

## Supporting Information

### Enantioselective synthesis of 2-amino-4*H*-chromene derivatives with antifungal activities on phytopathogenic fungi

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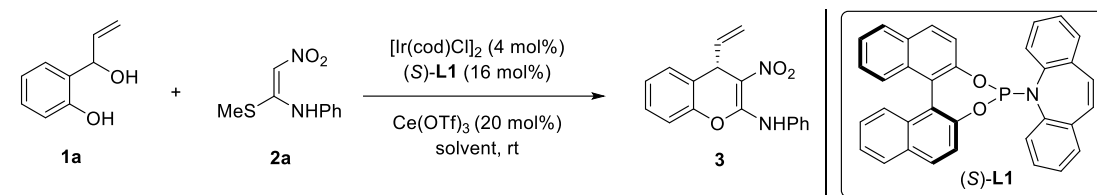
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## 1. General information

<sup>1</sup>H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in CDCl<sub>3</sub>. Chemical shifts are reported in ppm with the internal CDCl<sub>3</sub> signal at 7.26 ppm as a standard. The spectra are interpreted as: s, singlet; brs, broad singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet; ddd, double double doublet; td, triple doublet; coupling constant(s) *J* are reported in Hz and relative integrations are reported. <sup>13</sup>C NMR (100 MHz) spectrum were recorded on a Bruker DPX 400 MHz spectrometer in CDCl<sub>3</sub>. Chemical shifts are reported in ppm with the internal chloroform signal at 77.16 ppm as a standard; <sup>19</sup>F NMR (376 MHz) spectra were recorded on a Bruker DPX 400 MHz spectrometer in CDCl<sub>3</sub> and referenced relative to CFCl<sub>3</sub>. Optical rotations were measured on an AUTOPOL V. Enantiomeric excesses were determined by analysis of HPLC traces, obtained by using Chiralpak AS-H, AD-H, IC, columns with *n*-hexane and ethanol as solvents (Chiralpak AS-H, AD-H, IC, were purchased from Daicel Chiral Technologies (China) Co., Ltd.). Melting points were obtained in open capillary tubes using Buchi melting point B540 which were uncorrected. High-resolution mass spectra (HRMS) were recorded on a Waters GCT Premier mass spectrometer using EI-TOF and ESI-TOF (electron ionization-time of flight). Commercially available materials purchased from Adamas-beta and Bidepharm, which were used as received. Solvent was purified according to the procedure from *Purification of Laboratory Chemicals*. [Ir(cod)Cl]<sub>2</sub> and malononitrile was purchased from Bidepharm. Carreira's ligand (*S*)-**L1** was prepared according to the literature procedure.<sup>[1]</sup> Substrates 2-(1-hydroxyallyl)phenols ( $\pm$ )-**1**<sup>[2]</sup> and (*E*)-1-(methylthio)-2-nitroenamines **2**<sup>[3]</sup> were prepared according to the literature procedures.

## 2. Optimization study

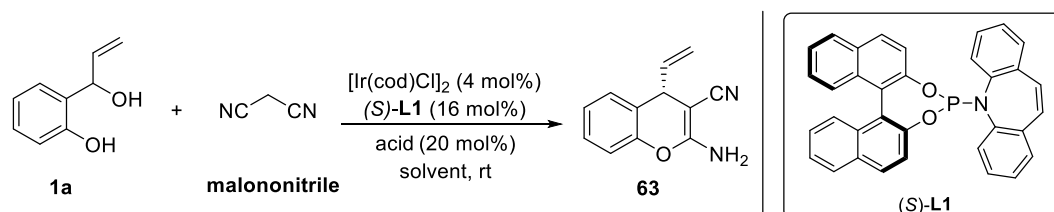
**Table S1 Screening of the solvents and additive**



entry <sup>[a]</sup>	solvent	additive	yield (%) <sup>[b]</sup>	ee (%) <sup>[c]</sup>
1	CH <sub>2</sub> Cl <sub>2</sub>	no	98	96
2	THF	no	83	95
3	CH <sub>3</sub> CN	no	68	92
4	DCE	no	91	95
5	toluene	no	84	95
6	CH <sub>2</sub> Cl <sub>2</sub>	3Å MS	59	85
7	CH <sub>2</sub> Cl <sub>2</sub>	4Å MS	64	84
8	CH <sub>2</sub> Cl <sub>2</sub>	5Å MS	74	86

[a] Unless others stated, the reactions were performed with **2a** (0.10 mmol), **1a** (0.20 mmol), [Ir(cod)Cl]<sub>2</sub> (4 mol %), (*S*)-L1 (16 mol %), and Ce(OTf)<sub>3</sub> (20 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) at room temperature. [b] Yield of isolated product **3**. [c] The ee value was determined by chiral HPLC analysis.

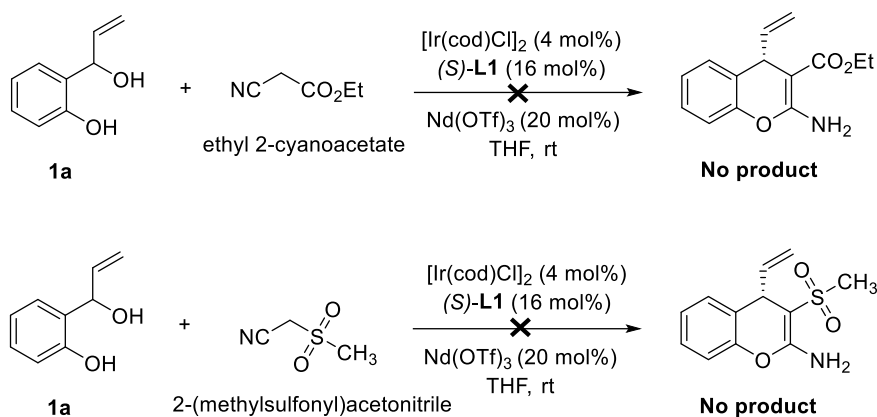
**Table S2 Optimization of the reaction conditions**



entry <sup>[a]</sup>	acid promoter	solvent	yield (%) <sup>[b]</sup>	ee (%) <sup>[c]</sup>
1	Ce(OTf) <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	40	56
2	Yb(OTf) <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	59	56
3	Yb(OTf) <sub>3</sub>	CH <sub>3</sub> CN	33	81
4	Yb(OTf) <sub>3</sub>	toluene	54	50
5	Yb(OTf) <sub>3</sub>	1,4-dioxane	53	82
6	Yb(OTf) <sub>3</sub>	THF	56	82
7	CF <sub>3</sub> CO <sub>2</sub> H	THF	32	69
8	<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	THF	42	86
9	Ce(OTf) <sub>3</sub>	THF	50	83
10	La(OTf) <sub>3</sub>	THF	48	81

11	Lu(OTf) <sub>3</sub>	THF	85	83
12	Dy(OTf) <sub>3</sub>	THF	39	81
13	Er(OTf) <sub>3</sub>	THF	46	79
14	Nd(OTf) <sub>3</sub>	THF	73	88

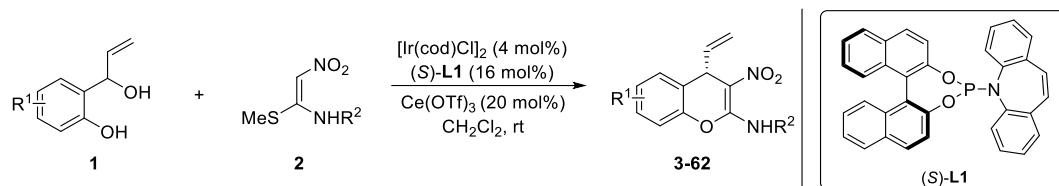
[a] Unless others stated, the reactions were performed with malononitrile (0.10 mmol), **1a** (0.20 mmol), [Ir(cod)Cl]<sub>2</sub> (4 mol %), (*S*)-**L1** (16 mol %), and Nd(OTf)<sub>3</sub> (20 mol %) in THF (1.5 mL) at room temperature. [b] Yield of isolated product **63**. [c] The ee value was determined by chiral HPLC analysis.



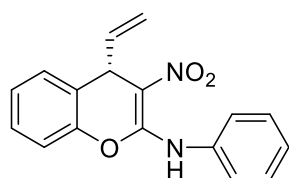
**Scheme S1** Unsuccessful reactions



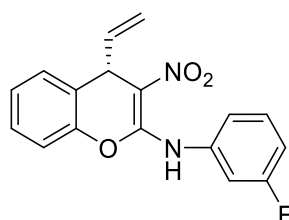
### 3. Synthesis and characterization data of 2-amino-4*H*-chromene derivatives



**General procedure A:** Under a nitrogen atmosphere, a flame dried 10 mL Schlenk tube was charged with  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (2.7 mg, 0.004 mmol, 4 mol%), Carreira's ligand (*S*)-**L1** (8.2 mg, 0.016 mmol, 16 mol%). After the tube was evacuated and backfilled with nitrogen, freshly distilled  $\text{CH}_2\text{Cl}_2$  (1.5 mL) was added, then stirred at room temperature for 15 minutes while the solution turned dark red. Then, 2-(1-hydroxyallyl)phenols **1** (0.2 mmol, 2.0 equiv) were added and the reaction mixture immediately turned light yellow. 1-(Methylthio)-2-nitroenamines **2** (0.1 mmol, 1.0 equiv) and  $\text{Ce}(\text{OTf})_3$  (11.74 mg, 0.02 mmol, 20 mol%) were added sequentially. The reaction mixture was stirred at room temperature until **2** were consumed (monitored by TLC), which was directly purified by flash column chromatography silica gel ( $\text{CH}_2\text{Cl}_2$  or petroleum ether/ethyl acetate = 4/1) to afford products **3-62**.

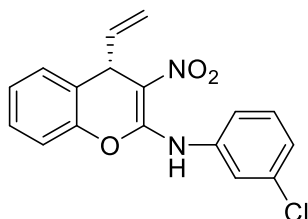


**(S)-3-Nitro-*N*-phenyl-4-vinyl-4*H*-chromen-2-amine (3):** Following the general procedure **A**, compound **3a** was obtained as a yellow solid in 98% yield (28.8 mg), 96% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 105 – 107 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.26 (brs, 1H), 7.45 – 7.42 (m, 4H), 7.32 – 7.25 (m, 3H), 7.24 – 7.19 (m, 1H), 7.08 (d,  $J = 8.0$  Hz, 1H), 5.92 (ddd,  $J = 16.7, 10.0, 6.6$  Hz, 1H), 5.10 (d,  $J = 9.8$  Hz, 1H), 5.04 (d,  $J = 16.8$  Hz, 1H), 5.02 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 148.1, 137.2, 135.2, 129.7, 129.5(2C), 128.6, 126.6, 126.1, 123.3(1), 123.3(0) (2C), 116.3, 115.8, 108.2, 39.6. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_3$ : 294.0999, found: 294.1006;  $[\alpha]_D^{25} = +19.0$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 8.466$  min (minor), 15.350 min (major).

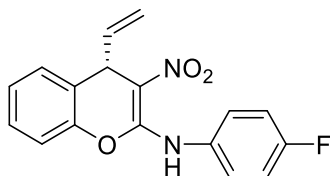


**(S)-*N*-(3-Fluorophenyl)-3-nitro-4-vinyl-4*H*-chromen-2-amine (4):** Following the general procedure **A**, compound **4** was obtained as a yellow solid in 83% yield (25.9 mg), 95% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 136 – 138 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.26 (brs, 1H), 7.45 – 7.35 (m, 1H), 7.33 – 7.24 (m, 4H), 7.17 (d,  $J = 8.0$  Hz, 1H), 7.12 (d,  $J = 7.9$  Hz, 1H), 7.02 – 6.97 (m, 1H), 5.91 (ddd,  $J = 16.8, 10.0, 6.6$  Hz, 1H), 5.12 (d,  $J = 10.0$  Hz, 1H), 5.07 (d,  $J = 17.1$  Hz, 1H),

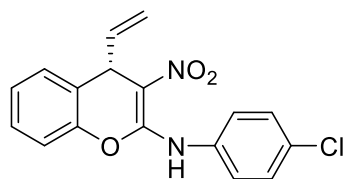
5.01 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1 (d,  $^1J_{\text{C-F}} = 246.9$  Hz), 156.6, 148.0, 137.1, 136.8 (d,  $^3J_{\text{C-F}} = 10.4$  Hz), 130.7 (d,  $^3J_{\text{C-F}} = 9.2$  Hz), 129.8, 128.7, 126.3, 123.2, 118.7 (d,  $^4J_{\text{C-F}} = 3.2$  Hz), 116.1 (d,  $^2J_{\text{C-F}} = 32.8$  Hz), 113.3 (d,  $^2J_{\text{C-F}} = 21.3$  Hz), 110.6, 110.4, 108.7, 39.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.48 – -110.55(m). HRMS (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}\text{FN}_2\text{O}_3$ : 312.0905, found: 312.0912;  $[\alpha]_{\text{D}}^{25} = +22.9$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 7.218$  min (minor), 13.914 min (major).



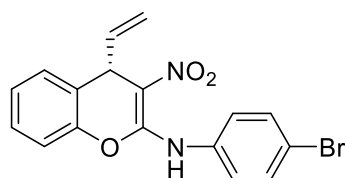
**(S)-N-(3-Chlorophenyl)-3-nitro-4-vinyl-4H-chromen-2-amine (5)**: Following the general procedure A, compound **5** was obtained as a yellow solid in 78% yield (25.6 mg), 89% ee;  $R_{\text{f}} = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 131 – 133 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.18 (brs, 1H), 7.49 (s, 1H), 7.39 – 7.35(m, 1H), 7.33 – 7.20 (m, 5H), 7.09 (d,  $J = 7.8$  Hz, 1H), 5.90 (ddd,  $J = 16.7$ , 10.0, 6.6 Hz, 1H), 5.10 (d,  $J = 10.3$  Hz, 1H), 5.04 (d,  $J = 17.2$  Hz, 1H), 5.00 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 147.9, 137.1, 136.5, 135.1, 130.5, 129.7, 128.7, 126.5, 126.3, 123.3, 123.2, 121.2, 116.3, 115.9, 108.7, 39.5. HRMS (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}^{35}\text{ClN}_2\text{O}_3$ : 328.0610, found: 328.0612;  $\text{C}_{17}\text{H}_{13}^{37}\text{ClN}_2\text{O}_3$ : 330.0580, found: 330.0585;  $[\alpha]_{\text{D}}^{25} = +30.2$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 7.182$  min (minor), 12.817 min (major).



**(S)-N-(4-Fluorophenyl)-3-nitro-4-vinyl-4H-chromen-2-amine (6)**: Following the general procedure A, compound **6** was obtained as a yellow solid in 95% yield (29.7 mg), 90% ee;  $R_{\text{f}} = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 142 – 144 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.17 (brs, 1H), 7.40 (dd,  $J = 9.0$ , 4.7 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.17 – 7.13 (m, 2H), 7.04 (d,  $J = 8.2$  Hz, 1H), 5.91 (ddd,  $J = 16.8$ , 10.0, 6.6 Hz, 1H), 5.10 (d,  $J = 10.0$  Hz, 1H), 5.06 (d,  $J = 16.4$  Hz, 1H), 5.01 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0 (d,  $^1J_{\text{C-F}} = 247.2$  Hz), 156.9, 148.1, 137.1, 131.1 (d,  $^4J_{\text{C-F}} = 3.2$  Hz), 129.8, 128.6, 126.2, 125.4 (d,  $^3J_{\text{C-F}} = 8.4$  Hz)(2C), 123.3, 116.5, 116.3 (d,  $^2J_{\text{C-F}} = 8.6$  Hz) (2C), 115.9, 108.2, 39.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.62 – -114.68 (m). HRMS (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}\text{FN}_2\text{O}_3$ : 312.0905, found: 312.0908;  $[\alpha]_{\text{D}}^{25} = +21.7$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); HPLC (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 10.287$  min (minor), 21.105 min (major).

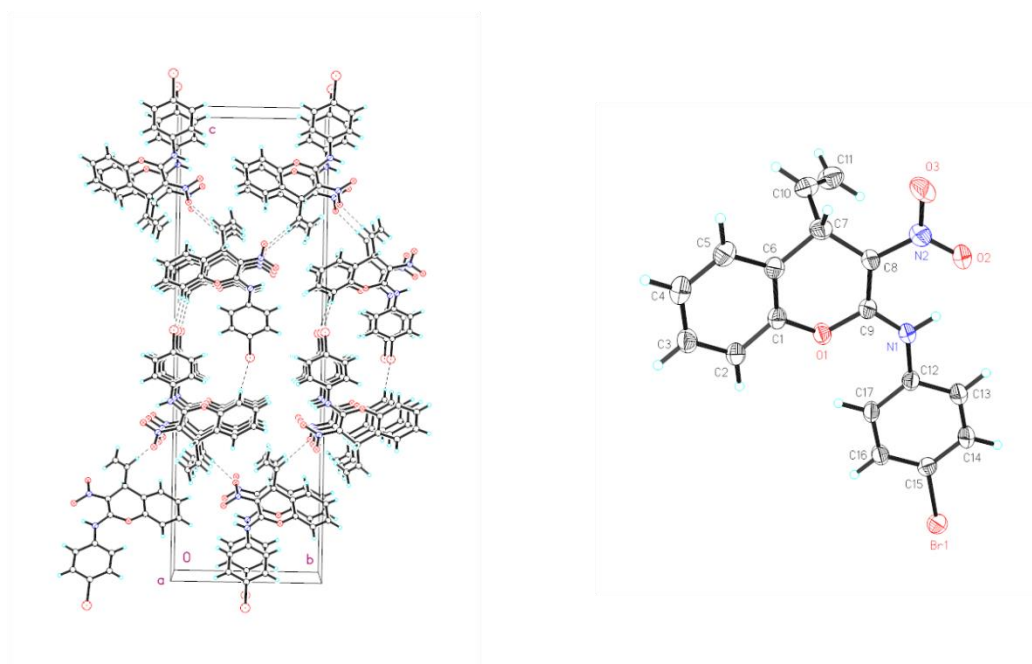


**(S)-N-(4-Chlorophenyl)-3-nitro-4-vinyl-4H-chromen-2-amine (7):** Following the general procedure A, compound **7** was obtained as a yellow solid in 89% yield (29.1 mg), 94% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 129 – 131 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.20 (brs, 1H), 7.42 – 7.35(m, 4H), 7.29 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 7.07 (d,  $J = 7.8$  Hz, 1H), 5.90 (ddd,  $J = 16.7, 10.0, 6.6$  Hz, 1H), 5.09 (d,  $J = 9.8$  Hz, 1H), 5.04 (d,  $J = 16.8$  Hz, 1H), 4.99 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 147.9, 137.1, 133.8, 132.0, 129.7, 129.6(2C), 128.6, 126.2, 124.5(2C), 123.1, 116.2, 115.9, 108.4, 39.5. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}^{35}\text{ClN}_2\text{O}_3$ : 328.0610, found: 328.0613;  $\text{C}_{17}\text{H}_{13}^{37}\text{ClN}_2\text{O}_3$ : 330.0580, found: 330.0579;  $[\alpha]_D^{25} = +29.7$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 9.144$  min (minor), 19.878 min (major).



**(S)-N-(4-Bromophenyl)-3-nitro-4-vinyl-4H-chromen-2-amine (8):** Following the general procedure A, compound **8** was obtained as a yellow solid in 89% yield (33.2 mg), 98% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 129 – 131 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.19 (brs, 1H), 7.57 (d,  $J = 8.7$  Hz, 2H), 7.33 – 7.25 (m, 5H), 7.07 (d,  $J = 7.7$  Hz, 1H), 5.91 (ddd,  $J = 16.8, 10.0, 6.6$  Hz, 1H), 5.10 (d,  $J = 10.7$  Hz, 1H), 5.05 (d,  $J = 17.6$  Hz, 1H), 5.01 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 148.1, 137.1, 134.4, 132.7(2C), 129.8, 128.7, 126.3, 124.9(2C), 123.2, 119.9, 116.3, 115.9, 108.6, 39.6. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}^{79}\text{BrN}_2\text{O}_3$ : 372.0104, found: 372.0111;  $\text{C}_{17}\text{H}_{13}^{81}\text{BrN}_2\text{O}_3$ : 374.0084, found: 374.0090;  $[\alpha]_D^{25} = +19.8$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 9.542$  min (minor), 23.178 min (major).

**The preparation and X-ray analysis of the single crystal:** Compound **8** (98% ee, 10.0 mg) was dissolved in 1.0 mL of acetone in a screw-top vial and drops of hexane were added. The lid was then loosely screwed on the vial, and a single crystal was obtained by natural volatilization at room temperature. The data set was collected by a Bruker APEX-II CCD at 293(2) K equipped with Mo radiation source ( $K\alpha = 0.71073$  Å). Applied with multi-scan absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package. CCDC 2342669 contains the supplementary crystallographic data, and can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

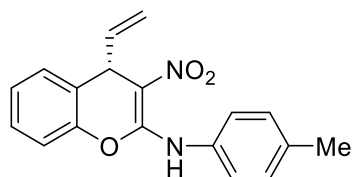


**Figure S1.** The thermal ellipsoid plot for X-ray structure of compound **8** with the ellipsoid contour at 30% probability levels

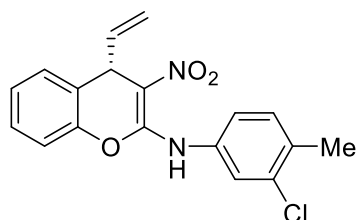
**The crystallographic data of compound 8**

Identification code	mo_dd22075_0m	
Empirical formula	$C_{17}H_{13}BrN_2O_3$	
Formula weight	373.20	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 4.8026(3) Å	a = 90 °
	b = 10.1124(6) Å	b = 90 °
	c = 31.8117(19) Å	g = 90 °
Volume	1544.96(16) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.604 Mg/m <sup>3</sup>	
Absorption coefficient	2.677 mm <sup>-1</sup>	
F(000)	752	
Crystal size	0.180 x 0.120 x 0.070 mm <sup>3</sup>	
Theta range for data collection	2.783 to 25.997 °	
Index ranges	-5 ≤ h ≤ 5, -9 ≤ k ≤ 12, -39 ≤ l ≤ 37	
Reflections collected	7304	
Independent reflections	3004 [R(int) = 0.0523]	
Completeness to theta = 25.242 °	99.5 %	

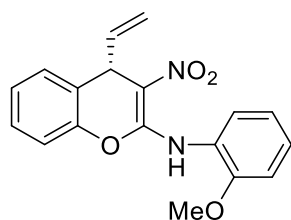
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4356
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3004 / 0 / 208
Goodness-of-fit on F <sup>2</sup>	1.001
Final R indices [I > 2σ(I)]	R1 = 0.0391, wR2 = 0.0895
R indices (all data)	R1 = 0.0533, wR2 = 0.0974
Absolute structure parameter	0.047(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.460 and -0.372 e.Å <sup>-3</sup>



**(S)-3-Nitro-N-(p-tolyl)-4-vinyl-4H-chromen-2-amine (9):** Following the general procedure **A**, compound **9** was obtained as a yellow solid in 98% yield (30.2 mg), 85% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 109 – 111 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.25 (brs, 1H), 7.31 – 7.18(m, 7H), 7.05 (d,  $J = 9.4$  Hz, 1H), 5.91 (ddd,  $J = 16.6, 9.9, 5.9$  Hz, 1H), 5.08 (d,  $J = 9.8$  Hz, 1H), 5.03 (d,  $J = 16.4$  Hz 1H), 4.99 (d,  $J = 6.6$  Hz, 1H), 2.38 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 148.1, 137.1, 136.6, 132.5, 129.9(2C), 129.6, 128.5, 125.9, 123.20, 123.1(2C), 116.2, 115.6, 107.9, 39.5, 21.1. **HRMS** (EI-TOF) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3$ : 308.1155, found: 308.1158;  $[\alpha]_{\text{D}}^{25} = +24.5$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 9.176$  min (minor), 14.421 min (major).

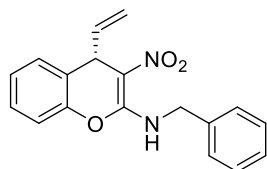


**(S)-N-(3-Chloro-4-methylphenyl)-3-nitro-4-vinyl-4H-chromen-2-amine (10):** Following the general procedure **A**, compound **10** was obtained as a yellow solid in 89% yield (30.4 mg), 93% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 114 – 116 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.17 (brs, 1H), 7.50 (d,  $J = 2.2$  Hz, 1H), 7.33 – 7.25 (m, 3H), 7.24 (d,  $J = 5.3$  Hz, 1H), 7.23 – 7.16 (m, 1H), 7.12 – 7.05 (m, 1H), 5.91 (ddd,  $J = 16.8, 10.0, 6.6$  Hz, 1H), 5.10 (d,  $J = 9.9$  Hz, 1H), 5.04 (d,  $J = 18.8$  Hz, 1H), 5.01 (d,  $J = 6.5$  Hz, 1H), 2.41 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 148.0, 137.1, 134.9, 134.5, 133.9, 131.5, 129.7, 128.7, 126.2, 123.8, 123.2, 121.5, 116.3, 115.9, 108.4, 39.5, 19.8. **HRMS** (EI-TOF) m/z:  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{15}^{35}\text{ClN}_2\text{O}_3$ : 342.0766, found: 342.0769;  $\text{C}_{18}\text{H}_{15}^{37}\text{ClN}_2\text{O}_3$ : 344.0737, found: 344.0749;  $[\alpha]_{\text{D}}^{25} = +27.9$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 6.863$  min (minor), 11.101 min (major).

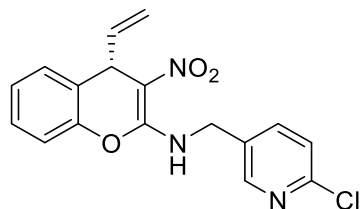


**(S)-N-(2-Methoxyphenyl)-3-nitro-4-vinyl-4H-chromen-2-amine (11):** Following the general procedure **A**, compound **11** was obtained as a yellow solid in 95% yield (30.8 mg), 50% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 170 – 172 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.61 (brs, 1H), 7.82 (d,  $J = 8.0$  Hz, 1H), 7.33 – 7.24 (m, 2H), 7.26 – 7.17 (m, 2H), 7.17 – 7.10 (m, 1H), 7.08 – 6.96 (m, 2H), 5.93 (ddd,  $J = 16.7, 10.8, 6.5$  Hz, 1H), 5.12 – 4.99 (m, 3H), 3.94 (s, 3H).  $^{13}\text{C NMR}$  (100

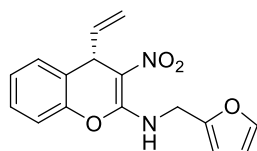
MHz, CDCl<sub>3</sub>)  $\delta$  156.7, 150.6, 148.2, 137.4, 129.7, 128.5, 126.6, 126.0, 125.3, 123.5, 122.4, 120.9, 116.3, 115.6, 111.2, 108.3, 56.2, 39.7. **HRMS** (EI-TOF)  $m/z$ : [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: 324.1105, found: 324.1112; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +16.3 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda$  = 220 nm)  $t_R$  = 8.152 min (minor), 16.787 min (major).



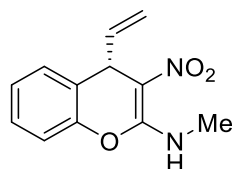
**(S)-N-Benzyl-3-nitro-4-vinyl-4H-chromen-2-amine (12)**: Following the general procedure **A**, compound **12** was obtained as a white solid in 55% yield (16.9 mg), 92% ee;  $R_f$  = 0.6 (petroleum ether/ethyl acetate = 4/1); m.p: 148 – 150 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.75 (brs, 1H), 7.43 – 7.30 (m, 5H), 7.30 – 7.22 (m, 2H), 7.24 – 7.14 (m, 1H), 7.08 – 7.01 (m, 1H), 5.88 (ddd,  $J$  = 16.7, 10.0, 6.5 Hz, 1H), 5.06 (d,  $J$  = 10.1 Hz, 1H), 5.02 (d,  $J$  = 16.9 Hz, 1H), 4.95 (d,  $J$  = 6.5 Hz, 1H), 4.85 – 4.69 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 148.2, 137.4, 136.4, 129.8, 129.2(2C), 128.5, 128.3, 127.6(2C), 125.9, 123.5, 116.1, 115.5, 107.4, 45.6, 39.6. **HRMS** (EI-TOF)  $m/z$ : [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: 308.1155, found: 308.1165; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +3.2 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda$  = 220 nm)  $t_R$  = 13.326 min (minor), 39.044 min (major).



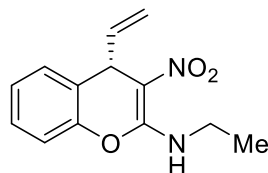
**(S)-N-((6-Chloropyridin-3-yl)methyl)-3-nitro-4-vinyl-4H-chromen-2-amine (13)**: Following the general procedure **A**, compound **13** was obtained as a yellow solid in 65% yield (22.4 mg), 96% ee;  $R_f$  = 0.5 (petroleum ether/ethyl acetate = 4/1); m.p: 109 – 111 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.72 (brs, 1H), 8.46 (d,  $J$  = 2.5 Hz, 1H), 7.71 (dd,  $J$  = 8.3, 2.5 Hz, 1H), 7.36 (d,  $J$  = 8.2 Hz, 1H), 7.27 – 7.16 (m, 3H), 7.03 (dd,  $J$  = 7.8, 1.9 Hz, 1H), 5.85 (ddd,  $J$  = 16.7, 10.0, 6.6 Hz, 1H), 5.06 (d,  $J$  = 10.0 Hz, 1H), 5.01 (d,  $J$  = 17.0 Hz, 1H), 4.92 (d,  $J$  = 6.6 Hz, 1H), 4.85 – 4.70 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.1, 151.4, 149.1, 147.9, 138.2, 137.2, 131.5, 129.8, 128.7, 126.1, 124.8, 123.2, 115.9, 115.7, 107.8, 42.3, 39.5. **HRMS** (EI-TOF)  $m/z$ : [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub><sup>35</sup>ClN<sub>3</sub>O<sub>3</sub>: 343.0719, found: 343.0727; C<sub>17</sub>H<sub>14</sub><sup>37</sup>ClN<sub>3</sub>O<sub>3</sub>: 345.0689, found: 345.0695; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +22.4 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda$  = 220 nm)  $t_R$  = 18.847 min (minor), 48.310 min (major).



**(S)-N-(Furan-2-ylmethyl)-3-nitro-4-vinyl-4H-chromen-2-amine (14):** Following the general procedure A, compound **14** was obtained as a yellow solid in 98% yield (29.2 mg), 91% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 165 – 167 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.58 (brs, 1H), 7.40 (dd,  $J = 1.8, 0.9$  Hz, 1H), 7.32 – 7.26 (m, 2H), 7.22 (d,  $J = 6.7$  Hz, 1H), 7.13 (d,  $J = 6.7$  Hz, 1H), 6.37 – 6.34 (m, 2H), 5.87 (ddd,  $J = 16.7, 10.0, 6.5$  Hz, 1H), 5.06 (d,  $J = 11.8$  Hz, 1H), 5.00 (d,  $J = 16.8$ , 1H), 4.94 (d,  $J = 6.6$  Hz, 1H), 4.82 – 4.69 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 149.3, 148.2, 143.1, 137.4, 129.8, 128.5, 125.9, 123.5, 116.2, 115.5, 110.8, 108.6, 107.6, 39.6, 38.4. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$ : 298.0948, found: 298.0951;  $[\alpha]_{\text{D}}^{25} = +6.3$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 13.716$  min (minor), 42.619 min (major).



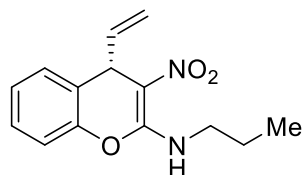
**(S)-N-Methyl-3-nitro-4-vinyl-4H-chromen-2-amine (15):** Following the general procedure A, compound **15** was obtained as a white solid in 96% yield (22.3 mg), 82% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 120 – 122 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.48 (brs, 1H), 7.32 – 7.24 (m, 2H), 7.22 – 7.18 (m 1H), 7.15 – 7.09 (m, 1H), 5.88 (ddd,  $J = 16.7, 9.9, 6.4$  Hz, 1H), 5.05 (d,  $J = 10.0$  Hz, 1H), 5.00 (d,  $J = 16.9$  Hz, 1H), 4.94 (d,  $J = 6.4$  Hz, 1H), 3.22 (d,  $J = 5.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 148.2, 137.4, 129.8, 128.5, 125.9, 123.4, 116.2, 115.3, 107.2, 39.6, 27.9. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$ : 232.0842, found: 232.0845;  $[\alpha]_{\text{D}}^{25} = +19.3$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak IC,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 28.767$  min (major), 36.700 min (minor).



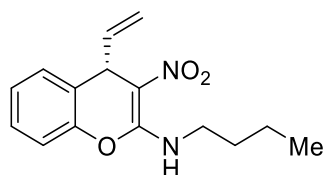
**(S)-N-Ethyl-3-nitro-4-vinyl-4H-chromen-2-amine (16):** Following the general procedure A, compound **16** was obtained as a yellow solid in 98% yield (24.1 mg), 65% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 103 – 105 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.50 (brs, 1H), 7.30 – 7.25 (m, 2H), 7.21 (d,  $J = 7.1$  Hz, 1H), 7.10 (d,  $J = 6.0$  Hz, 1H), 5.88 (ddd,  $J = 16.9, 9.9, 6.1$  Hz, 1H), 5.05 (d,  $J = 9.6$  Hz, 1H), 4.99 (d,  $J = 16.6$  Hz, 1H), 4.95 (d,  $J = 7.0$  Hz, 1H), 3.71 – 3.59 (m, 2H), 1.38 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 148.3, 137.4, 129.8, 128.5, 125.8, 123.5, 116.1, 115.3, 106.9, 39.6, 36.7, 15.2. **HRMS** (EI-TOF)



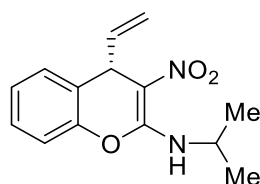
m/z:  $[M]^+$  calcd for  $C_{13}H_{14}N_2O_3$ : 246.0999, found: 246.1001;  $[\alpha]_D^{25} = +16.9$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 8.319$  min (minor), 36.278 min (major).



**(S)-3-Nitro-N-propyl-4-vinyl-4H-chromen-2-amine (17)**: Following the general procedure **A**, compound **17** was obtained as a yellow solid in 95% yield (24.6 mg), 69% ee;  $R_f = 0.6$  (petroleum ether/ethyl acetate = 4/1); m.p: 82 – 84 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  10.59 (brs, 1H), 7.26 (d,  $J = 6.8$  Hz, 2H), 7.21 (d,  $J = 7.4$  Hz, 1H), 7.11 (d,  $J = 8.1$  Hz, 1H), 5.92 – 5.84 (m, 1H), 5.05 (d,  $J = 10.0$  Hz, 1H), 5.00 (d,  $J = 17.0$  Hz, 1H), 4.95 (d,  $J = 6.3$  Hz, 1H), 3.58 (t,  $J = 6.3$  Hz, 2H), 1.80 – 1.71 (m, 2H), 1.05 (t,  $J = 7.5$  Hz, 3H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  159.4, 148.2, 137.3, 129.7, 128.4, 125.8, 123.4, 116.1, 115.3, 106.9, 43.3, 39.6, 23.1, 11.5. **HRMS** (EI-TOF) m/z:  $[M]^+$  calcd for  $C_{14}H_{16}N_2O_3$ : 260.1155, found: 260.1159;  $[\alpha]_D^{25} = +5.4$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 7.287$  min (minor), 18.508 min (major).

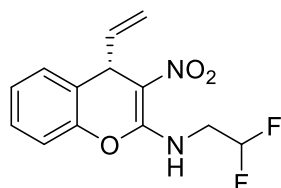


**(S)-N-Butyl-3-nitro-4-vinyl-4H-chromen-2-amine (18)**: Following the general procedure **A**, compound **18** was obtained as a yellow solid in 90% yield (24.6 mg), 75% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 77 – 79 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  10.57 (brs, 1H), 7.30 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 7.10 (dd,  $J = 8.2, 1.3$  Hz, 1H), 5.88 (ddd,  $J = 16.7, 10.0, 6.4$  Hz, 1H), 5.05 (d,  $J = 10.0$  Hz, 1H), 5.00 (d,  $J = 16.9$  Hz, 1H), 4.95 (d,  $J = 6.6$  Hz, 1H), 3.65 – 3.57 (m, 2H), 1.77 – 1.65 (m, 2H), 1.54 – 1.40 (m, 2H), 0.99 (t,  $J = 7.4$  Hz, 3H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  159.4, 148.3, 137.4, 129.8, 128.5, 125.8, 123.5, 116.1, 115.3, 107.0, 41.4, 39.6, 31.8, 20.1, 13.8. **HRMS** (EI-TOF) m/z:  $[M]^+$  calcd for  $C_{15}H_{18}N_2O_3$ : 274.1312, found: 274.1315;  $[\alpha]_D^{25} = +13.5$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 6.707$  min (minor), 13.253 min (major).

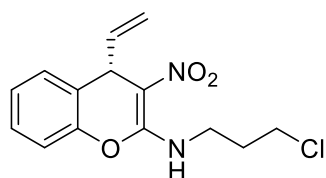


**(S)-N-Isopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (19)**: Following the general procedure **A**, compound **19** was obtained as a yellow solid in 88% yield (22.9 mg), 72% ee;  $R_f$

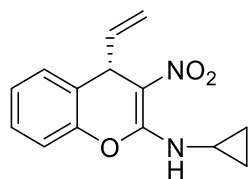
= 0.3 (petroleum ether/ethyl acetate = 4/1); m.p: 134 – 136 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.46 (brs, 1H), 7.31 – 7.26 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 5.88 (ddd, *J* = 16.7, 10.0, 6.4 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 2H), 4.95 (d, *J* = 6.3 Hz, 1H), 4.38 – 4.22 (m, 1H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.38 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.6, 148.3, 137.4, 129.7, 128.4, 125.8, 123.5, 116.1, 115.3, 106.8, 44.5, 39.6, 23.4, 23.2. HRMS (EI-TOF) *m/z*: [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: 260.1155, found: 260.1158; [α]<sub>D</sub><sup>25</sup> = +14.1 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); HPLC (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 5.879 min (minor), 20.802 min (major).



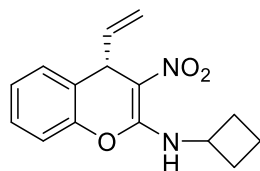
**(*R*)-*N*-(2,2-Difluoroethyl)-4-vinyl-4*H*-chromen-2-amine (20):** Following the general procedure A, compound **20** was obtained as a white solid in 98% yield (27.6 mg), 83% ee; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 4/1); m.p: 134 – 136 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.40 (brs, 1H), 7.34 – 7.18 (m, 3H), 7.11 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.02 (tt, *J*<sub>H-F</sub> = 55.2 Hz, *J* = 3.8 Hz, 1H), 5.85 (ddd, *J* = 16.8, 10.0, 6.8 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 4.92 (d, *J* = 6.6 Hz, 1H), 3.98 (td, *J*<sub>H-F</sub> = 14.5 Hz, *J* = 6.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.1, 147.9, 137.2, 129.8, 128.6, 126.2, 123.3, 116.1, 115.7, 113.2(t, <sup>1</sup>*J*<sub>C-F</sub> = 242.0 Hz), 108.2, 43.4(t, <sup>2</sup>*J*<sub>C-F</sub> = 26.8 Hz), 39.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -122.59 (dtd, *J* = 55.4, 14.4, 7.0 Hz). HRMS (EI-TOF) *m/z*: [M]<sup>+</sup> calcd for C<sub>13</sub>H<sub>12</sub>F<sub>2</sub>N<sub>2</sub>O<sub>3</sub>: 282.0811, found: 282.0811; [α]<sub>D</sub><sup>25</sup> = +12.9 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); HPLC (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 10.387 min (minor), 49.030 min (major).



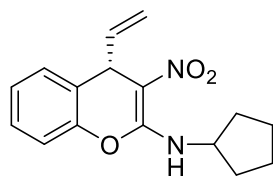
**(*S*)-*N*-(3-Chloropropyl)-3-nitro-4-vinyl-4*H*-chromen-2-amine (21):** Following the general procedure A, compound **21** was obtained as a yellow solid in 62% yield (18.3 mg), 77% ee; R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 4/1); m.p: 94 – 96 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.54 (brs, 1H), 7.33 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.14 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.87 (ddd, *J* = 16.8, 10.0, 6.5 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 5.01 (d, *J* = 17.0 Hz, 1H), 4.94 (d, *J* = 6.5 Hz, 1H), 3.88 – 3.75 (m, 2H), 3.67 (t, *J* = 6.0 Hz, 2H), 2.23 – 2.16 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.4, 148.1, 137.3, 129.7, 128.5, 125.9, 123.3, 116.2, 115.5, 107.3, 41.8, 39.6, 38.7, 32.5. HRMS (EI-TOF) *m/z*: [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>15</sub><sup>35</sup>ClN<sub>2</sub>O<sub>3</sub>: 294.0766, found: 294.0766; C<sub>14</sub>H<sub>15</sub><sup>37</sup>ClN<sub>2</sub>O<sub>3</sub>: 296.0737, found: 296.0748; [α]<sub>D</sub><sup>25</sup> = +18.5 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); HPLC (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 12.271 min (minor), 28.732 min (major).



**(S)-N-Cyclopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (22):** Following the general procedure A, compound **22** was obtained as a yellow solid in 93% yield (24.1 mg), 60% ee;  $R_f = 0.6$  (petroleum ether/ethyl acetate = 4/1); m.p: 128 – 130 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.35 (brs, 1H), 7.35 – 7.23 (m, 2H), 7.21 (d,  $J = 7.4$  Hz, 1H), 7.15 (d,  $J = 8.1$  Hz, 1H), 5.91 – 5.83 (m, 1H), 5.05 (d,  $J = 10.0$  Hz, 1H), 5.00 (d,  $J = 17.0$  Hz, 1H), 4.93 (d,  $J = 6.4$  Hz, 1H), 3.03 (tt,  $J = 7.8, 3.9$  Hz, 1H), 0.95 – 1.00 (m, 2H), 0.87 – 0.74 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.88, 148.28, 137.34, 129.72, 128.48, 125.83, 123.33, 116.33, 115.42, 107.37, 39.55, 23.94, 7.41(2C). **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_3$ : 258.0999, found: 258.1007;  $[\alpha]_{\text{D}}^{25} = +2.4$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 7.778$  min (minor), 27.845 min (major).

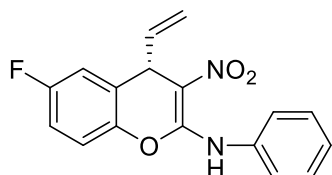


**(S)-N-Cyclobutyl-3-nitro-4-vinyl-4H-chromen-2-amine (23):** Following the general procedure A, compound **23** was obtained as a yellow solid in 93% yield (25.3 mg), 70% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 131 – 133 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.56 (brs, 1H), 7.30 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 7.08 (dd,  $J = 8.0, 1.2$  Hz, 1H), 5.87 (ddd,  $J = 16.7, 10.0, 6.4$  Hz, 1H), 5.05 (d,  $J = 9.9$  Hz, 1H), 4.99 (d,  $J = 16.9$  Hz, 1H), 4.93 (d,  $J = 6.4$  Hz, 1H), 4.56 – 4.46 (m, 1H), 2.52 – 2.45 (m, 2H), 2.27 – 2.09 (m, 2H), 1.97 – 1.79 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 148.2, 137.4, 129.7, 128.4, 125.8, 123.4, 116.1, 115.3, 106.9, 46.6, 39.5, 31.5, 31.3, 15.5. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3$ : 272.1155, found: 272.1157;  $[\alpha]_{\text{D}}^{25} = +10.0$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 7.547$  min (minor), 19.735 min (major).

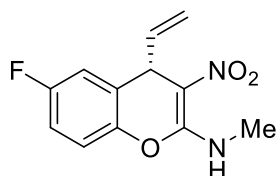


**(S)-N-Cyclopentyl-3-nitro-4-vinyl-4H-chromen-2-amine (24):** Following the general procedure A, compound **24** was obtained as a yellow solid in 91% yield (26.0 mg), 69% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 93 – 95 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.59 (brs, 1H), 7.30 – 7.25 (m, 2H), 7.22 – 7.17 (m, 1H), 7.11 (dd,  $J = 8.1, 1.3$  Hz, 1H), 5.88 (ddd,  $J = 16.7, 10.0, 6.4$  Hz, 1H), 5.05 (d,  $J = 9.9$  Hz, 1H), 4.99 (d,  $J = 16.9$  Hz, 1H), 4.94 (d,  $J = 6.3$  Hz, 1H), 4.43 – 4.35 (m, 1H), 2.22 – 2.07 (m, 2H), 1.90 – 1.79 (m, 2H), 1.78 – 1.67 (m,

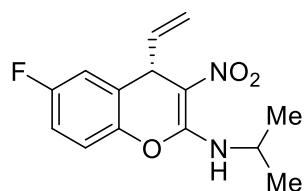
4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 148.3, 137.4, 129.8, 128.4, 125.8, 123.5, 116.1, 115.3, 106.9, 53.6, 39.6, 34.0, 33.8, 23.9. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3$ : 286.1312, found: 286.1314;  $[\alpha]_{\text{D}}^{25} = +10.9$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 6.577$  min (minor), 16.542 min (major).



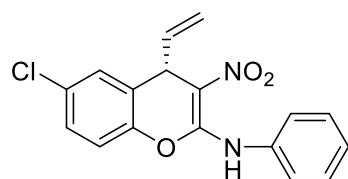
**(S)-6-Fluoro-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (25)**: Following the general procedure A, compound **25** was obtained as a yellow solid in 98% yield (30.6 mg), 87% ee;  $R_{\text{f}} = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 138 – 140 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.18 (brs, 1H), 7.47 – 7.40 (m, 4H), 7.32 – 7.29 (m, 1H), 7.05 (dd,  $J = 8.7, 4.5$  Hz, 1H), 6.99 (d,  $J = 8.1$  Hz, 2H), 5.90 (ddd,  $J = 16.6, 9.9, 6.6$  Hz, 1H), 5.14 (d,  $J = 9.2$  Hz, 1H), 5.10 (d,  $J = 15.6$  Hz, 1H), 4.99 (d,  $J = 6.7$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0 (d,  $^1J_{\text{C-F}} = 245.6$  Hz), 156.7, 144.2, 136.6, 135.1, 129.6 (2C), 126.8, 125.3 (d,  $^3J_{\text{C-F}} = 7.9$  Hz), 123.4 (2C), 117.8 (d,  $^3J_{\text{C-F}} = 8.4$  Hz), 116.4, 115.9 (d,  $^2J_{\text{C-F}} = 23.9$  Hz), 115.7 (d,  $^2J_{\text{C-F}} = 24.1$  Hz), 107.6, 39.9.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.76 – -115.82 (m). **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}\text{FN}_2\text{O}_3$ : 312.0905, found: 312.0909;  $[\alpha]_{\text{D}}^{25} = +23.8$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 8.241$  min (minor), 13.449 min (major).



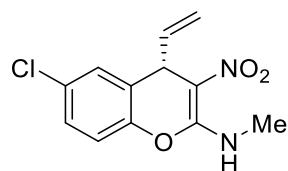
**(S)-6-Fluoro-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (26)**: Following the general procedure A, compound **26** was obtained as a yellow solid in 98% yield (24.5mg), 88% ee;  $R_{\text{f}} = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 139 – 141 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.42 (brs, 1H), 7.11 (dd,  $J = 8.7, 4.5$  Hz, 1H), 7.03 – 6.93 (m, 2H), 5.85 (ddd,  $J = 16.7, 10.0, 6.6$  Hz, 1H), 5.09 (d,  $J = 10.0$  Hz, 1H), 5.04 (d,  $J = 16.9$  Hz, 1H), 4.91 (d,  $J = 6.5$  Hz, 1H), 3.22 (d,  $J = 5.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.4 (d,  $^1J_{\text{C-F}} = 140.8$  Hz), 158.6, 144.3, 136.8, 125.3 (d,  $^3J_{\text{C-F}} = 8.0$  Hz), 117.7 (d,  $^3J_{\text{C-F}} = 8.7$  Hz), 115.9 (d,  $^2J_{\text{C-F}} = 12.7$  Hz), 115.7 (d,  $^2J_{\text{C-F}} = 15.7$  Hz), 115.4, 106.6, 39.9, 28.0.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.21 – -116.24(m). **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{11}\text{FN}_2\text{O}_3$ : 250.0748, found: 250.0752;  $[\alpha]_{\text{D}}^{25} = +16.9$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 11.028$  min (minor), 55.533 min (major).



**(S)-6-Fluoro-N-isopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (27):** Following the general procedure A, compound **27** was obtained as a yellow solid in 90% yield (25.0mg), 79% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 140 – 142 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.39 (brs, 1H), 7.09 (dd,  $J = 8.6, 4.5$  Hz, 1H), 7.01 – 6.95 (m, 2H), 5.86 (ddd,  $J = 16.8, 10.0, 6.5$  Hz, 1H), 5.09 (d,  $J = 10.0$  Hz, 1H), 5.03 (d,  $J = 16.9$  Hz, 1H), 4.92 (d,  $J = 6.6$  Hz, 1H), 4.32 – 4.24 (m, 1H), 1.40 (d,  $J = 6.5$  Hz, 3H), 1.37 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8 (d,  $^1J_{\text{C-F}} = 245.2$  Hz), 158.4, 144.3 (d,  $^4J_{\text{C-F}} = 2.6$  Hz), 136.8, 125.4 (d,  $^3J_{\text{C-F}} = 8.0$  Hz), 117.5 (d,  $^3J_{\text{C-F}} = 8.6$  Hz), 115.9 (d,  $^2J_{\text{C-F}} = 17.5$  Hz), 115.8, 115.5 (d,  $^2J_{\text{C-F}} = 24.1$  Hz), 106.2, 44.5, 39.8, 23.4, 23.2.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.29 – -116.40 (m). **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{14}\text{H}_{15}\text{FN}_2\text{O}_3$ : 278.1061, found: 278.1064;  $[\alpha]_{\text{D}}^{25} = +10.6$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 5.905$  min (minor), 17.752 min (major).

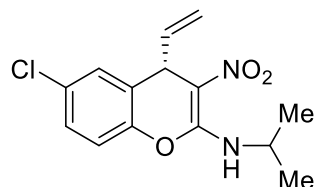


**(S)-6-Chloro-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (28):** Following the general procedure A, compound **28** was obtained as a yellow solid in 98% yield (32.1mg), 96% ee;  $R_f = 0.5$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 146 – 148 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.18 (brs, 1H), 7.47 – 7.39 (m, 4H), 7.31 (d,  $J = 7.2$  Hz, 1H), 7.28 – 7.22 (m, 2H), 7.02 (d,  $J = 8.5$  Hz, 1H), 5.88 (ddd,  $J = 16.8, 10.0, 6.7$  Hz, 1H), 5.14 (d,  $J = 10.0$  Hz, 1H), 5.11 (d,  $J = 16.8$  Hz, 1H), 4.97 (d,  $J = 6.7$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 146.6, 136.6, 134.9, 131.2, 129.6(2C), 129.4, 128.7, 126.8, 125.1, 123.4(2C), 117.7, 116.4, 107.7, 39.6. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}^{35}\text{ClN}_2\text{O}_3$ : 328.0610, found: 328.0611;  $\text{C}_{17}\text{H}_{13}^{37}\text{ClN}_2\text{O}_3$ : 330.0580, found: 328.0589;  $[\alpha]_{\text{D}}^{25} = +23.9$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 8.652$  min (minor), 11.454 min (major).

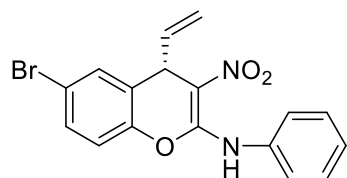


**(S)-6-Chloro-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (29):** Following the general procedure A, compound **29** was obtained as a yellow solid in 99% yield (26.3mg), 86% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 156 – 158 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.41 (brs, 1H), 7.29 – 7.22 (m, 2H), 7.11 – 7.04 (m, 1H), 5.83 (ddd,  $J = 16.8, 10.0, 6.6$  Hz, 1H), 5.09 (d,  $J = 10.0$  Hz, 1H), 5.04 (d,  $J = 16.9$  Hz, 1H), 4.89 (d,  $J = 6.6$  Hz, 1H), 3.22 (d,  $J =$

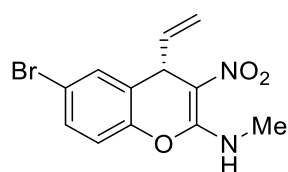
5.2 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 146.7, 136.8, 130.9, 129.5, 128.6, 125.2, 117.6, 116.0, 106.7, 39.6, 28.1. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{11}^{35}\text{ClN}_2\text{O}_3$ : 266.0453, found: 266.0457;  $\text{C}_{12}\text{H}_{11}^{37}\text{ClN}_2\text{O}_3$ : 268.0424, found: 268.0427;  $[\alpha]_{\text{D}}^{25} = +27.6$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda$  = 220 nm)  $t_{\text{R}}$  = 10.521 min (minor), 21.262 min (major).



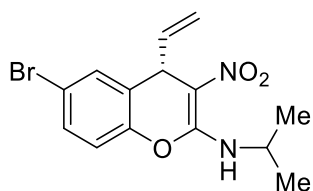
**(S)-6-Chloro-N-isopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (30)**: Following the general procedure A, compound **30** was obtained as a yellow solid in 85% yield (24.9mg), 90% ee;  $R_{\text{f}}$  = 0.4 (petroleum ether/ethyl acetate = 4/1); m.p: 153 – 155 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.37 (brs, 1H), 7.25 (d,  $J$  = 7.6 Hz, 2H), 7.10 – 7.03 (m, 1H), 5.84 (ddd,  $J$  = 16.8, 10.0, 6.6 Hz, 1H), 5.08 (d,  $J$  = 9.9 Hz, 1H), 5.04 (d,  $J$  = 16.9 Hz, 1H), 4.89 (d,  $J$  = 6.7 Hz, 1H), 4.33 – 4.24 (m, 1H), 1.40 (d,  $J$  = 6.6 Hz, 3H), 1.38 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 146.7, 136.7, 130.8, 129.3, 128.5, 125.2, 117.5, 115.9, 106.2, 44.5, 39.5, 23.3, 23.2. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{14}\text{H}_{15}^{35}\text{ClN}_2\text{O}_3$ : 294.0766, found: 294.0774;  $\text{C}_{14}\text{H}_{15}^{37}\text{ClN}_2\text{O}_3$ : 296.0737, found: 294.0743;  $[\alpha]_{\text{D}}^{25} = -0.1$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda$  = 220 nm)  $t_{\text{R}}$  = 6.428 min (minor), 16.698 min (major).



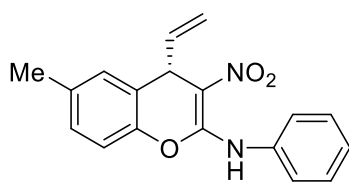
**(S)-6-Bromo-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (31)**: Following the general procedure A, compound **31** was obtained as a yellow solid in 99% yield (36.8mg), 95% ee;  $R_{\text{f}}$  = 0.6 ( $\text{CH}_2\text{Cl}_2$ ); m.p: 135 – 137 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.18 (brs, 1H), 7.52 – 7.35 (m, 6H), 7.35 – 7.26 (m, 1H), 6.96 (d,  $J$  = 8.7 Hz, 1H), 5.88 (ddd,  $J$  = 16.8, 10.0, 6.7 Hz, 1H), 5.14 (d,  $J$  = 7.2 Hz, 1H), 5.11 (d,  $J$  = 14.1 Hz, 1H), 4.97 (d,  $J$  = 6.8 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 147.1, 136.6, 134.9, 132.4, 131.6, 129.6(2C), 126.8, 125.5, 123.4(2C), 118.7, 118.1, 116.5, 107.7, 39.5. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}^{79}\text{BrN}_2\text{O}_3$ : 372.0105, found: 372.0112;  $\text{C}_{17}\text{H}_{13}^{81}\text{BrN}_2\text{O}_3$ : 374.0084, found: 374.0085;  $[\alpha]_{\text{D}}^{25} = +18.2$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda$  = 220 nm)  $t_{\text{R}}$  = 8.859 min (minor), 11.241 min (major).



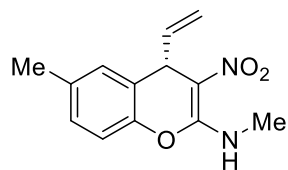
**(S)-6-Bromo-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (32):** Following the general procedure A, compound **32** was obtained as a yellow solid in 98% yield (30.3mg), 78% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 188 – 190 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.41 (brs, 1H), 7.43 – 7.36 (m, 2H), 7.06 – 6.99 (m, 1H), 5.83 (ddd,  $J = 16.8, 9.9, 6.7$  Hz, 1H), 5.09 (d,  $J = 10.0$  Hz, 1H), 5.04 (d,  $J = 16.9$  Hz, 1H), 4.88 (d,  $J = 6.7$  Hz, 1H), 3.22 (d,  $J = 5.3$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 147.2, 136.8, 132.4, 131.5, 125.6, 118.4, 117.9, 116.0, 106.6, 39.5, 28.1. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{11}^{79}\text{BrN}_2\text{O}_3$ : 309.9948, found: 309.9957;  $\text{C}_{12}\text{H}_{11}^{81}\text{BrN}_2\text{O}_3$ : 311.9928, found: 311.9934;  $[\alpha]_{\text{D}}^{25} = +20.9$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 10.335$  min (minor), 17.279 min (major).



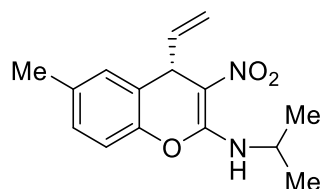
**(S)-6-Bromo-N-isopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (33):** Following the general procedure A, compound **33** was obtained as a yellow solid in 88% yield (29.7mg), 84% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 144 – 146 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.38 (brs, 1H), 7.41 – 7.38 (m, 2H), 7.00 (d,  $J = 9.2$  Hz, 1H), 5.84 (ddd,  $J = 16.8, 10.0, 6.6$  Hz, 1H), 5.09 (d,  $J = 10.0$  Hz, 1H), 5.04 (d,  $J = 17.0$  Hz, 1H), 4.90 (d,  $J = 6.6$  Hz, 1H), 4.33 – 4.20 (m, 1H), 1.40 (d,  $J = 6.6$  Hz, 3H), 1.37 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 147.4, 136.8, 132.4, 131.5, 125.8, 118.4, 117.9, 116.0, 106.3, 44.6, 39.5, 23.4, 23.3. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{14}\text{H}_{15}^{79}\text{BrN}_2\text{O}_3$ : 338.0261, found: 338.0265;  $\text{C}_{14}\text{H}_{15}^{81}\text{BrN}_2\text{O}_3$ : 340.0241, found: 340.0248;  $[\alpha]_{\text{D}}^{25} = +8.3$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 6.076$  min (minor), 12.532 min (major).



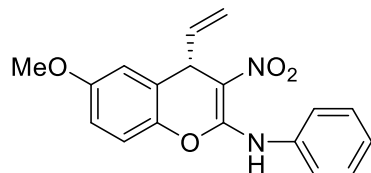
**(S)-6-Methyl-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (34):** Following the general procedure A, compound **34** was obtained as a yellow solid in 98% yield (30.2 mg), 89% ee;  $R_f = 0.5$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 168 – 170 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.31 (brs, 1H), 7.46 – 7.41 (m, 4H), 7.31 – 7.26 (m, 1H), 7.06 (dd,  $J = 5.7, 2.4$  Hz, 2H), 6.96 (d,  $J = 8.9$  Hz, 1H), 5.90 (ddd,  $J = 17.4, 9.5, 6.6$  Hz, 1H), 5.11 (d,  $J = 10$  Hz, 1H), 5.07 (d,  $J = 16.8$  Hz, 1H), 4.95 (d,  $J = 6.6$  Hz, 1H), 2.34 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 146.0, 137.2, 135.9, 135.2, 129.8, 129.5(2C), 129.2, 126.5, 123.2(2C), 122.9, 115.9, 115.7, 108.2, 39.6, 20.9. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3$ : 308.1155, found: 308.1158;  $[\alpha]_{\text{D}}^{25} = +22.1$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 8.094$  min (minor), 14.282 min (major).



**(S)-N,6-Dimethyl-3-nitro-4-vinyl-4H-chromen-2-amine (35):** Following the general procedure A, compound **35** was obtained as a yellow solid in 98% yield (24.1mg), 64% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 151 – 153 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.49 (brs, 1H), 7.14 – 6.95 (m, 3H), 5.85 (ddd,  $J = 16.8, 10.0, 6.6$  Hz, 1H), 5.04 (d,  $J = 10.0$  Hz, 1H), 5.01 (d,  $J = 16.4$  Hz, 1H), 4.87 (d,  $J = 6.7$  Hz, 1H), 3.21 (d,  $J = 5.2$  Hz, 3H), 2.34 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 146.1, 137.4, 135.6, 129.8, 129.0, 122.9, 115.9, 115.2, 107.2, 39.6, 27.9, 20.8. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$ : 246.0999, found: 246.1006;  $[\alpha]_{\text{D}}^{25} = +22.6$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 9.497$  min (minor), 29.834 min (major).



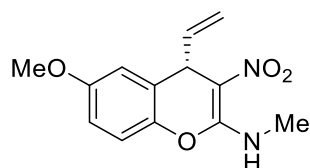
**(S)-N-Isopropyl-6-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (36):** Following the general procedure A, compound **36** was obtained as a yellow solid in 82% yield (22.5mg), 65% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 104 – 106 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.48 (brs, 1H), 7.06 (d,  $J = 8.1$  Hz, 1H), 7.04 (s, 1H), 6.99 (d,  $J = 8.2$  Hz, 1H), 5.86 (ddd,  $J = 16.7, 10.0, 6.5$  Hz, 1H), 5.05 (d,  $J = 8.8$  Hz, 1H), 5.01 (d,  $J = 15.8$  Hz, 1H), 4.89 (d,  $J = 6.4$  Hz, 1H), 4.32 – 4.24 (m, 1H), 2.34 (s, 3H), 1.39 (d,  $J = 6.6$  Hz, 3H), 1.37 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 146.3, 137.4, 135.6, 129.9, 129.0, 123.1, 115.8, 115.2, 106.9, 44.4, 39.7, 23.4, 23.2, 20.9. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_3$ : 274.1312, found: 274.1320;  $[\alpha]_{\text{D}}^{25} = +15.8$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 5.824$  min (minor), 22.793 min (major).



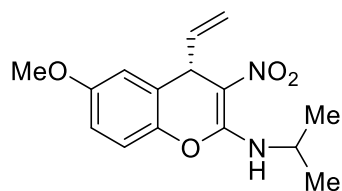
**(S)-6-Methoxy-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (37):** Following the general procedure A, compound **37** was obtained as a yellow solid in 97% yield (31.4 mg), 99% ee;  $R_f = 0.5$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 155 – 157 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.29 (brs, 1H), 7.49 – 7.38 (m, 4H), 7.33 – 7.27 (m, 1H), 7.01 (d,  $J = 8.9$  Hz, 1H), 6.84 – 6.73 (m, 2H), 5.91 (ddd,  $J = 16.7, 9.7, 6.6$  Hz, 1H), 5.12 (d,  $J = 9.6$  Hz, 1H), 5.09 (d,  $J = 17.2$  Hz, 1H), 4.98 (d,  $J = 6.6$  Hz, 1H), 3.81 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4, 157.0, 142.1, 136.9, 135.2, 129.5(2C), 126.5, 124.2, 123.2(2C), 117.2, 115.9, 114.5, 113.5, 107.9, 55.9, 40.0. **HRMS** (EI-TOF)  $m/z$ :



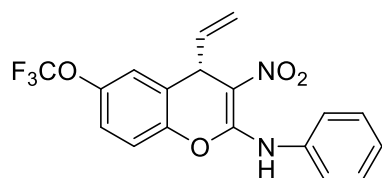
[M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: 324.1105, found: 324.1113; [α]<sub>D</sub><sup>25</sup> = +14.5 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 12.304 min (minor), 19.211 min (major).



**(S)-6-Methoxy-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (38)**: Following the general procedure A, compound **38** was obtained as a yellow solid in 80% yield (20.9mg), 52% ee; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 4/1); m.p: 155 – 157 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.47 (brs, 1H), 7.05 (d, *J* = 8.9 Hz, 1H), 6.81 (d, *J* = 9.1 Hz, 1H), 6.73 (s, 1H), 5.86 (ddd, *J* = 15.8, 8.7, 6.6 Hz, 1H), 5.06 (d, *J* = 8.0 Hz, 1H), 5.03 (d, *J* = 15.3 Hz, 1H), 4.89 (d, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 3.20 (d, *J* = 5.2 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.0, 157.2, 142.2, 137.2, 124.3, 117.1, 115.4, 114.4, 113.5, 106.9, 55.8, 39.9, 27.9. **HRMS** (EI-TOF) m/z: [M]<sup>+</sup> calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: 262.0948, found: 262.0951; [α]<sub>D</sub><sup>25</sup> = +15.7 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak IC-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 35.147 min (major), 47.328 min (minor).

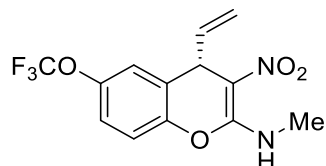


**(S)-N-Isopropyl-6-methoxy-3-nitro-4-vinyl-4H-chromen-2-amine (39)**: Following the general procedure A, compound **39** was obtained as a yellow solid in 86% yield (24.9mg), 41% ee; R<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate = 4/1); m.p: 103 – 105 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.45 (brs, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 6.81 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.74 (d, *J* = 3.0 Hz, 1H), 5.87 (ddd, *J* = 16.5, 10.3, 6.2 Hz, 1H), 5.06 (d, *J* = 8.8 Hz, 1H), 5.03 (d, *J* = 14.6 Hz, 1H), 4.90 (d, *J* = 6.4 Hz, 1H), 4.32 – 4.23 (m, 1H), 3.80 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H), 1.37 (d, *J* = 6.4 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.8, 157.1, 142.3, 137.1, 124.4, 116.9, 115.4, 114.4, 113.5, 106.6, 55.8, 44.4, 39.9, 23.3, 23.2. **HRMS** (EI-TOF) m/z: [M]<sup>+</sup> calcd for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: 290.1261, found: 290.1265; [α]<sub>D</sub><sup>25</sup> = +4.8 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 7.312 min (minor), 26.847 min (major).

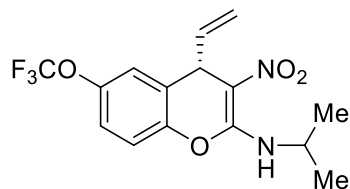


**(S)-3-Nitro-N-phenyl-6-(trifluoromethoxy)-4-vinyl-4H-chromen-2-amine (40)**: Following the general procedure A, compound **40** was obtained as a yellow solid in 97% yield (36.7mg),

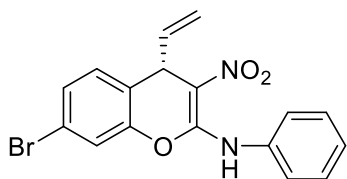
90% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 96 – 98 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.16 (brs, 1H), 7.48 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 7.34 – 7.29 (m, 1H), 7.17 – 7.09 (m, 3H), 5.90 (ddd,  $J = 16.8, 10.0, 6.7$  Hz, 1H), 5.15 (d,  $J = 10.0$  Hz, 1H), 5.11 (d,  $J = 16.9$  Hz, 1H), 5.02 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 146.5, 146.3, 136.5, 134.9, 129.6(2C), 126.9, 125.2, 123.5(2C), 122.2, 121.5, 120.5 (q,  $^1J_{\text{C-F}} = 256.5$  Hz), 117.8, 116.5, 107.5, 39.7.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -58.23(s). **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_4$ : 378.0822, found: 378.0824;  $[\alpha]_{\text{D}}^{25} = +16.2$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 5.547$  min (minor), 7.354 min (major).



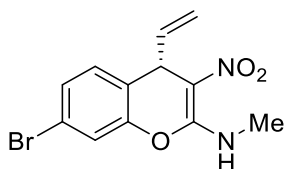
**(S)-N-Methyl-3-nitro-6-(trifluoromethoxy)-4-vinyl-4H-chromen-2-amine (41)**: Following the general procedure A, compound **41** was obtained as a yellow solid in 98% yield (30.9mg), 77% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 133 – 135 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.40 (brs, 1H), 7.19 – 7.16 (m, 2H), 7.13 (s), 5.85 (ddd,  $J = 16.7, 10.0, 6.5$  Hz, 1H), 5.10 (d,  $J = 9.9$  Hz, 1H), 5.03 (d,  $J = 16.9$  Hz, 1H), 4.93 (d,  $J = 6.6$  Hz, 1H), 3.23 (d,  $J = 5.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 146.4, 146.3, 136.7, 125.3, 122.2, 121.3, 120.5 (q,  $^1J_{\text{C-F}} = 256.3$  Hz), 117.7, 116.0, 106.5, 39.7, 28.1.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -58.25(s). **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_3\text{N}_2\text{O}_4$ : 316.0665, found: 316.0673;  $[\alpha]_{\text{D}}^{25} = +16.1$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 7.580$  min (minor), 10.998 min (major).



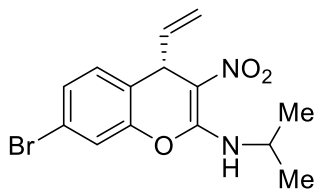
**(S)-N-Isopropyl-3-nitro-6-(trifluoromethoxy)-4-vinyl-4H-chromen-2-amine (42)**: Following the general procedure A, compound **42** was obtained as a yellow solid in 92% yield (31.6mg), 84% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 77 – 79 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.37 (brs, 1H), 7.17 – 7.12 (m, 3H), 5.86 (ddd,  $J = 16.8, 10.0, 6.4$  Hz, 1H), 5.10 (d,  $J = 9.7$  Hz, 1H), 5.03 (d,  $J = 16.8$  Hz, 1H), 4.95 (d,  $J = 6.7$  Hz, 1H), 4.32 – 4.24 (m, 1H), 1.41 (d,  $J = 6.2$  Hz, 3H), 1.38 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3, 146.5, 146.3, 136.7, 125.4, 122.3, 121.4, 120.5 (q,  $^1J_{\text{C-F}} = 247.2$  Hz), 117.5, 116.1, 106.1, 44.6, 39.8, 23.4, 23.3.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -58.25(s). **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_4$ : 344.0978, found: 344.0986;  $[\alpha]_{\text{D}}^{25} = +10.9$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 4.586$  min (minor), 8.490 min (major).



**(S)-7-Bromo-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (43):** Following the general procedure A, compound **43** was obtained as a yellow solid in 99% yield (36.8mg), 95% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 154 – 156 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.16 (brs, 1H), 7.48 – 7.44 (m, 2H), 7.39 (d,  $J = 7.9$  Hz, 2H), 7.37 – 7.29 (m, 2H), 7.24 (s), 7.16 (d,  $J = 8.2$  Hz, 1H), 5.89 (ddd,  $J = 16.8, 10.0, 6.6$  Hz, 1H), 5.12 (d,  $J = 10.0$  Hz, 1H), 5.07 (d,  $J = 16.9$  Hz, 1H), 4.97 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 148.4, 136.8, 134.9, 130.9, 129.6(2C), 129.3, 126.9, 123.5(2C), 122.5, 121.3, 119.6, 116.2, 107.9, 39.29. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}^{79}\text{BrN}_2\text{O}_3$ : 372.0105, found: 372.0115;  $\text{C}_{17}\text{H}_{13}^{81}\text{BrN}_2\text{O}_3$ : 374.0084, found: 374.0085;  $[\alpha]_{\text{D}}^{25} = +12.8$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 8.658$  min (minor), 12.162 min (major).

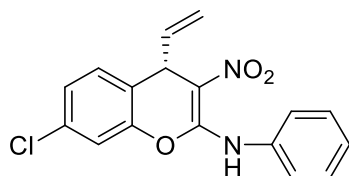


**(S)-7-Bromo-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (44):** Following the general procedure A, compound **44** was obtained as a yellow solid in 97% yield (29.9mg), 74% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 126 – 128 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.41 (brs, 1H), 7.34 – 7.32 (m, 2H), 7.14 (d,  $J = 8.5$  Hz, 1H), 5.84 (ddd,  $J = 16.7, 10.0, 6.5$  Hz, 1H), 5.06 (d,  $J = 10.0$  Hz, 1H), 5.00 (d,  $J = 17.0$  Hz, 1H), 4.88 (d,  $J = 6.4$  Hz, 1H), 3.22 (d,  $J = 5.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 148.4, 136.9, 130.9, 128.9, 122.5, 121.1, 119.5, 115.8, 106.8, 39.2, 28.1. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{11}^{79}\text{BrN}_2\text{O}_3$ : 309.9948, found: 309.9952;  $\text{C}_{12}\text{H}_{11}^{81}\text{BrN}_2\text{O}_3$ : 311.9928, found: 311.9934;  $[\alpha]_{\text{D}}^{25} = +9.8$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 12.740$  min (minor), 34.731 min (major).

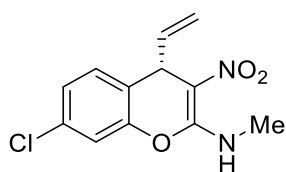


**(S)-7-Bromo-N-isopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (45):** Following the general procedure A, compound **45** was obtained as a yellow solid in 92% yield (31.1mg), 64% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 156 – 158 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.38 (brs, 1H), 7.35 – 7.29 (m, 2H), 7.14 (d,  $J = 8.2$  Hz, 1H), 5.85 (ddd,  $J = 16.7, 10.0, 6.4$  Hz, 1H), 5.07 (d,  $J = 10.0$  Hz, 1H), 5.00 (d,  $J = 16.9$  Hz, 1H), 4.90 (d,  $J = 6.4$  Hz, 1H), 4.35 – 4.18 (m, 1H), 1.40 (d,  $J = 6.6$  Hz, 3H), 1.37 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 148.6, 136.9, 131.0, 128.9, 122.7, 121.2, 119.5, 115.8, 106.5, 44.6, 39.3, 23.4, 23.3.

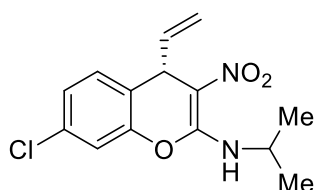
**HRMS** (EI-TOF)  $m/z$ :  $[M]^+$  calcd for  $C_{14}H_{15}^{79}BrN_2O_3$ : 338.0261, found: 338.0262;  $C_{14}H_{15}^{81}BrN_2O_3$ : 340.0241, found: 340.0249;  $[\alpha]_D^{25} = +5.0$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 6.125$  min (minor), 13.359 min (major).



**(S)-7-Chloro-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (46)**: Following the general procedure A, compound **46** was obtained as a yellow solid in 96% yield (31.6mg), 88% ee;  $R_f = 0.6$  ( $CH_2Cl_2$ ); m.p: 163 – 165 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  12.16 (brs, 1H), 7.48 – 7.44 (m, 2H), 7.39 (d,  $J = 7.8$  Hz, 2H), 7.33 – 7.30 (m, 1H), 7.24 – 7.19 (m, 2H), 7.09 (d,  $J = 1.9$  Hz, 1H), 5.89 (ddd,  $J = 16.7, 10.0, 6.6$  Hz, 1H), 5.12 (d,  $J = 9.8$  Hz, 1H), 5.07 (d,  $J = 17.2$  Hz, 1H), 4.98 (d,  $J = 6.6$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  156.5, 148.3, 136.9, 134.9, 133.9, 130.7, 129.6(2C), 126.9, 126.4, 123.5(2C), 121.9, 116.7, 116.2, 107.9, 39.2. **HRMS** (EI-TOF)  $m/z$ :  $[M]^+$  calcd for  $C_{17}H_{13}^{35}ClN_2O_3$ : 328.0610, found: 328.0612;  $C_{17}H_{13}^{37}ClN_2O_3$ : 330.0580, found: 328.0583;  $[\alpha]_D^{25} = +21.6$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 8.275$  min (minor), 11.256 min (major).

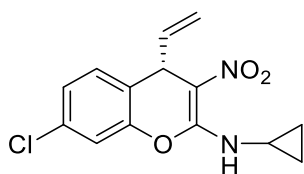


**(S)-7-Chloro-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (47)**: Following the general procedure A, compound **47** was obtained as a yellow solid in 87% yield (23.1mg), 89% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 138 – 140 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  10.42 (brs, 1H), 7.19 (d,  $J = 1.6$  Hz, 2H), 7.17 (s, 1H), 5.84 (ddd,  $J = 16.7, 10.0, 6.5$  Hz, 1H), 5.07 (d,  $J = 10.0$  Hz, 1H), 5.00 (d,  $J = 16.9$  Hz, 1H), 4.90 (d,  $J = 6.6$  Hz, 1H), 3.22 (d,  $J = 5.2$  Hz, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  159.4, 148.4, 137.0, 133.7, 130.7, 126.1, 122.0, 116.7, 115.8, 106.9, 39.2, 28.1. **HRMS** (EI-TOF)  $m/z$ :  $[M]^+$  calcd for  $C_{12}H_{11}^{35}ClN_2O_3$ : 266.0453, found: 266.0454;  $C_{12}H_{11}^{37}ClN_2O_3$ : 268.0424, found: 268.0430;  $[\alpha]_D^{25} = -9.7$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 10.726$  min (minor), 25.968 min (major).

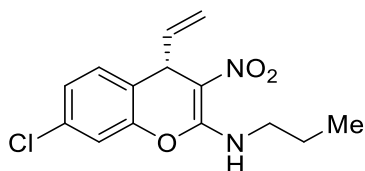


**(S)-7-Chloro-N-isopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (48)**: Following the general procedure A, compound **48** was obtained as a yellow solid in 78% yield (22.9mg), 78% ee;  $R_f$

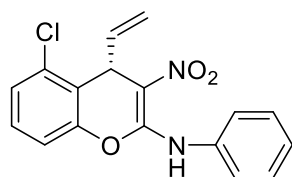
= 0.4 (petroleum ether/ethyl acetate = 4/1); m.p: 157 – 159 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.39 (brs, 1H), 7.22 – 7.19 (m, 2H), 7.15 (d, *J* = 1.7 Hz, 1H), 5.85 (ddd, *J* = 16.7, 10.0, 6.5 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 5.00 (d, *J* = 17.0 Hz, 1H), 4.91 (d, *J* = 6.4 Hz, 1H), 4.34 – 4.21 (m, 1H), 1.40 (d, *J* = 6.6 Hz, 3H), 1.38 (d, *J* = 6.5 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.2, 148.5, 136.9, 133.7, 130.7, 126.1, 122.1, 116.6, 115.7, 106.5, 44.6, 39.2, 23.4, 23.2. **HRMS** (EI-TOF) *m/z*: [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>15</sub><sup>35</sup>ClN<sub>2</sub>O<sub>3</sub>: 294.0766, found: 294.0773; C<sub>14</sub>H<sub>15</sub><sup>37</sup>ClN<sub>2</sub>O<sub>3</sub>: 296.0737, found: 294.0739; [α]<sub>D</sub><sup>25</sup> = +33.3 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) *t*<sub>R</sub> = 6.020 min (minor), 12.457 min (major).



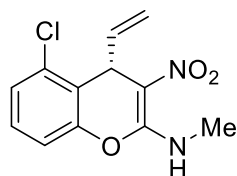
**(S)-7-Chloro-N-cyclopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (49):** Following the general procedure A, compound **49** was obtained as a yellow solid in 86% yield (25.1 mg), 69% ee; *R*<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 4/1); m.p: 164 – 166 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.27 (brs, 1H), 7.21 – 7.17(m, 3H), 5.84 (ddd, *J* = 16.7, 10.0, 6.6 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 5.01 (d, *J* = 16.9 Hz, 1H), 4.89 (d, *J* = 6.6 Hz, 1H), 2.97 – 3.03 (m, 1H), 1.02 – 0.97 (m, 2H), 0.91 – 0.72 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.5, 148.5, 137.1, 133.8, 130.7, 126.1, 122.1, 116.8, 115.9, 107.2, 39.2, 24.0, 7.5, 7.5. **HRMS** (EI-TOF) *m/z*: [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>13</sub><sup>35</sup>ClN<sub>2</sub>O<sub>3</sub>: 292.0610, found: 292.0611; C<sub>14</sub>H<sub>13</sub><sup>37</sup>ClN<sub>2</sub>O<sub>3</sub>: 294.0580, found: 294.0586; [α]<sub>D</sub><sup>25</sup> = +7.7 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) *t*<sub>R</sub> = 7.562 min (minor), 16.631 min (major).



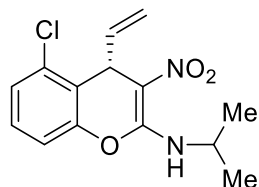
**(S)-7-Chloro-3-nitro-N-propyl-4-vinyl-4H-chromen-2-amine (50):** Following the general procedure A, compound **50** was obtained as a yellow solid in 90% yield (25.1 mg), 58% ee; *R*<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 4/1); m.p: 113 – 115 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.51 (brs, 1H), 7.19 (d, *J* = 2.4 Hz, 2H), 7.15 (s, 1H), 5.85 (ddd, *J* = 16.7, 9.9, 6.4 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 5.00 (d, *J* = 17.0 Hz, 1H), 4.91 (d, *J* = 6.4 Hz, 1H), 3.60 – 3.51 (m, 2H), 1.80 – 1.71 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.9, 148.4, 137.0, 133.7, 130.7, 126.1, 122.1, 116.6, 115.7, 106.7, 43.4, 39.2, 23.1, 11.5. **HRMS** (EI-TOF) *m/z*: [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>15</sub><sup>35</sup>ClN<sub>2</sub>O<sub>3</sub>: 294.0766, found: 294.0768; C<sub>14</sub>H<sub>15</sub><sup>37</sup>ClN<sub>2</sub>O<sub>3</sub>: 296.0737; found: 296.0735, [α]<sub>D</sub><sup>25</sup> = +10.7 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) *t*<sub>R</sub> = 7.017 min (minor), 12.371 min (major).



**(S)-5-Chloro-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (51):** Following the general procedure A, compound **51** was obtained as a yellow solid in 84% yield (27.7 mg), 99% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 146 – 148 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.09 (brs, 1H), 7.48 – 7.39 (m, 4H), 7.34 – 7.24 (m, 3H), 7.02 (d,  $J = 8.0$  Hz, 1H), 5.98 (ddd,  $J = 16.6, 10.1, 5.9$  Hz, 1H), 5.30 (d,  $J = 5.8$  Hz, 1H), 5.15 (d,  $J = 10.0$  Hz, 1H), 5.01 (d,  $J = 17.1$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 149.4, 135.0, 134.3, 134.1, 129.6(2C), 128.9, 127.0, 126.8, 123.4(2C), 122.7, 116.3, 115.0, 108.4, 37.4. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}^{35}\text{ClN}_2\text{O}_3$ : 328.0610, found: 328.0620;  $\text{C}_{17}\text{H}_{13}^{37}\text{ClN}_2\text{O}_3$ : 330.0580, found: 330.0588;  $[\alpha]_{\text{D}}^{25} = +29.2$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 8.431$  min (minor), 11.118 min (major).

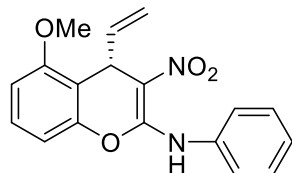


**(S)-5-Chloro-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (52):** Following the general procedure A, compound **52** was obtained as a yellow solid in 92% yield (24.5mg), 92% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 156 – 158 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.34 (brs, 1H), 7.30 – 7.24 (m, 2H), 7.08 (dd,  $J = 7.4, 1.9$  Hz, 1H), 5.95 (ddd,  $J = 17.1, 10.0, 5.8$  Hz, 1H), 5.22 (d,  $J = 5.8$  Hz, 1H), 5.10 (d,  $J = 10.0$  Hz, 1H), 4.93 (d,  $J = 17.1$  Hz, 1H), 3.23 (d,  $J = 5.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 149.4, 134.4, 134.1, 128.8, 126.8, 122.7, 115.8, 114.9, 107.3, 37.3, 28.1. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{11}^{35}\text{ClN}_2\text{O}_3$ : 266.0453, found: 266.0461;  $\text{C}_{12}\text{H}_{11}^{37}\text{ClN}_2\text{O}_3$ : 268.0424, found: 268.0432;  $[\alpha]_{\text{D}}^{25} = +23.9$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 10.575$  min (minor), 36.027 min (major).

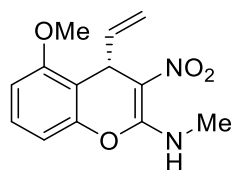


**(S)-5-Chloro-N-isopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (53):** Following the general procedure A, compound **53** was obtained as a yellow solid in 74% yield (21.8mg), 57% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 100 – 102 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.30 (brs, 1H), 7.28 (d,  $J = 7.2$  Hz, 1H), 7.23 (d,  $J = 8.0$  Hz, 1H), 7.05 (dd,  $J = 7.8, 1.7$  Hz, 1H), 5.95 (ddd,  $J = 16.6, 10.0, 5.8$  Hz, 1H), 5.24 (d,  $J = 5.8$  Hz, 1H), 5.10 (d,  $J = 10.0$  Hz, 1H), 4.93 (d,  $J = 18.1$  Hz, 1H), 4.32 – 4.24 (m, 1H), 1.41 (d,  $J = 6.6$  Hz, 3H), 1.37 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 149.6, 134.4, 134.2, 128.8, 126.8, 122.9, 115.8,

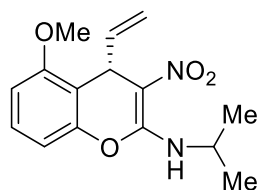
114.8, 107.0, 44.7, 37.4, 23.5, 23.3. **HRMS** (EI-TOF)  $m/z$ :  $[M]^+$  calcd for  $C_{14}H_{15}^{35}ClN_2O_3$ : 294.0766, found: 294.0770;  $C_{14}H_{15}^{37}ClN_2O_3$ : 296.0737, found: 294.0738;  $[\alpha]_D^{25} = +13.9$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 5.864$  min (minor), 15.092 min (major).



**(S)-5-Methoxy-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (54)**: Following the general procedure A, compound **54** was obtained as a yellow solid in 80% yield (25.8 mg), 72% ee;  $R_f = 0.5$  ( $CH_2Cl_2$ ); m.p: 157 – 159 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  12.25 (brs, 1H), 7.43 (d,  $J = 5.8$  Hz, 4H), 7.34 – 7.19 (m, 2H), 6.72 (dd,  $J = 13.3, 8.3$  Hz, 2H), 6.02 (ddd,  $J = 17.1, 10.0, 5.6$  Hz, 1H), 5.23 (d,  $J = 5.7$  Hz, 1H), 5.05 (d,  $J = 10.0$  Hz, 1H), 4.97 (d,  $J = 17.1$  Hz, 1H), 3.88 (s, 3H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  157.2, 157.1, 149.1, 135.8, 135.3, 129.5(2C), 128.7, 126.5, 123.2(2C), 114.7, 112.9, 108.8, 108.5, 107.7, 56.1, 34.3. **HRMS** (EI-TOF)  $m/z$ :  $[M]^+$  calcd for  $C_{18}H_{16}N_2O_4$ : 324.1105, found: 324.1111;  $[\alpha]_D^{25} = +26.9$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 10.010$  min (minor), 10.624 min (major).

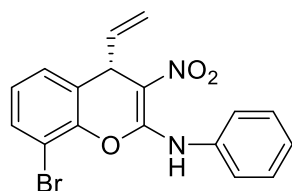


**(S)-5-Methoxy-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (55)**: Following the general procedure A, compound **55** was obtained as a yellow solid in 61% yield (15.9mg), 70% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 149 – 151 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  10.46 (brs, 1H), 7.28 – 7.19 (m, 1H), 6.76 – 6.71 (m, 2H), 5.99 (ddd,  $J = 17.2, 10.0, 5.5$  Hz, 1H), 5.17 (d,  $J = 5.5$  Hz, 1H), 5.00 (d,  $J = 10.1$  Hz, 1H), 4.89 (d,  $J = 17.1$  Hz, 1H), 3.86 (s, 3H), 3.21 (d,  $J = 5.2$  Hz, 3H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  160.3, 157.1, 149.2, 136.0, 128.6, 114.3, 113.1, 108.4, 107.8, 107.5, 56.1, 34.3, 28.0. **HRMS** (EI-TOF)  $m/z$ :  $[M]^+$  calcd for  $C_{13}H_{14}N_2O_4$ : 262.0948, found: 262.0956;  $[\alpha]_D^{25} = +41.4$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak IC-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 27.667$  min (major), 42.084 min (minor).

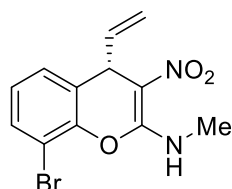


**(S)-N-Isopropyl-5-methoxy-3-nitro-4-vinyl-4H-chromen-2-amine (56)**: Following the general procedure A, compound **56** was obtained as a yellow solid in 77% yield (22.3mg), 90%

ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 102 – 104 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.43 (brs, 1H), 7.25 – 7.21 (m, 1H), 6.73 (d,  $J = 8.2$  Hz, 2H), 5.98 (ddd,  $J = 17.4, 10.1, 5.6$  Hz, 1H), 5.17 (d,  $J = 5.5$  Hz, 1H), 5.00 (d,  $J = 10.1$  Hz, 1H), 4.89 (d,  $J = 17.2$  Hz, 1H), 4.35 – 4.20 (m, 1H), 3.86 (s, 3H), 1.40 (d,  $J = 6.5$  Hz, 3H), 1.37 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 157.1, 149.3, 135.9, 128.6, 114.2, 113.2, 108.3, 107.4, 107.4, 56.1, 44.5, 34.3, 23.4, 23.2. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4$ : 290.1261, found: 290.1265;  $[\alpha]_{\text{D}}^{25} = +19.2$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 6.278$  min (minor), 8.570 min (major).

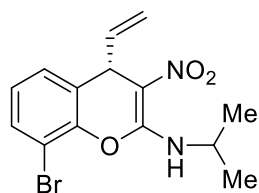


**(S)-8-Bromo-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (57)**: Following the general procedure A, compound **57** was obtained as a yellow solid in 96% yield (35.6mg), 97% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 150 – 152 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.31 (brs, 1H), 7.58 (d,  $J = 7.9$  Hz, 2H), 7.54 – 7.40 (m, 3H), 7.34 – 7.19 (m, 2H), 7.10 – 7.07 (m, 1H), 5.89 (ddd,  $J = 16.7, 10.0, 6.6$  Hz, 1H), 5.13 (d,  $J = 10.8$  Hz, 1H), 5.08 (d,  $J = 17.6$  Hz, 1H), 5.03 (d,  $J = 6.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 145.5, 136.9, 134.7, 132.6, 129.4(2C), 128.8, 126.9, 126.8, 125.3, 123.9(2C), 116.2, 110.1, 107.9, 39.9. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}^{79}\text{BrN}_2\text{O}_3$ : 372.0105, found: 372.0108;  $\text{C}_{17}\text{H}_{13}^{81}\text{BrN}_2\text{O}_3$ : 374.0084, found: 372.0093;  $[\alpha]_{\text{D}}^{25} = +18.0$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 8.177$  min (minor), 15.913 min (major).

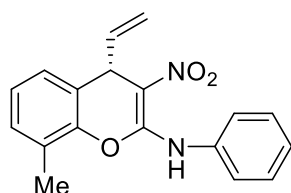


**(S)-8-Bromo-N-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (58)**: Following the general procedure A, compound **58** was obtained as a yellow solid in 97% yield (29.9mg), 61% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 135 – 137 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.28 (brs, 1H), 7.50 (d,  $J = 7.9$  Hz, 1H), 7.21 (d,  $J = 7.6$  Hz, 1H), 7.08 (dd,  $J = 8.0$  Hz, 8.0 Hz, 1H), 5.86 (ddd,  $J = 16.8, 10.0, 6.4$  Hz, 1H), 5.07 (d,  $J = 10.2$  Hz, 1H), 5.01 (d,  $J = 17.7$  Hz, 1H), 4.96 (d,  $J = 7.0$  Hz, 1H), 3.31 (d,  $J = 5.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 145.1, 136.9, 132.1, 128.7, 126.5, 125.4, 115.7, 110.3, 106.9, 39.9, 28.5. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{11}^{79}\text{BrN}_2\text{O}_3$ : 309.9948, found: 309.9950;  $\text{C}_{12}\text{H}_{11}^{81}\text{BrN}_2\text{O}_3$ : 311.9928, found: 311.9937;  $[\alpha]_{\text{D}}^{25} = +14.6$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 11.440$  min (minor), 43.566 min (major).

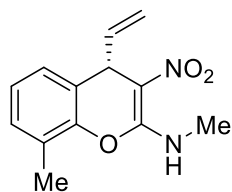




**(S)-8-Bromo-N-isopropyl-3-nitro-4-vinyl-4H-chromen-2-amine (59):** Following the general procedure A, compound **59** was obtained as a yellow solid in 86% yield (29.1mg), 59% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 149 – 151 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.24 (brs, 1H), 7.50 (d,  $J = 6.4$  Hz, 1H), 7.21 (d,  $J = 5.7$  Hz, 1H), 7.10 – 7.06 (m, 1H), 5.86 (ddd,  $J = 16.7, 10.0, 6.4$  Hz, 1H), 5.07 (d,  $J = 10.0$  Hz, 1H), 5.01 (d,  $J = 16.9$  Hz, 1H), 4.97 (d,  $J = 6.4$  Hz, 1H), 4.48 – 4.40 (m, 1H), 1.44 (d,  $J = 6.6$  Hz, 3H), 1.42 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 145.3, 136.9, 132.1, 128.8, 126.5, 125.5, 115.7, 110.3, 106.5, 45.1, 39.9, 23.3, 23.1. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{14}\text{H}_{15}^{79}\text{BrN}_2\text{O}_3$ : 338.0261, found: 338.0265;  $\text{C}_{14}\text{H}_{15}^{81}\text{BrN}_2\text{O}_3$ : 340.0241, found: 340.0247;  $[\alpha]_{\text{D}}^{25} = +8.3$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 5.785$  min (minor), 15.419 min (major).

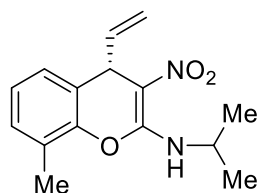


**(S)-8-Methyl-3-nitro-N-phenyl-4-vinyl-4H-chromen-2-amine (60):** Following the general procedure A, compound **60** was obtained as a yellow solid in 90% yield (27.6mg), 99% ee;  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ); m.p: 109 – 111 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.25 (brs, 1H), 7.48 – 7.42 (m, 4H), 7.33 – 7.30 (m, 1H), 7.12 – 7.07 (m, 3H), 5.92 (ddd,  $J = 16.7, 9.5, 6.6$  Hz, 1H), 5.09 (d,  $J = 7.2$  Hz, 1H), 5.04 (d,  $J = 16.0$  Hz, 1H), 5.00 (d,  $J = 4.2$  Hz, 1H), 2.17 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 146.9, 137.4, 135.0, 130.1, 129.4(2C), 127.2, 126.9, 125.8, 125.7, 124.1(2C), 123.1, 115.6, 108.2, 39.7, 16.3. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3$ : 308.1155, found: 308.1160;  $[\alpha]_{\text{D}}^{25} = +15.2$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 8.088$  min (minor), 23.630 min (major).

