Supplementary Information

Stereoselective total syntheses of (−)-hygrophorone A[12], 4-*O*-acetyl-hygrophorone A[12] and (+)-hygrophorone B[12]

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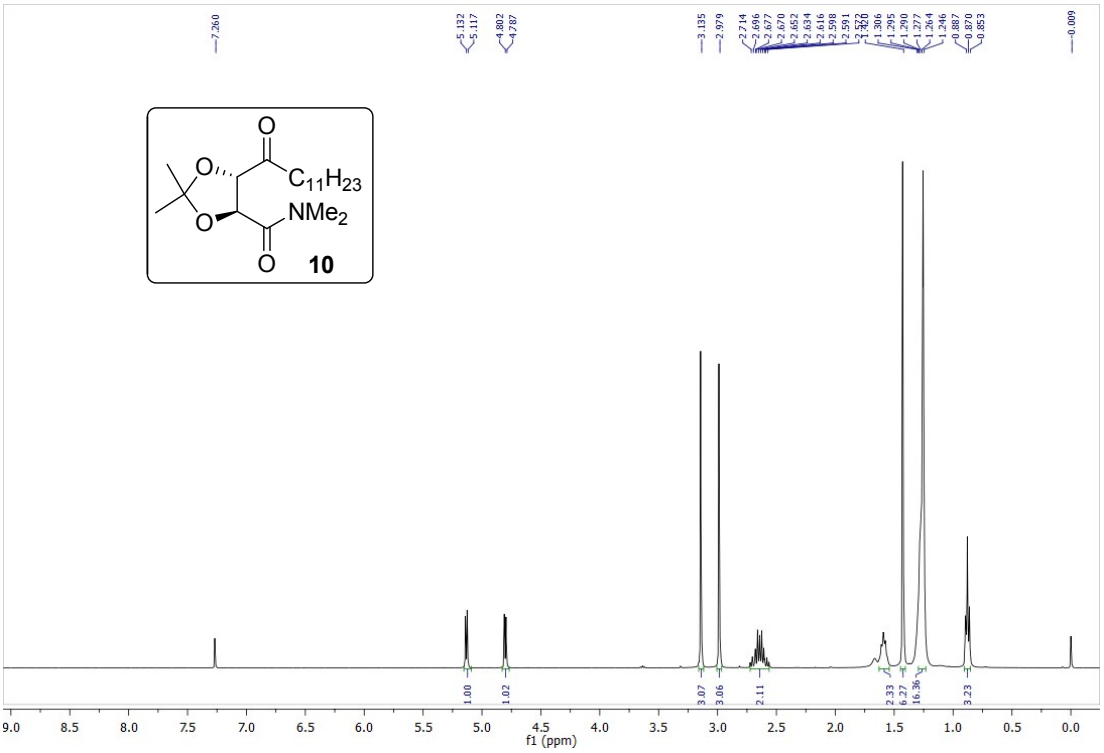
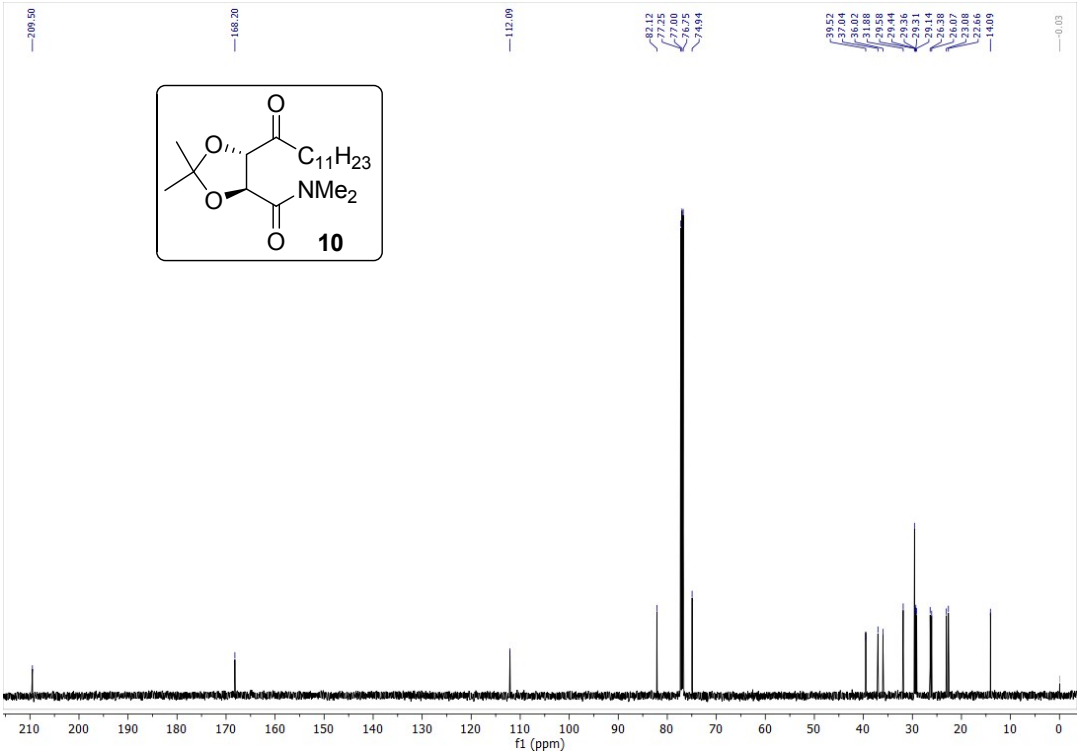
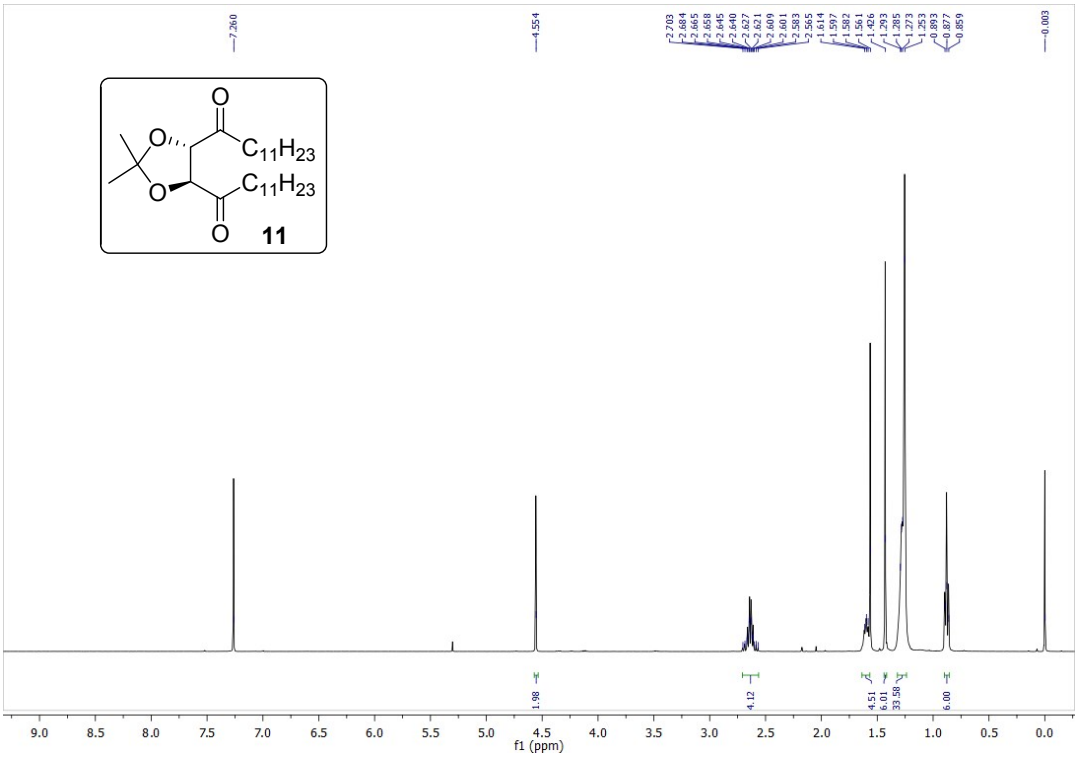
^{1}H NMR of compound **10** (400 MHz) in $CDCl_3$



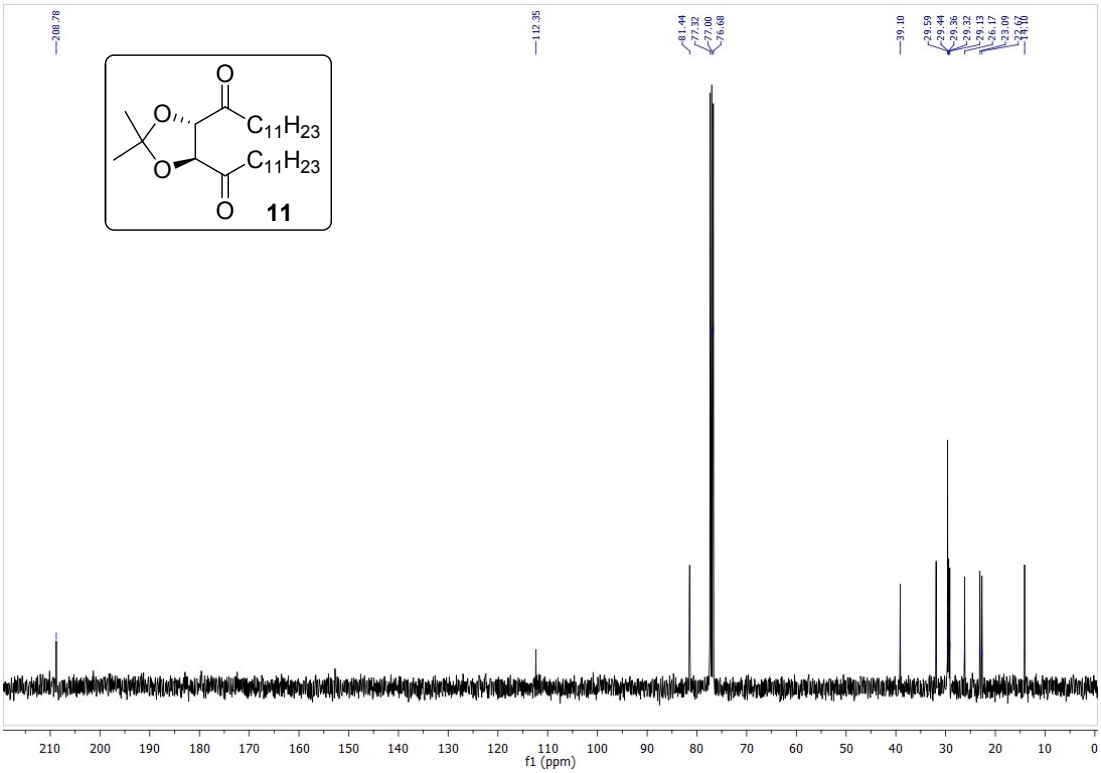
^{13}C NMR of compound **10** (125 MHz) in $CDCl_3$



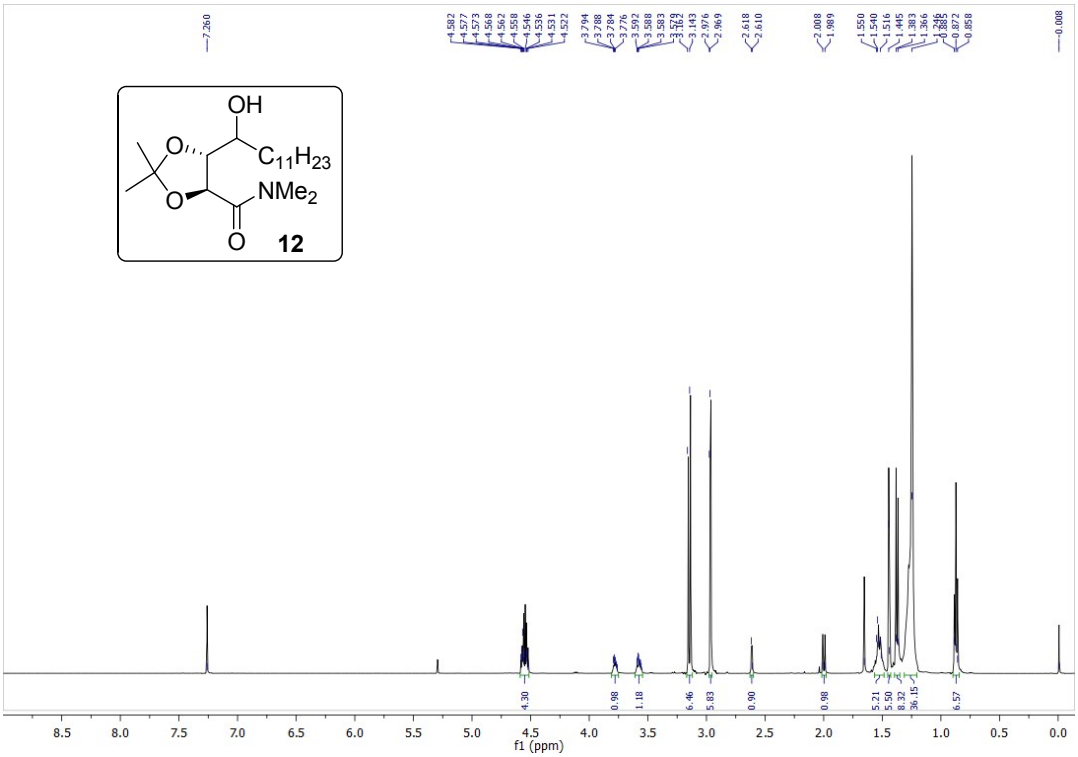
^{1}H NMR of compound **11** (400 MHz) in $CDCl_3$



