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Supporting Information-I

Sequential Combination of Michael and Acetalization Reactions: Direct Catalytic Asymmetric Synthesis of Functionalized 4-Nitromethyl-chromans as Drug Intermediates

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα ($\lambda = 0.71073$ 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

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graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

The enantiomeric excess (ee) of the *SMA* products was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column and hexane/2-propanol as the eluent or using a Daicel Chiralpak AD-H column and hexane/2-propanol as the eluent. Retention times and solvent ratios are indicated in the respective entries.

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

General Experimental Procedures for the SMA Reactions:

Procedure A: ***General procedure for amine-catalyzed asymmetric SMA reaction of acetone 1 with 2-(2-nitro-vinyl)-phenols 2:*** In an ordinary glass vial equipped with a magnetic stirring bar, to a mixture of 9-amino-9-deoxyepiquinine **3h** (16 mg, 0.05 mmol) and diphenylacetic acid (11 mg, 0.05 mmol) in DCM (2.0 mL), was added acetone **1** (1.0 mL, 7.0 mmol) and of 2-hydroxy-nitro styrene **2** (83 mg, 0.5 mmol). After stirring the reaction mixture at 25 °C for 3 days, the crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure chiral products **4↔5↔6** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: ***General procedure for amino acid-catalyzed SMA reaction of acetone 1 with 2-(2-nitro-vinyl)-phenols 2:*** In an ordinary glass vial equipped with a magnetic stirring bar, to *S*-proline **3a** (6 mg, 0.05 mmol) in DMSO (2.0 mL), was added acetone **1** (1.0 mL, 7.0 mmol) and of 2-(2-nitro-vinyl)-phenols **2** (83 mg, 0.5 mmol). After stirring the reaction mixture at 25 °C for 2h, the crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. The crude mixture was dissolved in of alcohol **7** (2.5 mL) and cooled to 0 °C, and added *p*-TSA (19 mg, 20 mol %). The mixture was stirred at the same temperature for 30 min and then brought to room temperature and stirred for another 90 min. The crude reaction mixture was worked up with aqueous $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined

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organic layers were dried (Na_2SO_4), filtered and concentrated. Pure achiral products (±)-**8** and (±)-**9** were separated by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure C: ***General procedure for amine-catalyzed asymmetric SMA reaction of acetone 1 with 2-(2-nitro-vinyl)-phenols 2:*** In an ordinary glass vial equipped with a magnetic stirring bar, to a mixture of 9-amino-9-deoxyepiquinine **3h** (16 mg, 0.05 mmol) and diphenylacetic acid (11 mg, 0.05 mmol) in DCM (2.0 mL), was added acetone **1** (1.0 mL, 7.0 mmol) and of 2-(2-nitro-vinyl)-phenols **2** (83 mg, 0.5 mmol). After stirring the reaction mixture at 25 °C for 3 days, the crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. The crude mixture was dissolved in alcohol **7** (2.5 mL) and cooled to 0 °C, and added *p*-TSA (19 mg, 20 mol %). The mixture was stirred at the same temperature for 30 min and then brought to room temperature and stirred for another 90 min. The crude reaction mixture was worked up with aqueous $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure chiral products **8** and **9** were separated by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure D: ***Brønsted acid-catalyzed hydrolysis of SMA products:*** In an oven dried round bottom flask, to the Michael adduct **4a↔5a↔6a** (46 mg, 0.2 mmol), added toluene (2 mL), and *p*-TSA.H_2O (7 mg, 20 mol%). After heating reaction mixture to 110 °C for 50 min, it was brought to 25 °C and the crude reaction mixture was worked up with aqueous $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure chiral product **10a** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure E: ***Base-catalyzed protection of SMA products:*** To a solution of Michael adduct **4a↔5a↔6a** (44 mg, 0.2 mmol) in dry DCM (4 mL) were added successively *i*-Pr_2NEt (0.13 mL, 0.8 mmol) and MOMCl (91 μL, 1.2 mmol) at 0 °C. The resulting mixture was stirred at 25 °C for 4 h. The reaction mixture was worked up with aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure product **11a** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure F: ***Methylenation of SMA products:*** In an oven dried round bottom flask, to triphenyl(bromomethyl)phosphonium bromide (457 mg, 1.28 mmol), in dry benzene (1 mL), under nitrogen, was added potassium *tert*-butoxide (134 mg, 1.28 mmol). After the mixture becomes deep yellow in colour, added the Michael adduct **4a↔5a↔6a** (46 mg, 0.2 mmol) in benzene (1 ml). After

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stirring the reaction mixture at 25 °C for 2h, the crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure product **12a** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure G: ***Iodine-catalyzed cyclization of olefin products:*** In an oven dried round bottom flask, was taken 2-(3-methyl-1-nitromethyl-but-3-enyl)-phenol (44 mg, 0.2 mmol) **12a** in DCM and it was cooled to 0 °C. To that added iodine (61 mg, 0.24 mmol) and stirred at same temperature for 15 min. The reaction mixture was worked up with aqueous sodium thiosulphate and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure product **13a** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure H: ***Hydrogenation followed by protection of nitro products:*** In an oven dried round bottom flask, was taken activated (10%) Pd/C (7 mg, 10 mol-%), with compound **13a** or **9aa** dissolved in MeOH (4 mL) and stirred under H_2 atmosphere at 25 °C for 5 h. The reaction mixture was passed through a pad of celite and concentrated to dryness. The crude mixture was taken in a dry oven dried round bottom flask in dry DCM (2 mL) and added successively dry triethylamine (42 µL, 0.3 mmol) and di-*tert*-butyl carbonate (65 mg, 0.3 mmol) at 0 °C. The resulting mixture was stirred at 25 °C for 2 h and then worked up with aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure product **14a** or **15aa** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure I: ***General procedure for diamine-catalyzed asymmetric SMA reaction of acetone 1 with 2-(2-nitro-vinyl)-phenols 2:*** In an ordinary glass vial equipped with a magnetic stirring bar, to a mixture of (*S*)-(+)-1-(2-pyrrolidinylmethyl)-pyrrolidine **3d** (8 mg, 0.05 mmol) and diphenylacetic acid (11 mg, 0.05 mmol) in DCM (2.0 mL), was added acetone **1** (1 mL, 7.0 mmol) and of 2-(2-nitro-vinyl)-phenol **2a** (83 mg, 0.5 mmol). After stirring the reaction mixture at 25 °C for 3 days, the crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. The crude mixture was dissolved in alcohol **7a** (2.5 mL) and cooled to 0 °C and added *p*-TSA (19 mg, 20 mol-%). The mixture was stirred at the same temperature for 30 min and then brought to room temperature and stirred for another 90 min. The crude reaction mixture was worked up with aqueous $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure products **8aa** and **9aa** were separated by column chromatography (silica gel, mixture of hexane/ethyl acetate).

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Procedure J: ***Base-catalyzed protection of SMA products:*** To a solution of Michael adduct **4a↔5a↔6a** (44 mg, 0.2 mmol) in dry THF (2 mL) were added successively NaH (6 mg, 0.24 mmol) and MeI (74 µL, 1.2 mmol) at 0 °C. The resulting mixture was stirred at same temperature for 30 min and then brought to 25 °C and stirred for 4.5 h. The reaction mixture was worked up with aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure product (+)-**11ab** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure K: ***Hydrogenation of nitro products:*** In an oven dried round bottom flask, was taken pre-activated 10% Pd/C (3 mg, 5 mol-%), with compound (+)-**11ab** (24 mg, 0.1 mmol) dissolved in dry ethyl acetate (1.0 mL) and stirred under H_2 atmosphere at 25 °C for 5 h. The reaction mixture was passed through a pad of celite and the pure product (+)-**16ab** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure L: ***Protection of hydrogenated products:*** In an oven dried round bottom flask, were taken (+)-**16ab** (30 mg, 0.16 mmol) in chloroform (0.2 mL) and triethylamine (45 µL, 0.32 mmol). To that reaction mixture, *p*-toluenesulphonyl chloride (33 mg, 0.176 mmol) was added drop wise in 0.3 mL chloroform under N_2 atmosphere at 0 °C. After 30 min, it was brought to 25 °C and stirred for overnight. The reaction mixture was then worked up with aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure product (+)-**17ab** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

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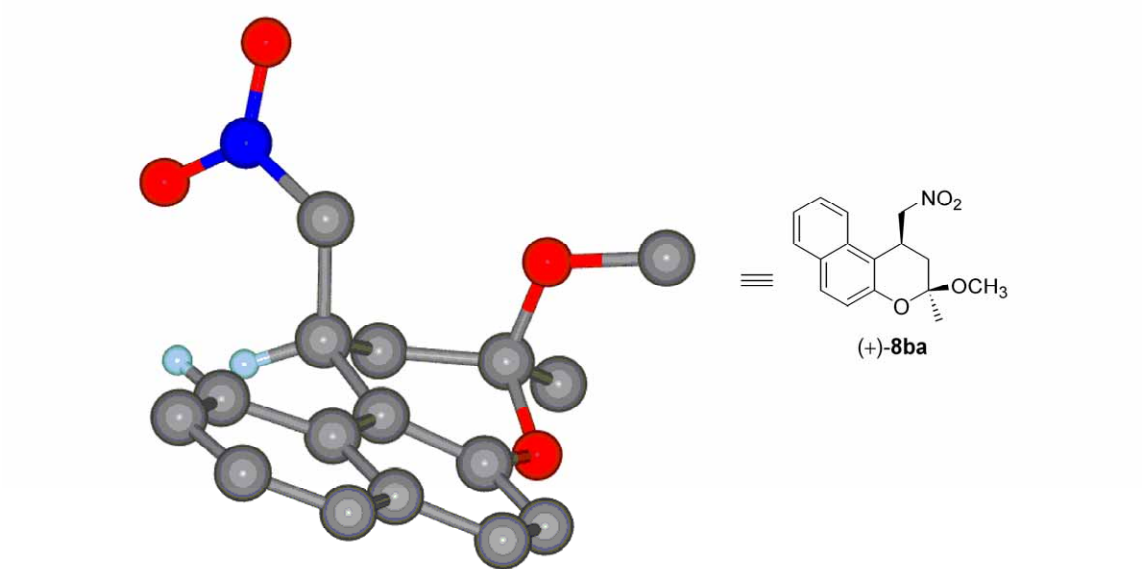

Figure S1. X-Ray crystal structure of chiral 3-methoxy-3-methyl-1-nitromethyl-2,3-dihydro-1*H*-benzo[*f*]chromene (**8ba**).

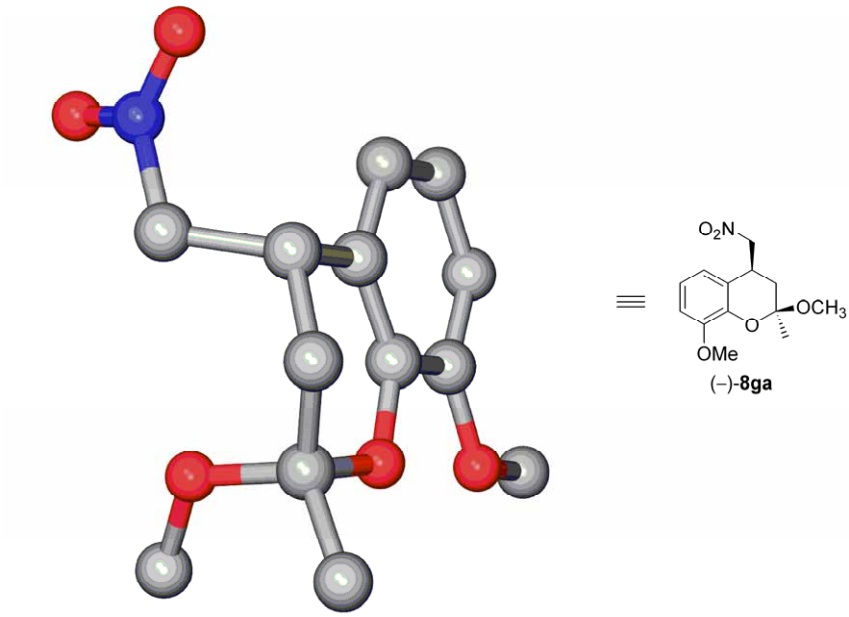

Figure S2. X-Ray crystal structure of chiral 2,8-dimethoxy-2-methyl-4-nitromethyl-chroman (**8ga**).

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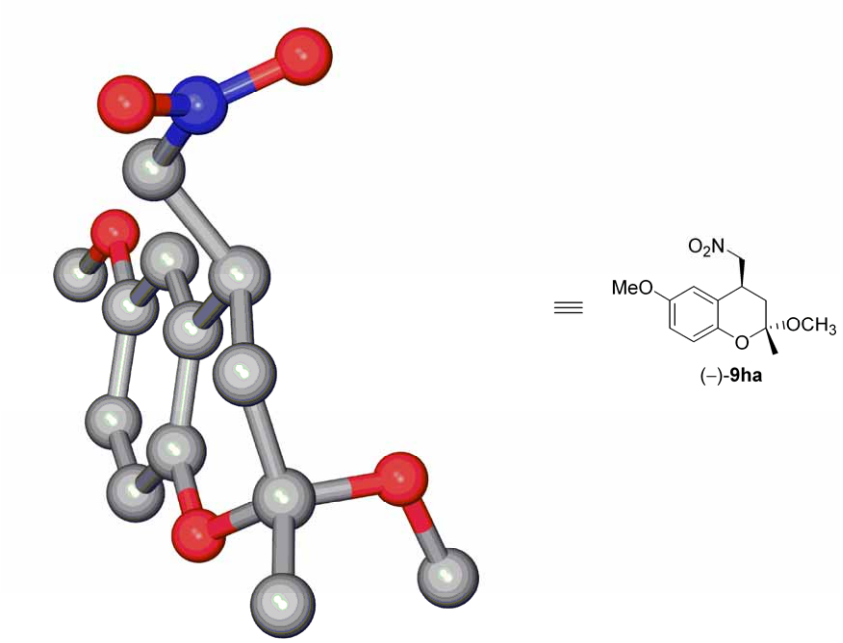

Figure S3. X-Ray crystal structure of chiral 2,6-dimethoxy-2-methyl-4-nitromethyl-chroman (**9ha**).

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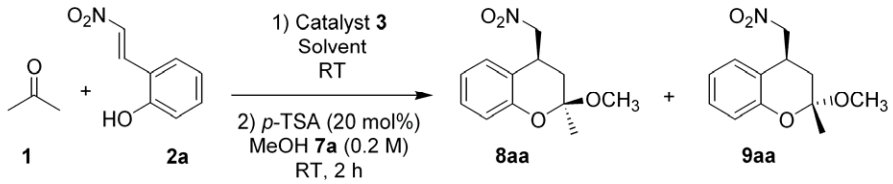
Table S1: Optimization for the *SMA* reaction of **1a**, **2a** and **7a**



Entry	Catalyst **3** [20 mol%]	Solvent [0.25 M]	Time [h]	Products yield [%][a]		ee [%][b]	
				8aa	**9aa**	**8aa**	**9aa**
1	**3h**/$PhCO_2H$	$C_6H_5CH_3$	24	42	43	60	58
2	**3h**/$PhCO_2H$	Hexane	48	44	46	49	52
3	**3h**/$PhCO_2H$	DCM	48	47	42	64	64
4	**3h**/$PhCO_2H$	DCE	48	19	11	64	64
5	**3h**/$PhCO_2H$	Neat	48	49	42	39	38
6	**3h**/CH_3CO_2H	DCM	72	47	36	75	72
7	**3h**/CCl_3CO_2H	DCM	96	–	–	–	–
8	**3h**/$C_2H_5CO_2H$	DCM	72	32	25	70	76
9	**3h**/$PhCH_2CO_2H$	DCM	72	38	33	82	80
10	**3h/Ph_2CHCO_2H**	**DCM**	**72**	**47**	**42**	**84**	**82**
11	**3h**/Ph_3CCO_2H	DCM	96	44	42	76	76
12[c]	**3h/Ph_2CHCO_2H**	**DCM**	**72**	**40**	**42**	**82**	**82**
13[c]	**3h/Naphthalen-1-yl-acetic acid**	**DCM**	**72**	**39**	**45**	**82**	**82**
14[c]	**3i**/$PhCO_2H$	$C_6H_5CH_3$	48	19	21	45	54
15[c]	**3j**/$PhCO_2H$	DCM	48	35	35	–60	–57
16[c]	**3j**/Naphthalen-1-yl-acetic acid	DCM	72	26	30	–73	–70
17[c]	**3k**/Naphthalen-1-yl-acetic acid	DCM	72	30	38	79	80
18[c]	**3l**/Naphthalen-1-yl-acetic acid	DCM	72	27	27	–76	–76

[a] Yield refers to the column purified product. [b] Ee determined by HPLC analysis. [c] Reactions were carried out with 10 mol% of catalyst **3** and 10 mol% of co-catalyst.

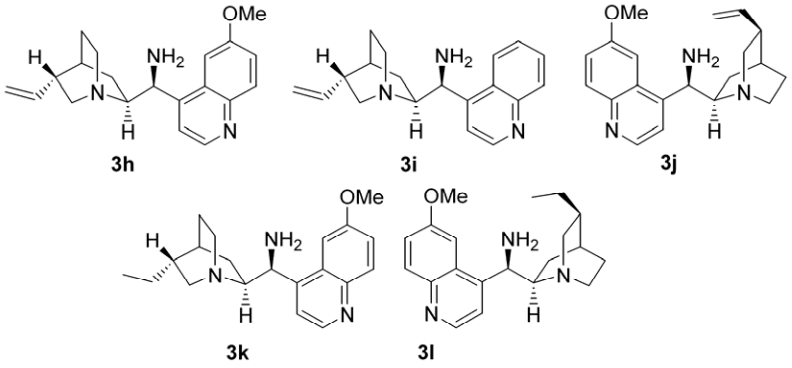


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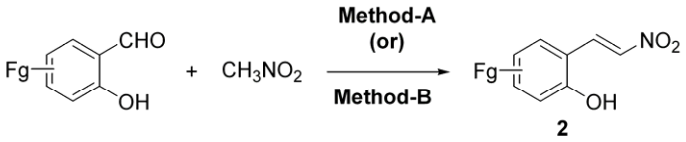
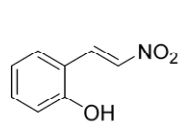
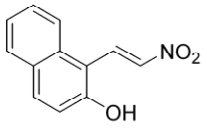
Table S2: Synthesis of 2-(2-nitro-vinyl)-phenols **2**



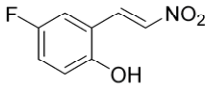
2



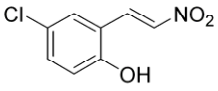
42% (2a)[b]
63% (2a)[c]



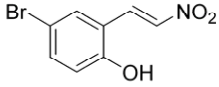
28% (2b)[c]



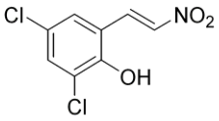
33% (2c)[b]



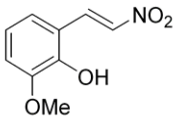
40% (2d)[b]



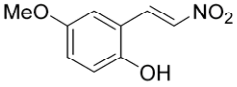
77% (2e)[c]



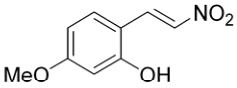
55% (2f)[b]



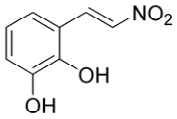
42% (2g)[b]



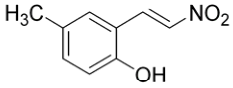
39% (2h)[b]



35% (2i)[c]



36% (2j)[c]



61% (2k)[b]

[a] Yield refers to column purified products. [b] Reagents and conditions for **Method-A:** To a mixture of 2-hydroxy-benzaldehydes (3 mmol) and nitromethane (15 mmol) in dry DCM (20 mL), added activated 4Å Molecular sieves (2g) followed by piperidine (20 mol%) and stirred at RT for overnight. [c] Reagents and conditions for **Method-B:** To a mixture of 2-hydroxy-benzaldehydes (3 mmol) and nitromethane (15 mmol) in AcOH (2.4 mL), added ammonium acetate and refluxed for 45 min.

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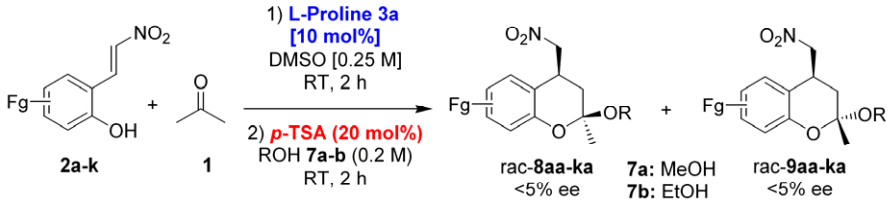
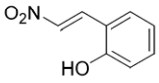
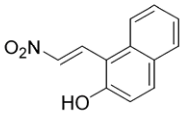
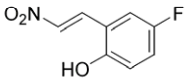
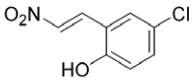
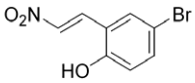
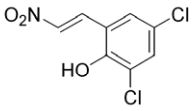
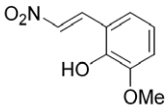
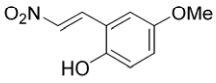
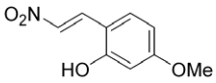
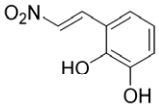
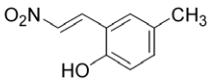
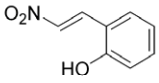
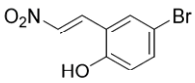
Table S3: Synthesis of achiral *SMA* products **8** and **9**[a]



Entry	2-(2-Nitro-vinyl)-phenols **2**	ROH **7a/7b**	Products **8/9**	Ratio[b] **[8/9]**	Products yield [%][c] **8**	**9**
1	 **2a**	**7a**	**8aa/9aa**	1:1	46	46
2	 **2b**	**7a**	**8ba/9ba**	99:1	82	<1
3	 **2c**	**7a**	**8ca/9ca**	1:1	44	44
4	 **2d**	**7a**	**8da/9da**	1:1	44	44
5	 **2e**	**7a**	**8ea/9ea**	1:1	46	46
6	 **2f**	**7a**	**8fa/9fa**	1:1	40	40
7	 **2g**	**7a**	**8ga/9ga**	1:1	42	42
8	 **2h**	**7a**	**8ha/9ha**	1:1	45	45
9	 **2i**	**7a**	**8ia/9ia**	1:1	48	48
10	 **2j**	**7a**	**8ja/9ja**	1:1	42	42
11	 **2k**	**7a**	**8ka/9ka**	1:1	46	46
12	 **2a**	**7b**	**8ab/9ab**	1:1	49	49
13	 **2e**	**7b**	**8eb/9eb**	1:1	46	46

[a] Reactions were carried out in DMSO (0.25 M) with 14 equiv. of **1** relative to the **2a-k** (0.5 mmol) in the presence of 10-mol% of catalyst **3a**. [b] Ratio is based on NMR analysis. [c] Yield refers to the column purified product.

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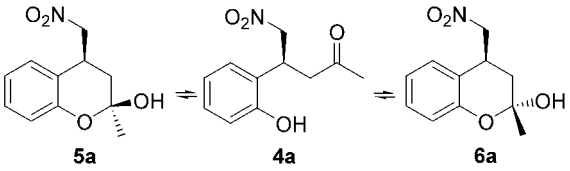
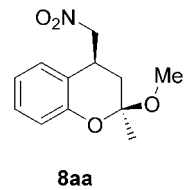


(2*S*, 4*S*)-2-Methyl-4-nitromethyl-chroman-2-ol (5a), (2*S*)-4-(2-Hydroxy-phenyl)-5-nitro-pentan-2-one (4a), and (2*S*, 4*R*)-2-Methyl-4-nitromethyl-chroman-2-ol (6a): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as liquid. The product **4a/5a/6a** was found to exist in rapid equilibrium with 1:1:1 ratio in solution. 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 = 43.21 min (major), t_R = 58.4 min (minor). **$[\alpha]_D^{25}$ = +15.0° (*c* = 0.3 g/100 mL, $CHCl_3$, 84% *ee*);** IR (Neat): ν_{max} 3350 (O-*H*), 1708 (*C*=O), 1547 (NO_2), 1491, 1454, 1378, 1227, 1166, 1117, 891, 758 and 663 cm^{-1}; ^1H NMR ($CDCl_3$, 1:1:1 mixture of δ-hydroxy ketone **4a** and lactols **5a/6a**) δ 7.21-7.16 (2H, m), 7.13-7.09 (3H, m), 7.06 (1H, d, *J* = 7.6 Hz), 6.96-6.92 (3H, m), 6.89-6.83 (2H, m), 6.78 (1H, d, *J* = 8.0 Hz), 6.37 (1H, s, Ar-O*H*), 5.07 (2H, dd, *J* = 12.8, 9.2 Hz), 4.95 (1H, dd, *J* = 12.2, 5.2 Hz), 4.72-4.66 (3H, m), 4.49 (1H, dd, *J* = 12.4, 9.2 Hz), 4.20 (1H, t, *J* = 6.8 Hz), 3.98-3.90 (1H, m), 3.72 (1H, dd, *J* = 14.6, 6.4 Hz), 3.01 (1H, d, *J* = 7.2 Hz), 2.84-2.80 (2H, m), 2.25-2.18 (3H, m), 2.13 (3H, s, CH_3), 2.08-2.02 (2H, m), 1.66 (3H, s, CH_3), 1.64 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 1:1:1 mixture of δ-hydroxy ketone **4a** and lactols **5a/6a**, DEPT-135) δ 207.6 (C, *C*=O), 153.5 (C), 152.1 (C), 152.0 (C), 128.94 (2 x CH), 128.91 (CH), 128.7 (CH), 128.6 (CH), 125.7 (CH), 125.1 (C), 121.4 (CH), 121.3 (CH), 119.9 (C), 119.4 (C), 117.9 (CH), 117.8 (2 x CH), 116.9 (CH), 96.4 (C), 95.8 (C), 80.2 (CH_2), 79.0 (CH_2), 77.8 (CH_2), 45.5 (CH_2), 35.6 (CH_2), 34.1 (CH), 33.0 (CH_2), 32.1 (CH_3), 30.2 (CH), 30.0 (CH), 29.5 (CH_3), 29.1 (CH_3); LRMS m/z 222.15 ($M - H^+$), calcd for $C_{11}H_{13}NO_4$ 223.0845; HRMS m/z 246.0740 (M + Na), calcd for $C_{11}H_{13}NO_4Na$ 246.0742; Anal. calcd for $C_{11}H_{13}NO_4$ (223.0845): C, 59.19; H, 5.87; N, 6.27. Found: C, 59.25; H, 5.91; N, 6.23%.



8aa

(2*S*, 4*S*)-2-Methoxy-2-methyl-4-nitromethyl-chroman (8aa): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 99:1, flow rate 0.8 mL/min, λ = 254 nm), t_R = 14.10 min (major), t_R = 15.2 min (minor). Mp 46 °C; **$[\alpha]_D^{25}$ = +52.5° (*c* = 0.25 g/100 mL, $CHCl_3$, 84% *ee*);** IR (Neat): ν_{max} 2924, 1581, 1550 (NO_2), 1489, 1379, 1251, 1216, 1148, 1122, 1058, 877 and 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (1H, t, *J* = 7.6 Hz), 7.12 (1H, d, *J* = 7.6 Hz), 6.95 (1H, t, *J* = 7.6 Hz), 6.89 (1H, d, *J* = 8.0 Hz), 5.01 (1H, dd, *J* = 12.6, 8.8 Hz), 4.63 (1H, dd, *J* = 12.8, 5.6 Hz), 3.69 (1H, dd, *J* = 14.6, 6.8 Hz), 3.24 (3H, s, O*CH*$_3$), 2.20 (1H, d, *J* = 14.4 Hz),

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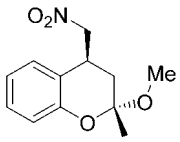
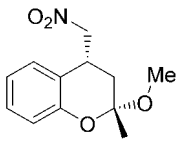
2.07 (1H, dd, *J* = 14.4, 6.8 Hz), 1.55 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 151.8 (C), 128.9 (CH), 128.88 (CH), 121.5 (CH), 120.2 (C), 117.8 (CH), 98.5 (C), 80.7 (CH_2), 48.8 (CH_3, O*C*H$_3$), 34.0 (CH_2), 32.0 (CH), 23.0 (CH_3); LRMS m/z 236 (M – H$^+$), calcd for $C_{12}H_{15}NO_4$ 237.1001; HRMS m/z 260.0888 (M + Na), calcd for $C_{12}H_{15}NO_4Na$ 260.0899; Anal. calcd for $C_{12}H_{15}NO_4$ (237.1001): C, 60.75; H, 6.37; N, 5.90. Found: C, 60.85; H, 6.35; N, 5.85%.



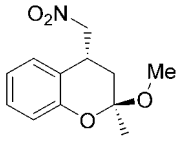
9aa

(2*S*, 4*R*)-2-Methoxy-2-methyl-4-nitromethyl-chroman (9aa): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 99:1, flow rate 0.8 mL/min, λ = 254 nm), t_R = 16.91 min (major), t_R = 29.16 min (minor). Mp 58 °C; **$[\alpha]_D^{25}$ = –22.6° (*c* = 0.50 g/100 mL, $CHCl_3$, 82% *ee*);** IR (Neat): ν_{max} 2989, 1551 (NO_2), 1490, 1452, 1379, 1257, 1223, 1188, 1067, 882, 756 and 646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.19 (1H, t, *J* = 7.6 Hz), 7.10 (1H, d, *J* = 7.6 Hz), 6.95 (1H, t, *J* = 7.2 Hz), 6.89 (1H, d, *J* = 8.0 Hz), 4.94 (1H, dd, *J* = 12.0, 4.8 Hz), 4.46 (1H, dd, *J* = 12.4, 9.6 Hz), 3.97-3.89 (1H, m), 3.23 (3H, s, O*CH*$_3$), 2.22 (1H, dd, *J* = 13.2, 6.4 Hz), 1.81 (1H, t, *J* = 12.8 Hz), 1.57 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 152.1 (C), 128.6 (CH), 125.8 (CH), 121.3 (CH), 120.6 (C), 117.9 (CH), 98.0 (C), 79.2 (CH_2), 49.0 (CH_3, O*C*H$_3$), 36.6 (CH_2), 30.2 (CH), 22.9 (CH_3); LRMS m/z 236 (M – H$^+$), calcd for $C_{12}H_{15}NO_4$ 237.1001; HRMS m/z 260.0891 (M + Na), calcd for $C_{12}H_{15}NO_4Na$ 260.0899; Anal. calcd for $C_{12}H_{15}NO_4$ (237.1001): C, 60.75; H, 6.37; N, 5.90. Found: C, 60.68; H, 6.32; N, 5.96%.



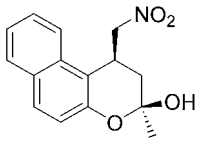
(–)-**8aa**

(2*R*, 4*R*)-2-Methoxy-2-methyl-4-nitromethyl-chroman (8aa): Prepared following the procedure **I** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 99:1, flow rate 0.8 mL/min, λ = 254 nm), t_R = 16.44 min (minor), t_R = 18.99 min (major). Mp 46 °C; **$[\alpha]_D^{25}$ = –17.4° (*c* = 0.42 g/100 mL, $CHCl_3$, 25% *ee*)**.



