29 (1H, s), 5.22 (1H, d, $J = 15.6$ Hz), 4.17 (1H, t, $J = 6.8$ Hz), 4.08 (2H, q, $J = 7.2$ Hz), 2.70-2.63 (1H, m), 2.19- 2.11 (1H, m), 1.49 (9H, s), 1.23 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 174.9 (C, N-C=O), 165.6 (C, O-C=O), 148.0 (C, N-CO_2), 145.0 (C), 144.7 (C), 141.5 (C), 140.4 (C), 133.8 (CH), 129.1 (CH), 128.8 (CH), 127.5 (2 x CH), 127.1 (2 x CH), 125.8 (CH), 124.2 (CH), 123.9 (C), 123.7 (C), 123.5 (CH), 122.3 (CH), 118.6 (CH), 114.7 (CH), 113.6 (CH), 84.0 (C), 82.8 (CH), 60.2 (CH_2), 56.1 (C), 40.1 (CH), 34.5 (CH_2), 27.9 (3 x CH_3), 14.2 (CH_3); HRMS m/z 578.2155 ($\text{M} + \text{Na}$), calcd for $\text{C}_{33}\text{H}_{33}\text{NO}_7\text{Na}$ 578.2155.

(2*S*,3*S*,4*R*)-tert-butyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-8-methoxy-2'-oxo-2-

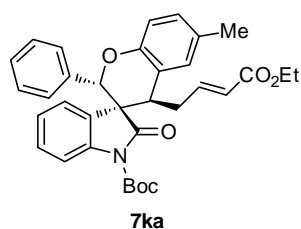


phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7ja):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as white gummy solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 95:5, flow rate 0.5 mL/min, λ = 254 nm), t_R = 14.43 min (major), t_R =

22.36 min (minor). $[\alpha]_D^{25} = -17.09^\circ$ ($c = 0.3$ g/100 mL, CHCl_3 , 96% *ee*); IR (Neat): ν_{max} 2978, 1764, 1724, 1707, 1350, 1253, 1151, 1048, 820 and 768 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.54 (1H, d, $J = 8.4$ Hz), 7.21-7.12 (2H, m), 7.07 (2H, t, $J = 7.6$ Hz), 7.02-6.91 (6H, m), 6.68 (2H, d, $J = 7.6$ Hz), 5.84 (1H, d, $J = 15.6$ Hz), 5.61 (1H, s), 4.16 (2H, q, $J = 7.2$ Hz), 3.91 (3H, s, OCH_3), 3.44 (1H, br td, $J = 14.4, 5.2$ Hz), 3.14 (1H, t, $J = 6.8$ Hz), 2.85 (1H, br td, $J = 14.8, 7.6$ Hz), 1.54 (9H, s), 1.27 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.8 (C, N-C=O), 166.3 (C, O-C=O), 148.4 (C, N-CO₂), 148.3 (C), 146.5 (CH), 143.7 (C), 138.8 (C), 135.2 (C), 128.6 (CH), 128.4 (CH), 128.0 (2 x CH), 127.7 (C), 127.5 (2 x CH), 125.1 (CH), 124.4 (CH), 123.5 (CH), 122.8 (C), 122.1 (CH), 120.8 (CH), 114.3 (CH), 110.6 (CH), 84.4 (C), 77.7 (CH), 60.2 (CH₂), 56.1 (CH₃, OCH_3), 53.6 (C), 43.0 (CH), 36.3 (CH₂), 28.0 (3 x CH₃), 14.3 (CH₃); HRMS m/z 592.2312 (M+Na), calcd for $\text{C}_{34}\text{H}_{35}\text{NO}_7\text{Na}$ 592.2312.

(2*S*,3*S*,4*R*)-tert-butyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methyl-2'-oxo-2-



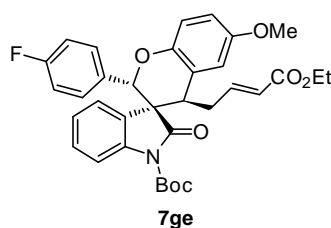
phenylspiro[chroman-3,3'-indoline]-1'-carboxylate (7ka):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2 column

(hexane/2-propanol = 98:2, flow rate 0.5 mL/min, λ = 254 nm), t_R = 23.19 min (major), t_R = 31.24 min (minor). $[\alpha]_D^{25} = -22.9^\circ$ ($c = 0.19$ g/100 mL, CHCl_3 , 95% *ee*); IR (Neat): ν_{max} 2986, 2926, 1770, 1731, 1709, 1644, 1605, 1496, 1479, 1255, 1156, 1041 and 876 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (1H, d, $J = 8.0$ Hz), 7.23-7.14 (2H, m), 7.11-7.05 (3H, m), 7.03-6.94 (5H, m), 6.87 (1H, br s), 6.75 (1H, d, $J = 7.2$ Hz), 5.87 (1H, d, $J = 16.0$ Hz), 5.53 (1H, s), 4.17 (2H, q, $J = 7.2$ Hz), 3.44 (1H, dtd, $J = 14.4, 6.0, 1.6$ Hz), 3.10 (1H, t, $J = 6.4$ Hz), 2.86 (1H, br td, $J = 14.8,$

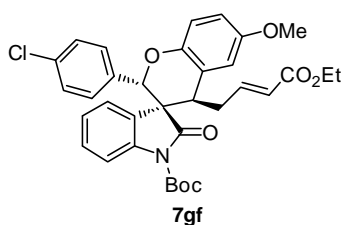
7.6 Hz), 2.31 (3H, s, Ar-CH₃), 1.53 (9H, s), 1.27 (3H, t, *J* = 7.2 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 173.7 (C, N-C=O), 166.2 (C, O-C=O), 151.8 (C, N-CO₂), 148.4 (C), 146.6 (CH), 138.7 (C), 135.3 (C), 130.7 (CH), 130.4 (C), 129.5 (CH), 128.5 (CH), 128.4 (CH), 127.8 (2 x CH), 127.5 (2 x CH), 125.0 (CH), 124.2 (CH), 123.4 (CH), 121.5 (C), 116.6 (CH), 114.2 (CH), 114.2 (C), 84.2 (C), 77.3 (CH), 60.1 (CH₂), 53.6 (C), 43.0 (CH), 36.4 (CH₂), 27.9 (3 x CH₃), 20.6 (CH₃), 14.2 (CH₃); HRMS *m/z* 576.2362 (M+Na), calcd for C₃₄H₃₅NO₆Na 576.2362.

