

**Reactivity Study of 4-Hydroxy-2*H*-chromene-2-thione with Symmetrical
1,4-Acetylene Dicarboxylate and Methyl Propiolate Using Ytterbium(III)
Triflate as Catalyst: Stereoselective Synthesis of Substituted Fumarate and
(*Z*) Acrylate Derivatives**

Electronic Supporting Information

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General information and methods

In this work, the starting material 4-Hydroxythiocumarin was synthesized in our laboratory followed by previously reported methods. The acetylene dicarboxylate derivatives were all Sigma Aldrich. ^1H and ^{13}C NMR spectra were recorded on 400, 500, and 600 MHz (Bruker) NMR spectrometers, respectively. TMS is used in internal reference: chemical shifts (δ scale) are reported in parts per million (ppm). ^1H NMR spectra are also noted in the order of multiplicity, coupling constant (J value) in Hertz (Hz), and the number of protons; signals were characterized as s (singlet), d (doublet), t (triplet), m (multiplet) and bs (broad). IR spectra were recorded on an IR spectrophotometer. Melting points were recorded using the melting point apparatus (Stuart Company). HRMS spectra were recorded on a TOF mass analyzer. The structure was also determined using a single-crystal XRD diffractometer.

X-ray crystallographic data of compound (**3fb**)

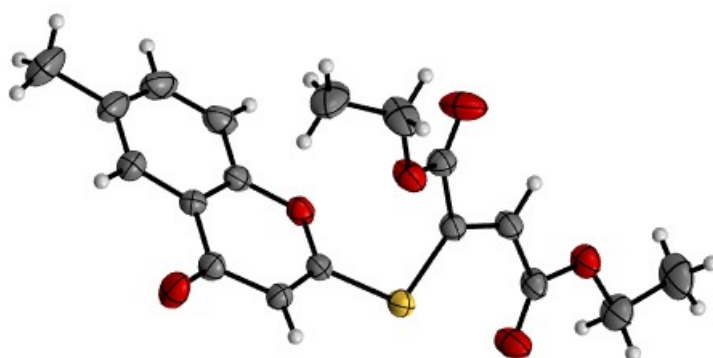


Figure: ORTEP Diagram of compound (**3fb**)

Table S1. Crystal data and structure refinement for compound (**3fb**)

Entry	Identification Code	Compound (3fb)
01	Empirical formula	C ₁₈ H ₁₈ O ₆ S
02	Formula weight	362.38
03	Temperature	295 K
04	Wavelength	0.71073
05	Radiation type	Mo K α
06	Radiation system	Fine-focus sealed tube
07	Crystal system	Monoclinic P
08	Space group	P 21/c
09	Cell length (Å)	(a)=9.2431(5), (b)=7.5910(4), (c)=26.1848(15)
10	Cell angle (°)	(α)=90, (β)=97.560(2), (γ)=90
11	Cell volume (Å ³)	1821.27(17)
12	Density	1.322
13	Absorption correction	Multi-scan
14	Reflection number	3192
15	Cell formula units Z	4
16	CCDC no	2390500

X-ray crystallographic data of compound (**3fc**)

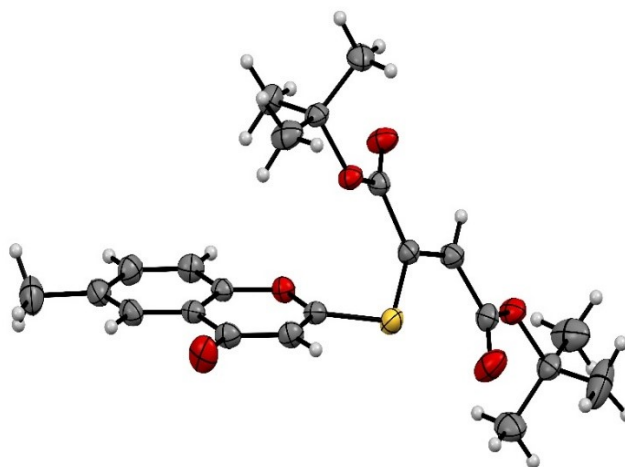


Table S1. Crystal data and structure refinement for compound (**3fc**)

Entry	Identification Code	Compound (3fc)
01	Empirical formula	C ₂₂ H ₂₆ O ₆ S
02	Formula weight	418.49
03	Temperature	295 K
04	Wavelength	0.71073
05	Radiation type	Mo K α
06	Radiation system	Fine-focus sealed tube
07	Crystal system	Monoclinic P
08	Space group	P 21/n
09	Cell length (Å)	(a)=11.1757(6), (b)=7.6127(4), (c)=26.4230(15)
10	Cell angle (°)	(α)=90, (β)=100.954(2), (γ)=90
11	Cell volume (Å ³)	2207.0(2)
12	Density	1.260
13	Absorption correction	Multi-scan
14	Reflection number	3877
15	Cell formula units Z	4
16	CCDC no	2390445

X-ray crystallographic data of compound (**7da**)

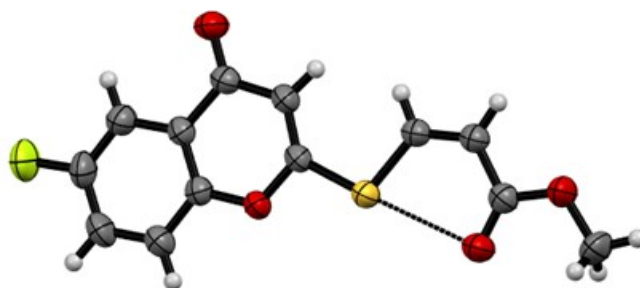


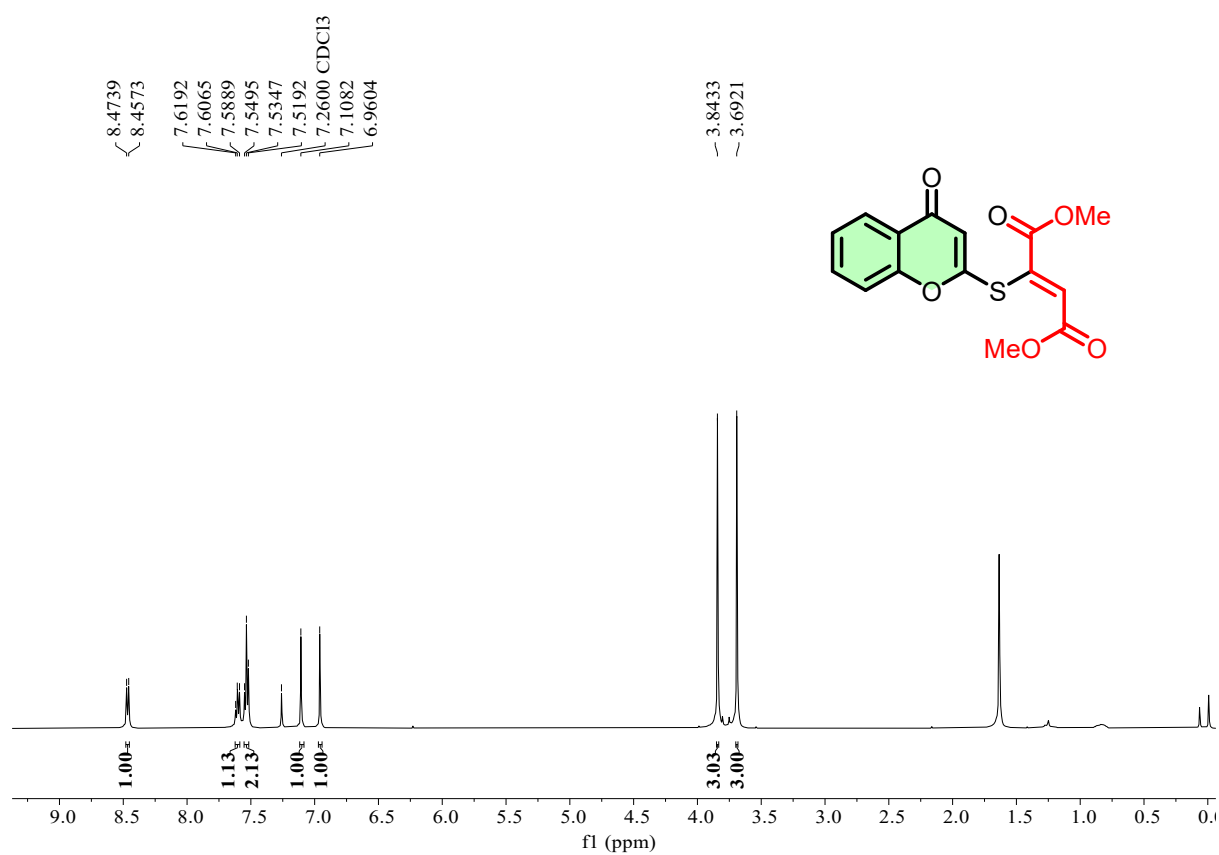
Figure. ORTEP Diagram of compound (**7da**)

Table S1. Crystal data and structure refinement for compound (**7da**)

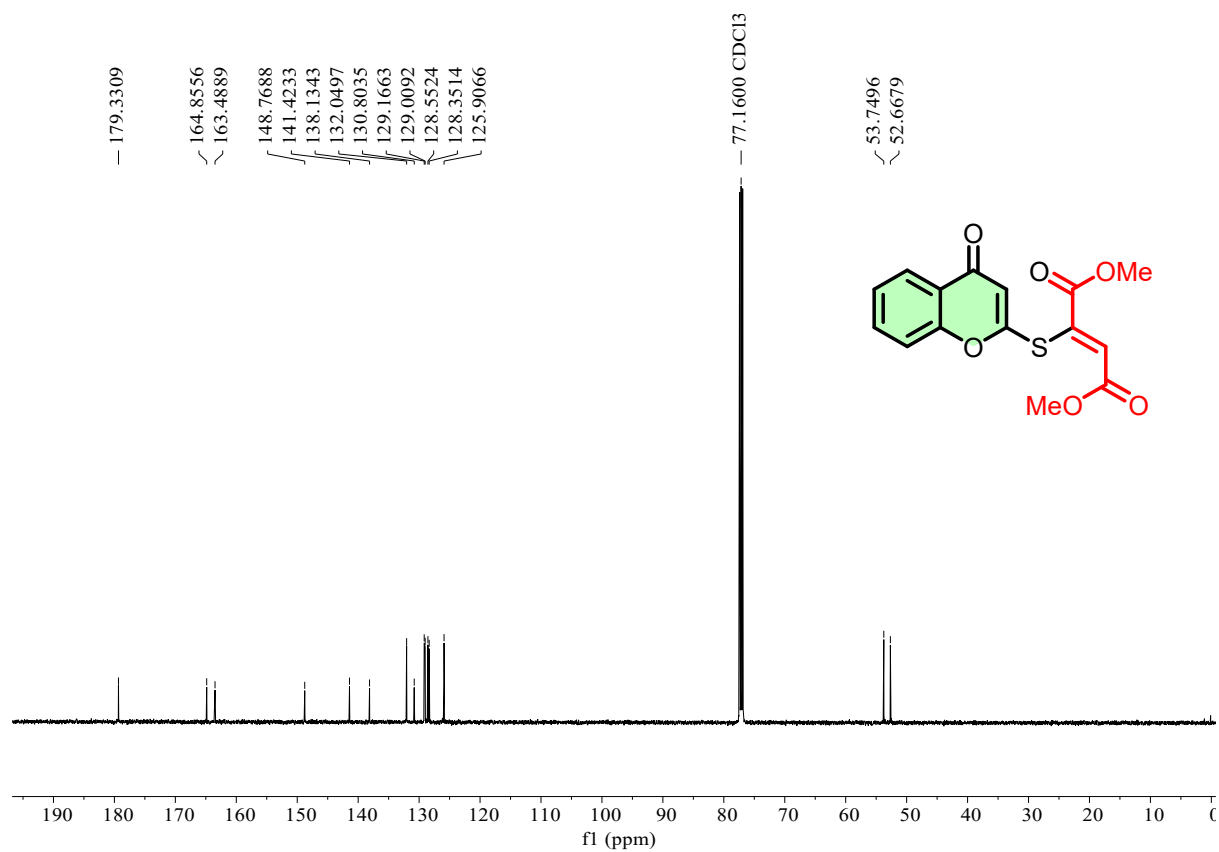
Entry	Identification Code	Compound (7da)
01	Empirical formula	C ₁₃ H ₉ F O ₄ S

02	Formula weight	280.26
03	Temperature	296 K
04	Wavelength	0.71073
05	Radiation type	Mo K α
06	Radiation system	Fine-focus sealed tube
07	Crystal system	Monoclinic P
08	Space group	P 2 ₁ /n
09	Cell length (Å)	<u>(a)=10.802(3), (b)=13.196(3),</u> <u>(c)=25.591(6)</u>
10	Cell angle (°)	(α)=90, (β)=90.479(7), (γ)=90
11	Cell volume (Å ³)	3647.7(16)
12	Density	1.531 g cm ⁻³
13	Absorption correction	Multi-scan
14	Reflection number	6426
15	Cell formula units Z	12
16	CCDC no	2487877

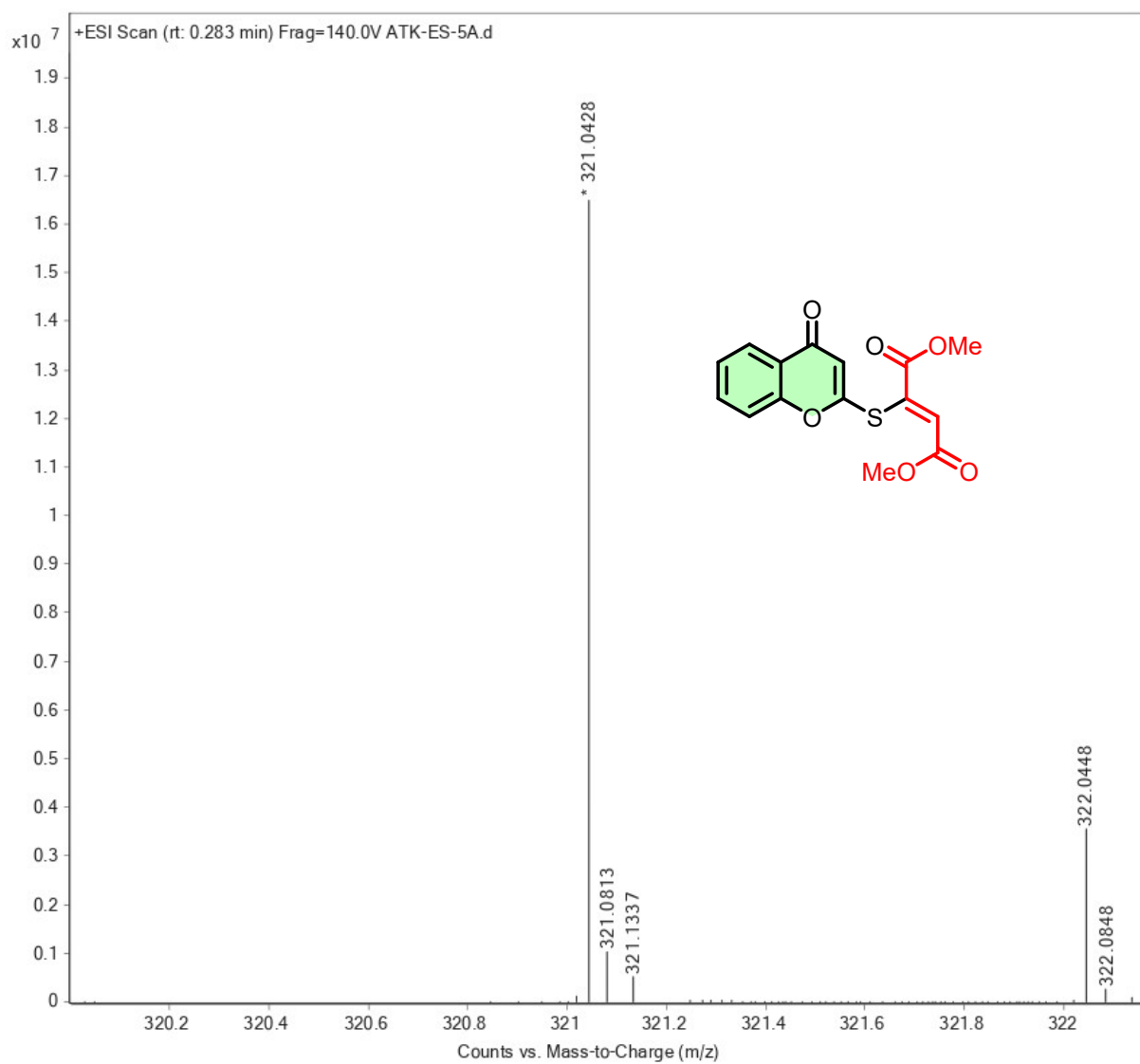
¹H NMR (500MHz, CDCl₃) spectrum of compound 3aa



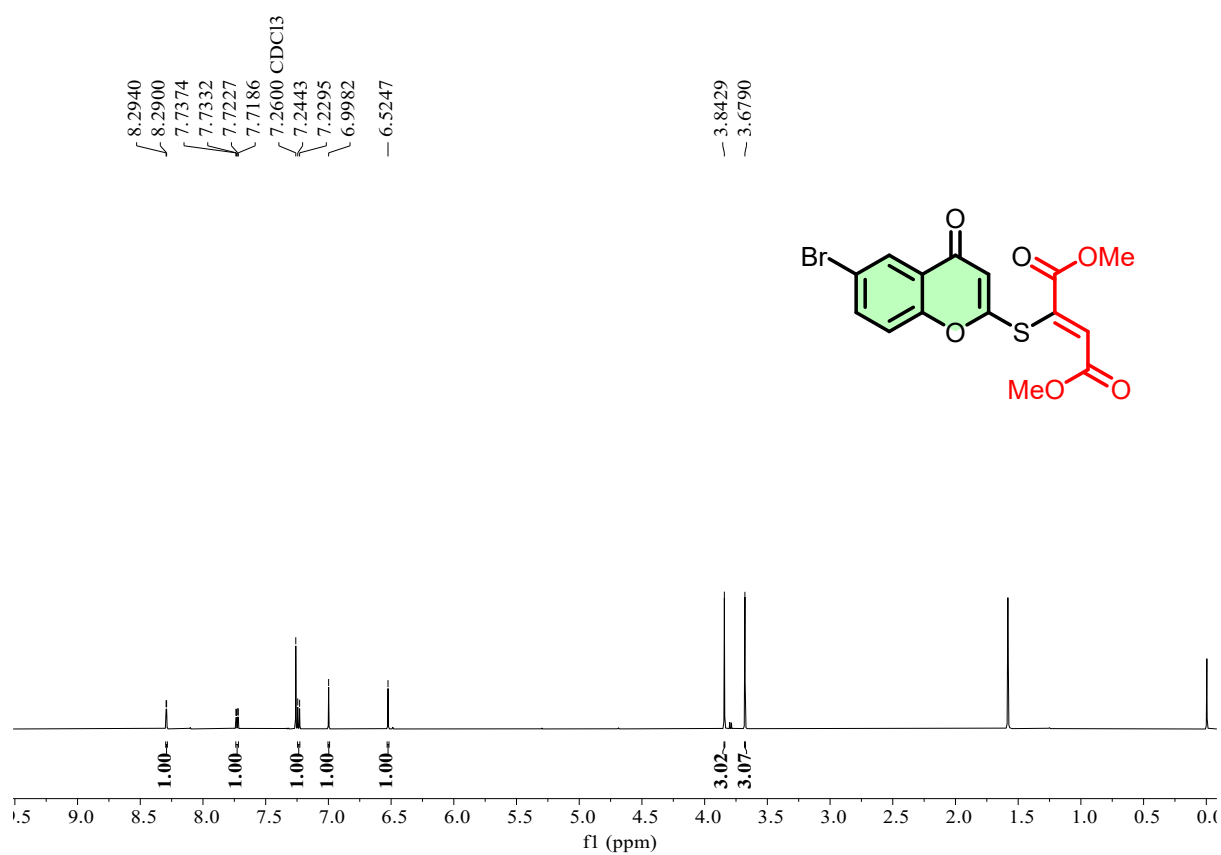
¹³C{¹H} NMR (125MHz, CDCl₃) spectrum of compound 3aa



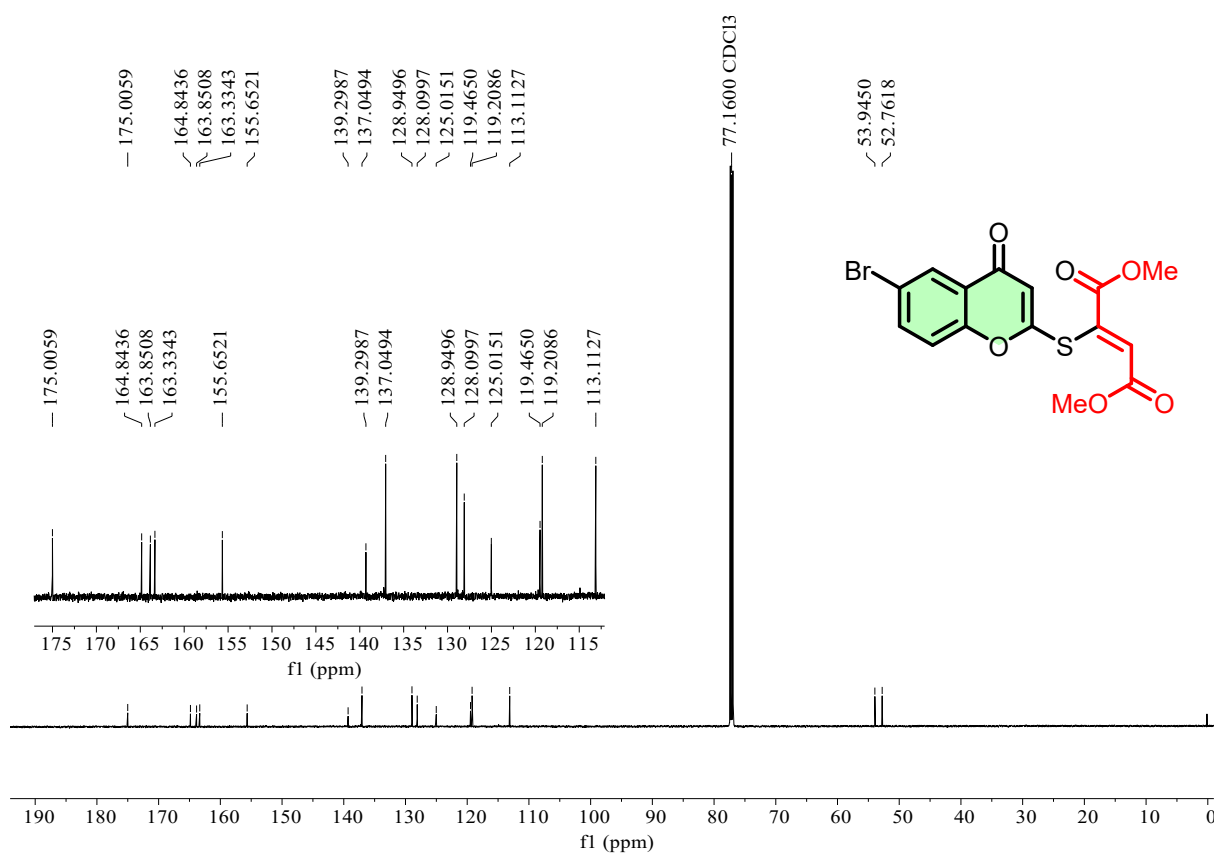
HRMS of compound 3aa



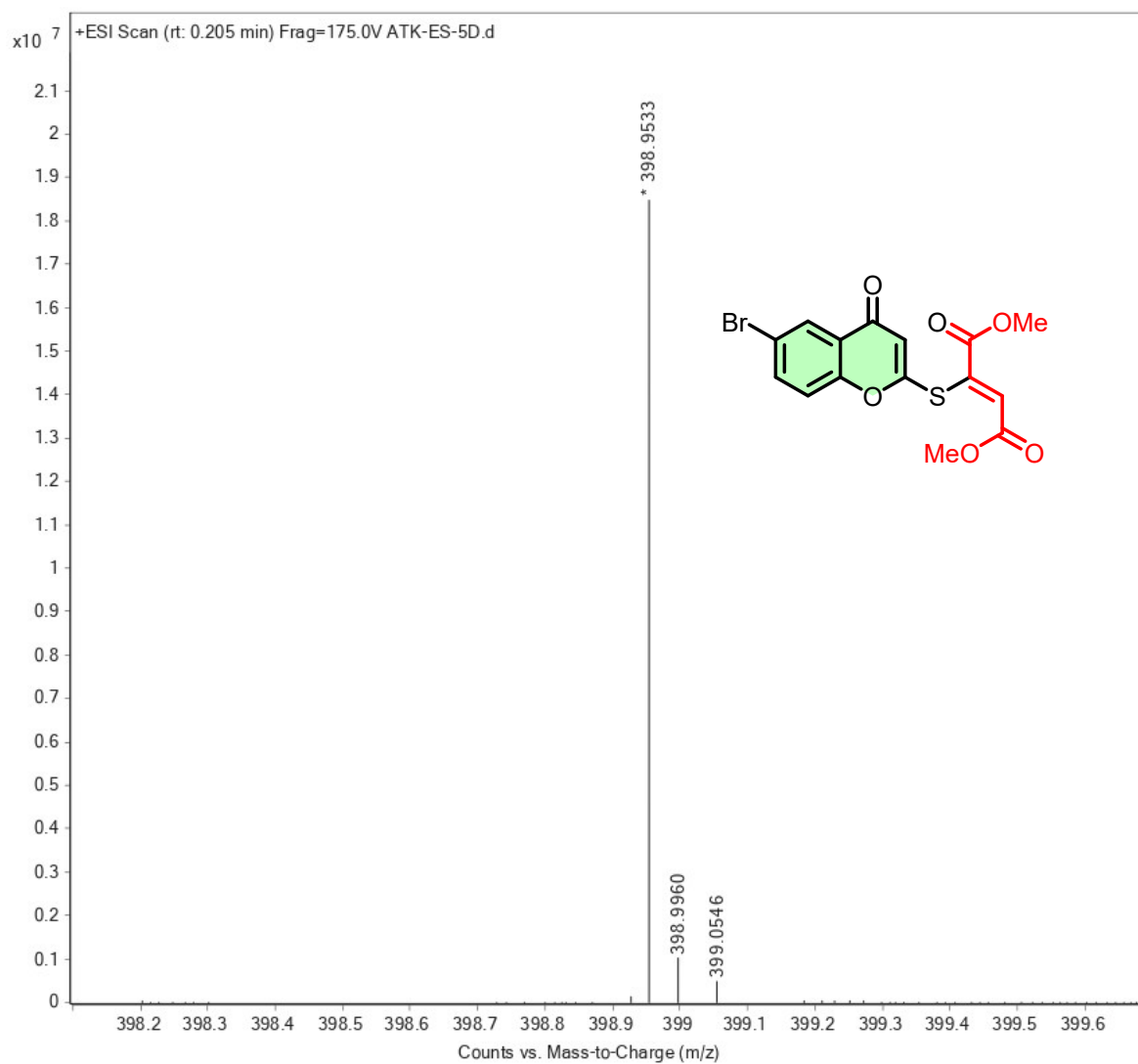
¹H NMR (600MHz, CDCl₃) spectrum of compound 3ba



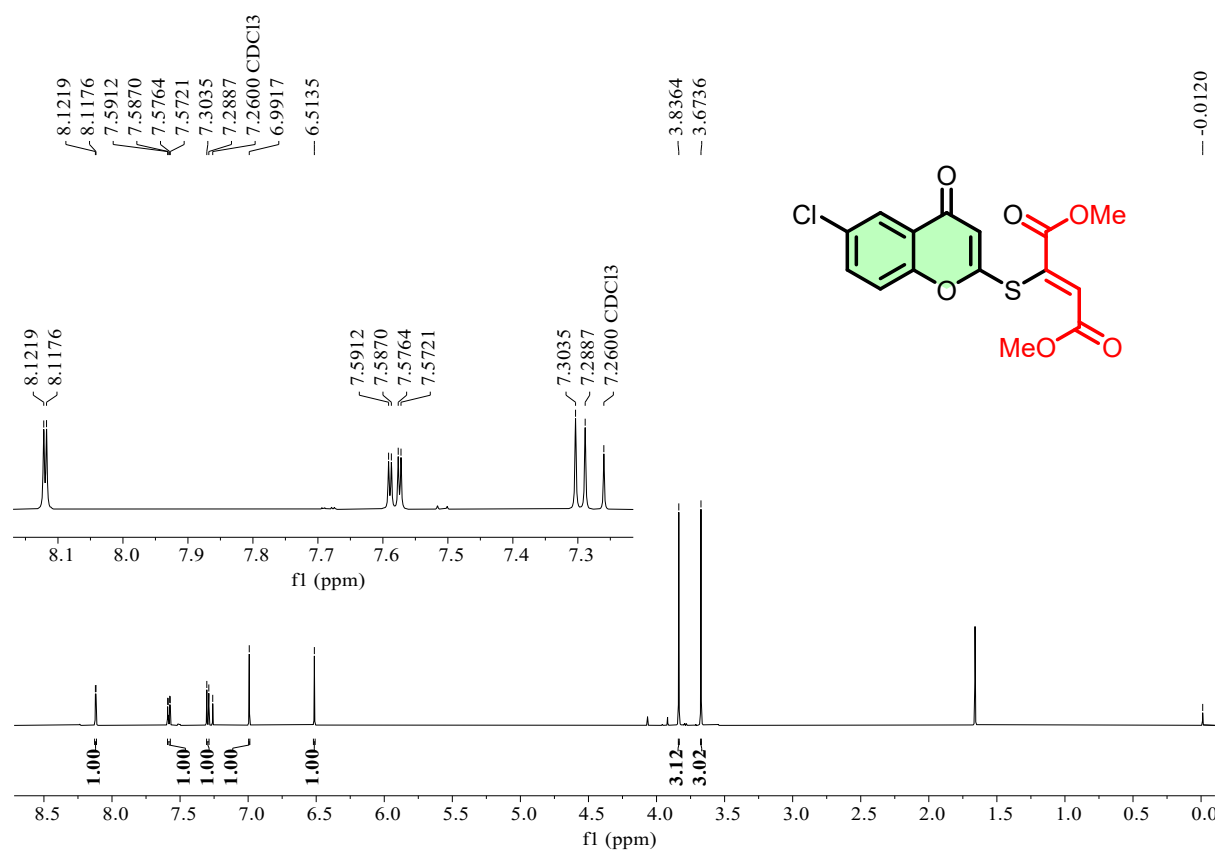
¹³C{¹H} NMR (125 MHz, CDCl₃) spectrum of compound 3ba



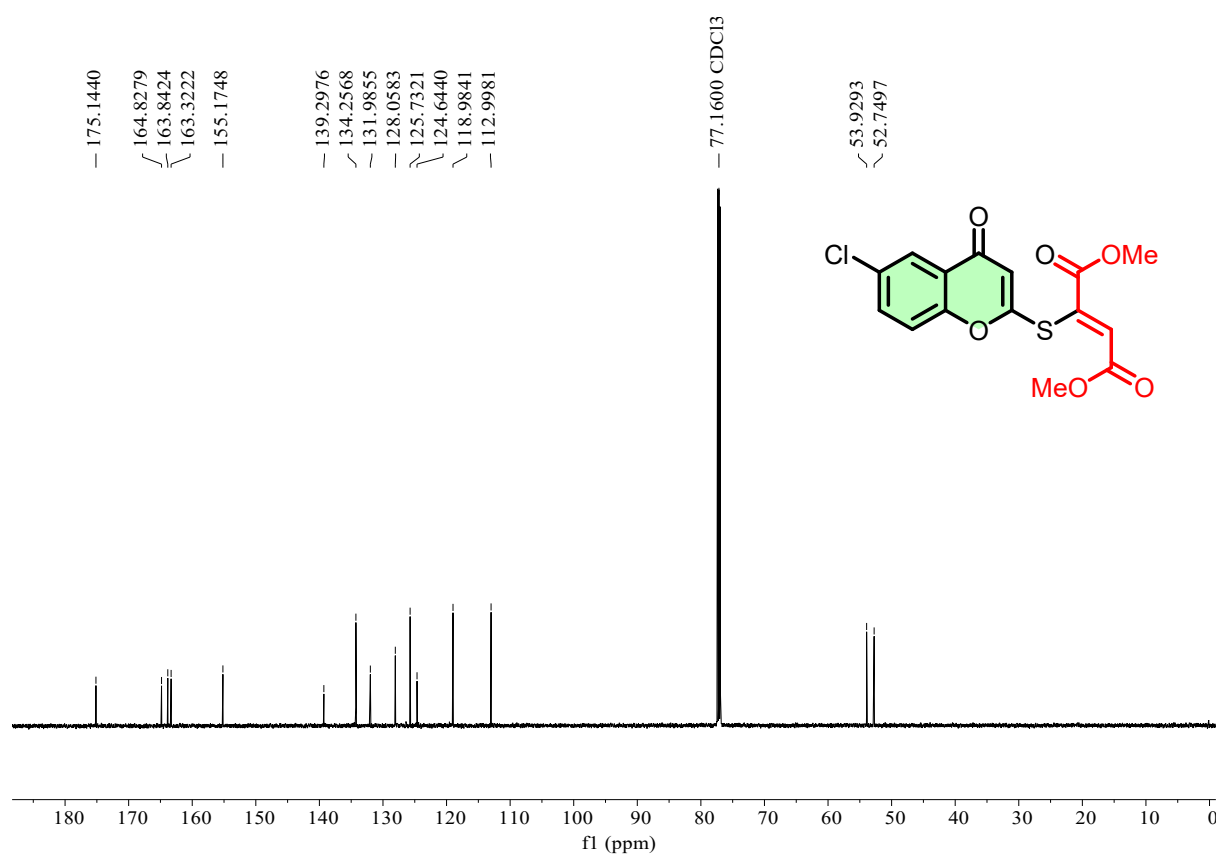
HRMS of compound 3ba



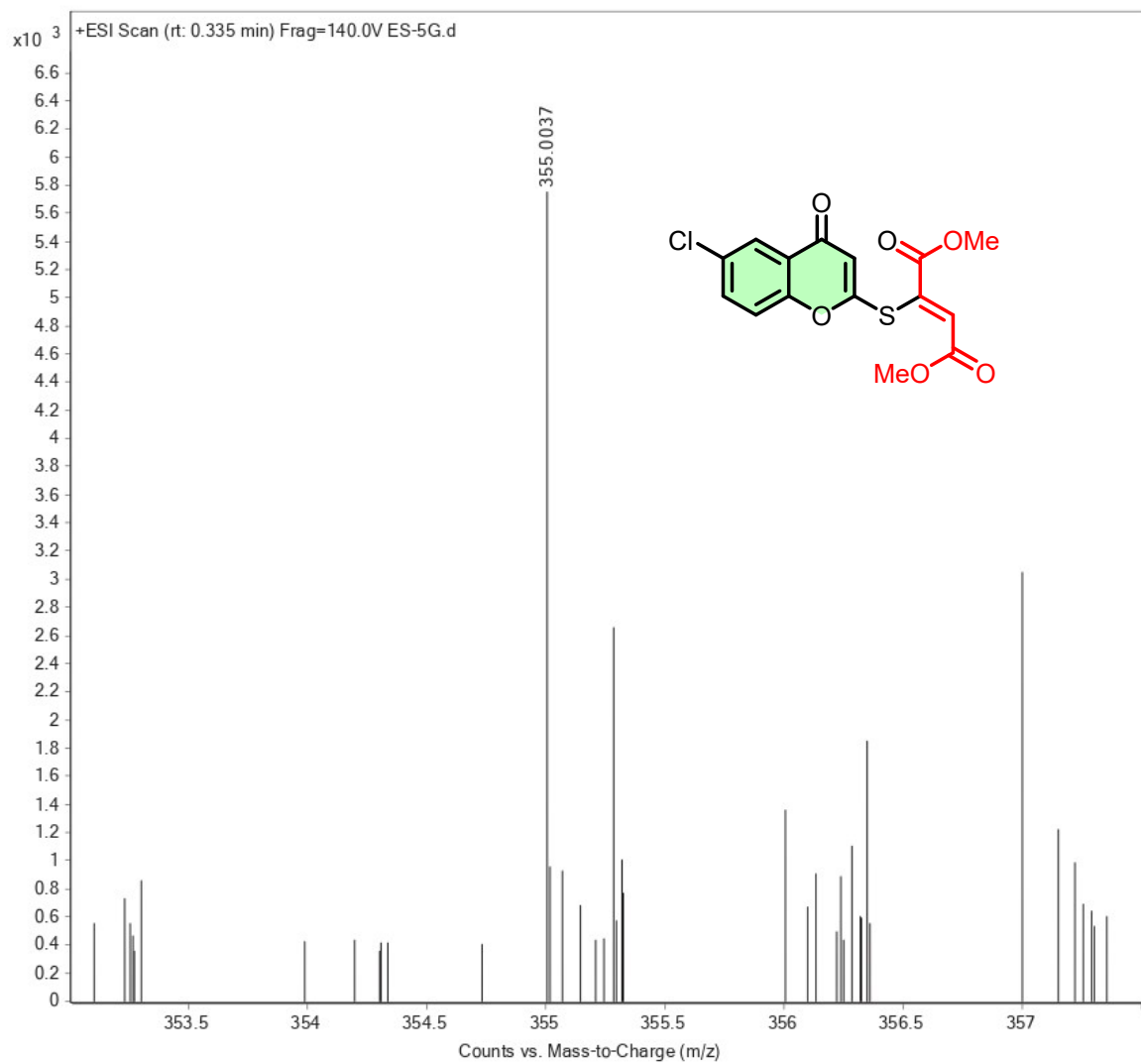
¹H NMR (600MHz, CDCl₃) spectrum of compound 3ca



