

**The Development of a Unified Enantioselective, Convergent Synthetic Approach
Toward the Furanobutenolide-Derived Polycyclic Norcembranoid Diterpenes:
Asymmetric Formation of the Polycyclic Norditerpenoid Carbocyclic Core by
Tandem Annulation Cascade**

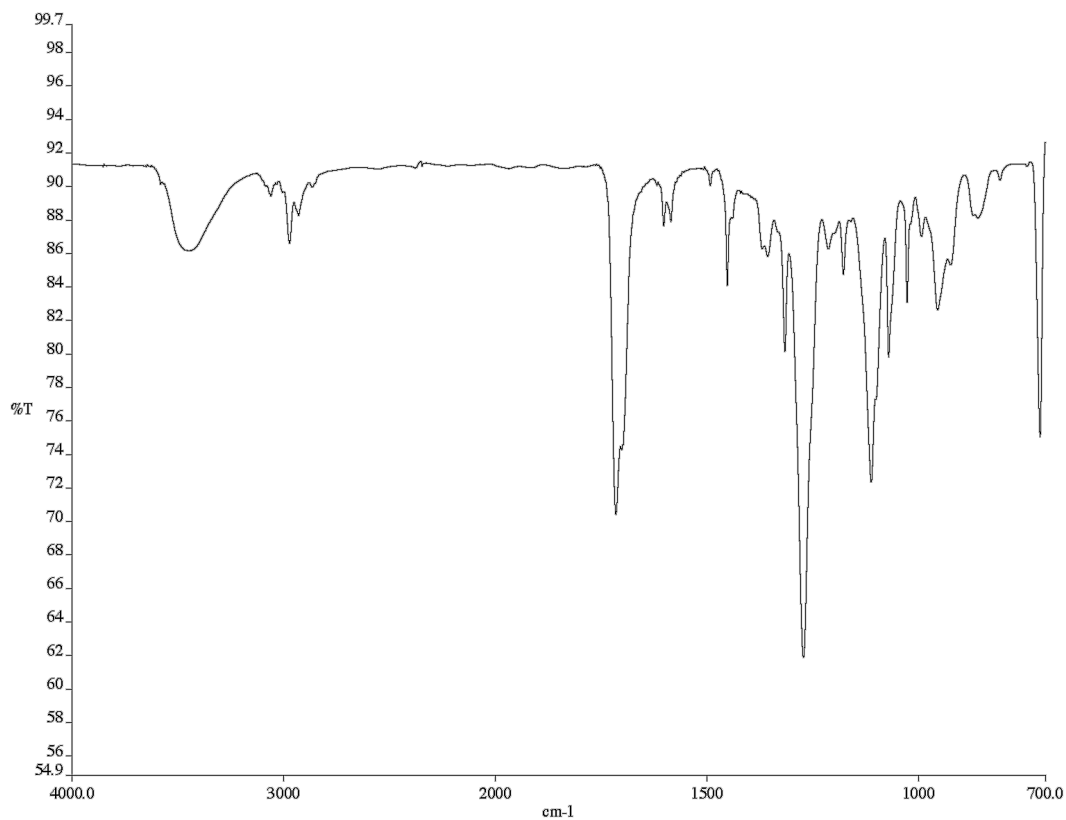
Robert A. Craig, II, Russell C. Smith, Jennifer L. Roizen,
Amanda C. Jones, Scott C. Virgil, and Brian M. Stoltz*

*Warren and Katharine Schlinger Laboratory for Chemistry and Chemical Engineering,
Division of Chemistry and Chemical Engineering, California Institute of Technology, MC
101-20, Pasadena, CA 91125, U.S.A.*

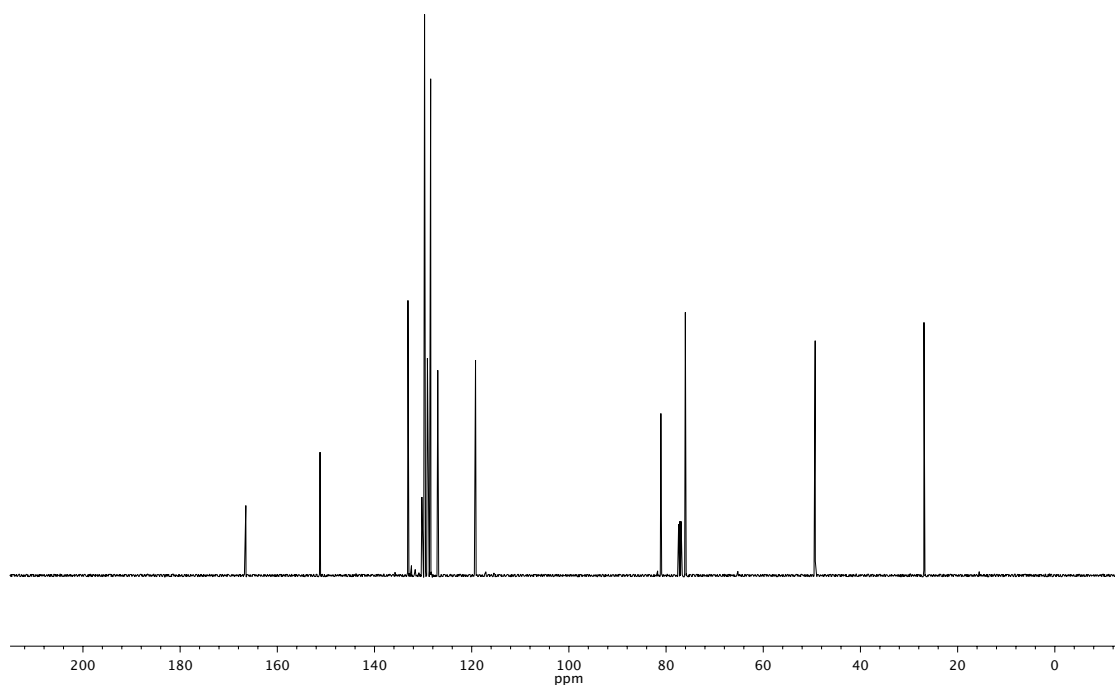
Table of Contents

¹ H, ¹³ C, and IR spectra for Diene 67	S3
¹ H, ¹³ C, and IR spectra for Diol <i>ent-18</i>	S5
¹ H, ¹³ C, and IR spectra for Ethyl Ester 32	S7
¹ H, ¹³ C, and IR spectra for α -Diazoester <i>ent-16</i>	S9
¹ H, ¹³ C, and IR spectra for Diene 34	S11
¹ H, ¹³ C, and IR spectra for Enone 35	S13
¹ H, ¹³ C, and IR spectra for <i>ent</i> -Isoineleganolide A (36)	S15
¹ H, ¹³ C, and IR spectra for Silyl Ether 37	S17
¹ H, ¹³ C, IR, ¹⁹ F, and ¹⁹ F – ¹³ C HSQC spectra for Triflate 39	S19
¹ H, ¹³ C, and IR spectra for Diol 44	S23
¹ H, ¹³ C, and IR spectra for Diol 45 , Diastereomer A	S25
¹ H, ¹³ C, and IR spectra for Diol 45 , Diastereomer B	S27
¹ H, ¹³ C, and IR spectra for Methyl Ketone 46	S29
¹ H, ¹³ C, and IR spectra for Methyl Ketone Diol <i>ent-43</i>	S31
¹ H, ¹³ C, and IR spectra for Methyl Ketone α -Diazoester 48	S33

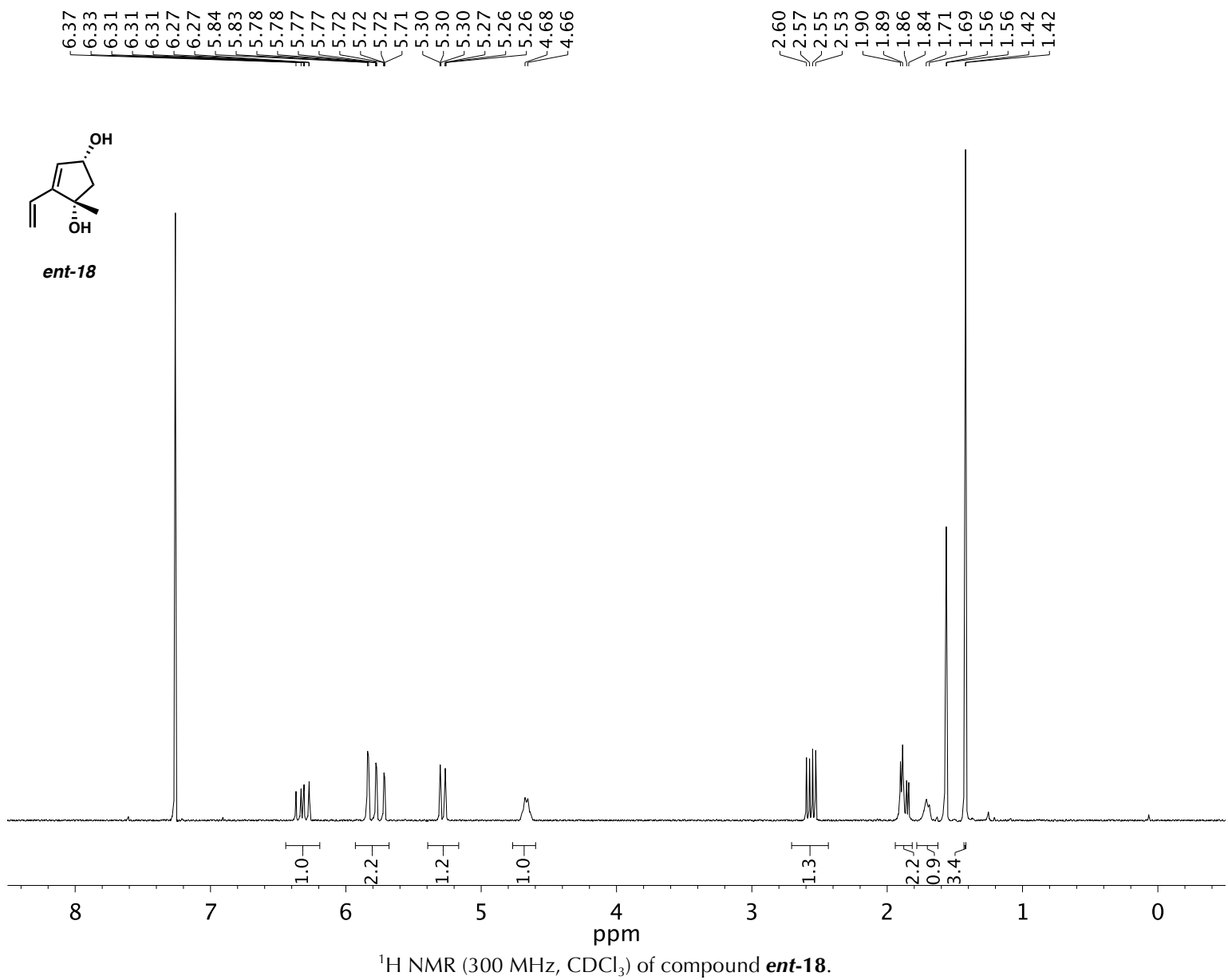
¹ H, ¹³ C, and IR spectra for Pyrazole 49	S35
¹ H, ¹³ C, and IR spectra for Ethyl Ether 52	S37
¹ H, ¹³ C, and IR spectra for Cycloheptatriene 53	S39
¹ H, ¹³ C, and IR spectra for Bromide 54	S41
¹ H, ¹³ C, and IR spectra for Ketopyran 55	S43
¹ H, ¹³ C, and IR spectra for Hemiketal 57 / Hydroxyketone 58	S45
¹ H, ¹³ C, and IR spectra for <i>ent-epi</i> -Isoineleganolide B (59)	S51
¹ H, ¹³ C, and IR spectra for <i>ent</i> -Isoineleganolide C (60)	S53
¹ H, ¹³ C, and IR spectra for Bisenone 61	S55

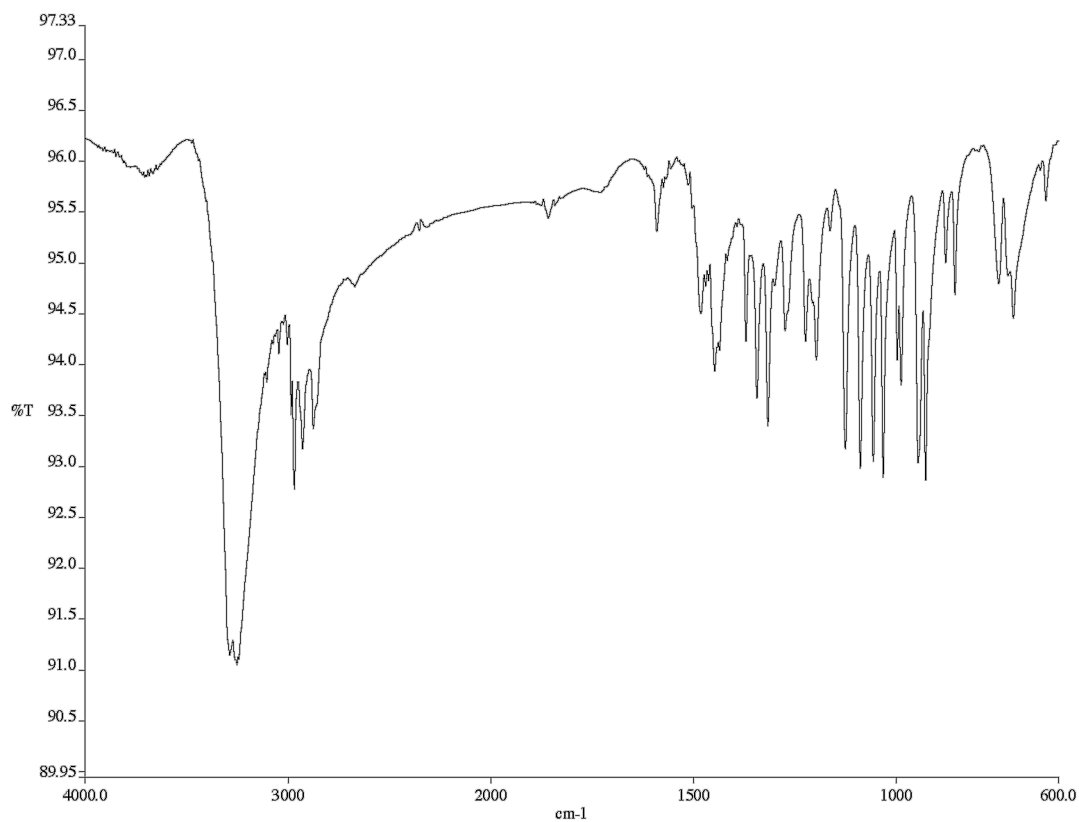


Infrared spectrum (Thin Film, NaCl) of compound **67**.

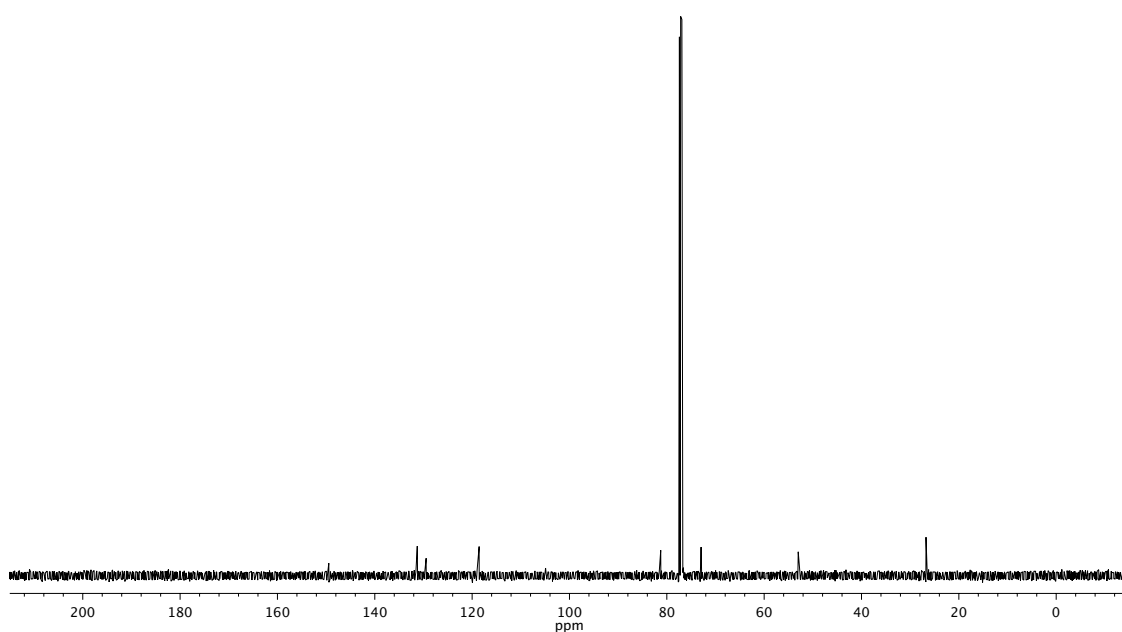


¹³C NMR (126 MHz, CDCl₃) of compound **67**.

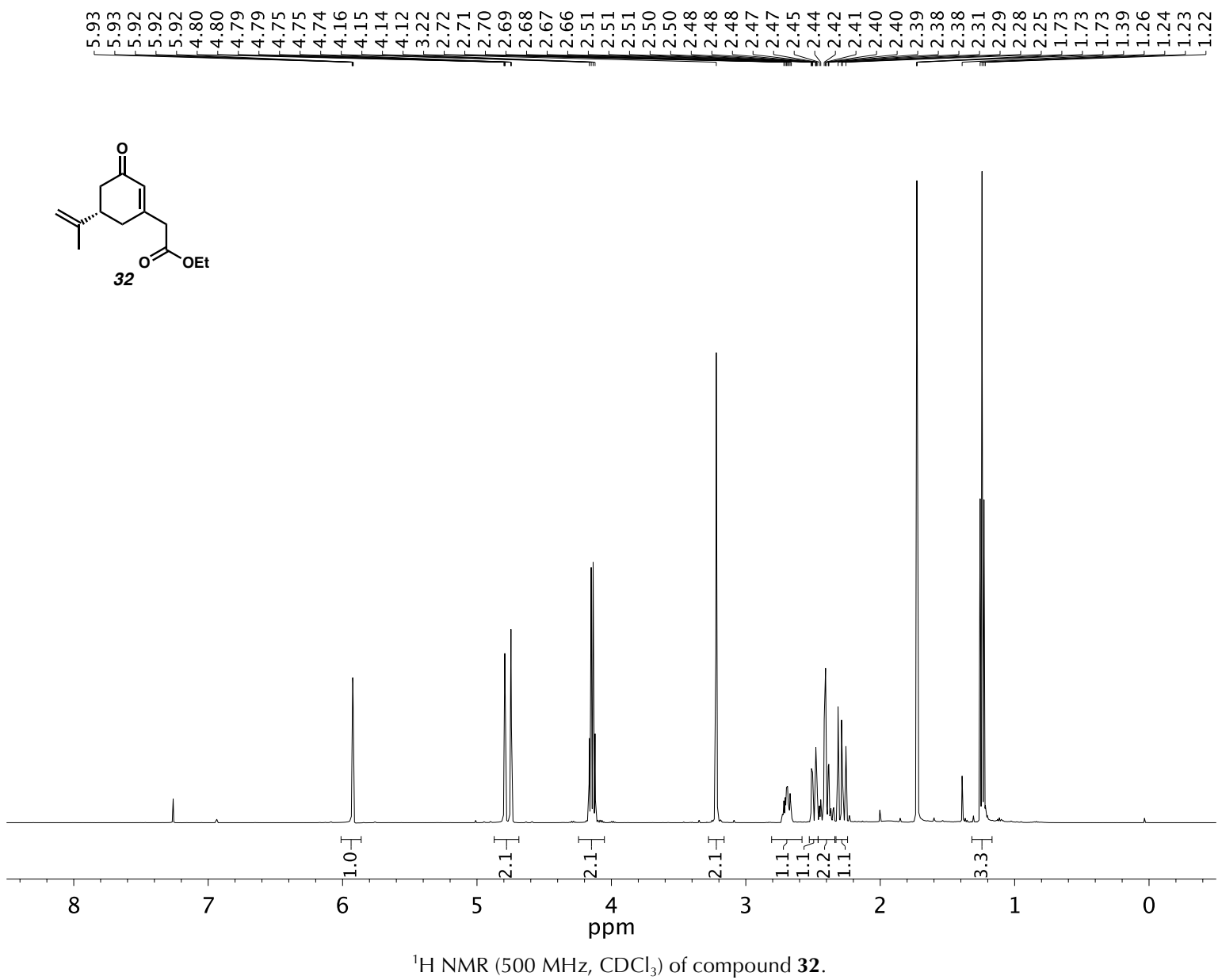


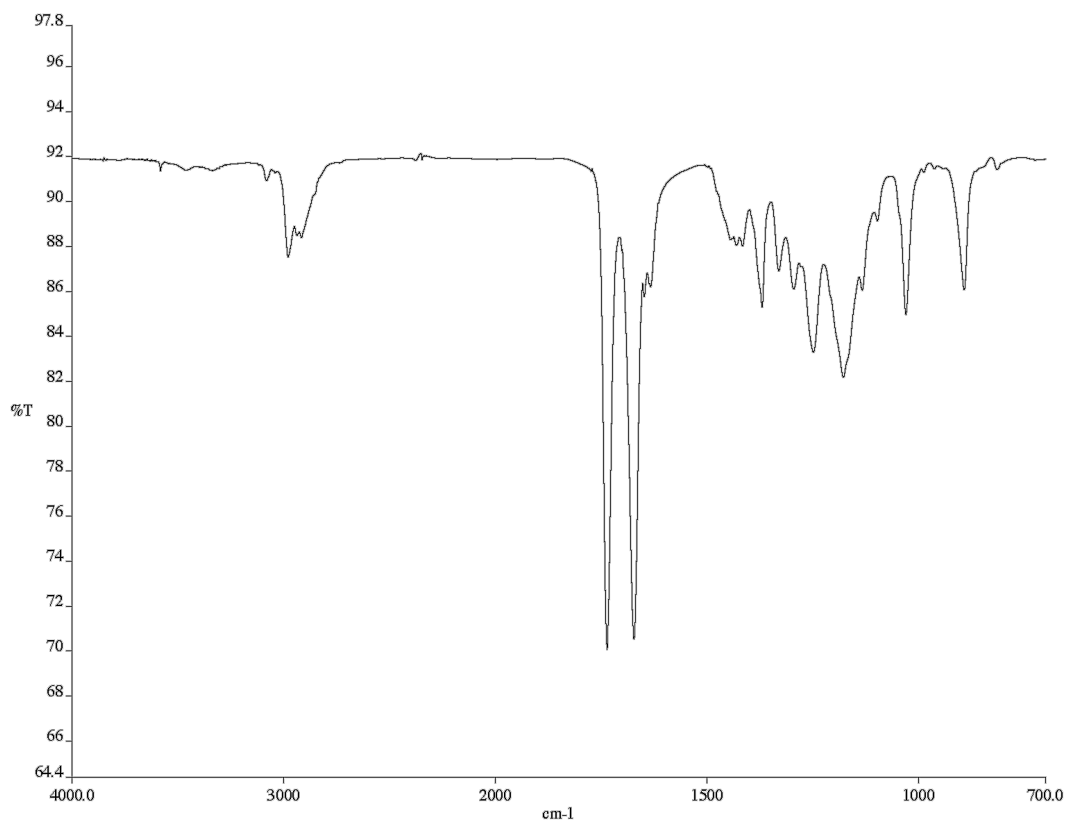


Infrared spectrum (Thin Film, NaCl) of compound **ent-18**.

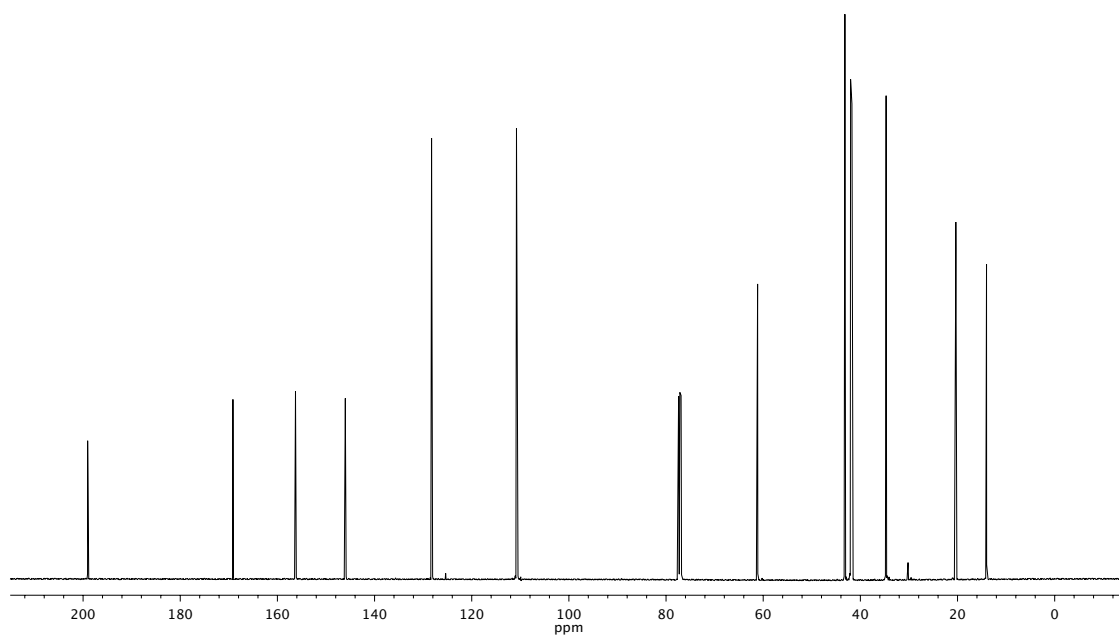


¹³C NMR (76 MHz, CDCl₃) of compound **ent-18**.