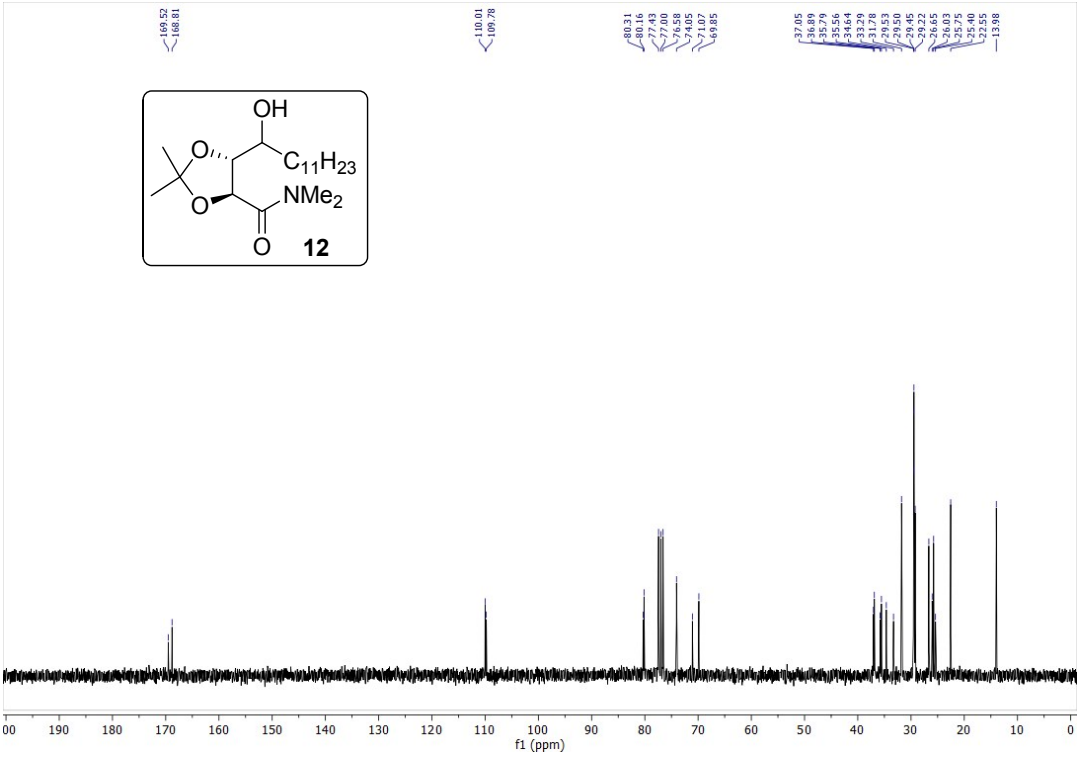
^{13}C NMR of compound **11** (100 MHz) in $CDCl_3$



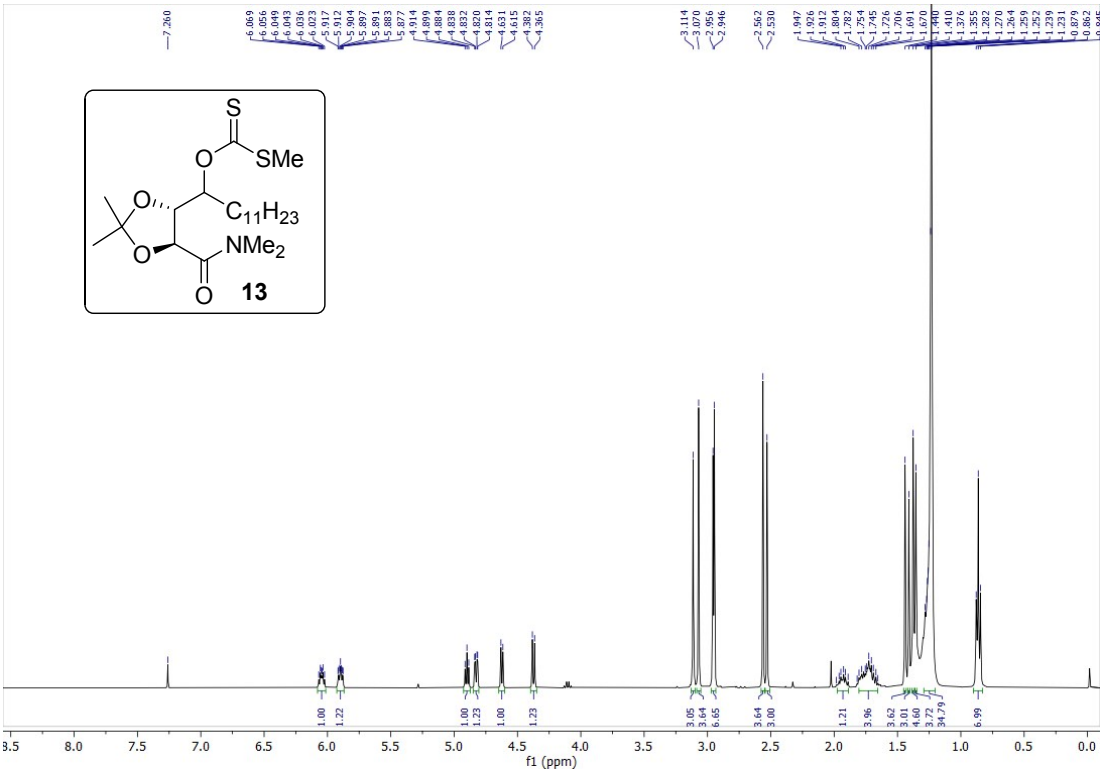
^{1}H NMR of compound **12** (500 MHz) in $CDCl_3$



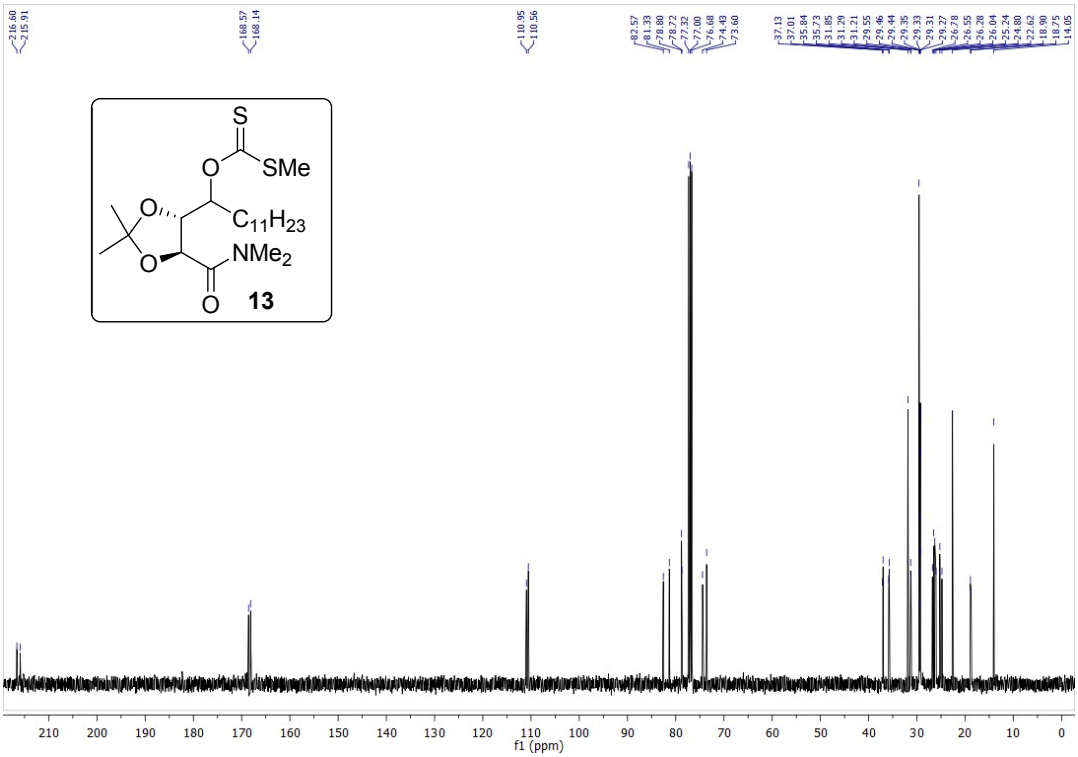
^{13}C NMR of compound **12** (75 MHz) in $CDCl_3$



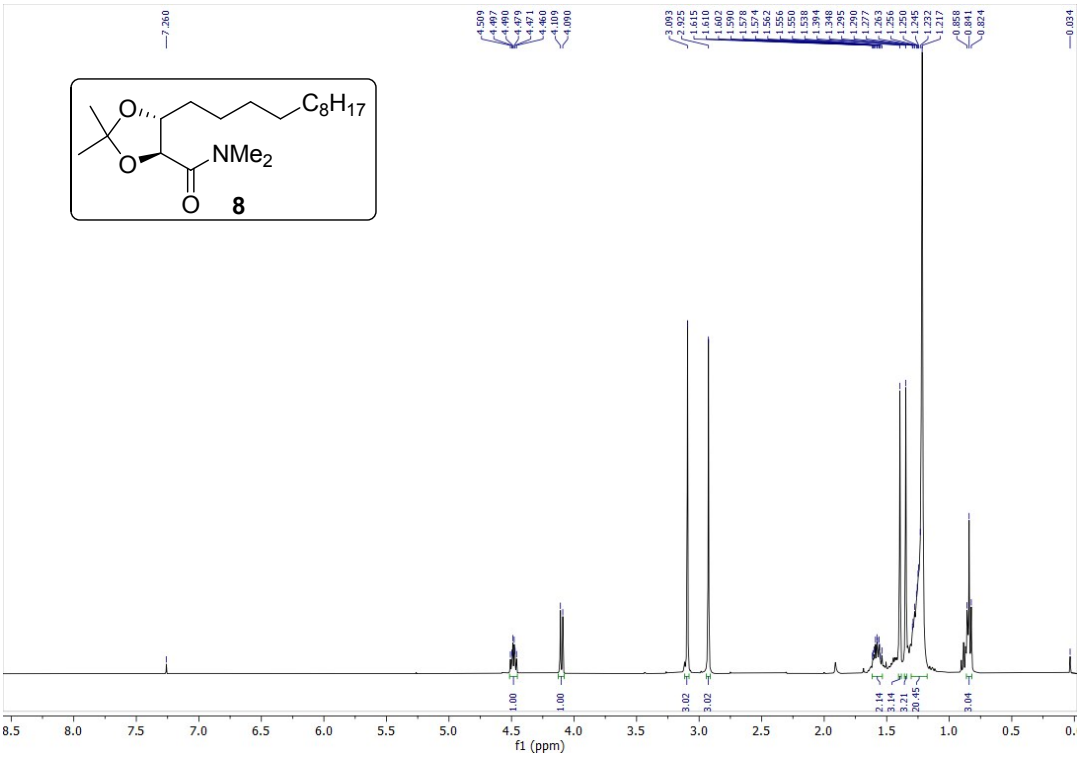
^{1}H NMR of compound **13** (400 MHz) in $CDCl_3$



^{13}C NMR of compound **13** (100 MHz) in $CDCl_3$



^{1}H NMR of compound **8** (400 MHz) in $CDCl_3$



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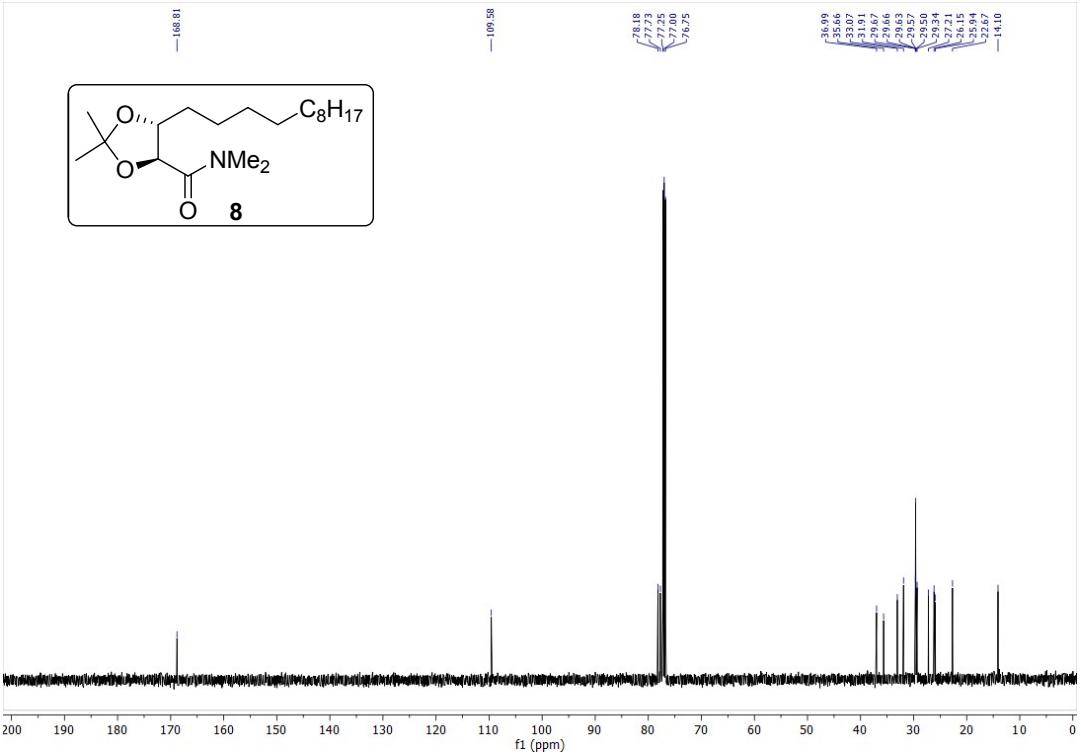

