Supporting Information

Regiodivergent Addition of Phenols to Allylic Oxides

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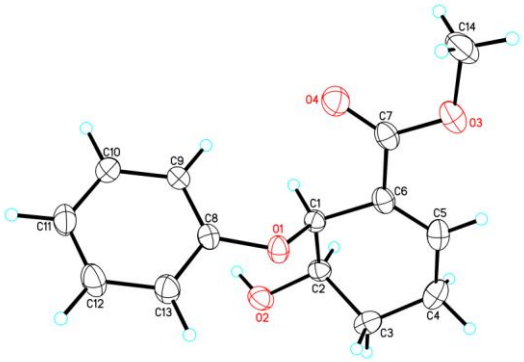
General Procedures. Where appropriate, reactions were carried out under an inert atmosphere of argon or nitrogen with dry solvents, using anhydrous conditions unless otherwise stated. Dry toluene, dichloromethane (DCM), diethyl ether, and triethylamine (Et_3N), were obtained by passing the previously 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 (^{1}H-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 (5μm, 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).

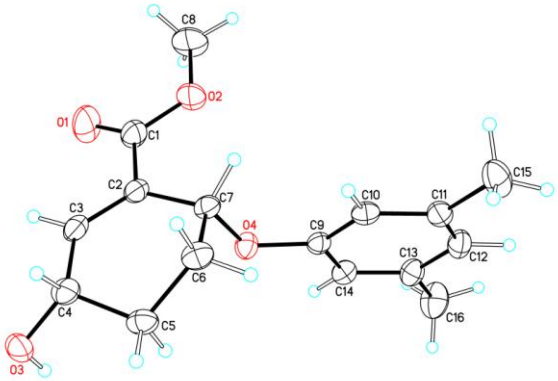


Crystal data for 2a

Selected parameters:

Empirical formula	$C_{14}H_{16}O_4$	
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) $Å^3$	
Z	4	
Final R indices [I>2sigma(I)]	R1 = 0.0323, wR2 = 0.0810	
R indices (all data)	R1 = 0.0400, wR2 = 0.0866	

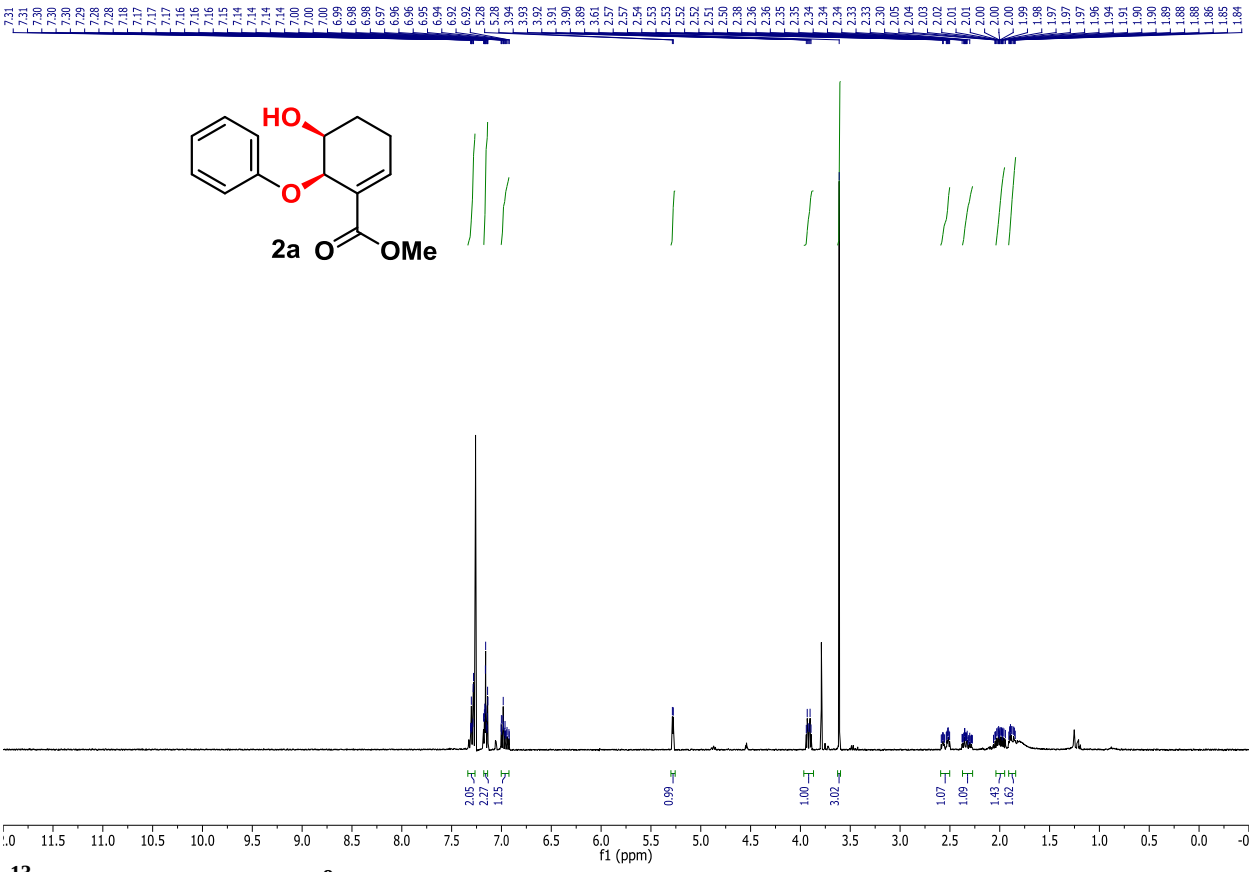
Crystal data for 3h



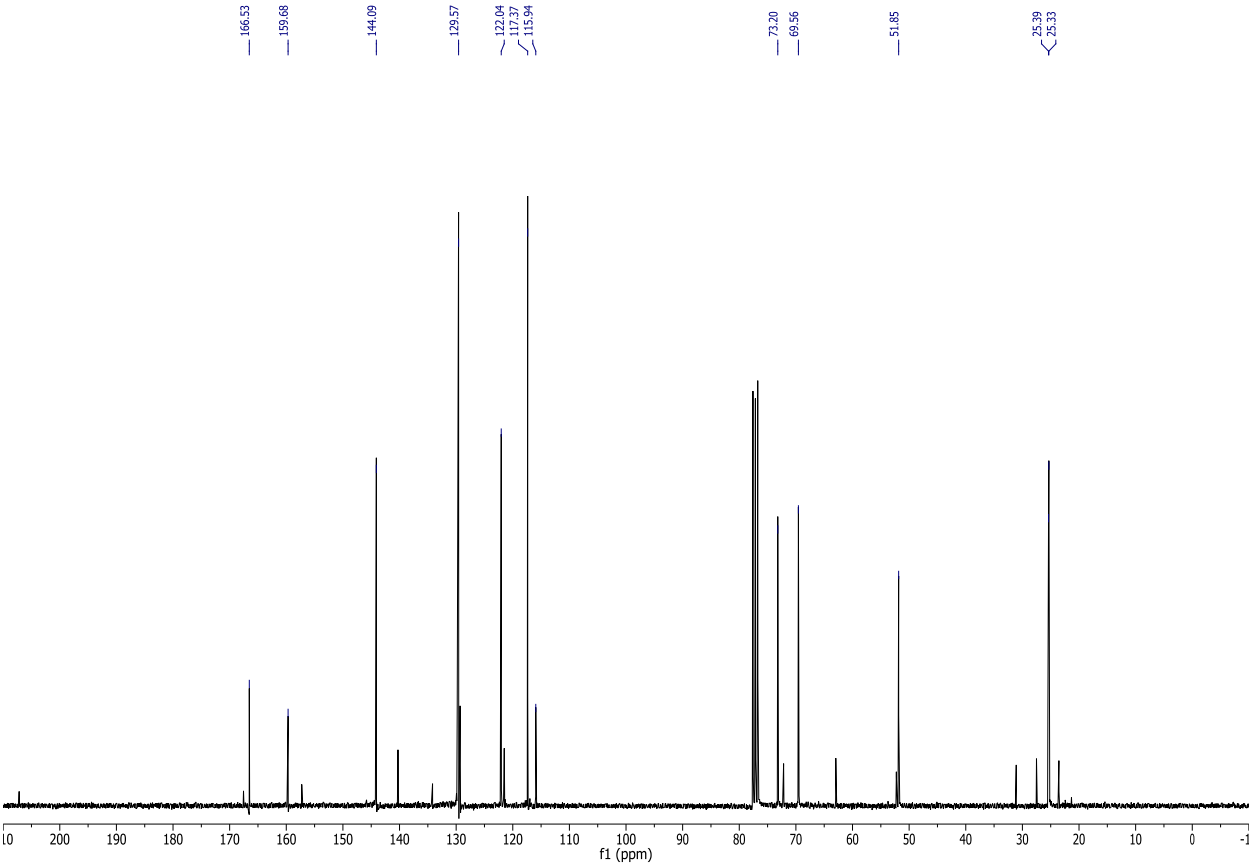
Selected parameters:

Empirical Formula	$C_{16}H_{20}O_4$	
Formula weight	276.32	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	a = 32.791(2) Å	α = 90°
	b = 32.791(2) Å	β = 90°
	c = 7.4776(3) Å	γ = 120°
Volume	6962.9(7) $Å^3$	
Z	18	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.0865	
R indices (all data)	R1 = 0.0974, wR2 = 0.1064	

^{1}H NMR (400 MHz, 23 ^{o}C, $CDCl_3$)



^{13}C NMR (75 MHz, 23 ^{o}C, $CDCl_3$)



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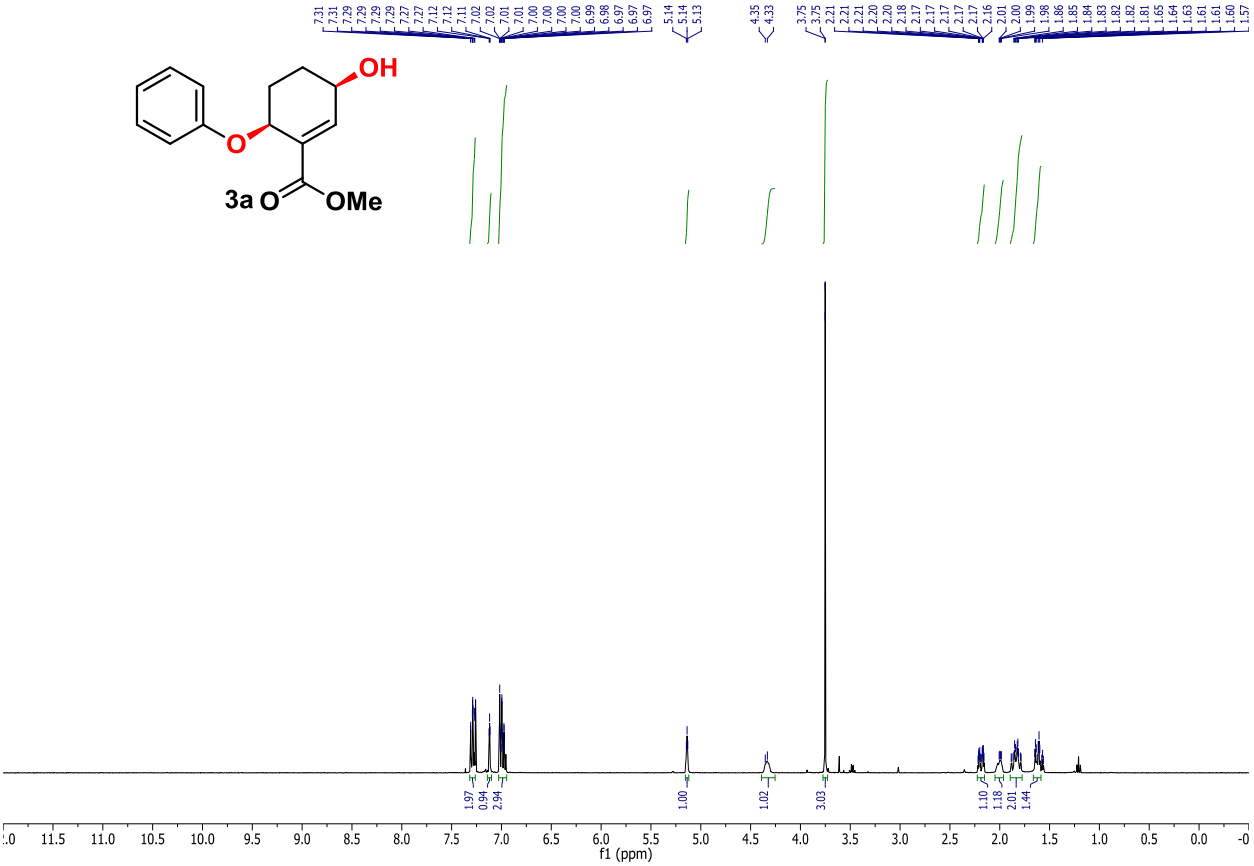

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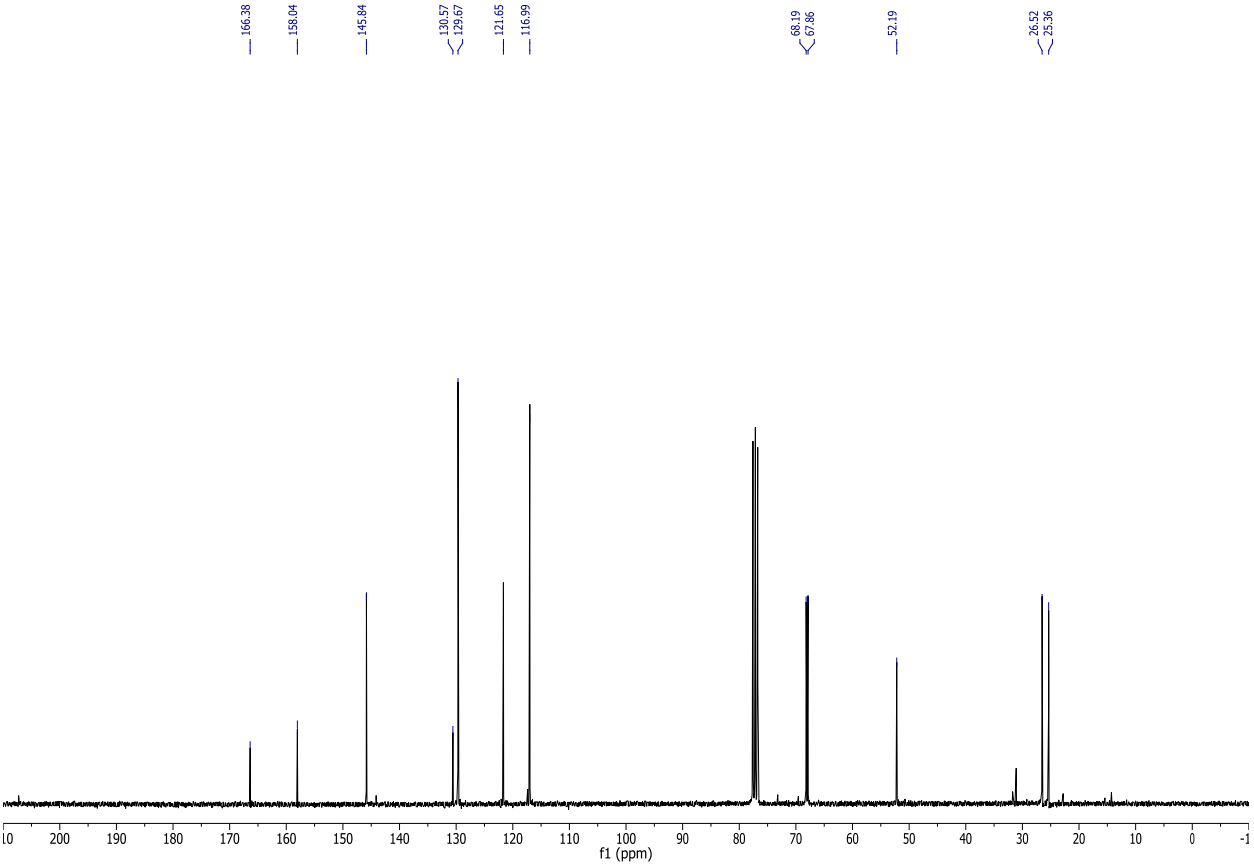

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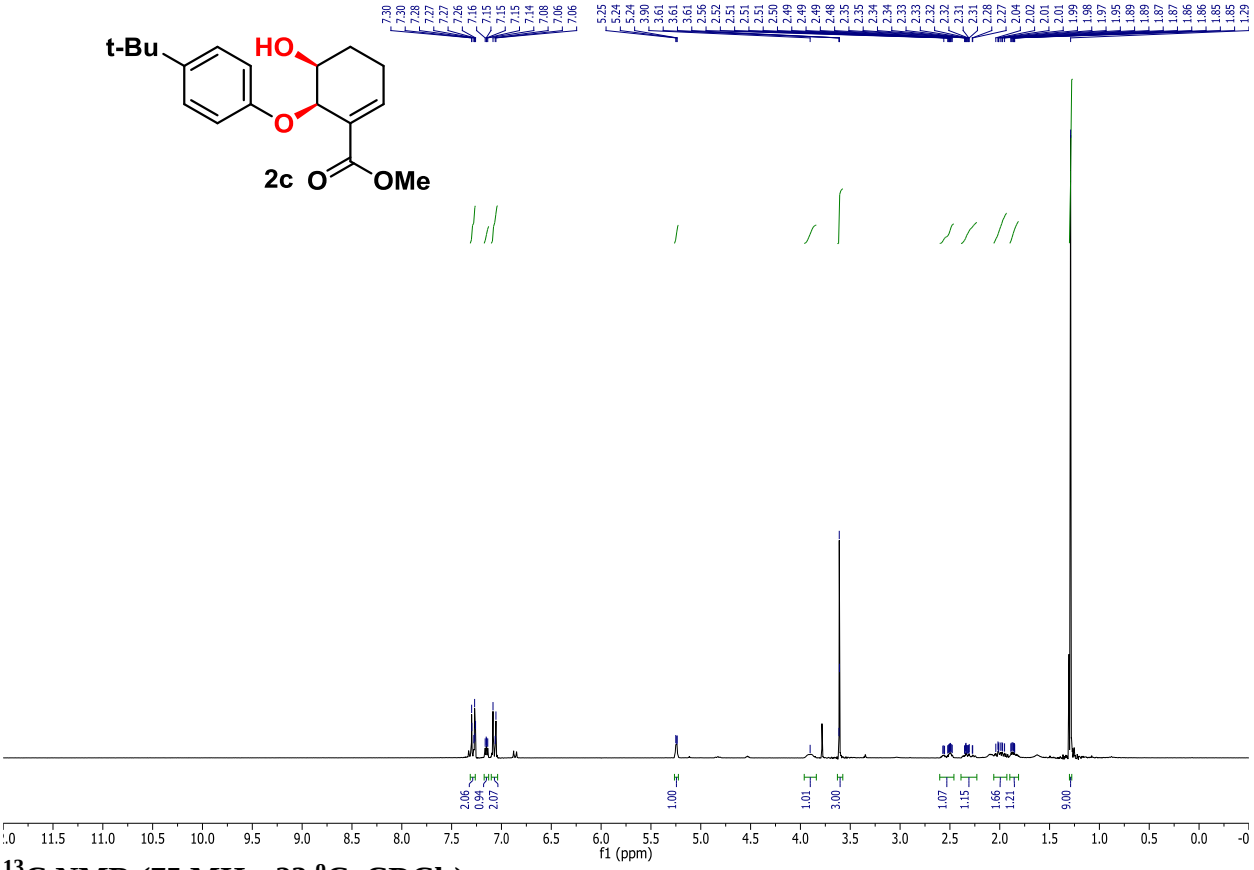

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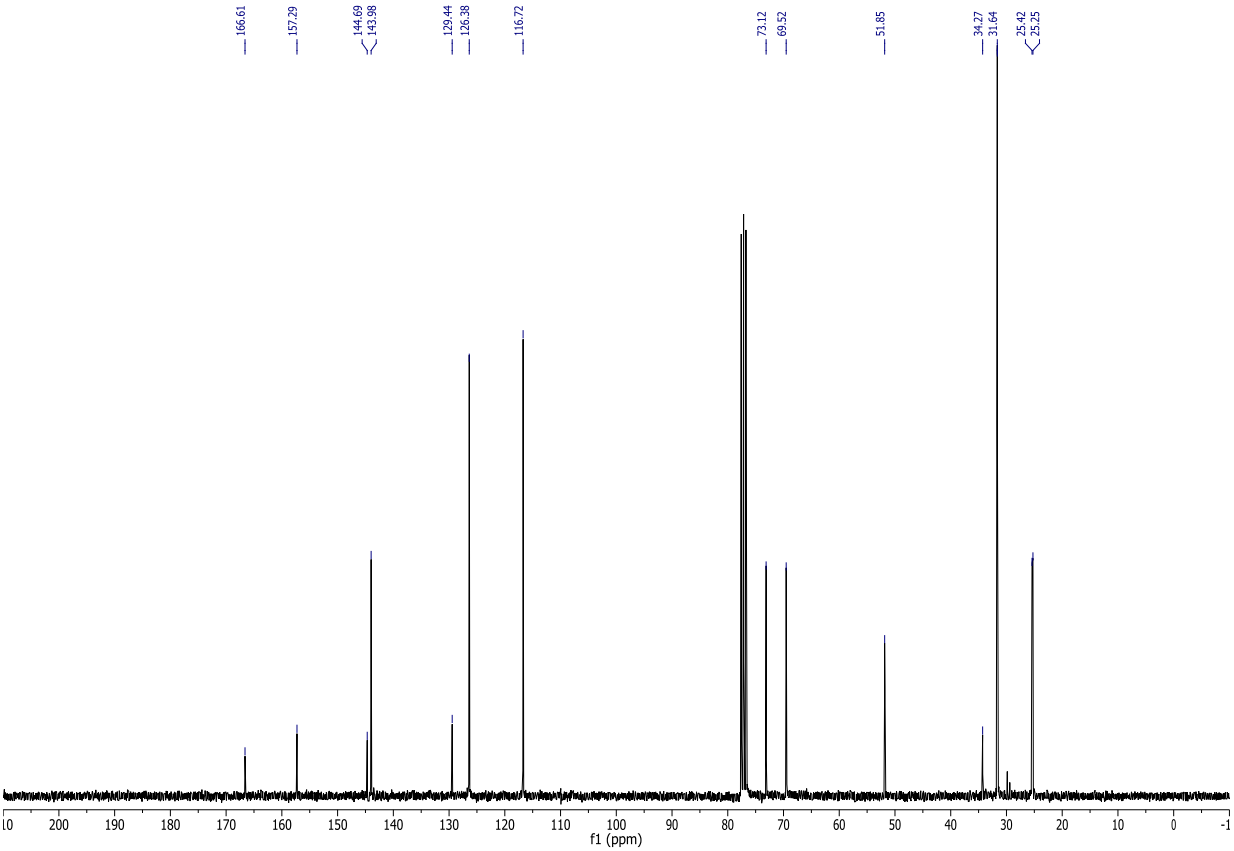

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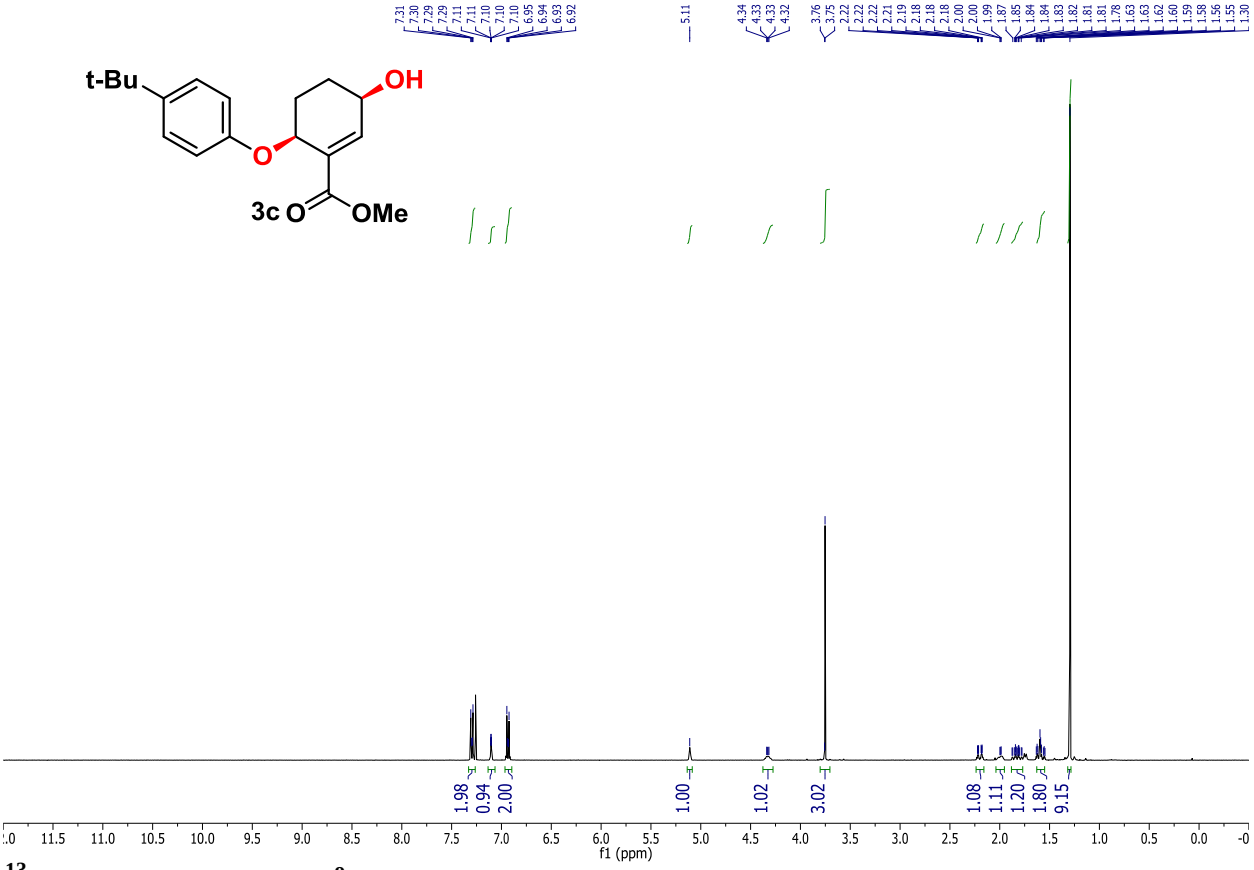

