

Supporting Information

Regiodivergent Addition of Phenols to Allylic Oxides

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Ithaca, New York, 14850*

Table of Contents

General Procedures	page	S-2
X-ray data for 2a	page	S-3
X-ray data for 3h	page	S-4

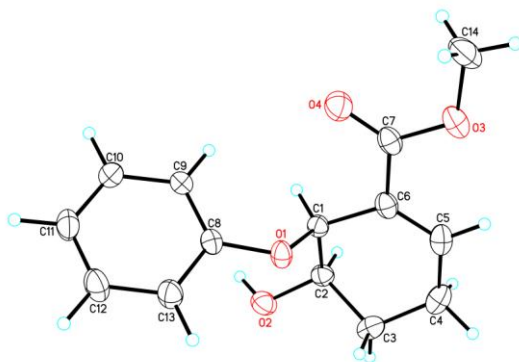
Spectra for Compounds

Compound 2a ¹ H and ¹³ C-NMR	page	S-20
Compound 3a ¹ H and ¹³ C-NMR	page	S-21
Compound 2c ¹ H and ¹³ C-NMR	page	S-22
Compound 3c ¹ H and ¹³ C-NMR	page	S-23
Compound 2e ¹ H and ¹³ C-NMR	page	S-24
Compound 3e ¹ H and ¹³ C-NMR	page	S-25
Compound 2f ¹ H and ¹³ C-NMR	page	S-26
Compound 3f ¹ H and ¹³ C-NMR	page	S-27
Compound 2g ¹ H and ¹³ C-NMR	page	S-28
Compound 3g ¹ H and ¹³ C-NMR	page	S-29
Compound 2h ¹ H and ¹³ C-NMR	page	S-30
Compound 3h ¹ H and ¹³ C-NMR	page	S-31
Compound 2i ¹ H and ¹³ C-NMR	page	S-32
Compound 3i ¹ H and ¹³ C-NMR	page	S-33
Compound 2j ¹ H and ¹³ C-NMR	page	S-34
Compound 3j ¹ H and ¹³ C-NMR	page	S-35
Compound 2k ¹ H and ¹³ C-NMR	page	S-36
Compound 3k ¹ H and ¹³ C-NMR	page	S-37
Compound 8 ¹ H and ¹³ C-NMR	page	S-38
Compound 9 ¹ H and ¹³ C-NMR	page	S-39
Compound 10 ¹ H and ¹³ C-NMR	page	S-40
Compound 11 ¹ H and ¹³ C-NMR	page	S-41
Compound 13 ¹ H and ¹³ C-NMR	page	S-42
Compound 14 ¹ H and ¹³ C-NMR	page	S-43
Compound 15 ¹ H and ¹³ C-NMR	page	S-44
Compound 16 ¹ H and ¹³ C-NMR	page	S-45
Compound 18 ¹ H and ¹³ C-NMR	page	S-46
Compound 19 ¹ H and ¹³ C-NMR	page	S-47
Compound 20 ¹ H and ¹³ C-NMR	page	S-48
Compound 21 ¹ H and ¹³ C-NMR	page	S-49

General Procedures. Where appropriate, reactions were carried out under an inert atmosphere of argon or nitrogen with dry solvents, using anhydrous conditions unless otherwise stated. Dry toluene, dichloromethane (DCM), diethyl ether, and triethylamine (Et₃N), were obtained by passing the previously degassed solvents through activated alumina columns. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketal before use. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (¹H-NMR) homogeneous material. Flash column chromatography was performed using Silicycle Silica Gel 60 Å (40-53 μm) or Florisil F-101 (100-200 mesh). Analytical thin-layer chromatography (TLC) was performed using Merck Silica Gel 60 Å F-254 precoated plates (0.25 mm thickness). Preparatory HPLC (P-HPLC) was performed with a single wavelength detector using either an Xterra Prep RP8 (5 μm, 7.6 x 100 mm) or Atlantis Prep T3 (10 μm, 19 x 150 mm) column. Proton NMR spectra were recorded on either a 300, 400, or 500 MHz spectrometer. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (δ 0.0). Data is reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q) and multiplet (m)], coupling constants [Hz], integration). Carbon NMR spectra were recorded on a 300 (75 MHz) or 400 (100 MHz) spectrometer with proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to deuterated chloroform (δ 77.16). NMR data was collected at 25 °C. Infrared spectra were obtained on a FT-IR spectrometer. Melting points are uncorrected. Analytical normal phase HPLC was performed with a single wavelength detector (230 nm) using a Chiralpak AD-RH column (5 μm, 4.6 x 150 mm, 20 °C). Analytical GC was performed on a chromatograph equipped with a FID detector using a J+W Scientific column (5 μm, 30 m x 0.250 mm). Low-resolution mass spectra (LRMS) were recorded on an LC/MSD TOF mass spectrometer by electrospray (ES) or atmospheric-pressure chemical ionization (ACPI) time of flight experiment. High-resolution mass spectra were obtained on a mass spectrometer (magnetic sector) using electron impact experiments or on a mass spectrometer with a DART SVP ion source. The method of ionization is given in parentheses. Optical rotations were recorded on a polarimeter at the sodium D line (path length 1 dm, corrected to 20.0 °C).

X-ray data

Samples of **2a** and **3h** were prepared for X-ray crystallography analysis by slow solvent evaporation (9:1 hexanes:isopropanol (v/v)).



Crystal data for 2a

Selected parameters:

Empirical formula

C₁₄H₁₆O₄

Formula weight

248.27

Crystal system

Orthorhombic

Space group

P2(1)2(1)2(1)

Unit cell dimensions

a = 8.1690(4) Å

α = 90°

b = 8.3603(4) Å

β = 90°

c = 18.2330(9) Å

γ = 90°

Volume

1245.23(11) Å³

Z

4

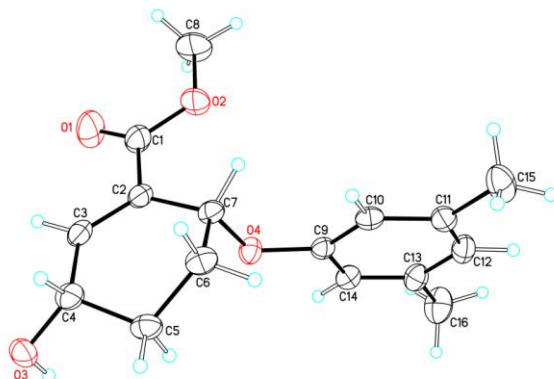
Final R indices [I > 2σ(I)]

R1 = 0.0323, wR2 = 0.0810

R indices (all data)

R1 = 0.0400, wR2 = 0.0866

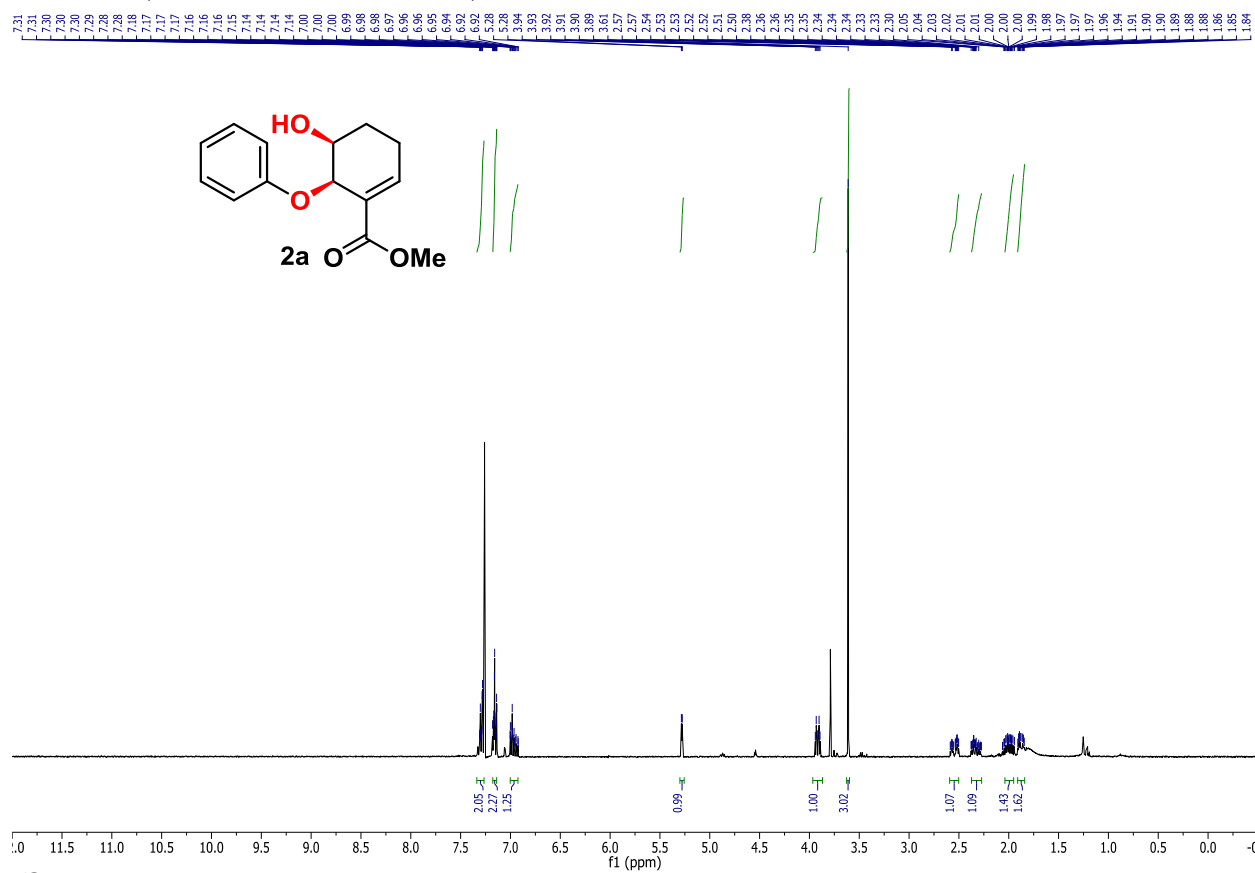
Crystal data for 3h



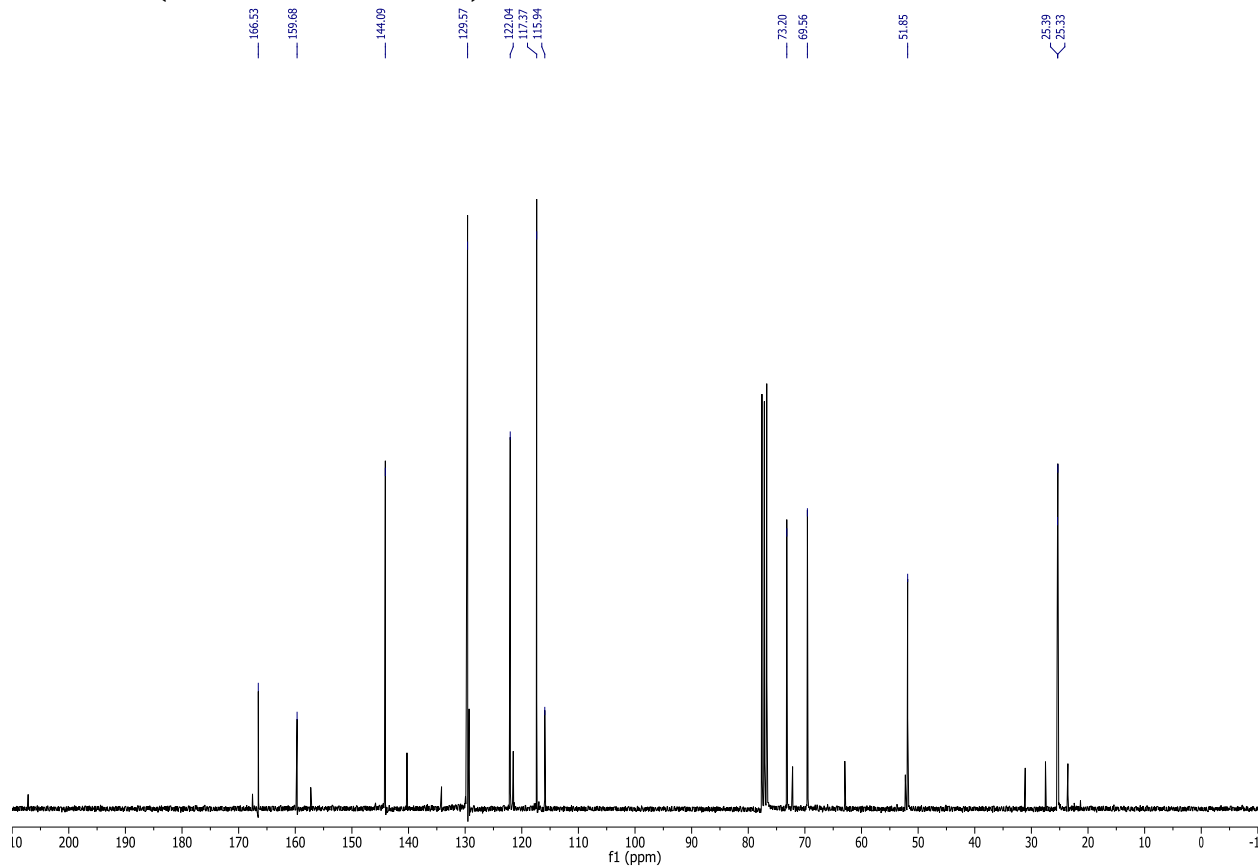
Selected parameters:

Empirical Formula	$\text{C}_{16}\text{H}_{20}\text{O}_4$	
Formula weight	276.32	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	$a = 32.791(2) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 32.791(2) \text{ \AA}$	$\beta = 90^\circ$
	$c = 7.4776(3) \text{ \AA}$	$\gamma = 120^\circ$
Volume	$6962.9(7) \text{ \AA}^3$	
Z	18	
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0422, wR2 = 0.0865$	
R indices (all data)	$R1 = 0.0974, wR2 = 0.1064$	

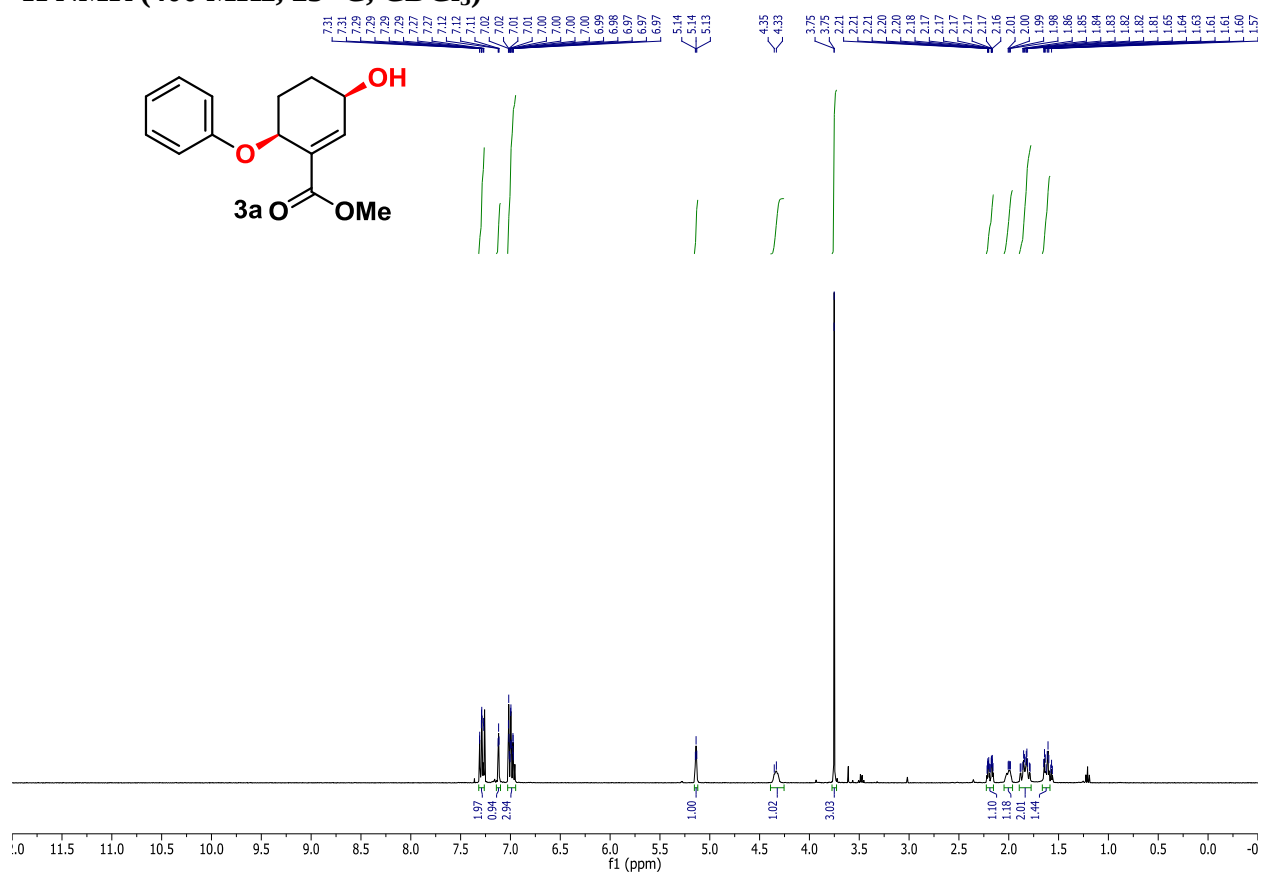
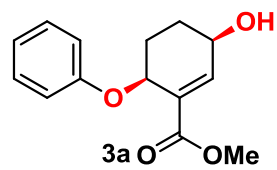
^1H NMR (400 MHz, 23 °C, CDCl_3)



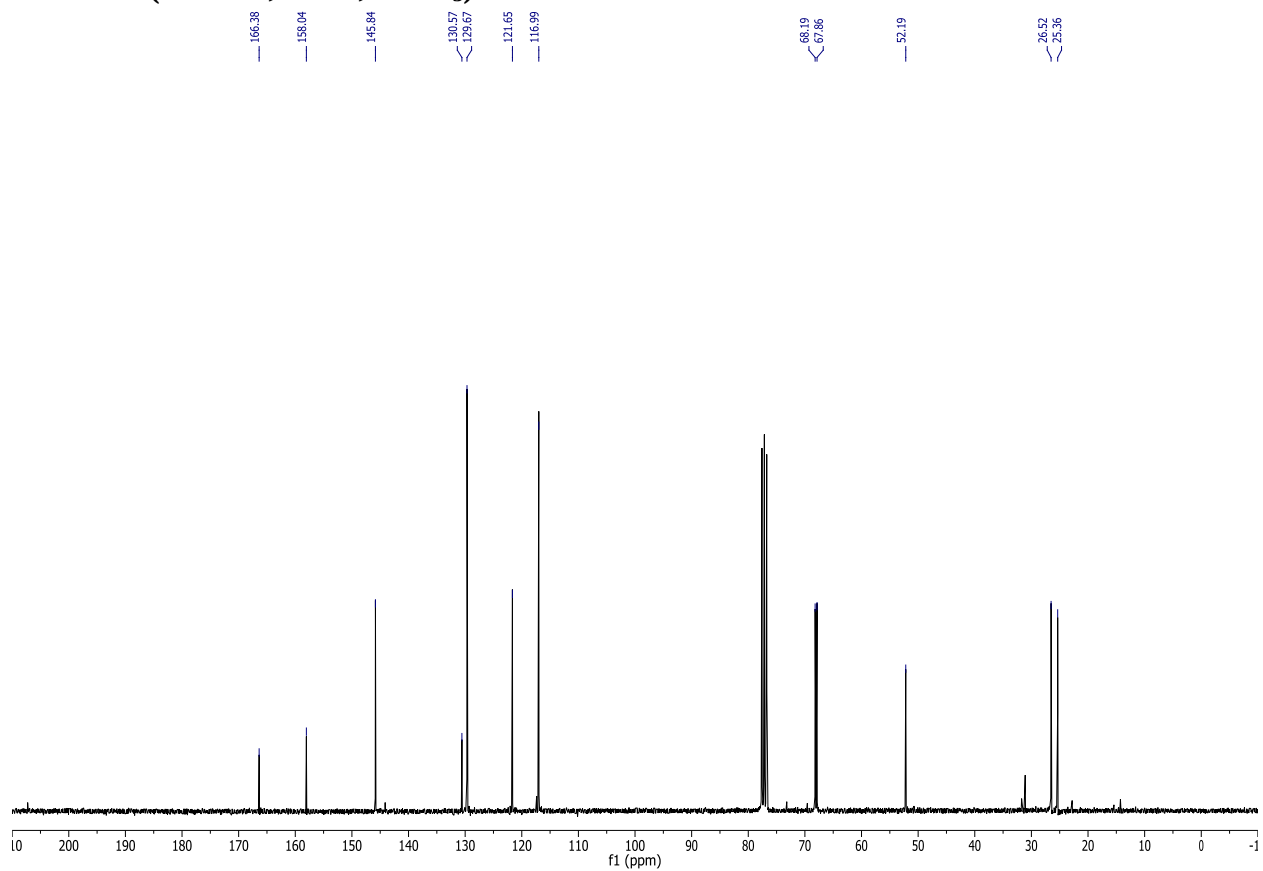
^{13}C NMR (75 MHz, 23 °C, CDCl_3)



^1H NMR (400 MHz, 23 °C, CDCl_3)



^{13}C NMR (75 MHz, 23 °C, CDCl_3)

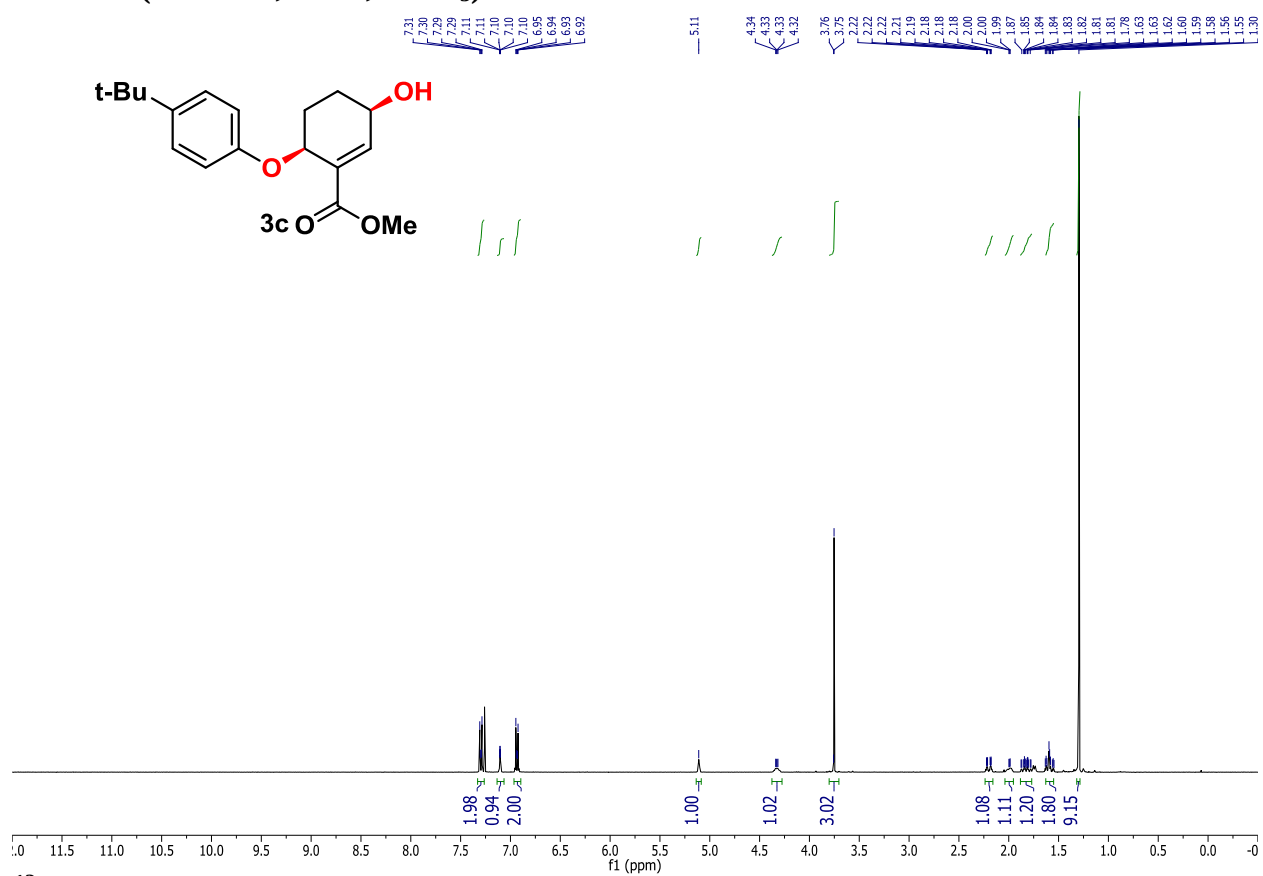


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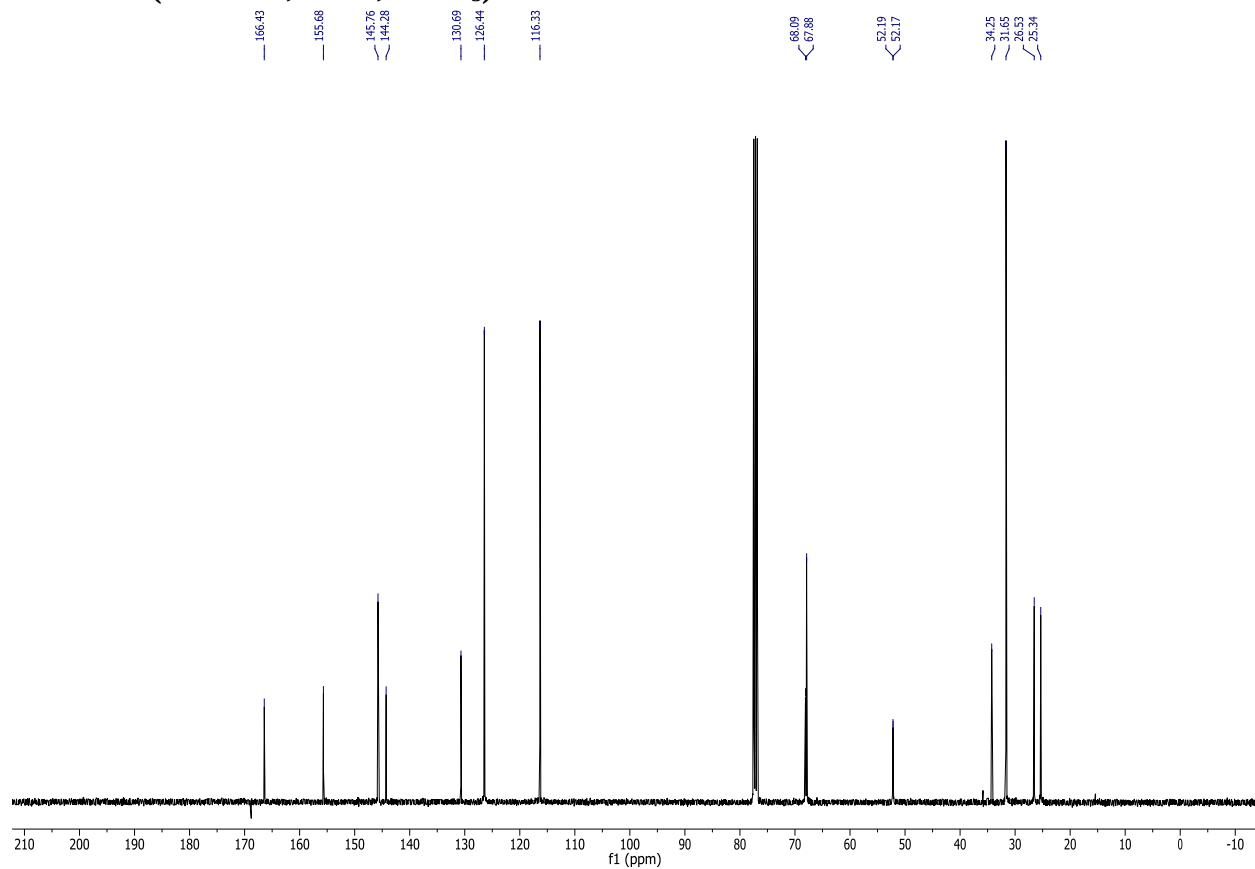
¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from 10 to -1. The spectrum shows several sharp peaks, with the following chemical shifts labeled above the corresponding peaks:

Chemical Shift (ppm)
166.61
157.29
144.69
143.98
129.44
126.38
116.72
73.12
69.52
51.85
34.27
31.64
25.42
25.25

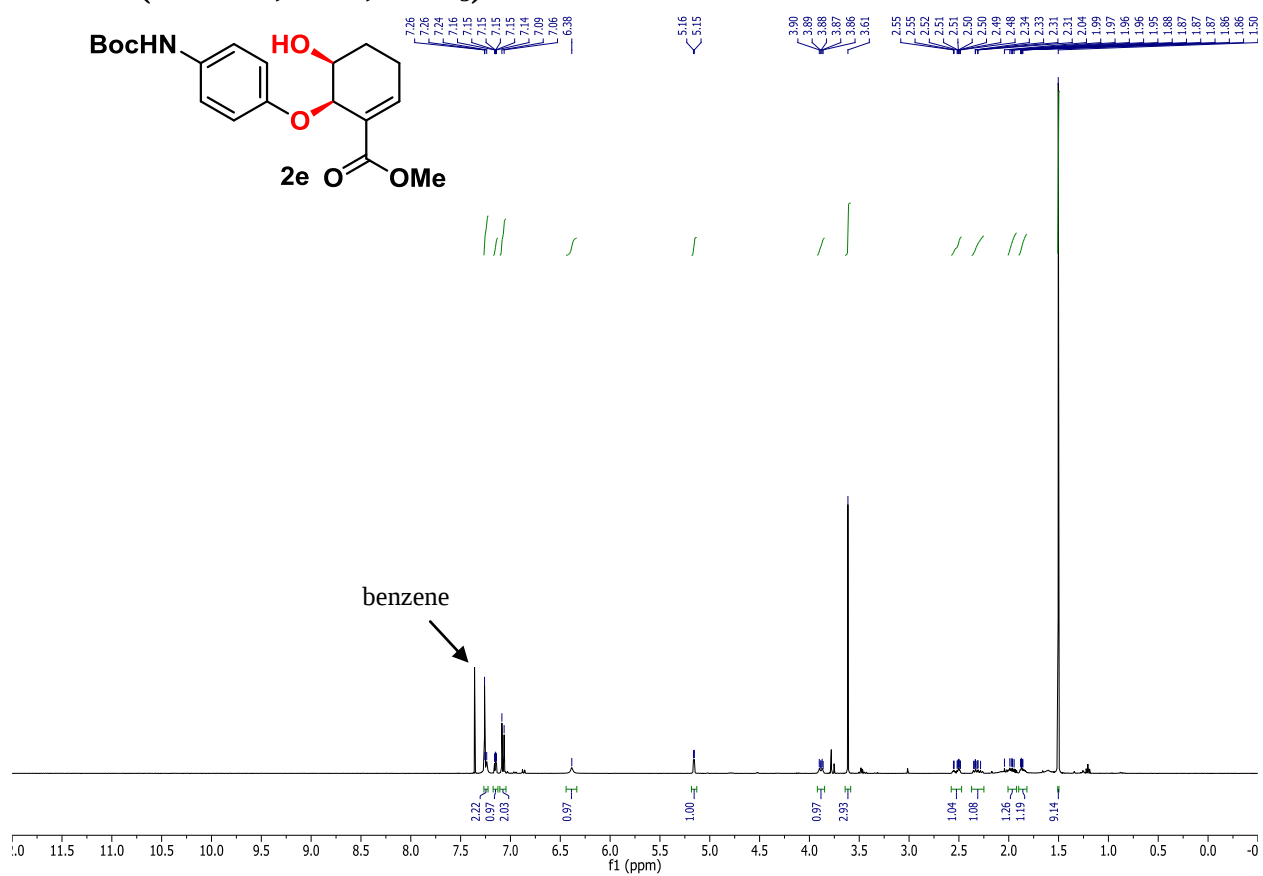
^1H NMR (400 MHz, 23 °C, CDCl_3)



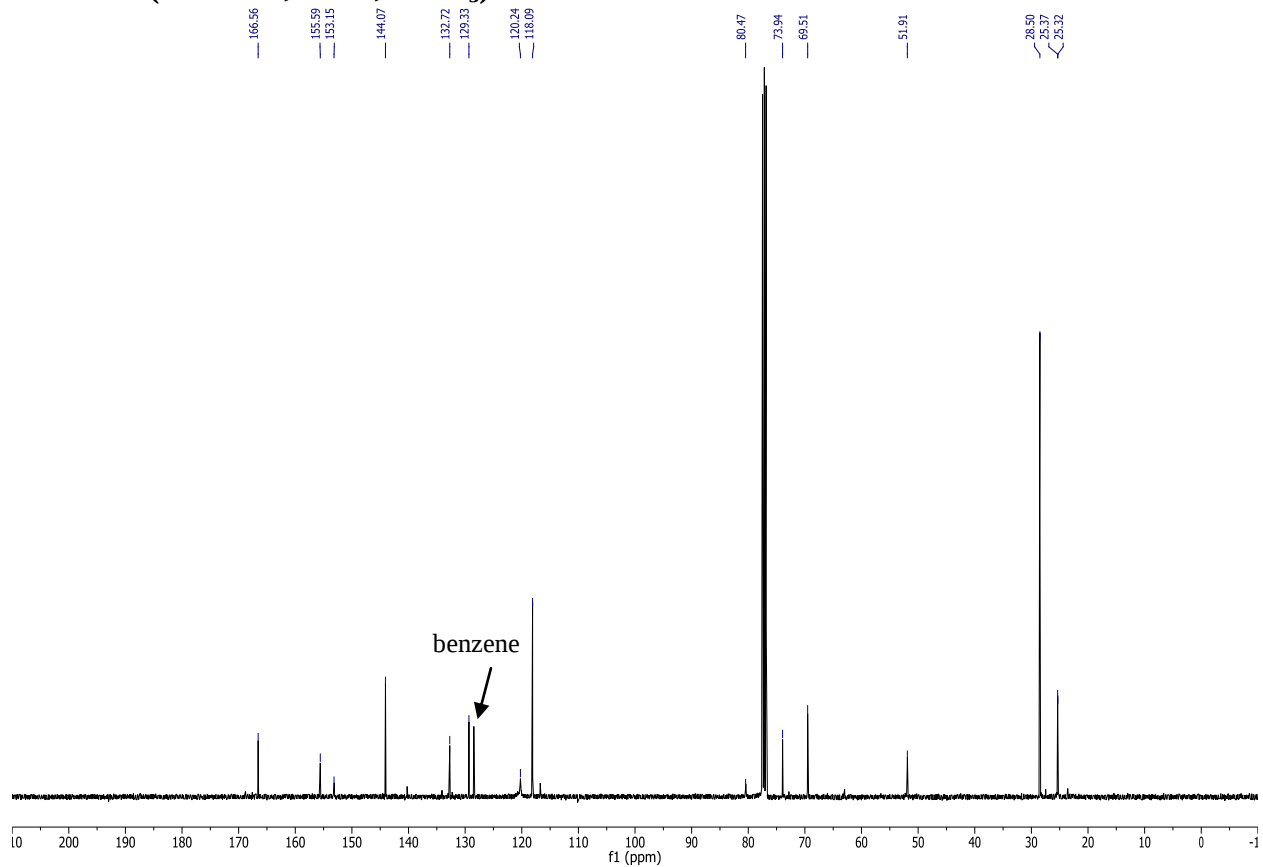
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



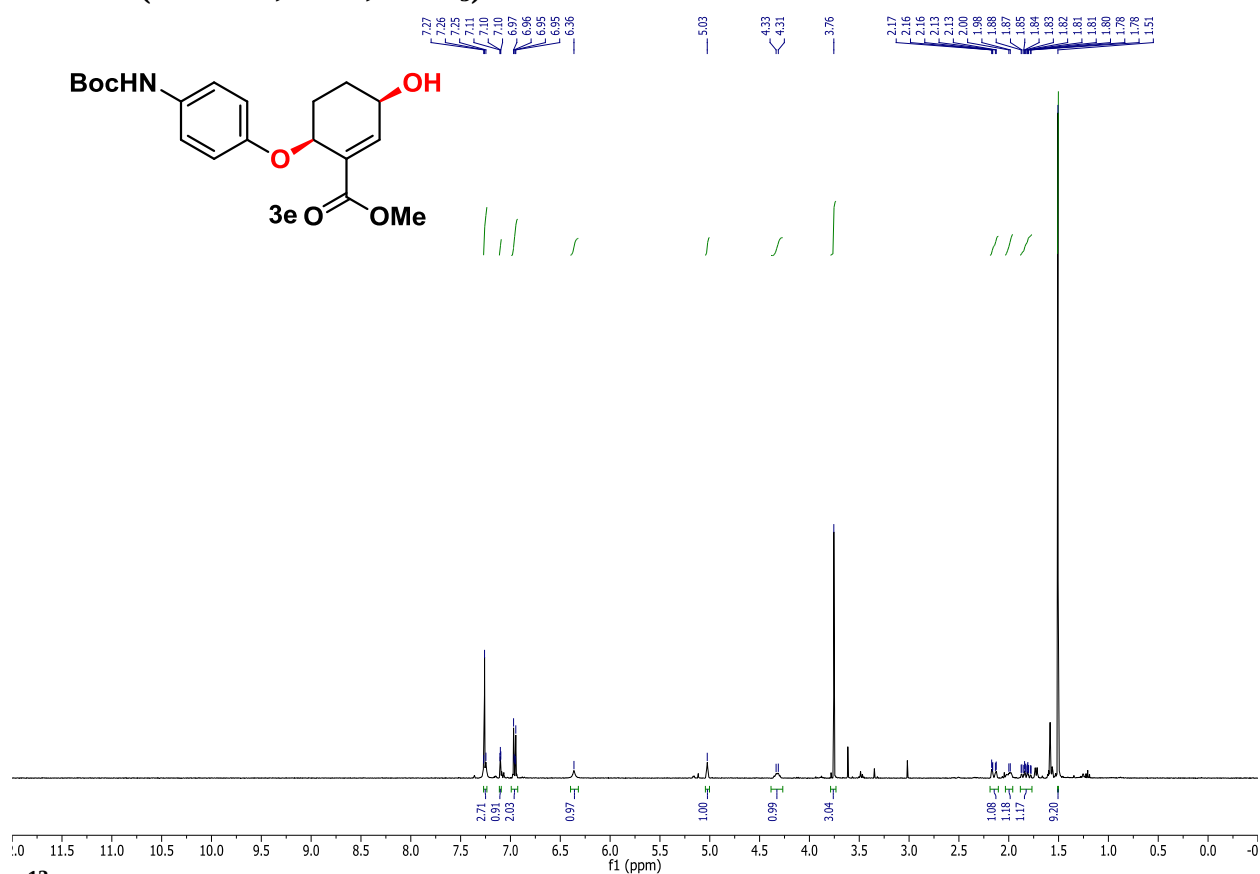
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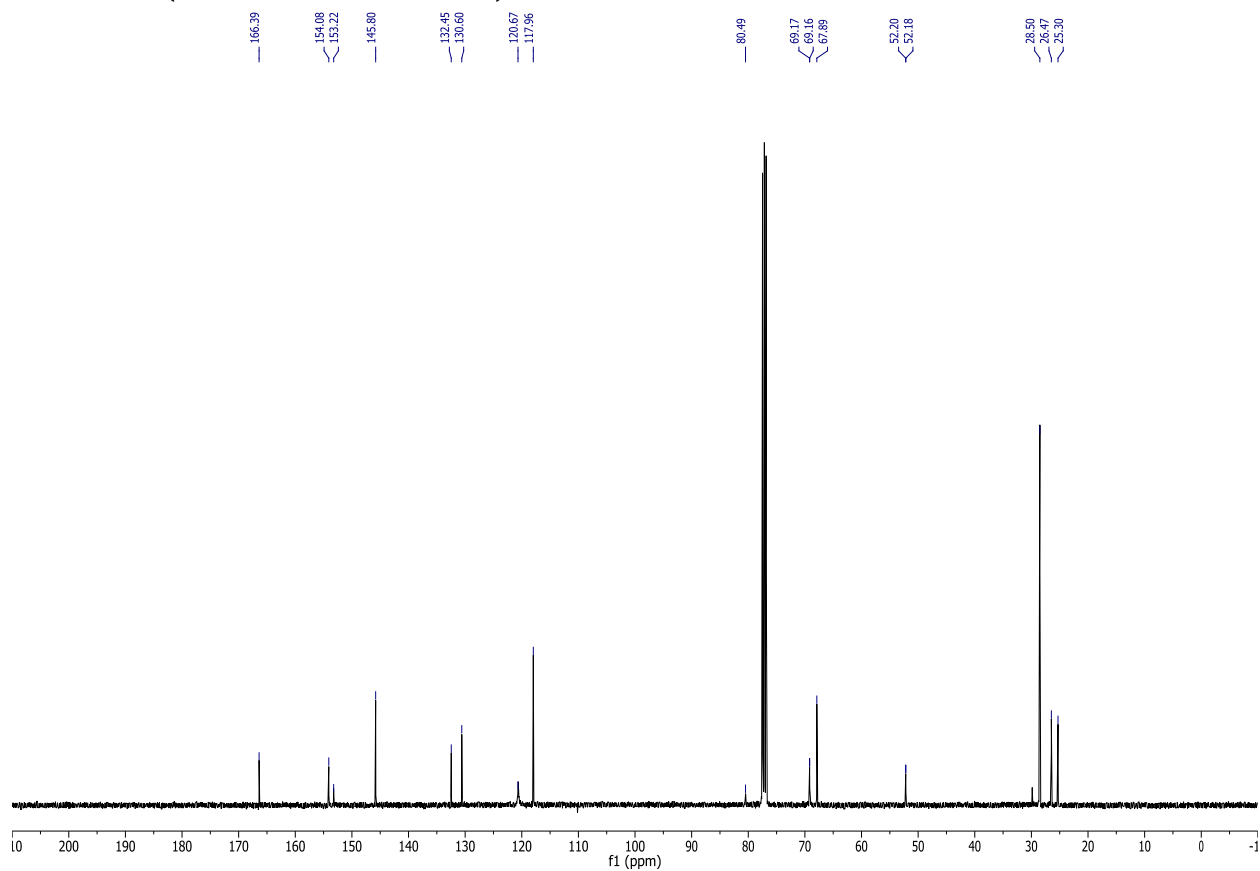
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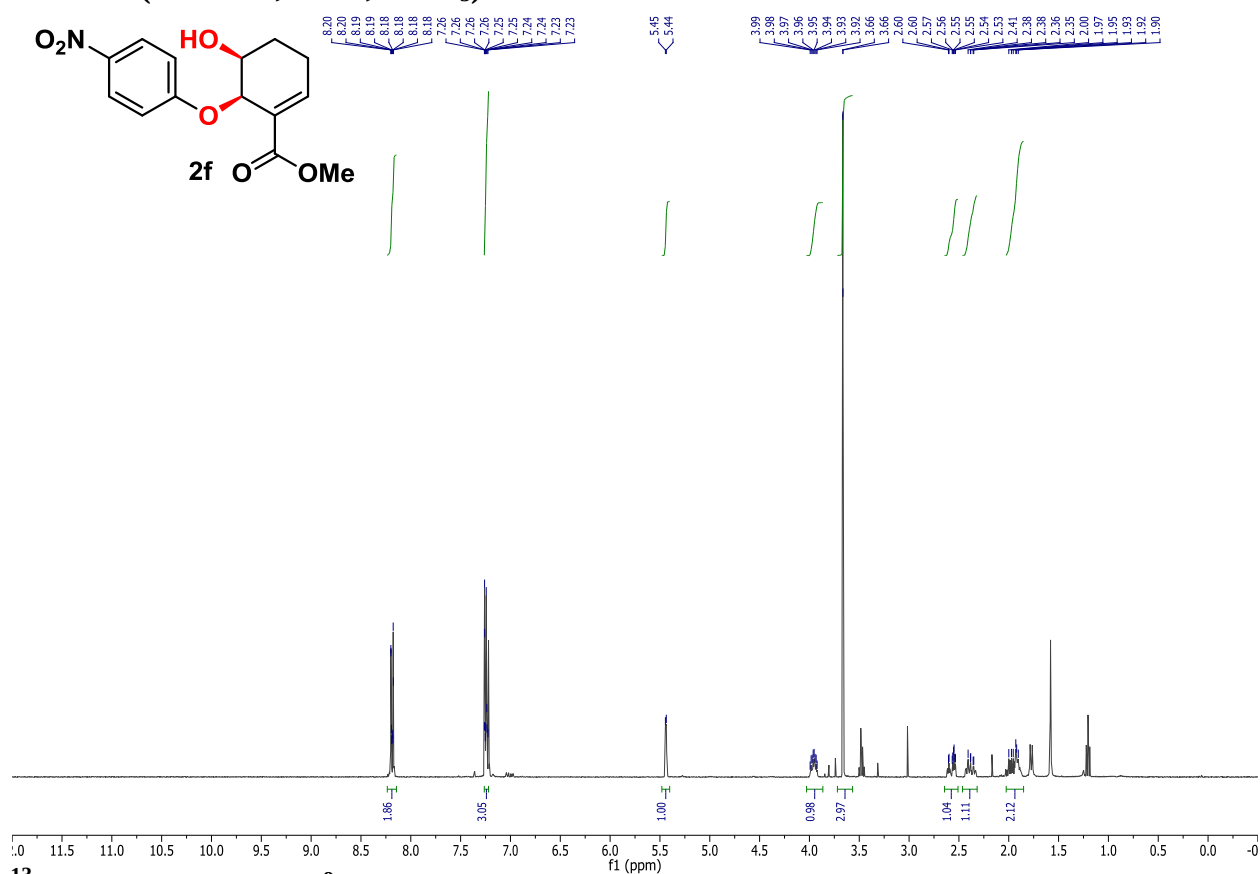
^1H NMR (400 MHz, 23 °C, CDCl_3)



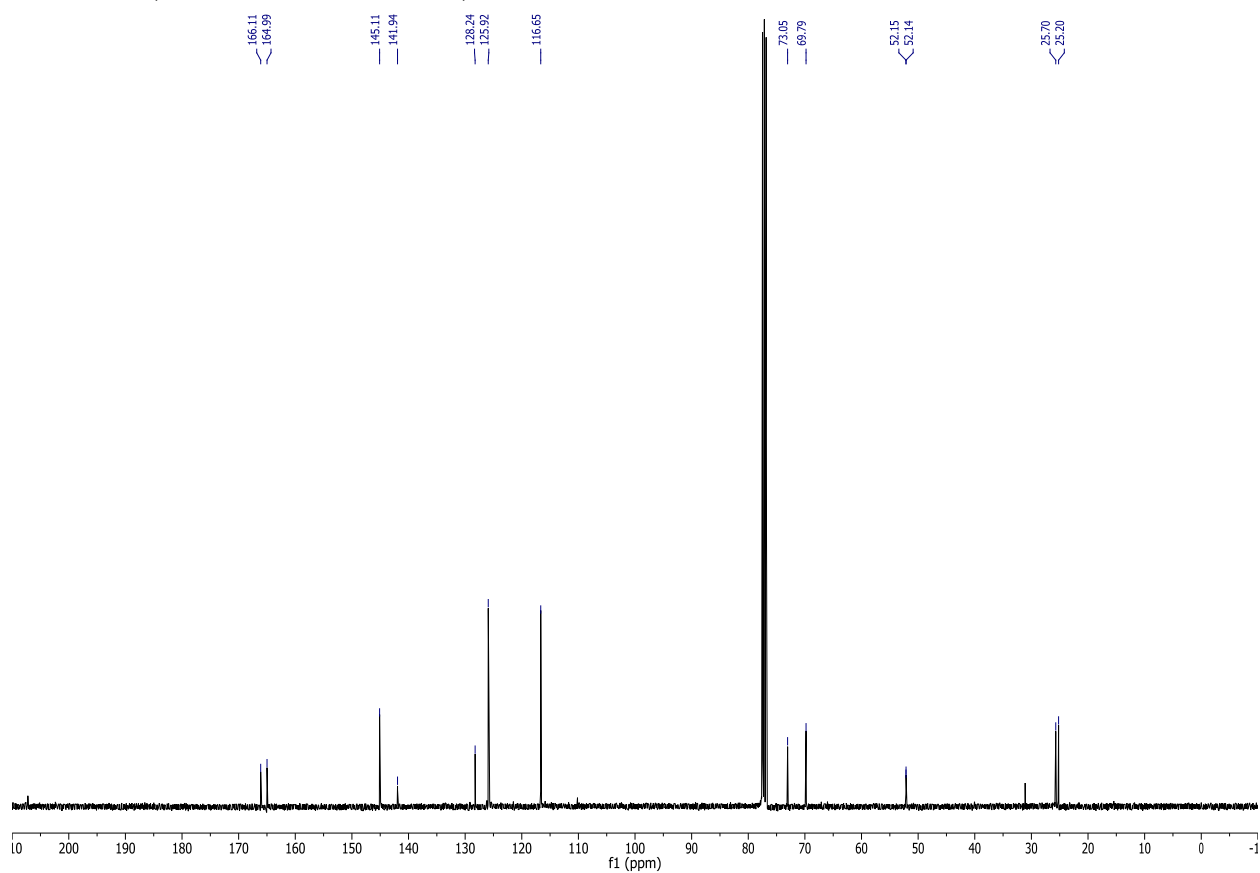
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