(2*S*,3*S*,4*R*)-tert-butyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-2-(4-fluorophenyl)-6-methoxy-2'-oxospiro[chroman-3,3'-indoline]-1'-carboxylate (7ge): Prepared by following the procedure



B and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous liquid. 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, λ = 254 nm), *t*_R = 25.92 min (major), *t*_R = 33.40 min (minor). [α]_D²⁵ = -13.6° (*c* = 0.74 g/100 mL, CHCl₃, 91% *ee*); IR (Neat): ν_{max} 2981, 1788, 1739, 1716, 1497, 1345, 1208, 1148, 839 and 749 cm⁻¹; ¹H NMR (CDCl₃) δ 7.55 (1H, d, *J* = 8.4 Hz), 7.22 (1H, t, *J* = 8.0 Hz), 7.06-6.84 (6H, m), 6.76 (3H, t, *J* = 8.4 Hz), 6.57 (1H, d, *J* = 2.8 Hz), 5.86 (1H, d, *J* = 15.6 Hz), 5.49 (1H, s), 4.16 (2H, q, *J* = 7.2 Hz), 3.75 (3H, s, OCH₃), 3.42 (1H, br td, *J* = 14.4, 5.2 Hz), 3.09 (1H, br t, *J* = 6.8 Hz), 2.86 (1H, br td, *J* = 14.8, 8.0 Hz), 1.54 (9H, s), 1.26 (3H, t, *J* = 7.2 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 173.9 (C, N-C=O), 166.3 (C, O-C=O), 162.6 (C, d, *J* = 245.6 Hz, C-F), 153.8 (C, N-CO₂), 148.3 (C), 147.8 (C), 146.5 (CH), 138.8 (C), 131.2 (C), 129.7 (2 x CH, d, *J* = 8.1 Hz), 128.8 (CH), 127.5 (C), 125.1 (CH), 124.5 (CH), 123.7 (CH), 121.6 (C), 117.7 (CH), 115.7 (CH), 114.6 (CH), 114.4 (2 x CH), 114.2 (CH), 84.6 (C), 76.7 (CH), 60.3 (CH₂), 55.6 (CH₃, OCH₃), 53.7 (C), 43.4 (CH), 36.4 (CH₂), 27.9 (3 x CH₃), 14.3 (CH₃); HRMS *m/z* 610.2217 (M +Na), calcd for C₃₄H₃₄FNO₇Na 610.2217.

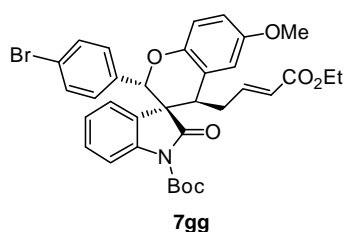
(2*S*,3*S*,4*R*)-tert-butyl-2-(4-chlorophenyl)-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2'-oxospiro[chroman-3,3'-indoline]-1'-carboxylate (7gf): Prepared



B and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2

column (hexane/2-propanol = 90:10, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 14.45$ min (major), $t_R = 26.95$ min (minor). $[\alpha]_D^{25} = -15.0^\circ$ ($c = 1.0$ g/100 mL, CHCl_3 , 94% *ee*); IR (Neat): ν_{max} 2923, 1750, 1730, 1716, 1496, 1307, 1208, 1152, 1061, 822 and 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (1H, d, $J = 8.0$ Hz), 7.22 (1H, t, $J = 8.0$ Hz), 7.06-6.87 (8H, m), 6.74 (1H, d, $J = 7.6$ Hz), 6.57 (1H, d, $J = 2.0$ Hz), 5.87 (1H, d, $J = 15.6$ Hz), 5.49 (1H, s), 4.16 (2H, q, $J = 7.2$ Hz), 3.76 (3H, s, OCH_3), 3.42 (1H, br td, $J = 14.4, 5.6$ Hz), 3.09 (1H, t, $J = 5.6$ Hz), 2.85 (1H, br td, $J = 14.4, 8.0$ Hz), 1.55 (9H, s), 1.26 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.8 (C, N-C=O), 166.3 (C, O-C=O), 153.8 (C, N-CO₂), 148.2 (C), 147.8 (C), 146.4 (CH), 138.8 (C), 134.3 (C), 134.0 (C), 129.3 (2 x CH), 129.0 (CH), 127.8 (2 x CH), 127.4 (C), 125.0 (CH), 124.5 (CH), 123.7 (CH), 122.2 (C), 117.7 (CH), 115.7 (CH), 114.4 (CH), 114.2 (CH), 84.6 (C), 76.8 (CH), 60.2 (CH₂), 55.6 (CH₃), 53.7 (C), 43.4 (CH), 36.4 (CH₂), 28.0 (3 x CH₃), 14.2 (CH₃); HRMS m/z 626.1922 (M + Na), calcd for $\text{C}_{34}\text{H}_{34}\text{ClNO}_7\text{Na}$ 626.1922.

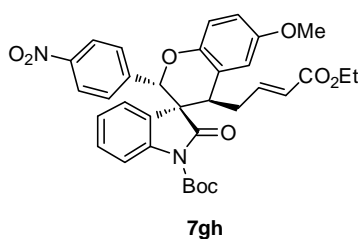
(2*S*,3*S*,4*R*)-tert-butyl-2-(4-bromophenyl)-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2'-



oxospiro[chroman-3,3'-indoline]-1'-carboxylate (7gg): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as gummy solid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2 column (hexane/2-

propanol = 90:10, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 16.28$ min (major), $t_R = 29.0$ min (minor). $[\alpha]_D^{25} = -12.1^\circ$ ($c = 1.0$ g/100 mL, CHCl_3 , 94% *ee*); IR (Neat): ν_{max} 2928, 1756, 1729, 1707, 1644, 1601, 1495, 1345, 1289, 1251, 1148, 1066, 845 and 752 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.55 (1H, d, $J = 8.0$ Hz), 7.24-7.20 (3H, m), 7.04-6.94 (3H, m), 6.90-6.84 (3H, m), 6.74 (1H, d, $J = 7.2$ Hz), 6.56 (1H, d, $J = 2.8$ Hz), 5.86 (1H, d, $J = 15.6$ Hz), 5.47 (1H, s), 4.16 (2H, q, $J = 7.2$ Hz), 3.76 (3H, s, OCH_3), 3.41 (1H, br td, $J = 14.4, 5.2$ Hz), 3.09 (1H, br t, $J = 5.6$ Hz), 2.85 (1H, td, $J = 14.4, 8.0$ Hz), 1.55 (9H, s), 1.26 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.8 (C, N-C=O), 166.3 (C, O-C=O), 153.8 (C, N-CO₂), 148.2 (C), 147.7 (C), 146.4 (CH), 138.8 (C), 134.5 (C), 130.7 (2 x CH), 129.6 (2 x CH), 128.9 (CH), 127.3 (C), 125.1 (CH), 124.5 (CH), 123.8 (CH), 122.7 (C), 122.2 (C), 117.8 (CH), 115.7 (CH), 114.5 (CH), 114.2 (CH), 84.7 (C), 76.7 (CH), 60.3 (CH₂), 55.6 (CH₃, OCH_3), 53.6 (C), 43.4 (CH), 36.4 (CH₂), 28.0 (3 x CH₃), 14.3 (CH₃); HRMS m/z 670.1418 (M + Na), calcd for $\text{C}_{34}\text{H}_{34}\text{BrNO}_7\text{Na}$ 670.1417.