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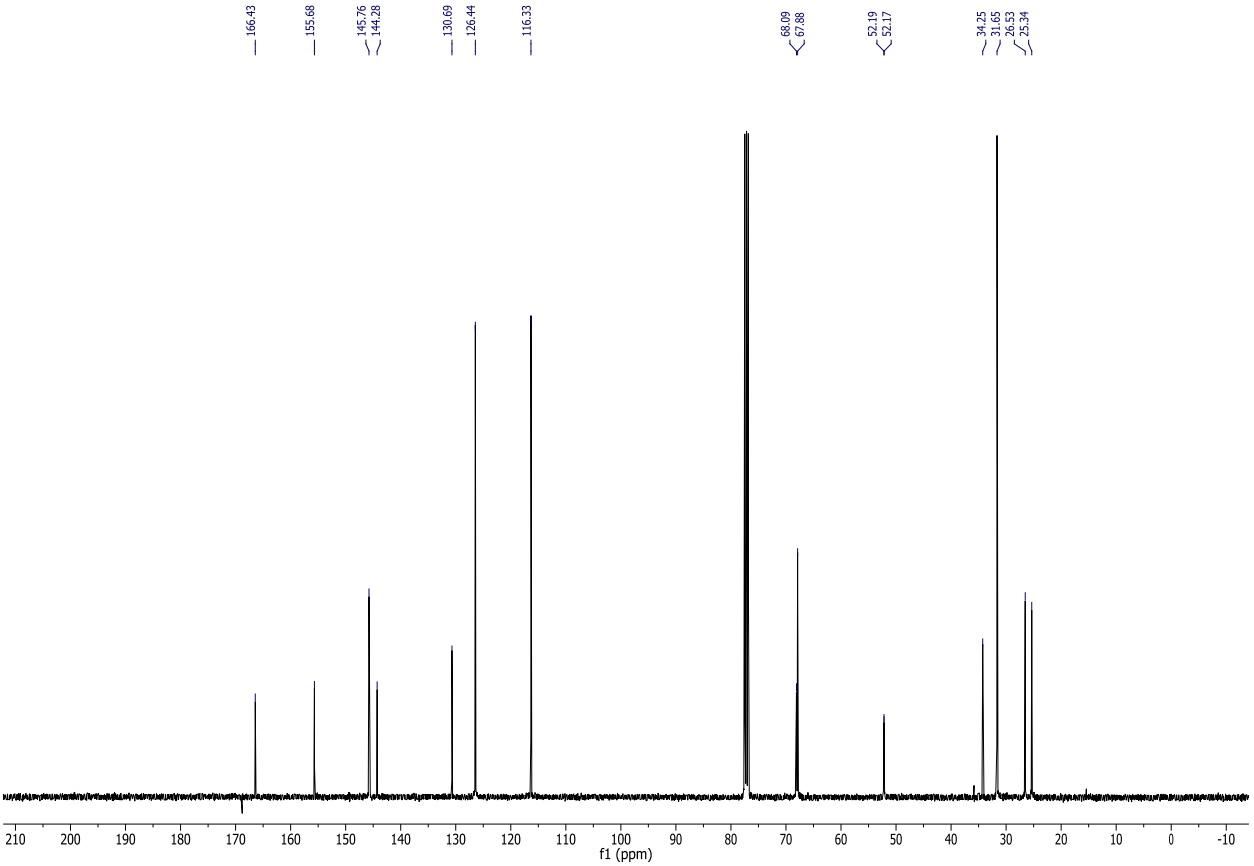

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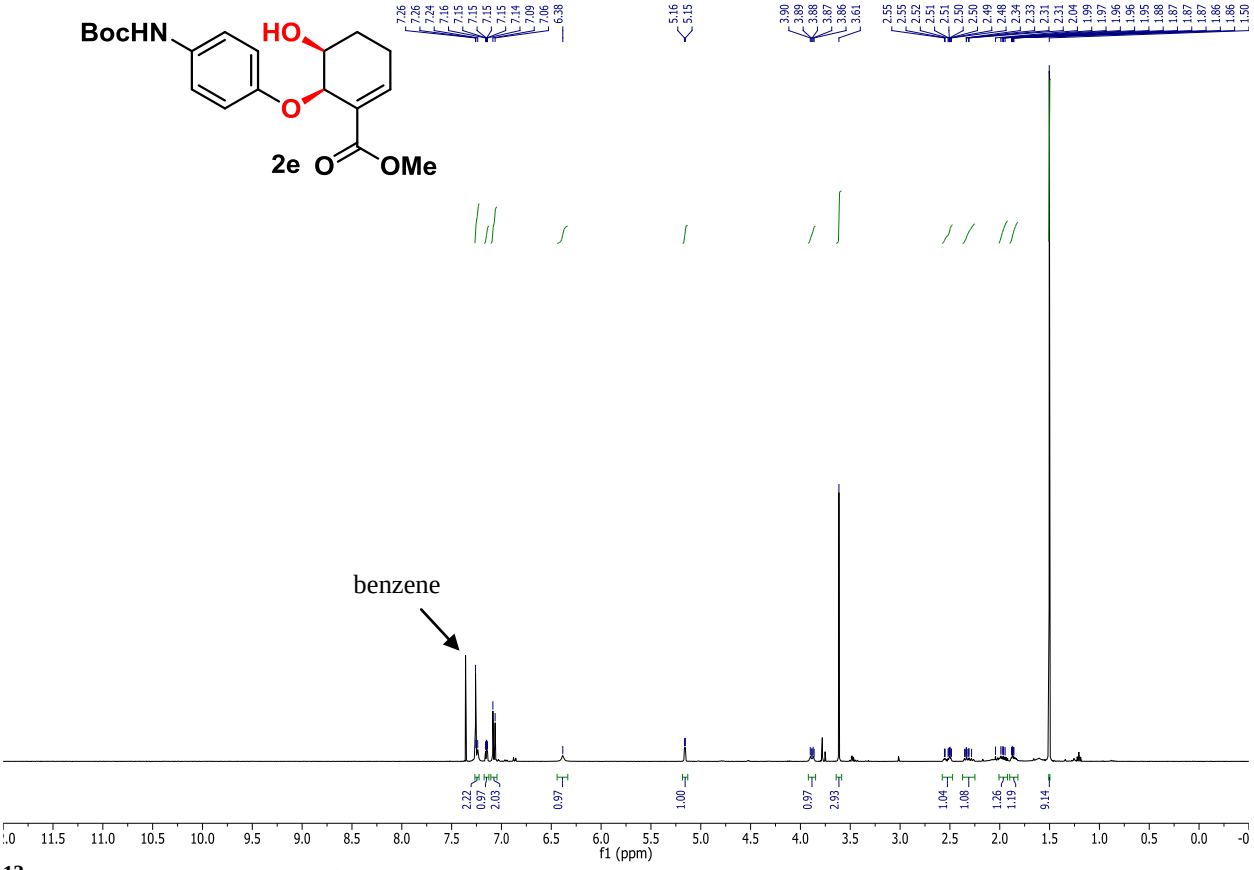
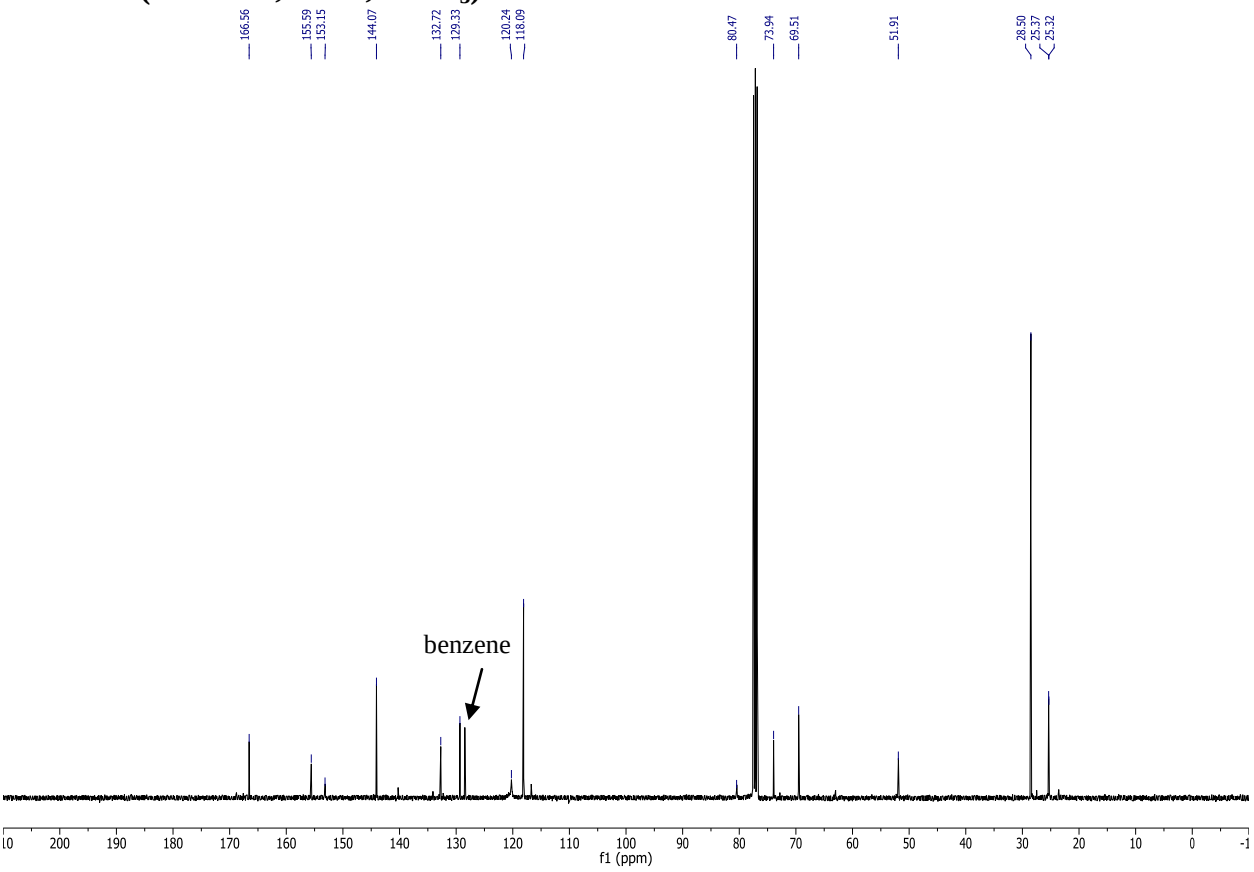
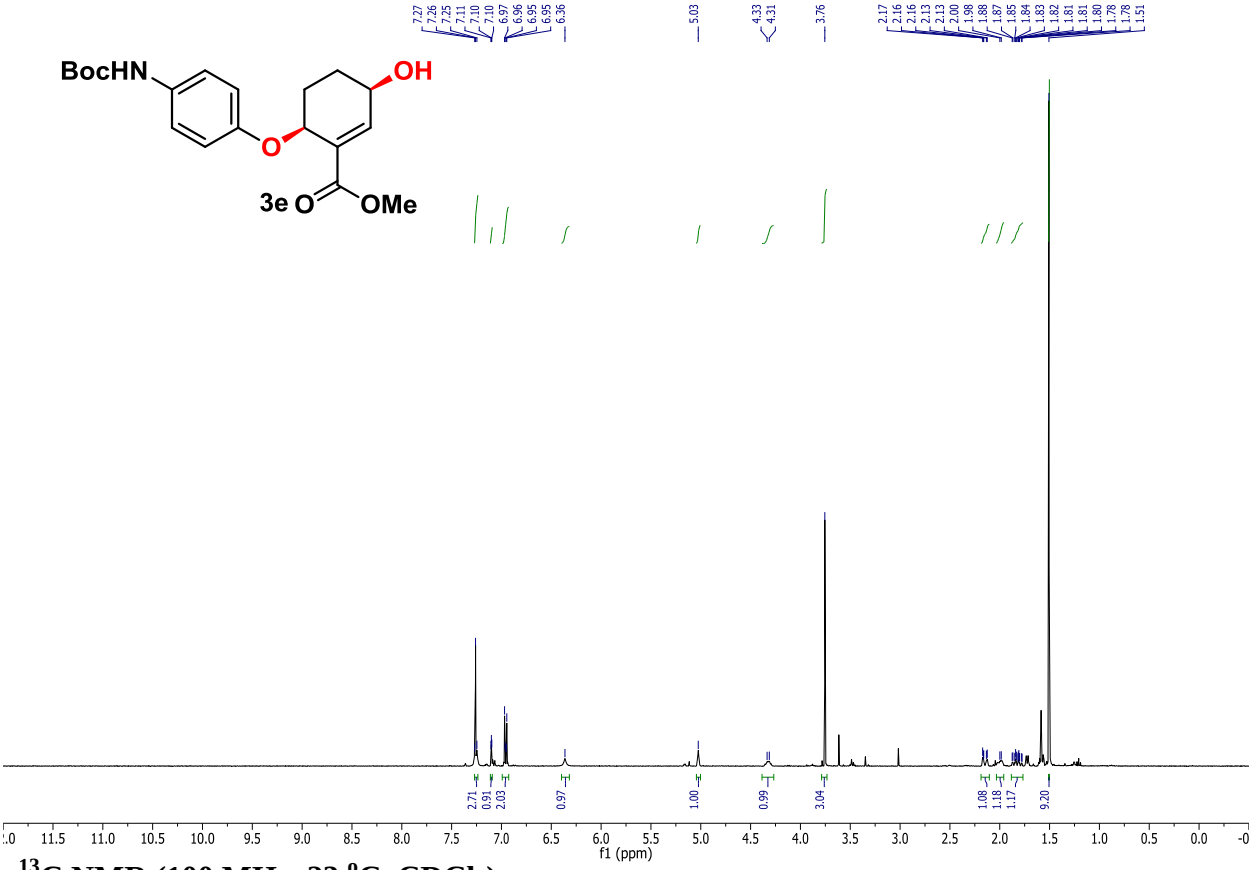


^{13}C NMR (100 MHz, 23 ^{o}C, $CDCl_3$)



^{1}H NMR (400 MHz, 23 ^{o}C, $CDCl_3$)



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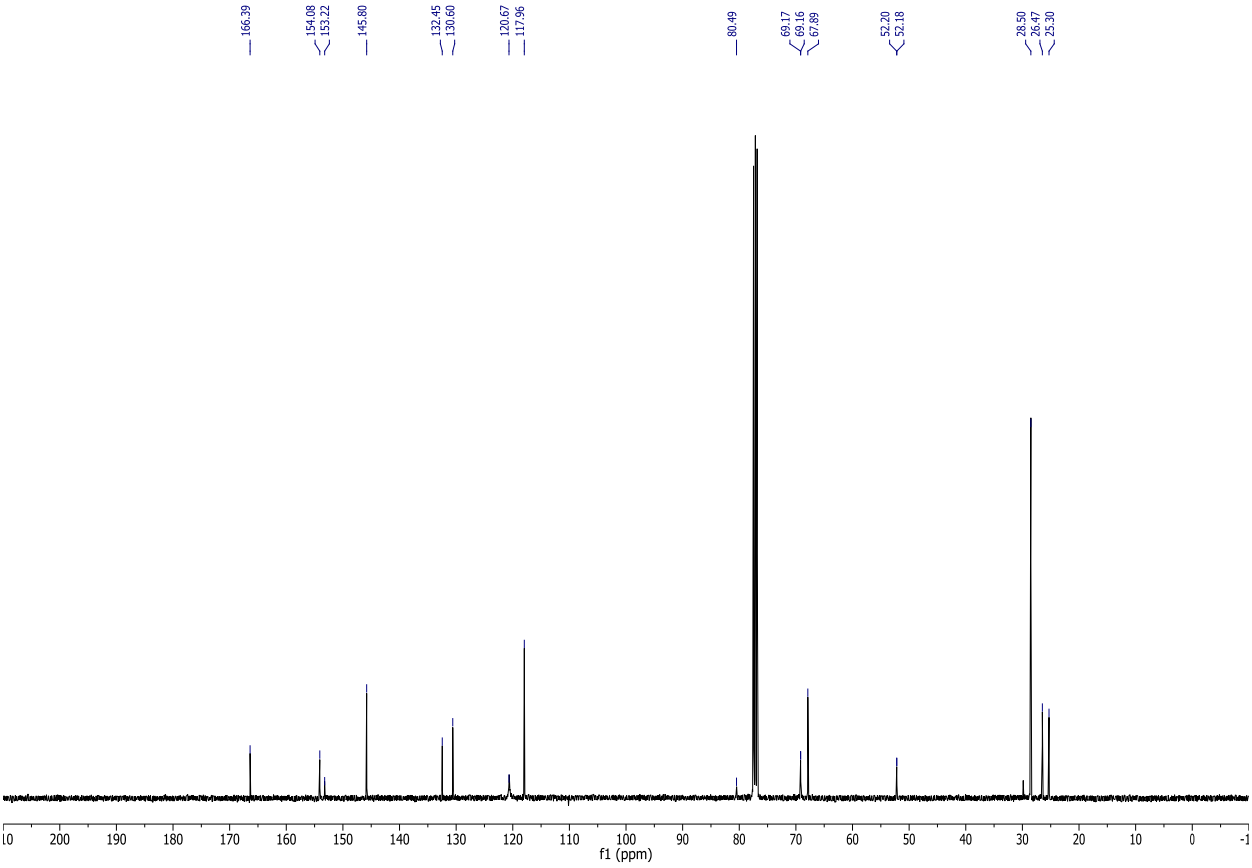

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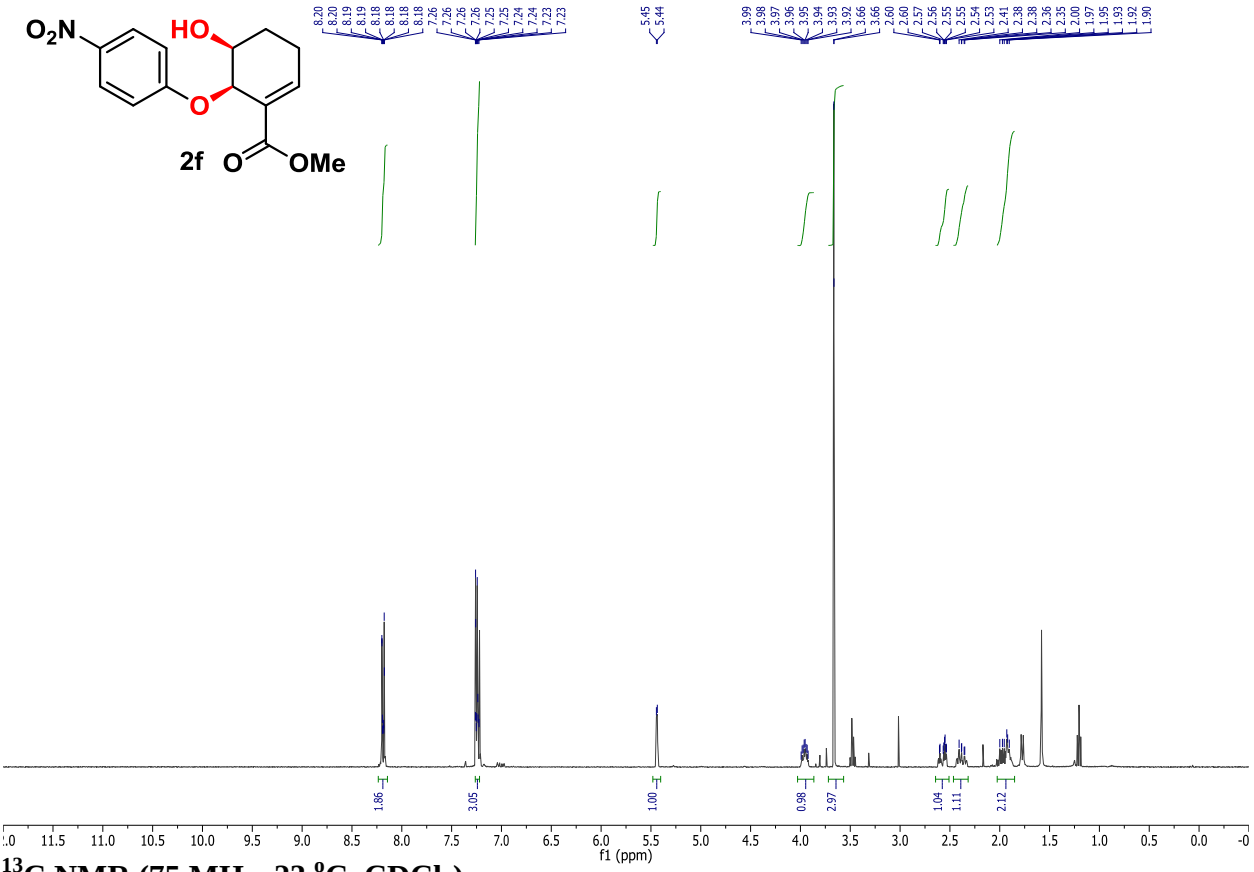

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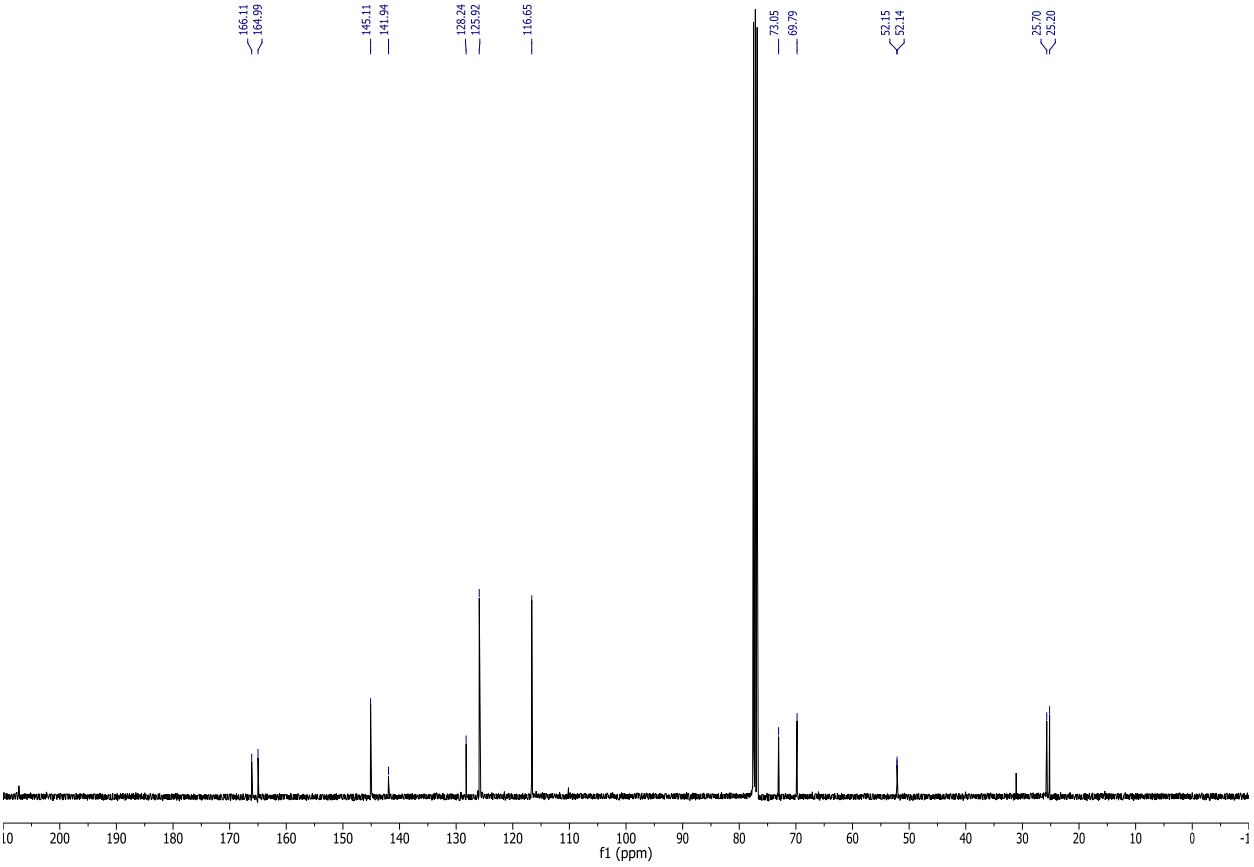