(+)-**9aa**

(2*R*, 4*S*)-2-Methoxy-2-methyl-4-nitromethyl-chroman (9aa): Prepared following the procedure **I** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 99:1, flow rate 0.8 mL/min, λ = 254 nm), t_R = 20.00 min (minor), t_R = 39.24 min (major). Mp 58 °C; **$[\alpha]_D^{25}$ = +10.8° (*c* = 0.53 g/100 mL, $CHCl_3$, 21% *ee*)**.



5b

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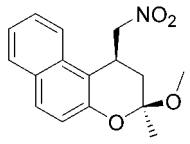
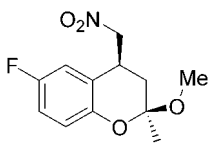
(1*S*, 3*S*)-3-Methyl-1-nitromethyl-2,3-dihydro-1*H*-benzo[f]chromen-3-ol (5b): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 13.69 min (minor), t_R = 16.42 min (major). Mp 116 °C; **$[\alpha]_D^{25}$ = +30.0° (*c* = 0.38 g/100 mL, $CHCl_3$, 98% *ee*);** IR (Neat): ν_{max} 2796, 2758, 1621, 1544 (NO_2), 1514, 1438, 1403, 1382, 1341, 1229, 1160, 1106, 1053, 1023, 975, 892, 819, 782, 682 and 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91 (1H, d, *J* = 8.0 Hz), 7.81 (1H, d, *J* = 8.0 Hz), 7.72 (1H, d, *J* = 8.0 Hz), 7.58 (1H, t, *J* = 8.0 Hz), 7.40 (1H, t, *J* = 8.0 Hz), 7.04 (1H, d, *J* = 8.0 Hz), 5.43 (1H, t, *J* = 12.0 Hz), 4.75 (1H, dd, *J* = 12.0, 4.0 Hz), 4.26 (1H, t, *J* = 4.0 Hz), 2.75 (1H, s), 2.45 (1H, d, *J* = 16.0 Hz), 2.08 (1H, dd, *J* = 14.0, 8.0 Hz), 1.73 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 150.3 (C), 131.4 (C), 129.9 (CH), 129.5 (C), 129.1 (CH), 127.5 (CH), 123.8 (CH), 121.0 (CH), 119.2 (CH), 110.0 (C), 96.6 (C), 76.9 (CH_2), 31.8 (CH_2), 30.2 (CH), 29.8 (CH_3); LRMS m/z 272.25 ($M - H^+$), calcd for $C_{15}H_{15}NO_4$ 273.1001; HRMS m/z 296.0898 (M + Na), calcd for $C_{15}H_{15}NO_4Na$ 296.0899; Anal. calcd for $C_{15}H_{15}NO_4$ (273.1001): C, 65.92, H; 5.53; N, 5.13. Found: C, 65.86; H, 5.49; N, 5.21%.



8ba

(1*S*, 3*S*)-3-Methoxy-3-methyl-1-nitromethyl-2,3-dihydro-1*H*-benzo[f]chromene (8ba): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 84 °C; **$[\alpha]_D^{25}$ = +71.5° (*c* = 0.23 g/100 mL, $CHCl_3$, 98% *ee*);** IR (Neat): ν_{max} 3738, 1624, 1549 (NO_2), 1378, 1176, 1115, 1052 and 817 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87 (1H, d, *J* = 8.4 Hz), 7.78 (1H, d, *J* = 8.0 Hz), 7.70 (1H, d, *J* = 8.8 Hz), 7.55 (1H, t, *J* = 7.2 Hz), 7.38 (1H, t, *J* = 7.2 Hz), 7.08 (1H, d, *J* = 8.8 Hz), 5.33 (1H, dd, *J* = 12.8, 11.2 Hz), 4.71 (1H, dd, *J* = 13.2, 2.0 Hz), 4.19-4.15 (1H, m), 3.30 (3H, s, OC*H*$_3$), 2.41 (1H, d, *J* = 14.4 Hz), 2.05 (1H, dd, *J* = 14.8, 6.4 Hz), 1.60 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 150.1 (C), 131.4 (C), 129.8 (CH), 129.5 (C), 129.0 (CH), 127.4 (CH), 123.7 (CH), 121.1 (CH), 119.1 (CH), 110.7 (C), 98.7 (C), 77.3 (CH_2), 48.8 (CH_3, O*C*H_3), 32.8 (CH_2), 29.7 (CH), 23.2 (CH_3); LRMS m/z 286 ($M - H^+$), calcd for $C_{16}H_{17}NO_4$ 287.1158; HRMS m/z 310.0975 (M + Na), calcd for $C_{16}H_{17}NO_4Na$ 310.1055; Anal. calcd for $C_{16}H_{17}NO_4$ (287.1158): C, 66.89; H, 5.96; N, 4.88. Found: C, 66.83; H, 5.91; N, 4.92%.



8ca

(2*S*, 4*S*)-6-Fluoro-2-methoxy-2-methyl-4-nitromethyl-chroman (8ca): Prepared following the procedure **C** 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 AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 6.00 min (major), t_R = 6.73 min (minor). **$[\alpha]_D^{25}$**

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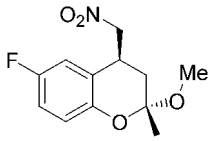
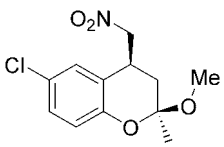
= +11.5° (*c* = 0.26 g/100 mL, $CHCl_3$, 82% *ee*); IR (Neat): ν_{max} 1530 (NO_2), 1492, 1427, 1379, 1248, 1195, 1145, 1120, 1056, 940, 877, 819 and 636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90 (1H, br dt, *J* = 9.0, 2.8 Hz), 6.86-6.82 (2H, m), 4.98 (1H, dd, *J* = 13.0, 8.8 Hz), 4.61 (1H, dd, *J* = 13.2, 5.6 Hz), 3.67 (1H, dd, *J* = 14.4, 6.8 Hz), 3.23 (3H, s, OC*H*$_3$), 2.18 (1H, d, *J* = 14.4 Hz), 2.04 (1H, dd, *J* = 14.6, 6.8 Hz), 1.55 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 157.1 (C, d, *J* = 238.4 Hz), 147.8 (C), 121.3 (C, d, *J* = 6.8 Hz), 118.8 (CH, d, *J* = 7.9 Hz), 115.8 (CH, d, *J* = 22.9 Hz), 114.8 (CH, d, *J* = 23.0 Hz), 98.6 (C), 80.5 (CH_2), 48.7 (CH_3, O*C*H$_3$), 33.8 (CH_2), 32.0 (CH), 22.8 (CH_3); LRMS m/z 254 ($M - H^+$), calcd for $C_{12}H_{14}FNO_4$ 255.0907; HRMS m/z 301.1362 (M + 2Na), calcd for $C_{12}H_{14}FNO_4Na_2$ 301.0703; Anal. calcd for $C_{12}H_{14}FNO_4$ (255.0907): C, 56.47; H, 5.53;N, 5.49. Found: C, 56.41; H, 5.54; N, 5.56%.



9ca

(2*S*, 4*R*)-6-Fluoro-2-methoxy-2-methyl-4-nitromethyl-chroman (9ca): Prepared following the procedure **C** 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 = 97:3, flow rate 1.0 mL/min, λ = 254 nm), t_R = 10.15 min (major), t_R = 10.75 min (minor). **$[\alpha]_D^{25}$ = –36.2° (*c* = 0.26 g/100 mL, $CHCl_3$, 76% *ee*);** IR (Neat): ν_{max} 2997, 1622, 1535 (NO_2), 1492, 1430, 1379, 1224, 1191, 1139, 1097, 1065, 883 and 802 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.89 (1H, br dt, *J* = 8.8, 2.8 Hz), 6.85-6.81 (2H, m), 4.85 (1H, dd, *J* = 12.4, 4.8 Hz), 4.47 (1H, dd, *J* = 12.4, 9.2 Hz), 3.93-3.85 (1H, m), 3.21 (3H, s, OC*H*$_3$), 2.20 (1H, dd, *J* = 13.4, 6.0 Hz), 1.79 (1H, t, *J* = 12.8 Hz), 1.55 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 157.1 (C, d, *J* = 238.2 Hz), 148.1 (C), 121.7 (C, d, *J* = 6.8 Hz), 118.9 (CH, d, *J* = 8.0 Hz), 115.4 (CH, d, *J* = 22.8 Hz), 112.3 (CH, d, *J* = 23.7 Hz), 98.1 (C), 78.8 (CH_2), 49.0 (CH_3, O*C*H$_3$), 36.2 (CH_2), 30.4 (CH), 22.7 (CH_3); LRMS m/z 254 ($M - H^+$), calcd for $C_{12}H_{14}FNO_4$ 255.0907; HRMS m/z 278.0805 (M + Na), calcd for $C_{12}H_{14}FNO_4Na$ 278.0805; Anal. calcd for $C_{12}H_{14}FNO_4$ (255.0907): C, 56.47; H, 5.53; N, 5.49. Found: C, 56.44; H, 5.49; N, 5.56%.



8da

(2*S*, 4*S*)-6-Chloro-2-methoxy-2-methyl-4-nitromethyl-chroman (8da): Prepared following the procedure **C** 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 AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 4.73 min (major), t_R = 5.50 min (minor). **$[\alpha]_D^{25}$ = +13.0° (*c* = 0.20 g/100 mL, $CHCl_3$, 69% *ee*);** IR (Neat): ν_{max} 2993, 2941, 1549 (NO_2), 1514, 1481, 1425, 1379, 1251, 1217, 1177, 1146, 1121, 1053, 877 and 821 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15 (1H, dd, *J* = 8.8, 2.4 Hz), 7.12 (1H, d, *J* = 2.4 Hz), 6.83 (1H, d, *J* = 8.8 Hz), 5.00 (1H, dd, *J* = 13.0, 9.2 Hz), 4.60 (1H, dd, *J* = 13.0, 5.2 Hz), 3.66 (1H, dd, *J* = 15.2, 6.4 Hz), 3.23 (3H, s, OC*H*$_3$), 2.19 (1H,

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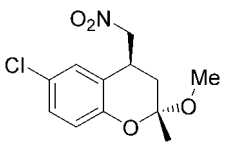
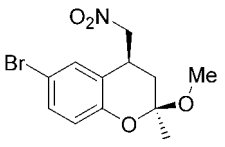
dd, *J* = 14.6, 0.8 Hz), 2.04 (1H, dd, *J* = 14.8, 7.2 Hz), 1.55 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 150.5 (C), 128.9 (CH), 128.5 (CH), 126.1 (C), 121.8 (C), 119.2 (CH), 98.8 (C), 80.3 (CH_2), 48.8 (CH_3, O*C*H$_3$), 33.7 (CH_2), 31.8 (CH), 22.8 (CH_3); LRMS m/z 270 (M – H$^+$), calcd for $C_{12}H_{14}ClNO_4$ 271.0611; HRMS m/z 294.0511 (M + Na), calcd for $C_{12}H_{14}ClNO_4Na$ 294.0509; Anal. calcd for $C_{12}H_{14}ClNO_4$ (271.0611): C, 53.05; H, 5.19; N, 5.16. Found: C, 53.12; H, 5.15, N, 5.22%.



9da

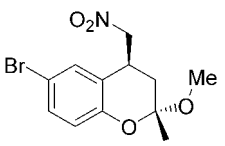
(2*R*, 4*S*)-6-Chloro-2-methoxy-2-methyl-4-nitromethyl-chroman (9da): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 8.25 min (major), t_R = 8.84 min (minor). **[α]$_D^{25}$ = –10.0° (*c* = 0.18 g/100 mL, $CHCl_3$, 70% *ee*);** IR (Neat): ν_{max} 2939, 2299, 1551 (NO_2), 1515, 1482, 1436, 1412, 1378, 1261, 1224, 1186, 1066, 881, 822, 680, 659 and 633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.15-7.13 (1H, m), 7.09-7.08 (1H, m), 6.83 (1H, d, *J* = 8.8 Hz), 4.88 (1H, dd, *J* = 12.4, 4.8 Hz), 4.47 (1H, dd, *J* = 12.4, 9.2 Hz), 3.93-3.89 (1H, m), 3.22 (3H, s, OC*H*$_3$), 2.20 (1H, dd, *J* = 11.2, 6.0 Hz), 1.79 (1H, dd, *J* = 13.2, 12.4 Hz), 1.56 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 150.8 (C), 128.6 (CH), 126.1 (C), 125.8 (CH), 122.2 (C), 119.2 (CH), 98.3 (C), 78.7 (CH_2), 49.1 (CH_3, O*C*H$_3$), 36.2 (CH_2), 30.2 (CH), 22.6 (CH_3); LRMS m/z 270 (M – H$^+$), calcd for $C_{12}H_{14}ClNO_4$ 271.0611; HRMS m/z 294.0505 (M + Na), calcd for $C_{12}H_{14}ClNO_4Na$ 294.0509; Anal. calcd for $C_{12}H_{14}ClNO_4$ (271.0611): C, 53.05; H, 5.19; N, 5.16. Found: C, 53.10; H, 5.16; N, 5.23%.

(2*S*, 4*S*)-6-Bromo-2-methoxy-2-methyl-4-nitromethyl-chroman (8ea): Prepared following the procedure **C** 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 AS-H column (hexane/2-propanol = 91:9, flow rate 1.0 mL/min, λ = 254 nm), t_R = 5.43 min (minor), t_R = 5.96 min (major).



8ea

[α]$_D^{25}$ = +63.2° (*c* = 0.23 g/100 mL, $CHCl_3$, 87% *ee*); IR (Neat): ν_{max} 1549 (NO_2), 1479, 1427, 1379, 1251, 1215, 1174, 1148, 1124, 1055, 877 and 818 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.30-7.26 (2H, m), 6.78 (1H, d, *J* = 8.4 Hz), 5.00 (1H, dd, *J* = 13.2, 9.2 Hz), 4.60 (1H, dd, *J* = 13.0, 5.2 Hz), 3.69-3.64 (1H, m), 3.23 (3H, s, OC*H*$_3$), 2.19 (1H, dd, *J* = 14.8, 1.2 Hz), 2.03 (1H, dd, *J* = 14.6, 7.2 Hz), 1.55 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 151.1 (C), 131.8 (CH), 131.5 (CH), 122.4 (C), 119.6 (CH), 113.4 (C), 98.8 (C), 80.4 (CH_2), 48.8 (CH_3, O*C*H$_3$), 33.8 (CH_2), 31.7 (CH), 22.8 (CH_3); LRMS m/z 314 (M – H$^+$), calcd for $C_{12}H_{14}BrNO_4$ 315.0106; HRMS m/z 338.0012 (M + Na), calcd for $C_{12}H_{14}BrNO_4Na$ 338.0004; Anal.



9ea

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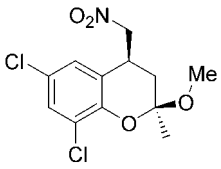
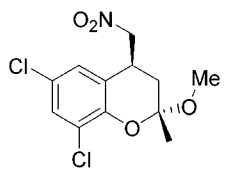
calcd for $C_{12}H_{14}BrNO_4$ (315.0106): C, 45.59; H, 4.46; N, 4.43. Found: C, 45.68; H, 4.39; N, 4.47%.

(2*S*, 4*R*)-6-Bromo-2-methoxy-2-methyl-4-nitromethyl-chroman (9ea): Prepared following the procedure **C** 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 = 95:5, flow rate 0.8 mL/min, λ = 254 nm), t_R = 11.10 min (major), t_R = 14.47 min (minor). **$[\alpha]_D^{25}$ = –15.6° (*c* = 0.18 g/100 mL, $CHCl_3$, 86% *ee*);** IR (Neat): ν_{max} 1551 (NO_2), 1514, 1481, 1379, 1255, 1224, 1186, 1066 and 881 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29-7.26 (1H, m), 7.23-7.22 (1H, m), 6.77 (1H, d, *J* = 8.8 Hz), 4.89 (1H, dd, *J* = 12.4, 4.8 Hz), 4.46 (1H, dd, *J* = 12.0, 9.2 Hz), 3.94-3.86 (1H, m), 3.22 (3H, s, OC*H*$_3$), 2.21 (1H, dd, *J* = 13.2, 6.4 Hz), 1.78 (1H, dd, *J* = 13.0, 12.4 Hz), 1.56 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 151.3 (C), 131.6 (CH), 128.7 (CH), 122.8 (C), 119.7 (CH), 113.4 (C), 98.3 (C), 78.7 (CH_2), 49.1 (CH_3, O*C*H$_3$), 36.2 (CH_2), 30.1(CH), 22.7 (CH_3); LRMS m/z 314 ($M - H^+$), calcd for $C_{12}H_{14}BrNO_4$ 315.0106; HRMS m/z 338.0004 (M + Na), calcd for $C_{12}H_{14}BrNO_4Na$ 338.0004; Anal. calcd for $C_{12}H_{14}BrNO_4$ (315.0106): C, 45.59; H, 4.46; N, 4.43. Found: C, 45.65; H, 4.41; N, 4.51%.



8fa

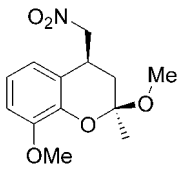
(2*S*, 4*S*)-6,8-Dichloro-2-methoxy-2-methyl-4-nitromethyl-chroman (8fa): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), t_R = 6.43 min (minor), t_R = 7.20 min (major). Mp 62 °C; **$[\alpha]_D^{25}$ = –7.6° (*c* = 0.30 g/100 mL, $CHCl_3$, 88% *ee*);** IR (Neat): ν_{max} 2962, 1548 (NO_2), 1450, 1380, 1235, 1177, 1090, 1050, 1024, 937, 882, 823 and 633 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (1H, br d, *J* = 2.0 Hz), 7.05-7.04 (1H, m), 4.98 (1H, dd, *J* = 13.4, 9.2 Hz), 4.59 (1H, dd, *J* = 13.4, 5.2 Hz), 3.70 (1H, dd, *J* = 14.2, 6.8 Hz), 3.25 (3H, s, OC*H*$_3$), 2.22 (1H, br d, *J* = 14.8 Hz), 2.09 (1H, dd, *J* = 14.6, 7.2 Hz), 1.62 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.6 (C), 129.2 (CH), 127.0 (CH), 125.9 (C), 123.7 (C), 123.3 (C), 99.6 (C), 80.3 (CH_2), 49.1 (CH_3, O*C*H$_3$), 33.8 (CH_2), 31.9 (CH), 22.7 (CH_3); LRMS m/z 304 ($M - H^+$), calcd for $C_{12}H_{13}Cl_2NO_4$ 305.0222; HRMS m/z 328.0110 (M + Na), calcd for $C_{12}H_{13}Cl_2NO_4Na$ 328.0119.



9fa

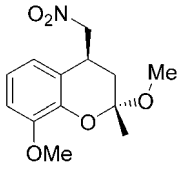
(2*R*, 4*S*)-6,8-Dichloro-2-methoxy-2-methyl-4-nitromethyl-chroman (9fa): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), t_R = 10.39 min (major), t_R =

11.34 min (minor). Mp 94 °C; **$[\alpha]_D^{25}$ = –64.6° (*c* = 0.22 g/100 mL, $CHCl_3$, 91% *ee*);** IR (Neat): ν_{max} 2963, 1557 (NO_2), 1455, 1382, 1278, 1239, 1181, 1082, 1051, 1026, 882, 678 and 636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29-7.28 (1H, m), 7.02-7.01 (1H, m), 4.85 (1H, dd, *J* = 12.6, 4.4 Hz), 4.50 (1H, dd, *J* = 12.8, 8.8 Hz), 3.94-3.86 (1H, m), 3.23 (3H, s, OC*H*$_3$), 2.25 (1H, dd, *J* = 13.2, 6.4 Hz), 1.86 (1H, t, *J* = 12.8 Hz), 1.63 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.9 (C), 128.9 (CH), 125.9 (C), 124.5 (CH), 123.8 (C), 123.7 (C), 99.2 (C), 78.5 (CH_2), 49.3 (CH_3, O*C*H$_3$), 36.2 (CH_2), 30.5 (CH), 22.5 (CH_3); LRMS m/z 306.30 (M + H^+), calcd for $C_{12}H_{13}Cl_2NO_4$ 305.0222; HRMS m/z 328.0110 (M + Na), calcd for $C_{12}H_{13}Cl_2NO_4Na$ 328.0119; Anal. calcd for $C_{12}H_{13}Cl_2NO_4$ (306.0222): C, 47.08; H, 4.28; N, 4.58. Found: C, 47.12; H, 4.23; N, 4.51%.



8ga

(2*S*, 4*S*)-2,8-Dimethoxy-2-methyl-4-nitromethyl-chroman (8ga): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 7.40 min (major), t_R = 8.38 min (minor). Mp 74 °C; **$[\alpha]_D^{25}$ = –43.1° (*c* = 0.23 g/100 mL, $CHCl_3$, 79% *ee*);** IR (Neat): ν_{max} 3729, 1584, 1546 (NO_2), 1479, 1378, 1262, 1212, 1086, 1053 and 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90 (1H, t, *J* = 8.0 Hz), 6.81 (1H, dd, *J* = 8.2, 1.2 Hz), 6.74-6.72 (1H, m), 5.00 (1H, dd, *J* = 12.8, 9.2 Hz), 4.63 (1H, dd, *J* = 12.8, 5.2 Hz), 3.86 (3H, s, Ar-OC*H*$_3$), 3.72-3.66 (1H, m), 3.25 (3H, s, OC*H*$_3$), 2.19 (1H, dd, *J* = 14.6, 1.6 Hz), 2.08 (1H, dd, *J* = 14.8, 6.8 Hz), 1.62 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 149.0 (C), 141.3 (C), 121.0 (C), 120.9 (CH), 120.4 (CH), 110.6 (CH), 98.5 (C), 80.6 (CH_2), 55.9 (CH_3, O*C*H$_3$), 48.8 (CH_3, O*C*H$_3$), 33.8 (CH_2), 31.9 (CH), 23.0 (CH_3); LRMS m/z 268 (M + H^+), calcd for $C_{13}H_{17}NO_5$ 267.1107; HRMS m/z 290.1001 (M + Na), calcd for $C_{13}H_{17}NO_5Na$ 290.1004; Anal. calcd for $C_{13}H_{17}NO_5$ (267.1107): C, 58.42; H, 6.41; N; 5.24. Found: C, 58.36; H, 6.45; N; 5.28%.



9ga

(2*R*, 4*S*)-2,8-Dimethoxy-2-methyl-4-nitromethyl-chroman (9ga): Prepared following the procedure **C** 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 AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 10.49 min (major), t_R = 12.27 min (minor). **$[\alpha]_D^{25}$ = –62.3° (*c* = 0.14 g/100 mL, $CHCl_3$, 79% *ee*);** IR (Neat): ν_{max} 2921, 2850, 1583, 1546 (NO_2), 1470, 1379, 1261, 1223, 1183, 1082, 1055, 1032, 906, 686 and 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90 (1H, t, *J* = 8.0 Hz), 6.81 (1H, d, *J* = 7.6 Hz), 6.71 (1H, dt, *J* = 8.0, 1.2 Hz), 4.91 (1H, dd, *J* = 12.4, 4.8 Hz), 4.44 (1H, dd, *J* = 12.4, 9.6 Hz), 3.96-3.88 (1H, m), 3.86 (3H, s, Ar-OC*H*$_3$), 3.23 (3H, s, OC*H*$_3$), 2.22 (1H, dd, *J* = 13.4, 6.0

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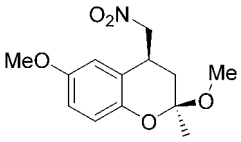
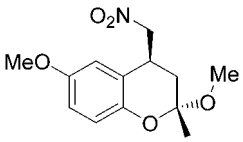
Hz), 1.84 (1H, dd, *J* = 13.2, 12.0 Hz), 1.63 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 149.1 (C), 141.5 (C), 121.5 (C), 120.8 (CH), 117.5 (CH), 110.6 (CH), 98.1 (C), 79.3 (CH_2), 56.0 (CH_3, O*C*H$_3$), 49.1 (CH_3, O*C*H$_3$), 36.5 (CH_2), 30.4 (CH), 22.9 (CH_3); LRMS m/z 268 (M + H$^+$), calcd for $C_{13}H_{17}NO_5$ 267.1107; HRMS m/z 290.1000 (M + Na), calcd for $C_{13}H_{17}NO_5Na$ 290.1004; Anal. calcd for $C_{13}H_{17}NO_5$ (267.1107): C, 58.42; H, 6.41; N, 5.24. Found: C, 58.36; H, 6.44; N, 5.32%.



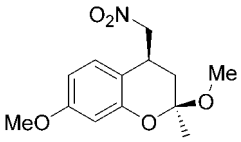
8ha

(2*S*, 4*S*)-2,6-Dimethoxy-2-methyl-4-nitromethyl-chroman (8ha): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 6.21 min (minor), t_R = 6.91 min (major). Mp 68 °C; **[α]$_D^{25}$ = +20.7° (*c* = 0.28 g/100 mL, $CHCl_3$, 79% *ee*);** IR (Neat): ν$_{max}$ 2956, 1727, 1550 (NO_2), 1495, 1426, 1380, 1251, 1207, 1147, 1107, 1049, 937, 874, 789, and 645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.83-6.76 (2H, m), 6.64 (1H, d, *J* = 2.0 Hz), 5.00 (1H, dd, *J* = 12.8, 9.2 Hz), 4.63 (1H, dd, *J* = 12.8, 5.6 Hz), 3.75 (3H, s, Ar-OC*H*$_3$), 3.65 (1H, dd, *J* = 14.2, 6.8 Hz), 3.22 (3H, s, OC*H*$_3$), 2.16 (1H, d, *J* = 14.8 Hz), 2.04 (1H, dd, *J* = 14.4, 6.8 Hz), 1.53 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 154.0 (C), 145.6 (C), 120.7 (C), 118.4 (CH), 115.1 (CH), 113.1 (CH), 98.3 (C), 80.7 (CH_2), 55.6 (CH_3, O*C*H$_3$), 48.6 (CH_3, O*C*H$_3$), 33.9 (CH_2), 32.3 (CH), 22.9 (CH_3); LRMS m/z 266 (M – H$^+$), calcd for $C_{13}H_{17}NO_5$ 267.1107; HRMS m/z 290.0992 (M + Na), calcd for $C_{13}H_{17}NO_5Na$ 290.1004; Anal. calcd for $C_{13}H_{17}NO_5$ (267.1107): C, 58.42; H, 6.41; N, 5.24. Found: C, 58.45; H, 6.38; N, 5.28%.



9ha

(2*R*, 4*S*)-2,6-Dimethoxy-2-methyl-4-nitromethyl-chroman (9ha): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 9.65 min (major), t_R = 11.11 min (minor). Mp 110 °C; **[α]$_D^{25}$ = –47.6° (*c* = 0.28 g/100 mL, $CHCl_3$, 79% *ee*);** IR (Neat): ν$_{max}$ 2940, 2340, 1546 (NO_2), 1499, 1379, 1281, 1251, 1220, 1150, 1106, 1068, 1037, 887, 821, 665 and 637 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.82 (1H, d, *J* = 8.8 Hz), 6.76 (1H, dd, *J* = 8.8, 2.4 Hz), 6.63 (1H, d, *J* = 2.0 Hz), 4.89 (1H, dd, *J* = 12.4, 4.8 Hz), 4.45 (1H, dd, *J* = 12.2, 9.2 Hz), 3.93-3.85 (1H, m), 3.75 (3H, s, Ar-OC*H*$_3$), 3.21 (3H, s, OC*H*$_3$), 2.19 (1H, dd, *J* = 13.2 , 6.0 Hz), 1.79 (1H, t, *J* = 12.4 Hz), 1.54 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 153.9 (C), 145.9 (C), 121.2 (C), 118.4 (CH), 114.1 (CH), 111.2 (CH), 97.8 (C), 79.2 (CH_2), 55.6 (CH_3, O*C*H$_3$), 48.9 (CH_3, O*C*H$_3$), 36.5 (CH_2), 30.6 (CH), 22.8 (CH_3); LRMS m/z 266 (M – H$^+$), calcd for $C_{13}H_{17}NO_5$ 267.1107; HRMS m/z 290.0975 (M + Na), calcd for $C_{13}H_{17}NO_5Na$



8ia

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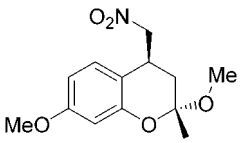
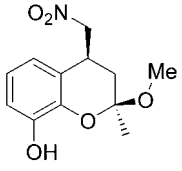
290.1004; Anal. calcd for $C_{13}H_{17}NO_5$ (267.1107): C, 58.42; H, 6.41; N, 5.24. Found: C, 58.32; H, 6.44; N, 5.28%.

(2*S*, 4*S*)-2,7-Dimethoxy-2-methyl-4-nitromethyl-chroman (8ia): Prepared following the procedure **C** 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 AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 6.64 min (minor), t_R = 7.19 min (major). **$[\alpha]_D^{25}$ = –10.9° (*c* = 0.18 g/100 mL, $CHCl_3$, 80% *ee*);** IR (Neat): ν_{max} 2960, 1620, 1548 (NO_2), 1504, 1439, 1379, 1335, 1268, 1197, 1149, 1119, 1055, 979, 804, 648 and 625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.01 (1H, d, *J* = 8.0 Hz), 6.54 (1H, dd, *J* = 8.0, 4.0 Hz), 6.45 (1H, d, *J* = 2.4, Hz), 4.95 (1H, dd, *J* = 12.0, 4.0 Hz), 4.60 (1H, dd, *J* = 12.0, 8.0 Hz), 3.78 (3H, s, Ar-OC*H*$_3$), 3.66-3.59 (1H, m), 3.26 (3H, s, OC*H*$_3$), 2.18 (1H, d, *J* = 16.0 Hz), 2.04 (1H, dd, *J* = 14.0, 8.0 Hz), 1.55 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.1 (C), 152.7 (C), 129.5 (CH), 112.2 (C), 108.3 (CH), 102.4 (CH), 98.6 (C), 80.8 (CH_2), 55.2 (CH_3, O*C*H$_3$), 48.8 (CH_3, O*C*H$_3$), 34.0 (CH_2), 31.5 (CH), 23.0 (CH_3); LRMS m/z 266 ($M - H^+$), calcd for $C_{13}H_{17}NO_5$ 267.1107; HRMS m/z 290.1003 (M + Na), calcd for $C_{13}H_{17}NO_5Na$ 290.1004; Anal. calcd for $C_{13}H_{17}NO_5$ (267.1107): C, 58.42; H, 6.41; N, 5.24. Found: C, 58.50; H, 6.35; N, 5.21%.



9ia

(2*R*, 4*S*)-2,7-Dimethoxy-2-methyl-4-nitromethyl-chroman (9ia): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 9.60 min (major), t_R = 11.33 min (minor). Mp 76 °C; **$[\alpha]_D^{25}$ = –45.5° (*c* = 0.18 g/100 mL, $CHCl_3$, 80% *ee*);** IR (Neat): ν_{max} 2922, 2851, 1621, 1551 (NO_2), 1511, 1381, 1301, 1279, 1223, 1192, 1157, 1117, 1059, 1030, 859, 795, 675, and 649 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.99 (1H, dd, *J* = 8.4, 0.8 Hz), 6.52 (1H, dd, *J* = 8.6, 2.4 Hz), 6.44 (1H, d, *J* = 4.8 Hz), 4.89 (1H, dd, *J* = 12.0, 4.8 Hz), 4.42 (1H, dd, *J* = 12.4, 9.2 Hz), 3.90-3.81 (1H, m), 3.76 (3H, s, Ar-OC*H*$_3$), 3.24 (3H, s, OC*H*$_3$), 2.19 (1H, dd, *J* = 13.2, 6.0 Hz), 1.76 (1H, dd, *J* = 13.0, 12.0 Hz), 1.55 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 159.8 (C), 153.1 (C), 126.4 (CH), 112.7 (C), 107.8 (CH), 102.7 (CH), 98.2 (C), 79.3 (CH_2), 55.2 (CH_3, O*C*H$_3$), 49.0 (CH_3, O*C*H$_3$), 36.7 (CH_2), 29.8 (CH), 22.8 (CH_3); LRMS m/z 266 ($M - H^+$), calcd for $C_{13}H_{17}NO_5$ 267.1107; HRMS m/z 290.1002 (M + Na), calcd for $C_{13}H_{17}NO_5Na$ 290.1004; Anal. calcd for $C_{13}H_{17}NO_5$ (267.1107): C, 58.42; H, 6.41; N, 5.24. Found: C, 58.51; H, 6.38; N, 5.31%.



