

Supporting Information

**A DOUBLE HEMIKETAL FORMATION/HETERO-MICHAEL ADDITION
APPROACH TO THE [6,5,5]-DISPIROKETAL SYSTEM OF SPIROLIDES**

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1. General Information

Optical rotations were recorded on a digital polarimeter with a sodium lamp (589 nm). Infrared (IR) spectra were recorded on an FT-IR spectrophotometer and absorbance bands are reported in wavenumber (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with tetramethylsilane (δ_{H} 0.00), C_6H_6 (δ_{H} 7.16) or CHCl_3 (δ_{H} 7.26) as an internal standard. Coupling constants (J) are reported in hertz (Hz). Abbreviations of multiplicity are as follows: s, singlet; d, doublet; t, triplet; q, quartet; sext, sextet; m, multiplet. Data are presented as follows: chemical shift, multiplicity, coupling constants, integration and assignment. Spirolide numbering is used for proton assignments of all intermediates. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded with CDCl_3 (δ_{C} 77.0) or C_6D_6 (δ_{C} 127.0) as an internal standard. High-resolution mass spectra (HRMS) were recorded by electrospray ionization (ESI) using a time-of-flight (TOF) analyzer.

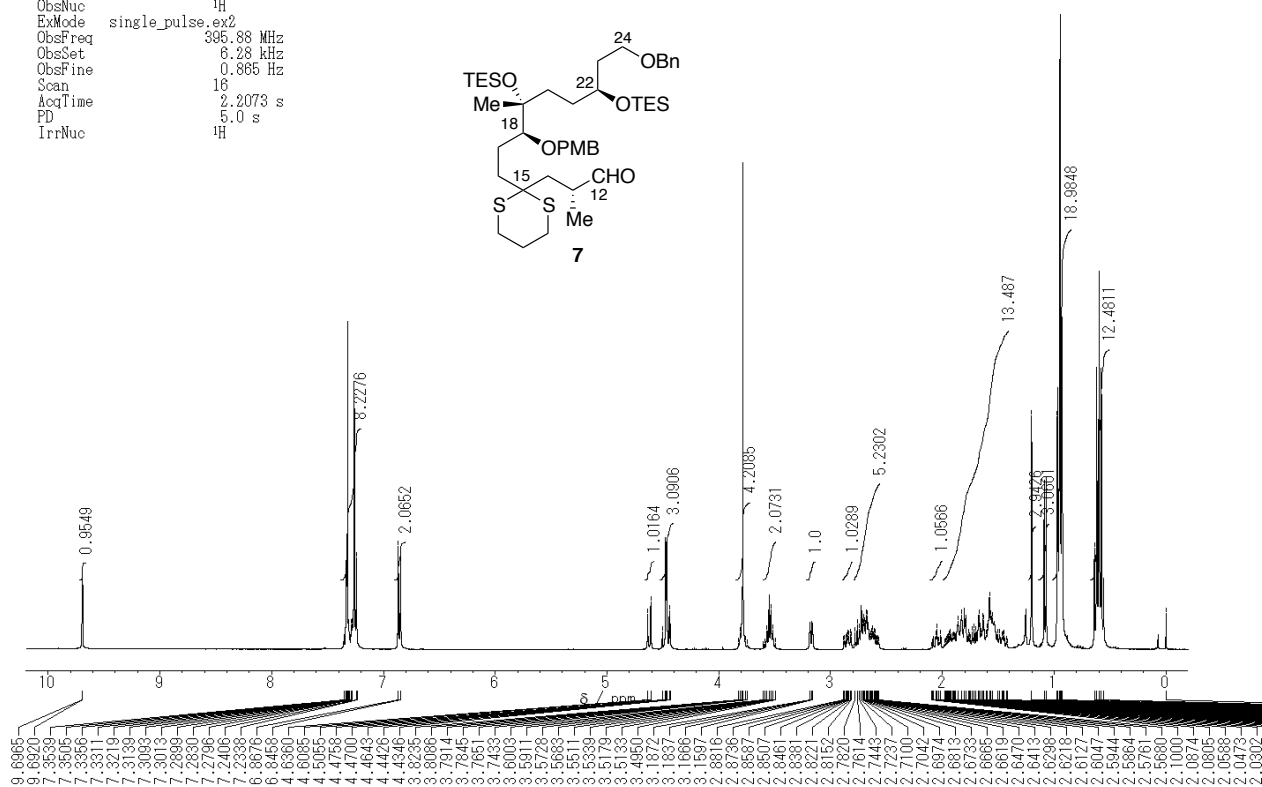
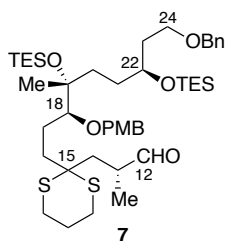
Column chromatography was carried out on silica gel 60 N (63–210 μm or 40–50 μm). Analytical thin layer chromatography (TLC) was carried out with 0.25 mm silica gel plates. Visualization was accomplished with ultraviolet light and anisaldehyde stain, followed by heating.