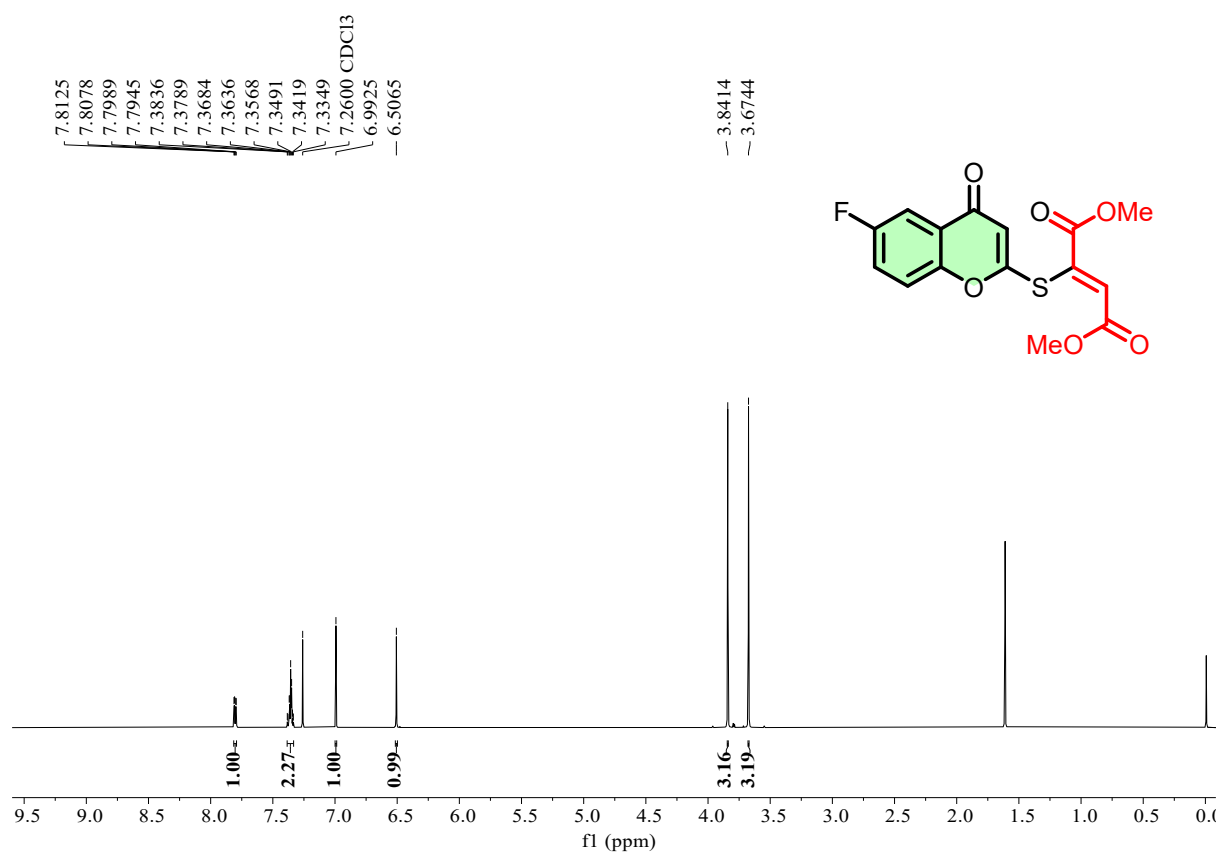
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 3ca



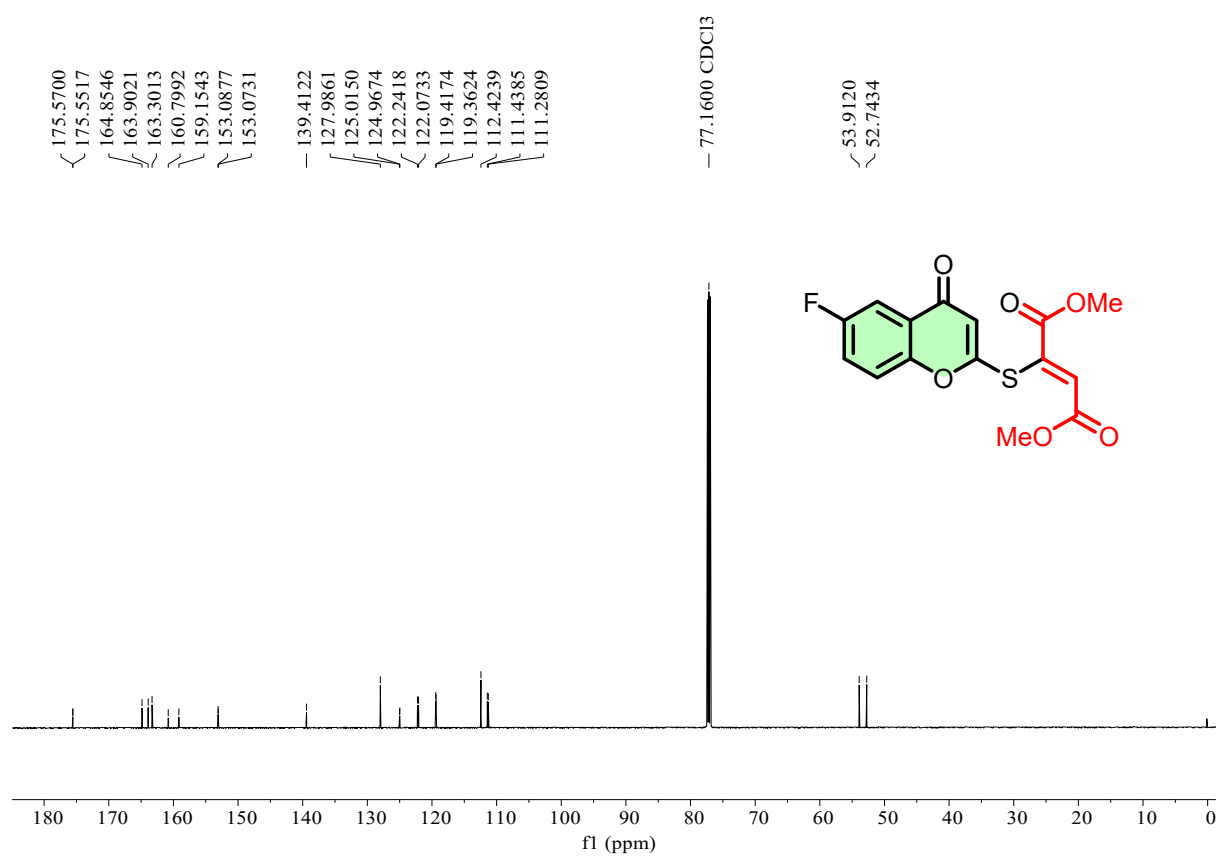
HRMS of compound 3ca



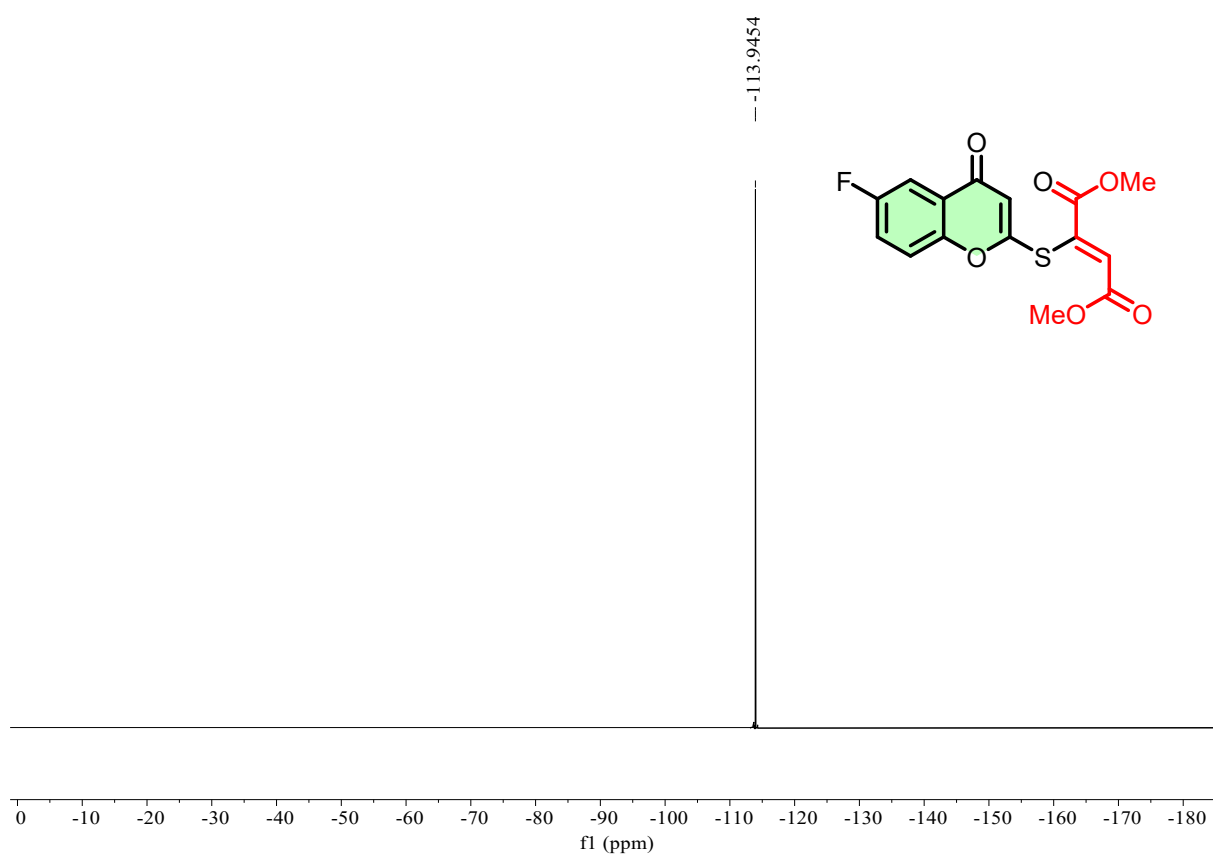
¹H NMR (600 MHz, CDCl₃) spectrum of compound 3da



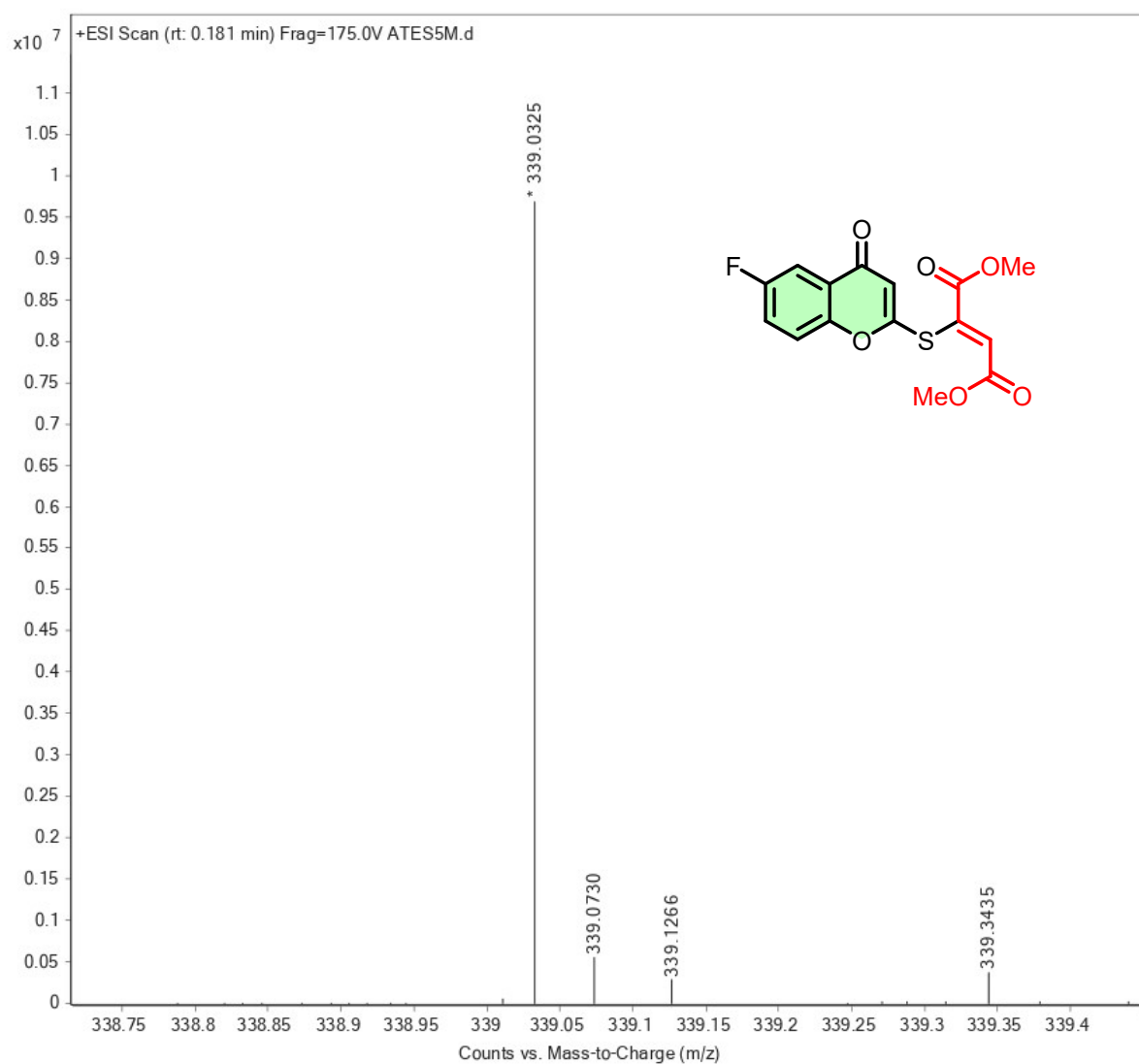
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 3da



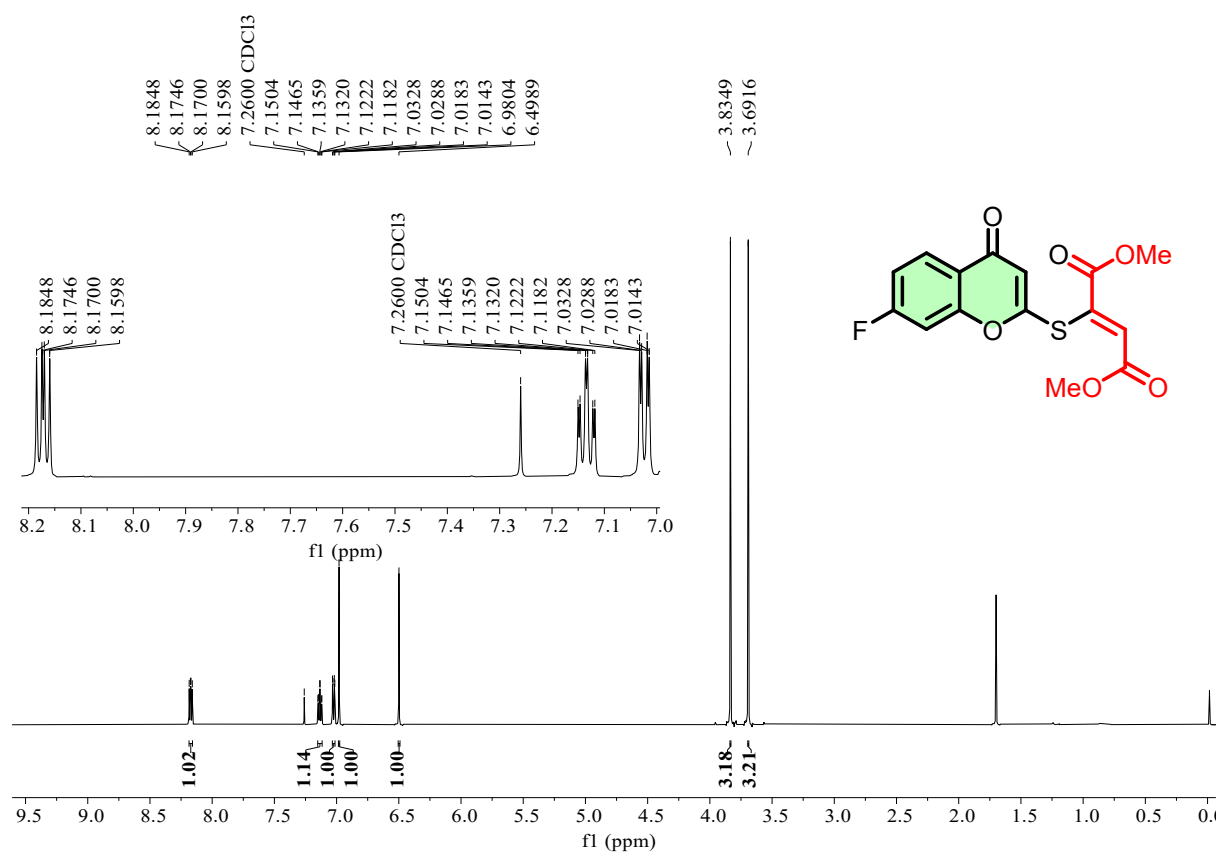
^{19}F NMR (470 MHz, CDCl_3) spectrum of compound 3da



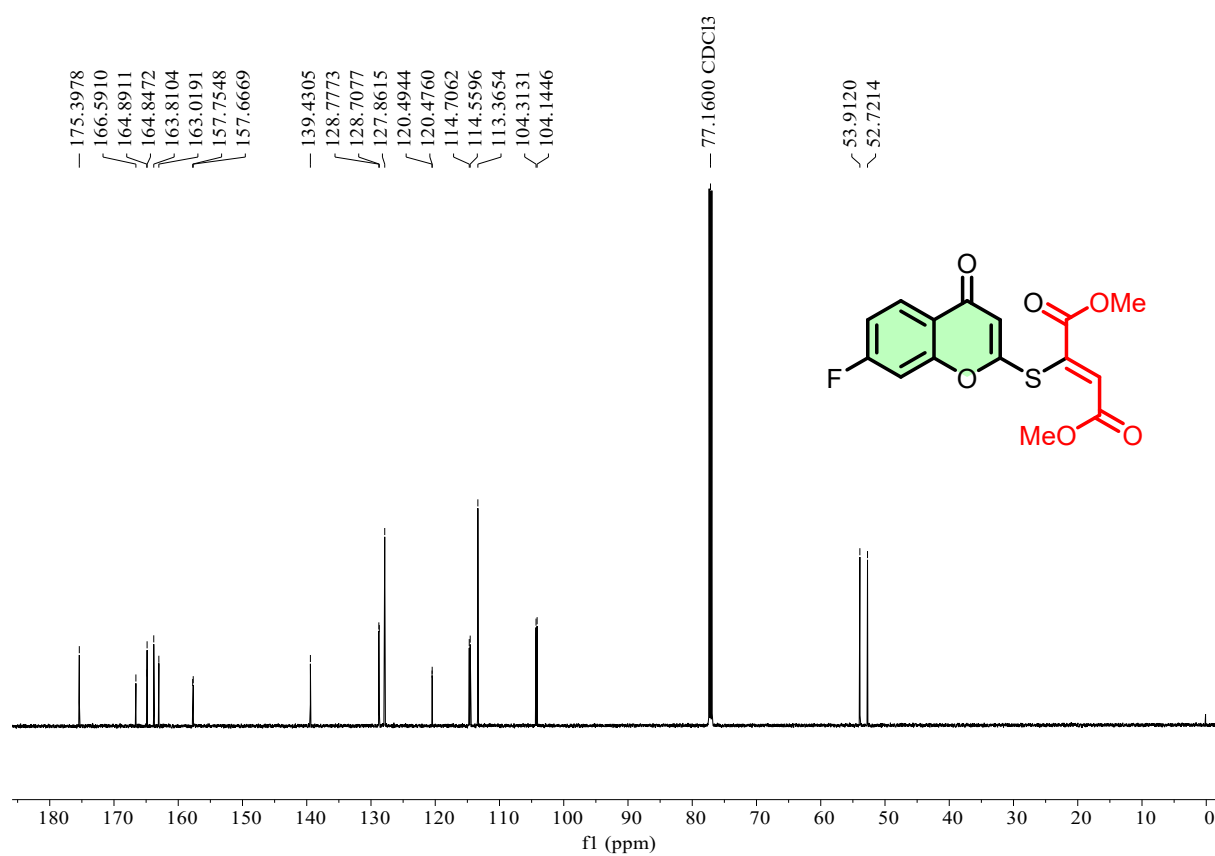
HRMS of compound 3da



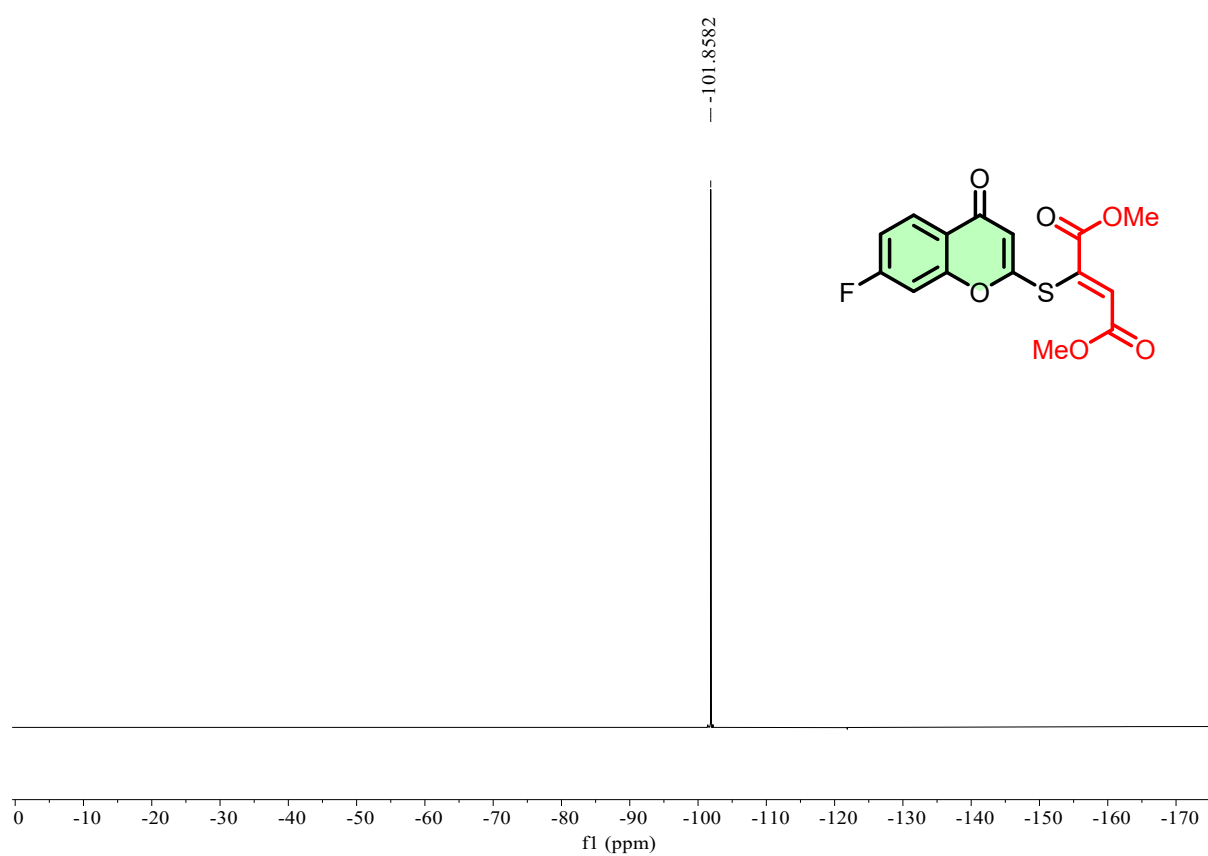
^1H NMR (600 MHz, CDCl_3) spectrum of compound 3ea



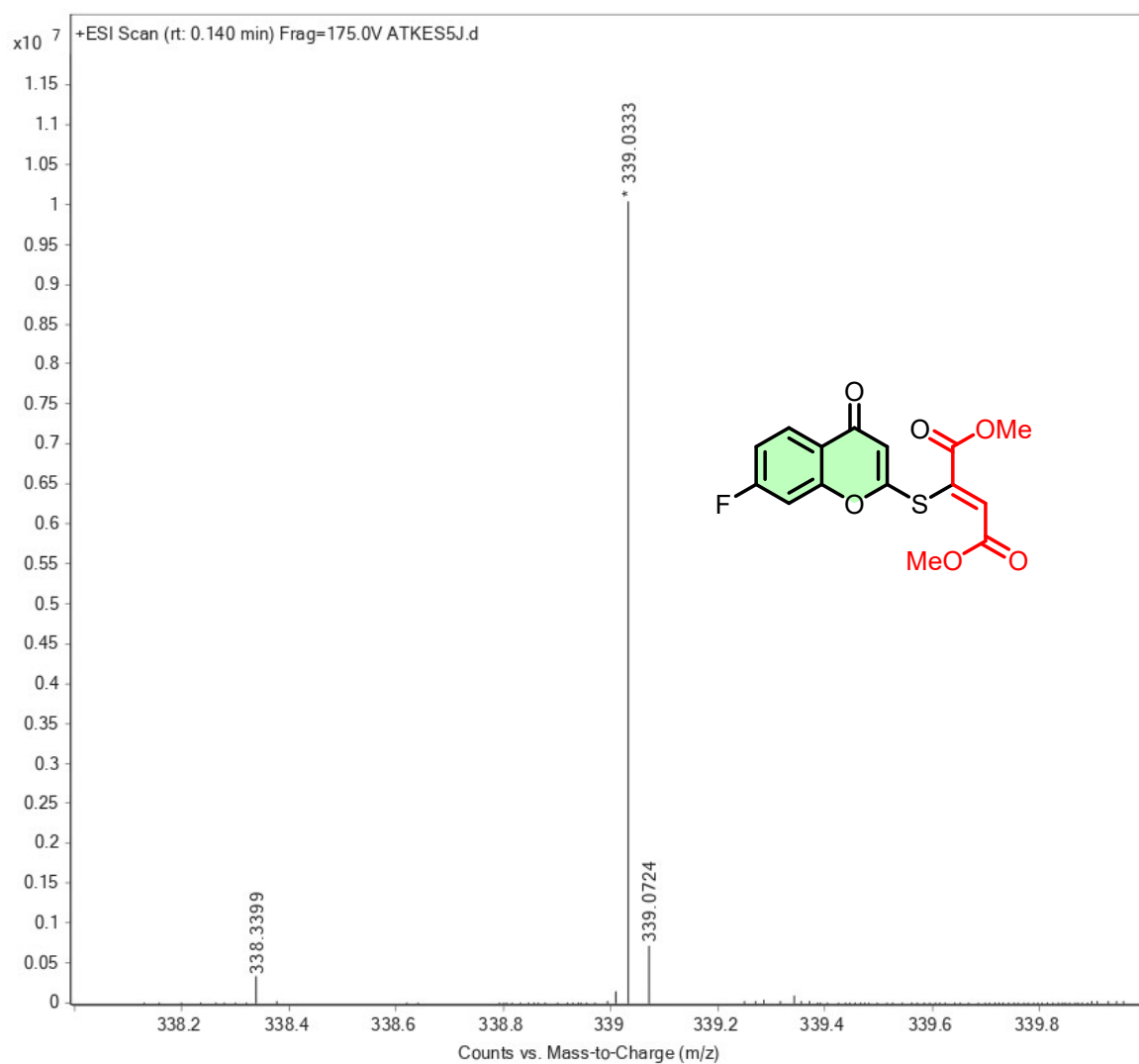
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 3ea



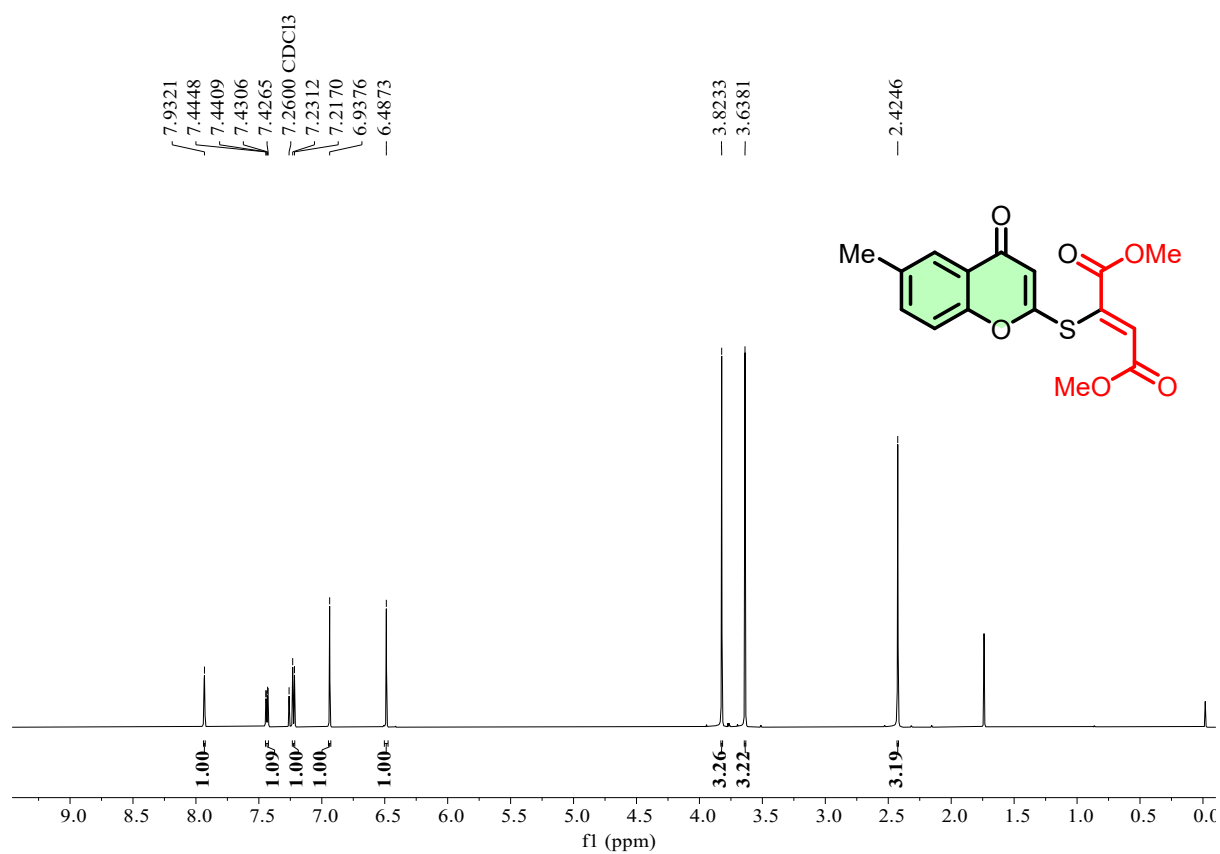
^{19}F NMR (564 MHz, CDCl_3) spectrum of compound 3ea



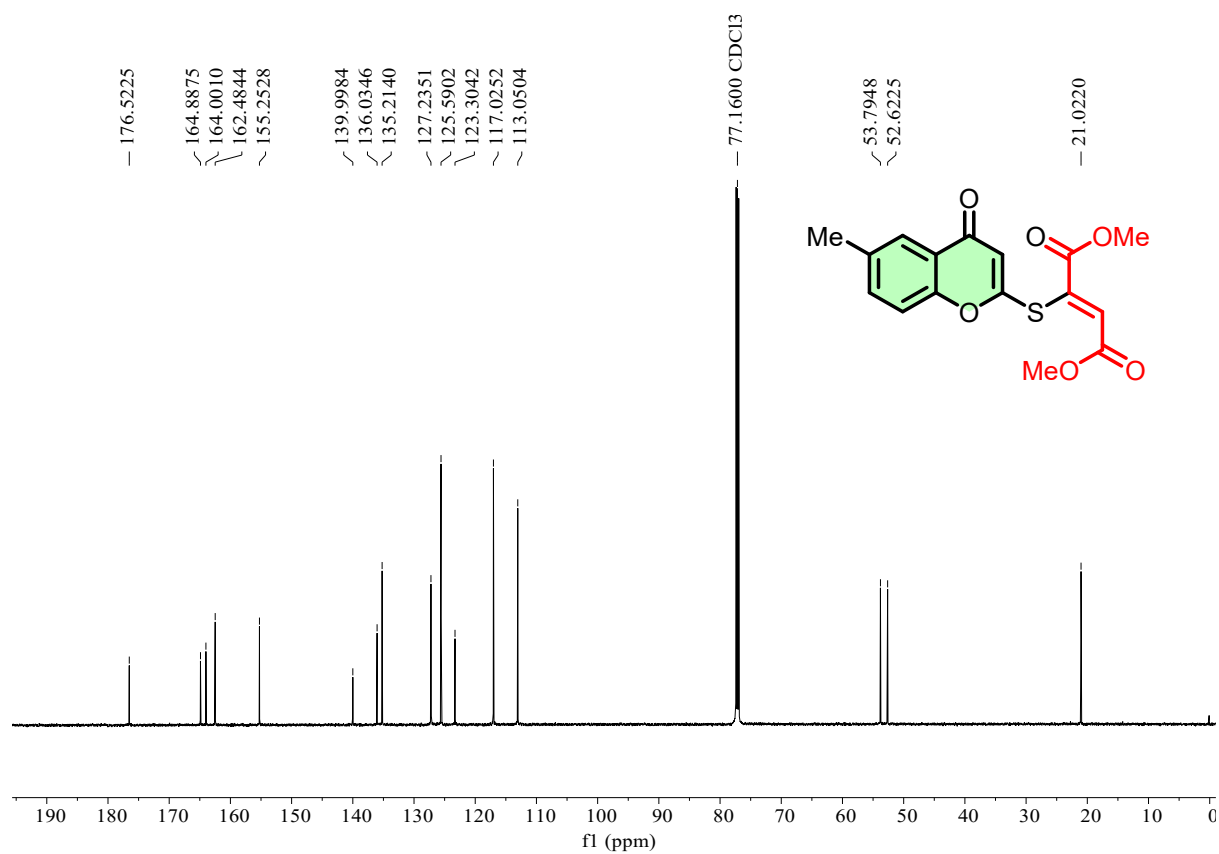
HRMS of compound 3ea



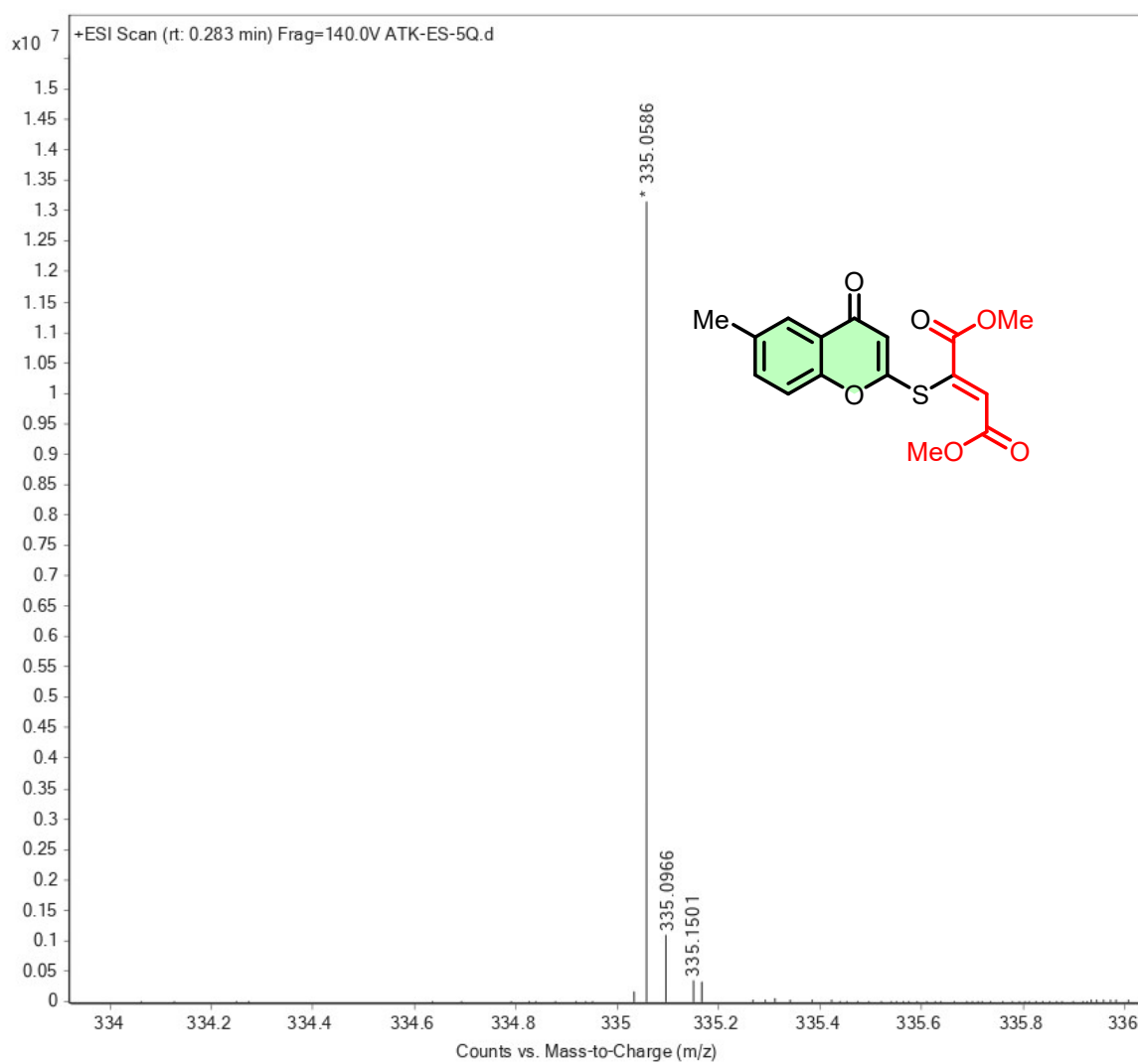
¹H NMR (600 MHz, CDCl₃) spectrum of compound 3fa



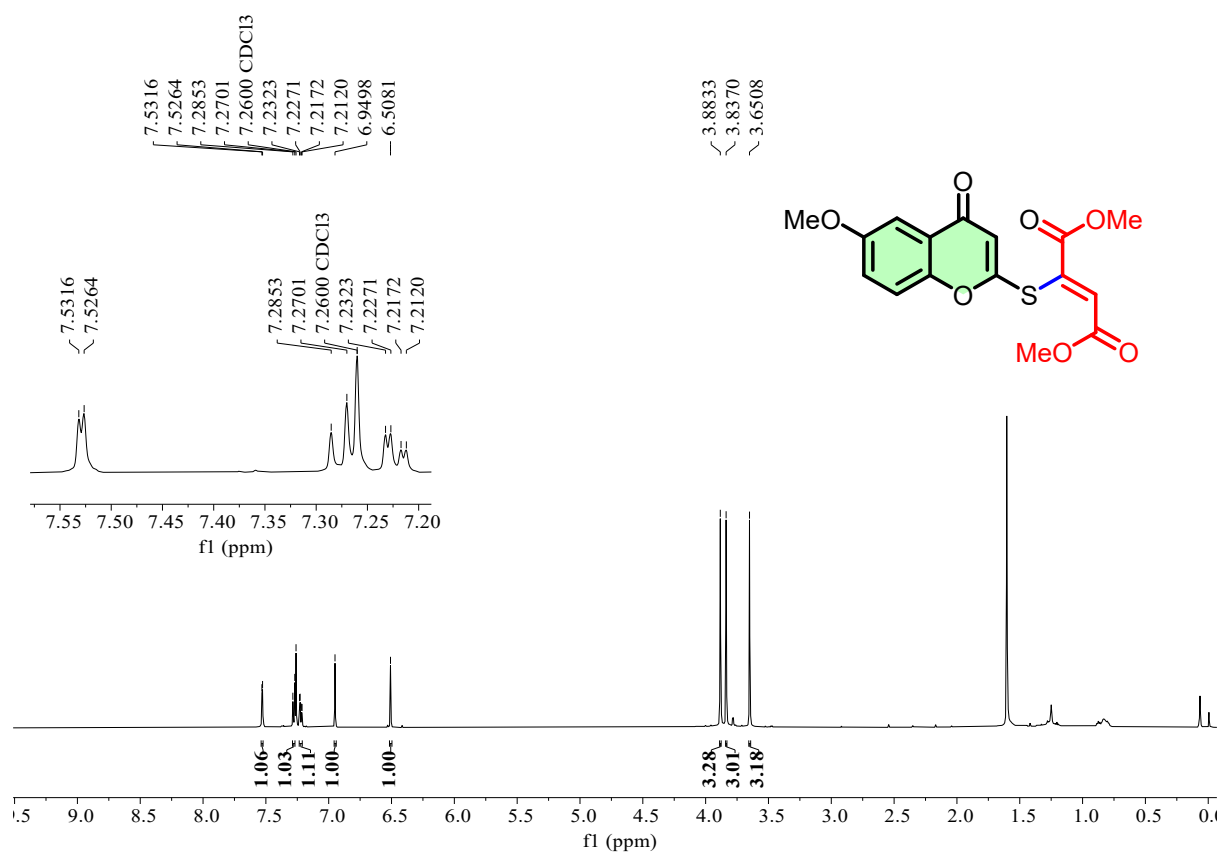
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 3fa