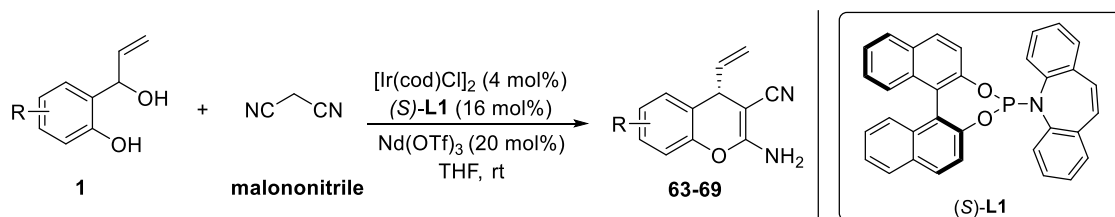


**(S)-N,8-Dimethyl-3-nitro-4-vinyl-4H-chromen-2-amine (61):** Following the general procedure A, compound **61** was obtained as a yellow solid in 90% yield (22.1mg), 62% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 136 – 138 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.43 (brs, 1H), 7.16 – 7.05 (m, 3H), 5.86 (ddd,  $J = 16.7, 10.0, 6.4$  Hz, 1H), 5.03 (d,  $J = 10.0$  Hz, 1H), 4.98 (d,  $J = 16.8$  Hz, 1H), 4.92 (d,  $J = 6.4$  Hz, 1H), 3.24 (d,  $J = 5.2$  Hz, 3H), 2.37 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 146.7, 137.4, 129.9, 127.2, 125.6, 125.4, 123.1,

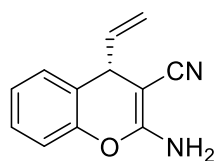
115.1, 107.3, 39.7, 28.0, 15.9. **HRMS** (EI-TOF)  $m/z$ :  $[M]^+$  calcd for  $C_{13}H_{14}N_2O_3$ : 246.0999, found: 246.1002;  $[\alpha]_D^{25} = +28.7$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak IC-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 27.711$  min (major), 36.674 min (minor).



**(S)-N-Isopropyl-8-methyl-3-nitro-4-vinyl-4H-chromen-2-amine (62)**: Following the general procedure A, compound **62** was obtained as a yellow solid in 90% yield (24.7mg), 55% ee;  $R_f = 0.4$  (petroleum ether/ethyl acetate = 4/1); m.p: 132 – 134 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  10.43 (brs, 1H), 7.15 – 7.06 (m, 3H), 5.87 (ddd,  $J = 16.6, 10.0, 6.4$  Hz, 1H), 5.04 (d,  $J = 9.9$  Hz, 1H), 4.99 (d,  $J = 16.9$  Hz, 1H), 4.93 (d,  $J = 6.3$  Hz, 1H), 4.36 – 4.23 (m, 1H), 2.37 (s, 3H), 1.43 (d,  $J = 6.5$  Hz, 3H), 1.40 (d,  $J = 6.5$  Hz, 3H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ )  $\delta$  158.5, 146.7, 137.4, 129.9, 127.2, 125.5, 125.3, 123.2, 115.1, 106.8, 44.6, 39.7, 23.2, 23.1, 15.9. **HRMS** (EI-TOF)  $m/z$ :  $[M]^+$  calcd for  $C_{15}H_{18}N_2O_3$ : 274.1312, found: 274.1320;  $[\alpha]_D^{25} = +5.8$  ( $c$  0.20,  $CH_2Cl_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 5.749$  min (minor), 68.704 min (major).

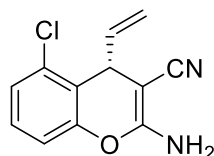


**General procedure B**: Under a nitrogen atmosphere, a flame dried 10 mL Schlenk tube was charged with  $[Ir(cod)Cl]_2$  (2.7 mg, 0.004 mmol, 4 mol%), Carreira's ligand (*S*)-**L1** (8.2 mg, 0.016 mmol, 16 mol%). After the tube was evacuated and backfilled with nitrogen, freshly distilled THF (1.5 mL) was added, then stirred at room temperature for 15 minutes while the solution turned dark red. Then, 2-(1-hydroxyallyl)phenols ( $\pm$ )-**1** (0.2 mmol, 2.0 equiv) were added and the reaction mixture immediately turned light yellow. Malononitrile (6.6 mg, 0.1 mmol, 1.0 equiv) and  $Nd(OTf)_3$  (13.9 mg, 0.02 mmol, 20 mol%) were added sequentially. The reaction mixture was stirred at room temperature until **1** were consumed (monitored by TLC), which was directly purified by flash column chromatography silica gel (petroleum ether/ethyl acetate = 4/1) to afford products **63-69**.

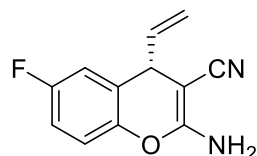


**(S)-2-Amino-4-vinyl-4H-chromene-3-carbonitrile (63)**: Following the general procedure B, compound **63** was obtained as a yellow solid in 73% yield (14.5 mg), 88% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 104 – 106 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.23

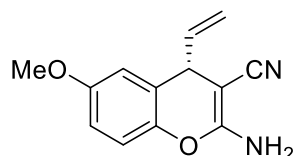
– 7.09 (m, 3H), 6.95 (d,  $J = 8.1$  Hz, 1H), 5.78 (ddd,  $J = 17.6, 9.1, 8.3$  Hz, 1H), 5.22 (d,  $J = 16.9$  Hz, 1H), 5.13 (d,  $J = 9.8$  Hz, 1H), 4.69 (brs, 2H), 4.13 (d,  $J = 8.3$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 148.5, 139.7, 129.4, 128.5, 125.0, 121.4, 120.1, 116.5, 115.9, 58.2, 39.5. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$ : 198.0788, found: 198.0791;  $[\alpha]_{\text{D}}^{25} = -0.6$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 6.609$  min (minor), 7.547 min (major).



**(R)-2-Amino-5-chloro-4-vinyl-4H-chromene-3-carbonitrile (64)**: Following the general procedure **B**, compound **64** was obtained as a white solid in 40% yield (9.3 mg), 89% ee;  $R_{\text{f}} = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 123 – 125 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 – 7.13 (m, 2H), 6.92 (dd,  $J = 6.7, 2.7$  Hz, 1H), 5.83 (ddd,  $J = 16.8, 9.9, 6.7$  Hz, 1H), 5.16 (d,  $J = 16.8$  Hz, 1H), 5.13 (d,  $J = 10.4$  Hz, 1H), 4.69 (brs, 2H), 4.32 (d,  $J = 6.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 150.1, 136.9, 133.9, 128.7, 126.2, 121.3, 119.5, 115.9, 115.3, 58.7, 37.5. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_9^{35}\text{ClN}_2\text{O}$ : 232.0398, found: 232.0404;  $\text{C}_{12}\text{H}_9^{37}\text{ClN}_2\text{O}$ : 234.0369, found: 234.0372;  $[\alpha]_{\text{D}}^{25} = -3.2$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 5.788$  min (major), 8.816 min (minor).

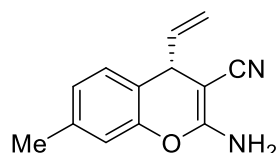


**(S)-2-Amino-6-fluoro-4-vinyl-4H-chromene-3-carbonitrile (65)**: Following the general procedure **B**, compound **65** was obtained as a yellow solid in 66% yield (15.3 mg), 71% ee;  $R_{\text{f}} = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 141 – 143 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.98 – 6.87 (m, 2H), 6.86 (d,  $J = 7.8$  Hz, 1H), 5.76 (ddd,  $J = 16.8, 9.6, 8.3$  Hz, 1H), 5.25 (d,  $J = 16.8$  Hz, 1H), 5.18 (d,  $J = 9.7$  Hz, 1H), 4.61 (brs, 2H), 4.12 (d,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 159.4 (d,  $^1J_{\text{C-F}} = 242.3$  Hz), 144.6, 138.9, 123.2 (d,  $^3J_{\text{C-F}} = 7.8$  Hz), 119.7, 117.9 (d,  $^3J_{\text{C-F}} = 8.6$  Hz), 116.8, 115.5 (d,  $^2J_{\text{C-F}} = 23.6$  Hz), 115.4 (d,  $^2J_{\text{C-F}} = 23.8$  Hz), 57.9, 39.8.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -117.32 – -117.41 (m). **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_9\text{FN}_2\text{O}$ : 216.0693, found: 216.0697;  $[\alpha]_{\text{D}}^{25} = -1.8$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AS-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_{\text{R}} = 6.630$  min (minor), 7.438 min (major).

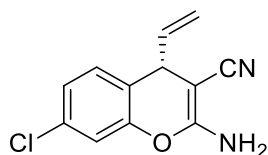


**(S)-2-Amino-6-methoxy-4-vinyl-4H-chromene-3-carbonitrile (66)**: Following the general procedure **B**, compound **66** was obtained as a yellow solid in 70% yield (15.9 mg), 90% ee;  $R_{\text{f}}$

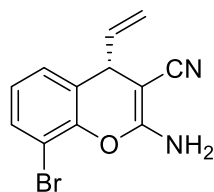
= 0.3 (petroleum ether/ethyl acetate = 4/1); m.p: 167 – 169 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.89 (d, *J* = 8.9 Hz, 1H), 6.76 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.64 (d, *J* = 2.9 Hz, 1H), 5.77 (ddd, *J* = 16.8, 9.8, 8.4 Hz, 1H), 5.24 (d, *J* = 16.8 Hz, 1H), 5.15 (d, *J* = 10.0 Hz, 1H), 4.57 (brs, 2H), 4.11 (d, *J* = 8.4 Hz, 1H), 3.77 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.8, 156.6, 142.6, 139.5, 122.2, 120.2, 117.4, 116.1, 114.4, 113.4, 57.9, 55.8, 39.9. HRMS (EI-TOF) m/z: [M]<sup>+</sup> calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: 228.0899, found: 228.0896; [α]<sub>D</sub><sup>25</sup> = -2.7 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); HPLC (Chiralpak AD-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 9.352 min (minor), 14.632 min (major).



**(S)-2-Amino-7-methyl-4-vinyl-4H-chromene-3-carbonitrile (67):** Following the general procedure B, compound 67 was obtained as a white solid in 54% yield (11.4 mg), 96% ee; R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 4/1); m.p: 140 – 142 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.03 (d, *J* = 7.8 Hz, 1H), 6.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.77 (s, 1H), 5.75 (ddd, *J* = 16.8, 9.7, 8.3 Hz, 1H), 5.21 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 9.7 Hz, 1H), 4.57 (brs, 2H), 4.10 (d, *J* = 8.3 Hz, 1H), 2.32 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 148.4, 139.8, 138.8, 129.1, 125.9, 120.1, 118.3, 116.8, 115.8, 58.6, 39.3, 21.1. HRMS (EI-TOF) m/z: [M]<sup>+</sup> calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O: 212.0944, found: 212.0948; [α]<sub>D</sub><sup>25</sup> = -3.1 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); HPLC (Chiralpak AD-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 7.529 min (minor), 12.306 min (major).

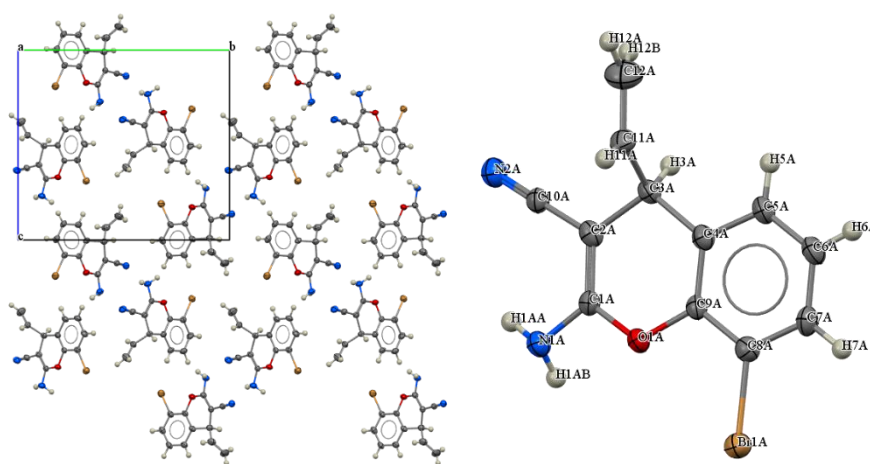


**(S)-2-Amino-7-chloro-4-vinyl-4H-chromene-3-carbonitrile (68):** Following the general procedure B, compound 68 was obtained as a white solid in 59% yield (13.7 mg), 97% ee; R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 4/1); m.p: 125 – 127 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.09 (d, *J* = 1.5 Hz, 2H), 6.98 (s, 1H), 5.74 (ddd, *J* = 16.8, 9.8, 8.3 Hz, 1H), 5.23 (d, *J* = 16.8 Hz, 1H), 5.16 (d, *J* = 9.8 Hz, 1H), 4.66 (brs, 2H), 4.10 (d, *J* = 8.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.2, 148.9, 139.2, 133.7, 130.4, 125.3, 120.1, 119.6, 116.8, 116.5, 58.6, 39.2. HRMS (EI-TOF) m/z: [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>9</sub><sup>35</sup>ClN<sub>2</sub>O: 232.0398, found: 232.0404; C<sub>12</sub>H<sub>9</sub><sup>37</sup>ClN<sub>2</sub>O: 234.0369, found: 234.0376; [α]<sub>D</sub><sup>25</sup> = +0.8 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); HPLC (Chiralpak AS-H, *n*-hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 6.026 min (minor), 6.994 min (major).



**(S)-2-Amino-8-bromo-4-vinyl-4H-chromene-3-carbonitrile (69):** Following the general procedure **B**, compound **69** was obtained as a yellow solid in 54% yield (12.3 mg), 95% ee;  $R_f = 0.3$  (petroleum ether/ethyl acetate = 4/1); m.p: 157 – 159 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.11 (d,  $J = 7.4$  Hz, 1H), 7.01 – 6.97 (m, 1H), 5.77 (ddd,  $J = 16.8, 9.8, 8.2$  Hz, 1H), 5.23 (d,  $J = 16.8$  Hz, 1H), 5.16 (d,  $J = 9.8$  Hz, 1H), 4.74 (brs, 2H), 4.16 (d,  $J = 8.3$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 145.6, 139.2, 132.4, 128.6, 125.7, 123.5, 119.4, 116.5, 110.5, 58.8, 40.0. **HRMS** (EI-TOF)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{12}\text{H}_9^{79}\text{BrN}_2\text{O}$ : 275.9893, found: 275.9901;  $\text{C}_{12}\text{H}_9^{81}\text{BrN}_2\text{O}$ : 277.9873, found: 277.9881;  $[\alpha]_D^{25} = -2.4$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ); **HPLC** (Chiralpak AD-H,  $n$ -hexane/ethanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 220$  nm)  $t_R = 7.398$  min (minor), 10.674 min (major).

**The preparation and X-ray analysis of the single crystal:** Compound **69** (95% ee, 10.0 mg) was dissolved in 1.0 mL of acetone in a screw-top vial and drops of hexane were added. The lid was then loosely screwed on the vial, and a single crystal was obtained by natural volatilization at room temperature. The data set was collected by a Bruker APEX-II CCD at 293(2) K equipped with Cu radiation source ( $K\alpha = 1.54178$  Å). Applied with multi-scan absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package. CCDC 2342670 contains the supplementary crystallographic data, and can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).



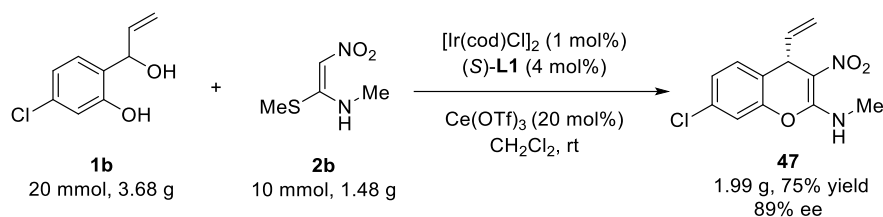
**Figure S2.** The thermal ellipsoid plot for X-ray structure of compound **69** with the ellipsoid contour at 30% probability levels

**Crystal data and structure refinement for 69**

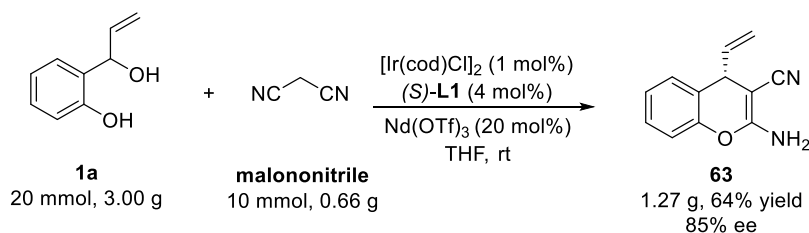
Identification code	zm_e123_0m	
Empirical formula	$\text{C}_{12}\text{H}_9\text{BrN}_2\text{O}$	
Formula weight	277.12	
Temperature	293.00 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P 1 2 1 1$	
Unit cell dimensions	$a = 4.9753(2)$ Å	$a = 90^\circ$

	$b = 16.0176(6) \text{ \AA}$	$b = 90.798(2)^\circ$
	$c = 14.3810(5) \text{ \AA}$	$g = 90^\circ$
Volume	1145.94(7) $\text{\AA}^3$	
Z	4	
Density (calculated)	1.606 $\text{Mg/m}^3$	
Absorption coefficient	4.724 $\text{mm}^{-1}$	
F(000)	552	
Crystal size	0.2 x 0.15 x 0.13 $\text{mm}^3$	
Theta range for data collection	3.073 to 68.389 $^\circ$	
Index ranges	-5 $\leq h \leq$ 5, -19 $\leq k \leq$ 19, -17 $\leq l \leq$ 15	
Reflections collected	14310	
Independent reflections	4023 [R(int) = 0.0910]	
Completeness to theta = 67.679 $^\circ$	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5321	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	4023 / 2 / 303	
Goodness-of-fit on $F^2$	0.940	
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0474, wR2 = 0.1241	
R indices (all data)	R1 = 0.0773, wR2 = 0.1295	
Absolute structure parameter	0.12(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.483 and -0.685 $\text{e.\AA}^{-3}$	

#### 4. Gram-scale preparation of products **47** and **63**

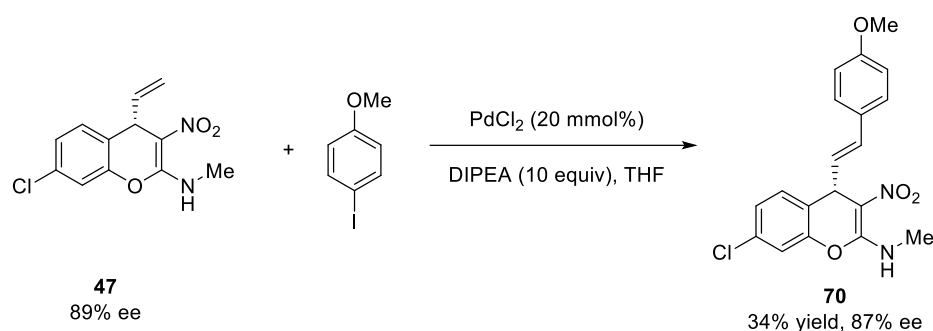


Under a nitrogen atmosphere, a flame dried 100 mL Schlenk tube was charged with  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (67 mg, 0.1 mmol, 1 mol %), Carreira's ligand (*S*)-**L1** (203 mg, 0.4 mmol, 4 mol %). After the tube was evacuated and backfilled with nitrogen, freshly distilled  $\text{CH}_2\text{Cl}_2$  (40 mL) was added, then stirred at room temperature for 15 minutes while the solution turned dark red. Then, 2-(1-hydroxyallyl)phenol **1b** (3.68 g, 20 mmol, 2.0 equiv) were added and the reaction mixture immediately turned light yellow. 1-(methylthio)-2-nitroenamine **2b** (1.48 g, 10 mmol, 1.0 equiv) and  $\text{Ce}(\text{OTf})_3$  (1.17 g, 2 mmol, 20 mol %) were added sequentially. The reaction mixture was stirred at room temperature until **2b** were consumed (monitored by TLC). After the solvent was removed in vacuo, the residue was directly purified by flash column chromatography silica gel (petroleum ether/ethyl acetate = 4/1) to afford product **47** in 75% yield (1.99 g, 89% ee).



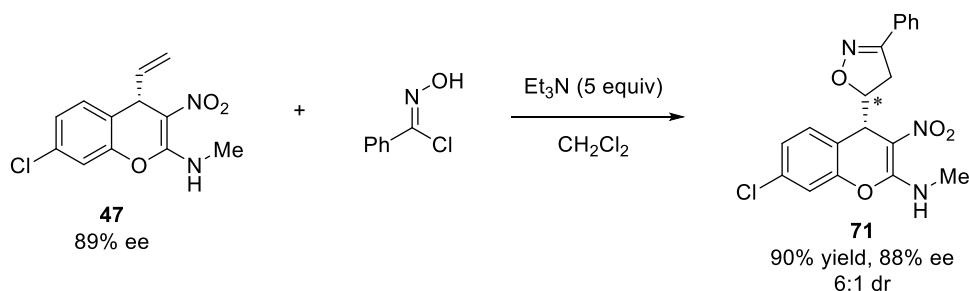
Under a nitrogen atmosphere, a flame dried 100 mL Schlenk tube was charged with  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (67 mg, 0.1 mmol, 1 mol %), Carreira's ligand (*S*)-**L1** (203 mg, 0.4 mmol, 4 mol %). After the tube was evacuated and backfilled with nitrogen, freshly distilled THF (40 mL) was added, then stirred at room temperature for 15 minutes while the solution turned dark red. Then, racemic allylic alcohol **1a** (3.00 g, 20 mmol, 2.0 equiv) were added and the reaction mixture immediately turned light yellow. Malononitrile (0.66 g, 10 mmol, 1.0 equiv) and  $\text{Nd}(\text{OTf})_3$  (1.39 g, 2 mmol, 20 mol %) were added sequentially. The reaction mixture was stirred at room temperature until **1a** were consumed (monitored by TLC). After the solvent was removed in vacuo, the residue was directly purified by flash column chromatography silica gel (petroleum ether/ethyl acetate = 4/1) to afford product **63** in 64% yield (1.27 g, 85% ee).

## 5. Synthetic transformation of product 47



Under a nitrogen atmosphere, a flame dried 10 mL Schlenk tube was charged with compound **47** (53.2 mg, 0.2 mmol, 1.0 equiv), 4-iodobenzyl ether (93.6 mg, 0.4 mmol, 2.0 equiv), DIPEA (258.5 mg, 2 mmol, 10.0 equiv) and PdCl<sub>2</sub> (7.1 mg, 0.04 mmol, 20 mmol%), after the tube was evacuated and backfilled with nitrogen, dry THF (3 mL) was added, then the reaction mixture was stirred at 60 °C for 12 hours. Afterwards, the solvent was removed *in vacuo*, and the crude product was extracted with EtOAc (5 mL) 3-5 times. The combined organics was washed with water and brine, then separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under the reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to give the desired product **70**.

**(S,E)-7-Chloro-4-(4-methoxystyryl)-N-methyl-3-nitro-4H-chromen-2-amine (70)**: yellow solid, 34% yield (25.3 mg), 87% ee;  $R_f = 0.2$  (petroleum ether/ethyl acetate = 4/1); m.p: 136 – 138 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.40 (brs, 1H), 7.26 – 7.16 (m, 5H), 6.79 (d,  $J = 8.5$  Hz, 2H), 6.29 (d,  $J = 15.7$  Hz, 1H), 6.03 (dd,  $J = 15.7, 7.0$  Hz, 1H), 5.04 (d,  $J = 7.0$  Hz, 1H), 3.77 (s, 3H), 3.22 (d,  $J = 5.2$  Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.5, 159.4, 148.5, 133.8, 130.9, 130.5, 129.4, 127.8 (2C), 126.5 (2C), 126.3, 122.5, 116.8, 114.0 (2C), 55.4, 38.6, 28.1. **HRMS** (EI-TOF)  $m/z$ : [M]<sup>+</sup> calcd for C<sub>19</sub>H<sub>17</sub><sup>35</sup>ClN<sub>2</sub>O<sub>4</sub>: 372.0871, found: 372.0881; C<sub>19</sub>H<sub>17</sub><sup>37</sup>ClN<sub>2</sub>O<sub>4</sub>: 374.0847, found: 374.0854; [α]<sub>D</sub><sup>25</sup> = +13.1 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AS-H, *n*-hexane/ethanol = 70/30, flow rate = 1.0 mL/min, λ = 220 nm)  $t_R = 17.555$  min (minor), 40.391 min (major).



A flame-dried Schlenk tube was charged compound **47** (53.2 mg, 0.2 mmol, 1.0 equiv) and purged with nitrogen. CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was added *via* syringe to the reaction tube. A second flame-dried tube was charged with α-chlorobenzaldoxime (155.6 mg, 1.00 mmol, 5.0 equiv.) and CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) and purged with nitrogen. Triethylamine (139.0 μL, 1.00 mmol, 5.0 equiv.) was added to the second tube, which was stirred 15 minutes at room temperature. The oxime chloride solution was then transferred to the tube containing **47** *via* syringe. The mixture was stirred 12 hours at room temperature. After completion, the reaction mixture was quenched with



water and extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times. The resulted filtrate was separated. The combined organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to give product **71** as a white solid in 90% yield (69.3 mg, 88% ee, 6:1 dr).

**(S)-7-Chloro-N-methyl-3-nitro-4-((S)-3-phenyl-4,5-dihydroisoxazol-5-yl)-4H-chromen-2-amine (71)**: white solid, 90% yield (69.3 mg), 88% ee; R<sub>f</sub> = 0.2 (petroleum ether/ethyl acetate = 4:1); m.p: 124 – 126 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.37 (brs, 1H), 7.50 – 7.42 (m, 3H), 7.38 – 7.32 (m, 3H), 7.21 – 7.16 (m, 1H), 7.13 (d, *J* = 2.1 Hz, 1H), 5.17 (ddd, *J* = 11.0, 8.1, 3.0 Hz, 1H), 4.90 (d, *J* = 3.0 Hz, 1H), 3.31 – 3.25 (dd, *J* = 11.0, 8.1 Hz, 1H), 3.23 (d, *J* = 5.2 Hz, 3H), 2.94 (dd, *J* = 17.0, 8.1 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.7, 156.9, 149.6, 134.4, 131.3, 130.3, 129.1, 128.8 (2C), 126.7 (2C), 126.4, 119.4, 116.4, 104.3, 82.5, 39.1, 36.9, 28.3. **HRMS** (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub><sup>35</sup>ClN<sub>3</sub>O<sub>4</sub>Na: 408.0722, found: 408.0726; C<sub>19</sub>H<sub>16</sub><sup>37</sup>ClN<sub>3</sub>O<sub>4</sub>Na: 410.0693, found: 410.0698; [α]<sub>D</sub><sup>25</sup> = +11.3 (*c* 0.20, CH<sub>2</sub>Cl<sub>2</sub>); **HPLC** (Chiralpak AD-H, *n*-hexane/ethanol = 70/30, flow rate = 1.0 mL/min, λ = 220 nm) t<sub>R</sub> = 18.260 min (minor-1), 21.850 min (major-1), 23.696 min (minor-2), 25.159 min (major-2).

## 6. Antifungal activities evaluation

*In-vitro* antifungal activities of 2-amino-4*H*-chromene compounds against *Fusarium graminearum*, *Botrytis cinerea*, *Rhizoctonia solani* and *Sclerotinia sclerotiorum*, which were provided by GreenTech Laboratory, were tested using the mycelium growth rate method. All compounds were tested at 100 mg/L as well as the positive control reagents boscalid and procymidone. Each compound was dissolved with dimethyl sulfoxide (DMSO) for preparing 1000 mg/L stock solution and diluted with the melted potato dextrose agar (PDA) media to prepared the target concentrations of compounds. A blank control was established by incorporating 0.5% DMSO (v/v) into PDA media. The mycelial disks, with a diameter of 5 mm, from phytopathogenic fungi were placed onto PDA plates and then were incubated at 25 °C under 80% moisturizing conditions in the dark. Diameters (mm) of the colony were measured by the cross-bracketing method. The growth inhibition rates were calculated according to the following formula percentage inhibition (%) = [(C – T)/(C – 5 mm)] × 100, where C and T represent diameters of the colony cultured on blank control and dosed PDA, respectively. The potent products, which average inhibitory rate >80% at 100 mg/L against *Rhizoctonia solani*, was further evaluated by the median effective concentrations (EC<sub>50</sub>). Each experiment was conducted three times, and the statistical analyses of the data were performed using Office Excel 19.0. EC<sub>50</sub> values were calculated with the IBM SPSS Statistics 27.0 software.

**Table S3** *In vitro* antifungal activities of 3-70

entry	compounds	Inhibition Rate (%) (100 mg/L)			
		<i>F. g.</i> <sup>a</sup>	<i>B. c.</i> <sup>b</sup>	<i>R. s.</i> <sup>c</sup>	<i>S. s.</i> <sup>d</sup>
1	<b>rac-3</b>	41.6	40.9	59.7	12.5
2	<b>rac-4</b>	9.1	10.1	11.2	12.0
3	<b>rac-5</b>	19.2	24.1	55.7	26.3
4	<b>rac-6</b>	11.9	-2.5	53.8	10.8
5	<b>rac-7</b>	23.6	9.2	52.4	-16.1
6	<b>rac-8</b>	28.3	10.3	57.9	9.6
7	<b>rac-9</b>	43.6	23.7	47.9	33.5
8	<b>rac-10</b>	28.8	5.4	38.4	18.1
9	<b>rac-11</b>	9.6	2.5	46.5	-5.1
10	<b>rac-12</b>	27.1	5.7	54.9	-4.6
11	<b>rac-13</b>	54.4	33.1	62.5	10.2
12	<b>rac-14</b>	32.0	24.4	43.0	25.4
13	<b>rac-15</b>	65.0	40.5	68.1	11.8
14	<b>rac-16</b>	52.2	59.0	79.5	42.4
15	<b>rac-17</b>	58.6	35.1	86.9	66.5
16	<b>rac-18</b>	49.4	47.0	86.8	48.3
17	<b>rac-19</b>	54.7	38.0	90.7	27.2
18	<b>rac-20</b>	-6.1	-3.1	24.9	2.8
19	<b>rac-21</b>	43.7	66.7	66.7	59.8
20	<b>rac-22</b>	57.7	68.4	85.9	64.1
21	<b>rac-23</b>	29.4	43.3	86.8	28.5
22	<b>rac-24</b>	15.5	18.0	83.1	5.6

23	<b>rac-25</b>	18.5	9.6	46.7	3.9
24	<b>rac-26</b>	62.6	37.6	61.8	29.2
25	<b>rac-27</b>	32	36.1	43.2	8.2
26	<b>rac-28</b>	21.9	22.5	56.4	44.9
27	<b>rac-29</b>	74.1	57.3	61.2	47.8
28	<b>rac-30</b>	23.7	18.6	41.6	10.8
29	<b>rac-31</b>	42.3	30.7	65.4	25.7
30	<b>rac-32</b>	64.9	39.1	64.8	33.9
31	<b>rac-33</b>	22.4	18.3	35.9	19.2
32	<b>rac-34</b>	-15.6	-19.5	2.4	-28.4
33	<b>rac-35</b>	61.3	66.4	67.9	48.8
34	<b>rac-36</b>	76.0	71.5	89.9	30.6
35	<b>rac-37</b>	-4.4	-15.7	25.5	17.9
36	<b>rac-38</b>	64.5	50.7	60.1	41.6
37	<b>rac-39</b>	57.5	61.7	72.7	51
38	<b>rac-40</b>	29.6	-14.6	47.3	-16.0
39	<b>rac-41</b>	67.4	50.7	78.4	27.8
40	<b>rac-42</b>	49.2	52.6	78.2	32.9
41	<b>rac-43</b>	35.7	12.0	40.0	22.5
42	<b>rac-44</b>	67.1	68.3	87.3	62.0
43	<b>rac-45</b>	1.6	10.2	20.0	4.9
44	<b>rac-46</b>	-11.3	-3.8	-4.9	5.5
45	<b>rac-47</b>	81.2	87.6	90.0	74.0
46	<b>rac-48</b>	30.7	8.0	22.1	4.7
47	<b>rac-49</b>	15.0	21.7	46.0	13.9
48	<b>rac-50</b>	45.3	34.7	75.8	32.5
49	<b>rac-51</b>	-14.7	-6.1	29.7	-10.7
50	<b>rac-52</b>	47.6	76.6	70.9	55.4
51	<b>rac-53</b>	49.2	32.5	58.5	16.1
52	<b>rac-54</b>	-10.4	-17.2	10.3	-18.2
53	<b>rac-55</b>	64.9	56.2	70.1	50.8
54	<b>rac-56</b>	41.5	39.1	62.9	29.6
55	<b>rac-57</b>	-8.7	8.8	16.4	1.9
56	<b>rac-58</b>	75.1	67.5	78.4	51.4
57	<b>rac-59</b>	6.1	12.1	40.4	5.5
58	<b>rac-60</b>	36.4	18.0	50.3	26.2
59	<b>rac-61</b>	71.9	69.0	86.4	49.6
60	<b>rac-62</b>	42.8	16.8	37.1	5.5
61	<b>rac-63</b>	18.7	44.7	52.9	33.5
62	<b>rac-64</b>	35.7	48.9	50.8	37.6
63	<b>rac-65</b>	34.3	46.7	56.1	26.4
64	<b>rac-66</b>	26.9	39.6	43.2	29.7
65	<b>rac-67</b>	44.6	56.2	49.8	12.5
66	<b>rac-68</b>	38.6	43.1	60.3	19.8

67	<b>rac-69</b>	39.5	33.7	63.2	20.4
68	<b>rac-70</b>	33.6	35.6	49.4	18.7
69 <sup>e</sup>	<b>Boscalid</b>	35.7	89.6	94.9	94.4
70 <sup>f</sup>	<b>Procymidone</b>	22.2	99.0	98.3	99.7

<sup>a</sup> *Fusarium graminearum*.

<sup>b</sup> *Botrytis cinerea*.

<sup>c</sup> *Rhizoctonia solani*.

<sup>d</sup> *Sclerotinia sclerotiorum*.

<sup>e,f</sup> positive control.

**Table S4** EC<sub>50</sub> Values against *Rhizoctonia solani*

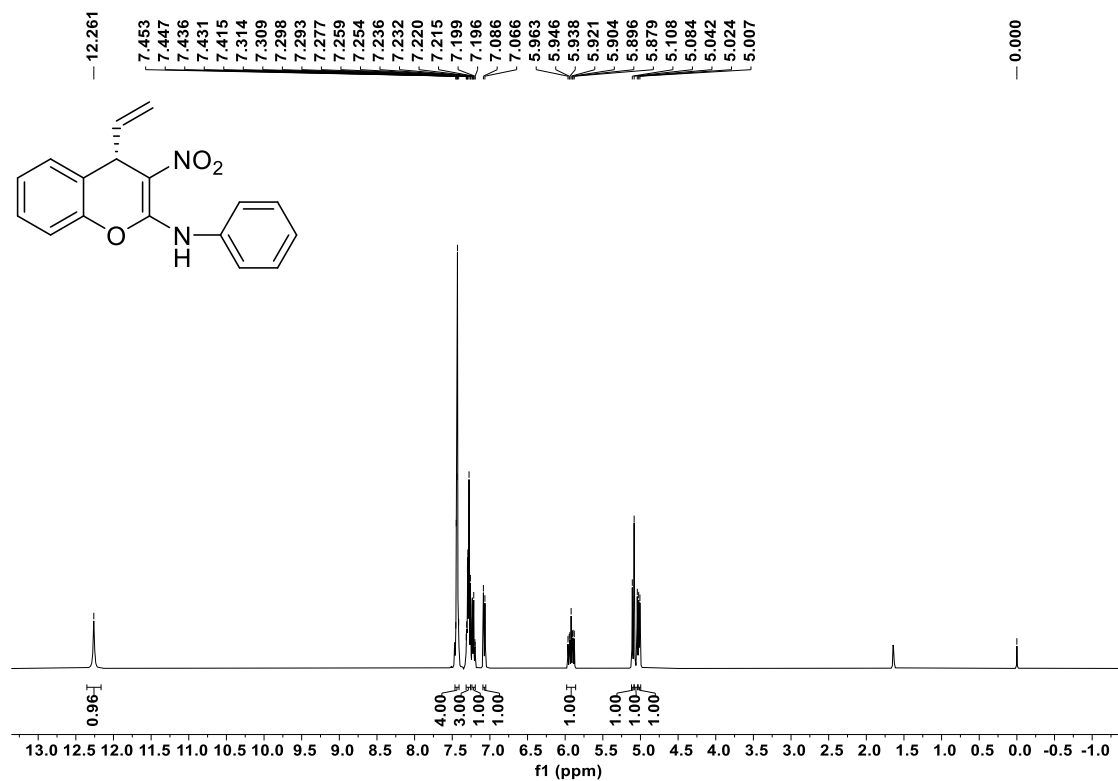
entry	compounds	<i>Rhizoctonia solani</i>			
		y=ax+b	EC <sub>50</sub> (mg/L)	R <sup>2</sup>	95%CI (mg/L)
1	<b>rac-15</b>	y=1.53x-2.58	47.03	0.97	38.99-58.81
2	<b>rac-16</b>	y=2.32x-3.95	49.15	0.97	43.15-56.78
3	<b>rac-17</b>	y=1.43x-1.96	23.88	0.98	19.64-28.97
4	<b>rac-18</b>	y=1.63x-2.46	31.77	0.89	16.98-71.86
5	<b>rac-19</b>	y=1.62x-2.25	24.21	0.98	20.30-28.80
6	<b>rac-22</b>	y=1.39x-2.13	35.37	0.91	20.03-83.38
7	<b>rac-23</b>	y=1.90x-2.94	32.93	0.84	19.69-50.28
8	<b>rac-24</b>	y=1.56x-2.15	24.08	0.99	20.14-28.75
9	<b>rac-36</b>	y=1.60x-2.21	24.17	0.99	20.30-28.72
10	<b>rac-44</b>	y=2.13x-2.79	22.35	0.95	21.59-29.65
11	<b>rac-47</b>	y=1.94x-2.65	22.01	0.99	18.65-25.89
12	<b>(S)-47</b>	y=1.20x-1.54	19.41	0.96	15.14-24.31
13	<b>(R)-47</b>	y=1.24x-1.53	17.43	0.93	8.59-28.73
14	<b>rac-61</b>	y=1.83x-2.55	25.29	0.98	21.59-29.65

## 7. References

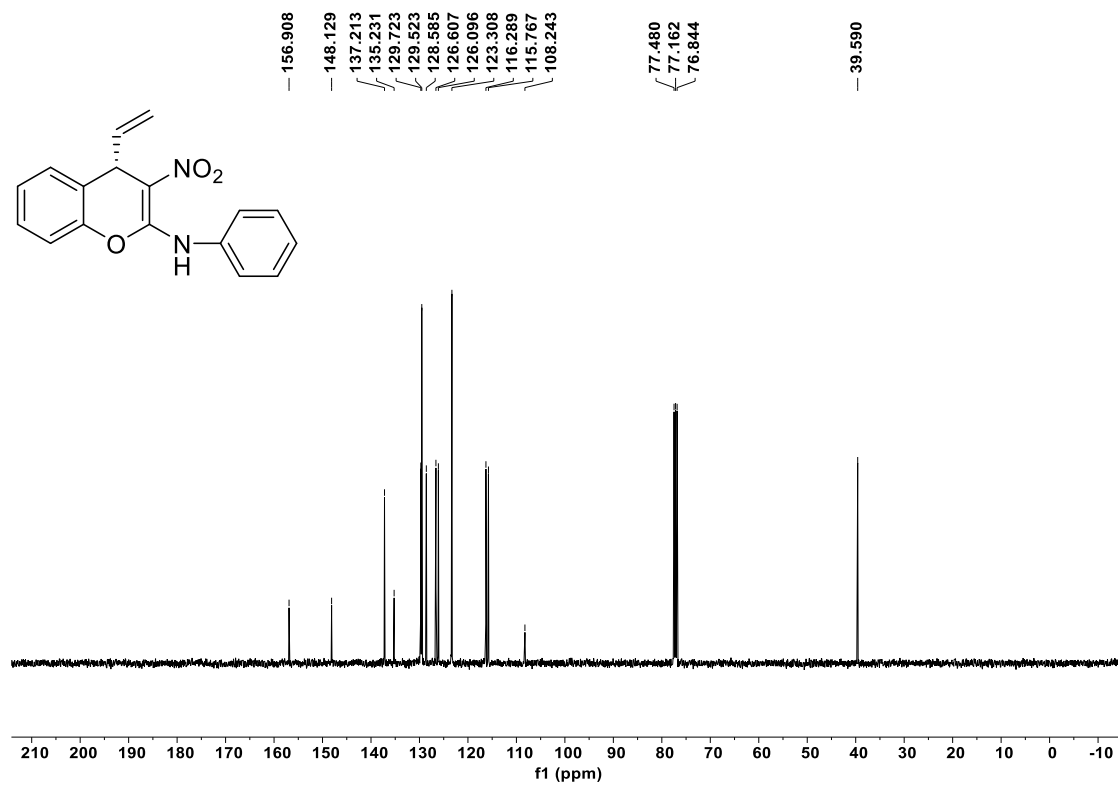
- [1] C. Defieber, M. A. Ariger, P. Moriel, E. M. Carreira, Iridium-Catalyzed Synthesis of Primary Allylic Amines from Allylic Alcohols: Sulfamic Acid as Ammonia Equivalent, *Angew. Chem. Int. Ed.* 2007, **46**, 3139-3143.
- [2] J. Zhang, W. L. Yang, H. Zheng, Y. Wang, W.-P. Deng, Regio- and Enantioselective  $\gamma$ -Allylic Alkylation of In Situ-Generated Free Dienolates via Scandium/Iridium Dual Catalysis, *Angew. Chem. Int. Ed.* 2022, **61**, e202117079.
- [3] C. Venkatesh, B. Singh, P. K. Mahata, H. Ila, H. Junjappa, Heteroannulation of Nitroketene *N,S*-Arylaminoacetals with  $\text{POCl}_3$ : A Novel Highly Regioselective Synthesis of Unsymmetrical 2,3-Substituted Quinoxalines, *Org. Lett.* 2005, **7**, 2169-2172.

## 8. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR spectra

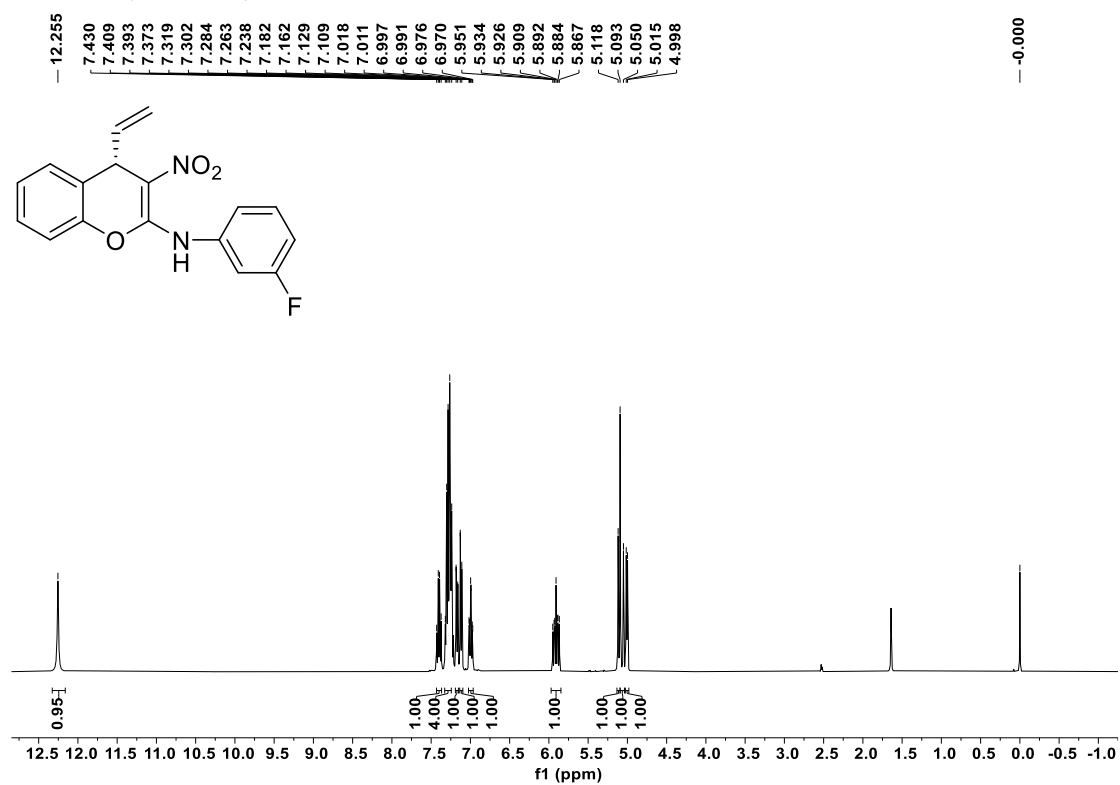
$^1\text{H}$  NMR (400 MHz) of **3** in  $\text{CDCl}_3$



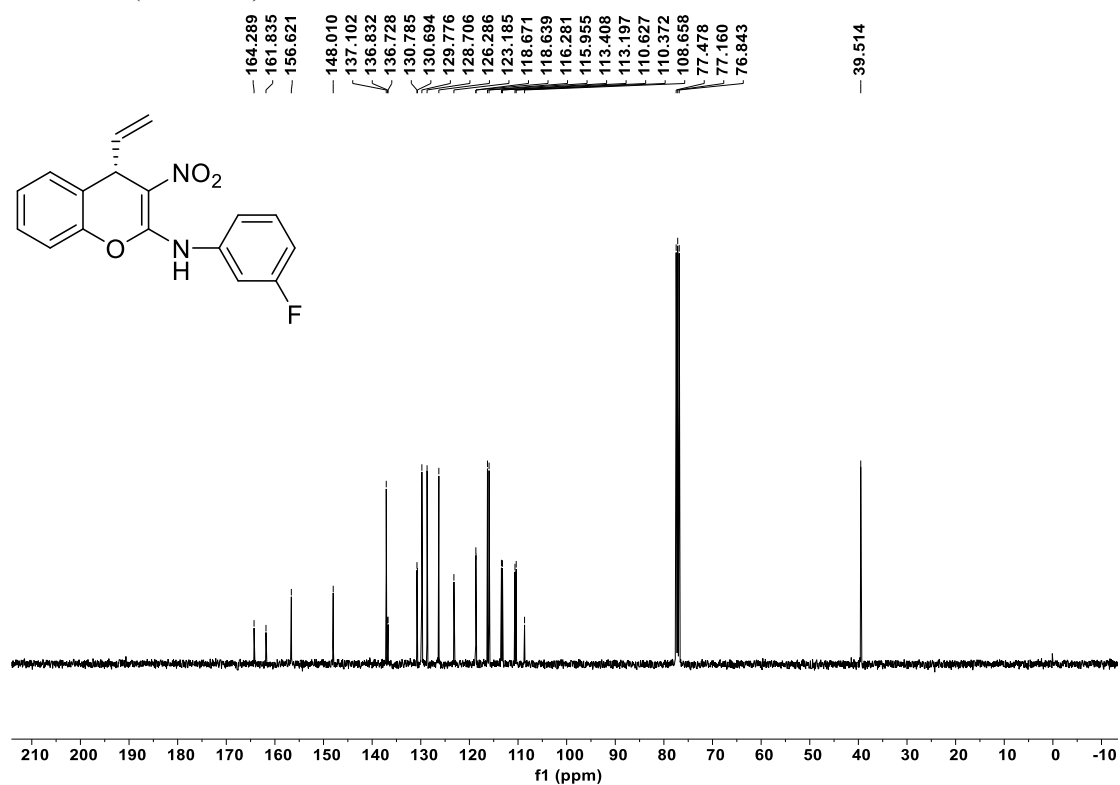
$^{13}\text{C}$  NMR (100 MHz) of **3** in  $\text{CDCl}_3$



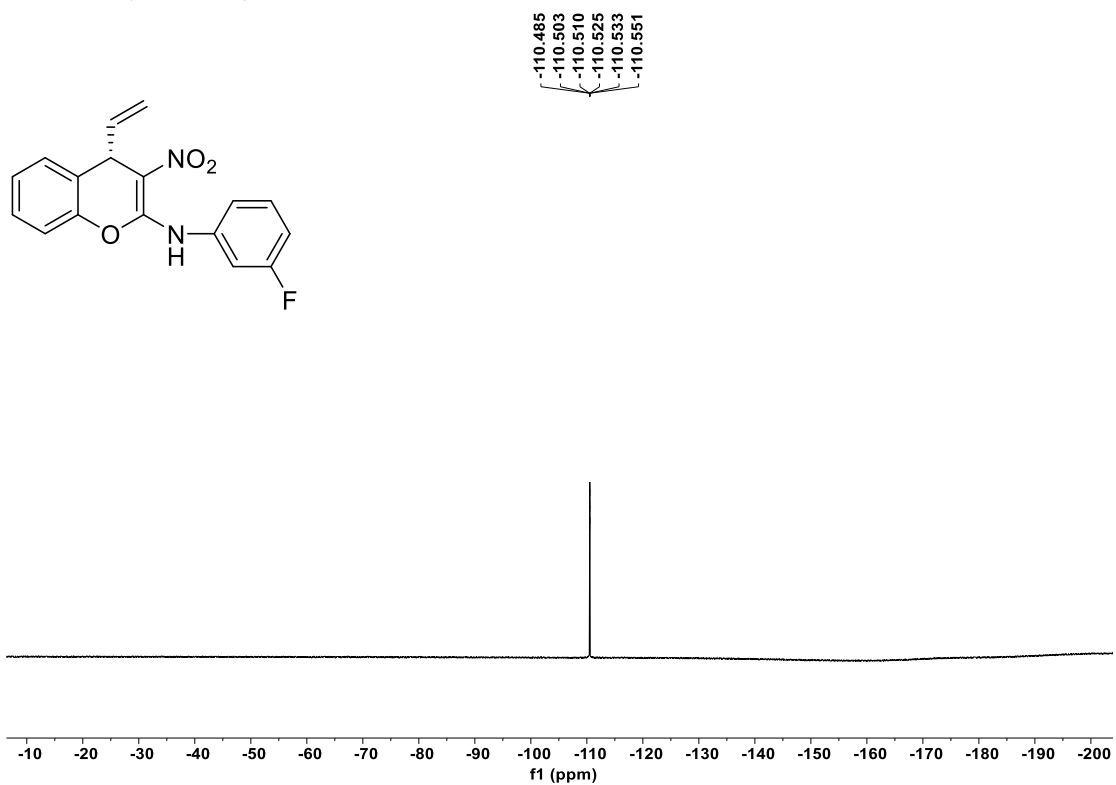
<sup>1</sup>H NMR (400 MHz) of **4** in CDCl<sub>3</sub>



<sup>13</sup>C NMR (100 MHz) of **4** in CDCl<sub>3</sub>



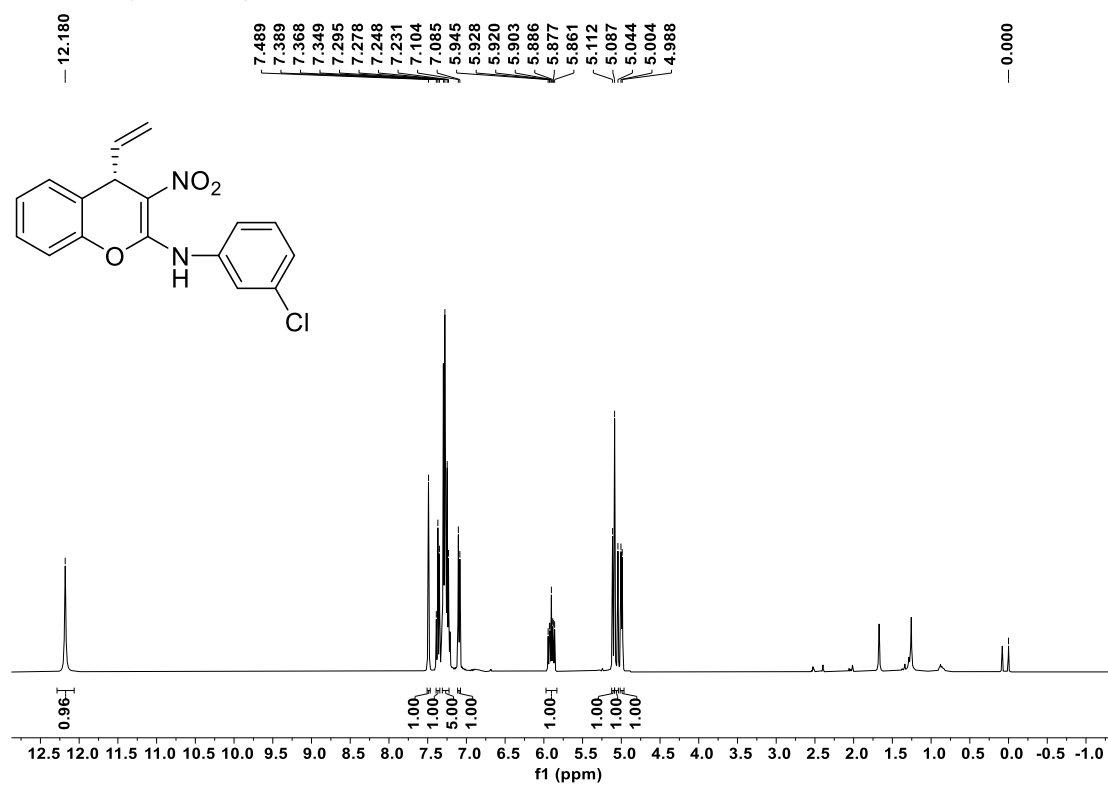
$^{19}\text{F}$  NMR (376 MHz) of **4** in  $\text{CDCl}_3$



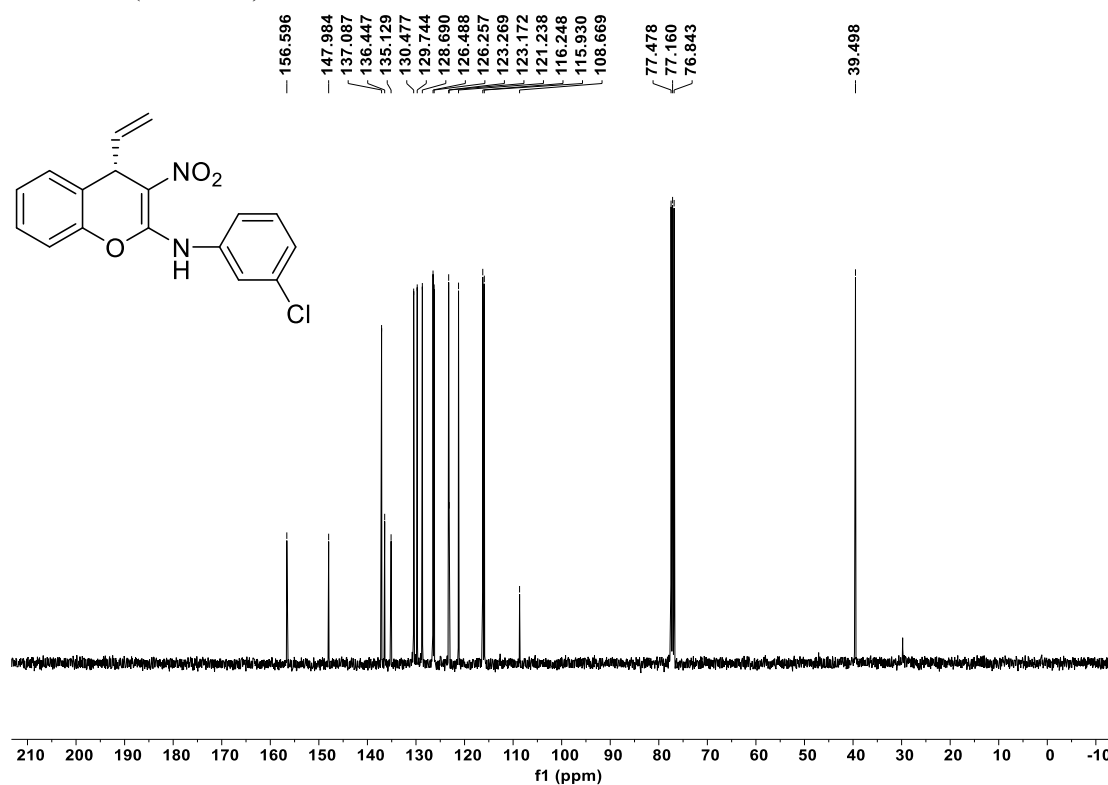
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.48 – -110.55(m).



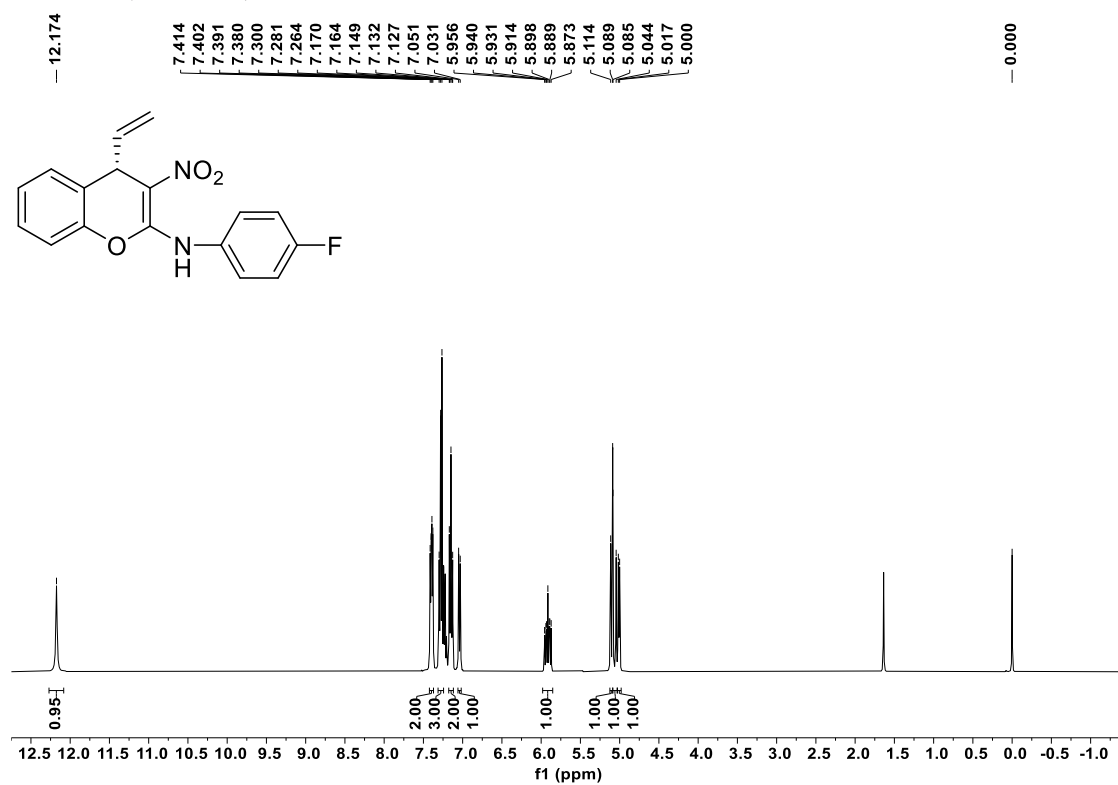
<sup>1</sup>H NMR (400 MHz) of **5** in CDCl<sub>3</sub>



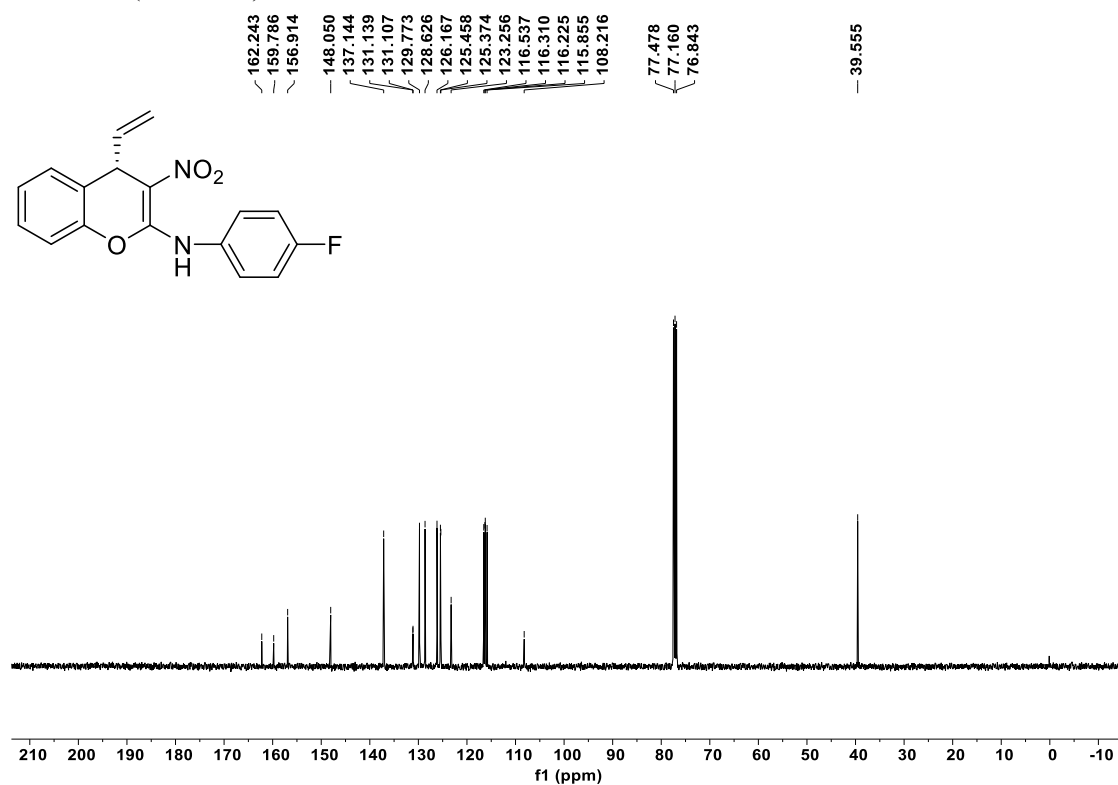
<sup>13</sup>C NMR (100 MHz) of **5** in CDCl<sub>3</sub>



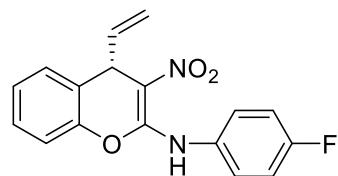
<sup>1</sup>H NMR (400 MHz) of **6** in CDCl<sub>3</sub>



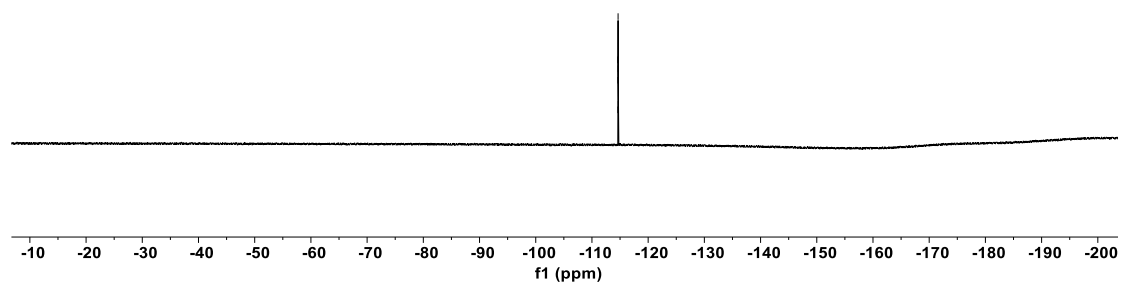
<sup>13</sup>C NMR (100 MHz) of **6** in CDCl<sub>3</sub>



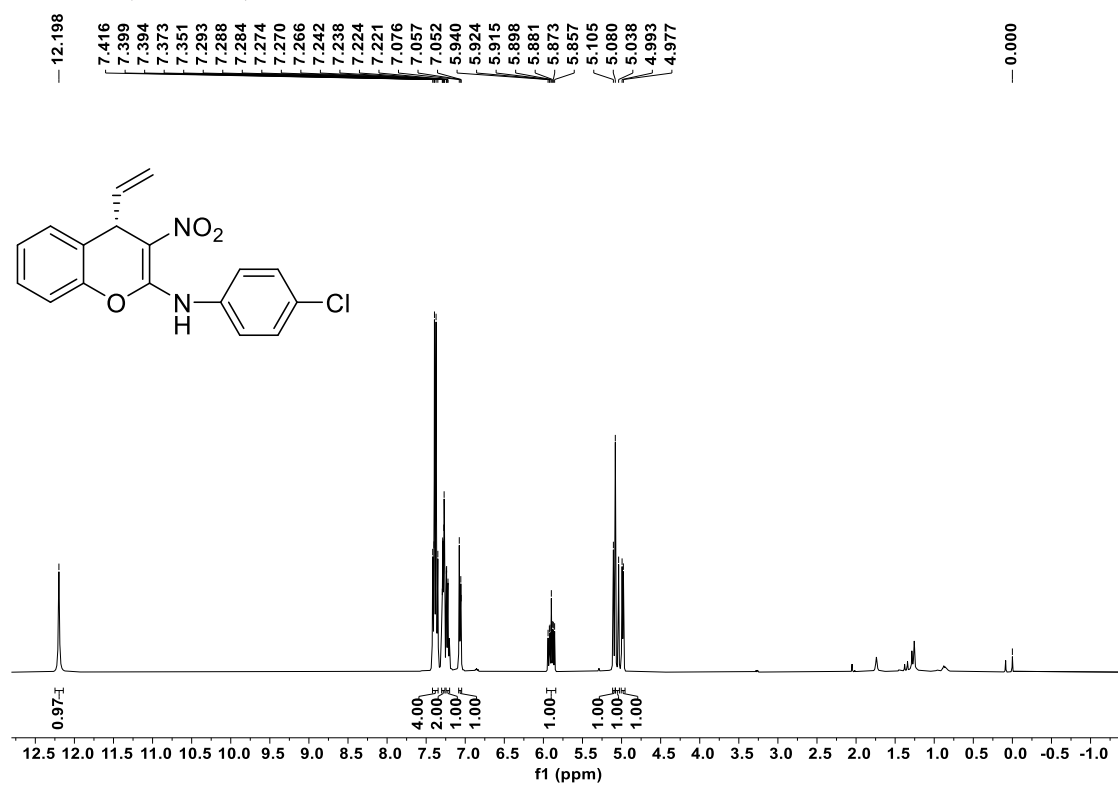
$^{19}\text{F}$  NMR (376 MHz) of **6** in  $\text{CDCl}_3$



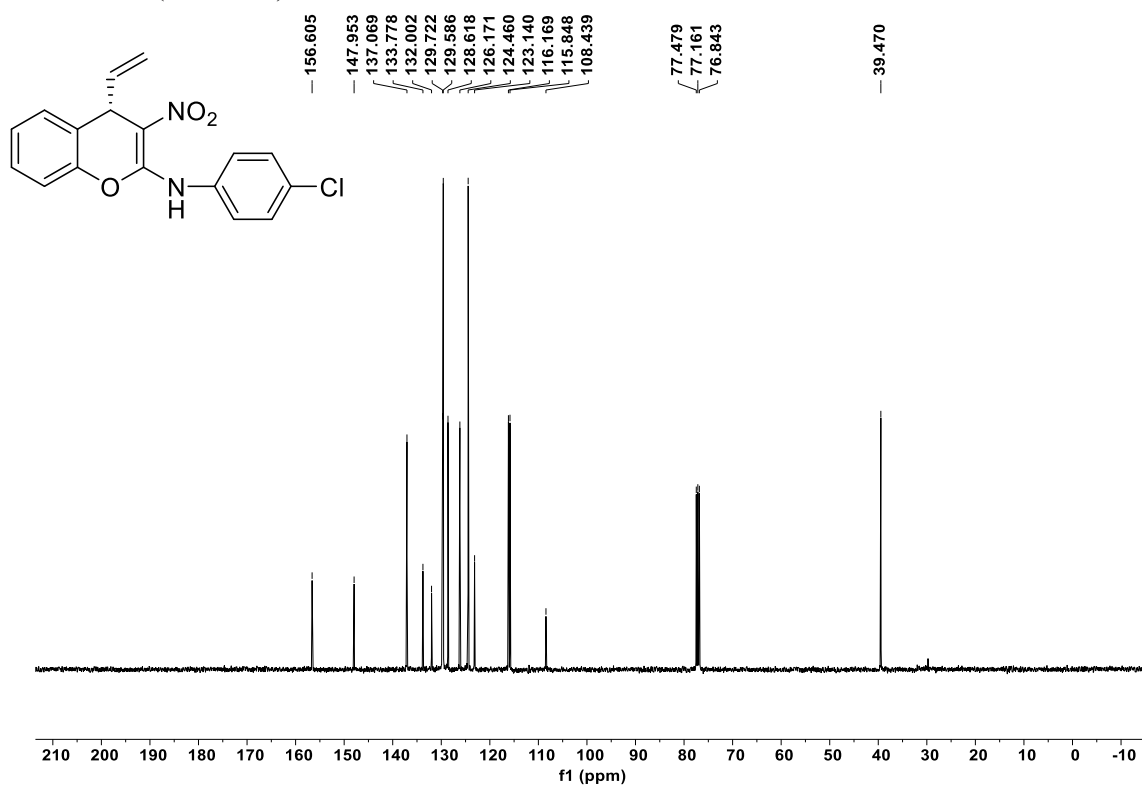
-114.616  
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-114.662  
-114.672  
-114.684



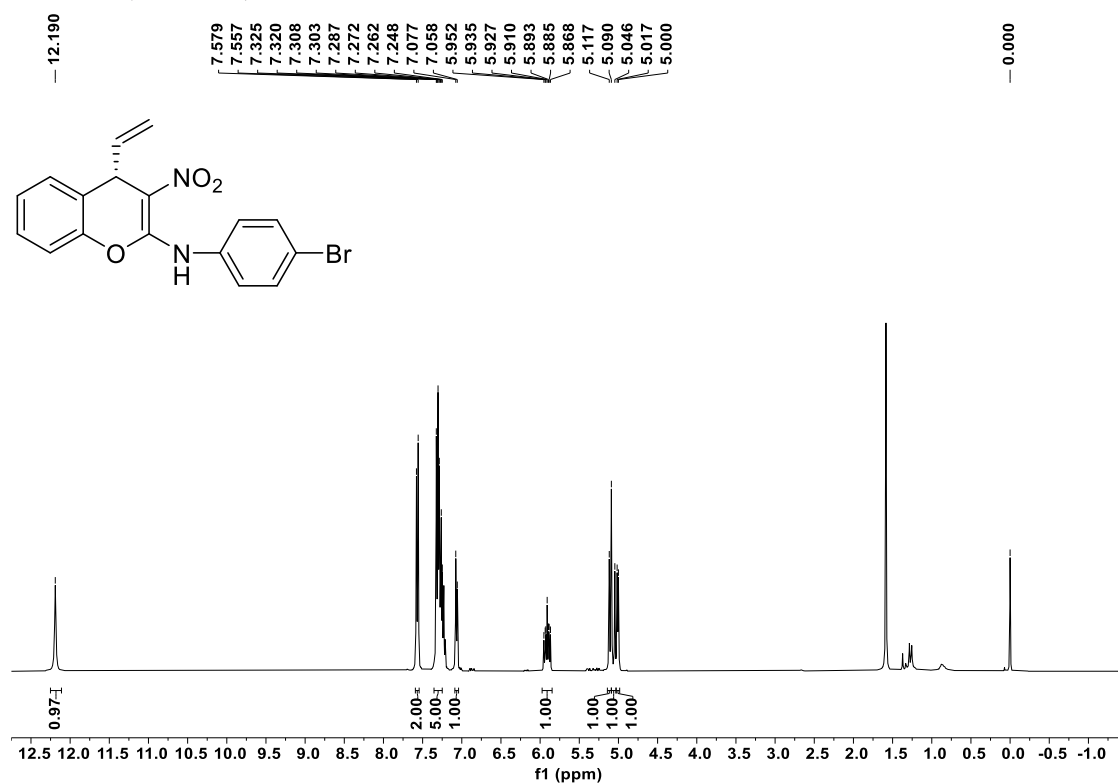
$^1\text{H}$  NMR (400 MHz) of **7** in  $\text{CDCl}_3$



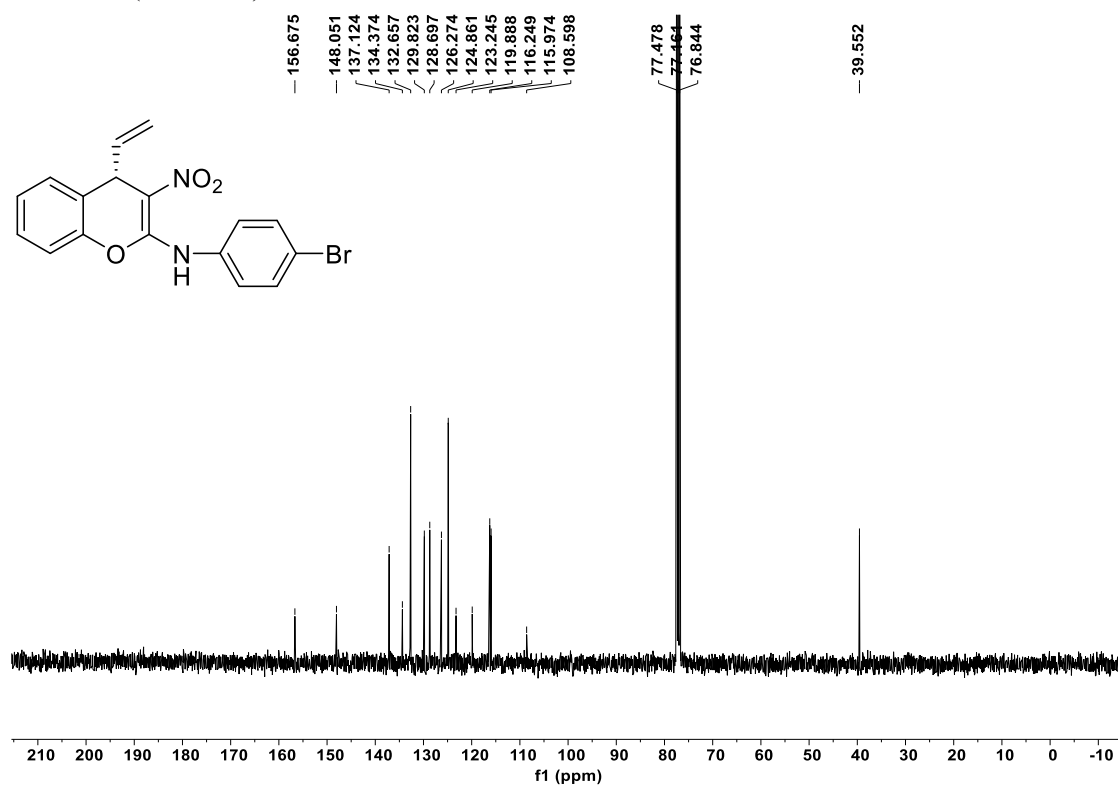
$^{13}\text{C}$  NMR (100 MHz) of **7** in  $\text{CDCl}_3$



$^1\text{H}$  NMR (400 MHz) of **8** in  $\text{CDCl}_3$

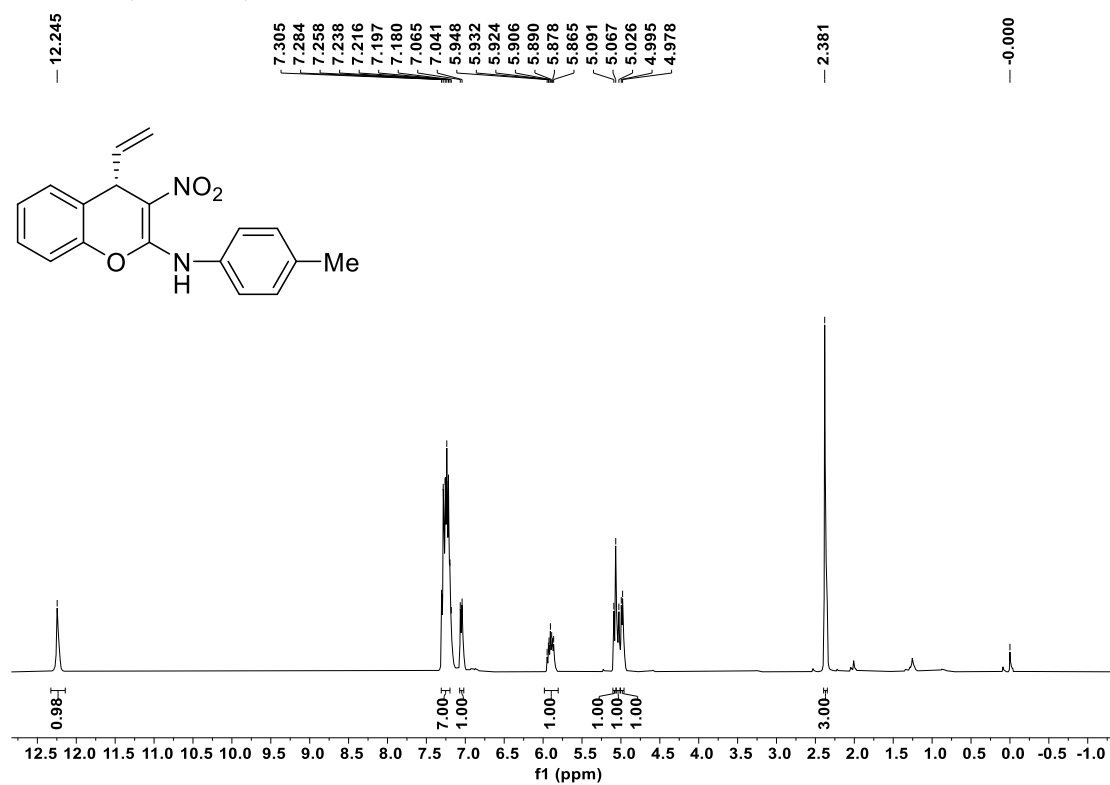


$^{13}\text{C}$  NMR (100 MHz) of **8** in  $\text{CDCl}_3$

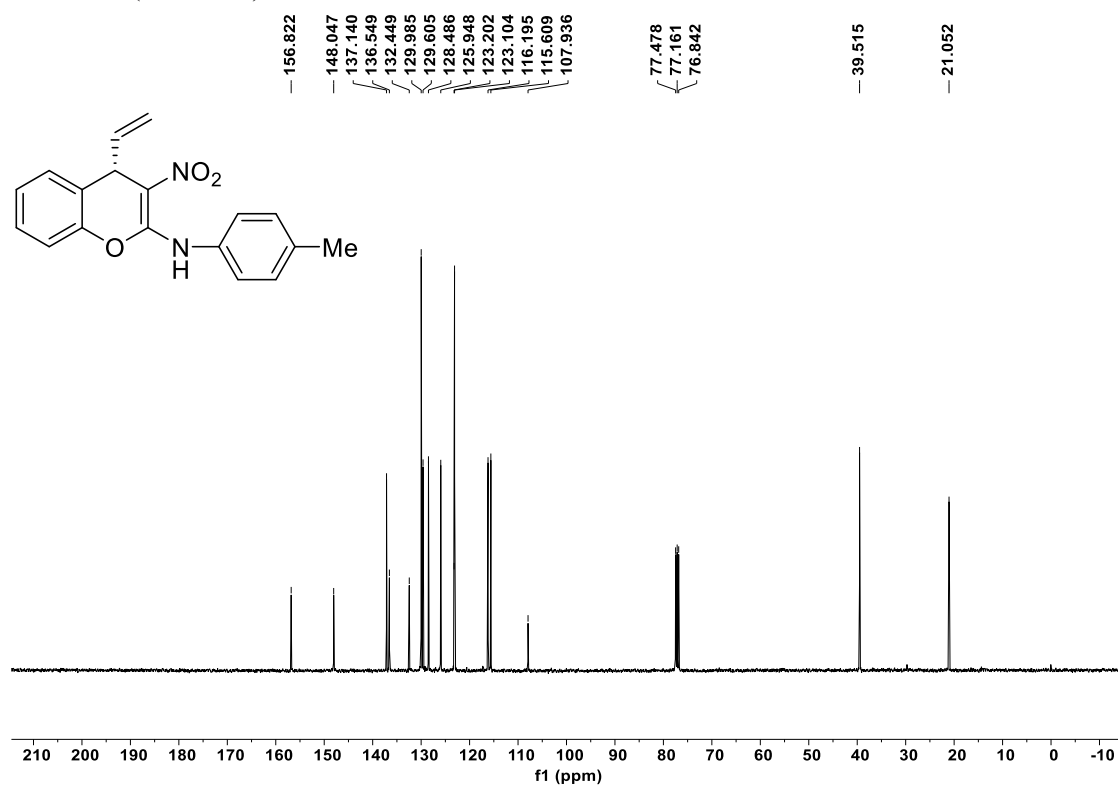


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 148.1, 137.1, 134.4, 132.7(2C), 129.8, 128.7, 126.3, 124.9(2C), 123.2, 119.9, 116.3, 115.9, 108.6, 39.6.

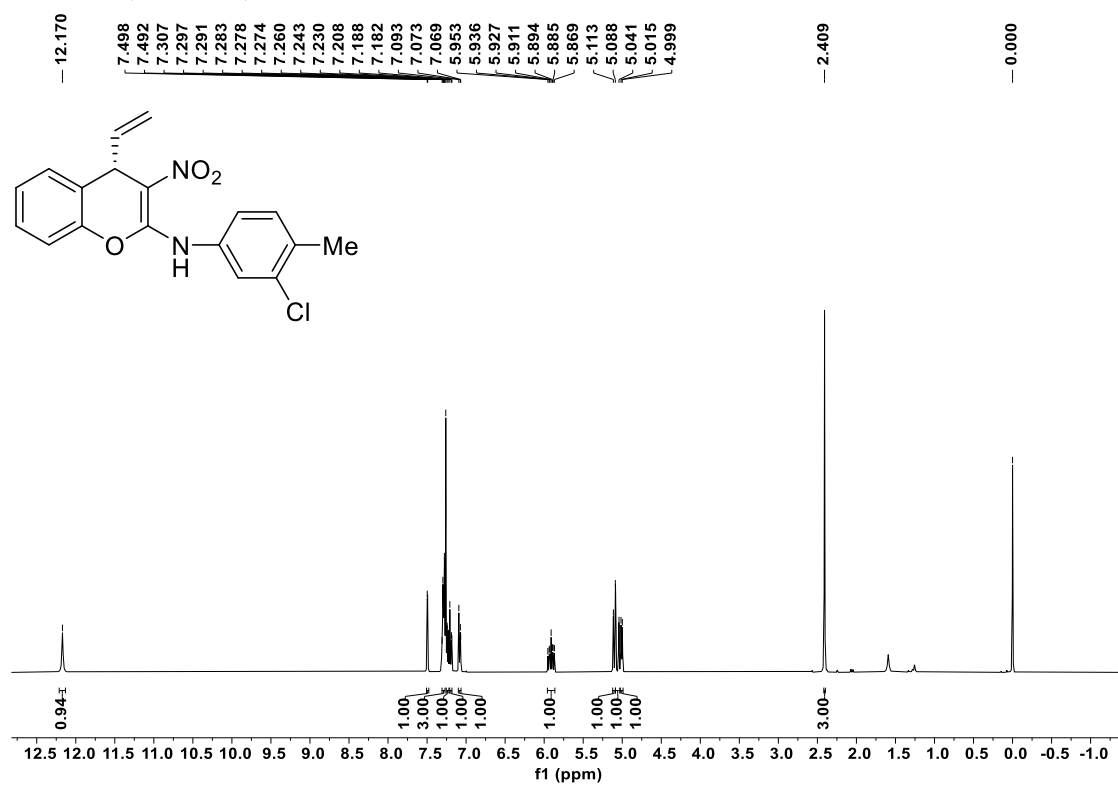
<sup>1</sup>H NMR (400 MHz) of **9** in CDCl<sub>3</sub>



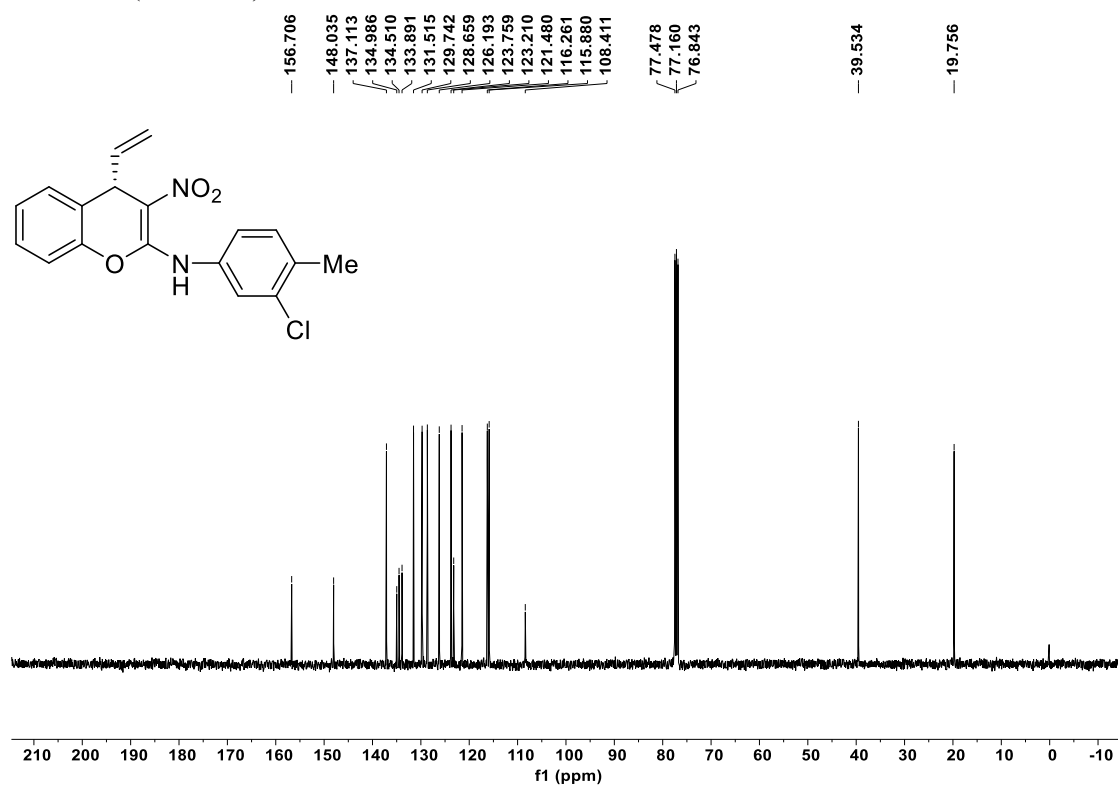
<sup>13</sup>C NMR (100 MHz) of **9** in CDCl<sub>3</sub>



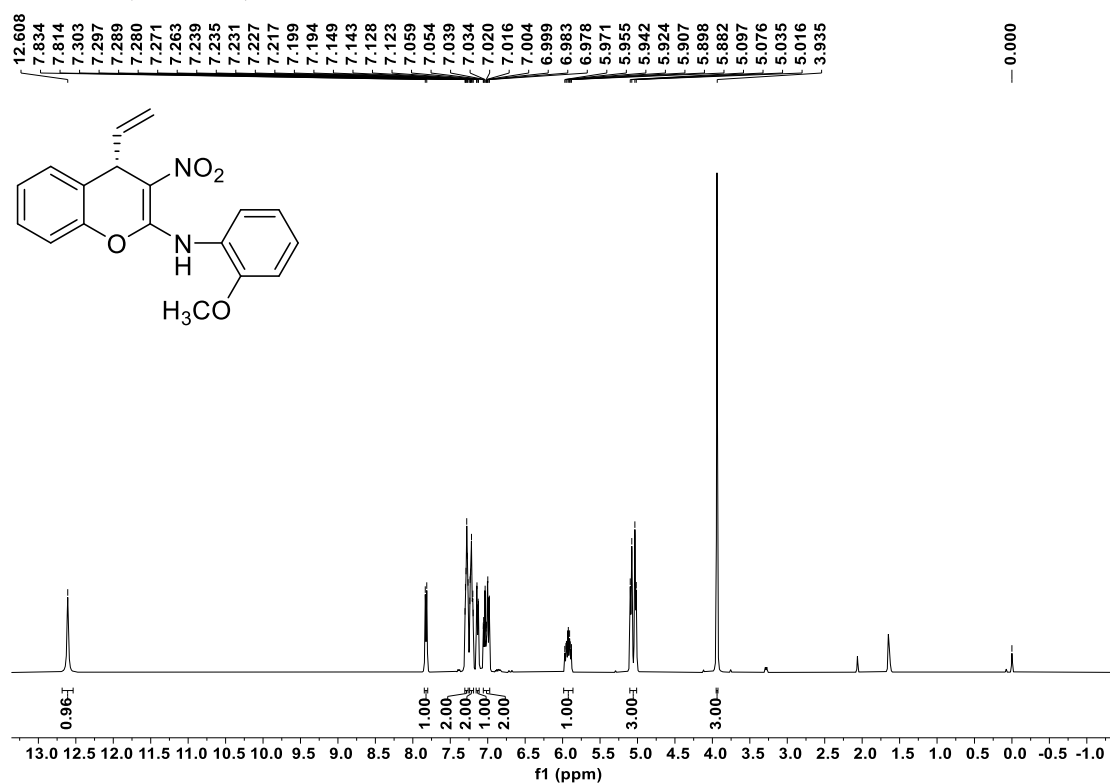
<sup>1</sup>H NMR (400 MHz) of **10** in CDCl<sub>3</sub>



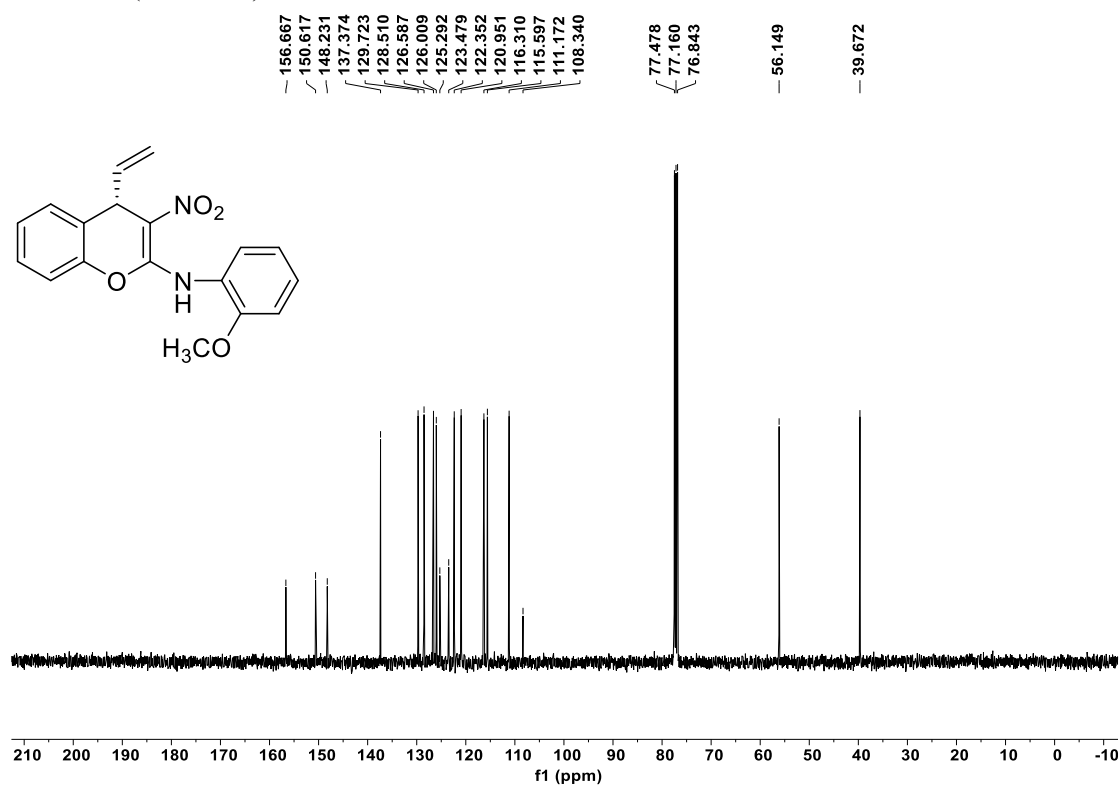
<sup>13</sup>C NMR (100 MHz) of **10** in CDCl<sub>3</sub>