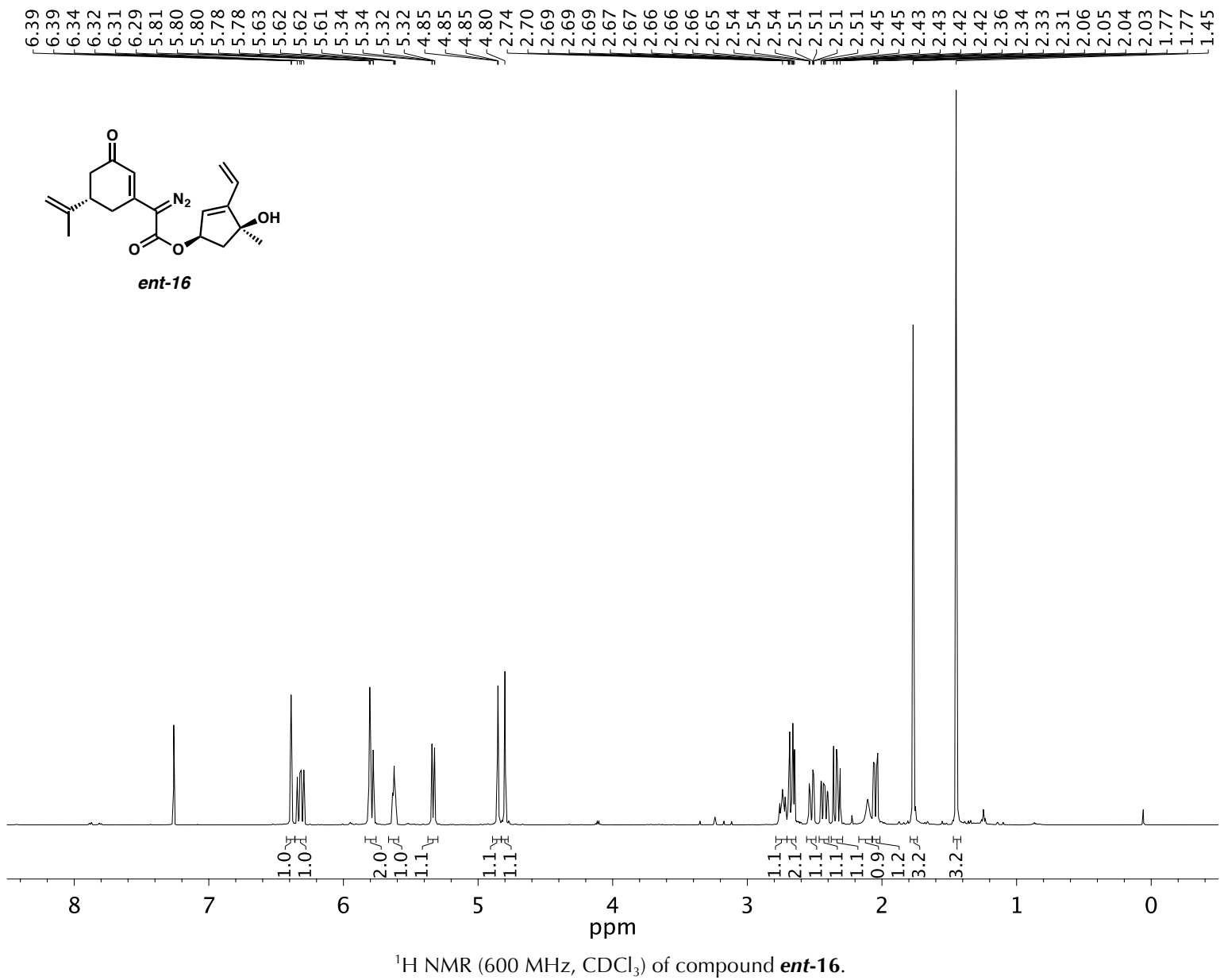


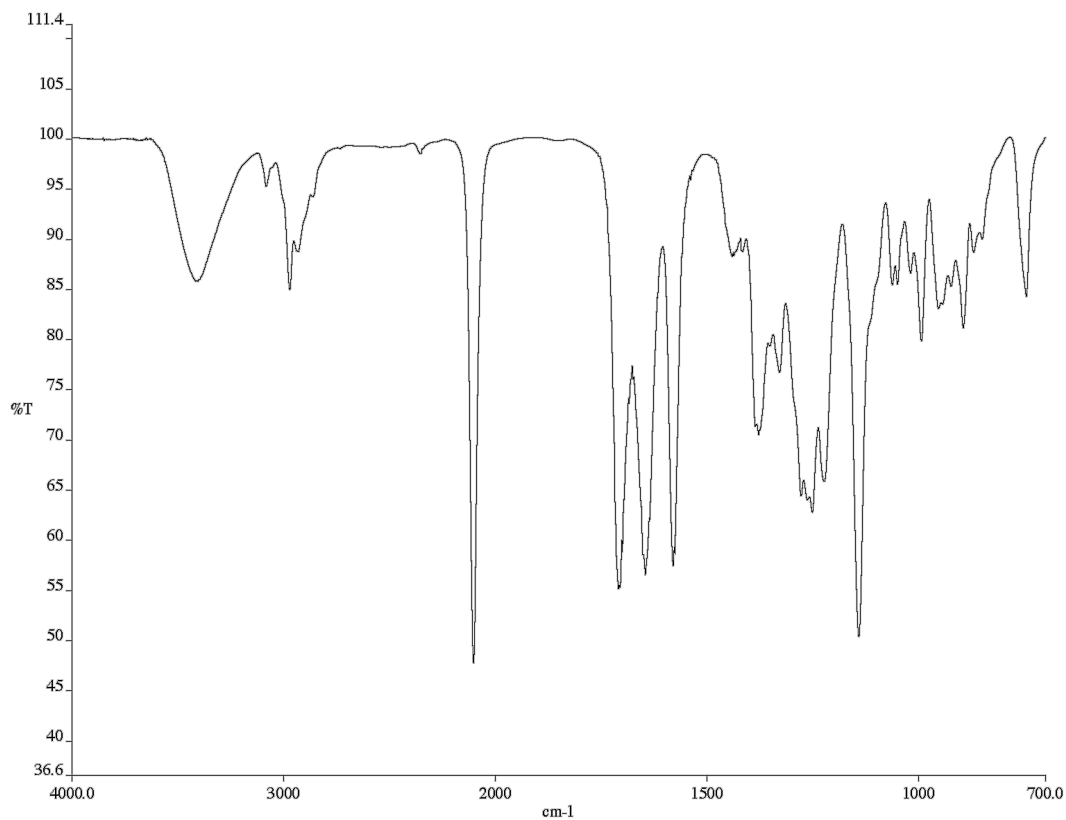
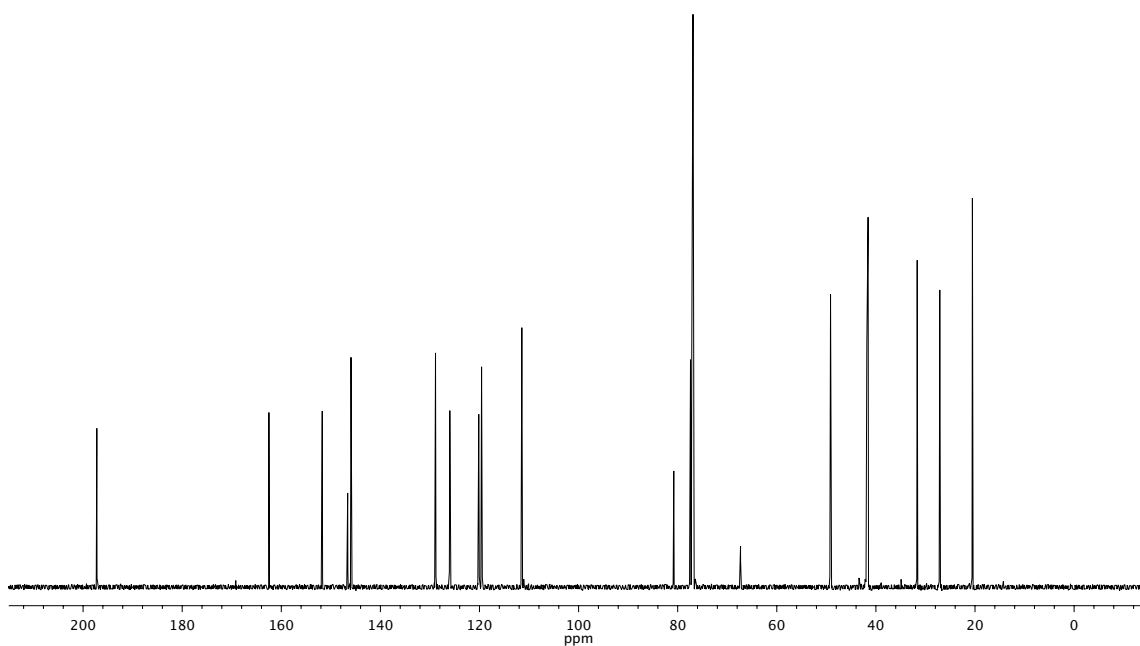


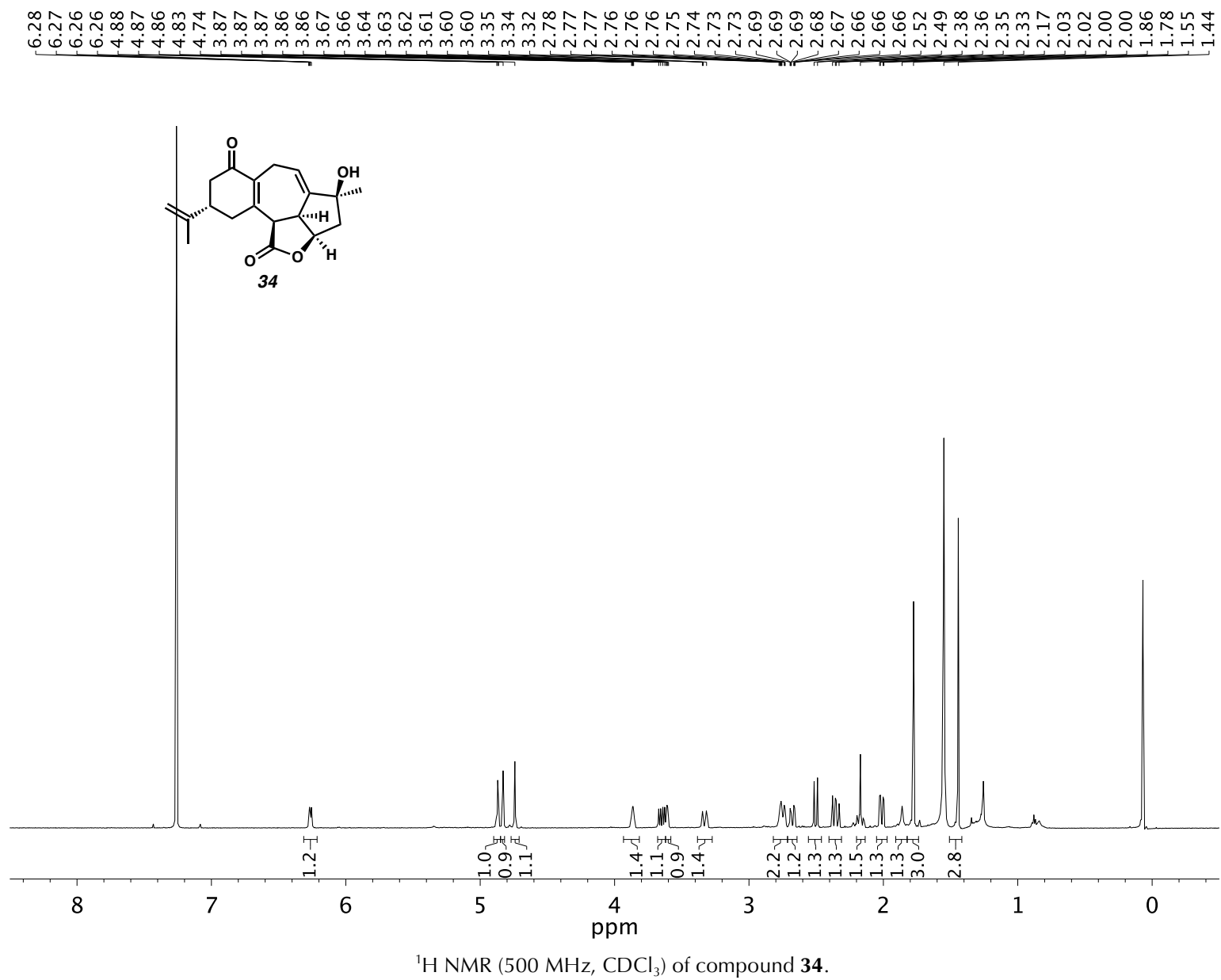
Infrared spectrum (Thin Film, NaCl) of compound **32**.

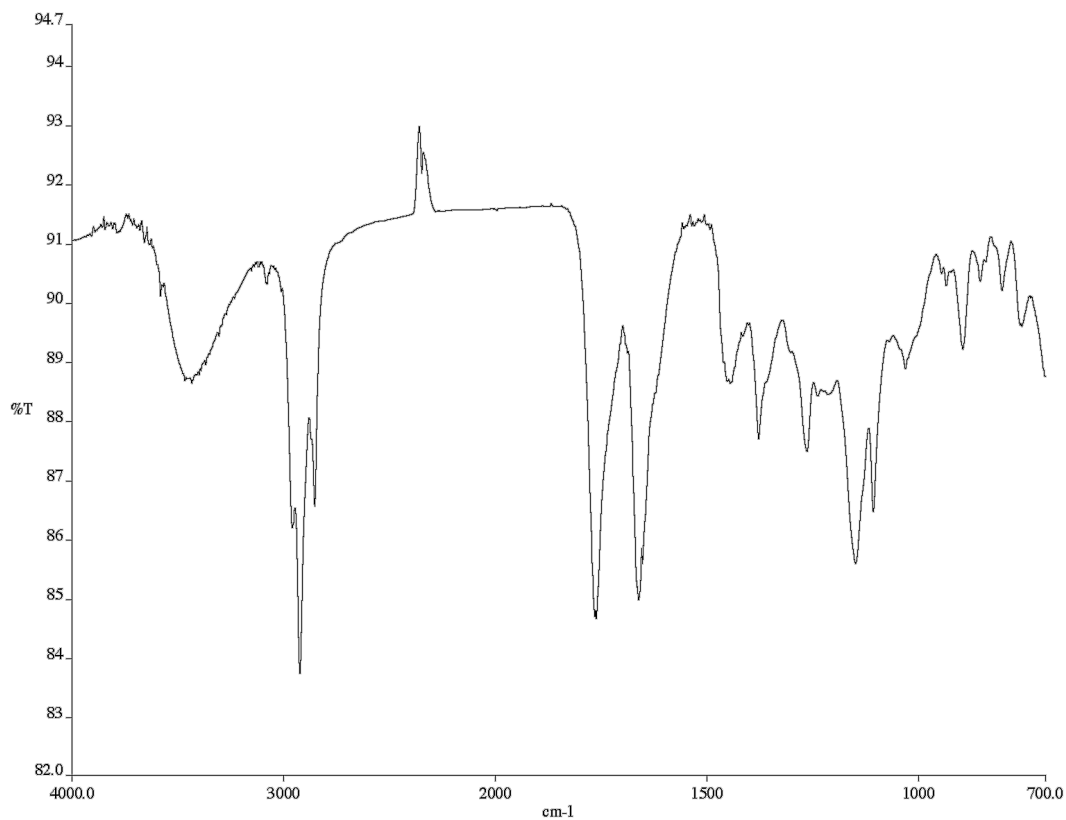


¹³C NMR (126 MHz, CDCl₃) of compound **32**.

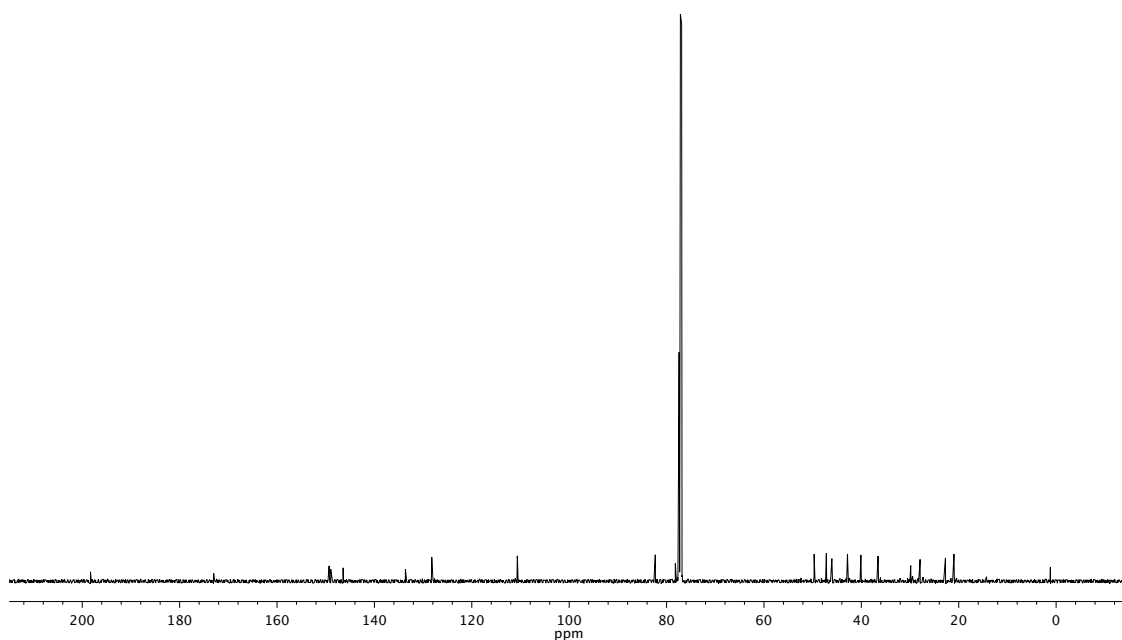


Infrared spectrum (Thin Film, NaCl) of compound **ent-16**.¹³C NMR (126 MHz, CDCl₃) of compound **ent-16**.

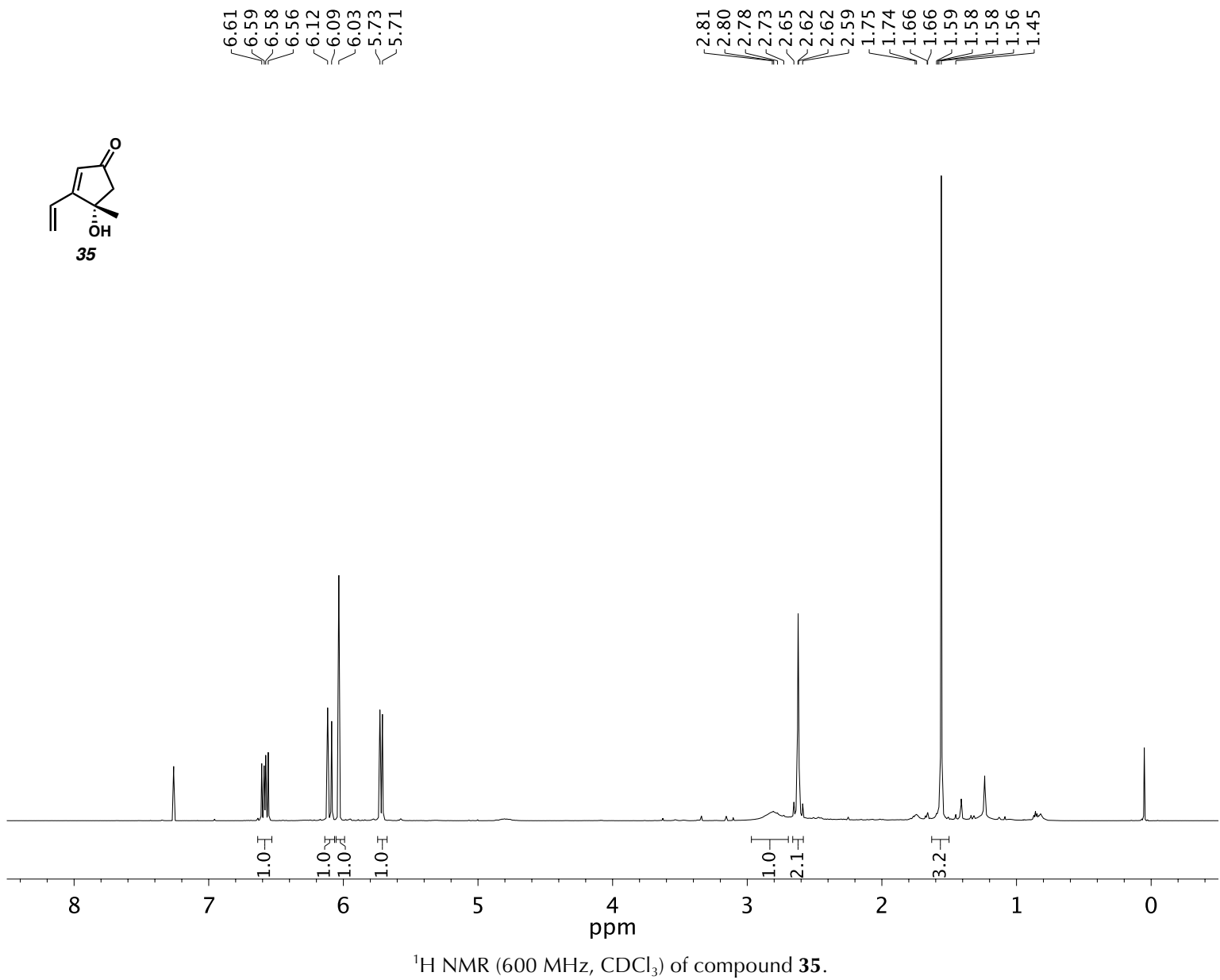


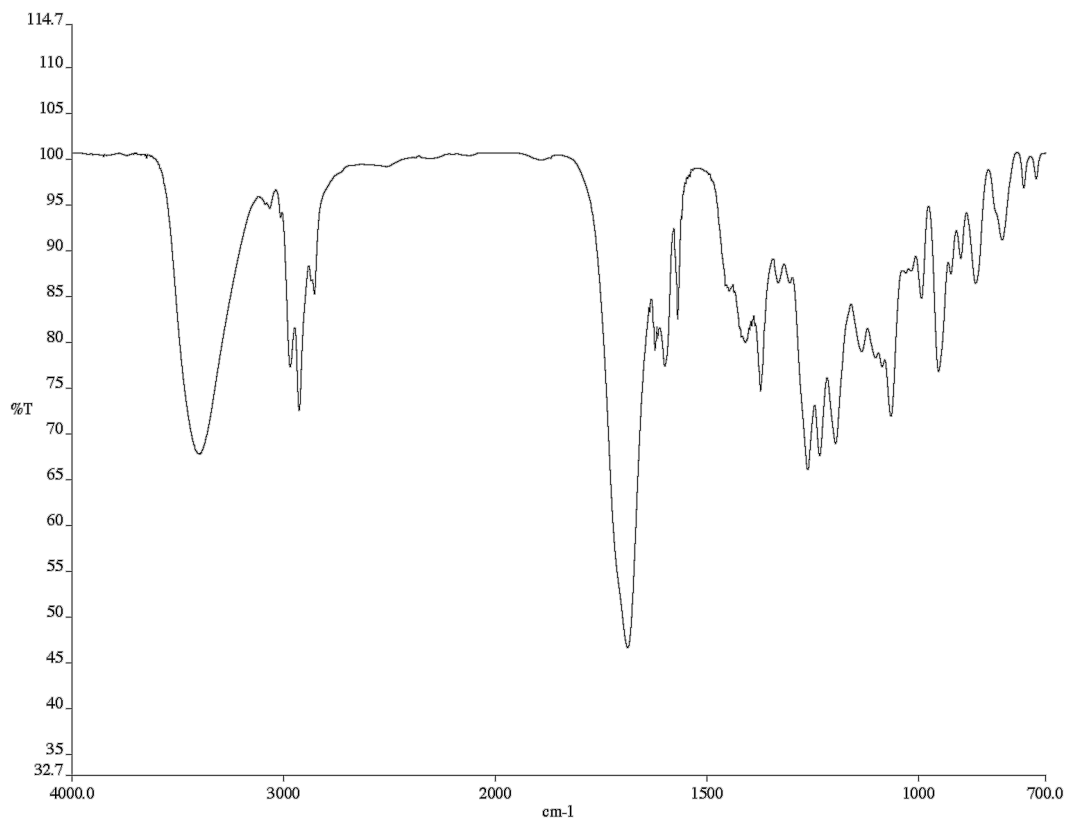


Infrared spectrum (Thin Film, NaCl) of compound **34**.

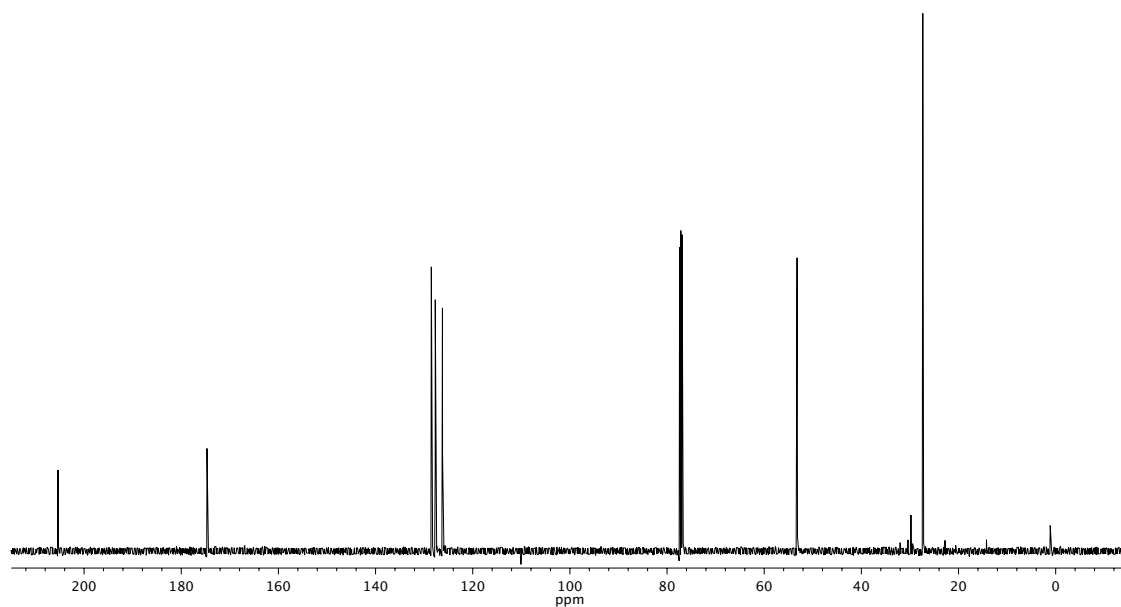


¹³C NMR (126 MHz, CDCl₃) of compound **34**.

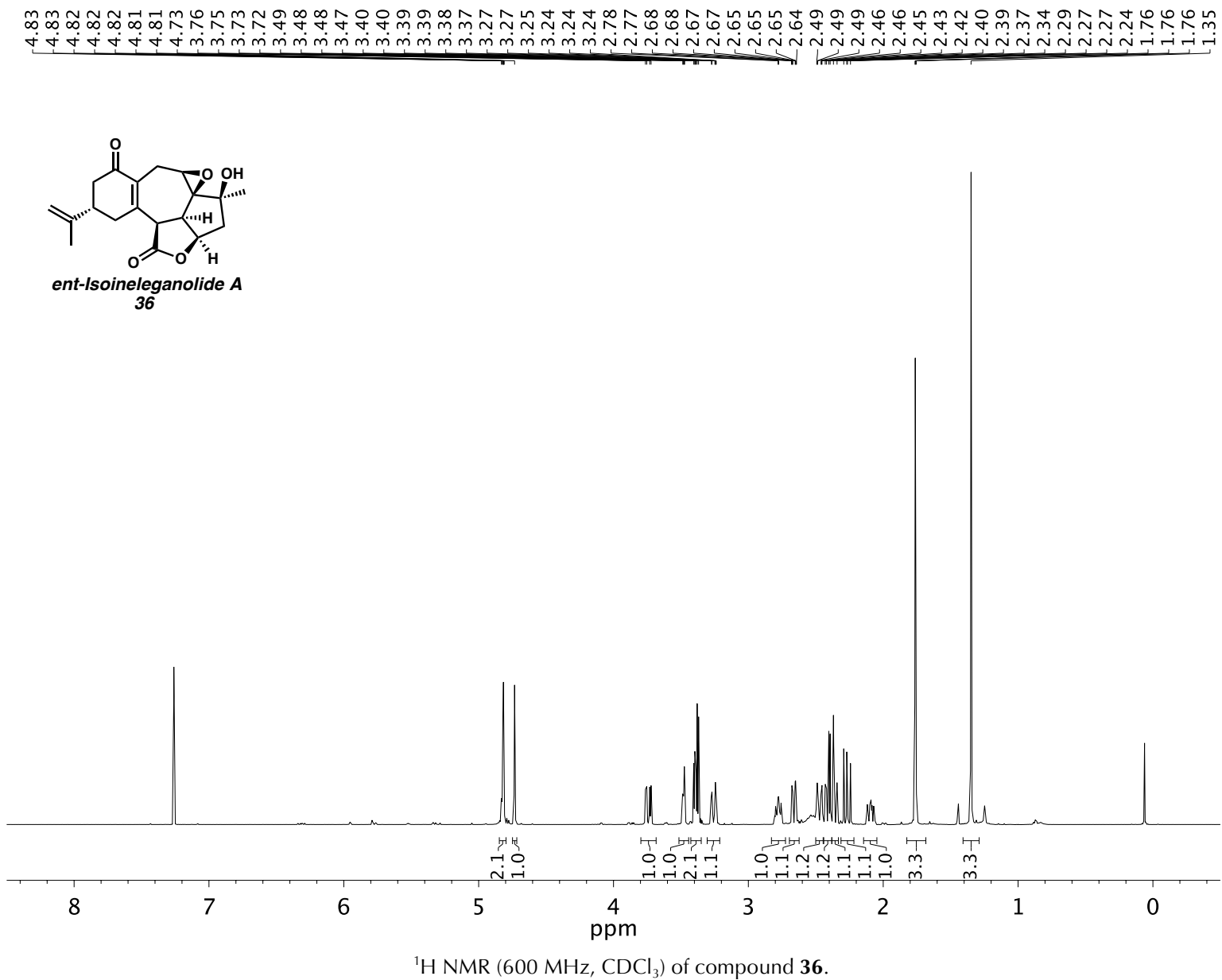


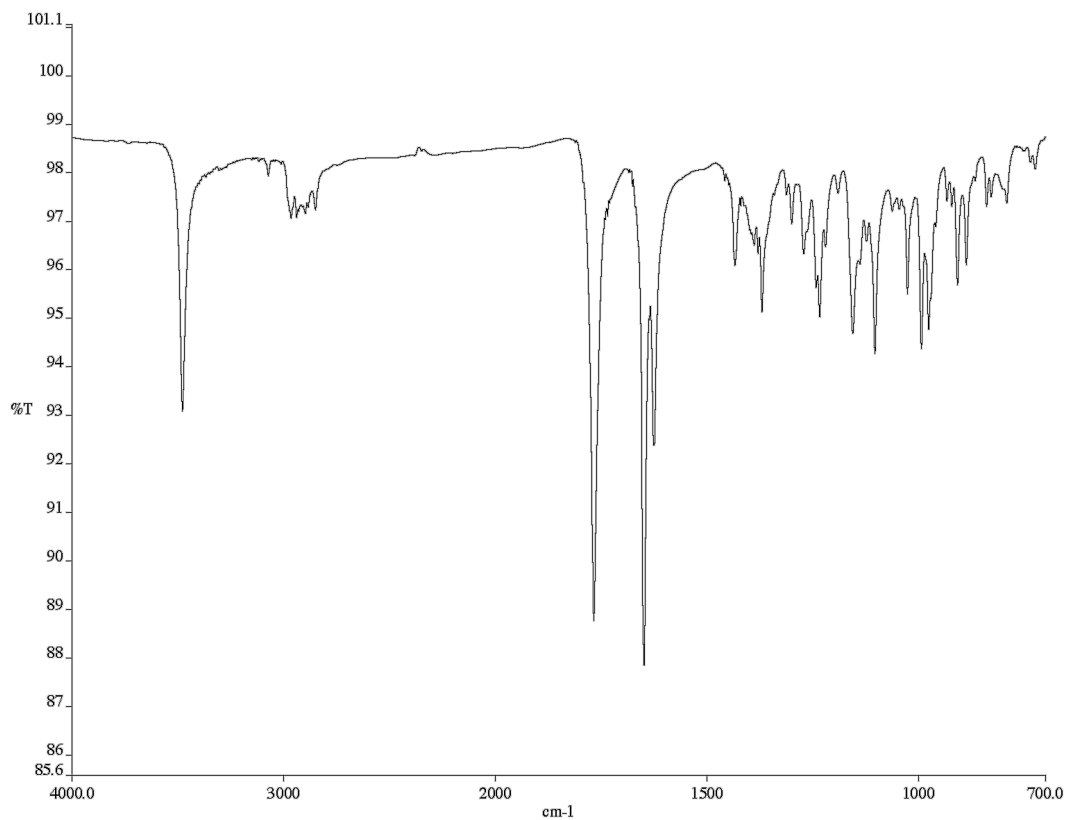


Infrared spectrum (Thin Film, NaCl) of compound **35**.