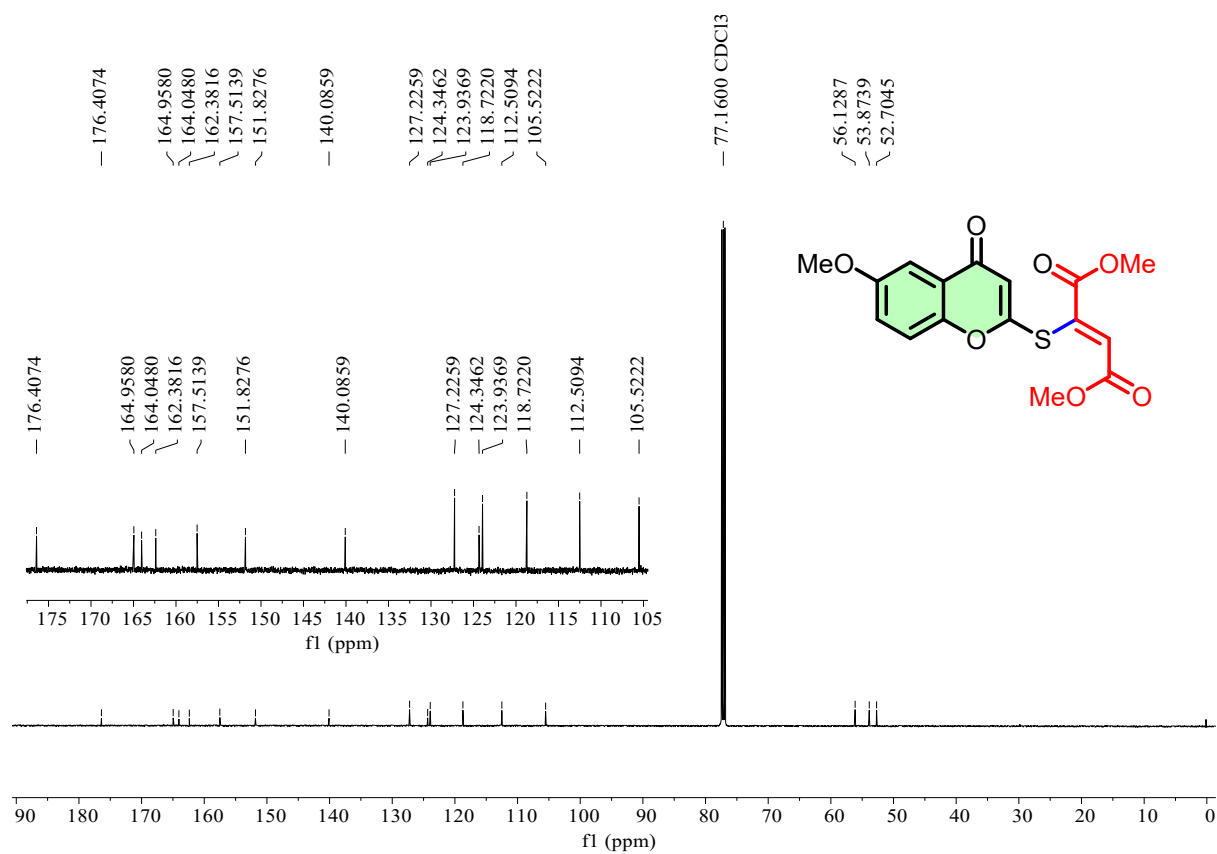
HRMS of compound 3fa



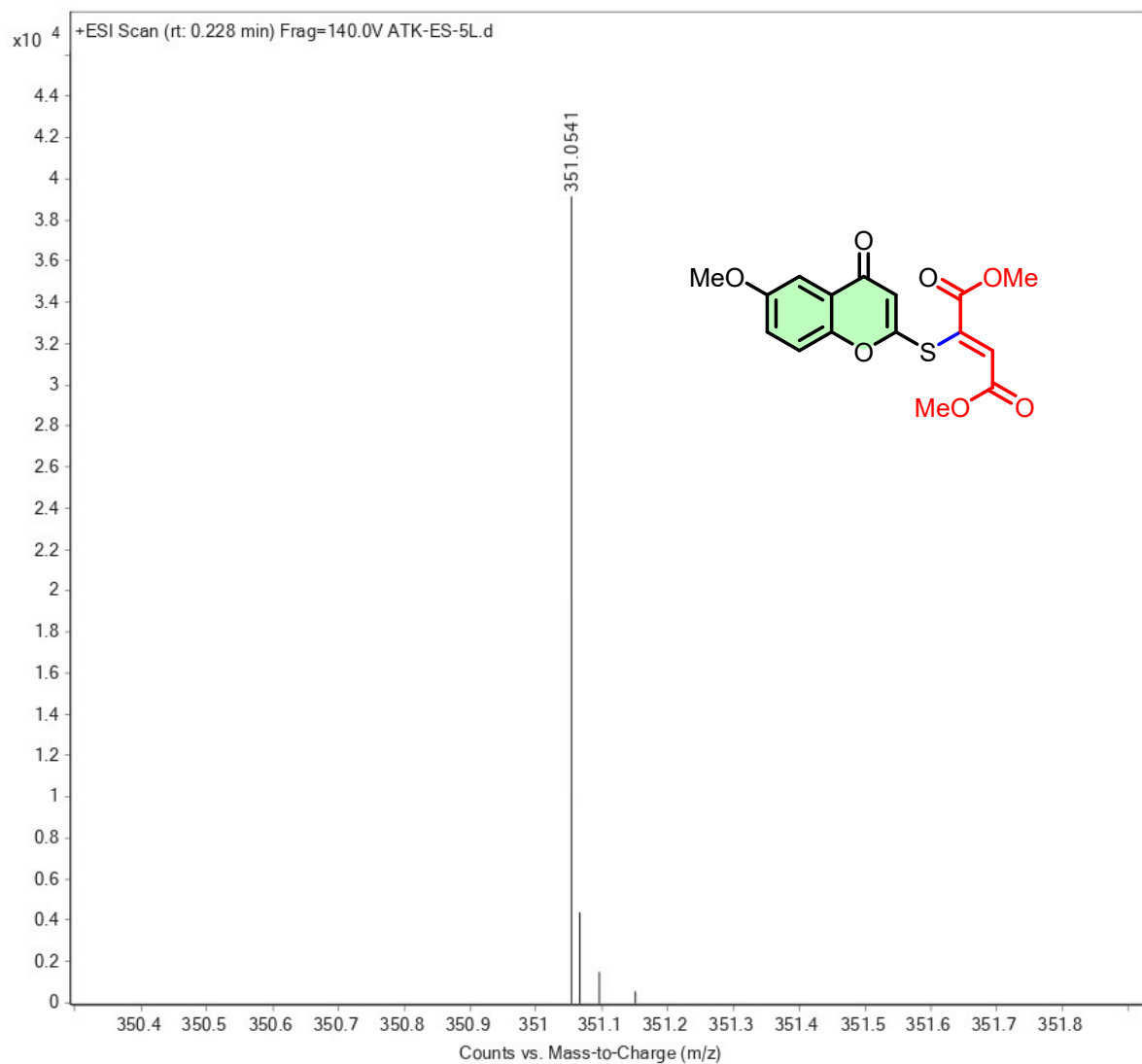
¹H NMR (600MHz, CDCl₃) spectrum of compound 3ga



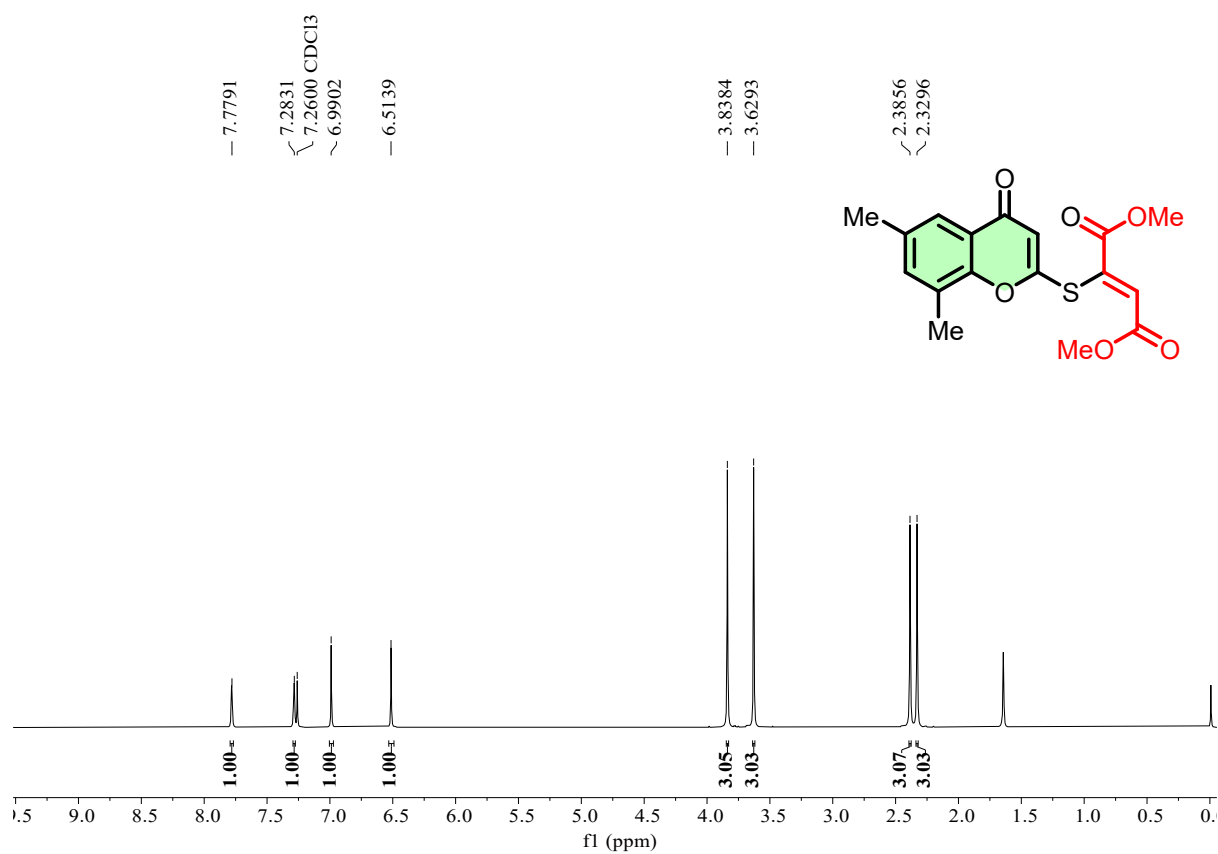
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of compound 3ga



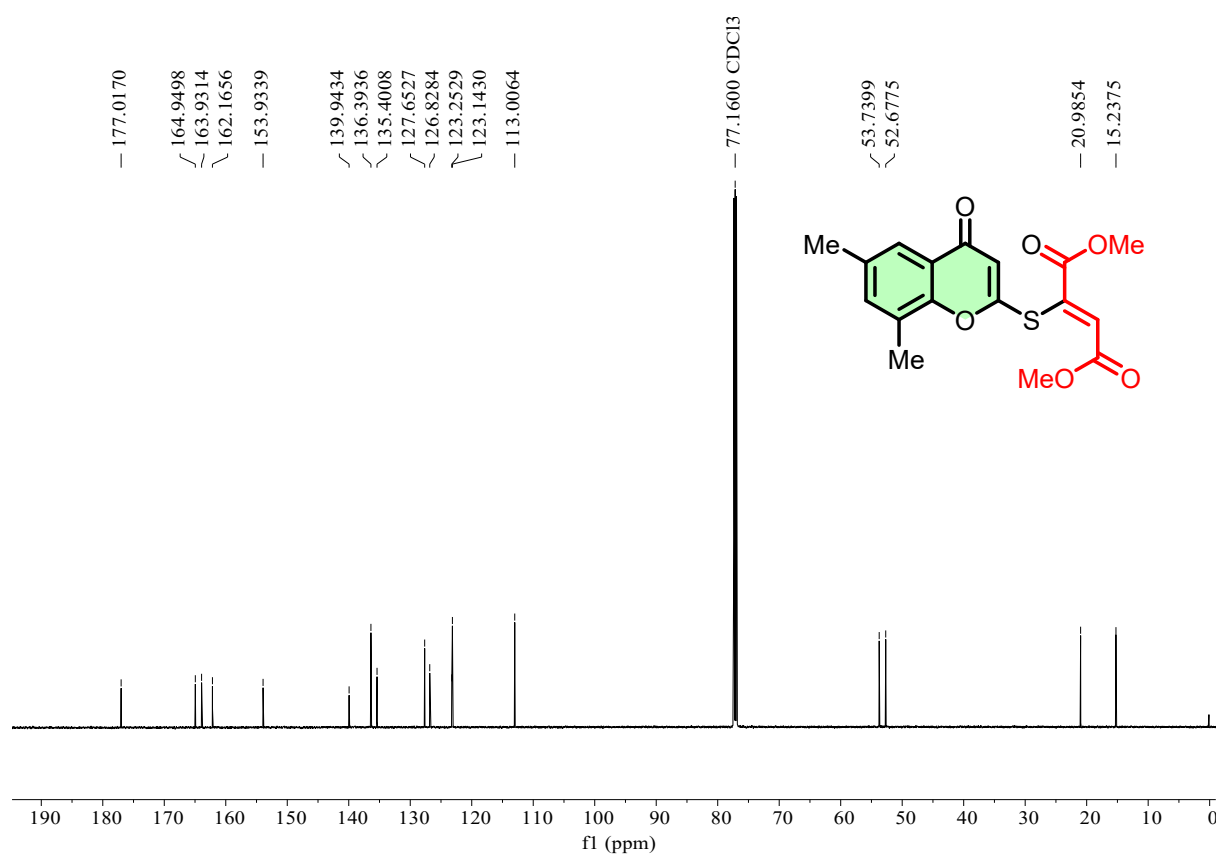
HRMS of compound 3ga



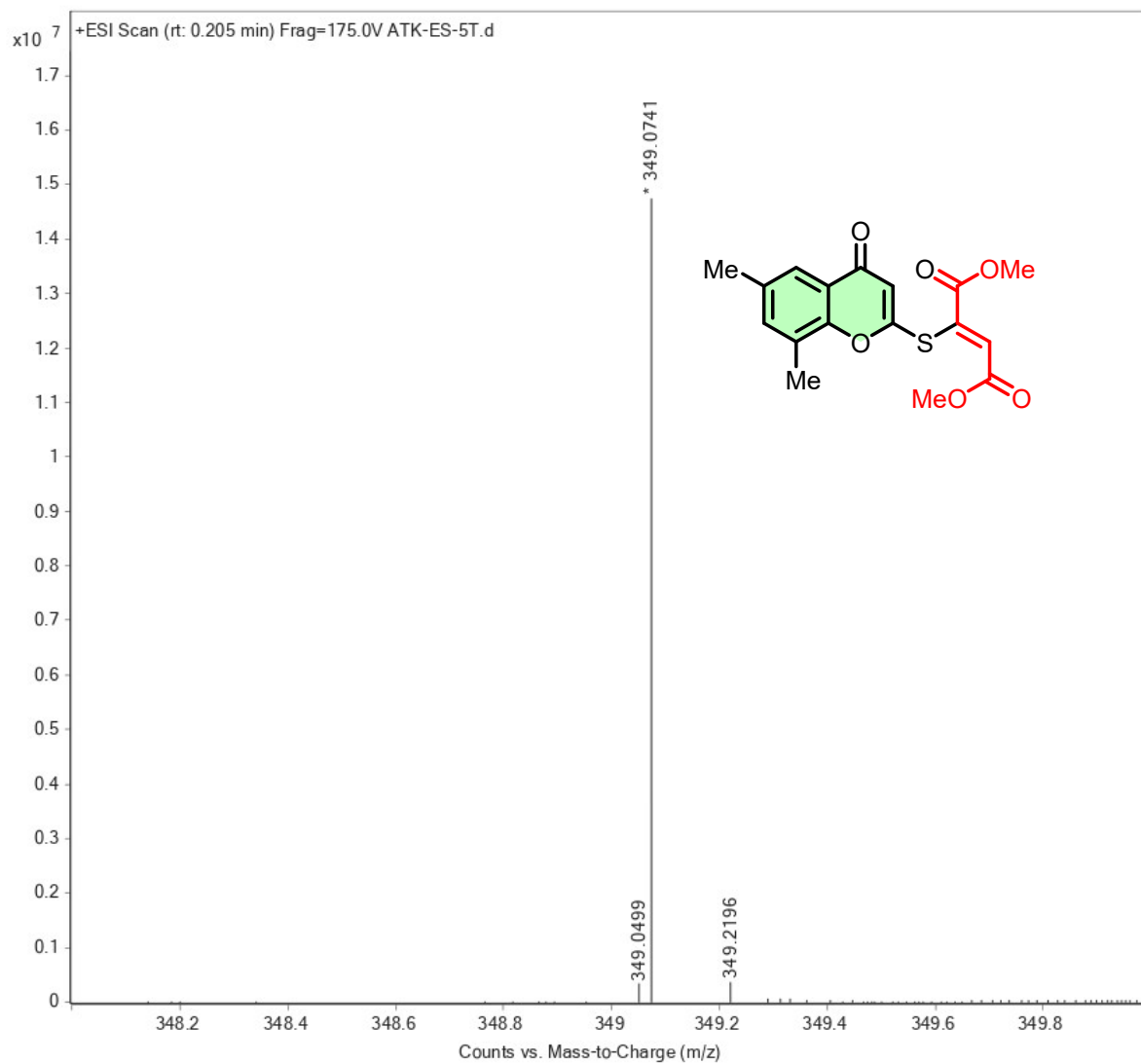
¹H NMR (500 MHz, CDCl₃) spectrum of compound 3ha



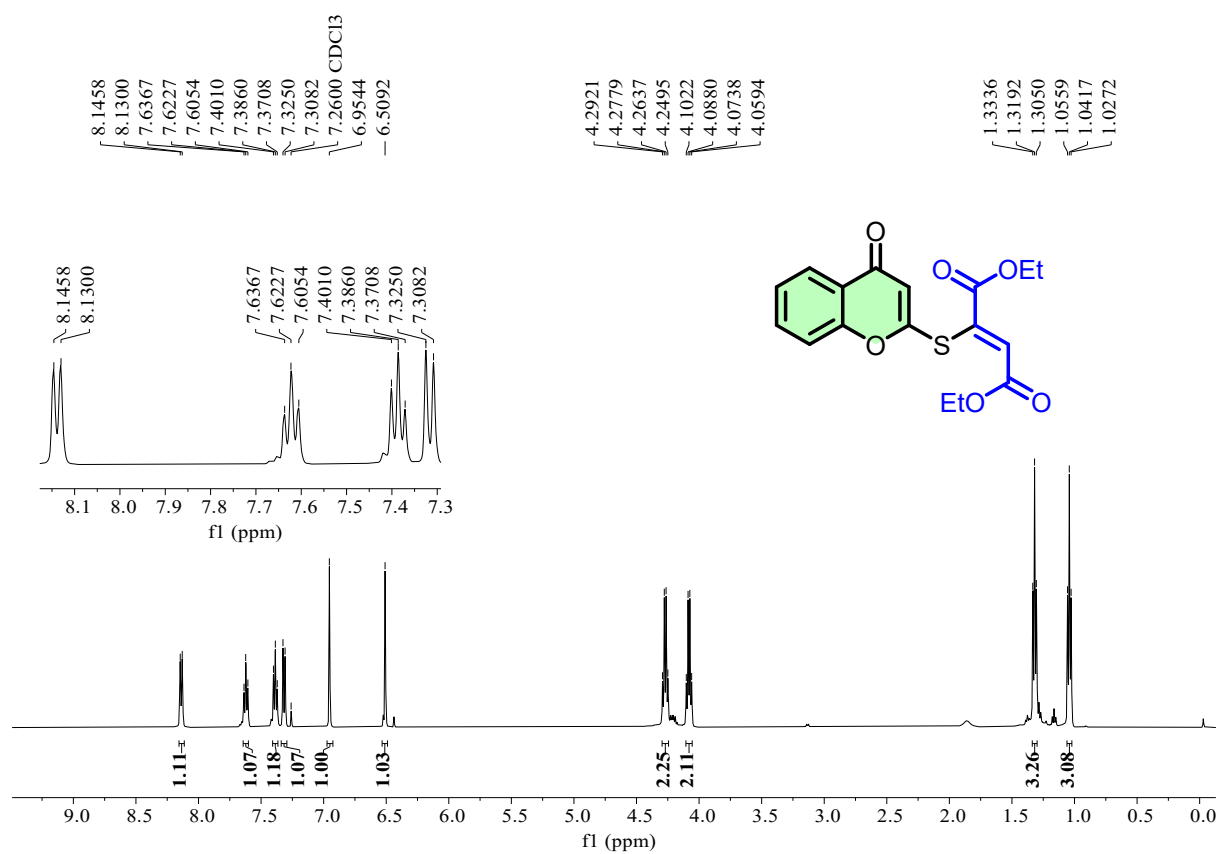
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 3ha



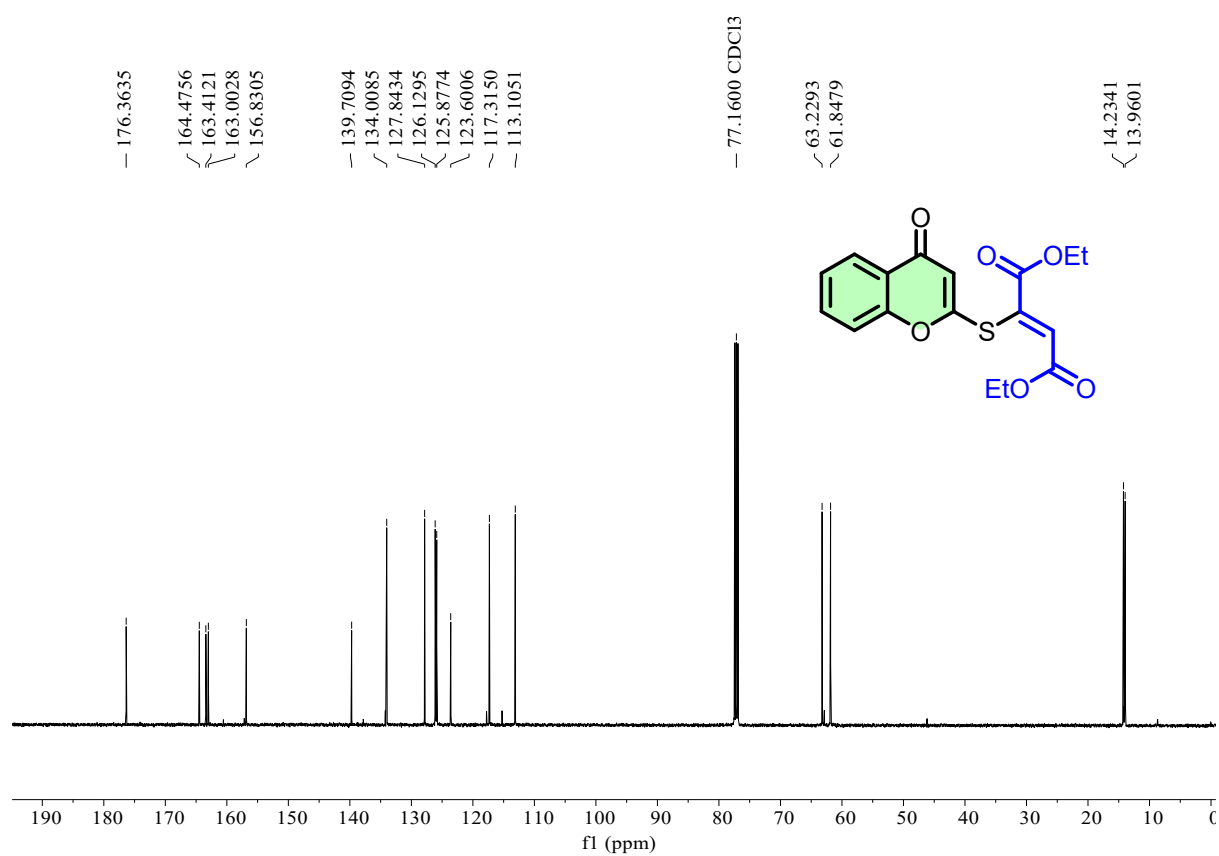
HRMS of compound 3ha



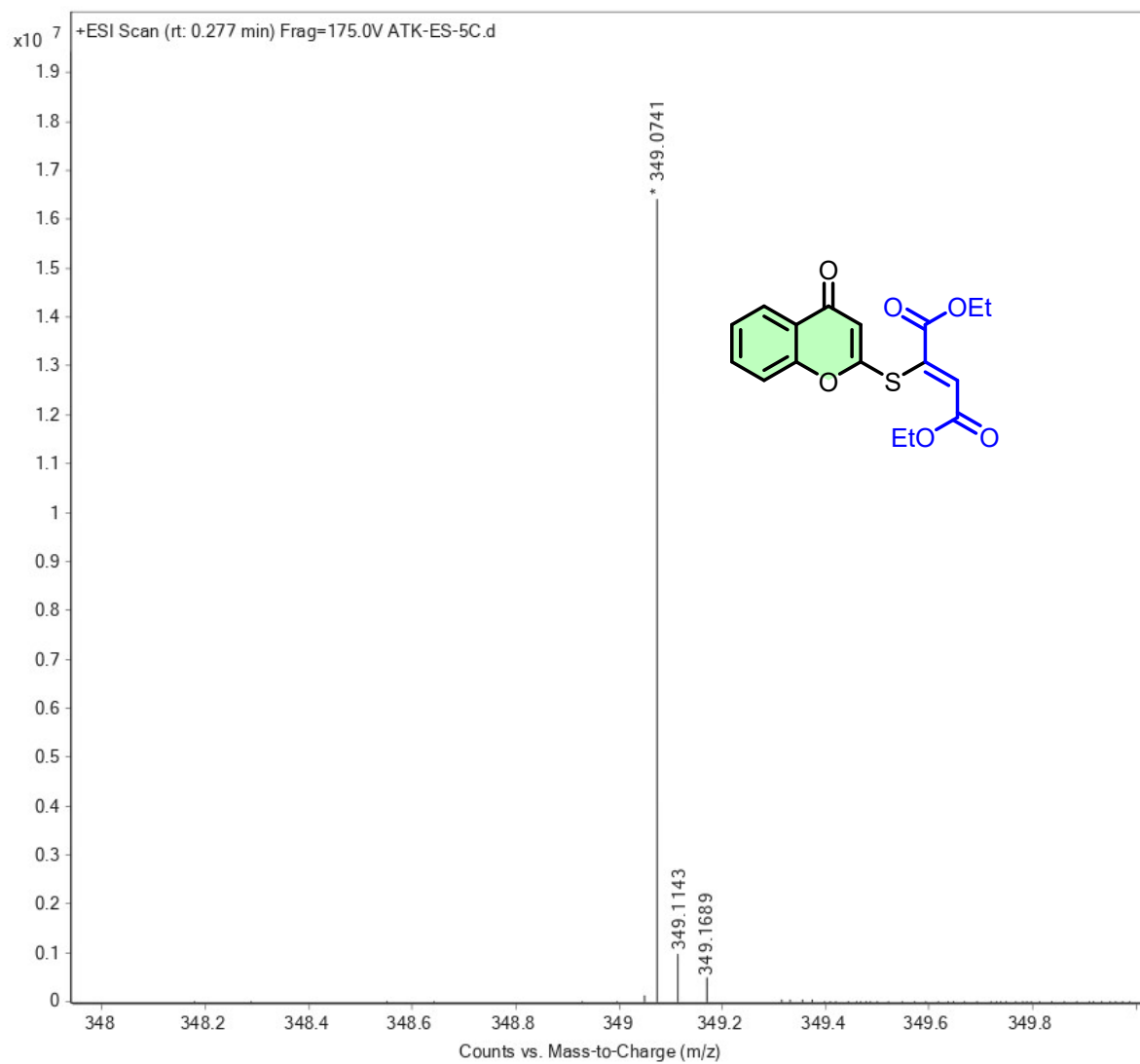
¹H NMR (500 MHz, CDCl₃) spectrum of compound 3ab



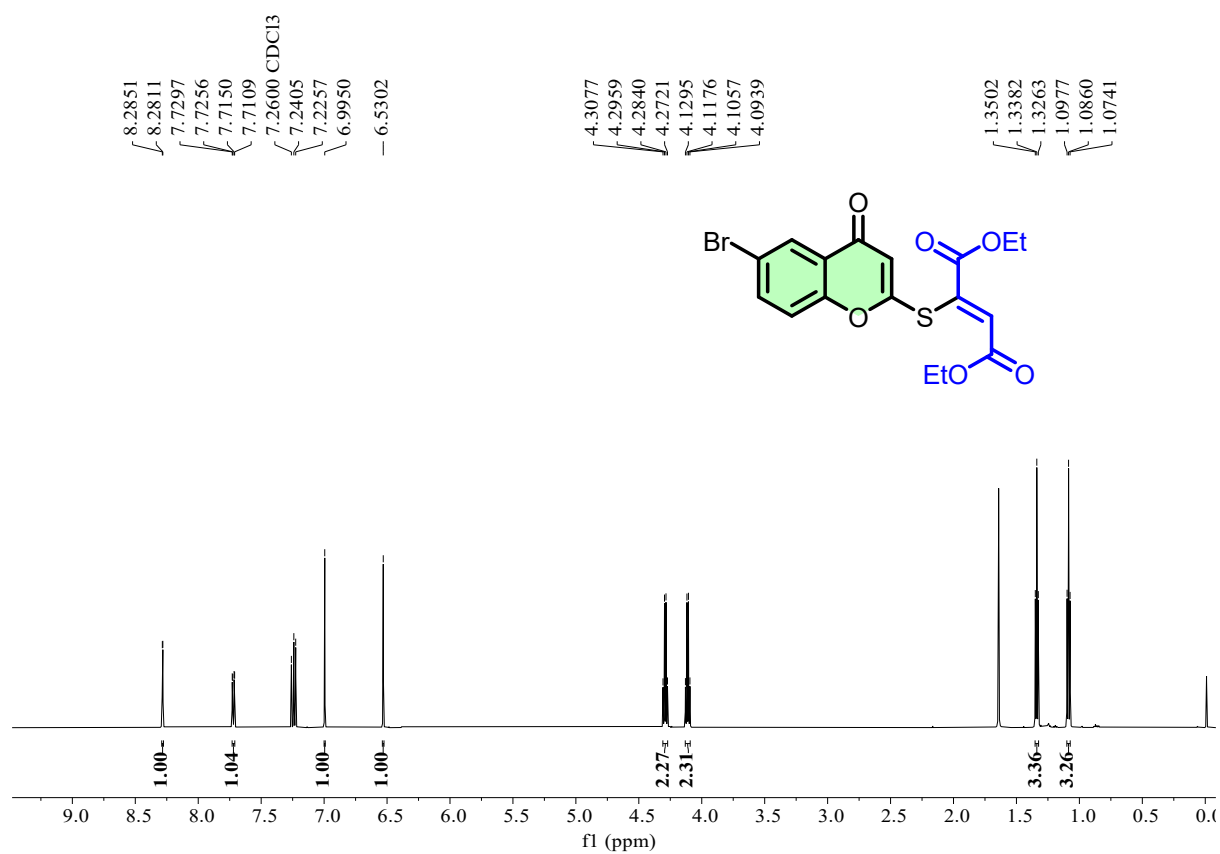
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of compound 3ab



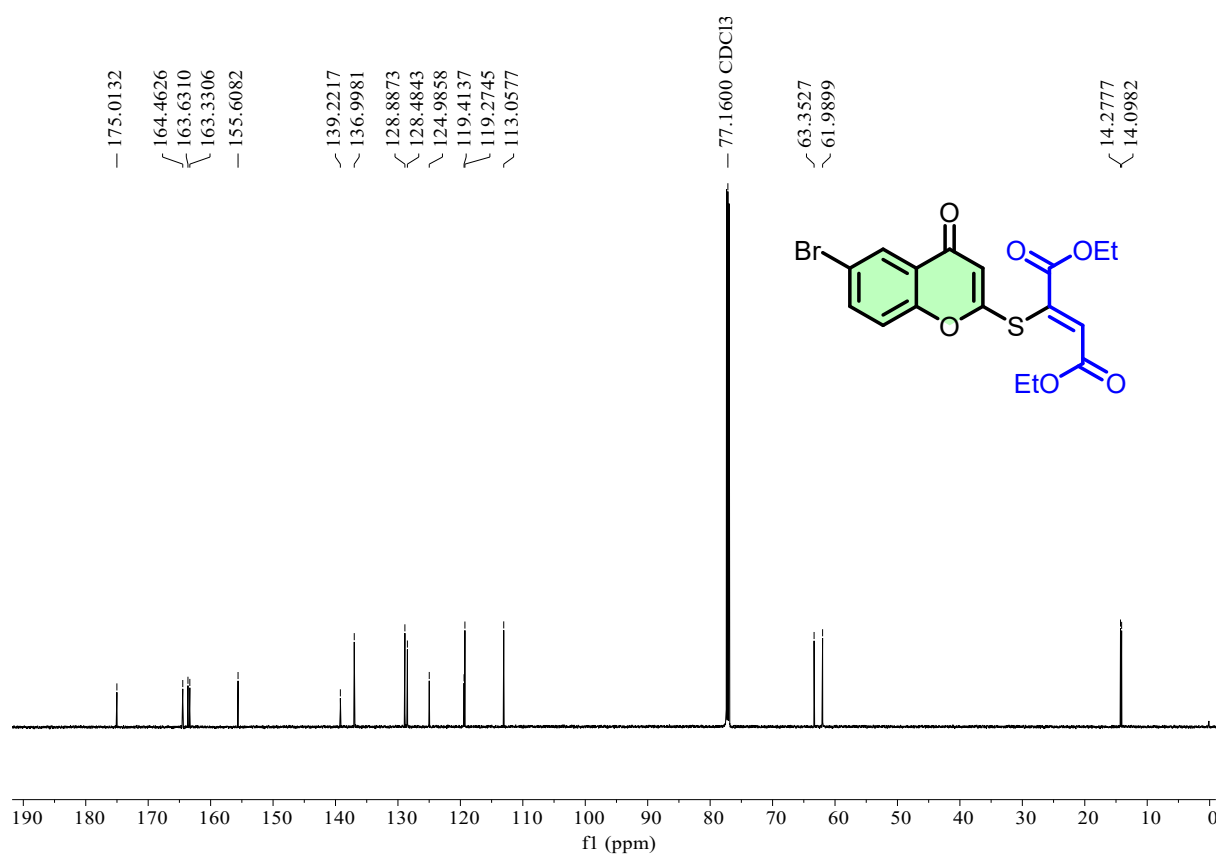
HRMS of compound 3ab



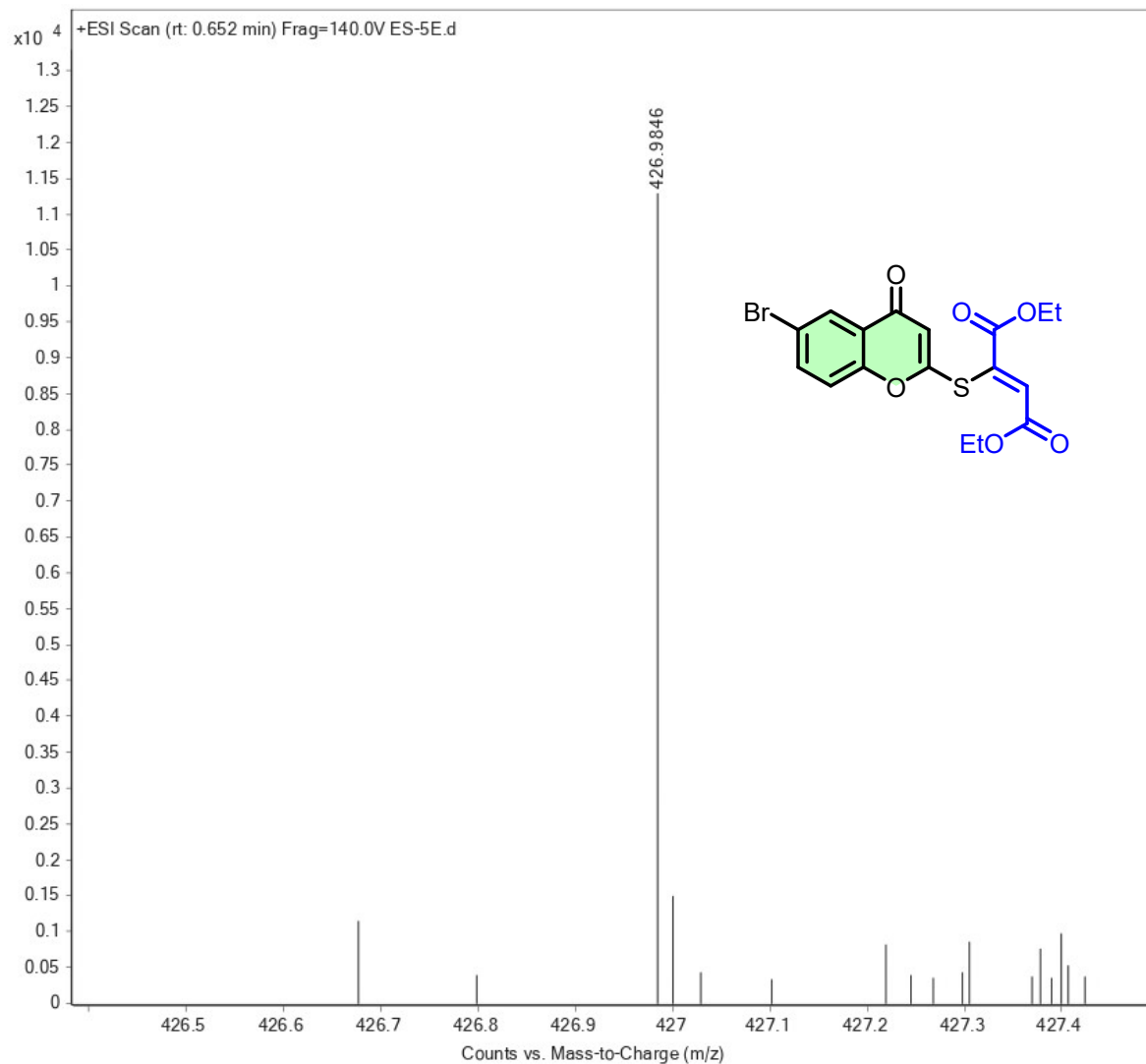
¹H NMR (600 MHz, CDCl₃) spectrum of compound 3bb