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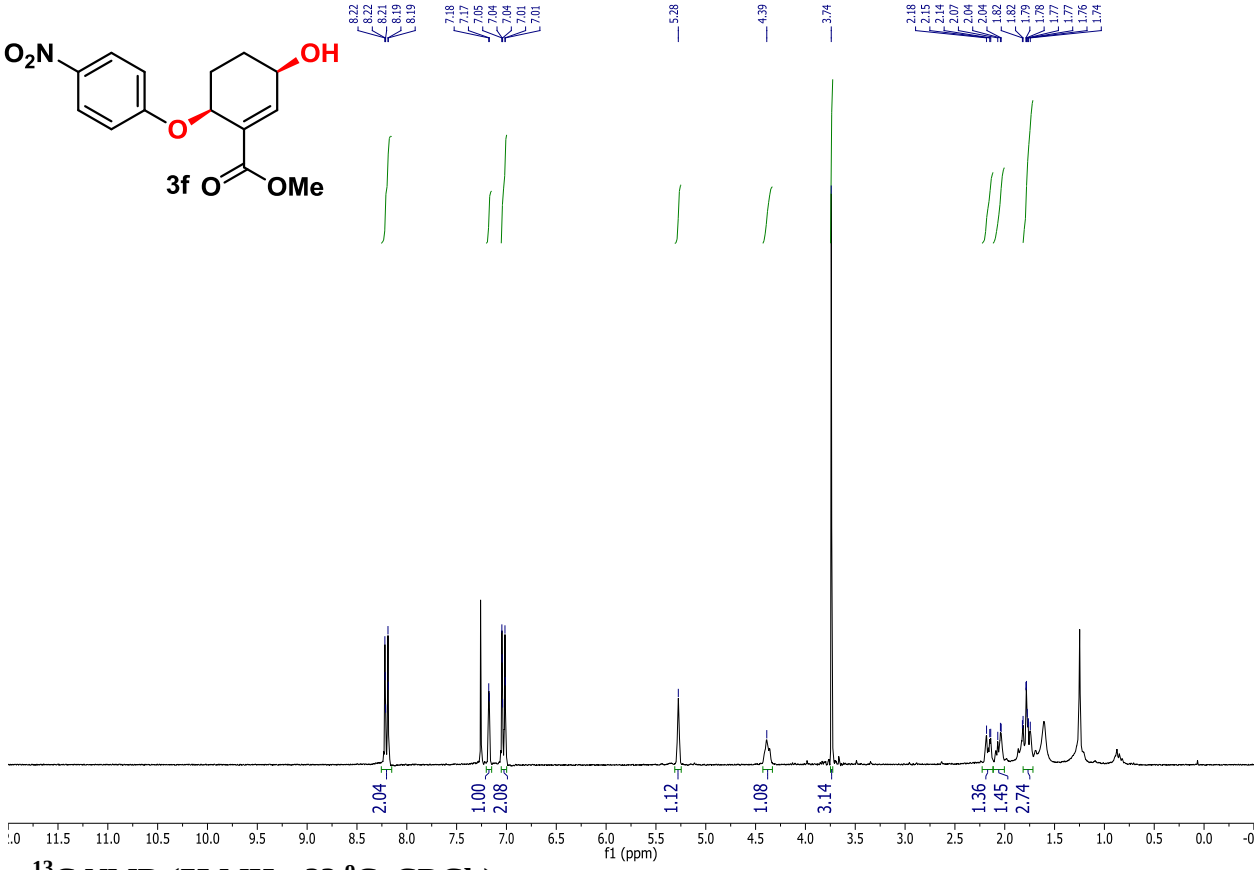

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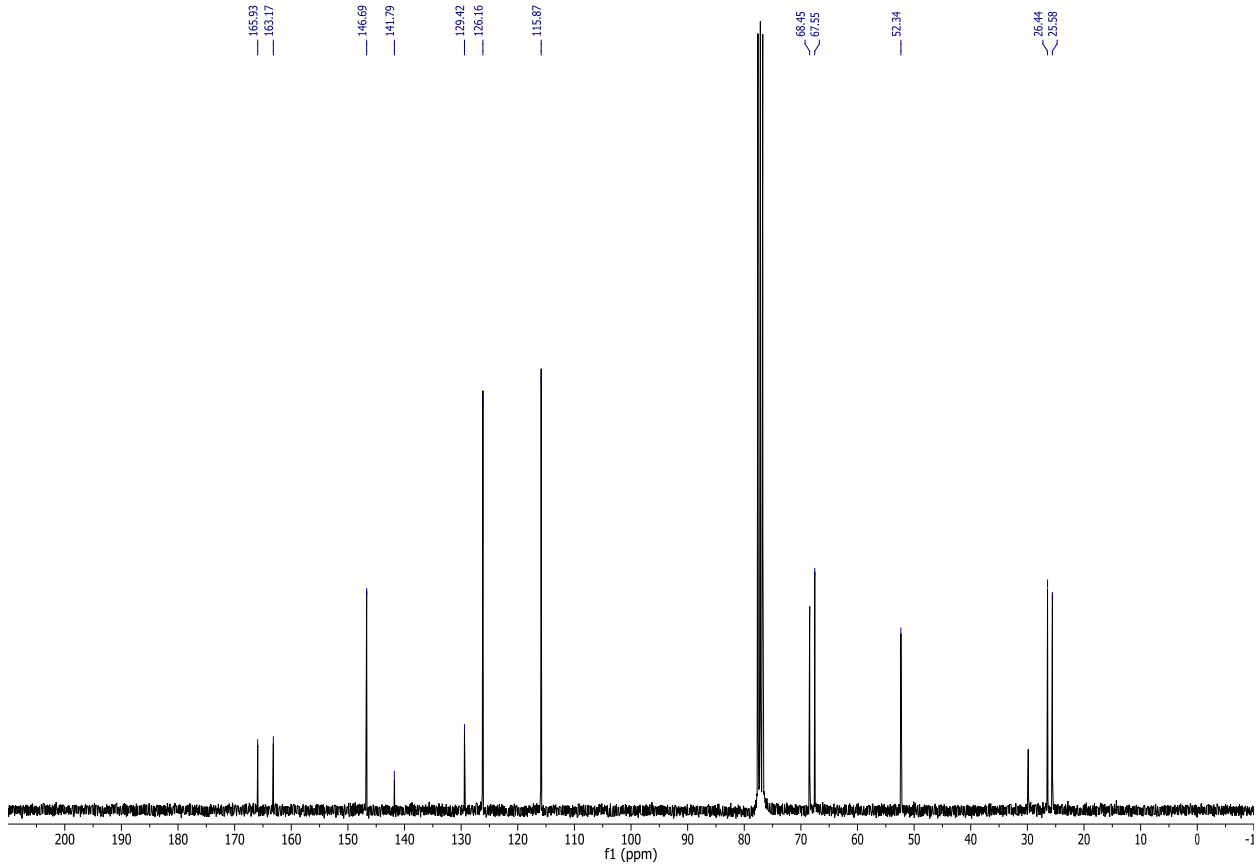

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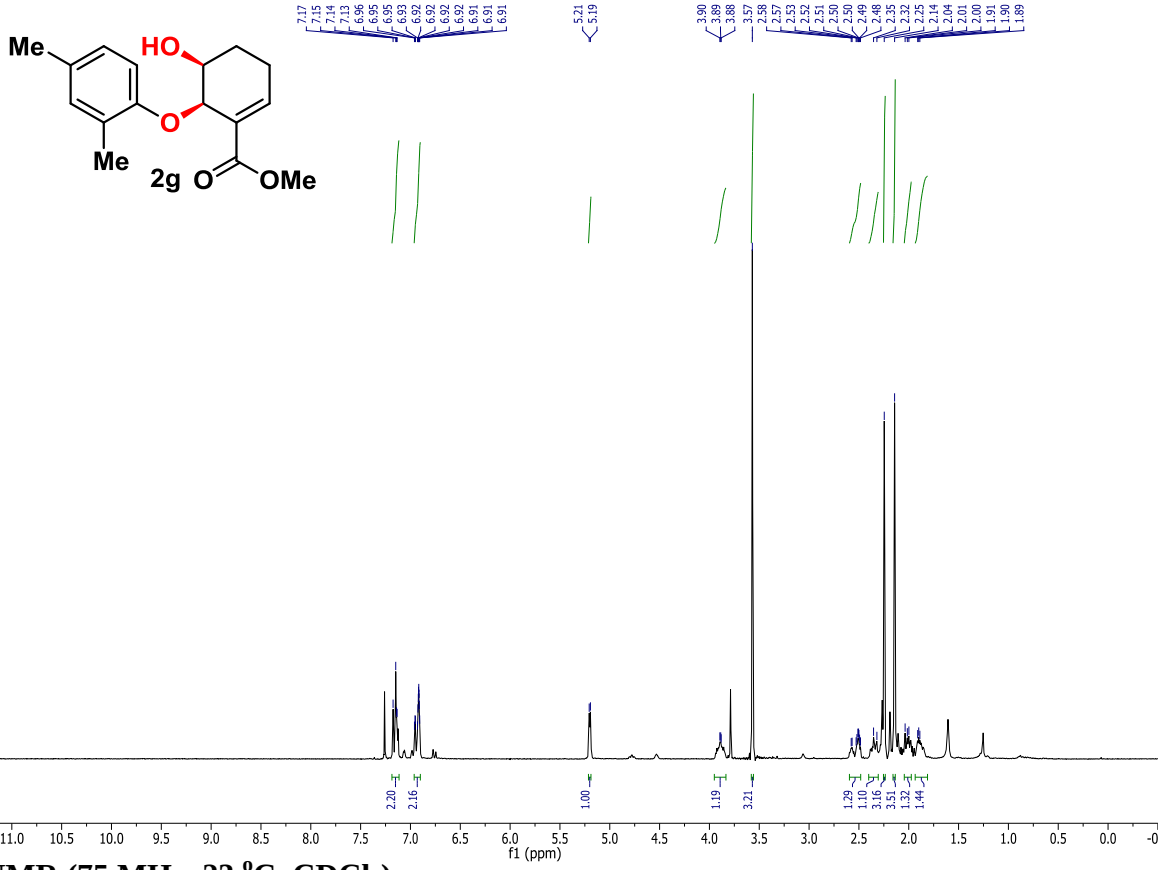

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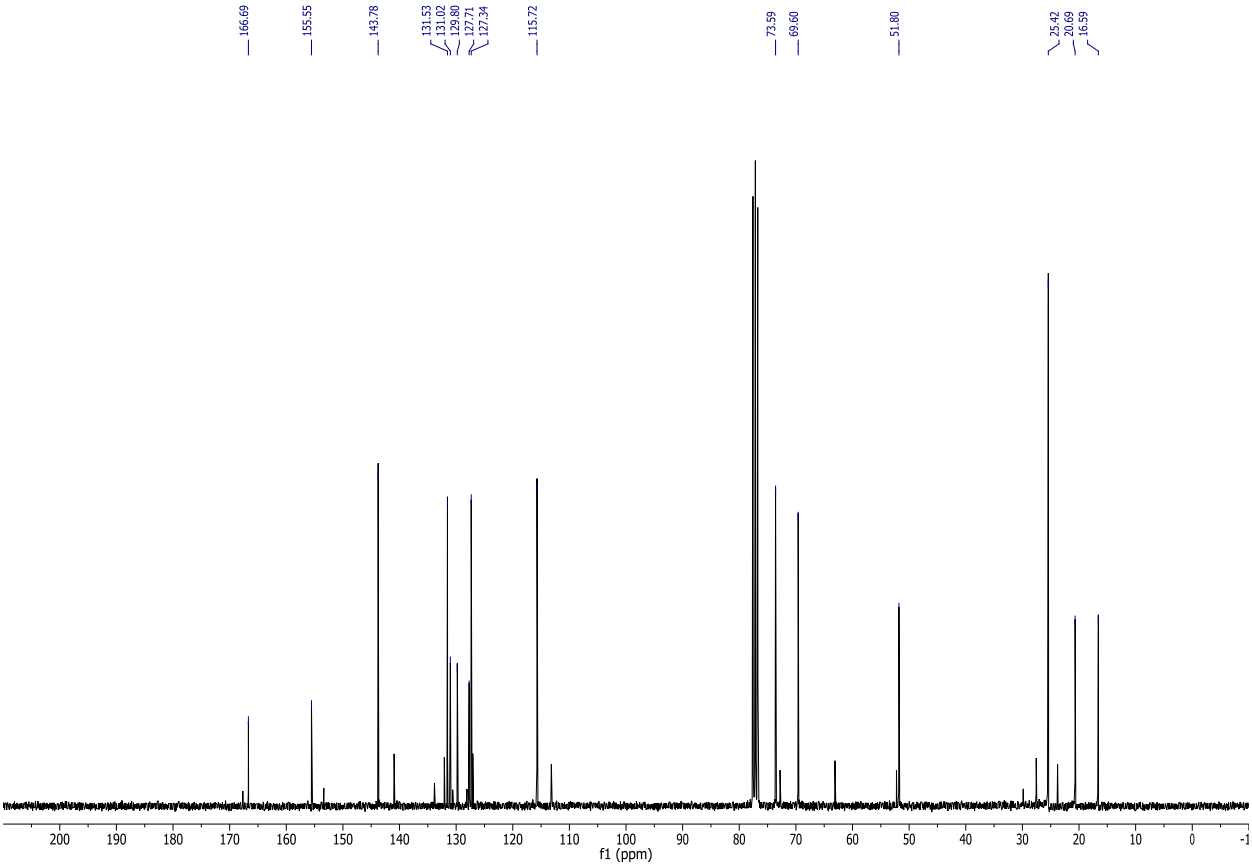

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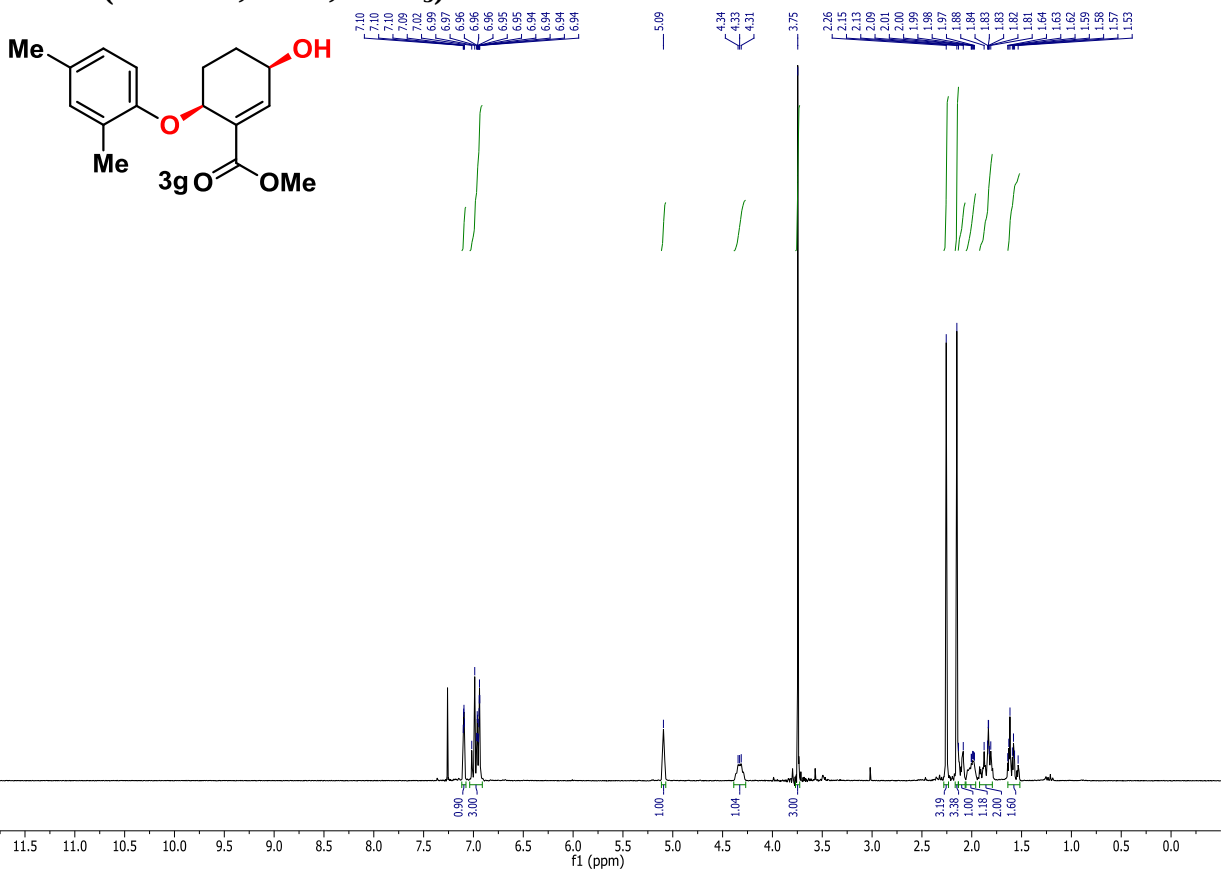

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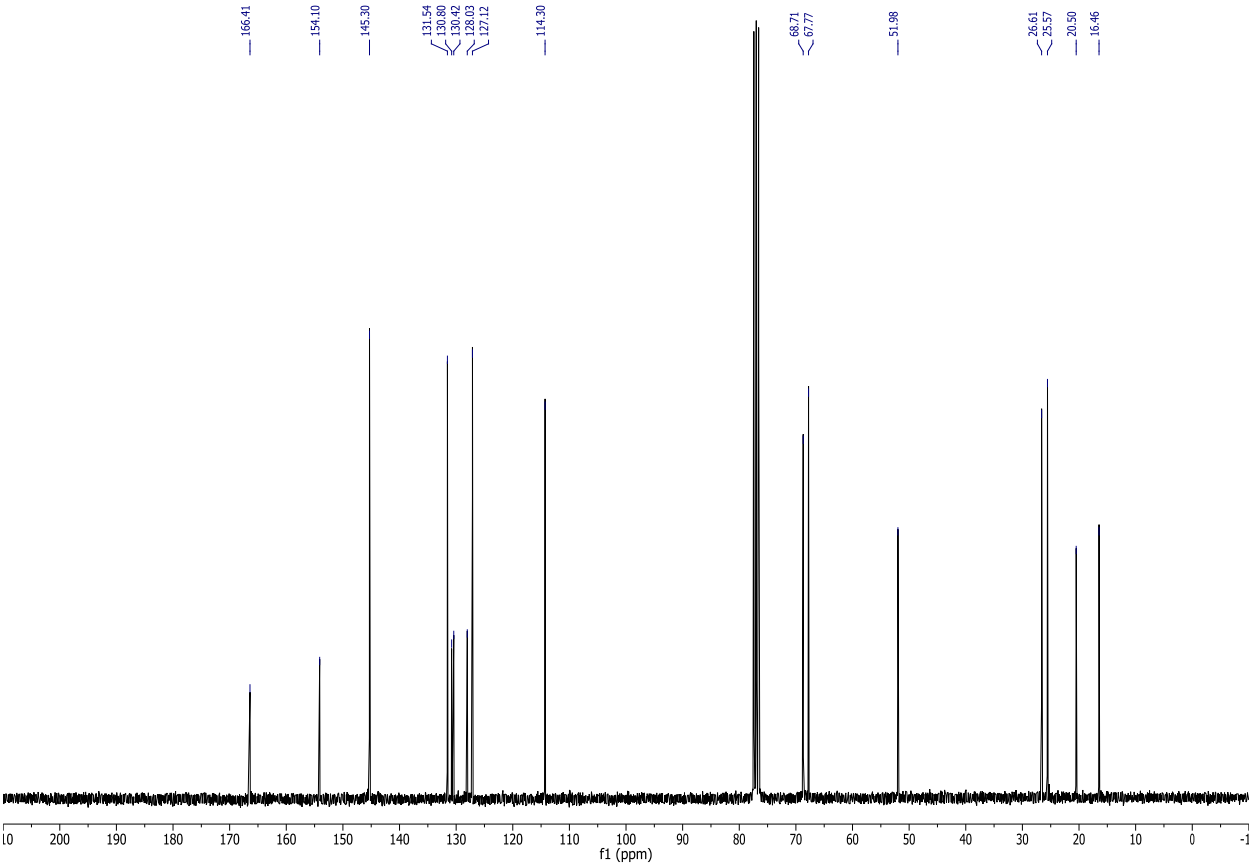

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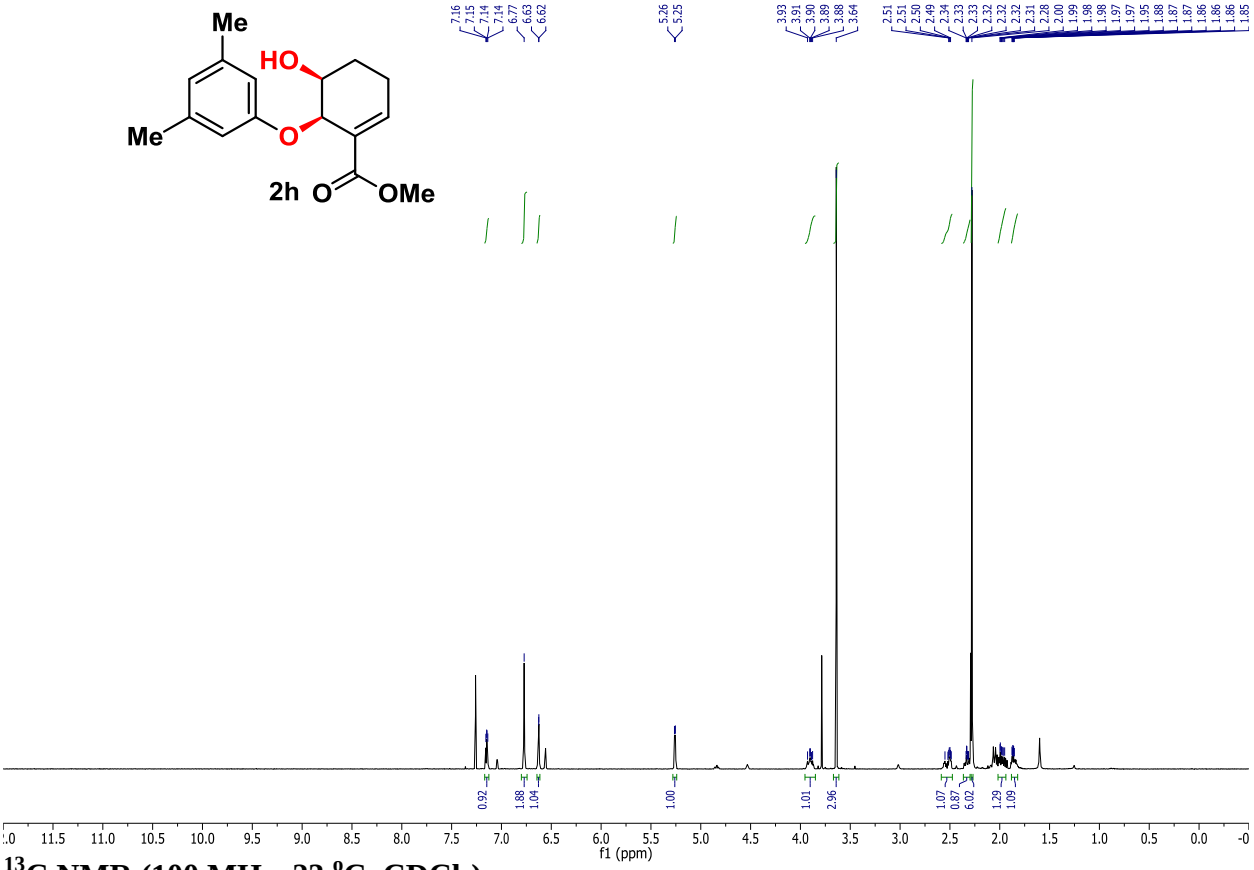
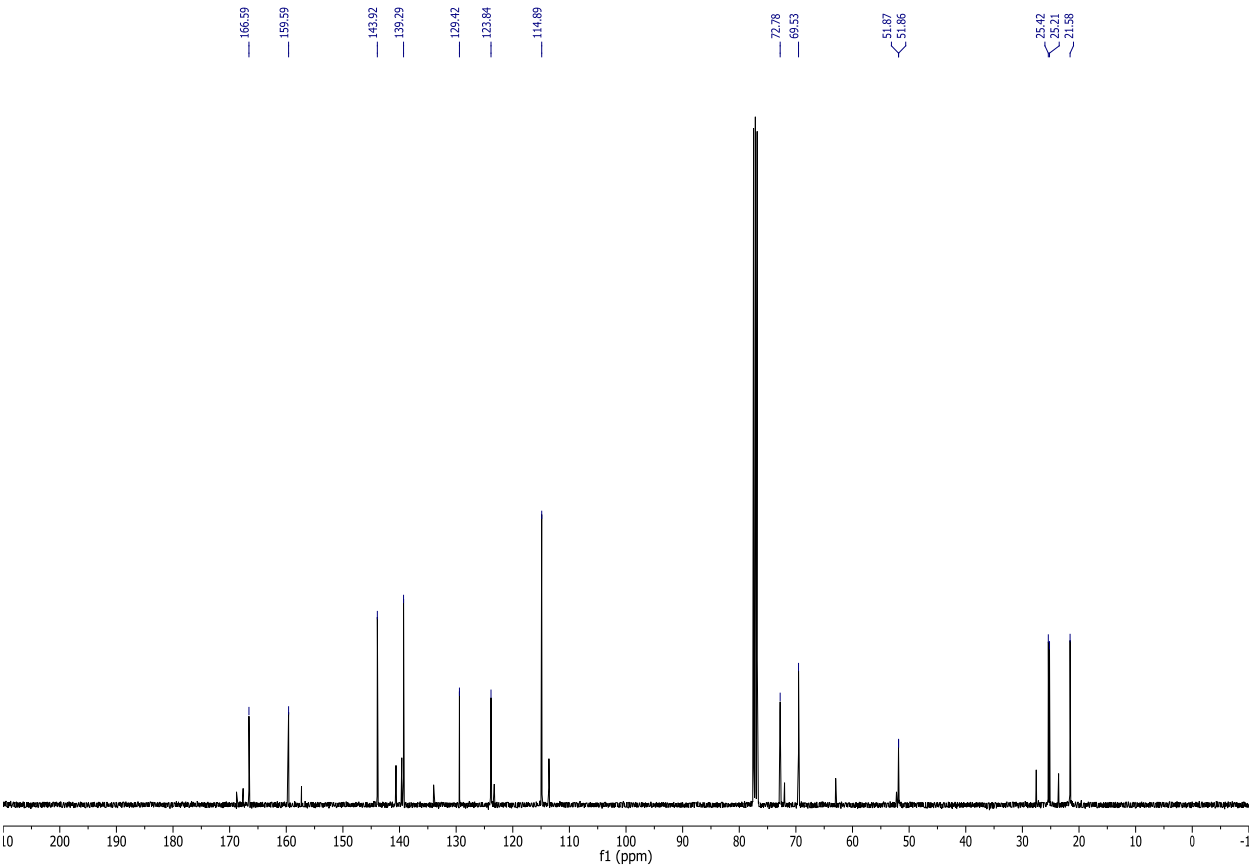


