Supporting Information for:

An Access to Chiral 3-Benzylchromanones and 2,6-Disubstituted Cyclohexanones *via* Rh-Catalyzed Chemo- and Enantioselective Hydrogenation of Arylidene Chromanones/Cyclohexanones

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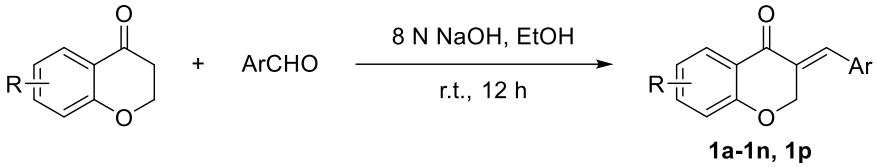
1. Experimental Section

General Information: All the air or moisture sensitive reactions and manipulations were performed by using standard Schlenk techniques and in a nitrogen-filled glovebox. THF, dioxane and toluene were distilled from sodium benzophenone ketyl. DCM was distilled from calcium hydride. Anhydrous MeOH was distilled from magnesium. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV (400 MHz) spectrometers and JEOL JNM-ECX600P and JNM-ECS600 (400 MHz or 600 MHz) spectrometers. ($CDCl_3$ was the solvent used for the NMR analysis, with TMS as the internal standard). Optical rotation was determined using Autopol III Automatic polarimeter (Rudolph research Analyical). HPLC analysis was conducted on Agilent 1260 series instrument. SFC analysis was conducted on Agilent 1260 series instrument. HRMS were recorded on a Waters LCT Premier XE mass spectrometer with TOF.

2. General procedure for the synthesis of substrates 1, 3, 5 and 6

General Procedure for Synthesis of Products 1



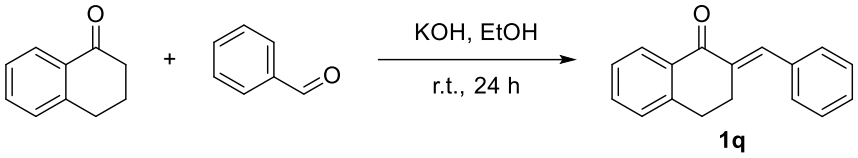
1a-1n, 1p

The chroman-4-one (10 mmol, 1.0 equiv.) was added to a single-necked flask, dissolved with EtOH (4 mL) and stirred, then the corresponding aldehyde (10 mmol, 1.0 equiv.) was added. The aqueous solution of NaOH (2.4 mmol, 8 N, 0.24 equiv.) was slowly added to the system and stirred at room temperature for 12 h. The solid precipitate was collected by filtration, the crude product was purified by column chromatography (PE : EA = 10 : 1). The corresponding products **1a**–**1n** and **1p** were obtained after recrystallization.[1]

1o

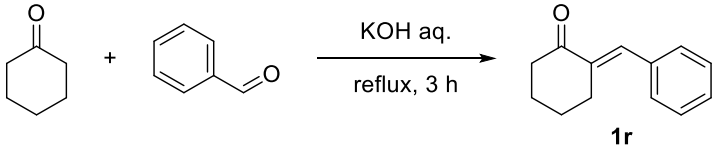
In the nitrogen atmosphere, chroman-4-one (10 mmol, 1.0 equiv.) was added to the dried three-necked bottle, and anhydrous DCM (30 mL) was added for stirring and dissolution. $TiCl_4$ (1.3 mL, 12 mmol, 1.2 equiv.) and Et_3N (2.0 mL, 14 mmol, 1.4 equiv.) were added to the system, the mixture was stirred at -78 °C for 30 minutes. Then isobutyraldehyde (12 mmol, 1.2 equiv.) was added to the

system, and stirred at -78 °C for 2 hours. The reaction was quenched by adding water (20 mL) and then cooled to room temperature. The water layer was extracted with DCM (3 × 30 mL), the combined organic layers were washed with 1 M HCl aqueous solution and dried with anhydrous Na_2SO_4. The solvent was evaporated, and the crude product was purified by column chromatography to obtain product **1o**.[19]



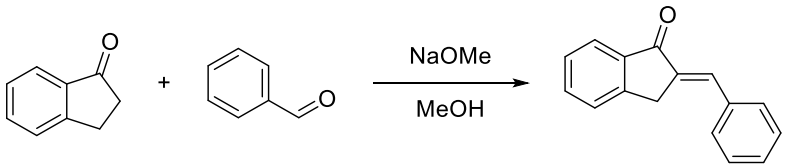
1q

KOH (1.1 g) was added to a round-bottomed flask and mixed with EtOH (100 mL), then 1-tetralone (20 mmol, 1.0 equiv.) and benzaldehyde (50 mmol, 2.5 equiv.) were slowly added to the system in turn and stirred at room temperature for 24 h. After the reaction was complete, the solid was filtered and separated. The crude product was purified by column chromatography (PE : EA = 10 : 1), and the corresponding product **1q** was obtained.[2]



1r

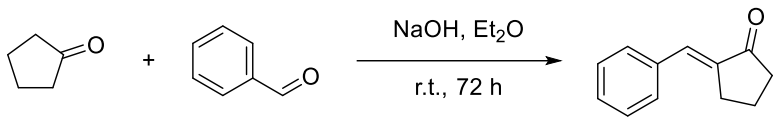
The mixture of benzaldehyde (25 mmol, 1.0 equiv.), cyclohexanone (37.5 mmol, 1.5 equiv.) and 1N KOH solution (25 mL) was refluxed for 3 h. After cooling to room temperature, EA (50 mL) was added, the water layer was separated and extracted with EA (3 × 30 mL). The combined organic phases were washed with brine and dried with Na_2SO_4. The solvent was evaporated and the crude product was purified by silica gel column chromatography (PE:EA = 10:1) to obtain the substrate **1r**.[2]



1s

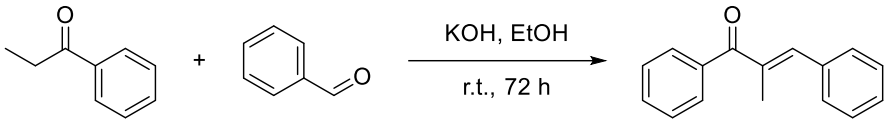
Under nitrogen atmosphere, the solution of NaOMe was added to the mixed solution of benzaldehyde (12 mmol, 1.1 equiv.) and MeOH (30 mL). 1-indanone (11.4 mmol, 1.0 equiv.) was dissolved in MeOH (30 mL), dropped into the mixture, and stirred at room temperature for 15 h. The reaction mixture was poured into water (50 mL), acidified with 2N HCl and extracted with DCM (3 × 30 mL). The combined organic layers were washed with brine, then dried with Na_2SO_4,

and the solvent was removed. The substrate **1s** was obtained by column chromatography (PE : EA = 10 : 1).[3]



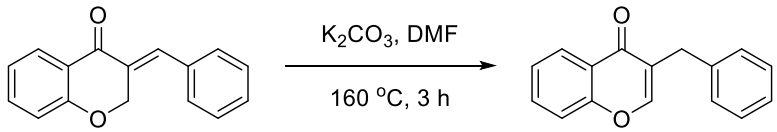
1t

Benzaldehyde (50 mmol, 1.0 equiv.), cyclopentanone (60 mmol, 1.2 equiv.), diethyl ether (50 mL) and 1N NaOH solution (50 mL) were sequentially added into a 250 mL single-necked flask, and the mixture was stirred at room temperature for 72 h. The reaction solution was extracted with EA (3 × 30 mL), the combined organic phases were washed with brine, dried with Na_2SO_4 and the solvent was evaporated. The crude product was purified by silica gel column chromatography to obtain substrate **1t**.[2]



1u

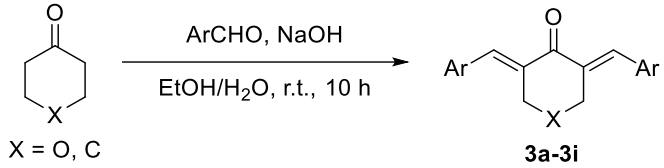
In a 250 mL flask, an aqueous solution of KOH (0.1 mol, 2.5 equiv.) was added to the EtOH (80 mL) solution of phenylacetone (40 mmol, 1.0 equiv.) and benzaldehyde (80 mmol, 2.0 equiv.) and stirred at room temperature for 72 h. EtOH was removed under reduced pressure and extracted with EA (3 × 30 mL). The combined organic layers were washed with aqueous HCl solution and brine, dried with Na_2SO_4, and the solvent was evaporated. The residue was purified by column chromatography (PE : EA = 20 : 1) to obtain the substrate **1u**.[2]



1a **2a'**

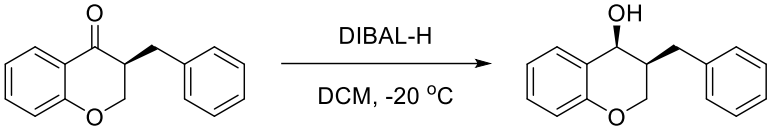
The mixture of **1a** (3.0 mmol, 1.0 equiv.), K_2CO_3 (5.1 mmol, 1.7 equiv.) and DMF (36 mL) was refluxed for 3 h, then poured into brine and extracted with EA (3 × 50 mL). The solvent was removed under reduced pressure, and the residue after drying was separated by column chromatography with (PE:EA = 15:1) to obtain the product **2a'**.[1]

General Procedure for Synthesis of Products 3

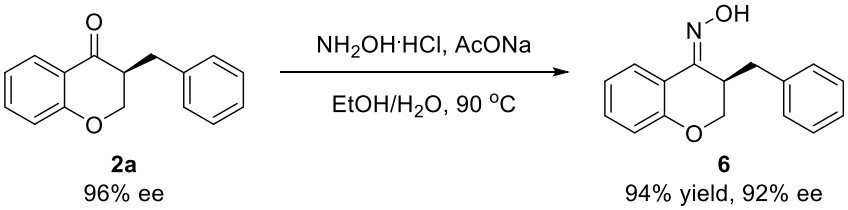


The corresponding mixed solution (10 mL) of aldehyde (15 mmol, 2.0 equiv.), tetrahydro-4*H*-pyran-4-one/cyclohexanone (7.5 mmol, 1.0 equiv.) and EtOH were slowly added to the EtOH/H_2O (v/v = 1/1, 28.5 mL) solution of NaOH (30 mmol, 4.0 equiv.). The reaction mixture was stirred at room temperature for 10 h, the yellow precipitate was filtered and recrystallized from DCM/PE, and dried in vacuum.[4]

General Procedure for Synthesis of Products 5 and 6



The chiral substrate **2a** was added to a dry three-neck flask equipped with a magnetic stirrer, nitrogen was replaced three times, dried DCM was added and cooled to -20 °C. Subsequently, a newly prepared solution of 1 M DIBAL-H (diisobutylaluminum hydride) in toluene (1.2 equiv.) was added. The reaction was stirred at -20 °C and the completion of the reaction was observed by TLC analysis. Subsequently, the reaction was cooled to 0 °C, and water was added to quench the reaction. The aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were dried with Na_2SO_4 and concentrated. The crude product was purified by column chromatography, and product **5** was obtained in 96% yield.

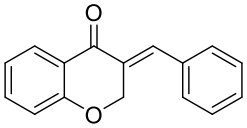


Sodium acetate (1.5 equiv.) was added to a stirred **2a** (1.0 equiv.) EtOH/H_2O solution (v/v = 1/3, 15 mL). Hydroxylamine hydrochloride (1.5 equiv.) was added, then heated to 90 °C by oil bath. and stirred for 16 h. The mixture was cooled to room temperature, diluted with EA and washed with water. The organic layer was separated, dried with Na_2SO_4, and separated by column

chromatography after vacuum concentration to obtain product **6** in 94% yield.

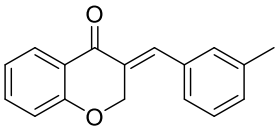
3. The characterization data for substrates 1 and 3

(*E*)-3-Benzylidenechroman-4-one (**1a**)



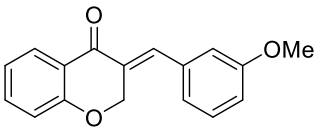
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 3.1 g, yield: 80%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.88 (d, *J* = 2.0 Hz, 1H), 7.51 – 7.40 (m, 4H), 7.32 (dd, *J* = 7.2, 1.9 Hz, 2H), 7.09 – 7.07 (m, 1H), 6.97 (dd, *J* = 8.3, 1.0 Hz, 1H), 5.36 (d, *J* = 1.9 Hz, 2H). The analytical data are consistent with the literature.[1b]

(*E*)-3-(3-Methylbenzylidene)chroman-4-one (**1b**)



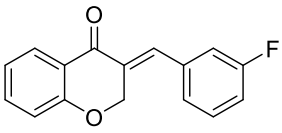
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 645 mg, yield: 82%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.13 – 7.10 (m, 2H), 7.09 – 7.06 (m, 1H), 6.97 (dd, *J* = 8.4, 1.0 Hz, 1H), 5.36 (d, *J* = 1.9 Hz, 2H), 2.41 (s, 3H). The analytical data are consistent with the literature.[5]

(*E*)-3-(3-Methoxybenzylidene)chroman-4-one (**1c**)



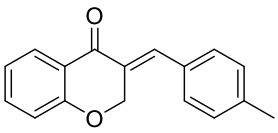
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 450 mg, yield: 73%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.84 (d, *J* = 2.0 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.97 – 6.95 (m, 2H), 6.89 (d, *J* = 6.7 Hz, 1H), 6.84 (t, *J* = 2.1 Hz, 1H), 5.35 (d, *J* = 1.9 Hz, 2H), 3.84 (s, 3H). The analytical data are consistent with the literature.[1a]

(*E*)-3-(3-Fluorobenzylidene)chroman-4-one (**1d**)



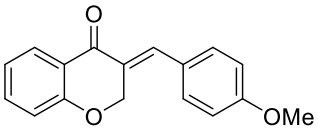
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 240 mg, yield: 62%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 – 8.02 (m, 1H), 7.81 (s, 1H), 7.53 – 7.49 (m, 1H), 7.45 – 7.41 (m, 1H), 7.27 – 7.26 (m, 1H), 7.14 – 7.07 (m, 3H), 7.02 – 6.97 (m, 2H), 5.33 – 5.32 (m, 2H). The analytical data are consistent with the literature.[6]

(*E*)-3-(4-Methylbenzylidene)chroman-4-one (**1e**)



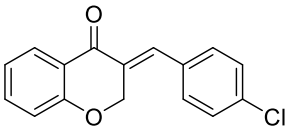
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 890 mg, yield: 79%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 5.35 (s, 2H), 2.39 (s, 3H). The analytical data are consistent with the literature.[1b]

(*E*)-3-(4-Methoxybenzylidene)chroman-4-one (**1f**)



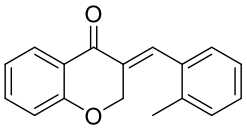
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 710 mg, yield: 75%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.84 (d, *J* = 1.9 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.29 – 7.27 (m, 2H), 7.08 – 7.05 (m, 1H), 6.98 – 6.95 (m, 3H), 5.38 (d, *J* = 1.9 Hz, 2H), 3.86 (s, 3H). The analytical data are consistent with the literature.[1b]

(*E*)-3-(4-Chlorobenzylidene)chroman-4-one (**1g**)



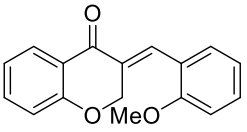
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 120 mg, yield: 56%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.82 – 7.81 (m, 1H), 7.52 – 7.48 (m, 1H), 7.45 – 7.41 (m, 2H), 7.25 (d, *J* = 8.6 Hz, 3H), 7.10 – 7.06 (m, 1H), 6.98 (dd, *J* = 8.4, 1.0 Hz, 1H), 5.31 (d, *J* = 1.9 Hz, 2H). The analytical data are consistent with the literature.[1b]

(*E*)-3-(2-Methylbenzylidene)chroman-4-one (**1h**)



Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 410 mg, yield: 78%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.97 (d, *J* = 1.8 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.33 – 7.30 (m, 1H), 7.28 – 7.23 (m, 2H), 7.09 – 7.07 (m, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.1 Hz, 1H), 5.21 (d, *J* = 1.8 Hz, 2H), 2.36 (s, 3H). The analytical data are consistent with the literature.[5]

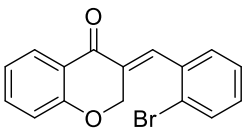
(*E*)-3-(2-Methoxybenzylidene)chroman-4-one (**1i**)



Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 805 mg, yield: 70%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.01

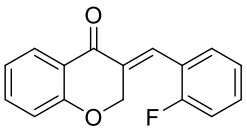
(d, *J* = 1.9 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.41 – 7.38 (m, 1H), 7.08 – 7.05 (m, 2H), 7.01 – 6.99 (m, 1H), 6.95 (d, *J* = 8.3 Hz, 2H), 5.22 (d, *J* = 1.8 Hz, 2H), 3.86 (s, 3H). The analytical data are consistent with the literature.[1b]

(*E*)-3-(2-Bromobenzylidene)chroman-4-one (**1j**)



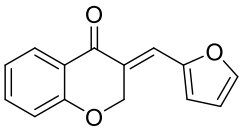
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 150 mg, yield: 60%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 – 8.04 (m, 1H), 7.90 (s, 1H), 7.68 – 7.67 (m, 1H), 7.51 – 7.48 (m, 1H), 7.39 – 7.36 (m, 1H), 7.28 – 7.25 (m, 1H), 7.13 – 7.07 (m, 2H), 6.98 – 6.96 (m, 1H), 5.16 (t, *J* = 1.8 Hz, 2H). The analytical data are consistent with the literature.[5]

(*E*)-3-(2-Fluorobenzylidene)chroman-4-one (**1k**)



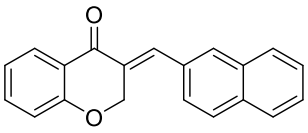
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 300 mg, yield: 62%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.85 (q, *J* = 1.6 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.43 – 7.39 (m, 1H), 7.22 – 7.20 (m, 2H), 7.18 – 7.14 (m, 1H), 7.09 – 7.07 (m, 1H), 6.97 (dd, *J* = 8.4, 1.1 Hz, 1H), 5.19 (t, *J* = 1.7 Hz, 2H). The analytical data are consistent with the literature.[7]

(*E*)-3-(Furan-2-ylmethylene)chroman-4-one (**1l**)



Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 680 mg, yield: 86%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.52 (t, *J* = 1.9 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.07 – 7.04 (m, 1H), 6.99 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.75 (d, *J* = 3.5 Hz, 1H), 6.55 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.60 (d, *J* = 1.9 Hz, 2H). The analytical data are consistent with the literature.[1b]

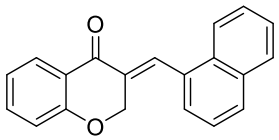
(*E*)-3-(Naphthalen-2-ylmethylene)chroman-4-one (**1m**)



Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as pale yellow solid; 980 mg, yield: 88%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.03 (d, *J* = 2.1 Hz, 1H), 7.91 – 7.87 (m, 3H), 7.76 (s, 1H), 7.58 – 7.54 (m, 2H), 7.52 – 7.49 (m, 1H), 7.44 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.11 – 7.08 (m, 1H), 6.99 (dd, *J* = 8.3, 1.1 Hz,

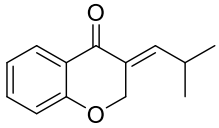
1H), 5.46 (d, *J* = 1.9 Hz, 2H). The analytical data are consistent with the literature.[1b]

(*E*)-3-(Naphthalen-1-ylmethylene)chroman-4-one (**1n**)



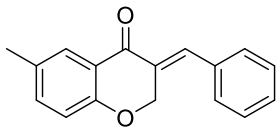
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as pale yellow solid; 500 mg, yield: 80%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.10 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.01 – 7.98 (m, 1H), 7.93 – 7.90 (m, 2H), 7.58 – 7.54 (m, 2H), 7.53 – 7.49 (m, 2H), 7.25 – 7.23 (m, 1H), 7.12 – 7.09 (m, 1H), 6.97 (dd, *J* = 8.3, 1.0 Hz, 1H), 5.23 (d, *J* = 1.8 Hz, 2H). The analytical data are consistent with the literature.[5]

(*E*)-3-(2-methylpropylidene)chroman-4-one (**1o**)



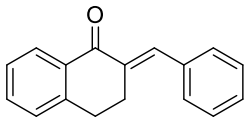
Purification by column chromatography (silica gel, PE:EA = 20:1) afforded the product as pale yellow oil; 254 mg, yield: 65%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.09 – 6.97 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.72 (dt, *J* = 10.2, 1.7 Hz, 1H), 5.00 (d, *J* = 1.8 Hz, 2H), 2.69 – 2.57 (m, 1H), 1.06 (d, *J* = 6.6 Hz, 6H). The analytical data are consistent with the literature.[20]

(*E*)-3-Benzylidene-6-methylchroman-4-one (**1p**)



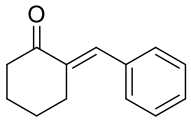
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as pale yellow solid; 202 mg, yield: 45%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.87 (m, 1H), 7.82 (dd, *J* = 2.3, 1.0 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.42 – 7.39 (m, 1H), 7.32 – 7.29 (m, 3H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.32 (d, *J* = 1.9 Hz, 2H), 2.34 (s, 3H). The analytical data are consistent with the literature.[1b]

(*E*)-2-Benzylidene-3,4-dihydronaphthalen-1(2*H*)-one (**1q**)



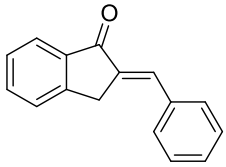
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 1.3 g, yield: 89%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.46 – 7.42 (m, 4H), 7.39 – 7.34 (m, 2H), 7.26 (d, *J* = 5.5 Hz, 2H), 3.15 – 3.13 (m, 2H), 2.97 – 2.94 (m, 2H). The analytical data are consistent with the literature.[2]

(*E*)-2-Benzylidenecyclohexan-1-one (**1r**)



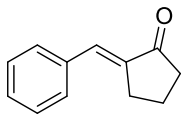
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 3.3 g, yield: 92%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (t, *J* = 2.3 Hz, 1H), 7.40 – 7.35 (m, 4H), 7.32 – 7.29 (m, 1H), 2.84 – 2.81 (m, 2H), 2.52 (t, *J* = 6.7 Hz, 2H), 1.95 – 1.89 (m, 2H), 1.77 – 1.73 (m, 2H). The analytical data are consistent with the literature.[2]

(*E*)-2-Benzylidene-2,3-dihydro-1*H*-inden-1-one (**1s**)



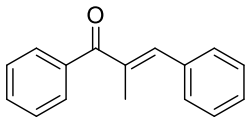
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as pale yellow solid; 1.1 g, yield: 85%; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.92 (dd, J = 7.9, 3.3 Hz, 1H), 7.69 – 7.68 (m, 3H), 7.63 – 7.61 (m, 1H), 7.57 – 7.55 (m, 1H), 7.48 – 7.39 (m, 4H), 4.06 (s, 2H). The analytical data are consistent with the literature.[3]

(*E*)-2-Benzylidenecyclopentan-1-one (**1t**)



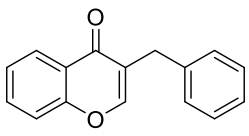
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as pale yellow solid; 1.5 g, yield: 88%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 2H), 7.44 – 7.34 (m, 4H), 3.00 – 2.96 (m, 2H), 2.41 (t, *J* = 7.9 Hz, 2H), 2.03 (p, *J* = 7.6 Hz, 2H). The analytical data are consistent with the literature.[2]

(*E*)-2-Methyl-1,3-diphenylprop-2-en-1-one (**1u**)



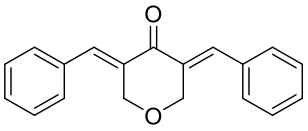
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as light yellow oil; 1.3 g, yield: 67%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.2 Hz, 2H), 7.57 – 7.33 (m, 8H), 7.20 (s, 1H), 2.29 (s, 3H). The analytical data are consistent with the literature.[2]

3-Benzyl-4*H*-chromen-4-one (**2a'**)



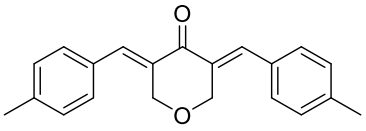
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as white solid; 460 mg, yield: 93%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.65 – 7.63 (m, 1H), 7.61 (t, *J* = 1.1 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.33 – 7.30 (m, 4H), 7.24 – 7.21 (m, 1H), 3.83 (d, *J* = 1.1 Hz, 2H). The analytical data are consistent with the literature.[1b]

3,5-di((*E*)-benzylidene)tetrahydro-4*H*-pyran-4-one (**3a**)



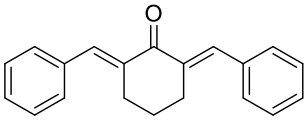
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 440 mg, yield: 65%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (s, 2H), 7.49 – 7.37 (m, 6H), 7.33 (d, *J* = 7.8 Hz, 4H), 4.94 (s, 4H). The analytical data are consistent with the literature.[4a]

3,5-bis((*E*)-4-methylbenzylidene)tetrahydro-4*H*-pyran-4-one (**3b**)



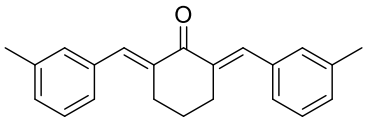
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 510 mg, yield: 68%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (s, 2H), 7.23 (s, 8H), 4.93 (d, *J* = 1.9 Hz, 4H), 2.39 (s, 6H). The analytical data are consistent with the literature.[4a]

2,6-Di((*E*)-benzylidene)cyclohexan-1-one (**3c**)



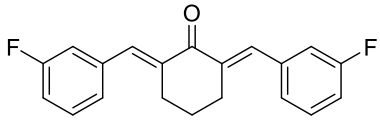
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 2.0 g, yield: 89%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (s, 2H), 7.47 (d, *J* = 7.6 Hz, 4H), 7.42 (d, *J* = 6.8 Hz, 4H), 7.36 – 7.33 (m, 2H), 2.94 (t, *J* = 6.5 Hz, 4H), 1.82 – 1.78 (m, 2H). The analytical data are consistent with the literature.[4b]

2,6-Bis((*E*)-3-methylbenzylidene)cyclohexan-1-one (**3d**)



Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 1.9 g, yield: 91%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 2.1 Hz, 2H), 7.32 – 7.27 (m, 6H), 7.17 – 7.15 (m, 2H), 2.94 – 2.92 (m, 4H), 2.39 (s, 6H), 1.81 – 1.77 (m, 2H). The analytical data are consistent with the literature.[4b]

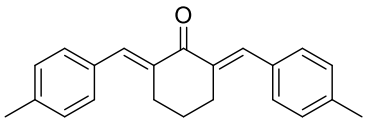
2,6-Bis((*E*)-3-fluorobenzylidene)cyclohexan-1-one (**3e**)



Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 1.8 g, yield: 90%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 2.2 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.17 – 7.14 (m, 2H), 7.06 – 7.03 (m, 2H), 2.93 – 2.90 (m, 4H), 1.83 – 1.79 (m, 2H). The analytical data are consistent with the

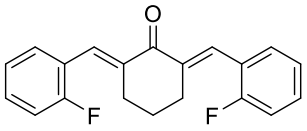
literature.[8]

2,6-Bis((*E*)-4-methylbenzylidene)cyclohexan-1-one (**3f**)



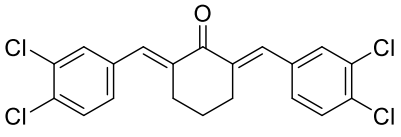
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 2.2 g, yield: 94%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (s, 2H), 7.39 – 7.38 (m, 4H), 7.22 (t, *J* = 5.7 Hz, 4H), 2.93 (q, *J* = 5.4 Hz, 4H), 2.39 (d, *J* = 4.0 Hz, 6H), 1.79 (p, *J* = 5.1 Hz, 2H). The analytical data are consistent with the literature.[4b]

2,6-Bis((*E*)-2-fluorobenzylidene)cyclohexan-1-one (**3g**)



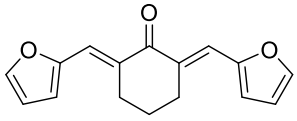
Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 1.5 g, yield: 86%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.43 – 7.28 (m, 4H), 7.17 (d, *J* = 6.7 Hz, 2H), 7.10 (d, *J* = 9.4 Hz, 2H), 2.81 (d, *J* = 6.1 Hz, 5H), 1.77 (q, *J* = 5.8 Hz, 2H). The analytical data are consistent with the literature.[9]

2,6-Bis((*E*)-3,4-dichlorobenzylidene)cyclohexan-1-one (**3h**)



Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 2.3 g, yield: 84%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 2.4 Hz, 2H), 7.52 (d, *J* = 2.1 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.26 (dd, *J* = 8.2, 2.1 Hz, 2H), 2.88 – 2.86 (m, 4H), 1.83 – 1.79 (m, 2H). The analytical data are consistent with the literature.[10]

(2*E*,6*E*)-2,6-Bis(furan-2-ylmethylene)cyclohexan-1-one (**3i**)



Purification by column chromatography (silica gel, PE:EA = 10:1) and recrystallization afforded the product as yellow solid; 413 mg, yield: 60%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 5.3 Hz, 4H), 6.66 (d, *J* = 4.4 Hz, 2H), 6.52 (s, 2H), 3.01 (d, *J* = 6.7 Hz, 4H), 1.89 (q, *J* = 6.1 Hz, 2H). The analytical data are consistent with the literature.[8]

4. General procedure for asymmetric hydrogenation of 1 and 3

General procedure: In a nitrogen-filled glove box, $[Rh(COD)Cl]_2$ (0.5 mol%) and (*S*,*S*)-f-spiroPhos (1.0 mol%) were mixed in MeOH at room temperature for 40 minutes to prepare a stock solution. Aliquots of catalyst solution (1.0 mL, 0.00125 mmol) were transferred to vials containing different substrates **1** or **3** (0.125 mmol) by syringe. Subsequently, the reaction vial was transferred

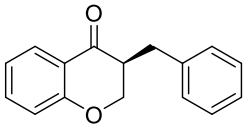
to an autoclave filled with hydrogen gas and the mixture was stirred at room temperature under H_2 (10 atm) for 2 h. After that, the hydrogen gas was released slowly and carefully and the reaction mixture was passed through a silica gel short column to remove the metal complex. (**4a** and **4b**: DCM was added for dissolution, and three equivalents of PCC and appropriate amount of diatomite were added. The reaction proceeded at room temperature for 4 h. After filtration, column chromatography was used for purification). The conversion was determined by ^{1}H NMR analysis. The crude products were concentrated and purified by silica gel column chromatography, and the ee values were determined by HPLC analysis on chiral stationary phase.

Gram scale experiment: In a nitrogen-filled glove box, $[Rh(COD)Cl]_2$ (0.025 mol%) and (*S*,*S*)-f-spiroPhos (0.05 mol%) were mixed in MeOH at room temperature and stirred for 40 minutes to prepare a stock solution. The catalyst solution (0.00215 mmol) was transferred by syringe into a vial containing substrate **1a** (4.3 mmol). Subsequently, the reaction vial was transferred to an autoclave filled with hydrogen gas and the reaction was carried out at room temperature and H_2 (10 atm) for 72 h. After the reaction, the hydrogen gas was released slowly and carefully. The reaction mixture was passed through a silica gel short column to remove the metal complex and the ee value was determined by HPLC analysis on chiral stationary phase. Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product **2a** as white soild; 0.99 g, yield: 97%; 90% ee; HPLC (Lux 5u Cellulose-1, *i*-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 7.0 min (minor), 7.6 min (major).

Deuteration experiment: In a nitrogen-filled glove box, $[Rh(COD)Cl]_2$ (0.5 mol%) and (*S*,*S*)-f-spiroPhos (1.0 mol%) were mixed in MeOH for 40 minutes at room temperature to prepare a stock solution. An aliquot of the catalyst solution (1.0 mL, 0.00125 mmol) was transferred to a vial containing the substrate **1a** (0.125 mmol) by syringe. The reaction vial was then transferred to an autoclave filled with D_2. Then the mixture was stirred at room temperature under D_2 (10 atm) for 4.5 h. After that, the D_2 gas was released slowly and carefully. The solution was subjected to silica gel column chromatography to remove metal complexes and purified. The product **2a-D** was analyzed by ^{1}H NMR. **2a-D**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.35 – 7.30 (m, 2H), 7.26 – 7.22 (m, 3H), 7.05 – 7.01 (m, 1H), 6.96 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.36 (d, *J* = 11.5 Hz, 1H), 4.17 (d, *J* = 11.6 Hz, 1H), 2.69 (s, 1H).

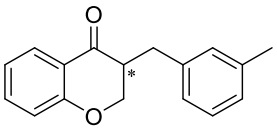
5. NMR, HPLC, optical rotation and HRMS data of compounds 2, 4, 5 and 6

(*S*)-3-Benzylchroman-4-one (**2a**)



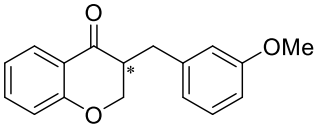
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 29.1 mg, yield: 98%; 96% ee; $[\alpha]_D^{25}$ = + 49.9 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-1, *i*-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 6.9 min (minor), 7.6 min (major); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.35 – 7.32 (m, 2H), 7.26 – 7.24 (m, 3H), 7.05 – 7.03 (m, 1H), 6.97 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.38 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.18 (dd, *J* = 11.5, 8.4 Hz, 1H), 3.30 (dd, *J* = 14.0, 4.5 Hz, 1H), 2.96 – 2.91 (m, 1H), 2.72 (dd, *J* = 14.0, 10.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.9, 161.7, 138.4, 136.0, 129.2, 128.8, 127.6, 126.8, 121.6, 120.6, 117.9, 69.5, 47.8, 32.5. The analytical data are consistent with the literature.[11]

3-(3-Methylbenzyl)chroman-4-one (**2b**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as yellow oil; 31.1 mg, yield: 99%; 97% ee; $[\alpha]_D^{25}$ = + 9.2 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 254 nm) t_R = 6.9 min (major), 9.5 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.24 – 7.20 (m, 1H), 7.07 – 7.03 (m, 4H), 6.98 (d, *J* = 8.3 Hz, 1H), 4.38 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.19 (dd, *J* = 11.5, 8.4 Hz, 1H), 3.26 (dd, *J* = 14.0, 4.3 Hz, 1H), 2.95 – 2.90 (m, 1H), 2.67 (dd, *J* = 14.0, 10.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 194.0, 161.7, 138.4, 138.3, 136.0, 129.9, 128.7, 127.6, 127.5, 126.2, 121.6, 120.7, 117.9, 69.5, 47.8, 32.4, 21.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{17}H_{17}O_2$ 253.1223; Found 253.1218.

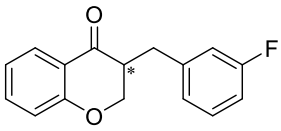
3-(3-Methoxybenzyl)chroman-4-one (**2c**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 32.2 mg, yield: 96%; 97% ee; $[\alpha]_D^{25}$ = + 10.2 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-1, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 254 nm) t_R = 9.9 min (major), 10.9 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.26 – 7.23 (m, 1H), 7.05 – 7.02 (m, 1H), 6.97 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.84 – 6.82 (m, 1H), 6.80

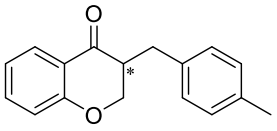
– 6.78 (m, 2H), 4.38 (dd, *J* = 11.5, 4.4 Hz, 1H), 4.18 (dd, *J* = 11.5, 8.5 Hz, 1H), 3.81 (s, 3H), 3.27 (dd, *J* = 14.0, 4.5 Hz, 1H), 2.96 – 2.91 (m, 1H), 2.68 (dd, *J* = 14.0, 10.5 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.9, 161.7, 160.0, 140.0, 136.0, 129.8, 127.6, 121.6, 121.5, 120.6, 117.9, 114.9, 112.1, 69.5, 55.3, 47.7, 32.5. The analytical data are consistent with the literature.[12]

3-(3-Fluorobenzyl)chroman-4-one (**2d**)



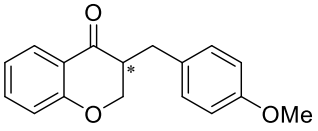
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 31.3 mg, yield: 98%; 97% ee; $[\alpha]_D^{25}$ = + 7.1 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 254 nm) t_R = 9.0 min (major), 10.8 min (minor). MP: 46-49 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.30 – 7.27 (m, 1H), 7.05 – 7.01 (m, 2H), 6.98 – 6.93 (m, 3H), 4.38 (dd, *J* = 11.5, 4.4 Hz, 1H), 4.17 (dd, *J* = 11.5, 8.7 Hz, 1H), 3.28 (dd, *J* = 14.1, 4.7 Hz, 1H), 2.96 – 2.92 (m, 1H), 2.72 (dd, *J* = 14.1, 10.2 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.5, 163.9, 162.3, 161.6, 140.9 (d, *J* = 7.3 Hz), 136.1, 130.3, 130.2, 127.6, 124.9, 124.8, 121.7, 120.6, 117.9, 116.2, 116.0, 113.8, 113.7, 69.5, 47.5, 32.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}FO_2$ 257.0972; Found 257.0967.

3-(4-methylbenzyl)chroman-4-one (**2e**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as yellow oil; 31.2 mg, yield: 99%; 97% ee; $[\alpha]_D^{25}$ = + 8.7 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 7.5 min (major), 9.7 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.14 (s, 4H), 7.06 – 7.02 (m, 1H), 6.97 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.37 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.18 (dd, *J* = 11.5, 8.2 Hz, 1H), 3.24 (dd, *J* = 14.0, 4.5 Hz, 1H), 2.94 – 2.87 (m, 1H), 2.69 (dd, *J* = 14.0, 10.4 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.0, 161.7, 136.3, 136.0, 135.2, 129.5, 129.1, 127.6, 121.5, 120.7, 117.9, 69.5, 47.9, 32.1, 21.1. The analytical data are consistent with the literature.[14]

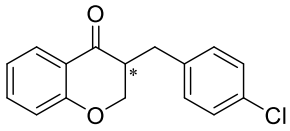
3-(4-Methoxybenzyl)chroman-4-one (**2f**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 32.8 mg, yield: 98%; 94% ee; $[\alpha]_D^{25}$ = + 14.0 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-

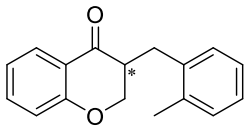
propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 12.8 min (major), 18.5 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.17 – 7.15 (m, 2H), 7.05 – 7.02 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.88 – 6.85 (m, 2H), 4.37 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.18 (dd, *J* = 11.5, 8.1 Hz, 1H), 3.80 (s, 3H), 3.21 (dd, *J* = 14.1, 4.6 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.69 (dd, *J* = 14.1, 10.3 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 194.0, 161.7, 158.5, 136.0, 130.2, 127.6, 121.6, 120.7, 117.9, 114.2, 69.5, 55.4, 48.0, 31.7. The analytical data are consistent with the literature.[14]

3-(4-Chlorobenzyl)chroman-4-one (**2g**)



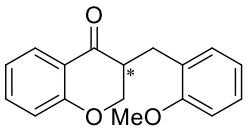
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 32.3 mg, yield: 95%; 96% ee; $[\alpha]_D^{25}$ = + 14.2 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 8.1 min (major), 9.4 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.30 – 7.28 (m, 2H), 7.19 – 7.16 (m, 2H), 7.05 – 7.03 (m, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 4.37 (dd, *J* = 11.6, 4.3 Hz, 1H), 4.16 (dd, *J* = 11.6, 8.5 Hz, 1H), 3.23 (dd, *J* = 14.1, 4.7 Hz, 1H), 2.92 – 2.88 (m, 1H), 2.72 (dd, *J* = 14.1, 10.0 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.5, 161.6, 136.8, 136.1, 132.6, 130.5, 128.9, 127.6, 121.7, 120.6, 117.9, 69.4, 47.6, 31.9. The analytical data are consistent with the literature.[14]

3-(2-Methylbenzyl)chroman-4-one (**2h**)



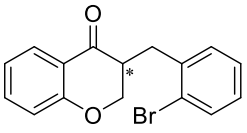
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as yellow oil; 30.3 mg, yield: 96%; 90% ee; $[\alpha]_D^{25}$ = - 15.7 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 6.8 min (major), 8.9 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.21 – 7.16 (m, 4H), 7.07 – 7.04 (m, 1H), 6.99 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.37 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.21 (dd, *J* = 11.5, 8.0 Hz, 1H), 3.34 (dd, *J* = 14.2, 4.2 Hz, 1H), 2.92 – 2.87 (m, 1H), 2.67 (dd, *J* = 14.2, 11.0 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.7, 136.6, 136.0, 130.8, 130.0, 127.6, 127.0, 126.2, 121.6, 120.6, 117.9, 69.5, 46.6, 29.9, 19.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_2$ 253.1223; Found 253.1220.

3-(2-Methoxybenzyl)chroman-4-one (**2i**)



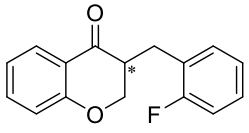
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 31.8 mg, yield: 95%; 88% ee; $[\alpha]_D^{25}$ = - 26.6 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 8.3 min (major), 10.7 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.25 – 7.22 (m, 1H), 7.18 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.04 – 7.01 (m, 1H), 6.95 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.92 – 6.90 (m, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 4.37 (dd, *J* = 11.5, 4.6 Hz, 1H), 4.19 (dd, *J* = 11.5, 9.4 Hz, 1H), 3.82 (s, 3H), 3.39 (dd, *J* = 13.7, 4.9 Hz, 1H), 3.11 – 3.07 (m, 1H), 2.67 (dd, *J* = 13.8, 9.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 194.3, 161.7, 157.7, 135.8, 131.2, 128.1, 127.5, 126.8, 121.4, 120.8, 120.6, 117.8, 110.4, 70.2, 55.3, 46.1, 27.4. The analytical data are consistent with the literature.[13]

3-(2-Bromobenzyl)chroman-4-one (**2j**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as yellow oil; 38.3 mg, yield: 97%; 92% ee; $[\alpha]_D^{25}$ = - 65.6 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 8.5 min (major), 10.7 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.29 – 7.27 (m, 2H), 7.14 – 7.10 (m, 1H), 7.04 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.41 (dd, *J* = 11.5, 4.6 Hz, 1H), 4.25 – 4.21 (m, 1H), 3.49 (dd, *J* = 14.1, 5.1 Hz, 1H), 3.16 – 3.12 (m, 1H), 2.81 (dd, *J* = 14.1, 9.7 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.5, 161.7, 138.0, 136.0, 133.3, 131.6, 128.6, 127.7, 127.6, 124.8, 121.6, 120.6, 117.9, 69.8, 46.0, 32.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}{}^{79}BrO_2$ 317.0172; Found 317.0170. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}{}^{81}BrO_2$ 319.0152; Found 318.0159.

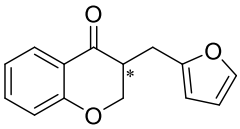
3-(2-Fluorobenzyl)chroman-4-one (**2k**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 31.0 mg, yield: 97%; 93% ee; $[\alpha]_D^{25}$ = - 19.7 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 8.1 min (major), 10.3 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.27 – 7.21 (m, 2H),

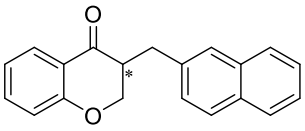
7.11 – 7.08 (m, 1H), 7.06 – 7.01 (m, 2H), 6.96 (dd, *J* = 8.4, 1.1 Hz, 1H), 4.41 (dd, *J* = 11.5, 4.6 Hz, 1H), 4.19 (dd, *J* = 11.5, 9.6 Hz, 1H), 3.37 – 3.33 (m, 1H), 3.05 – 3.00 (m, 1H), 2.78 (dd, *J* = 14.8, 9.2 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.4, 162.2, 161.7, 160.6, 136.0, 131.7, 131.6, 128.7, 128.6, 127.6, 125.5, 125.4, 124.4 (d, *J* = 3.5 Hz), 121.6, 120.6, 117.9, 115.6, 115.5, 69.9, 46.5, 25.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}FO_2$ 257.0972; Found 257.0967.

3-(Furan-2-ylmethyl)chroman-4-one (**2l**)



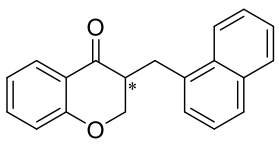
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as yellow oil; 27.4 mg, yield: 96%; 98% ee; $[\alpha]_D^{25}$ = -29.7 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 7.0 min (minor), 7.4 min (major); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.33 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.04 – 7.01 (m, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.12 (d, *J* = 2.3 Hz, 1H), 4.52 (dd, *J* = 11.5, 4.7 Hz, 1H), 4.20 (dd, *J* = 11.5, 10.1 Hz, 1H), 3.30 (dd, *J* = 15.4, 4.4 Hz, 1H), 3.11 – 3.06 (m, 1H), 2.82 (dd, *J* = 15.4, 9.6 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.1, 161.8, 152.2, 141.8, 136.0, 127.6, 121.6, 120.6, 117.9, 110.5, 107.2, 70.2, 45.4, 24.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}O_3$ 229.0859; Found 229.0856.

3-(Naphthalen-2-ylmethyl)chroman-4-one (**2m**)



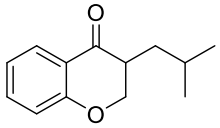
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 34.2 mg, yield: 95%; 89% ee; $[\alpha]_D^{25}$ = + 12.6 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 11.1 min (major), 12.7 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 – 7.95 (m, 1H), 7.84 – 7.80 (m, 3H), 7.70 (s, 1H), 7.51 – 7.45 (m, 3H), 7.39 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.39 (dd, *J* = 11.6, 4.3 Hz, 1H), 4.21 (dd, *J* = 11.5, 8.4 Hz, 1H), 3.46 (dd, *J* = 14.0, 4.4 Hz, 1H), 3.07 – 3.02 (m, 1H), 2.89 (dd, *J* = 14.1, 10.5 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.9, 161.7, 136.1, 135.8, 133.6, 132.4, 128.6, 127.8, 127.6, 127.3, 126.3, 125.8, 121.6, 120.7, 117.9, 69.5, 47.7, 32.7. The analytical data are consistent with the literature.[15]

3-(Naphthalen-1-ylmethyl)chroman-4-one (**2n**)



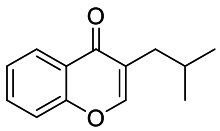
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 34.6 mg, yield: 96%; 97% ee; $[\alpha]_D^{25}$ = - 46.5 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 8.7 min (major), 11.4 min (minor). MP: 97-100 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.2 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.53 – 7.49 (m, 2H), 7.44 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.39 (d, *J* = 6.3 Hz, 1H), 7.08 – 7.05 (m, 1H), 6.99 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.33 (dd, *J* = 11.6, 4.4 Hz, 1H), 4.23 (dd, *J* = 11.6, 8.0 Hz, 1H), 3.93 (dd, *J* = 14.2, 3.7 Hz, 1H), 3.13 – 3.09 (m, 1H), 3.00 (dd, *J* = 14.2, 11.0 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 194.0, 161.8, 136.1, 134.4, 134.2, 131.8, 129.1, 127.8, 127.7, 127.7, 126.5, 125.9, 125.5, 123.7, 121.6, 120.6, 118.0, 69.7, 46.9, 29.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{17}O_2$ 289.1223; Found 289.1220.

3-Isobutylchroman-4-one (**2o**)



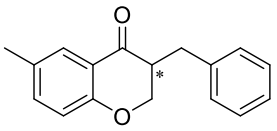
Purification by flash column chromatography (silica gel, PE:EA = 20:1) afforded the product as colorless oil; 12.3 mg, yield: 48%; rac; HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 5.8 min, 6.1 min. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 4.49 (dd, *J* = 11.5, 4.1 Hz, 1H), 4.27 – 4.18 (m, 1H), 2.74 – 2.69 (m, 1H), 1.79 – 1.69 (m, 2H), 1.32 (d, *J* = 5.2 Hz, 1H), 0.96 (d, *J* = 6.1 Hz, 3H), 0.92 (d, *J* = 6.1 Hz, 3H). The analytical data are consistent with the literature.[20]

3-isobutyl-4*H*-chromen-4-one (**2o'**)



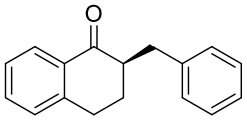
Purification by flash column chromatography (silica gel, PE:EA = 20:1) afforded the product as colorless oil; 11.9 mg, yield: 47%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.71 (s, 1H), 7.65 – 7.59 (m, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.39 – 7.33 (m, 1H), 2.30 (d, *J* = 7.0 Hz, 2H), 2.01 – 1.98 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 6H). The analytical data are consistent with the literature.[20]

3-Benzyl-6-methylchroman-4-one (**2p**)



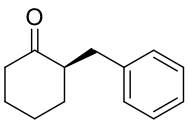
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 30.9 mg, yield: 98%; 96% ee; $[\alpha]_D^{25}$ = + 9.4 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 6.7 min (major), 7.1 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 2.2, 1.0 Hz, 1H), 7.35 – 7.22 (m, 7H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.34 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.15 (dd, *J* = 11.5, 8.2 Hz, 1H), 3.28 (dd, *J* = 13.9, 4.4 Hz, 1H), 2.93 – 2.87 (m, 1H), 2.71 (dd, *J* = 13.9, 10.4 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.2, 159.7, 138.4, 137.1, 131.0, 129.2, 128.8, 127.1, 126.7, 120.2, 117.7, 69.5, 47.8, 32.6, 20.5. The analytical data are consistent with the literature.[16]

(*R*)-2-Benzyl-3,4-dihydronaphthalen-1(2*H*)-one (**2q**)



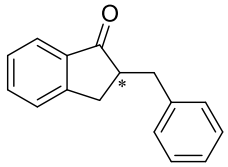
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 29.2 mg, yield: 99%; 92% ee; $[\alpha]_D^{25}$ = + 8.8 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 2/98, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 10.4 min (major), 11.0 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.34 – 7.30 (m, 3H), 7.25 – 7.22 (m, 4H), 3.51 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.99 – 2.89 (m, 2H), 2.78 – 2.73 (m, 1H), 2.66 (dd, *J* = 13.8, 9.6 Hz, 1H), 2.14 – 2.09 (m, 1H), 1.83 – 1.76 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.5, 144.1, 140.2, 133.4, 132.6, 129.4, 128.8, 128.5, 127.7, 126.7, 126.2, 49.6, 35.8, 28.7, 27.8. The analytical data are consistent with the literature.[2]

(*R*)-2-Benzylcyclohexan-1-one (**2r**)



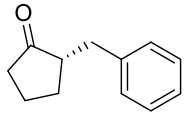
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 22.6 mg, yield: 96%; 93% ee; $[\alpha]_D^{25}$ = + 35.0 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-3, *i*-propanol/*n*-hexane = 3/97, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 7.1 min (major), 7.5 min (minor); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 2H), 7.20 – 7.13 (m, 3H), 3.26 – 3.20 (m, 1H), 2.59 – 2.51 (m, 1H), 2.46 – 2.28 (m, 3H), 2.09 – 1.98 (m, 2H), 1.85 – 1.78 (m, 1H), 1.73 – 1.51 (m, 2H), 1.40 – 1.26 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.6, 140.5, 129.2, 128.4, 126.1, 52.6, 42.3, 35.6, 33.5, 28.2, 25.2. The analytical data are consistent with the literature.[2]

2-Benzyl-2,3-dihydro-1*H*-inden-1-one (**2s**)



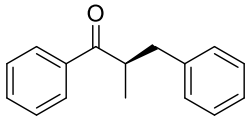
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as yellow oil; 26.9 mg, yield: 97%; 69% ee; $[\alpha]_D^{25}$ = + 20.3 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 8.5 min (major), 9.7 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.41 – 7.36 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.21 (m, 3H), 3.41 (dd, *J* = 14.0, 4.3 Hz, 1H), 3.17 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.03 – 2.98 (m, 1H), 2.87 (dd, *J* = 17.1, 4.1 Hz, 1H), 2.68 (dd, *J* = 14.0, 10.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 207.9, 153.8, 139.8, 136.7, 134.9, 129.0, 128.7, 127.6, 126.7, 126.5, 124.1, 49.0, 37.1, 32.3. The analytical data are consistent with the literature.[3]

(*S*)-2-Benzylcyclopentan-1-one (**2t**)



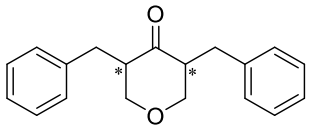
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 20.2 mg, yield: 93%; 69% ee; $[\alpha]_D^{25}$ = + 68.9 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 6.3 min (major), 6.7 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 3.14 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.53 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.38 – 2.28 (m, 2H), 2.14 – 2.02 (m, 2H), 1.98 – 1.90 (m, 1H), 1.77 – 1.65 (m, 1H), 1.59 – 1.49 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 220.3, 140.1, 129.0, 128.5, 126.3, 51.1, 38.3, 35.7, 29.2, 20.7. The analytical data are consistent with the literature.[2]

(*R*)-2-methyl-1,3-diphenylpropan-1-one (**2u**)



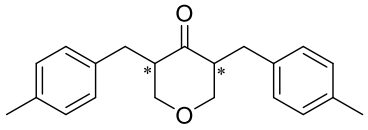
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 27.4 mg, yield: 98%; 89% ee; $[\alpha]_D^{25}$ = - 47.5 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 5.1 min (minor), 5.5 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.56 – 7.52 (m, 1H), 7.51 – 7.40 (m, 2H), 7.29 – 7.17 (m, 5H), 3.76 (h, *J* = 7.0 Hz, 1H), 3.19 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.71 (dd, *J* = 13.7, 7.8 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 203.9, 140.1, 136.6, 133.1, 129.2, 128.8, 128.5, 128.4, 126.3, 42.9, 39.5, 17.5. The analytical data are consistent with the literature.[2]

3,5-dibenzyltetrahydro-4*H*-pyran-4-one (**4a**)



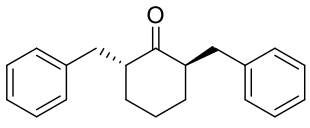
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 34.3 mg, yield: 98%; *trans*:*cis* = 13:1; >99% ee; $[\alpha]_D^{25}$ = + 40.6 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-1, *i*-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 9.6 min (minor), 10.4 min (major); *trans*-**4a**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.5 Hz, 4H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 4H), 3.89 (dd, *J* = 11.4, 4.8 Hz, 2H), 3.66 (dd, *J* = 11.5, 6.3 Hz, 2H), 3.14 (dd, *J* = 14.0, 5.3 Hz, 2H), 2.92 – 2.85 (m, 2H), 2.71 (dd, *J* = 13.9, 9.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 210.0, 138.6, 129.0, 128.7, 126.6, 72.0, 51.9, 33.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}O_2$ 281.1536; Found 281.1533.

3,5-bis(4-methylbenzyl)tetrahydro-4*H*-pyran-4-one (**4b**)



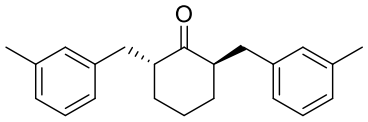
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 38.1 mg, yield: 99%; *trans*:*cis* >20:1; >99% ee; $[\alpha]_D^{25}$ = - 38.0 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 7.1 min (major), 7.8 min (minor); MP: 59-61°C. *trans*-**4b**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 7.7 Hz, 4H), 7.05 (d, *J* = 8.0 Hz, 4H), 3.88 (dd, *J* = 11.4, 4.8 Hz, 2H), 3.65 (dd, *J* = 11.4, 6.3 Hz, 2H), 3.09 (dd, *J* = 14.0, 5.4 Hz, 2H), 2.88 – 2.82 (m, 2H), 2.67 (dd, *J* = 14.0, 9.4 Hz, 2H), 2.33 (s, 7H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 210.2, 136.1, 135.5, 129.4, 128.9, 72.0, 52.0, 33.3, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_2$ 309.1849; Found 308.1850.

(+)-(2*R*,6*R*)-2,6-Dibenzylcyclohexan-1-one (**4c**)



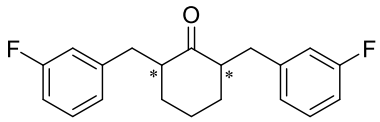
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 34.4 mg, yield: 99%; *trans*:*cis* >20:1; >99% ee; $[\alpha]_D^{25}$ = + 60.3 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-1, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 5.4 min (major), 6.1 min (minor); *trans*-**4c**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 4H), 7.22 – 7.17 (m, 2H), 7.13 (dd, *J* = 6.8, 1.6 Hz, 4H), 3.10 (dd, *J* = 13.7, 5.7 Hz, 2H), 2.81 – 2.74 (m, 2H), 2.61 (dd, *J* = 13.7, 8.9 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.77 – 1.71 (m, 2H), 1.64 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.8, 139.7, 129.1, 128.5, 126.3, 50.9, 36.3, 32.0, 20.4. The analytical data are consistent with the literature.[4]

(+)-(2*R*,6*R*)-2,6-Bis(3-methylbenzyl)cyclohexan-1-one (**4d**)



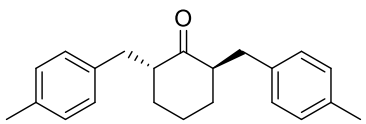
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 37.1 mg, yield: 97%; *trans*:*cis* = 18:1; >99% ee; $[\alpha]_D^{25}$ = + 50.4 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-1, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 4.6 min (major), 6.5 min (minor); *trans*-**4d**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.97 – 6.93 (m, 4H), 3.08 (dd, *J* = 13.7, 5.4 Hz, 2H), 2.81 – 2.74 (m, 2H), 2.57 (dd, *J* = 13.7, 9.2 Hz, 2H), 2.33 (s, 6H), 1.93 – 1.85 (m, 2H), 1.75 (p, *J* = 5.9 Hz, 2H), 1.64 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.1, 139.7, 138.1, 129.9, 128.4, 127.1, 126.1, 50.8, 36.2, 31.9, 21.5, 20.4. The analytical data are consistent with the literature.[4]

2,6-Bis(3-fluorobenzyl)cyclohexan-1-one (**4e**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 38.4 mg, yield: 98%; *trans*:*cis* >20:1; 99% ee; $[\alpha]_D^{25}$ = + 30.5 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-1, *i*-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 6.4 min (minor), 6.9 min (major); *trans*-**4e**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.19 (m, 2H), 6.91 – 6.81 (m, 6H), 3.09 (dd, *J* = 13.7, 6.1 Hz, 2H), 2.80 – 2.73 (m, 2H), 2.61 (dd, *J* = 13.7, 8.6 Hz, 2H), 1.94 – 1.86 (m, 2H), 1.76 (p, *J* = 5.9 Hz, 2H), 1.65 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.0, 164.2, 161.7, 142.2, 142.1, 130.0, 129.9, 124.7 (d, *J* = 2.7 Hz), 116.0, 115.8, 113.4, 113.2, 50.6, 36.0, 32.0, 20.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}F_2O$ 315.1555; Found 315.1553.