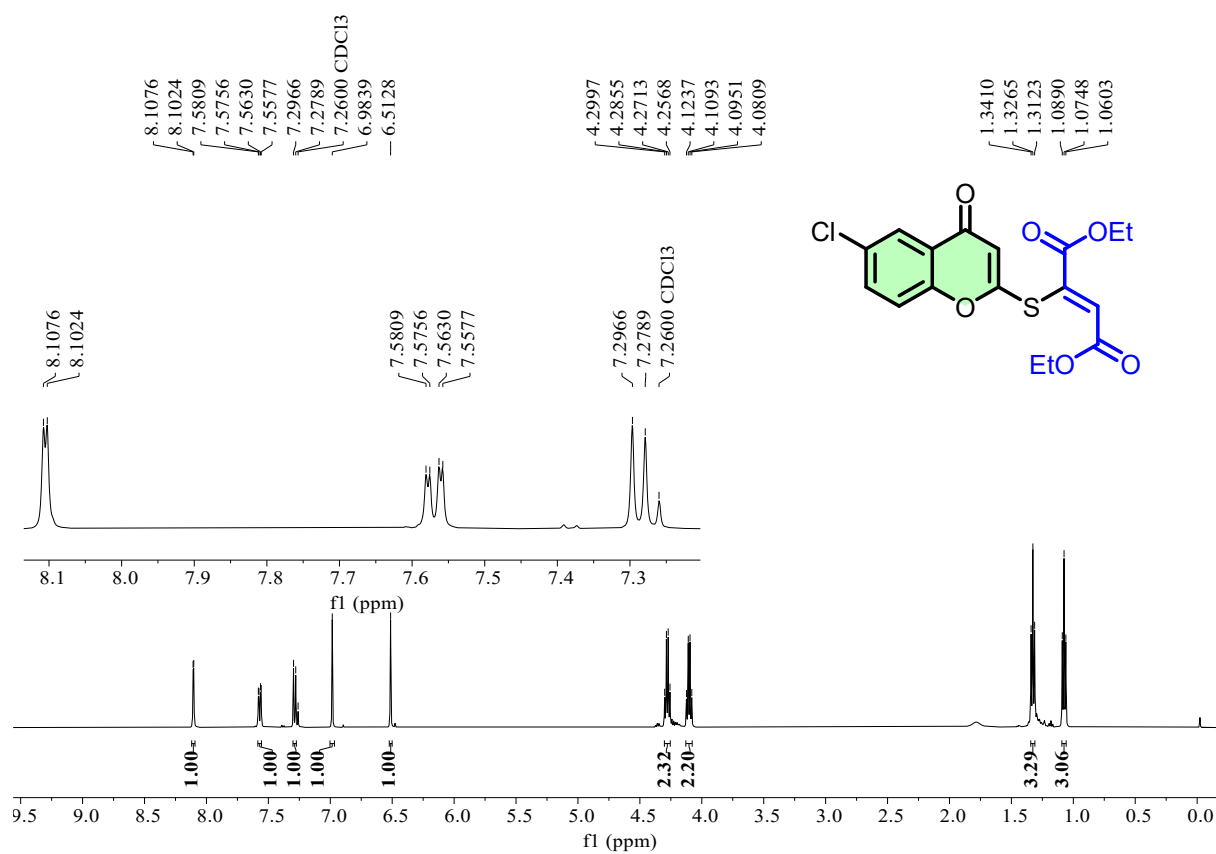
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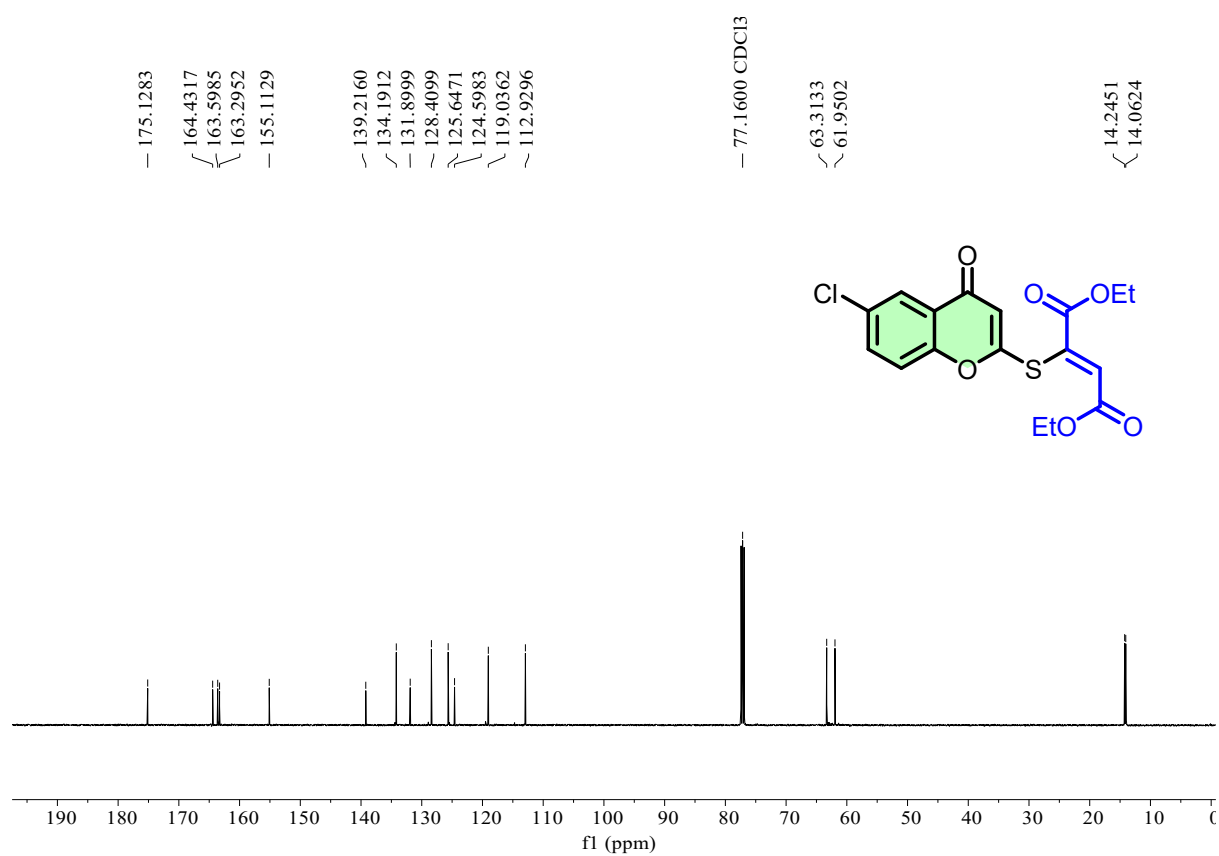
HRMS of compound 3bb



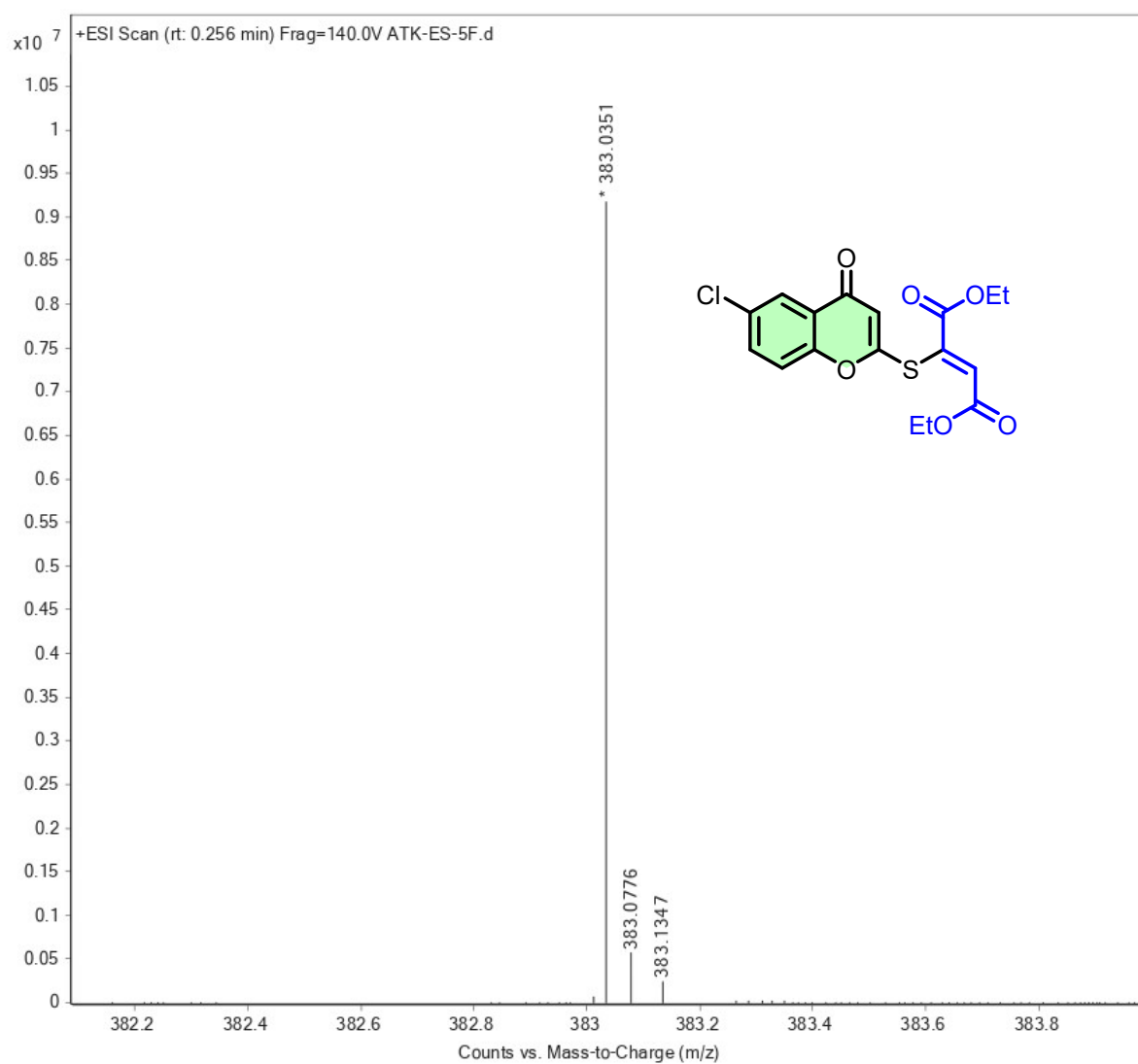
¹H NMR (500 MHz, CDCl₃) spectrum of compound 3cb



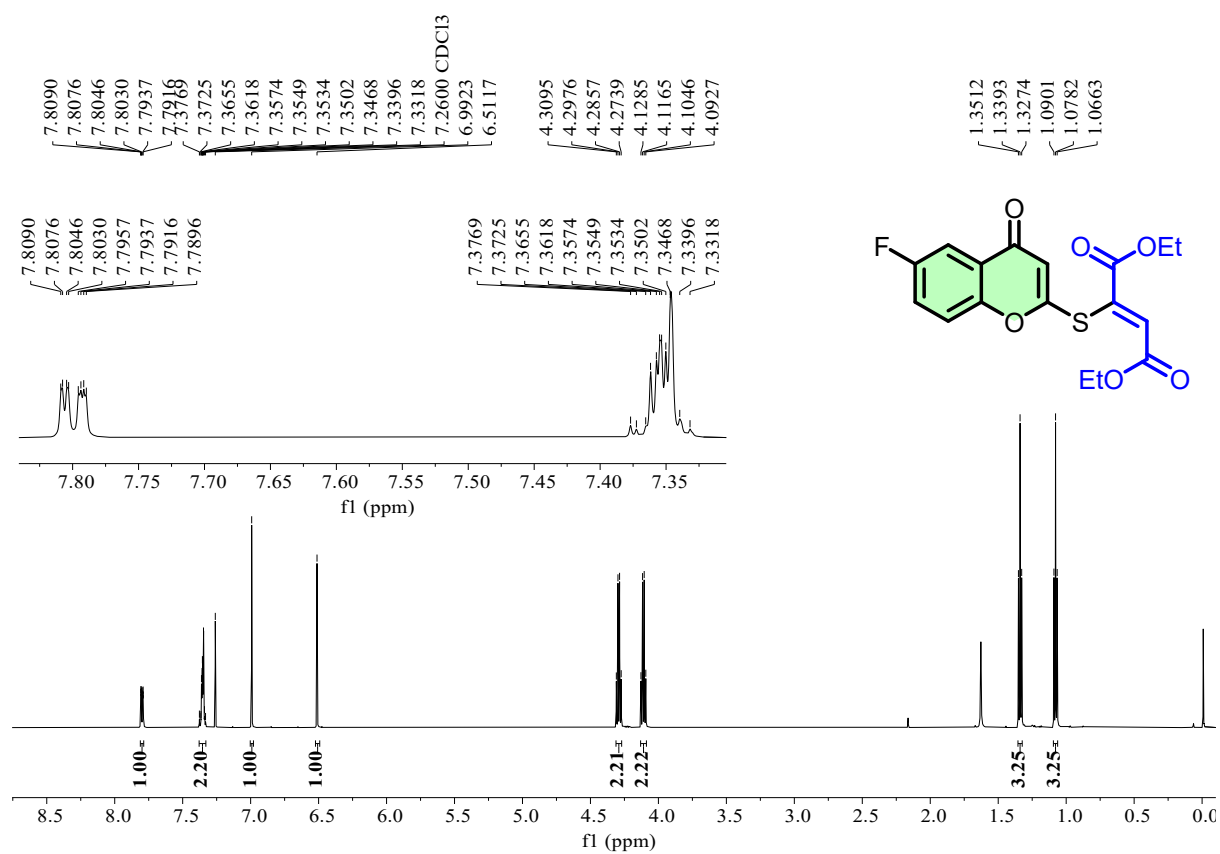
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of compound 3cb



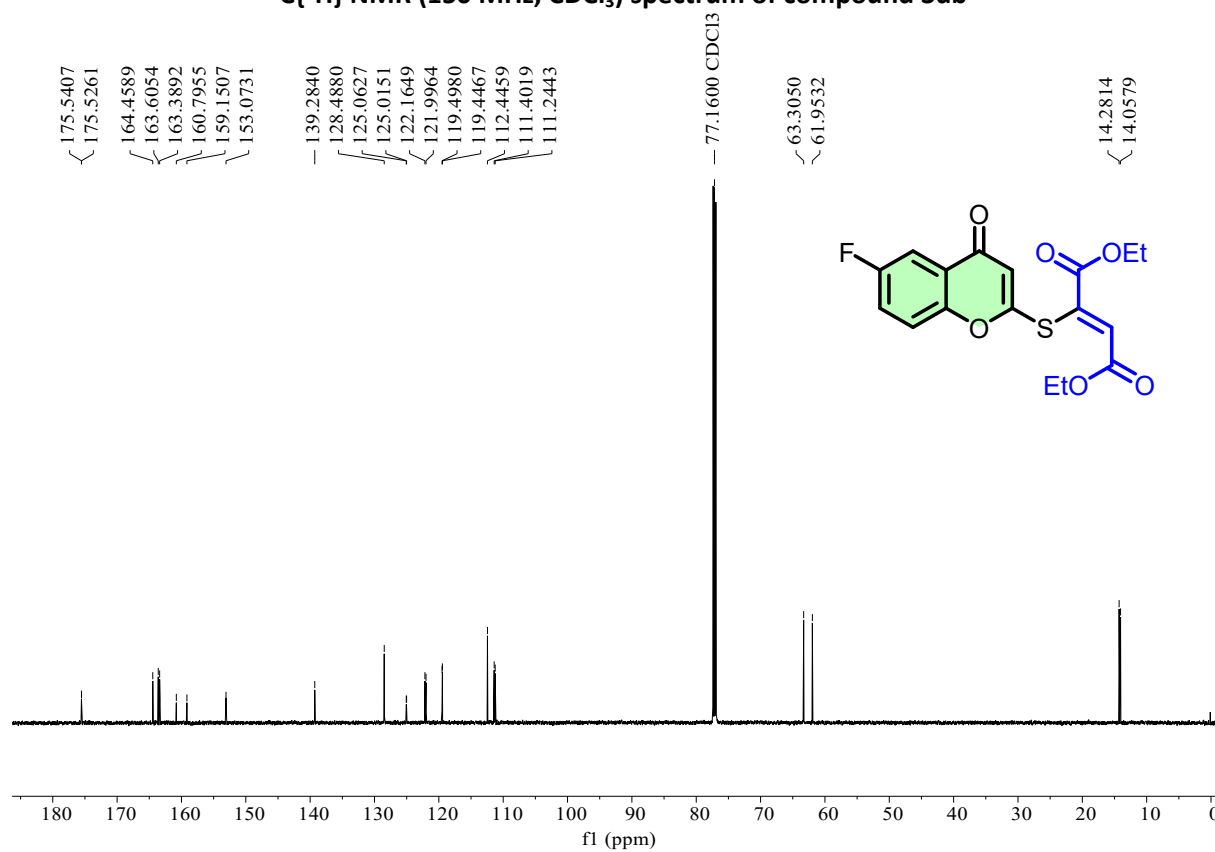
HRMS of compound 3cb



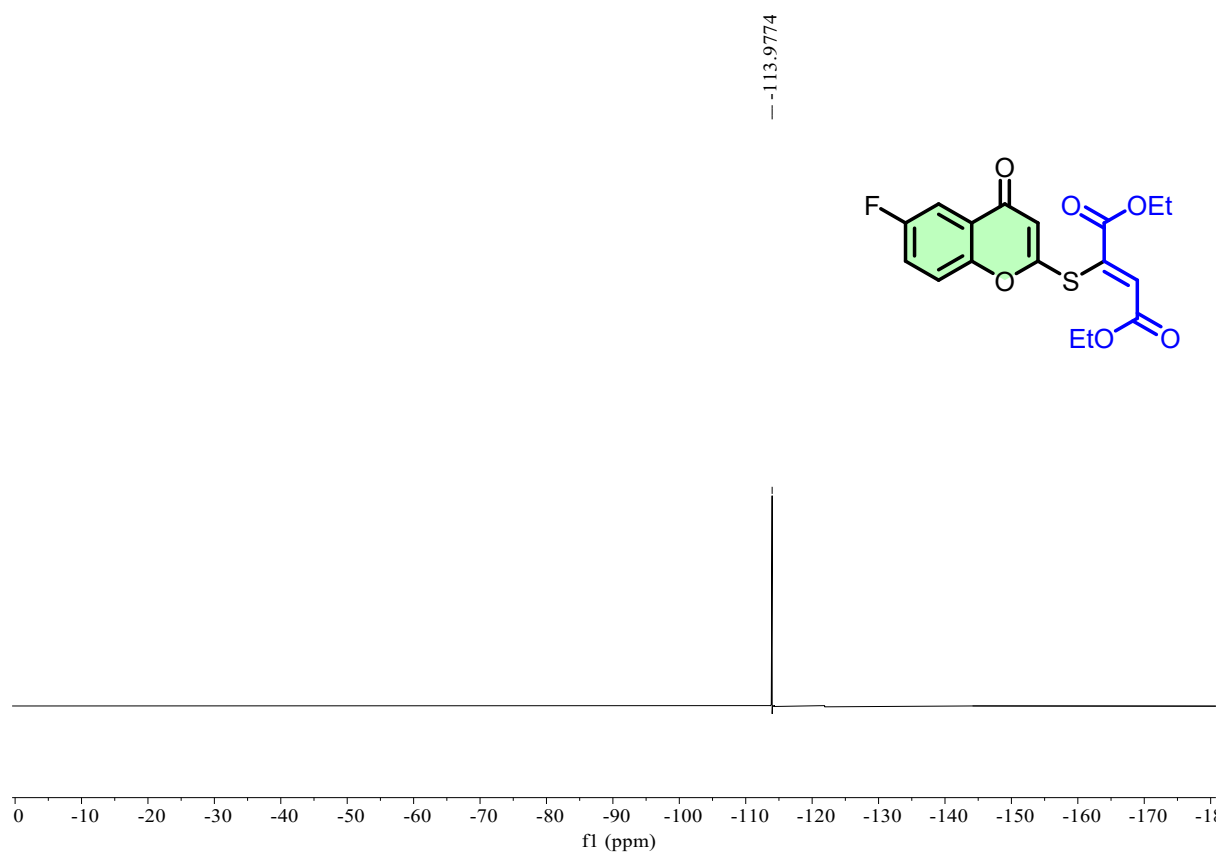
¹H NMR (600 MHz, CDCl₃) spectrum of compound 3db



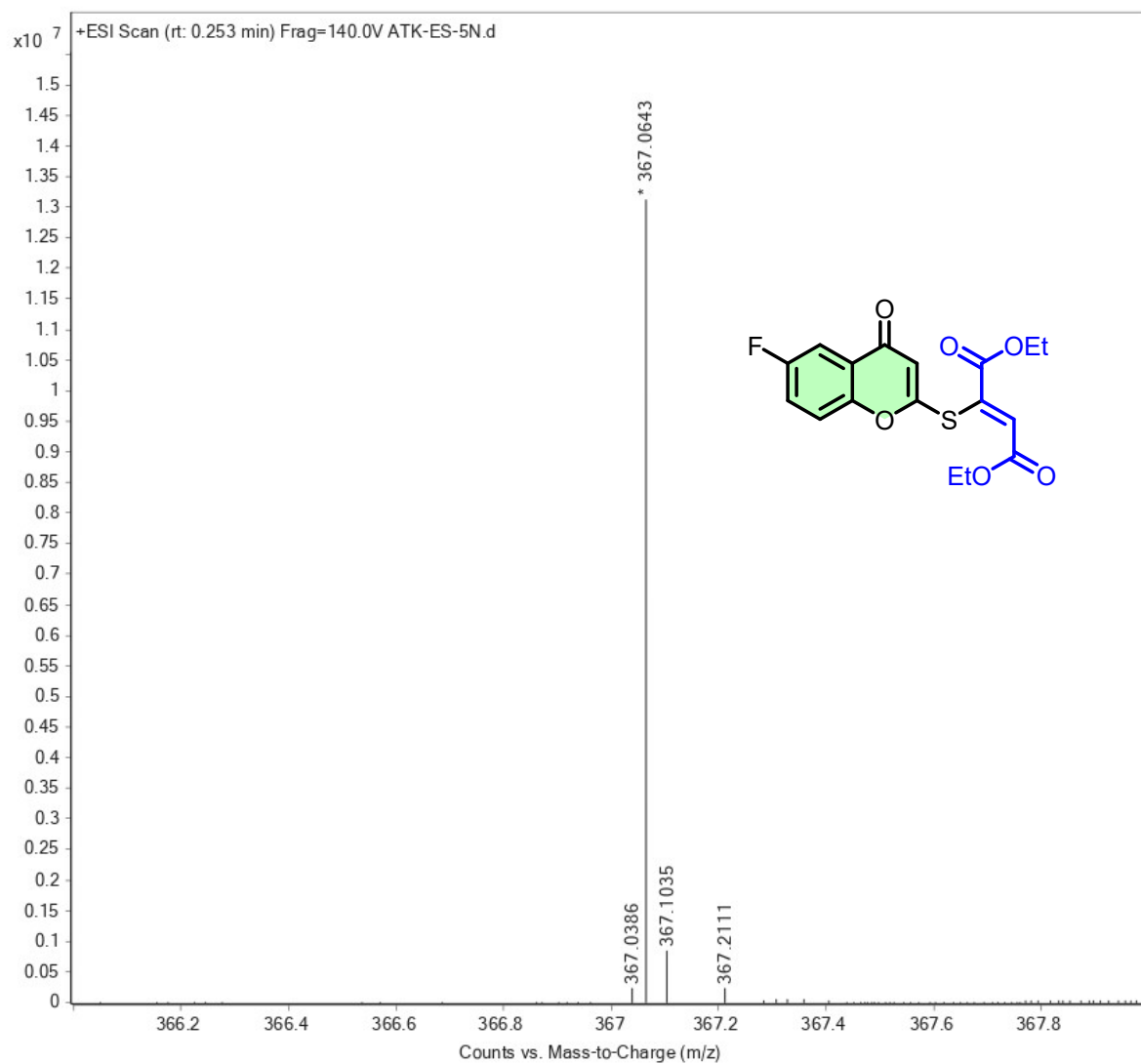
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 3db



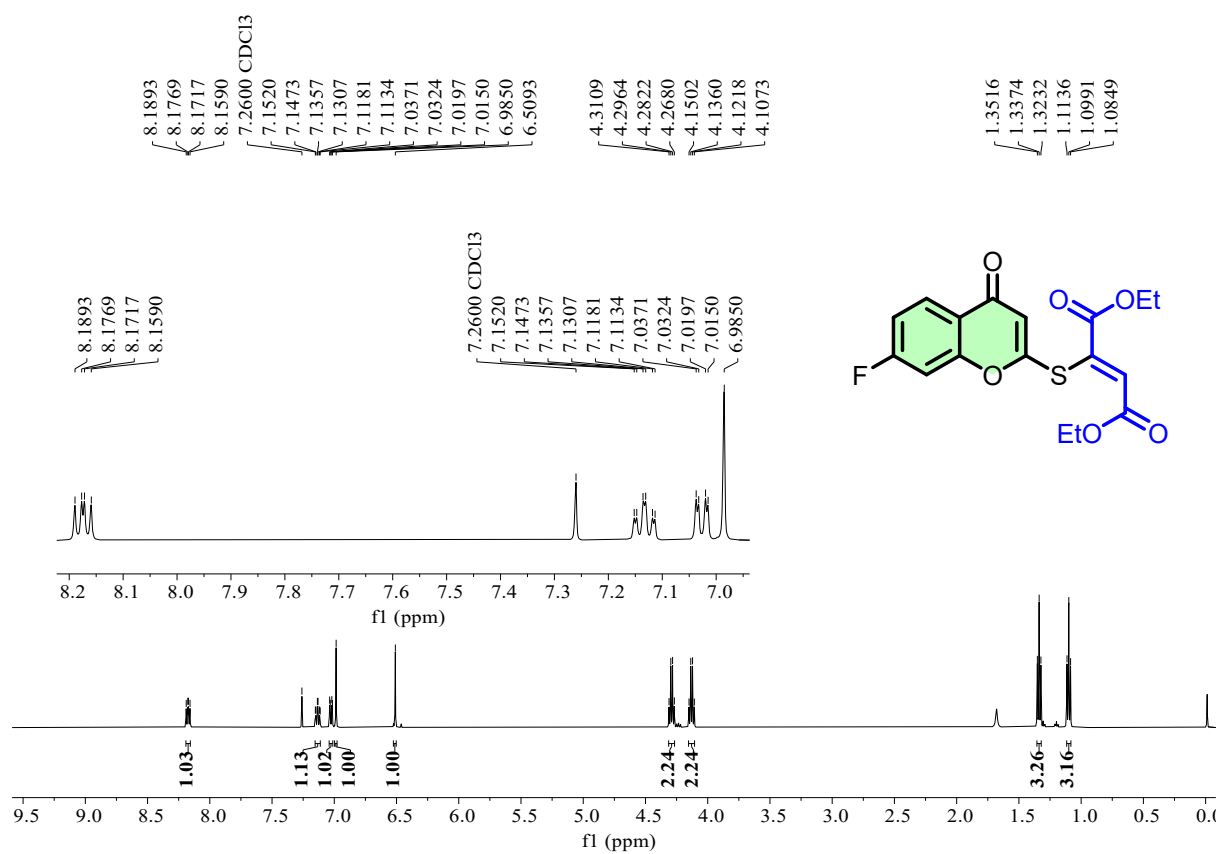
^{19}F NMR (564 MHz, CDCl_3) spectrum of compound 3db



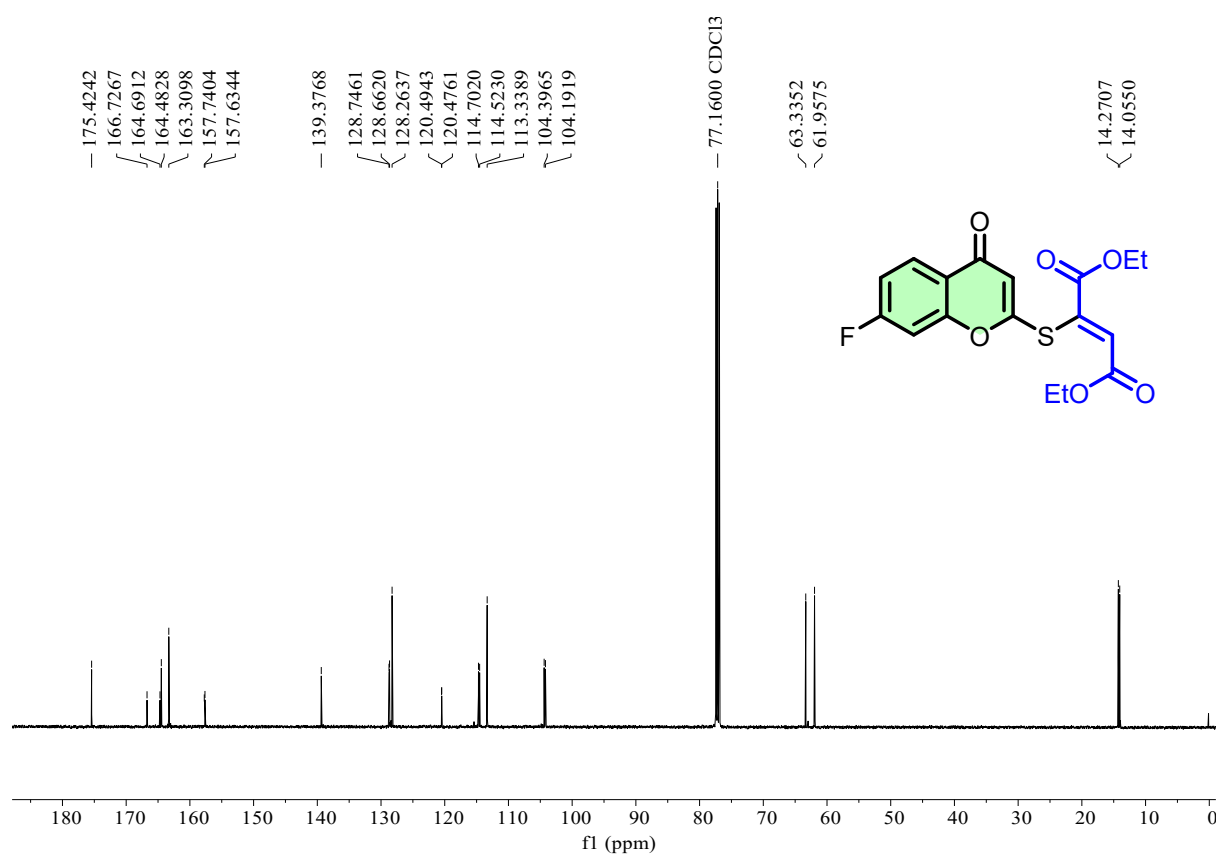
HRMS of compound 3db



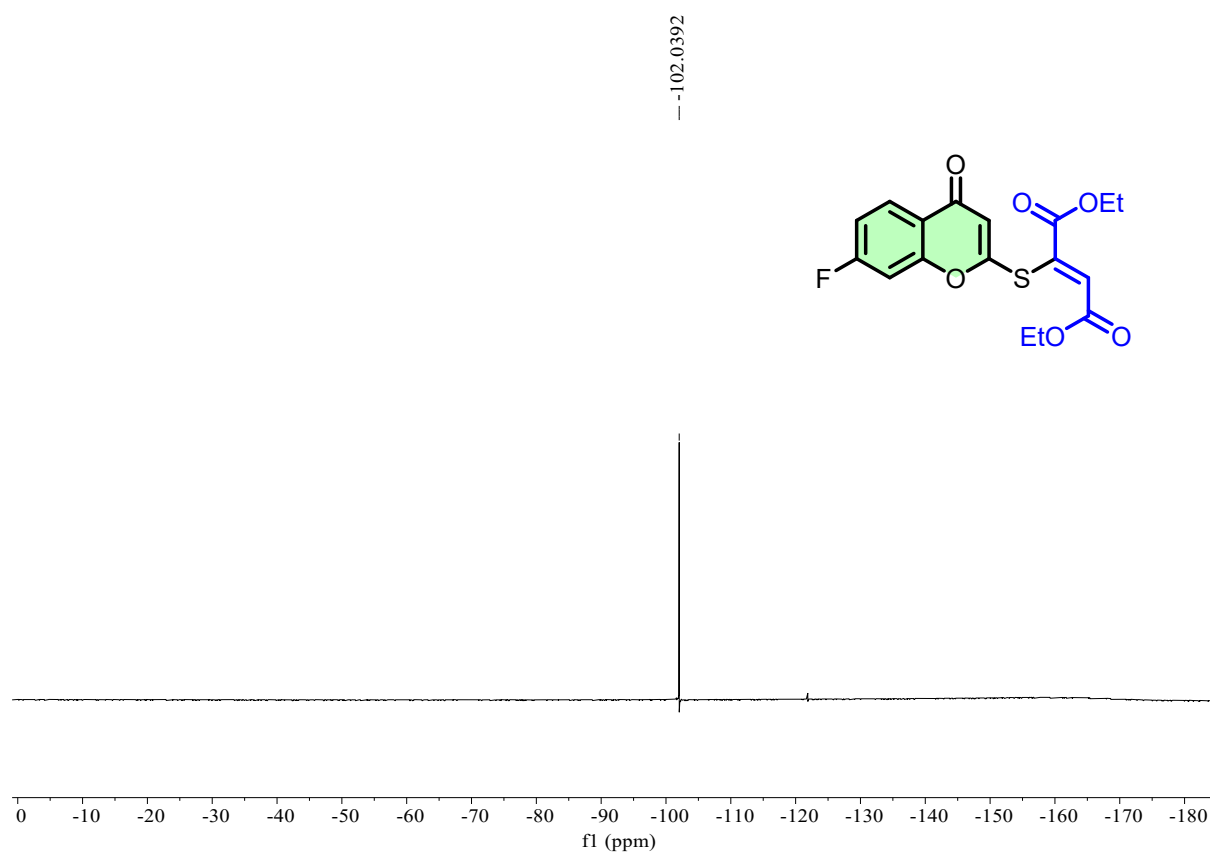
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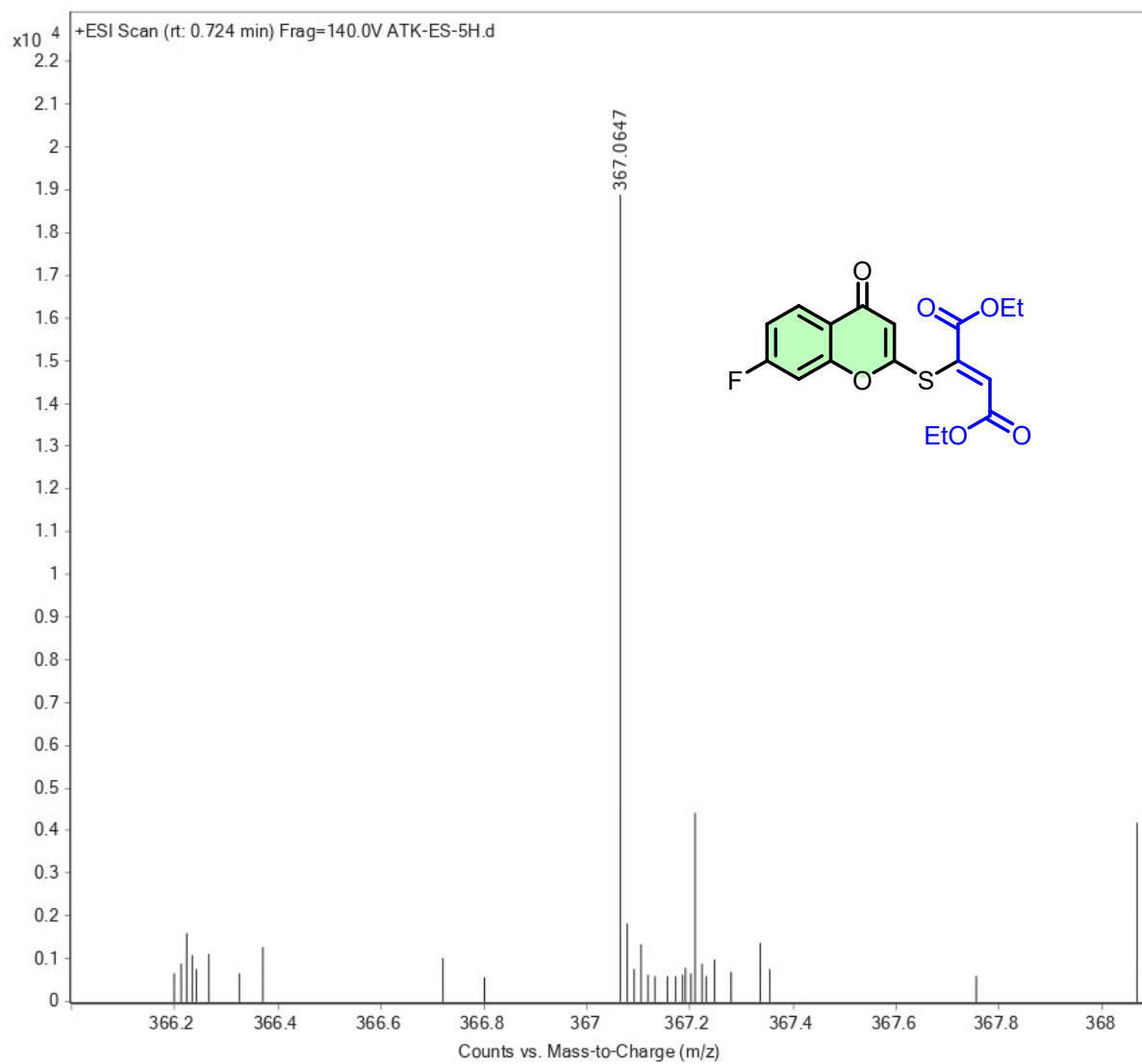
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of compound 3eb