8ja

(2*S*, 4*S*)-2-Methoxy-2-methyl-4-nitromethyl-chroman-8-ol (8ja): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and

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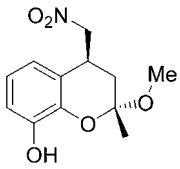
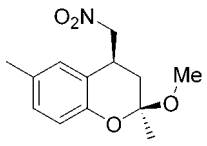
isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 98:2, flow rate 0.5 mL/min, λ = 254 nm), t_R = 59.74 min (minor), t_R = 64.77 min (major). **$[\alpha]_D^{25}$ = +14.2° (*c* = 0.25 g/100 mL, $CHCl_3$, 83% *ee*);** IR (Neat): ν_{max} 3509 (O*H*), 1596, 1547 (NO_2), 1474, 1426, 1378, 1239, 1202, 1148, 1119, 1058, 949, 863, 789, 731, 651, and 606 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.86 (2H, d, *J* = 3.5 Hz), 6.68 (1H, d, *J* = 4.0 Hz), 5.58 (1H, br s, Ar-O*H*), 4.99 (1H, dd, *J* = 12.2, 7.6 Hz), 4.63 (1H, dd, *J* = 12.7, 4.5 Hz), 3.71 (1H, d, *J* = 6.5 Hz), 3.24 (3H, s, OCH_3), 2.23 (1H, d, *J* = 14.5 Hz), 2.10 (1H, dd, *J* = 14.5, 7.0 Hz), 1.61 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.2 (C), 138.9 (C), 121.6 (CH), 120.5 (C), 119.7 (CH), 113.9 (CH), 99.6 (C), 80.4 (CH_2), 48.9 (CH_3), 34.2 (CH_2), 31.7 (CH), 23.0 (CH_3); LRMS m/z 252.15 ($M - H^+$), calcd for $C_{12}H_{15}NO_5$ 253.0950; HRMS m/z 276.0841 (M + Na), calcd for $C_{12}H_{15}NO_5Na$ 276.0848; Anal. calcd for $C_{12}H_{15}NO_5$ (253.0950): C, 56.91; H, 5.97; N, 5.53. Found: C, 56.95; H, 5.88; N, 5.65%.



9ja

(2*R*, 4*S*)-2-Methoxy-2-methyl-4-nitromethyl-chroman-8-ol (9ja): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AD-H column (hexane/2-propanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), t_R = 17.93 min (major), t_R = 23.49 min (minor). Mp 92 °C; **$[\alpha]_D^{25}$ = –54.1° (*c* = 0.27 g/100 mL, $CHCl_3$, 82% *ee*);** IR (Neat): ν_{max} 3348 (O*H*), 2940, 1596, 1547 (NO_2), 1475, 1437, 1382, 1255, 1219, 1194, 1105, 1067, 1031, 954, 926, 864, 728, 651, 630, and 608 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.86-6.85 (2H, m), 6.66-6.64 (1H, m), 5.75 (1H, br s, Ar-O*H*), 4.93 (1H, dd, *J* = 12.2, 5.0 Hz), 4.46 (1H, dd, *J* = 12.2, 9.5 Hz), 3.96-3.90 (1H, m), 3.23 (3H, s, OCH_3), 2.25 (1H, dd, *J* = 13.5, 6.0 Hz), 1.85 (1H, dd, *J* = 13.5, 12.0 Hz), 1.62 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 145.3 (C), 139.0 (C), 121.5 (CH), 120.9 (C), 116.7 (CH), 113.8 (CH), 99.0 (C), 78.9 (CH_2), 49.2 (CH_3, OCH_3), 36.8 (CH_2), 30.1 (CH), 22.8 (CH_3); LRMS m/z 252.15 ($M - H^+$), calcd for $C_{12}H_{15}NO_5$ 253.0950; HRMS m/z 276.0843 (M + Na), calcd for $C_{12}H_{15}NO_5Na$ 276.0848; Anal. calcd for $C_{12}H_{15}NO_5$ (253.0950): C, 56.91; H, 5.97; N, 5.53. Found: C, 56.95; H, 5.91; N, 5.49%.



8ka

(2*S*, 4*S*)-2-Methoxy-2,6-dimethyl-4-nitromethyl-chroman (8ka): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), t_R = 5.02 min (major), t_R = 5.70 min (minor). Mp 60 °C; **$[\alpha]_D^{25}$ = +16.0° (*c* = 0.30 g/100 mL, $CHCl_3$, 92% *ee*);** IR (Neat): ν_{max} 2951, 1547 (NO_2), 1498, 1378, 1251, 1213, 1153, 1123, 1056, 882 and 819 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.99 (1H,

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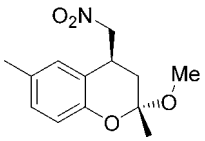
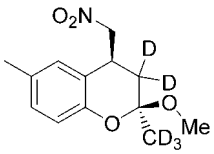
dd, *J* = 8.4, 2.0 Hz), 6.92 (1H, d, *J* = 1.6 Hz), 6.79 (1H, d, *J* = 8.0 Hz), 5.00 (1H, dd, *J* = 12.8, 9.6 Hz), 4.61 (1H, dd, *J* = 12.8, 5.6 Hz), 3.66-3.61 (1H, m), 3.22 (3H, s, OC*H*$_3$), 2.26 (3H, s, Ar-C*H*$_3$), 2.17 (1H, dd, *J* = 14.4, 1.2 Hz), 2.02 (1H, dd, *J* = 14.6, 6.8 Hz), 1.53 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 149.6 (C), 130.7 (C), 129.5 (CH), 129.1 (CH), 119.8 (C), 117.5 (CH), 98.4 (C), 80.7 (CH_2), 48.6 (CH_3, OC*H*$_3$), 33.9 (CH_2), 32.0 (CH), 23.0 (CH_3), 20.4 (CH_3); LRMS m/z 250 ($M - H^+$), calcd for $C_{13}H_{17}NO_4$ 251.1158; HRMS m/z 274.1050 (M + Na), calcd for $C_{13}H_{17}NO_4Na$ 274.1055; Anal. calcd for $C_{13}H_{17}NO_4$ (251.1158): C, 62.14; H, 6.82; N, 5.57. Found: C, 62.21; H, 6.78; N, 5.61%.



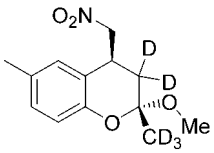
9ka

(2*R*, 4*S*)-2-Methoxy-2,6-dimethyl-4-nitromethyl-chroman (9ka): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), t_R = 6.58 min (major), t_R = 7.07 min (minor). Mp 58 °C; **$[\alpha]_D^{25}$ = –42.5° (*c* = 0.20 g/100 mL, $CHCl_3$, 89% *ee*);** IR (Neat): ν_{max} 2990, 1551 (NO_2), 1498, 1435, 1378, 1284, 1228, 1179, 1067, 887, 820 and 639 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.99-6.97 (1H, m), 6.89 (1H, br s), 6.78 (1H, d, *J* = 8.4 Hz), 4.92 (1H, dd, *J* = 12.4, 4.8 Hz), 4.42 (1H, dd, *J* = 12.2, 9.2 Hz), 3.92-3.84 (1H, m), 3.21 (3H, s, OC*H*$_3$), 2.26 (3H, s, Ar-C*H*$_3$), 2.19 (1H, dd, *J* = 13.2, 6.4 Hz), 1.78 (1H, dd, *J* = 13.2, 12.0 Hz), 1.54 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 149.8 (C), 130.5 (C), 129.2 (CH), 126.2 (CH), 120.2 (C), 117.6 (CH), 97.8 (C), 79.2 (CH_2), 48.9 (CH_3), 36.6 (CH_2), 30.2 (CH), 22.8 (CH_3), 20.6 (CH_3); LRMS m/z 250 ($M - H^+$), calcd for $C_{13}H_{17}NO_4$ 251.1158; HRMS m/z 274.1051 (M + Na), calcd for $C_{13}H_{17}NO_4Na$ 274.1055; Anal. calcd for $C_{13}H_{17}NO_4$ (251.1158): C, 62.14; H, 6.82; N, 5.57. Found: C, 62.25; H, 6.88; N, 5.51%.



8ka-D_5

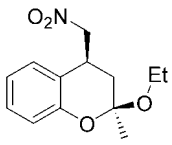
(2*S*, 4*S*)-2-Methoxy-2,6-dimethyl-4-nitromethyl-chroman-1,1,1,3,3-d_5 (8ka-d_5): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), t_R = 5.17 min (major), t_R = 6.12 min (minor). Mp 56 °C; **$[\alpha]_D^{25}$ = +23.0° (*c* = 0.27 g/100 mL, $CHCl_3$, 89% *ee*);** IR (Neat): ν_{max} 2962, 1539 (NO_2), 1498, 1378, 1235, 1178, 1143, 1075, 1035 and 817 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.01 (1H, d, *J* = 8.0 Hz), 6.94 (1H, s), 6.81 (1H, d, *J* = 8.4 Hz), 5.00 (1H, d, *J* = 9.2 Hz, proton resolution is very poor), 4.61 (1H, s, proton resolution is very poor), 3.62 (1H, s), 3.24 (3H, s, OC*H*$_3$), 2.28 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 149.6 (C), 130.7 (C), 129.5 (CH), 129.1 (CH), 119.7 (C), 117.5 (CH), 98.3 (C), 80.7 (CH_2, peak resolution is very poor), 48.6 (CH_3, OC*H*$_3$), 33.9 (CH_2, peak resolution is very poor), 31.7 (CH),



9ka-D_5

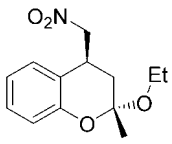
23.0 (CH_3, peak resolution is very poor), 20.5 (CH_3); LRMS m/z 257 ($M + H^+$), calcd for $C_{13}H_{12}D_5NO_4$ 256.1466.

(2*R*, 4*S*)-2-Methoxy-2,6-dimethyl-4-nitromethyl-chroman-1,1,1,3,3-d$_5$ (9ka-d$_5$): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), t_R = 6.84 min (major), t_R = 7.41 min (minor). Mp 66 °C; **$[\alpha]_D^{25}$ = –54.9° (*c* = 0.37 g/100 mL, $CHCl_3$, 91% *ee*);** IR (Neat): ν_{max} 2939, 1543 (NO_2), 1496, 1378, 1248, 1196, 1072, 1037, 820 and 642 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00 (1H, d, *J* = 8.0 Hz), 6.91 (1H, s), 6.80 (1H, d, *J* = 8.2 Hz), 4.92 (1H, s, proton resolution is very poor), 4.43 (1H, d, *J* = 9.6 Hz, proton resolution is very poor), 3.87 (1H, s), 3.23 (3H, s, OC*H*$_3$), 2.28 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 149.8 (C), 130.5 (C), 129.3 (CH), 126.2 (CH), 120.2 (C), 117.7 (CH), 97.7 (C), 79.0 (CH_2, peak resolution is very poor), 49.0 (CH_3, OC*H*$_3$), 36.0 (CH_2, peak resolution is very poor), 30.0 (CH), 22.1 (CH_3, peak resolution is very poor), 20.7 (CH_3); LRMS m/z 257.10 ($M + H^+$), calcd for $C_{13}H_{12}D_5NO_4$ 256.1466.



8ab

(2*S*, 4*S*)-2-Ethoxy-2-methyl-4-nitromethyl-chroman (8ab): Prepared following the procedure **C** 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 1.0 mL/min, λ = 254 nm), t_R = 5.12 min (minor), t_R = 5.52 min (major). **$[\alpha]_D^{25}$ = +74.8° (*c* = 0.67 g/100 mL, $CHCl_3$, 80% *ee*);** IR (Neat): ν_{max} 2974, 2937, 1582, 1550 (NO_2), 1488, 1454, 1379, 1247, 1156, 1126, 1101, 1057 and 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18 (1H, dt, *J* = 7.2, 1.0 Hz), 7.11 (1H, br d, *J* = 7.2 Hz), 6.94 (1H, br t, *J* = 7.2 Hz), 6.87 (1H, d, *J* = 8.0 Hz), 5.06 (1H, dd, *J* = 13.0, 9.2 Hz), 4.65 (1H, dd, *J* = 12.8, 5.6 Hz), 3.69 (1H, q, *J* = 6.4 Hz), 3.59 (2H, q, *J* = 6.8 Hz, OC*H*$_2$CH$_3$), 2.22 (1H, d, *J* = 14.4 Hz), 2.04 (1H, dd, *J* = 14.4, 6.8 Hz), 1.56 (3H, s, C*H*$_3$), 1.03 (3H, t, *J* = 6.8 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 152.0 (C), 128.9 (CH), 128.8 (CH), 121.3 (CH), 120.2 (C), 117.7 (CH), 98.4 (C), 80.9 (CH_2), 56.8 (CH_2, OC*H*$_2$CH$_3$), 34.2 (CH_2), 32.1 (CH), 23.7 (CH_3), 15.4 (CH_3, OCH$_2$C*H*$_3$); LRMS m/z 250 ($M - H^+$), calcd for $C_{13}H_{17}NO_4$ 251.1158; Anal. calcd for $C_{13}H_{17}NO_4$ (251.1158): C, 62.14; H, 6.82; N, 5.57. Found: C, 62.25; H, 6.88; N, 5.61%.



9ab

(2*R*, 4*S*)-2-Ethoxy-2-methyl-4-nitromethyl-chroman (9ab): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 90:10, flow rate 1.0

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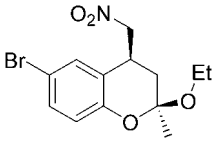
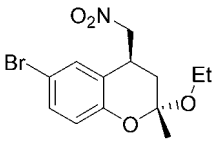
mL/min, λ = 254 nm), t_R = 5.72 min (major), t_R = 8.69 min (minor). Mp 60 °C; **$[\alpha]_D^{25}$ = –54.8° (*c* = 0.83 g/100 mL, $CHCl_3$, 80% *ee*);** IR (Neat): ν_{max} 2979, 1552 (NO_2), 1489, 1452, 1379, 1256, 1224, 1188, 1097, 1063, 938, 879, 756 and 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17 (1H, t, *J* = 7.6 Hz), 7.10 (1H, d, *J* = 7.6 Hz), 6.93 (1H, t, *J* = 7.2 Hz), 6.86 (1H, d, *J* = 8.0 Hz), 4.93 (1H, dd, *J* = 12.4, 4.8 Hz), 4.47 (1H, dd, *J* = 12.0, 9.2 Hz), 4.00-3.92 (1H, m), 3.64-3.47 (2H, m, OCH_2CH_3), 2.22 (1H, dd, *J* = 13.4, 6.0 Hz), 1.79 (1H, t, *J* = 12.8 Hz), 1.57 (3H, s, CH_3), 0.97 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 152.2 (C), 128.5 (CH), 125.7 (CH), 121.1 (CH), 120.6 (C), 117.8 (CH), 97.9 (C), 79.2 (CH_2), 56.8 (CH_2, OCH_2CH_3), 36.8 (CH_2), 30.3 (CH), 23.7 (CH_3), 15.3 (CH_3, OCH_2CH_3); LRMS m/z 250 ($M - H^+$), calcd for $C_{13}H_{17}NO_4$ 251.1158; HRMS m/z 274.1053 (M + Na), calcd for $C_{13}H_{17}NO_4Na$ 274.1055; Anal. calcd for $C_{13}H_{17}NO_4$ (251.1158): C, 62.14; H, 6.82; N, 5.57. Found: C, 62.10; H, 6.88; N, 5.65%.



8eb

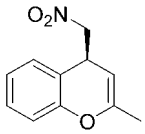
(2*S*, 4*S*)-6-Bromo-2-ethoxy-2-methyl-4-nitromethyl-chroman (8eb): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 4.54 min (minor), t_R = 4.90 min (major). **$[\alpha]_D^{25}$ = +65.5° (*c* = 0.83 g/100 mL, $CHCl_3$, 88% *ee*);** IR (Neat): ν_{max} 2974, 2934, 2893, 1739, 1545 (NO_2), 1483, 1381, 1253, 1215, 1180, 1059, 951, 881, 818, 739, 681, 582 and 490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30-7.26 (2H, m), 6.76 (1H, d, *J* = 8.8 Hz), 5.07 (1H, dd, *J* = 13.2, 9.2 Hz), 4.61 (1H, dd, *J* = 13.0, 5.2 Hz), 3.70-3.61 (1H, m), 3.59-3.51 (2H, m, OCH_2CH_3), 2.20 (1H, dd, *J* = 14.8, 1.2 Hz), 2.01 (1H, dd, *J* = 14.6, 7.2 Hz), 1.56 (3H, s, CH_3), 1.03 (3H, t, *J* = 8.4 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 151.2 (C), 131.8 (CH), 131.5 (CH), 122.4 (C), 119.6 (CH), 113.3 (C), 98.6 (C), 80.5 (CH_2), 57.0 (CH_2, OCH_2CH_3), 33.9 (CH_2), 31.8 (CH), 23.6 (CH_3), 15.3 (CH_3, OCH_2CH_3); LRMS m/z 330.15 ($M + H^+$), calcd for $C_{13}H_{16}BrNO_4$ 329.0263; Anal. calcd for $C_{13}H_{16}BrNO_4$ (329.0263): C, 47.29; H, 4.88; N, 4.24. Found: C, 47.32; H, 4.84; N, 4.28%.

(2*R*, 4*S*)-6-Bromo-2-ethoxy-2-methyl-4-nitromethyl-chroman (9eb): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 5.34 min (major), t_R = 6.09 min (minor). Mp 70 °C; **$[\alpha]_D^{25}$ = –41.2° (*c* = 0.83 g/100 mL, $CHCl_3$, 82% *ee*);** IR (Neat): ν_{max} 2974, 2922, 1736, 1548 (NO_2), 1483, 1381, 1217, 1064, 939, 885, 814, 673 and 470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29-7.26 (1H, m), 7.23-7.22 (1H, m), 6.75 (1H, d, *J* = 8.8 Hz), 4.89 (1H, dd, *J* = 12.2, 4.4 Hz), 4.48 (1H, dd, *J* = 12.4, 9.2 Hz), 3.97-3.89 (1H, m),



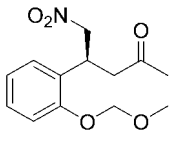
9eb

3.68-3.44 (2H, m, OC*H*$_2$CH$_3$), 2.21 (1H, dd, *J* = 13.2, 6.0 Hz), 1.77 (1H, t, *J* = 12.4 Hz), 1.56 (3H, s, C*H*$_3$), 0.98 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 151.5 (C), 131.5 (CH), 128.7 (CH), 122.8 (C), 119.6 (CH), 113.2 (C), 98.2 (C), 78.8 (CH$_2$), 57.0 (CH$_2$, O*C*H$_2$CH$_3$), 36.4 (CH$_2$), 30.2 (CH), 23.5 (CH$_3$), 15.2 (CH$_3$, OCH$_2$*C*H$_3$); LRMS m/z 330.15 (M + H$^+$), calcd for $C_{13}H_{16}BrNO_4$ 329.0263; Anal. calcd for $C_{13}H_{16}BrNO_4$ (329.0263): C, 47.29; H, 4.88; N, 4.24. Found: C, 47.32; H, 4.91; N, 4.31%.



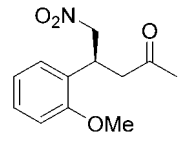
10a

(4*S*)-2-Methyl-4-nitromethyl-4*H*-chromene (10a): Prepared following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as solid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), t_R = 8.09 min (major), t_R = 8.74 min (minor). Mp 58 °C; **[α]$_D^{25}$ = –15.5° (*c* = 0.23 g/100 mL, CHCl$_3$, 81% *ee*);** IR (Neat): ν$_{max}$ 3623, 3602, 1688, 1544 (NO$_2$), 1485, 1380, 1314, 1263, 1227, 1193, 1105, 1069, 1022, 801 and 767 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.23 (1H, t, *J* = 7.6 Hz), 7.11-7.05 (2H, m), 6.96 (1H, d, *J* = 8.4 Hz), 4.75 (1H, d, *J* = 3.6 Hz), 4.45 (1H, dd, *J* = 11.6, 5.6 Hz), 4.43-4.38 (1H, m), 4.27-4.26 (1H, m), 1.95 (3H, s, C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 151.6 (C), 150.7 (C), 128.8 (CH), 128.0 (CH), 123.7 (CH), 118.2 (C), 116.9 (CH), 94.5 (CH), 82.0 (CH$_2$), 33.9 (CH), 19.3 (CH$_3$); LRMS m/z 204 (M – H$^+$), calcd for $C_{11}H_{11}NO_3$ 205.0739; Anal. calcd for $C_{11}H_{11}NO_3$ (205.0739): C, 64.38; H, 5.40; N, 6.83. Found: C, 64.25; H, 5.46; N, 6.89%.



11aa

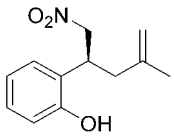
(4*S*)-4-(2-Methoxymethoxy-phenyl)-5-nitro-pentan-2-one (11aa): Prepared following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as liquid. **[α]$_D^{25}$ = –44.6° (*c* = 0.20 g/100 mL, CHCl$_3$, 82% *ee*);** IR (Neat): ν$_{max}$ 2918, 2851, 1712 (*C*=O), 1550 (NO$_2$), 1489, 1375, 1232, 1151, 1078, 999 and 758 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.23 (1H, dt, *J* = 7.2, 2.3 Hz), 7.15 (1H, dd, *J* = 7.6, 1.6 Hz), 7.11 (1H, br d, *J* = 7.6 Hz), 6.96 (1H, dt, *J* = 7.2, 1.6 Hz), 5.25 (2H, s), 4.74 (2H, d, *J* = 6.8 Hz), 4.30 (1H, quintet, *J* = 6.8 Hz), 3.52 (3H, s, OC*H*$_3$), 3.01 (2H, dABq, *J* = 17.6, 7.6 Hz), 2.14 (3H, s, C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 205.9 (C, *C*=O), 154.8 (C), 129.0 (CH), 128.9 (CH), 126.9 (C), 122.0 (CH), 114.3 (CH), 94.4 (CH$_2$), 78.0 (CH$_2$), 56.3 (CH$_3$, O*C*H$_3$), 44.7 (CH$_2$), 34.7 (CH), 30.2 (CH$_3$); LRMS m/z 268.50 (M + H$^+$), calcd for $C_{13}H_{17}NO_5$ 267.1107; Anal. calcd for $C_{13}H_{17}NO_5$ (267.1107): C, 58.24; H, 6.41; N, 5.24. Found: C, 58.25; H, 6.44; N, 5.32%.



11ab

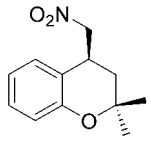
(4*S*)-4-(2-Methoxy-phenyl)-5-nitro-pentan-2-one (11ab):♣ Prepared following the procedure **J** and purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralpak AS-H column (hexane/2-propanol = 60:40, flow rate 1.0

mL/min, λ = 210 nm), t_R = 10.62 min (major), t_R = 12.00 min (minor). **$[\alpha]_D^{25}$ = +33.2°** (*c* = 0.50 g/100 mL, $CHCl_3$, 80% *ee*); IR (Neat): ν_{max} 1716 (*C*=O), 1551 (NO_2), 1494, 1462, 1376, 1245, 1165, 1122, 1028, 910 and 656 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25-7.21 (1H, m), 7.12 (1H, d, *J* = 4.0 Hz), 6.90-6.86 (2H, m), 4.75-4.66 (2H, m), 4.20 (1H, quintet, *J* = 6.8 Hz), 3.84 (3H, s, O*CH*$_3$), 3.04-2.91 (2H, m), 2.10 (3H, s, *CH*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 206.1 (C, *C*=O), 156.9 (C), 129.1 (CH), 128.8 (CH), 126.2 (C), 120.6 (CH), 110.8 (CH), 77.6 (CH_2), 55.1 (CH_3, O*C*H$_3$), 44.3 (CH_2), 35.2 (CH), 30.0 (CH_3).



12a

(1*S*)-2-(3-Methyl-1-nitromethyl-but-3-enyl)-phenol (12a): 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 AS-H column (hexane/2-propanol = 94:6, flow rate 0.8 mL/min, λ = 254 nm), t_R = 7.57 min (major), t_R = 8.75 min (minor). **$[\alpha]_D^{25}$ = –26.5° (*c* = 0.20 g/100 mL, $CHCl_3$, 82% *ee*);** IR (Neat): ν_{max} 3518 (O*H*), 1600, 1550 (NO_2), 1454, 1378, 1260, 1105, 894, 755, 679, 646 and 601 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13-7.10 (2H, m), 6.89 (1H, t, *J* = 7.2 Hz), 6.72 (1H, t, *J* = 8.0 Hz), 5.39 (1H, s, Ar-O*H*), 4.81-4.73 (3H, m), 4.67-4.62 (1H, m), 3.98 (1H, quintet, *J* = 6.8 Hz), 2.53-2.49 (2H, m), 1.75 (3H, s, *CH*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 153.5 (C), 142.1 (C), 129.1 (CH), 128.5 (CH), 125.5 (C), 121.1 (CH), 116.0 (CH), 113.5 (CH_2, C=*C*H$_2$), 78.6 (CH_2), 39.9 (CH_2), 37.6 (CH), 22.0 (CH_3); LRMS m/z 222.00 (M + H^+), calcd for $C_{12}H_{15}NO_3$ 221.1052; HRMS m/z 244.0945 (M + Na), calcd for $C_{12}H_{15}NO_3Na$ 244.0950; Anal. calcd for $C_{12}H_{15}NO_3$ (221.1052): C, 65.14; H, 6.83; N, 6.33. Found: C, 65.25; H, 6.87; N, 6.42%.



13a

(4*S*)-2,2-Dimethyl-4-nitromethyl-chroman (13a): Prepared following the procedure **G** 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 1.0 mL/min, λ = 254 nm), t_R = 6.44 min (major), t_R = 8.15 min (minor). **$[\alpha]_D^{25}$ = –65.8° (*c* = 0.57 g/100 mL, $CHCl_3$, 81% *ee*);** IR (Neat): ν_{max} 2963, 2930, 2865, 1730, 1552 (NO_2), 1483, 1444, 1376, 1260, 1087, 1025, 800 and 651 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17 (1H, t, *J* = 7.6 Hz), 7.08 (1H, d, *J* = 7.6 Hz), 6.89 (1H, t, *J* = 7.2 Hz), 6.84 (1H, d, *J* = 8.4 Hz), 4.95 (1H, dd, *J* = 12.0, 4.8 Hz), 4.40 (1H, t, *J* = 10.0 Hz), 3.78-3.73 (1H, m), 1.98 (1H, dd, *J* = 13.4, 6.4 Hz), 1.74 (1H, t, *J* = 11.6 Hz), 1.44 (3H, s, *CH*$_3$), 1.27 (3H, s, *CH*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 153.8 (C), 128.8 (CH), 126.3 (CH), 120.4 (CH), 118.7 (C), 118.4 (CH), 80.1 (CH_2), 73.9 (C), 37.5 (CH_2), 31.2 (CH), 29.5 (CH_3), 24.1 (CH_3); LRMS m/z 221.80 (M + H^+), calcd for $C_{12}H_{15}NO_3$ 221.1052; HRMS m/z 244.0942 (M + Na), calcd for $C_{12}H_{15}NO_3Na$ 244.0950; Anal. calcd for $C_{12}H_{15}NO_3$ (221.1052): C, 65.14; H, 6.83; N, 6.33. Found: C, 65.08; H, 6.77; N, 6.25%.

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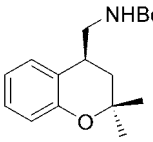
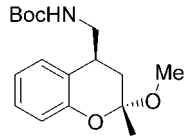


14a

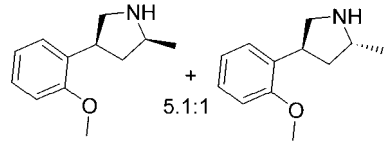
(4*S*)-(2,2-Dimethyl-chroman-4-ylmethyl)-carbamic acid *tert*-butyl ester (14a): Prepared following the procedure **H** and purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 68 °C; **$[\alpha]_D^{25}$ = –24.7° (*c* = 0.5 g/100 mL, $CHCl_3$, 81% *ee*);** IR (Neat): ν_{max} 3350 (N*H*), 2982, 2924, 2492, 1678 (*C*=O), 1606, 1577, 1525 (NO_2), 1487, 1423, 1365, 1251, 1157, 1041, 935, 754, 638 and 403 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (1H, br d, *J* = 7.2 Hz), 7.12 (1H, t, *J* = 7.2 Hz), 6.88 (1H, t, *J* = 7.2 Hz), 6.81 (1H, dd, *J* = 7.2, 1.0 Hz), 4.50 (1H, s, N*H*), 3.82-3.77 (1H, m), 3.40-3.36 (1H, m), 3.09 (1H, m), 1.88 (1H, dd, *J* = 13.6, 6.0 Hz), 1.68 (1H, t, *J* = 12.8 Hz), 1.43 (12H, s, 4 x CH_3), 1.23 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 156.1 (C), 154.4 (C), 127.9 (CH), 126.7 (CH), 121.6 (C), 120.2 (CH), 117.8 (CH), 79.4 (C), 74.2 (C), 43.6 (CH_2), 37.3 (CH_2), 31.9 (CH), 30.0 (CH_3), 28.3 (3 x CH_3), 24.1 (CH_3); LRMS m/z 292.10 (M + H^+), calcd for $C_{17}H_{25}NO_3$ 291.1834; Anal. calcd for $C_{17}H_{25}NO_3$ (291.1834): C, 70.07; H, 8.65; N, 4.81. Found: C, 70.15; H, 8.61; N, 4.85%.



15aa

(*2R*, *4S*)-(2-Methoxy-2-methyl-chroman-4-ylmethyl)-carbamic acid *tert*-butyl ester (15aa): Prepared following the procedure **H** and purified by column chromatography using EtOAc/hexane and isolated as liquid. The enantiomeric excess (ee) was determined by chiral stationary phase HPLC using a Daicel Chiralcel OD-H column (hexane/2-propanol = 94:6, flow rate 0.6 mL/min, λ = 254 nm), t_R = 9.83 min (major), t_R = 11.39 min (minor). **$[\alpha]_D^{25}$ = –44.5° (*c* = 0.22 g/100 mL, $CHCl_3$, 81% *ee*);** IR (Neat): ν_{max} 3627 (N*H*), 3361, 2977, 2936, 1704 (*C*=O), 1491, 1454, 1370, 1256, 1168, 1107, 1067 and 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (1H, d, *J* = 8.0 Hz), 7.15 (1H, t, *J* = 8.0 Hz), 6.94 (1H, dt, *J* = 8.0, 0.8 Hz), 6.86 (1H, dd, *J* = 8.2, 1.2 Hz), 4.44 (1H, s, N*H*), 3.80-3.73 (1H, m), 3.51-3.45 (1H, m), 3.29-3.22 (1H, m), 3.24 (3H, s, OCH_3), 2.13 (1H, dd, *J* = 13.4, 6.0 Hz), 1.75 (1H, t, *J* = 13.2 Hz), 1.56 (3H, s, C*H*$_3$), 1.47-1.41 (9H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 156.1 (C), 152.8 (C), 127.8 (CH), 126.2 (CH), 123.0 (C), 121.1 (CH), 117.4 (CH), 98.4 (C), 79.3 (C), 49.0 (CH_3, O*C*H$_3$), 42.4 (CH_2), 36.2 (CH_2), 31.0 (CH), 28.3 (3 x CH_3), 23.1 (CH_3); HRMS m/z 330.1682 (M + Na), calcd for $C_{17}H_{25}NO_4Na$ 330.1681; Anal. calcd for $C_{17}H_{25}NO_4$ (307.1784): C, 66.43; H, 8.20; N, 4.56. Found: C, 66.56; H, 8.25; N, 4.51%.