(2*S*,3*S*,4*R*)-tert-butyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2-(4-nitrophenyl)-2'-

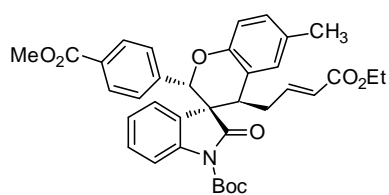


7gh

oxospiro[chroman-3,3'-indoline]-1'-carboxylate (7gh):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous liquid. 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), $t_R = 58.49$ min (minor), $t_R = 67.10$ min (major). $[\alpha]_D^{25} = -8.83^\circ$ ($c = 1.0$ g/100 mL, CHCl_3 , 96% *ee*); IR (Neat): ν_{max} 2918, 1787, 1732, 1712, 1523, 1497, 1368, 1149, 1066, 823 and 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.94 (2H, d, $J = 8.8$ Hz), 7.52 (1H, d, $J = 8.4$ Hz), 7.26- 7.20 (3H, m), 7.03-6.89 (4H, m), 6.76 (1H, d, $J = 7.6$ Hz), 6.57 (1H, d, $J = 2.8$ Hz), 5.88 (1H, d, $J = 15.2$ Hz), 5.63 (1H, s), 4.16 (2H, q, $J = 7.2$ Hz), 3.76 (3H, s, OCH_3), 3.41 (1H, br td, $J = 14.8, 5.6$ Hz), 3.11 (1H, t, $J = 5.6$ Hz), 2.86 (1H, br td, $J = 14.8, 7.6$ Hz), 1.54 (9H, s), 1.27 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.6 (C, N-C=O), 166.2 (C, O-C=O), 154.1 (C, N-CO₂), 148.1 (C), 147.8 (C), 147.3 (C), 146.0 (CH), 142.8 (C), 138.5 (C), 129.2 (CH), 128.9 (2 x CH), 126.8 (C), 125.1 (CH), 124.7 (CH), 123.9 (CH), 122.7 (2 x CH), 122.0 (C), 117.7 (CH), 115.9 (CH), 114.5 (CH), 114.2 (CH), 85.0 (C), 76.4 (CH), 60.3 (CH₂), 55.7 (CH₃, OCH_3), 53.7 (C), 43.4 (CH), 36.3 (CH₂), 27.9 (3 x CH₃), 14.3 (CH₃); HRMS m/z 637.2160 (M + Na), calcd for C₃₄H₃₄N₂O₉Na 637.2162.

(2*S*,3*S*,4*R*)-tert-butyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-2-(4-(methoxycarbonyl)phenyl)-6-methyl-2'-oxospiro[chroman-3,3'-indoline]-1'-carboxylate (7ki):

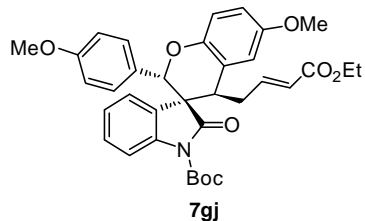


7ki

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow solid with M.P. 52°C. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2 column (hexane/2-propanol = 95:5, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 30.69$ min (major), $t_R = 41.52$ min (minor). $[\alpha]_D^{25} = -6.32^\circ$ ($c = 1.0$ g/100 mL, CHCl_3 , 98% *ee*); IR (Neat): ν_{max} 2981, 1789, 1749, 1719, 1652, 1606, 1498, 1479, 1369, 1277, 1150, 816 and 752 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.77 (2H, d, $J = 7.6$ Hz), 7.53 (1H, d, $J = 8.0$ Hz), 7.21 (1H, t, $J = 8.0$ Hz), 7.14-7.09 (3H, m), 7.04-6.95 (3H, m), 6.88 (1H, s), 6.75 (1H, d, $J = 7.6$ Hz), 5.88 (1H, d, $J = 15.6$ Hz), 5.61 (1H, s), 4.18 (2H, q, $J = 7.2$ Hz), 3.86 (3H, s, CO_2CH_3), 3.43

(1H, br td, $J = 14.8, 5.6$ Hz), 3.09 (1H, t, $J = 5.6$ Hz), 2.86 (1H, br td, $J = 14.4, 7.6$ Hz), 2.32 (3H, s, Ar-CH₃), 1.54 (9H, s), 1.29 (3H, t, $J = 7.2$ Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 173.7 (C, N-C=O), 166.7 (C, O-C=O), 166.3 (C, O-C=O), 151.6 (C, N-CO₂), 148.3 (C), 146.4 (CH), 140.5 (C), 138.7 (C), 130.84 (C), 130.80 (CH), 130.0 (C), 129.7 (CH), 128.8 (CH), 128.8 (2 x CH), 127.9 (2 x CH), 127.4 (C), 125.0 (CH), 124.4 (CH), 123.6 (CH), 121.5 (C), 116.6 (CH), 114.4 (CH), 84.6 (C), 77.1 (CH), 60.2 (CH₂), 53.7 (C), 52.1 (CH₃, OCH₃), 43.1 (CH), 36.5 (CH₂), 27.9 (3 x CH₃), 20.7 (CH₃), 14.3 (CH₃); HRMS m/z 634.2418 (M + Na), calcd for C₃₆H₃₇NO₈Na 634.2417.

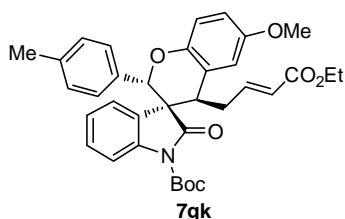
(2*S*,3*S*,4*R*)-tert-butyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2-(4-methoxyphenyl)-2'-oxospiro[chroman-3,3'-indoline]-1'-carboxylate (7gj):



Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as colour less viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2

column (hexane/2-propanol = 95:5, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 32.5$ min (major), $t_R = 57.4$ min (minor). $[\alpha]_D^{25} = -7.46^\circ$ ($c = 0.24$ g/100 mL, CHCl₃, 96% *ee*); IR (Neat): ν_{\max} 2932, 1788, 1716, 1652, 1612, 1514, 1497, 1478, 1346, 1306, 1247, 1209, 1148, 1034, 834 and 751 cm⁻¹; ¹H NMR (CDCl₃) δ 7.59 (1H, d, $J = 8.0$ Hz), 7.24 (1H, dt, $J = 6.4, 0.8$ Hz), 7.06-6.97 (3H, m), 6.91-6.89 (3H, m), 6.78 (1H, dd, $J = 8.0, 0.8$ Hz), 6.62 (2H, td, $J = 7.2, 1.6$ Hz), 6.58 (1H, d, $J = 3.0$ Hz), 5.88 (1H, d, $J = 15.5$ Hz), 5.48 (1H, s), 4.18 (2H, q, $J = 7.5$ Hz), 3.78 (3H, s, OCH₃), 3.72 (3H, s, OCH₃), 3.45 (1H, br td, $J = 14.5, 5.5$ Hz), 3.10 (1H, t, $J = 6.5$ Hz), 2.87 (1H, br td, $J = 15.0, 7.5$ Hz), 1.55 (9H, s), 1.28 (3H, t, $J = 7.5$ Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 173.9 (C, N-C=O), 166.3 (C, O-C=O), 159.6 (C, N-CO₂), 153.7 (C), 148.5 (C), 148.2 (C), 146.6 (CH), 138.9 (CH), 129.2 (2 x CH), 128.6 (CH), 127.9 (C), 127.5 (C), 125.1 (CH), 124.3 (CH), 123.6 (CH), 122.4 (C), 117.8 (CH), 115.7 (CH), 114.4 (CH), 114.2 (C), 113.0 (2 x CH), 84.3 (C), 77.2 (CH), 60.2 (CH₂), 55.7 (CH₃, OCH₃), 55.1 (CH₃, OCH₃), 53.7 (C), 43.6 (CH), 36.4 (CH₂), 28.0 (3 x CH₃), 14.2 (CH₃); HRMS m/z 622.2418 (M + Na), calcd for C₃₅H₃₇NO₈Na 622.2417.