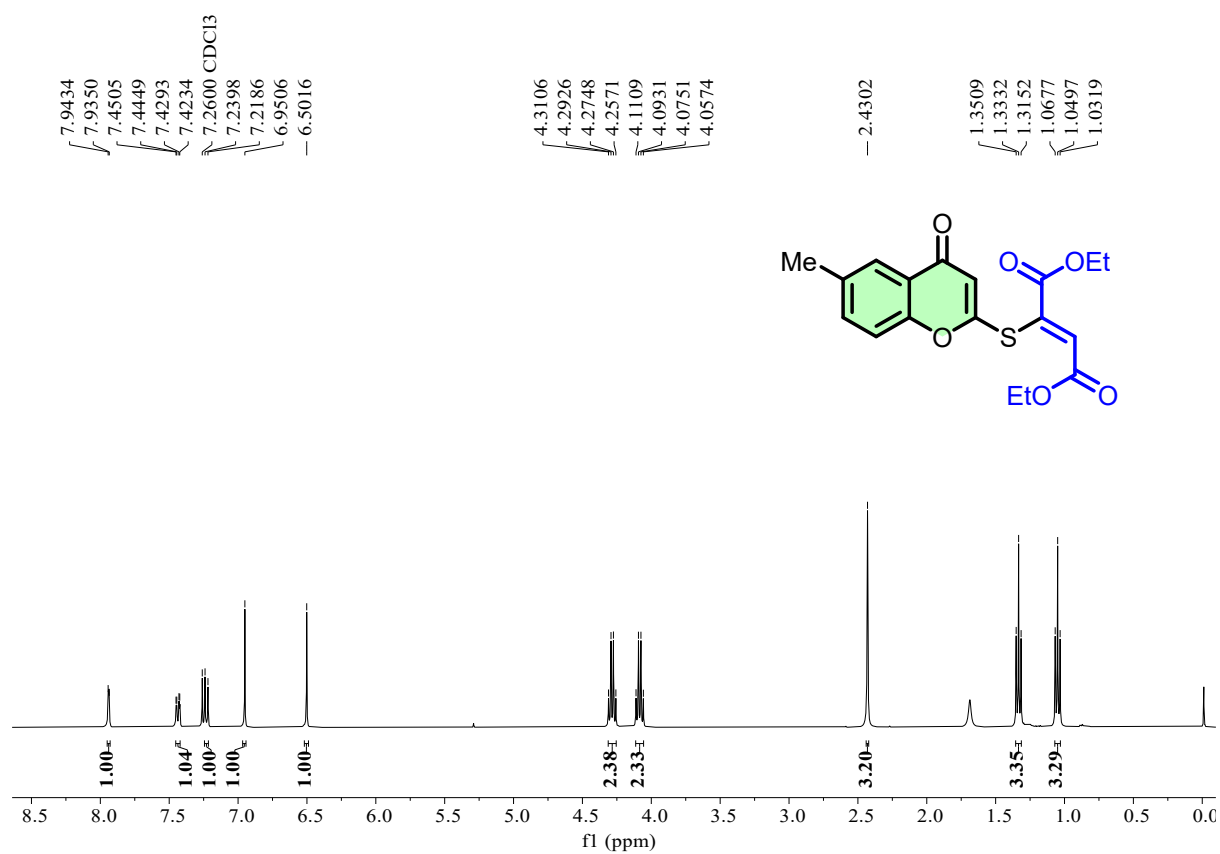
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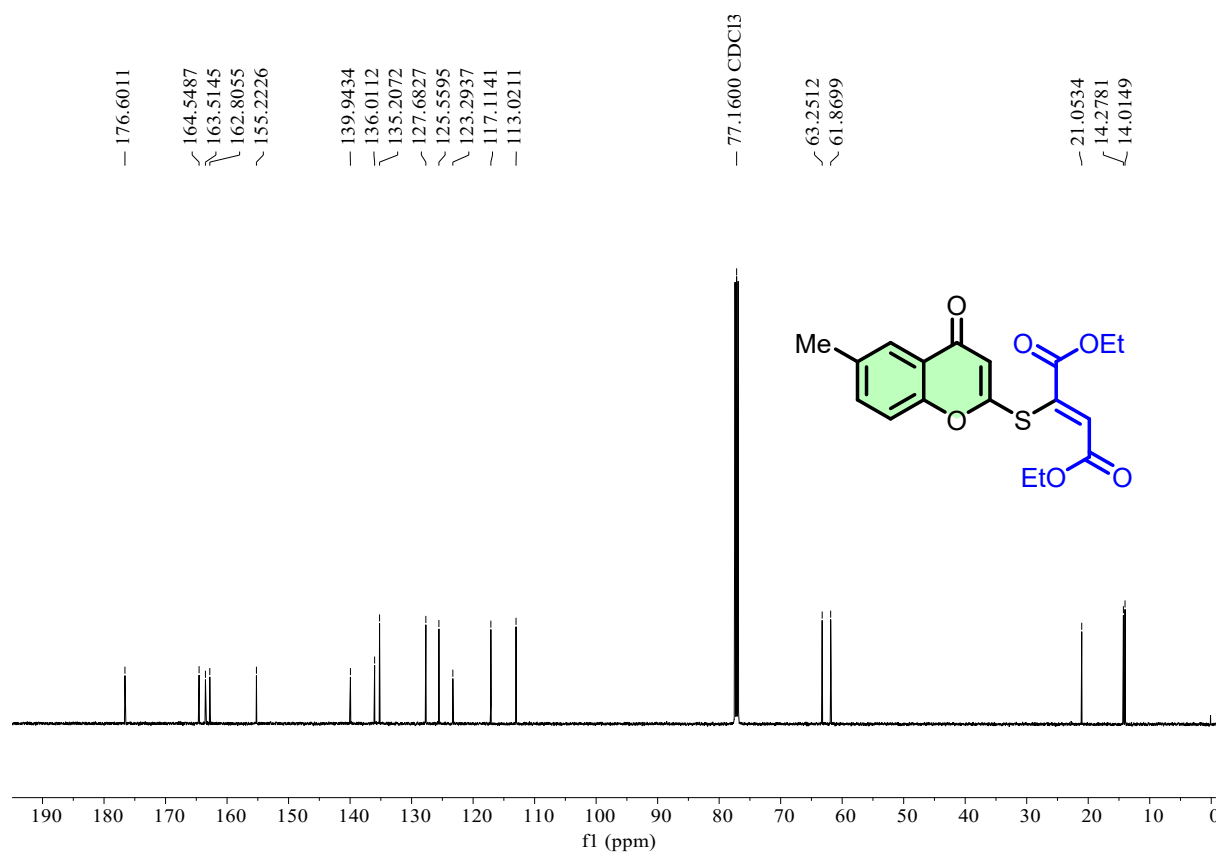
HRMS of compound 3eb



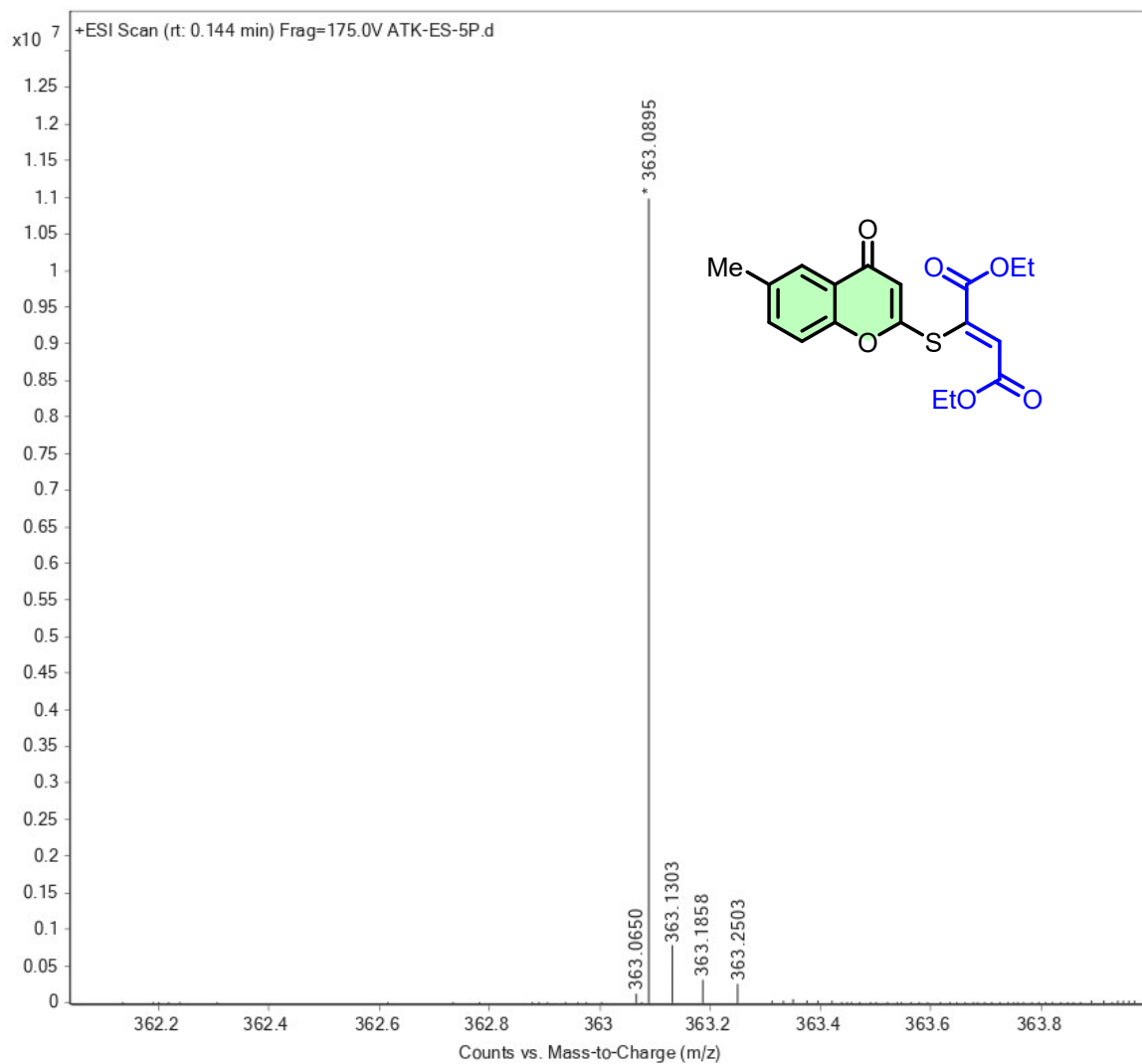
¹H NMR (400 MHz, CDCl₃) spectrum of compound 3fb



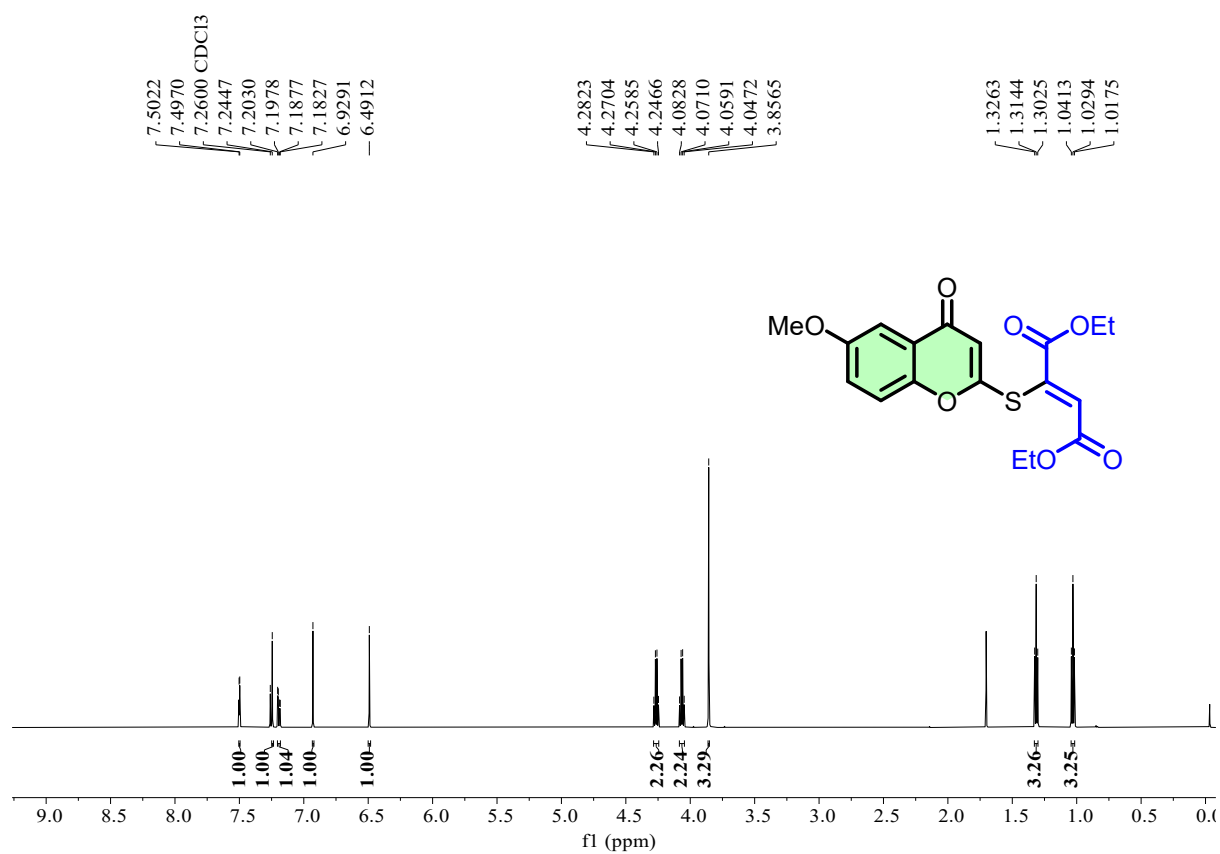
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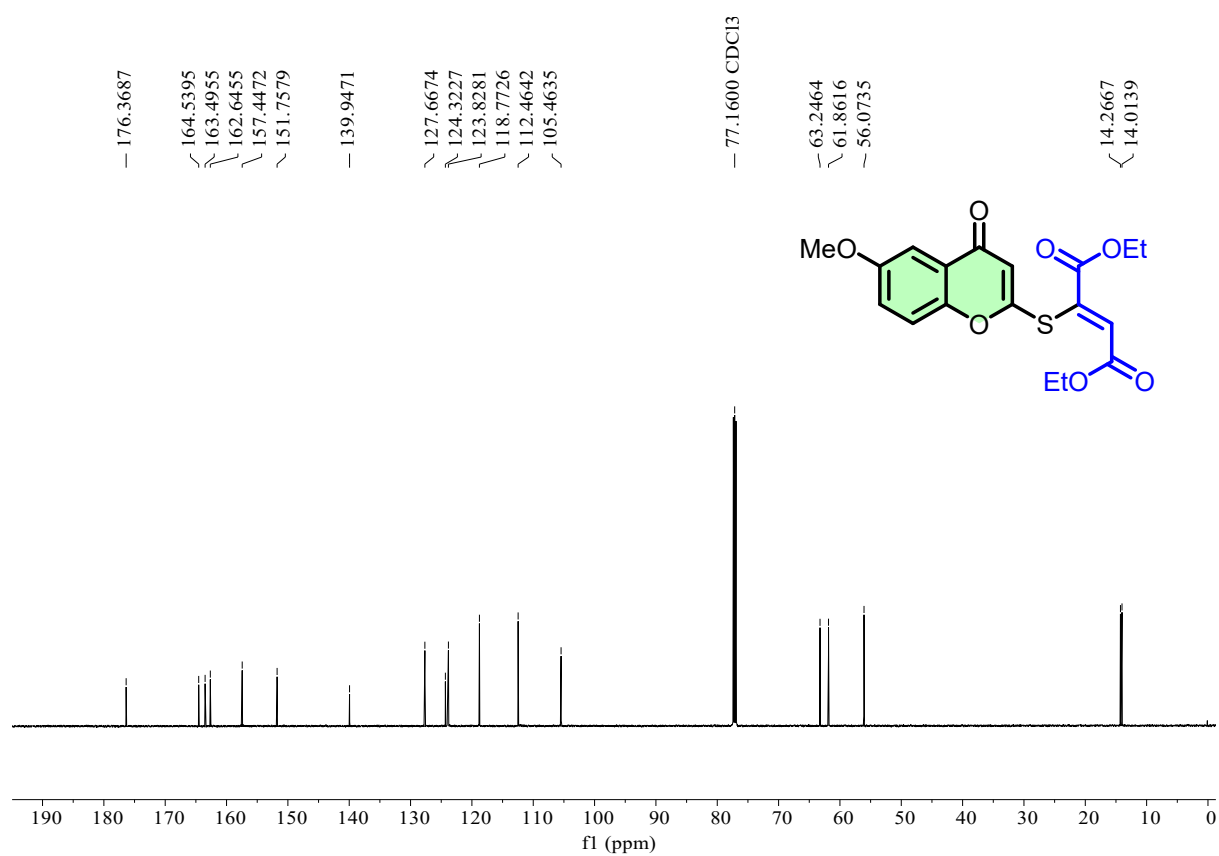
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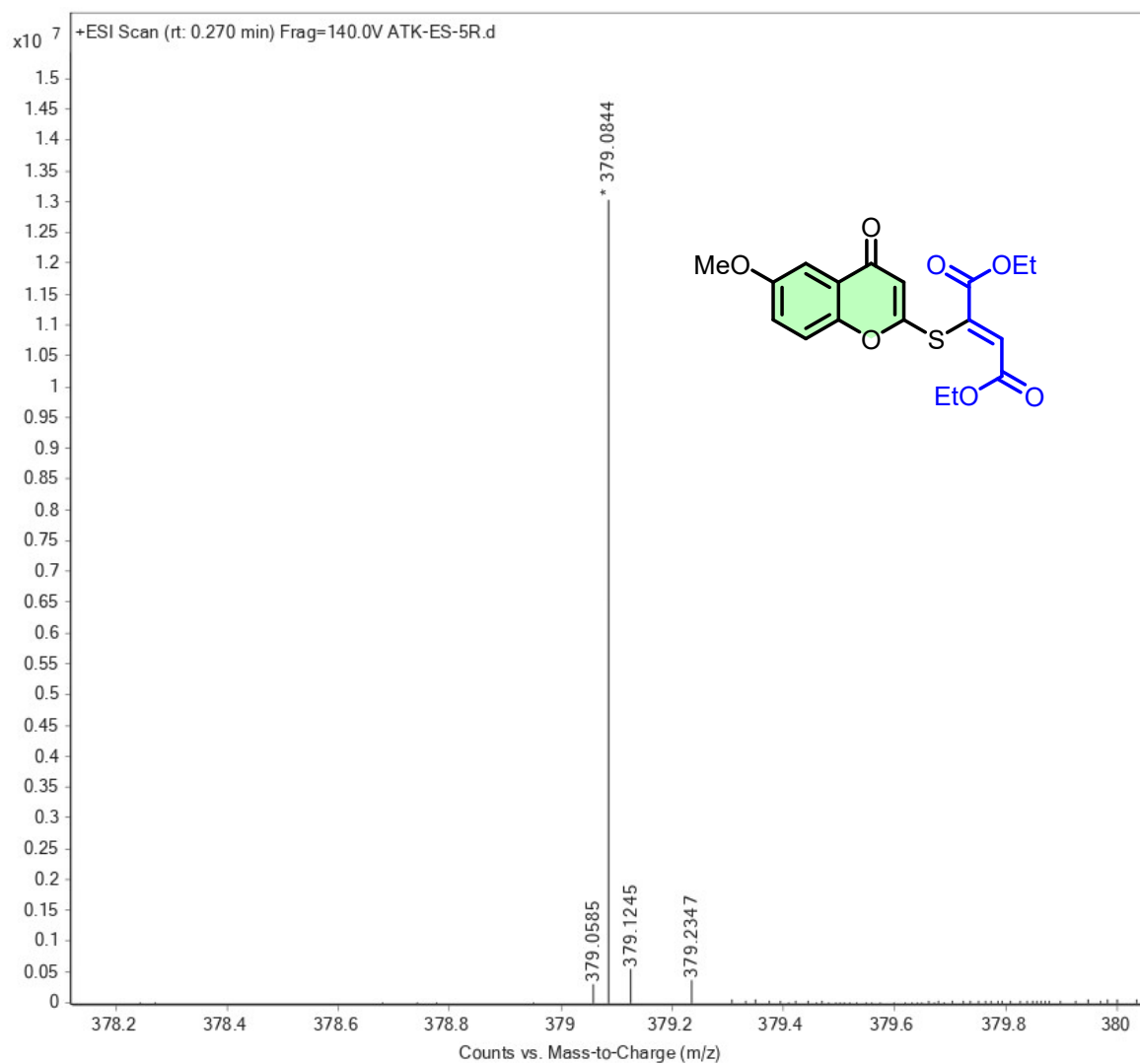
^1H NMR (600 MHz, CDCl_3) spectrum of compound 3gb



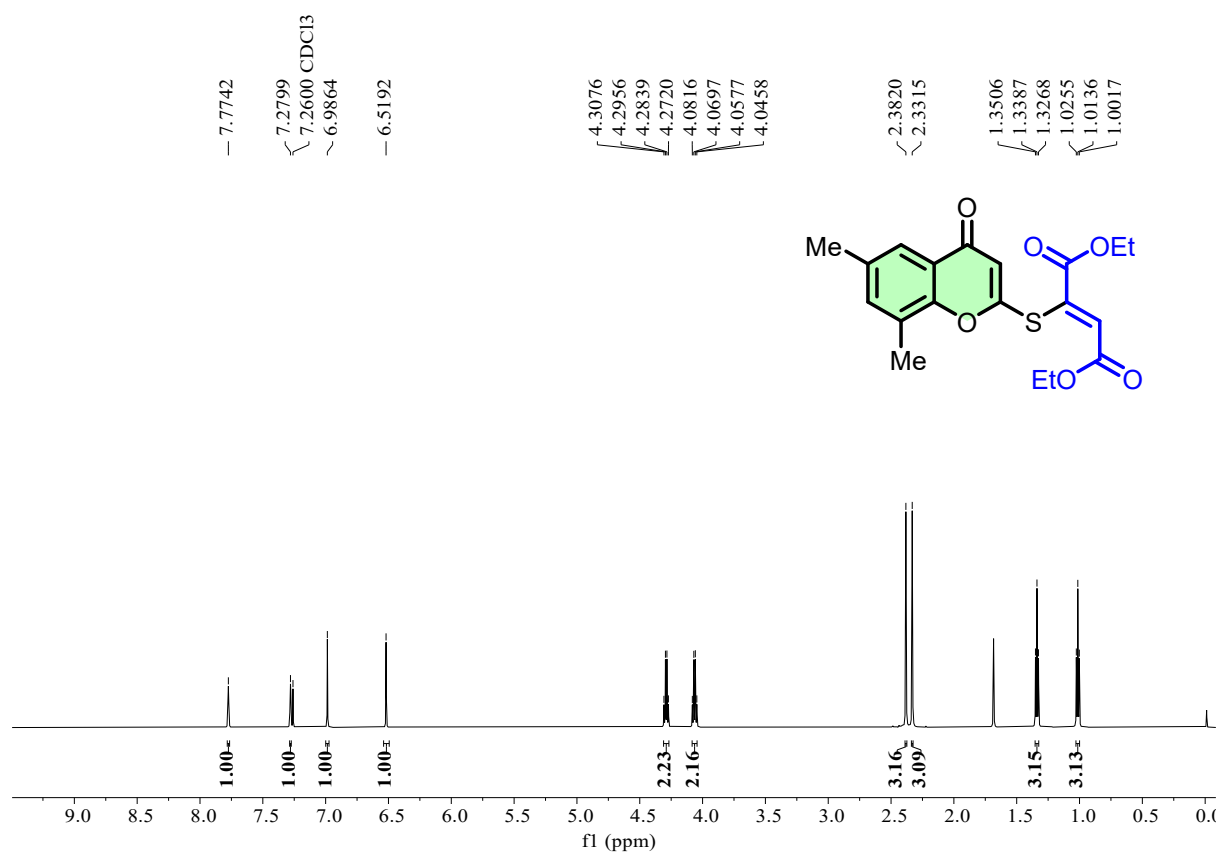
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 3gb