Analytical high performance liquid chromatography (HPLC) was carried out equipped with a UV detector. Detection was performed at 254 nm. Zorbax[®] Sil (4.6 \times 250 mm) was used. *n*-Hexane and AcOEt were distilled, filtered and degassed prior to use.

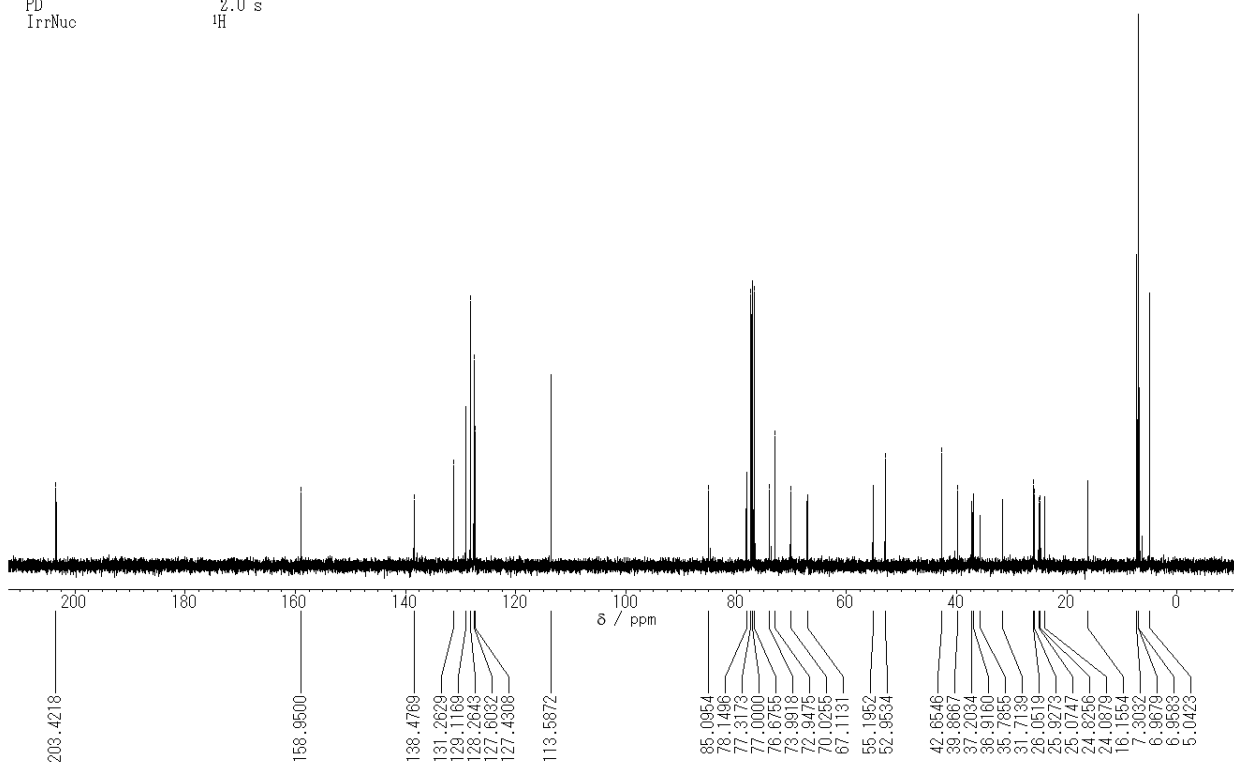
Reagents and solvents were purified by standard means or used as received unless otherwise noted. Dehydrated dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF, stabilizer free) were purchased. All reactions were conducted under an argon atmosphere unless otherwise noted.