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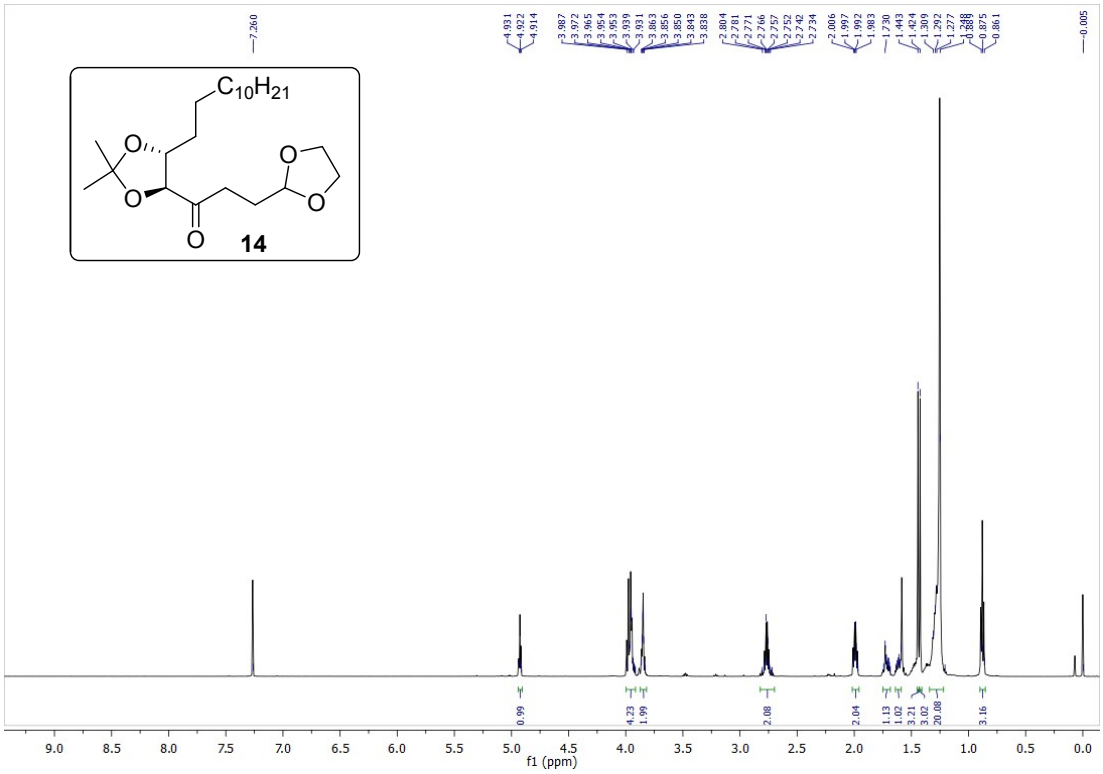
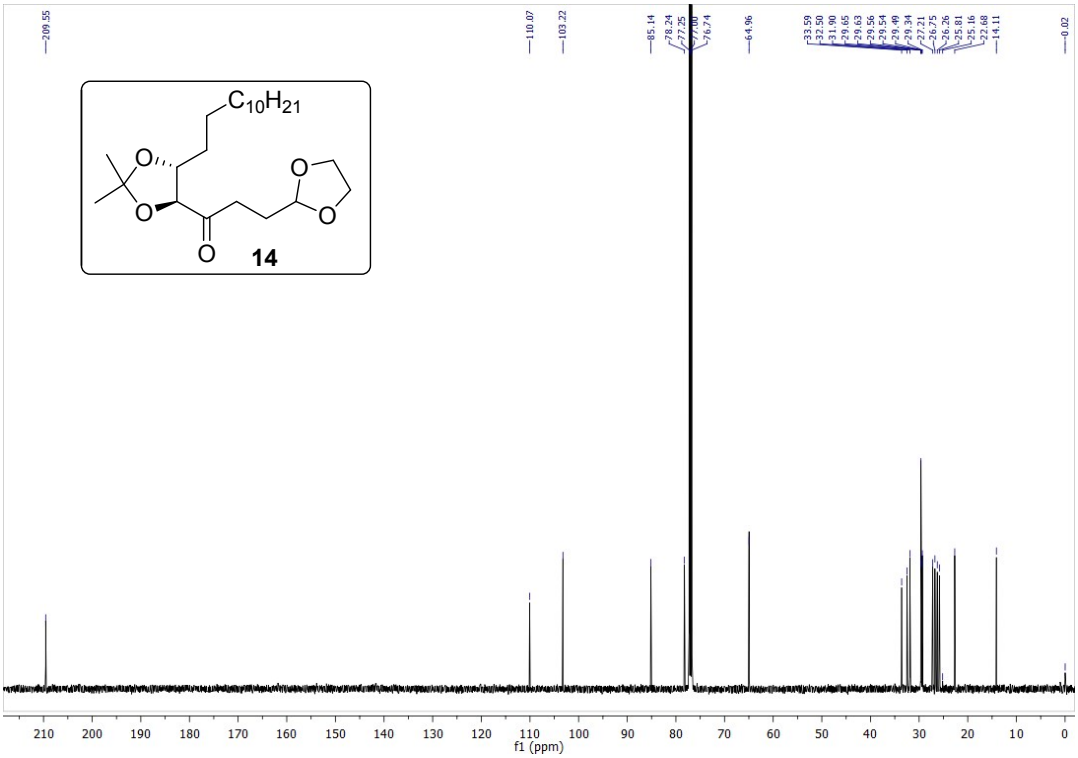


^{13}C NMR of compound **14** (125 MHz) in $CDCl_3$



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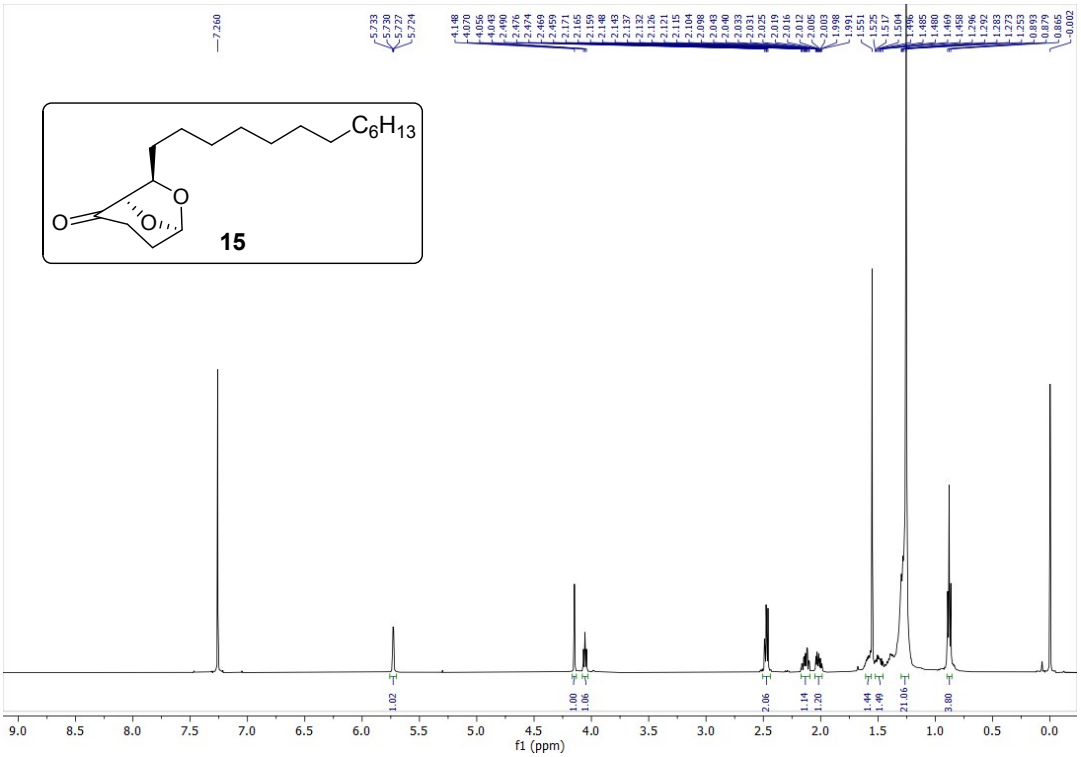

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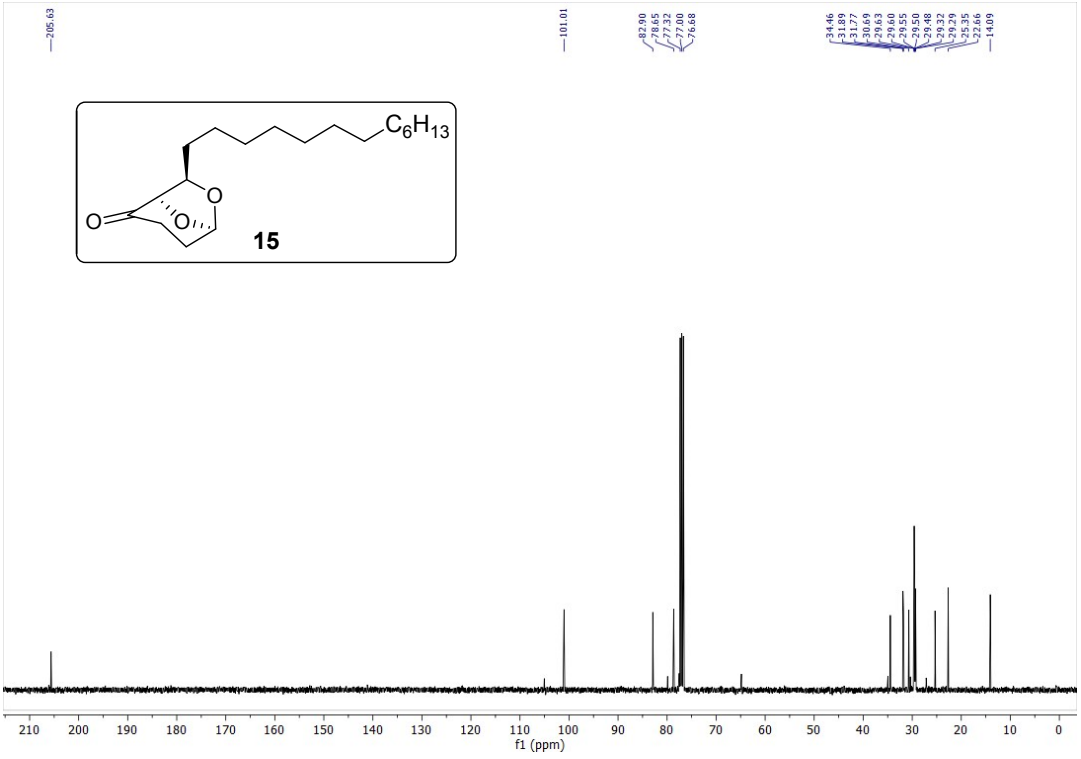