<sup>1</sup>H NMR (400 MHz) of **11** in CDCl<sub>3</sub>

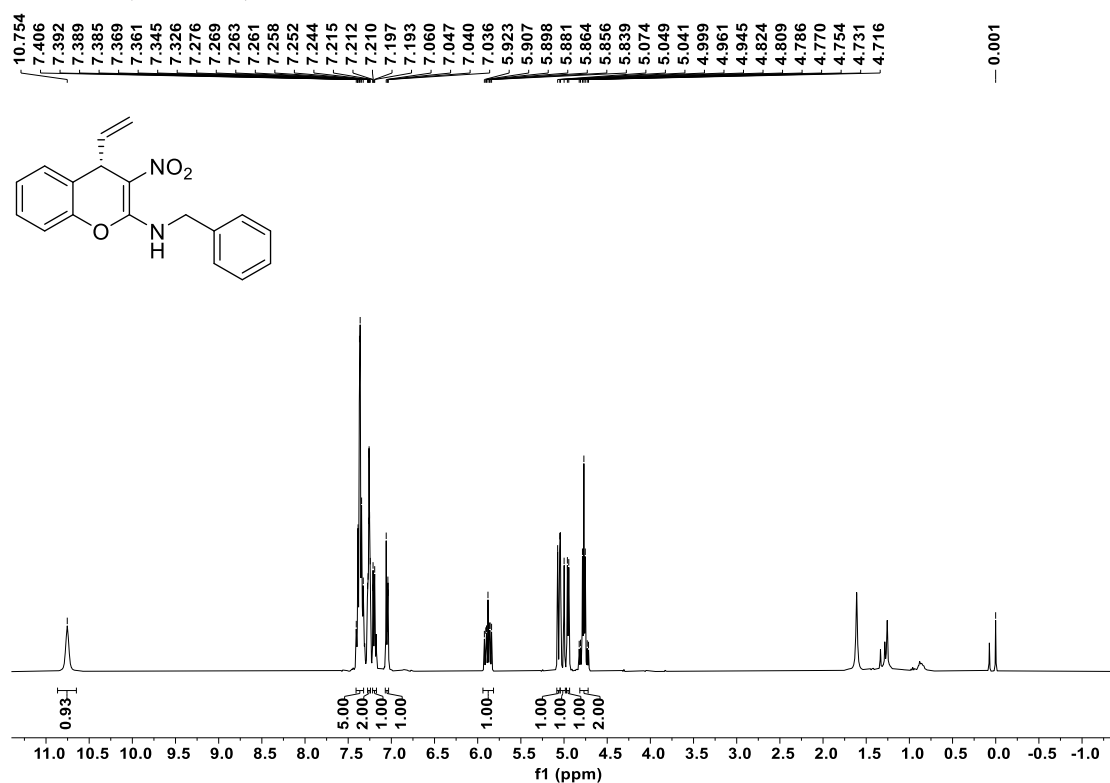


<sup>13</sup>C NMR (100 MHz) of **11** in CDCl<sub>3</sub>

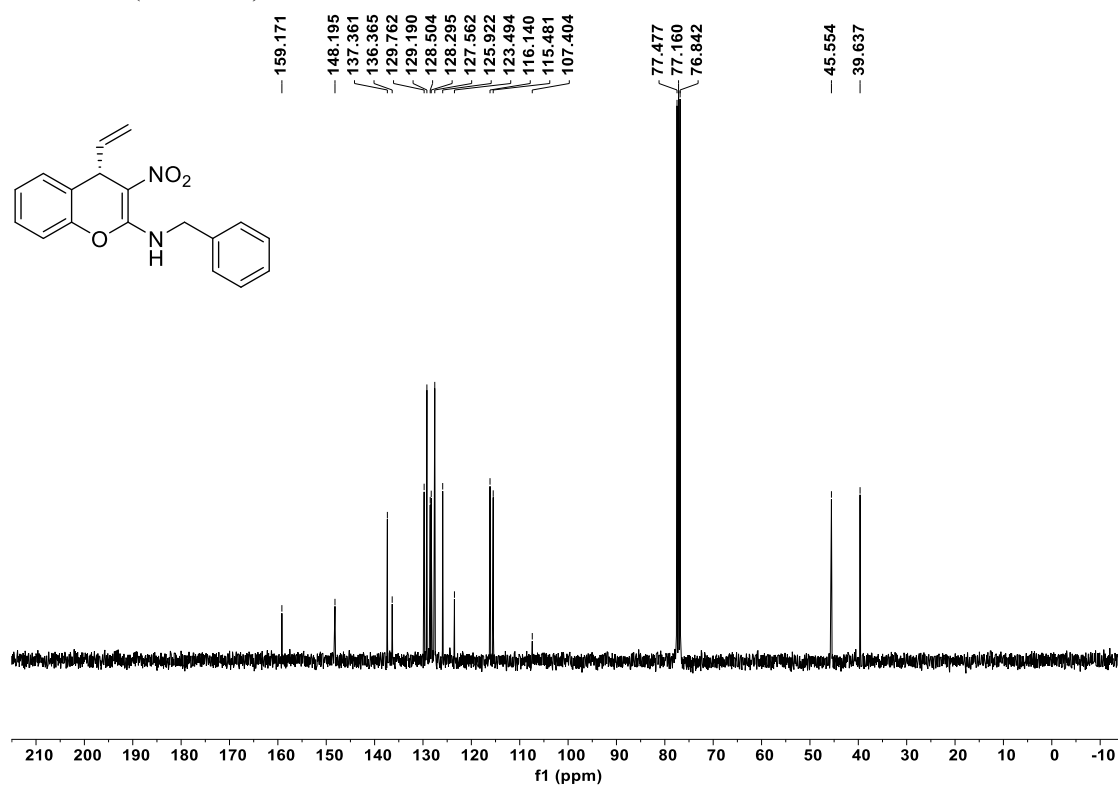




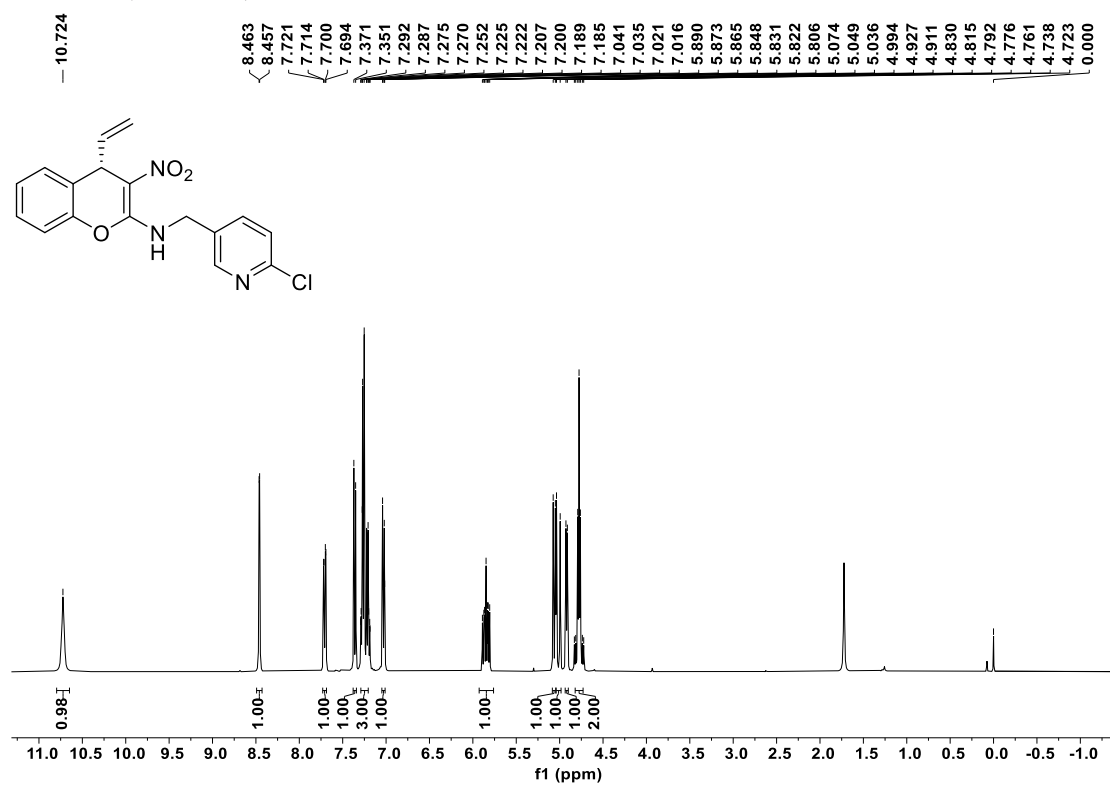
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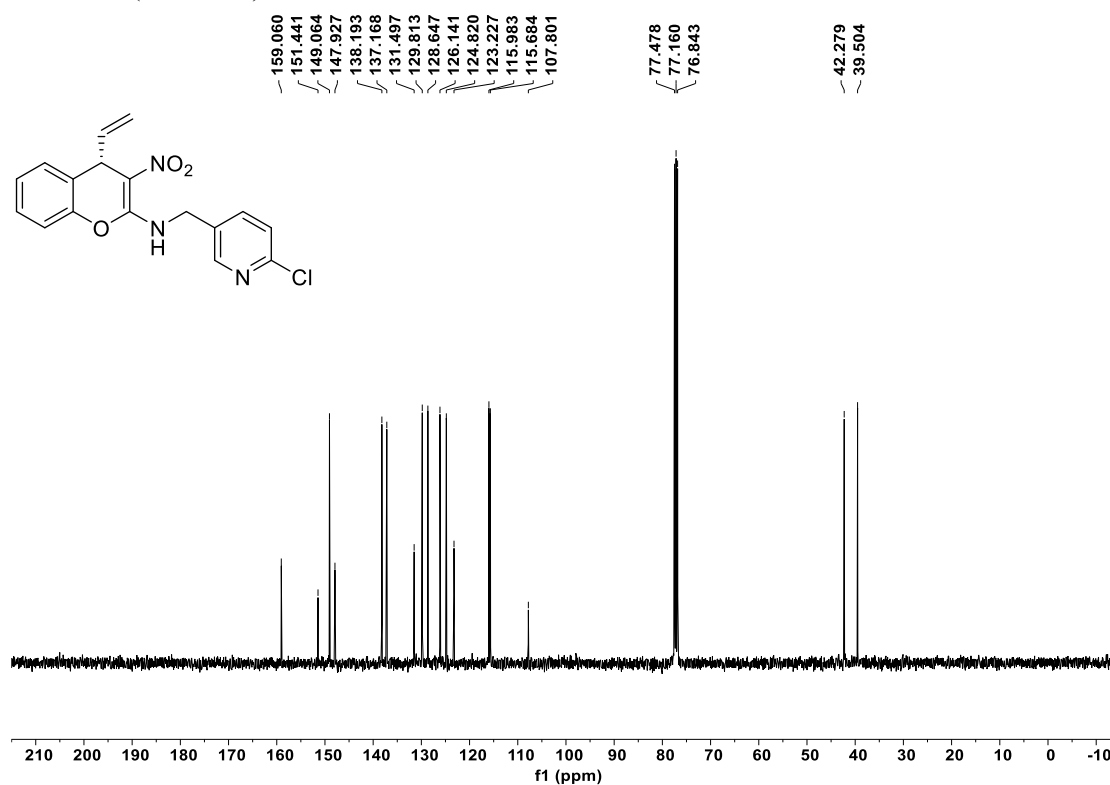
<sup>13</sup>C NMR (100 MHz) of **12** in CDCl<sub>3</sub>



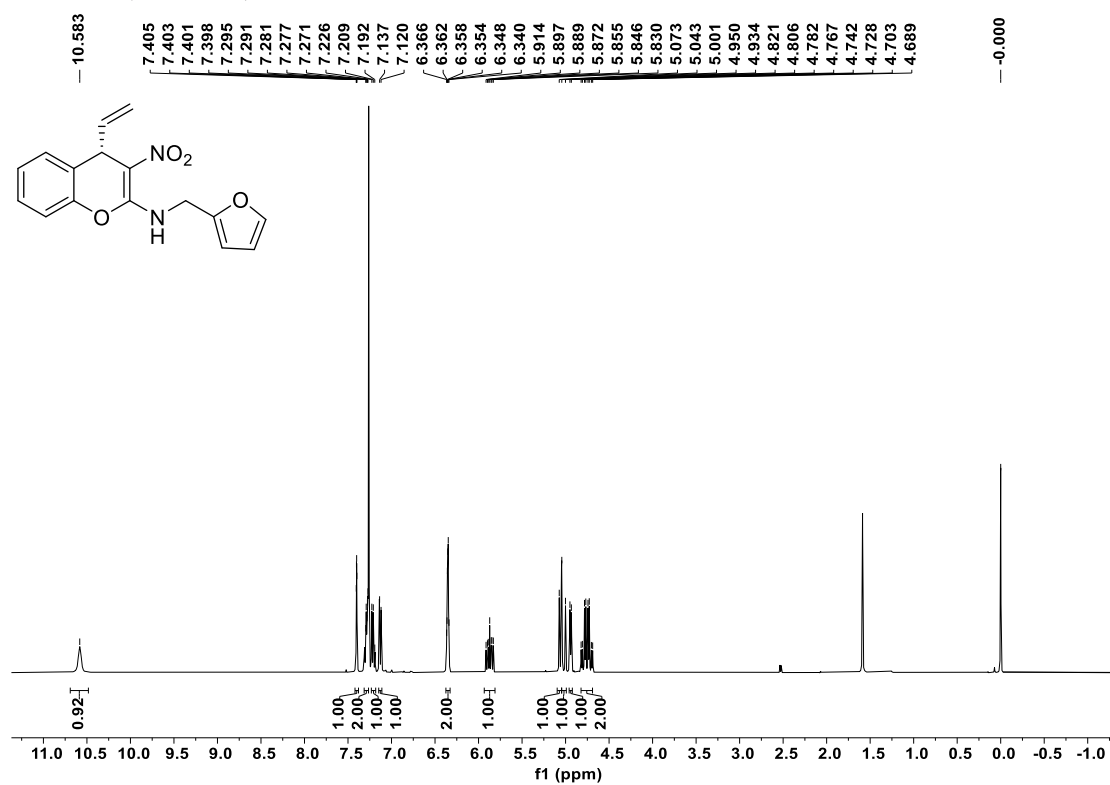
<sup>1</sup>H NMR (400 MHz) of **13** in CDCl<sub>3</sub>



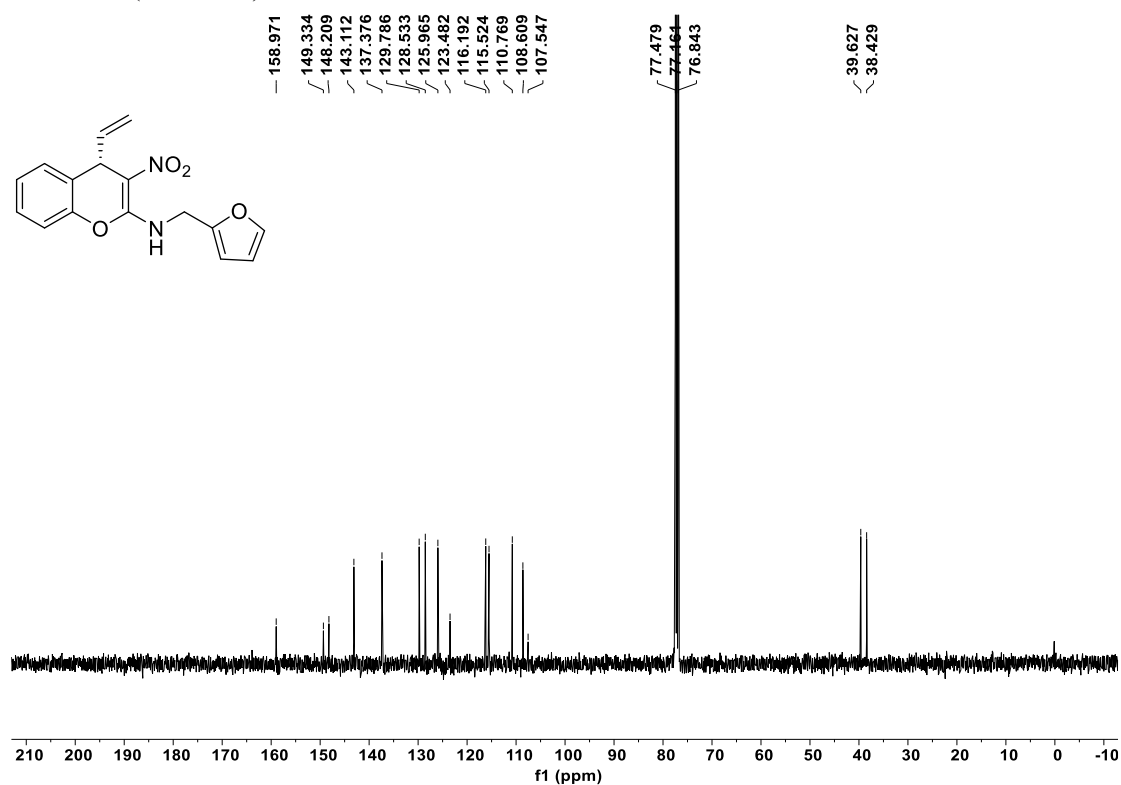
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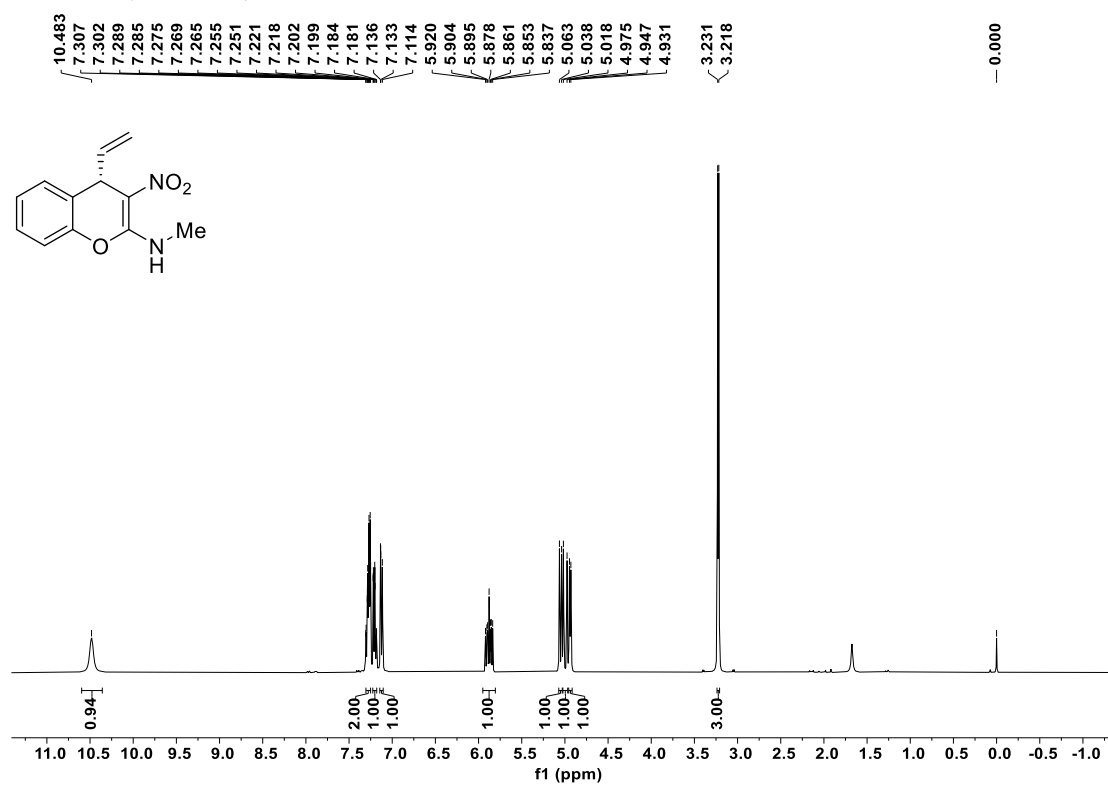
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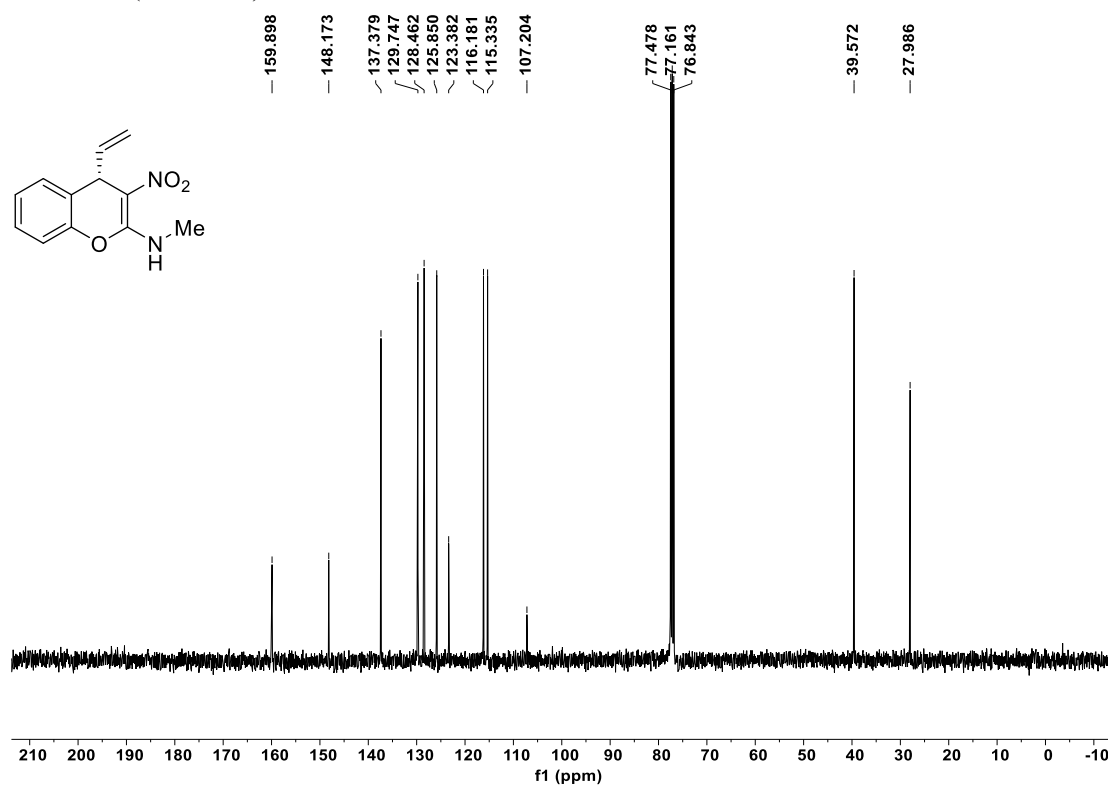
<sup>13</sup>C NMR (100 MHz) of **14** in CDCl<sub>3</sub>



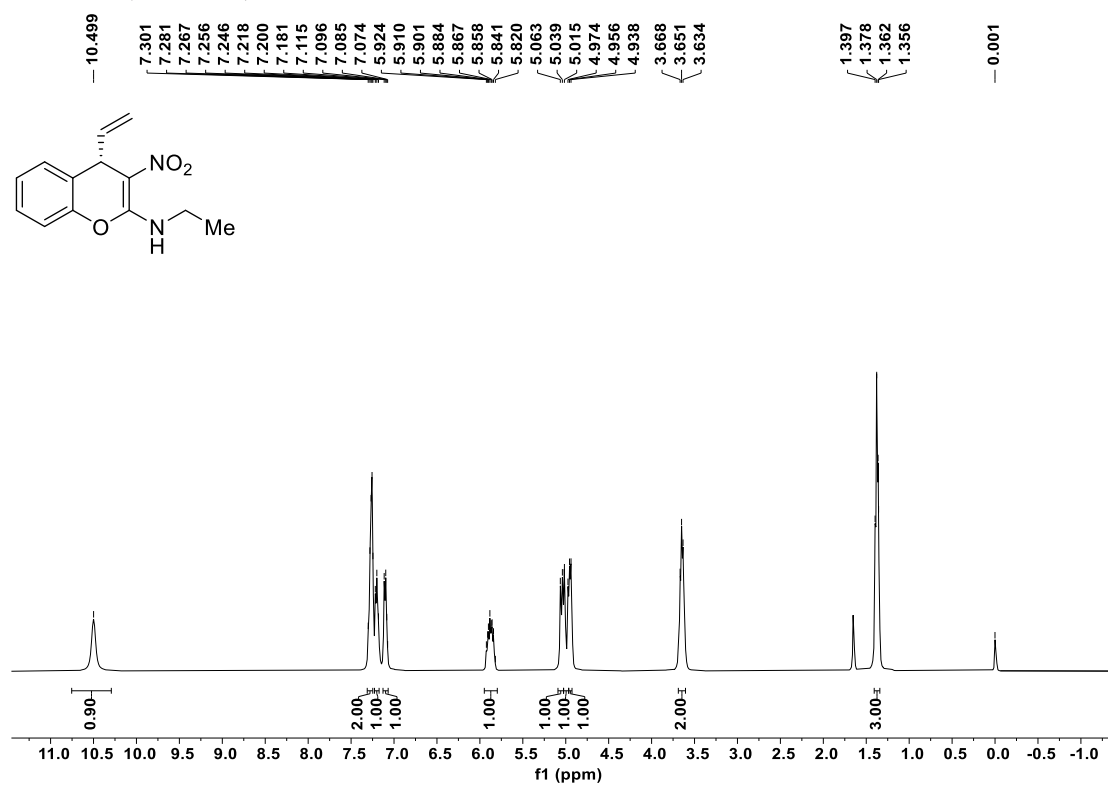
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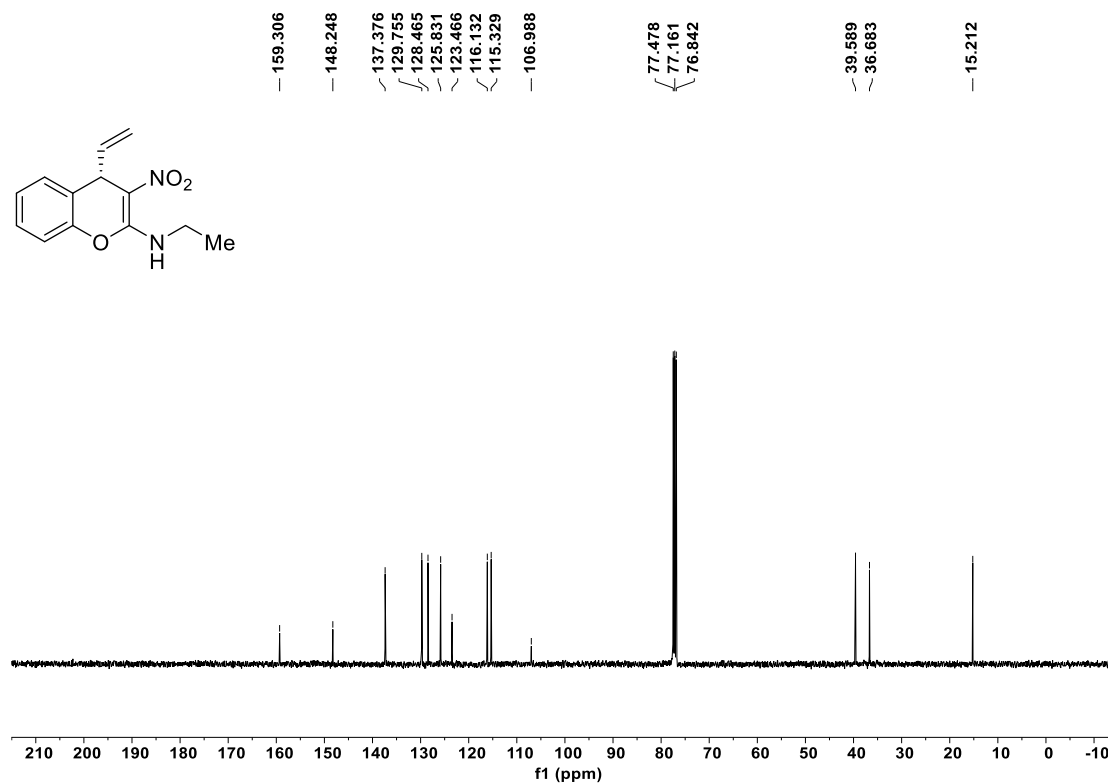
<sup>13</sup>C NMR (100 MHz) of **15** in CDCl<sub>3</sub>



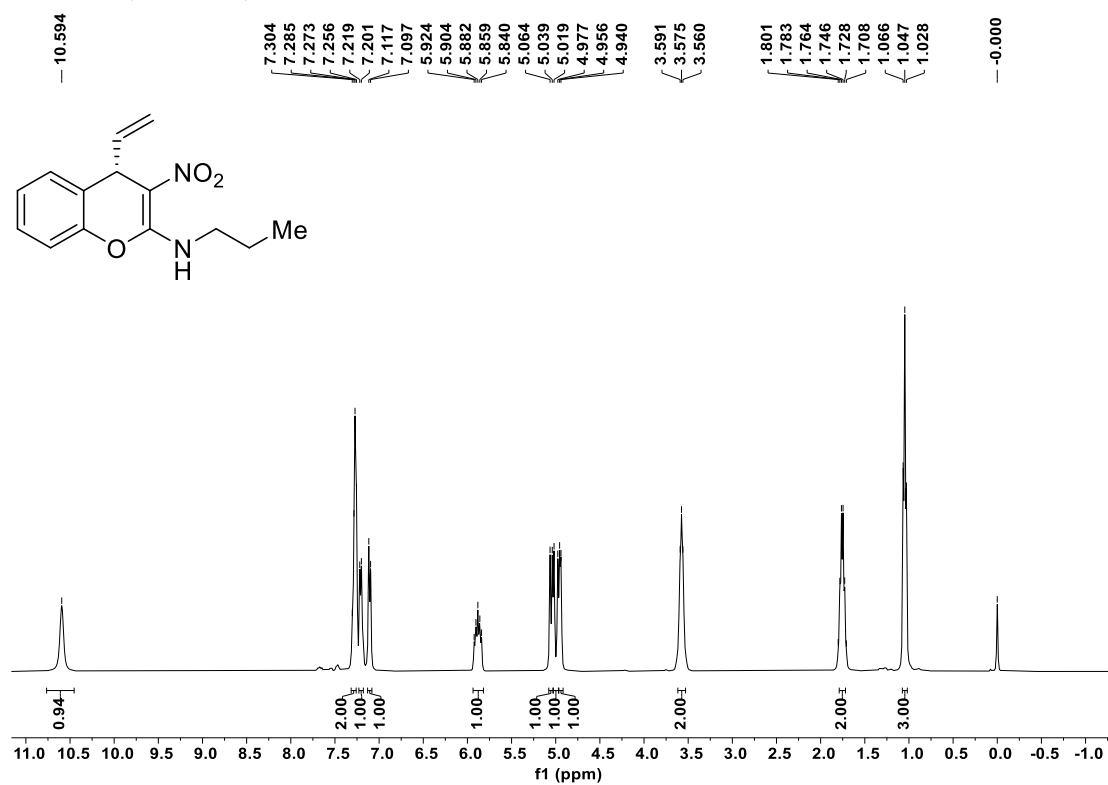
<sup>1</sup>H NMR (400 MHz) of **16** in CDCl<sub>3</sub>



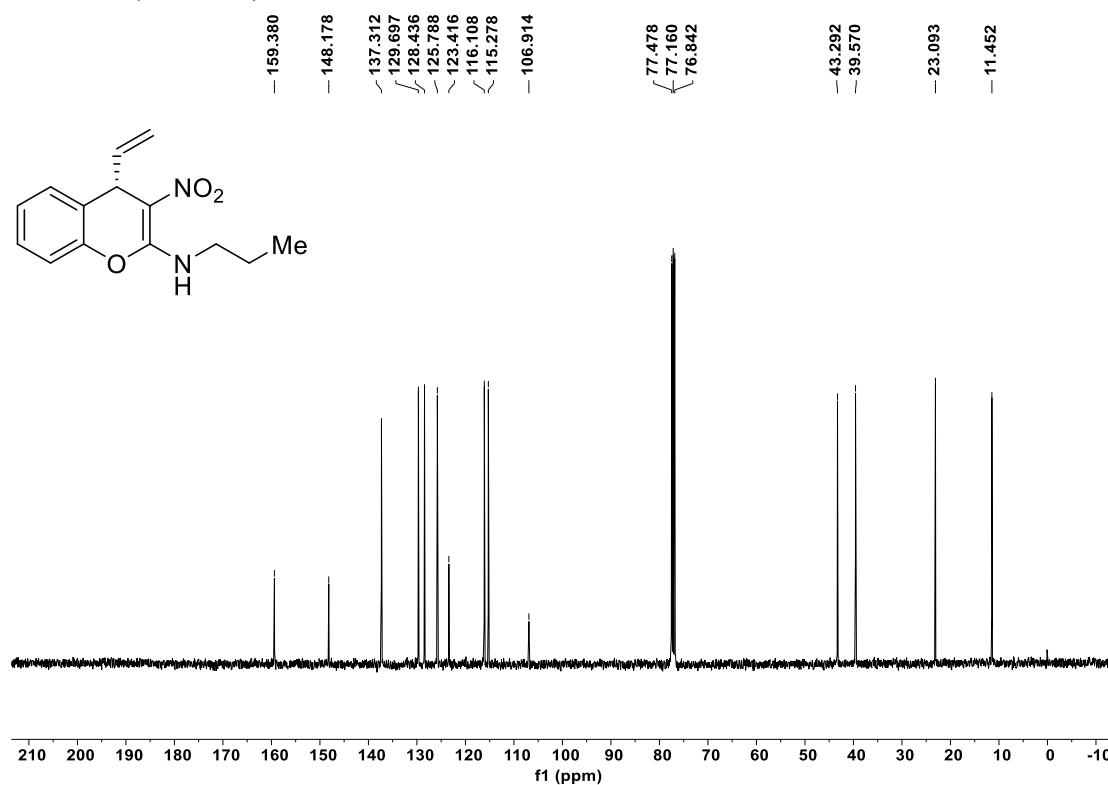
<sup>13</sup>C NMR (100 MHz) of **16** in CDCl<sub>3</sub>



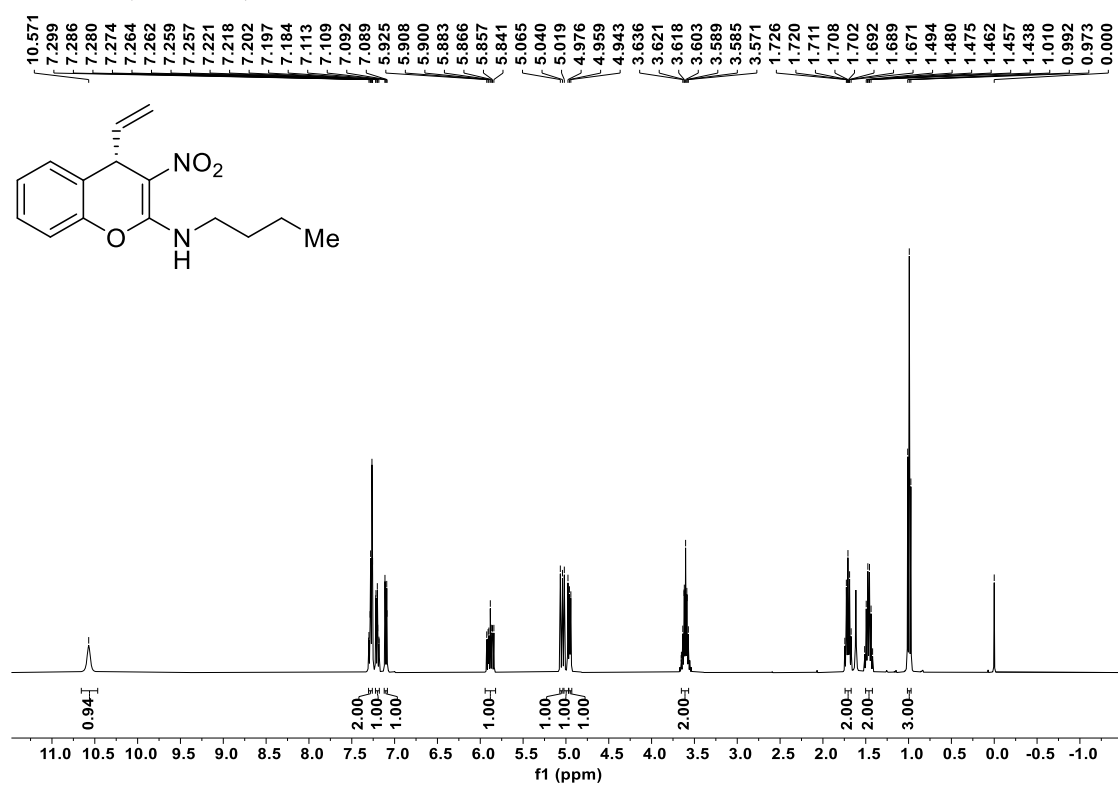
<sup>1</sup>H NMR (400 MHz) of **17** in CDCl<sub>3</sub>



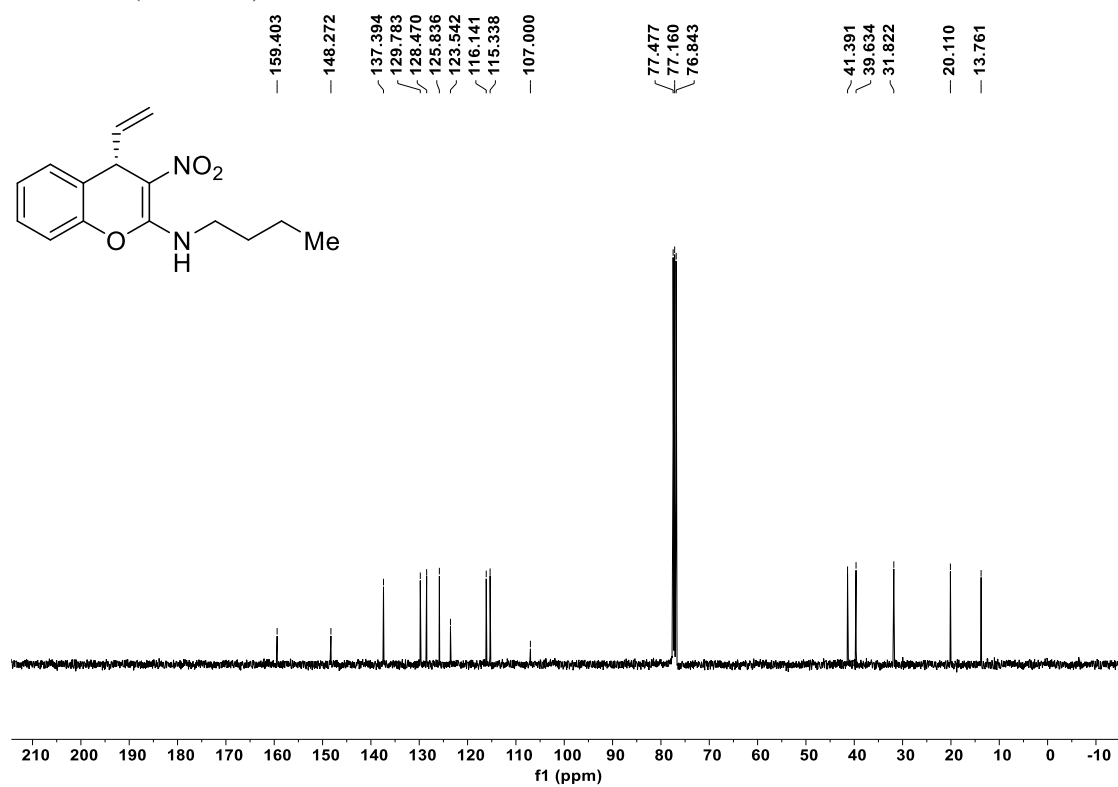
<sup>13</sup>C NMR (100 MHz) of **17** in CDCl<sub>3</sub>



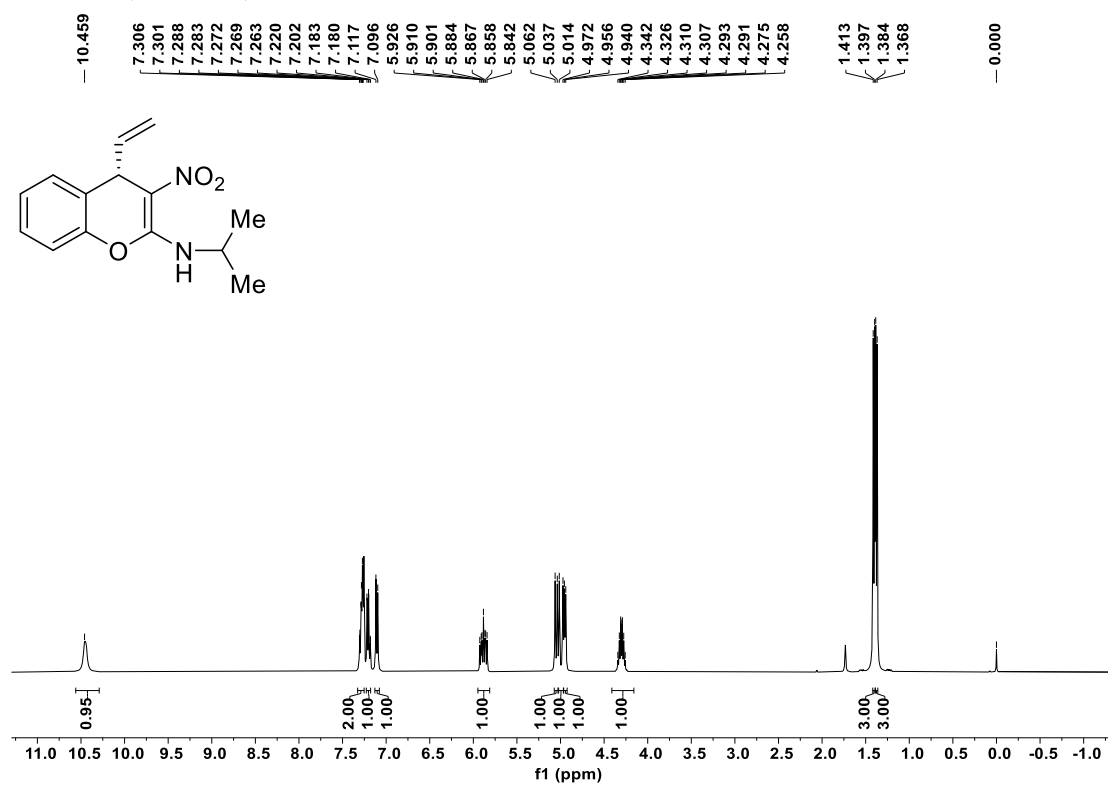
<sup>1</sup>H NMR (400 MHz) of **18** in CDCl<sub>3</sub>



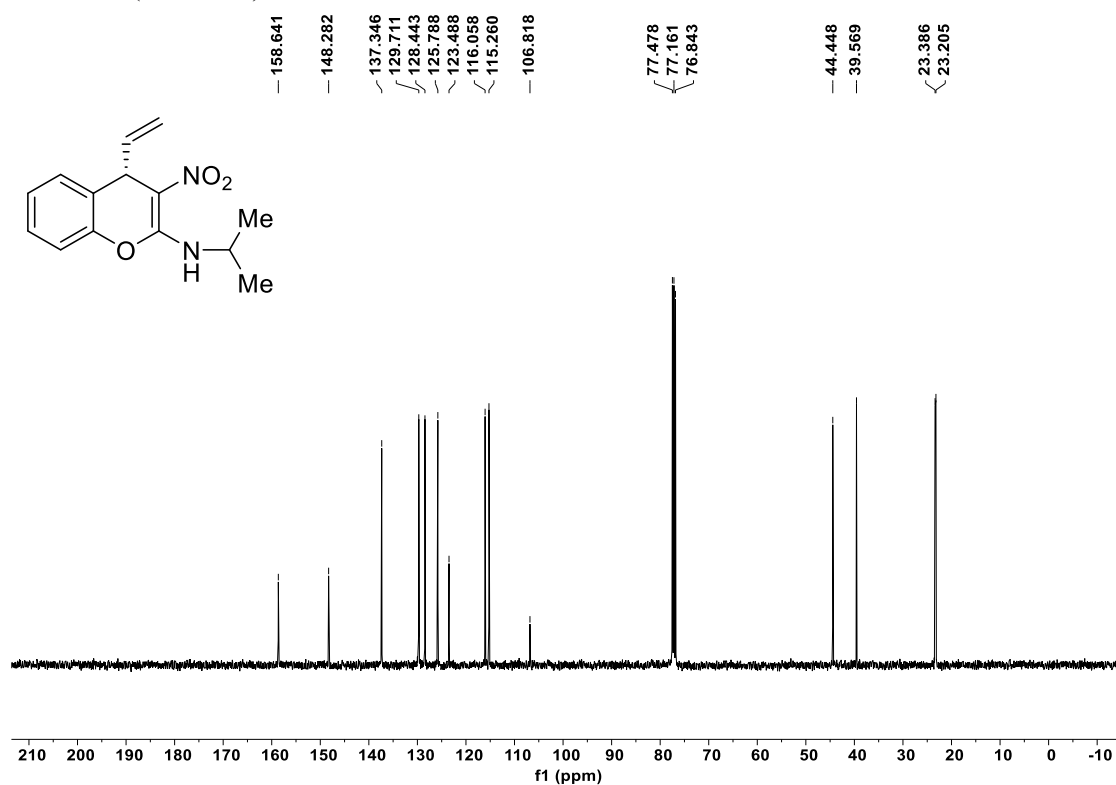
<sup>13</sup>C NMR (100 MHz) of **18** in CDCl<sub>3</sub>



<sup>1</sup>H NMR (400 MHz) of **19** in CDCl<sub>3</sub>

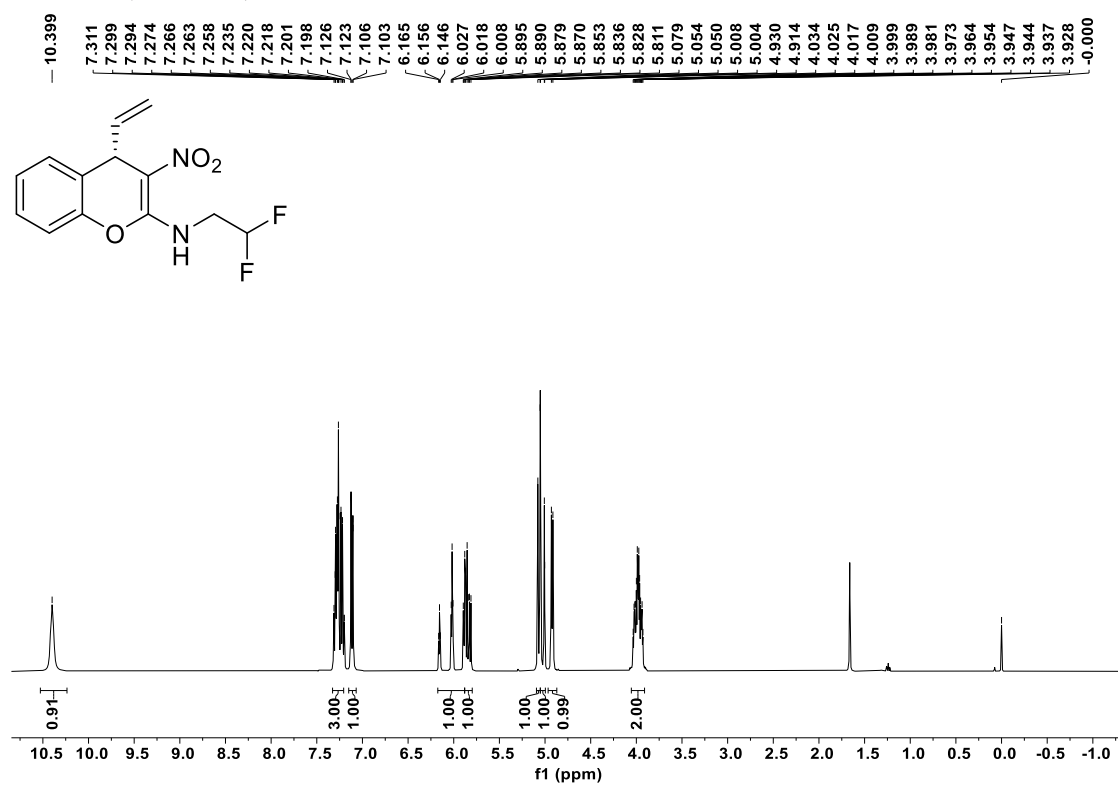


<sup>13</sup>C NMR (100 MHz) of **19** in CDCl<sub>3</sub>

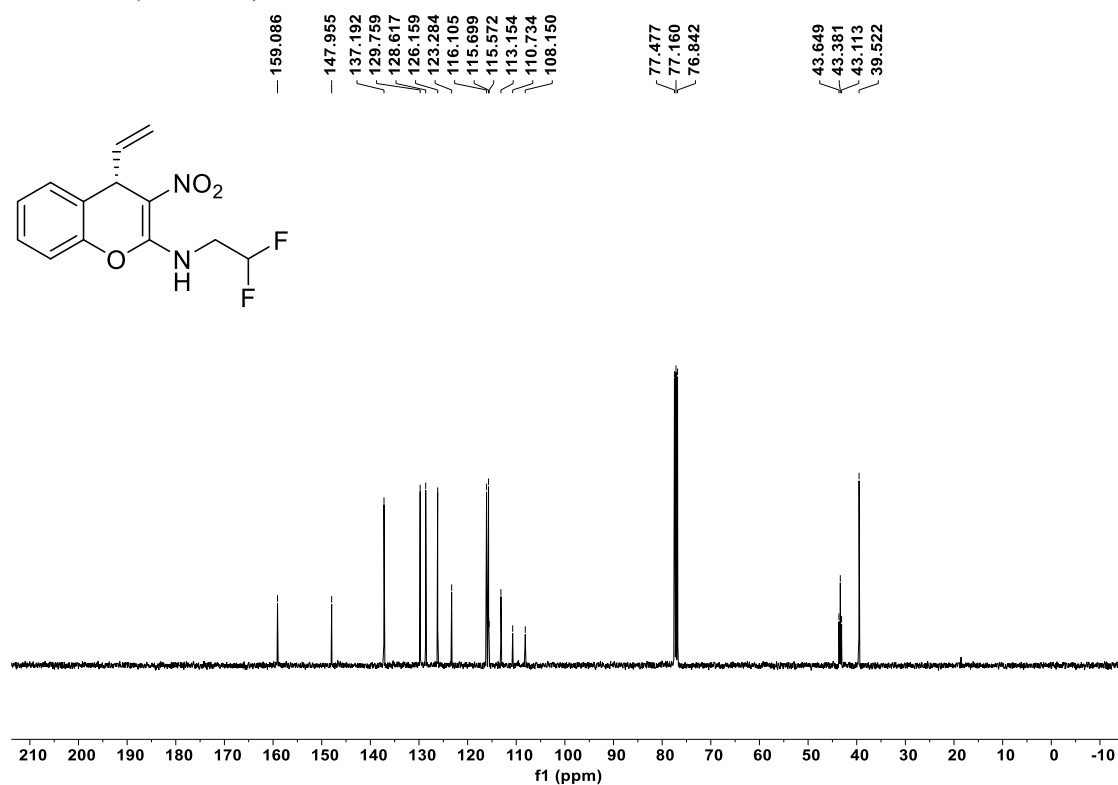




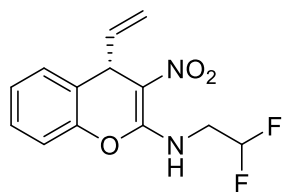
<sup>1</sup>H NMR (400 MHz) of **20** in CDCl<sub>3</sub>



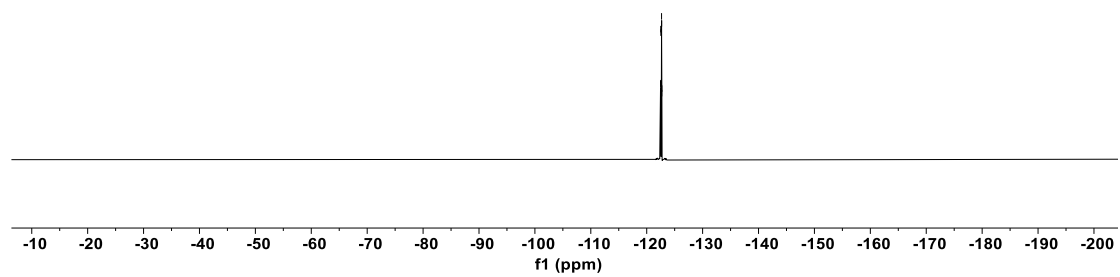
<sup>13</sup>C NMR (100 MHz) of **20** in CDCl<sub>3</sub>



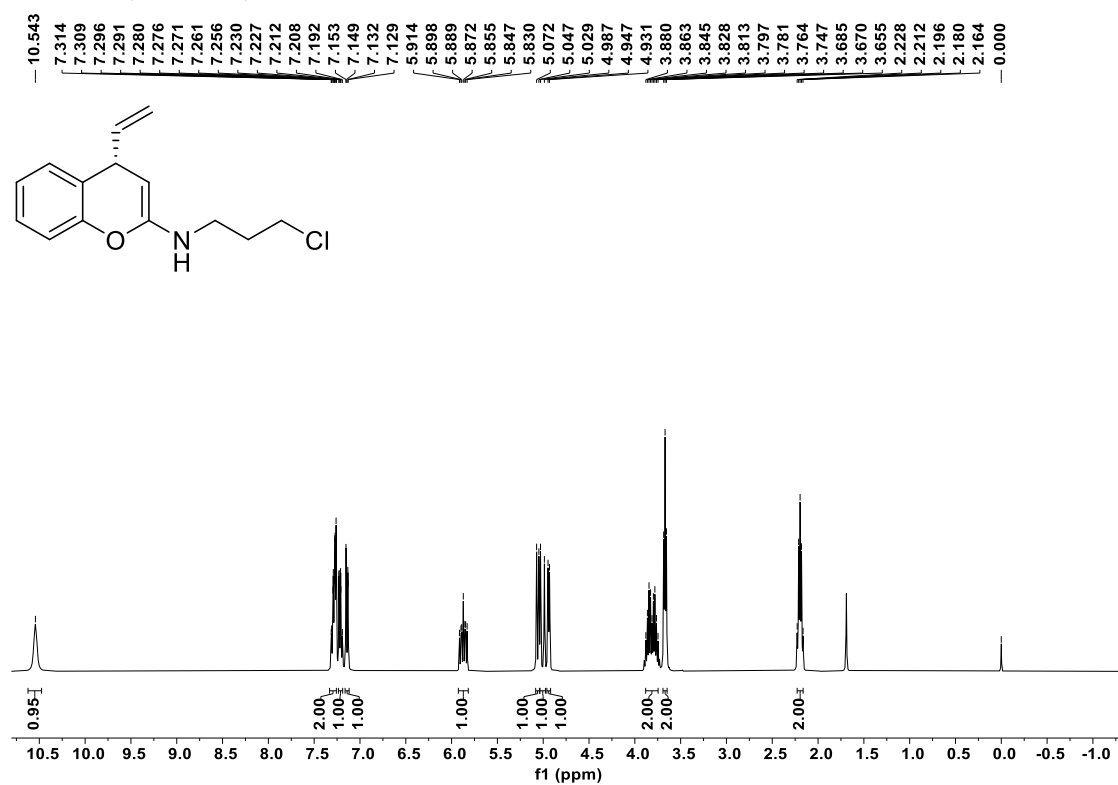
$^{19}\text{F}$  NMR (376 MHz) of **20** in  $\text{CDCl}_3$



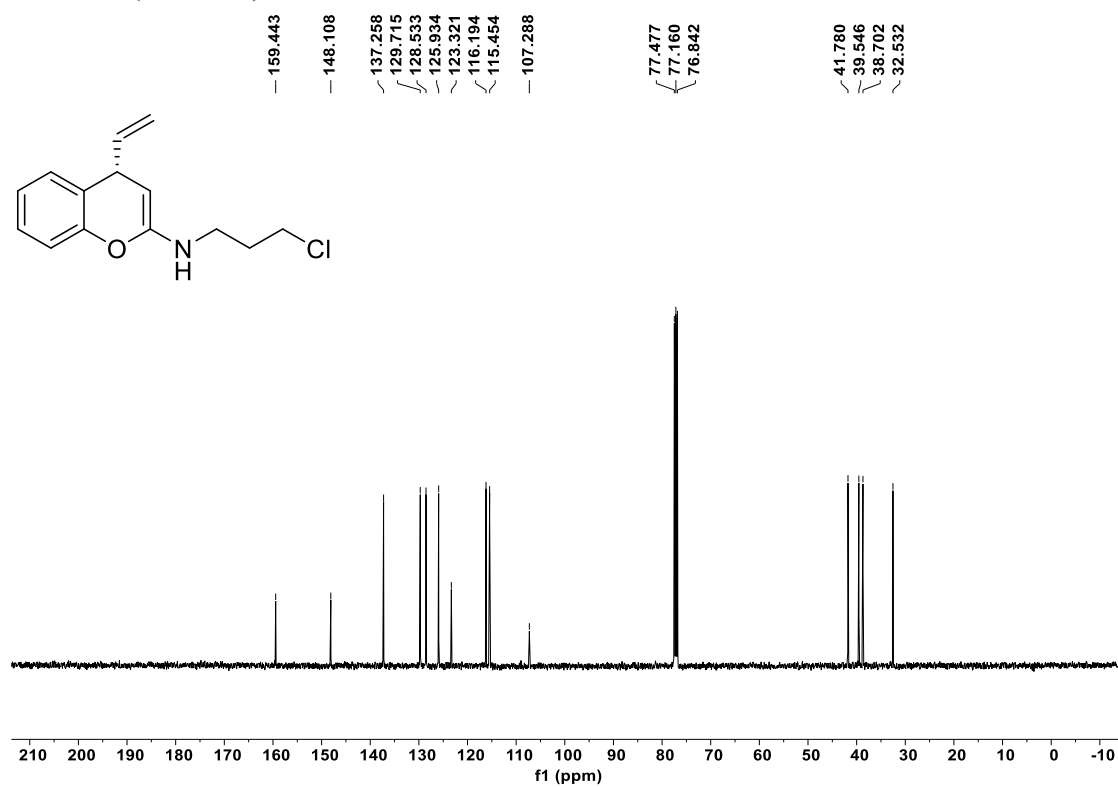
-122.471  
-122.489  
-122.509  
-122.527  
-122.546  
-122.565  
-122.618  
-122.635  
-122.655  
-122.673  
-122.693  
-122.712



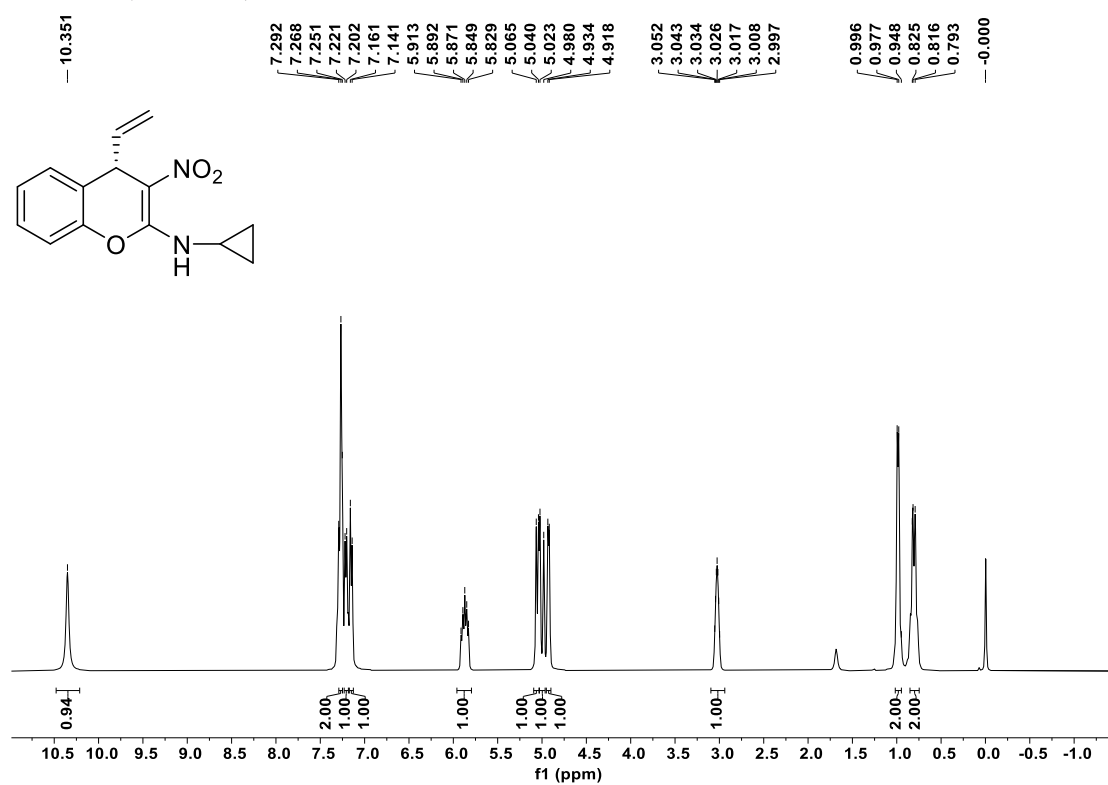
<sup>1</sup>H NMR (400 MHz) of **21** in CDCl<sub>3</sub>



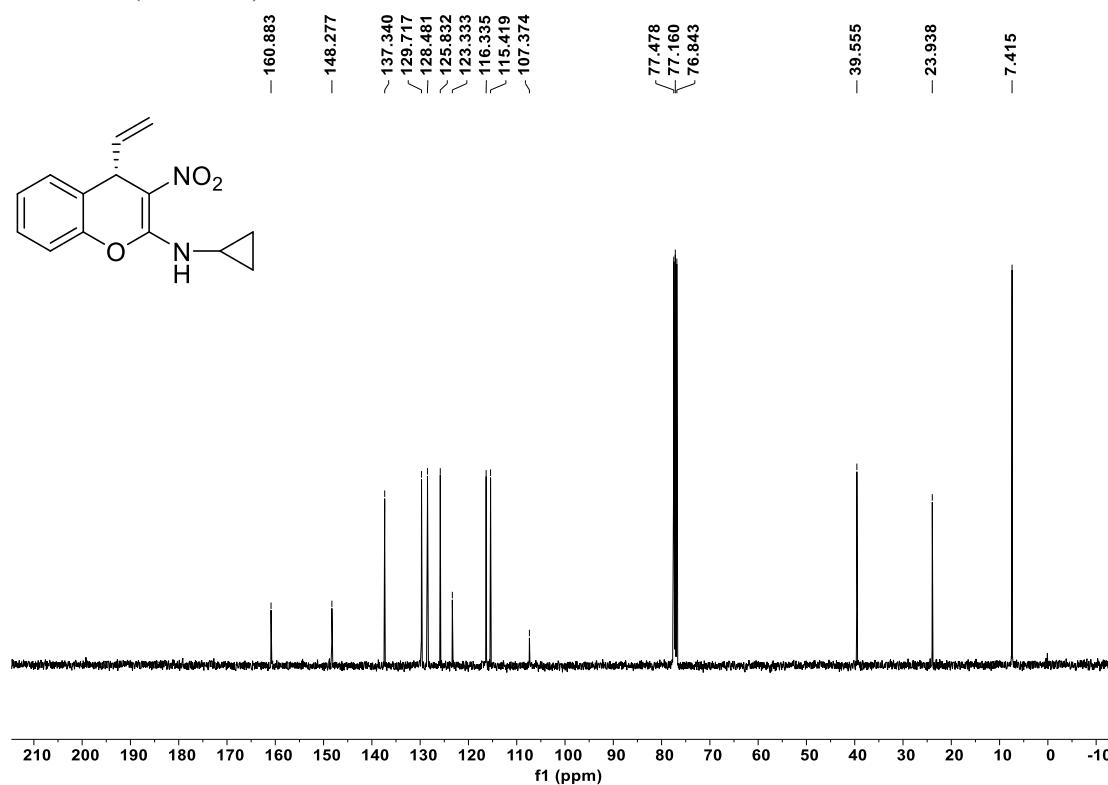
<sup>13</sup>C NMR (100 MHz) of **21** in CDCl<sub>3</sub>



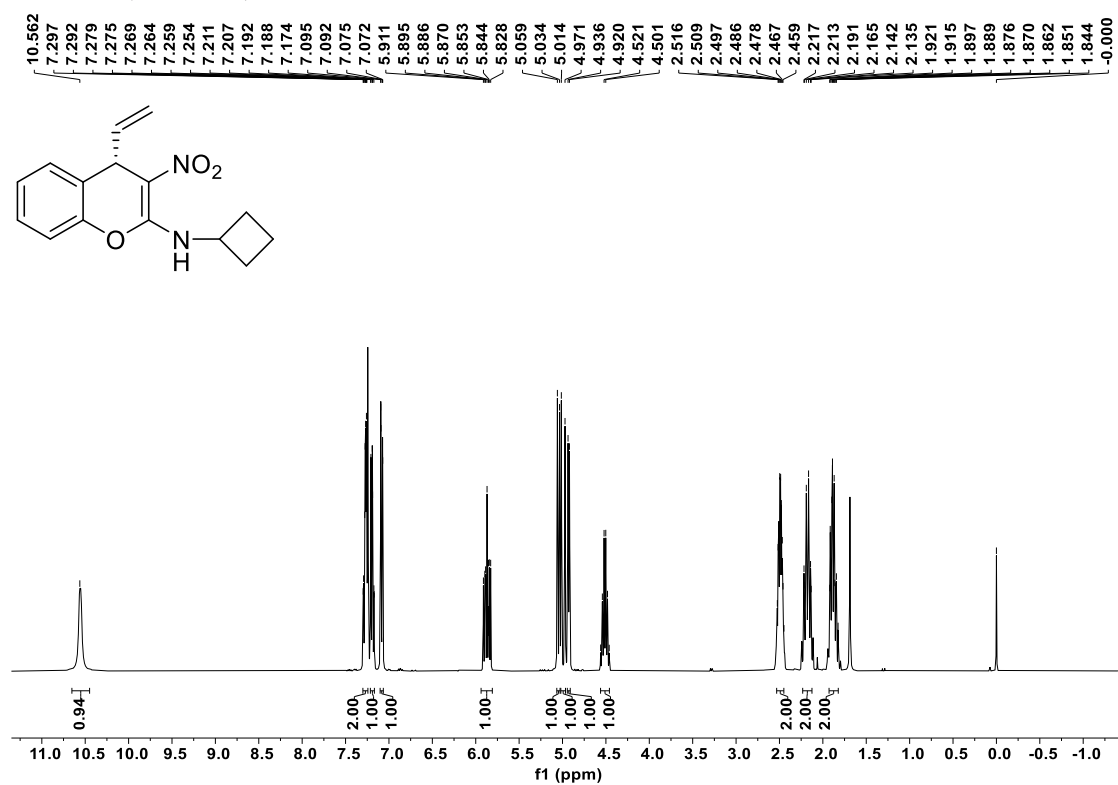
<sup>1</sup>H NMR (400 MHz) of **22** in CDCl<sub>3</sub>



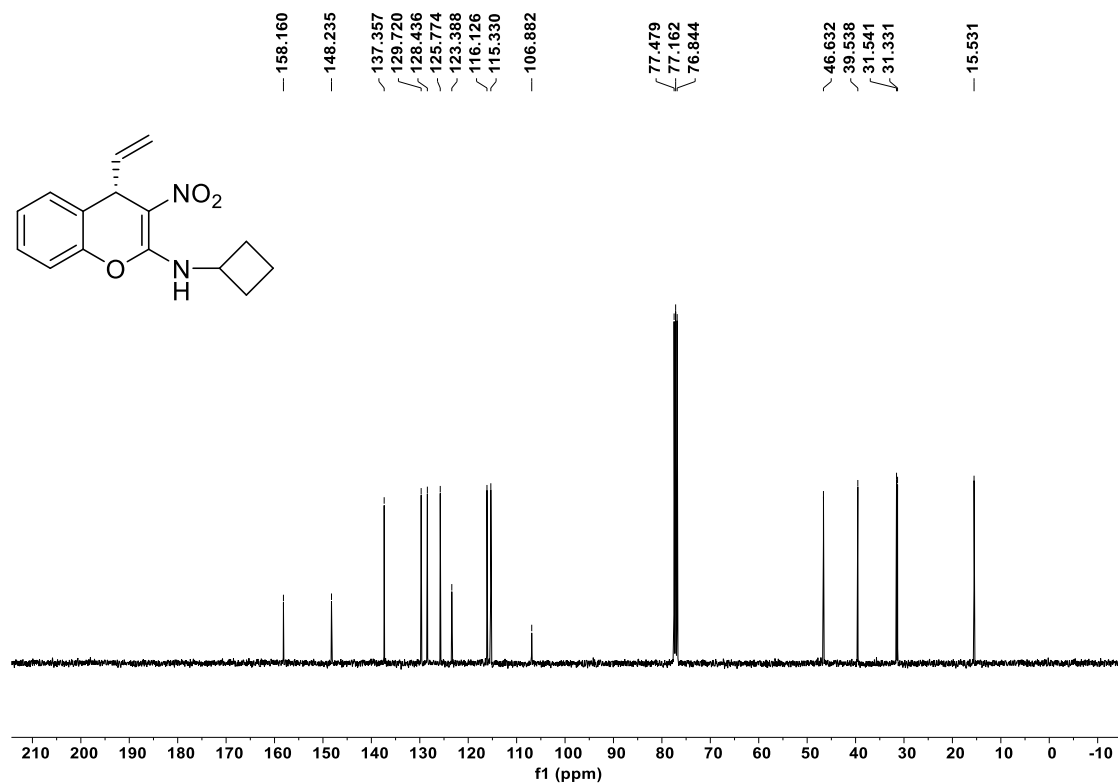
<sup>13</sup>C NMR (100 MHz) of **22** in CDCl<sub>3</sub>



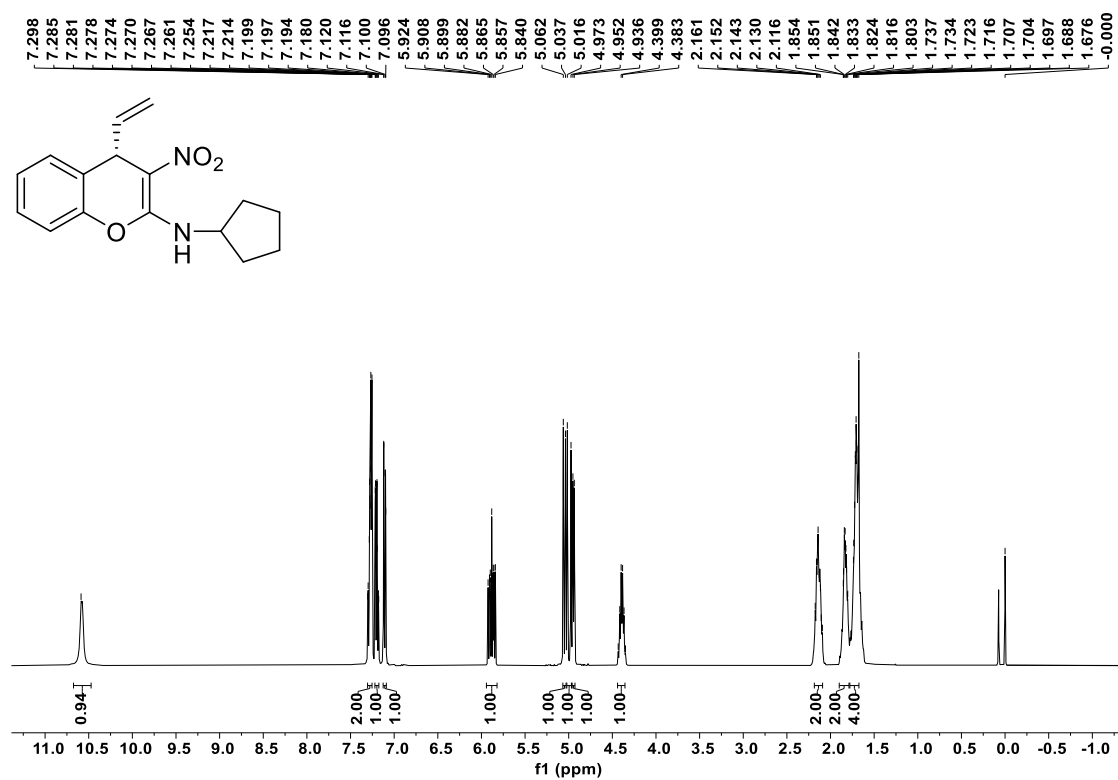
<sup>1</sup>H NMR (400 MHz) of **23** in CDCl<sub>3</sub>



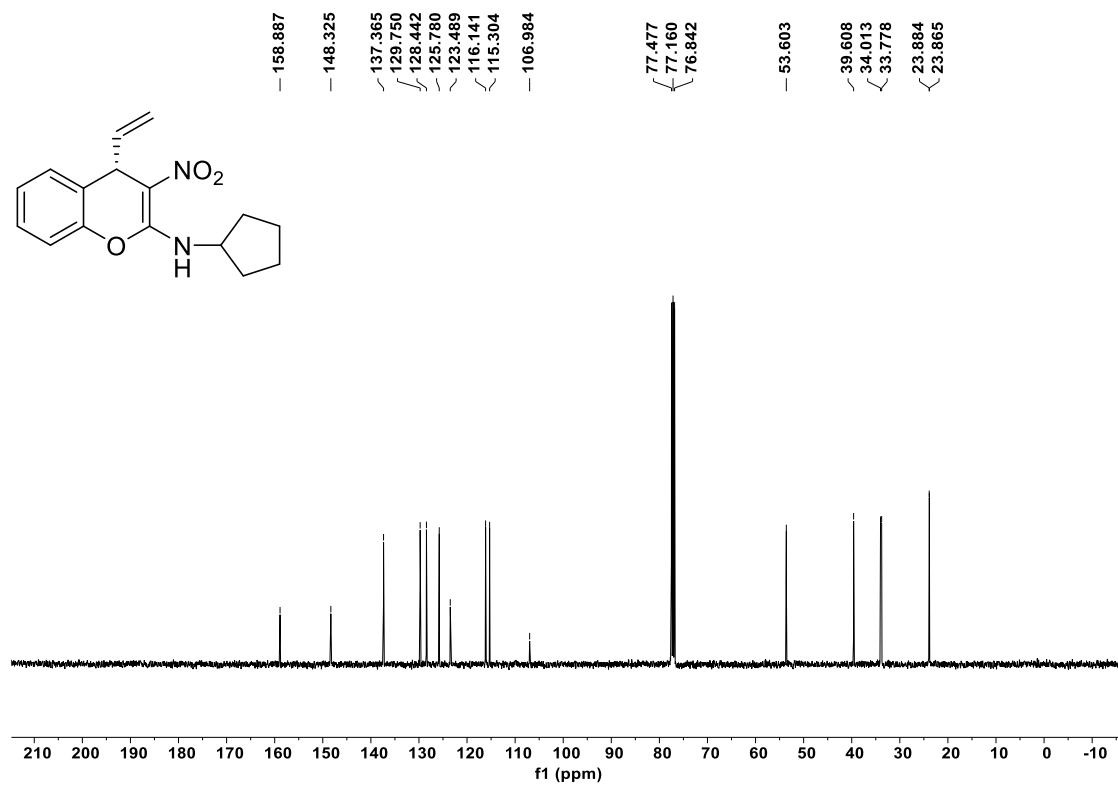
<sup>13</sup>C NMR (100 MHz) of **23** in CDCl<sub>3</sub>



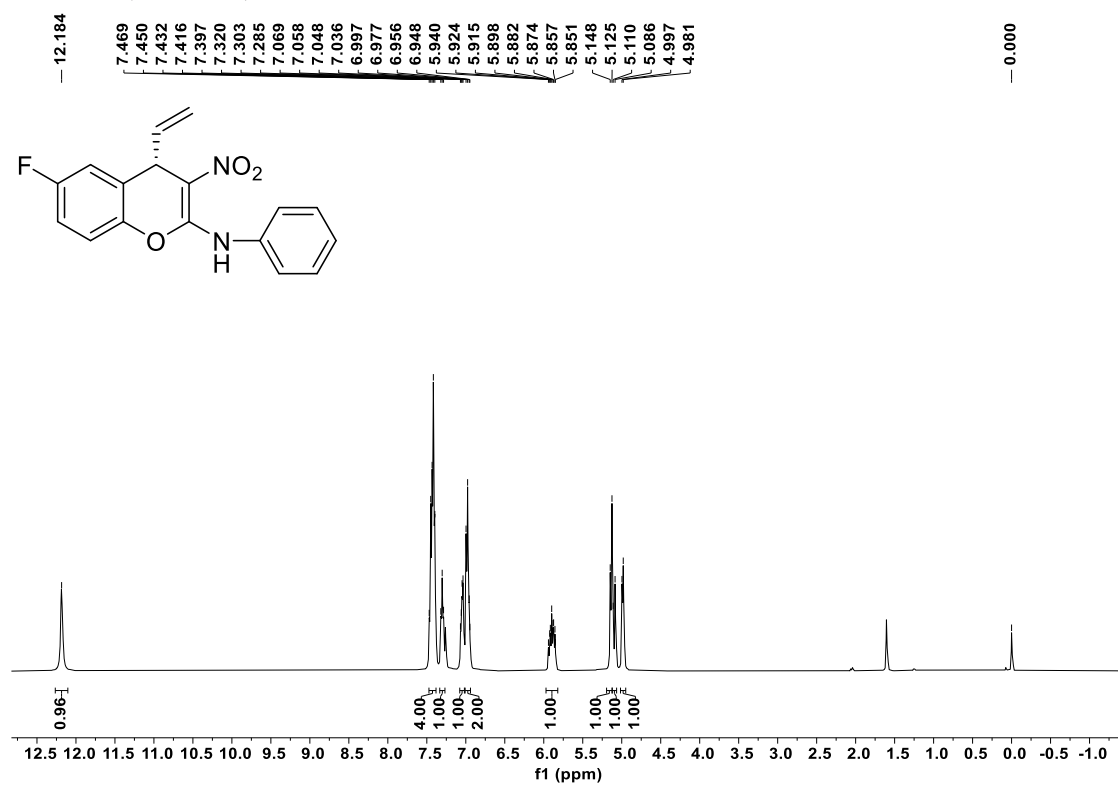
<sup>1</sup>H NMR (400 MHz) of **24** in CDCl<sub>3</sub>



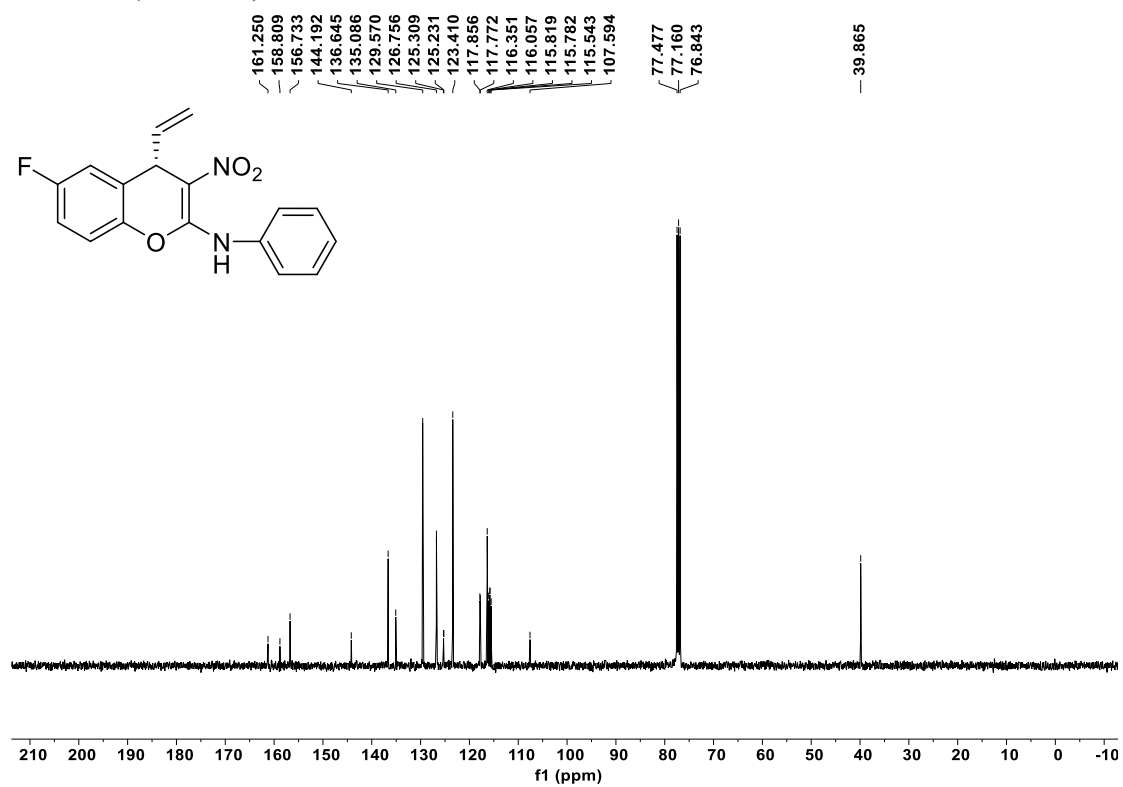
<sup>13</sup>C NMR (100 MHz) of **24** in CDCl<sub>3</sub>



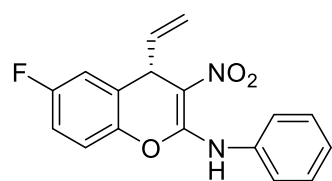
<sup>1</sup>H NMR (400 MHz) of **25** in CDCl<sub>3</sub>



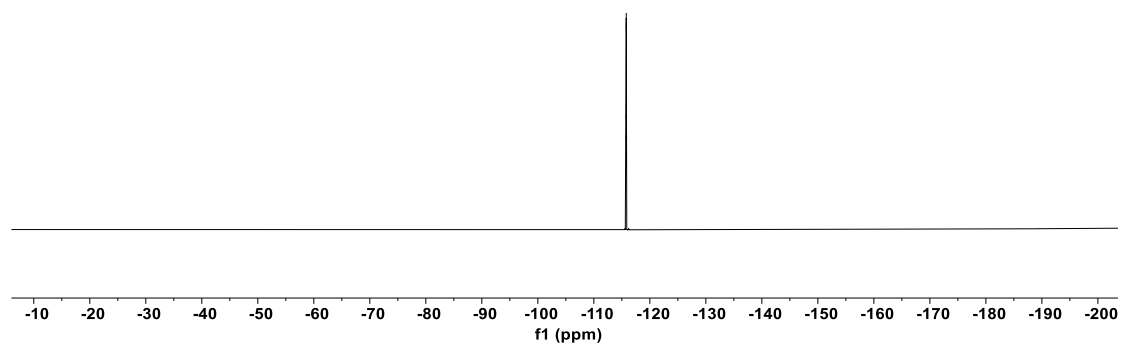
<sup>13</sup>C NMR (100 MHz) of **25** in CDCl<sub>3</sub>



$^{19}\text{F}$  NMR (376 MHz) of **25** in  $\text{CDCl}_3$

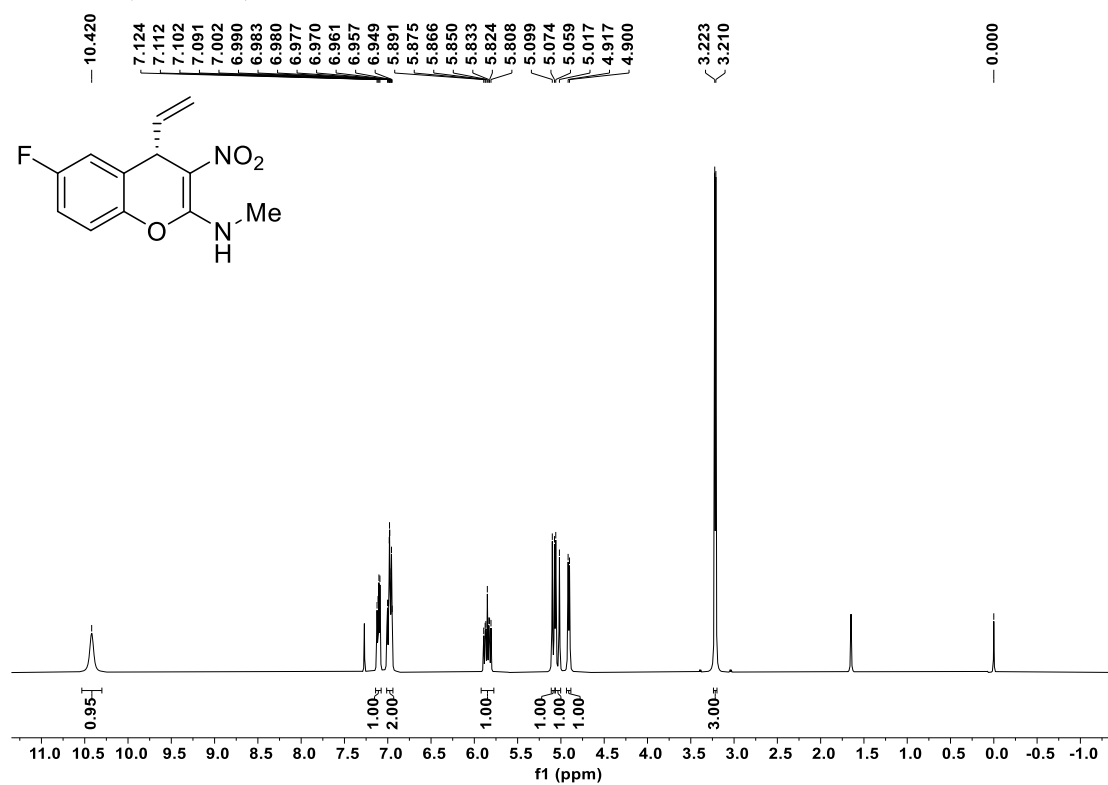


-115.764  
-115.777  
-115.786  
-115.797  
-115.806  
-115.819

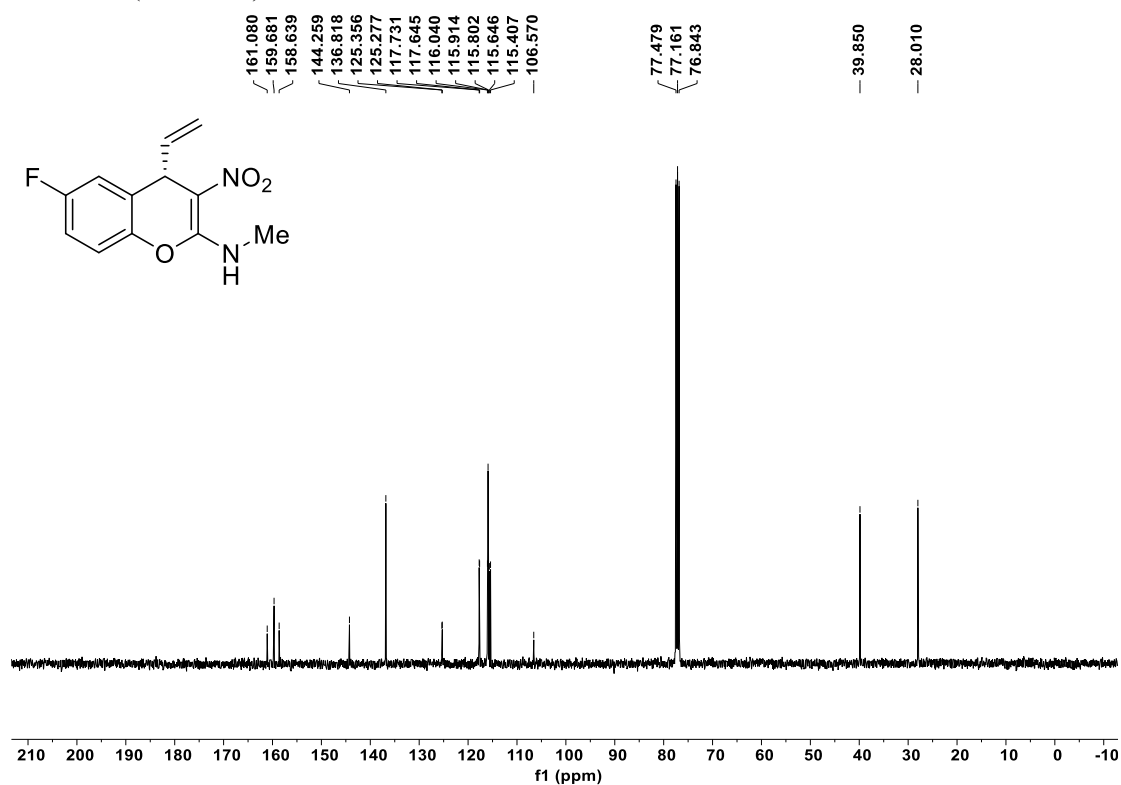




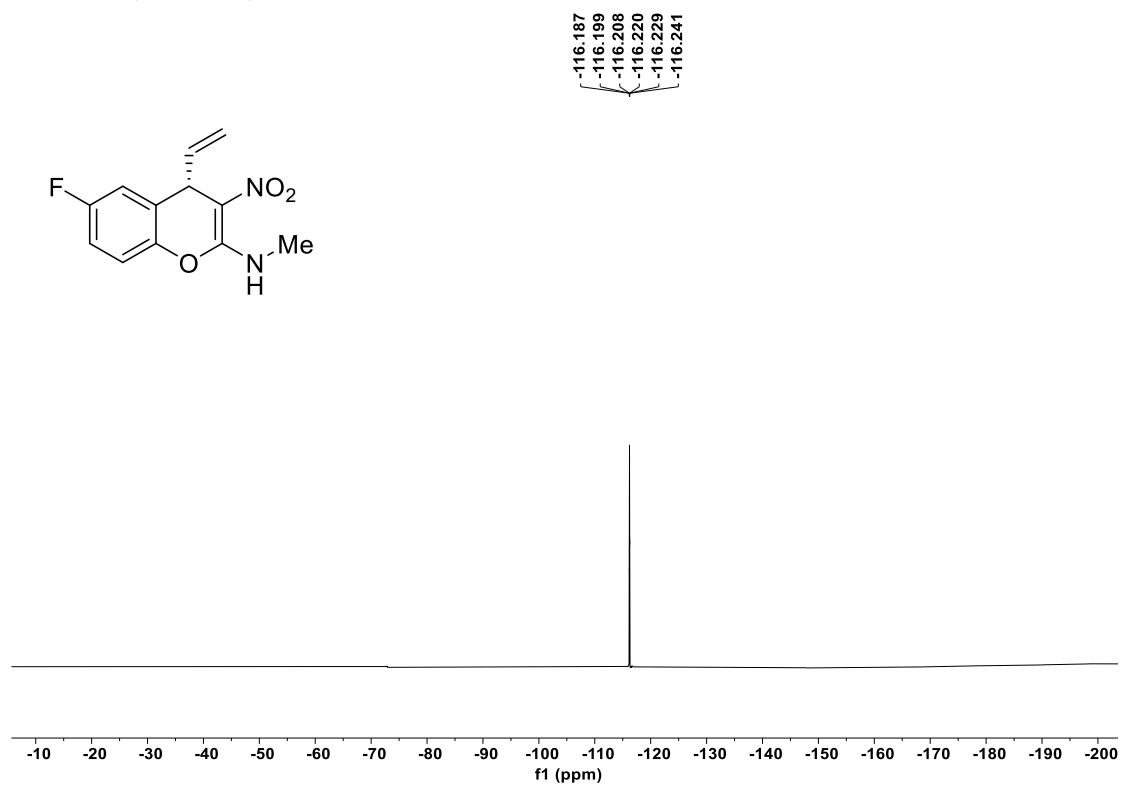
<sup>1</sup>H NMR (400 MHz) of **26** in CDCl<sub>3</sub>



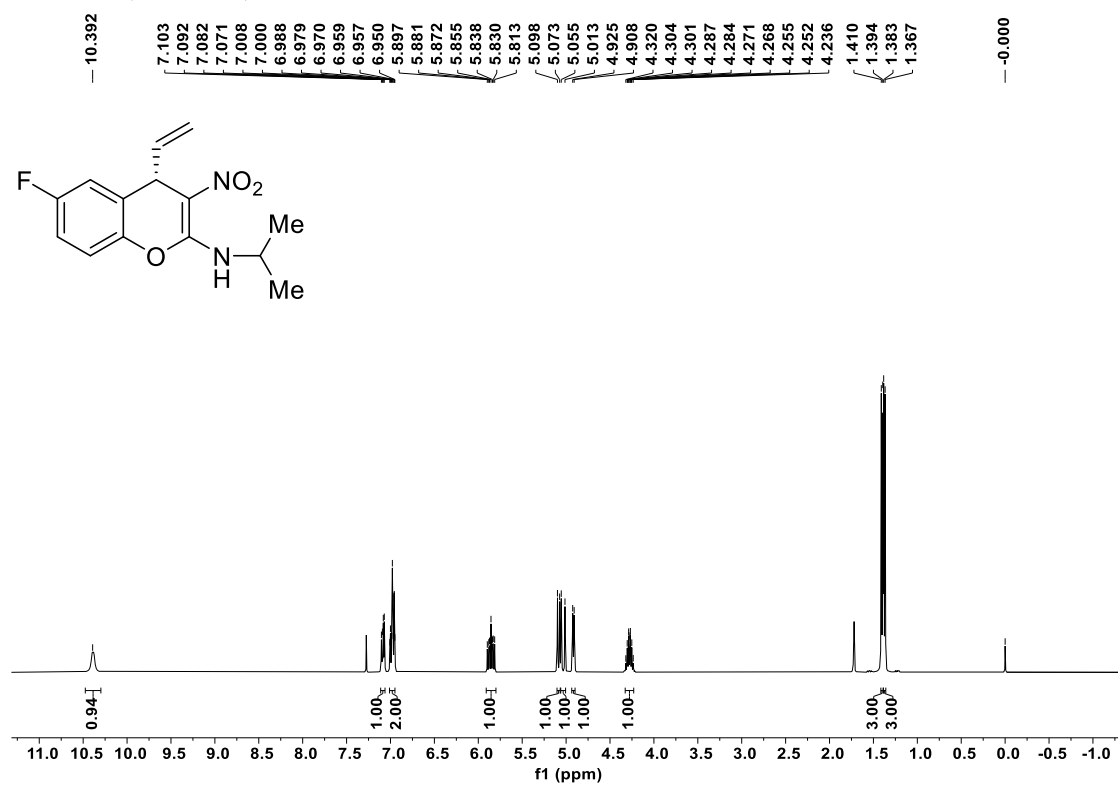
<sup>13</sup>C NMR (100 MHz) of **26** in CDCl<sub>3</sub>



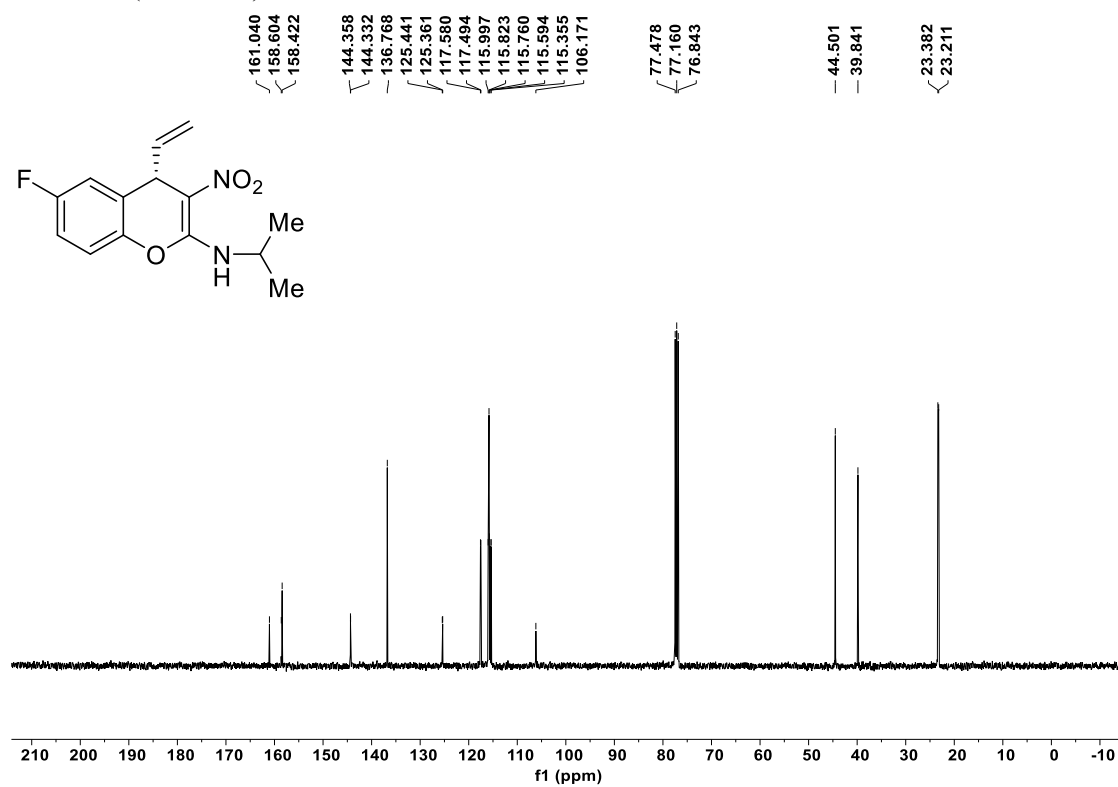
$^{19}\text{F}$  NMR (376 MHz) of **26** in  $\text{CDCl}_3$



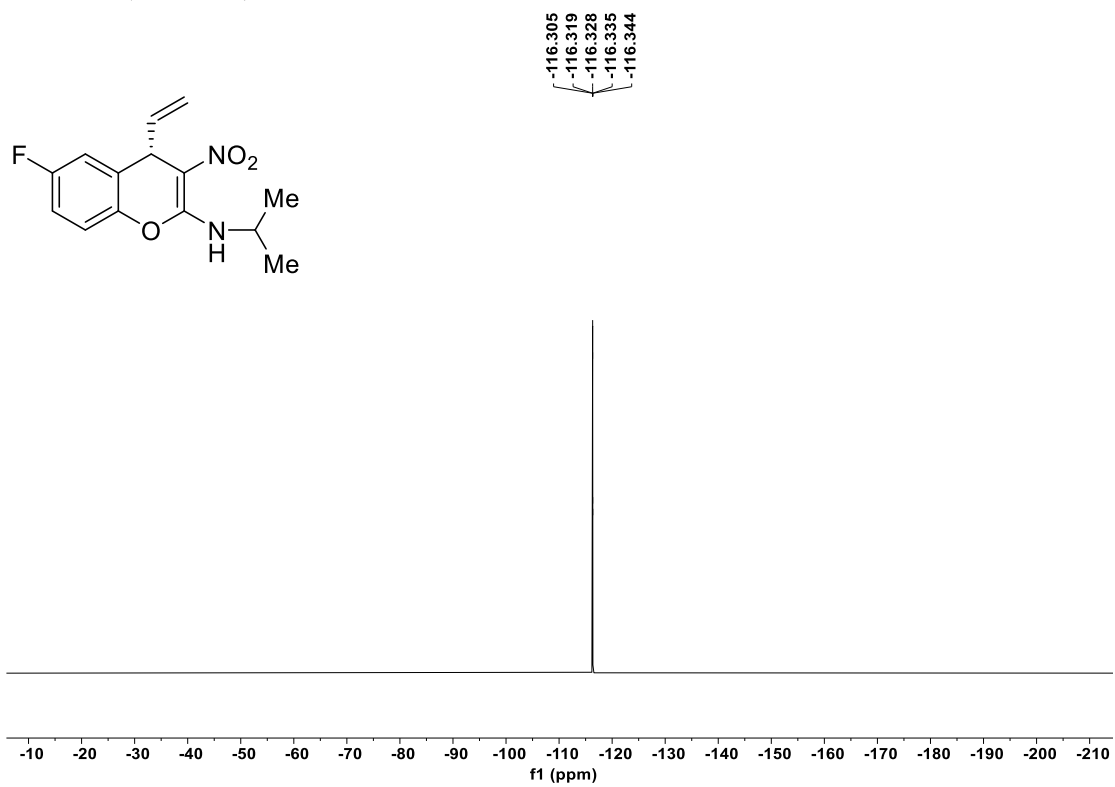
<sup>1</sup>H NMR (400 MHz) of **27** in CDCl<sub>3</sub>