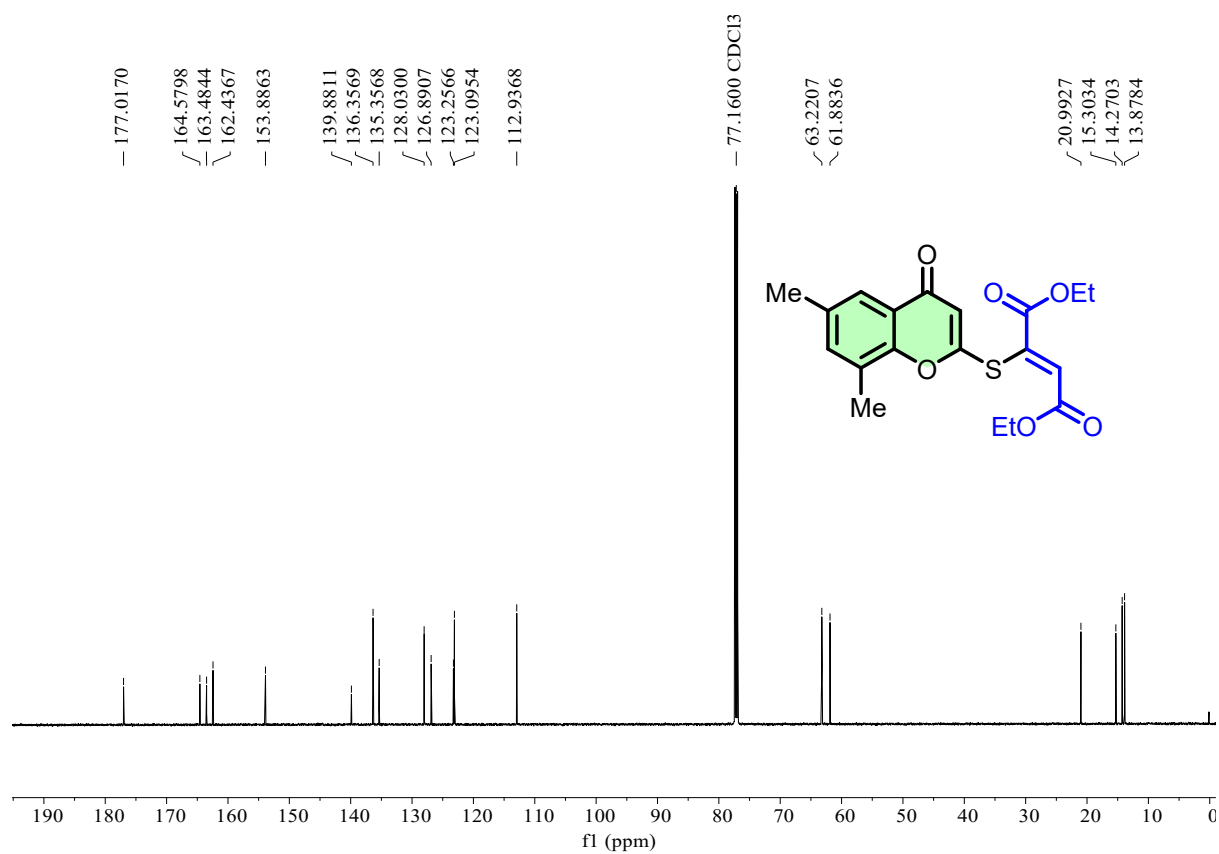
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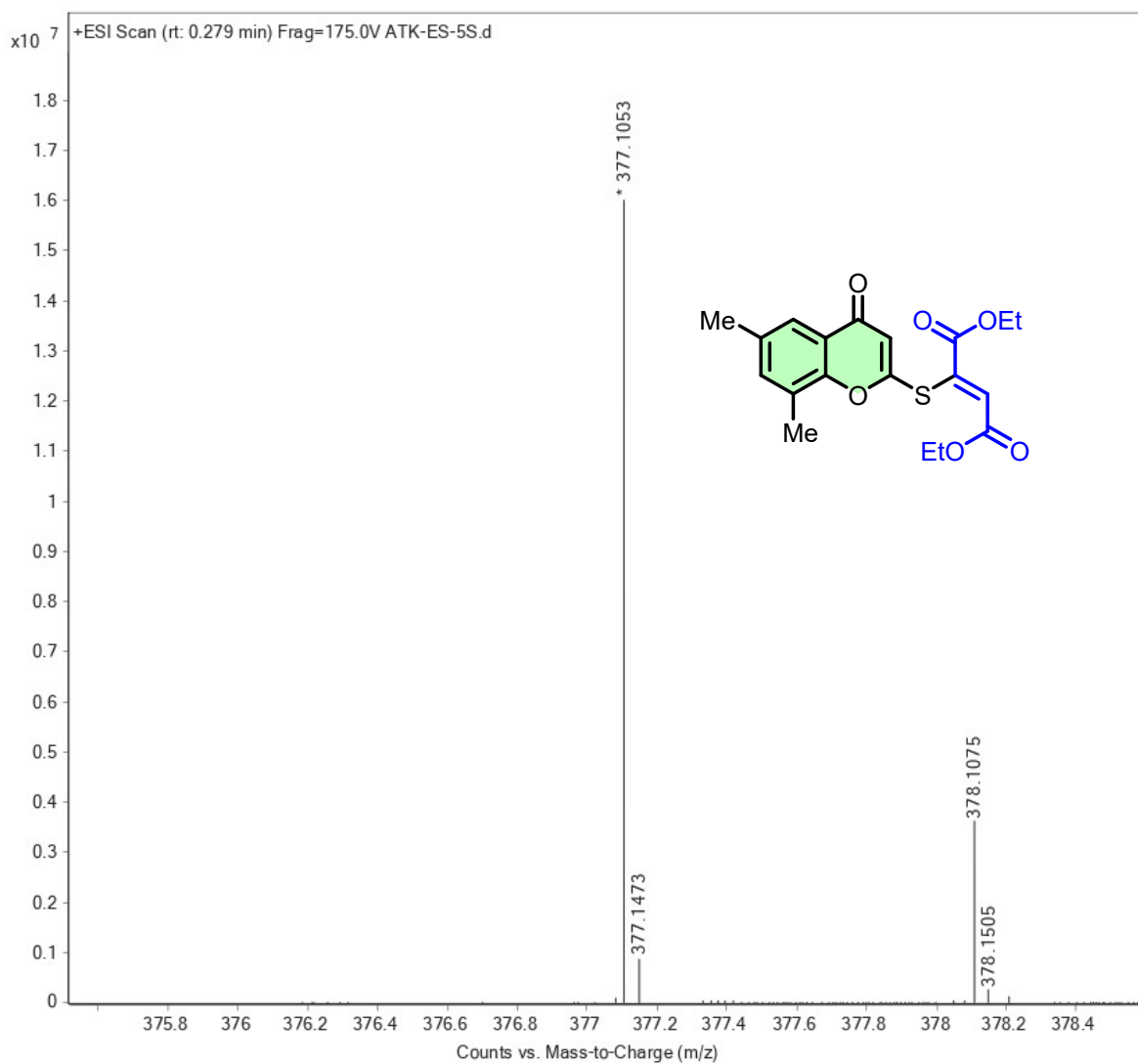
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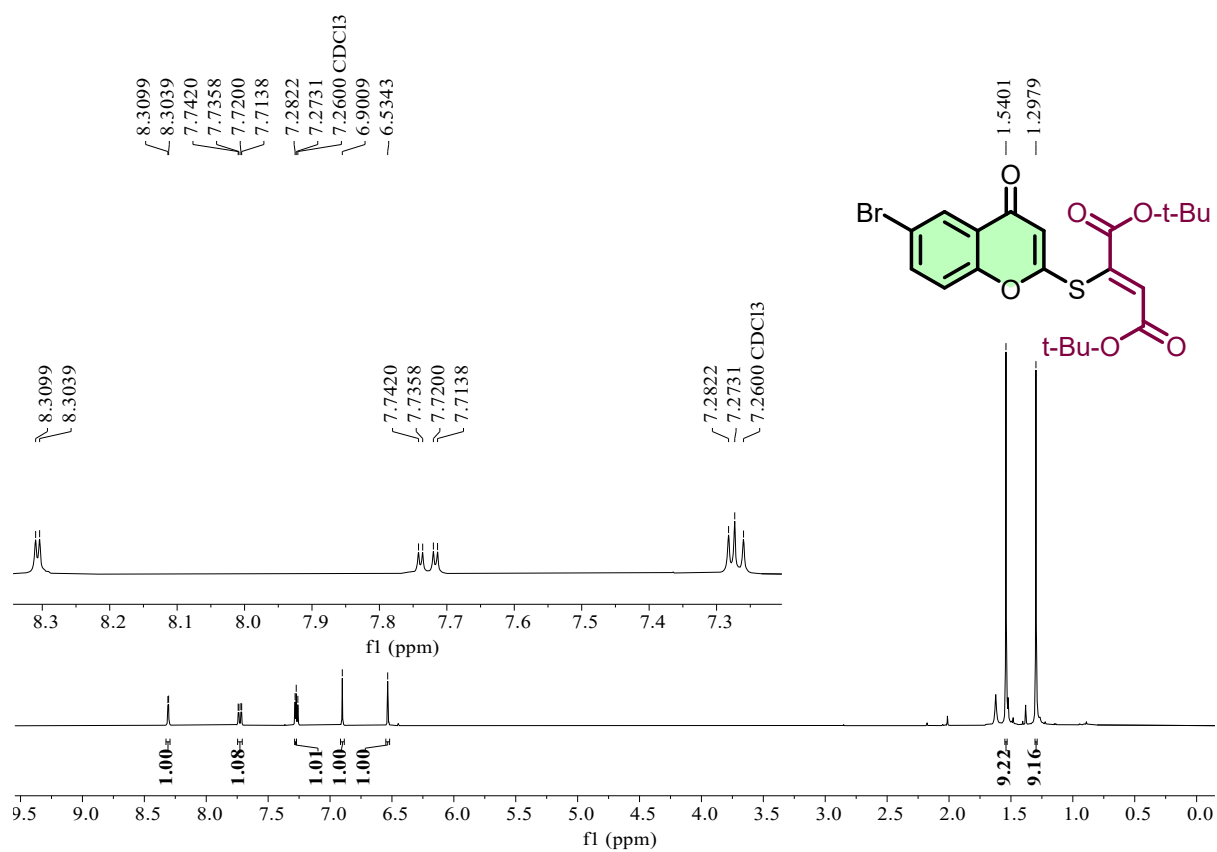
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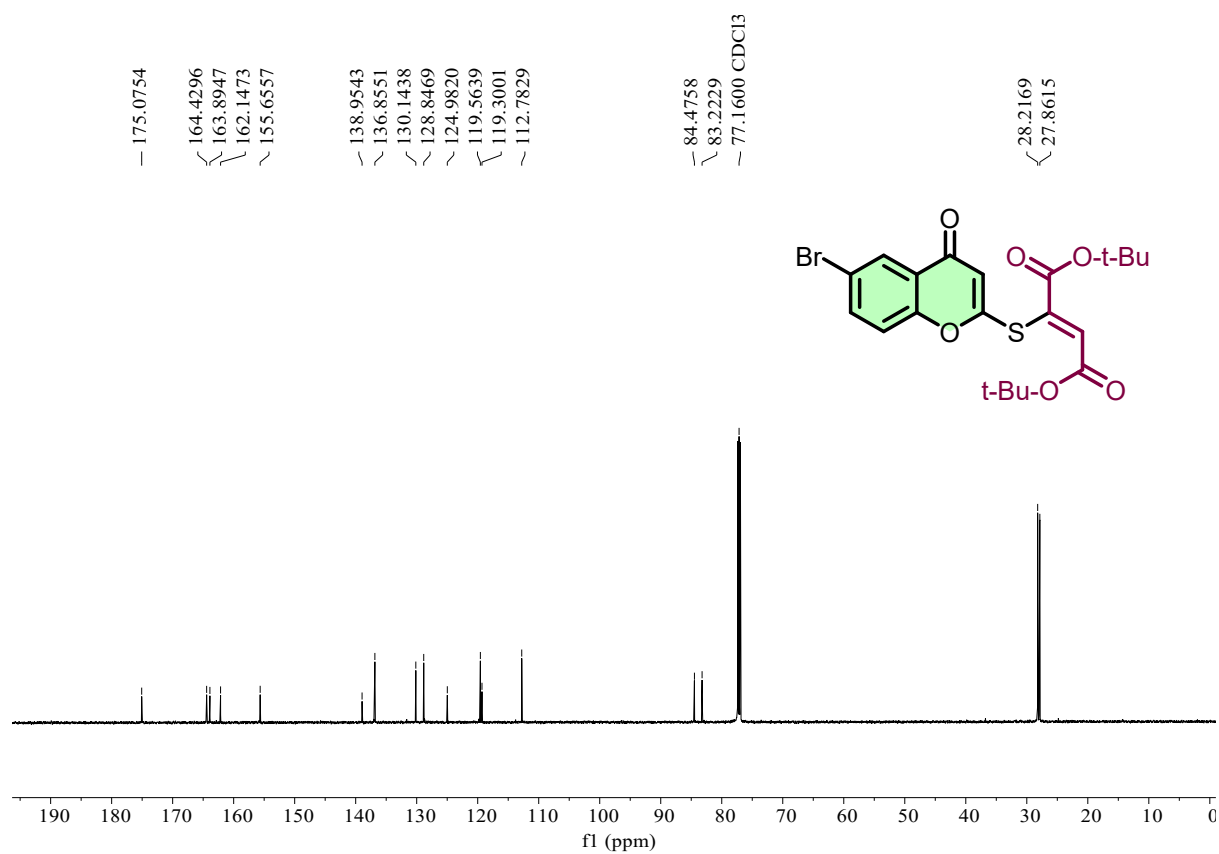
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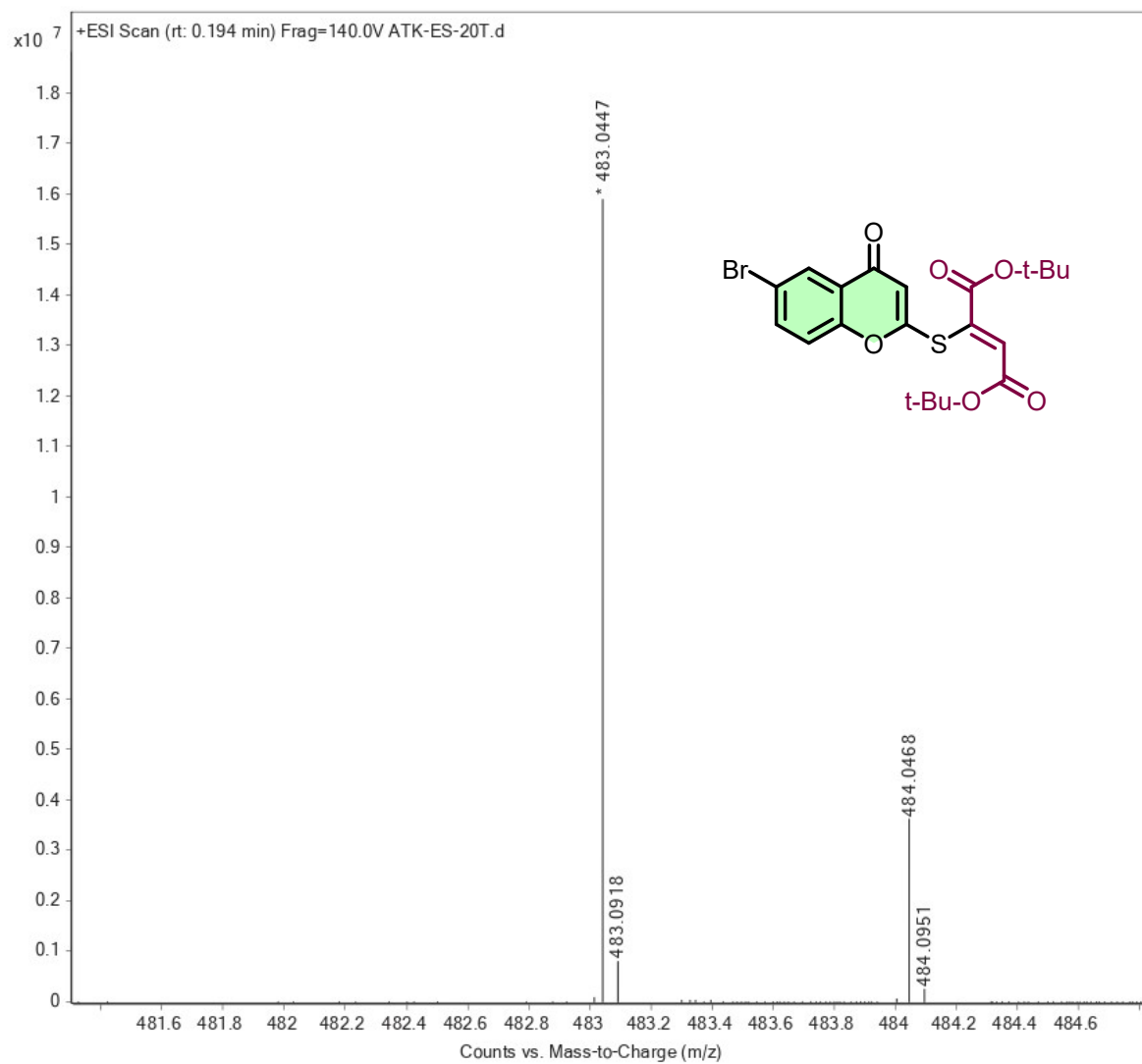
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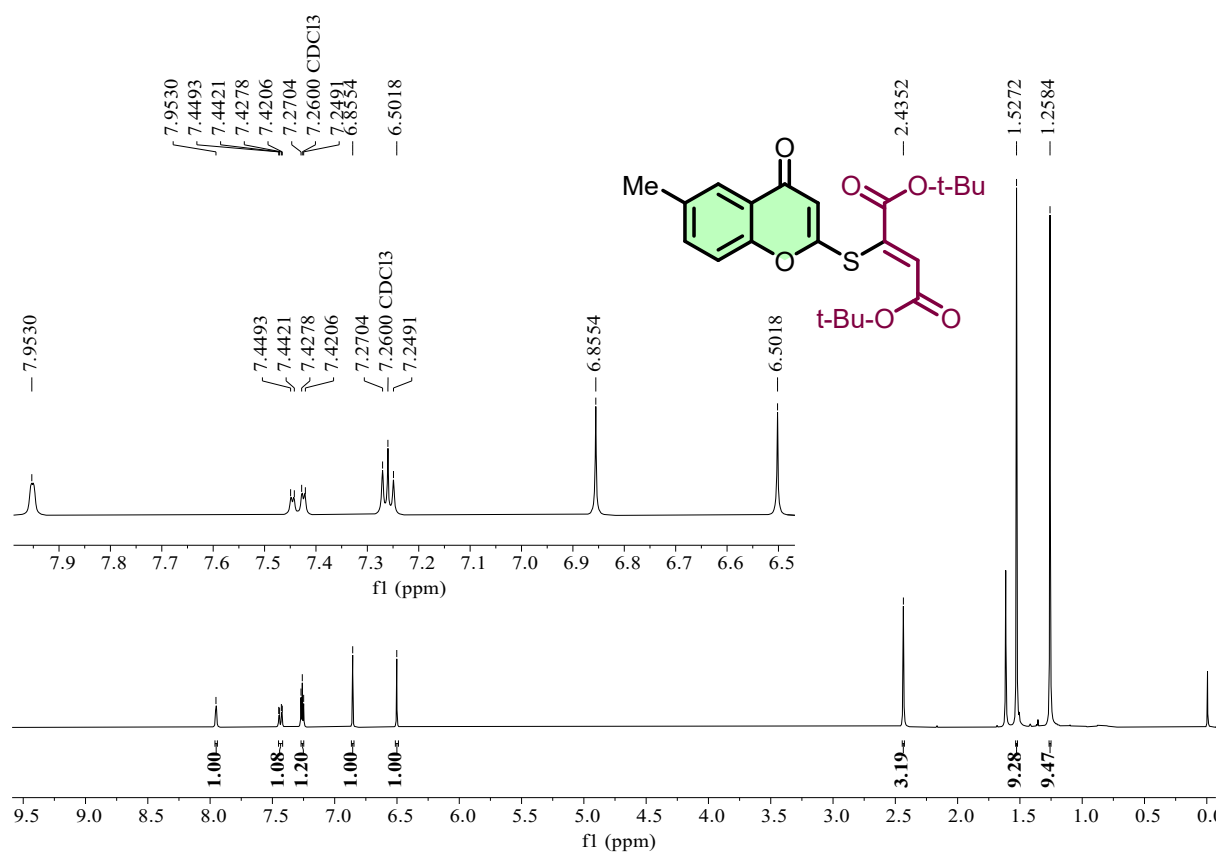
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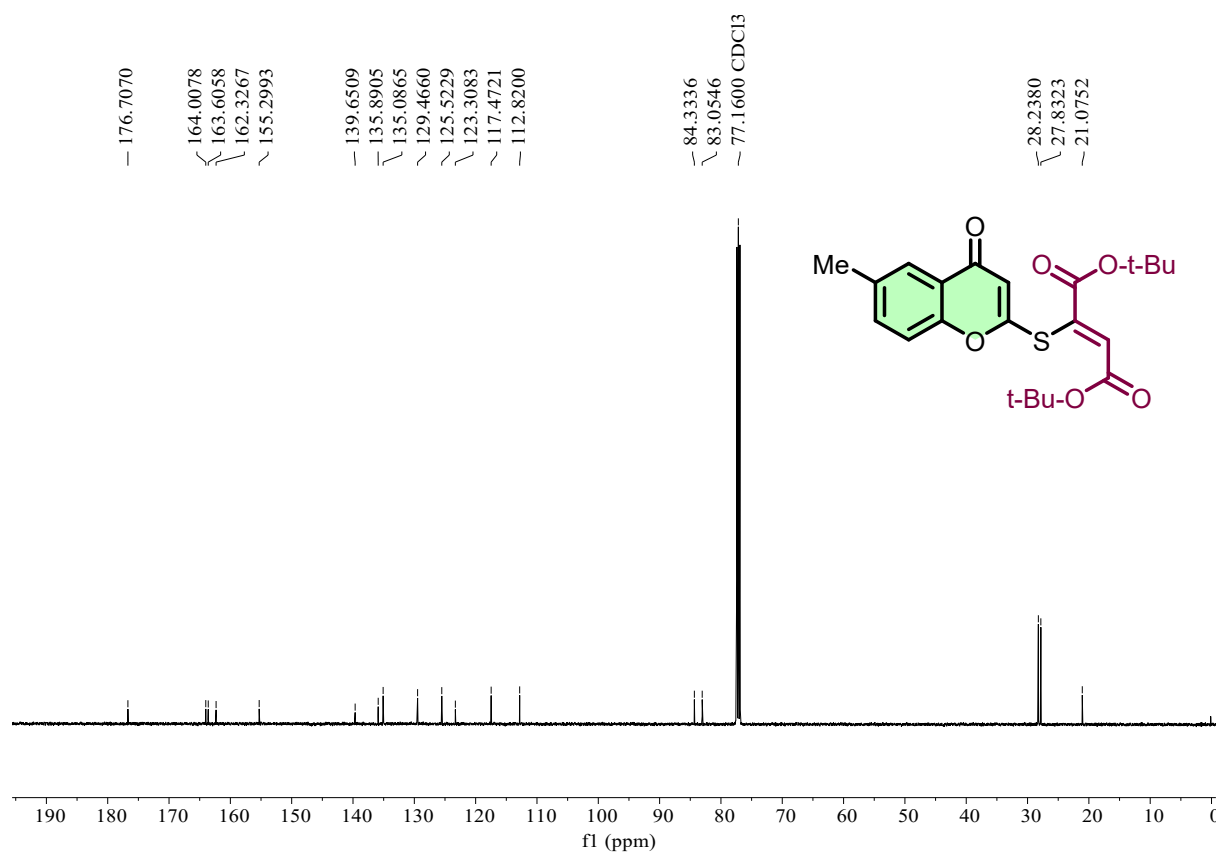
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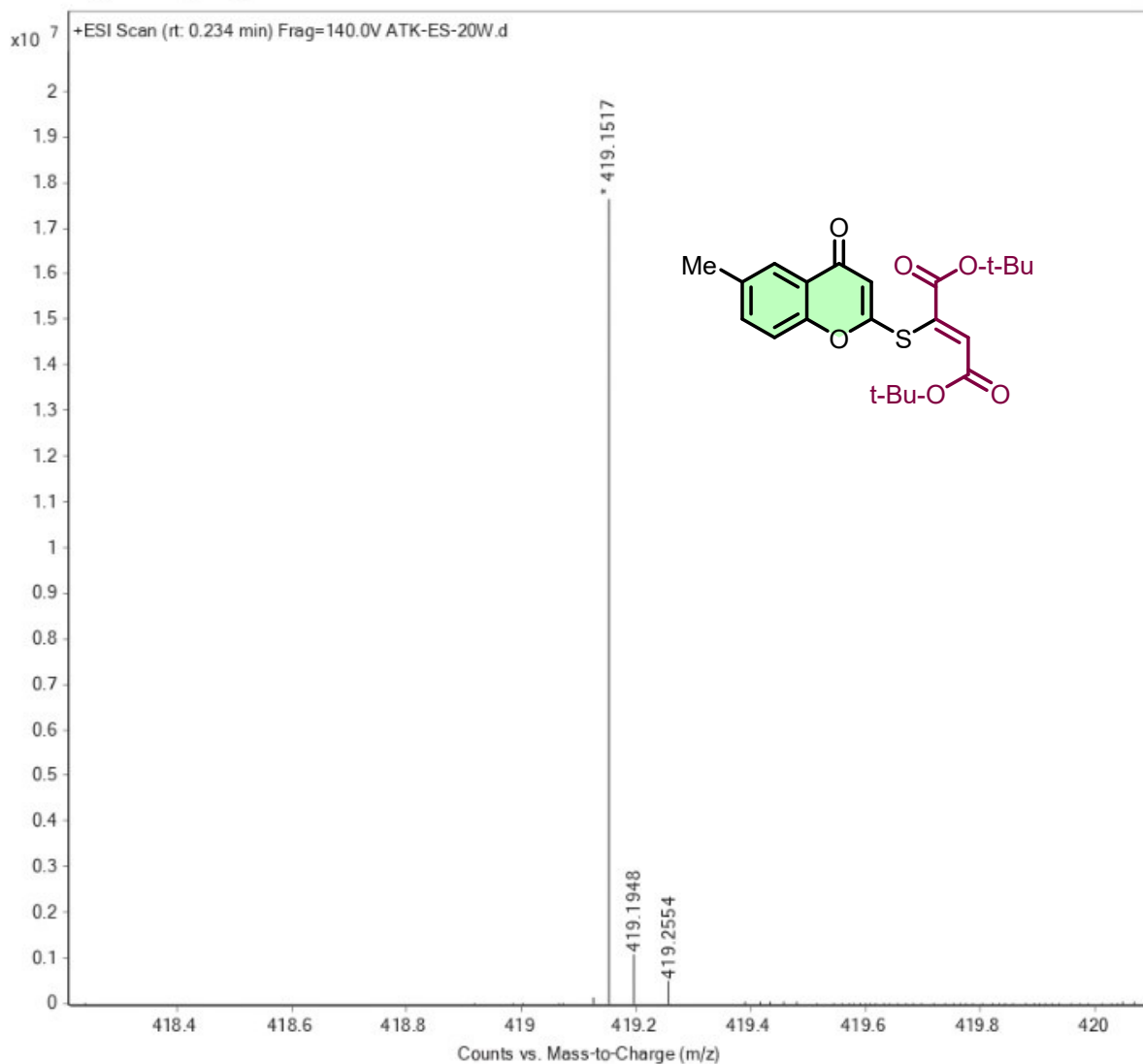
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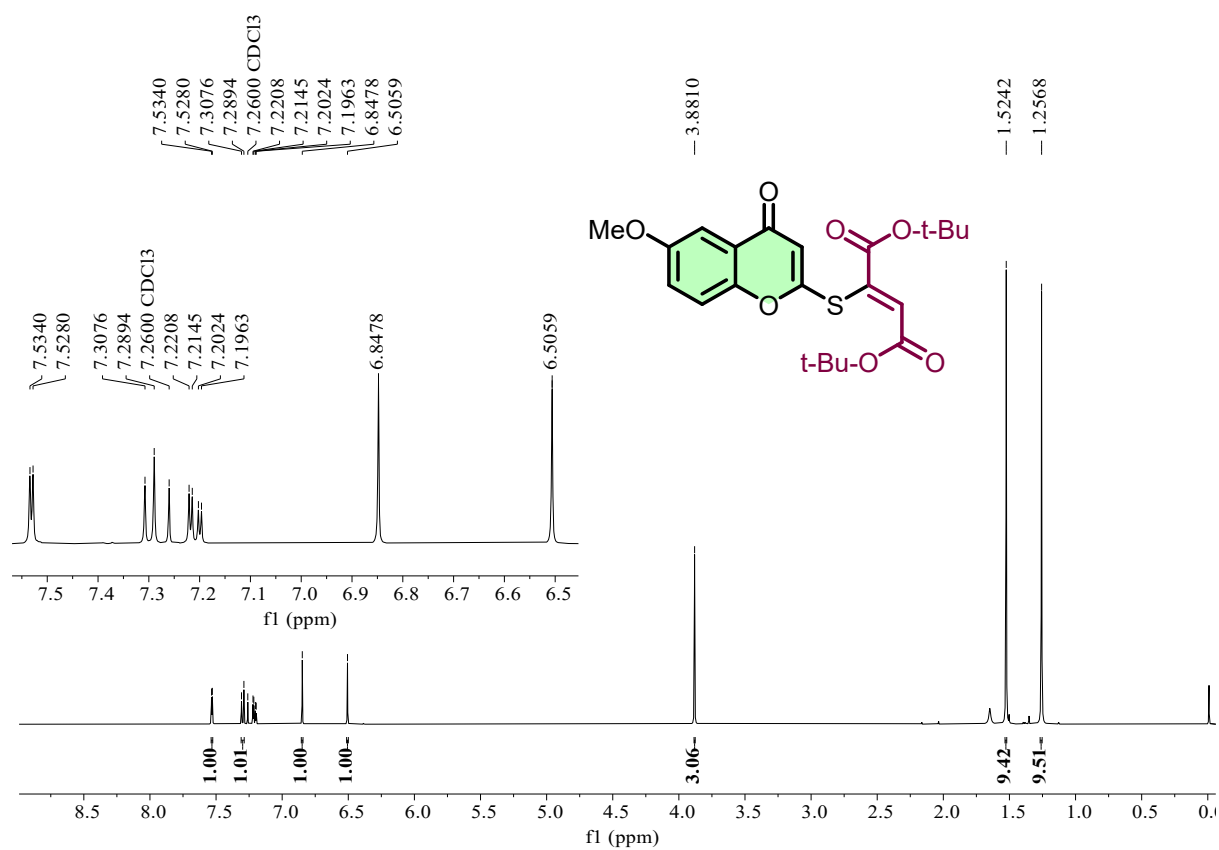
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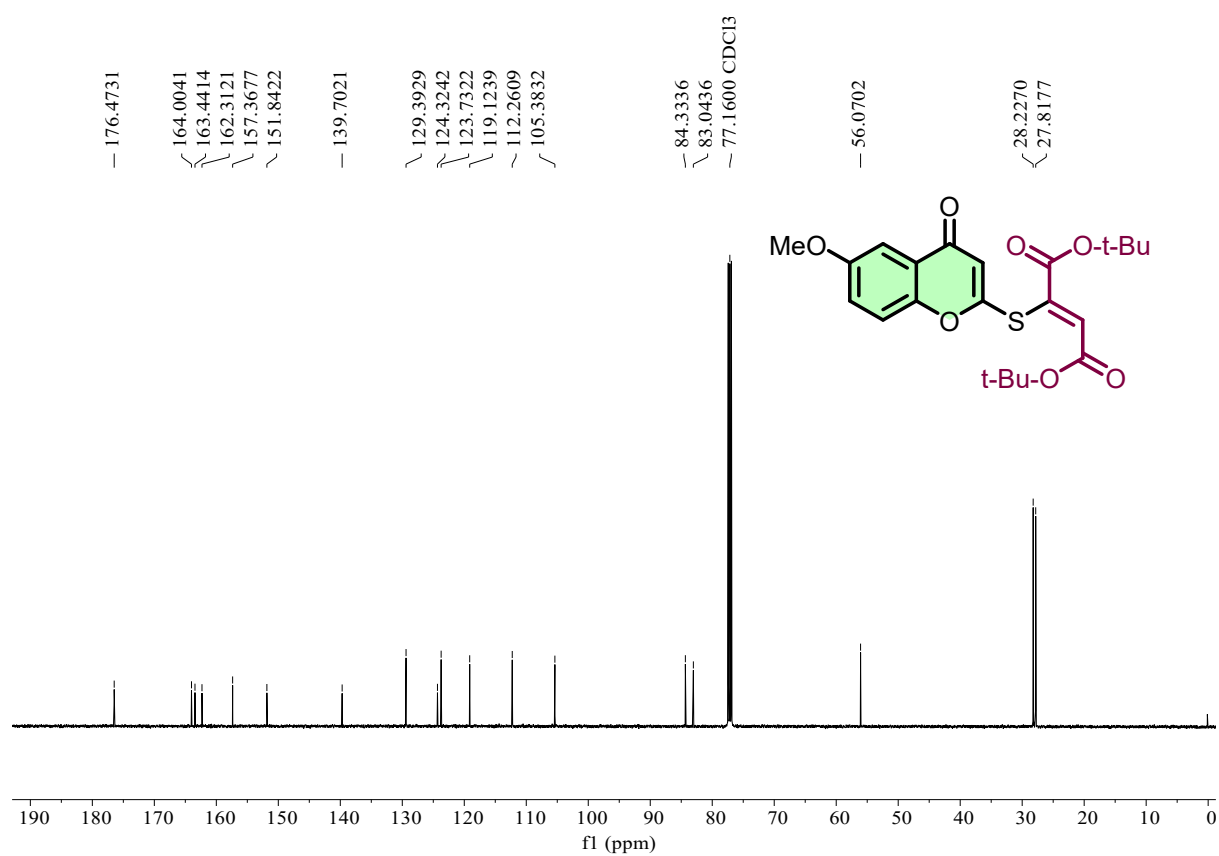
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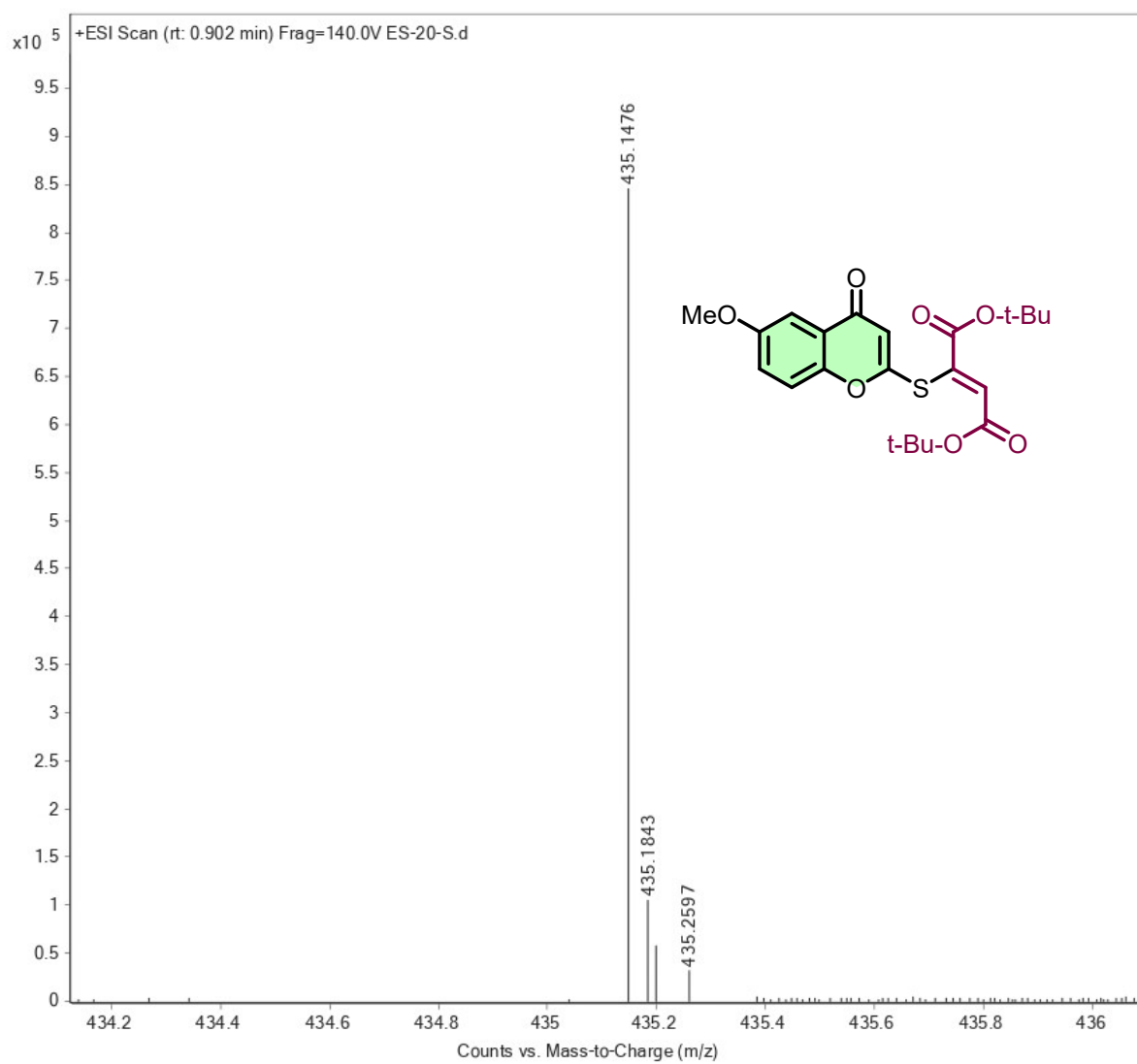
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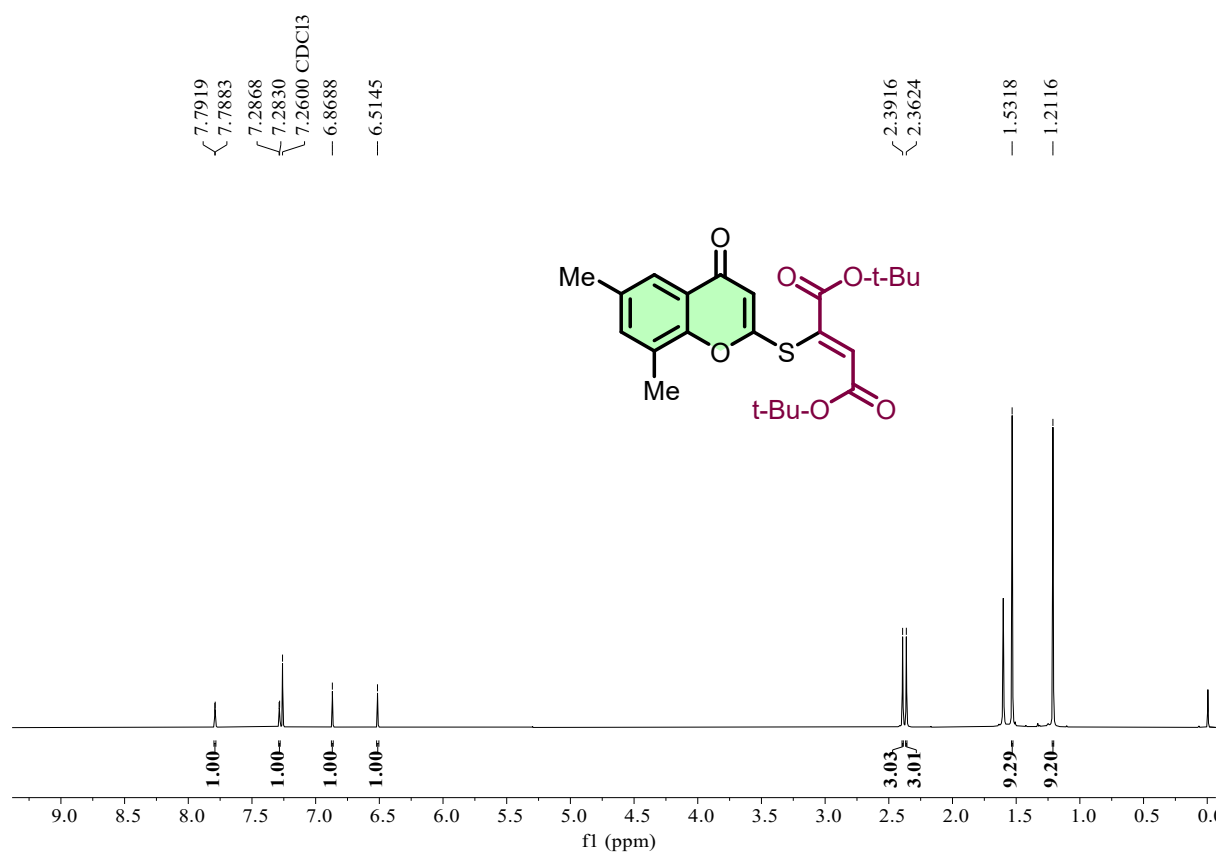
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of compound 3gc



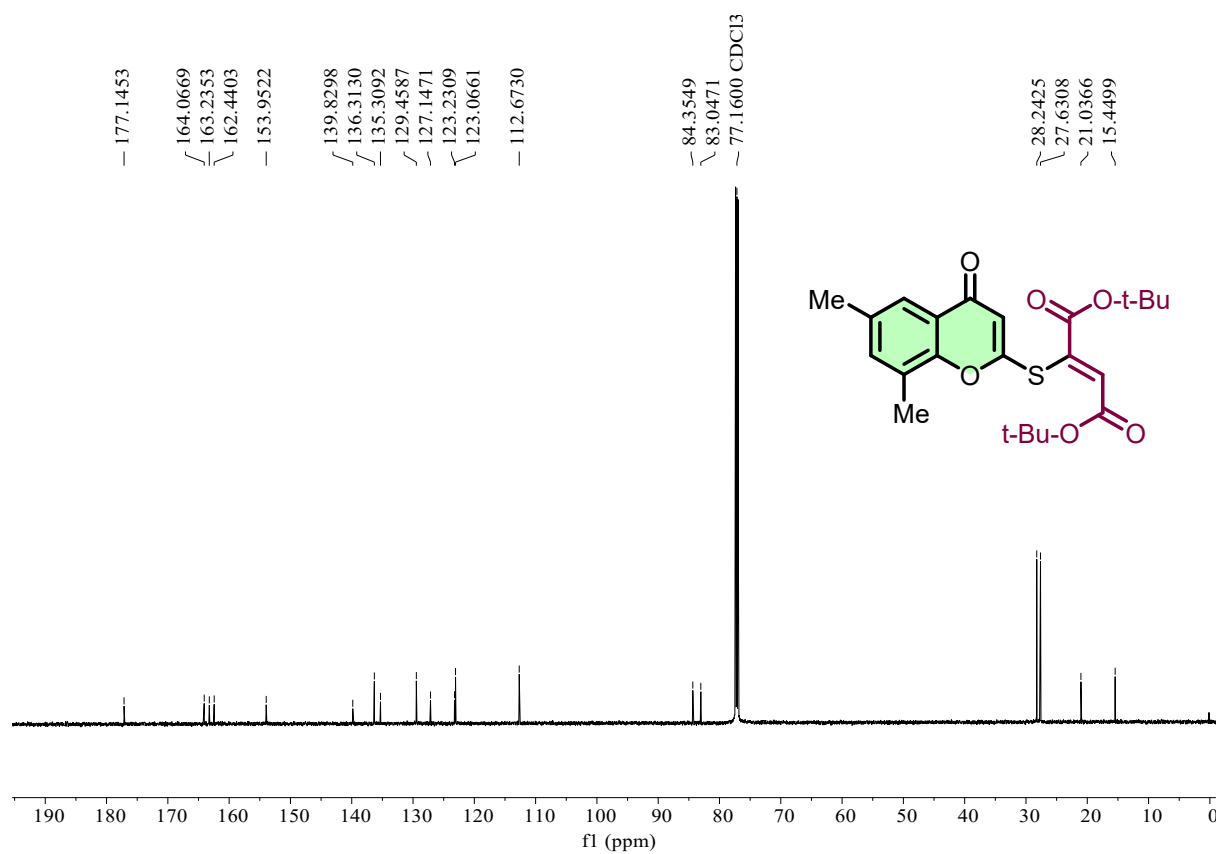
HRMS of compound 3gc



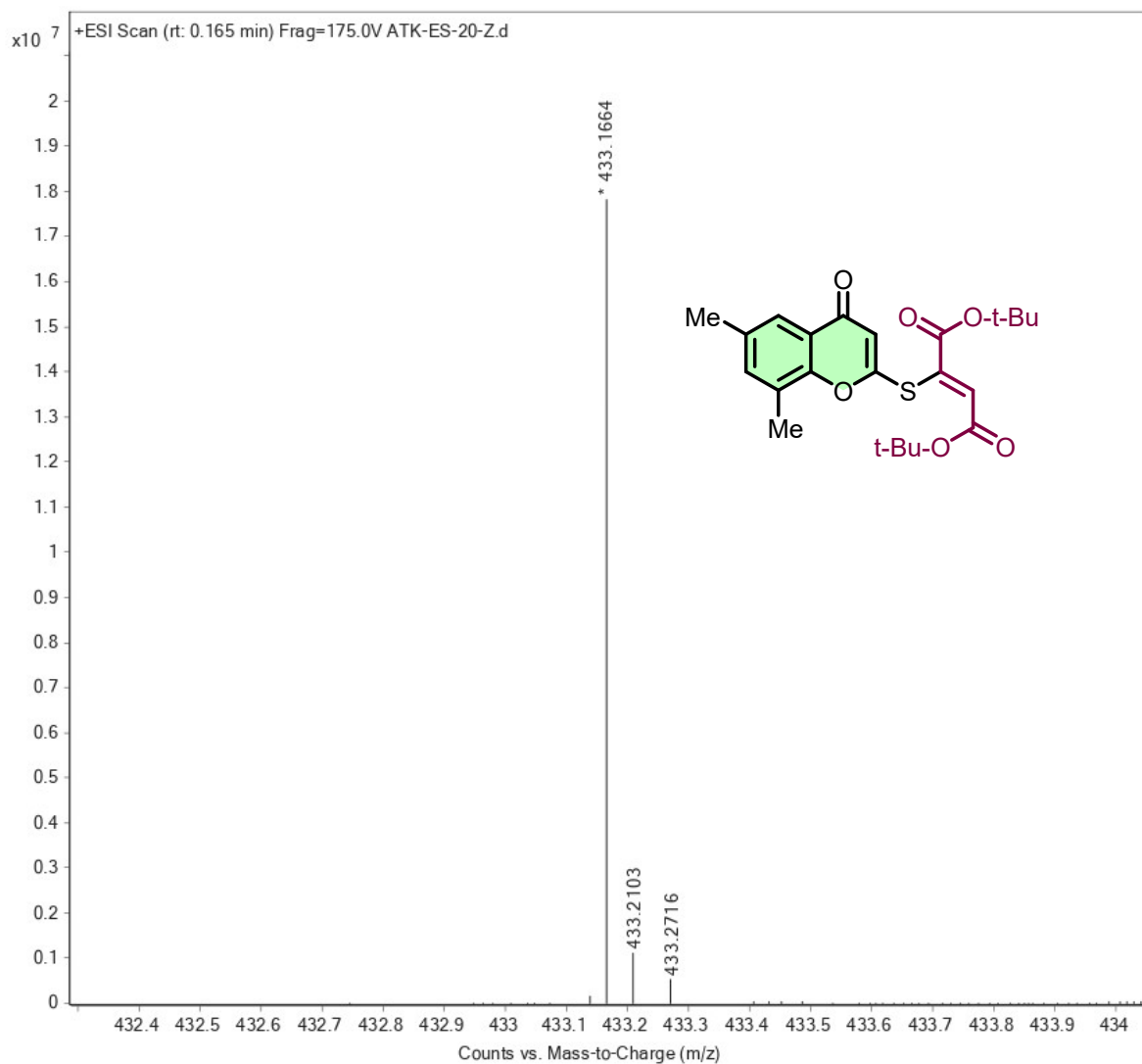
¹H NMR (600 MHz, CDCl₃) spectrum of compound 3hc



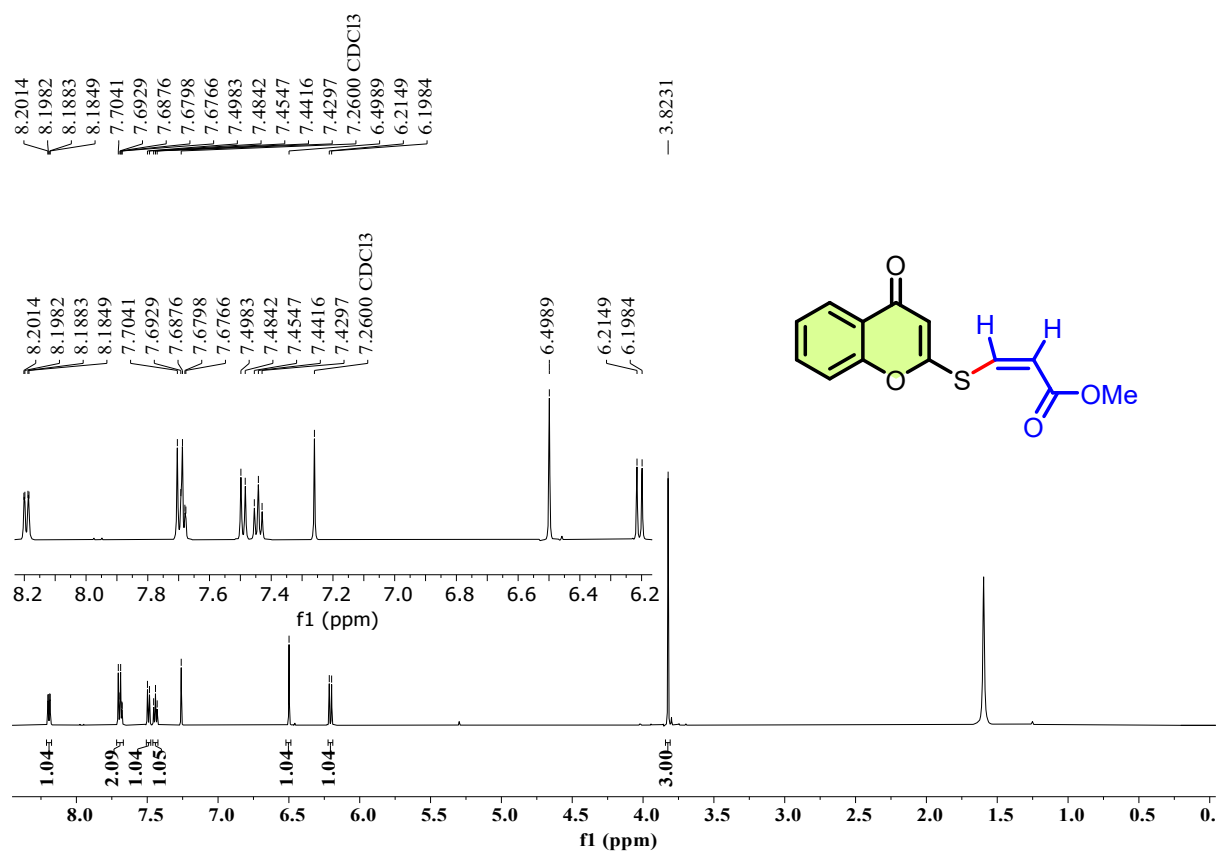
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 3hc



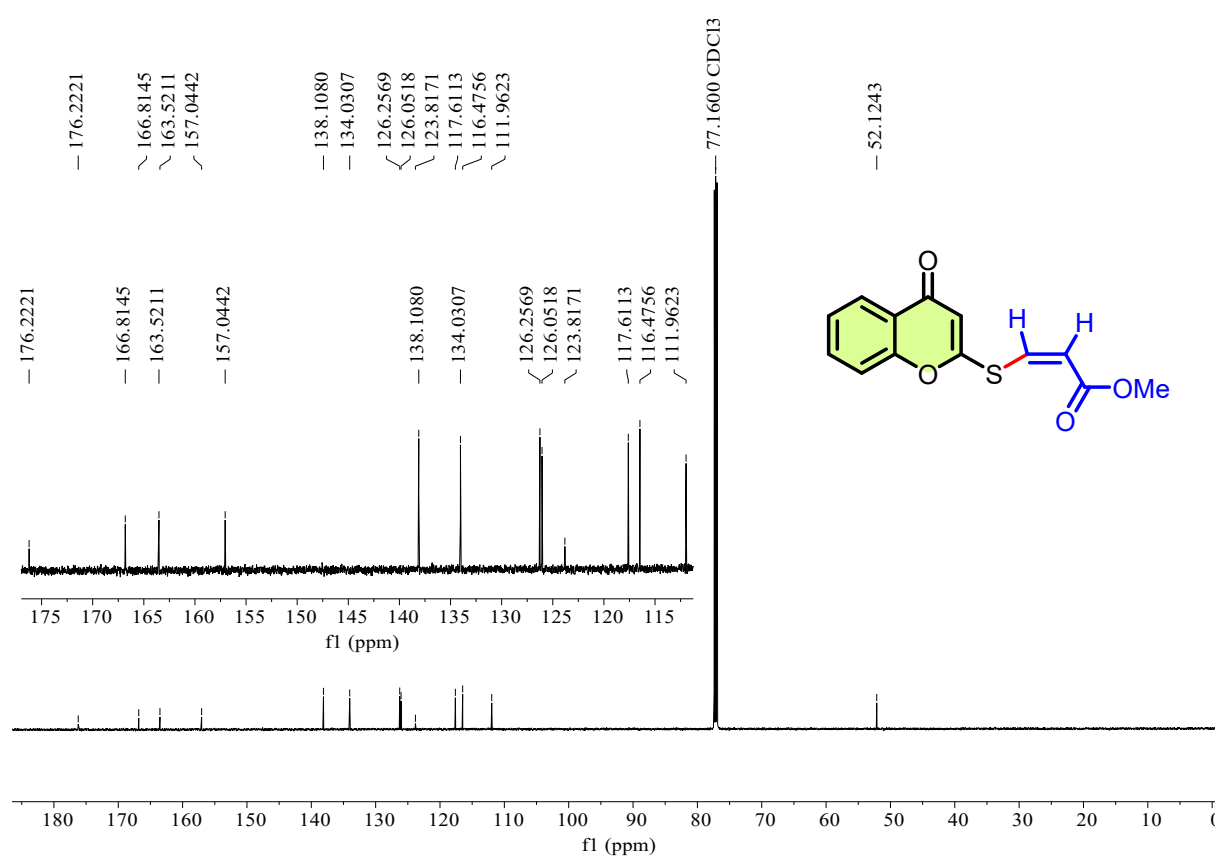
HRMS of compound 3hc



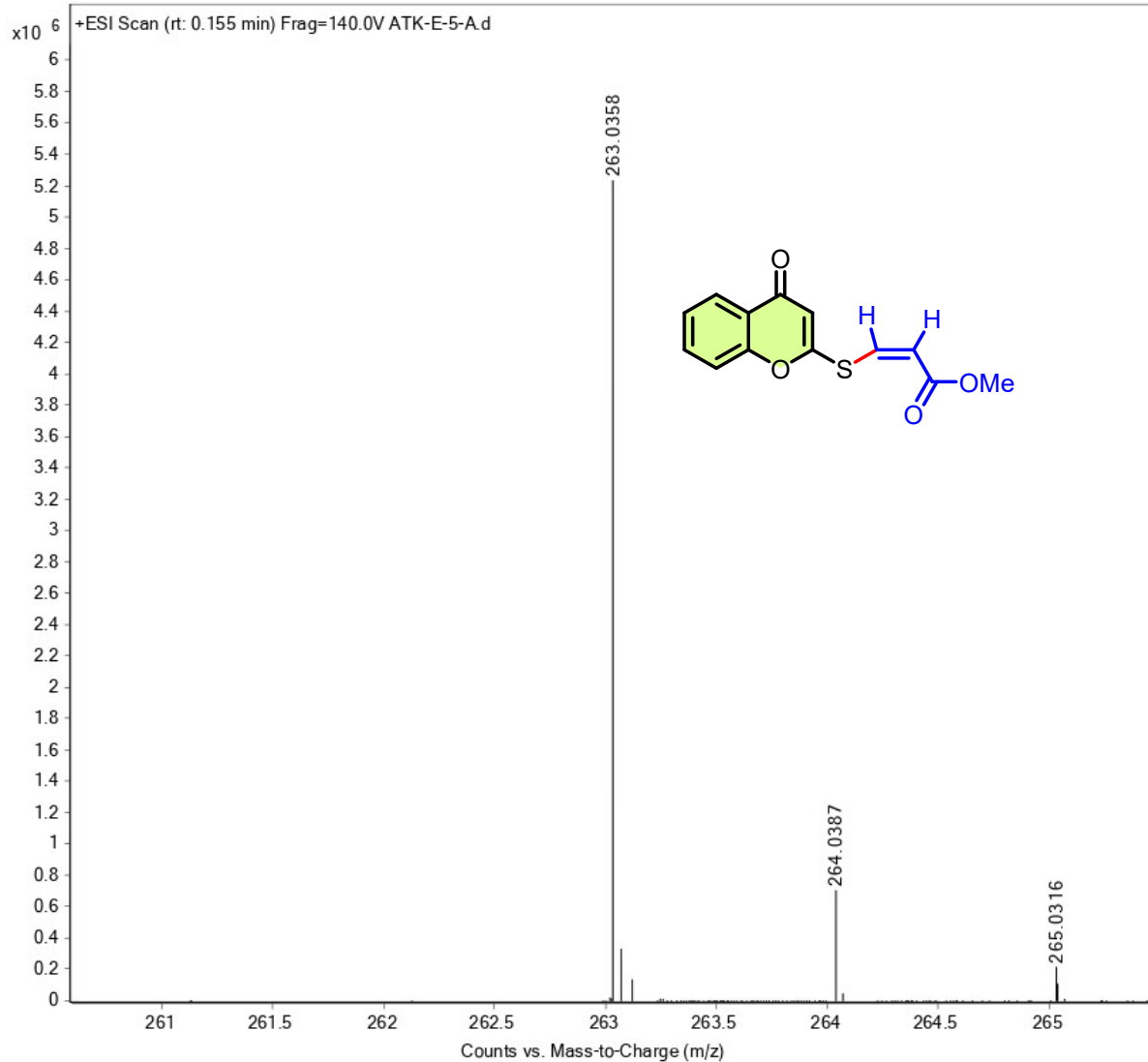
¹H NMR (600 MHz, CDCl₃) spectrum of compound 7aa