(4*S*, 2*S*)-4-(2-Methoxy-phenyl)-2-methyl-pyrrolidine (*cis*-16ab) and (4*S*, 2*R*)-4-(2-Methoxy-phenyl)-2-methyl-pyrrolidine (*trans*-16ab): Prepared following the procedure **K** and purified by column chromatography using EtOAc/hexane and isolated as liquid. **$[\alpha]_D^{25}$ = +31.0° (*c* = 0.35 g/100 mL, $CHCl_3$, 80% *ee*);** IR (Neat): ν_{max} 1598, 1493, 1459, 1243, 1095, 1026, 799, 641 and 605 cm^{-1}; ^1H NMR ($CDCl_3$, major *cis*-isomer) δ 7.22-7.09 (2H, m),



16ab

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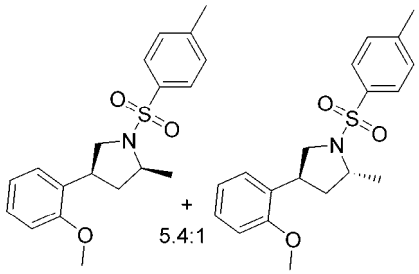
6.93-6.84 (2H, m), 3.82 (3H, s, OC*H*$_3$), 3.88-3.70 (1H, m), 3.64-3.56 (1H, m), 3.34-3.25 (1H, m), 2.99-2.95 (1H, m), 2.64-2.57 (1H, br s, N*H*), 2.32-2.23 (1H, m), 1.54-1.43 (1H, m), 1.27 (3H, d, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major *cis*-isomer) δ 157.3 (C), 132.4 (C), 127.2 (CH), 127.1 (CH), 120.5 (CH), 110.4 (CH), 55.5 (CH), 55.3 (CH_3, O*C*H$_3$), 53.0 (CH_2), 41.5 (CH_2), 40.6 (CH), 21.0 (CH_3); LRMS m/z 192.15 (M + H$^+$), calcd for $C_{12}H_{17}NO$ 191.1310; Anal. calcd for $C_{12}H_{17}NO$ (191.1310): C, 75.35; H, 8.96; N, 7.32. Found: C, 75.48; H, 8.88; N, 7.42%.

(4*S*, 2*S*)-4-(2-Methoxy-phenyl)-2-methyl-1-(toluene-4-sulfonyl)-pyrrolidine (*cis*-17ab) and (4*S*, 2*R*)-4-(2-Methoxy-phenyl)-2-methyl-1-(toluene-4-sulfonyl)-pyrrolidine (*trans*-17ab): Prepared following the procedure **L** and purified by column chromatography using EtOAc/hexane and isolated as liquid.



17ab

[α]$_D^{25}$ = +38.5° (*c* = 0.33 g/100 mL, $CHCl_3$, 80% *ee*); IR (Neat): ν$_{max}$ 1597, 1493, 1461, 1341, 1243, 1092, 1032, 817, 755, 724, 658, 642 and 625 cm^{-1}; ^{1}H NMR ($CDCl_3$, major *cis*-isomer) δ 7.82 (2H, d, *J* = 8.2 Hz), 7.36 (2H, d, *J* = 8.0 Hz), 7.24-7.19 (1H, m), 7.12-7.10 (1H, m), 6.93-6.89 (1H, m), 6.85-6.82 (1H, m), 3.96 (1H, ddd, *J* = 11.6, 7.4, 1.2 Hz), 3.79 (3H, s, Ar-OC*H*$_3$), 3.76-3.71 (1H, m), 3.27 (1H, t, *J* = 11.2 Hz), 2.97-2.87 (1H, m), 2.47 (3H, s, Ar-C*H*$_3$), 2.96-2.23 (1H, m), 1.82-1.74 (1H, m), 1.49 (3H, d, *J* = 6.2 Hz); ^{1}H NMR ($CDCl_3$, minor *trans*-isomer) δ 7.74 (2H, d, *J* = 8.2 Hz), 7.31 (2H, d, *J* = 8.0 Hz), 7.24-7.19 (1H, m), 7.12-7.10 (1H, m), 6.93-6.89 (1H, m), 6.85-6.82 (1H, m), 3.99-3.92 (1H, m), 3.79 (3H, s), 3.76-3.71 (1H, m), 3.27 (1H, t, *J* = 11.0 Hz), 2.97-2.87 (1H, m), 2.45 (3H, s), 2.96-2.23 (1H, m), 2.00-1.85 (1H, m), 1.44 (3H, d, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135, major *cis*-isomer) δ 157.5 (C), 143.1 (C), 135.4 (C), 129.5 (2 x CH), 127.9 (CH), 127.7 (C), 127.6 (2 x CH), 126.6 (CH), 120.5 (CH), 110.3 (CH), 56.7 (CH), 55.2 (CH_3, O*C*H$_3$), 53.9 (CH_2), 39.9 (CH_2), 37.3 (CH), 22.8 (CH_3), 21.5 (CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, minor *trans*-isomer) δ 157.6 (C), 143.1 (C), 134.6 (C), 129.5 (2 x CH), 127.9 (CH), 127.6 (2 x CH), 127.5 (C), 126.6 (CH), 120.4 (CH), 110.36 (CH), 56.7 (CH), 55.7 (CH_3, O*C*H$_3$), 53.8 (CH_2), 37.9 (CH_2), 36.1 (CH), 23.4 (CH_3), 21.5 (CH_3); LRMS m/z 346.25 (M + H$^+$), calcd for $C_{19}H_{23}NO_3S$ 345.1399; Anal. calcd for $C_{19}H_{23}NO_3S$ (345.1399): C, 66.06; H, 6.71; N, 4.05. Found: C, 66.25; H, 6.62; N, 4.12%.

♣ The absolute configuration of chiral products **8aa-eb** and **9aa-eb** were also established by comparison of **(+)-11ab** with the chiral product synthesized from direct asymmetric Michael reaction (see Fei Xue et. al. *Adv. Synth. Catal.*, **2008**, *350*, 2194-2198).

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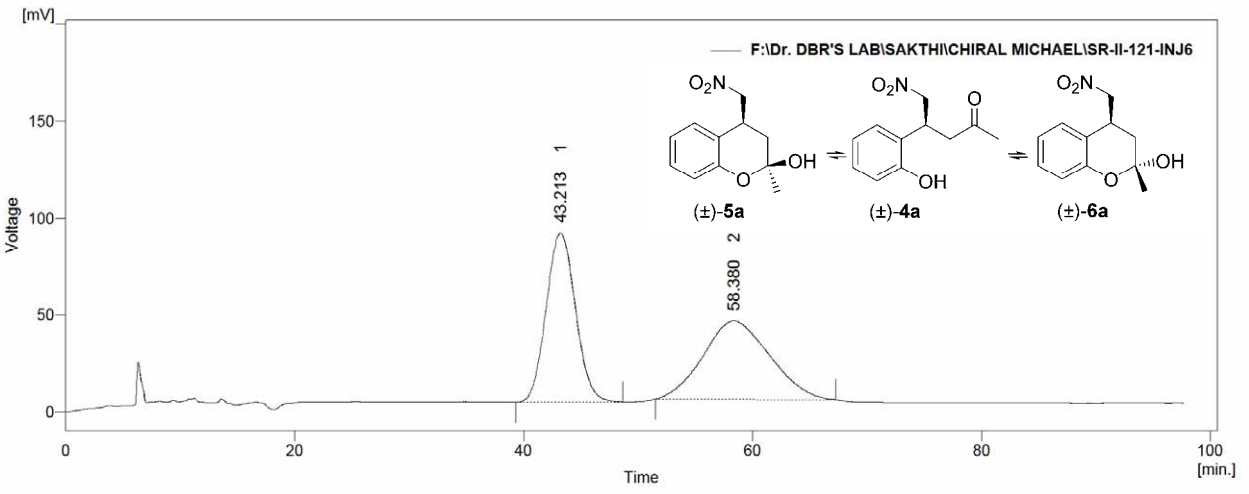
RACEMIC **5a↔4a↔6a**:

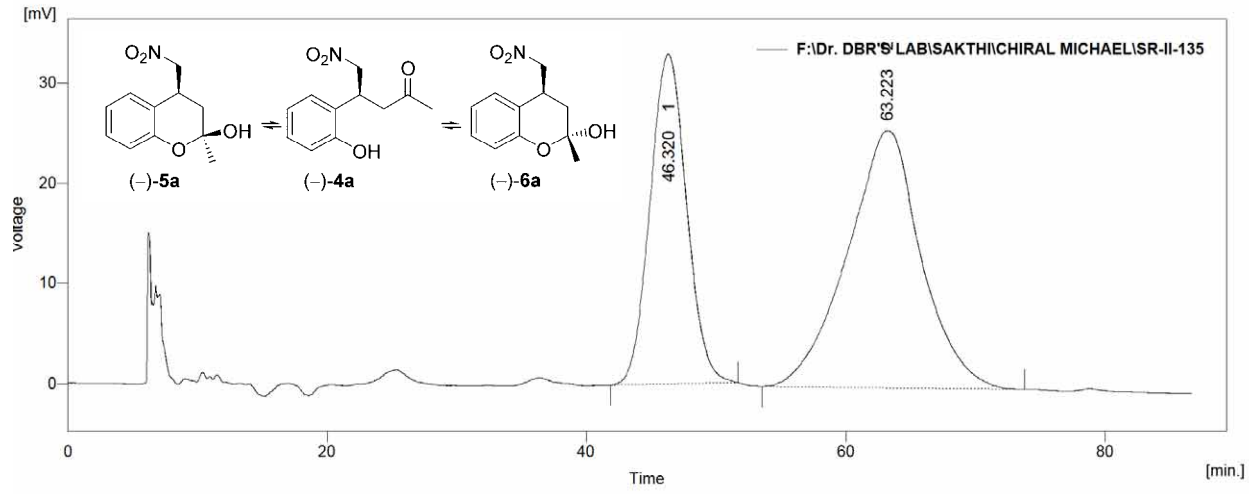


Daicel chiralpak AD-H, Hexane/i-PrOH = 95:5, Flow Rate 0.5 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-121-INJ6)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	43.213	10318.546	58.262	48.7	68.4	2.77
2	58.380	10879.922	26.908	51.3	31.6	6.38
	Total	21198.468	85.170	100.0	100.0	

CHIRAL **5a↔4a↔6a** (22% ee):



Daicel chiralpak AD-H, Hexane/i-PrOH = 95:5, Flow Rate 0.5 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-135)

	Reten. Time	Area	Height	Area	Height	W05

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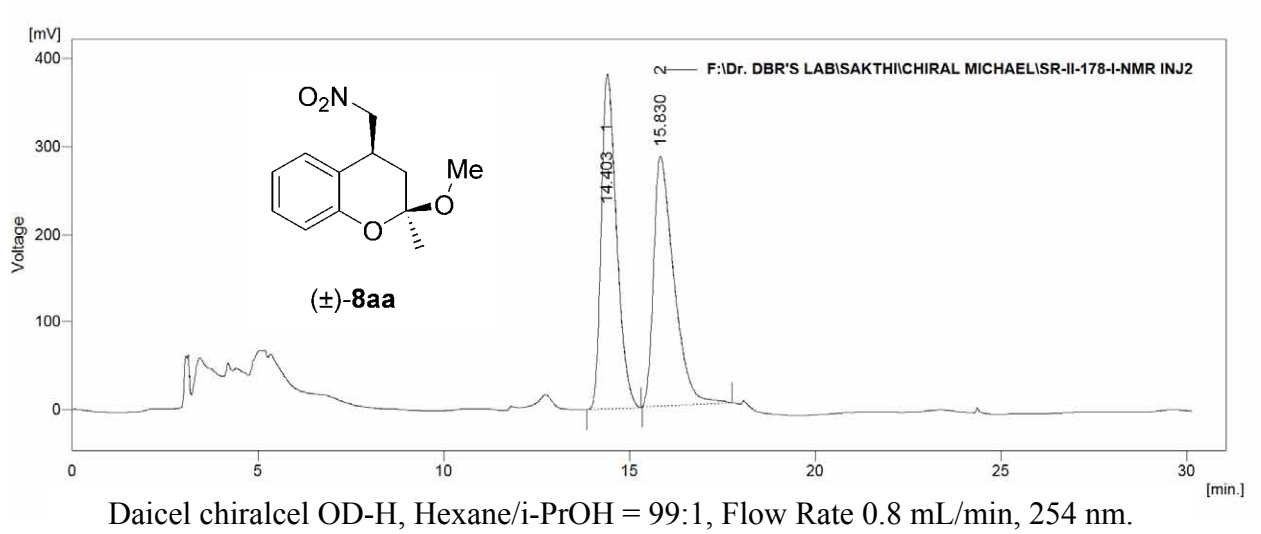
RACEMIC **8aa**:

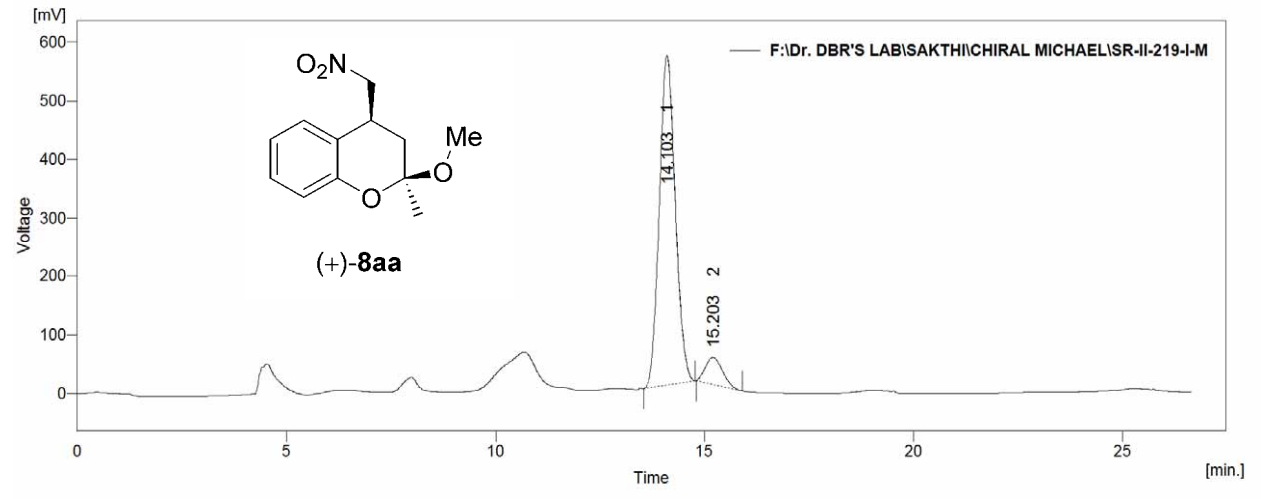


Daicel chiralcel OD-H, Hexane/i-PrOH = 99:1, Flow Rate 0.8 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-178-I-NMR INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	14.403	7267.009	254.500	50.2	57.3	0.44
2	15.830	7207.534	190.025	49.8	42.7	0.57
	Total	14474.543	444.525	100.0	100.0	

CHIRAL **8aa** (84% ee):



Daicel chiralcel OD-H, Hexane/i-PrOH = 99:1, Flow Rate 0.8 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-219-I-M)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	14.103	9914.923	375.320	91.9	92.4	0.41
2	15.203	879.379	30.667	8.1	7.6	0.46
	Total	10794.302	405.987	100.0	100.0	

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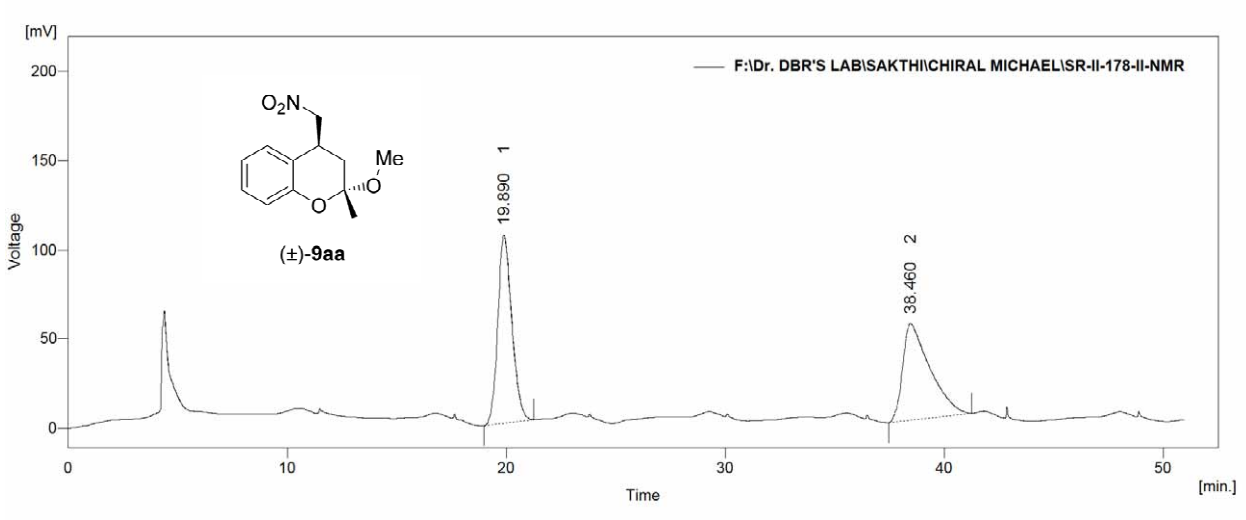
RACEMIC **9aa**:

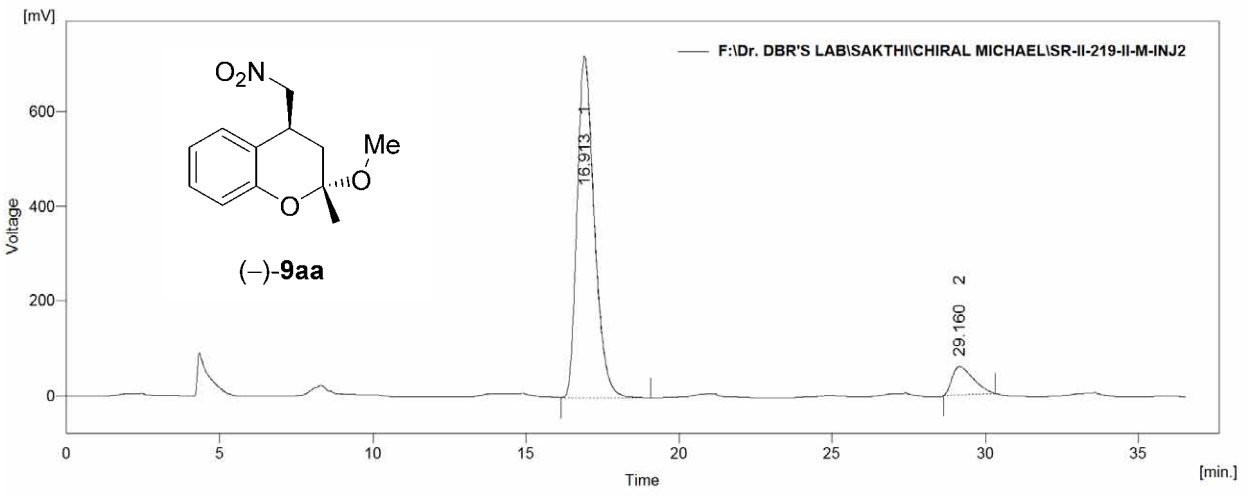


Daicel chiralcel OD-H, Hexane/i-PrOH = 99:1, Flow Rate 0.8 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-178-II-NMR)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	19.890	3121.366	70.465	50.3	66.2	0.68
2	38.460	3086.682	35.926	49.7	33.8	1.35
	Total	6208.048	106.391	100.0	100.0	

CHIRAL **9aa** (82% ee):



Daicel chiralcel OD-H, Hexane/i-PrOH = 99:1, Flow Rate 0.8 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-219-II-M-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	16.913	18743.042	480.605	90.8	92.4	0.60
2	29.160	1894.363	39.584	9.2	7.6	0.78
	Total	20637.404	520.188	100.0	100.0	

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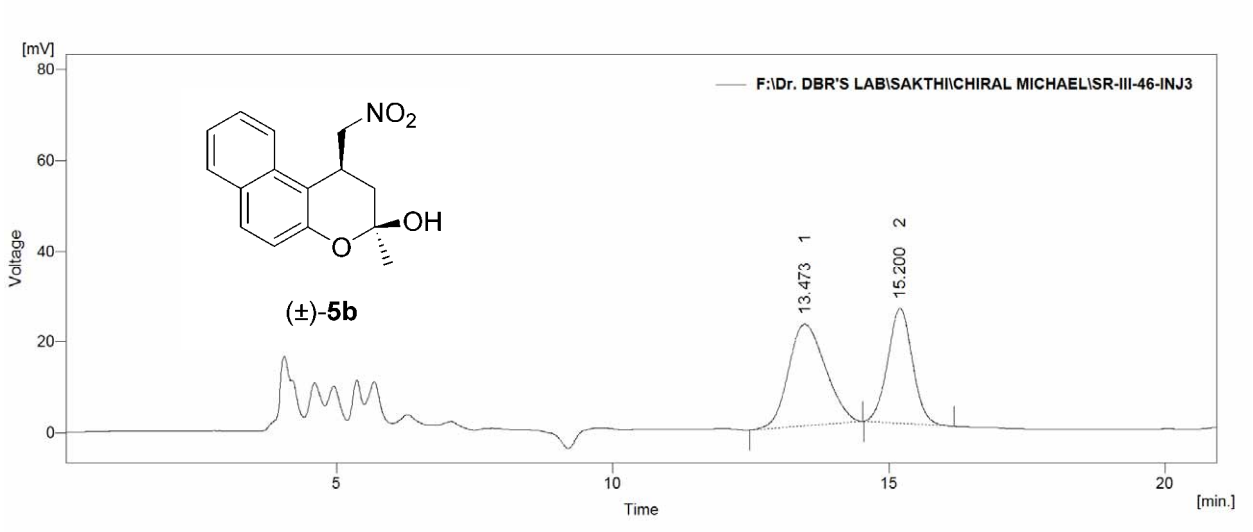
RACEMIC **5b**:

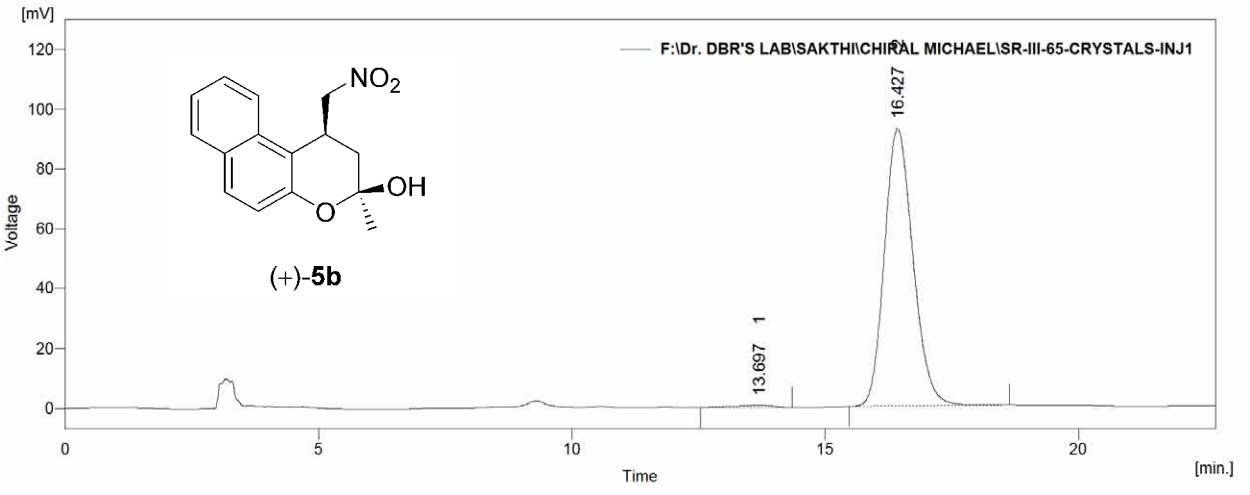


Daicel chiralcel OD-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-46-INJ3)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	13.473	692.512	14.928	56.7	46.9	0.74
2	15.200	527.822	16.918	43.3	53.1	0.48
	Total	1220.334	31.847	100.0	100.0	

CHIRAL **5b** (98% ee):



Daicel chiralcel OD-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-65-CRYSTALS-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	13.697	24.119	0.454	1.0	0.7	0.88
2	16.427	2425.580	61.868	99.0	99.3	0.60
	Total	2449.699	62.322	100.0	100.0	

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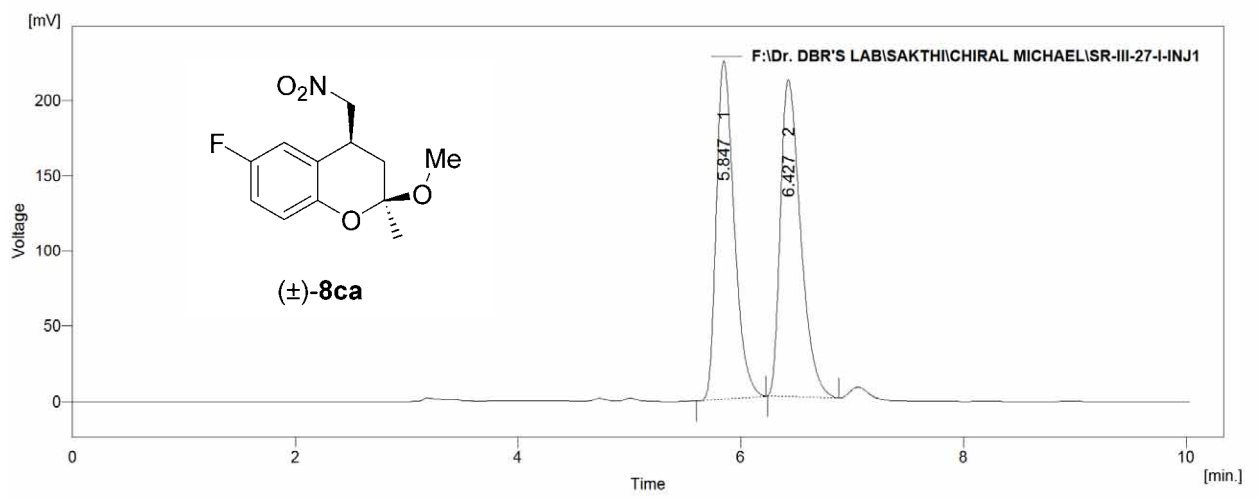
RACEMIC **8ca**:

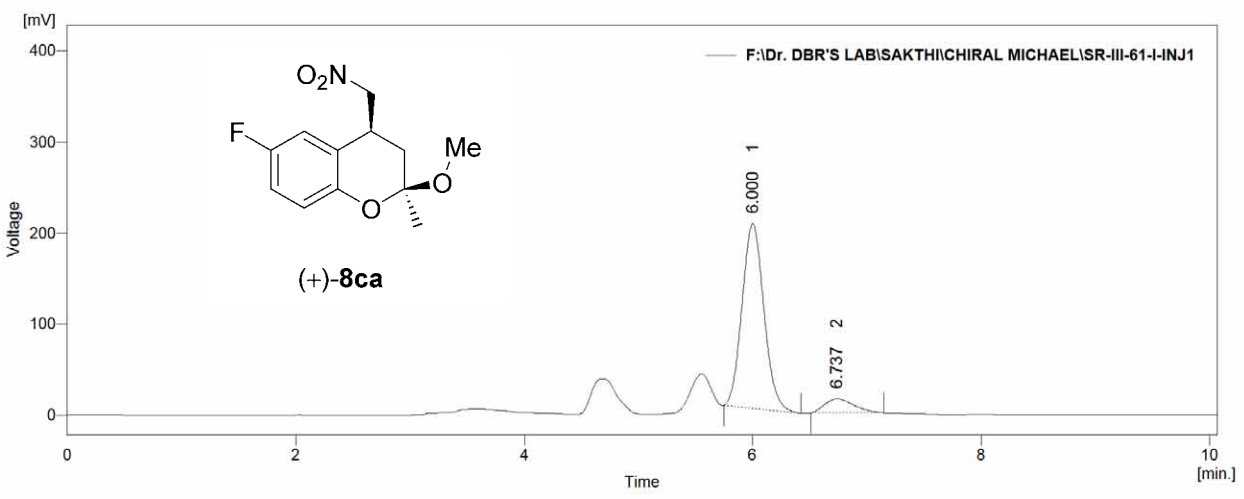


Daicel chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-27-I-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.847	1660.629	149.464	48.5	51.6	0.18
2	6.427	1765.566	140.133	51.5	48.4	0.20
	Total	3426.195	289.597	100.0	100.0	

CHIRAL **8ca** (82% ee):



Daicel chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-61-I-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.000	1797.229	135.714	91.0	93.0	0.21
2	6.737	178.300	10.179	9.0	7.0	0.28
	Total	1975.529	145.893	100.0	100.0	

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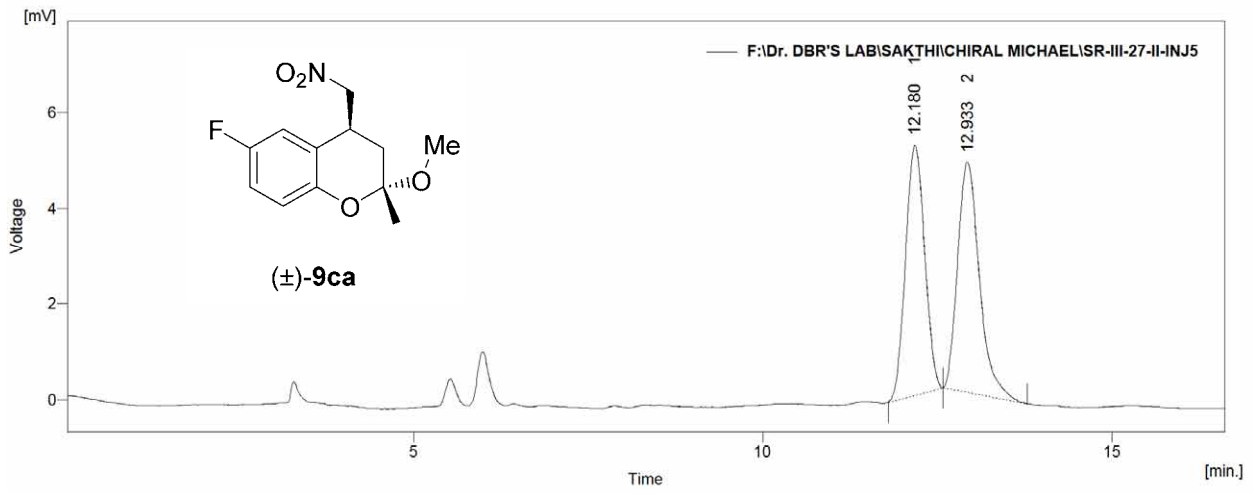
RACEMIC **9ca**:

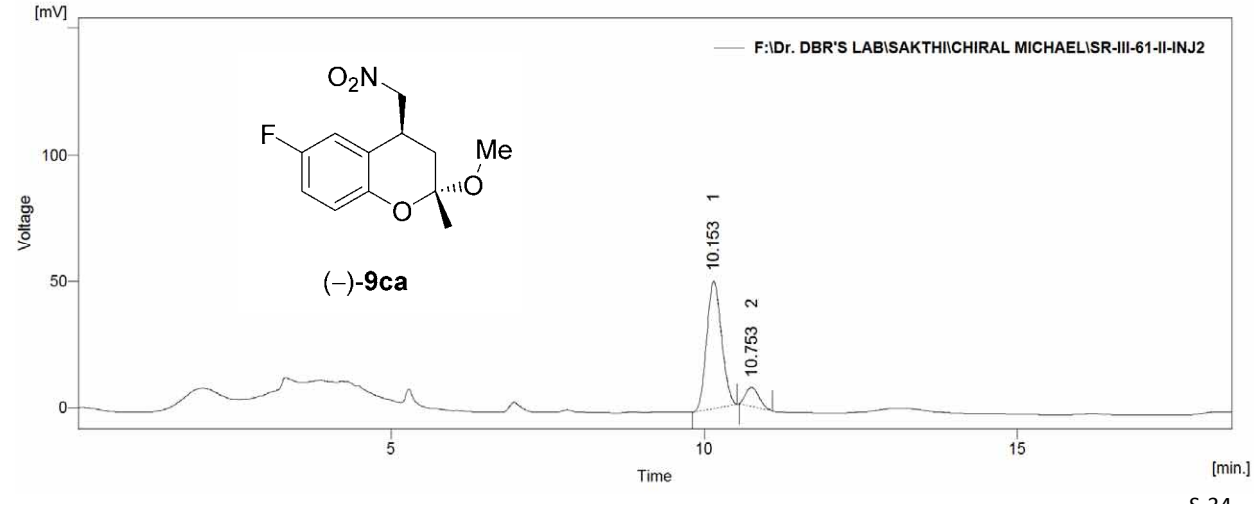


Daicel chiralcel OD-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-27-II-INJ5)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	12.180	66.175	3.490	48.7	52.1	0.31
2	12.933	69.599	3.210	51.3	47.9	0.33
	Total	135.775	6.700	100.0	100.0	

CHIRAL **9ca** (76% ee):



Daicel chiralcel OD-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-61-II-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.153	549.336	33.409	88.0	87.0	0.26
2	10.753	74.868	4.991	12.0	13.0	0.24

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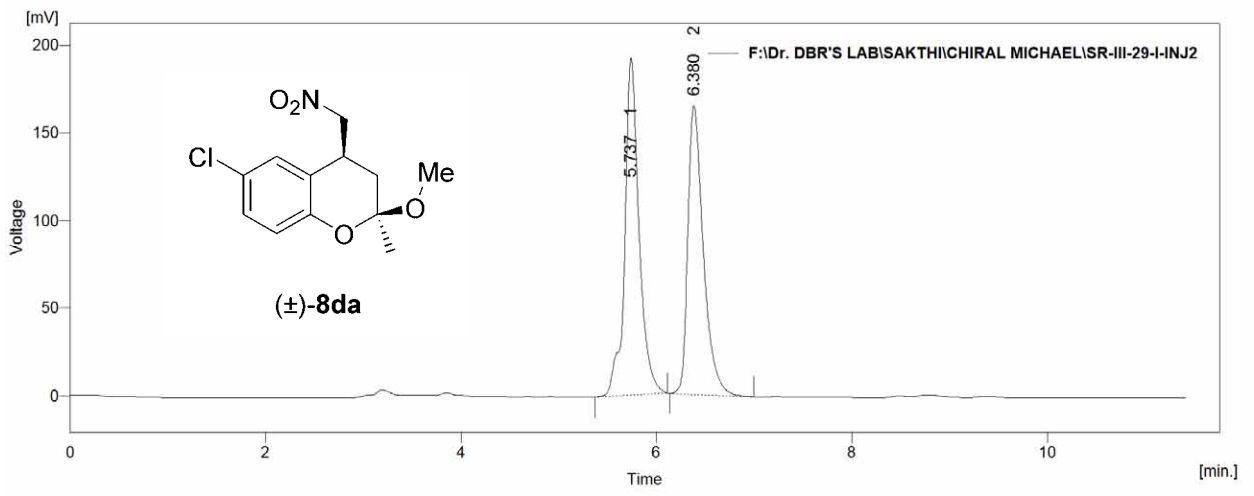
RACEMIC **8da**:

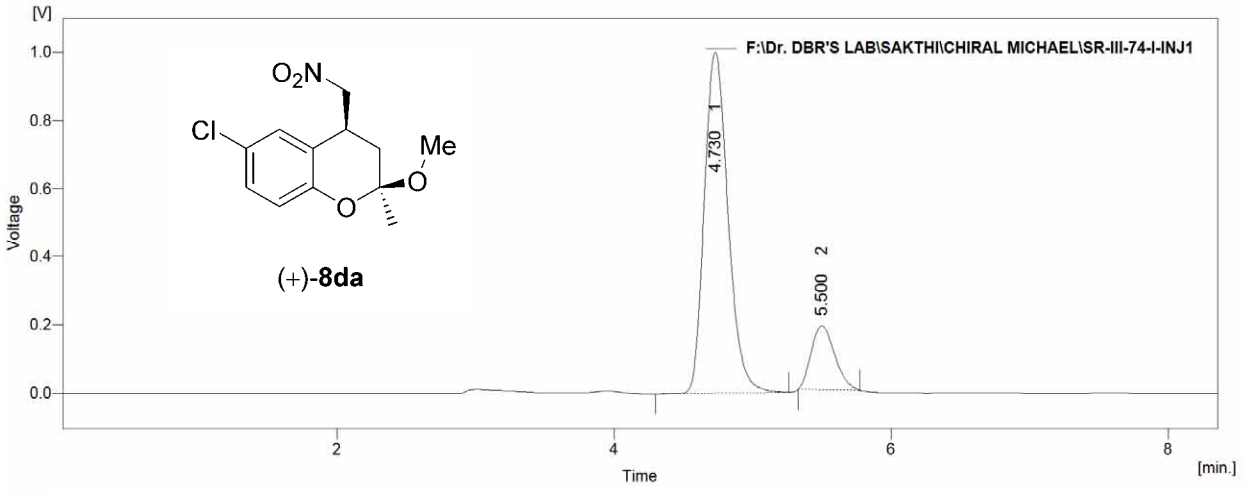


Daicel chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-29-I-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.737	1308.769	128.240	51.9	53.9	0.14
2	6.380	1212.254	109.864	48.1	46.1	0.17
	Total	2521.023	238.105	100.0	100.0	

CHIRAL **8da** (69% ee):



Daicel chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

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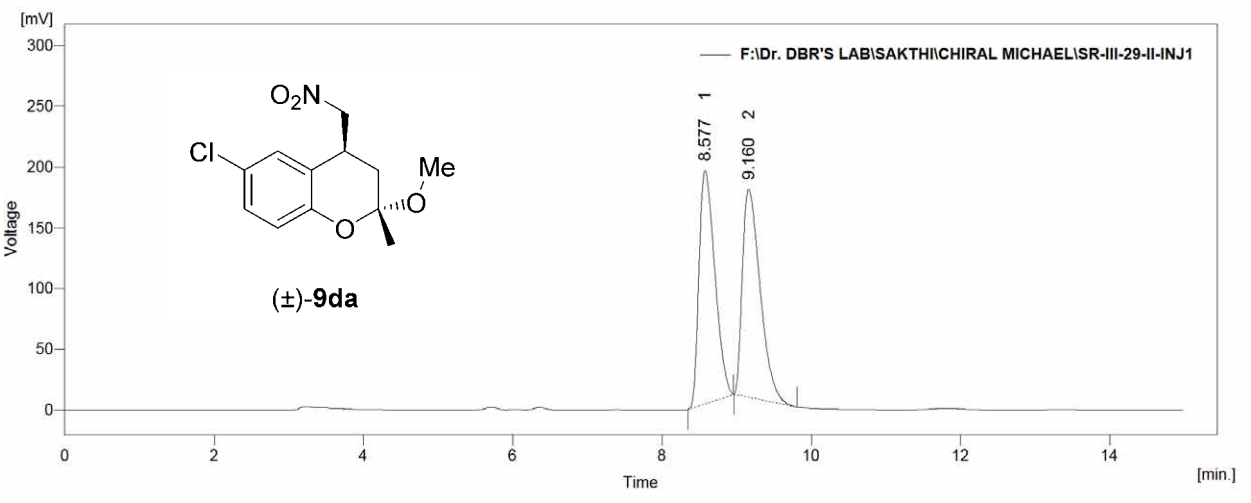
RACEMIC **9da**:

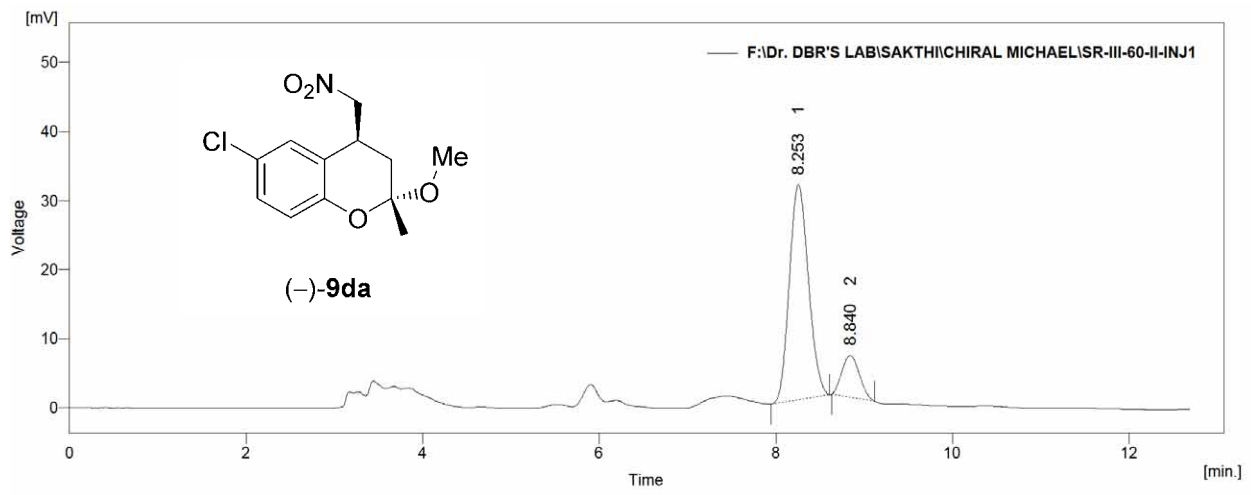


Daicel chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-29-II-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	8.577	1882.576	127.911	49.9	52.9	0.24
2	9.160	1886.995	114.052	50.1	47.1	0.26
	Total	3769.571	241.963	100.0	100.0	

CHIRAL **9da** (70% ee):



Daicel chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

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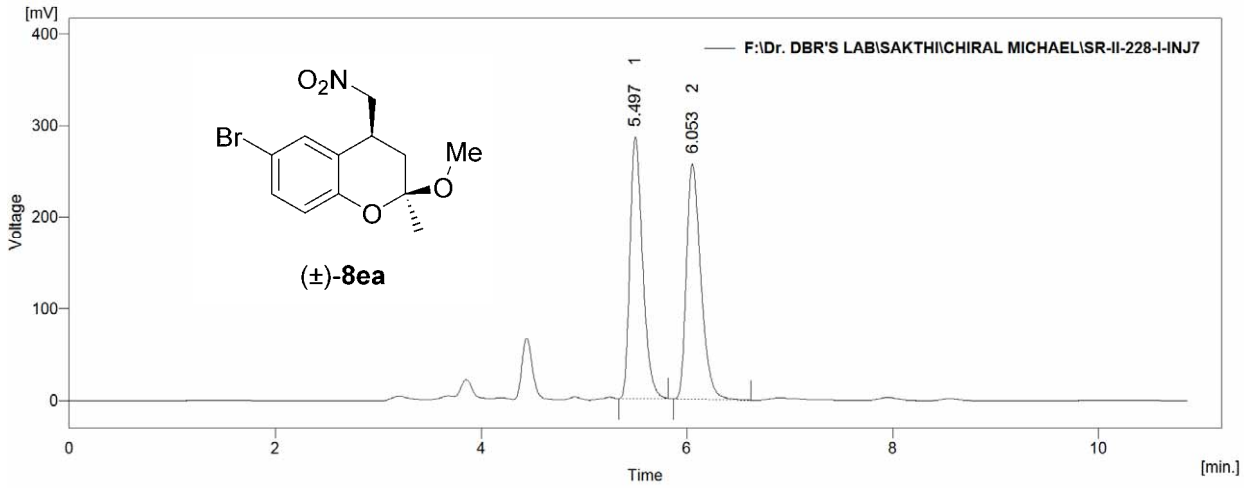
RACEMIC **8ea**:

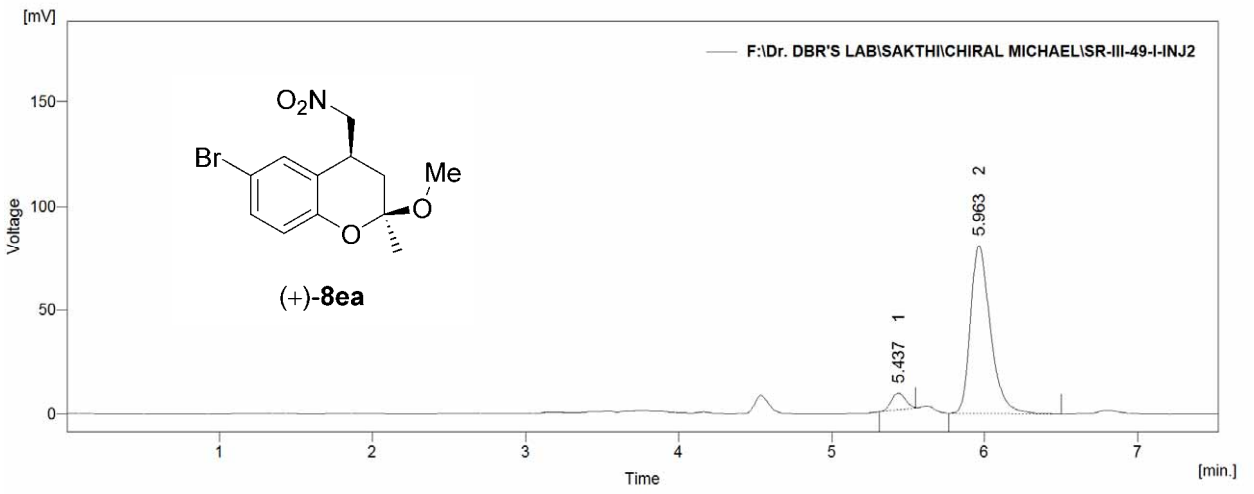


Daicel Chiralpak AS-H, Hexane/i-PrOH = 91:9, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-228-I-INJ7)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.497	1624.272	190.149	49.5	52.7	0.13
2	6.053	1659.037	170.785	50.5	47.3	0.15
	Total	3283.309	360.934	100.0	100.0	

CHIRAL **8ea** (87% ee):



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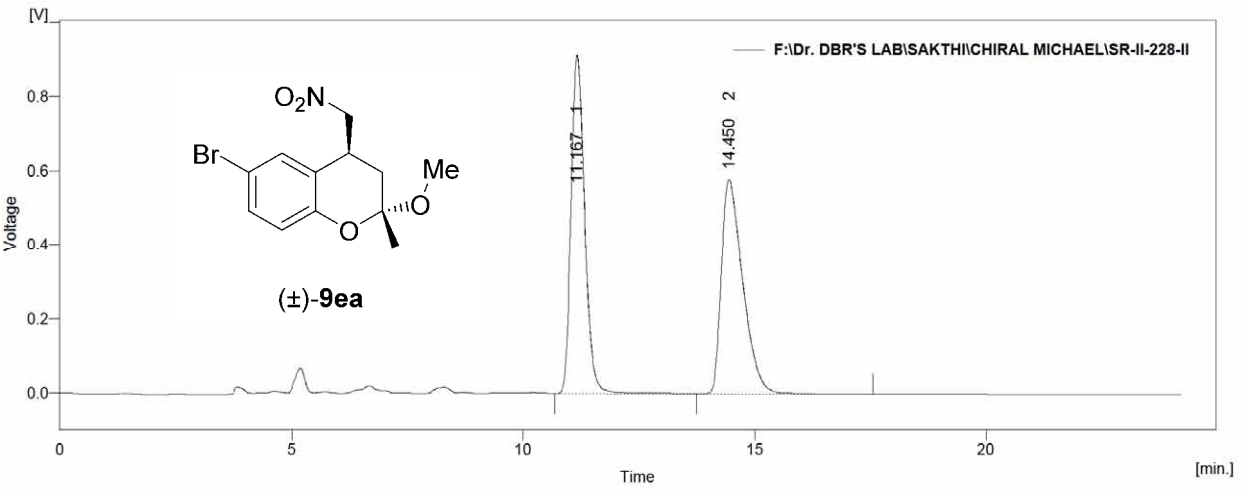
RACEMIC **9ea**:

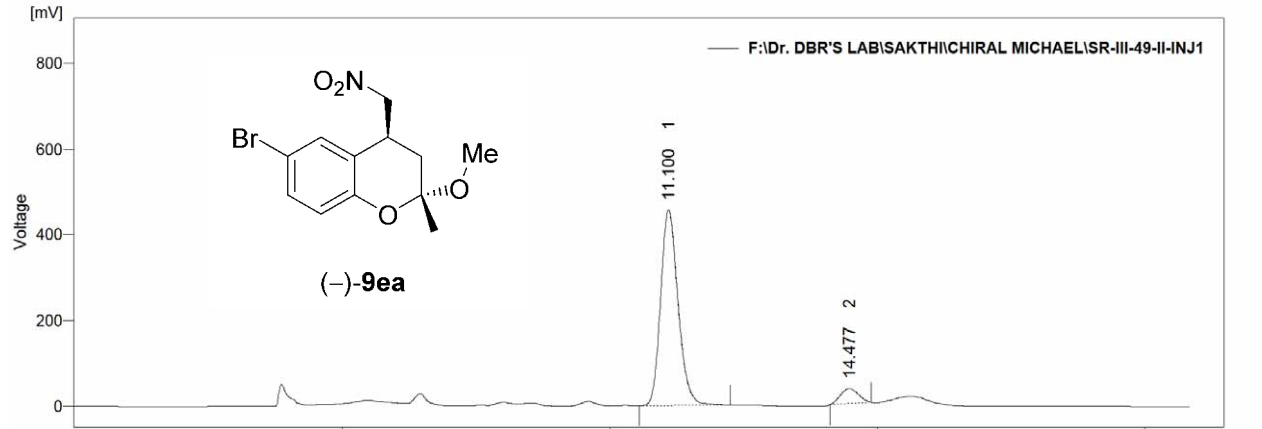


Daicel Chiralcel OD-H, Hexane/i-PrOH = 95:5, Flow Rate 0.8 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-228-II)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	11.167	12544.448	609.489	50.3	61.2	0.32
2	14.450	12408.256	385.931	49.7	38.8	0.50
	Total	24952.704	995.419	100.0	100.0	

CHIRAL **9ea** (86% ee):



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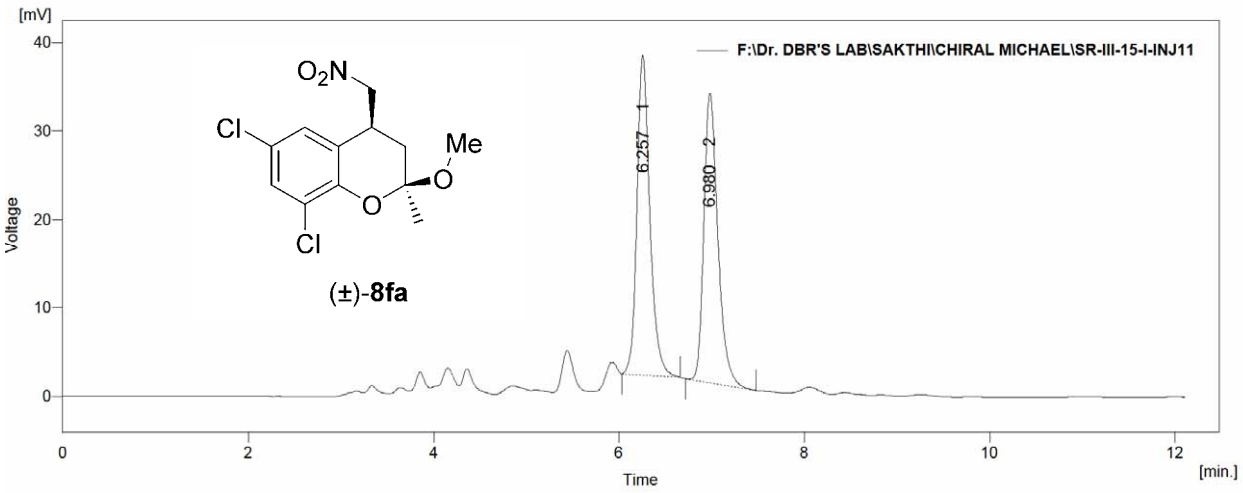
RACEMIC **8fa**:

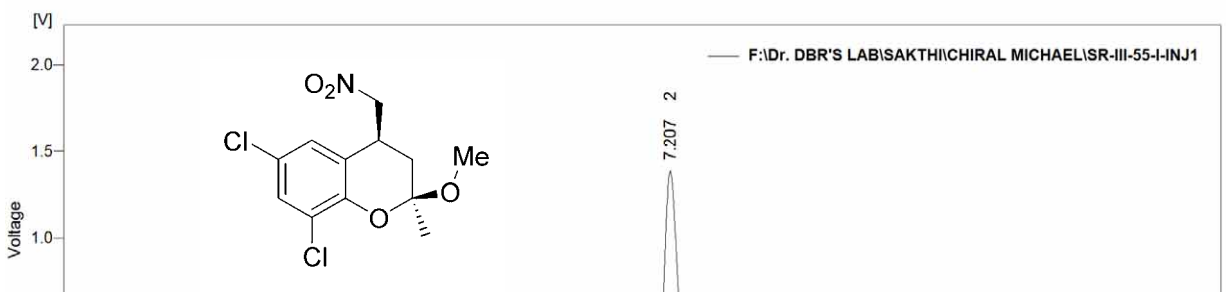


Daicel Chiralpak AS-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-15-I-INJ11)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.257	231.409	24.097	50.3	52.5	0.14
2	6.980	228.256	21.820	49.7	47.5	0.16
	Total	459.664	45.918	100.0	100.0	

CHIRAL **8fa** (88% ee):



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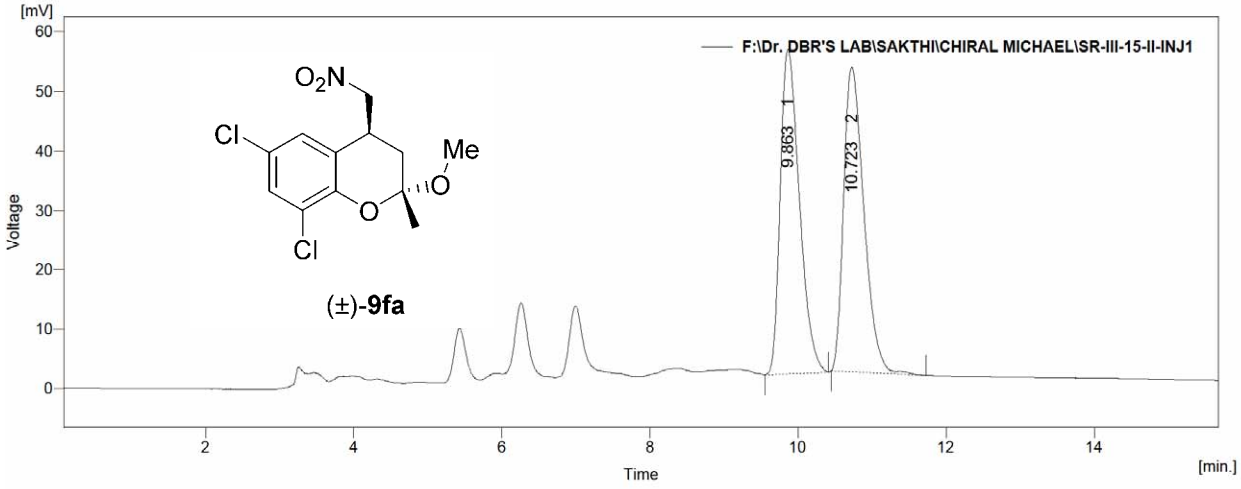
RACEMIC **9fa**:

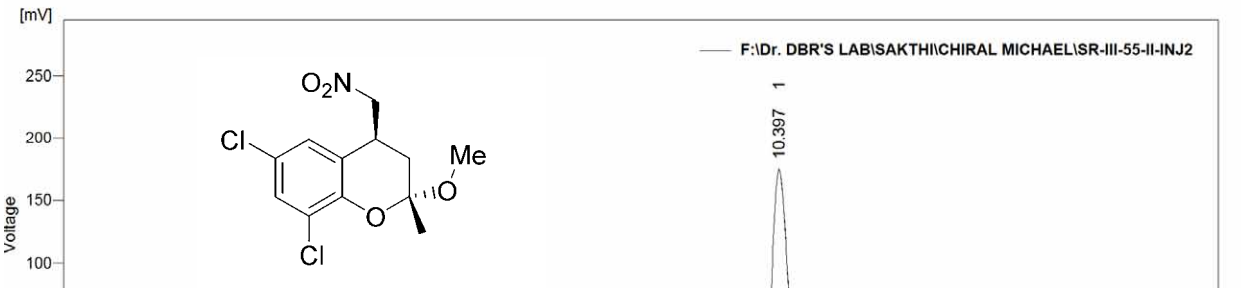


Daicel Chiralpak AS-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-15-II-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	9.863	650.836	36.316	50.0	51.5	0.28
2	10.723	651.696	34.149	50.0	48.5	0.30
	Total	1302.532	70.465	100.0	100.0	

CHIRAL **9fa** (91% ee):



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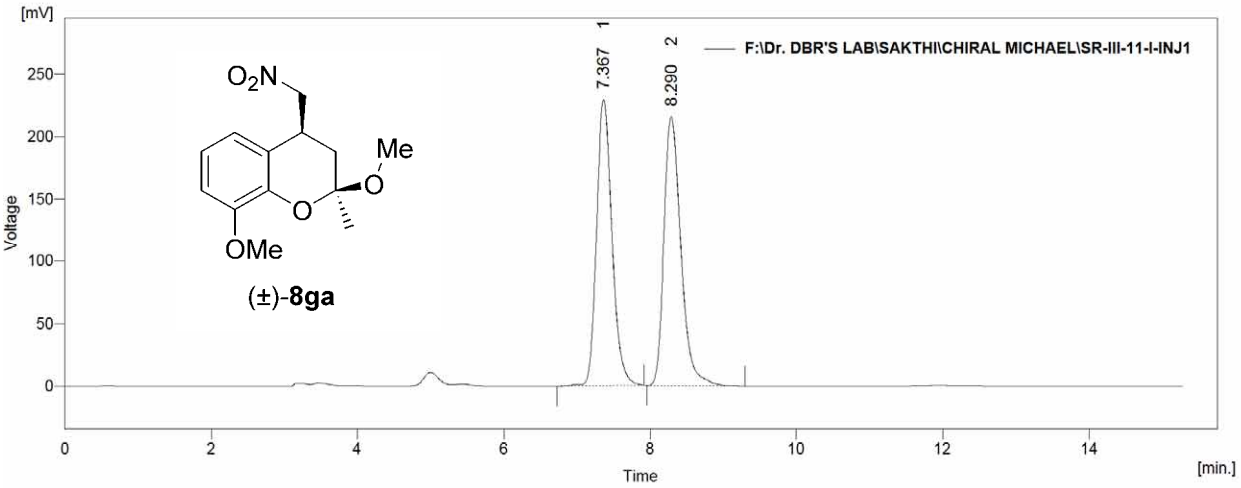
RACEMIC **8ga**:



Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-11-I-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	7.367	2275.419	152.987	49.5	51.6	0.23
2	8.290	2320.886	143.724	50.5	48.4	0.25
	Total	4596.305	296.712	100.0	100.0	

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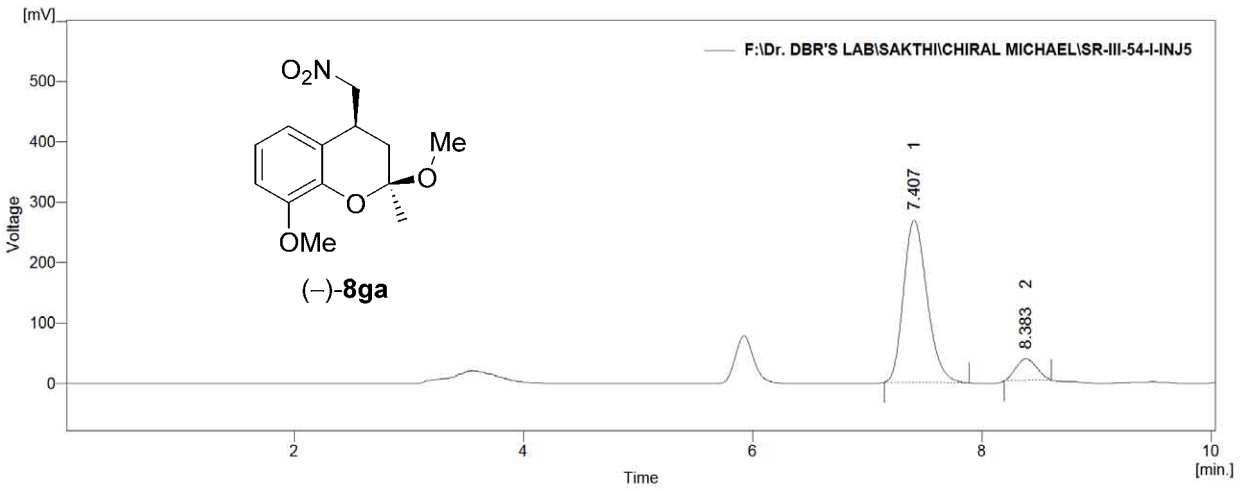
CHIRAL **8ga** (79% ee):