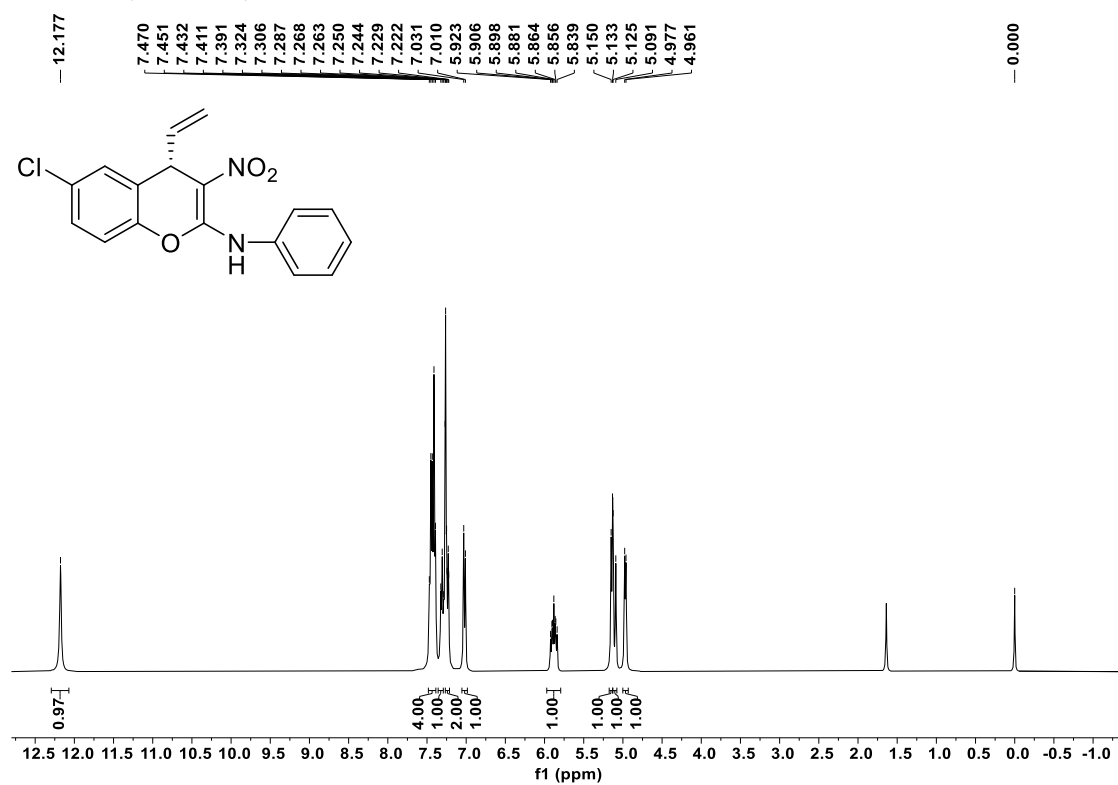
<sup>13</sup>C NMR (100 MHz) of **27** in CDCl<sub>3</sub>



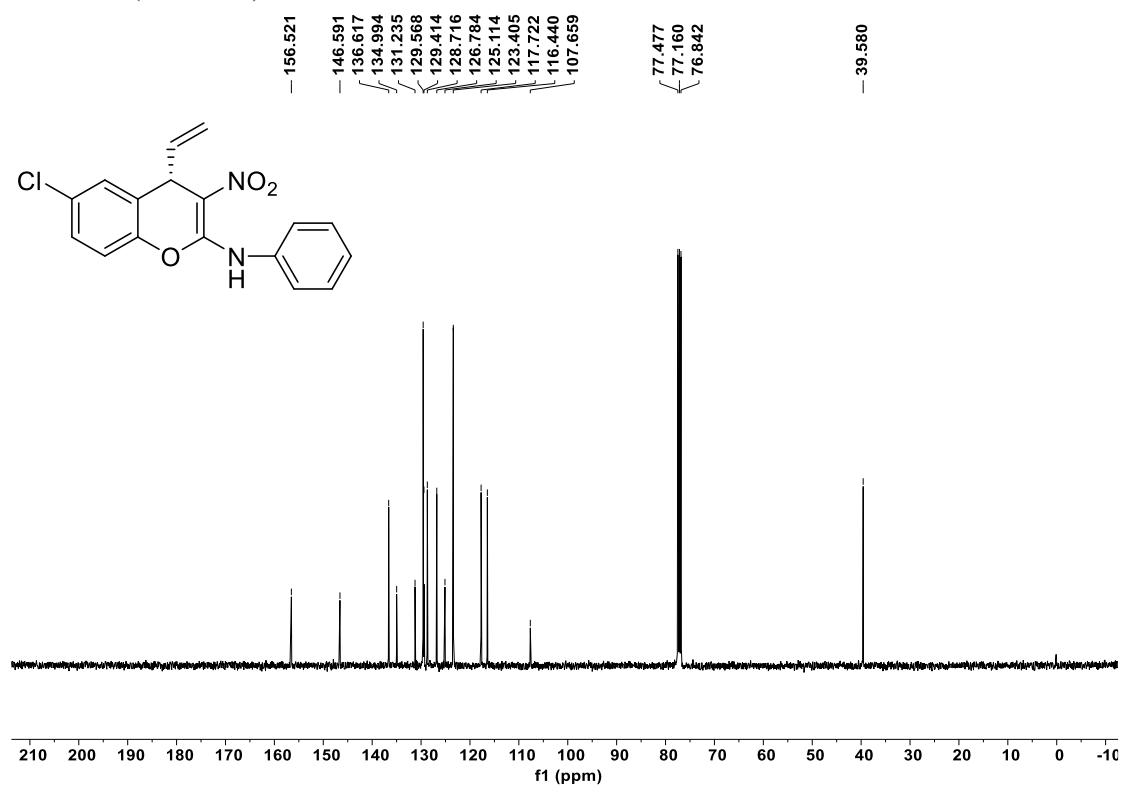
$^{19}\text{F}$  NMR (376 MHz) of **27** in  $\text{CDCl}_3$



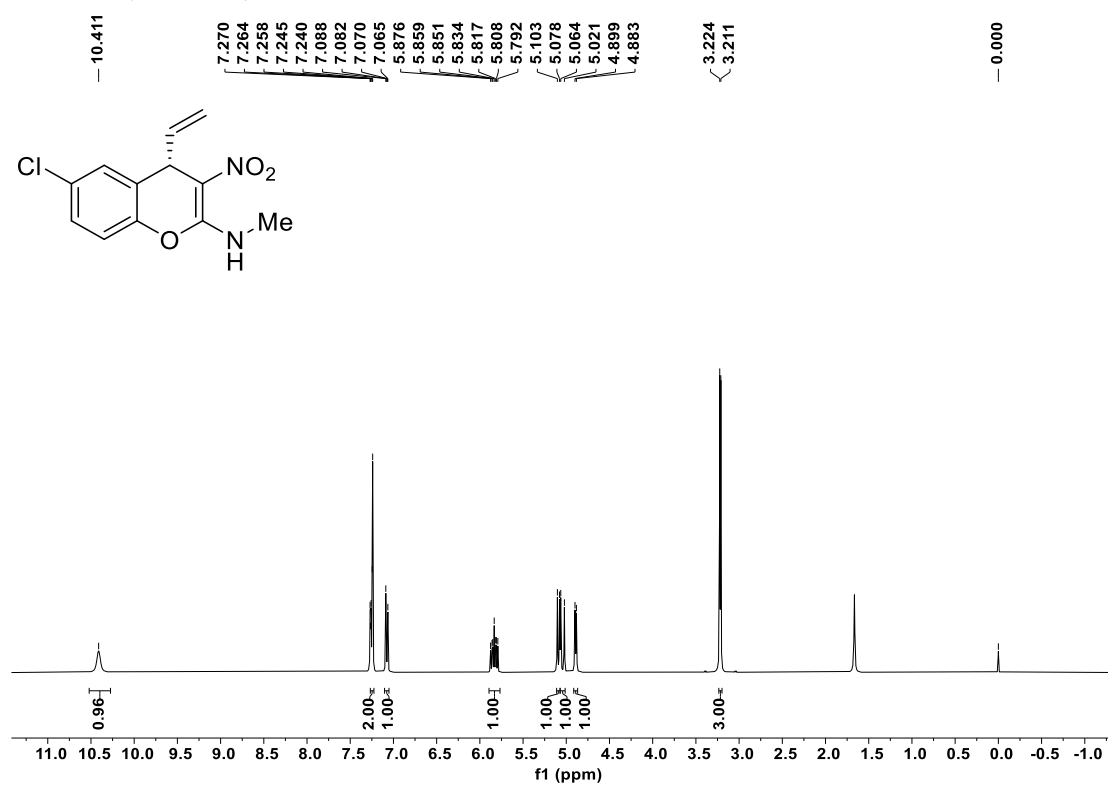
$^1\text{H}$  NMR (400 MHz) of **28** in  $\text{CDCl}_3$



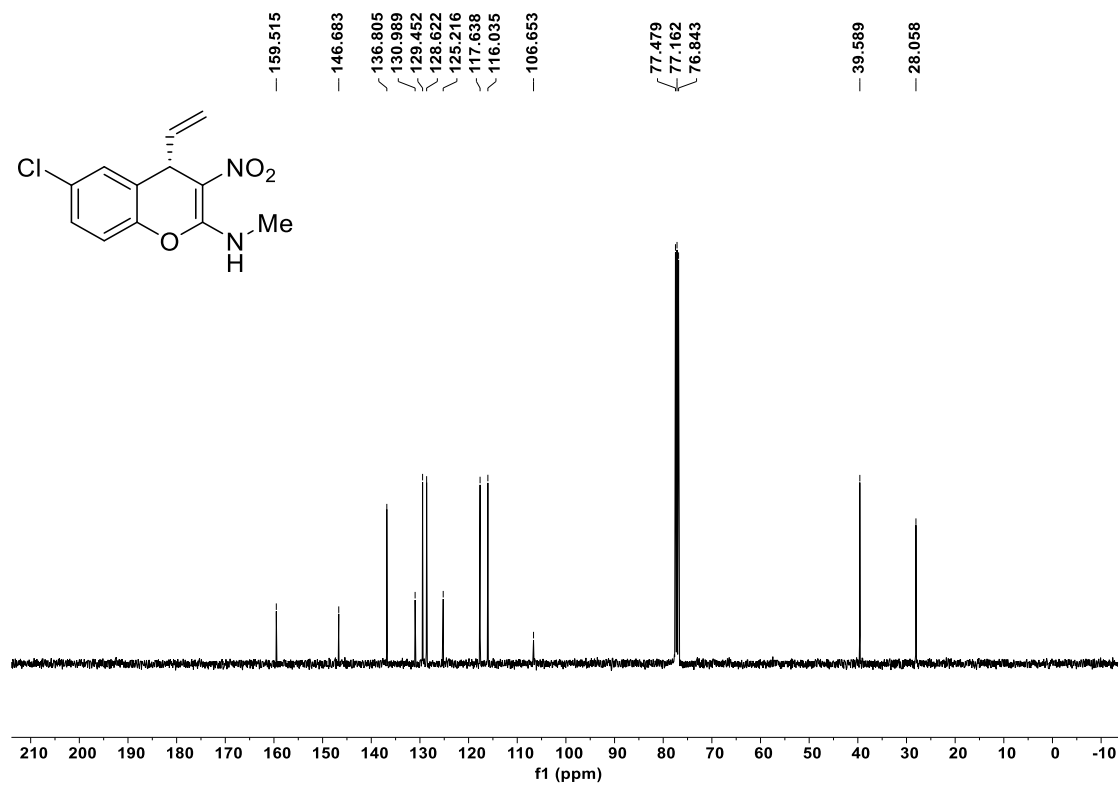
$^{13}\text{C}$  NMR (100 MHz) of **28** in  $\text{CDCl}_3$



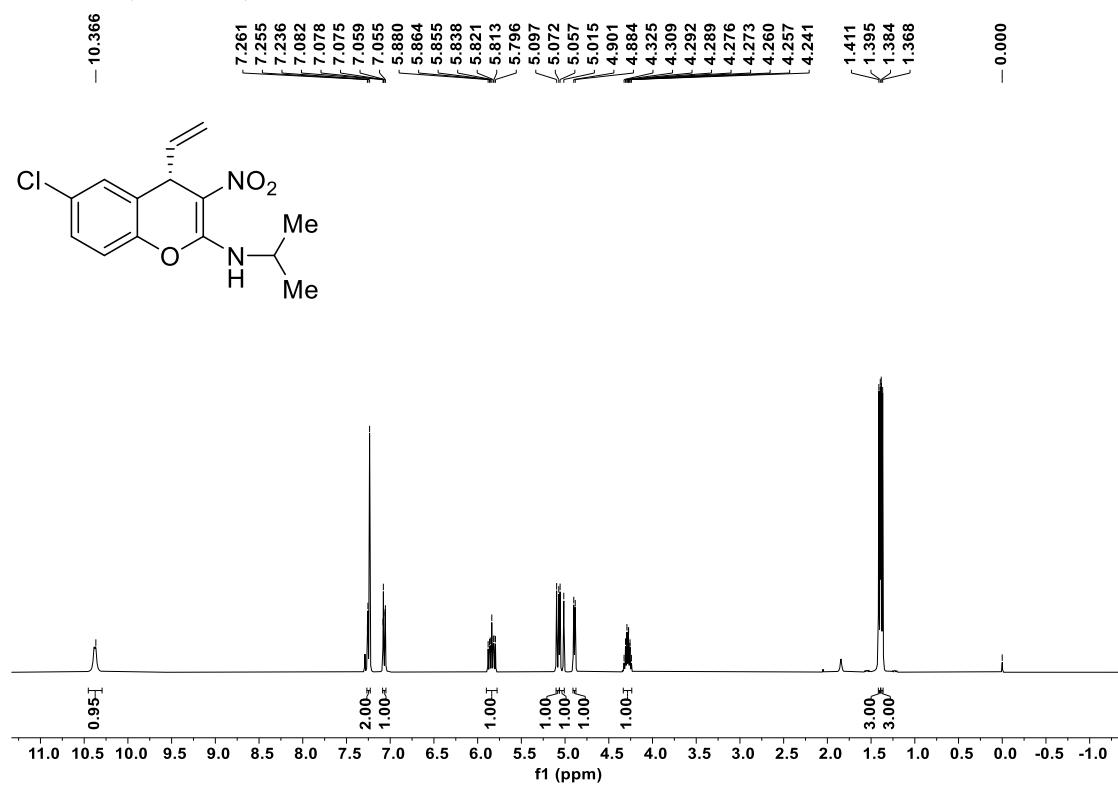
$^1\text{H}$  NMR (400 MHz) of **29** in  $\text{CDCl}_3$



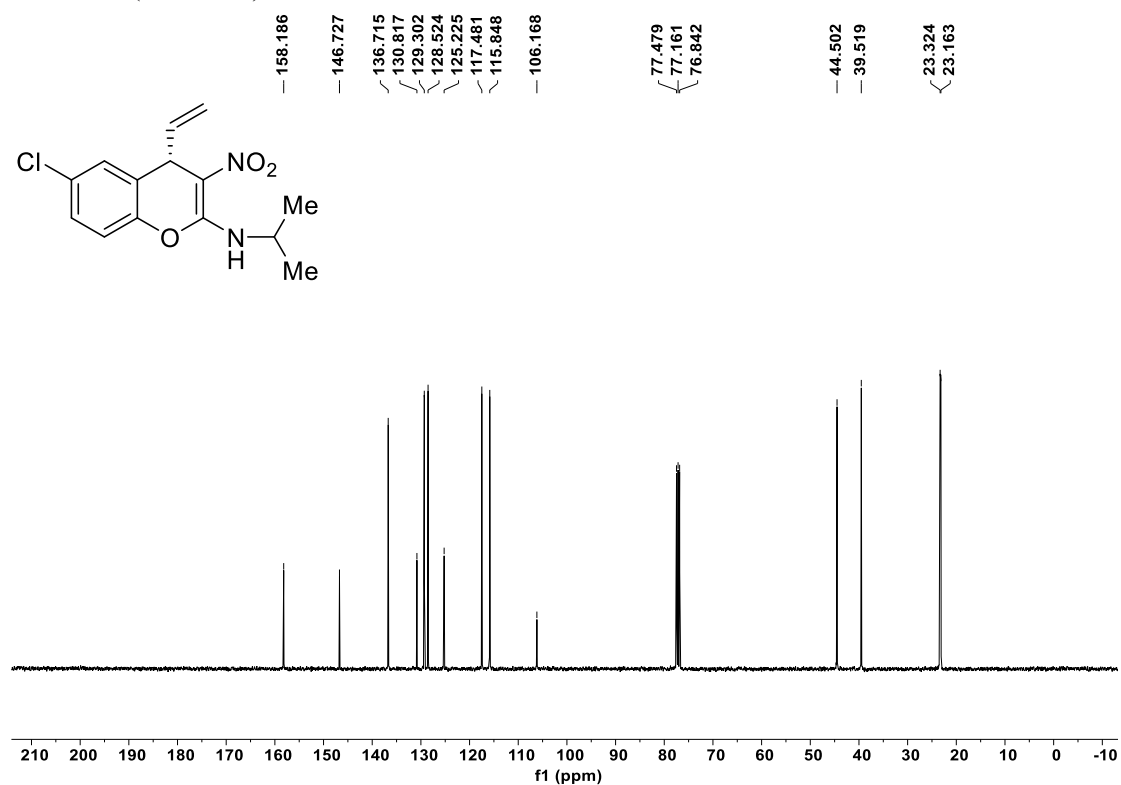
$^{13}\text{C}$  NMR (100 MHz) of **29** in  $\text{CDCl}_3$



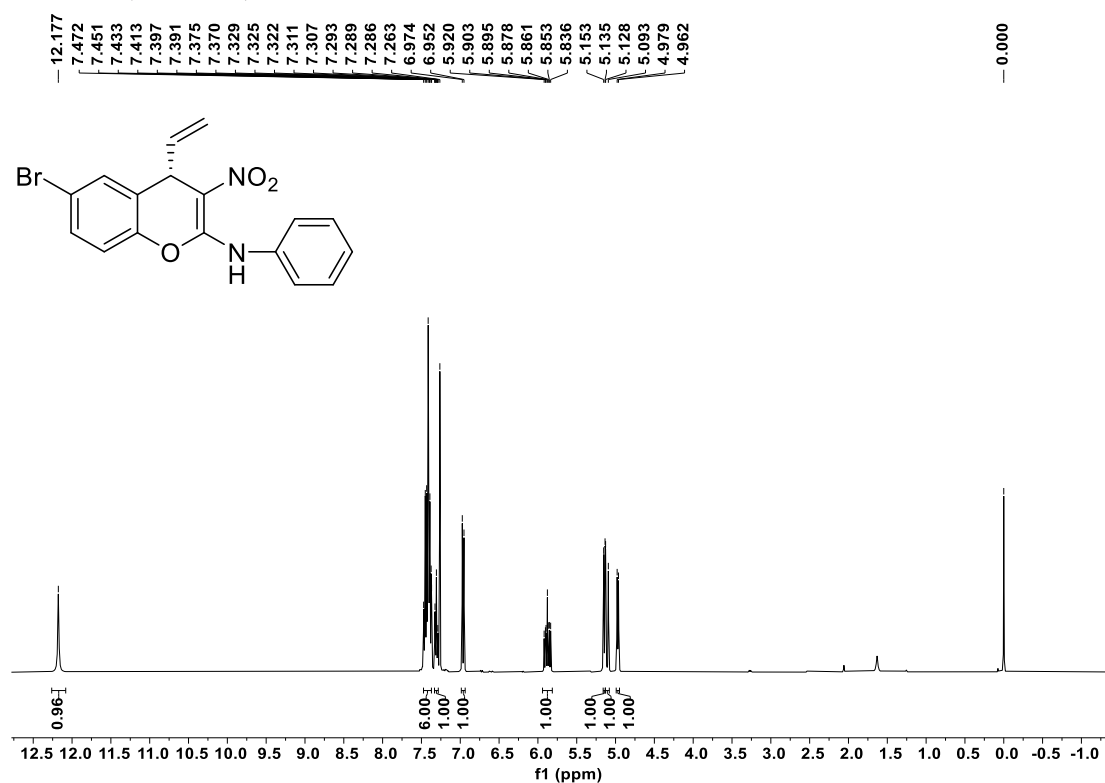
<sup>1</sup>H NMR (400 MHz) of **30** in CDCl<sub>3</sub>



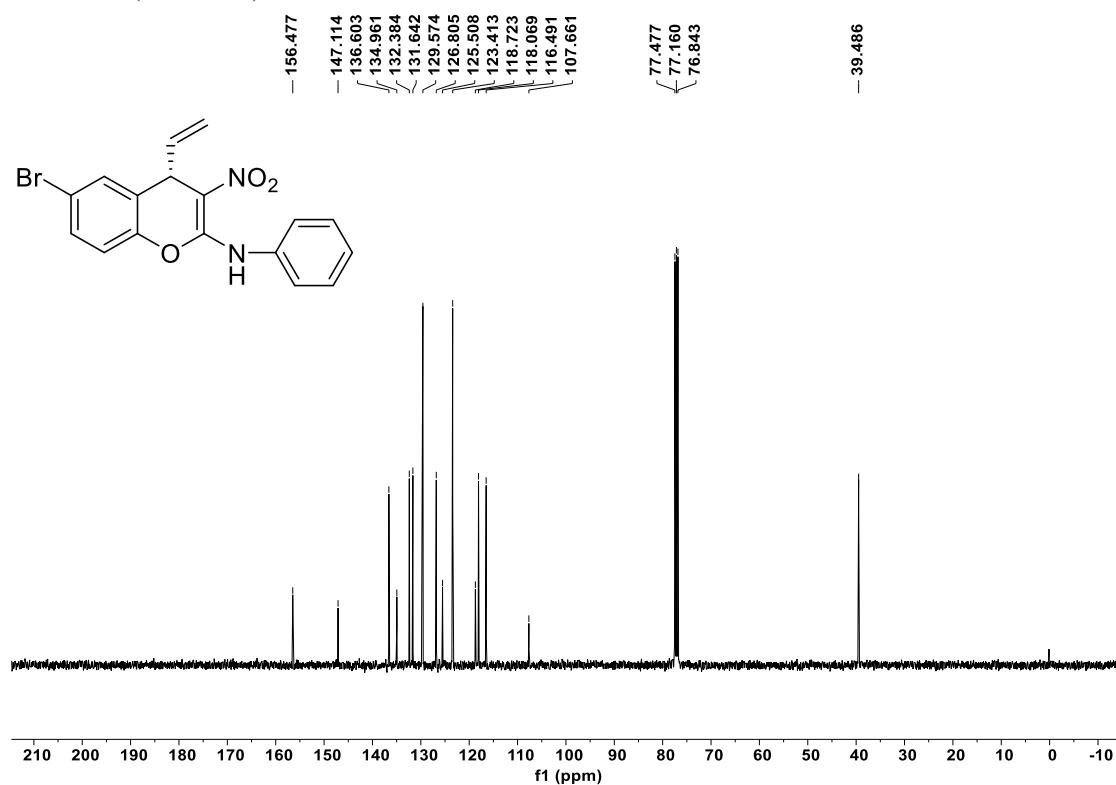
<sup>13</sup>C NMR (100 MHz) of **30** in CDCl<sub>3</sub>



<sup>1</sup>H NMR (400 MHz) of **31** in CDCl<sub>3</sub>

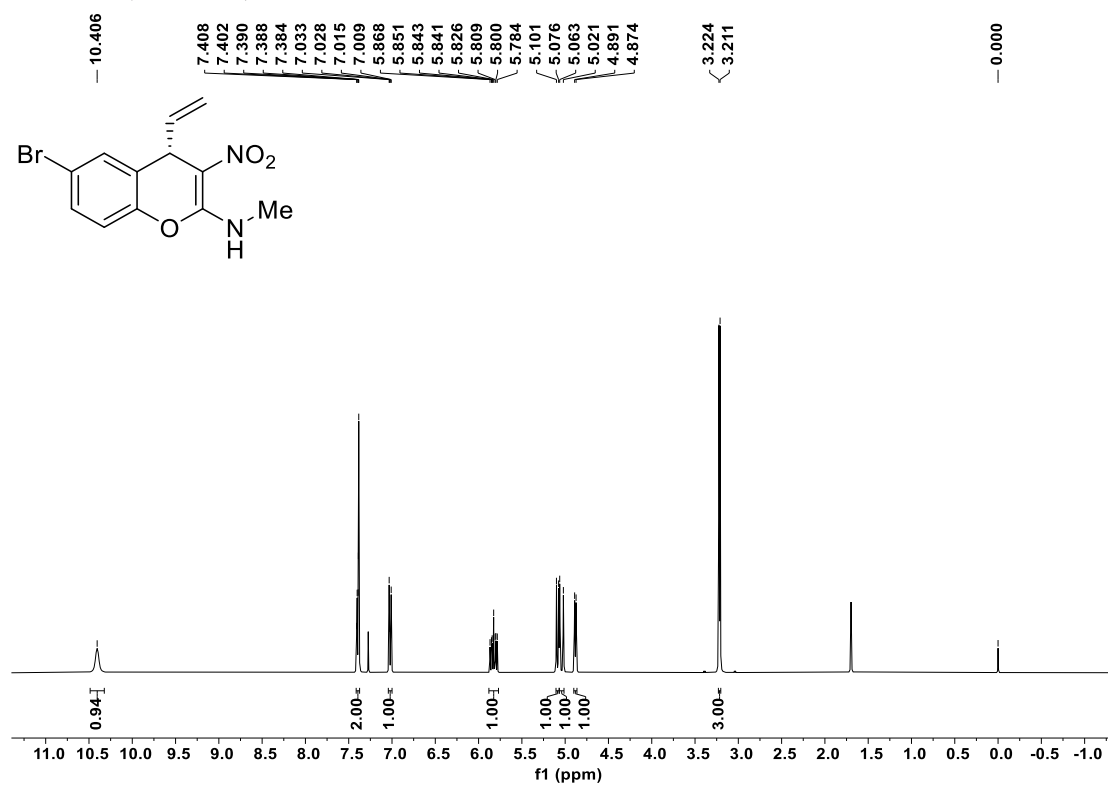


<sup>13</sup>C NMR (100 MHz) of **31** in CDCl<sub>3</sub>

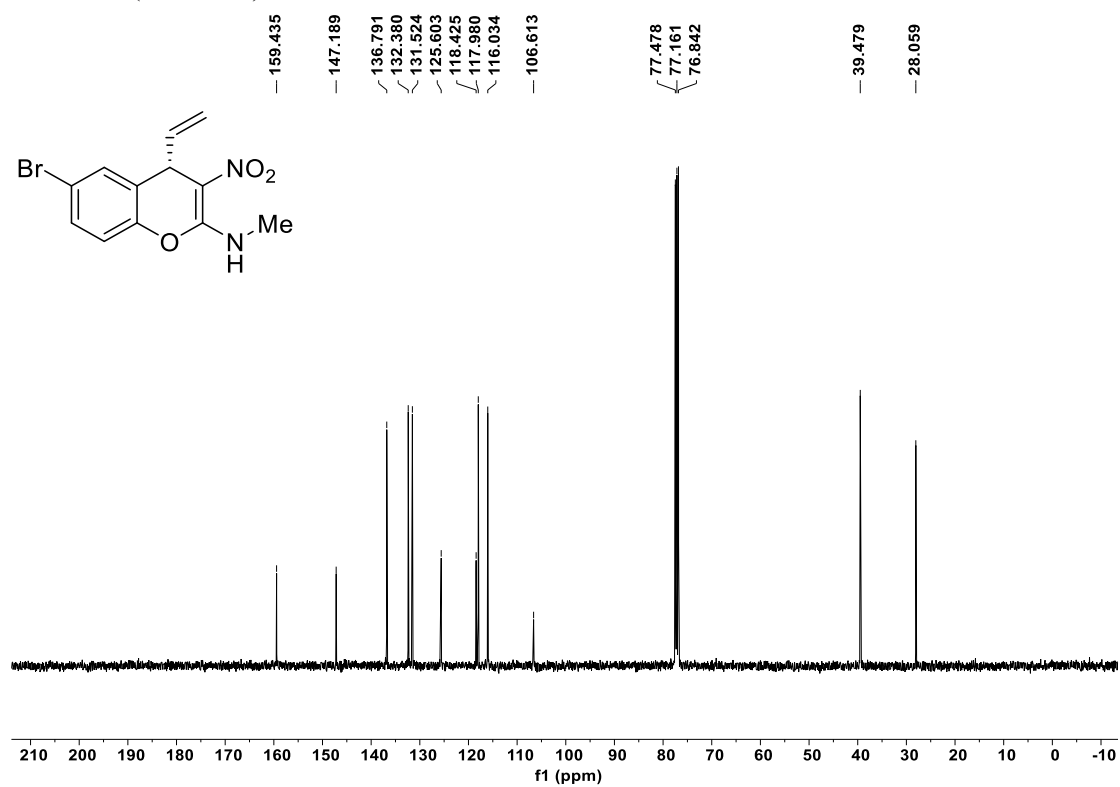




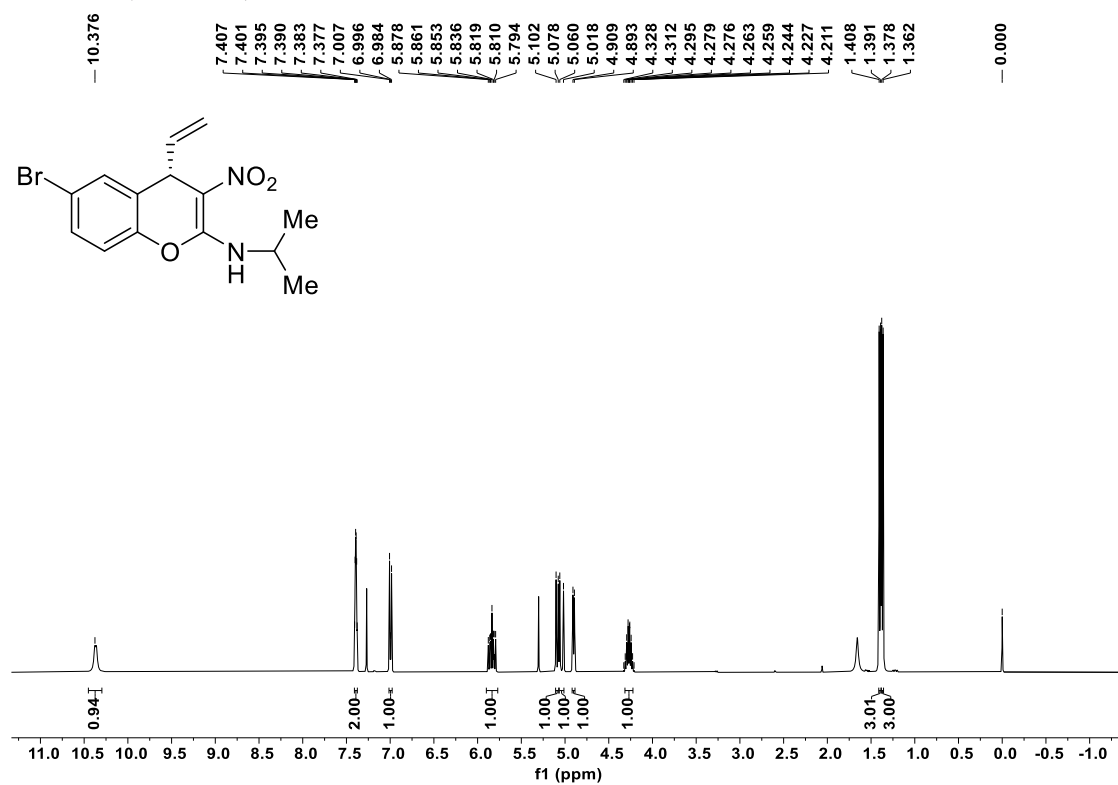
<sup>1</sup>H NMR (400 MHz) of **32** in CDCl<sub>3</sub>



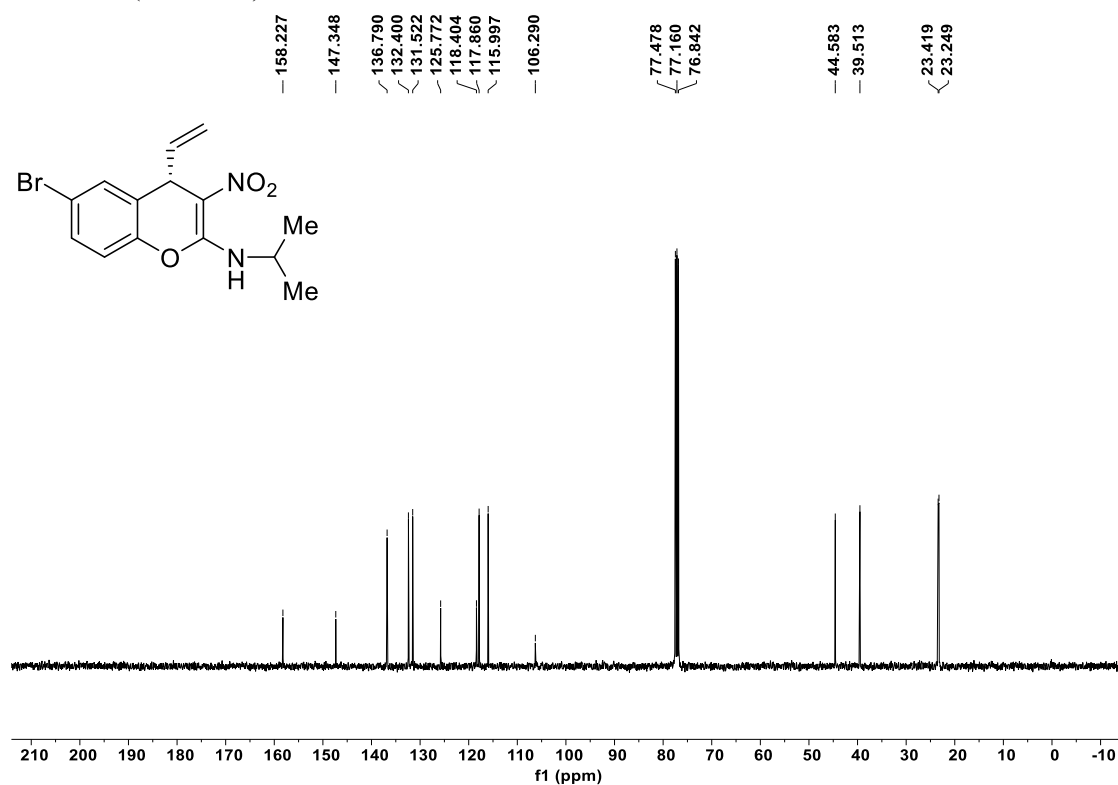
<sup>13</sup>C NMR (100 MHz) of **32** in CDCl<sub>3</sub>



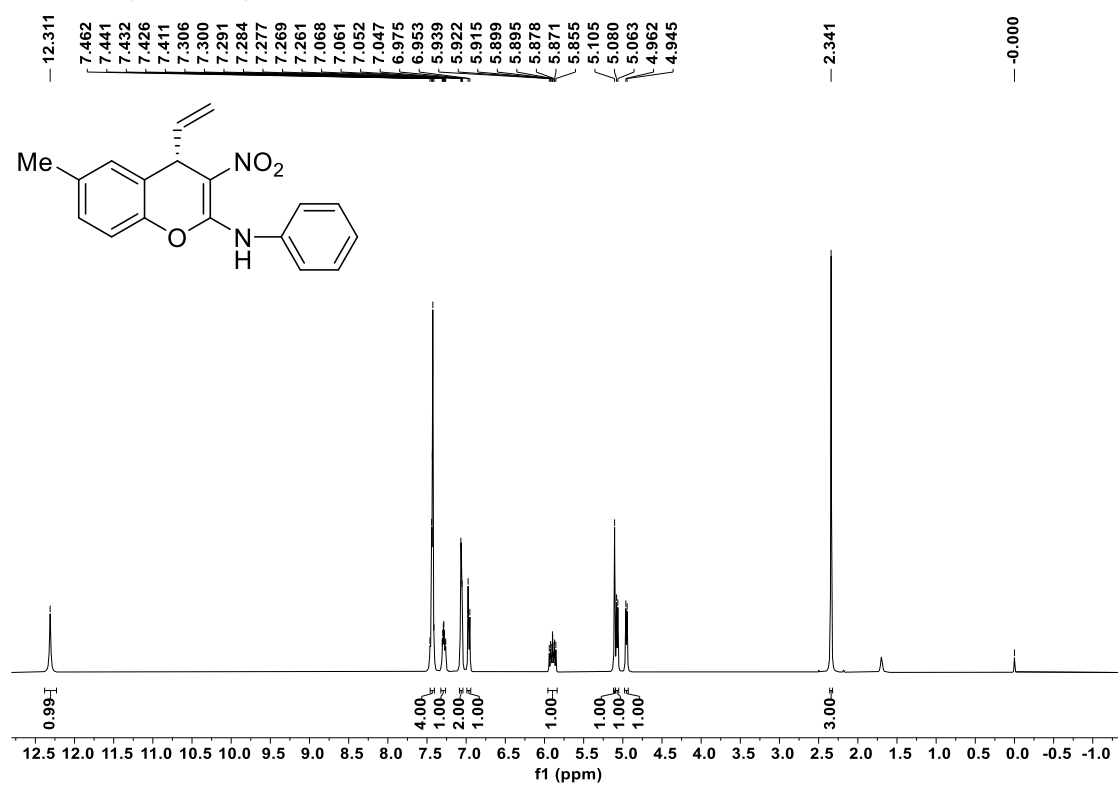
<sup>1</sup>H NMR (400 MHz) of **33** in CDCl<sub>3</sub>



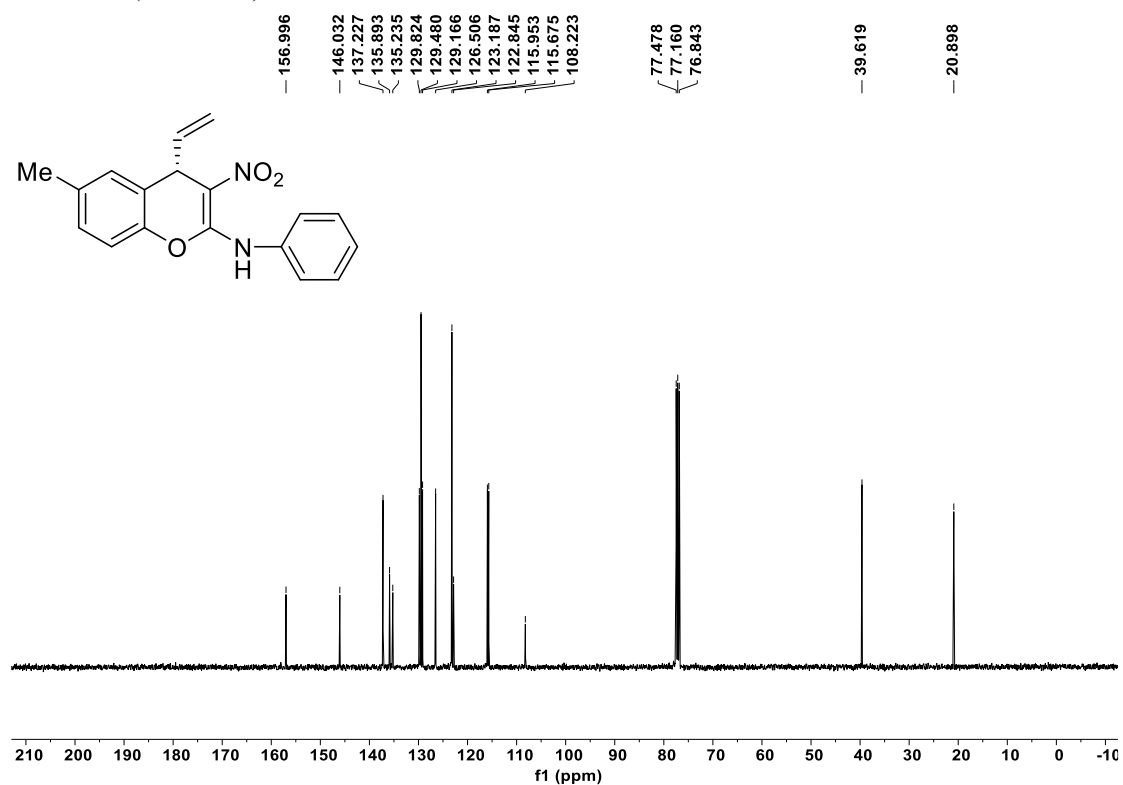
<sup>13</sup>C NMR (100 MHz) of **33** in CDCl<sub>3</sub>



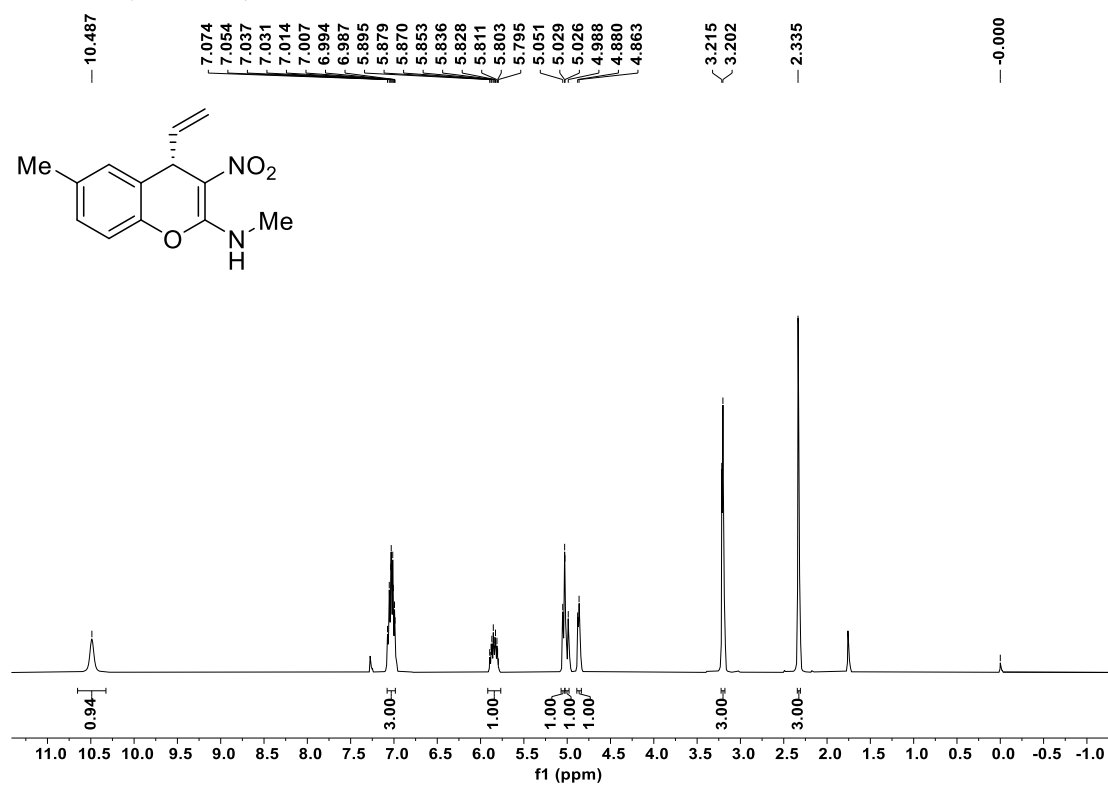
<sup>1</sup>H NMR (400 MHz) of **34** in CDCl<sub>3</sub>



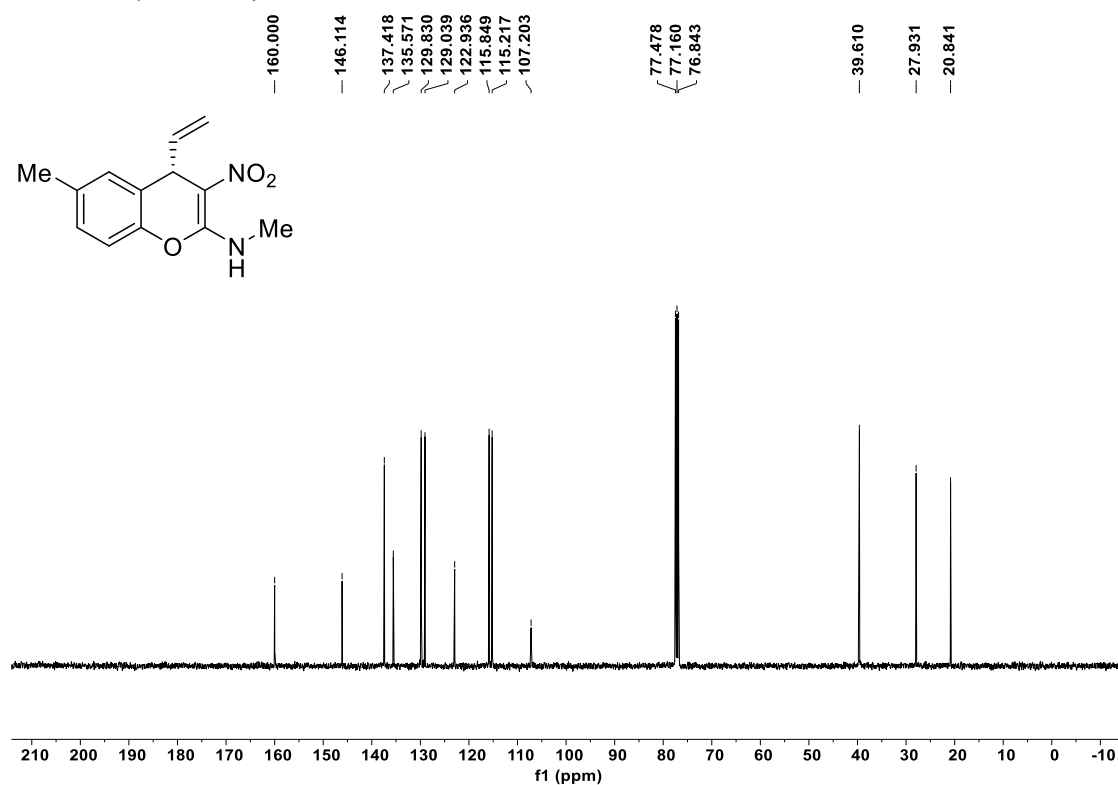
<sup>13</sup>C NMR (100 MHz) of **34** in CDCl<sub>3</sub>



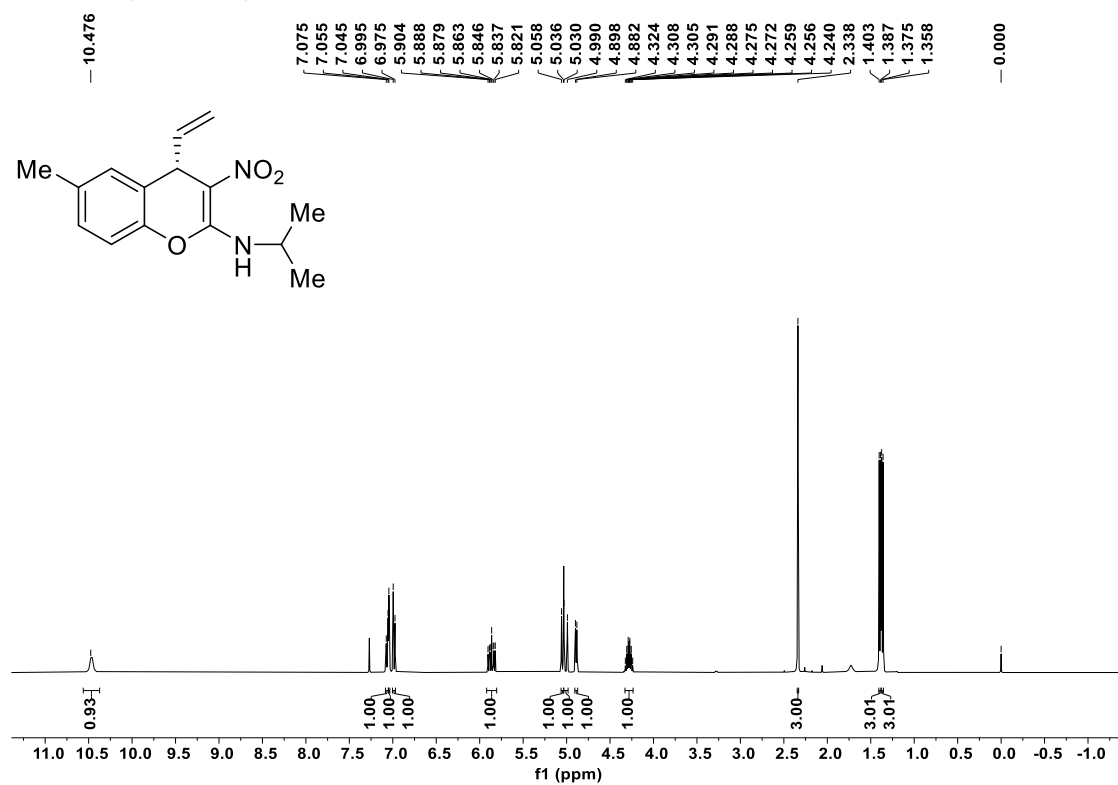
$^1\text{H}$  NMR (400 MHz) of **35** in  $\text{CDCl}_3$



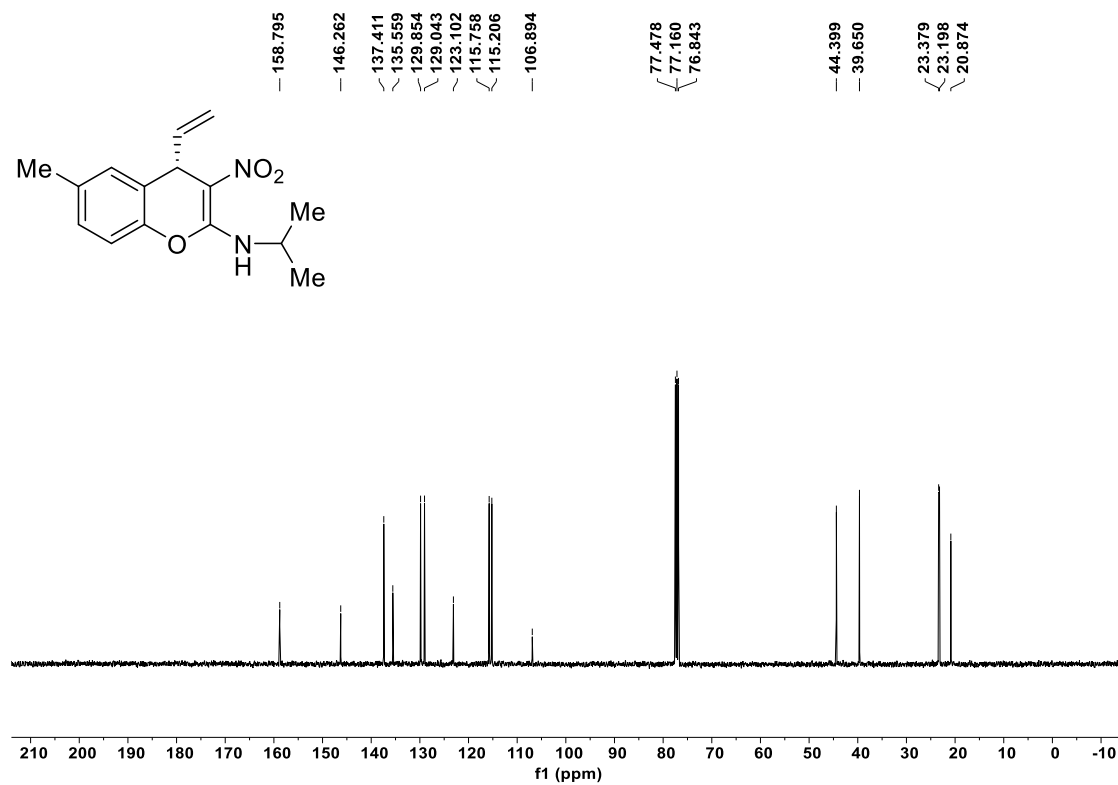
$^{13}\text{C}$  NMR (100 MHz) of **35** in  $\text{CDCl}_3$



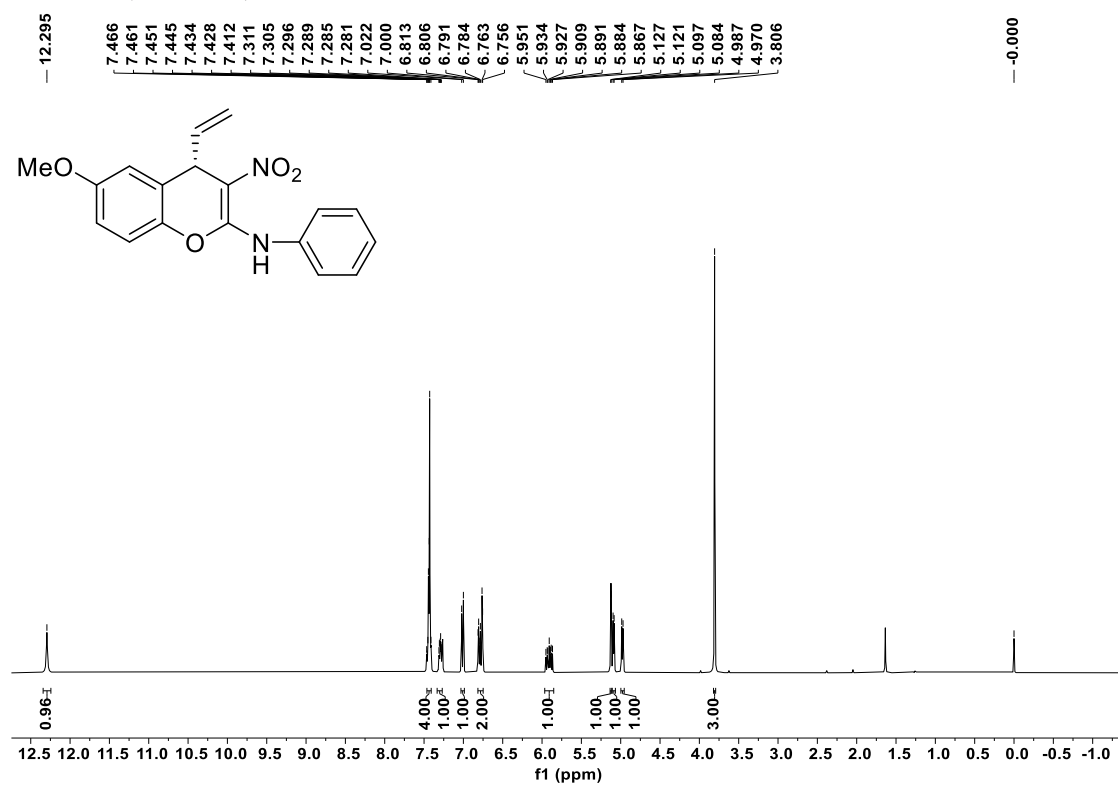
$^1\text{H}$  NMR (400 MHz) of **36** in  $\text{CDCl}_3$



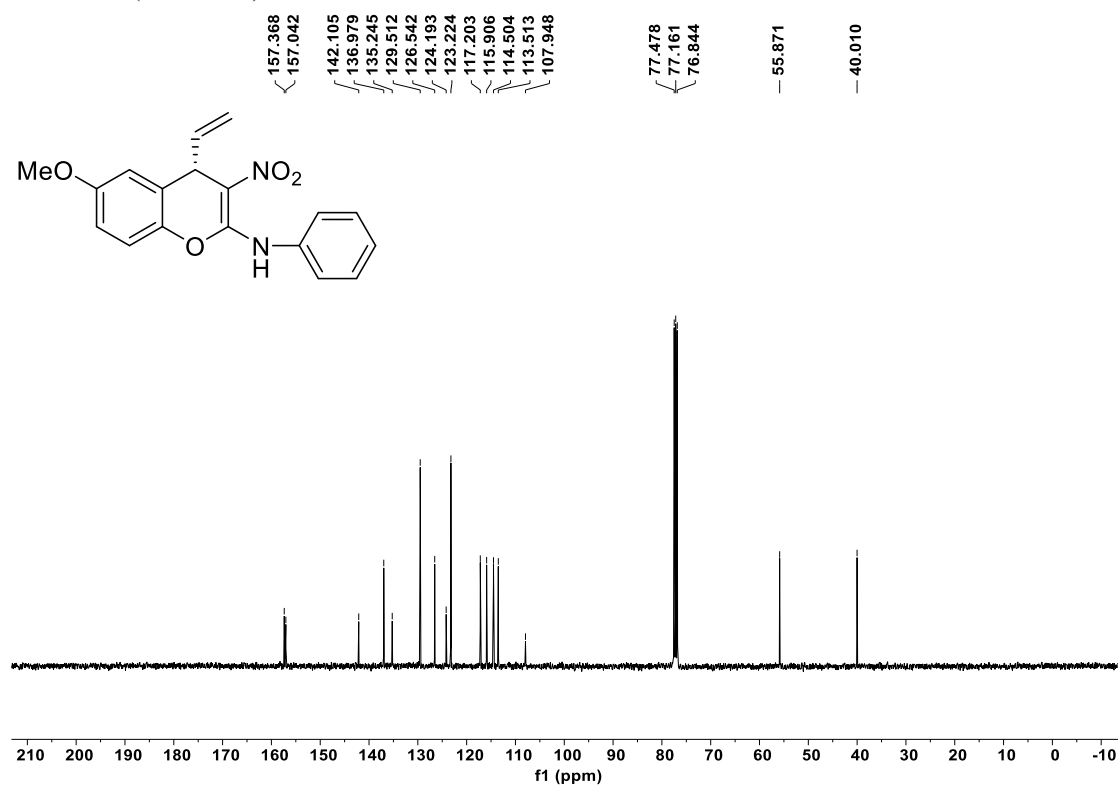
$^{13}\text{C}$  NMR (100 MHz) of **36** in  $\text{CDCl}_3$



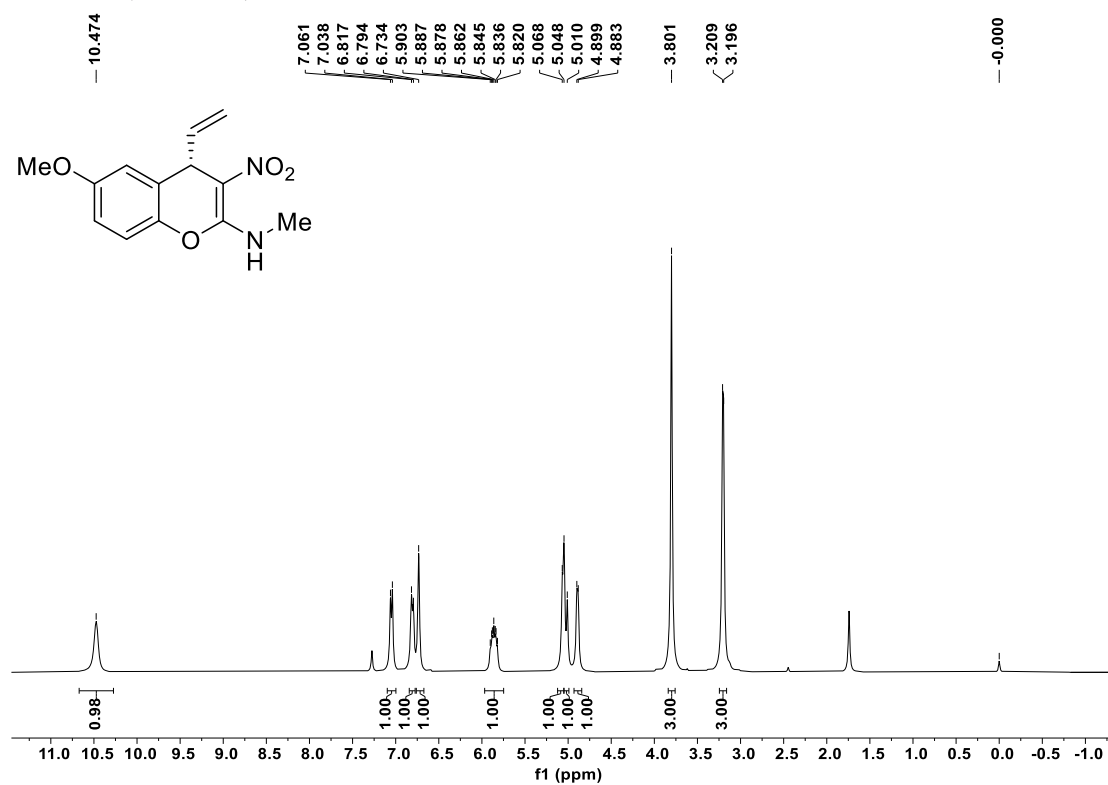
<sup>1</sup>H NMR (400 MHz) of **37** in CDCl<sub>3</sub>



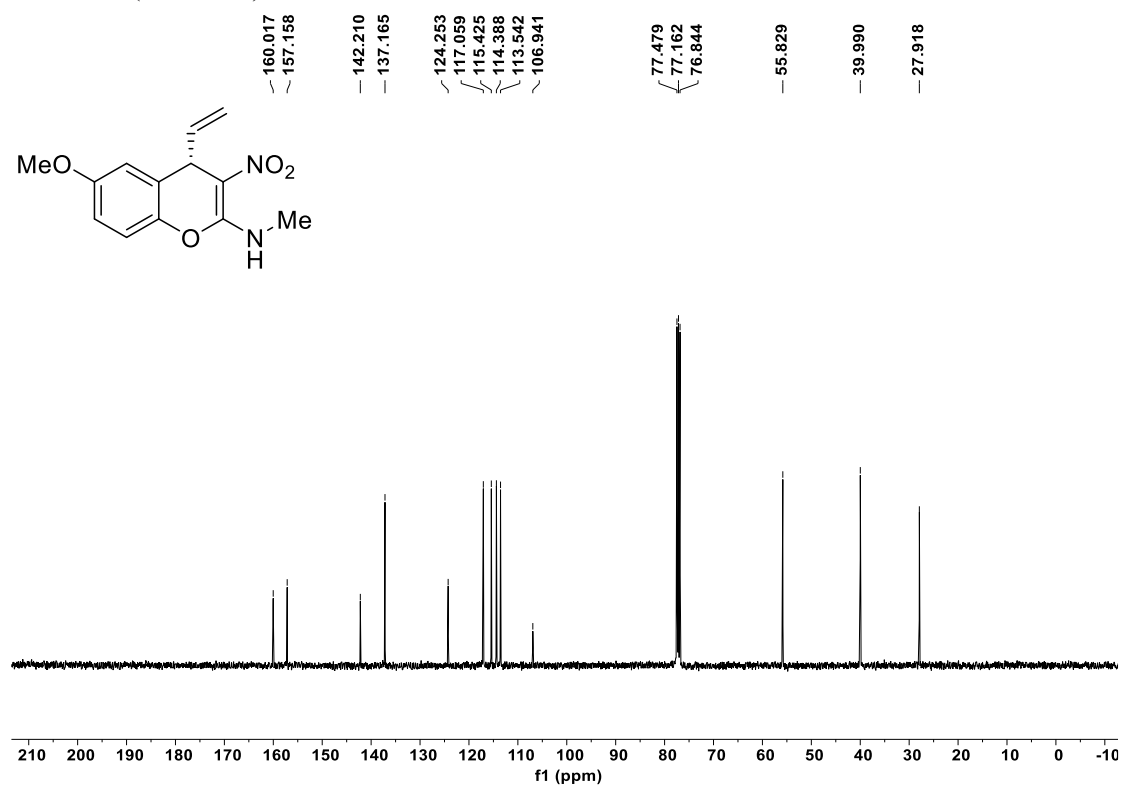
<sup>13</sup>C NMR (100 MHz) of **37** in CDCl<sub>3</sub>



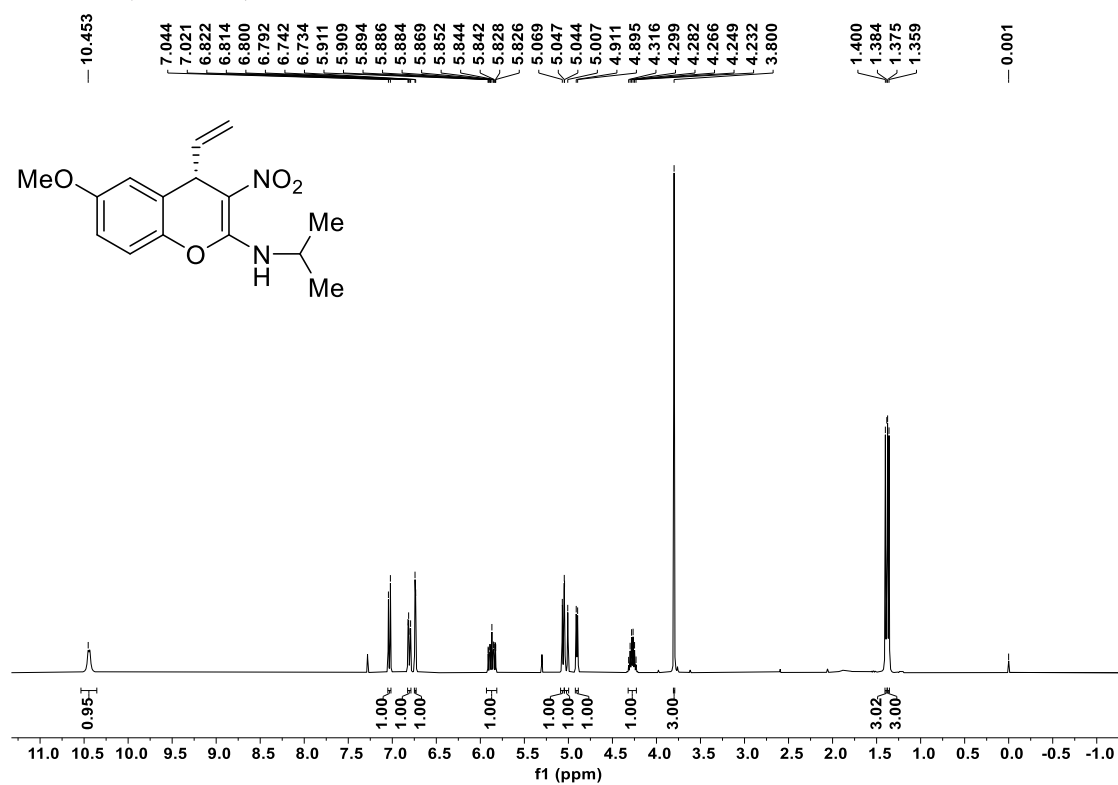
<sup>1</sup>H NMR (400 MHz) of **38** in CDCl<sub>3</sub>



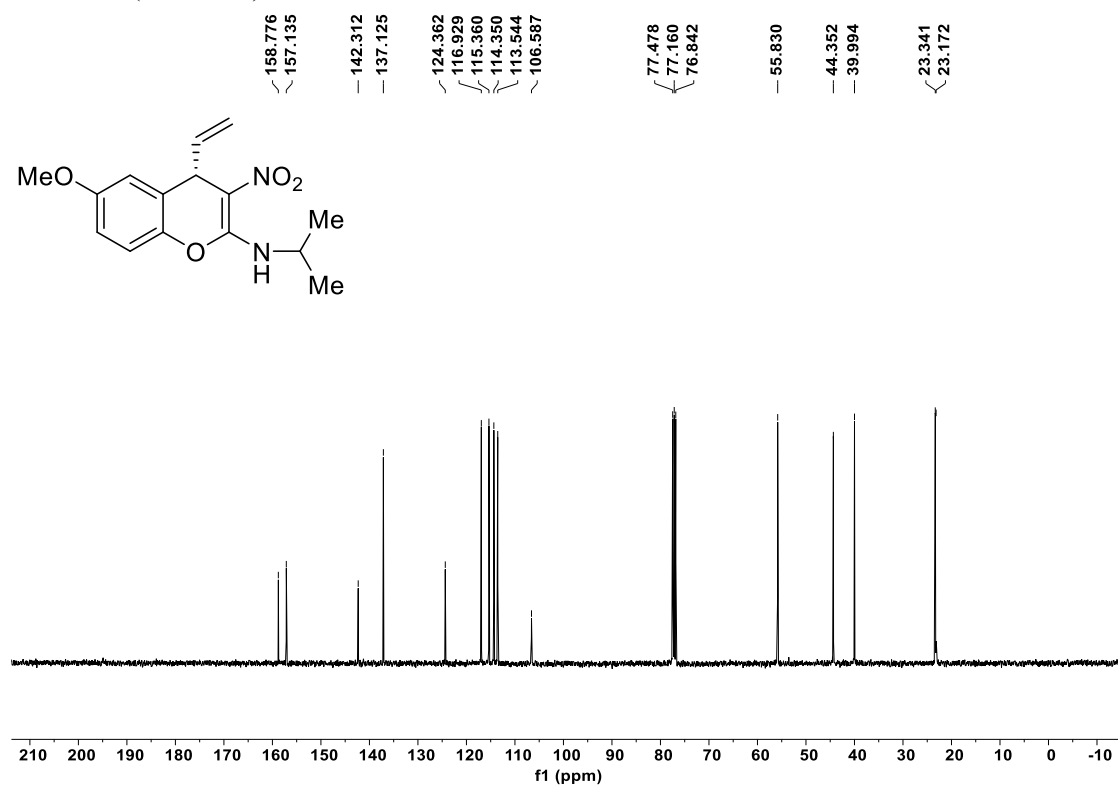
<sup>13</sup>C NMR (100 MHz) of **38** in CDCl<sub>3</sub>



<sup>1</sup>H NMR (400 MHz) of **39** in CDCl<sub>3</sub>

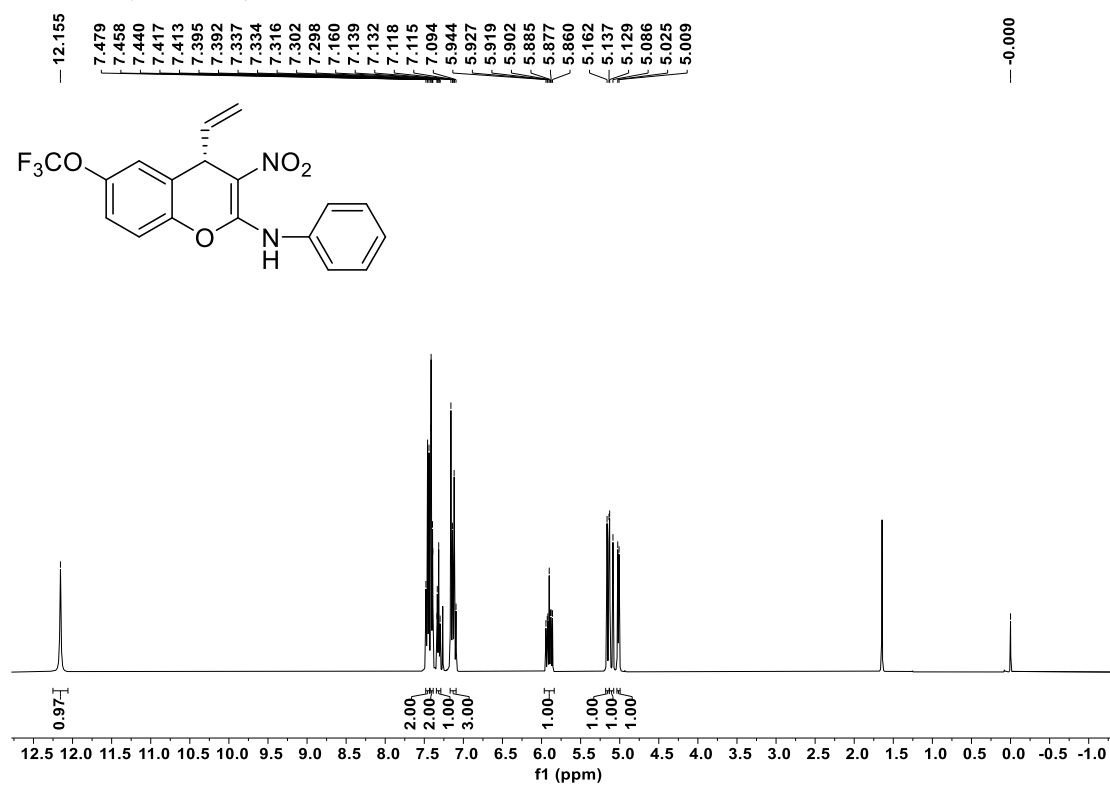


<sup>13</sup>C NMR (100 MHz) of **39** in CDCl<sub>3</sub>

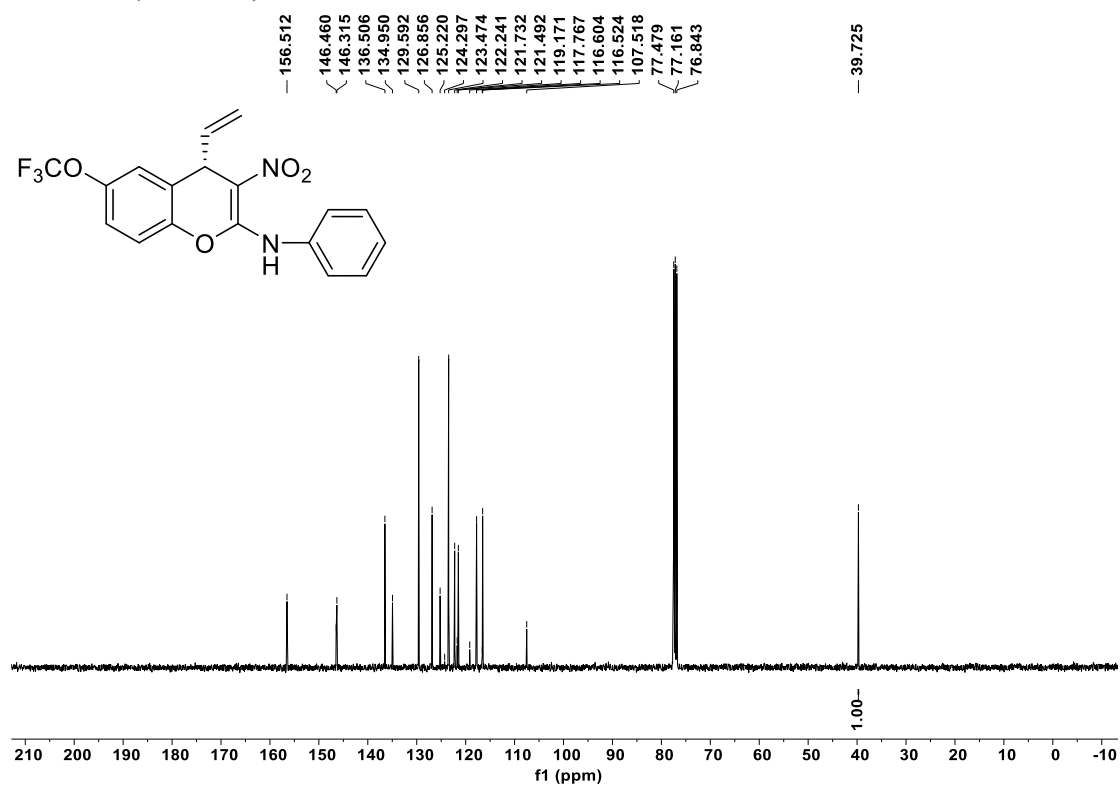




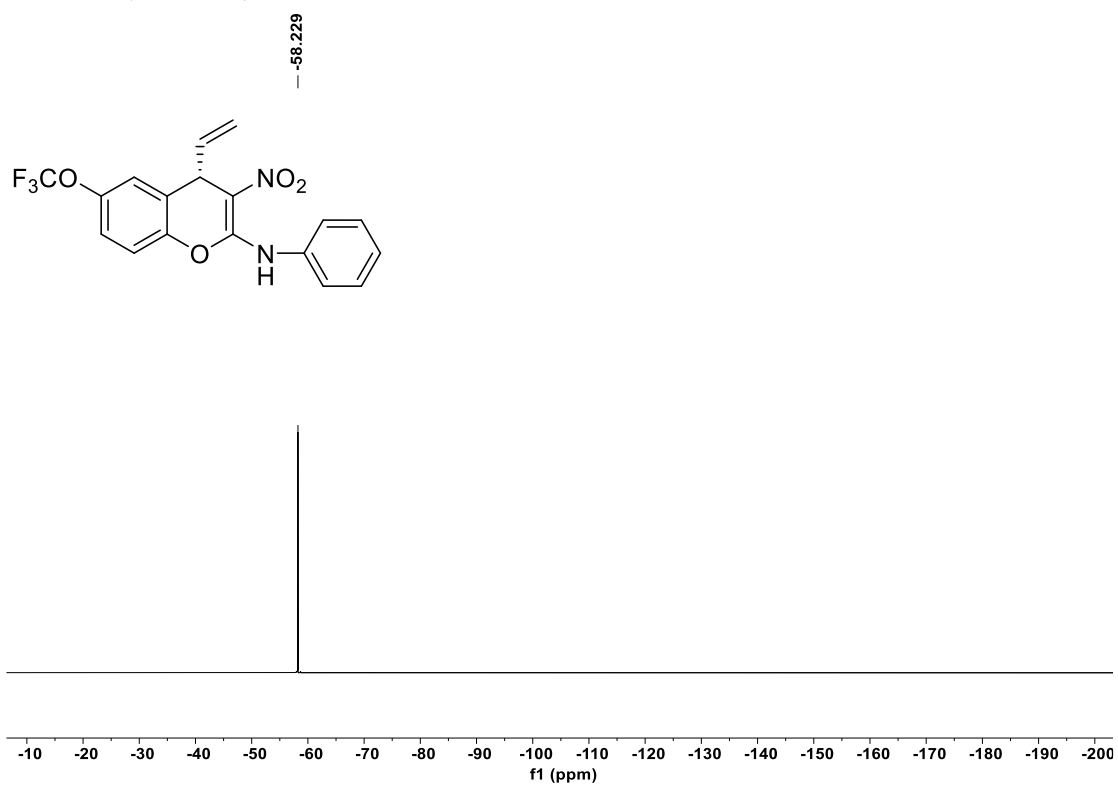
<sup>1</sup>H NMR (400 MHz) of **40** in CDCl<sub>3</sub>



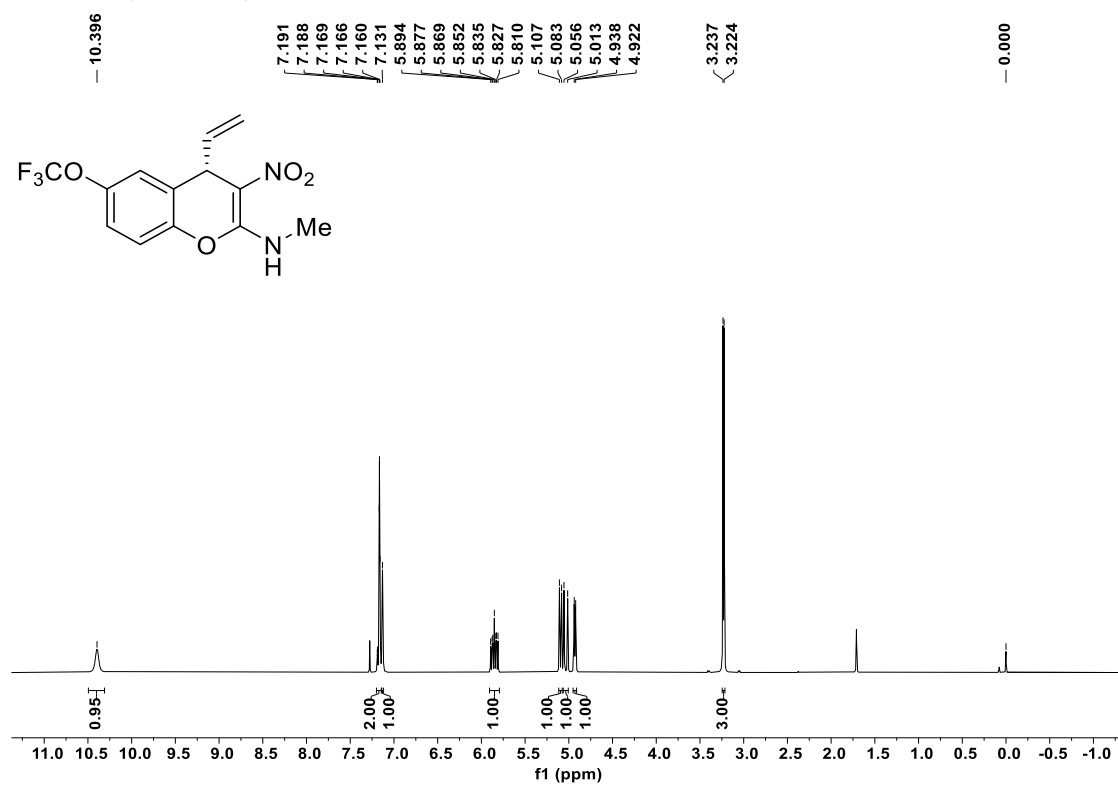
<sup>13</sup>C NMR (100 MHz) of **40** in CDCl<sub>3</sub>



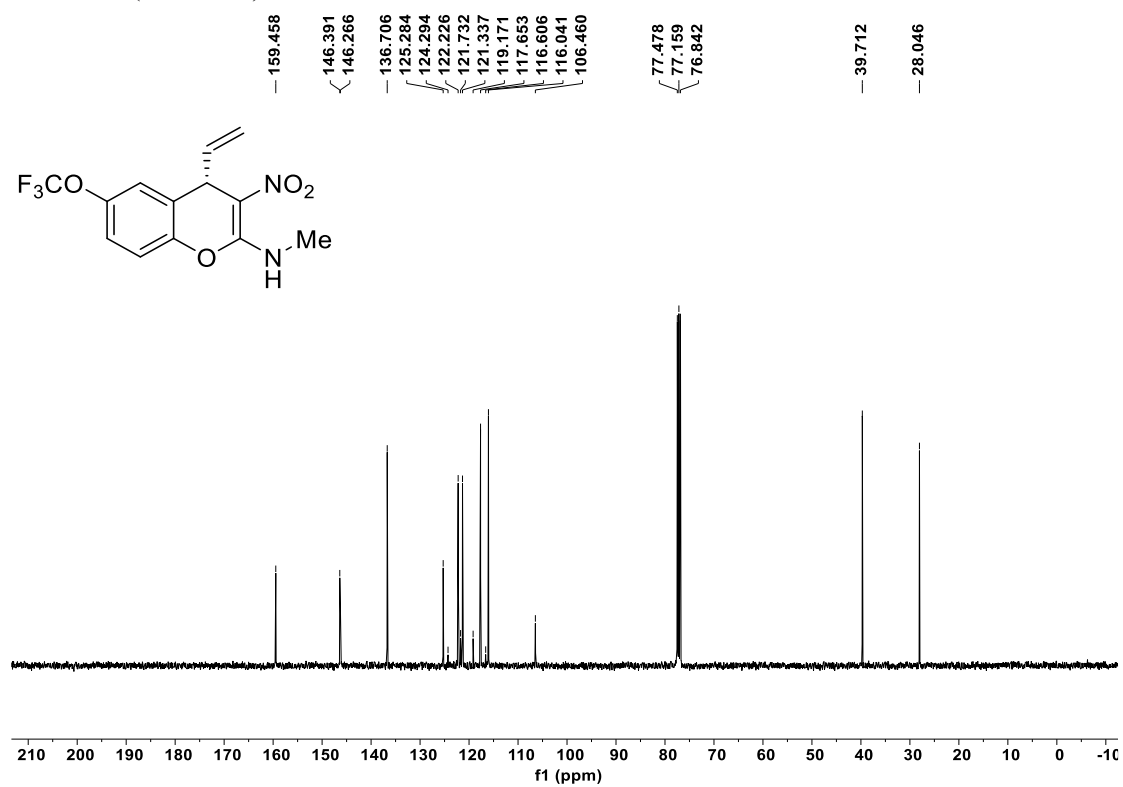
$^{19}\text{F}$  NMR (376 MHz) of **40** in  $\text{CDCl}_3$



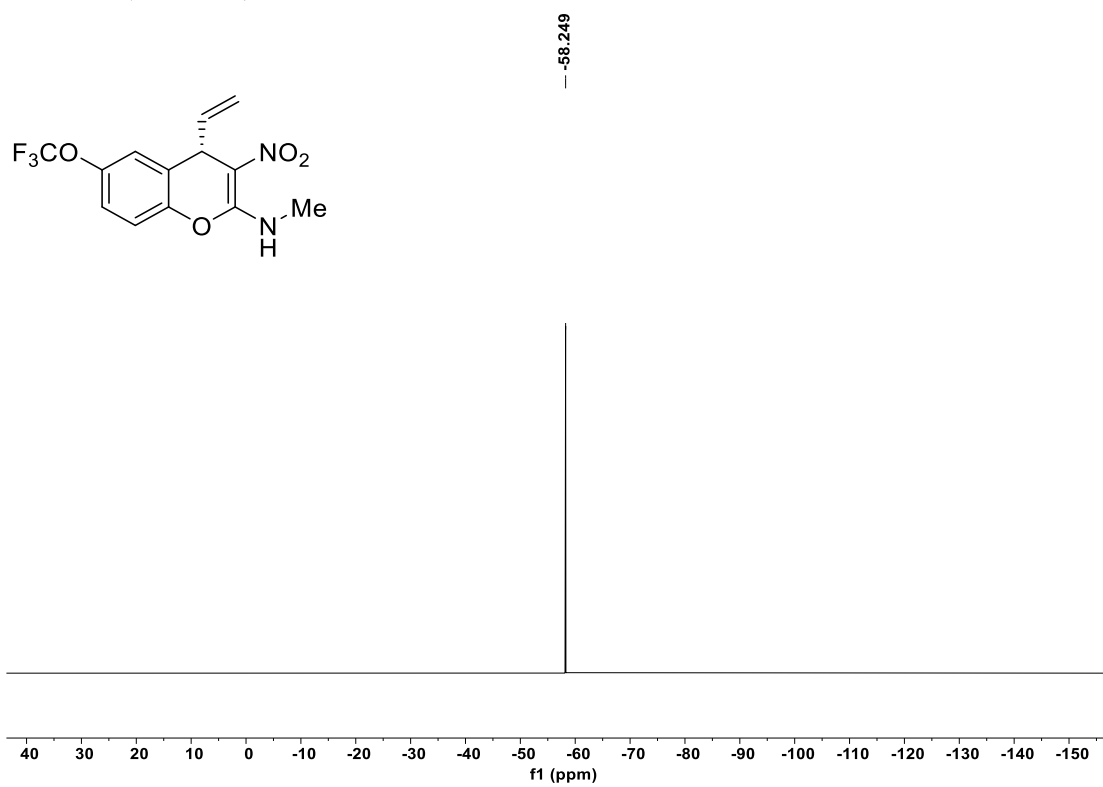
$^1\text{H}$  NMR (400 MHz) of **41** in  $\text{CDCl}_3$



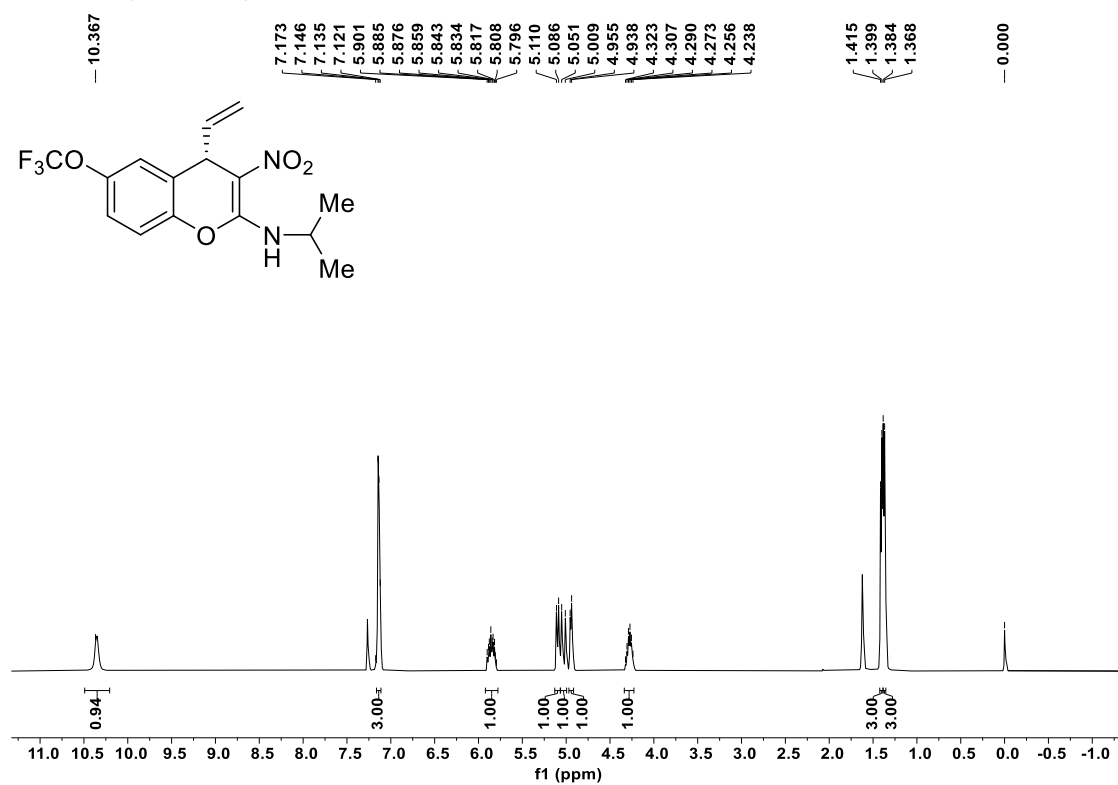
$^{13}\text{C}$  NMR (100 MHz) of **41** in  $\text{CDCl}_3$



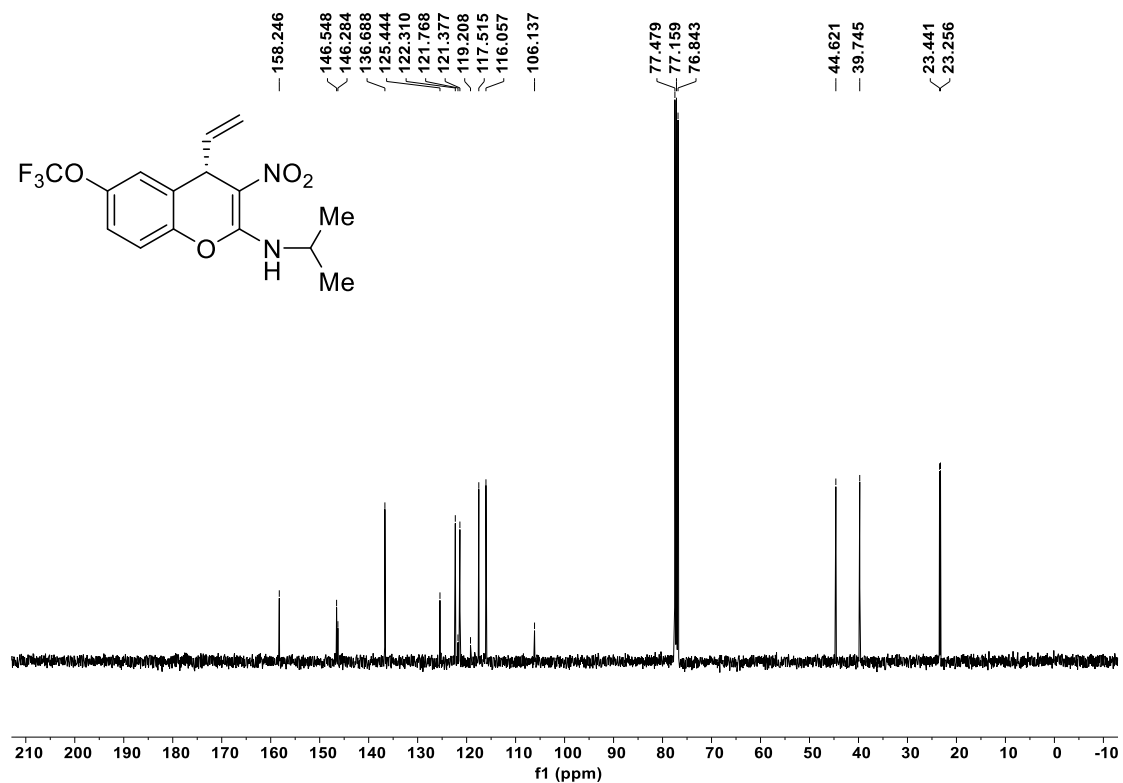
$^{19}\text{F}$  NMR (376 MHz) of **41** in  $\text{CDCl}_3$



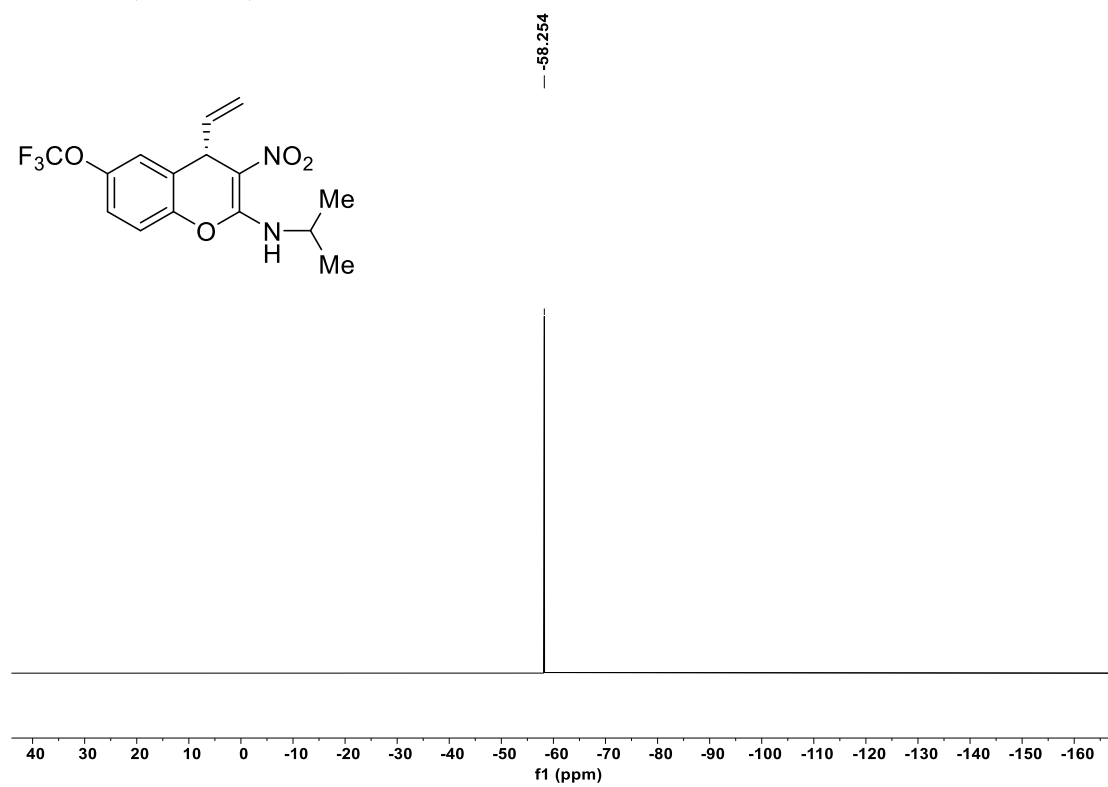
<sup>1</sup>H NMR (400 MHz) of **42** in CDCl<sub>3</sub>



