Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Harmonization of an incompatible aqueous Aldol condensation/oxa-Michael addition/reduction cascade process over a core-shell-structured thermoresponsive catalyst

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CONTENTS

Experimental

1. General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware using standard Schlenk techniques. All commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI Chemicals, Acros Organics, or ABCR in the highest purity grade and used without further purification.

2. Characterization: Ru loading amounts in the catalysts were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian VISTA−MPX). Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 ℃), employing a series of three linear Styragel columns (HR1, HR2, and HR4) at an oven temperature of 45 ℃. The eluent was DMF at a flow rate of 1.0 mL/min. A series of low polydispersity polystyrene standards were employed for calibration. Solid-state NMR experiments were explored on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with ^{1}H frequency of 400.1 MHz, and ^{13}C frequency of 100.5 MHz with 4 mm rotor at two spinning frequencies of 5.5 kHz and 8.0 kHz, TPPM decoupling is applied in the during the acquisition period. ^{1}H cross-polarization in the solid-state NMR experiments was employed using a contact time of 2 ms and pulse lengths of 4μs. Liquid-state NMR (^{1}H NMR and ^{13}C NMR) spectra were performed on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with a ^{1}H frequency of 400 MHz and a ^{13}C frequency of 100 MHz. Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, brs = broad single, m = multiplet), coupling constants (Hz), and integration. Mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics Micro Tof, and a Waters-Micromass Quatro LCZ (ESI); peaks are given in m/z (% of basis peak).

3. General procedure for the Aldol condensation/oxa-Michael addition process. A typical procedure was as follows: The base (0.12 mmol of DBU salt-loadings based on ICP analysis), **4aa** (0.10 mmol), **5aa** (0.12 mmol), HCO_2Na (1.0 mmol), and/or 2.50 mol% of additive in 4.0 mL of $H_2O/^{i}PrOH$ (v/v = 1:3) were added sequentially to a 10.0 mL round−bottom flask purged with nitrogen in turn. The mixture was stirred at 70 ℃ for 12 h. After completion of the reaction, the aqueous solution was extracted by Et_2O (3 × 3.0 mL). The combined Et_2O was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of Et_2O, the residue was purified by silica gel flash column chromatography to afford **6aa** as a white solid.

4. General procedure for the DKR-ATH process. A typical procedure was as follows: The catalyst (2.50 mol% of Ru-loading), **6aa** (0.10 mmol), HCO_2Na (1.0 mmol), and/or additive (0.12 mmol) in 4.0 mL of $H_2O/^{i}PrOH$ (v/v = 1:3) were added sequentially to a

10.0 mL round–bottom flask purged with nitrogen in turn at room temperature. The resulting mixture was stirred at 40 ℃ for 18 h. After completion of the reaction, The aqueous solution was extracted by Et_2O (3 × 3.0 mL). The combined Et_2O was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of Et_2O, the residue was purified by silica gel flash column chromatography to afford (*S,S*)-**7aa** as a white solid.

5. Reusability of catalyst 3 in the Aldol/addition/DKR-ATH cascade process of 4aa and 5aa. A typical procedure was as follows: The catalyst **3** (0.12 mmol of DBU salt-loadings and 2.50 mol% of Ru-loadings based on ICP analyses), 1.0 equivalent of **4aa**, 1.20 equivalent of **5aa**, and 10.0 equivalent of HCOONa in 4.0 mL of $H_2O/^iPrOH$ (v/v = 1:3), and the mixture stirred at 70 ℃ for the first 12 h followed at 40 ℃ for 10 h. After completion of the reaction, the heterogeneous catalyst was separated for the recycling experiment. The aqueous solution was extracted by Et_2O (3 × 3.0 mL). The combined Et_2O was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of Et_2O, the residue was purified by silica gel flash column chromatography to afford (*S,S*)-**7aa**.

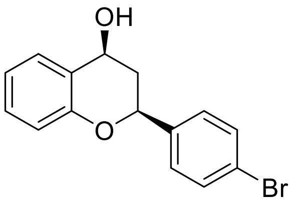
6. Deuterium experiments

6.1 A typical procedure for the aldol/addition reaction of **4aa** and 5**aa**-d_1 in deuterated D_2O/CD_3OD is as follows: The catalyst **3** (0.12 mmol of DBU salt-loadings based on ICP analysis), **4aa** (0.10 mmol), **5aa** (0.12 mmol), and HCO_2Na (1.0 mmol) in 4.0 mL of D_2O/CD_3OD (v/v = 1:3) were added sequentially to a 10.0 mL round–bottom flask purged with nitrogen in turn. The mixture was stirred at 70 ℃ for 12 h. After completion of the reaction, the aqueous solution was extracted by Et_2O (3 × 3.0 mL). The combined Et_2O was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of Et_2O, the residue was purified by silica gel flash column chromatography to afford the desired product **6aa** in a 95% isolated yield.

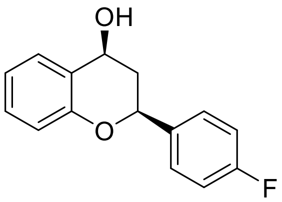
6.2 A typical procedure for the DKR-ATH reaction of **6aa** in deuterated D_2O/CD_3OD is as follows: The catalyst **3** (0.12 mmol of DBU salt-loadings and 2.50 mol% of Ru based on ICP analyses), **6aa** (0.10 mmol), and HCO_2Na (1.0 mmol) in 4.0 mL of D_2O/CD_3OD (v/v = 1:3) were added sequentially to a 10.0 mL round–bottom flask purged with nitrogen in turn. The resulting mixture was stirred at 40 ℃ for 18 h. After completion of the reaction, The aqueous solution was extracted by Et_2O (3 × 3.0 mL). The combined Et_2O was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of Et_2O, the residue was purified by silica gel flash column chromatography to afford (*S,S*)-**7aa**-d_3 in a 93% isolated yield.

9. Data of chiral products.

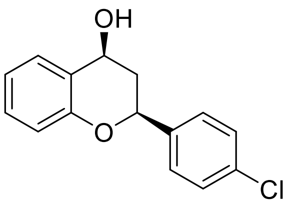
7aa: (2*S*,4*S*)-2-(4-bromophenyl)chroman-4-ol. White solid, 91% yield, 99% *ee*, 37/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.56 – 6.80 (m, 8H), 5.17 (dd, *J* = 12.0, 1.8 Hz, 1H), 5.09 – 5.04 (m, 1H), 2.44 – 1.94 (m, 2H).^{13}C NMR (100 MHz, Methanol-d_4) δ 155.77, 141.95, 132.66, 129.69, 128.22, 127.62, 122.65, 121.87, 117.34, 77.61, 66.12, 41.05. HRMS (APCI): m/z $[M\text{-}OH^+]$ calcd. for $C_{15}H_{12}OBr^+$ 287.00660; found 287.00698. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



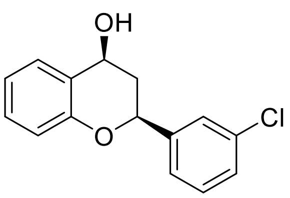
7ab: (2*S*,4*S*)-2-(4-fluorophenyl)chroman-4-ol. White solid, 86% yield, 99% *ee*, 39/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.51 – 6.79 (m, 8H), 5.16 (dd, *J* = 12.1, 1.8 Hz, 1H), 5.06 – 5.04 (m, 1H), 2.39 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 165.08, 162.64, 155.86, 138.63 (d, *J* = 3.2 Hz), 129.67, 129.18, 129.10, 128.21, 127.60, 121.80, 117.33, 116.30, 116.08, 77.65, 66.19, 41.10. HRMS (APCI): m/z $[M\text{-}OH^+]$ calcd. for $C_{15}H_{12}OF^+$ 227.08667; found 227.08615. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).

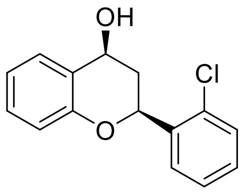


7ac: (2*S*,4*S*)-2-(4-chlorophenyl)chroman-4-ol. White solid, 92% yield, 99% *ee*, 17/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.66 – 6.84 (m, 8H), 5.20 (dd, *J* = 12.0, 1.9 Hz, 1H), 5.08 (dd, *J* = 10.8, 6.2 Hz, 1H), 2.47 – 1.93 (m, 2H) .^{13}C NMR (100 MHz, Methanol-d_4) δ 154.36, 140.02, 133.26, 128.28, 128.23, 127.36, 126.81, 126.20, 120.45, 115.92, 76.16, 64.71, 39.65. HRMS (APCI): m/z $[M\text{-}OH^+]$ calcd. for $C_{15}H_{12}OCl^+$ 243.05712; found 243.05752. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).

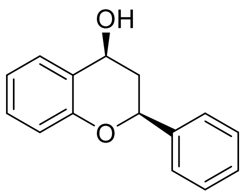


7ad: (2*S*,4*S*)-2-(3-chlorophenyl)chroman-4-ol. White solid, 87% yield, 99% *ee*, 14/1*dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.53 – 6.84 (m, 8H), 5.20 (dd, *J* = 12.0, 1.8 Hz, 1H), 5.09 (ddt, *J* = 10.8, 6.2, 0.9 Hz, 1H), 2.47 – 1.95 (m, 2H).^{13}C NMR (100 MHz, Methanol-d_4) δ 154.27, 143.58, 134.02, 129.72, 128.31, 127.60, 126.81, 126.20, 125.71, 124.04, 120.50, 115.94, 76.08, 64.66, 39.70. HRMS (APCI): m/z $[M\text{-}OH^+]$ calcd. for $C_{15}H_{12}OCl^+$ 243.05712; found 243.05627. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).

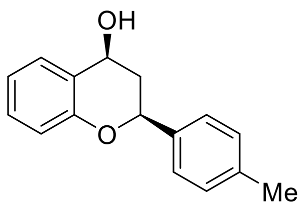




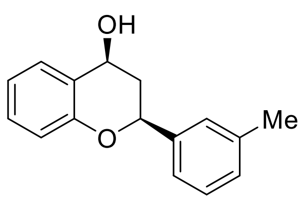
7ae: (2*S*,4*S*)-2-(2-chlorophenyl)chroman-4-ol. White solid, 82% yield, 99% *ee*, 37/1*dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.52 – 7.40 (m, 5H), 7.17 – 7.16 (m, 1H), 6.83 (dd, J = 8.2, 1.2 Hz, 1H), 5.19 (dd, J = 12.0, 1.9 Hz, 1H), 5.08 (ddt, J = 10.8, 6.2, 0.9 Hz, 1H), 2.45 – 1.92 (m, 2H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.10, 142.05, 132.02, 131.20, 130.30, 128.35, 127.77, 126.85, 126.16, 125.51, 120.62, 115.94, 75.45, 64.55, 39.50. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{15}H_{12}OCl^+$ 243.05712; found 243.05739. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



7af: (2*S*,4*S*)-2-phenylchroman-4-ol. White solid, 86% yield, 99% *ee*, 23/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.53 – 6.82 (m, 9H), 5.18 (dd, J = 12.0, 1.8 Hz, 1H), 5.20 – 5.06 (m, 1H), 2.45 – 2.01 (m, 2H).^{13}C NMR (100 MHz, Methanol-d_4) δ 154.58, 141.18, 128.24, 128.13, 127.64, 126.78, 126.25, 125.73, 120.31, 115.93, 76.96, 64.87, 39.80. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{15}H_{13}O^+$ 209.09609; found 209.09560. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).

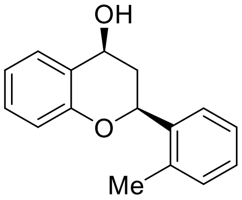


7ag: (2*S*,4*S*)-2-(p-tolyl)chroman-4-ol. White solid, 90% yield, 99% *ee*, 21/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.52 – 6.80 (m, 8H), 5.14 (dd, J = 12.0, 1.8 Hz, 1H), 5.08 (dd, J = 10.9, 6.2 Hz, 1H), 2.42 – 2.37 (m, 4H), 2.05 (ddd, J = 13.0, 12.0, 10.9 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.65, 138.16, 137.48, 128.69, 128.20, 126.77, 126.24, 125.74, 120.23, 115.90, 76.88, 64.91, 39.71, 19.81. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{16}H_{15}O^+$ 223.11174; found 223.11207. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).

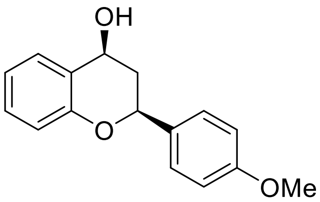


7ah: (2*S*,4*S*)-2-(m-tolyl)chroman-4-ol. White solid, 83% yield, 99% *ee*, 20/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.51 – 6.79 (m, 8H), 5.03 (ddd, J = 12.7, 10.1, 4.0 Hz, 2H), 2.38 – 2.33 (m, 4H), 2.02 (ddd, J = 13.0, 12.1, 10.9 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4)δ 158.56, 144.99, 141.83, 132.27 (d, J = 8.0 Hz), 132.04, 130.79, 130.37, 130.20, 126.83, 124.28, 119.95, 80.95, 68.86, 43.70, 24.20. HRMS(APCI) calcd. for [M-OH$^+$]: $C_{16}H_{15}O^+$ 223.11174 found 223.11210. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).

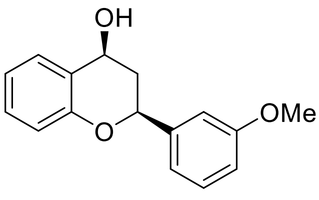
7ai: (2*S*,4*S*)-2-(o-tolyl)chroman-4-ol. White solid, 80% yield, 99% *ee*, 25/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.54 – 6.16 (m, 6H), 6.98 – 6.81 (m, 2H), 5.38 (d, *J* = 10.2 Hz, 1H), 5.09 (dd, *J* = 10.9, 6.2 Hz, 1H), 2.41 – 2.37 (m, 4H), 2.05 (ddd, *J* = 13.0, 11.9, 10.9 Hz, 1H).^{13}C NMR (100 MHz, Methanol-d_4) δ 154.73, 138.79, 134.75, 130.13, 128.24, 127.50, 126.86, 126.33, 125.87, 125.32, 120.31, 115.95, 74.01, 65.00, 38.14, 17.68. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{16}H_{15}O^+$ 223.11174; found 223.11112. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



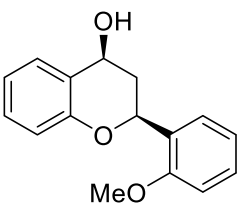
7aj: (2*S*,4*S*)-2-(4-methoxyphenyl)chroman-4-ol. White solid, 85% yield, 99% *ee*, 35/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.28 – 6.78 (m, 8H), 5.14 – 5.05 (m, 2H), 3.82 (s, 3H), 2.41 – 2.03 (m, 2H).^{13}C NMR (100 MHz, Methanol-d_4) δ 159.61, 154.68, 133.14, 128.19, 127.17, 126.78, 126.22, 120.22, 115.89, 113.45, 76.71, 64.95, 54.32, 39.56. HRMS(APCI) calcd. for [M-OH$^+$]: $C_{16}H_{15}O_2^+$ 239.10666 found 239.10698. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



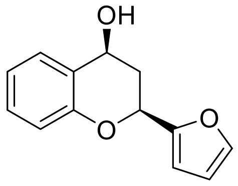
7ak: (2*S*,4*S*)-2-(3-methoxyphenyl)chroman-4-ol. White solid, 83% yield, 99% *ee*, 21/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δδ 7.47 – 6.76 (m, 8H), 5.12– 5.03 (m, 2H), 3.80 (d, *J* = 1.4 Hz, 3H), 2.40 – 2.00(m, 2H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 160.58, 155.65, 134.11, 129.16, 128.13, 127.74, 127.19, 121.18, 116.86, 114.41, 77.67, 65.92, 55.29, 40.53. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{16}H_{15}O_2^+$ 239.10666; found 239.10522. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



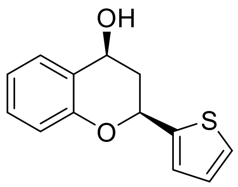
7al: (2*S*,4*S*)-2-(2-methoxyphenyl)chroman-4-ol. White solid, 79% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.54 – 7.47 (m, 2H), 7.22 (dtd, *J* = 62.1, 7.8, 1.7 Hz, 2H), 7.00 – 7.00 (m, 4H), 5.49 (dd, *J* = 11.7, 1.7 Hz, 1H), 5.03 (dd, *J* = 11.0, 6.2 Hz, 1H), 3.86 (s, 3H), 2.46 (ddd, *J* = 12.8, 6.2, 1.8 Hz, 1H), 1.88 (dt, *J* = 12.8, 11.3 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 155.93, 154.77, 129.23, 128.49, 128.17, 126.79, 126.36, 125.80, 120.33, 120.19, 115.95, 110.21, 71.56, 64.93, 54.55, 38.34. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{16}H_{15}O_2^+$ 239.10666; found 239.10588. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



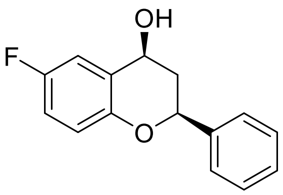
7am: (2*S*,4*S*)-2-(furan-2-yl)chroman-4-ol. White solid, 86% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.52 – 6.42 (m, 7H), 5.19 (dd, *J* = 12.1, 1.9 Hz, 1H), 5.01 (dd, *J* = 10.9, 6.3 Hz, 1H), 2.30 – 2.21 (m, 2H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 155.79, 154.98, 144.28, 130.07, 128.62, 127.84, 122.22, 117.66, 111.75, 109.09, 71.82, 66.18, 37.24. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{13}H_{11}O_2^+$ 199.07536; found 199.07475. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



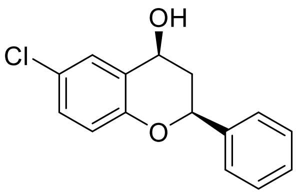
7an: (2*S*,4*S*)-2-(thiophen-2-yl)chroman-4-ol. White solid, 85% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.52 – 6.80 (m, 8H), 5.16 – 5.05 (m, 2H), 2.42 – 2.37 (m, 4H), 2.05 (ddd, *J* = 13.0, 12.0, 10.9 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.15, 143.94, 128.26, 126.82, 126.15, 126.10, 124.82, 124.43, 120.50, 115.89, 72.78, 64.51, 39.79. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{13}H_{11}OS^+$ 215.05251; found 215.05165. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



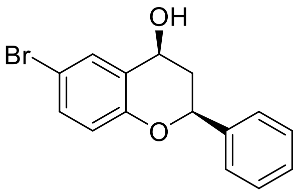
7ao: (2*S*,4*S*)-6-fluoro-2-phenylchroman-4-ol. White solid, 88% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.46 – 6.78 (m, 8H), 5.17 – 5.01 (m, 2H), 2.39 – 1.96 (m, 2H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 162.33, 159.98, 154.60 (d, *J* = 2.1 Hz), 144.90, 132.09, 131.67 (d, *J* = 4.7 Hz), 129.65, 121.07 (d, *J* = 7.9 Hz), 118.75 (d, *J* = 23.6 Hz), 116.57 (d, *J* = 23.7 Hz), 81.07, 68.68, 43.30. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{15}H_{12}OF^+$ 227.08667; found 227.08701. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



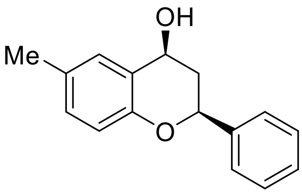
7ap: (2*S*,4*S*)-6-chloro-2-phenylchroman-4-ol. White solid, 85% yield, 99% *ee*, 37/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.47 – 6.78 (m, 8H), 5.18 (dd, *J* = 12.0, 1.8 Hz, 1H), 5.03 (ddt, *J* = 11.0, 6.2, 1.0 Hz, 1H), 2.42 – 1.96(m, 2H).^{13}C NMR (100 MHz, Methanol-d_4) δ 157.22, 144.71, 132.18, 132.11, 132.05, 131.71, 130.45, 129.66, 129.07, 121.51, 81.18, 68.49, 43.18. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{15}H_{12}OCl^+$ 243.05712; found 243.05721. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



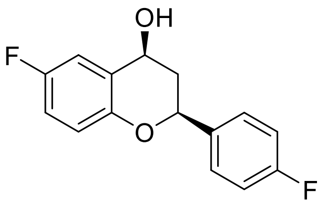
7aq: (2*S*,4*S*)-6-bromo-2-phenylchroman-4-ol. White solid, 83% yield, 99% *ee*, 28/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.61 (d, *J* = 2.4 Hz, 1H), 7.42 – 6.72 (m, 8H), 5.15 (dd, *J* = 12.1, 1.8 Hz, 1H), 5.01 (dd, *J* = 11.0, 6.2 Hz, 1H), 2.00 (dd, *J* = 12.2, 1.5 Hz, 2H).^{13}C NMR (101 MHz, Methanol-d_4) δ 153.76, 140.70, 131.08, 129.55, 128.74, 128.20, 127.80, 125.75, 118.04, 112.31, 77.24, 64.51, 39.17. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{15}H_{12}OBr^+$ 287.00660; found 287.00711. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



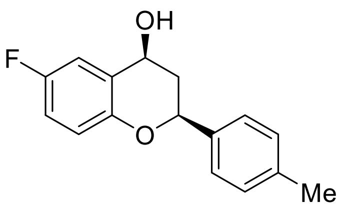
7ar: (2*S*,4*S*)-6-methyl-2-phenylchroman-4-ol. White solid, 73% yield, 99% *ee*, 46/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.48 – 6.71 (m, 8H), 5.12 – 5.02 (m, 2H), 2.39 (ddd, *J* = 12.9, 6.3, 1.8 Hz, 1H), 2.29 (s, 3H), 2.03 (ddd, *J* = 13.0, 12.0, 10.8 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 152.40, 141.28, 129.51, 128.84, 128.12, 127.60, 127.02, 125.80, 125.74, 115.75, 76.87, 64.93, 39.91, 19.40. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{16}H_{15}O^+$ 223.11174; found 223.11115. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



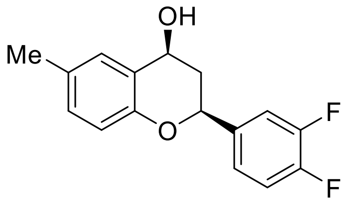
7as: (2*S*,4*S*)-6-fluoro-2-(4-fluorophenyl)chroman-4-ol. White solid, 89% yield, 99% *ee*, 23/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.49 – 6.78 (m, 7H), 5.16 – 5.02 (m, 2H), 2.42 – 1.96 (m, 2H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 165.08, 162.64, 159.81, 157.45, 151.91 (d, *J* = 2.1 Hz), 138.35 (d, *J* = 3.2 Hz), 129.08, 118.53 (d, *J* = 7.9 Hz), 116.23 (dd, *J* = 22.7, 4.2 Hz), 114.07 (d, *J* = 23.8 Hz), 77.80, 66.04, 40.62. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{15}H_{11}OF_2^+$ 245.07725; found 245.07672. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



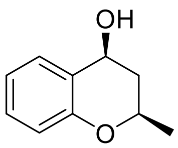
7at: (2*S*,4*S*)-6-fluoro-2-(p-tolyl)chroman-4-ol. White solid, 95% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.35 – 7.19 (m, 5H), 6.92 – 6.76 (m, 2H), 5.12 (dd, *J* = 12.0, 1.8 Hz, 1H), 5.08 – 4.99 (m, 1H), 2.41 – 2.36 (m, 4H), 2.02 (ddd, *J* = 13.0, 12.0, 10.9 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 158.36, 156.00, 150.73 (d, *J* = 2.0 Hz), 137.75 (d, *J* = 38.5 Hz), 128.72, 127.74, 125.73, 117.06, 114.78 (d, *J* = 23.7 Hz), 112.62 (d, *J* = 23.9 Hz), 77.05, 64.78, 39.26, 19.82. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{16}H_{14}OF^+$ 241.10232; found 241.10170. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



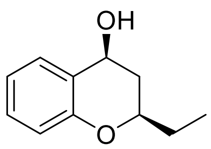
7au: (2*S*,4*S*)-2-(3,4-difluorophenyl)-6-methylchroman-4-ol. White solid, 76% yield, 99% *ee*, 36/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.41 – 6.70 (m, 6H), 5.14 – 5.00 (m, 2H), 2.40 (ddd, J = 13.0, 6.3, 1.9 Hz, 1H), 2.27 (s, 3H), 1.99 – 1.90 (m, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 155.95, 155.30 (d, J = 12.8 Hz), 154.81 (d, J = 12.7 Hz), 152.85 (d, J = 12.7 Hz), 152.36 (d, J = 12.7 Hz), 142.87 (dd, J = 5.6, 3.8 Hz), 133.72, 132.83, 130.97, 129.66, 126.08 (dd, J = 6.5, 3.6 Hz), 120.91, 79.45 (d, J = 1.5 Hz), 68.59, 43.67, 23.29. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{16}H_{13}OF_2^+$ 259.09290; found 259.09218. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



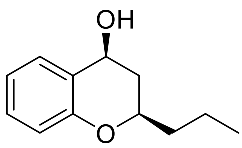
7ba: (2*R*,4*S*)-2-methylchroman-4-ol. White solid, 82% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.46 – 6.71 (m, 4H), 4.88 (d, J = 7.4 Hz, 1H), 4.25 (dqd, J = 12.6, 6.3, 1.7 Hz, 1H), 2.26 (ddd, J = 12.9, 6.4, 1.7 Hz, 1H), 1.71 (dt, J = 12.9, 11.2 Hz, 1H), 1.40 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.57, 128.05, 126.84, 126.04, 119.89, 115.71, 71.15, 64.48, 39.06, 20.44. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{10}H_{11}O^+$ 147.08044; found 147.08010. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



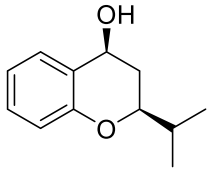
7bb: (2*R*,4*S*)-2-ethylchroman-4-ol. White solid, 81% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.45 – 6.72 (m, 4H), 4.88 (d, J = 6.5 Hz, 1H), 2.25 (ddd, J = 12.8, 6.3, 1.7 Hz, 1H), 2.25 (ddd, J = 12.8, 6.3, 1.7 Hz, 1H), 1.85 – 1.65 (m, 3H), 1.07 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.62, 128.06, 126.80, 126.30, 119.83, 115.73, 76.04, 64.64, 36.84, 28.24, 8.39. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{11}H_{13}O^+$ 161.09609; found 161.09570. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



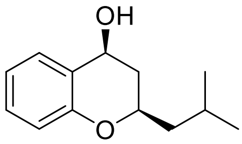
7bc: (2*R*,4*S*)-2-propylchroman-4-ol. White solid, 85% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.45 – 6.71 (m, 4H), 4.88 (d, J = 6.5 Hz, 1H), 4.12 (dddd, J = 11.6, 7.6, 4.5, 1.7 Hz, 1H), 2.24 (ddd, J = 12.9, 6.3, 1.7 Hz, 1H), 1.80 – 1.45 (m, 5H), 1.01 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.60, 128.05, 126.82, 126.29, 119.83, 115.74, 74.57, 64.61, 37.57, 37.34, 17.99, 12.99. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{12}H_{15}O^+$ 175.11174; Found 175.11104. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



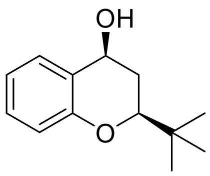
7bd: (2*S*,4*S*)-2-isopropylchroman-4-ol. White solid, 83% yield, 99% *ee*, 19/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.45 – 6.72 (m, 4H), 3.89 (ddd, *J* = 11.7, 5.4, 1.6 Hz, 1H), 2.23 (ddd, *J* = 12.8, 6.3, 1.6 Hz, 1H), 1.94 (pd, *J* = 6.9, 5.4 Hz, 1H), 1.72 (dt, *J* = 12.6, 11.2 Hz, 1H), 1.06 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.77, 128.04, 126.65, 126.40, 119.75, 115.70, 79.45, 65.01, 34.03, 32.31, 17.07, 16.66. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{12}H_{14}O^+$ 175.1117; found 175.1119. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



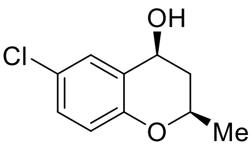
7be: (2*R*,4*S*)-2-isobutylchroman-4-ol. White solid, 88% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.45 – 6.71 (m, 4H), 4.91 (d, *J* = 6.7 Hz, 1H), 4.19 (dddd, *J* = 11.3, 8.7, 4.5, 1.7 Hz, 1H), 2.23 (ddd, *J* = 12.9, 6.4, 1.7 Hz, 1H), 2.04 – 1.91 (m, 1H), 1.76 – 1.66 (m, 2H), 1.46 – 1.39 (m, 1H), 1.00 (dd, *J* = 6.7, 3.7 Hz, 6H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.56, 128.05, 126.87, 126.30, 119.87, 115.77, 73.04, 64.54, 44.59, 37.88, 24.05, 22.26, 21.19. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{13}H_{17}O^+$ 189.12739; found 189.12656. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



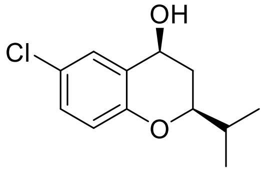
7bf: (2*S*,4*S*)-2-(tert-butyl)-chroman-4-ol. White solid, 95% yield, 99% *ee*, >50/1 *dr*.^{1}H NMR (400 MHz, Methanol-d_4) δ 7.45 – 6.72 (m, 1H), 4.87 (s, 4H), 3.75 (dd, *J* = 12.0, 1.5 Hz, 1H), 2.27 (ddd, *J* = 12.6, 6.2, 1.5 Hz, 1H), 1.68 (td, *J* = 12.3, 11.0 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.95, 128.05, 126.47, 126.44, 119.71, 115.67, 82.31, 65.43, 33.49, 32.23, 24.70. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{13}H_{17}O^+$ 189.12739; found 189.12626. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



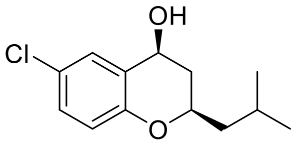
7bg: (2*R*,4*S*)-6-chloro-2-methylchroman-4-ol. White solid, 91% yield, 99% *ee*, 35/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.42 – 6.70 (m, 3H), 4.85 (dd, *J* = 11.2, 6.6 Hz, 1H), 4.26 (dd, *J* = 5.2, 1.7 Hz, 1H), 2.28 – 1.63 (m, 2H), 1.40 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 153.30, 128.03, 127.93, 126.55, 124.68, 117.33, 71.54, 64.17, 38.54, 20.32. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{10}H_9OCl^+$ 181.0415; found 181.0418. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



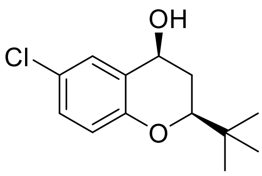
7bh: (2*S*,4*S*)-6-chloro-2-isopropylchroman-4-ol. White solid, 87% yield, 99% *ee*, 45/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.41 – 6.71 (m, 3H), 4.84 (ddt, *J* = 11.0, 6.2, 1.0 Hz,1H), 3.91 (ddd, *J* = 11.8, 5.4, 1.6 Hz, 1H), 2.22 (ddd, *J* = 12.8, 6.2, 1.7 Hz, 1H), 1.93 (heptd, *J* = 6.8, 5.2 Hz, 1H), 1.69 (ddd, *J* = 12.8, 11.8, 10.9 Hz, 1H), 1.05 (dd, *J* = 6.9, 5.7 Hz, 6H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 153.47, 128.38, 127.92, 126.38, 124.55, 117.30, 79.78, 64.67, 33.57, 32.25, 17.05, 16.57. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{12}H_{14}OCl^+$ 209.07277; found 209.07227. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



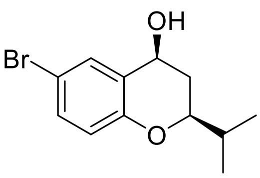
7bi: (2*R*,4*S*)-6-chloro-2-isobutylchroman-4-ol. White solid, 86% yield, 99% *ee*, 21/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.42 – 6.70 (m, 3H), 4.87 – 4.84 (m, 1H), 4.21 (dddd, *J* = 11.3, 8.6, 4.4, 1.7 Hz, 1H), 2.25 – 2.20 (m, 2H), 1.75 – 1.43 (m, 3H), 0.99 (dd, *J* = 6.7, 3.4 Hz, 6H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 153.26, 128.29, 127.92, 126.56, 124.65, 117.37, 73.44, 64.22, 44.45, 37.37, 24.03, 22.22, 21.14. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{13}H_{15}OCl^+$ 223.0884; found 223.0885. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



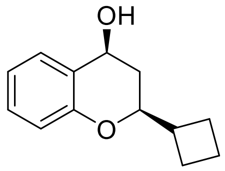
7bj: (2*S*,4*S*)-2-(tert-butyl)-6-chlorochroman-4-ol. White solid, 93% yield, 99% *ee*, 42/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.41 – 6.71 (m, 3H), 4.82 (s, 1H), 3.79 (dd, *J* = 12.0, 1.5 Hz, 1H), 2.30 – 1.64 (m, 2H), 1.04 (s, 9H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 153.61, 128.42, 127.91, 126.22, 124.52, 117.24, 82.67, 65.04, 33.48, 31.76, 24.59. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{13}H_{15}OCl^+$ 223.0884; found 223.0885. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



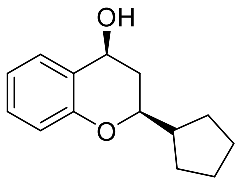
7bk: (2*S*,4*S*)-6-bromo-2-isopropylchroman-4-ol White solid, 85% yield, 99% *ee*,16/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.55 – 6.66 (m, 3H), 4.85 (ddt, *J* = 11.0, 6.3, 1.0 Hz, 1H), 3.93 – 3.89 (m, 1H), 2.25 (s, 1H), 1.93 (pd, *J* = 6.9, 5.4 Hz, 1H), 1.69 (ddd, *J* = 12.8, 11.8, 11.0 Hz, 1H), 1.07 – 1.03 (m, 6H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 153.96, 130.87, 129.41, 128.93, 117.77, 111.68, 79.79, 64.61, 33.54, 32.25, 17.05, 16.57. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{12}H_{14}OBr^+$ 253.02225; found 253.02227. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



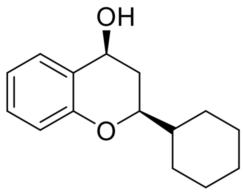
7bl: (2*S*,4*S*)-2-cyclobutylchroman-4-ol. White solid, 76% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.43 – 6.71 (m, 4H), 4.86 – 4.84 (m, 1H), 4.01 (ddd, *J* = 11.5, 7.1, 1.7 Hz, 1H), 2.63 – 2.18 (m, 1H), 2.18 (s, 7H), 1.56 (dt, *J* = 12.8, 11.2 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.62, 128.07, 126.75, 126.31, 119.79, 115.74, 77.90, 64.56, 39.69, 34.47, 23.77, 23.06, 17.66. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{13}H_{15}O^+$ 187.11174; found 187.11112. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 99/1, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



7bm: (2*S*,4*S*)-2-cyclopentylchroman-4-ol. White solid, 81% yield, 99% *ee*, 42/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.45 – 6.71 (m, 4H), 4.90 (s, 1H), 3.92 (ddd, *J* = 11.5, 7.4, 1.7 Hz, 1H), 2.31 – 2.09 (m, 2H), 1.94 – 1.40 (m, 9H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.71, 128.05, 126.74, 126.35, 119.75, 115.75, 78.59, 64.69, 44.56, 36.31, 28.21, 25.19 (d, *J* = 3.2 Hz). HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{14}H_{17}O^+$ 201.12739; found 201.12656. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



7bn: (2*S*,4*S*)-2-cyclohexylchroman-4-ol. White solid, 88% yield, 99% *ee*, 16/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.44 – 6.71 (m, 4H), 4.88 – 4.85 (m, 1H), 3.89 (ddd, *J* = 11.7, 5.6, 1.6 Hz, 1H), 2.23 (ddd, *J* = 12.7, 6.2, 1.7 Hz, 1H), 1.98 (dtt, *J* = 13.4, 4.5, 2.3 Hz, 1H), 1.85 – 1.62 (m, 6H), 1.37 – 1.12 (m, 5H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 154.77, 128.03, 126.67, 126.43, 119.73, 115.71, 78.94, 65.05, 42.32, 34.22, 28.23, 27.91, 26.29, 25.96, 25.89. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{15}H_{19}O^+$ 215.14304; found 215.14213. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 97/3, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).



7bo: tert-butyl 4-((2*S*,4*S*)-7-bromo-4-hydroxychroman-2-yl)piperidine-1-carboxylate. White solid, 78% yield, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.34 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.05 – 6.92 (m, 2H), 4.83 (dd, *J* = 10.7, 6.1 Hz, 1H), 4.17 (d, *J* = 13.3 Hz, 2H), 3.99 (dd, *J* = 11.6, 5.9 Hz, 1H), 2.79 (s, 2H), 2.26 (ddd, *J* = 13.0, 6.1, 1.8 Hz, 1H), 1.95 (d, *J* = 13.1 Hz, 1H), 1.78 – 1.72 (m, 3H), 1.49 (d, *J* = 1.1 Hz, 9H), 1.44 – 1.26 (m, 2H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 155.33, 155.13, 128.44, 125.92, 123.01, 120.83, 118.65, 79.65, 78.61, 64.33, 40.37, 33.79, 27.35, 27.00. HRMS (APCI): m/z [M-OH$^+$] calcd. for $C_{19}H_{25}O_3NBr^+$ 394.10123; found 394.10060. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 210 nm, flow rate: 1.0 mL/min, 25 ℃).

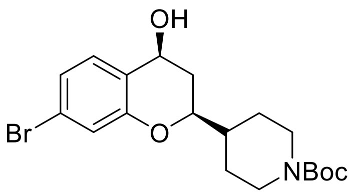


Figure 1. DLS traces of **1** (green) and **2** (red) and catalyst **3** (blue) indicated at 25, 45, and 70 °.

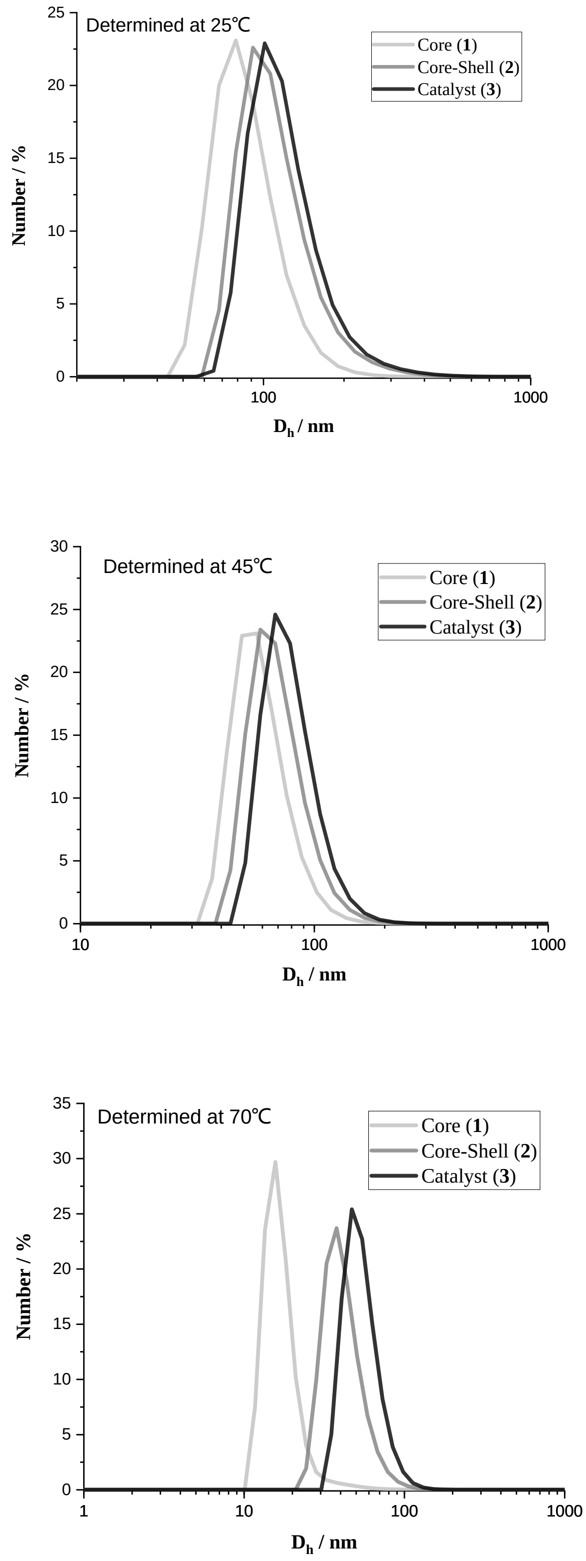


Figure S2. Temperature-dependent transmittance of **3** using a turbidity measurement (a) This turbidity measurement was performed on a custom-modified Tepper turbidity photometer TP1-D at a wavelength of 670 nm, a cell path length of 10 mm, and magnetic stirring. The heating program started at a high temperature, and it was cooled to 10 ℃ at a constant cooling rate of 1.0 ℃/min. (b) Temperature-dependent transmittance for the determination of the the volume phase transition temperature (VPTT) as the temperature corresponding to the transmittance decrease at the wavelength of 680 nm).

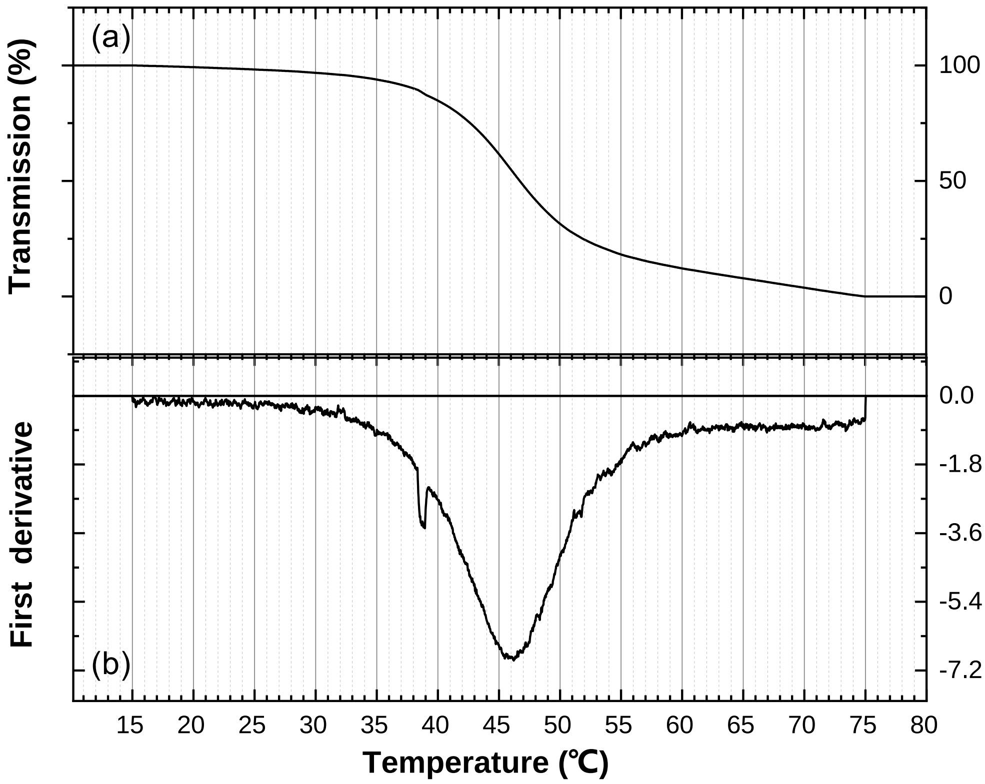


Figure S3. The SEM images and dispersive situations of catalyst **3**. (a) The scanning electron microscopy (SEM) images of catalyst **3**. (b) The dispersive situations of catalyst **3** at indicated 25, 40, and 80 ℃ in $H_2O/^i PrOH$ (v/v = 1:3) system.

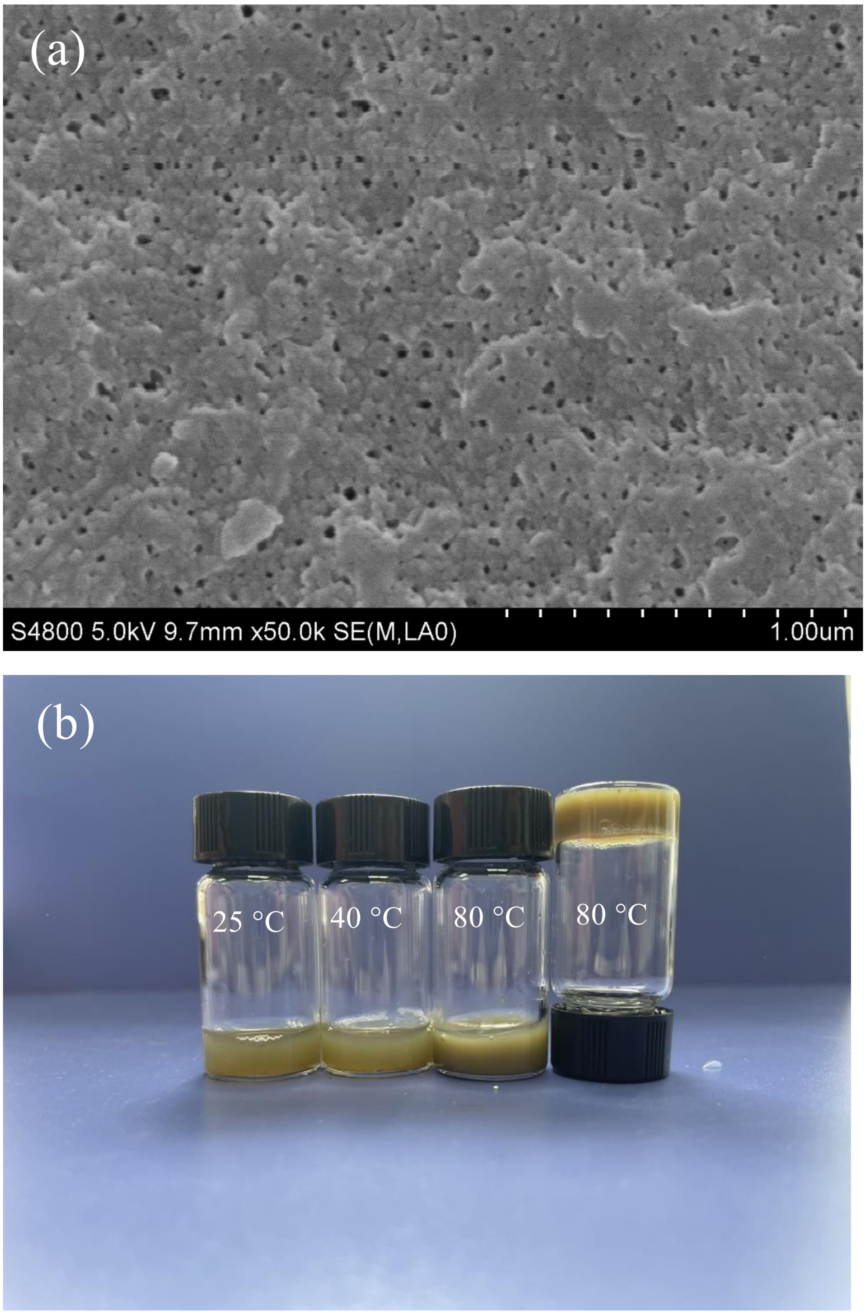
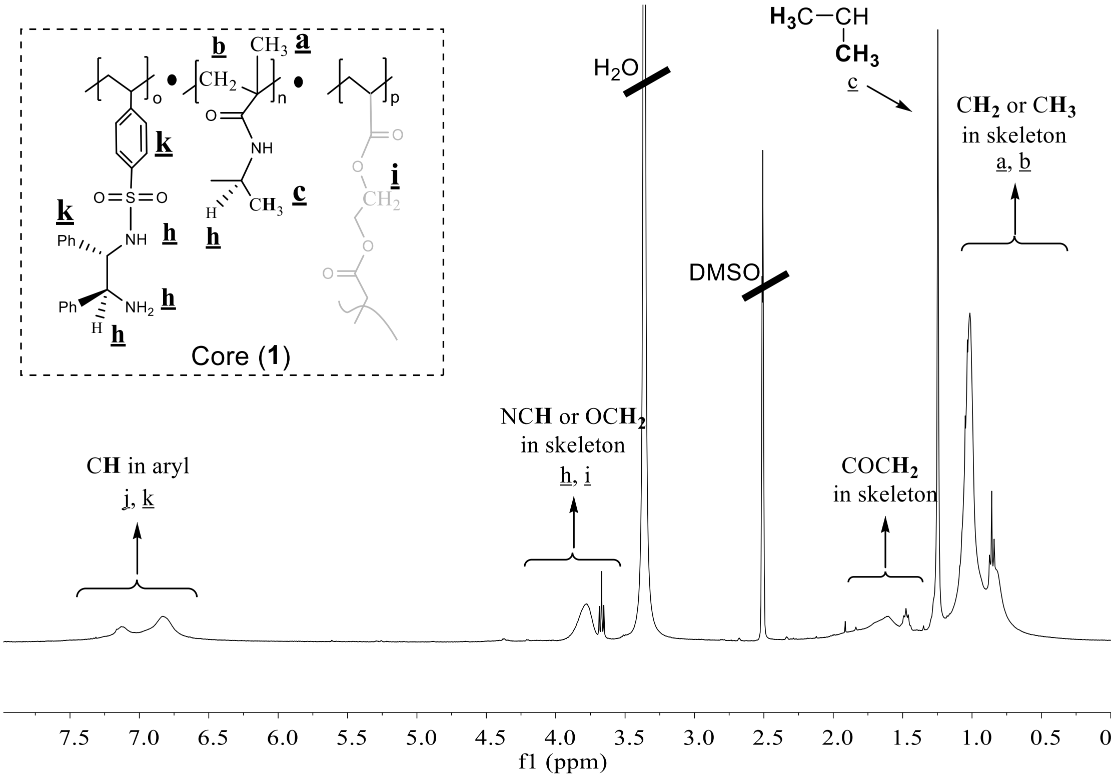
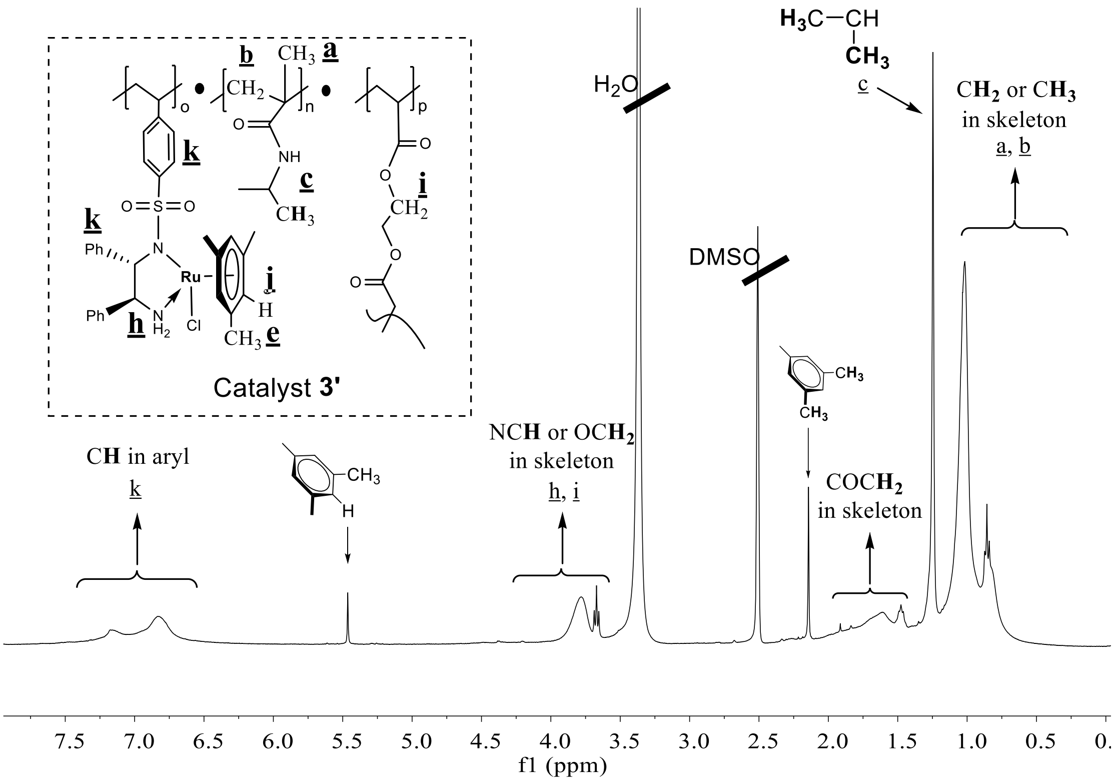
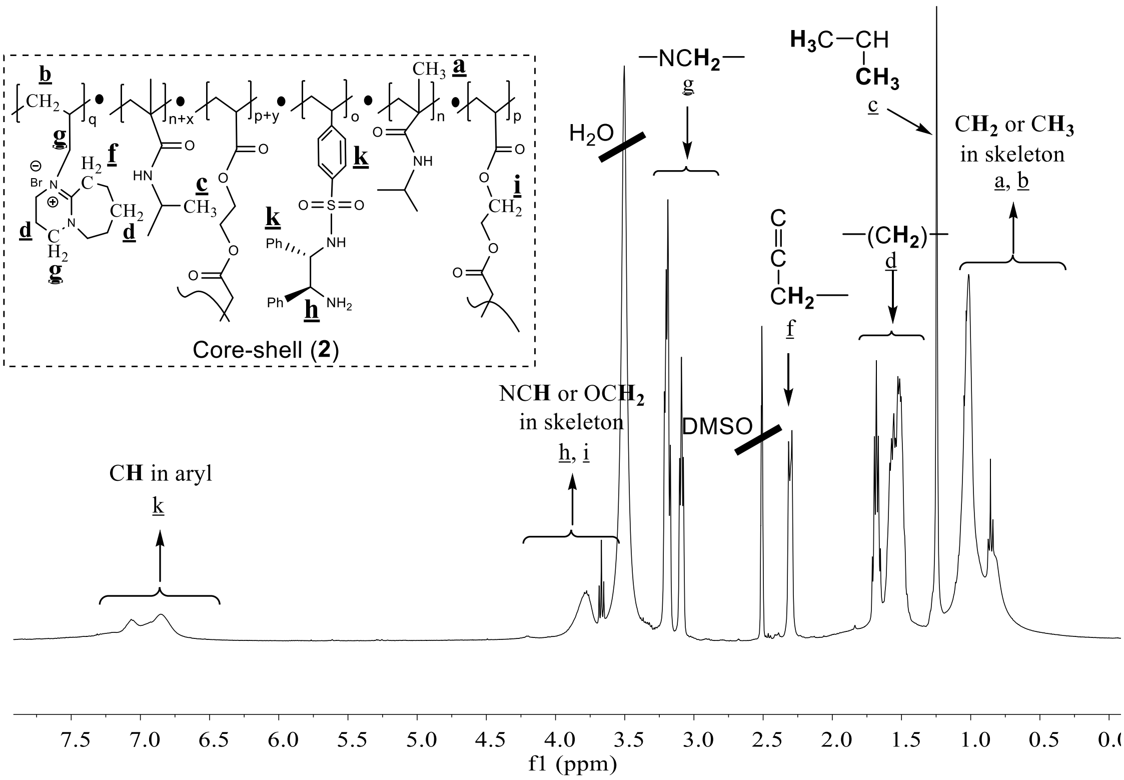


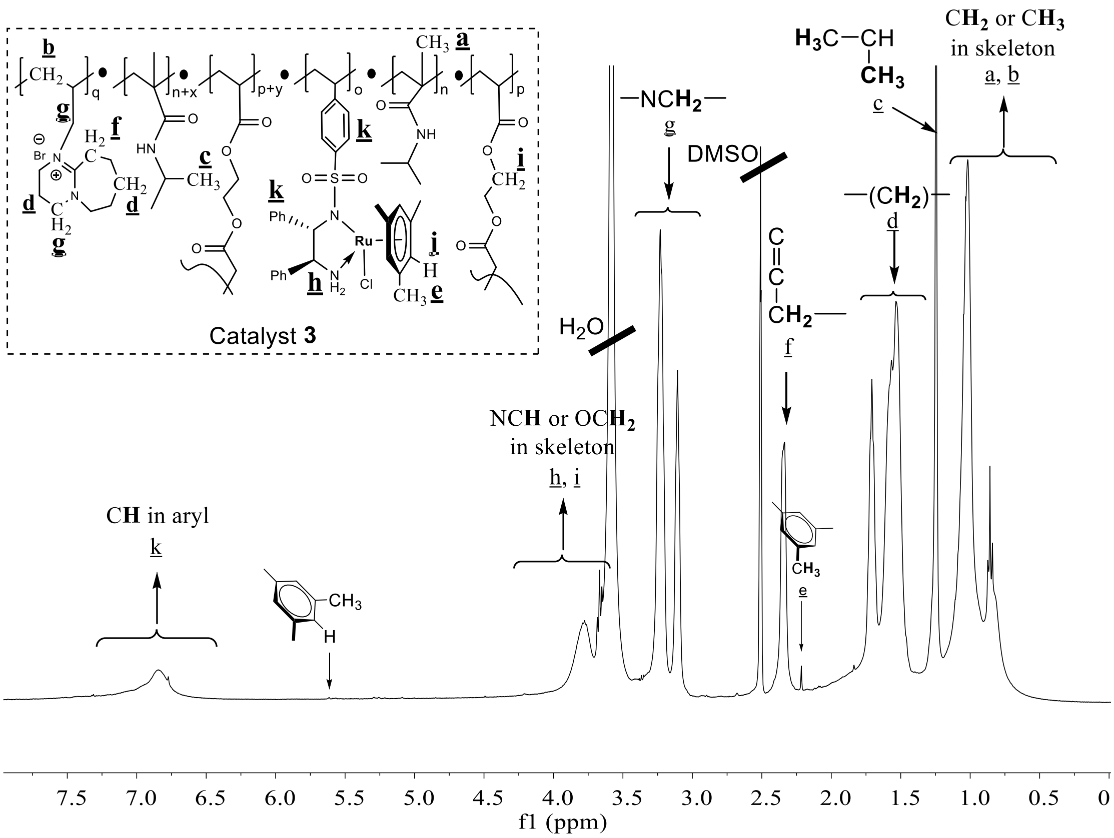
Figure S4. The NMR spectra. (a) The liquid-state [1]H-NMR of **1-2**, catalysts **3** and **3′**. (b) The solid-state [13]C MAS NMR spectra of **1-2,** and catalysts **3** and **3′.**

(a) The liquid-state [1]H-NMR of the core (**1**), catalyst **3′,** core-shell (**2**), and catalyst **3.**

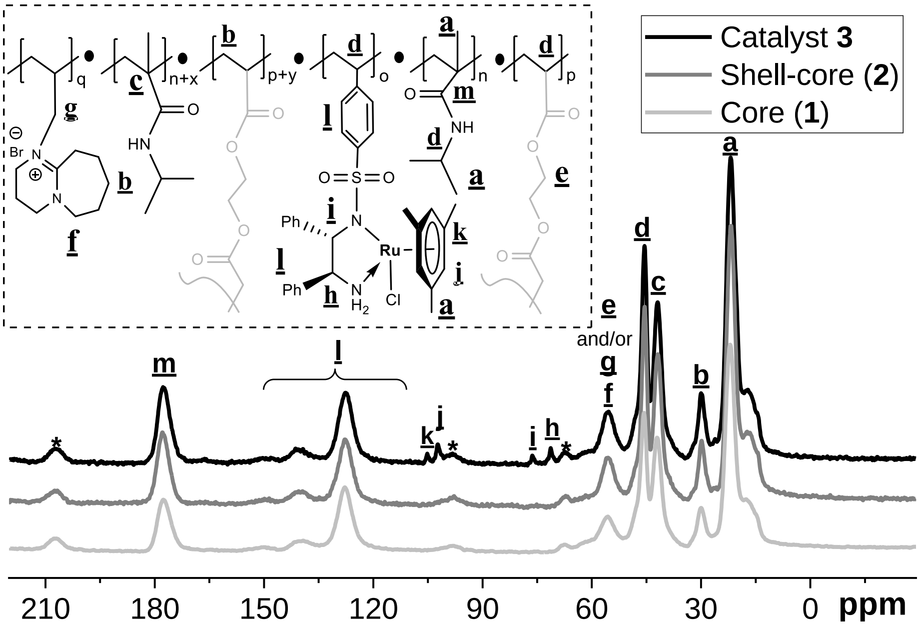





Core-shell (2)
H2O
—NCH2—
g
H3C—CH
CH3
c
CH2 or CH3
in skeleton
a, b
C≡C
CH2—
f
—(CH2)—
d
DMSO
NCH or OCH2
in skeleton
h, i
CH in aryl
k
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Catalyst 3
H2O
—NCH2—
g
DMSO
H3C—CH
CH3
c
CH2 or CH3
in skeleton
a, b
C≡C
CH2—
f
—(CH2)—
d
NCH or OCH2
in skeleton
h, i
CH in aryl
k
CH3
H
CH3
e
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

(b) Solid-state ^{13}C MAS NMR spectra of **1, 2,** and catalysts **3** and **3′.**



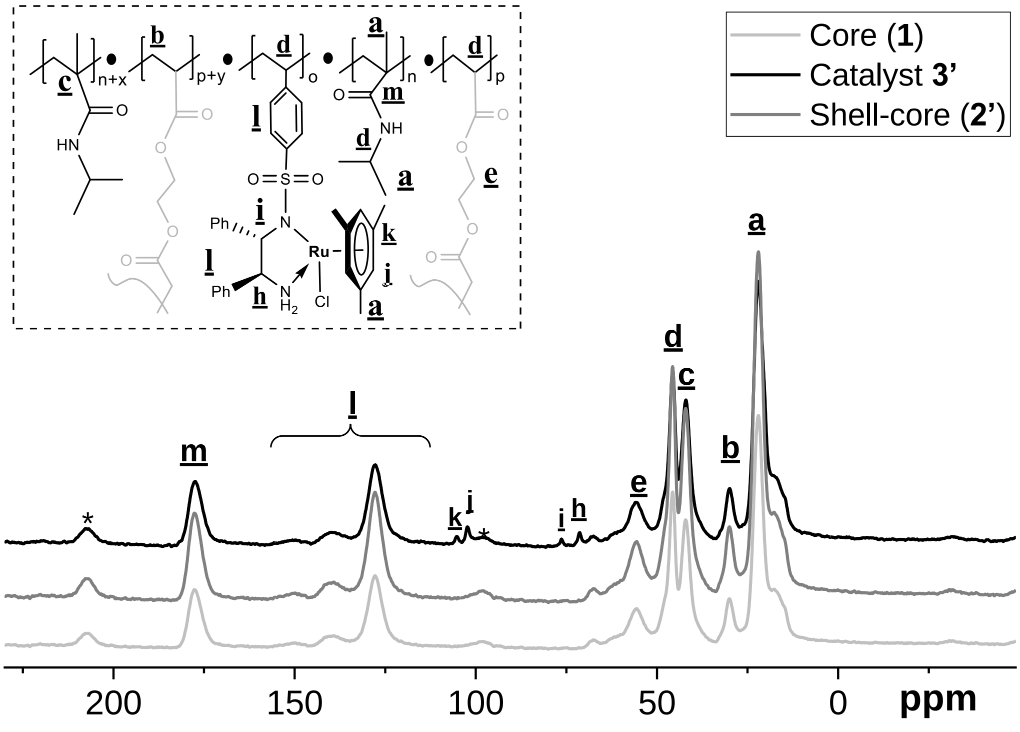
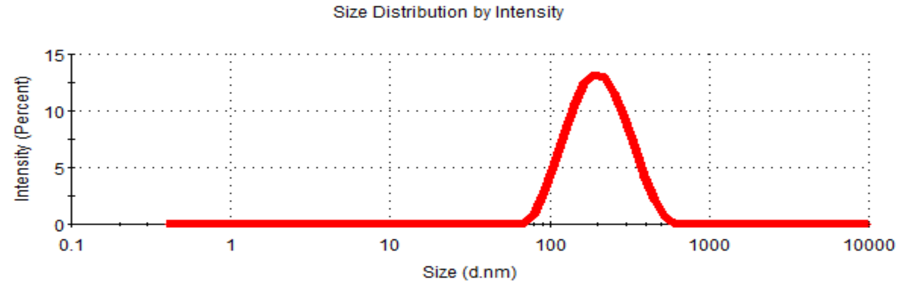


Figure S5. Average hydrodynamic diameters distribution measurement of **3**.

Run 1.

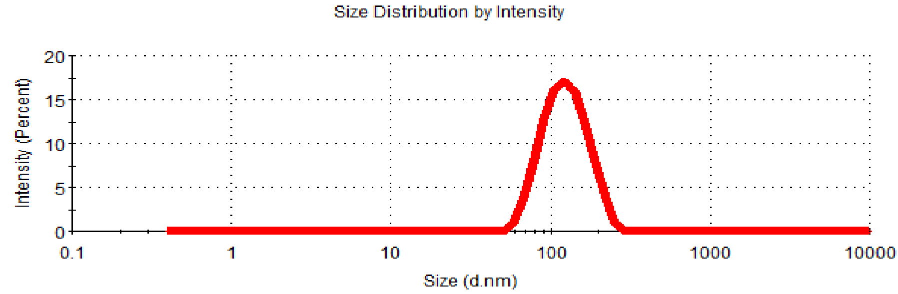
Results (25 °C for the first run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	181.4	Peak 1:	216.0	100.0	88.49
PdI:	0.159	Peak 2:	0.000	0.0	0.000
Intercept:	0.921	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



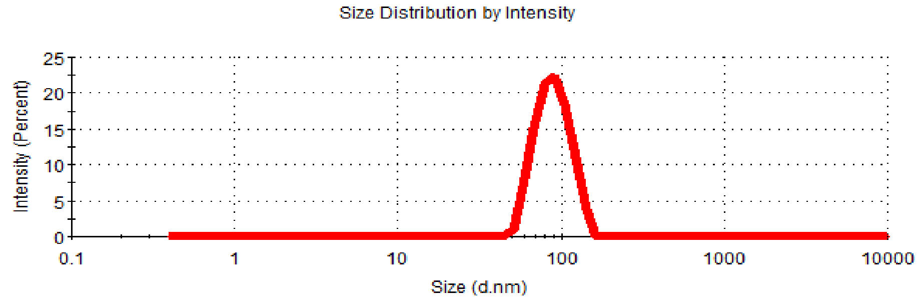
Results (45 °C for the first run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	116.7	Peak 1:	127.8	100.0	40.16
PdI:	0.074	Peak 2:	0.000	0.0	0.000
Intercept:	0.920	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Results (70 °C for the first run)

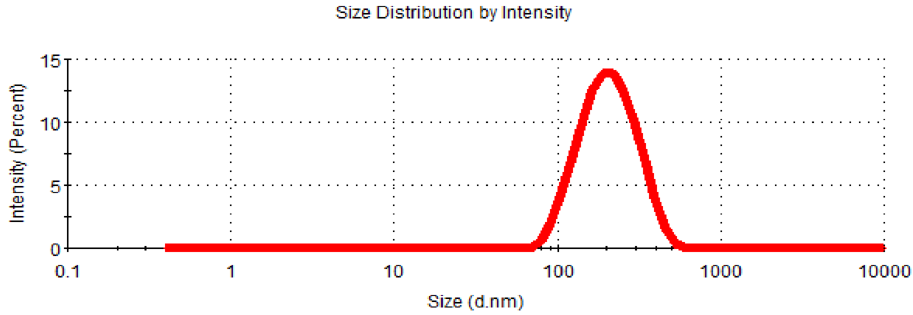
			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	86.24	Peak 1:	90.51	100.0	21.14
PdI:	0.025	Peak 2:	0.000	0.0	0.000
Intercept:	0.944	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Run 2.