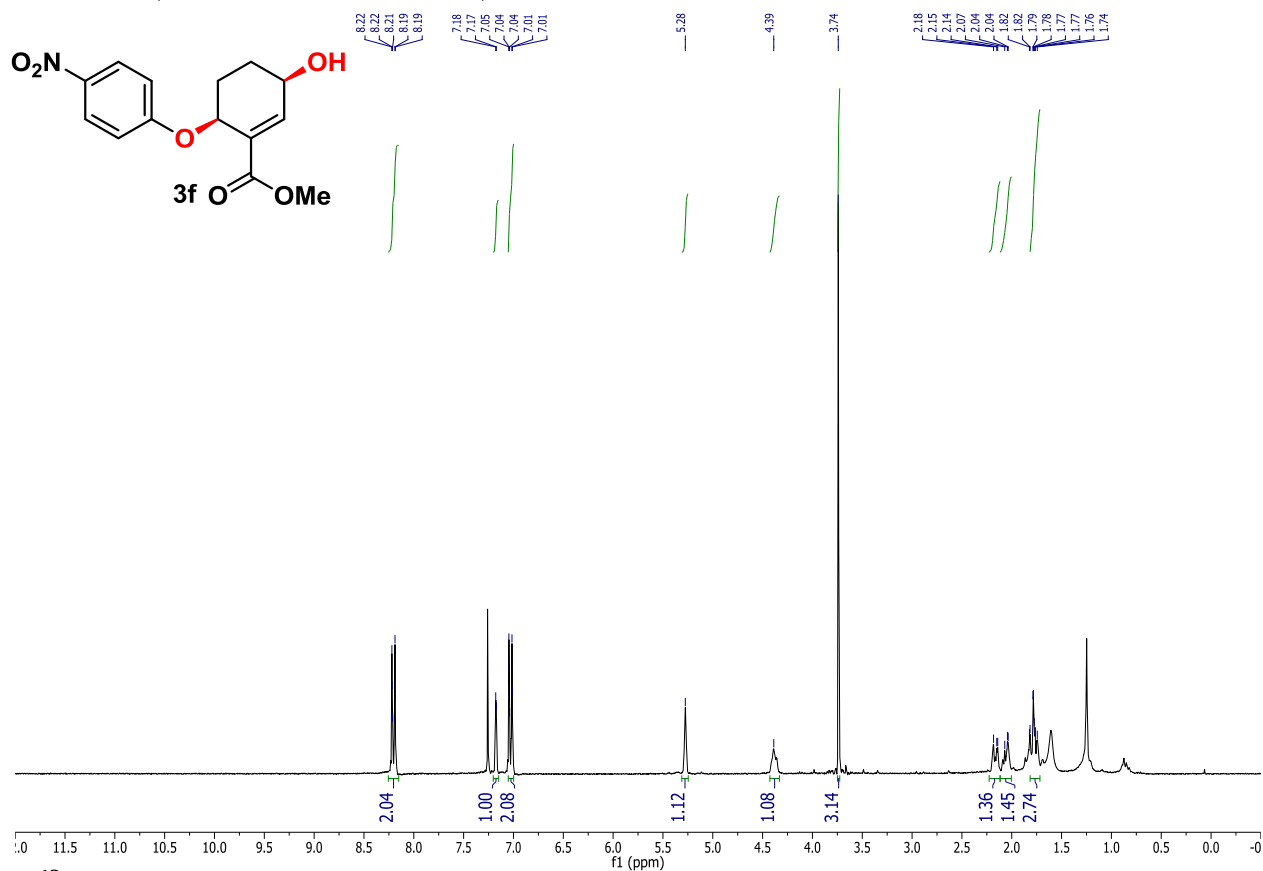
^1H NMR (400 MHz, 23 °C, CDCl_3)



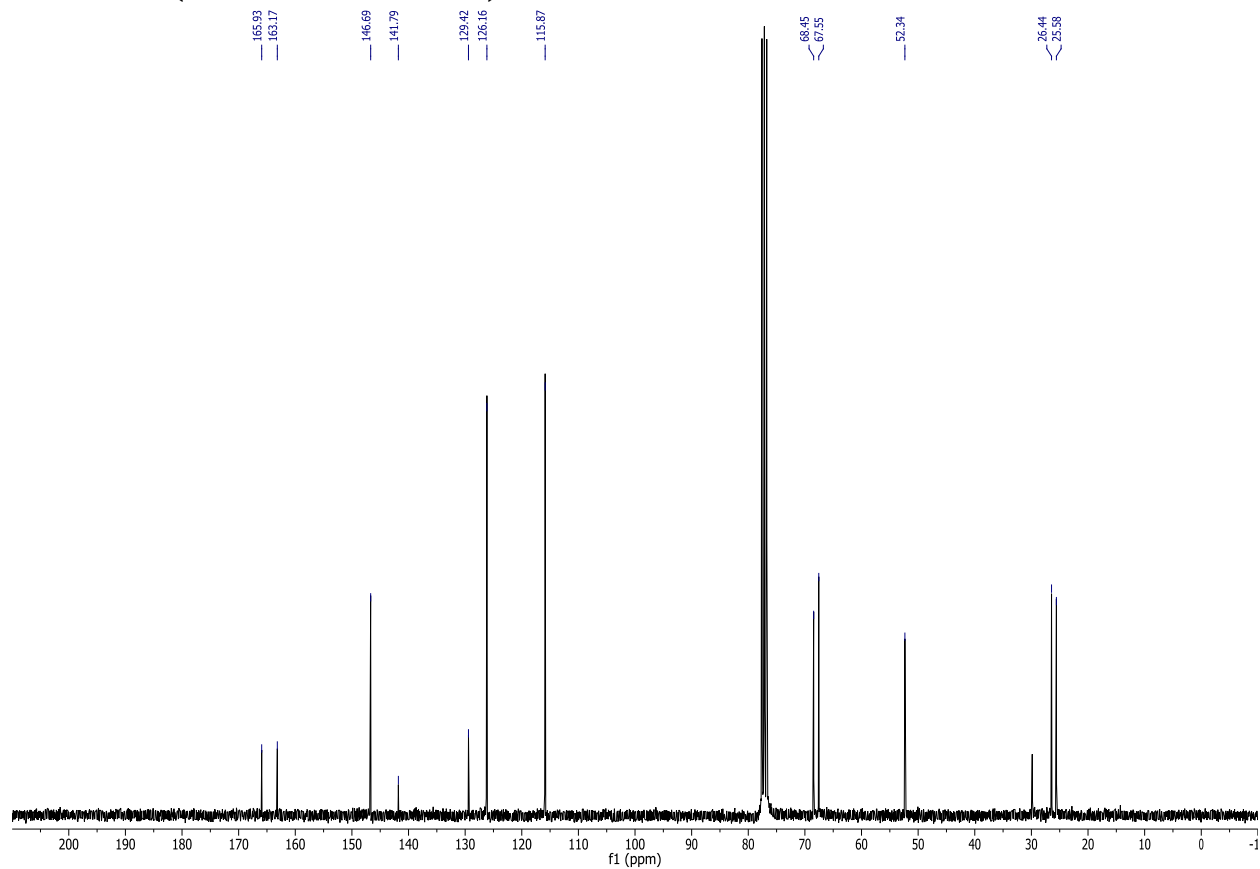
^{13}C NMR (75 MHz, 23 °C, CDCl_3)



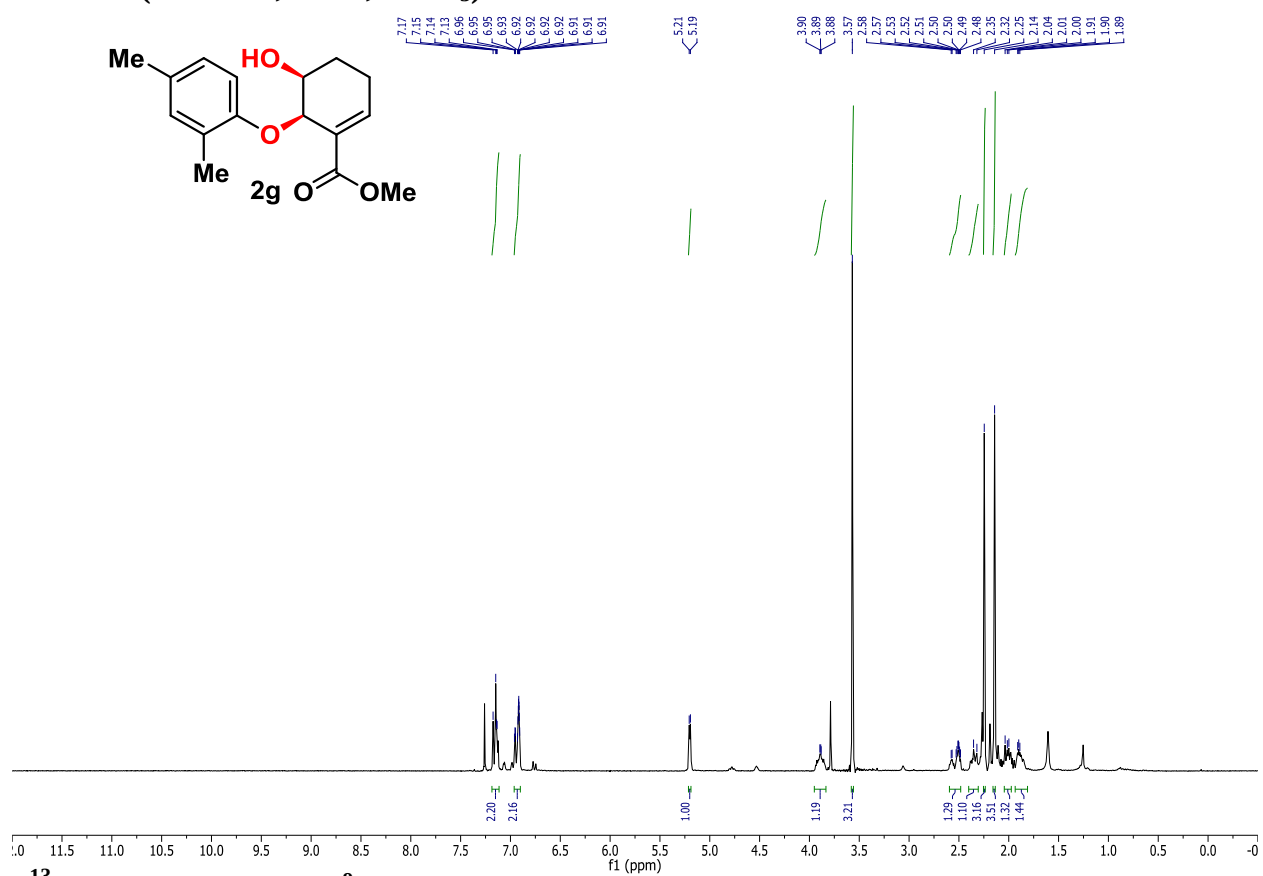
¹H NMR (300 MHz, 23 °C, CDCl₃)



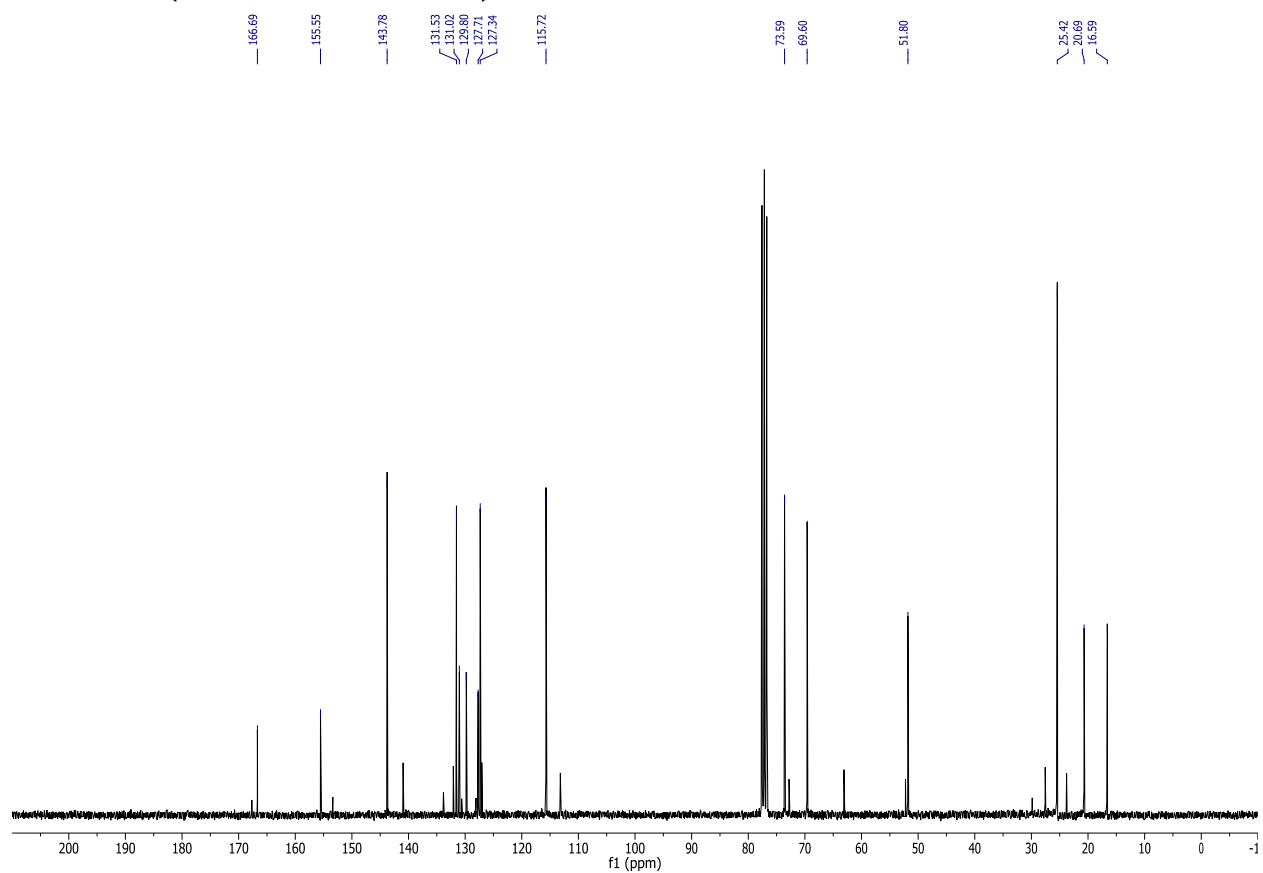
¹³C NMR (75 MHz, 23 °C, CDCl₃)



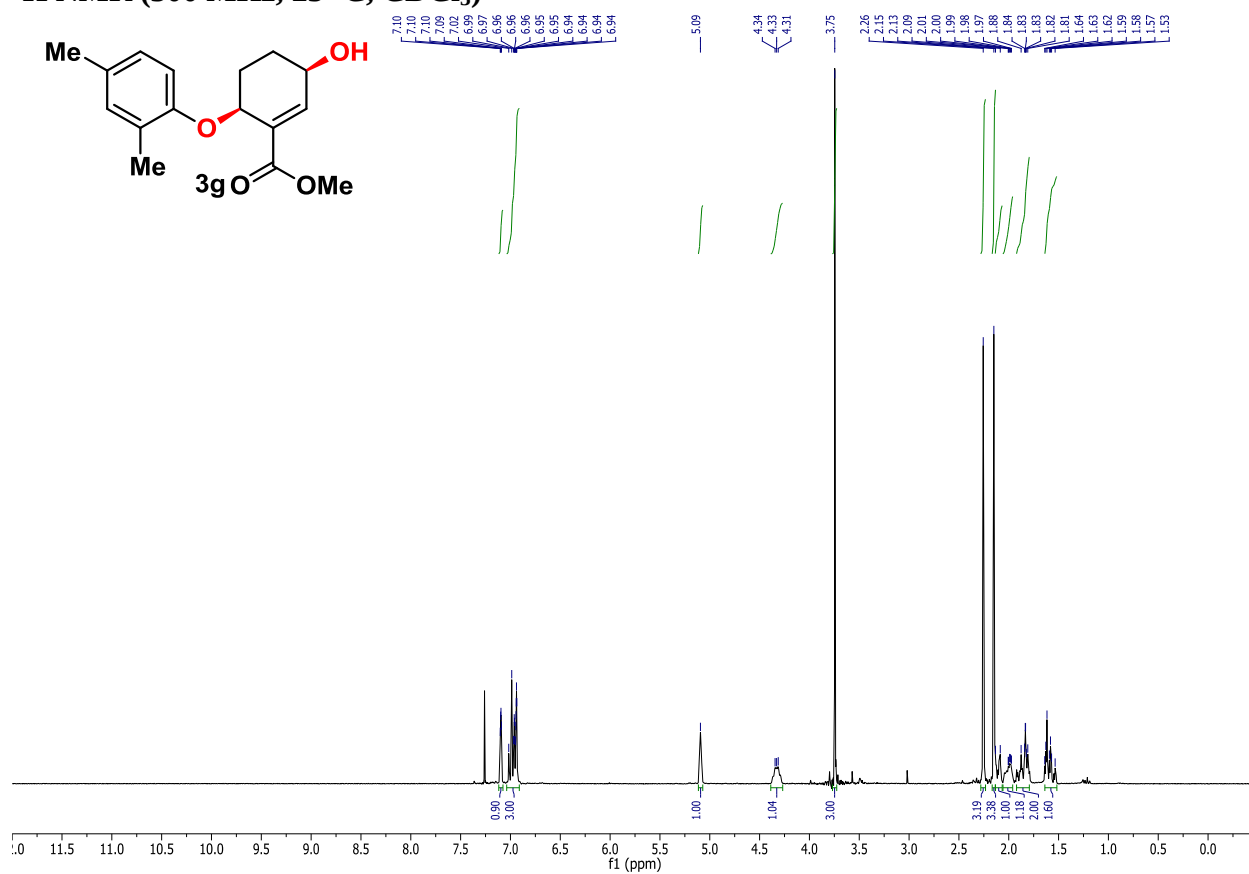
^1H NMR (300 MHz, 23 °C, CDCl_3)



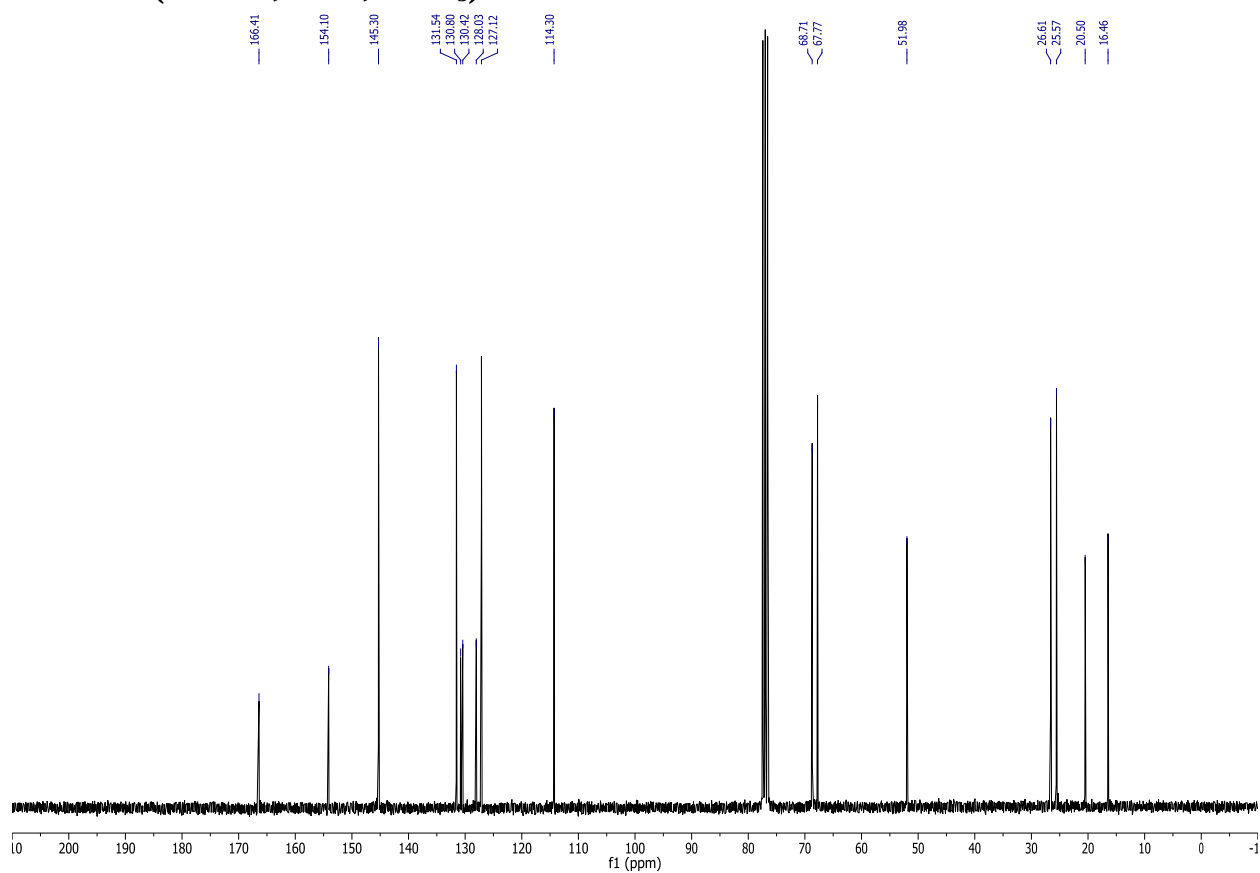
^{13}C NMR (75 MHz, 23 °C, CDCl_3)



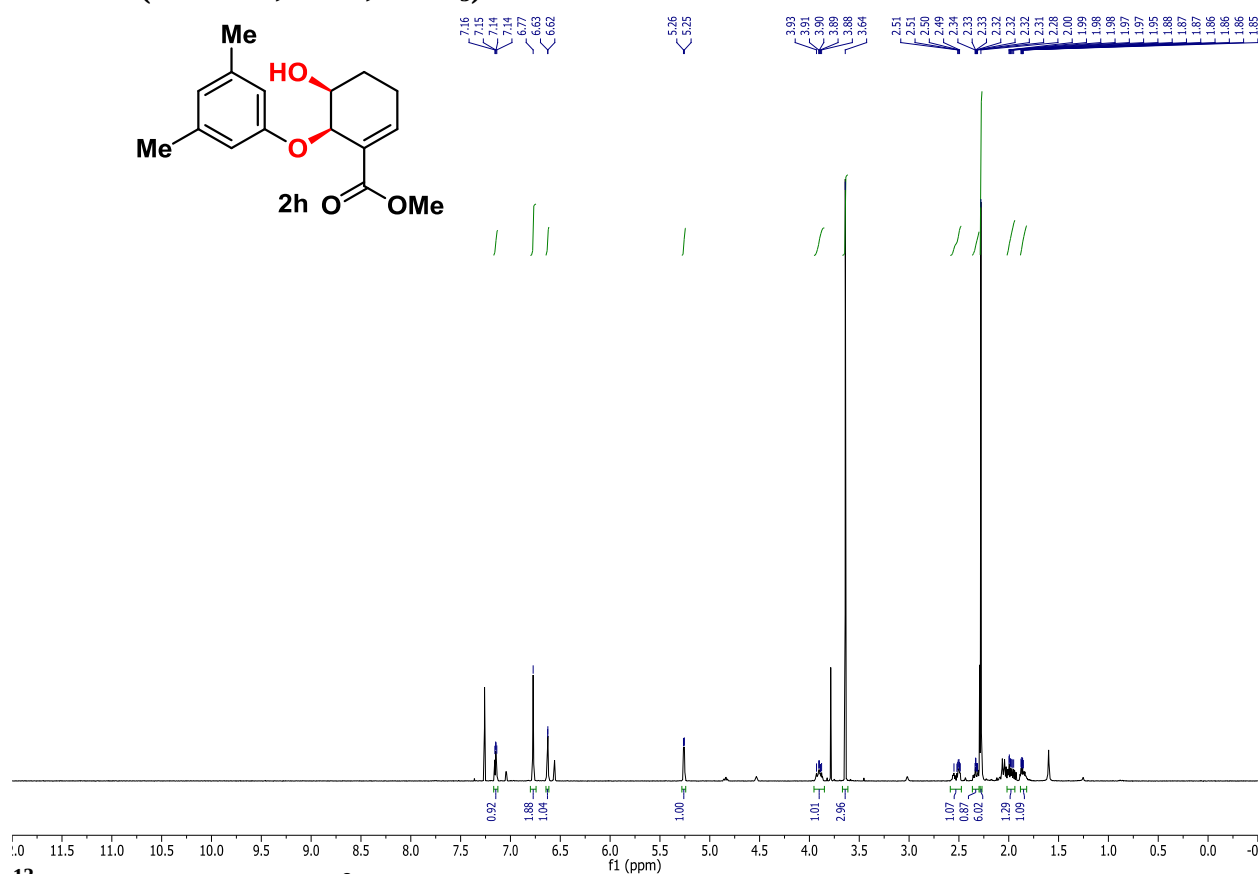
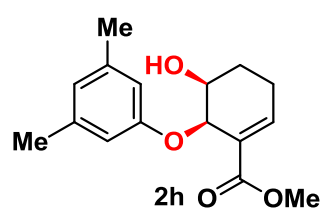
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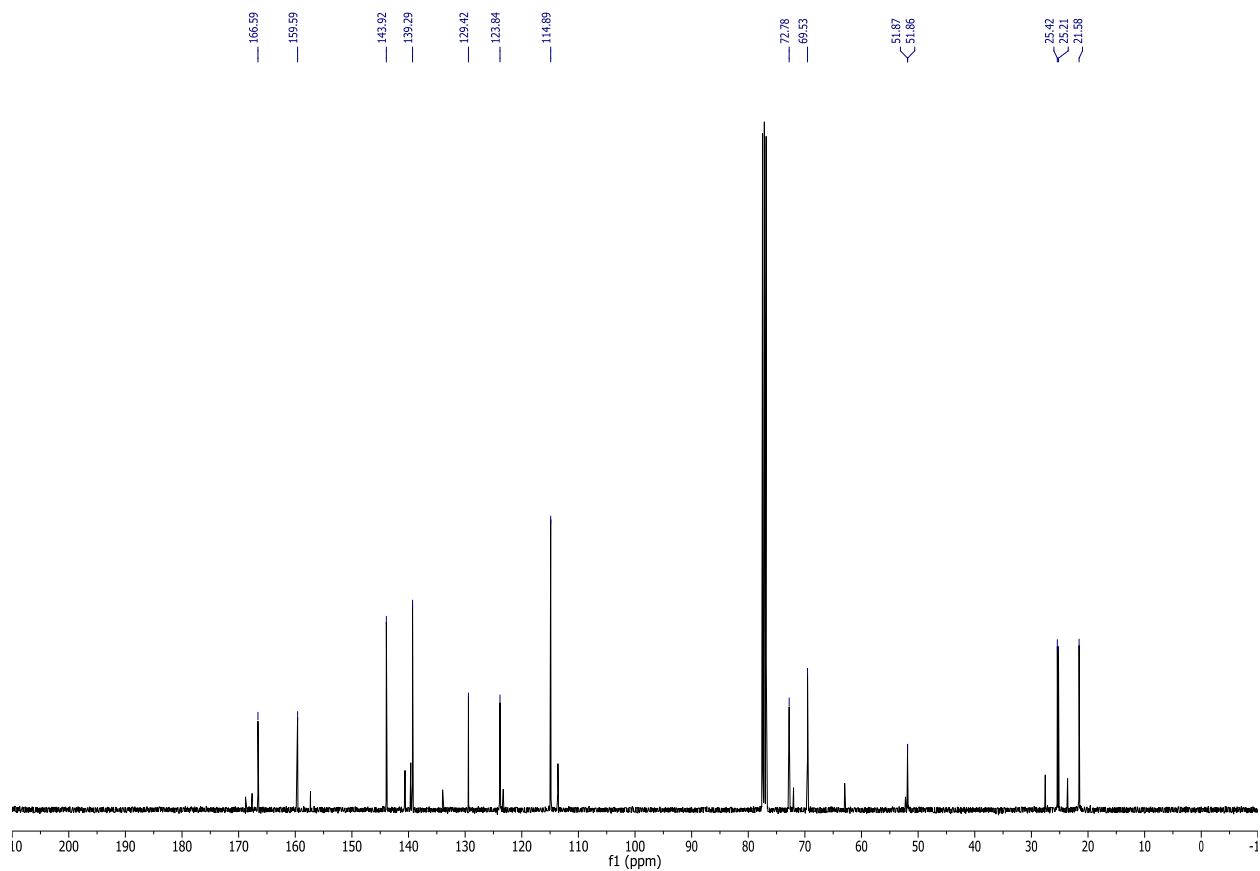
^{13}C NMR (75 MHz, 23 °C, CDCl_3)