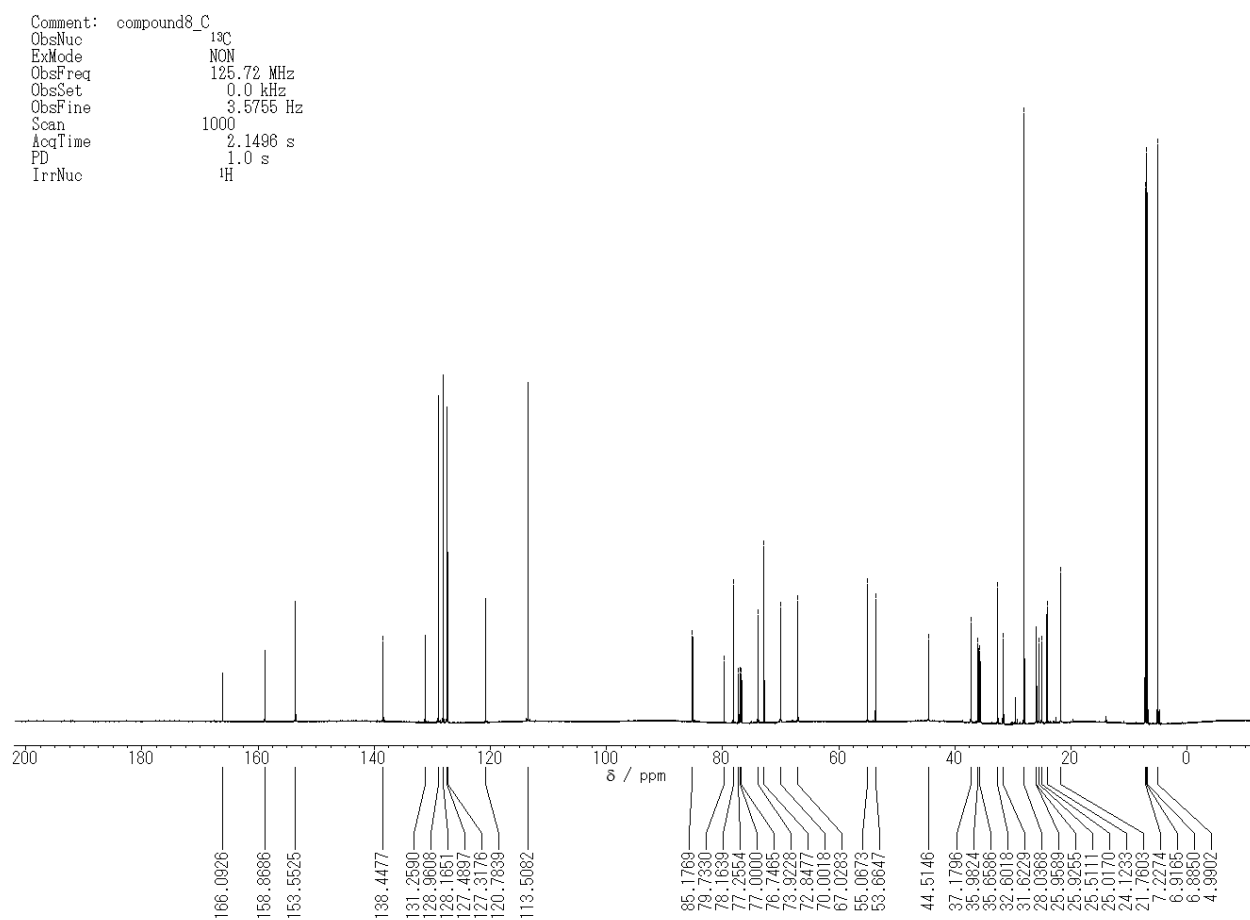
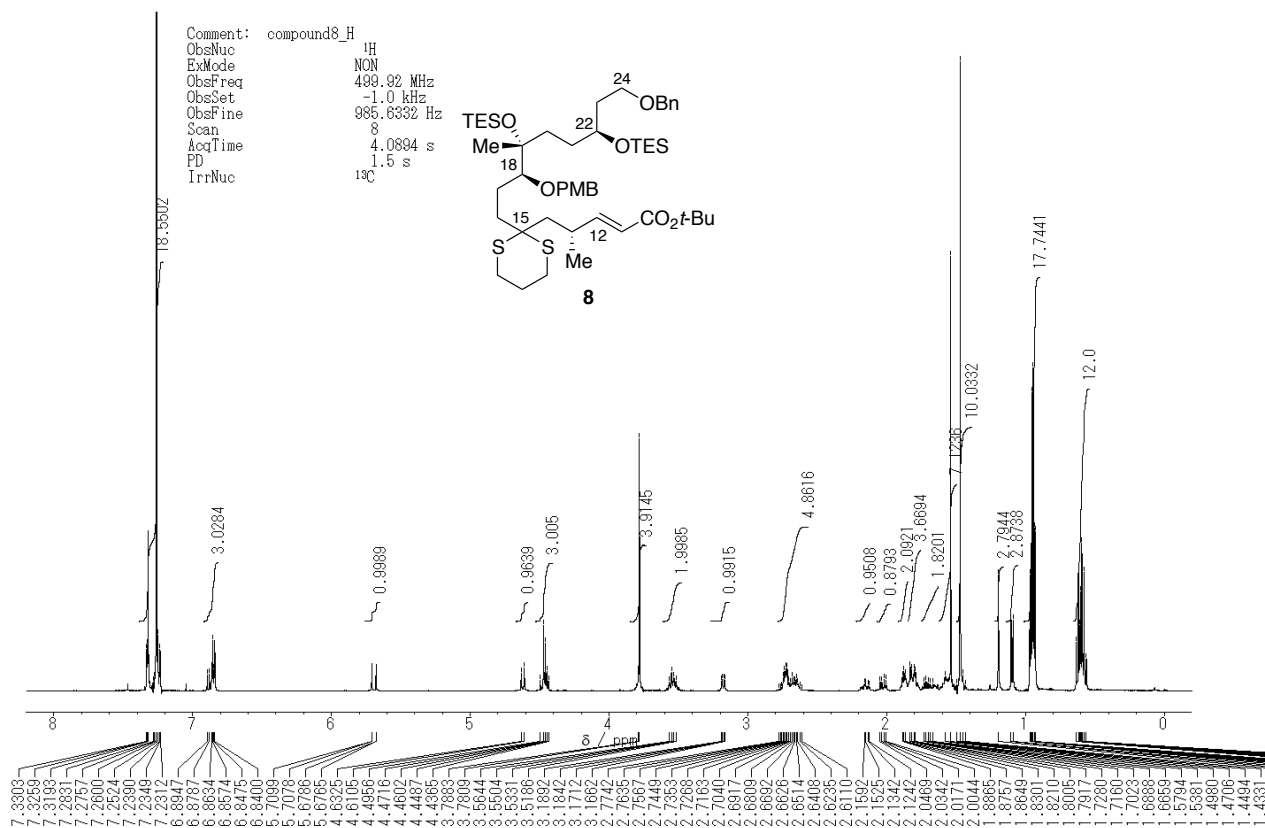
2. Copies of ^1H and ^{13}C NMR Spectra