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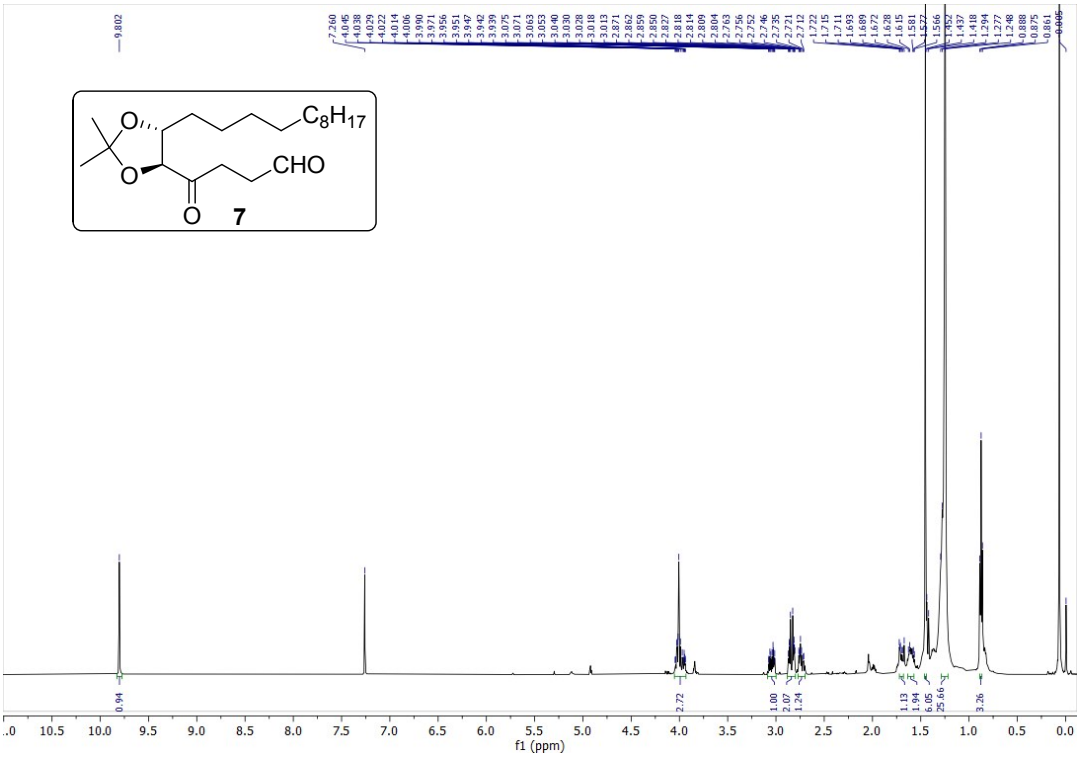
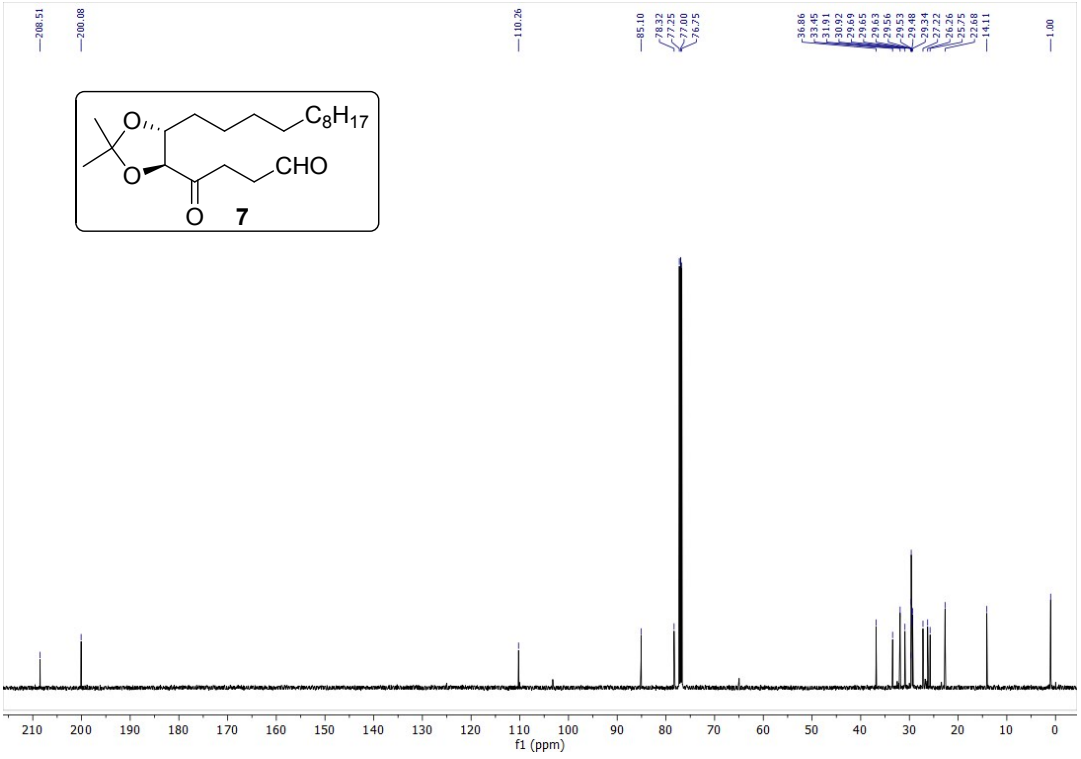
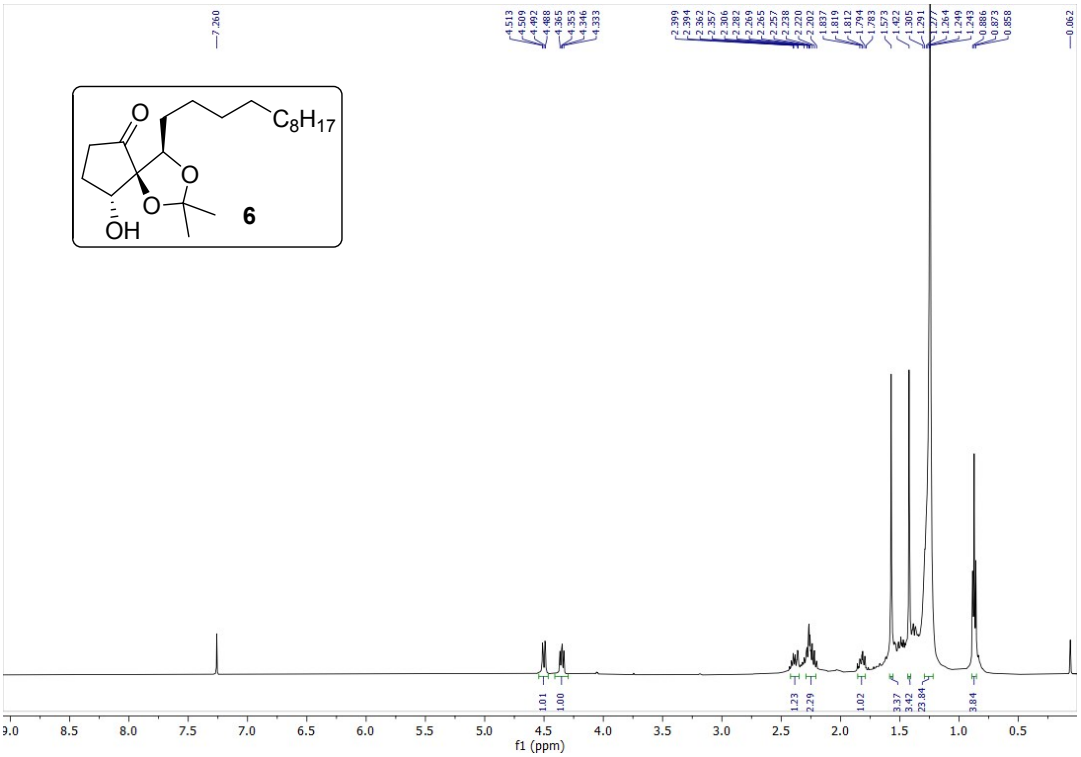


^{13}C NMR of compound **7** (125 MHz) in $CDCl_3$



^{1}H NMR of compound **6** (500 MHz) in $CDCl_3$



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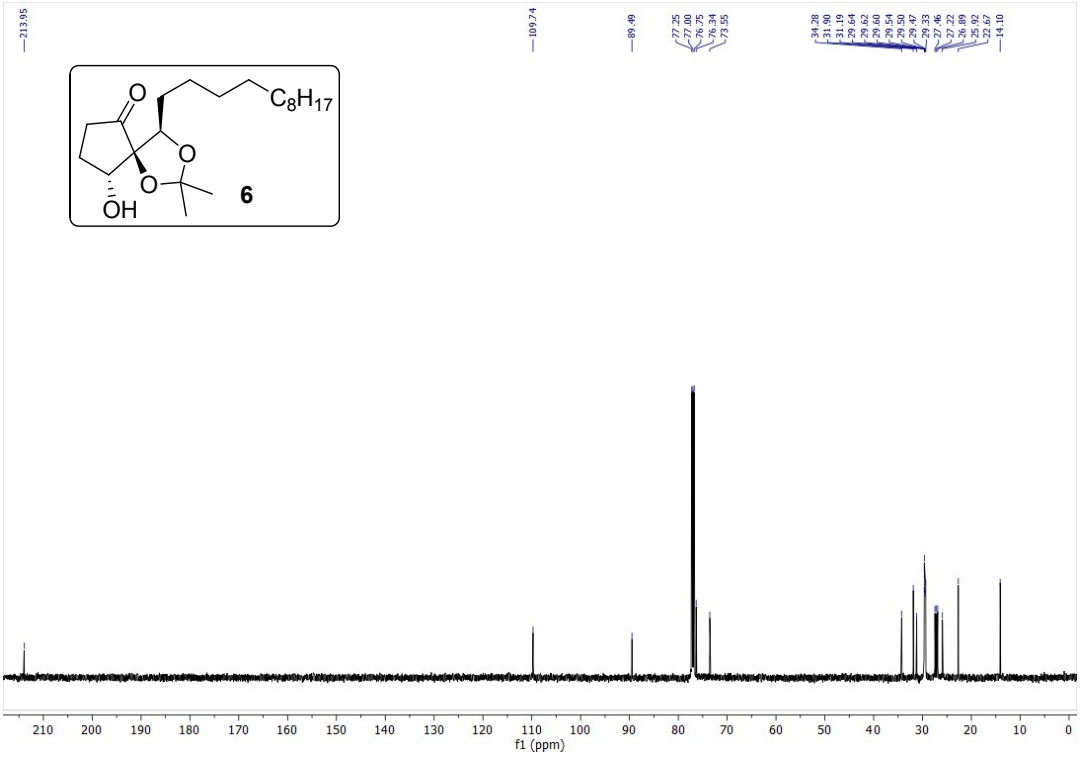

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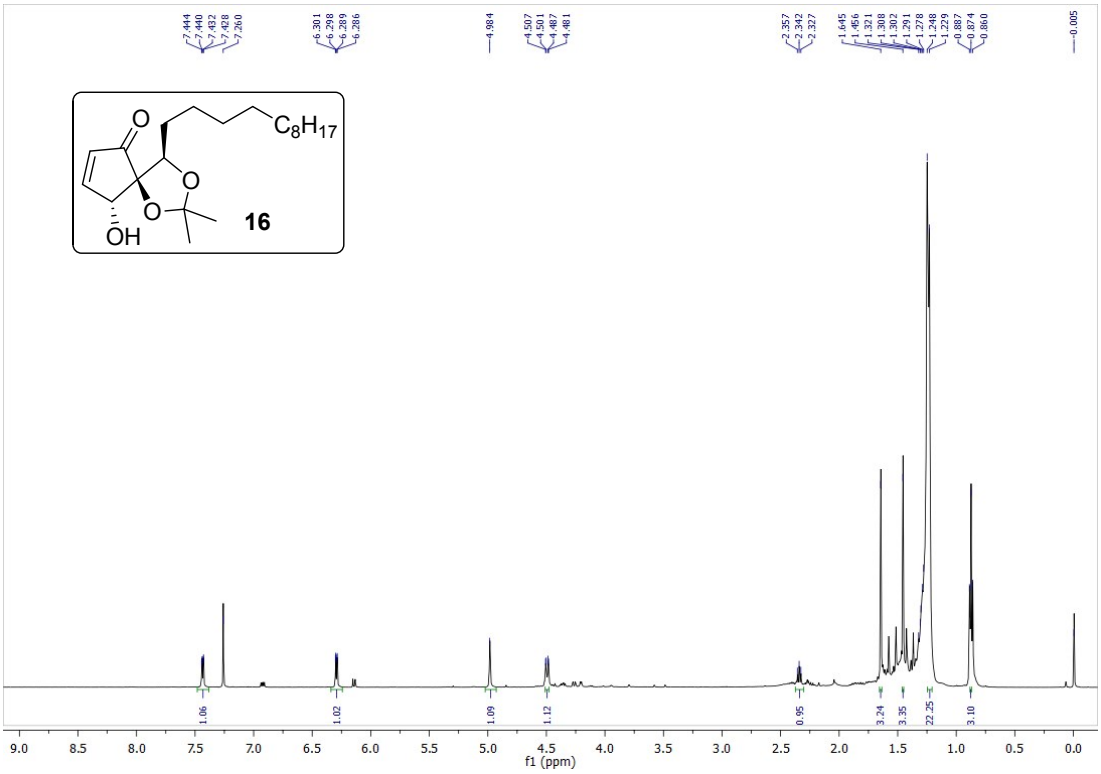
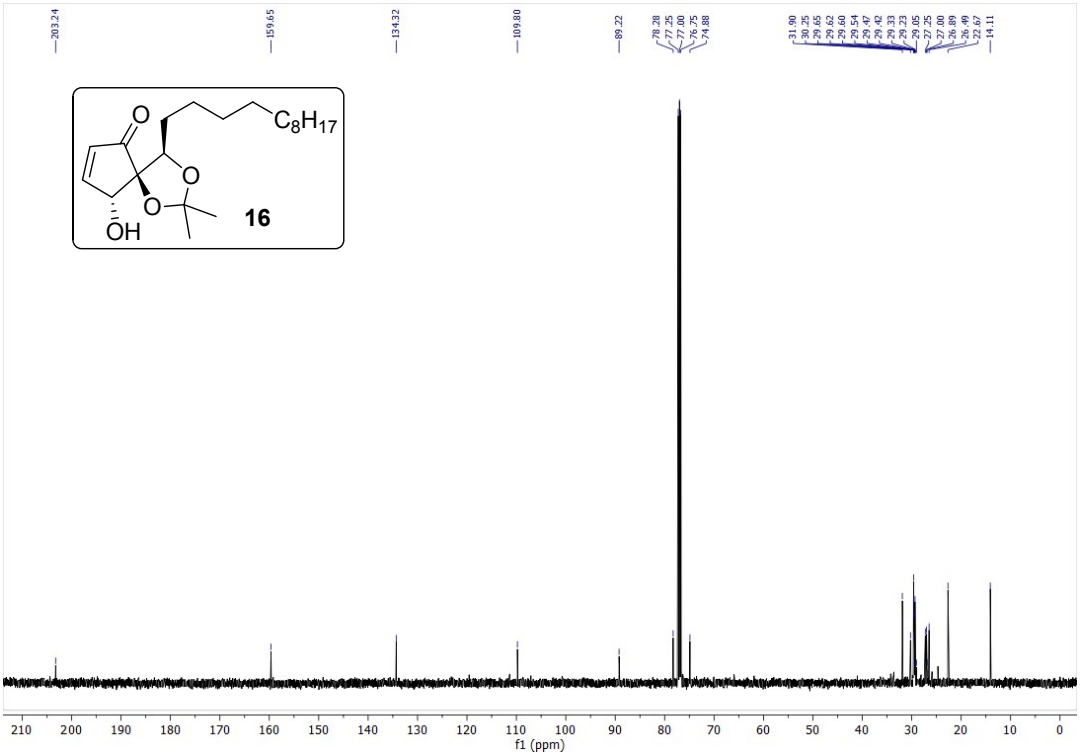
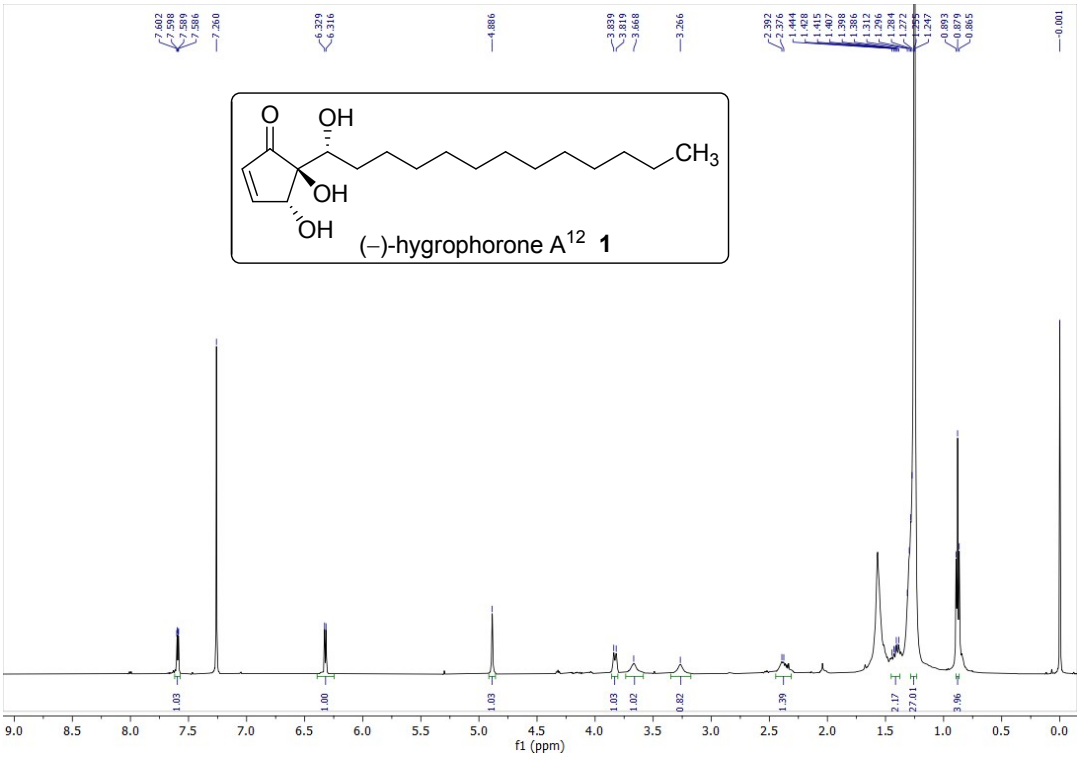