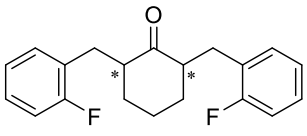
(+)-(2*R*,6*R*)-2,6-Bis(4-methylbenzyl)cyclohexan-1-one (**4f**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 37.1 mg, yield: 97%; *trans*:*cis* = 11:1; >99% ee; $[\alpha]_D^{25}$ = + 43.8 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-1, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 4.5 min (major), 5.3 min (minor); *trans*-**4f**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 – 7.03 (m, 9H), 3.08 (dd, *J* = 13.7, 5.6 Hz, 2H), 2.80 – 2.73 (m, 2H), 2.59 (dd, *J* = 13.8, 9.0 Hz, 2H), 2.34 (s, 6H), 1.94 – 1.86 (m, 2H), 1.75 (p, *J* = 5.9 Hz, 2H), 1.65 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.1, 136.6, 135.8, 129.2, 129.0, 50.9, 35.9, 32.0, 21.1, 20.5. The analytical data

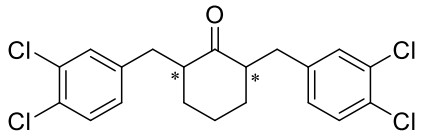
are consistent with the literature.[4]

2,6-Bis(2-fluorobenzyl)cyclohexan-1-one (**4g**)



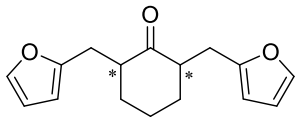
Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 37.3 mg, yield: 95%; *trans*:*cis* = 11:1; >99% ee; $[\alpha]_D^{25}$ = + 38.3 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-1, *i*-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 6.2 min (major), 6.8 min (minor); *trans*-**4g**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 – 7.15 (m, 2H), 7.14 – 7.11 (m, 2H), 7.04 – 6.99 (m, 4H), 3.09 (dd, *J* = 15.0, 6.8 Hz, 2H), 2.87 – 2.82 (m, 2H), 2.70 (dd, *J* = 13.3, 8.1 Hz, 2H), 1.93 – 1.88 (m, 2H), 1.78 (p, *J* = 6.0 Hz, 2H), 1.65 – 1.61 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 214.2, 162.1, 160.5, 131.5, 131.4, 128.1, 128.1, 126.6, 126.5, 124.1, 124.1, 115.4, 115.3, 49.7, 32.4, 29.7, 20.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}F_2O$ 315.1555; Found 315.1554.

2,6-Bis(3,4-dichlorobenzyl)cyclohexan-1-one (**4h**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 50.7 mg, yield: 98%; *trans*:*cis* >20:1; >99% ee; $[\alpha]_D^{25}$ = + 45.4 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Amylose-2, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 8.0 min (major), 9.4 min (minor); *trans*-**4h**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 2.1 Hz, 2H), 6.92 (dd, *J* = 8.2, 2.1 Hz, 2H), 3.01 (dd, *J* = 13.8, 6.6 Hz, 2H), 2.74 – 2.67 (m, 2H), 2.56 (dd, *J* = 13.8, 8.0 Hz, 2H), 1.94 – 1.87 (m, 2H), 1.77 (p, *J* = 5.9 Hz, 2H), 1.65 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.4, 139.7, 132.4, 130.9, 130.4, 128.5, 50.5, 35.4, 32.0, 20.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}Cl_4O$ 415.0185; Found 415.0183.

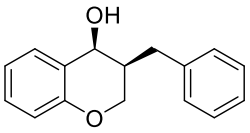
2,6-Bis(furan-2-ylmethyl)cyclohexan-1-one (**4i**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as colorless oil; 31.0 mg, yield: 96%; *trans*:*cis* = 5:1; 98% ee; $[\alpha]_D^{25}$ = + 32.2 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-2, *i*-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 4.8 min (minor), 5.3 min (major); *trans*-**4i**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 1.9, 0.8 Hz, 2H), 6.26 (dd, *J* = 3.2, 1.9 Hz, 2H), 6.00 (dd, *J* = 3.2, 0.9 Hz, 2H), 3.09 (dd, *J* = 14.6, 5.9 Hz, 2H), 2.91 – 2.84

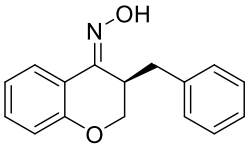
(m, 2H), 2.70 (dd, *J* = 15.1, 8.3 Hz, 2H), 1.99 – 1.91 (m, 2H), 1.80 – 1.74 (m, 2H), 1.66 – 1.58 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.8, 153.4, 141.4, 110.3, 106.6, 48.0, 32.4, 288, 20.3. The analytical data are consistent with the literature.[18]

(3*S*,4*S*)-3-Benzylchroman-4-ol (**5**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 115 mg, yield: 96%; dr = 7:1; 94% ee; $[\alpha]_D^{25}$ = - 94.8 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-1, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 7.0 min (major), 8.0 min (minor); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.19 (m, 7H), 6.91 – 6.83 (m, 2H), 4.51 (t, *J* = 3.7 Hz, 1H), 4.09 (d, *J* = 8.9 Hz, 2H), 2.89 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.68 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.37 – 2.28 (m, 1H), 1.65 (dd, *J* = 51.5, 10.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.4, 139.3, 130.3, 130.1, 129.2, 128.7, 126.4, 124.3, 120.6, 117.0, 65.1, 65.0, 40.1, 32.9. The analytical data are consistent with the literature.[1a]

(*R*,*E*)-3-benzylchroman-4-one oxime (**6**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as white solid; 105 mg, yield: 94%; 92% ee; $[\alpha]_D^{25}$ = + 60.8 (c = 1.0, CH_2Cl_2); HPLC (Lux 5u Cellulose-1, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, *l* = 210 nm) t_R = 5.2 min (minor), 6.3 min (major); MP: 80-83 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 107.9 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.35 – 7.30 (m, 5H), 7.28 – 7.24 (m, 1H), 7.01 – 6.95 (m, 2H), 4.15 – 4.12 (m, 1H), 3.95 – 3.92 (m, 1H), 3.65 – 3.62 (m, 1H), 3.05 – 3.02 (m, 1H), 2.79 – 2.74 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.3, 153.3, 139.1, 131.4, 129.6, 128.6, 126.6, 124.5, 121.6, 117.9, 117.2, 66.3, 34.8, 33.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_2$ 254.1176; Found 254.1174.

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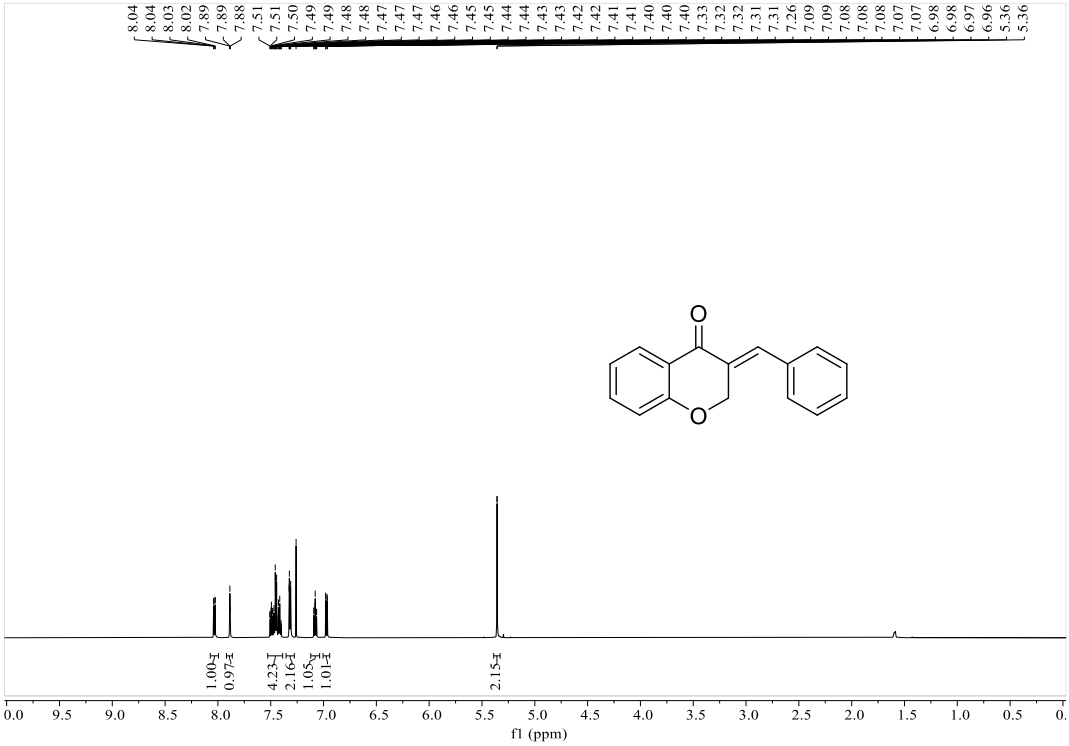
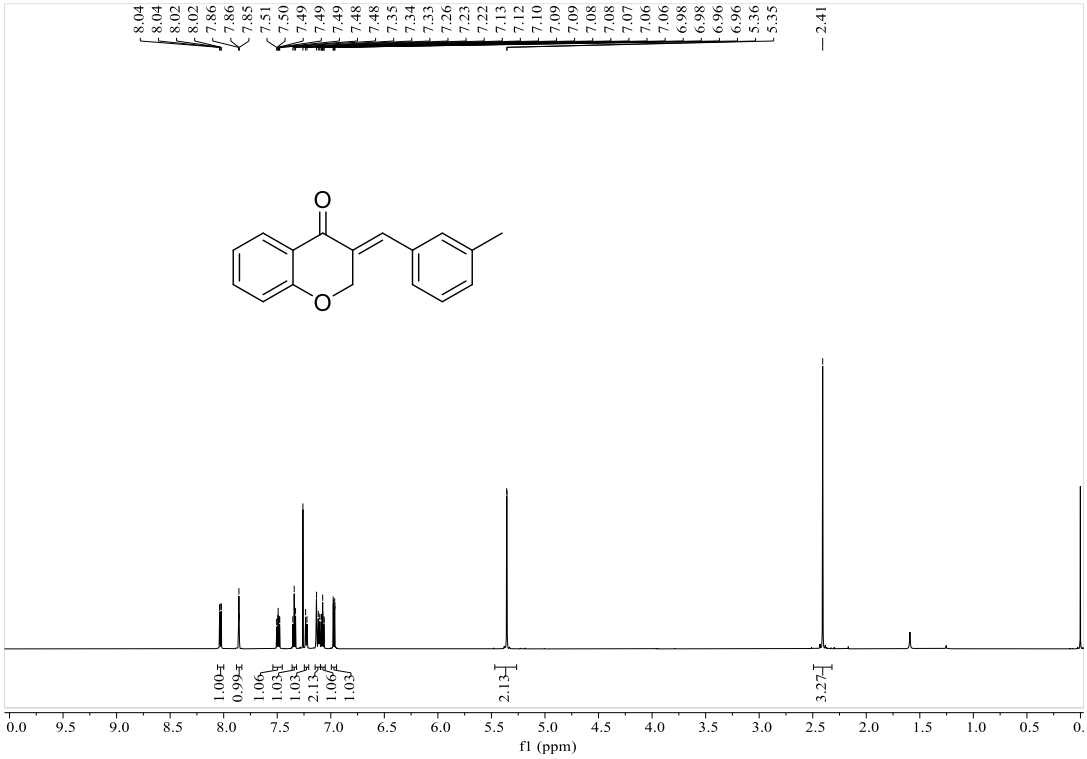
7. NMR, SFC and HPLC spectra

(*E*)-3-Benzylidenechroman-4-one (**1a**)



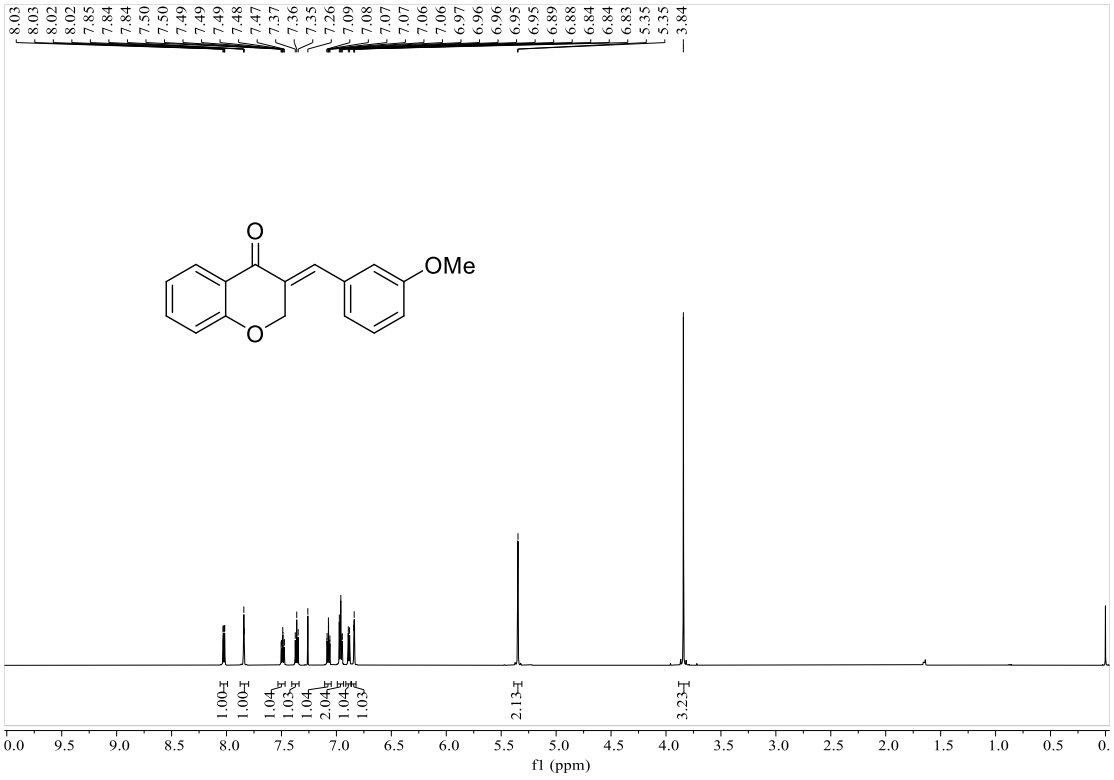
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(3-Methylbenzylidene)chroman-4-one (**1b**)



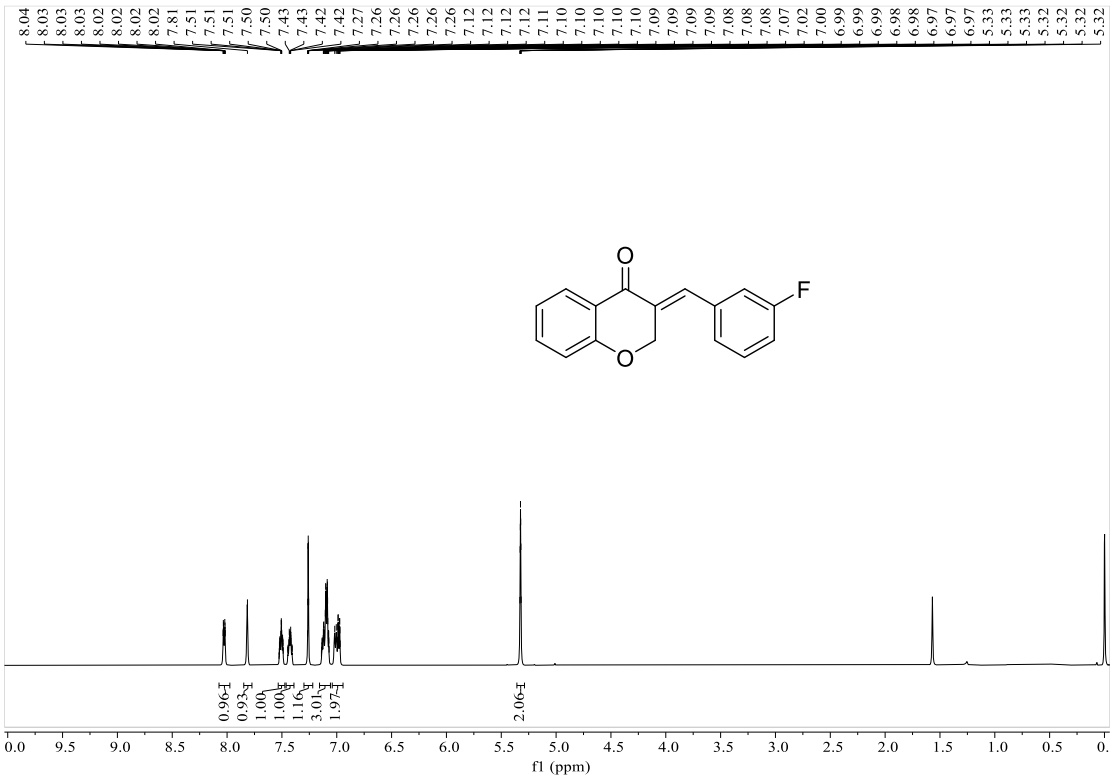
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(3-Methoxybenzylidene)chroman-4-one (**1c**)



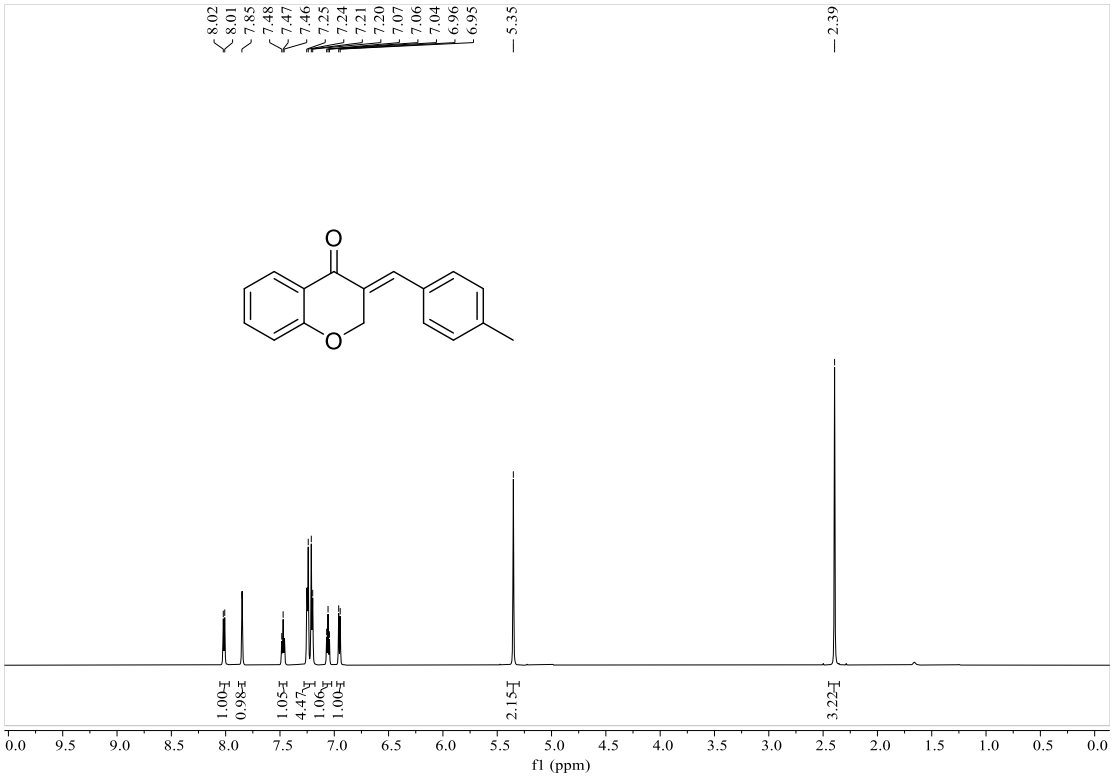
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(3-Fluorobenzylidene)chroman-4-one (**1d**)



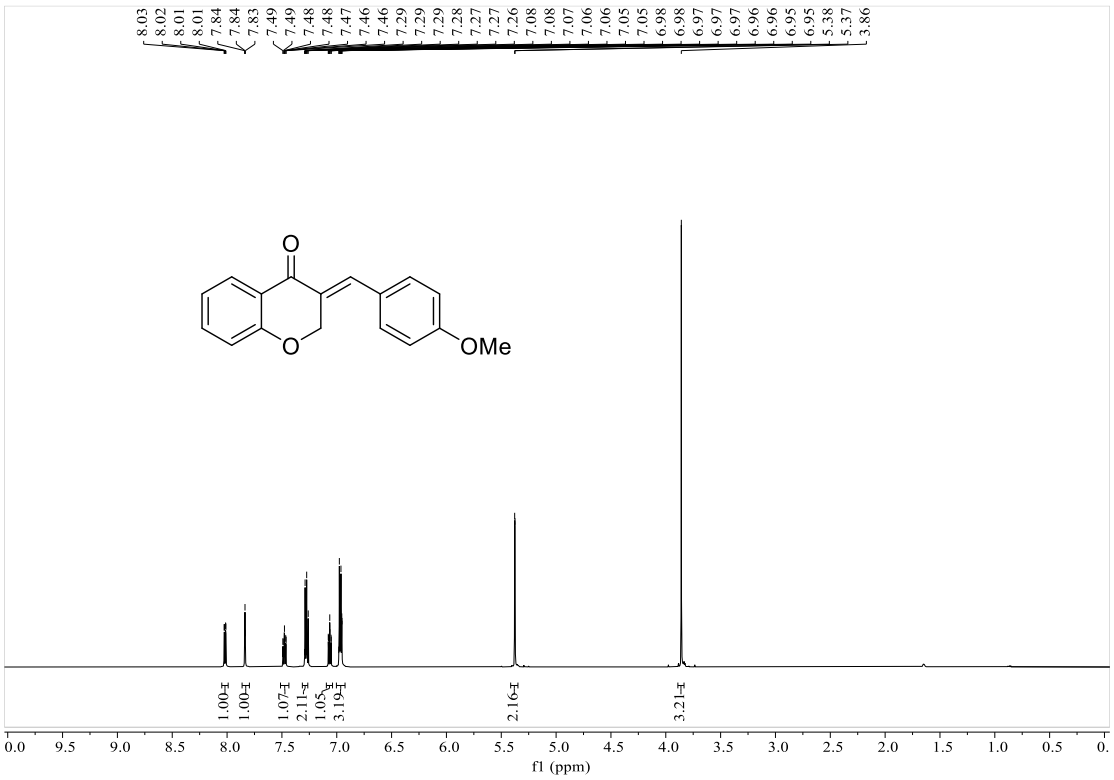
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(4-Methylbenzylidene)chroman-4-one (**1e**)



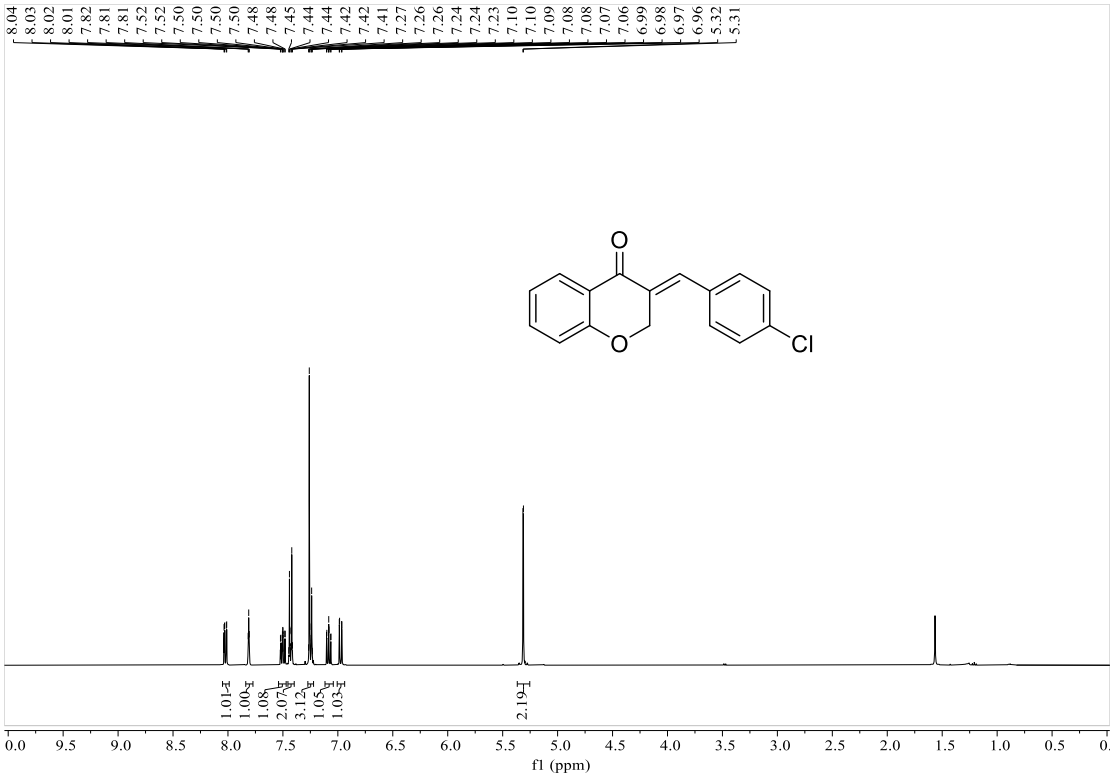
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(4-Methoxybenzylidene)chroman-4-one (**1f**)



^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(4-Chlorobenzylidene)chroman-4-one (**1g**)

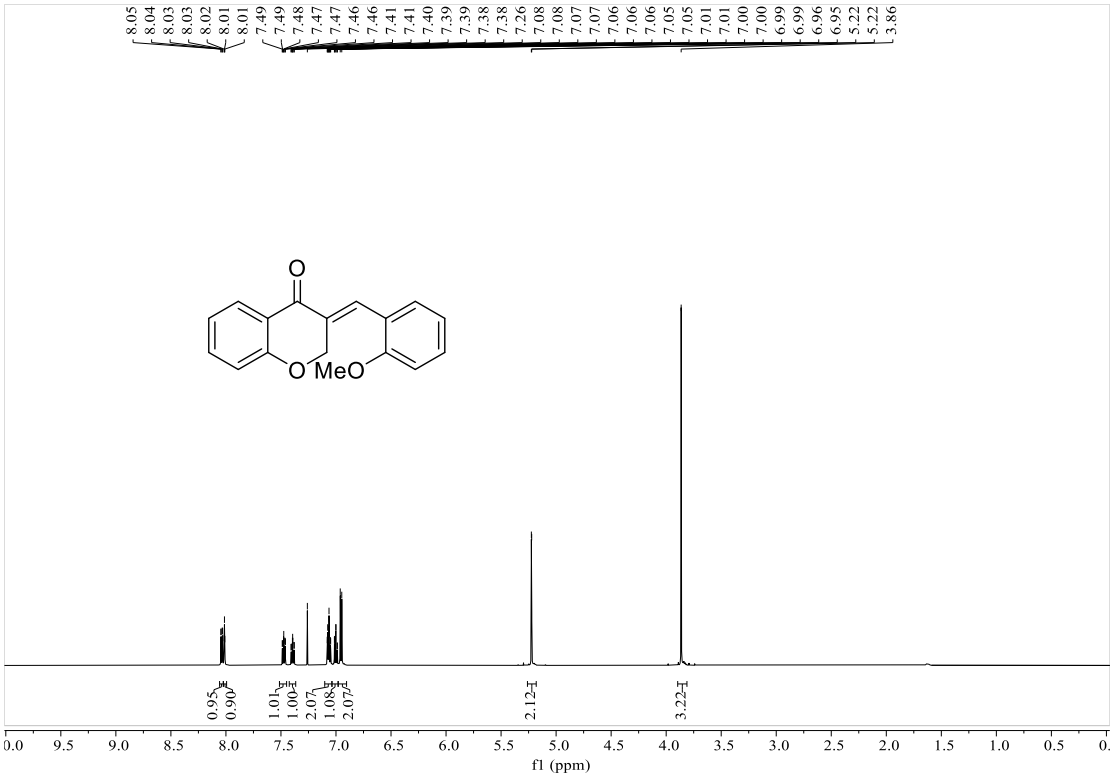


^{1}H NMR (400 MHz, Chloroform-*d*)

(*E*)-3-(2-Methylbenzylidene)chroman-4-one (**1h**)

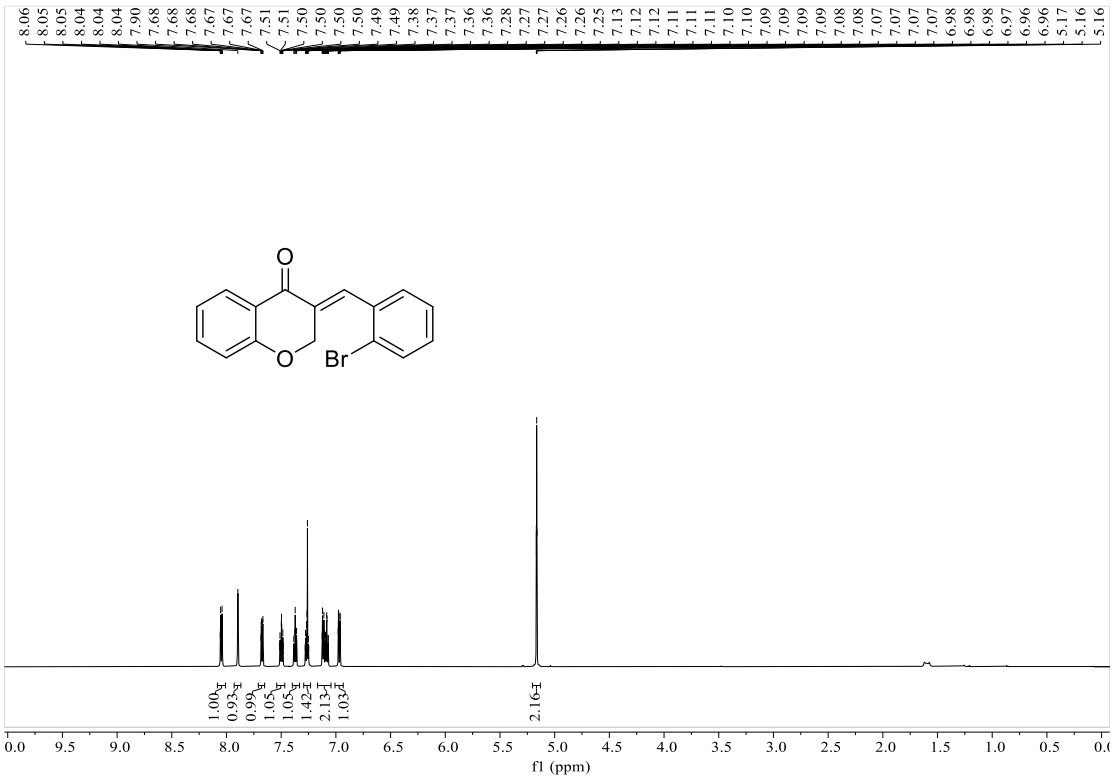
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(2-Methoxybenzylidene)chroman-4-one (**1i**)



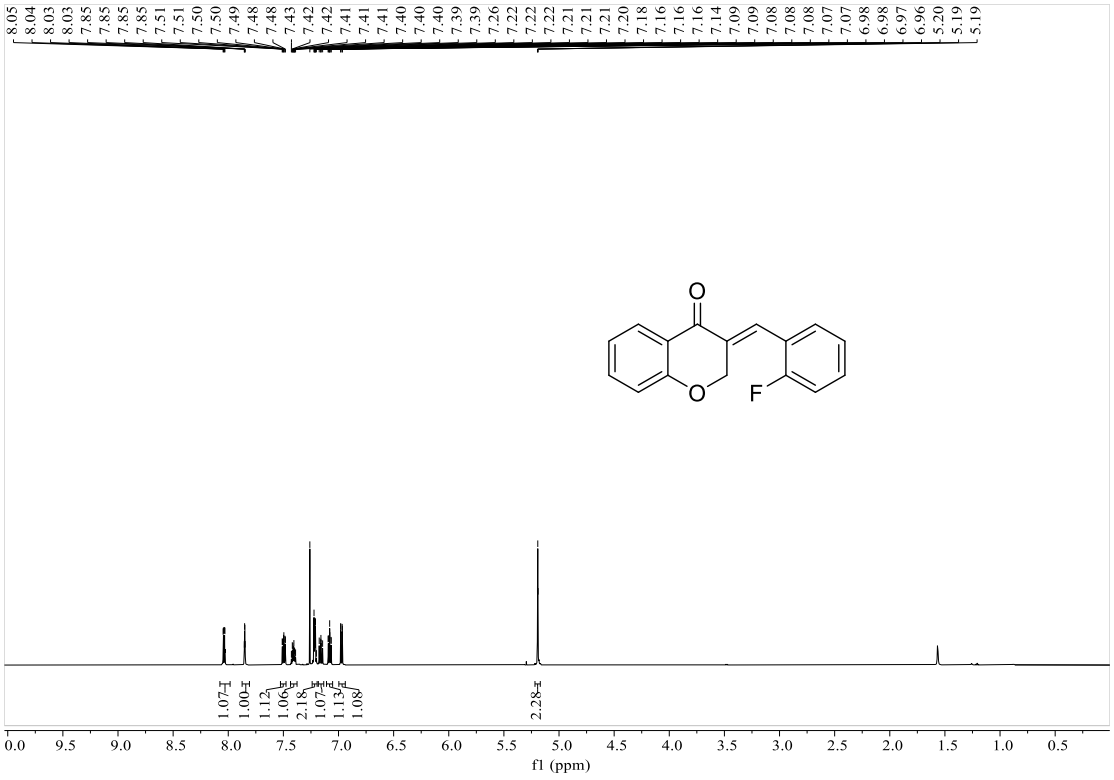
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(2-Bromobenzylidene)chroman-4-one (**1j**)



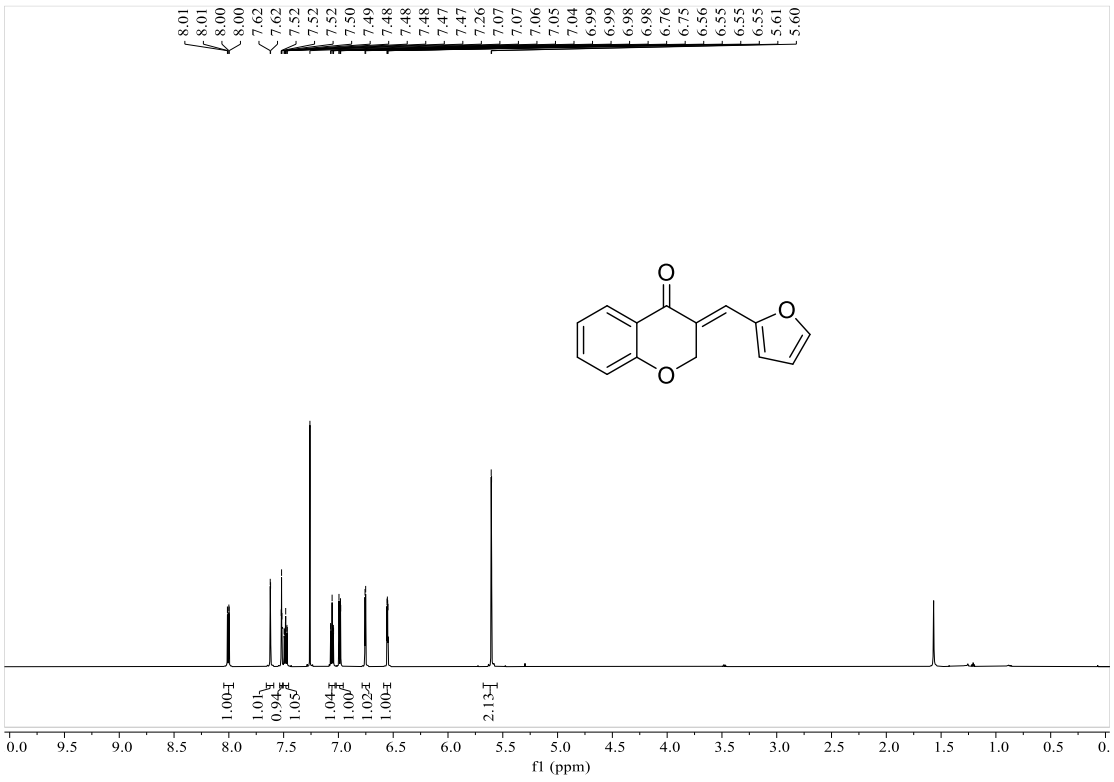
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(2-Fluorobenzylidene)chroman-4-one (**1k**)



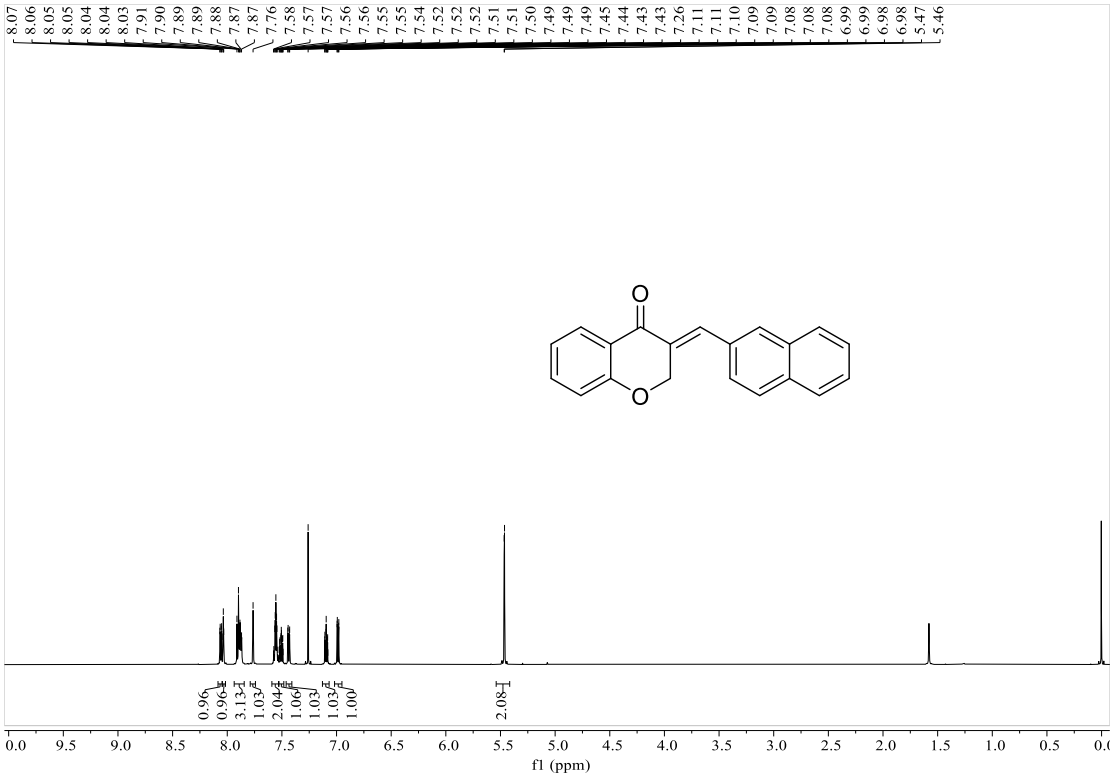
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(Furan-2-ylmethylene)chroman-4-one (**1l**)



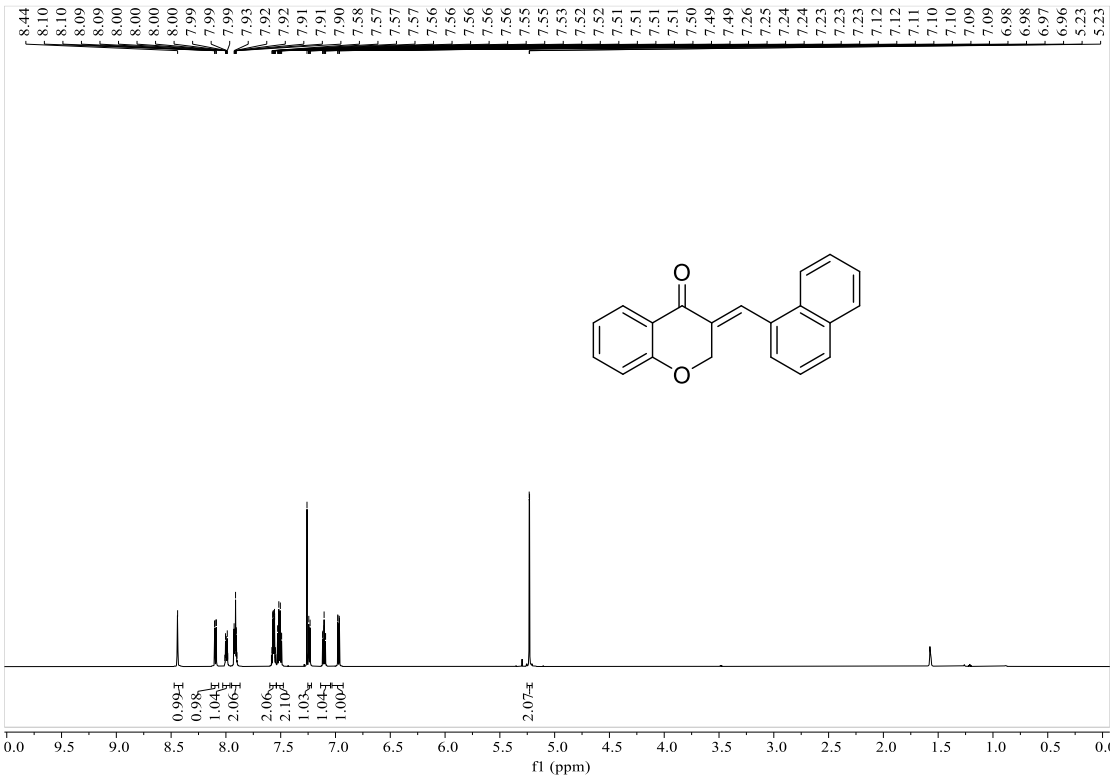
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(Naphthalen-2-ylmethylene)chroman-4-one (**1m**)



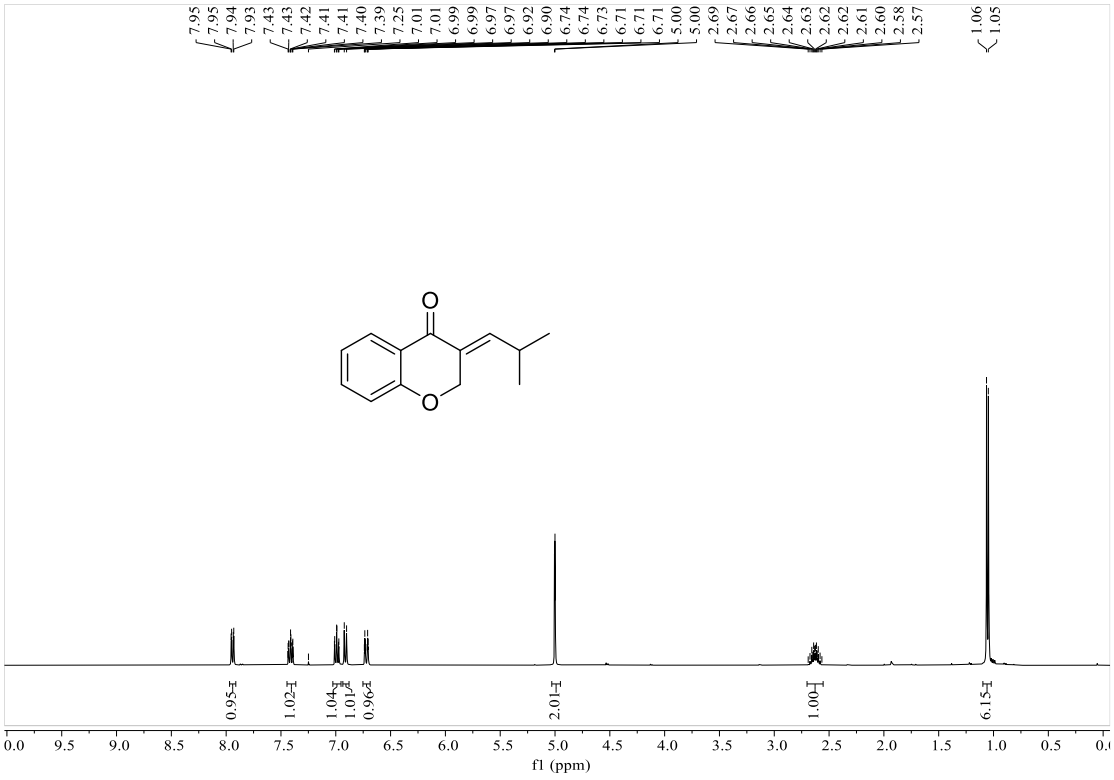
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(Naphthalen-1-ylmethylene)chroman-4-one (**1n**)



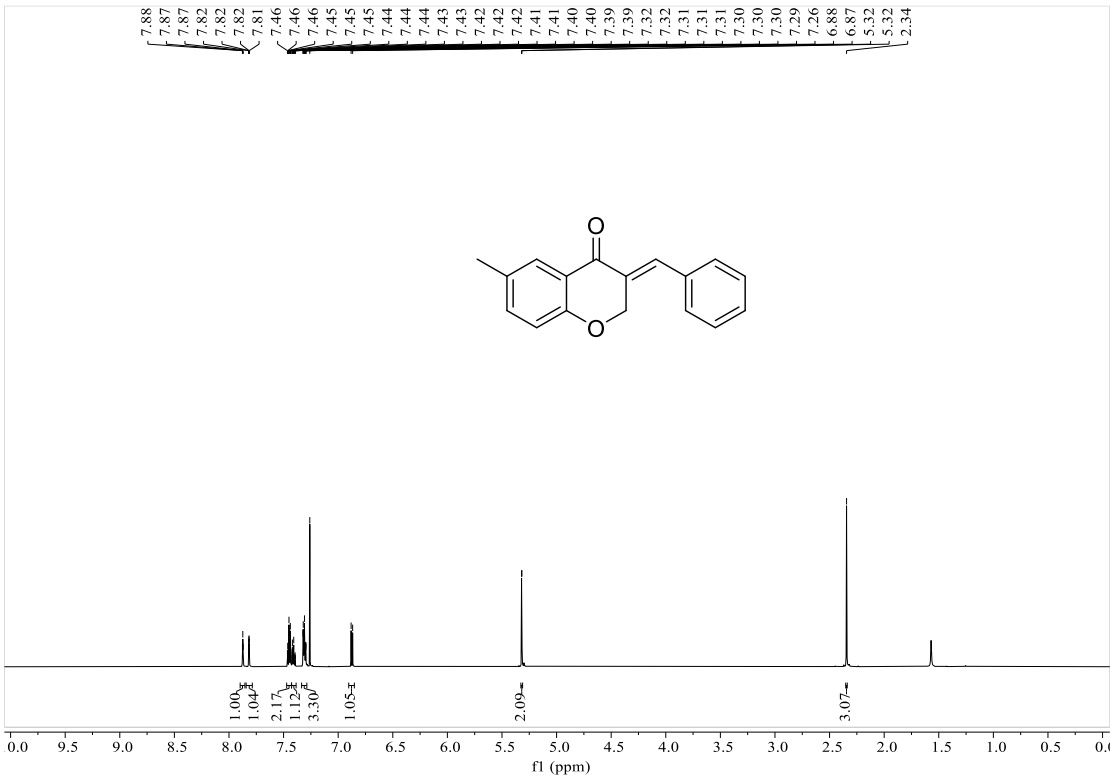
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-3-(2-methylpropylidene)chroman-4-one (**1o**)



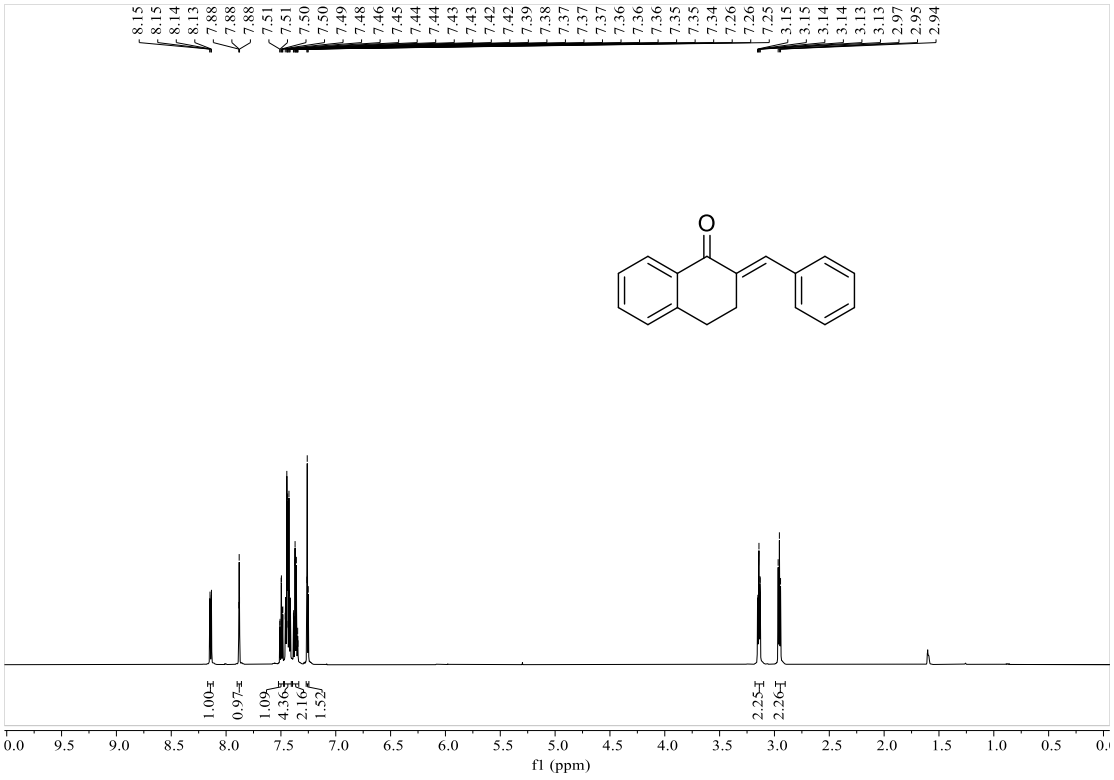
^{1}H NMR (400 MHz, Chloroform-*d*)

(*E*)-3-Benzylidene-6-methylchroman-4-one (**1p**)



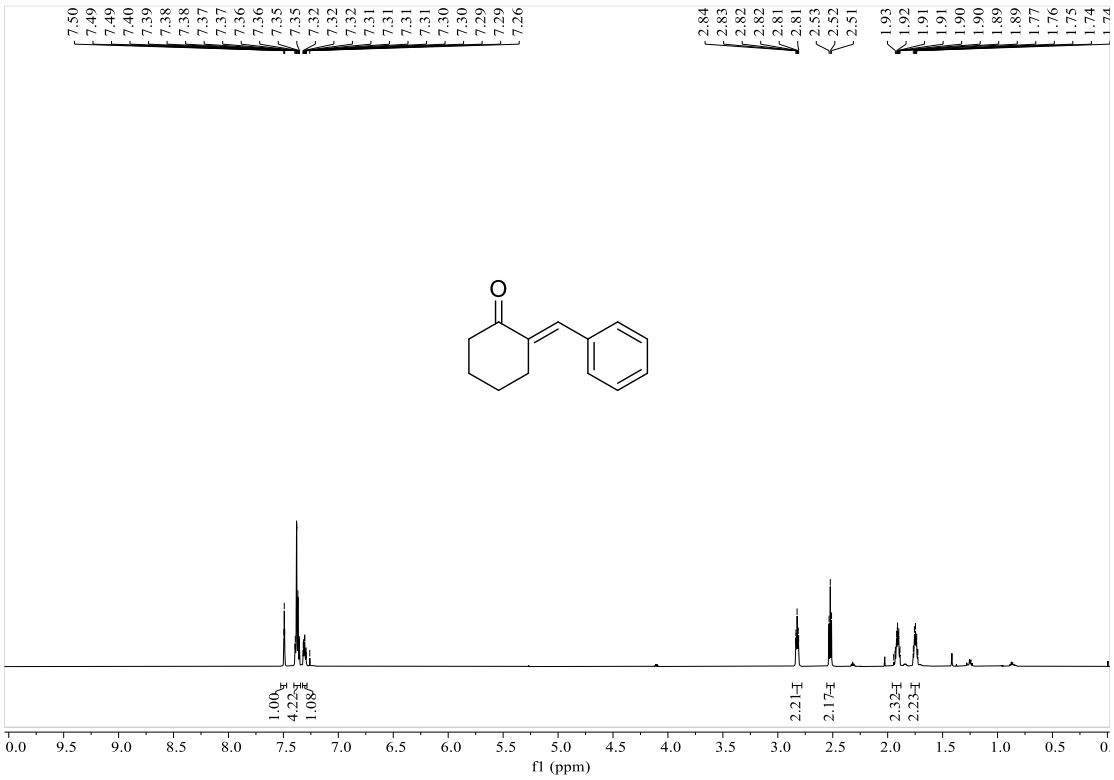
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-2-Benzylidene-3,4-dihydronaphthalen-1(2*H*)-one (**1q**)



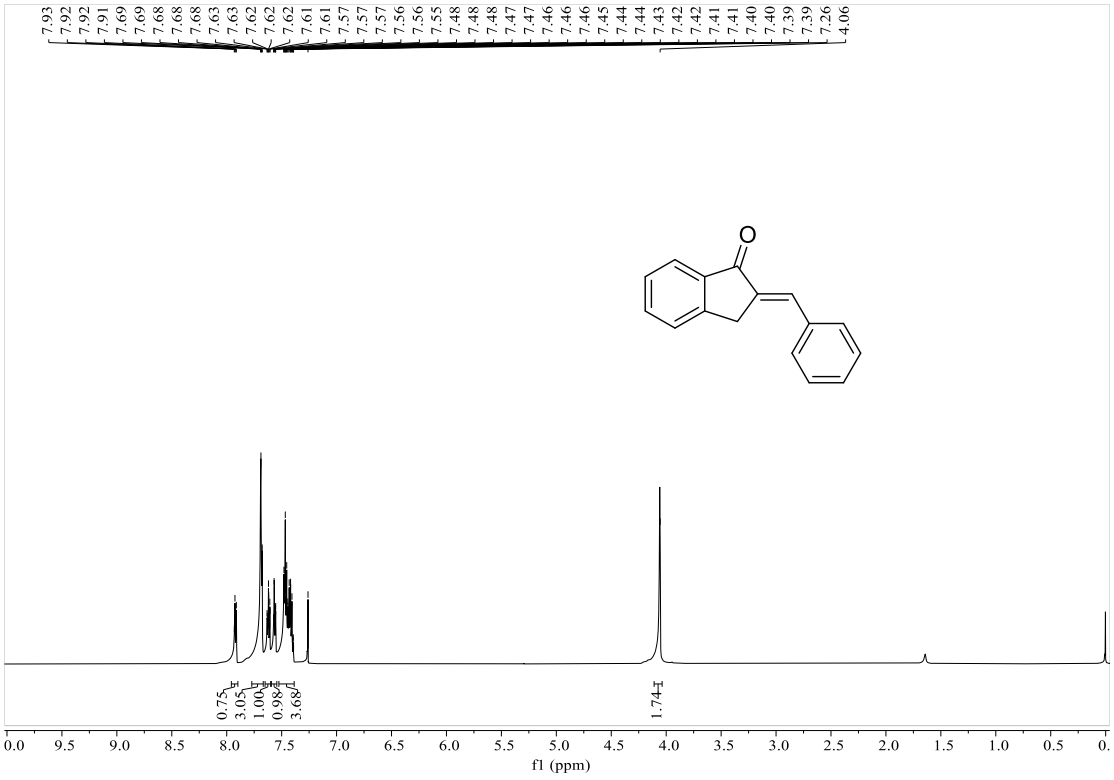
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-2-Benzylidenecyclohexan-1-one (**1r**)