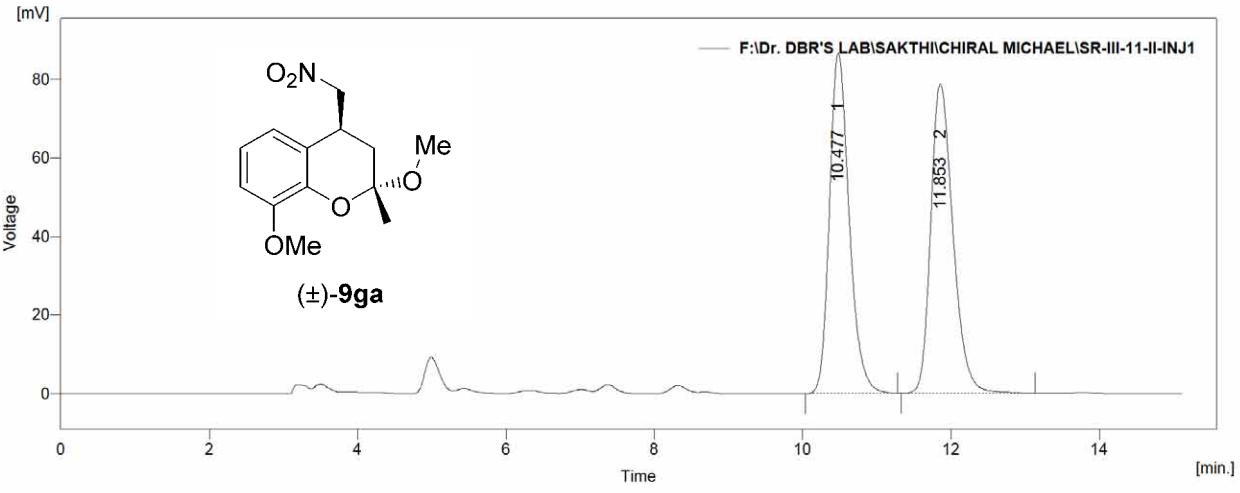


Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-54-I-INJ5)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	7.407	2555.666	178.894	89.5	88.3	0.22
2	8.383	300.186	23.719	10.5	11.7	0.21
	Total	2855.853	202.613	100.0	100.0	

RACEMIC **9ga**:



Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-11-II-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.477	1067.374	57.706	49.6	52.4	0.28
2	11.853	1084.214	52.452	50.4	47.6	0.32
	Total	2151.588	110.158	100.0	100.0	

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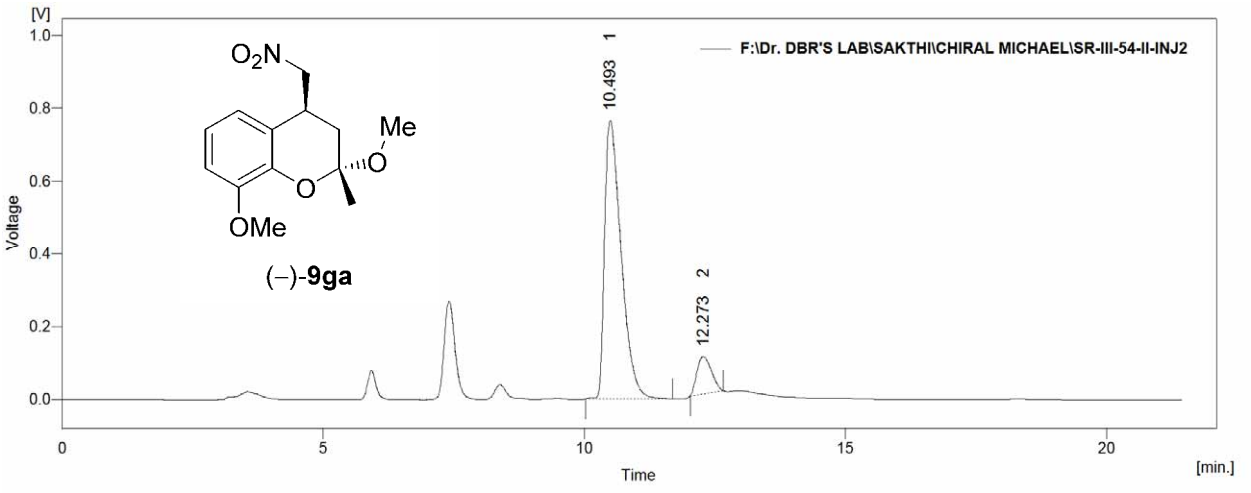
CHIRAL **9ga** (79% ee):

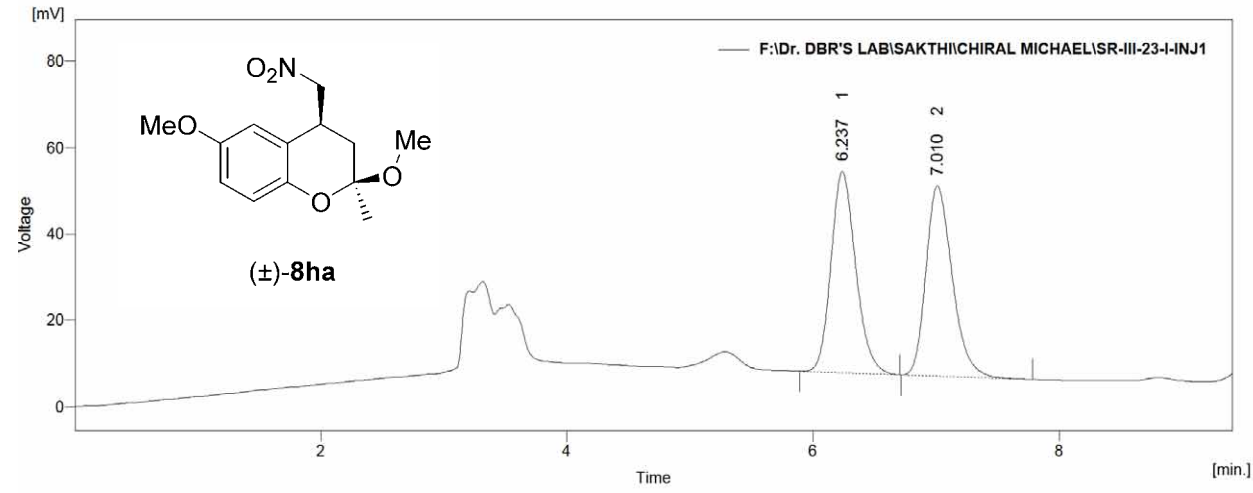


Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-54-II-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.493	11227.933	510.300	89.6	88.3	0.34
2	12.273	1302.253	67.913	10.4	11.7	0.33
	Total	12530.186	578.213	100.0	100.0	

RACEMIC **8ha**:



Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-23-I-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.237	434.580	31.141	49.8	51.4	0.22
2	7.010	437.651	29.391	50.2	48.6	0.23
	Total	872.231	60.532	100.0	100.0	

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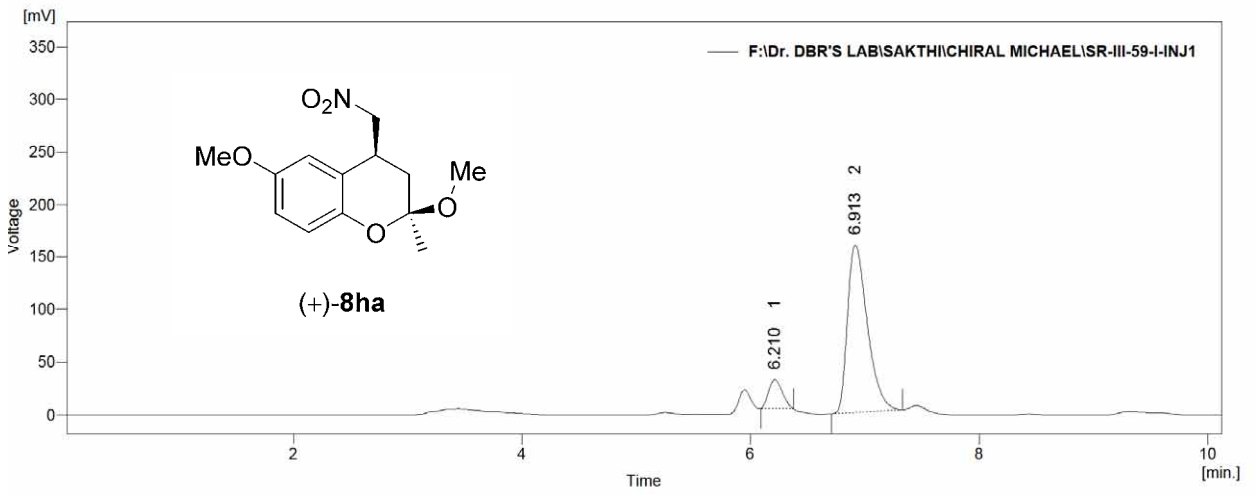
CHIRAL **8ha** (79% ee):

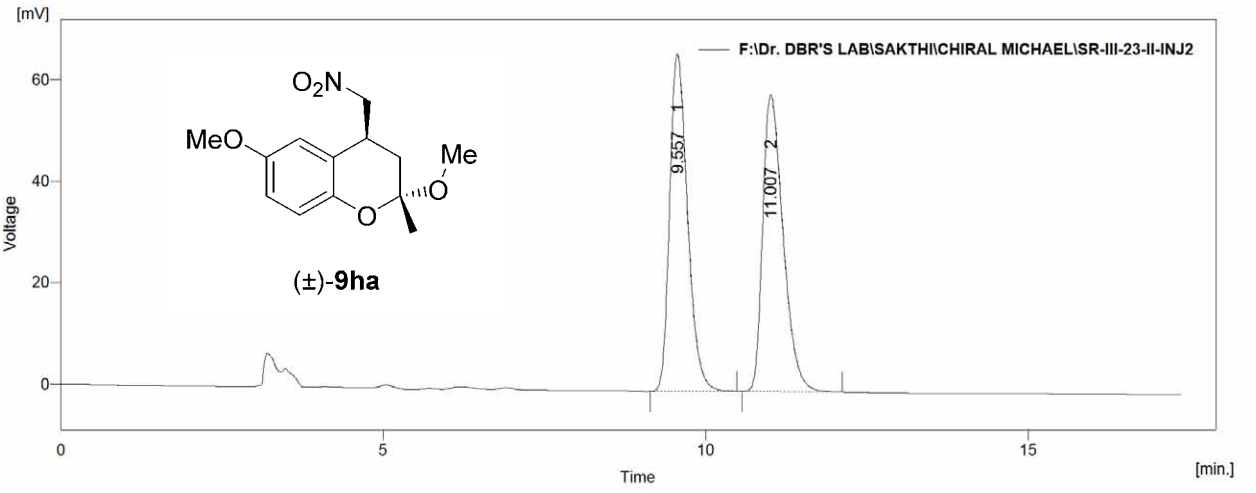


Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-59-I-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.210	152.052	18.166	10.6	14.6	0.14
2	6.913	1276.552	106.159	89.4	85.4	0.19
	Total	1428.604	124.325	100.0	100.0	

RACEMIC **9ha**:



Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-23-II-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	9.557	851.832	44.296	49.8	53.2	0.30
2	11.007	857.264	38.965	50.2	46.8	0.34
	Total	1709.097	83.261	100.0	100.0	

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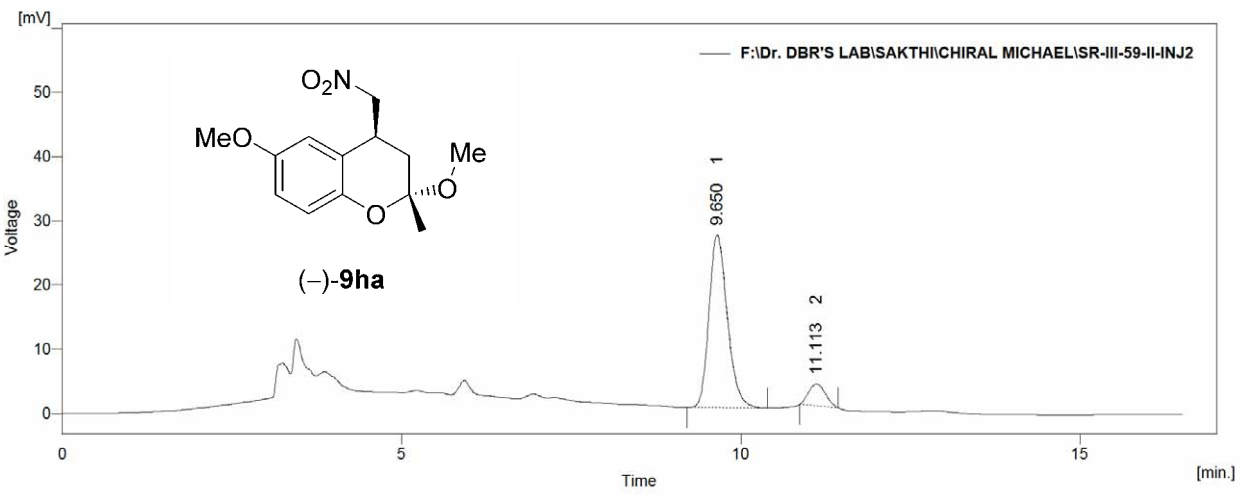
CHIRAL **9ha** (79% ee):

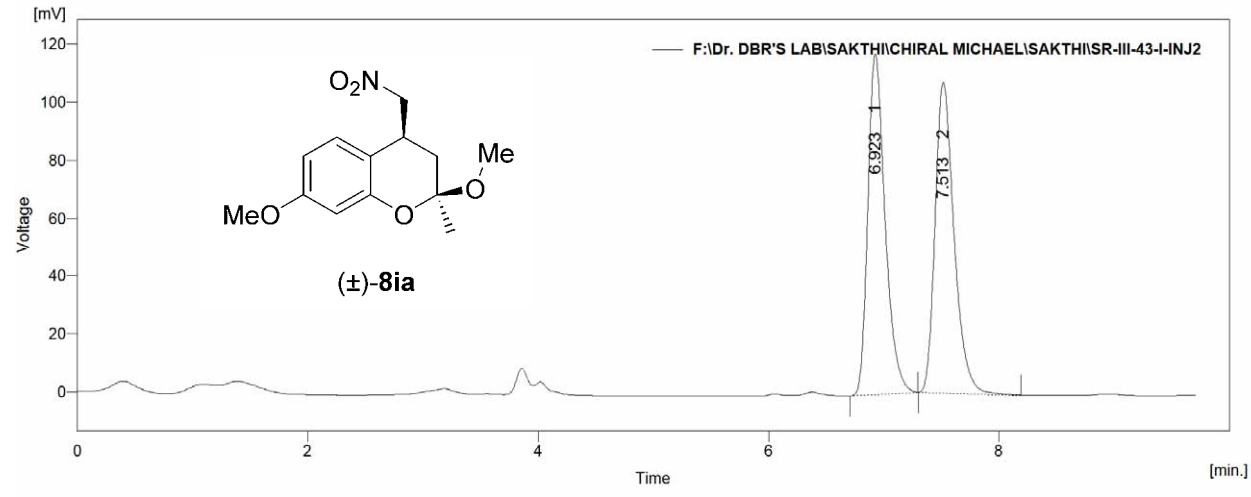


Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-59-II-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	9.650	337.052	17.943	89.6	88.8	0.29
2	11.113	39.166	2.264	10.4	11.2	0.28
	Total	376.219	20.207	100.0	100.0	

RACEMIC **8ia**:



Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SAKTHI\SR-III-43-I-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.923	813.479	78.344	49.9	52.3	0.16
2	7.513	818.152	71.508	50.1	47.7	0.17
	Total	1631.631	149.852	100.0	100.0	

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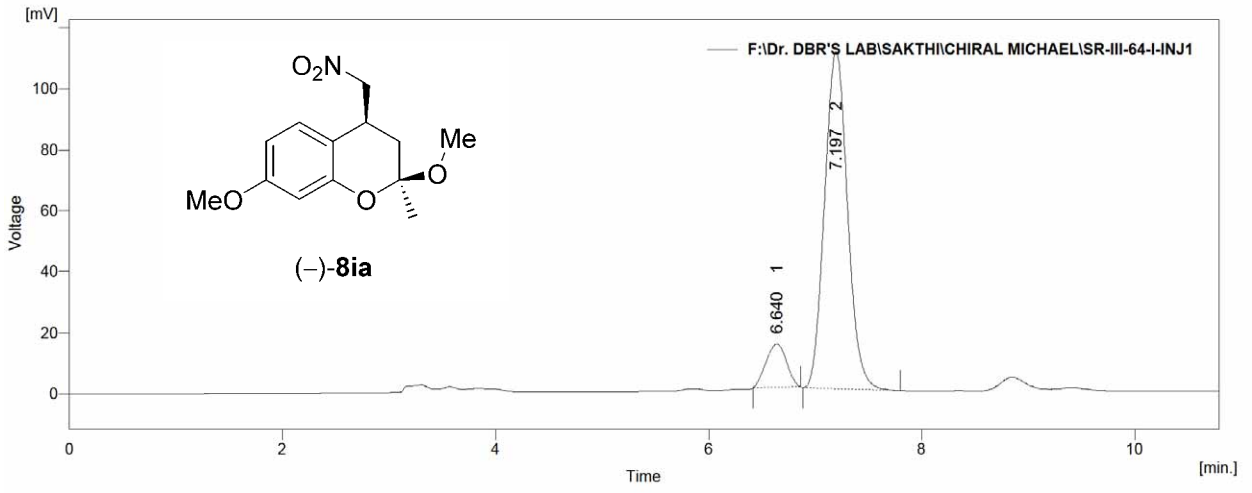
CHIRAL **8ia** (80% ee):

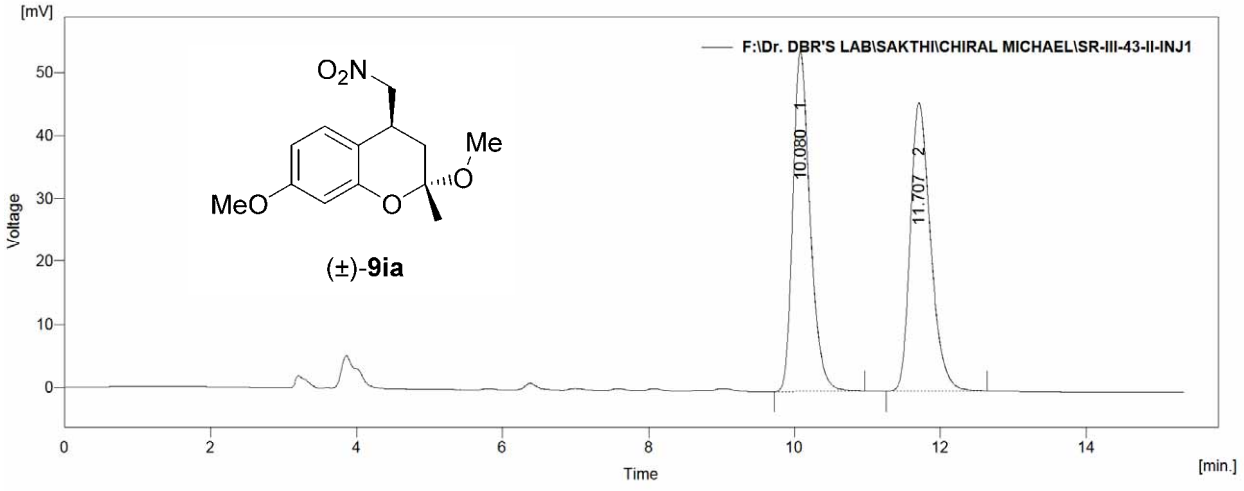


Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-64-I-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.640	124.179	9.365	10.1	11.3	0.22
2	7.197	1100.346	73.668	89.9	88.7	0.24
	Total	1224.525	83.033	100.0	100.0	

RACEMIC **9ia**:



Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-43-II-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.080	584.144	35.934	49.9	54.1	0.25
2	11.707	585.317	30.472	50.1	45.9	0.29
	Total	1169.461	66.407	100.0	100.0	

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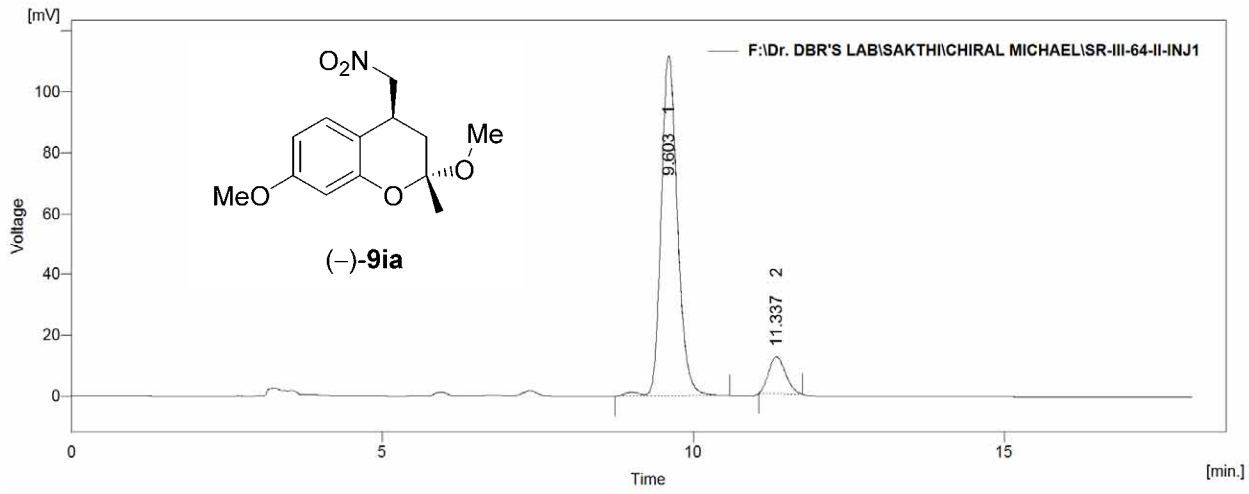
CHIRAL **9ia** (80% ee):

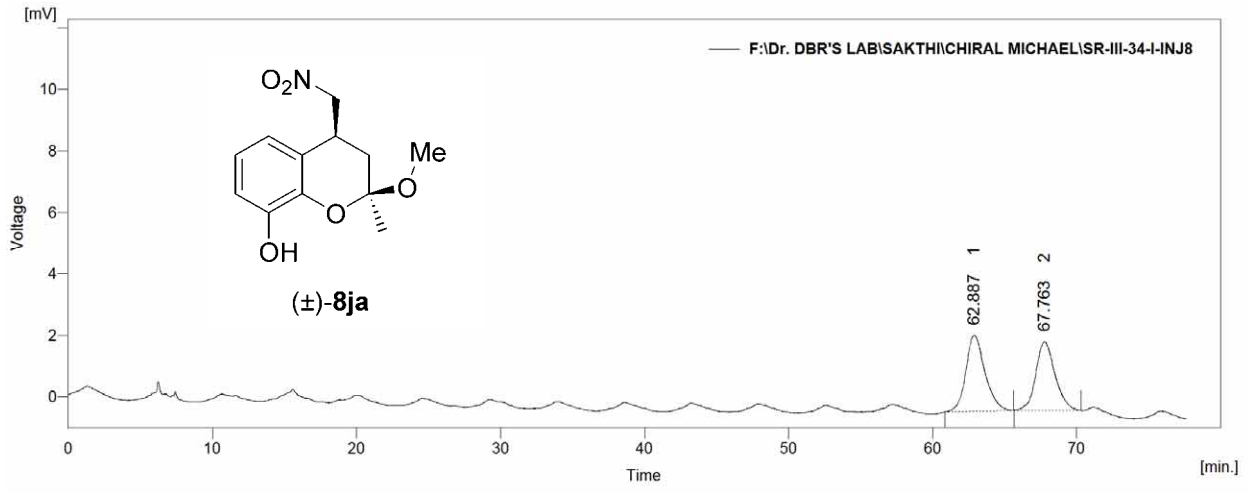


Daicel Chiralpak AS-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-64-II-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	9.603	1358.717	74.588	89.9	90.2	0.28
2	11.337	152.684	8.117	10.1	9.8	0.30
	Total	1511.401	82.706	100.0	100.0	

RACEMIC **8ja**:



Daicel Chiralpak AD-H, Hexane/i-PrOH = 98:2, Flow Rate 0.5 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-34-I-INJ8)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]

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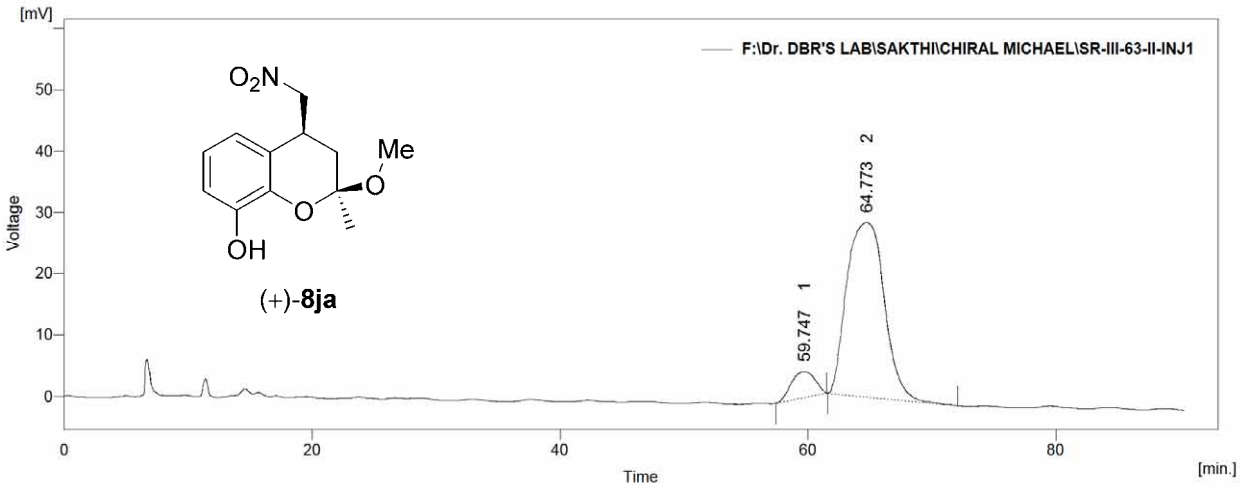
CHIRAL **8ja** (83% ee):

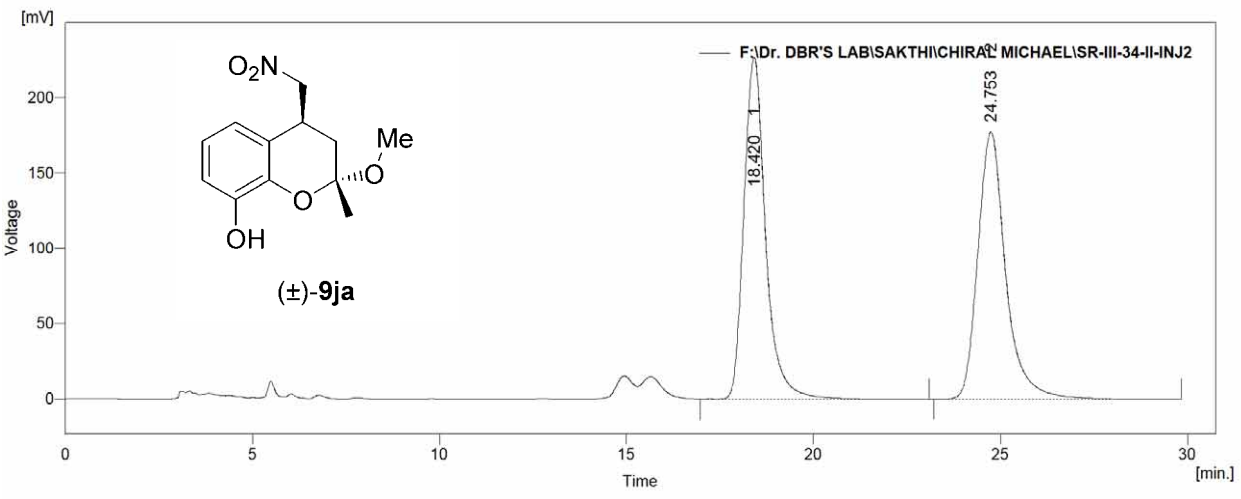


Daicel Chiralpak AD-H, Hexane/i-PrOH = 98:2, Flow Rate 0.5 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-63-II-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	59.747	379.144	2.810	8.7	12.9	2.27
2	64.773	3986.933	19.011	91.3	87.1	3.38
	Total	4366.077	21.822	100.0	100.0	

RACEMIC **9ja**:



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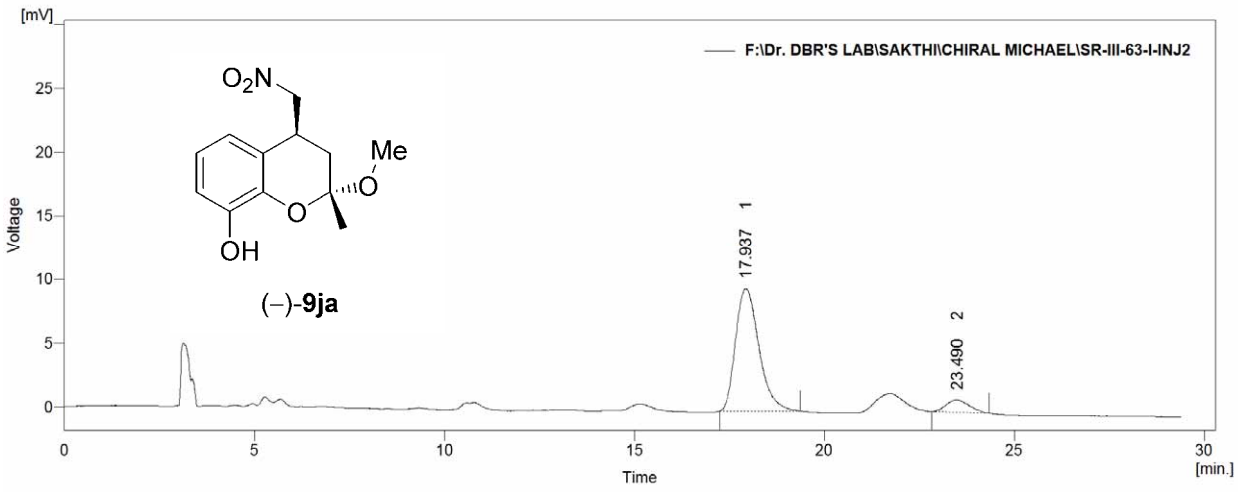
Daicel Chiralpak AD-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-34-II-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	18.420	6080.990	151.245	49.8	56.1	0.60
2	24.753	6124.138	118.452	50.2	43.9	0.75
	Total	12205.128	269.696	100.0	100.0	

CHIRAL **9ja** (82% ee):

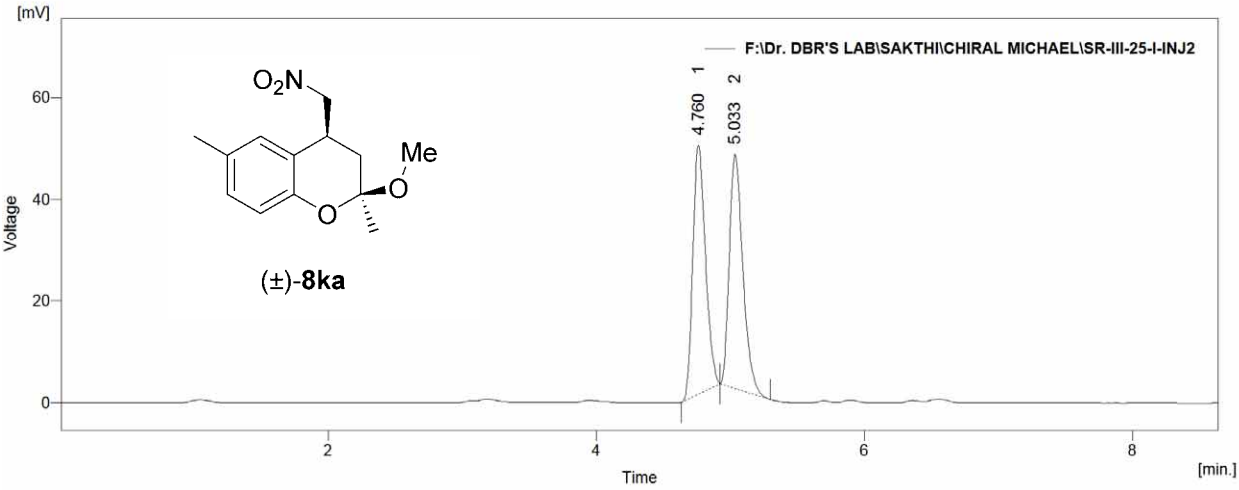


Daicel Chiralpak AD-H, Hexane/i-PrOH = 95:5, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-63-I-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	17.937	273.949	6.380	91.0	90.9	0.66
2	23.490	27.204	0.638	9.0	9.1	0.68
	Total	301.154	7.018	100.0	100.0	