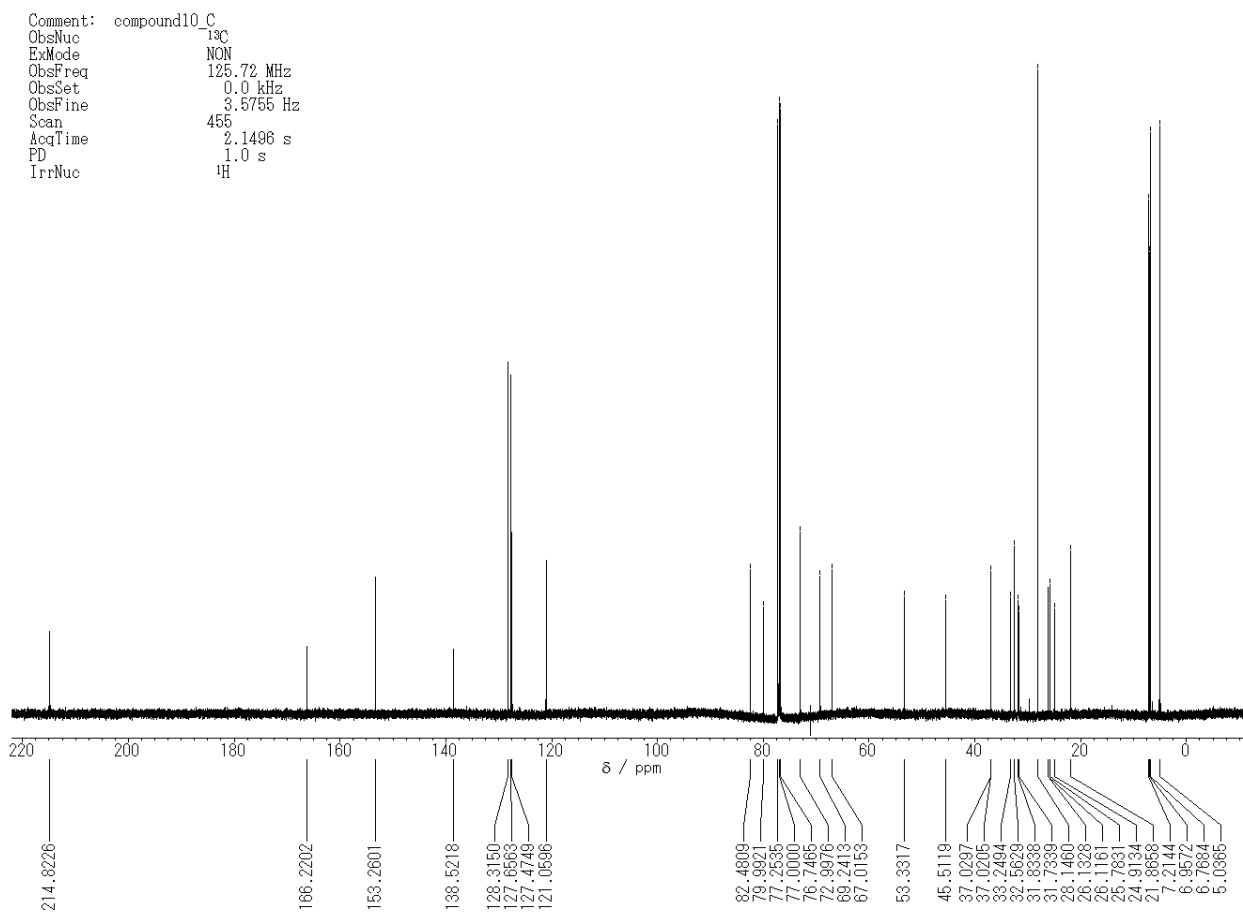
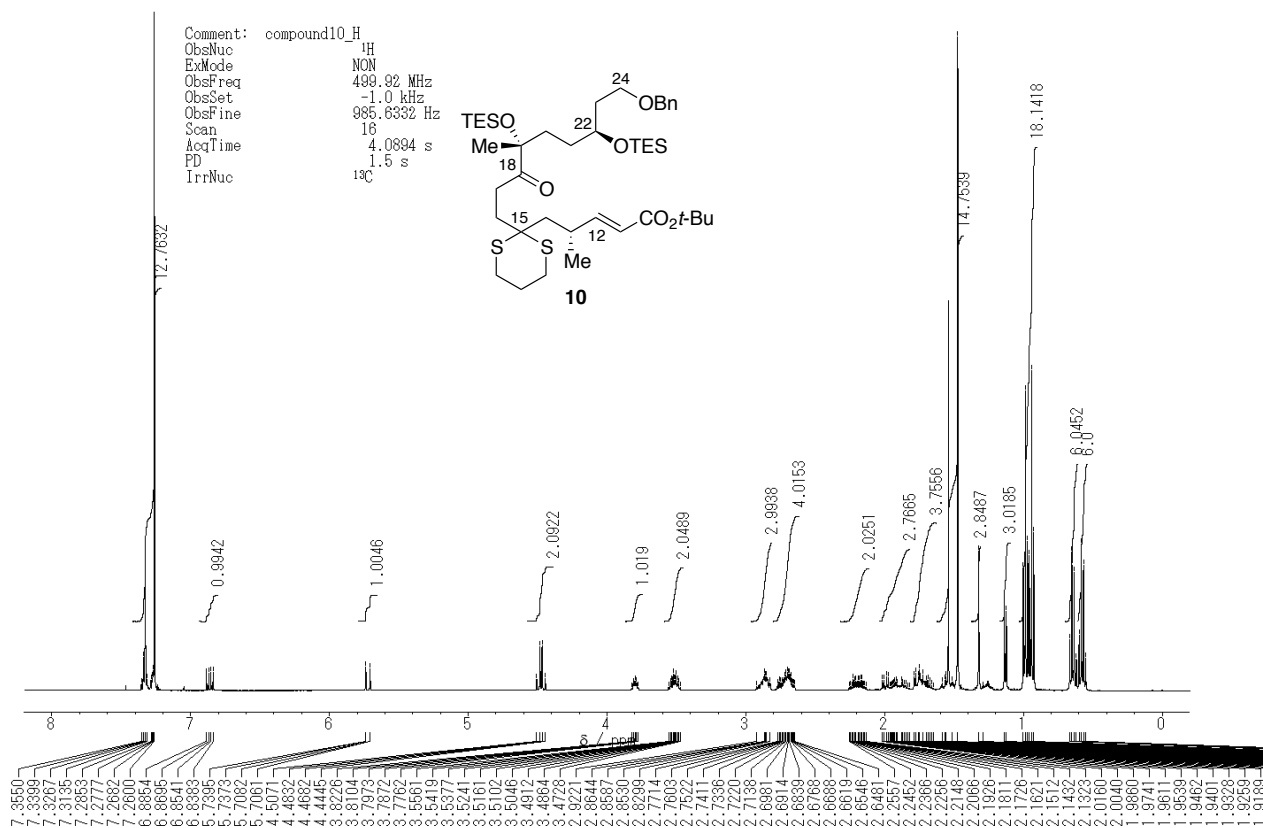
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 IrrNuc ^1H