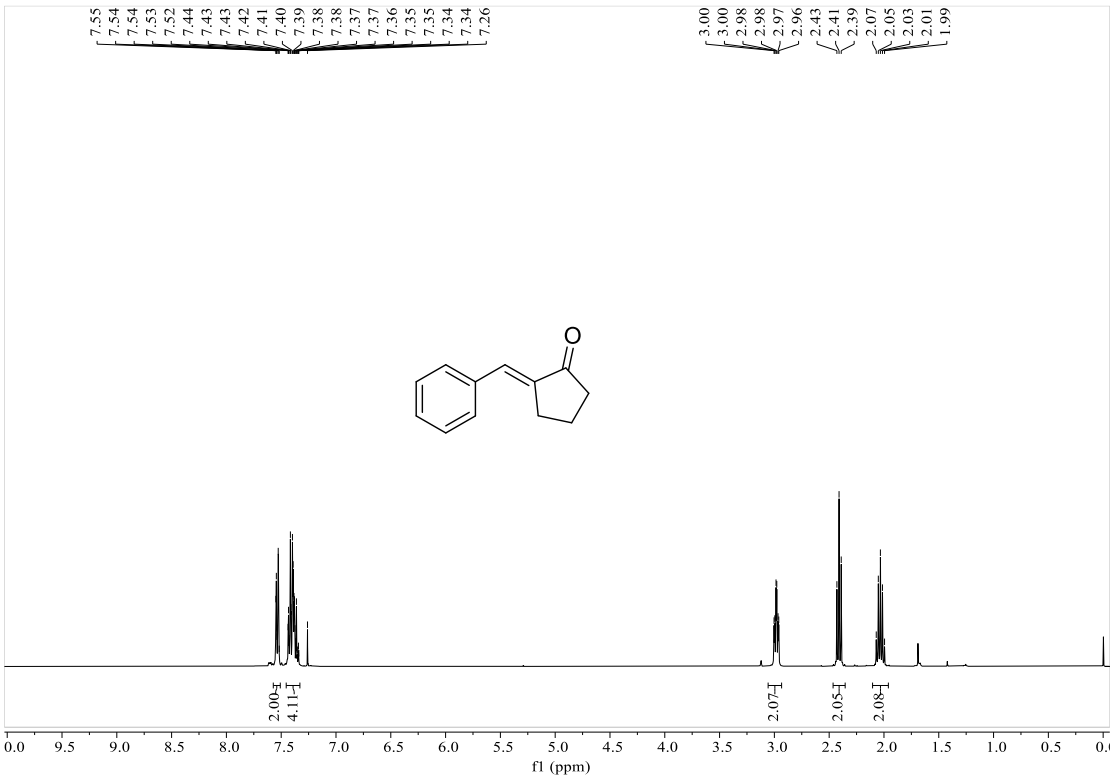
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-2-Benzylidene-2,3-dihydro-1*H*-inden-1-one (**1s**)



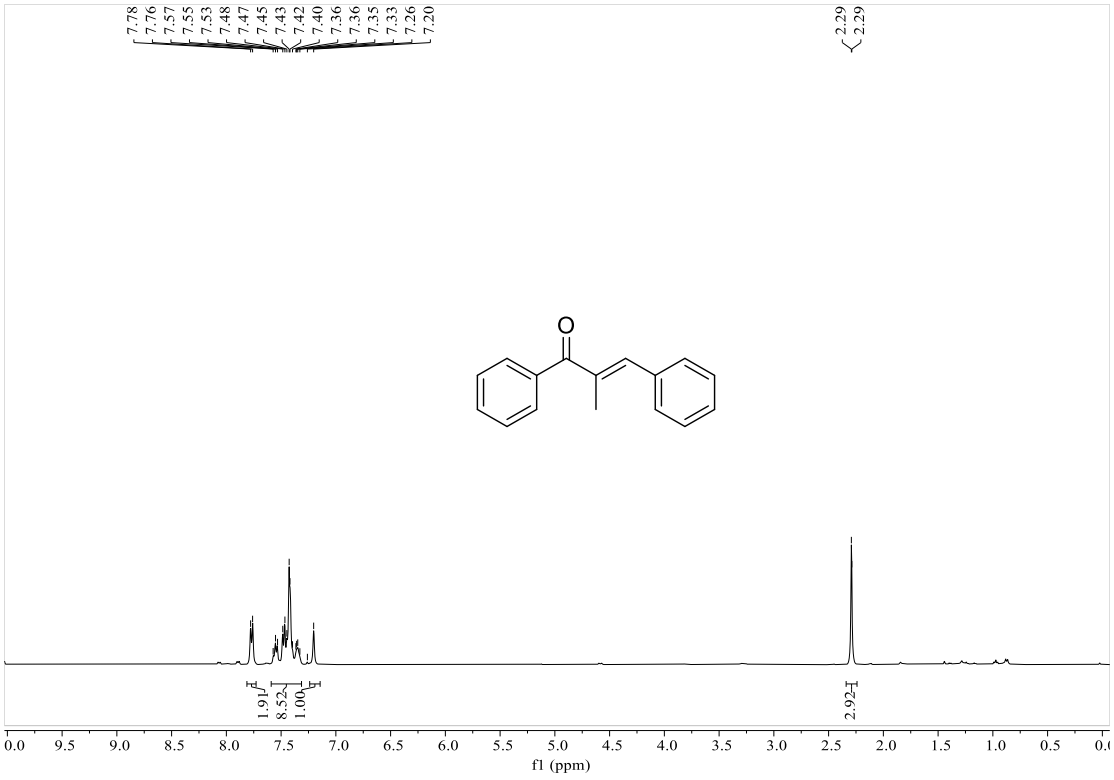
^{1}H NMR (600 MHz, Chloroform-*d*)

(*E*)-2-Benzylidenecyclopentan-1-one (**1t**)



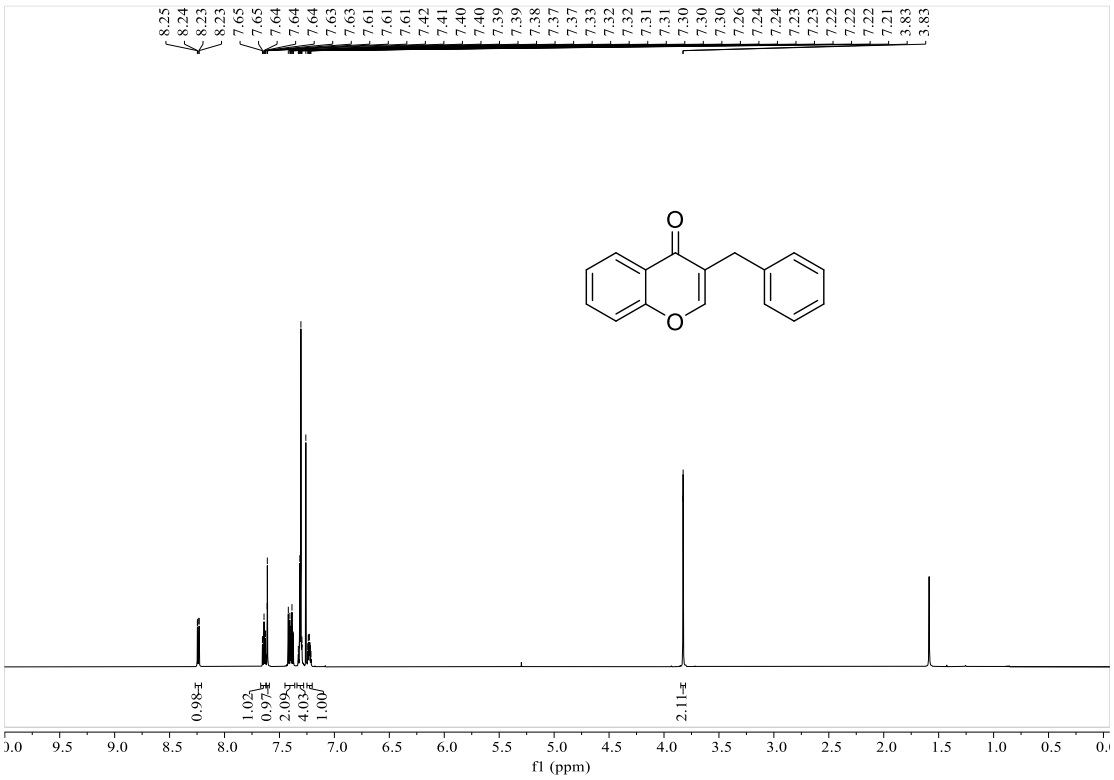
^{1}H NMR (400 MHz, Chloroform-*d*)

(*E*)-2-Methyl-1,3-diphenylprop-2-en-1-one (**1u**)



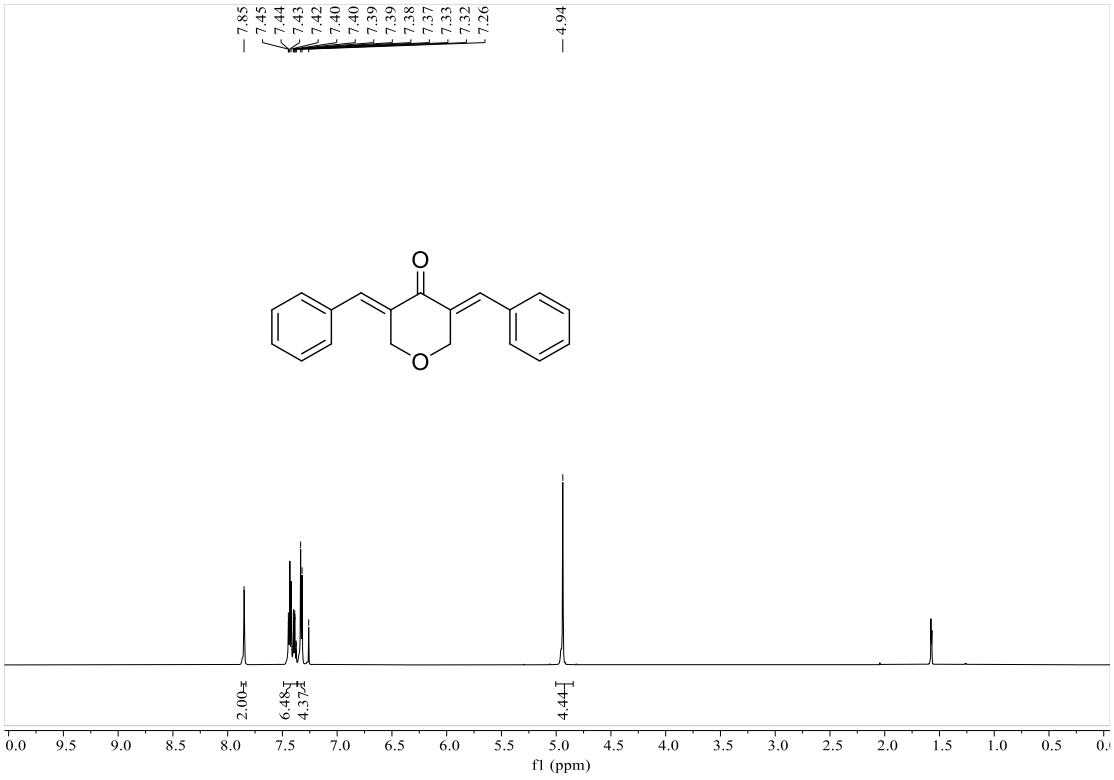
^{1}H NMR (400 MHz, Chloroform-*d*)

3-Benzyl-4*H*-chromen-4-one (**2a'**)



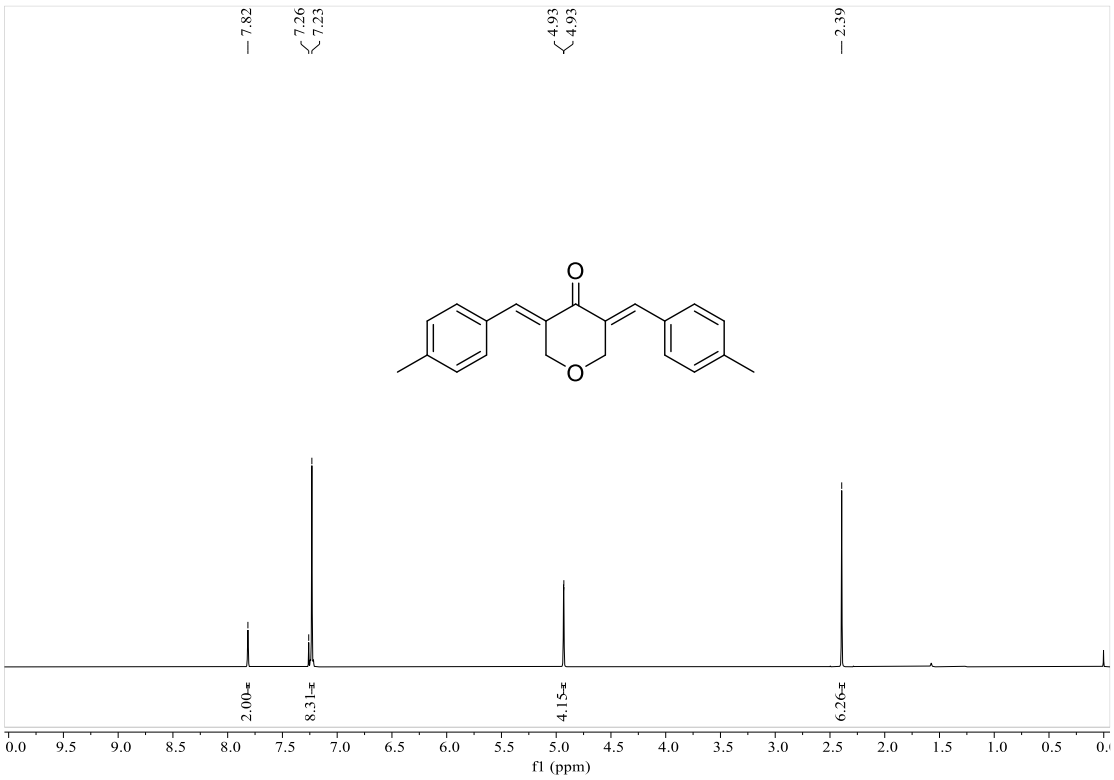
^{1}H NMR (600 MHz, Chloroform-*d*)

3,5-di((*E*)-benzylidene)tetrahydro-4*H*-pyran-4-one (**3a**)



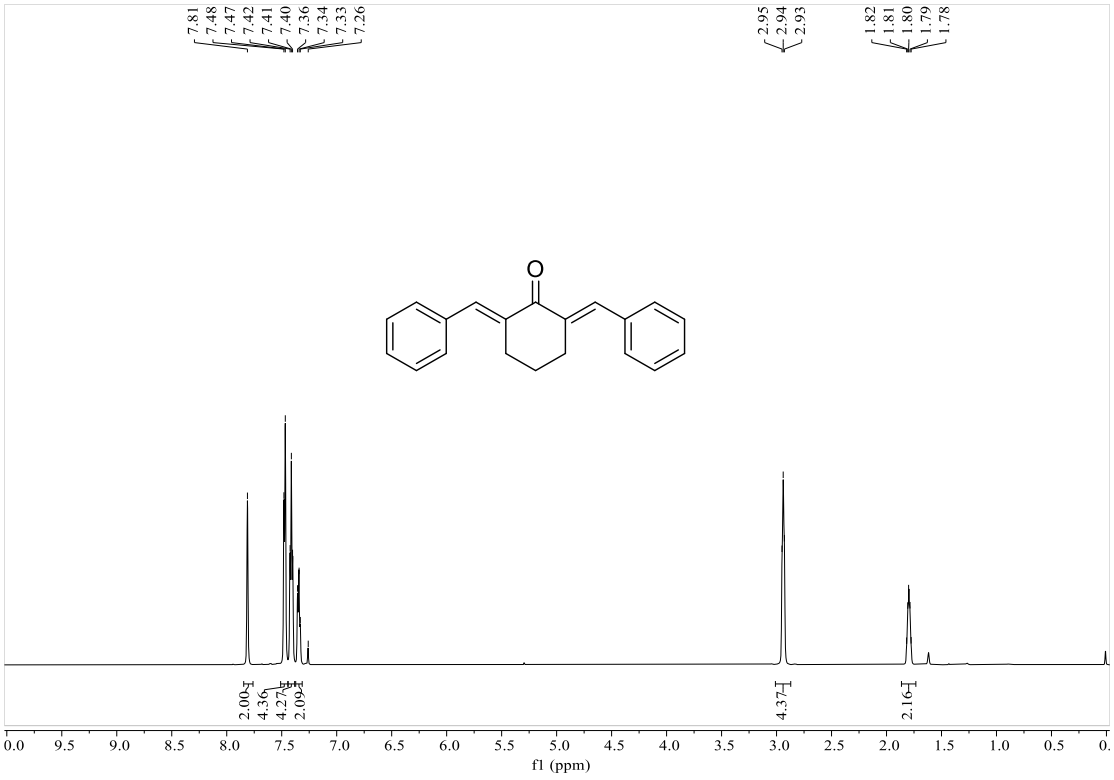
^{1}H NMR (600 MHz, Chloroform-*d*)

3,5-bis((*E*)-4-methylbenzylidene)tetrahydro-4*H*-pyran-4-one (**3b**)



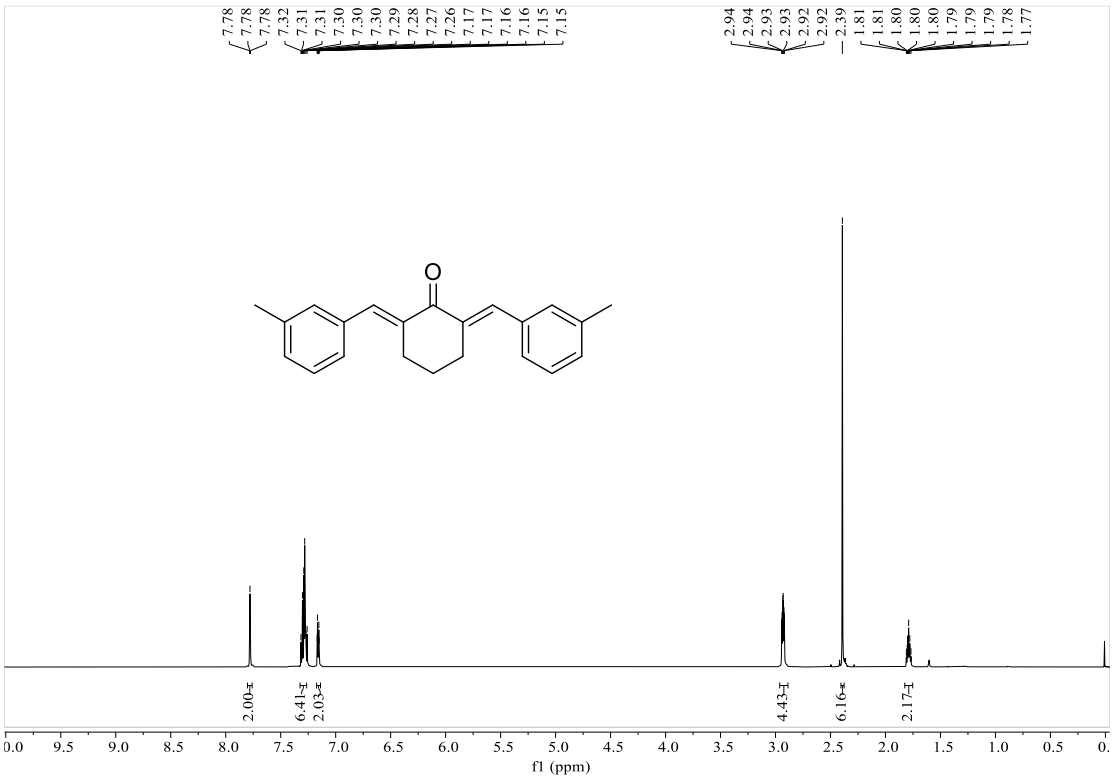
^{1}H NMR (600 MHz, Chloroform-*d*)

2,6-Di((*E*)-benzylidene)cyclohexan-1-one (**3c**)



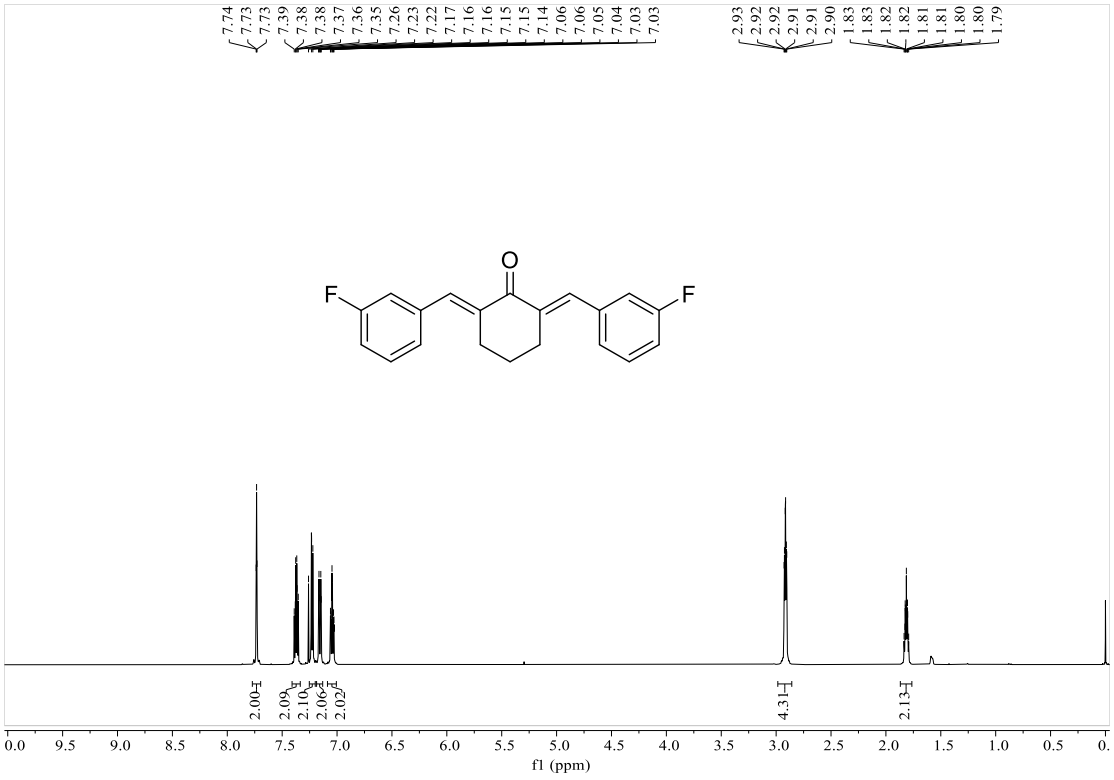
^{1}H NMR (600 MHz, Chloroform-*d*)

2,6-Bis((*E*)-3-methylbenzylidene)cyclohexan-1-one (**3d**)



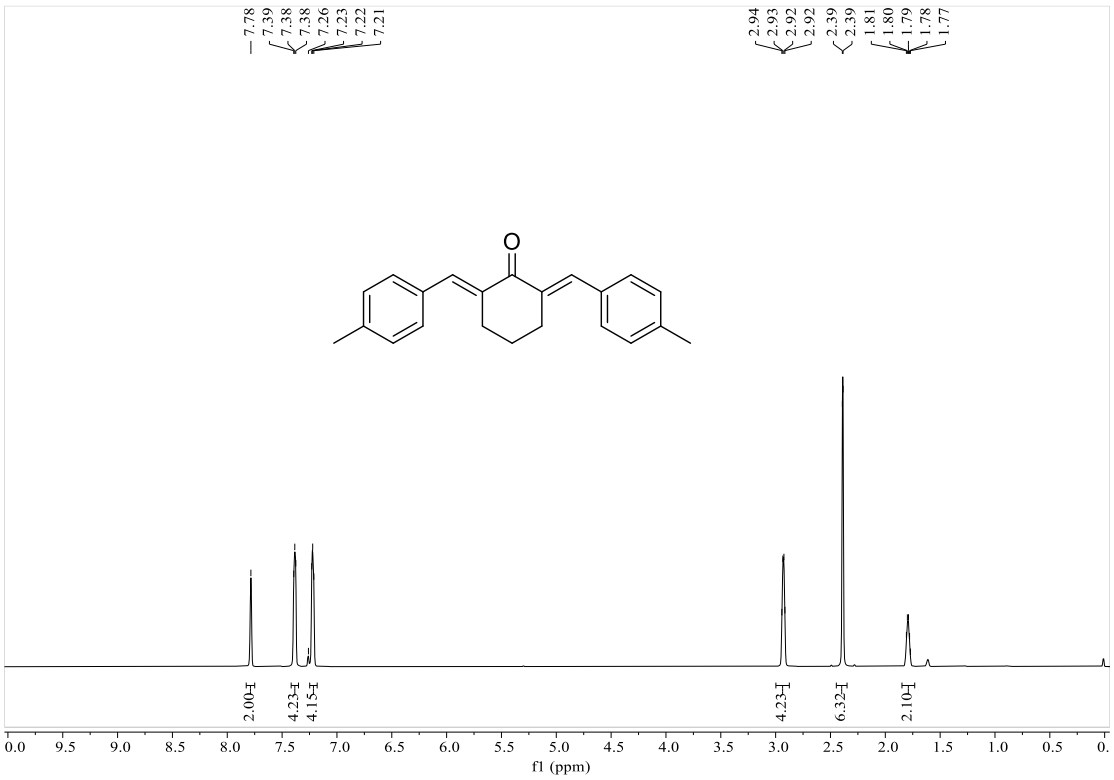
^{1}H NMR (600 MHz, Chloroform-*d*)

2,6-Bis((*E*)-3-fluorobenzylidene)cyclohexan-1-one (**3e**)



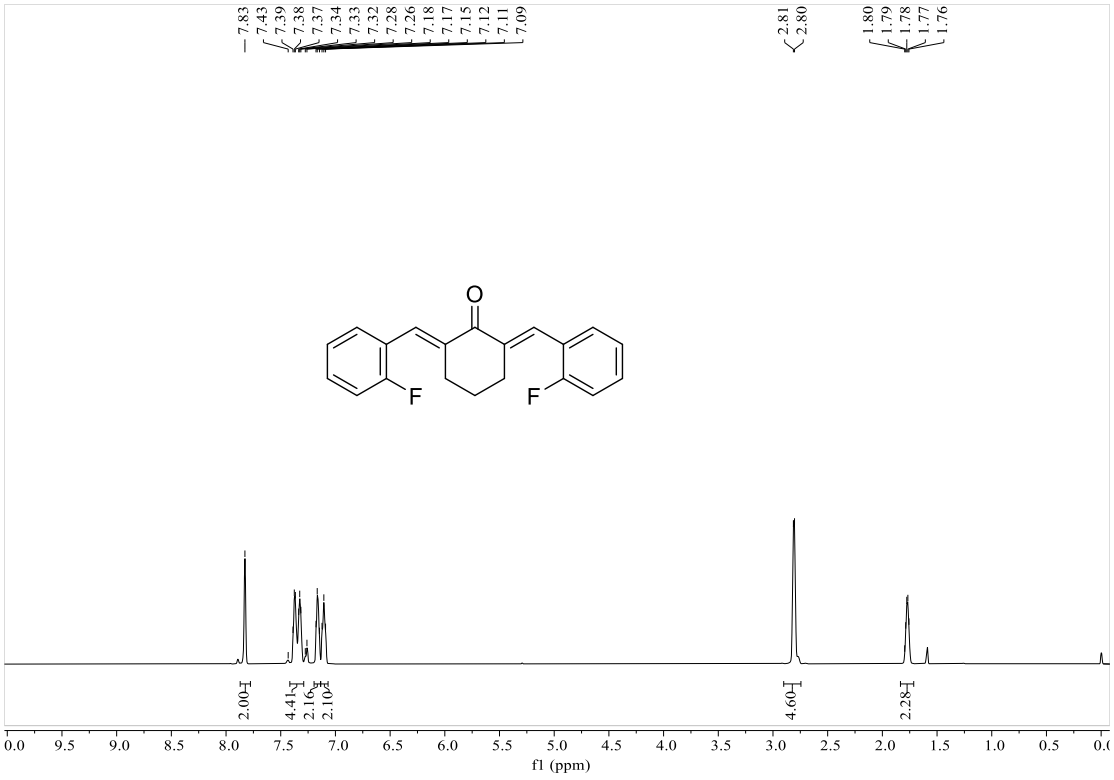
^{1}H NMR (600 MHz, Chloroform-*d*)

2,6-Bis((*E*)-4-methylbenzylidene)cyclohexan-1-one (**3f**)



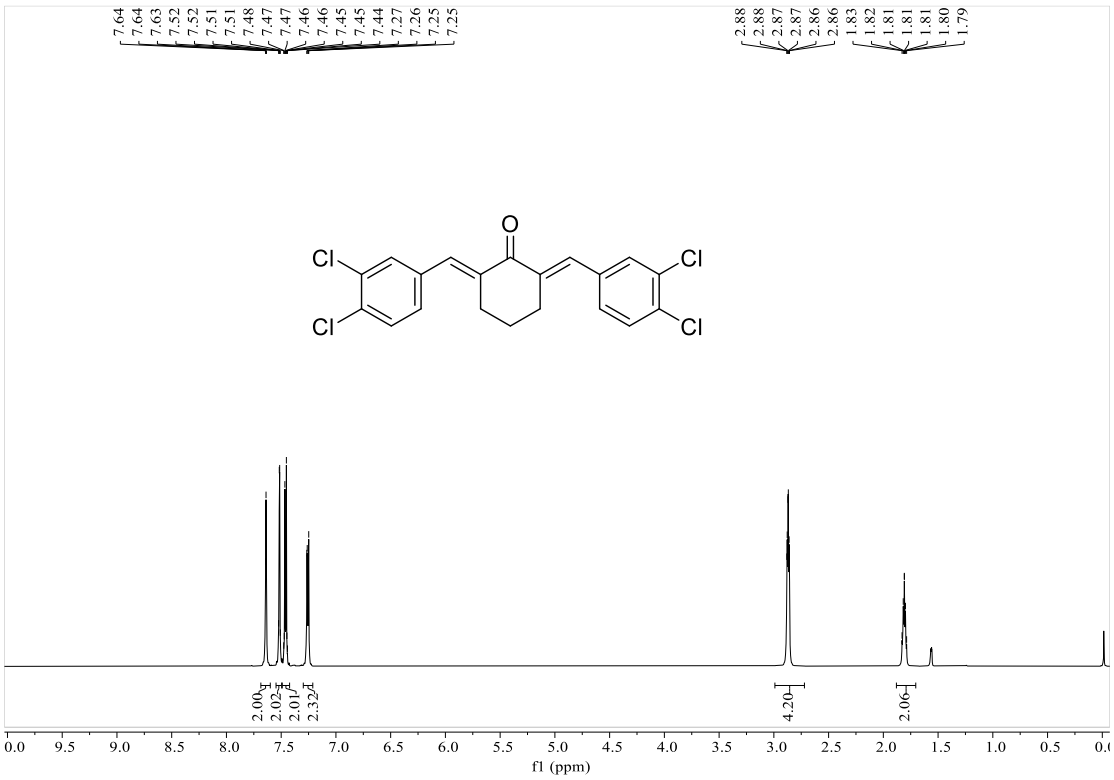
^{1}H NMR (600 MHz, Chloroform-*d*)

2,6-Bis((*E*)-2-fluorobenzylidene)cyclohexan-1-one (**3g**)



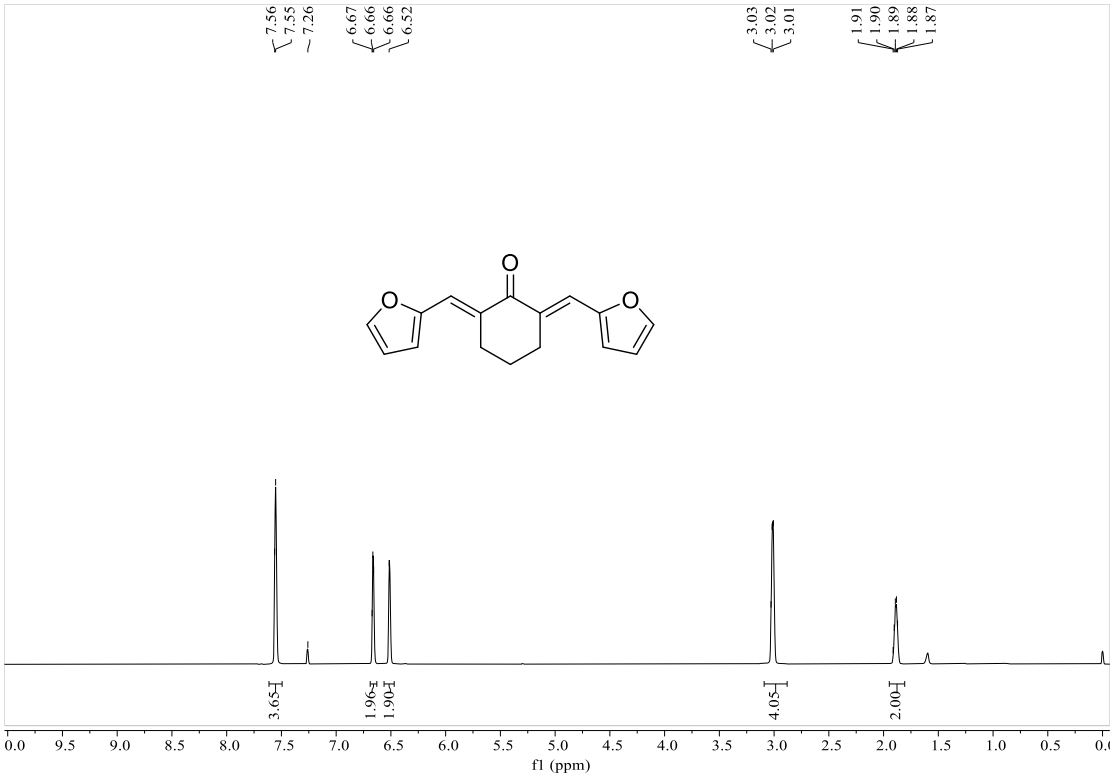
^{1}H NMR (600 MHz, Chloroform-*d*)

2,6-Bis((*E*)-3,4-dichlorobenzylidene)cyclohexan-1-one (**3h**)



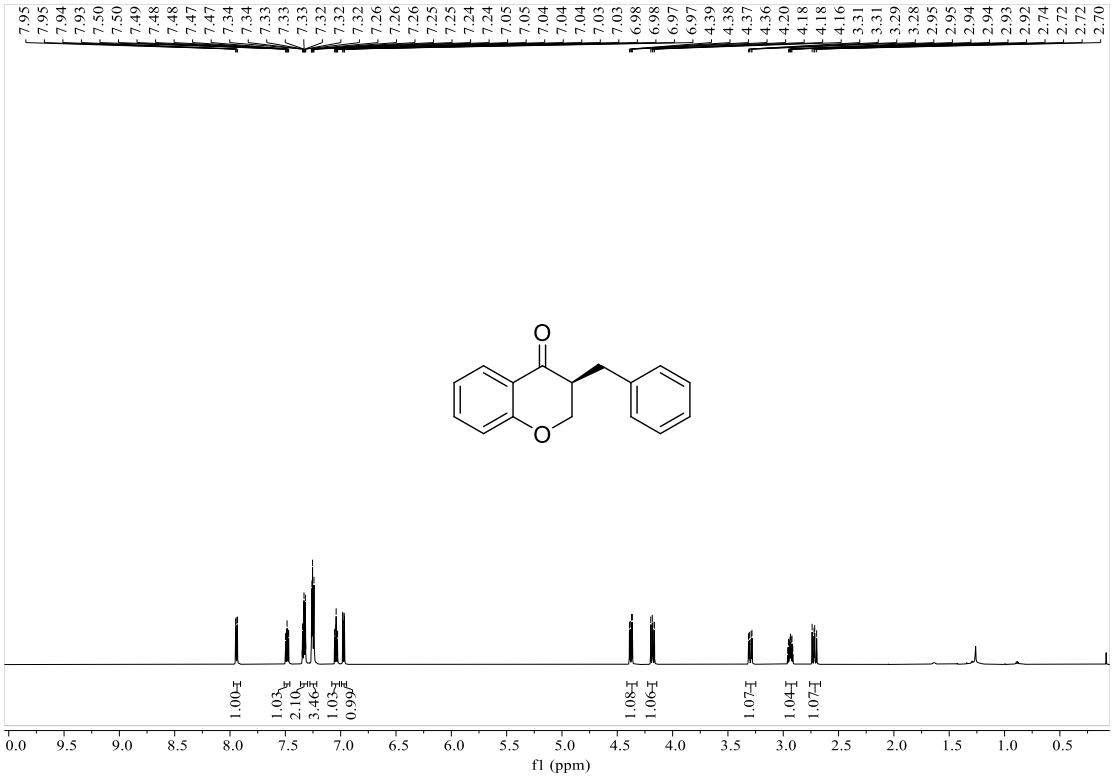
^{1}H NMR (600 MHz, Chloroform-*d*)

(2*E*,6*E*)-2,6-Bis(furan-2-ylmethylene)cyclohexan-1-one (**3i**)

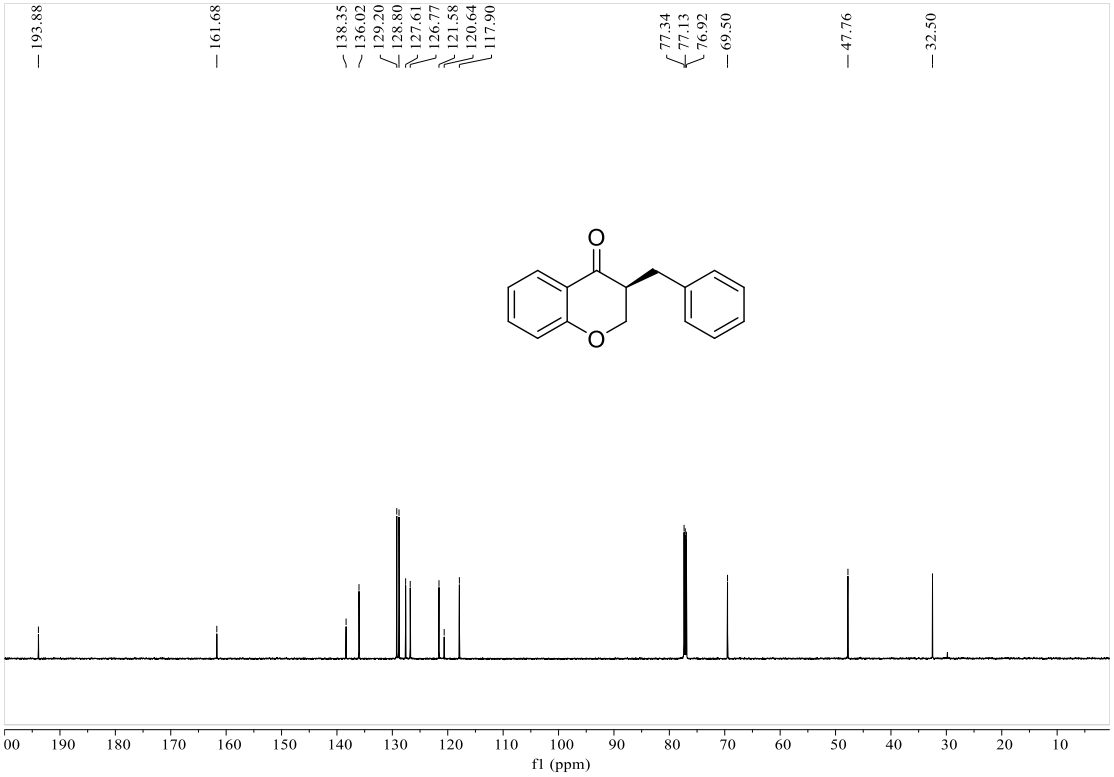


^{1}H NMR (600 MHz, Chloroform-*d*)

(*S*)-3-Benzylchroman-4-one (**2a**)

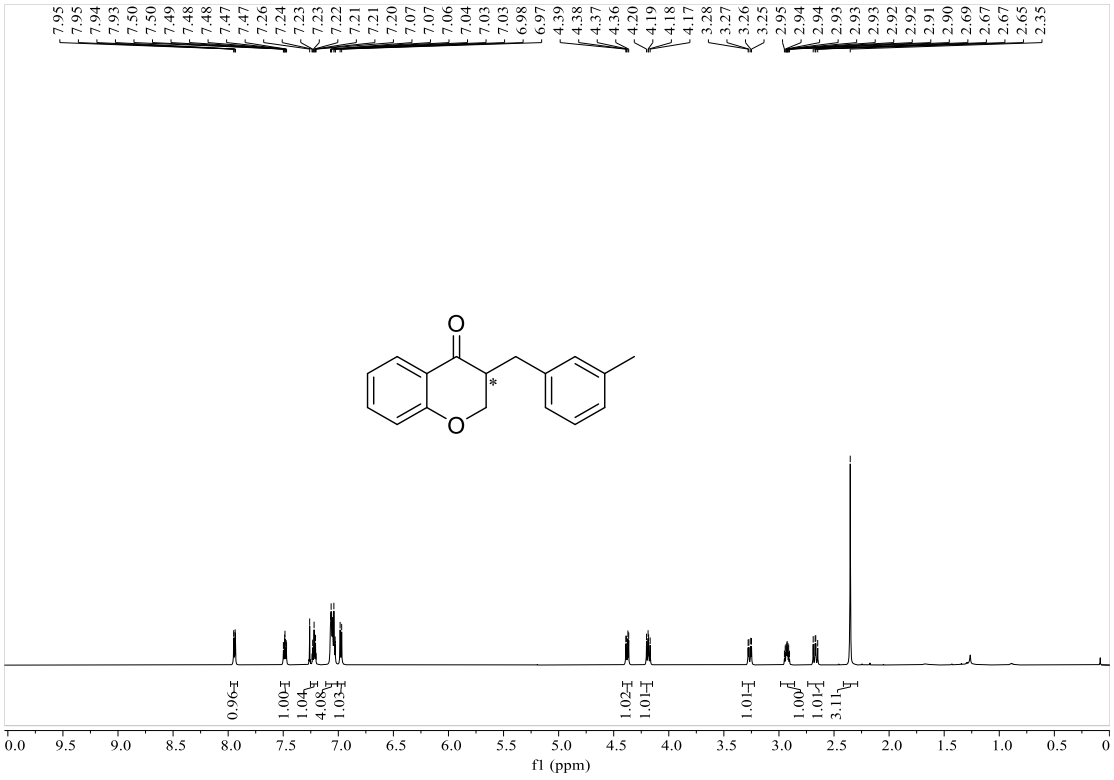


^{1}H NMR (600 MHz, Chloroform-*d*)

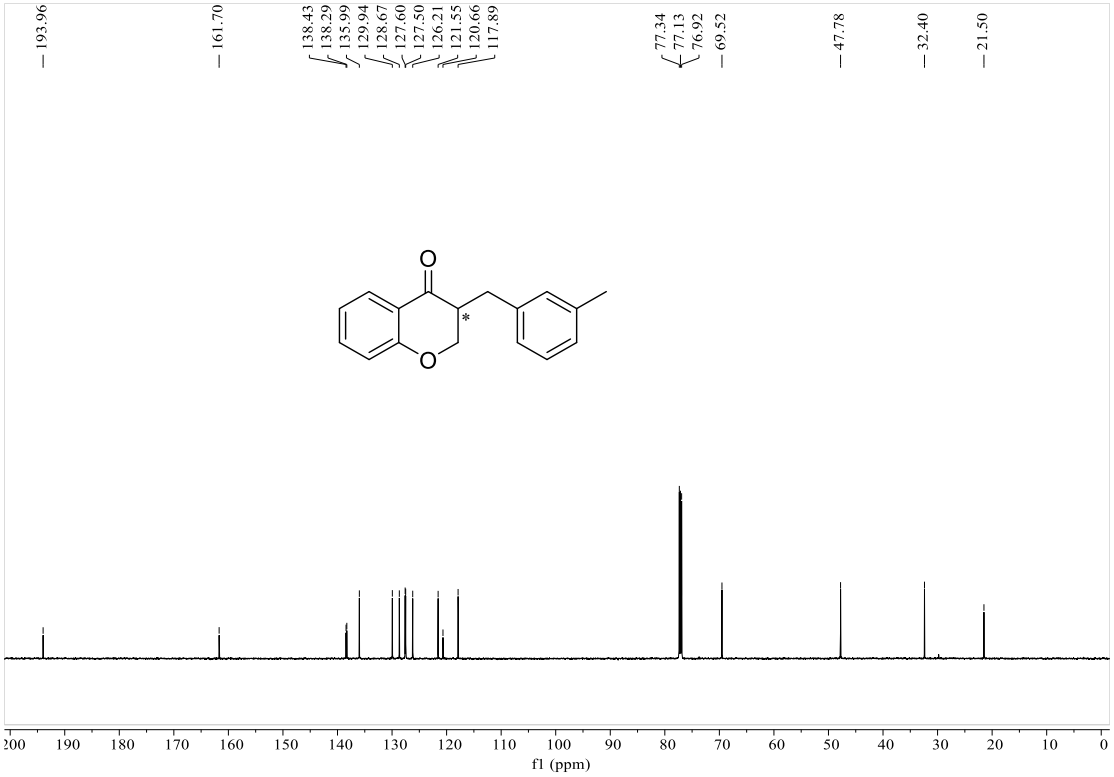


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(3-Methylbenzyl)chroman-4-one (**2b**)

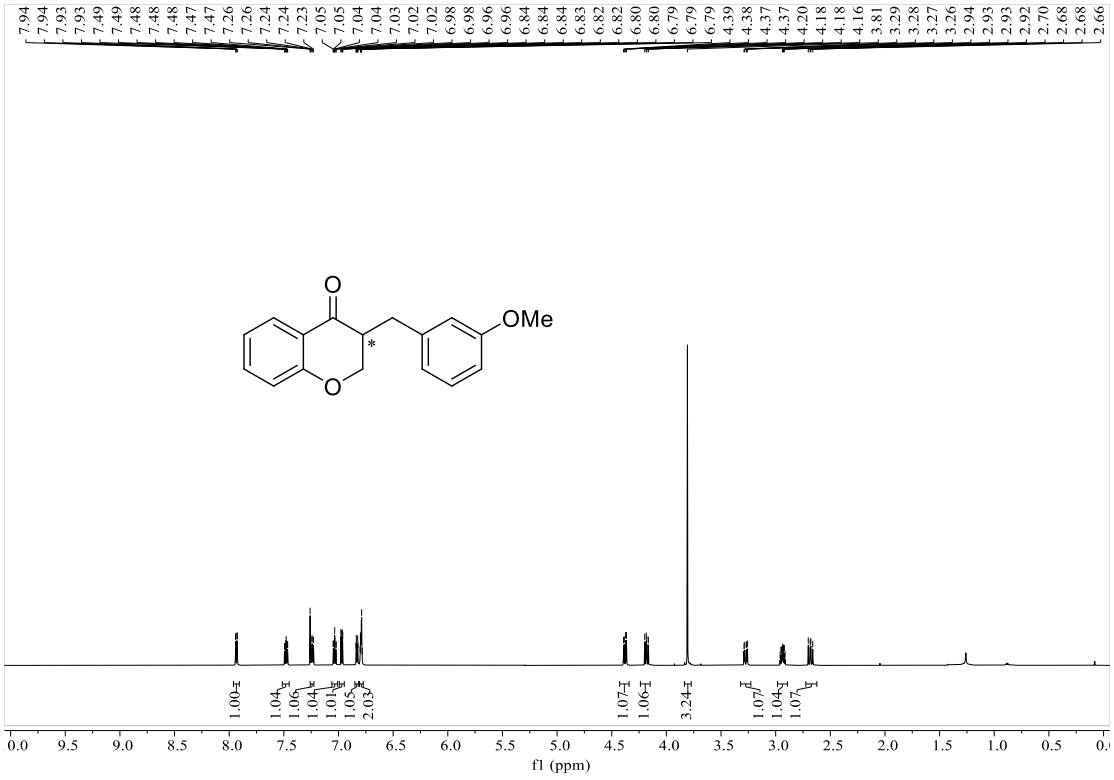


^{1}H NMR (600 MHz, Chloroform-*d*)

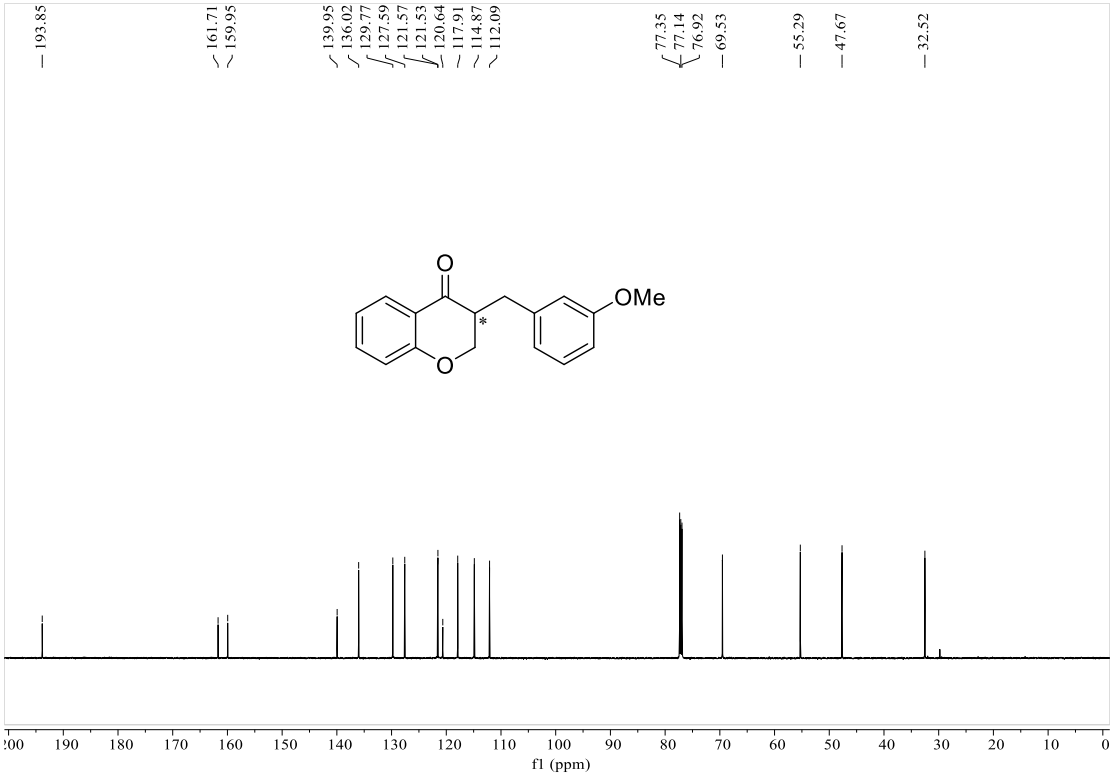


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(3-Methoxybenzyl)chroman-4-one (**2c**)

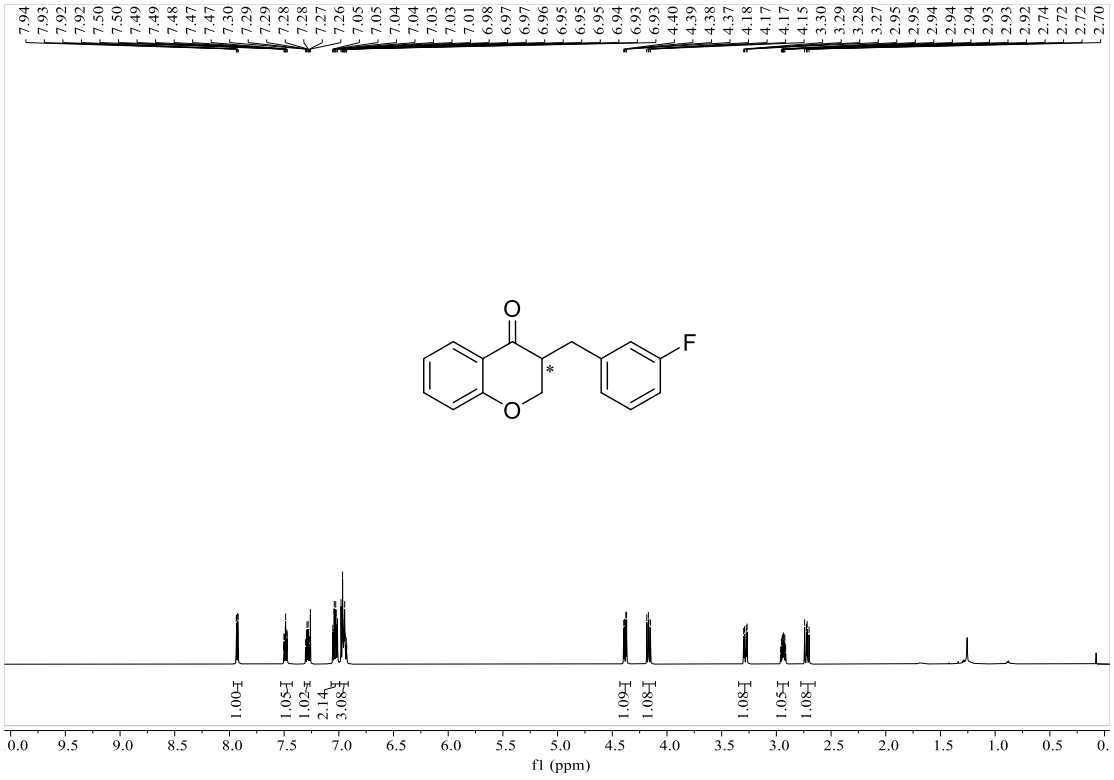


^{1}H NMR (600 MHz, Chloroform-*d*)

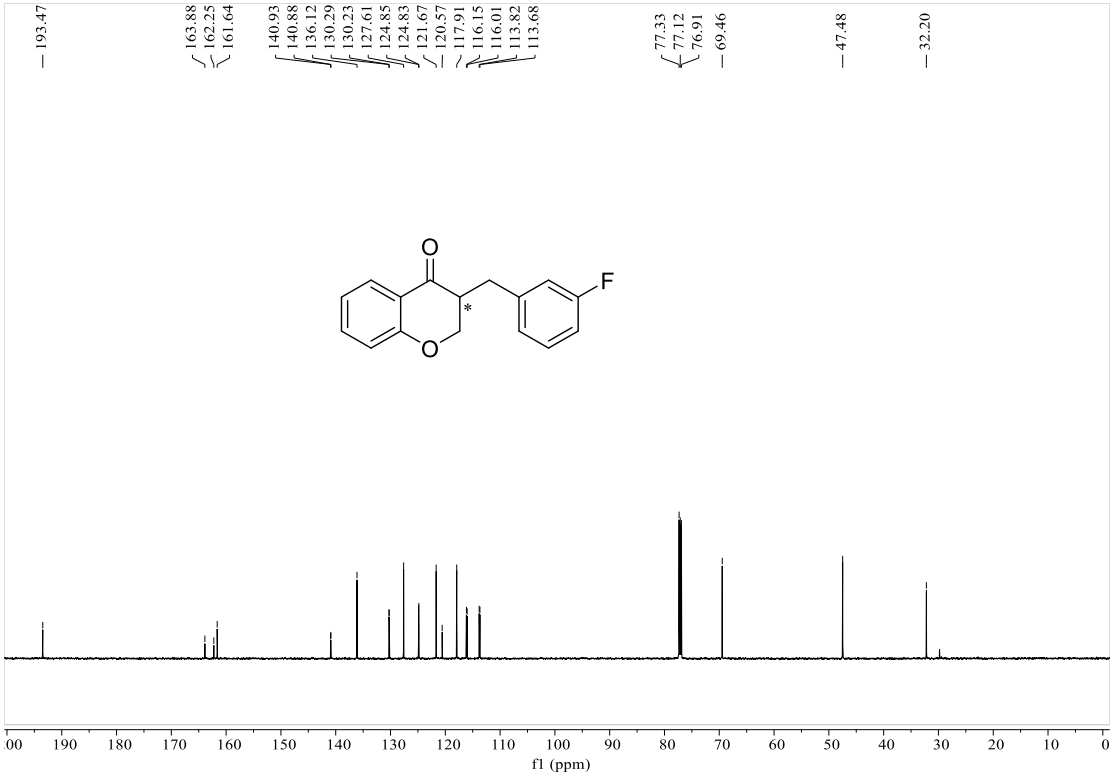


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(3-Fluorobenzyl)chroman-4-one (**2d**)

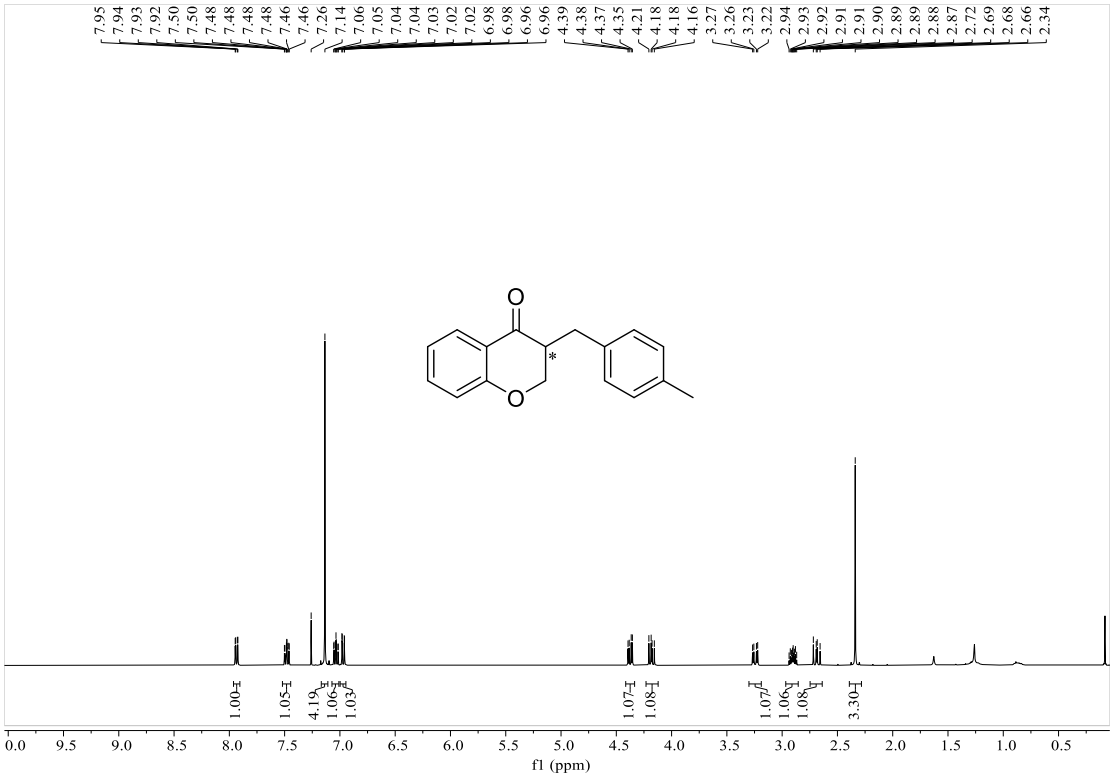


^{1}H NMR (600 MHz, Chloroform-*d*)