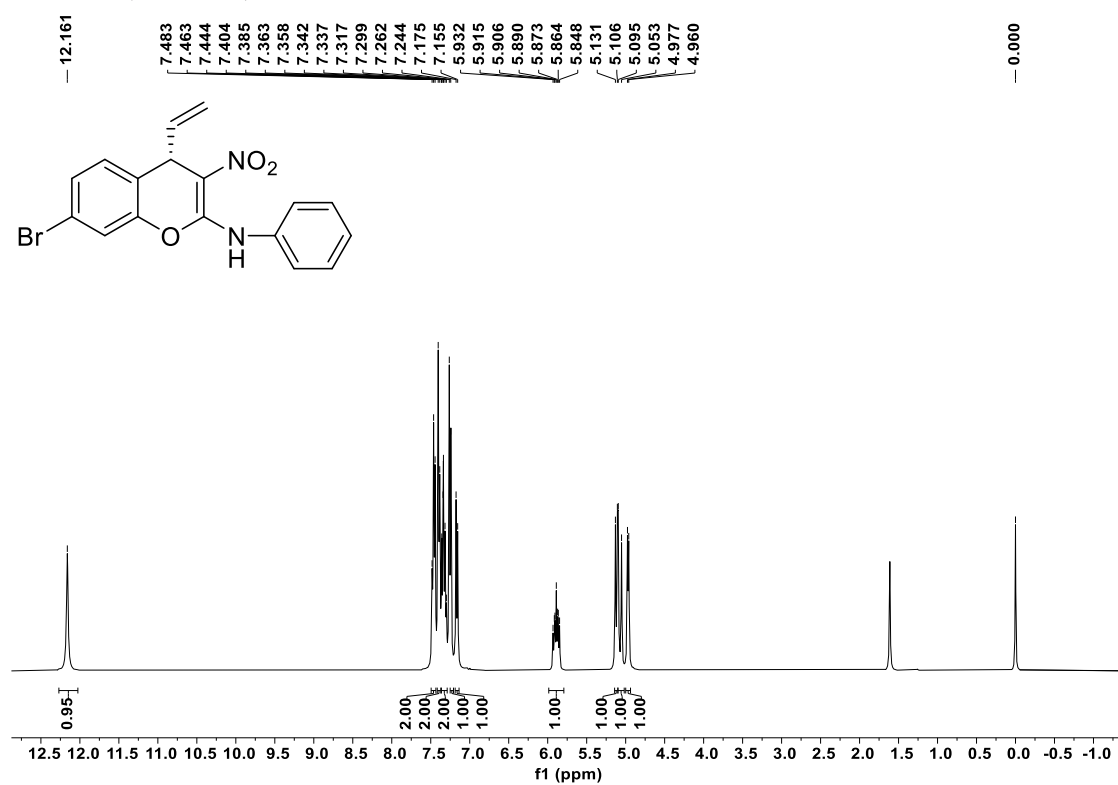
<sup>13</sup>C NMR (100 MHz) of **42** in CDCl<sub>3</sub>



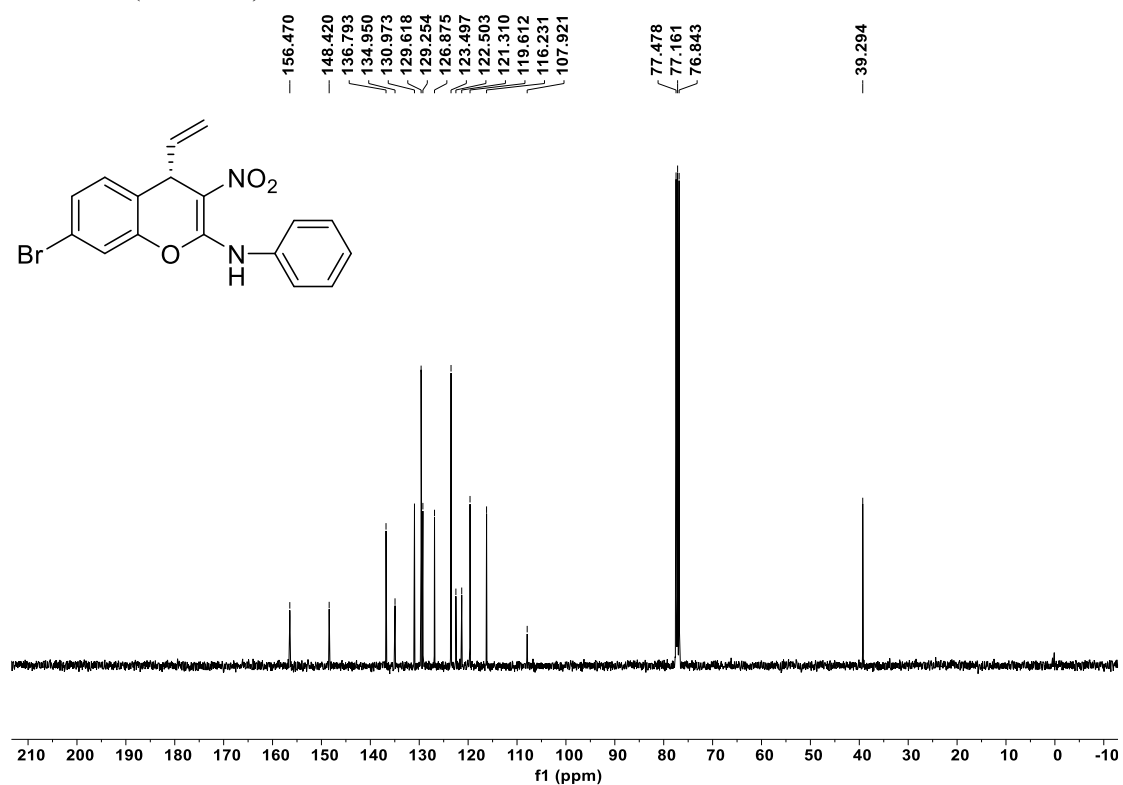
$^{19}\text{F}$  NMR (376 MHz) of **42** in  $\text{CDCl}_3$



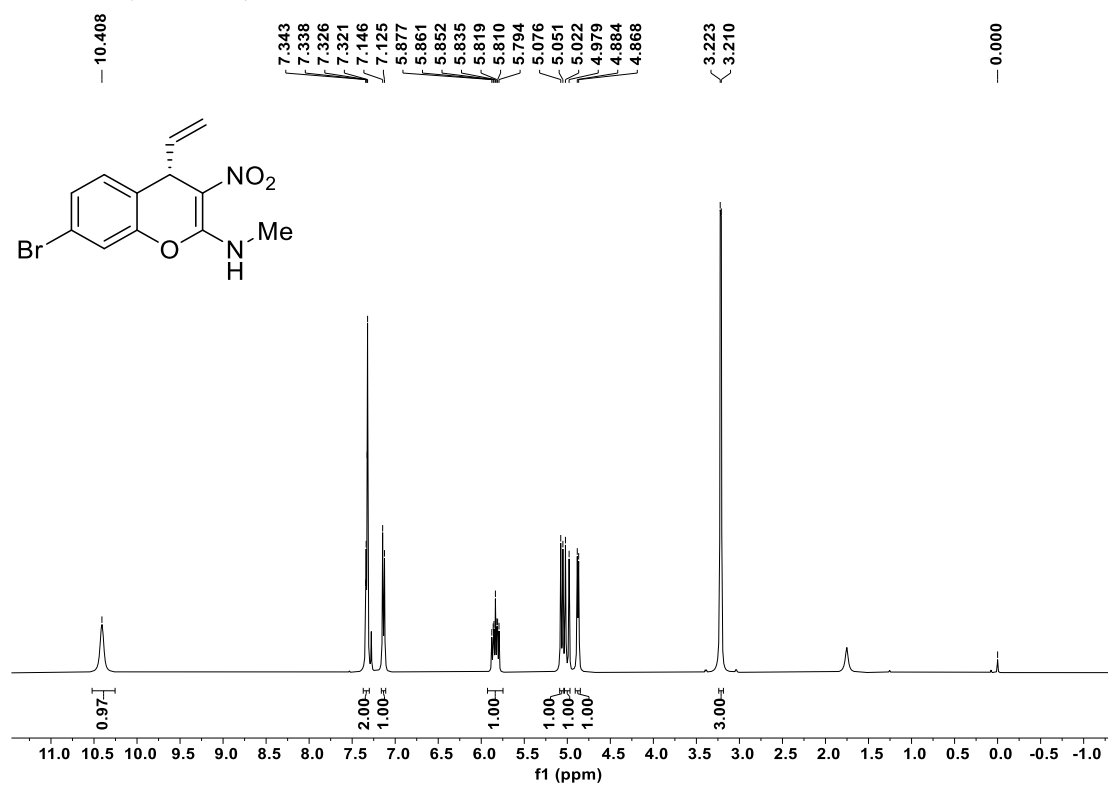
<sup>1</sup>H NMR (400 MHz) of **43** in CDCl<sub>3</sub>



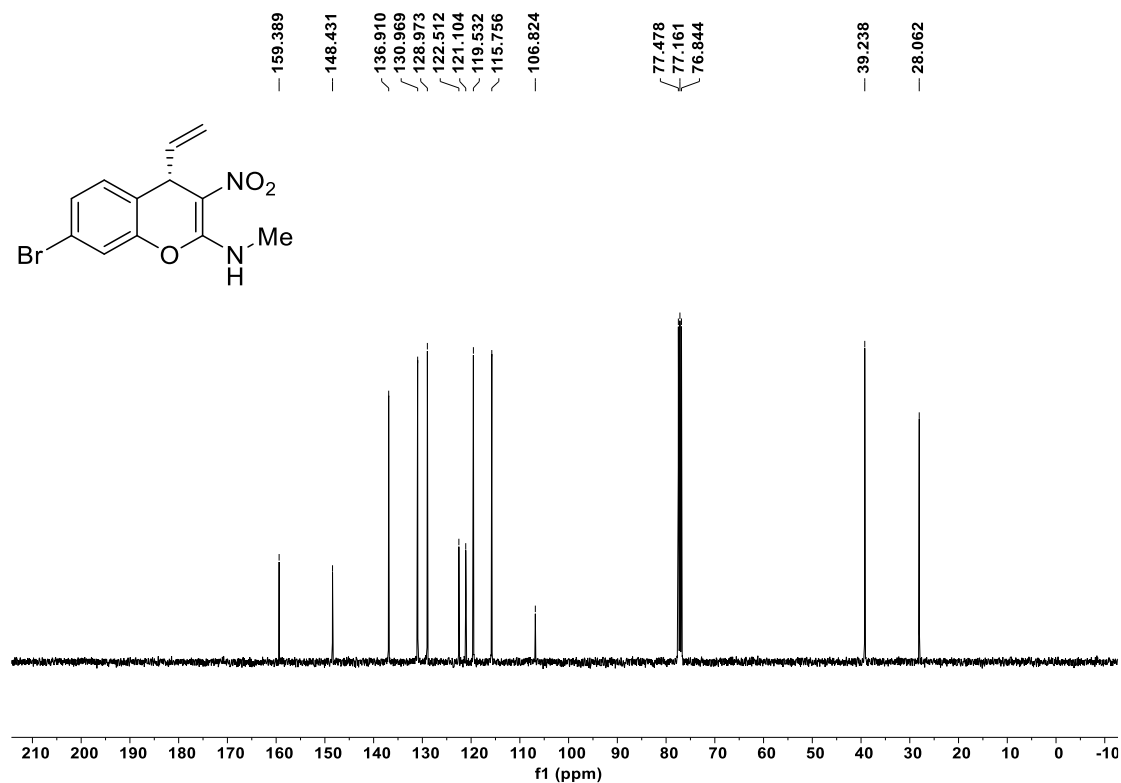
<sup>13</sup>C NMR (100 MHz) of **43** in CDCl<sub>3</sub>



$^1\text{H}$  NMR (400 MHz) of **44** in  $\text{CDCl}_3$

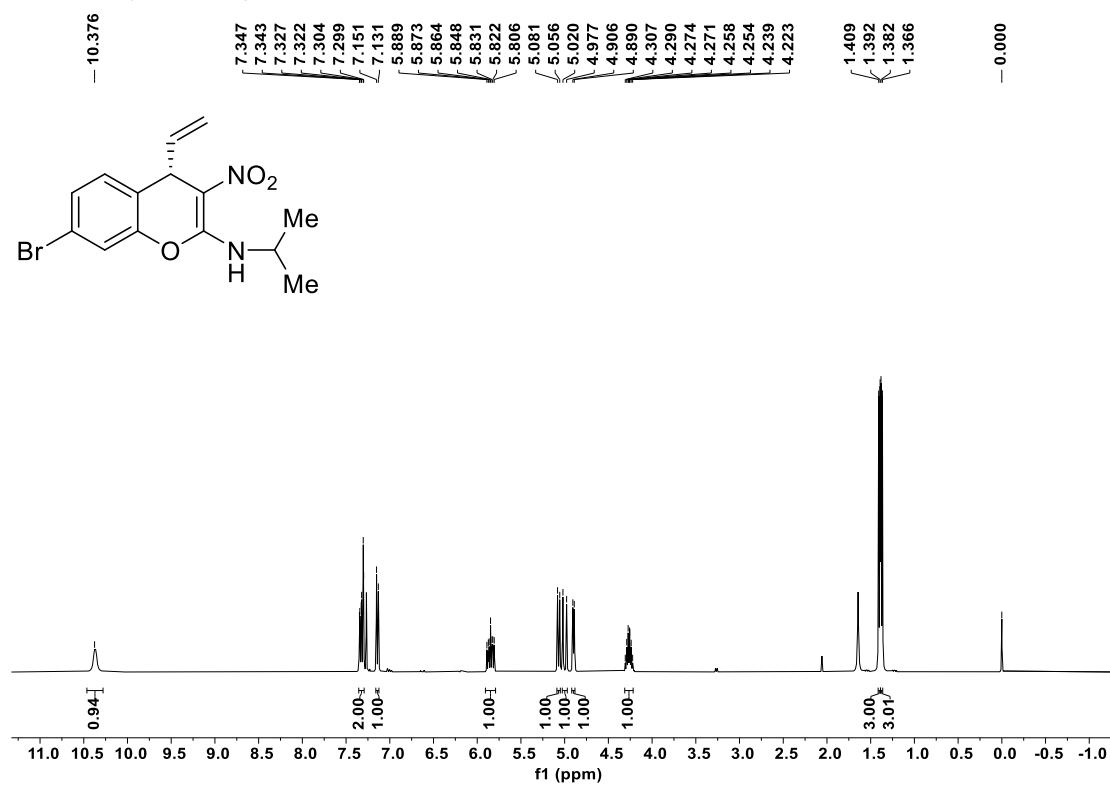


$^{13}\text{C}$  NMR (100 MHz) of **44** in  $\text{CDCl}_3$

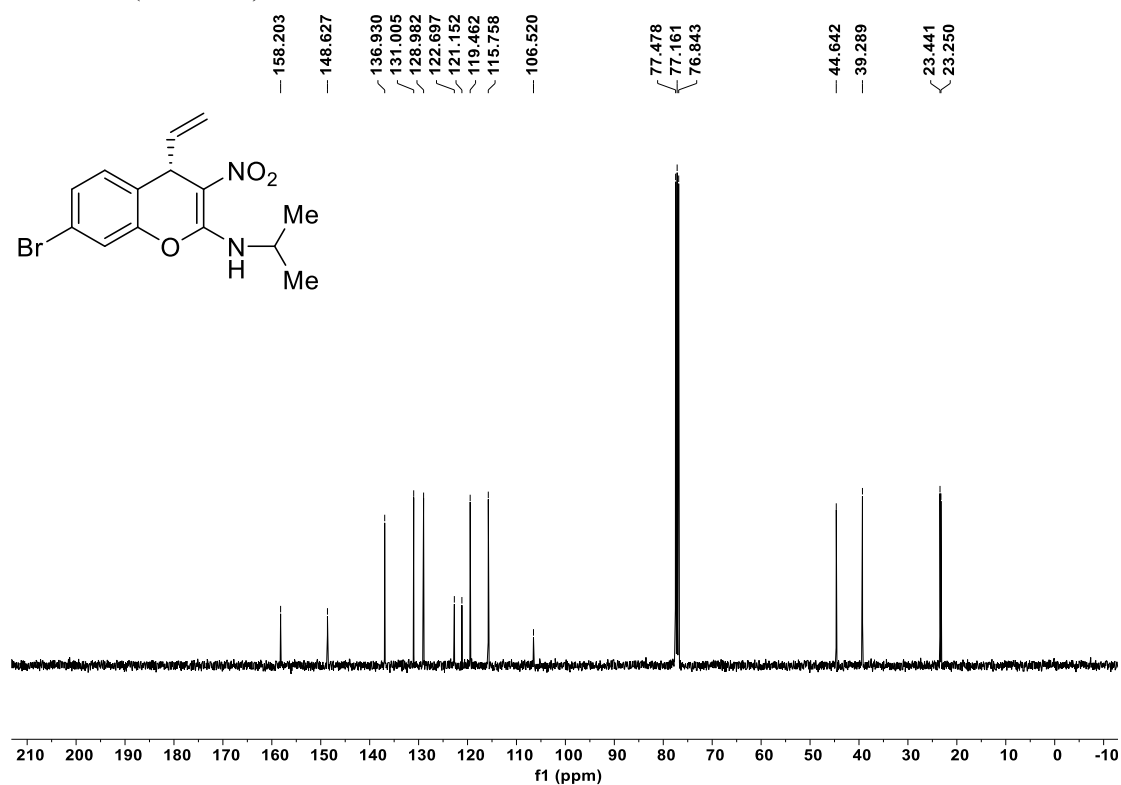




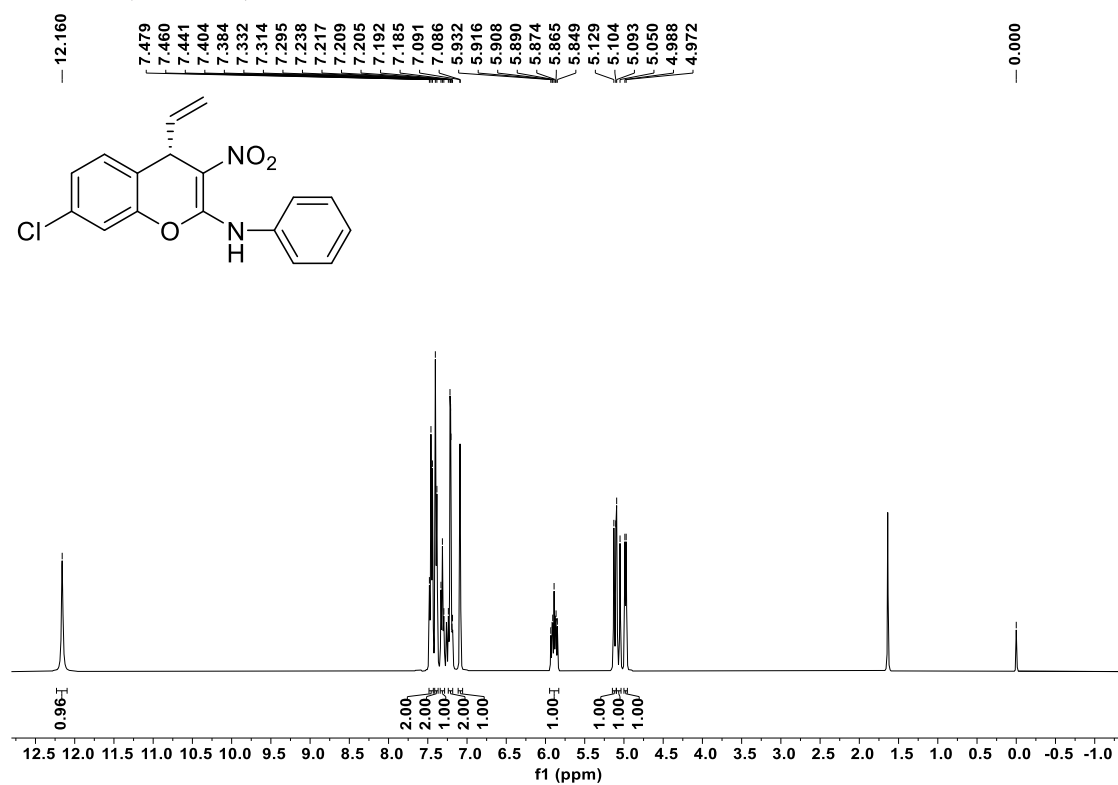
<sup>1</sup>H NMR (400 MHz) of **45** in CDCl<sub>3</sub>



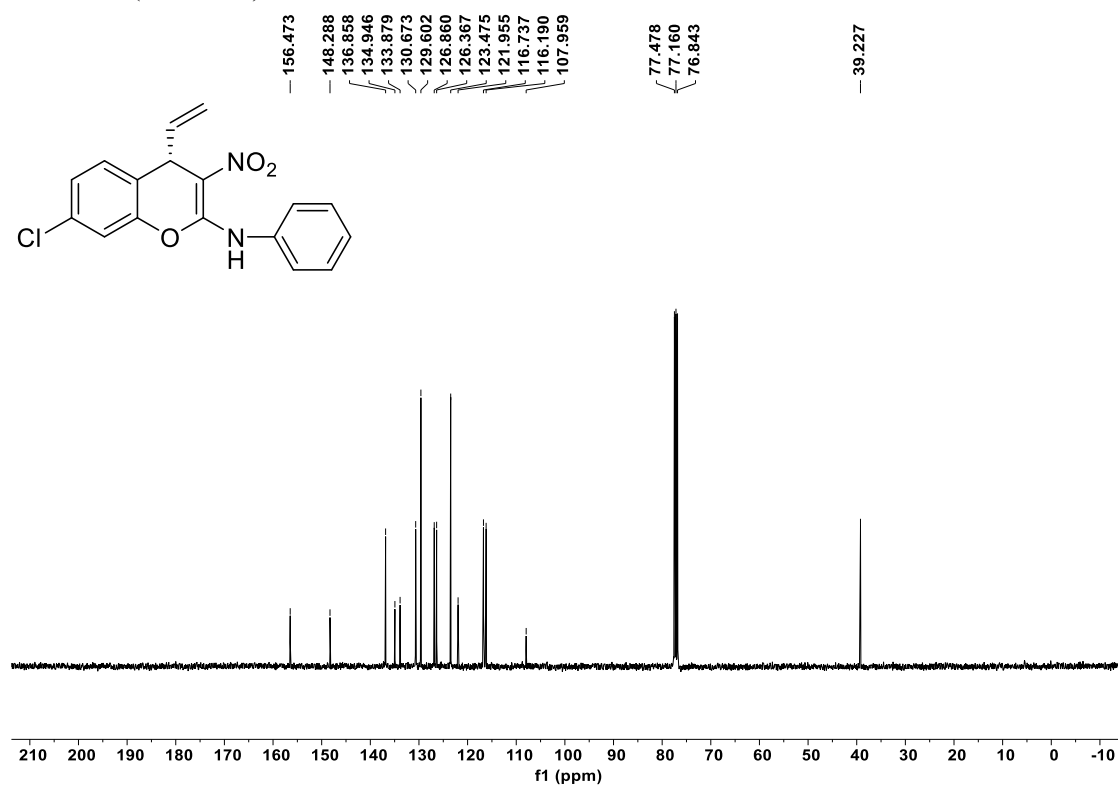
<sup>13</sup>C NMR (100 MHz) of **45** in CDCl<sub>3</sub>



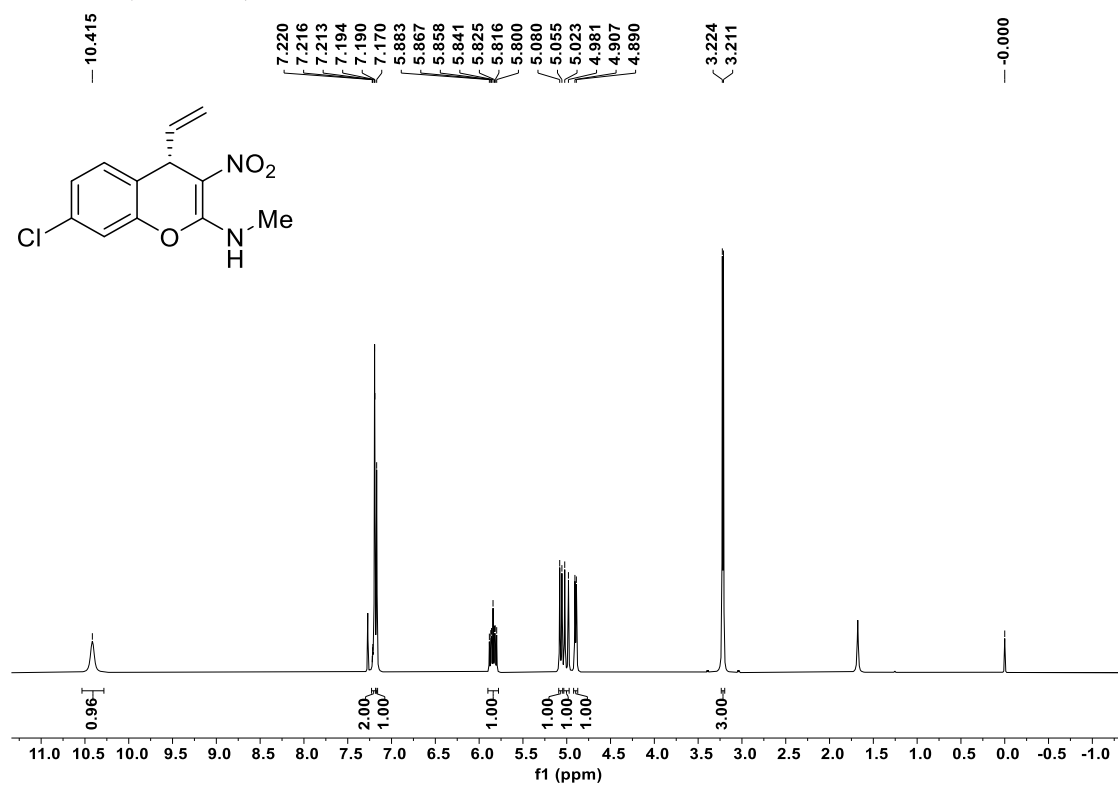
$^1\text{H}$  NMR (400 MHz) of **46** in  $\text{CDCl}_3$



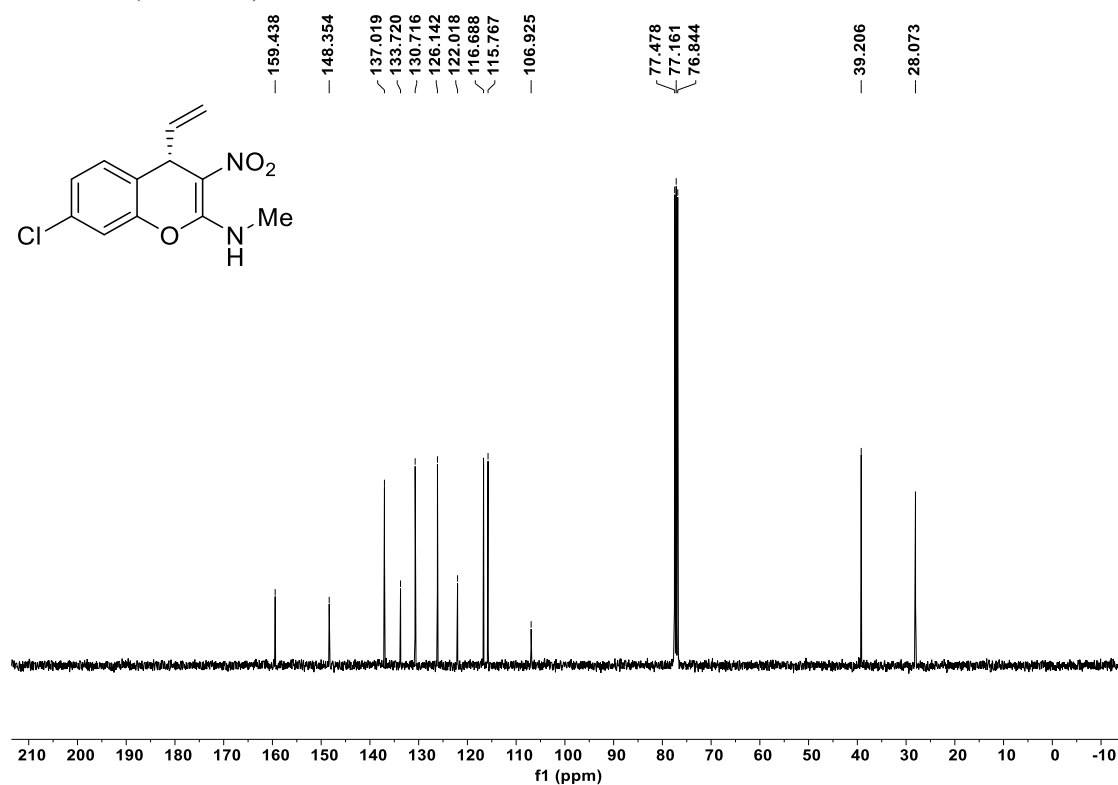
$^{13}\text{C}$  NMR (100 MHz) of **46** in  $\text{CDCl}_3$



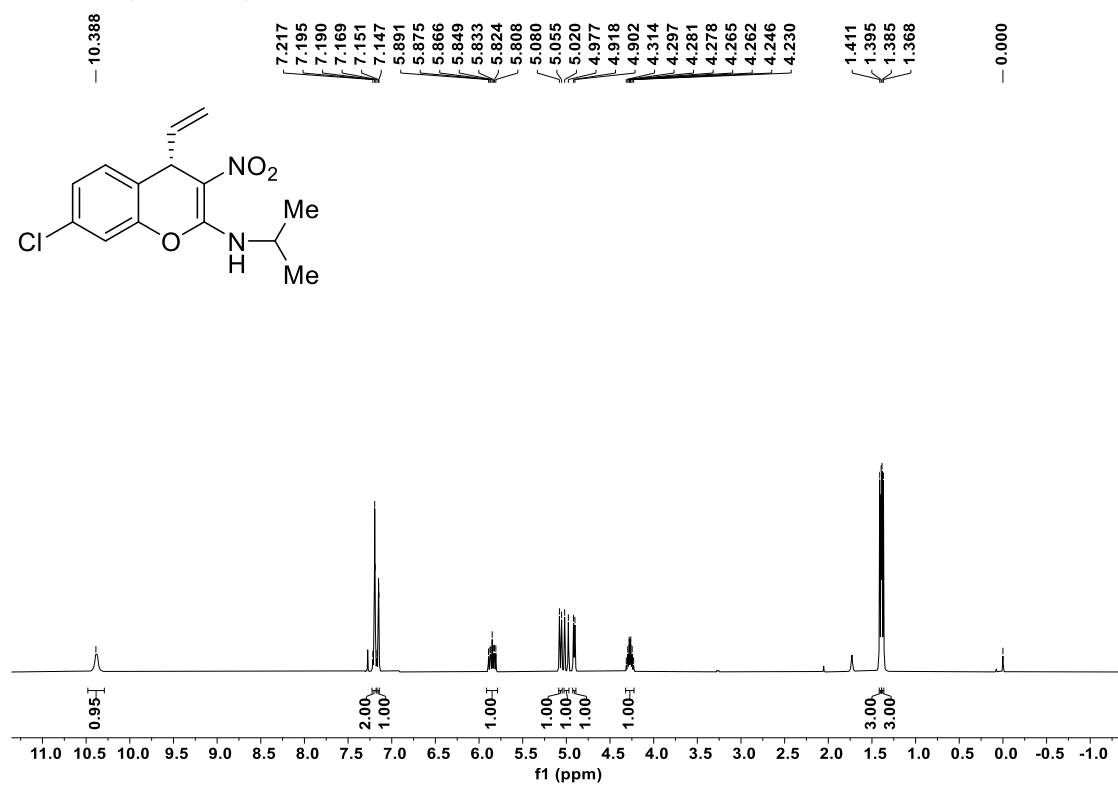
<sup>1</sup>H NMR (400 MHz) of **47** in CDCl<sub>3</sub>



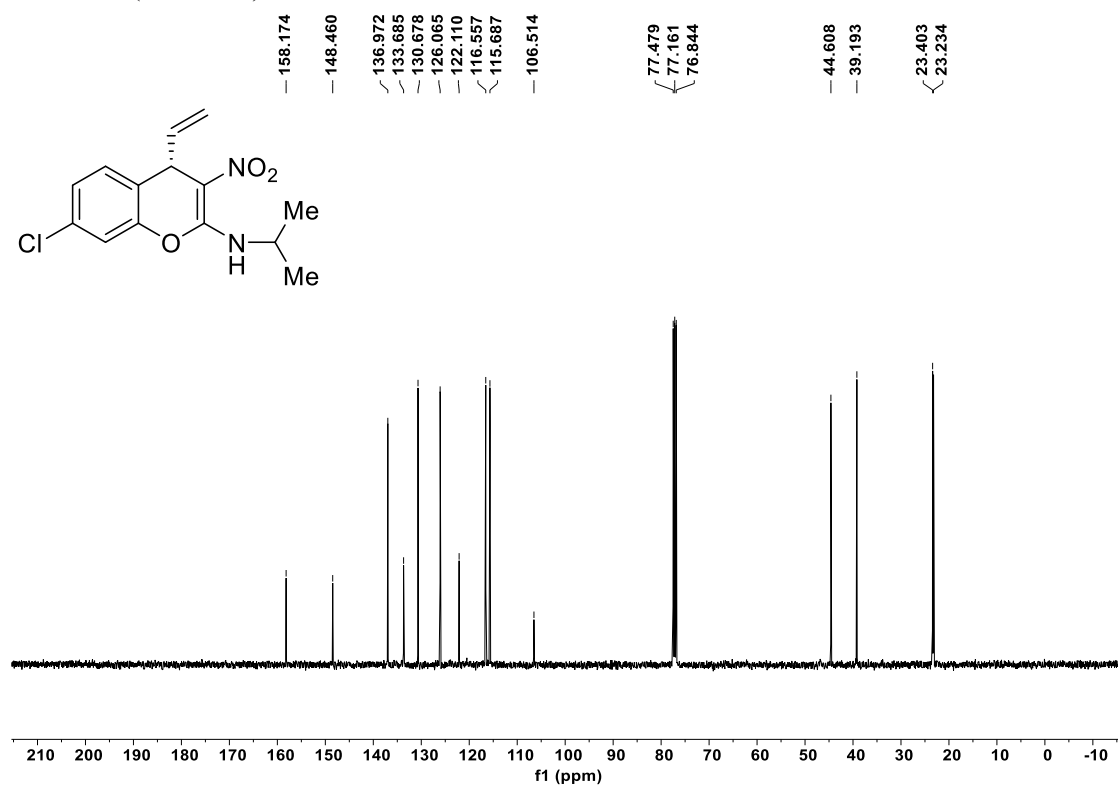
<sup>13</sup>C NMR (100 MHz) of **47** in CDCl<sub>3</sub>



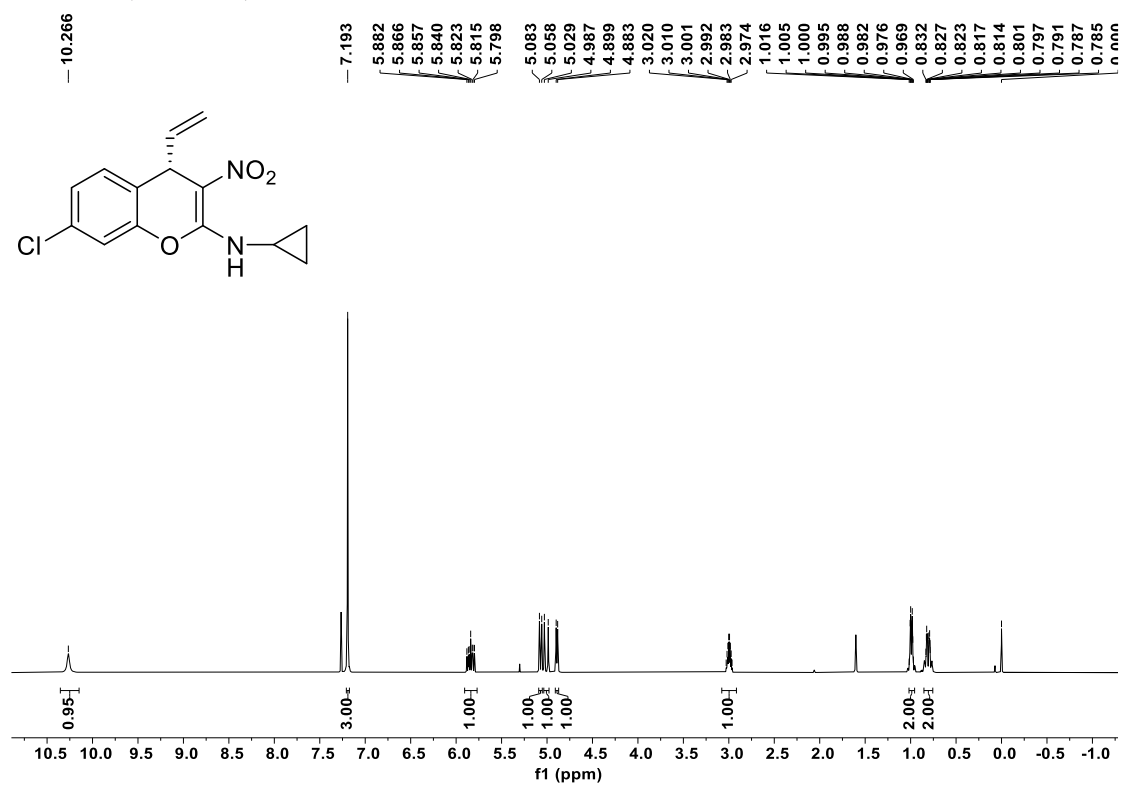
$^1\text{H}$  NMR (400 MHz) of **48** in  $\text{CDCl}_3$



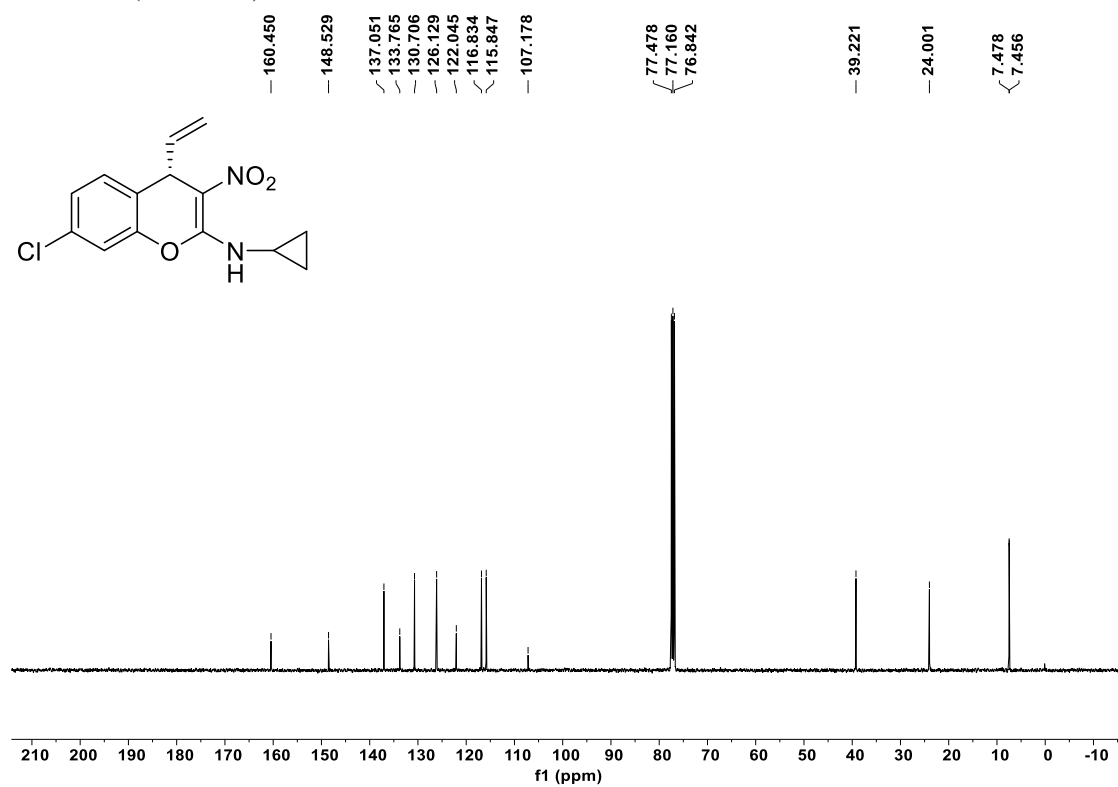
$^{13}\text{C}$  NMR (100 MHz) of **48** in  $\text{CDCl}_3$



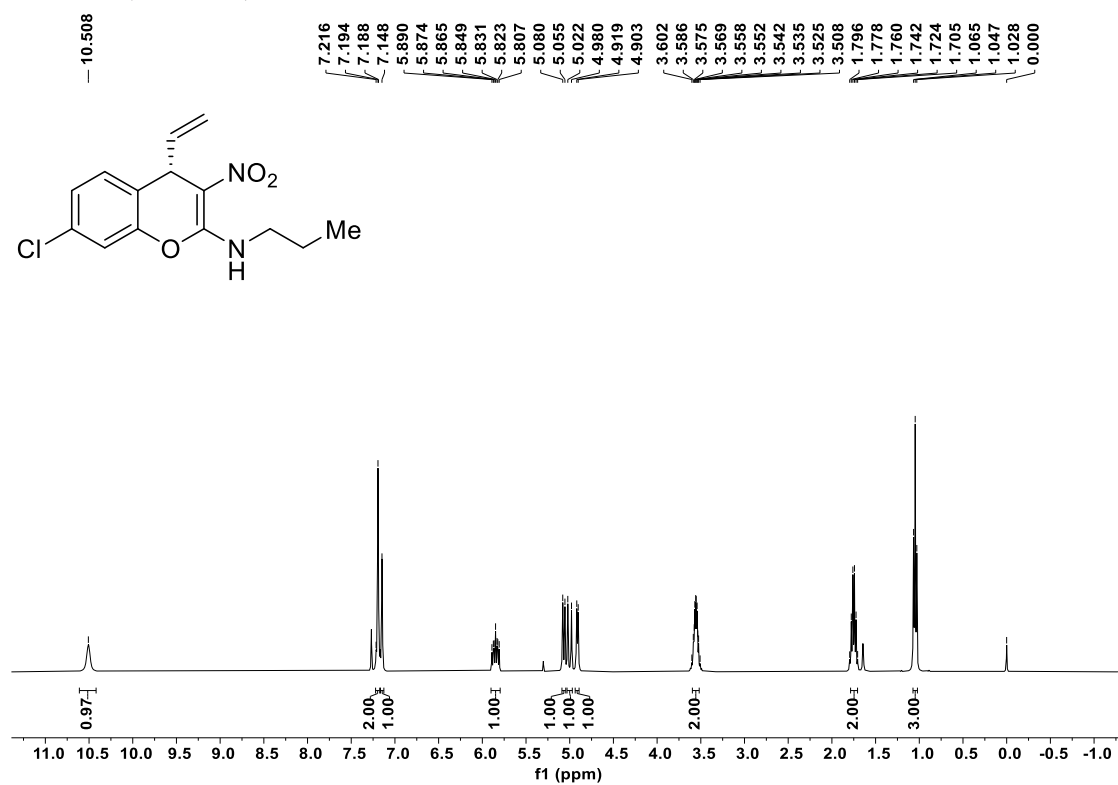
<sup>1</sup>H NMR (400 MHz) of **49** in CDCl<sub>3</sub>



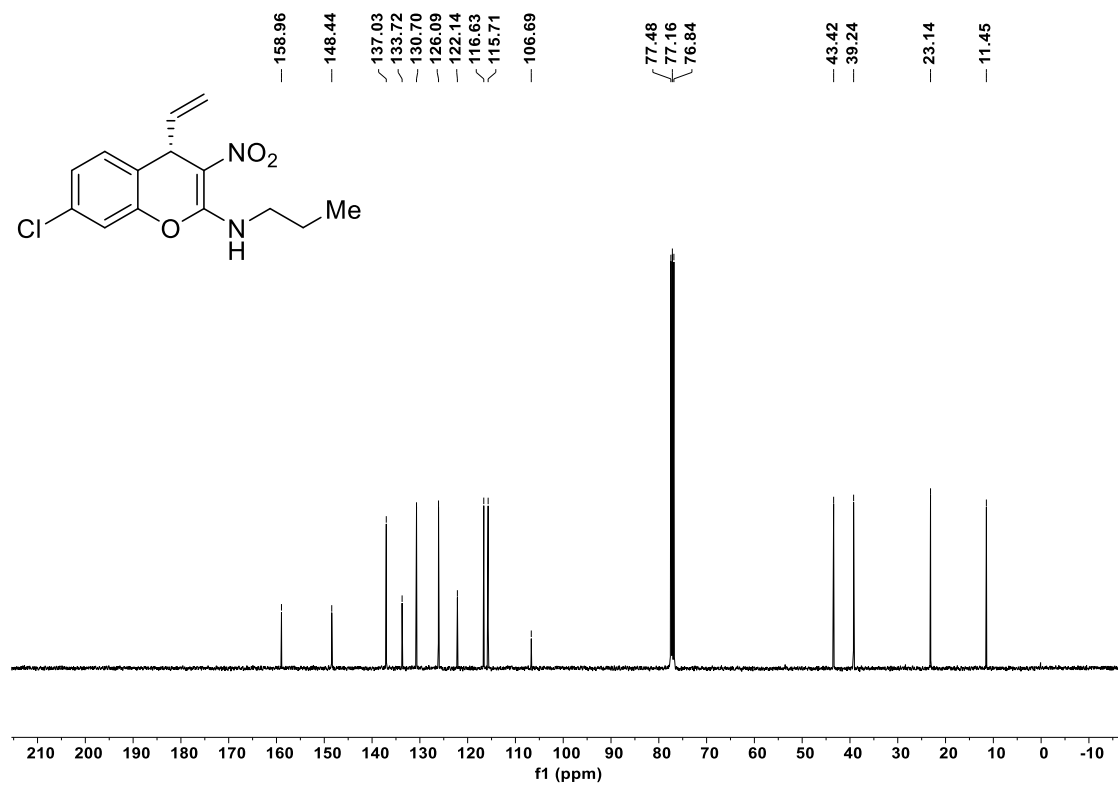
<sup>13</sup>C NMR (100 MHz) of **49** in CDCl<sub>3</sub>



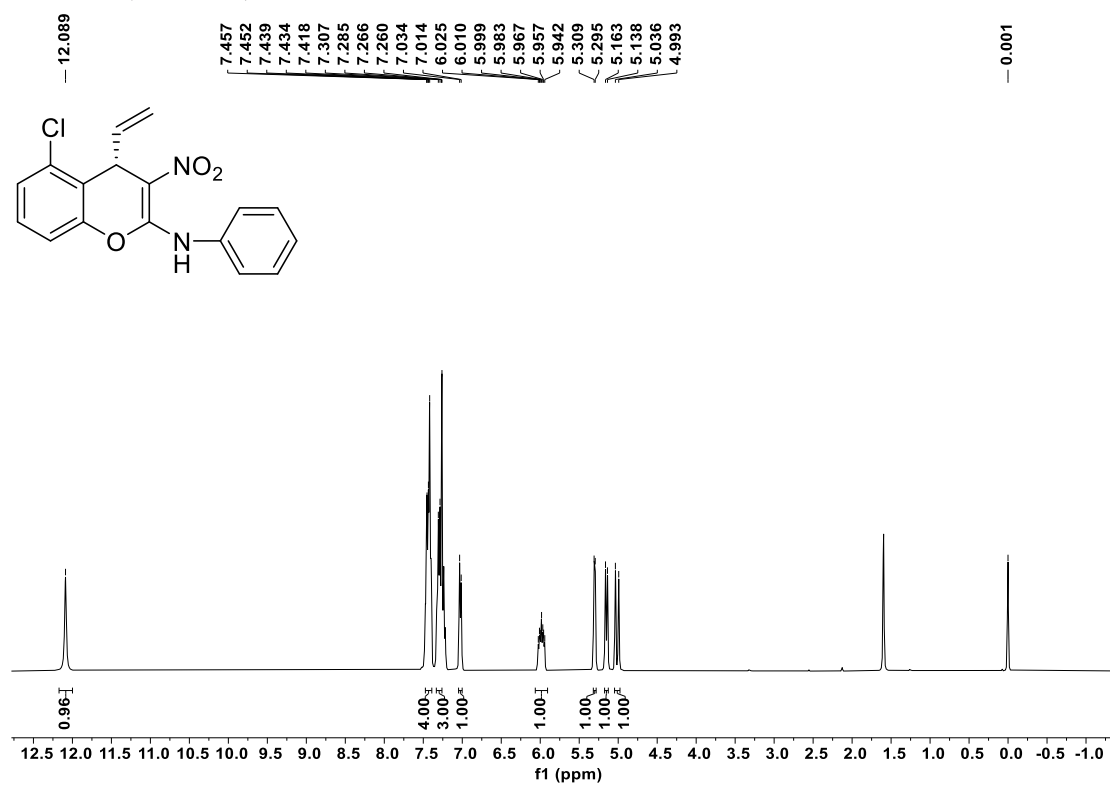
$^1\text{H}$  NMR (400 MHz) of **50** in  $\text{CDCl}_3$



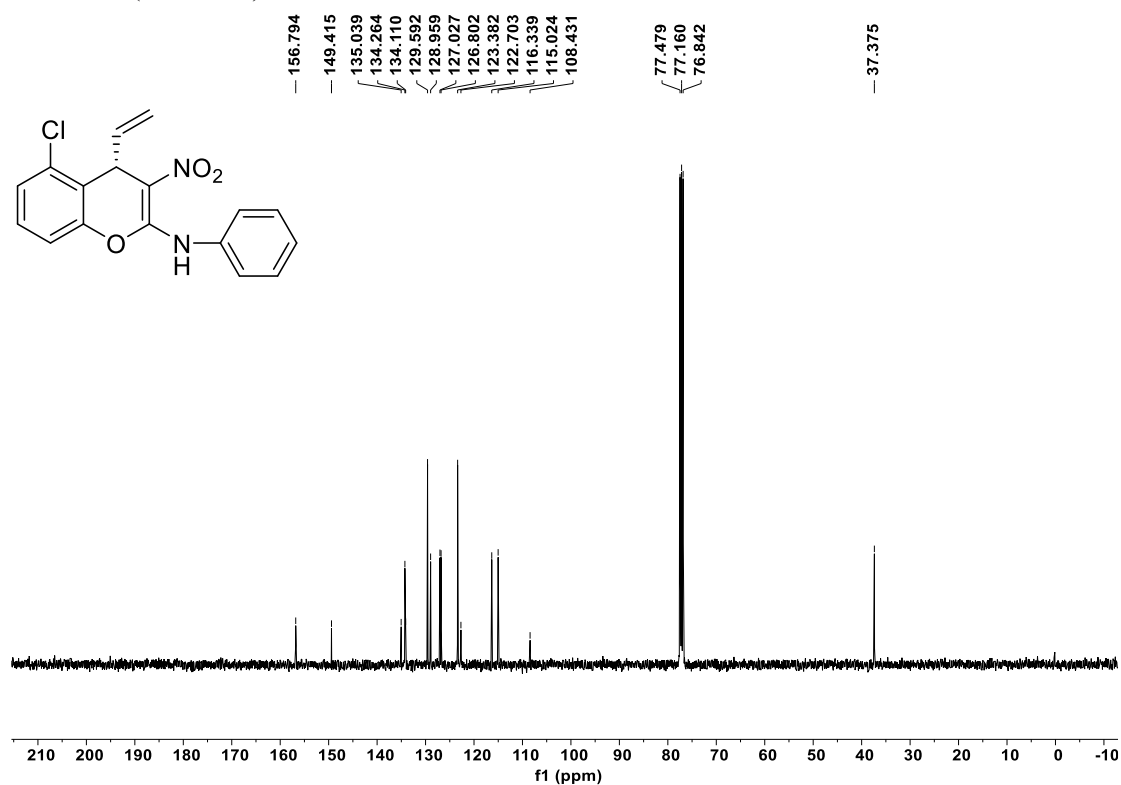
$^{13}\text{C}$  NMR (100 MHz) of **50** in  $\text{CDCl}_3$



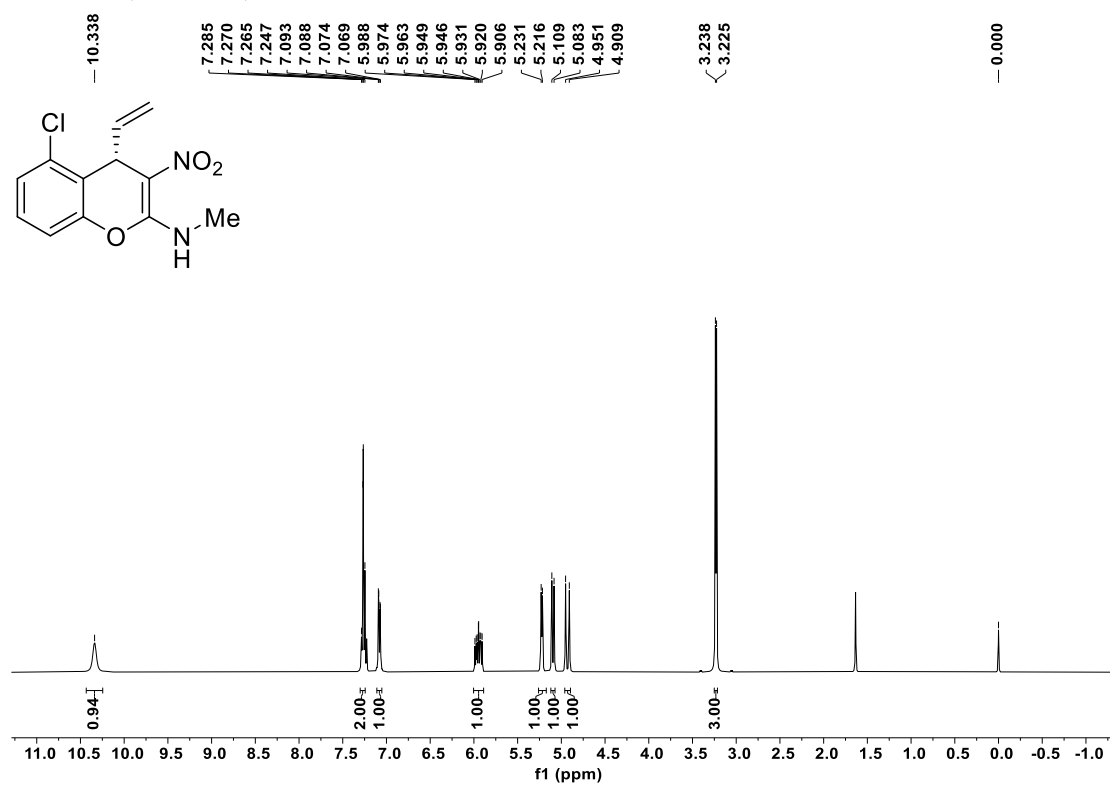
$^1\text{H}$  NMR (400 MHz) of **51** in  $\text{CDCl}_3$



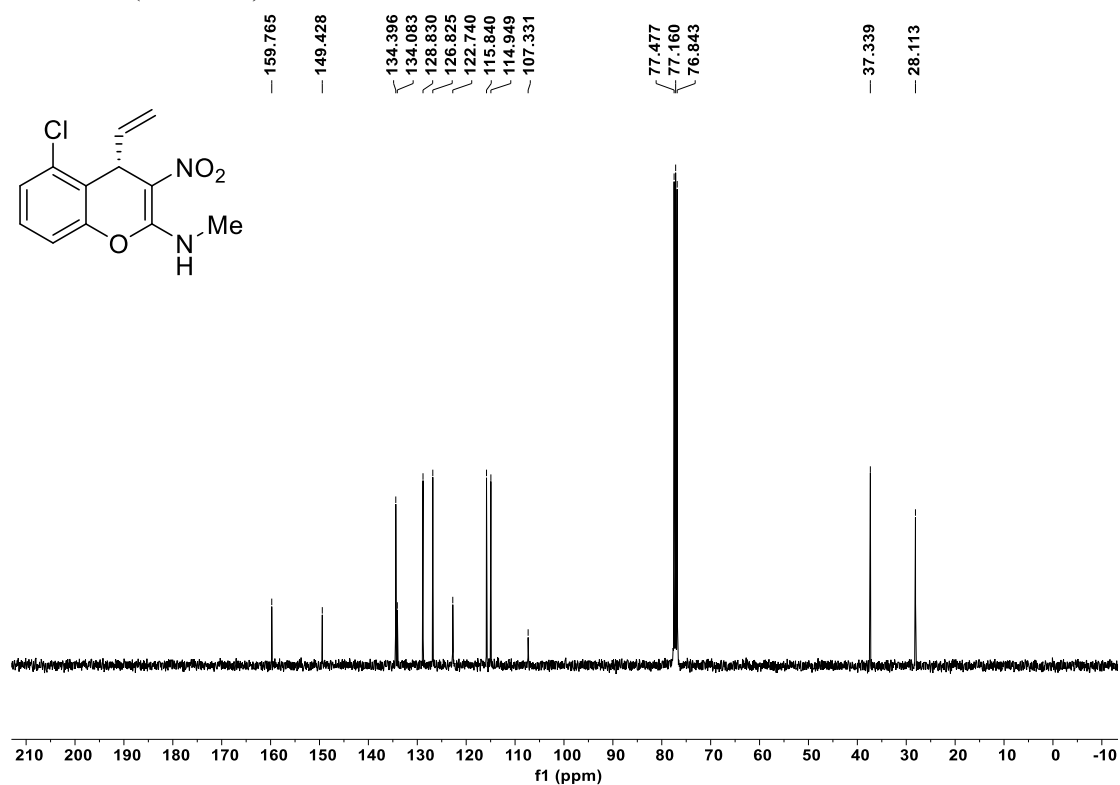
$^{13}\text{C}$  NMR (100 MHz) of **51** in  $\text{CDCl}_3$



<sup>1</sup>H NMR (400 MHz) of **52** in CDCl<sub>3</sub>

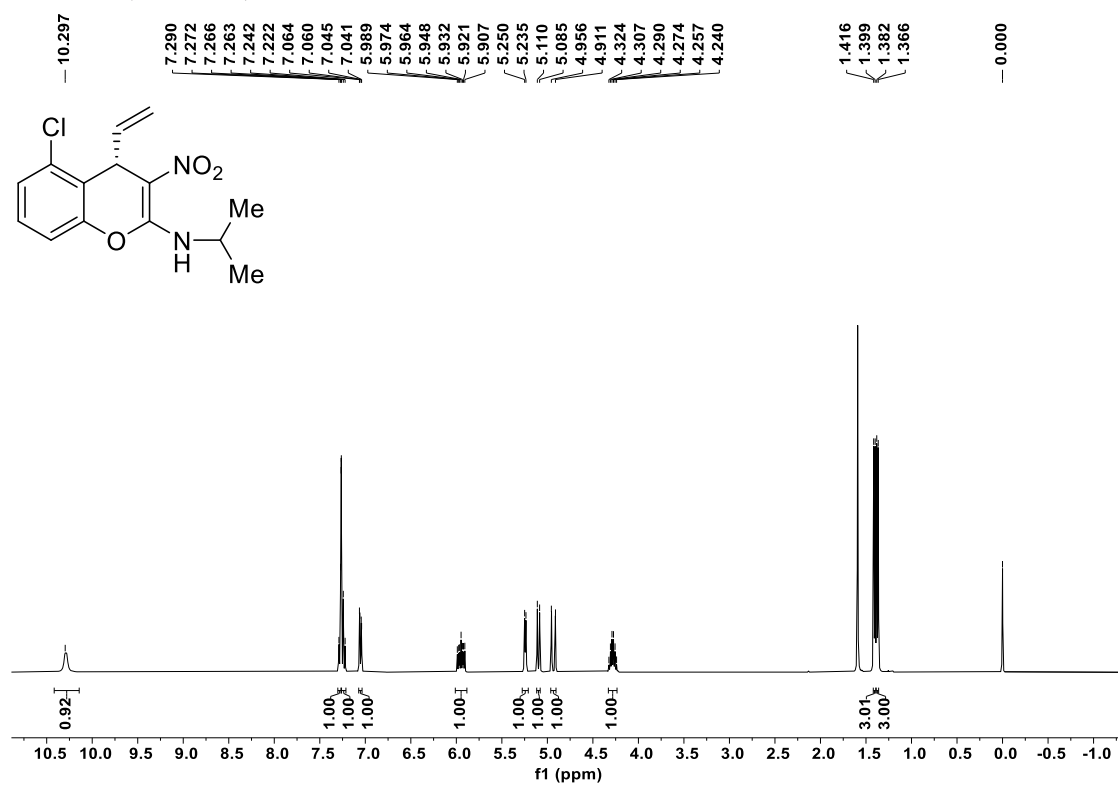


<sup>13</sup>C NMR (100 MHz) of **52** in CDCl<sub>3</sub>

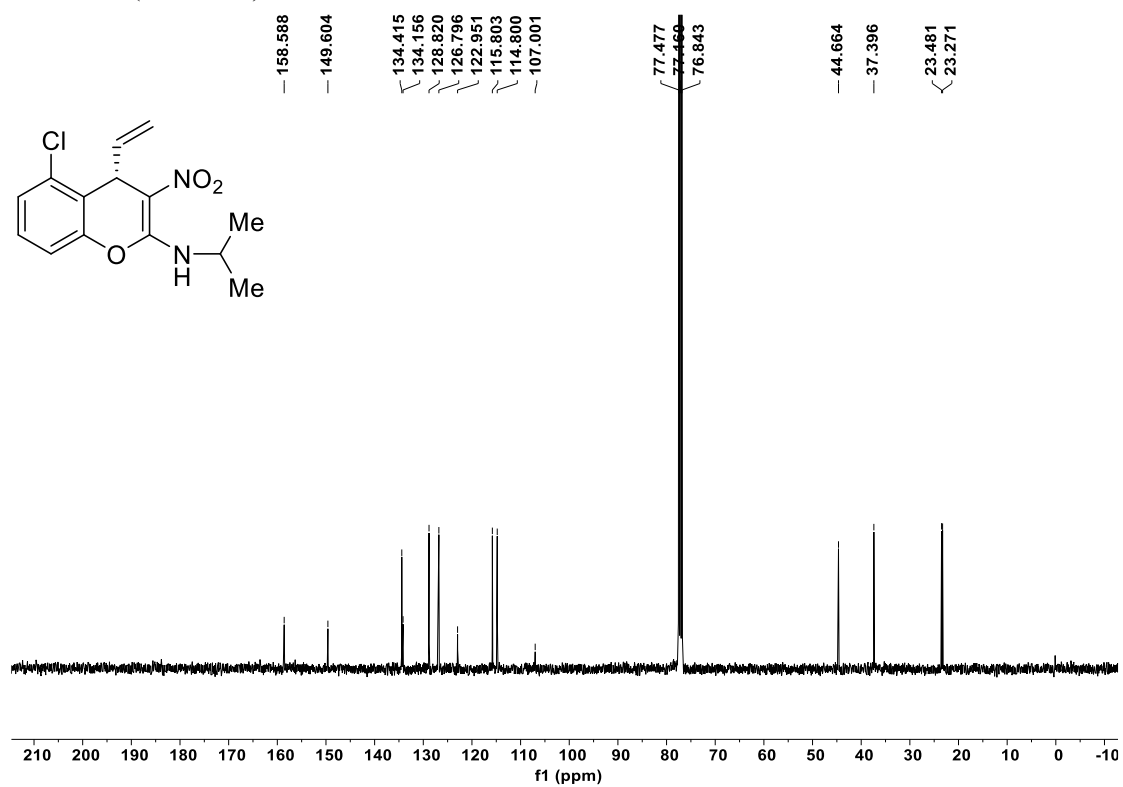




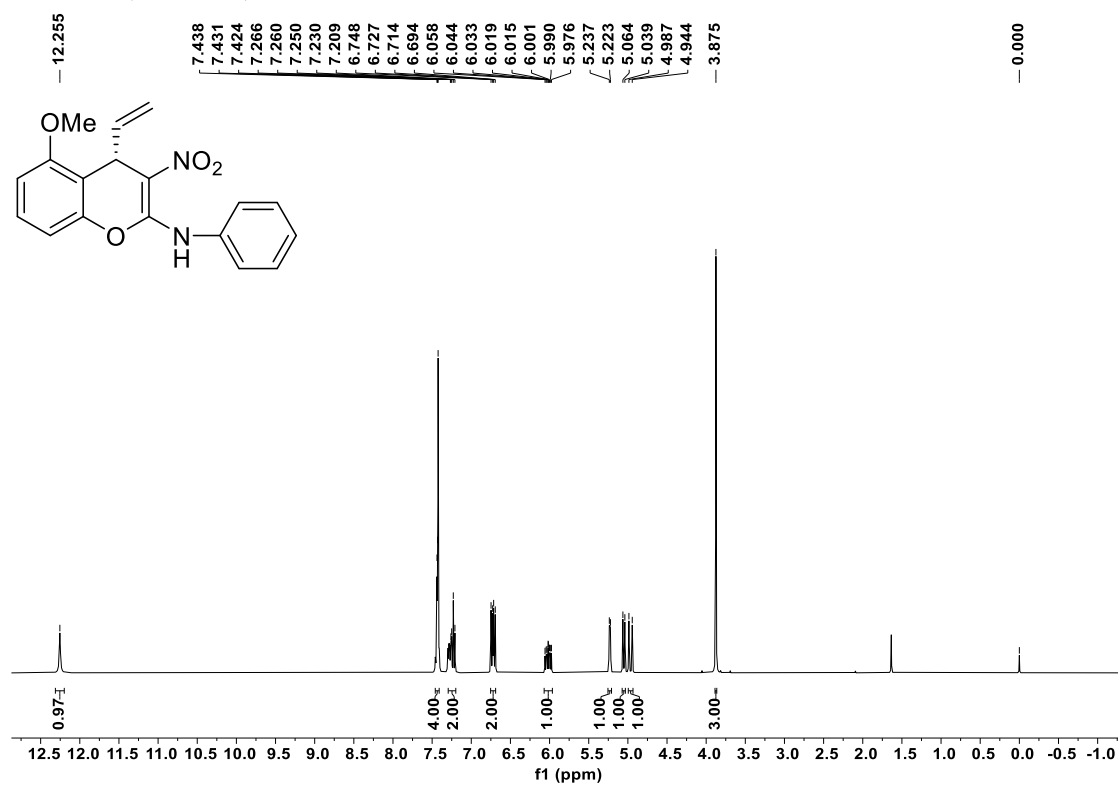
<sup>1</sup>H NMR (400 MHz) of **53** in CDCl<sub>3</sub>



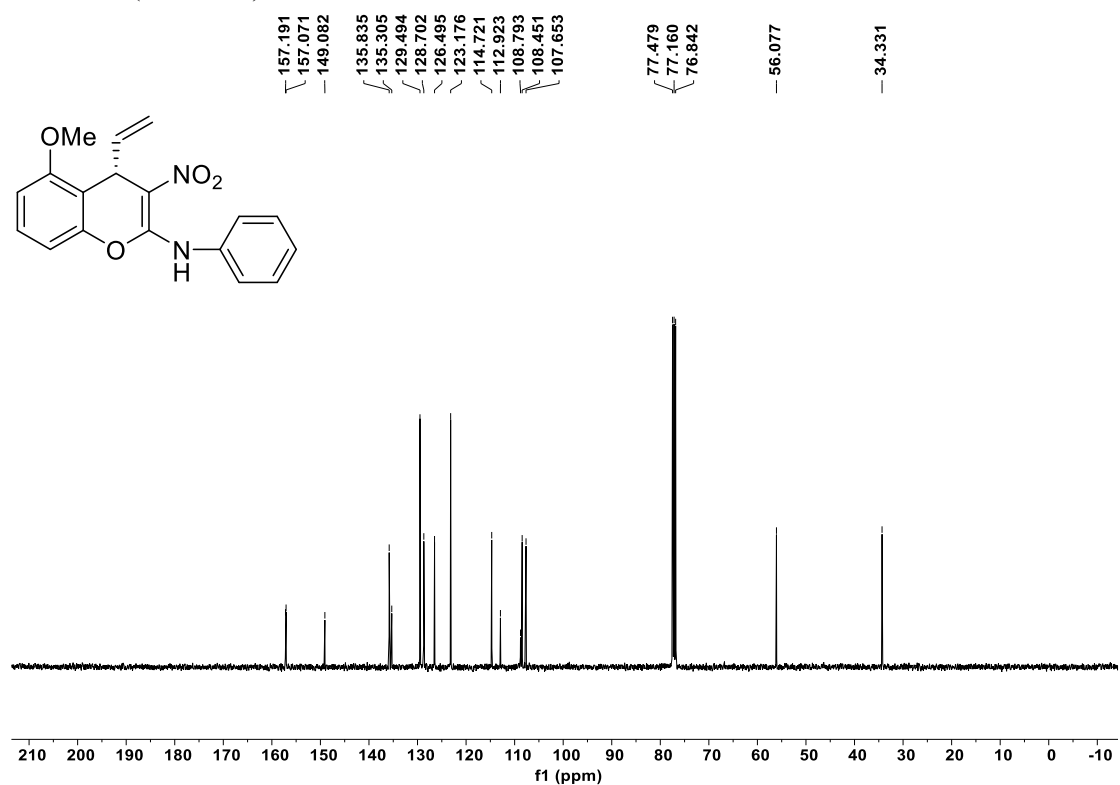
<sup>13</sup>C NMR (100 MHz) of **53** in CDCl<sub>3</sub>



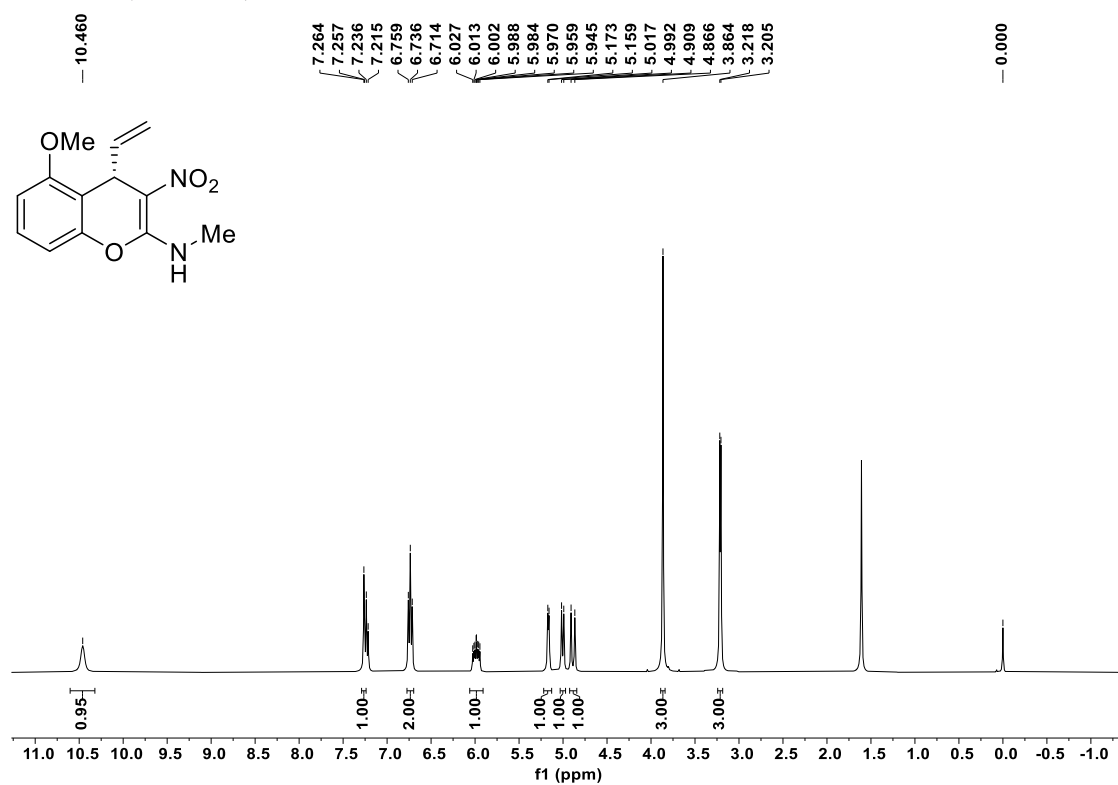
<sup>1</sup>H NMR (400 MHz) of **54** in CDCl<sub>3</sub>



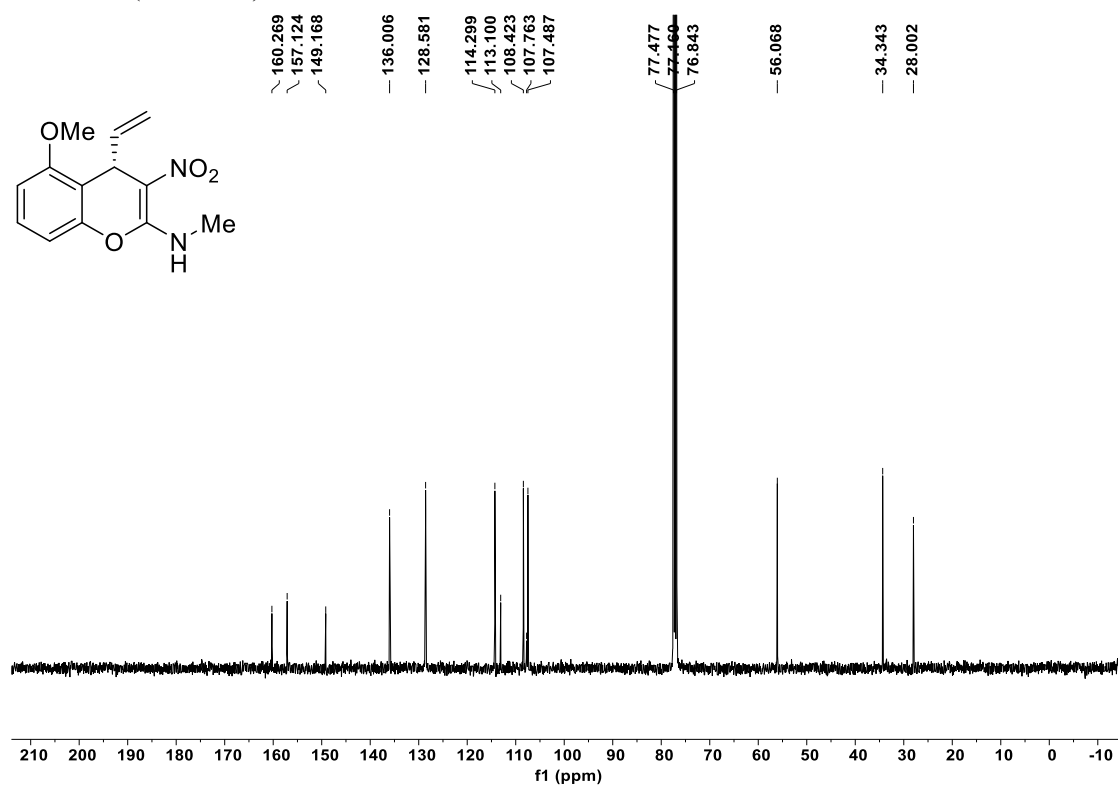
<sup>13</sup>C NMR (100 MHz) of **54** in CDCl<sub>3</sub>



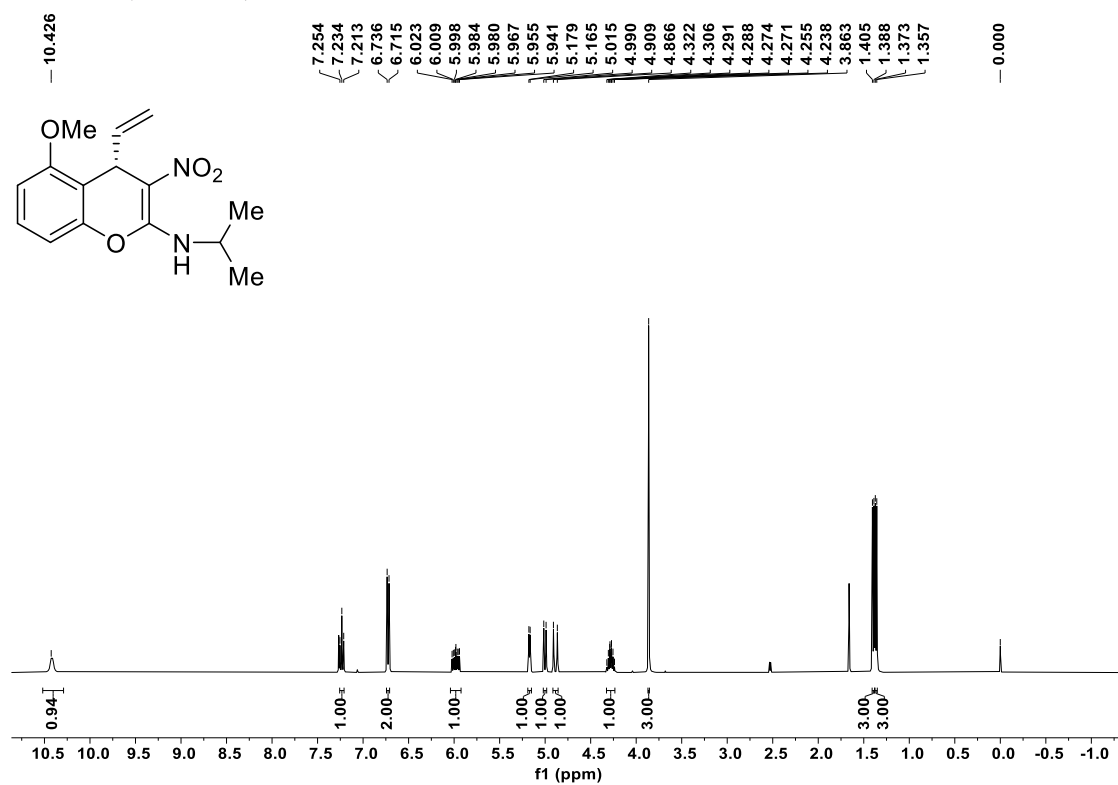
<sup>1</sup>H NMR (400 MHz) of **55** in CDCl<sub>3</sub>



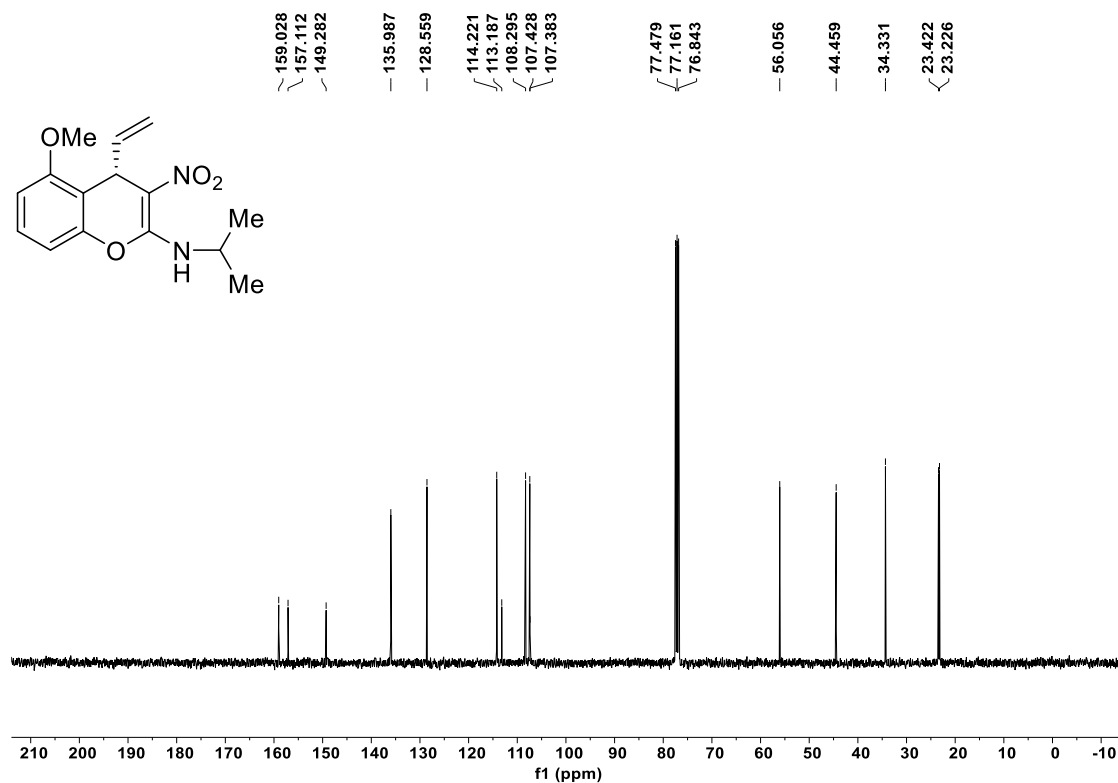
<sup>13</sup>C NMR (100 MHz) of **55** in CDCl<sub>3</sub>



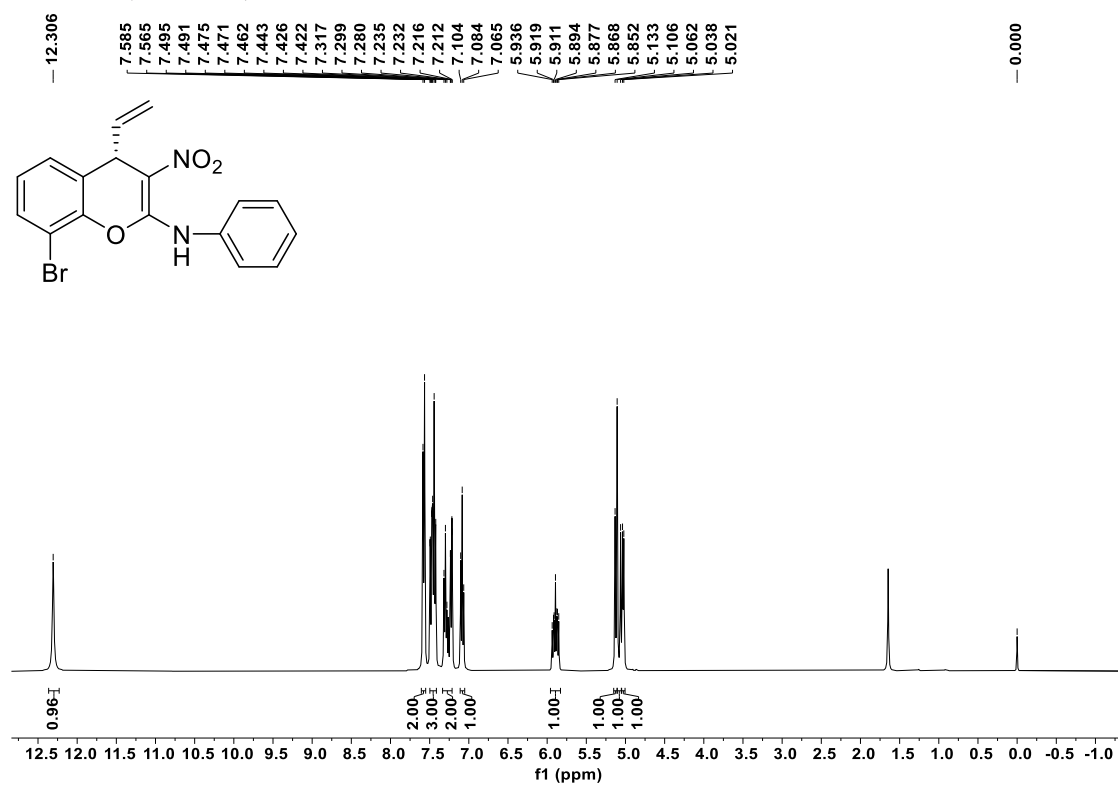
<sup>1</sup>H NMR (400 MHz) of **56** in CDCl<sub>3</sub>



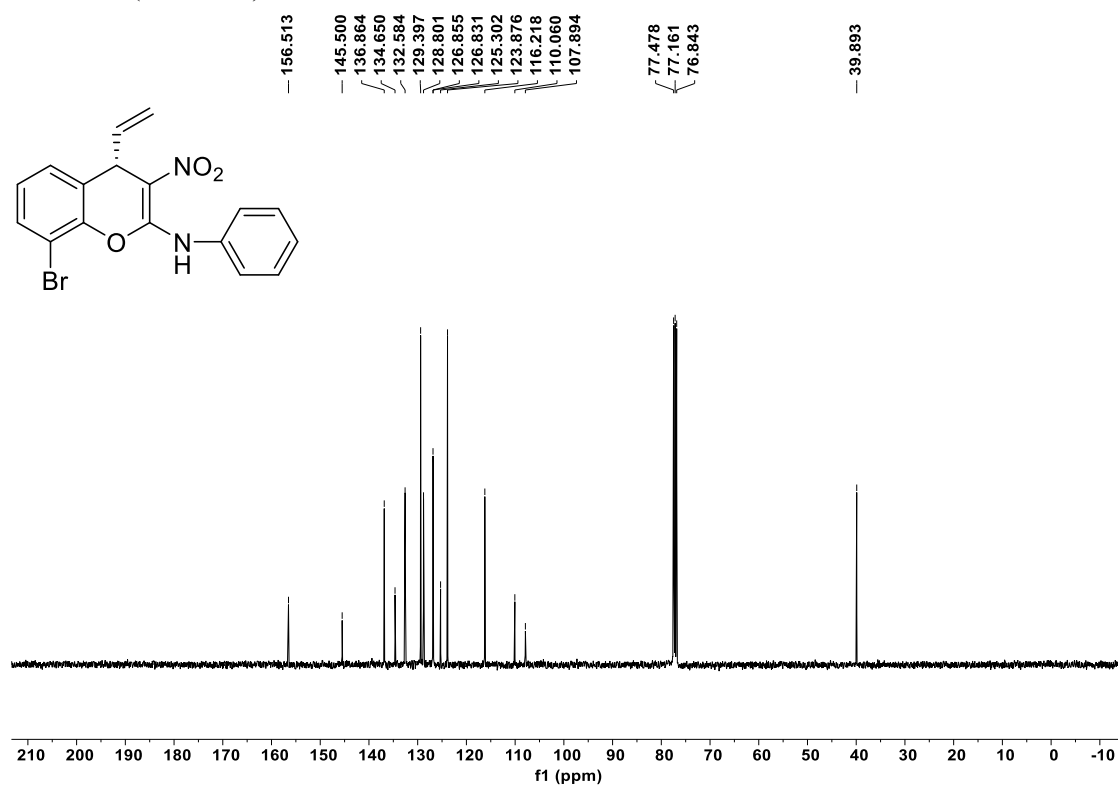
<sup>13</sup>C NMR (100 MHz) of **56** in CDCl<sub>3</sub>



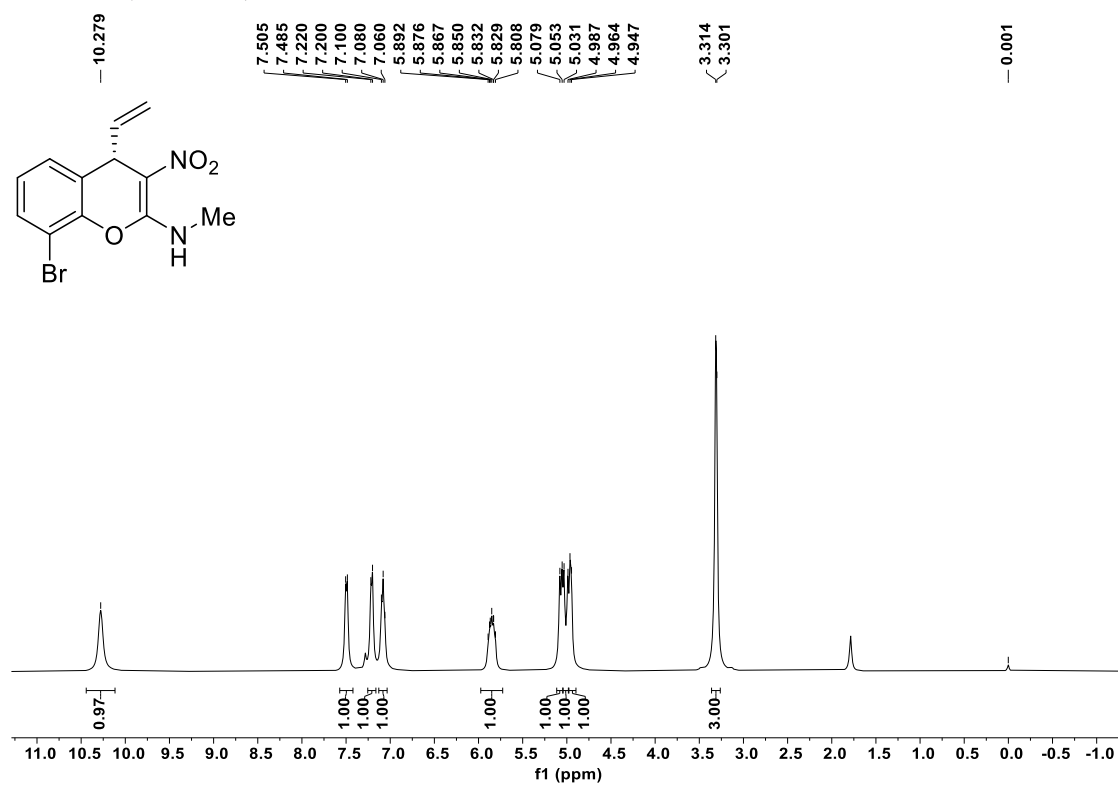
<sup>1</sup>H NMR (400 MHz) of **57** in CDCl<sub>3</sub>



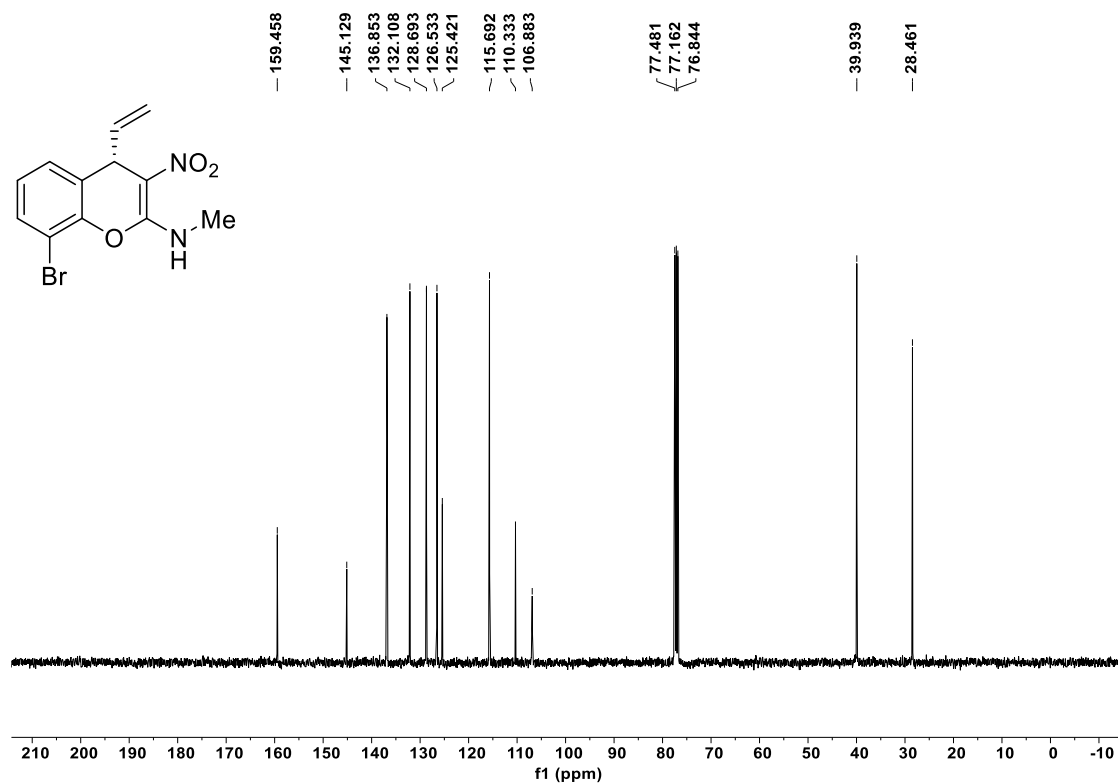
<sup>13</sup>C NMR (100 MHz) of **57** in CDCl<sub>3</sub>



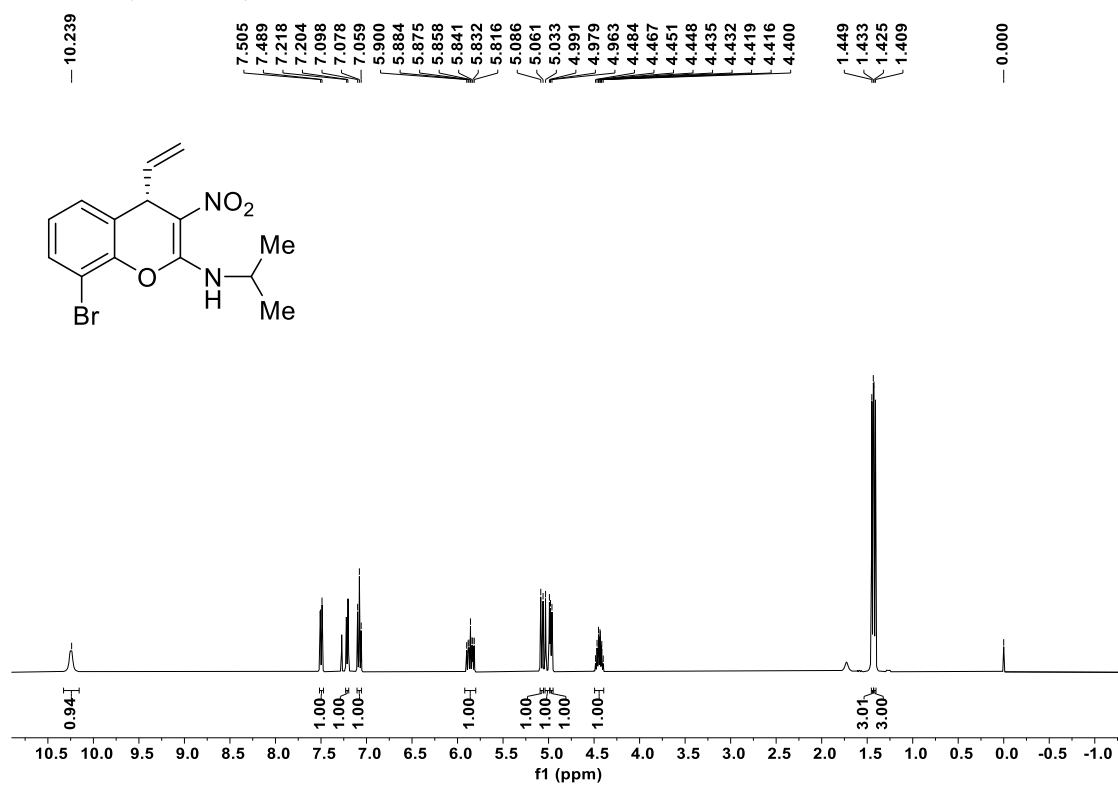
$^1\text{H}$  NMR (400 MHz) of **58** in  $\text{CDCl}_3$



