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Direct Enantioselective Allylic Substitution of 4-Hydroxycoumarin Derivatives with Branched Allylic Alcohols via Iridium Catalysis

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I General information:

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash column chromatography was performed using Merck aluminium oxide90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-d (7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-d (77.0, triplet).

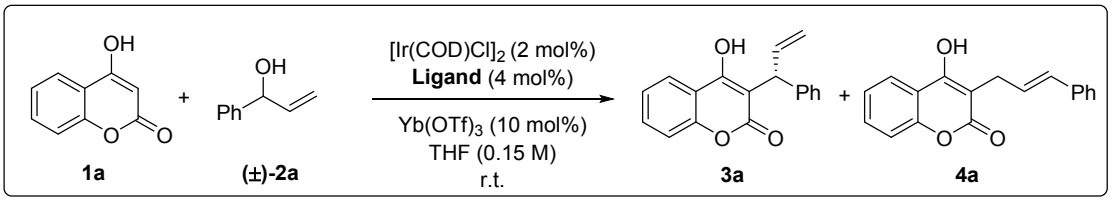
Enantiomeric excesses were determined by high performance liquid chromatography (HPLC) analysis on a chiral stationary phase, CHIRALCEL AD-H, CHIRALCEL OD-H or CHIRALCEL IC. Optical rotations were measured in $CHCl_3$ on a Schmidt + Haensdchpolarimeter (Polartronic MH8) with a 10 cm cell (*c* given ing/100 mL).

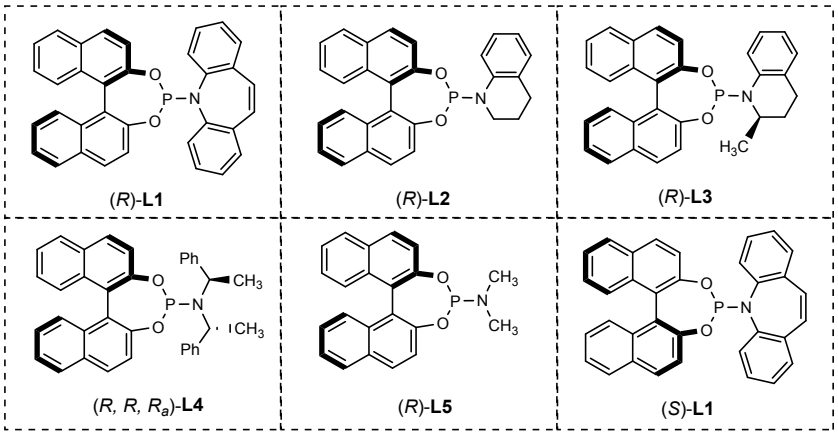
High resolution mass spectrometry (HRMS) was recorded on QTOF perimer for ESI^+.

The racemic products used to determine the *ee* values were synthesized by using equivalent mixture of both enantiomers of the chiral ligand.

II Optimization of reaction condition

Table S1. Screening of various chiral phosphoramidite ligands.[a]

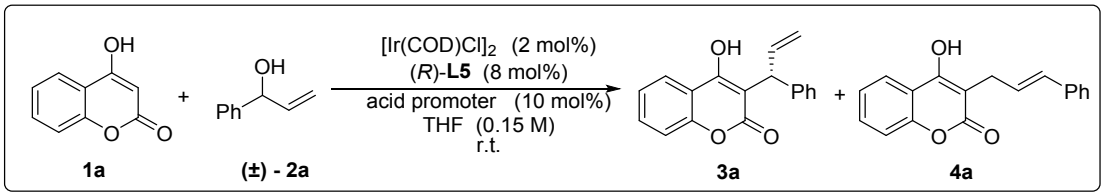




entry	ligand	time (h)	yield (%)[b]	**3a**/**4a**[c]	*ee* (%)[d]
1	(*R*)-**L2**	18	< 5	-	-
2	(*R*)-**L3**	18	< 5	-	-
3	(*R, R, Ra*)-**L4**	18	8	-	n.d.
4	(*R*)-**L5**	18	n.r.	-	-
5[e]	(*R*)-**L1**	18	93	> 25/1	>99
6[e]	(*S*)-**L1**	18	92	> 25/1	>-99

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 4 mol% of Ligand, 10 mol% of $Yb(OTf)_3$, 0.2 mmol of **1a**, 0.4 mmol of **2a** in THF (0.15 M) at room temperature. [b]Isolated yields of **3a**. [c]Measured by ^1H NMR. [d]Determined by HPLC analysis. [e]8 mol% of Ligand. n.r. = no reaction, n.d. = not determined.

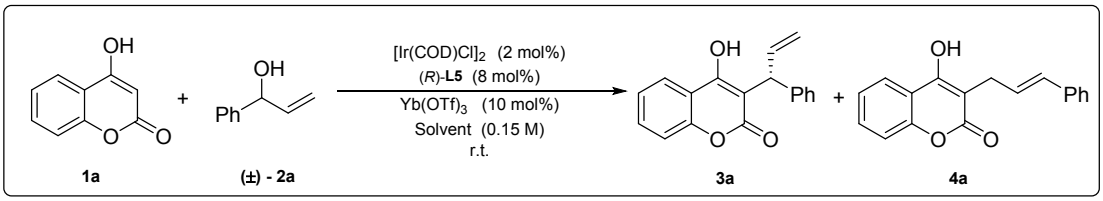
Table S2. Comparison of various acid promoters.[a]



entry	acid	time (h)	yield (%)[b]	**3a**/**4a**[c]	*ee* (%)[d]
1	none	24	n.r.	-	-
2	$(PhO)_2POOH$	18	78	> 25/1	> 99
3	$TsOH \cdot H_2O$	24	50	> 25/1	93
4	(+/-) - CSA	24	11	n.d.	n.d.
5	CF_3COOH	24	61	> 25/1	> 99
6	$La(OTf)_3$	24	39	> 25/1	> 99
7	$Cu(OTf)_2$	36	< 5	-	-
8	$Sc(OTf)_3$	36	53	> 25/1	98
9	$Zn(OTf)_2$	36	56	> 25/1	99
10	$In(OTf)_3$	36	< 5	-	-
11	$Yb(OTf)_3$	18	93	> 25/1	> 99
12	$Yb(OTf)_3$	24	94	> 25/1	> 99
13[e]	$Yb(OTf)_3$	18	83	> 25/1	> 99
14[f]	$Yb(OTf)_3$	18	78	> 25/1	> 99

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of Ligand, 10 mol% of $Yb(OTf)_3$, 0.2 mmol of **1a**, 0.4 mmol of **2a** in THF (0.15 M) at room temperature. [b]Isolated yields of **3a**. [c]Measured by ^1H NMR. [d]Determined by HPLC analysis. [e]5 mol% of $Yb(OTf)_3$. [f]20 mol% of $Yb(OTf)_3$. (+/-) - CSA = (+/-) - camphorsulfonic acid, n.r. = no reaction, n.d. = not determined.

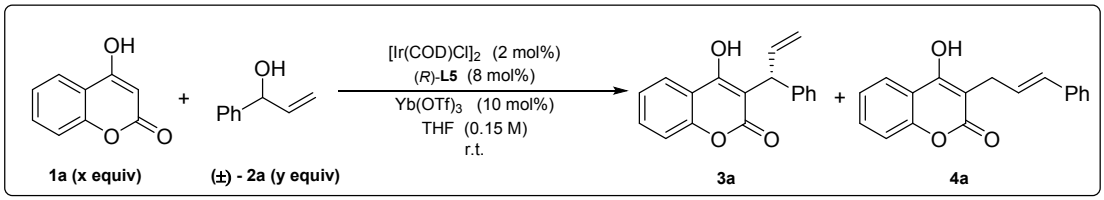
Table S3. Comparison of various solvents.[a]



entry	solvent	Time (h)	yield (%)[b]	**3a**/**4a**[c]	*ee* (%)[d]
1	DCM	18	66	> 25/1	96
2	DCE	18	57	> 25/1	96
3	Dioxane	18	26	> 25/1	97
4	Et_2O	18	91	> 25/1	97
5	Toluene	24	71	> 25/1	98
6	H_2O	18	74	> 25/1	84
7	DMF	24	< 10	-	-
8	$CHCl_3$	24	< 5	-	-
9	THF	18	93	> 25/1	> 99
10[e]	THF	24	82	> 25/1	> 99
11[f]	THF	18	89	> 25/1	> 99

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of Ligand, 10 mol% of $Yb(OTf)_3$, 0.2 mmol of **1a**, 0.4 mmol of **2a** in THF (0.15 M) at room temperature. [b]Isolated yields of **3a**. [c]Measured by ^1H NMR. [d]Determined by HPLC analysis. [e]1 mol% of $[Ir(COD)Cl]_2$, 4 mol% of Ligand. [f]0.2 M of THF.

Table S4. Comparison of the equavalent of starting materials.[a]



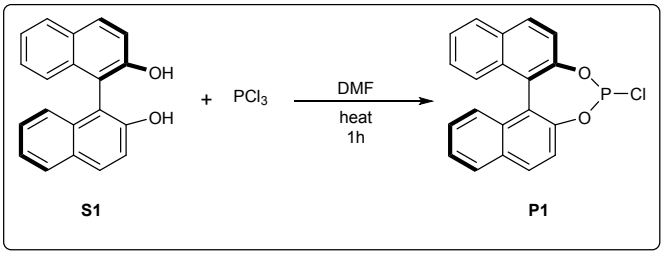
entry	x / y	time (h)	yield (%)[b]	**3a**/**4a**[c]	*ee* (%)[d]
1	1.0 / 1.2	18	63	> 25/1	93
2	1.0 / 1.5	18	68	> 25/1	97
3	1.0 / 2.0	18	93	> 25/1	> 99
4	2.0 / 1.0	24	36	> 25/1	88
5	1.5 / 1.0	24	45	> 25/1	89

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of Ligand, 10 mol% of $Yb(OTf)_3$, 0.2 mmol of **1a**, 0.4 mmol of **2a** in THF (0.15 M) at room temperature. [b]Isolated yields of **3a**. [c]Measured by ^1H NMR. [d]Determined by HPLC analysis.

Ⅲ Experimental section

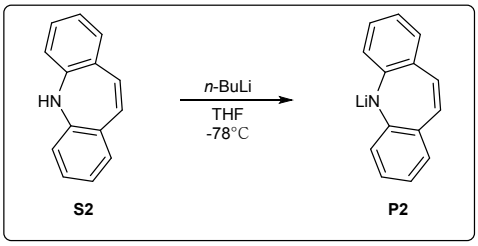
3.1. General procedure for the synthesis of phosphoramidite ligand (*R*)-L1:

Synthesis of **P1:**



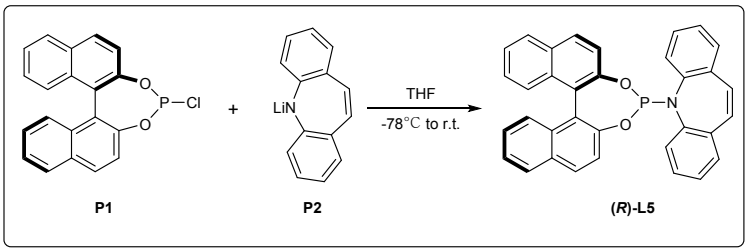
To an oven-dried flask charged with stir bar and **S1** (1.145g, 4.0 mmol), then refilled with argon 3 times. PCl_3 (5.24 mL, 60.0 mmol, 15.0 equiv) and DMF (9.2 μL, 0.12 mmol, 0.03 equiv) were added sequentially. The system was heated to 50-55°C smoothly and stirred for 1 hour to give colorless oil. After reaction completion, the residue was removed under the reduced pressure to afford product **P1** with white foam.

Synthesis of product **P2:**



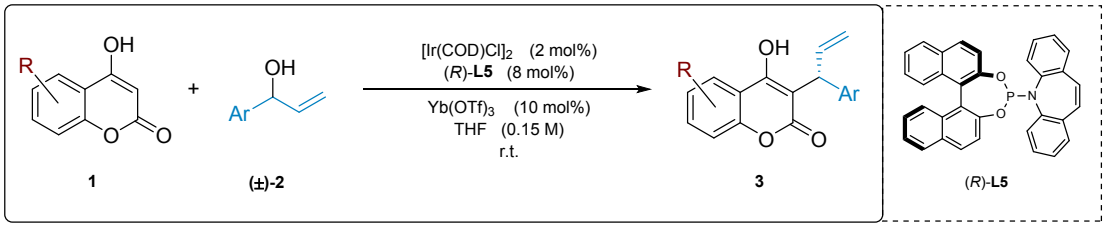
To an oven-dried flask charged with stir bar and **S2** (0.85 g, 4.4 mmol, 1.1 equiv), then refilled with argon 3 times. Anhydrous THF (25 mL) was added and the solution was cooled at -78°C. The reaction was stirred for 1 hour after *n*-BuLi (1.84 mL, 4.4 mmol, 1.1 equiv, 2.0 M in hexane) was added dropwise via syringe to afford the solution of product **P2**.

Synthesis of product (*R*)-**L1:**



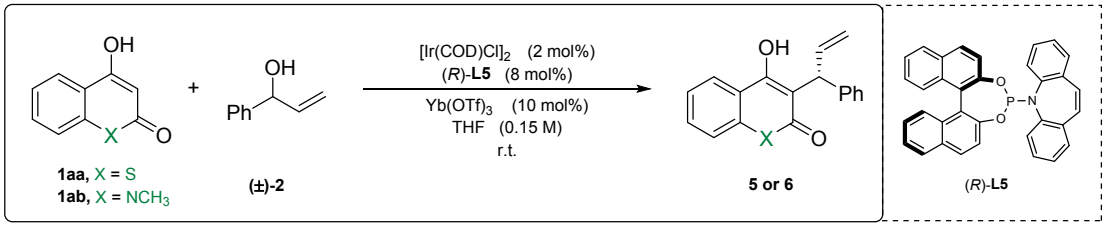
The above product **P1** was dissolved in anhydrous THF (20 mL) and added dropwise to the solution of **P2** by syringe. The dark blue homogeneous solution was raised to ambient temperature slowly and stirred for 6-8 hours. Afterwards, the organics was quenched by water. The mixture was extracted with EtOAc 3 times, then separated. The organic mixture was washed with water and brine, then dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography with eluent (PE/EA/Et_3N = 20/1/0.1% to 8/1/0.1%) to give the final product, then recrystallized with DCM/pentane to afford the high ee value (>99%) compound (R)-**L1**. The characterization data of compound (R)-**L1** was reported as reference.

3.2. General procedure A: the synthesis of compound 3a-3u:



An oven-dried flask fitted with septum and charged with stir bar, $[Ir(COD)Cl]_2$ (0.004 mmol, 2 mol%) and (*R*)-**L1** (0.016 mmol, 8 mol%) were then added. The system was refilled with argon 3 times. To this flask was added anhydrous THF (1.3 mL, 0.15 M) with syringe. The mixture was stirred at ambient temperature for 30 min. Afterwards, the orange solution was followed by the addition of **1** (0.2 mmol, 1.0 equiv), **(±)-2** (0.4 mmol 2.0 equiv) and $Yb(OTf)_3$ (0.02 mmol, 10 mol%). The reaction was stirred for 18 hours at room temperature. After completion, the mixture was directly concentrated under the reduced pressure. The ratio of branched and linear compounds was determined by ^1H NMR of the crude organic mixture. The residue was purified by silica gel column chromatography rapidly to afford the desired compounds. The characterization data of the products **3a-3u** are listed as follows.

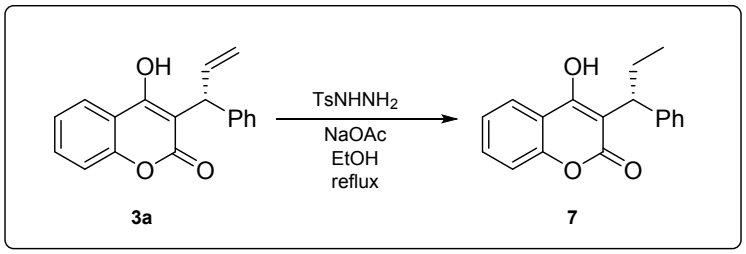
3.3. General procedure B: the synthesis of compound 5 or 6:



An oven-dried flask fitted with septum and charged with stir bar, $[Ir(COD)Cl]_2$ (0.004 mmol, 2 mol%) and (*R*)-**L1** (0.016 mmol, 8 mol%) were then added. The system was refilled with argon 3 times. To this flask was added anhydrous THF (1.3 mL, 0.15 M) with syringe. The mixture was stirred at ambient temperature for 30 min. Afterwards, the orange solution was followed by the addition of **1aa** or **1ab** (0.2 mmol, 1.0 equiv), **(±)-2** (0.4 mmol 2.0 equiv) and $Yb(OTf)_3$ (0.02 mmol, 10 mol%). The reaction was stirred for 24 hours at room temperature. After completion, the mixture was directly concentrated under the reduced pressure. The ratio of branched and linear compounds was determined by ^1H NMR of the crude organic mixture. The residue was purified by

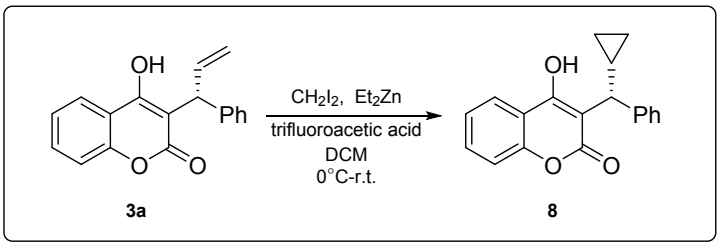
silica gel column chromatography rapidly to afford the desired compounds. The characterization data of the product **5** or **6** are listed as follows.

3.4. General procedure for olefin reduction of compound 7:



Compound 7 was synthesized according to a literature procedure. A mixture of compound **3a** (27.8 mg, 0.1 mmol), $TsNHNH_2$ (93.1 mg, 0.5 mmol, 5.0 equiv) and NaOAc (41.0 mg, 0.5 mmol, 5.0 equiv) was added ethanol (2 mL, 0.05 M). The mixture was refluxed for 6 hours. Afterwards, the solvent was removed in vacuo, and the crude product was quenched with saturated NH_4Cl solution (2 mL) and extracted with EtOAc (5 mL) 3-5 times. The combined organics was washed with water and brine, then separated, dried over anhydrous Na_2SO_4 and evaporated under the reduced pressure. The residue was purified by silica gel column chromatography to give the desired product **7**. The characterization data of the product **7** is listed as follows.

3.5. General procedure for cyclopropanation of compound **8**:

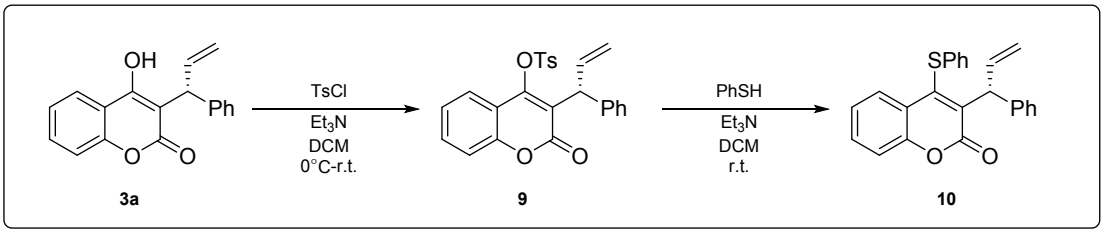


To an oven-dried round bottom fitted with septum and charged with stir bar, then refilled with argon 3 times. Et_2Zn (0.5 mL, 0.5 mmol, 5.0 equiv, 1.0 M in hexane) and anhydrous DCM (1 mL) were added into the bottom, the solution was then cooled at 0 °C. A solution of trifluoroacetic acid (0.5 mmol, 5.0 equiv) in anhydrous DCM (0.25 mL) was added dropwise into the above system over 5 min via syringe. Upon stirring for 20 min, a solution of CH_2I_2 (134 mg, 0.5 mmol, 5.0 equiv) in anhydrous DCM (0.25 mL) was added dropwise into the system over 10 min via syringe.

After

completion, a solution of compound **3a** (27.8 mg, 0.5 mmol, 5.0 equiv) in anhydrous DCM (0.25 mL) was added dropwise into the system over 10 min, and the reaction was rise to room temperature slowly and stirred for additional 4-6 hours. The reaction mixture was quenched with saturated NH_4Cl solution and extracted with DCM 3 times. After separated, the combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated under the reduced pressure to give the desired compound **8** of quantitative yield as colorless oil without further purification. The characterization data of the product **8** is listed as follows.

3.6. General procedure for functionalization of compound **9** & **10**:

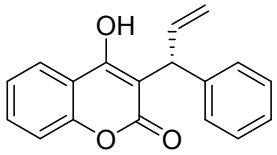


To a solution of starting material **3a** (55.7 mg, 0.2 mmol) in anhydrous DCM (4 mL, 0.05 M) was added into triethylamide (0.4 mmol, 2.0 equiv). After stirring for 10-15 min at 0 °C, TsCl (76.3 mg, 0.2 mmol, 2.0 equiv) was then added. The reaction was then removed to ambient temperature and stirred for another 4-6 hours. After completion, the crude product was directly purified by flash column chromatography on silica gel to afford the corresponding product **9**. The characterization data of the product **9** is listed as follows.

To a solution of compound **9** (43.2 mg, 0.1 mmol) in DCM (1 mL, 0.1 M) was added into triethylamide (0.11 mmol, 1.1 equiv). Thiophenol (0.11 mmol, 1.1 equiv) was then added into the above solution before the reaction was stirred for 6-8 hours. Afterwards, the solvent was directly evaporated in vacuo and purified by flash column chromatography on silica gel to give the desired compound **10** as colorless oil. The characterization data of the product **10** is listed as follows.

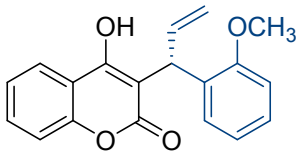
Ⅳ Characterization of products:

(*R*)-4-hydroxy-3-(1-phenylallyl)-2*H*-chromen-2-one



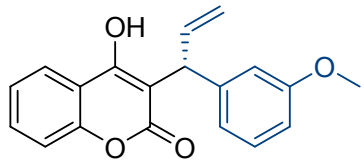
3a, white solid, 51.6 mg, yield 93%; m.p. = 140.6-141.4 °C; $[\alpha]_D^{20}$ = -31.5 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9 Hz, 1H), 7.57-7.51 (m, 1H), 7.40-7.25 (m, 7H), 7.01(bs, 1H), 6.51-6.41 (m, 1H), 5.53-5.47 (dt, *J* = 10.3 Hz, 1H), 5.34-5.30 (m, 1H), 5.24-5.17 (dt, *J* = 17.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 161.0, 152.7, 138.7, 137.7, 132.2, 129.3, 128.2, 127.7, 123.9, 123.1, 119.4, 116.5, 115.9, 105.6, 44.7;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 11.515 min, t_r (minor) = 10.022 min; HRMS (ESI) calcd for $C_{18}H_{15}O_3$ $(M+H)^+$: 279.1016, Found: 279.1020.

(*R*)-4-hydroxy-5-methoxy-3-(1-phenylallyl)-2*H*-chromen-2-one



3b, white solid, 60.4 mg, yield 98%; m.p. = 134.5-136.2 °C; $[\alpha]_D^{20}$ = +41.1 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.83 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.51-7.46 (m, 1H), 7.30-7.21 (m, 3H), 7.01 (td, *J* = 7.5, 1.2 Hz, 1H), 6.49 (m, 1H), 5.36-5.32 (m, 1H), 5.29-5.25 (m, 1H), 5.13-5.07 (m, 1H), 3.92 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 159.4, 154.7, 151.6, 135.7, 130.7, 129.9, 127.6, 122.7, 122.3, 121.1, 115.3, 115.2, 115.1, 110.4, 104.9, 54.9, 39.7;
>99% *ee* as determined by HPLC (Chiralcel OD-H, 95:5 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 14.755 min, t_r (minor) = 17.825 min; HRMS (ESI) calcd for $C_{19}H_{17}O_4$ $(M+H)^+$: 309.1121, Found: 309.1124.

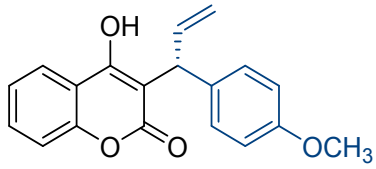
(*R*)-4-hydroxy-3-(1-(3-methoxyphenyl)allyl)-2*H*-chromen-2-one



3c, white solid, 56.1 mg, yield 91%; m.p. = 133.2-133.5 °C; $[\alpha]_D^{20}$ = +19.0 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.57-7.51 (m, 1H), 7.34-7.24 (m, 3H), 7.05-6.93 (m, 1H), 6.91-6.88 (m, 1H), 6.87-6.82 (m, 1H), 6.45-6.37 (m, 1H), 5.50-5.45 (m, 1H), 5.32-5.27 (m, 1H), 5.26-5.20 (m, 1H), 3.79 (s, 3H);

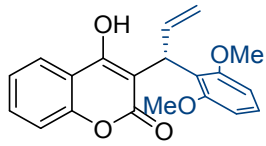
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 160.0, 159.3, 151.7, 139.7, 136.0, 131.1, 129.4, 122.9, 122.1, 119.1, 118.2, 115.5, 114.8, 113.1, 111.9, 104.5, 54.2, 43.6;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 15.448 min, t_r (minor) = 17.721 min;
HRMS (ESI) calcd for $C_{19}H_{17}O_4$ $(M+H)^+$: 309.1121, Found: 309.1124.

(*R*)-4-hydroxy-3-(1-(4-methoxyphenyl)allyl)-2*H*-chromen-2-one



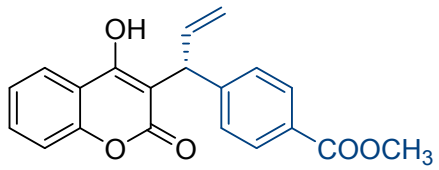
3d, colorless oil, 58.0 mg, yield 94%; $[\alpha]_D^{20}$ = -21.4 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56-7.49 (m, 1H), 7.32-7.23 (m, 1H), 7.22-7.14 (m, 1H), 6.90-6.87 (m, 2H), 6.48-6.39 (m, 1H), 5.44 (dt, *J* = 10.2, 1.5 Hz, 1H), 5.25-5.18 (m, 2H), 3.80 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 160.9, 159.1, 152.7, 137.8, 132.1, 130.6, 129.3, 123.9, 123.1, 119.1, 116.5, 115.9, 114.7, 105.8, 55.3, 43.0;
99% *ee* as determined by HPLC (Chiralcel AD-H, 80:20 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 7.539 min, t_r (minor) = 5.763 min;
HRMS (ESI) calcd for $C_{19}H_{17}O_4$ $(M+H)^+$: 309.1121, Found: 309.1121.

(*R*)-3-(1-(2,6-dimethoxyphenyl)allyl)-4-hydroxy-2*H*-chromen-2-one



3e, colorless oil, 59.6 mg, yield 88%; $[\alpha]_D^{20}$ = +6.2 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50-7.44 (m, 1H), 7.29-7.20 (m, 3H), 6.63 (d, *J* = 8.3 Hz, 2H), 6.25-6.17 (m, 1H), 5.92-5.88 (m, 1H), 5.14 (ddd, *J* = 10.3, 2.8, 1.2 Hz, 1H), 4.99 (ddd, *J* = 17.3, 2.6, 1.3 Hz, 1H), 3.89 (s, 6H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 160.0, 157.0, 151.5, 136.0, 130.5, 127.6, 122.5, 122.2, 116.0, 115.5, 115.2, 112.1, 104.1, 103.5, 55.1, 34.0;
97% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 9.095 min, t_r (minor) = 7.678 min;
HRMS (ESI) calcd for $C_{20}H_{19}O_5$ $(M+H)^+$: 339.1227, Found:339.1221.

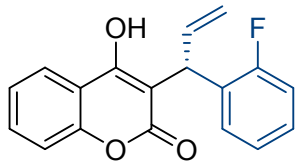
(*R*)-methyl-4-(1-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)allyl)benzoate



3f, white solid, 60.0 mg, yield 89%; m.p. = 125.9-127.1 °C; $[\alpha]_D^{20}$ = +93.8 (c = 0.4, $CHCl_3$);

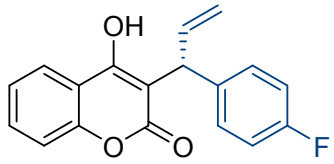
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.84-7.82 (m, 1H), 7.56 (d, *J* = 7.0 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.32-7.29 (m, 2H), 6.56-6.49 (m, 1H), 5.53 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.35-5.33 (m, 1H), 5.20-5.16 (m, 1H), 3.90 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 161.9, 160.3, 151.7, 143.3, 136.8, 131.3, 129.2, 128.2, 127.2, 123.0, 122.1, 119.0, 115.6, 114.7, 104.0, 51.1, 43.9;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1mL/min), t_r (minor) = 19.730 min, t_r (major) = 33.816 min;
HRMS (ESI) calcd for $C_{20}H_{17}O_5$ $(M+H)^+$: 337.0998, Found: 337.0995.

(*S*)-3-(1-(2-fluorophenyl)allyl)-4-hydroxy-2*H*-chromen-2-one



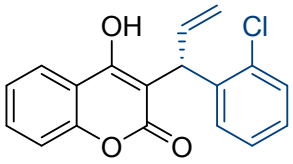
3g, white solid, 45.0 mg, yield 76%; m.p. = 156.9-157.7 °C; $[\alpha]_D^{20}$ = +196.5 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.57-7.52 (m, 1H), 7.50 (s, 1H), 7.37-7.25 (m, 4H), 7.16-7.11 (m, 1H), 7.10-7.05 (m, 1H), 6.54-6.46 (m, 1H), 5.54-5.50 (m, 1H), 5.46-5.41 (m, 1H), 5.22-5.15 (m, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 160.3, 159.9 (d, *J* = 245.4 Hz), 151.7, 136.1, 131.2, 128.9 (d, *J* = 4.1 Hz), 128.4 (d, *J* = 8.3 Hz), 124.6 (d, *J* = 14.4 Hz), 123.6 (d, *J* = 3.5 Hz), 122.9, 122.2, 118.2, 115.5, 115.0, 114.8 (d, *J* = 2.6 Hz), 102.9, 38.9 (d, *J* = 2.6 Hz);
^{19}F NMR (471 MHz, $CDCl_3$) δ -114.7;
94% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 12.030 min, t_r (minor) = 9.883 min;
HRMS (ESI) calcd for $C_{18}H_{14}O_3F$ $(M+H)^+$: 297.0921, Found: 297.0922.

(*R*)-3-(1-(4-fluorophenyl)allyl)-4-hydroxy-2*H*-chromen-2-one



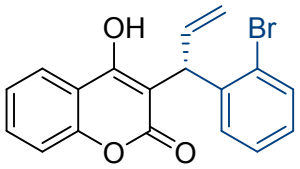
3h, colorless oil, 51.6 mg, yield 87%; $[\alpha]_D^{20}$ = -260.8 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57-7.52 (m, 1H), 7.41 (s, 1H), 7.32-7.25 (m, 4H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.54-6.45 (m, 1H), 5.53-5.47 (m, 1H), 5.28-5.24 (m, 1H), 5.22-5.16 (m, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0 (d, *J* = 6.9 Hz), 160.1 (d, *J* = 14.7 Hz), 151.7, 137.2, 133.5 (d, *J* = 3.2 Hz), 131.3, 128.8 (d, *J* = 8.0 Hz), 123.0, 122.1, 118.7, 115.5, 115.0, 114.8, 114.8, 104.5, 43.2;
^{19}F NMR (471 MHz, $CDCl_3$) δ -115.0;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 11.637 min, t_r (minor) = 8.825 min;
HRMS (ESI) calcd for $C_{18}H_{15}O_3$ $(M+H)^+$: 279.1016, Found: 279.1020.