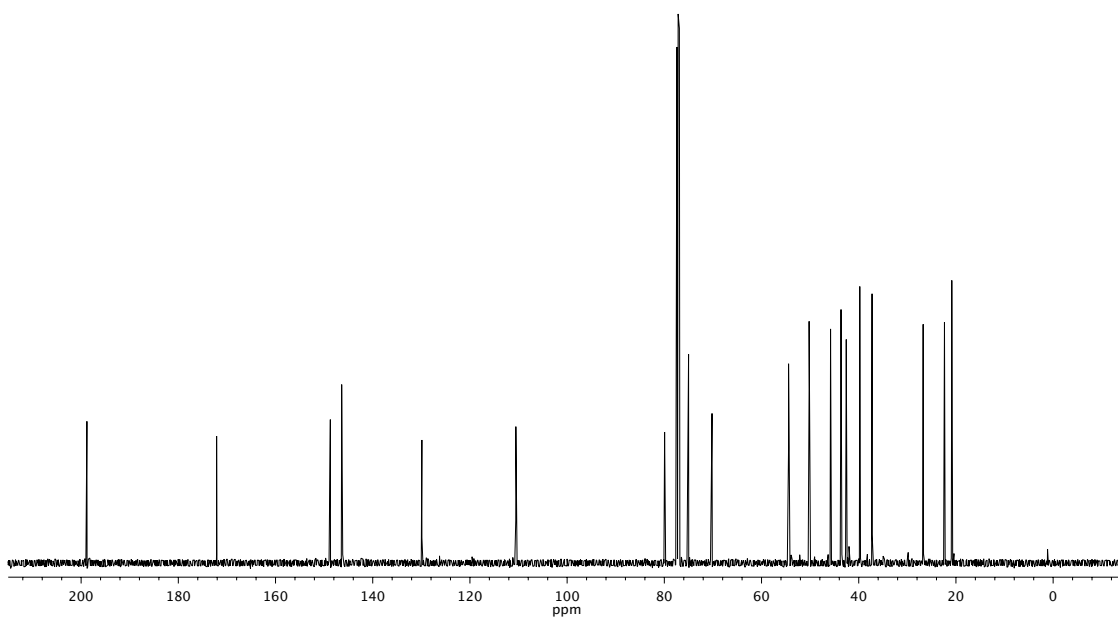


¹³C NMR (126 MHz, CDCl₃) of compound **35**.

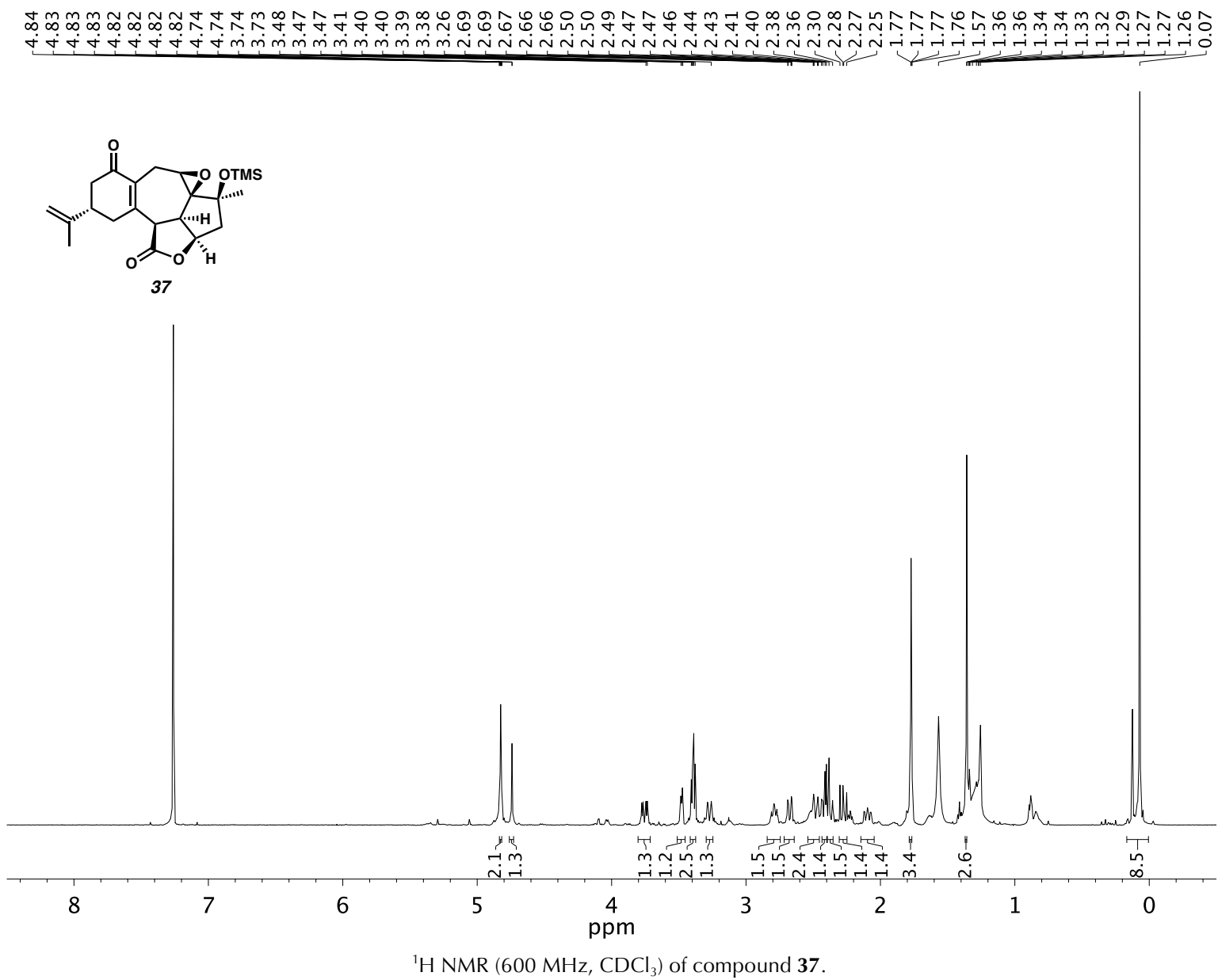


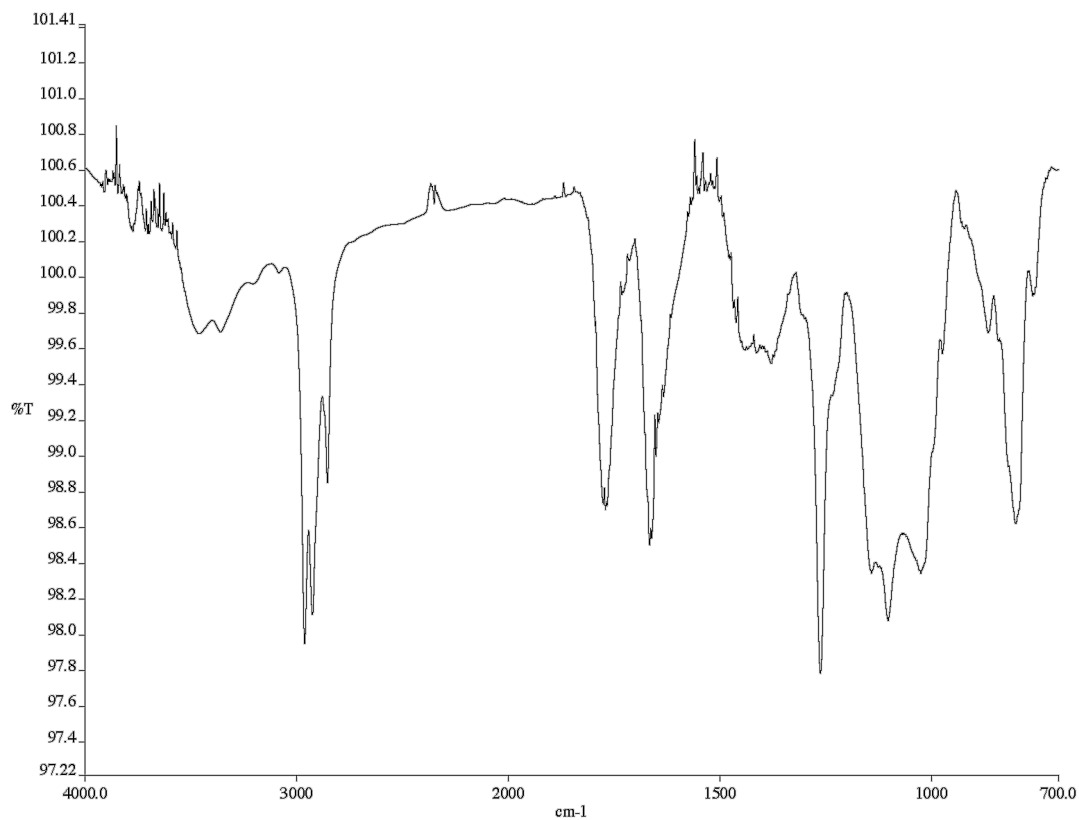


Infrared spectrum (Thin Film, NaCl) of compound **36**.

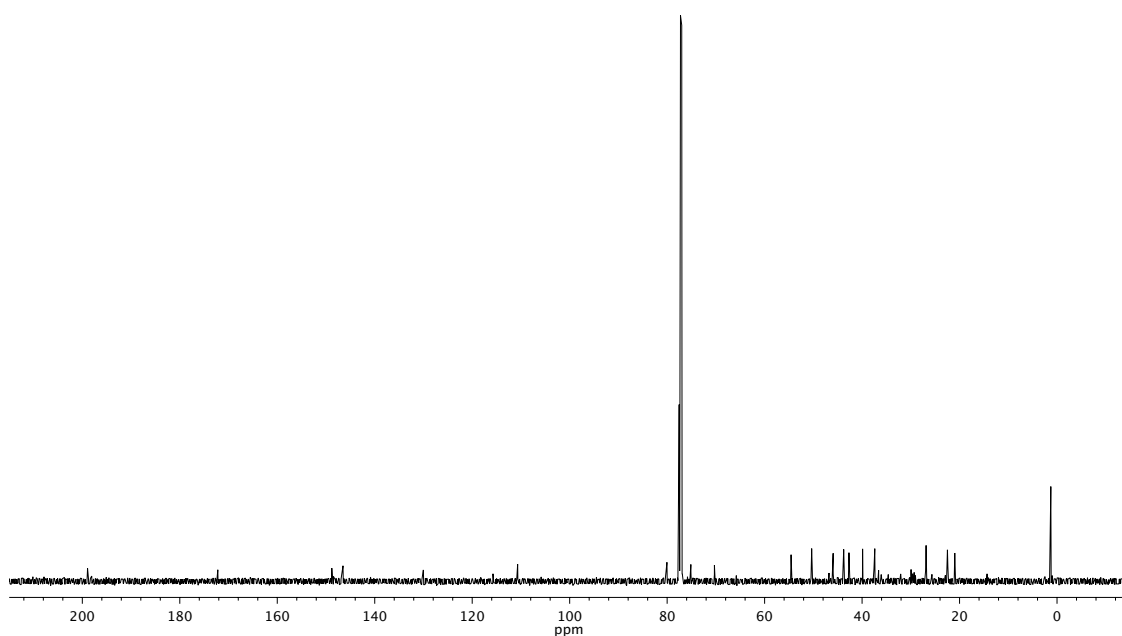


¹³C NMR (126 MHz, CDCl₃) of compound **36**.

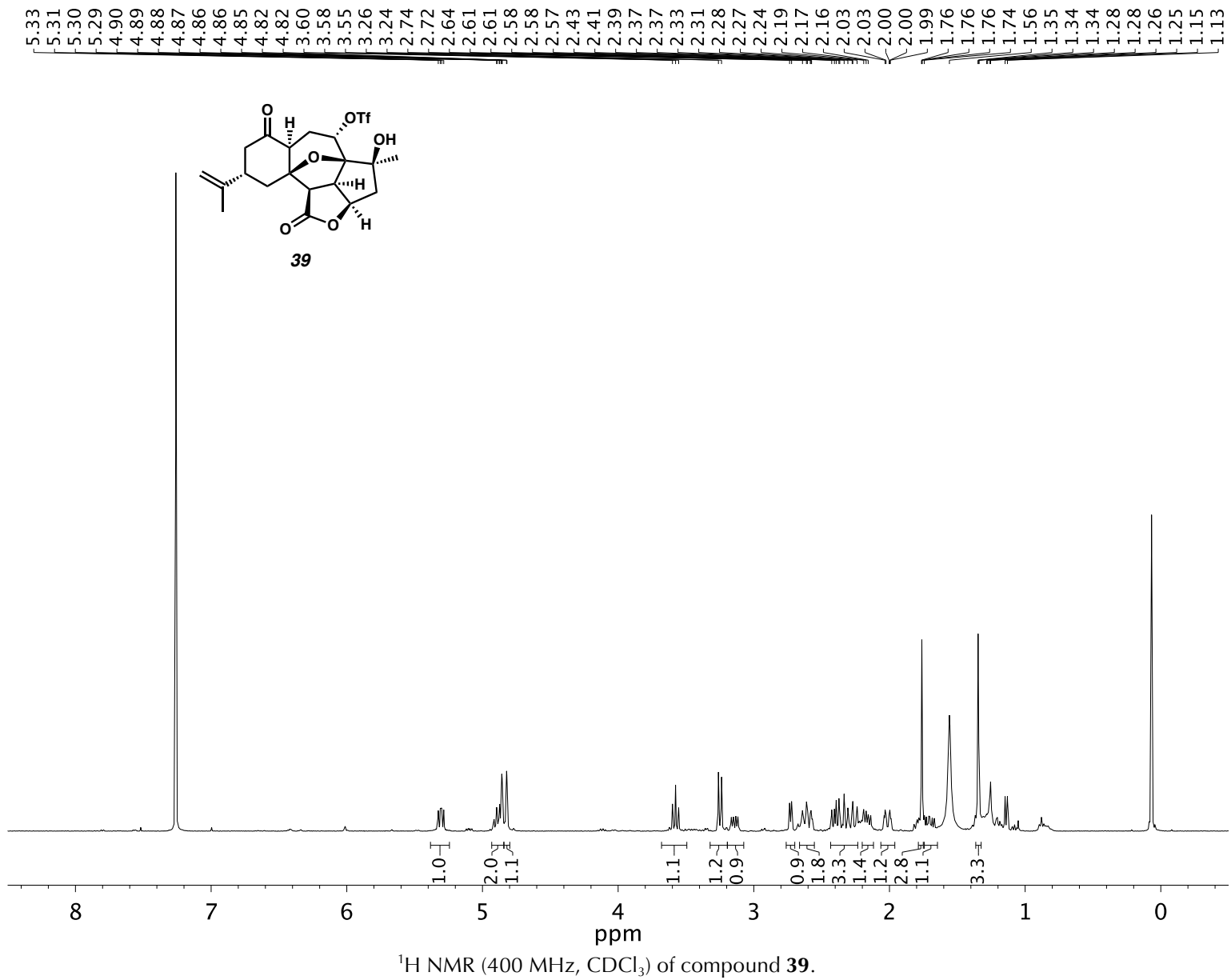


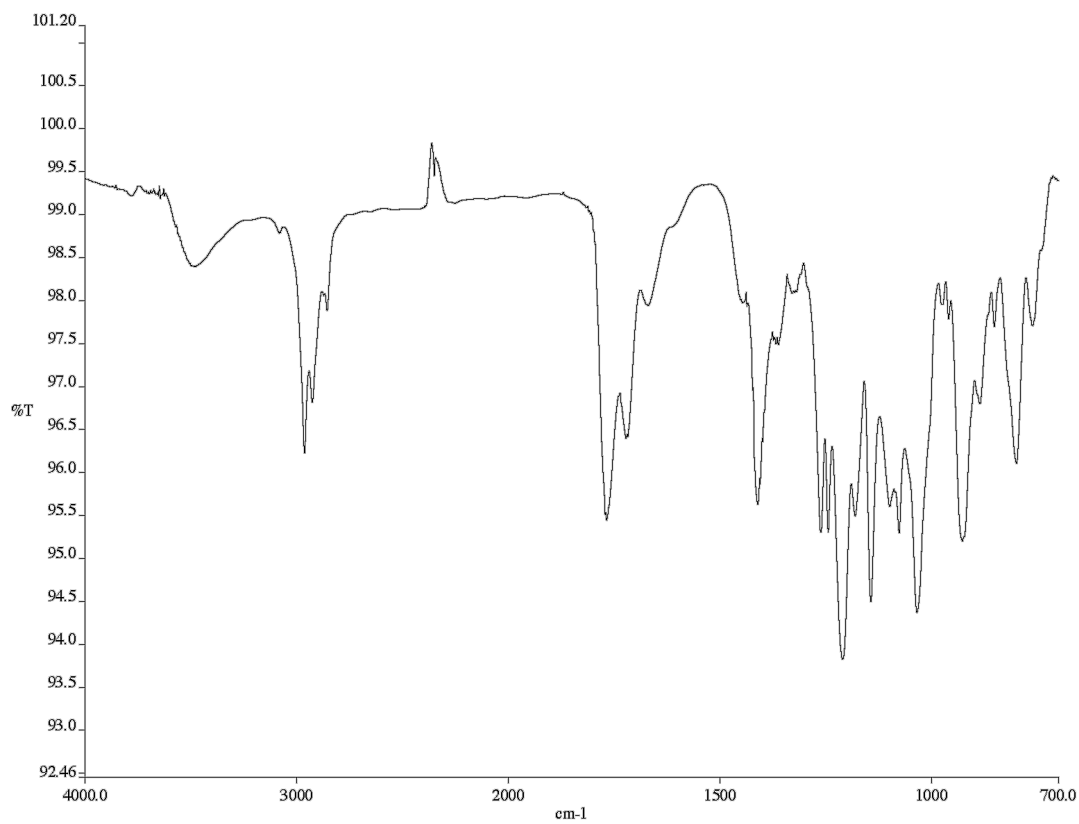


Infrared spectrum (Thin Film, NaCl) of compound **37**.

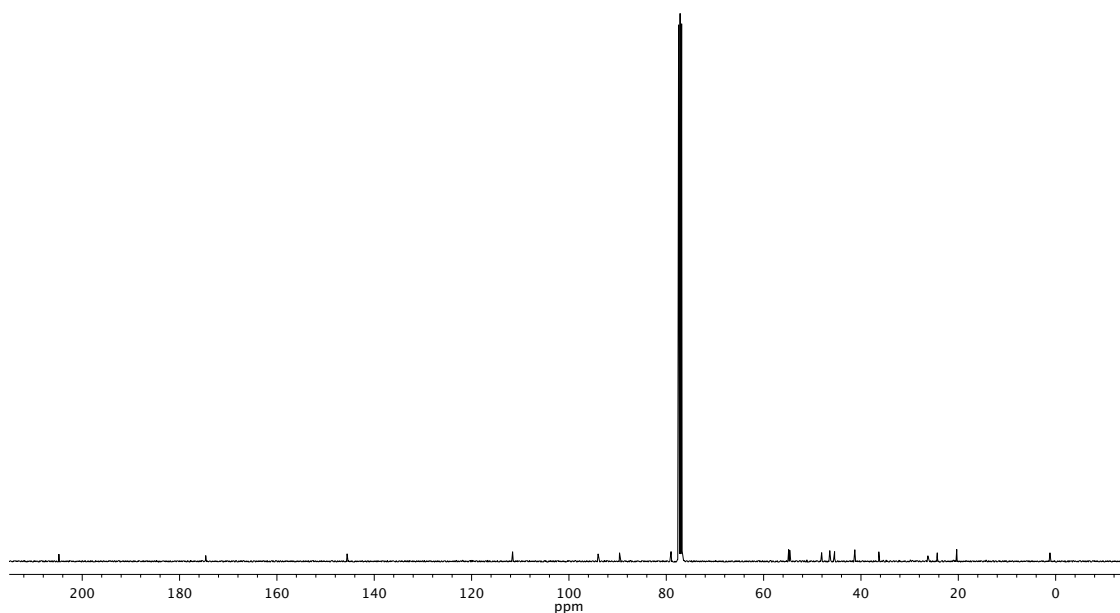


¹³C NMR (126 MHz, CDCl₃) of compound **37**.

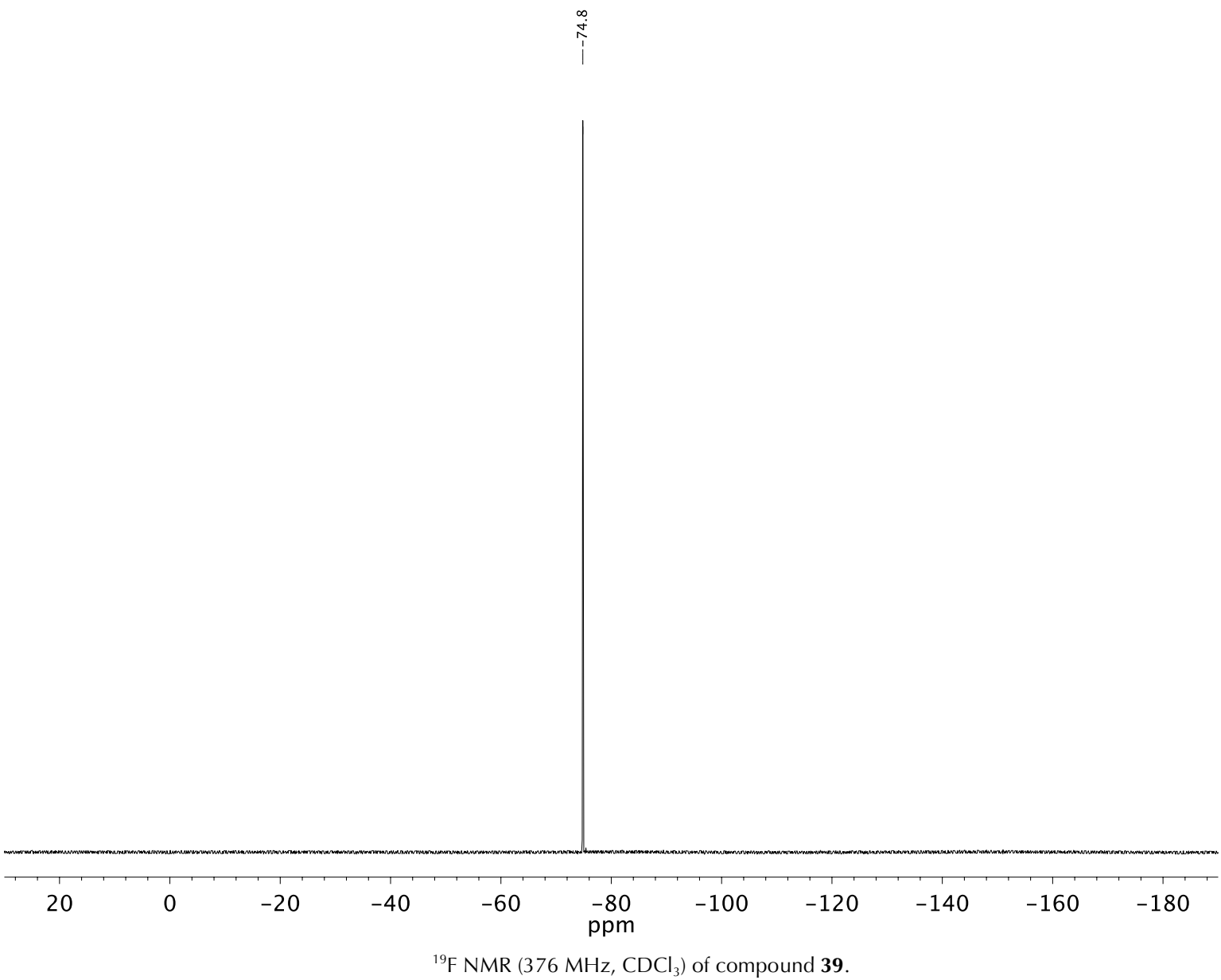


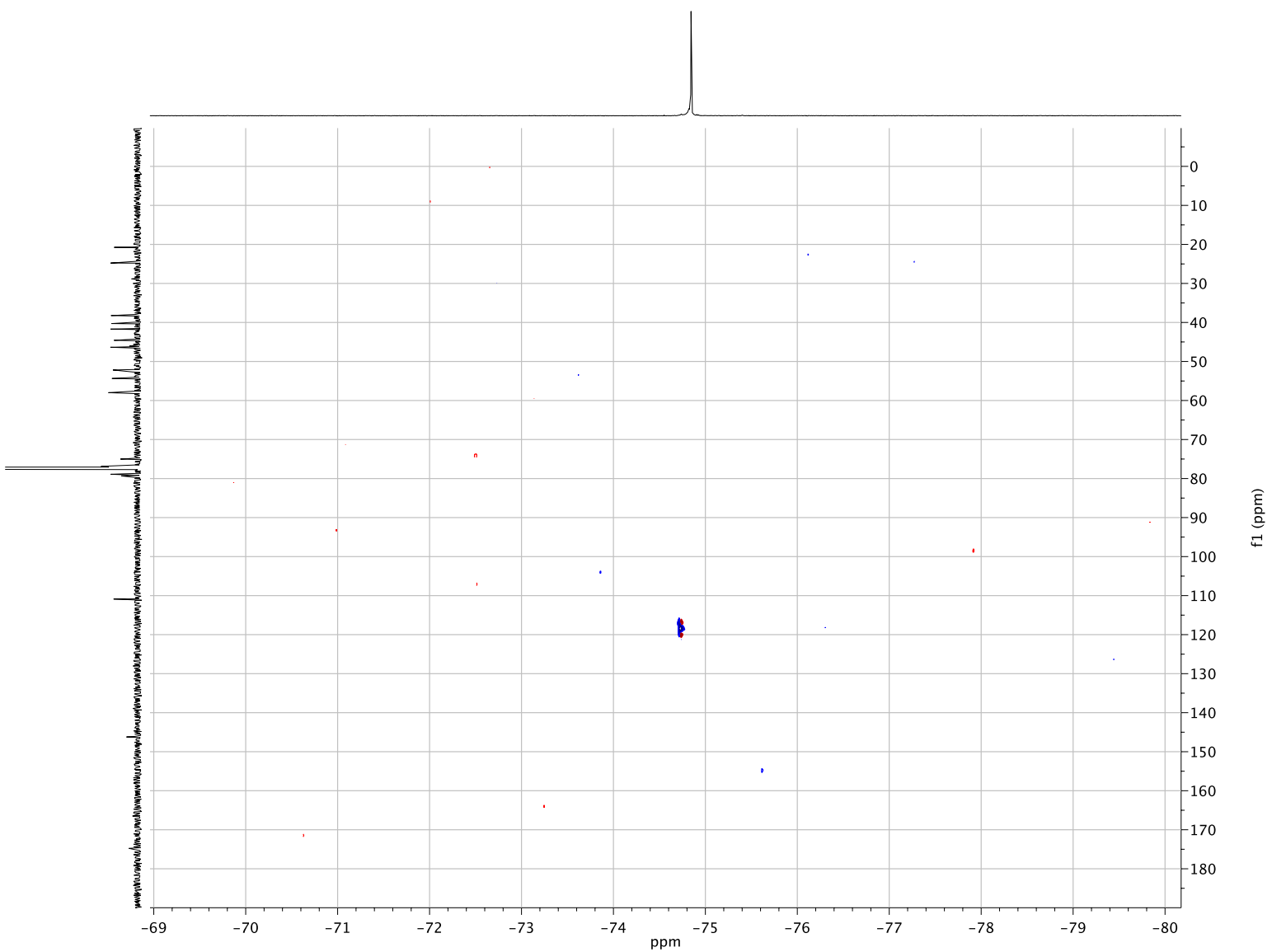


Infrared spectrum (Thin Film, NaCl) of compound **39**.