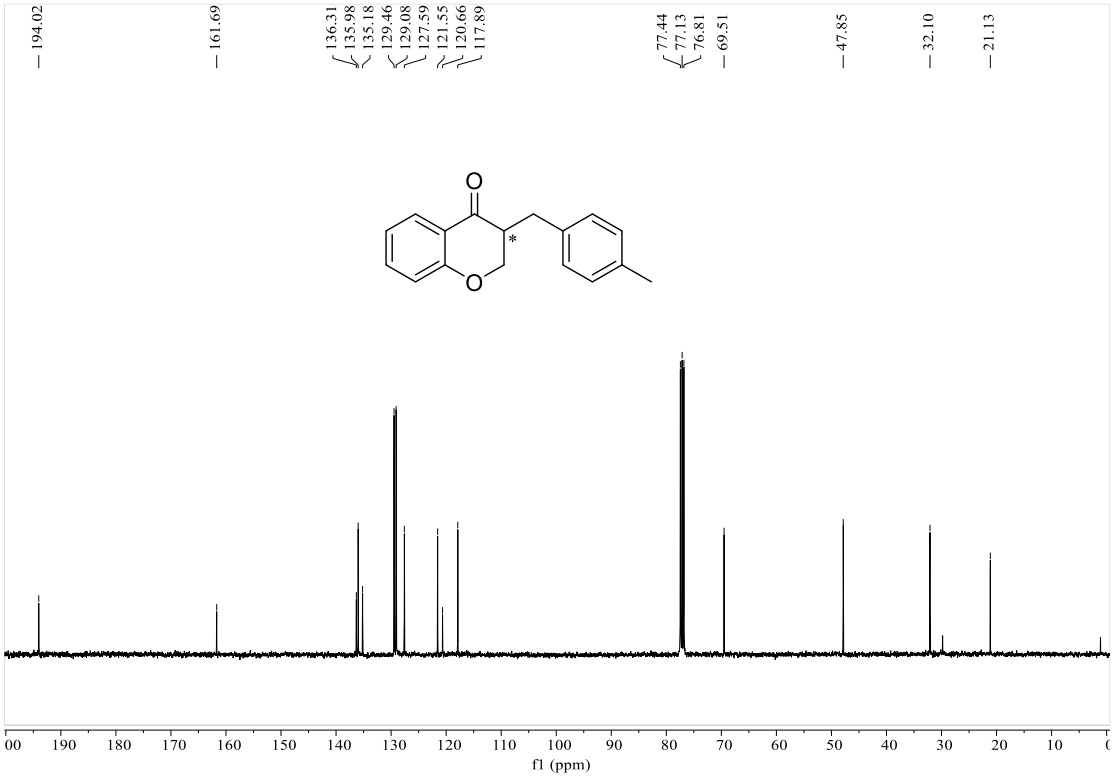


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(4-Methylbenzyl)chroman-4-one (**2e**)

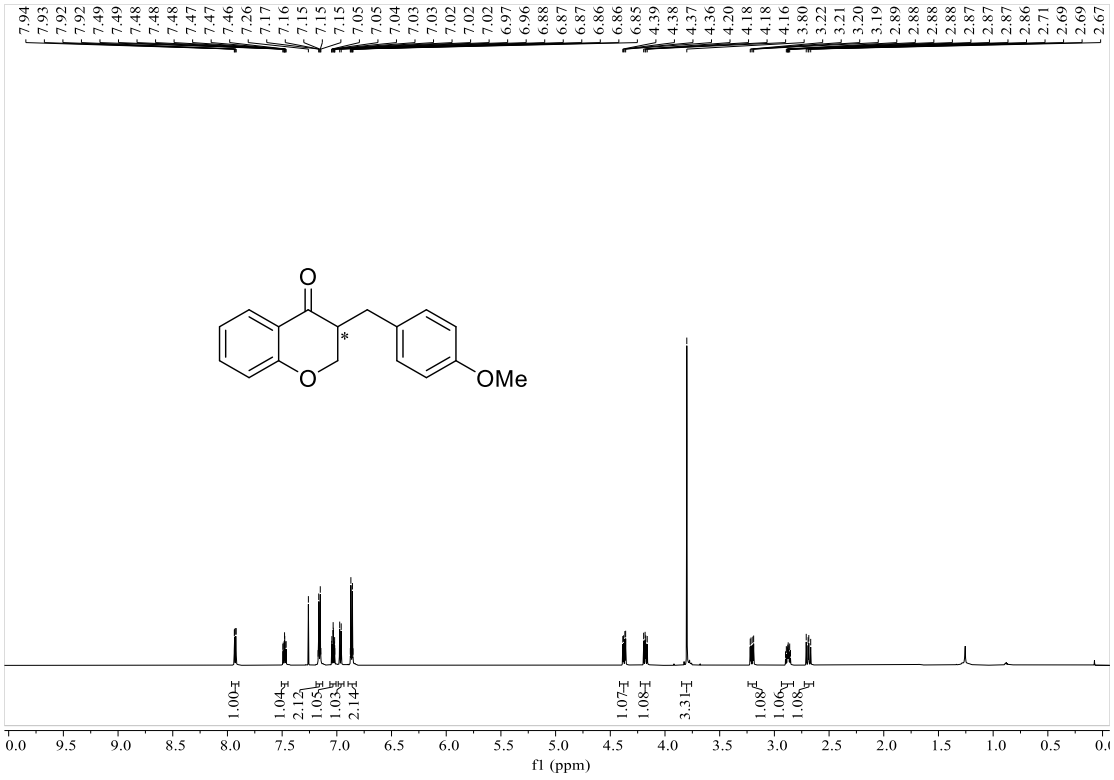


^{1}H NMR (400 MHz, Chloroform-*d*)

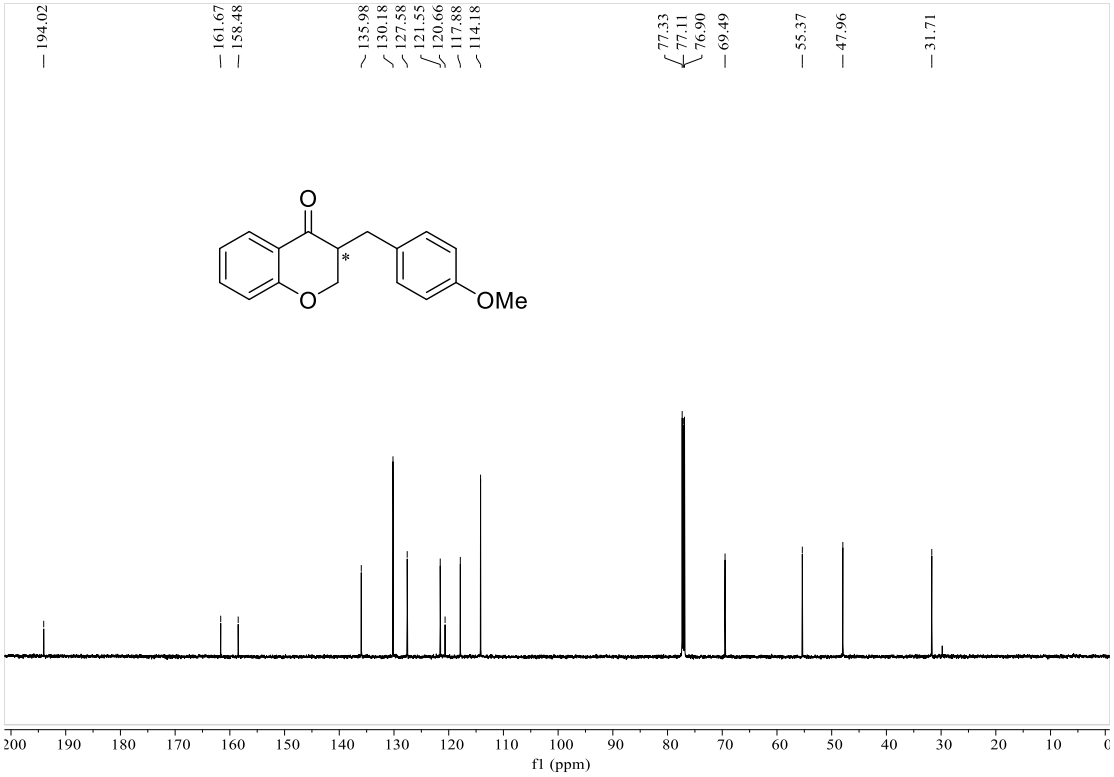


^{13}C NMR (101 MHz, Chloroform-*d*)

3-(4-Methoxybenzyl)chroman-4-one (**2f**)

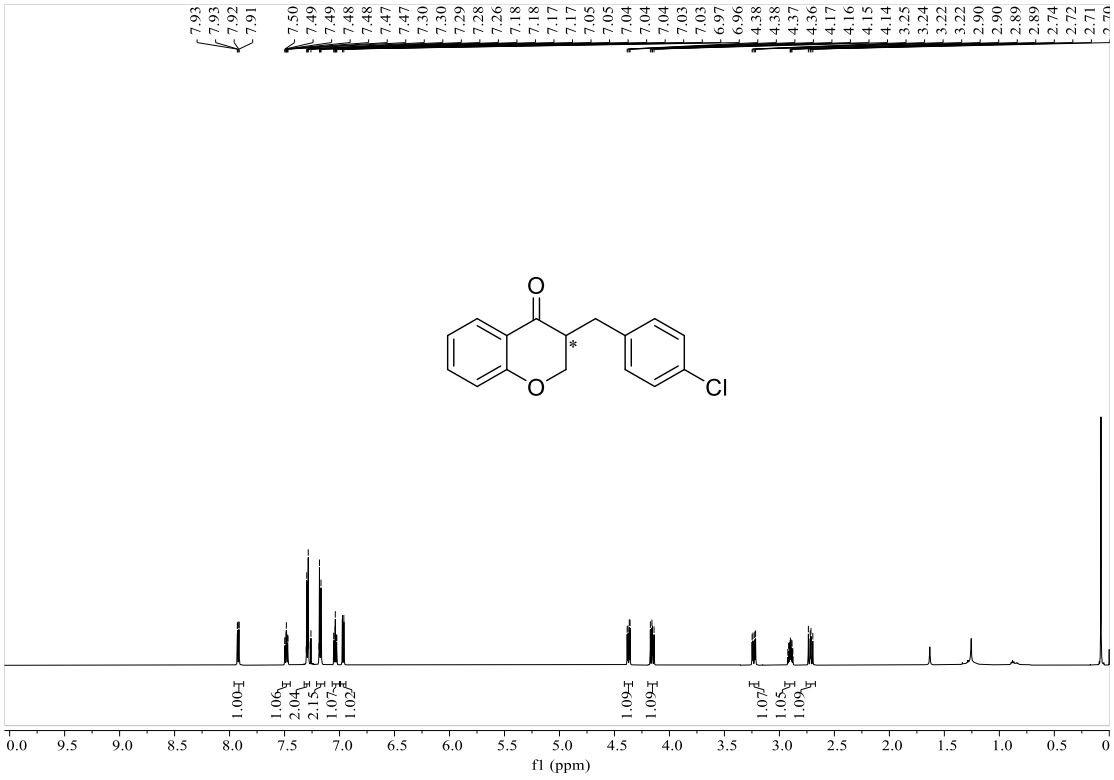


^{1}H NMR (600 MHz, Chloroform-*d*)

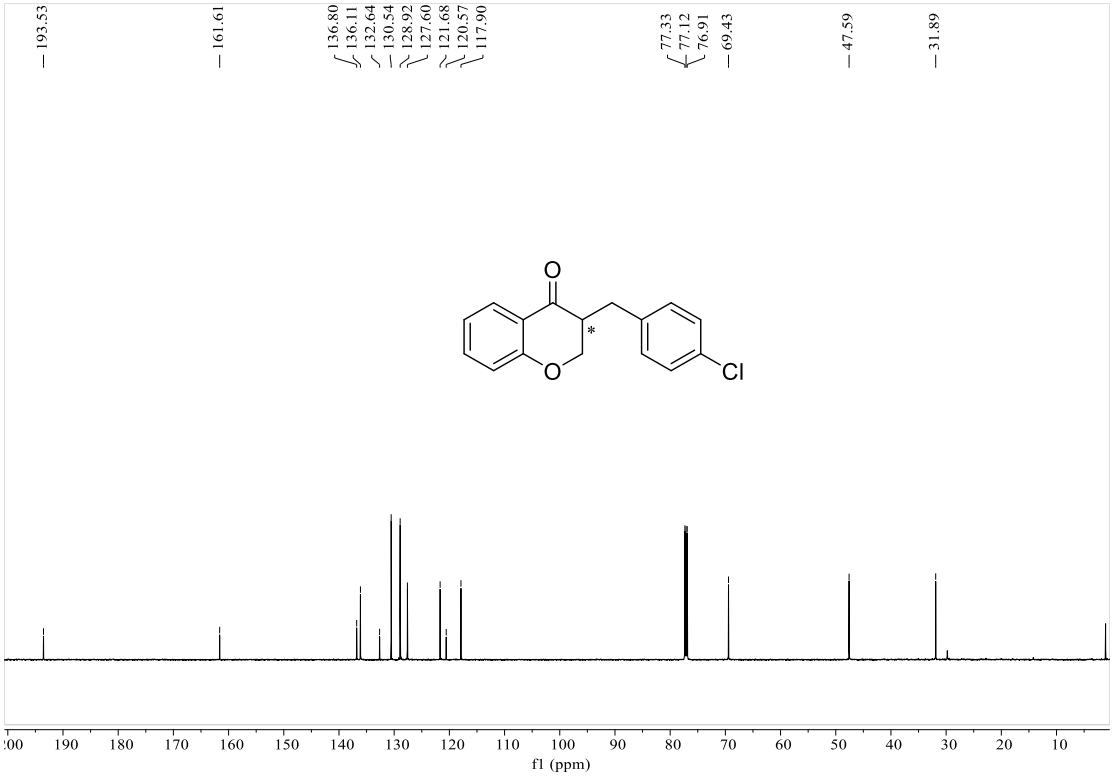


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(4-Chlorobenzyl)chroman-4-one (**2g**)

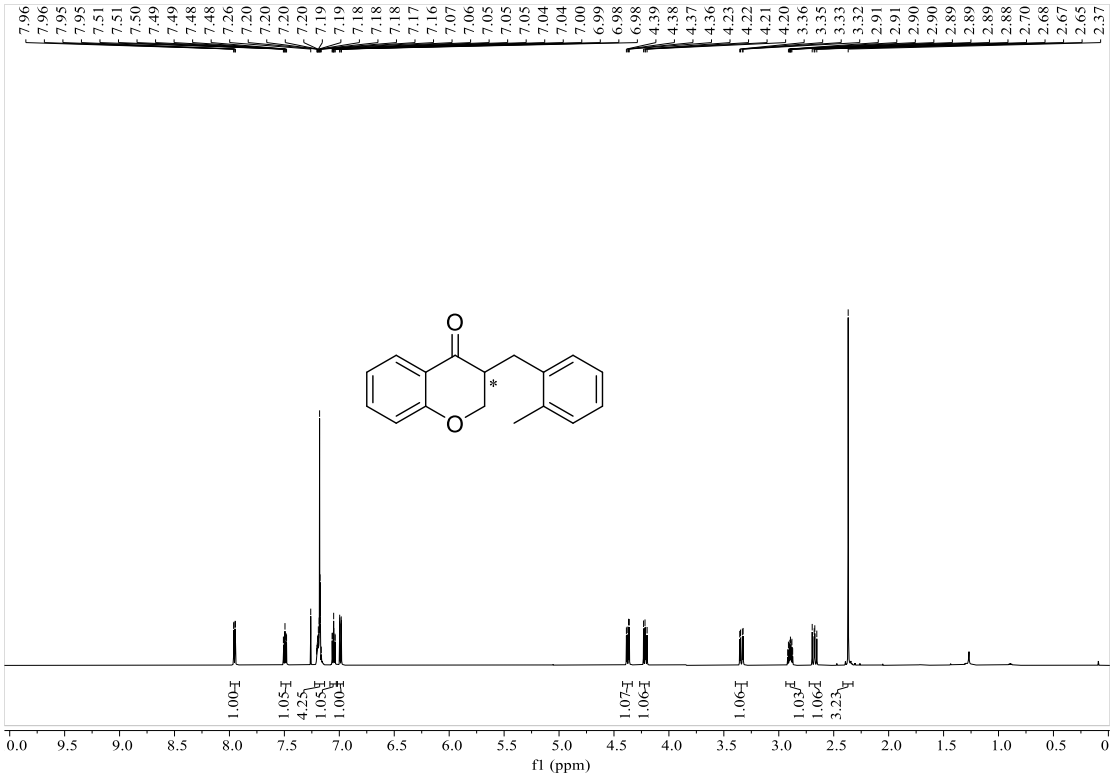


^{1}H NMR (600 MHz, Chloroform-*d*)

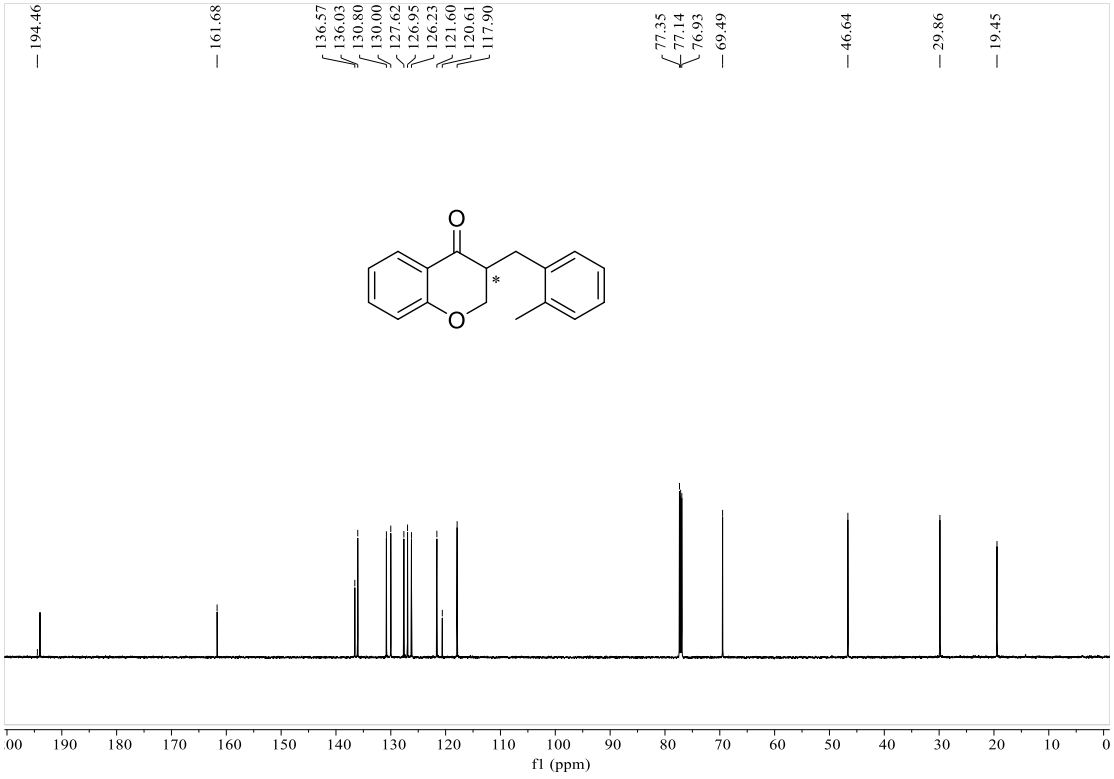


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(2-Methylbenzyl)chroman-4-one (**2h**)

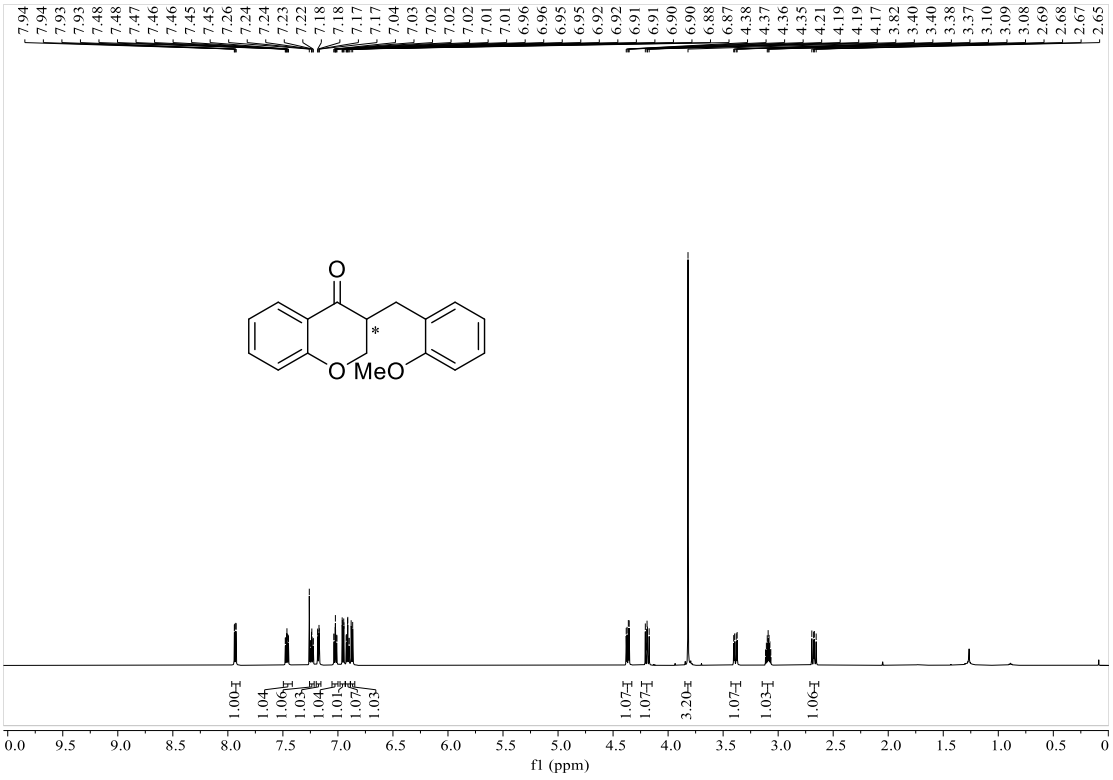


^{1}H NMR (600 MHz, Chloroform-*d*)

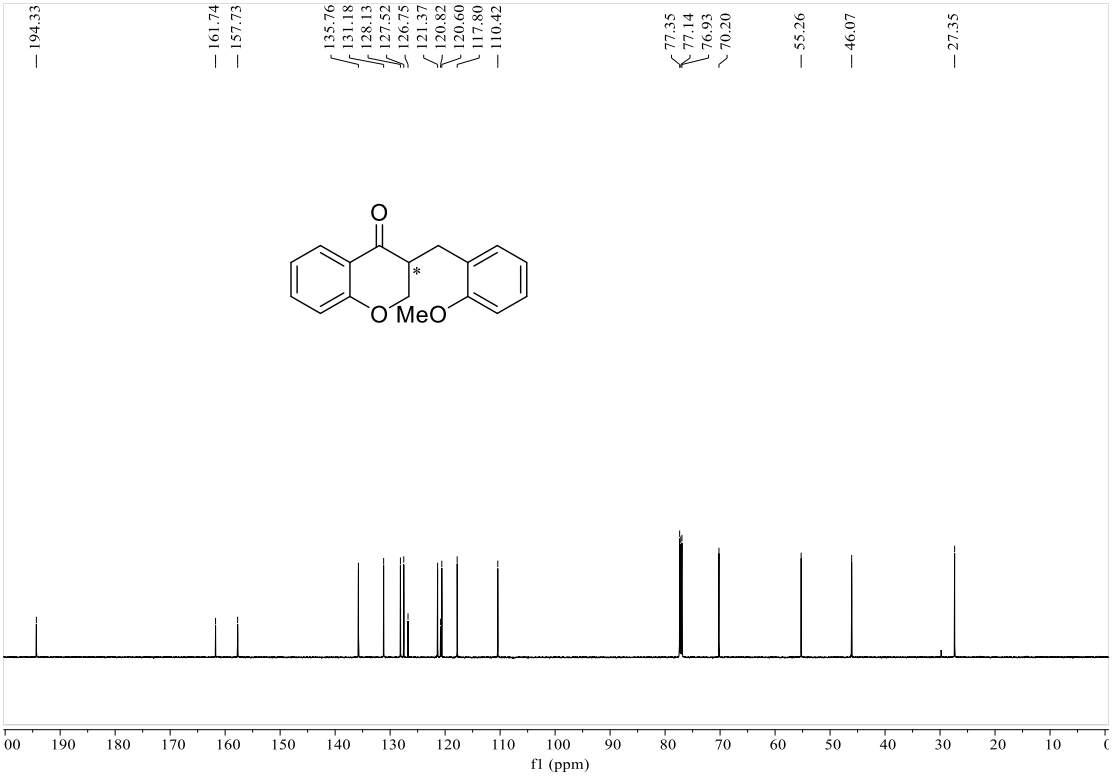


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(2-Methoxybenzyl)chroman-4-one (**2i**)

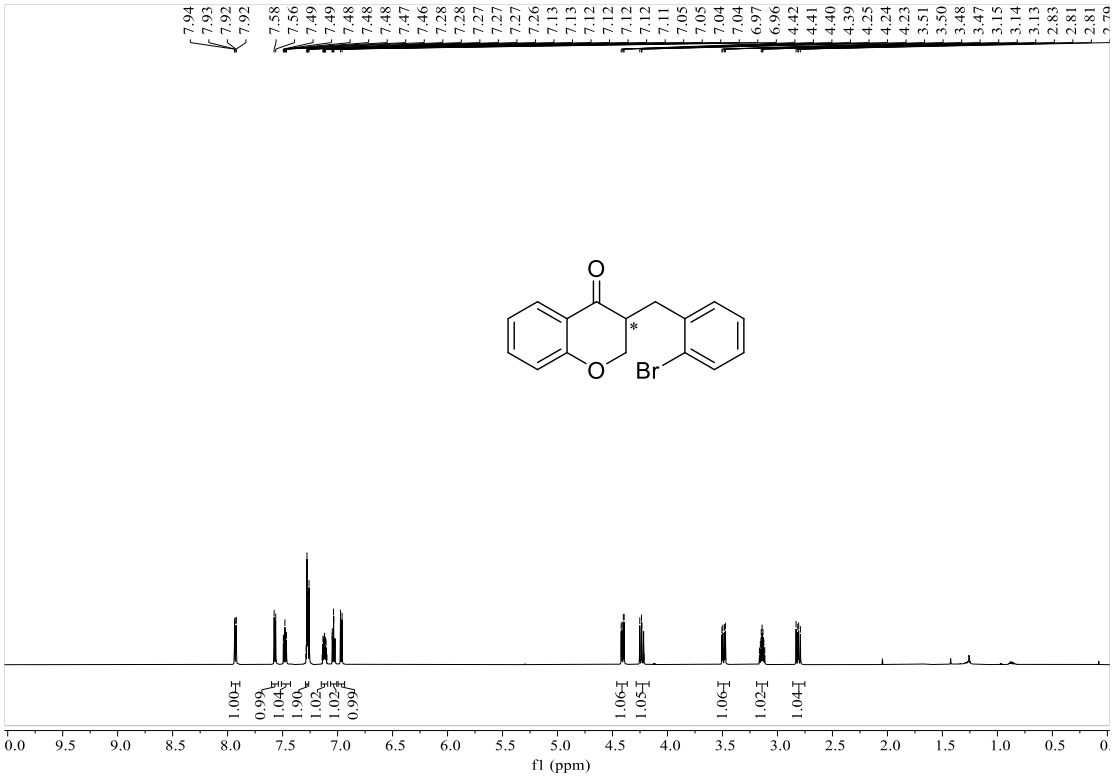


^{1}H NMR (600 MHz, Chloroform-*d*)

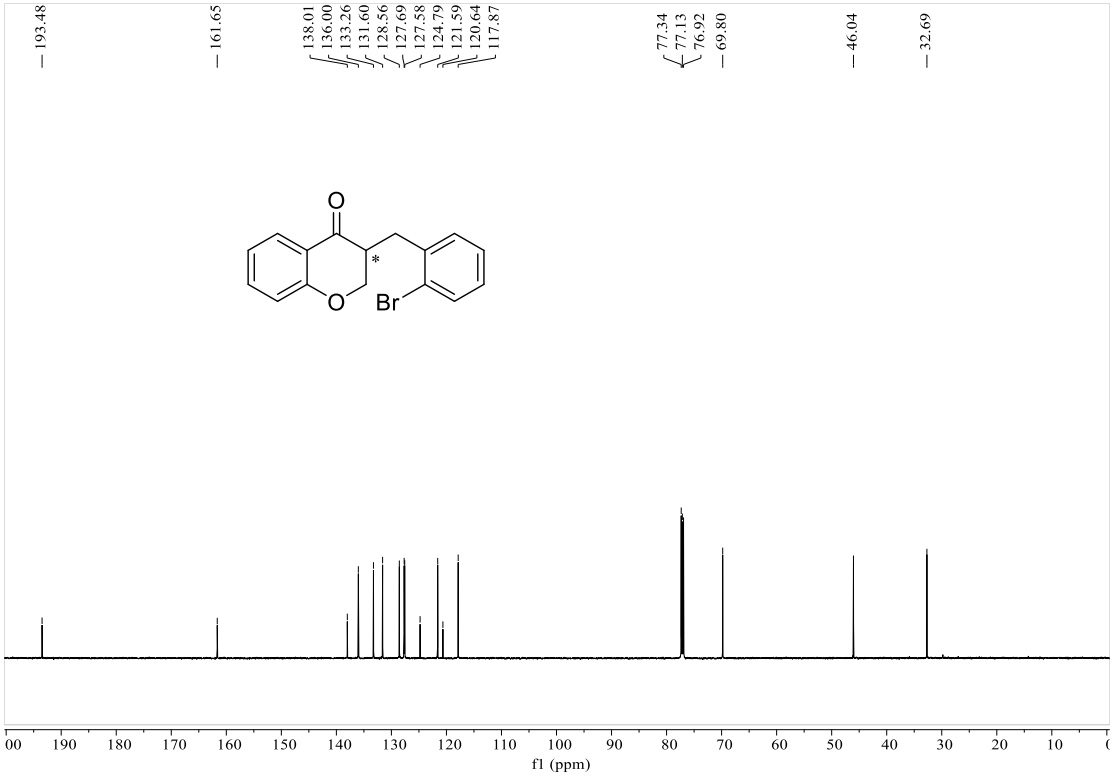


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(2-Bromobenzyl)chroman-4-one (**2j**)

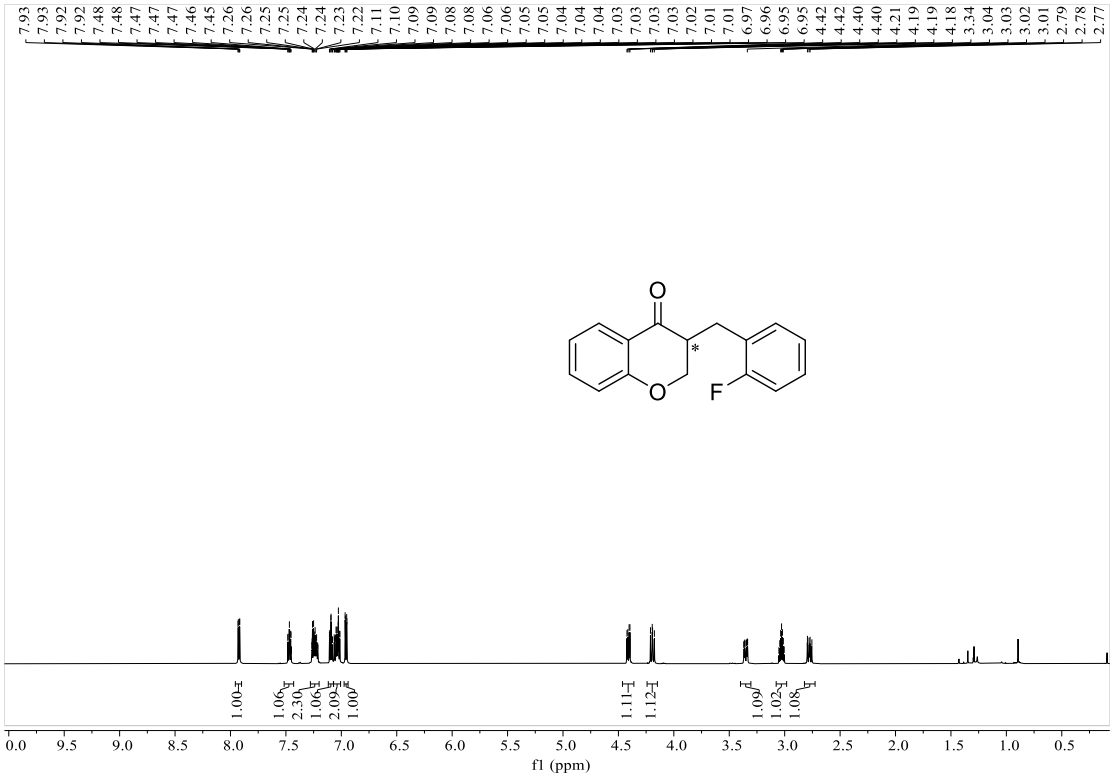


^{1}H NMR (600 MHz, Chloroform-*d*)

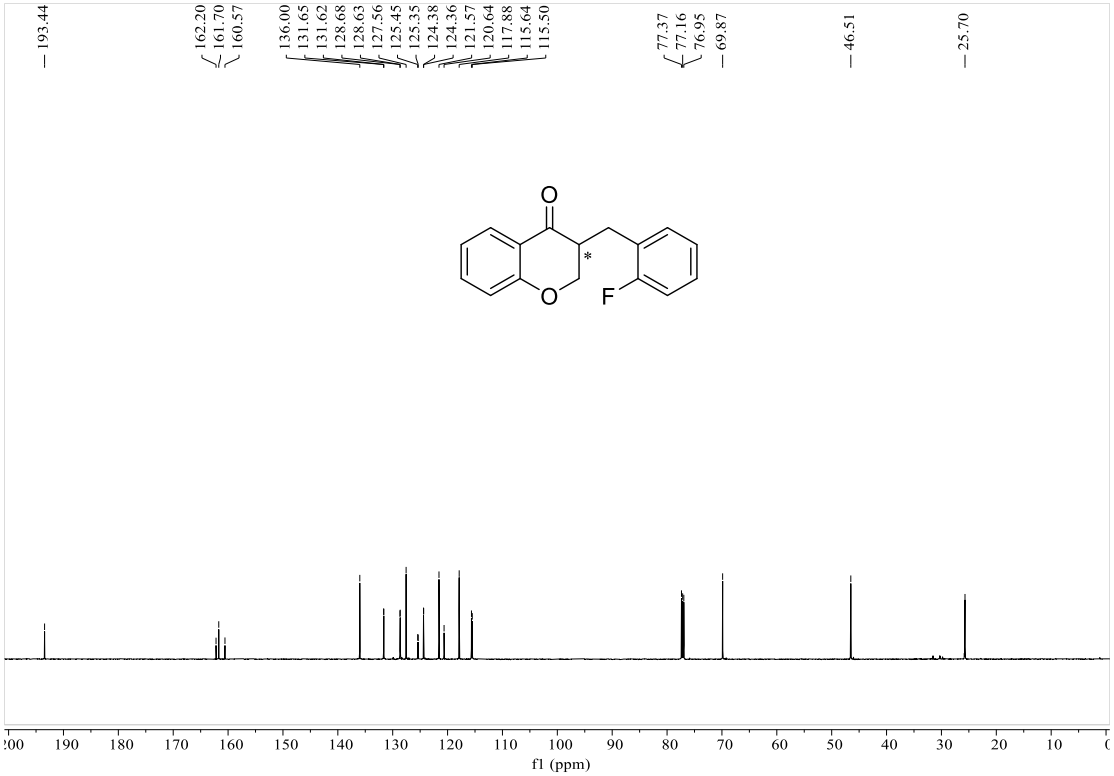


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(2-Fluorobenzyl)chroman-4-one (**2k**)

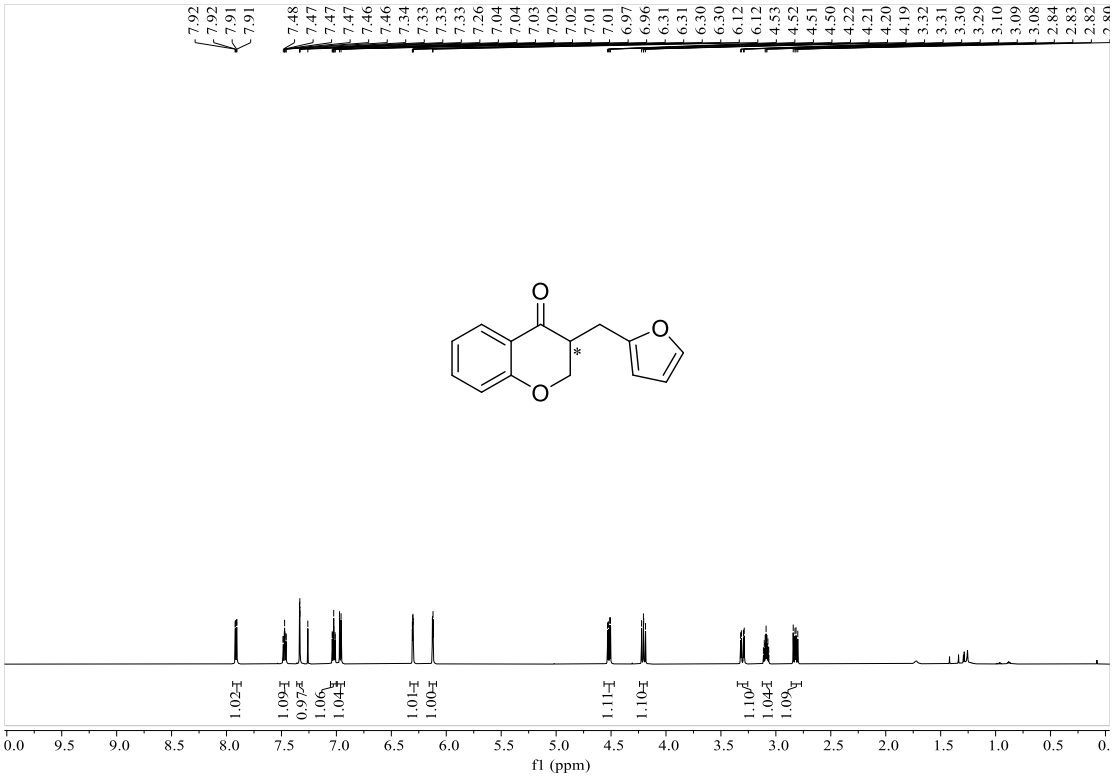


^{1}H NMR (600 MHz, Chloroform-*d*)

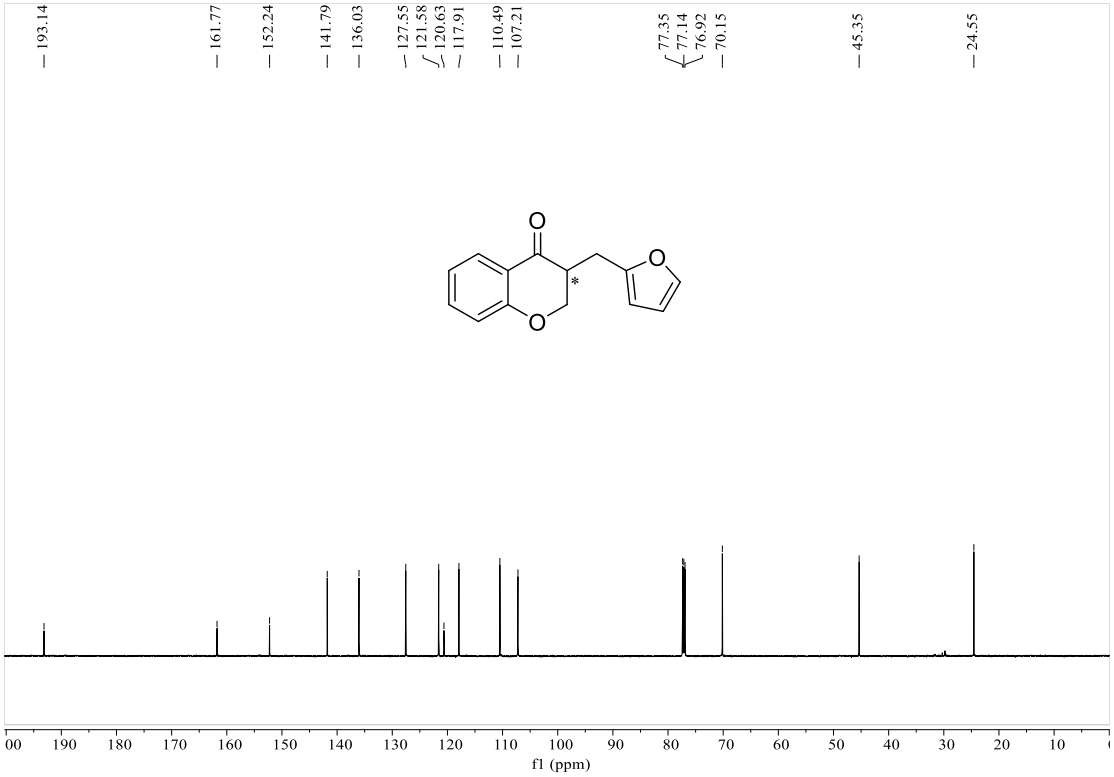


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(Furan-2-ylmethyl)chroman-4-one (**2l**)

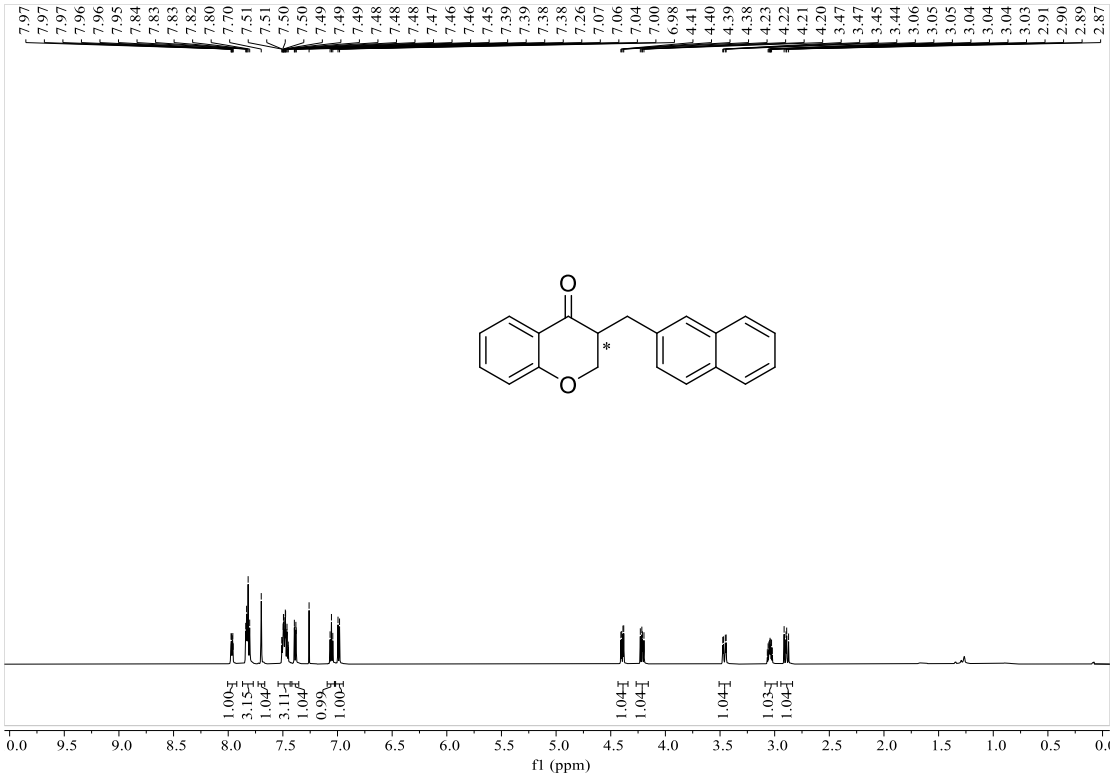


^{1}H NMR (600 MHz, Chloroform-*d*)

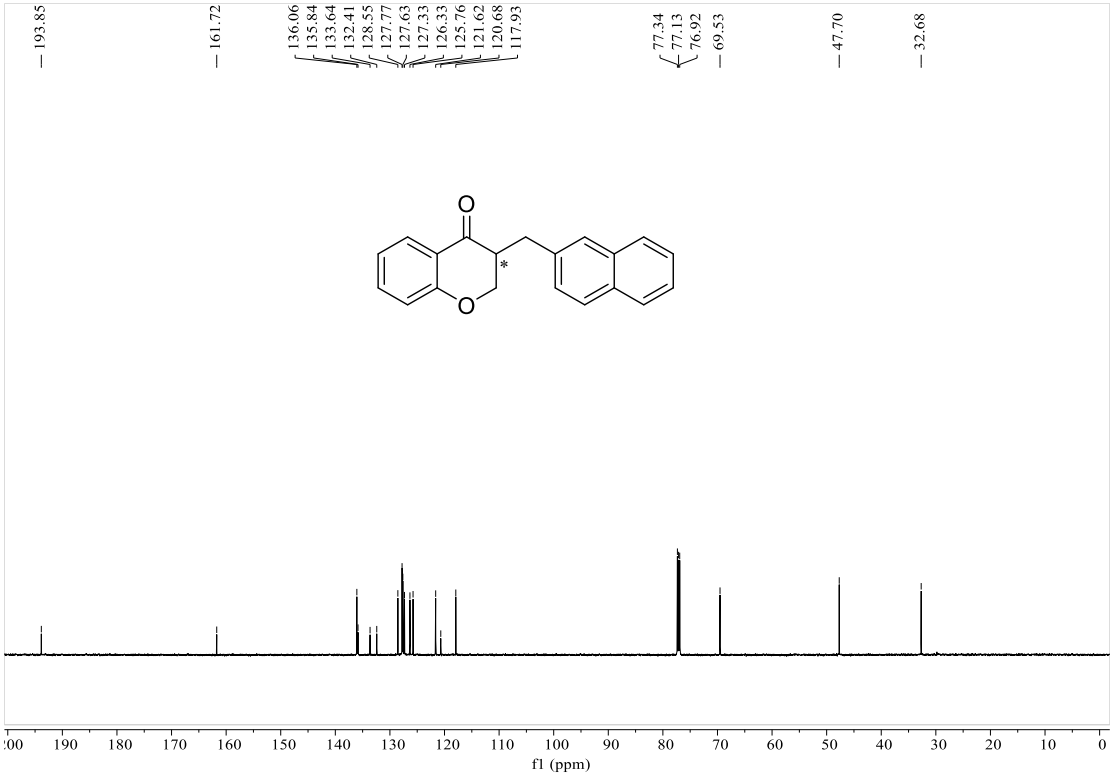


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(Naphthalen-2-ylmethyl)chroman-4-one (**2m**)

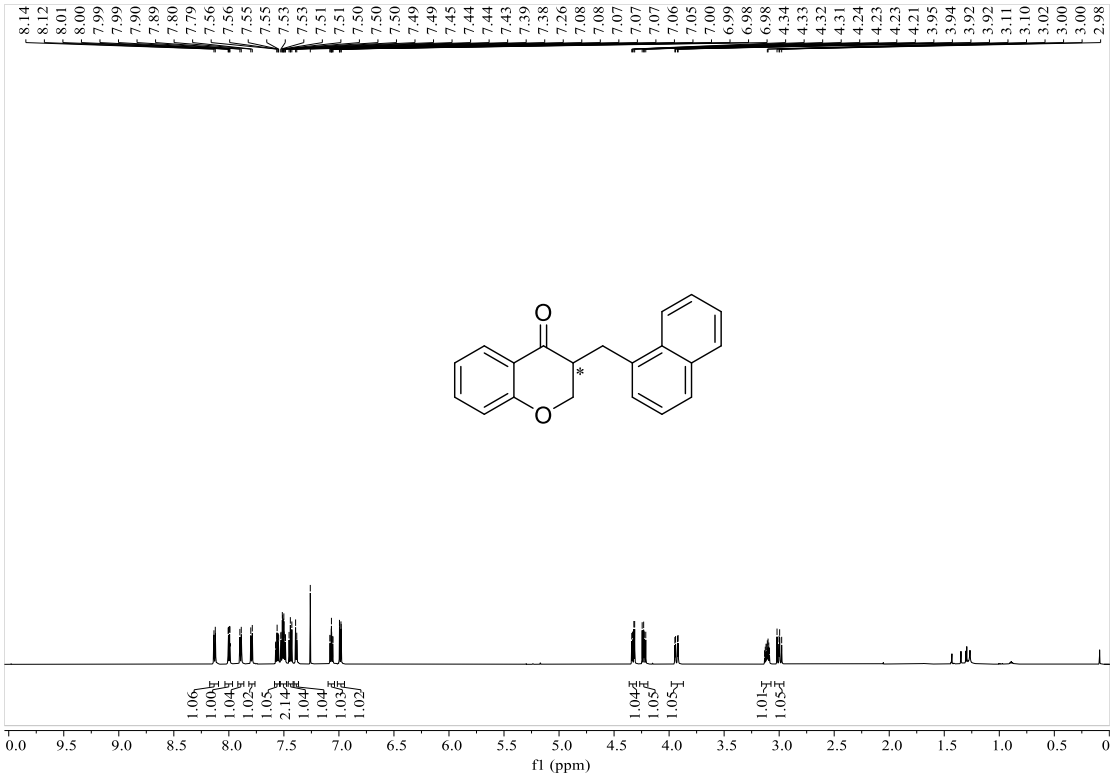


^{1}H NMR (600 MHz, Chloroform-*d*)

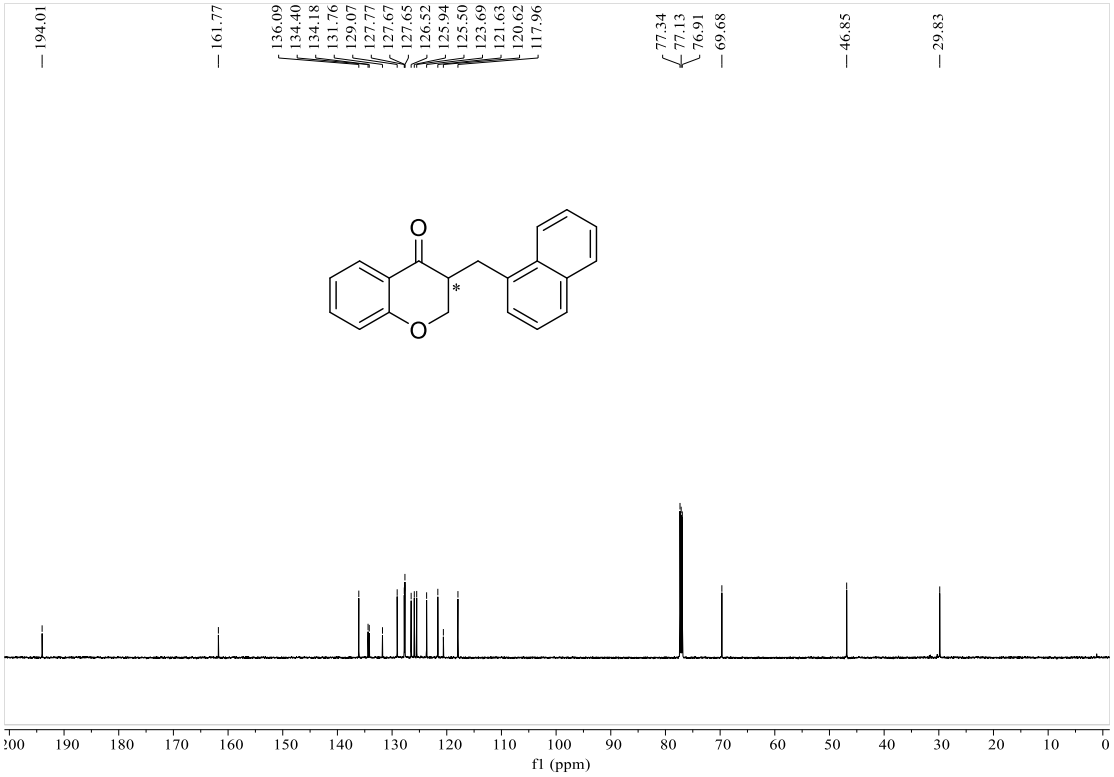


^{13}C NMR (151 MHz, Chloroform-*d*)

3-(Naphthalen-1-ylmethyl)chroman-4-one (**2n**)

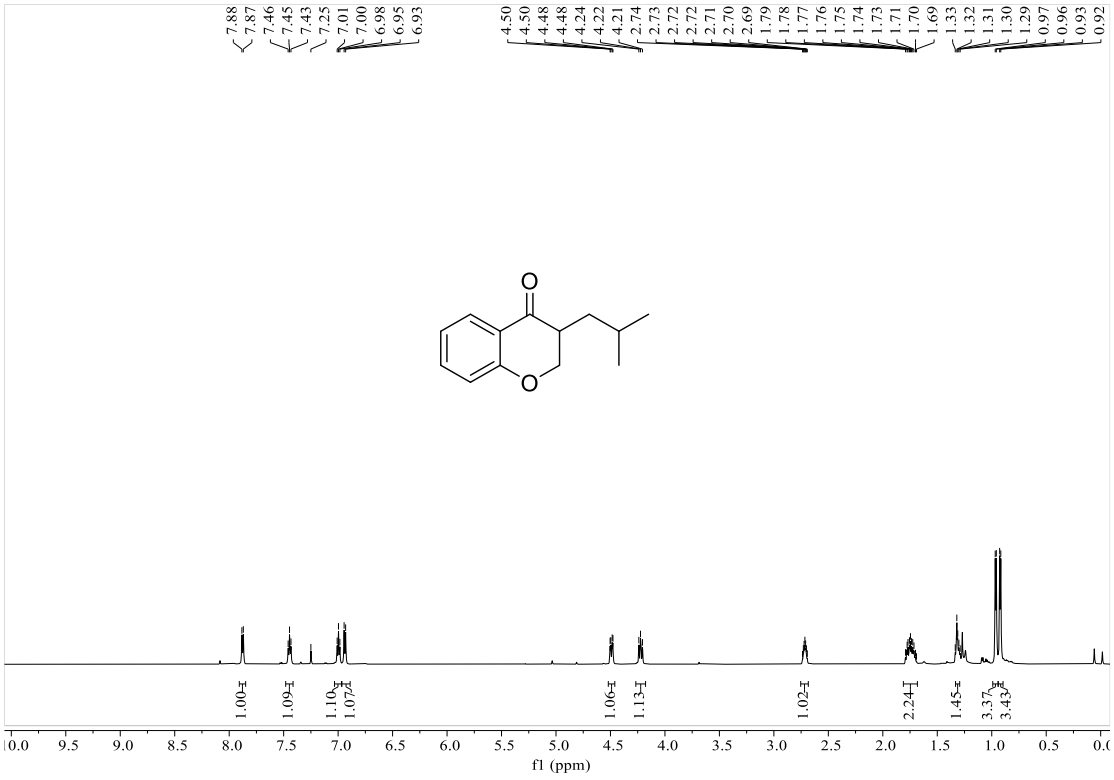


^{1}H NMR (600 MHz, Chloroform-*d*)



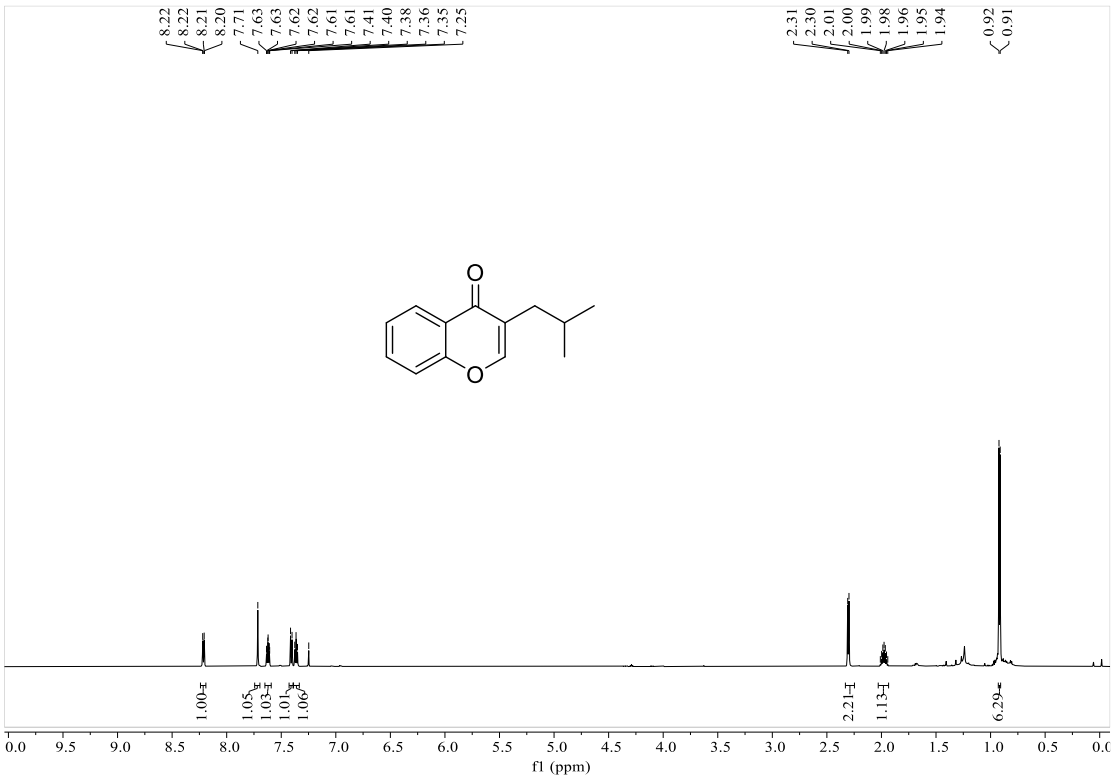
^{13}C NMR (151 MHz, Chloroform-*d*)