(*S*)-3-(1-(2-chlorophenyl)allyl)-4-hydroxy-2*H*-chromen-2-one



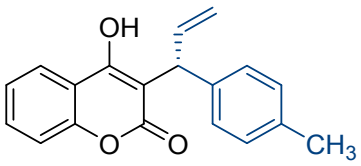
3i, white solid, 43.2 mg, yield 69%; m.p. = 169.0-169.4 °C; $[\alpha]_D^{20}$ = -75.8 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58-7.52 (m, 1H), 7.46-7.42 (m, 1H), 7.37-7.23 (m, 5H), 6.53-6.44 (m, 1H), 5.58-5.54 (m, 1H), 5.54-5.50 (m, 1H), 5.14-5.08 (m, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 161.6, 152.8, 137.3, 136.5, 134.9, 132.2, 130.6, 129.0, 128.8, 127.3, 124.0, 123.2, 119.6, 116.5, 115.7, 104.1, 42.9;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 11.429 min, t_r (minor) = 9.766 min;
HRMS (ESI) calcd for $C_{18}H_{14}O_3Cl$ $(M+H)^+$: 313.0626, Found: 313.0629.

(*S*)-3-(1-(2-bromophenyl)allyl)-4-hydroxy-2*H*-chromen-2-one



3j, white solid, 50.7 mg, yield 71%; m.p. = 176.9-178.1 °C; $[\alpha]_D^{20}$ = -56.9 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58-7.53 (m, 1H), 7.38-7.27 (m, 5H), 7.18 (td, *J* = 7.6, 1.9 Hz, 1H), 6.52-6.44 (m, 1H), 5.58-5.50 (m, 2H), 5.14-5.08 (m, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 160.5, 151.9, 137.2, 136.5, 133.0, 131.2, 128.2, 127.8, 127.0, 124.6, 122.9, 122.2, 118.8, 115.5, 114.7, 103.2, 44.5;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 11.650 min, t_r (minor) = 9.792 min;
HRMS (ESI) calcd for $C_{18}H_{14}O_3Br$ $(M+H)^+$: 357.0121, Found: 357.0128.

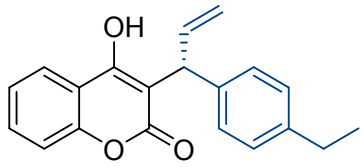
(*R*)-4-hydroxy-3-(1-(p-tolyl)allyl)-2*H*-chromen-2-one



3k, colorless oil, 53.8 mg, yield 87%; $[\alpha]_D^{20}$ = -316.8 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.56-7.51 (m, 1H), 7.32 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.29-7.23 (m, 4H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.88 (s, 1H), 6.46-6.37 (m, 1H), 5.50-5.45 (m, 1H), 5.30-5.26 (m, 1H), 5.24-5.19 (m, 1H), 2.34 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 160.9, 152.8, 137.5, 137.5, 135.8, 132.1, 130.1, 128.0, 123.9, 123.1, 119.1, 116.5, 115.9, 105.8, 44.3, 21.1;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic

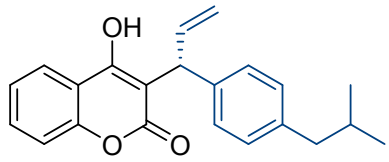
acid, 1 mL/min), t_r (major) = 15.150 min, t_r (minor) = 10.178 min;
HRMS (ESI) calcd for $C_{19}H_{17}O_3$ $(M+H)^+$: 293.1172, Found: 293.1173.

(*R*)-3-(1-(4-ethylphenyl)allyl)-4-hydroxy-2*H*-chromen-2-one



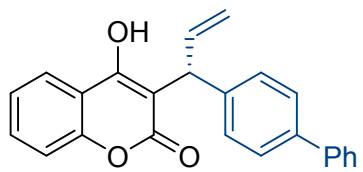
3l, light yellow oil, 54.5 mg, yield 89%; $[\alpha]_D^{20}$ = +11.4 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56-7.50 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.29-7.24 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 1H), 6.47-6.38 (m, 1H), 5.47 (dt, *J* = 10.3, 1.5 Hz, 1H), 5.32 – 5.26 (m, 1H), 5.22 (dt, *J* = 17.4, 1.6 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 159.9, 151.7, 142.8, 136.4, 135.0, 131.0, 127.8, 127.0, 122.9, 122.0, 118.0, 115.4, 114.9, 104.8, 43.3, 27.4, 14.4;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 14.669 min, t_r (minor) = 9.794 min;
HRMS (ESI) calcd for $C_{20}H_{19}O_3$ $(M+H)^+$: 307.1329, Found: 307.1328.

(*R*)-4-hydroxy-3-(1-(4-isobutylphenyl)allyl)-2*H*-chromen-2-one



3m, colorless oil, 65.5 mg, yield 98%; $[\alpha]_D^{20}$ = +60.1 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.56-7.50 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.29-7.24 (m, 3H), 7.18-7.12 (m, 2H), 6.93 (s, 1H), 6.47-6.38 (m, 1H), 5.46 (dt, *J* = 10.3, 1.5 Hz, 1H), 5.31-5.27 (m, 1H), 5.21(dt, *J* = 17.4, 1.5 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.90-1.80 (m, 1H), 0.89 (d, *J* = 6.7 Hz, 6H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 159.9, 151.7, 140.3, 136.4, 135.0, 131.0, 129.0, 126.8, 122.9, 122.1, 118.0, 115.4, 114.9, 104.8, 44.0, 43.3, 29.1, 21.3;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 11.123 min, t_r (minor) = 8.046 min;
HRMS (ESI) calcd for $C_{22}H_{23}O_3$ $(M+H)^+$: 335.1642, Found: 335.1651.

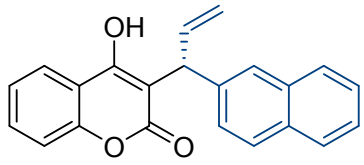
(*R*)-3-(1-([1,1'-biphenyl]-4-yl)allyl)-4-hydroxy-2*H*-chromen-2-one



3n, white solid, 69.5 mg, yield 98%; m.p. = 126.9-128.1 °C; $[\alpha]_D^{20}$ = -35.9 (c = 0.4, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59-7.52 (m, 5H), 7.45-7.39 (m, 4H),

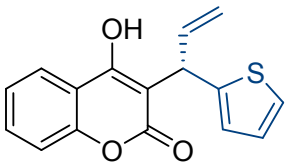
7.38-7.13 (m, 4H), 6.54-6.46 (m, 1H), 5.51 (dt, *J* = 10.2, 1.6 Hz, 1H), 5.37-5.33 (m, 1H), 5.29-5.23 (m, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 161.1, 152.7, 140.5, 140.4, 137.9, 137.8, 132.2, 128.8, 128.6, 127.8, 127.4, 127.0, 124.0, 123.1, 119.5, 116.5, 115.9, 105.6, 44.5;
99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 17.155 min, t_r (minor) = 12.914 min;
HRMS (ESI) calcd for $C_{24}H_{19}O_3$ $(M+H)^+$: 355.1329, Found: 355.1325.

(*R*)-4-hydroxy-3-(1-(naphthalen-2-yl)allyl)-2*H*-chromen-2-one



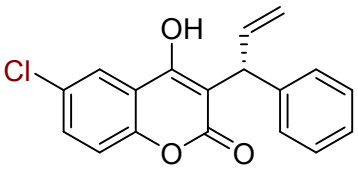
3o, colorless oil, 61.1 mg, yield 93%; $[\alpha]_D^{20}$ = +89.5 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.75 (m, 5H), 7.54-7.41 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.27-7.22 (m, 1H), 6.58-6.49 (m, 1H), 5.53-5.49 (m, 1H), 5.48-5.44 (m, 1H), 5.28-5.21 (m, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 161.2, 152.8, 137.2, 136.8, 133.5, 132.7, 132.2, 129.2, 127.9, 127.7, 126.7, 126.5, 126.0, 124.0, 123.1, 119.4, 116.5, 115.9, 105.5, 44.8;
99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 16.129 min, t_r (minor) = 12.885 min;
HRMS (ESI) calcd for $C_{22}H_{17}O_3$ $(M+H)^+$: 329.1172, Found: 329.1172.

(*S*)-4-hydroxy-3-(1-(thiophen-2-yl)allyl)-2*H*-chromen-2-one



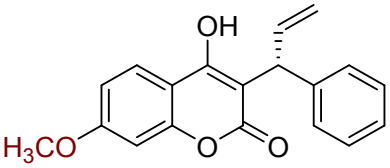
3p, brown solid, 50.6 mg, yield 89%; m.p. = 131.1-131.5 °C; $[\alpha]_D^{20}$ = -4.7 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.58-7.52 (m, 1H), 7.35-7.25 (m, 3H), 7.08-7.05 (m, 1H), 7.04-7.00 (m, 1H), 6.98-6.88 (m, 1H), 6.44-6.35 (m, 1H), 5.53-5.49 (m, 1H), 5.48-5.43 (m, 1H), 5.40-5.33 (m, 1H); For minor linear product: 7.13-7.11 (m, 1H), 6.78-6.71 (m, 1H), 6.64-6.57 (m, 1H), 6.19-6.12 (m, 1H), 3.67-3.60 (m, 2H). (branch/linear = 8.3/1)
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 161.2, 152.8, 142.8, 136.1, 132.3, 127.2, 126.3, 125.9, 124.0, 123.2, 118.7, 116.5, 115.8, 105.6, 40.2;
97% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 11.623 min, t_r (minor) = 10.354 min;
HRMS (ESI) calcd for $C_{16}H_{13}O_3S$ $(M+H)^+$: 285.0580, Found: 285.0579.

(*R*)-6-chloro-4-hydroxy-3-(1-phenylallyl)-2*H*-chromen-2-one



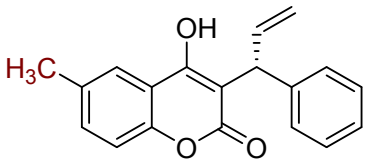
3q, white solid, 69.5 mg, yield 98%; m.p. = 143.4-144.4 °C; $[\alpha]_D^{20}$ = -73.6 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.51-7.44 (m, 1H), 7.42-7.22 (m, 6H), 7.21-7.00 (m, 1H), 6.50-6.39 (m, 1H), 5.50 (d, *J* = 10.3 Hz, 1H), 5.31-5.26 (m, 1H), 5.21 (d, *J* = 17.4 Hz, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 159.9, 151.1, 138.6, 137.4, 132.1, 129.5, 129.3, 128.1, 127.8, 122.8, 119.7, 117.9, 117.0, 106.5, 44.8;
>99% *ee* as determined by HPLC (Chiralcel IC, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 17.347 min, t_r (minor) = 14.490 min;
HRMS (ESI) calcd for $C_{18}H_{14}O_3Cl$ $(M+H)^+$: 313.0626, Found: 313.0626.

(*R*)-4-hydroxy-7-methoxy-3-(1-phenylallyl)-2*H*-chromen-2-one



3r, white solid, 59.2 mg, yield 96%; m.p. = 149.2-151.0 °C; $[\alpha]_D^{20}$ = -74.2 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 1H), 7.39-7.27 (m, 5H), 6.98 (s, 1H), 6.84 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.50-6.40 (m, 1H), 5.48 (dt, *J* = 10.2, 1.6 Hz, 1H), 5.30-5.26 (m, 1H), 5.19 (dt, *J* = 17.4, 1.7 Hz, 1H), 3.86 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 162.1, 160.5, 153.5, 138.1, 137.0, 128.2, 127.2, 126.5, 123.2, 118.2, 111.3, 108.0, 101.9, 99.2, 54.7, 43.6;
97% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 7.414 min, t_r (minor) = 5.631 min;
HRMS (ESI) calcd for $C_{19}H_{17}O_4$ $(M+H)^+$: 309.1121, Found: 309.1121.

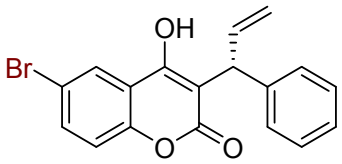
(*R*)-4-hydroxy-6-methyl-3-(1-phenylallyl)-2*H*-chromen-2-one



3s, white solid, 36.2 mg, yield 62%; m.p. = 135.9-136.7 °C; $[\alpha]_D^{20}$ = -69.1 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.39-7.27 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 6H), 6.99 (s, 1H), 6.50-6.41 (m, 1H), 5.49 (dt, *J* = 10.3, 1.6 Hz, 1H), 5.34-5.29 (m 1H), 5.20 (dt, *J* = 17.4, 1.6 Hz, 1H), 2.39 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 160.0, 149.9, 137.9, 136.7, 132.6, 132.1, 128.2, 127.1, 126.6, 121.7, 118.3, 115.2, 114.5, 104.5, 43.7, 19.9;
98% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 13.189 min, t_r (minor) = 11.955 min;

HRMS (ESI) calcd for $C_{19}H_{17}O_3$ $(M+H)^+$: 293.1172, Found: 293.1172.

(*R*)-6-bromo-4-hydroxy-3-(1-phenylallyl)-2*H*-chromen-2-one



3t, light yellow oil, 45.0 mg, yield 63%; $[\alpha]_D^{20}$ = -80.2 (c = 0.4, $CHCl_3$).

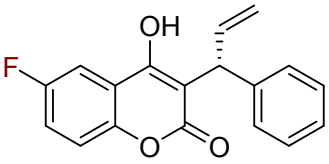
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.3 Hz, 1H), 7.62 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.40 – 7.29 (m, 5H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.06 (s, 1H), 6.48-6.40 (m, 1H), 5.51 (dt, *J* = 10.2, 1.5 Hz, 1H), 5.31-5.26 (m, 1H), 5.24-5.17 (m, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 159.8, 151.5, 138.5, 137.4, 134.9, 129.4, 128.1, 127.8, 125.8, 119.7, 118.2, 117.4, 116.8, 106.5, 44.8;

93% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 10.148 min, t_r (minor) = 9.126 min;

HRMS (ESI) calcd for $C_{18}H_{14}O_3Br$ $(M+H)^+$: 357.0121, Found: 357.0116.

(*R*)-6-fluoro-4-hydroxy-3-(1-phenylallyl)-2*H*-chromen-2-one



3u, white solid, 33.8 mg, yield 57%; m.p. = 161.8-163.6 °C; $[\alpha]_D^{20}$ = -66.7 (c = 0.4, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.4, 2.9 Hz, 1H), 7.41-7.23 (m, 7H), 7.03 (s, 1H), 6.49-6.40 (m, 1H), 5.52 (dt, *J* = 10.3, 1.5 Hz, 1H), 5.32-5.28 (m, 1H), 5.24-5.18 (m, 1H);

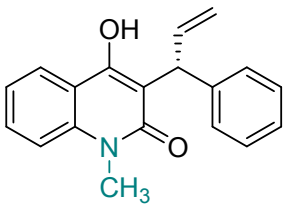
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 160.1 (d, *J* = 2.5 Hz),158.7 (d, *J* = 242.3 Hz), 148.8 (d, *J* = 2.1 Hz), 138.5, 137.4, 129.4, 128.1, 127.8, 119.7 (d, *J* = 3.5 Hz), 119.5, 118.1 (d, *J* = 8.3 Hz), 116.8 (d, *J* = 8.9 Hz), 108.9 (d, *J* = 25.3 Hz), 106.4, 44.8;

^{19}F NMR (471 MHz, $CDCl_3$) δ -117.3;

>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 9.286 min, t_r (minor) = 8.264 min;

HRMS (ESI) calcd for $C_{18}H_{14}O_3F$ $(M+H)^+$: 297.0921, Found: 297.0922.

(*R*)-4-hydroxy-1-methyl-3-(1-phenylallyl)quinolin-2(1*H*)-one



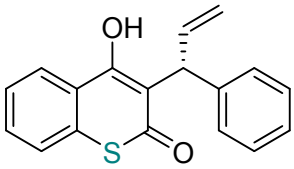
5, colorless oil, 59.2 mg, yield 88%; $[\alpha]_D^{20}$ = -73.3 (c = 0.4, $CHCl_3$);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60-7.55 (m, 1H), 7.40-7.21 (m, 7H), 6.65

(s, 1H), 6.52-6.44 (m, 1H), 5.64-5.59 (m, 1H), 5.46 (dt, *J* = 10.3, 1.7 Hz, 1H), 5.20-5.14 (m, 1H), 3.71 (s, 3H); 6.40-6.34 (m, 1H).

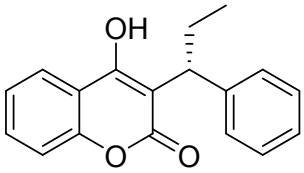
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 157.5, 139.8, 139.1, 138.6, 130.9, 129.0, 128.3, 127.2, 123.5, 121.7, 118.8, 116.1, 113.8, 111.1, 44.7, 29.9;
98% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 9.551 min, t_r (minor) = 13.691 min;
HRMS (ESI) calcd for $C_{19}H_{18}O_2N$ $(M+H)^+$: 292.1332, Found: 292.1331.

(*R*)-4-hydroxy-3-(1-phenylallyl)-2*H*-thiochromen-2-one



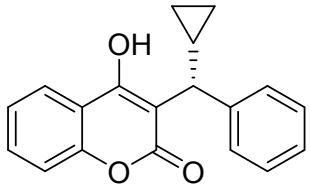
6, light yellow oil, 51.2 mg, yield 87%; $[\alpha]_D^{20}$ = -11.5 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dt, *J* = 8.2, 1.7 Hz, 1H), 7.51-7.47 (m, 1H), 7.44-7.25 (m, 8H), 6.95 (s, 1H), 6.47-6.38 (m, 1H), 5.72-5.66 (s, 1H), 5.52-5.46 (s, 1H), 5.27-5.20 (s, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 183.1, 161.1, 137.8, 136.1, 134.9, 129.3, 128.2, 127.1, 126.6, 125.2, 125.2, 124.1, 122.6, 118.5, 116.1, 42.1;
98% *ee* as determined by HPLC (Chiralcel OD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 7.380 min, t_r (minor) = 8.076 min;
HRMS (ESI) calcd for $C_{18}H_{15}O_2S$ $(M+H)^+$: 295.0787, Found: 295.0784.

(*R*)-4-hydroxy-3-(1-phenylpropyl)-2*H*-chromen-2-one



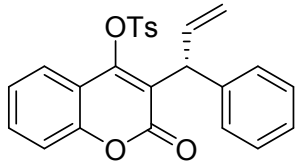
7, white solid, 53.8 mg, yield 96%; m.p. = 173.2-175.1 °C; $[\alpha]_D^{20}$ = +112.9 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.54-7.46 (m, 3H), 7.43-7.37 (m, 2H), 7.33-7.28 (m, 2H), 7.27-7.20 (m, 1H), 6.53 (s, 1H), 4.54 (t, *J* = 8.5 Hz, 1H), 2.30-2.20 (m, 1H), 2.18-2.08 (m, 1H), 1.07 (td, *J* = 7.4, 2.1 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 160.0, 152.6, 141.2, 131.8, 129.6, 127.7, 127.6, 123.8, 122.8, 116.4, 116.0, 108.9, 41.7, 24.0, 12.3;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 10.898 min, t_r (minor) = 9.179 min;
HRMS (ESI) calcd for $C_{18}H_{17}O_3$ $(M+H)^+$: 281.1172, Found: 281.1173.

(*R*)-3-(cyclopropyl(phenyl)methyl)-4-hydroxy-2*H*-chromen-2-one



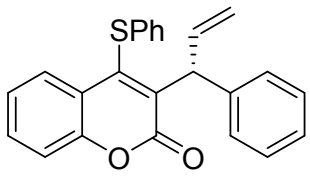
8, colorless oil, yield: 57.9 mg (99%); $[\alpha]_D^{20}$ = +61.8 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.58-7.50 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.33-7.22 (m, 3H), 6.73 (s, 1H), 4.09 (d, *J* = 8.9 Hz, 1H), 1.49-1.40 (m, 1H), 0.84-0.76 (m, 1H), 0.68-0.60 (m, 2H), 0.37-0.32 (m, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 158.9, 151.6, 139.6, 130.8, 128.3, 127.0, 126.7, 122.8, 121.9, 115.4, 115.1, 107.9, 43.3, 12.2, 4.1, 3.0;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, with 0.1% trifluoroacetic acid, 1 mL/min), t_r (major) = 13.498 min, t_r (minor) = 9.897 min;
HRMS (ESI) calcd for $C_{19}H_{17}O_3$ $(M+H)^+$: 293.1172, Found: 293.1173.

(*R*)-2-oxo-3-(1-phenylallyl)-2*H*-chromen-4-yl 4-methylbenzenesulfonate



9, white solid, 82.0 mg, yield 95%; m.p. = 154.9-155.6 °C; $[\alpha]_D^{20}$ = +54.9 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.83 (m, 2H), 7.66 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55-7.50 (m, 1H), 7.35-7.29 (m, 3H), 7.28-7.17 (m, 6H), 6.54-6.55 (m, 1H), 5.26-5.22 (m, 1H), 5.16-5.10 (m, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 2.46 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 154.1, 152.5, 146.5, 140.1, 136.0, 133.0, 132.2, 130.2, 128.2, 128.2, 127.6, 126.7, 124.7, 124.3, 123.0, 118.5, 116.7, 116.48, 46.5, 21.8;
98% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, 1 mL/min), t_r (major) = 12.295 min, t_r (minor) = 9.570 min;
HRMS (ESI) calcd for $C_{25}H_{21}O_5S$ $(M+H)^+$: 433.1104, Found: 433.1103.

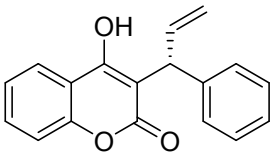
(*R*)-3-(1-phenylallyl)-4-(phenylthio)-2*H*-chromen-2-one



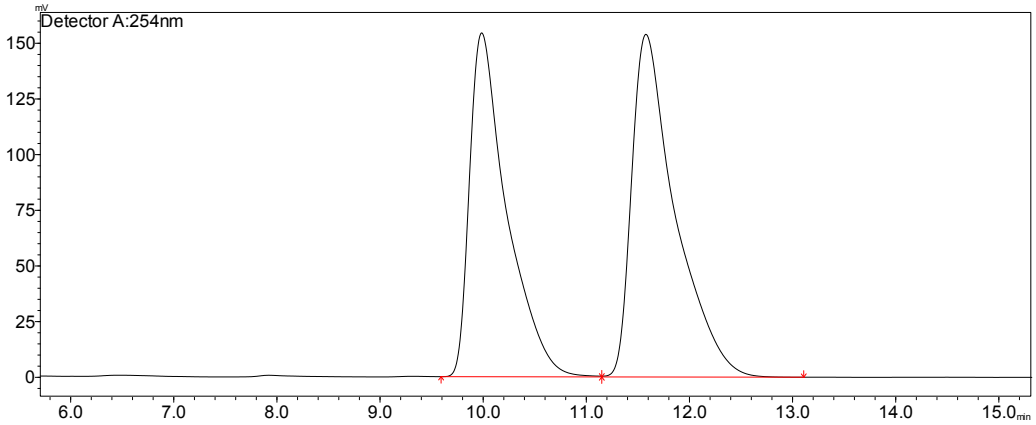
10, colorless oil, 64.5 mg, yield 87%; $[\alpha]_D^{20}$ = +195.0 (c = 0.4, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.45-7.40 (m, 1H), 7.35-7.11 (m, 12H), 6.76-6.67 (m, 1H), 5.81 (d, *J* = 8.3 Hz, 1H), 5.23 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.15 (d, *J* = 17.1 Hz, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 151.6, 144.1, 140.0, 136.0, 135.8, 133.5, 130.2, 128.5, 127.3, 127.3, 127.3, 126.4, 125.8, 125.5, 123.3, 118.8, 117.4, 115.6, 50.0;
>99% *ee* as determined by HPLC (Chiralcel AD-H, 90:10 hexanes/*i*-PrOH, 1 mL/min), t_r (major) = 9.012

min, t_r (minor) = 6.587 min;
HRMS (ESI) calcd for $C_{24}H_{19}O_2S$ $(M+H)^+$: 371.1100, Found: 371.1099.

Ⅴ Data of HPLC Chromatographs:



3a



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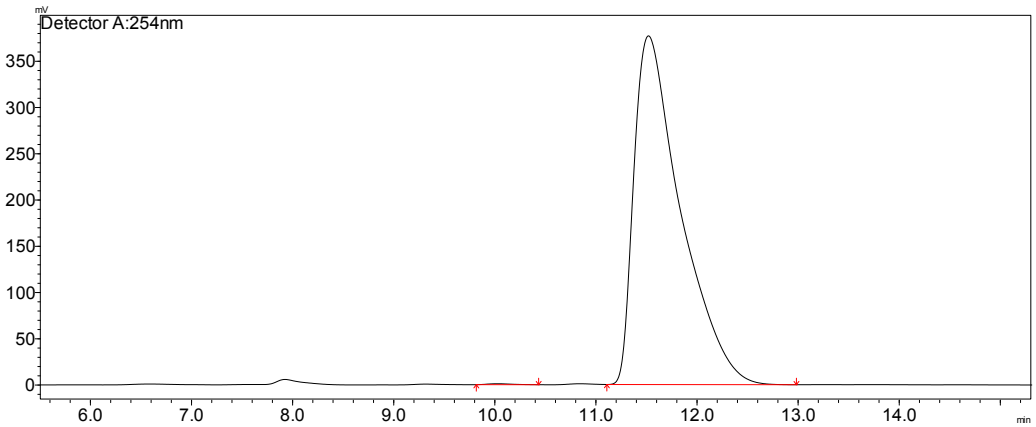

Peak#	Ret. Time	Area	Height	Area %	Height %
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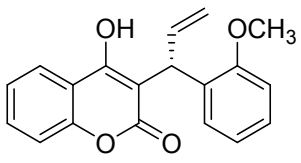
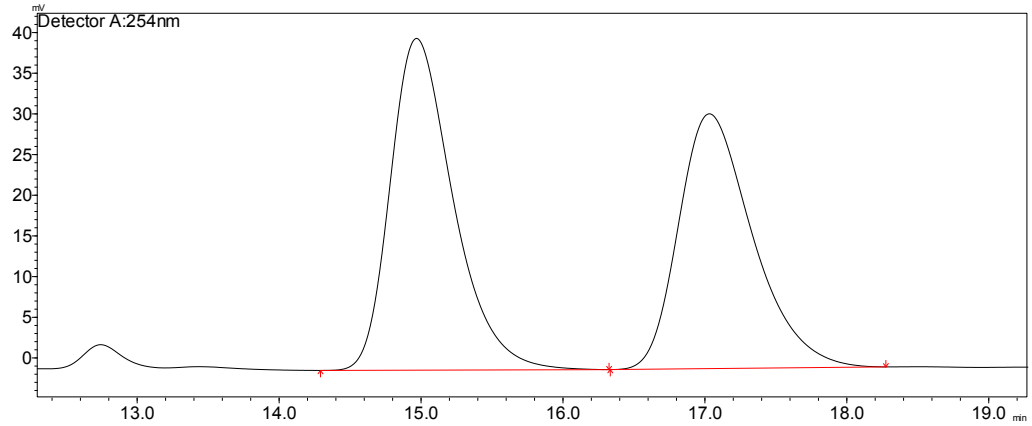
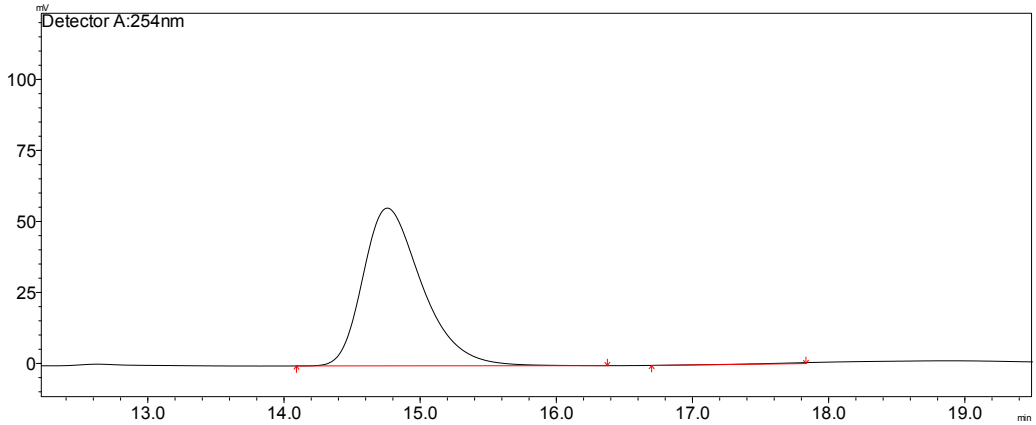
Total		12117714	377901	100.000	100.000



3b



Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.964	1257543	40781	52.563	56.557
2	17.028	1134908	31325	47.437	43.443
Total		2392450	72107	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
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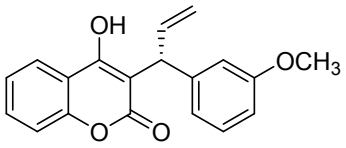
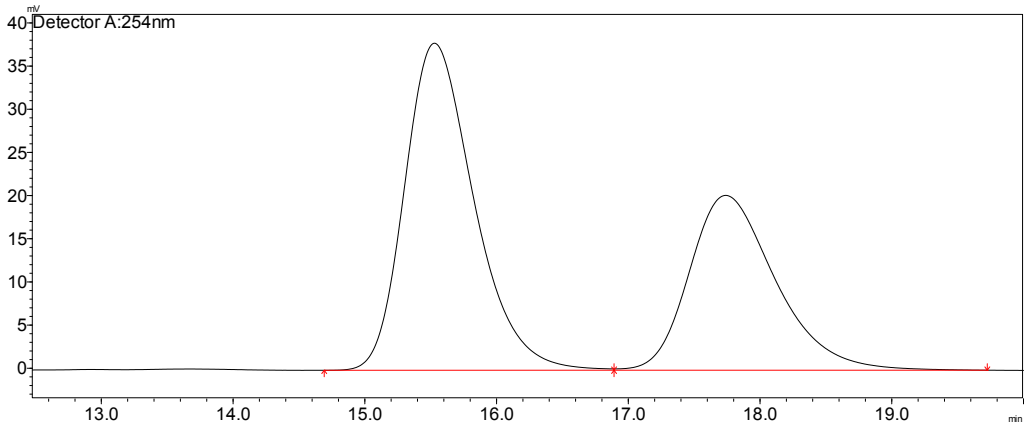
2	17.825	6749	323	0.401	0.578
Total		1682328	55881	100.000	100.000