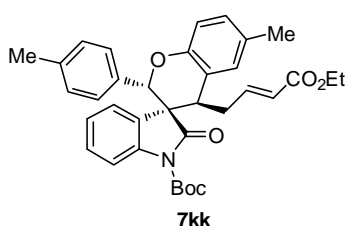
(2S,3S,4R)-tert-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2'-oxo-2-(p-



tolyl)spiro[chroman-3,3'-indoline]-1'-carboxylate (7gk):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2 column (hexane/2-propanol = 98:2, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 23.83$ min (major), $t_R = 58.65$ min (minor). $[\alpha]_D^{25} = -18.2^\circ$ ($c = 1.0$ g/100 mL, CHCl_3 , 96% *ee*); IR (Neat): ν_{max} 2923, 1789, 1755, 1720, 1604, 1479, 1277, 1252, 1148, 1105, 1045, 841 and 751 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.57 (1H, d, $J = 8.0$ Hz), 7.22 (1H, t, $J = 7.8$ Hz), 7.06-6.94 (3H, m), 6.89-6.83 (5H, m), 6.76 (1H, d, $J = 7.2$ Hz), 6.57 (1H, d, $J = 3.2$ Hz), 5.86 (1H, d, $J = 15.6$ Hz), 5.48 (1H, s), 4.16 (2H, q, $J = 7.2$ Hz), 3.76 (3H, s, OCH_3), 3.44 (1H, br td, $J = 14.4, 5.2$ Hz), 3.09 (1H, t, $J = 6.4$ Hz), 2.85 (1H, br td, $J = 14.4, 8.0$ Hz), 2.21 (3H, s, Ar- CH_3), 1.53 (9H, s), 1.27 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 173.8 (C, N-C=O), 166.3 (C, O-C=O), 153.7 (C, N-CO₂), 148.5 (C), 148.1 (CH), 146.7 (CH), 138.9 (C), 138.1 (CH), 132.4 (CH), 128.6 (C), 128.3 (2 x CH), 127.9 (C), 127.8 (2 x CH), 125.1 (CH), 124.3 (C), 123.6 (CH), 122.4 (C), 117.8 (CH), 115.6 (CH), 114.3 (C), 114.2 (CH), 84.2 (C), 77.4 (CH), 60.2 (CH₂), 55.7 (CH₃, OCH₃), 53.7 (C), 43.5 (CH), 36.4 (CH₂), 27.9 (3 x CH₃), 21.1 (CH₃, Ar- CH_3), 14.2 (CH₃); HRMS m/z 606.2468 (M + Na), calcd for C₃₅H₃₇NO₇Na 606.2468.

(2S,3S,4R)-tert-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methyl-2'-oxo-2-(p-

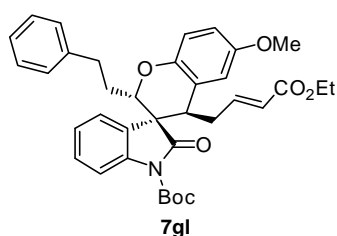


tolyl)spiro[chroman-3,3'-indoline]-1'-carboxylate (7kk):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Chiral Lux 5u Cellulose-2 column (hexane/2-propanol = 95:5, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 12.86$ min (major), $t_R = 17.12$ min (minor). $[\alpha]_D^{25} = -20.7^\circ$ ($c = 0.58$ g/100 mL, CHCl_3 , 96% *ee*); IR (Neat): ν_{max} 2977, 2361, 1763, 1723, 1697, 1347, 1251, 1149, 1100, 820 and 770 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.57 (1H, d, $J = 8.0$ Hz), 7.21 (1H, t, $J = 8.0$ Hz), 7.09 (1H, d, $J = 8.4$ Hz), 7.02-6.93 (3H, m), 6.90-6.84 (5H, m), 6.74 (1H, d, $J = 7.6$ Hz), 5.85 (1H, d, $J = 15.6$ Hz), 5.48 (1H, s), 4.17 (2H, q,

$J = 7.2$ Hz), 3.43 (1H, br td, $J = 14.8, 5.6$ Hz), 3.07 (1H, t, $J = 6.4$ Hz), 2.84 (1H, br td, $J = 14.8, 7.6$ Hz), 2.30 (3H, s, Ar-CH₃), 2.22 (3H, s, Ar-CH₃), 1.53 (9H, s), 1.27 (3H, t, $J = 7.2$ Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 173.8 (C, N-C=O), 166.4 (C, O-C=O), 152.0 (C, N-CO₂), 148.5 (C), 146.8 (CH), 138.9 (C), 138.1 (C), 132.4 (C), 130.8 (CH), 130.5 (C), 129.5 (CH), 128.6 (CH), 128.3 (2 x CH), 128.0 (C), 127.8 (2 x CH), 125.1 (CH), 124.3 (CH), 123.4 (CH), 121.7 (C), 116.7 (CH), 114.3 (CH), 84.2 (C), 77.3 (CH), 60.2 (CH₂), 53.7 (C), 43.2 (CH), 36.6 (CH₂), 27.9 (3 x CH₃), 21.1 (CH₃), 20.7 (CH₃), 14.3 (CH₃); HRMS m/z 590.2517 (M + Na), calcd for C₃₅H₃₇NO₆Na 590.2519.

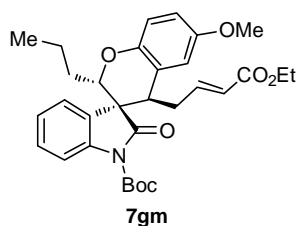
(2S,3S,4R)-tert-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2'-oxo-2-



phenethylspiro[chroman-3,3'-indoline]-1'-carboxylate (7gl):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale colourless liquid. 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), $t_R = 15.52$ min (major), $t_R = 19.18$ min (minor). $[\alpha]_D^{25} = -13.6^\circ$ ($c = 0.42$ g/100 mL, CHCl₃, 98% *ee*); IR (Neat): ν_{\max} 2922, 1789, 1736, 1711, 1676, 1616, 1596, 1456, 1304, 1245, 1177, 1149, 1001 and 751 cm⁻¹; ¹H NMR (CDCl₃) δ 7.81 (1H, d, $J = 8.4$ Hz), 7.27-7.23 (3H, m), 7.17-7.14 (3H, m), 6.99-6.85 (4H, m), 6.68 (1H, d, $J = 7.2$ Hz), 6.46 (1H, d, $J = 2.8$ Hz), 5.78 (1H, d, $J = 15.6$ Hz), 4.49 (1H, dd, $J = 10.4, 1.6$ Hz), 4.16 (2H, q, $J = 7.2$ Hz), 3.73 (3H, s, OCH₃), 3.19 (1H, br td, $J = 14.4, 5.6$ Hz), 3.05-2.98 (1H, m), 2.89 (1H, t, $J = 6.8$ Hz), 2.76-2.68 (1H, m), 2.63 (1H, br td, $J = 14.8, 7.6$ Hz), 1.71-1.56 (1H, m), 1.66 (9H, s), 1.52-1.36 (1H, m), 1.26 (3H, t, $J = 7.2$ Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 174.7 (C, N-C=O), 166.2 (C, O-C=O), 153.5 (C, N-CO₂), 148.8 (C), 147.5 (C), 146.6 (CH), 141.4 (C), 138.8 (C), 128.6 (3 x CH), 128.4 (C), 128.4 (2 x CH), 125.9 (CH), 124.8 (CH), 124.7 (CH), 123.4 (CH), 122.3 (C), 117.5 (CH), 115.5 (CH), 114.6 (CH), 114.2 (CH), 84.8 (C), 74.4 (CH), 60.2 (CH₂), 55.6 (CH₃, OCH₃), 52.1 (C), 43.8 (CH), 36.4 (CH₂), 33.1 (CH₂), 32.1 (CH₂), 28.1 (3 x CH₃), 14.3 (CH₃); HRMS m/z 620.2628 (M + Na), calcd for C₃₆H₃₉NO₇Na 620.2625.