3-Isobutylchroman-4-one (**2o**)



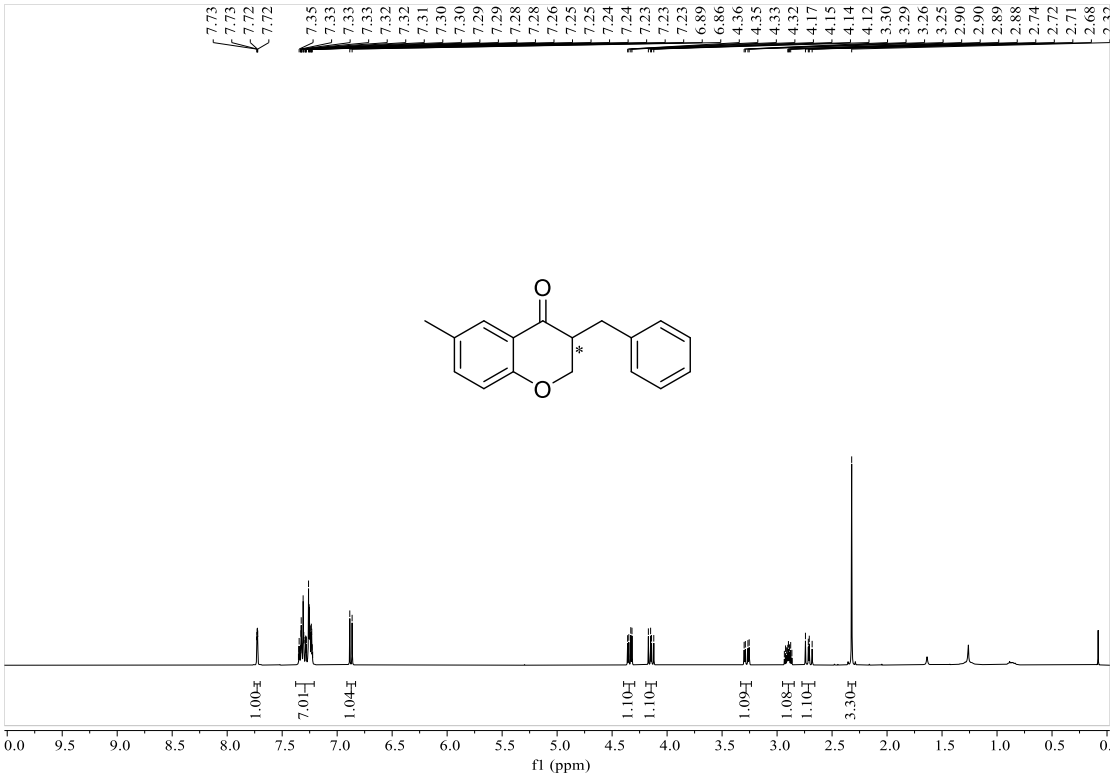
^{1}H NMR (600 MHz, Chloroform-*d*)

3-isobutyl-4*H*-chromen-4-one (**2o'**)

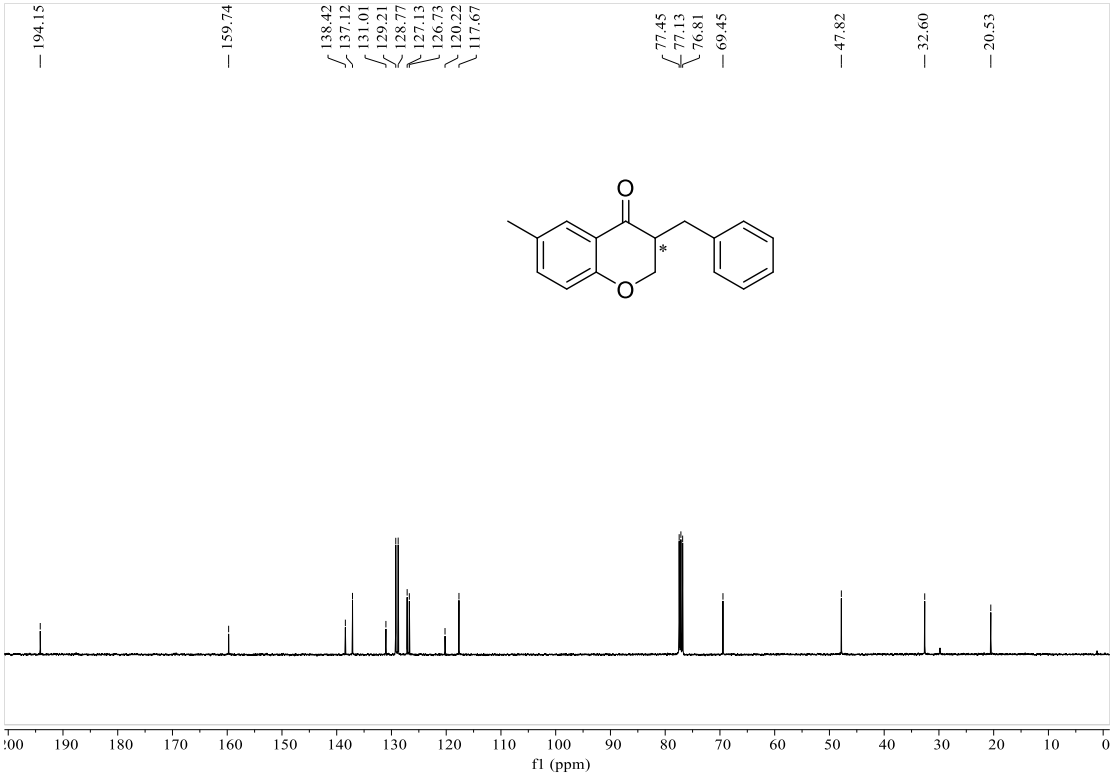


^{1}H NMR (600 MHz, Chloroform-*d*)

3-Benzyl-6-methylchroman-4-one (**2p**)

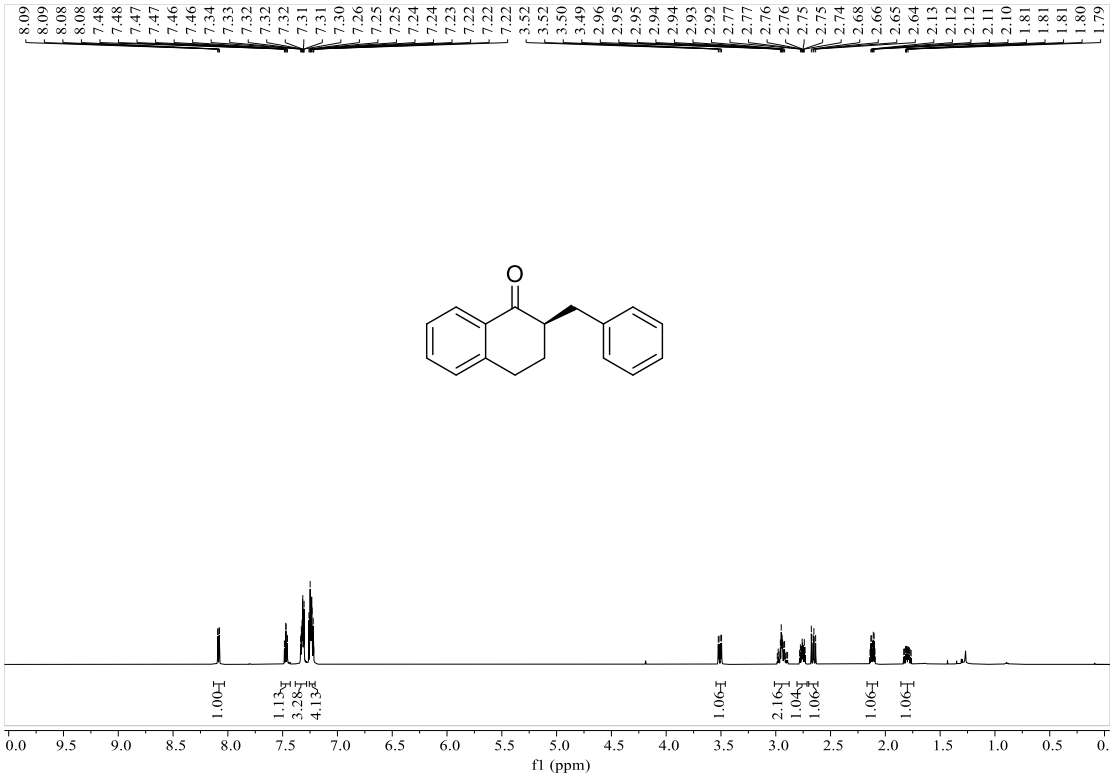


^{1}H NMR (400 MHz, Chloroform-*d*)

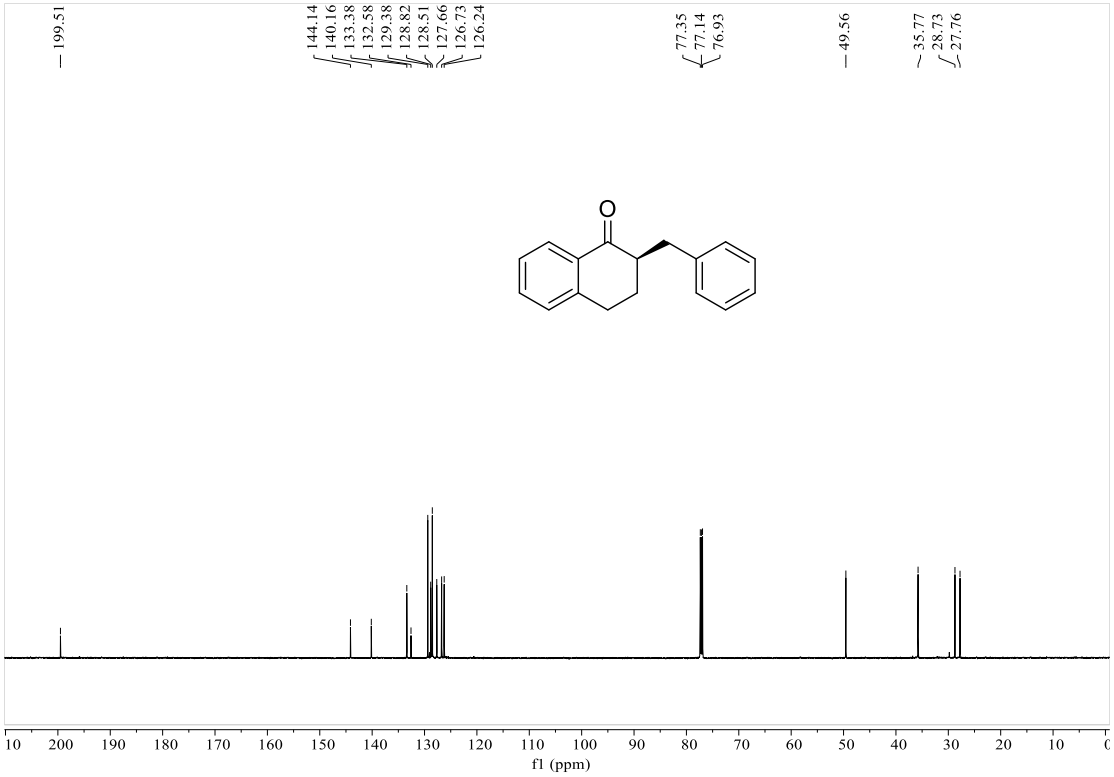


^{13}C NMR (101 MHz, Chloroform-*d*)

(*R*)-2-Benzyl-3,4-dihydronaphthalen-1(2*H*)-one (**2q**)

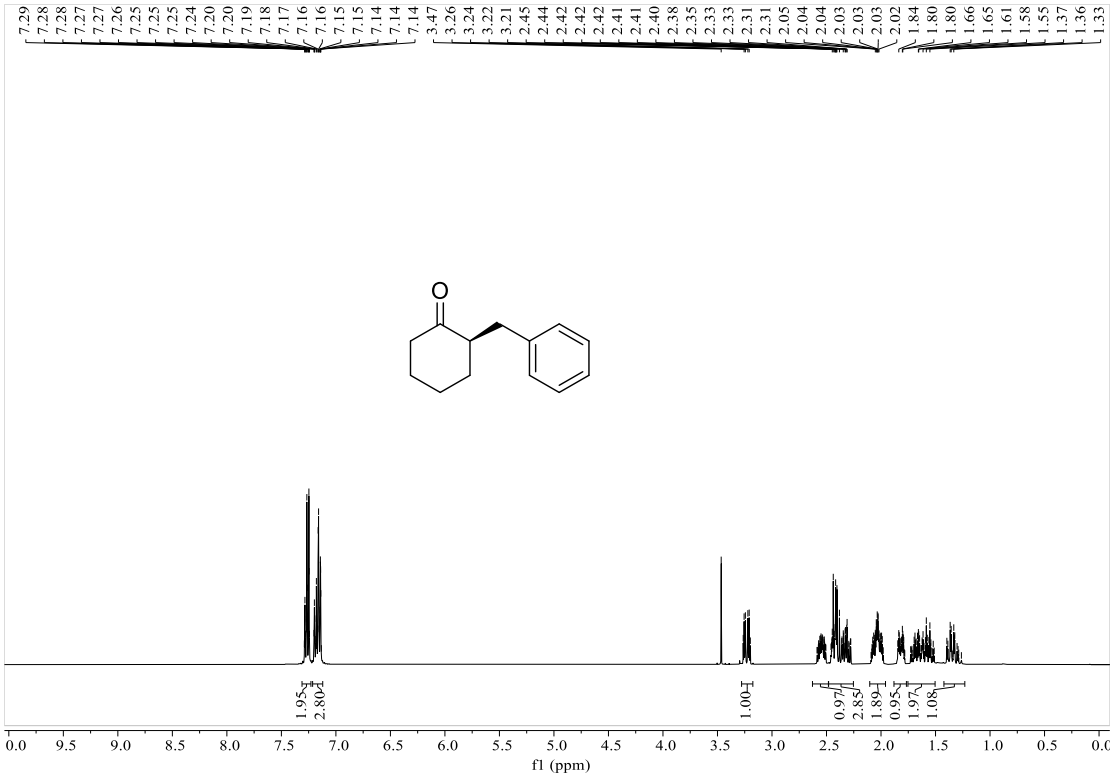


^{1}H NMR (600 MHz, Chloroform-*d*)

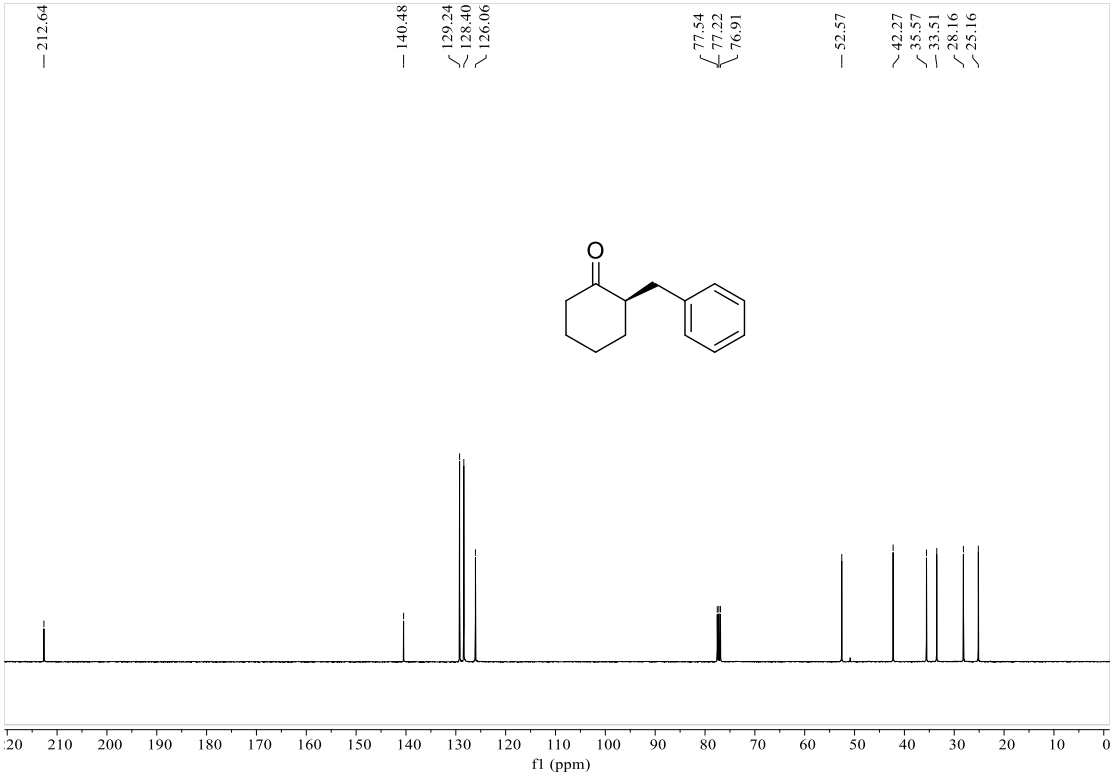


^{13}C NMR (151 MHz, Chloroform-*d*)

(*R*)-2-Benzylcyclohexan-1-one (**2r**)

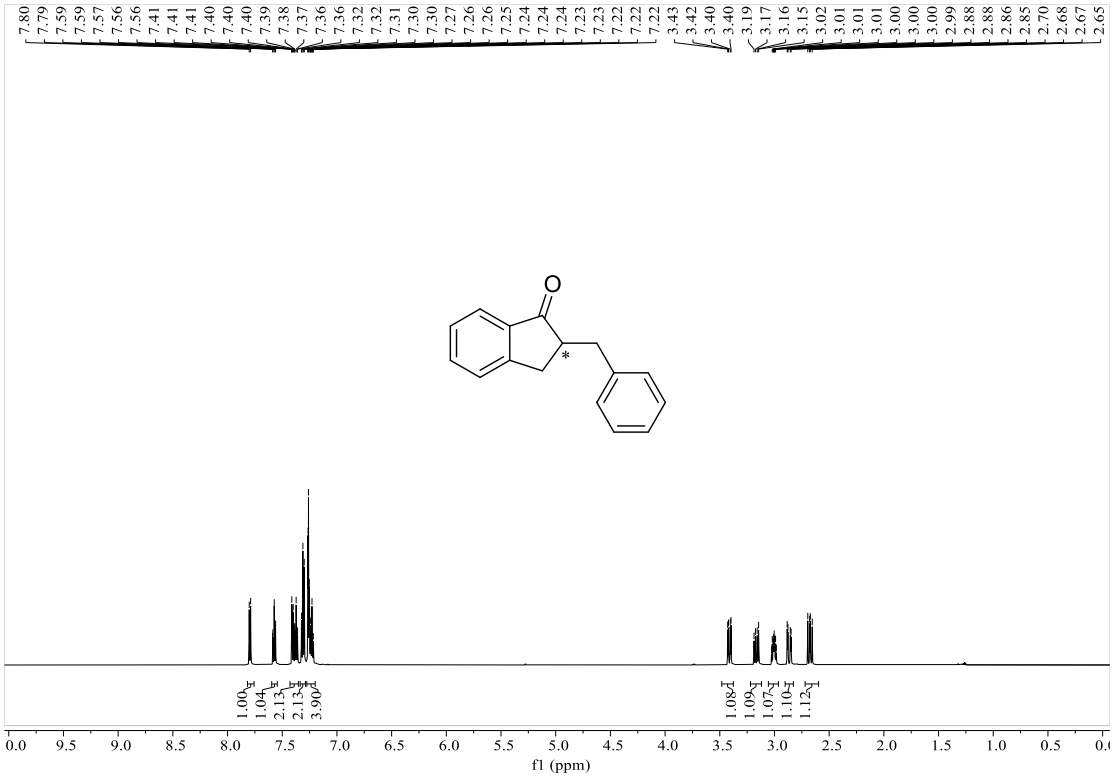


^{1}H NMR (400 MHz, Chloroform-*d*)

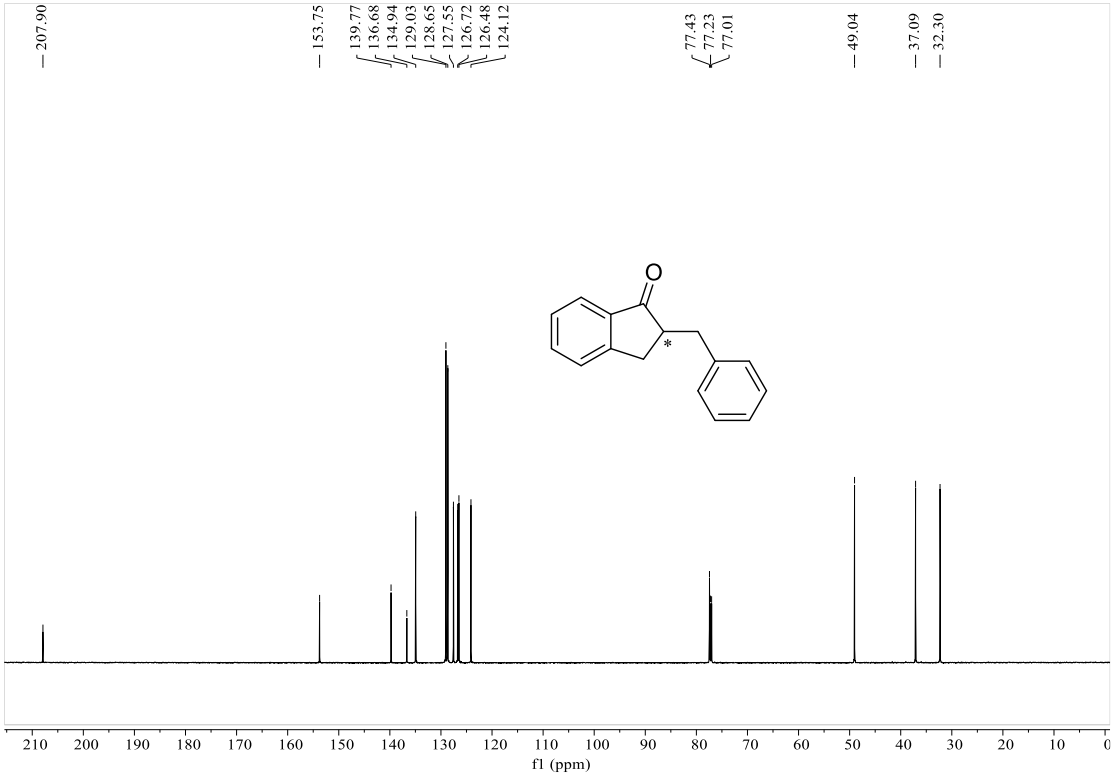


^{13}C NMR (101 MHz, Chloroform-*d*)

2-Benzyl-2,3-dihydro-1*H*-inden-1-one (**2s**)

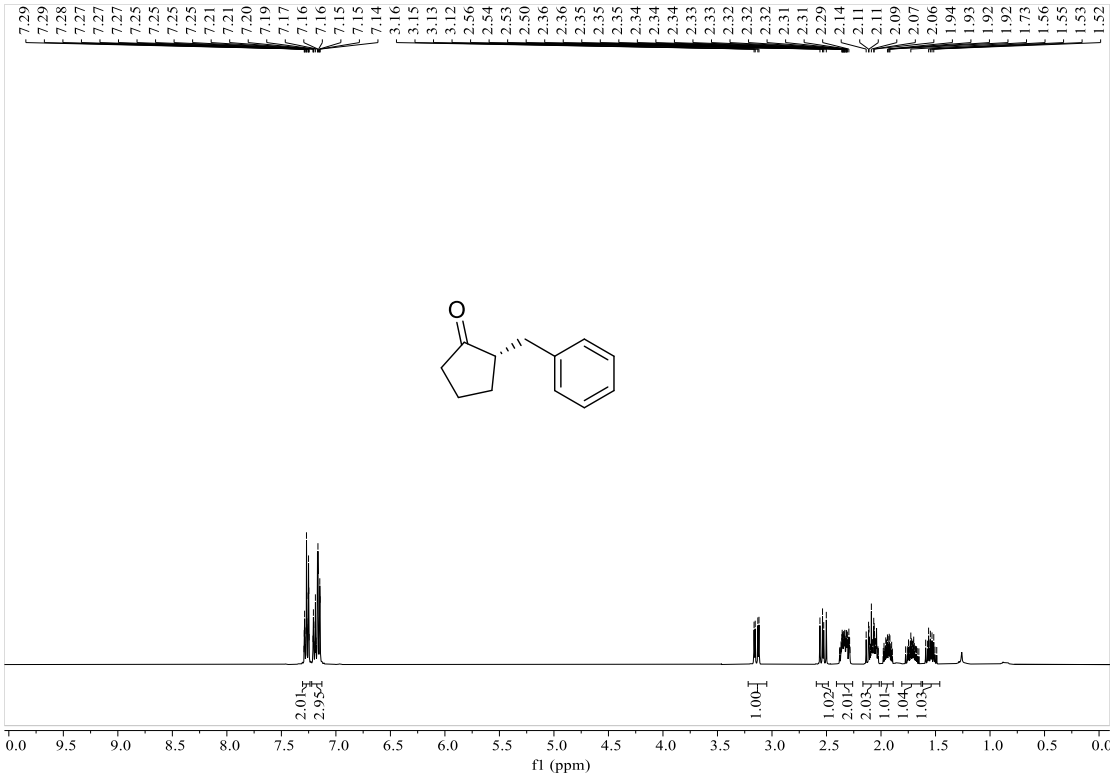


^{1}H NMR (600 MHz, Chloroform-*d*)

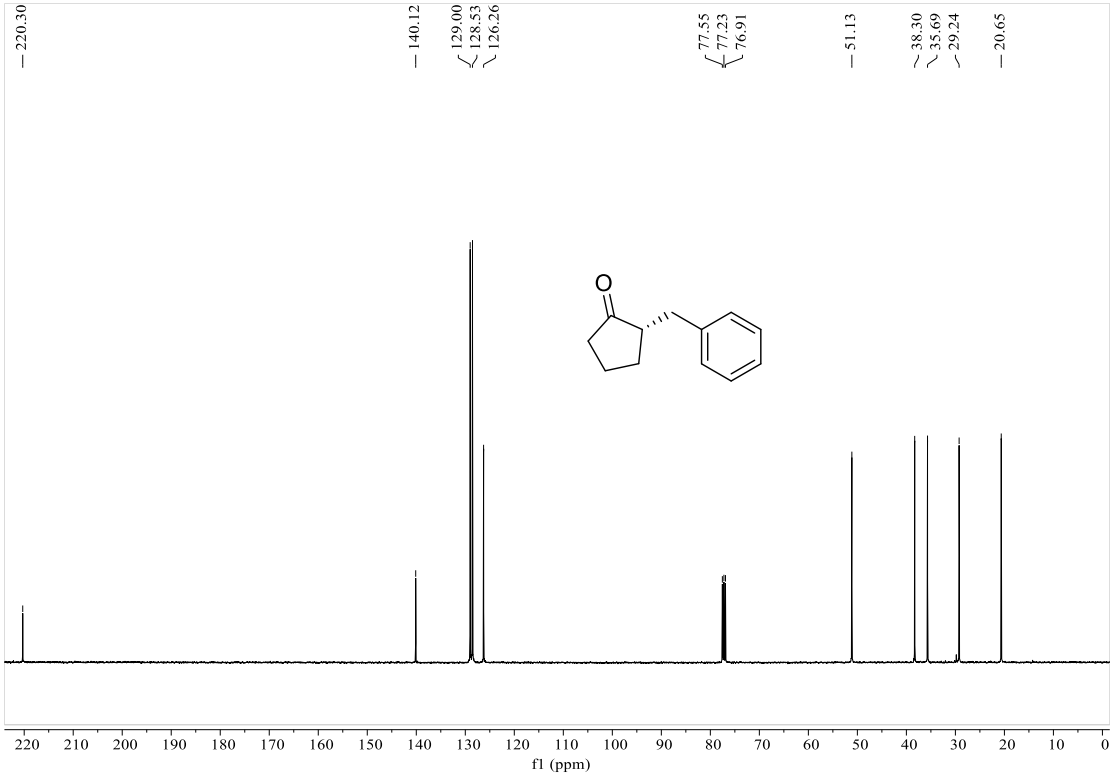


^{13}C NMR (151 MHz, Chloroform-*d*)

(*S*)-2-Benzylcyclopentan-1-one (**2t**)

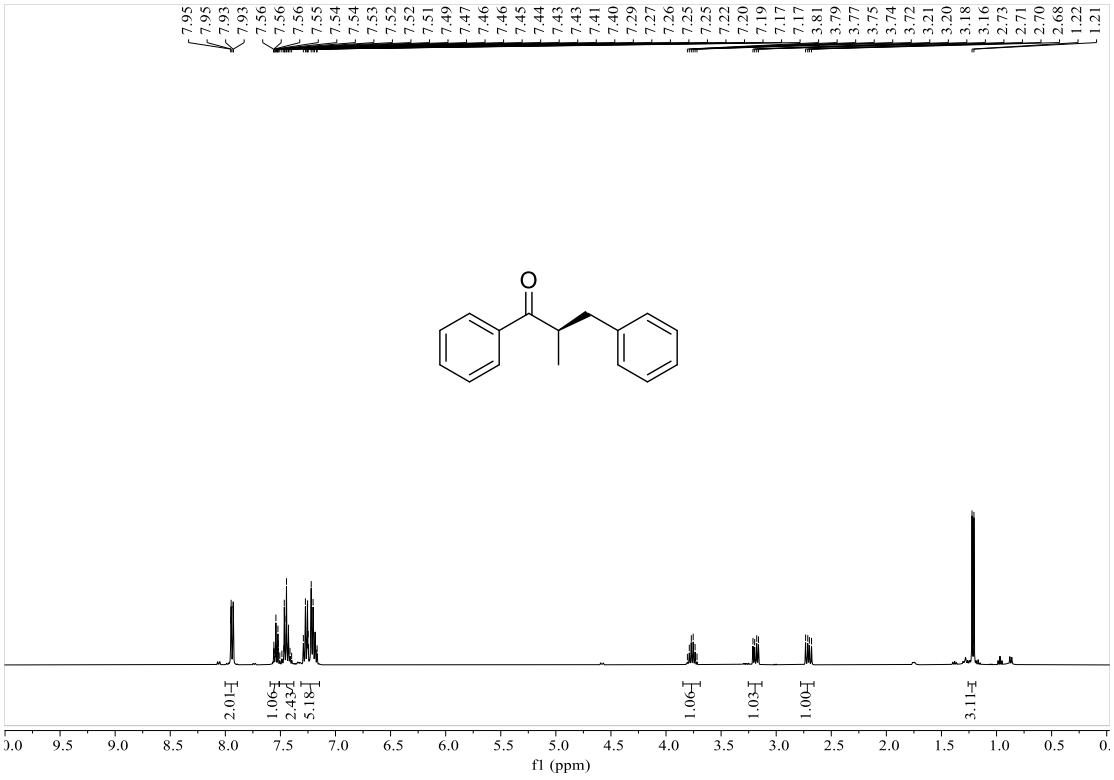


^{1}H NMR (400 MHz, Chloroform-*d*)

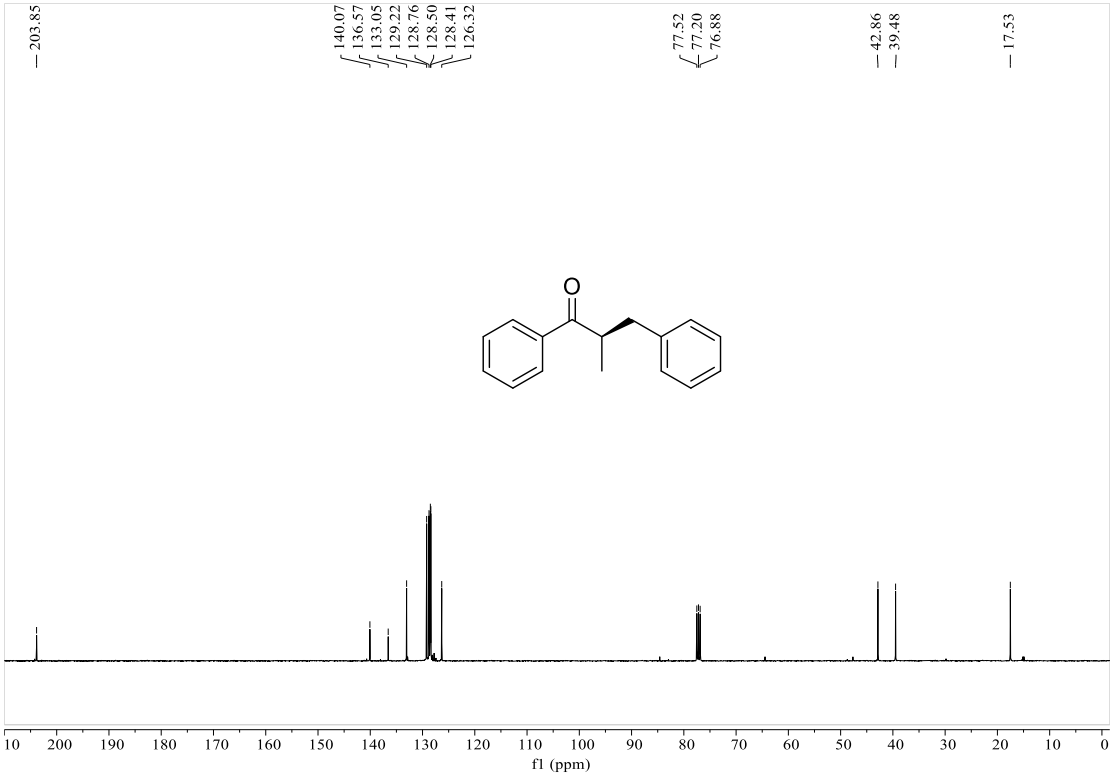


^{13}C NMR (101 MHz, Chloroform-*d*)

(*R*)-2-Methyl-1,3-diphenylpropan-1-one (**2u**)

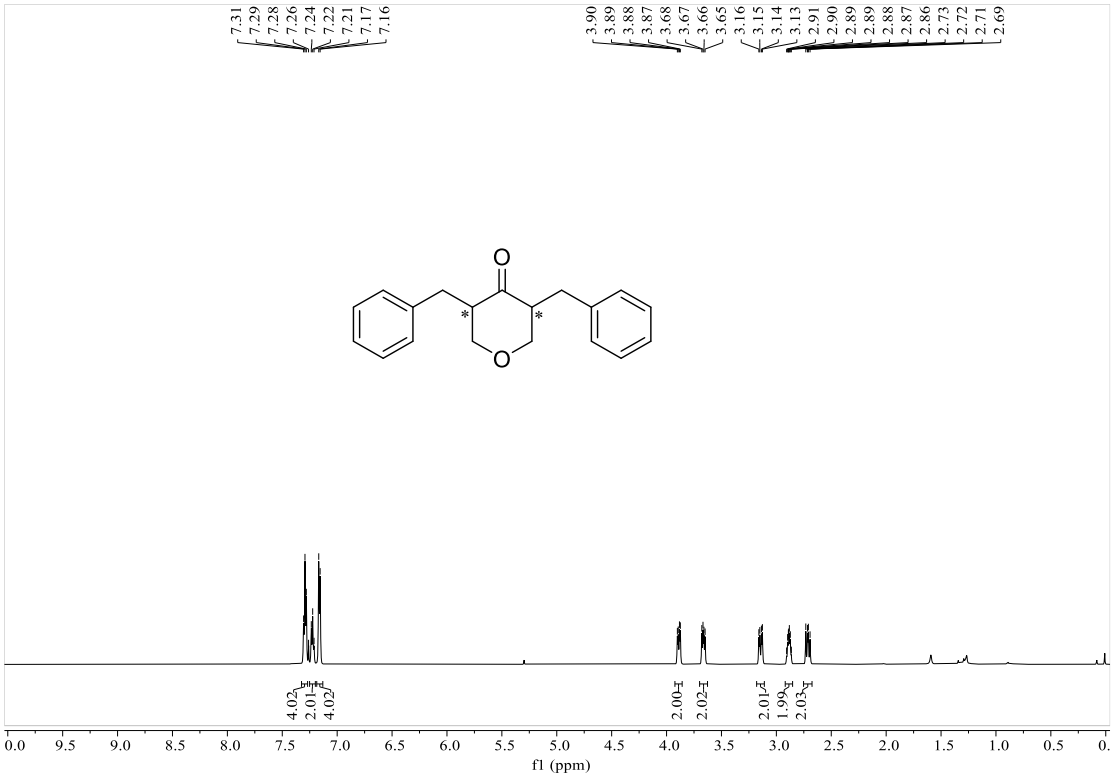


^{1}H NMR (400 MHz, Chloroform-*d*)

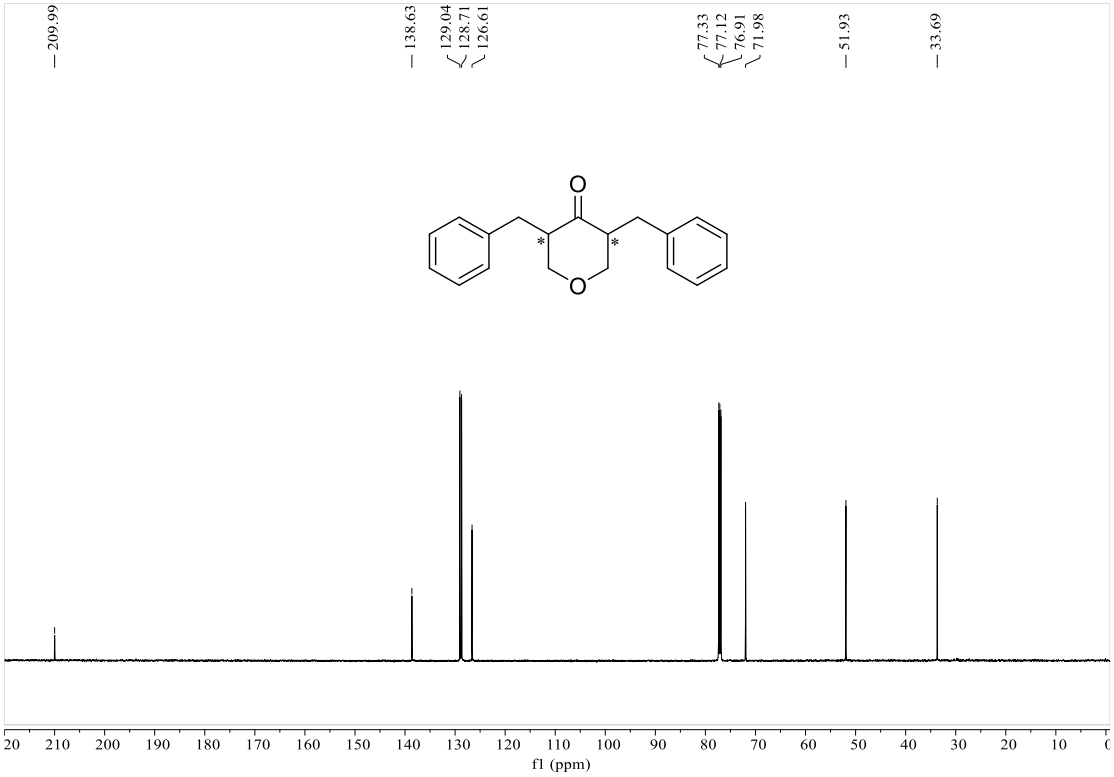


^{13}C NMR (101 MHz, Chloroform-*d*)

3,5-dibenzyltetrahydro-4*H*-pyran-4-one (**4a**)

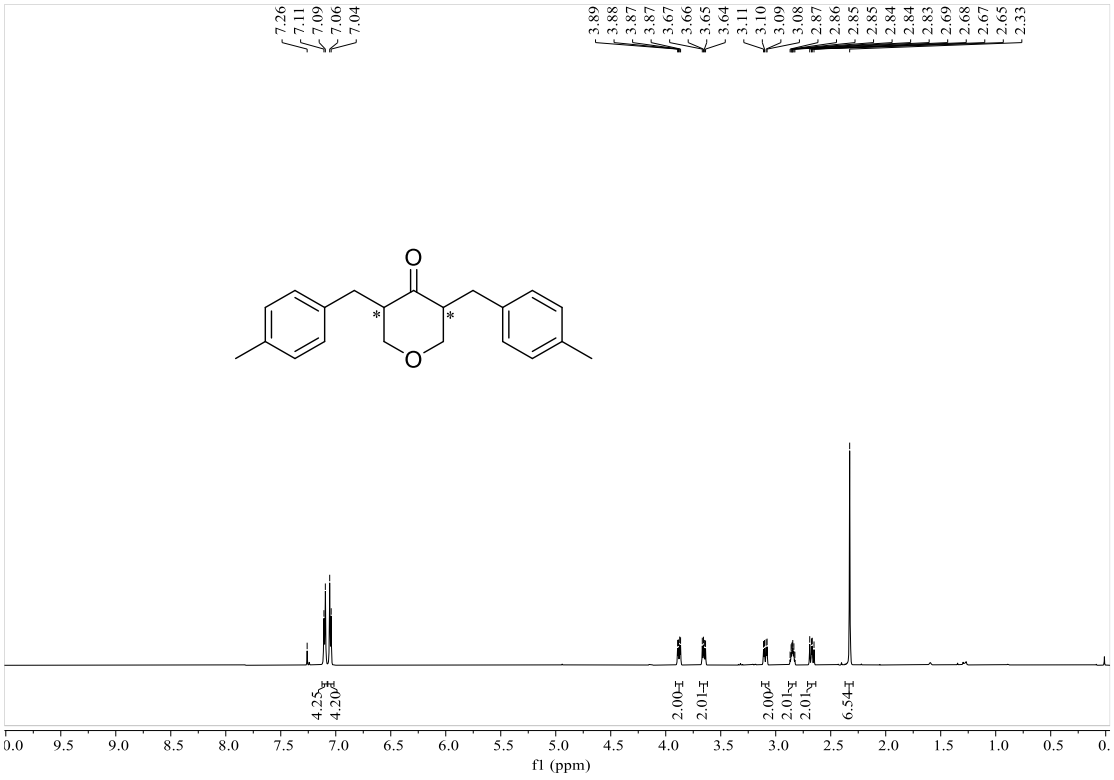


^{1}H NMR (600 MHz, Chloroform-*d*)

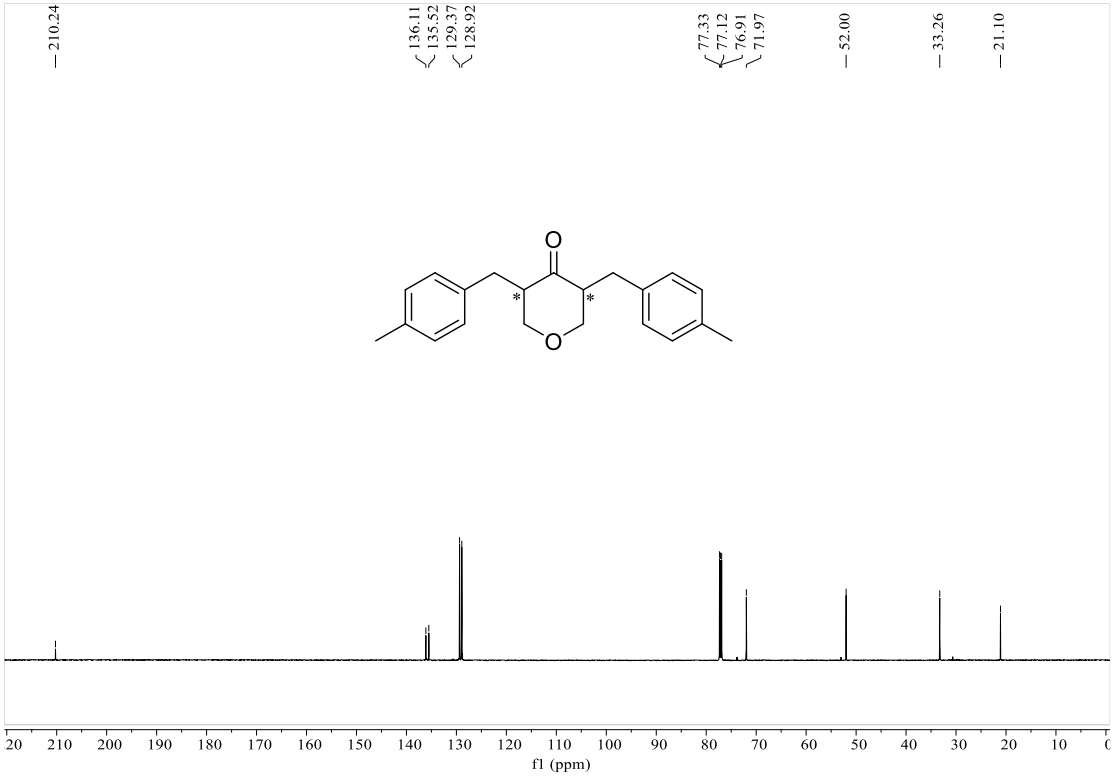


^{13}C NMR (151 MHz, Chloroform-*d*)

3,5-bis(4-methylbenzyl)tetrahydro-4*H*-pyran-4-one (**4b**)

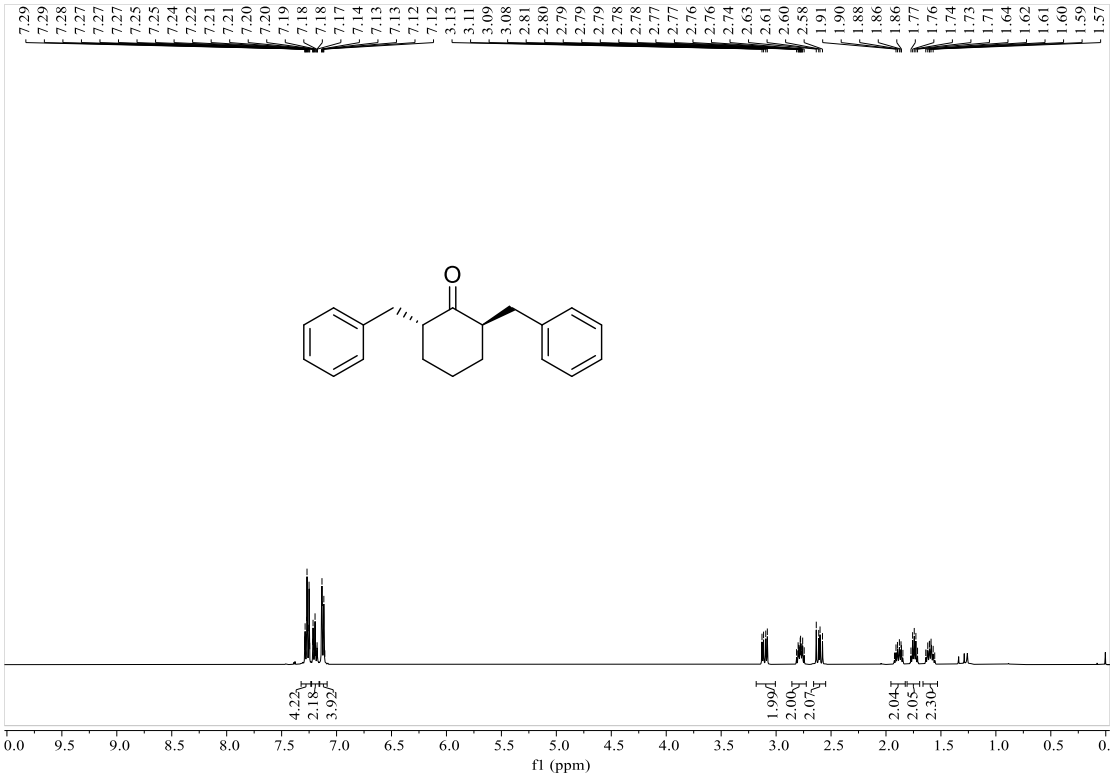


^{1}H NMR (600 MHz, Chloroform-*d*)

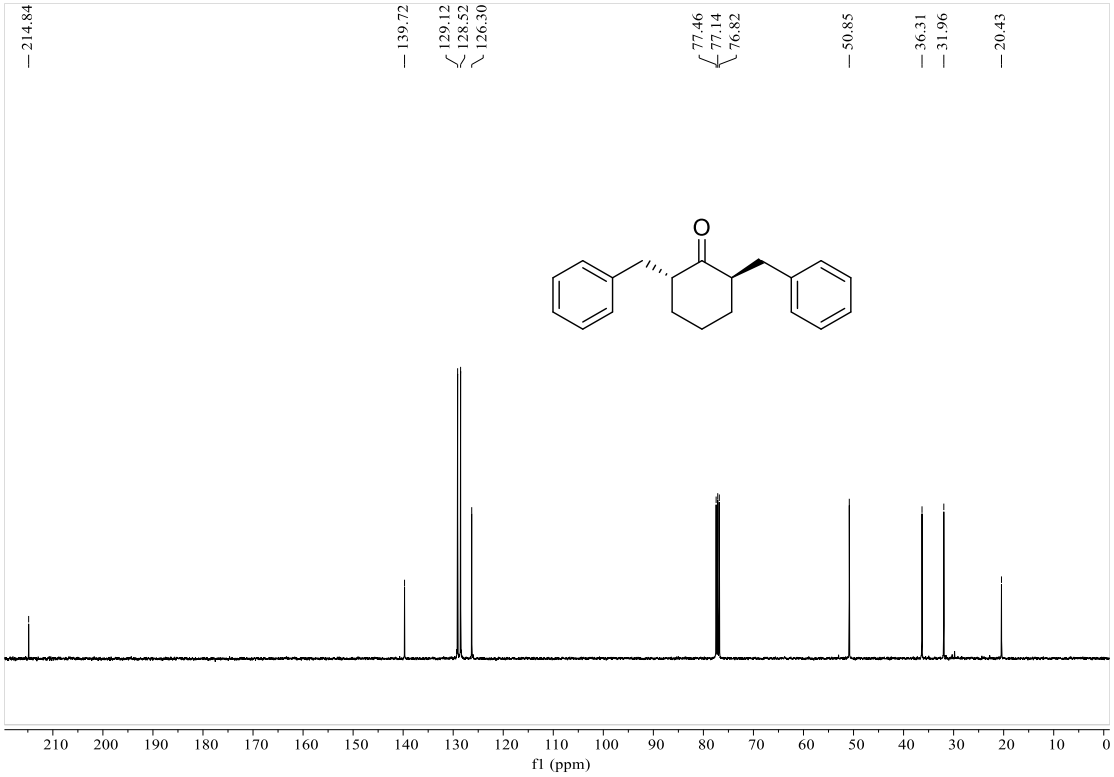


^{13}C NMR (151 MHz, Chloroform-*d*)

(+)-(2*R*,6*R*)-2,6-Dibenzylcyclohexan-1-one (**4c**)

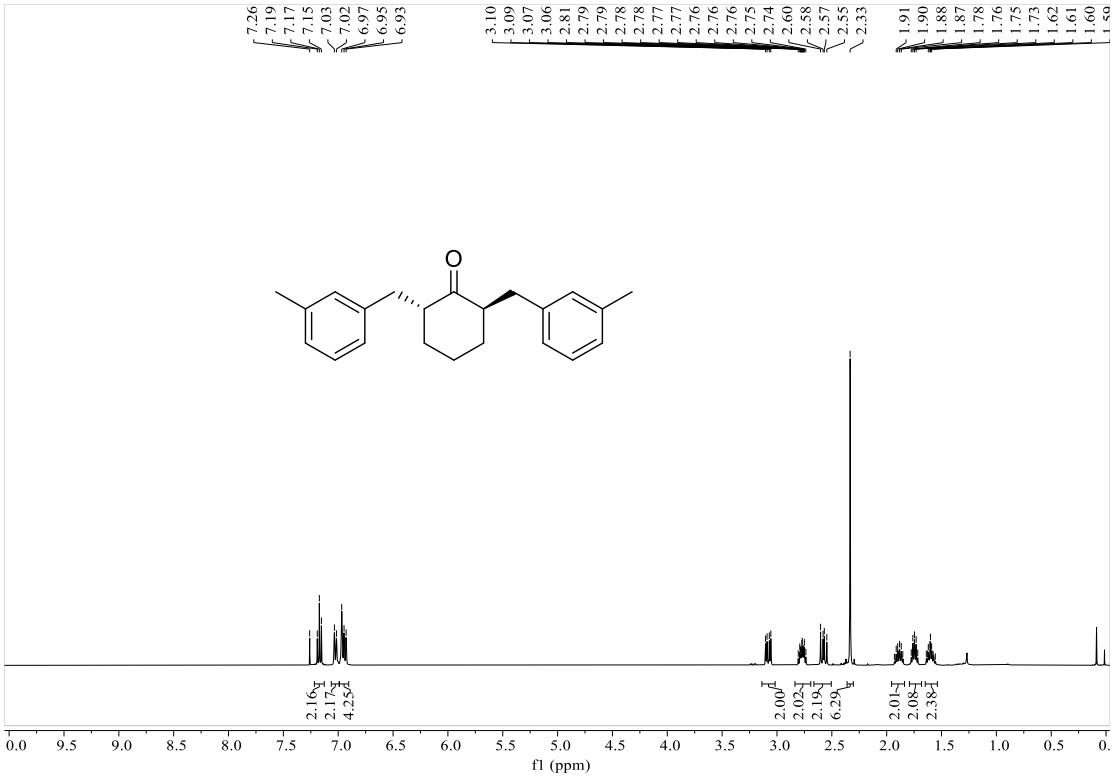


^{1}H NMR (400 MHz, Chloroform-*d*)

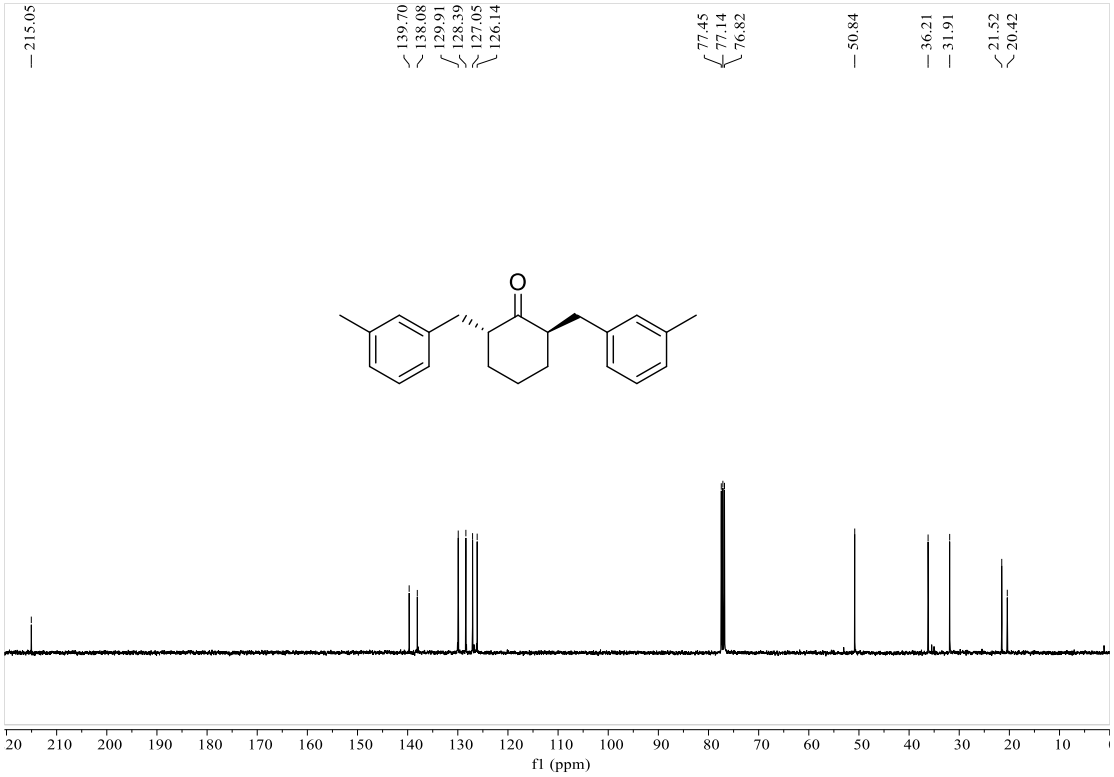


^{13}C NMR (101 MHz, Chloroform-*d*)

(+)-(2*R*,6*R*)-2,6-Bis(3-methylbenzyl)cyclohexan-1-one (**4d**)