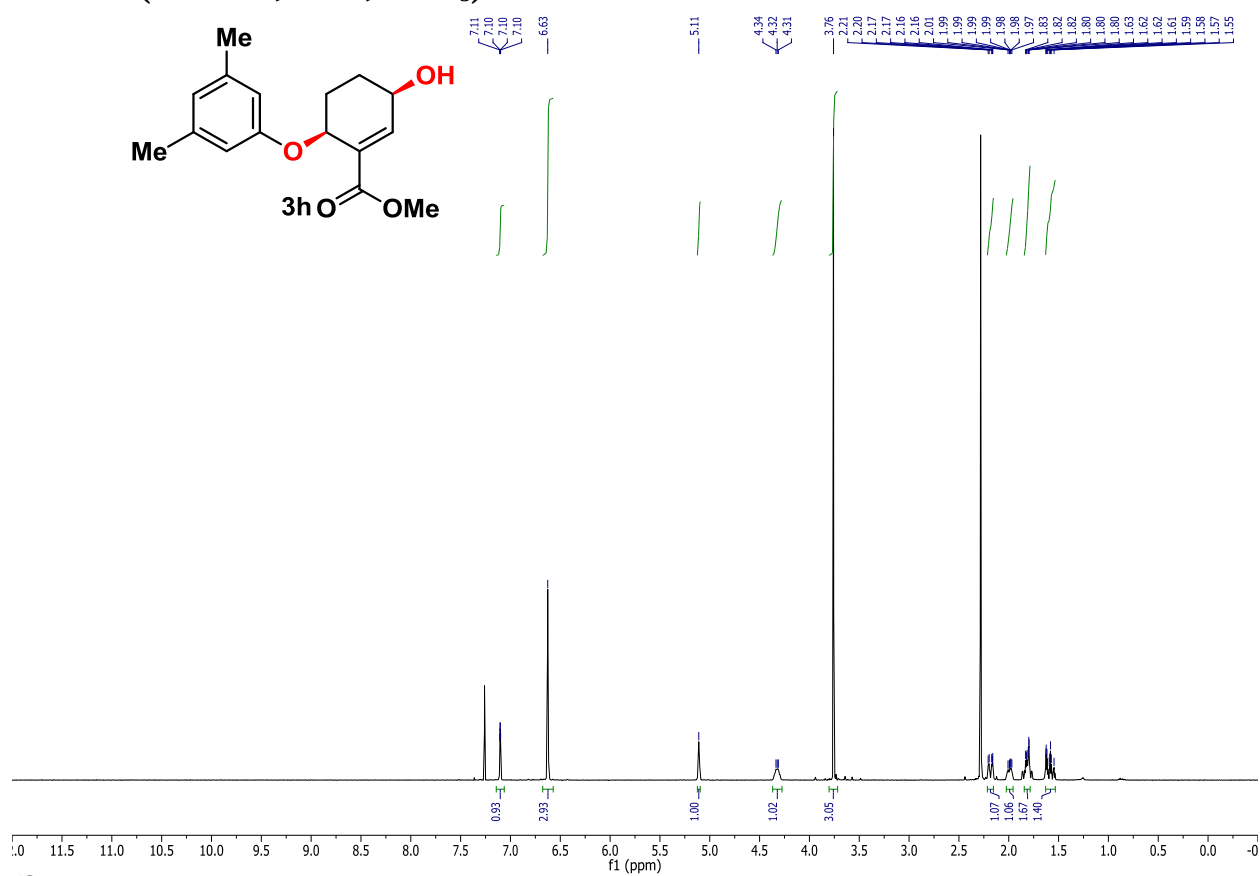
^1H NMR (400 MHz, 23 °C, CDCl_3)



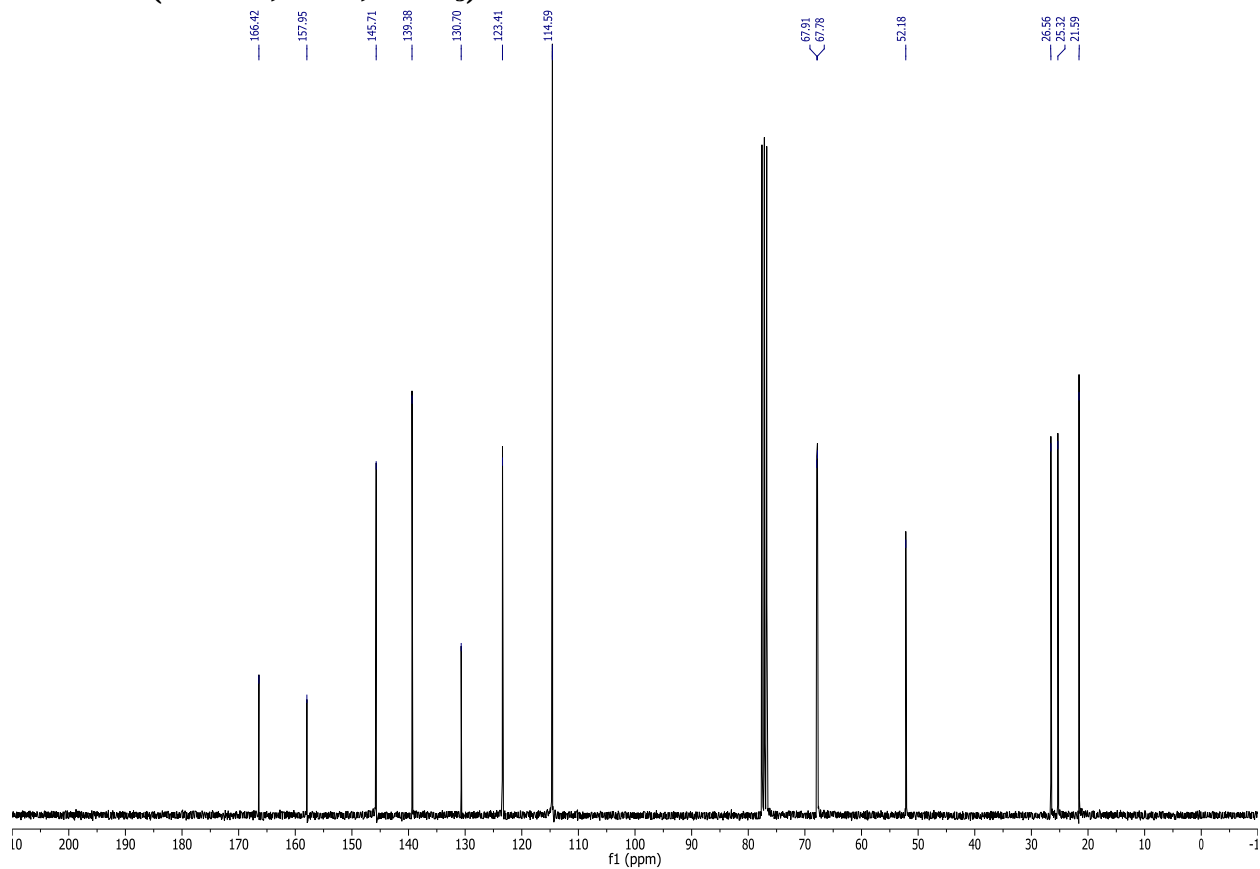
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



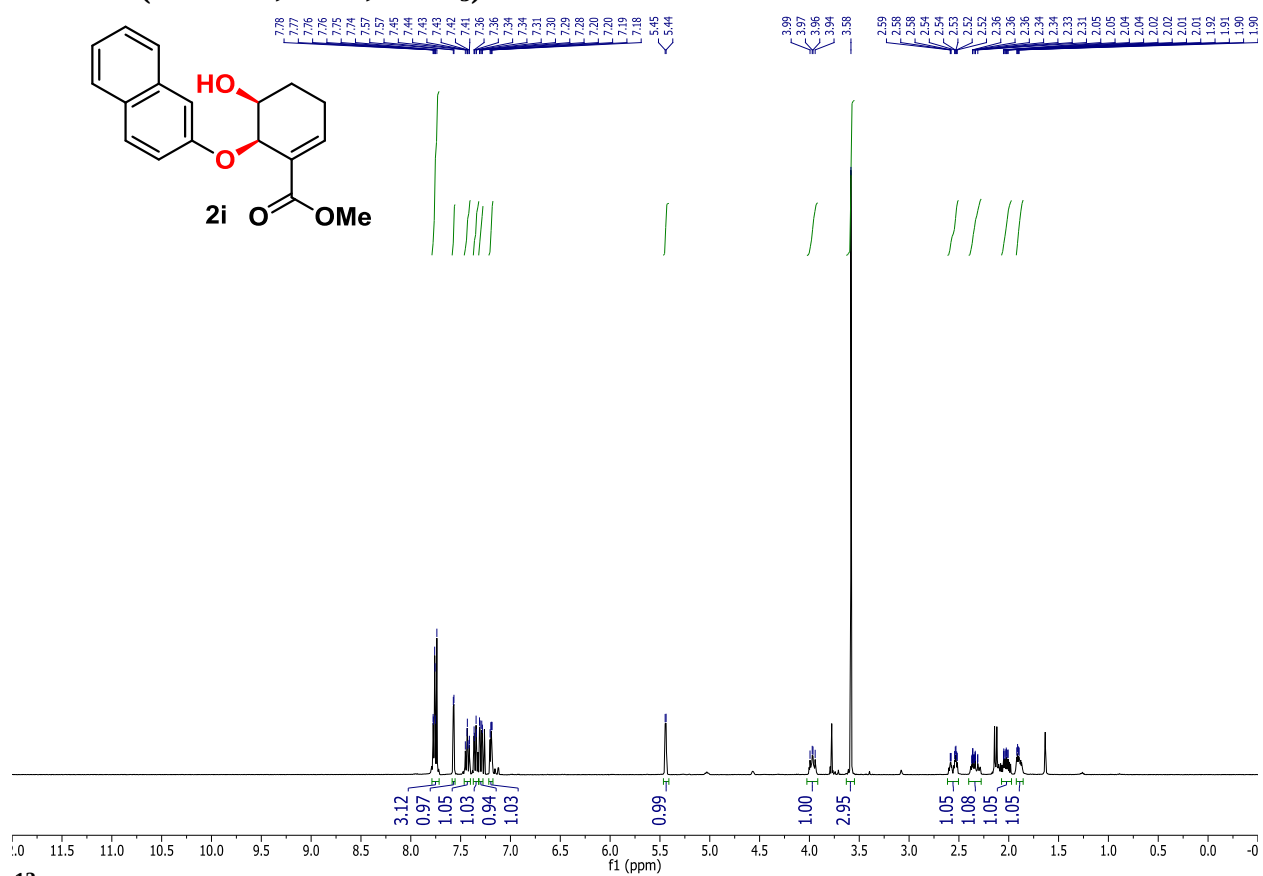
^1H NMR (400 MHz, 23 °C, CDCl_3)



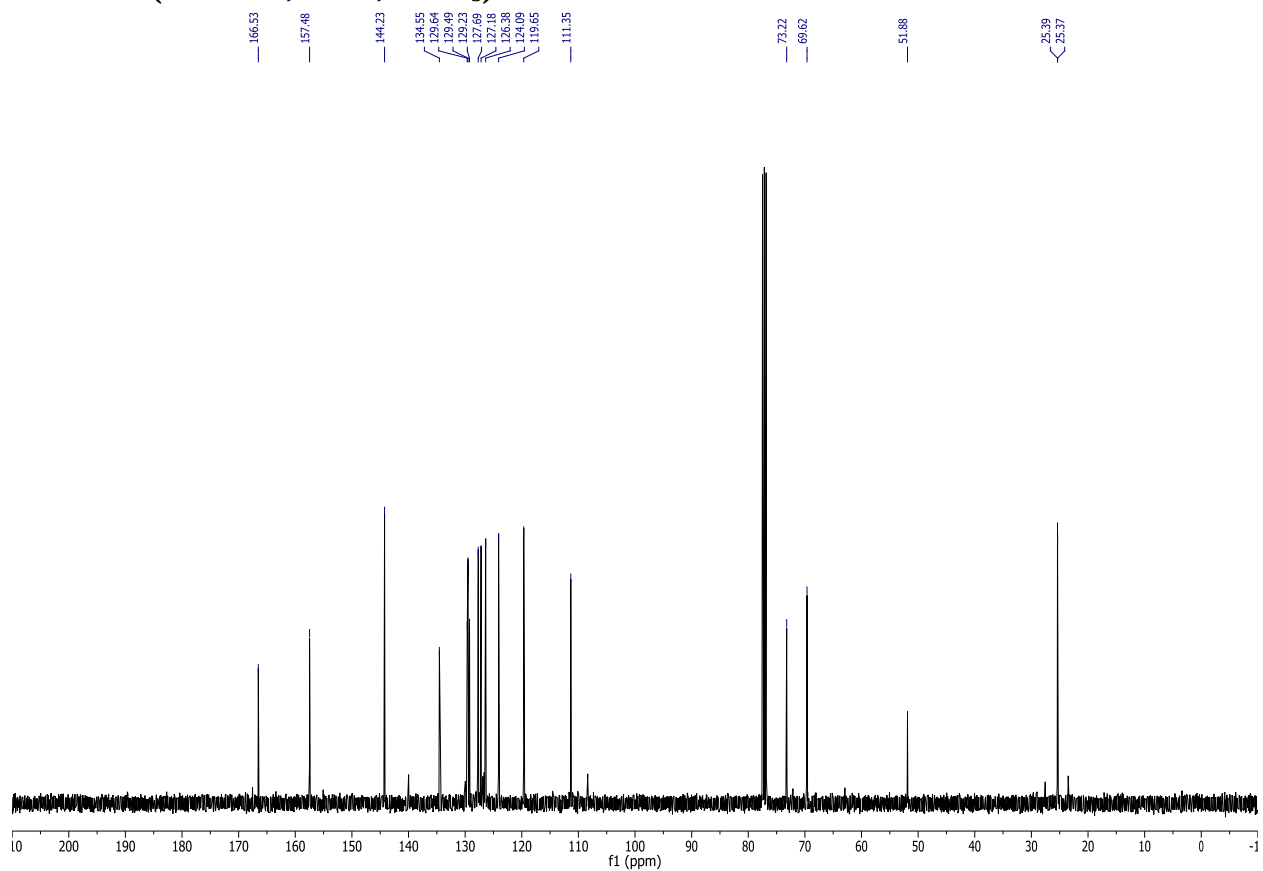
^{13}C NMR (75 MHz, 23 °C, CDCl_3)



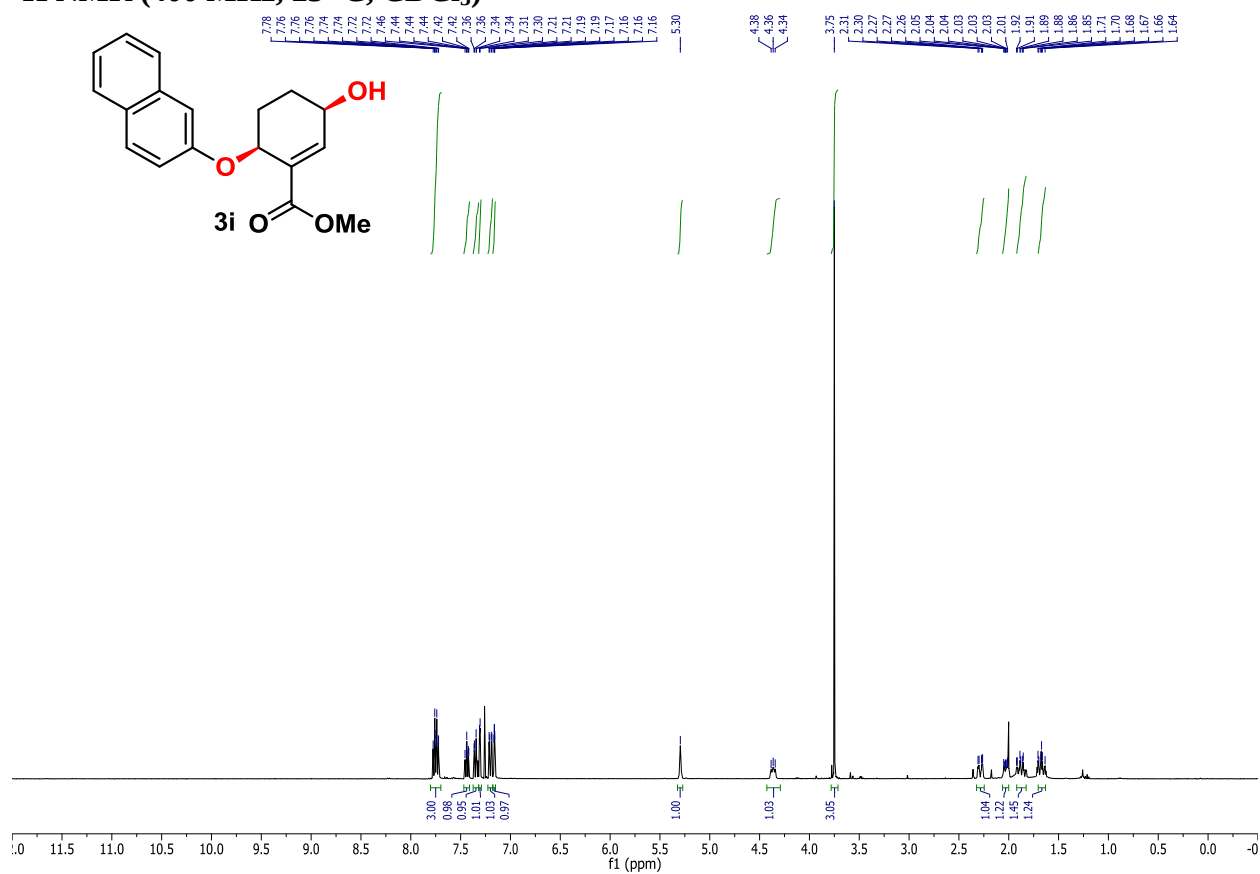
^1H NMR (400 MHz, 23 °C, CDCl_3)



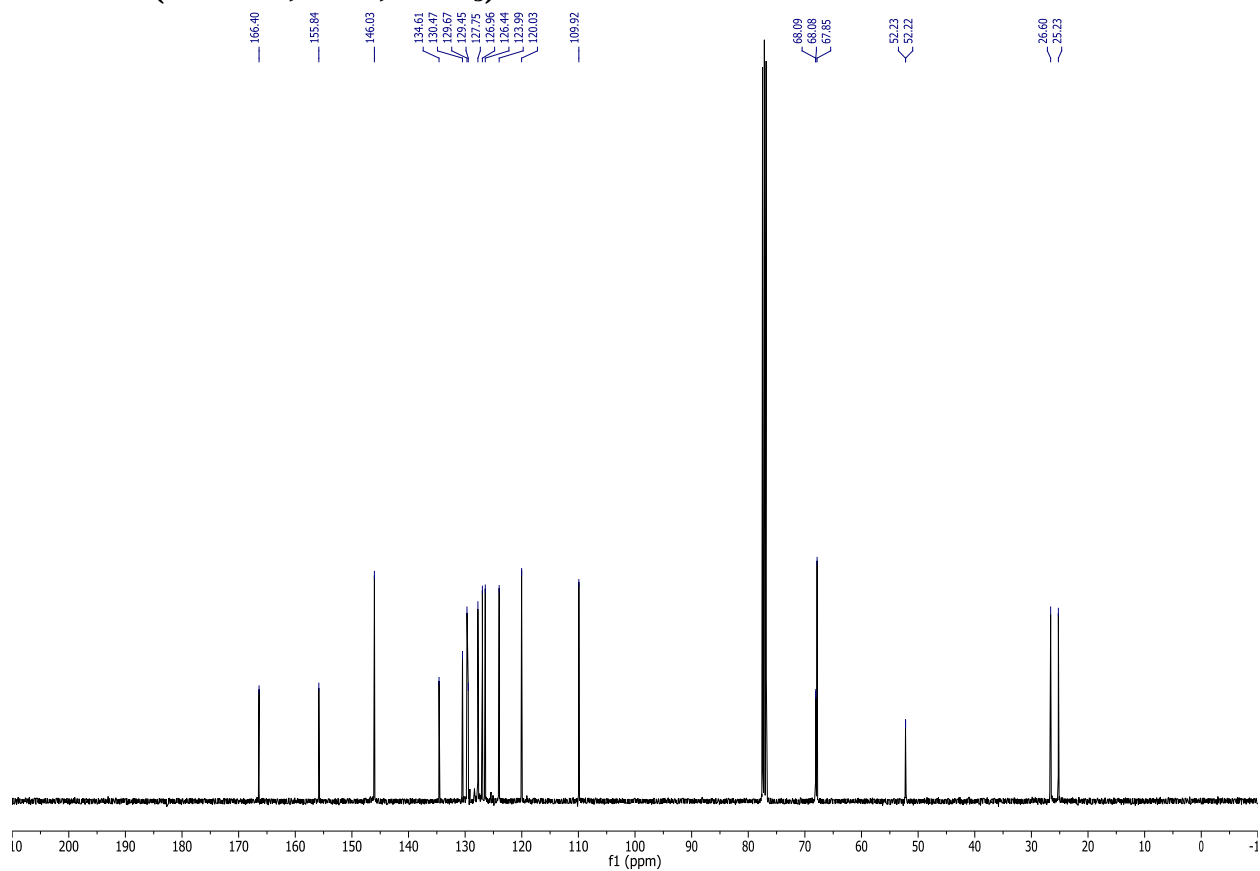
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



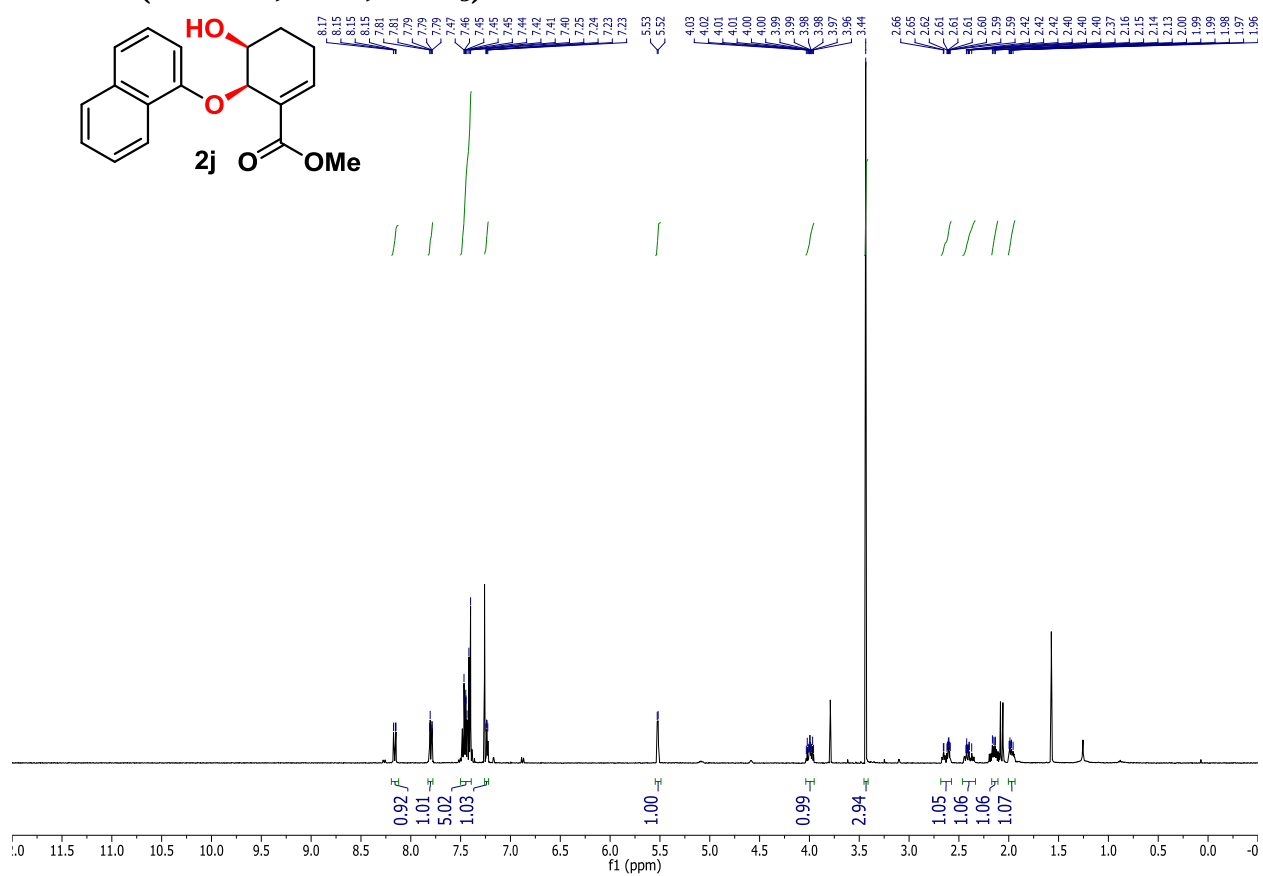
^1H NMR (400 MHz, 23 °C, CDCl_3)