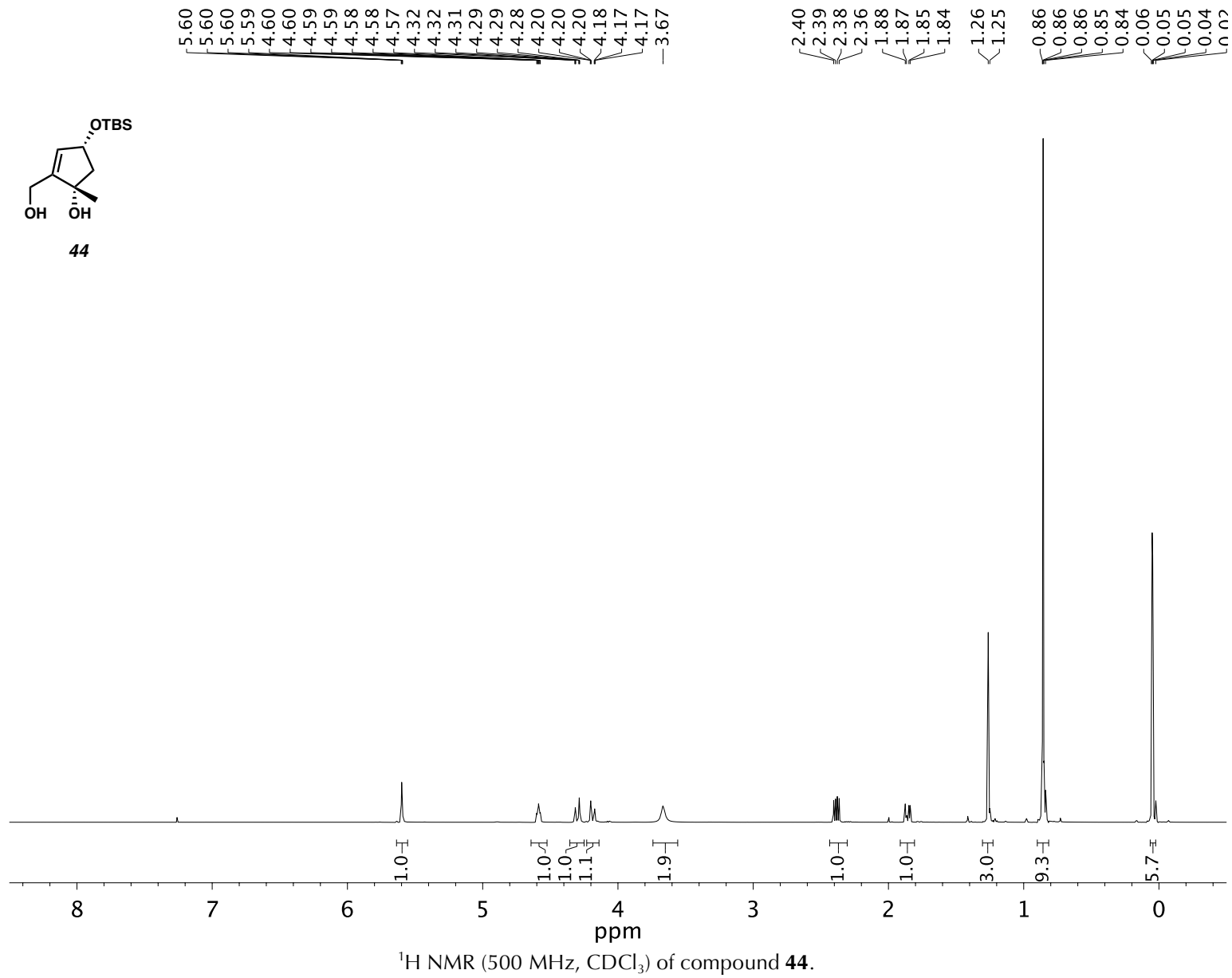


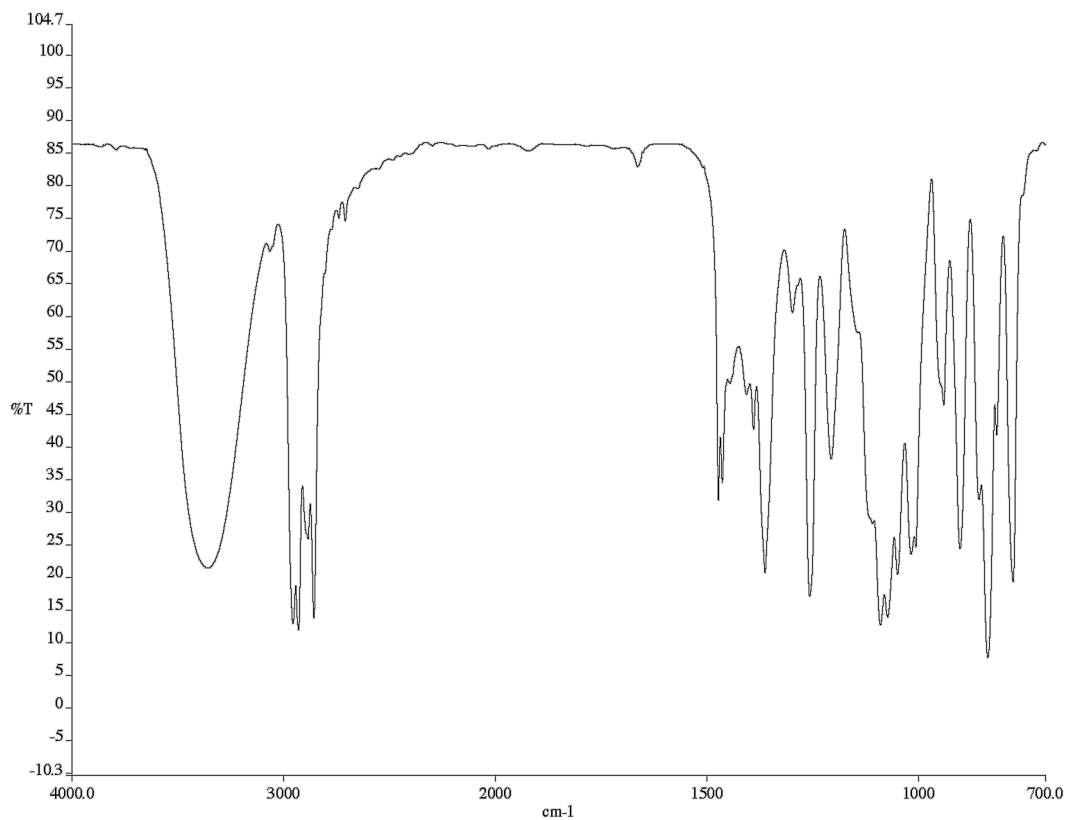
¹³C NMR (101 MHz, CDCl₃) of compound **39**.



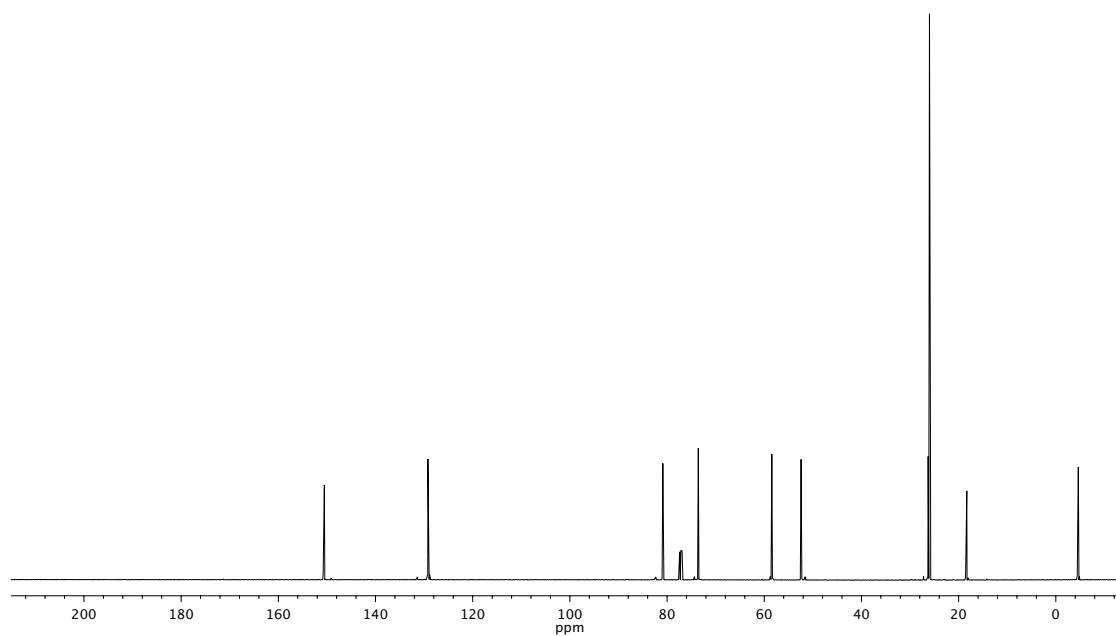


^{19}F - ^{13}C HSQC NMR (376 and 101 MHz, respectively, CDCl_3) of compound **39**.

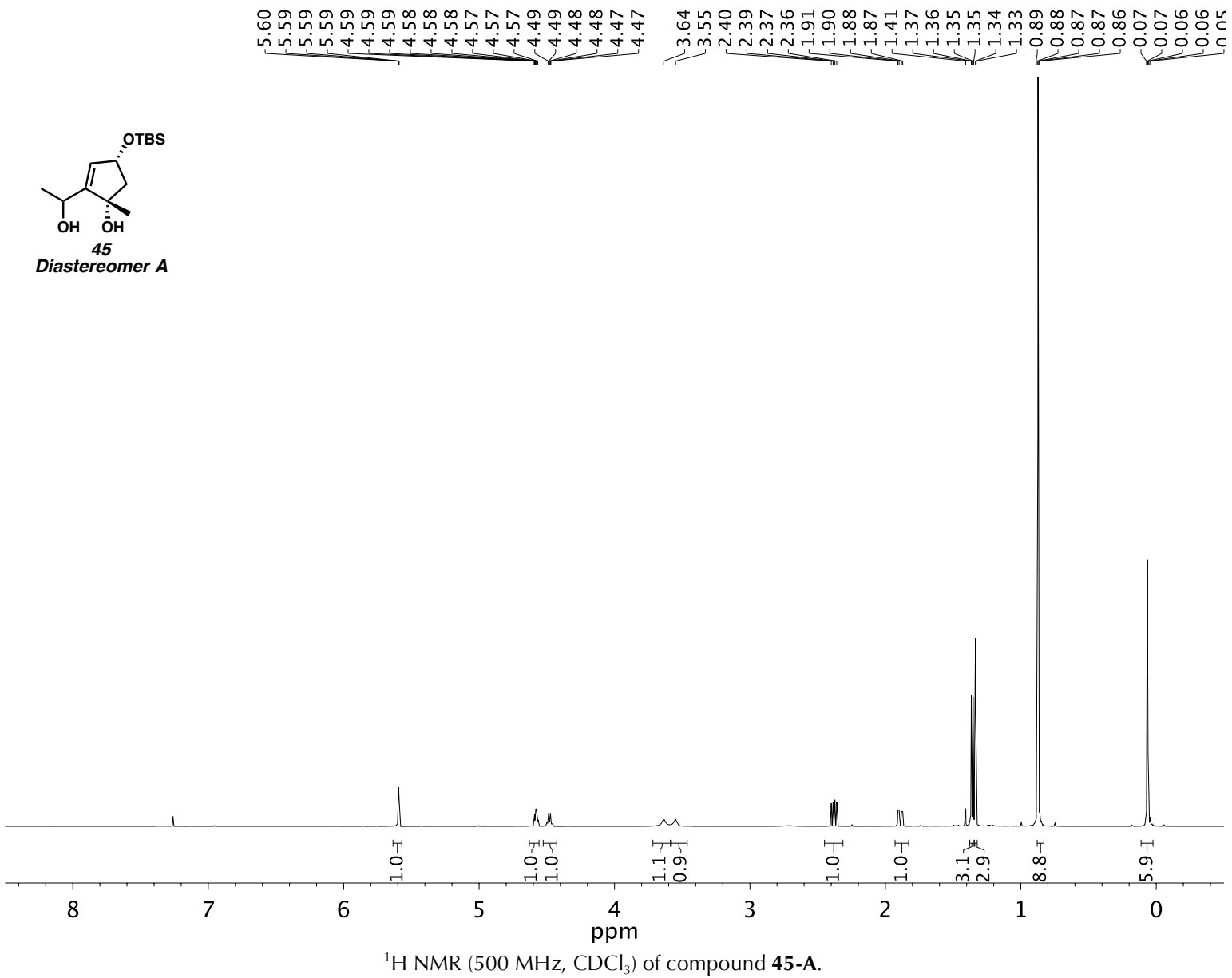


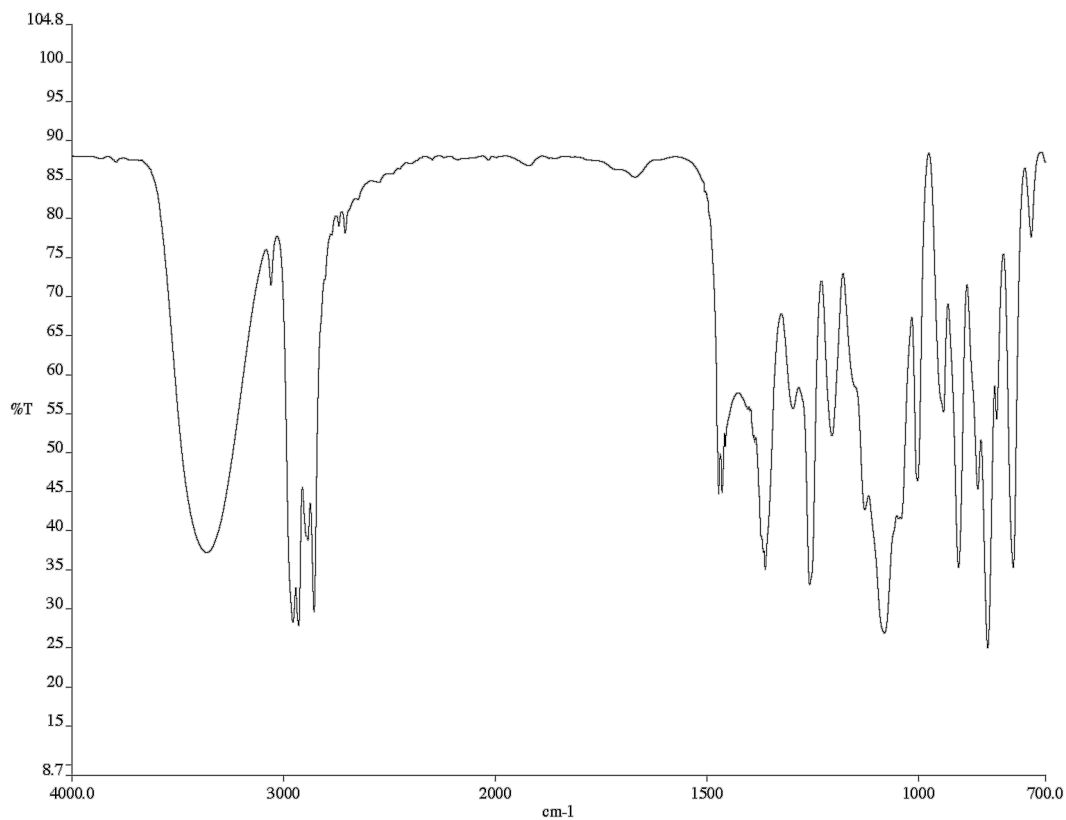


Infrared spectrum (Thin Film, NaCl) of compound **44**.

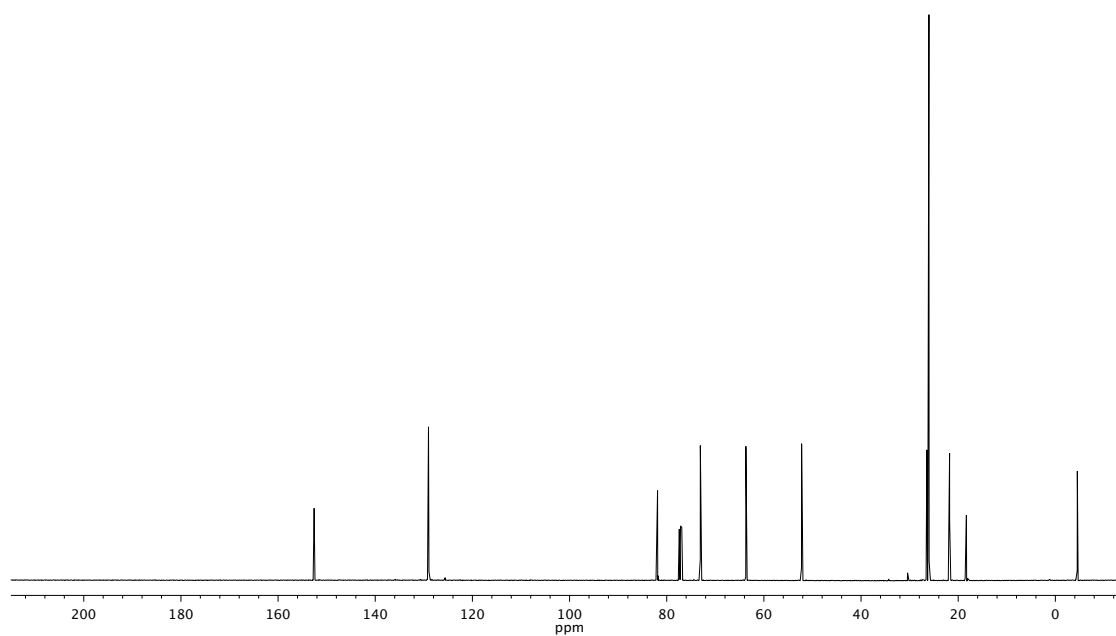


¹³C NMR (126 MHz, CDCl₃) of compound **44**.

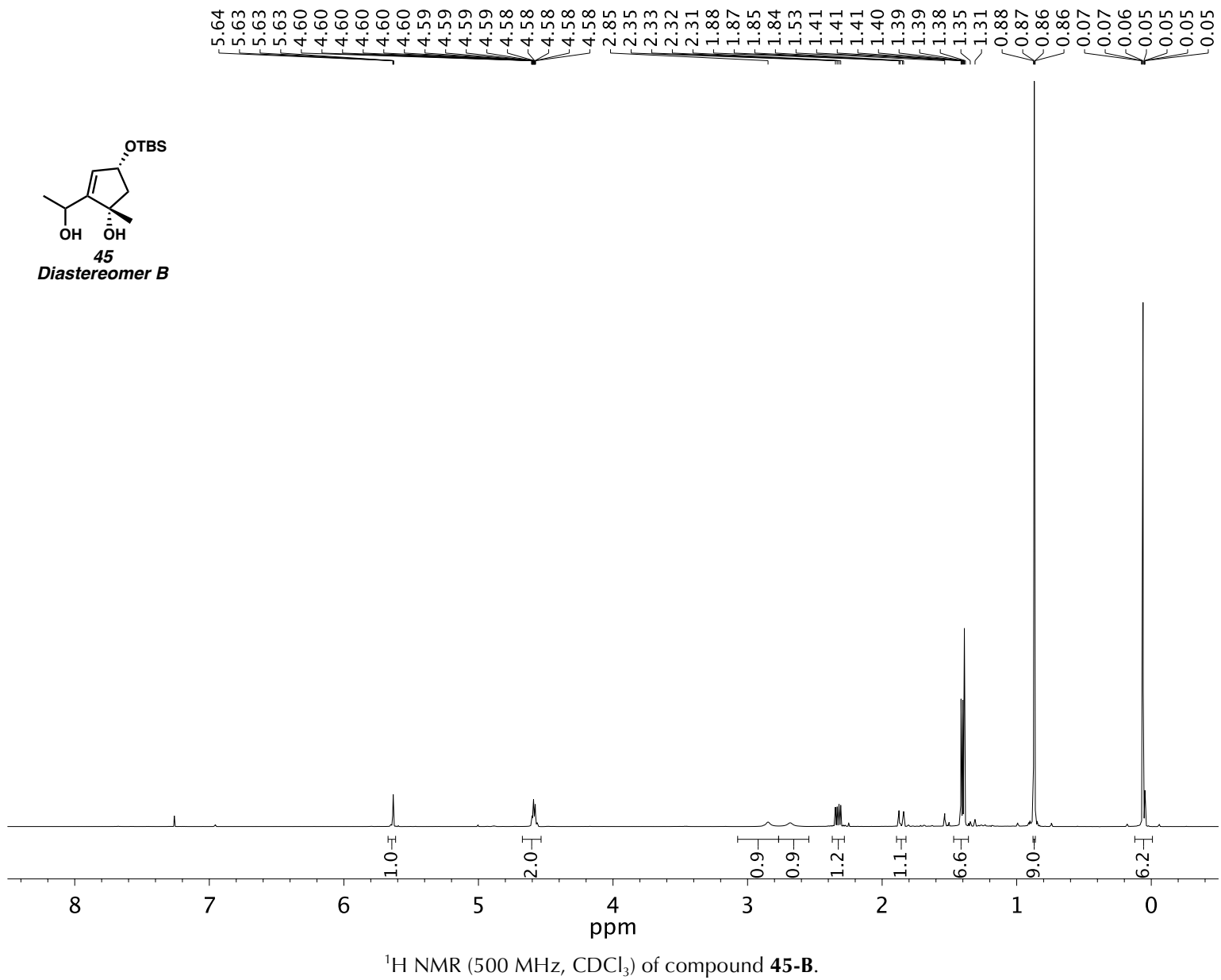


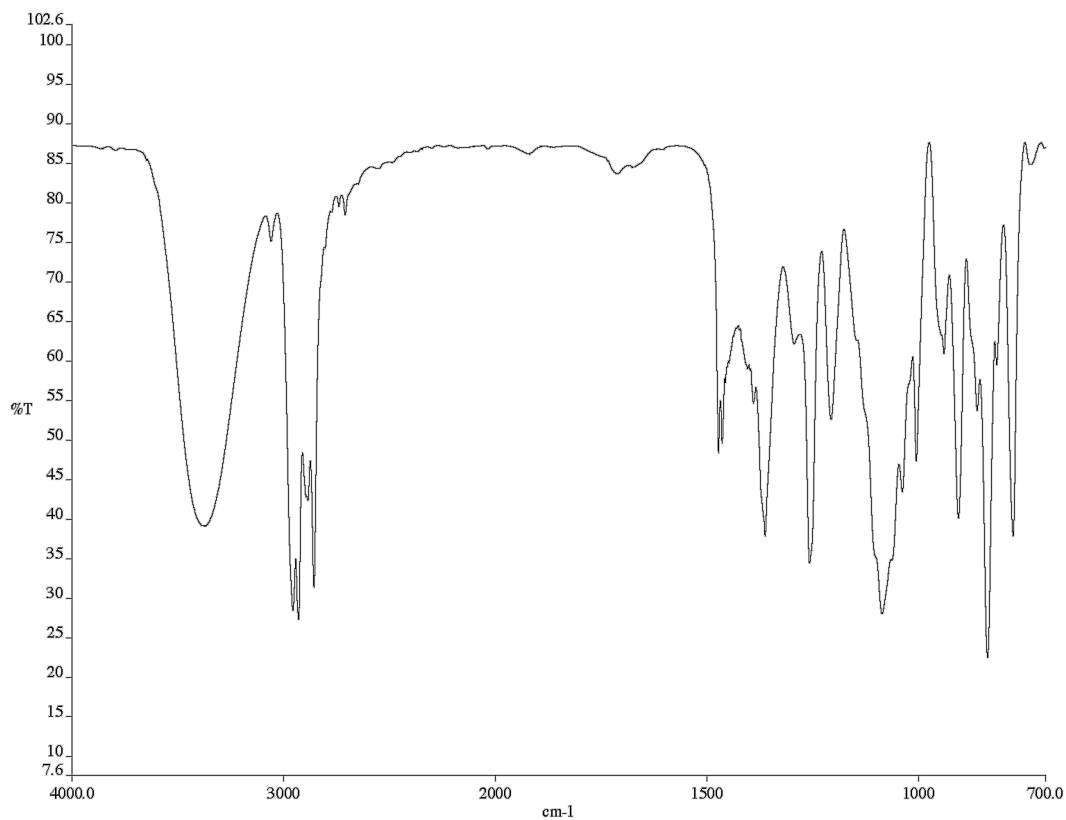


Infrared spectrum (Thin Film, NaCl) of compound **45-A**.

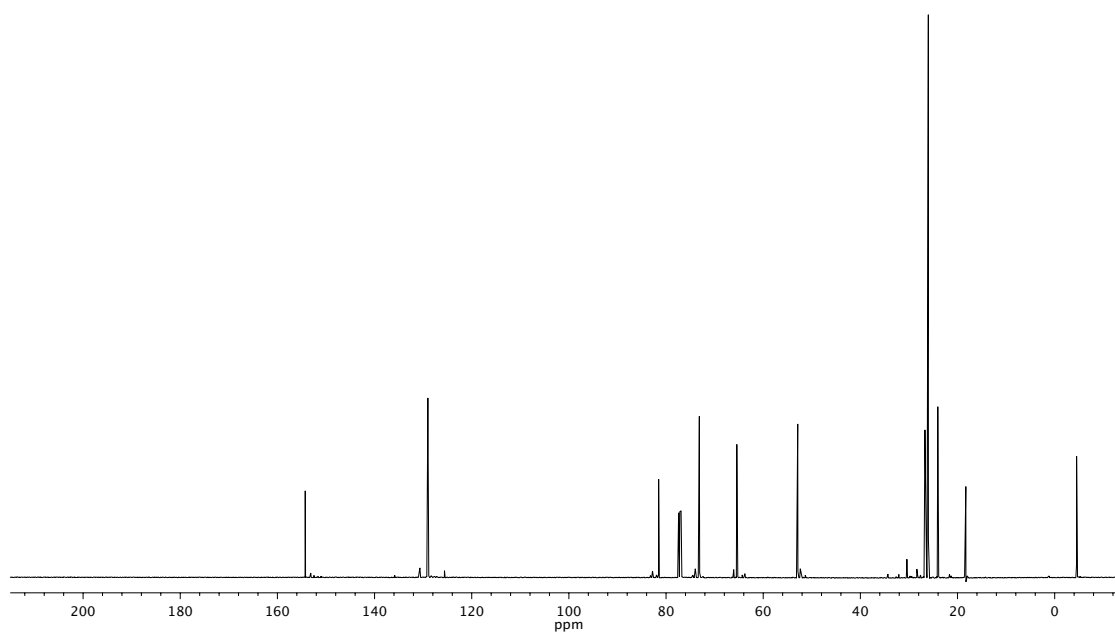


¹³C NMR (126 MHz, CDCl₃) of compound **45-A**.

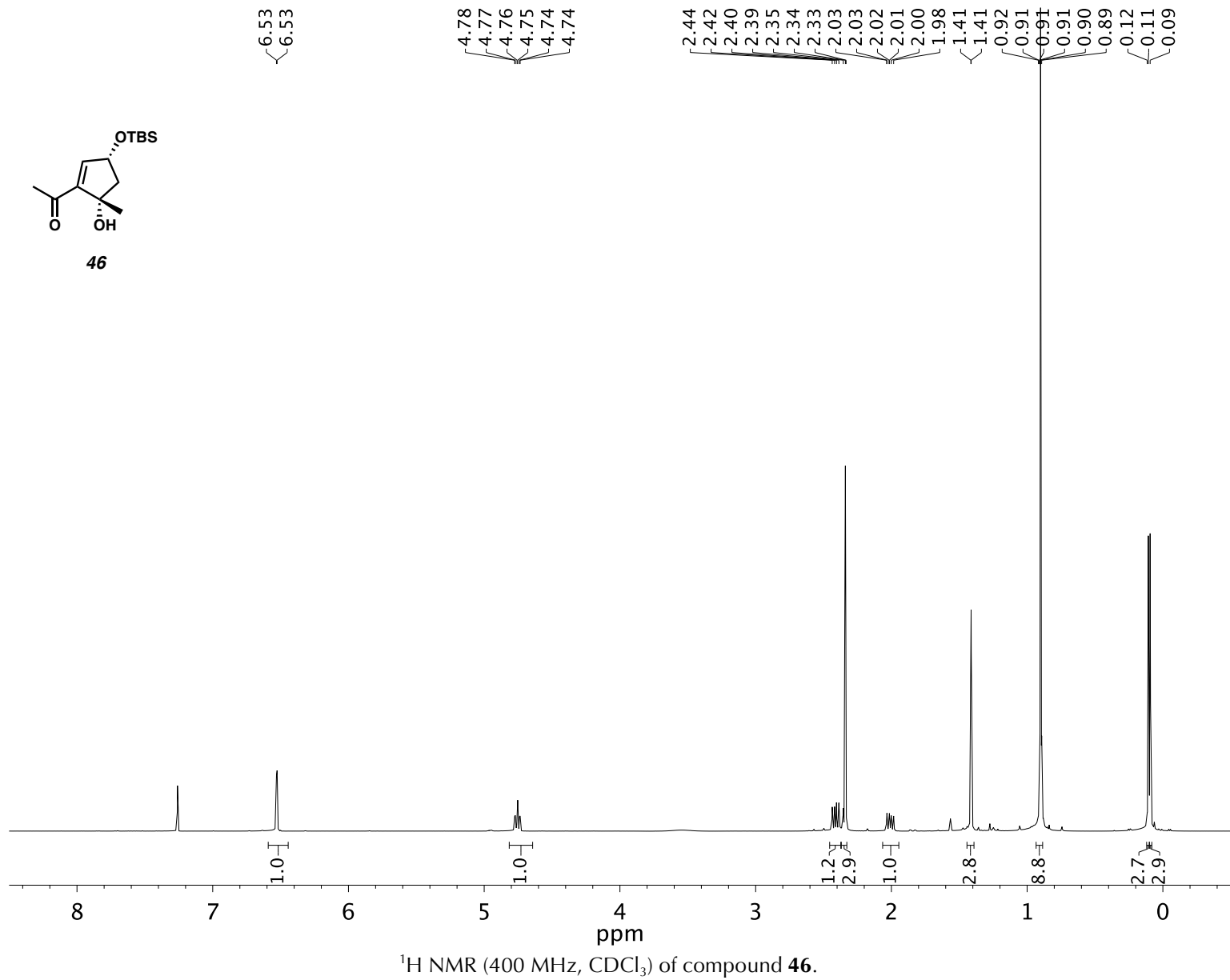


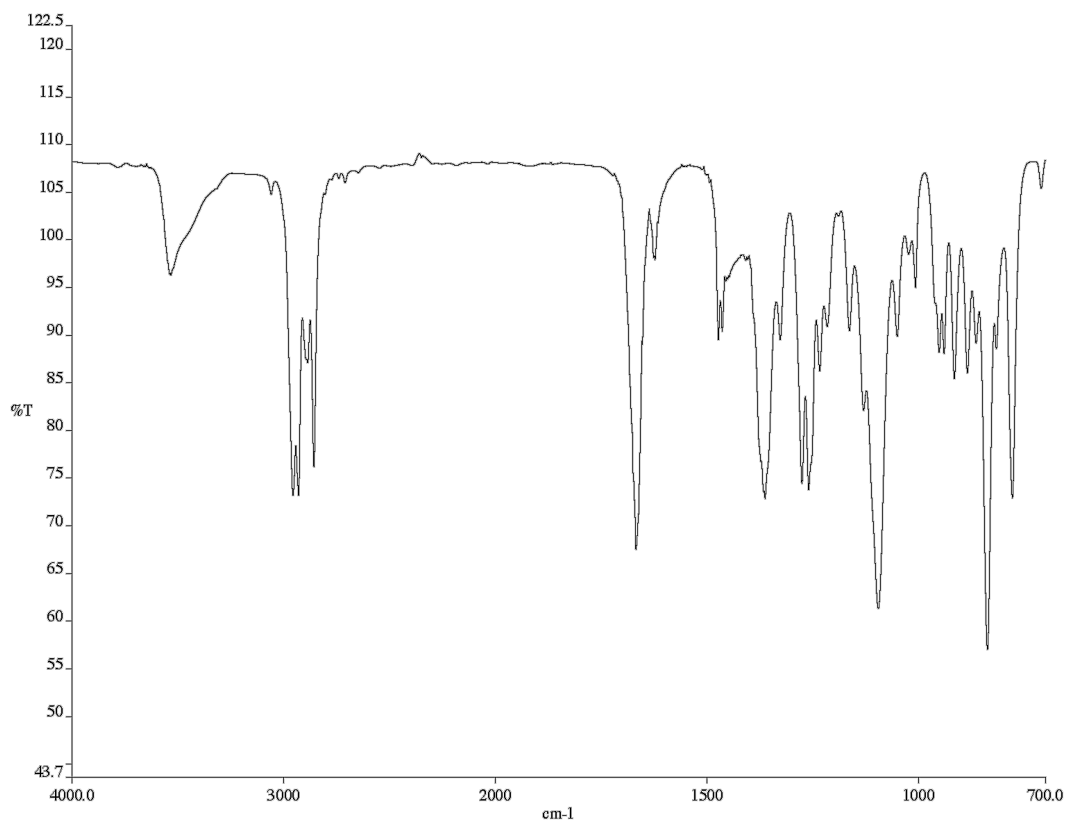


Infrared spectrum (Thin Film, NaCl) of compound **45-B**.