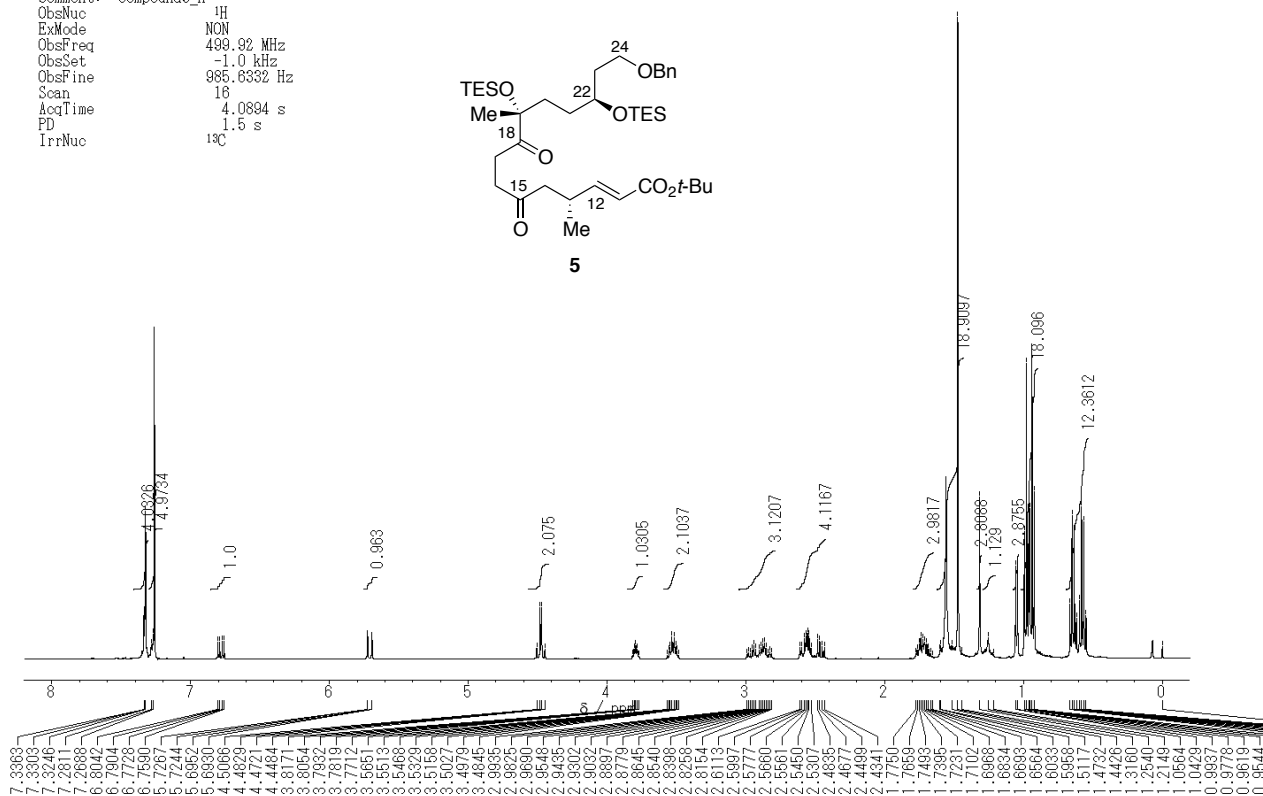
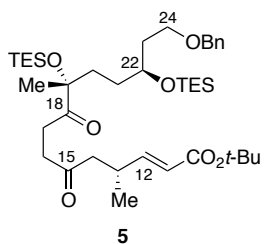
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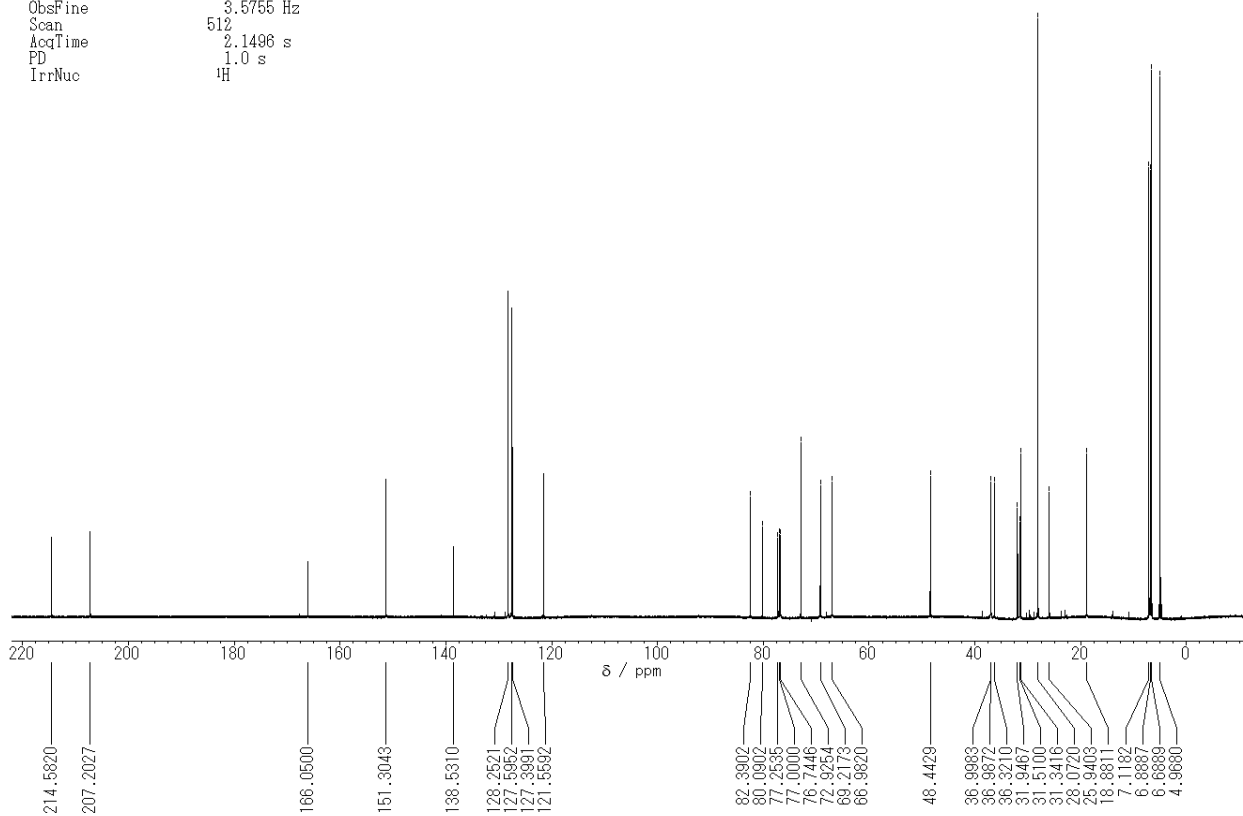