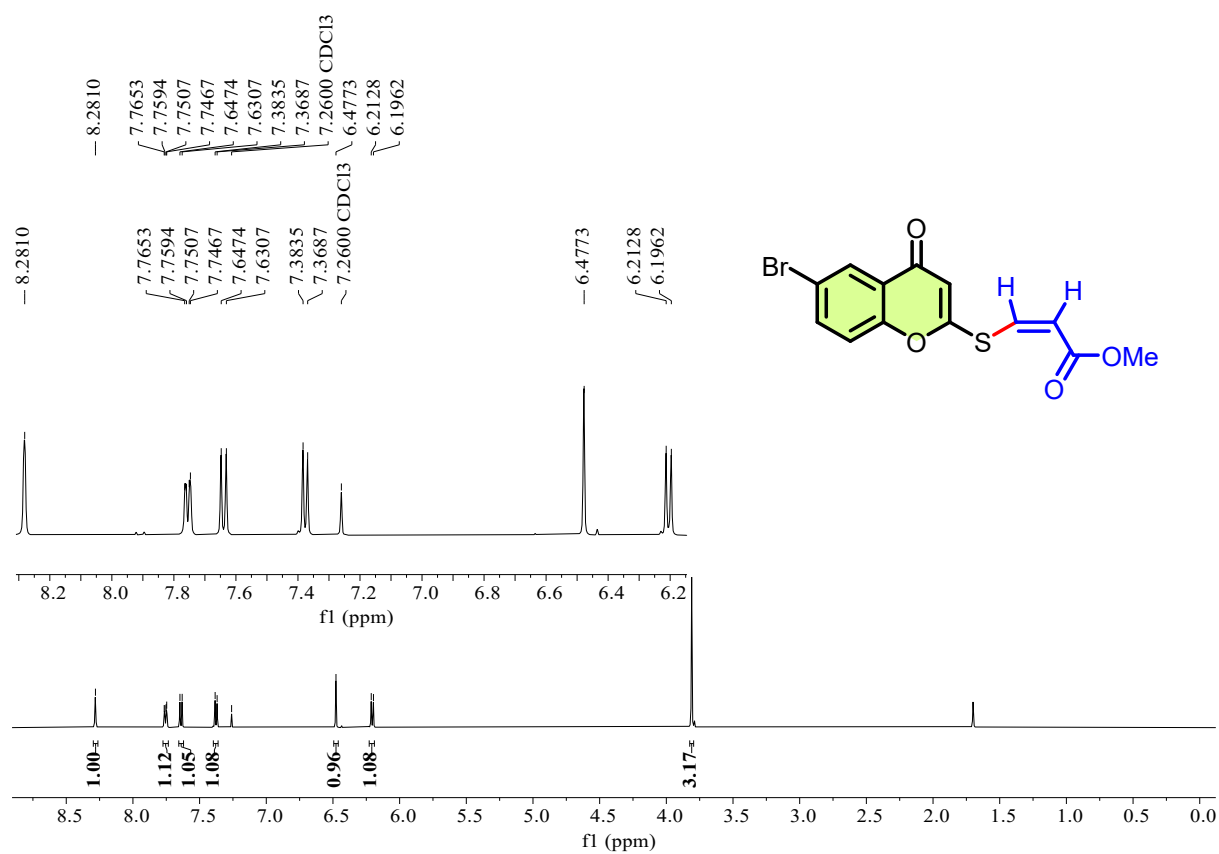
¹³C{¹H} NMR (150 MHz, CDCl₃) spectrum of compound 7aa



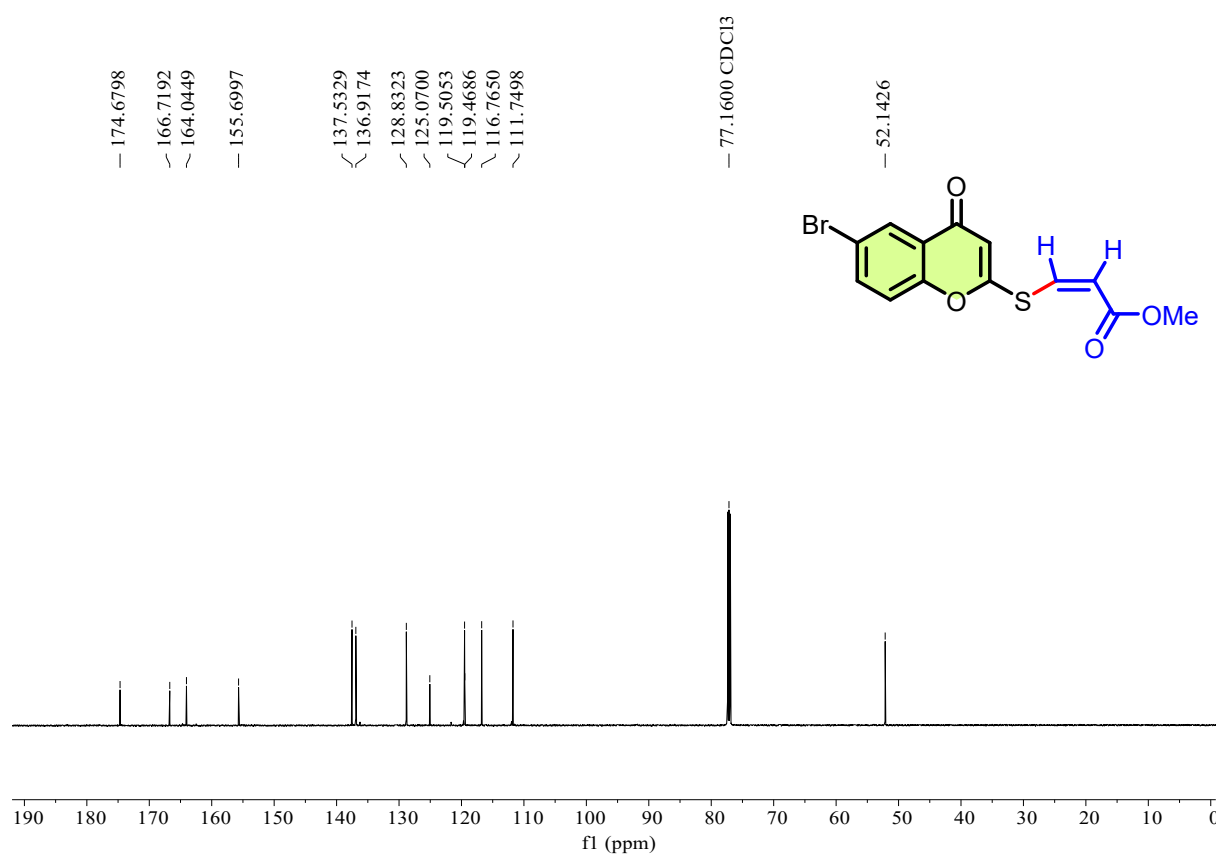
HRMS of compound 7aa



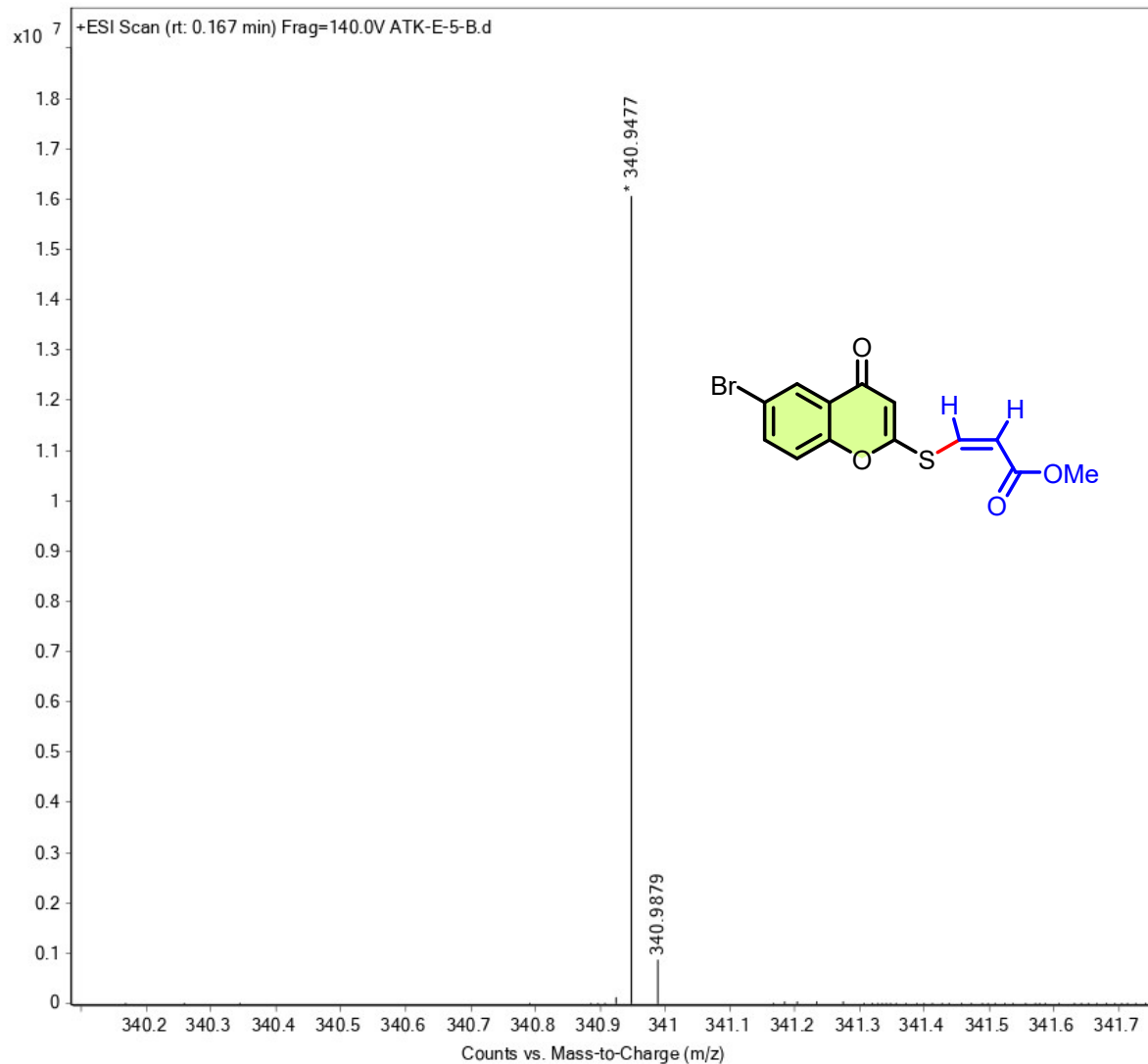
¹H NMR (600 MHz, CDCl₃) spectrum of compound 7ba



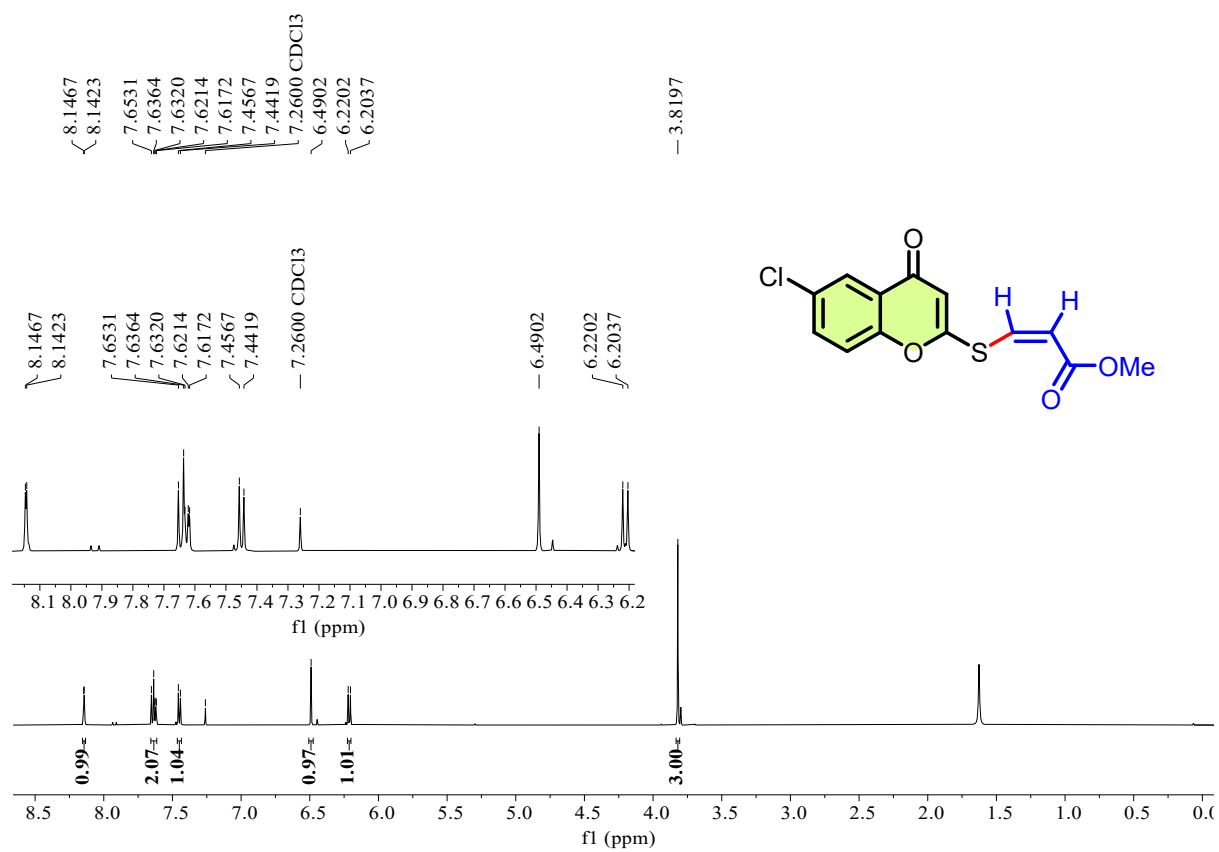
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 7ba



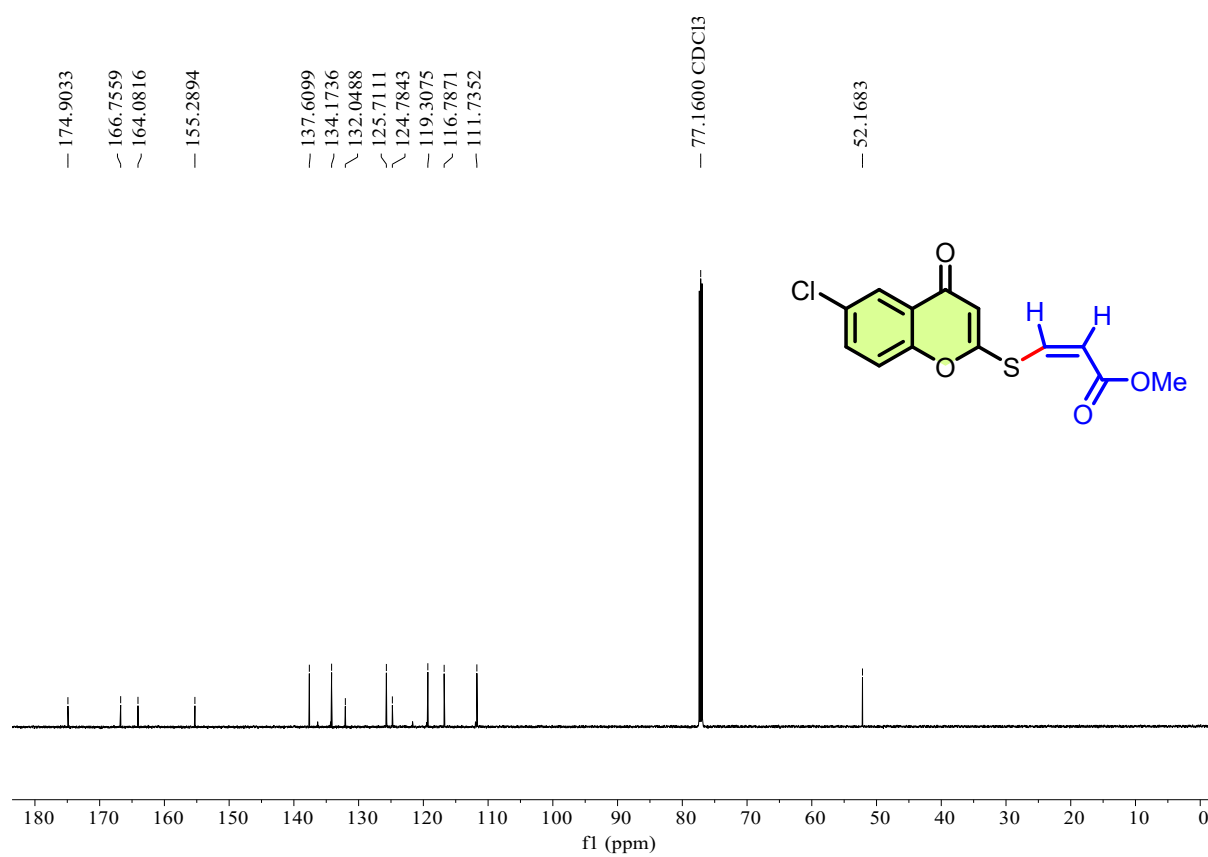
HRMS of compound 7ba



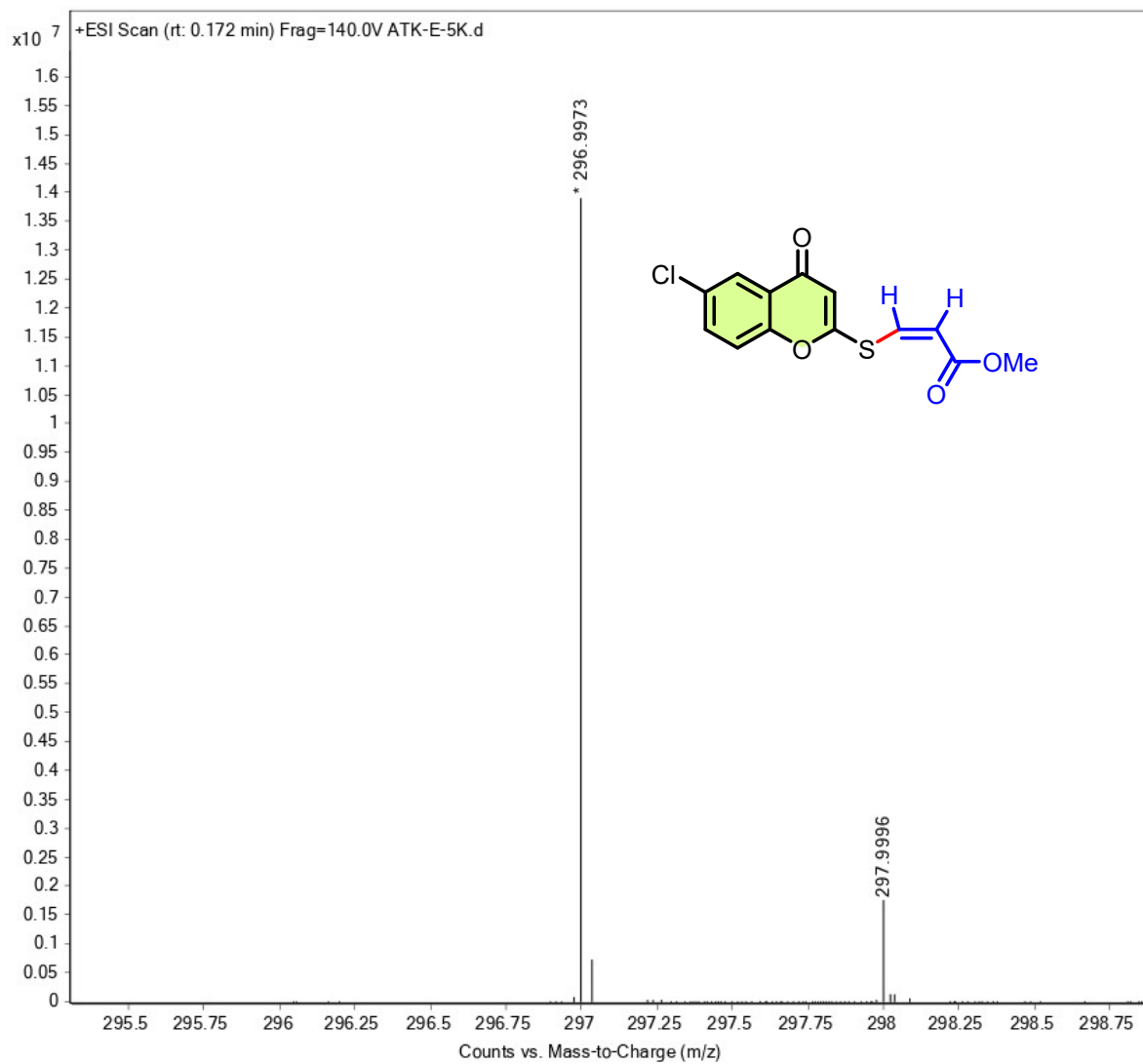
¹H NMR (600 MHz, CDCl₃) spectrum of compound 7ca



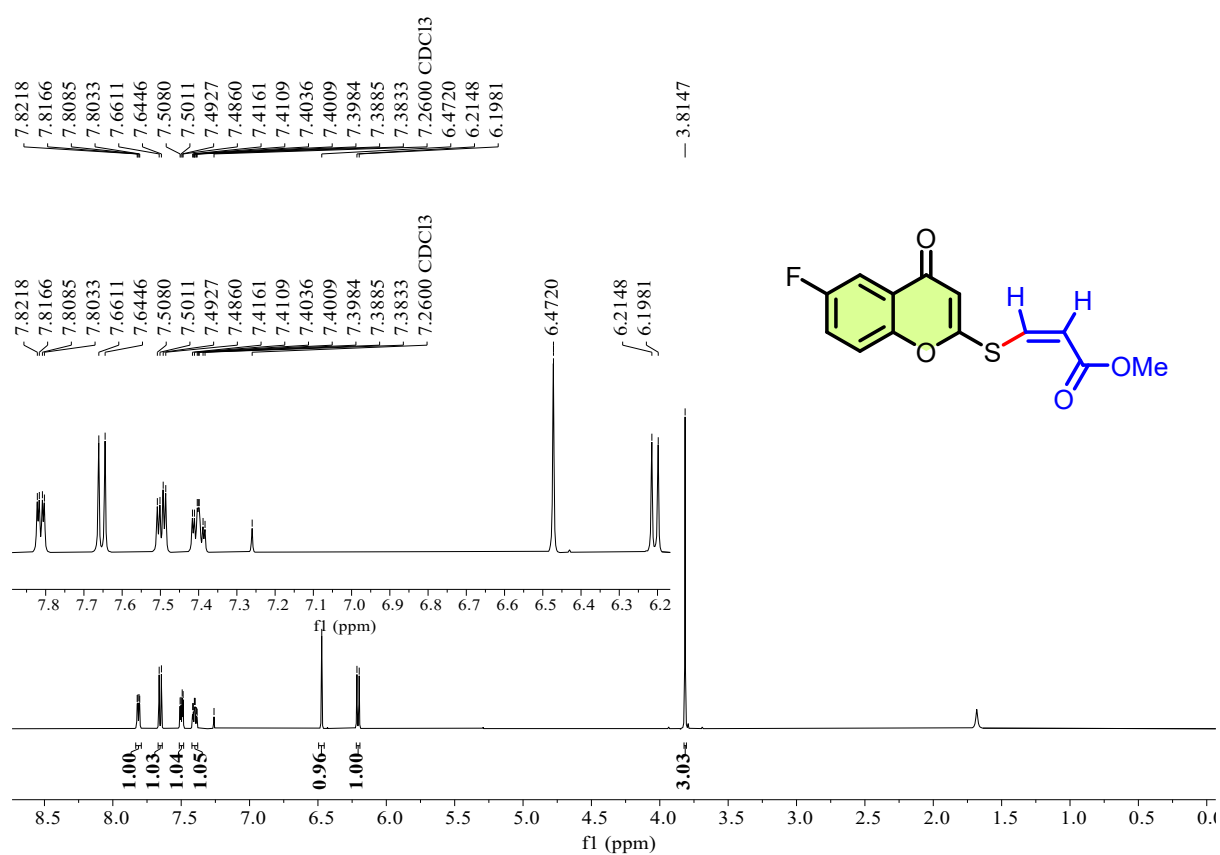
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 7ca



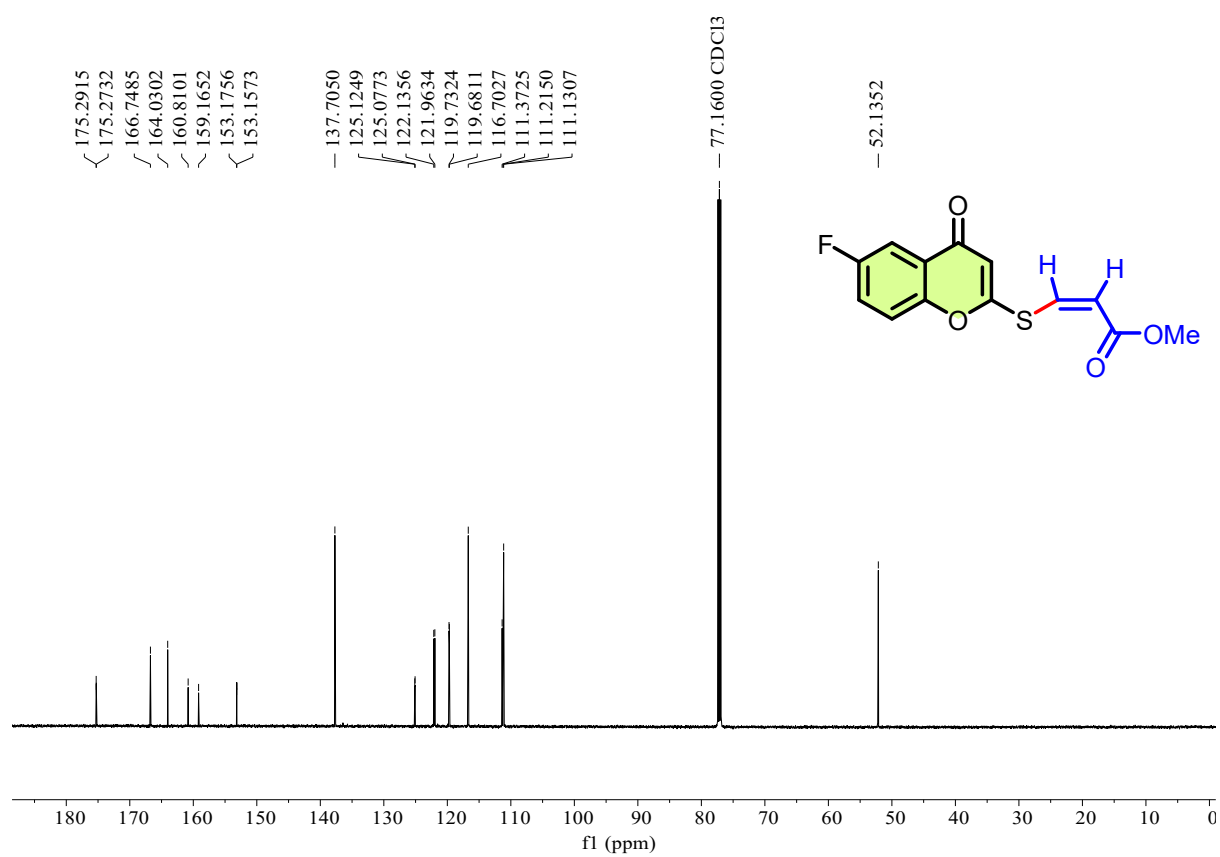
HRMS of compound 7ca



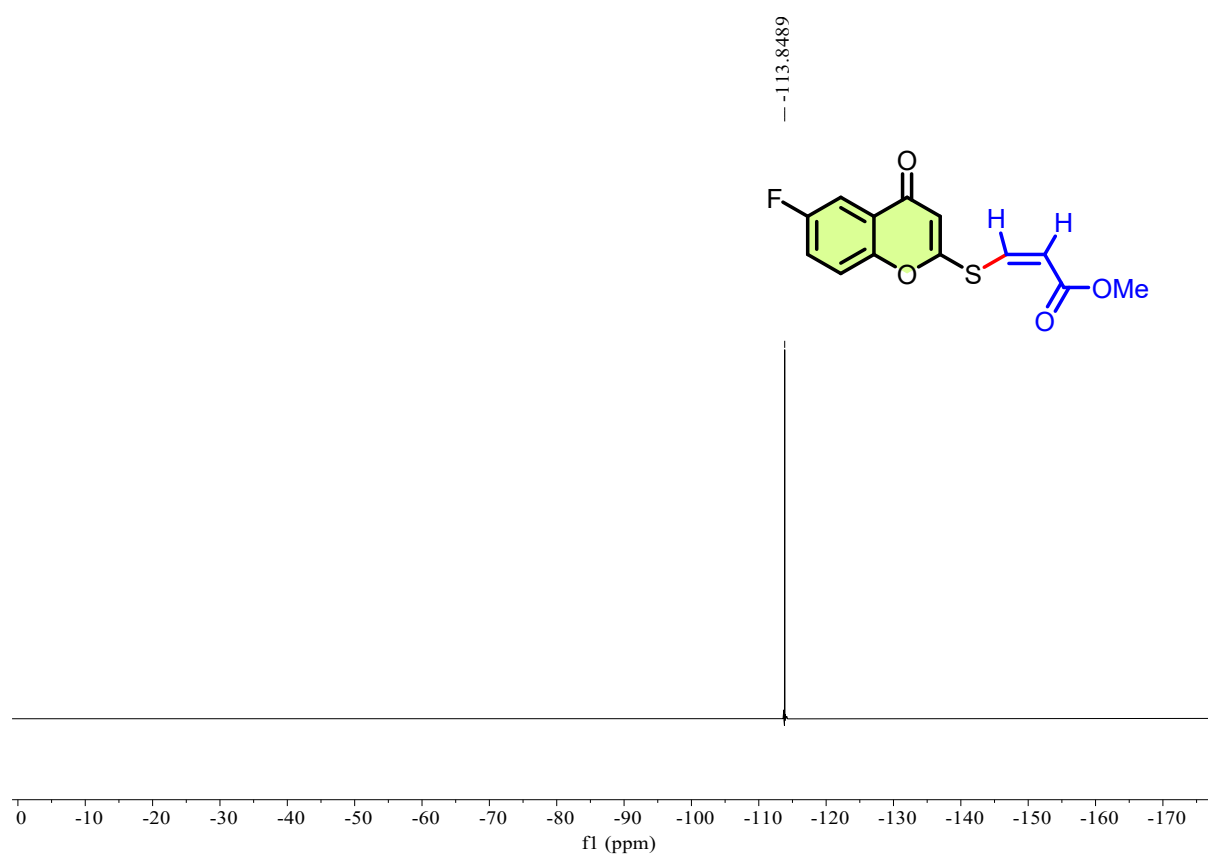
¹H NMR (600 MHz, CDCl₃) spectrum of compound 7da



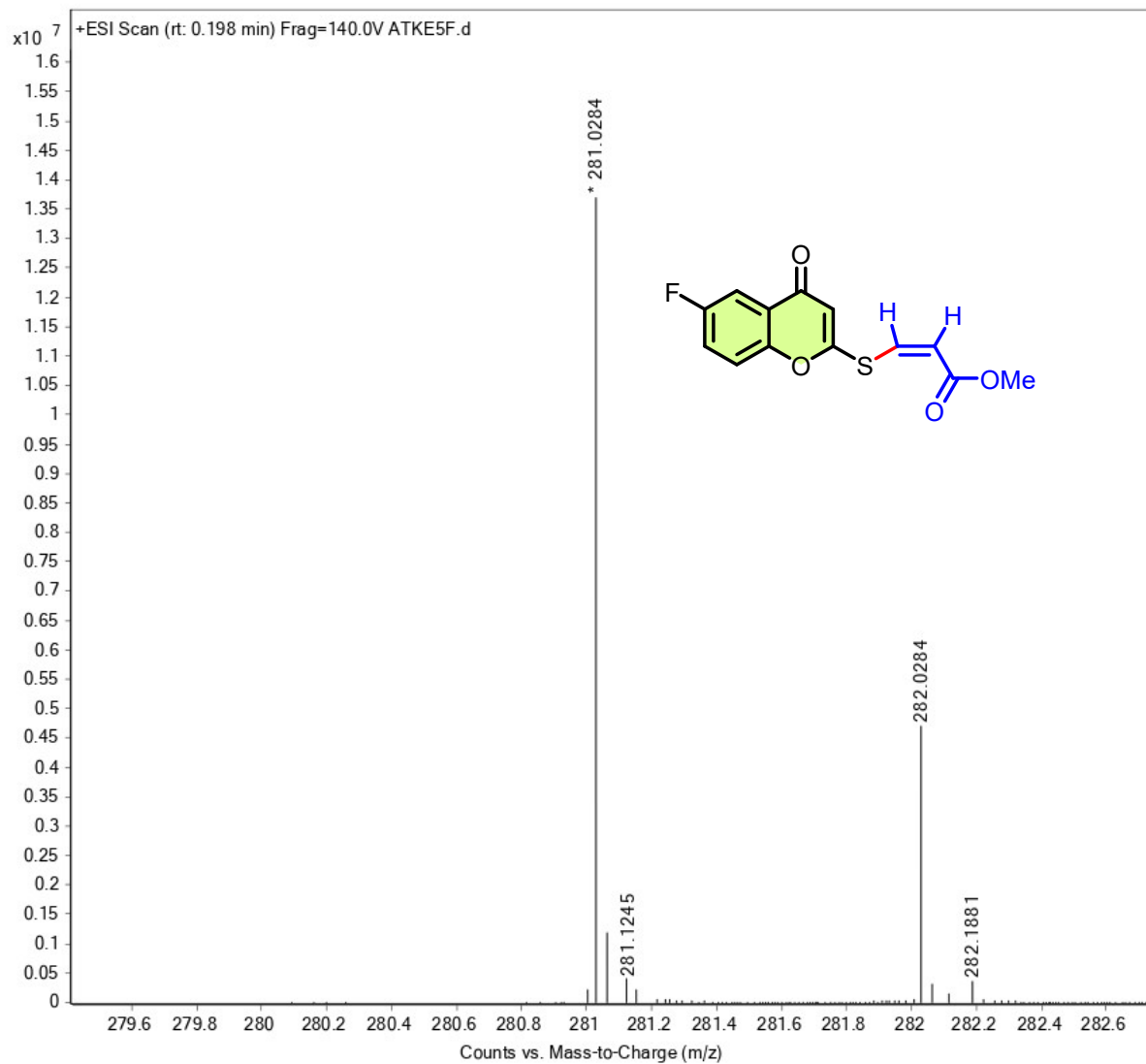
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 7da



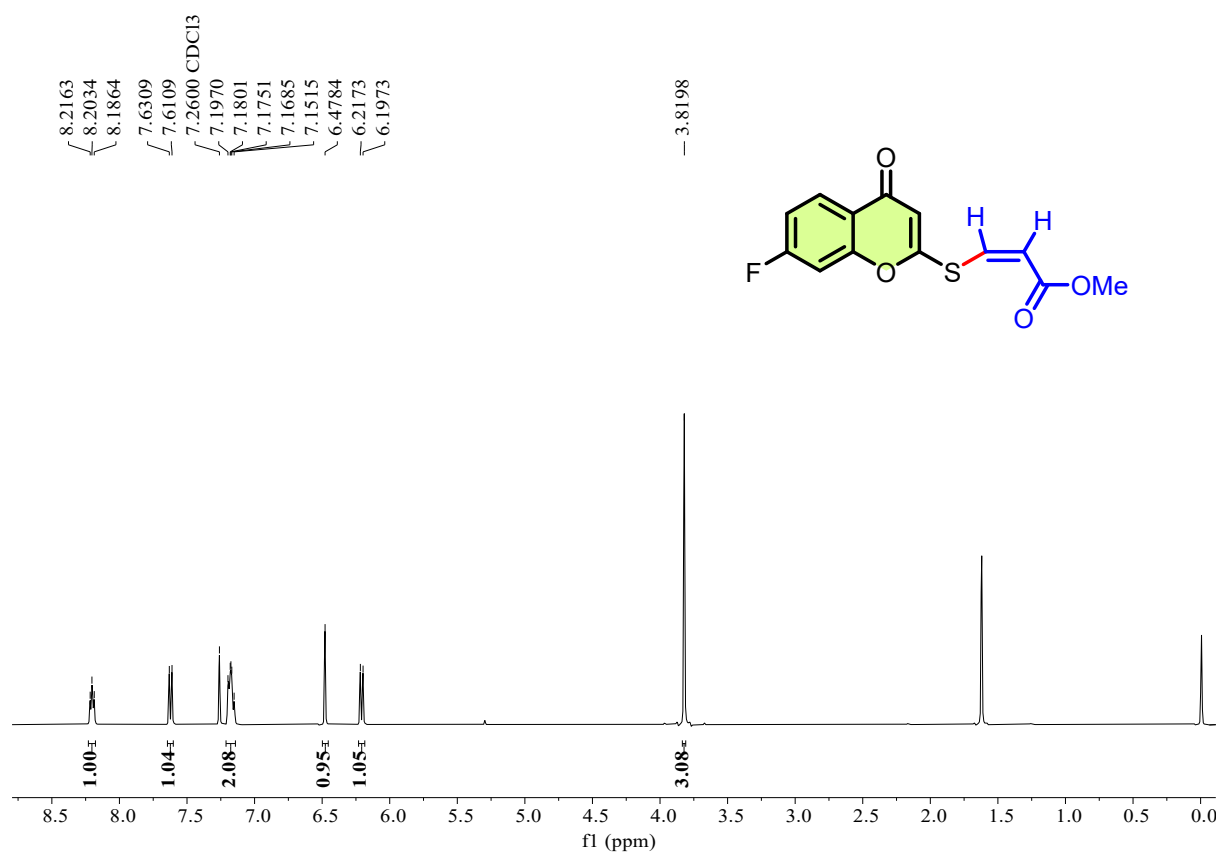
^{19}F NMR (564 MHz, CDCl_3) spectrum of compound 7da