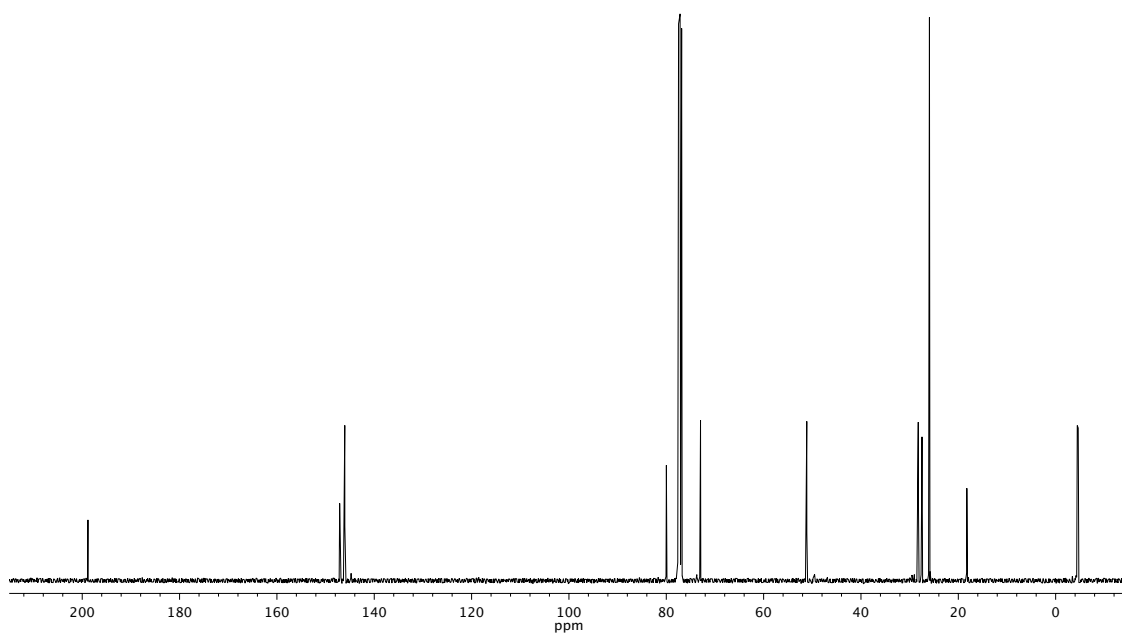


¹³C NMR (126 MHz, CDCl₃) of compound **45-B**.

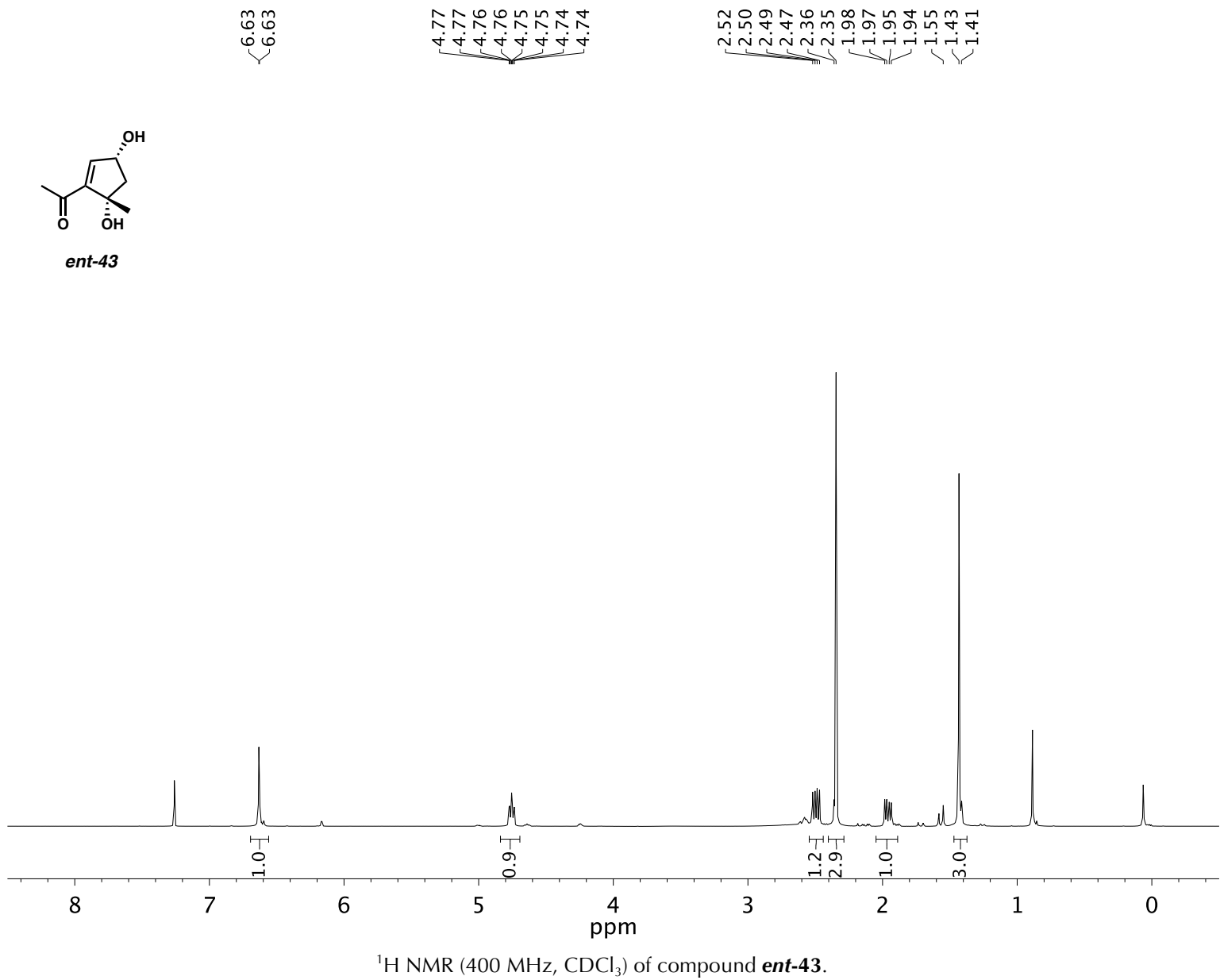


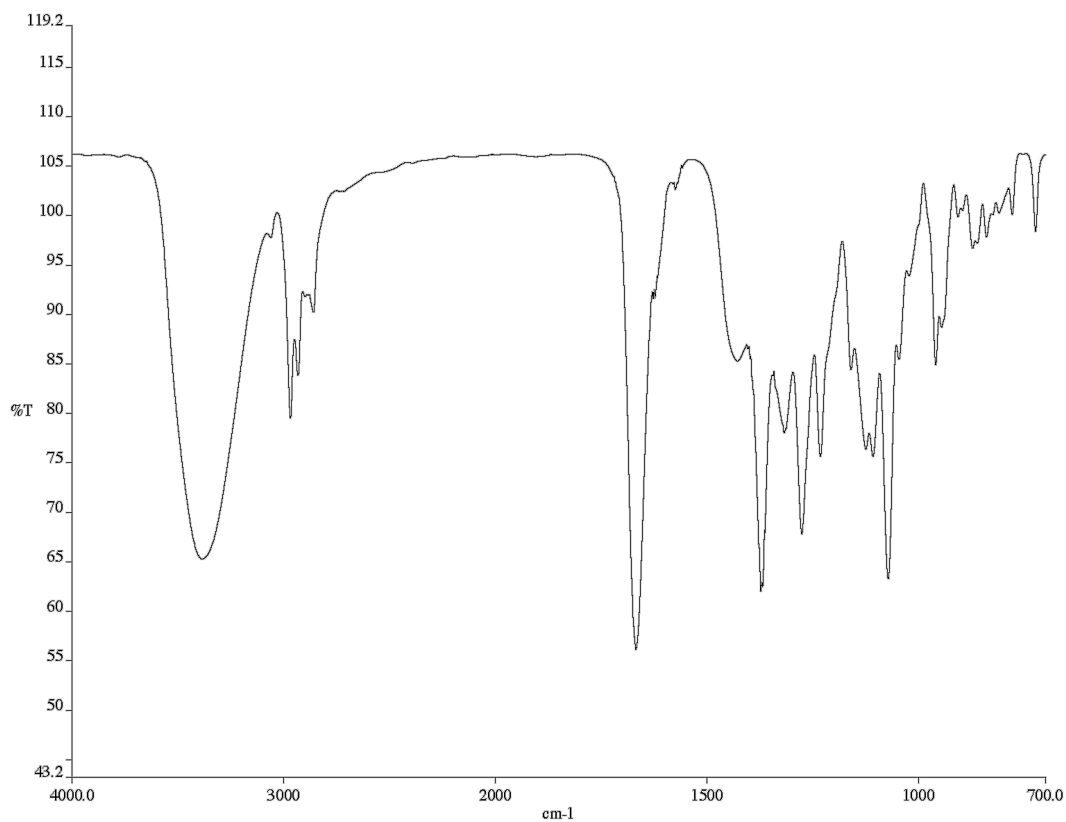


Infrared spectrum (Thin Film, NaCl) of compound **46**.

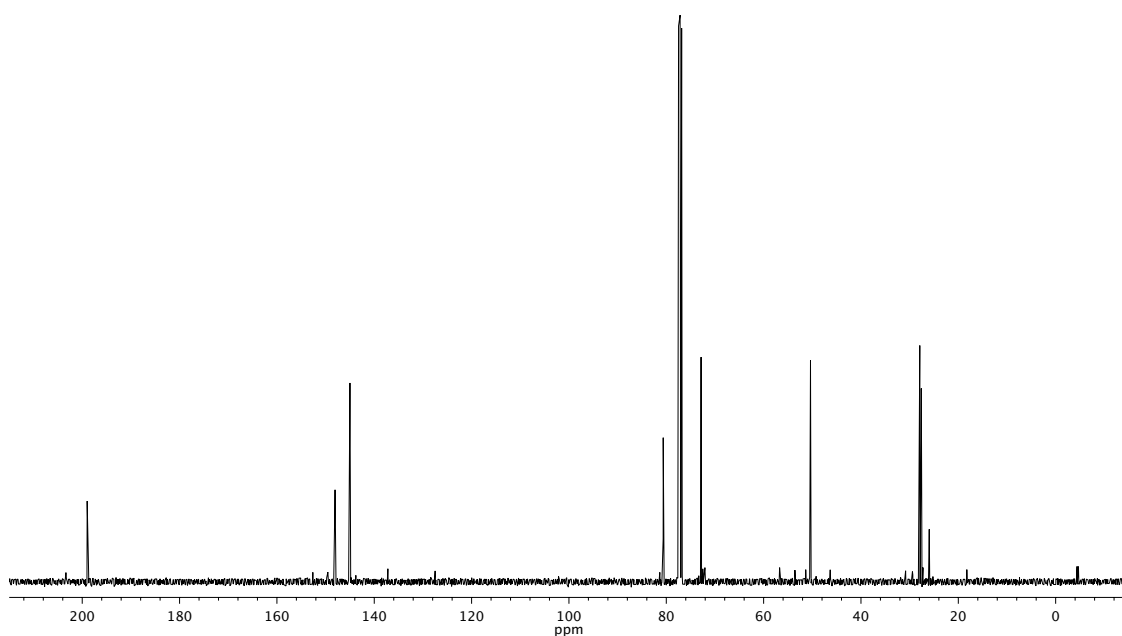


¹³C NMR (101 MHz, CDCl₃) of compound **46**.

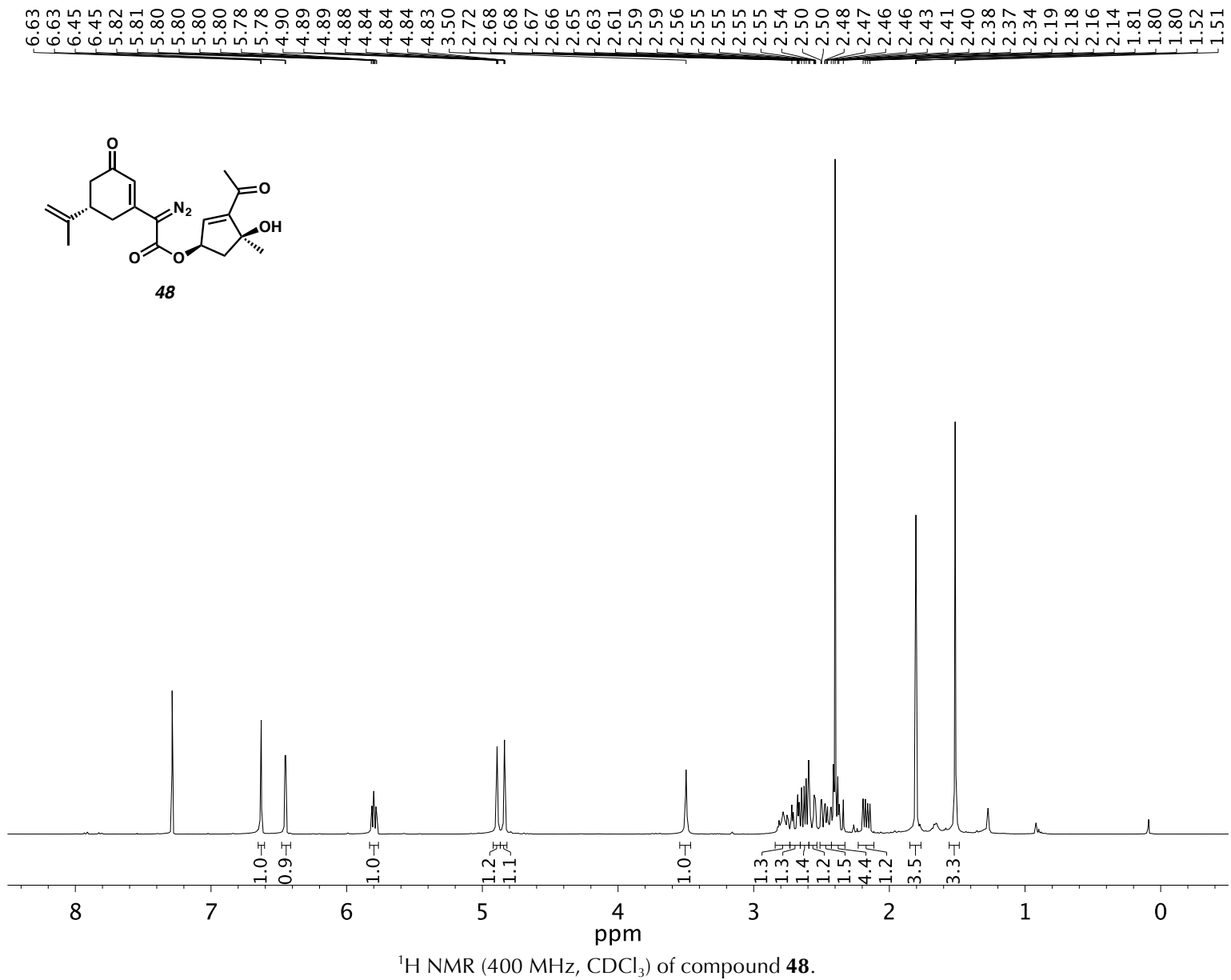


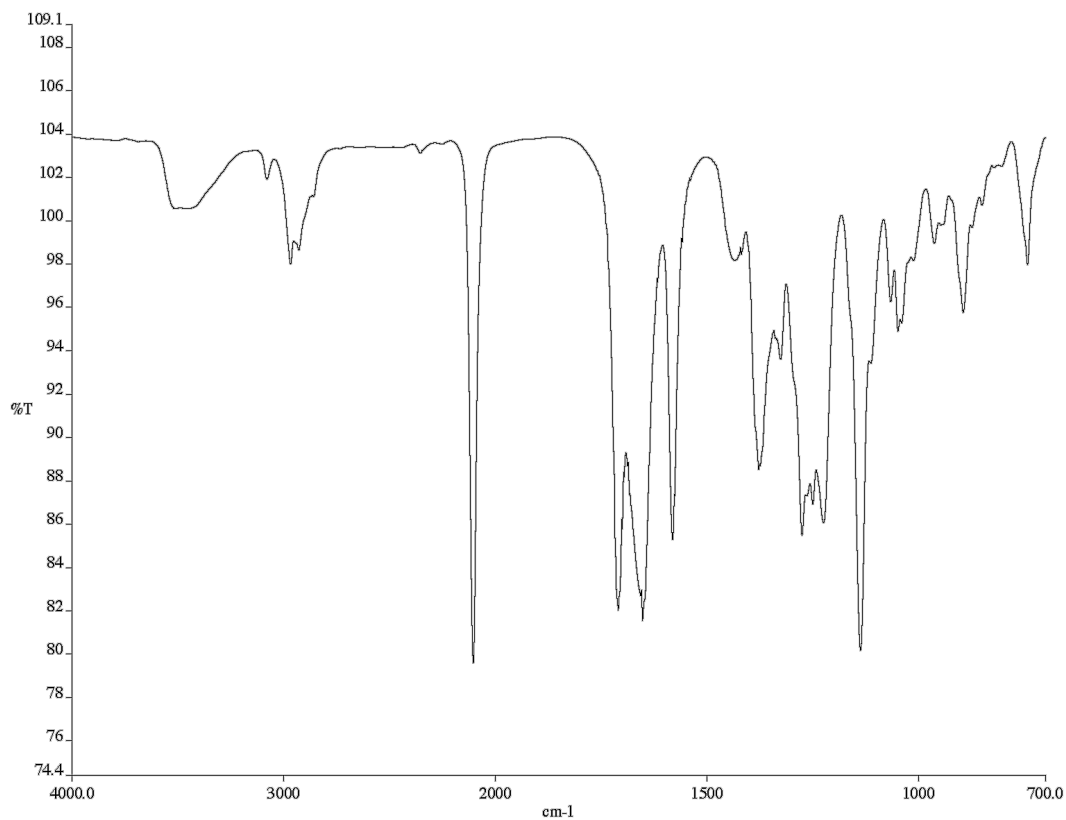


Infrared spectrum (Thin Film, NaCl) of compound **ent-43**.

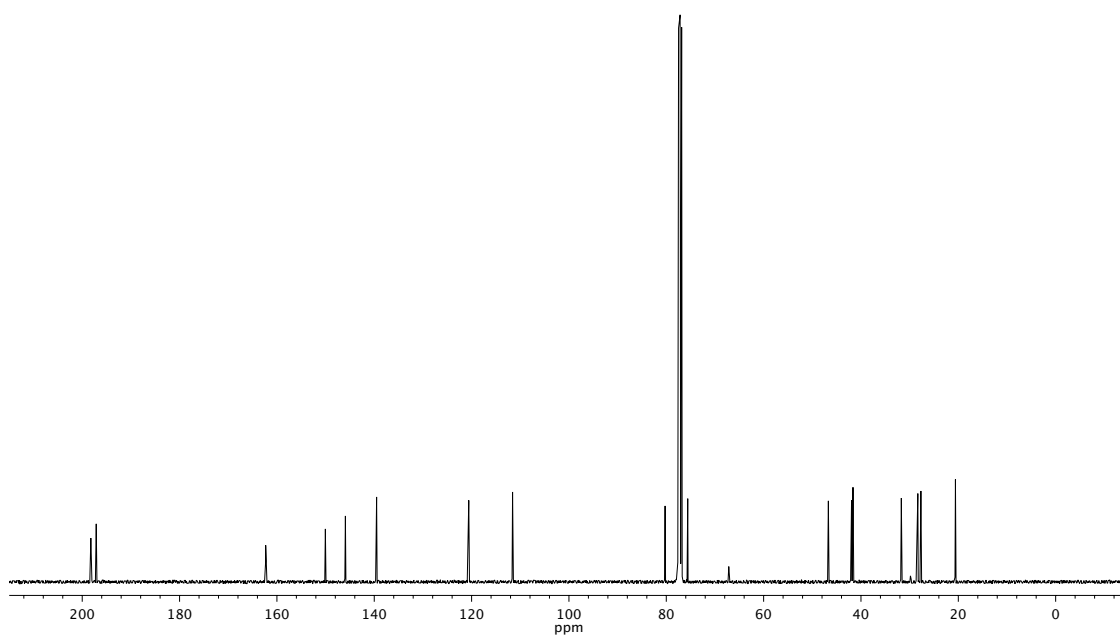


¹³C NMR (101 MHz, CDCl₃) of compound **ent-43**.

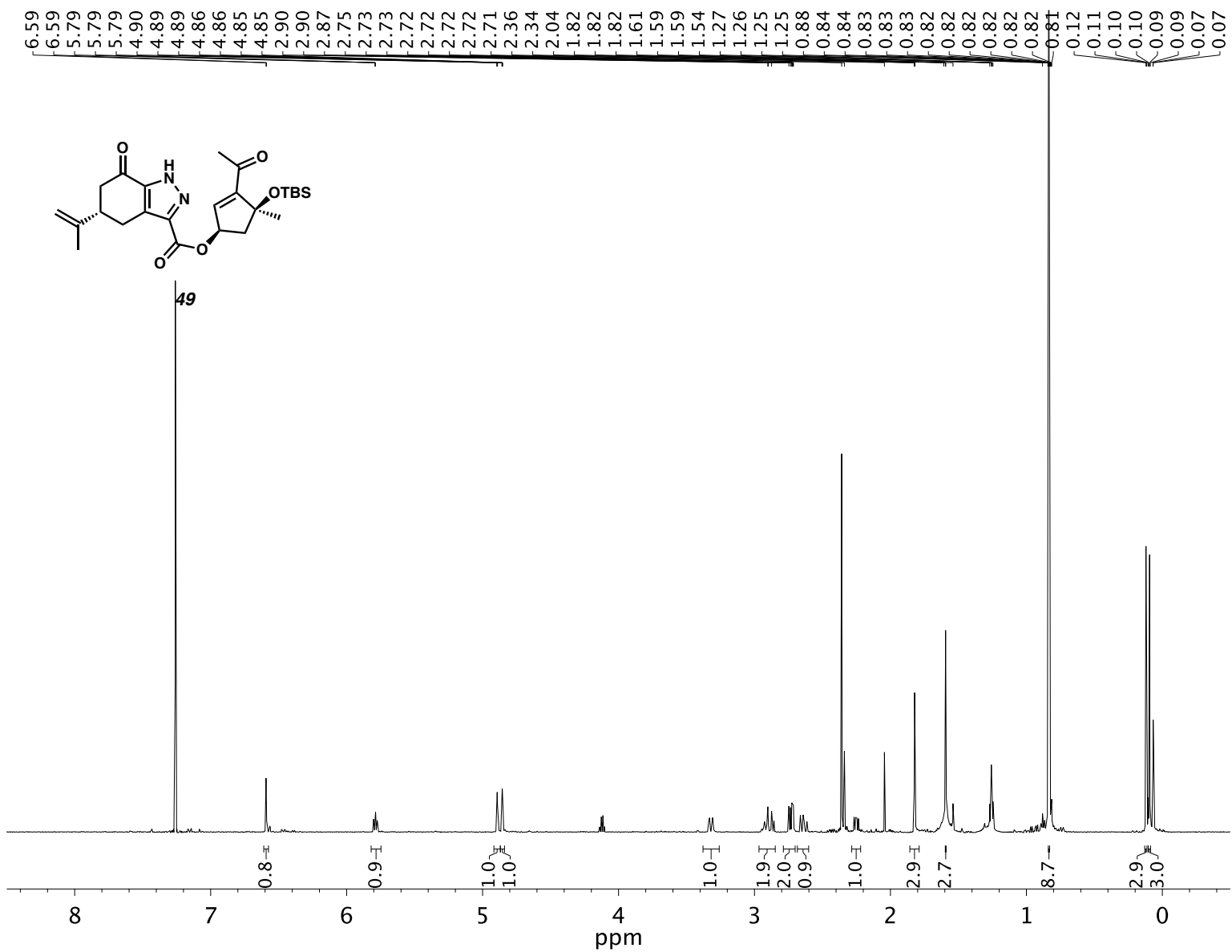


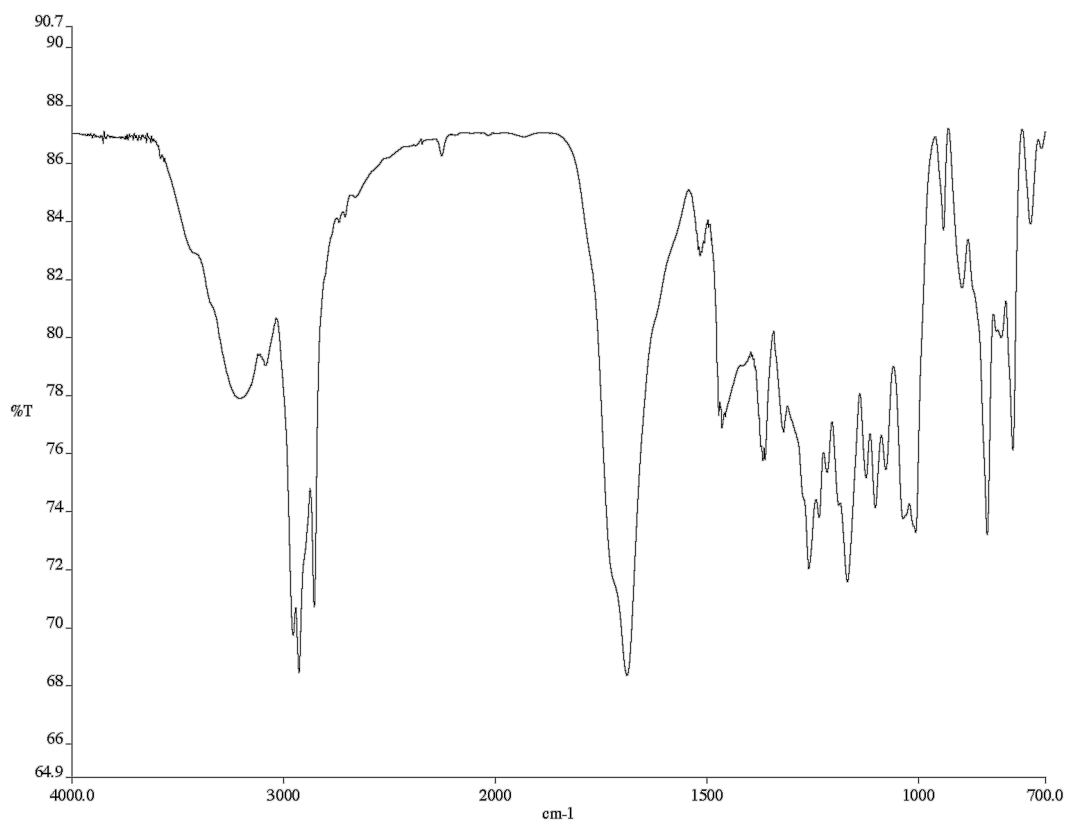


Infrared spectrum (Thin Film, NaCl) of compound **48**.