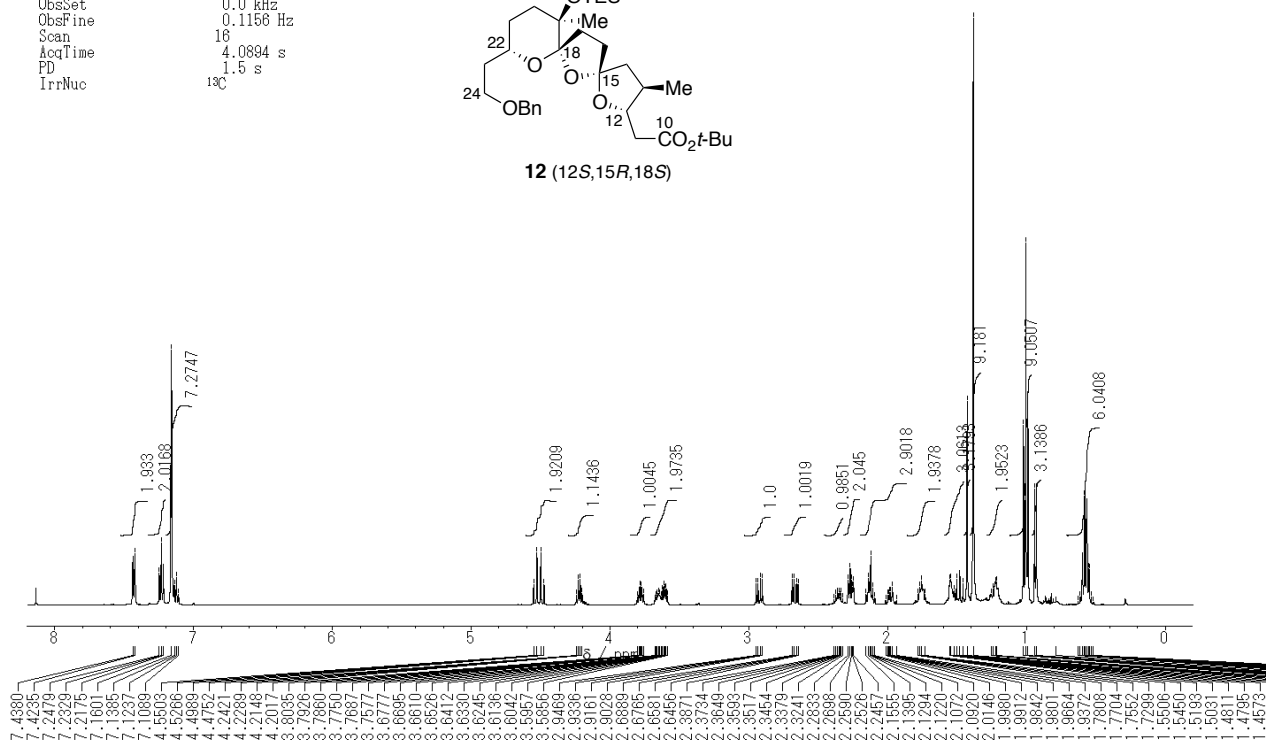
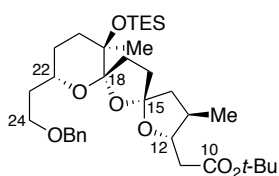
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 IrrNuc: ¹³C