3c



Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.524	1386604	37880	60.071	65.163
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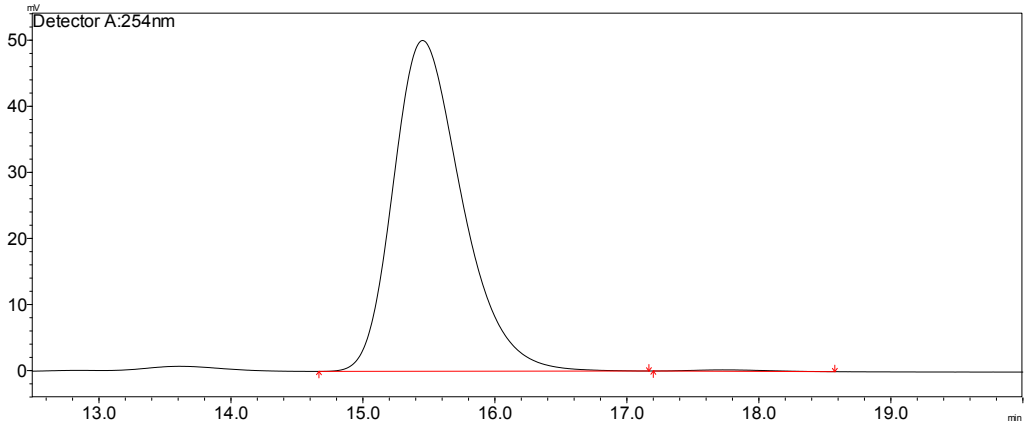
Total		2308276	58131	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.448	1814996	50059	99.554	99.584
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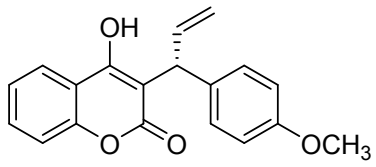
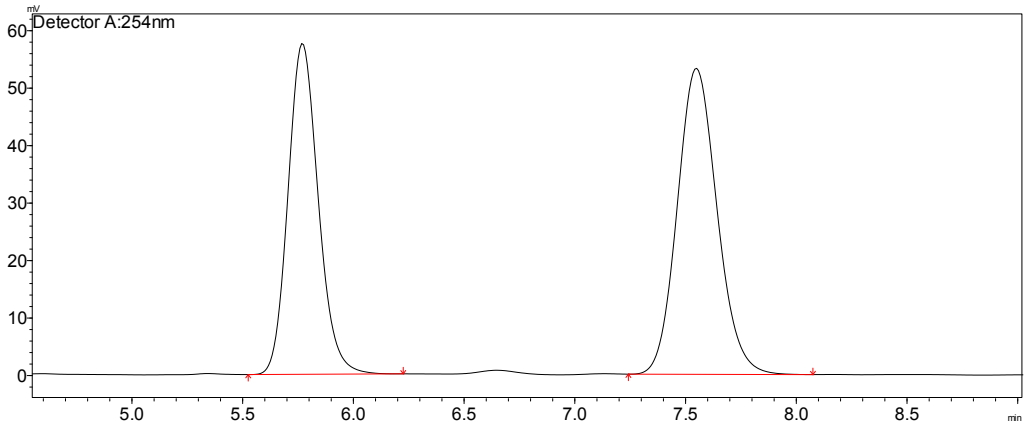


3d



Peak#	Ret. Time	Area	Height	Area %	Height %
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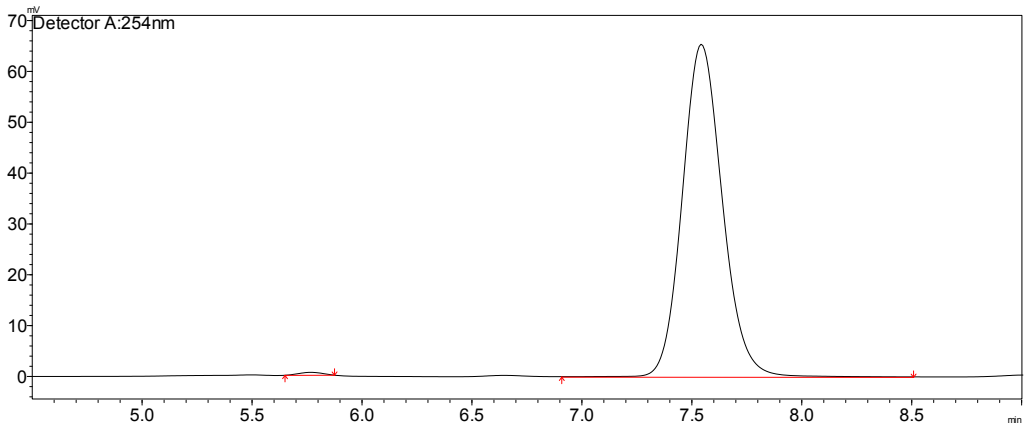
Total		1211837	110797	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
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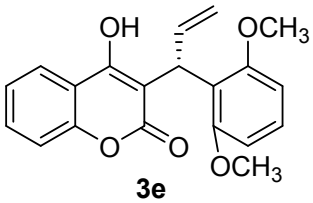
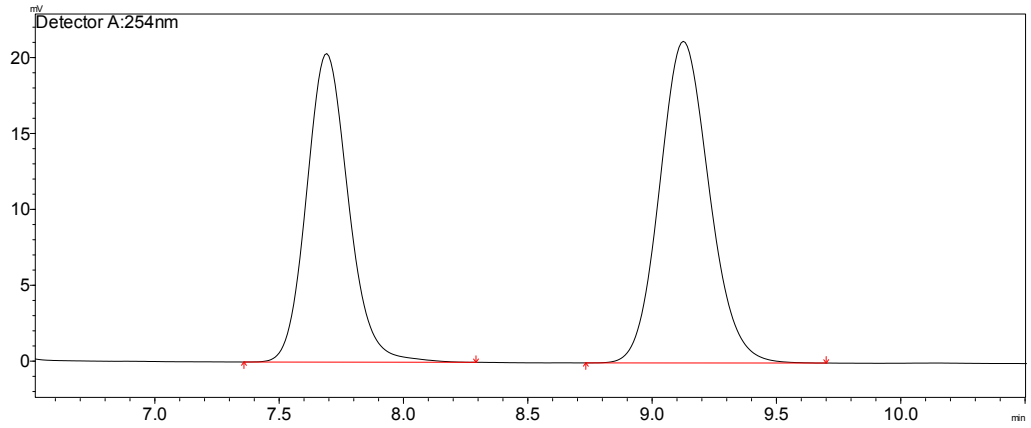
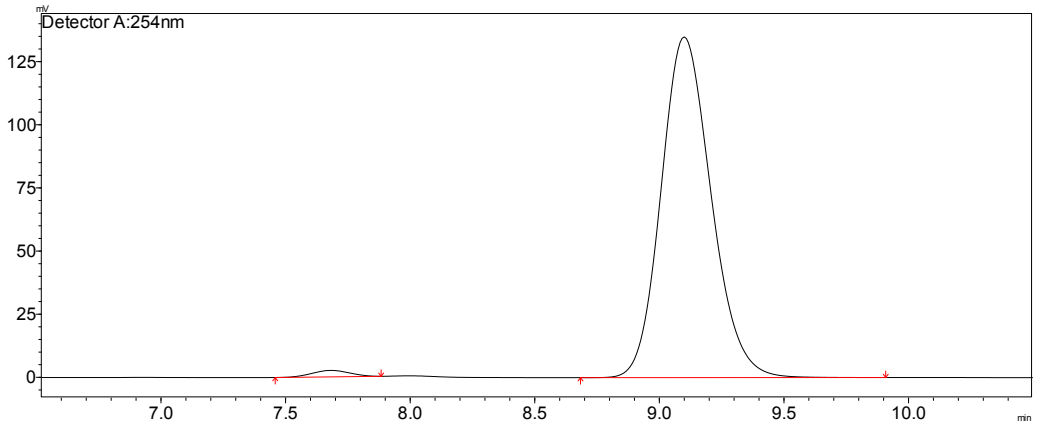
Total		840069	66085	100.000	100.000



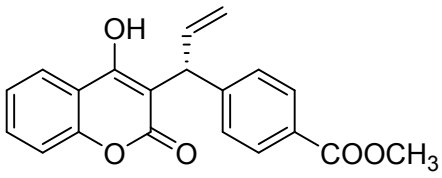
3e



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.686	238250	20325	44.731	48.958
2	9.122	294374	21191	55.269	51.042
Total		532624	41516	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.678	27092	2562	1.417	1.863
2	9.095	1884222	134900	98.583	98.137
Total		1911314	137462	100.000	100.000



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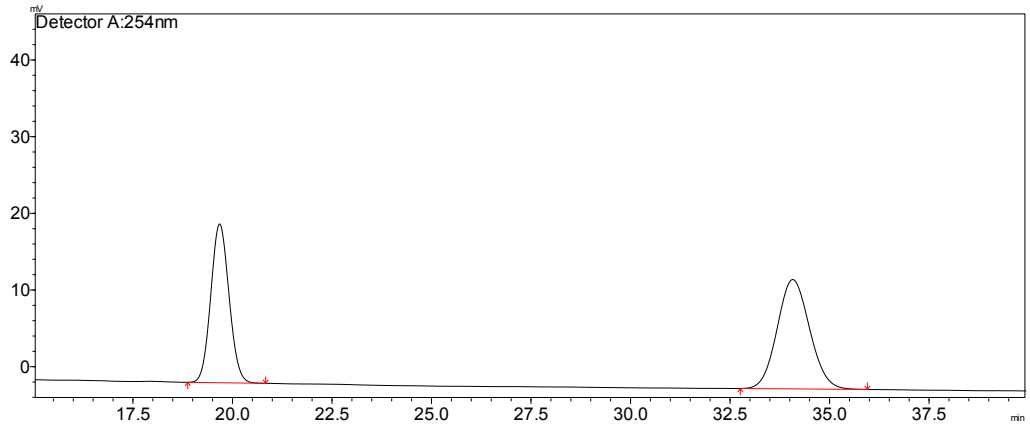
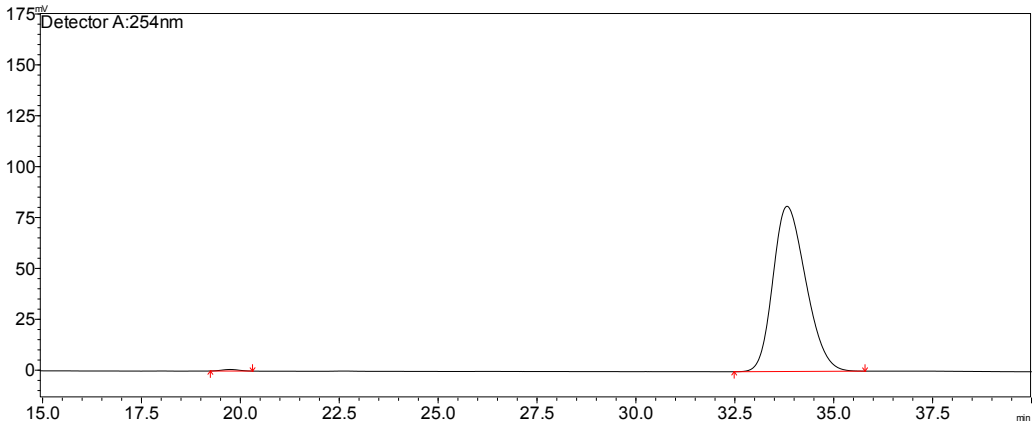
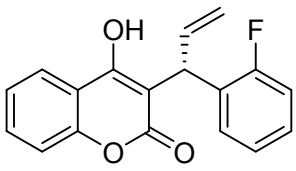


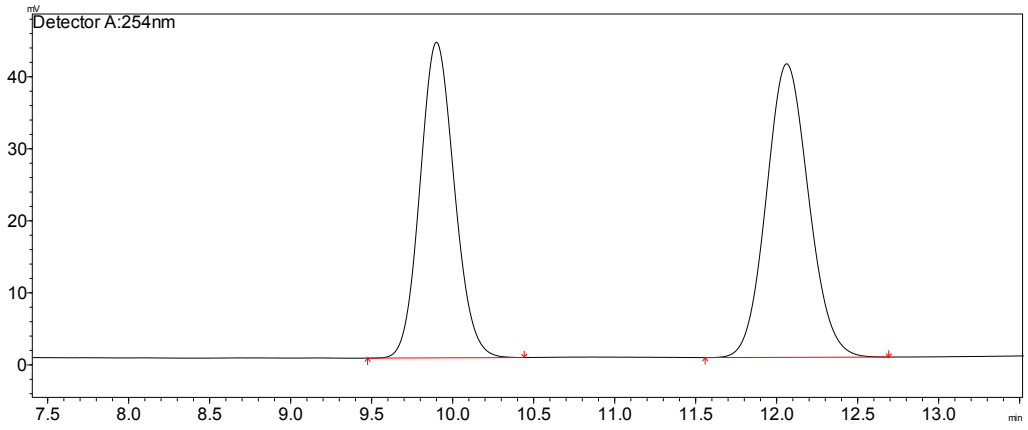
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.673	661183	20705	44.963	59.210
2	34.070	809337	14264	55.037	40.790
Total		1470520	34968	100.000	100.000



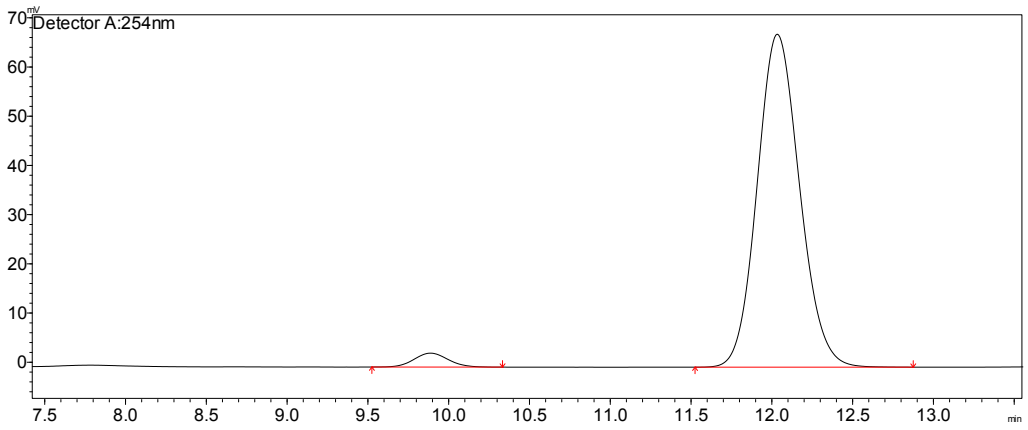
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.730	22912	768	0.485	0.937
2	33.816	4696643	81160	99.515	99.063
Total		4719555	81928	100.000	100.000



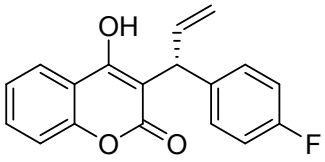
3g



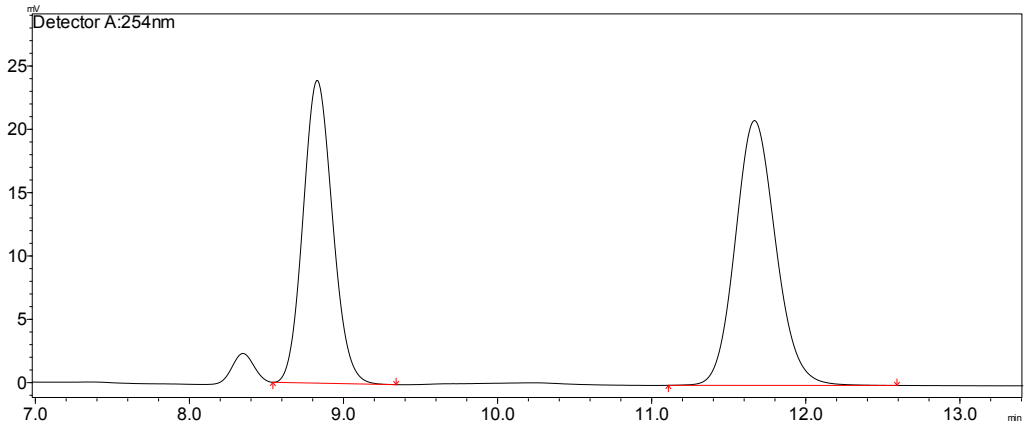
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.896	645507	43842	46.529	51.827
2	12.057	741814	40750	53.471	48.173
Total		1387320	84591	100.000	100.000



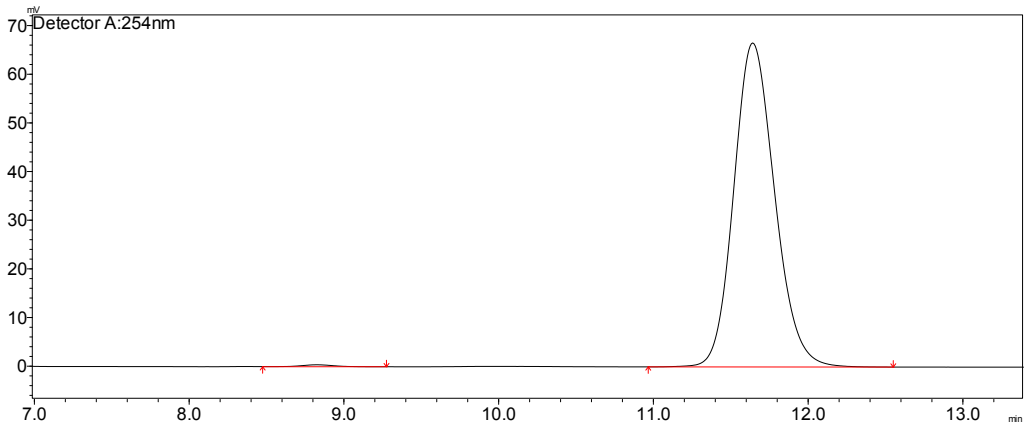
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.883	41425	2825	3.248	4.007
2	12.030	1233800	67678	96.752	95.993
Total		1275225	70503	100.000	100.000



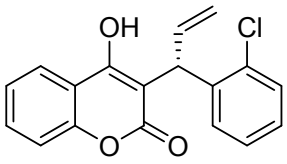
3h



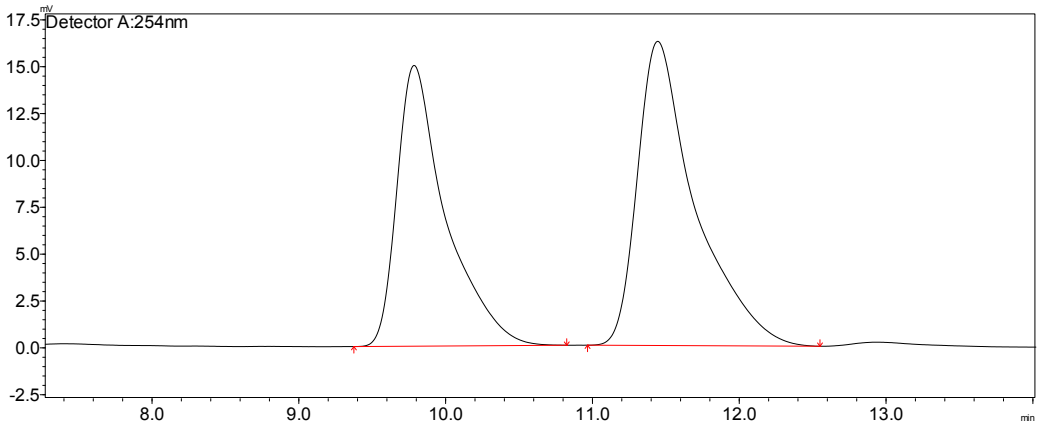
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.825	318163	23895	45.378	53.326
2	11.663	382978	20914	54.622	46.674
Total		701140	44809	100.000	100.000



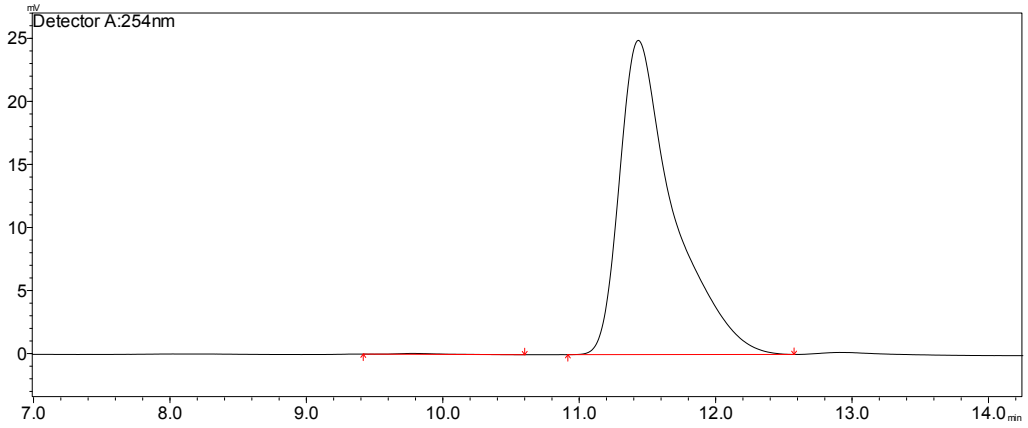
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.825	6001	397	0.488	0.592
2	11.637	1223169	66594	99.512	99.408
Total		1229170	66991	100.000	100.000



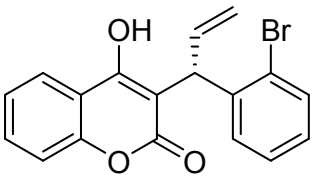
3i



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.781	345331	14979	43.825	48.000
2	11.440	442648	16228	56.175	52.000
Total		787980	31207	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.766	1326	67	0.194	0.267
2	11.429	683605	24923	99.806	99.733
Total		684931	24990	100.000	100.000



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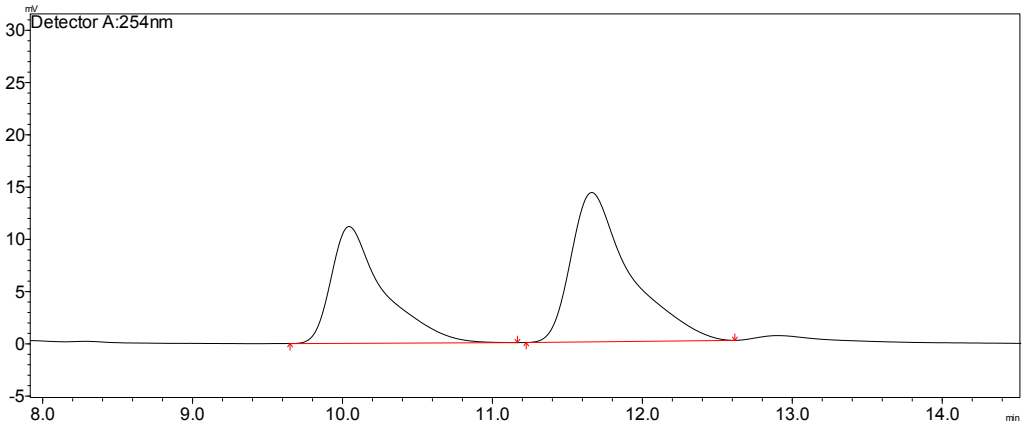
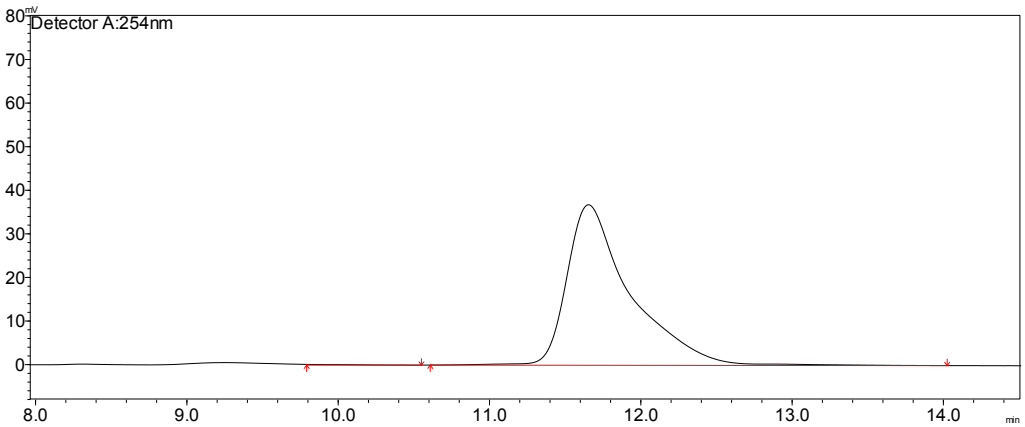
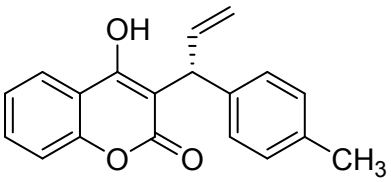


Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.040	271402	11177	40.991	43.889
2	11.658	390702	14290	59.009	56.111
Total		662104	25467	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.792	3248	162	0.302	0.437
2	11.650	1072312	36794	99.698	99.563
Total		1075560	36956	100.000	100.000



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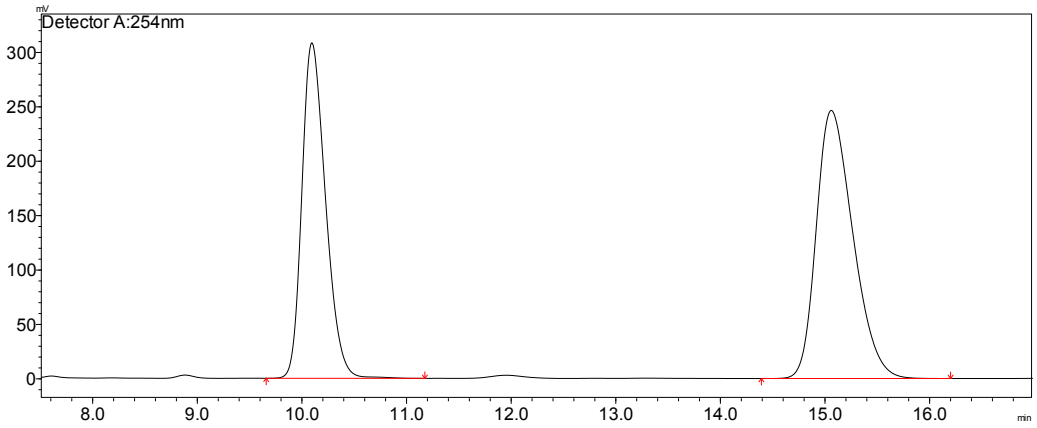
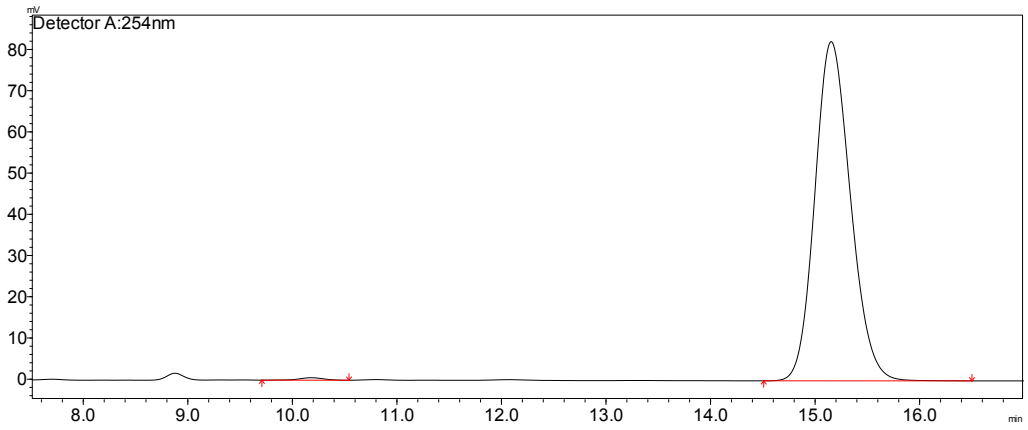
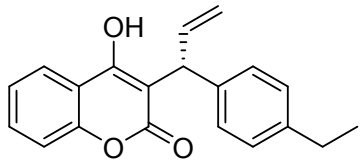


Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.091	4845384	308325	44.705	55.575
2	15.056	5993230	246466	55.295	44.425
Total		10838613	554792	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.178	9605	594	0.490	0.716
2	15.150	1949309	82288	99.510	99.284
Total		1958914	82882	100.000	100.000



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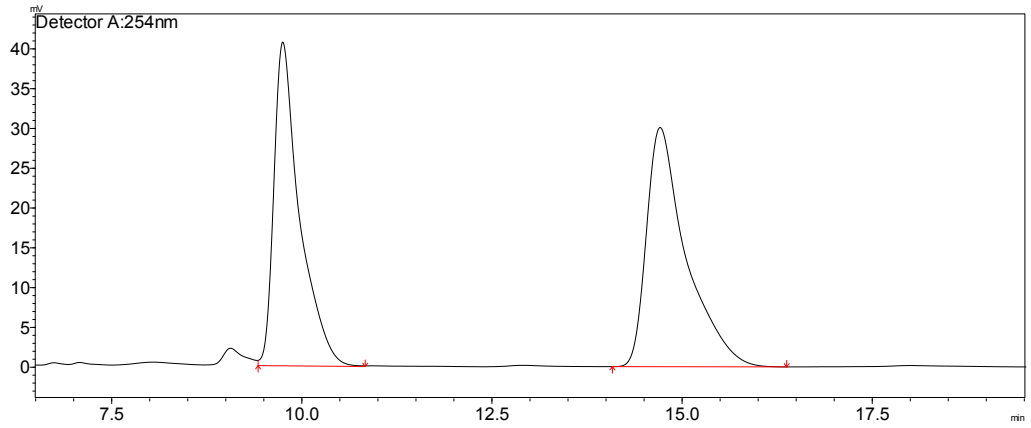
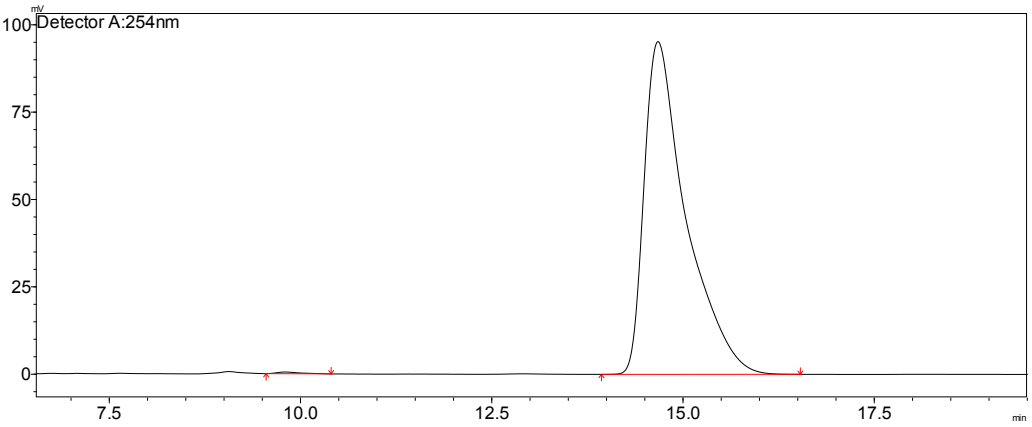
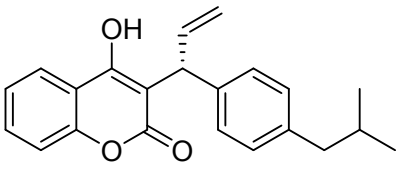


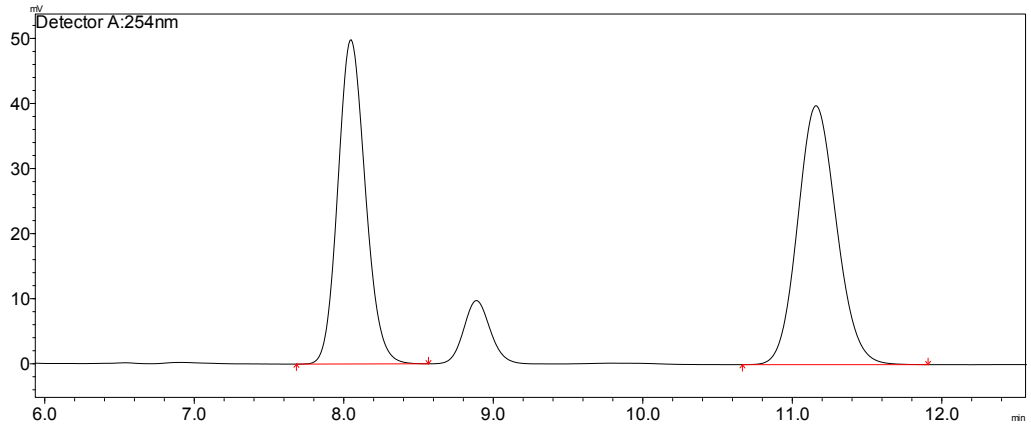
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.745	957120	40693	46.842	57.517
2	14.707	1086180	30057	53.158	42.483
Total		2043300	70750	100.000	100.000