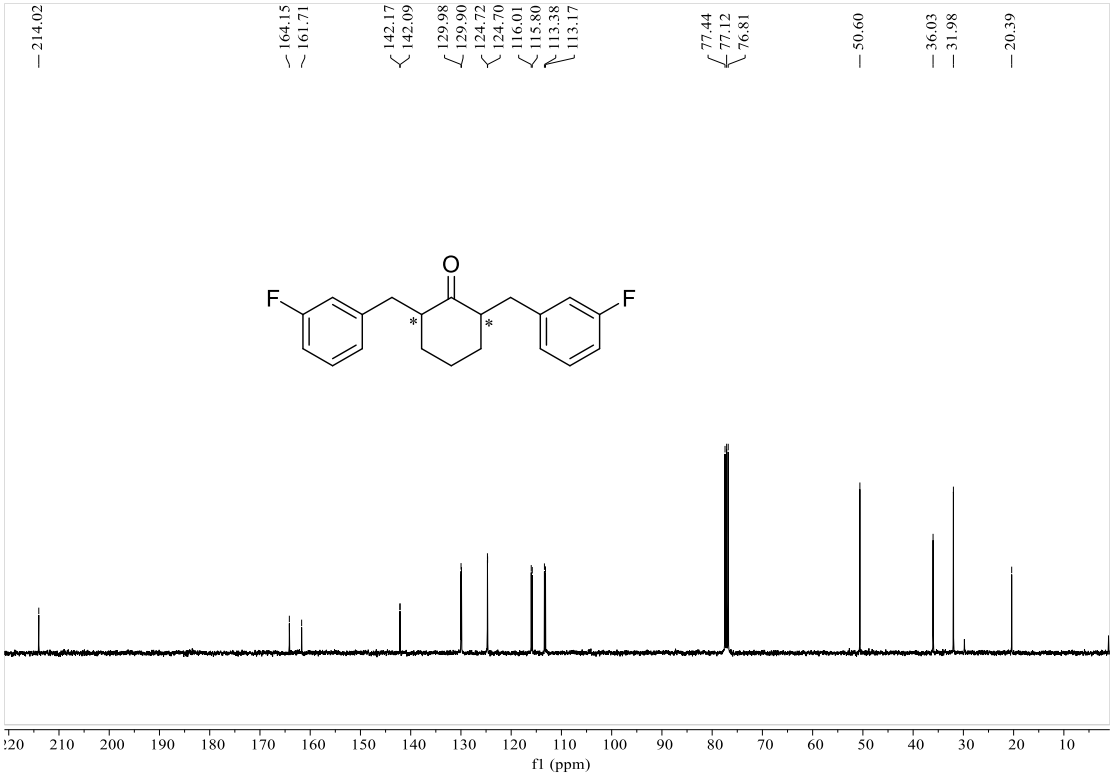
^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)

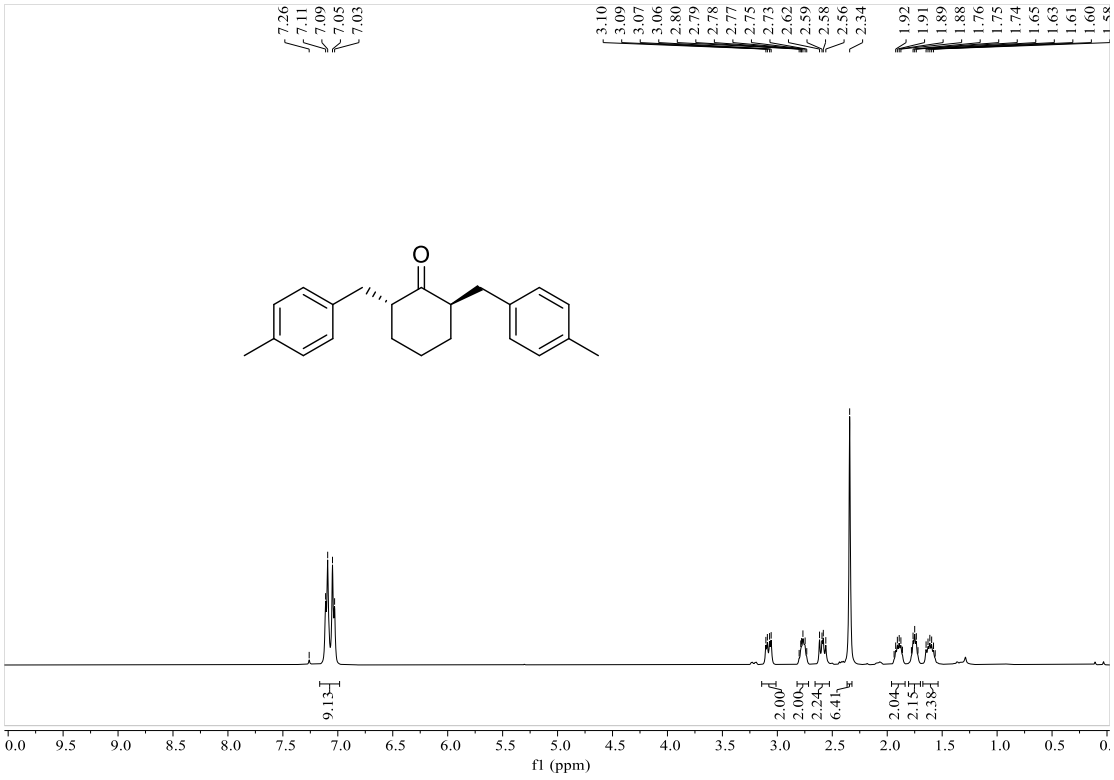
2,6-Bis(3-fluorobenzyl)cyclohexan-1-one (**4e**)

^{1}H NMR (400 MHz, Chloroform-*d*)

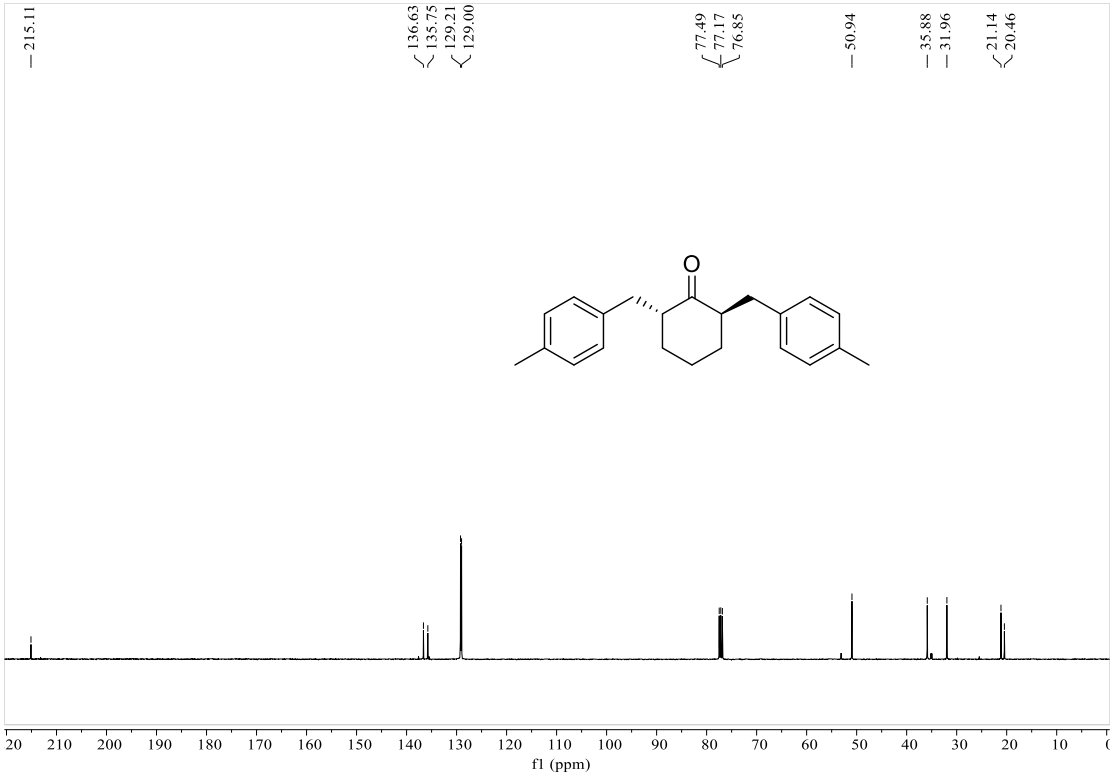


^{13}C NMR (101 MHz, Chloroform-*d*)

(+)-(2*R*,6*R*)-2,6-Bis(4-methylbenzyl)cyclohexan-1-one (**4f**)

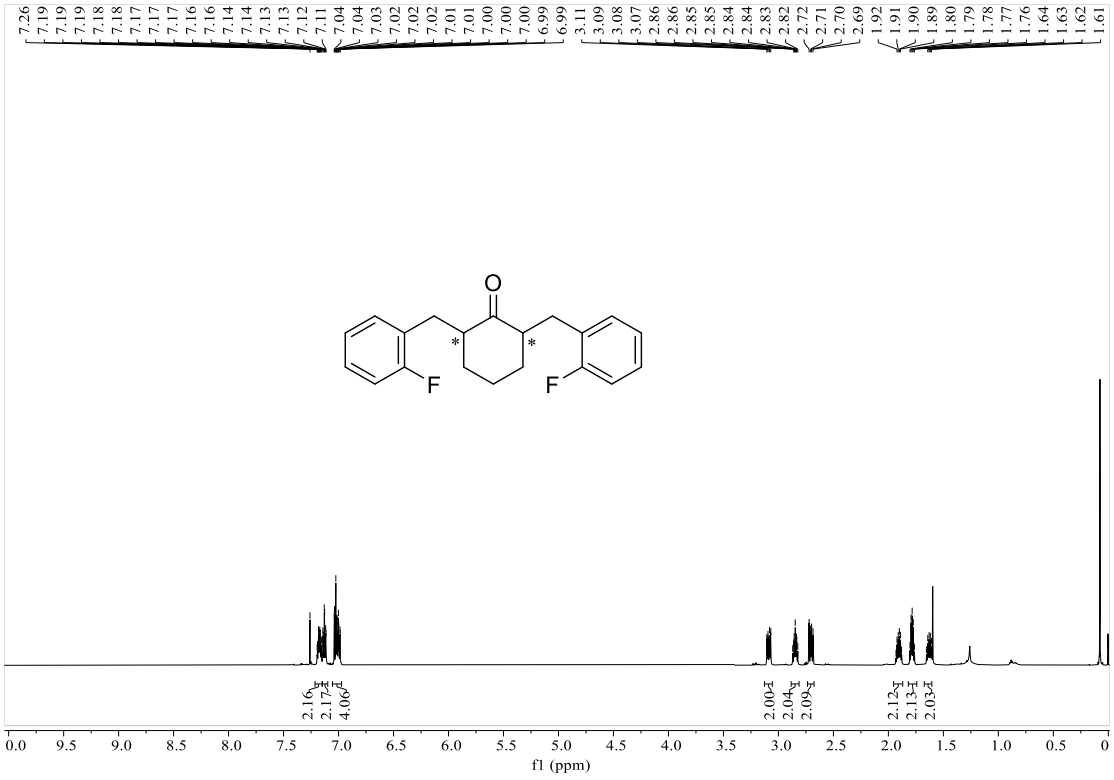


^{1}H NMR (400 MHz, Chloroform-*d*)

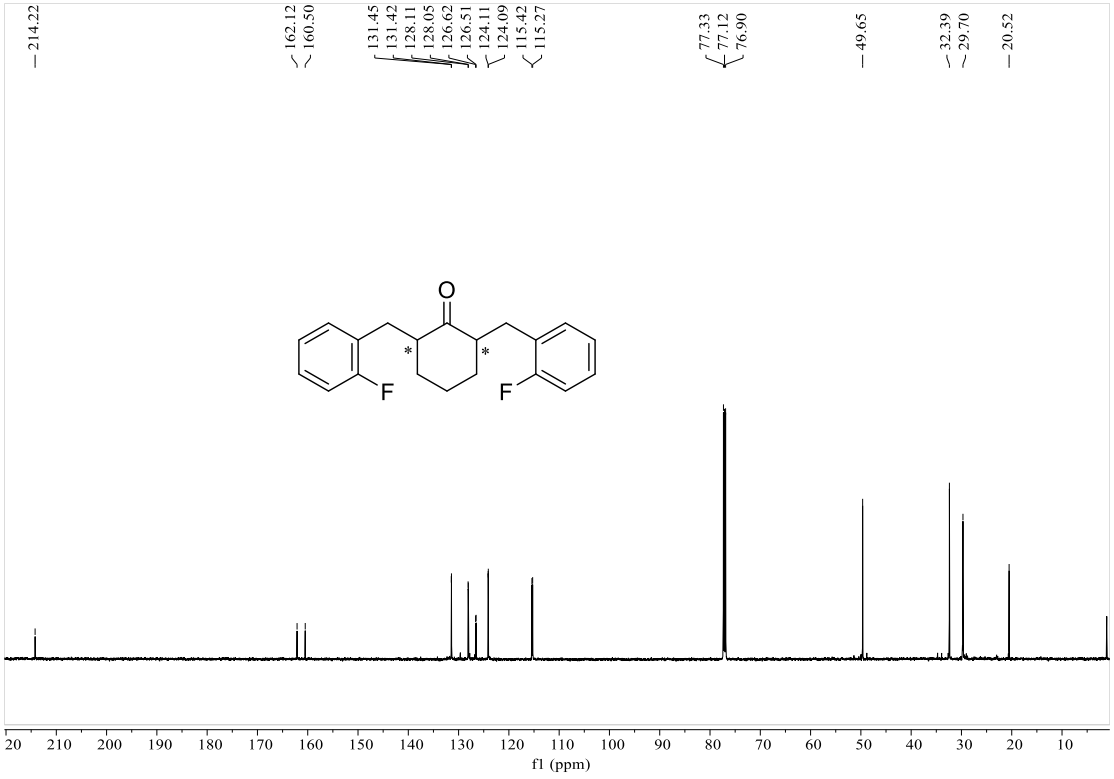


^{13}C NMR (101 MHz, Chloroform-*d*)

2,6-Bis(2-fluorobenzyl)cyclohexan-1-one (**4g**)

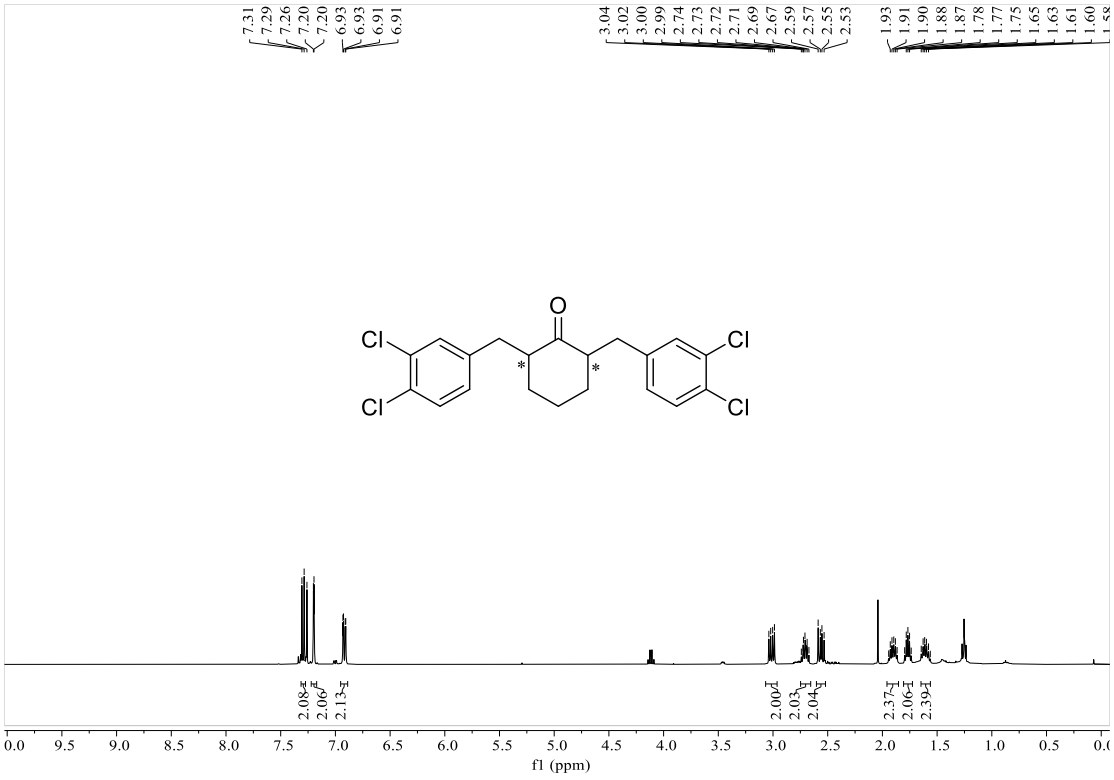


^{1}H NMR (600 MHz, Chloroform-*d*)

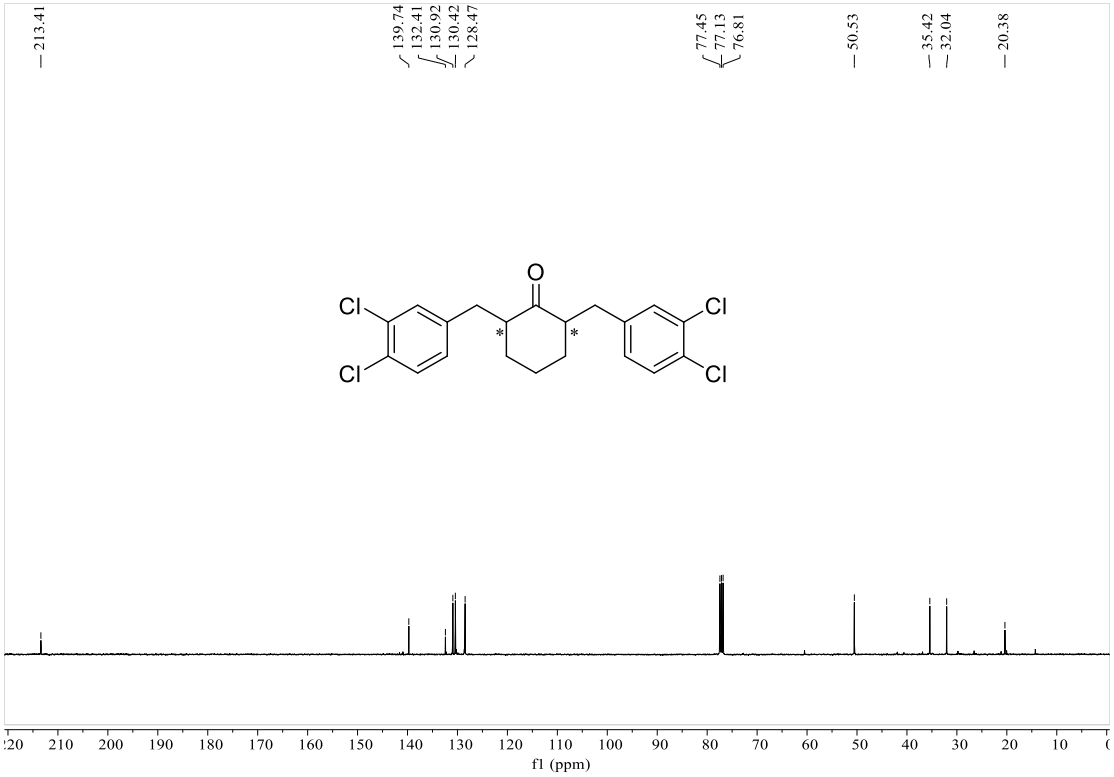


^{13}C NMR (151 MHz, Chloroform-*d*)

2,6-Bis(3,4-dichlorobenzyl)cyclohexan-1-one (**4h**)

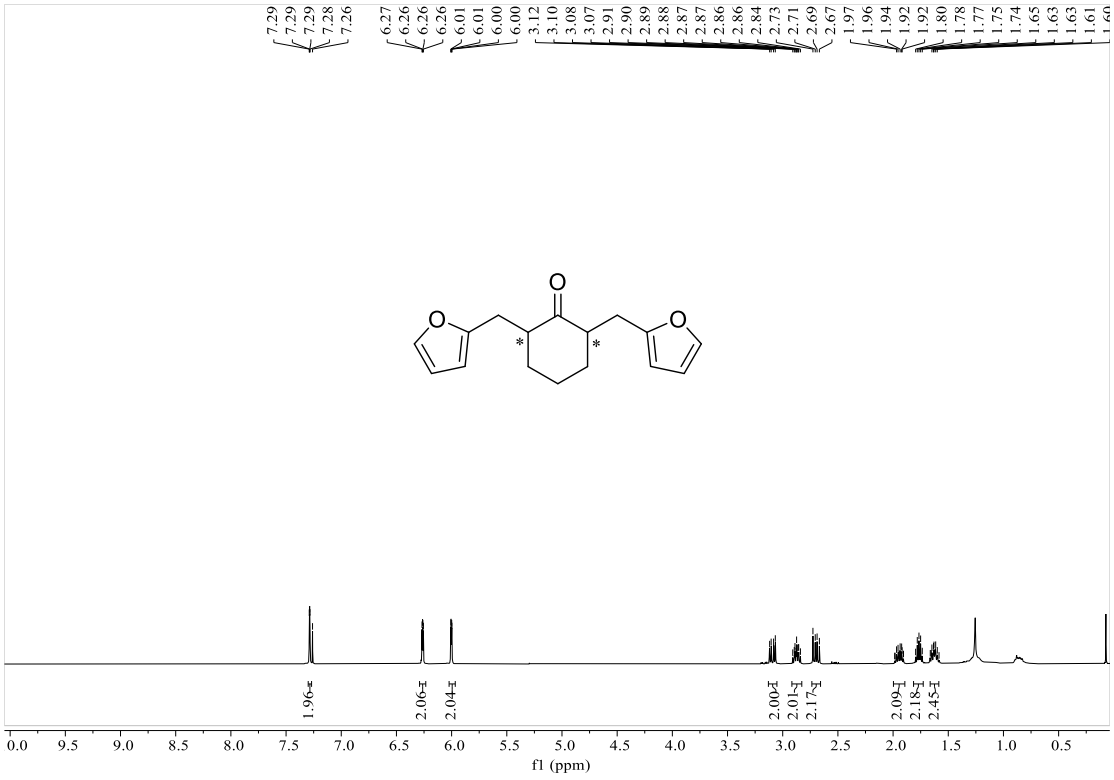


^{1}H NMR (400 MHz, Chloroform-*d*)

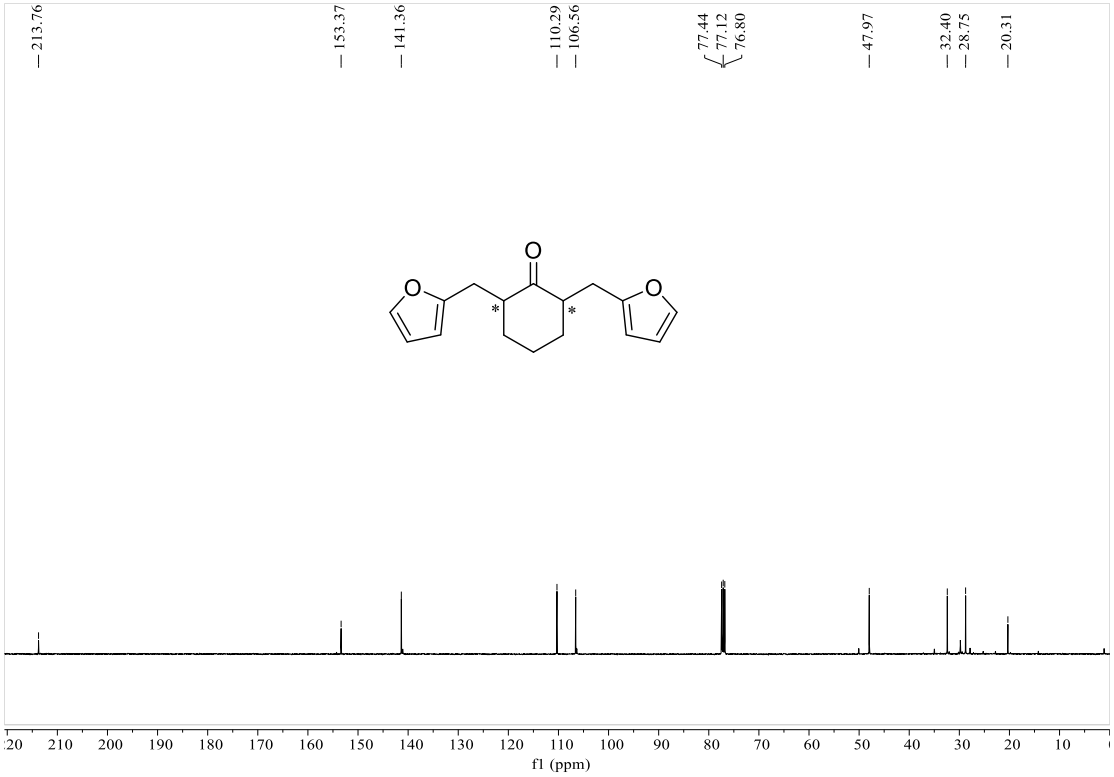


^{13}C NMR (101 MHz, Chloroform-*d*)

2,6-Bis(furan-2-ylmethyl)cyclohexan-1-one (**4i**)

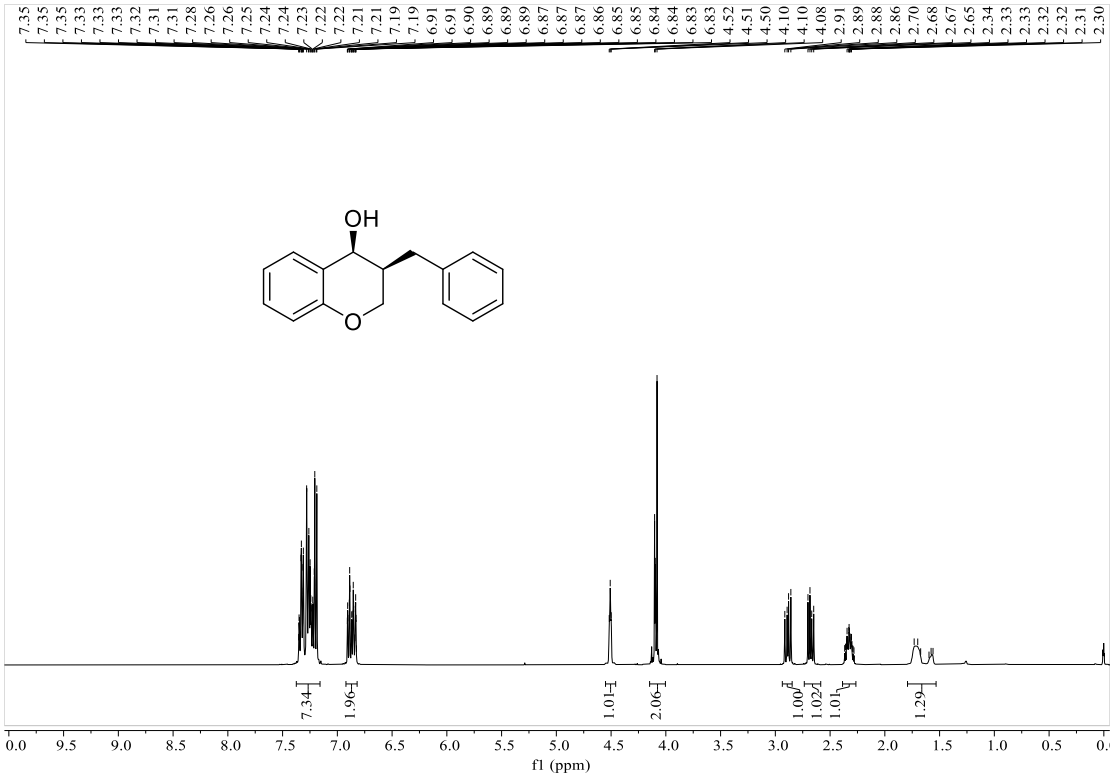


^{1}H NMR (400 MHz, Chloroform-*d*)

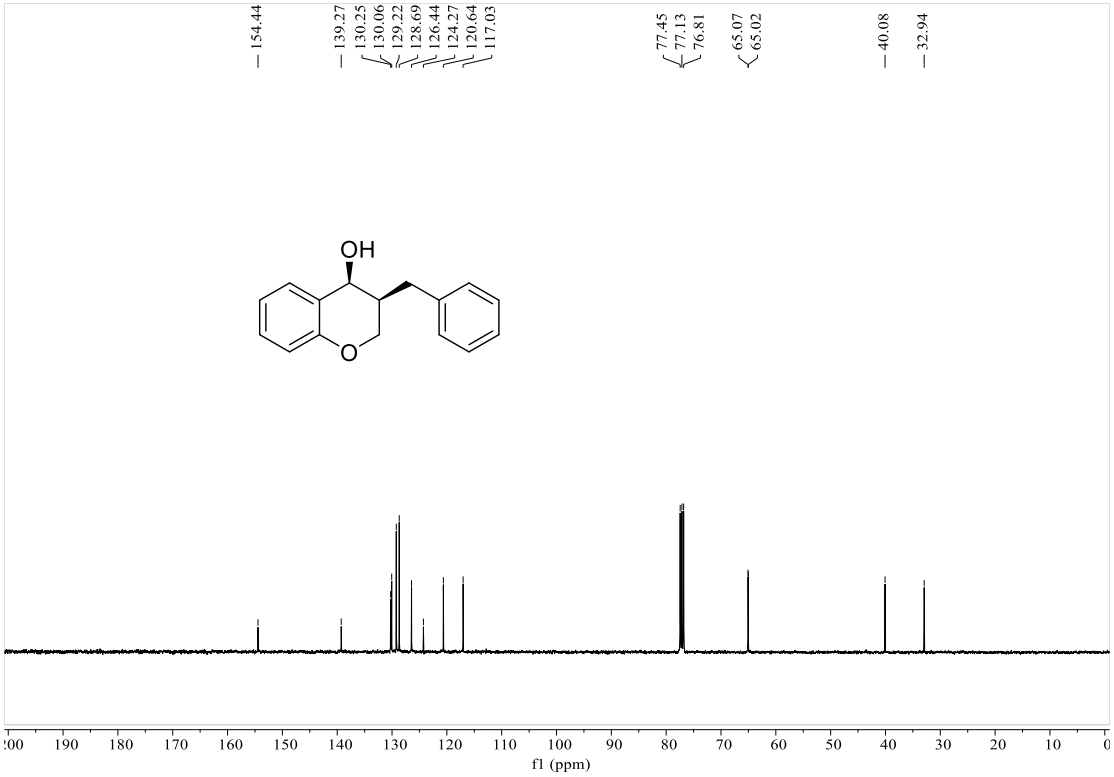


^{13}C NMR (101 MHz, Chloroform-*d*)

(3*S*,4*S*)-3-Benzylchroman-4-ol (**5**)

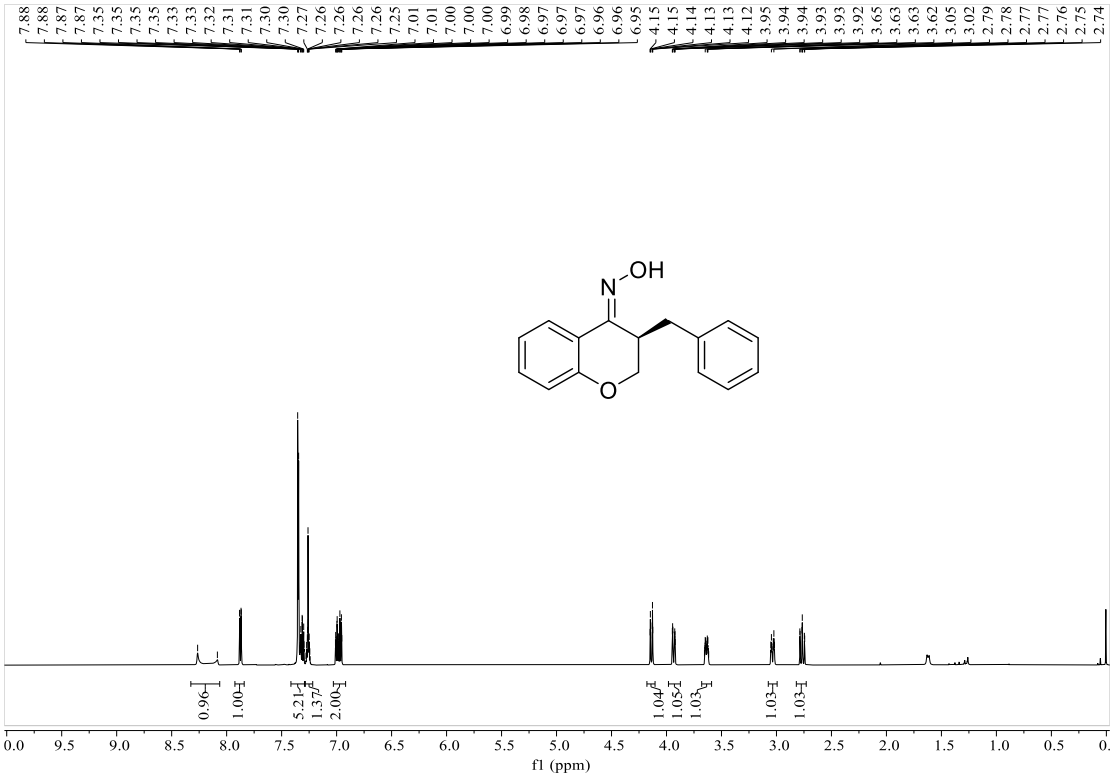


^{1}H NMR (400 MHz, Chloroform-*d*)

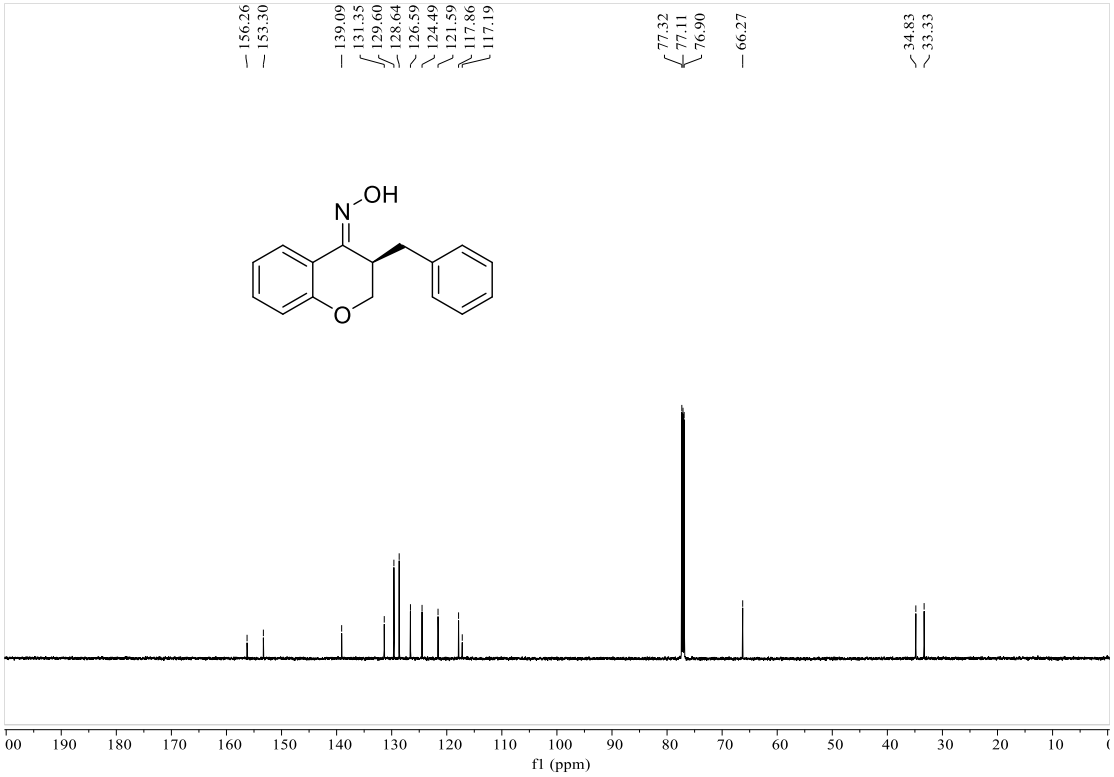


^{13}C NMR (101 MHz, Chloroform-*d*)

(*R*,*E*)-3-benzylchroman-4-one oxime (**6**)

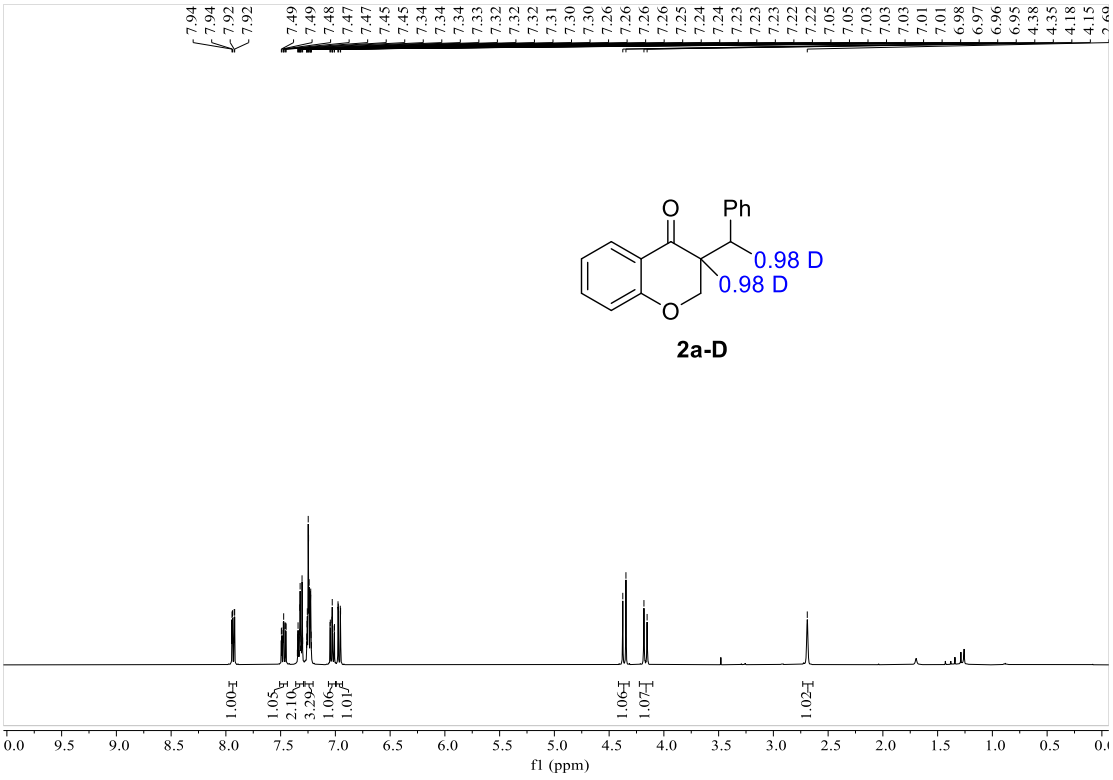


^{1}H NMR (600 MHz, Chloroform-*d*)



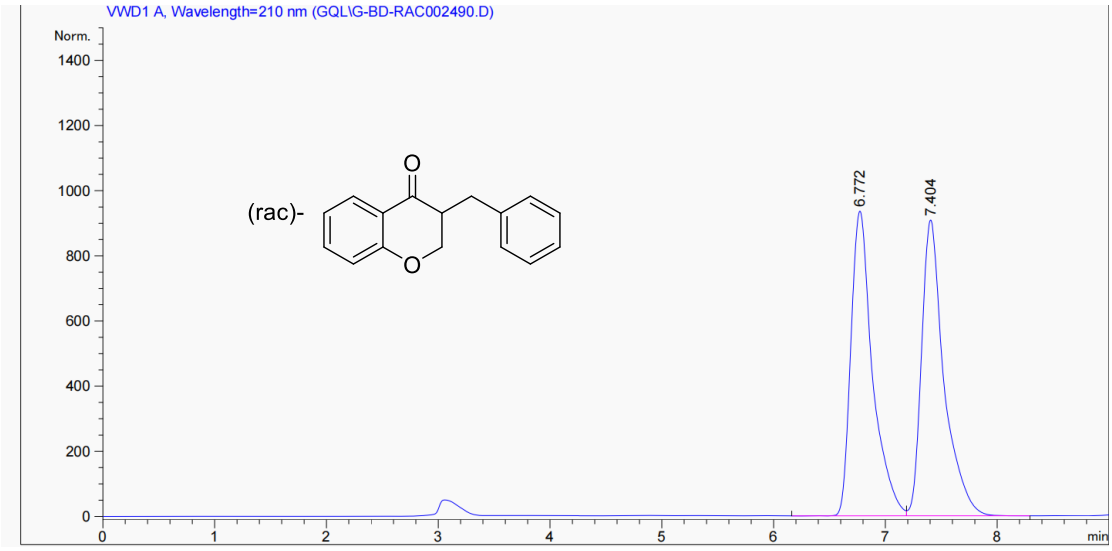
^{13}C NMR (151 MHz, Chloroform-*d*)

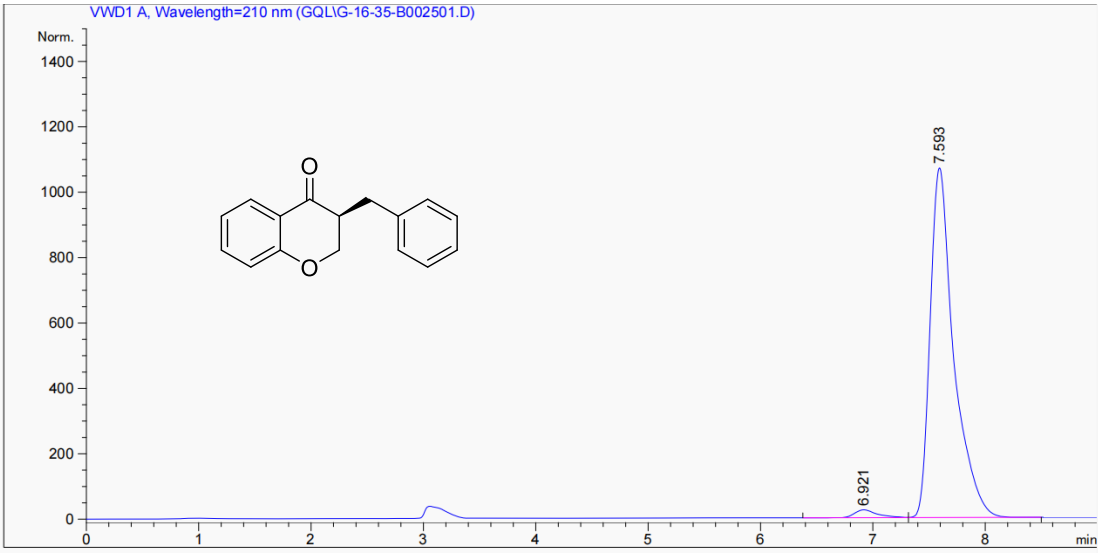
Deuteration experiment (**2a-D**)



^{1}H NMR (400 MHz, Chloroform-*d*)

(*S*)-3-Benzylchroman-4-one (**2a**)

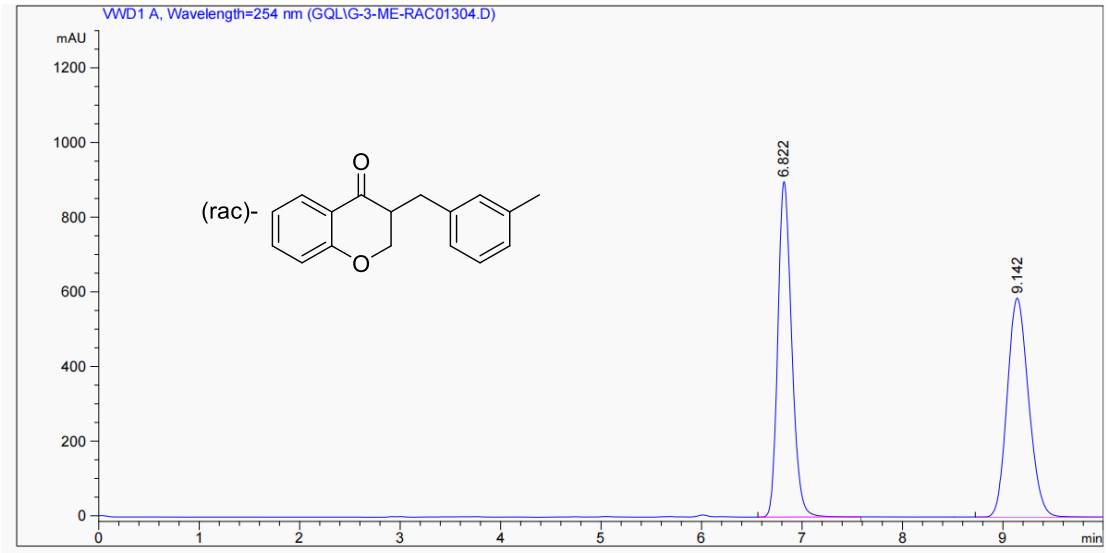


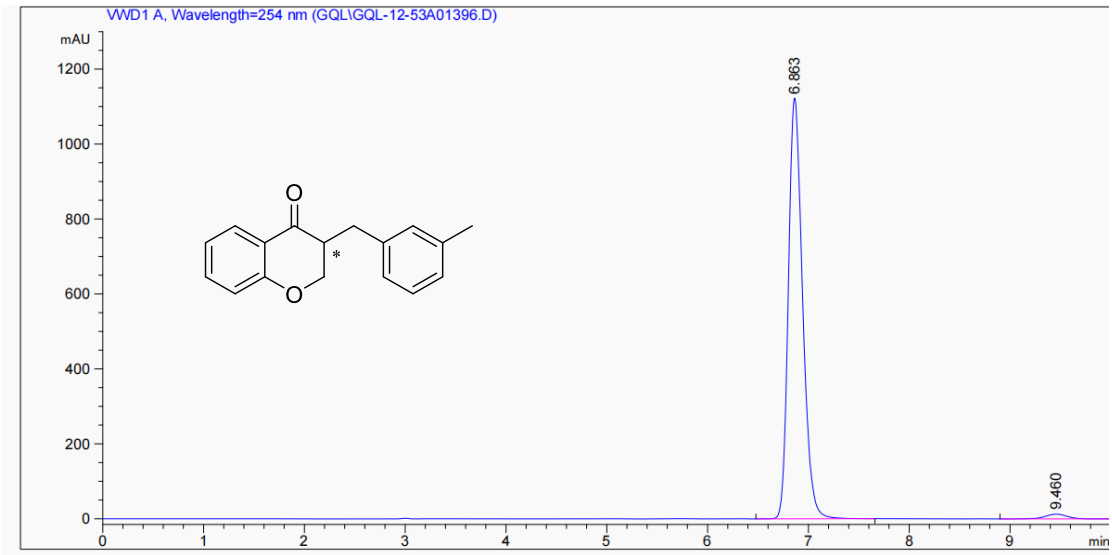


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.921	BV	0.2070	335.56378	24.16871	2.1052
2	7.593	VB	0.2162	1.56044e4	1069.33105	97.8948
Totals :				1.59400e4	1093.49976	

3-(3-Methylbenzyl)chroman-4-one (**2b**)

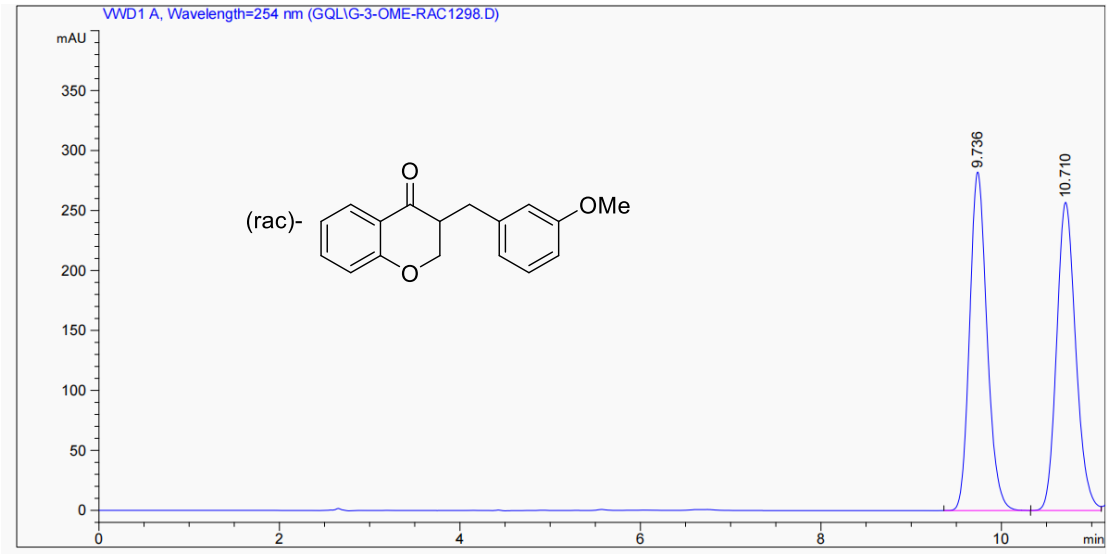


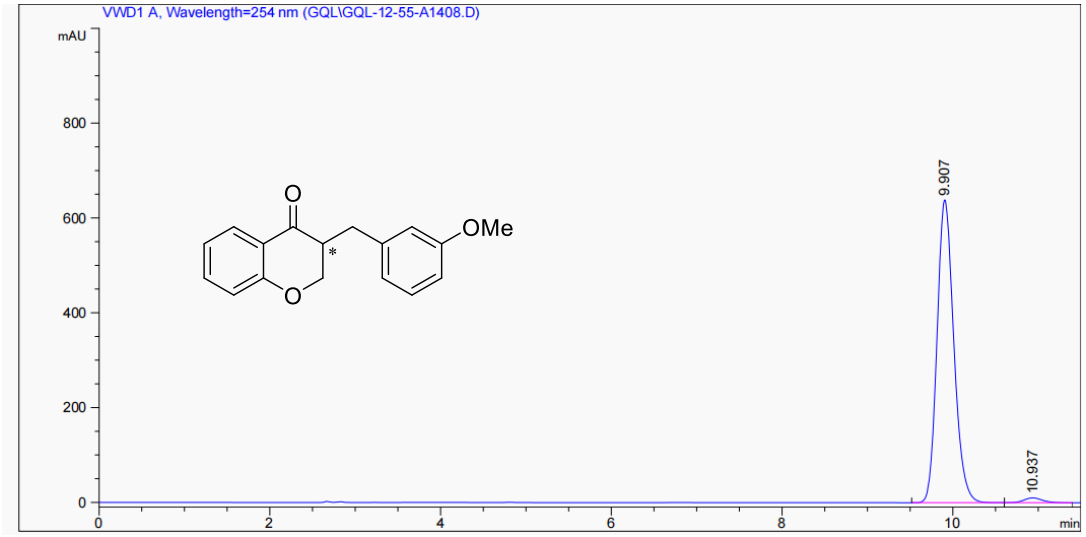


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.863	BB	0.1498	1.09555e4	1122.67407	98.3005
2	9.460	BBA	0.2323	189.40291	12.67885	1.6995
Totals :				1.11449e4	1135.35292	

3-(3-Methoxybenzyl)chroman-4-one (**2c**)

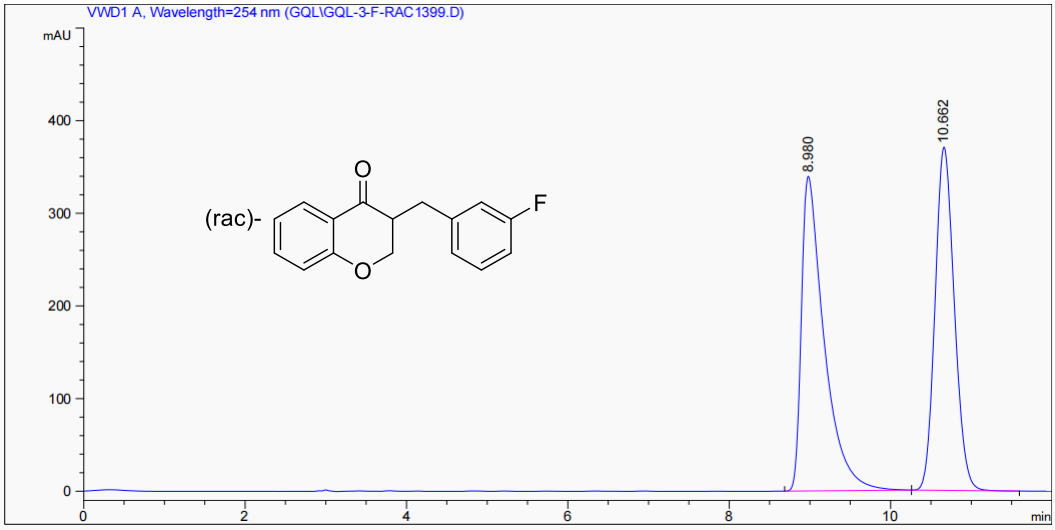


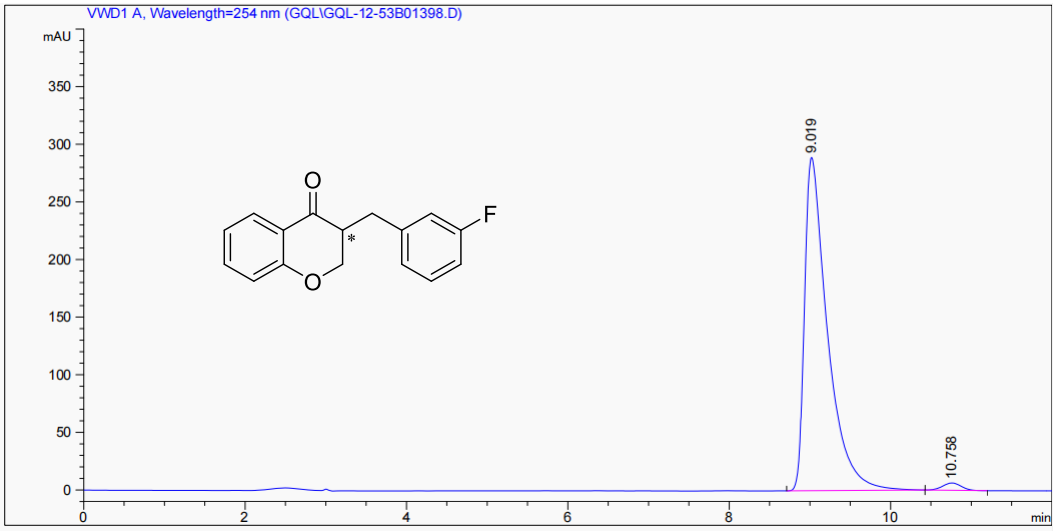


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.907	BB	0.2110	8706.12500	638.71991	98.2964
2	10.937	BB	0.2287	150.88564	10.19224	1.7036
Totals :				8857.01064	648.91215	

3-(3-Fluorobenzyl)chroman-4-one (**2d**)

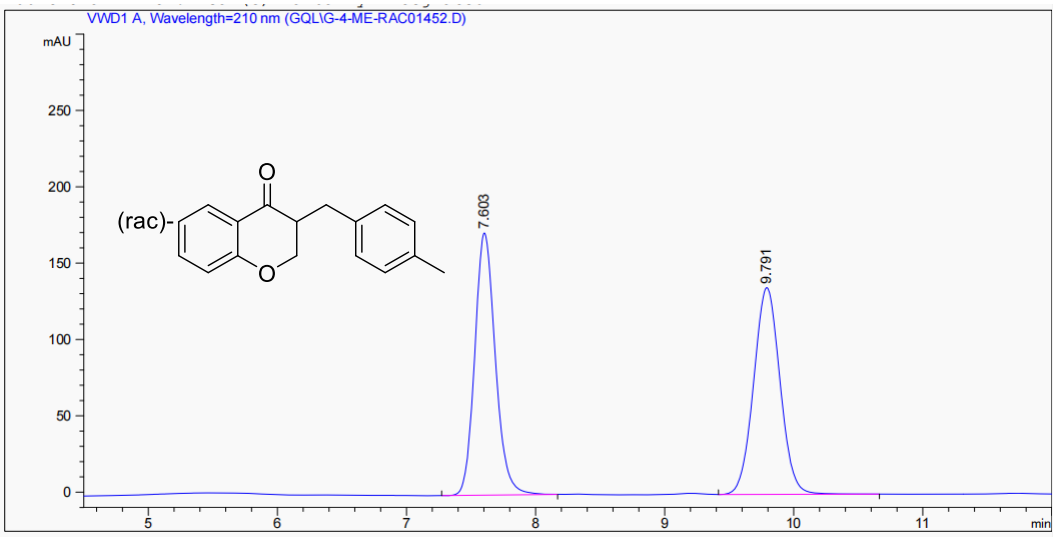


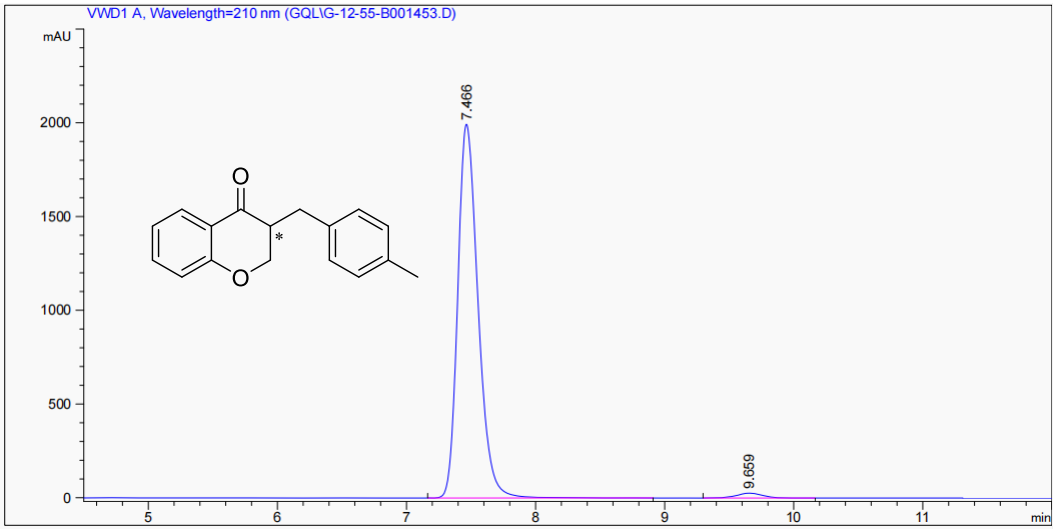


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.019	BB	0.2867	5692.09766	289.12540	98.2457
2	10.758	BB	0.2505	101.63803	6.35916	1.7543
Totals :				5793.73569	295.48456	