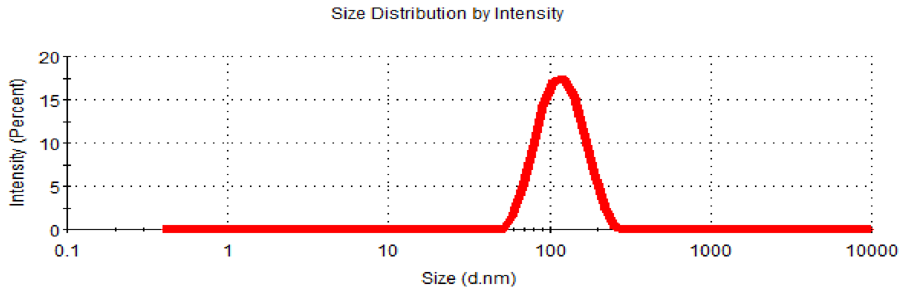
Results (25 °C for the second run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	182.6	Peak 1:	217.4	100.0	83.98
PdI:	0.168	Peak 2:	0.000	0.0	0.000
Intercept:	0.919	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



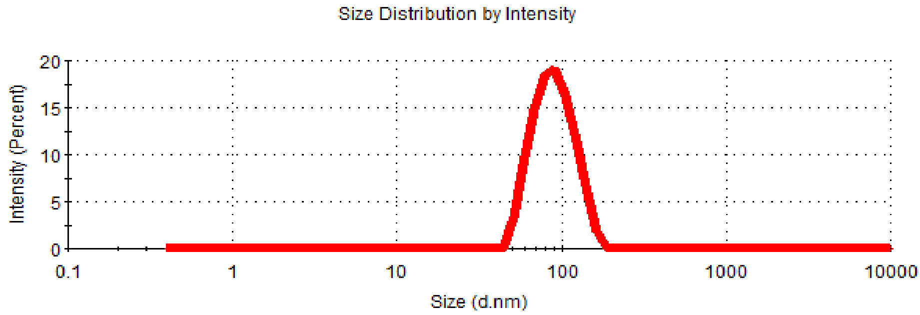
Results (45 °C for the second run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	111.9	Peak 1:	121.8	100.0	37.32
PdI:	0.062	Peak 2:	0.000	0.0	0.000
Intercept:	0.883	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Results (70 °C for the second run)

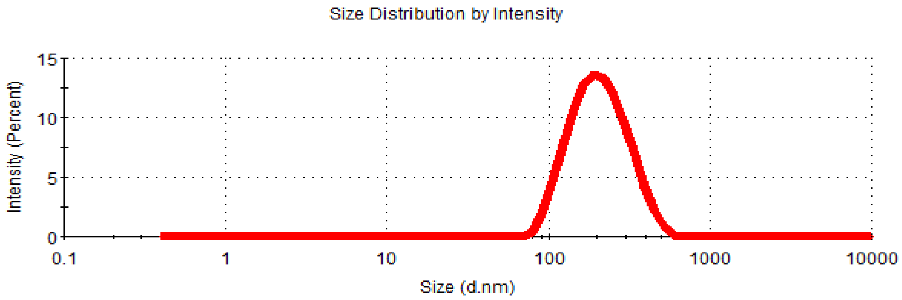
			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	84.65	Peak 1:	91.45	100.0	25.47
PdI:	0.076	Peak 2:	0.000	0.0	0.000
Intercept:	0.939	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Run 3.

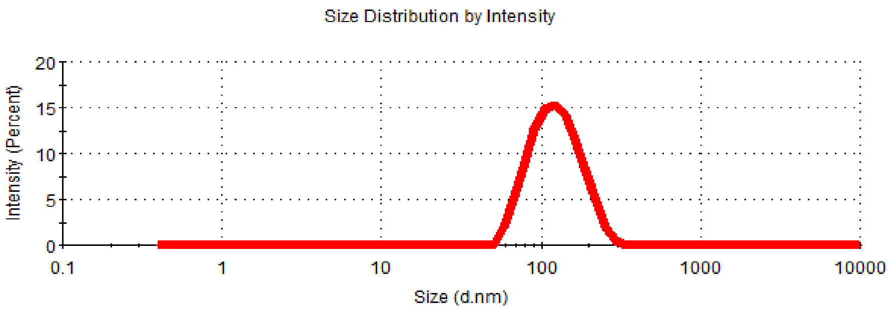
Results (25 °C for the third run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	183.7	Peak 1:	218.7	100.0	88.33
PdI:	0.163	Peak 2:	0.000	0.0	0.000
Intercept:	0.919	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



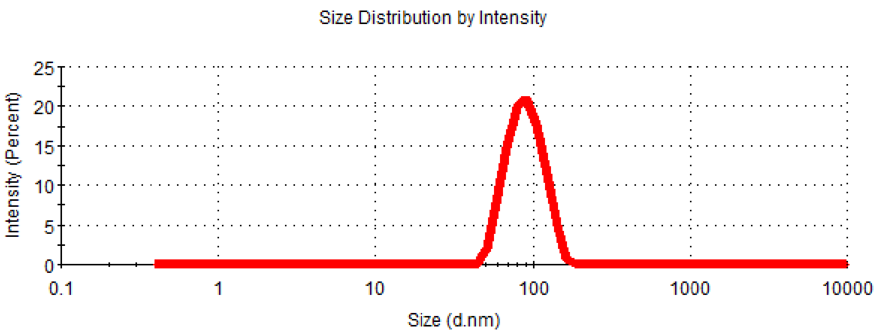
Results (45 °C for the third run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	114.6	Peak 1:	128.9	100.0	45.90
PdI:	0.104	Peak 2:	0.000	0.0	0.000
Intercept:	0.880	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Results (70 °C for the third run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	85.90	Peak 1:	91.11	100.0	23.19
PdI:	0.040	Peak 2:	0.000	0.0	0.000
Intercept:	0.943	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

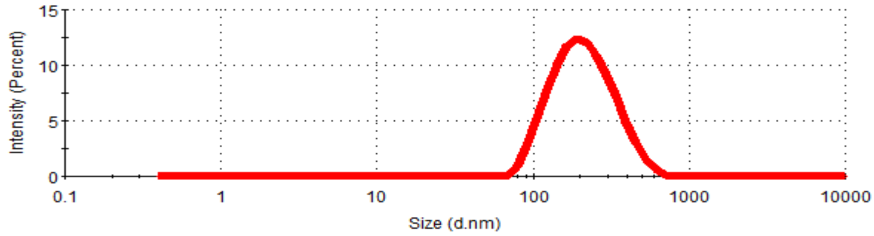


Run 4.

Results (25 °C for the fourth run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	183.1	Peak 1:	225.7	100.0	103.1
PdI:	0.197	Peak 2:	0.000	0.0	0.000
Intercept:	0.922	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

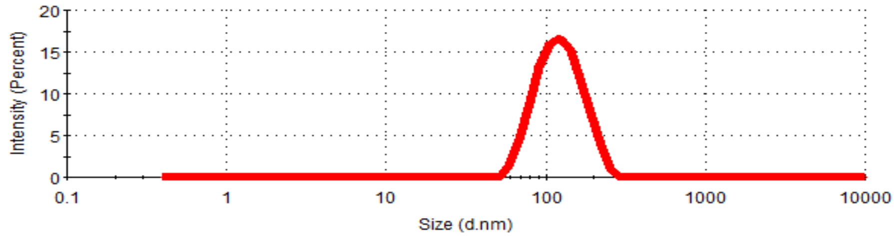
Size Distribution by Intensity



Results (45 °C for the fourth run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	114.7	Peak 1:	126.6	100.0	40.85
PdI:	0.087	Peak 2:	0.000	0.0	0.000
Intercept:	0.913	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

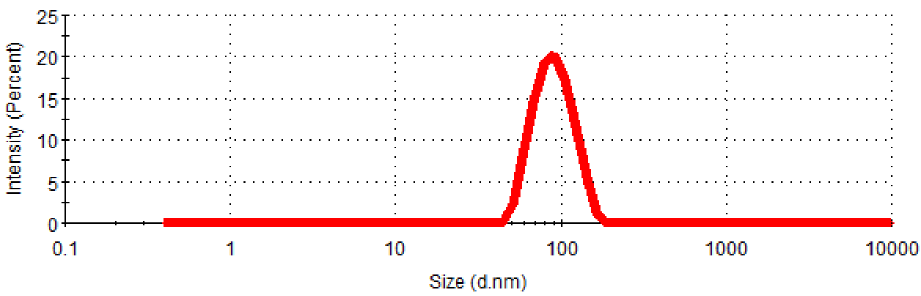
Size Distribution by Intensity



Results (70 °C for the fourth run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	85.69	Peak 1:	91.76	100.0	24.29
PdI:	0.064	Peak 2:	0.000	0.0	0.000
Intercept:	0.941	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

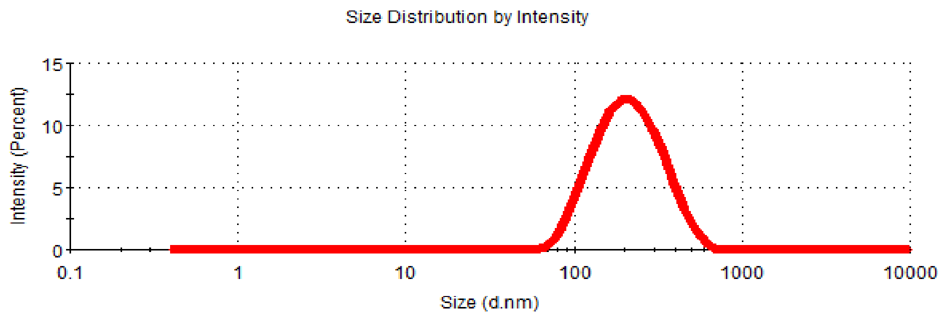
Size Distribution by Intensity



Run 5.

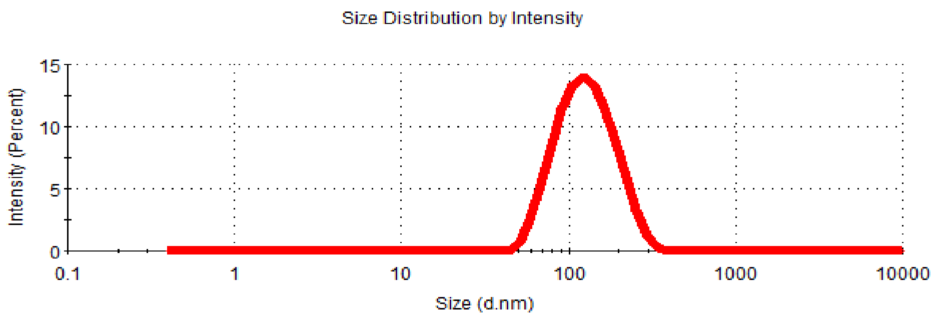
Results (25 °C for the fifth run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	185.0	Peak 1:	228.5	100.0	102.6
PdI:	0.185	Peak 2:	0.000	0.0	0.000
Intercept:	0.922	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



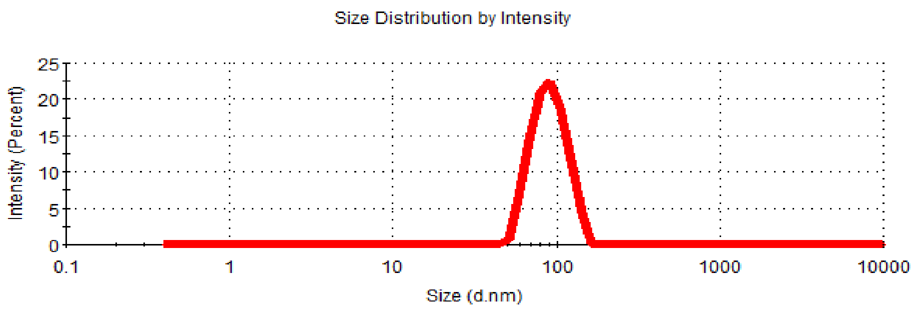
Results (45 °C for the fifth run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	116.0	Peak 1:	134.1	100.0	52.52
PdI:	0.128	Peak 2:	0.000	0.0	0.000
Intercept:	0.915	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Results (70 °C for the fifth run)

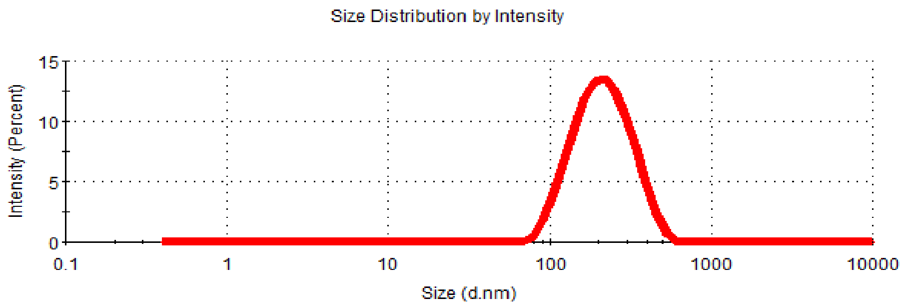
			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	87.13	Peak 1:	91.63	100.0	21.58
PdI:	0.028	Peak 2:	0.000	0.0	0.000
Intercept:	0.946	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Run 6.

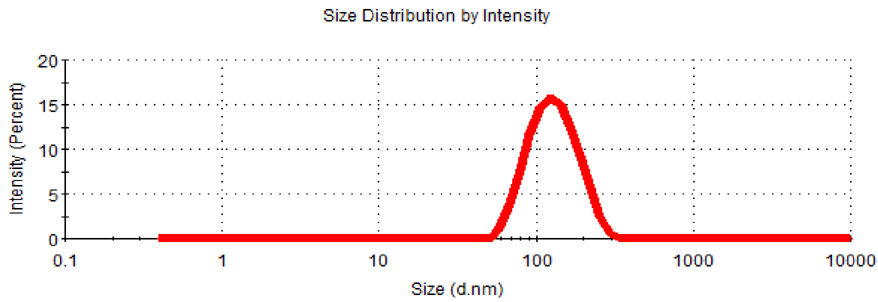
Results (25 °C for the sixth run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	185.1	Peak 1:	225.7	100.0	89.90
PdI:	0.182	Peak 2:	0.000	0.0	0.000
Intercept:	0.921	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Results (45 °C for the sixth run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	120.0	Peak 1:	134.3	100.0	46.48
PdI:	0.099	Peak 2:	0.000	0.0	0.000
Intercept:	0.906	Peak 3:	0.000	0.0	0.000
Result quality :	Good				



Results (70 °C for the sixth run)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	86.91	Peak 1:	93.14	100.0	25.35
PdI:	0.053	Peak 2:	0.000	0.0	0.000
Intercept:	0.941	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

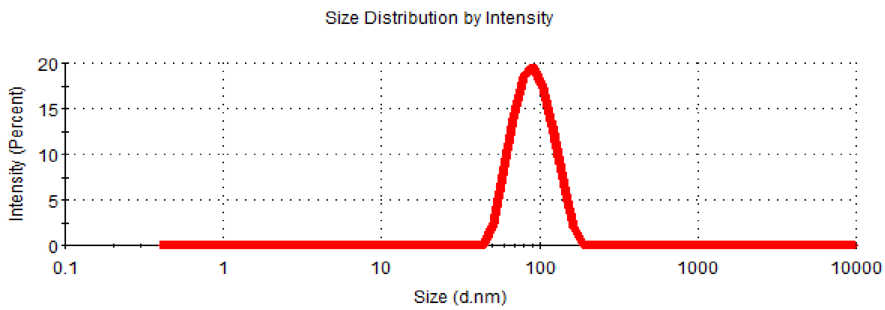
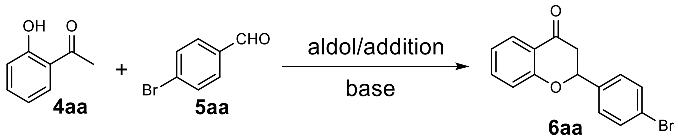


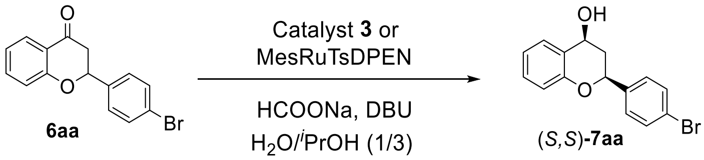
Table S1. Optimizing reaction conditions for the Aldol/addition reaction.[a]



Entry	Base	Solvent(s)	℃	h	Yield (%) of **6aa**
1	allylDBU	^{i}PrOH	70	12	98
2	allylDBU	^{i}PrOH-H_2O (4:1)	70	12	98
3	allylDBU	^{i}PrOH-H_2O (2:1)	70	12	91
4	allylDBU	^{i}PrOH/H_2O (3:1)	70	12	98
5	allylDBU	^{i}PrOH/H_2O (3:1)	65	12	92
6	allylDBU	^{i}PrOH/H_2O (3:1)	75	12	98
7	DBU	^{i}PrOH/H_2O (3:1)	70	12	76
8	DABCO	^{i}PrOH/H_2O (3:1)	70	12	45
9	NEt_3	^{i}PrOH/H_2O (3:1)	70	12	52

[a] Reaction conditions: base (0.12 mmol of base), **4aa** (0.10 mmol), **5aa** (0.12 mmol), HCO_2Na (1.0 mmol), and 4.0 mL of solvent. The ^{1}H-NMR yield.

Table S2. Optimizing reaction conditions for the DKR-ATH reaction.[a]

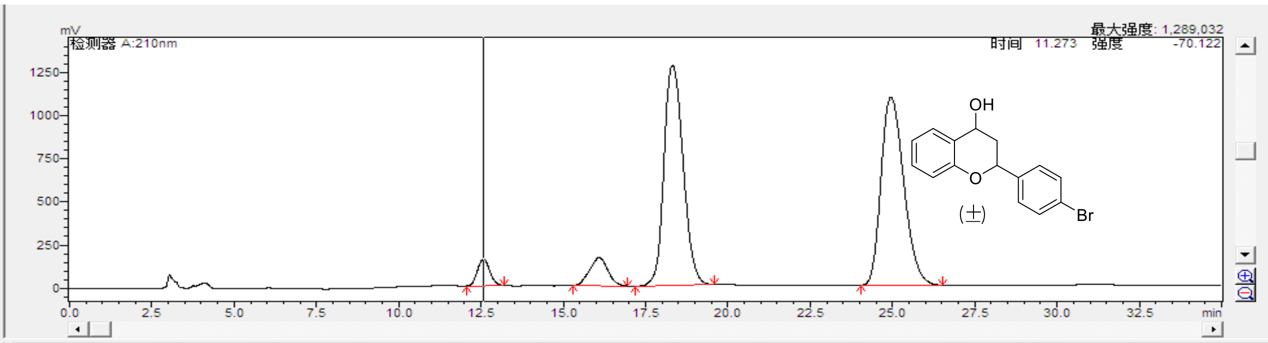


Entry	Catalyst	H-resource, Solvent, base	ºC	h	%Yield	*%ee/dr*
1	MesRuTsDPEN	HCO_2Na, ^{i}PrOH/H_2O (3:1), NEt_3	40	18	98	99/1:1
2	MesRuTsDPEN	HCO_2Na, ^{i}PrOH/H_2O (3:1), DBU	40	18	98	99/16:1
3	MesRuTsDPEN	HCO_2Na, ^{i}PrOH/H_2O (3:1), DABCO	40	18	98	99/4:1
4	MesRuTsDPEN	HCO_2Na, ^{i}PrOH/H_2O (3:1), allylDBU	40	18	96	99/16:1
5	**3**	HCO_2Na, ^{i}PrOH/H_2O (3:1), allylDBU	40	18	95	99/37:1
6	**3**	HCO_2Na, ^{i}PrOH/H_2O (3:1), allylDBU	35	18	90	99/37:1
7	**3**	HCO_2Na, ^{i}PrOH/H_2O (3:1), allylDBU	45	18	99	99/20:1

[a] Reaction conditions: catalyst (2.50 mol% of Ru-loading), **6aa** (0.10 mmol), base (0.12 mmol), HCO_2Na (1.0 mmol), and 4.0 mL of the mixed H_2O/^{i}PrOH co-solvents. The ^{1}H-NMR yield, the *%ee/dr* values were determined by chiral HPLC analysis.

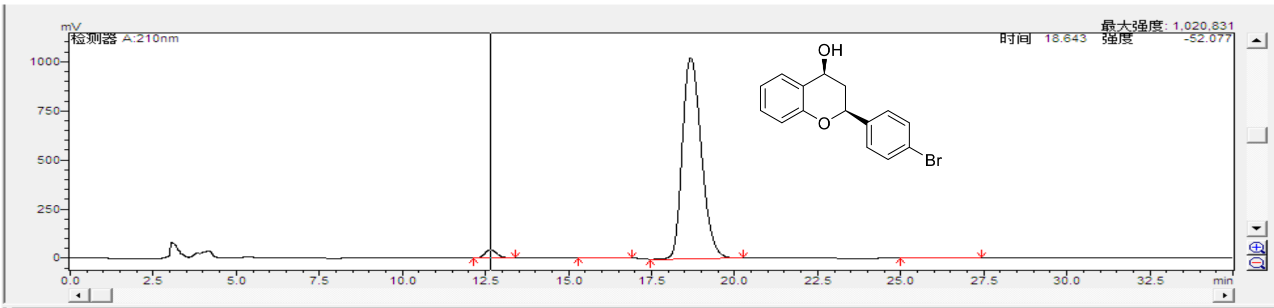
Figure S6. HPLC analyses of chiral products

(*S*,*S*)-7aa: (2S,4S)-2-(4-bromophenyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

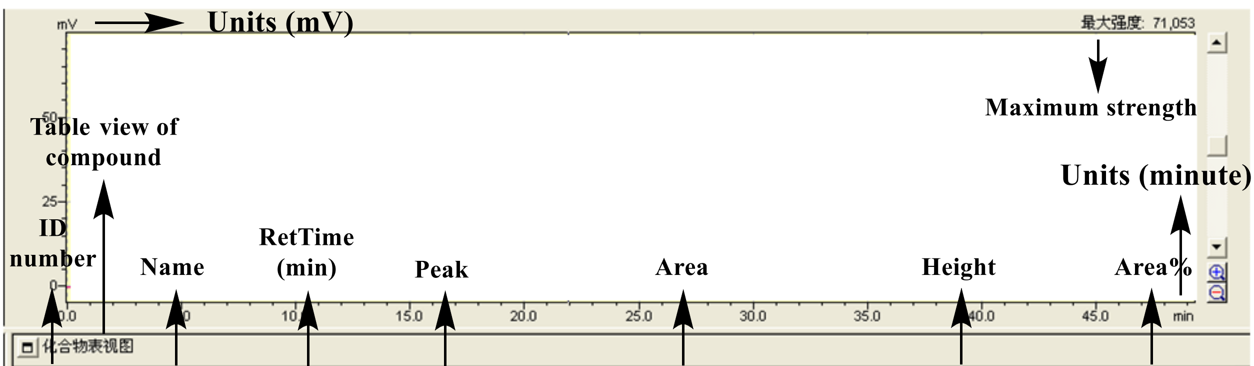
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.570	12.570	1	4042364	155575	3.5252
2	RT16.091	16.091	2	6305224	162875	5.4986
3	RT18.316	18.316	3	51778979	1272917	45.1550
4	RT24.949	24.949	4	52542892	1088882	45.8212



化合物表视图

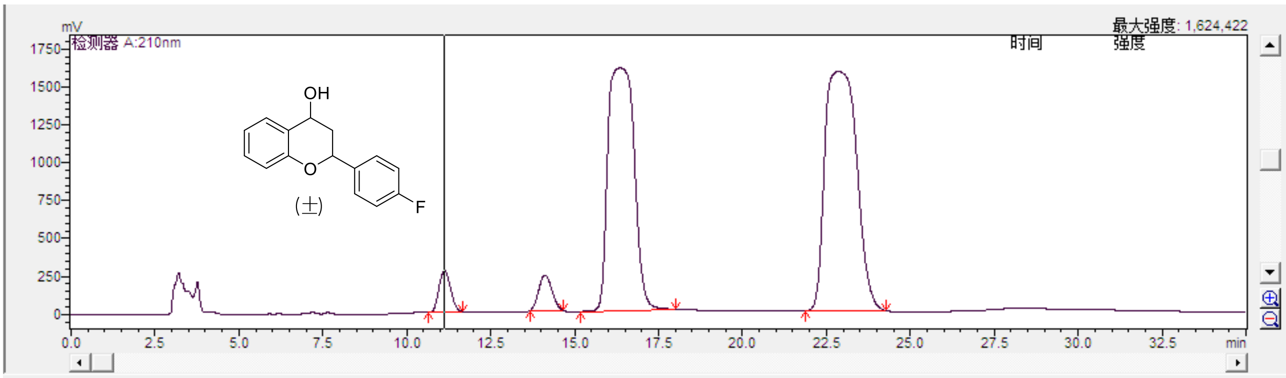
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.649	12.649	1	1074374	41506	2.5669
2	RT16.050	16.050	2	15076	313	0.0360
3	RT18.676	18.676	3	40701156	1023798	97.2442
4	RT25.917	25.917	4	63972	1275	0.1528

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>



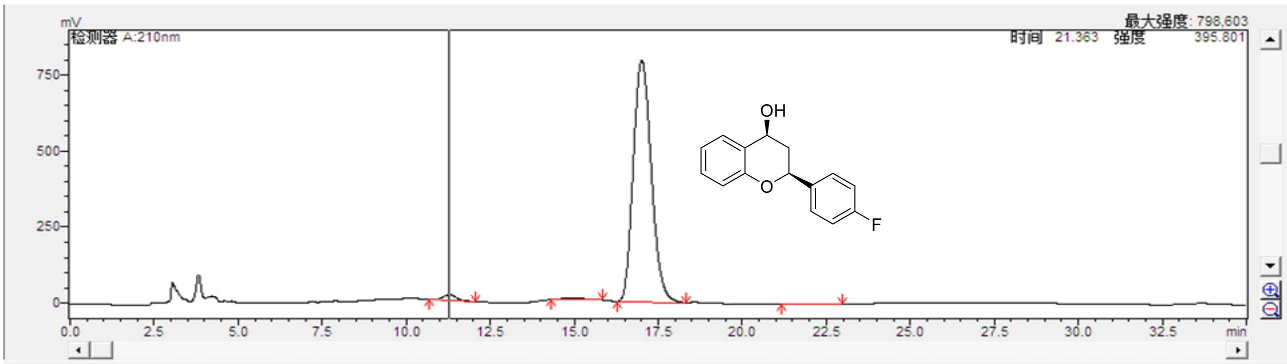
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7ab: (2S,4S)-2-(4-fluorophenyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

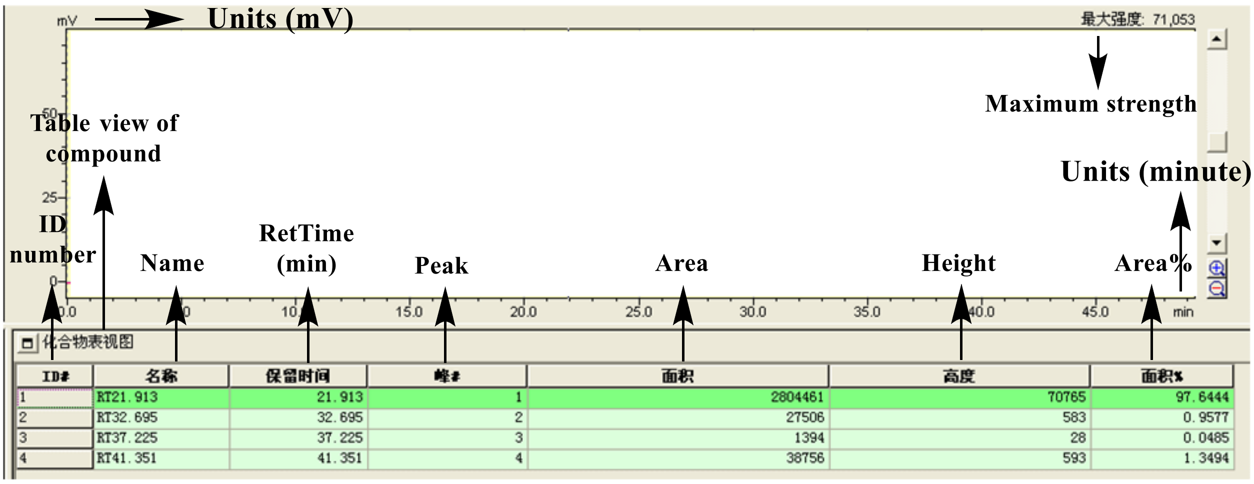
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.121	11.121	1	6604303	273980	3.2305
2	RT14.115	14.115	2	6390378	233758	3.1259
3	RT16.340	16.340	3	87270823	1600001	42.6886
4	RT22.848	22.848	4	104170220	1578330	50.9550



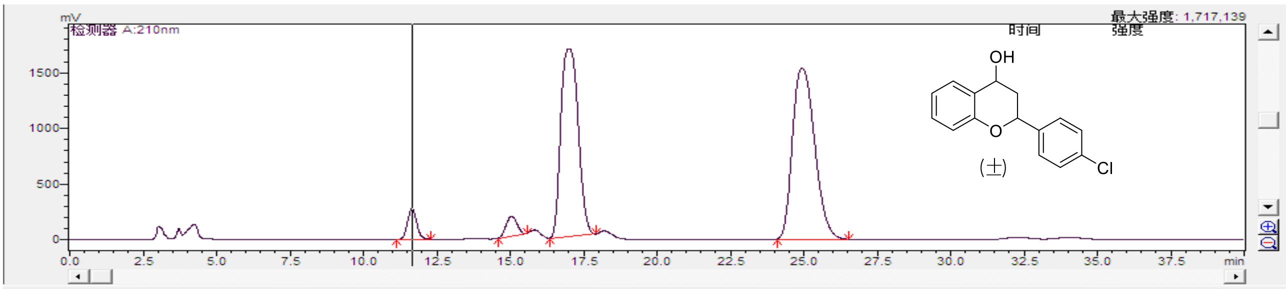
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.279	11.279	1	481024	18257	1.5764
2	RT14.930	14.930	2	259846	4276	0.8515
3	RT17.006	17.006	3	29764469	795086	97.5414
4	RT22.954	22.954	4	9361	7	0.0307

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>

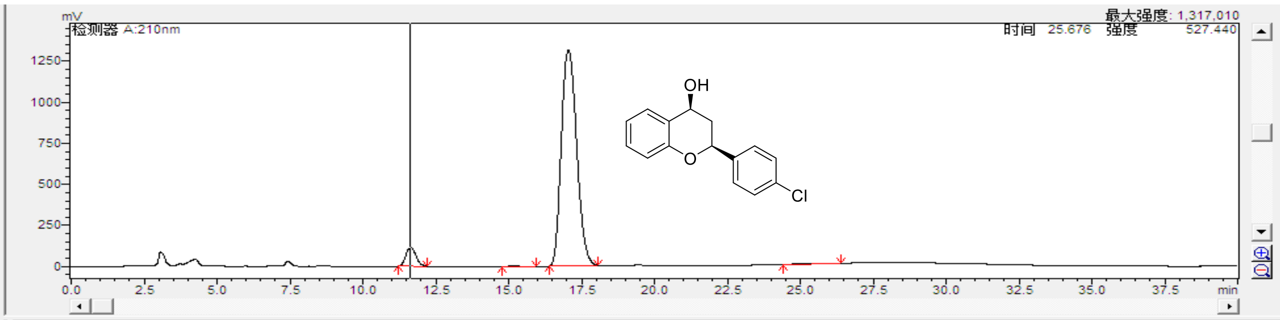


(*S*,*S*)-7ac: (2S,4S)-2-(4-chlorophenyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

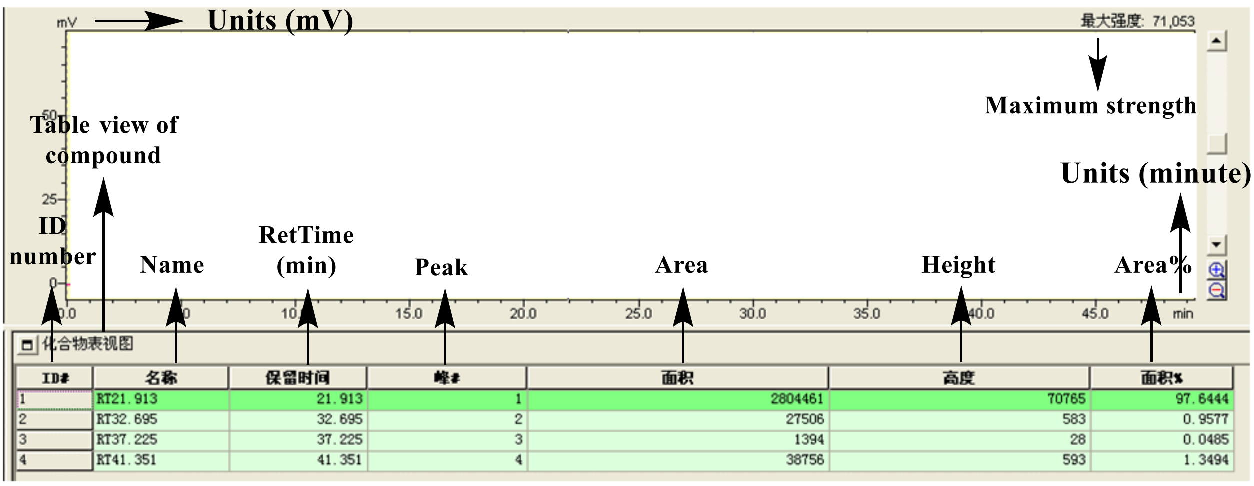
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.652	11.652	1	5947376	275238	3.7063
2	RT15.046	15.046	2	4542426	176831	2.8308
3	RT16.998	16.998	3	69135114	1686690	43.0840
4	RT24.941	24.941	4	80841098	1536827	50.3790



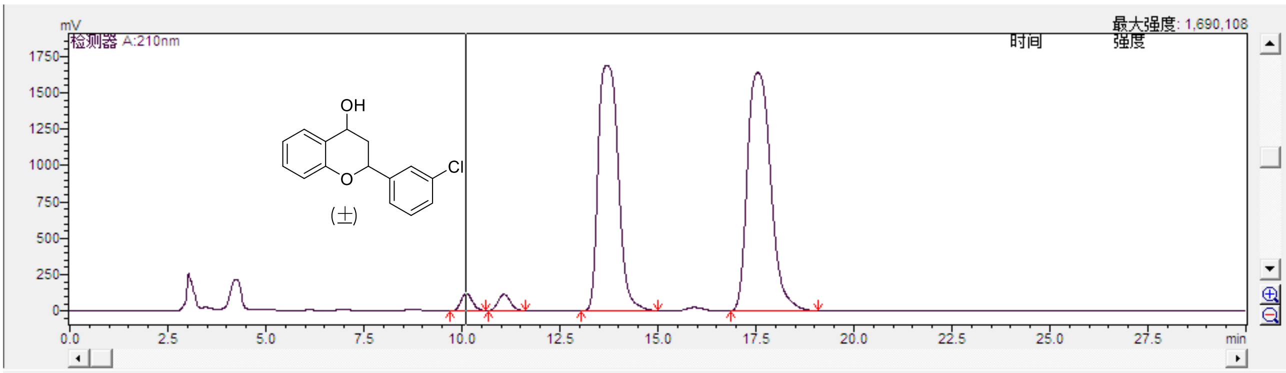
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.639	11.639	1	2768450	115882	5.4171
2	RT15.183	15.183	2	35519	1249	0.0695
3	RT17.047	17.047	3	48099351	1313317	94.1178
4	RT26.400	26.400	4	202175	1	0.3956

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>

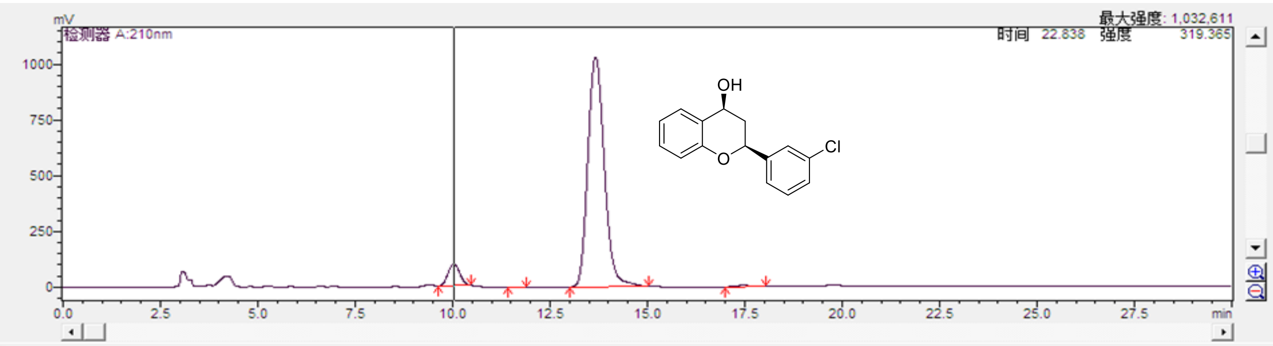


(*S,S*)-7ad: (2S,4S)-2-(3-chlorophenyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

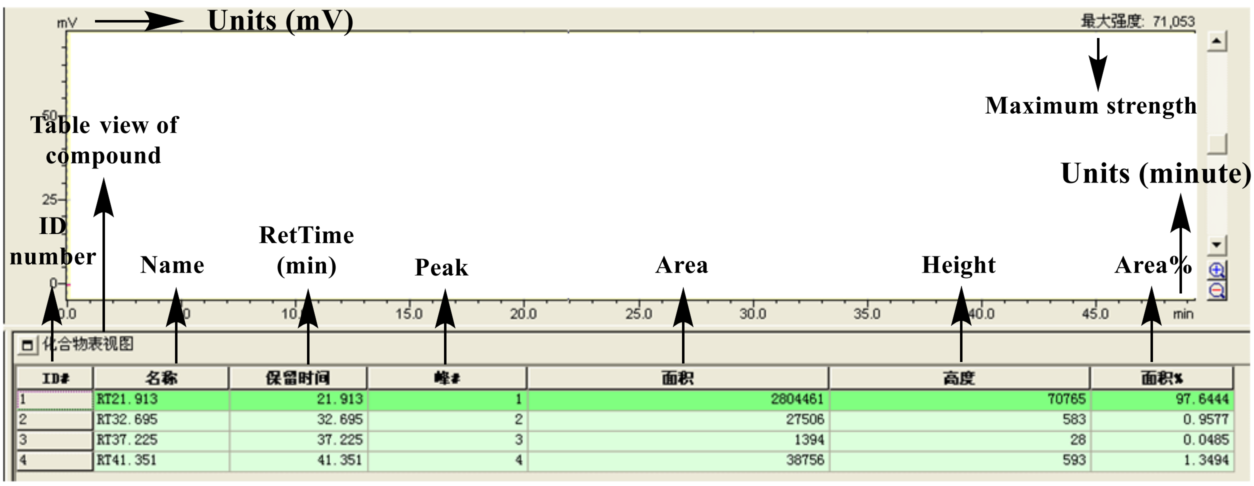
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.111	10.111	1	2381586	118887	1.7942
2	RT11.068	11.068	2	2427687	111471	1.8289
3	RT13.703	13.703	3	60155020	1688136	45.3183
4	RT17.541	17.541	4	67774720	1637115	51.0586



化合物表视图

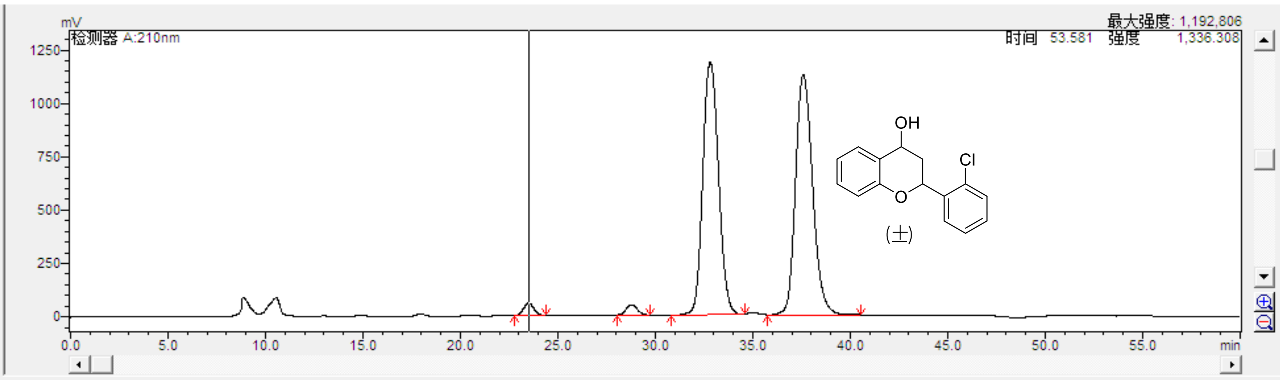
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.027	10.027	1	2086985	98521	6.3917
2	RT11.564	11.564	2	11337	668	0.0347
3	RT13.665	13.665	3	30364894	1030493	92.9973
4	RT17.457	17.457	4	188155	6033	0.5763

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>

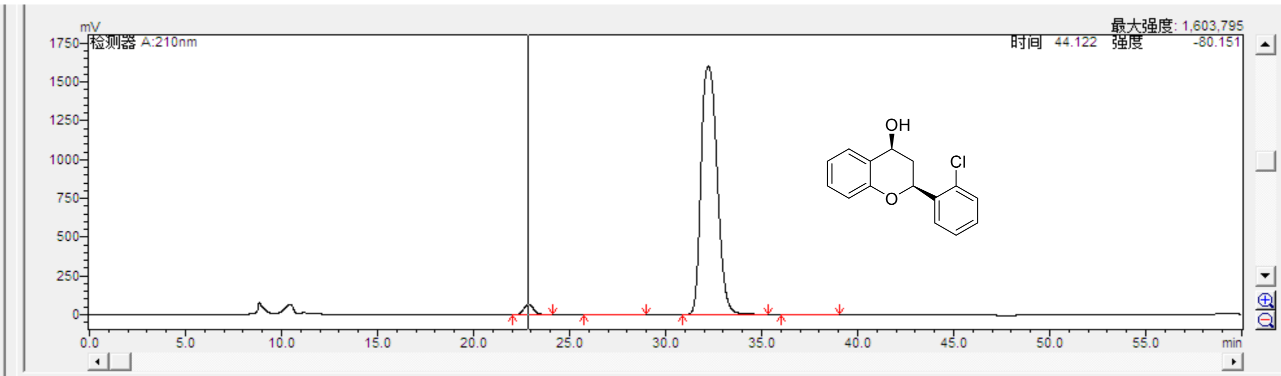


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7ae: (2S,4S)-2-(2-chlorophenyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).

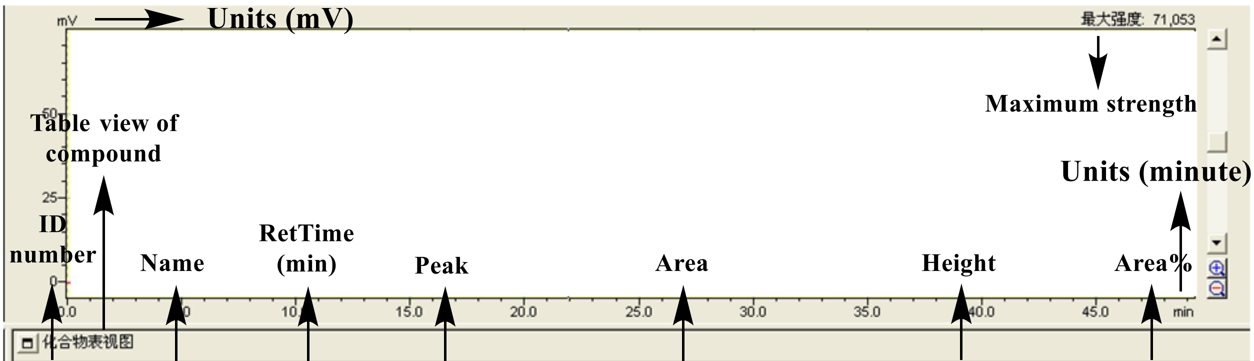


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT23.497	23.497	1	2019522	56348	1.4492
2	RT28.771	28.771	2	1964784	48934	1.4099
3	RT32.811	32.811	3	66518825	1182702	47.7332
4	RT37.584	37.584	4	68852420	1125002	49.4077



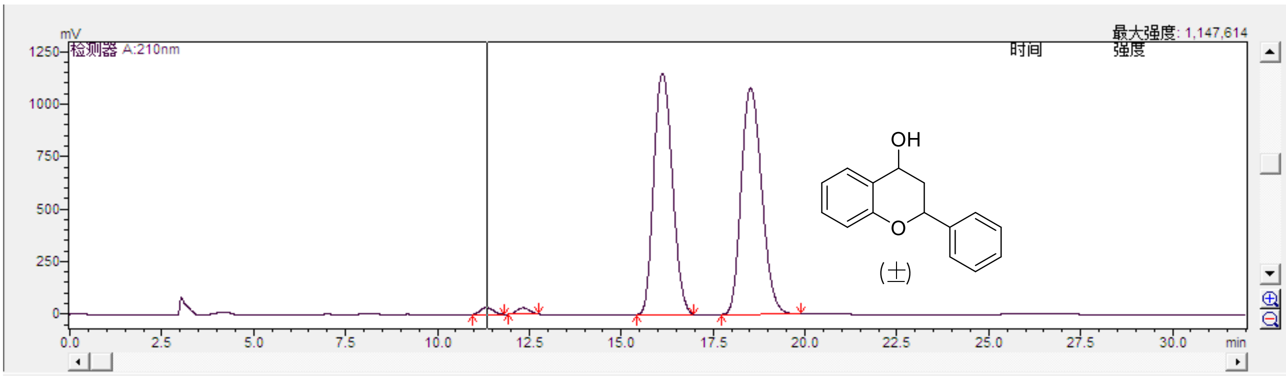
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.861	22.861	1	2441840	66987	2.5334
2	RT26.101	26.101	2	90386	1252	0.0938
3	RT32.214	32.214	3	93854473	1604456	97.3721
4	RT37.119	37.119	4	710	1926	0.0007

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>



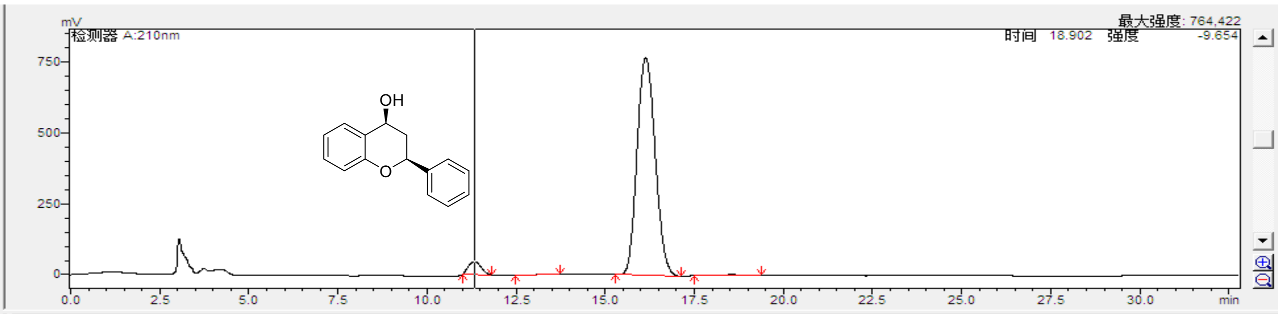
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7af: (2S,4S)-2-phenylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

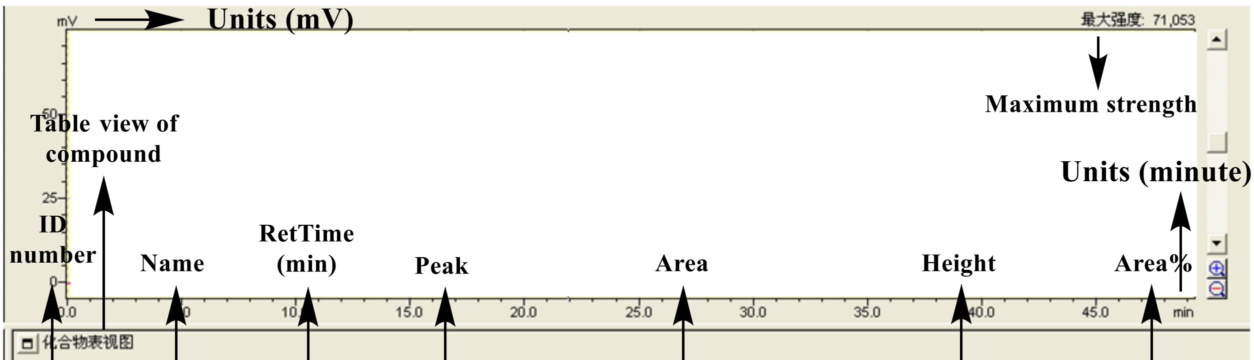
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.339	11.339	1	767011	32255	0.9131
2	RT12.328	12.328	2	733267	30129	0.8729
3	RT16.121	16.121	3	40554873	1150421	48.2802
4	RT18.521	18.521	4	41943825	1077800	49.9337



化合物表视图

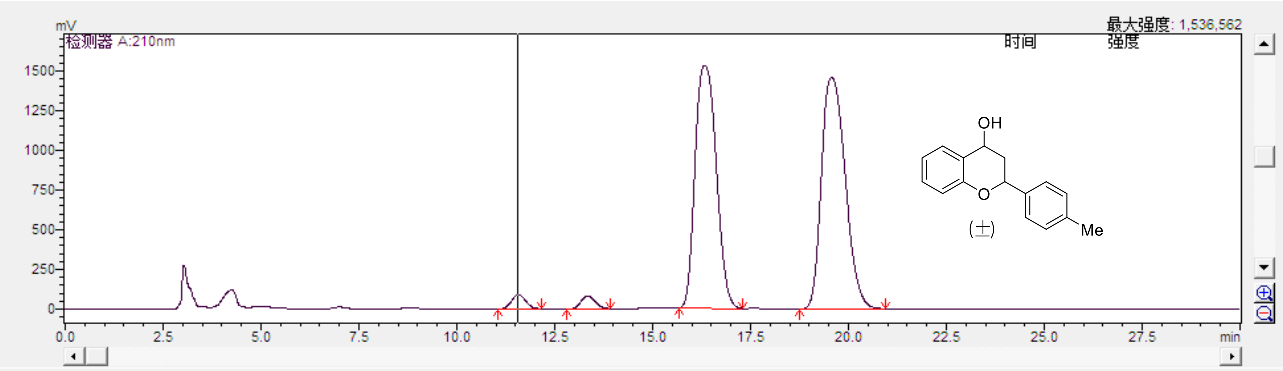
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.324	11.324	1	1142748	46386	4.0139
2	RT13.708	13.708	2	16614	15	0.0584
3	RT16.133	16.133	3	27166087	766833	95.4198
4	RT18.554	18.554	4	144619	3730	0.5080

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



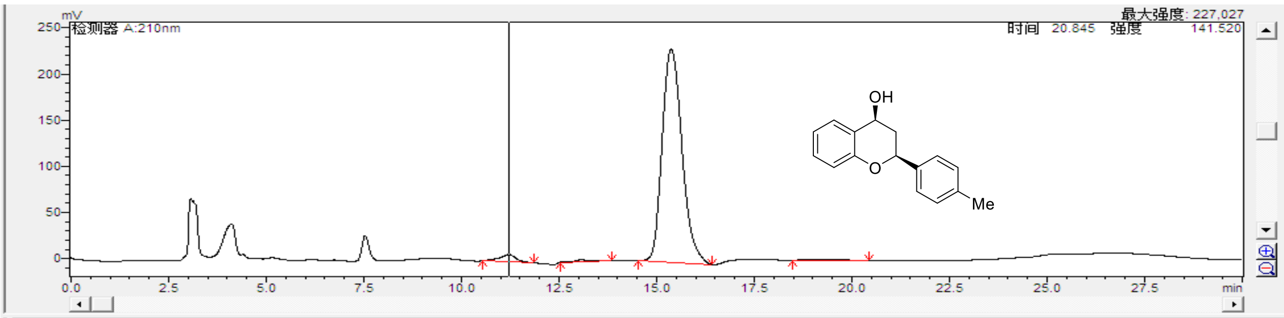
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7ag: (2S,4S)-2-(p-tolyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

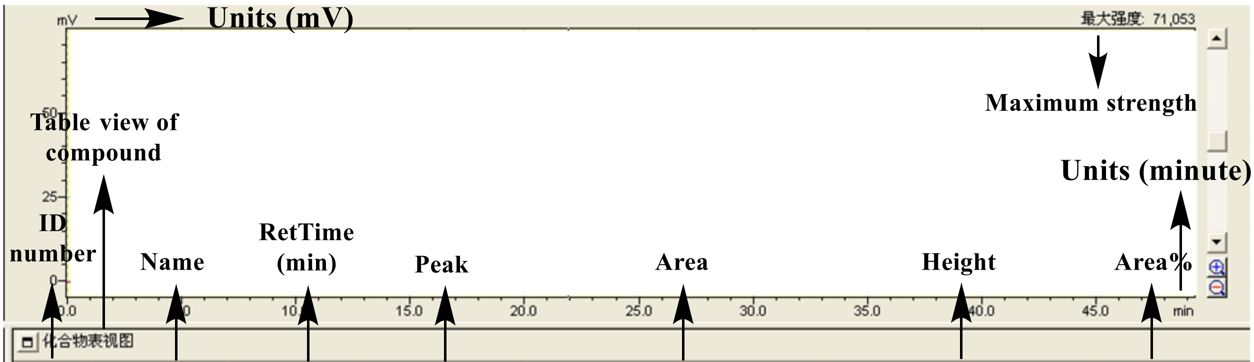
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.569	11.569	1	2193528	90138	1.7727
2	RT13.339	13.339	2	2051376	81070	1.6578
3	RT16.329	16.329	3	57683080	1530077	46.6158
4	RT19.567	19.567	4	61813513	1458259	49.9537



化合物表视图

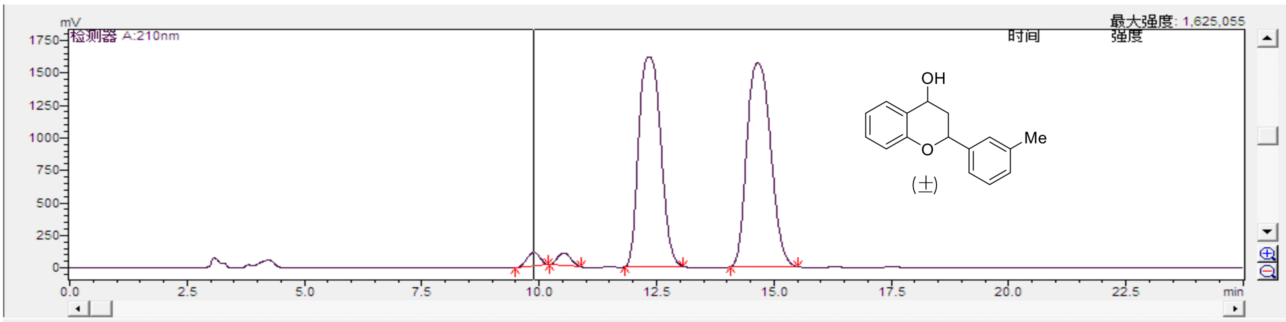
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.202	11.202	1	242794	7986	2.8497
2	RT13.073	13.073	2	53520	2026	0.6282
3	RT15.369	15.369	3	8159541	230935	95.7694
4	RT19.417	19.417	4	64136	1155	0.7528

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>



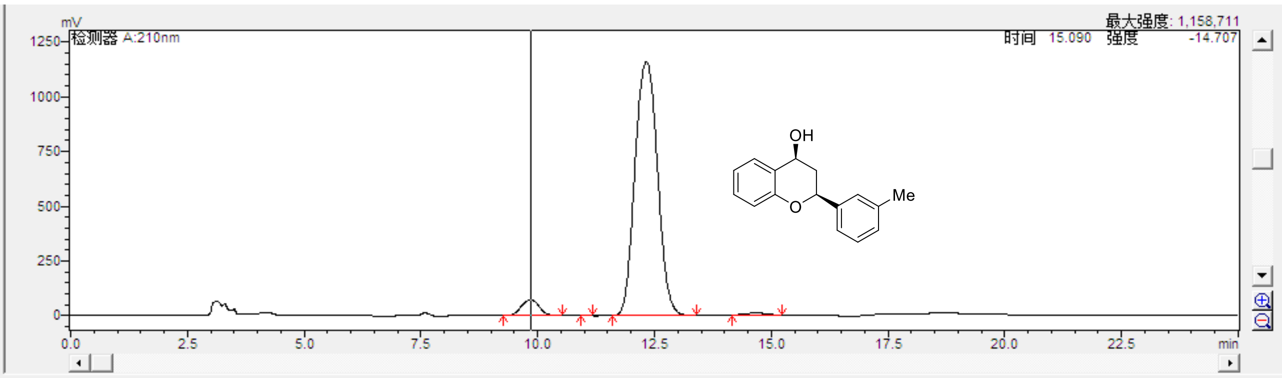
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7ah: (2S,4S)-2-(m-tolyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

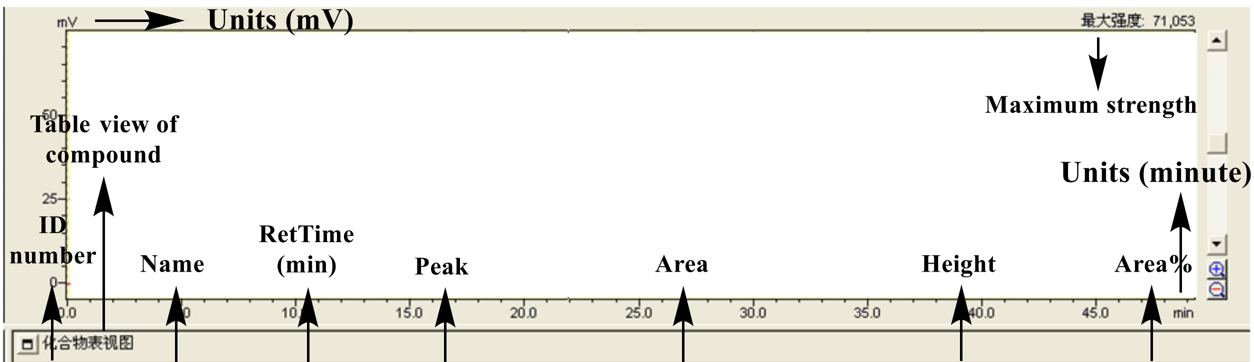
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT9.883	9.883	1	2052243	105047	1.8344
2	RT10.522	10.522	2	1935265	97631	1.7299
3	RT12.339	12.339	3	52484736	1613398	46.9147
4	RT14.657	14.657	4	55400508	1565426	49.5210



化合物表视图

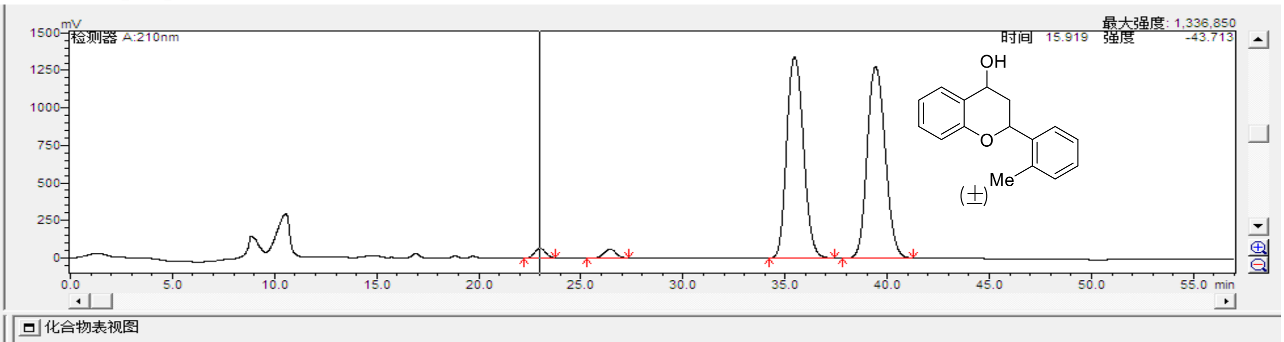
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT9.845	9.845	1	1949852	72631	4.7346
2	RT10.925	10.925	2	81	-2	0.0002
3	RT12.324	12.324	3	38922258	1157822	94.5112
4	RT14.668	14.668	4	310522	9569	0.7540

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

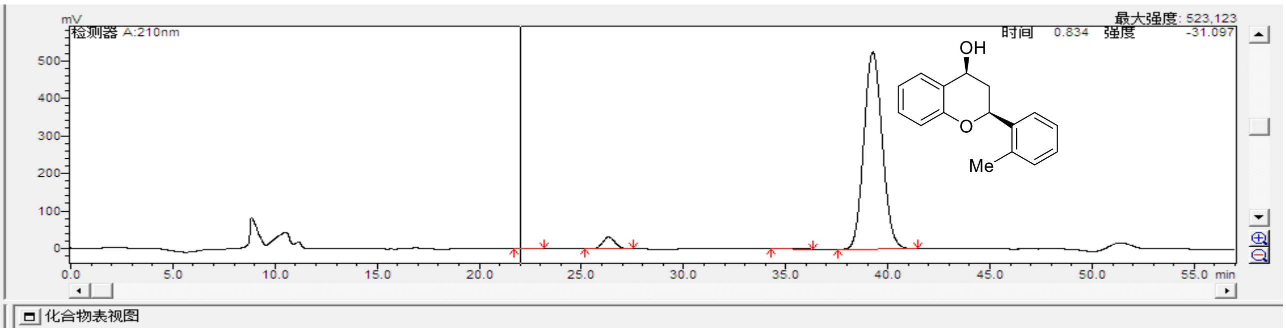


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7ai: (2S,4S)-2-(o-tolyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).

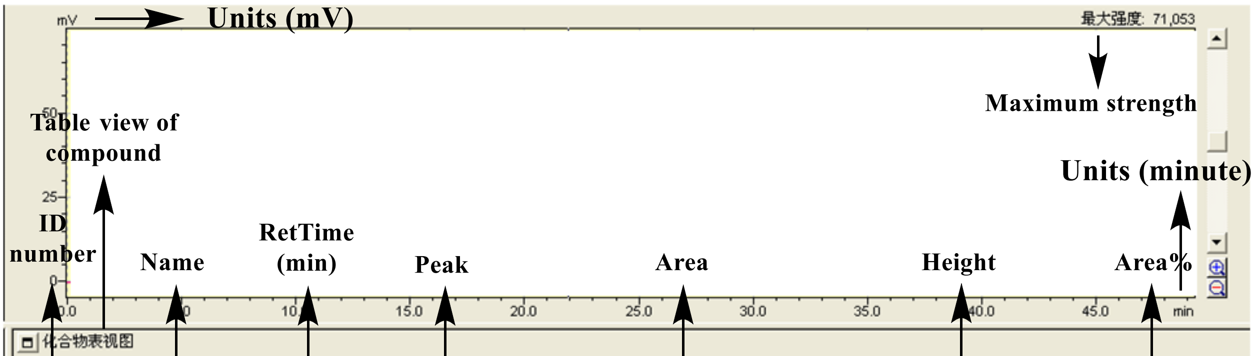


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.995	22.995	1	2415158	65370	1.5077
2	RT26.415	26.415	2	2549873	60486	1.5918
3	RT35.461	35.461	3	76766339	1337730	47.9220
4	RT39.424	39.424	4	78458850	1275477	48.9786



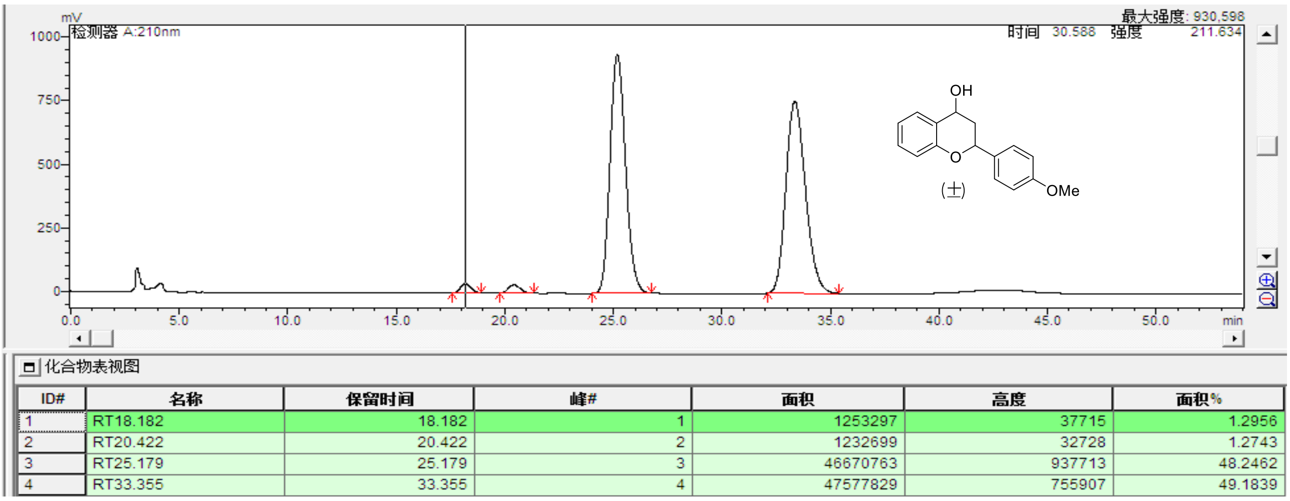
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.030	22.030	1	5736	470	0.0167
2	RT26.341	26.341	2	1311369	31436	3.8203
3	RT35.304	35.304	3	84926	1488	0.2474
4	RT39.260	39.260	4	32924578	524653	95.9156

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>

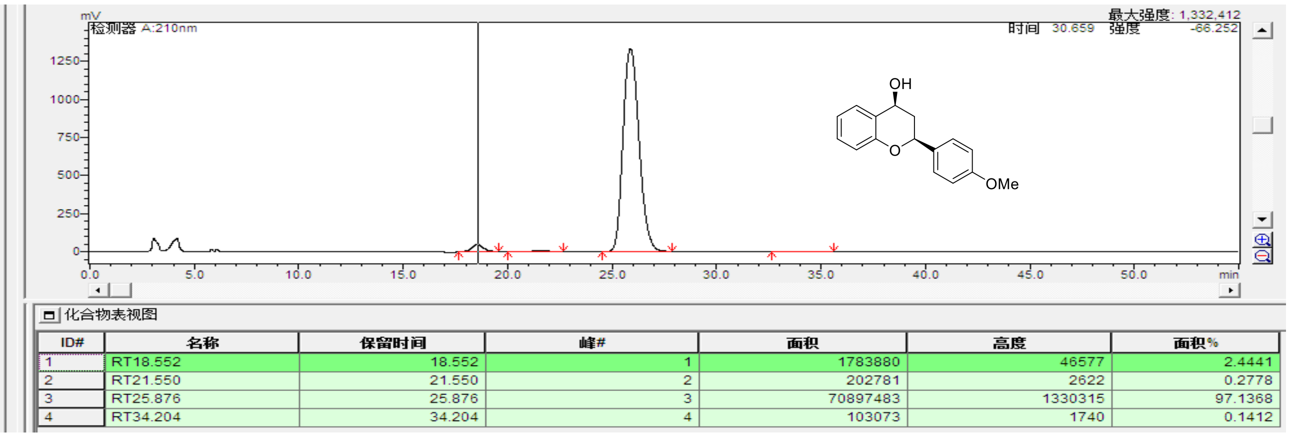


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,S*)-7aj: (2S,4S)-2-(4-methoxyphenyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).