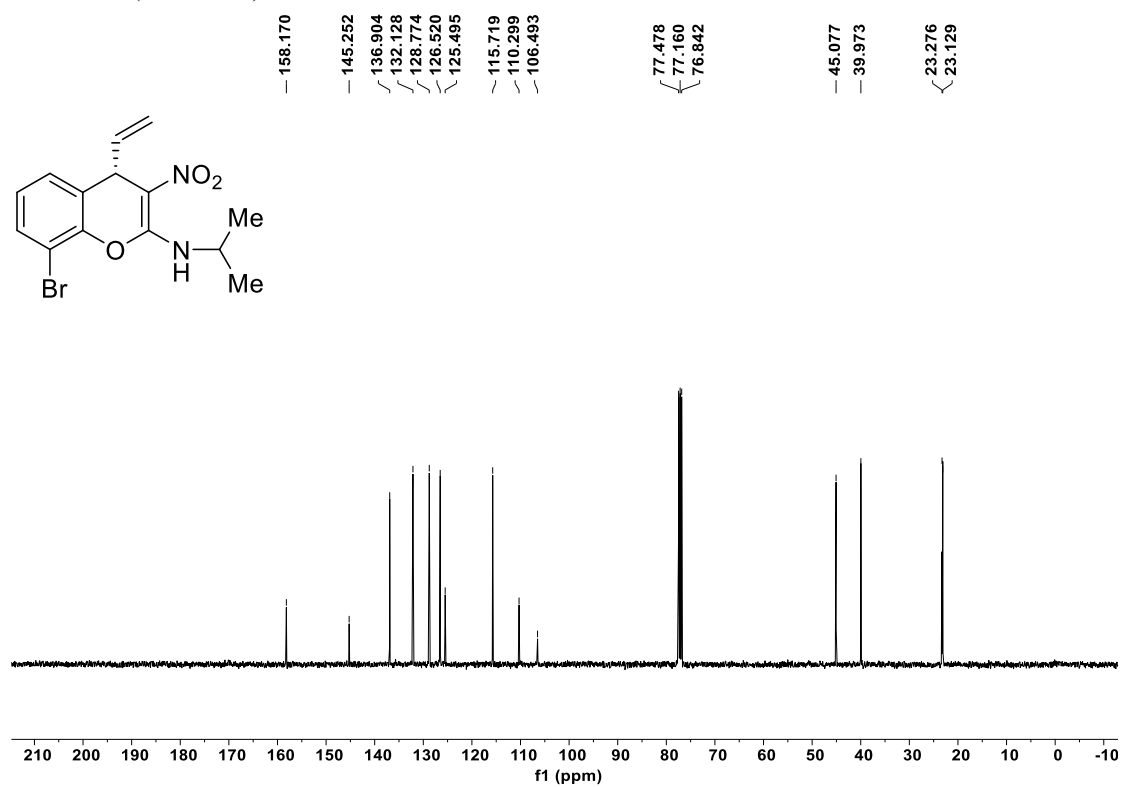
$^{13}\text{C}$  NMR (100 MHz) of **58** in  $\text{CDCl}_3$



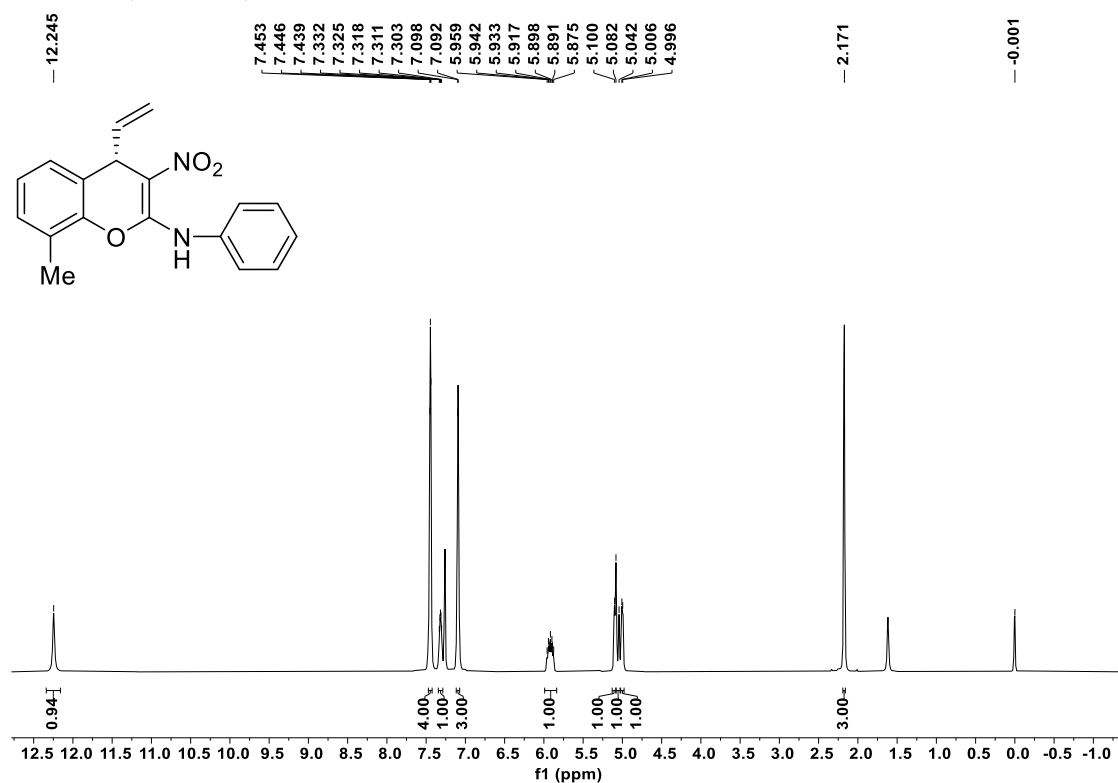
<sup>1</sup>H NMR (400 MHz) of **59** in CDCl<sub>3</sub>



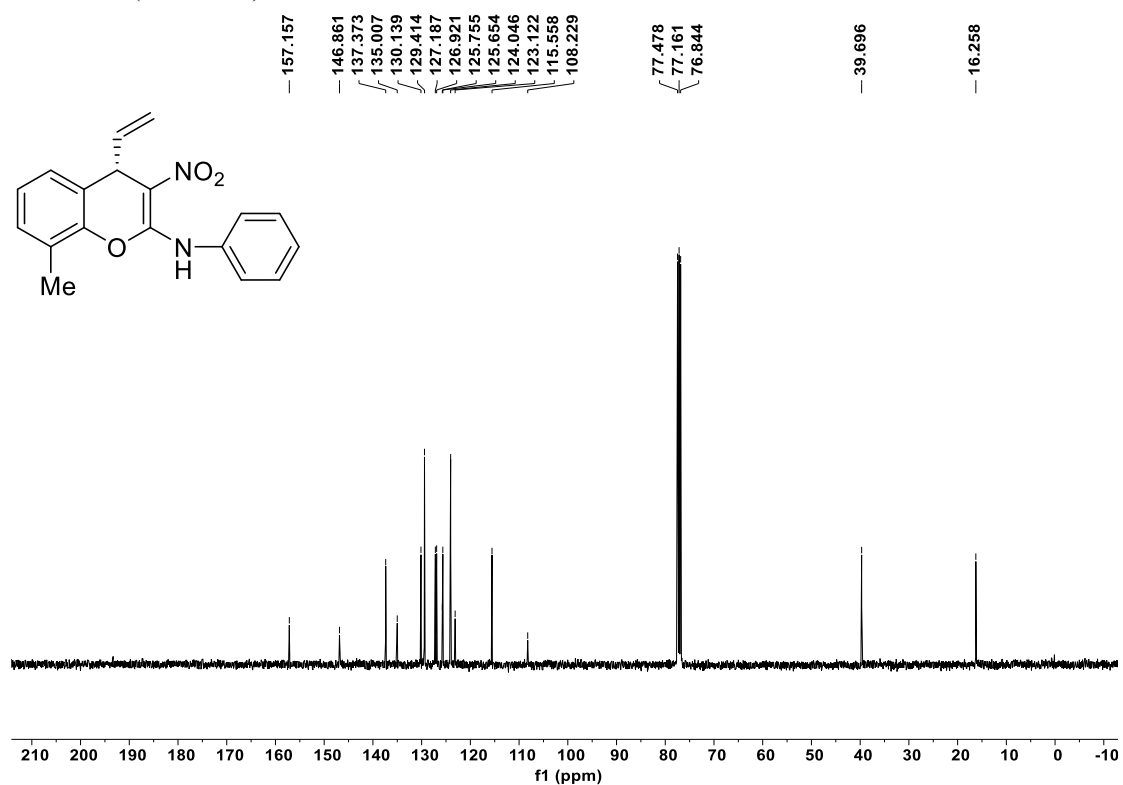
<sup>13</sup>C NMR (100 MHz) of **59** in CDCl<sub>3</sub>



<sup>1</sup>H NMR (400 MHz) of **60** in CDCl<sub>3</sub>

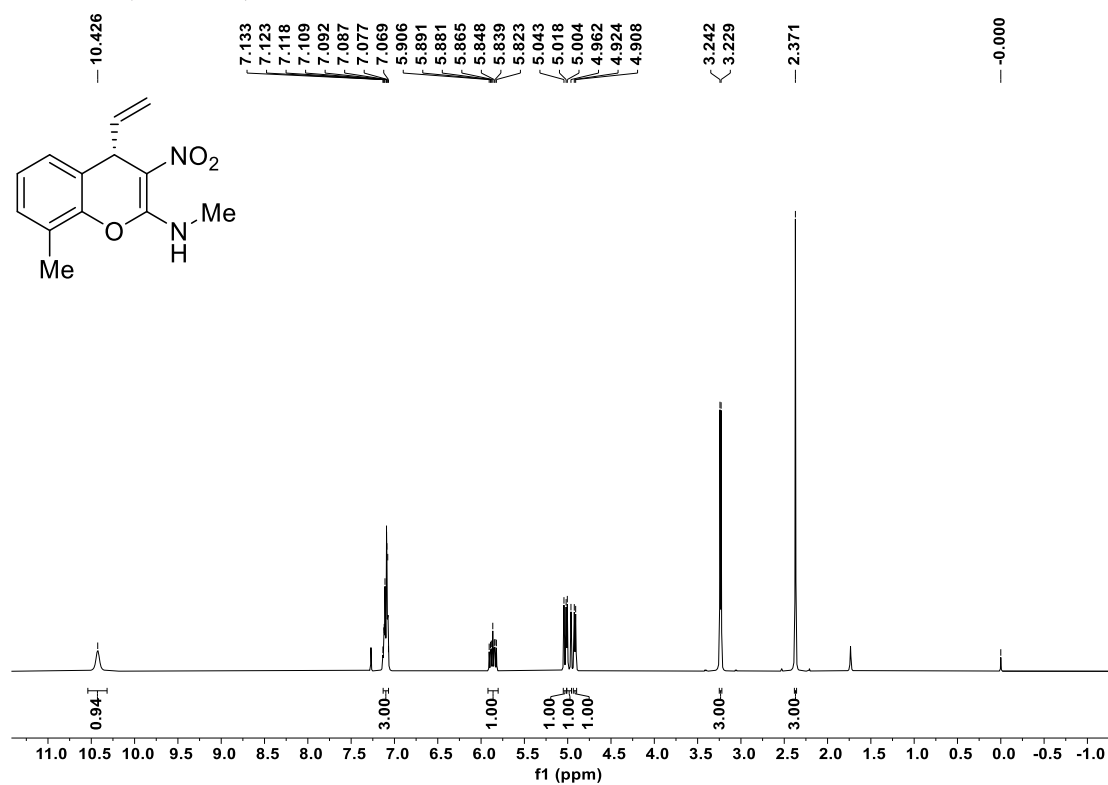


<sup>13</sup>C NMR (100 MHz) of **60** in CDCl<sub>3</sub>

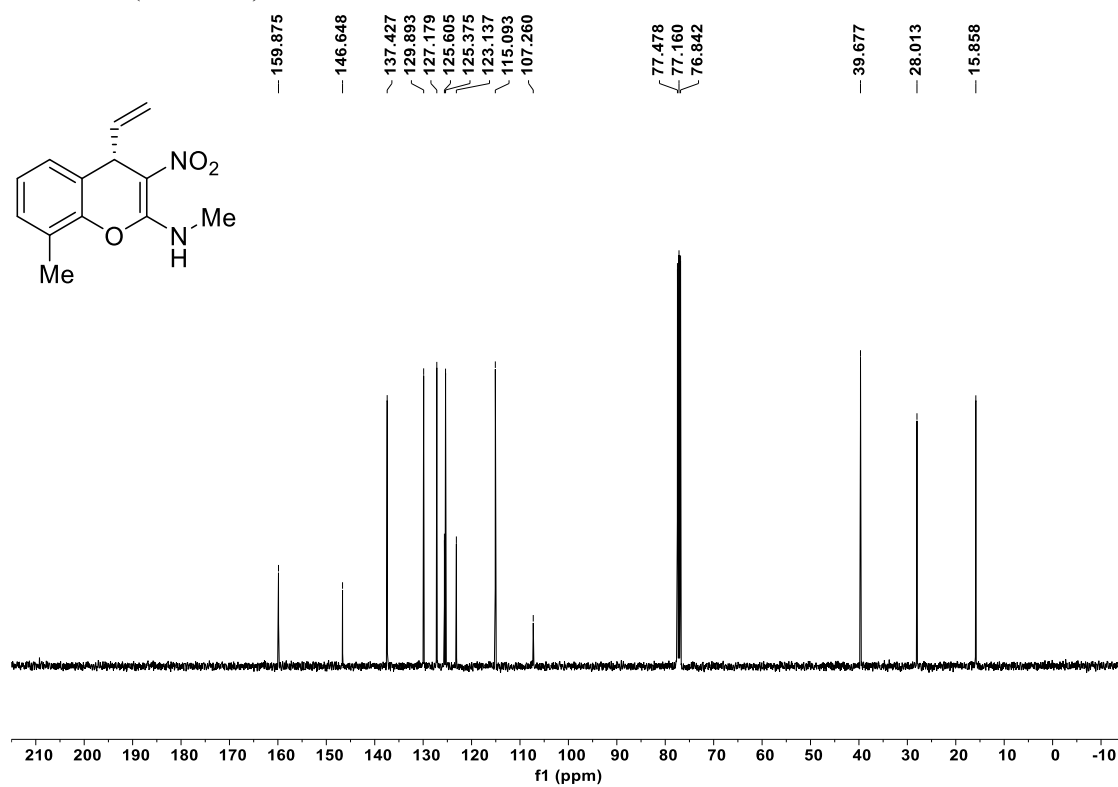




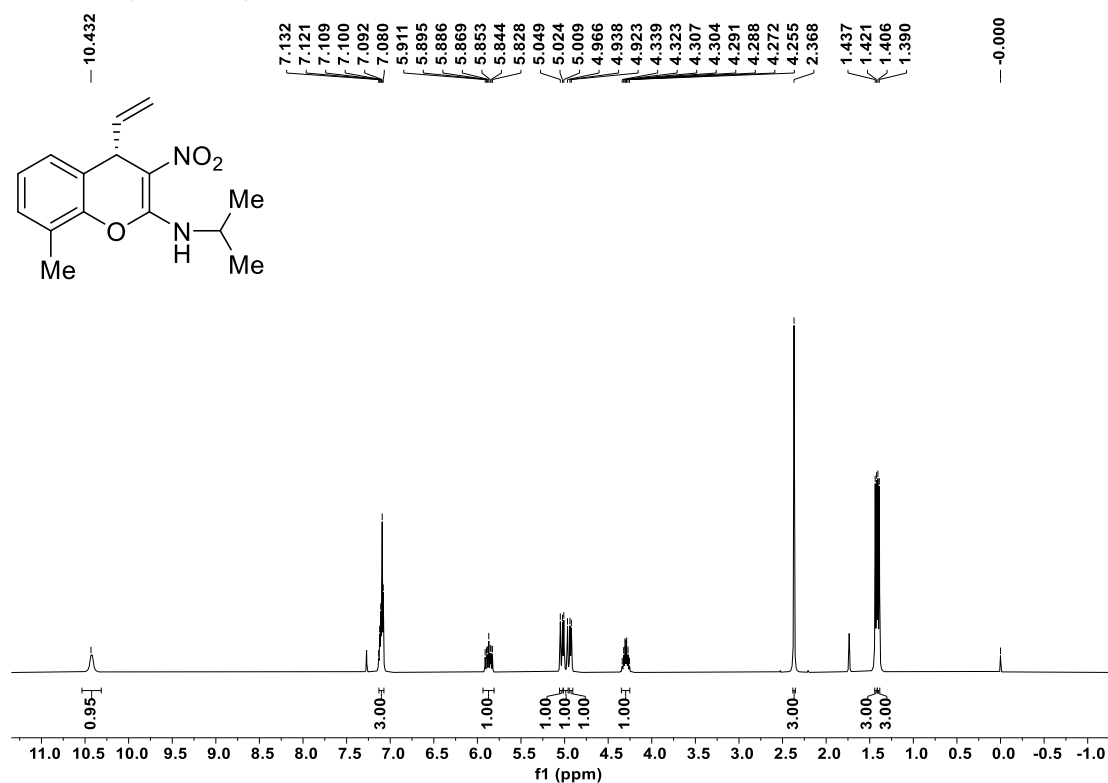
$^1\text{H}$  NMR (400 MHz) of **61** in  $\text{CDCl}_3$



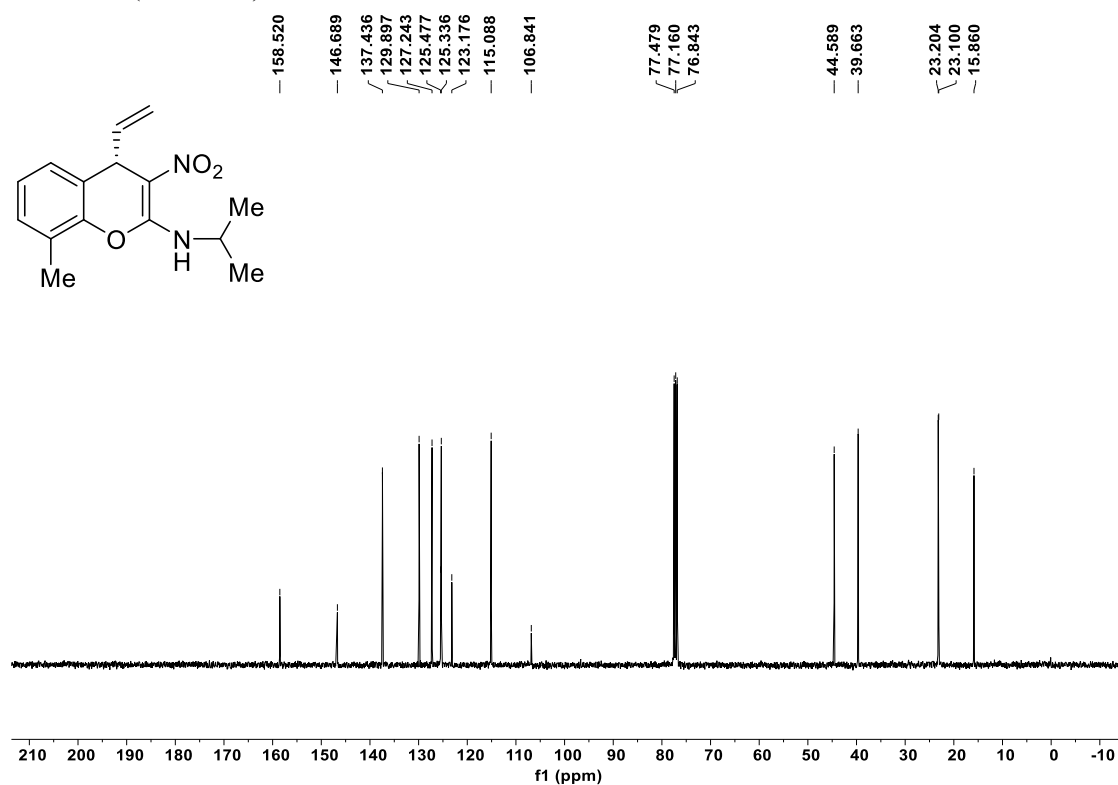
$^{13}\text{C}$  NMR (100 MHz) of **61** in  $\text{CDCl}_3$



<sup>1</sup>H NMR (400 MHz) of **62** in CDCl<sub>3</sub>

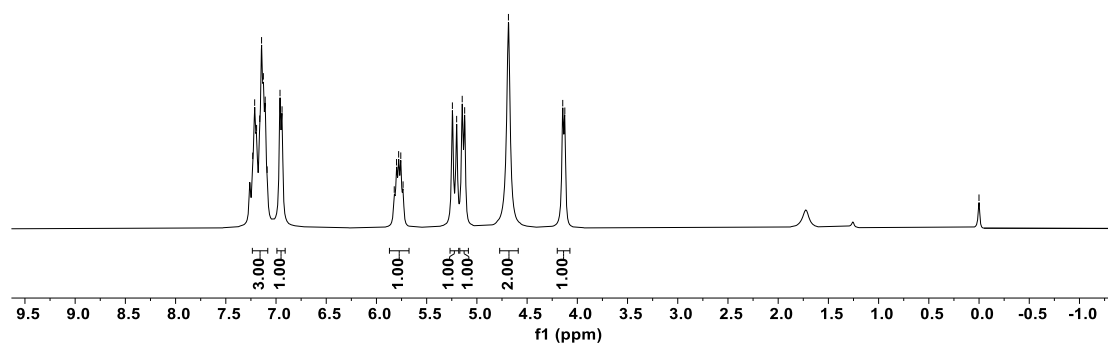
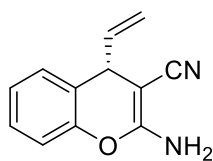


<sup>13</sup>C NMR (100 MHz) of **62** in CDCl<sub>3</sub>



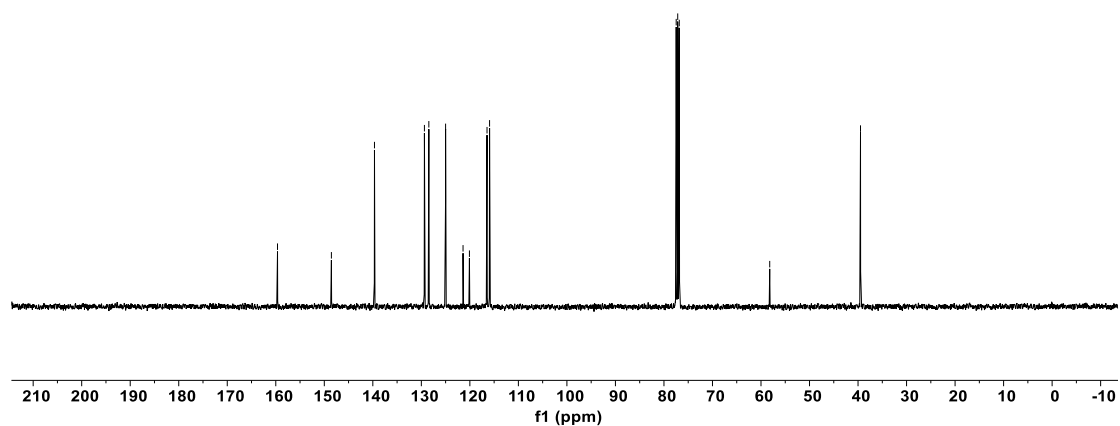
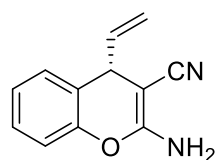
$^1\text{H}$  NMR (400 MHz) of **63** in  $\text{CDCl}_3$

7.232  
7.213  
7.193  
7.162  
7.144  
7.126  
7.108  
7.089  
6.960  
6.940  
5.823  
5.800  
5.779  
5.758  
5.735  
5.244  
5.201  
5.146  
5.122  
4.686  
4.145  
4.124  
-0.000

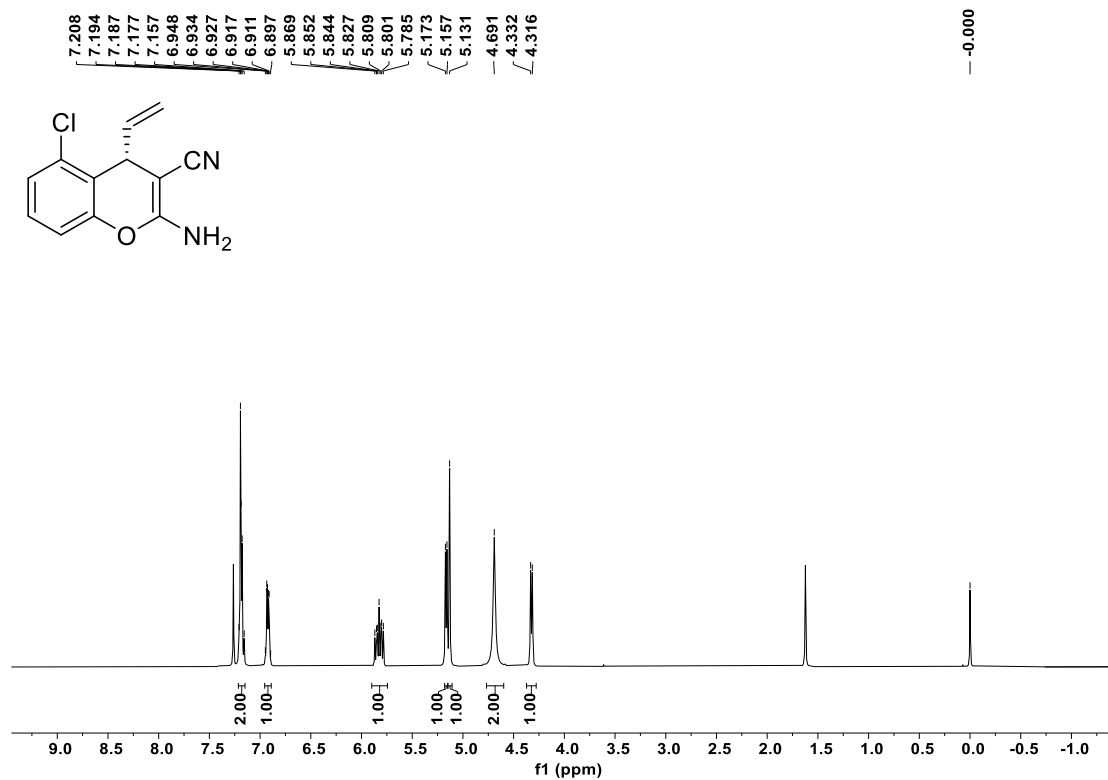


$^{13}\text{C}$  NMR (100 MHz) of **63** in  $\text{CDCl}_3$

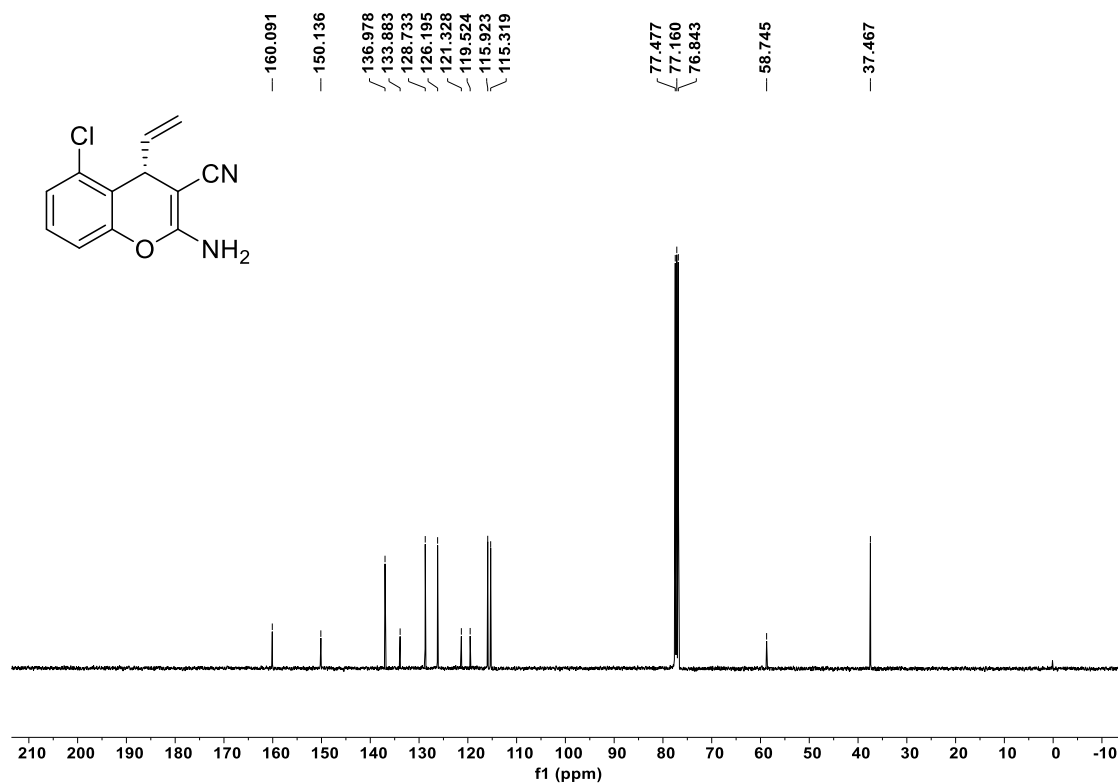
159.645  
148.537  
139.658  
129.365  
128.454  
125.003  
121.408  
120.092  
116.463  
115.940  
77.479  
77.161  
76.844  
58.202  
39.491



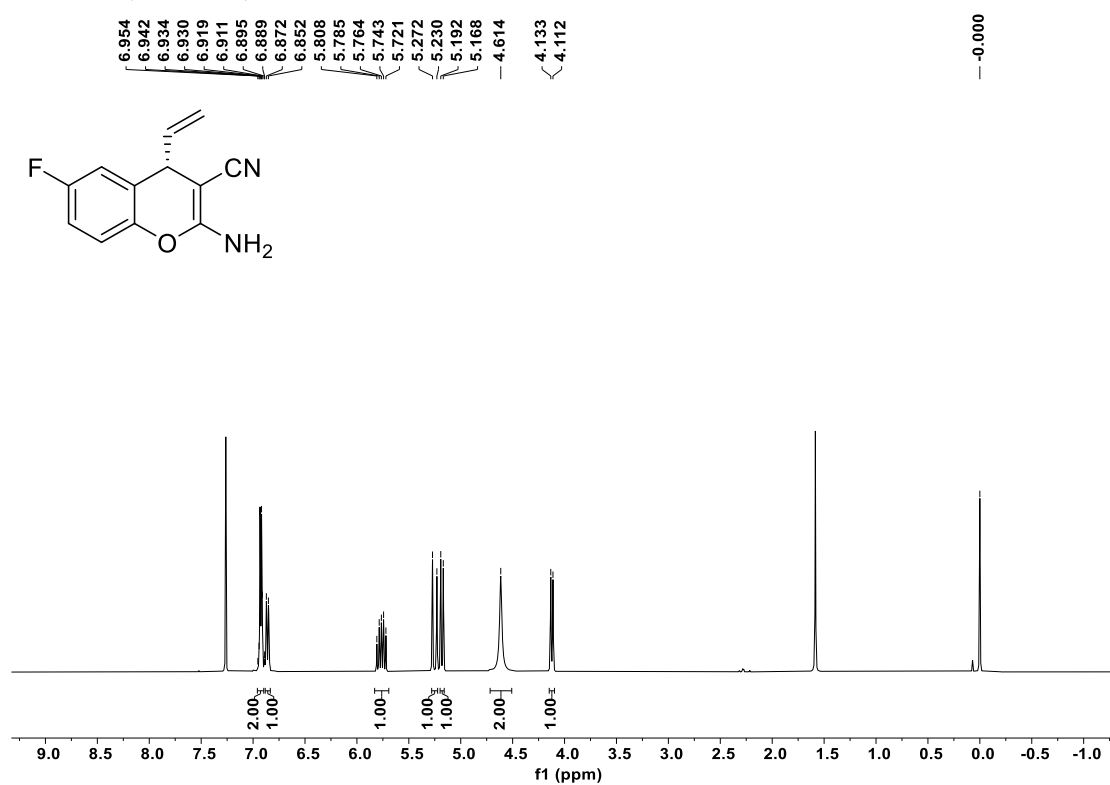
<sup>1</sup>H NMR (400 MHz) of **64** in CDCl<sub>3</sub>



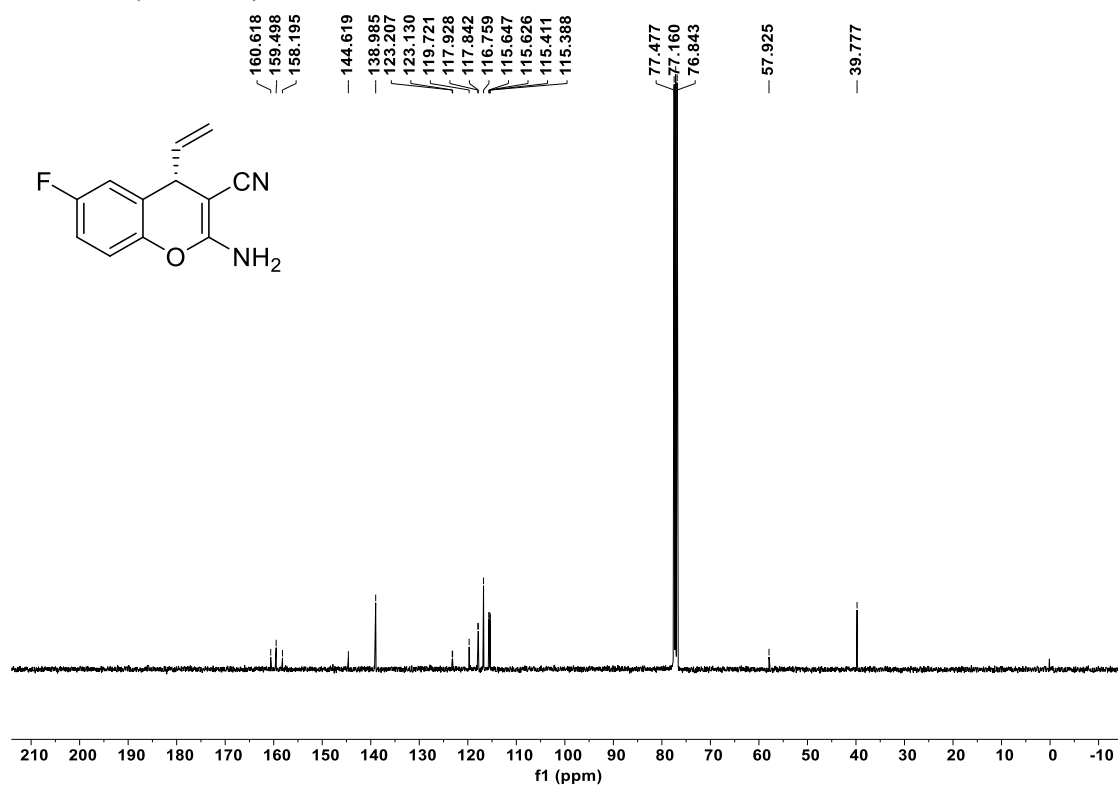
<sup>13</sup>C NMR (100 MHz) of **64** in CDCl<sub>3</sub>



$^1\text{H}$  NMR (400 MHz) of **65** in  $\text{CDCl}_3$

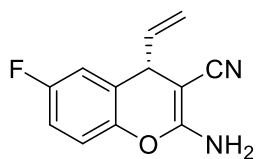


$^{13}\text{C}$  NMR (100 MHz) of **65** in  $\text{CDCl}_3$



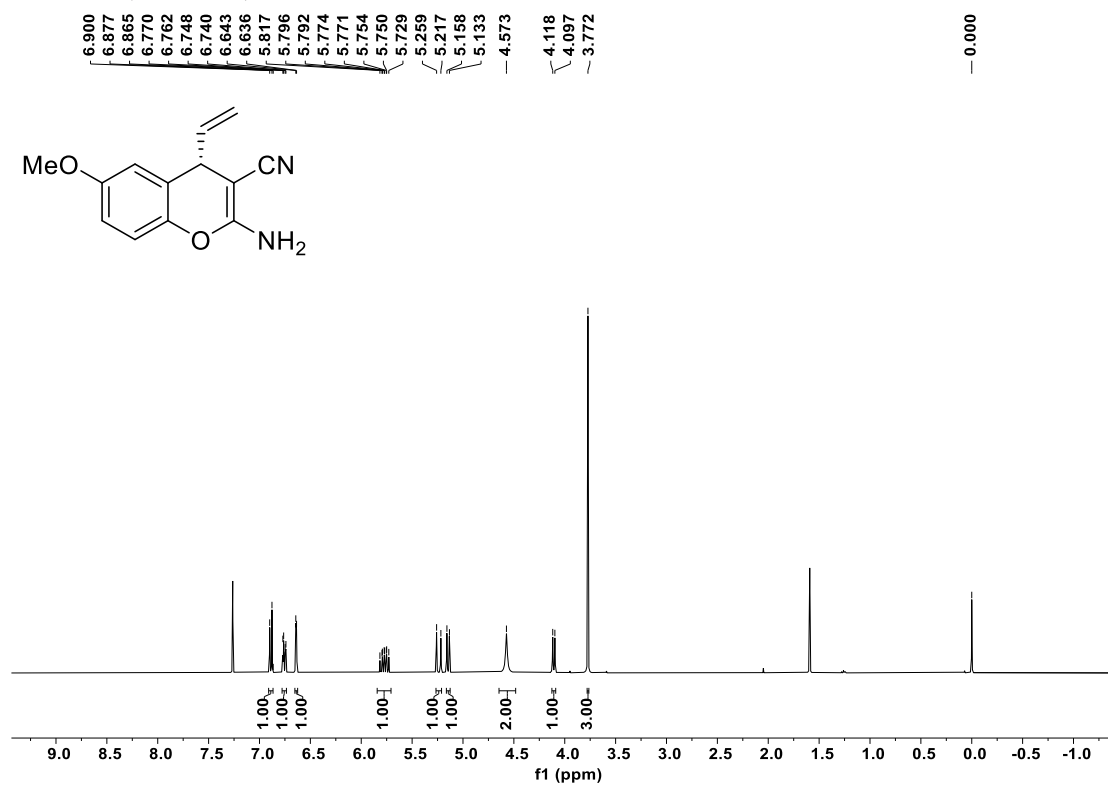
$^{19}\text{F}$  NMR (376 MHz) of **65** in  $\text{CDCl}_3$

-117.335  
-117.352  
-117.369  
-117.375  
-117.391

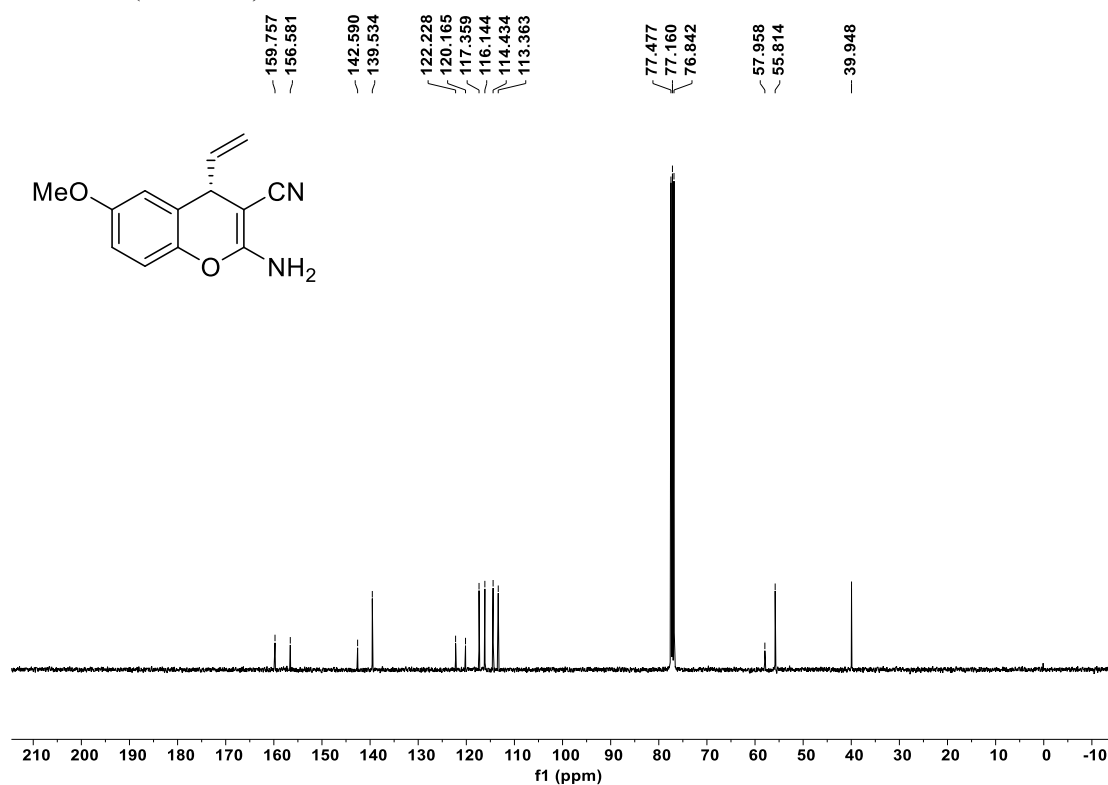


-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210  
f1 (ppm)

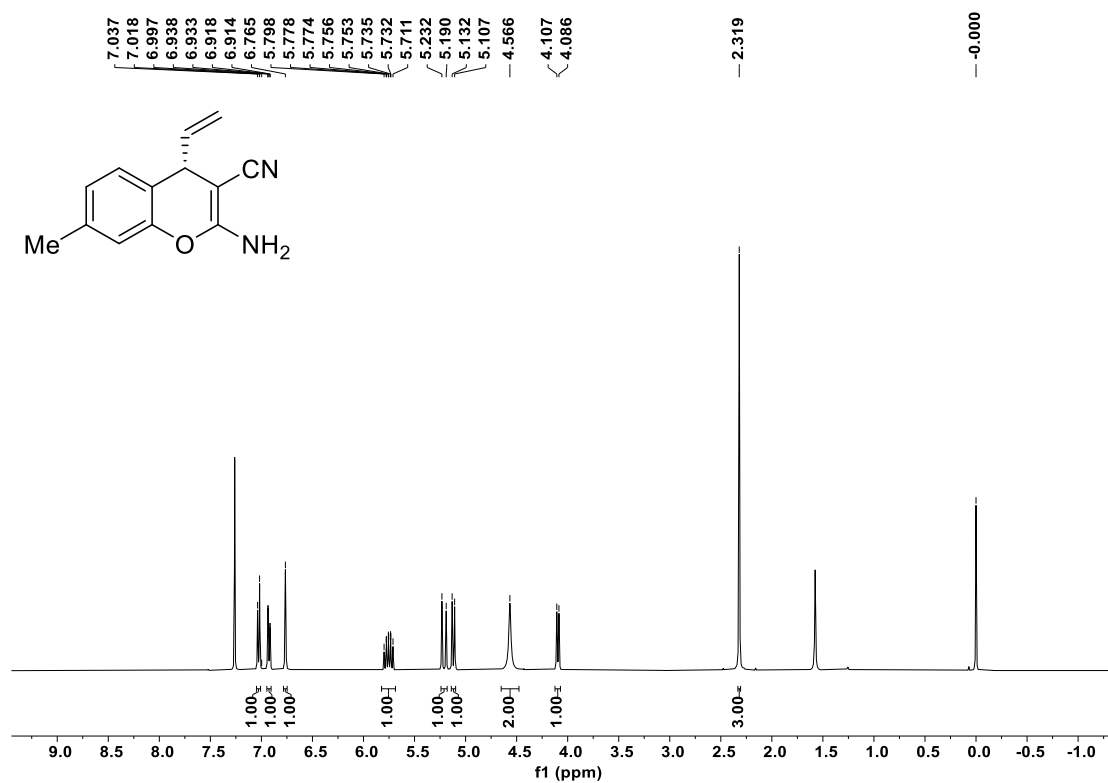
$^1\text{H}$  NMR (400 MHz) of **66** in  $\text{CDCl}_3$



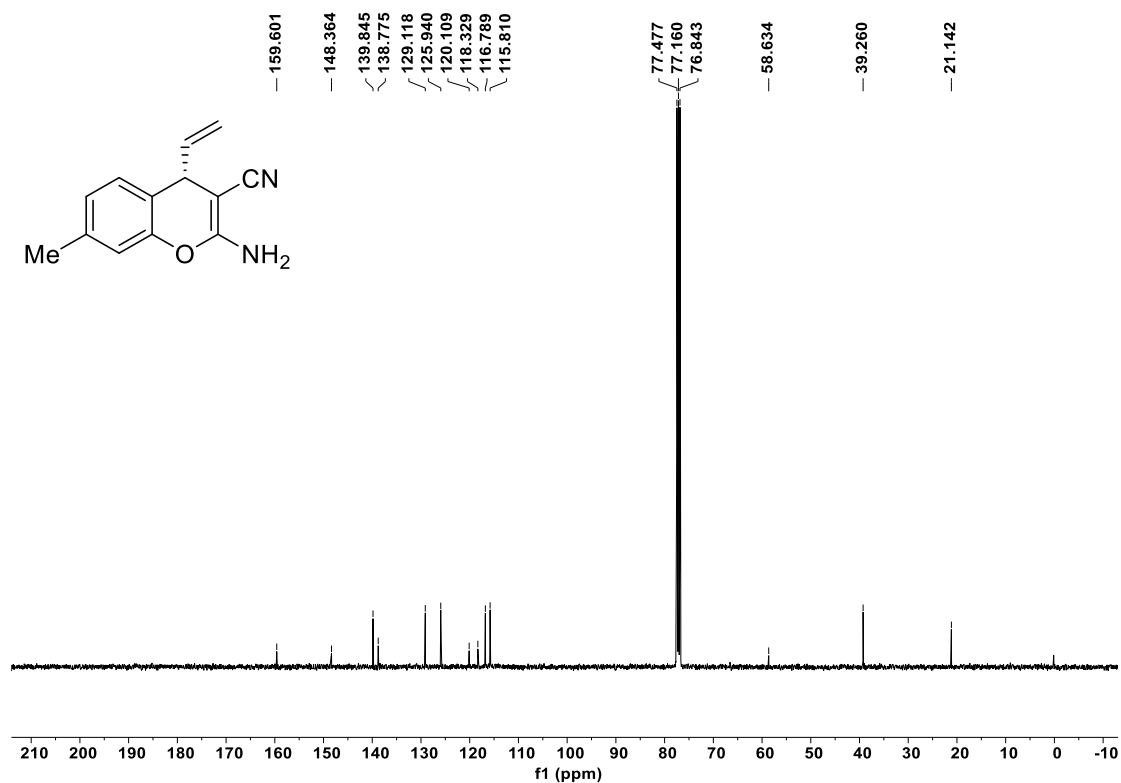
$^{13}\text{C}$  NMR (100 MHz) of **66** in  $\text{CDCl}_3$



<sup>1</sup>H NMR (400 MHz) of **67** in CDCl<sub>3</sub>

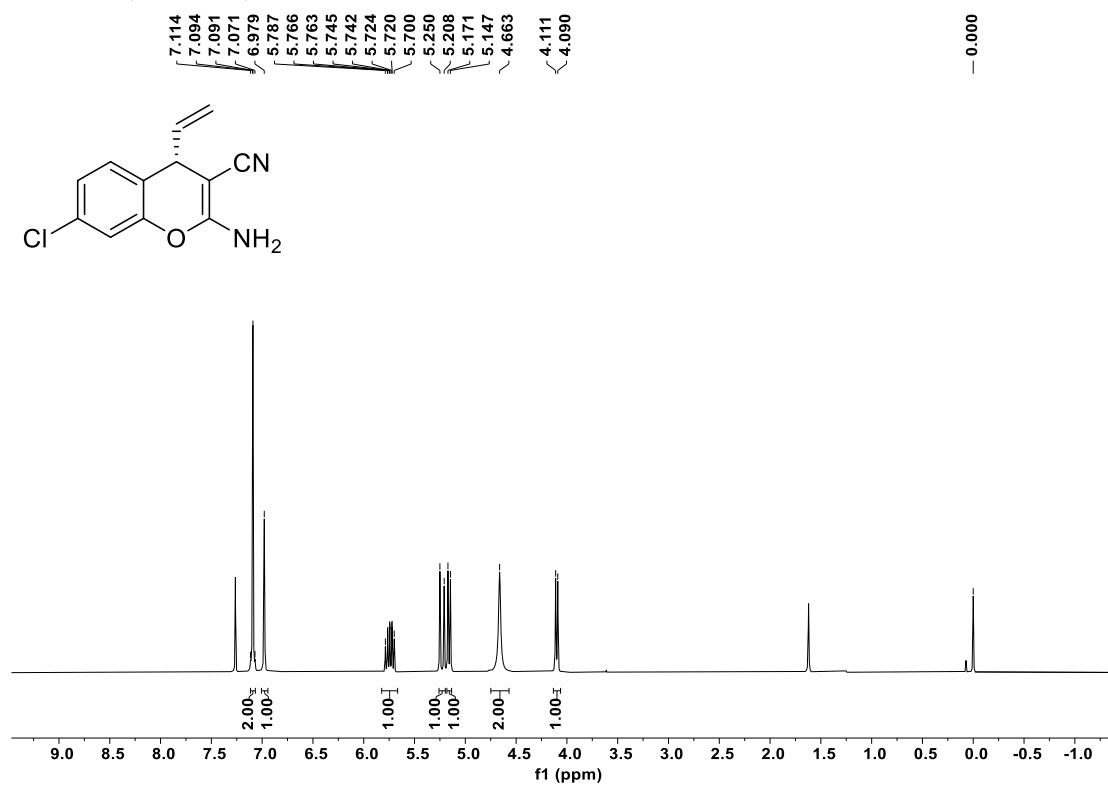


<sup>13</sup>C NMR (100 MHz) of **67** in CDCl<sub>3</sub>

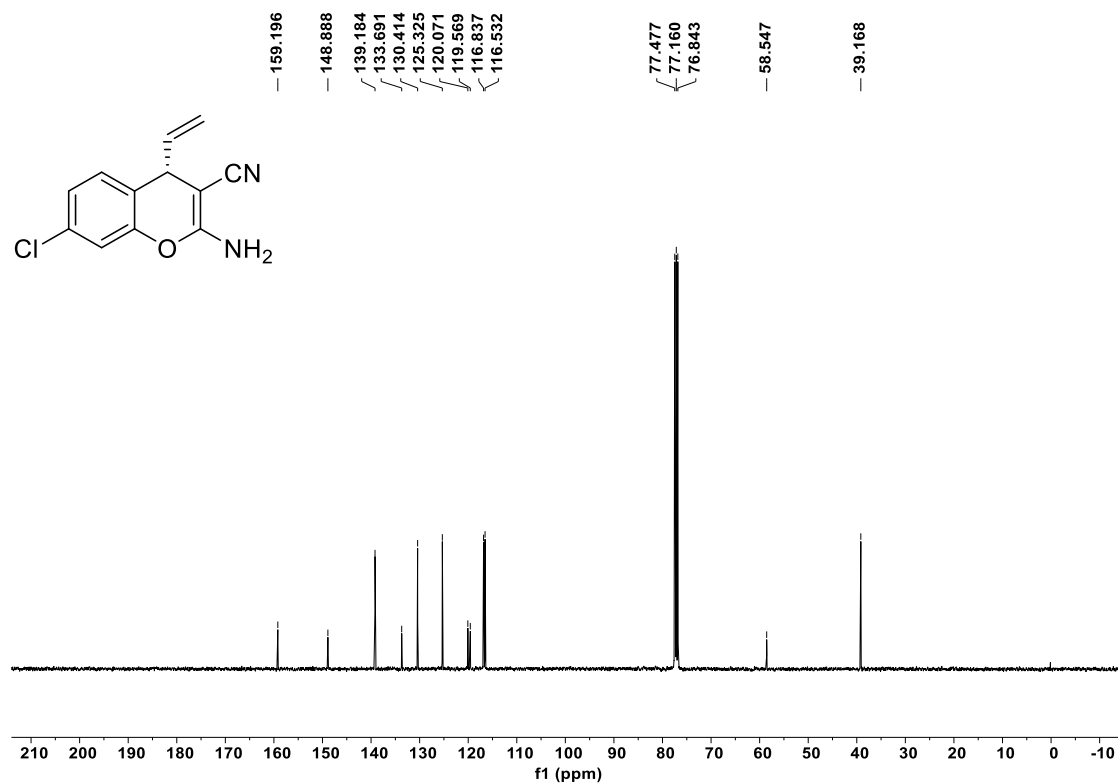




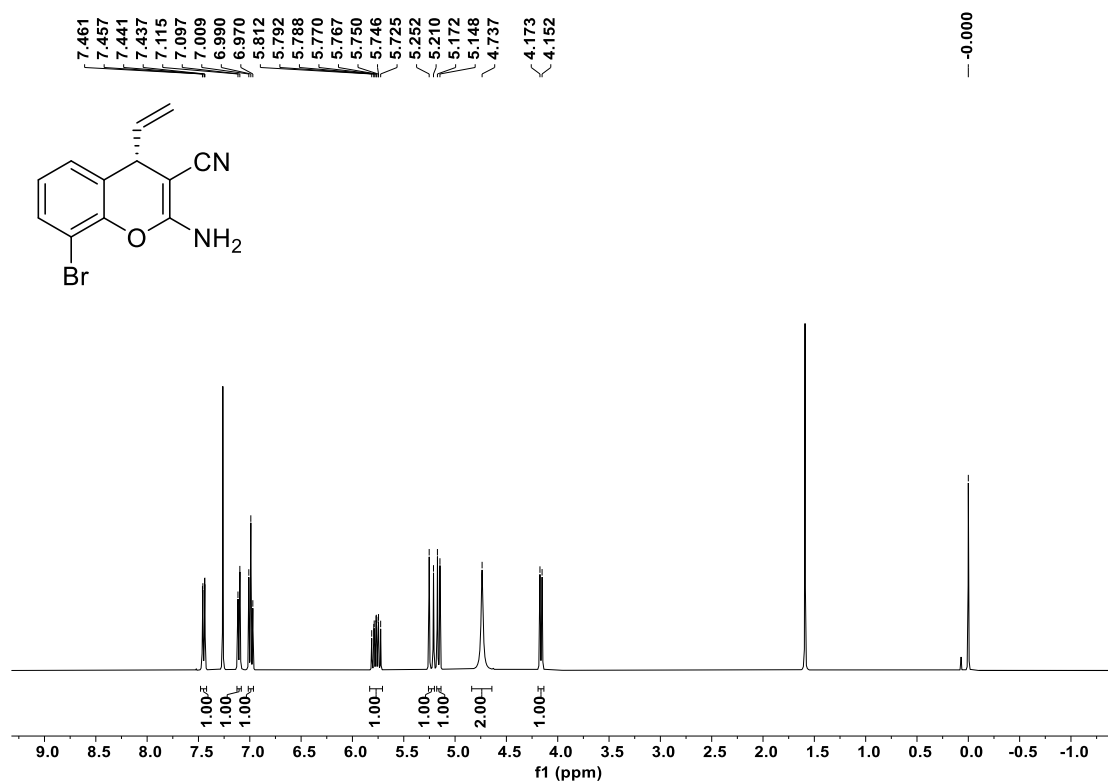
<sup>1</sup>H NMR (400 MHz) of **68** in CDCl<sub>3</sub>



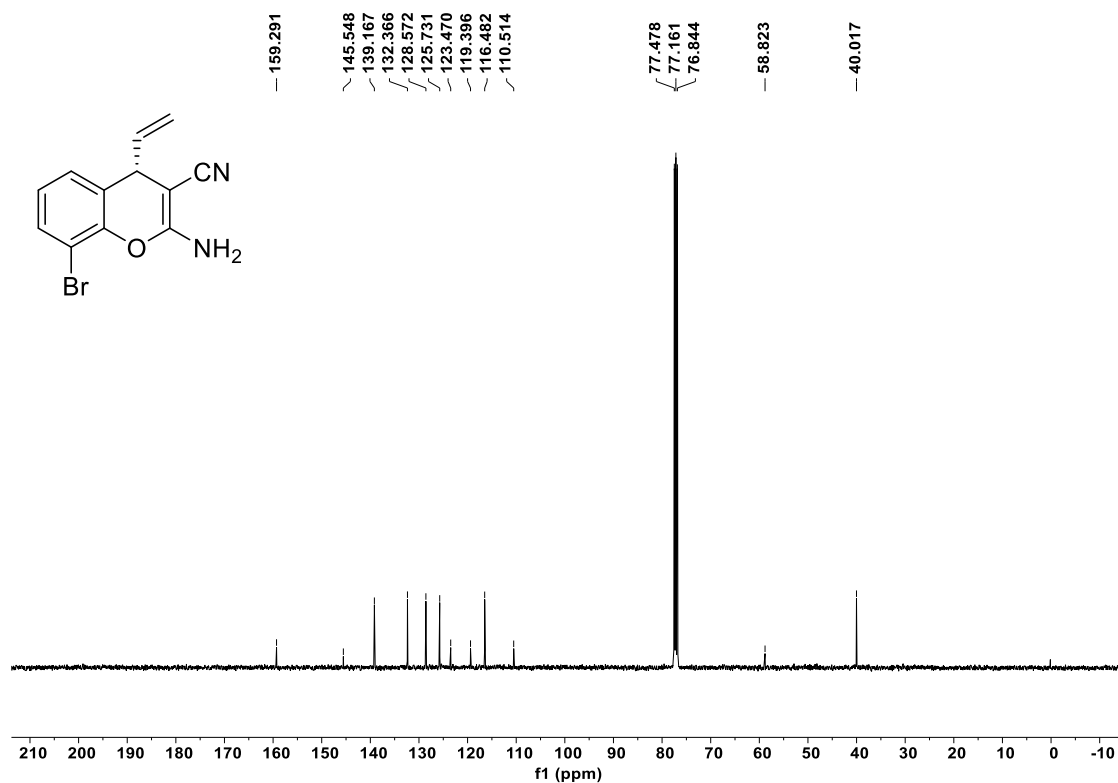
<sup>13</sup>C NMR (100 MHz) of **68** in CDCl<sub>3</sub>



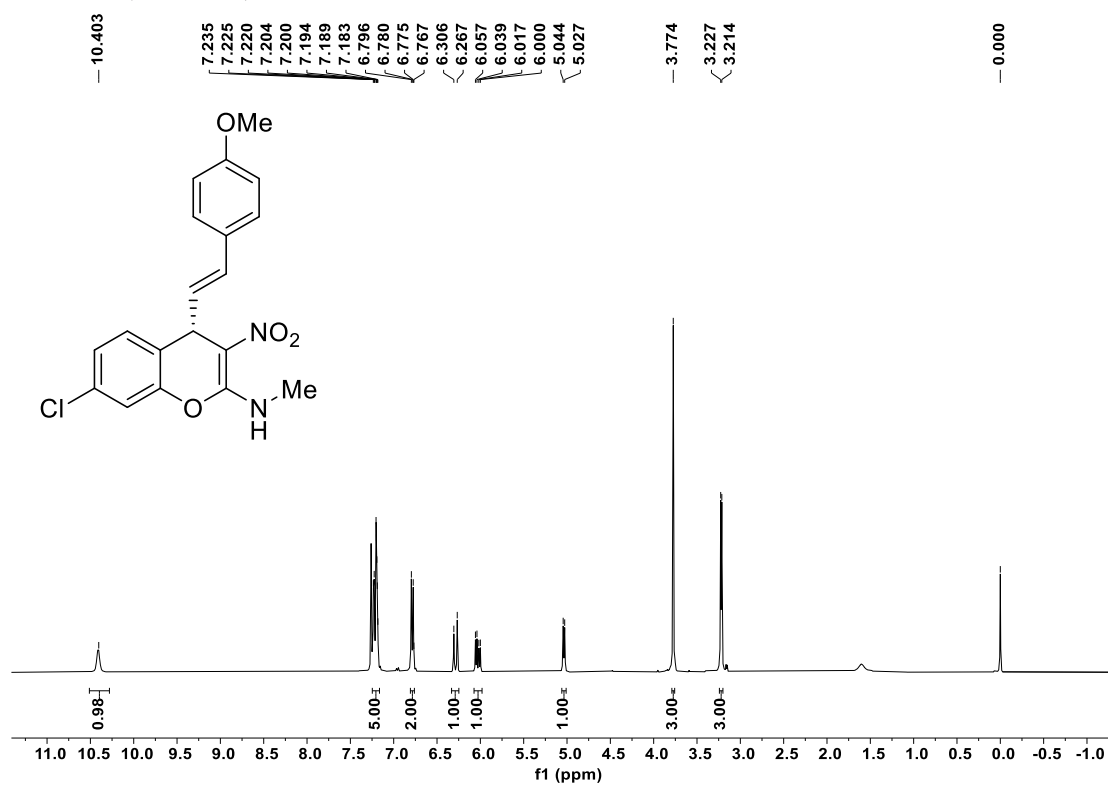
<sup>1</sup>H NMR (400 MHz) of **69** in CDCl<sub>3</sub>



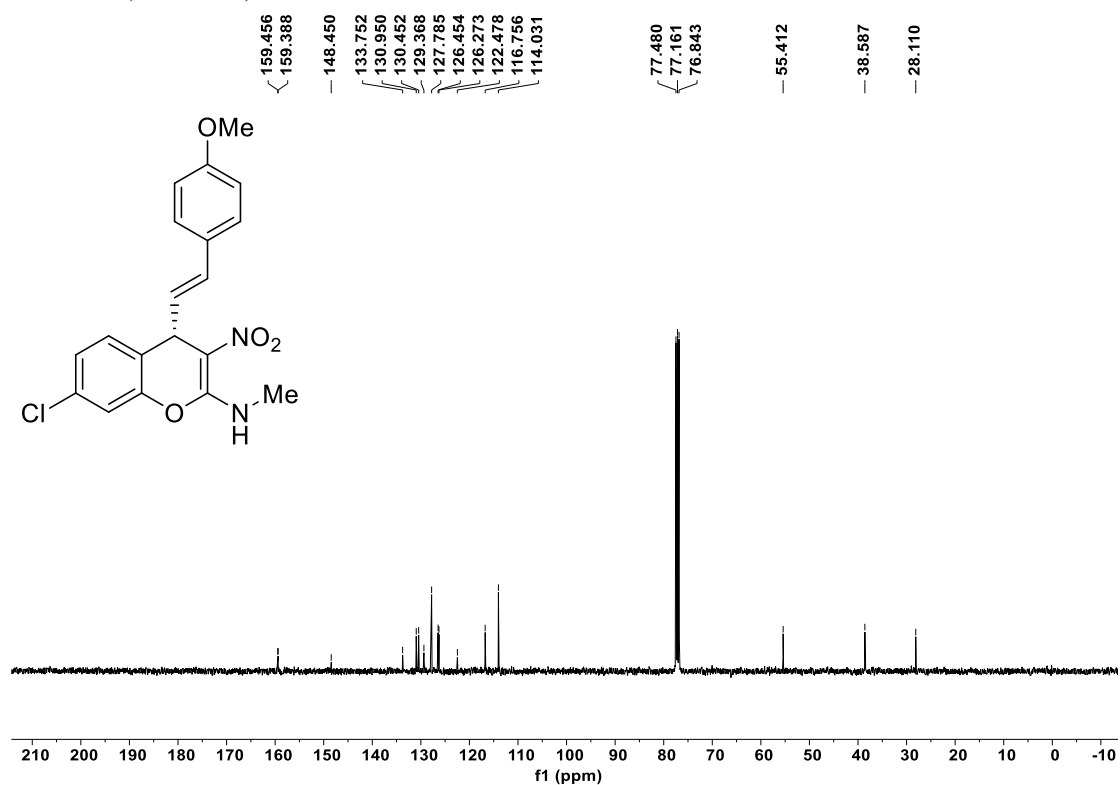
<sup>13</sup>C NMR (100 MHz) of **69** in CDCl<sub>3</sub>



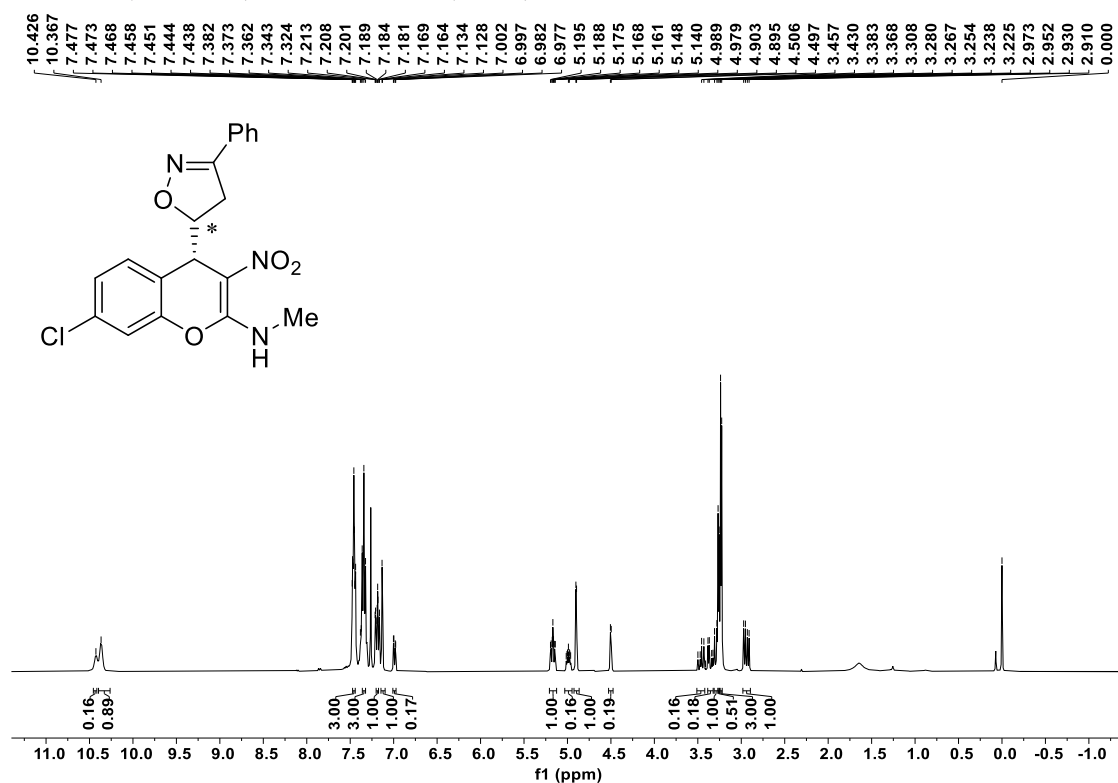
<sup>1</sup>H NMR (400 MHz) of **70** in CDCl<sub>3</sub>



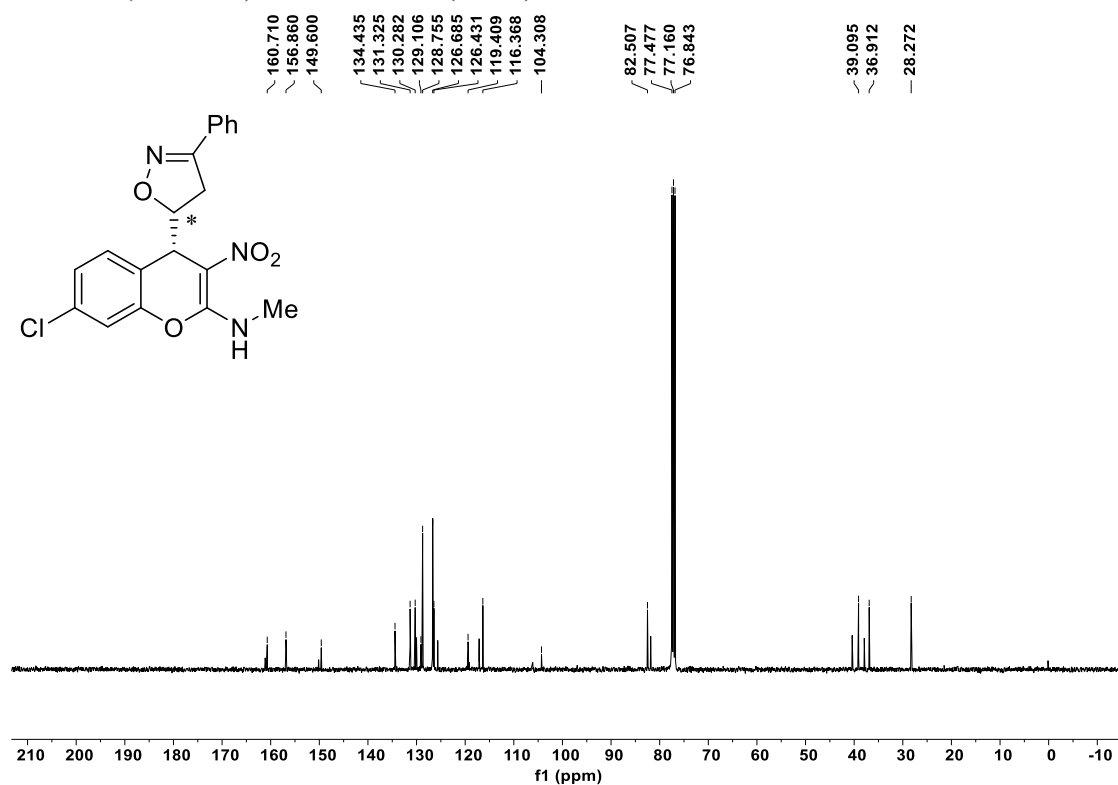
<sup>1</sup>H NMR (400 MHz) of **70** in CDCl<sub>3</sub>



$^1\text{H}$  NMR (400 MHz) of **71** in  $\text{CDCl}_3$  (6:1 dr)

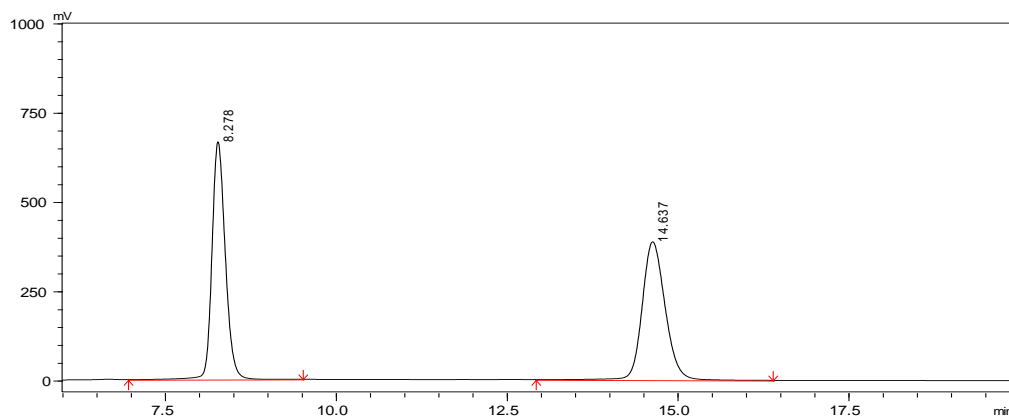
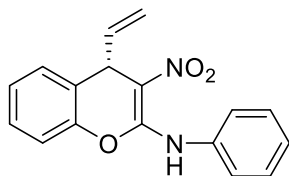


$^1\text{H}$  NMR (400 MHz) of **71** in  $\text{CDCl}_3$  (6:1 dr)

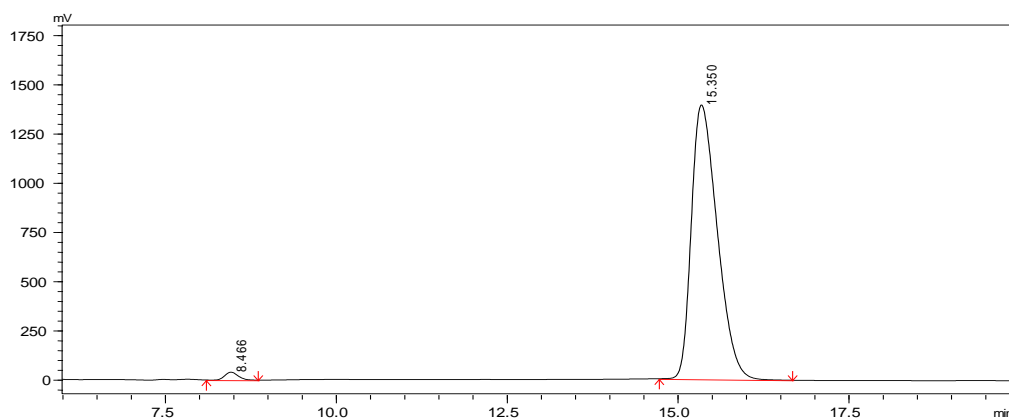


## 9. HPLC Chromatograms

HPLC chromatogram of compound **3** (96% ee)

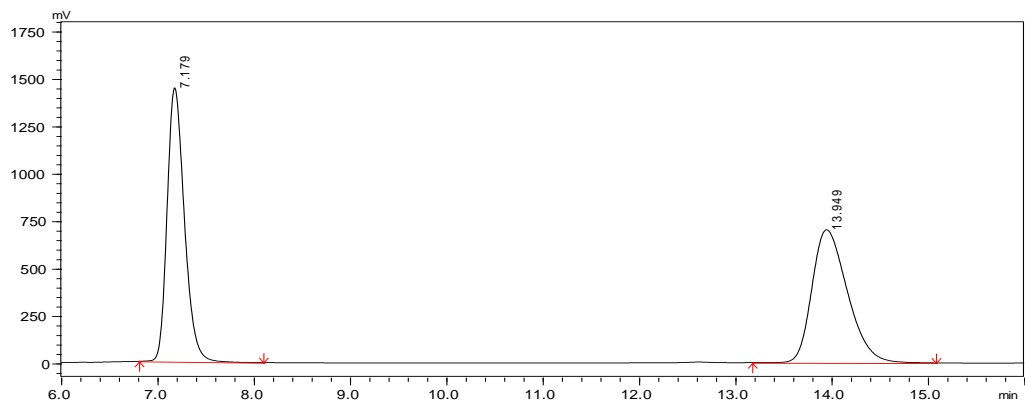
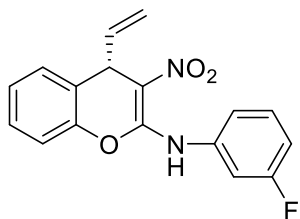


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	8.278	665368	9061535	50.084
2	14.637	386812	9031009	49.916
total		1052180	18092545	100.000

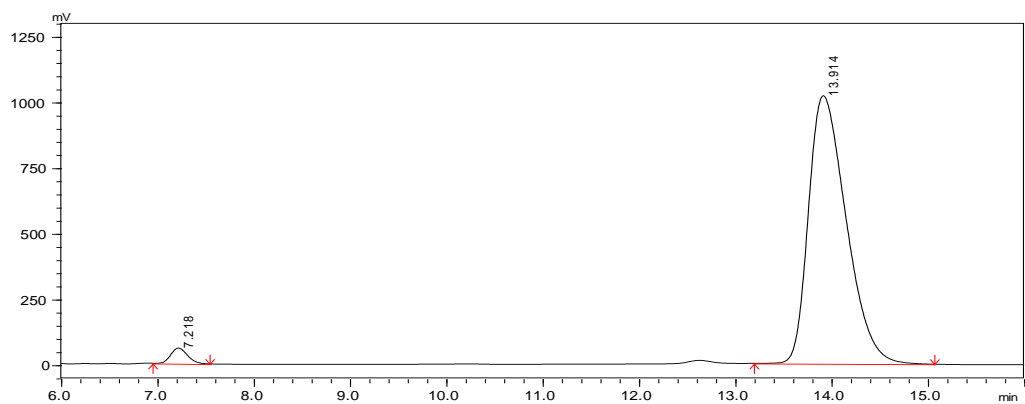


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	8.466	40142	535279	1.434
2	15.350	1393668	36781912	98.566
total		1433810	37317191	100.000

HPLC chromatogram of compound **4** (95% ee)

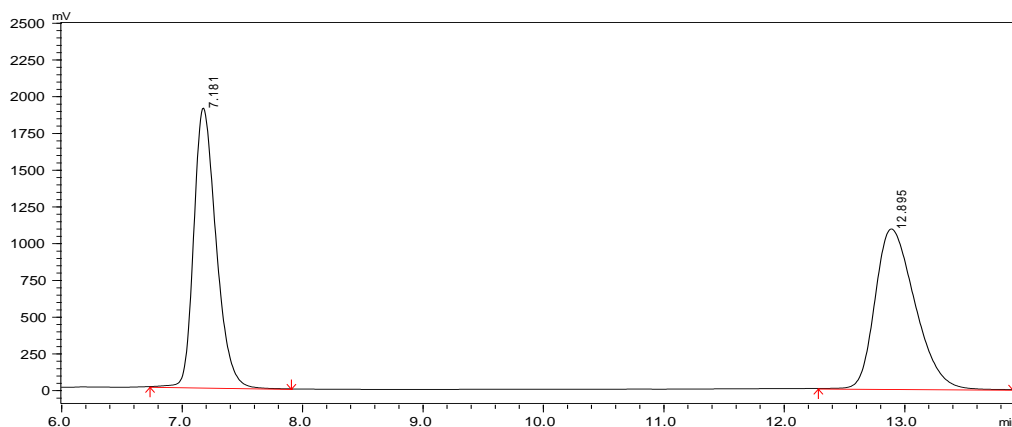
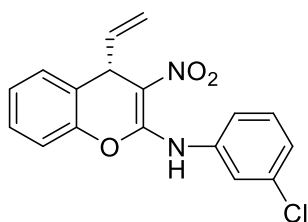


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.179	1443052	17958905	50.020
2	13.949	701107	17944632	49.980
total		2144159	35903537	100.000

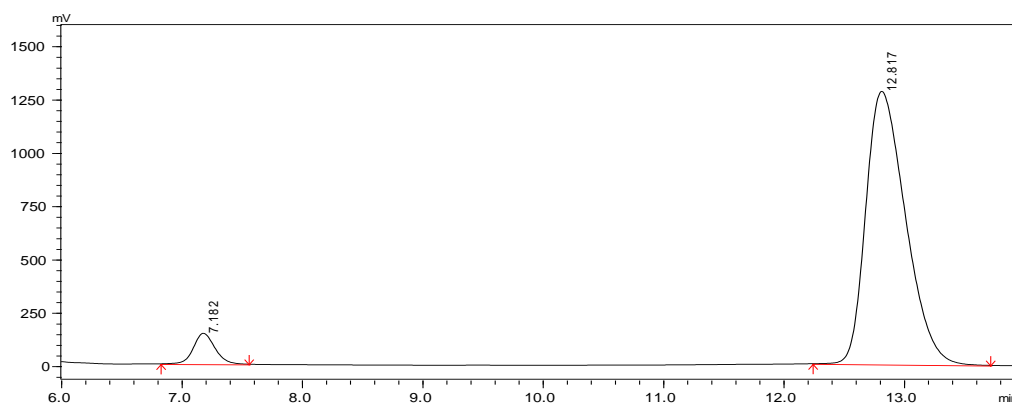


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.218	59046	704580	2.478
2	13.914	1019996	27731713	97.522
total		1079042	28436293	100.000

HPLC chromatogram of compound **5** (89% ee)

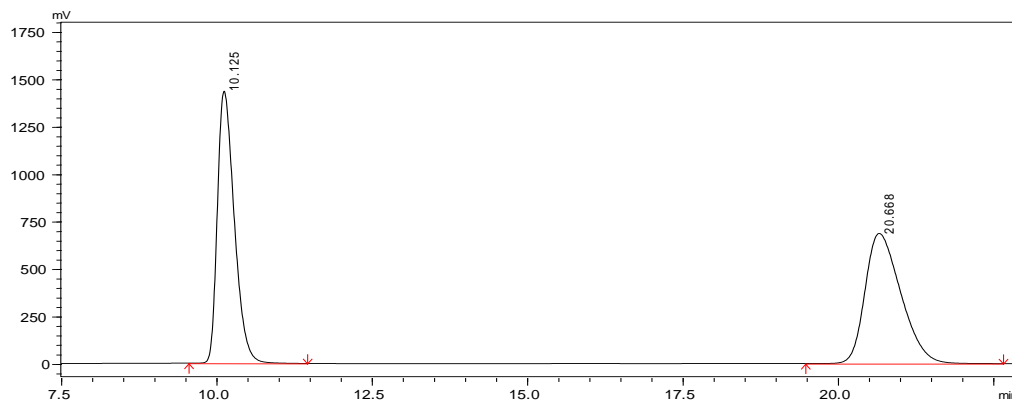
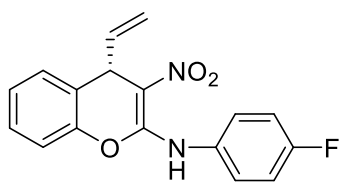


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.181	1900463	24467001	49.594
2	12.895	1087398	24867959	50.406
total		2987861	49334960	100.000

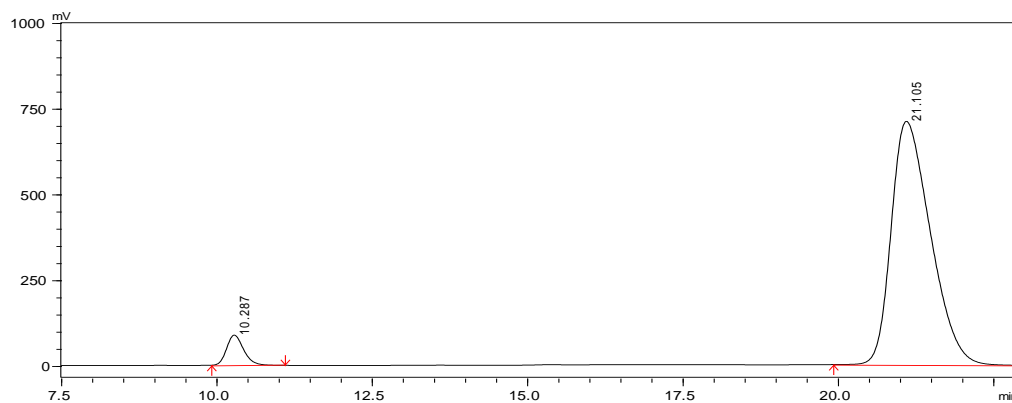


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.182	144067	1777913	5.713
2	12.817	1280006	29341512	94.287
total		1424073	31119425	100.000

HPLC chromatogram of compound **6** (90% ee)



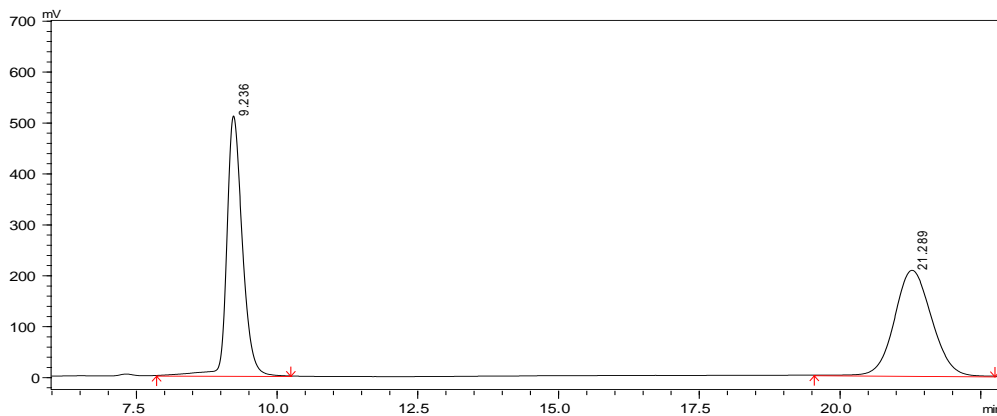
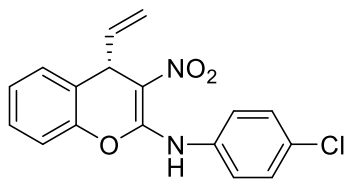
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.125	1434833	27226993	49.821
2	20.668	685887	27422931	50.179
total		2120720	54649924	100.000



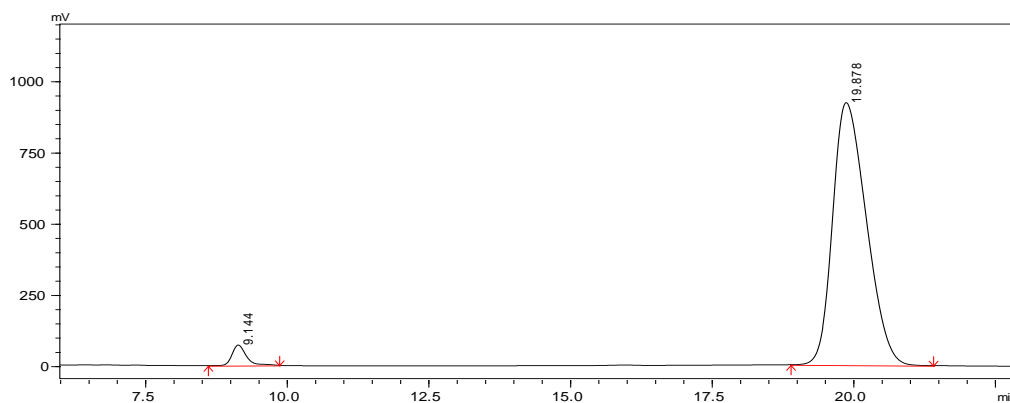
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.287	87008	1585724	4.839
2	21.105	710257	31186276	95.161
total		797265	32772000	100.000



HPLC chromatogram of compound 7 (94% ee)

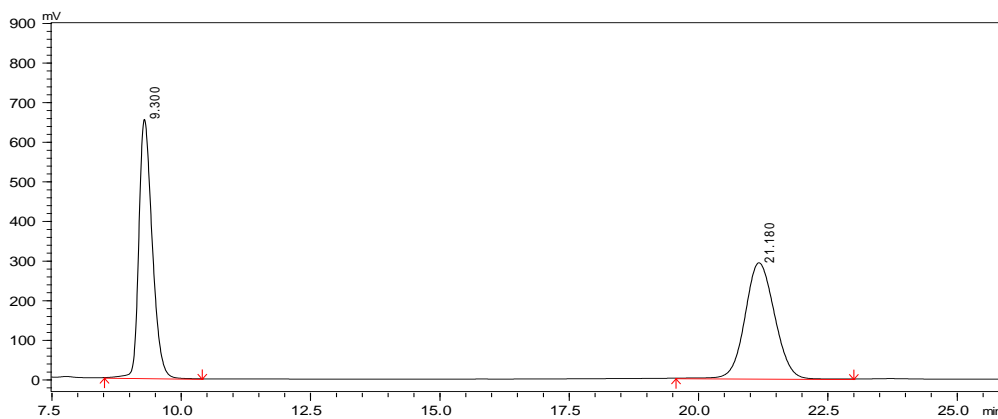
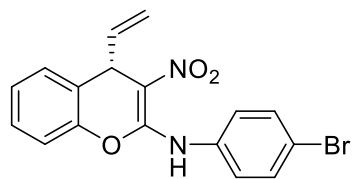


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	9.236	510279	9786964	50.926
2	21.289	206995	9431192	49.074
total		717274	19218156	100.000

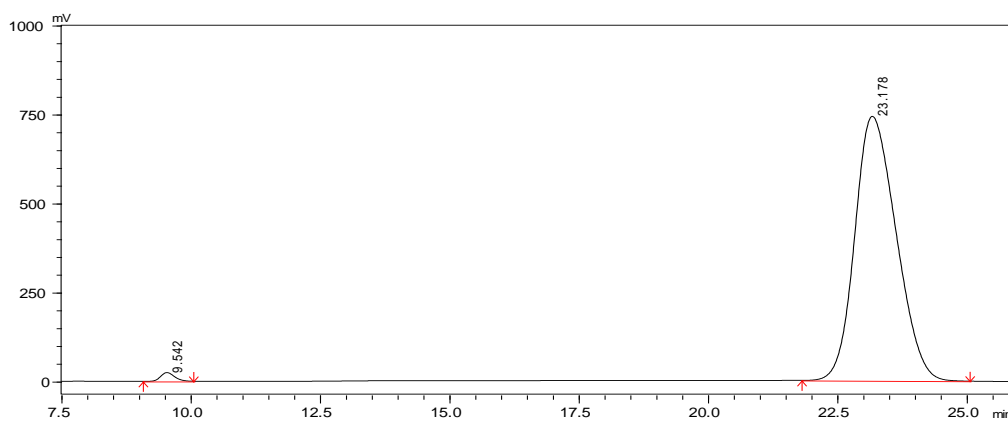


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	9.144	71688	1241611	3.158
2	19.878	921396	38069305	96.842
total		993083	39310916	100.000

HPLC chromatogram of compound **8** (98% ee)

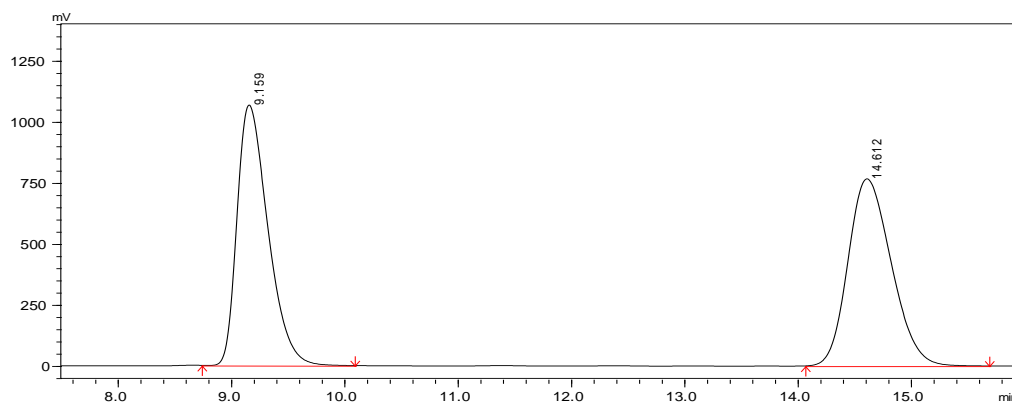
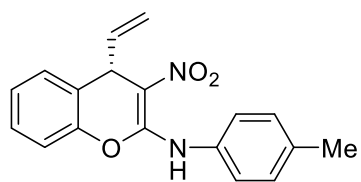


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.300	653567	11699755	50.359
2	21.180	292355	11532887	49.641
total		945923	23232641	100.000

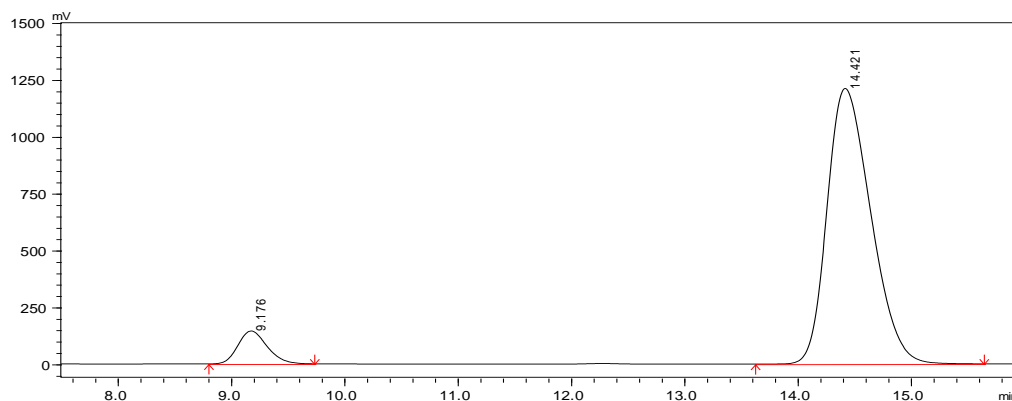


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.542	24475	455031	1.090
2	23.178	742487	41296646	98.910
total		766962	41751677	100.000

HPLC chromatogram of compound **9** (85% ee)

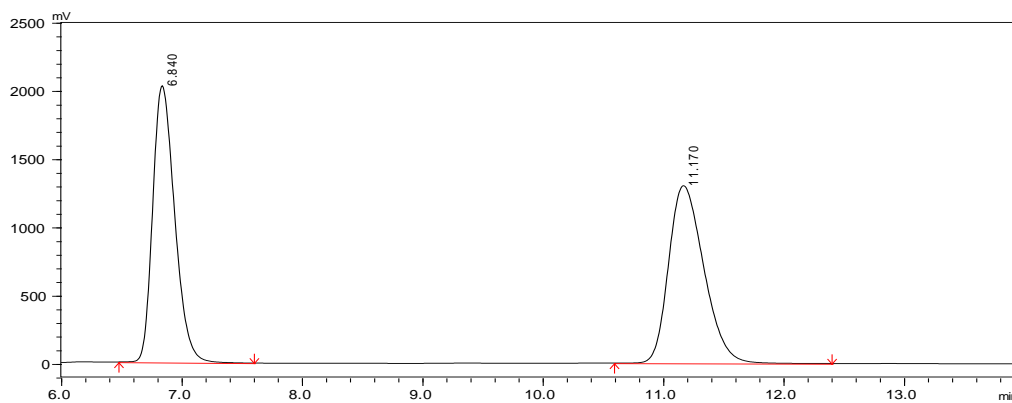
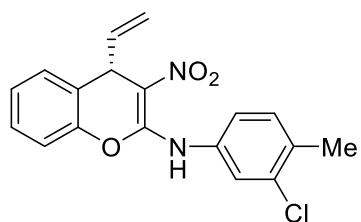


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.159	1066560	20238223	49.900
2	14.612	765863	20319219	50.100
total		1832423	40557442	100.000

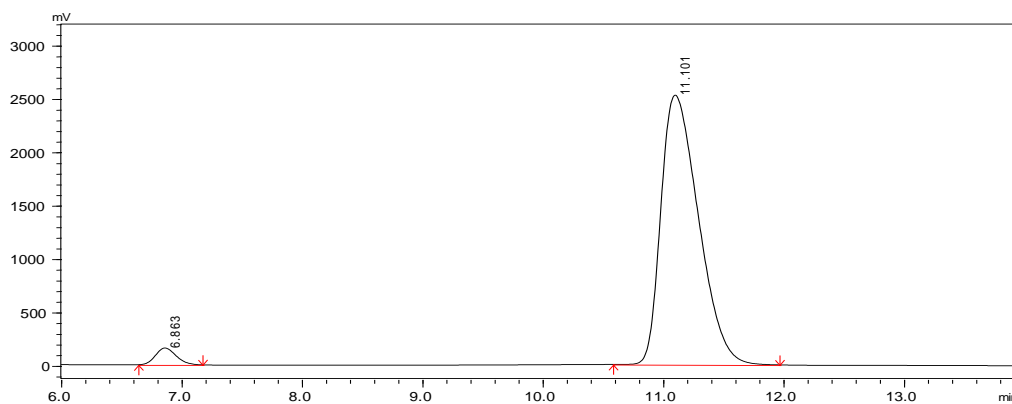


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.176	144348	2588824	7.390
2	14.421	1210705	32440281	92.610
total		1355053	35029106	100.000

HPLC chromatogram of compound **10** (93% ee)

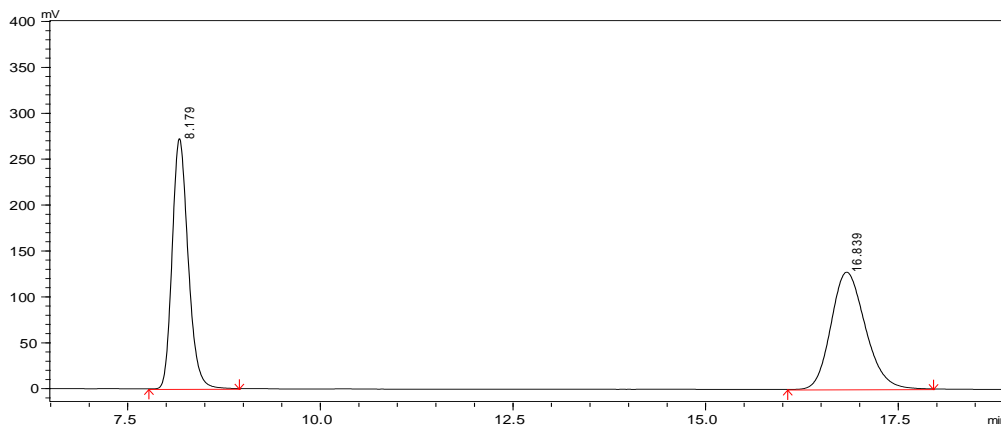
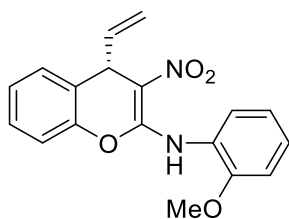