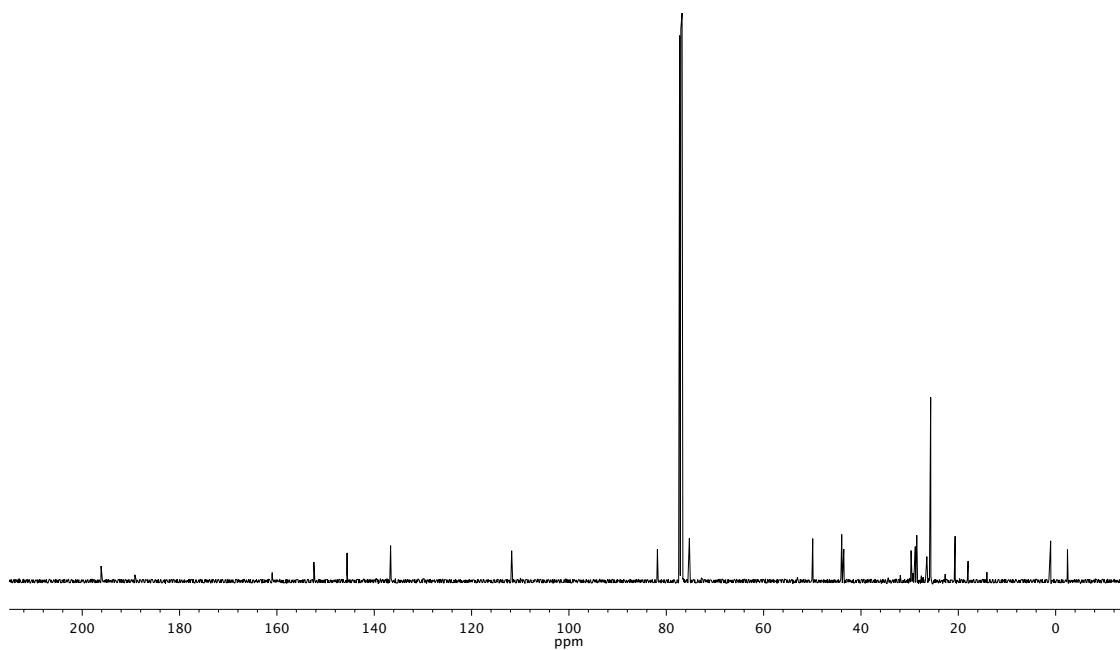


¹³C NMR (101 MHz, CDCl₃) of compound **48**.

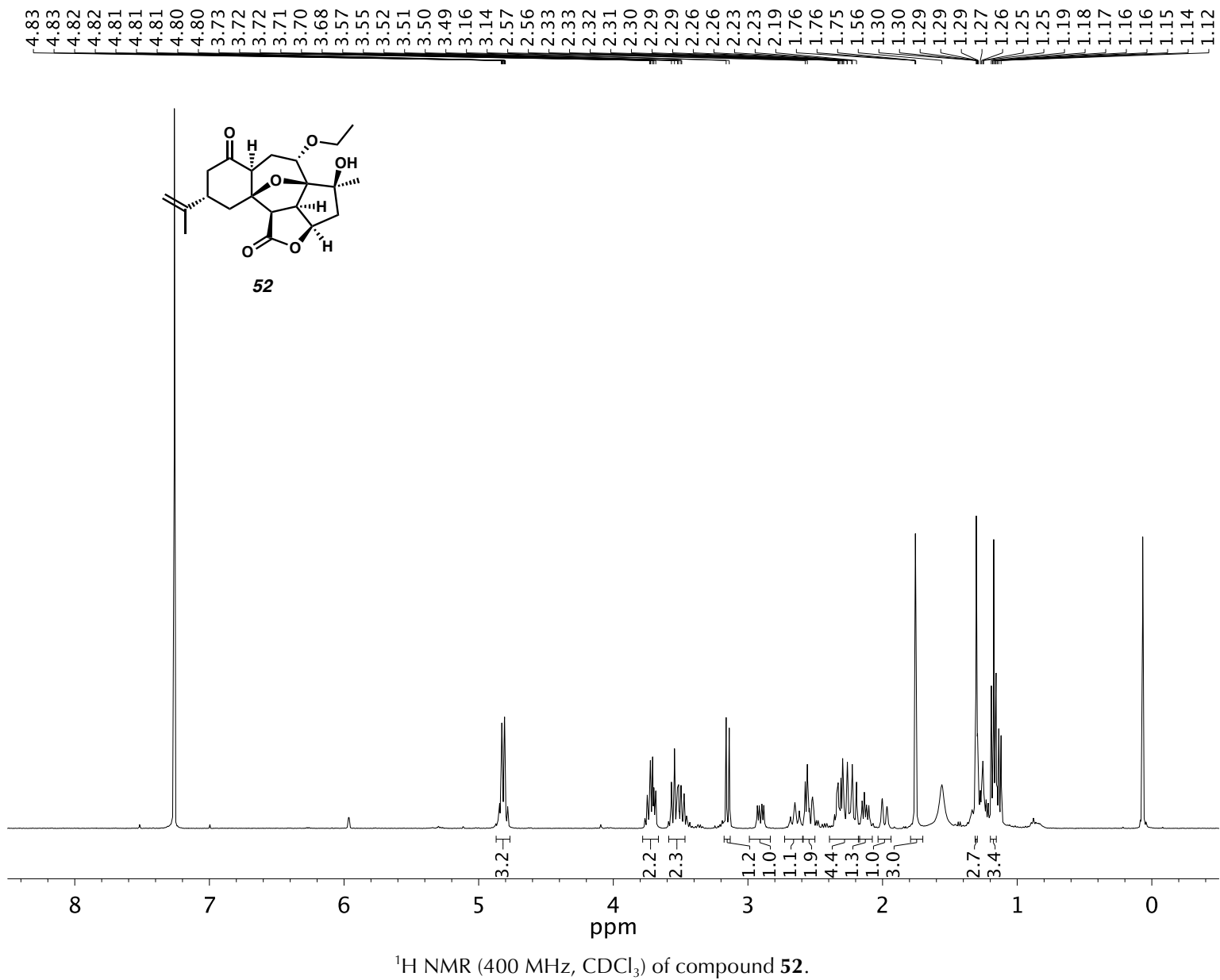


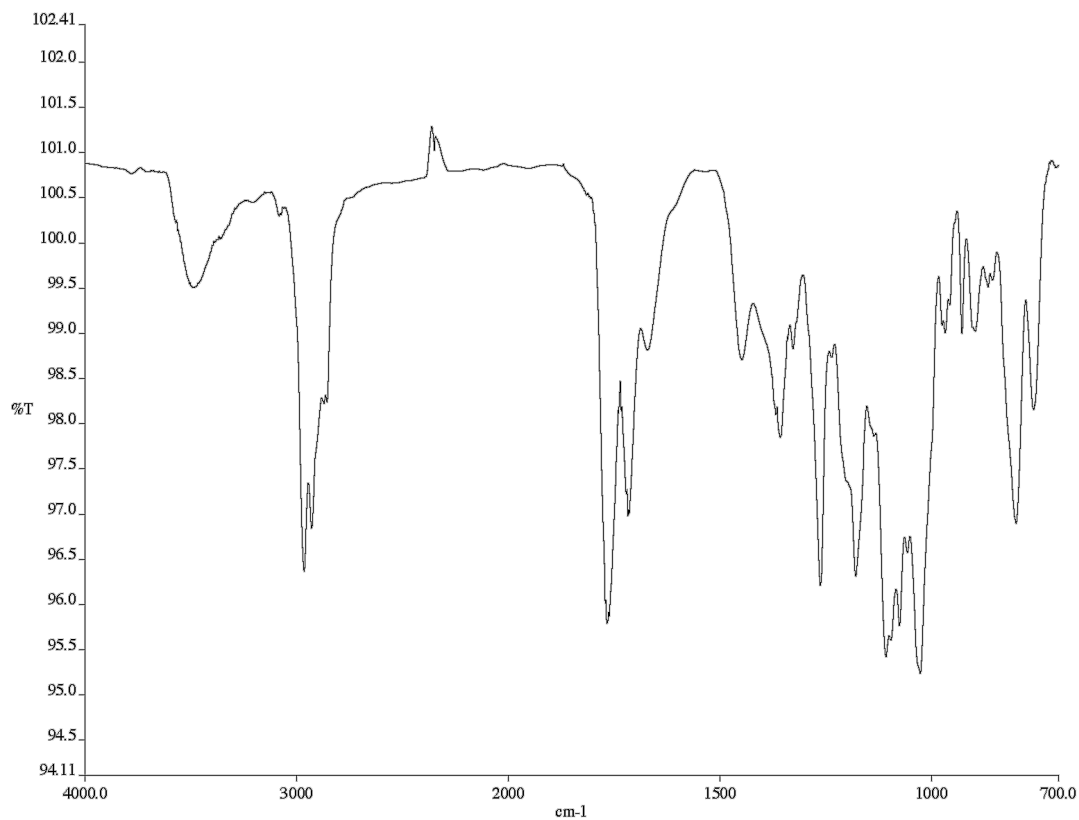


Infrared spectrum (Thin Film, NaCl) of compound **49**.

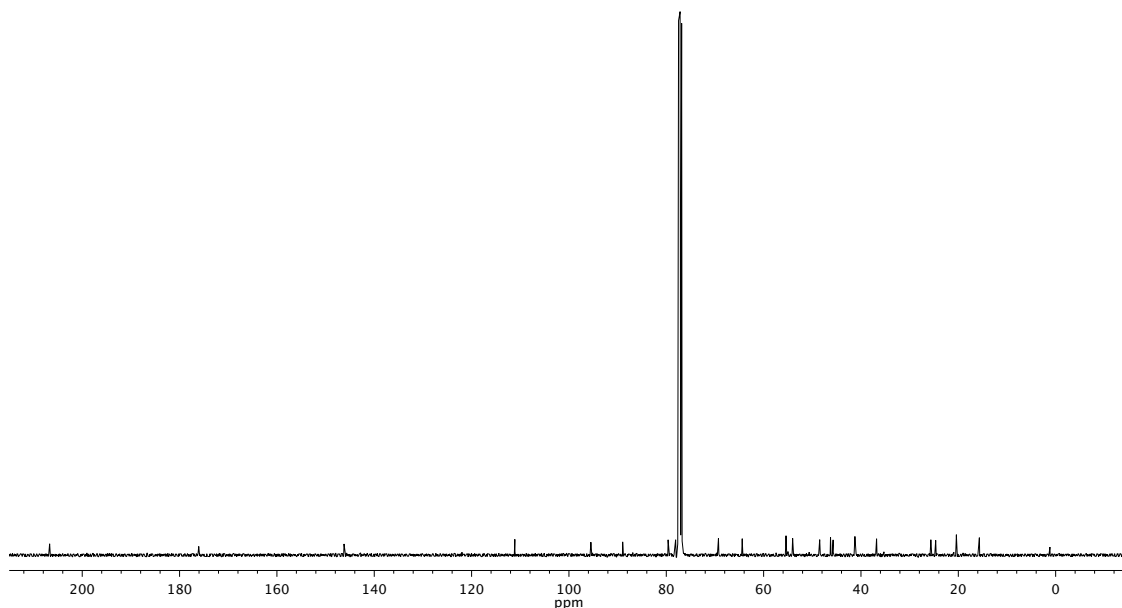


¹³C NMR (126 MHz, CDCl₃) of compound **49**.

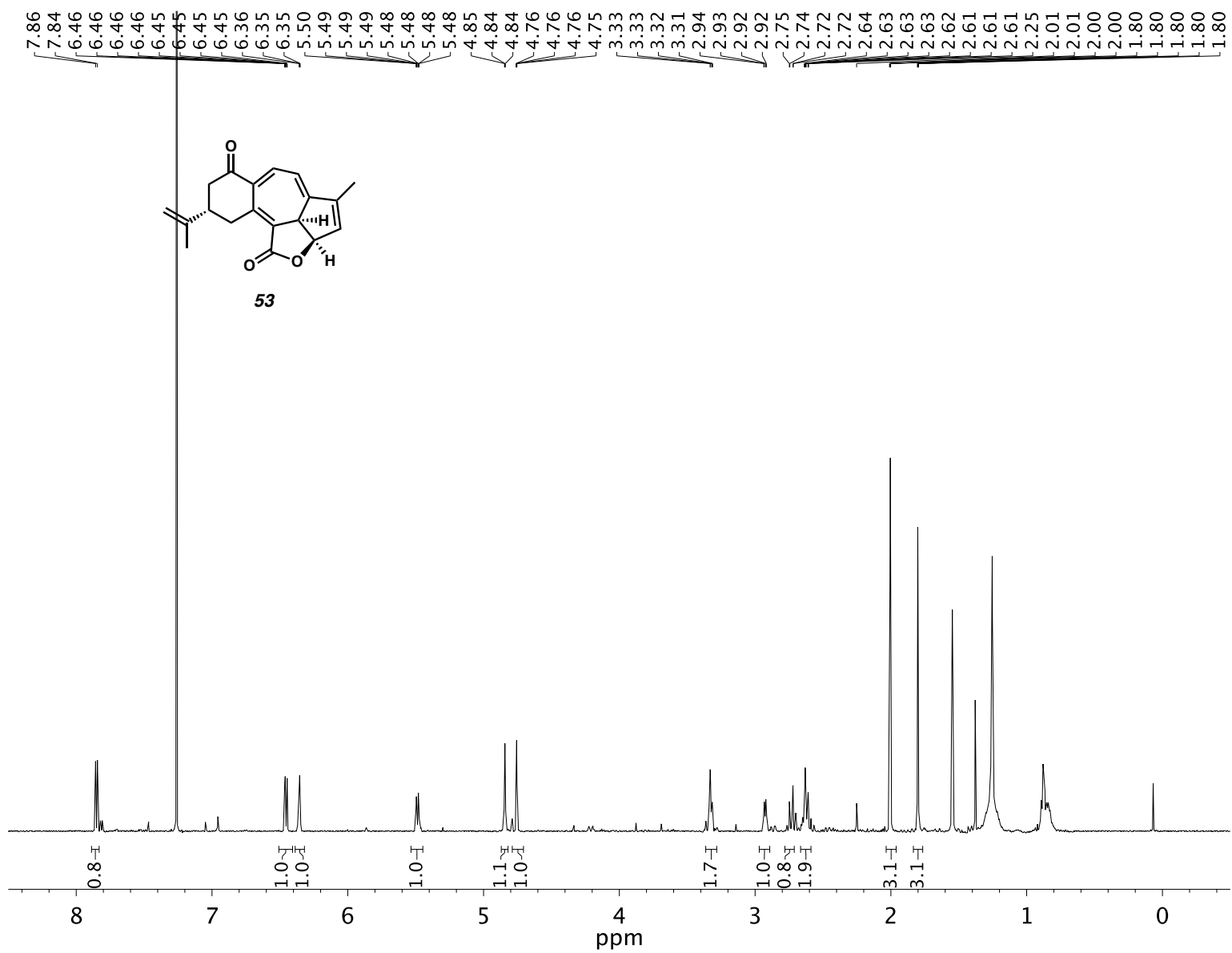


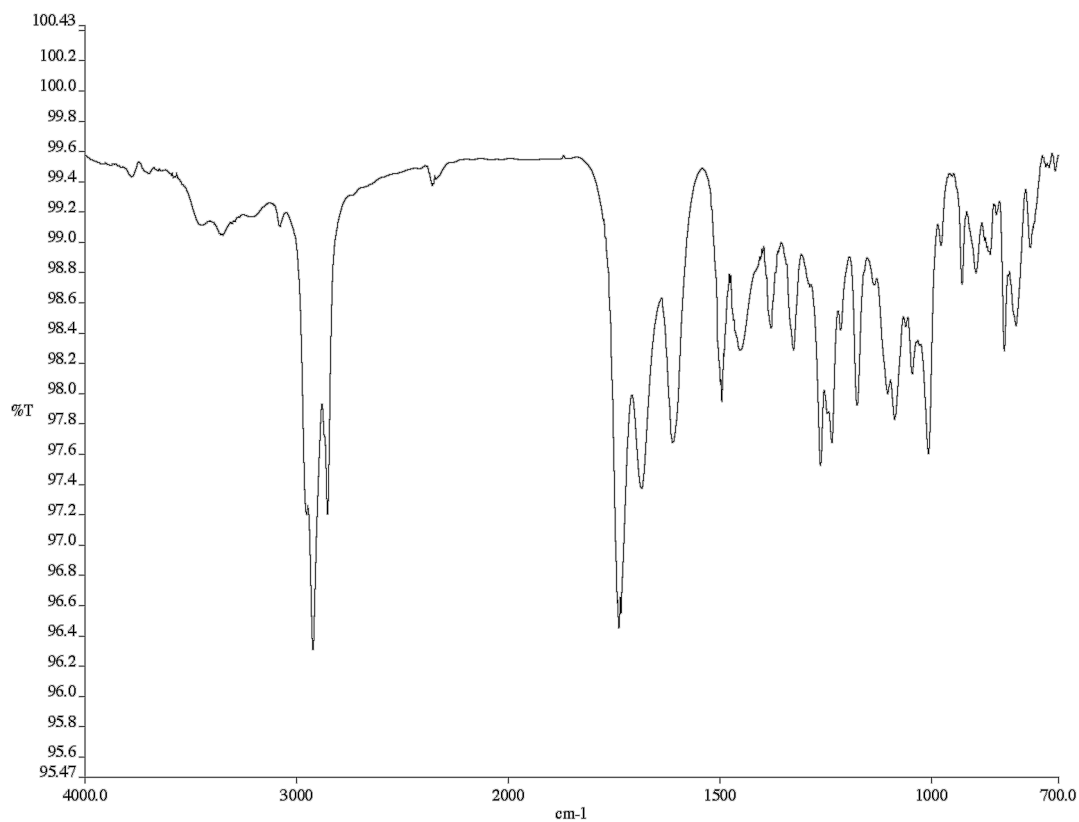


Infrared spectrum (Thin Film, NaCl) of compound **52**.

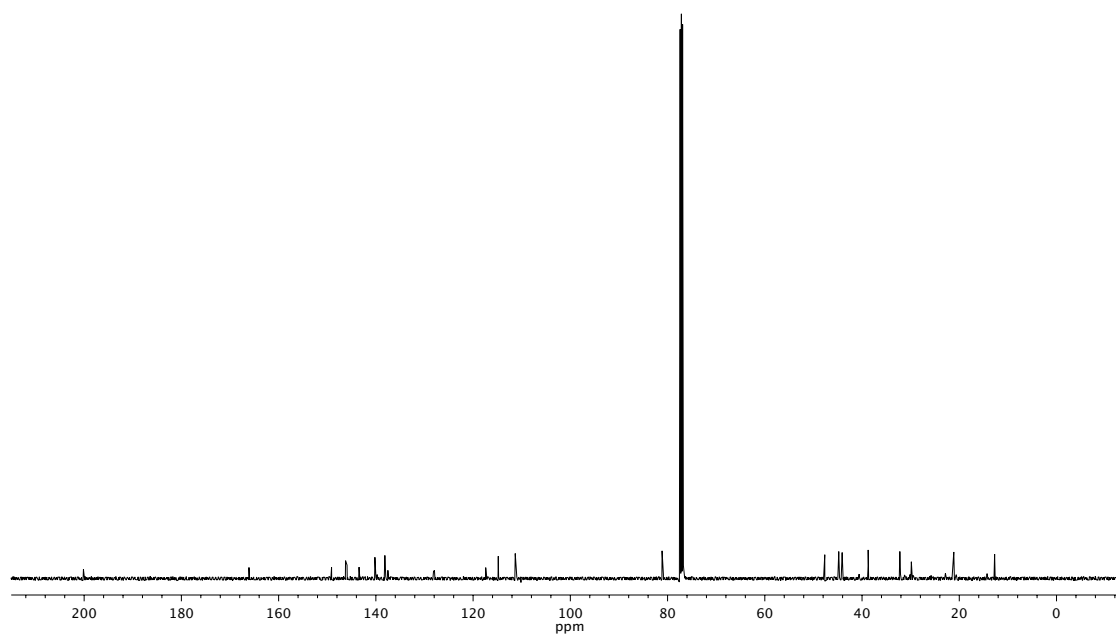


¹³C NMR (101 MHz, CDCl₃) of compound **52**.

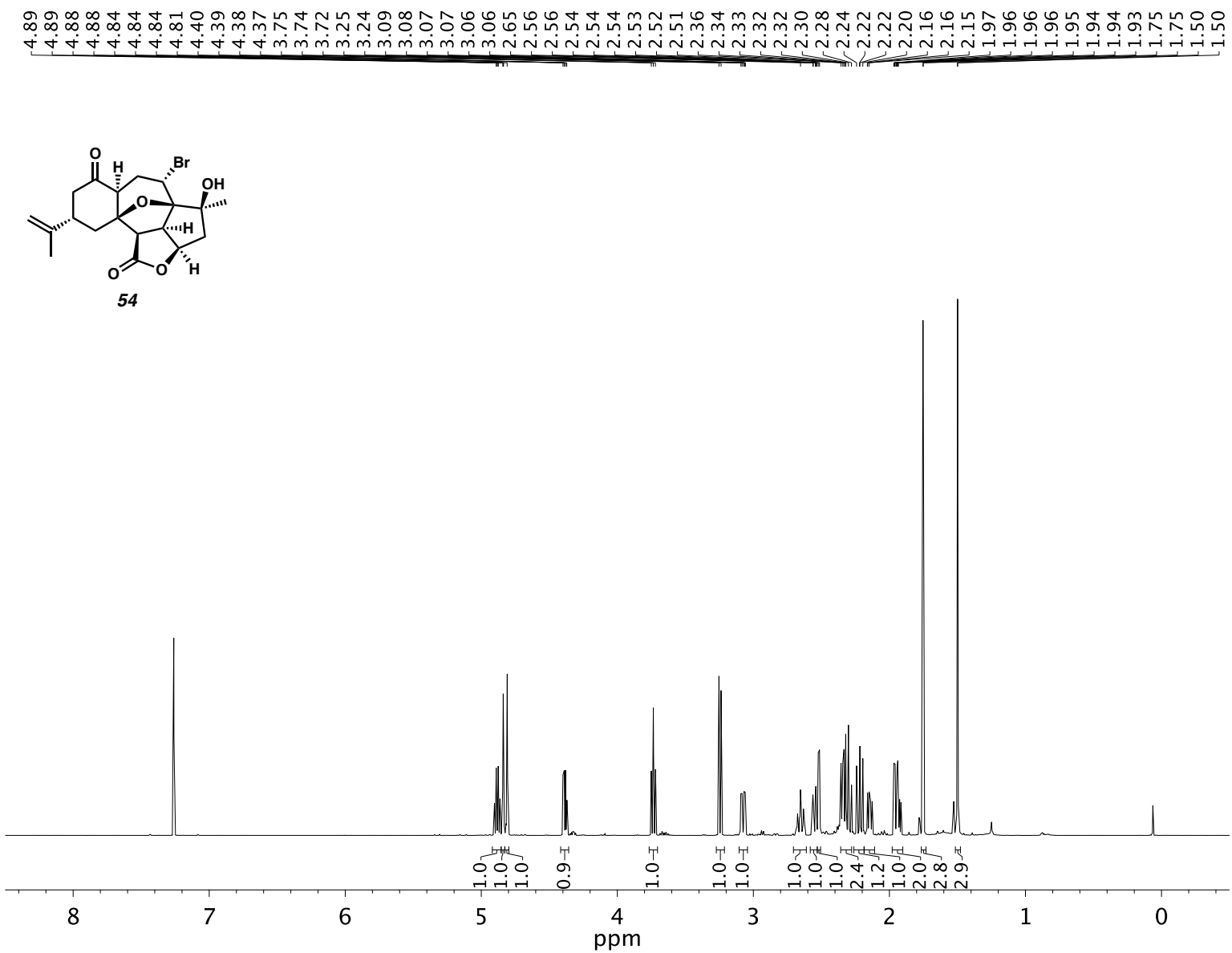
 ^1H NMR (500 MHz, CDCl_3) of compound 53.

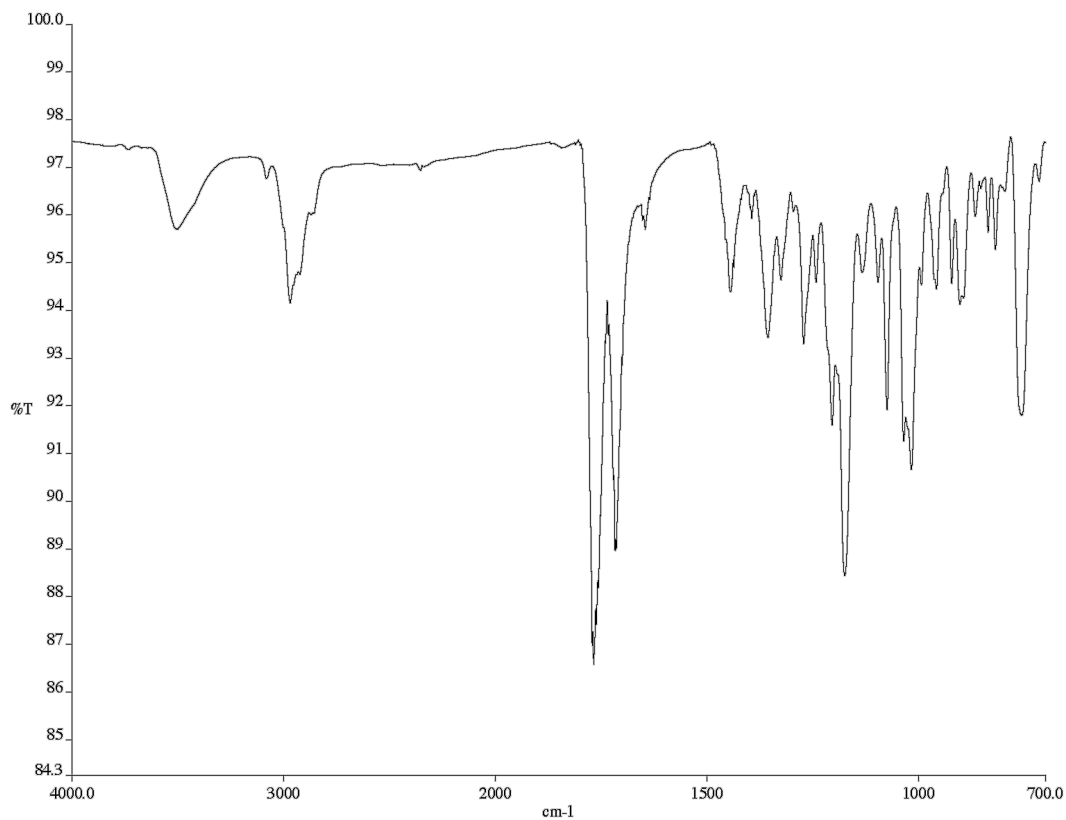


Infrared spectrum (Thin Film, NaCl) of compound **53**.

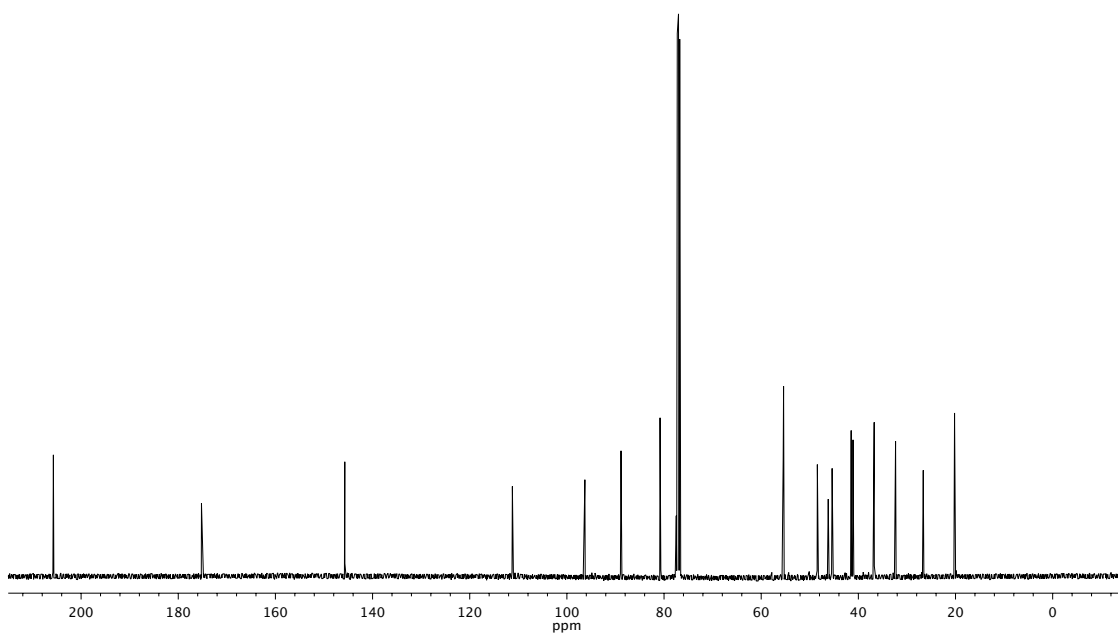


¹³C NMR (126 MHz, CDCl₃) of compound **53**.