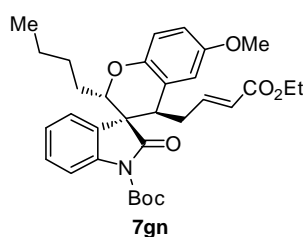
(2S,3S,4R)-tert-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2'-oxo-2-



propylspiro[chroman-3,3'-indoline]-1'-carboxylate (7gm):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as colour less viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Lux 5u Amylose-2 column (hexane/2-propanol = 99.4:0.6, flow rate 1.0 mL/min, $\lambda = 220$ nm), $t_R = 21.6$ min (minor), $t_R = 25.3$ min (major). $[\alpha]_D^{25} = -36.2^\circ$ ($c = 0.70$ g/100 mL, CHCl_3 , 94% *ee*); IR (Neat): ν_{max} 2955, 1789, 1752, 1721, 1652, 1498, 1346, 1212, 1148, 1039 and 751 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.84 (1H, d, $J = 8.0$ Hz), 7.27 (1H, t, $J = 6.8$ Hz), 6.95-6.88 (3H, m), 6.84-6.81 (1H, m), 6.64 (1H, d, $J = 7.2$ Hz), 6.45 (1H, d, $J = 2.8$ Hz), 5.77 (1H, d, $J = 15.6$ Hz), 4.43 (1H, dd, $J = 10.4, 1.6$ Hz), 4.14 (2H, q, $J = 7.2$ Hz), 3.71 (3H, s, OCH_3), 3.19 (1H, br td, $J = 14.8, 5.6$ Hz), 2.88 (1H, t, $J = 6.4$ Hz), 2.64 (1H, br td, $J = 14.4, 8.0$ Hz), 1.72-1.66 (1H, m), 1.66 (9H, s), 1.53-1.37 (1H, m), 1.25 (3H, t, $J = 7.2$ Hz), 1.27-1.18 (1H, m), 1.15-1.03 (1H, m), 0.85 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 174.8 (C, N-C=O), 166.2 (C, O-C=O), 153.4 (C, N-CO₂), 149.0 (C), 147.6 (C), 146.6 (CH), 138.8 (C), 128.6 (C), 128.5 (CH), 124.8 (CH), 124.6 (CH), 123.3 (CH), 122.3 (C), 117.4 (CH), 115.4 (CH), 114.5 (CH), 114.2 (CH), 84.7 (C), 74.7 (CH), 60.2 (CH₂), 55.6 (CH₃, OCH₃), 52.2 (C), 43.8 (CH), 36.4 (CH₂), 33.1 (CH₂), 28.1 (3 x CH₃), 19.0 (CH₂), 14.2 (CH₃), 13.7 (CH₃); HRMS m/z 536.2647 (M + H), calcd for C₃₁H₃₇NO₇H 536.2648.

(2S,3S,4R)-tert-butyl-2-butyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-6-methoxy-2'-

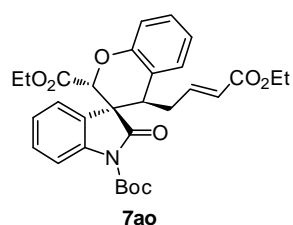


oxospiro[chroman-3,3'-indoline]-1'-carboxylate (7gn):

Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as colour less viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Lux 5u Amylose-2 column (hexane/2-propanol = 98.5:1.5, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R = 22.2$ min (minor), $t_R = 23.3$ min (major). $[\alpha]_D^{25} = -46.6^\circ$ ($c = 1.0$ g/100 mL, CHCl_3 , 96% *ee*); IR (Neat): ν_{max} 2955, 1790, 1749, 1721, 1652, 1498, 1346, 1212, 1148, 1039 and 752 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.84 (1H, d, $J = 8.4$ Hz), 7.26 (1H, br t, $J = 6.4$ Hz), 6.95-6.87 (3H, m), 6.84-6.81 (1H, m), 6.64 (1H, d, $J = 7.6$ Hz), 6.45 (1H, d, $J = 2.8$ Hz), 5.77 (1H, d, $J = 15.6$ Hz), 4.42 (1H, dd, $J = 10., 0.8$ Hz), 4.14 (2H, q, $J = 7.2$ Hz),

3.71 (3H, s, OCH₃), 3.19 (1H, br td, *J* = 14.8, 6.0 Hz), 2.88 (1H, t, *J* = 6.4 Hz), 2.63 (1H, br td, *J* = 14.8, 8.0 Hz), 1.66 (9H, s), 1.62-1.54 (1H, m), 1.43-1.35 (1H, m), 1.30-1.20 (3H, m), 1.25 (3H, t, *J* = 7.2 Hz), 1.15-1.06 (1H, m), 0.84 (3H, t, *J* = 7.6 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 174.8 (C, N-C=O), 166.2 (C, O-C=O), 153.4 (C, N-CO₂), 149.0 (C), 147.6 (C), 146.6 (CH), 138.8 (C), 128.6 (C), 128.5 (CH), 124.8 (CH), 124.6 (CH), 123.3 (CH), 122.3 (C), 117.4 (CH), 115.4 (CH), 114.4 (CH), 114.2 (CH), 84.7 (C), 74.9 (CH), 60.2 (CH₂), 55.6 (CH₃, OCH₃), 52.3 (C), 43.8 (CH), 36.4 (CH₂), 30.9 (CH₂), 28.1 (3 x CH₃), 28.0 (CH₂), 22.3 (CH₂), 14.2 (CH₃), 14.0 (CH₃); HRMS *m/z* 572.2625 (M + Na), calcd for C₃₂H₃₉NO₇Na 572.2625.

(2*R*,3*S*,4*R*)-1'-*tert*-butyl-2-ethyl-4-((*E*)-4-ethoxy-4-oxobut-2-en-1-yl)-2'-oxospiro[chroman-

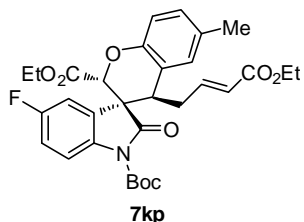


7ao

3,3'-indoline]-1',2-dicarboxylate (7ao): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as colour less viscous liquid. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol =

95:5, flow rate 1.0 mL/min, λ = 254 nm), *t_R* = 8.35 min (minor), *t_R* = 11.16 min (major). [α]_D²⁵ = -33.96° (*c* = 0.83 g/100 mL, CHCl₃, 94% *ee*); IR (Neat): ν_{max} 2922, 2852, 1790, 1736, 1711, 1676, 1616, 1596, 1456, 1304, 1248, 1177, 1149, 1086, 1001 and 751 cm⁻¹; ¹H NMR (CDCl₃) δ 7.82 (1H, d, *J* = 8.0 Hz), 7.34-7.17 (3H, m), 6.95 (1H, t, *J* = 7.6 Hz), 6.89-6.80 (3H, m), 6.70 (1H, d, *J* = 7.2 Hz), 5.74 (1H, d, *J* = 15.6 Hz), 5.31 (1H, s), 4.13 (2H, q, *J* = 7.2 Hz), 3.85 (2H, m), 3.21-3.13 (1H, m), 2.92 (1H, dd, *J* = 8.8, 4.4 Hz), 2.61 (1H, br td, *J* = 14.4, 8.4 Hz), 1.68 (9H, s), 1.24 (3H, t, *J* = 7.2 Hz), 0.89 (3H, t, *J* = 7.2 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 173.4 (C, N-C=O), 167.5 (C, O-C=O), 165.7 (C, O-C=O), 153.0 (C, N-CO₂), 149.0 (C), 145.3 (CH), 139.0 (C), 130.0 (CH), 129.2 (CH), 129.0 (CH), 128.0 (C), 124.3 (CH), 124.2 (CH), 123.9 (CH), 122.2 (C), 121.8 (CH), 117.3 (CH), 114.5 (CH), 84.8 (C), 75.8 (CH), 61.6 (CH₂), 60.2 (CH₂), 51.4 (C), 43.6 (CH), 34.2 (CH₂), 28.1 (3 x CH₃), 14.2 (CH₃), 13.4 (CH₃); HRMS *m/z* 558.2104 (M + Na), calcd for C₃₀H₃₃NO₈Na 558.2104.