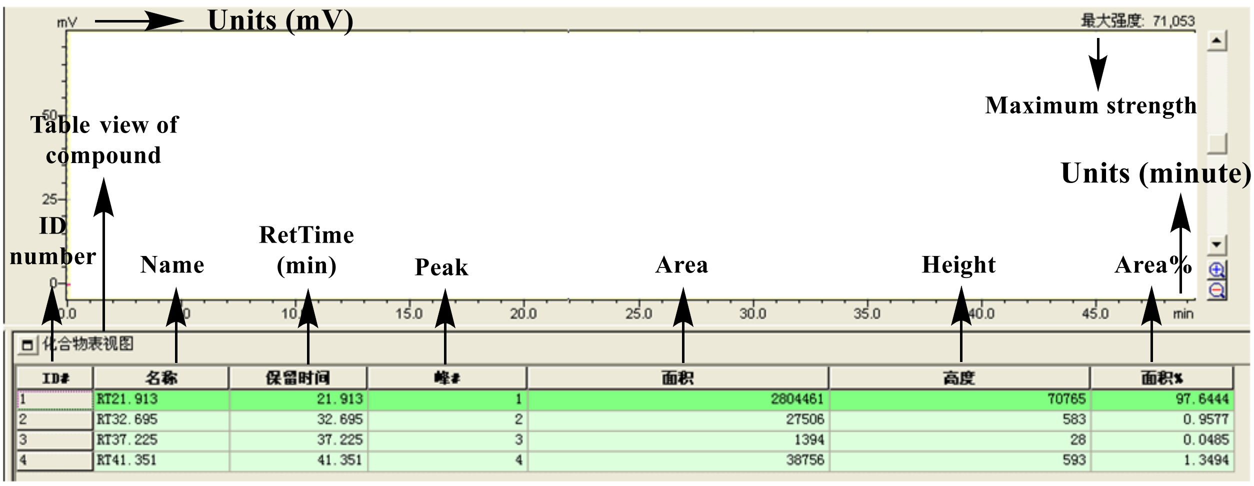


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.182	18.182	1	1253297	37715	1.2956
2	RT20.422	20.422	2	1232699	32728	1.2743
3	RT25.179	25.179	3	46670763	937713	48.2462
4	RT33.355	33.355	4	47577829	755907	49.1839



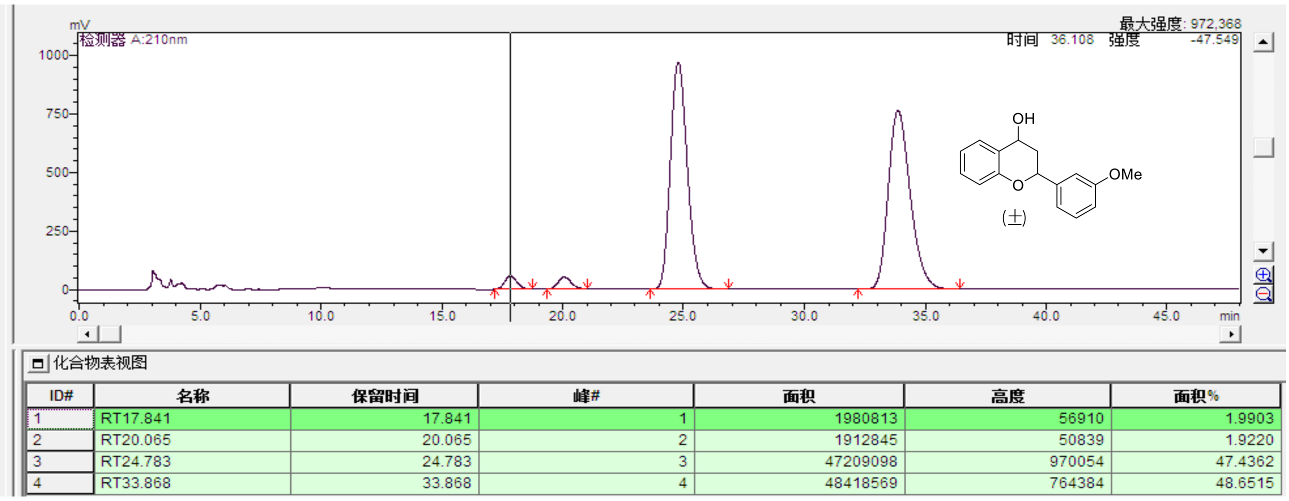
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.552	18.552	1	1783880	46577	2.4441
2	RT21.550	21.550	2	202781	2622	0.2778
3	RT25.876	25.876	3	70897483	1330315	97.1368
4	RT34.204	34.204	4	103073	1740	0.1412

__**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**__

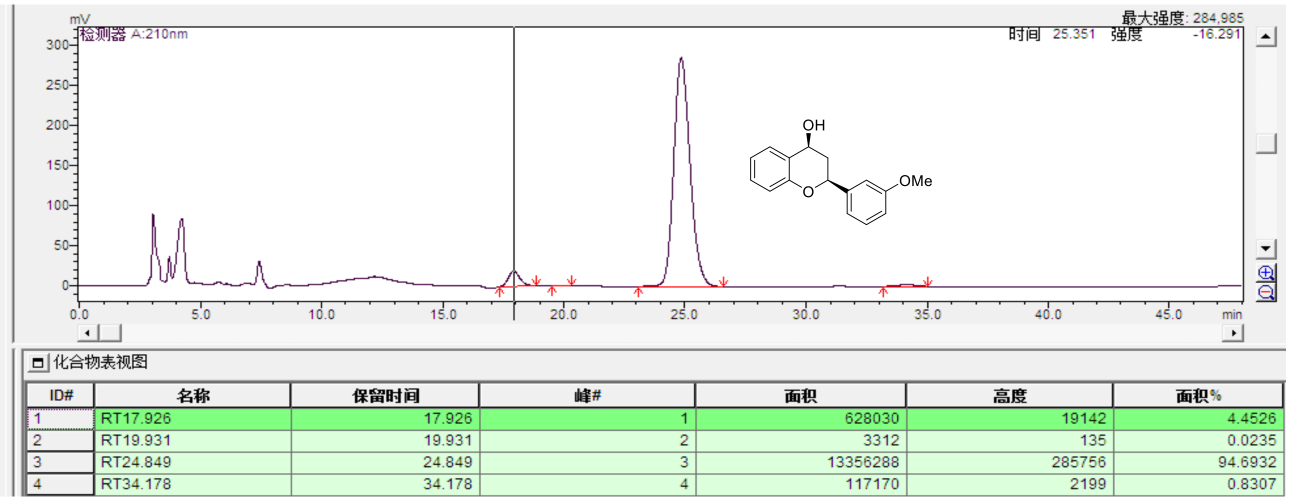


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7ak: (2S,4S)-2-(3-methoxyphenyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).

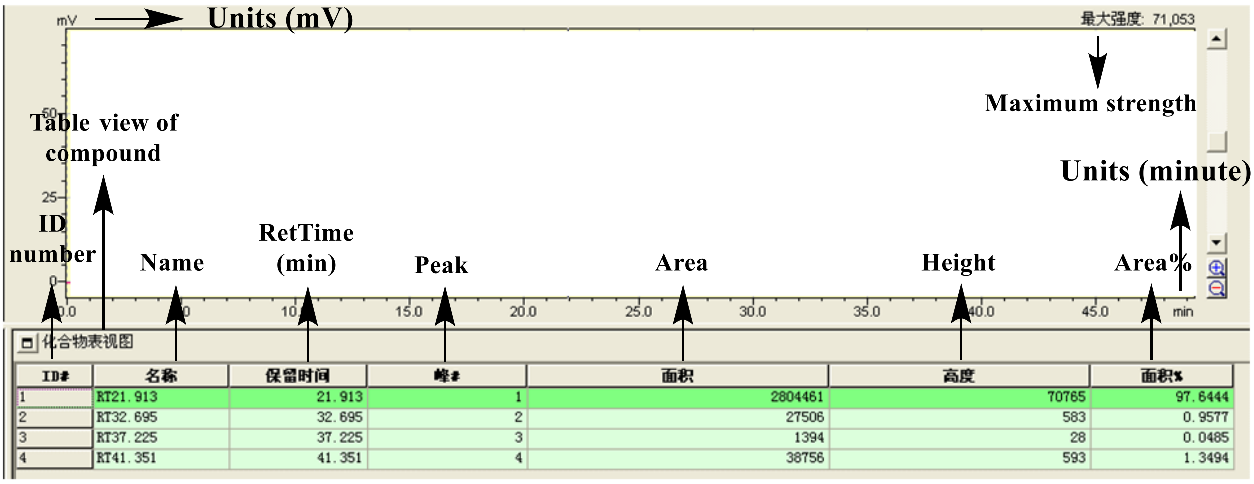


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT17.841	17.841	1	1980813	56910	1.9903
2	RT20.065	20.065	2	1912845	50839	1.9220
3	RT24.783	24.783	3	47209098	970054	47.4362
4	RT33.868	33.868	4	48418569	764384	48.6515



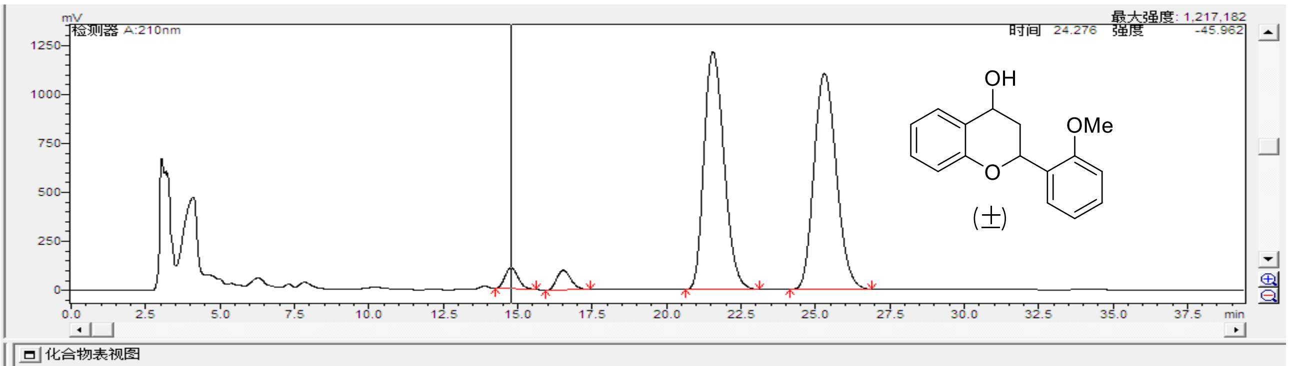
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT17.926	17.926	1	628030	19142	4.4526
2	RT19.931	19.931	2	3312	135	0.0235
3	RT24.849	24.849	3	13356288	285756	94.6932
4	RT34.178	34.178	4	117170	2199	0.8307

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

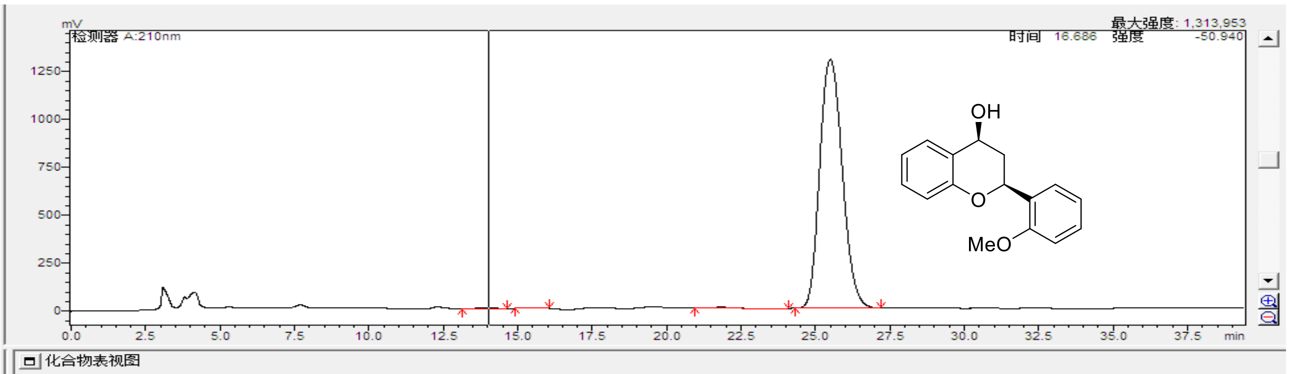


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,S*)-7al: (2S,4S)-2-(2-methoxyphenyl)chroman-4-ol**:** (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).

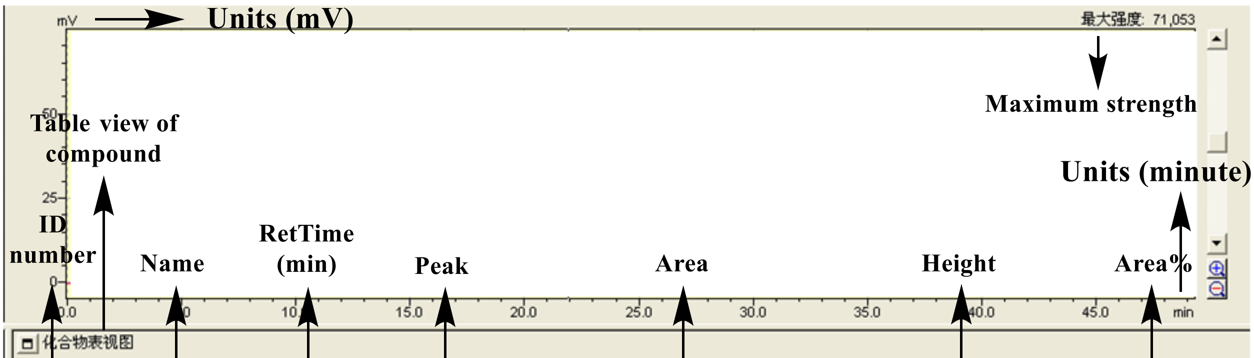


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT14.775	14.775	1	3335524	108601	2.7488
2	RT16.527	16.527	2	3394267	101565	2.7972
3	RT21.555	21.555	3	56853524	1212769	46.8530
4	RT25.300	25.300	4	57761267	1101541	47.6010



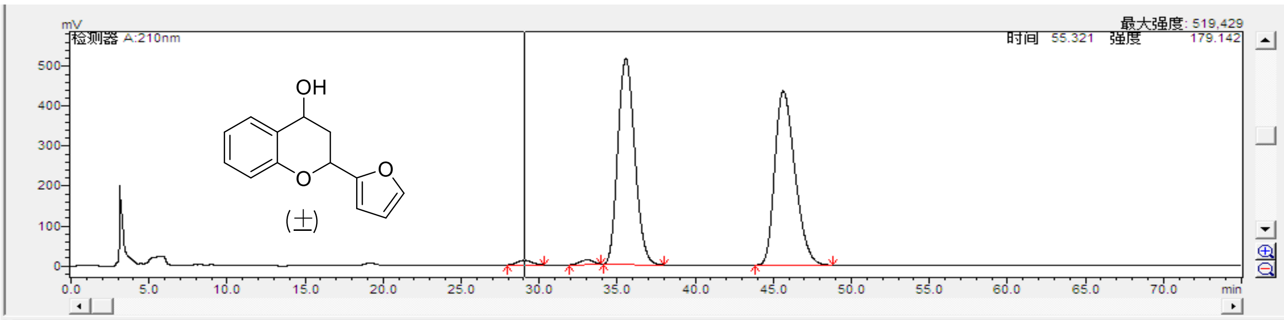
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT14.011	14.011	1	29974	669	0.0435
2	RT15.857	15.857	2	10548	395	0.0153
3	RT21.837	21.837	3	129780	5132	0.1884
4	RT25.496	25.496	4	68705509	1297830	99.7527

Translation of all characters (Chinese) in the above two frameworks to English is as follows:



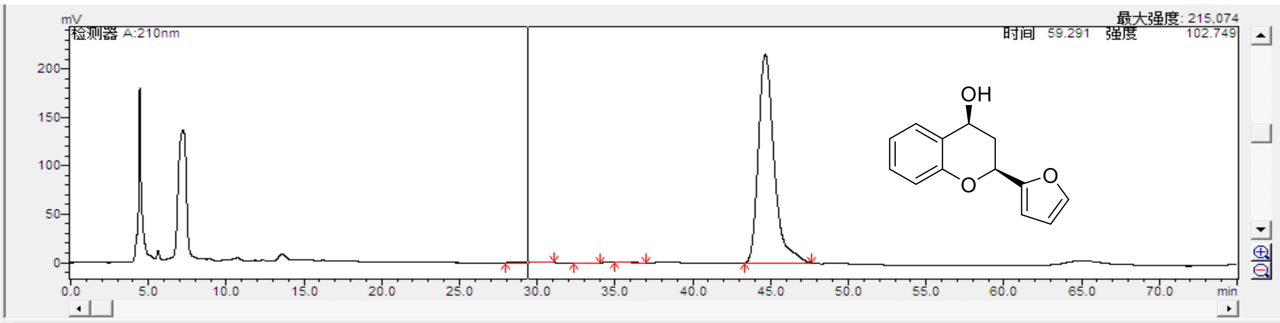
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*S*,*S*)-7am: (2S,4S)-2-(furan-2-yl)chroman-4-ol: (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

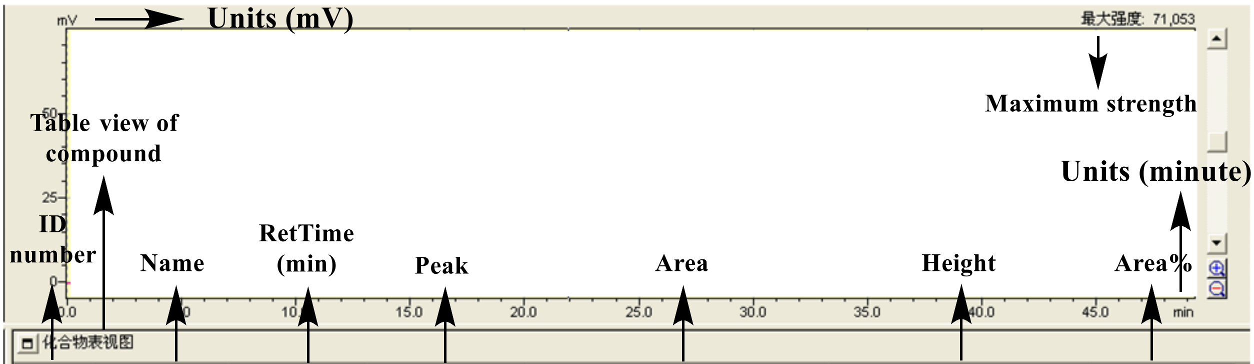
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT29.062	29.062	1	753213	11491	0.9475
2	RT33.083	33.083	2	660761	10782	0.8312
3	RT35.551	35.551	3	38827798	515149	48.8421
4	RT45.638	45.638	4	39254771	436158	49.3792



化合物表视图

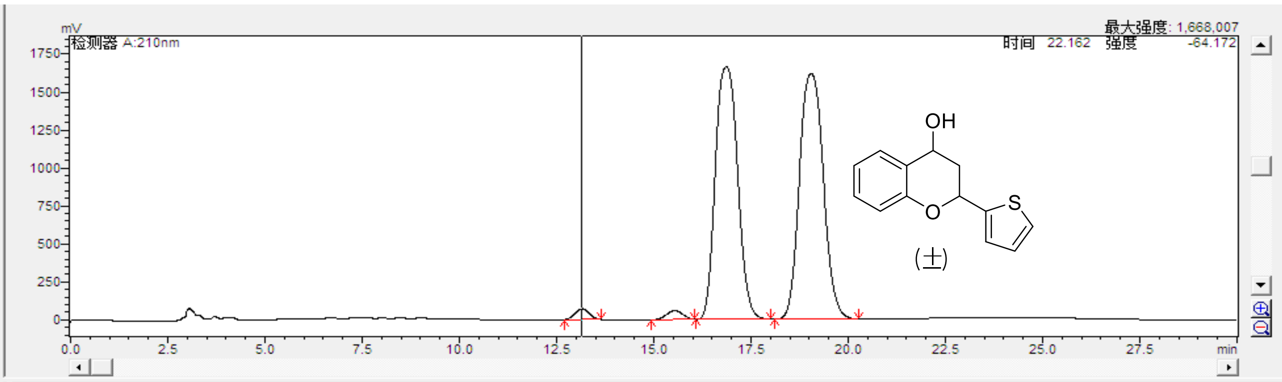
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT29.420	29.420	1	118802	1096	0.7706
2	RT32.959	32.959	2	14770	330	0.0958
3	RT35.957	35.957	3	18560	367	0.1204
4	RT44.656	44.656	4	15263984	215580	99.0132

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>

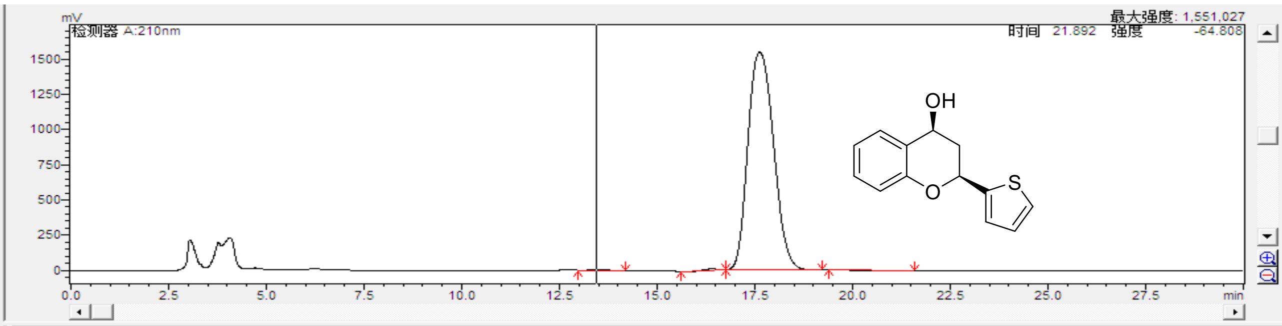


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*S*,*S*)-7an: (2S,4S)-2-(thiophen-2-yl)chroman-4-ol: (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).

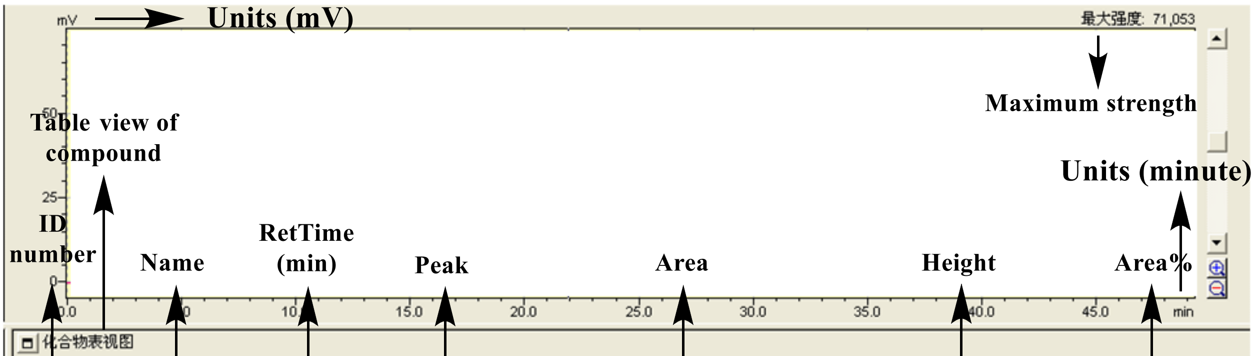


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT13.147	13.147	1	1804667	71438	1.2958
2	RT15.534	15.534	2	1741023	60097	1.2501
3	RT16.856	16.856	3	66445531	1665216	47.7105
4	RT19.047	19.047	4	69276969	1617591	49.7436



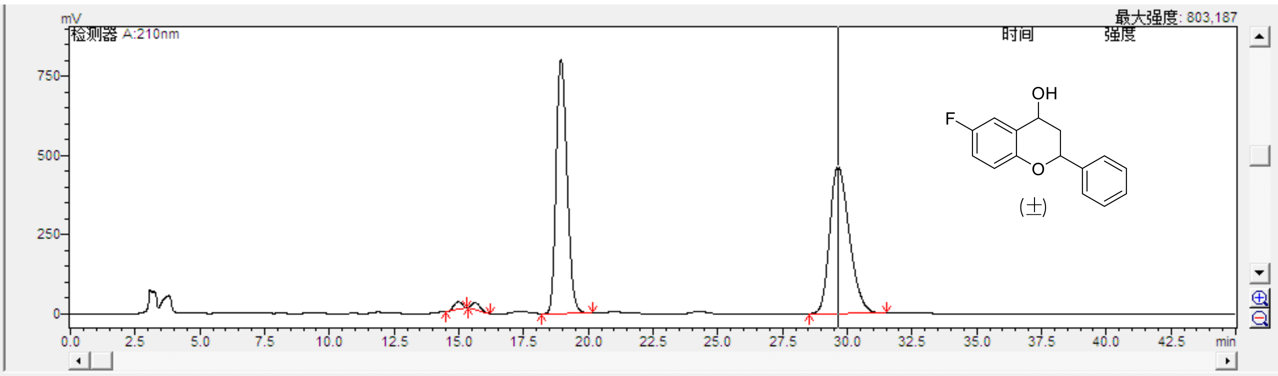
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT13.454	13.454	1	70715	2651	0.0996
2	RT16.401	16.401	2	168278	9585	0.2370
3	RT17.623	17.623	3	70770759	1547843	99.6519
4	RT19.408	19.408	4	8236	-1	0.0116

__**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**__



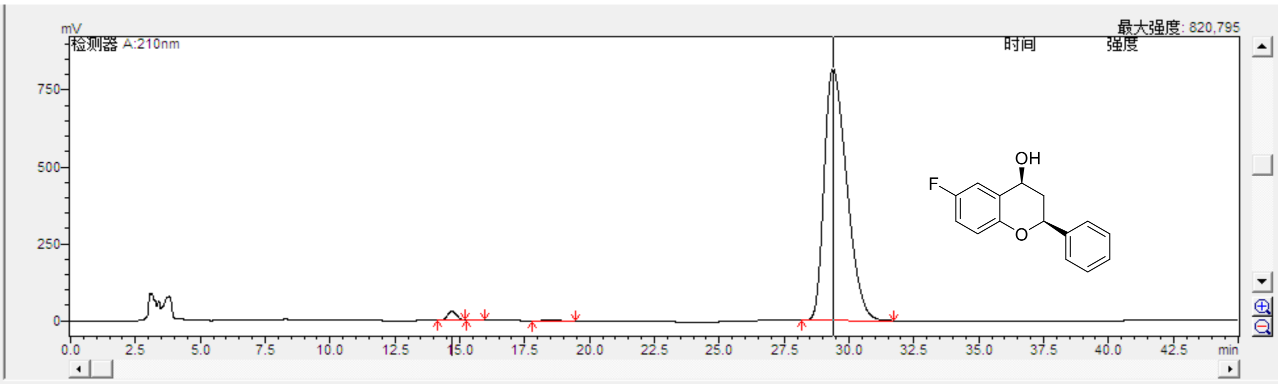
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7ao: (2S,4S)-6-fluoro-2-phenylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

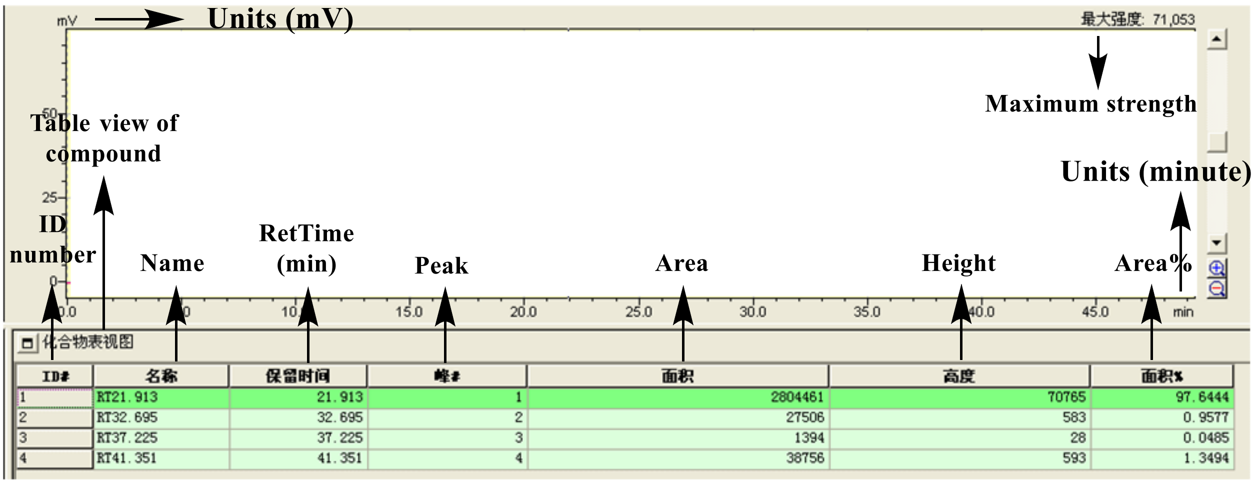
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT14.977	14.977	1	561693	25043	1.1459
2	RT15.628	15.628	2	494223	22363	1.0082
3	RT18.942	18.942	3	23483661	802620	47.9066
4	RT29.639	29.639	4	24480057	465242	49.9393



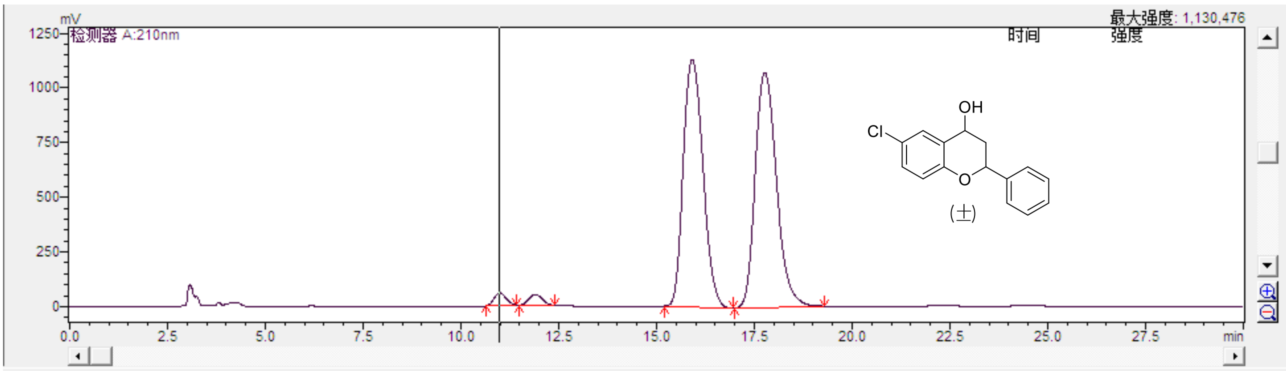
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT14.696	14.696	1	713892	29010	1.4155
2	RT15.461	15.461	2	29217	1382	0.0579
3	RT18.519	18.519	3	77534	1848	0.1537
4	RT29.381	29.381	4	49613921	820189	98.3729

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

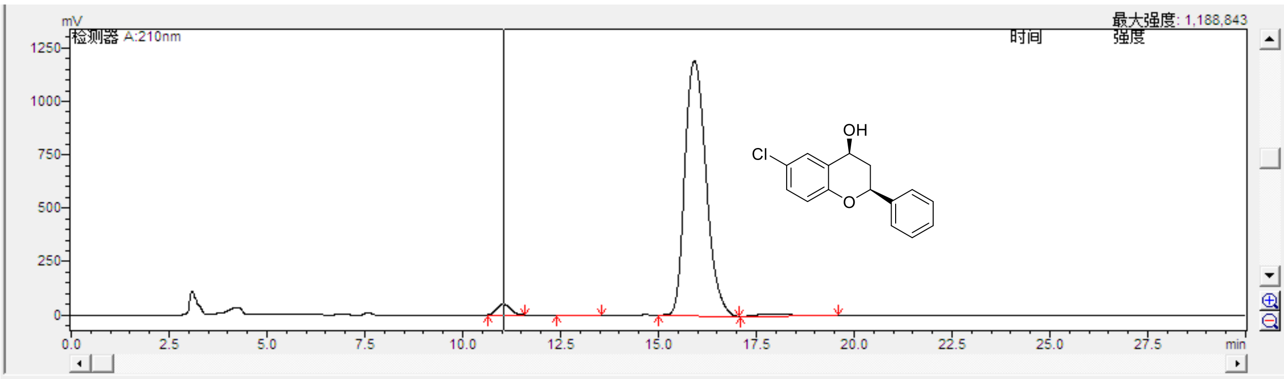


(*S*,*S*)-7ap: (2S,4S)-6-chloro-2-phenylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

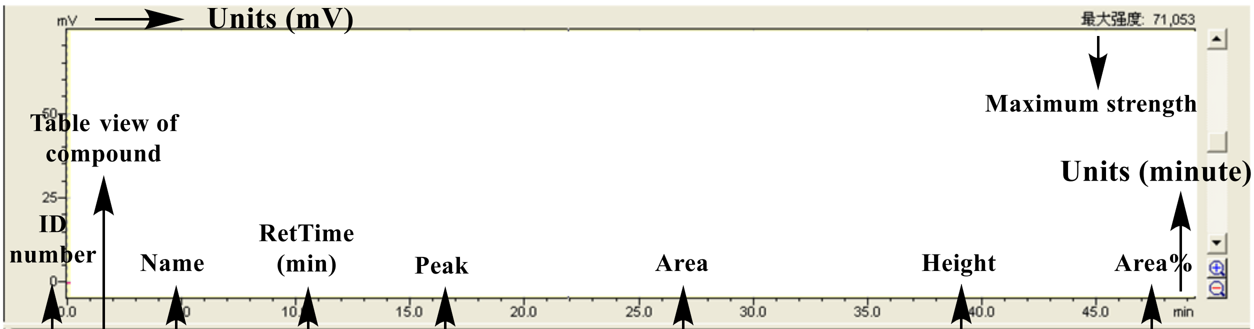
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.990	10.990	1	1203343	57663	1.4506
2	RT11.895	11.895	2	1176300	48948	1.4180
3	RT15.909	15.909	3	39729393	1132246	47.8932
4	RT17.765	17.765	4	40845122	1075474	49.2382



化合物表视图

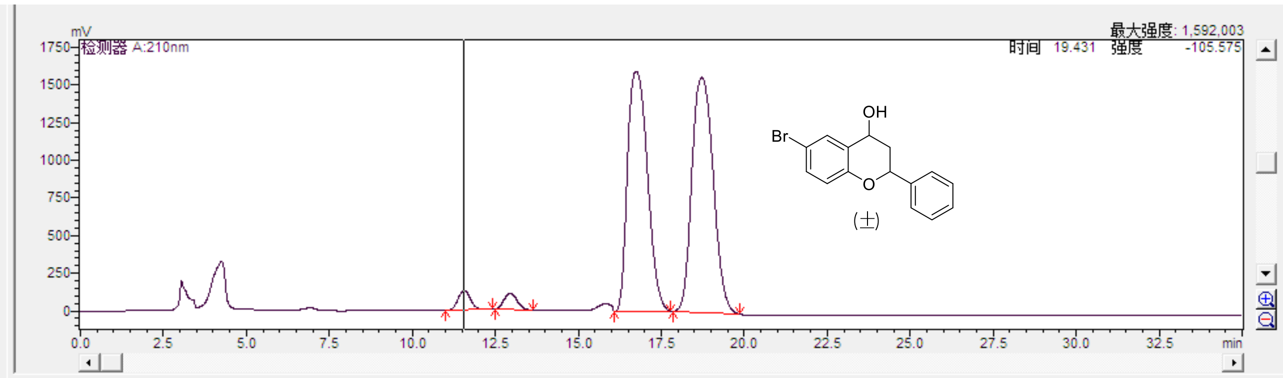
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.032	11.032	1	1214796	50157	2.5904
2	RT13.226	13.226	2	760	132	0.0016
3	RT15.917	15.917	3	45028382	1191935	96.0173
4	RT17.841	17.841	4	652151	10525	1.3906

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



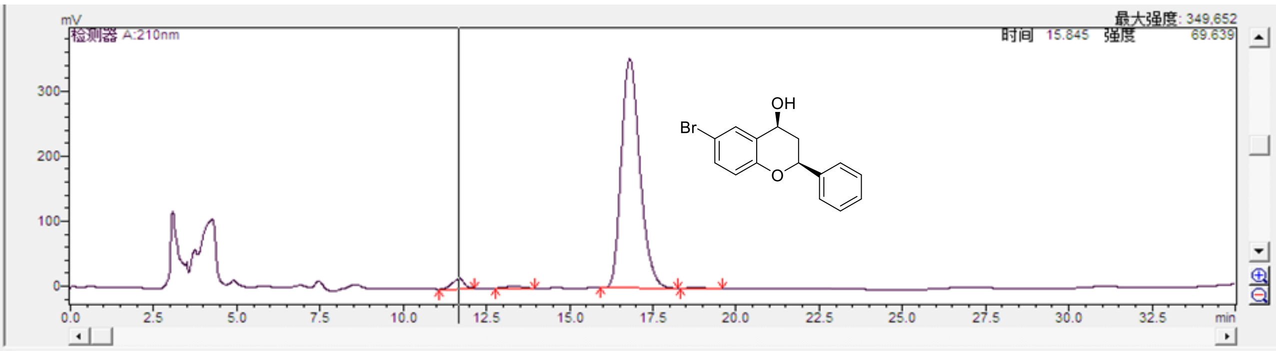
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7aq: (2*S*,4*S*)-6-bromo-2-phenylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

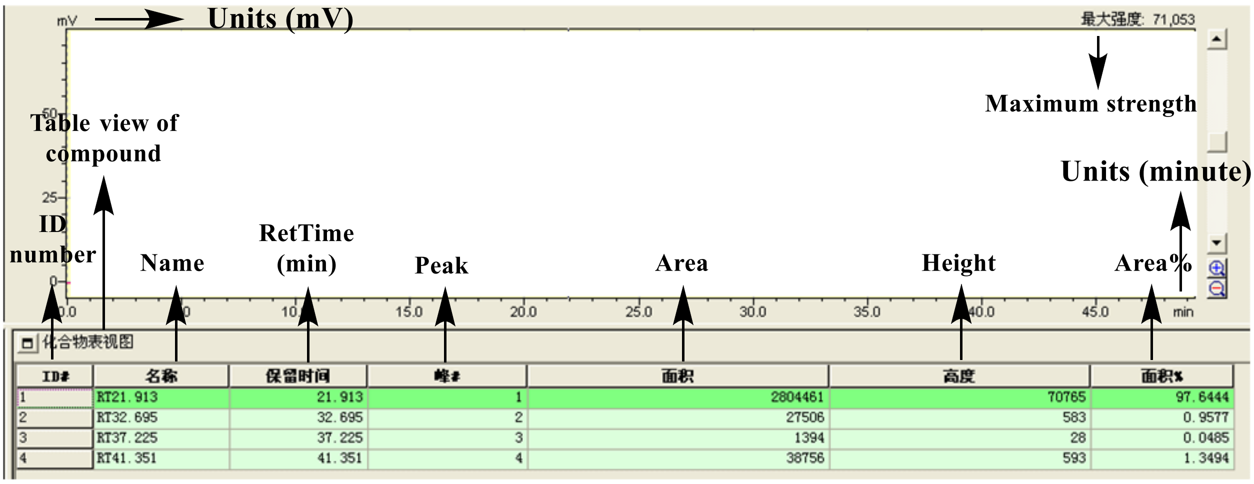
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.559	11.559	1	3362070	128987	2.3445
2	RT12.947	12.947	2	2988660	109190	2.0841
3	RT16.743	16.743	3	66675553	1593877	46.4947
4	RT18.712	18.712	4	70378286	1562477	49.0767



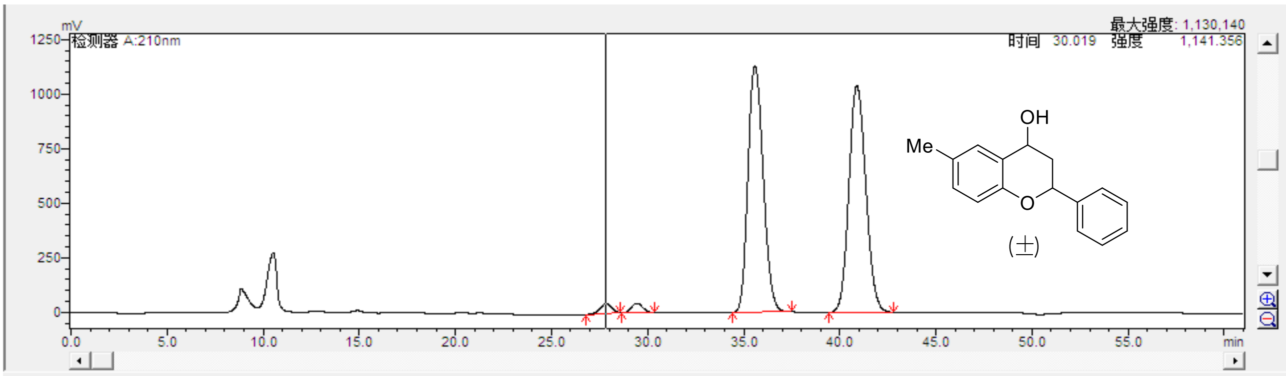
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.679	11.679	1	374977	16297	2.6356
2	RT13.329	13.329	2	109664	2986	0.7708
3	RT16.802	16.802	3	13707615	352496	96.3485
4	RT18.806	18.806	4	34867	926	0.2451

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

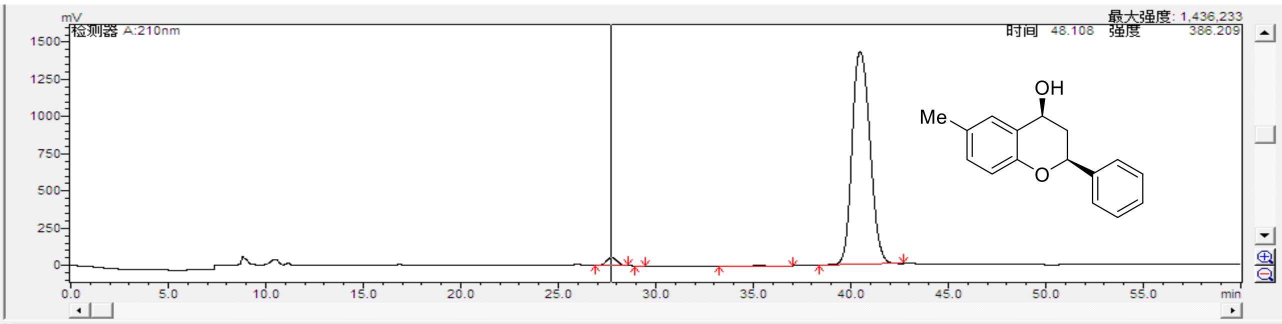


(*S*,*S*)-7ar: (2S,4S)-6-methyl-2-phenylchroman-4-ol: (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

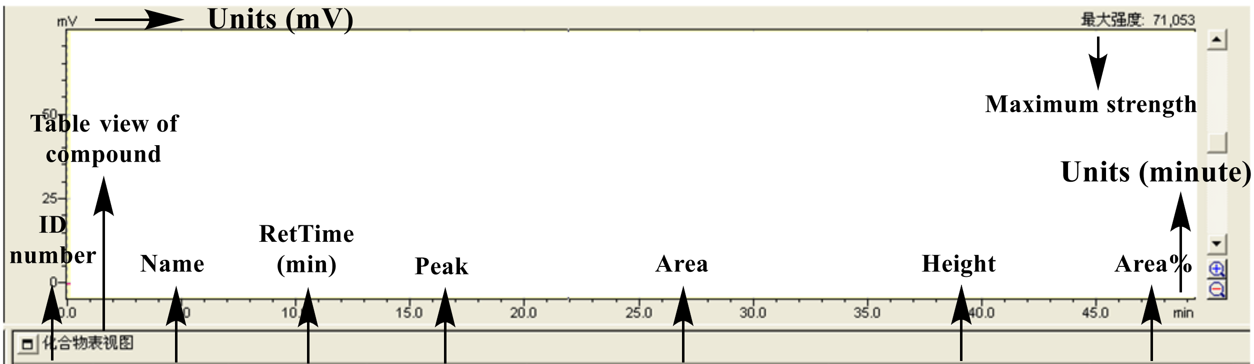
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.844	27.844	1	1865553	45723	1.4357
2	RT29.428	29.428	2	1723099	42692	1.3261
3	RT35.580	35.580	3	62458532	1129490	48.0677
4	RT40.883	40.883	4	63891564	1040119	49.1705



化合物表视图

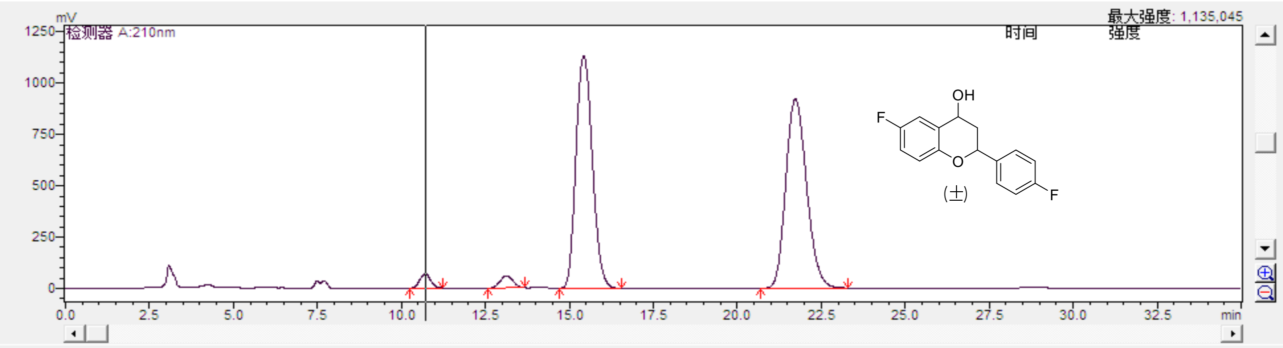
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.729	27.729	1	2023983	55769	2.1625
2	RT28.900	28.900	2	208	-1	0.0002
3	RT35.289	35.289	3	28869	2561	0.0308
4	RT40.478	40.478	4	91542154	1428845	97.8064

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

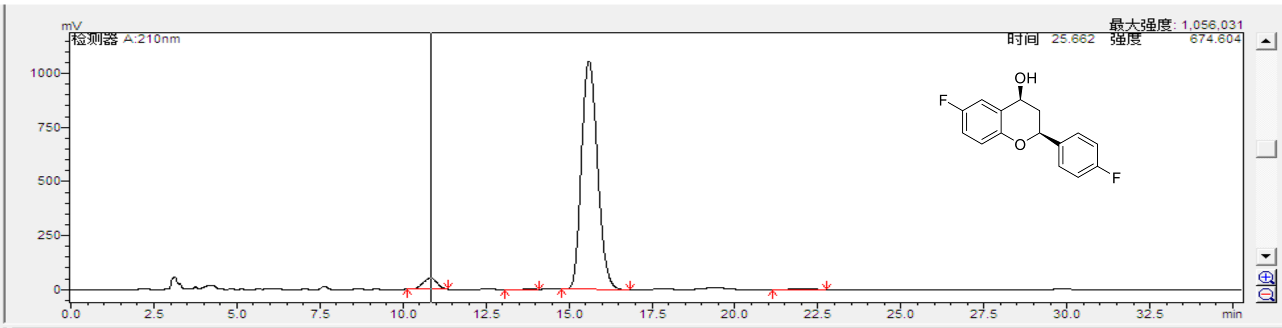


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,S*)-7as: (2S,4S)-6-fluoro-2-(4-fluorophenyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).

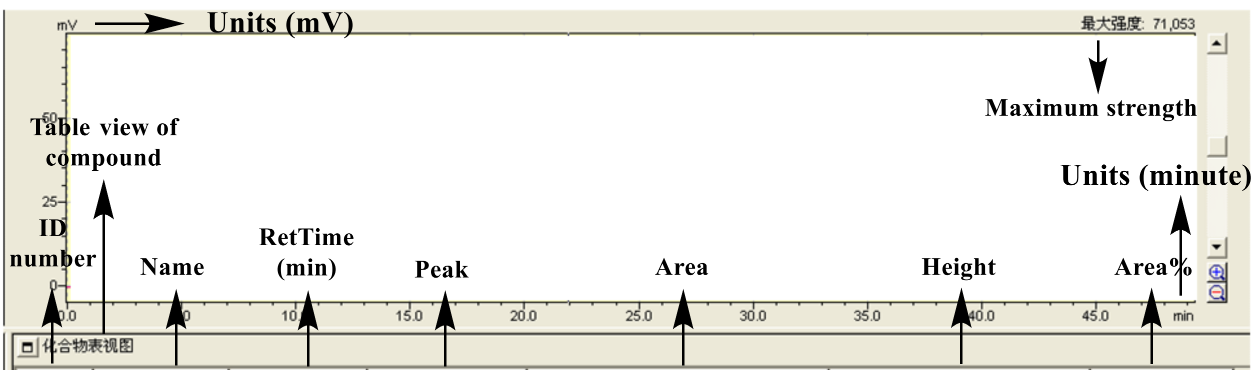


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.705	10.705	1	1550193	68510	1.9015
2	RT13.130	13.130	2	1605428	59459	1.9693
3	RT15.426	15.426	3	38556878	1134807	47.2958
4	RT21.724	21.724	4	39810297	921566	48.8333



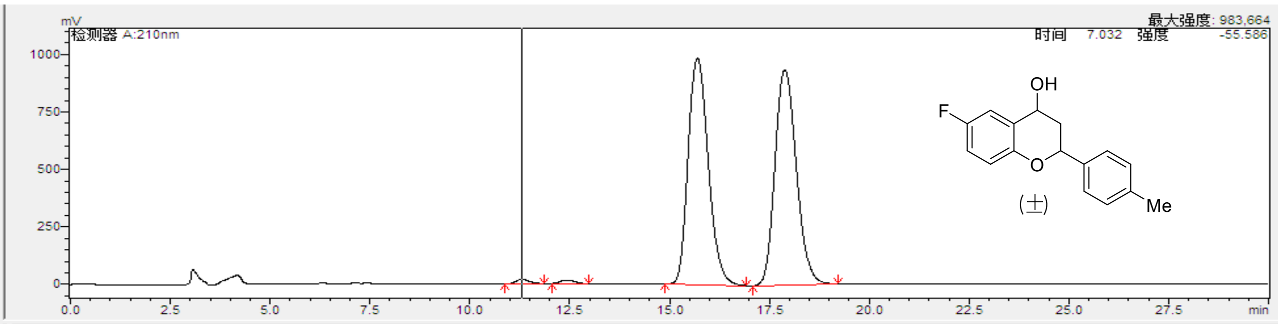
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.831	10.831	1	1528633	52559	4.0898
2	RT13.802	13.802	2	13661	989	0.0366
3	RT15.601	15.601	3	35679313	1056200	95.4598
4	RT22.011	22.011	4	154668	3690	0.4138

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



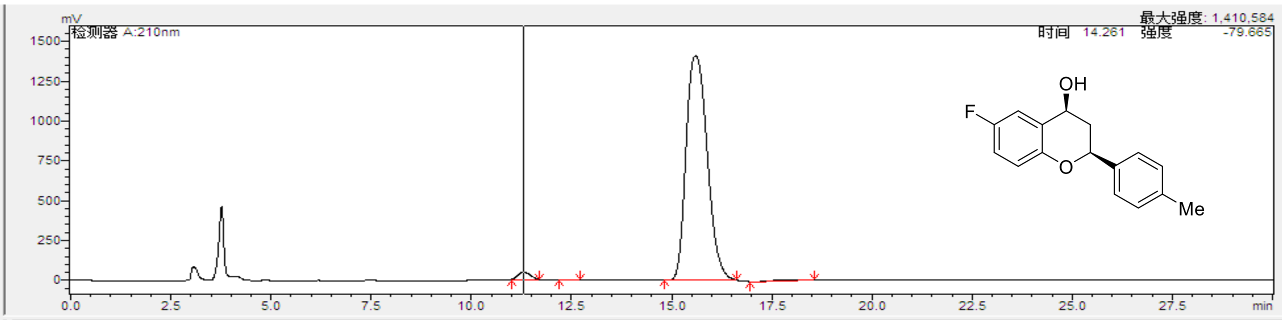
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*S*,*S*)-7at: (2S,4S)-6-fluoro-2-(p-tolyl)chroman-4-ol: (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

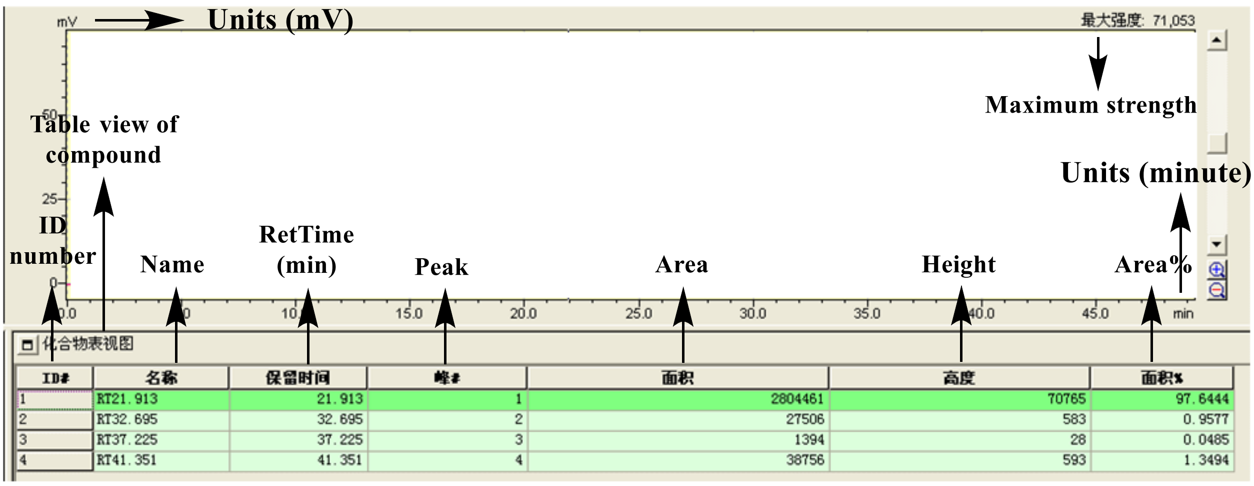
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.300	11.300	1	449915	18355	0.6406
2	RT12.444	12.444	2	400204	15550	0.5698
3	RT15.694	15.694	3	34562083	984584	49.2069
4	RT17.885	17.885	4	34826104	935551	49.5828



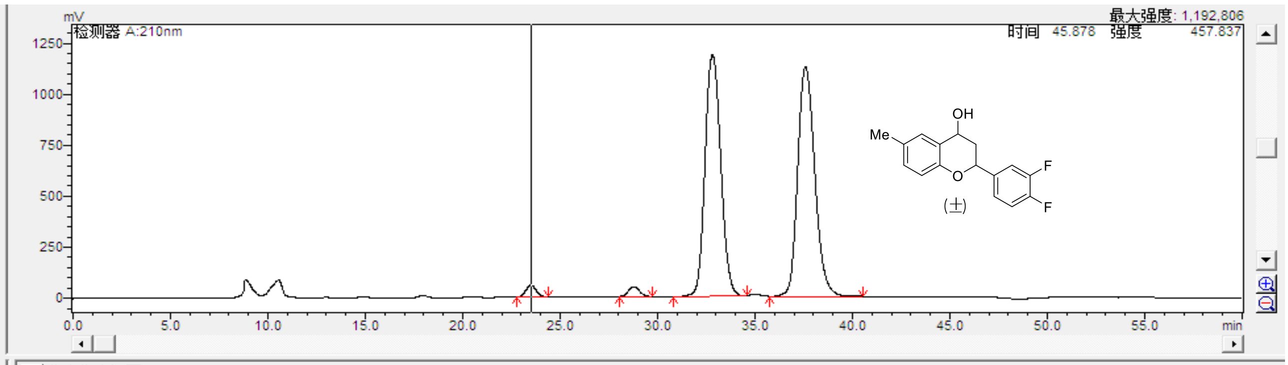
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.311	11.311	1	999142	46263	1.8786
2	RT12.193	12.193	2	24	1	0.0000
3	RT15.596	15.596	3	51942666	1410084	97.6621
4	RT17.860	17.860	4	244278	6079	0.4593

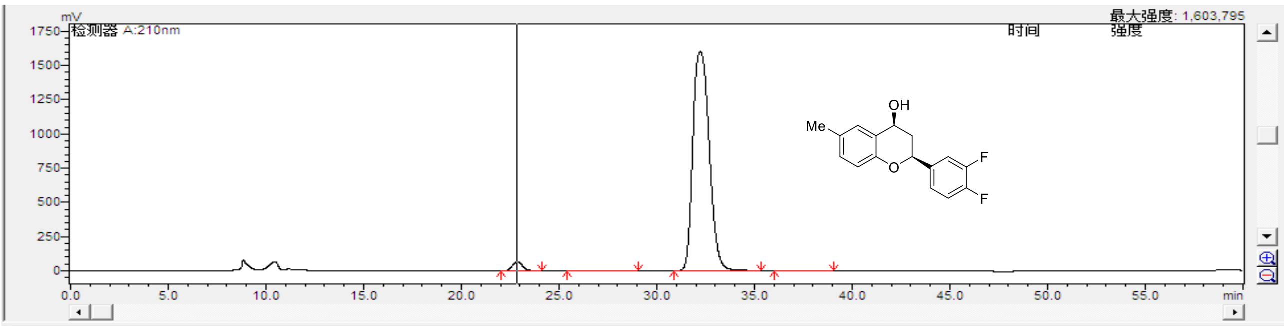
<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>



(*S*,*S*)-7au: (2S,4S)-2-(3,4-difluorophenyl)-6-methylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).

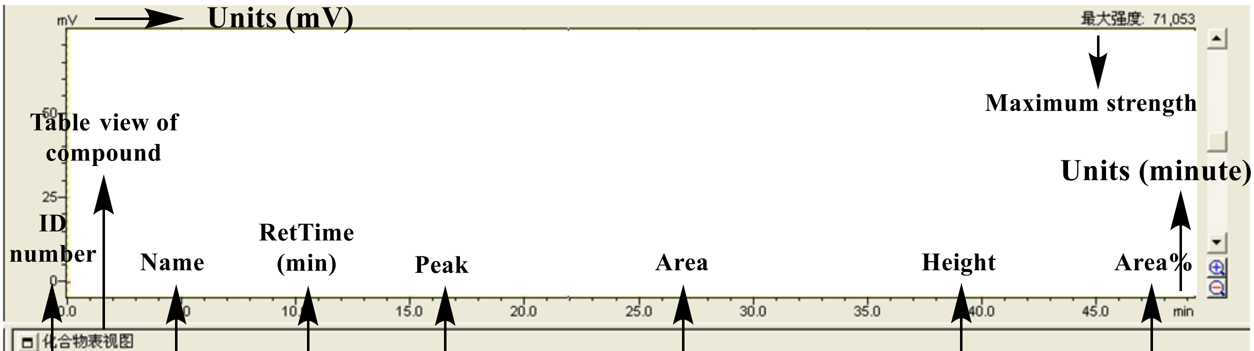


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT23.497	23.497	1	2019522	56348	1.4492
2	RT28.771	28.771	2	1964784	48934	1.4099
3	RT32.811	32.811	3	66518825	1182702	47.7332
4	RT37.584	37.584	4	68852420	1125002	49.4077



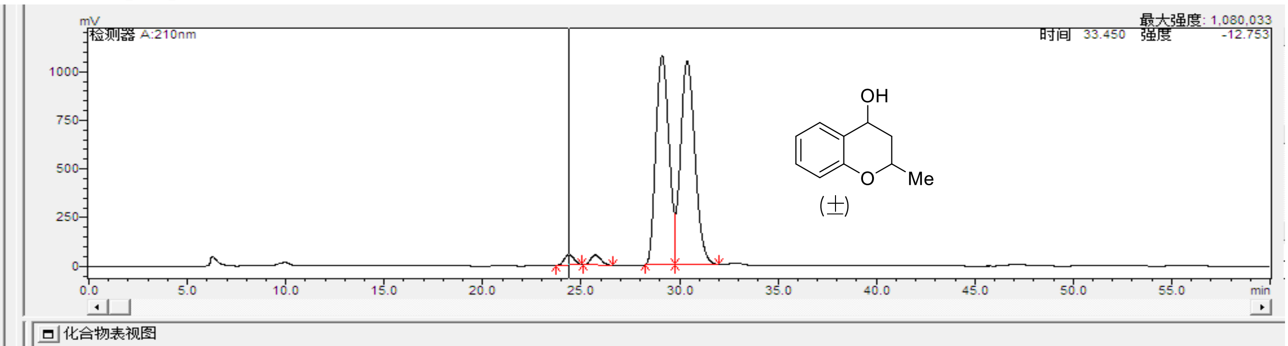
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.861	22.861	1	2441840	66987	2.5315
2	RT26.101	26.101	2	160368	1801	0.1663
3	RT32.214	32.214	3	93854473	1604456	97.3015
4	RT37.119	37.119	4	710	1926	0.0007

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>

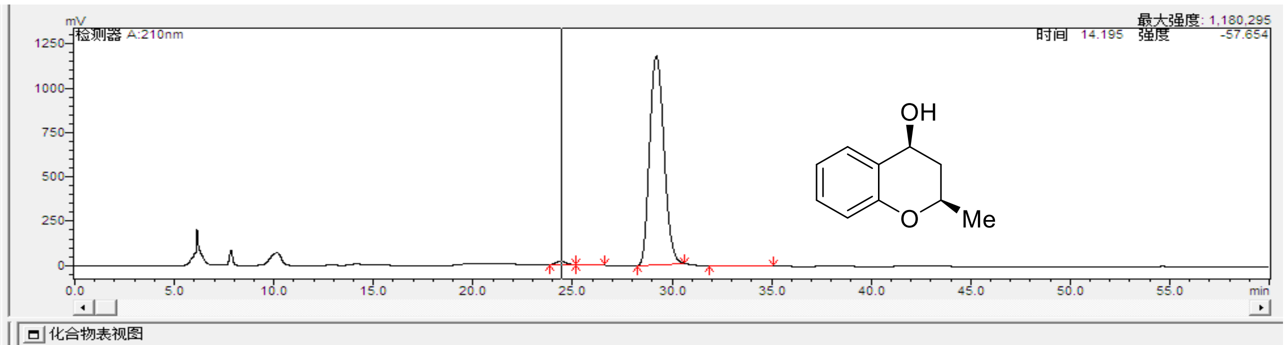


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*R*,*S*)-7ba: (2*R*,4*S*)-2-methylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).

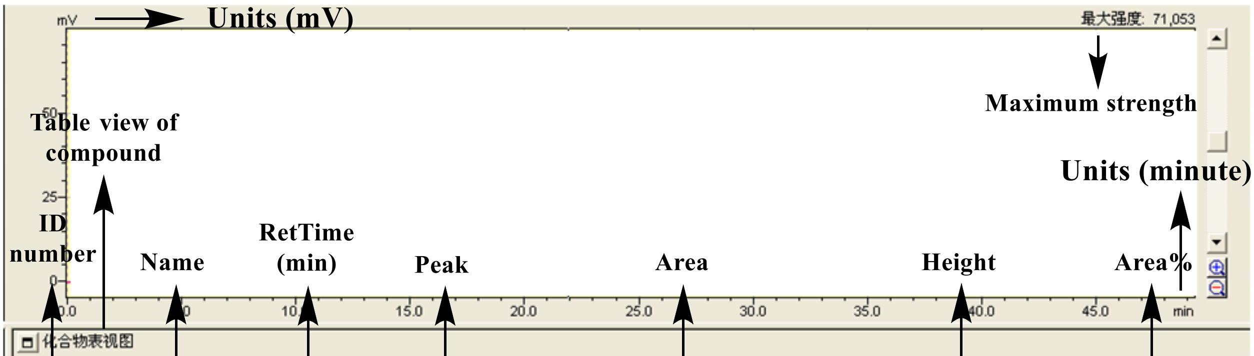


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT24.389	24.389	1	1884222	53907	1.7593
2	RT25.728	25.728	2	1870505	51335	1.7465
3	RT29.110	29.110	3	50039350	1071101	46.7227
4	RT30.388	30.388	4	53304514	1045608	49.7714



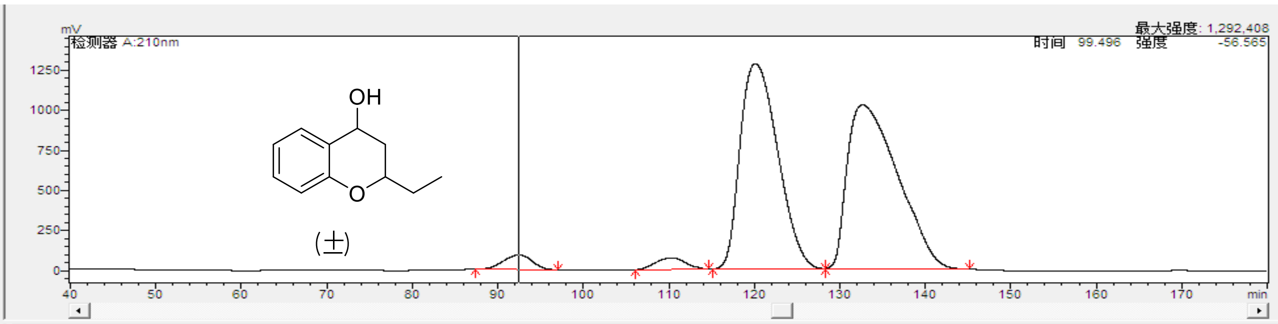
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT24.414	24.414	1	696999	19279	1.1647
2	RT25.570	25.570	2	20790	748	0.0347
3	RT29.211	29.211	3	59036112	1175391	98.6475
4	RT32.586	32.586	4	91598	712	0.1531

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



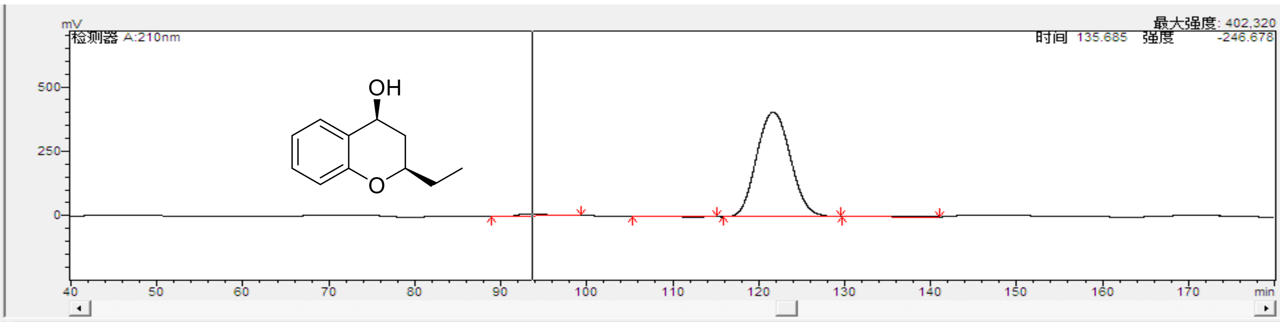
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*R*,*S*)-7bb: (2*R*,4*S*)-2-ethylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, 25 ℃).