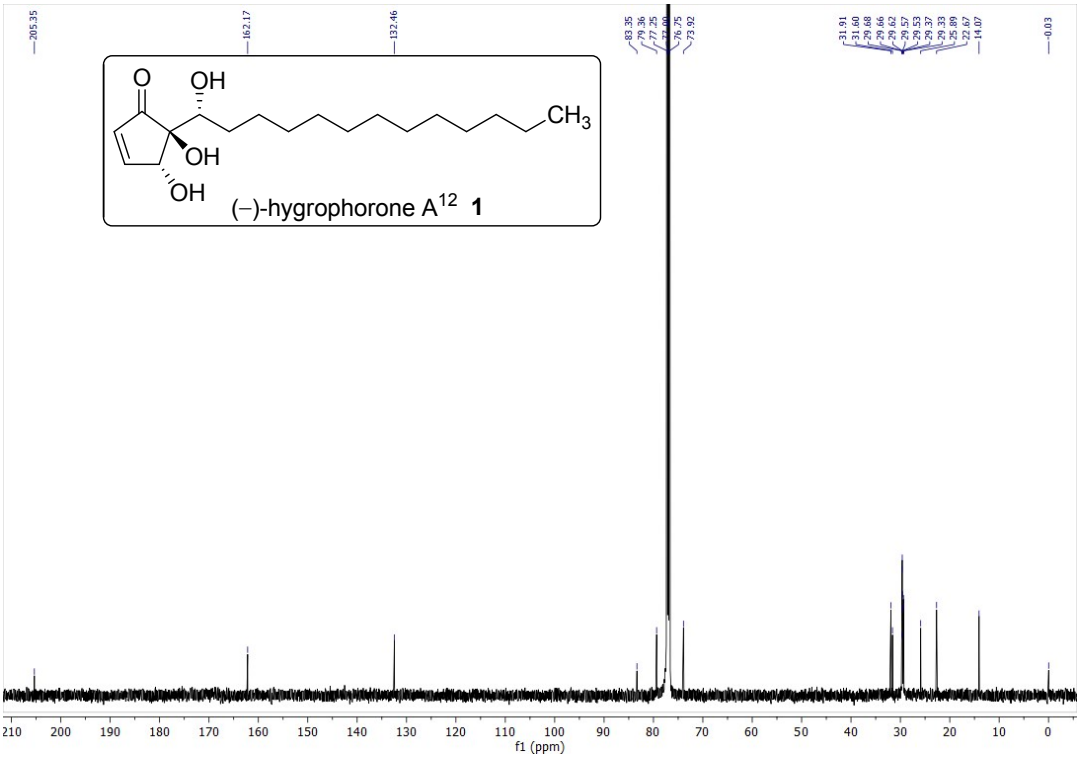
^{13}C NMR of compound **16** (125 MHz) in $CDCl_3$



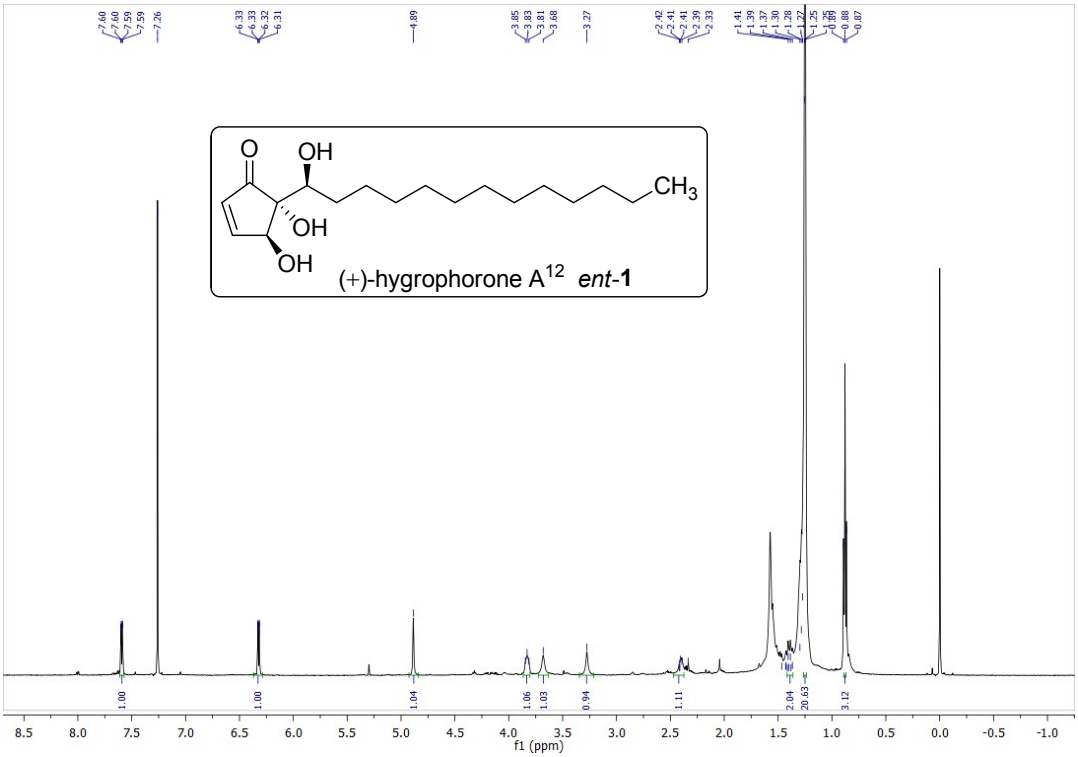
^{1}H NMR of (−)-hygrophorone A[12] **1** (500 MHz) in $CDCl_3$



^{13}C NMR of (−)-hygrophorone A[12] **1** (125 MHz) in $CDCl_3$



^{1}H NMR of (+)-hygrophorone A^{12} *ent*-**1** (500 MHz) in $CDCl_3$



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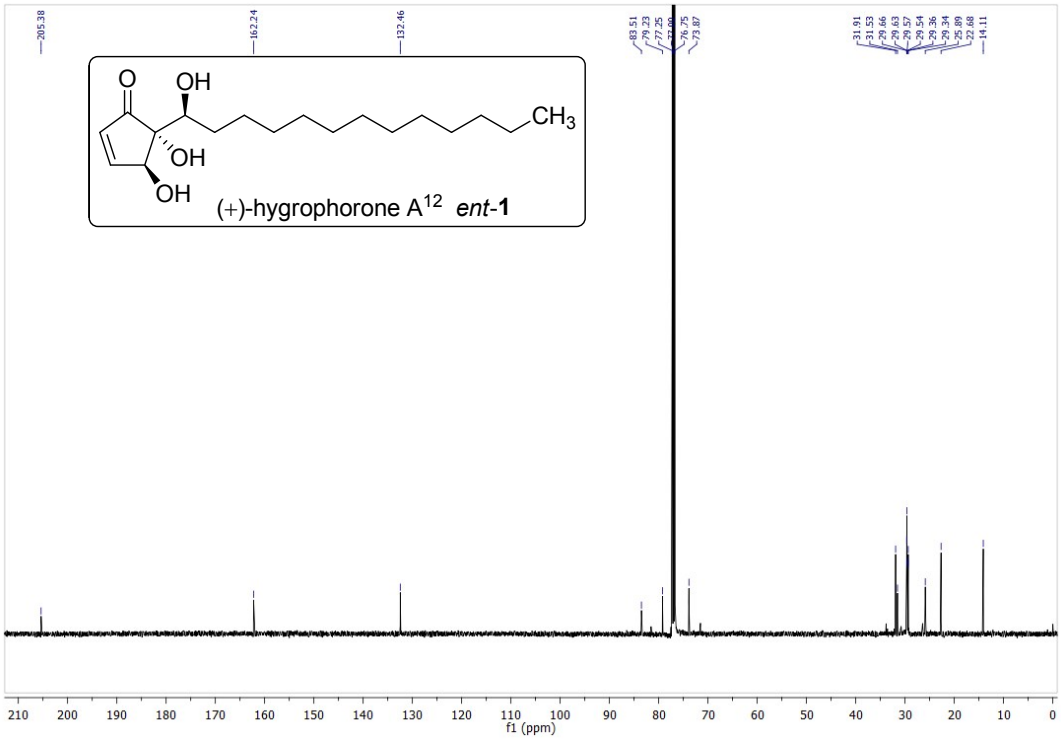
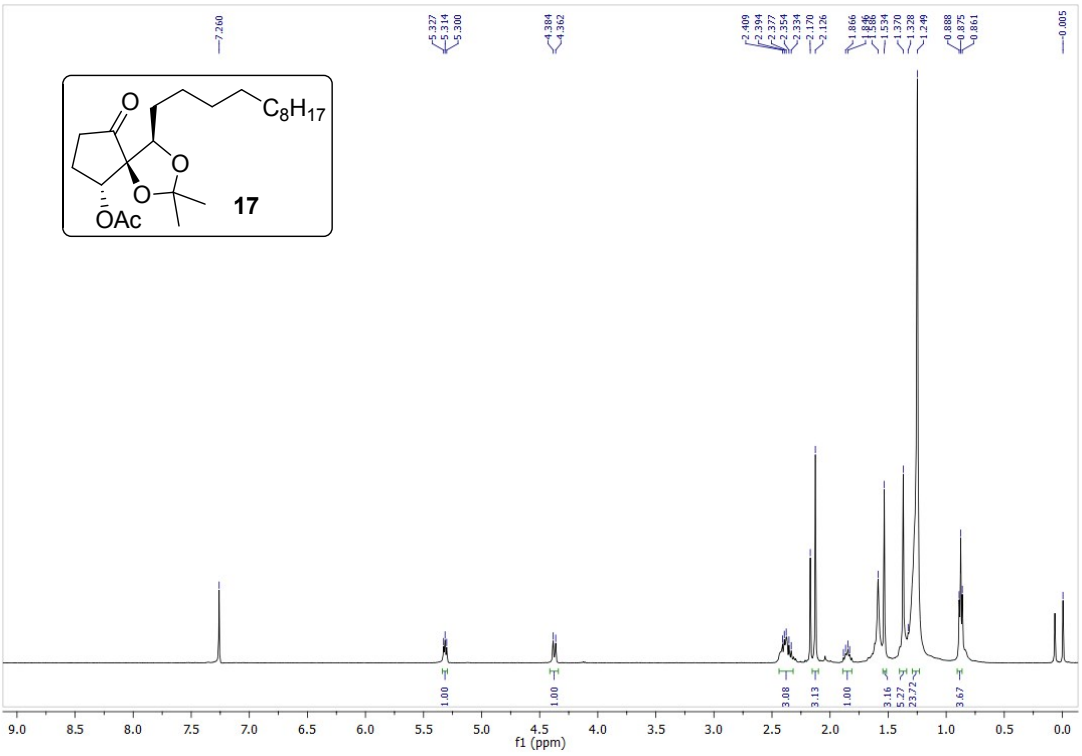
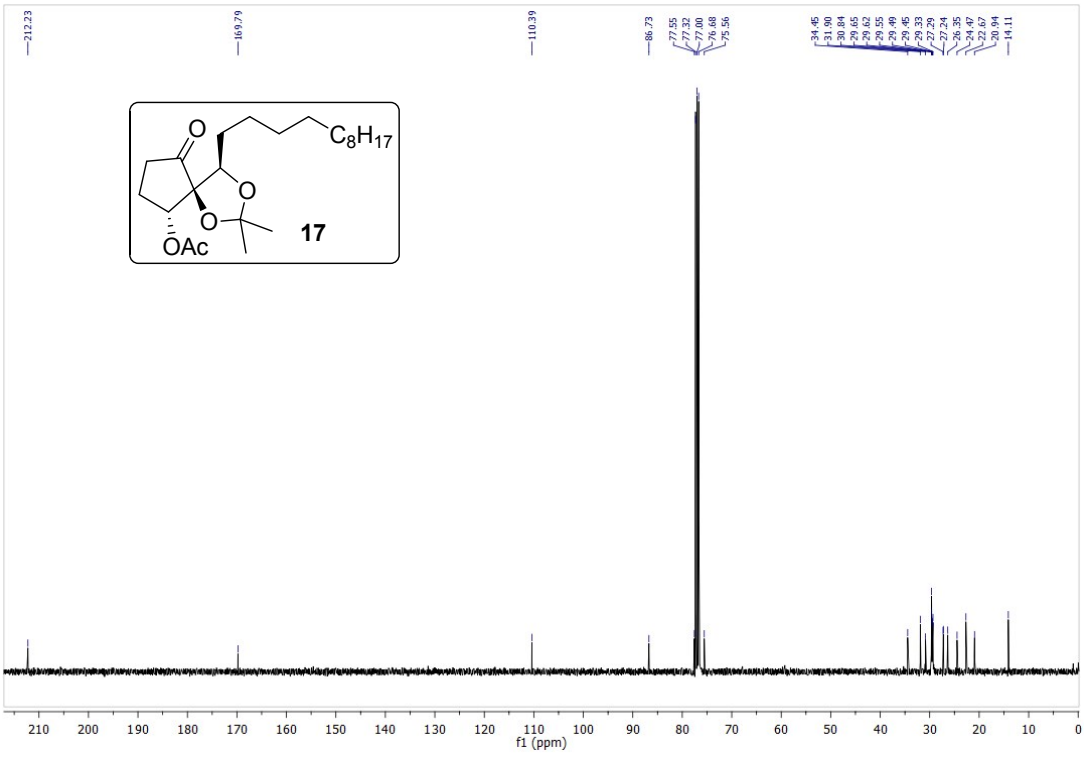