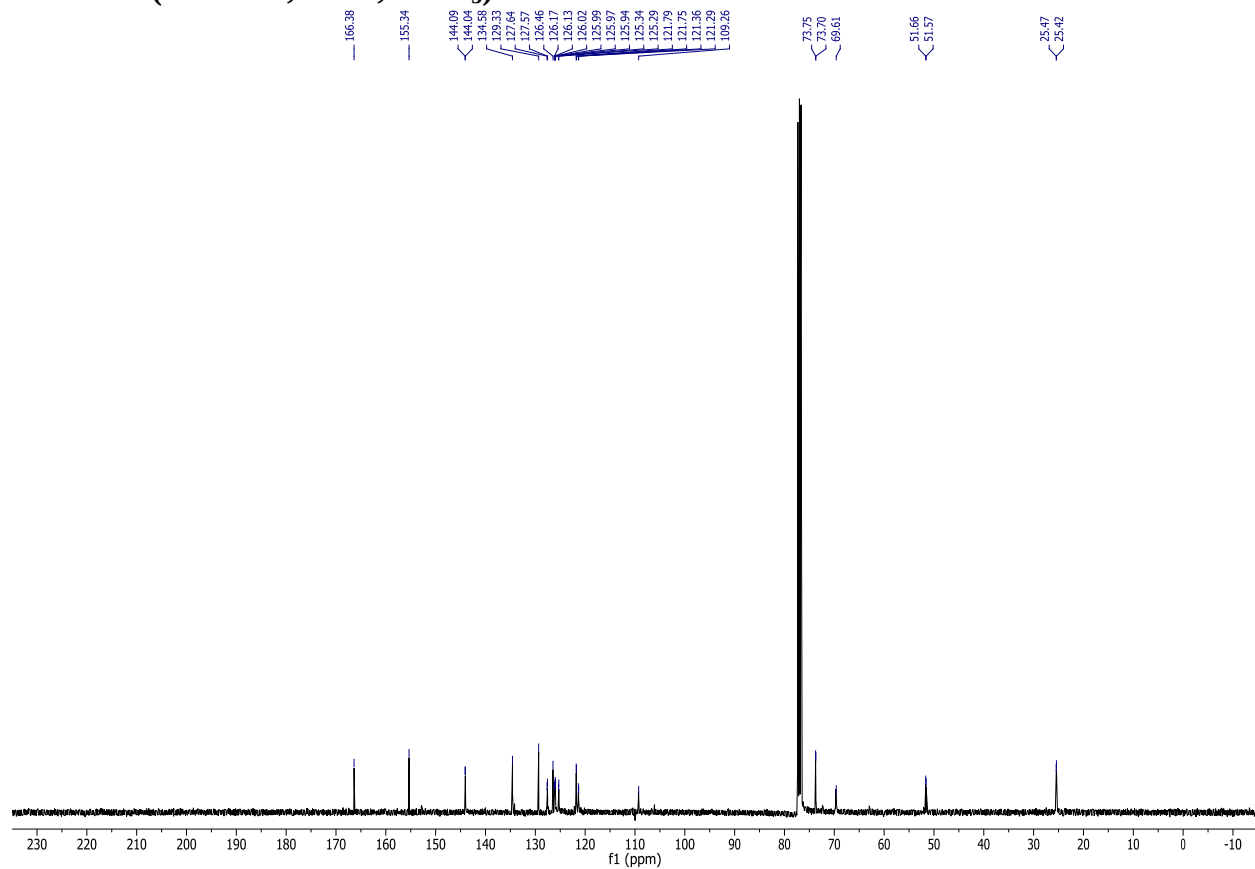
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



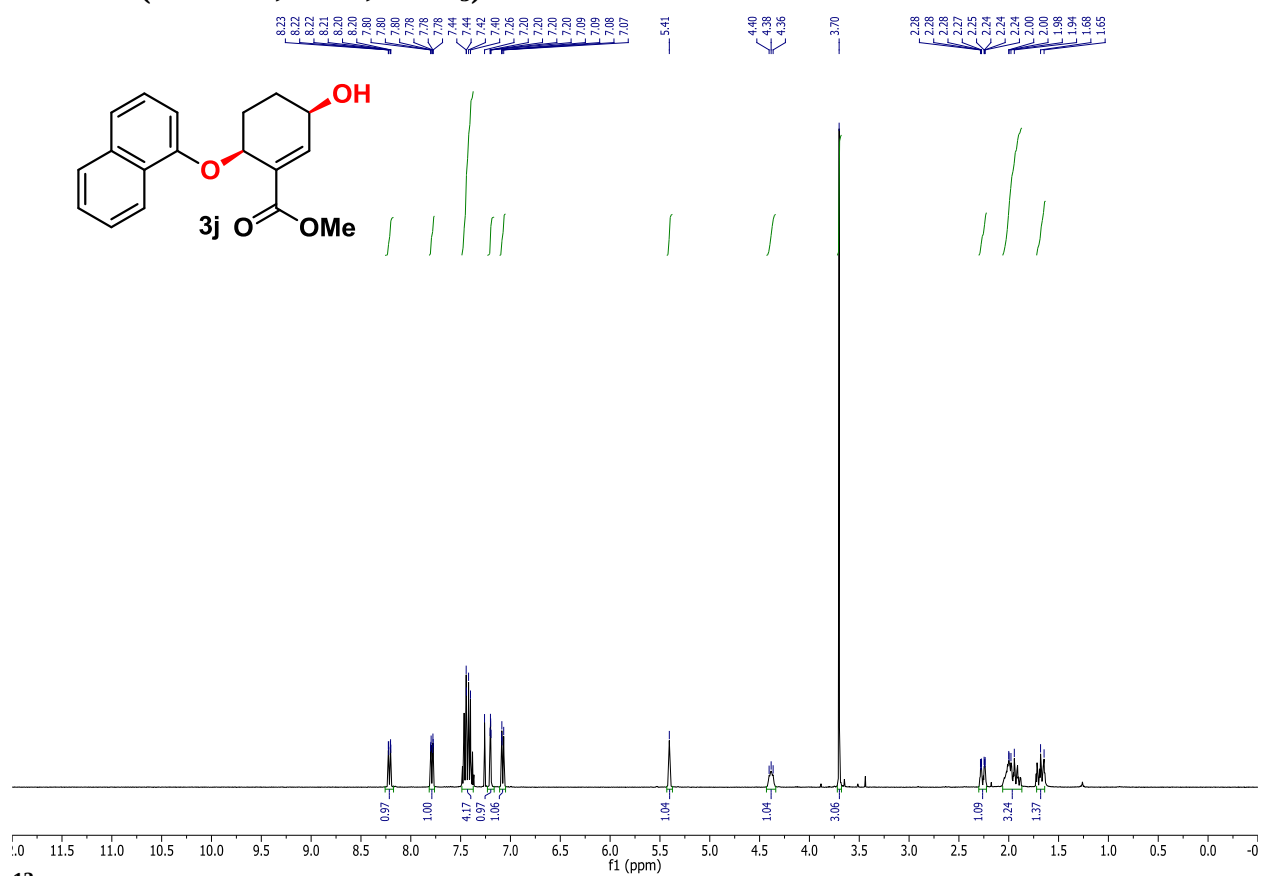
^1H NMR (400 MHz, 23 $^\circ\text{C}$, CDCl_3)



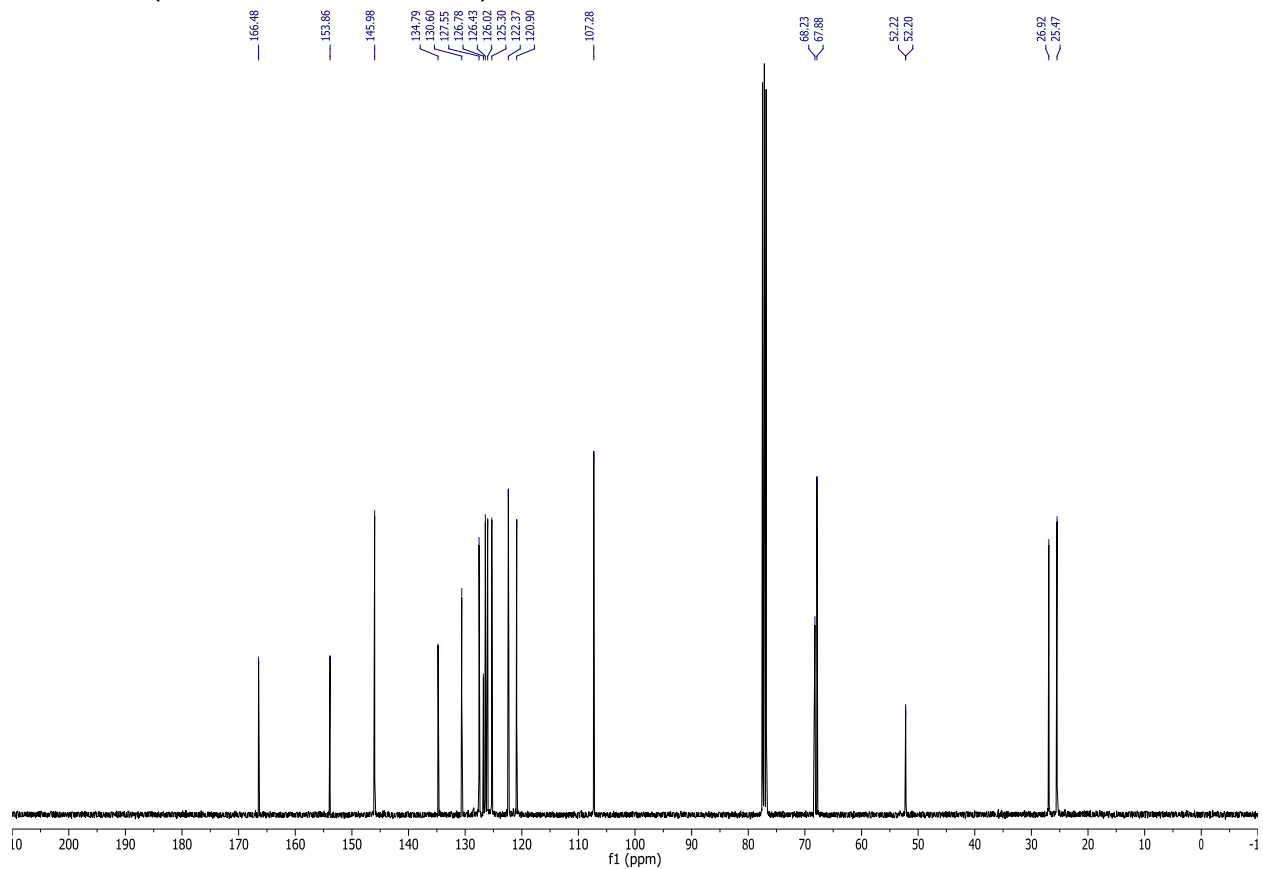
^{13}C NMR (100 MHz, 23 $^\circ\text{C}$, CDCl_3)



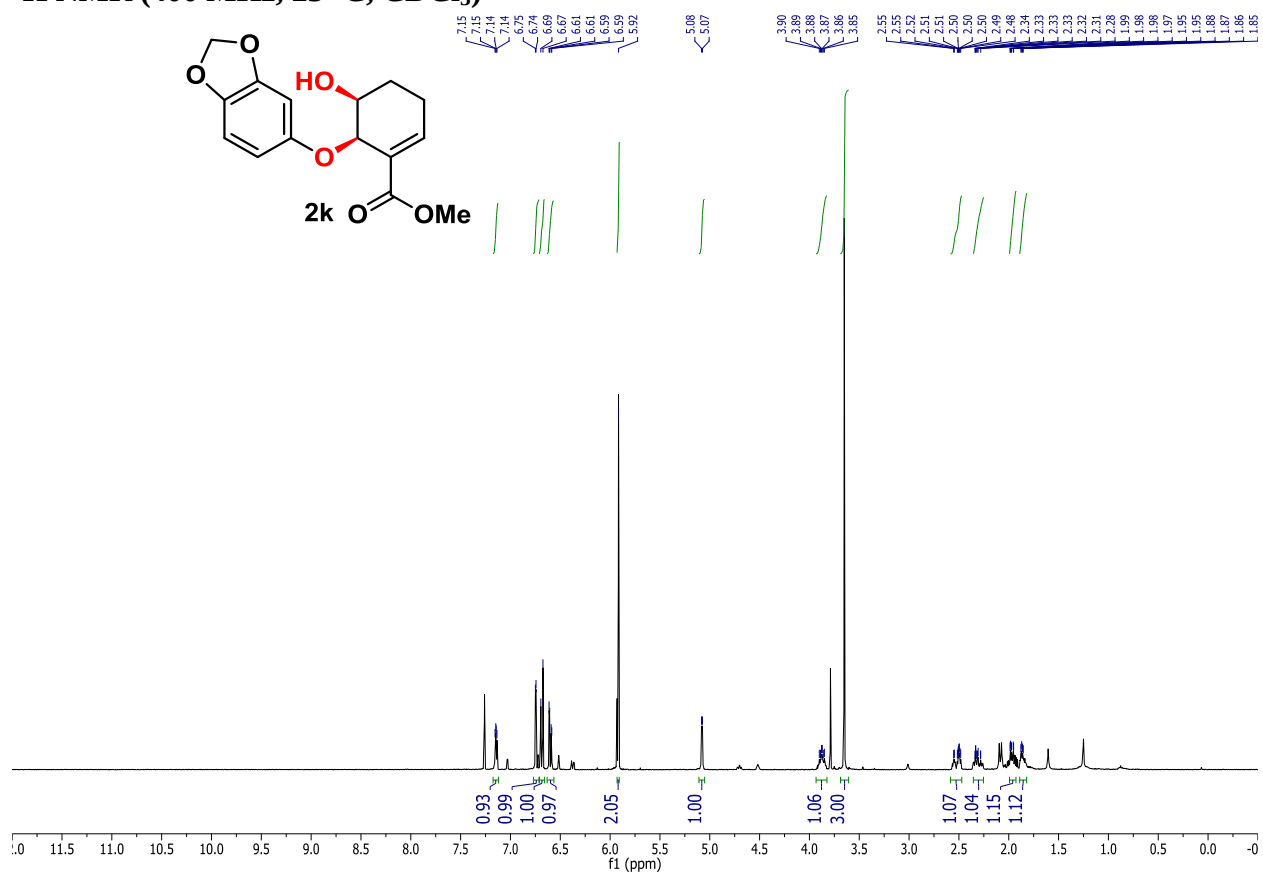
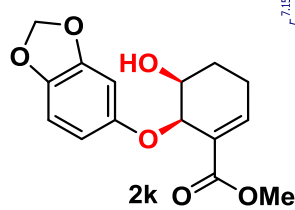
¹H NMR (400 MHz, 23 °C, CDCl₃)



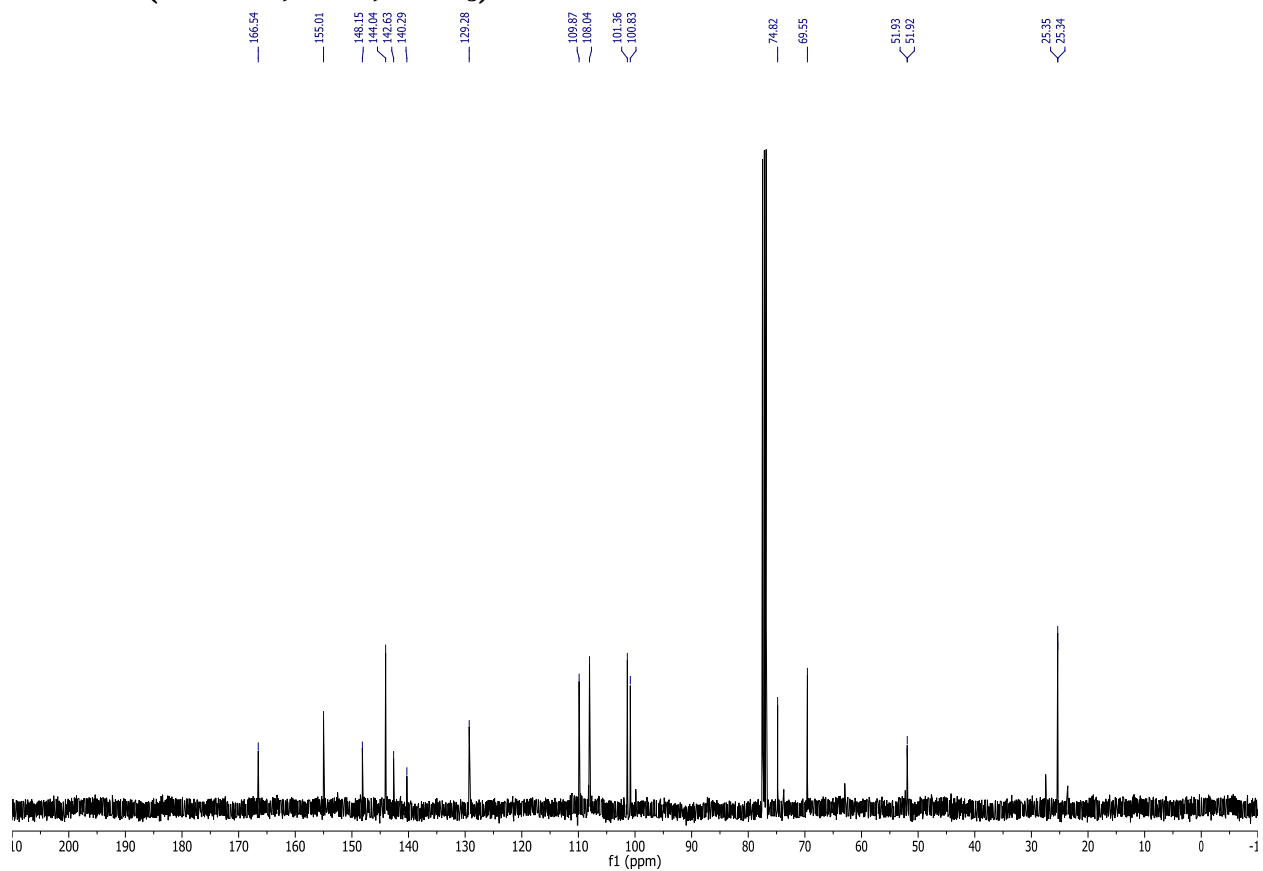
¹³C NMR (100 MHz, 23 °C, CDCl₃)



¹H NMR (400 MHz, 23 °C, CDCl₃)



¹³C NMR (100 MHz, 23 °C, CDCl₃)



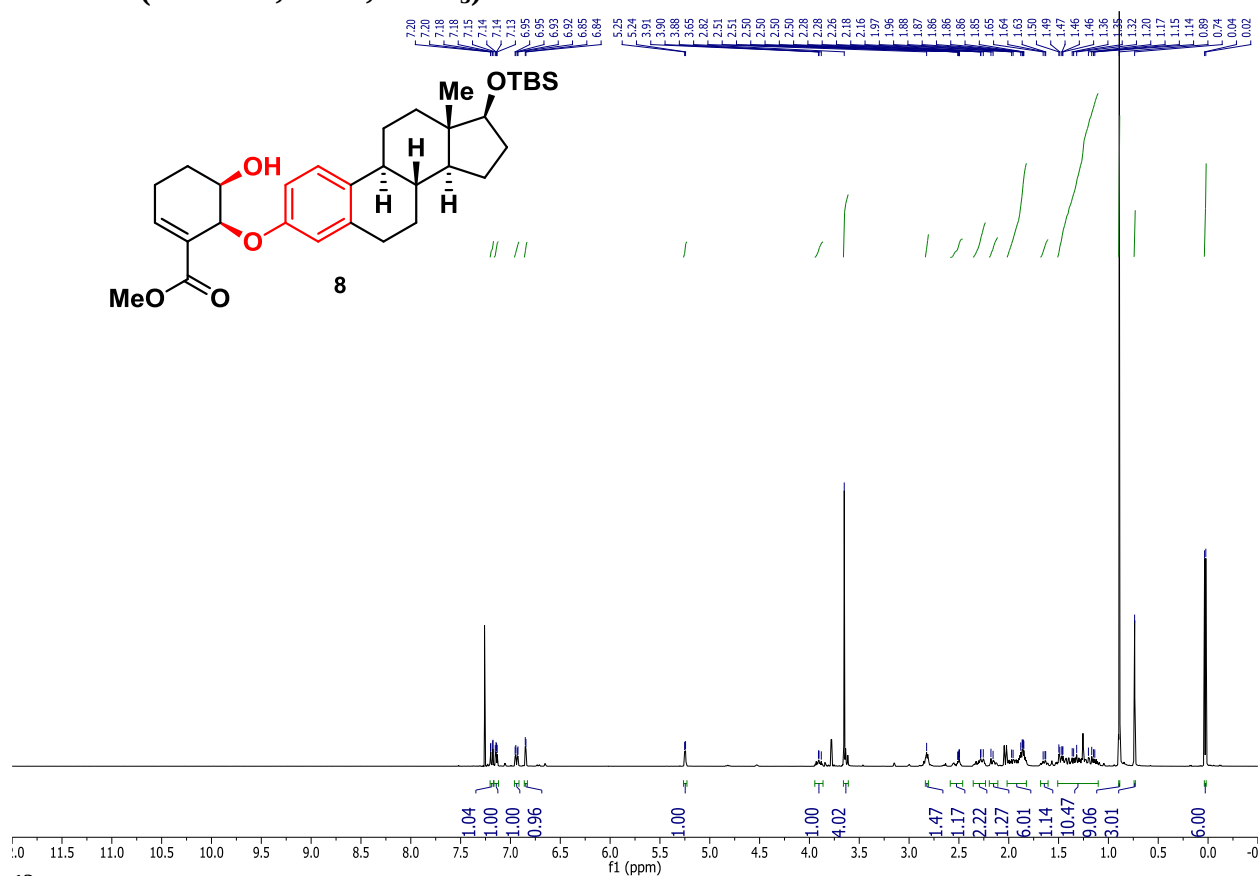
COC(=O)C1=CC=C(C=C1OC2=CC=CC3=C2OC3)O

¹H NMR spectrum (CDCl₃) of compound 3k. The spectrum shows peaks in the aromatic region (6.46–7.09 ppm), a methoxy singlet (3.76 ppm), and aliphatic signals (1.49–2.20 ppm). Integration values are provided below the peaks.