化合物表视图

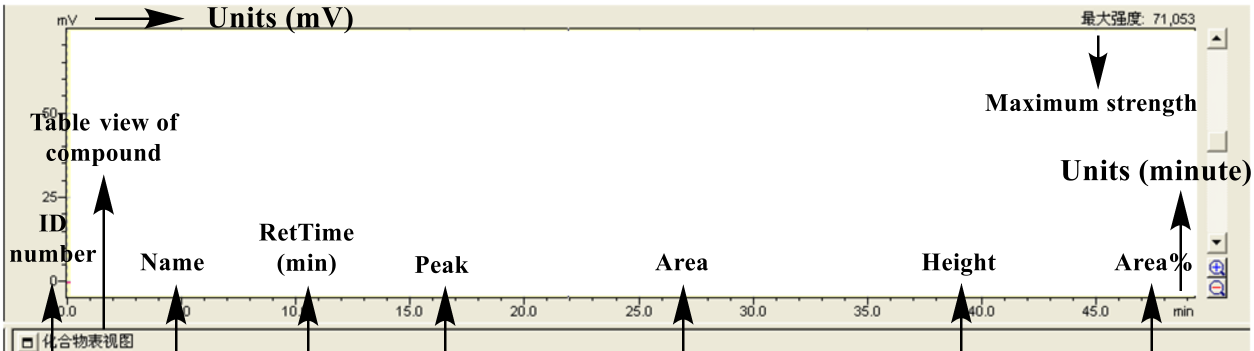
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT92.495	92.495	1	21517241	91545	2.5202
2	RT110.246	110.246	2	17896361	72686	2.0961
3	RT120.161	120.161	3	392857211	1280759	46.0124
4	RT132.616	132.616	4	421535931	1023403	49.3714



化合物表视图

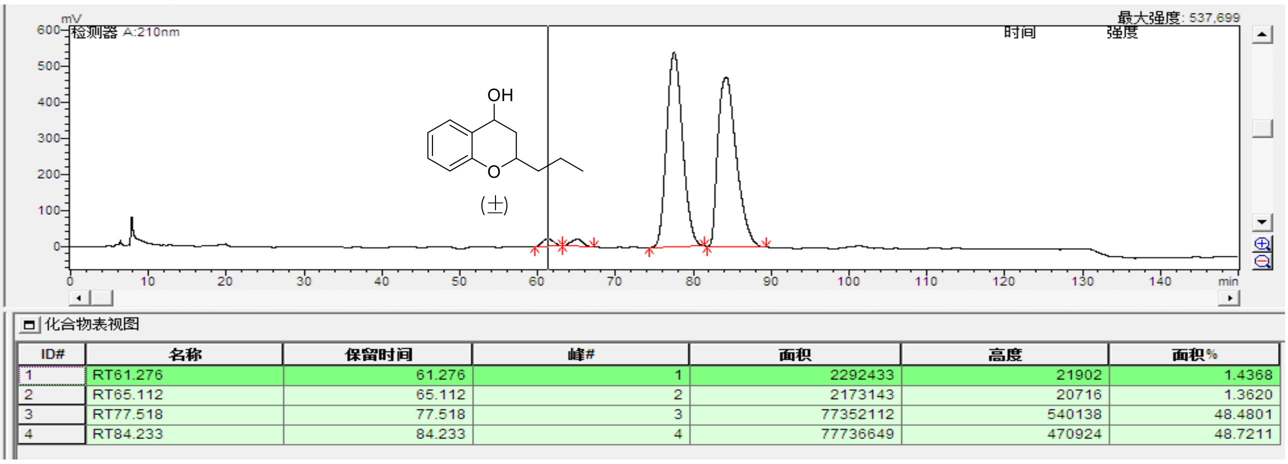
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT93.600	93.600	1	2143163	8994	1.8833
2	RT107.530	107.530	2	217735	1614	0.1913
3	RT121.710	121.710	3	111194212	406552	97.7105
4	RT132.963	132.963	4	244547	1496	0.2149

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

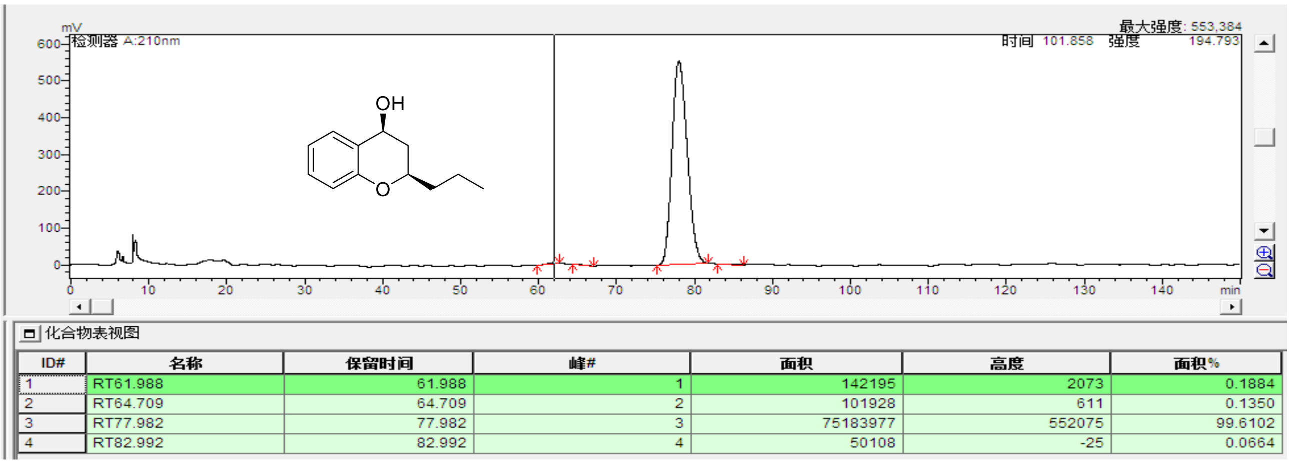


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*R*,*S*)-7bc: (2*R*,4*S*)-2-propylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 99/1, flow rate = 1.0mL/min, 25 ℃).

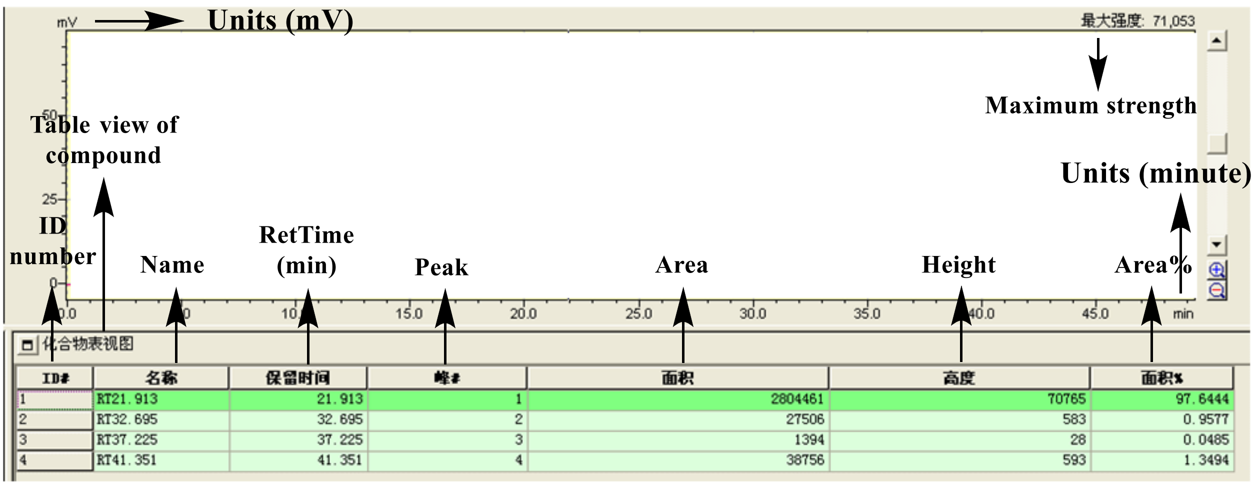


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT61.276	61.276	1	2292433	21902	1.4368
2	RT65.112	65.112	2	2173143	20716	1.3620
3	RT77.518	77.518	3	77352112	540138	48.4801
4	RT84.233	84.233	4	77736649	470924	48.7211



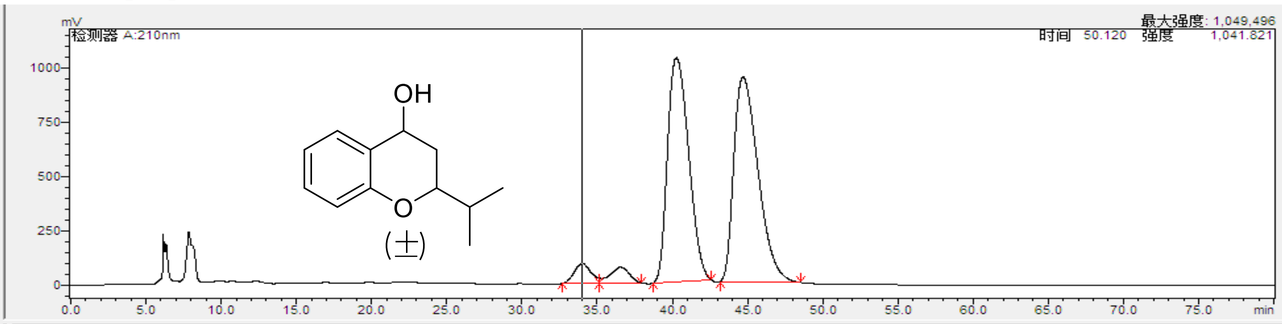
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT61.988	61.988	1	142195	2073	0.1884
2	RT64.709	64.709	2	101928	611	0.1350
3	RT77.982	77.982	3	75183977	552075	99.6102
4	RT82.992	82.992	4	50108	-25	0.0664

<u>**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**</u>



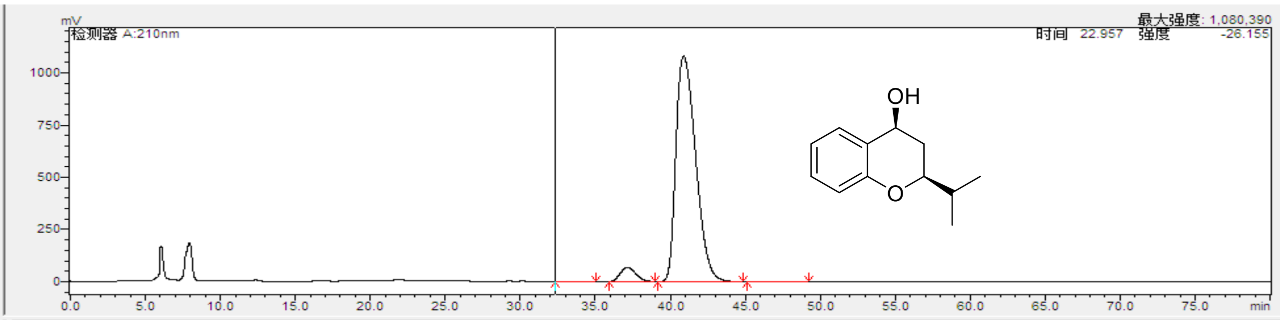
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7bd: (2S,4S)-2-isopropylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

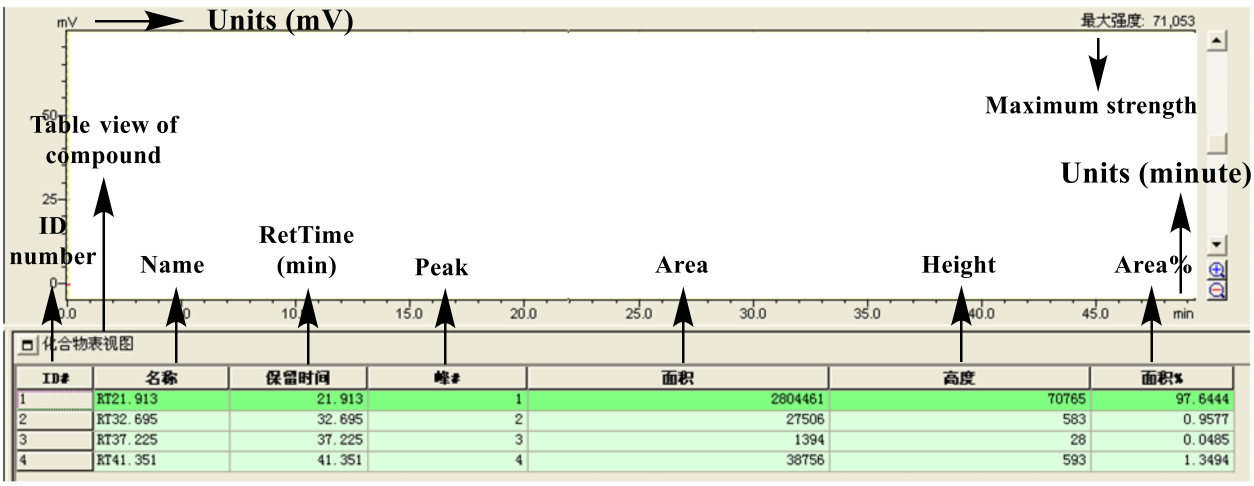
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT33.996	33.996	1	7128287	91685	3.2226
2	RT36.564	36.564	2	6570463	73456	2.9704
3	RT40.269	40.269	3	101209306	1032889	45.7547
4	RT44.696	44.696	4	106291813	944656	48.0524



化合物表视图

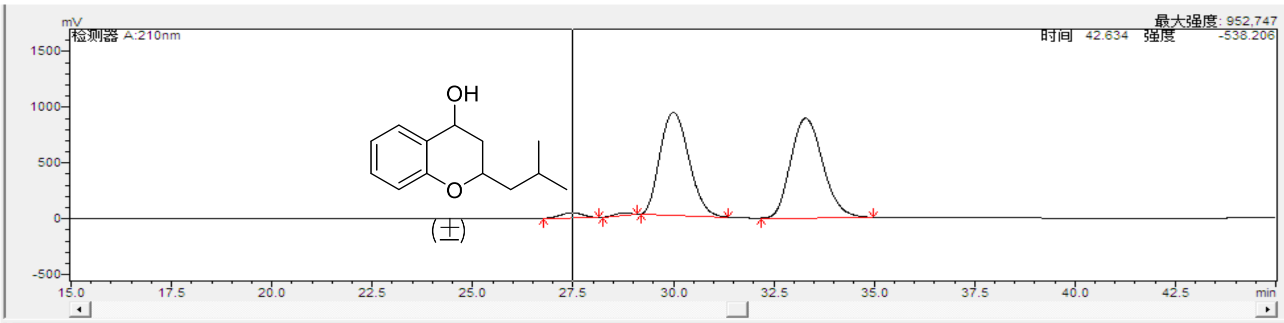
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.317	32.317	1	7714	0	0.0074
2	RT37.144	37.144	2	5067105	69457	4.8622
3	RT40.895	40.895	3	99085038	1080854	95.0782
4	RT46.035	46.035	4	54451	1171	0.0522

__**Translation of all characters (Chinese) in the above two frameworks to English is as follows:**__



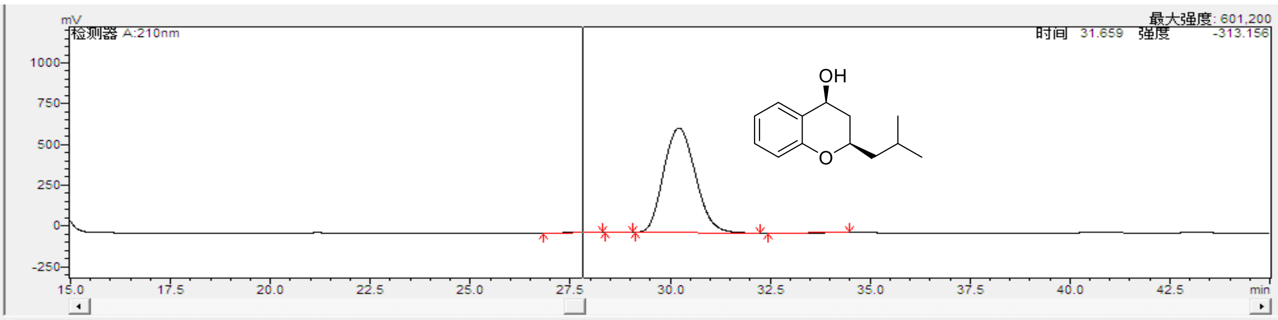
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*R*,*S*)-7be: (2R,4S)-2-isobutylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

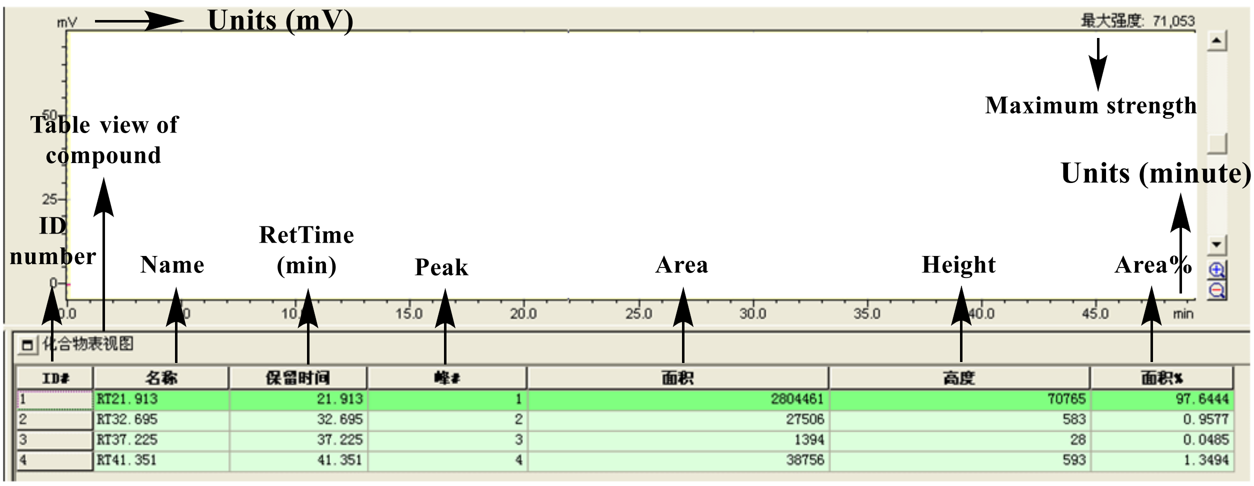
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.473	27.473	1	1768821	46114	1.7929
2	RT28.783	28.783	2	735798	25579	0.7458
3	RT29.995	29.995	3	46338900	922460	46.9708
4	RT33.291	33.291	4	49811086	893342	50.4904



化合物表视图

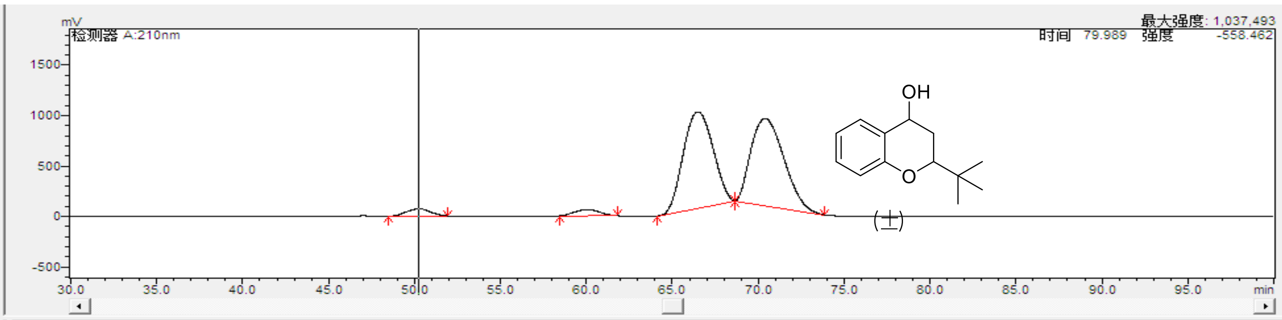
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.807	27.807	1	216668	5192	0.6036
2	RT28.863	28.863	2	18324	748	0.0510
3	RT30.214	30.214	3	35581135	642150	99.1181
4	RT34.229	34.229	4	81591	569	0.2273

Translation of all characters (Chinese) in the above two frameworks to English is as follows:



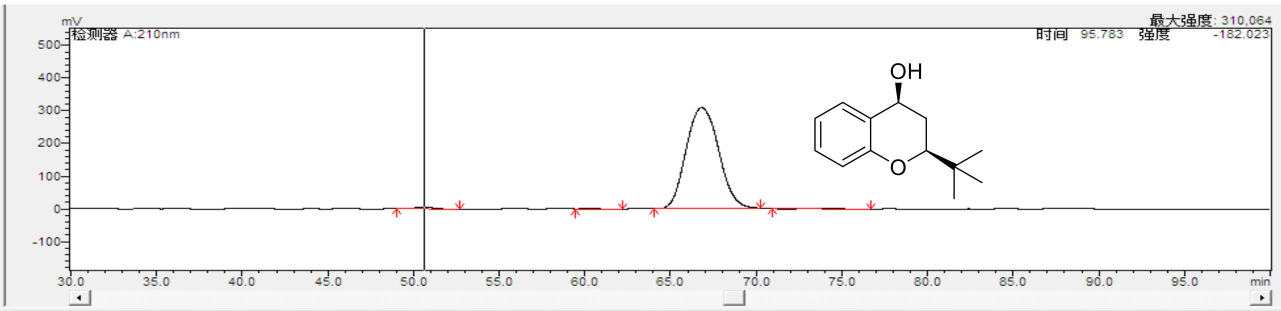
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*S*,*S*)-7bf: (2*S*,4*S*)-2-(*tert*-butyl)chroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 99/1, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

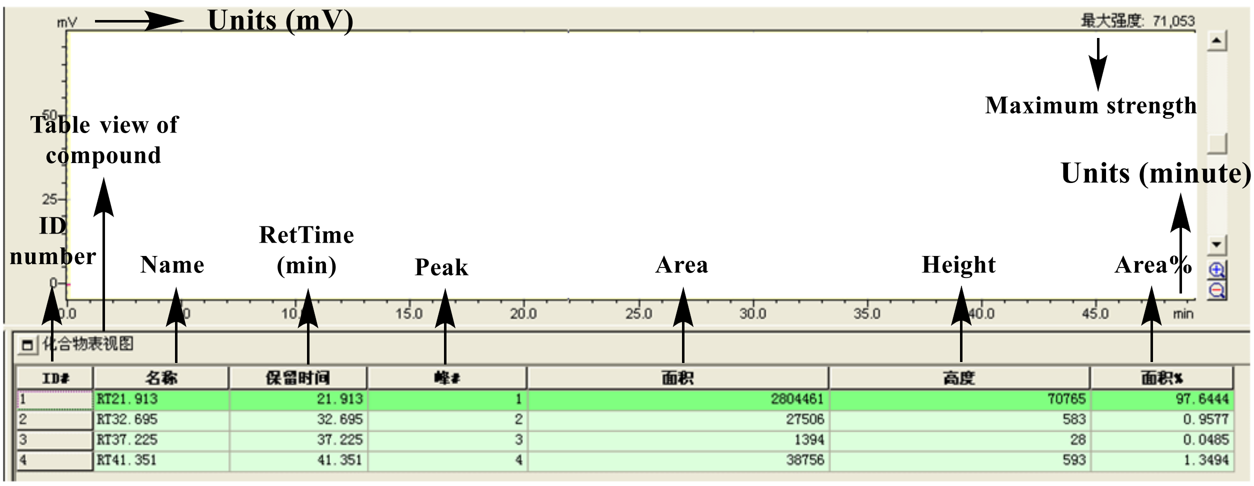
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT50.254	50.254	1	7053301	72612	2.8914
2	RT60.025	60.025	2	6250736	60318	2.5624
3	RT66.483	66.483	3	114919427	954869	47.1095
4	RT70.388	70.388	4	115717378	863899	47.4367



化合物表视图

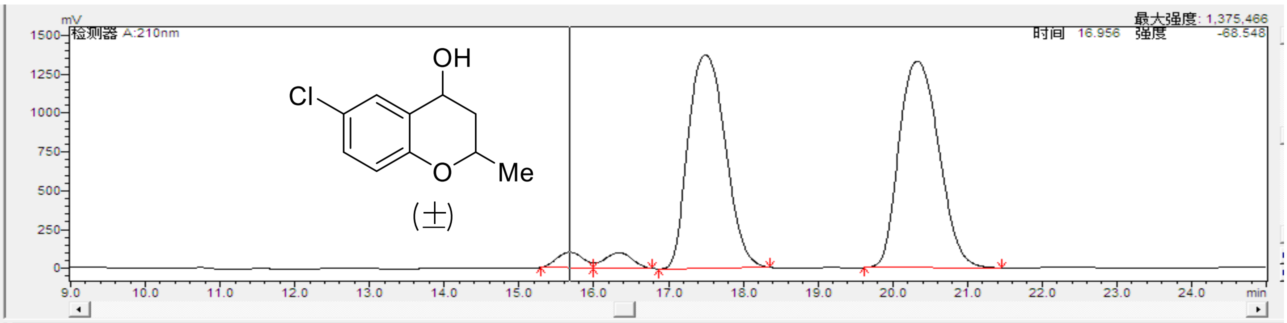
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT50.610	50.610	1	505557	5668	1.2177
2	RT60.286	60.286	2	36214	750	0.0872
3	RT66.809	66.809	3	40830733	308772	98.3453
4	RT70.950	70.950	4	145204	0	0.3497

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>

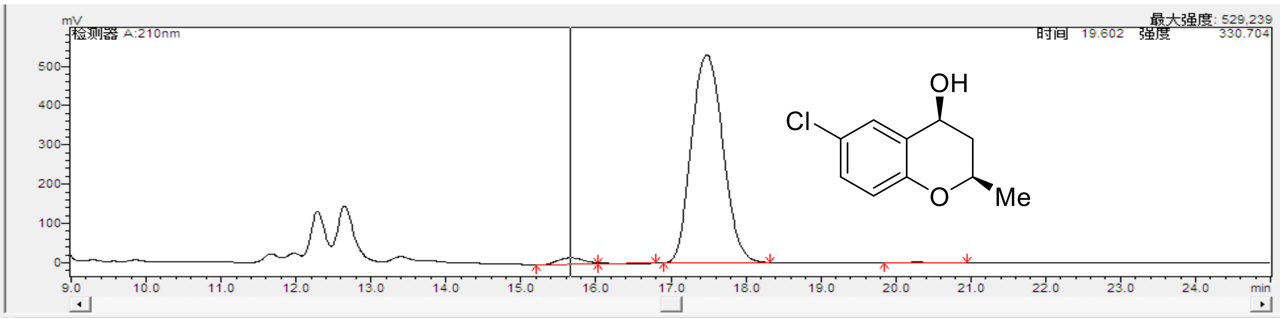


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*R*,*S*)-7bg: (2*R*,4S)-6-chloro-2-methylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).

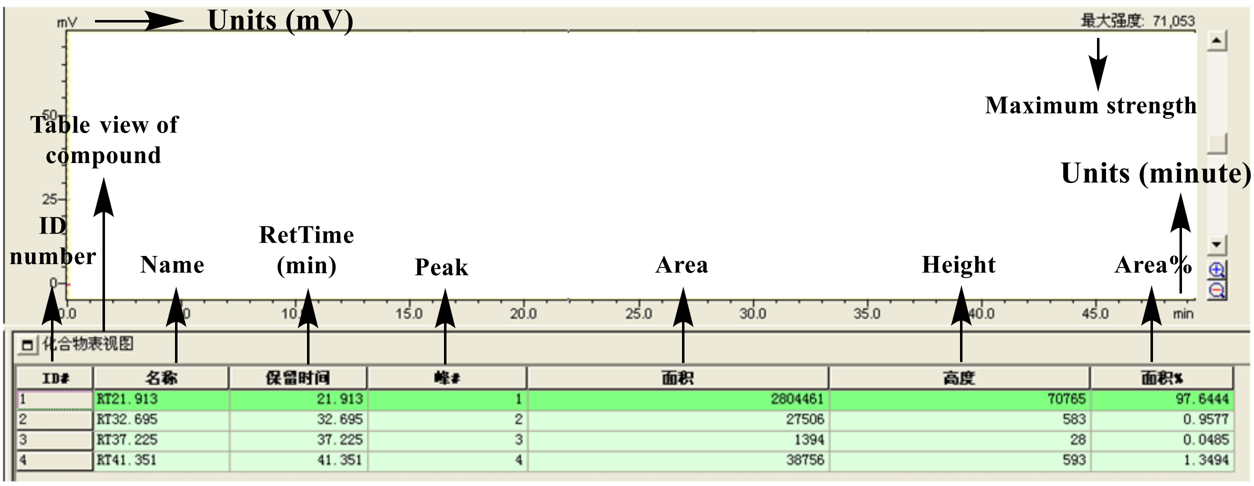


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT15.676	15.676	1	2477975	99723	2.4258
2	RT16.334	16.334	2	2556945	99132	2.5031
3	RT17.491	17.491	3	47651113	1374736	46.6480
4	RT20.327	20.327	4	49464357	1329842	48.4231



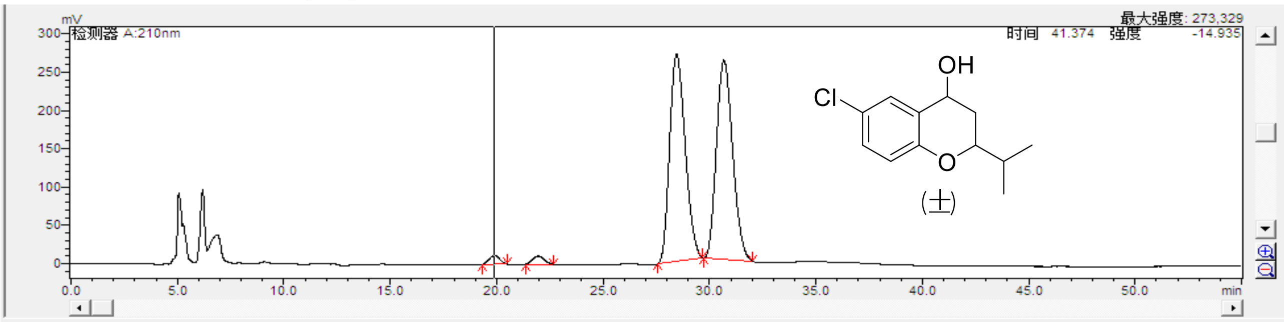
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT15.661	15.661	1	423475	17003	2.6497
2	RT16.033	16.033	2	16790	3066	0.1051
3	RT17.476	17.476	3	15486994	528910	96.9028
4	RT20.279	20.279	4	54736	2072	0.3425

__Translation of all characters (Chinese) in the above two frameworks to English is as follows:__



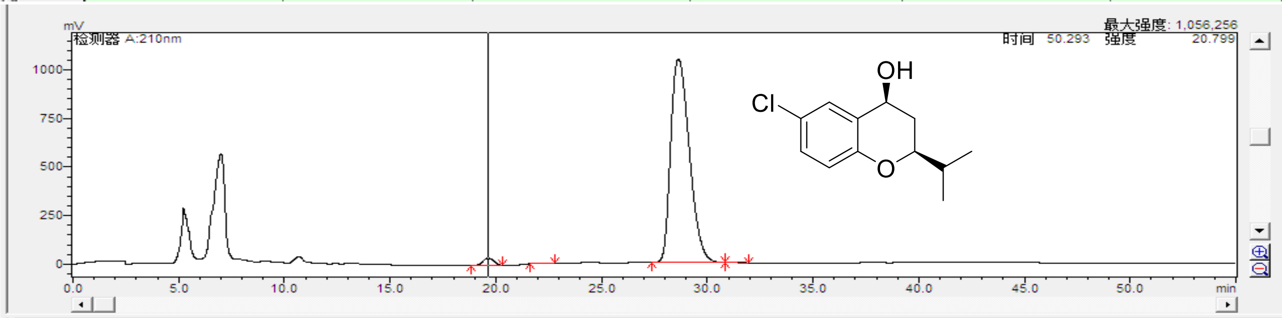
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7bh: (2S,4S)-6-chloro-2-isopropylchroman-4-ol: (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

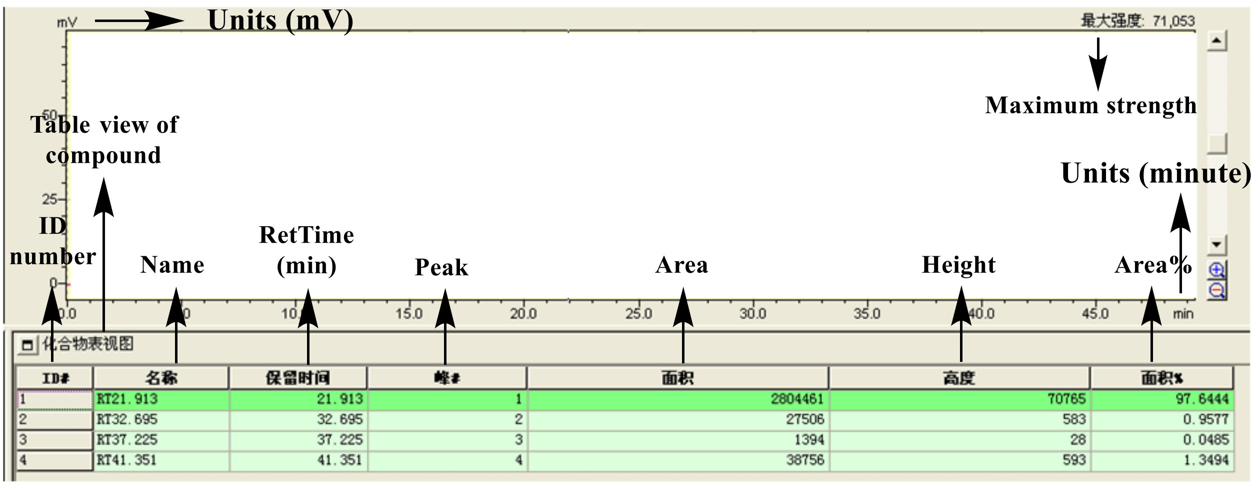
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.891	19.891	1	391103	11226	1.3778
2	RT21.941	21.941	2	412379	10733	1.4527
3	RT28.454	28.454	3	13736704	270359	48.3912
4	RT30.678	30.678	4	13846598	260429	48.7783



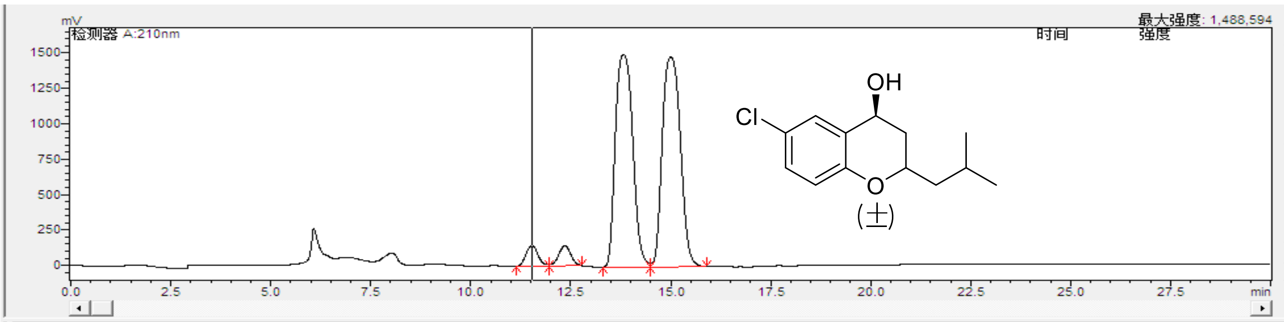
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.632	19.632	1	1352507	38116	2.0563
2	RT22.337	22.337	2	52596	1750	0.0800
3	RT28.630	28.630	3	64365632	1047963	97.8583
4	RT30.875	30.875	4	3598	8	0.0055

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

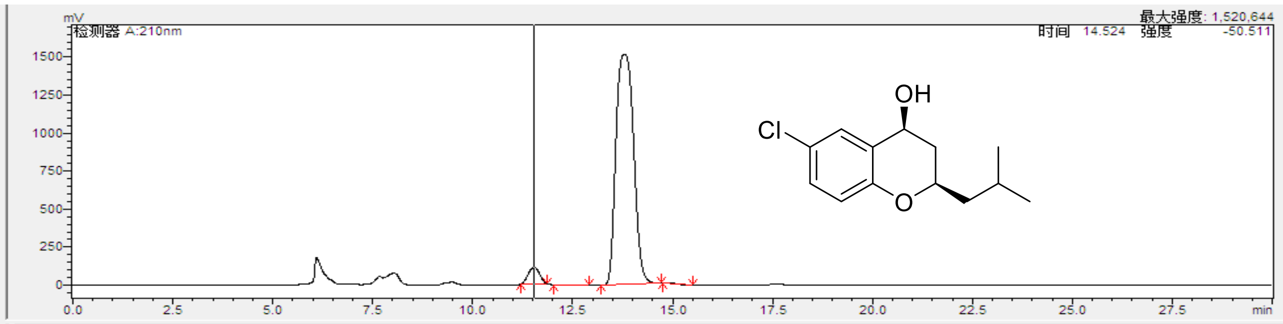


(*R*,*S*)-7bi: (2*R*,4*S*)-6-chloro-2-isobutylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25 ℃).



□ 化合物表视图

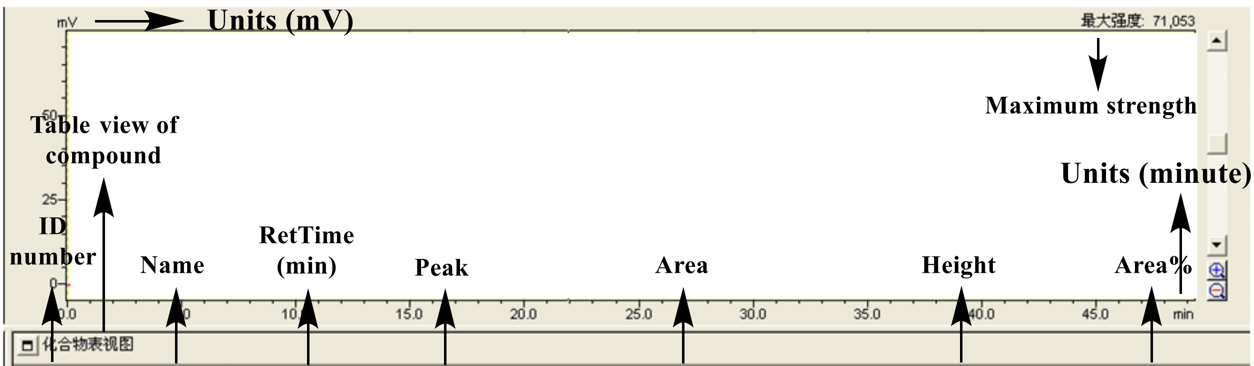
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.529	11.529	1	2988315	142669	3.0468
2	RT12.351	12.351	2	3014040	139803	3.0730
3	RT13.821	13.821	3	45370192	1501677	46.2583
4	RT15.002	15.002	4	46707478	1482224	47.6218



□ 化合物表视图

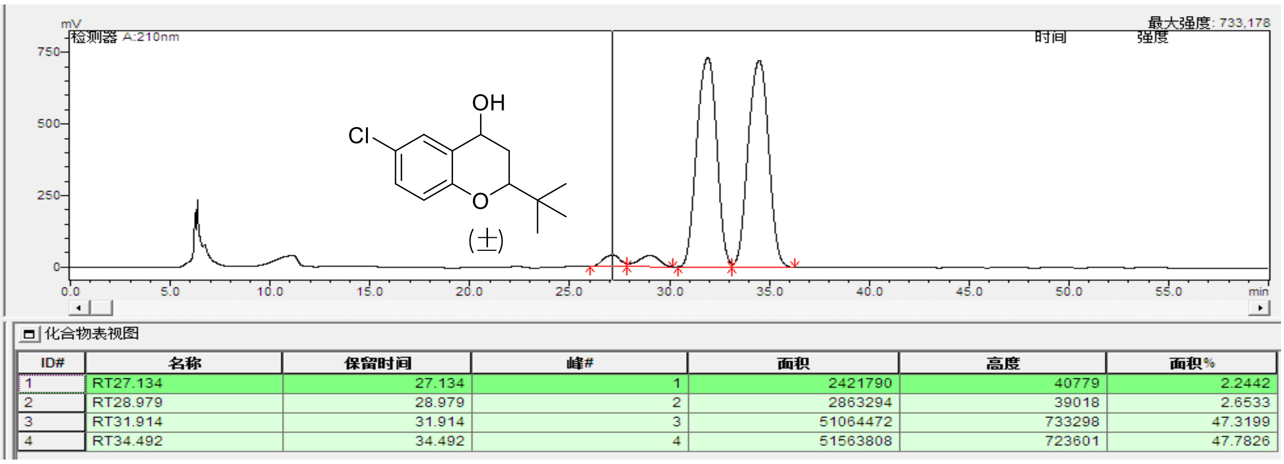
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.535	11.535	1	2139207	108518	4.3895
2	RT12.412	12.412	2	2799	694	0.0057
3	RT13.793	13.793	3	46584708	1518235	95.5877
4	RT14.903	14.903	4	8348	3626	0.0171

__Translation of all characters (Chinese) in the above two frameworks to English is as follows:__

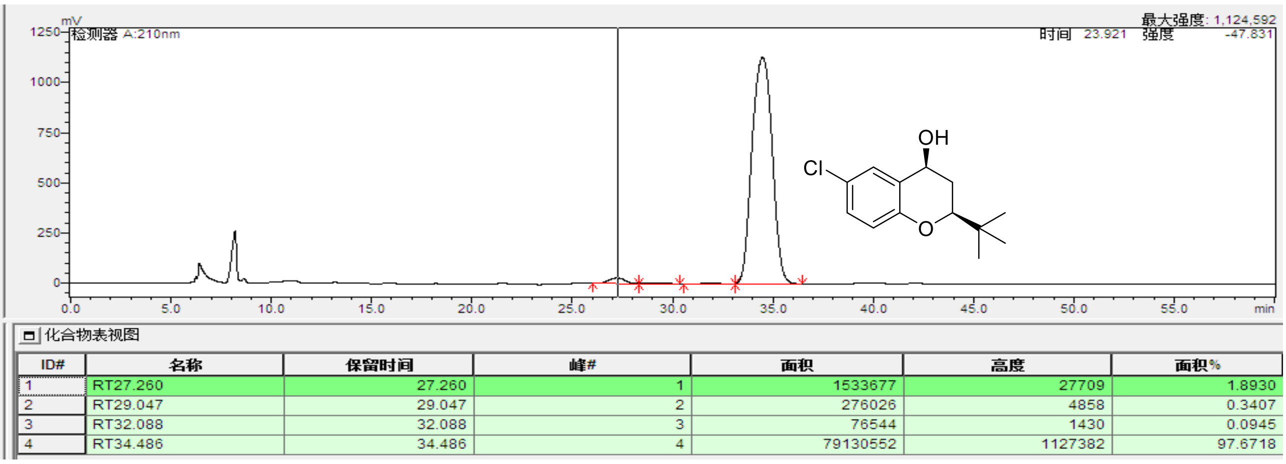


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,S*)-7bj: (2*S*,4*S*)-2-(*tert*-butyl)-6-chlorochroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).

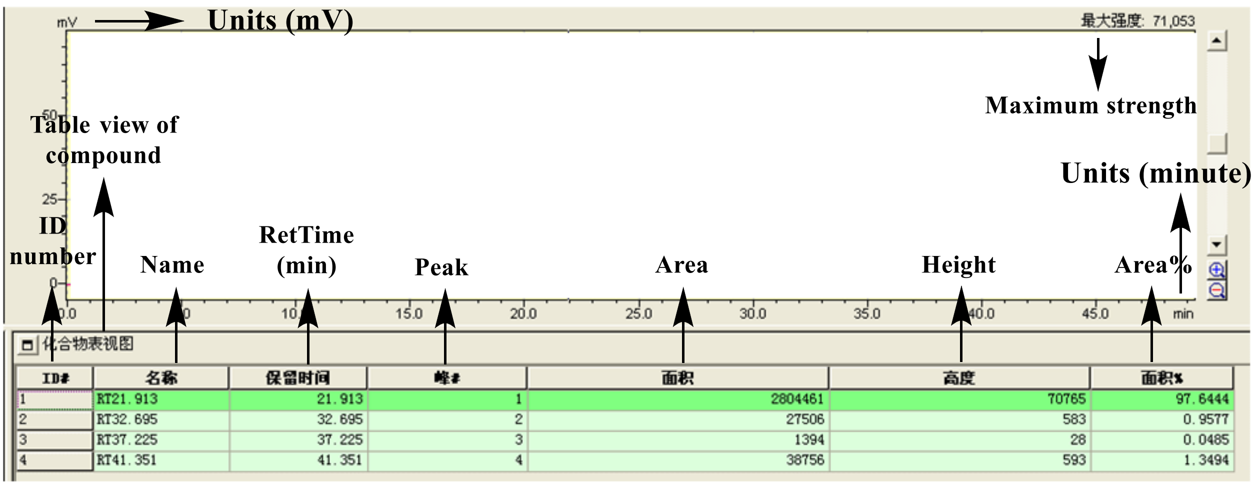


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.134	27.134	1	2421790	40779	2.2442
2	RT28.979	28.979	2	2863294	39018	2.6533
3	RT31.914	31.914	3	51064472	733298	47.3199
4	RT34.492	34.492	4	51563808	723601	47.7826



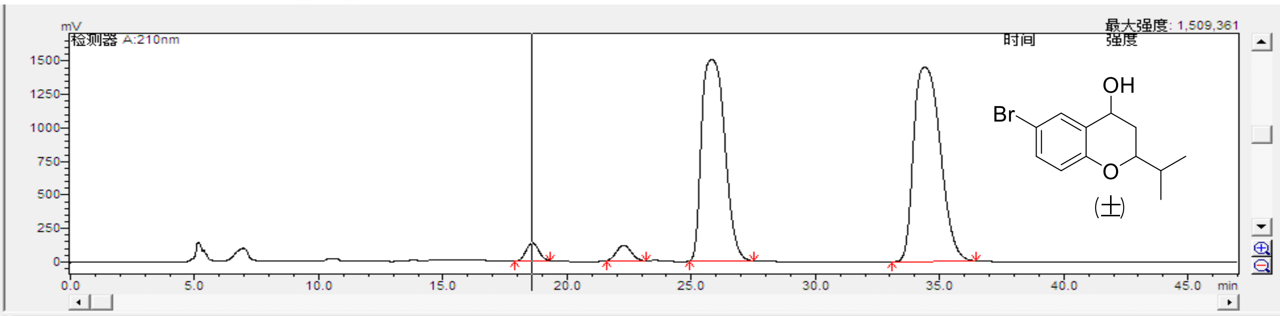
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.260	27.260	1	1533677	27709	1.8930
2	RT29.047	29.047	2	276026	4858	0.3407
3	RT32.088	32.088	3	76544	1430	0.0945
4	RT34.486	34.486	4	79130552	1127382	97.6718

Translation of all characters (Chinese) in the above two frameworks to English is as follows:



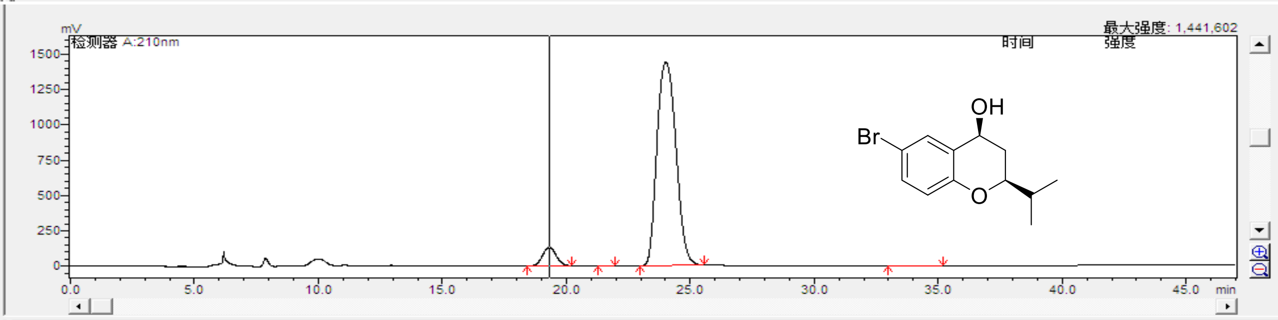
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*S*,*S*)-7bk: (2*S*,4*S*)-6-bromo-2-isopropylchroman-4-ol: (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

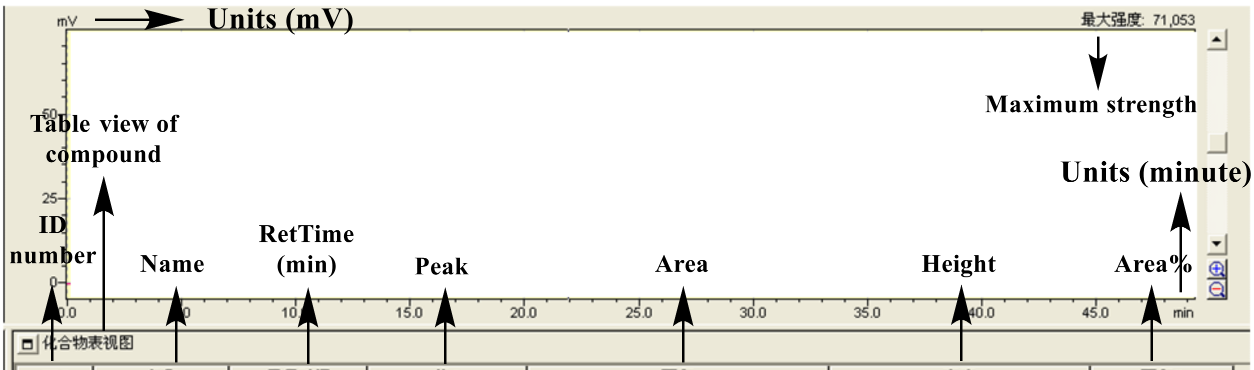
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.602	18.602	1	4696688	133876	2.1765
2	RT22.278	22.278	2	4697310	114525	2.1768
3	RT25.826	25.826	3	97790605	1501434	45.3180
4	RT34.391	34.391	4	108602768	1451831	50.3286



化合物表视图

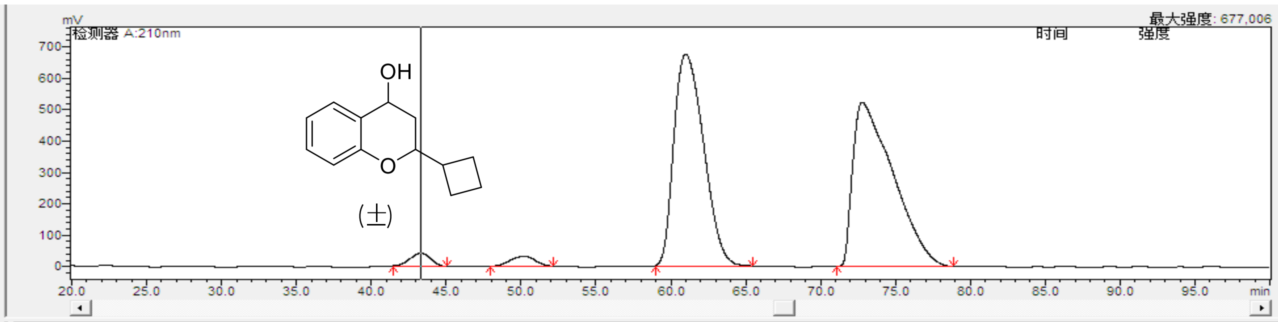
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.312	19.312	1	4882692	130080	5.9767
2	RT21.782	21.782	2	5873	242	0.0072
3	RT24.017	24.017	3	76795717	1437084	94.0024
4	RT34.397	34.397	4	11238	430	0.0138

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



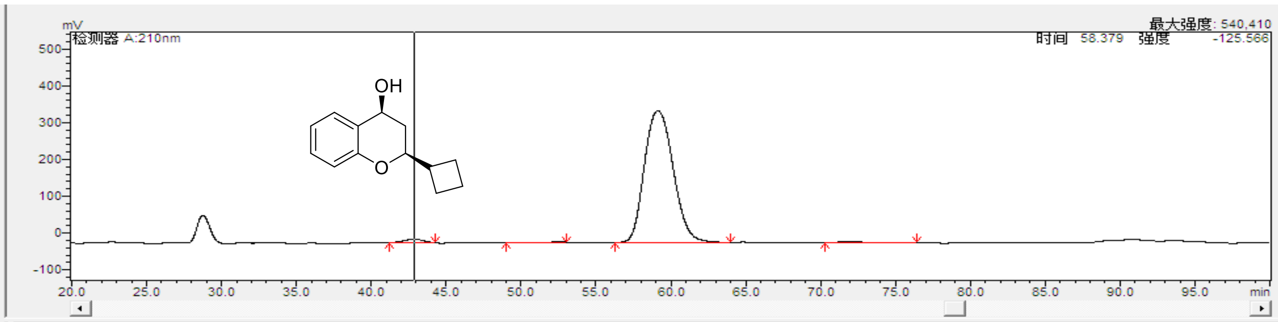
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*S*)-7bl: (2S,4S)-2-cyclobutylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 99/1, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

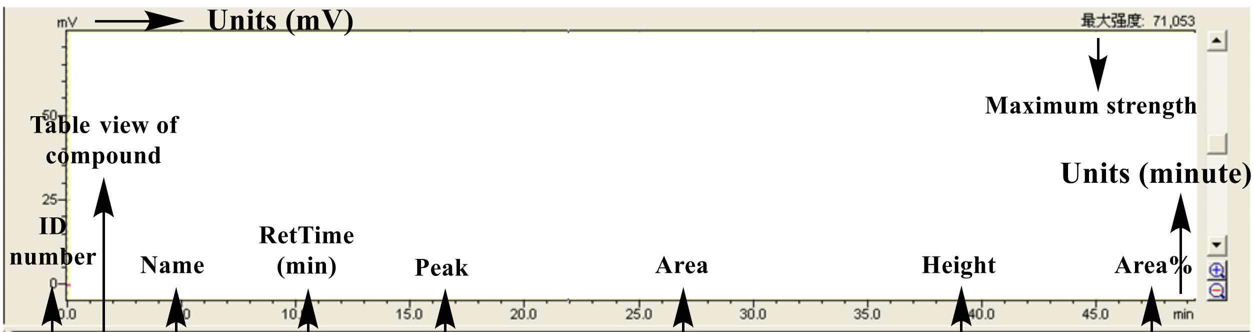
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT43.342	43.342	1	3933525	40905	1.9785
2	RT50.201	50.201	2	3655494	32107	1.8387
3	RT60.991	60.991	3	93326789	674510	46.9424
4	RT72.788	72.788	4	97895422	522851	49.2404



化合物表视图

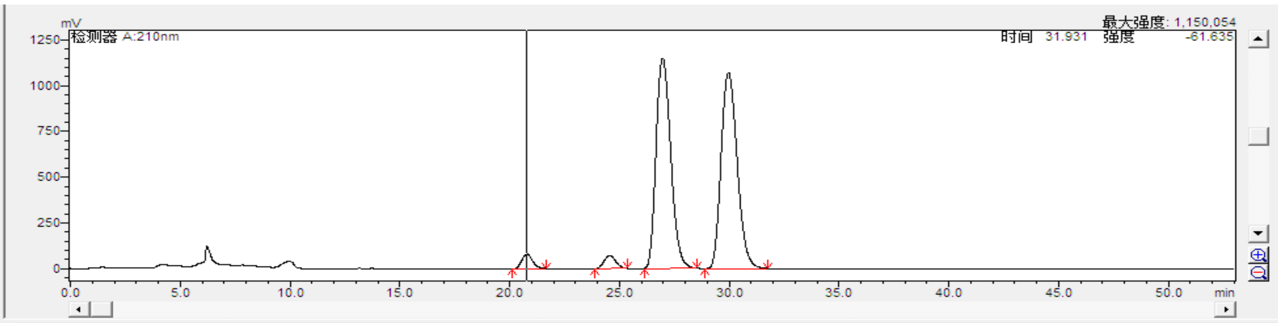
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT42.851	42.851	1	842013	9221	1.7205
2	RT52.458	52.458	2	49742	650	0.1016
3	RT59.124	59.124	3	47969524	357484	98.0158
4	RT71.955	71.955	4	79323	1599	0.1621

Translation of all characters (Chinese) in the above two frameworks to English is as follows:



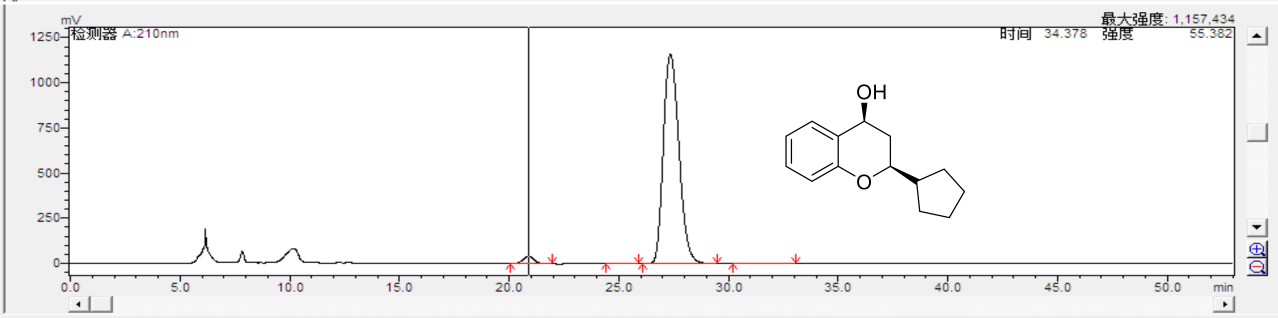
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*S*,*S*)-7bm: (2*S*,4*S*)-2-cyclopentylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).



化合物表视图

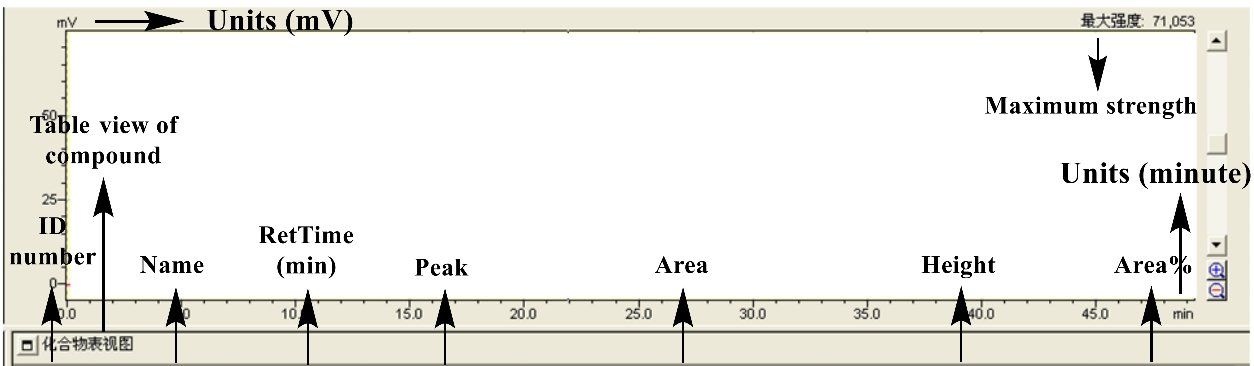
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.780	20.780	1	2776674	82292	2.4493
2	RT24.548	24.548	2	2633373	71353	2.3229
3	RT26.965	26.965	3	53389214	1149148	47.0950
4	RT29.960	29.960	4	54565680	1072049	48.1328



化合物表视图

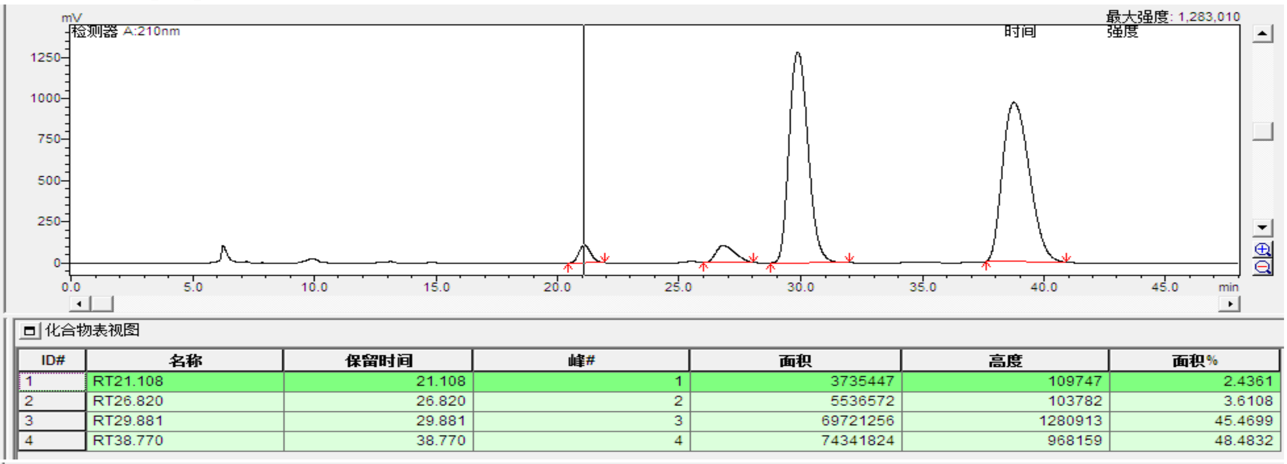
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.864	20.864	1	1270840	38379	2.1646
2	RT24.856	24.856	2	49028	982	0.0835
3	RT27.348	27.348	3	57342524	1158838	97.6723
4	RT31.045	31.045	4	46729	1888	0.0796

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>

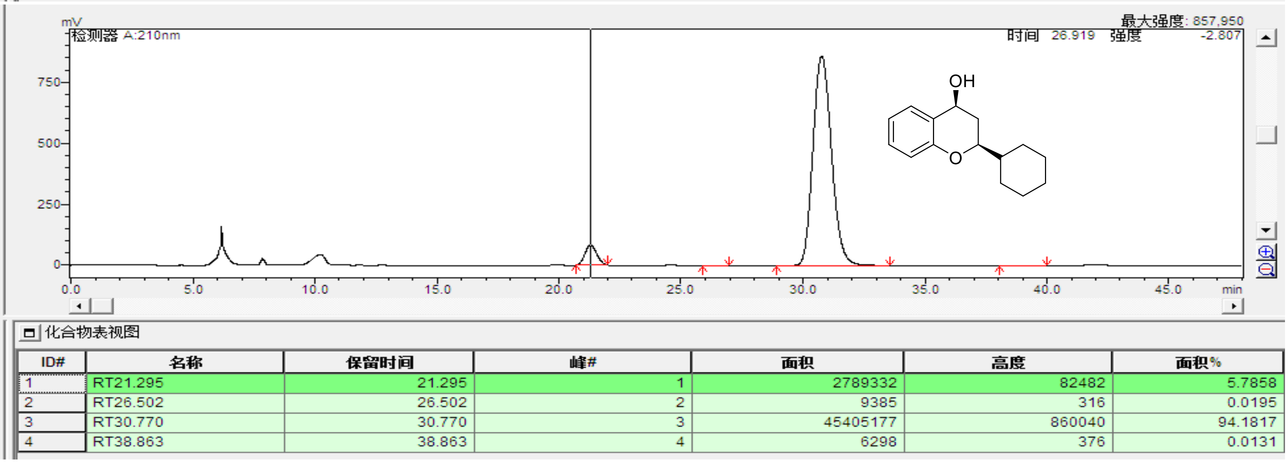


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*S*,*S*)-7bn: (2*S*,4*S*)-2-cyclohexylchroman-4-ol (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).

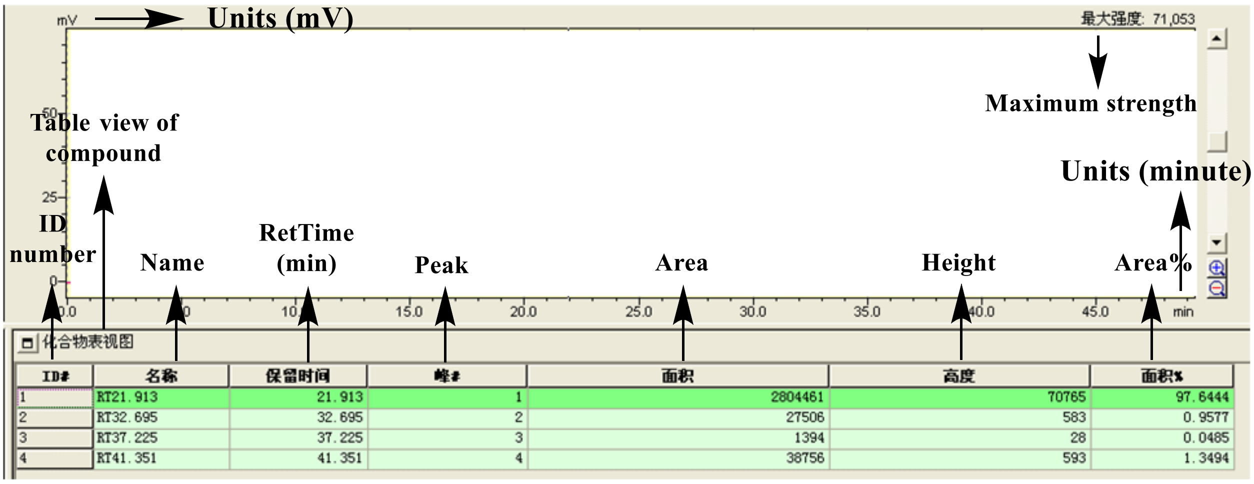


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.108	21.108	1	3735447	109747	2.4361
2	RT26.820	26.820	2	5536572	103782	3.6108
3	RT29.881	29.881	3	69721256	1280913	45.4699
4	RT38.770	38.770	4	74341824	968159	48.4832



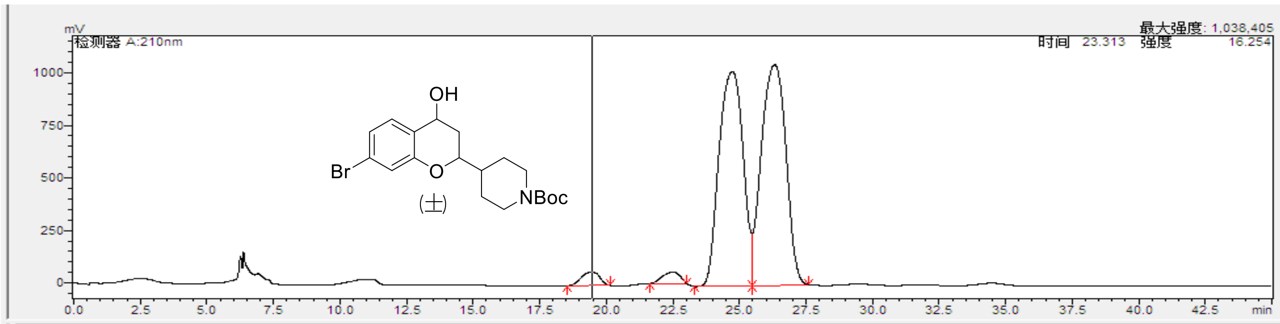
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.295	21.295	1	2789332	82482	5.7858
2	RT26.502	26.502	2	9385	316	0.0195
3	RT30.770	30.770	3	45405177	860040	94.1817
4	RT38.863	38.863	4	6298	376	0.0131

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>

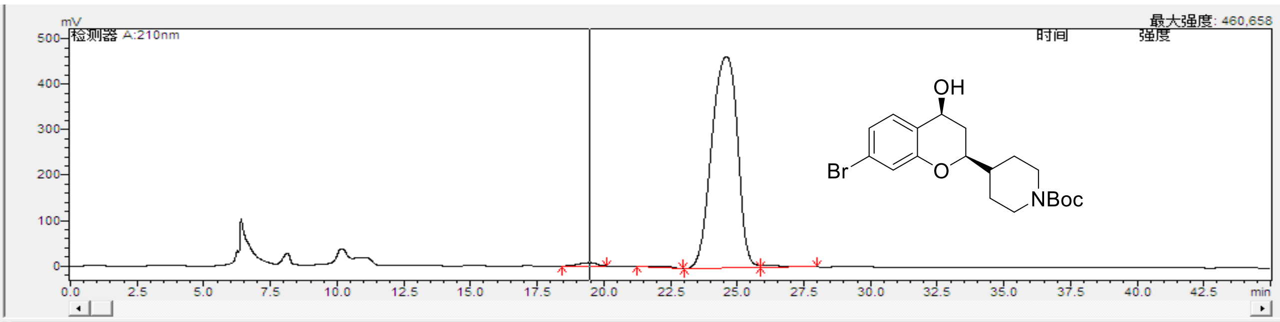


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

(*S*,*S*)-7bo: tert-butyl 4-((2*S*,4*S*)-7-bromo-4-hydroxychroman-2-yl)piperidine-1-carboxylate (HPLC: Chiracel AD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0mL/min, 25 ℃).