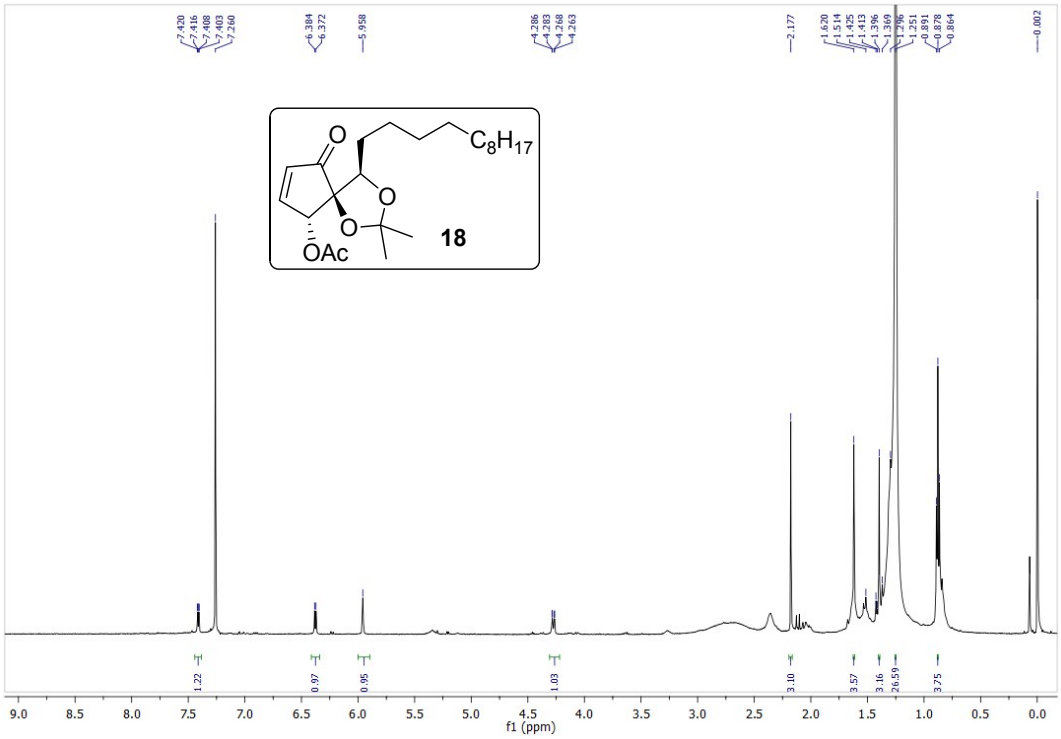
^{1}H NMR of compound **17** (500 MHz) in $CDCl_3$



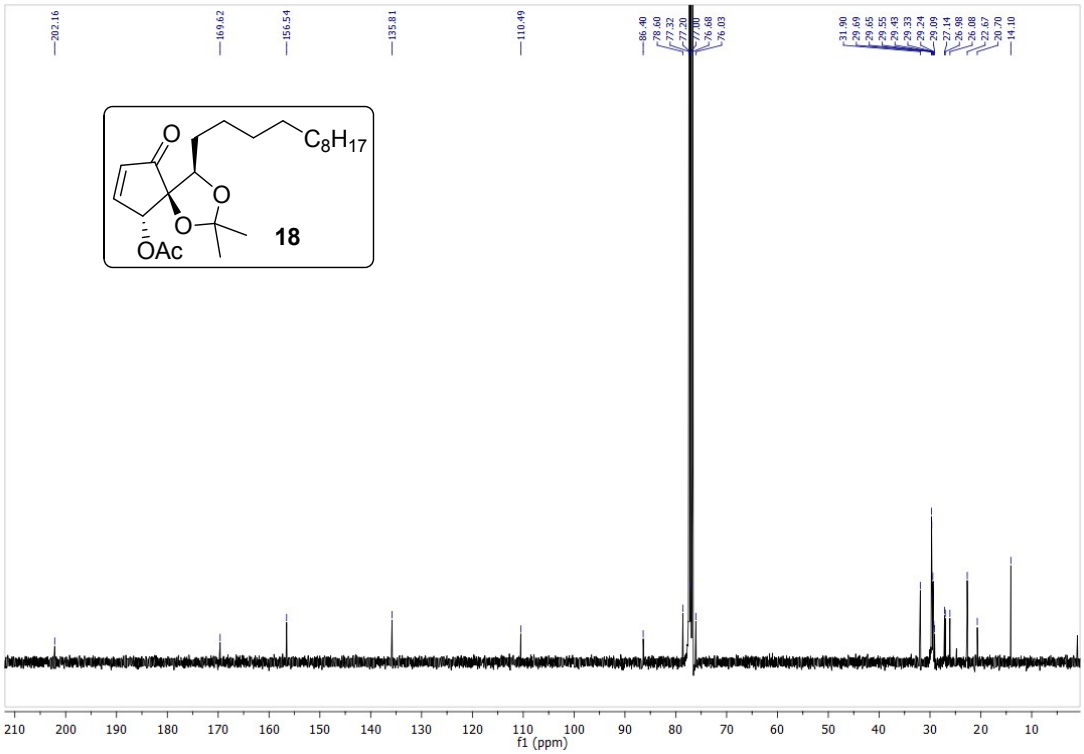
^{13}C NMR of compound **17** (100 MHz) in $CDCl_3$



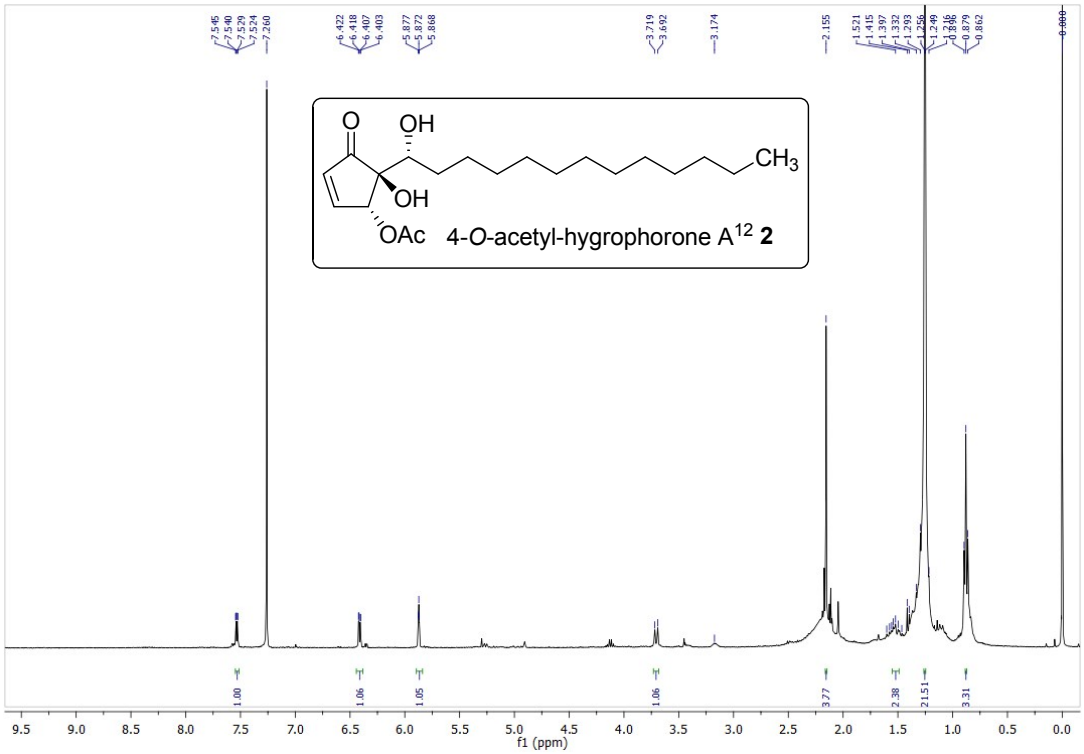
^{1}H NMR of compound **18** (500 MHz) in $CDCl_3$



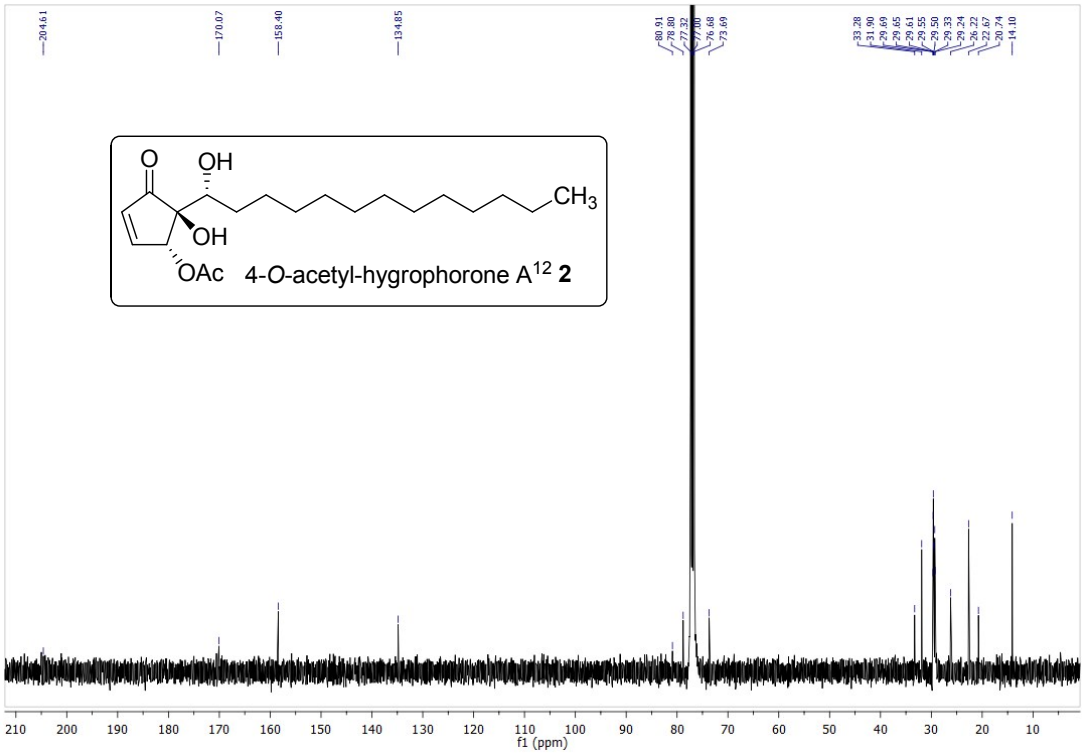
^{13}C NMR of compound **18** (100 MHz) in $CDCl_3$