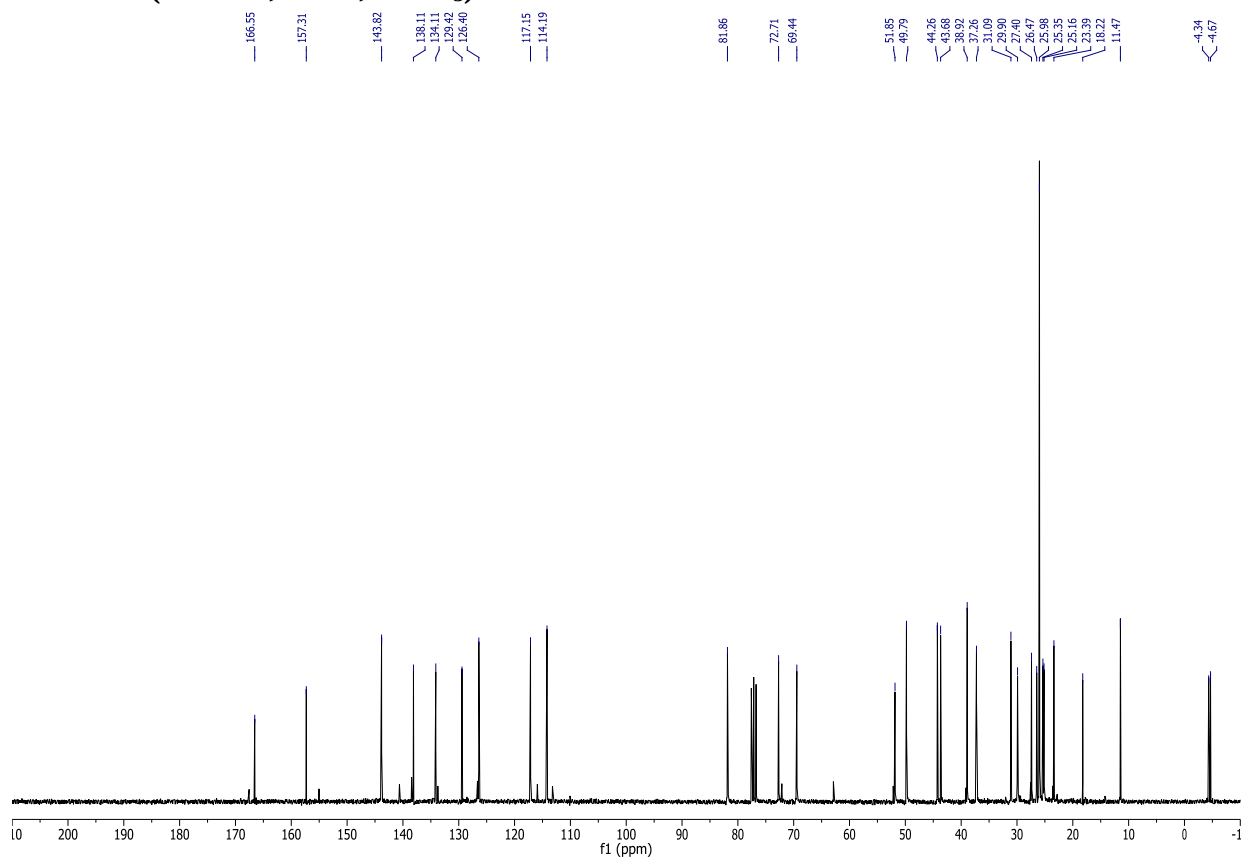
Chemical Shift (ppm)	Integration
7.09	1.04
6.70	1.06
6.68	1.00
6.63	1.09
6.47	2.20
5.00	1.06
4.31	1.09
3.76	3.09
2.15	1.91
2.12	1.14
2.11	1.12
1.98	1.07
1.97	-
1.96	-
1.88	-
1.80	-
1.79	-
1.57	-
1.56	-
1.55	-
1.53	-
1.52	-
1.51	-
1.49	-

13C NMR spectrum of compound 10. The x-axis is labeled 'f1 (ppm)' and ranges from -1 to 210. The spectrum shows several peaks with chemical shifts labeled above them: 166.38, 153.39, 148.31, 147.59, 146.60, 130.55, 109.84, 108.15, 101.34, 100.55, 70.22, 67.89, 52.21, 52.20, 26.45, and 25.23. A large solvent peak is visible at approximately 77 ppm.

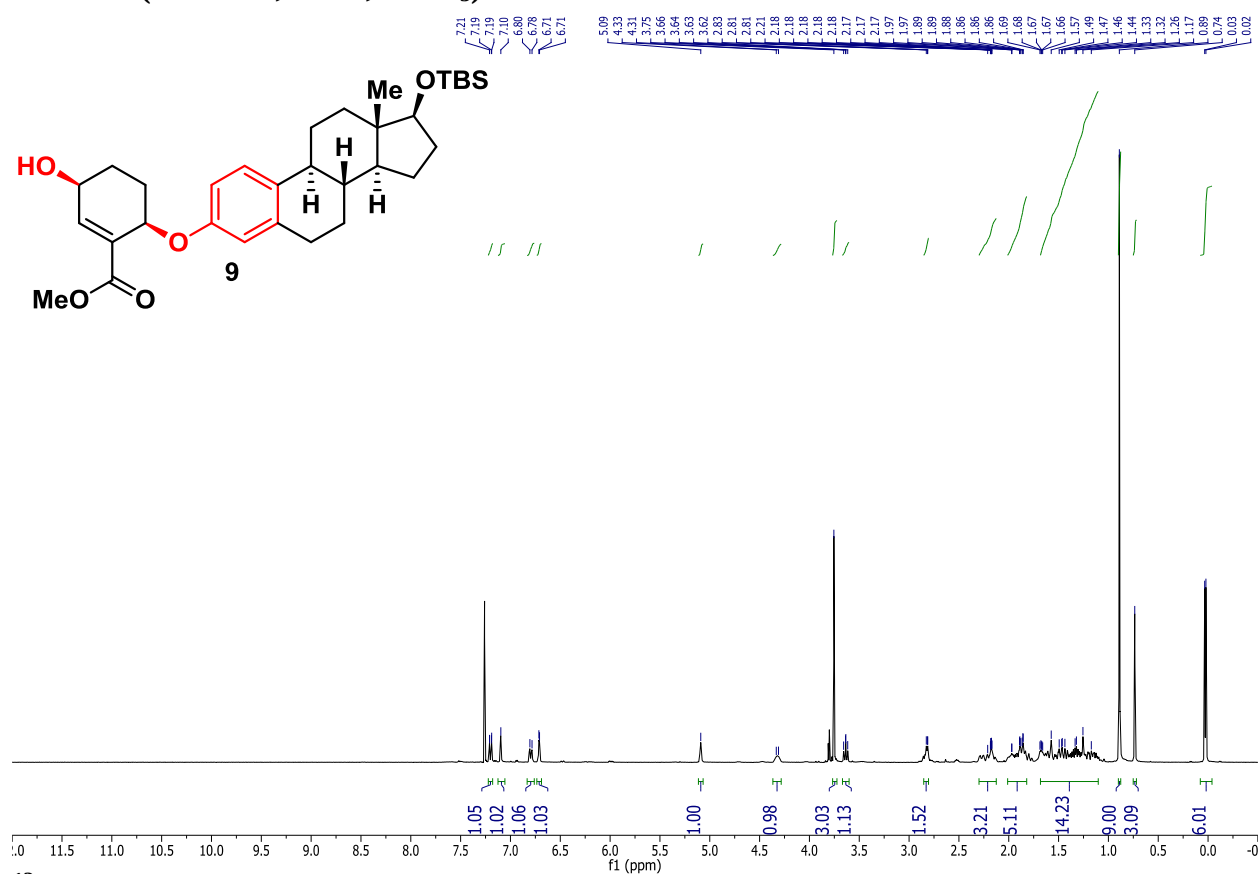
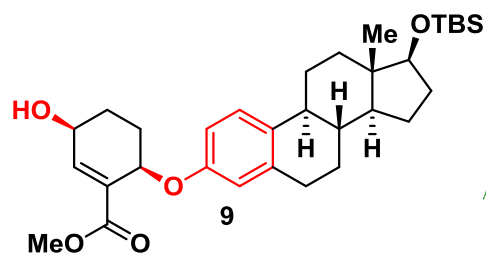
^1H NMR (400 MHz, 23 °C, CDCl_3)



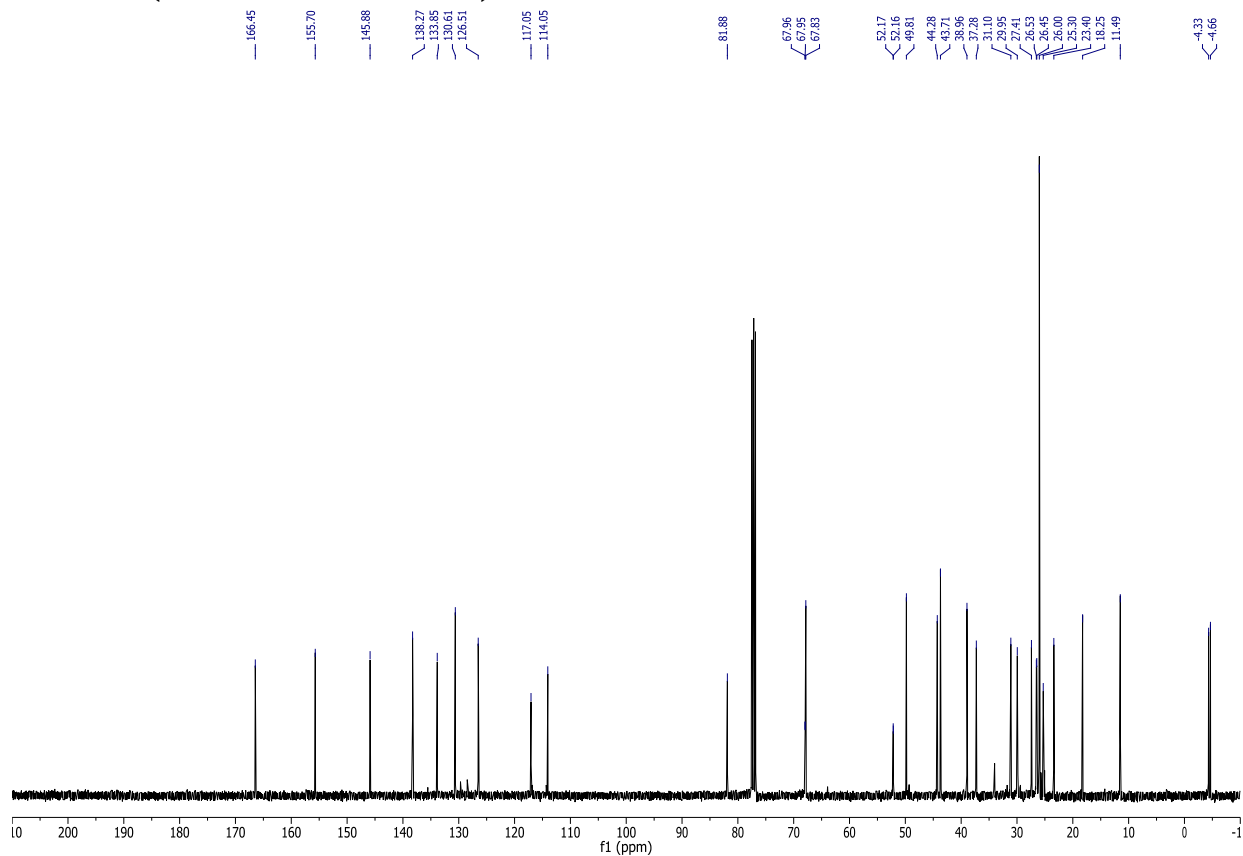
^{13}C NMR (75 MHz, 23 °C, CDCl_3)



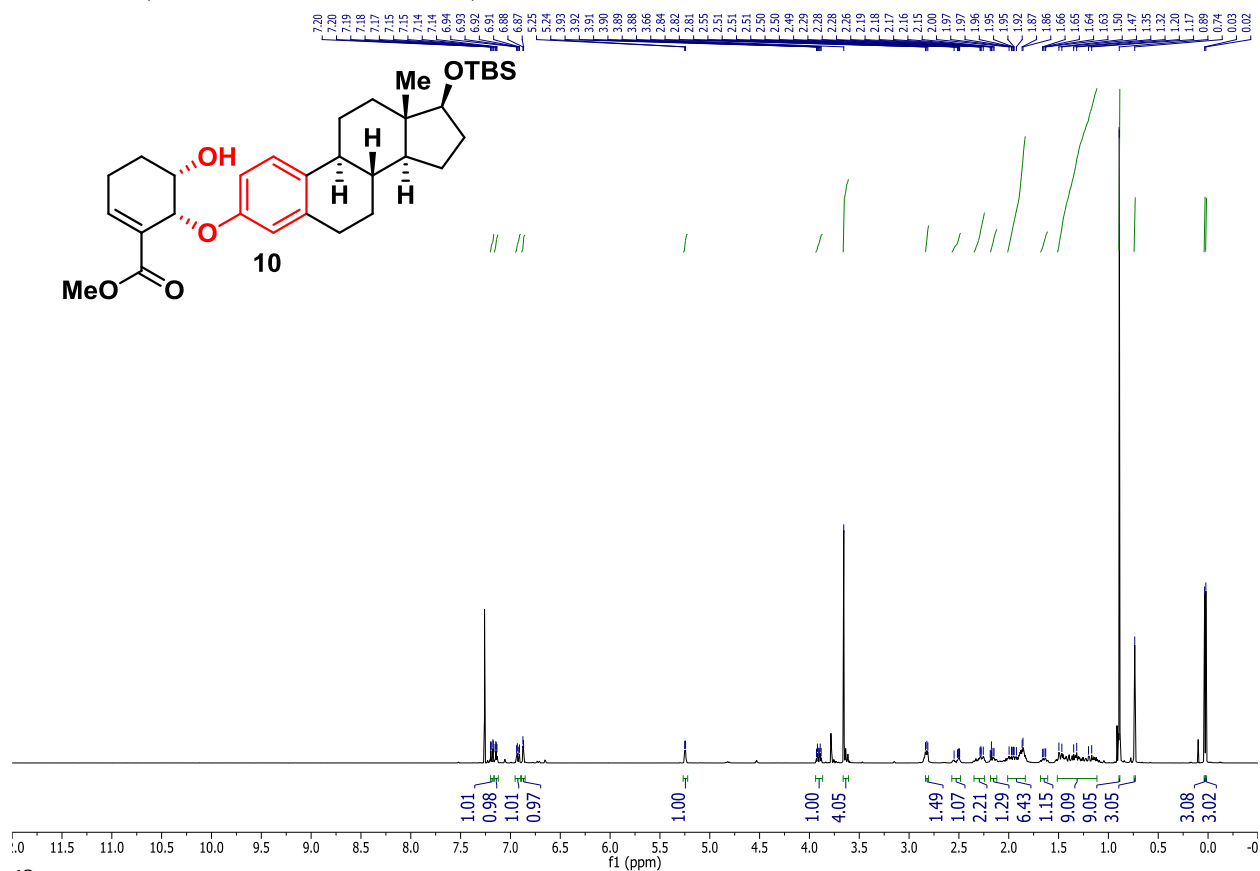
^1H NMR (400 MHz, 23 °C, CDCl_3)



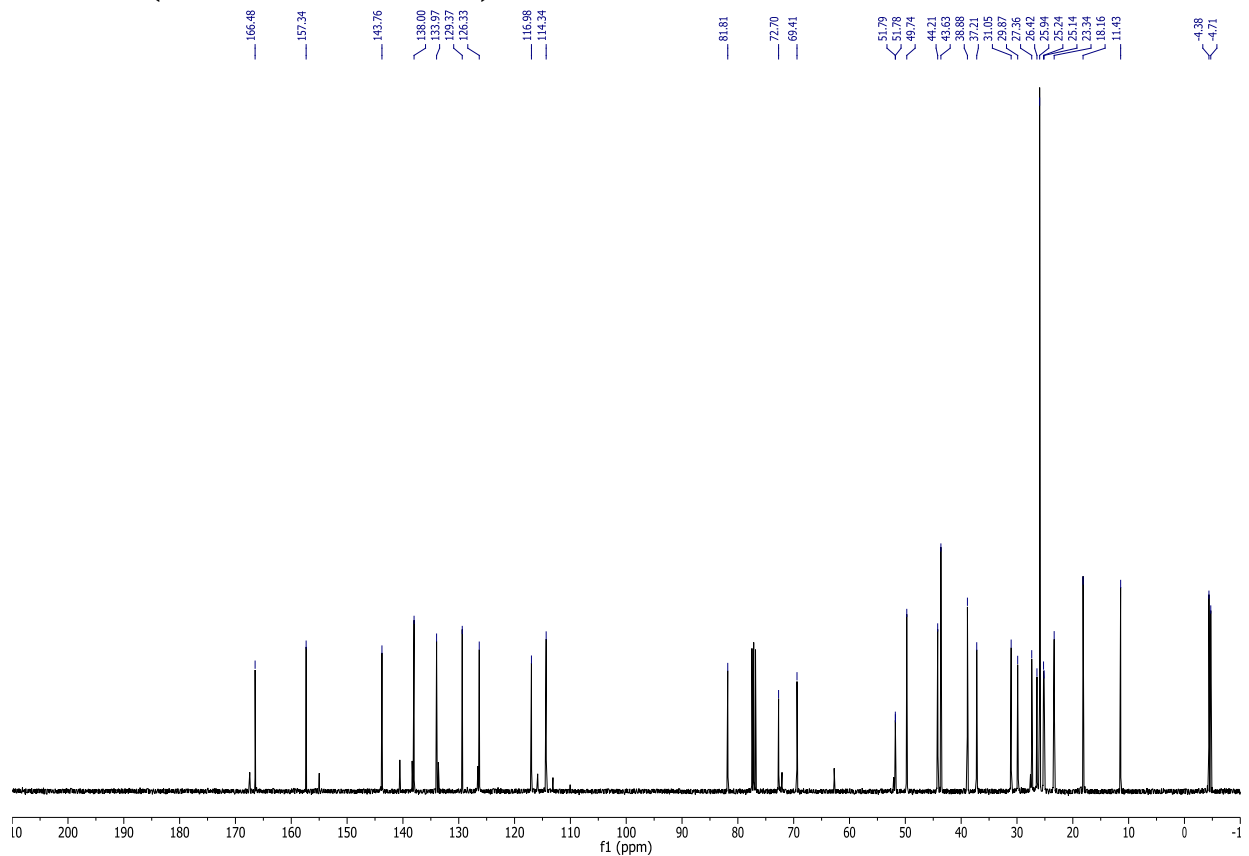
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