RACEMIC **8ka**:



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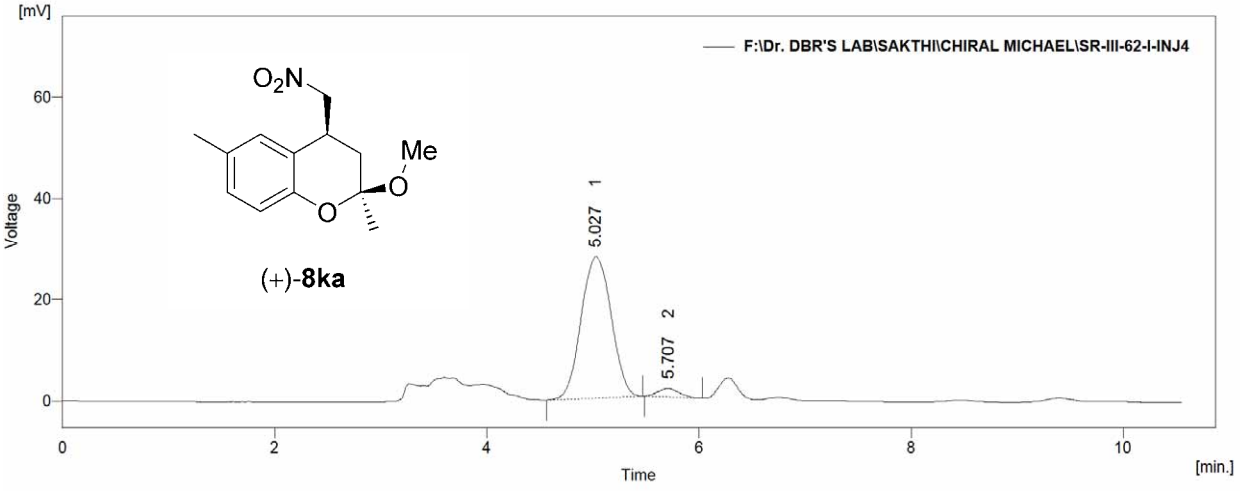
CHIRAL **8ka** (92% ee):

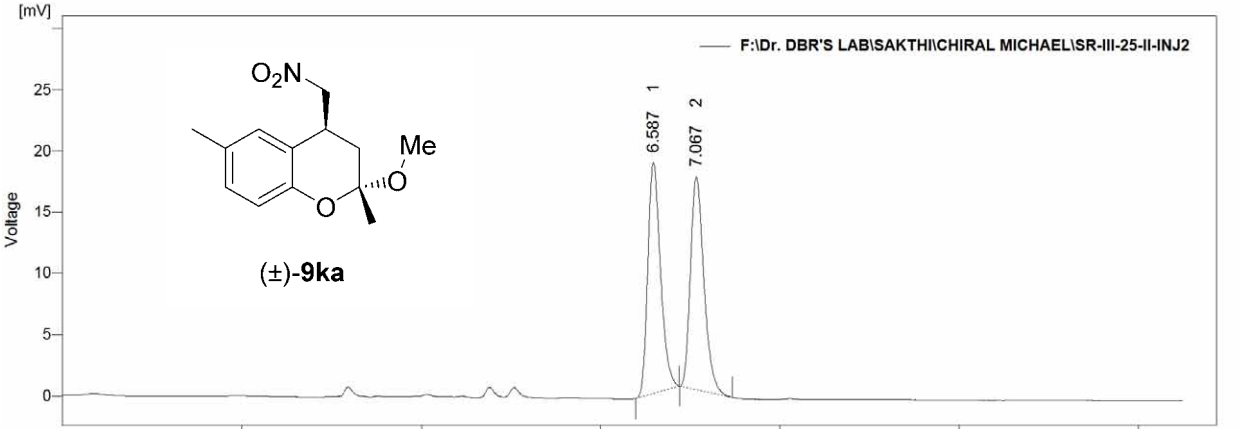


Daicel Chiralpak AS-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-62-I-INJ4)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.027	364.215	18.507	95.9	94.4	0.32
2	5.707	15.573	1.088	4.1	5.6	0.23
	Total	379.788	19.595	100.0	100.0	

RACEMIC **9ka**.



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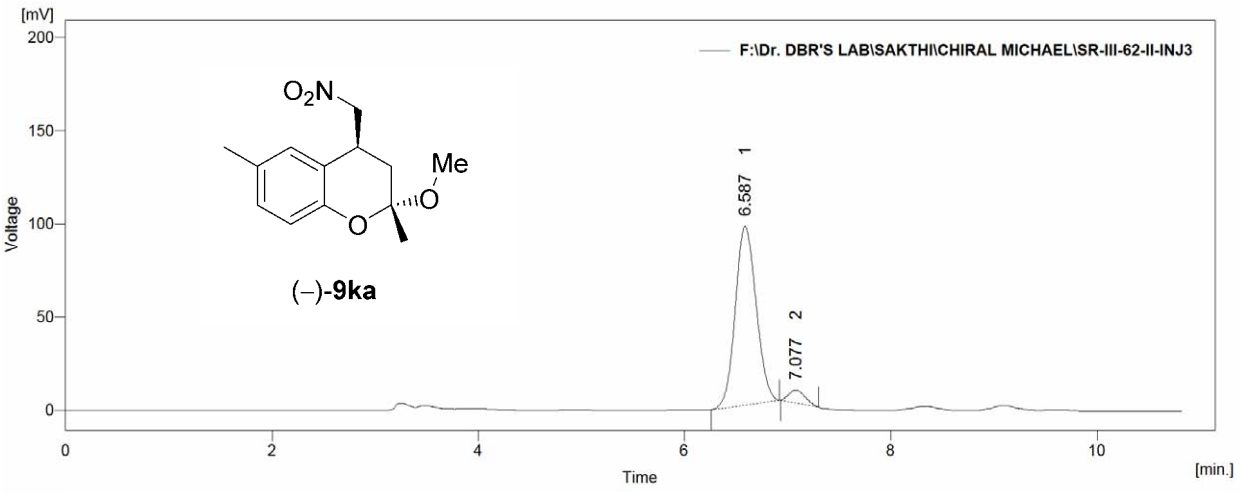
CHIRAL **9ka** (89% ee):

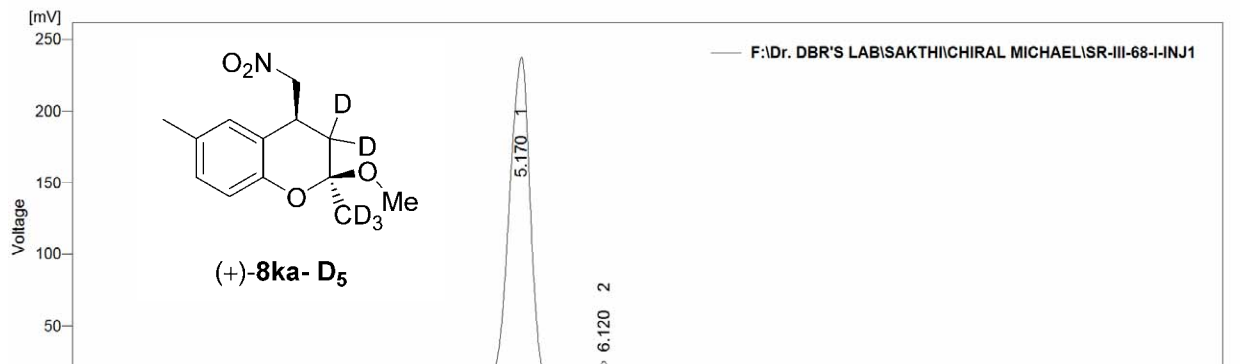


Daicel Chiralpak AS-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-62-II-INJ3)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.587	894.877	63.995	94.7	93.5	0.22
2	7.077	50.331	4.452	5.3	6.5	0.18
	Total	945.208	68.447	100.0	100.0	

CHIRAL **8ka-D$_5$** (89% ee):



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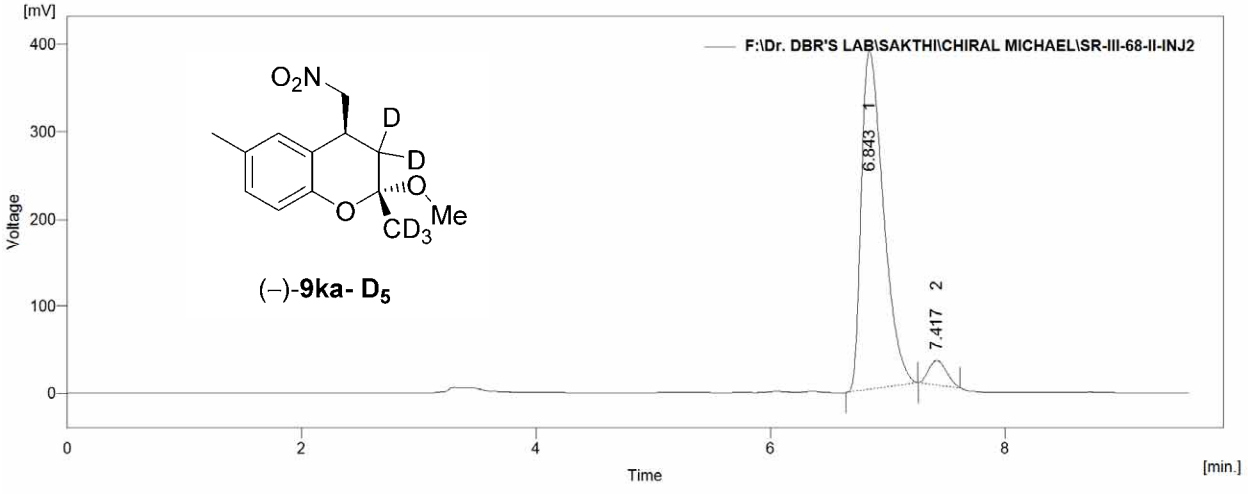
CHIRAL **9ka-D$_5$** (89% ee):

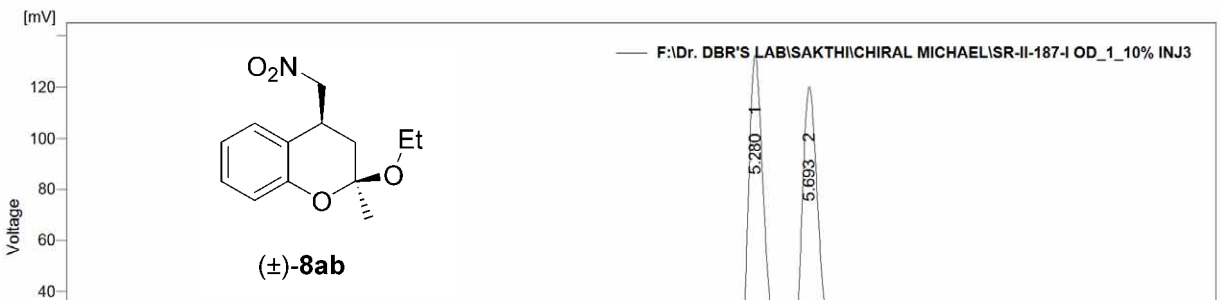


Daicel Chiralpak AS-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-68-II-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.843	3390.845	258.803	94.5	93.3	0.21
2	7.417	198.563	18.684	5.5	6.7	0.18
	Total	3589.408	277.487	100.0	100.0	

RACEMIC **8ab**:



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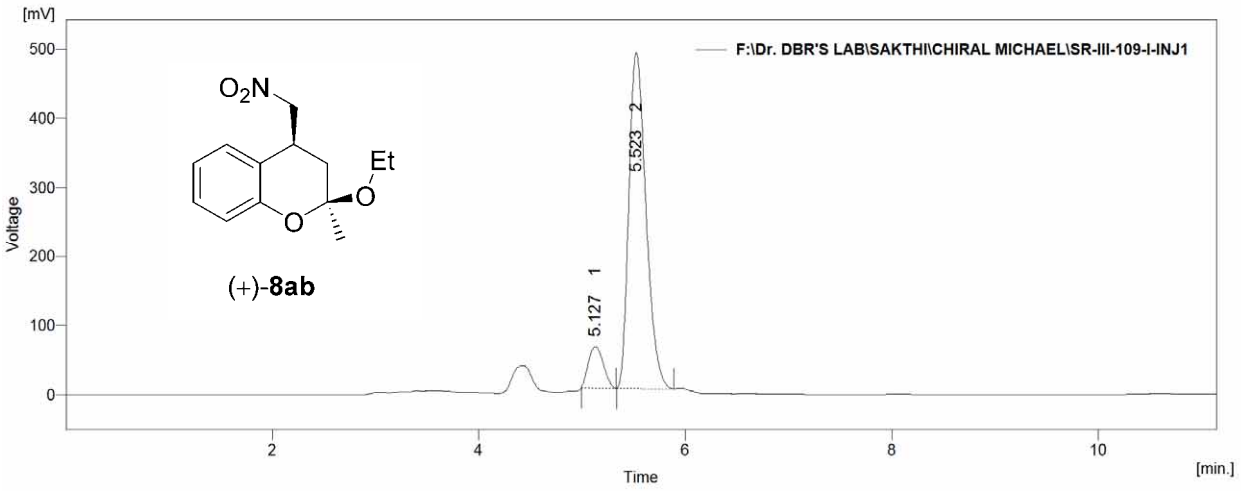
CHIRAL **8ab** (80% ee):



Daicel Chiralcel OD-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-109-I-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.127	401.974	40.009	9.7	11.0	0.17
2	5.523	3724.883	324.028	90.3	89.0	0.18
	Total	4126.857	364.038	100.0	100.0	

RACEMIC **9ab**:

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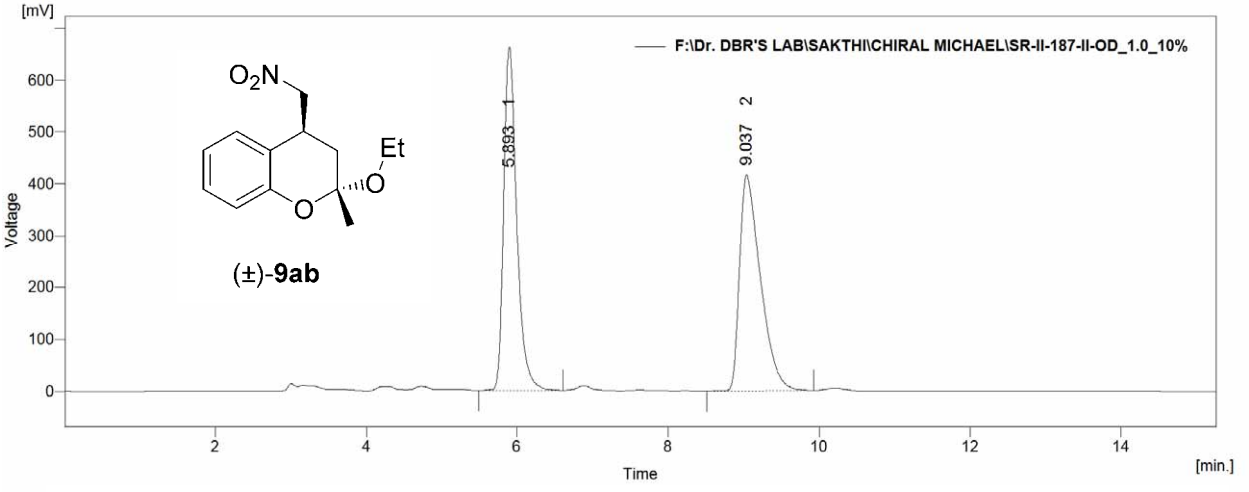
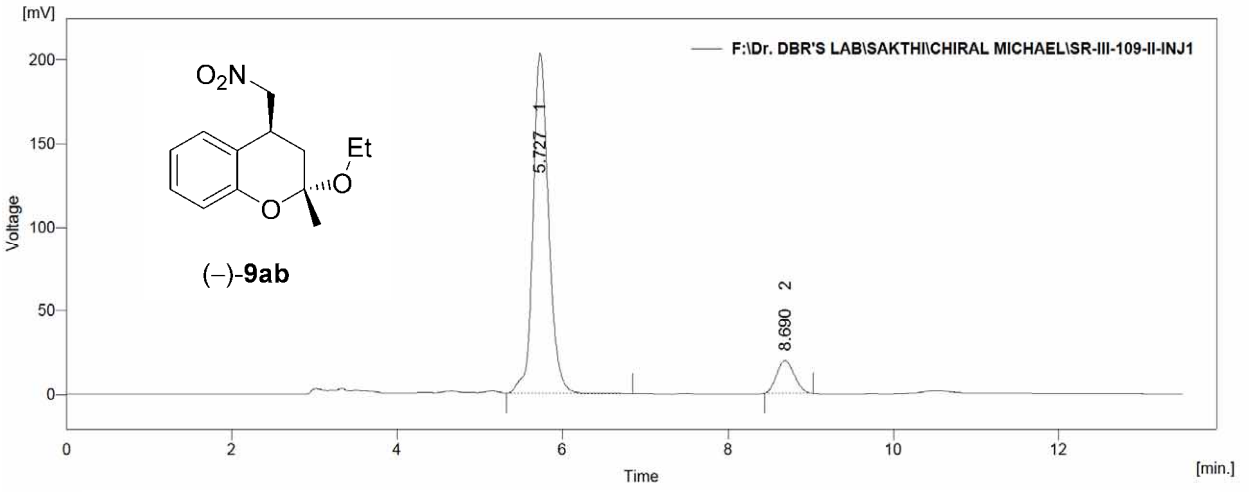


Daicel Chiralcel OD-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-II-187-II-OD_1.0_10%)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.893	5284.193	441.731	49.9	61.4	0.18
2	9.037	5312.705	277.583	50.1	38.6	0.30
	Total	10596.898	719.314	100.0	100.0	

CHIRAL **9ab** (80% ee):



Daicel Chiralcel OD-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-109-II-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.727	1771.027	135.481	90.2	91.2	0.20
2	8.690	193.345	13.046	9.8	8.8	0.24
	Total	1964.372	148.528	100.0	100.0	

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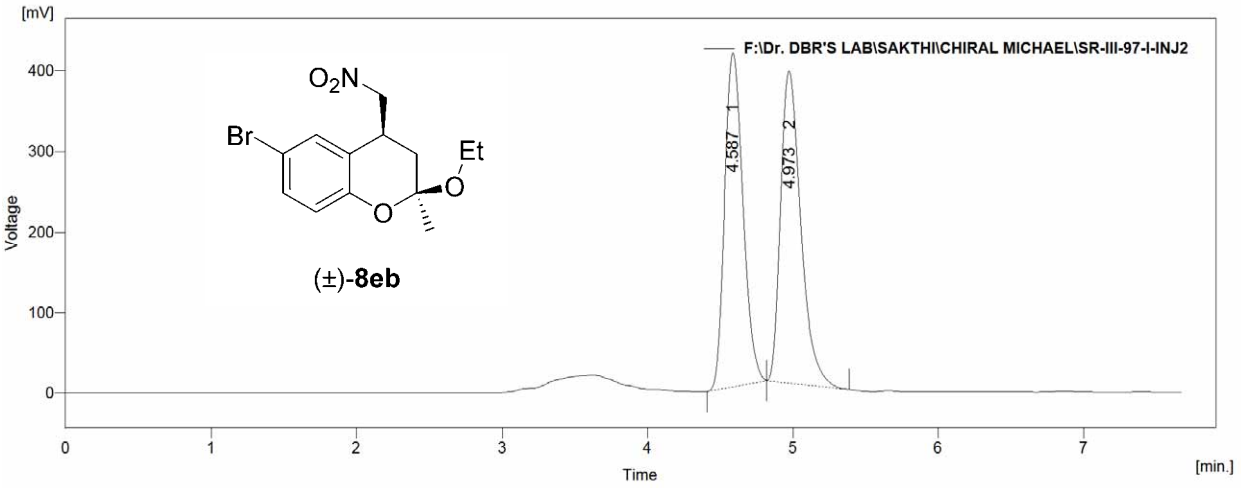
RACEMIC **8eb**:

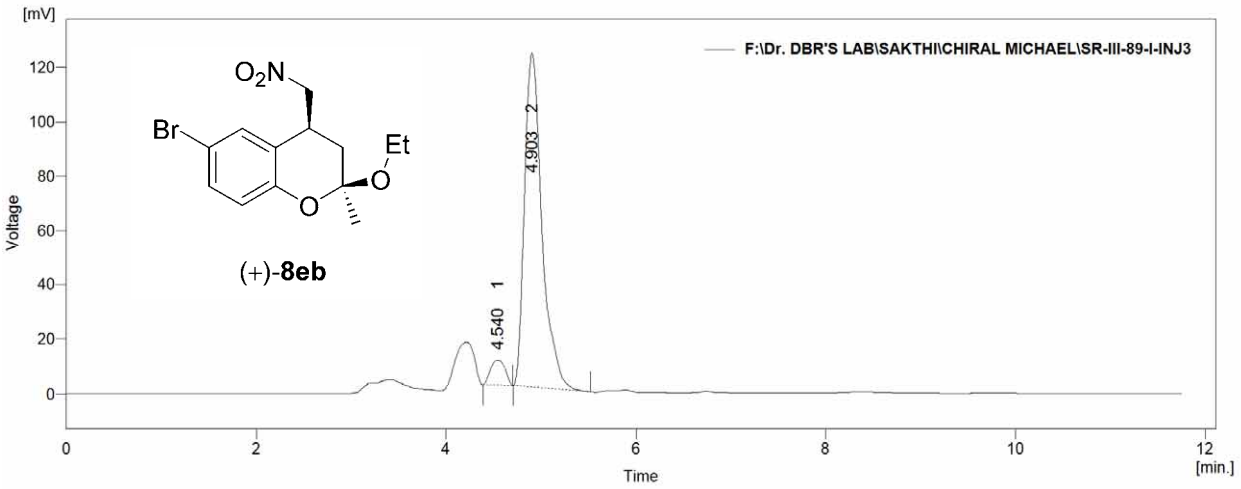


Daicel Chiralpak AS-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-97-I-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	4.587	2421.094	276.036	49.5	51.7	0.14
2	4.973	2471.258	258.029	50.5	48.3	0.15
	Total	4892.352	534.065	100.0	100.0	

CHIRAL **8eb** (88% ee):



Daicel Chiralpak AS-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-89-I-INJ3)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	4.540	65.507	6.125	5.9	7.0	0.19
2	4.903	1041.022	81.594	94.1	93.0	0.19
	Total	1106.530	87.719	100.0	100.0	

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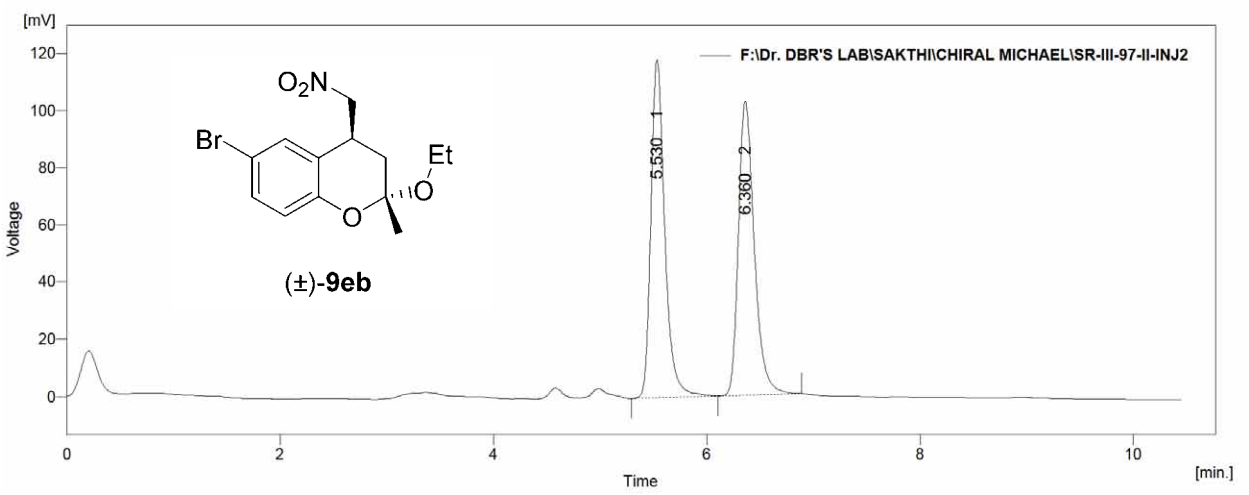
RACEMIC **9eb**:

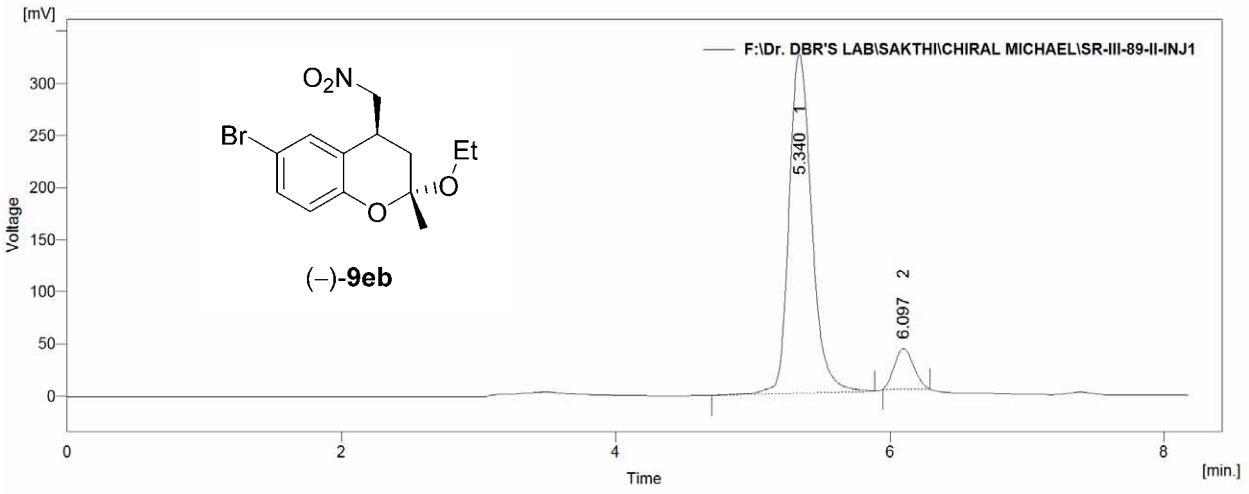


Daicel Chiralpak AS-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-97-II-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.530	709.787	78.651	50.1	53.4	0.14
2	6.360	706.892	68.562	49.9	46.6	0.16
	Total	1416.679	147.214	100.0	100.0	

CHIRAL **9eb** (82% ee):



Daicel Chiralpak AS-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-89-II-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	5.340	2481.844	216.504	90.8	89.4	0.18
2	6.097	251.696	25.696	9.2	10.6	0.16
	Total	2733.540	242.201	100.0	100.0	

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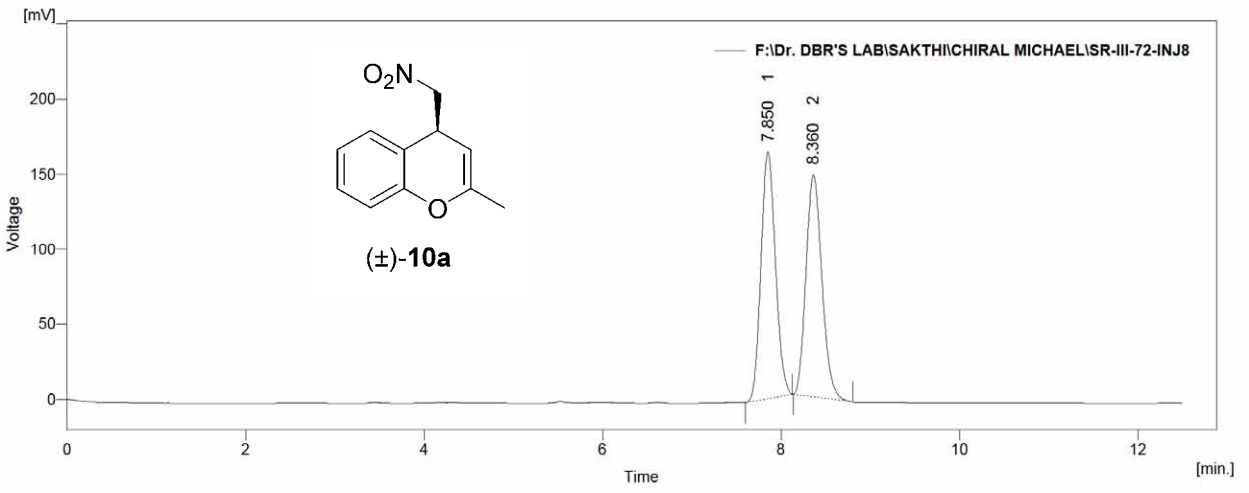
RACEMIC **10a**:

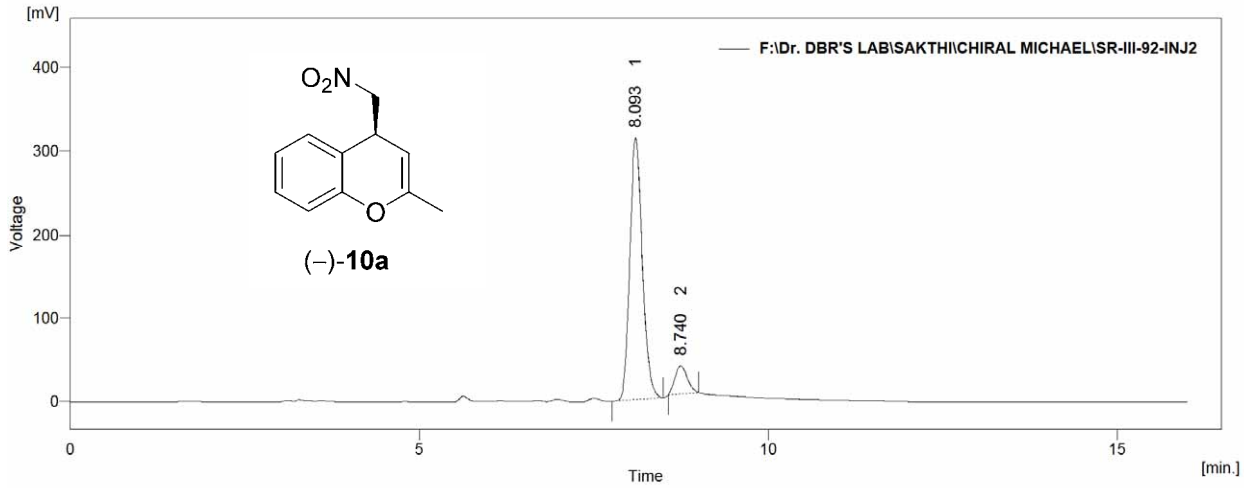


Daicel Chiralcel OD-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-72-INJ8)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	7.850	1228.327	109.324	50.2	52.6	0.18
2	8.360	1218.691	98.350	49.8	47.4	0.19
	Total	2447.018	207.674	100.0	100.0	