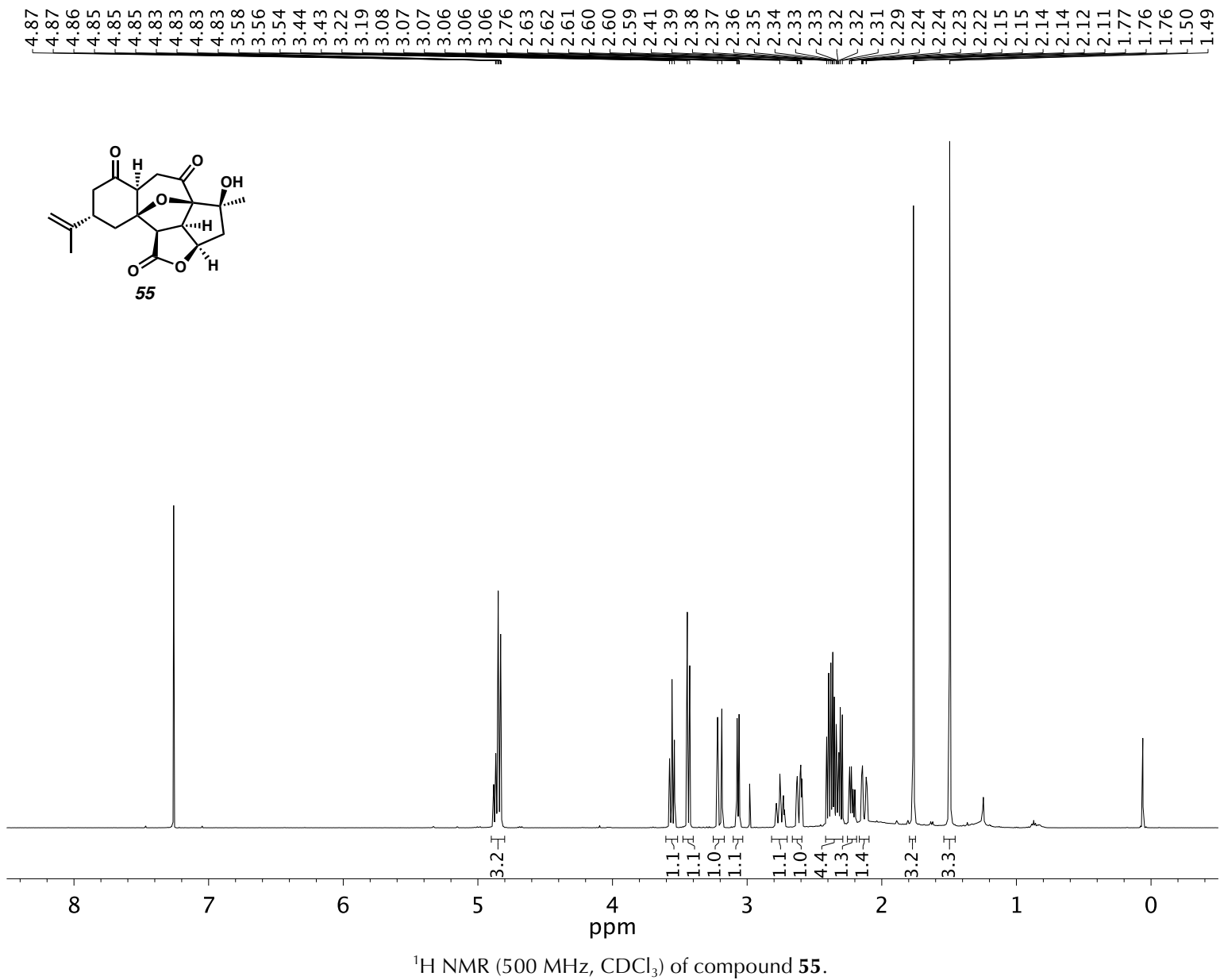


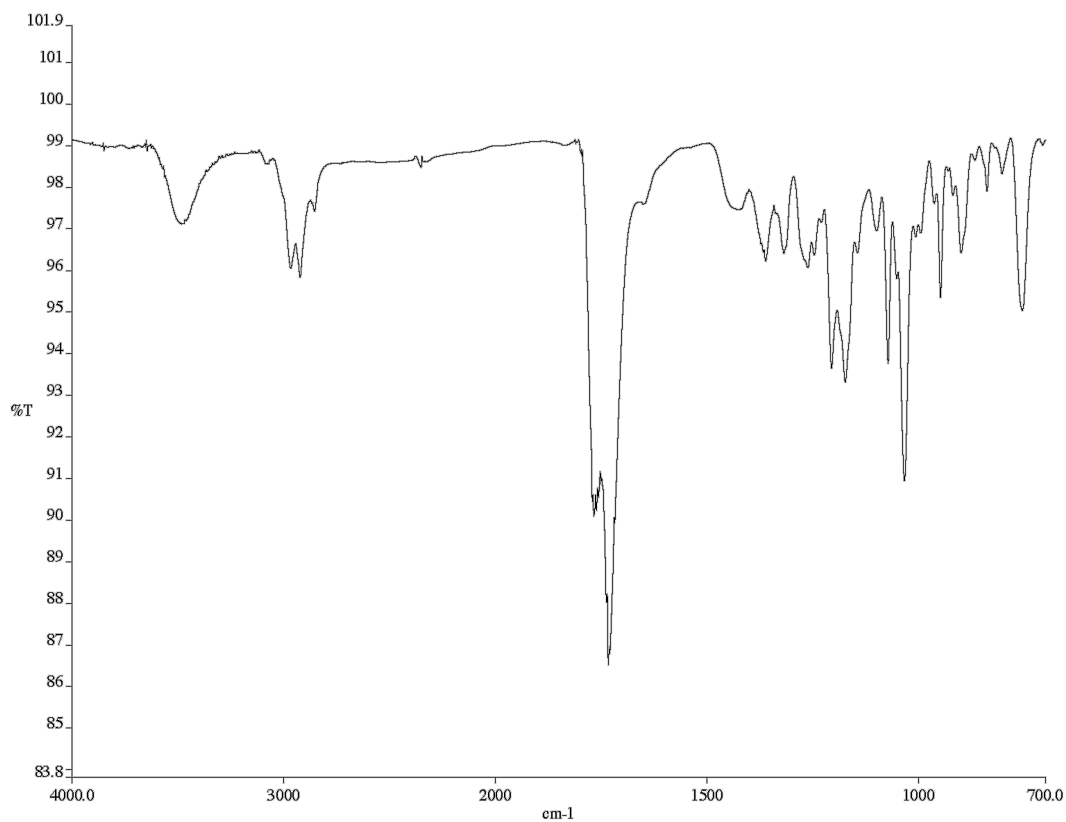


Infrared spectrum (Thin Film, NaCl) of compound **54**.

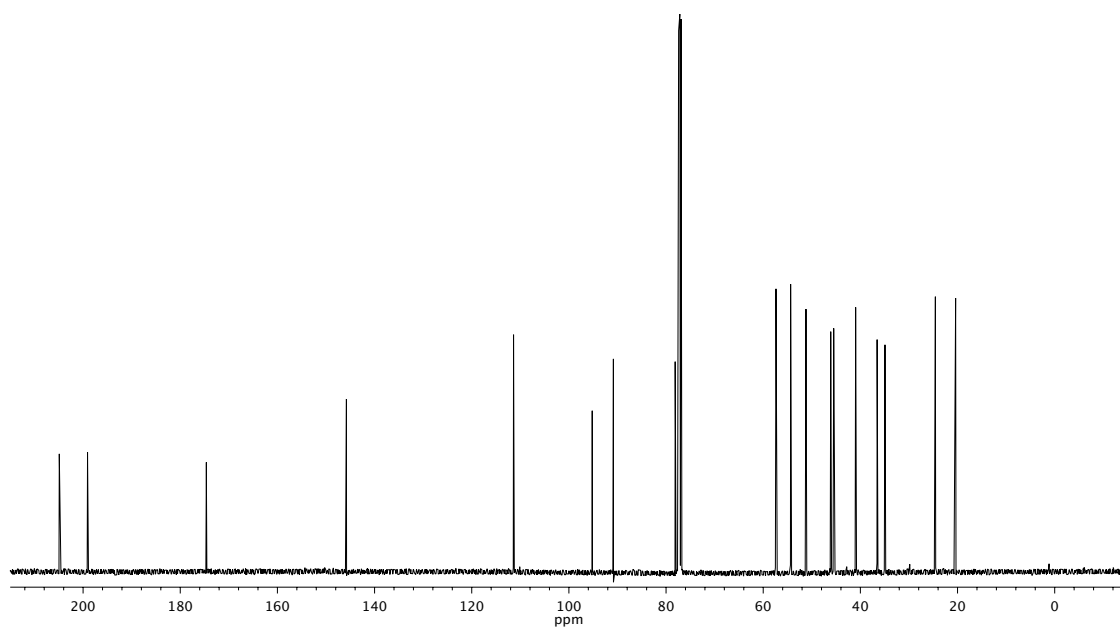


¹³C NMR (126 MHz, CDCl₃) of compound **54**.

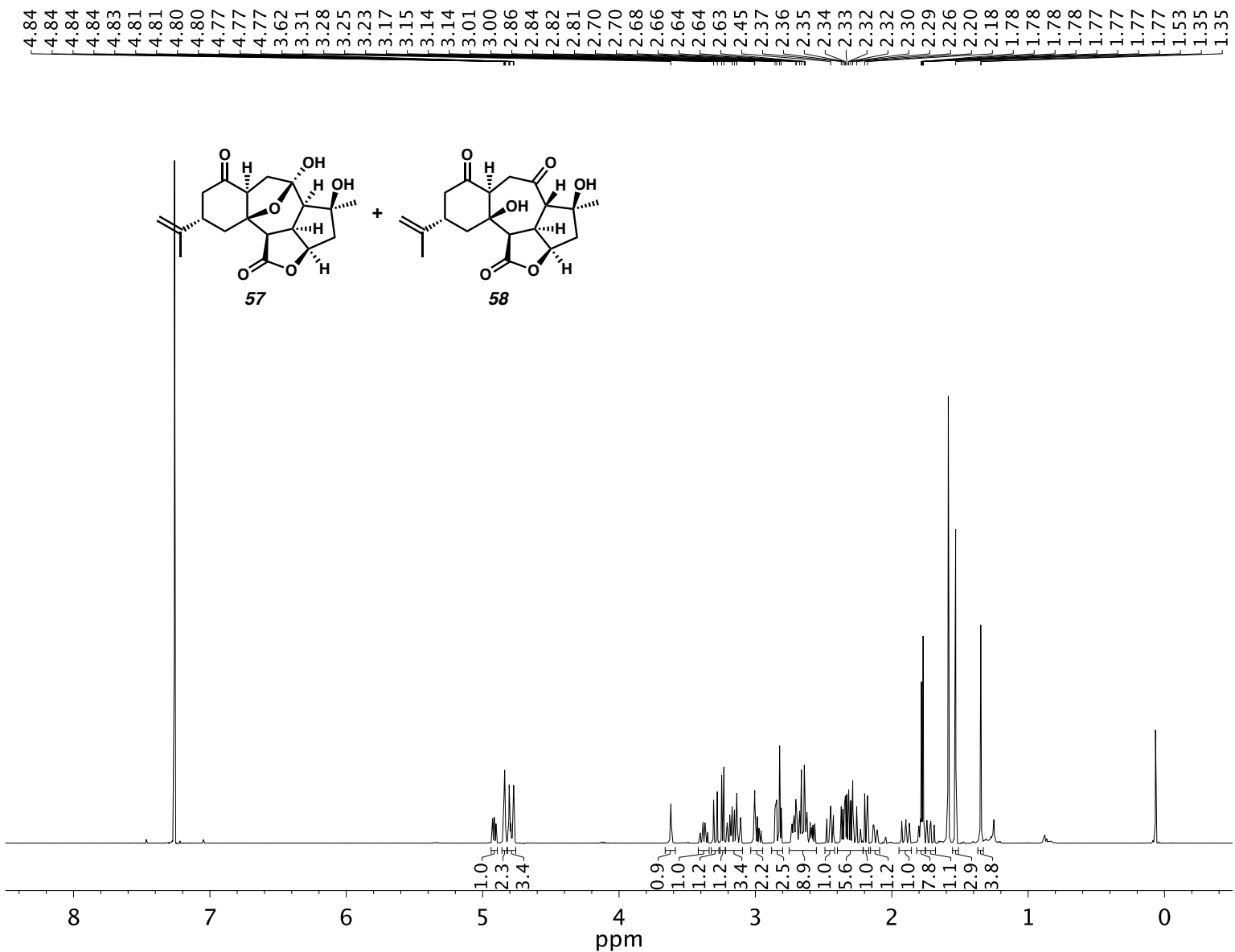




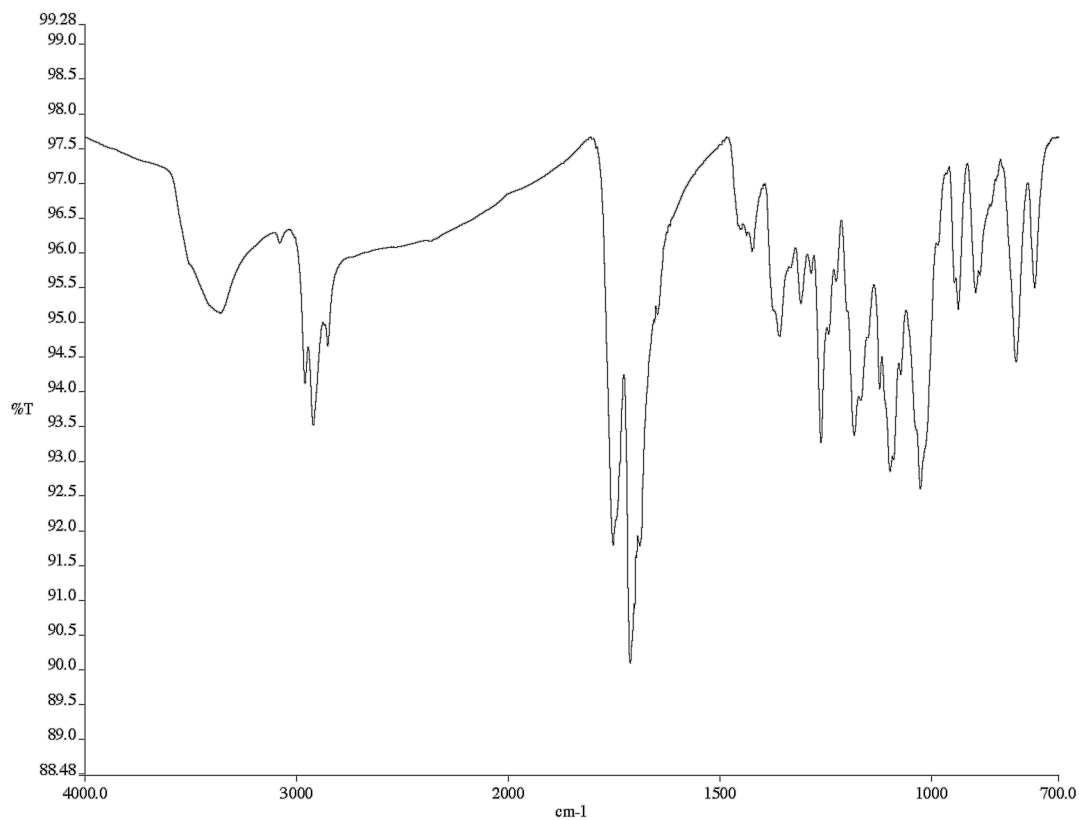
Infrared spectrum (Thin Film, NaCl) of compound **55**.



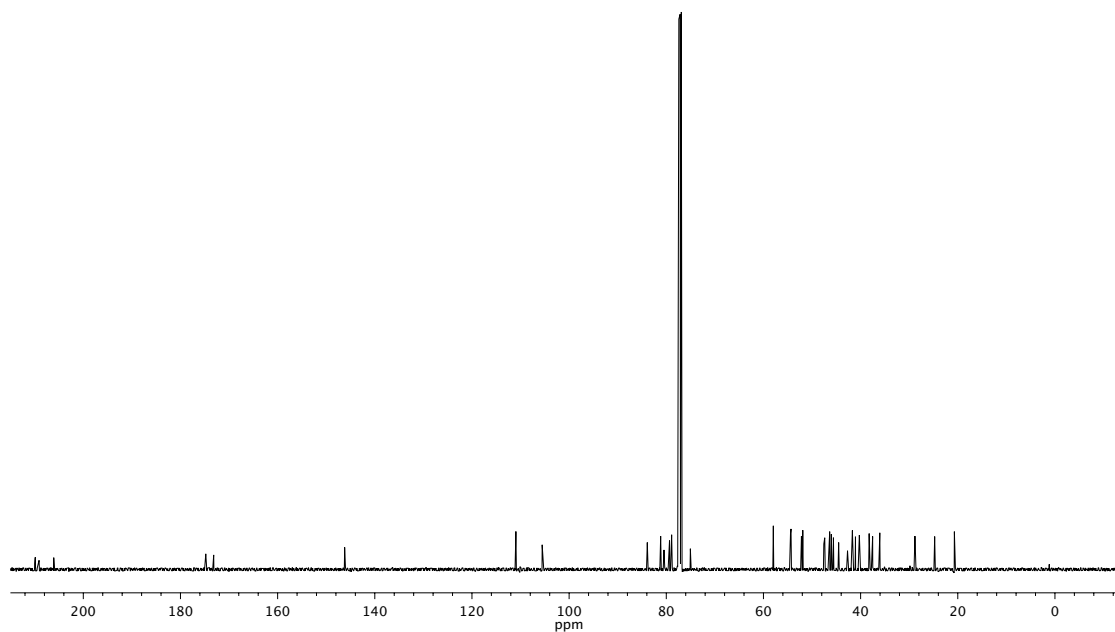
¹³C NMR (126 MHz, CDCl₃) of compound **55**.



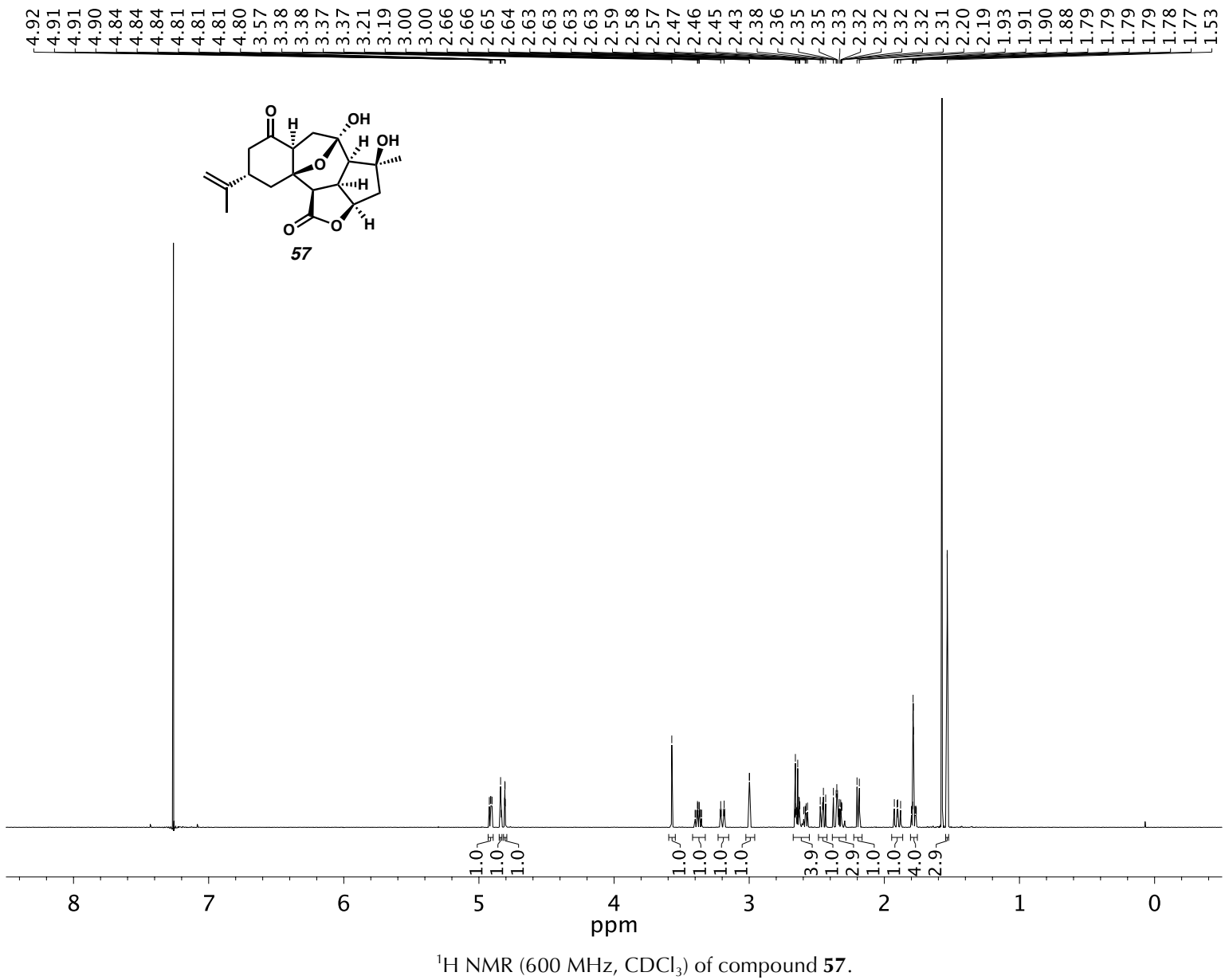
$^1\text{H NMR}$ (500 MHz, CDCl_3) of compound 57/58.

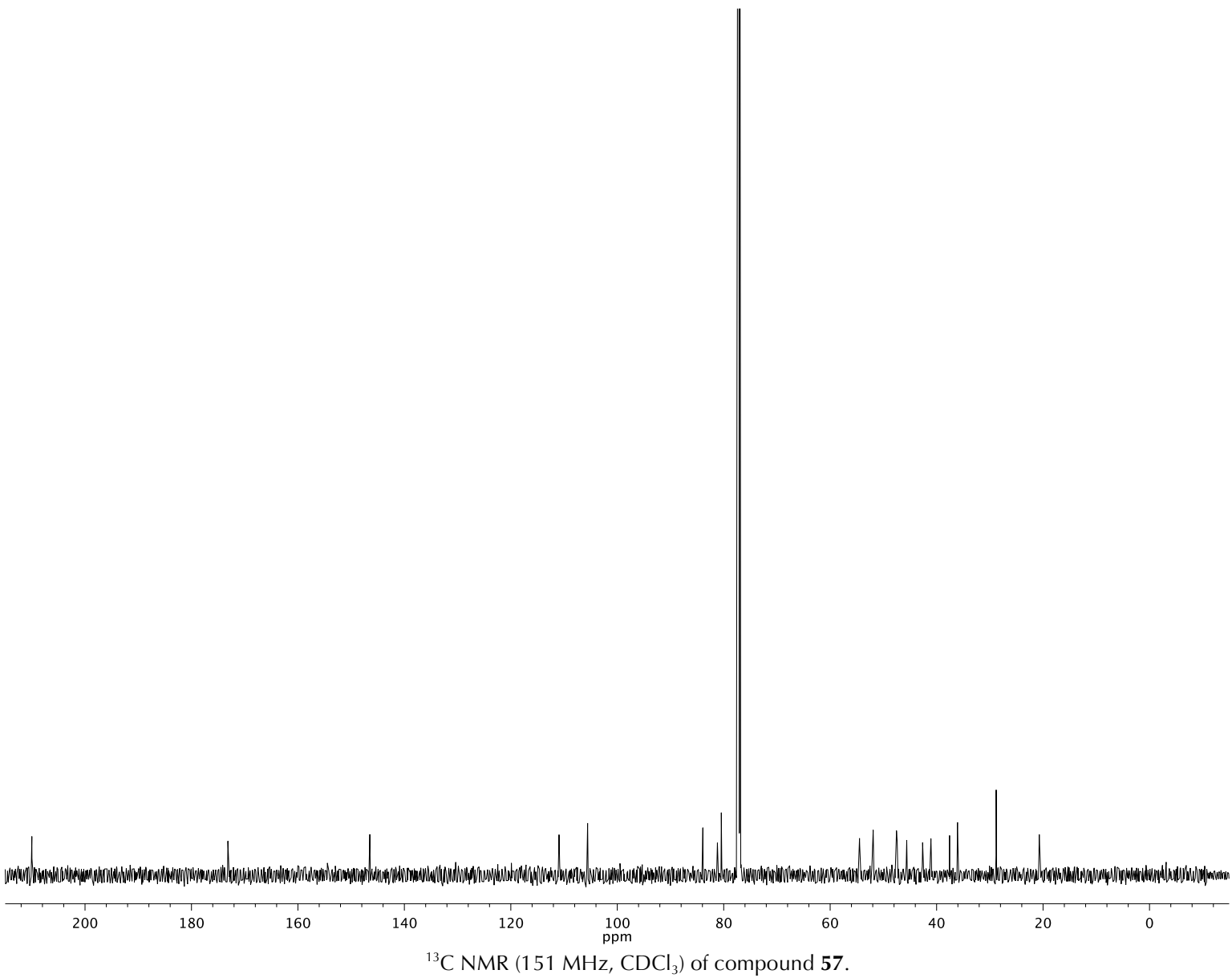


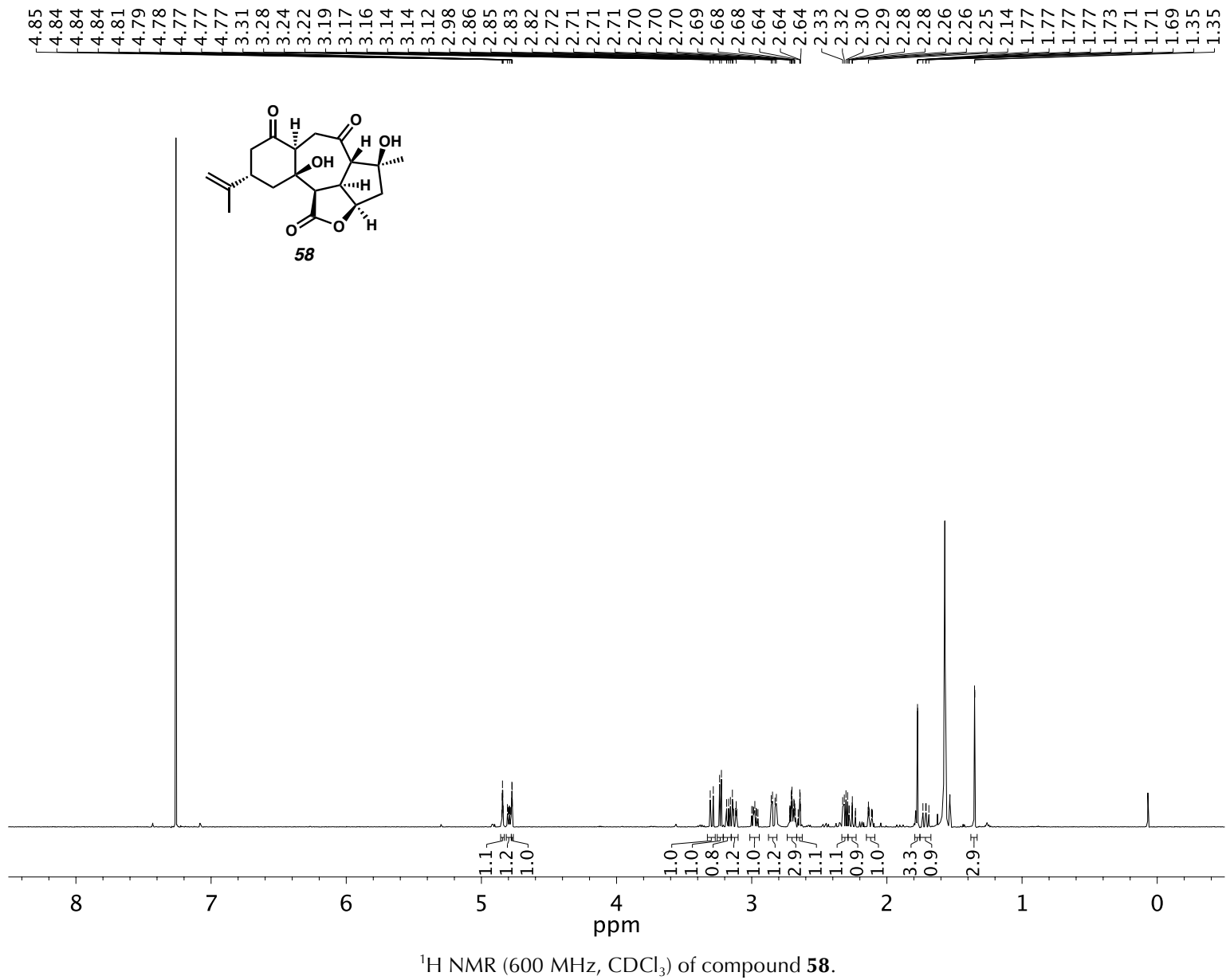
Infrared spectrum (Thin Film, NaCl) of compound **57/58**.