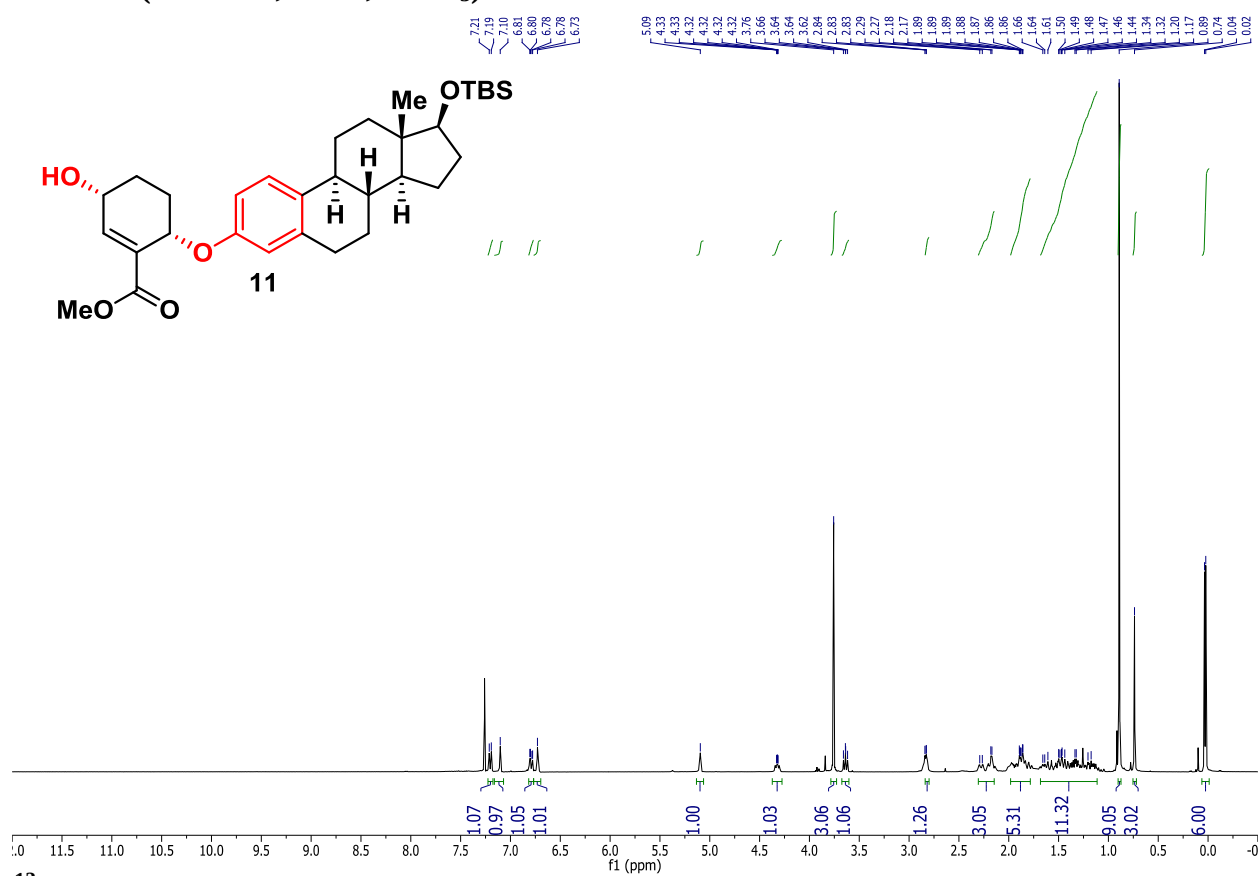
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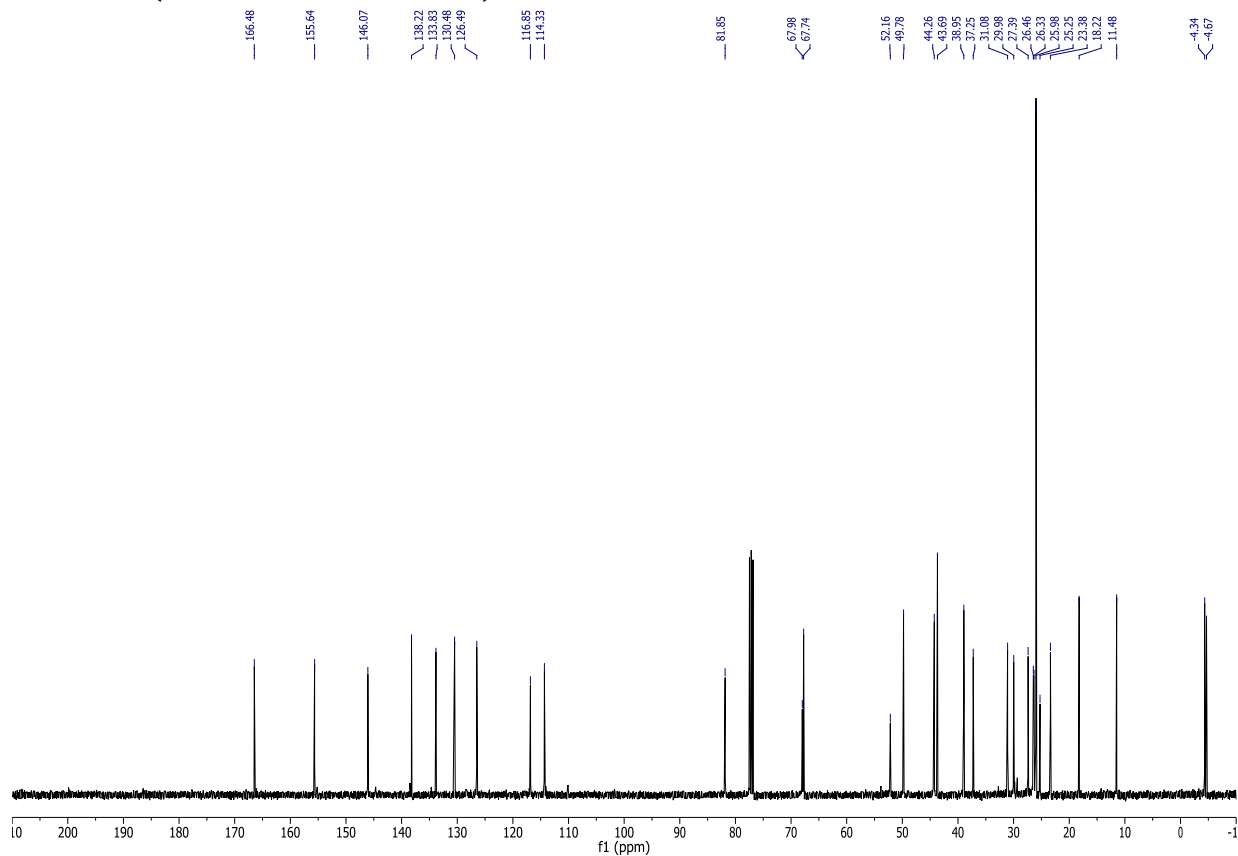
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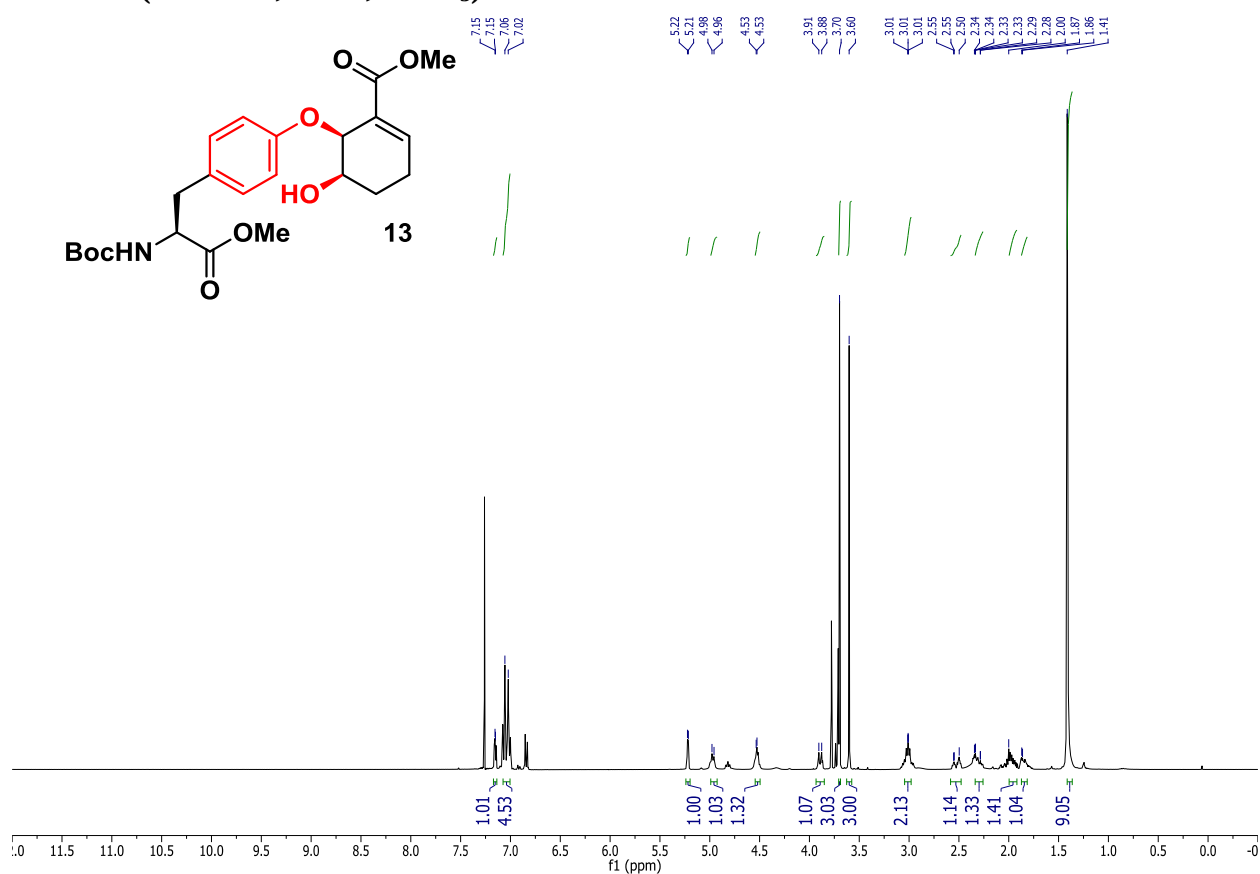
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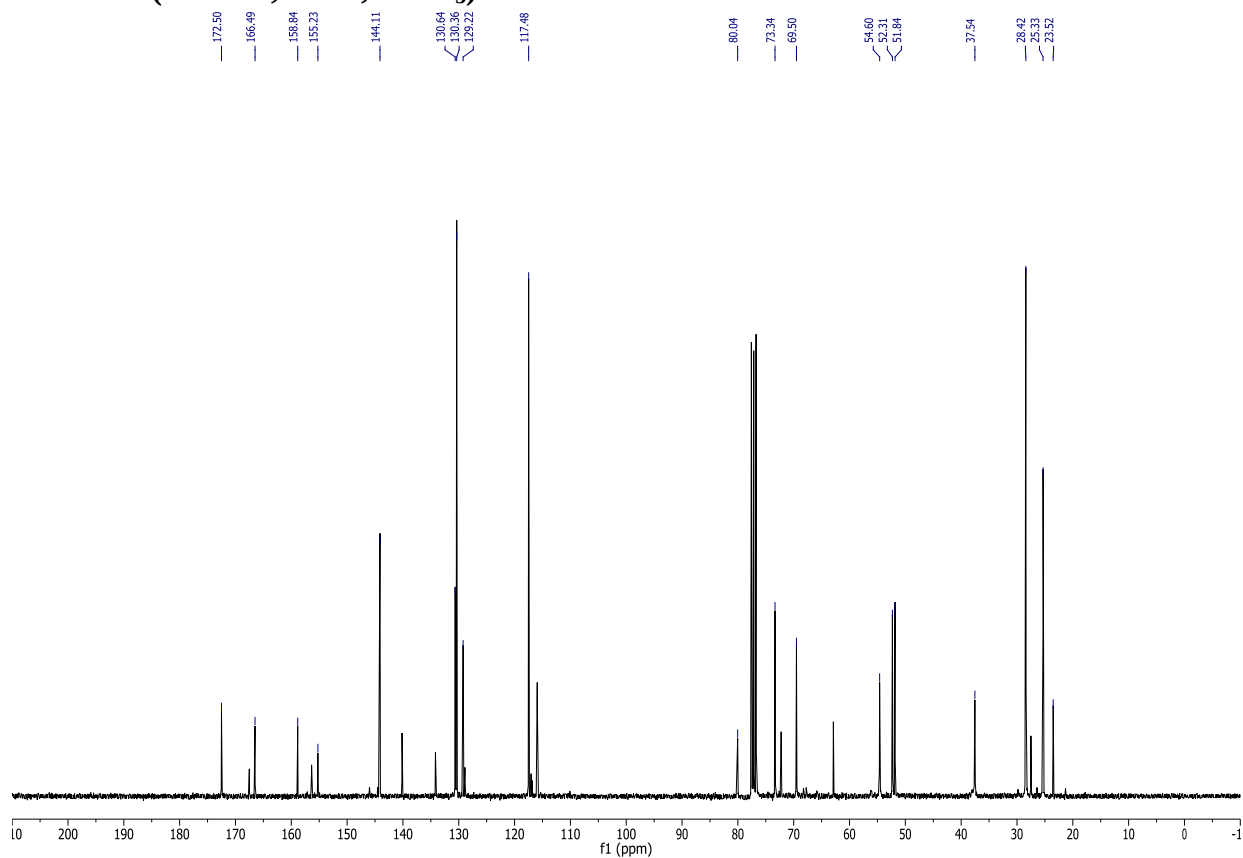
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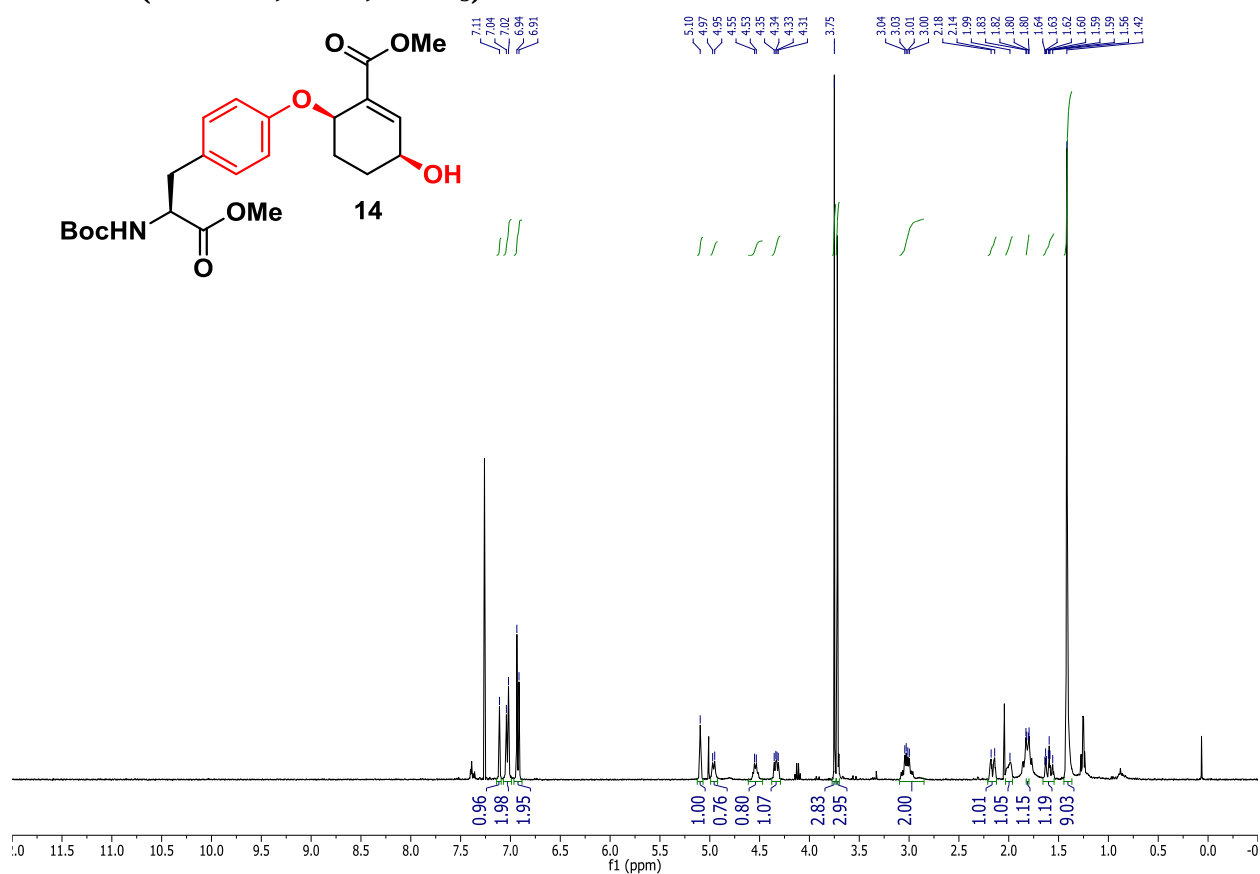
^1H NMR (400 MHz, 23 °C, CDCl_3)



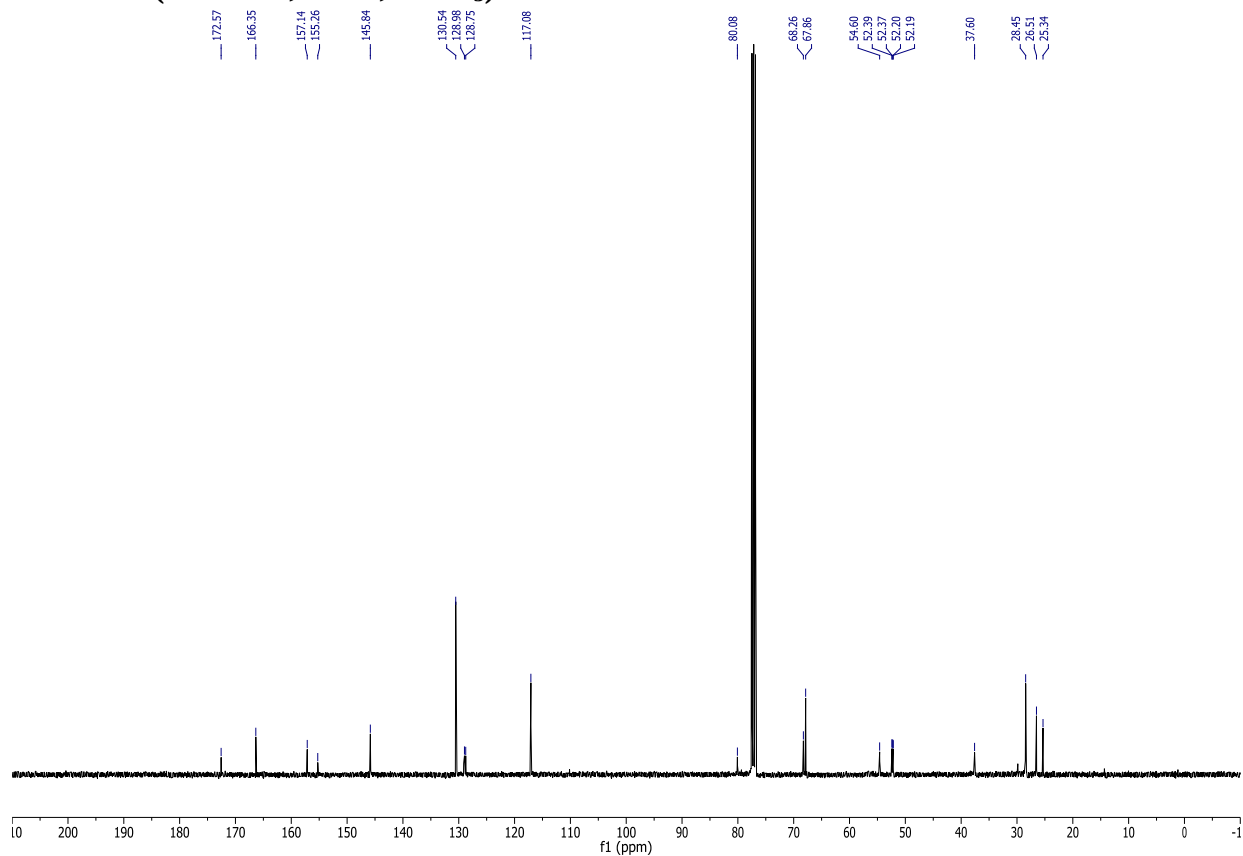
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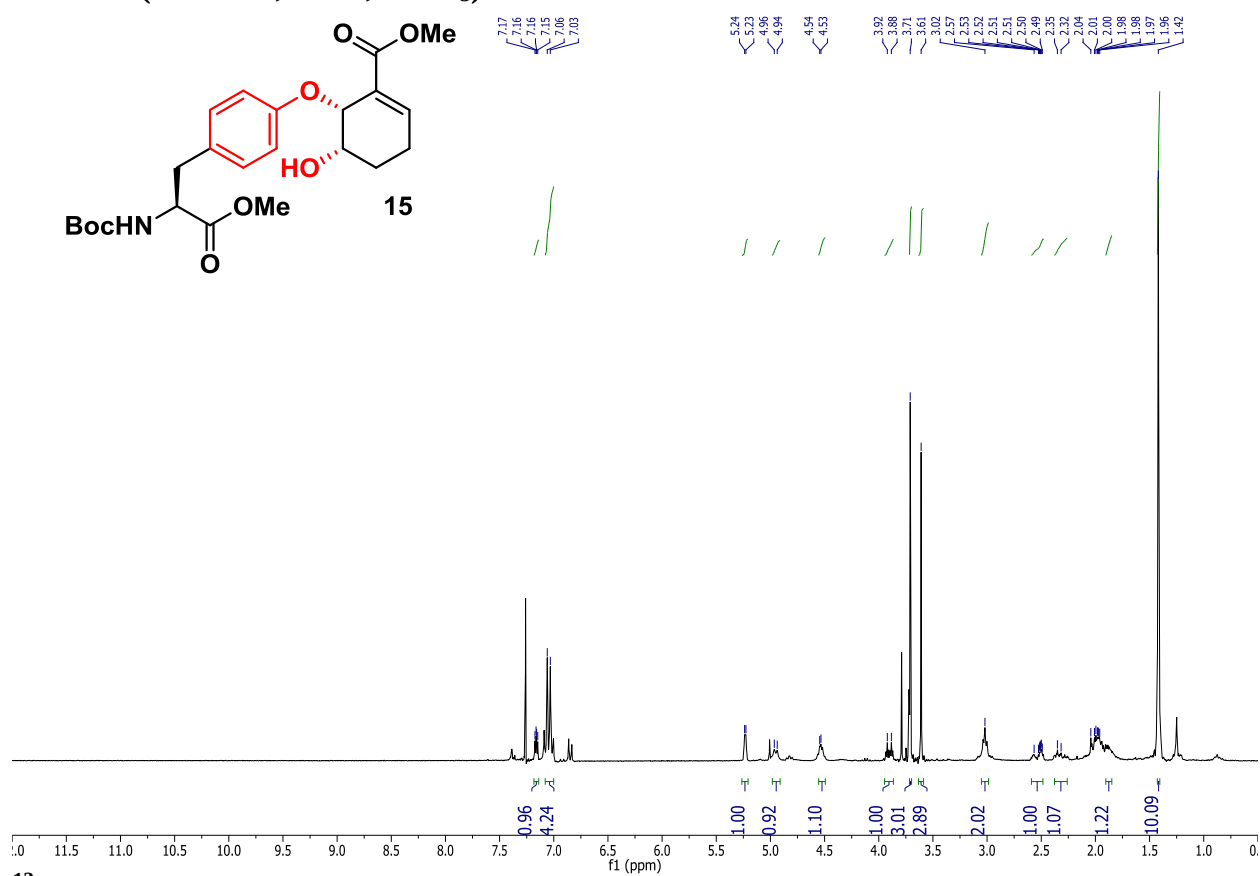
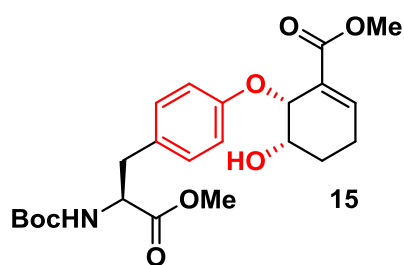
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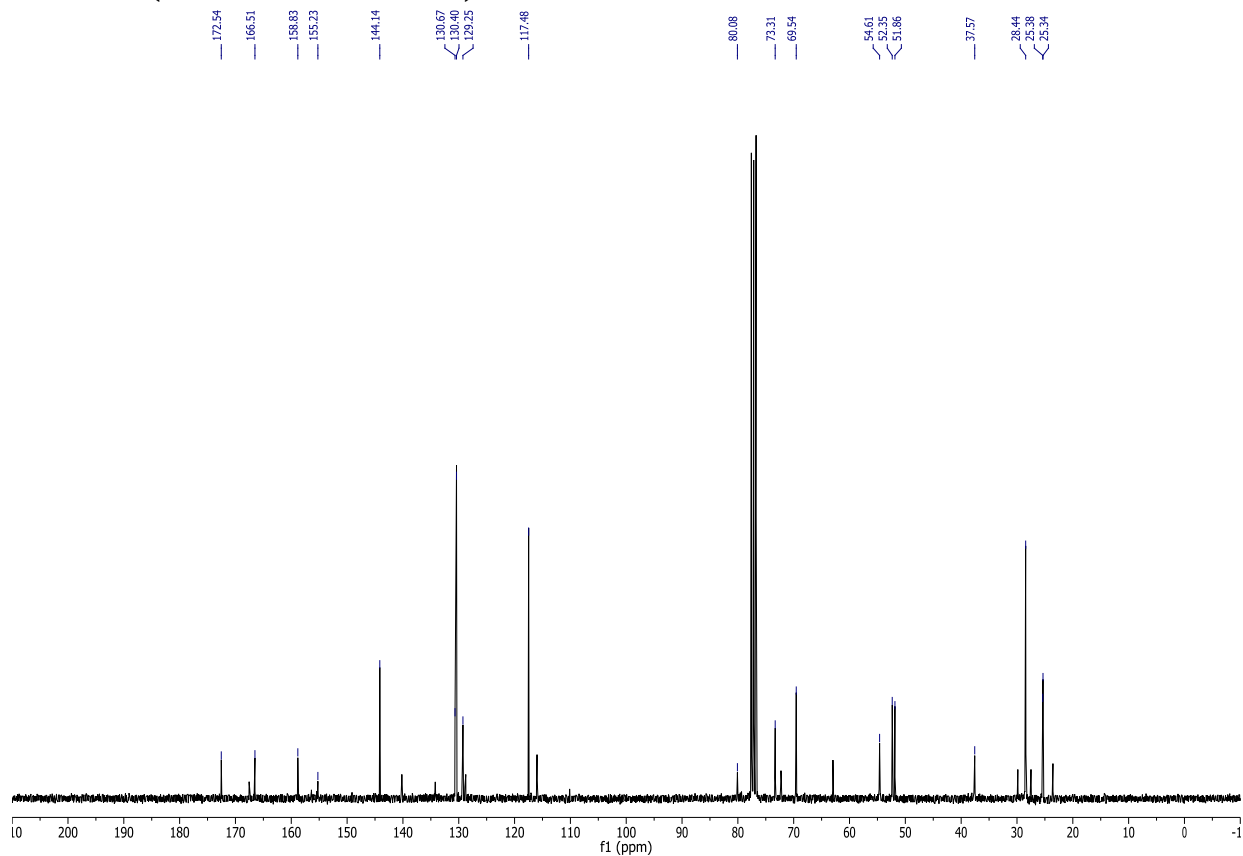
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



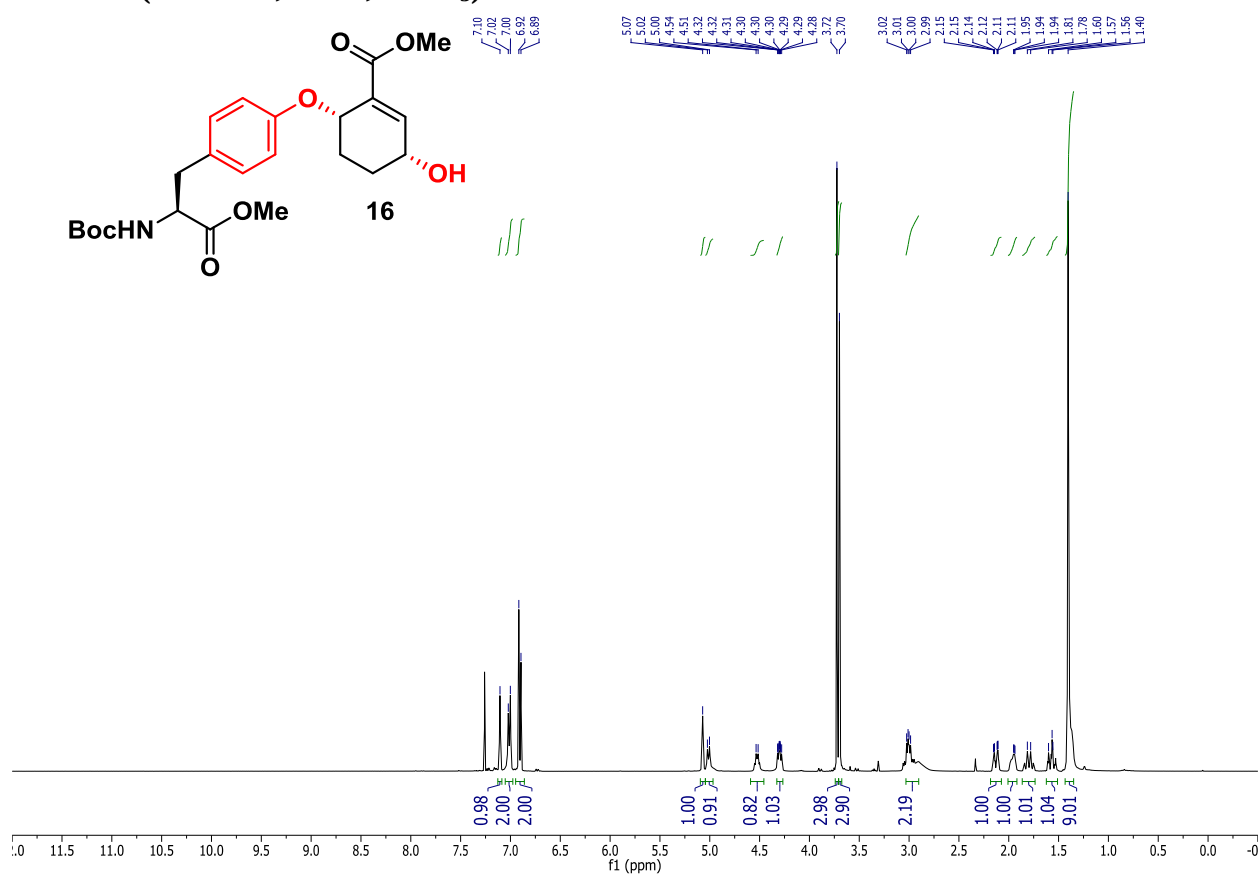
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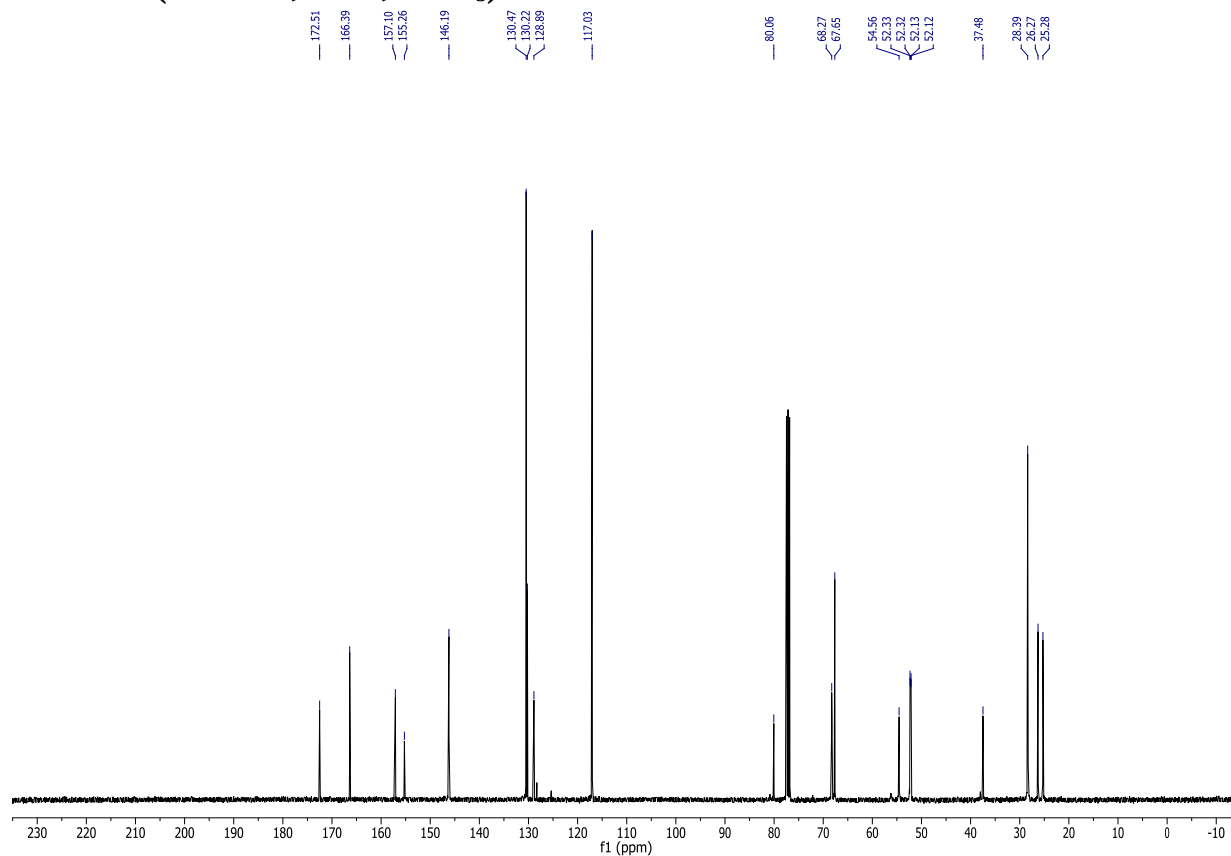
^{13}C NMR (75 MHz, 23 °C, CDCl_3)