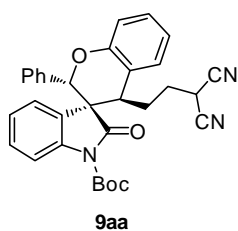
(2R,3S,4R)-1'-tert-butyl-2-ethyl-4-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-5'-fluoro-6-methyl-2'-oxospiro[chroman-3,3'-indoline]-1',2-dicarboxylate (7kp): Prepared by following the



procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow viscous 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, $\lambda = 254$ nm), $t_R = 17.4$ min (major), $t_R =$

28.8 min (minor). $[\alpha]_D^{25} = -18.8^\circ$ ($c = 0.36$ g/100 mL, CHCl_3 , 92% *ee*); IR (Neat): ν_{max} 2978, 1790, 1762, 1729, 1480, 1247, 1147, 1090, 817 and 734 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.84 (1H, dd, $J = 9.2, 4.8$ Hz), 7.11-7.06 (3H, m), 6.99 (1H, dt, $J = 8.8, 2.8$ Hz), 6.71-6.64 (1H, m), 6.60 (1H, dd, $J = 8.0, 2.8$ Hz), 5.36 (1H, d, $J = 15.6$ Hz), 4.92 (1H, s), 4.10 (2H, q, $J = 7.2$ Hz), 4.04-3.97 (2H, m), 3.92 (1H, t, $J = 6.4$ Hz), 2.48 (1H, br td, $J = 16.0, 6.4$ Hz), 2.31 (3H, s, Ar- CH_3), 2.25 (1H, br td, $J = 16.4, 1.8$ Hz), 1.65 (9H, s), 1.24 (3H, t, $J = 7.2$ Hz), 1.03 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 174.5 (C, N-C=O), 166.3 (C, O-C=O), 165.6 (C, O-C=O), 159.6 (C, d, $J = 243$ Hz, C-F), 150.3 (C, N-CO₂), 148.7 (C), 144.3 (CH), 136.4 (C), 132.1 (C), 129.5 (CH), 127.5 (CH), 126.0 (C, d, $J = 9.0$ Hz), 122.8 (CH), 121.6 (C), 117.3 (CH), 116.1 (CH, d, $J = 5.0$ Hz), 116.0 (CH, d, $J = 19$ Hz), 113.3 (CH, d, $J = 24$ Hz), 84.9 (C), 78.2 (CH), 61.9 (CH₂), 60.2 (CH₂), 52.1 (C), 41.4 (CH), 32.9 (CH₂), 28.1 (3 x CH₃), 20.1 (CH₃), 14.2 (CH₃), 13.6 (CH₃); HRMS m/z 568.2348 (M + H), calcd for C₃₁H₃₄FNO₈H 568.2346.

(2S,3S,4R)-tert-butyl-4-(3,3-dicyanopropyl)-2'-oxo-2-phenylspiro[chroman-3,3'-indoline]-

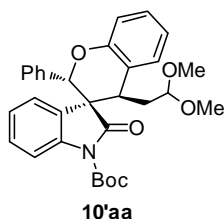


1'-carboxylate (9aa): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as pale brown solid with M.P 69°C. The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 95:5, flow rate 0.6 mL/min, $\lambda = 254$ nm), $t_R = 28.45$

min (major), $t_R = 33.63$ min (minor). $[\alpha]_D^{25} = +1.45^\circ$ ($c = 0.41$ g/100 mL, CHCl_3 , 98% *ee*); IR (Neat): ν_{max} 2926, 2252, 1784, 1744, 1607, 1484, 1313, 1252, 1151, 840 and 755 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.53 (1H, d, $J = 8.4$ Hz), 7.36 (1H, t, $J = 7.2$ Hz), 7.24-7.06 (7H, m), 6.99- 6.95 (3H, m), 6.70 (1H, d, $J = 7.6$ Hz), 5.50 (1H, s), 3.81 (1H, t, $J = 7.6$ Hz), 3.04 (1H, t, $J = 5.6$ Hz), 2.81-2.74 (1H, m), 2.44-2.35 (1H, m), 2.29-2.20 (1H, m), 2.10-2.02 (1H, m), 1.54 (9H, s); ^{13}C NMR

(CDCl₃, DEPT-135) δ 174.1 (C, N-C=O), 154.1 (C, N-CO₂), 148.2 (C), 138.7 (C), 134.9 (C), 130.0 (CH), 129.2 (CH), 128.9 (CH), 128.7 (CH), 127.8 (2 x CH), 127.7 (C), 127.6 (2 x CH), 124.9 (CH), 124.5 (CH), 122.0 (CH), 121.8 (C), 117.4 (CH), 114.3 (CH), 112.4 (2 x C, CN), 84.7 (C), 77.8 (CH), 53.7 (C), 43.1 (CH), 31.4 (CH₂), 29.9 (CH₂), 28.0 (3 x CH₃), 22.7 (CH); HRMS *m/z* 542.2058 (M+Na), calcd for C₃₂H₂₉N₃O₄Na 542.2056.

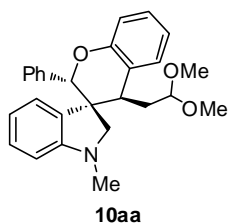
(2*S*,3*S*,4*R*)-tert-butyl-4-(2,2-dimethoxyethyl)-2'-oxo-2-phenylspiro[chroman-3,3'-indoline]-



1'-carboxylate (10'aa): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as colour less viscous liquid; $[\alpha]_D^{25} = +18.1^\circ$ (*c* = 0.71 g/100 mL, CHCl₃, 99% *ee*); IR (Neat): ν_{\max} 2980, 1786, 1731, 1483, 1249, 1150, 1056, 909 and 728 cm⁻¹; ¹H NMR (CDCl₃) δ 7.56 (1H, d, *J* = 8.0 Hz), 7.32-7.28 (1H, m), 7.21-

7.14 (3H, m), 7.11-6.90 (7H, m), 6.64 (1H, d, *J* = 8.0 Hz), 5.61 (1H, s), 4.43 (1H, t, *J* = 6.0 Hz), 3.36 (3H, s, OCH₃), 3.34 (3H, s, OCH₃), 3.17-3.10 (2H, m), 2.04-1.96 (1H, m), 1.54 (9H, s); ¹³C NMR (CDCl₃, DEPT-135) δ 173.9 (C, N-C=O), 154.0 (C, N-CO₂), 148.6 (C), 138.8 (C), 135.6 (C), 130.7 (CH), 128.5 (2 x CH), 128.4 (CH), 128.1 (C), 128.0 (2 x CH), 127.6 (2 x CH), 125.1 (CH), 124.1 (CH), 123.6 (C), 121.4 (CH), 116.8 (CH), 114.2 (CH), 103.0 (CH, CH(OCH₃)₂), 84.2 (C), 77.4 (CH), 53.5 (CH₃, OCH₃), 53.3 (C), 52.7 (CH₃, OCH₃), 39.8 (CH), 36.4 (CH₂), 28.0 (3 x CH₃); HRMS *m/z* 538.2207 (M+Na), calcd for C₃₁H₃₃NO₆Na 538.2206.