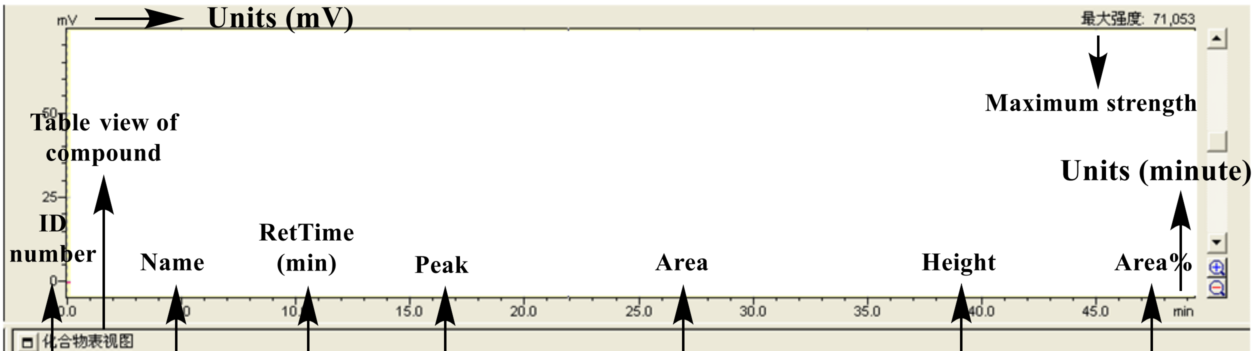


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.458	19.458	1	3071635	64557	2.2327
2	RT22.493	22.493	2	2457290	53305	1.7862
3	RT24.727	24.727	3	64538483	1019441	46.9120
4	RT26.323	26.323	4	67505986	1048613	49.0691



ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.473	19.473	1	342721	7479	1.0643
2	RT22.128	22.128	2	198235	3442	0.6156
3	RT24.591	24.591	3	31349527	465276	97.3503
4	RT25.883	25.883	4	312312	4701	0.9698

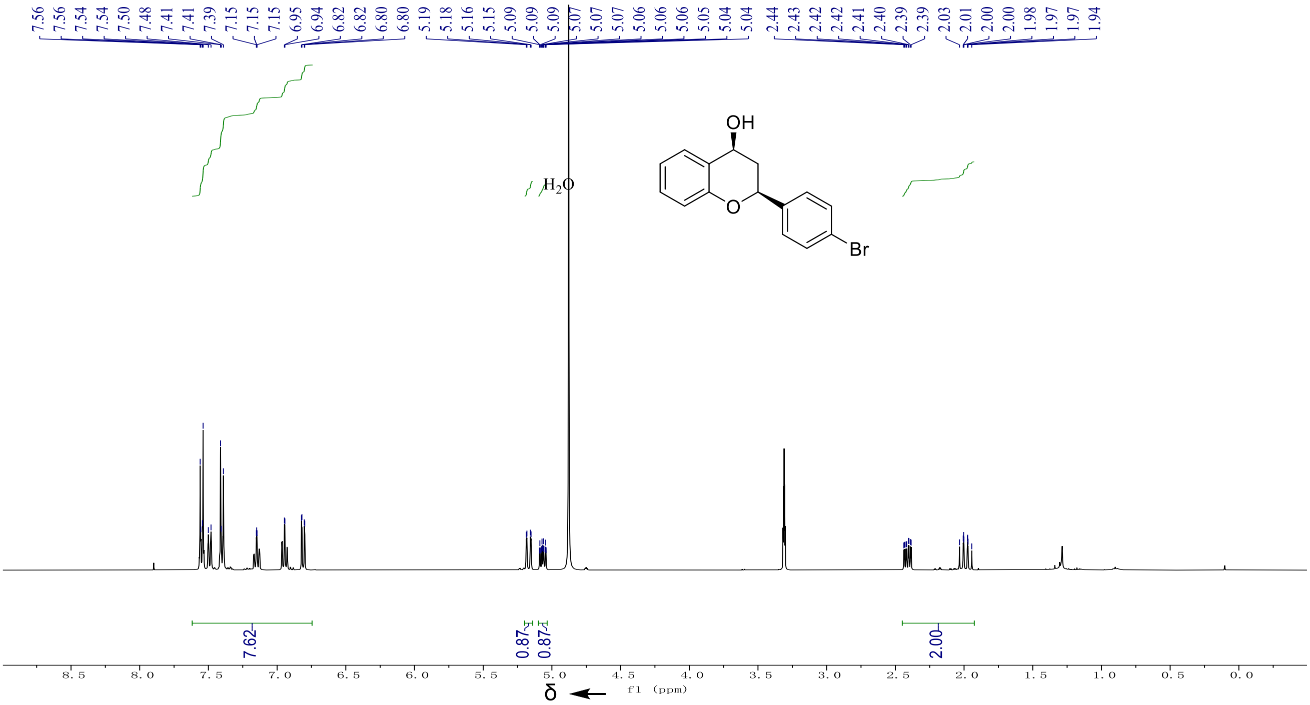
<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>

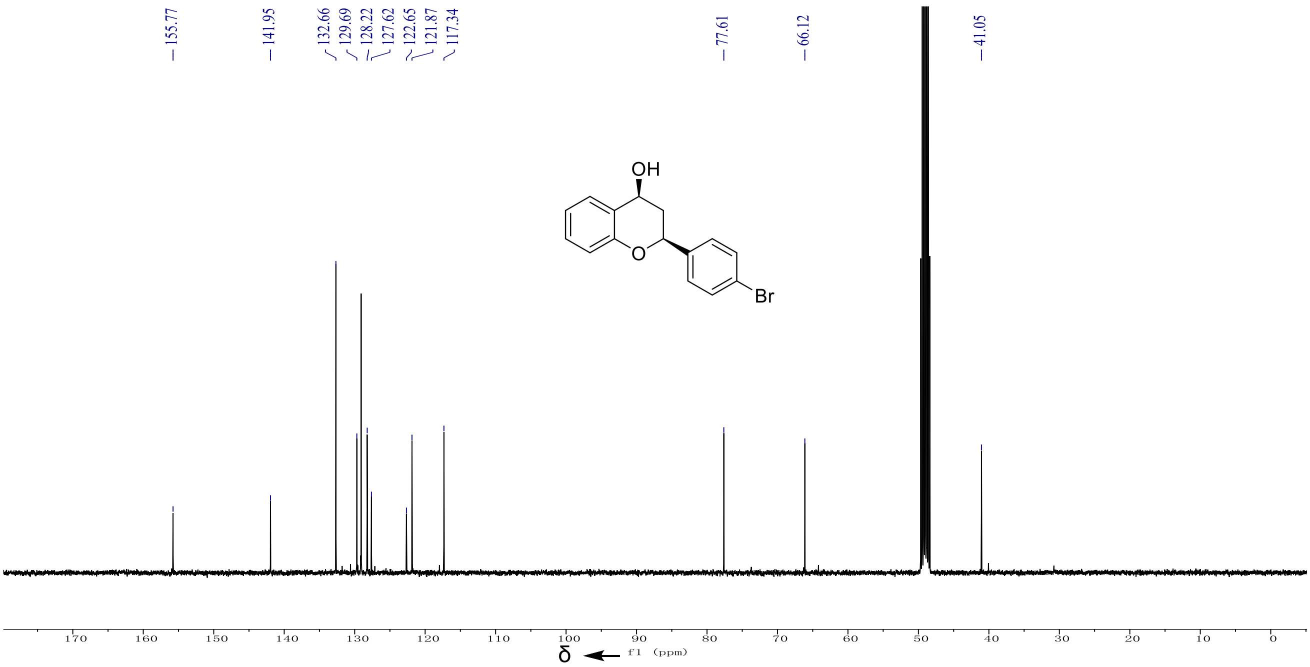


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

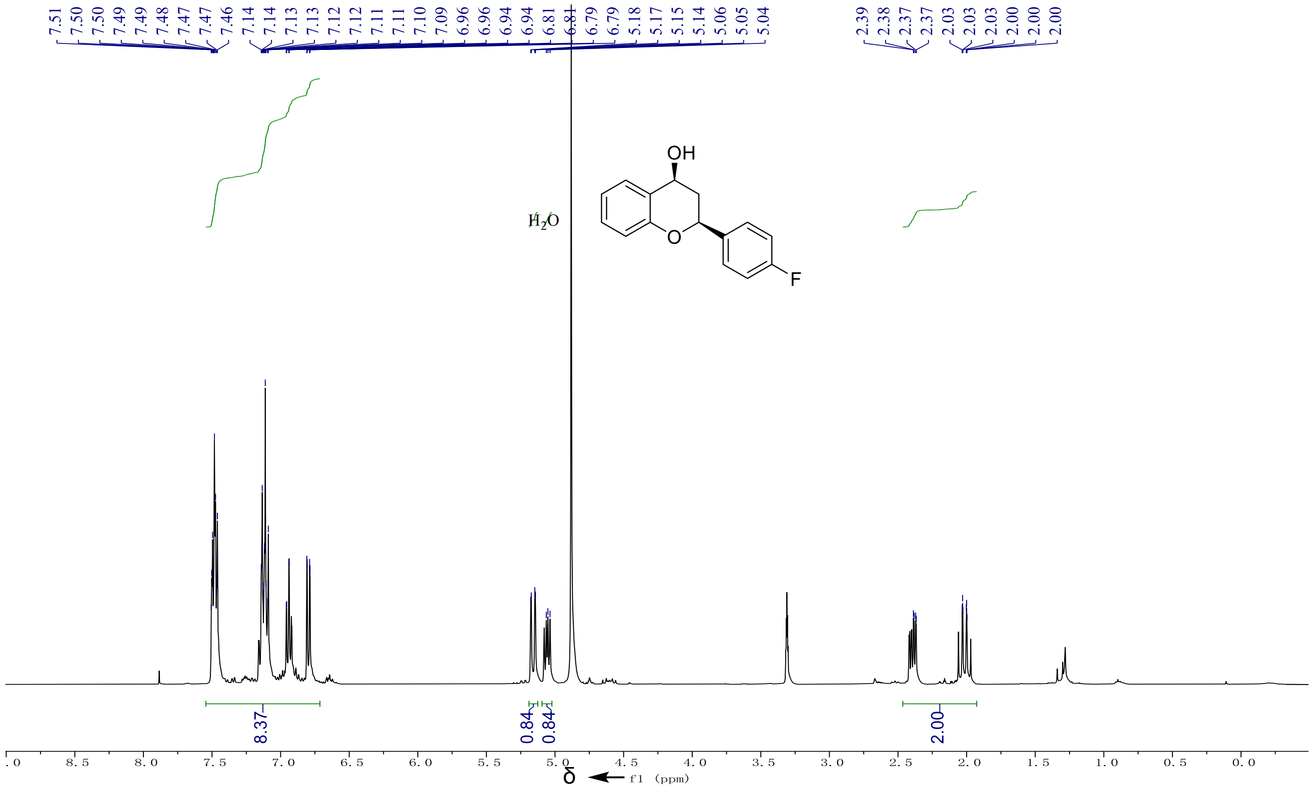
Figure S7. Characterizations of chiral products (^{1}H NMR, ^{13}C NMR, and LC/MS spectra).

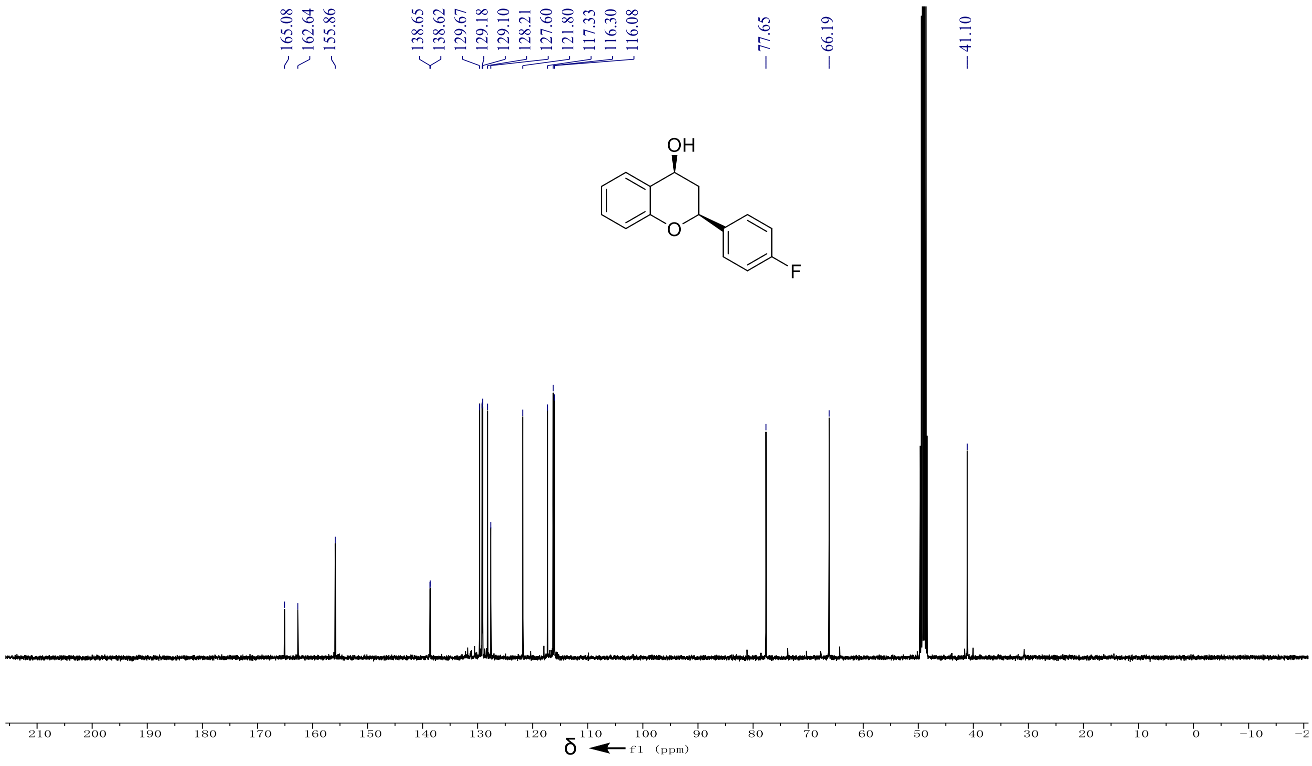
(*S*,*S*)-7aa: (2S,4S)-2-(4-bromophenyl)chroman-4-ol.



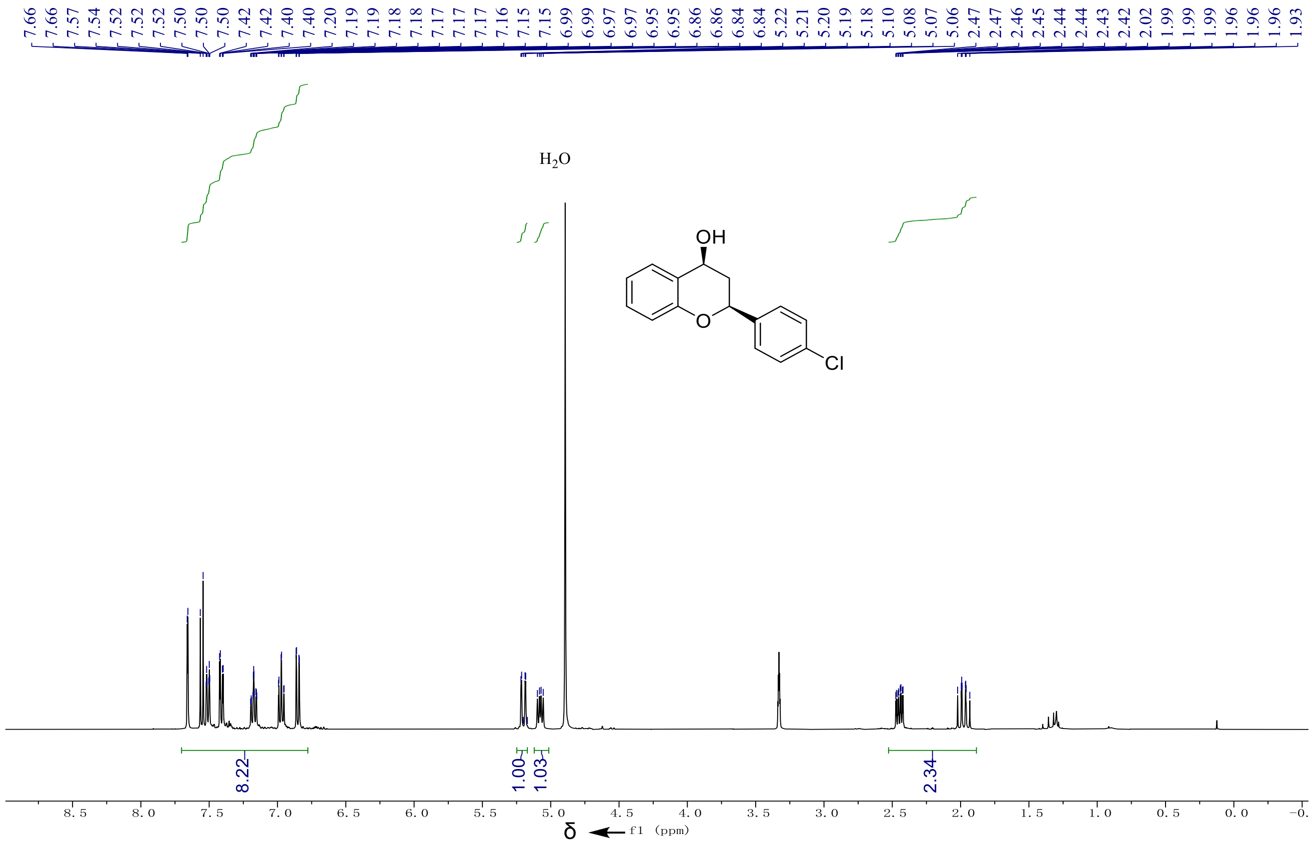


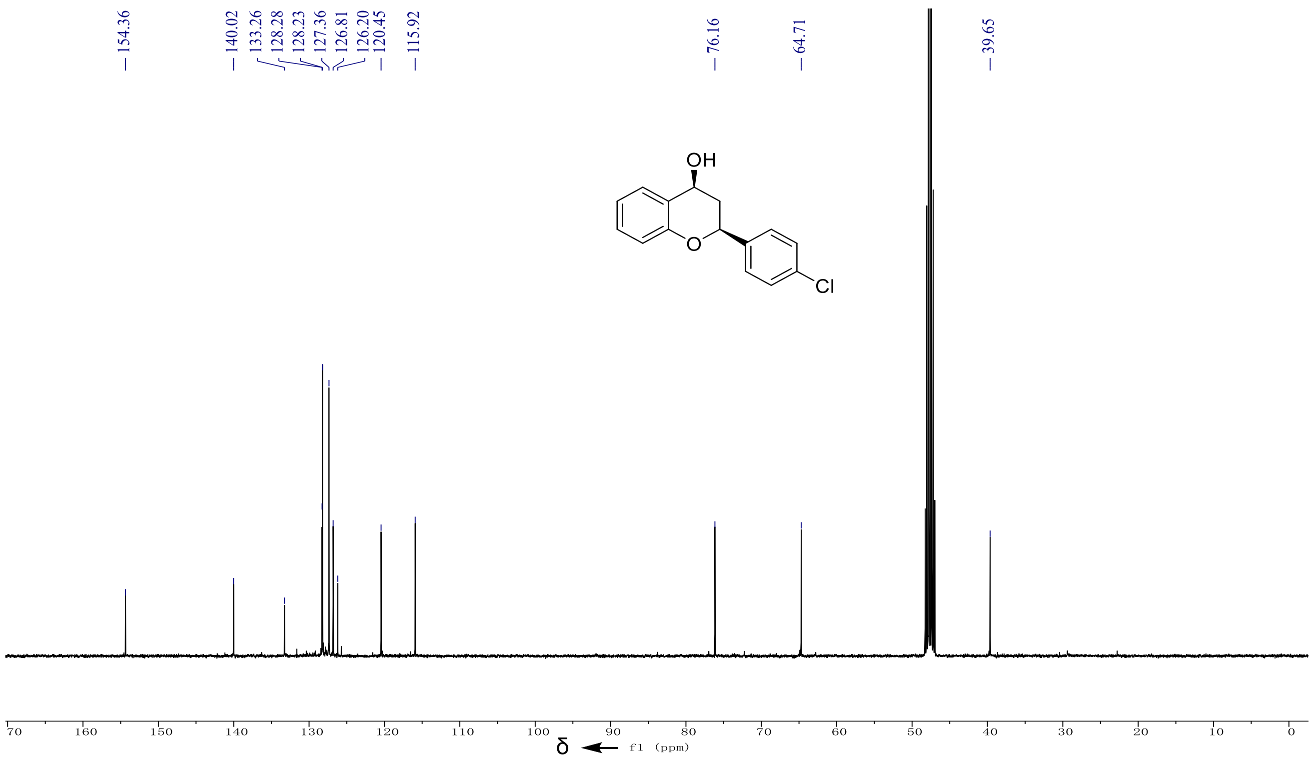
(*S*,*S*)-7ab: (2S,4S)-2-(4-fluorophenyl)chroman-4-ol.



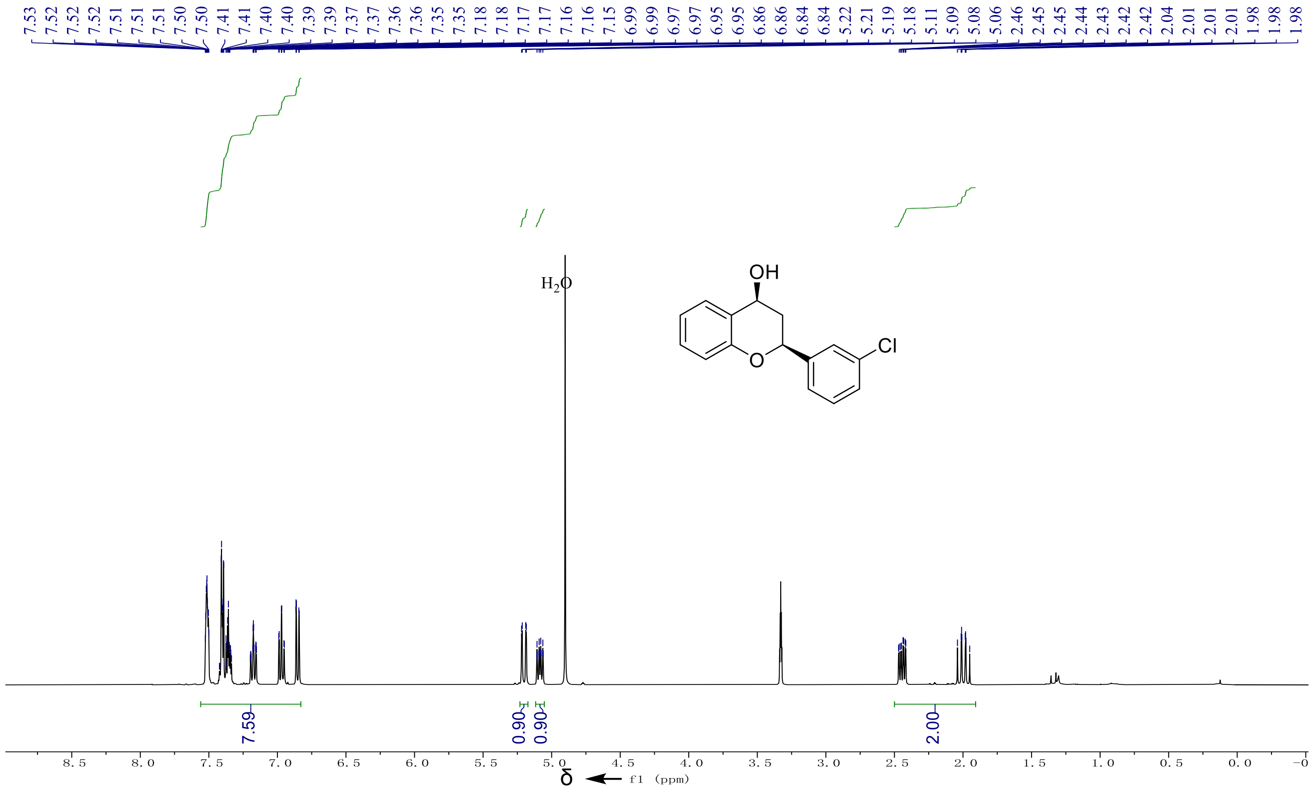


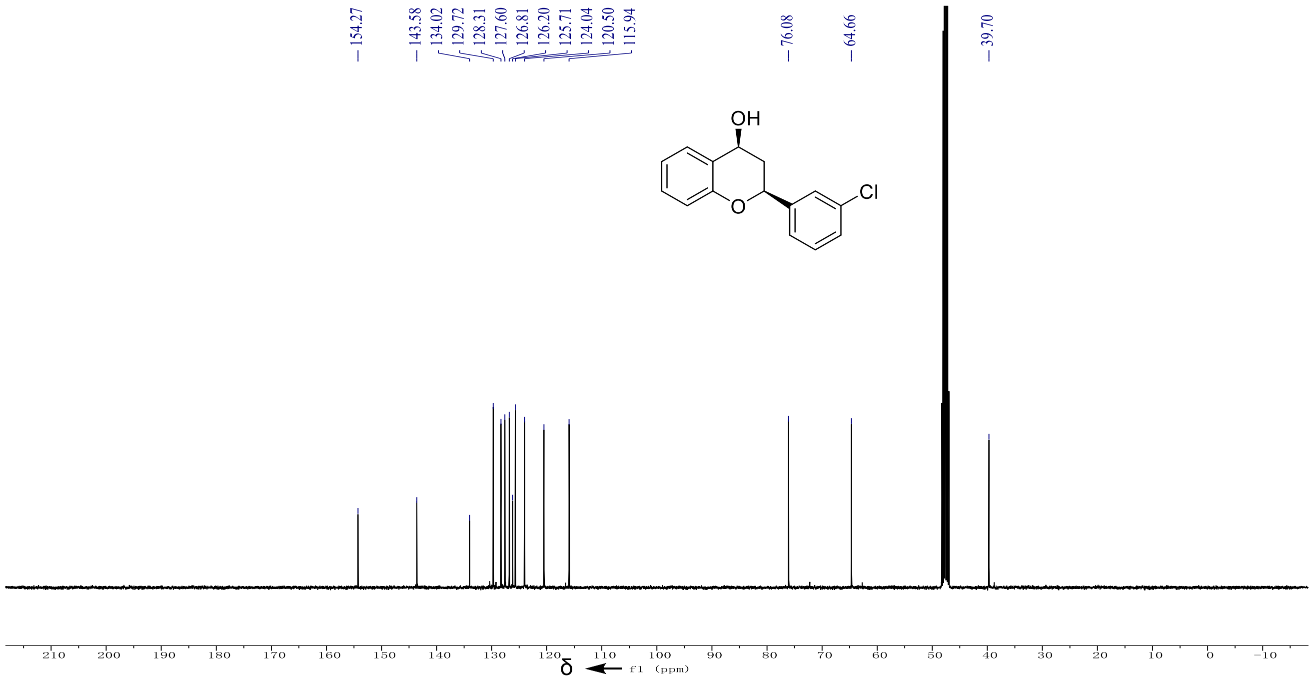
(*S*,*S*)-7ac: (2S,4S)-2-(4-chlorophenyl)chroman-4-ol.



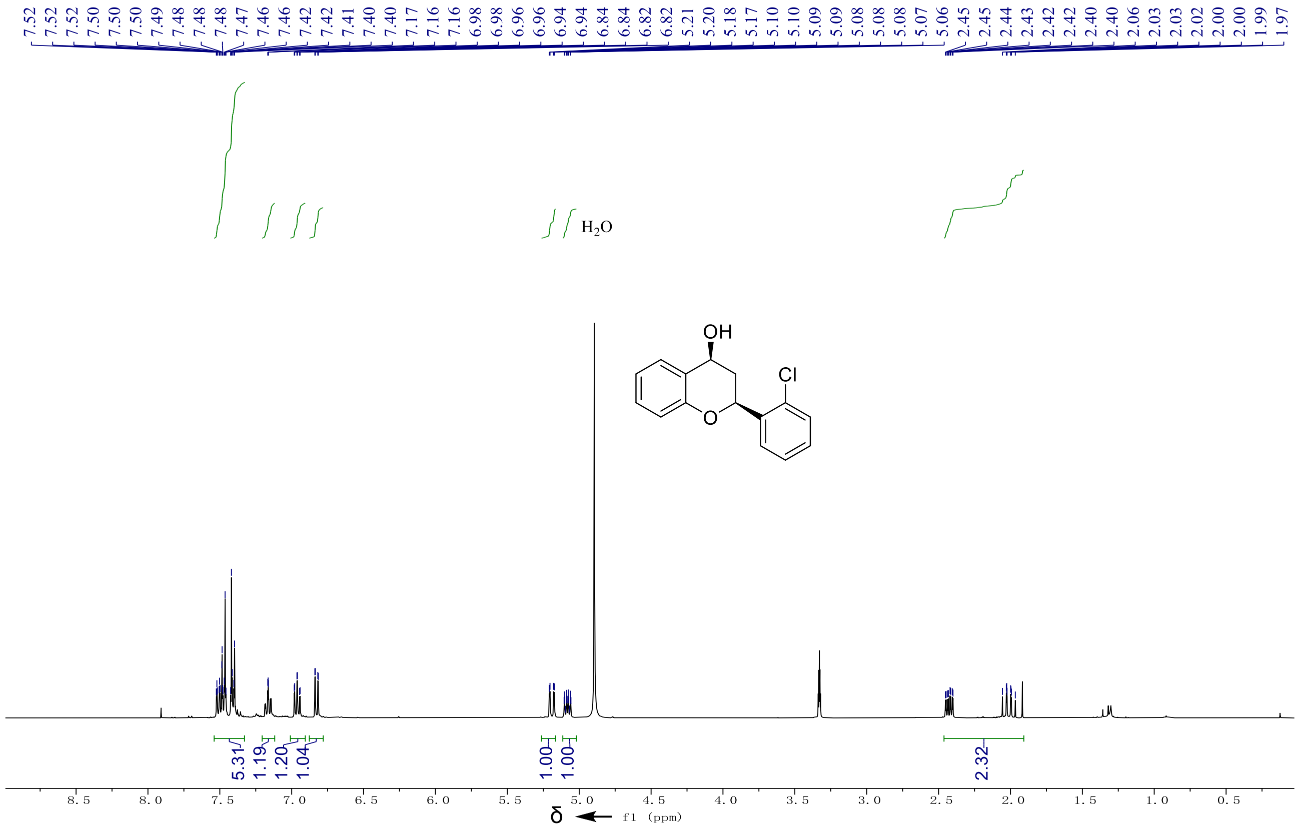


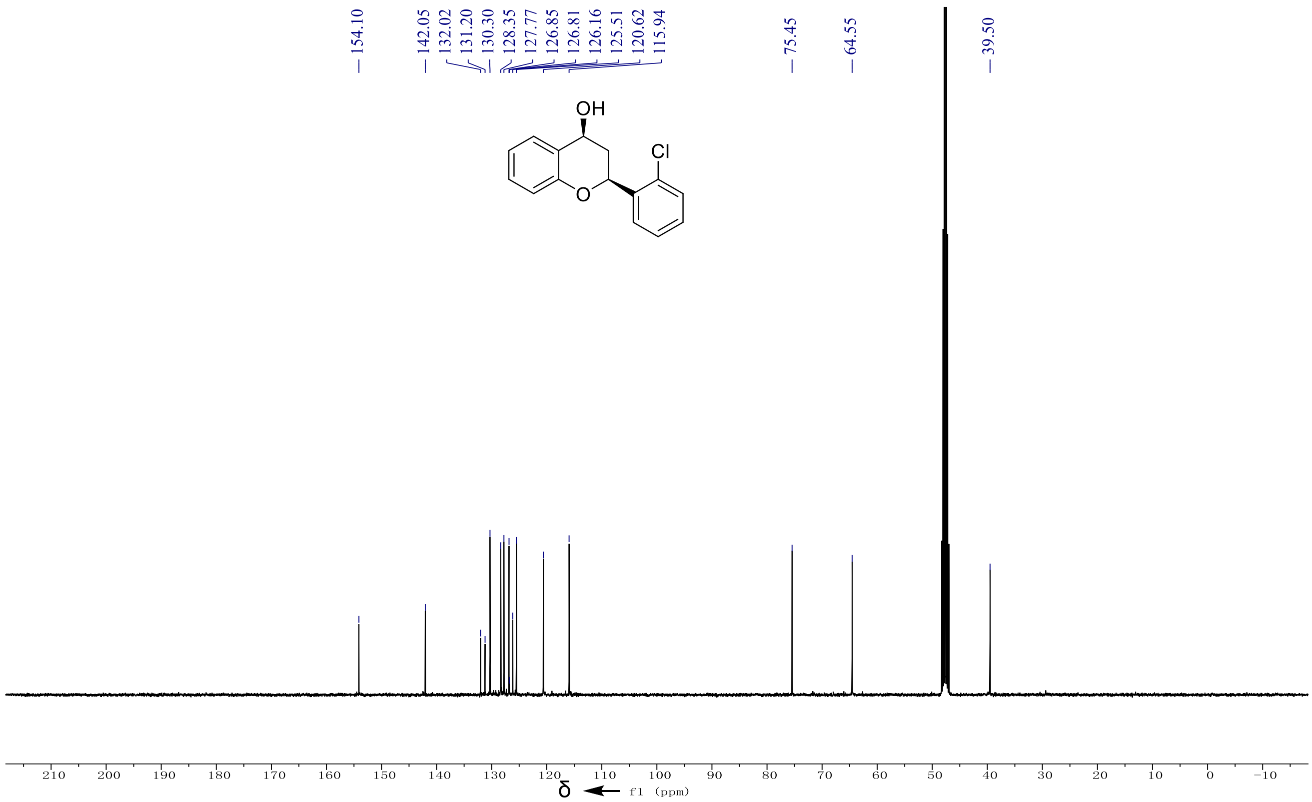
(*S*,*S*)-7ad: (2S,4S)-2-(3-chlorophenyl)chroman-4-ol.



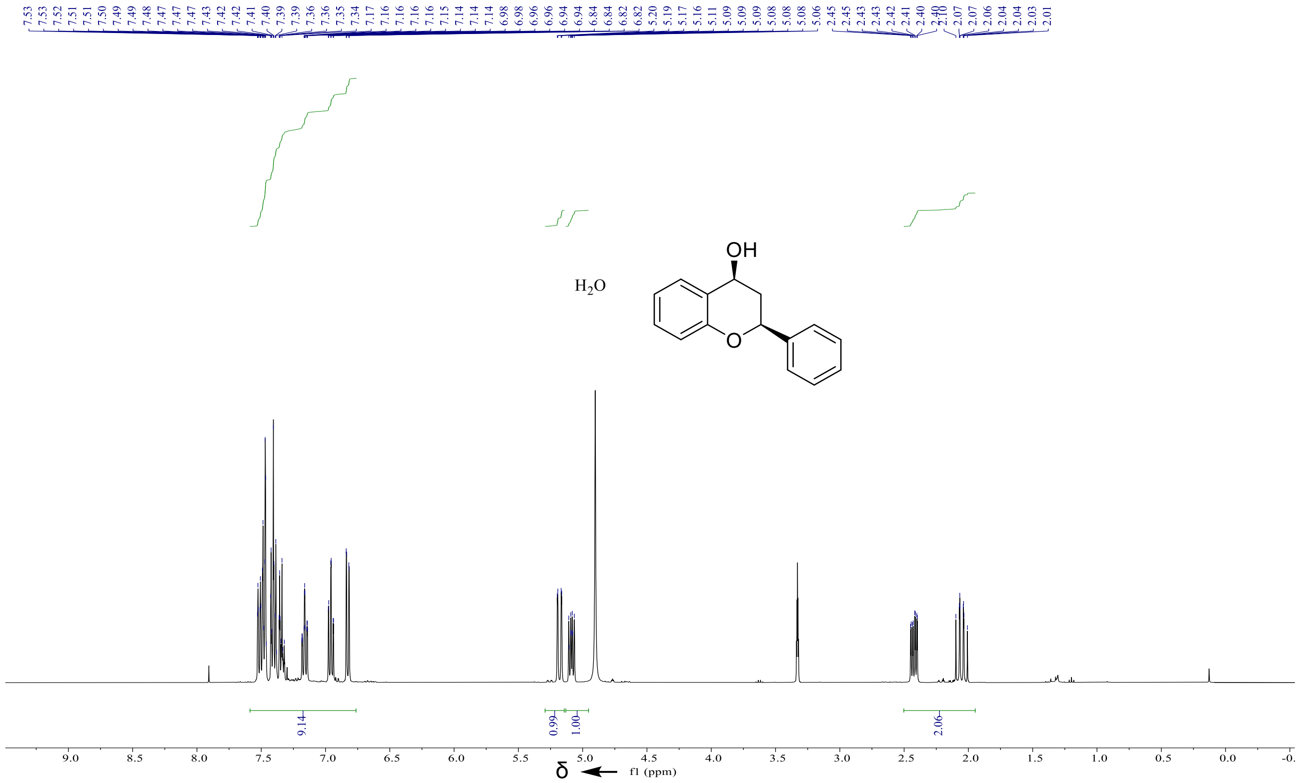


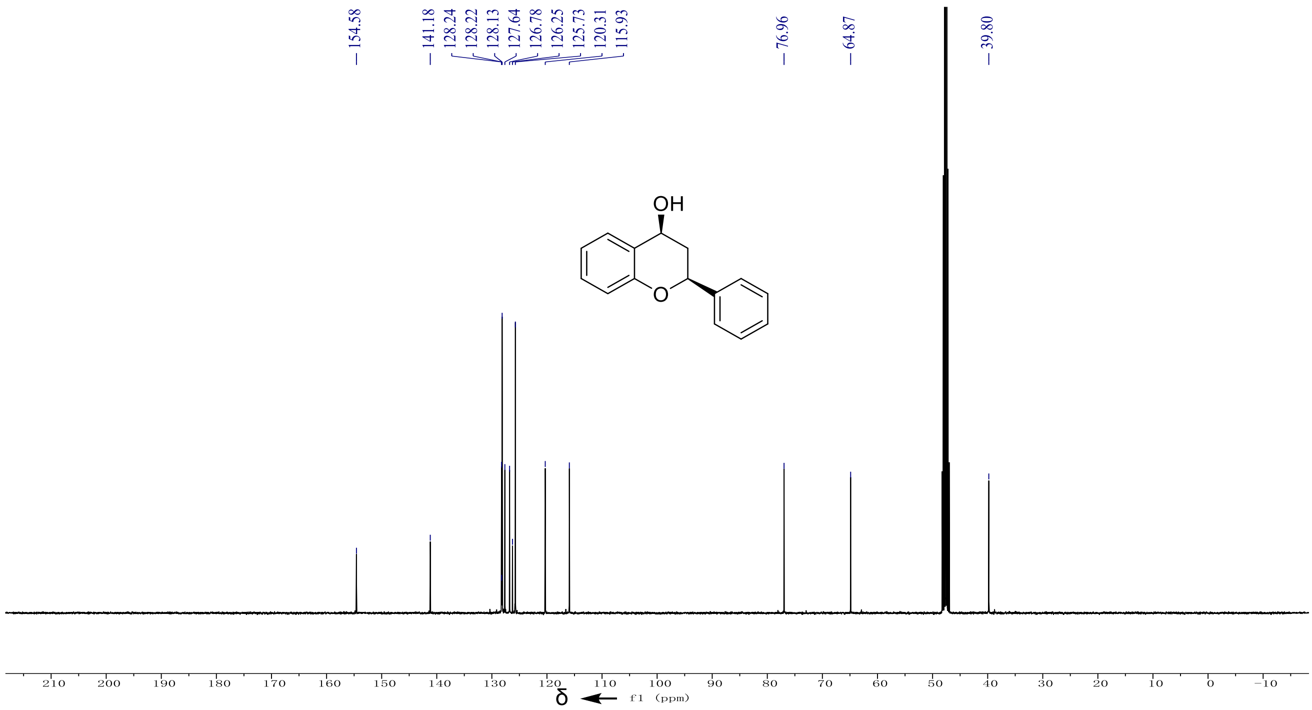
(*S*,*S*)-7ae:(2S,4S)-2-(3,4-dichlorophenyl)chroman-4-ol.



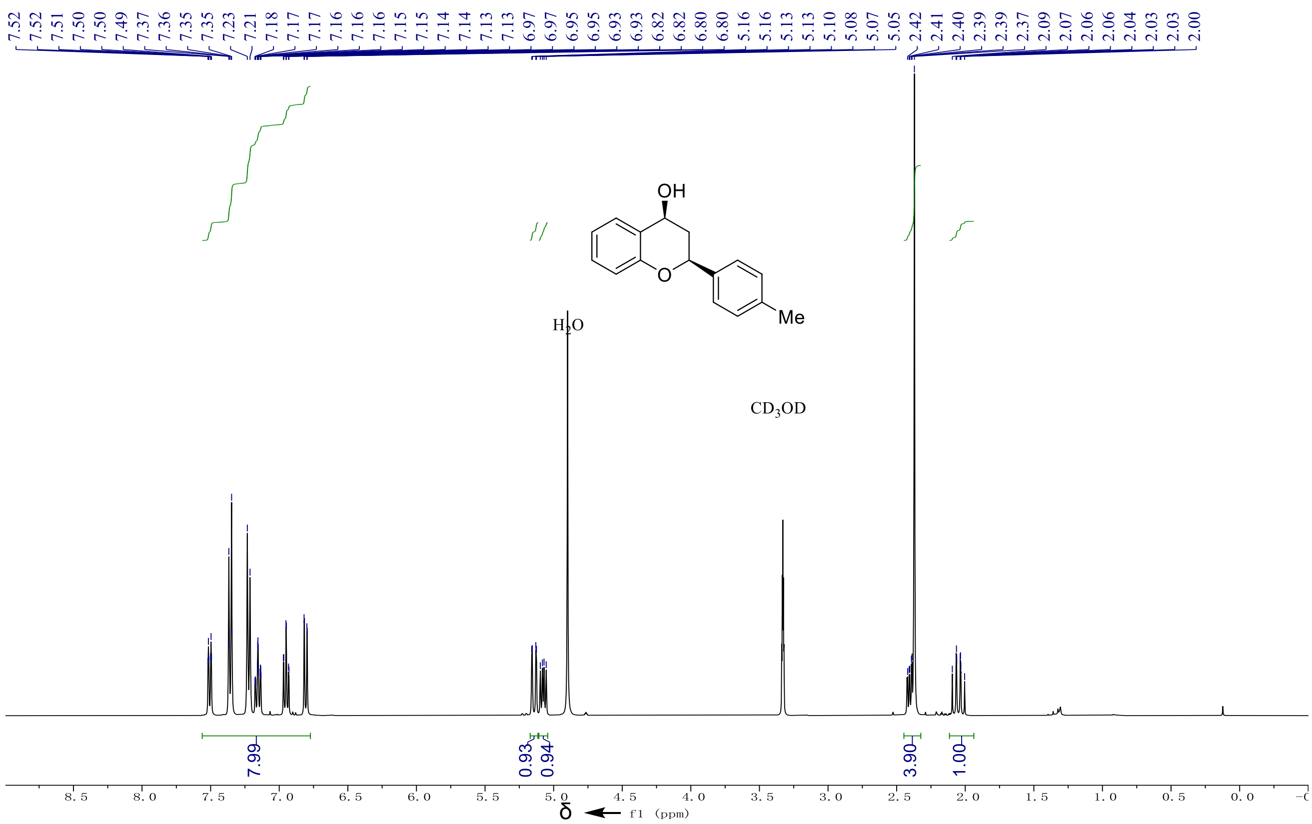


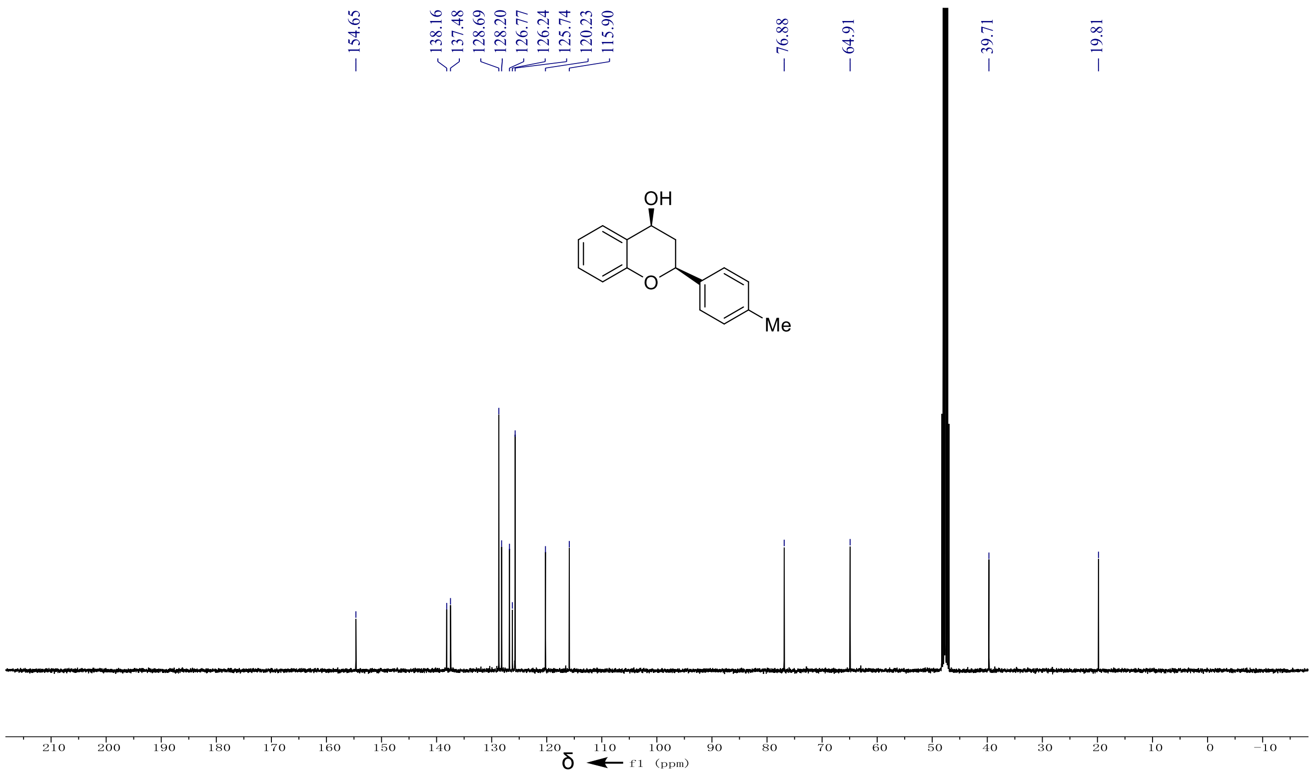
(*S*,*S*)-7af: (2S,4S)-2-phenylchroman-4-ol.



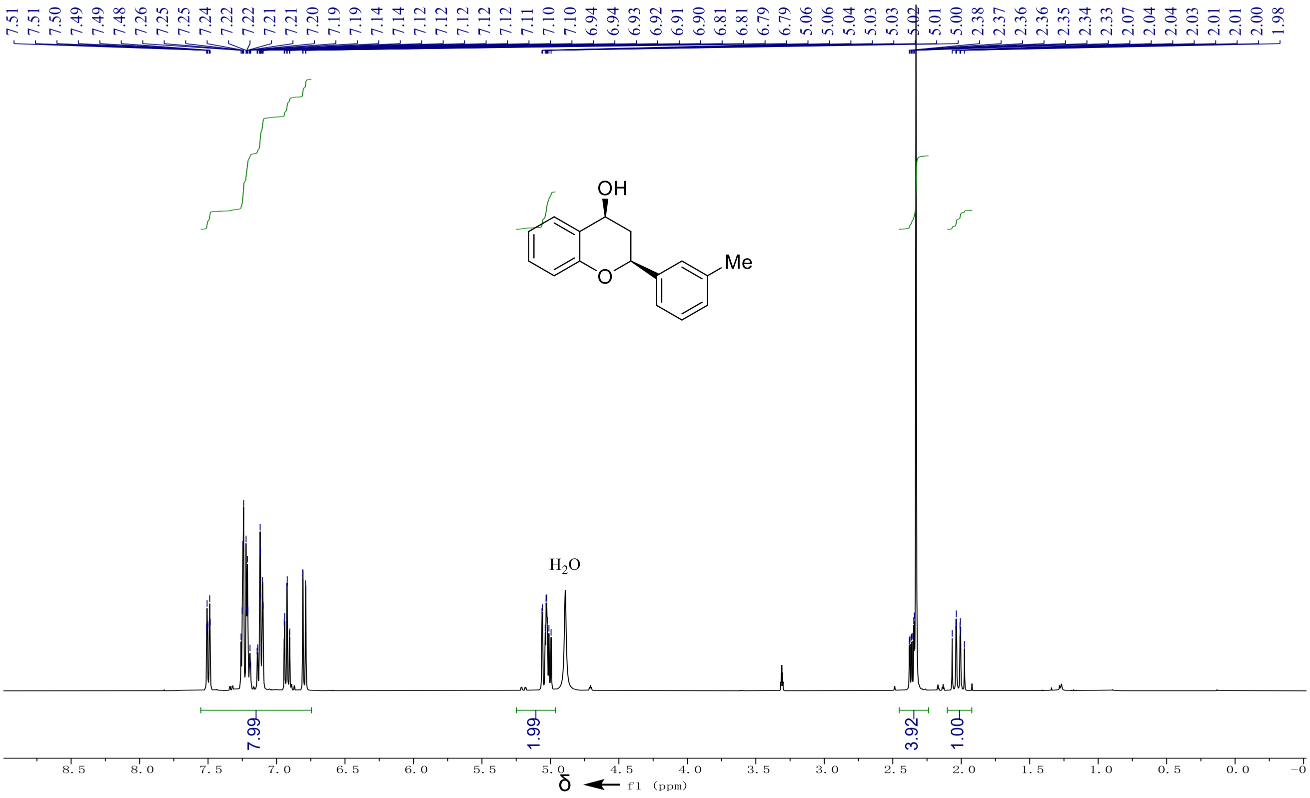


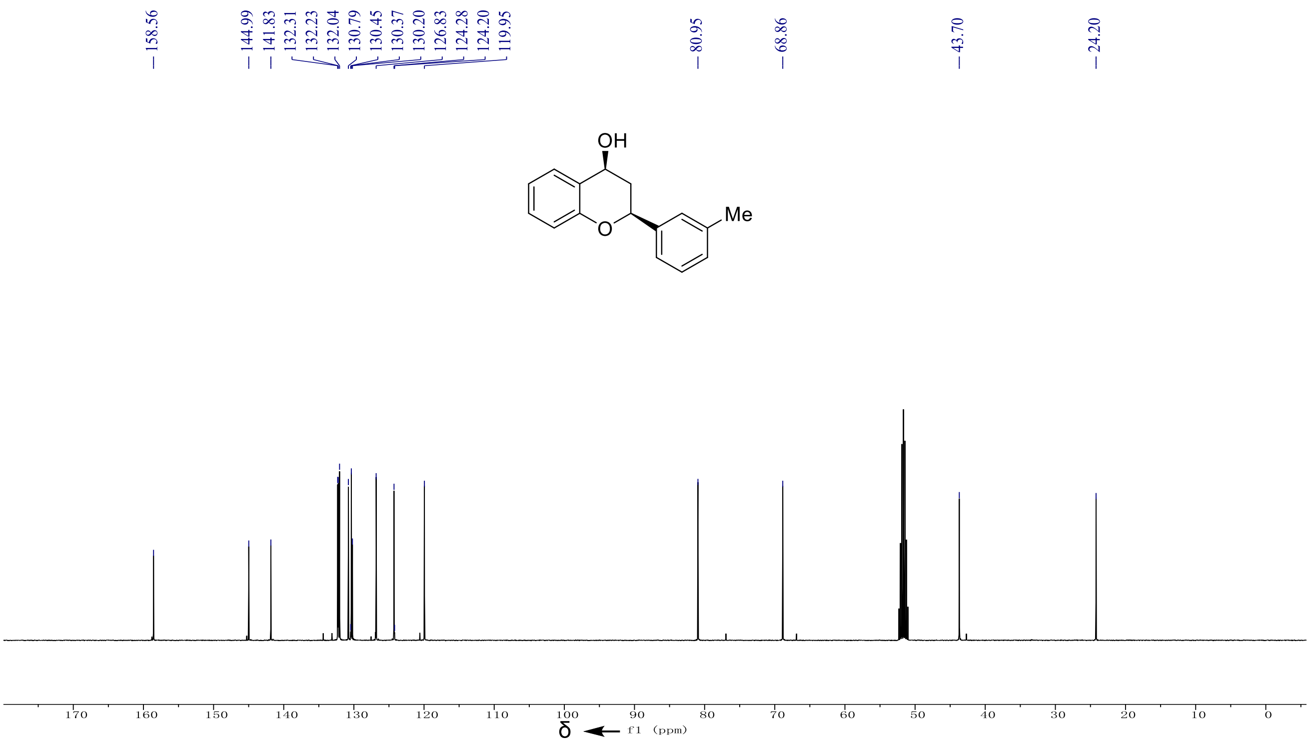
(*S*,*S*)-7ag: (2S,4S)-2-(p-tolyl)chroman-4-ol.



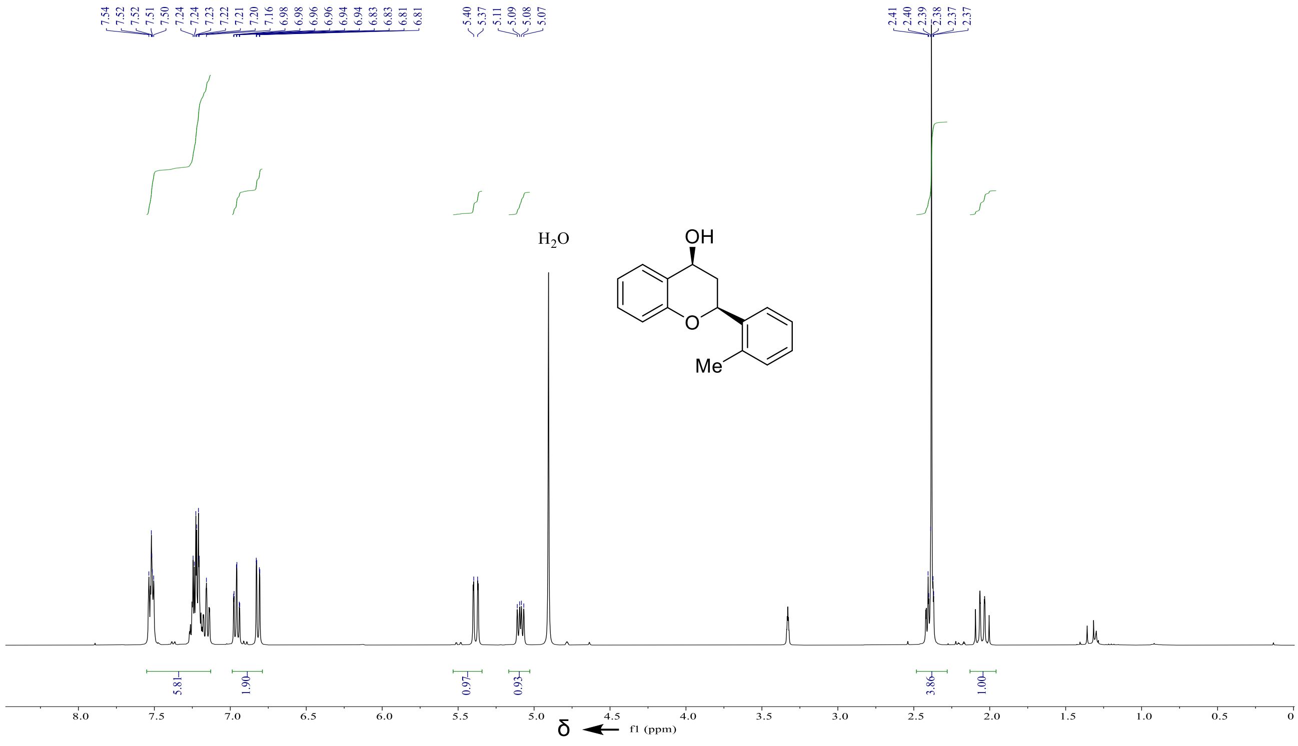


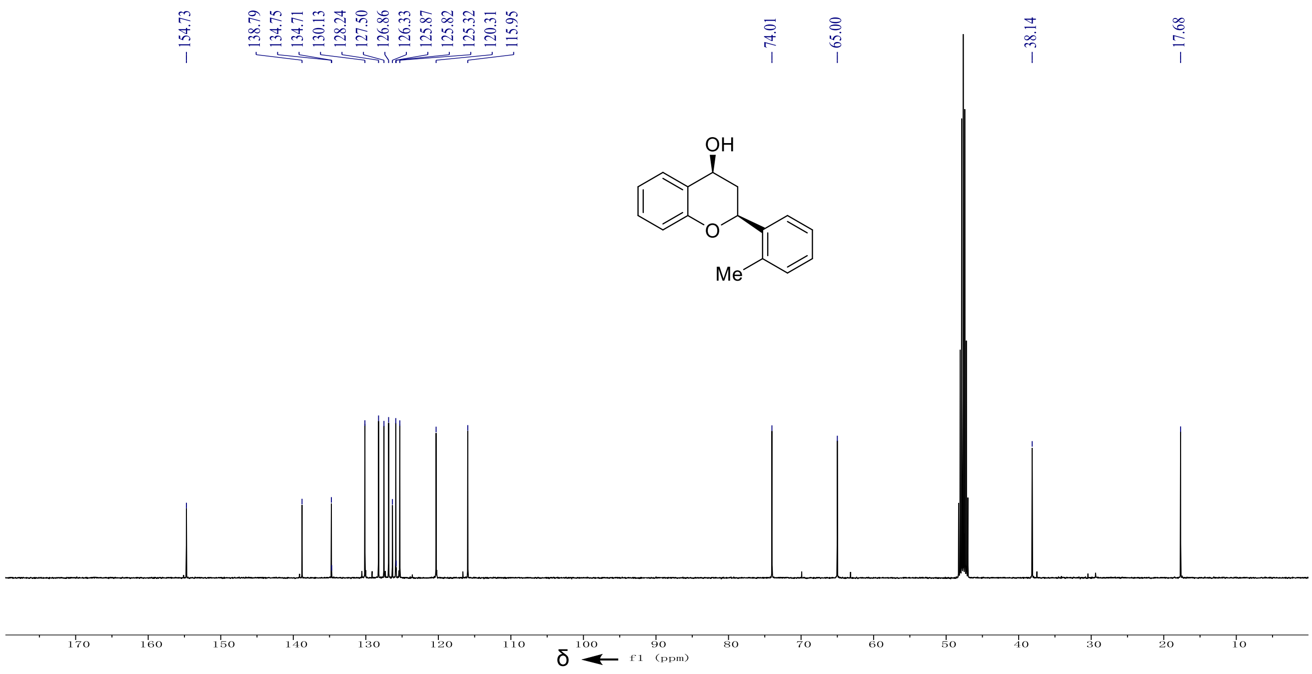
(*S*,*S*)-7ah: (2S,4S)-2-(m-tolyl)chroman-4-ol.



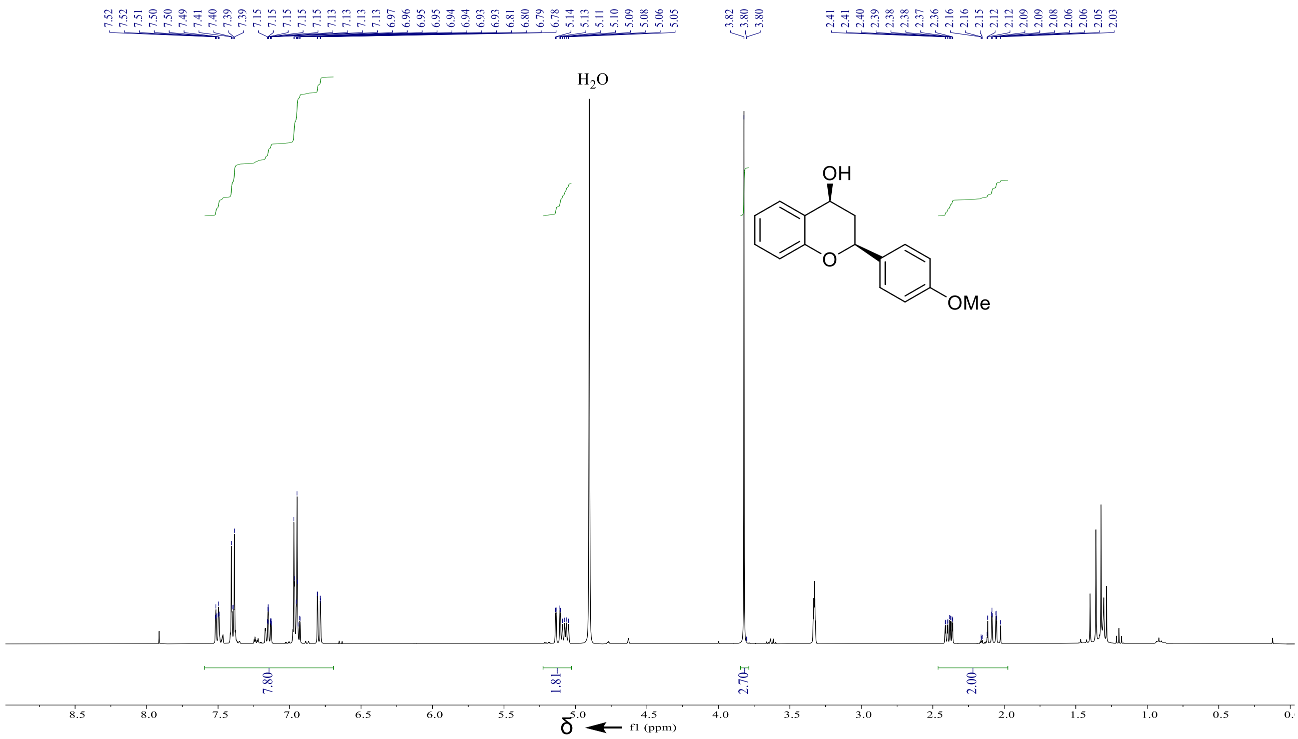


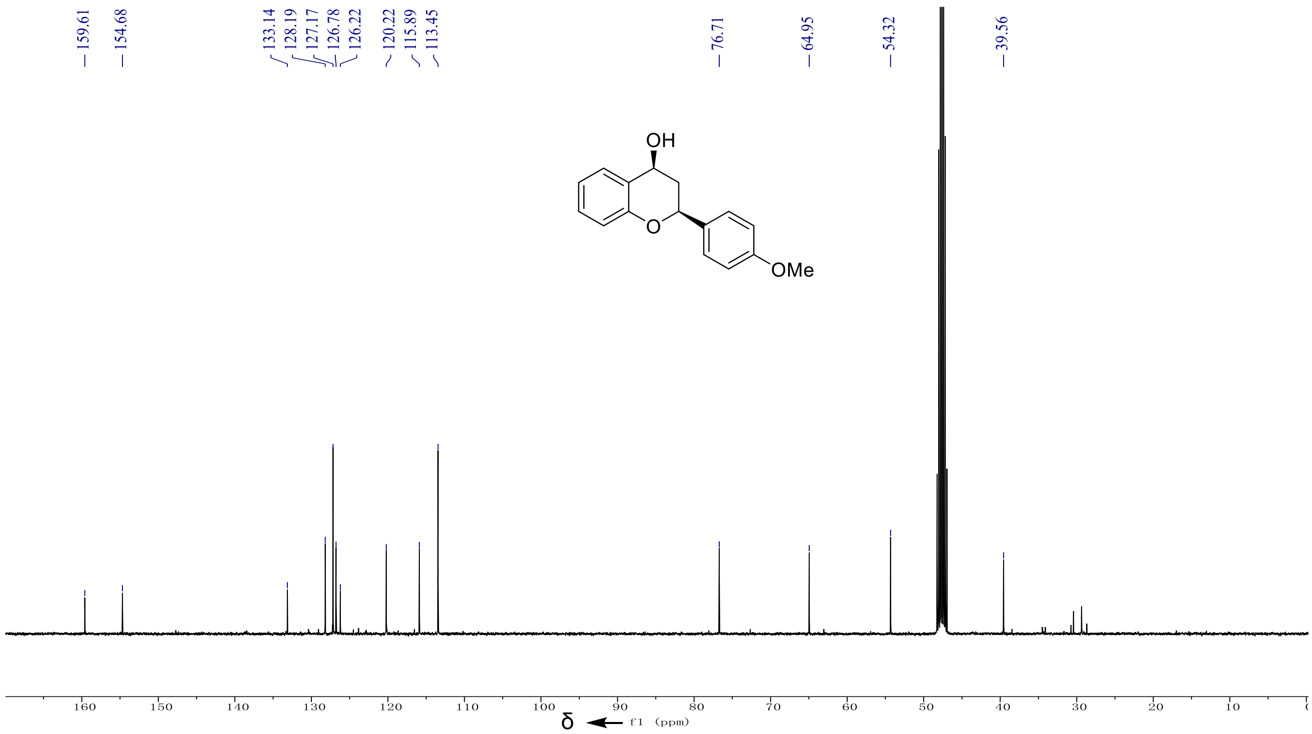
(*S*,*S*)-7ai: (2S,4S)-2-(o-tolyl)chroman-4-ol.



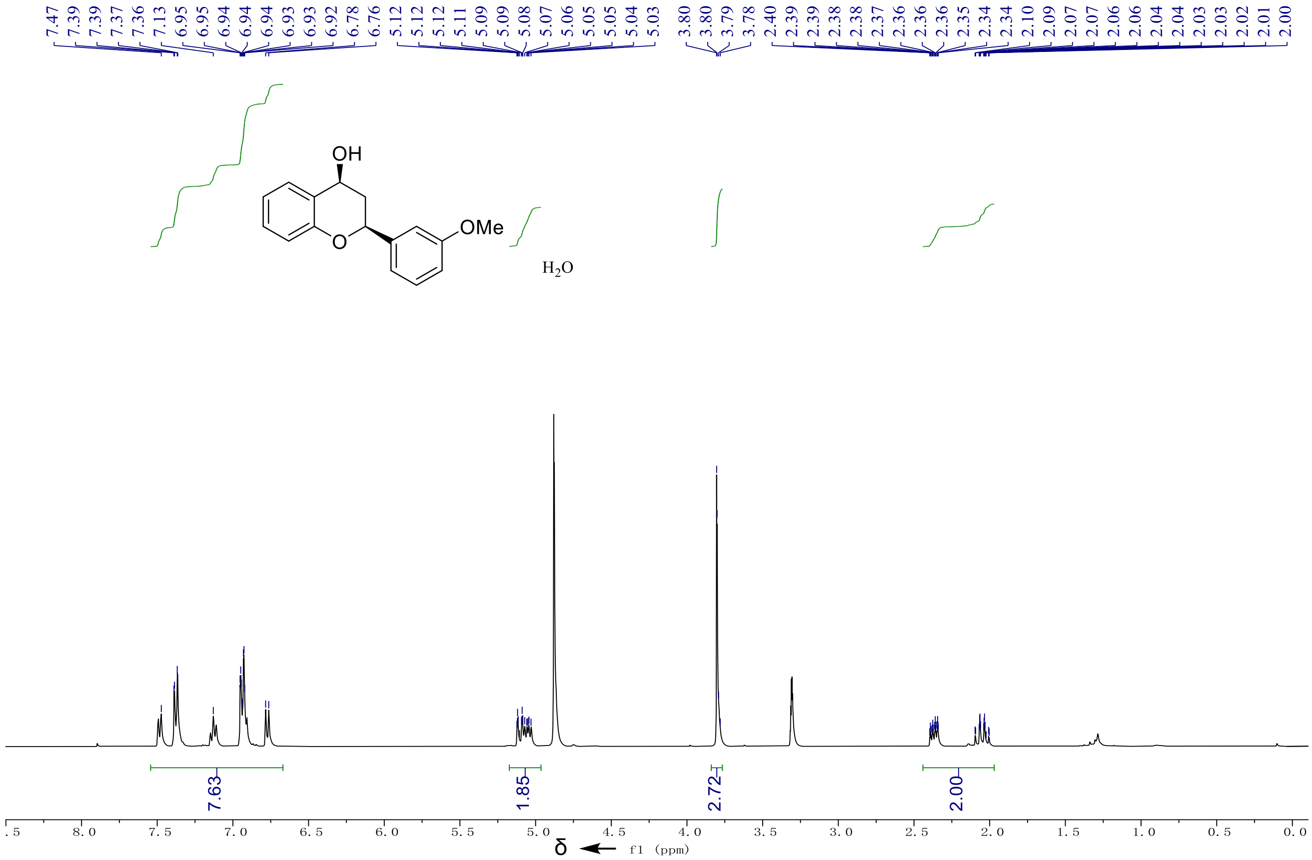


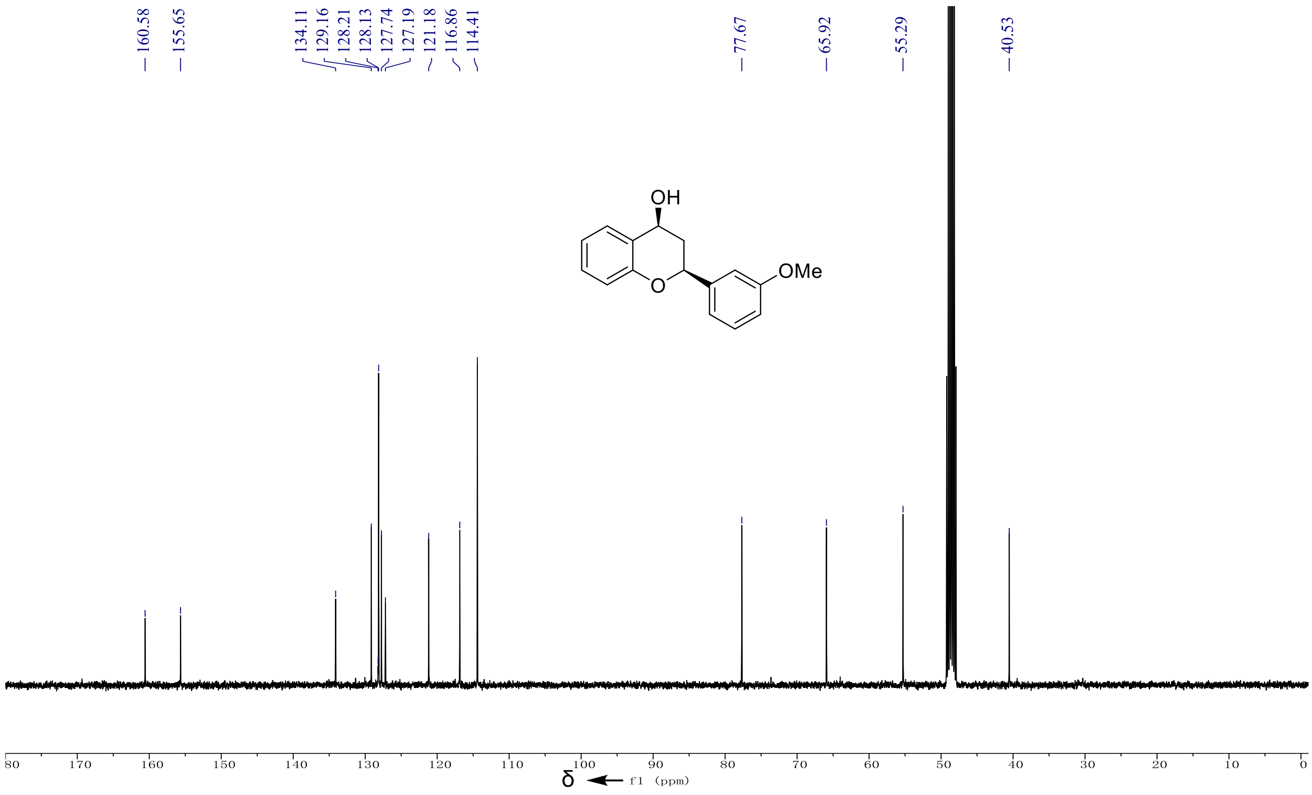
(*S*,*S*)-7aj: (2S,4S)-2-(4-methoxyphenyl)chroman-4-ol.