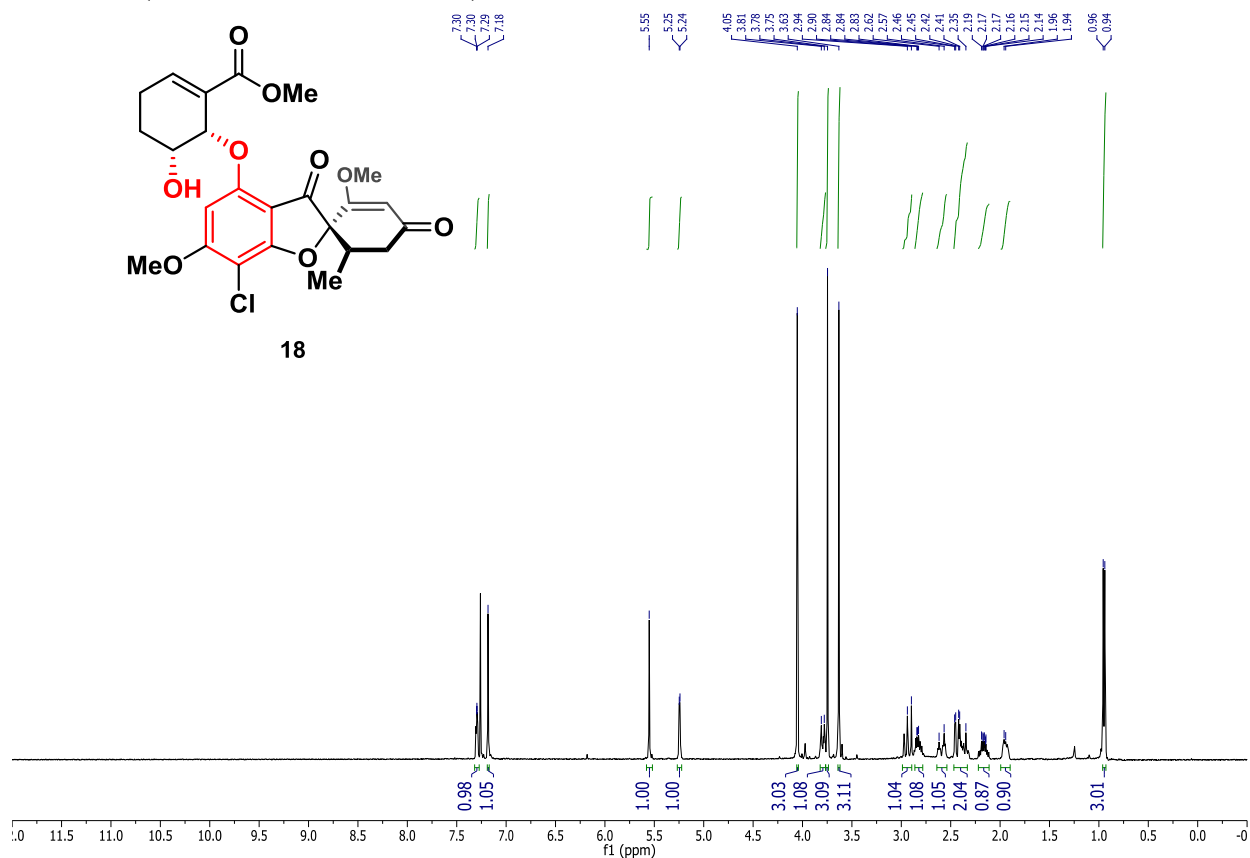
^1H NMR (400 MHz, 23 °C, CDCl_3)



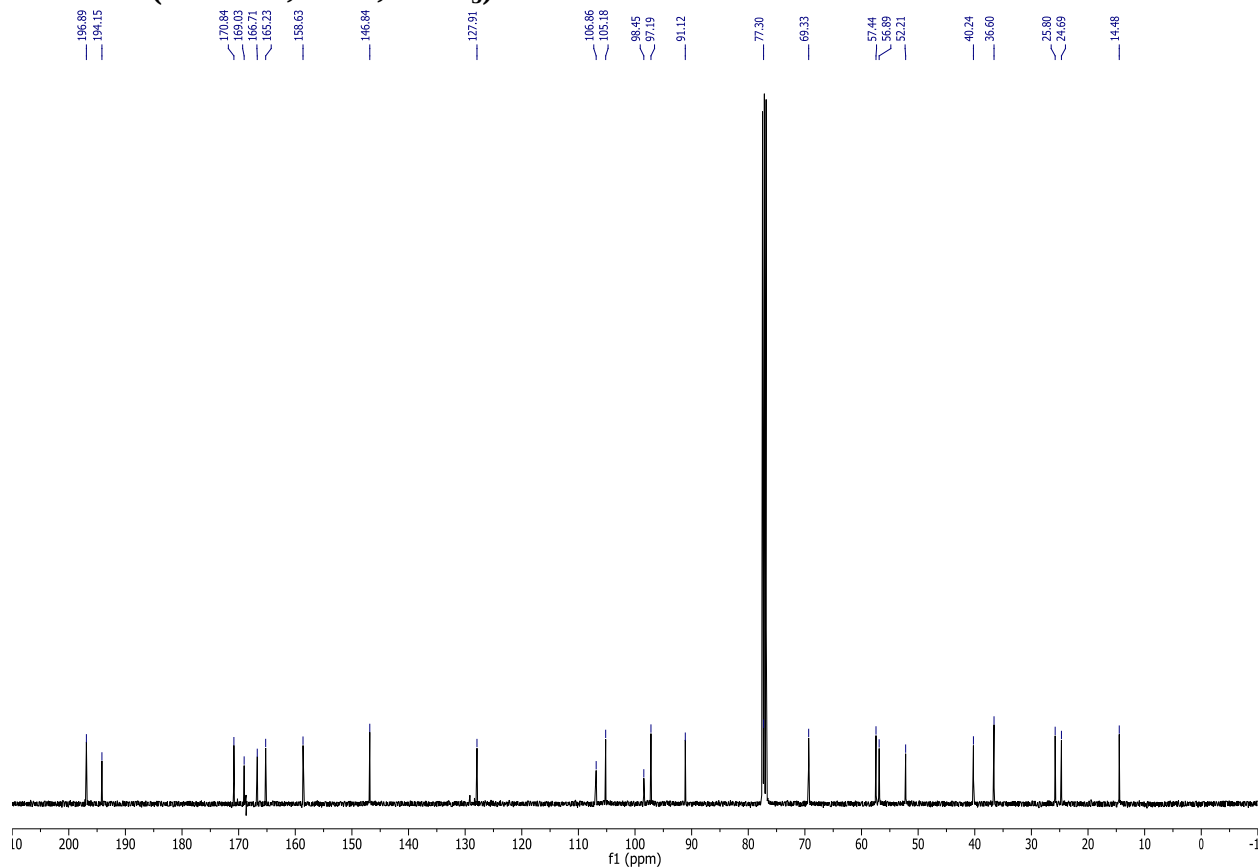
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



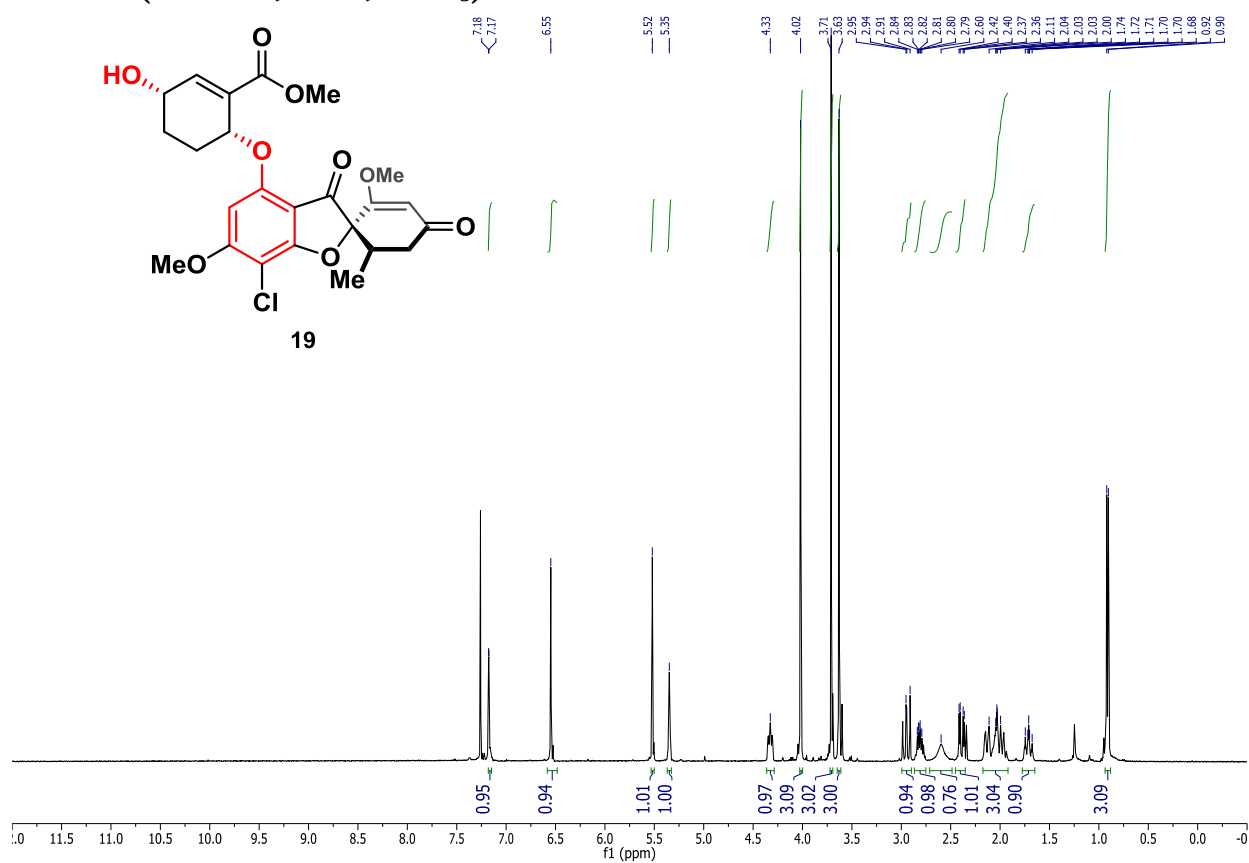
^1H NMR (400 MHz, 23 °C, CDCl_3)



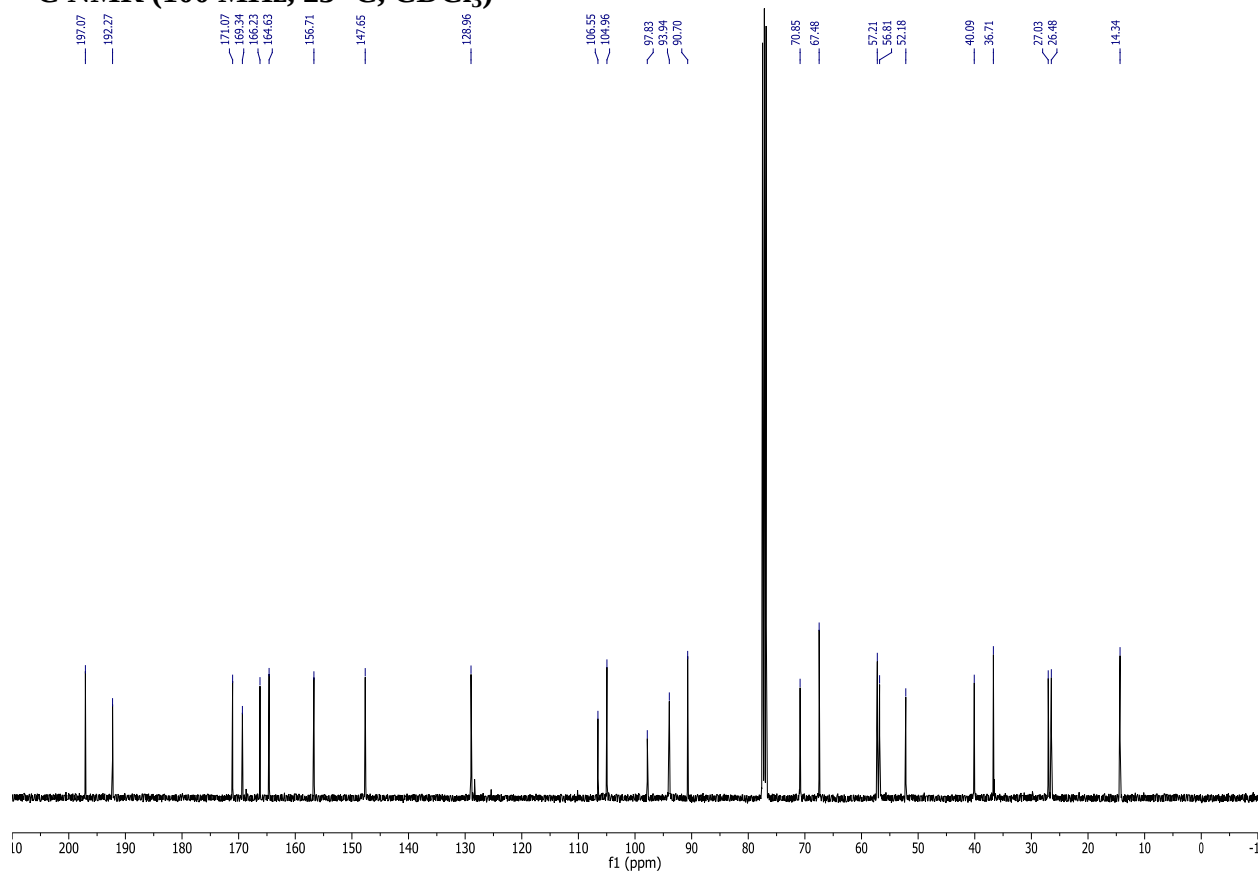
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



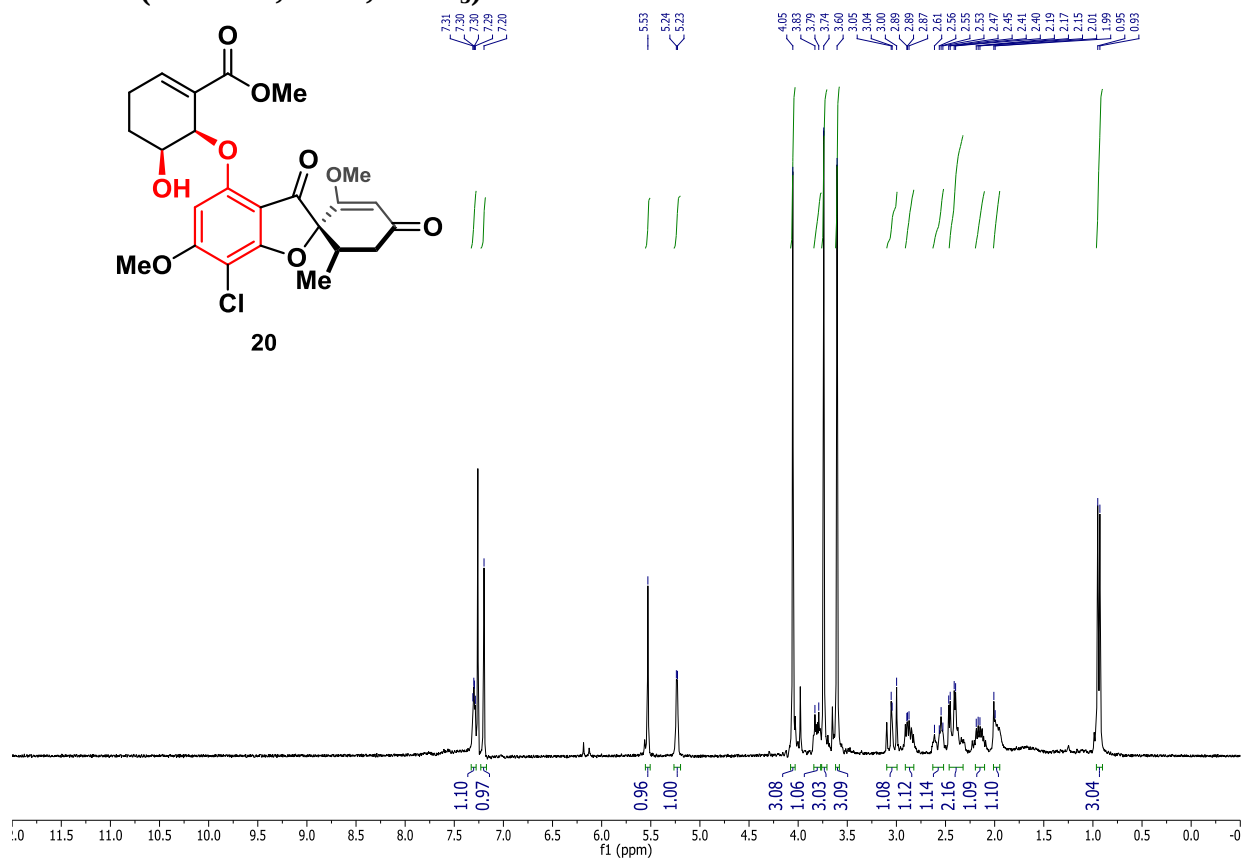
^1H NMR (400 MHz, 23 °C, CDCl_3)



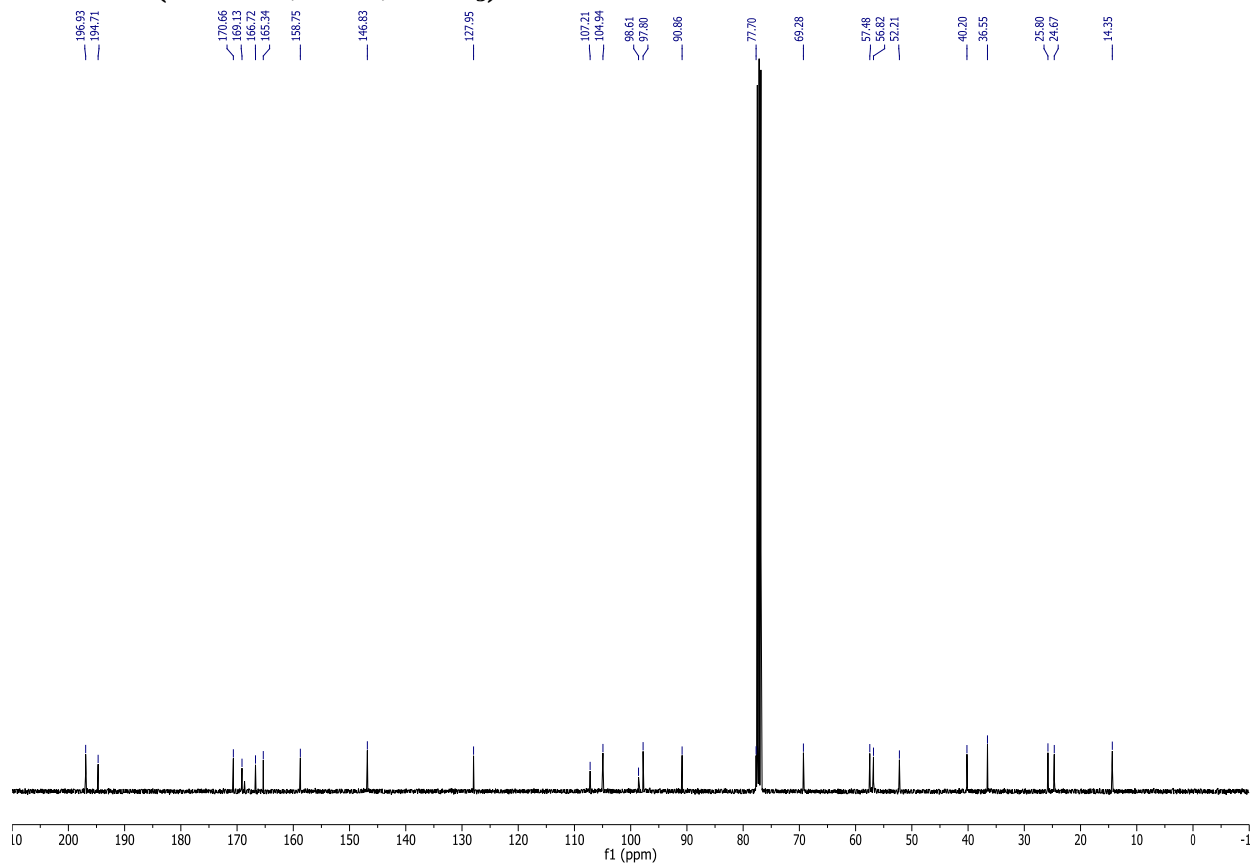
^{13}C NMR (100 MHz, 23 °C, CDCl_3)



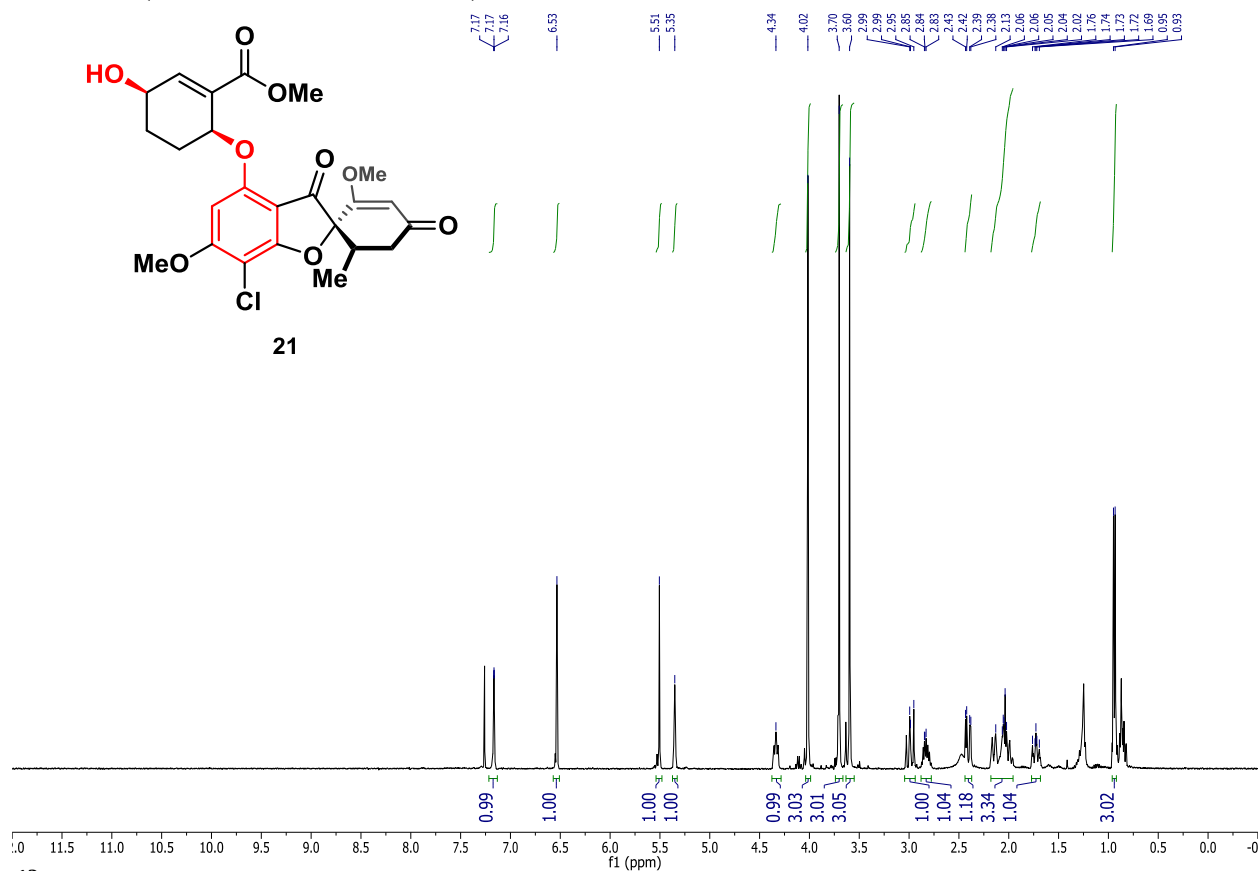
^1H NMR (300 MHz, 23 °C, CDCl_3)



^{13}C NMR (100 MHz, 23 °C, CDCl_3)



^1H NMR (400 MHz, 23 $^\circ\text{C}$, CDCl_3)



^{13}C NMR (100 MHz, 23 $^\circ\text{C}$, CDCl_3)