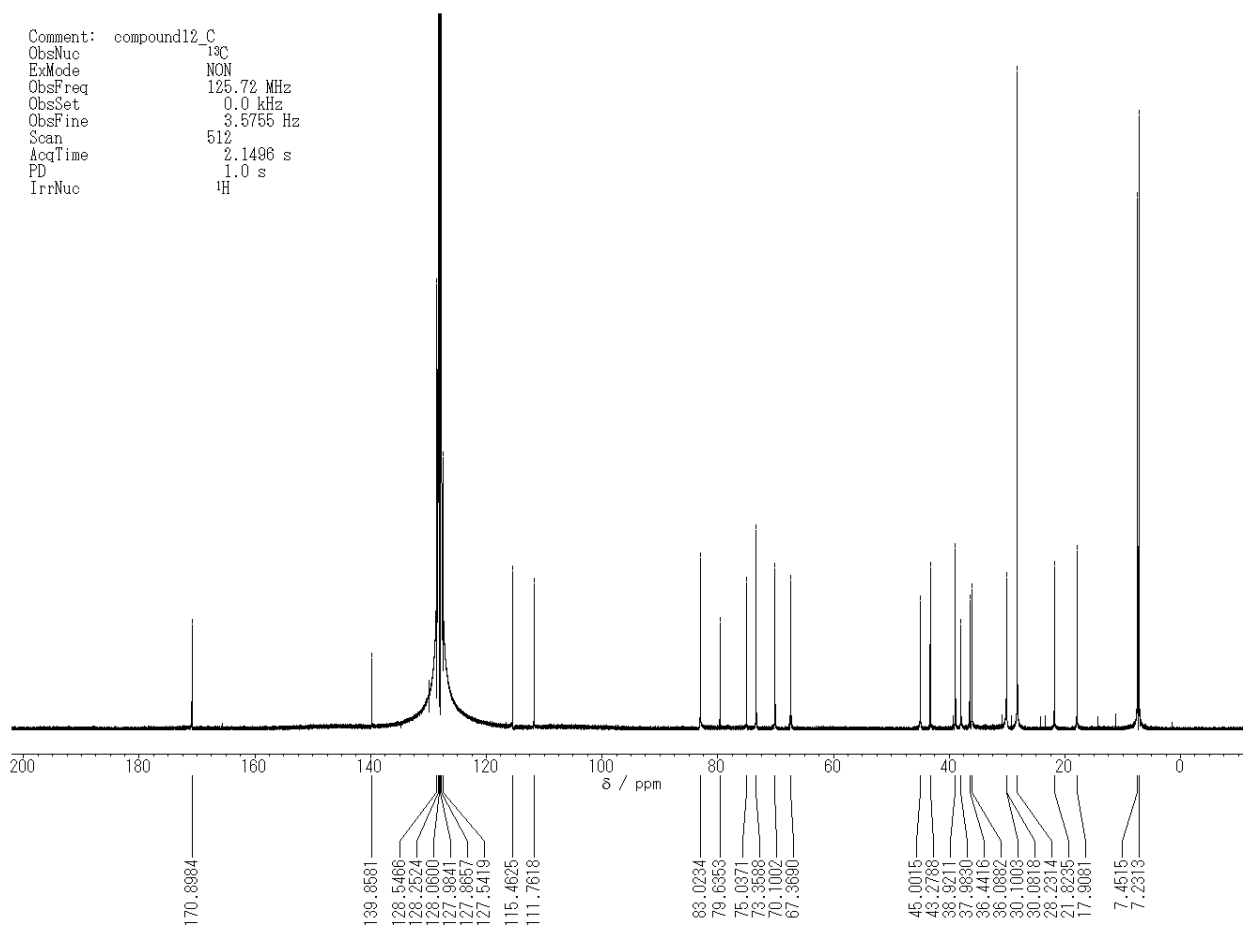
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 IrrNuc: ¹H