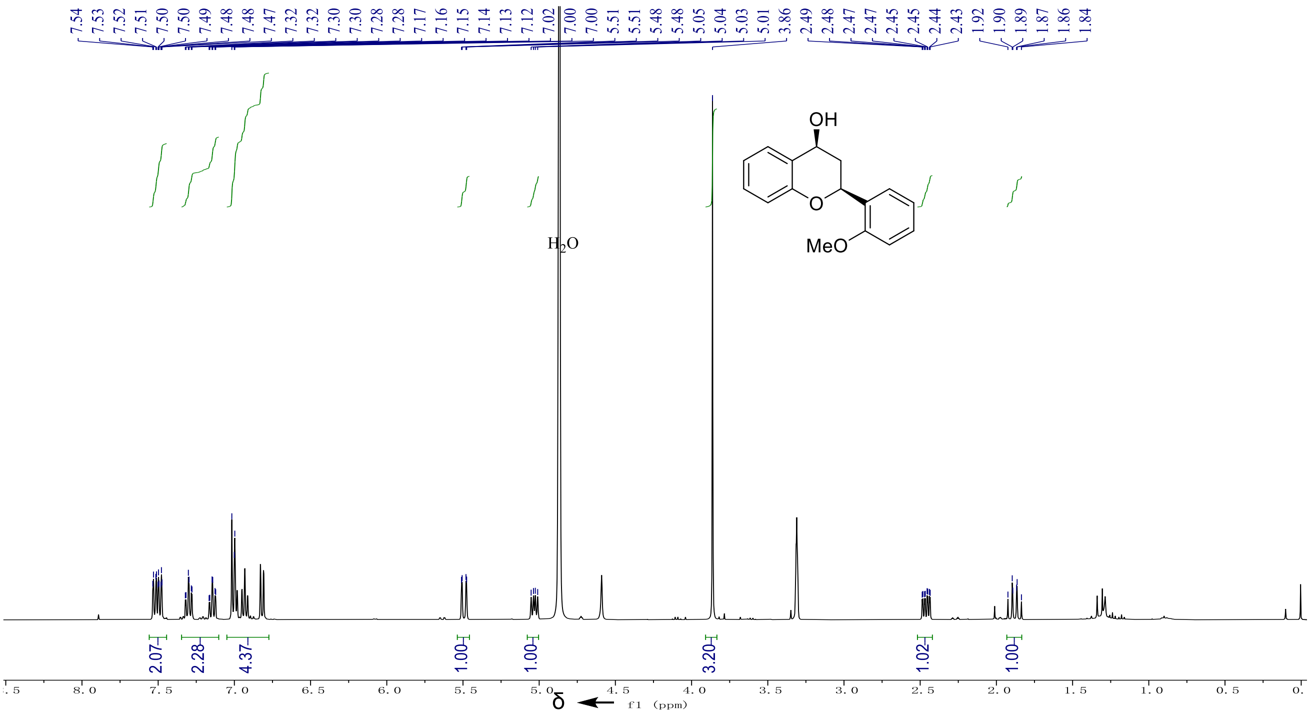


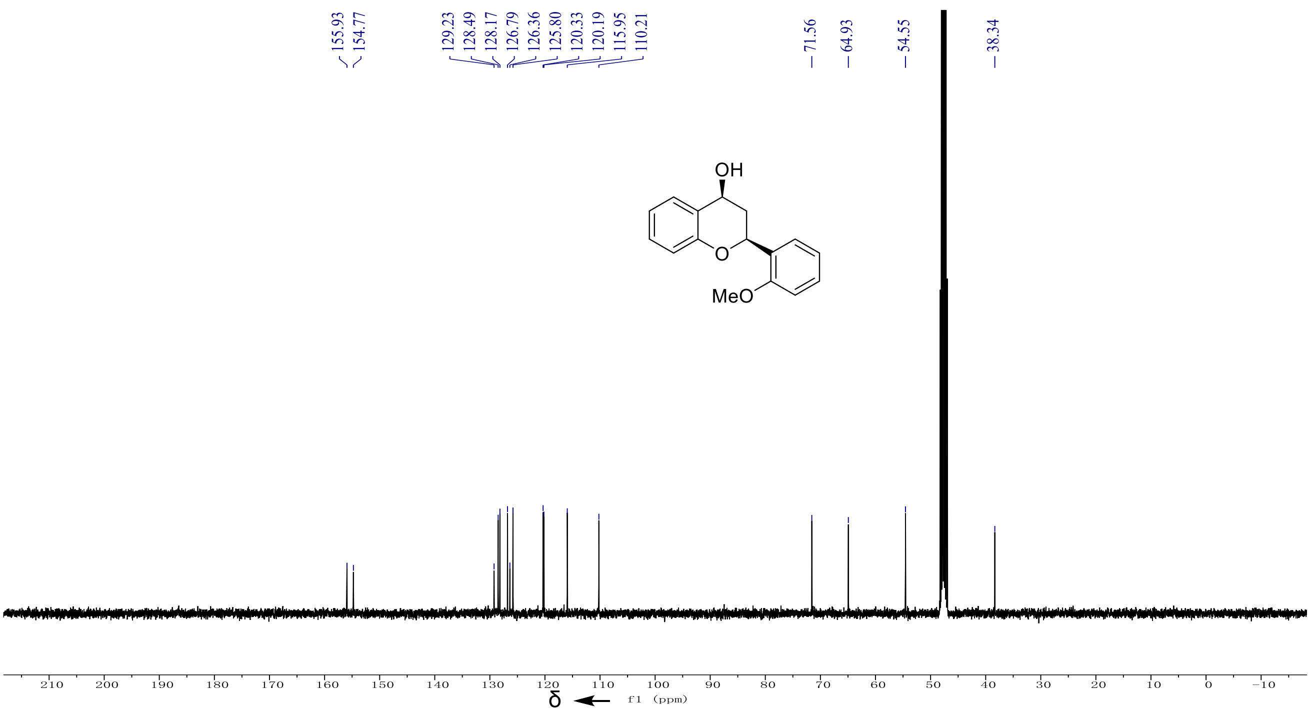
(*S*,*S*)-7ak: (2S,4S)-2-(3-methoxyphenyl)chroman-4-ol.



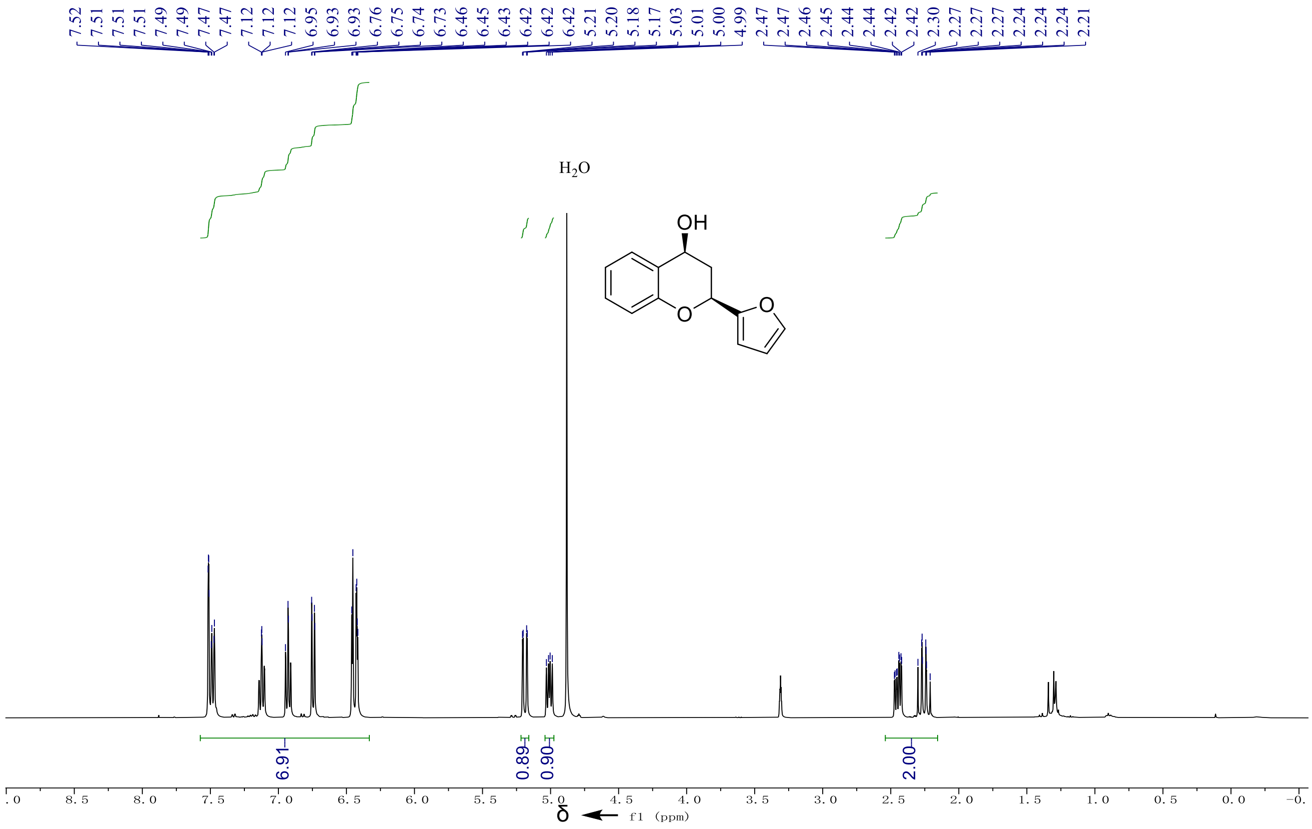


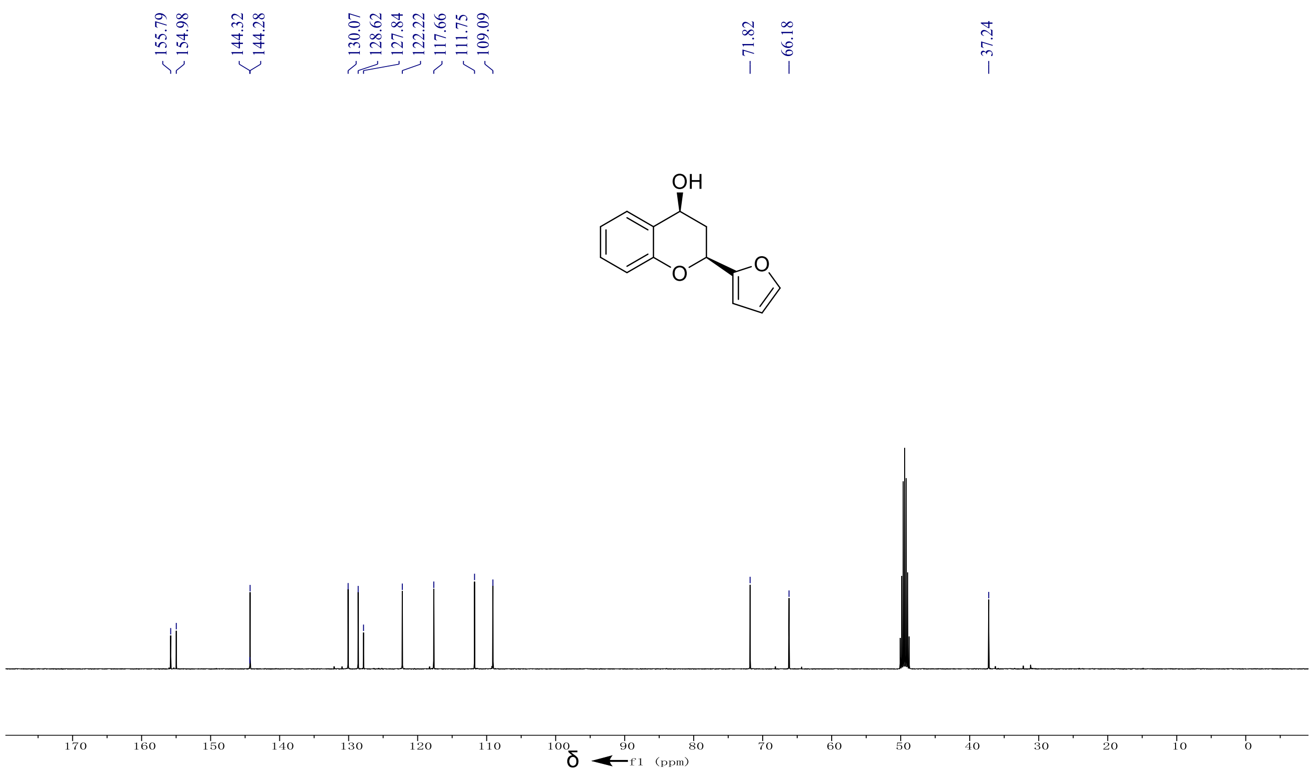
(*S*,*S*)-7al: (2S,4S)-2-(2-methoxyphenyl)chroman-4-ol.



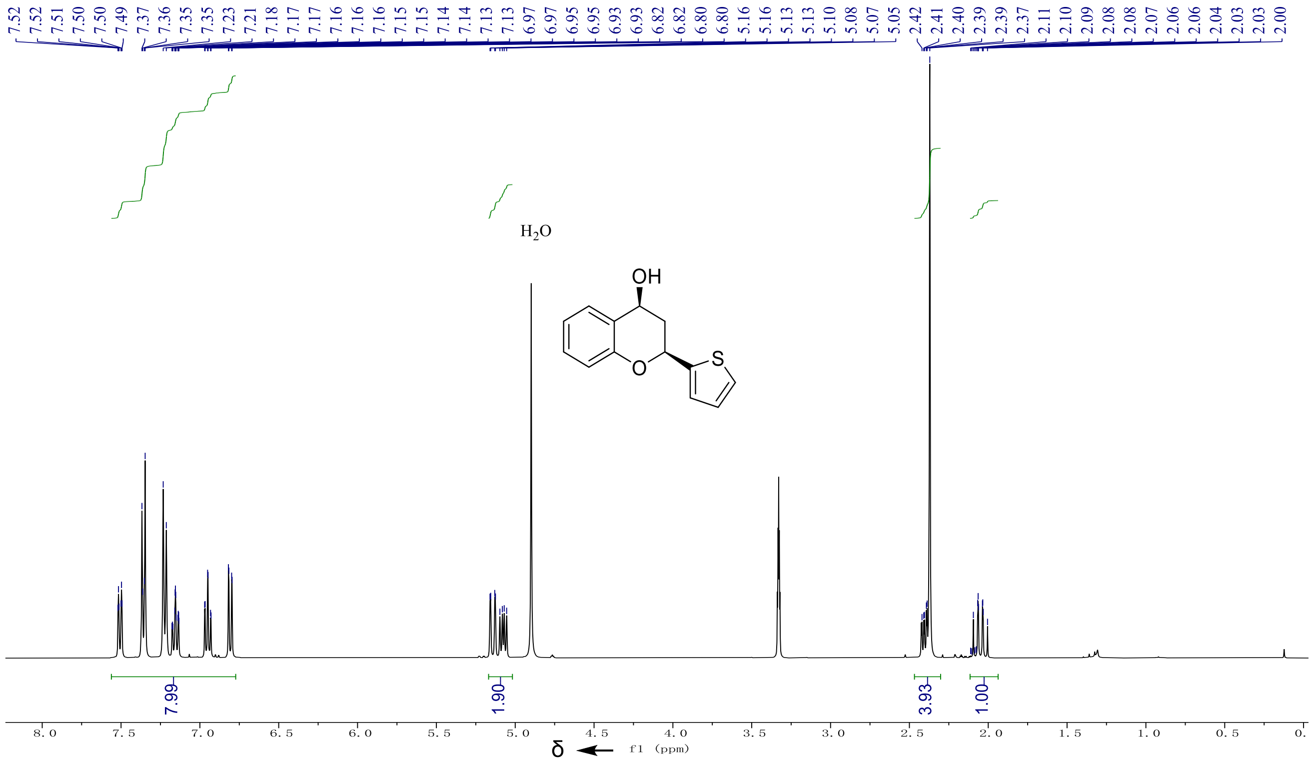


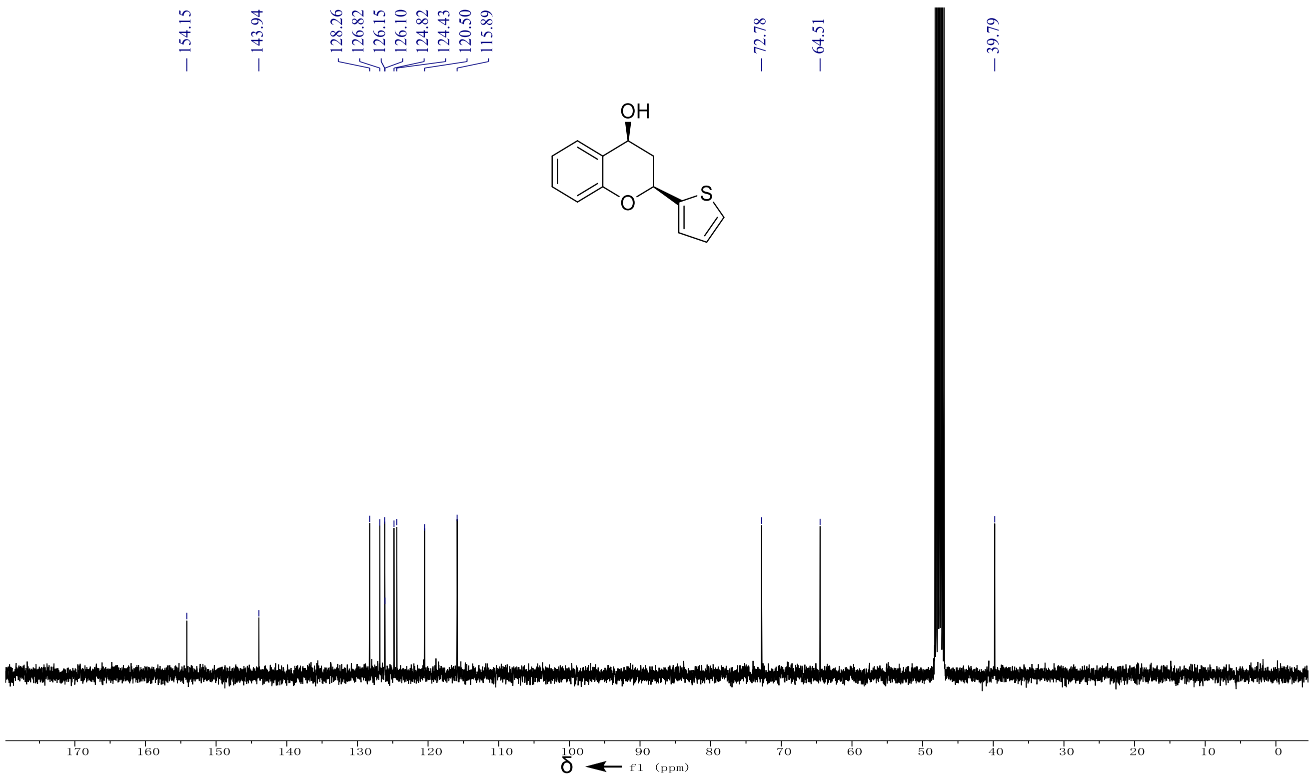
(*S*,*S*)-7am: (2S,4S)-2-(furan-2-yl)chroman-4-ol.



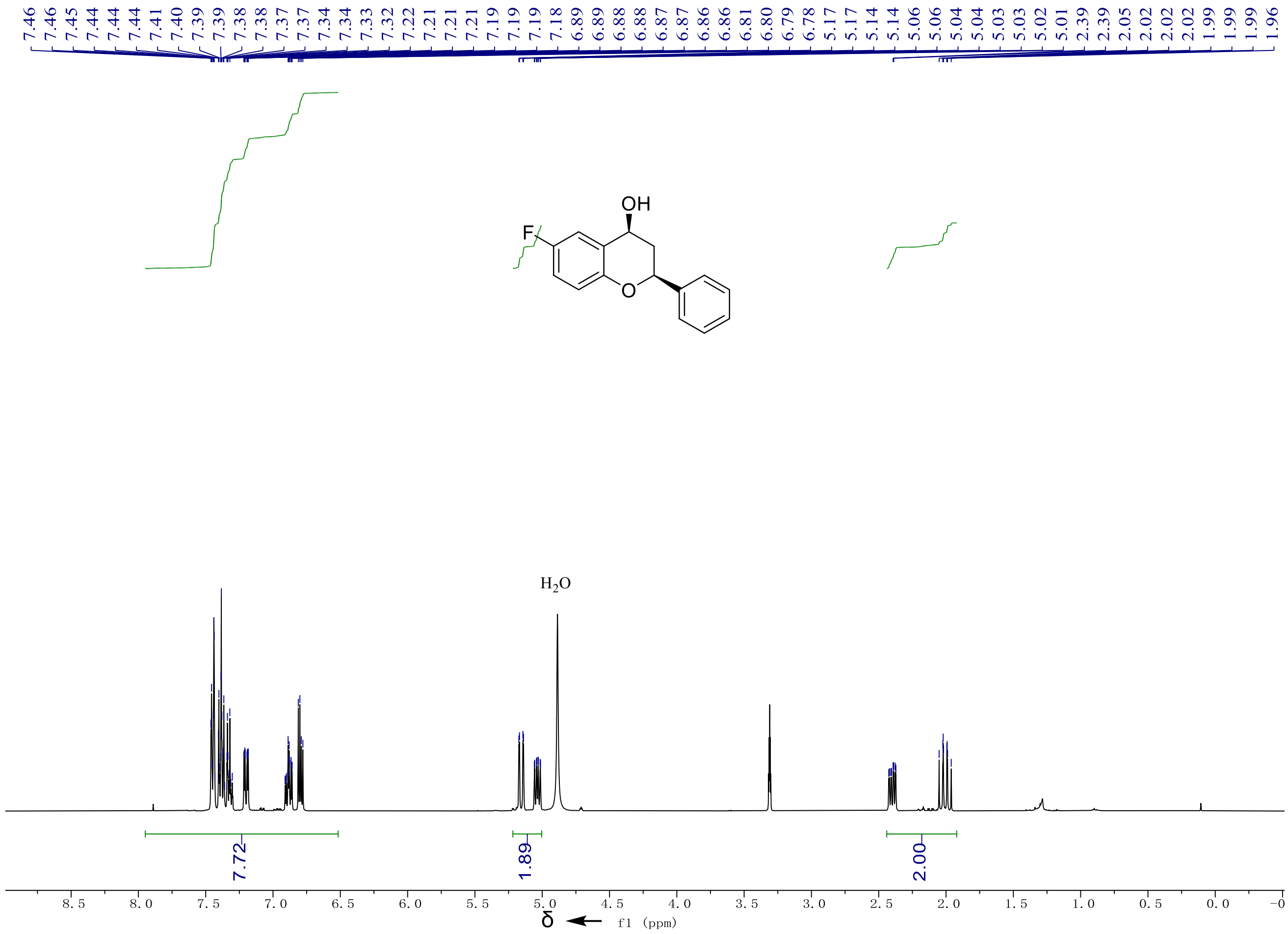


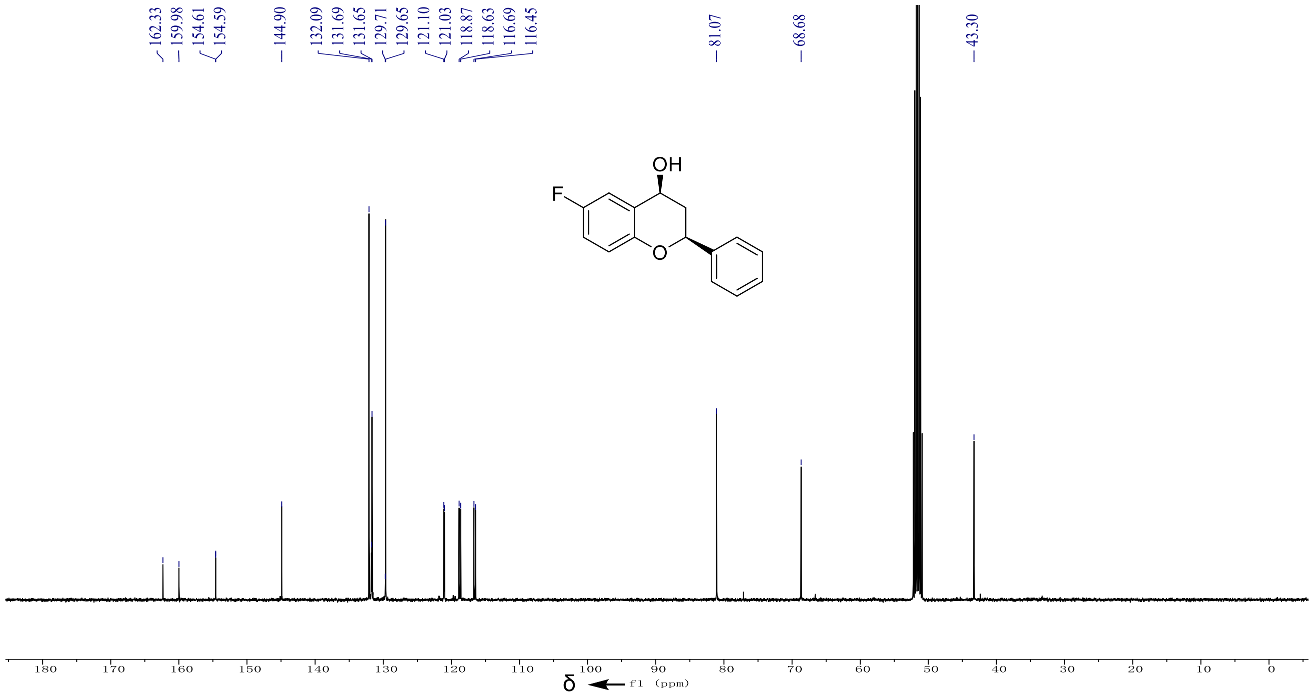
(*S*,*S*)-7an: (2S,4S)-2-(thiophen-2-yl)chroman-4-ol.



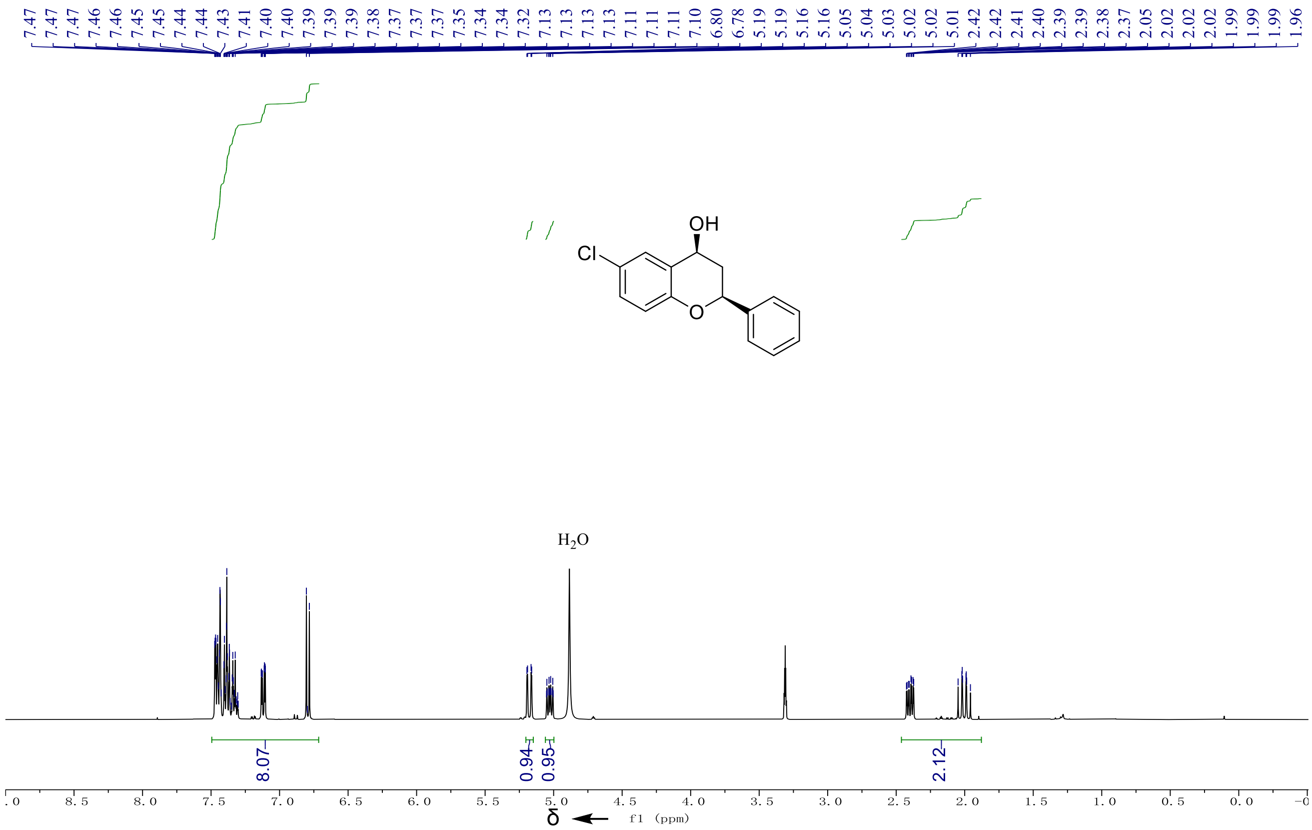


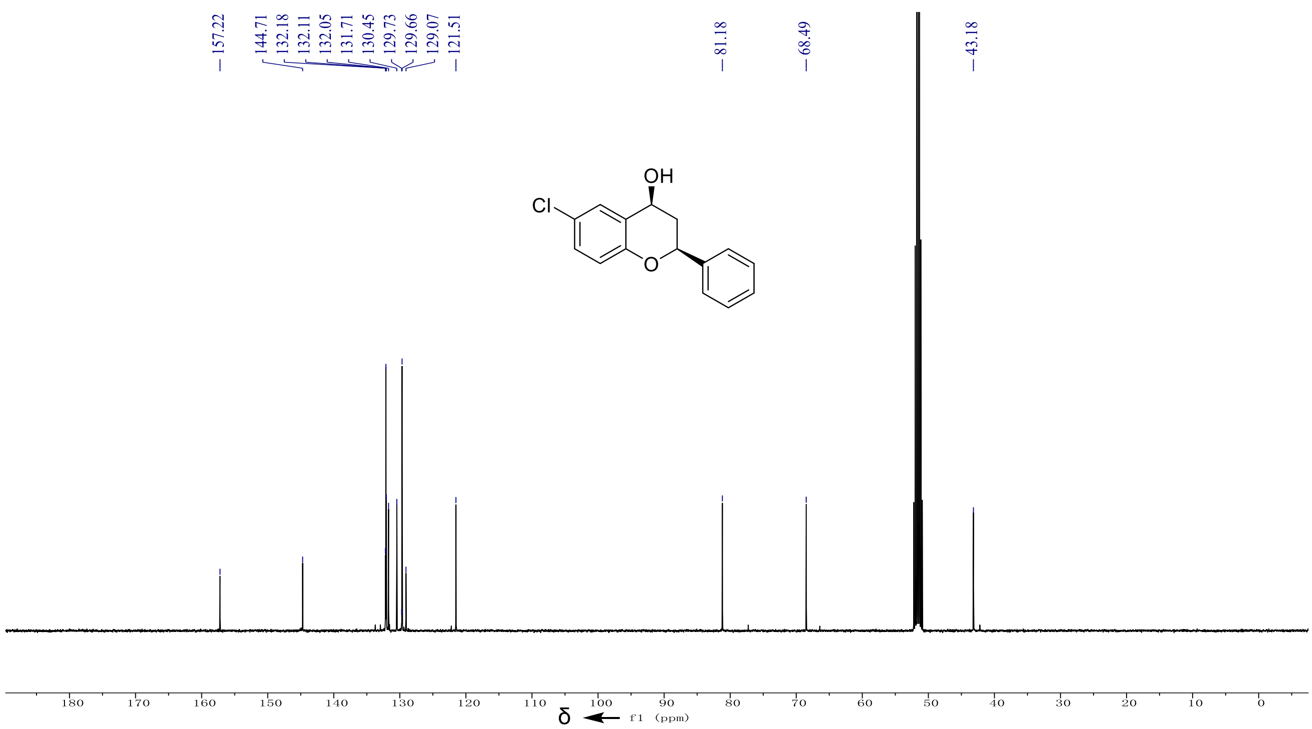
(*S*,*S*)-7ao: (2S,4S)-6-fluoro-2-phenylchroman-4-ol.



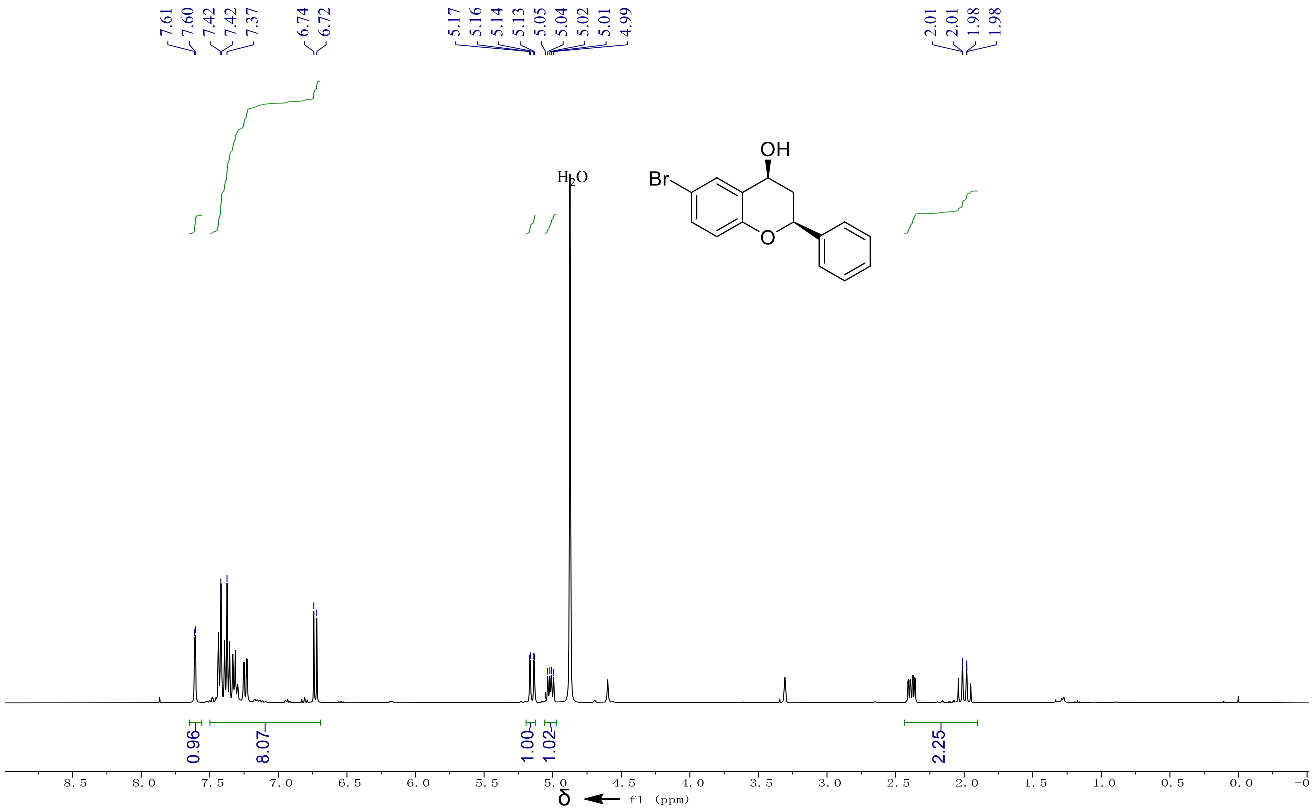


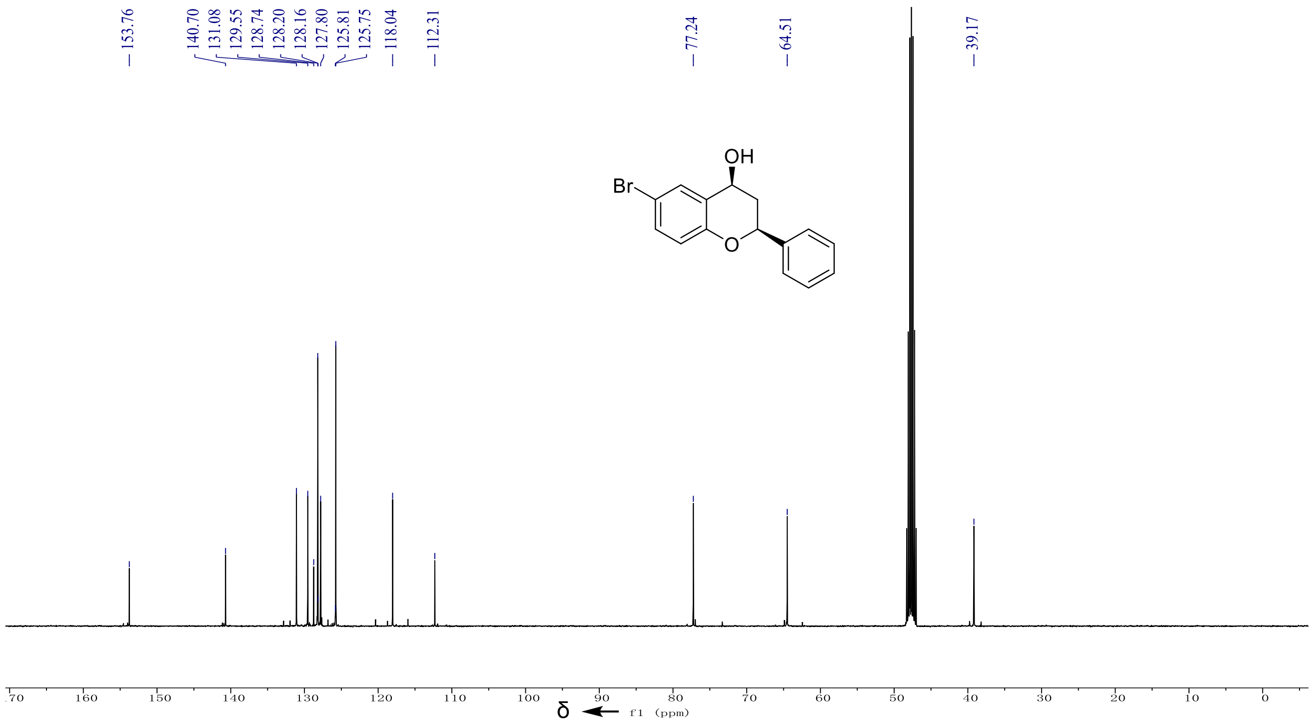
(*S*,*S*)-7ap: (2S,4S)-6-chloro-2-phenylchroman-4-ol.



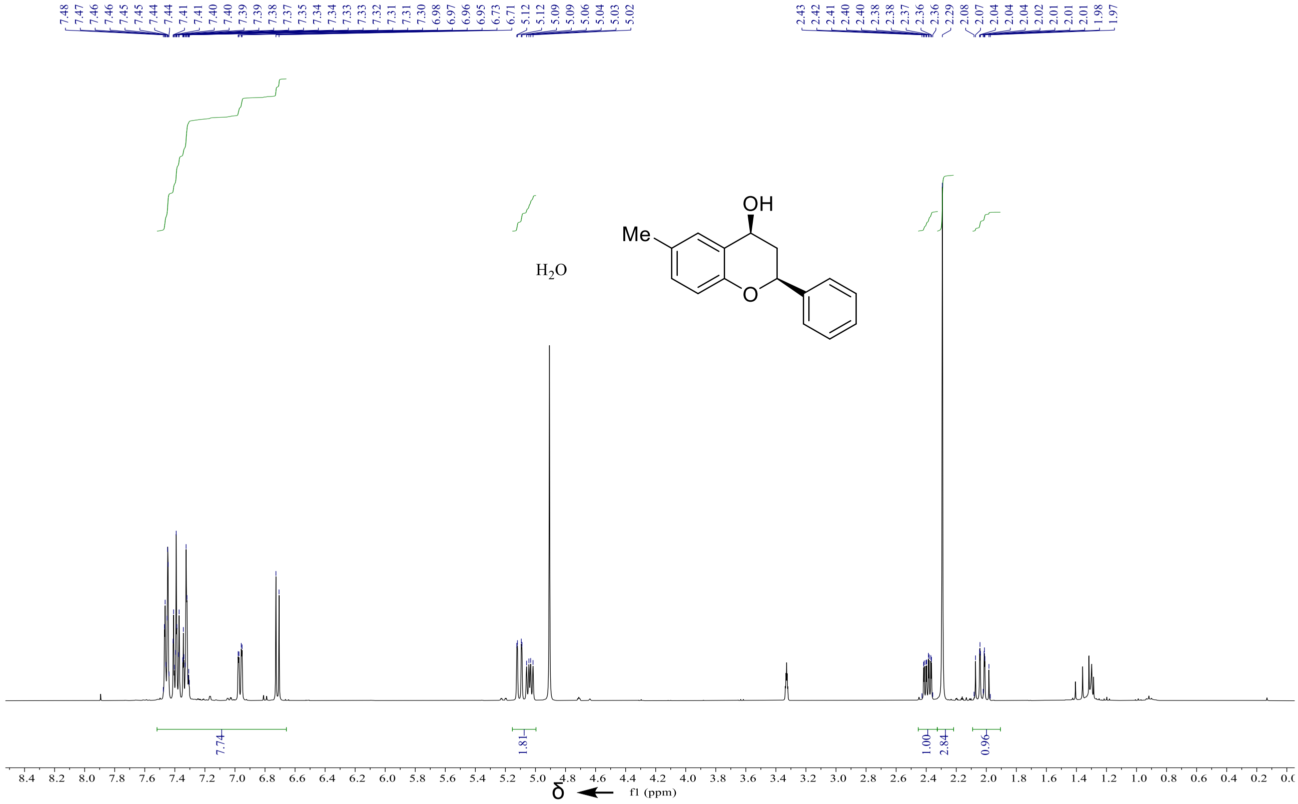


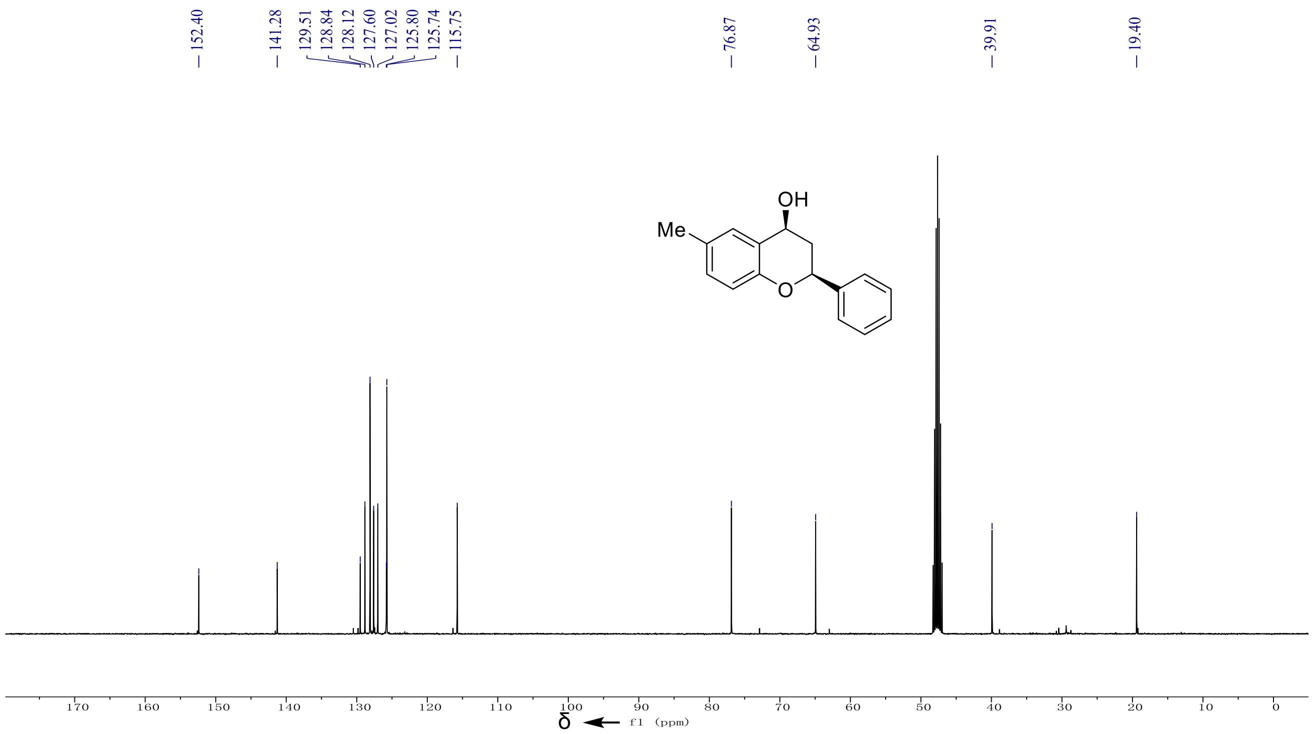
(*S*,*S*)-7aq: (2*S*,4*S*)-6-bromo-2-phenylchroman-4-ol



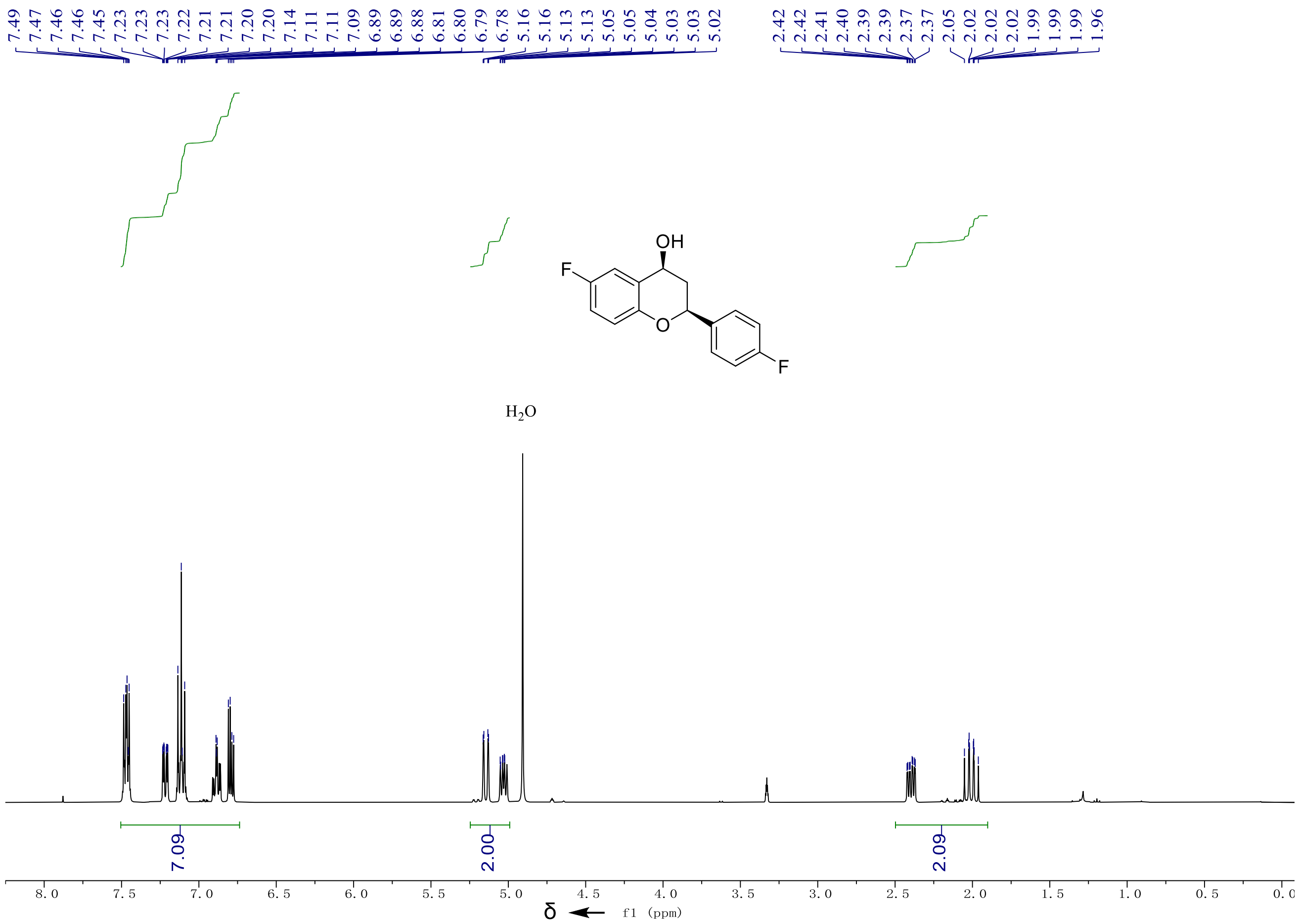


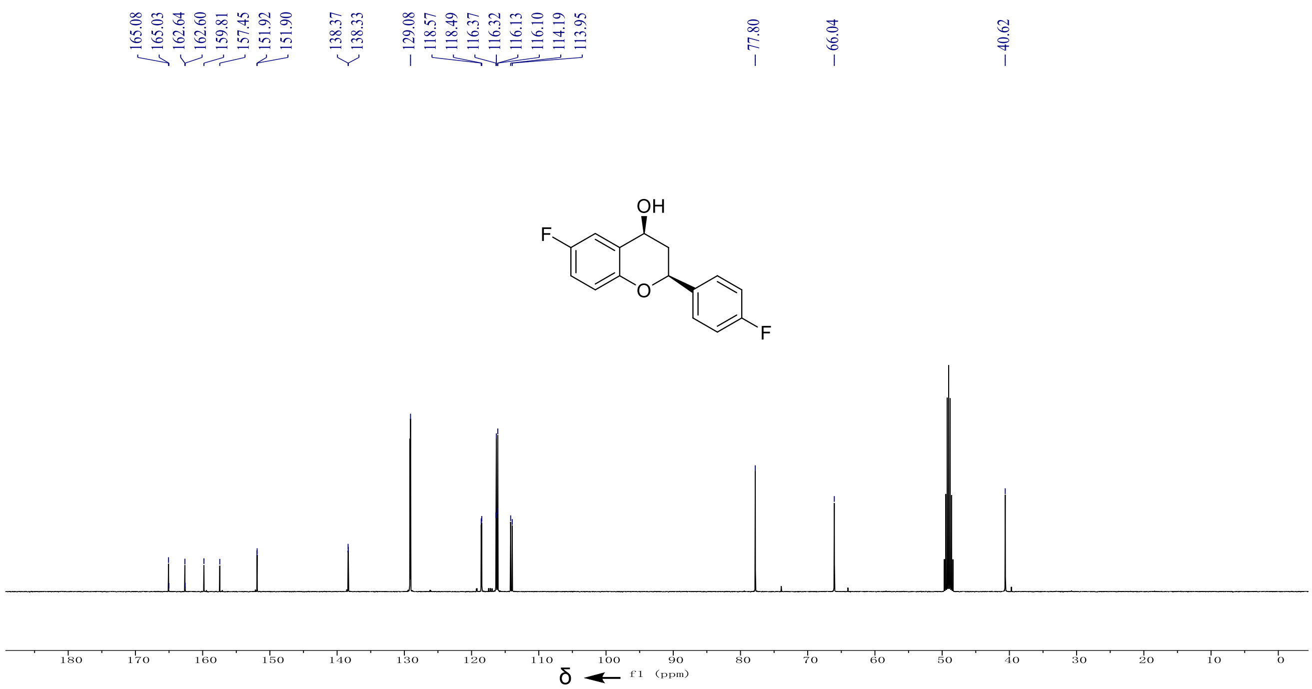
(*S*,*S*)-7ar: (2S,4S)-6-methyl-2-phenylchroman-4-ol.



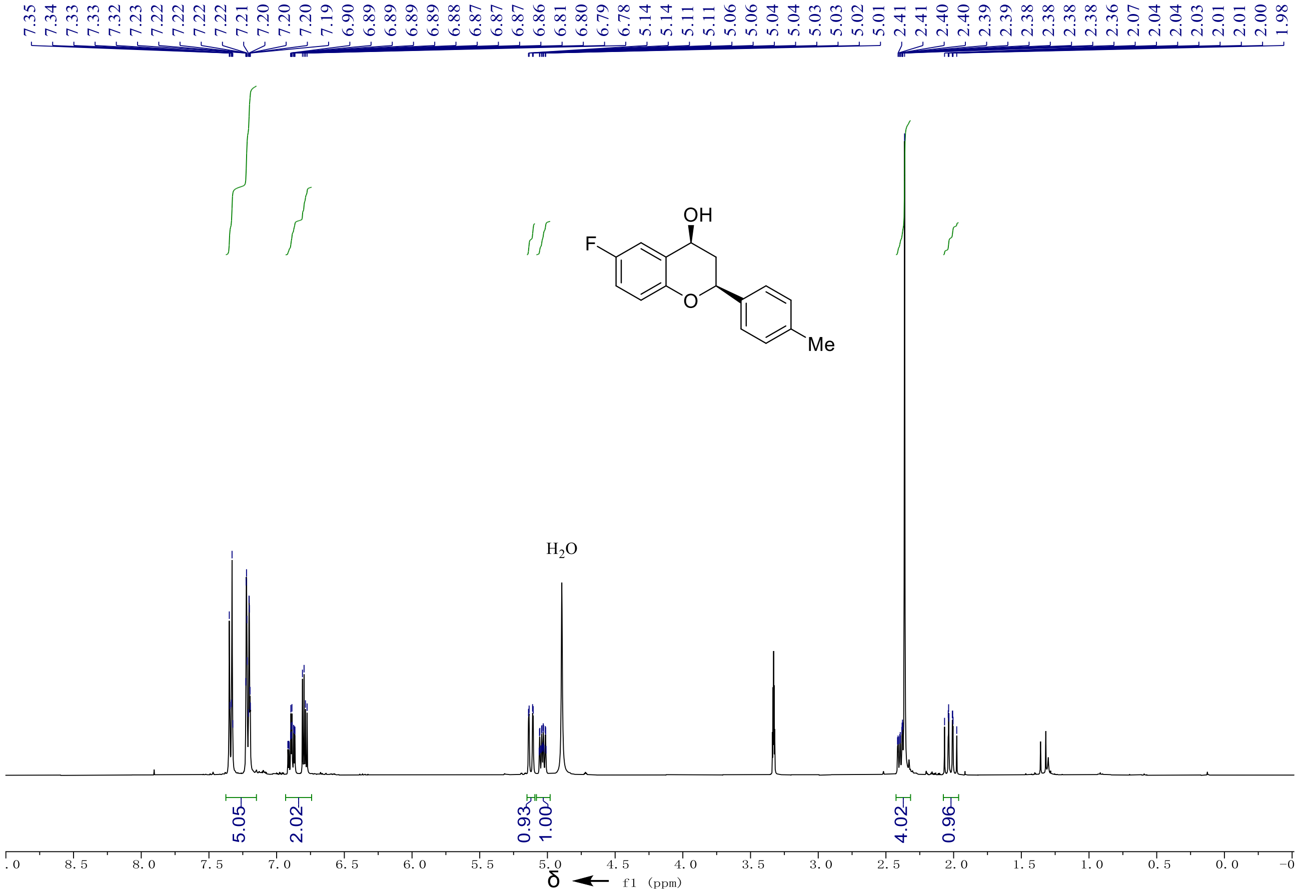


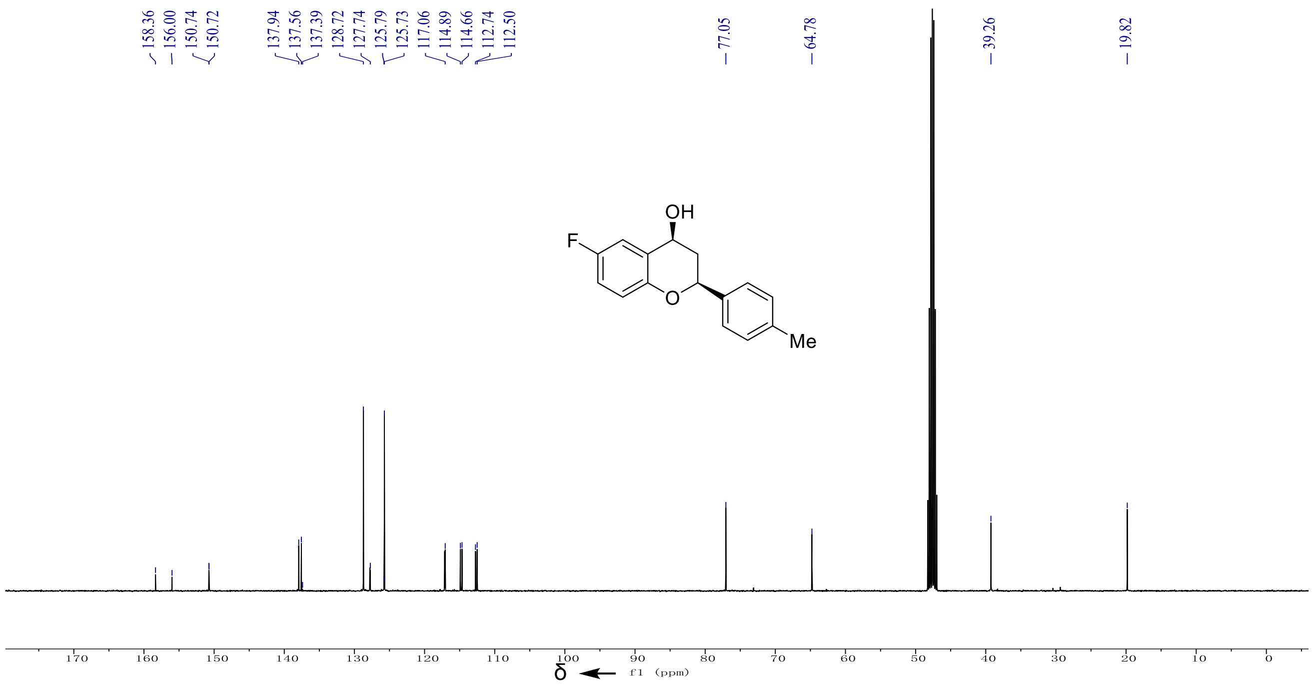
(*S*,*S*)-7as: (2S,4S)-6-fluoro-2-(4-fluorophenyl)chroman-4-ol.



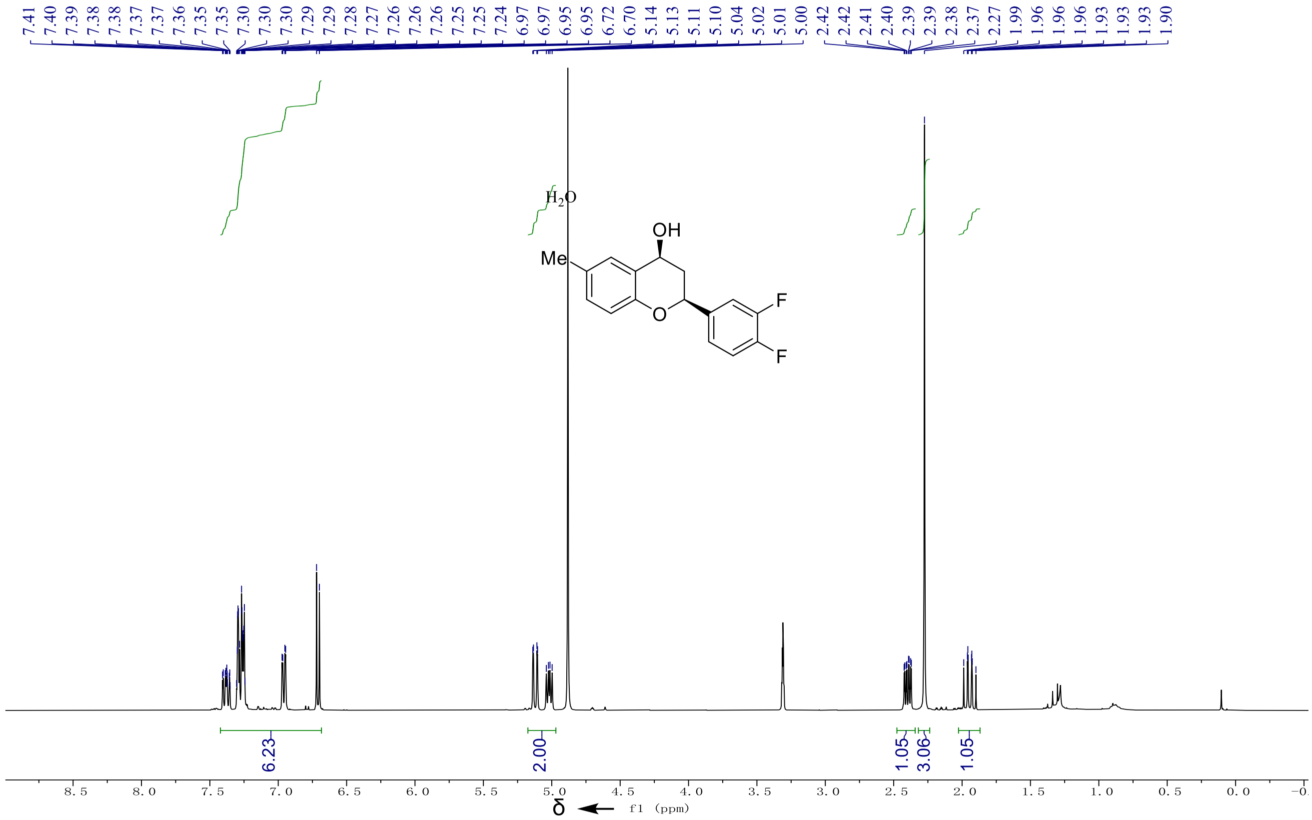


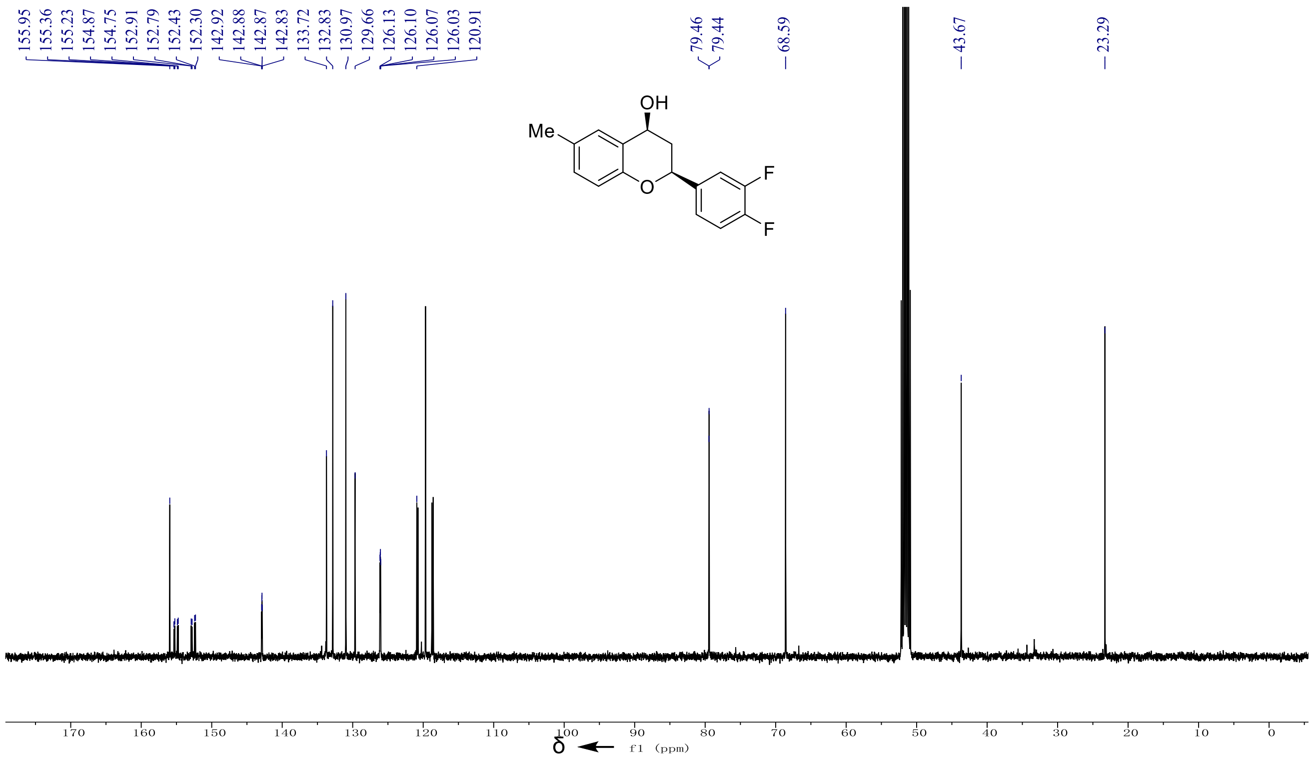
(*S*,*S*)-7at: (2S,4S)-6-fluoro-2-(p-tolyl)chroman-4-ol.