3-(4-Methylbenzyl)chroman-4-one (**2e**)

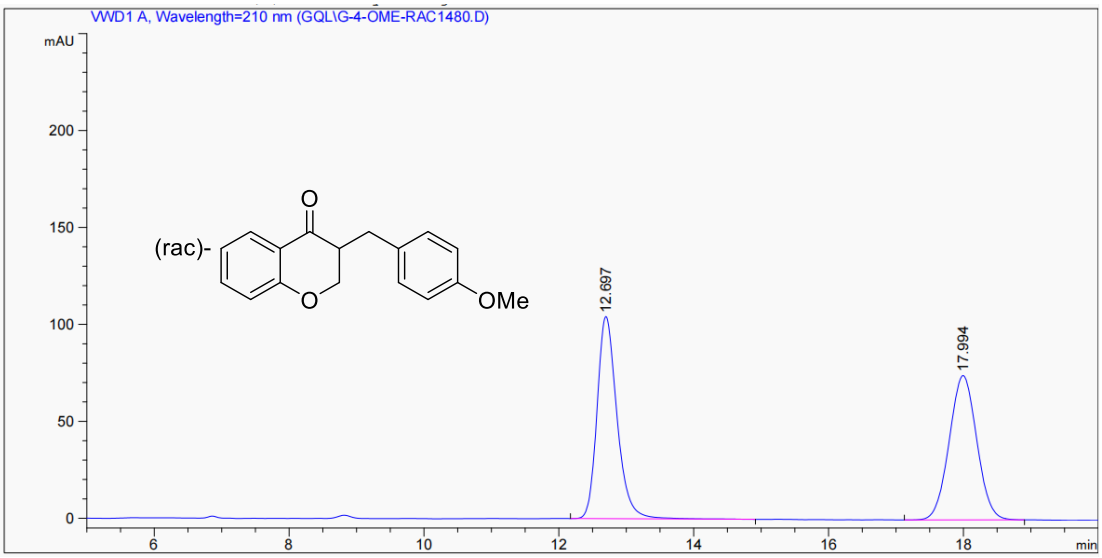


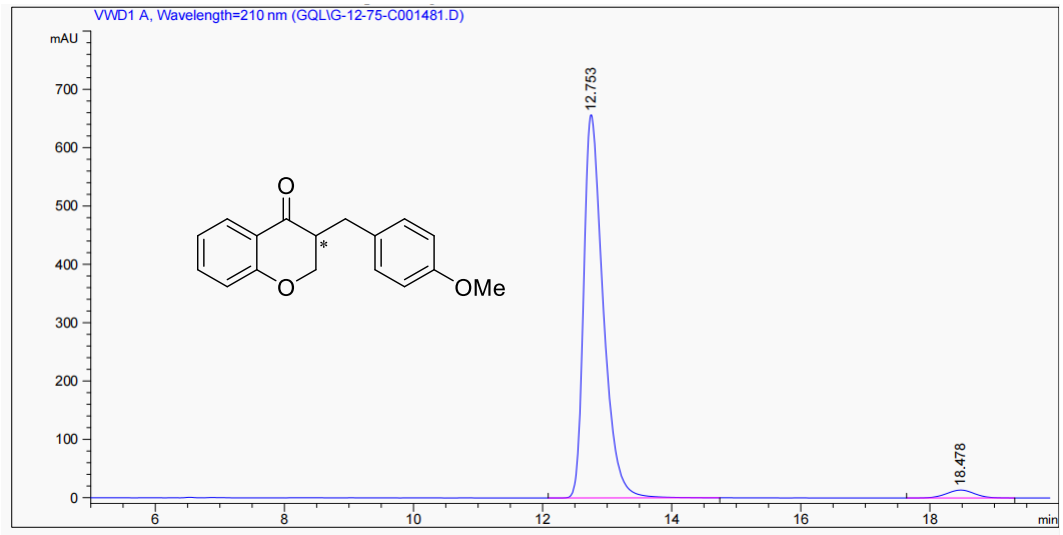


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.466	BB	0.1684	2.17704e4	1992.99316	98.3588
2	9.659	BB	0.2179	363.25912	25.85127	1.6412
Totals :				2.21337e4	2018.84443	

3-(4-Methoxybenzyl)chroman-4-one (**2f**)

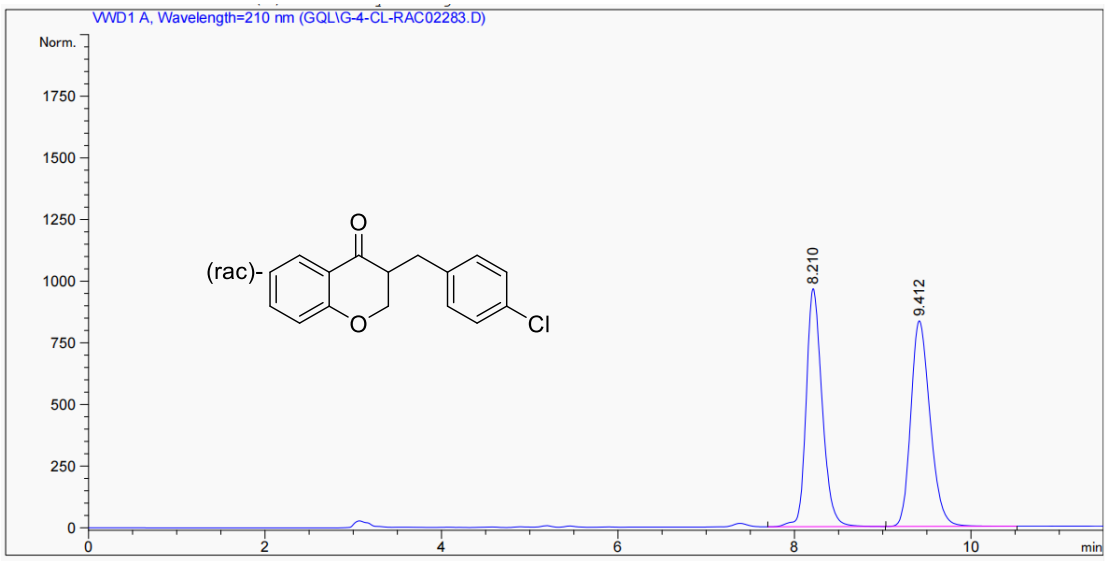


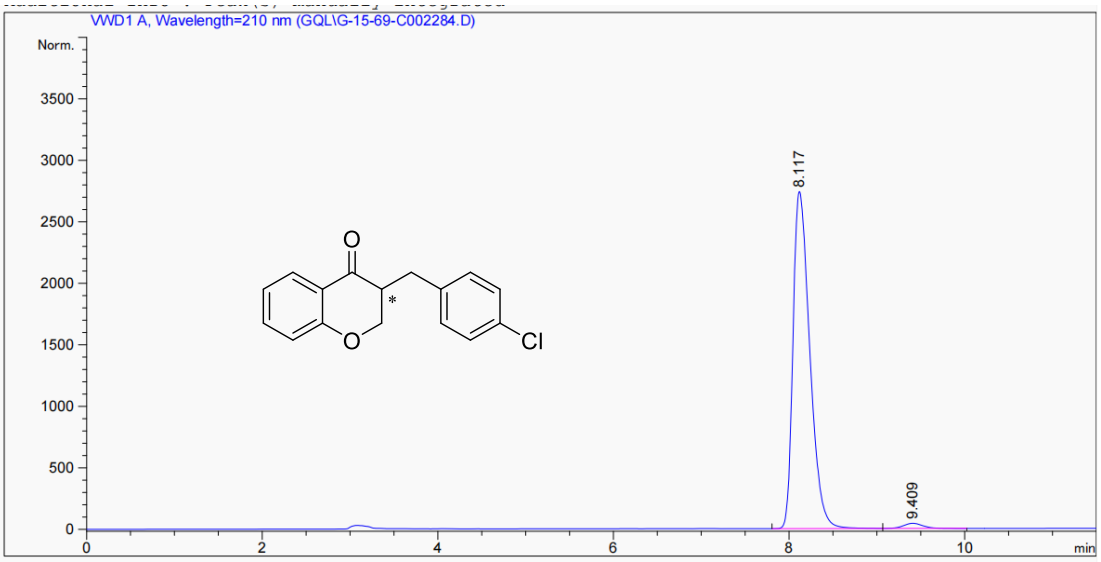


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.753	BB	0.3146	1.37154e4	656.84009	97.1242
2	18.478	BB	0.4696	406.11346	13.47568	2.8758
Totals :				1.41215e4	670.31577	

3-(4-Chlorobenzyl)chroman-4-one (**2g**)

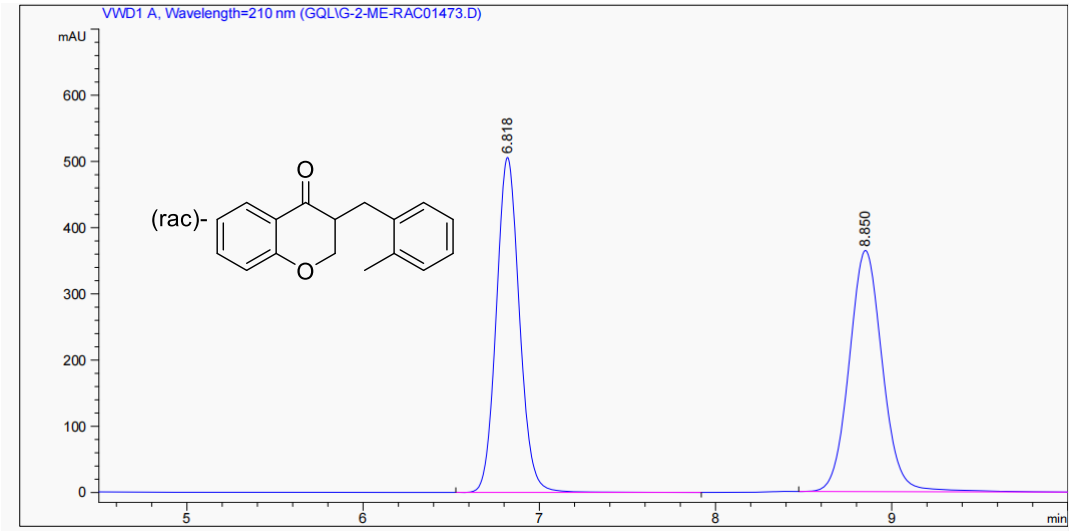


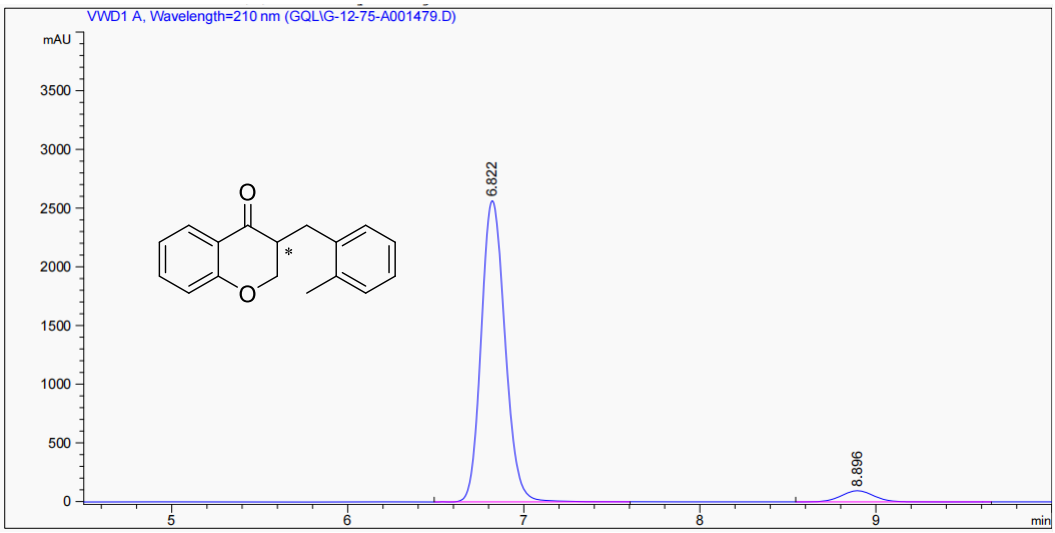


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.117	BV	0.2050	3.63914e4	2739.77051	98.2240
2	9.409	VB	0.2395	657.97827	42.06408	1.7760
Totals :				3.70493e4	2781.83458	

3-(2-Methylbenzyl)chroman-4-one (**2h**)

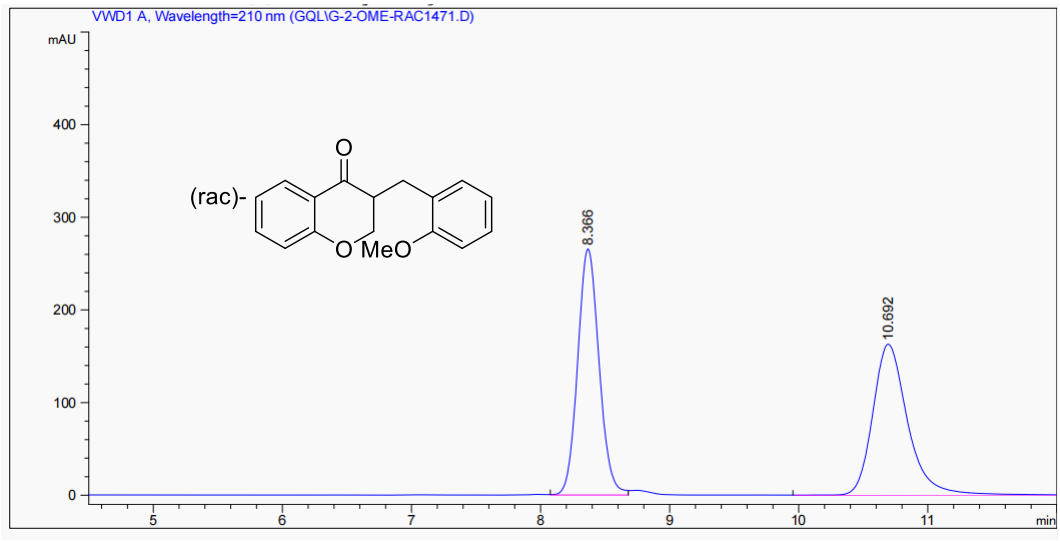


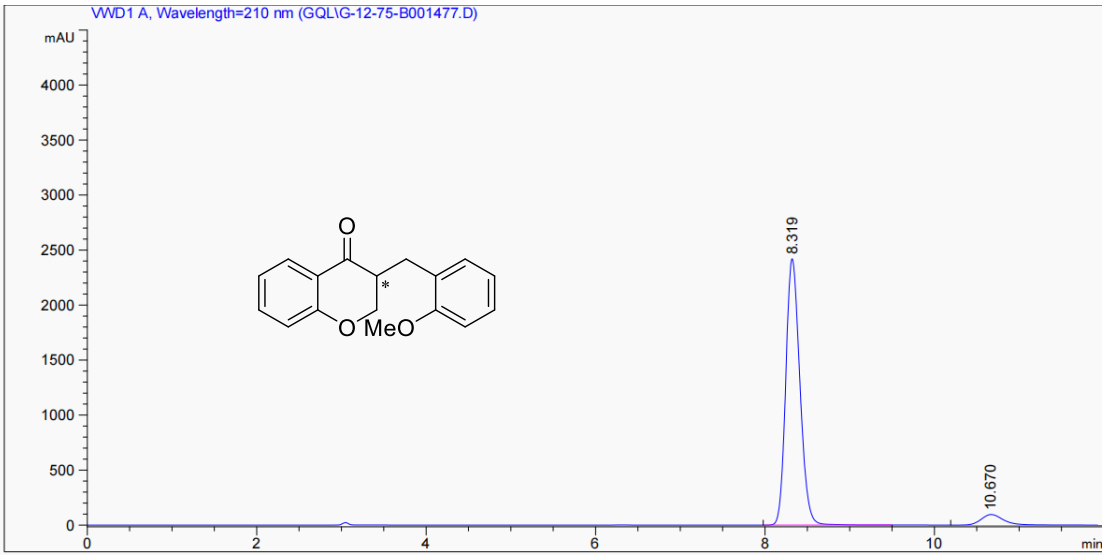


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.822	BV	0.1467	2.41312e4	2565.40796	95.1457
2	8.896	VB	0.2009	1231.17529	95.20234	4.8543
Totals :				2.53624e4	2660.61030	

3-(2-Methoxybenzyl)chroman-4-one (**2i**)



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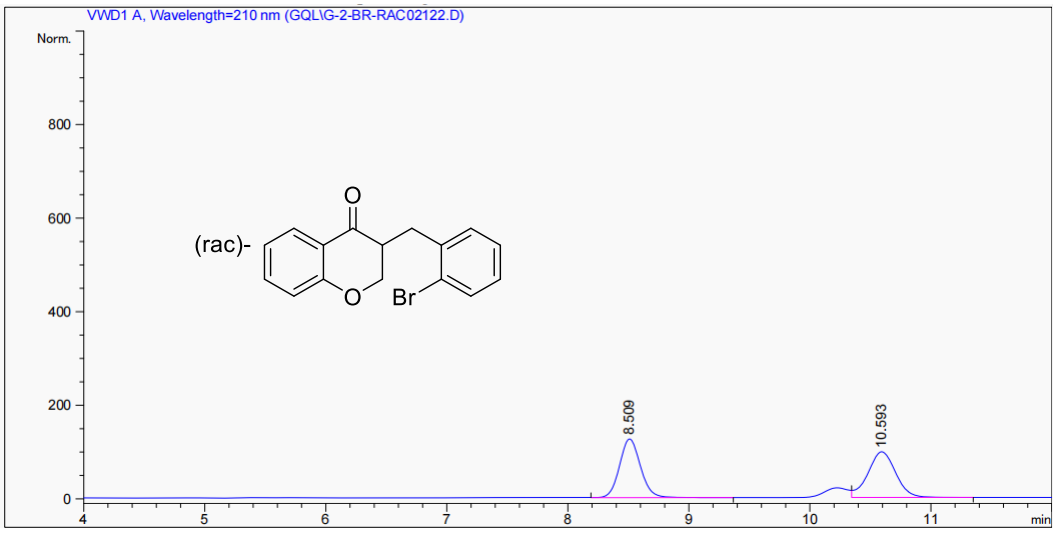
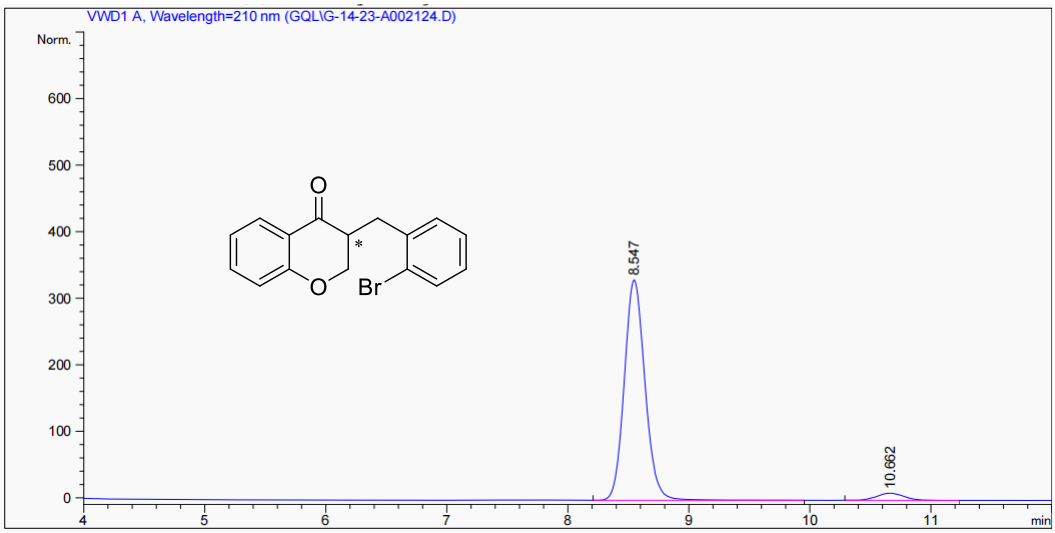
Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.319 BB    0.1797 2.79509e4  2420.52344  94.0106
   2  10.670 BB    0.2808 1780.75342   96.27020   5.9894