^{13}C NMR (100 MHz, 23 ^{o}C, $CDCl_3$)



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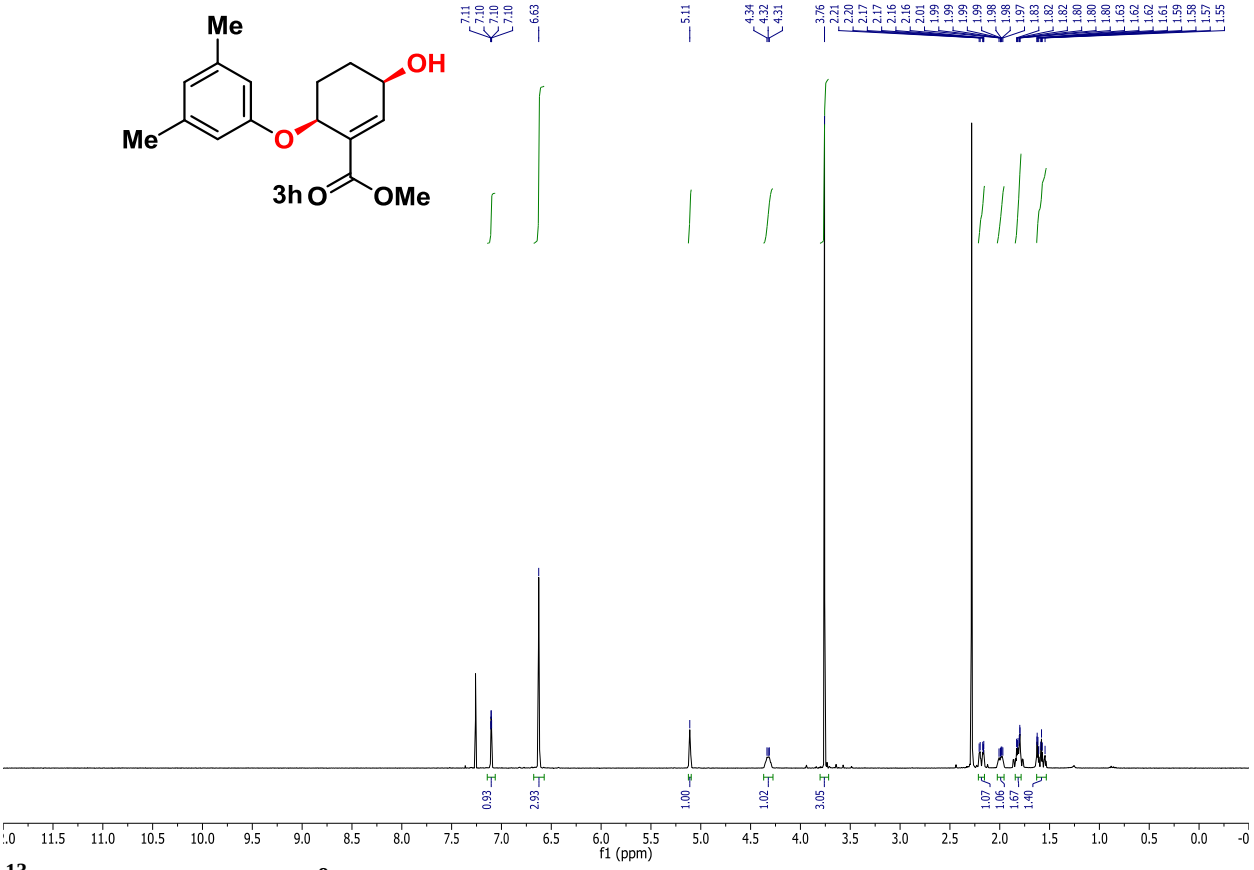

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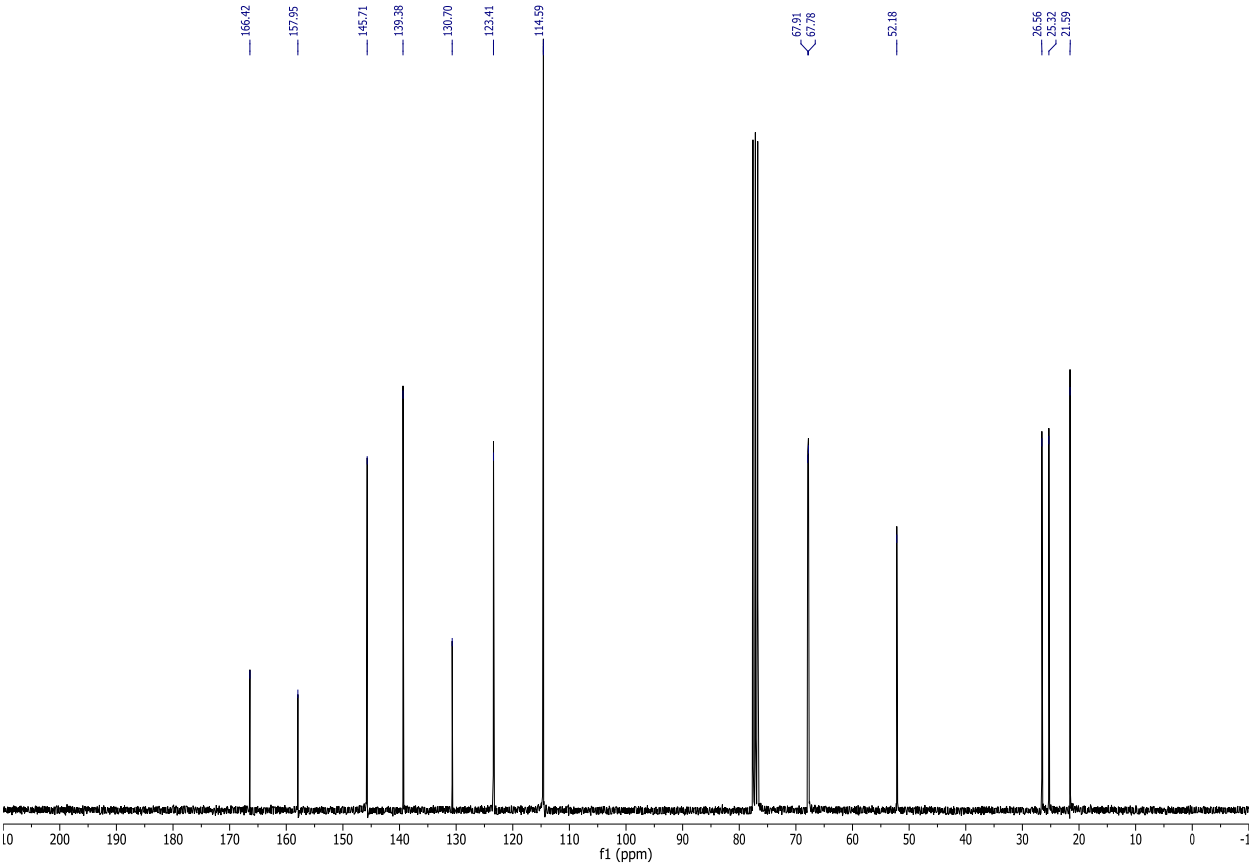

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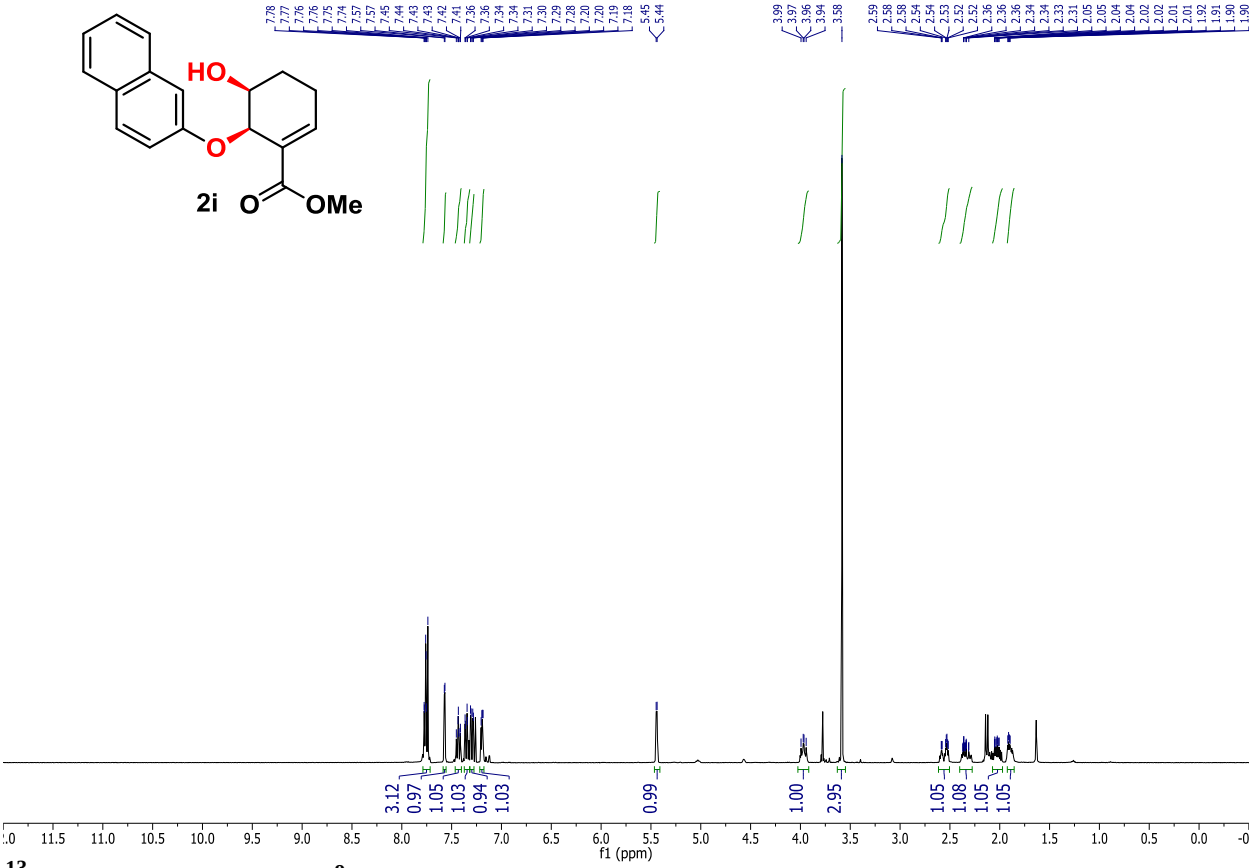

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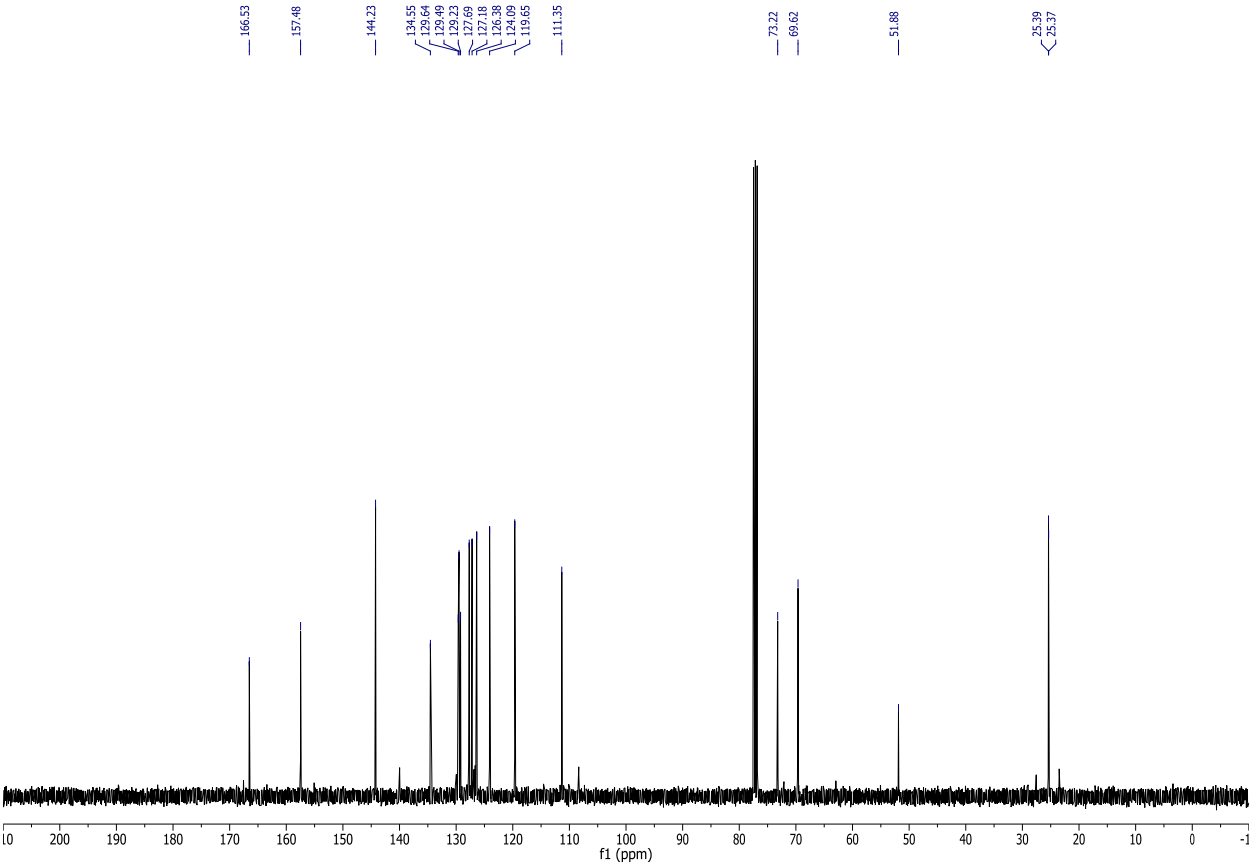

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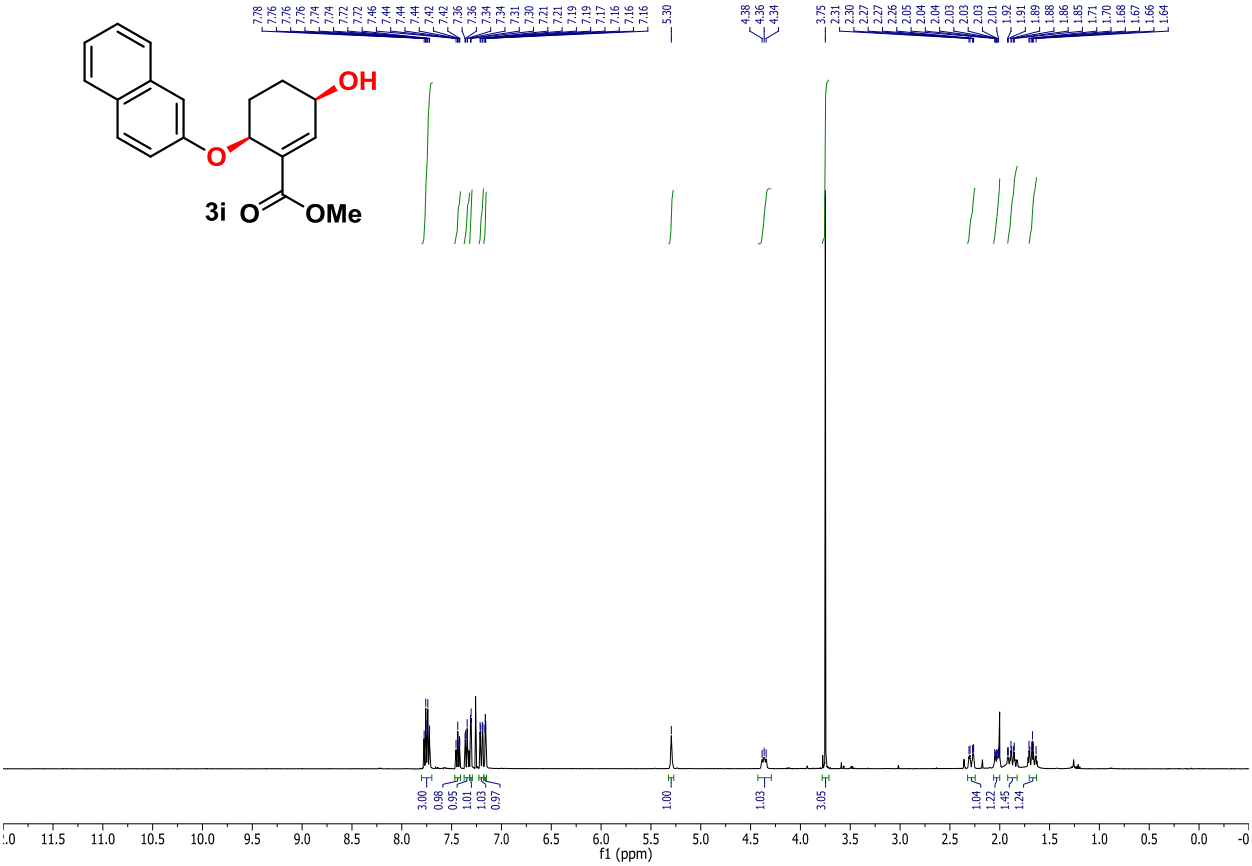

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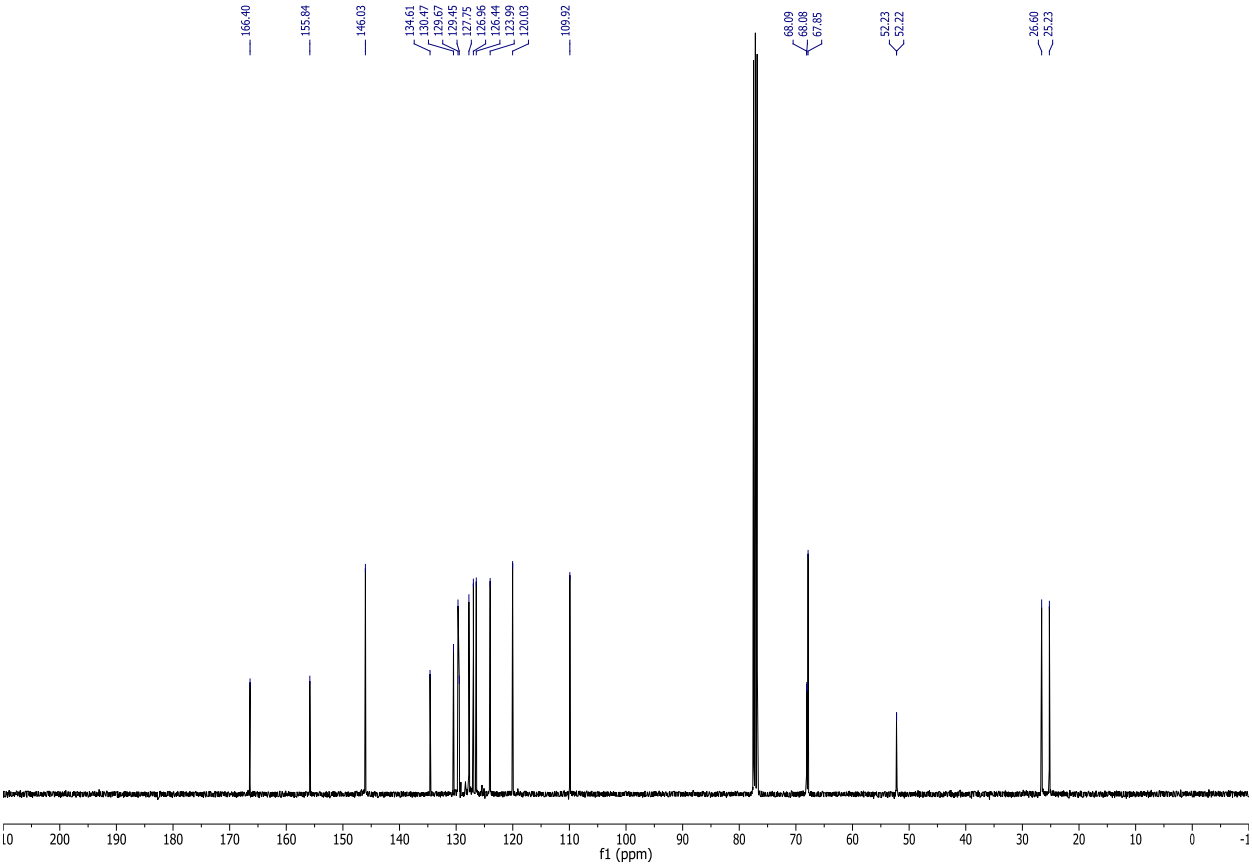