CHIRAL **10a** (81% ee):



Daicel Chiralcel OD-H, Hexane/i-PrOH = 97:3, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-92-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	8.093	2595.290	208.697	90.5	90.3	0.19
2	8.740	273.255	22.291	9.5	9.7	0.20
	Total	2868.544	230.988	100.0	100.0	

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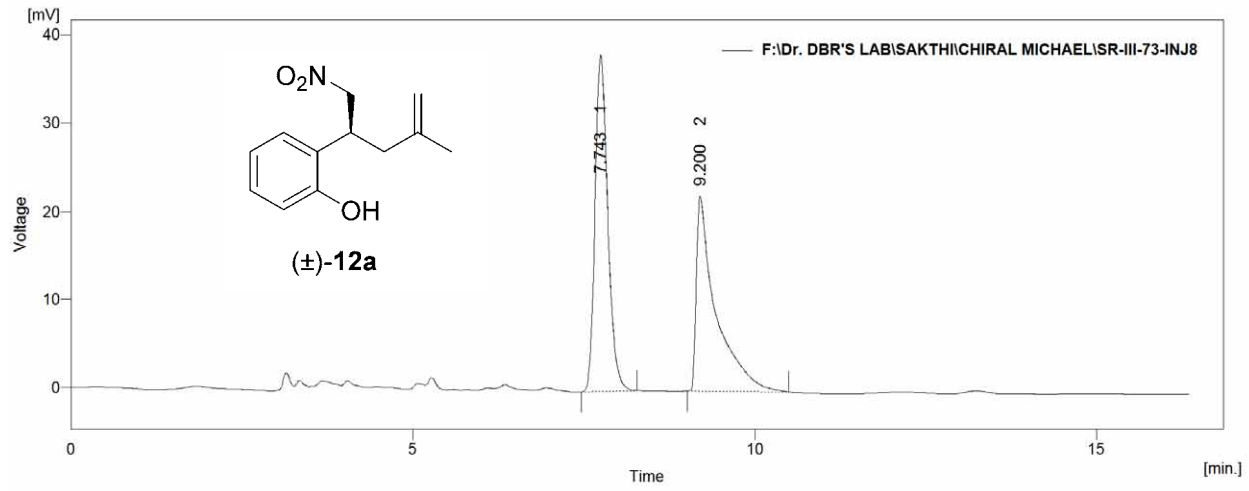
RACEMIC **12a**:

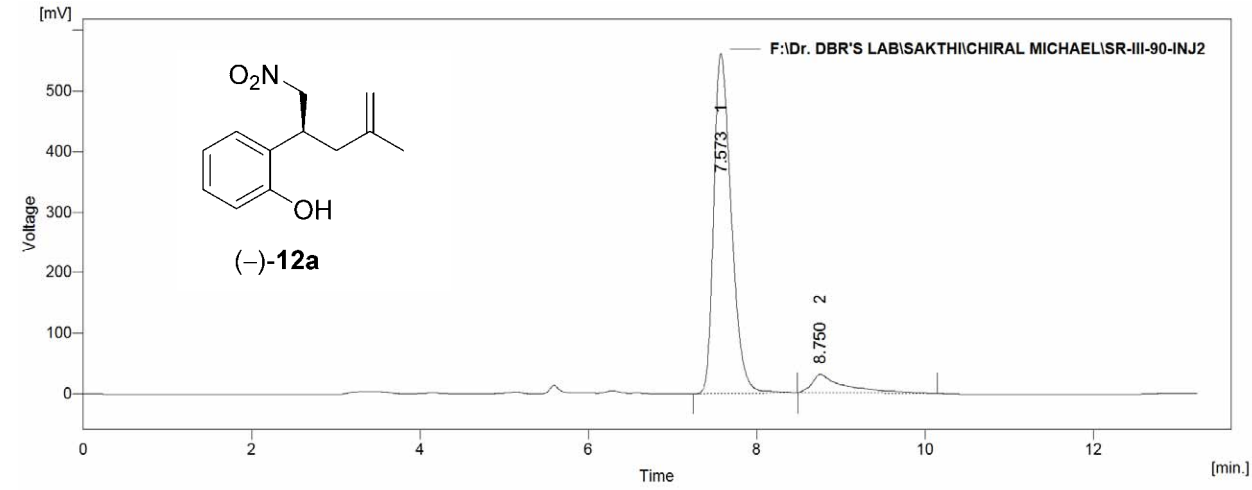


Daicel Chiralpak AS-H, Hexane/i-PrOH = 94:6, Flow Rate 0.8 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-73-INJ8)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	7.743	328.404	25.456	52.9	63.3	0.20
2	9.200	292.699	14.763	47.1	36.7	0.23
	Total	621.103	40.219	100.0	100.0	

CHIRAL **12a** (82% ee):



Daicel Chiralpak AS-H, Hexane/i-PrOH = 94:6, Flow Rate 0.8 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-90-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	7.573	5409.210	373.695	90.9	94.8	0.22
2	8.750	543.297	20.546	9.1	5.2	0.30
	Total	5952.507	394.242	100.0	100.0	

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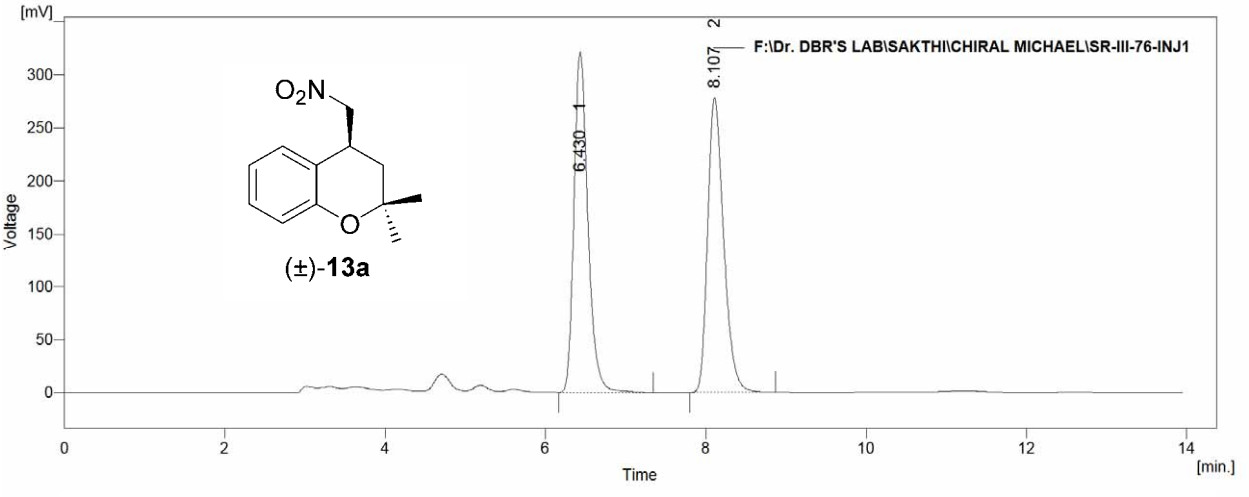
RACEMIC **13a**:

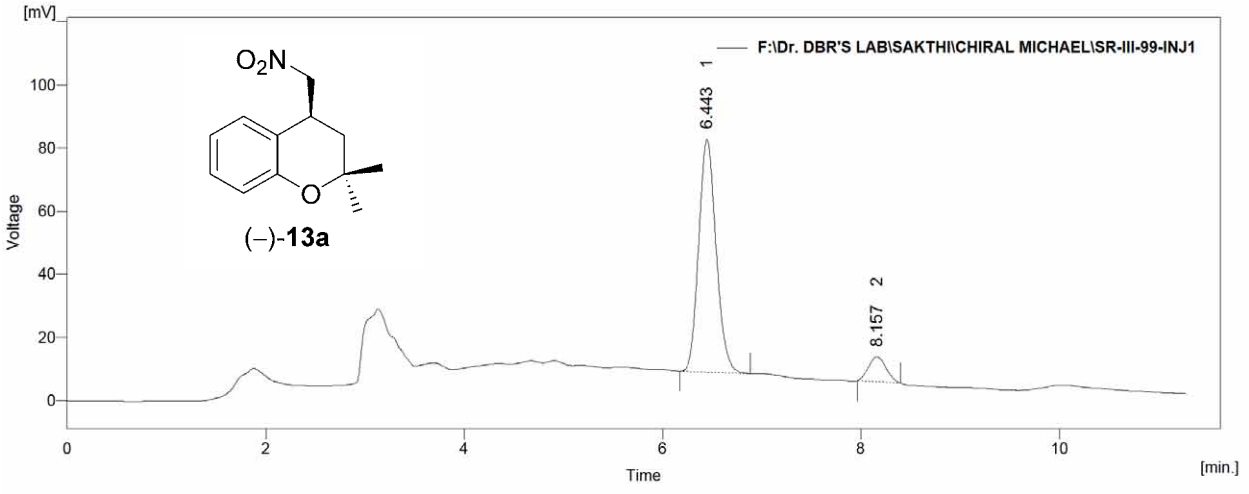


Daicel Chiralcel OD-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-76-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.430	2568.866	214.114	50.0	53.6	0.18
2	8.107	2572.321	185.233	50.0	46.4	0.21
	Total	5141.187	399.347	100.0	100.0	

CHIRAL **13a** (81% ee):



Daicel Chiralcel OD-H, Hexane/i-PrOH = 90:10, Flow Rate 1.0 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-99-INJ1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	6.443	598.692	49.135	90.4	90.5	0.19
2	8.157	63.913	5.182	9.6	9.5	0.20
	Total	662.606	54.317	100.0	100.0	

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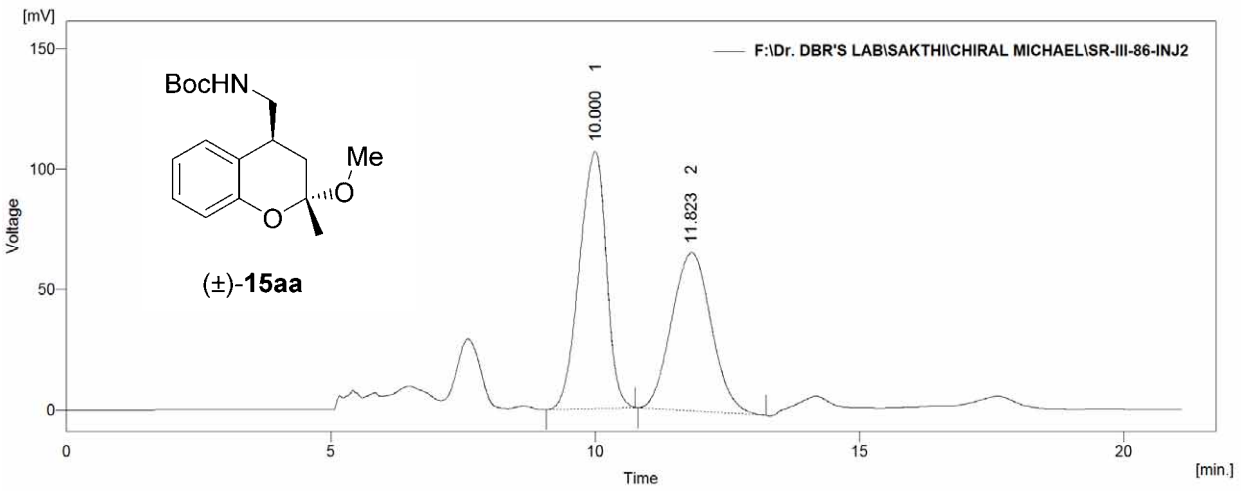
RACEMIC **15aa**:

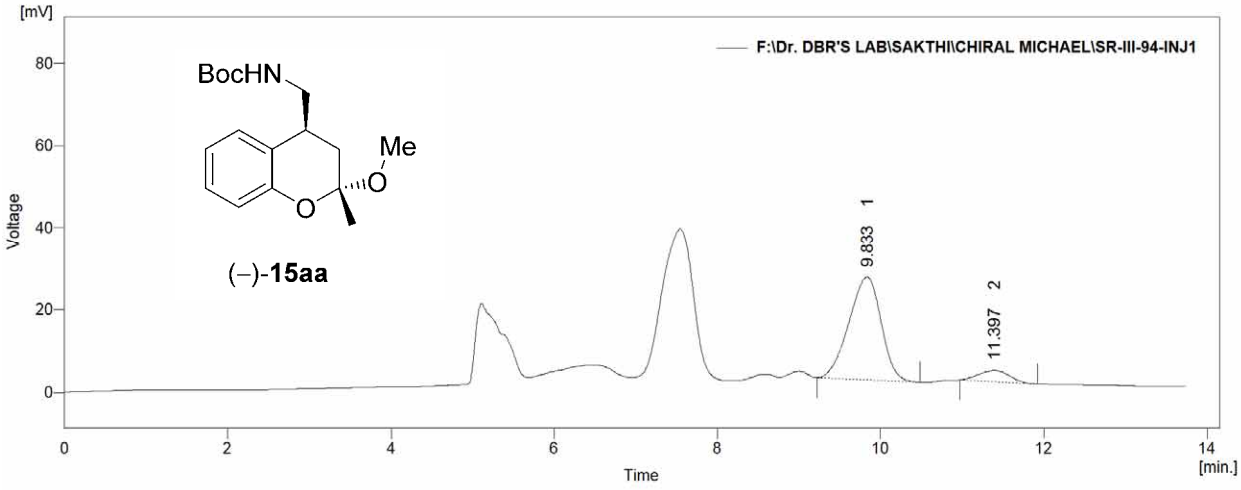


Daicel Chiralcel OD-H, Hexane/i-PrOH = 94:6, Flow Rate 0.6 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-86-INJ2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.000	2514.574	71.070	52.4	61.9	0.56
2	11.823	2280.239	43.704	47.6	38.1	0.82
	Total	4794.813	114.774	100.0	100.0	

CHIRAL **15aa** (81% ee):



Daicel Chiralcel OD-H, Hexane/i-PrOH = 94:6, Flow Rate 0.6 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-94-INJ1)

	Reten. Time	Area	Height	Area	Height	W05

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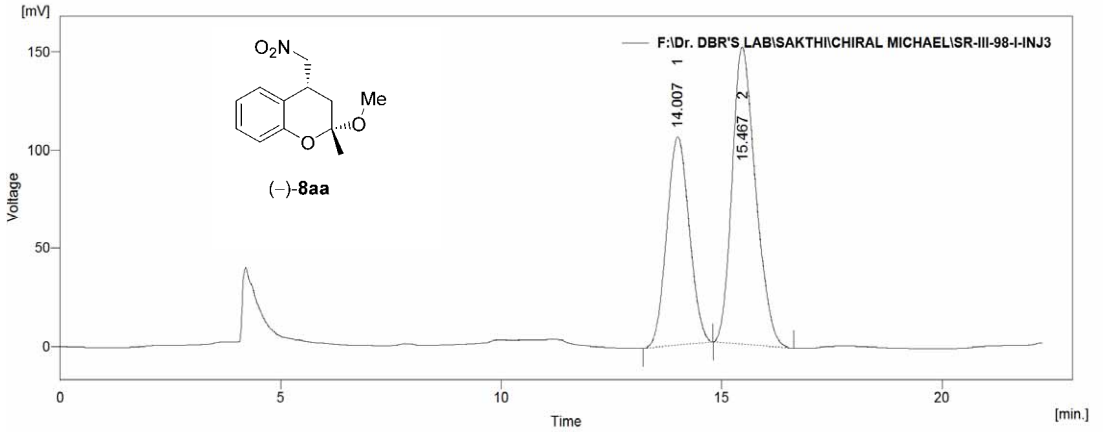
CHIRAL **(-)-8aa** (25% ee):

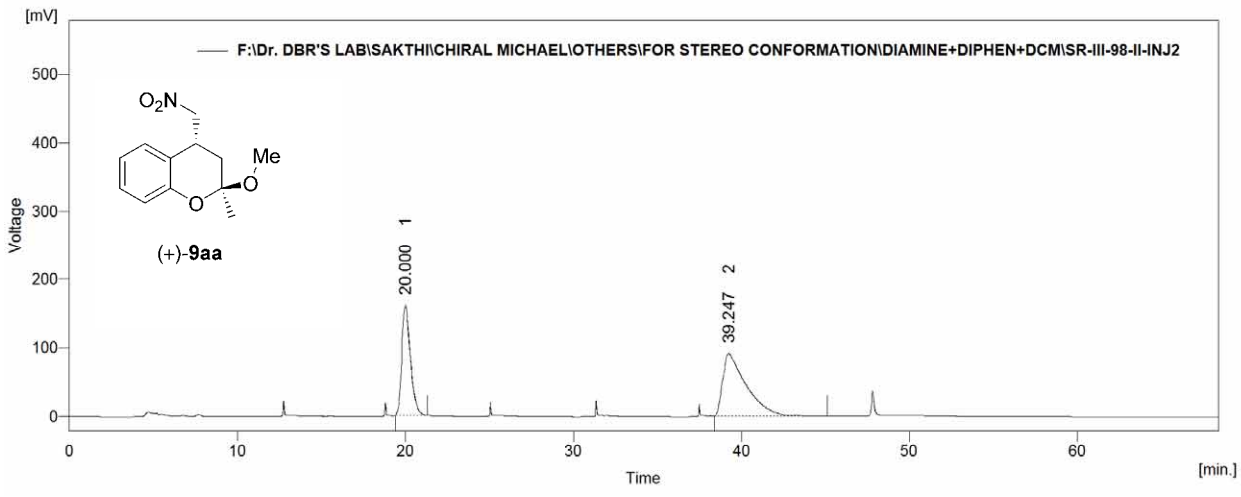


Daicel chiralcel OD-H, Hexane/i-PrOH = 99:1, Flow Rate 0.8 mL/min, 254 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-98-I-INJ4)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	14.007	2236.190	67.269	37.5	40.0	0.54
2	15.467	3727.687	100.838	62.5	60.0	0.57
	Total	5963.876	168.107	100.0	100.0	

CHIRAL **(+)-9aa** (21% ee):



Daicel chiralcel OD-H, Hexane/i-PrOH = 99:1, Flow Rate 0.8 mL/min, 254 nm.

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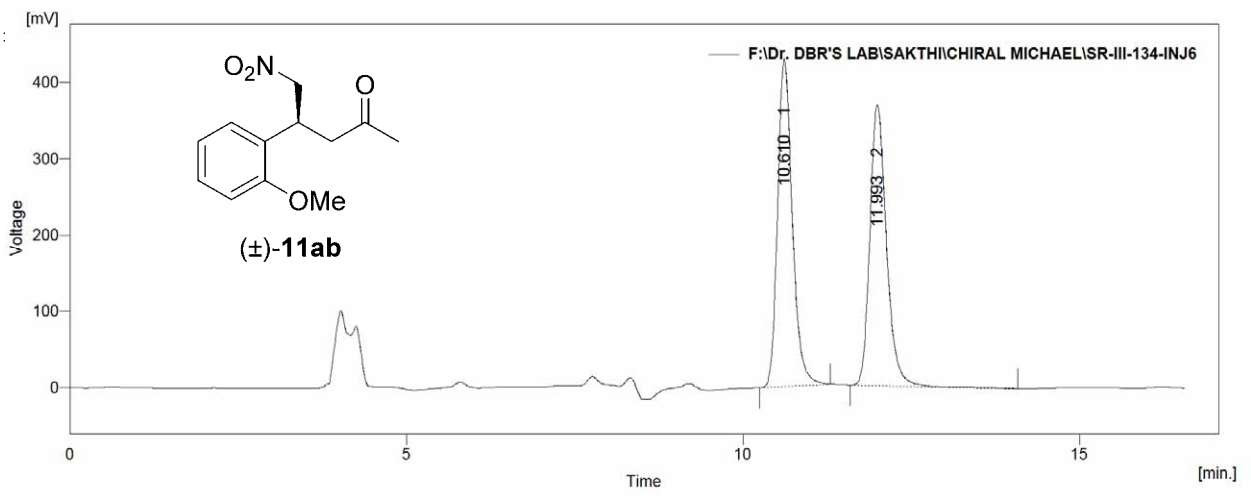
RACEMIC **11ab**:

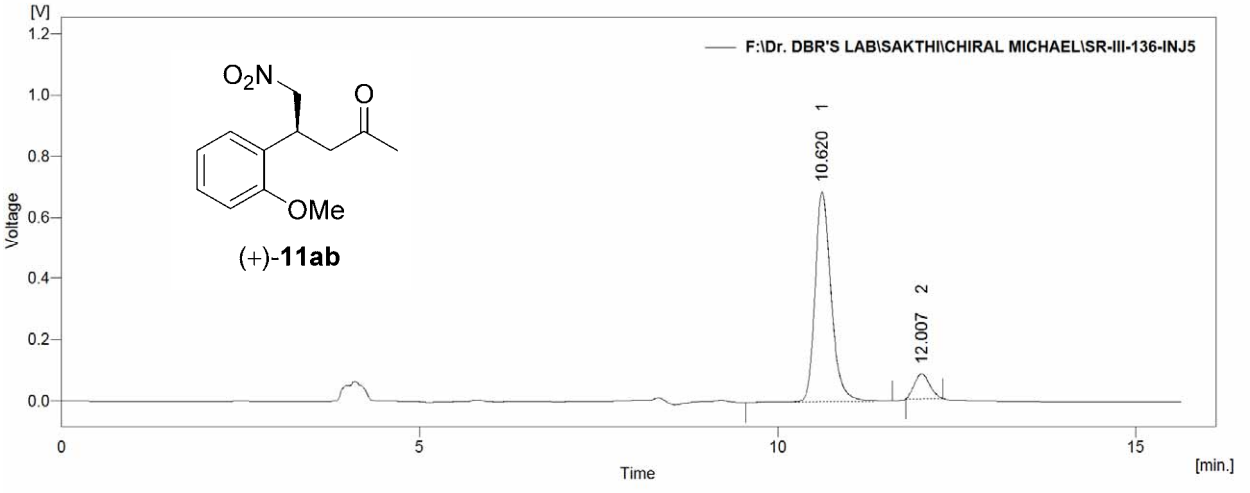


Daicel chiralpak AS-H, Hexane/i-PrOH = 60:40, Flow Rate 1.0 mL/min, 210 nm.

Result Table (Uncal - F:\Dr. DBR'S LAB\SAKTHI\CHIRAL MICHAEL\SR-III-134-INJ6)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.610	4339.270	286.476	50.9	53.9	0.23
2	11.993	4191.352	245.307	49.1	46.1	0.26
	Total	8530.622	531.784	100.0	100.0	

CHIRAL **11ab** (**80% ee**):



Daicel chiralpak AS-H, Hexane/i-PrOH = 60:40, Flow Rate 1.0 mL/min, 210 nm.

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Datablock: dbr11 (Compound 8ba)

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=10.7266(17) b=11.6724(15) c=11.4931(13)

alpha=90 beta=93.195(15) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1436.8(3)	1436.8(3)
Space group	P 21/n	P21/n
Hall group	-P 2yn	?
Moiety formula	C16 H17 N O4	?
Sum formula	C16 H17 N O4	C16 H17 N O4
Mr	287.31	287.31
Dx,g cm-3	1.328	1.328
Z	4	4
Mu (mm-1)	0.096	0.096

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```
F000                608.0                           608.0

F000'               608.32

h,k,lmax            13,14,14                        13,14,14

Nref                2943                            2939

Tmin,Tmax           0.977,0.986                     0.834,1.000

Tmin'               0.962

Correction method= MULTI-SCAN

Data completeness= 0.999       Theta(max)= 26.370

R(reflections)= 0.0499( 2042)     wR2(reflections)= 0.1317( 2939)

S = 1.033             Npar= 192
```

Datablock dbr11 - ellipsoid plot

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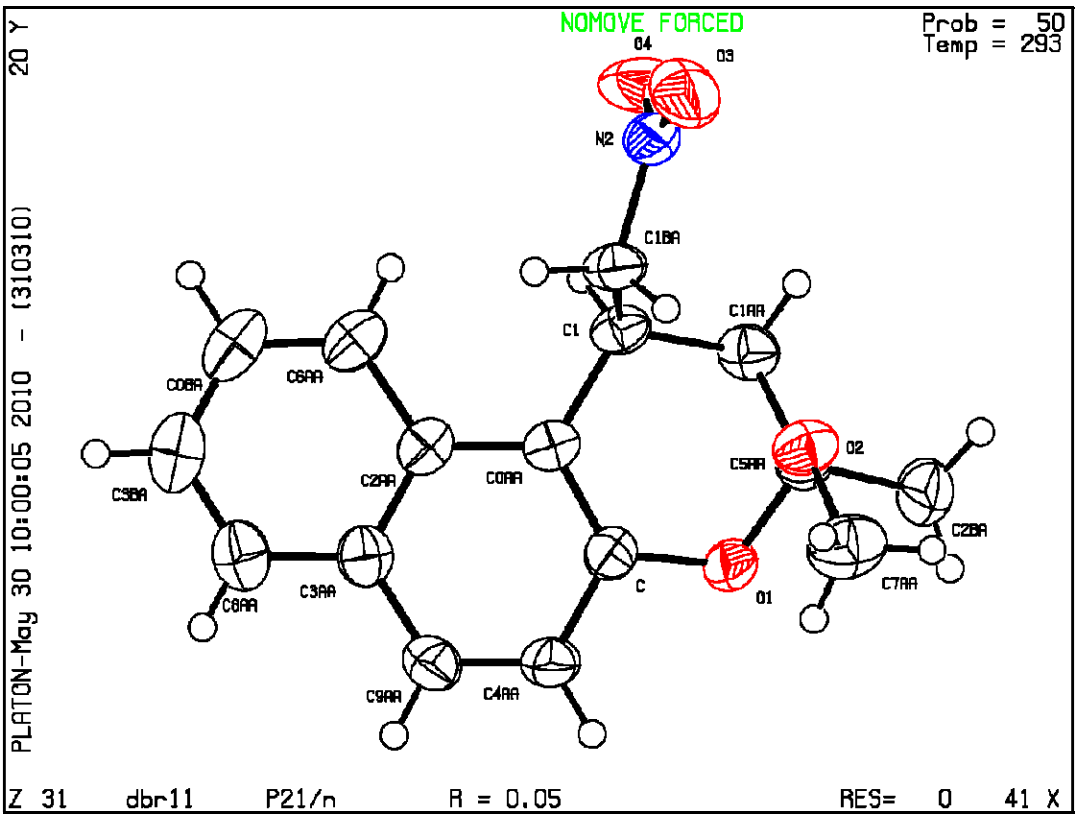

Datablock: dbr77_m (Compound 8ga)

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Bond precision: C-C = 0.0019 A Wavelength=0.71073

Cell: a=11.2657(18) b=6.0004(10) c=19.842(3)

alpha=90 beta=94.626(2) gamma=90

Temperature: 298 K

	Calculated	Reported
Volume	1336.9(4)	1336.9(4)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C13 H17 N O5	?
Sum formula	C13 H17 N O5	C13 H17 N O5
Mr	267.28	267.28
Dx,g cm-3	1.328	1.328
Z	4	4
Mu (mm-1)	0.102	0.102
F000	568.0	568.0
F000'	568.33	
h,k,lmax	14,7,26	14,7,26
Nref	3275	3178
Tmin,Tmax	0.964,0.975	0.960,0.975
Tmin'	0.960	

Correction method= MULTI-SCAN

Data completeness= 0.970 Theta(max)= 28.180

R(reflections)= 0.0558(2688) wR2(reflections)= 0.1526(3178)

S = 1.056 Npar= 175

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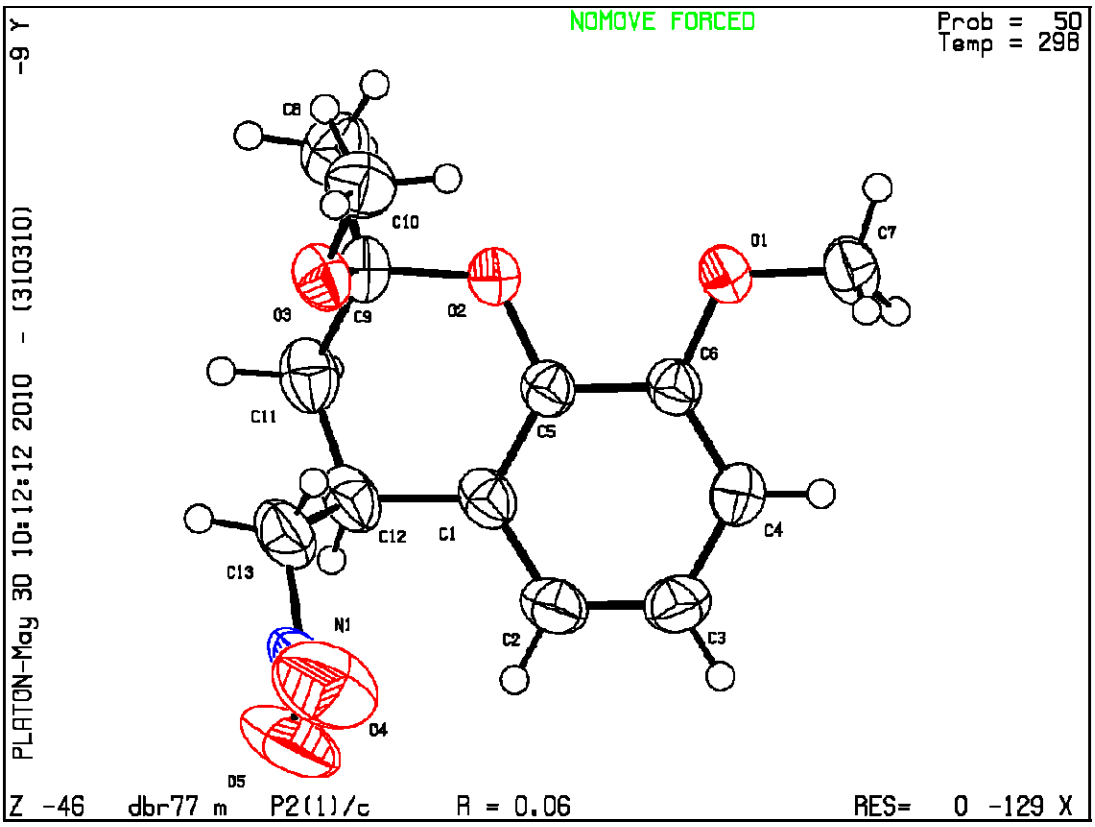
Datablock dbr77_m - ellipsoid plot



Datablock: dbr76_m (Compound 9ha)

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Bond precision: C-C = 0.0029 A Wavelength=0.71073

Cell: a=8.850(3) b=6.326(2) c=23.884(9)

alpha=90 beta=95.201(6) gamma=90

Temperature: 298 K

	Calculated	Reported
Volume	1331.6(8)	1331.5(9)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C13 H17 N O5	?
Sum formula	C13 H17 N O5	C13 H17 N O5
Mr	267.28	267.28
Dx,g cm-3	1.333	1.333
Z	4	4
Mu (mm-1)	0.103	0.103
F000	568.0	568.0
F000'	568.33	
h,k,lmax	11,8,31	11,8,31
Nref	3271	3150
Tmin,Tmax	0.970,0.984	0.130,1.000
Tmin'	0.970	

Correction method= MULTI-SCAN

Data completeness= 0.963 Theta(max)= 28.150

R(reflections)= 0.0656(2629) wR2(reflections)= 0.1493(3150)

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S = 1.181 Npar= 175

Datablock dbr76_m - ellipsoid plot