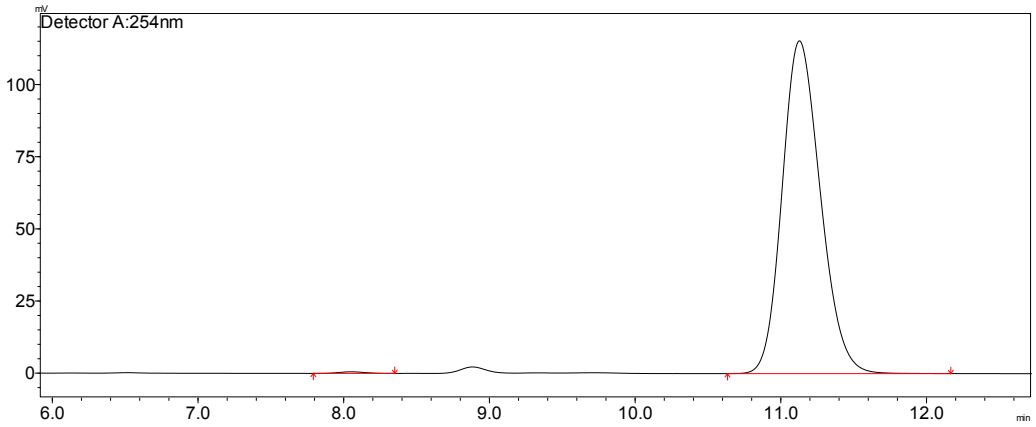
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.794	10442	482	0.288	0.503
2	14.669	3618119	95240	99.712	99.497
Total		3628561	95721	100.000	100.000



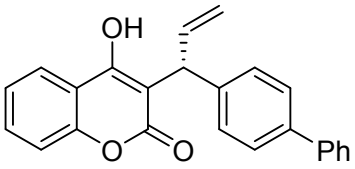
3m



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.043	637348	49841	46.957	55.596
2	11.155	719947	39808	53.043	44.404
Total		1357294	89649	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.046	6655	546	0.315	0.471
2	11.123	2105179	115314	99.685	99.529
Total		2111834	115860	100.000	100.000



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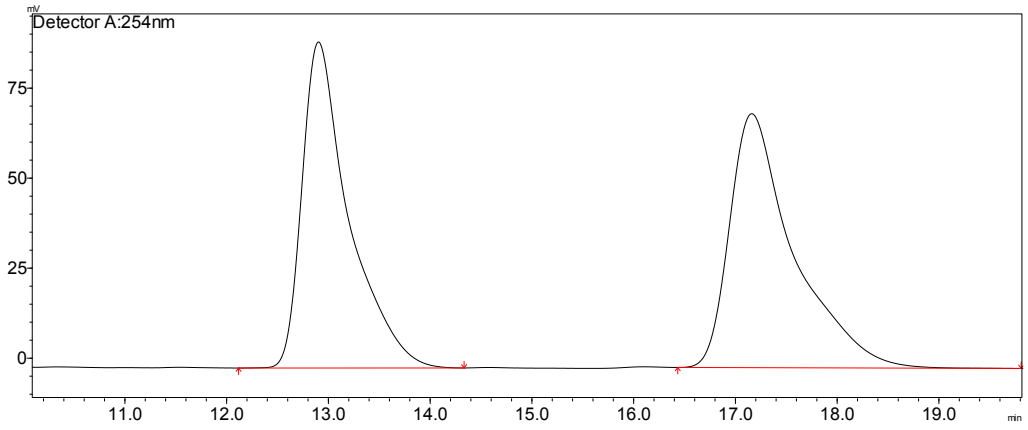
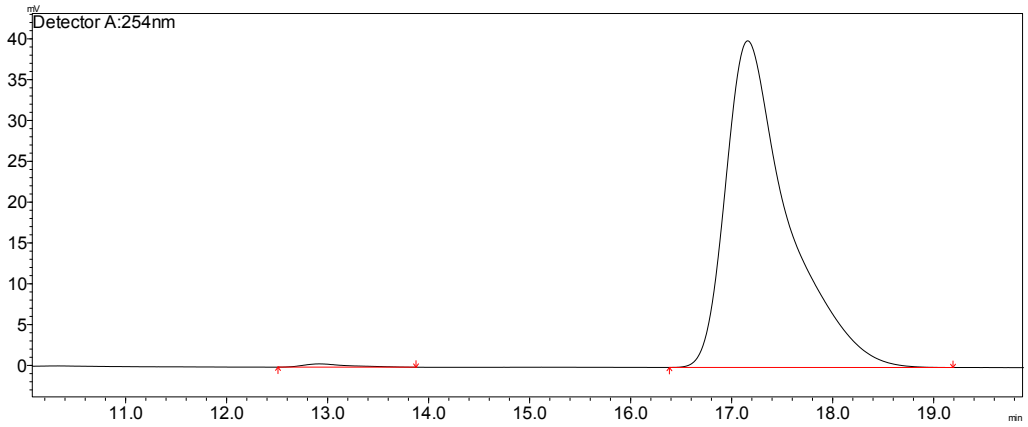
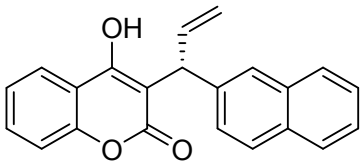


Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.899	2890738	90552	48.458	56.215
2	17.157	3074737	70529	51.542	43.785
Total		5965474	161081	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.914	9995	373	0.581	0.923
2	17.155	1709964	40011	99.419	99.077
Total		1719959	40383	100.000	100.000



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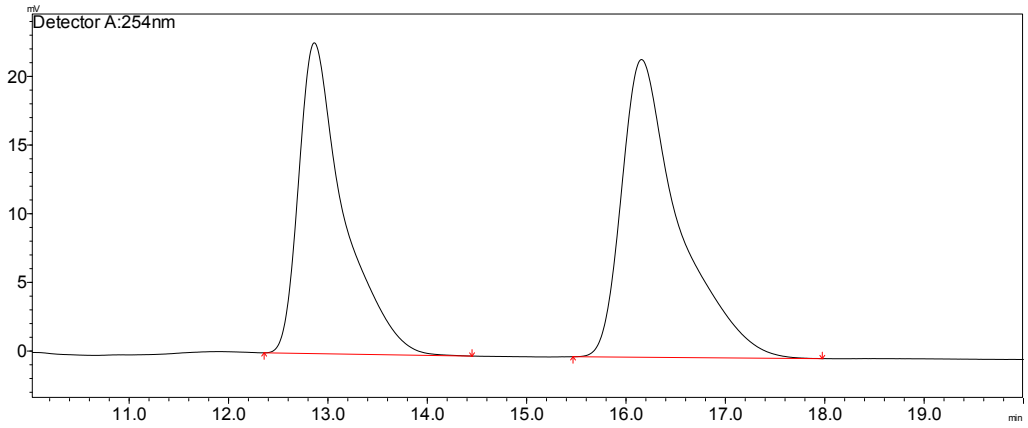
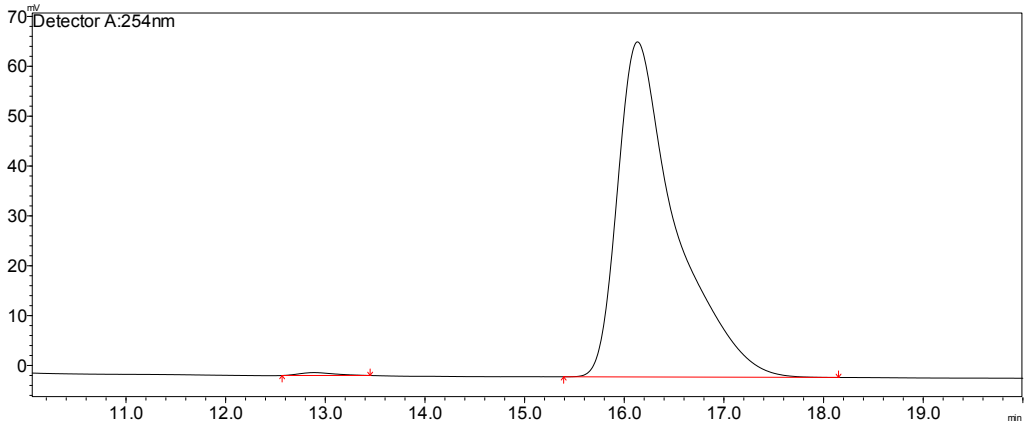
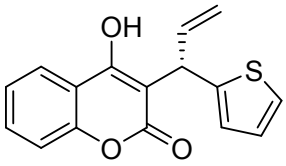


Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.859	711949	22629	45.070	51.073
2	16.152	867716	21679	54.930	48.927
Total		1579665	44308	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.885	14368	579	0.526	0.854
2	16.129	2717264	67204	99.474	99.146
Total		2731632	67783	100.000	100.000



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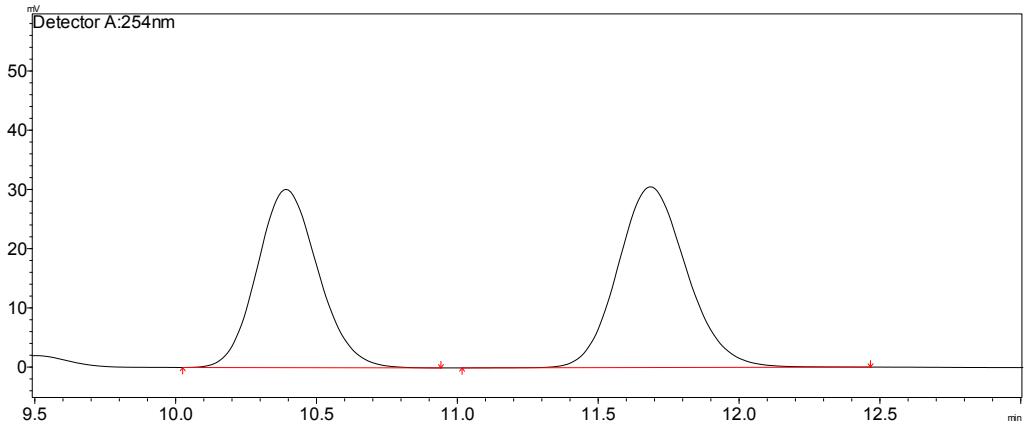
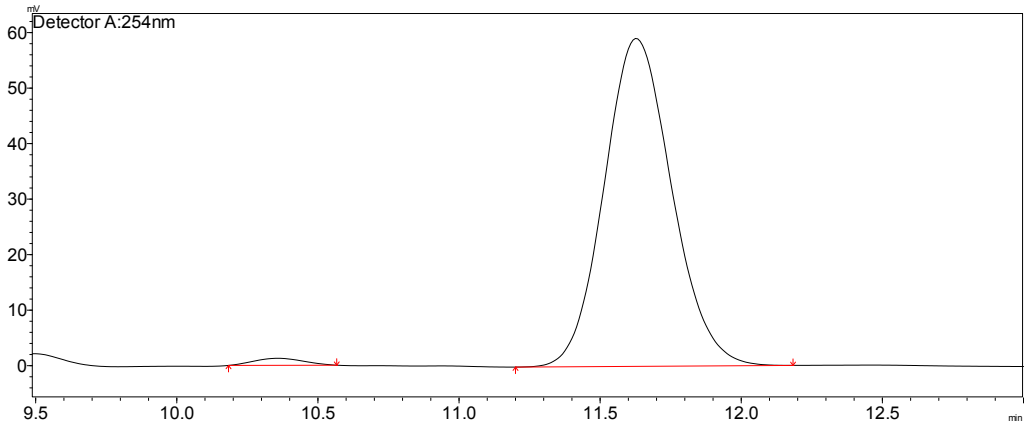
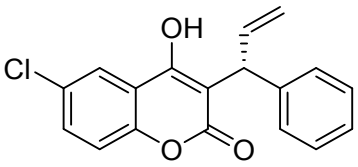


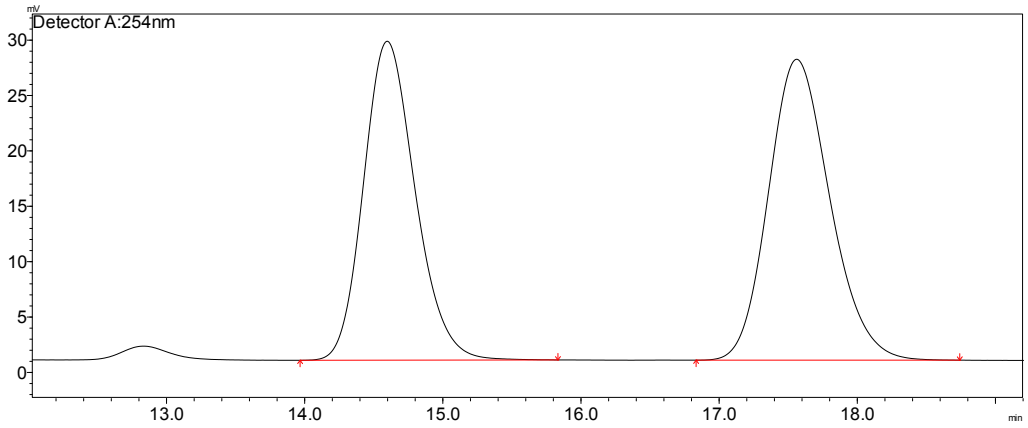
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.388	454578	30097	46.615	49.657
2	11.682	520598	30512	53.385	50.343
Total		975175	60609	100.000	100.000



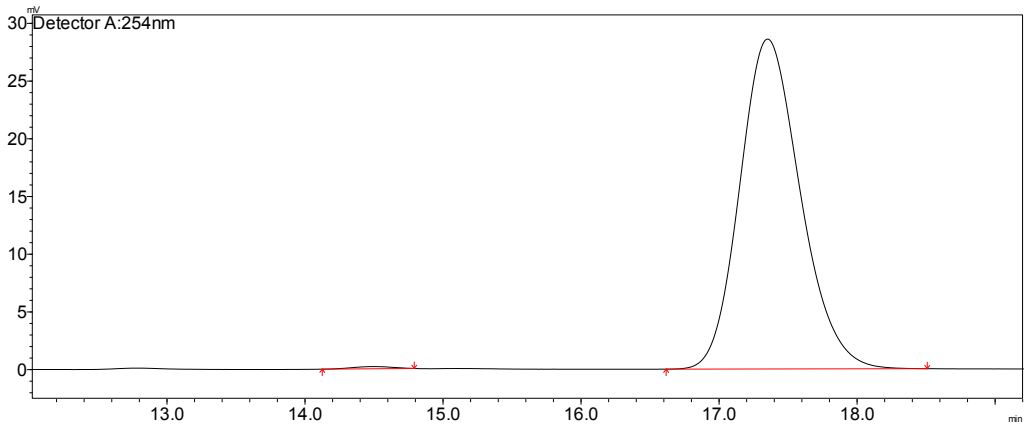
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.354	15272	1265	1.527	2.097
2	11.623	985025	59068	98.473	97.903
Total		1000297	60333	100.000	100.000



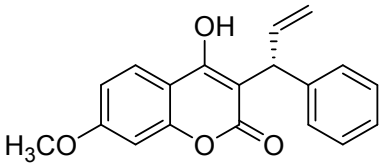
3q



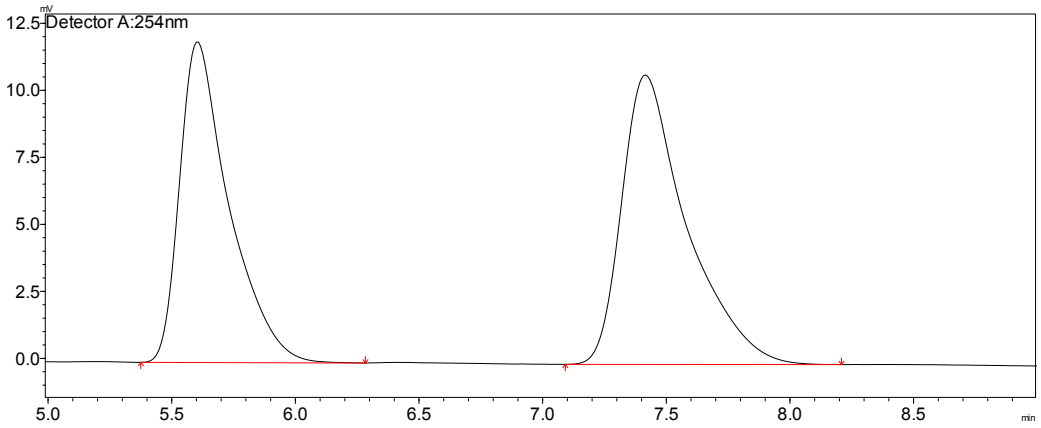
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.593	748252	28792	47.081	51.455
2	17.557	841047	27163	52.919	48.545
Total		1589300	55955	100.000	100.000



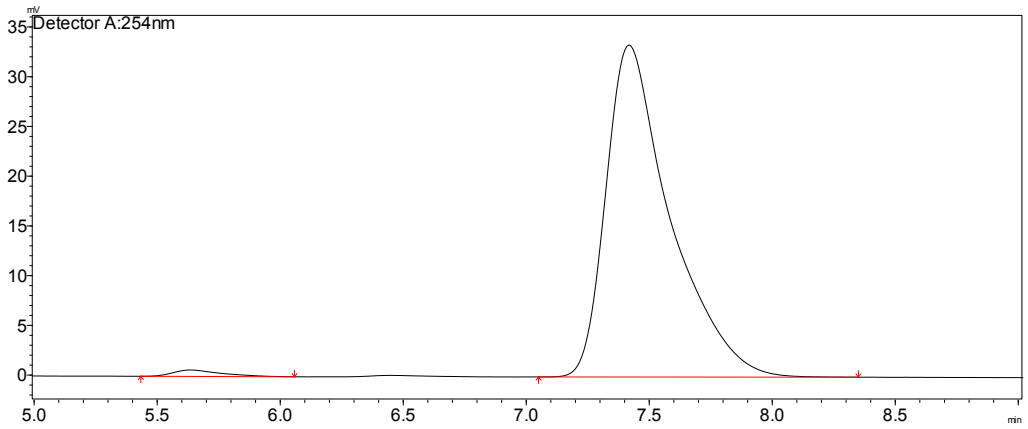
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.490	3832	190	0.438	0.660
2	17.347	872040	28588	99.562	99.340
Total		875872	28778	100.000	100.000



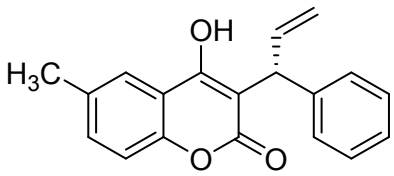
3r



Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.599	166203	11956	45.795	52.541
2	7.411	196724	10800	54.205	47.459
Total		362927	22756	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.631	8865	649	1.444	1.907
2	7.414	605254	33379	98.556	98.093
Total		614119	34028	100.000	100.000



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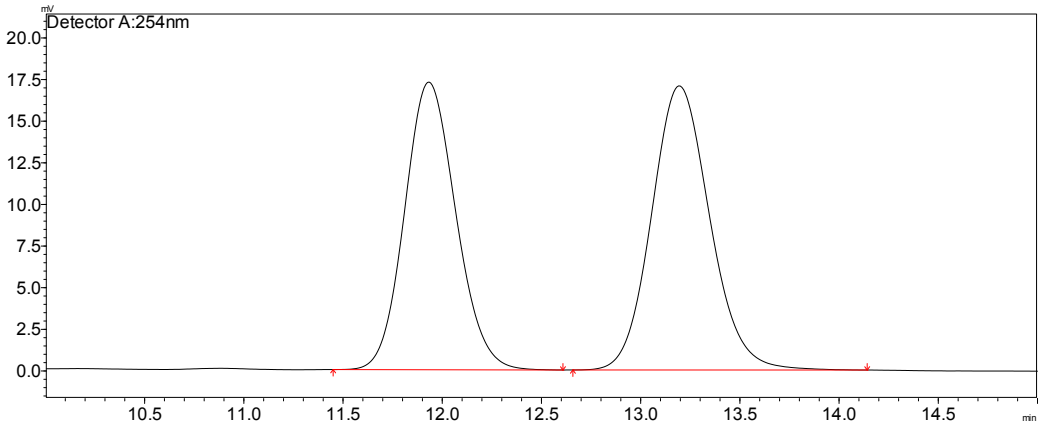
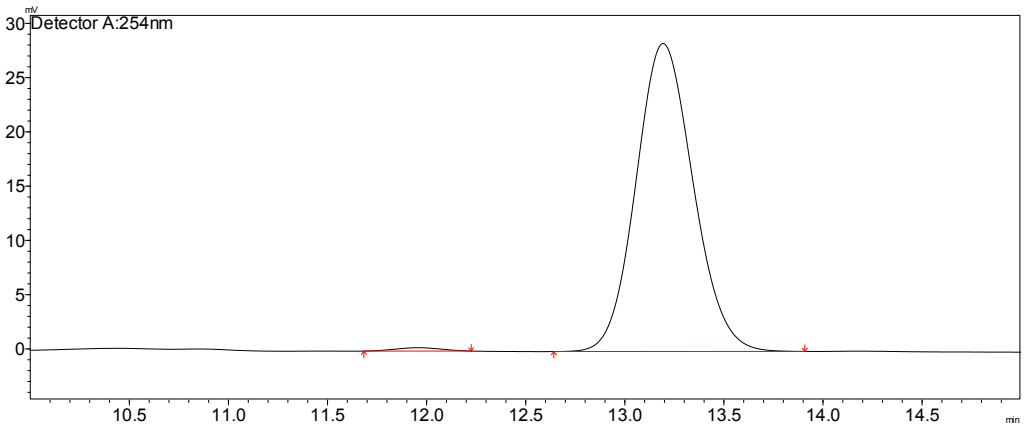
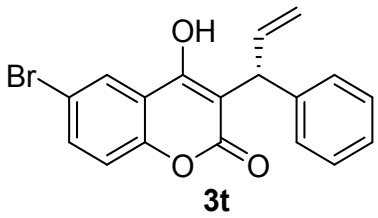


Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.928	310487	17277	47.130	50.312
2	13.190	348302	17062	52.870	49.688
Total		658789	34339	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.955	4979	310	0.866	1.080
2	13.189	570071	28386	99.134	98.920
Total		575050	28696	100.000	100.000



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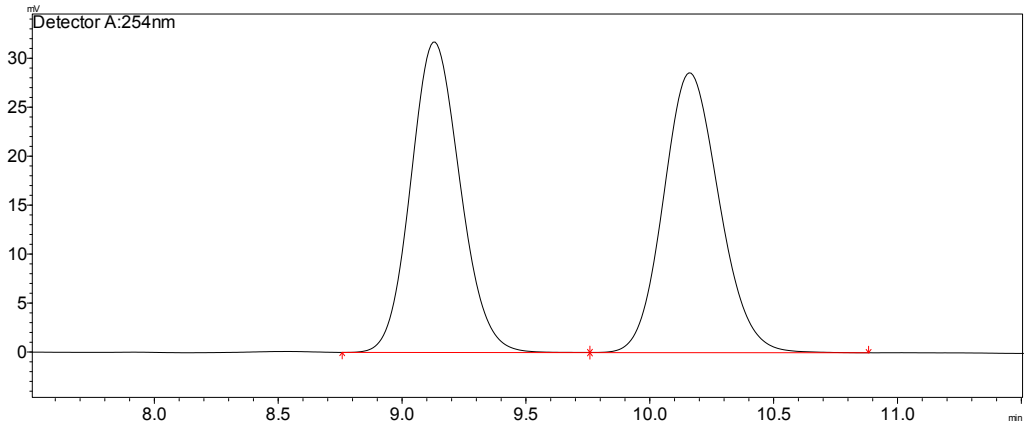
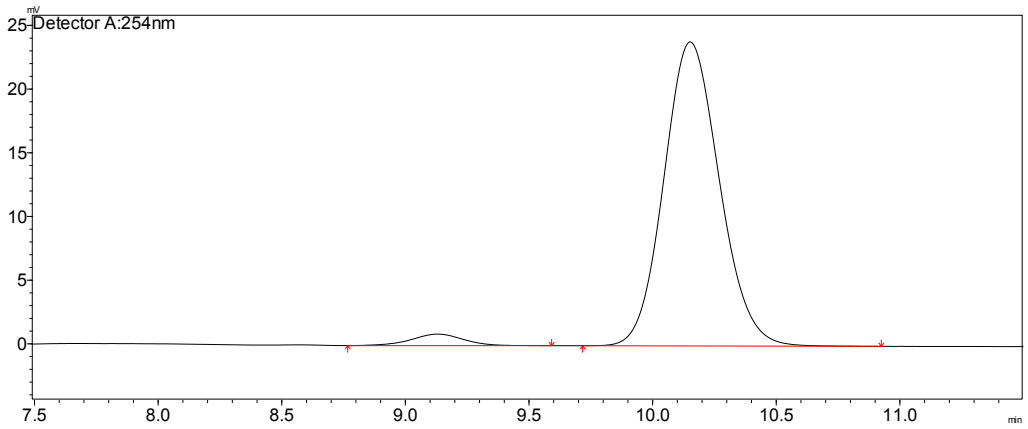
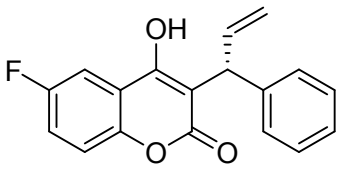


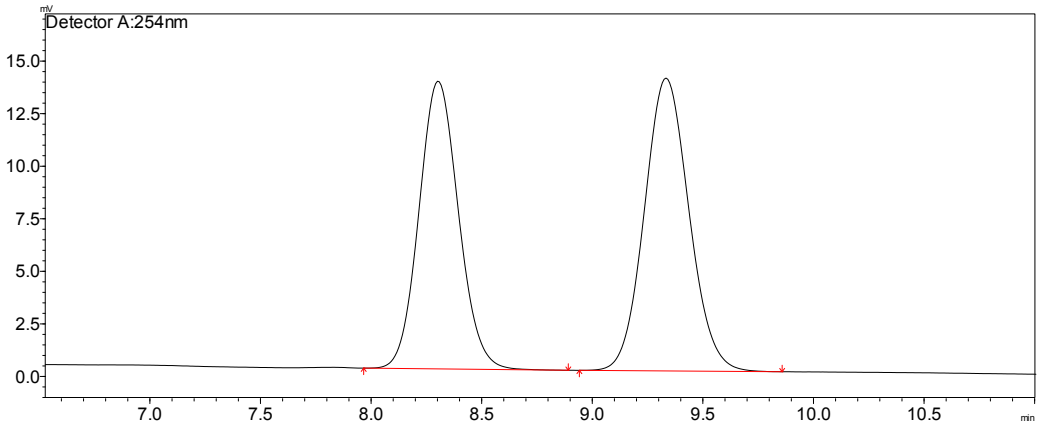
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.125	440126	31700	49.543	52.592
2	10.157	448241	28576	50.457	47.408
Total		888367	60275	100.000	100.000



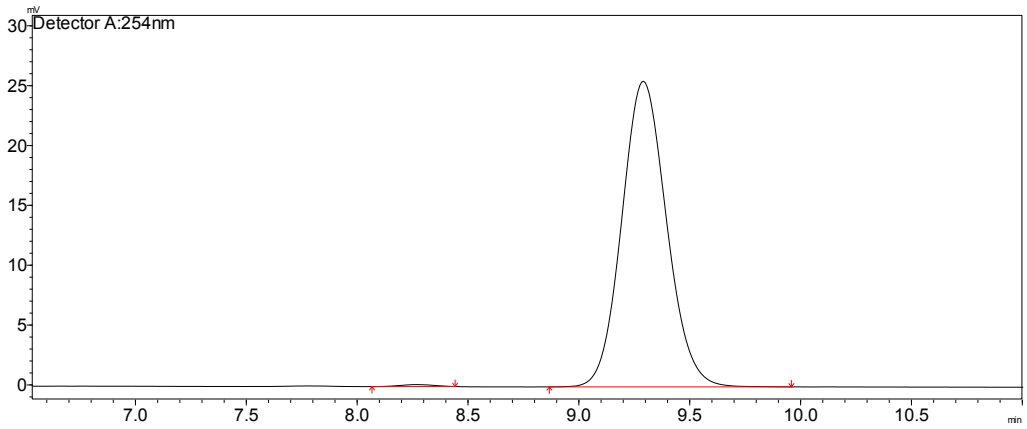
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.126	13394	904	3.468	3.649
2	10.148	372853	23875	96.532	96.351
Total		386247	24779	100.000	100.000



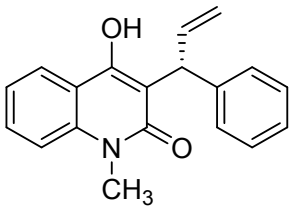
3u



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.299	170101	13683	46.506	49.553
2	9.329	195660	13930	53.494	50.447
Total		365761	27612	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.264	1721	162	0.477	0.629
2	9.286	358798	25534	99.523	99.371
Total		360519	25696	100.000	100.000



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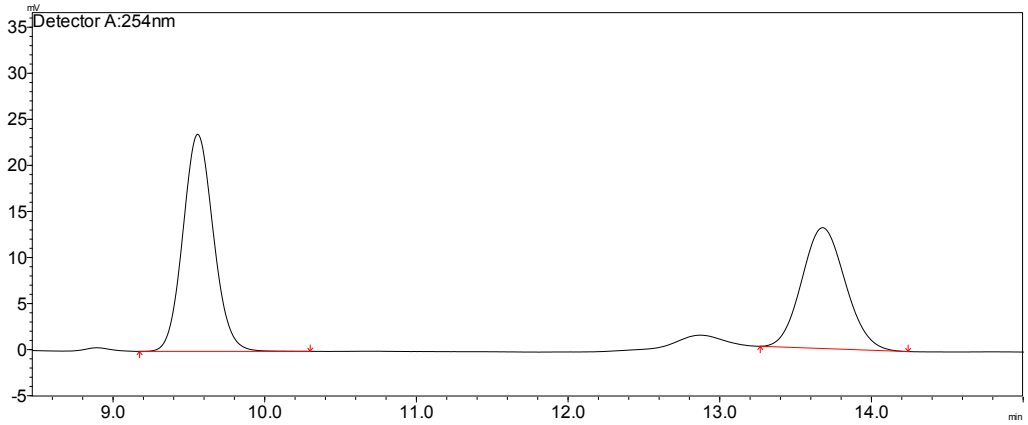
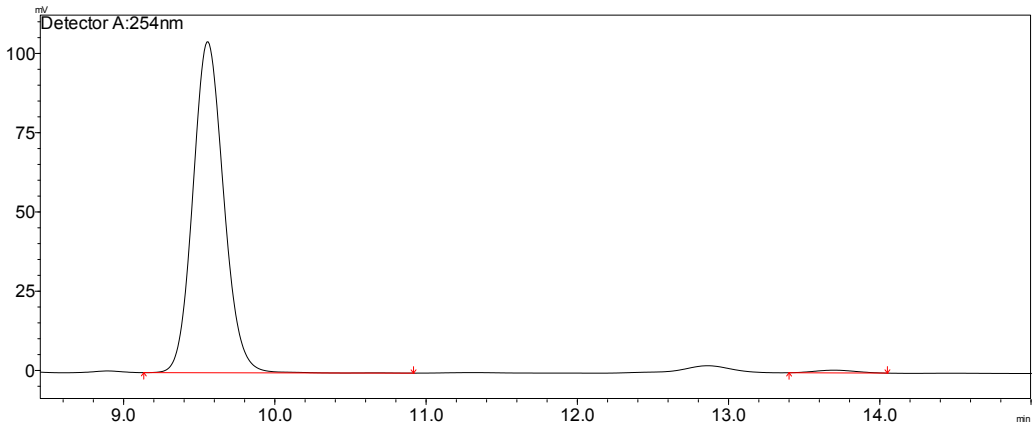
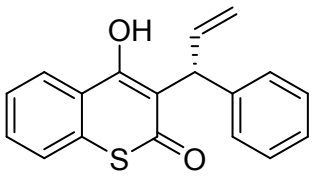


Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.554	329483	23578	55.650	64.259
2	13.674	262577	13114	44.350	35.741
Total		592061	36693	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.551	1475118	104464	98.926	99.188
2	13.691	16018	855	1.074	0.812
Total		1491136	105319	100.000	100.000



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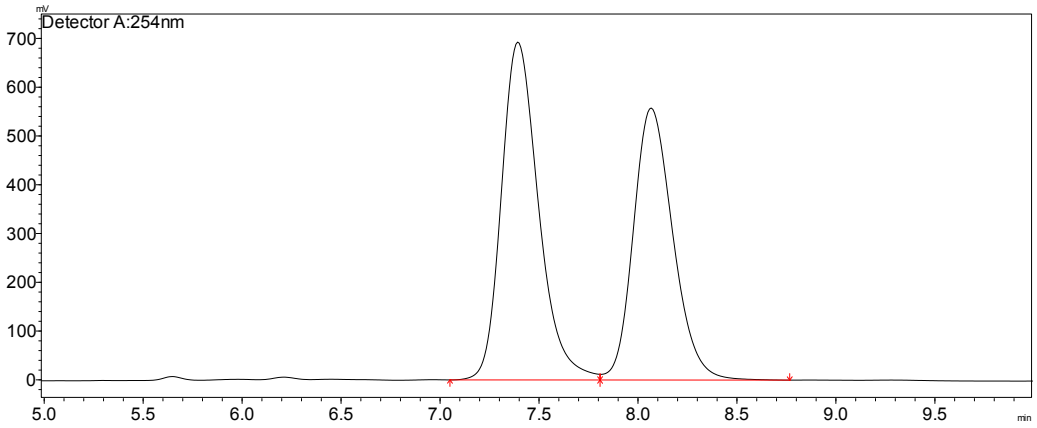
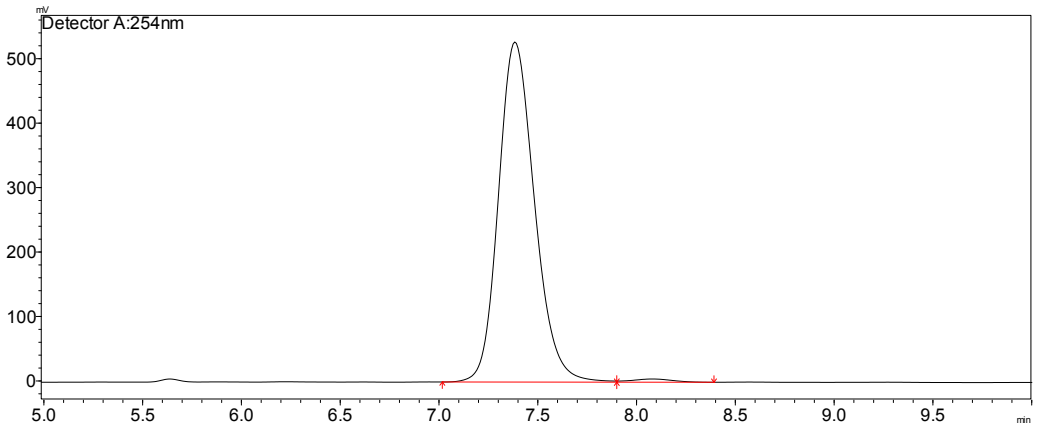
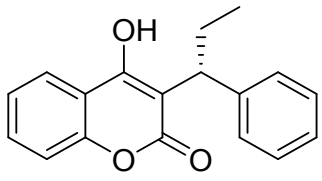


Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.389	9058614	692875	53.907	55.398
2	8.062	7745425	557852	46.093	44.602
Total		16804039	1250727	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.380	6697507	527755	98.971	99.069
2	8.076	69645	4961	1.029	0.931
Total		6767151	532716	100.000	100.000



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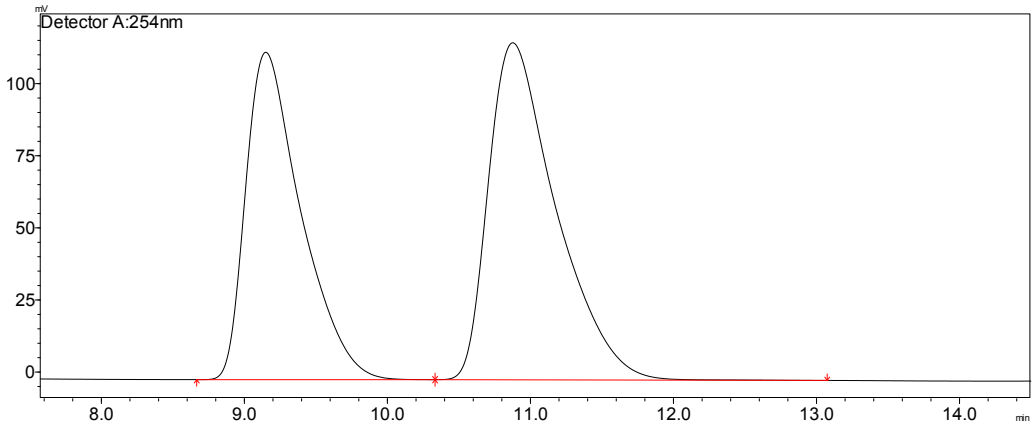
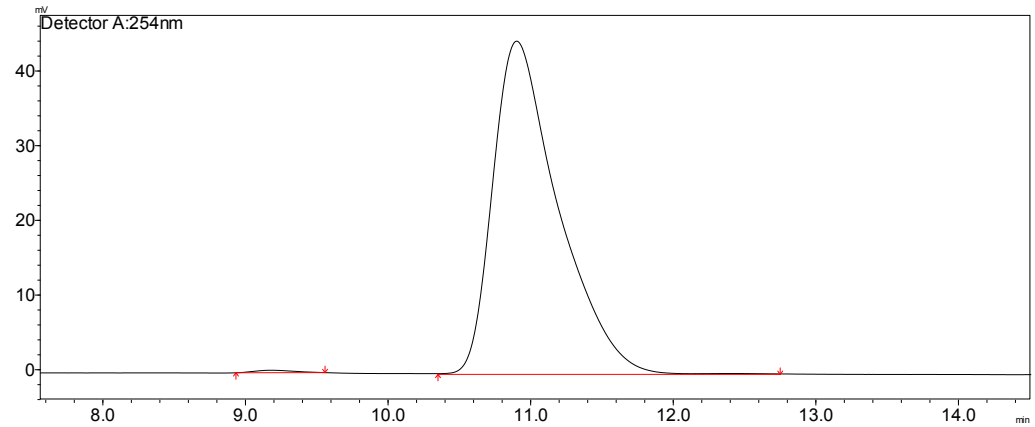
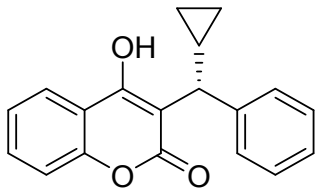


Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.145	3046394	113508	44.310	49.274
2	10.872	3828788	116853	55.690	50.726
Total		6875181	230361	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.179	6370	331	0.445	0.736
2	10.898	1424508	44614	99.555	99.264
Total		1430878	44945	100.000	100.000



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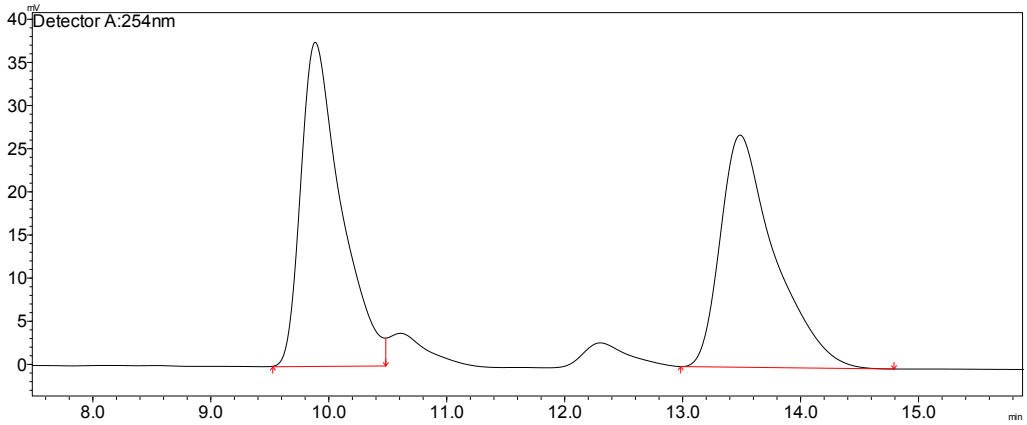
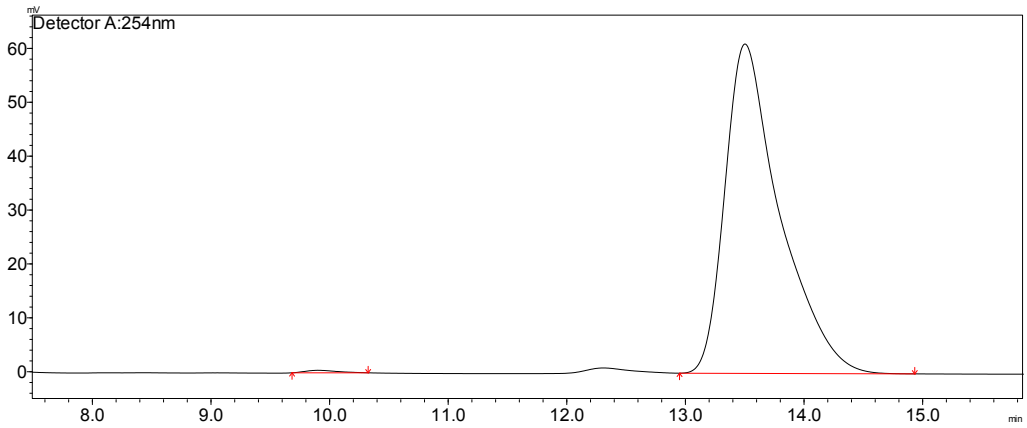
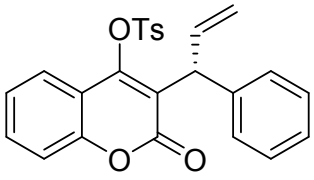


Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.881	891932	37580	50.911	58.279
2	13.483	860021	26903	49.089	41.721
Total		1751953	64483	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.897	8662	467	0.439	0.758
2	13.498	1965055	61129	99.561	99.242
Total		1973717	61596	100.000	100.000



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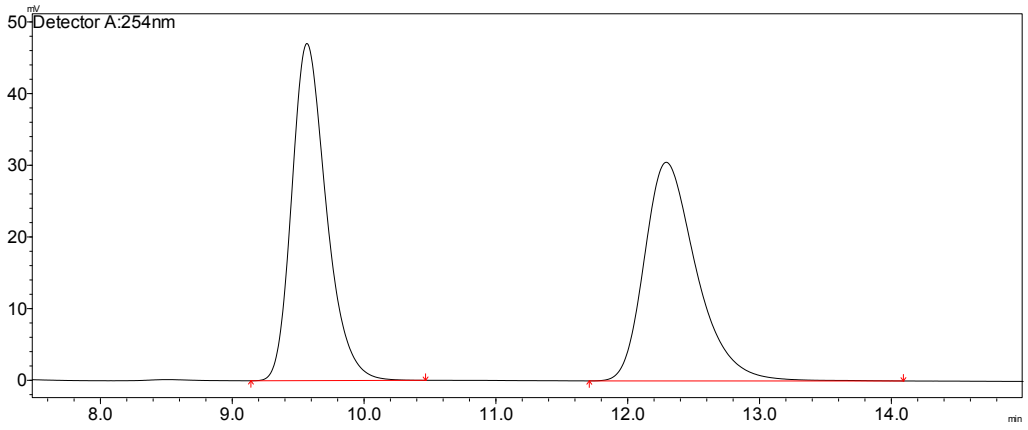
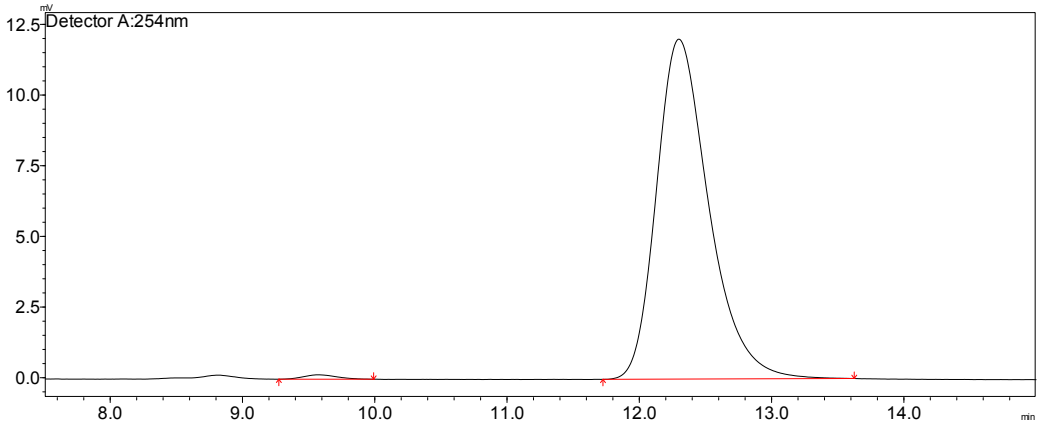
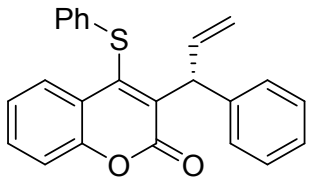


Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.562	856371	47042	50.560	60.666
2	12.289	837413	30500	49.440	39.334
Total		1693784	77542	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.570	2731	156	0.818	1.279
2	12.295	331016	12028	99.182	98.721
Total		333748	12183	100.000	100.000



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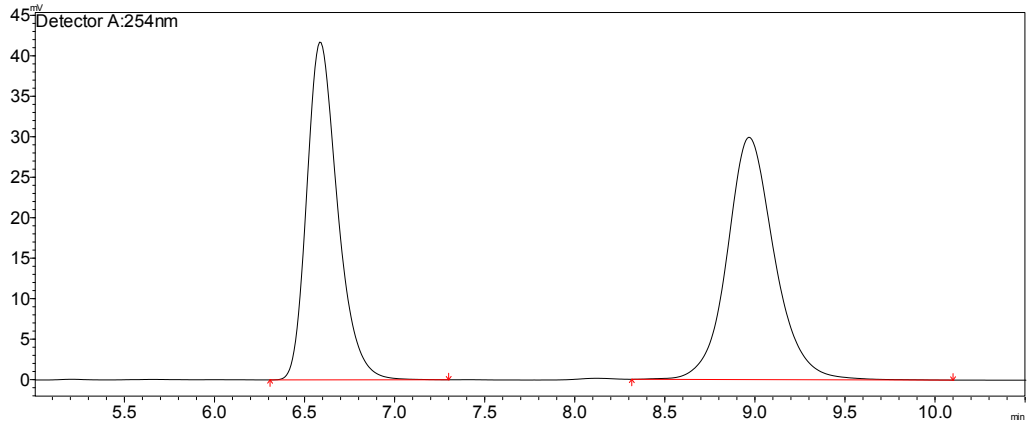
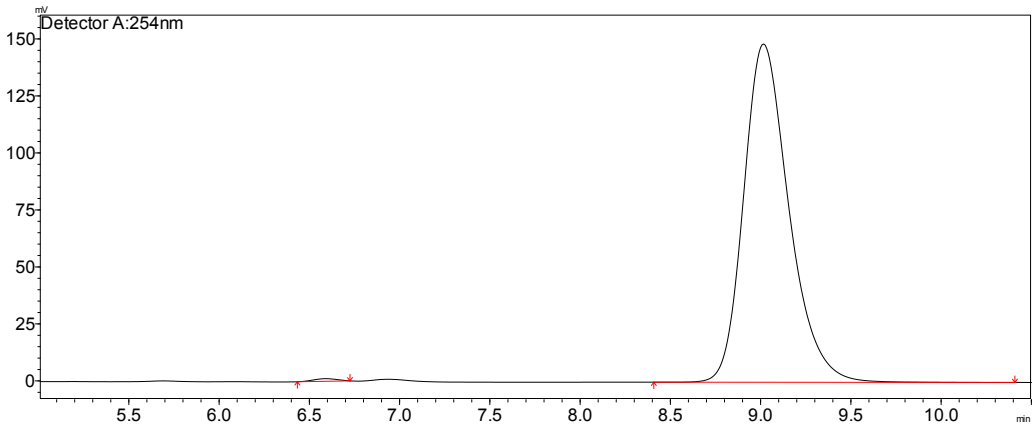


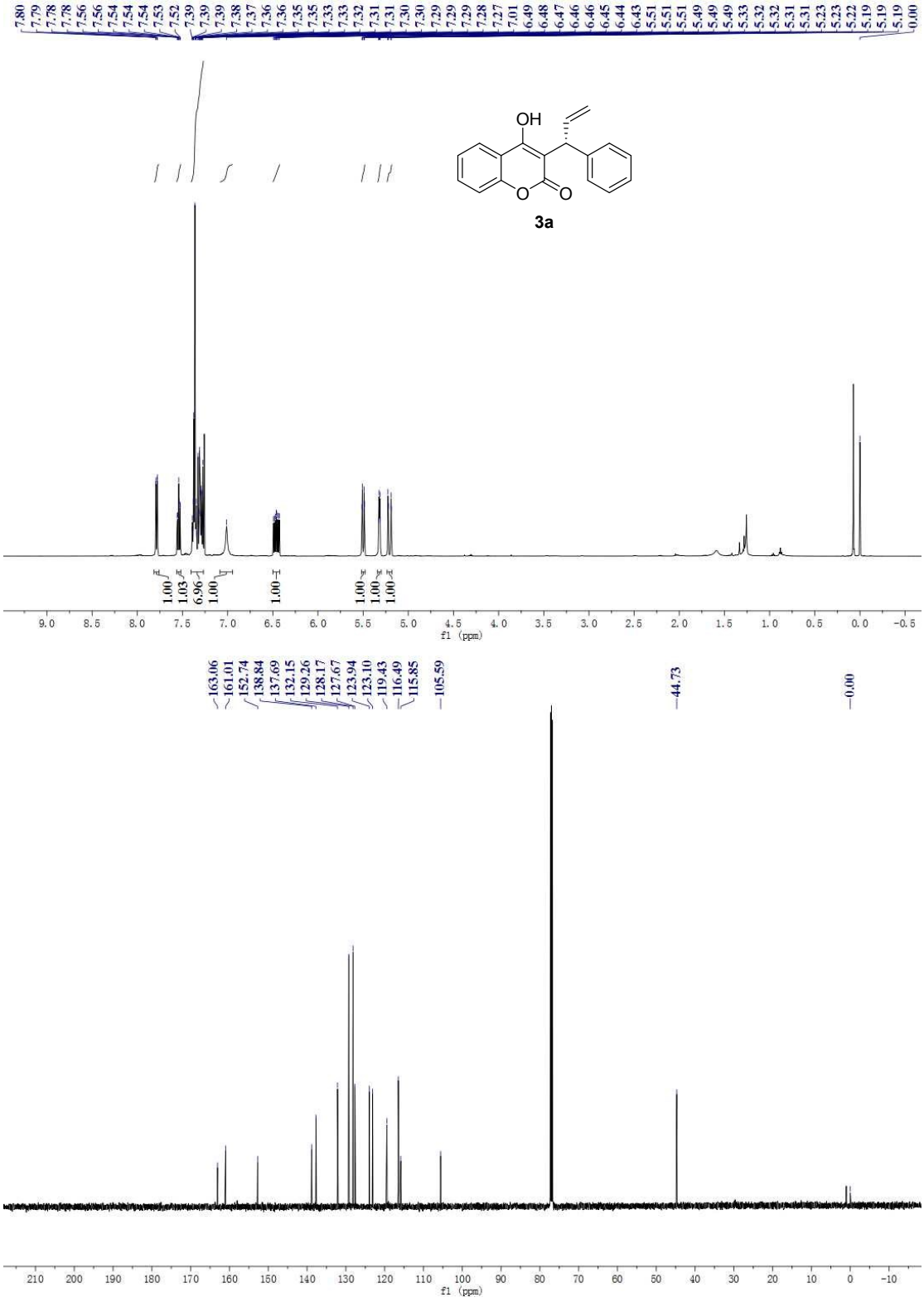
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.583	497327	41720	47.597	58.223
2	8.964	547548	29935	52.403	41.777
Total		1044875	71654	100.000	100.000



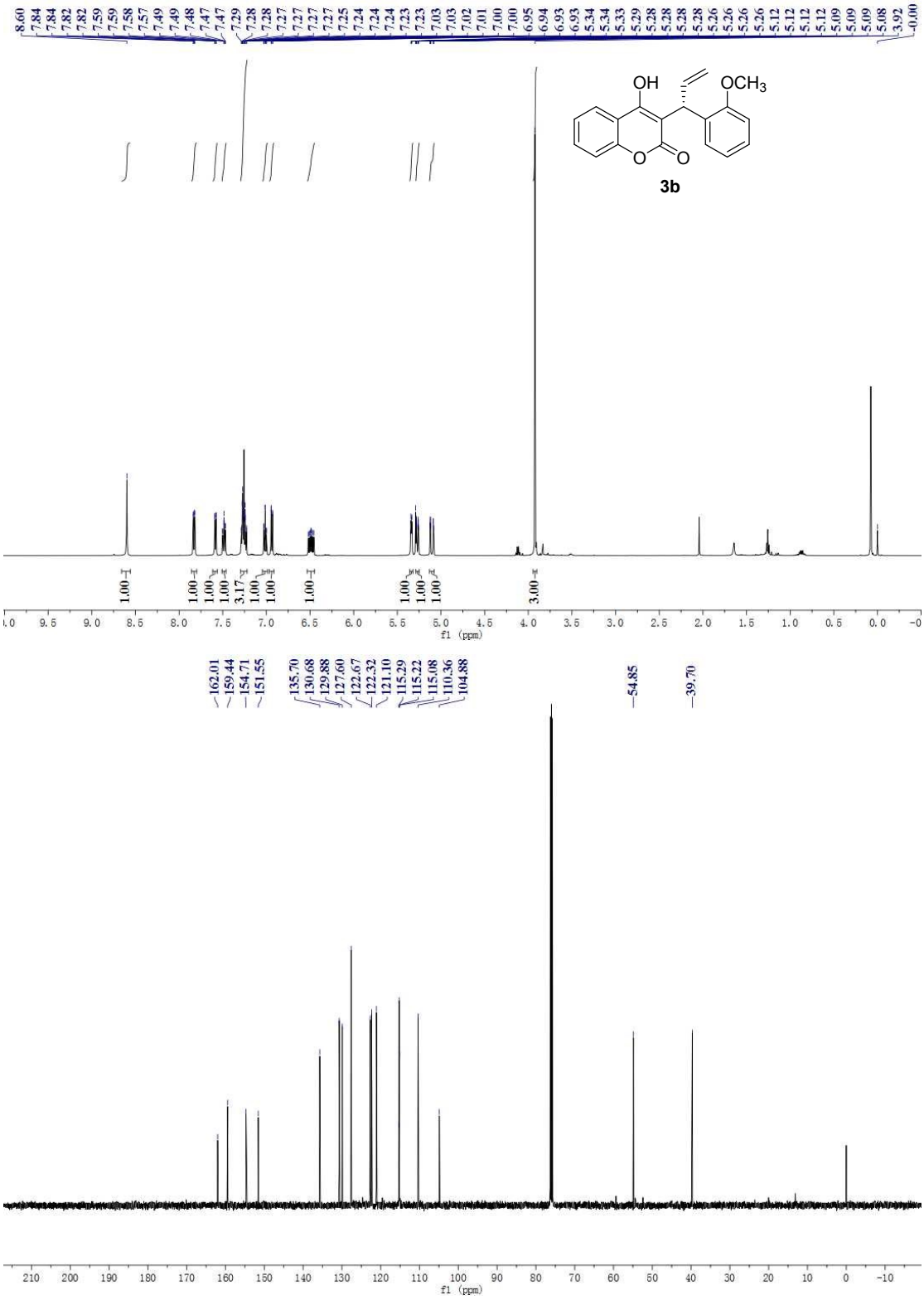
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.587	10457	1146	0.402	0.766
2	9.012	2588293	148408	99.598	99.234
Total		2598750	149554	100.000	100.000

VI Data of NMR Spectra:

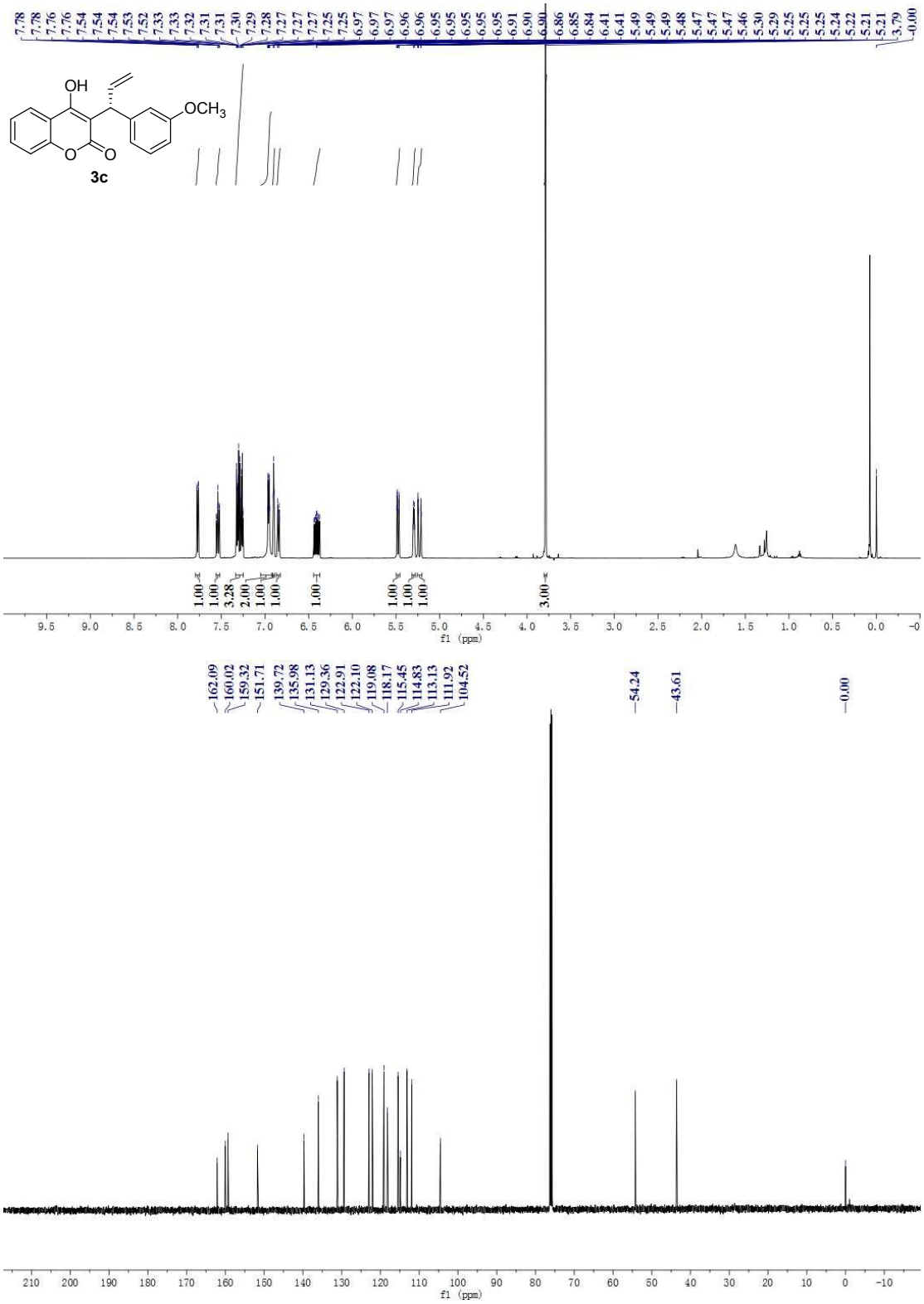
NMR Spectra of **3a**



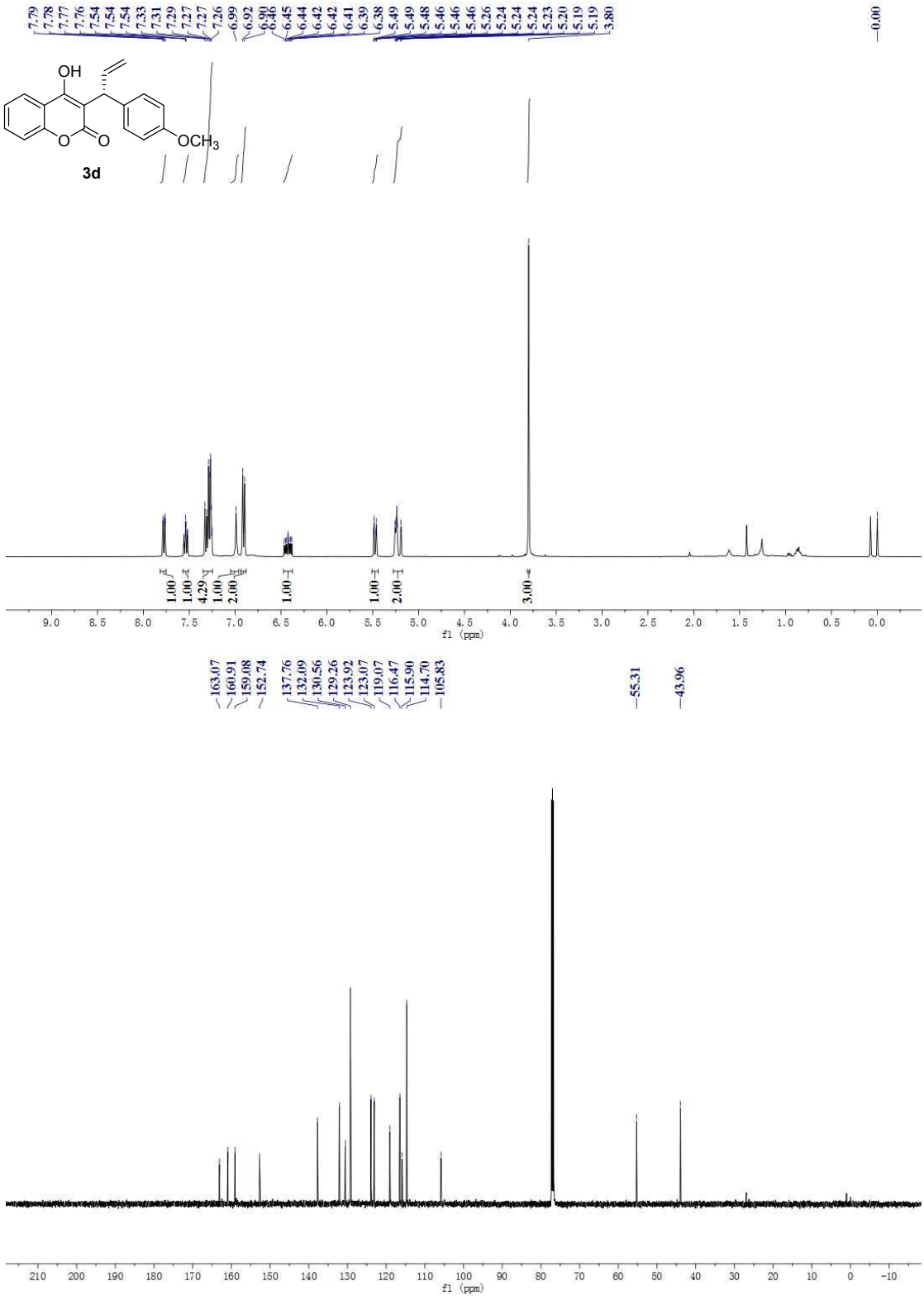
NMR Spectra of **3b**



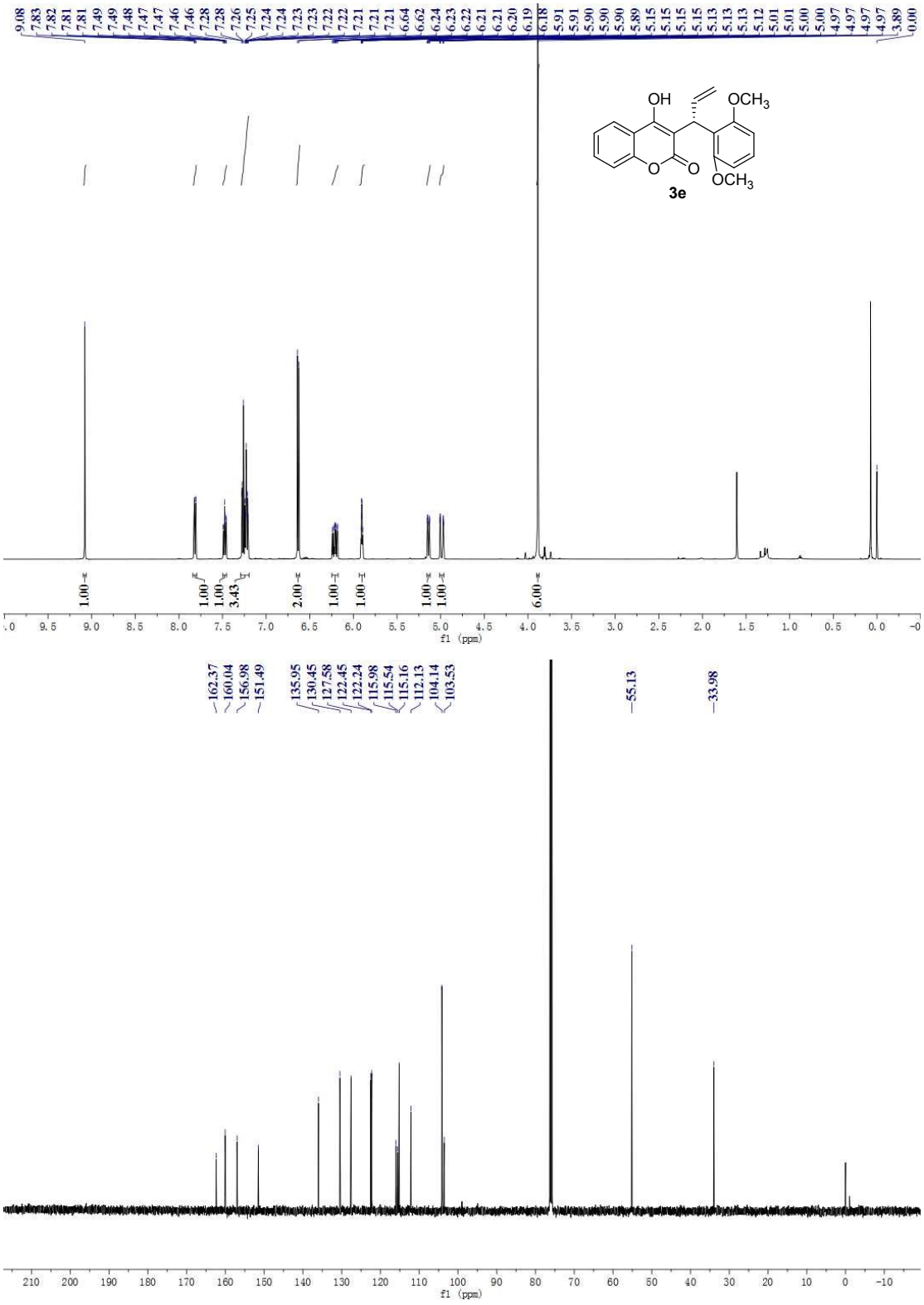
NMR Spectra of **3c**



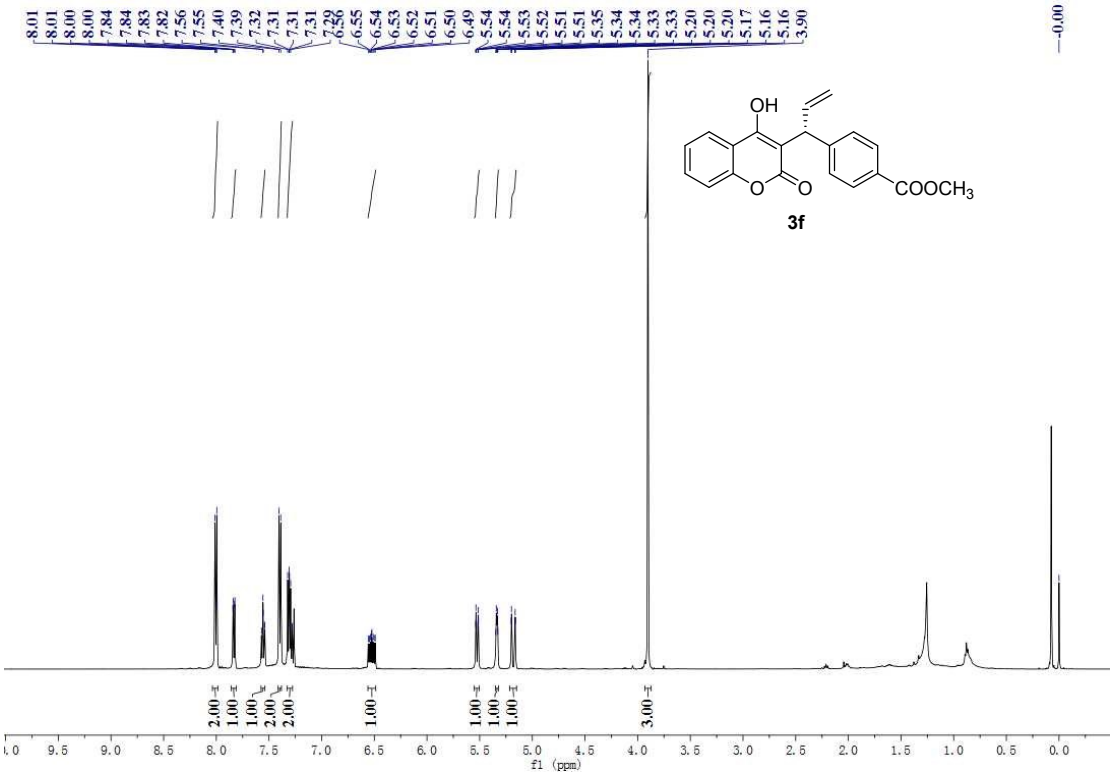
NMR Spectra of **3d**

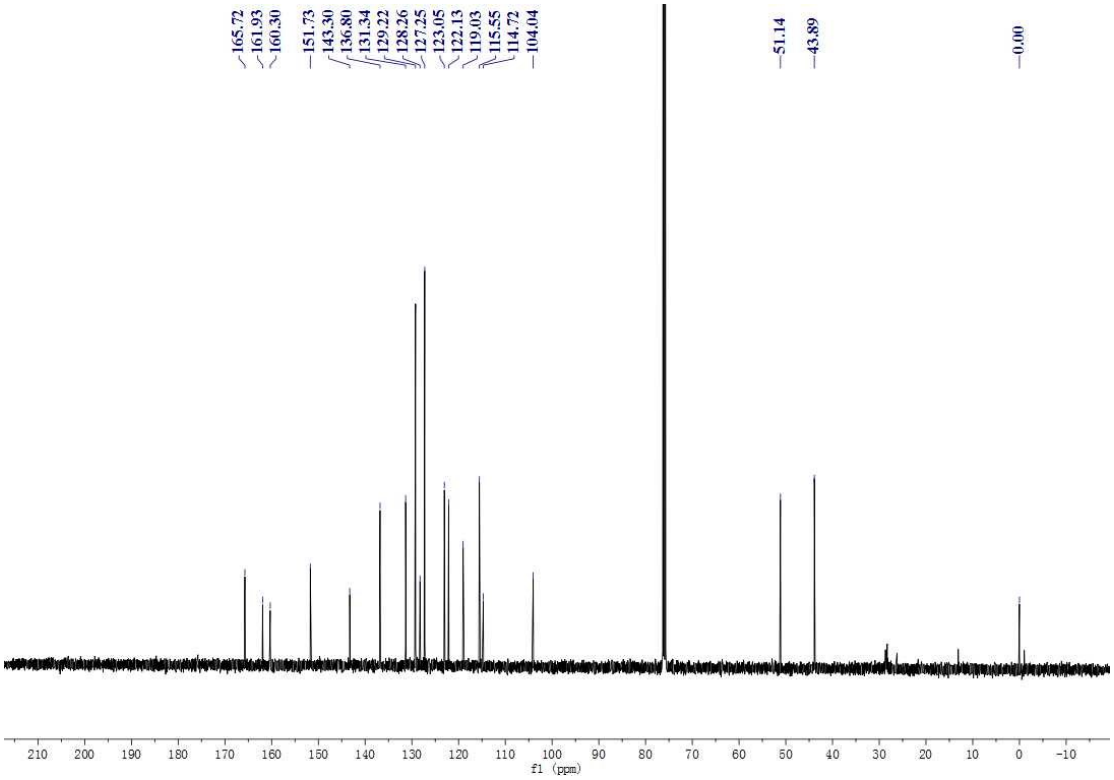


NMR Spectra of **3e**

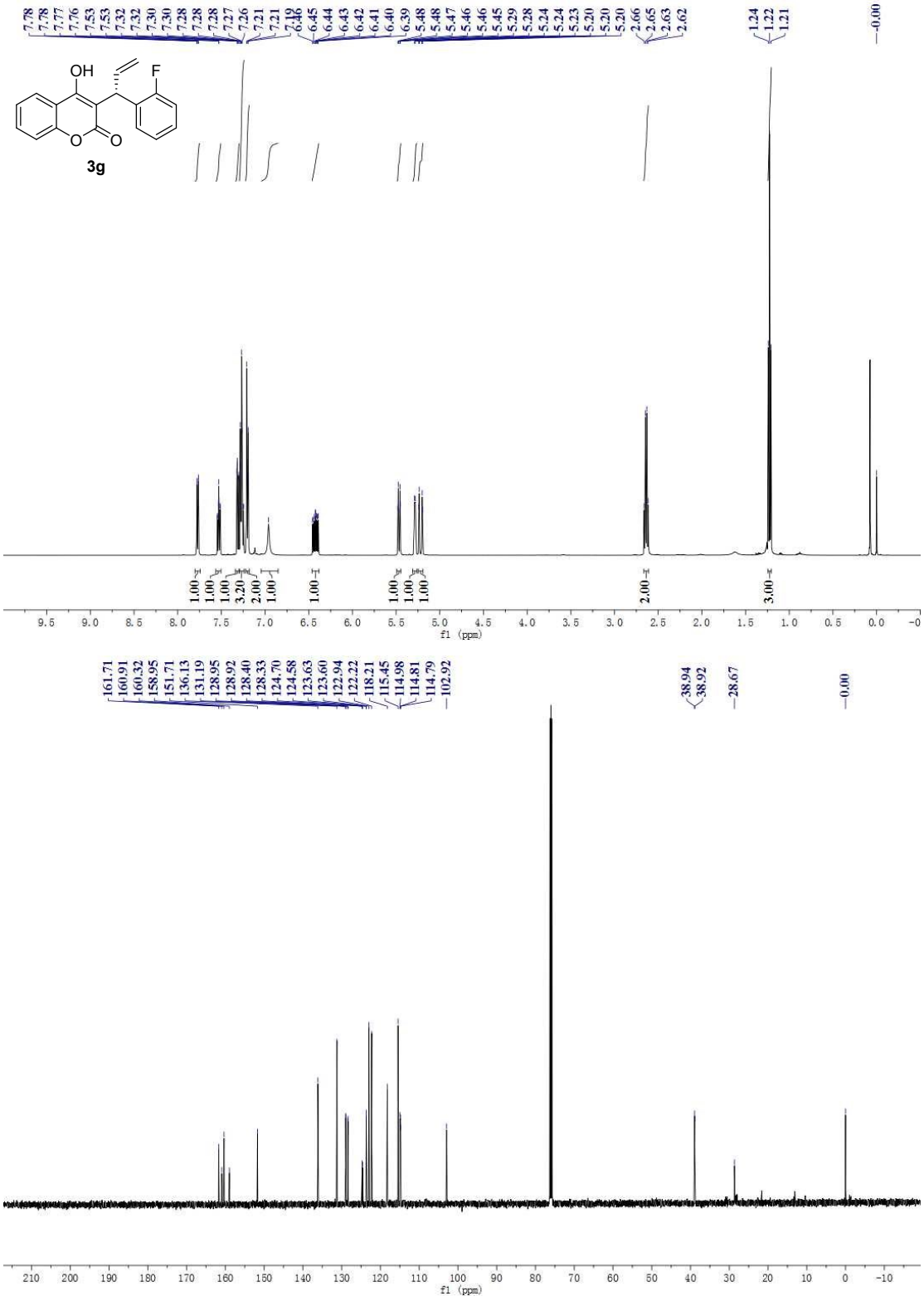


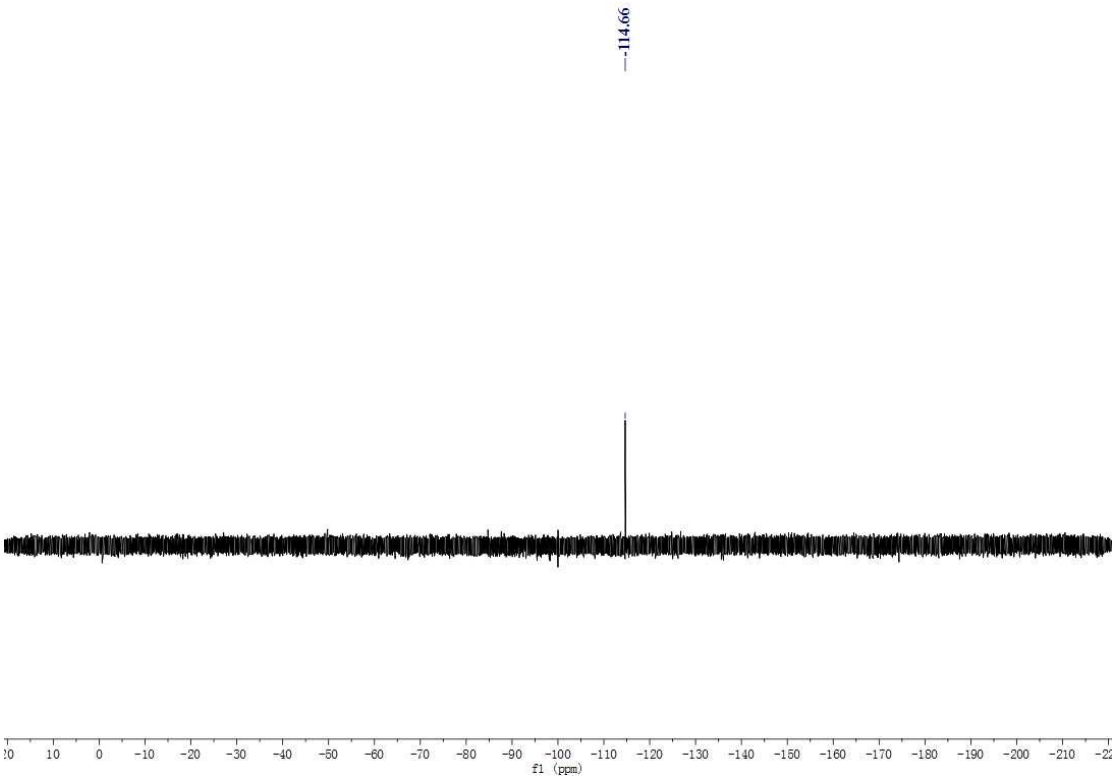
NMR Spectra of **3f**



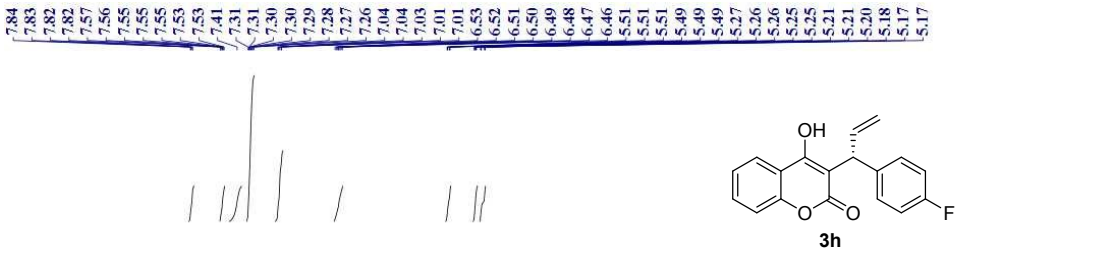


NMR Spectra of **3g**

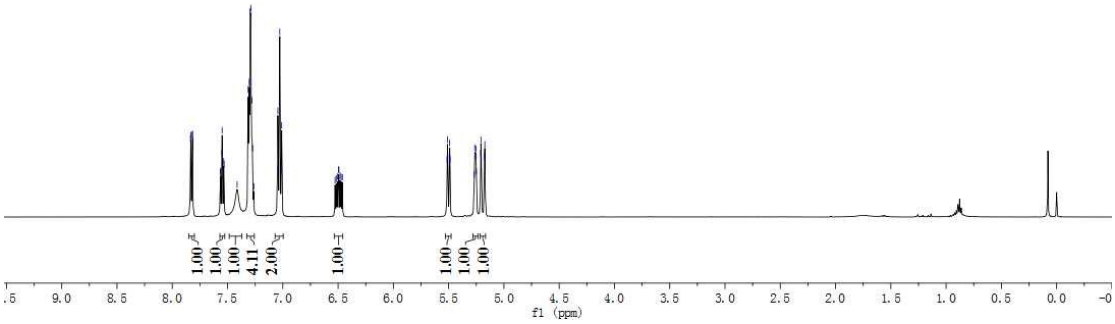


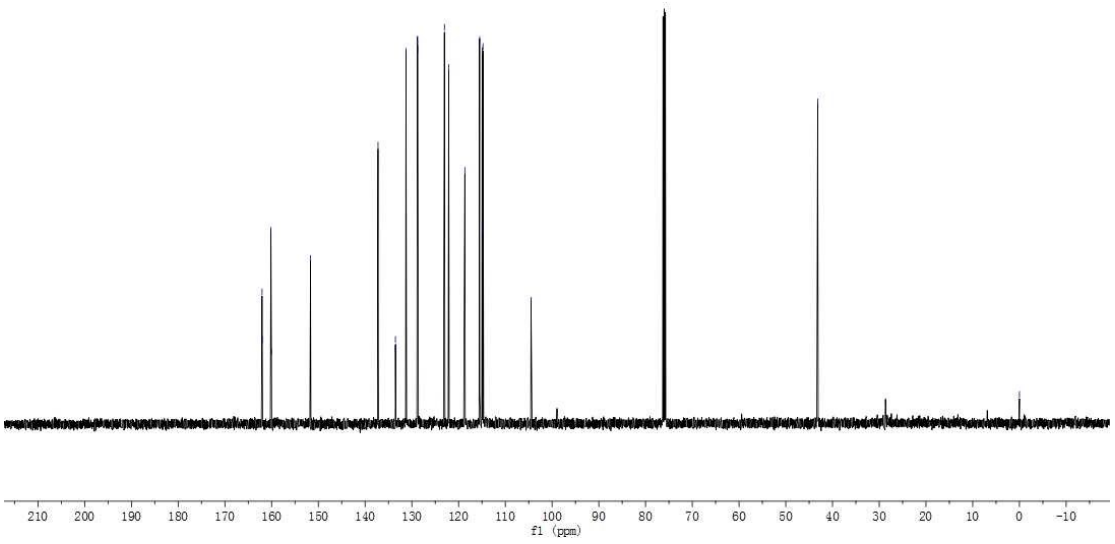

-114.66
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

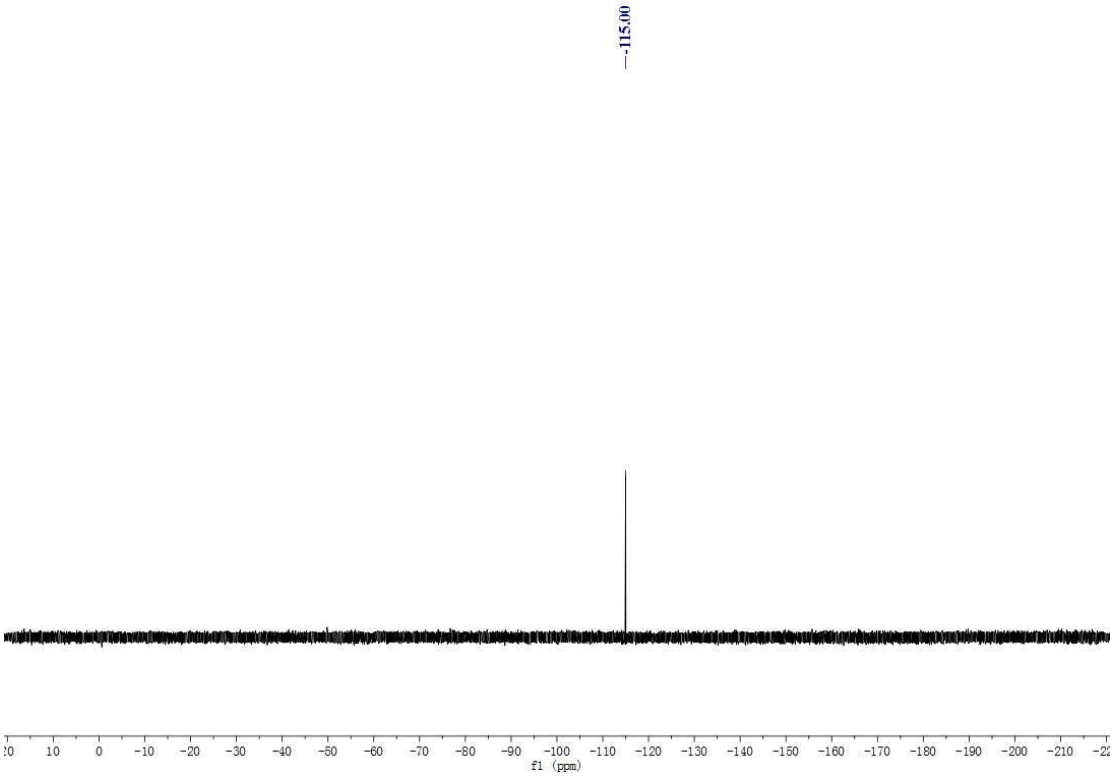
NMR Spectra of **3h**



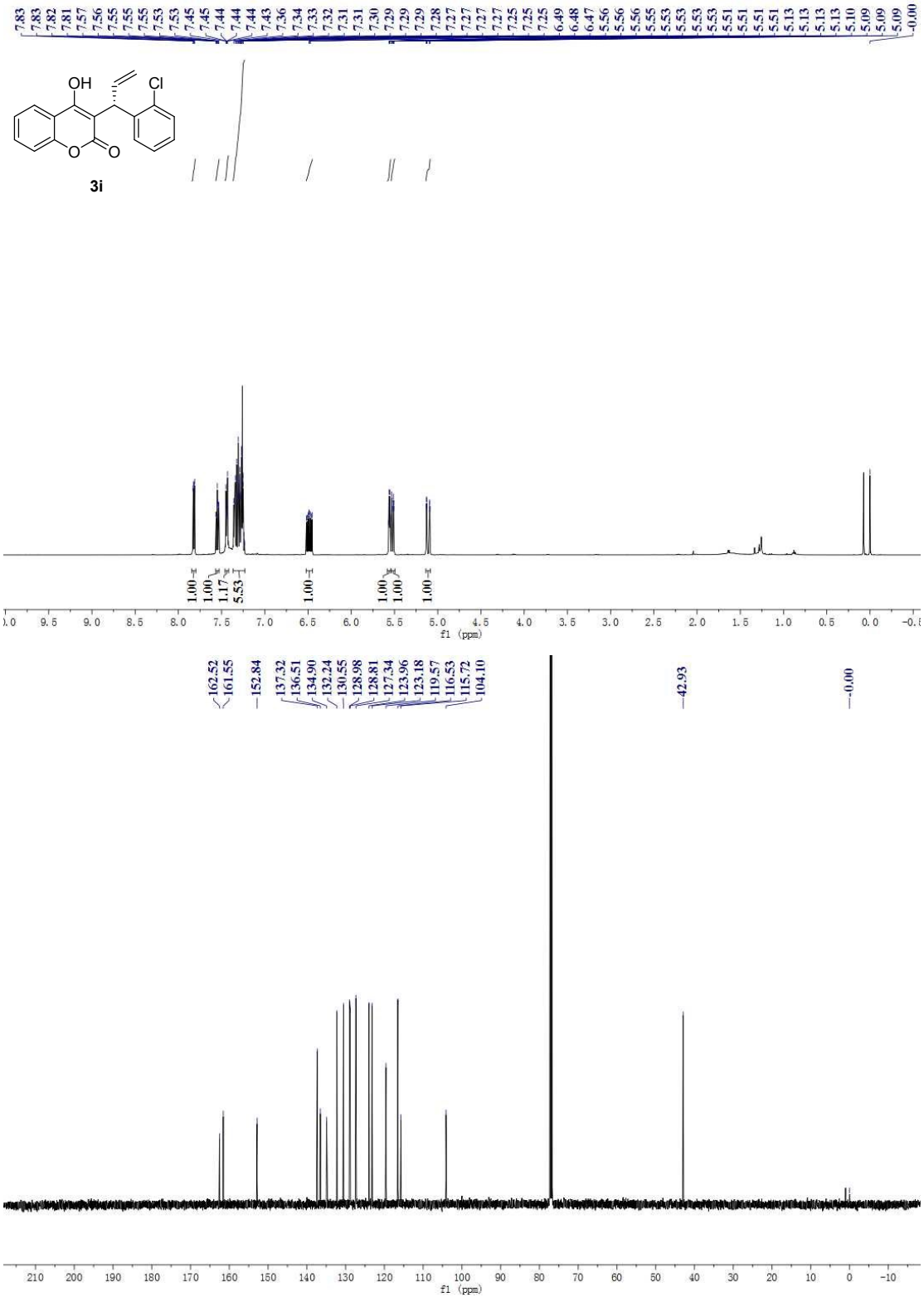
3h