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.840	2026953	25743629	49.404
2	11.170	1300633	26365044	50.596
total		3327586	52108673	100.000

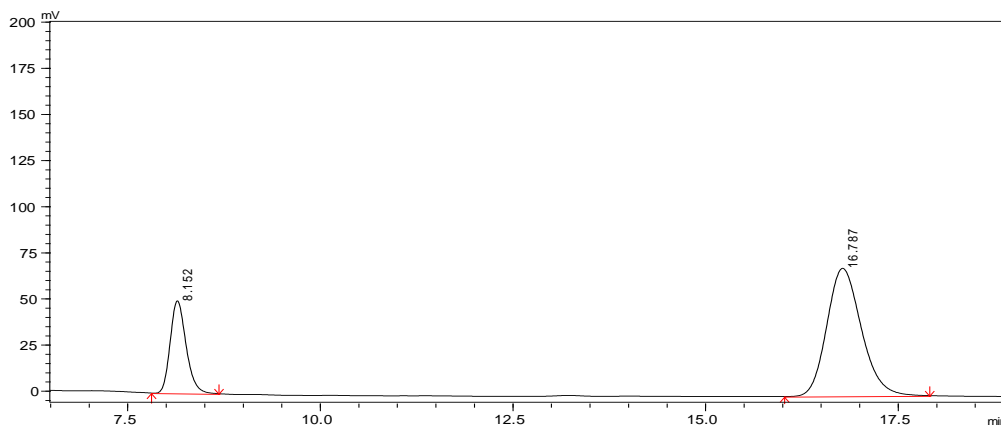


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.863	156845	1859463	3.285
2	11.101	2525037	54746618	96.715
total		2681882	56606081	100.000

HPLC chromatogram of compound **11** (50% ee)

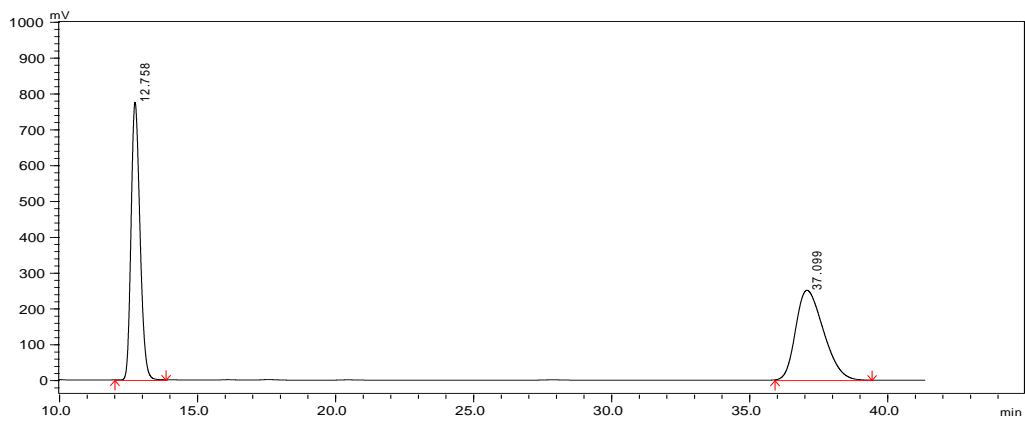
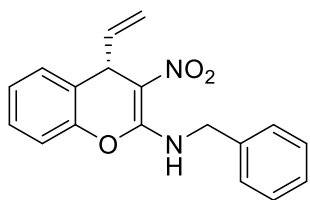


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.179	272333	3922060	49.897
2	16.839	127442	3938198	50.103
total		399775	7860258	100.000

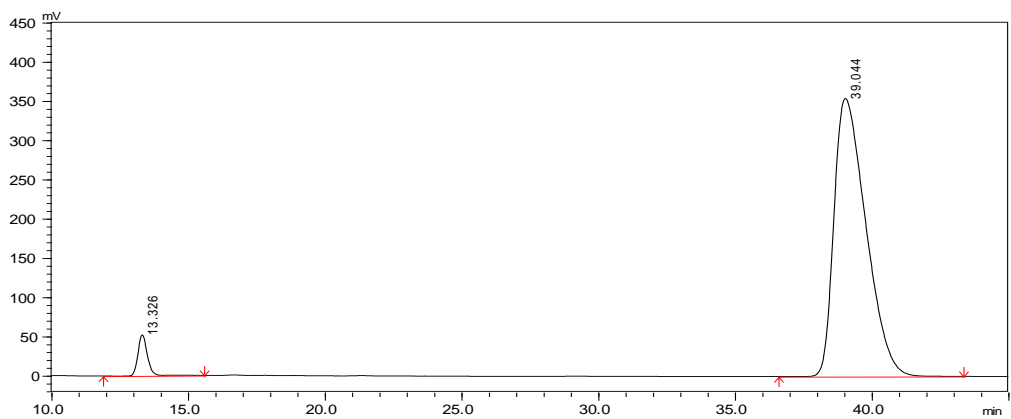


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.152	50105	717116	24.926
2	16.787	69254	2159852	75.074
total		119359	2876968	100.000

HPLC chromatogram of compound **12** (92% ee)

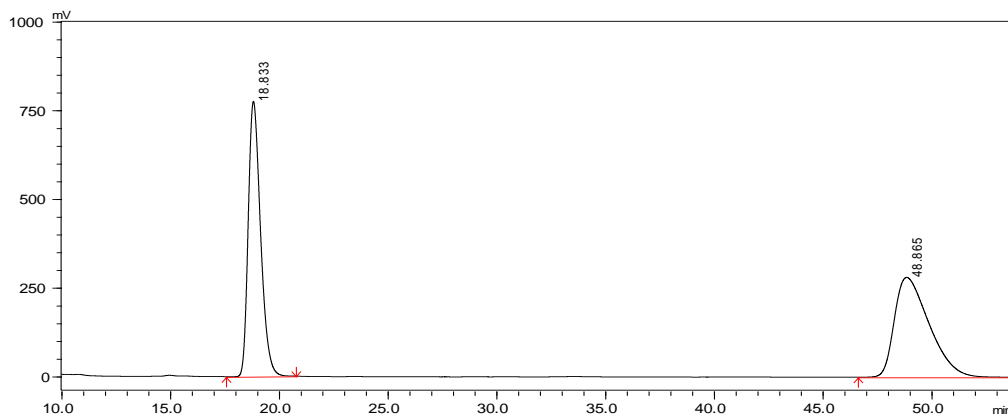
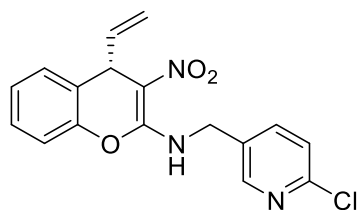


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	12.758	17374541	774483	49.812
2	37.099	17505443	250372	50.188
total		34879984	1024855	100.000

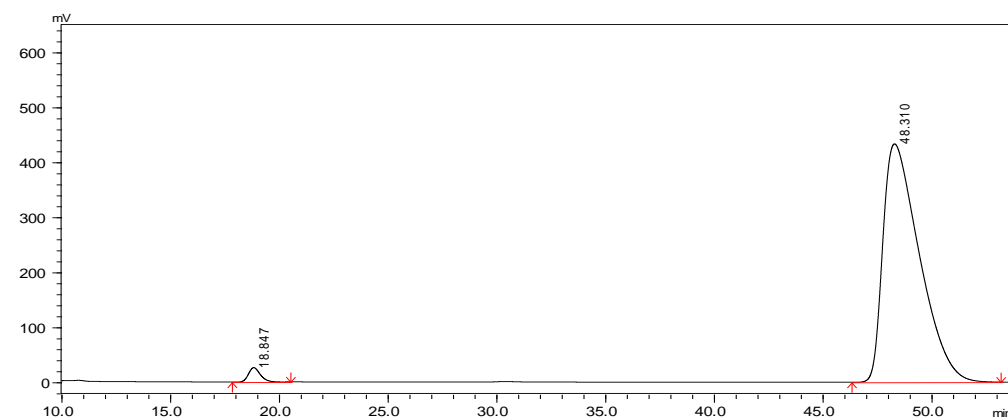


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	13.326	1234587	51985	4.120
2	39.044	28730828	354169	95.880
total		29965415	406153	100.000

HPLC chromatogram of compound **13** (96% ee)

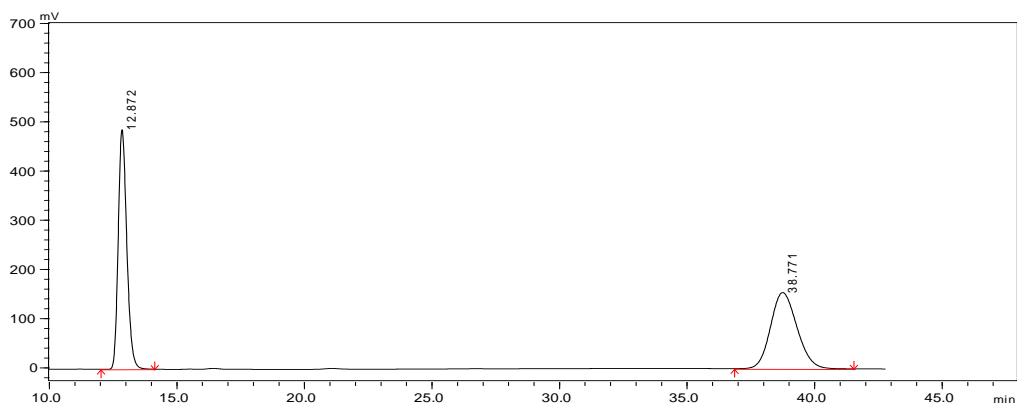
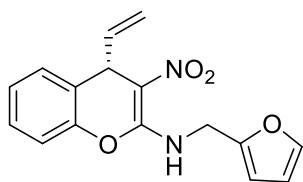


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	18.833	30506618	775136	49.544
2	48.865	31068088	281096	50.456
total		61574706	1056232	100.000

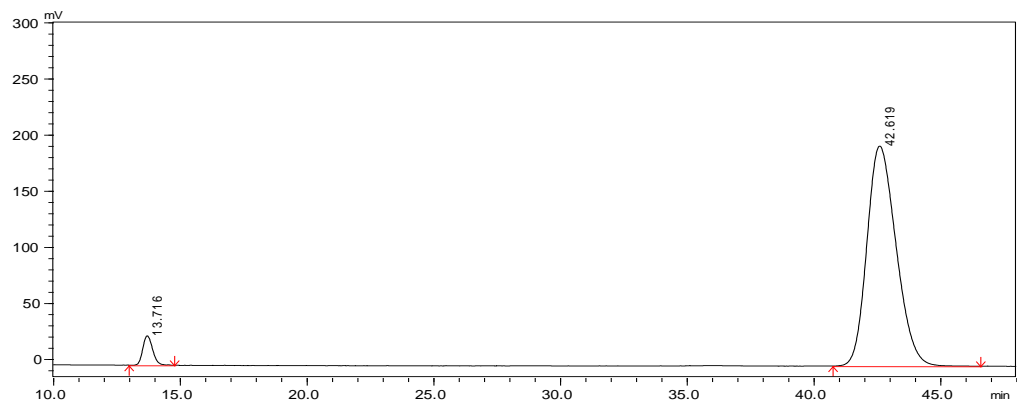


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	18.847	978150	26082	1.900
2	48.310	50516790	433424	98.100
total		51494941	459505	100.000

HPLC chromatogram of compound **14** (91% ee)



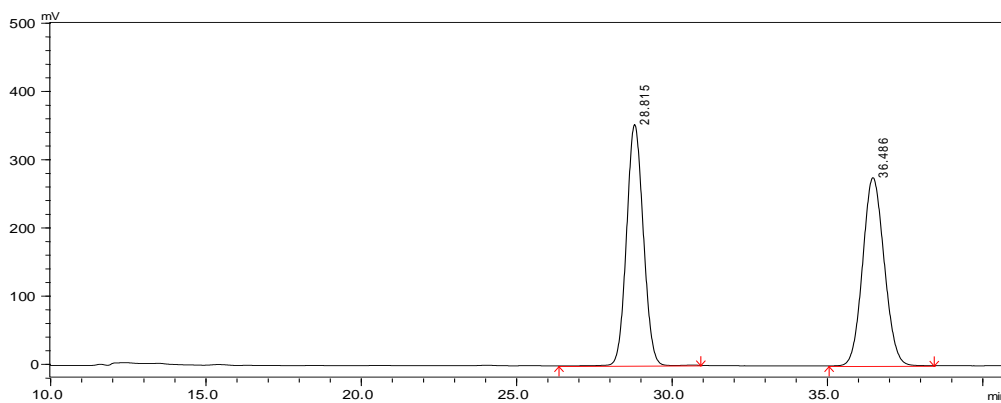
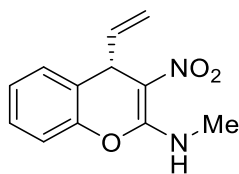
#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	12.872	486622	11381800	50.569
2	38.771	154687	11125501	49.431
total		641308	22507301	100.000



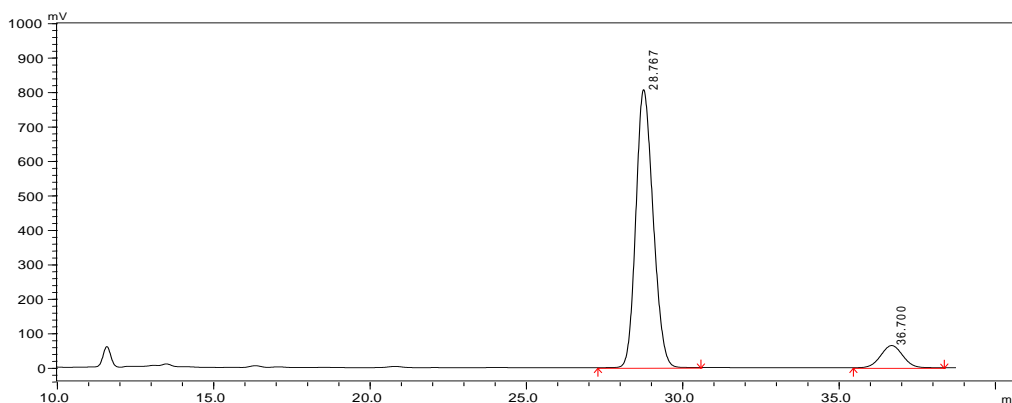
#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	13.716	26135	705581	4.306
2	42.619	196002	15680422	95.694
total		222137	16386004	100.000



HPLC chromatogram of compound **15** (82% ee)

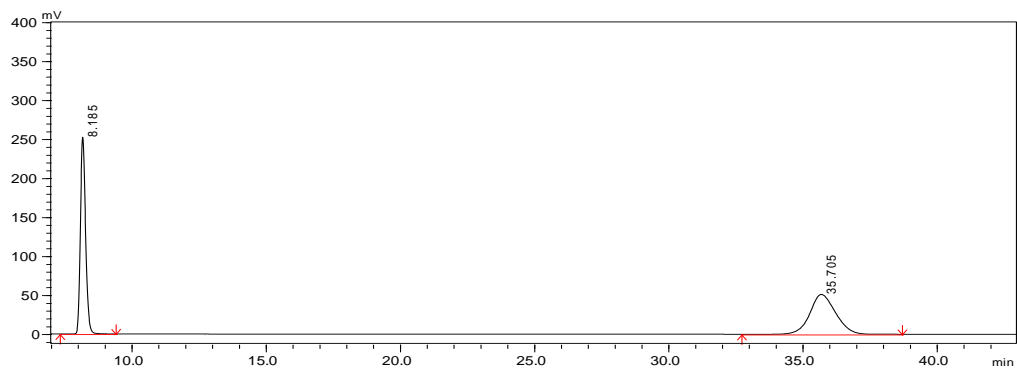
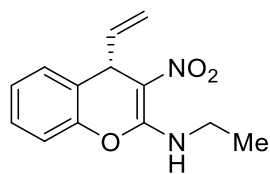


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	28.815	353114	13195412	49.840
2	36.486	275653	13280166	50.160
total		628767	26475578	100.000

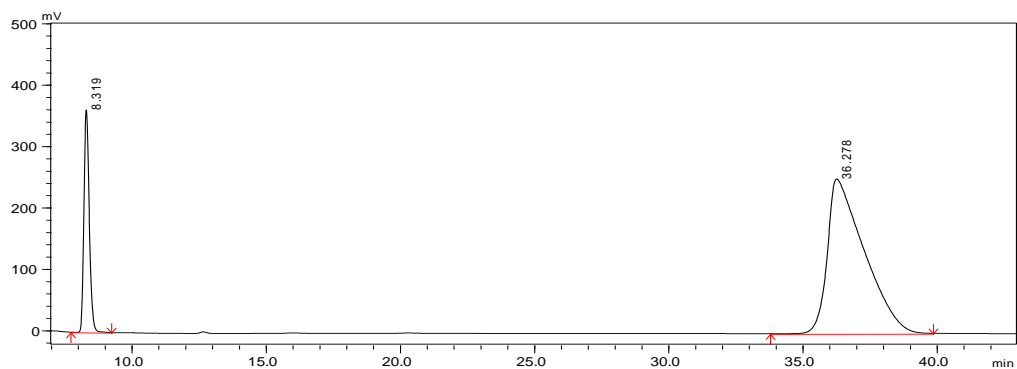


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	28.767	806115	30868500	90.786
2	36.700	64311	3132844	9.214
total		870426	34001345	100.000

HPLC chromatogram of compound **16** (65% ee)

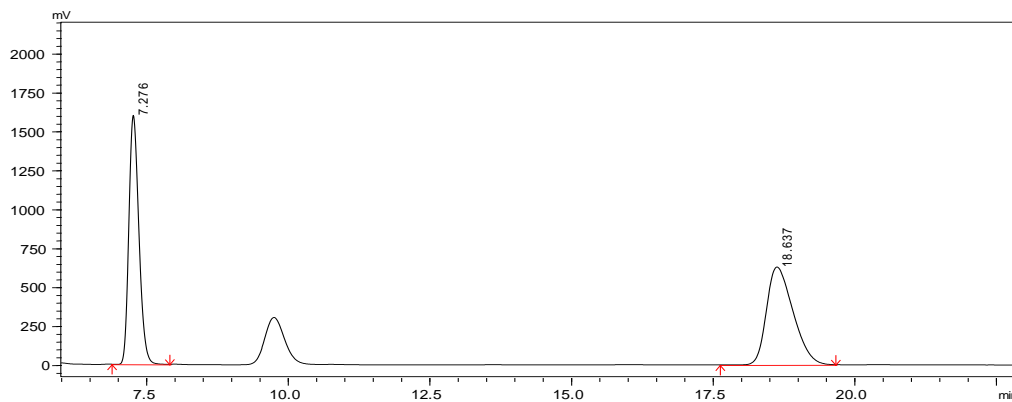
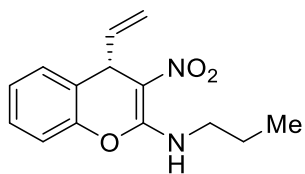


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.185	252169	3390068	49.897
2	35.705	51005	3404018	50.103
total		303173	6794086	100.000

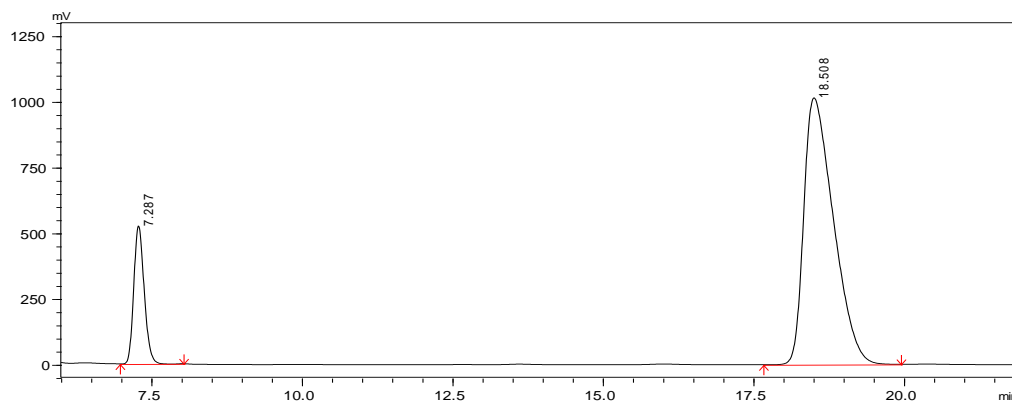


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.319	362578	5016750	17.282
2	36.278	251727	24012842	82.718
total		614305	29029592	100.000

HPLC chromatogram of compound **17** (69% ee)

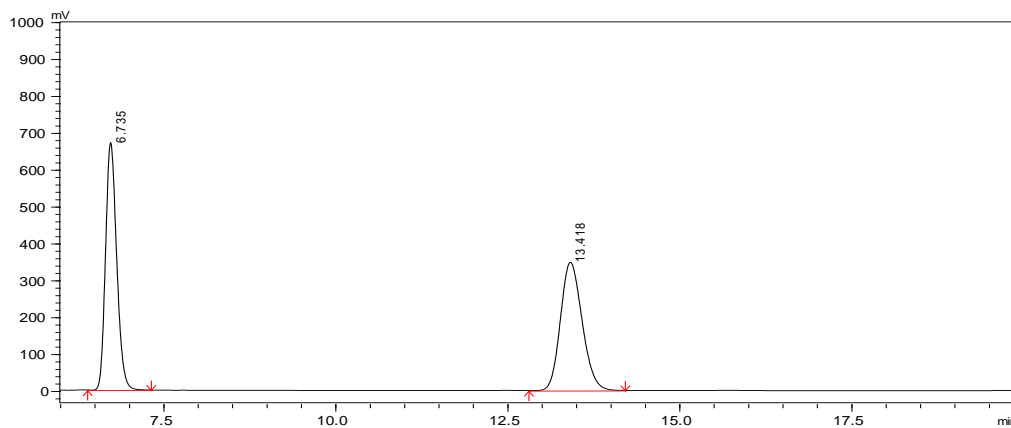
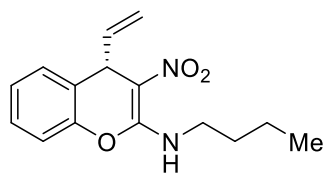


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.276	1598393	19603537	49.103
2	18.637	627745	20319377	50.897
total		2226138	39922914	100.000

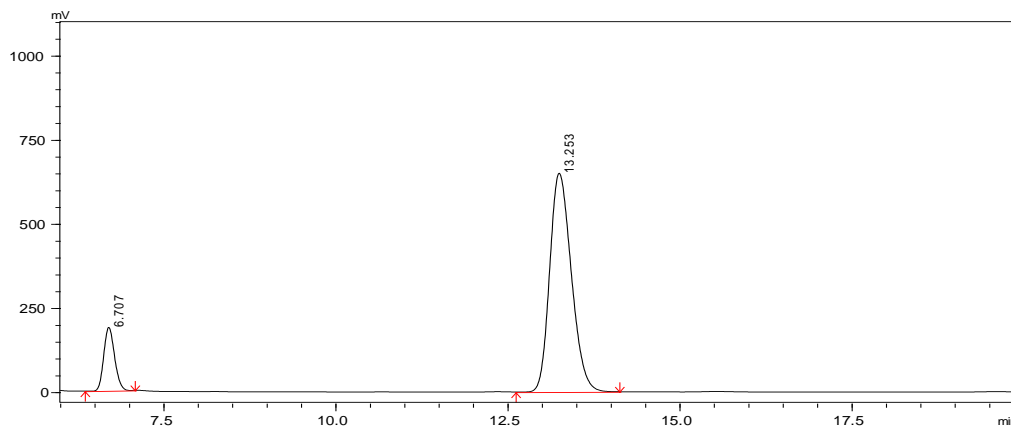


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.287	523900	6293852	15.330
2	18.508	1014498	34761559	84.670
total		1538399	41055411	100.000

HPLC chromatogram of compound **18** (75% ee)

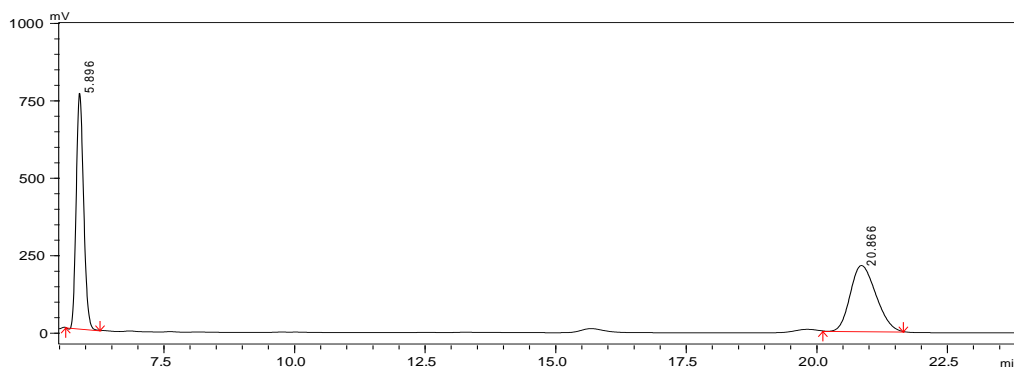
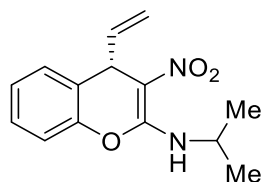


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.735	670868	7549701	49.817
2	13.418	347626	7605054	50.183
total		1018494	15154756	100.000

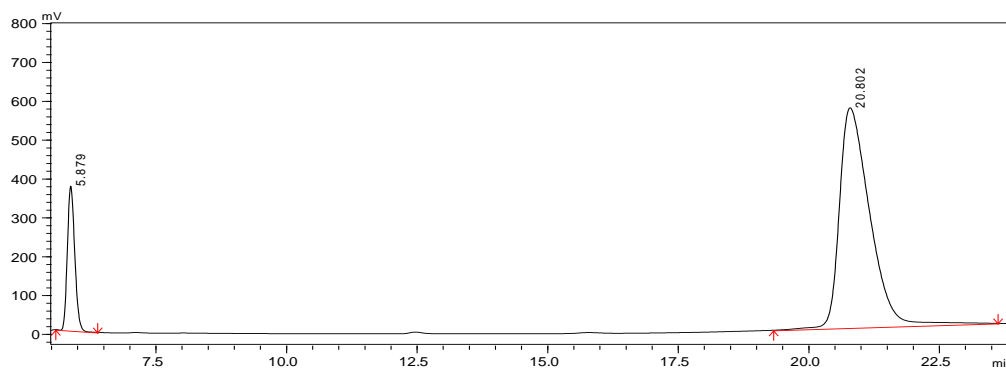


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.707	188250	2040167	12.557
2	13.253	649839	14206549	87.443
total		838090	16246716	100.000

HPLC chromatogram of compound **19** (72% ee)

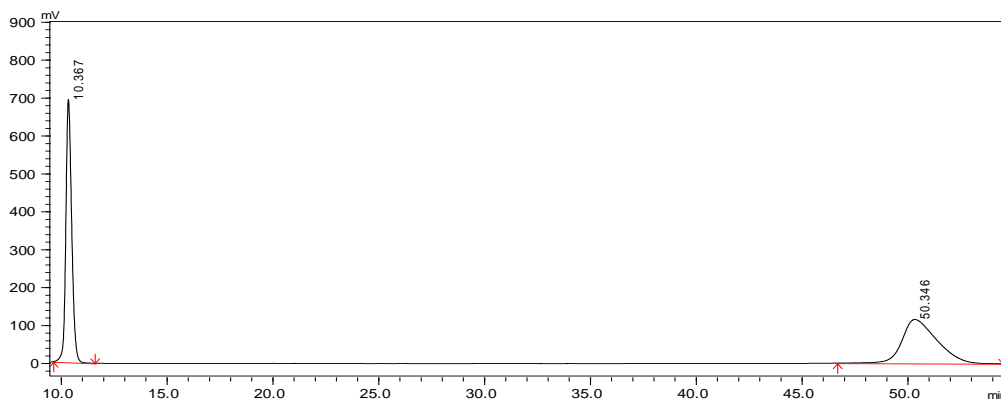
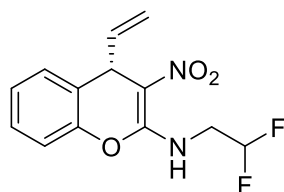


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.896	759152	7448156	50.884
2	20.866	211881	7189402	49.116
total		971033	14637558	100.000

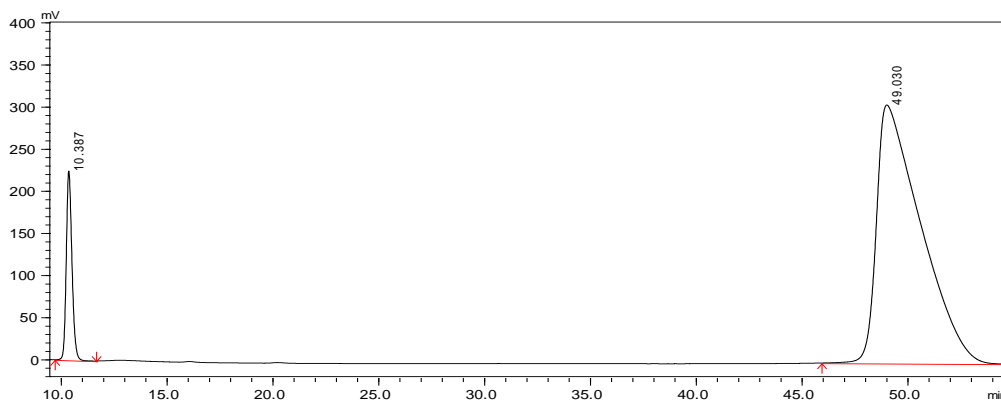


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.879	371654	3641534	13.706
2	20.802	566416	22927632	86.294
total		938070	26569165	100.000

HPLC chromatogram of compound **20** (83% ee)

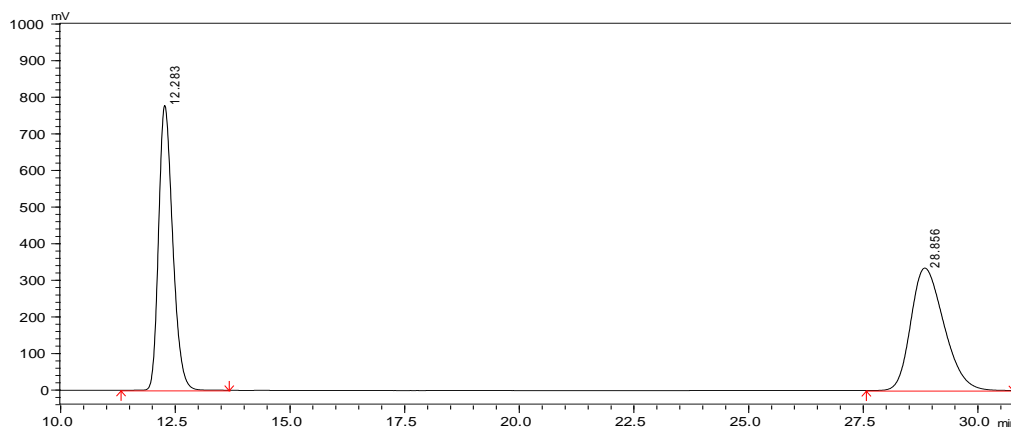
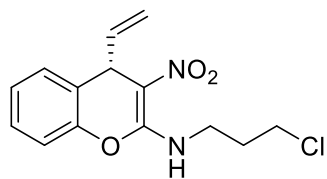


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.367	693217	13330797	50.329
2	50.346	115845	13156597	49.671
total		809061	26487394	100.000

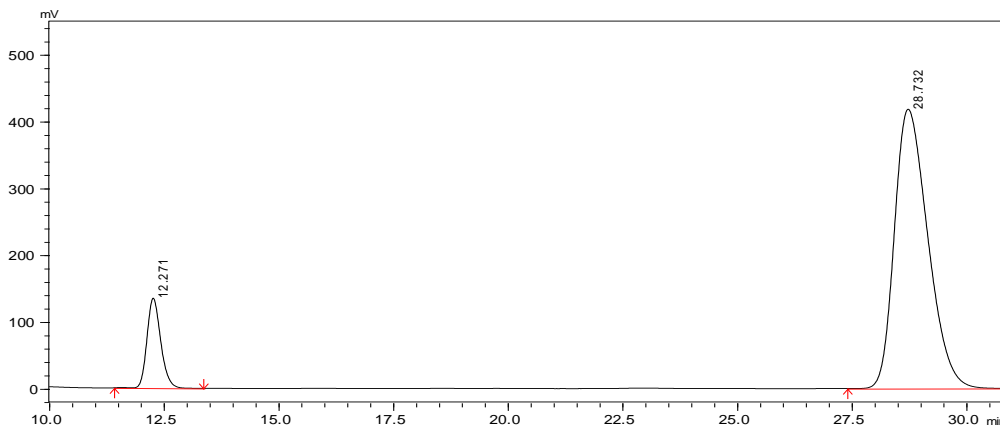


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.387	224508	4188166	8.601
2	49.030	306647	44506410	91.399
total		531155	48694575	100.000

HPLC chromatogram of compound **21** (77% ee)

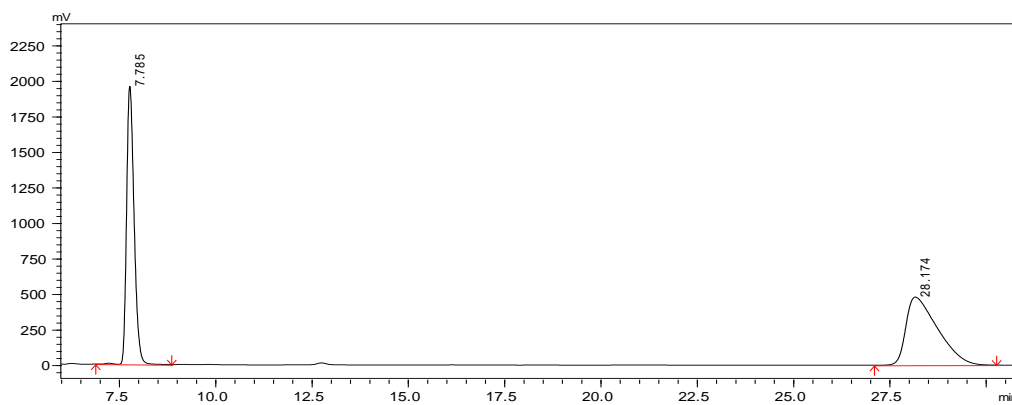
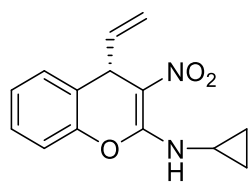


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.283	778052	16623158	49.817
2	28.856	334311	16745013	50.183
total		1112363	33368171	100.000

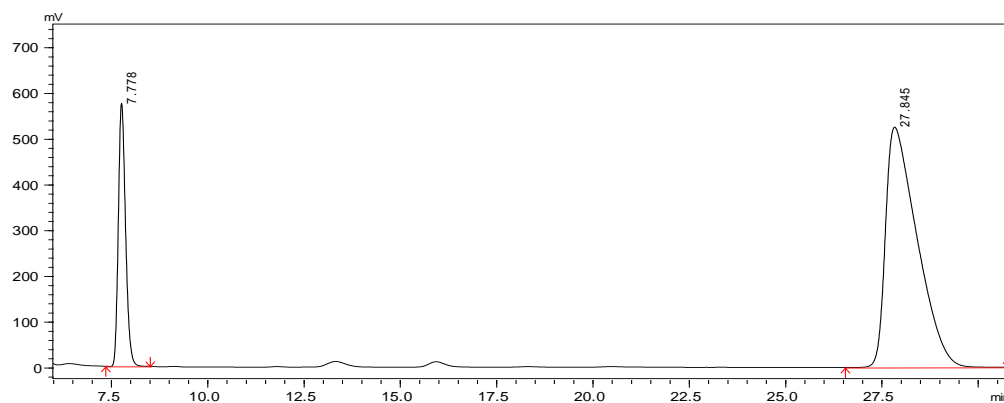


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.271	134425	2797913	11.670
2	28.732	418187	21176382	88.330
total		552612	23974295	100.000

HPLC chromatogram of compound **22** (60% ee)



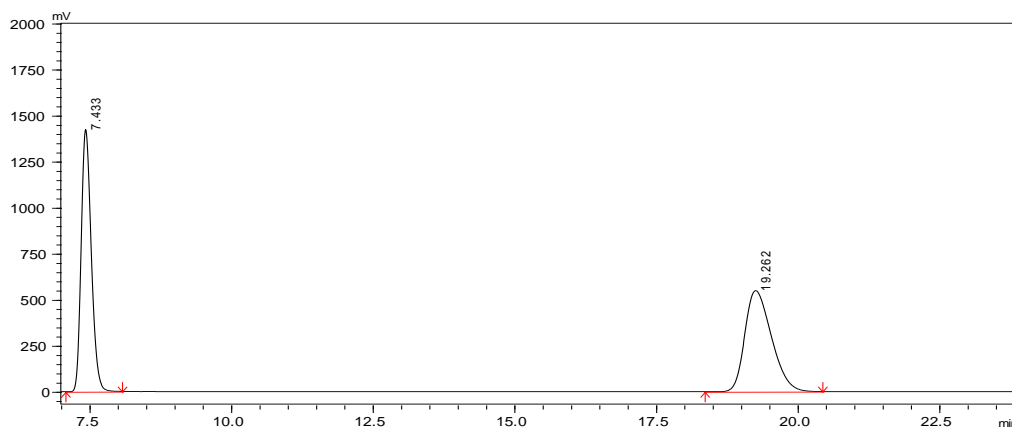
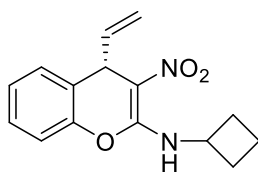
#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	7.785	1956541	26411047	49.232
2	28.174	479196	27235521	50.768
total		2435738	53646567	100.000



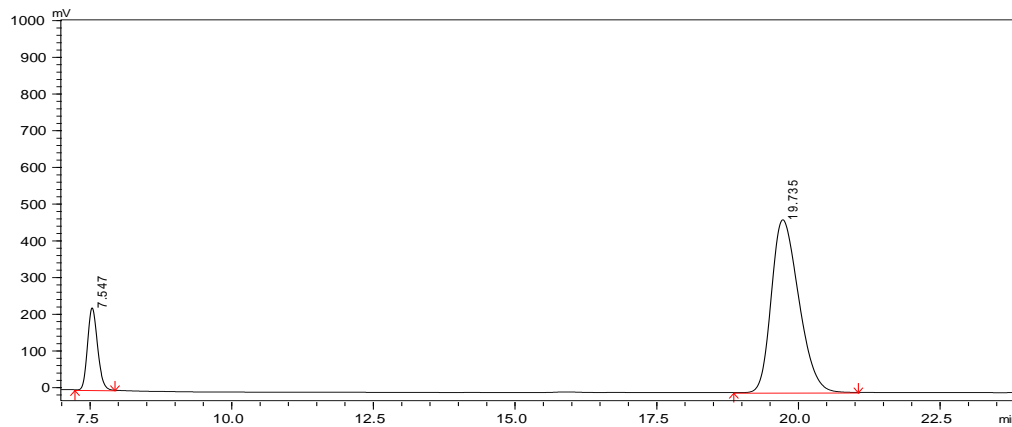
#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	7.778	574364	7483138	20.064
2	27.845	525118	29812745	79.936
total		1099482	37295883	100.000



HPLC chromatogram of compound **23** (70% ee)

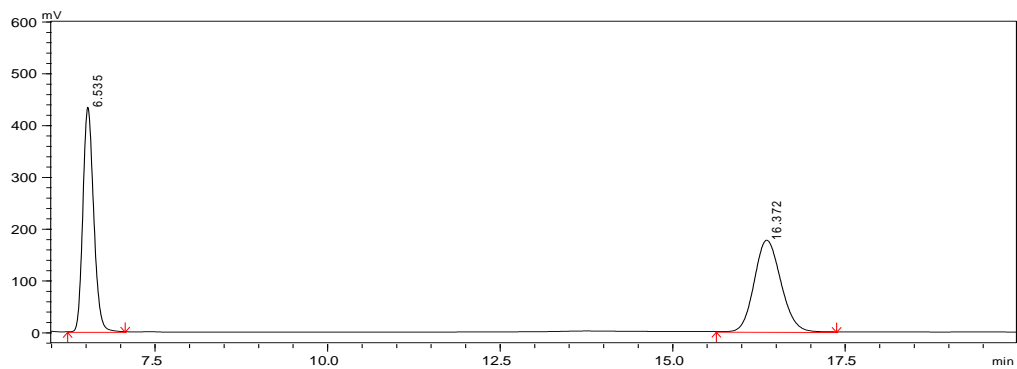
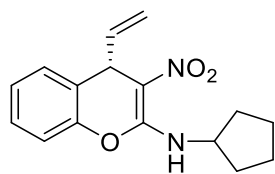


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.433	1423299	17597122	49.548
2	19.262	548545	17918438	50.452
total		1971844	35515560	100.000

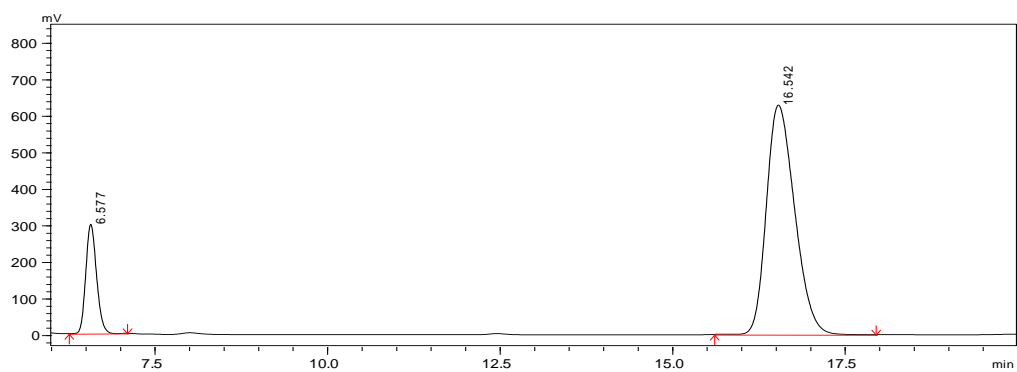


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.547	223415	2744417	14.811
2	19.735	470871	15784654	85.189
total		694286	18529071	100.000

HPLC chromatogram of compound **24** (69% ee)

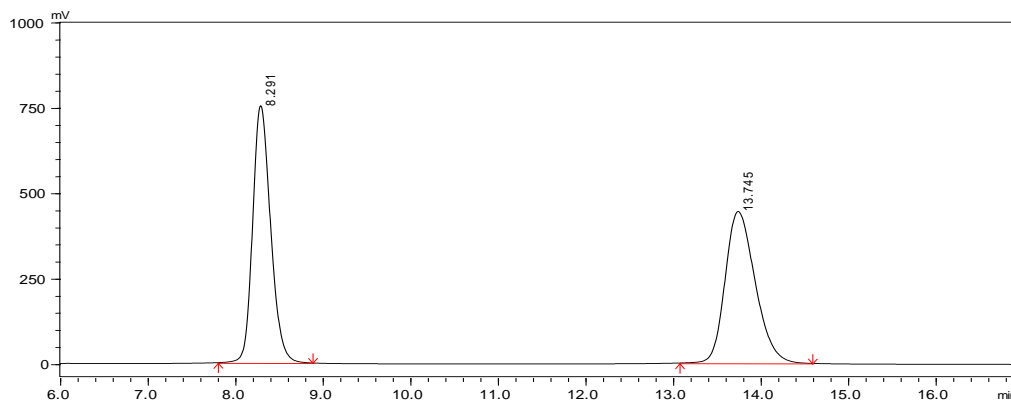
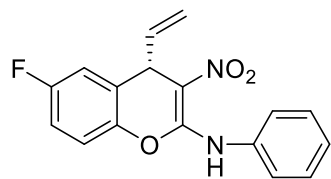


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	6.535	433603	4703663	49.942
2	16.372	176600	4714681	50.058
total		610203	9418344	100.000

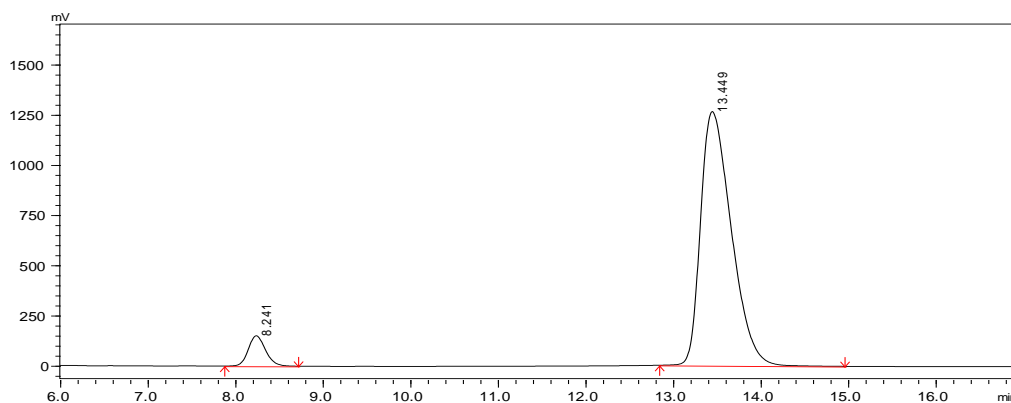


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	6.577	299162	3229740	15.306
2	16.542	628058	17871697	84.694
total		927220	21101436	100.000

HPLC chromatogram of compound **25** (87% ee)

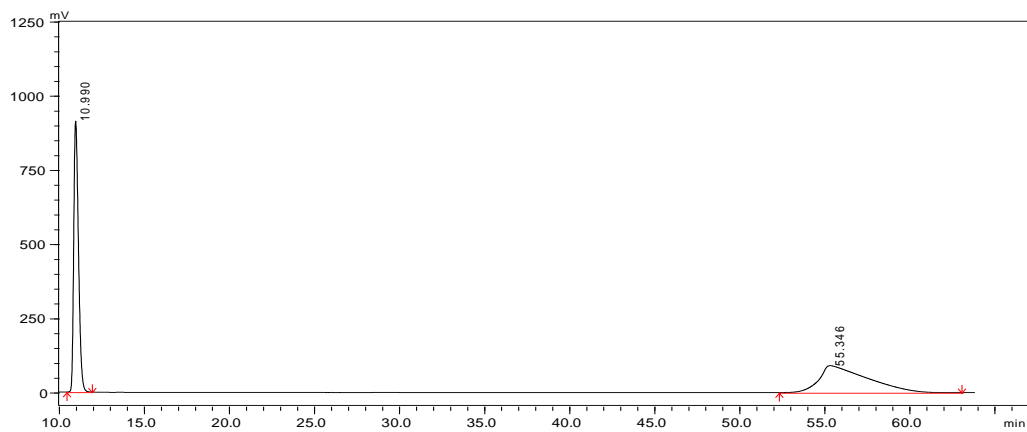
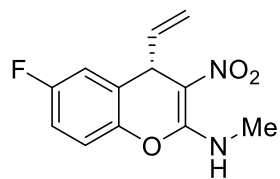


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.291	752515	10748595	50.340
2	13.745	444090	10603295	49.660
total		1196604	21351890	100.000

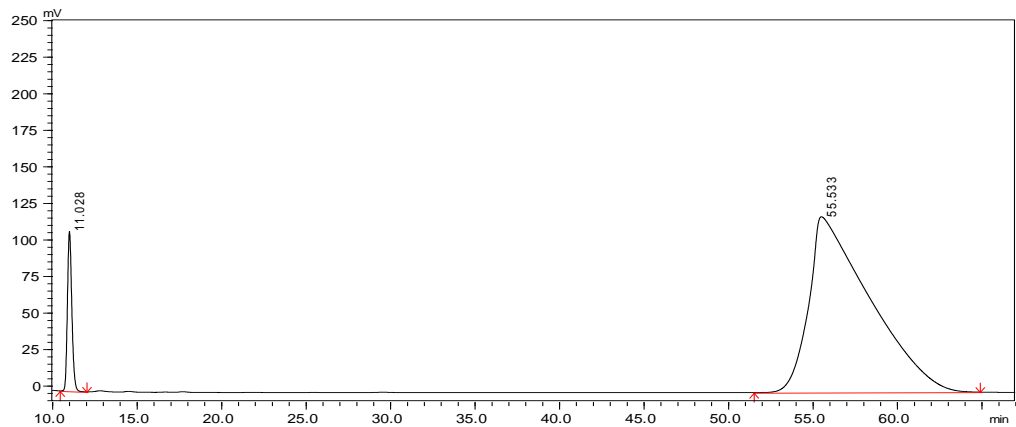


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.241	151220	2065435	6.282
2	13.449	1264868	30810990	93.718
total		1416088	32876425	100.000

HPLC chromatogram of compound **26** (88% ee)

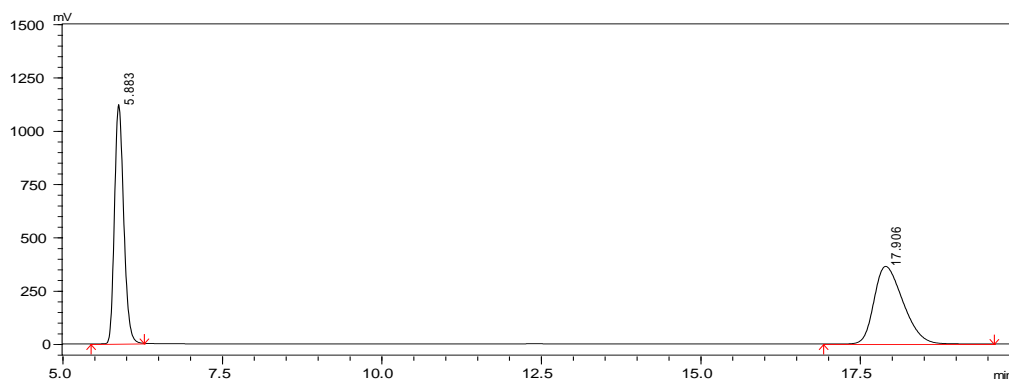
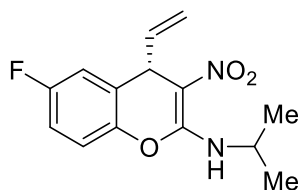


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.990	912175	17592891	49.751
2	55.346	90733	17769066	50.249
total		1002908	35361956	100.000

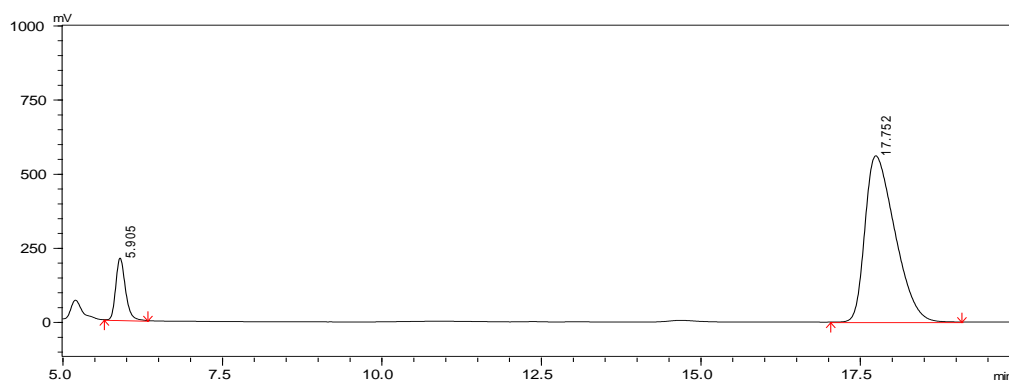


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.028	109262	1986498	6.163
2	55.533	120183	30244984	93.837
total		229445	32231482	100.000

HPLC chromatogram of compound **27** (79% ee)

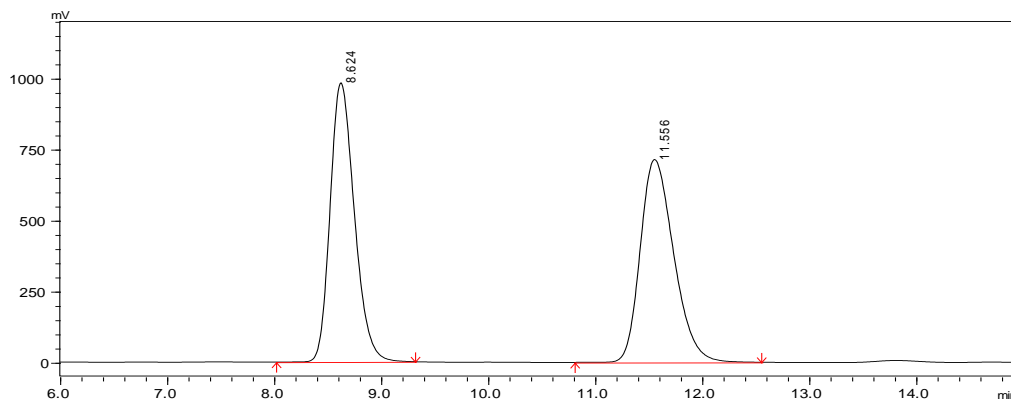
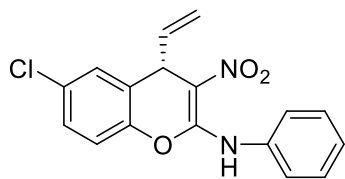


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.883	1120377	11255867	49.579
2	17.906	363606	11447038	50.421
total		1483983	22702905	100.000

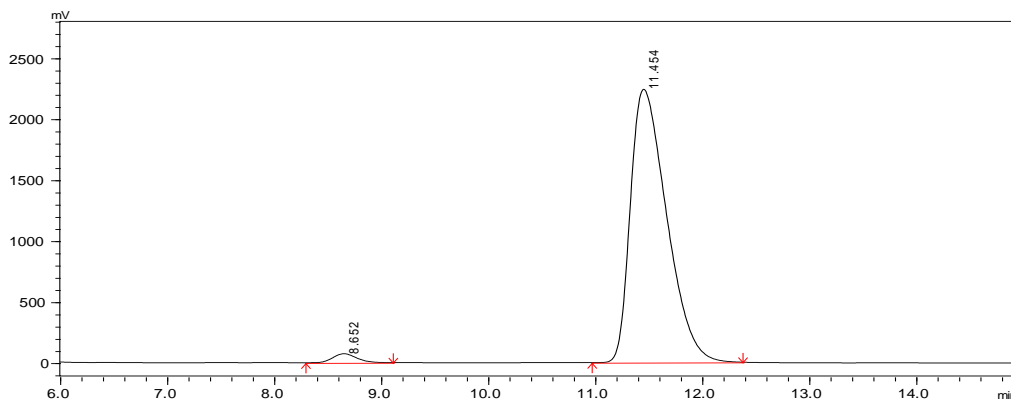


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.905	208647	2183942	10.690
2	17.752	560621	18245914	89.310
total		769268	20429856	100.000

HPLC chromatogram of compound **28** (96% ee)

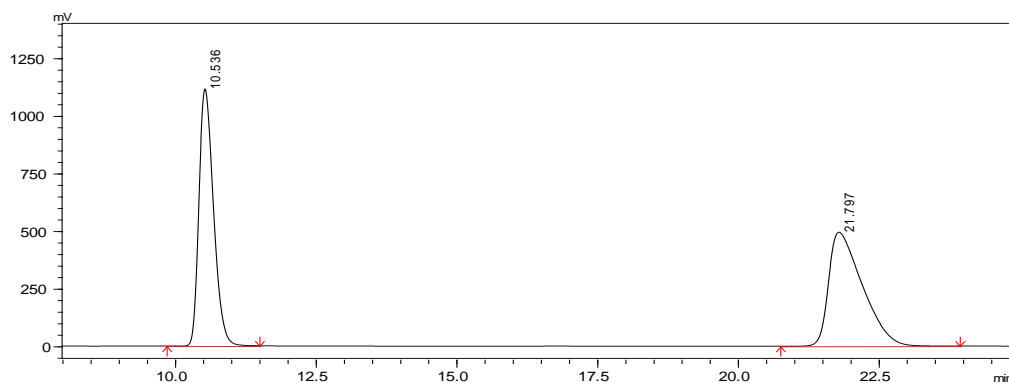
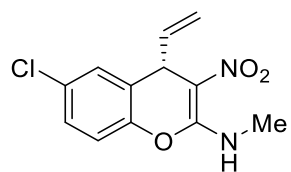


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.624	982347	15480405	49.940
2	11.556	713612	15517604	50.060
total		1695959	30998009	100.000

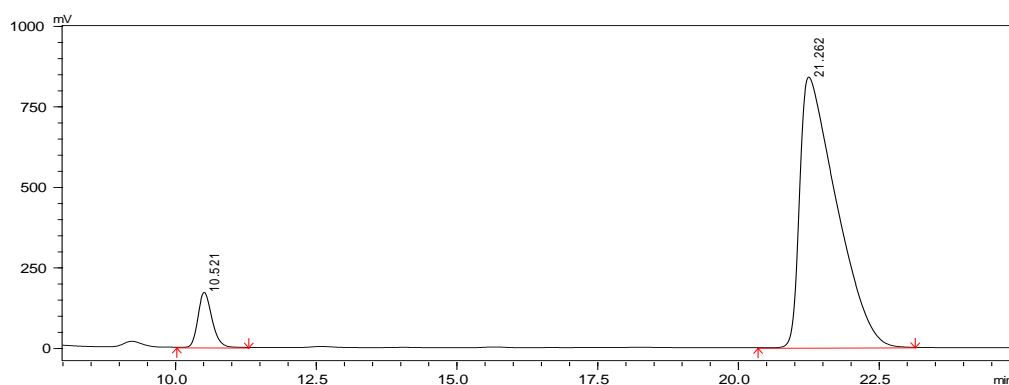


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.652	73442	1132526	2.103
2	11.454	2239642	52714023	97.897
total		2313085	53846549	100.000

HPLC chromatogram of compound **29** (86% ee)

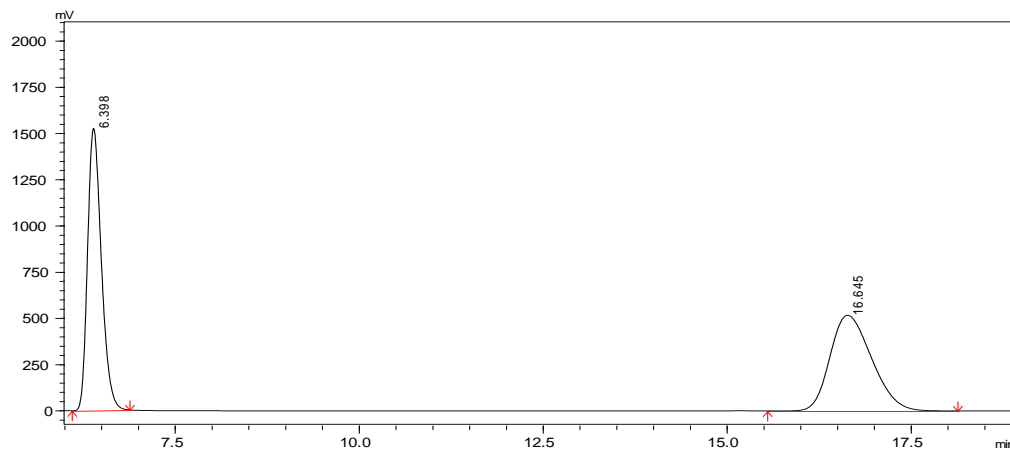
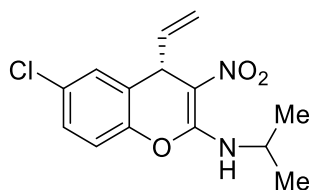


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.536	1114441	20124548	49.491
2	21.797	494586	20538577	50.509
total		1609027	40663124	100.000

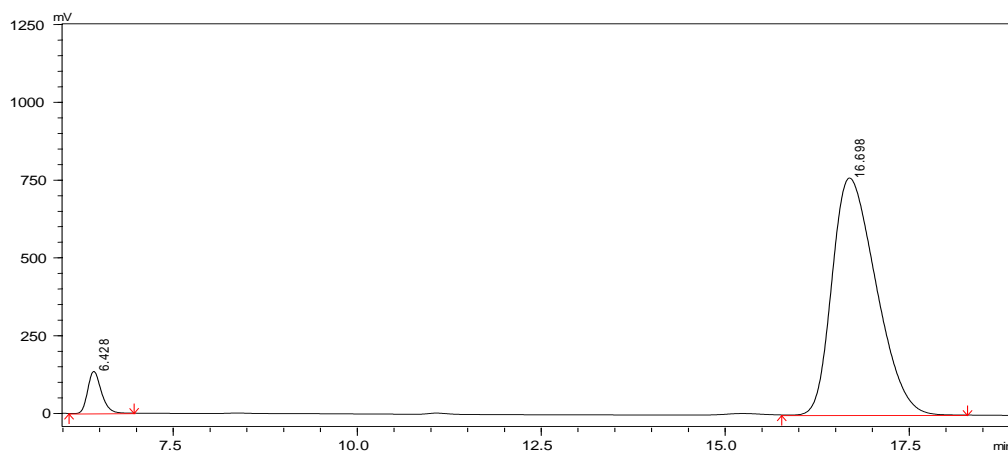


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.521	170476	2937038	7.158
2	21.262	840009	38096801	92.842
total		1010484	41033840	100.000

HPLC chromatogram of compound **30** (90% ee)



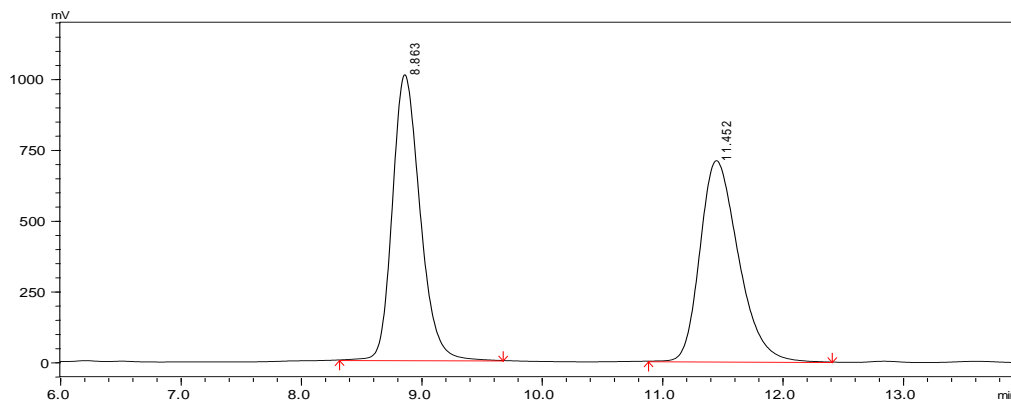
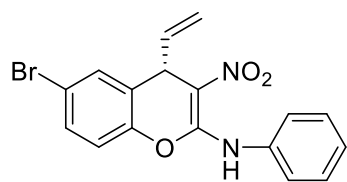
#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	6.398	1525611	19890080	49.476
2	16.645	516908	20310992	50.524
total		2042519	40201072	100.000



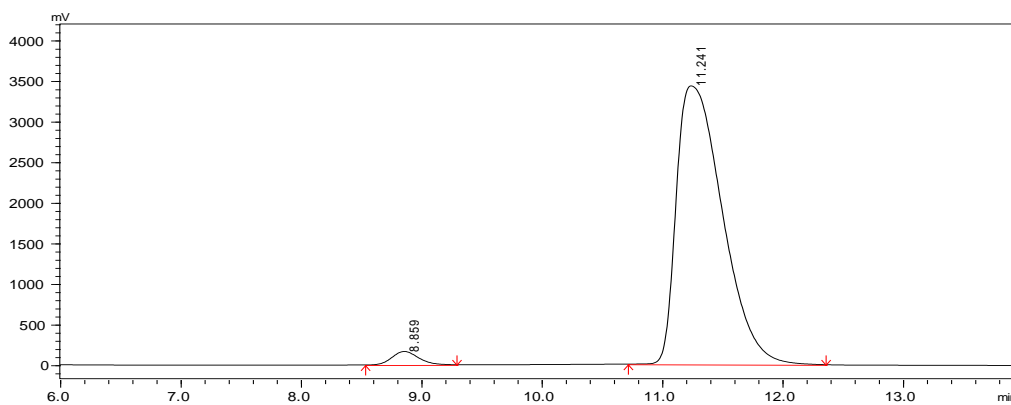
#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	6.428	134726	1725784	5.172
2	16.698	761855	31644702	94.828
total		896582	33370486	100.000



HPLC chromatogram of compound **31** (95% ee)

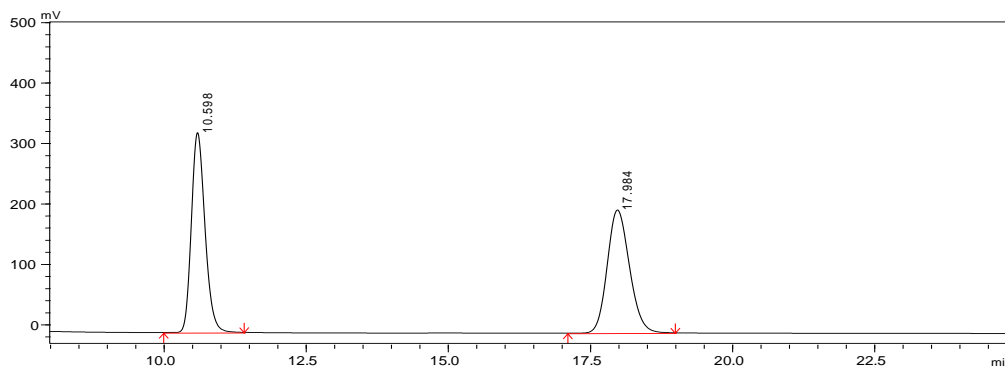
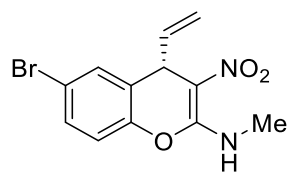


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.863	1007857	16065706	50.545
2	11.452	709040	15719147	49.455
total		1716898	31784853	100.000

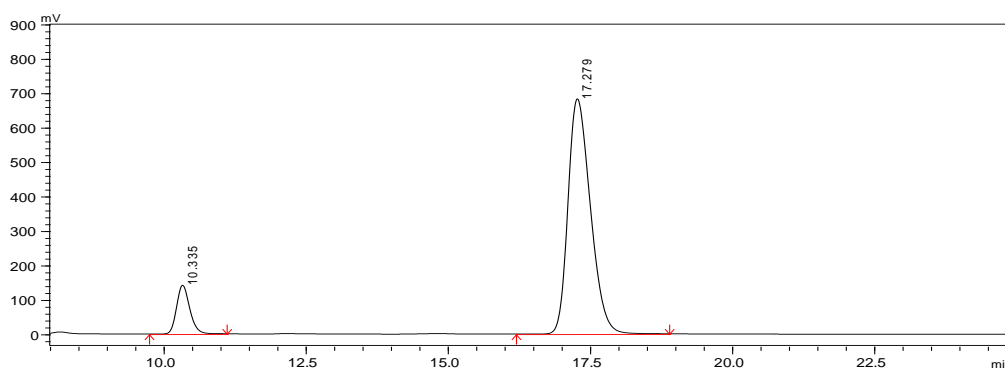


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.859	165136	2509727	2.680
2	11.241	3430427	91142137	97.320
total		3595563	93651864	100.000

HPLC chromatogram of compound **32** (78% ee)

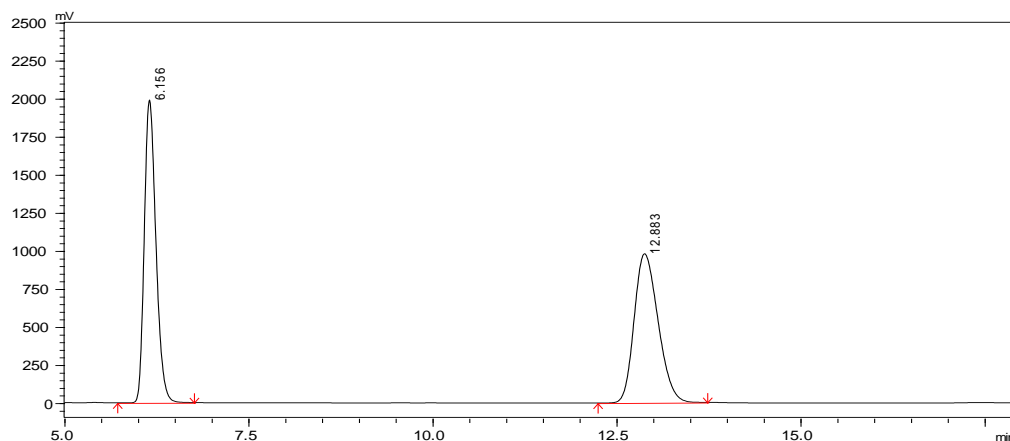
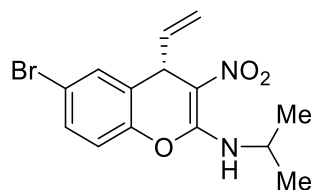


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	10.598	330648	5506764	49.879
2	17.984	203583	5533393	50.121
total		534231	11040157	100.000

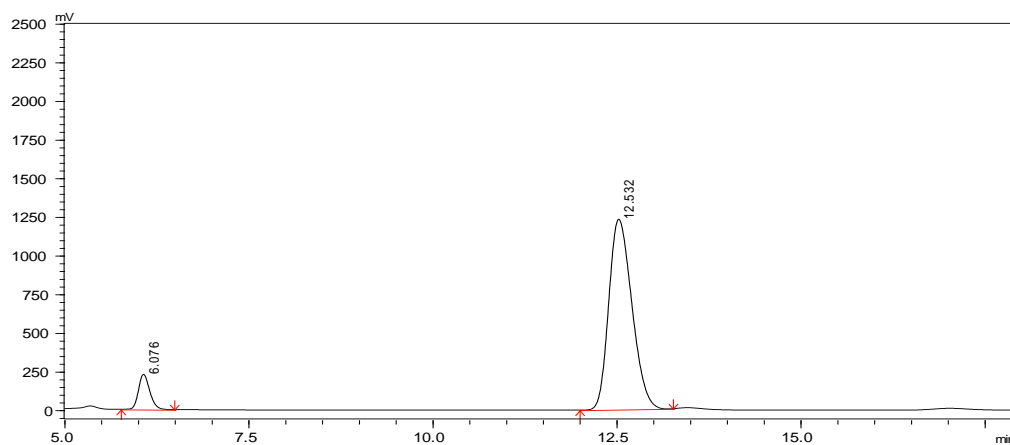


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	10.335	141219	2263635	10.785
2	17.279	682869	18724401	89.215
total		824088	20988036	100.000

HPLC chromatogram of compound **33** (84% ee)

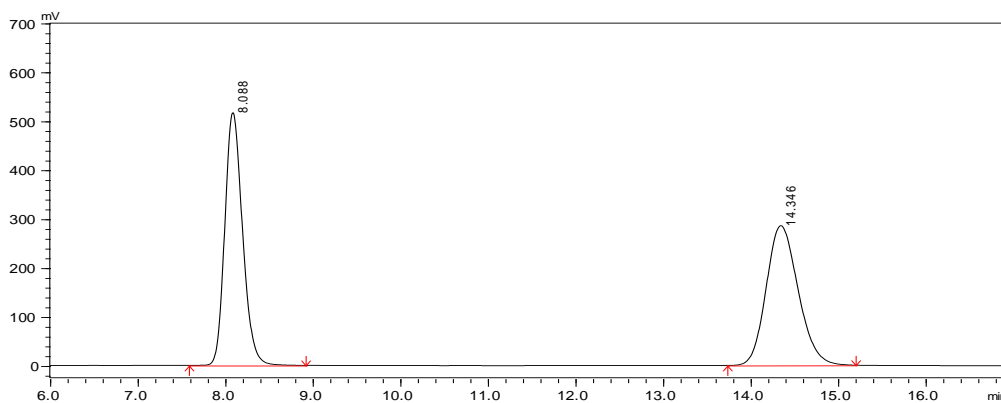
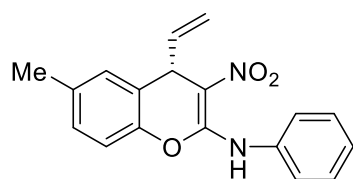


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.156	1989005	21828064	49.726
2	12.883	978733	22068828	50.274
total		2967738	43896893	100.000

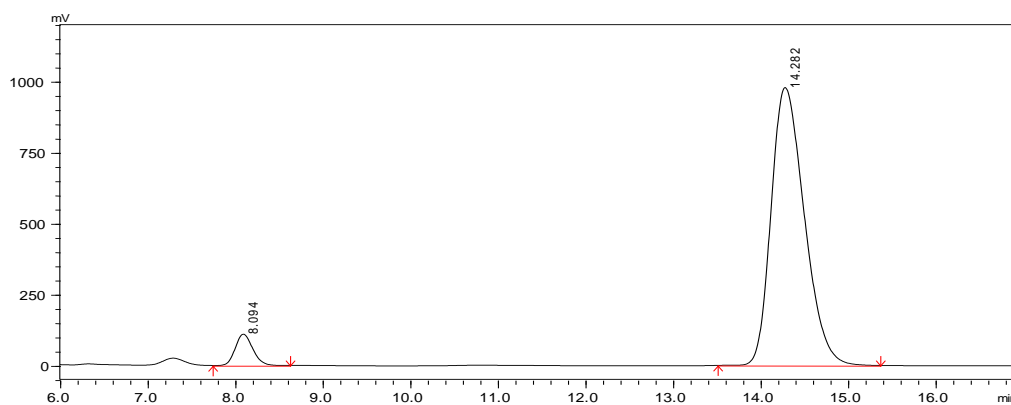


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.076	227166	2408286	8.233
2	12.532	1231284	26841627	91.767
total		1458451	29249913	100.000

HPLC chromatogram of compound **34** (89% ee)

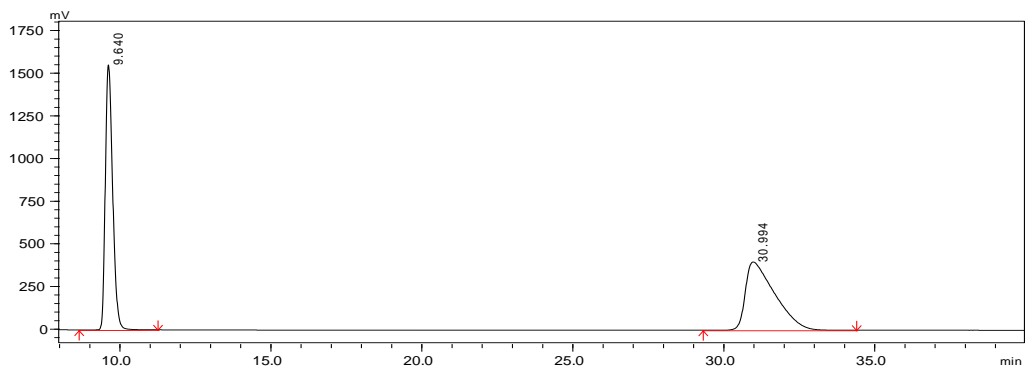
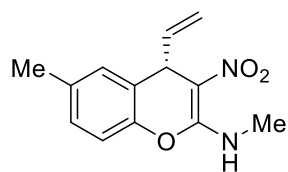


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	8.088	515845	7274033	50.117
2	14.346	285520	7239946	49.883
total		801365	14513980	100.000

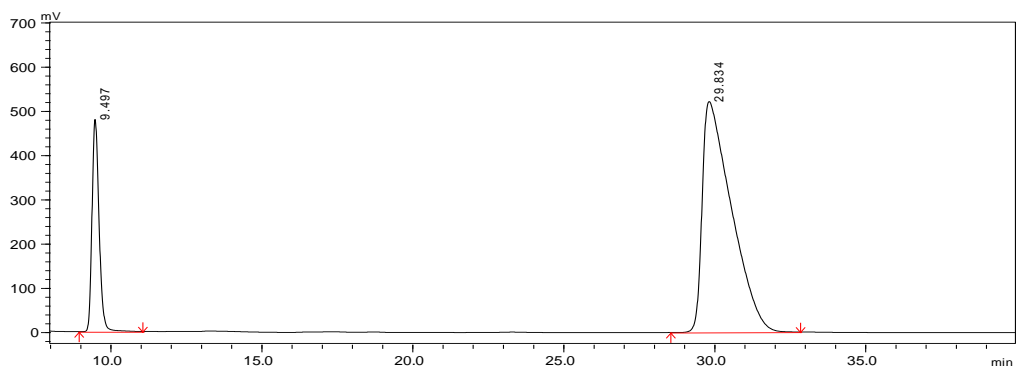


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	8.094	110105	1521948	5.576
2	14.282	978247	25774975	94.424
total		1088353	27296923	100.000

HPLC chromatogram of compound **35** (64% ee)

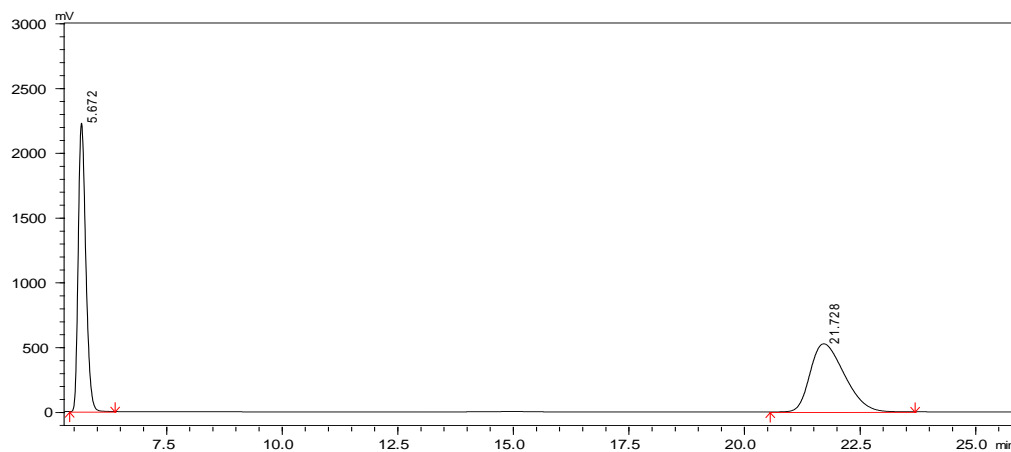
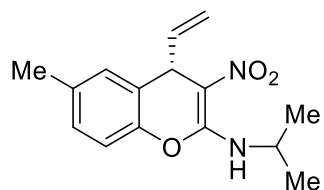


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	9.640	1552308	26197899	49.379
2	30.994	399847	26856817	50.621
total		1952155	53054716	100.000

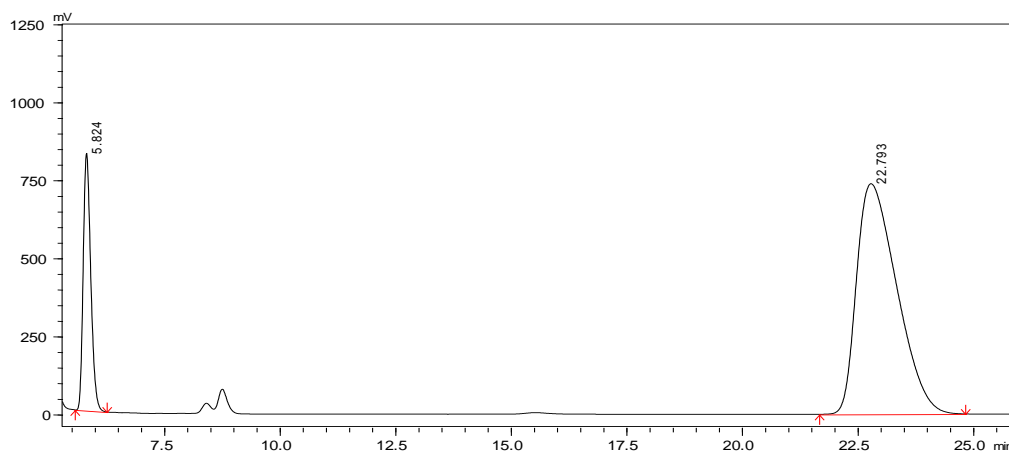


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	9.497	479351	7804469	18.216
2	29.834	521435	35038696	81.784
total		1000786	42843165	100.000

HPLC chromatogram of compound **36** (65% ee)

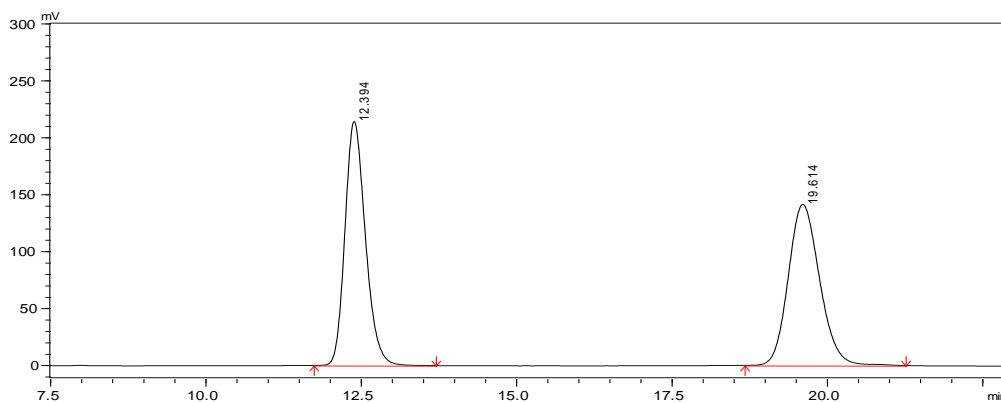
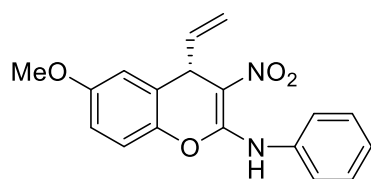


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.672	2226840	25337790	48.450
2	21.728	525253	26959475	51.550
total		2752093	52297266	100.000

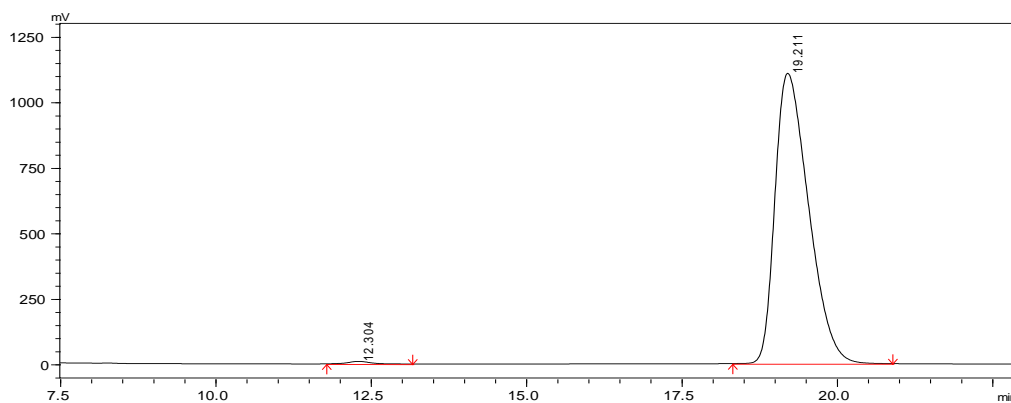


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.824	824478	9337194	17.310
2	22.793	738604	44604995	82.690
total		1563082	53942189	100.000

HPLC chromatogram of compound **37** (99% ee)

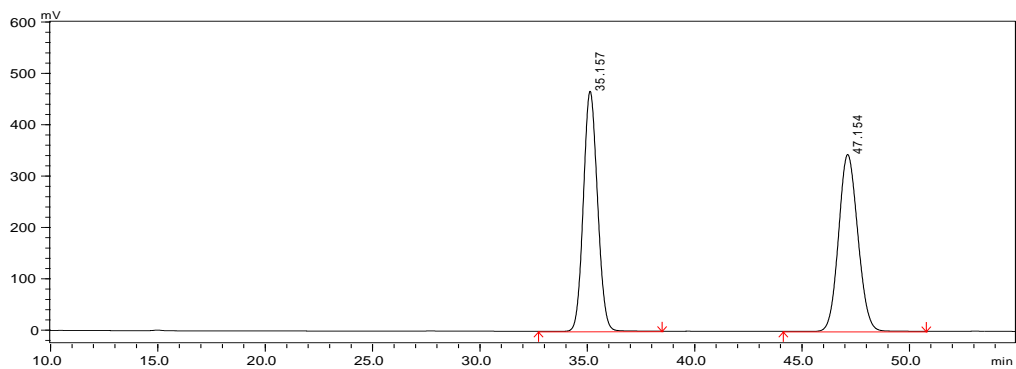
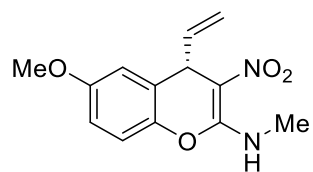


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	12.394	214218	4905610	49.761
2	19.614	141352	4952637	50.239
total		355571	9858248	100.000

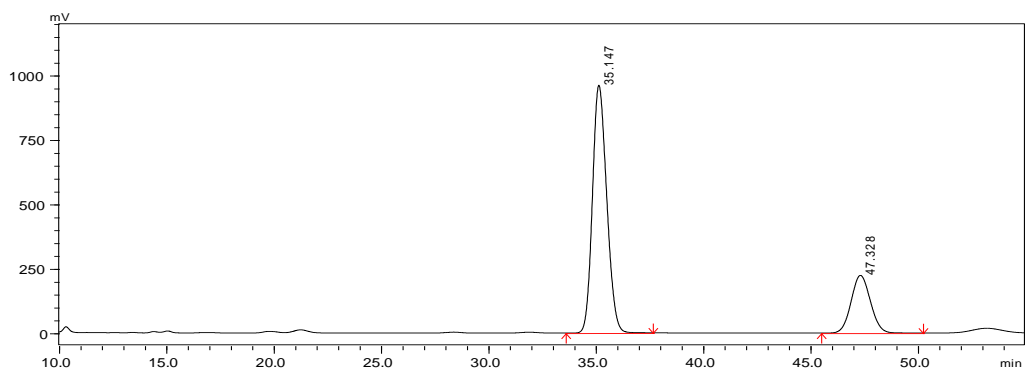


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	12.304	9517	226452	0.541
2	19.211	1107837	41637041	99.459
total		1117354	41863493	100.000

HPLC chromatogram of compound **38** (52% ee)



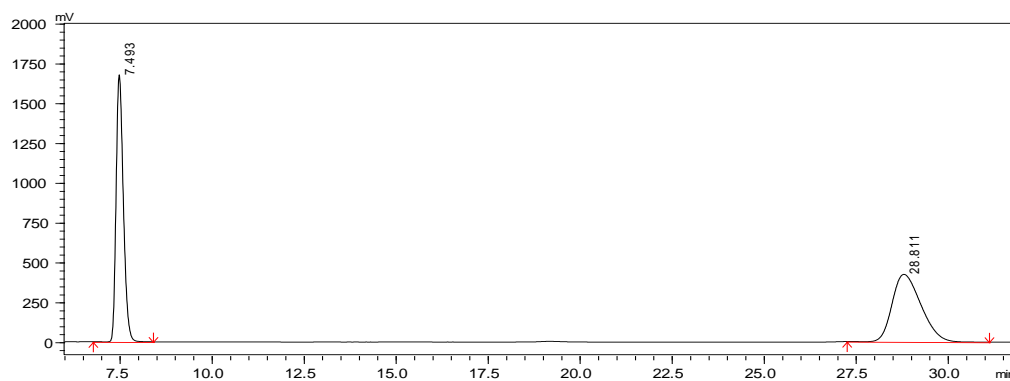
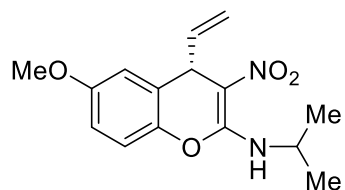
#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	35.157	467342	21403098	49.973
2	47.154	344353	21426524	50.027
total		811695	42829621	100.000



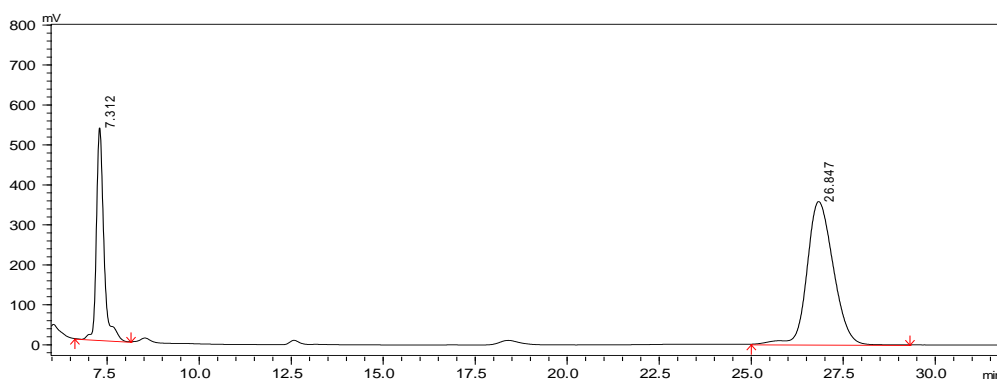
#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	35.147	961228	44452459	76.102
2	47.328	223788	13959346	23.898
total		1185017	58411805	100.000



HPLC chromatogram of compound **39** (41% ee)

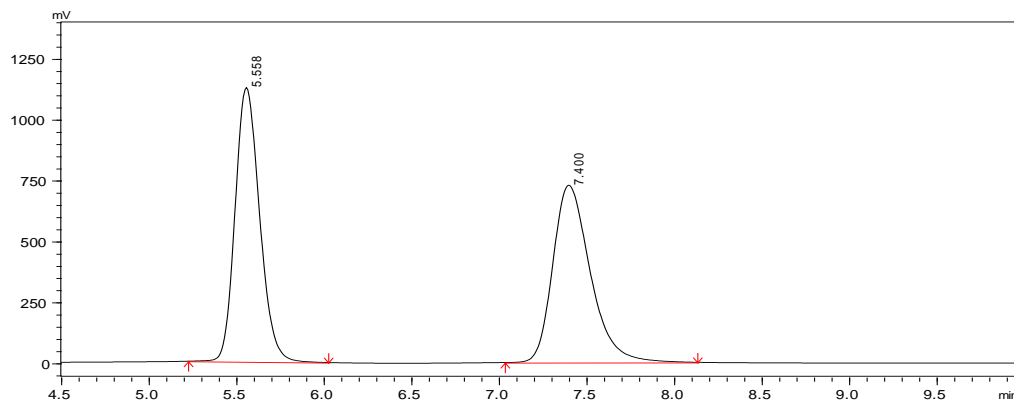
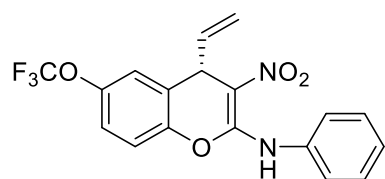


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.493	1675805	22911516	49.958
2	28.811	423218	22949976	50.042
total		2099023	45861493	100.000

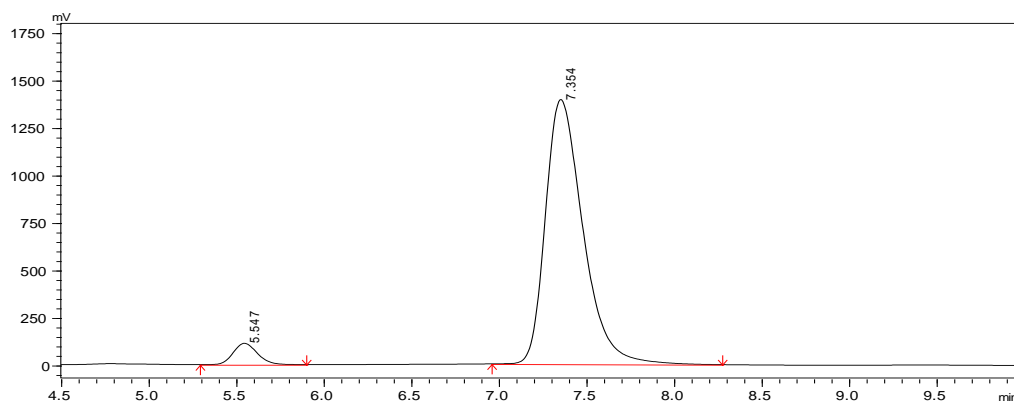


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.312	530629	7439217	29.659
2	26.847	357610	17643676	70.341
total		888239	25082893	100.000

HPLC chromatogram of compound **40** (90% ee)

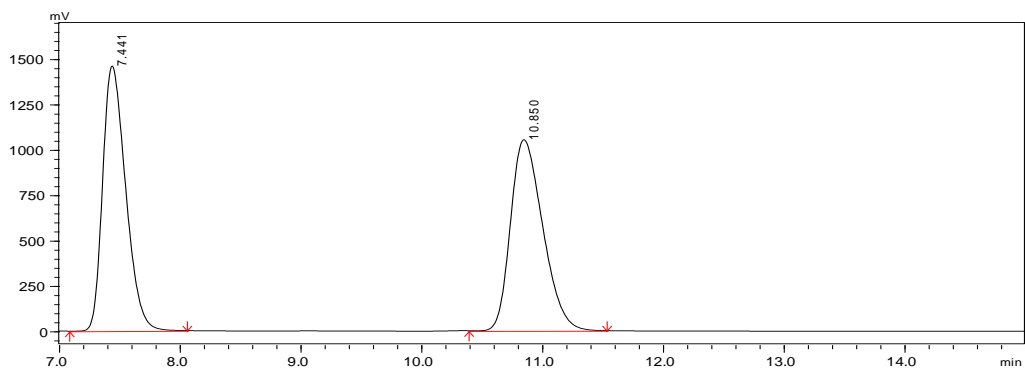
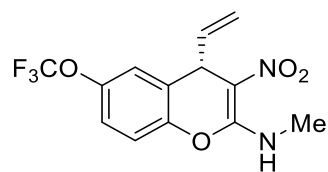


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.558	1125806	10958656	50.368
2	7.400	727850	10798667	49.632
total		1853656	21757323	100.000

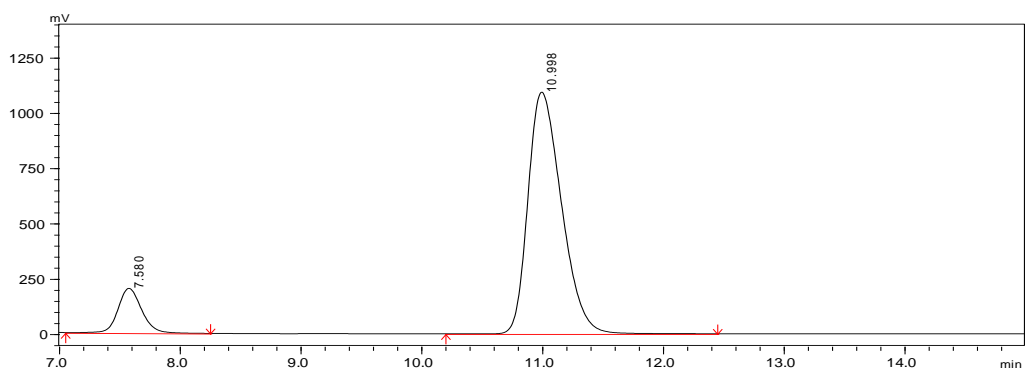


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.547	111723	1069342	4.889
2	7.354	1393405	20803295	95.111
total		1505127	21872637	100.000