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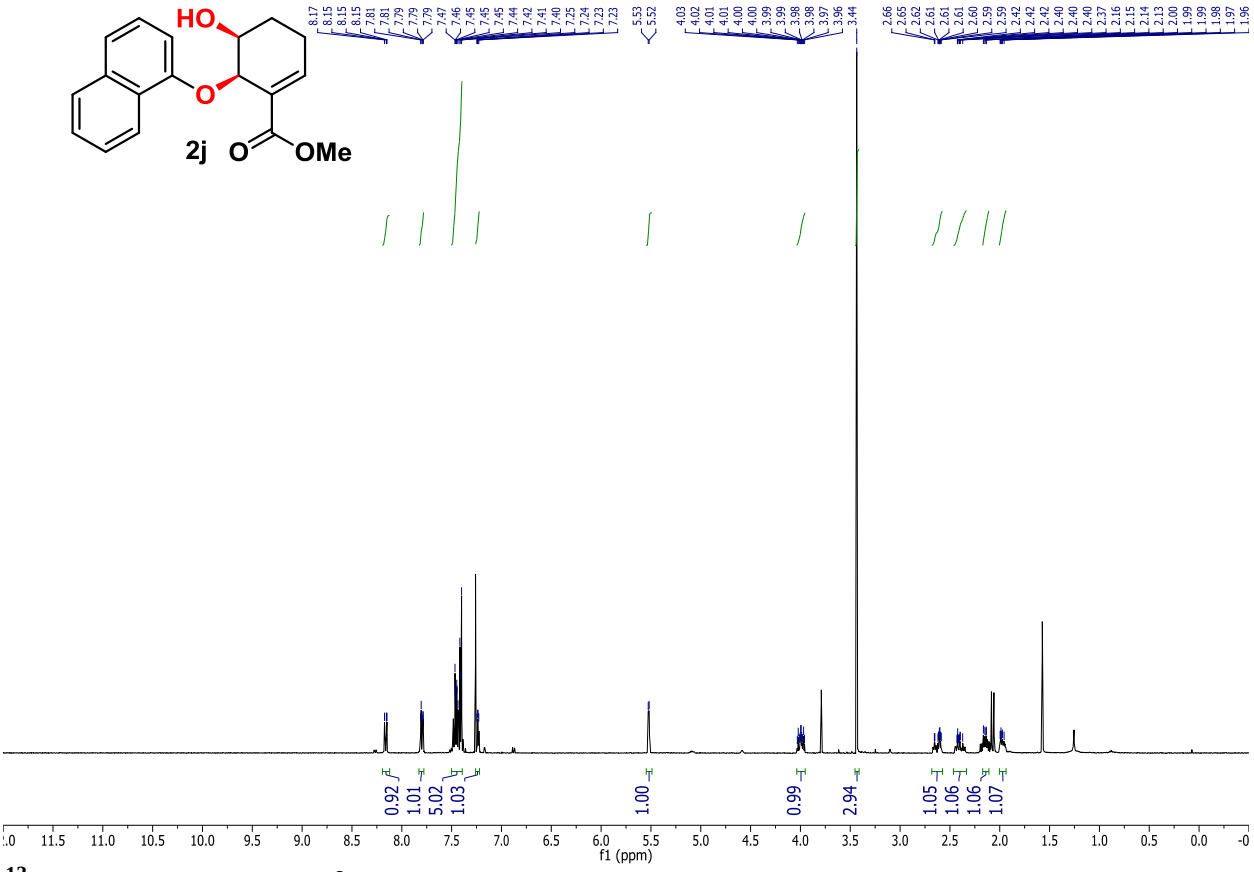

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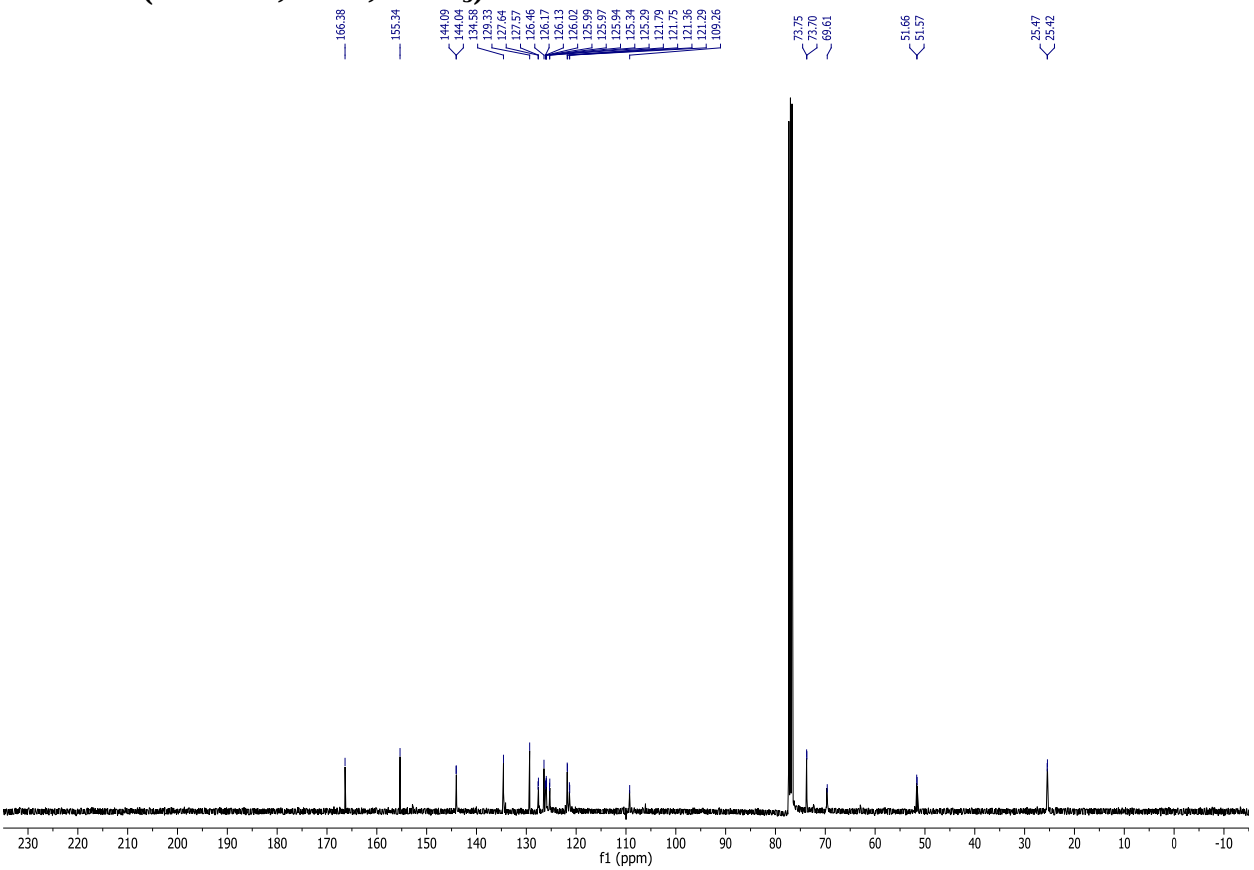

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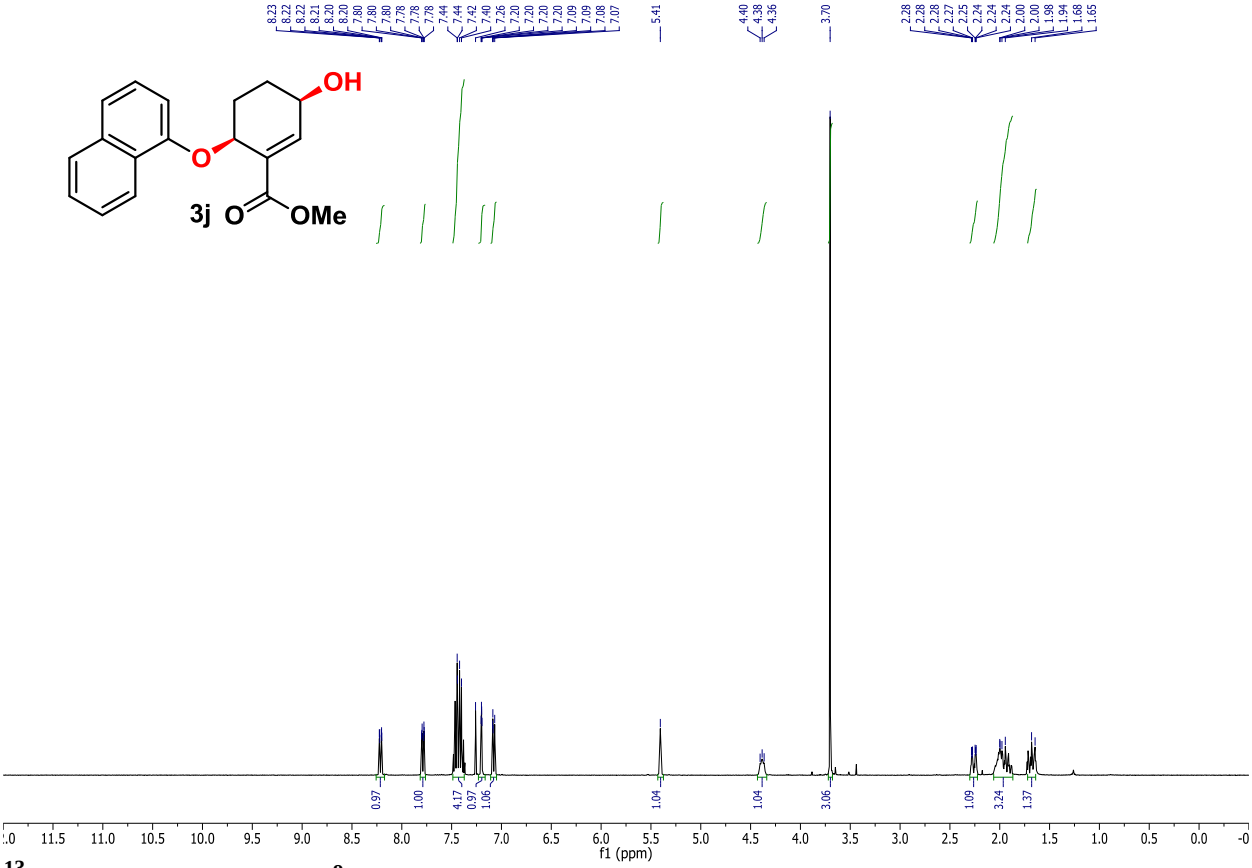

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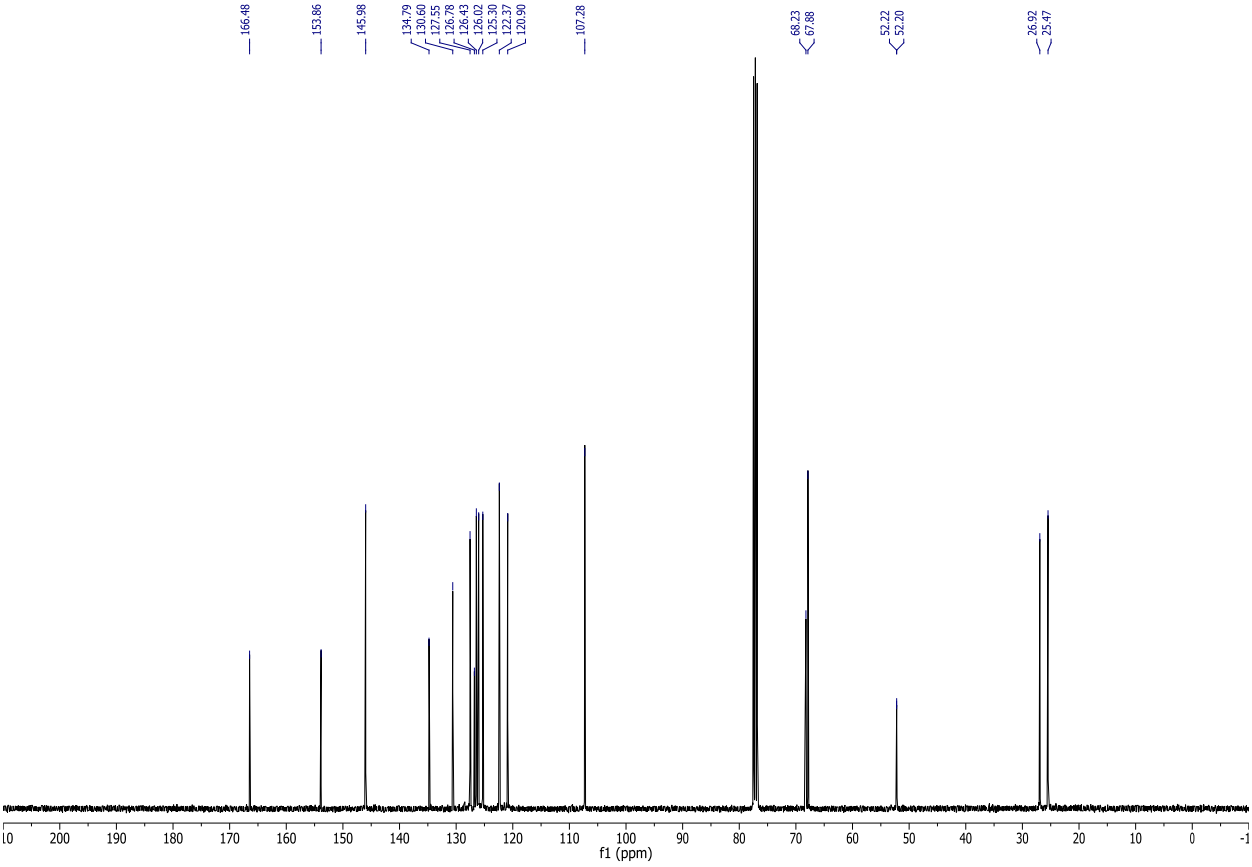

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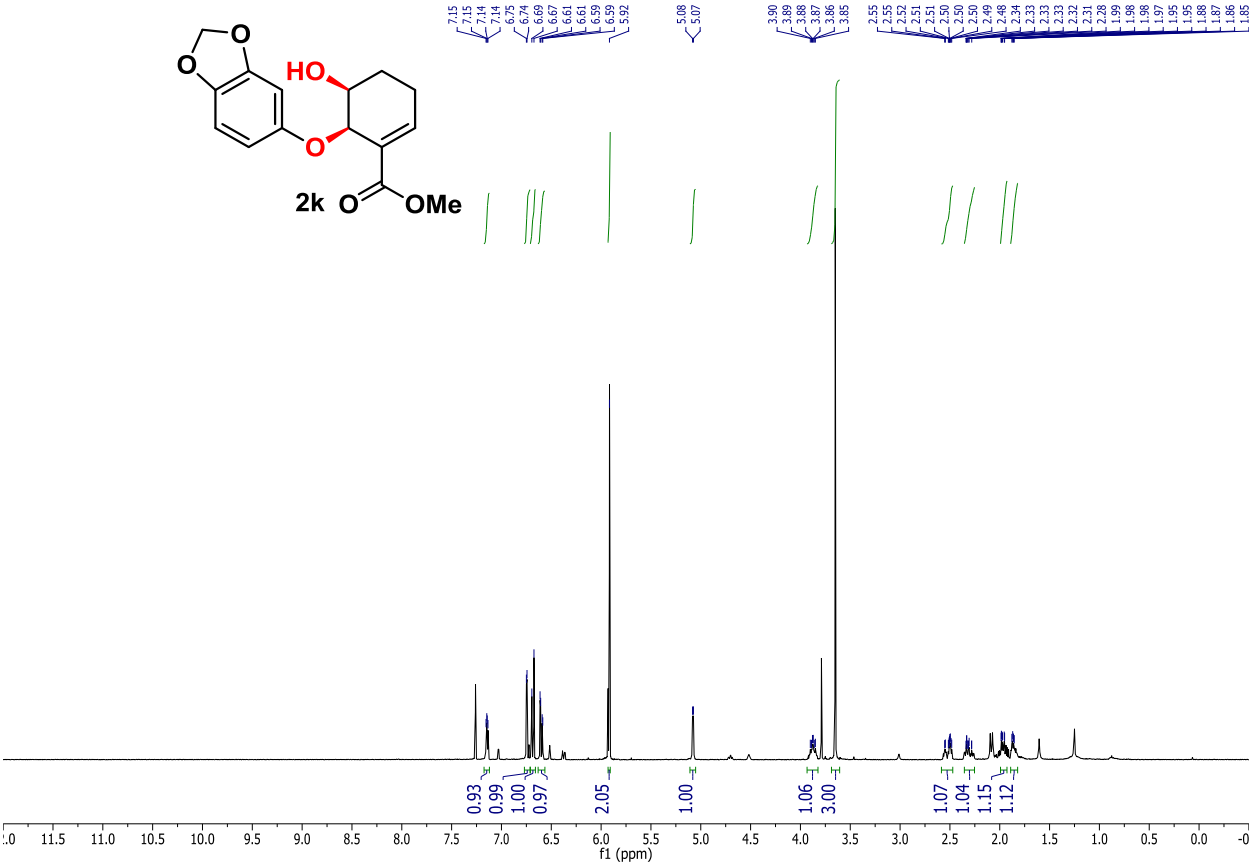

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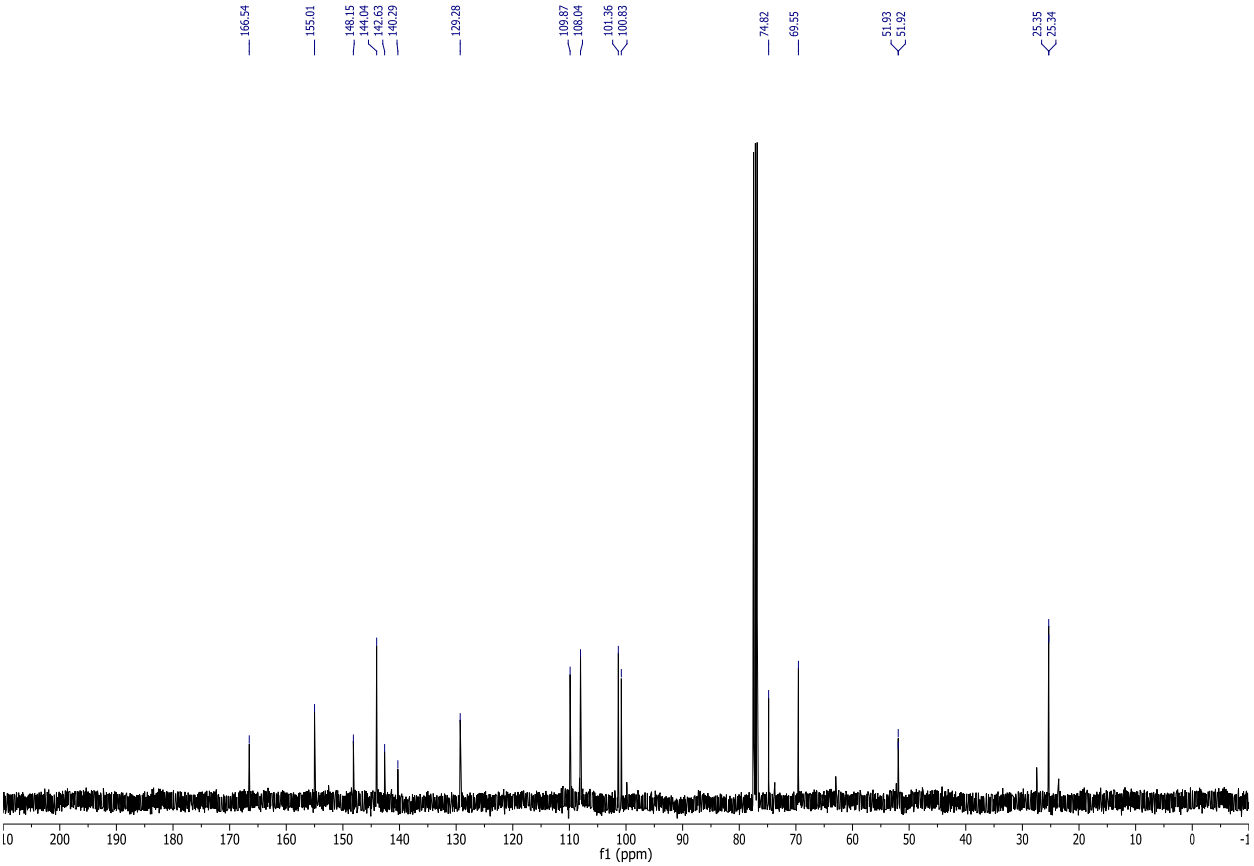

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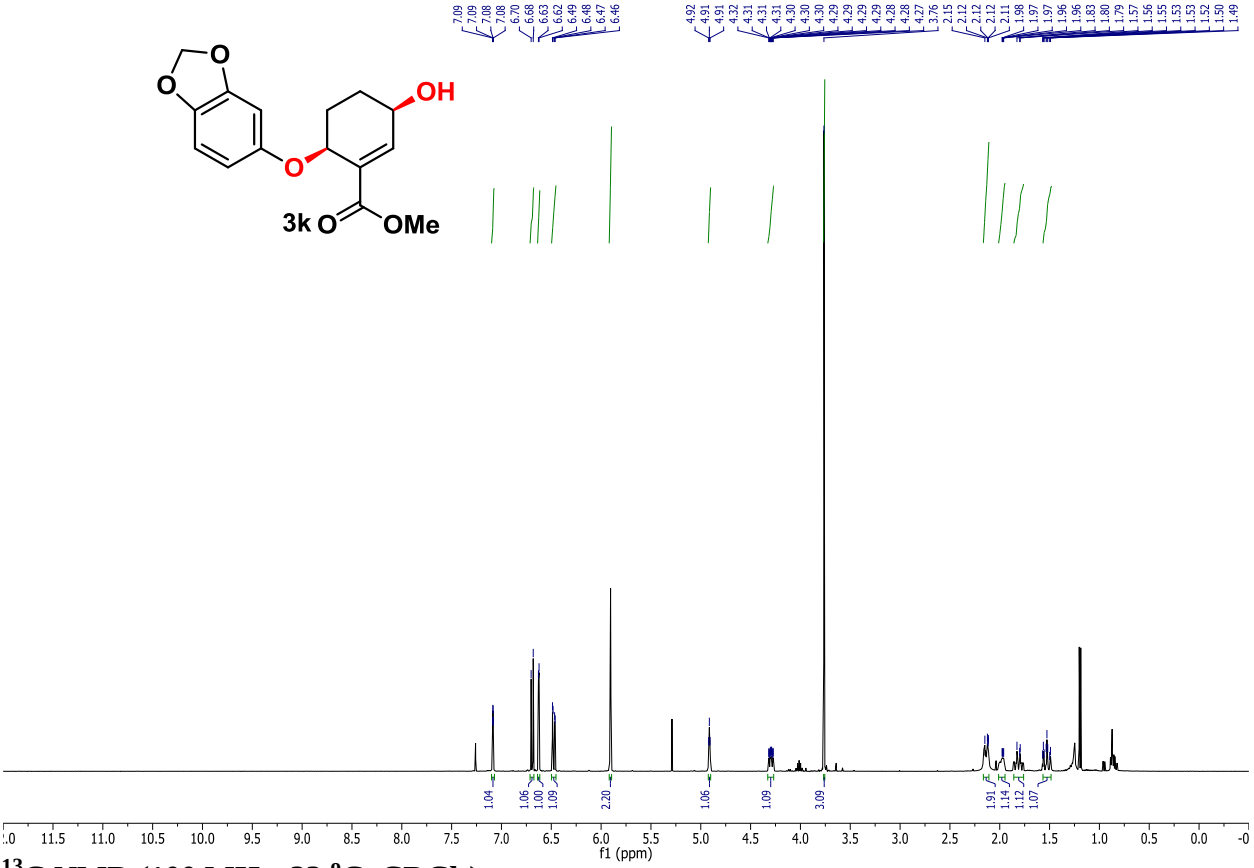

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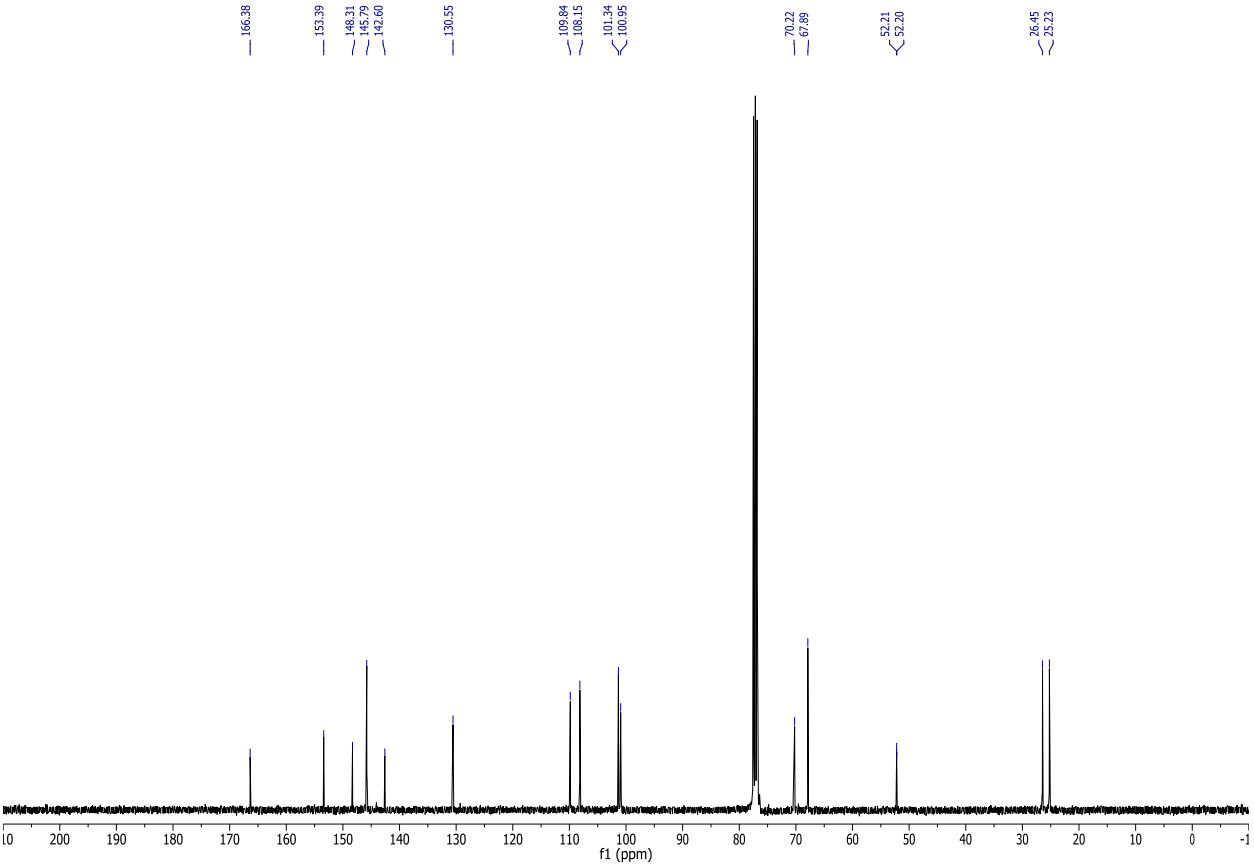