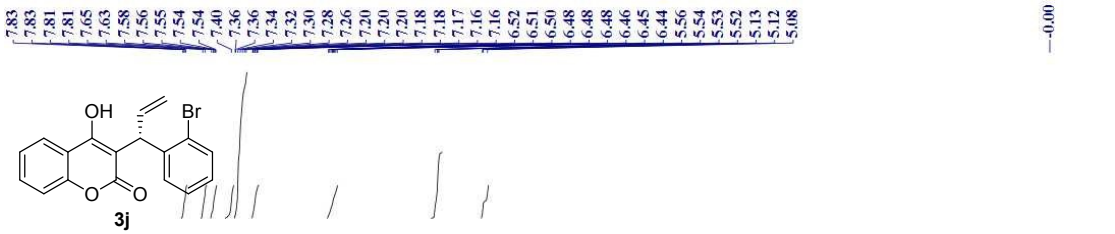



-115.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

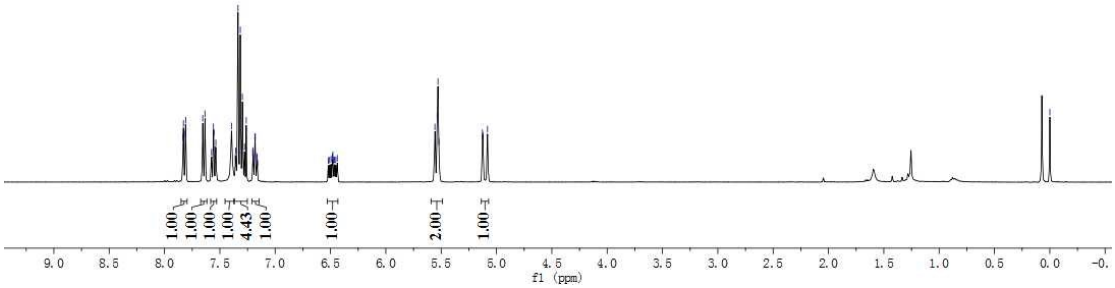
NMR Spectra of **3i**

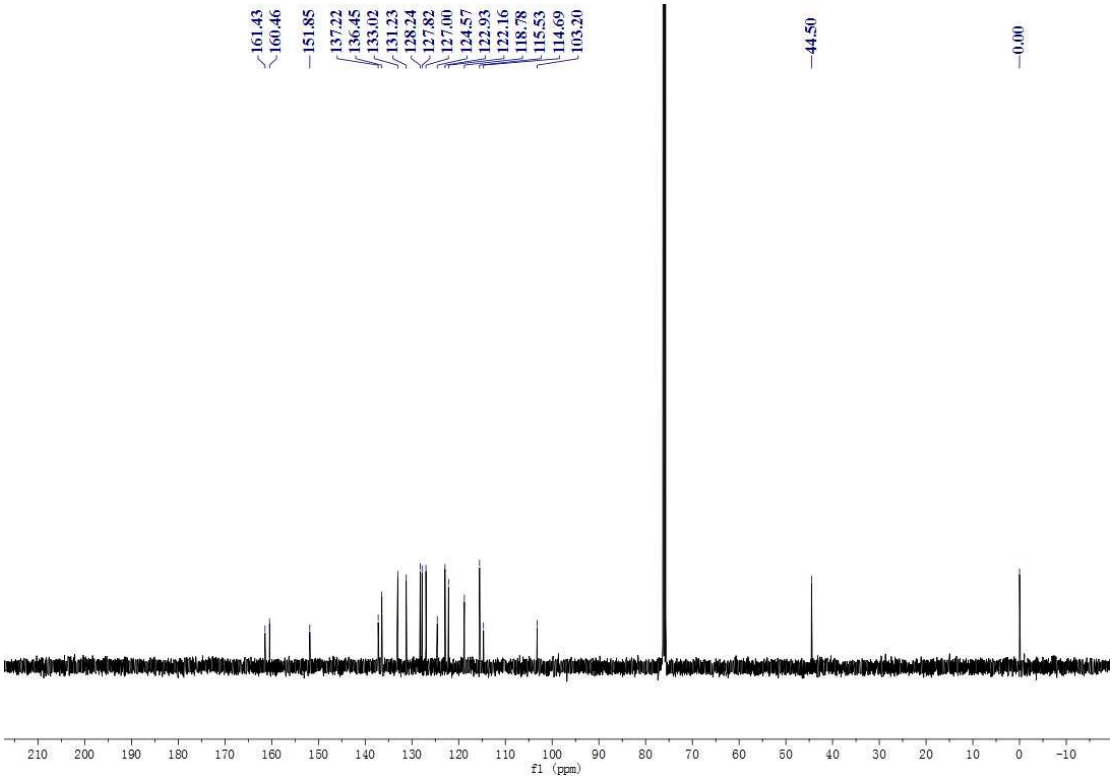


NMR Spectra of **3j**

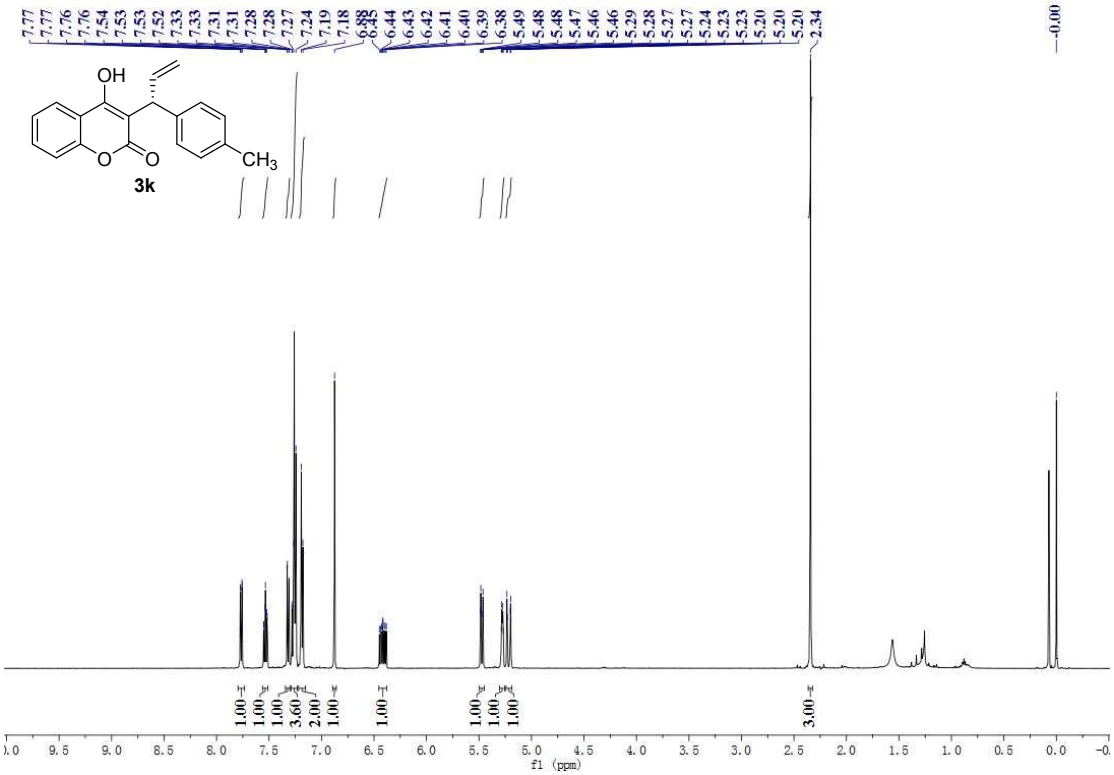


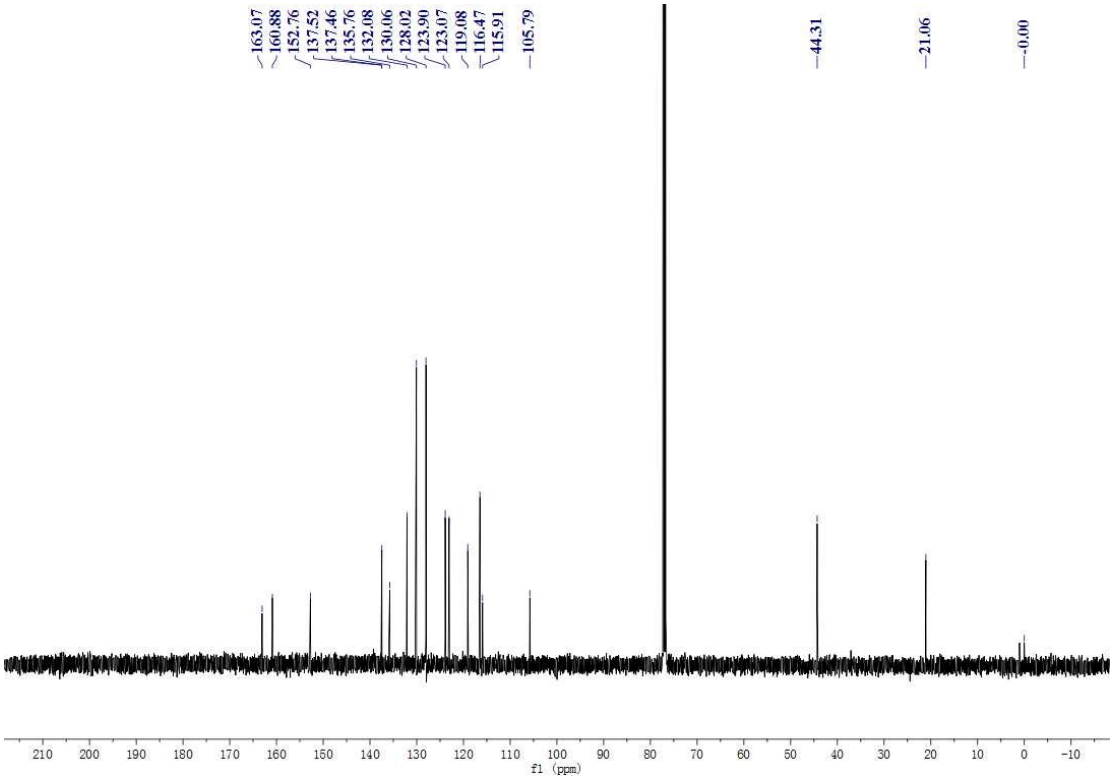
3j



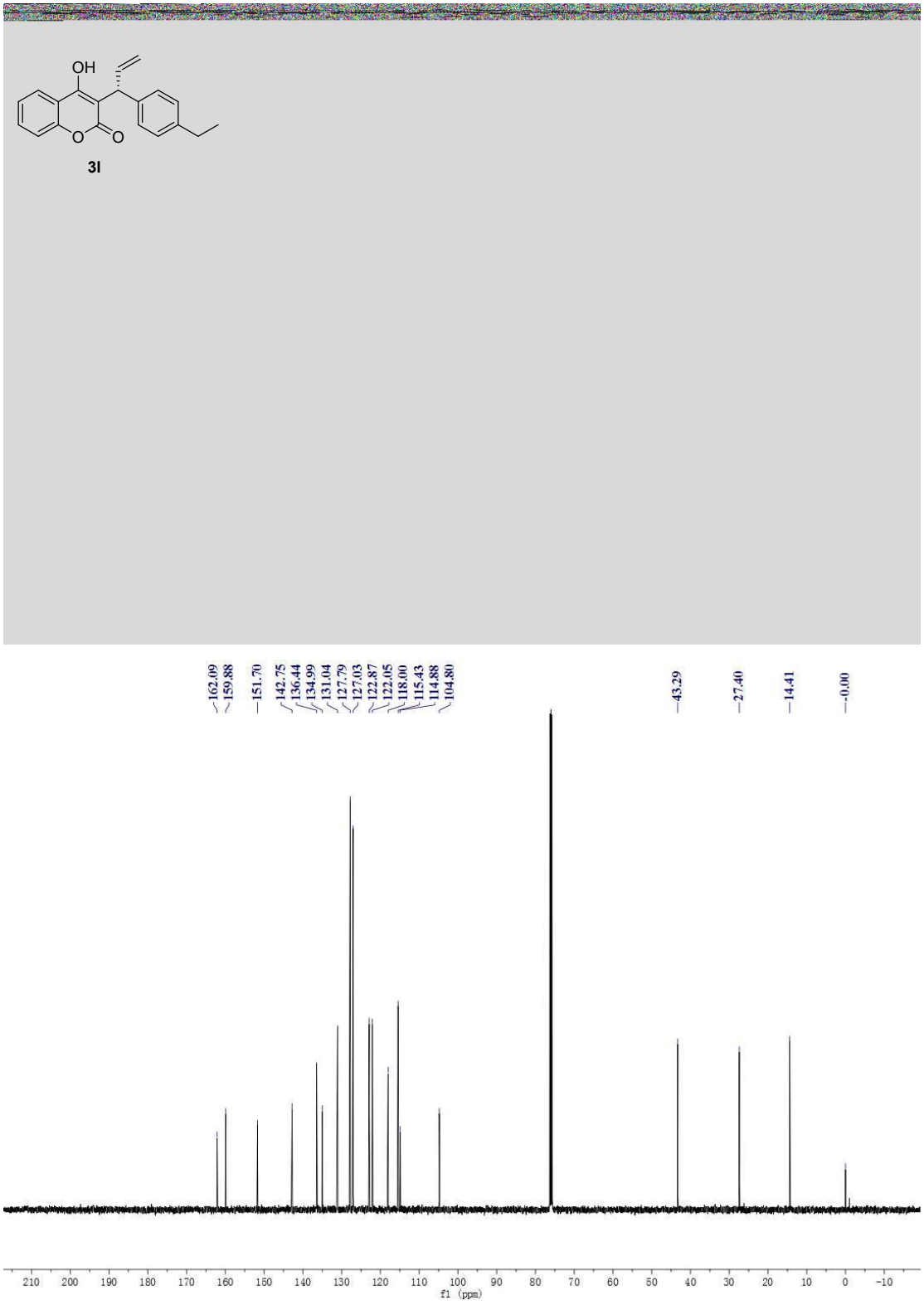


NMR Spectra of **3k**

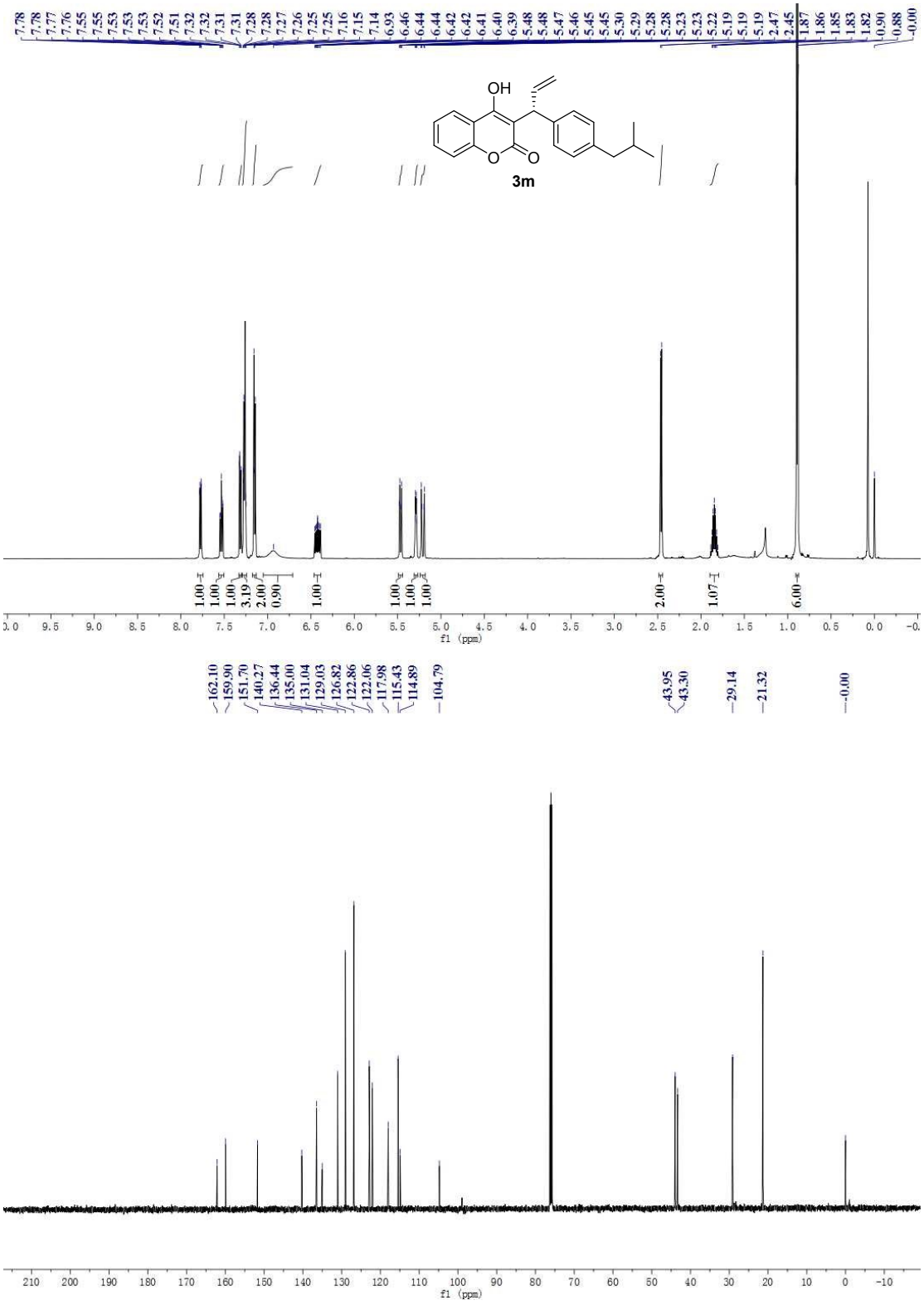




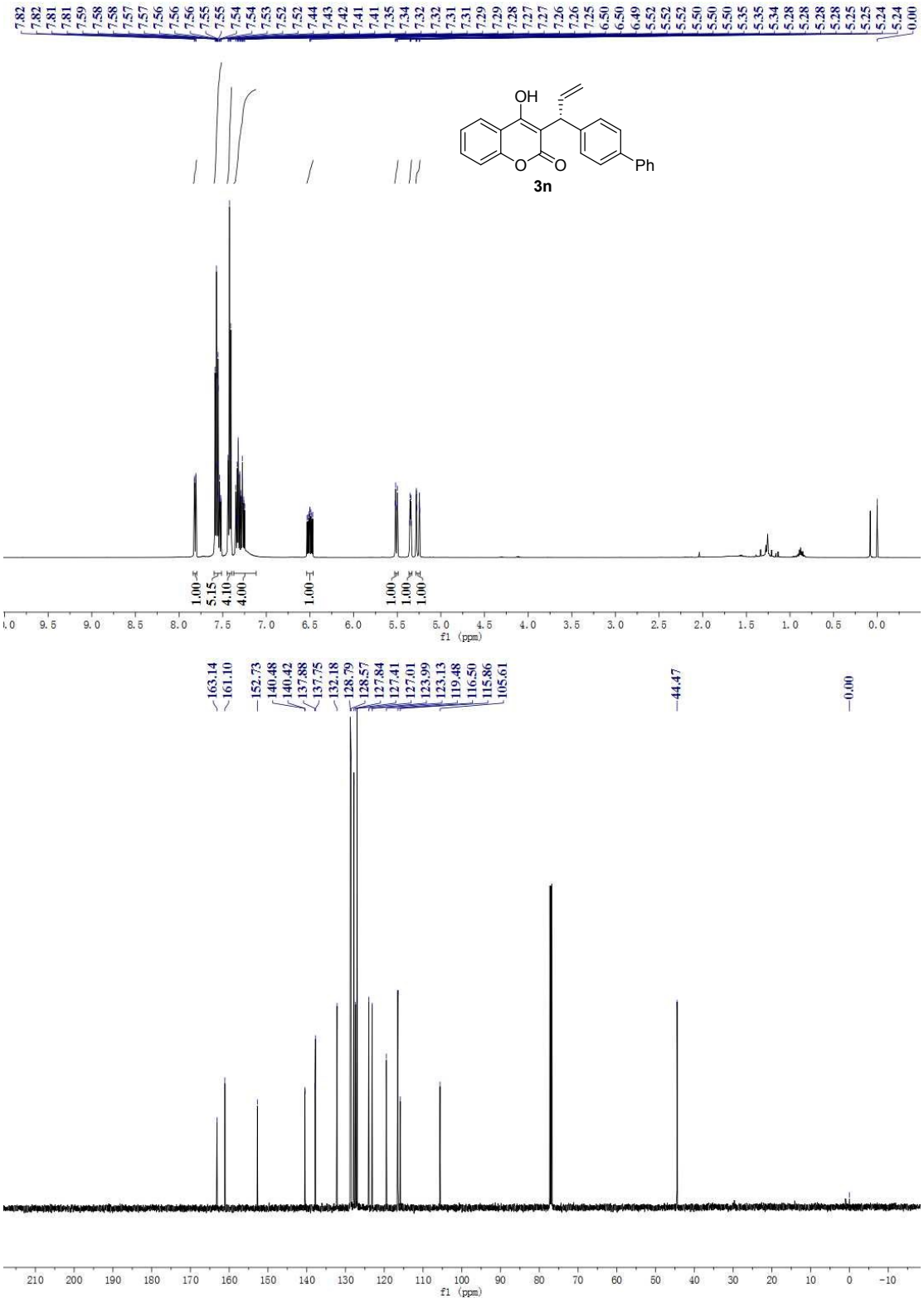
NMR Spectra of **3l**



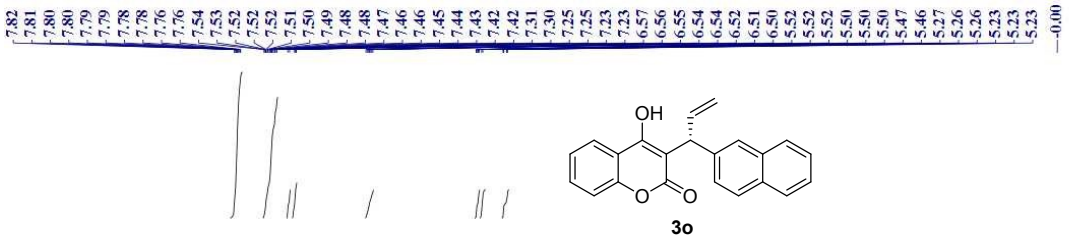
NMR Spectra of **3m**



NMR Spectra of **3n**

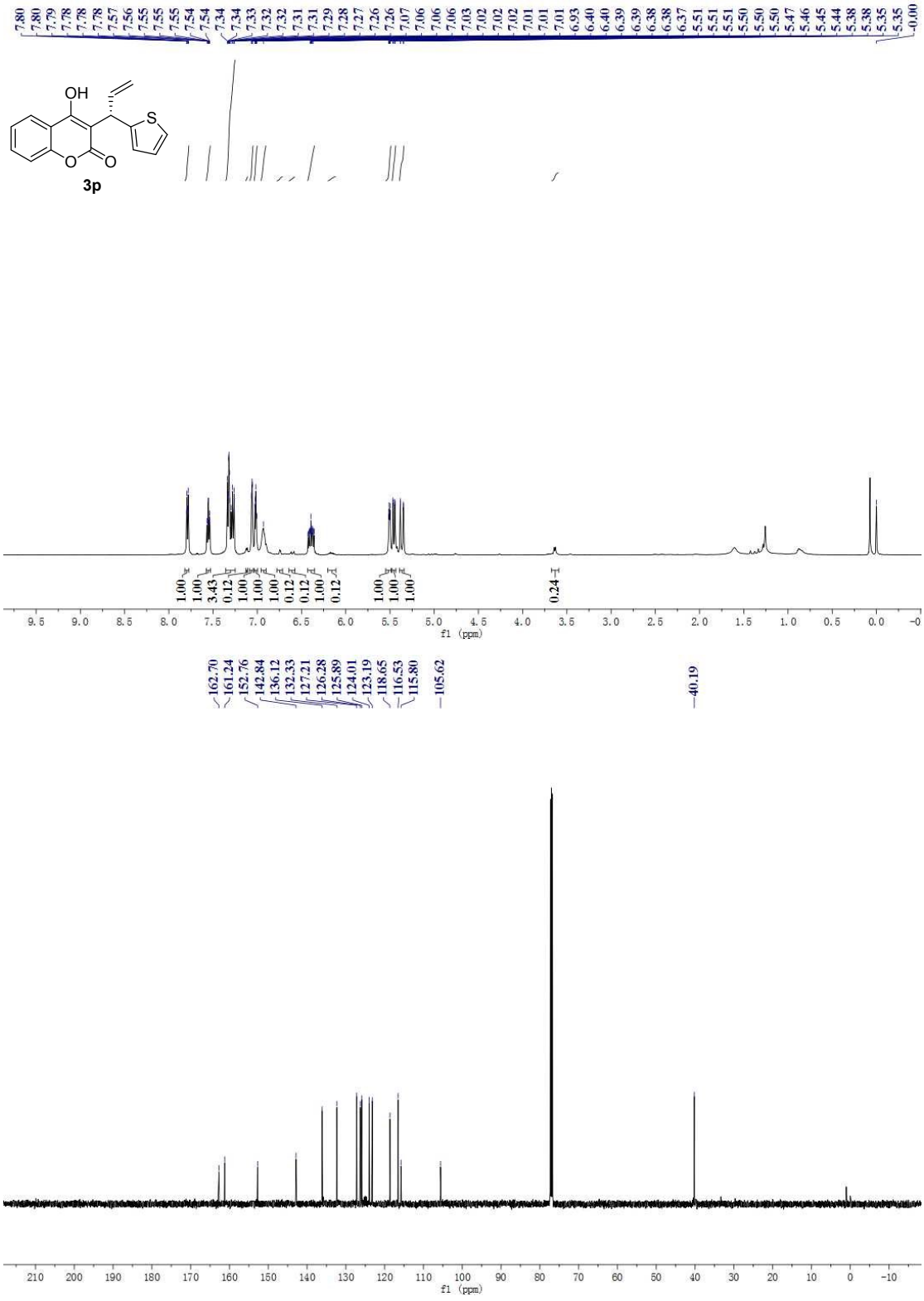


NMR Spectra of **3o**

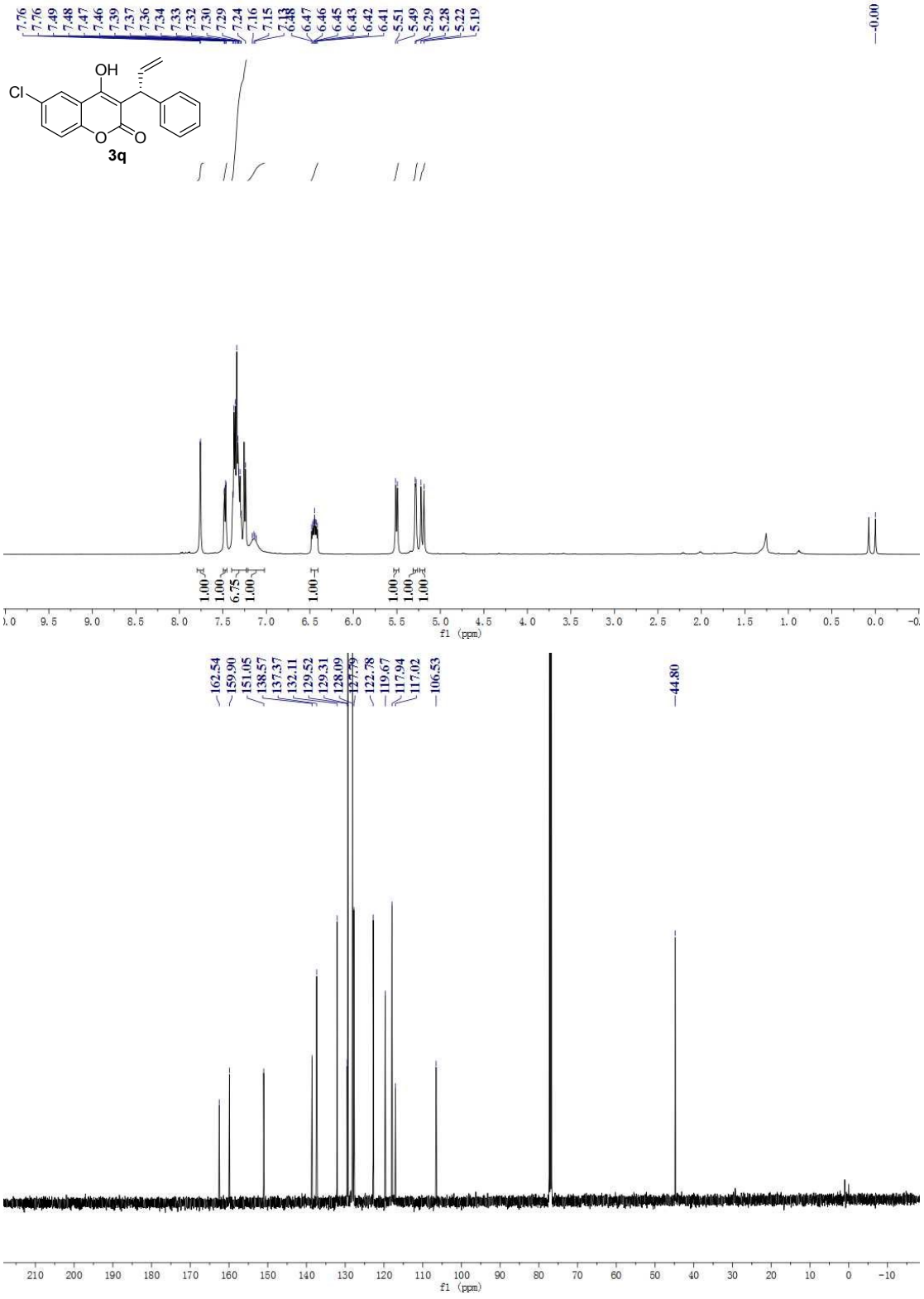


3o

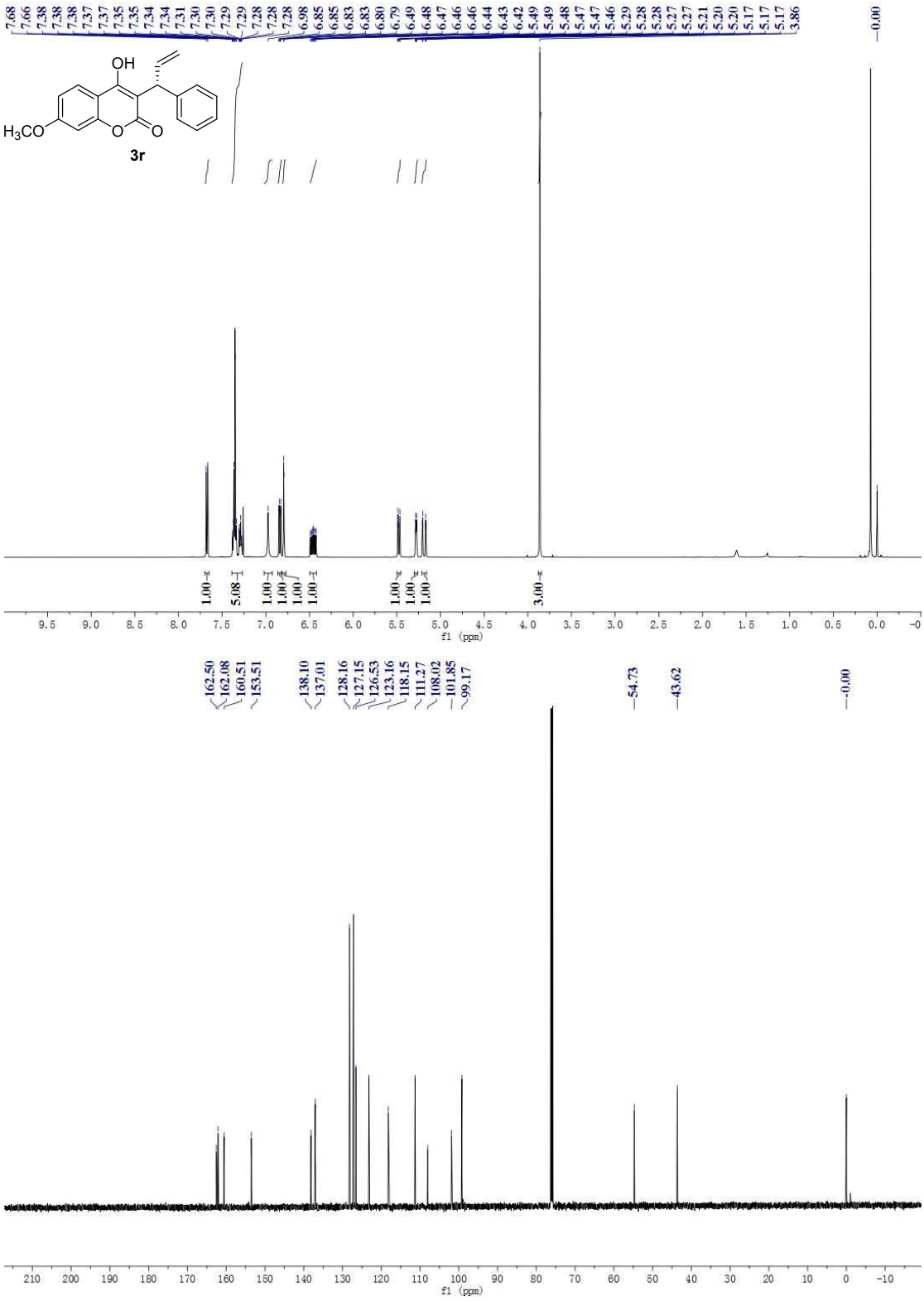
NMR Spectra of **3p**