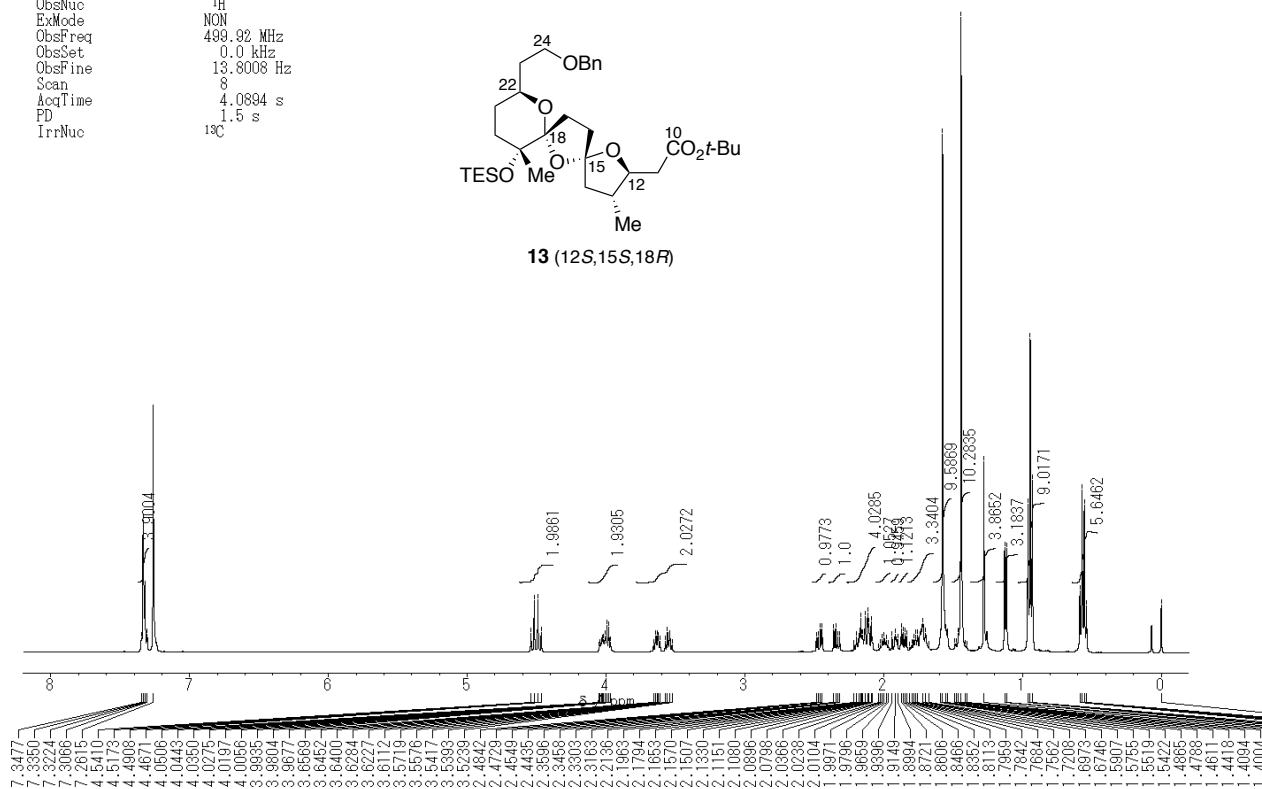
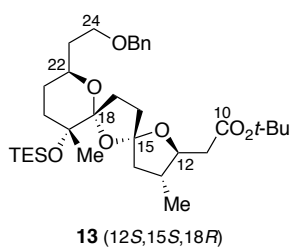
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 PD 1.5 s
 IrrNuc ¹³C



Comment: compound12_C
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 ExMode NON
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 ObsSet 0.0 kHz
 ObsFine 3.5755 Hz
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 PD 1.0 s
 IrrNuc ¹H



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 IrrNuc: ¹³C



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 IrrNuc: ¹H