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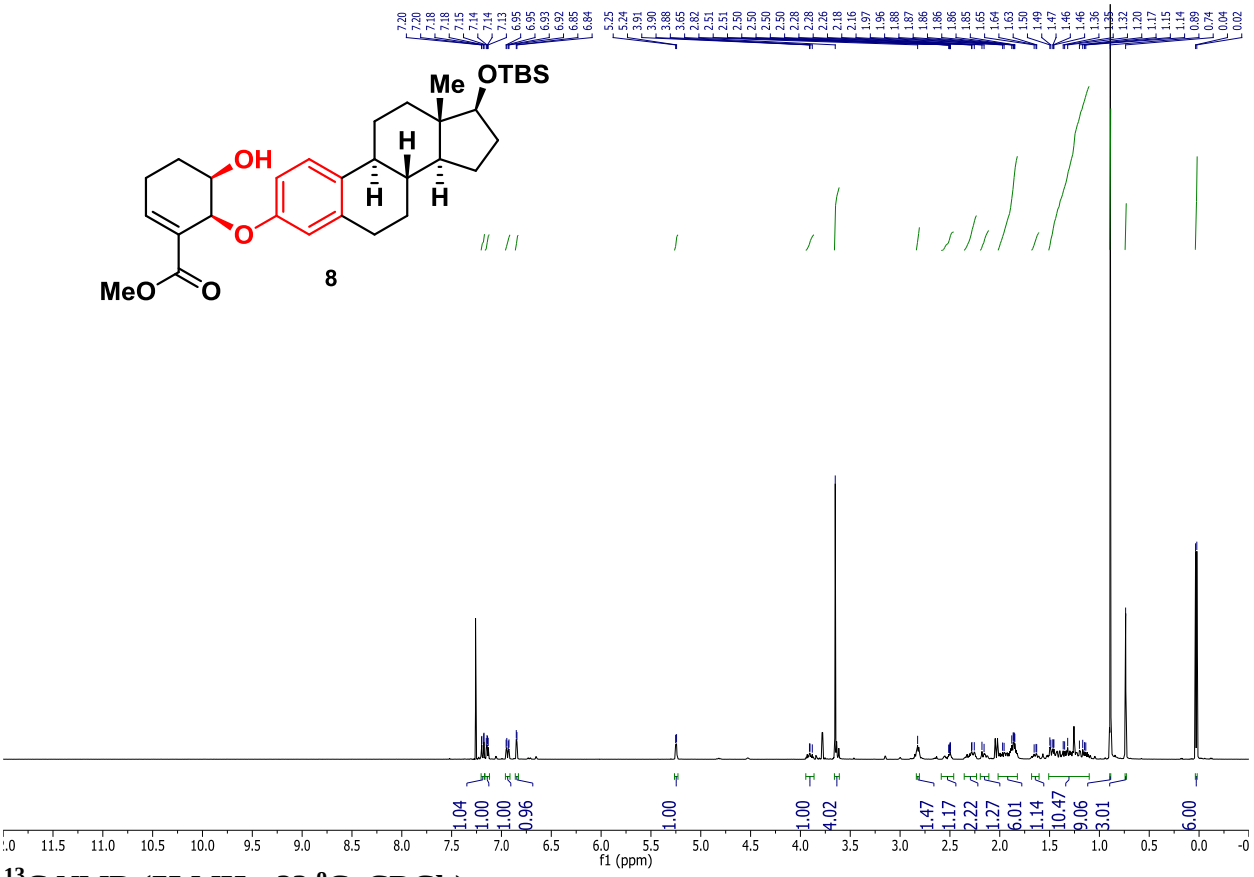

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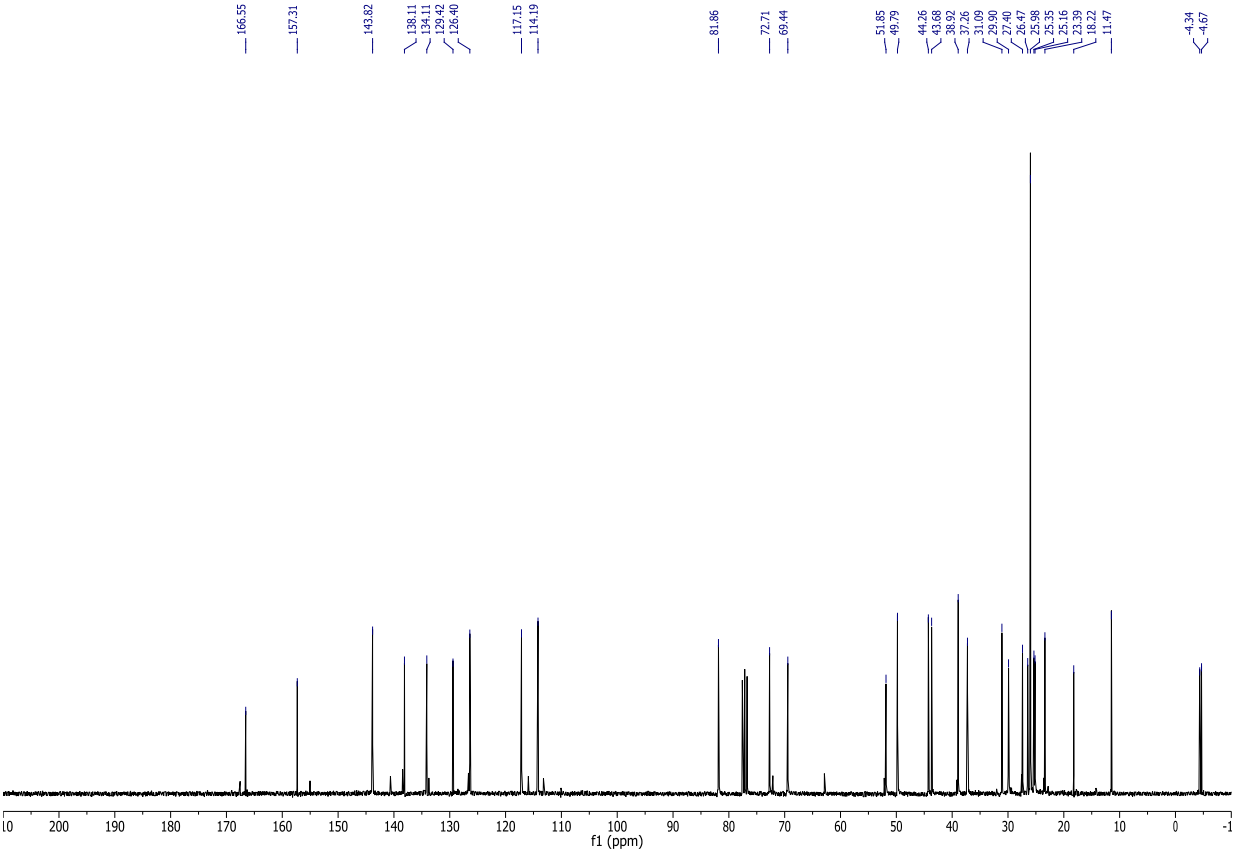

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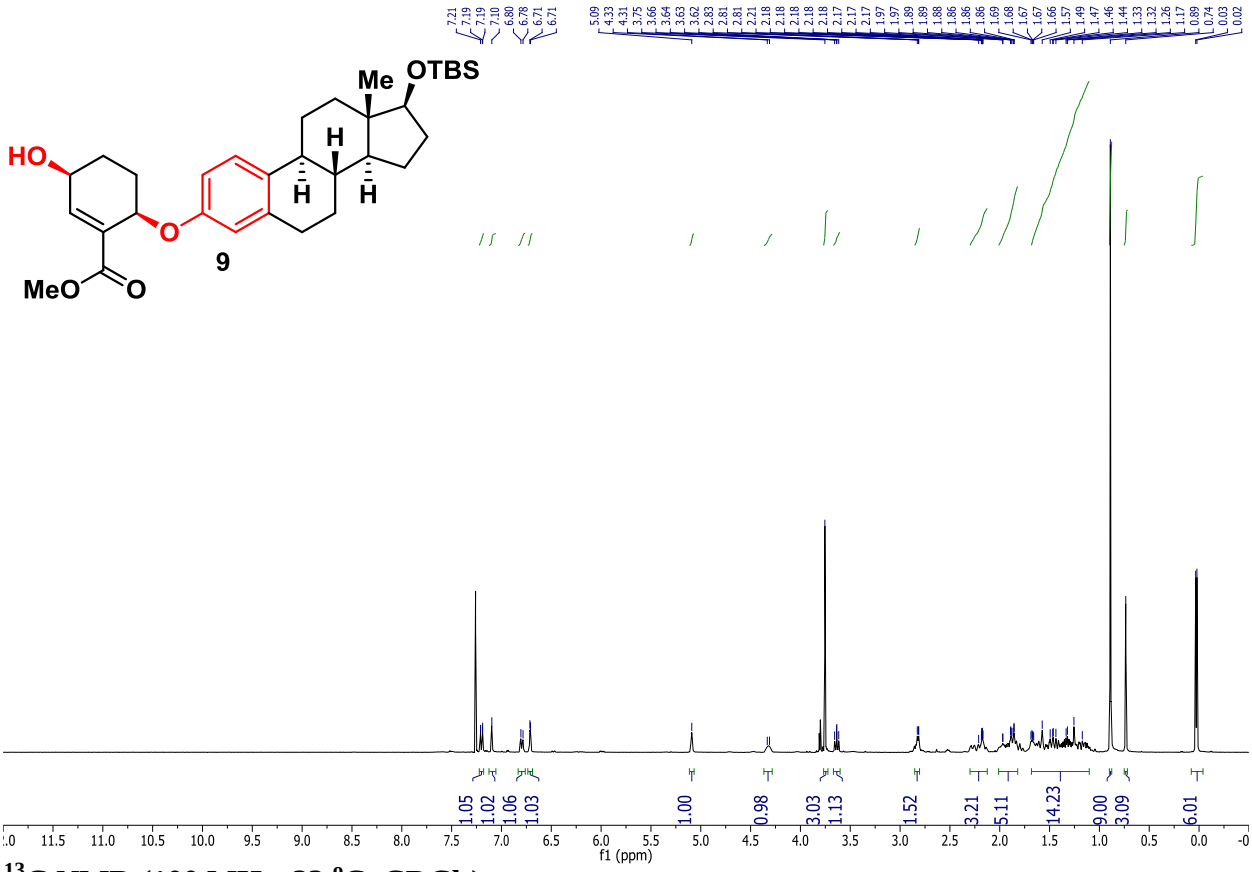

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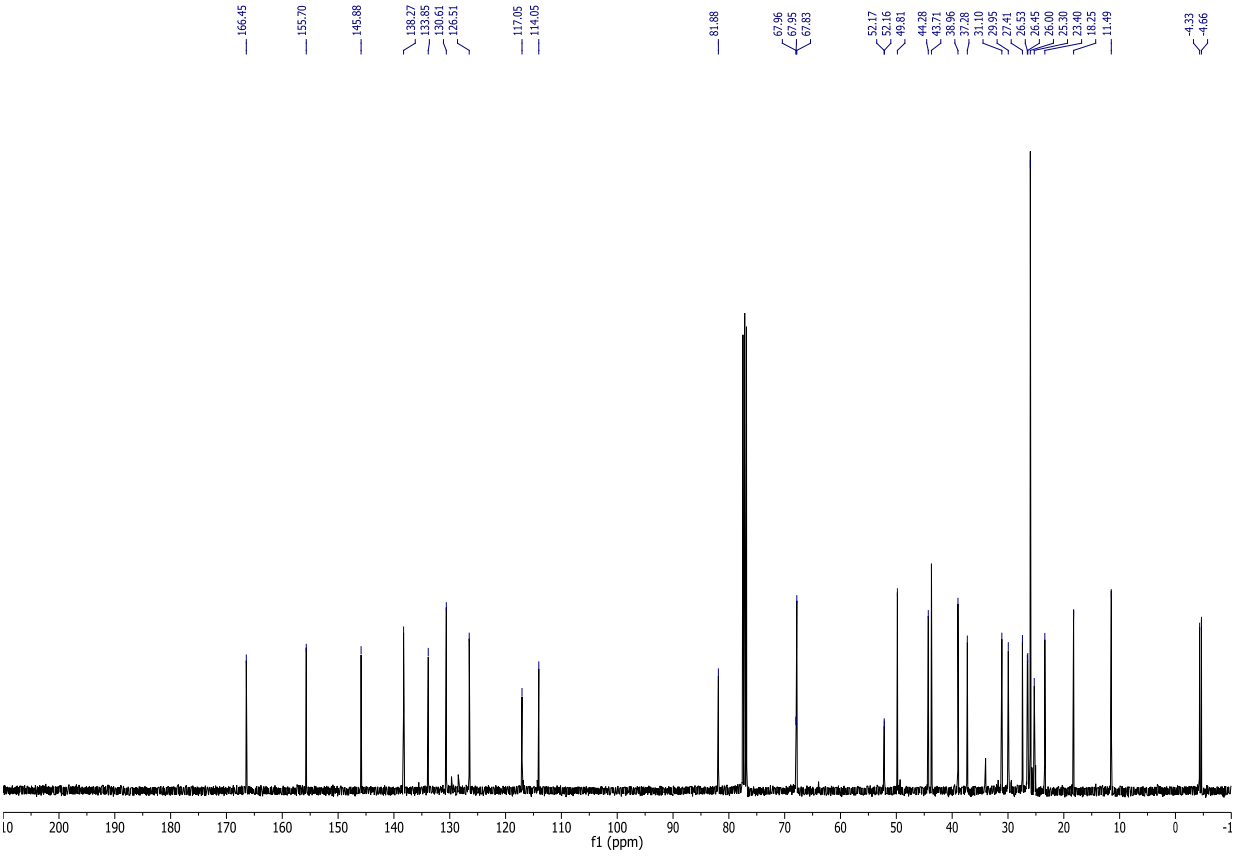

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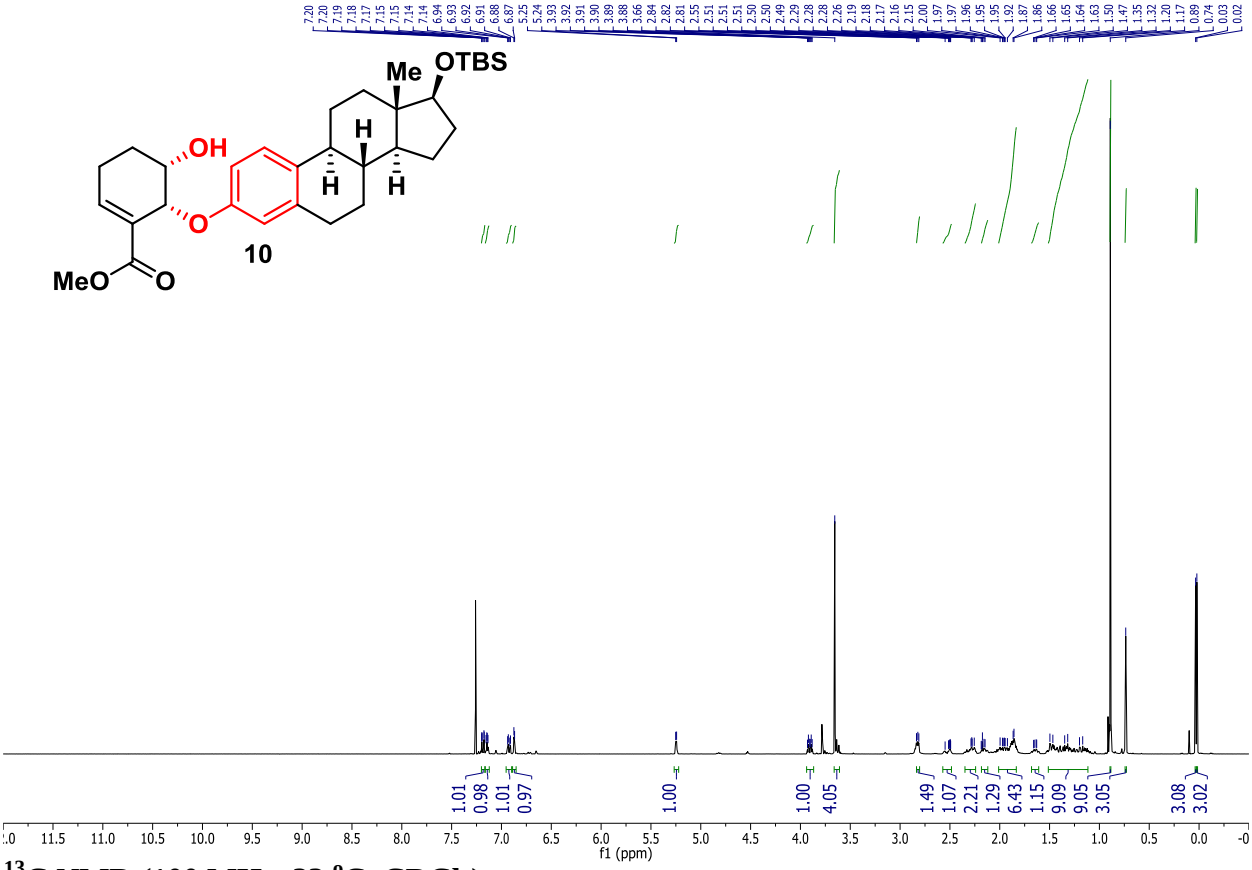

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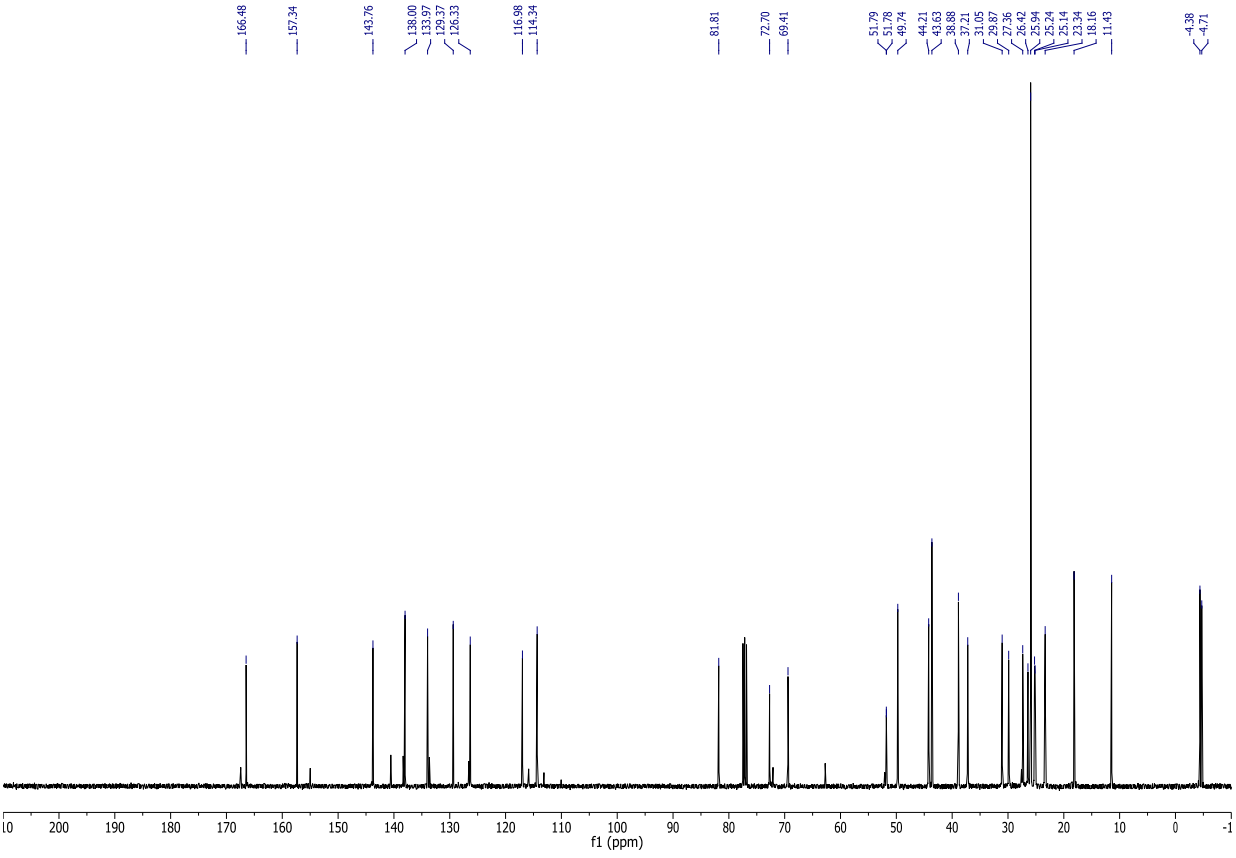