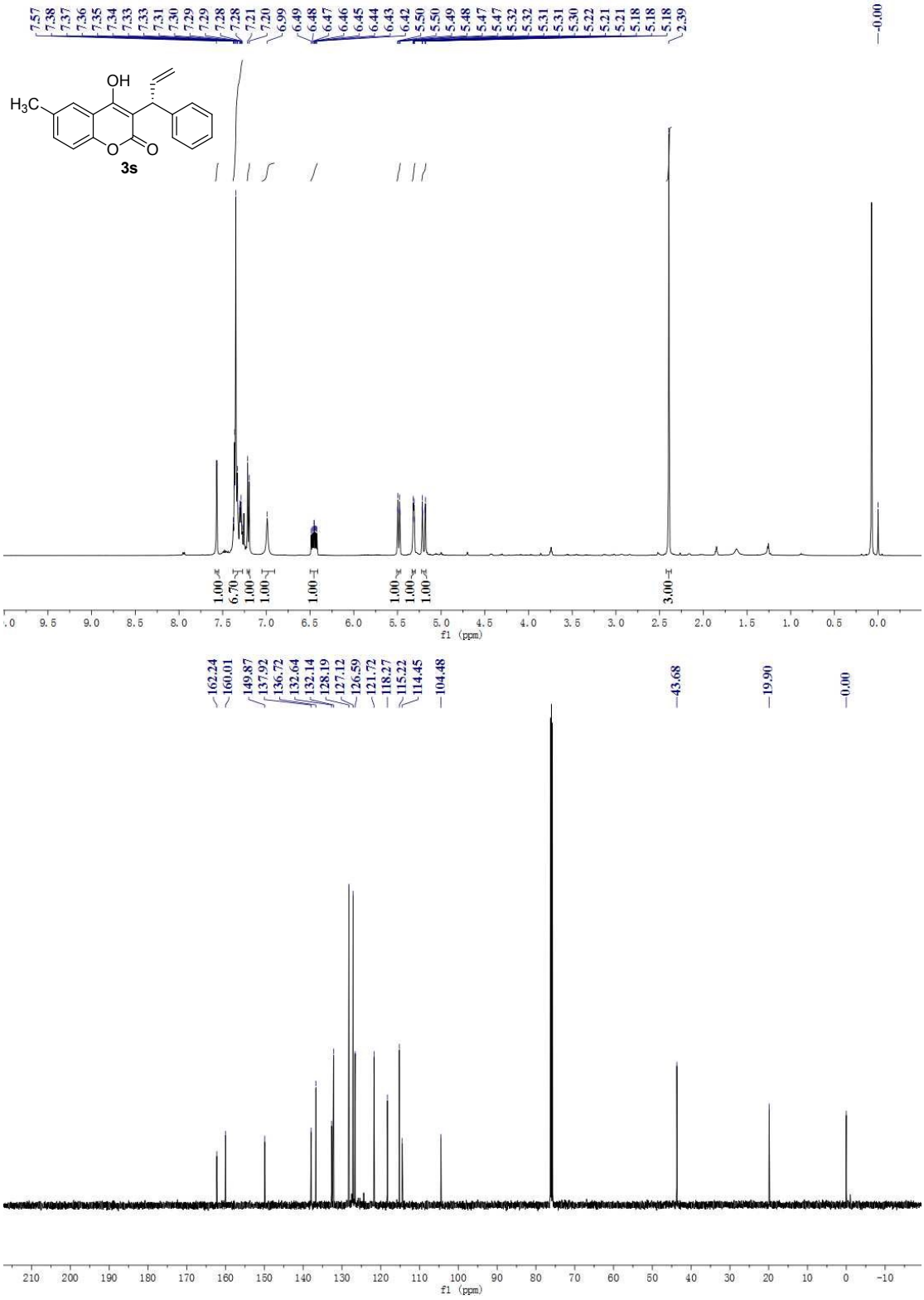
NMR Spectra of **3q**



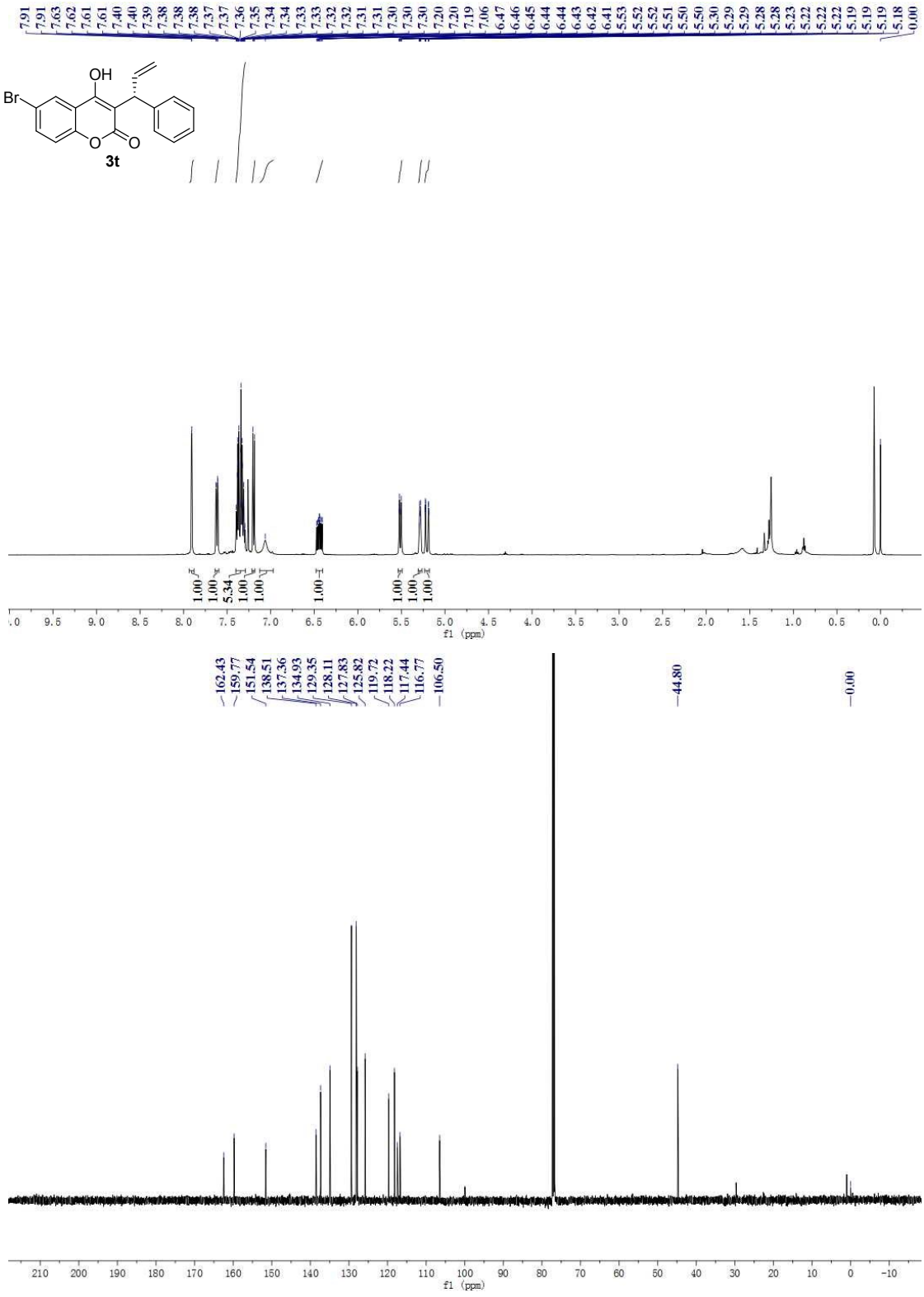
NMR Spectra of **3r**



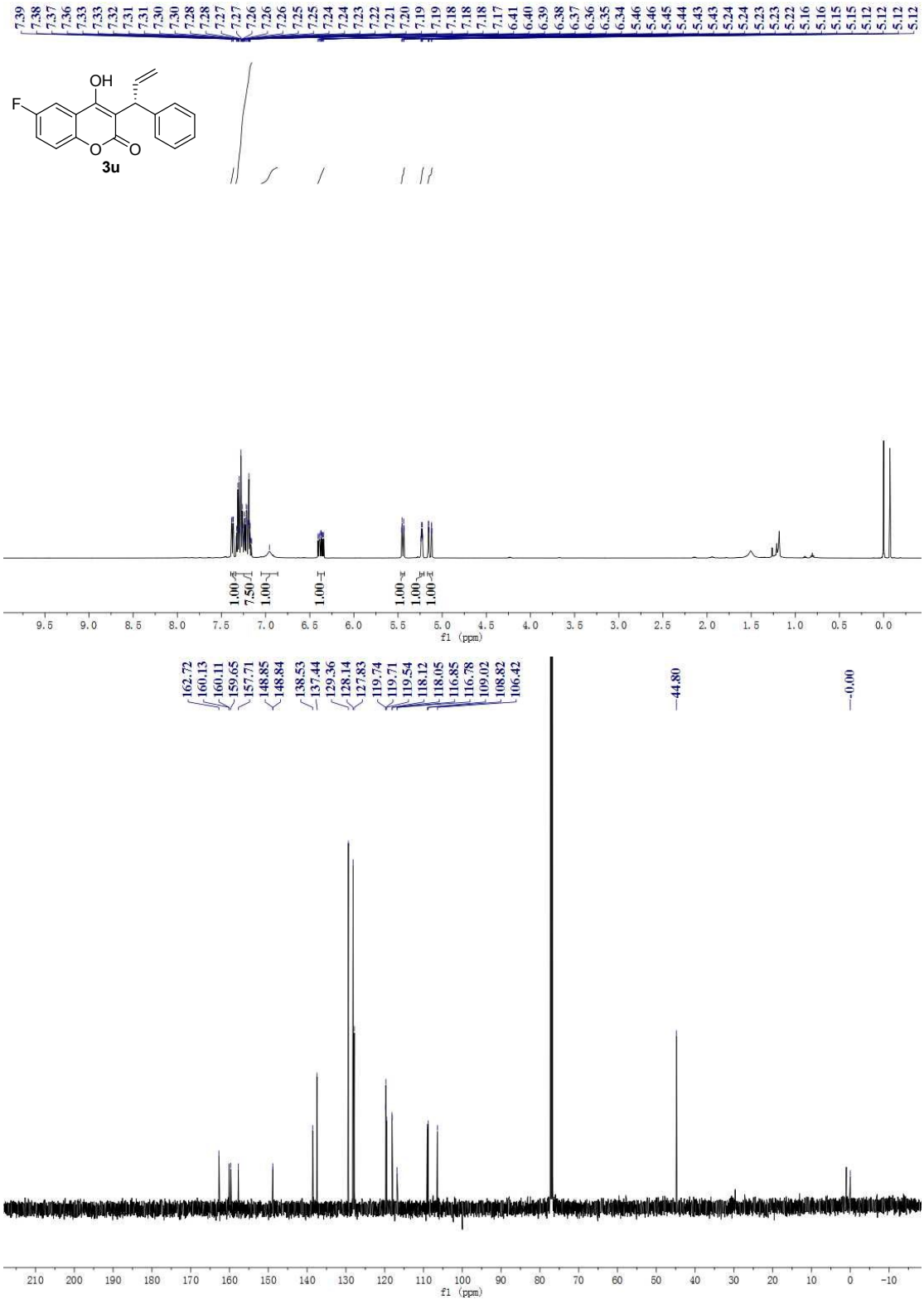
NMR Spectra of **3s**

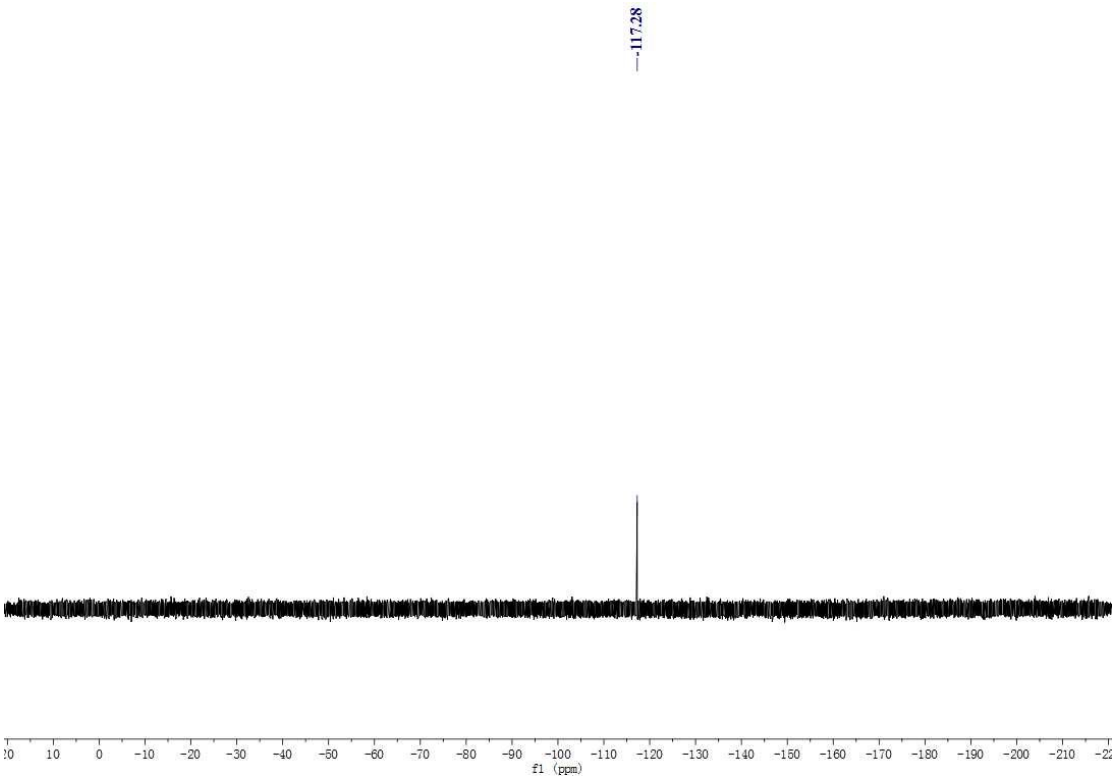


NMR Spectra of **3t**

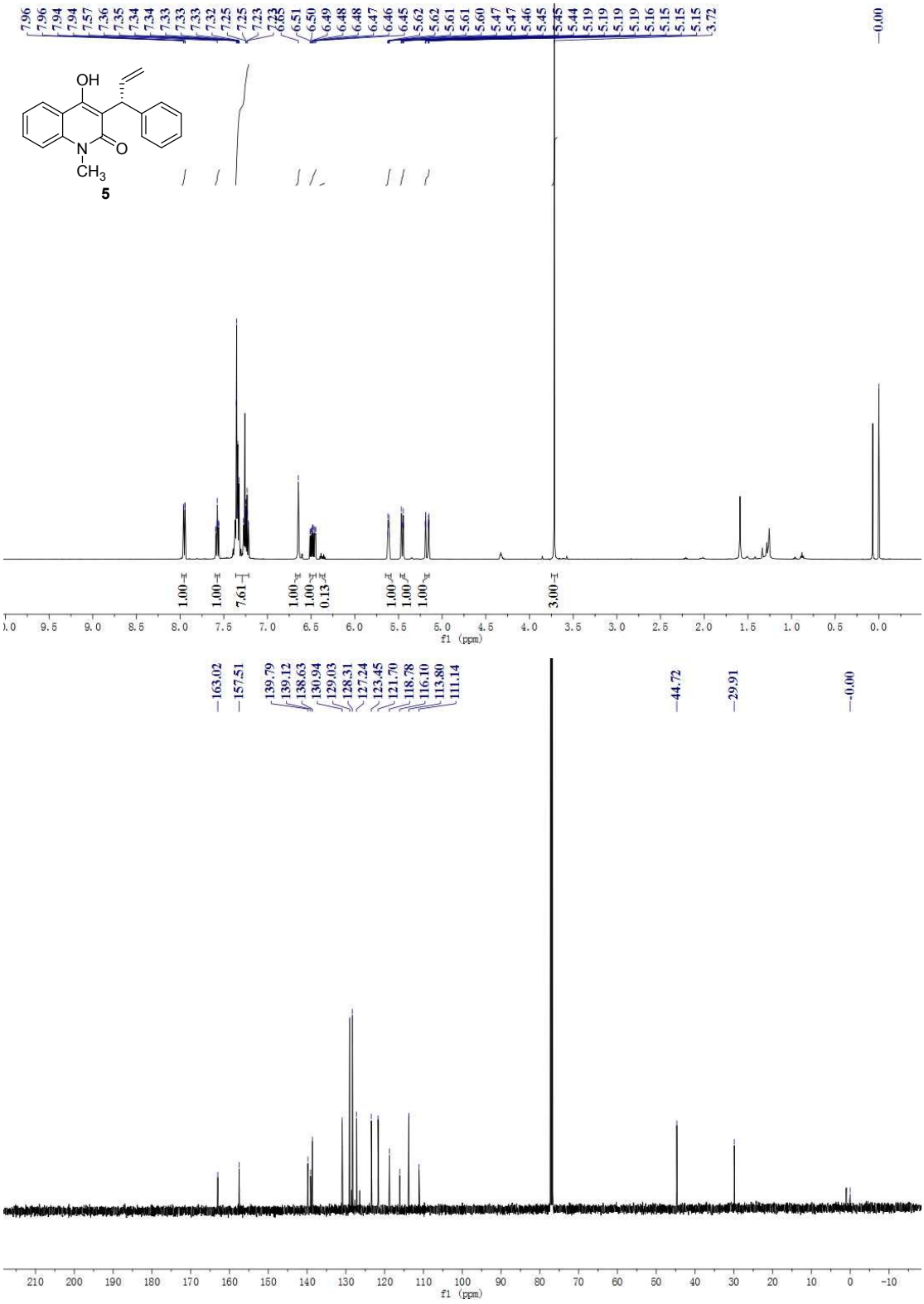


NMR Spectra of **3u**

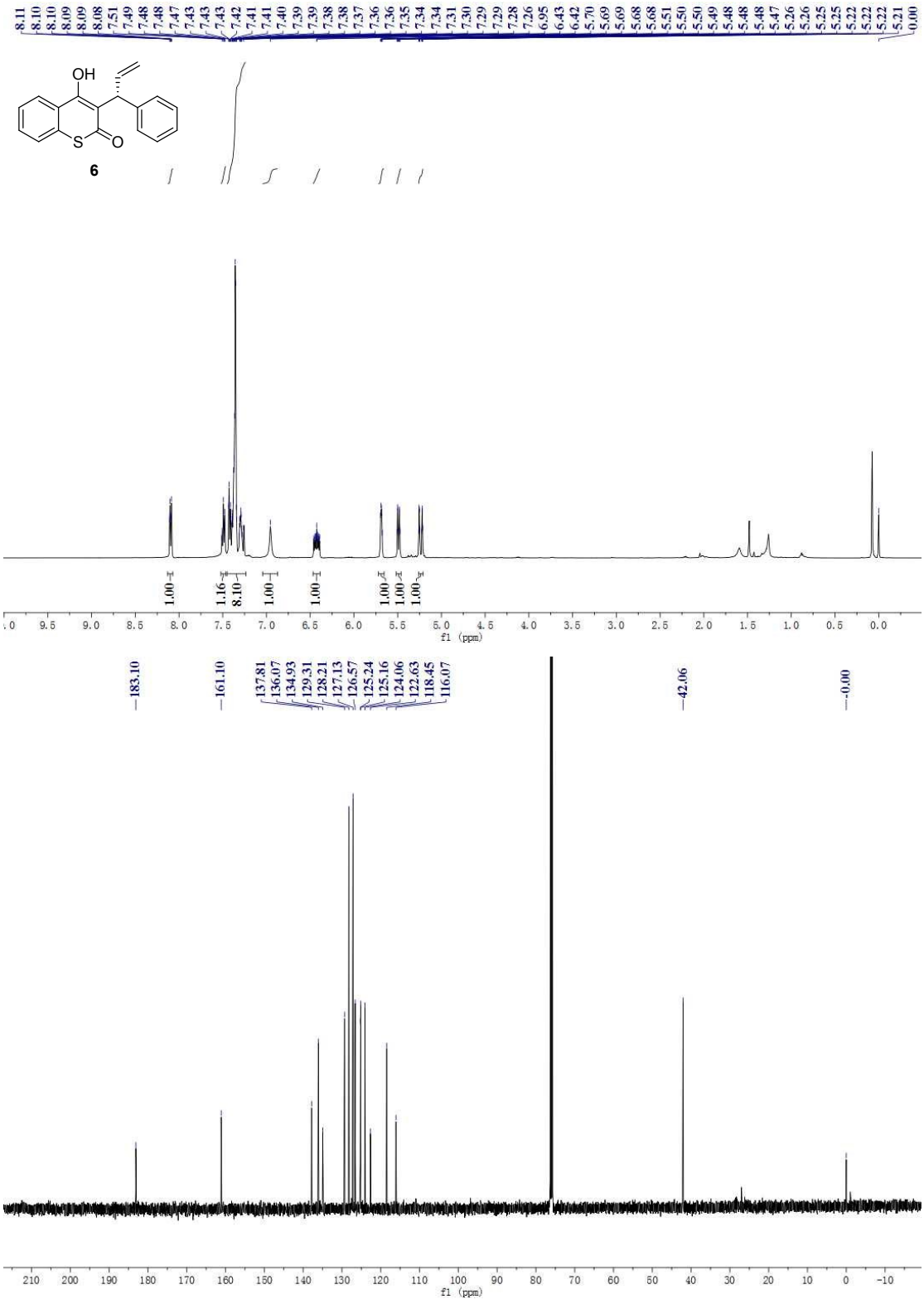



-117.28
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

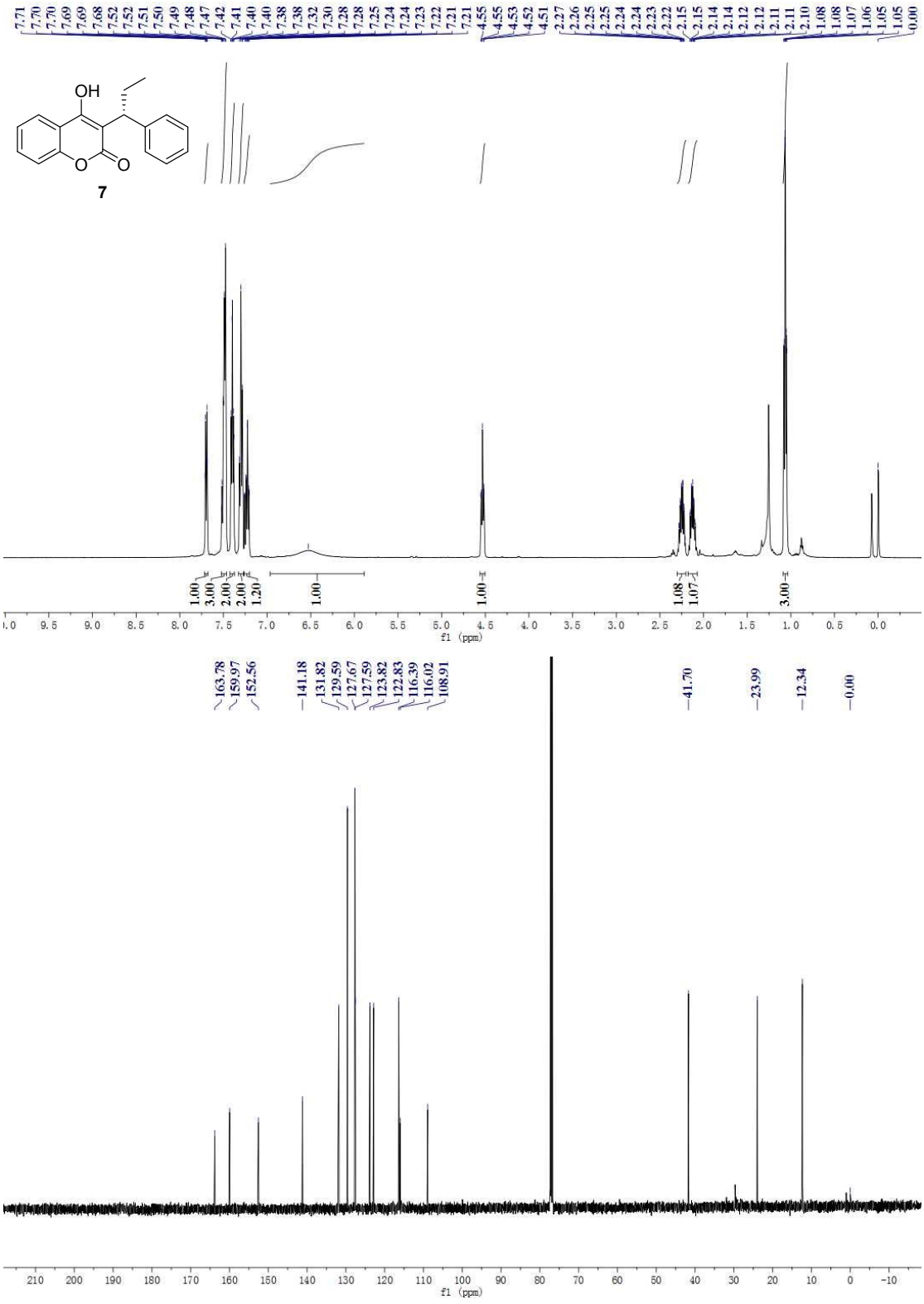
NMR Spectra of **5**



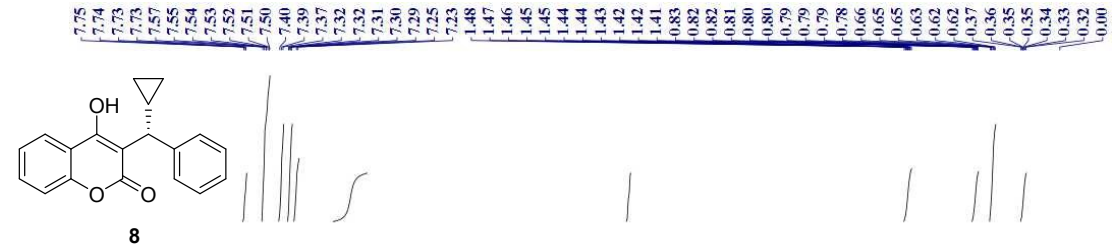
NMR Spectra of **6**



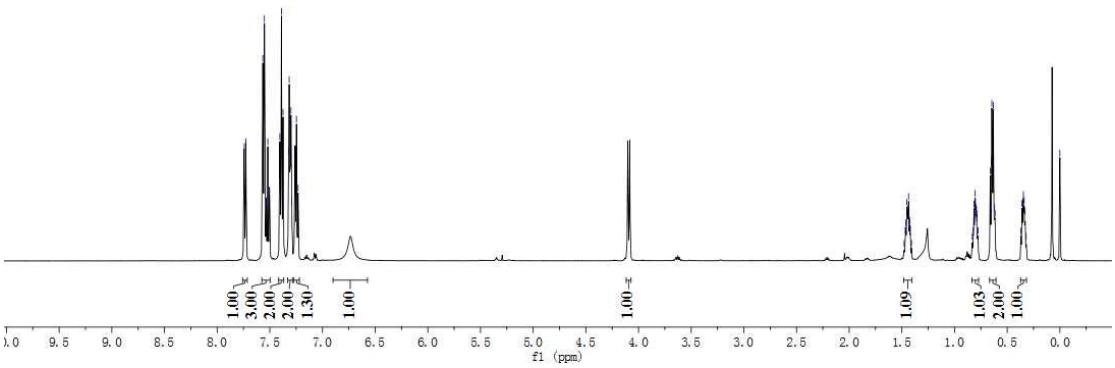
NMR Spectra of **7**

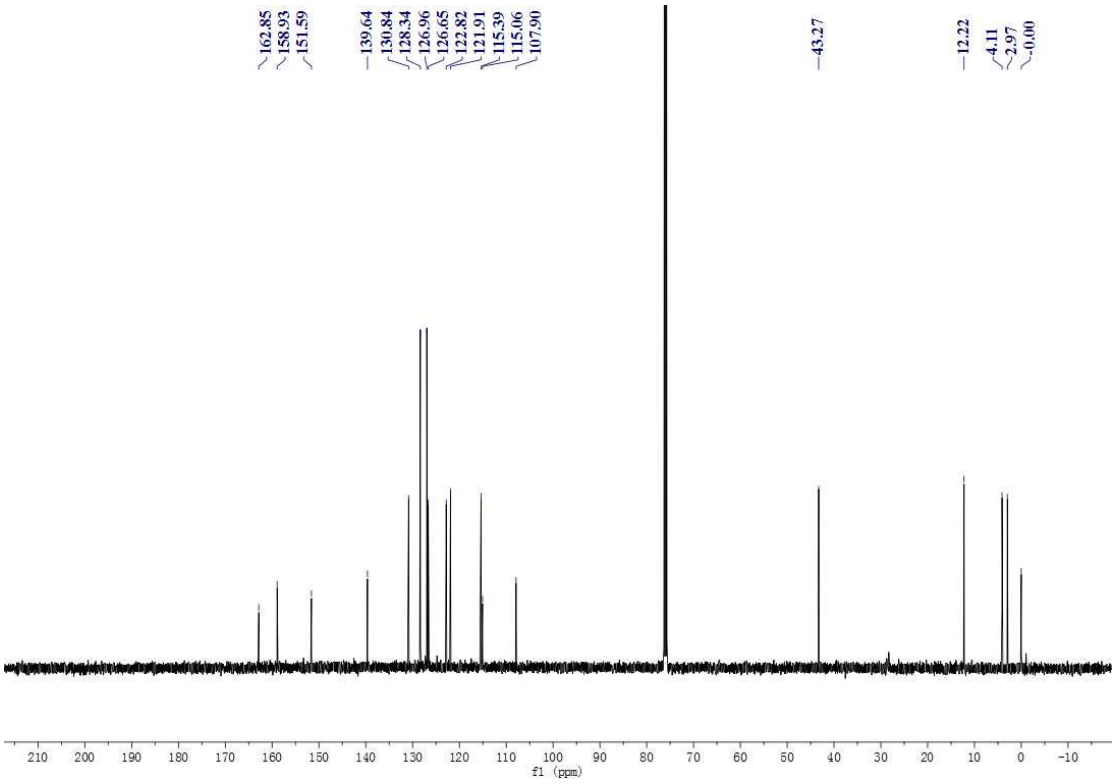


NMR Spectra of **8**

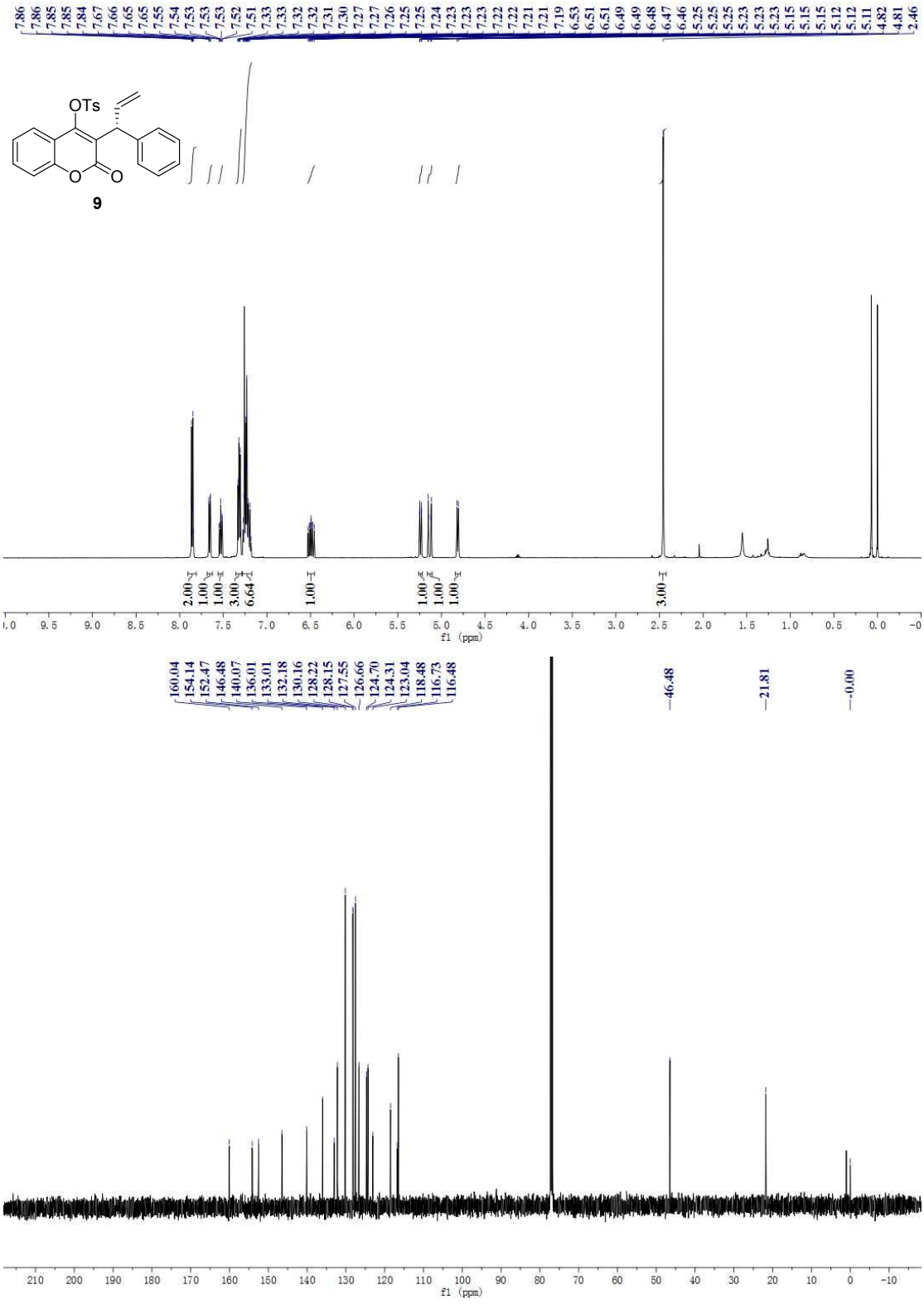


8





NMR Spectra of **9**



NMR Spectra of **10**