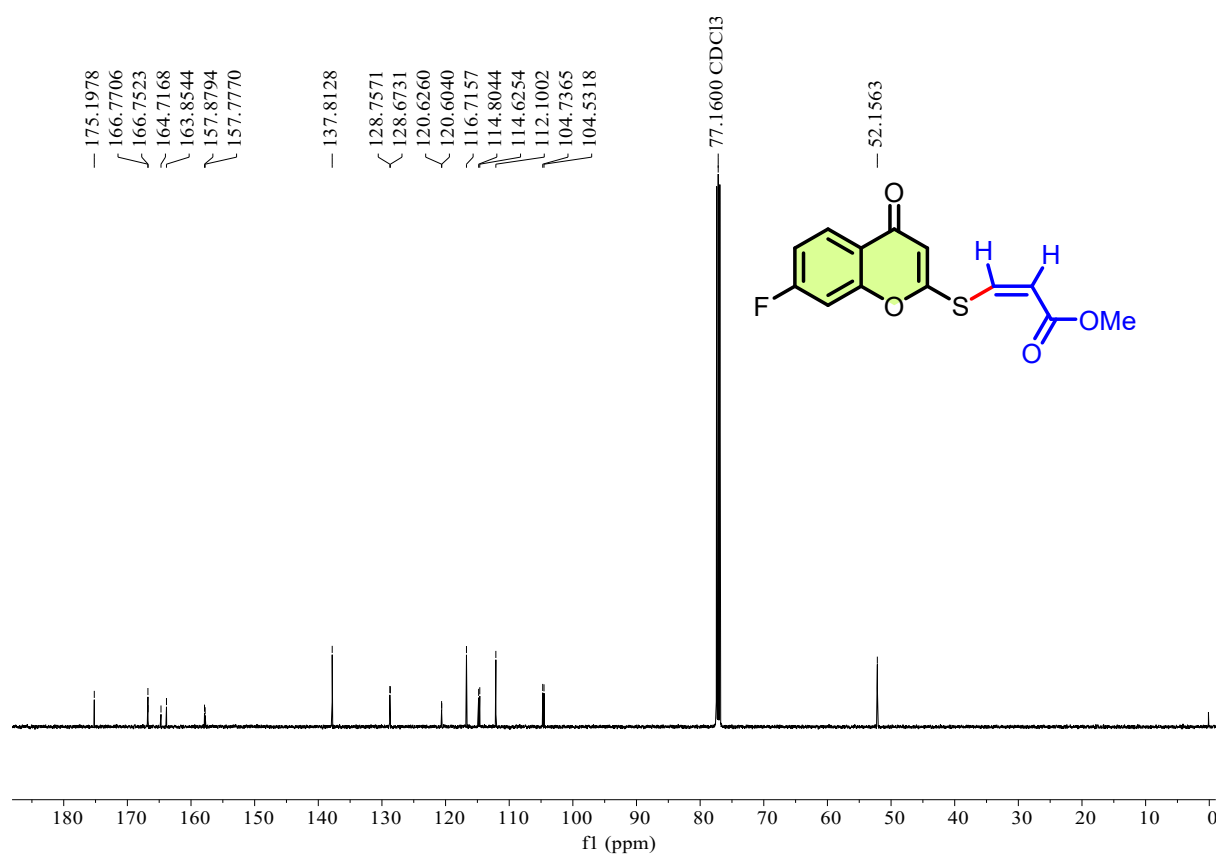
HRMS of compound 7da



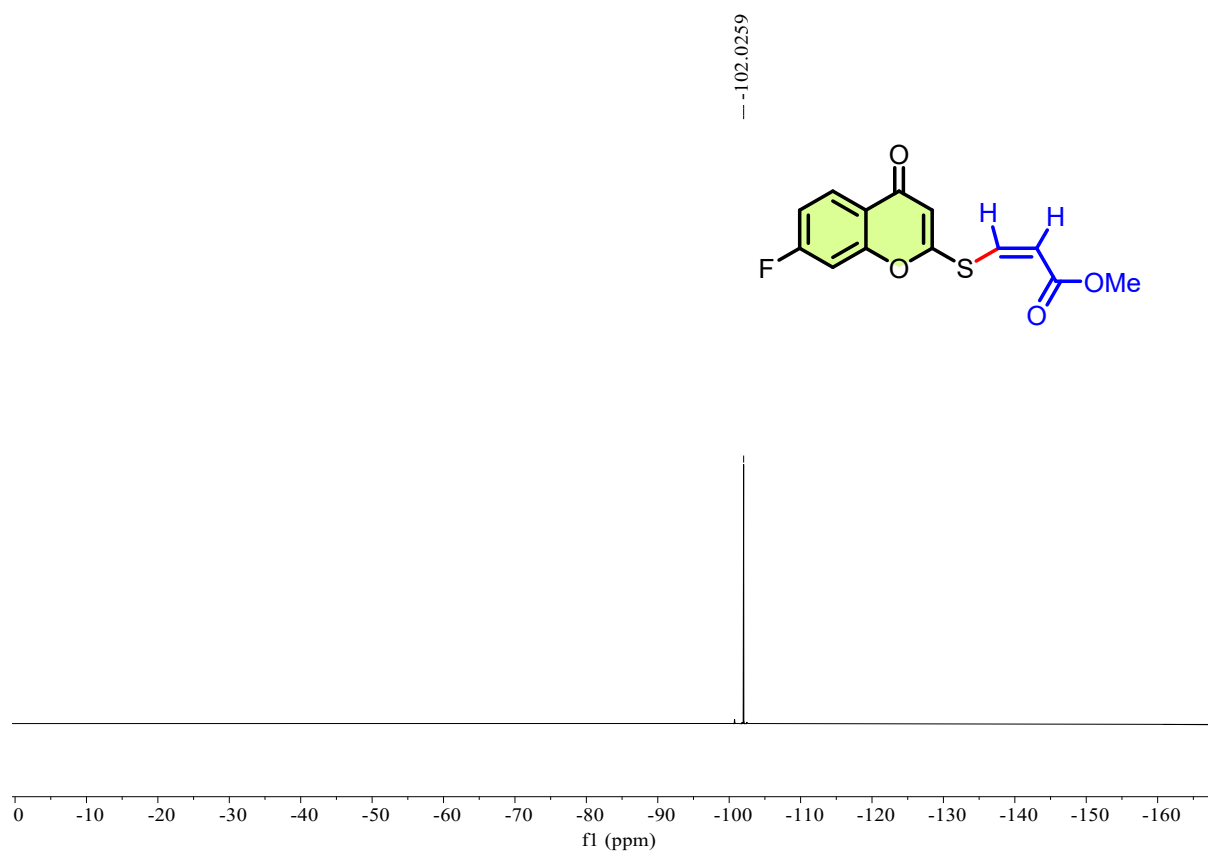
¹H NMR (500 MHz, CDCl₃) spectrum of compound 7ea



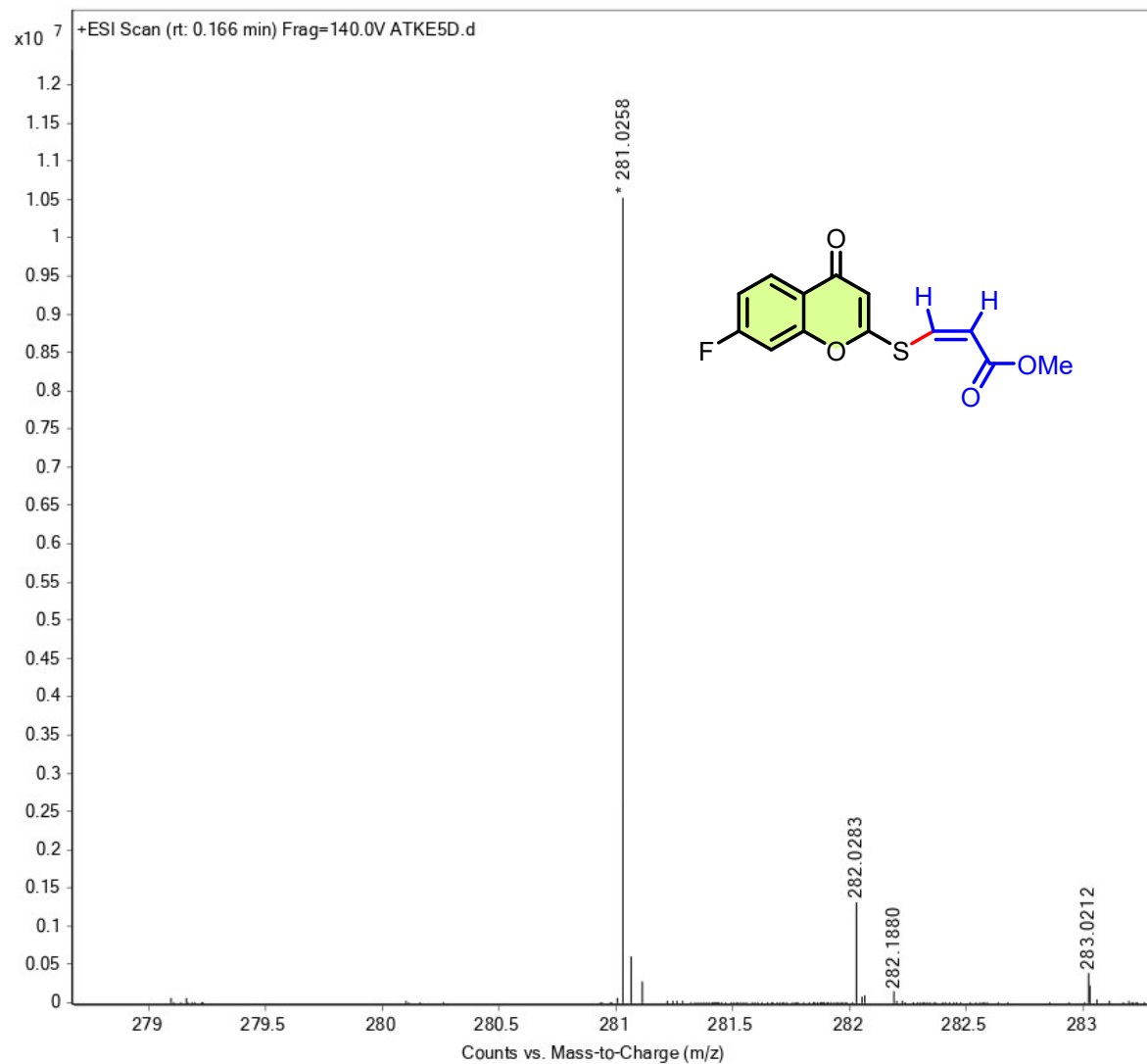
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) spectrum of compound 7ea



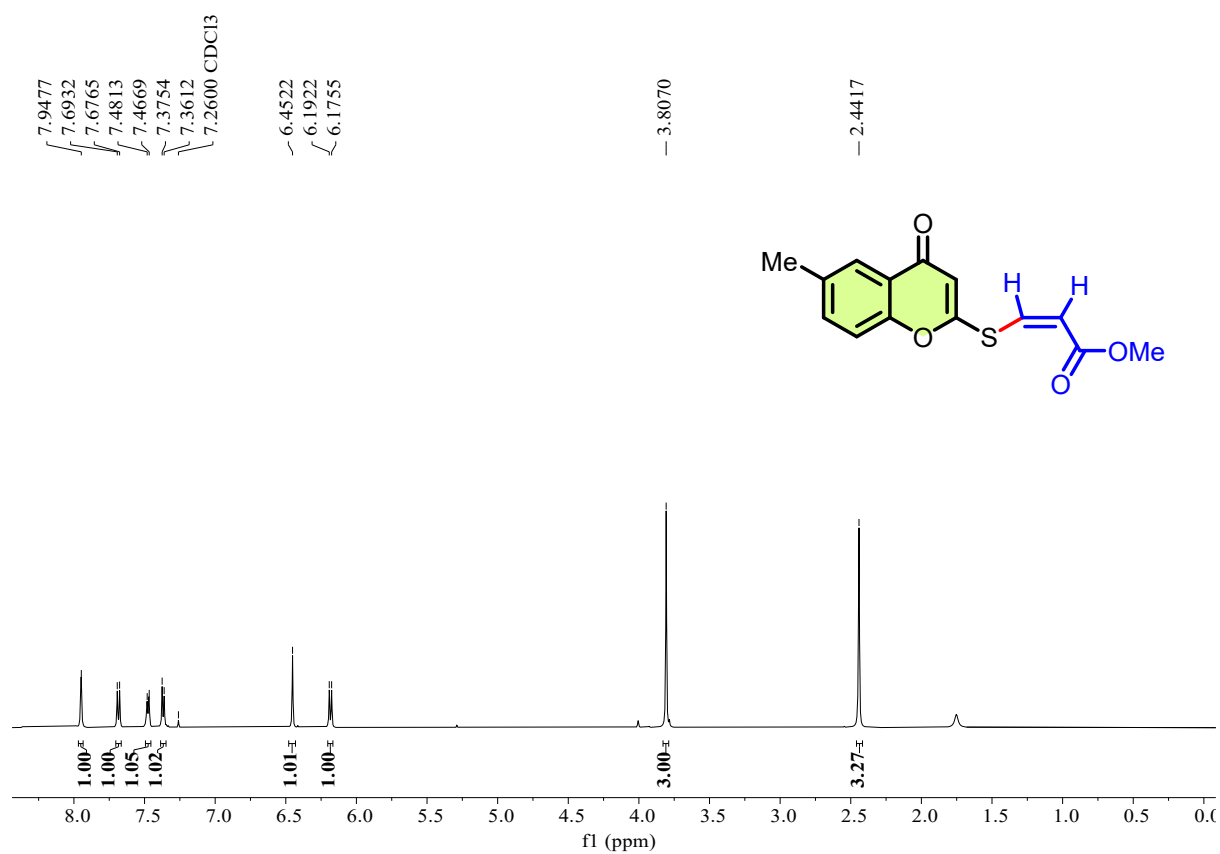
^{19}F NMR (377 MHz, CDCl_3) spectrum of compound 7ea



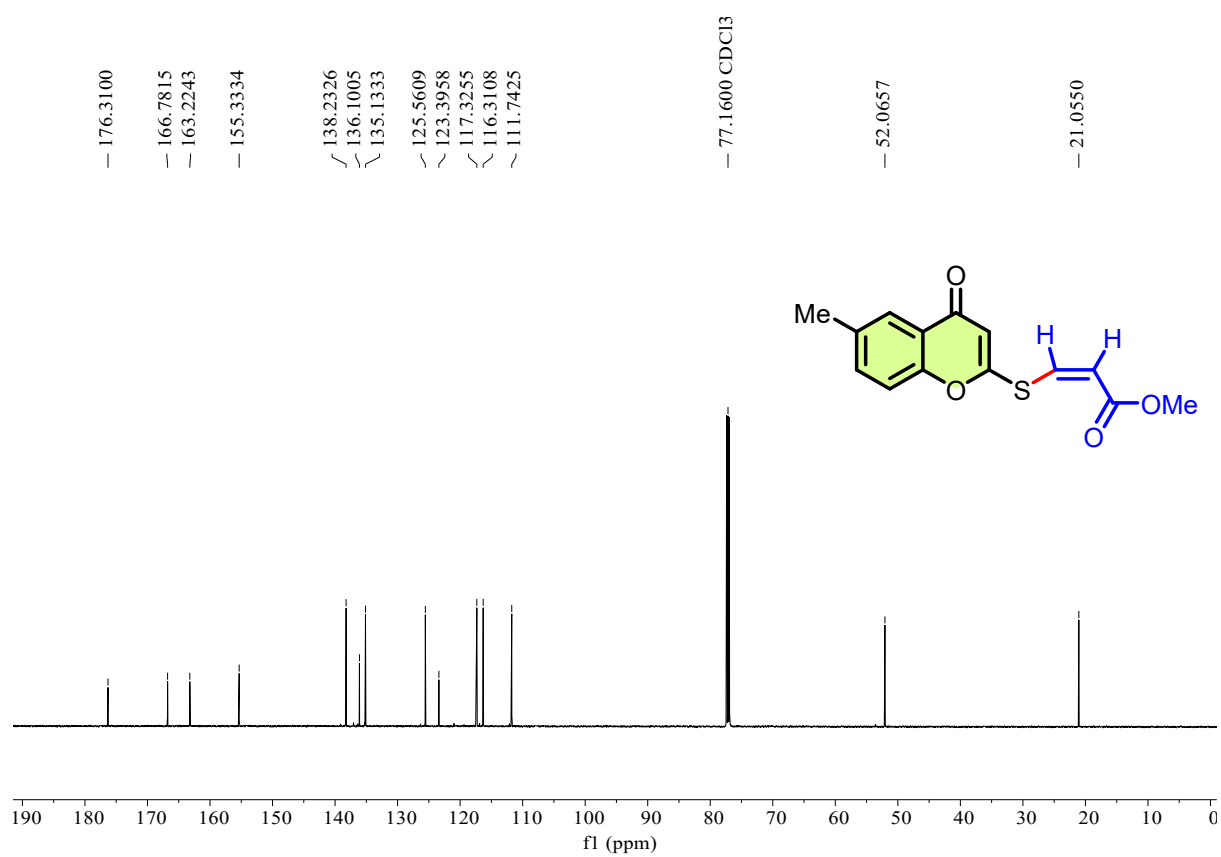
HRMS of compound 7ea



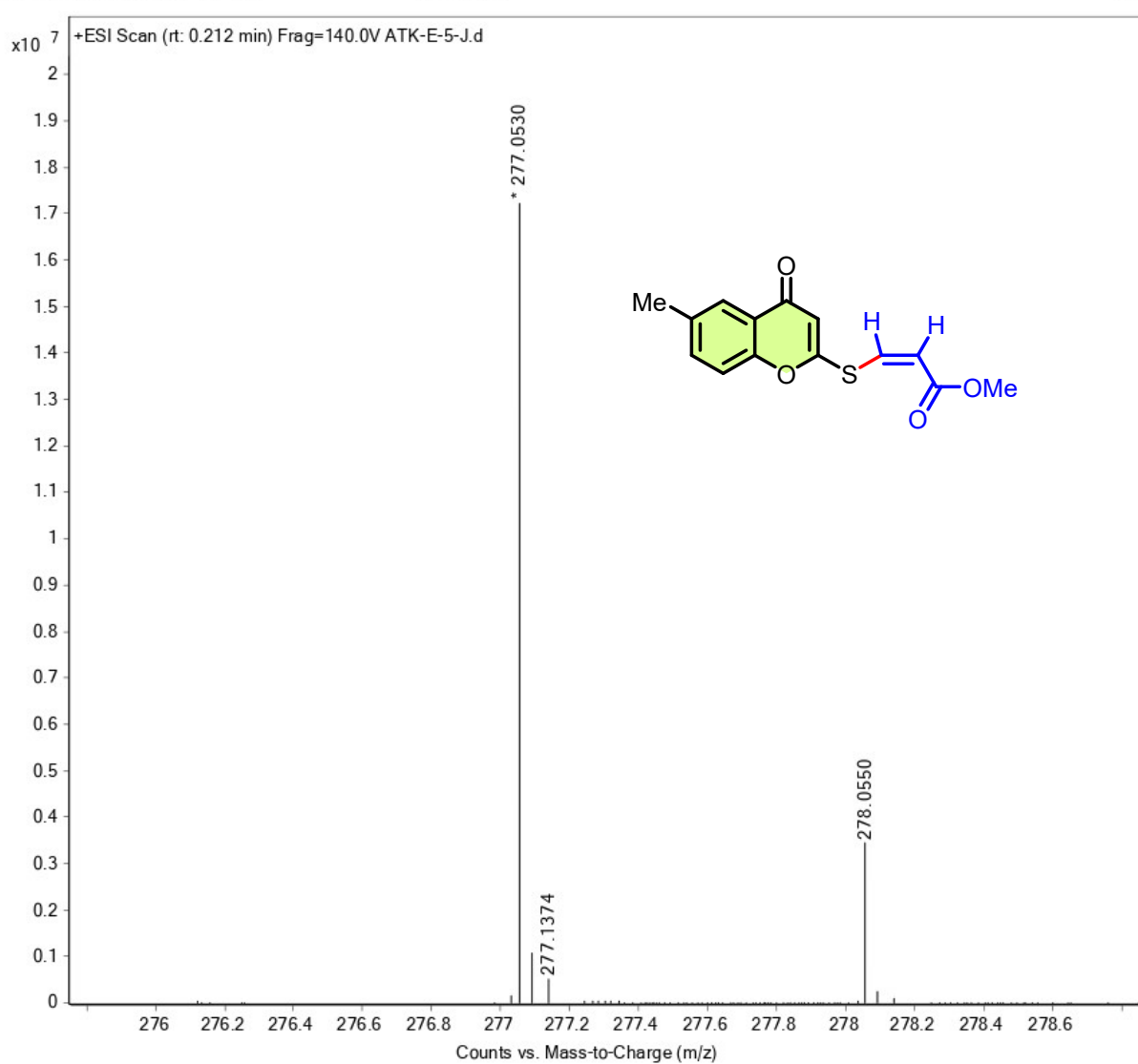
¹H NMR (600 MHz, CDCl₃) spectrum of compound 7fa



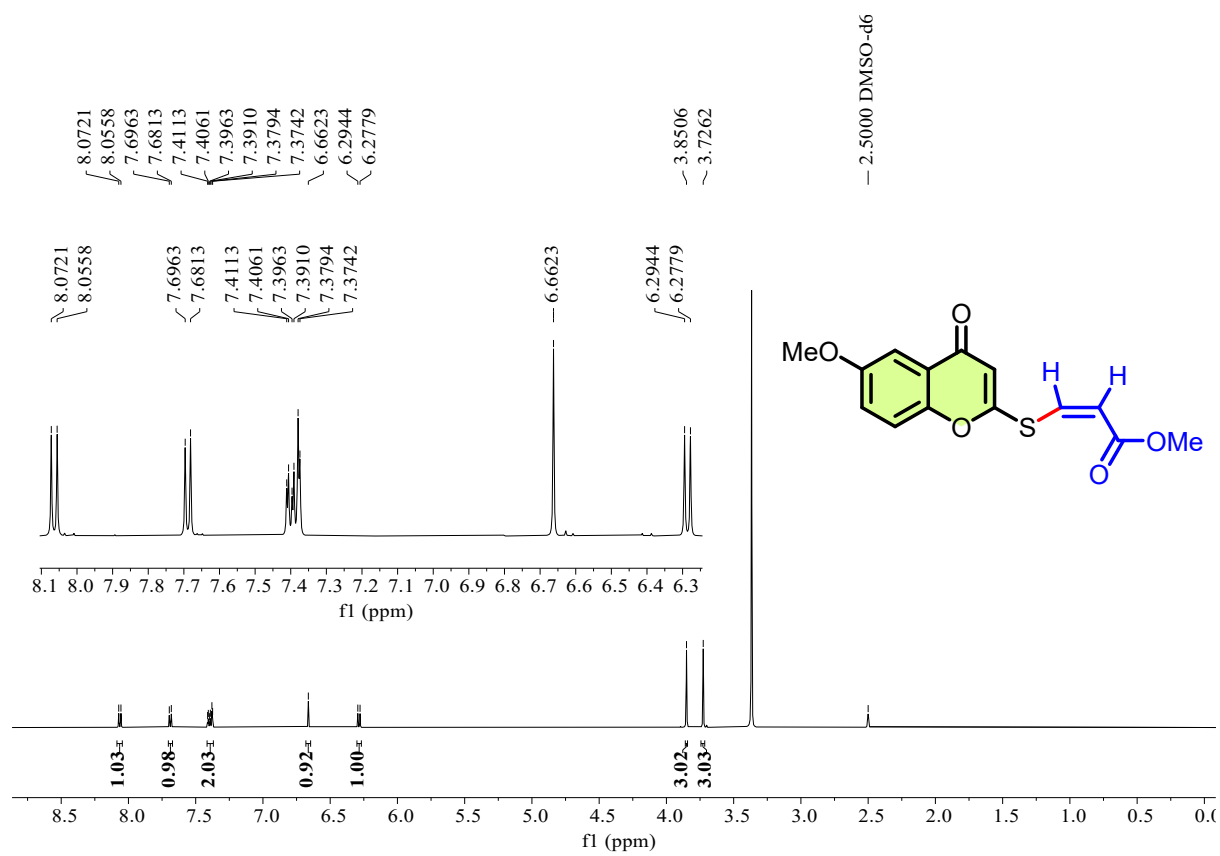
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) spectrum of compound 7fa



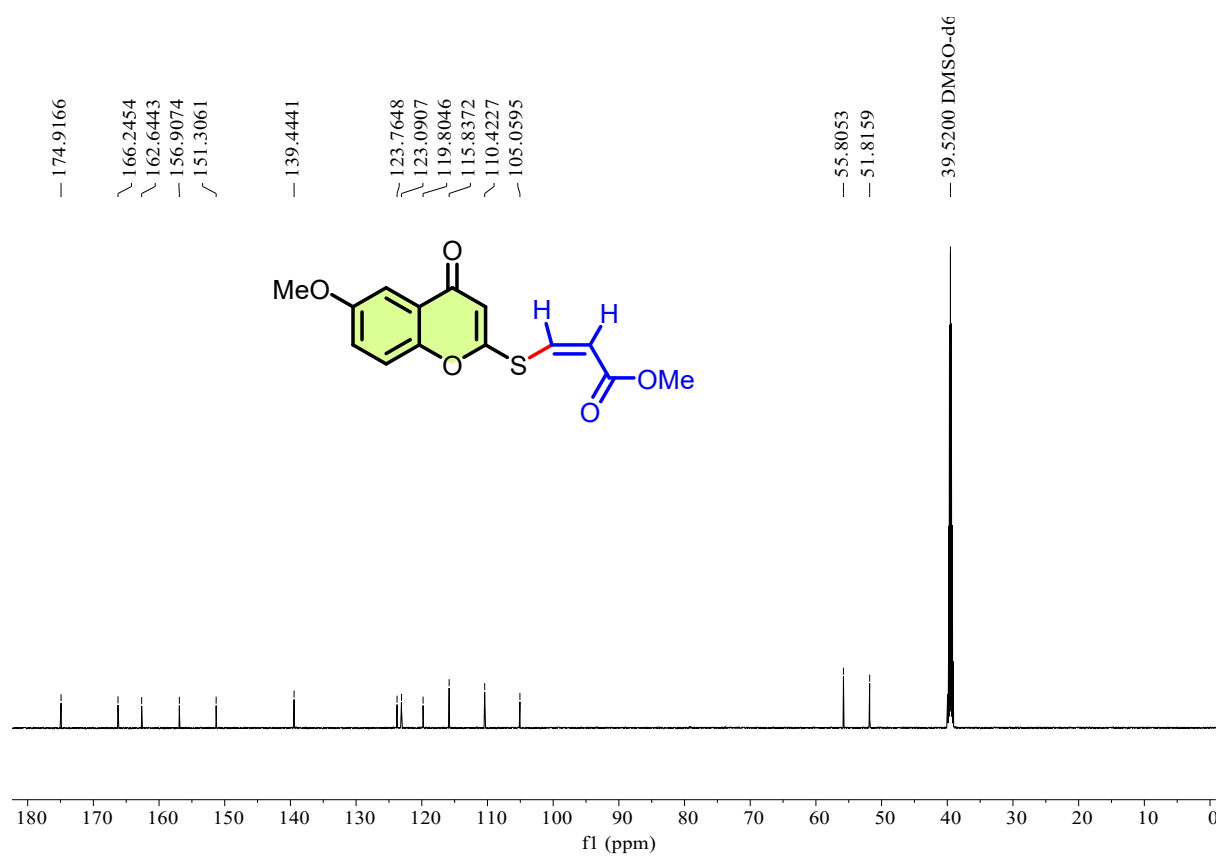
HRMS of compound 7fa



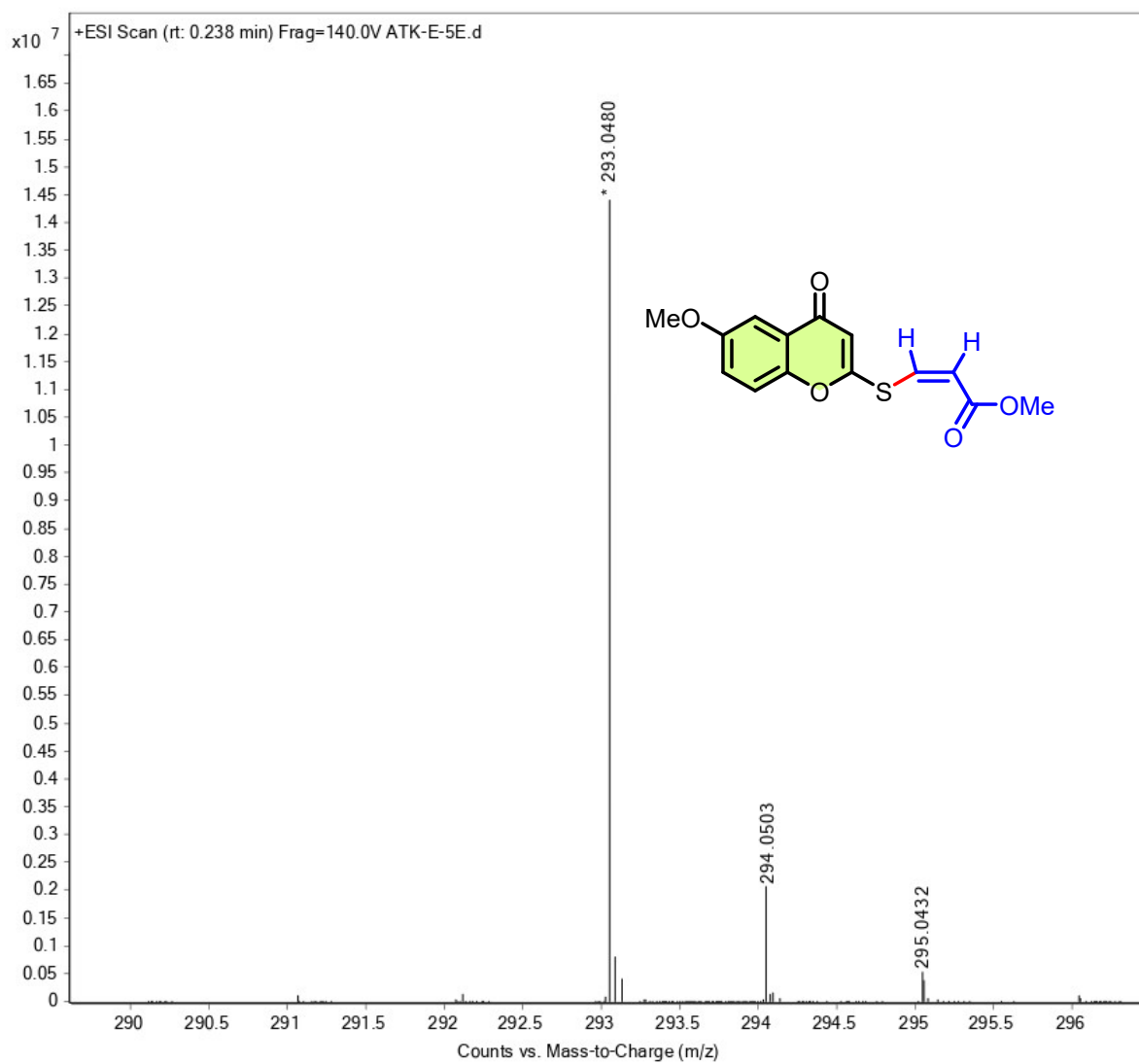
¹H NMR (600 MHz, CDCl₃) spectrum of compound 7ga



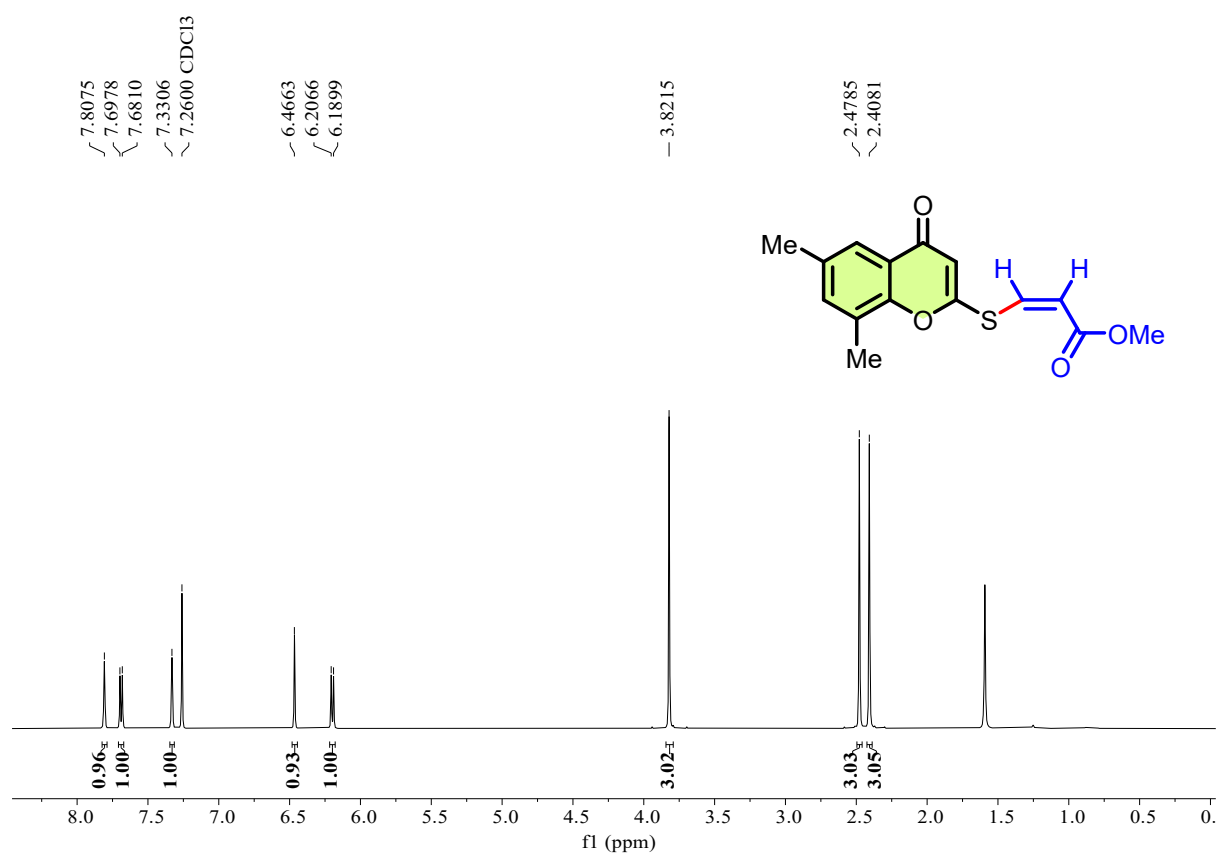
¹³C{¹H} NMR (150 MHz, CDCl₃) spectrum of compound 7ga



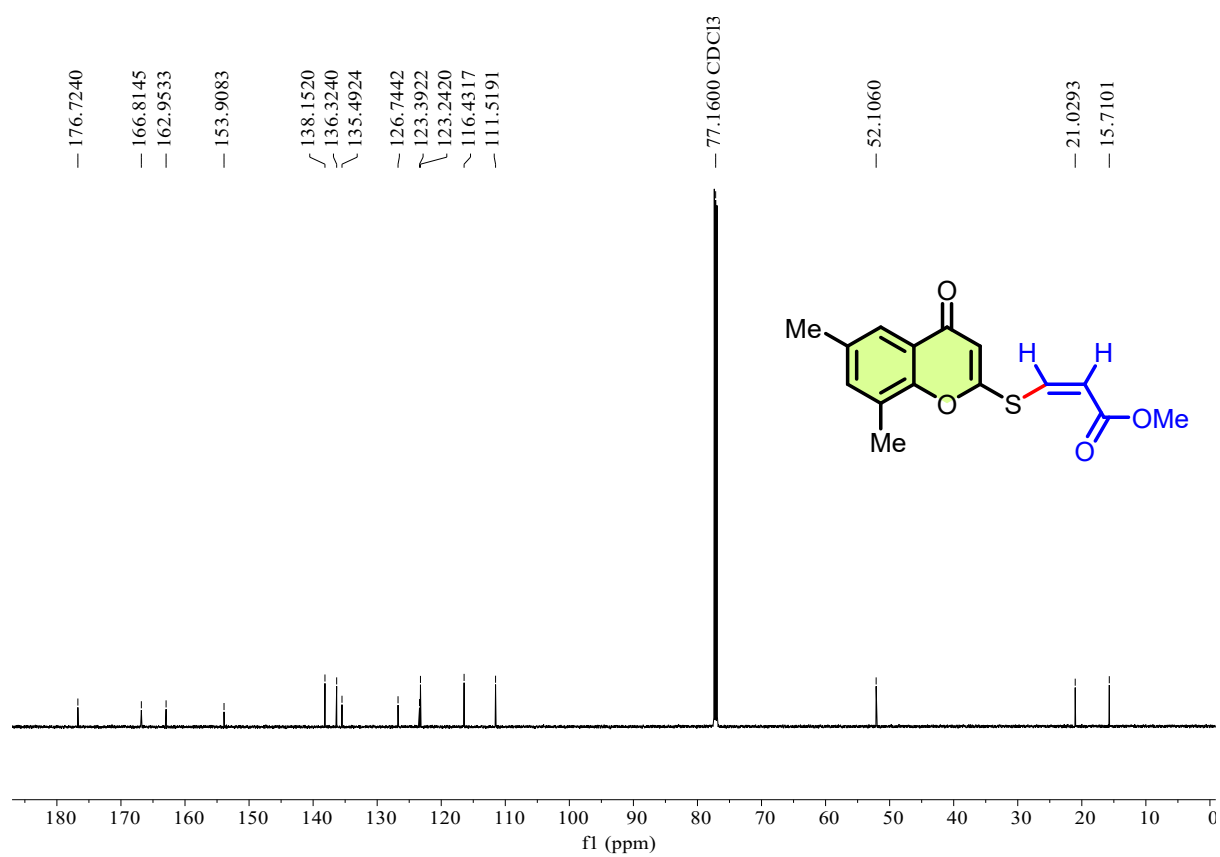
HRMS of compound 7ga



¹H NMR (600 MHz, CDCl₃) spectrum of compound 7ha



¹³C NMR (150 MHz, CDCl₃) spectrum of compound 7ha



HRMS of compound 7ha