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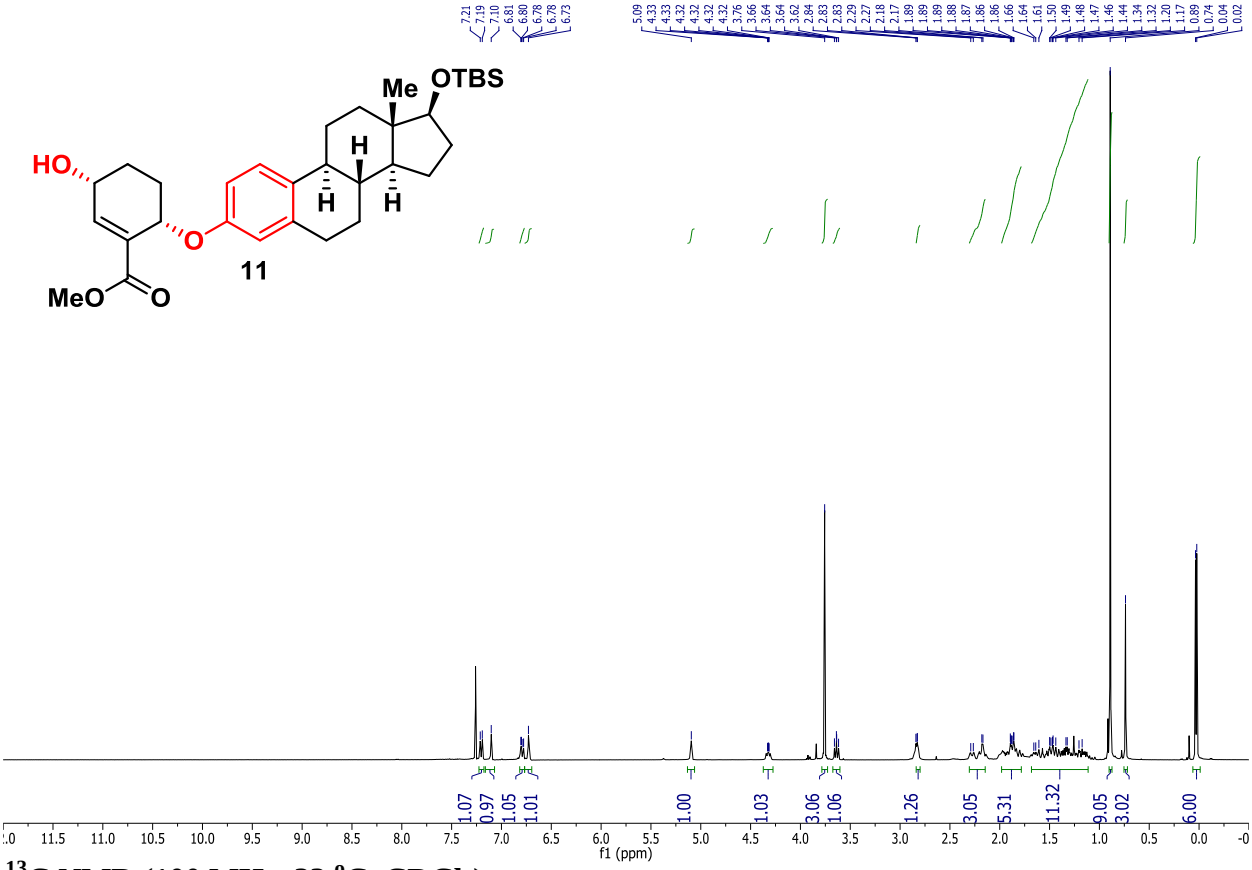
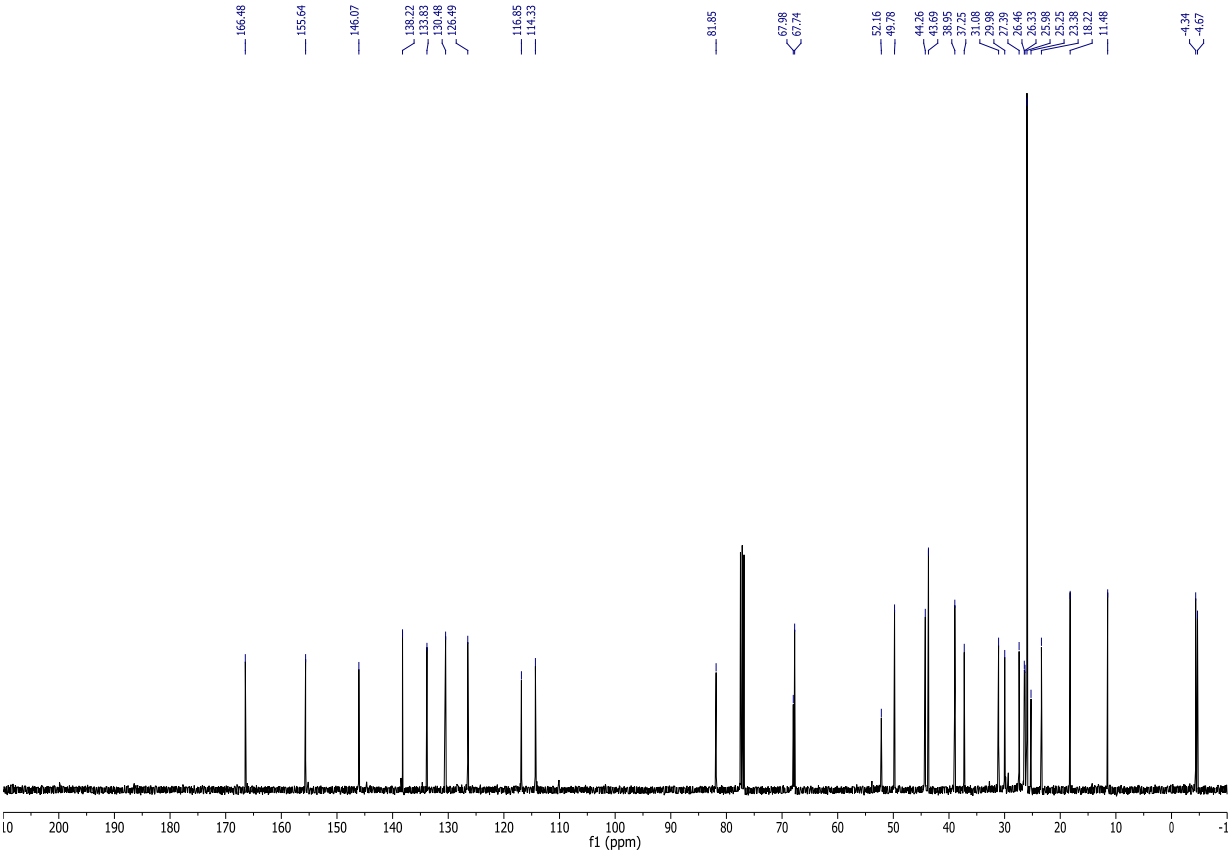
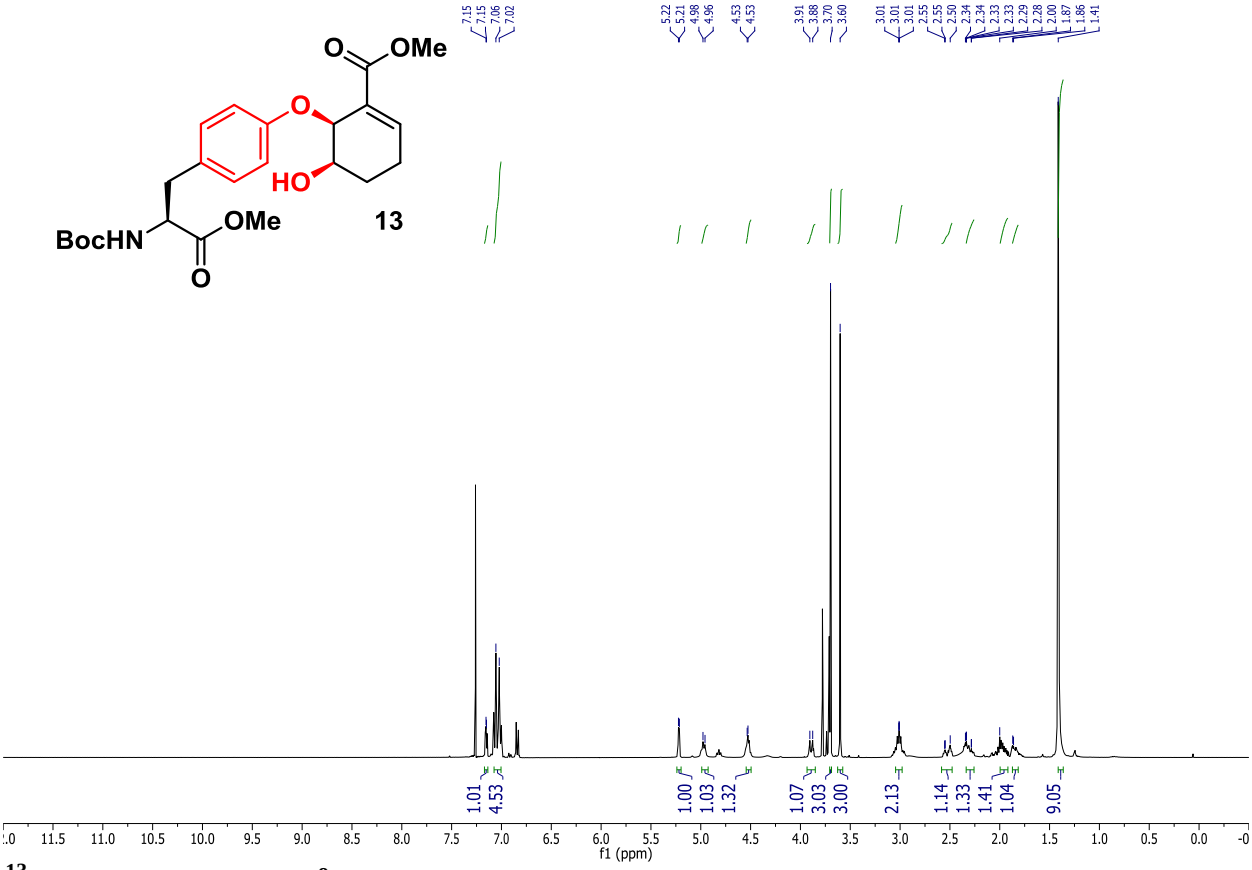


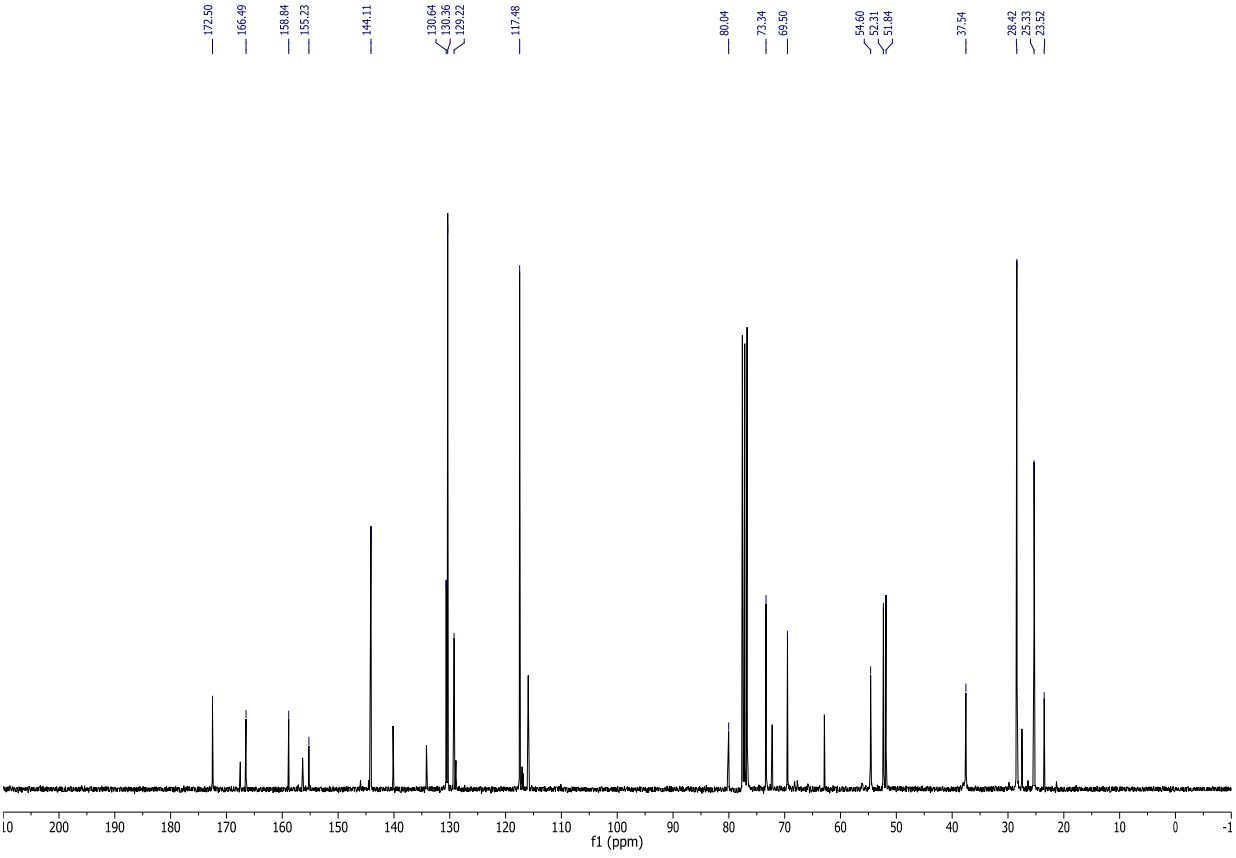
^{13}C NMR (100 MHz, 23 ^{o}C, $CDCl_3$)



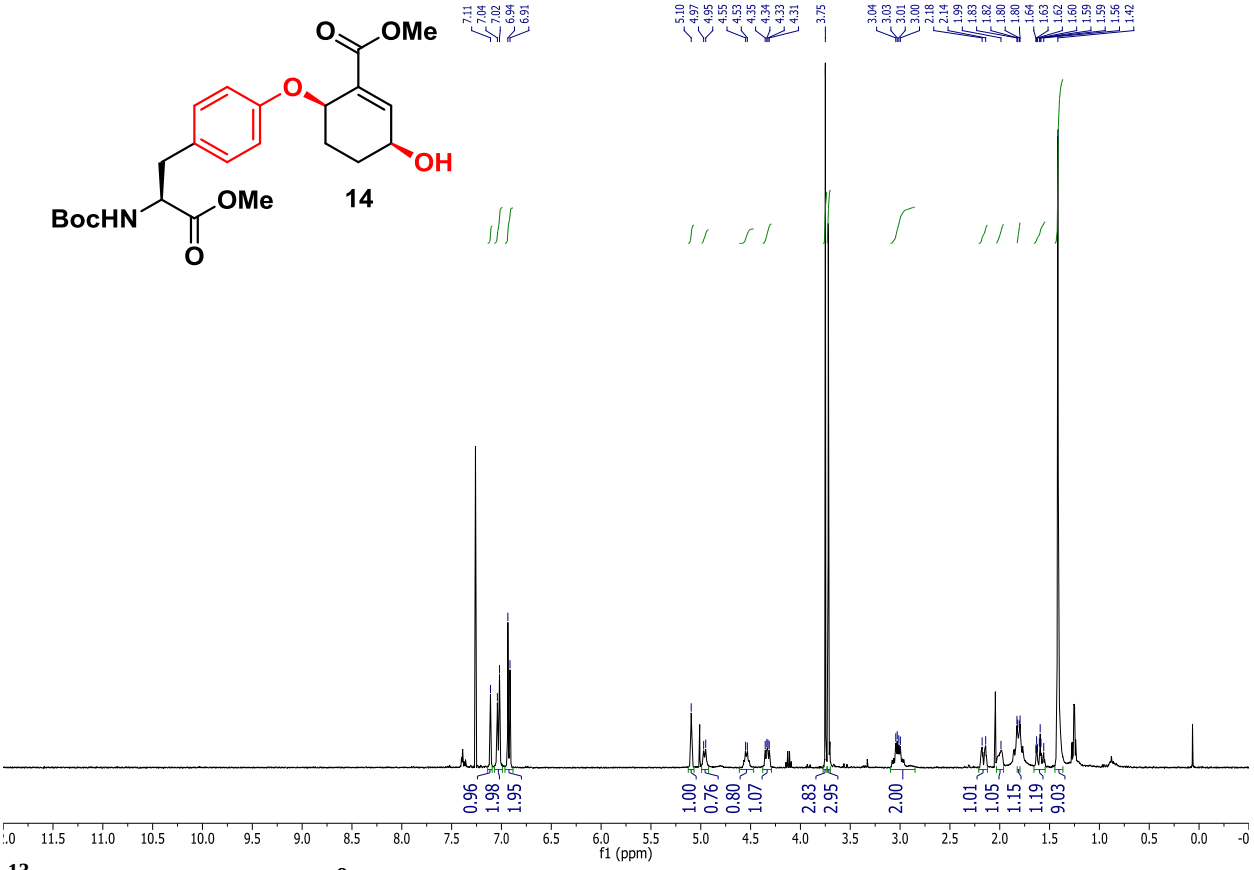
^{1}H NMR (400 MHz, 23 ^{o}C, $CDCl_3$)



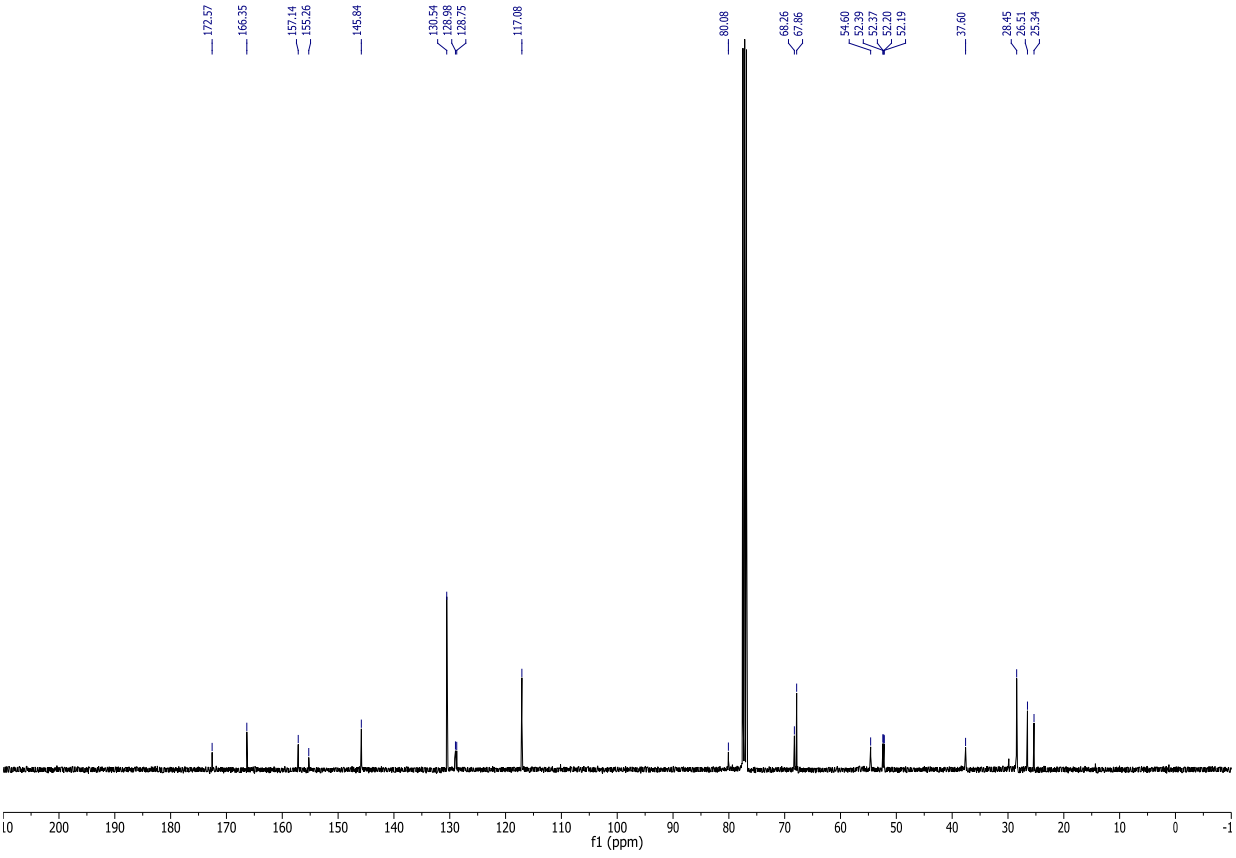
^{13}C NMR (75 MHz, 23 ^{o}C, $CDCl_3$)



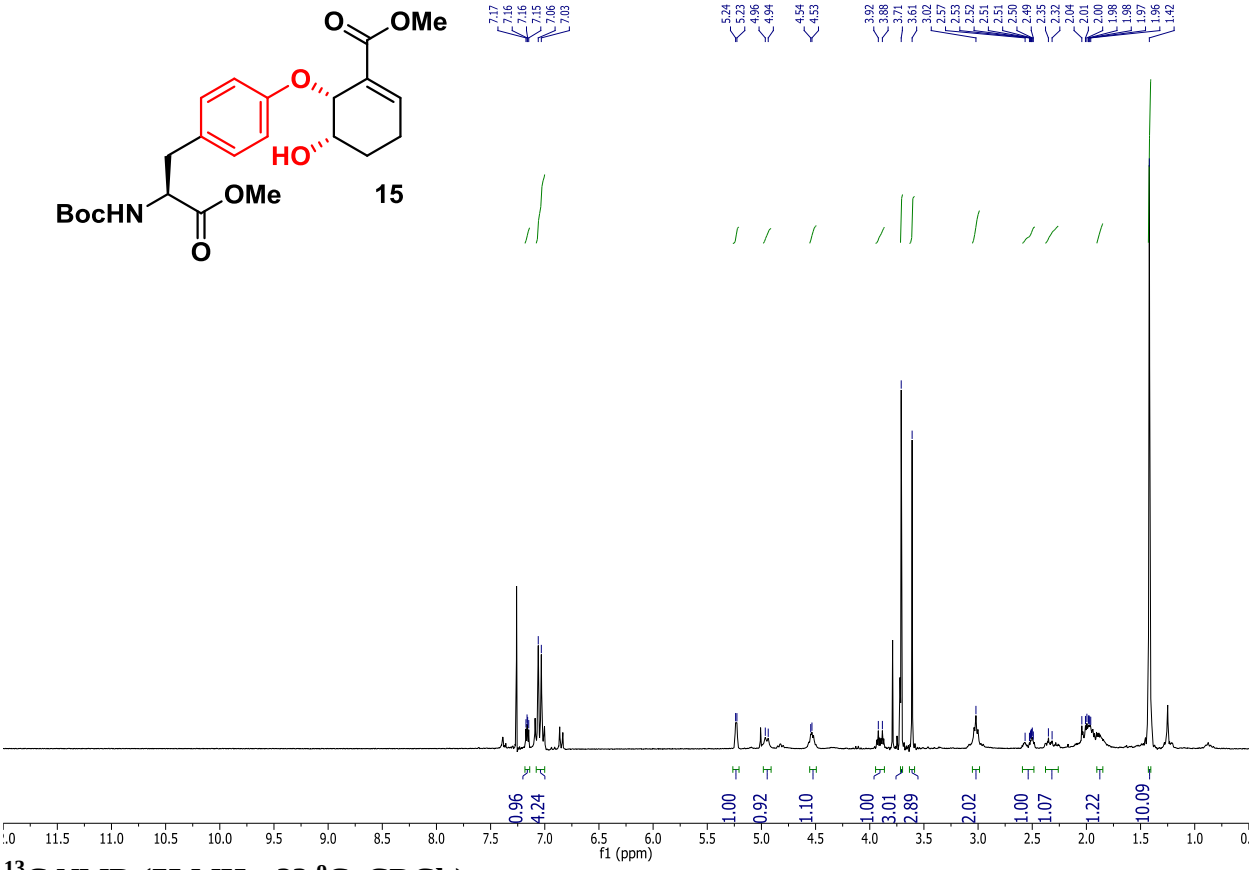
^{1}H NMR (400 MHz, 23 ^{o}C, $CDCl_3$)



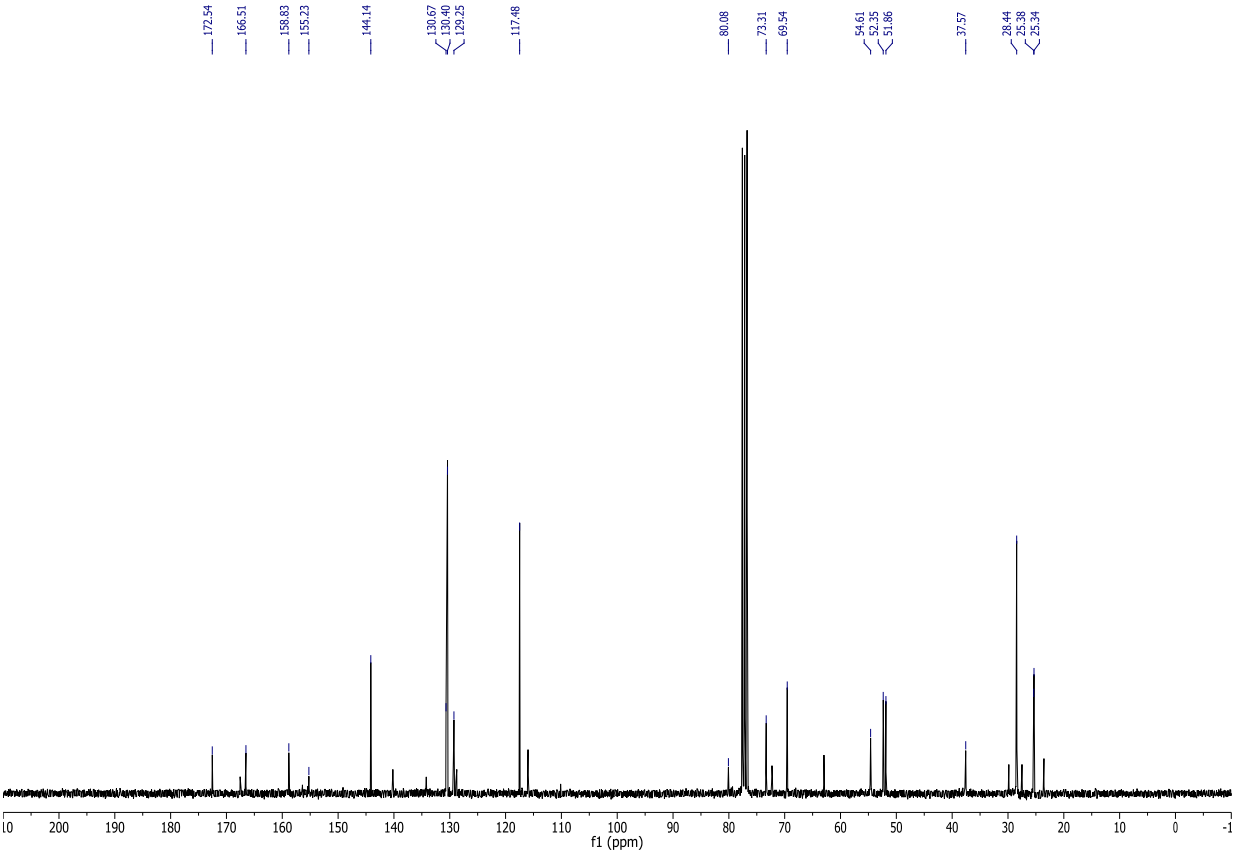
^{13}C NMR (100 MHz, 23 ^{o}C, $CDCl_3$)