(2*S*,3*R*,4*S*)-tert-butyl-4-(2,2-dimethoxyethyl)-2-phenylspiro[chroman-3,3'-indoline]-1'-

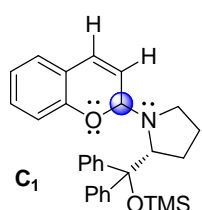


carboxylate (10aa): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as pale yellow gummy solid. $[\alpha]_D^{25} = -23.85^\circ$ (*c* = 0.21 g/100 mL, CHCl₃, 99% *ee*); IR (Neat): ν_{\max} 3035, 2934, 1605, 1584, 1487, 1454, 1233, 1123, 1053, and 751 cm⁻¹; ¹H NMR (C₆D₆) δ 7.41 (1H, d, *J* = 7.5 Hz), 7.15-7.10 (1H, m),

7.02-6.89 (8H, m), 6.69 (1H, d, *J* = 7.5 Hz), 6.48 (1H, t, *J* = 7.5 Hz), 6.03 (1H, d, *J* = 8.0 Hz), 5.16 (1H, s), 4.59 (1H, dd, *J* = 8.0, 3.5 Hz), 3.33 (1H, dd, *J* = 9.5, 2.5 Hz), 3.10 (3H, s, OCH₃), 3.06 (3H, s, OCH₃), 3.06 (1H, d, *J* = 9.5 Hz), 2.98 (1H, d, *J* = 9.0 Hz), 2.02 (3H, s, NCH₃), 2.01 (1H, ddd, *J* = 12.5, 10.5, 3.0 Hz), 1.87 (1H, ddd, *J* = 14.0, 10.0, 4.0 Hz); ¹³C NMR (C₆D₆, DEPT-135) δ 155.4 (C), 153.9 (C), 138.4 (C), 130.4 (C), 130.4 (CH), 129.0 (CH), 128.6 (CH), 128.3 (2 x CH), 128.0 (CH), 127.3 (2 x CH), 126.0 (CH), 125.6 (C), 120.7 (CH), 117.6 (CH), 117.0 (CH),

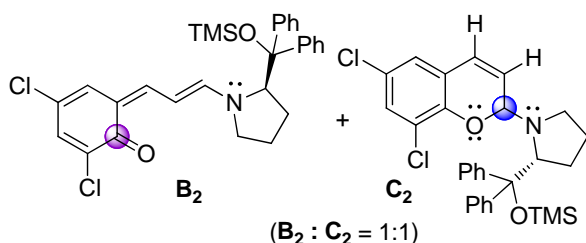
106.9 (CH), 103.3 (CH, CH(OCH₃)₂), 80.3 (CH), 62.5 (CH₂), 53.6 (CH₃, OCH₃), 51.6 (CH₃, OCH₃), 49.6 (C), 39.3 (CH), 37.2 (CH₂), 34.5 (CH₃, NCH₃); HRMS m/z 416.2225 (M+H), calcd for C₂₇H₂₉NO₃H 416.2225.

In situ formation and detection of aiminal intermediate (C₁): Experiment performed in NMR



tube with the each 0.05 mmol of **1a** and (*R*)-**3** in CDCl₃ (0.4 mL) at room temperature, within 10 min crude compound NMR recorded in 500 MHz NMR machine. Analysis of crude compound NMR revealed that intermediate **C₁** is formed almost as single compound along with starting material. IR (Neat): ν_{\max} 3058, 2954, 1665, 1585, 1487, 1447, 1250, 1069, 839 and 703 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.56 (2H, d, *J* = 7.0 Hz), 7.50 (2H, d, *J* = 6.5 Hz), 7.37-7.28 (6H, m), 7.12 (1H, dt, *J* = 8.0, 1.5 Hz), 6.97 (1H, dd, *J* = 7.5, 1.5 Hz), 6.87-6.79 (2H, m), 6.48 (1H, d, *J* = 10.0 Hz, olefinic-*H*), 5.92 (1H, br s, O-CH-N), 5.58 (1H, dd, *J* = 10.0, 3.0 Hz, olefinic-*H*), 4.66 (1H, dd, *J* = 9.0, 4.0 Hz, N-CH), 2.66 (1H, q, *J* = 7.5 Hz), 2.37-2.31 (1H, m), 2.10-2.06 (1H, m), 1.80-1.75 (1H, m), 1.30-1.24 (1H, m), 0.70-0.66 (1H, m), -0.14 (9H, s, 3 x CH₃); ¹³C NMR (CDCl₃, 125 MHz, DEPT-135) δ 155.2 (C), 143.9 (C), 143.6 (C), 129.8 (2 x CH), 129.6 (2 x CH), 129.1 (CH), 127.3 (2 x CH), 127.2 (CH), 127.0 (CH), 126.9 (2 x CH), 126.6 (CH), 125.1 (CH), 122.8 (CH), 120.4 (C), 119.7 (CH), 115.0 (CH), 89.0 (CH, O-CH-N), 84.8 (C), 67.1 (CH, N-CH), 46.0 (CH₂), 29.6 (CH₂), 24.7 (CH₂), 1.9 (3 x CH₃); HRMS m/z 456.2359 (M + H), calcd for C₂₉H₃₄NO₂Si 456.2359.

In situ formation and detection of *o*-quinone methide and aiminal intermediates (B₂ and C₂): Experiment performed in NMR tube with **1e** and (*R*)-**3** (each 0.1 mmol) in CDCl₃ (0.4 mL)

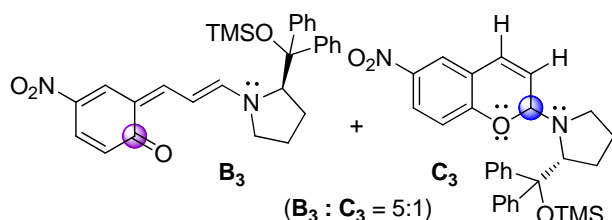


at room temperature, within 10-20 min crude compound NMR was recorded in 400 MHz NMR machine. Analysis of crude compound NMR revealed that intermediates **B₂** and **C₂** are there in almost 1:1 ratio. IR (Neat): ν_{\max} 3060, 2953, 1588, 1491, 1457, 1250, 1068, 875, 839 and 703 cm⁻¹; **Intermediate B₂**: ¹H NMR (CDCl₃, 400 MHz) δ 7.85 (1H, d, *J* = 11.2 Hz), 7.40-7.33 (5H, m), 7.26-7.23 (6H, m), 7.16 (1H, d, *J* = 2.4 Hz), 6.97 (1H, s), 6.84 (1H, d, *J* = 2.0 Hz), 4.68 (1H, br d, *J* = 4.8 Hz), 3.39-3.34 (1H, m),

2.44-2.39 (1H, m), 2.38-2.33 (1H, m), 2.13-2.07 (1H, m), 1.70-1.66 (1H, m), 1.09-1.04 (1H, m), -0.17 (9H, s, 3 x CH₃); ¹³C NMR (CDCl₃, 100 MHz, DEPT-135) δ 171.9 (C, C=O), 160.0 (CH), 149.4 (C), 143.9 (C), 139.9 (C), 134.0 (CH), 129.5 (CH), 128.8 (3 x CH), 128.76 (2 x CH), 128.67 (2 x CH), 128.5 (CH), 128.0 (2 x CH), 127.7 (CH), 124.4 (CH), 123.0 (C), 122.6 (C), 83.6 (C, TMSO-C), 73.6 (CH, N-CH), 50.4 (CH₂), 26.8 (CH₂), 22.4 (CH₂), 1.6 (3 x CH₃).