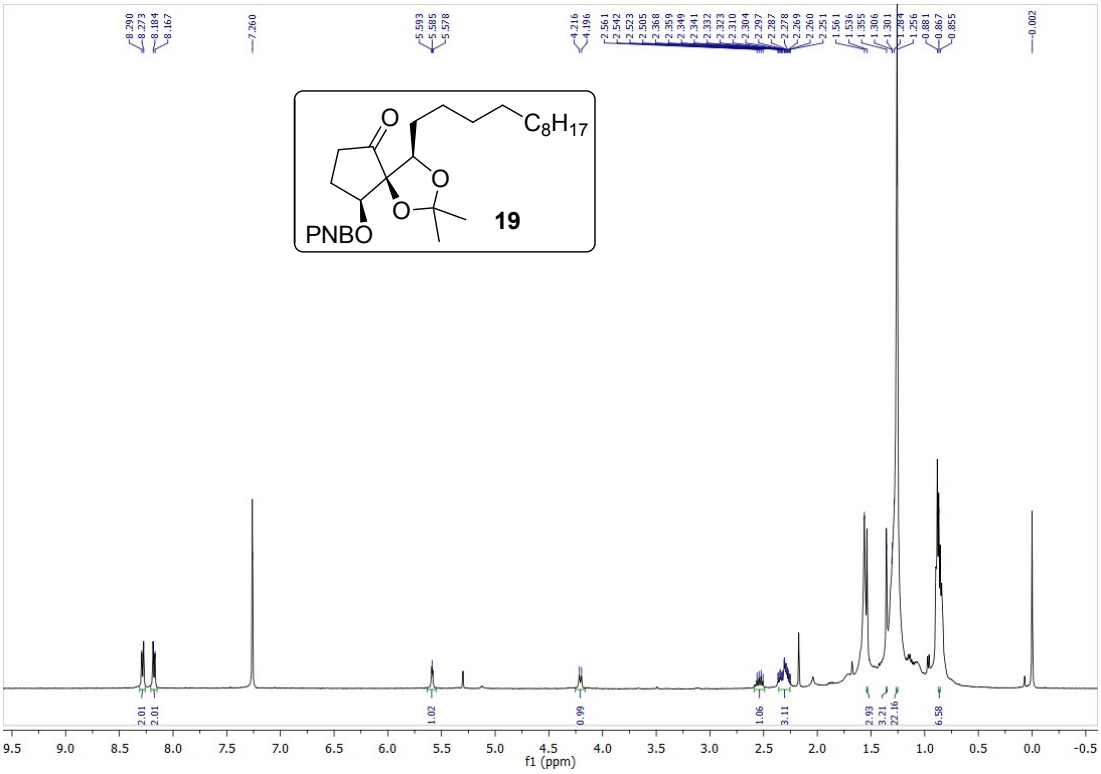
^{1}H NMR of 4-*O*-acetyl-hygrophorone A^{12} **2** (400 MHz) in $CDCl_3$



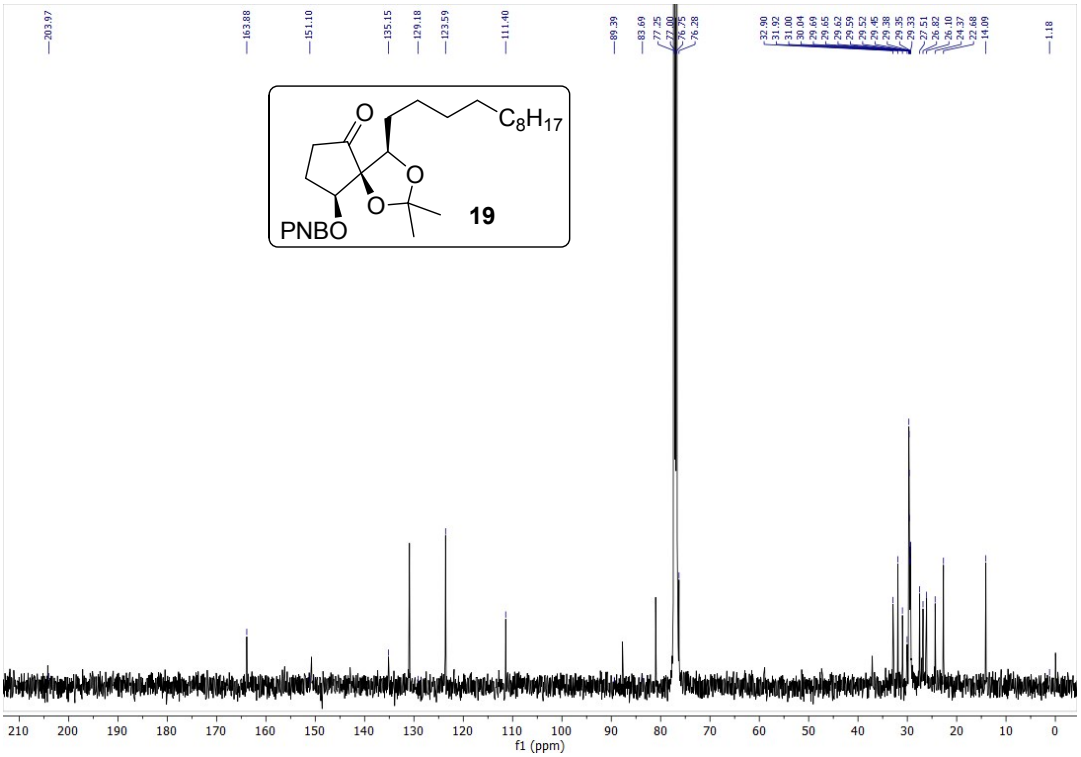
^{13}C NMR of 4-*O*-acetyl-hygrophorone A^{12} **2** (100 MHz) in $CDCl_3$



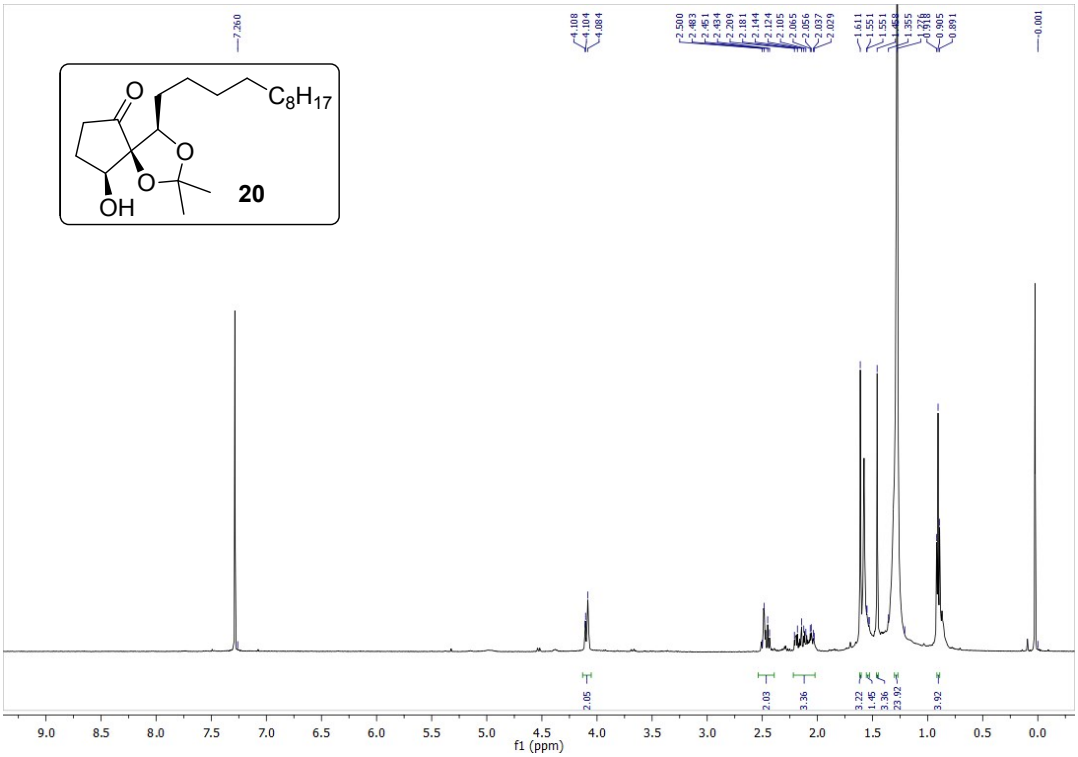
^{1}H NMR of compound **19** (500 MHz) in $CDCl_3$



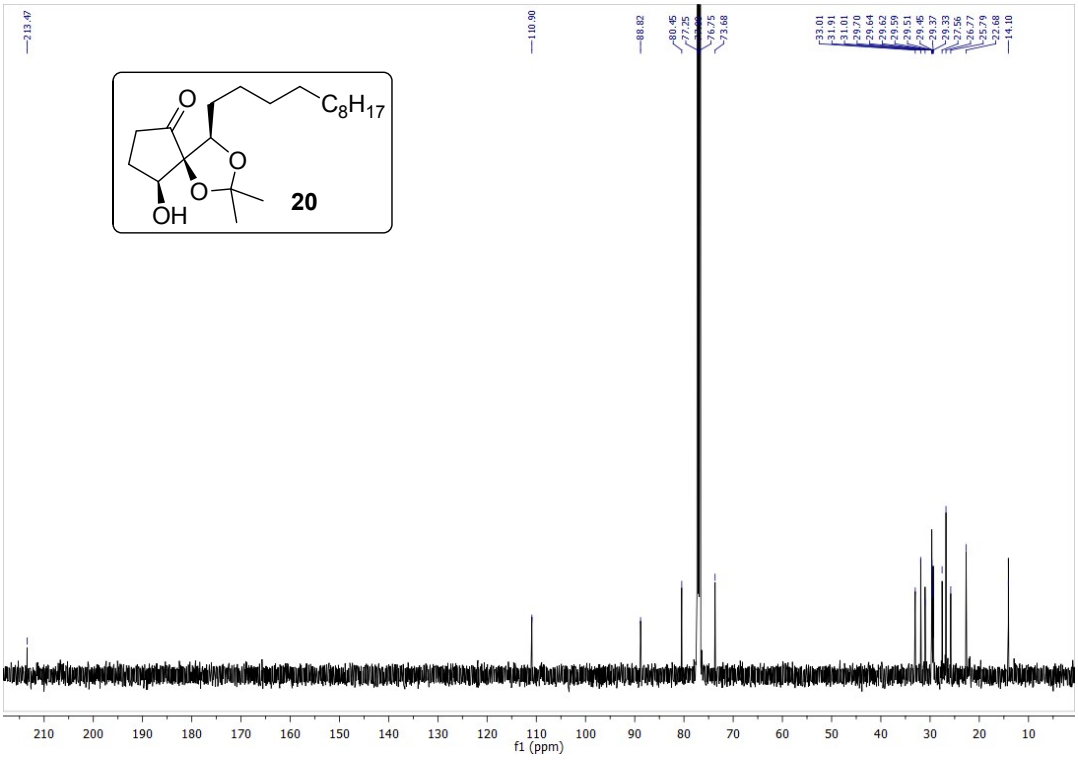
^{13}C NMR of compound **19** (125 MHz) in $CDCl_3$



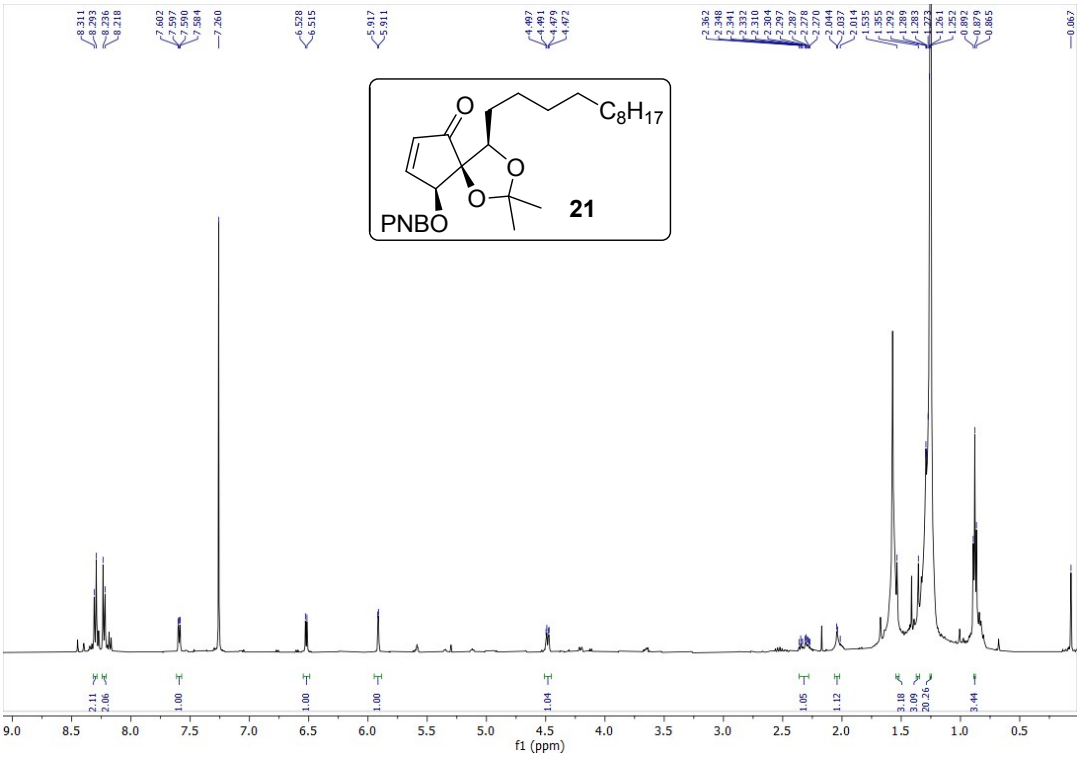
^{1}H NMR of compound **20** (500 MHz) in $CDCl_3$