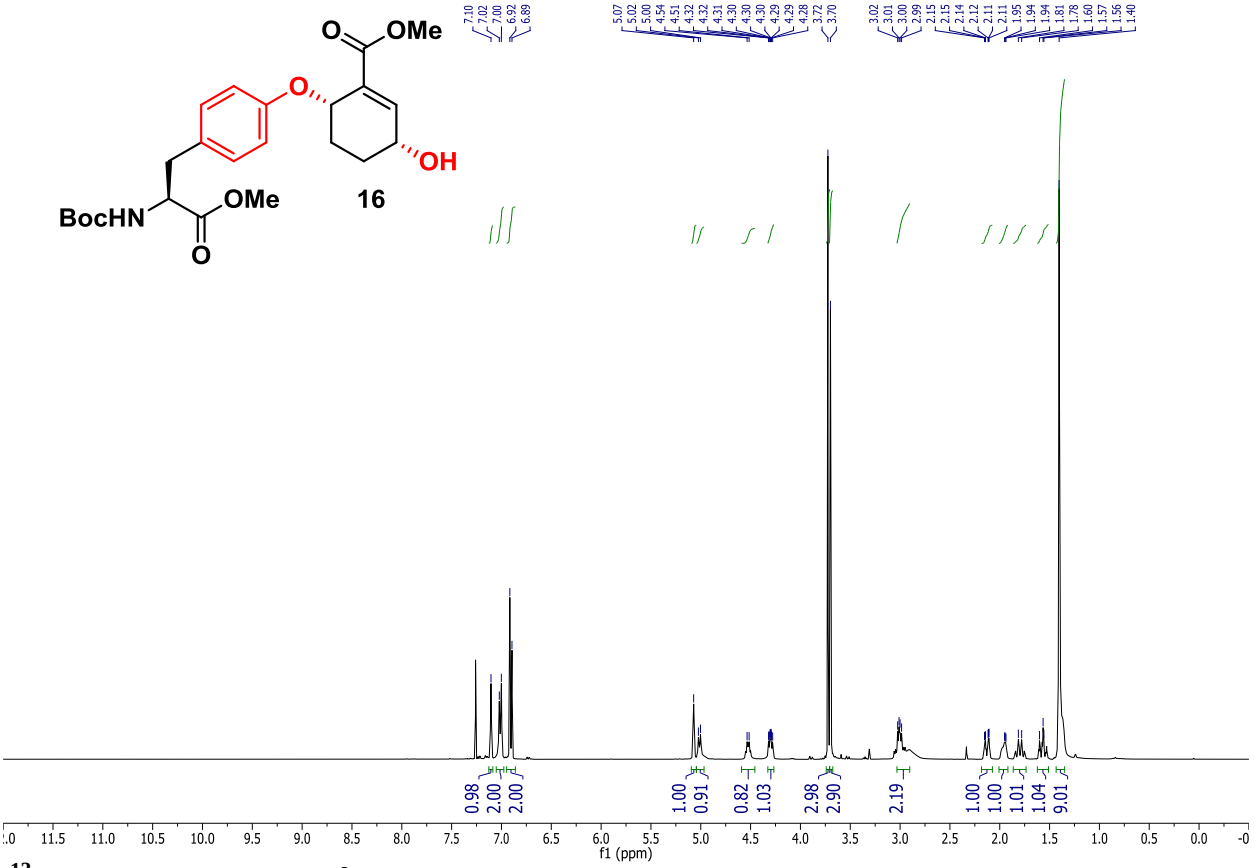
^{1}H NMR (300 MHz, 23 ^{o}C, $CDCl_3$)



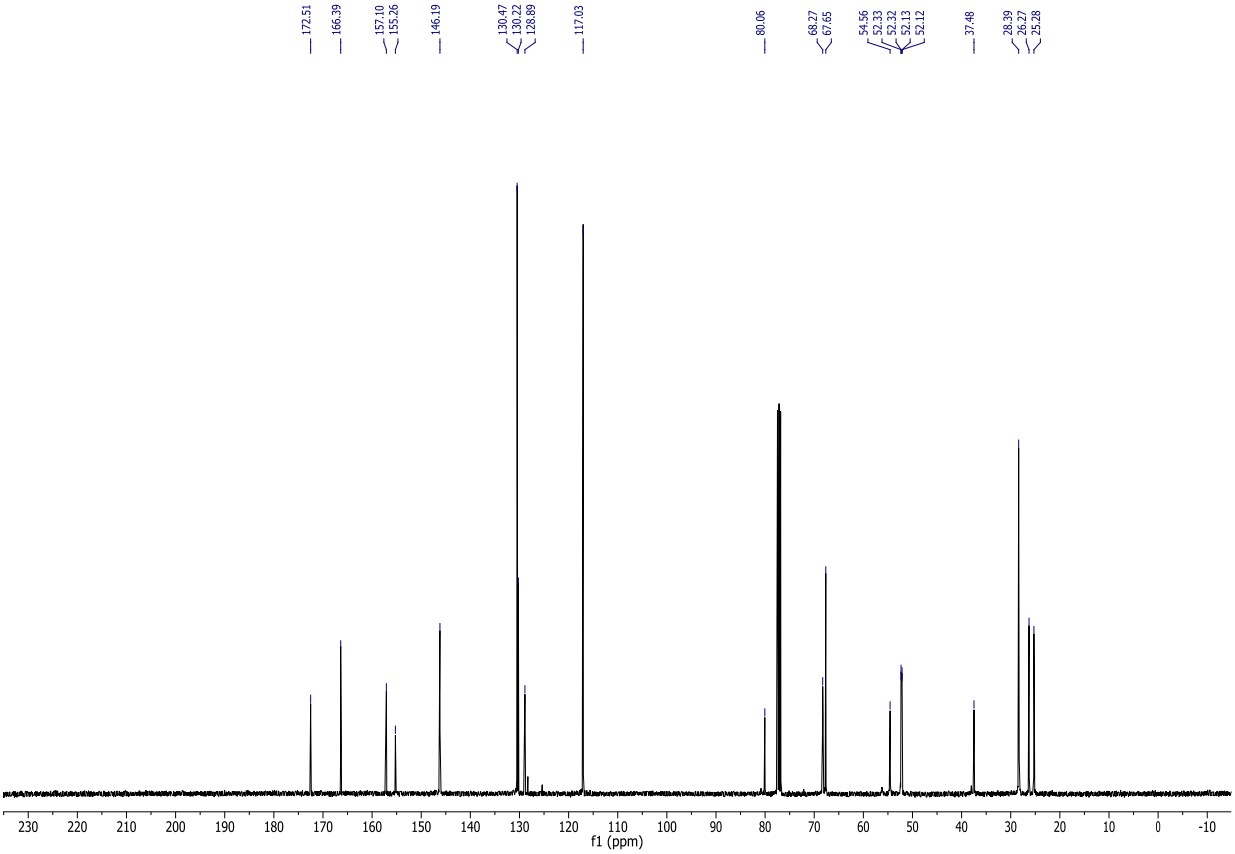
^{13}C NMR (75 MHz, 23 ^{o}C, $CDCl_3$)



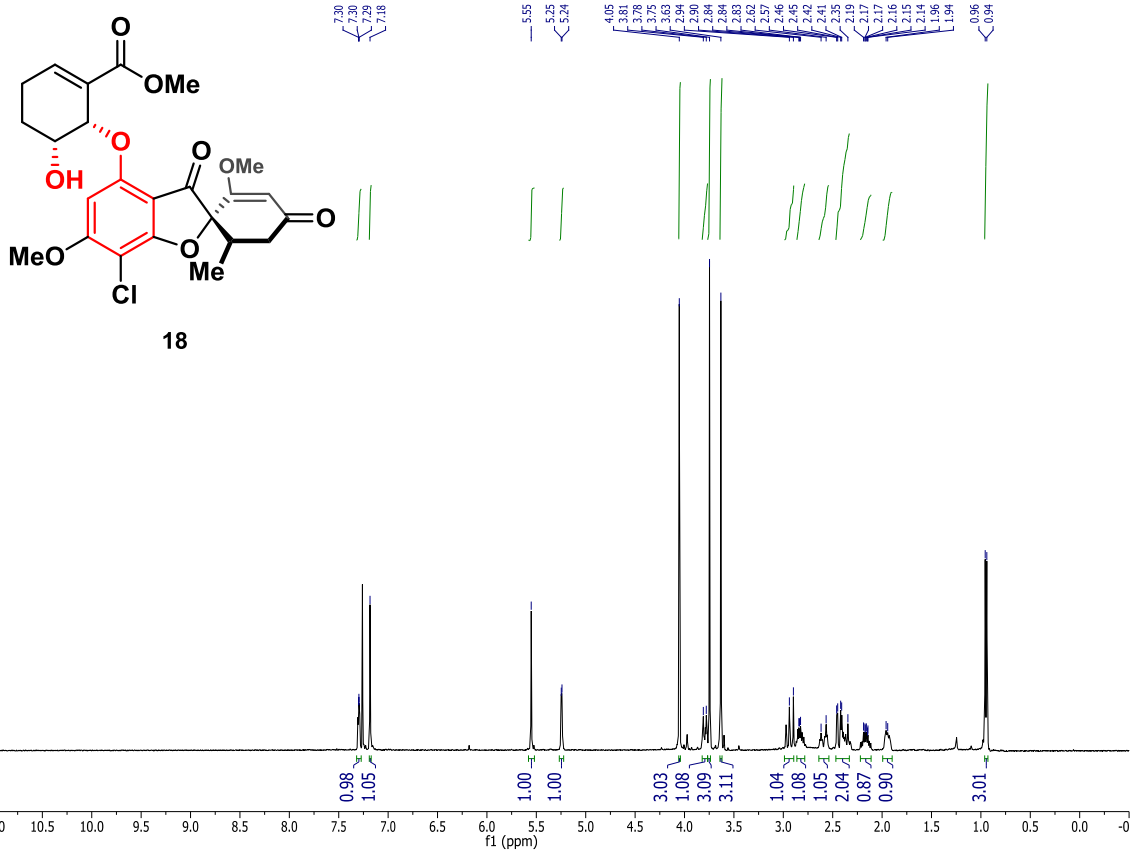
^{1}H NMR (400 MHz, 23 ^{o}C, $CDCl_3$)



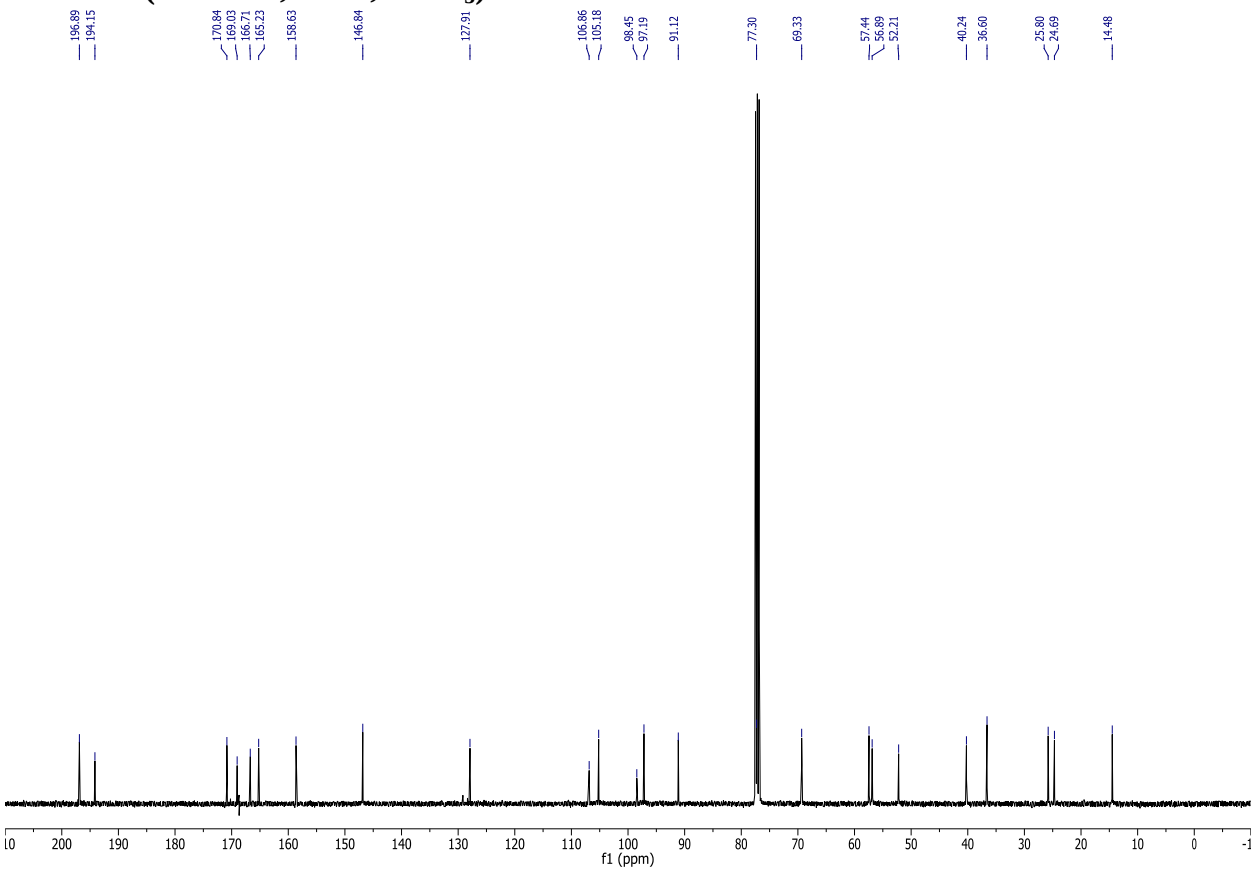
^{13}C NMR (100 MHz, 23 ^{o}C, $CDCl_3$)



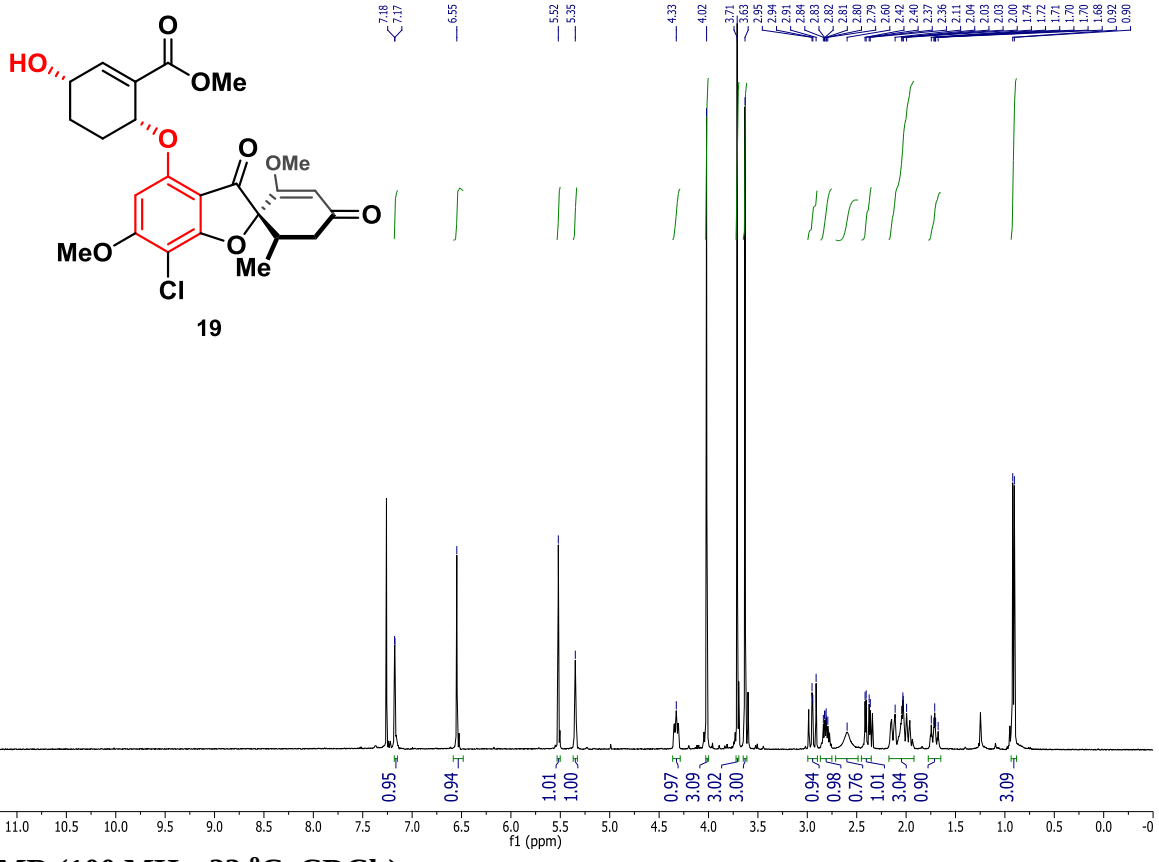
^{1}H NMR (400 MHz, 23 ^{o}C, $CDCl_3$)



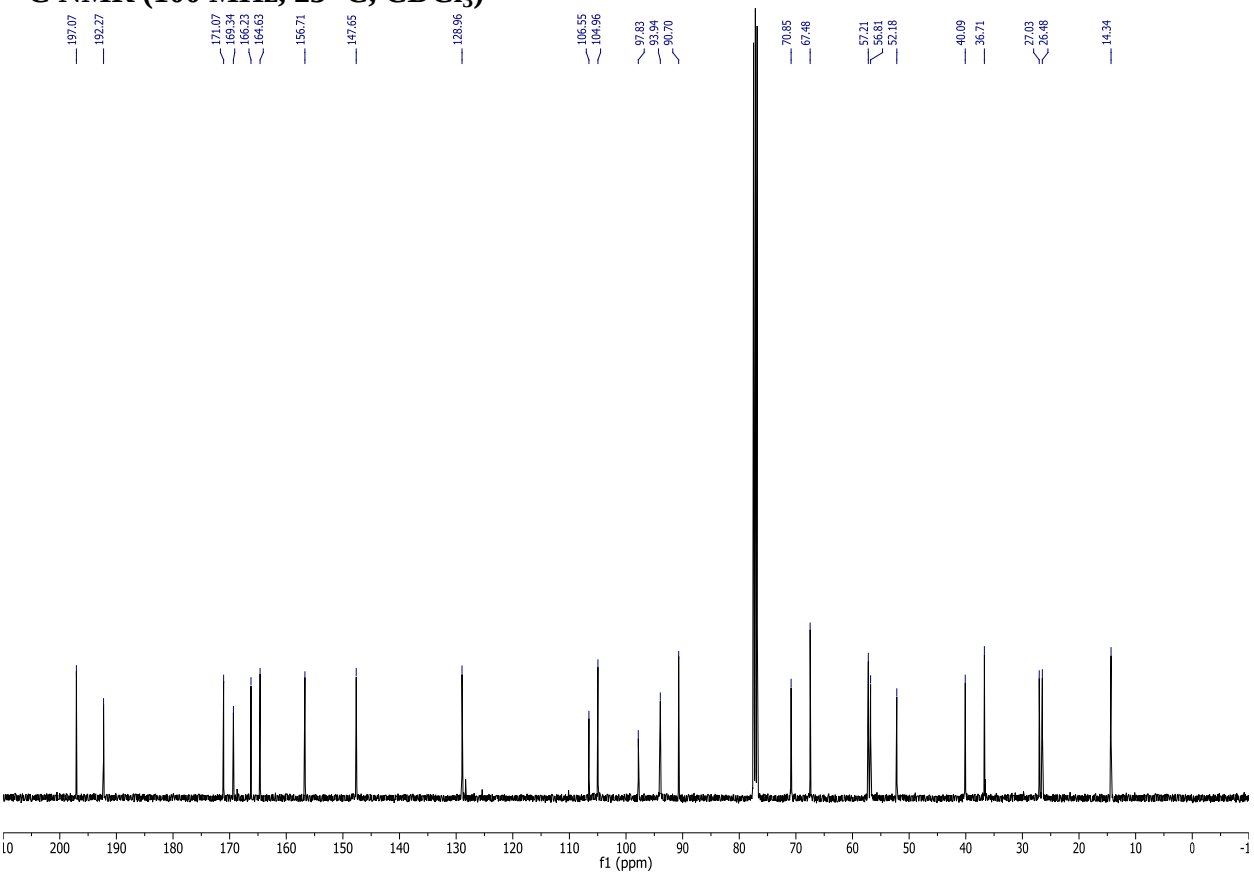
^{13}C NMR (100 MHz, 23 ^{o}C, $CDCl_3$)



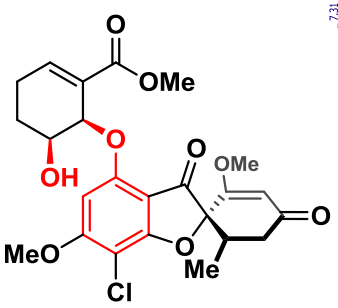
^{1}H NMR (400 MHz, 23 ^{o}C, $CDCl_3$)



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



^{1}H NMR (300 MHz, 23 ^{o}C, $CDCl_3$)



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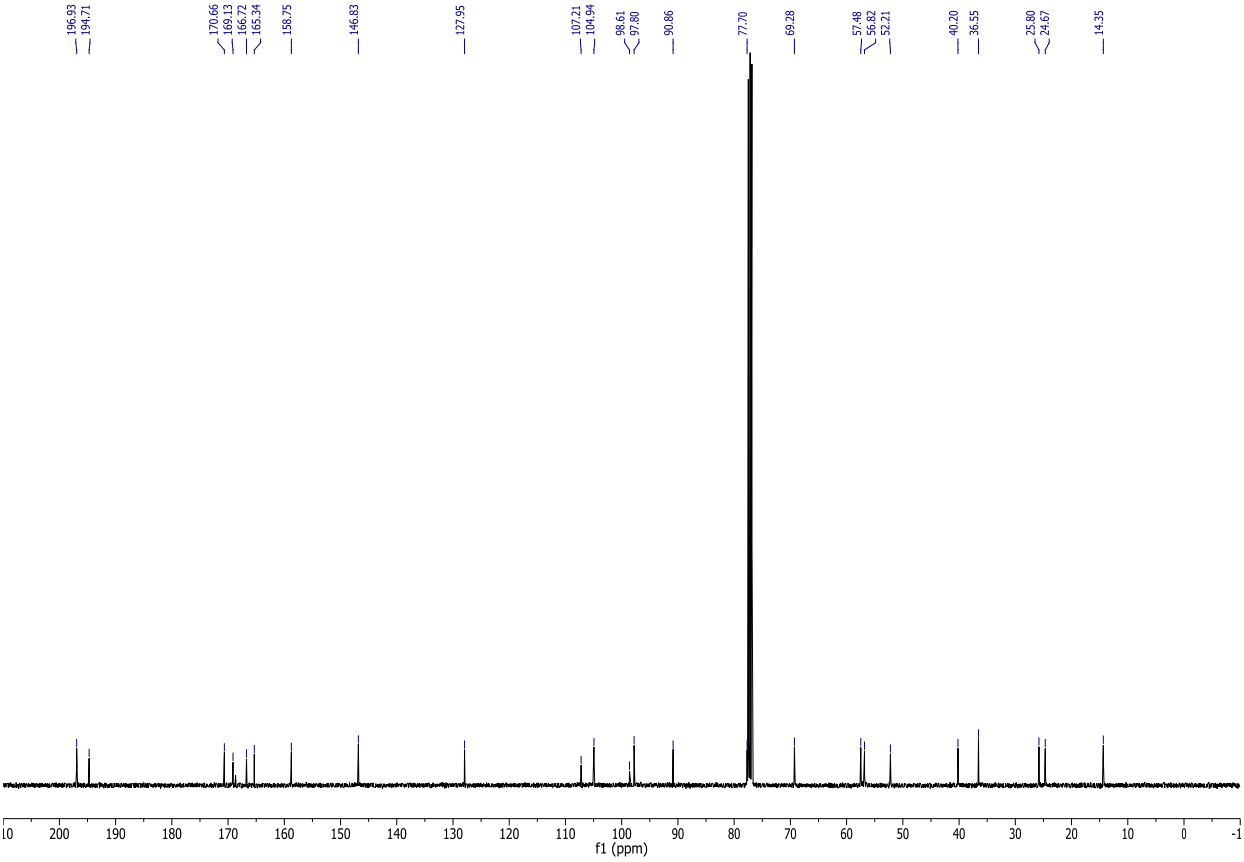
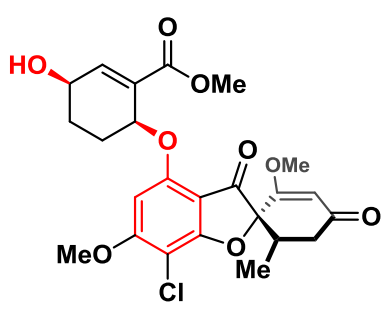
^{13}C NMR (100 MHz, 23 ^{o}C, $CDCl_3$)



^{1}H NMR (400 MHz, 23 ^{o}C, $CDCl_3$)



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