Intermediate C₂: ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (2H, d, *J* = 7.2 Hz), 7.46 (2H, d, *J* = 8.0 Hz), 7.34-7.32 (4H, m), 7.30-7.28 (4H, m), 6.38 (1H, d, *J* = 10.0 Hz, olefinic-*H*), 6.00 (1H, br s, O-CH-N), 5.63 (1H, br d, *J* = 8.4 Hz, olefinic-*H*), 4.75 (1H, d, *J* = 8.0 Hz), 2.47-2.45 (1H, m), 2.30-2.27 (1H, m), 2.05-1.97 (1H, m), 1.78-1.75 (1H, m), 1.30-1.20 (1H, m), 0.71 (1H, br s), -0.19 (9H, s, 3 x CH₃); ¹³C NMR (CDCl₃, 100 MHz, DEPT-135) δ 164.4 (C), 143.4 (C), 140.8 (C), 129.7 (2 x CH), 129.5 (2 x CH), 129.2 (CH), 127.4 (2 x CH), 127.3 (CH), 127.1 (CH), 127.0 (2 x CH), 124.7 (CH), 124.0 (CH), 123.9 (2 x C), 120.6 (CH), 114.6 (C), 90.3 (CH, br s, O-CH-N), 84.7 (C, TMSO-C), 67.1 (CH, N-CH), 46.1 (CH₂), 29.4 (CH₂), 24.5 (CH₂), 1.9 (3 x CH₃); HRMS *m/z* 524.1579 (M + H), calcd for C₂₉H₃₂Cl₂NO₂Si 524.1579.

In situ formation and detection of *o*-quinone methide and amination intermediates (B₃ and C₃):



Experiment performed in NMR tube with **1f** and (*R*)-**3** (each 0.1 mmol) in CDCl₃ (0.4 mL) at room temperature, within 10-20 min crude compound NMR was recorded in 500 MHz NMR machine. Analysis of crude

compound NMR revealed that intermediates B₃ and C₃ are there in almost 5:1 ratio.

Intermediate B₃: ¹H NMR (CDCl₃, 500 MHz) δ 8.20 (1H, d, *J* = 3.0 Hz), 8.11 (1H, d, *J* = 11.0 Hz), 7.93 (1H, dd, *J* = 10.0, 3.0 Hz), 7.42-7.40 (3H, m), 7.38-7.36 (4H, m), 7.34 (1H, br s), 7.33-7.32 (1H, m), 7.29-7.26 (3H, m), 6.49 (1H, d, *J* = 10.0 Hz), 4.95 (1H, br d, *J* = 6.5 Hz), 3.52 (1H, quin, *J* = 8.5 Hz), 2.58-2.52 (1H, m), 2.44-2.37 (1H, m), 2.13-2.08 (1H, m), 1.76-1.73 (1H, m), 1.24-1.21 (1H, m), -0.17 (9H, s, 3 x CH₃); ¹³C NMR (CDCl₃, 125 MHz, DEPT-135) δ 181.4 (C, C=O), 166.1 (CH), 162.2 (CH), 140.5 (C), 139.6 (C), 133.3 (C), 129.11 (2 x CH), 129.07 (CH), 128.8 (3 x CH), 128.75 (3 x CH), 128.71 (CH), 128.2 (2 x CH), 125.4 (CH), 121.3 (C), 115.4 (CH), 83.6 (C, TMSO-C), 74.4 (CH, N-CH), 51.0 (CH₂), 26.7 (CH₂), 22.5 (CH₂), 1.6 (3 x CH₃).

Intermediate C₃: ¹H NMR (CDCl₃, 500 MHz) δ 8.00 (1H, dd, *J* = 9.0, 3.0 Hz), 7.87 (1H, d, *J* =

3.0 Hz), 7.49 (2H, d, $J = 2.0$ Hz), 7.47 (2H, d, $J = 1.5$ Hz), 7.45-7.42 (3H, m), 7.31-7.30 (1H, m), 7.24 (1H, br s), 7.23 (1H, t, $J = 1.5$ Hz), 7.22-7.20 (1H, m), 6.85 (1H, d, $J = 9.0$ Hz, olefinic- H), 6.09 (1H, br s, O-CH-N), 5.67 (1H, dd, $J = 10.0, 3.0$ Hz, olefinic- H), 4.59 (1H, dd, $J = 9.0, 4.0$ Hz), 2.52-2.46 (1H, m), 2.37-2.30 (1H, m), 2.06-2.00 (1H, m), 1.72-1.65 (1H, m), 1.21-1.18 (1H, m), 0.91-0.82 (1H, m), -0.18 (9H, s, 3 x CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 161.0 (C), 143.6 (C), 129.6 (2 x CH), 129.5 (2 x CH), 129.4 (2 x CH), 128.3 (CH), 127.8 (2 x C), 127.7 (2 x CH), 127.5 (CH), 127.0 (CH), 124.4 (CH), 124.0 (CH), 122.6 (CH), 120.0 (C), 112.3 (CH), 91.4 (CH, O-CH-N), 84.8 (C, TMSO-C), 67.1 (CH, N-CH), 45.9 (CH_2), 29.4 (CH_2), 25.0 (CH_2), 1.8 (3 x CH_3); HRMS m/z 501.2209 (M + H), calcd for $C_{29}H_{33}N_2O_4Si$ 501.2210.

References:

1. (a) Z. Chen, J. Fan, A. S. Kende, *J. Org. Chem.* **2004**, *69*, 79. (b) I. P. Petrounia, J. Goldberg, E. J. Brush, *Biochemistry* **1994**, *33*, 2891. (c) T. Ishimaru, N. Shibata, J. Nagai, S. Nakamura, T. Toru, S. Kanemasa, *J. Am. Chem. Soc.* **2006**, *128*, 16488.
2. L. Zu, S. Zhang, H. Xie, W. Wang, *Org. Lett.* **2009**, *11*, 1627.

Datablock: dbr34

Bond precision: C-C = 0.0056 Å Wavelength=1.54184
Cell: a=9.2088(3) b=11.1545(3) c=13.3119(5)
alpha=90 beta=106.479(3) gamma=90
Temperature: 298 K

	Calculated	Reported
Volume	1311.23(8)	1311.23(7)
Space group	P 21	P21
Hall group	2yb	?
Moiety formula	C29 H26 Br N O5	?
Sum formula	C29 H26 Br N O5	C29 H26 Br N O5
Mr	548.41	548.42
Dx, g cm ⁻³	1.389	1.389
Z	2	2
Mu (mm ⁻¹)	2.458	2.458
F000	564.0	564.0
F000'	564.18	
h, k, lmax	11, 13, 16	10, 13, 16
Nref	5134 [2708]	4989
Tmin, Tmax	0.737, 0.782	0.271, 1.000
Tmin'	0.434	

Correction method= MULTI-SCAN
Data completeness= 1.84/0.97 Theta(max)= 71.600
R(reflections)= 0.0404(4549) wR2(reflections)= 0.1134(4989)
S = 0.819 Npar= 328

Data block dbr-34 - ellipsoid plot