HPLC chromatogram of compound **41** (77% ee)

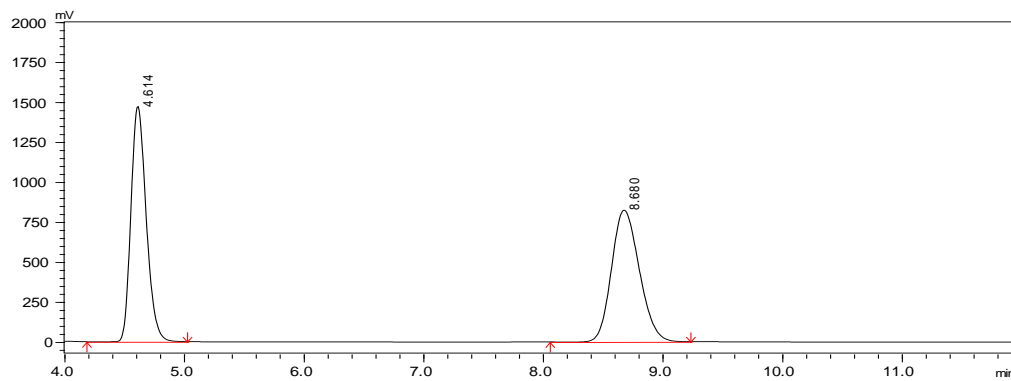
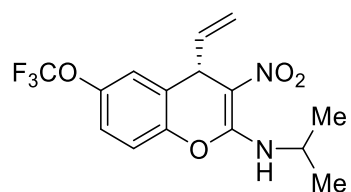


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.441	1460040	19354704	49.793
2	10.850	1052696	19515503	50.207
total		2512736	38870207	100.000

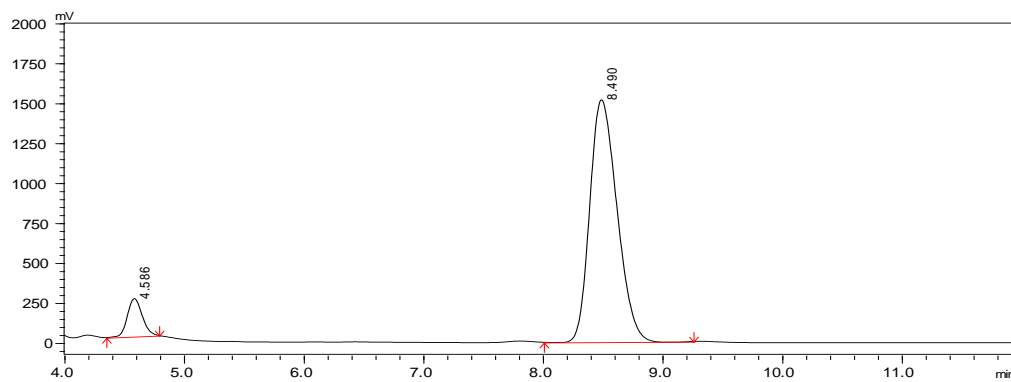


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.580	201239	2726261	11.476
2	10.998	1092736	21029778	88.524
total		1293975	23756039	100.000

HPLC chromatogram of compound **42** (84% ee)

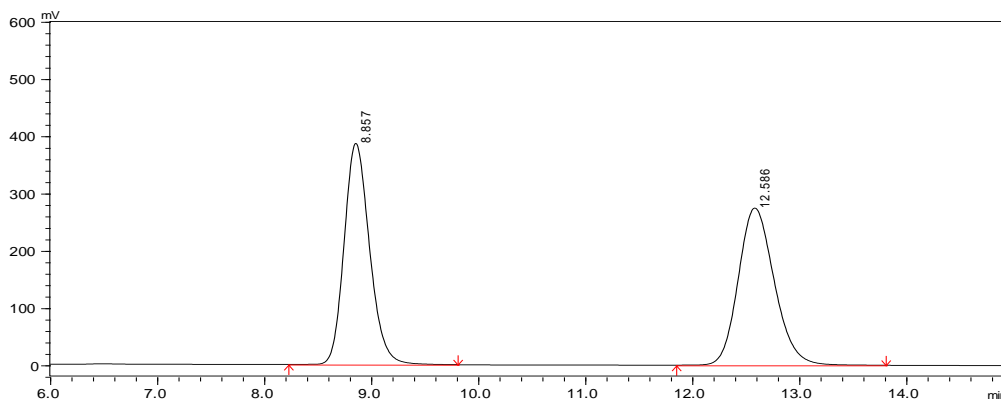
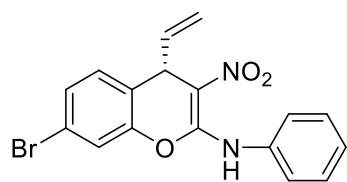


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.614	1470601	13053224	49.515
2	8.680	823377	13308758	50.485
total		2293977	26361982	100.000

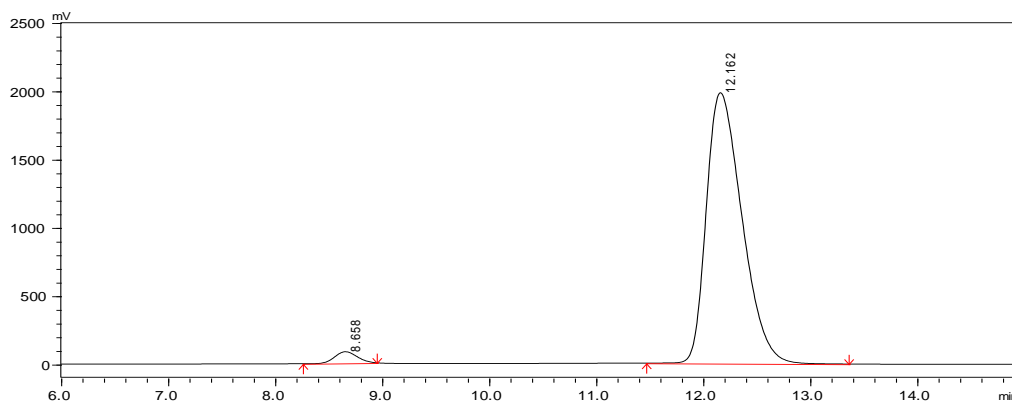


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.586	236945	2039891	7.861
2	8.490	1516389	23908939	92.139
total		1753334	25948830	100.000

HPLC chromatogram of compound **43** (95% ee)

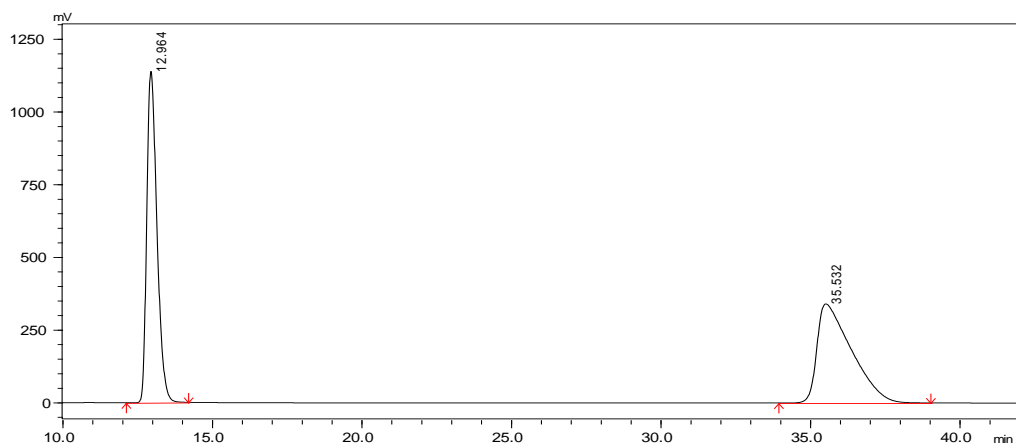
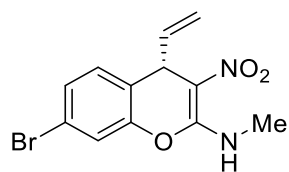


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	8.857	386252	6382161	49.881
2	12.586	274444	6412624	50.119
total		660696	12794784	100.000

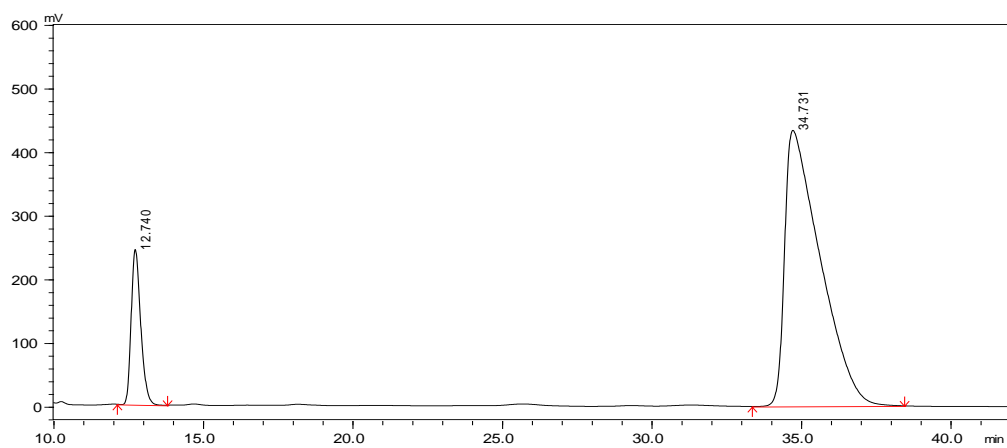


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	8.658	83965	1215526	2.584
2	12.162	1981474	45831851	97.416
total		2065440	47047377	100.000

HPLC chromatogram of compound **44** (74% ee)

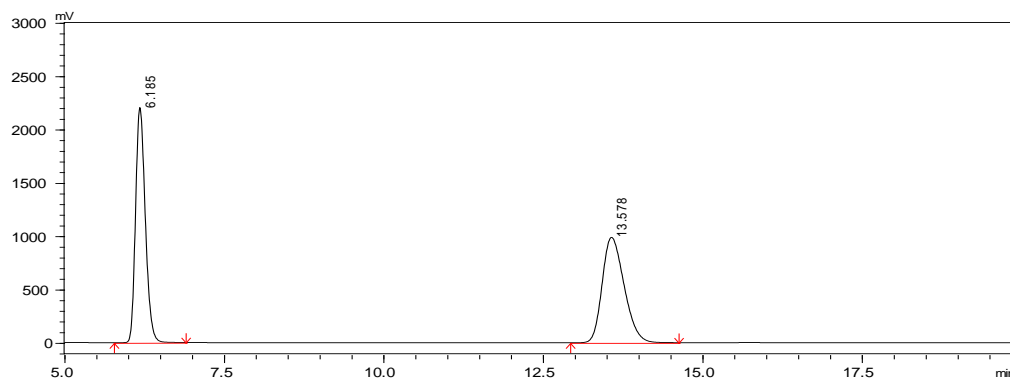
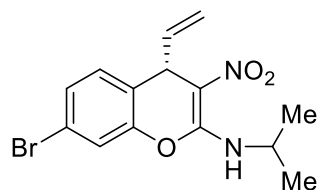


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.964	1138159	26950117	49.809
2	35.532	340561	27156369	50.191
total		1478719	54106487	100.000

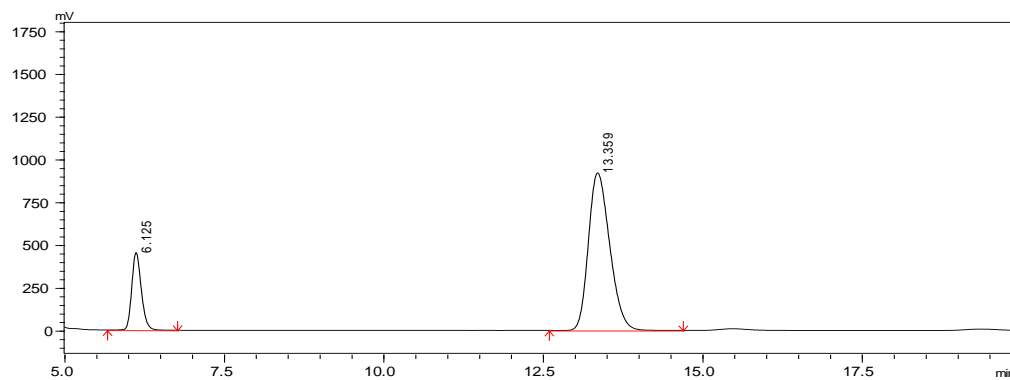


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.740	243671	5394425	13.085
2	34.731	433618	35830557	86.915
total		677288	41224983	100.000

HPLC chromatogram of compound **45** (64% ee)

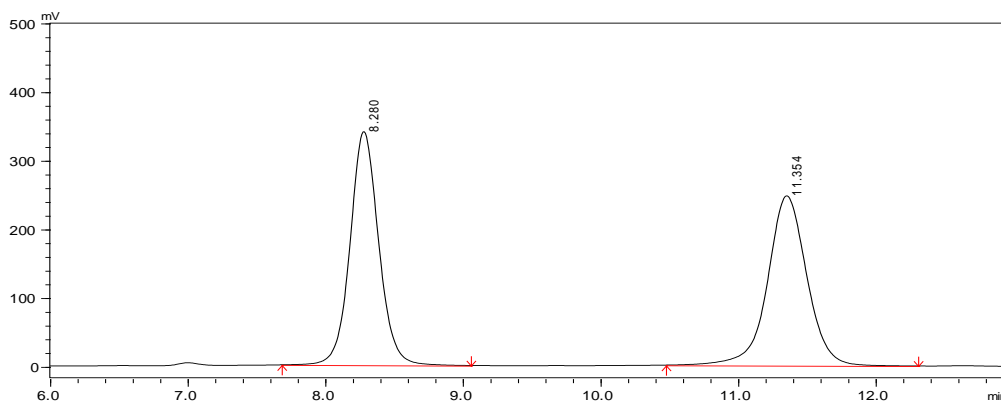
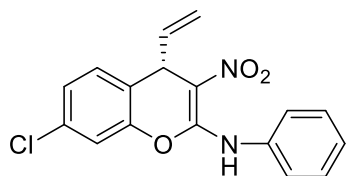


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	6.185	2203015	23402583	49.771
2	13.578	987202	23617967	50.229
total		3190217	47020550	100.000

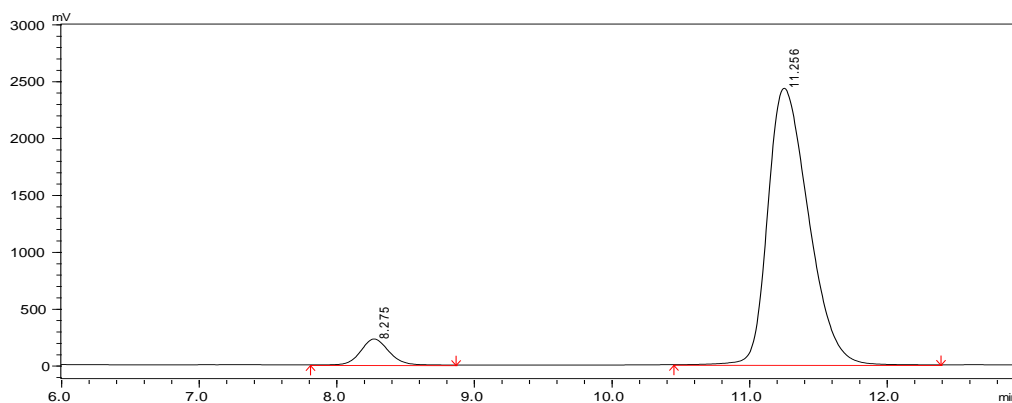


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	6.125	453023	4720150	18.071
2	13.359	920958	21400425	81.929
total		1373981	26120576	100.000

HPLC chromatogram of compound **46** (88% ee)



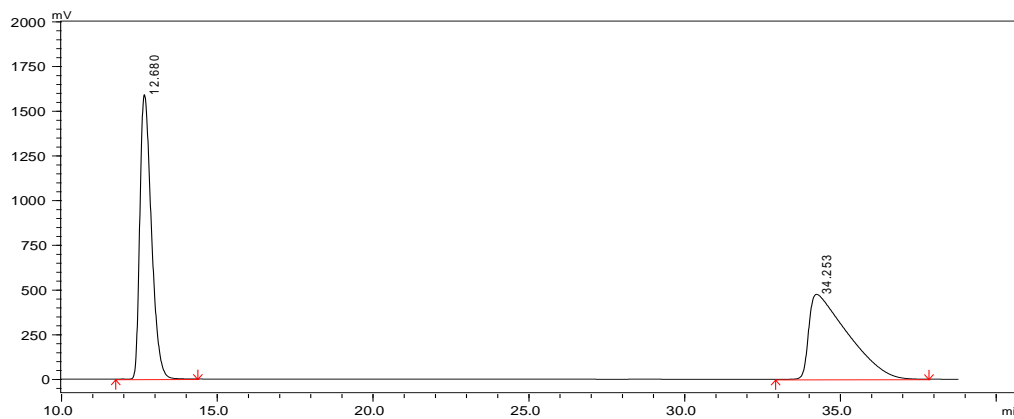
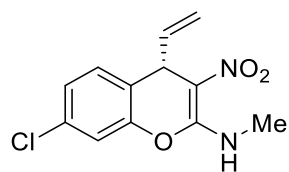
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.280	339992	4920512	50.125
2	11.354	246908	4896025	49.875
total		586900	9816537	100.000



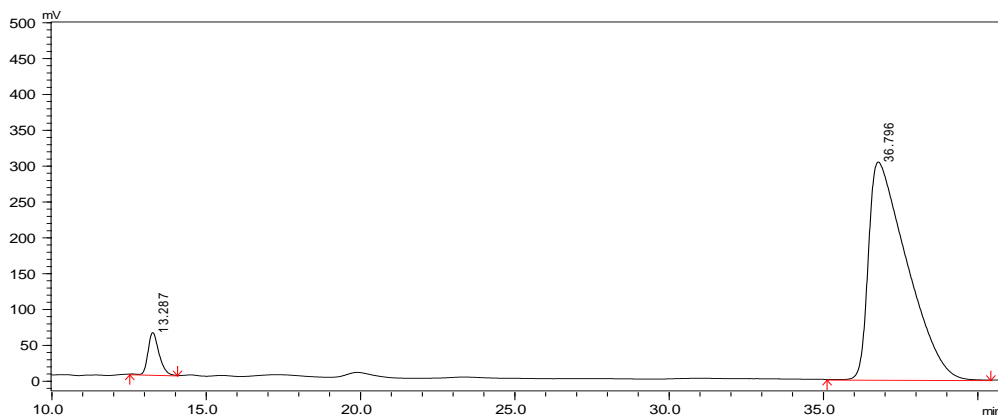
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.275	227988	3220365	6.068
2	11.256	2430018	49855048	93.932
total		2658006	53075413	100.000



HPLC chromatogram of compound **47** (89% ee)

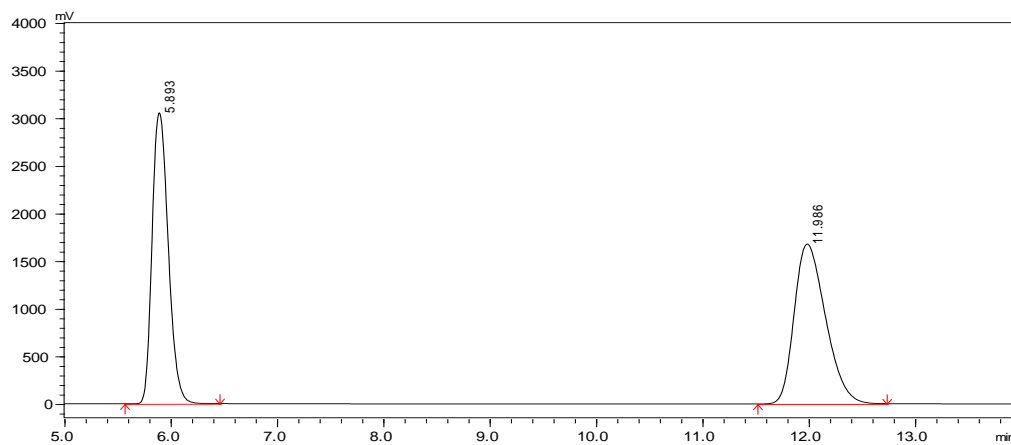
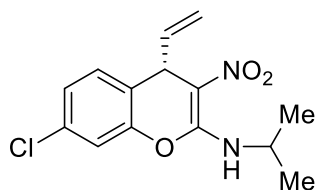


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.680	1590278	40908556	49.924
2	34.253	474724	41033360	50.076
total		2065001	81941916	100.000

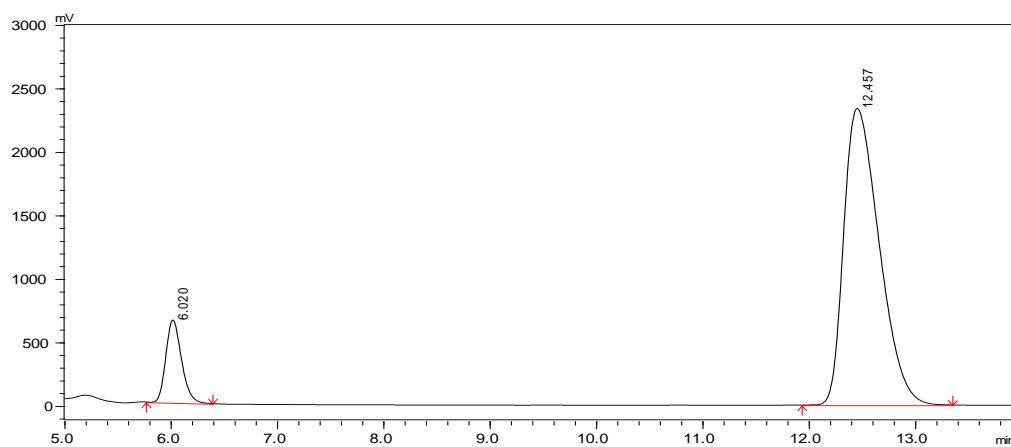


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	13.287	58803	1427212	5.257
2	36.796	303472	26248762	94.743
total		362275	27675974	100.000

HPLC chromatogram of compound **48** (78% ee)

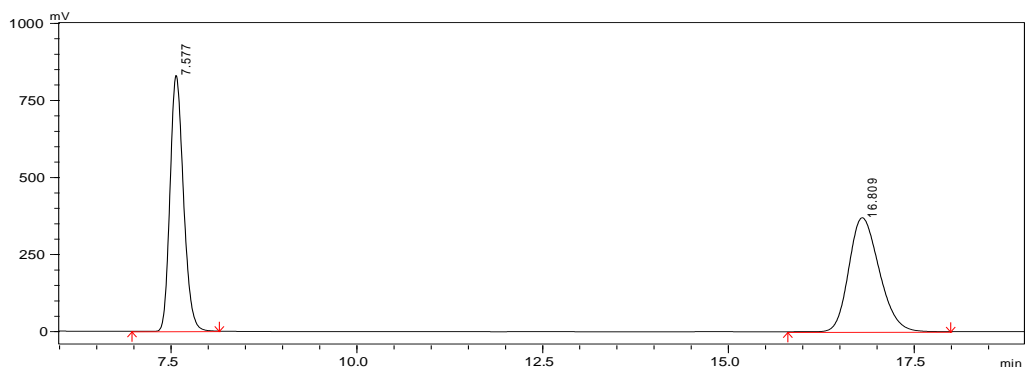
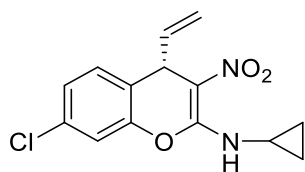


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.893	3054885	32308342	48.465
2	11.986	1677372	34354721	51.535
total		4732256	66663063	100.000

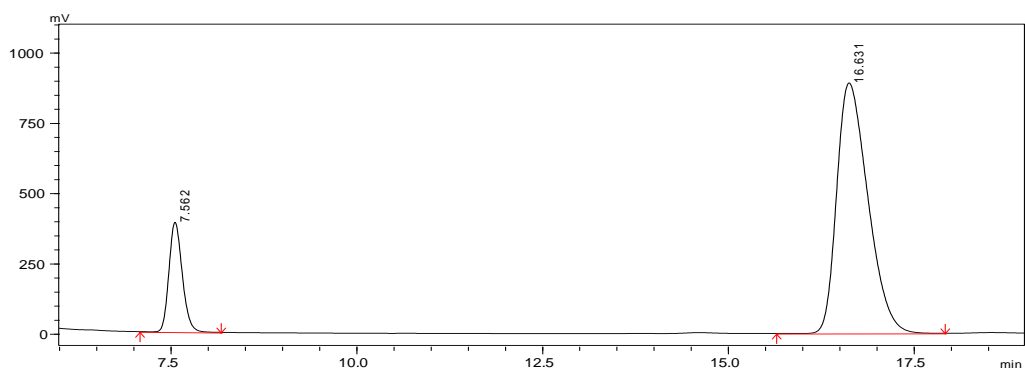


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.020	650157	6632355	10.929
2	12.457	2335613	54051271	89.071
total		2985770	60683626	100.000

HPLC chromatogram of compound **49** (69% ee)

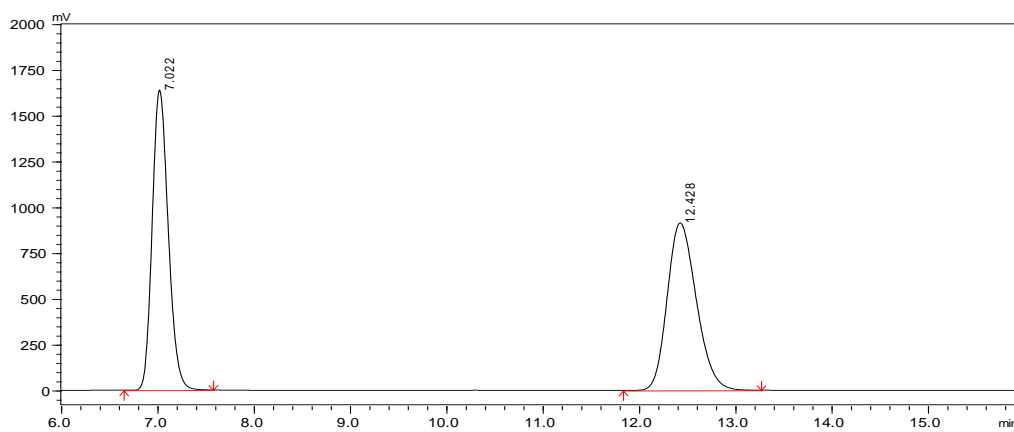
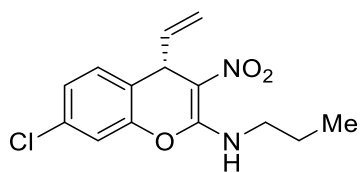


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.577	829487	10425470	49.825
2	16.809	369662	10498529	50.175
total		1199149	20923999	100.000

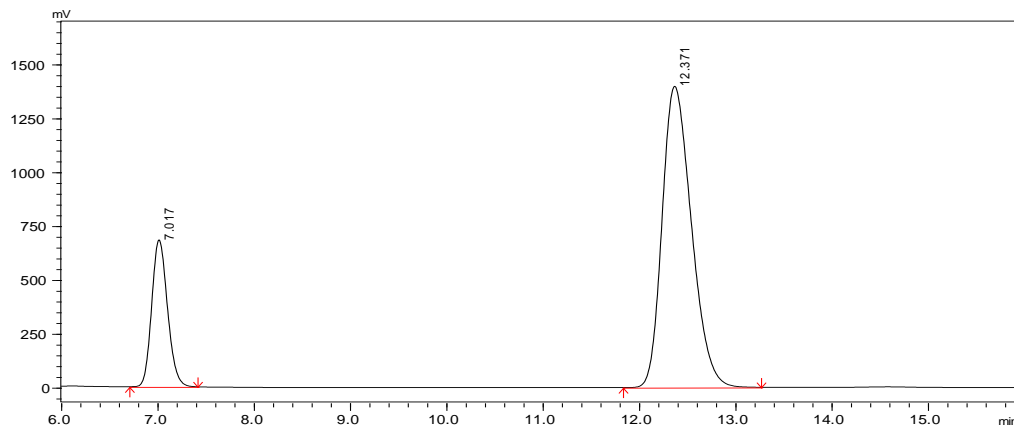


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.562	390108	4850589	15.732
2	16.631	890663	25982111	84.268
total		1280771	30832700	100.000

HPLC chromatogram of compound **50** (58% ee)

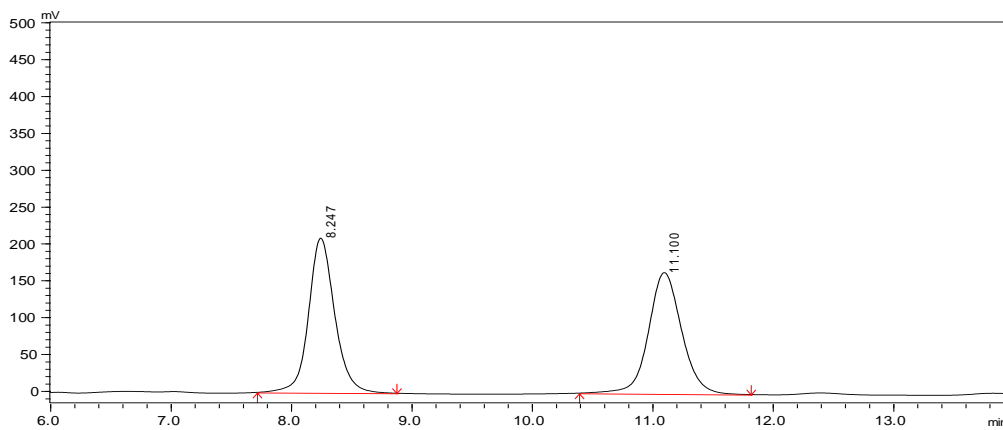
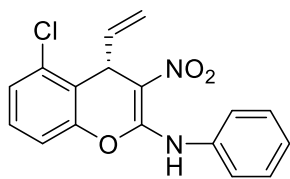


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.022	1639262	18992151	49.729
2	12.428	914206	19199178	50.271
total		2553468	38191330	100.000

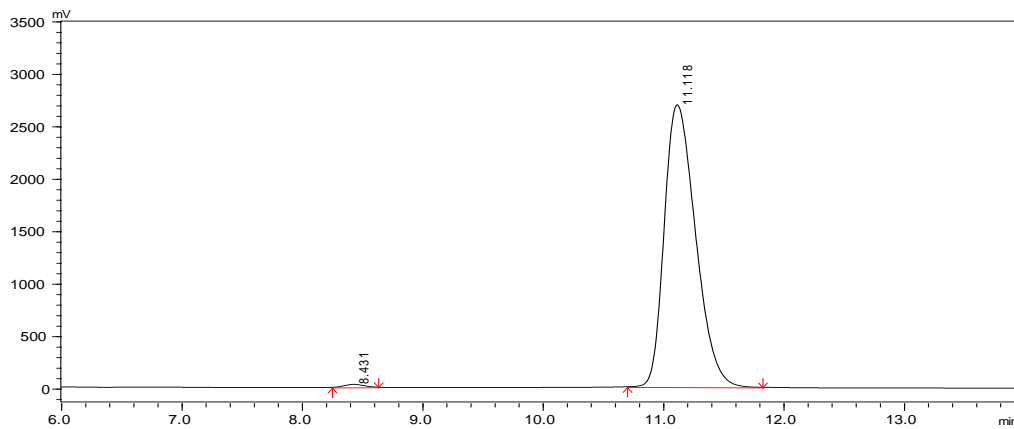


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.017	682150	7780533	20.845
2	12.371	1397638	29545194	79.155
total		2079789	37325727	100.000

HPLC chromatogram of compound **51** (99% ee)

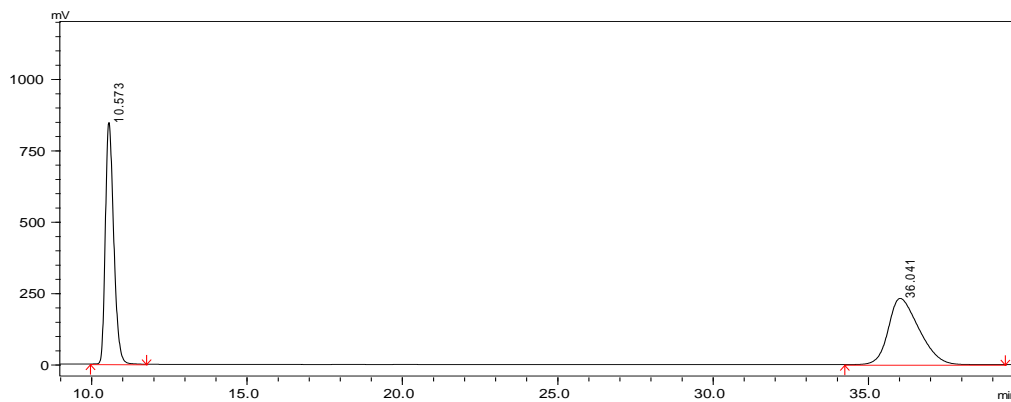
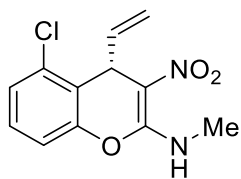


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.247	209724	3166081	50.203
2	11.100	164486	3140478	49.797
total		374211	6306559	100.000

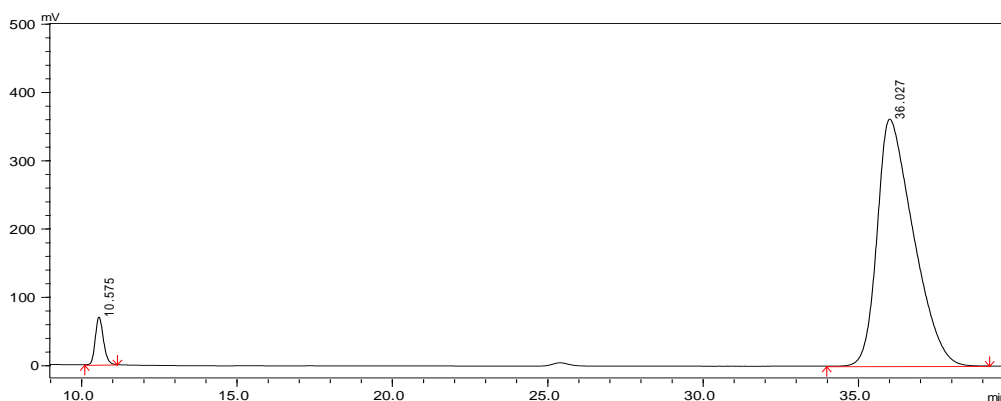


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.431	27916	312867	0.640
2	11.118	2689129	48568585	99.360
total		2717045	48881452	100.000

HPLC chromatogram of compound **52** (92% ee)

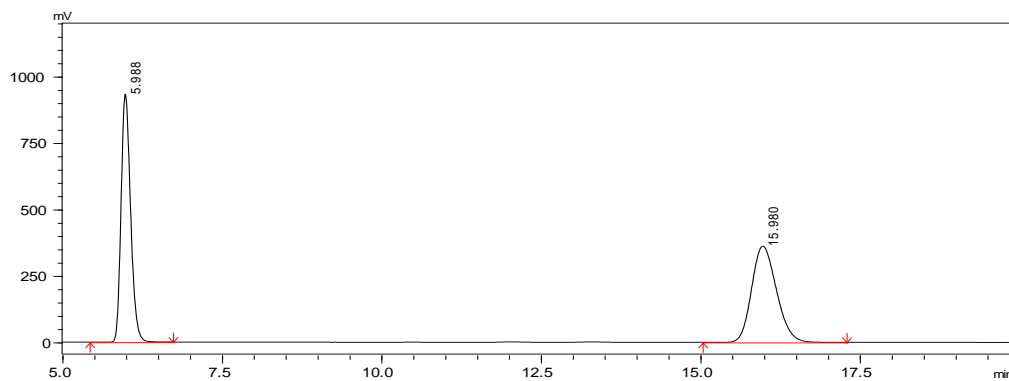
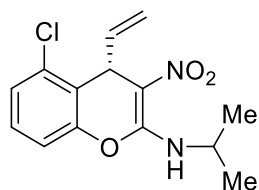


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.573	845758	15812878	49.878
2	36.041	231900	15889979	50.122
total		1077658	31702856	100.000

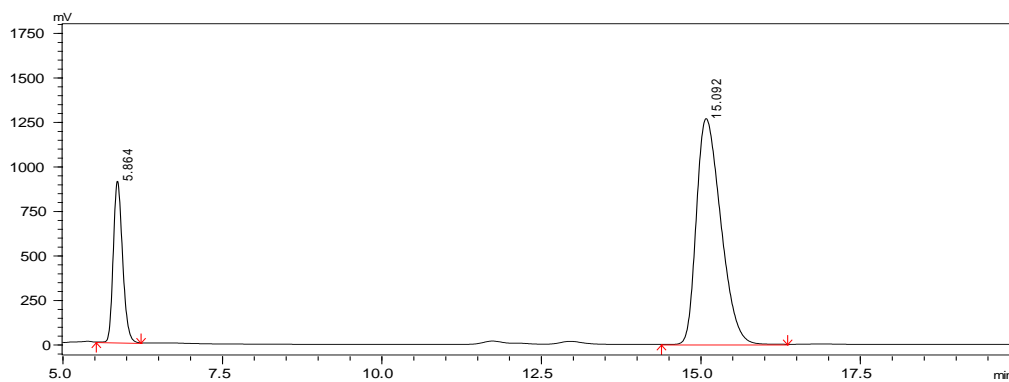


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.575	69686	1267136	4.147
2	36.027	361584	29291276	95.853
total		431270	30558413	100.000

HPLC chromatogram of compound **53** (57% ee)

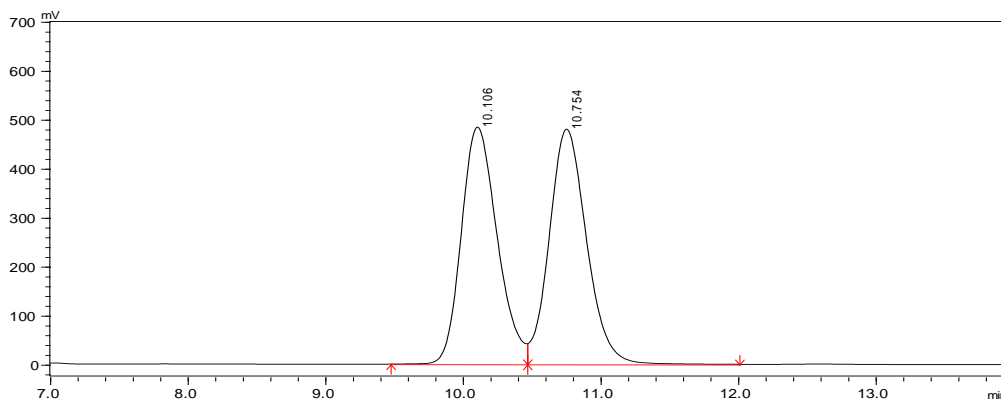
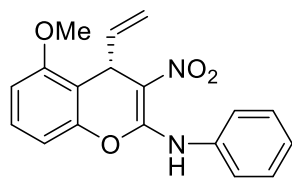


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.988	932159	9711519	49.812
2	15.980	361754	9784699	50.188
total		1293913	19496218	100.000

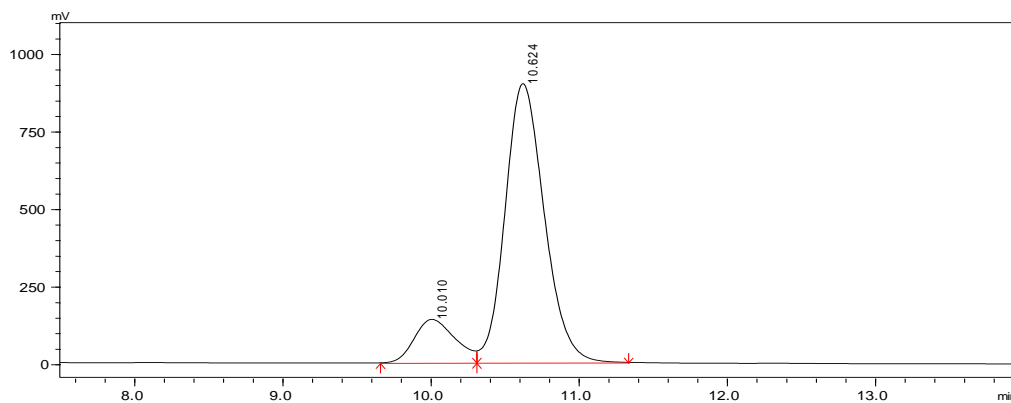


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.864	905563	9150006	21.367
2	15.092	1268308	33672950	78.633
total		2173871	42822956	100.000

HPLC chromatogram of compound **54** (72% ee)



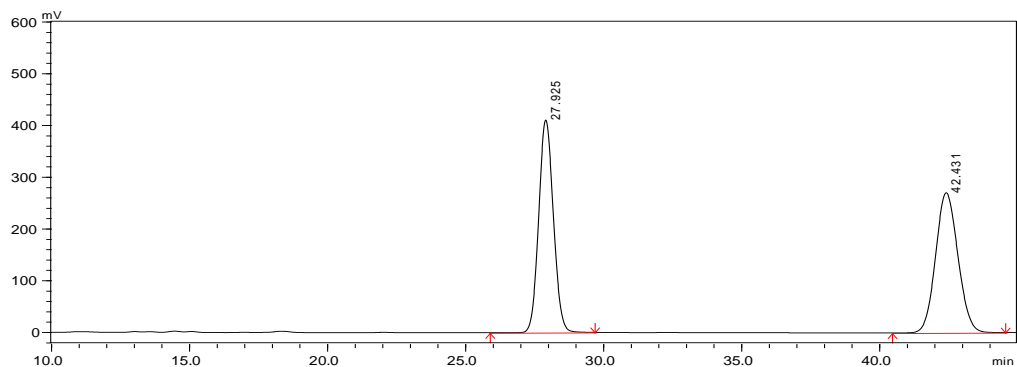
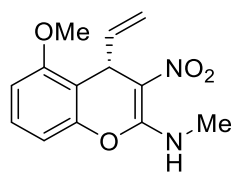
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.106	484215	8773943	49.302
2	10.754	479761	9022529	50.698
total		963976	17796472	100.000



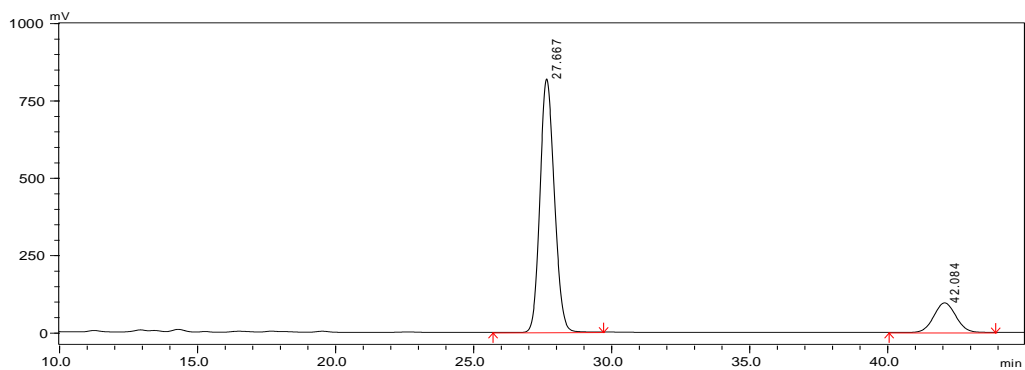
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.010	139948	2677369	13.939
2	10.624	899600	16529884	86.061
total		1039548	19207253	100.000



HPLC chromatogram of compound **55** (70% ee)

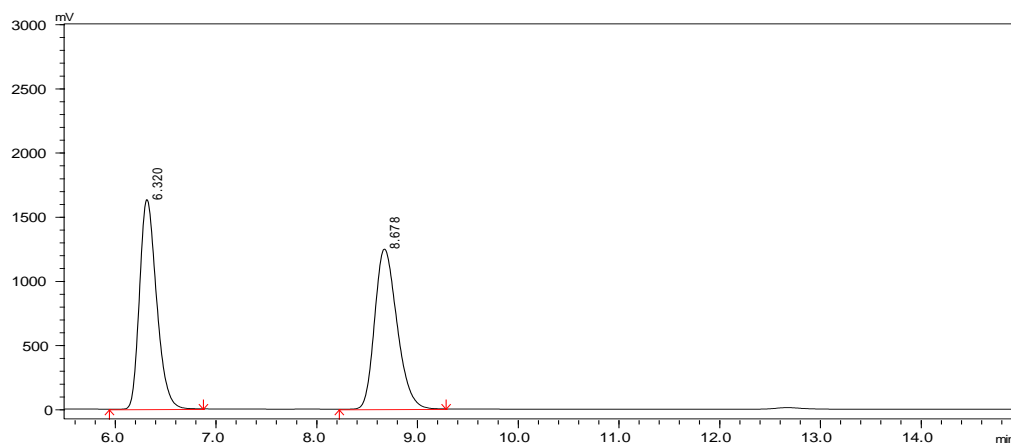
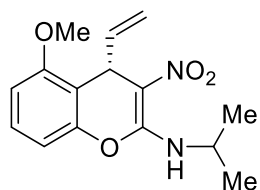


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	27.925	410695	15167657	49.983
2	42.431	270394	15177820	50.017
total		681089	30345477	100.000

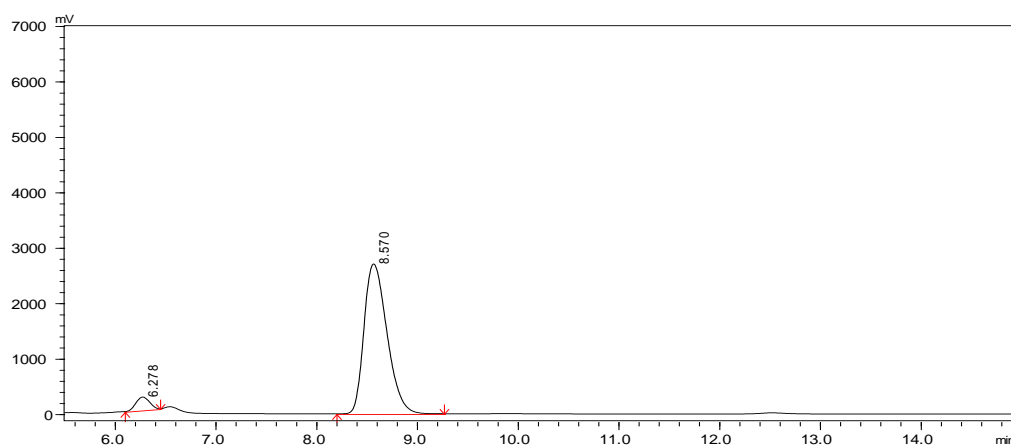


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	27.667	818148	29501904	84.829
2	42.084	95260	5276082	15.171
total		913408	34777986	100.000

HPLC chromatogram of compound **56** (90% ee)

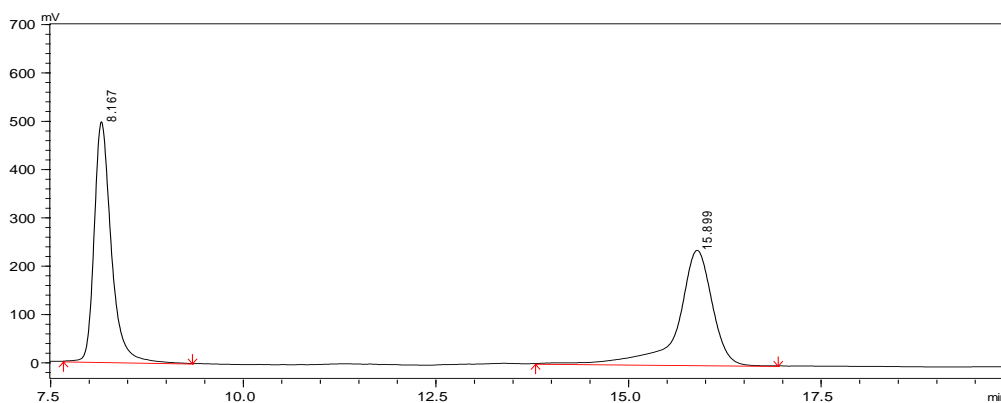
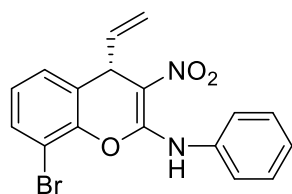


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.320	1630529	19144478	49.908
2	8.678	1246053	19214937	50.092
total		2876582	38359415	100.000

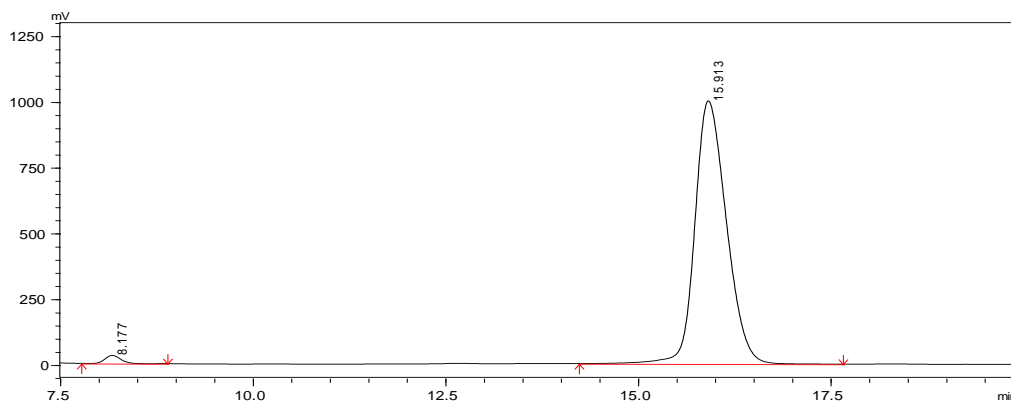


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.278	236525	2226875	4.934
2	8.570	2702701	42907033	95.066
total		2939226	45133907	100.000

HPLC chromatogram of compound **57** (97% ee)

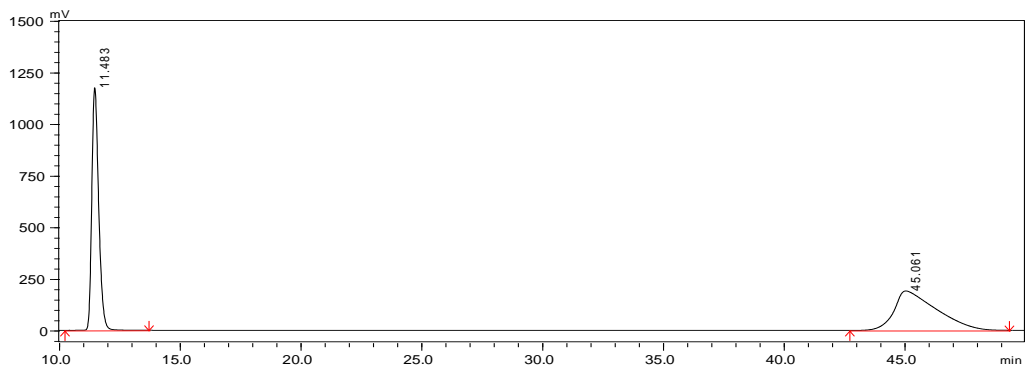
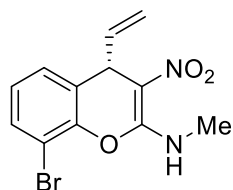


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.167	497054	7628208	51.158
2	15.899	237588	7282936	48.842
total		734642	14911144	100.000

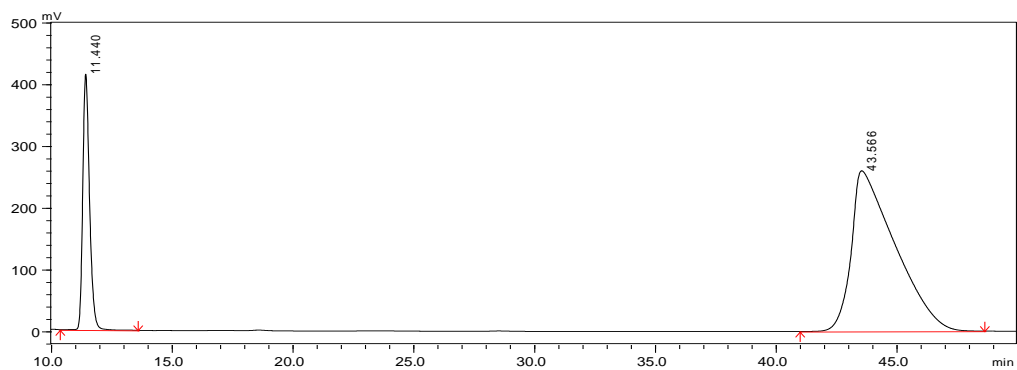


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.177	30456	410294	1.422
2	15.913	999409	28436709	98.578
total		1029865	28847003	100.000

HPLC chromatogram of compound **58** (61% ee)

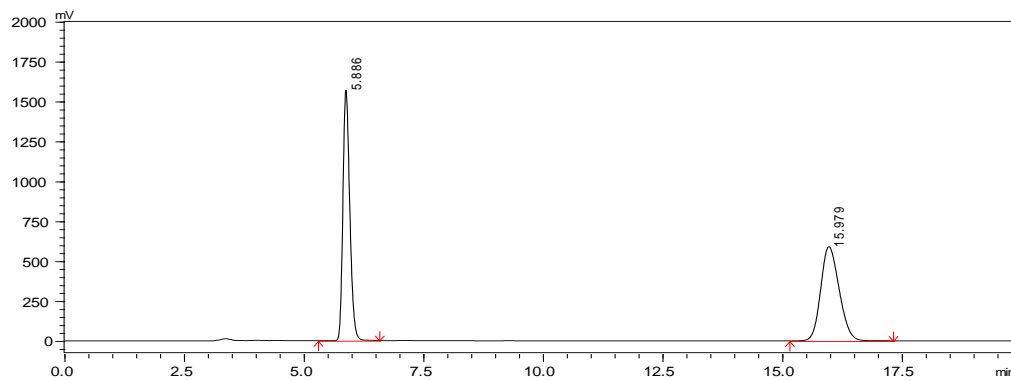
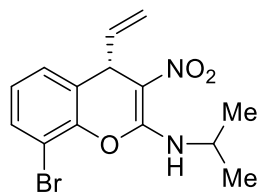


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.483	1175022	23270458	50.077
2	45.061	190944	23198612	49.923
total		1365966	46469070	100.000

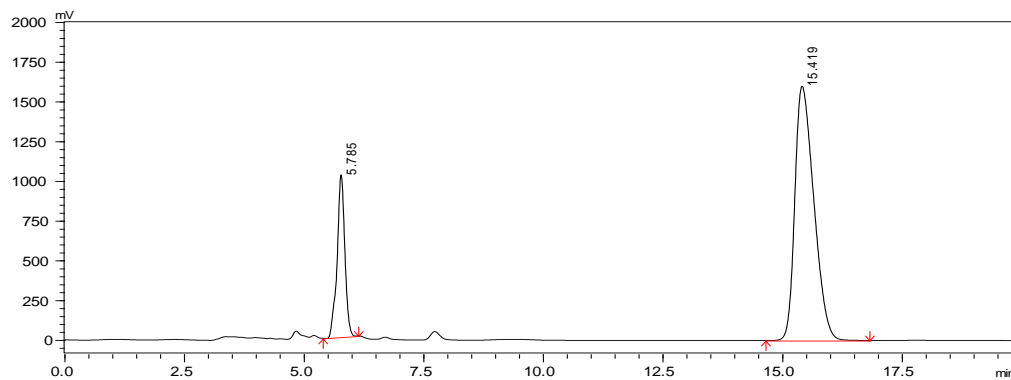


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.440	413950	8064769	19.713
2	43.566	259863	32846614	80.287
total		673814	40911383	100.000

HPLC chromatogram of compound **59** (59% ee)

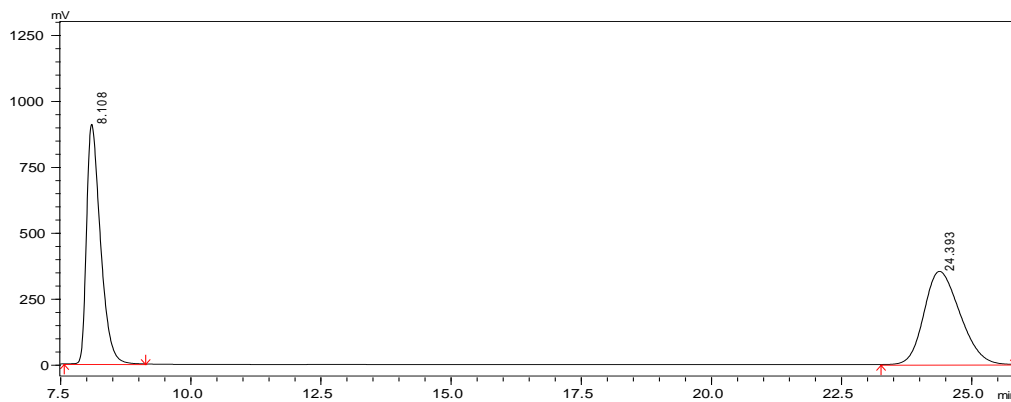
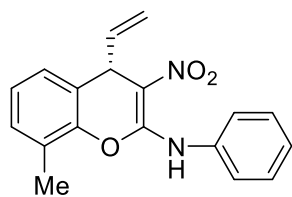


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	5.886	1570205	15690538	49.865
2	15.979	588768	15775576	50.135
total		2158974	31466114	100.000

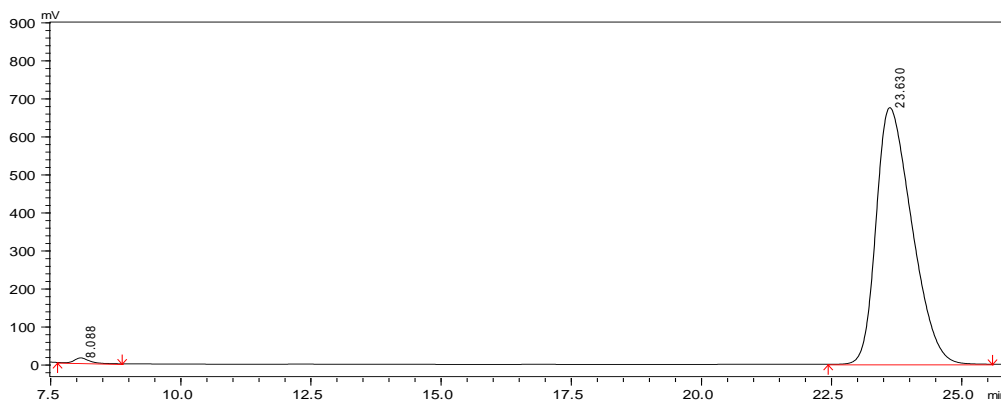


#	Ret Time (min)	Height ( $\mu$ V)	Area ( $\mu$ V.sec)	Area (%)
1	5.785	1021280	11426360	20.560
2	15.419	1599034	44149104	79.440
total		2620314	55575464	100.000

HPLC chromatogram of compound **60** (99% ee)

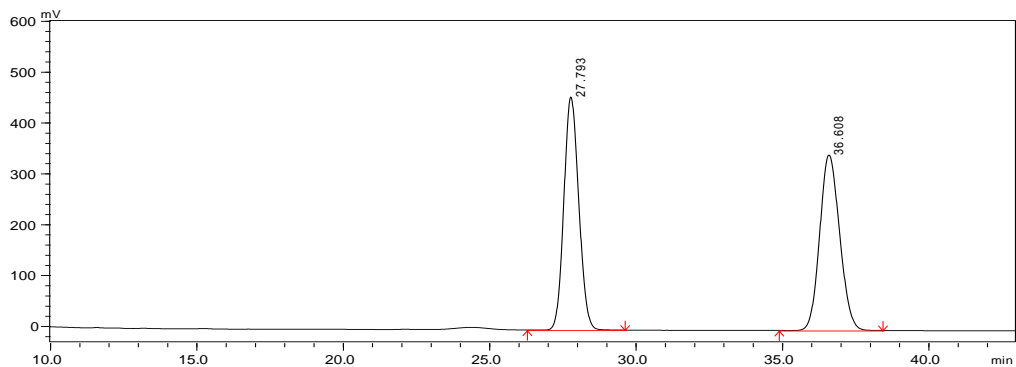
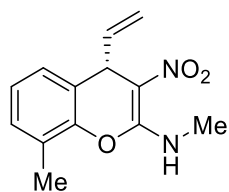


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	8.108	908409	16853260	49.917
2	24.393	352874	16909509	50.083
total		1261282	33762770	100.000

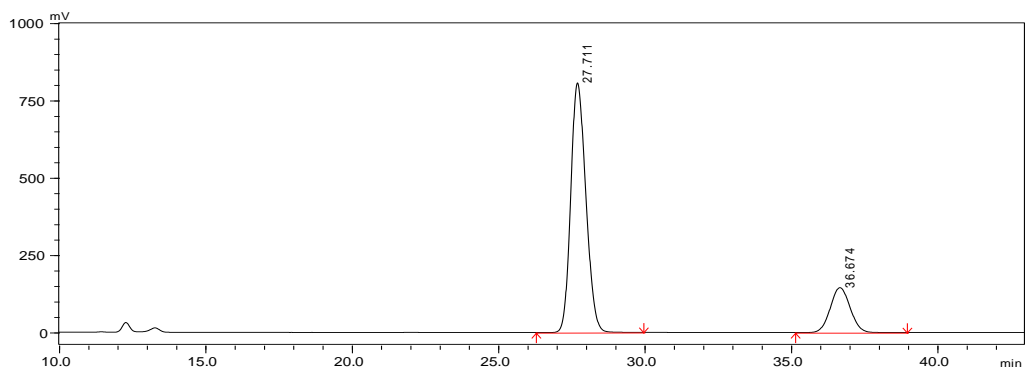


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	8.088	13319	231900	0.716
2	23.630	674766	32145773	99.284
total		688086	32377673	100.000

HPLC chromatogram of compound **61** (62% ee)

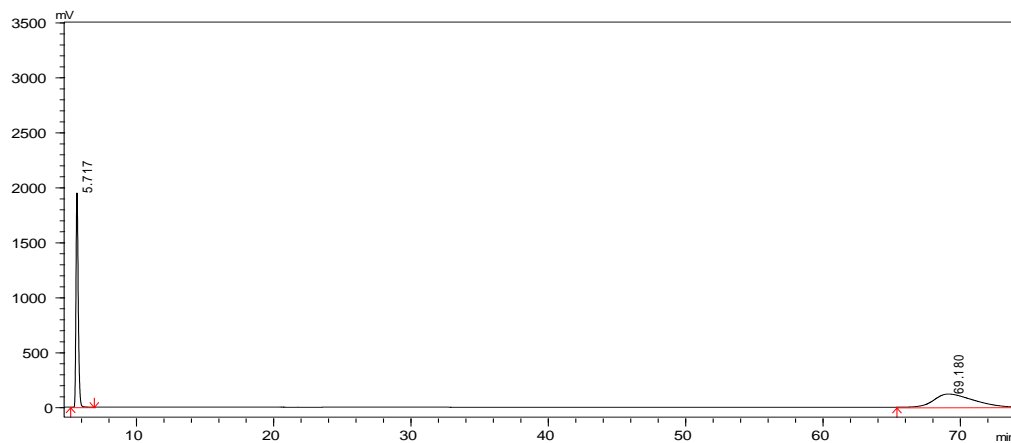
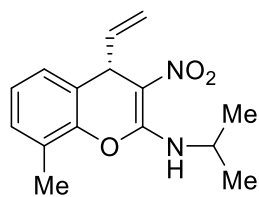


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	27.793	458182	16246322	49.902
2	36.608	344859	16309828	50.098
total		803041	32556150	100.000

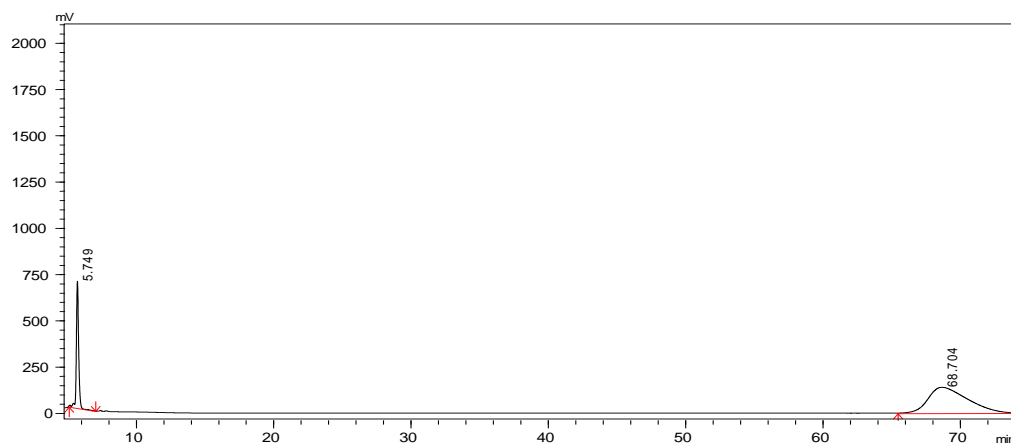


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	27.711	806834	29002216	80.901
2	36.674	145284	6846785	19.099
total		952118	35849001	100.000

HPLC chromatogram of compound **62** (55% ee)



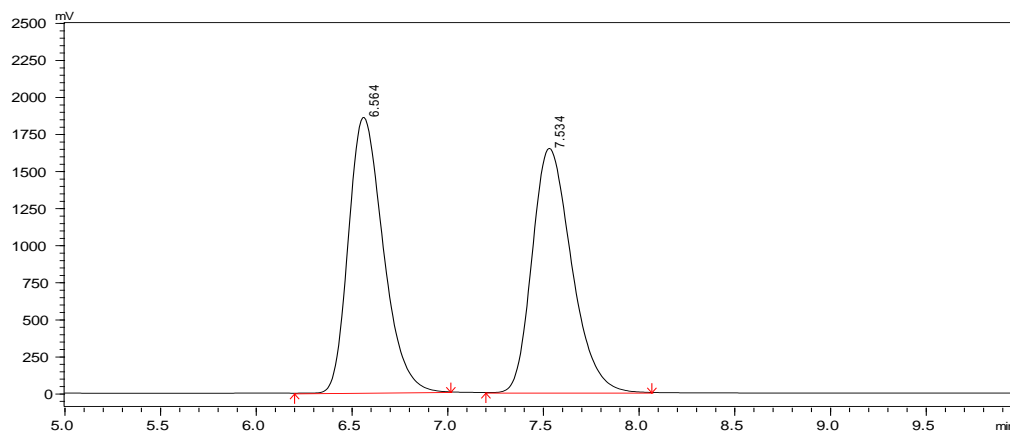
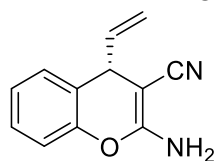
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.717	1947162	22420905	49.127
2	69.180	119070	23217326	50.873
total		2066232	45638232	100.000



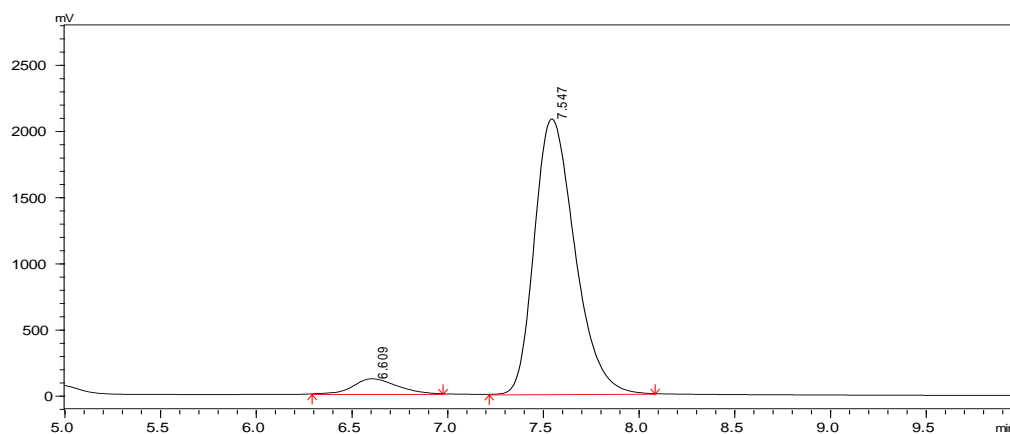
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.749	685279	7890151	22.302
2	68.704	139018	27488918	77.698
total		824297	35379069	100.000



HPLC chromatogram of compound **63** (88% ee)

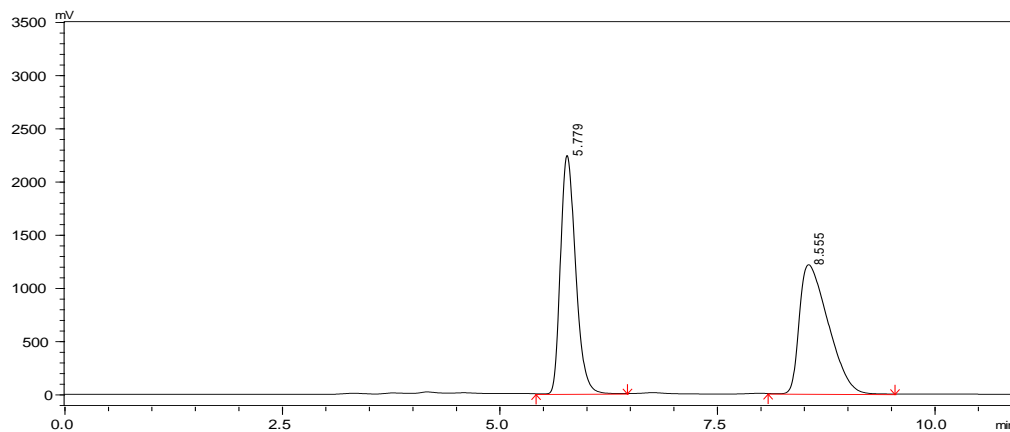
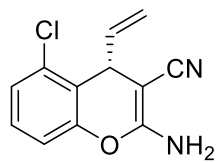


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.564	1856976	23418372	49.904
2	7.534	1646764	23508269	50.096
total		3503741	46926641	100.000

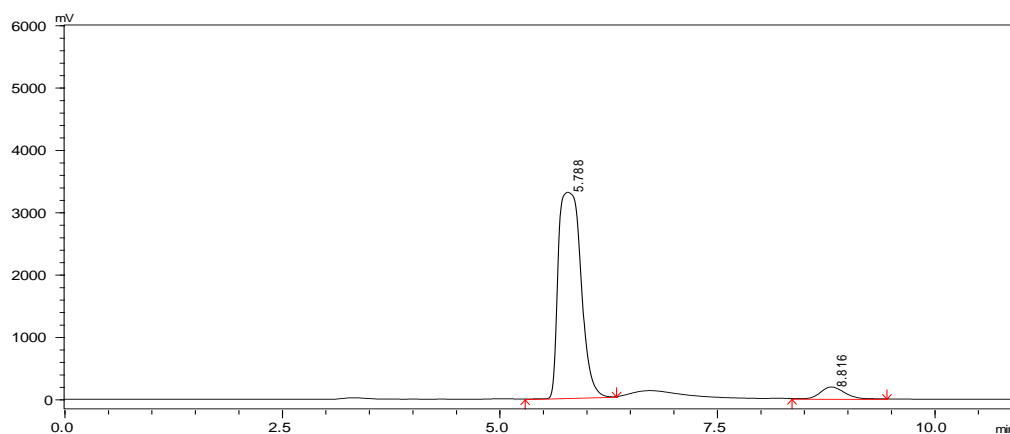


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.609	114134	1781156	5.522
2	7.547	2080142	30475161	94.478
total		2194276	32256317	100.000

HPLC chromatogram of compound **64** (89% ee)

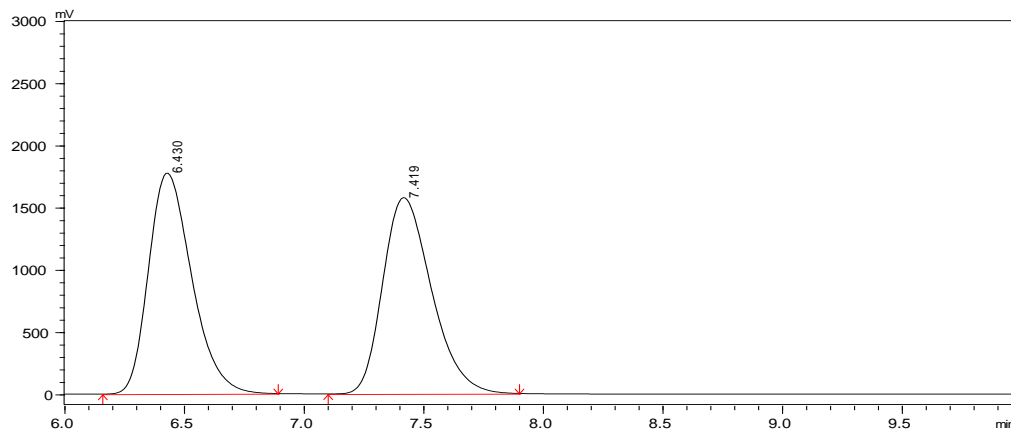
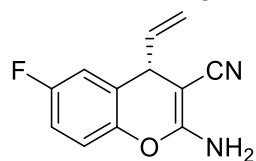


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.779	2236953	27021428	49.337
2	8.555	1211549	27747133	50.663
total		3448503	54768561	100.000

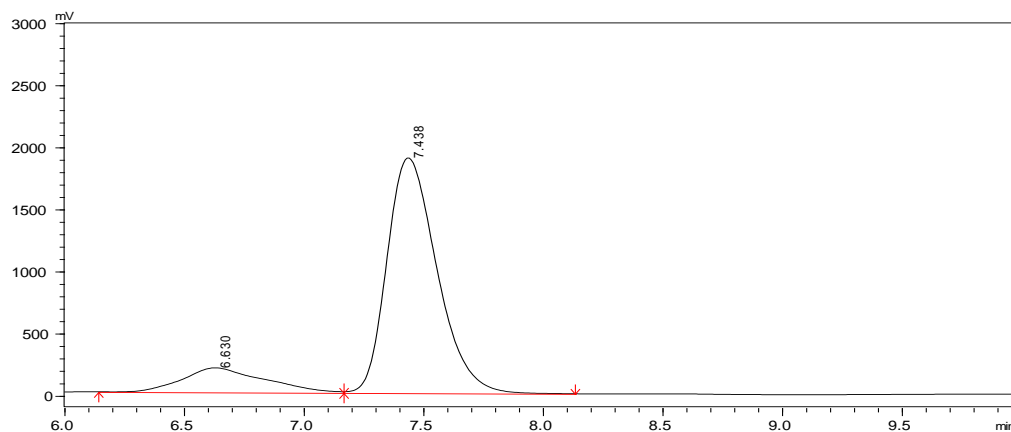


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.788	3297332	59363782	94.491
2	8.816	187183	3460987	5.509
total		3484515	62824769	100.000

HPLC chromatogram of compound **65** (71% ee)

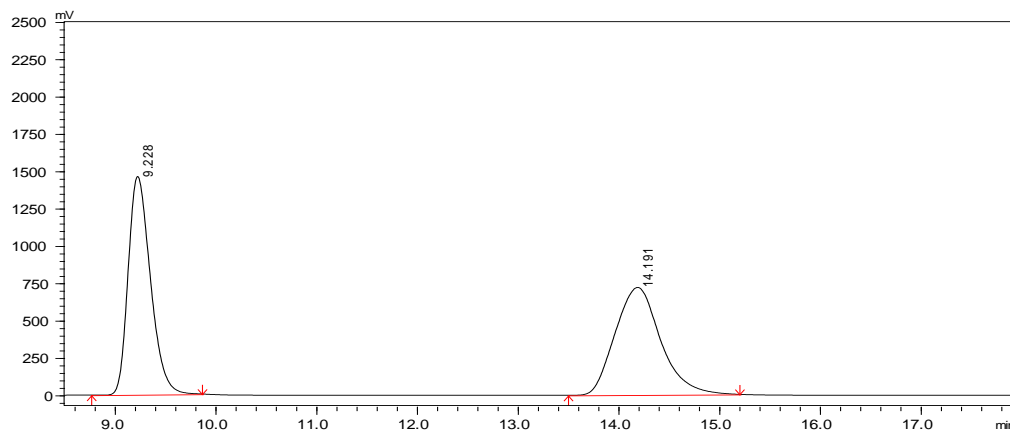
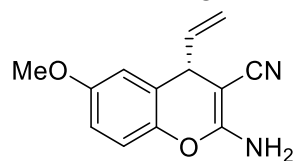


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.430	1773485	22275325	49.984
2	7.419	1575834	22289470	50.016
total		3349319	44564796	100.000

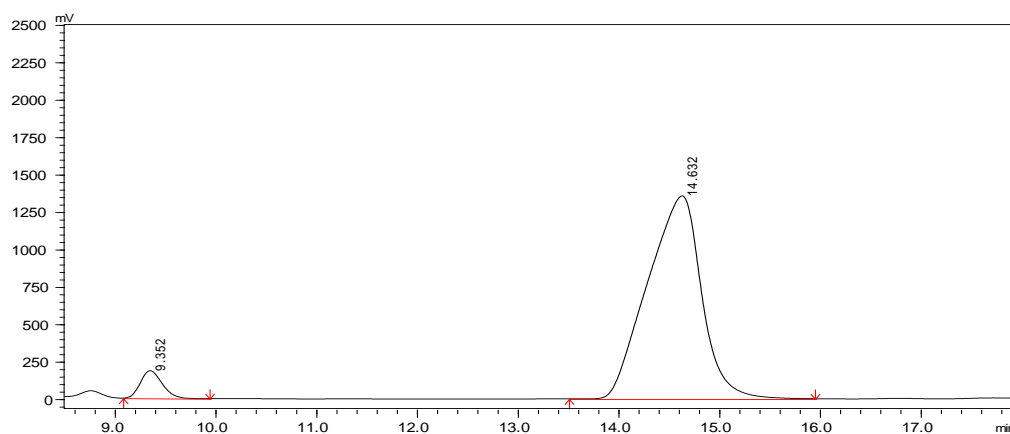


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.630	196880	4666152	14.517
2	7.438	1893389	27476572	85.483
total		2090270	32142724	100.000

HPLC chromatogram of compound **66** (90% ee)

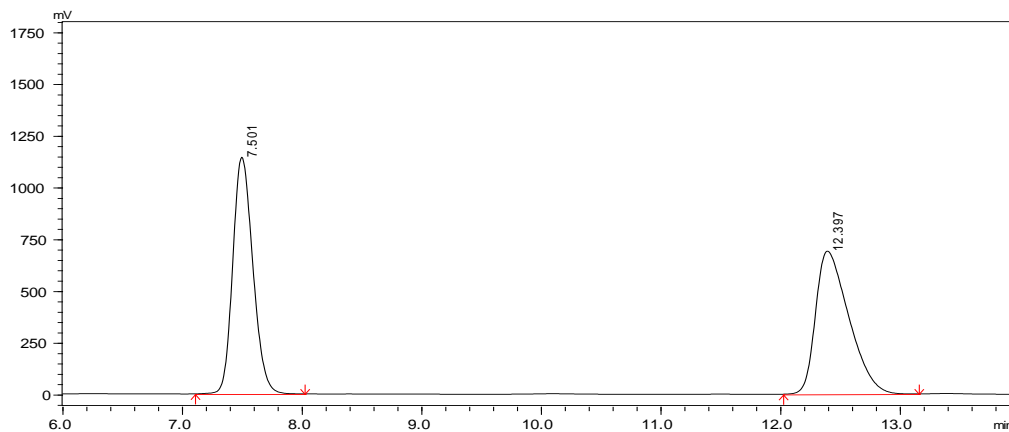
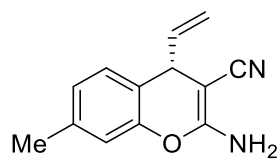


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.228	1459811	22419007	49.852
2	14.191	719611	22552535	50.148
total		2179422	44971542	100.000

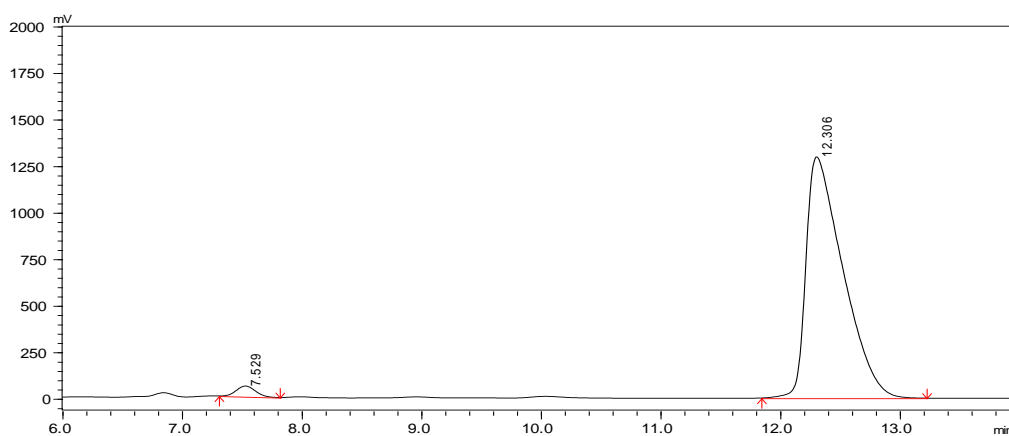


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.352	184317	2753668	5.176
2	14.632	1355056	50450040	94.824
total		1539373	53203709	100.000

HPLC chromatogram of compound **67** (96% ee)

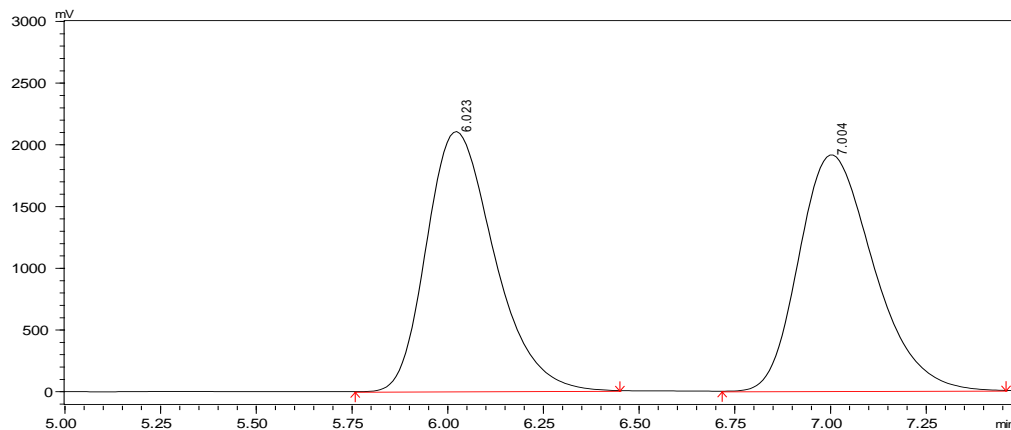
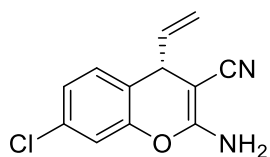


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	7.501	1143863	13386782	50.084
2	12.397	690661	13342135	49.916
total		1834524	26728917	100.000

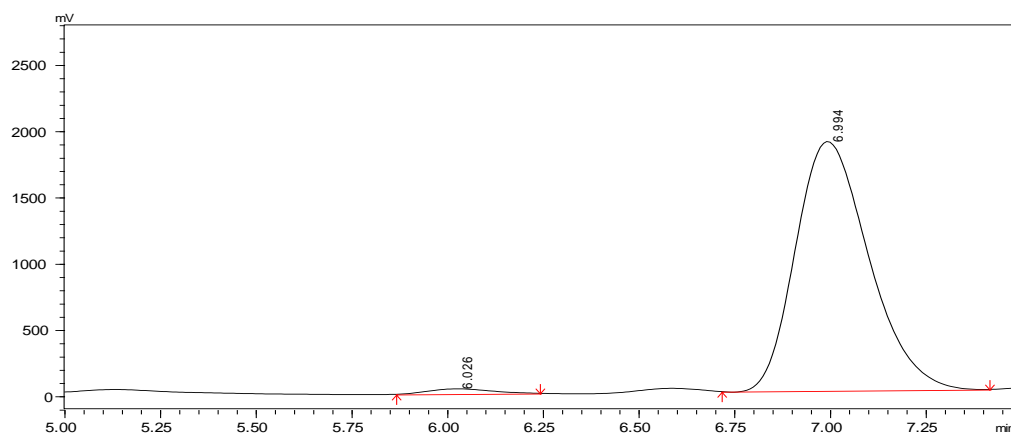


#	Ret Time (min)	Height ( $\mu\text{V}$ )	Area ( $\mu\text{V}\cdot\text{sec}$ )	Area (%)
1	7.529	56993	629319	2.212
2	12.306	1295780	27822376	97.788
total		1352773	28451695	100.000

HPLC chromatogram of compound **68** (97% ee)

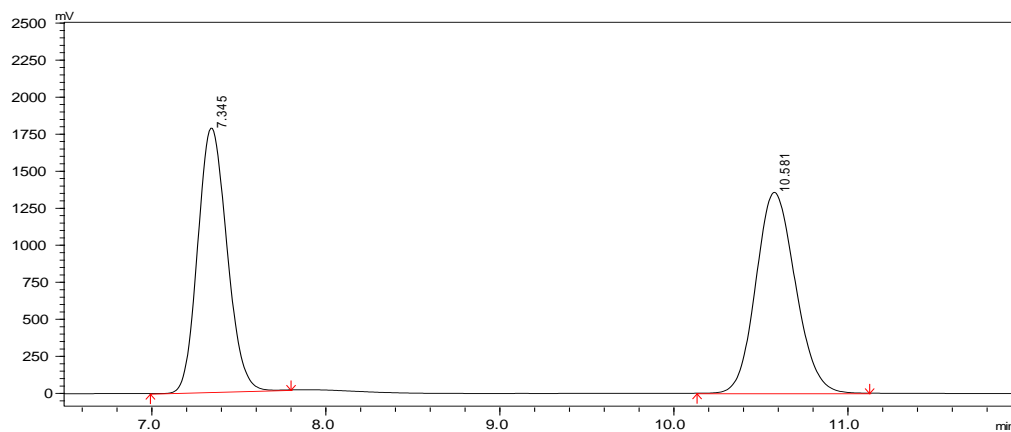
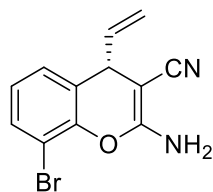


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.023	2103387	25870332	49.934
2	7.004	1910976	25938503	50.066
total		4014363	51808835	100.000

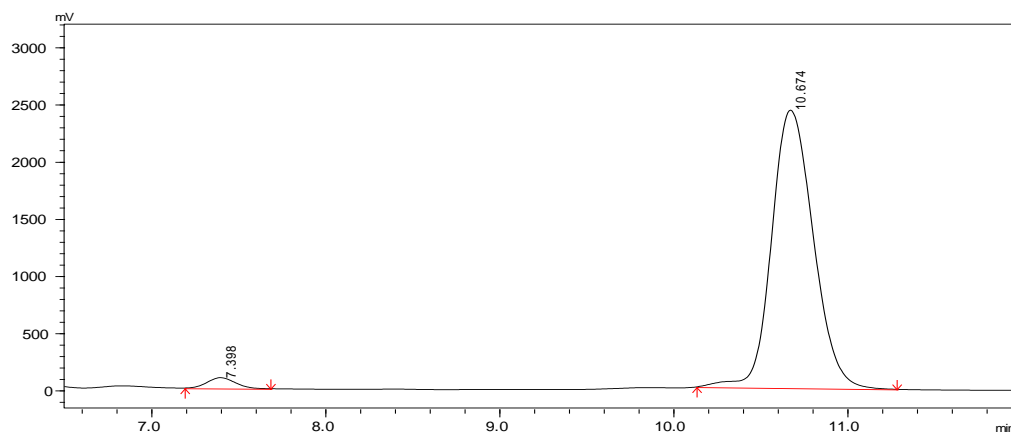


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.026	38104	416645	1.642
2	6.994	1879884	24963842	98.358
total		1917988	25380487	100.000

HPLC chromatogram of compound **69** (95% ee)

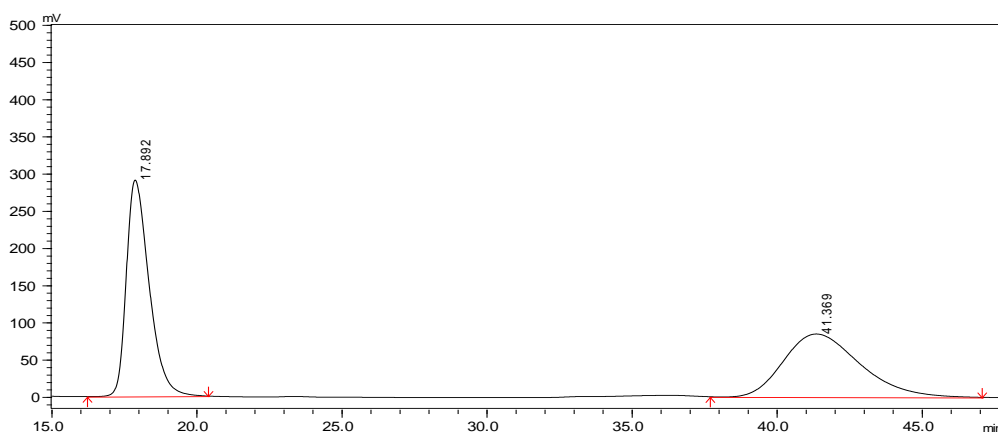
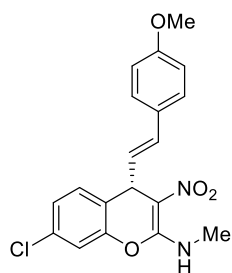


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.345	1781443	20733076	49.209
2	10.581	1356084	21399858	50.791
total		3137528	42132934	100.000

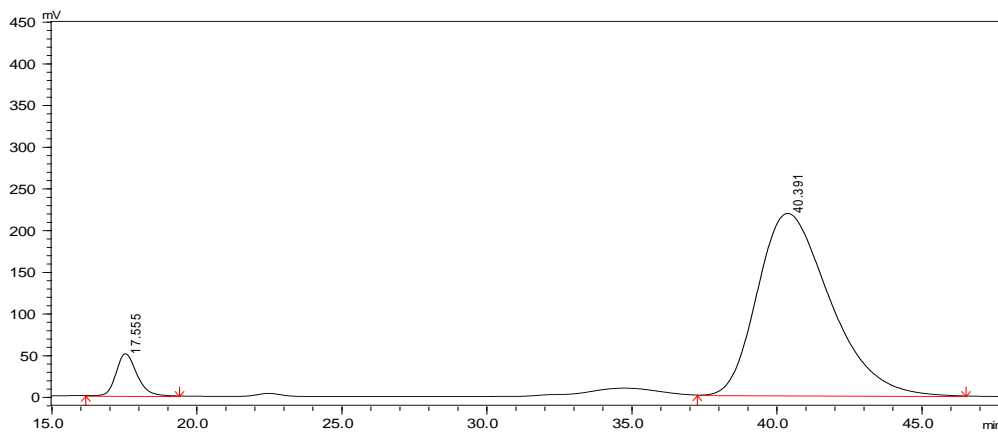


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.398	92826	1024113	2.463
2	10.674	2430202	40555189	97.537
total		2523028	41579302	100.000

HPLC chromatogram of compound **70** (87% ee)



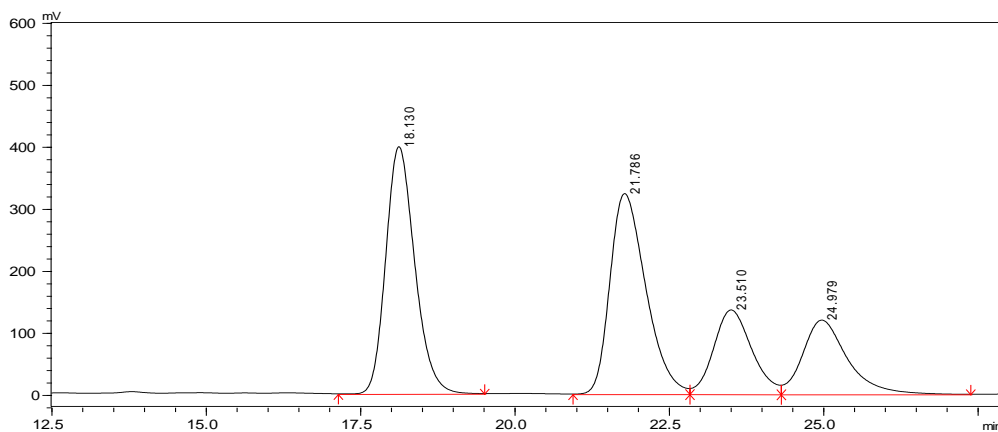
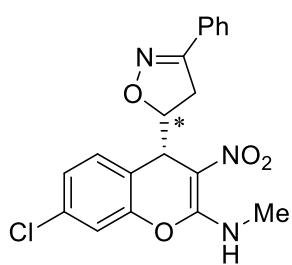
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	17.892	290743	15895387	50.736
2	41.369	84643	15434384	49.264
total		375386	31329771	100.000



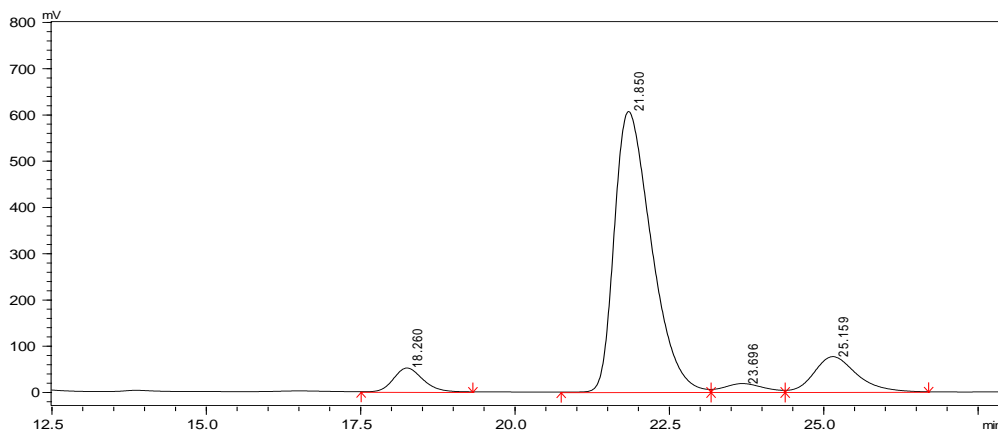
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	17.555	50411	2496822	6.177
2	40.391	218234	37925402	93.823
total		268645	40422224	100.000



HPLC chromatogram of compound **71** (88% ee, 6:1 dr)



#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	18.130	398418	12998543	34.355
2	21.786	323321	13040919	34.467
3	23.510	135789	5810826	15.358
4	24.979	119483	5985219	15.819
total		977011	37835507	100.000



#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	18.260	51291	1674975	5.348
2	21.850	606359	25232907	80.561
3	23.696	17977	772535	2.466
4	25.159	76066	3640882	11.624
total		751693	31321299	100.000