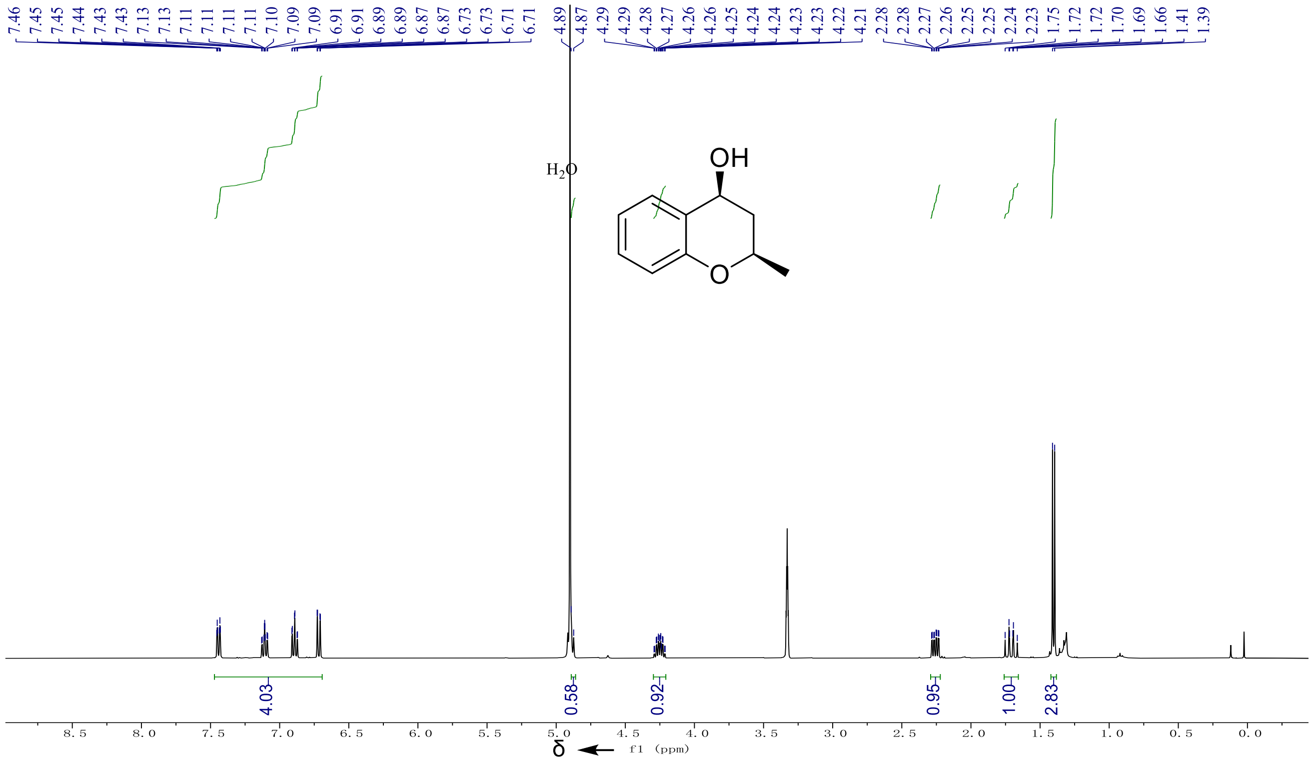


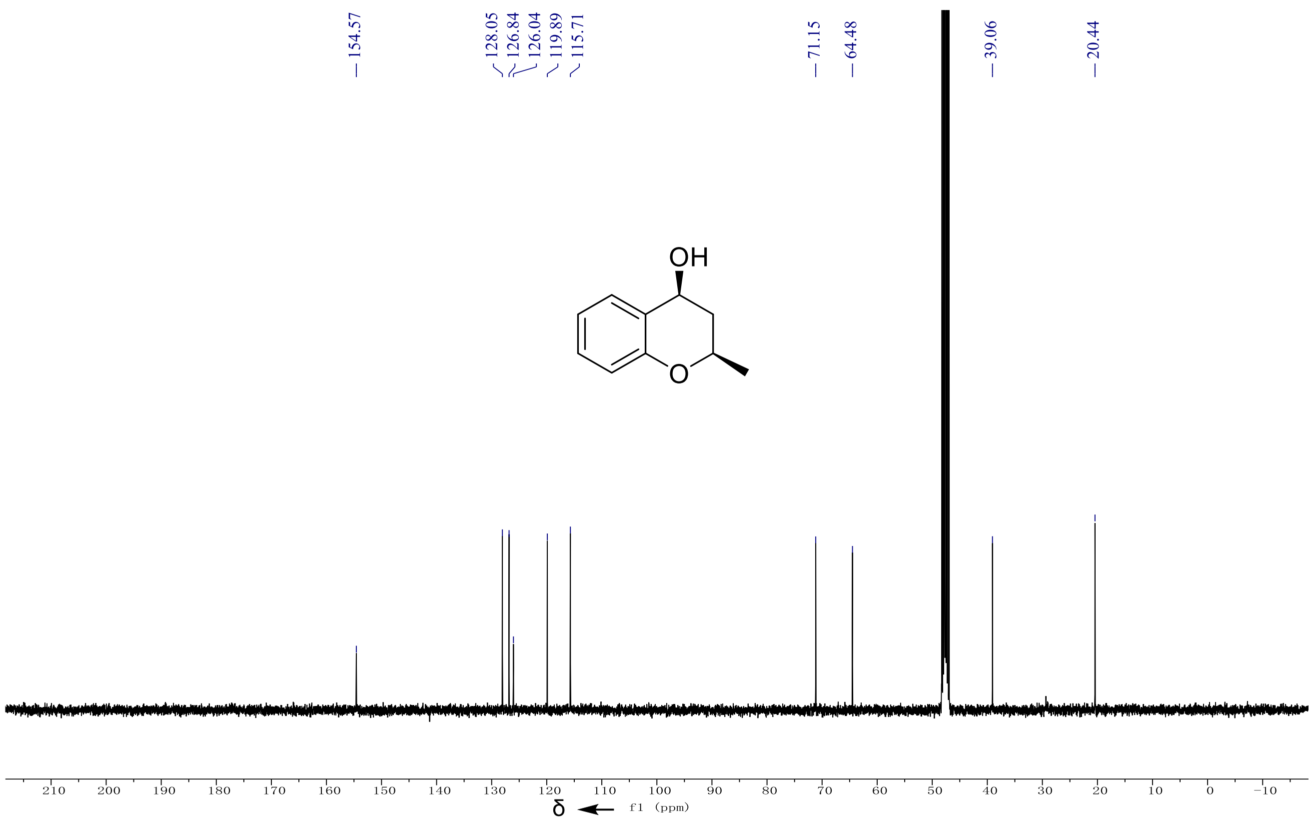
(*S*,*S*)-4au: (2S,4S)-2-(3,4-difluorophenyl)-6-methylchroman-4-ol.



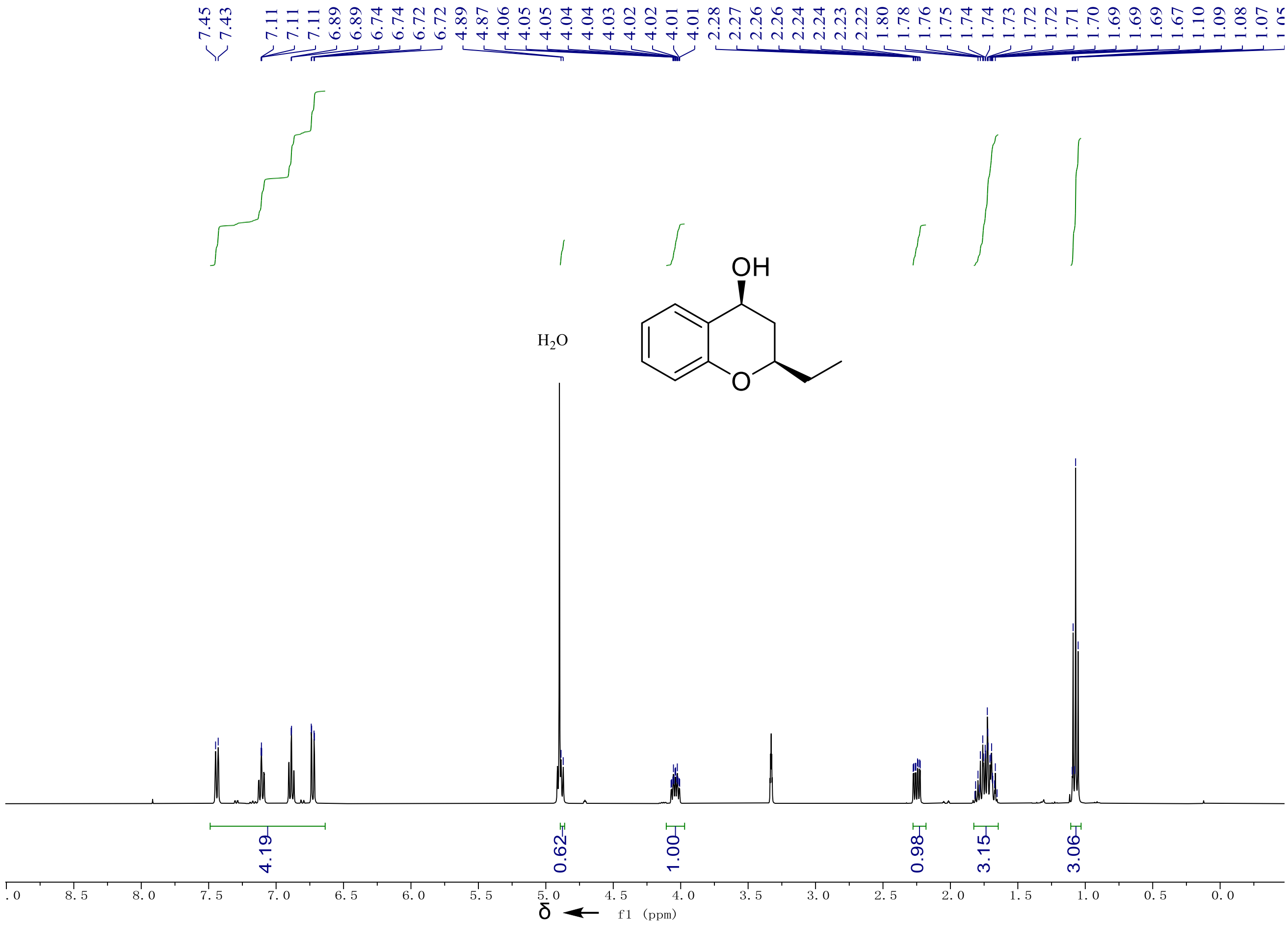


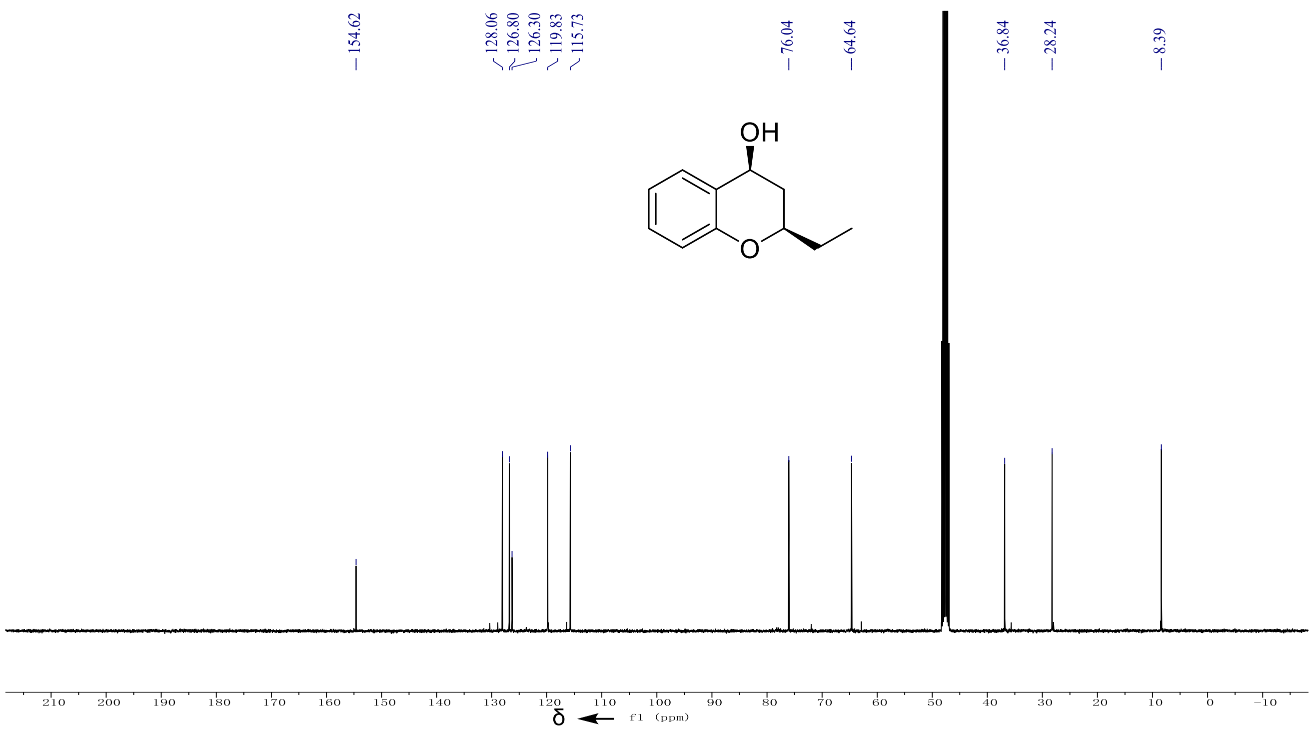
(*R*,*S*)-7ba: (2*R*,4*S*)-2-methylchroman-4-ol.



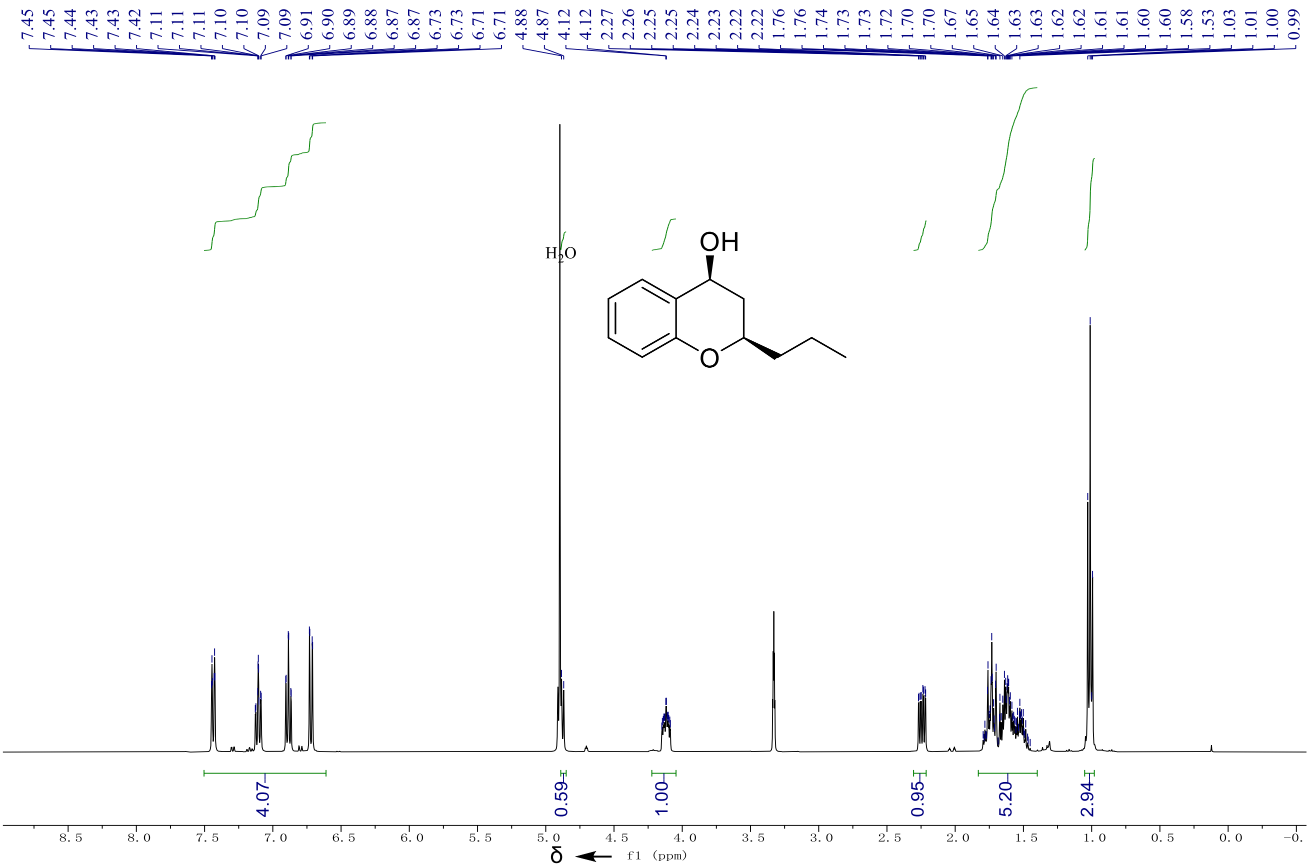


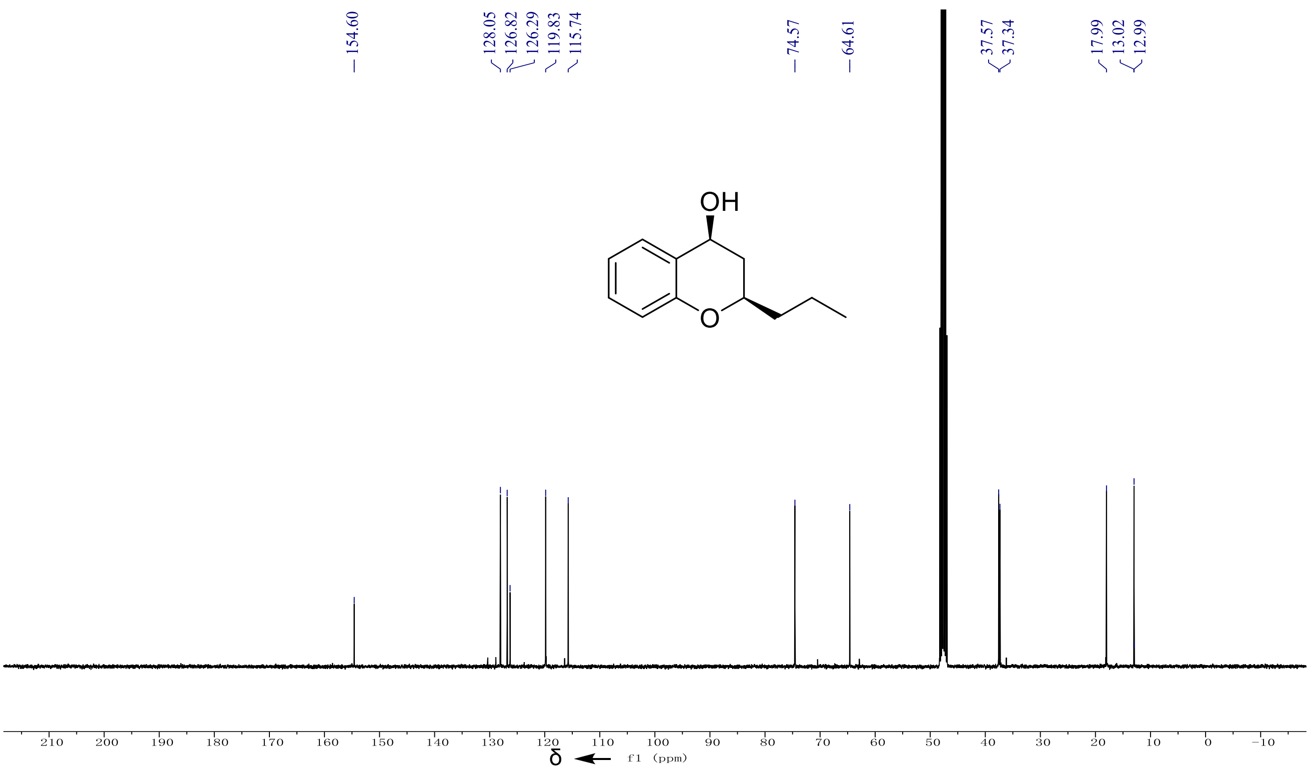
(*R*,*S*)-7bb: (2*R*,4*S*)-2-ethylchroman-4-ol.



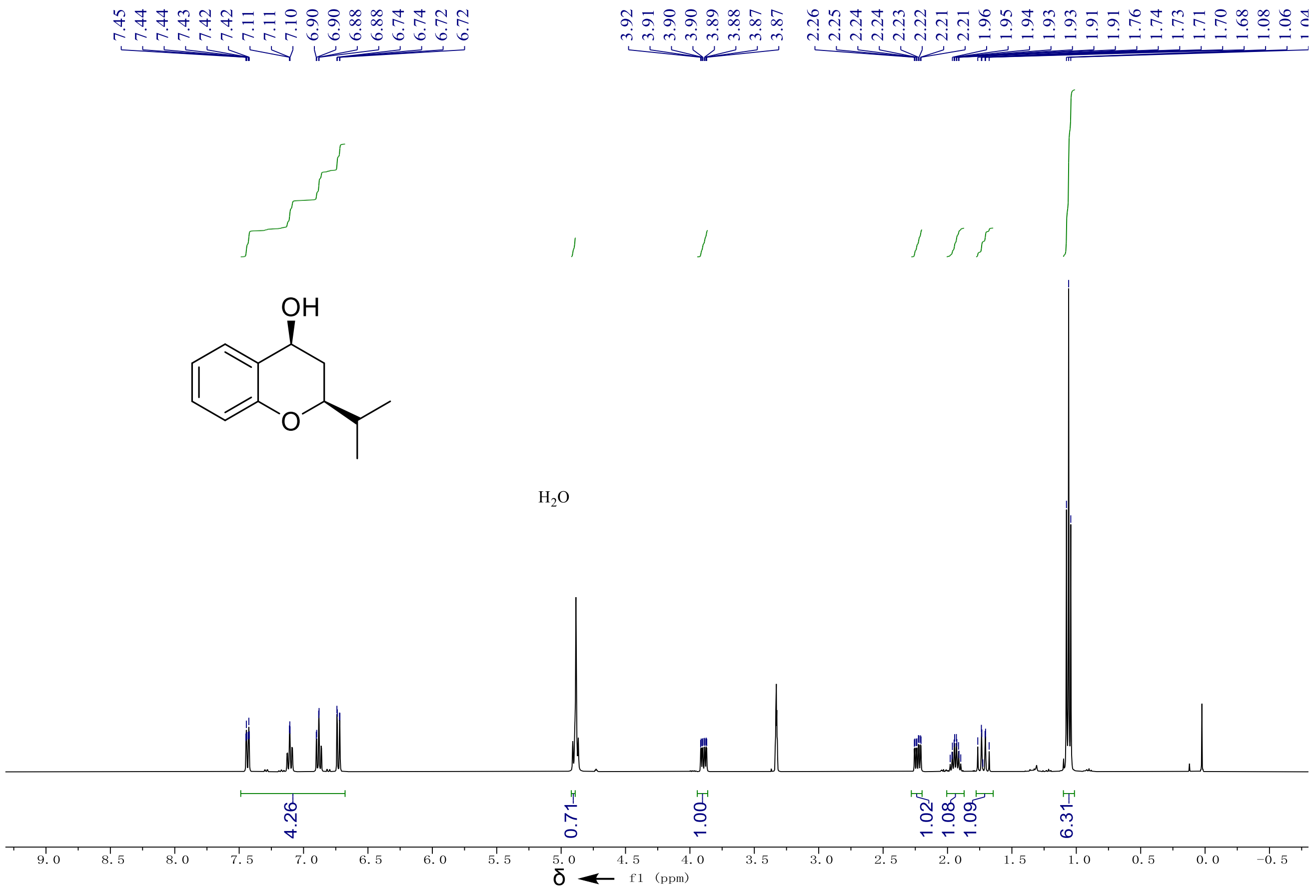


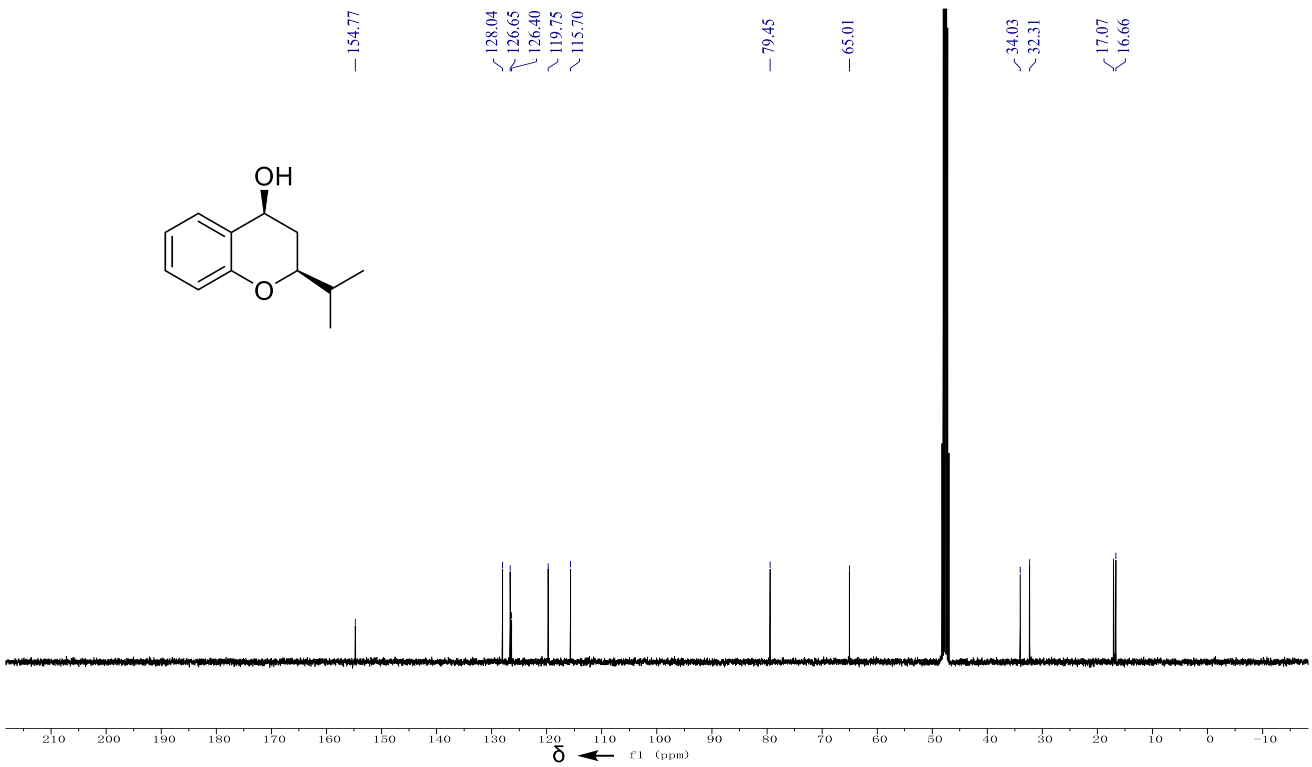
(*R*,*S*)-7bc: (2*R*,4*S*)-2-propylchroman-4-ol.



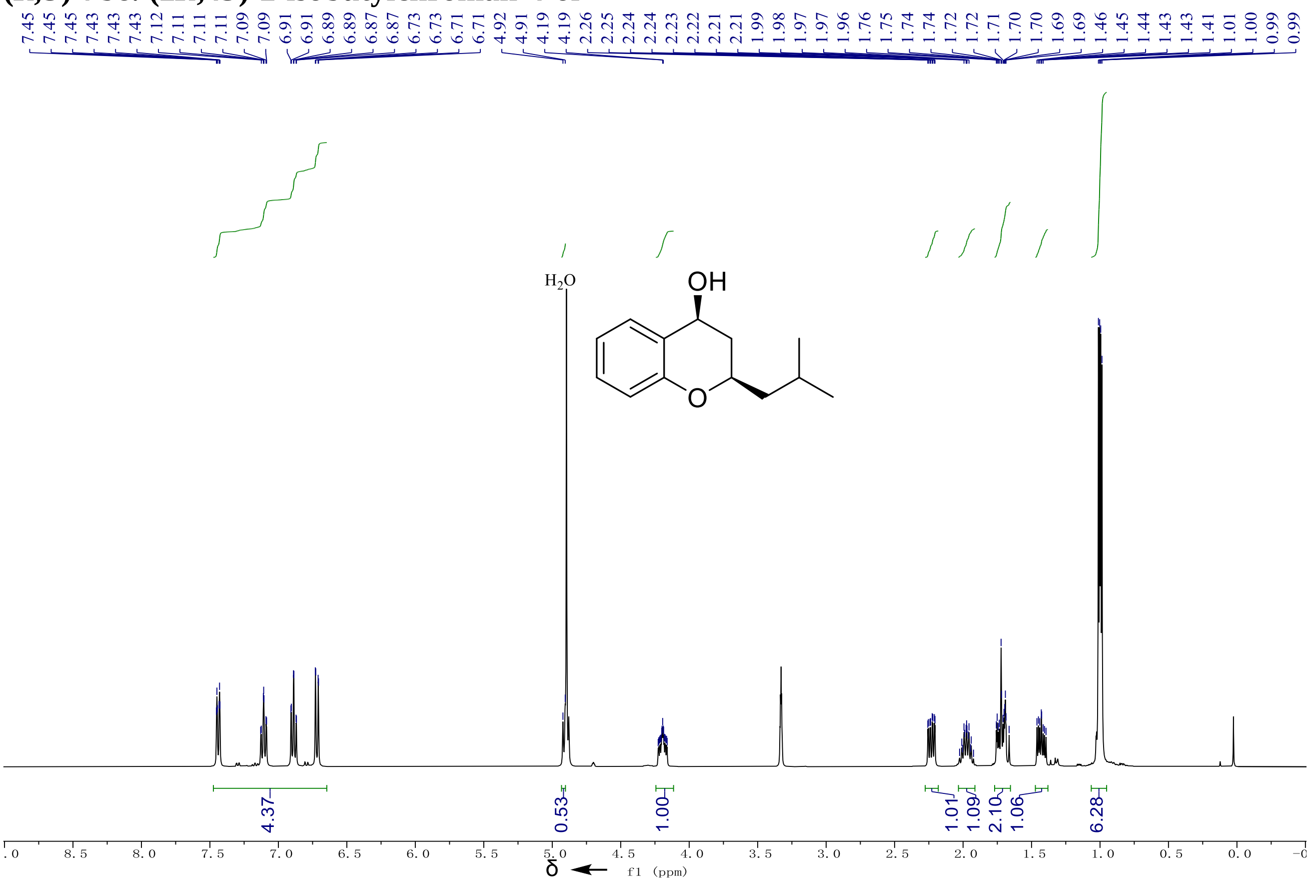


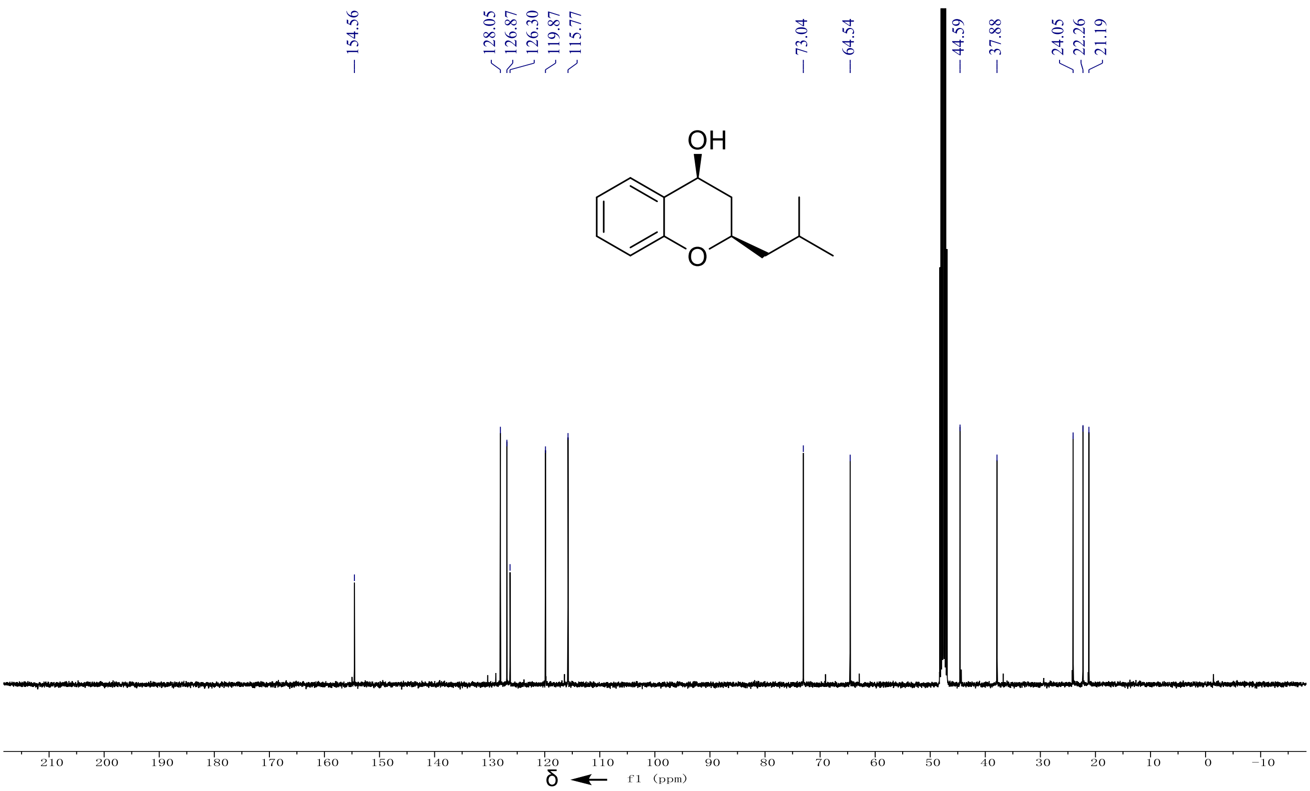
(*S*,*S*)-7bd: (2S,4S)-2-isopropylchroman-4-ol



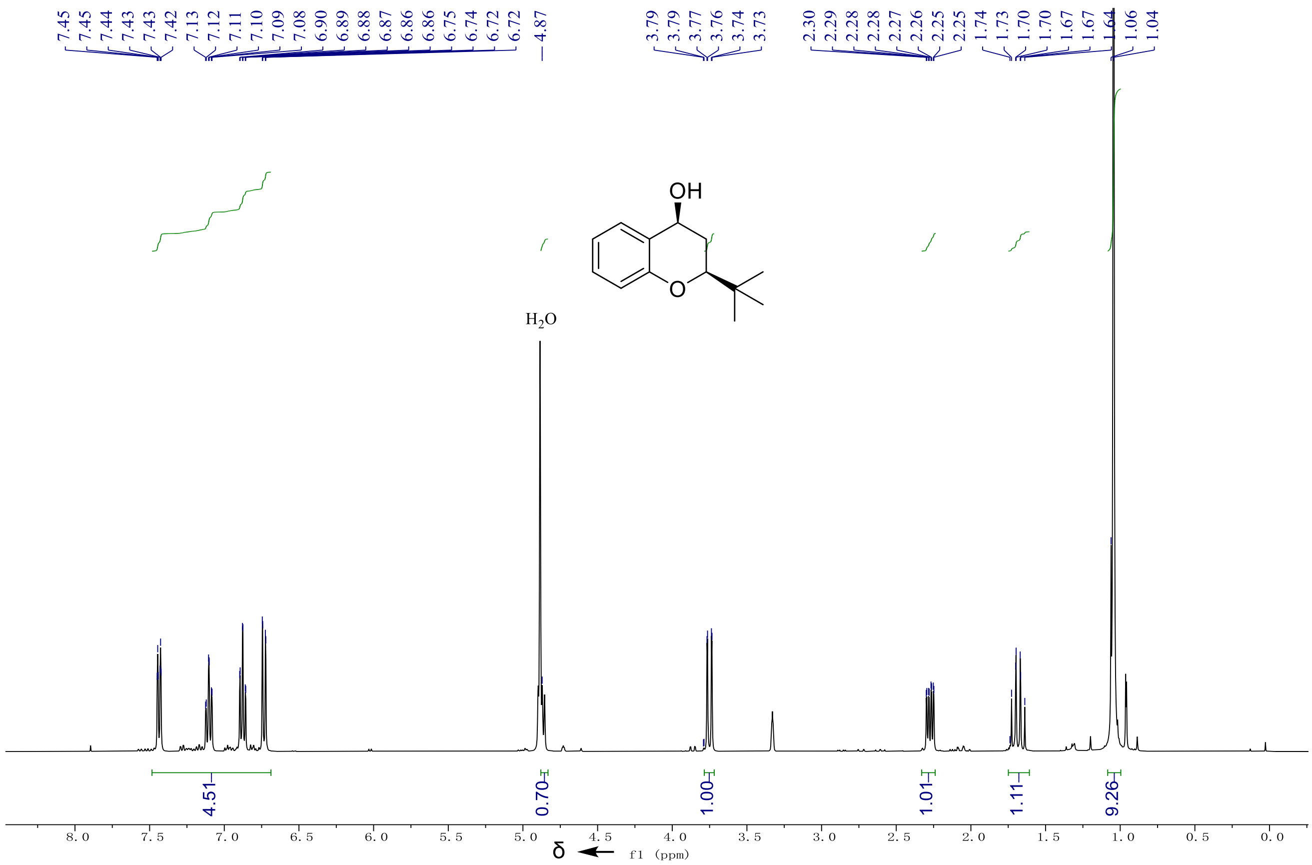


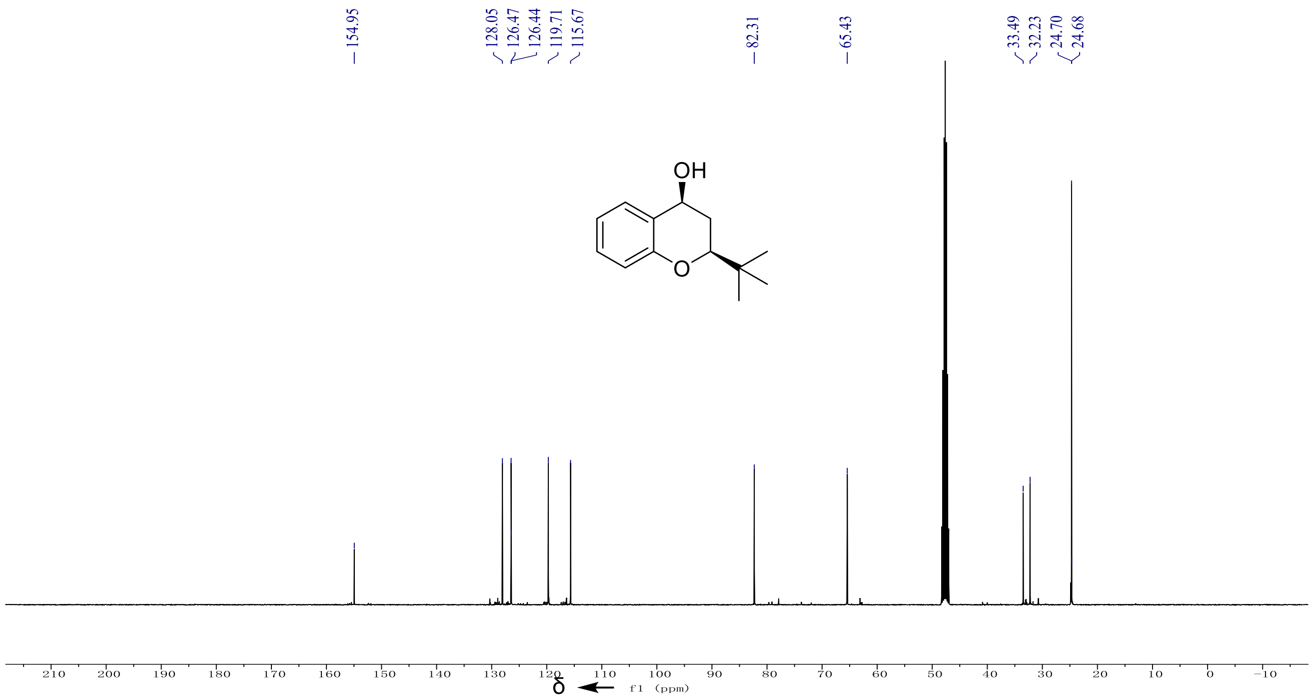
(*R*,*S*)-7be: (2*R*,4*S*)-2-isobutylchroman-4-ol



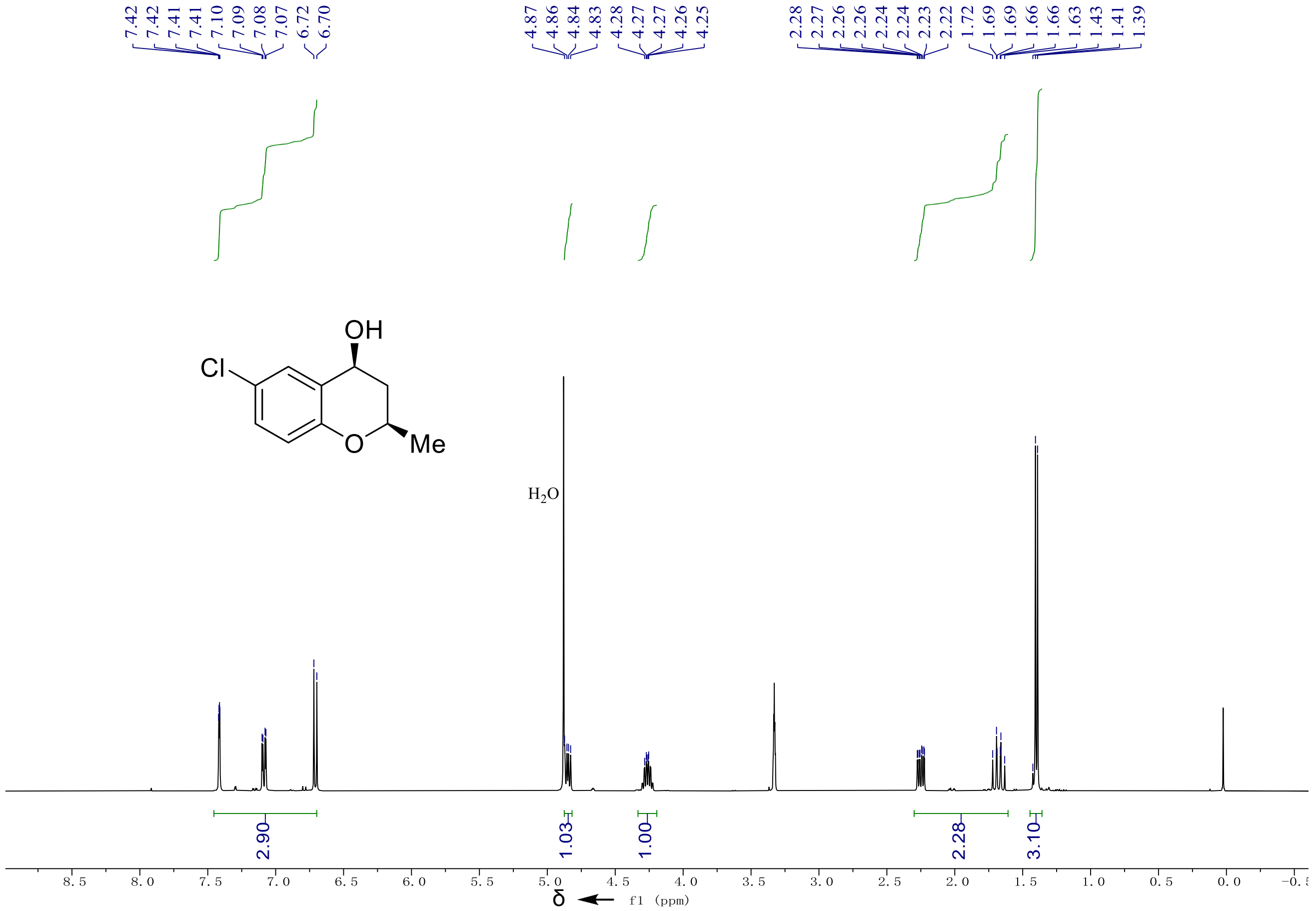


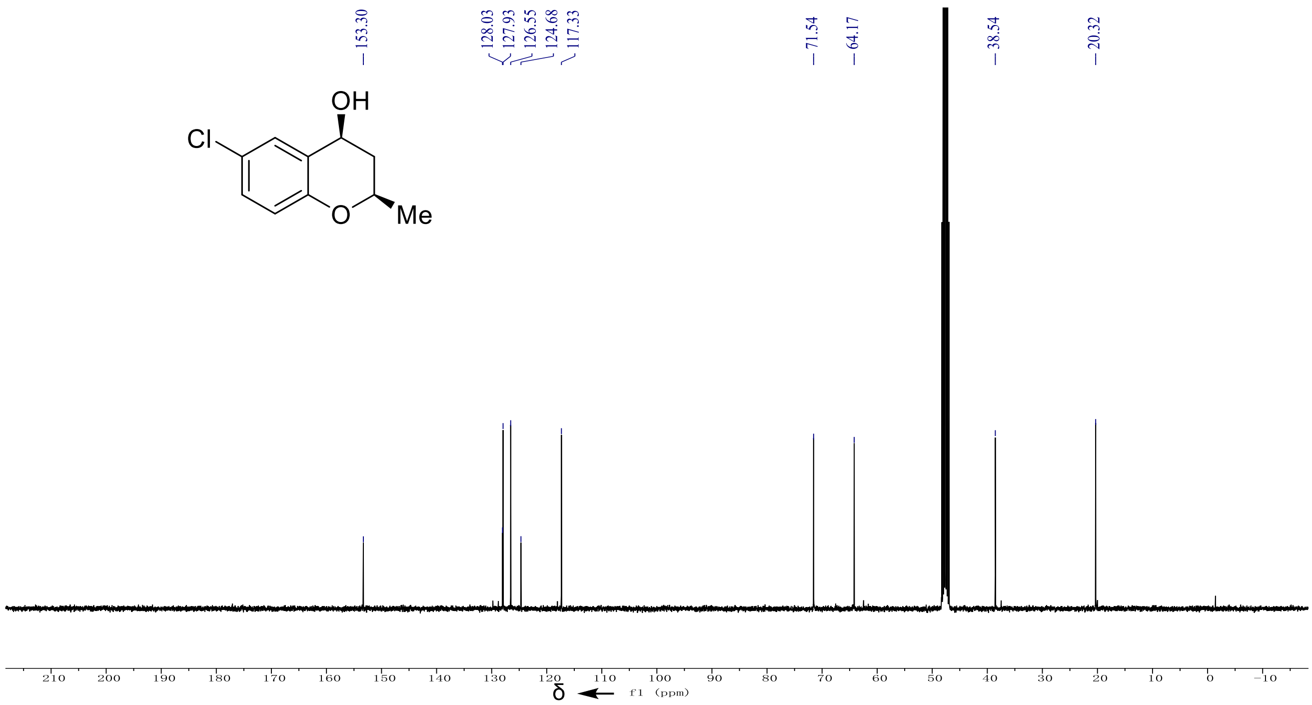
(***S***,***S***)**-7bf: (2S,4S)-2-(3,4-difluorophenyl)-6-methylchroman-4-ol.**



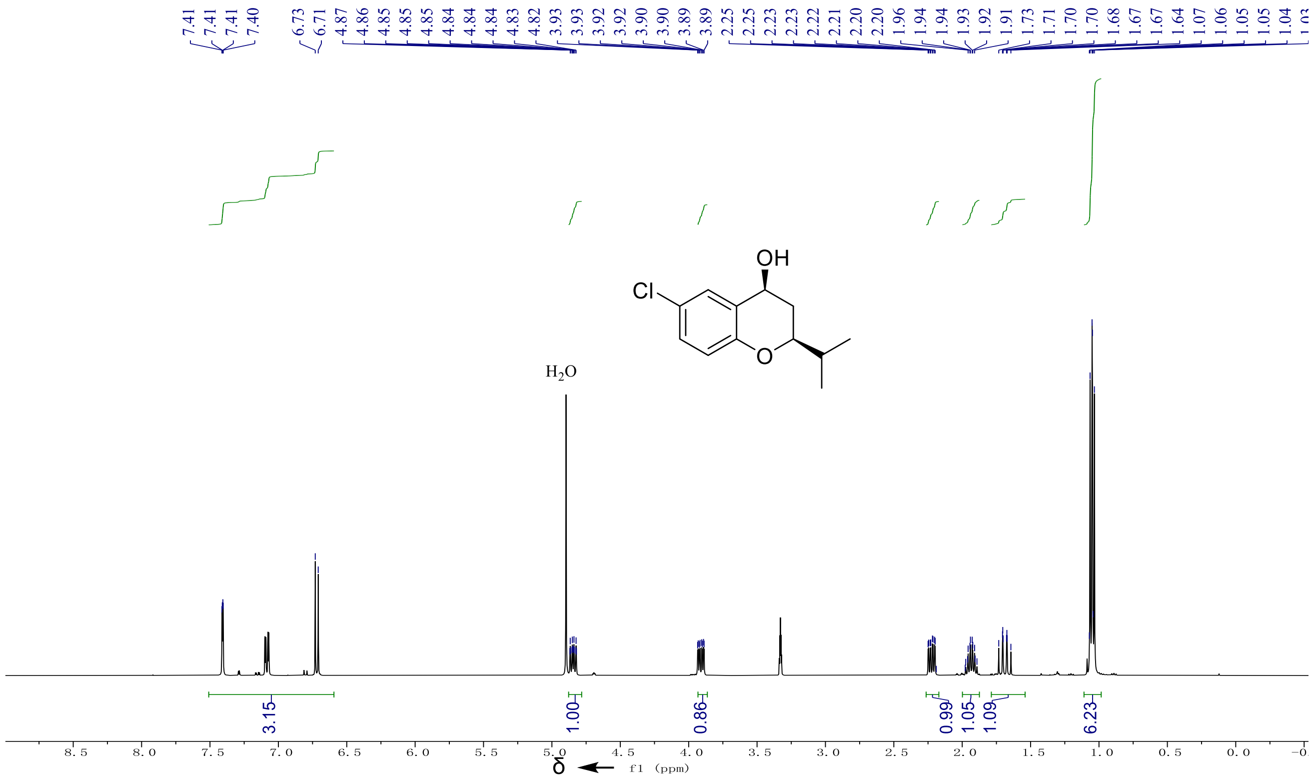


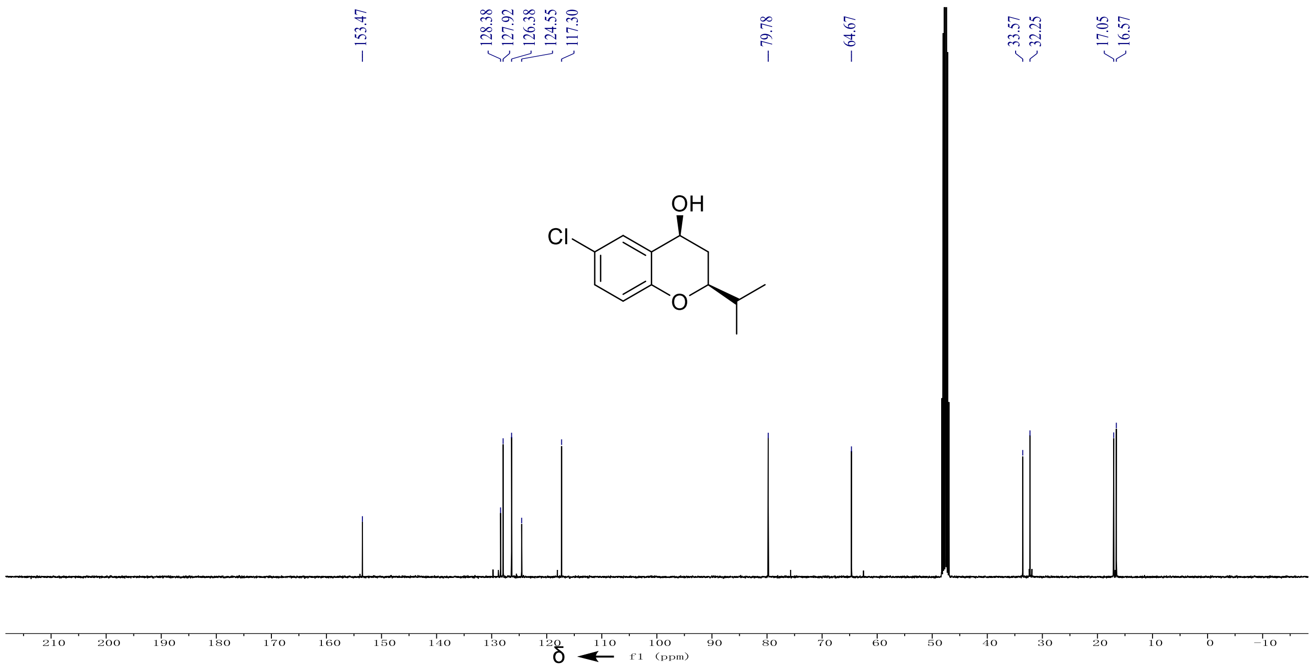
(*R*,*S*)-7bg: (2R,4S)-6-chloro-2-methylchroman-4-ol



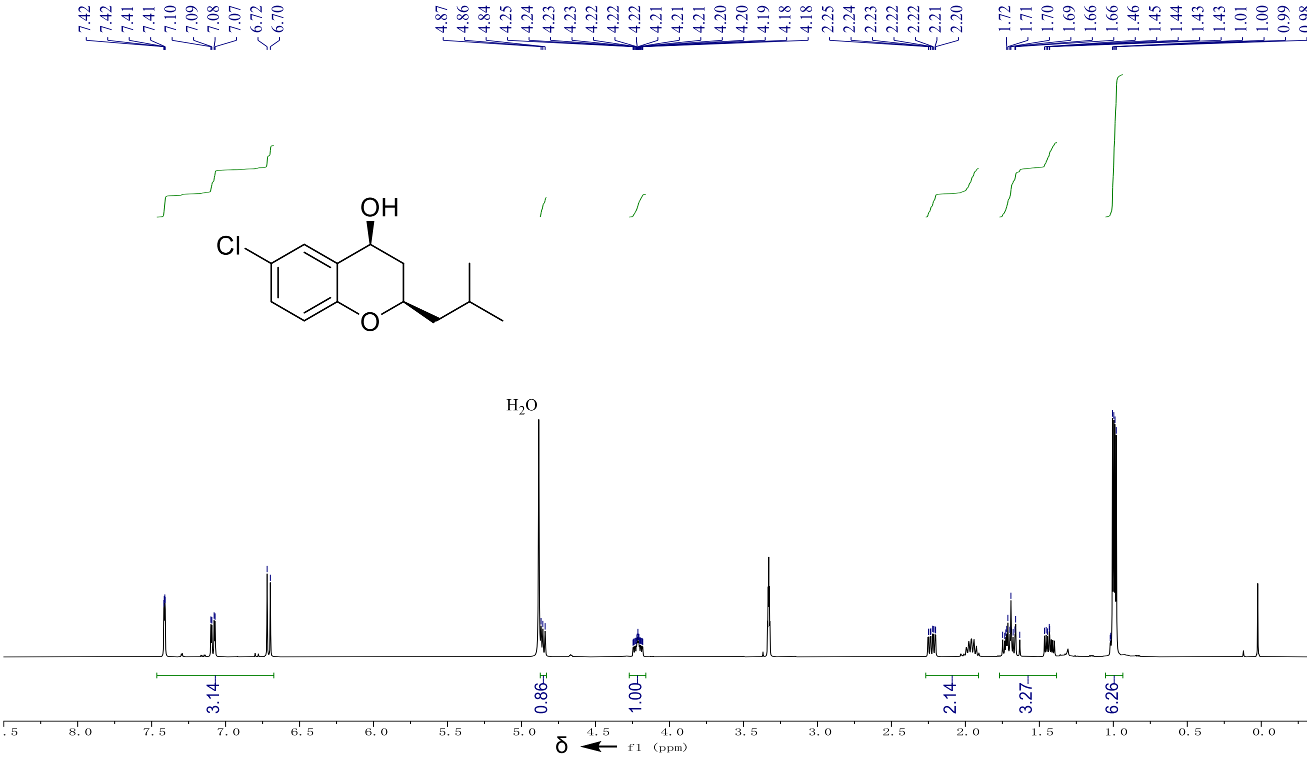


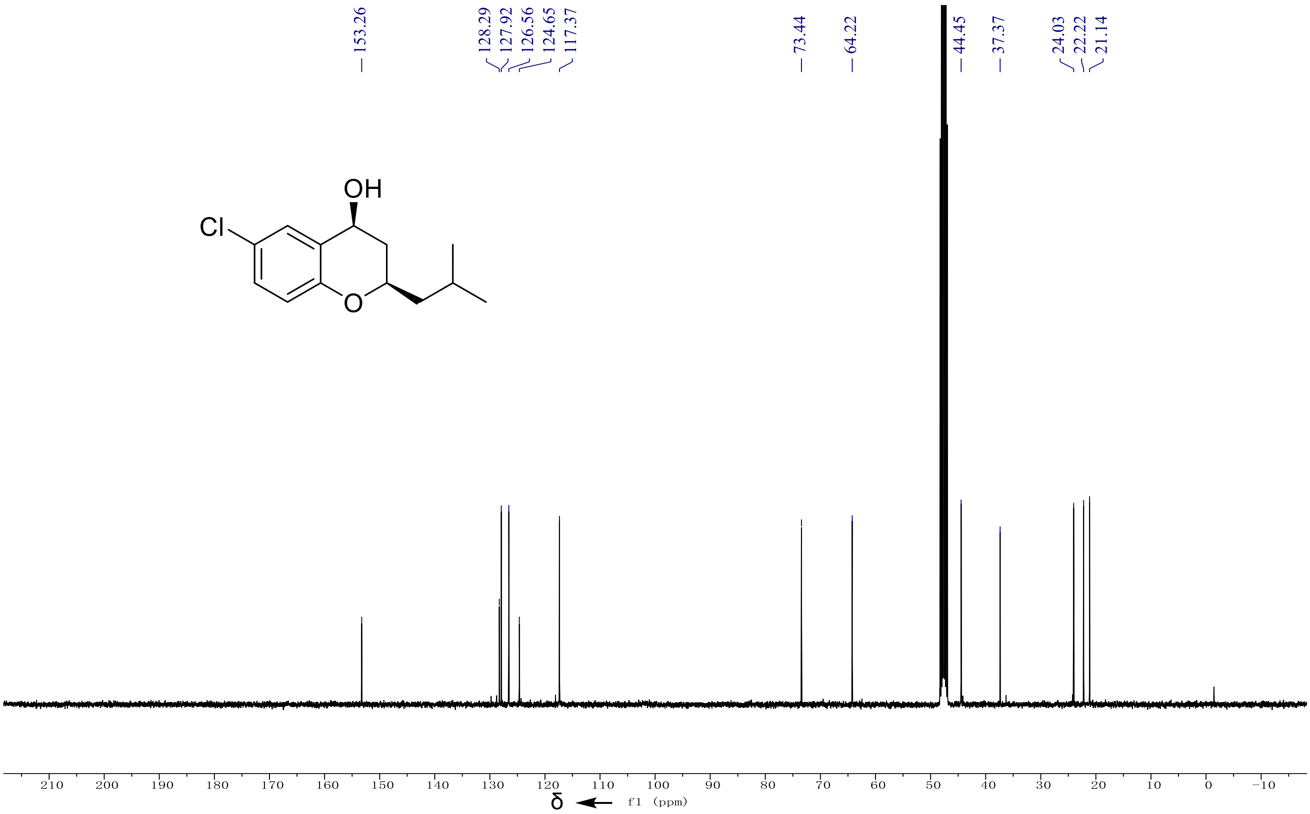
(*S*,*S*)-4bh: (2S,4S)-6-chloro-2-isopropylchroman-4-ol.