Totals :                  2.97317e4  2516.79363
```

3-(2-Bromobenzyl)chroman-4-one (**2j**)

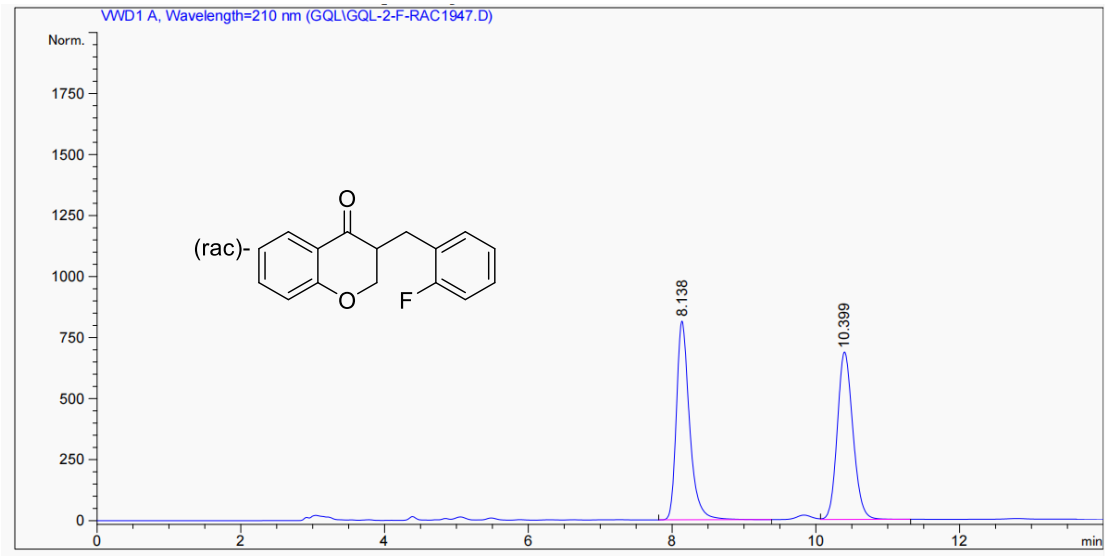


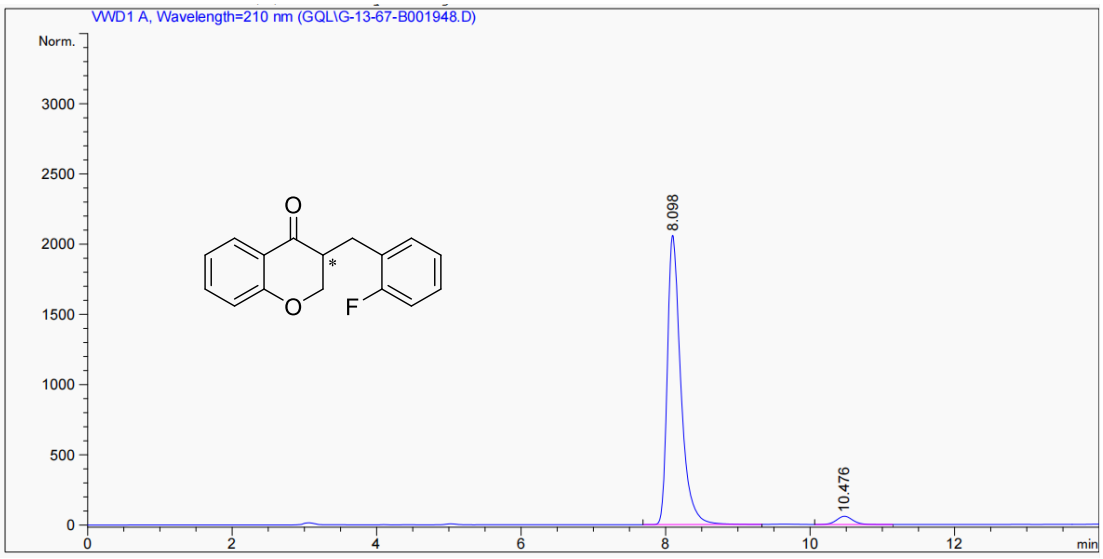


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.547	BB	0.1839	3940.78125	331.03705	95.8732
2	10.662	BB	0.2439	169.62752	10.81828	4.1268
Totals :				4110.40877	341.85533	

3-(2-Fluorobenzyl)chroman-4-one (**2k**)

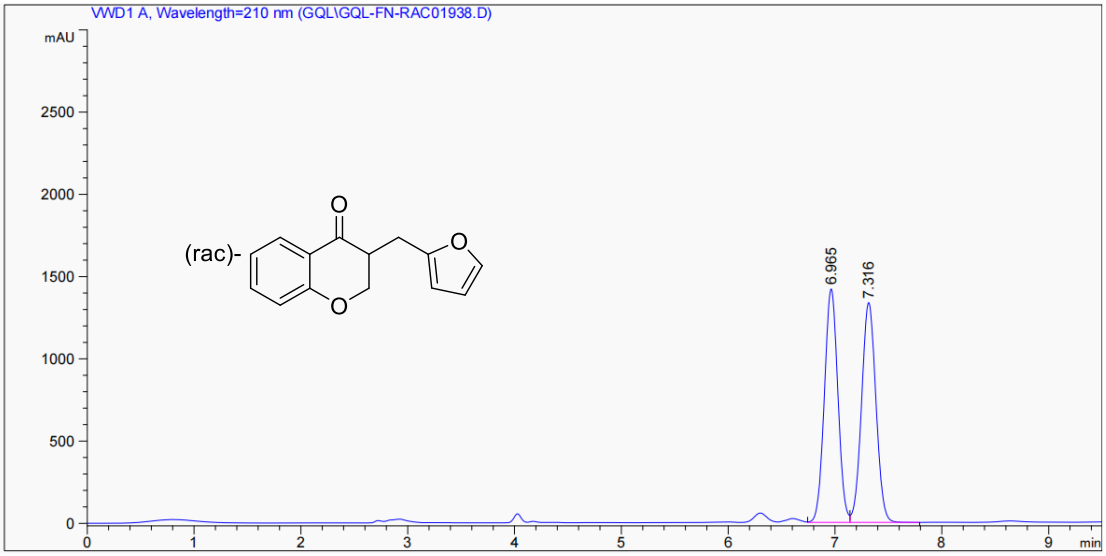


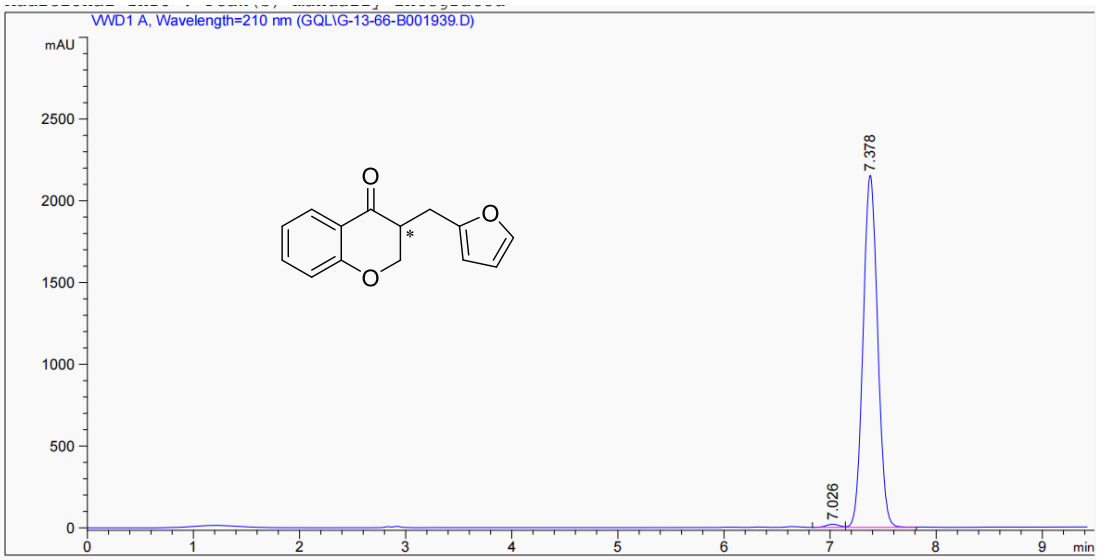


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.098	BB	0.1960	2.66591e4	2059.64771	96.6929
2	10.476	BB	0.2401	911.80908	58.40668	3.3071
Totals :				2.75709e4	2118.05439	

3-(Furan-2-ylmethyl)chroman-4-one (**2l**)

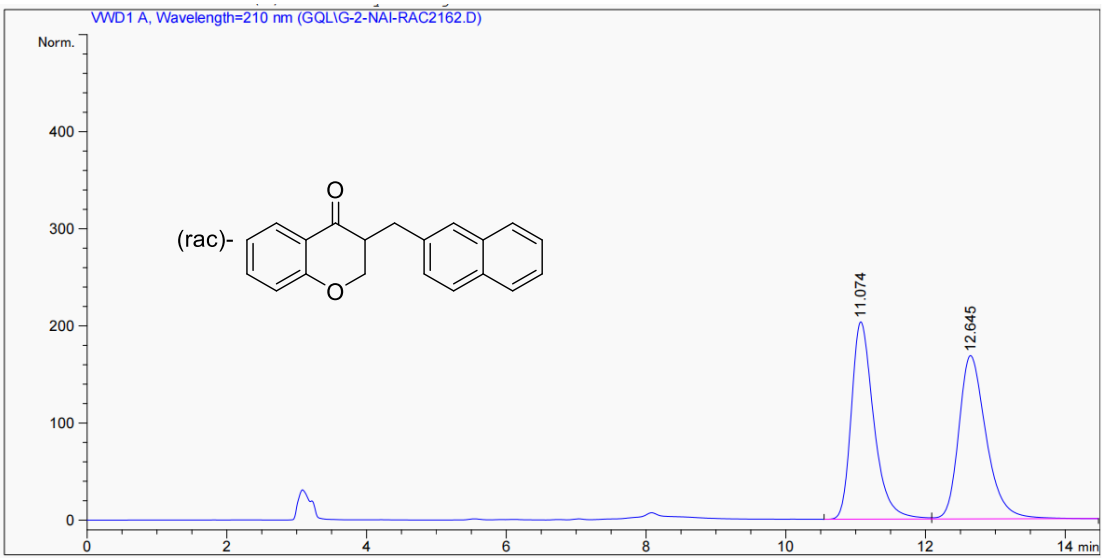


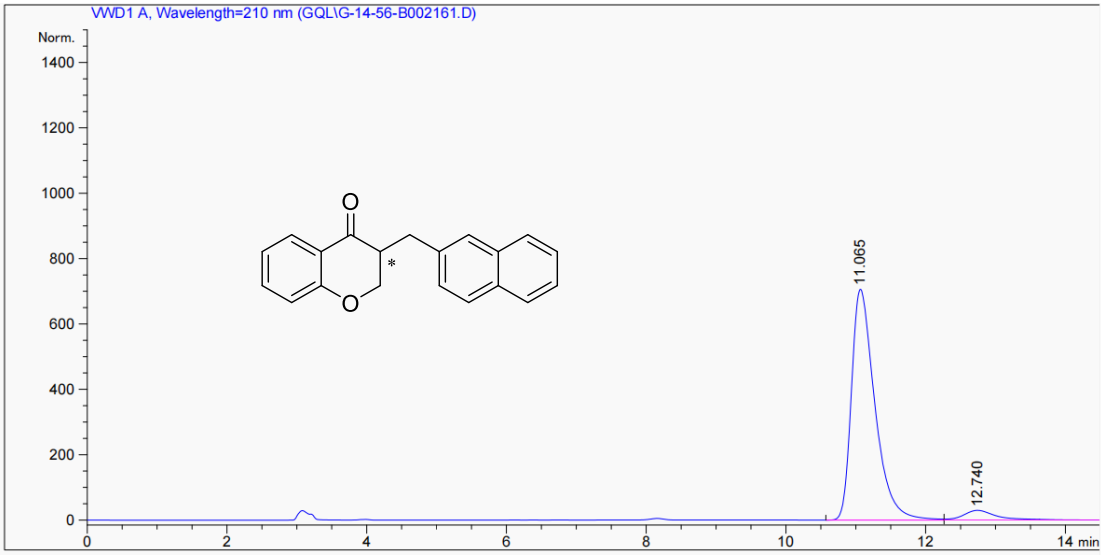


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.026	BV	0.1336	164.18068	19.23017	0.7939
2	7.378	VV	0.1492	2.05162e4	2153.14746	99.2061
Totals :				2.06804e4	2172.37763	

3-(Naphthalen-2-ylmethyl)chroman-4-one (**2m**)

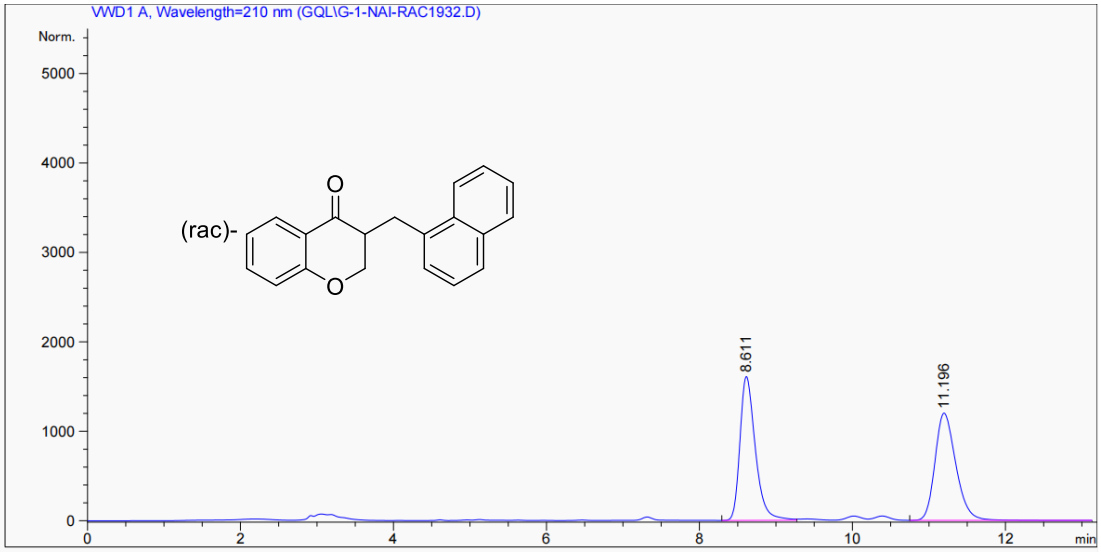


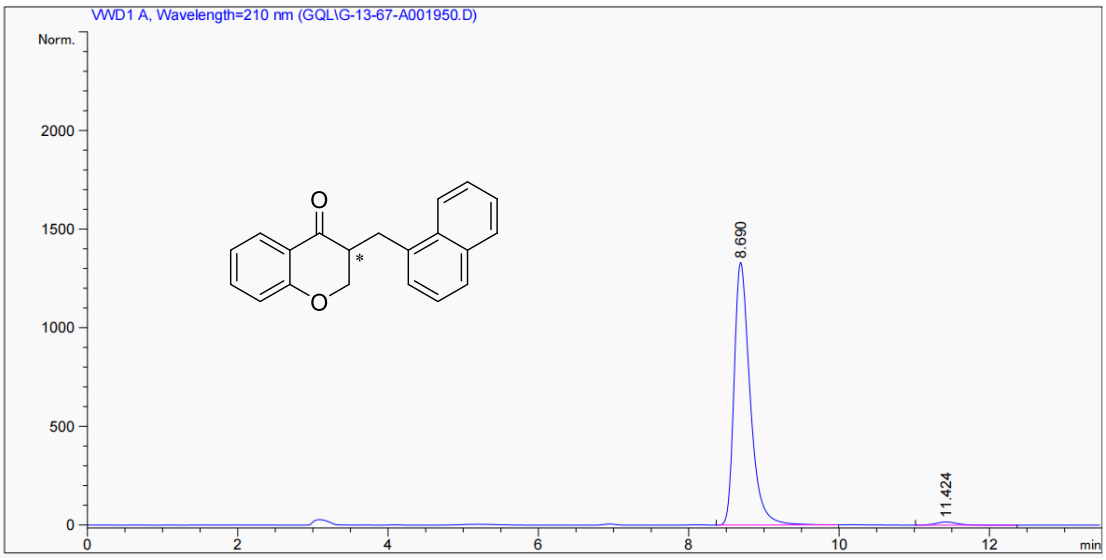


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.065	BV	0.3525	1.64334e4	706.07458	94.2730
2	12.740	VB	0.4924	998.31915	29.68058	5.7270
Totals :				1.74318e4	735.75517	

3-(Naphthalen-1-ylmethyl)chroman-4-one (**2n**)

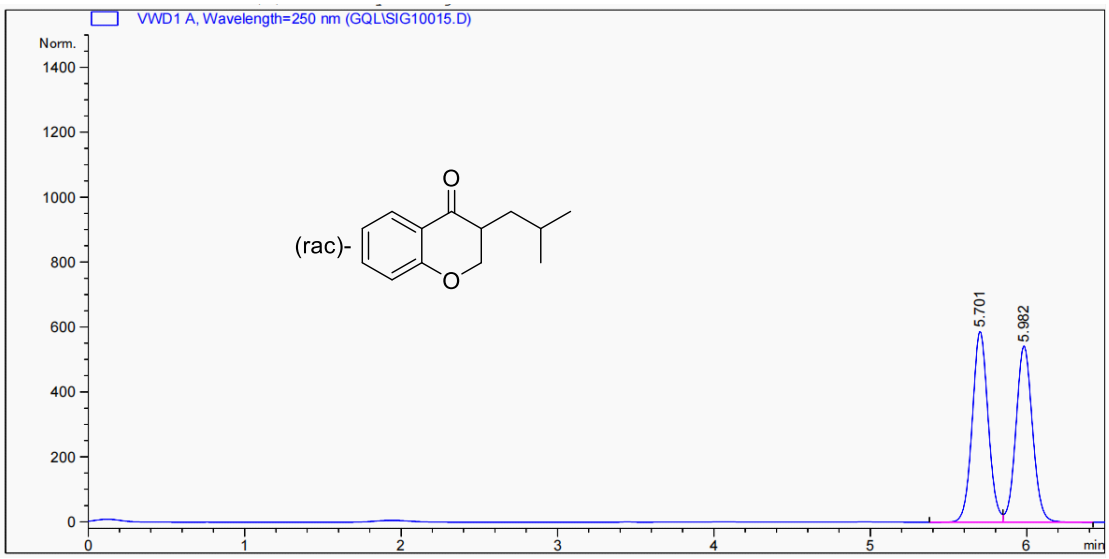


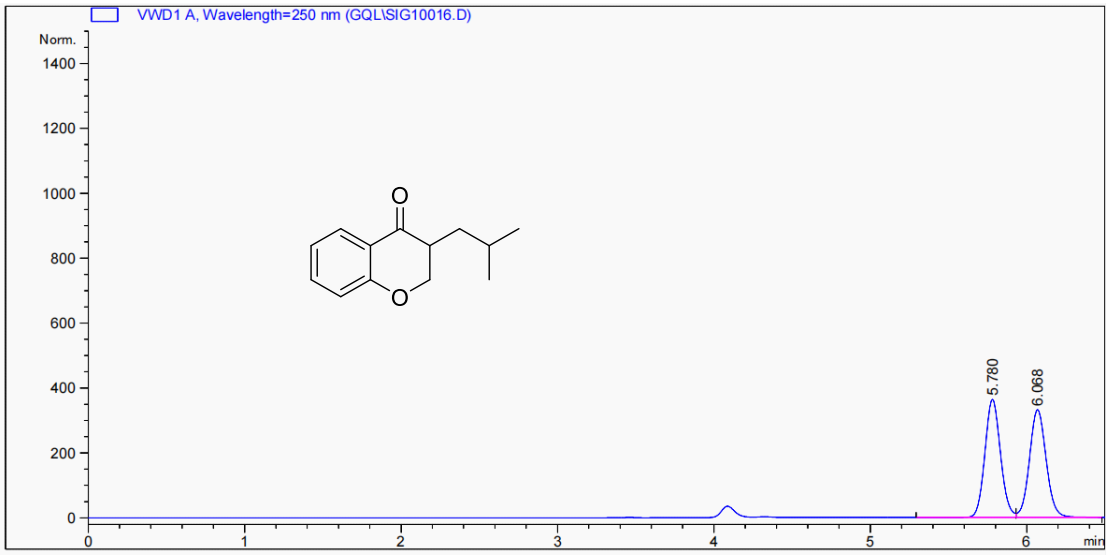


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.690	BB	0.2238	1.96081e4	1331.23035	98.4233
2	11.424	BB	0.3050	314.11801	15.93201	1.5767
Totals :				1.99222e4	1347.16235	

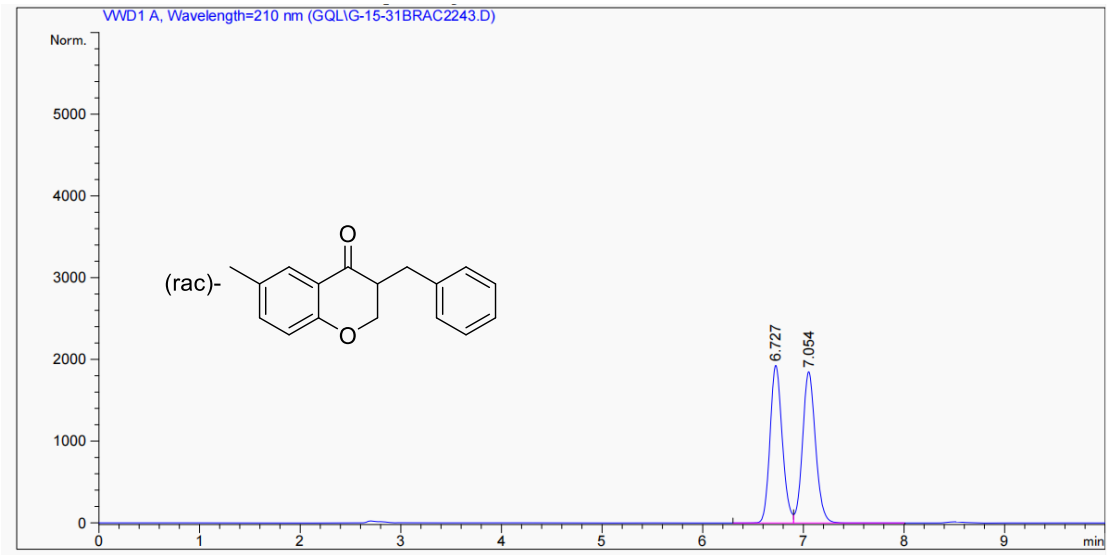
3-isobutylchroman-4-one (**2o**)

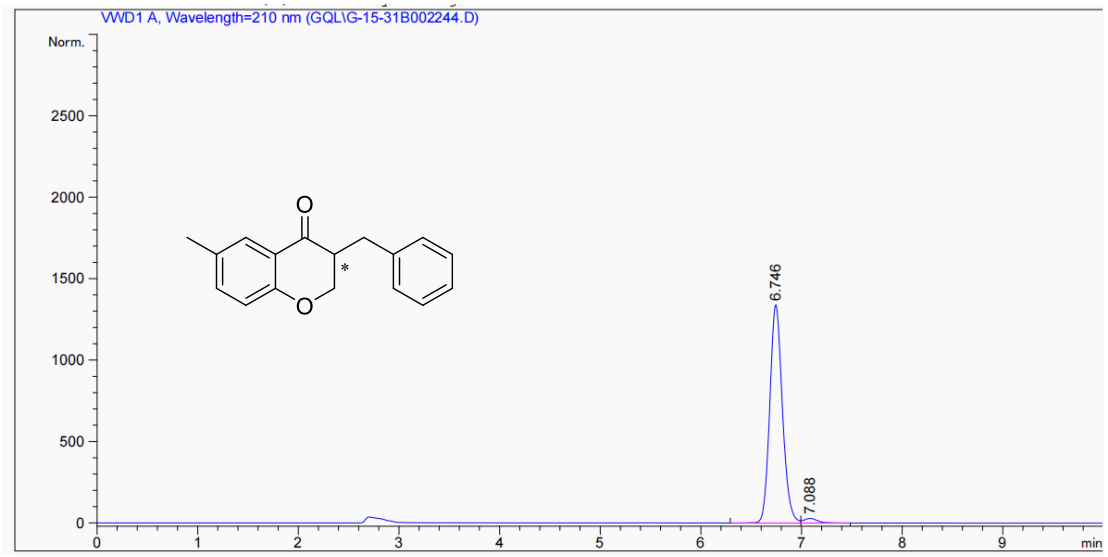




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.780	BV	0.1079	2523.54199	363.77313	50.5865
2	6.068	VB	0.1147	2465.02344	331.88086	49.4135
Totals :				4988.56543	695.65399	

3-Benzyl-6-methylchroman-4-one (**2p**)

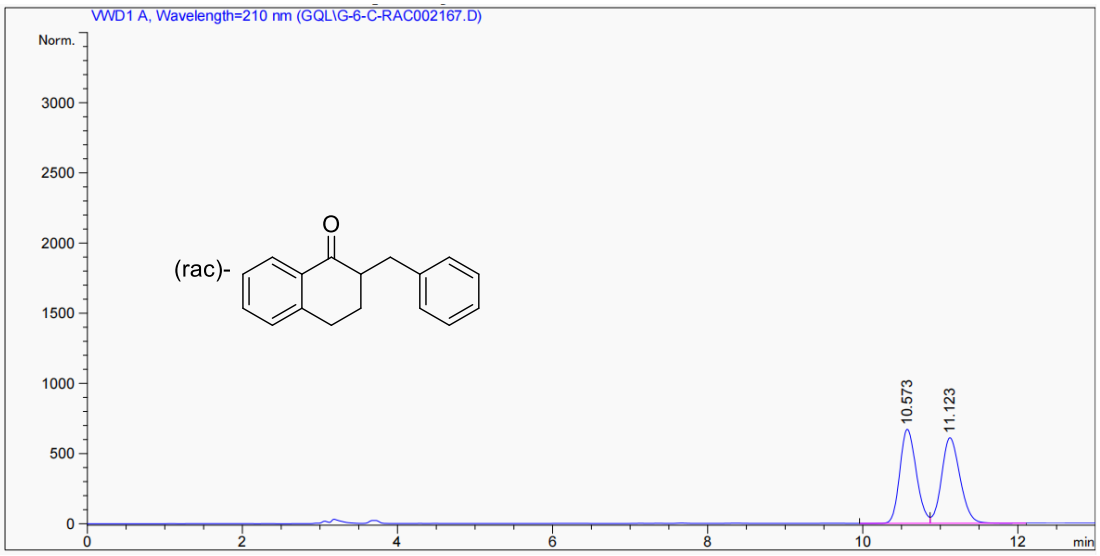


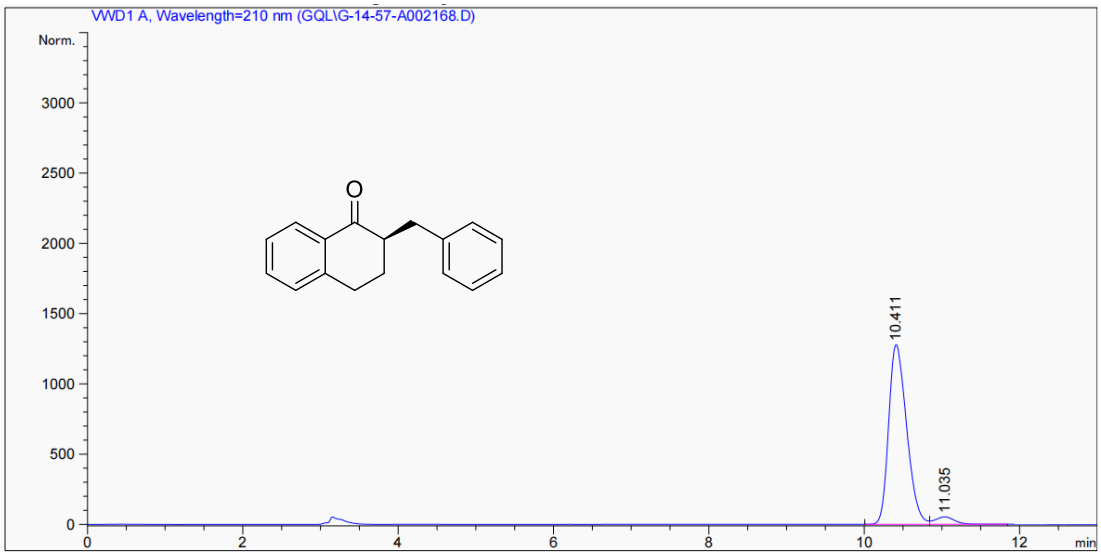


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.746	BV	0.1347	1.16765e4	1339.11902	97.8558
2	7.088	VB	0.1378	255.85263	27.93857	2.1442
Totals :				1.19323e4	1367.05759	

(*R*)-2-Benzyl-3,4-dihydronaphthalen-1(2*H*)-one (**2q**)

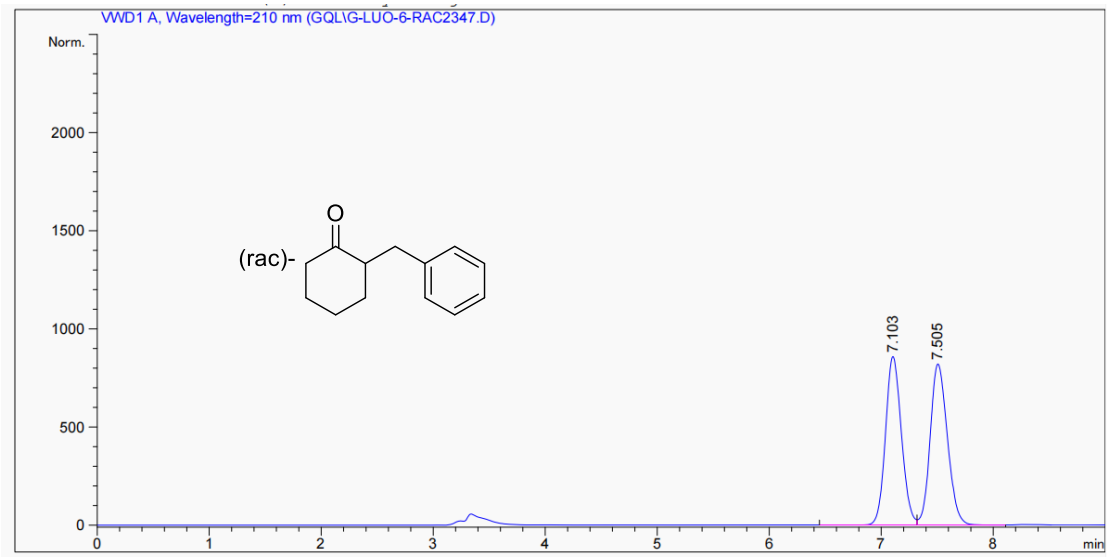


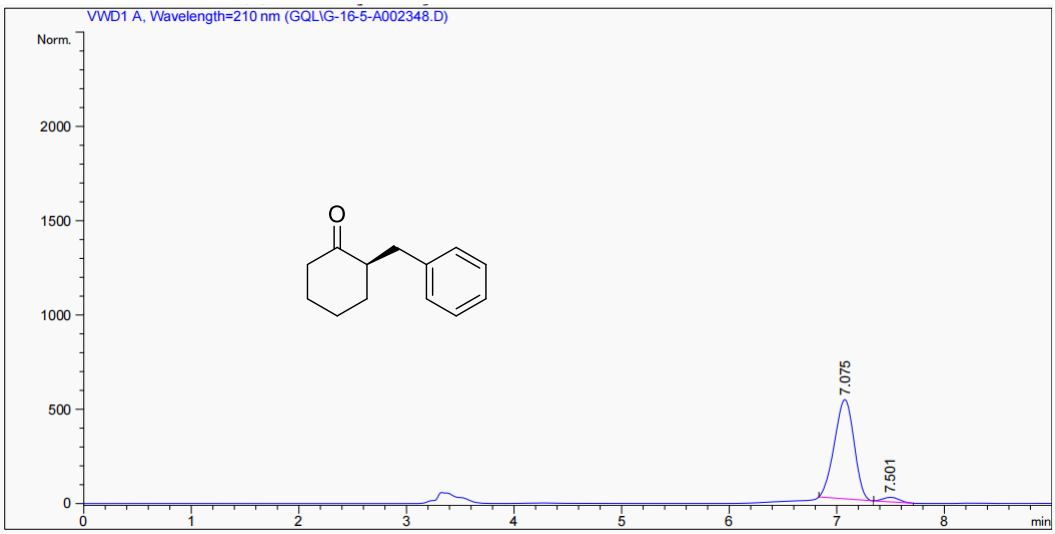


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.411	BV	0.2502	2.05015e4	1277.49866	95.7771
2	11.035	VB	0.2616	903.92493	52.57127	4.2229
Totals :				2.14054e4	1330.06992	

(*R*)-2-Benzylcyclohexan-1-one (**2r**)

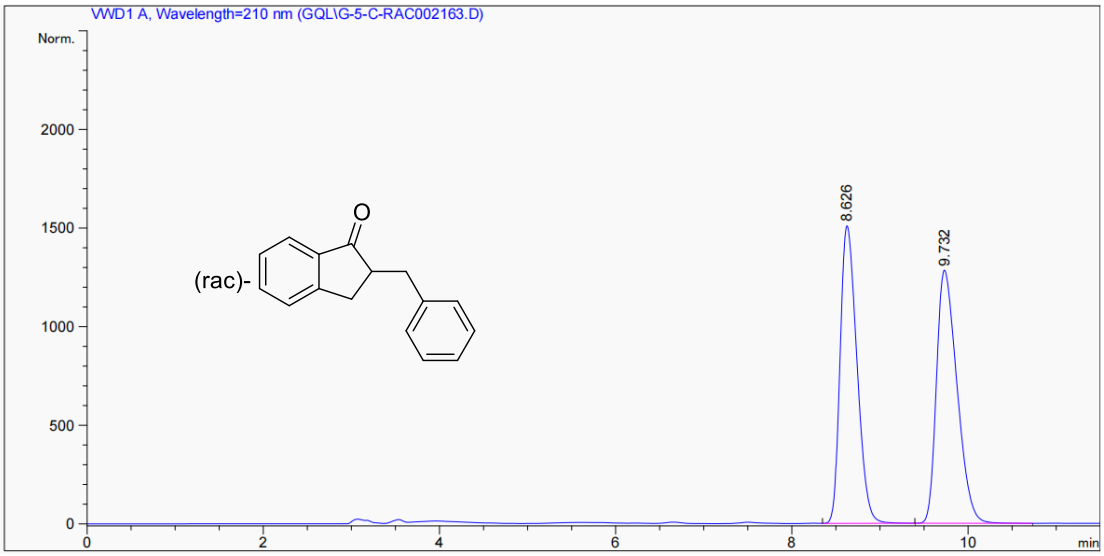


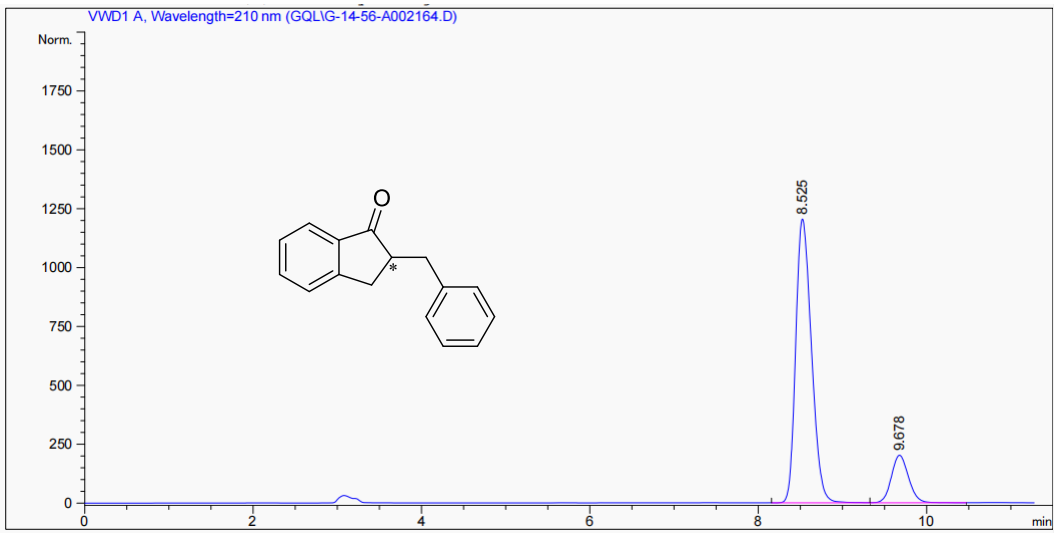


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.075	BB	0.1874	6645.47266	525.92828	96.3688
2	7.501	BB	0.1678	250.40022	24.19187	3.6312
Totals :				6895.87288	550.12015	

2-Benzyl-2,3-dihydro-1*H*-inden-1-one (**2s**)

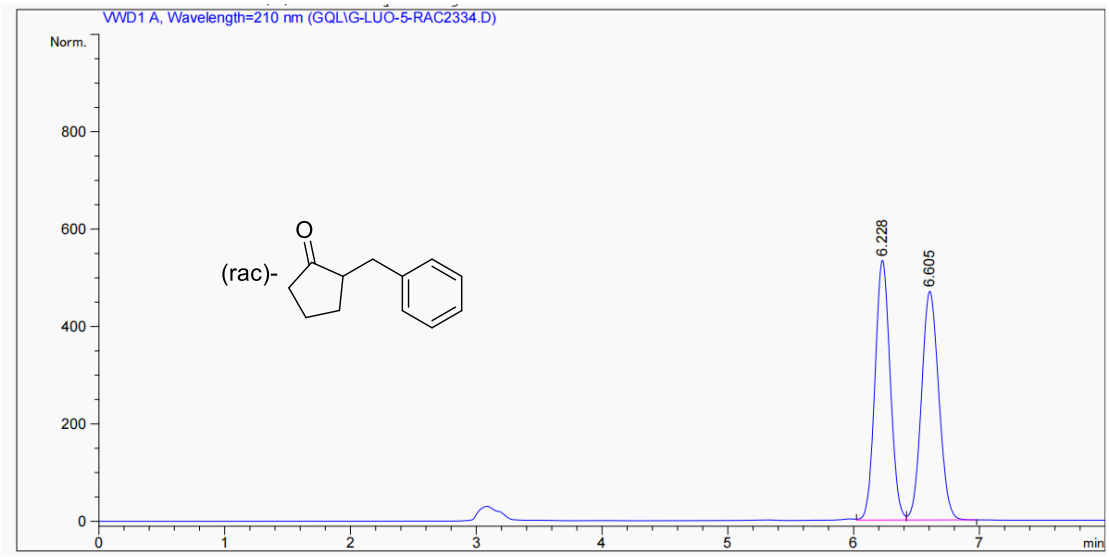


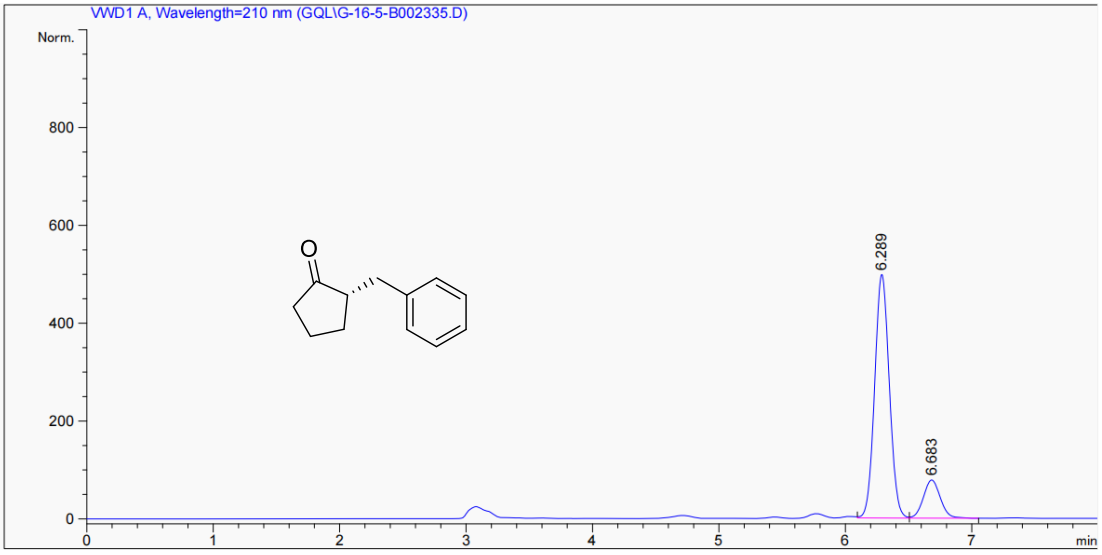


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.525	BV	0.2032	1.56166e4	1204.97974	84.5529
2	9.678	VB	0.2188	2853.02466	201.99254	15.4471
Totals :				1.84697e4	1406.97227	

(*S*)-2-Benzylcyclopentan-1-one (**2t**)

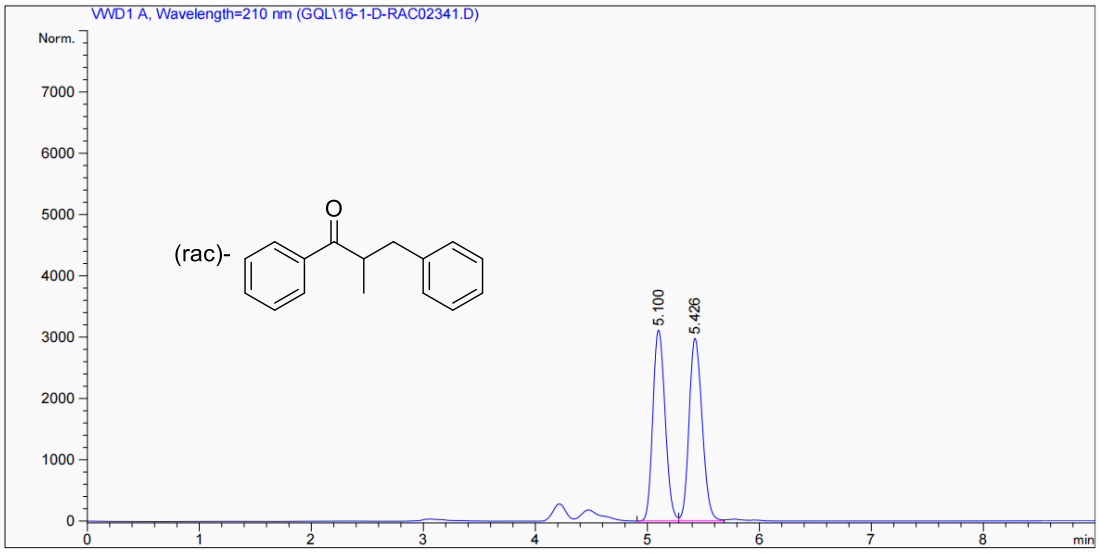


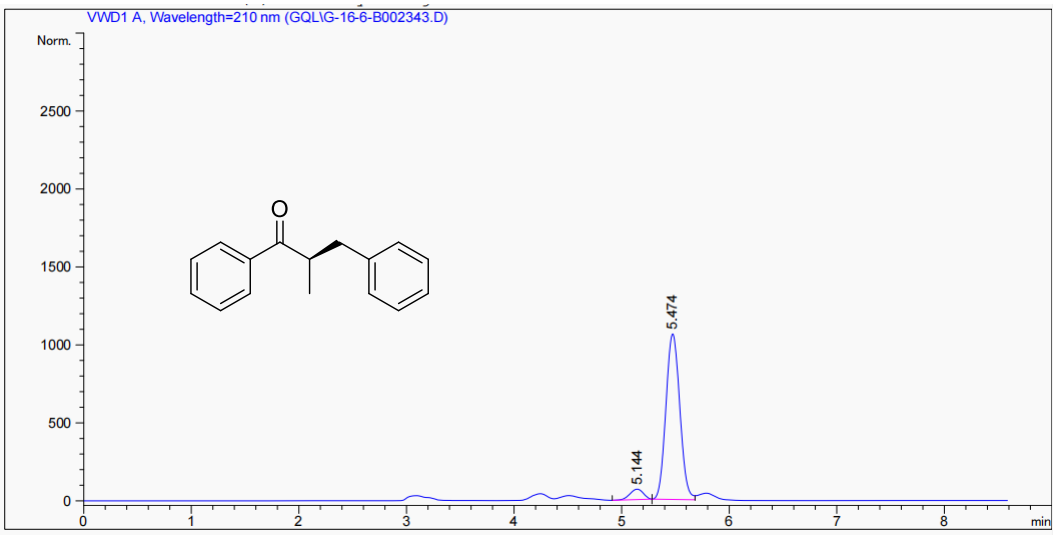


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.289	VV	0.1259	4007.26855	497.99661	84.6791
2	6.683	VB	0.1444	725.03284	78.00783	15.3209
Totals :				4732.30139	576.00444	

(*R*)-2-Methyl-1,3-diphenylpropan-1-one (**2u**)

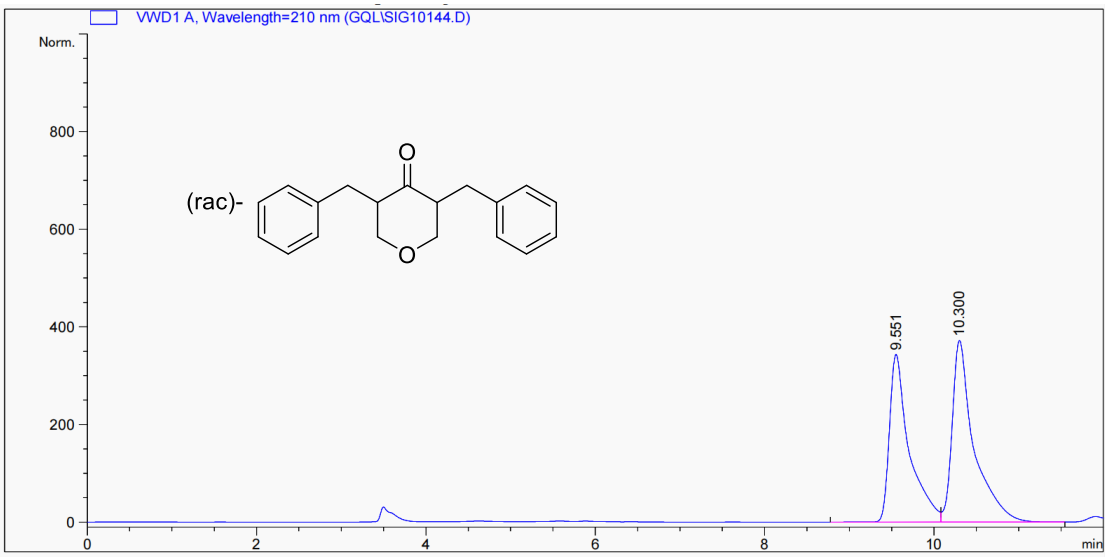


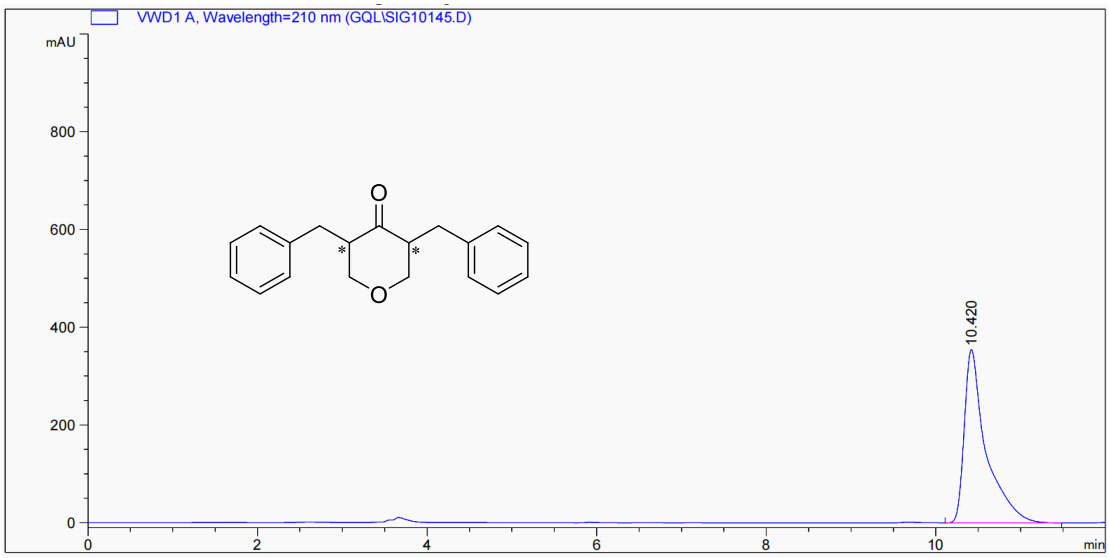


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.144	BB	0.1383	575.14771	66.89952	5.6778
2	5.474	BV	0.1430	9554.57520	1061.21436	94.3222
Totals :				1.01297e4	1128.11388	

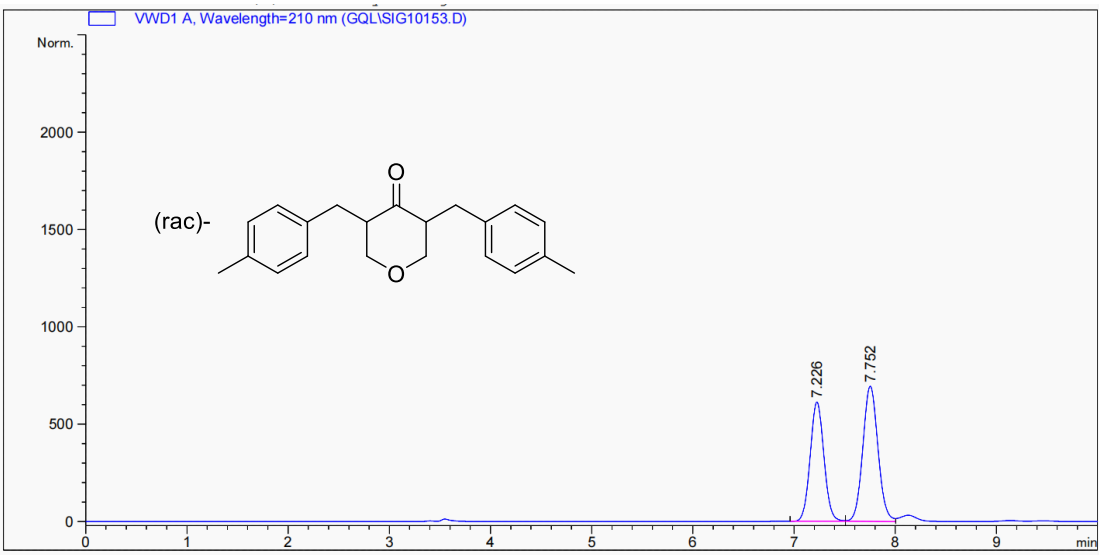
3,5-dibenzyltetrahydro-4*H*-pyran-4-one (**4a**)

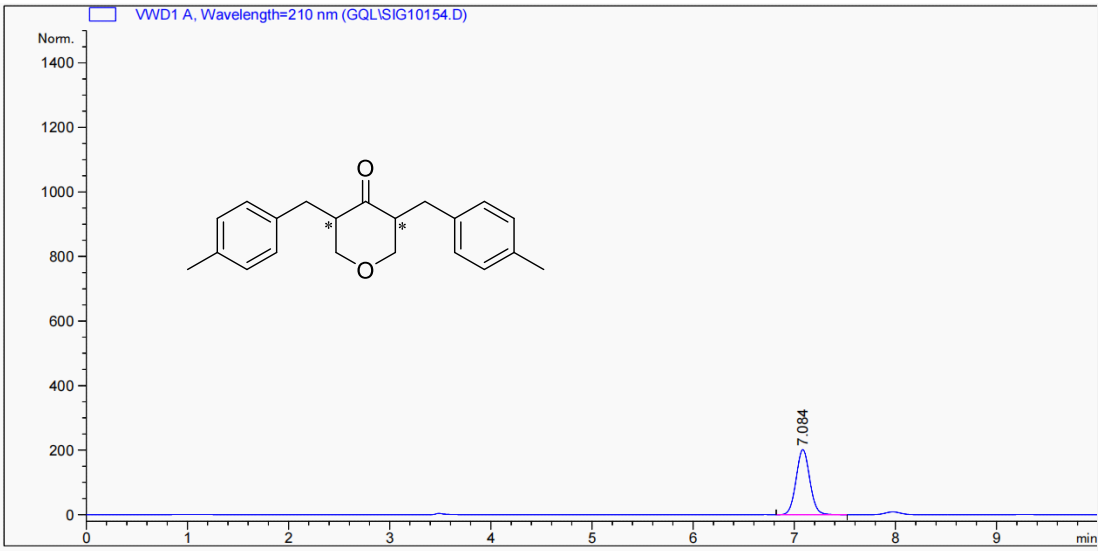




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.420	VB	0.2526	6309.24121	354.61420	100.0000
Totals :				6309.24121	354.61420	

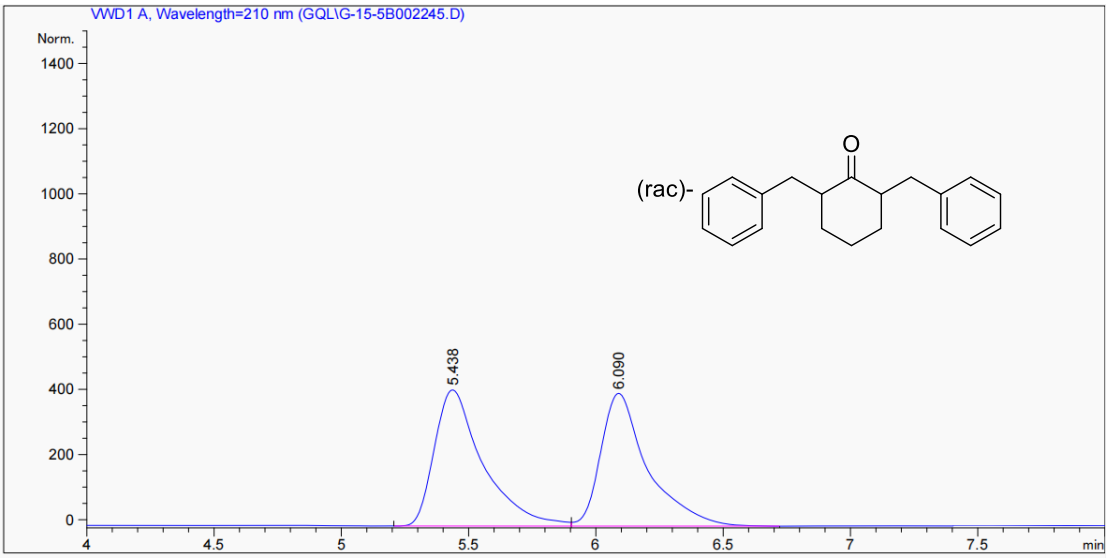
3,5-bis(4-methylbenzyl)tetrahydro-4*H*-pyran-4-one (**4b**)

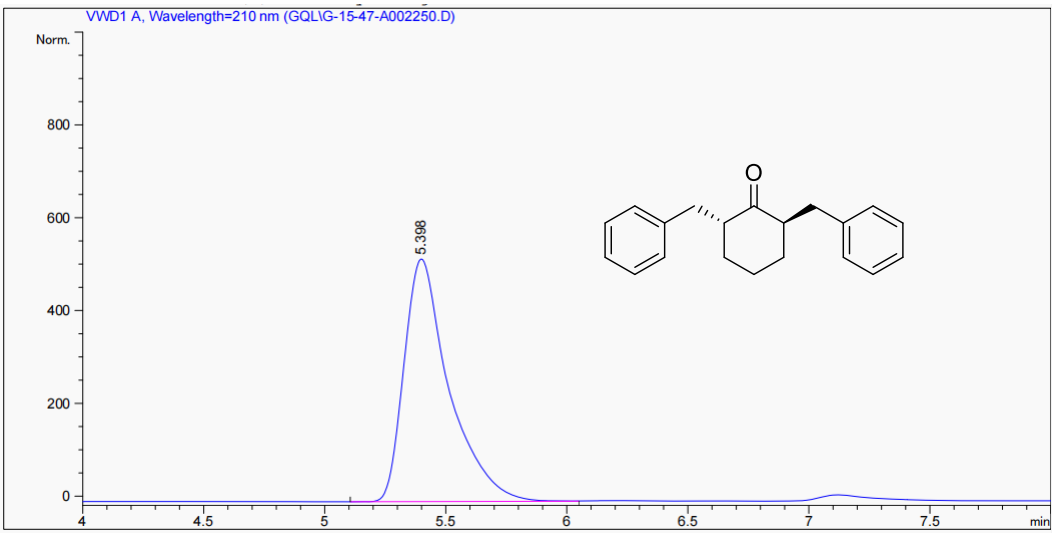




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.084	VB	0.1456	1895.08313	201.64590	100.0000
Totals :				1895.08313	201.64590	

(+)-(2*R*,6*R*)-2,6-Dibenzylcyclohexan-1-one (**4c**)

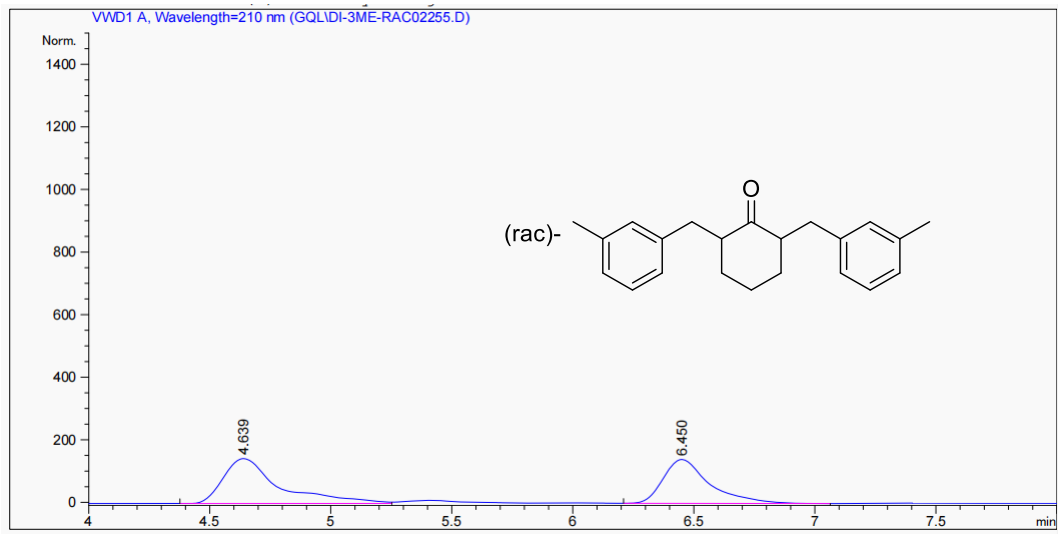


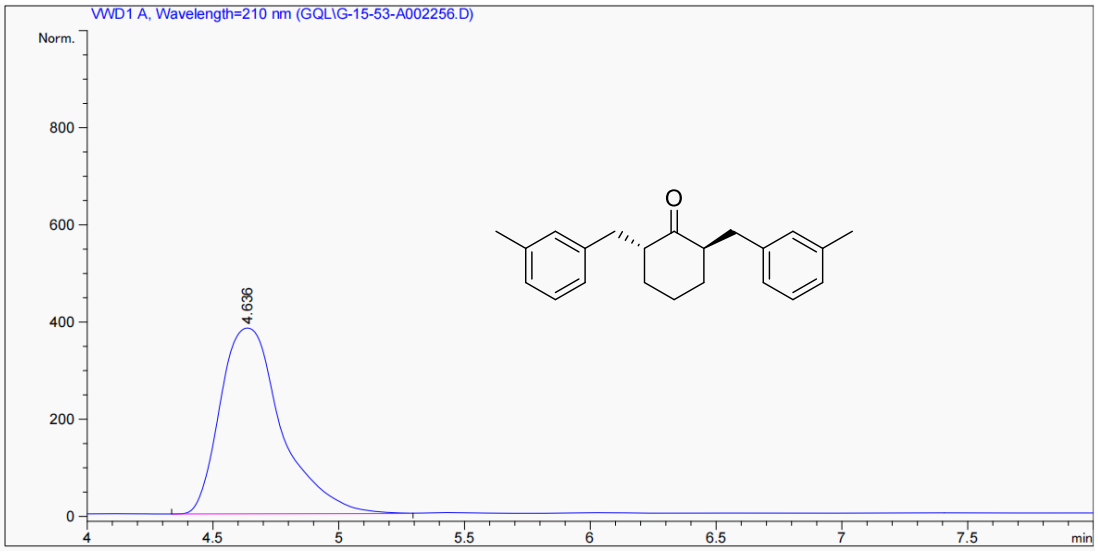


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.398	BV	0.1894	6735.31982	522.56036	100.0000
Totals :				6735.31982	522.56036	

(+)-(2*R*,6*R*)-2,6-Bis(3-methylbenzyl)cyclohexan-1-one (**4d**)

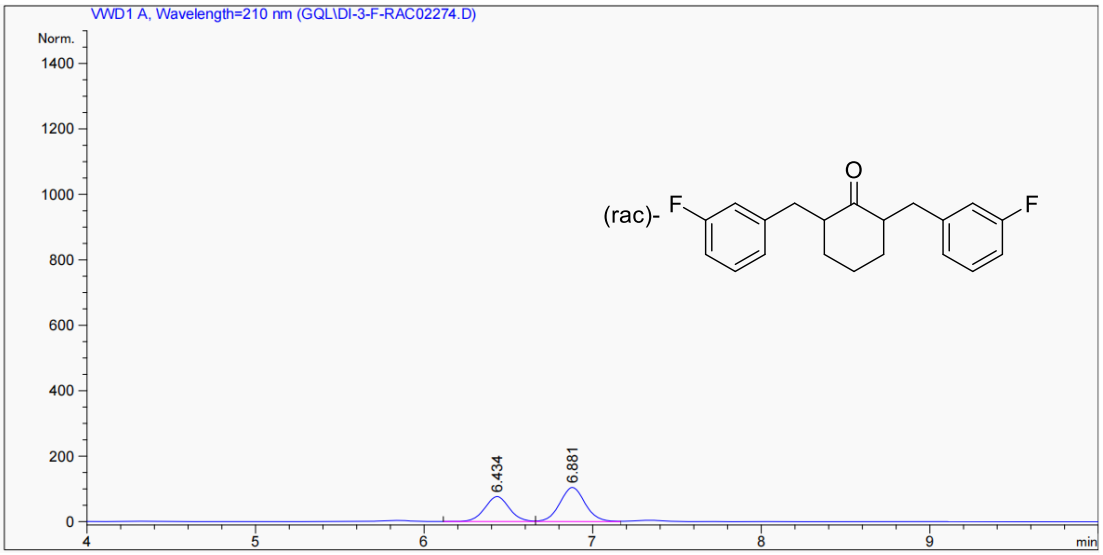


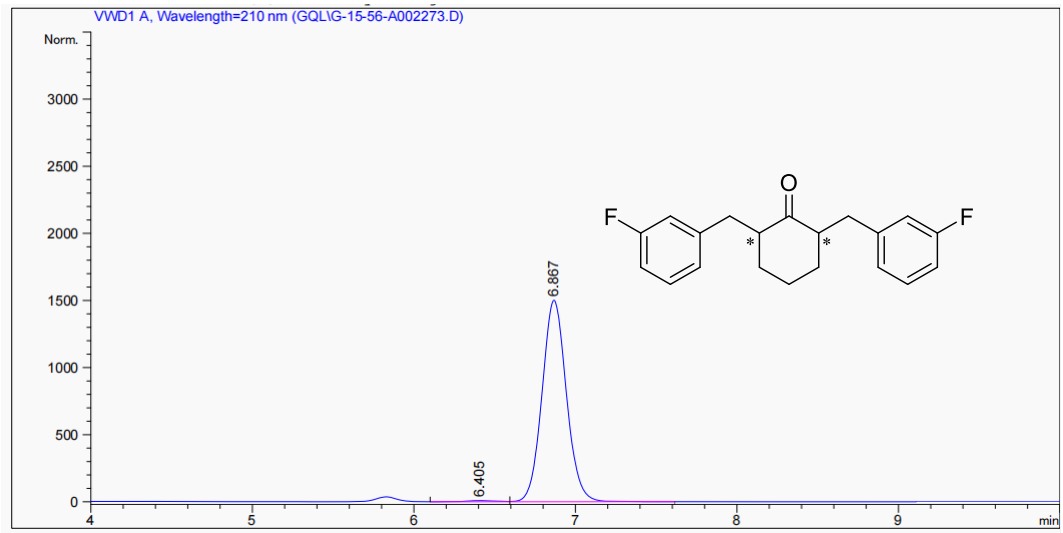


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.636	BV	0.2599	6487.35986	382.41516	100.0000
Totals :				6487.35986	382.41516	

2,6-Bis(3-fluorobenzyl)cyclohexan-1-one (**4e**)

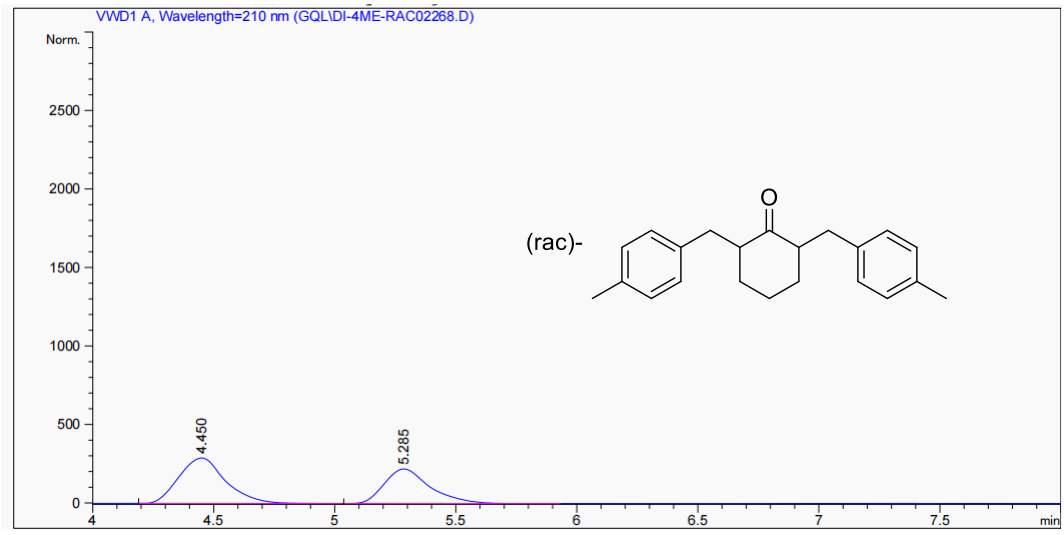


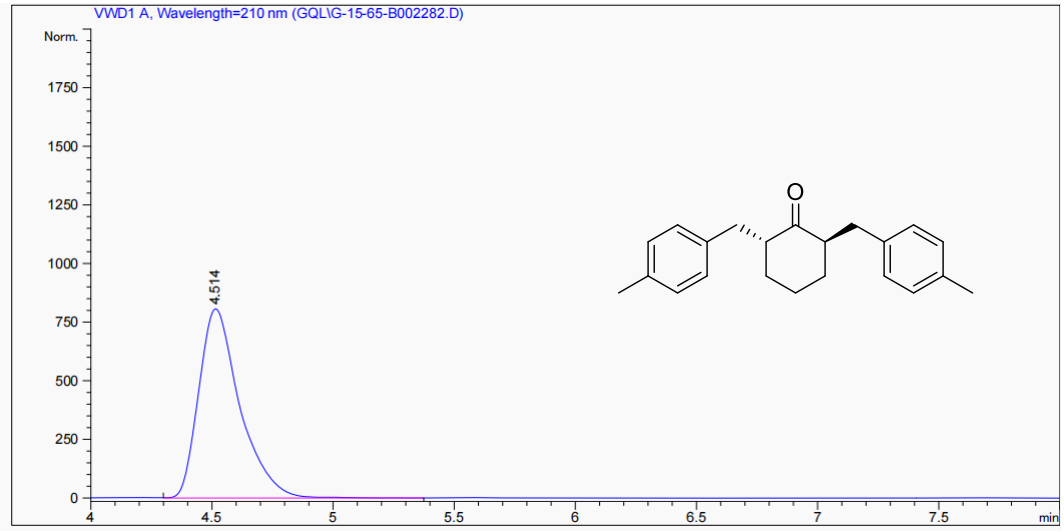


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.405	VV	0.1817	104.22371	8.34756	0.6574
2	6.867	VB	0.1614	1.57496e4	1500.91772	99.3426
Totals :				1.58539e4	1509.26528	

(+)-(2*R*,6*R*)-2,6-Bis(4-methylbenzyl)cyclohexan-1-one (**4f**)

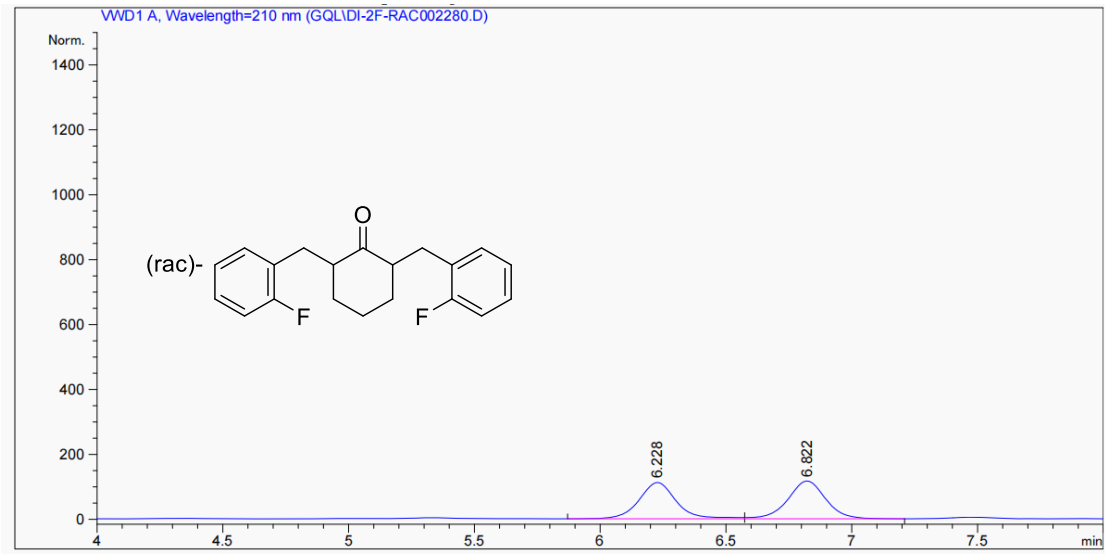


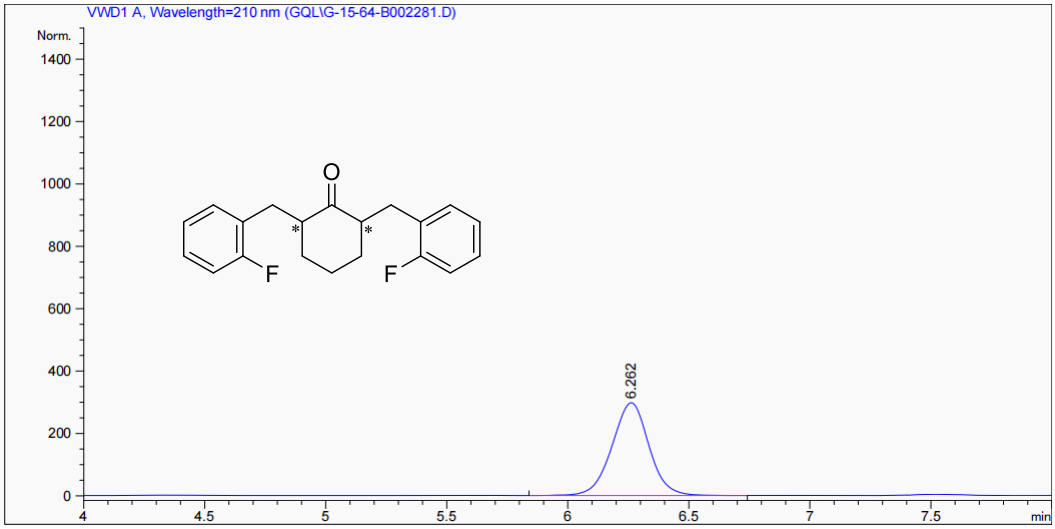


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.514	VV	0.1775	9503.42480	806.51422	100.0000
Totals :				9503.42480	806.51422	

2,6-Bis(2-fluorobenzyl)cyclohexan-1-one (**4g**)

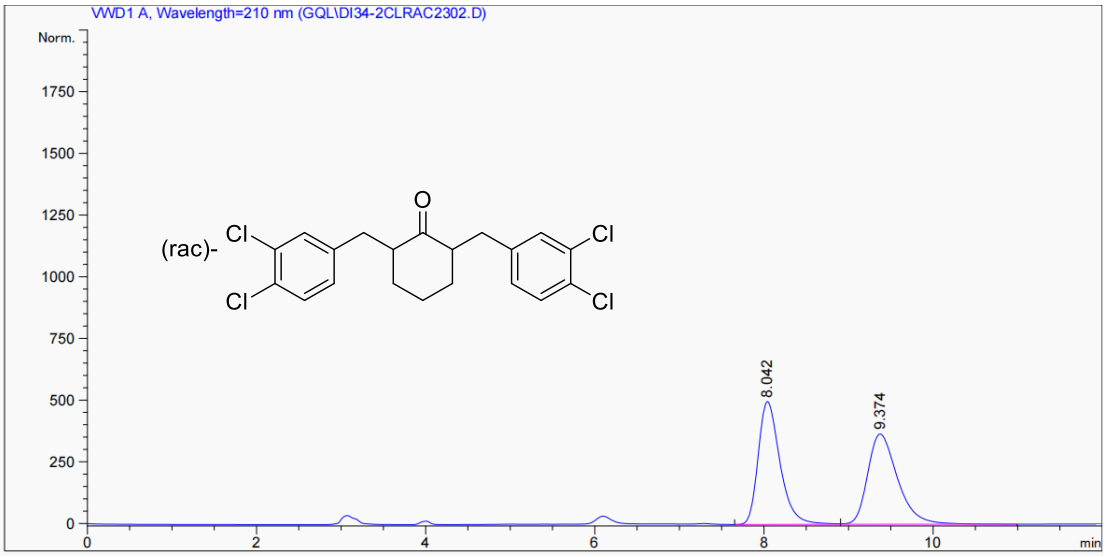


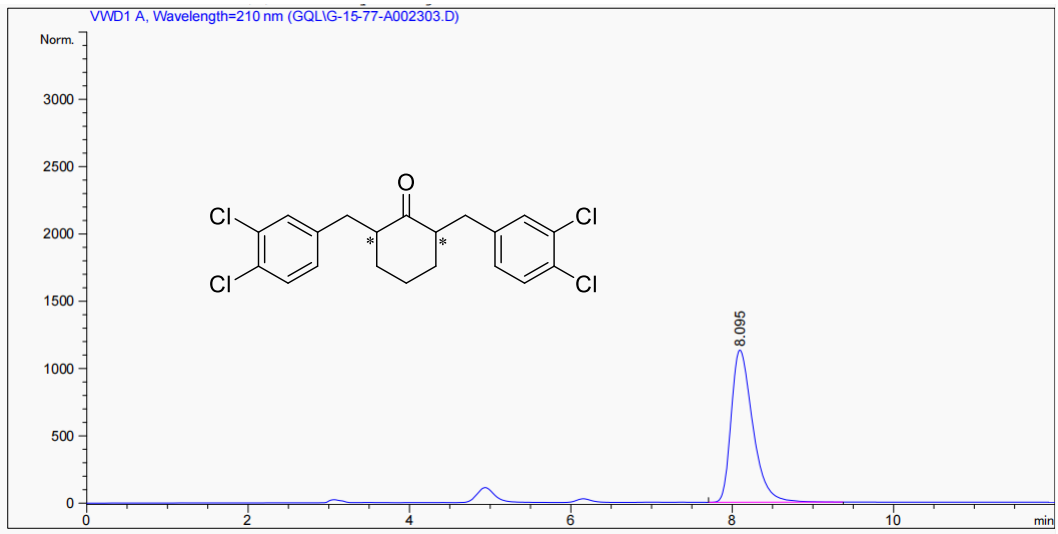


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.262	VB	0.1636	3174.77222	297.36655	100.0000
Totals :				3174.77222	297.36655	

2,6-Bis(3,4-dichlorobenzyl)cyclohexan-1-one (**4h**)

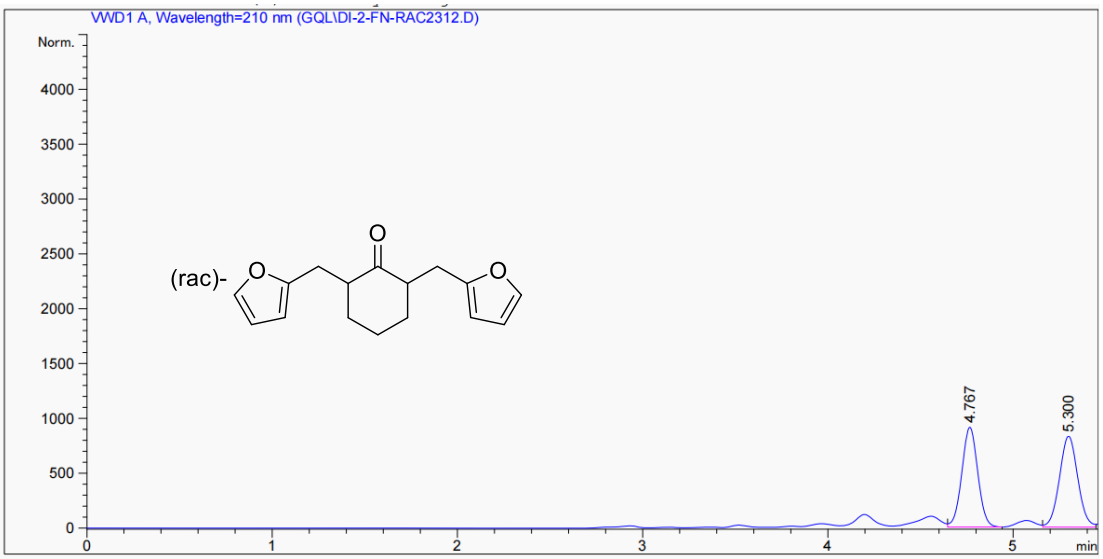


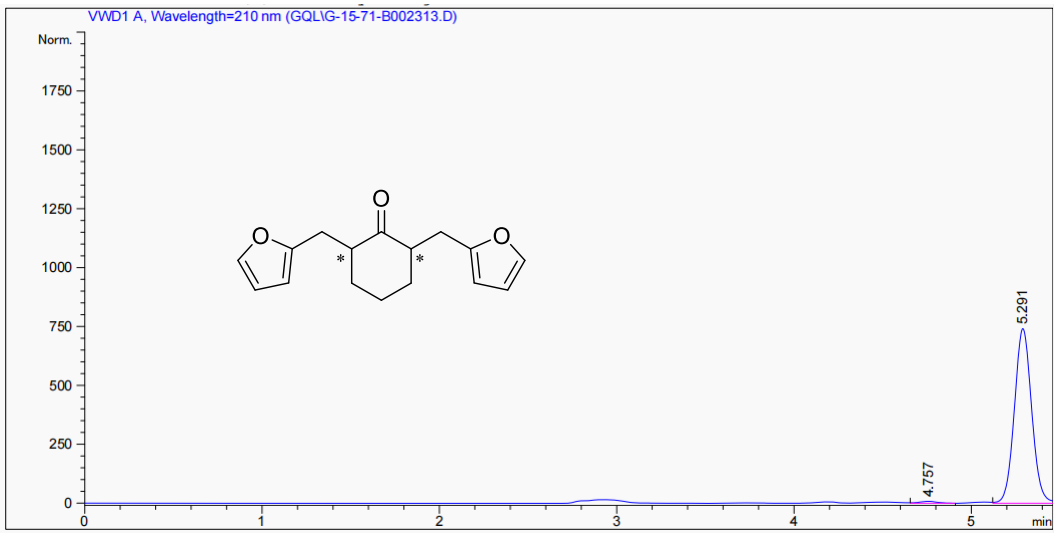


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.095	BB	0.2846	2.09887e4	1130.39001	100.0000
Totals :				2.09887e4	1130.39001	

2,6-Bis(furan-2-ylmethyl)cyclohexan-1-one (**4i**)

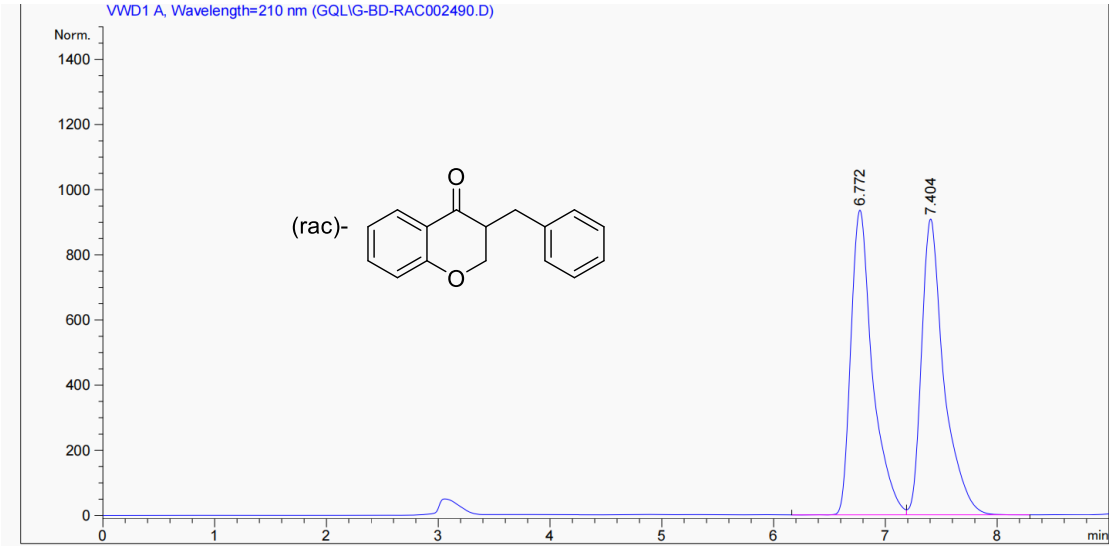


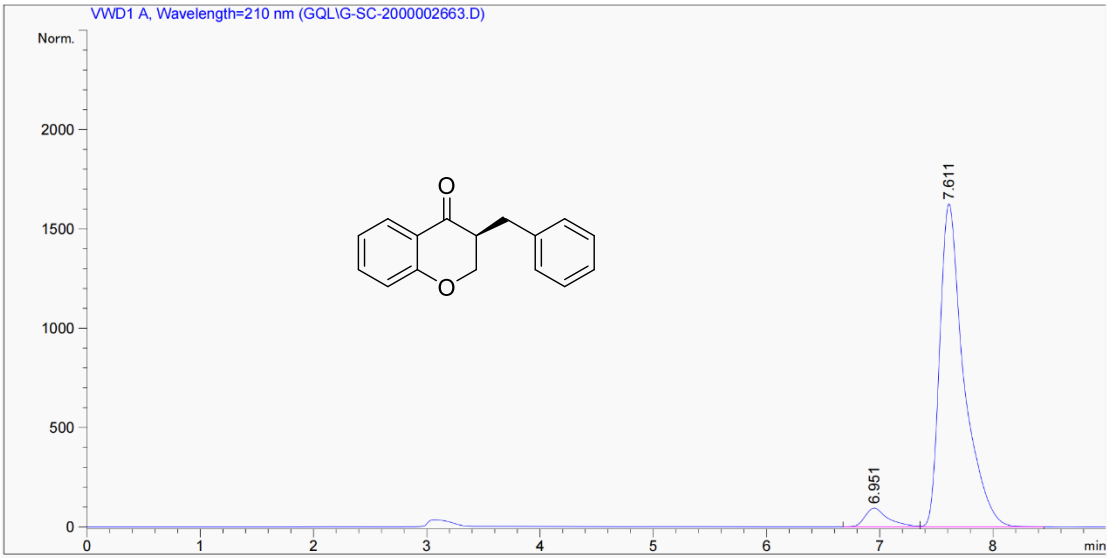


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.757	VB	0.1042	53.67749	7.90409	1.0594
2	5.291	VV	0.1049	5013.00439	741.34015	98.9406
Totals :				5066.68189	749.24424	

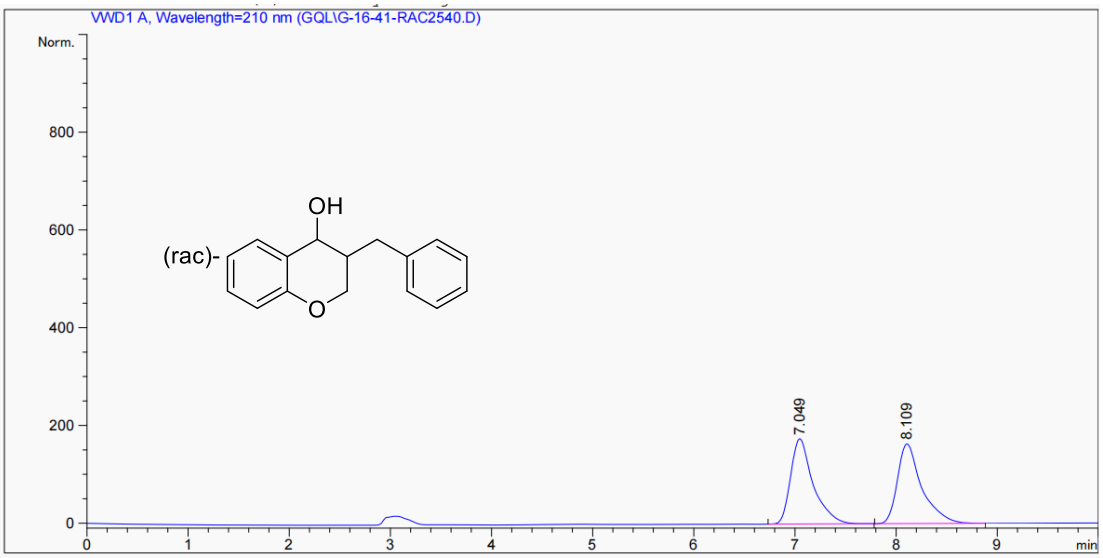
Gram scale experiment

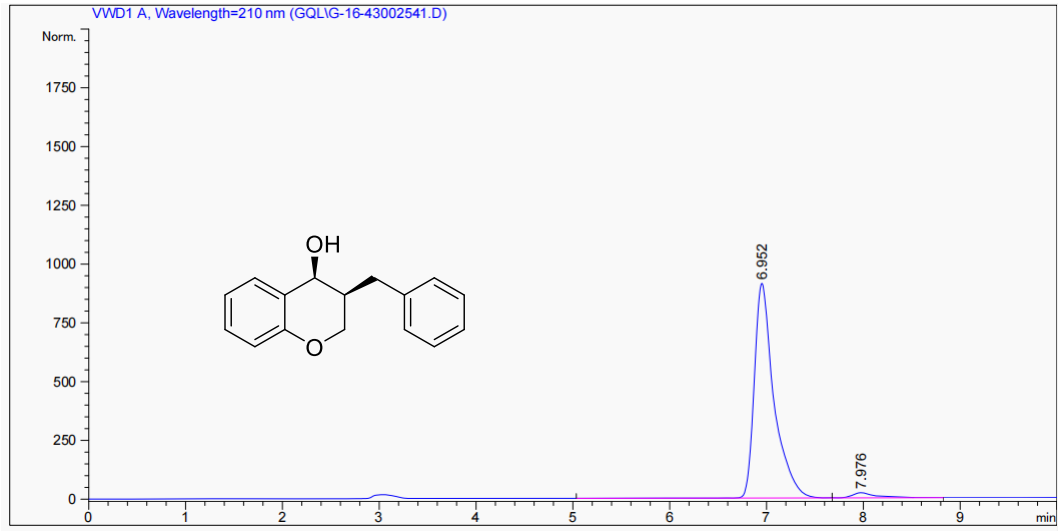




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.951	BV	0.2051	1301.94519	93.71024	5.1502
2	7.611	VB	0.2172	2.39775e4	1624.64355	94.8498
Totals :				2.52795e4	1718.35380	

(3*S*,4*S*)-3-Benzylchroman-4-ol (**5**)

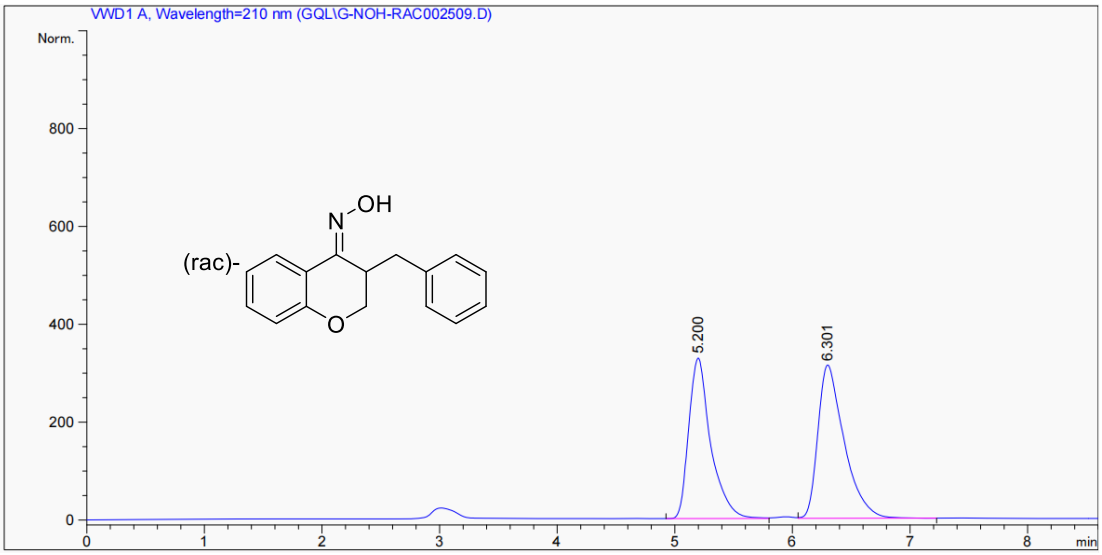


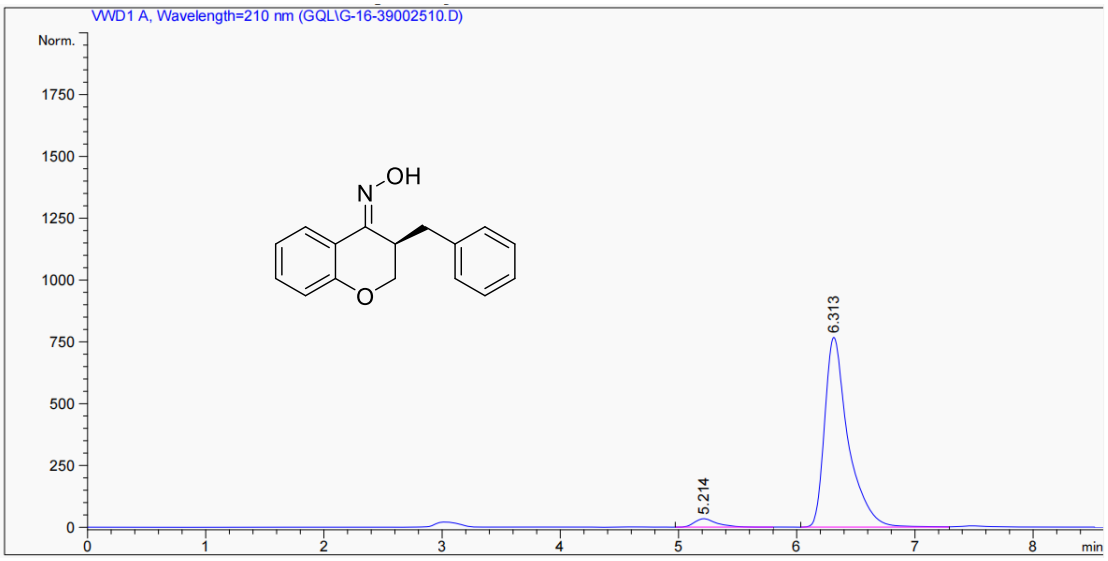


Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.952	BV	0.2068	1.28229e4	913.04211	97.0524
2	7.976	VB	0.2526	389.45102	21.99629	2.9476
Totals :				1.32124e4	935.03840	

(*R*,*E*)-3-benzylchroman-4-one oxime (**6**)






```
Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.214 BV    0.1986  453.10150   34.20211   4.0865
   2   6.313 VV    0.2036 1.06348e4   767.71741  95.9135

Totals :                  1.10879e4   801.91952
```

8. X-ray crystallographic analysis of compound 2a.

The structure of **2a** was determined by the X-ray diffraction analysis of single crystal, which recrystallized from a mixed solution of dichloromethane and *n*-hexane.

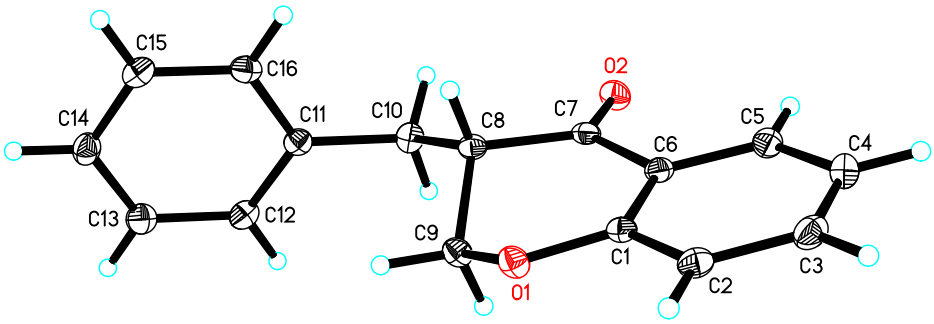


Table S1. Crystal Data and Experimental Parameters for Compound 2a.

Compound	**2a**
Empirical formula	$C_{16}H_{14}O_2$
Formula weight	238.27
Crystal system	Monoclinic
Space group	P 1 21 1
a (Å)	12.1858(3)
b (Å)	5.49205(11)
c (Å)	18.8339(4)
α (deg)	90
β (deg)	106.712(2)
γ (deg)	90
V (Å^3)	1207.22(5)
Z	4
F(000)	504
size (mm)	0.4 x 0.2 x 0.2
2θ range (deg)	3.787 to 75.898
Reflections collected	13010
Reflections unique	4789

abscorr (T_{max}, T_{min})	1.00, 0.91
Data / restraints / parameters	4789 / 1 / 325
R	0.0373
R_w	0.0987
R_{all}	0.0390
Absolute structure parameter	0.11(9)
CCDC	2417594