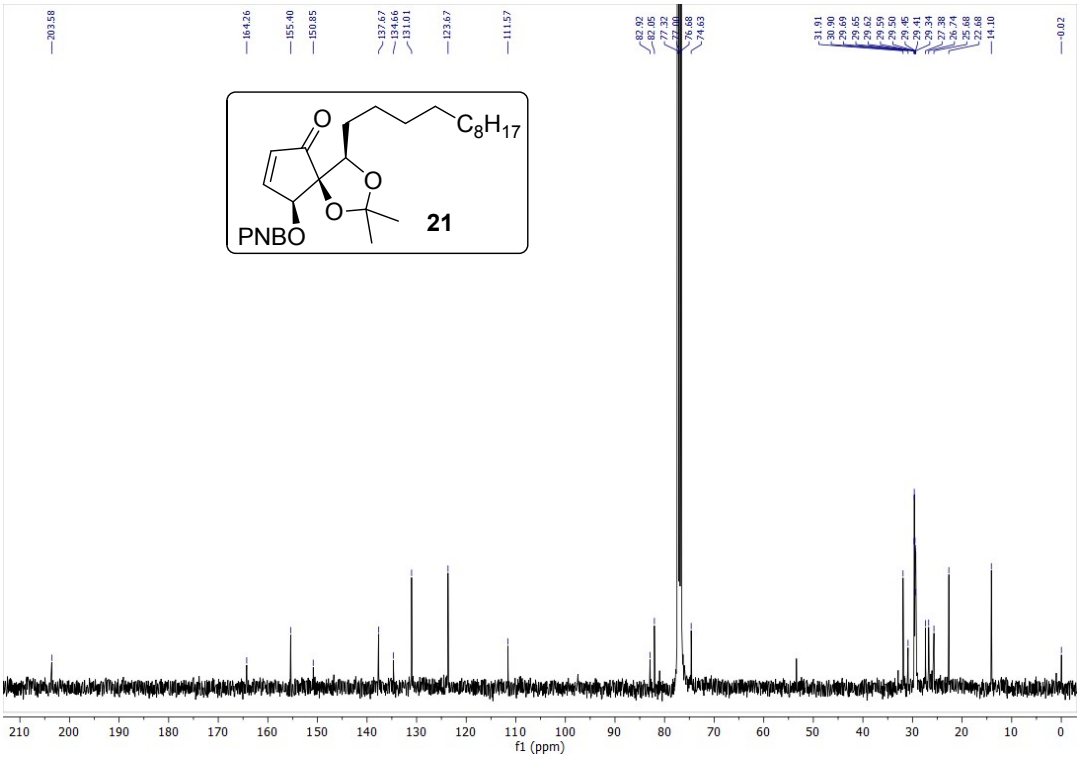
^{13}C NMR of compound **20** (125 MHz) in $CDCl_3$



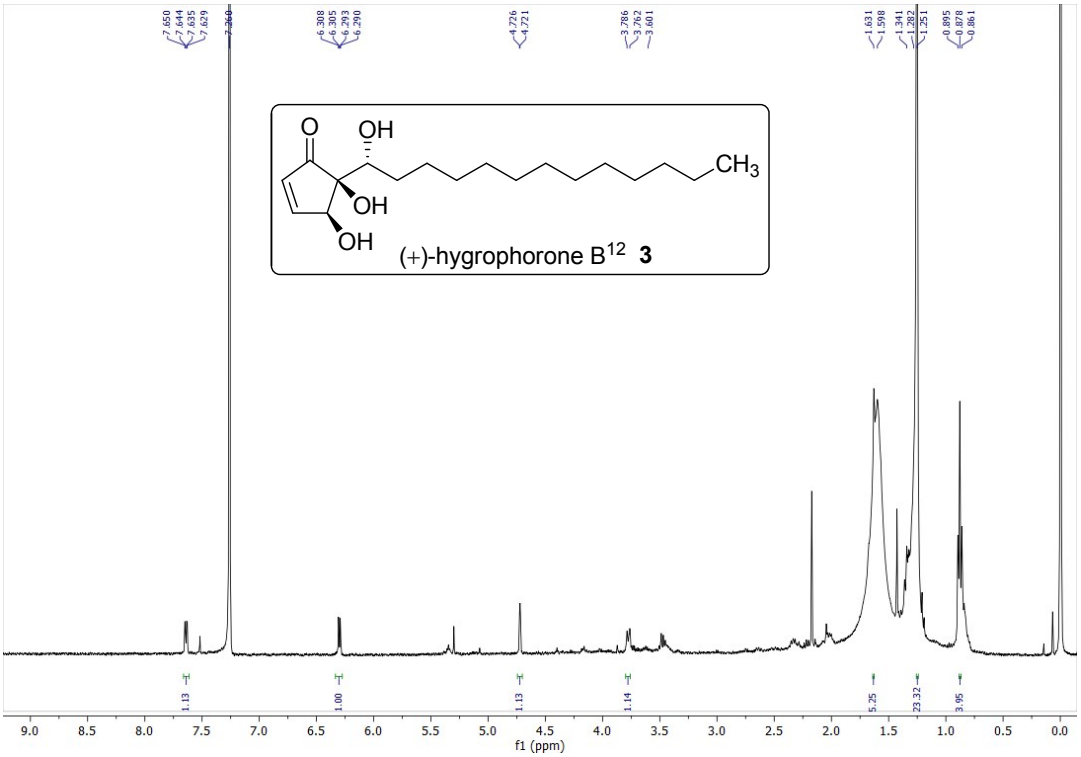
^{1}H NMR of compound **21** (500 MHz) in $CDCl_3$



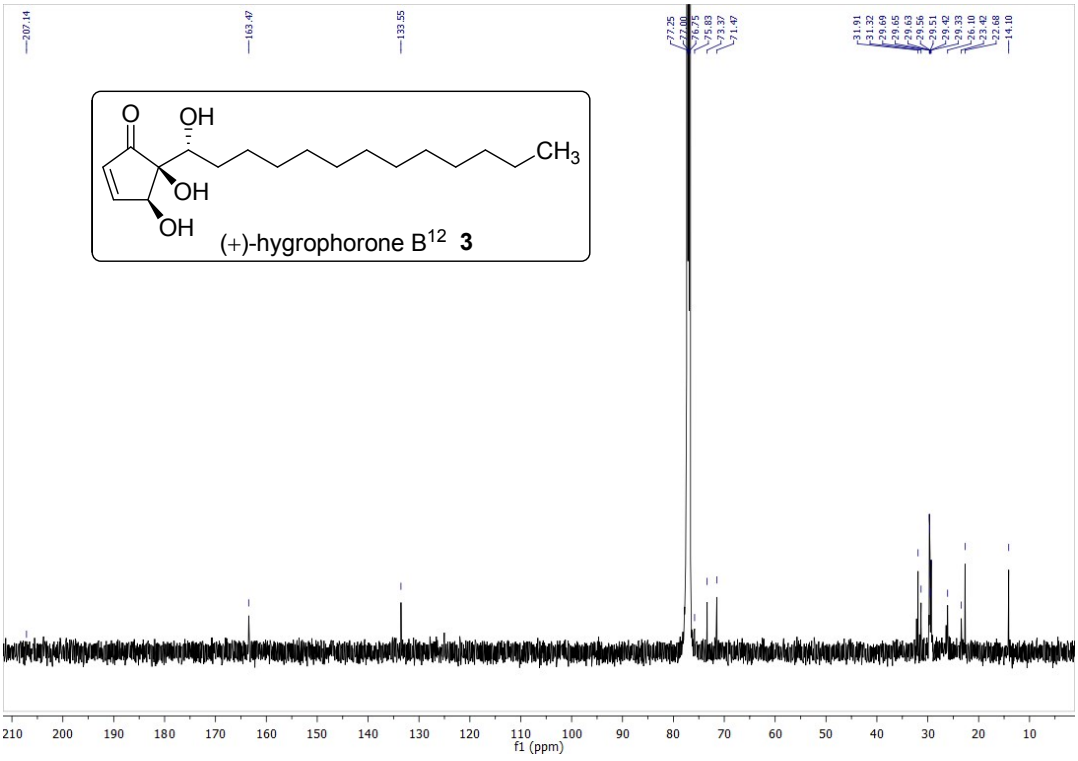
^{13}C NMR of compound **21** (100 MHz) in $CDCl_3$



^{1}H NMR of (+)-hygrophorone B^{12} **3** (400 MHz) in $CDCl_3$



^{13}C NMR of (+)-hygrophorone B^{12} **3** (125 MHz) in $CDCl_3$



Single crystal X-ray diffraction data for (+)-hygrophorone A^{12} *ent*-1 was collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer (Table S1).[1] The crystals were covered with Paratone-N and mounted on a glass capillary. The data was collected at 273 K using Mo Kα radiation (λ = 0.71073 Å). The integration of data was performed using the SAINT. Empirical absorption correction was applied using SADABS.[2] Structural solution was accomplished by direct method and refined by full-matrix least-square on F 2 using either SHELXTL[3] or SHELXL-2013 incorporated in OLEX2. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were fixed according to a riding model and were refined isotropically. Important crystallographic data are provided in Table S1.[4]

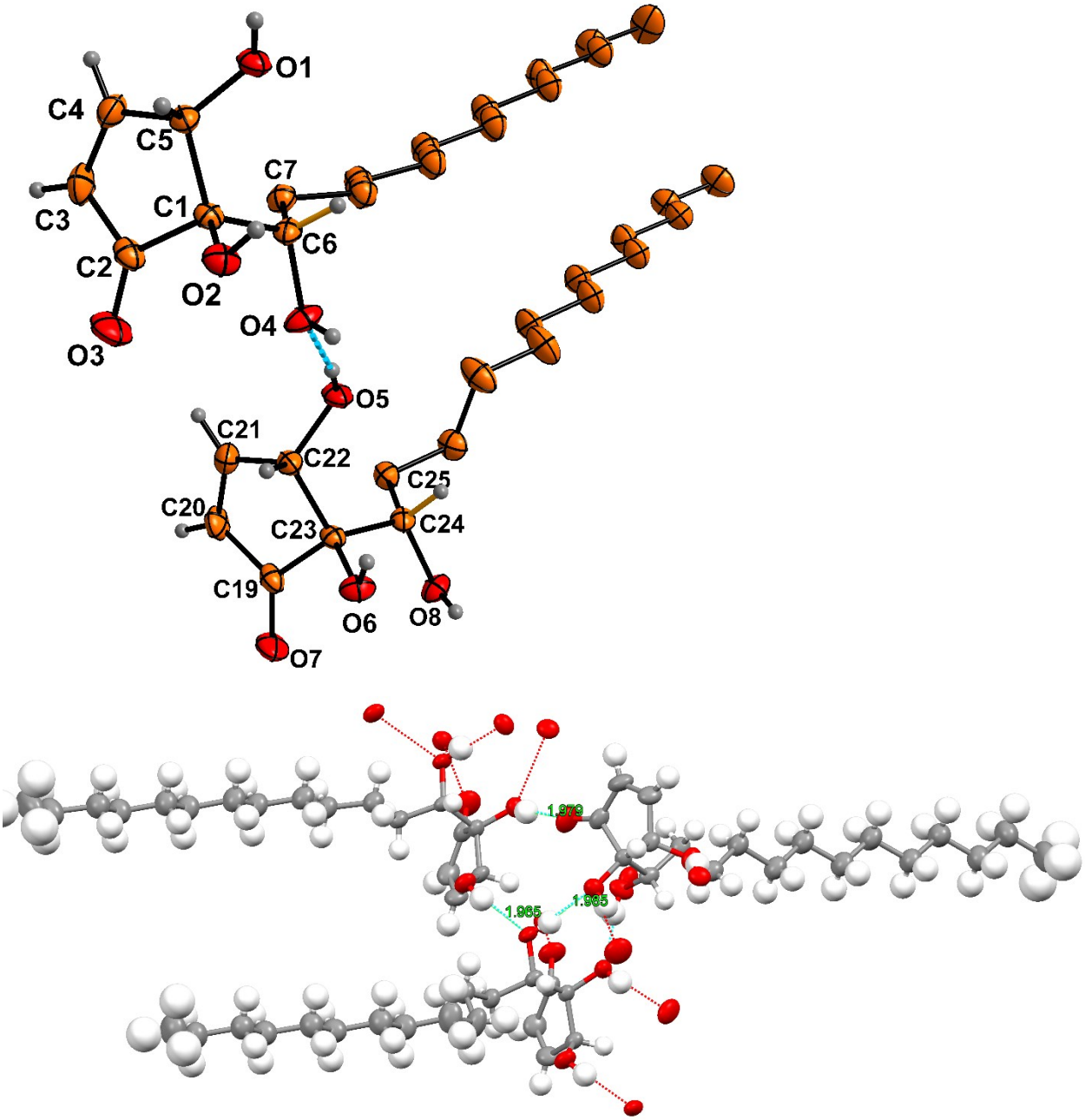


Figure 1. Molecular structure of (+)-hygrophorone A[12] *ent*-**1** from X-ray crystallography. All hydrogen atoms of alkyl chains are omitted for clarity and and thermal ellipsoids are shown at the 30% probability level. Data collection temperature: 273 K.

Table S1. Crystal data and structure refinement for (+)-hygrophorone *ent*-1

Empirical formula	$C_{18}H_{32}O_4$
Formula weight	312.44
Temperature, K	273.15
Wavelength, Å	0.71073
Crystal system	monoclinic
Space group	$P2_1$
a, Å	7.9985(6)
b, Å	10.3197(6)
c, Å	22.4140(14)
α, deg	90
β, deg	93.464(2)
γ, deg	90
Volume, $Å^3$	1846.7(2)
Z	4
Density (calcd), mg/m^3	1.124
Absorption coefficient, mm^{-1}	0.077
F(000)	688.0
Crystal size, mm^3	0.17 × 0.12 × 0.11
θ range for data collection, deg	4.346 to 56.612
Limiting indices	$-10 \le h \le 10$, $-13 \le k \le 13$, $-29 \le l \le 29$
No. of reflection collected	48074
No. of independent reflection	9176
Refinement method	Full-matrix least-squares on F^2
No. of data/restraints/ parameters	9176/1/405
Goodness-of-fit on F^2	1.025
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0501$, $wR_2 = 0.1023$
R indices (all data)	$R_1 = 0.0862$, $wR_2 = 0.1169$
Largest diff peak and hole, e $Å^{-3}$	0.14/-0.16

References:

1. SMART, Bruker Molecular Analysis Research Tool, Version 5.618, Bruker AXS, Madison, WI (2000).

2. SAINT-NT, Version 6.04; Bruker AXS, WI (2001).

3. SHELXTL-NT, Version 6.10, Bruker AXS, Madison, WI (2000).

4. **CCDC 2035478** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.