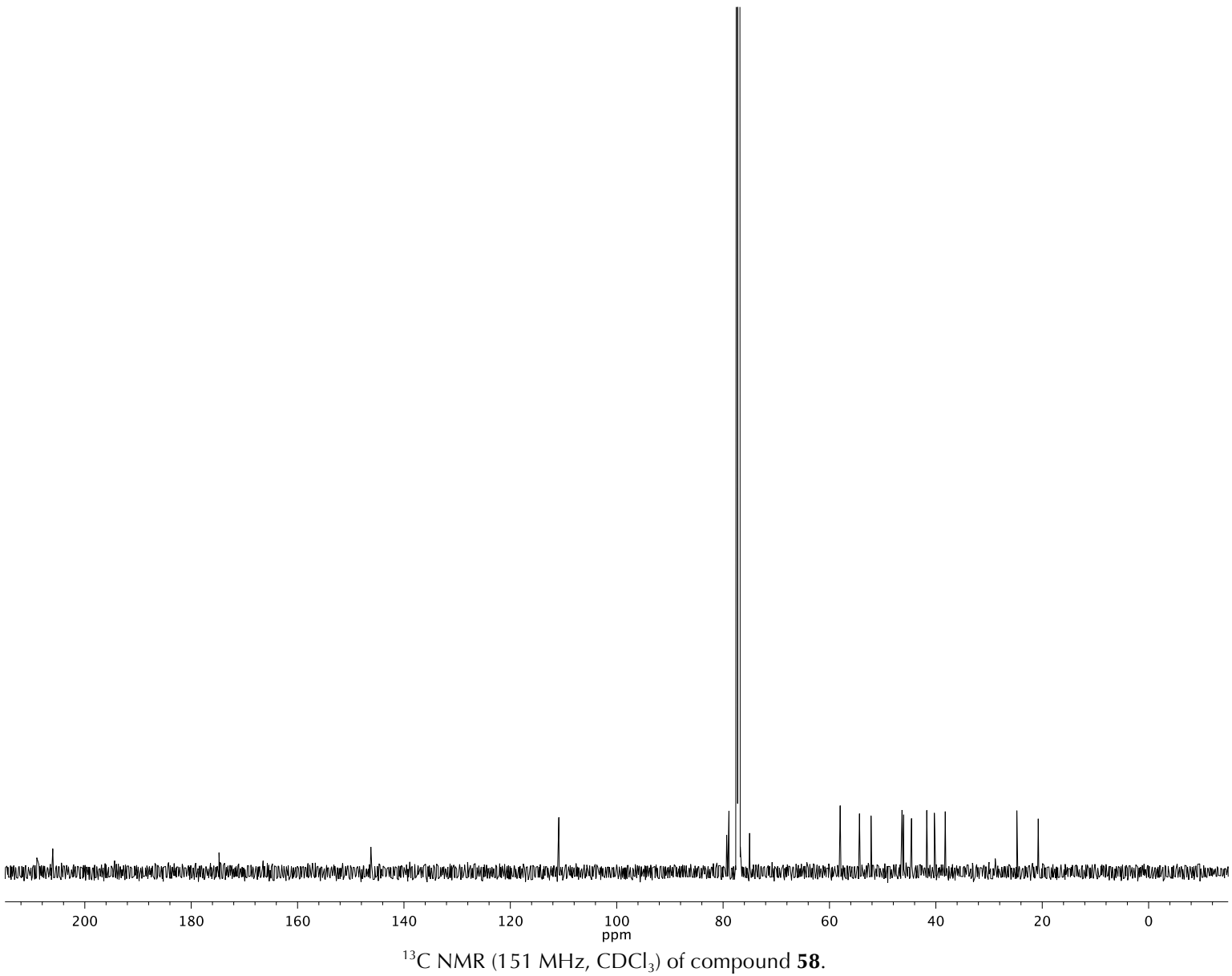


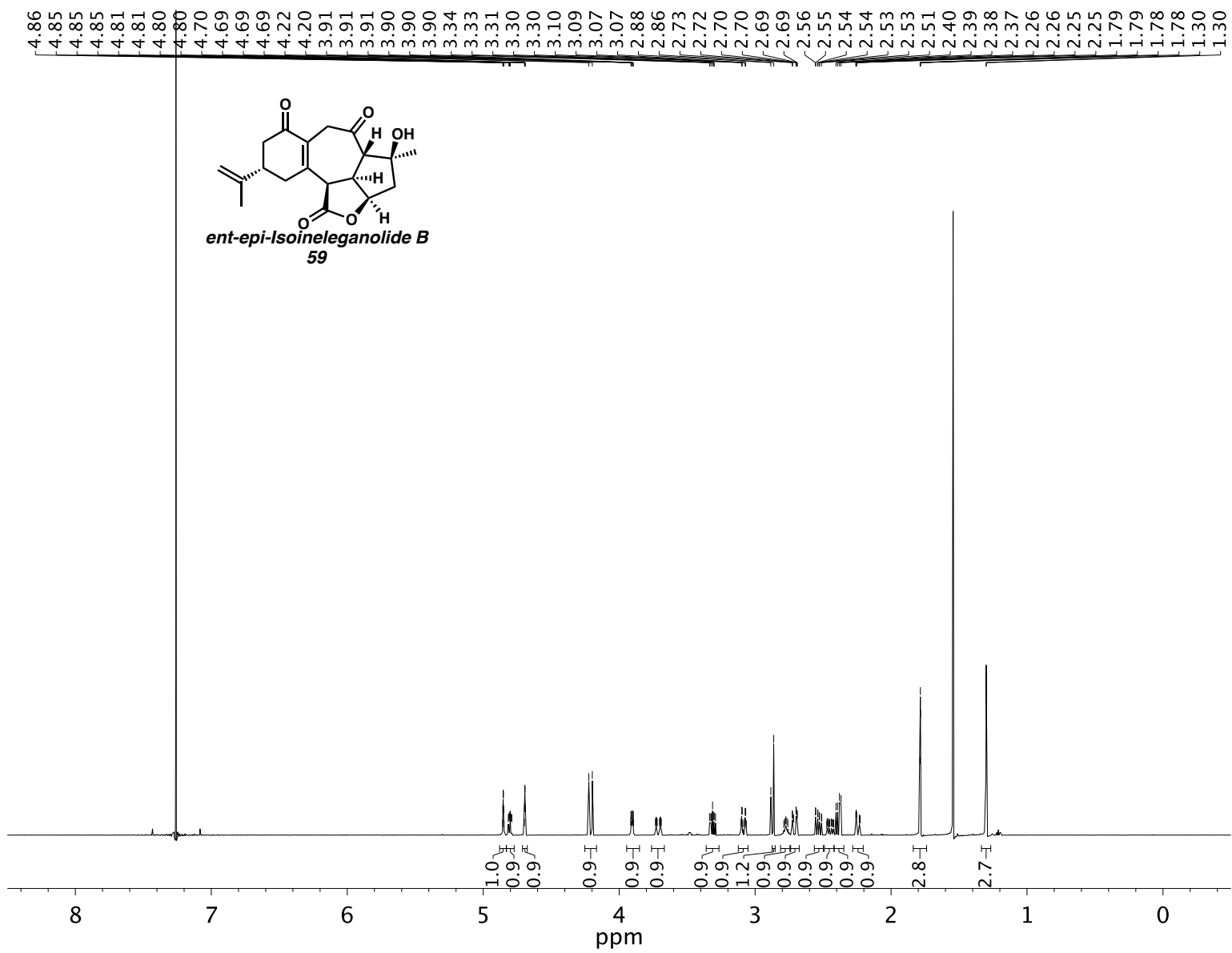
¹³C NMR (126 MHz, CDCl₃) of compound **57/58**.

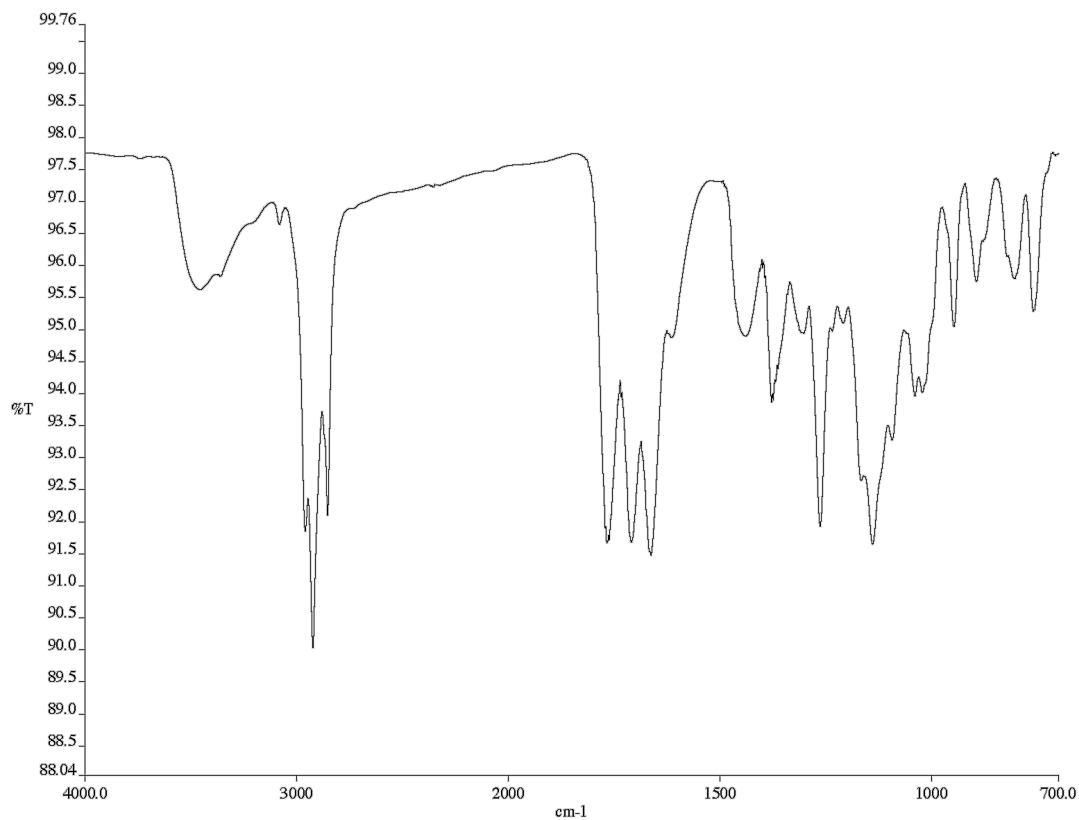




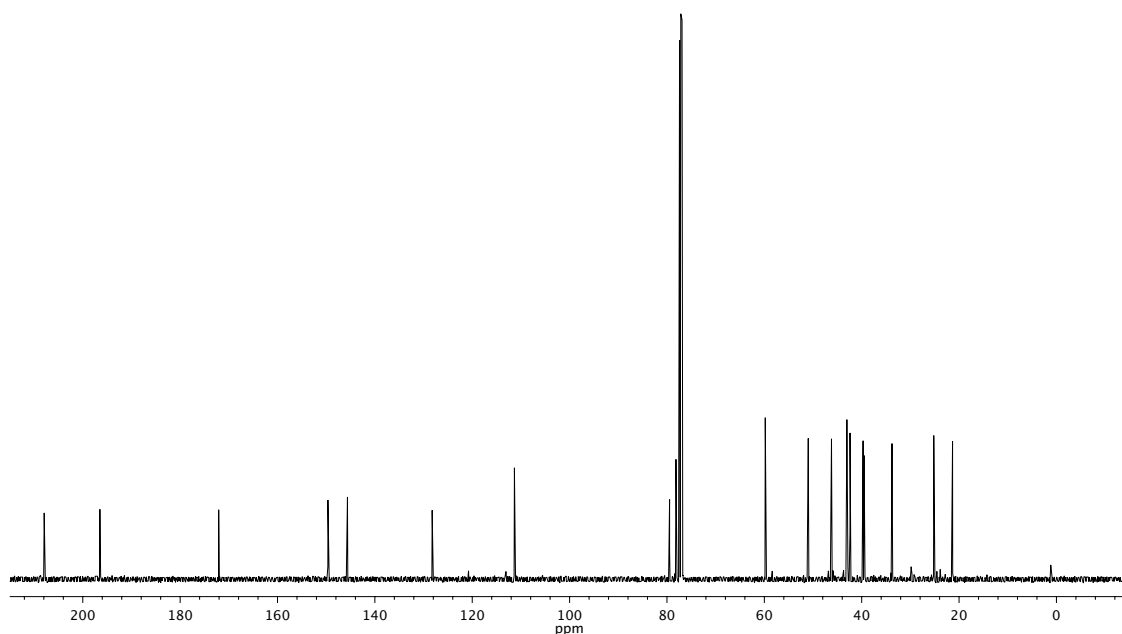




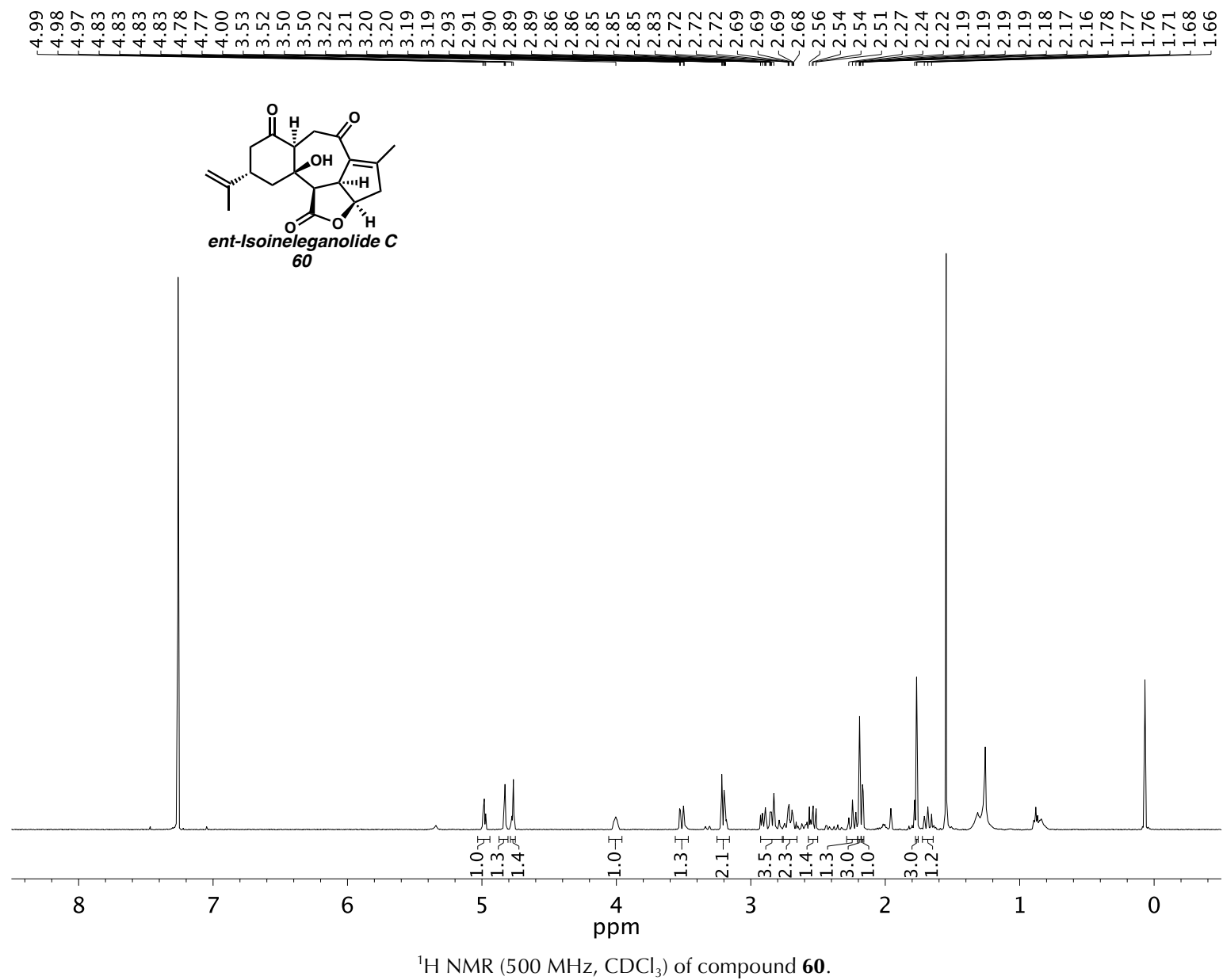


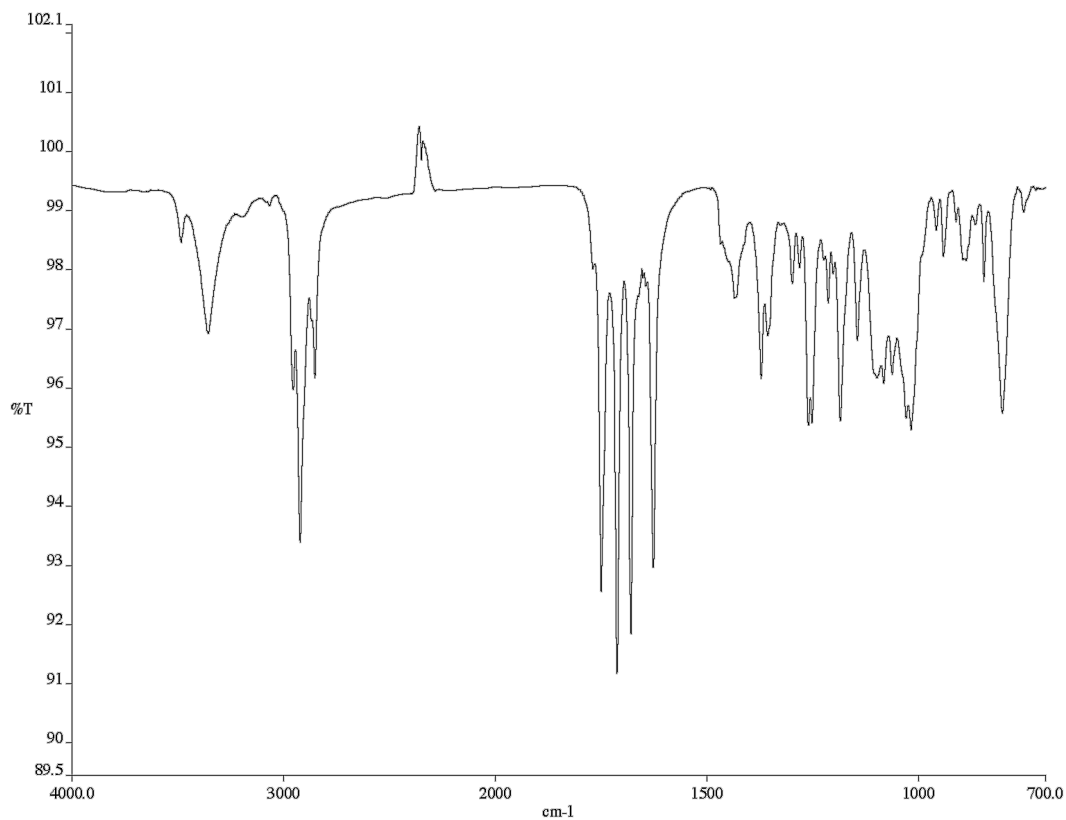


Infrared spectrum (Thin Film, NaCl) of compound **59**.

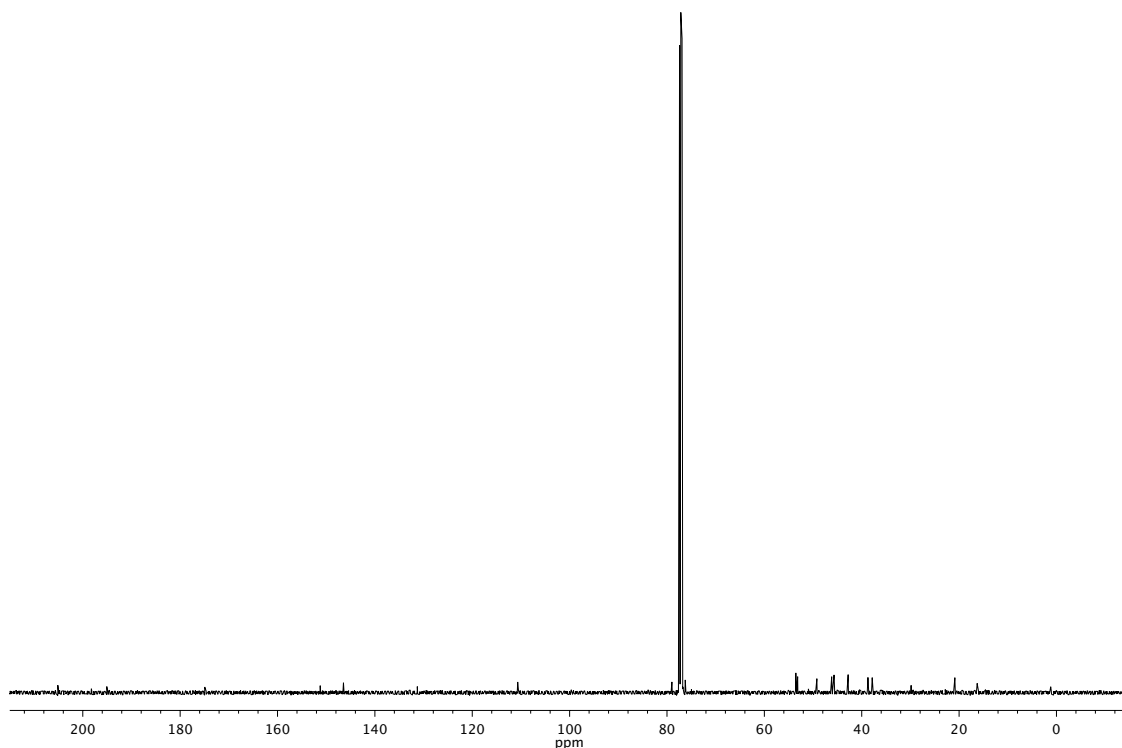


¹³C NMR (126 MHz, CDCl₃) of compound **59**.

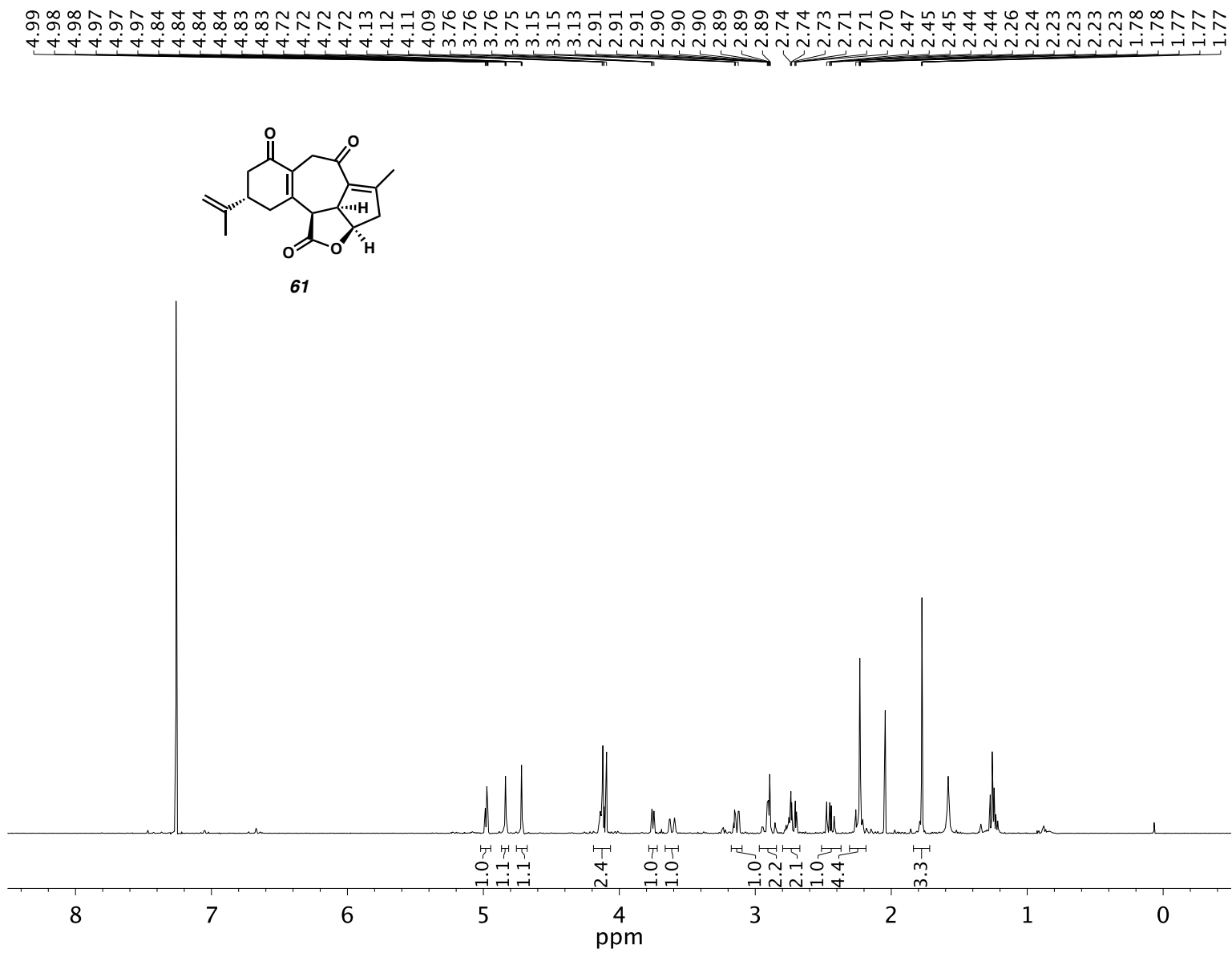


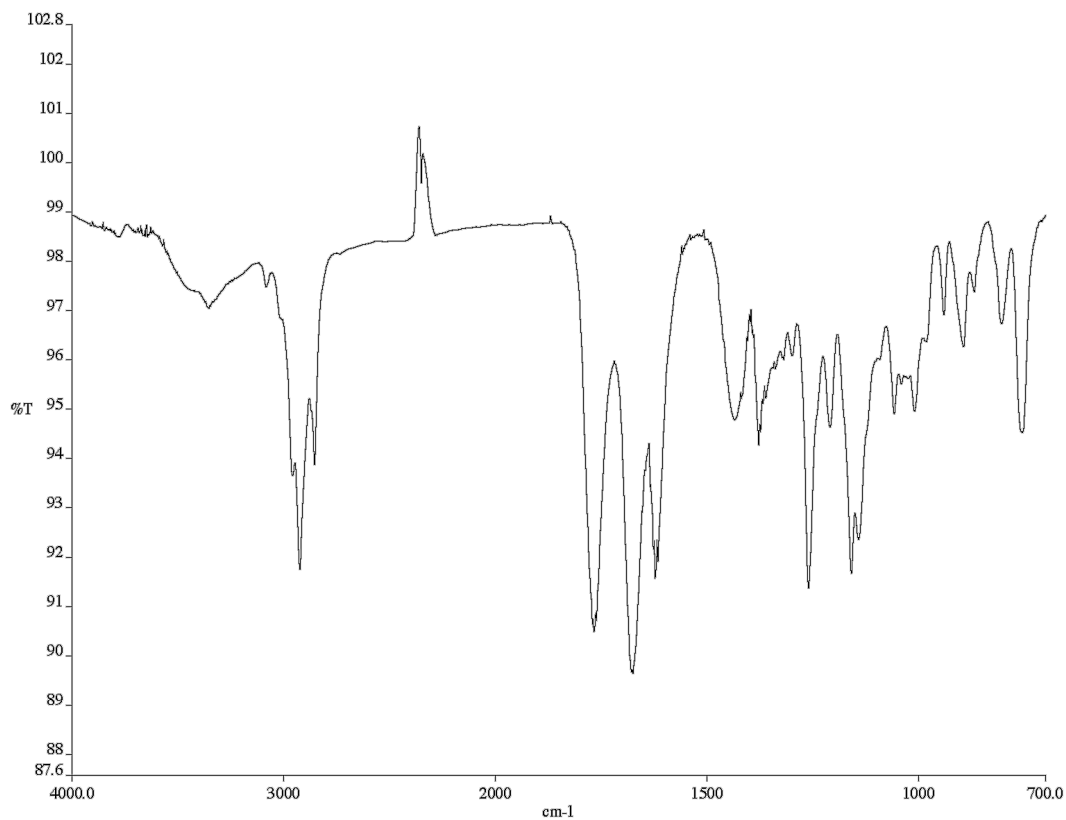


Infrared spectrum (Thin Film, NaCl) of compound **60**.

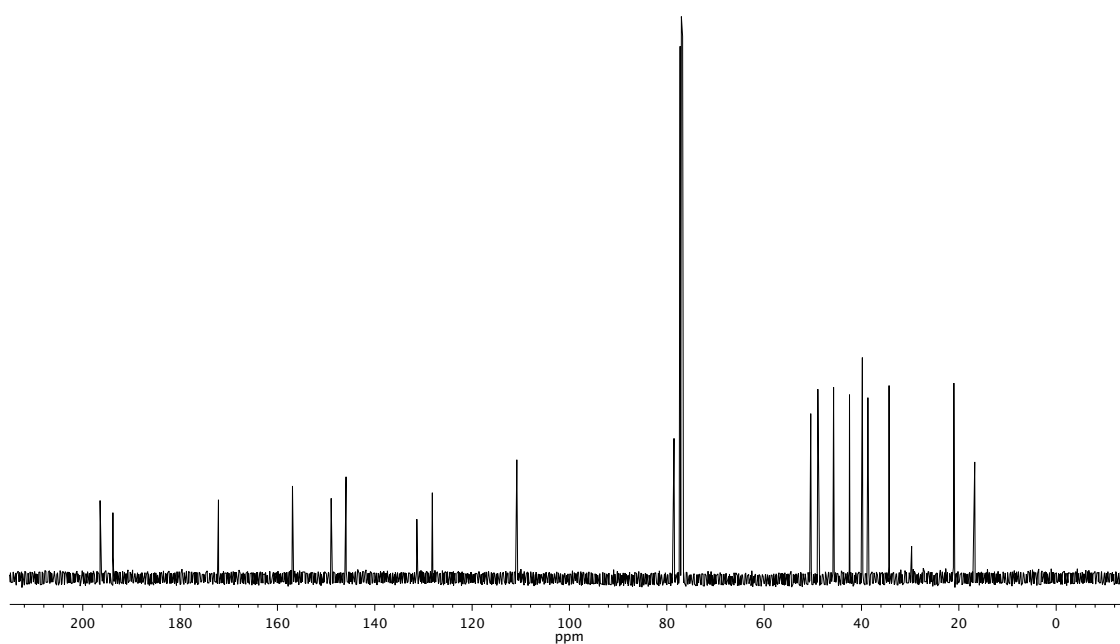


¹³C NMR (126 MHz, CDCl₃) of compound **60**.





Infrared spectrum (Thin Film, NaCl) of compound **61**.



¹³C NMR (126 MHz, CDCl₃) of compound **61**.