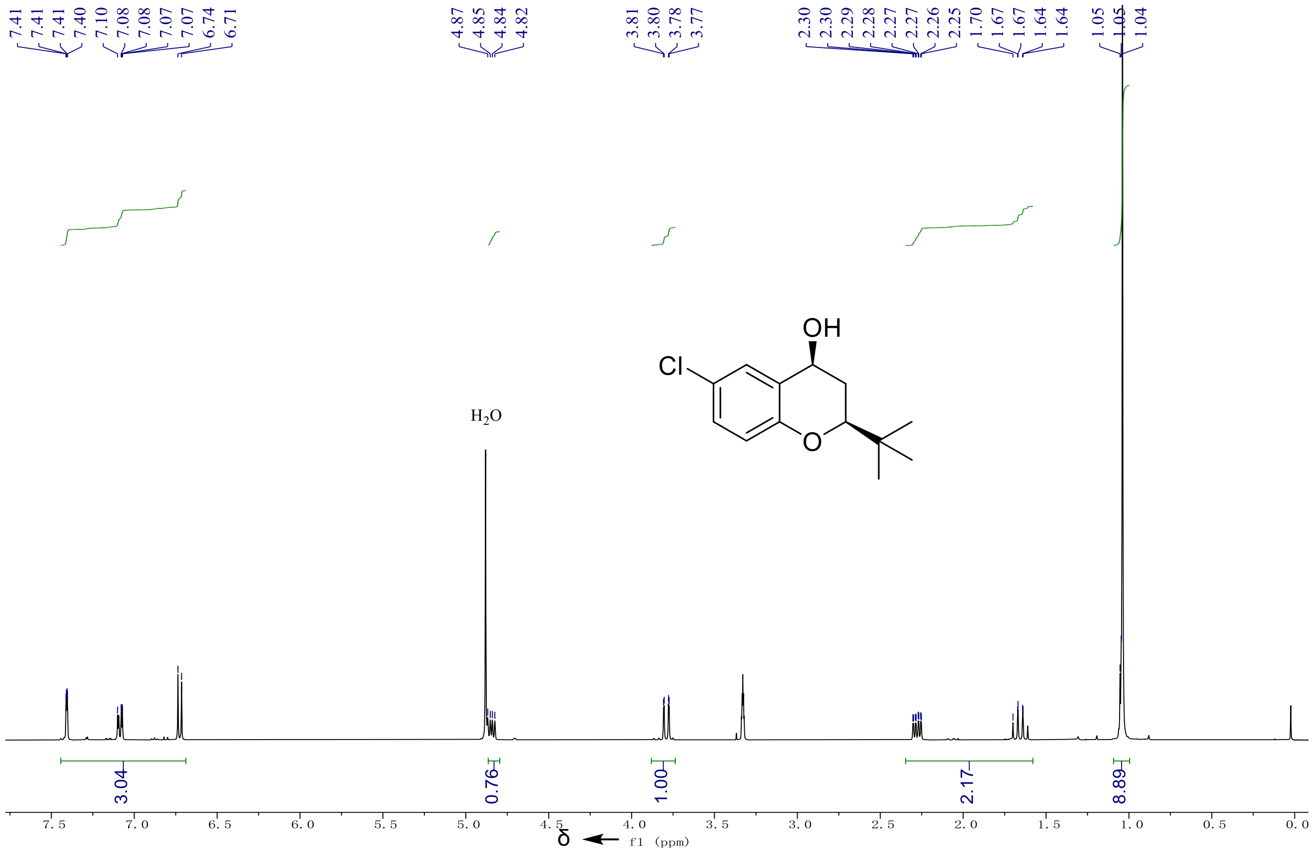


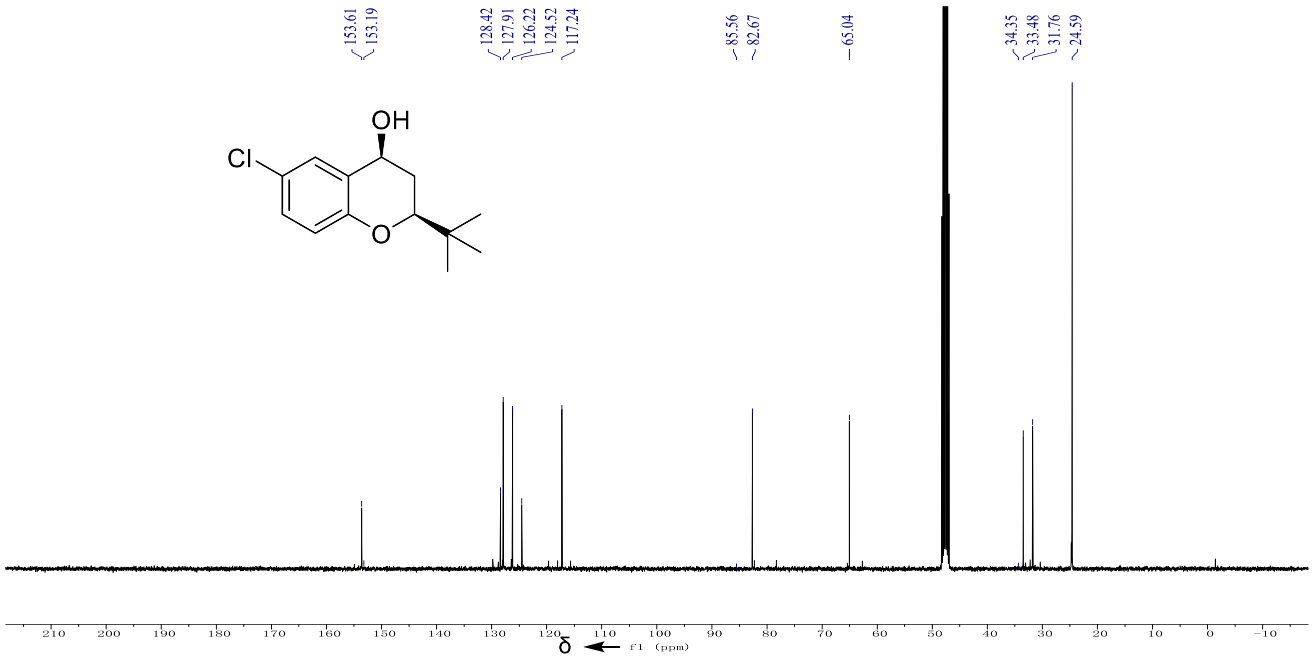
(*R*,*S*)-7bi: (2R,4S)-6-chloro-2-isobutylchroman-4-ol



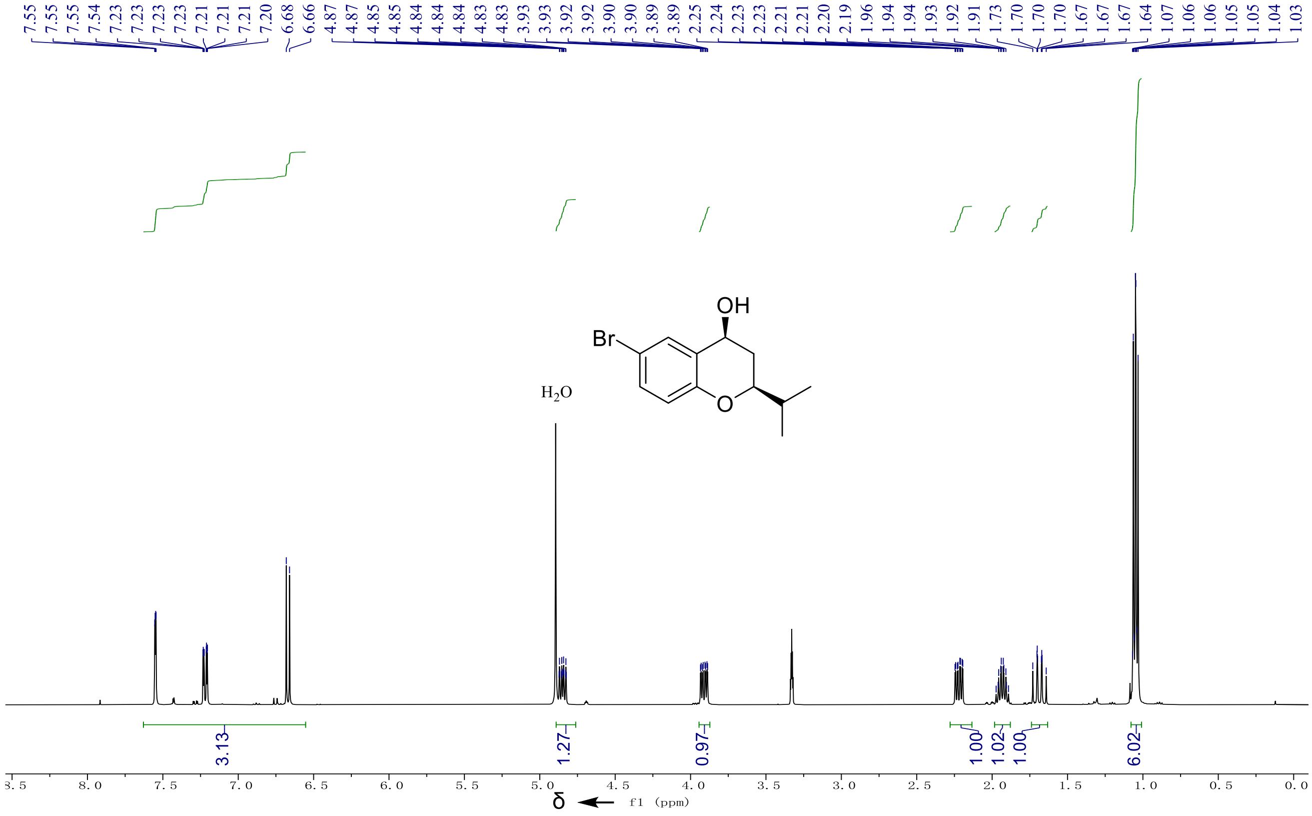


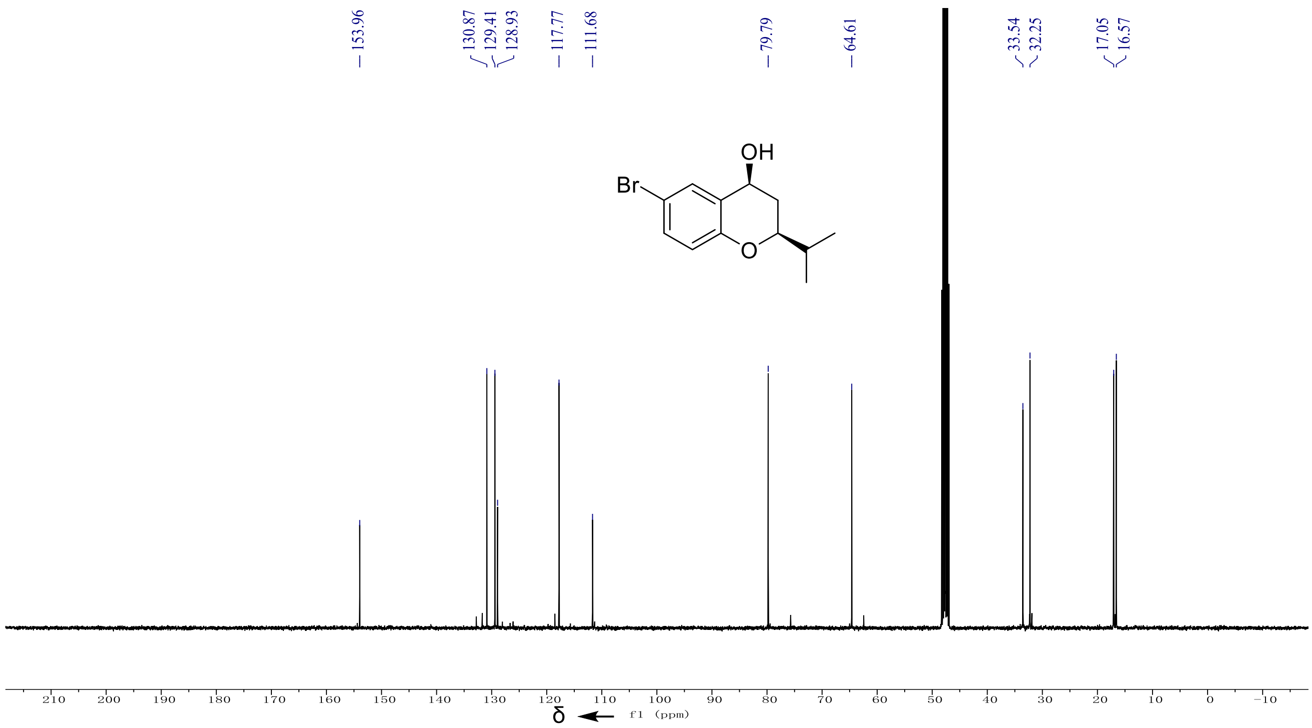
(*S*,*S*)-7bj: (2S,4S)-2-(tert-butyl)-6-chlorochroman-4-ol



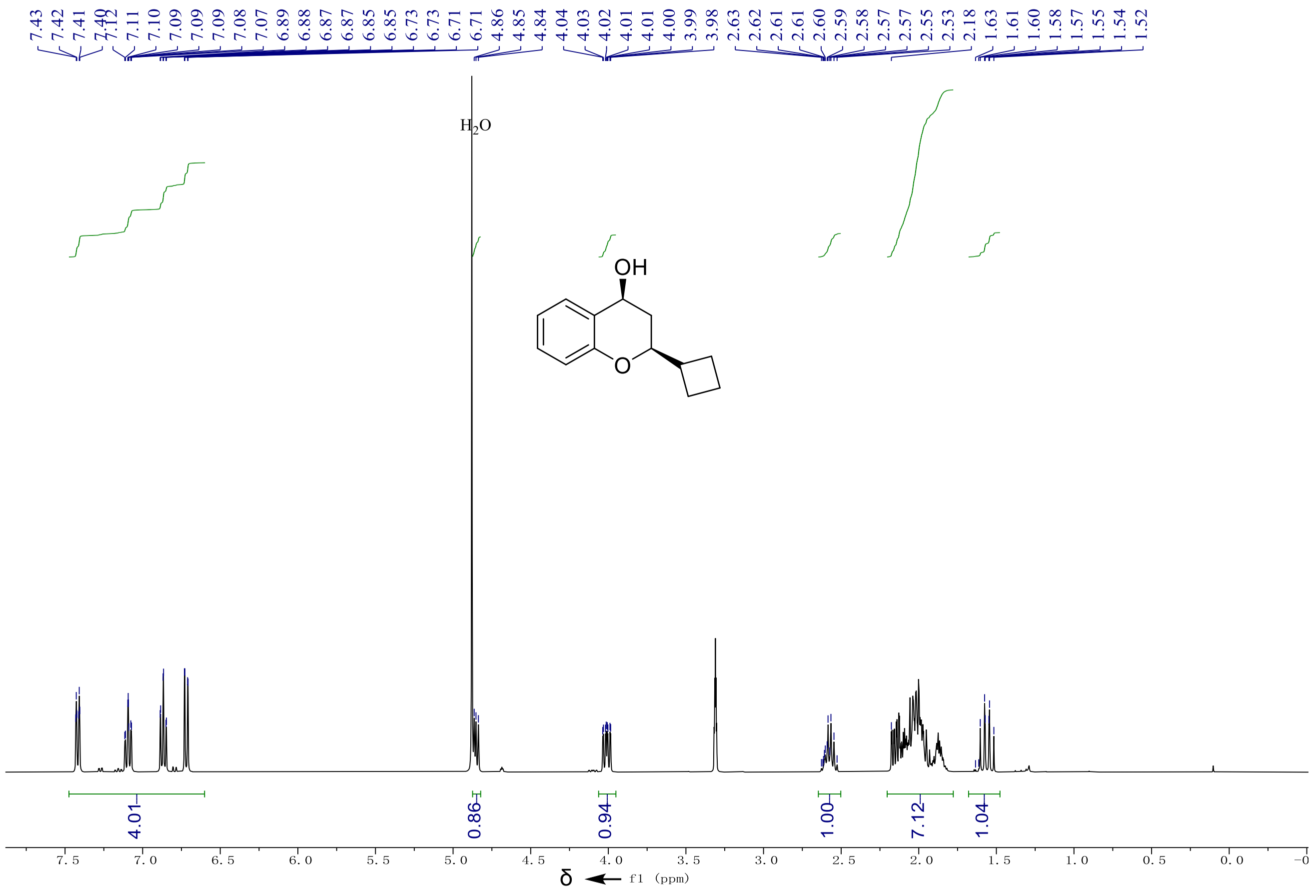


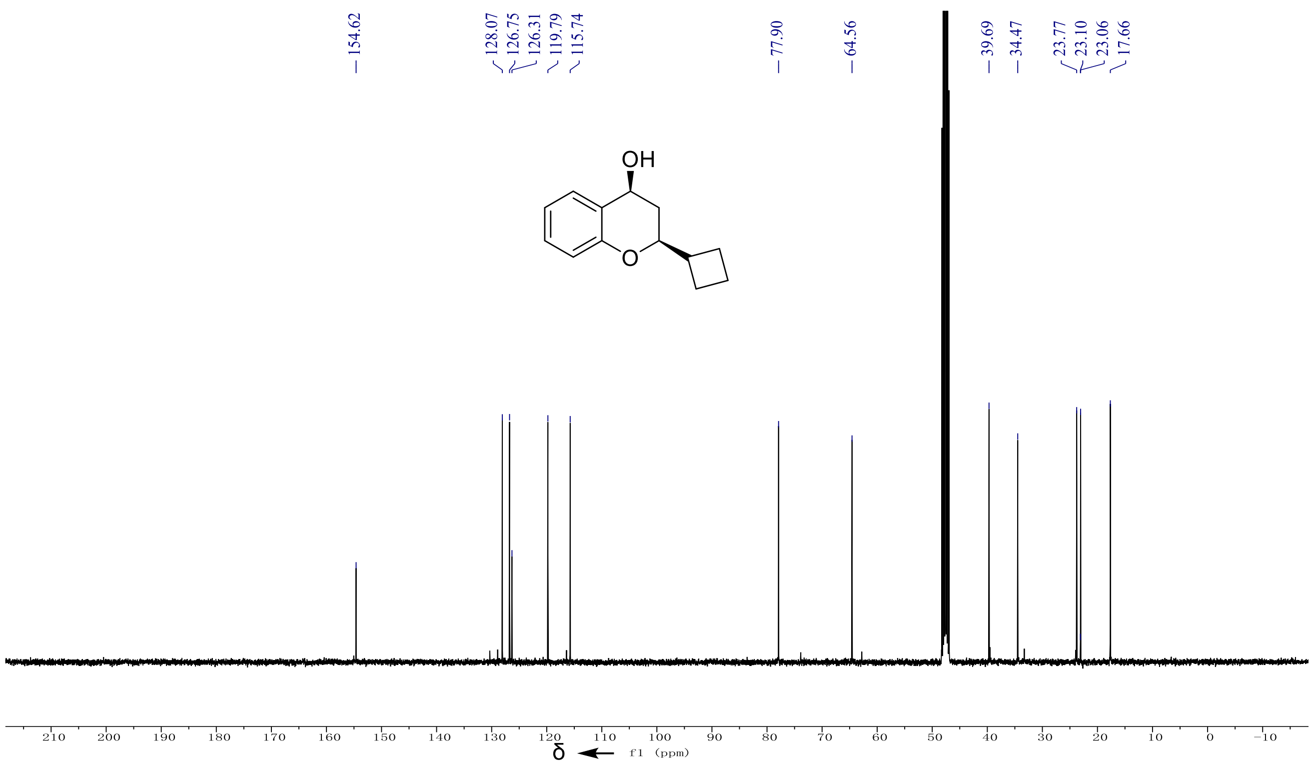
(*S*,*S*)-7bk: (2S,4S)-6-bromo-2-isopropylchroman-4-ol.



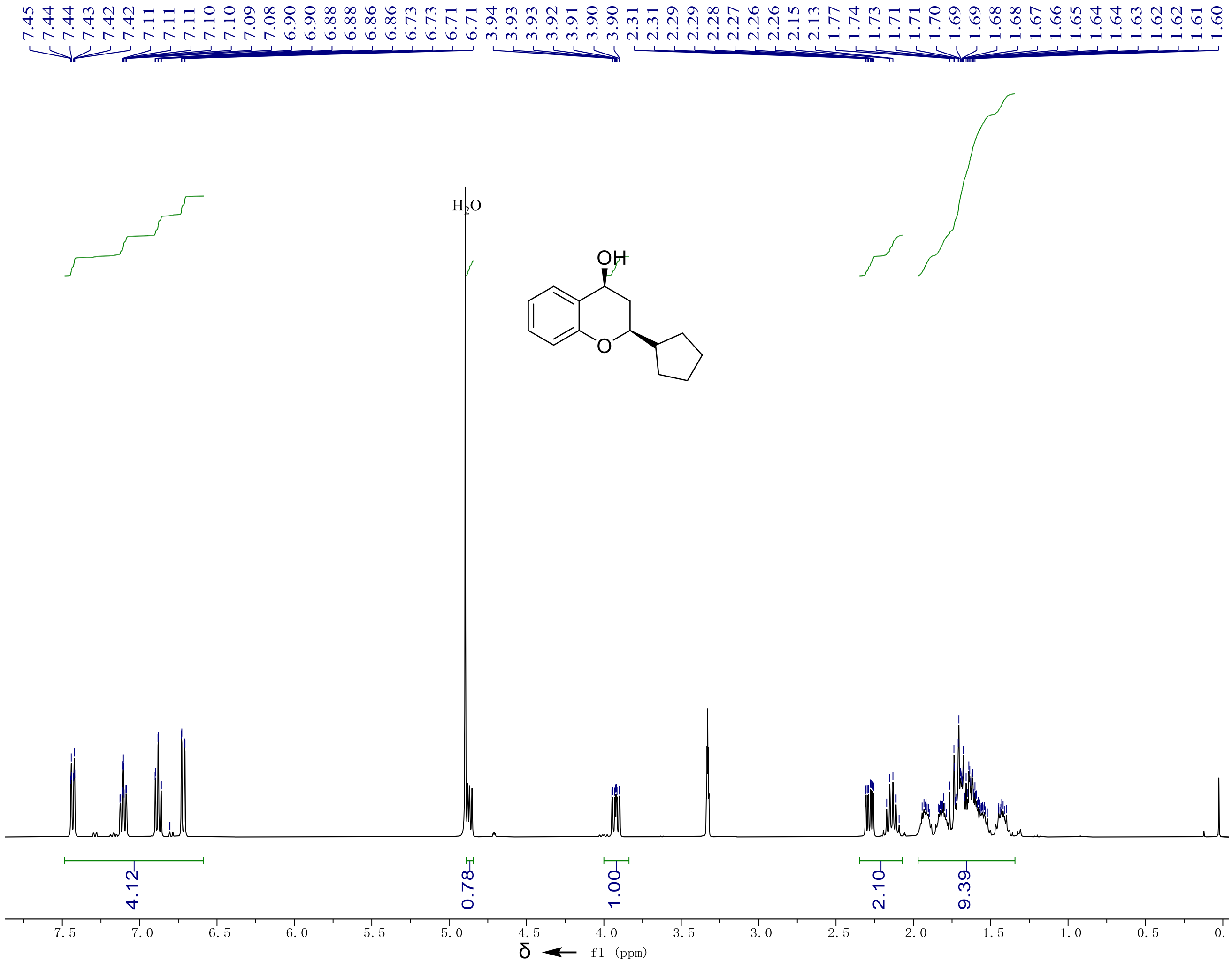


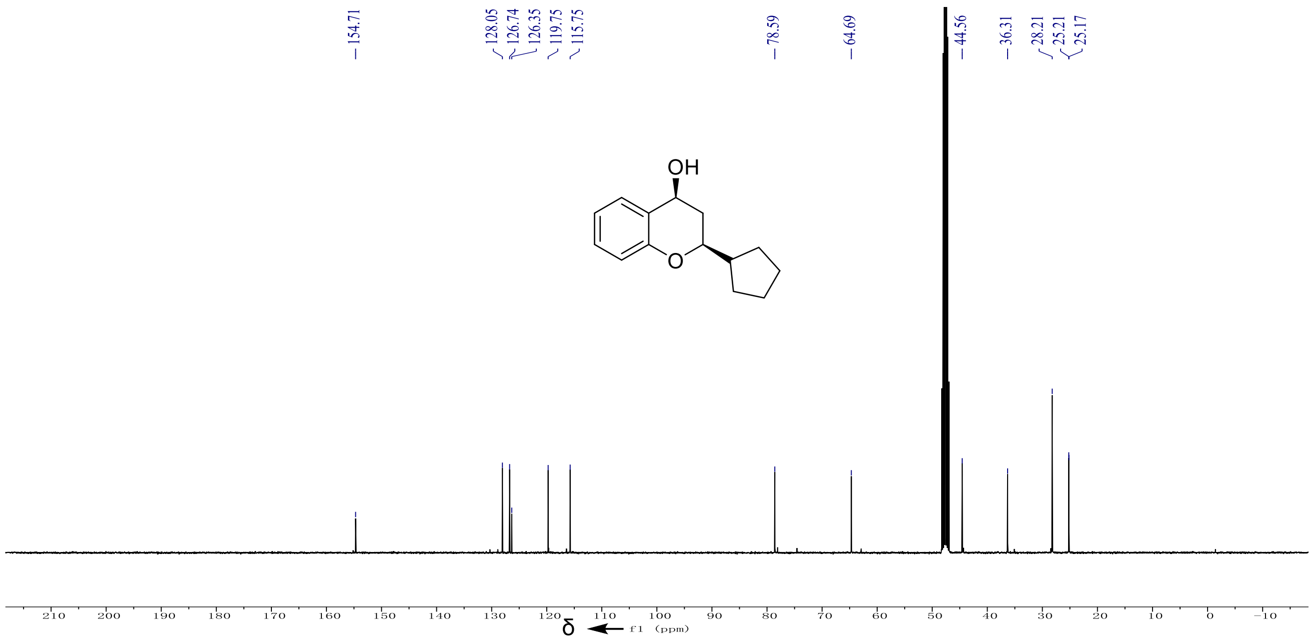
(*S*,*S*)-7bl: (2S,4S)-2-cyclobutylchroman-4-ol.



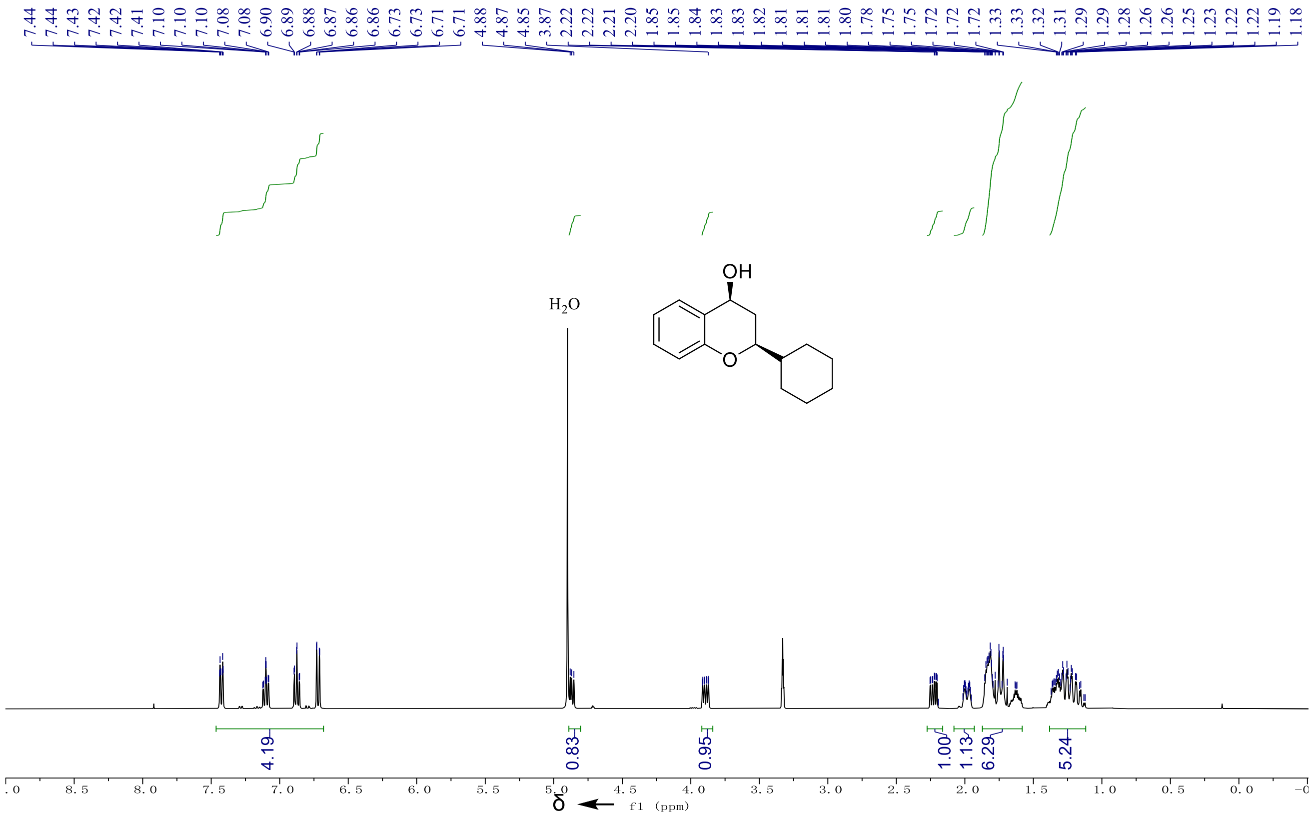


(*S*,*S*)-7bm: (2S,4S)-2-cyclopentylchroman-4-ol.

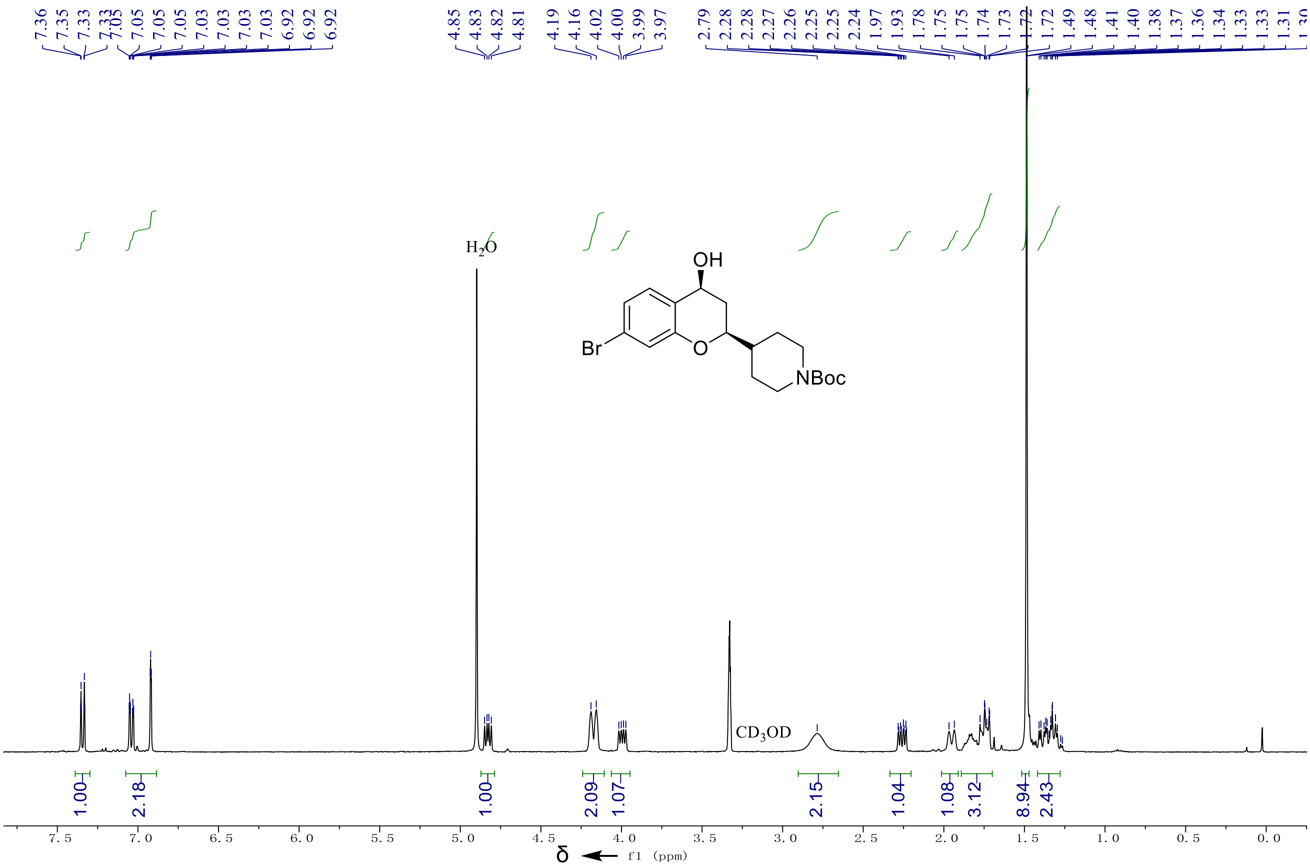




(*S*,*S*)-7bn: (2S,4S)-2-cyclohexylchroman-4-ol.



(*S*,*S*)-7bo: tert-butyl 4-((2S,4S)-7-bromo-4-hydroxychroman-2-yl)piperidine-1-carboxylate.



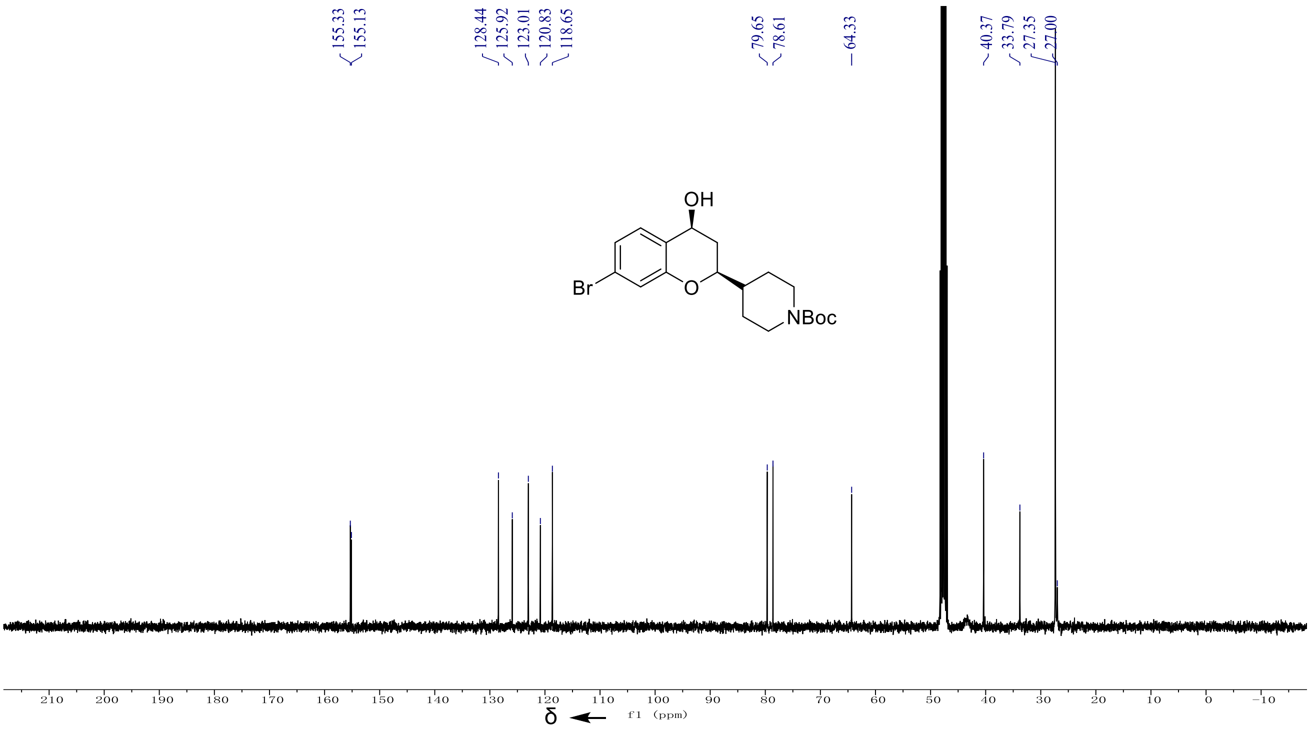


Table S3. The single-crystal structure data of (*S*,*S*)-**7ah**.

Datablock: (2*S*,4*S*)-2-(m-tolyl)chroman-4-ol ((*S*,*S*)-**7ah).**

Bond precision:	C-C = 0.0126 A		Wavelength=0.71073
Cell:	a=11.9068(17)	b=4.8812(7)	c=22.718(4)
	alpha=90	beta=94.231(4)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	1316.8(4)	1316.8(3)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C16 H16 O2	?
Sum formula	C16 H16 O2	C16 H16 O2
Mr	240.29	240.29
Dx,g cm-3	1.212	1.212
Z	4	4
Mu (mm-1)	0.079	0.079
F000	512.0	512.0
F000’	512.24	
h,k,lmax	14,5,27	14,5,27
Nref	4639[2619]	4440
Tmin,Tmax	0.993,0.996	0.550,0.746
Tmin’	0.985	

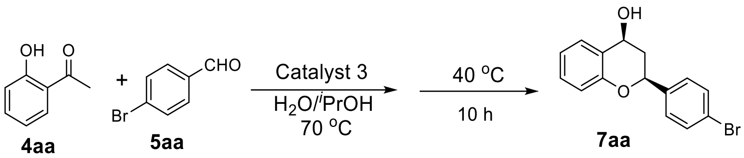
Correction method= # Reported T Limits: Tmin=0.550 Tmax=0.746
AbsCorr = MULTI-SCAN

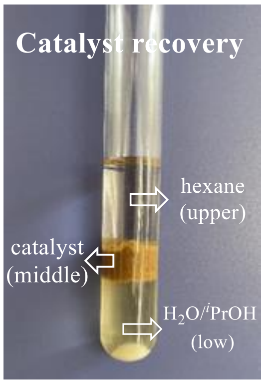
Data completeness= 1.70/0.96 Theta(max)= 24.998

R(reflections)= 0.0702(2296) wR2(reflections)= 0.2035(4440)

S = 1.041 Npar= 340

Table S4. Reusability of catalyst (for the Aldol condensation /oxa-addition/reduction cascade of **4aa** and **5aa**).

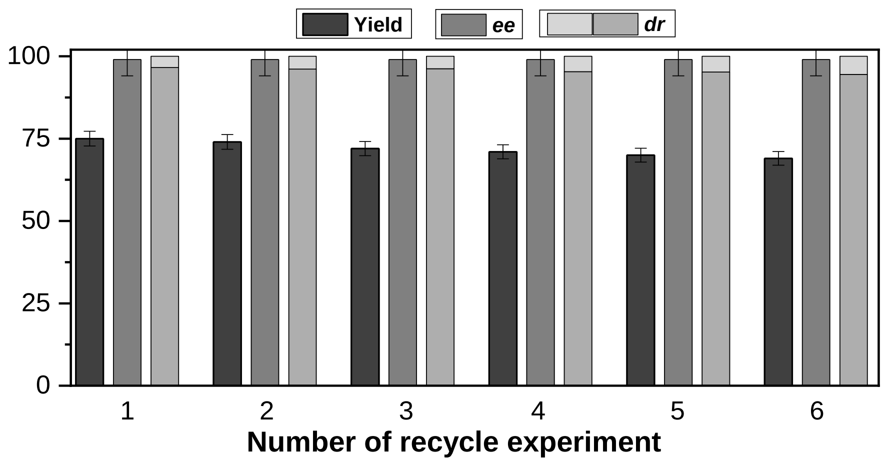


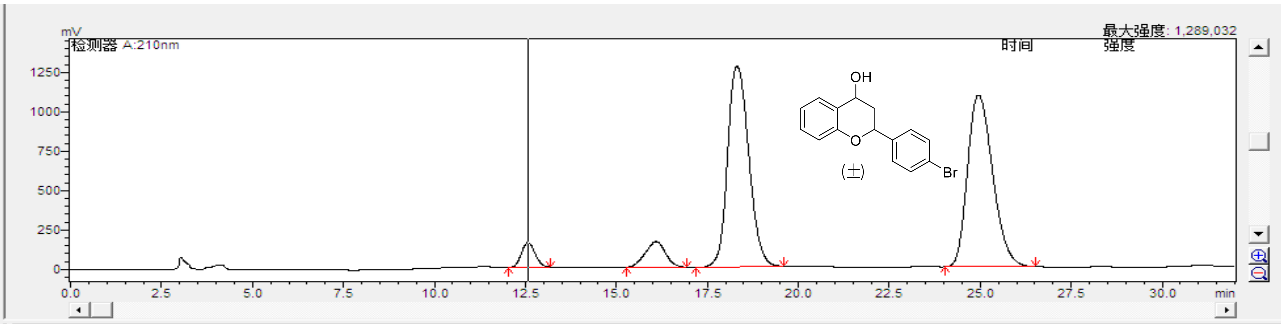


Entry	1	2	3	4	5	6
%Yield	75	74	72	71	70	69
%*ee*	99	99	99	99	99	99
dr	28	25	25	20	20	17

Reaction conditions: Catalyst **3** (0.12 mmol of DBU salt-loadings and 2.50 mol% of Ru-loadings based on ICP analyses), 1.0 equivalent of **4aa**, 1.20 equivalent of **5aa**, and 10.0 equivalent of HCOONa in 4.0 mL of H_2O/^{i}PrOH (v/v = 1:3), and the mixture stirred at 70 ℃ for the first 12 h followed at 40 ℃ for 10 h. Yields were determined by ^{1}H-NMR analysis, and *ee* and *dr* values were determined by chiral HPLC analysis.

Figure S8. Reusability of catalyst **3** in the Aldol condensation /oxa-addition/reduction cascade process of **4aa** and **5aa** (The error bars represent the standard deviation).

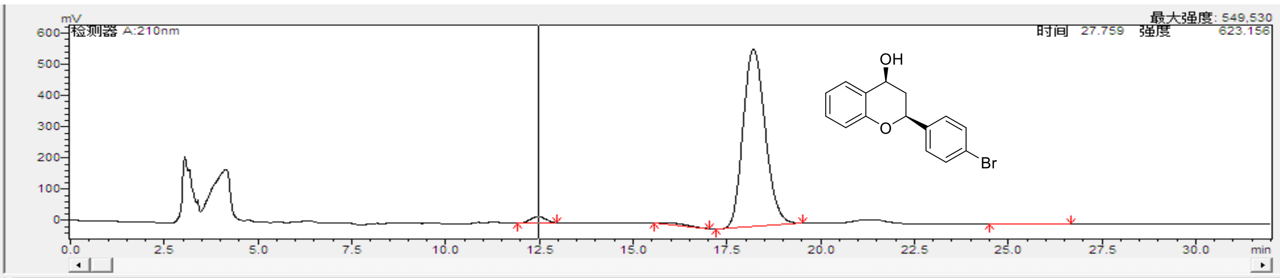




化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.570	12.570	1	4042364	155575	3.5252
2	RT16.091	16.091	2	6305224	162875	5.4986
3	RT18.316	18.316	3	51778979	1272917	45.1550
4	RT24.949	24.949	4	52542892	1088882	45.8212

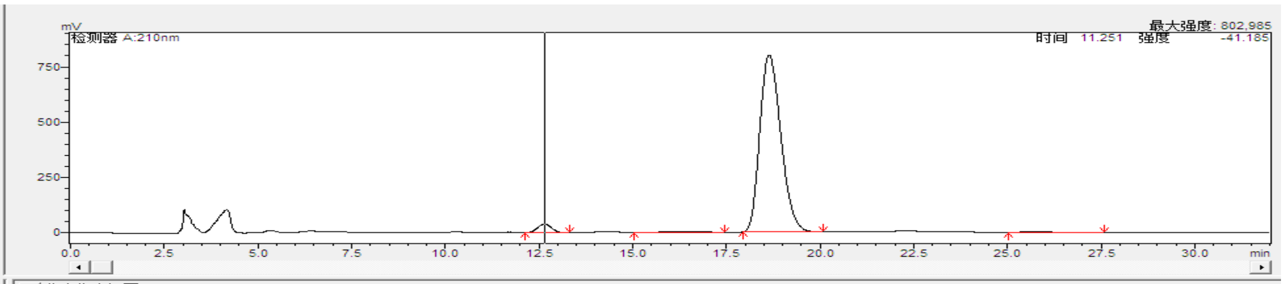
Recycle 1.



化合物表视图

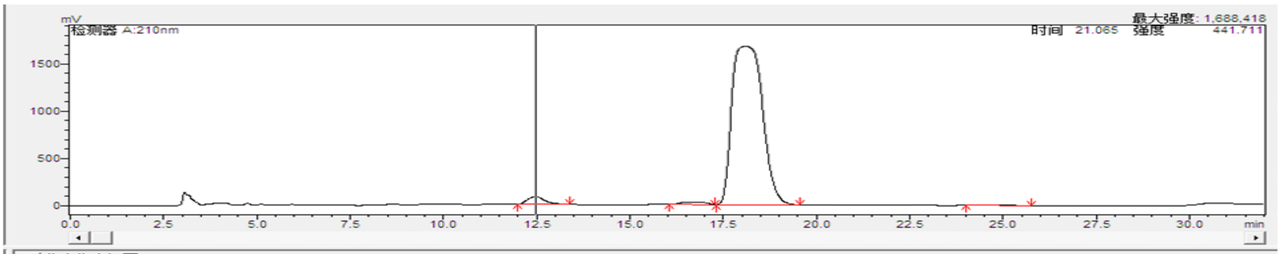
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.467	12.467	1	581009	19806	2.3915
2	RT15.821	15.821	2	238971	3451	0.9836
3	RT18.207	18.207	3	23424128	569386	96.4157
4	RT25.058	25.058	4	50832	1099	0.2092

Recycle 2.



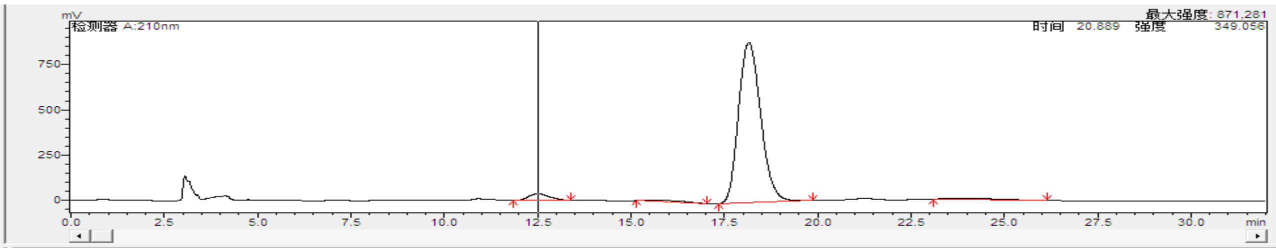
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.638	12.638	1	995245	39380	3.0551
2	RT16.924	16.924	2	270619	4303	0.8307
3	RT18.639	18.639	3	31248620	799927	95.9248
4	RT25.794	25.794	4	61695	1154	0.1894

Recycle 3.



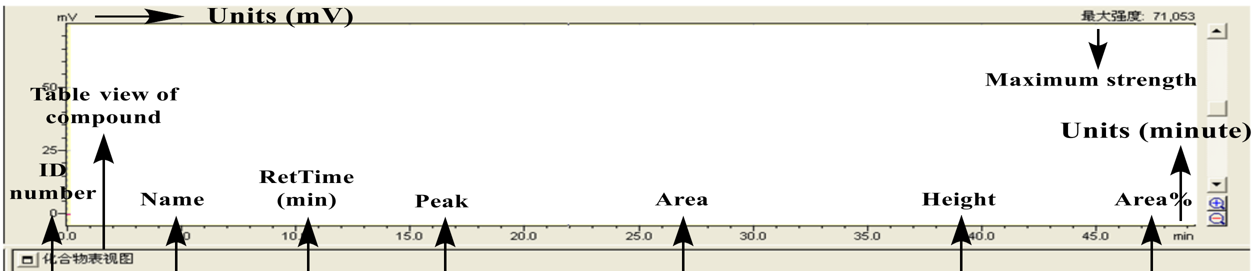
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.462	12.462	1	2604650	80450	2.6158
2	RT16.523	16.523	2	1188614	27008	1.1937
3	RT18.074	18.074	3	95616277	1679683	96.0267
4	RT24.929	24.929	4	163038	4005	0.1637

Recycle 4.



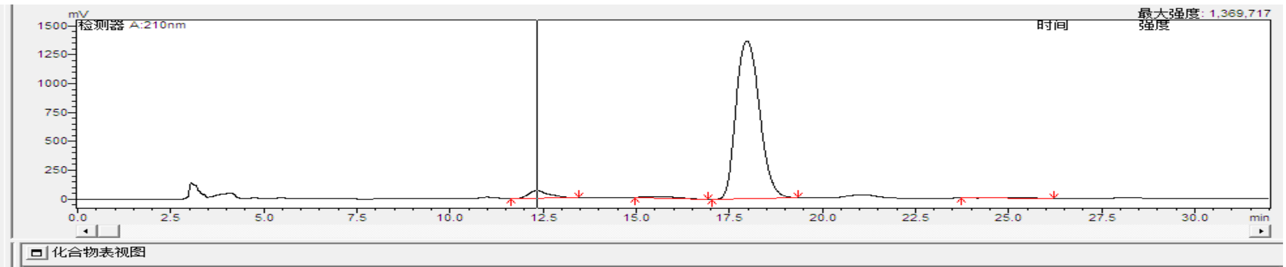
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.507	12.507	1	1311448	35989	3.3671
2	RT15.614	15.614	2	504898	4983	1.2963
3	RT18.153	18.153	3	36562494	883671	93.8720
4	RT23.865	23.865	4	570461	4987	1.4646

<u>Translation of all characters (Chinese) in the above all frameworks to English is as follows:</u>



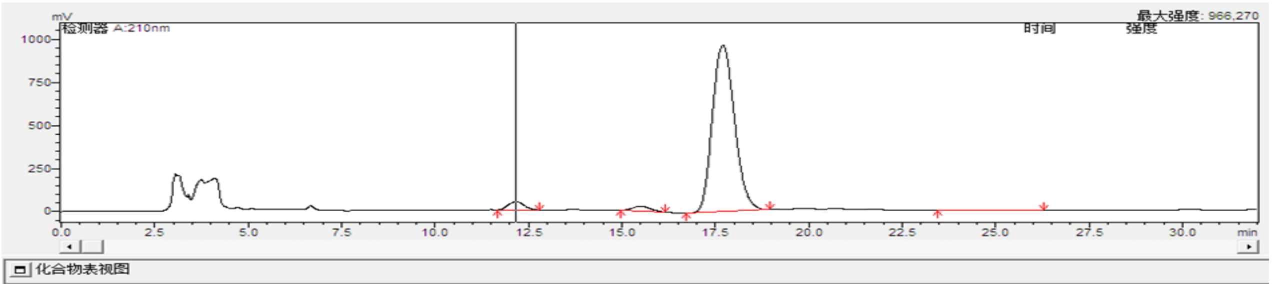
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 913	21. 913	1	2804461	70765	97. 6444
2	RT32. 695	32. 695	2	27506	583	0. 9577
3	RT37. 225	37. 225	3	1394	28	0. 0485
4	RT41. 351	41. 351	4	38756	593	1. 3494

Recycle 5.



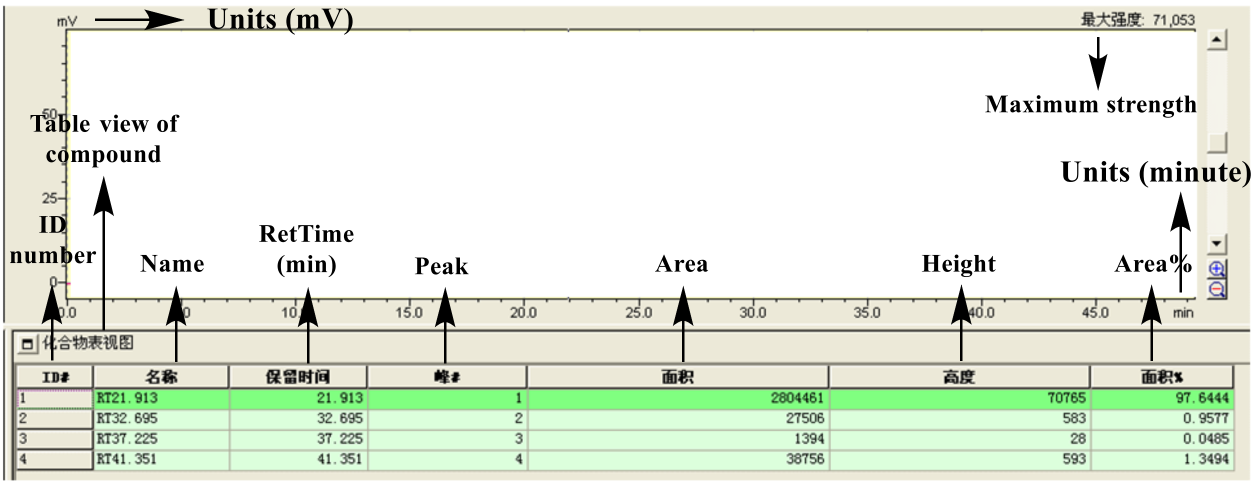
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.323	12.323	1	2477433	65763	3.9109
2	RT15.620	15.620	2	578667	8738	0.9135
3	RT17.969	17.969	3	60178008	1366528	94.9965
4	RT24.854	24.854	4	113496	2544	0.1792

Recycle 6.



ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.170	12.170	1	1419407	47510	3.3544
2	RT15.498	15.498	2	908717	28249	2.1475
3	RT17.696	17.696	3	39847698	966049	94.1699
4	RT24.533	24.533	4	138855	2711	0.3281

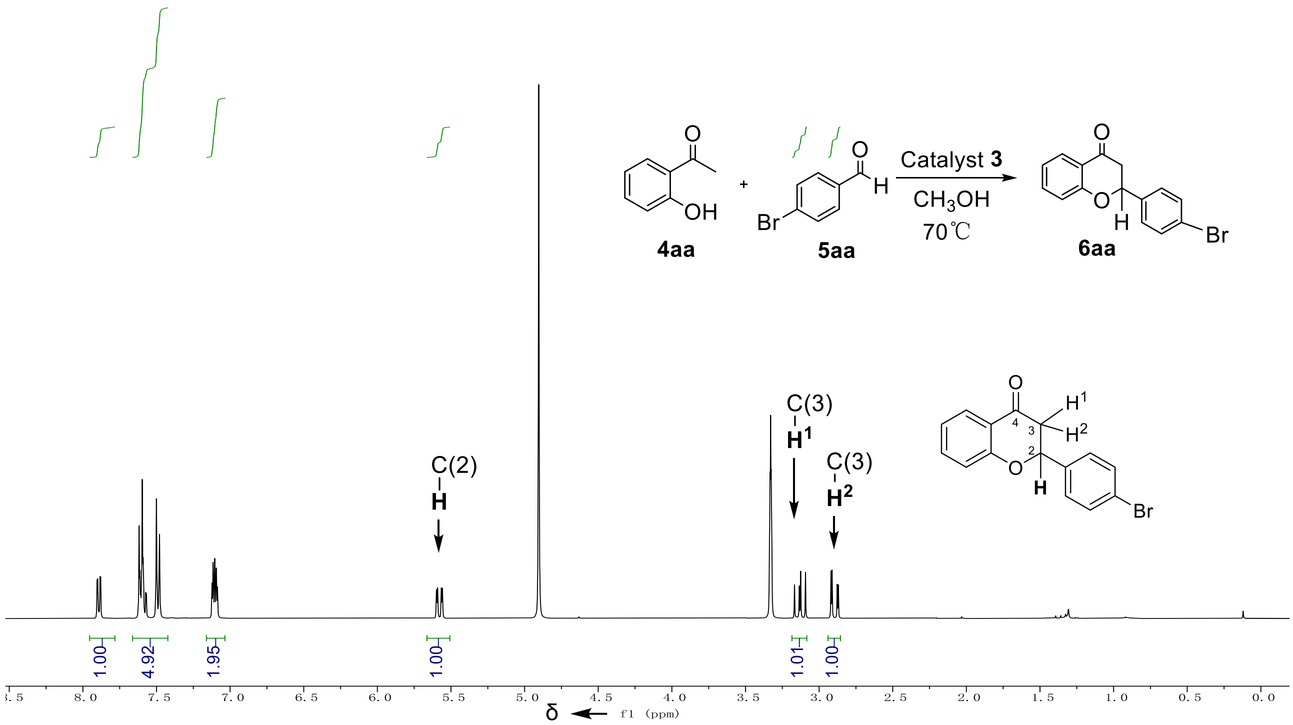
<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



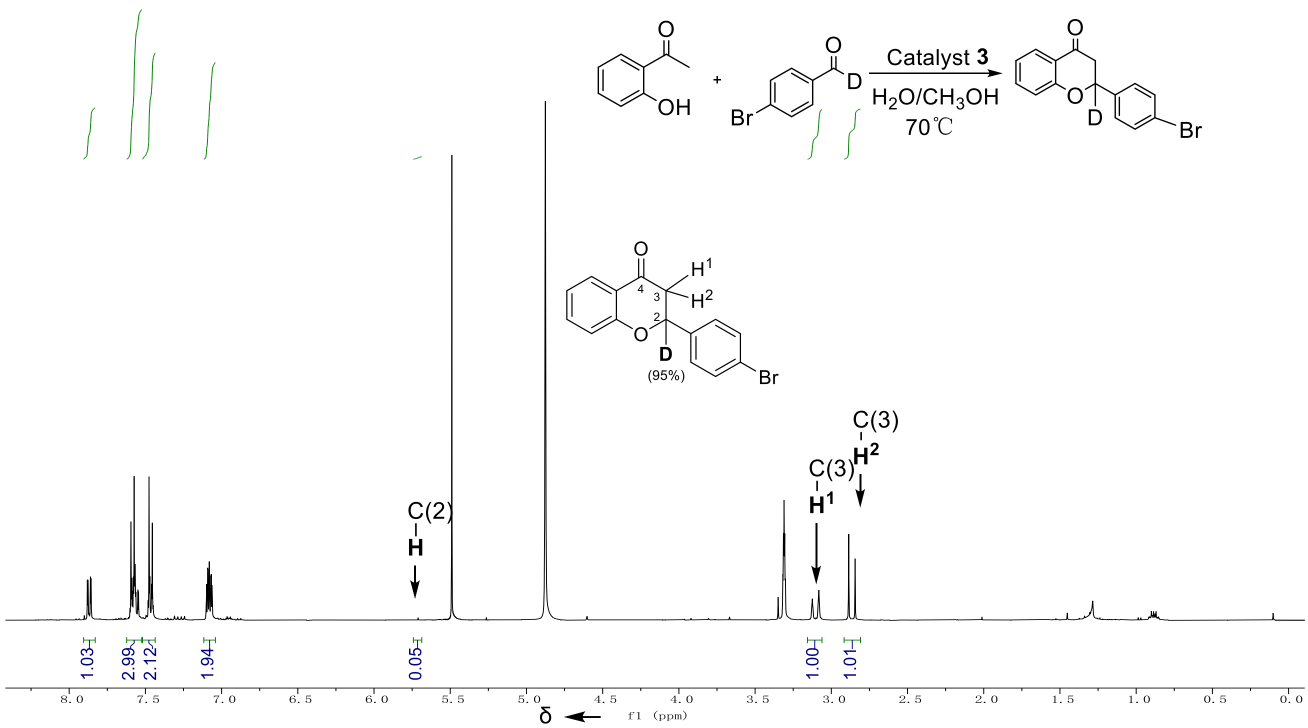
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

Figure S9. Contrastive ^{1}H-NMR spectra for deuterium labeling experiments.

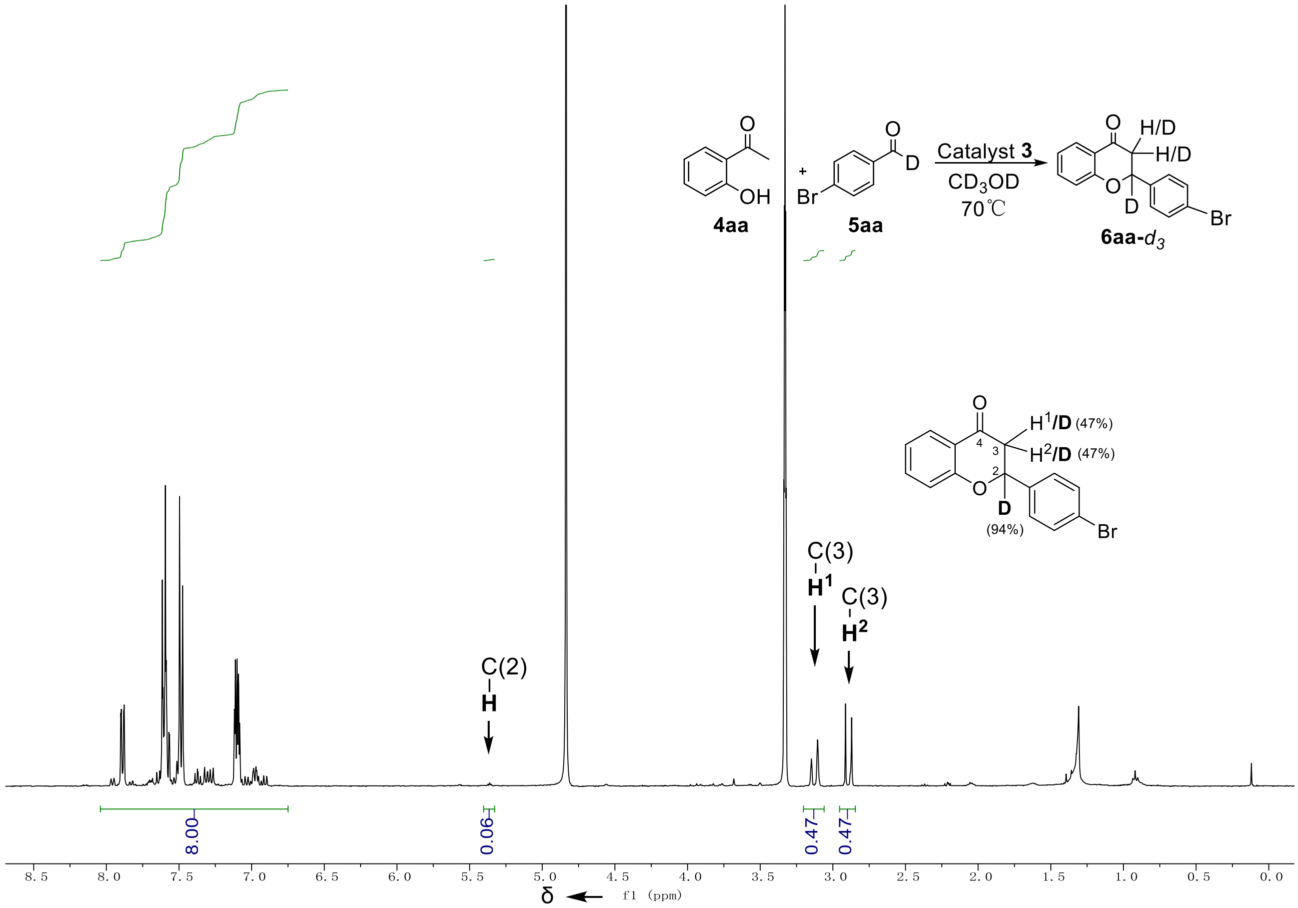
(a) The standard ^{1}H-NMR spectrum of **6aa** in the normal reaction of **4aa** and **5aa.**



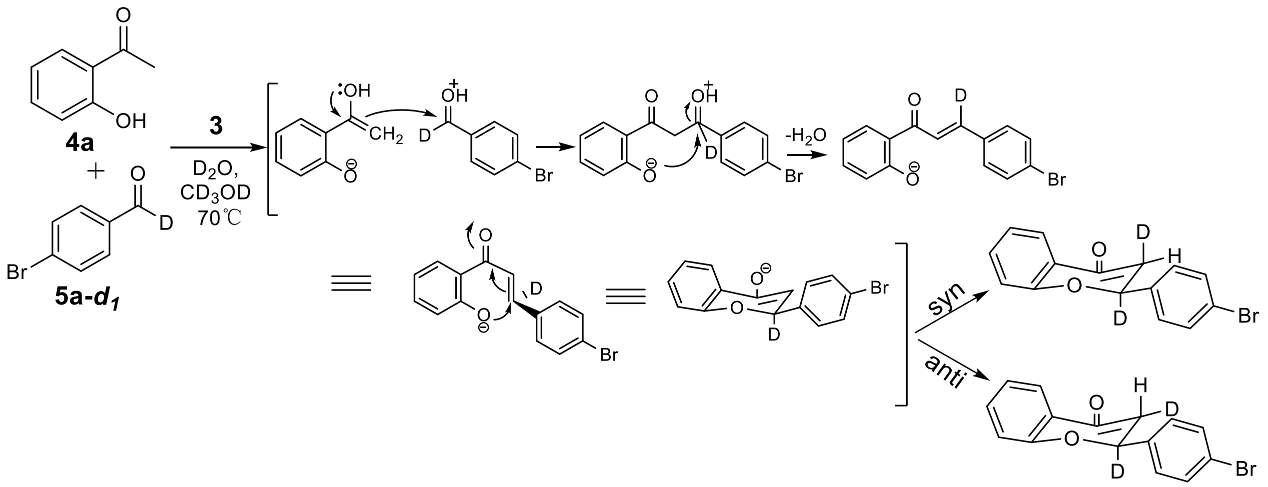
(b) The ^{1}H-NMR spectrum of ***6aa-d$_1$*** in the deuterium labeling reaction of **4aa** and **5aa-*d$_1$*** in H_2O/CH_3OH.



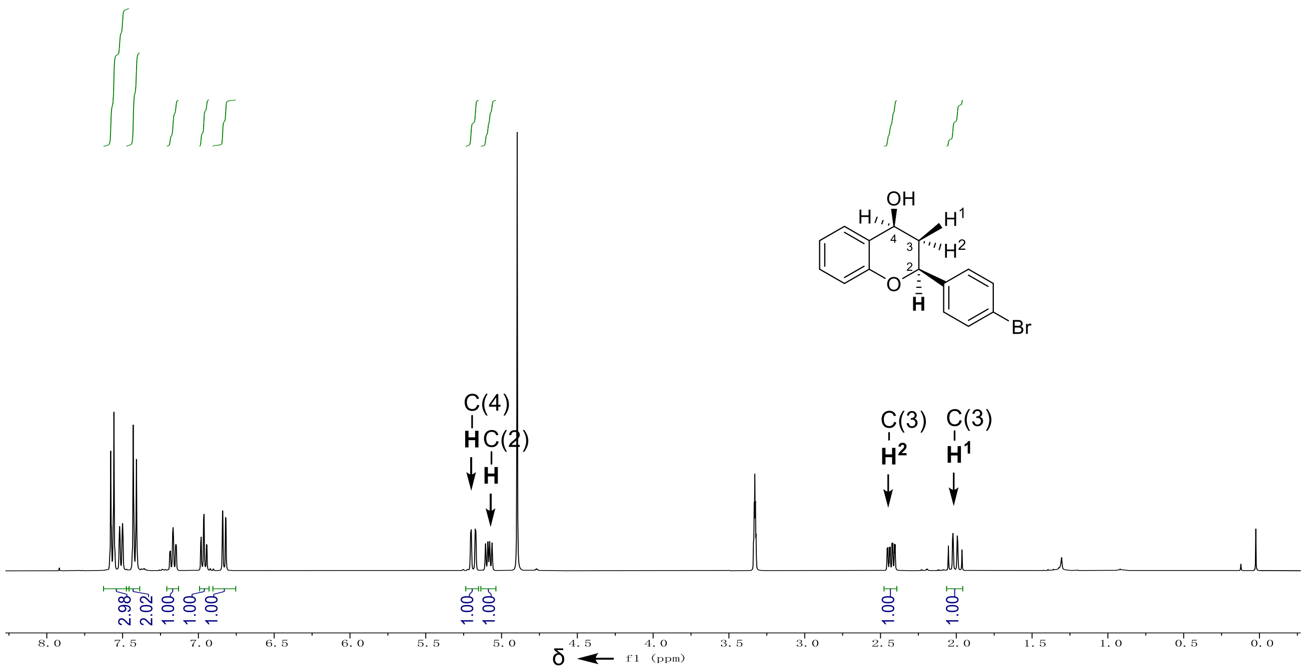
(c) The [1]H-NMR spectrum of **6aa-*d*$_3$** in the deuterium labeling reaction of **4aa** and **5aa**-*d*$_1$ reaction in deuterated D_2O/CD_3OD**.**



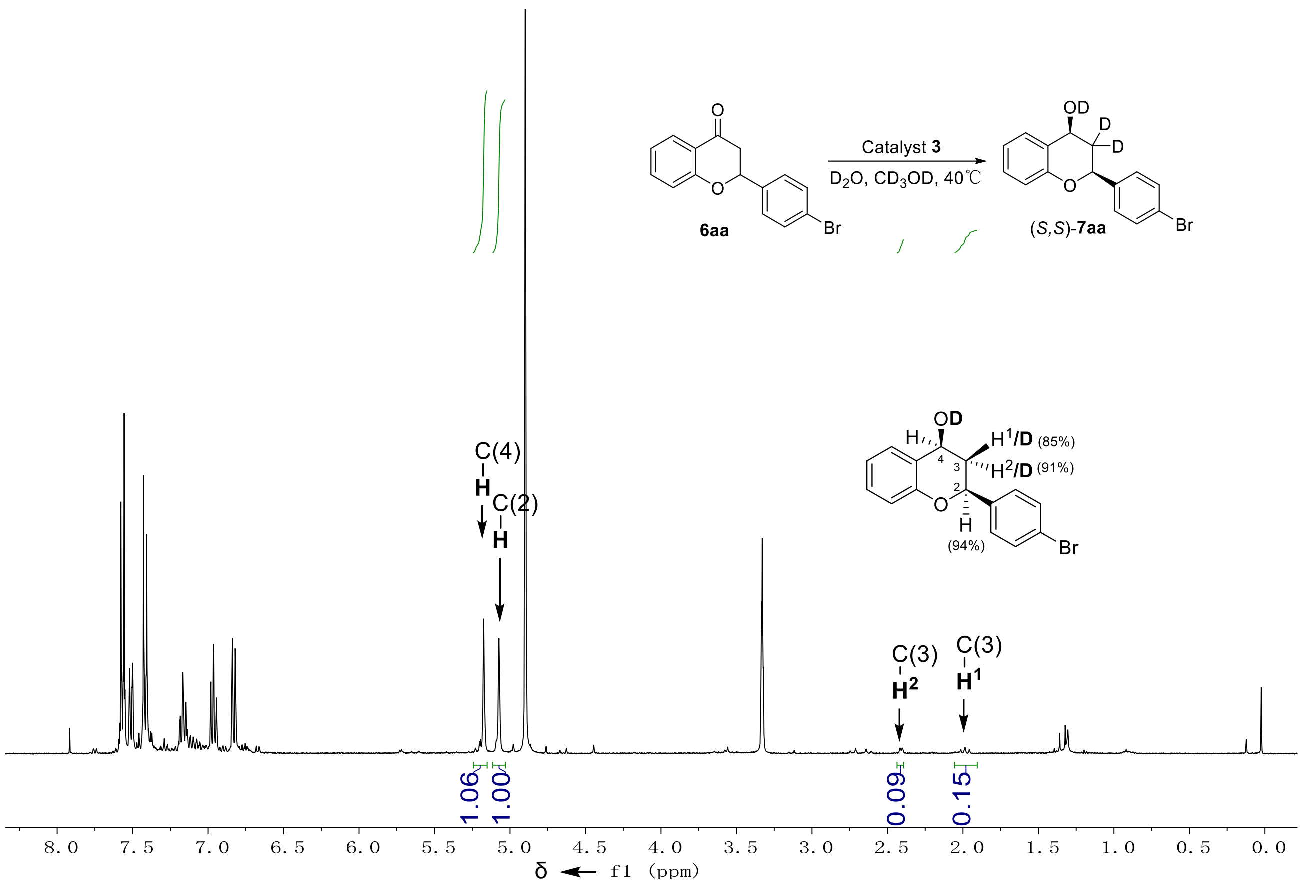
Explanation: Through the comparison of the above three [1]H-NMR spectra, it easily arrivals at a conclusion below. The Aldol condensation of **4aa** and **5aa** generates deuterated chalcone. The intramolecular conjugate addition (oxa-Michael cyclization) affords **6aa**-*d*$_3$ with equal attacks from both *syn*-face and *anti*-face of the double bond, leading to the same deuterium ratio that is possibly abstracted by D^+ from D_2O.



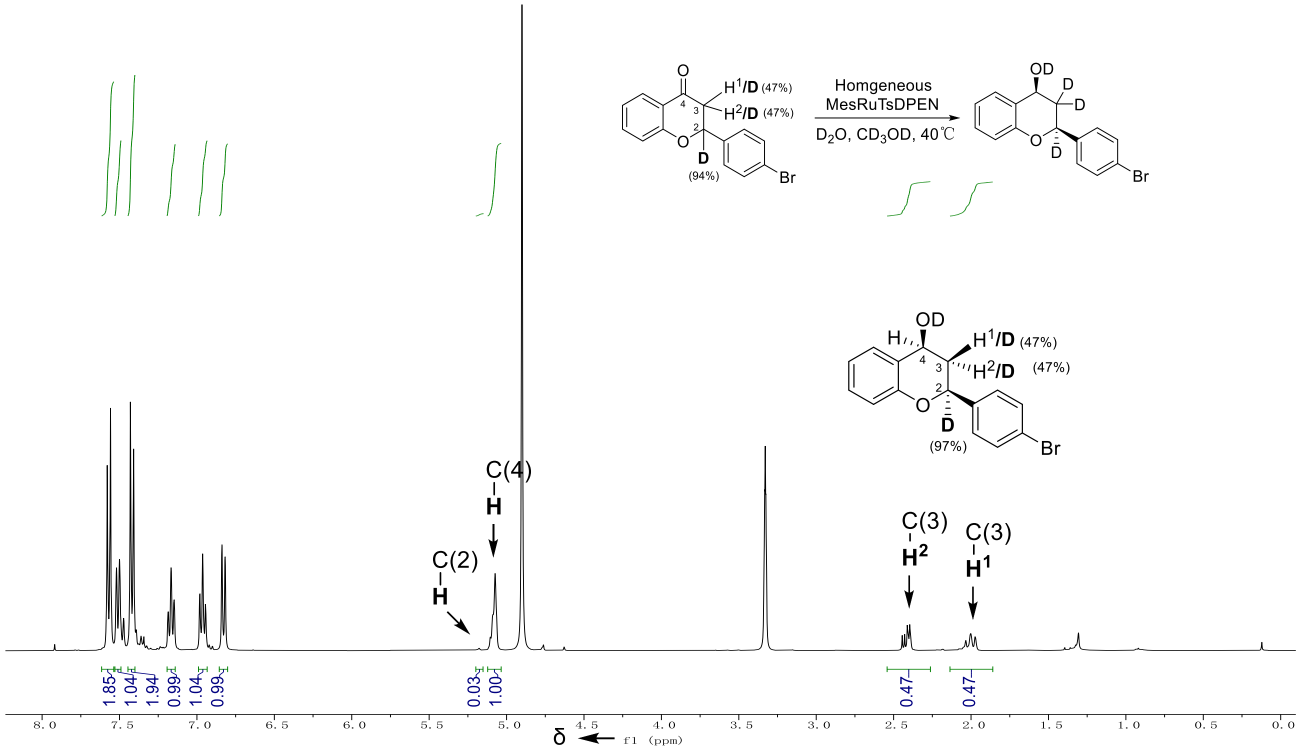
(d) The standard ^{1}H-NMR spectrum of (*S,S*)-**7aa**.



(e) The ^{1}H-NMR spectrum of **7aa-*d*₃** in the reaction of **6aa** in deuterated D_2O/CD_3OD.



(f) The [1]H-NMR spectrum of **7aa-*d₄*** in the deuterium labeling reaction (control reaction) of **6aa**-d_3 with homogeneous MesRuTsDPEN as a catalyst in the deuterated D_2O/CD_3OD.



(g) The [1]H-NMR spectrum of **7aa-*d₄*** in the deuterium labeling reaction (control reaction) of **6aa**-d_3 with **3** as a catalyst in the deuterated D_2O/CD_3OD.