Supplementary Material

Application of intramolecular carbonyl-ene reaction towards the synthesis of idarubicinone scaffold

Shyam Basak, Sutapa Ray and Dipakranjan Mal*

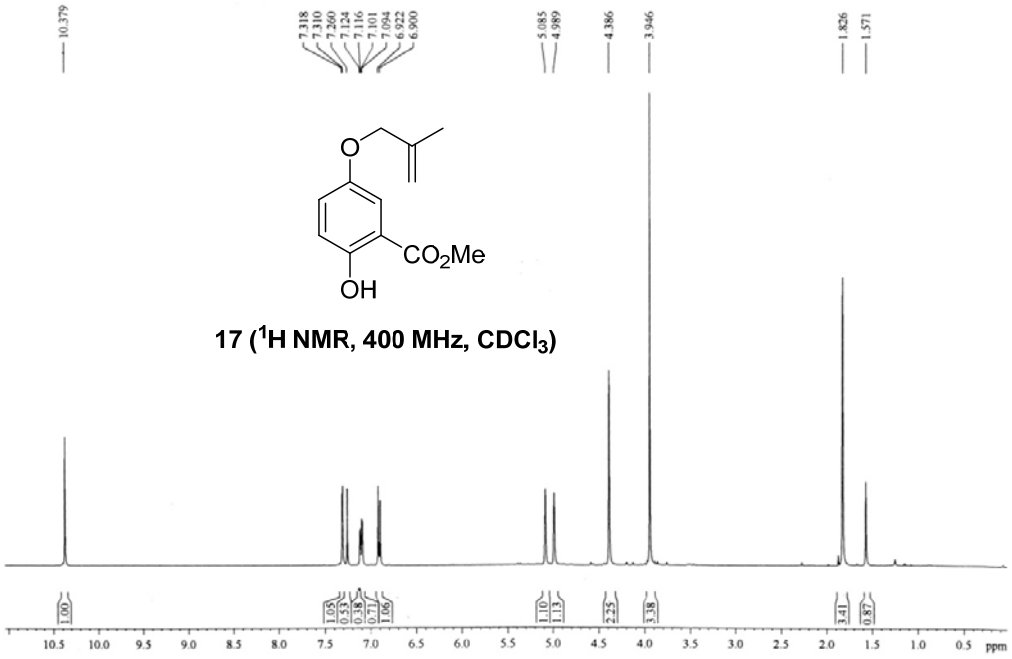
Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India
E-mail: dmal@chem.iitkgp.ernet.in

Table of Contents

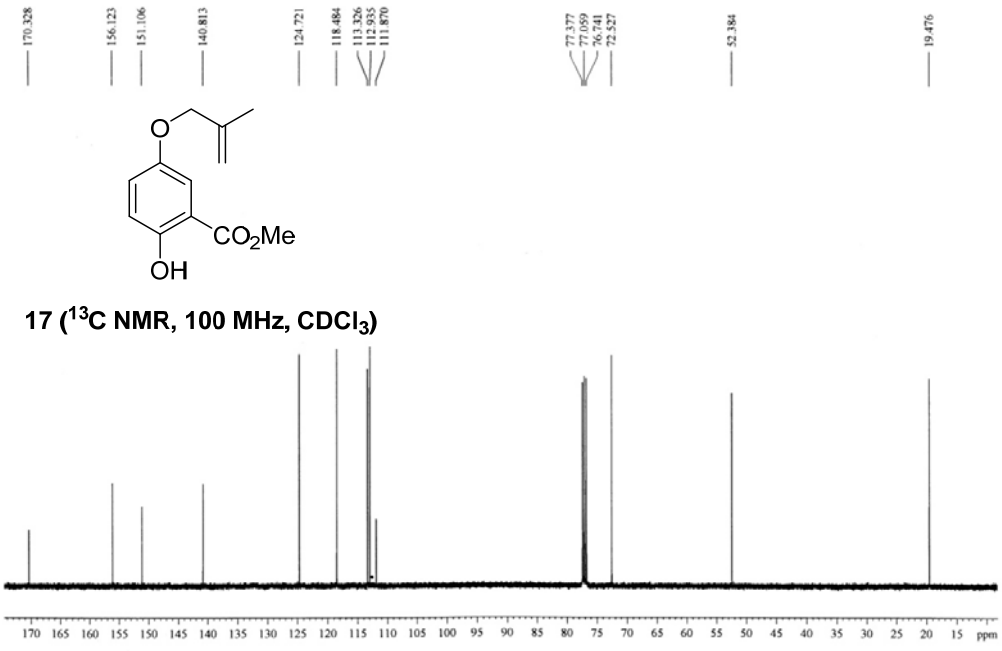
Spectra S2
References S28

©ARKAT USA, Inc

^{1}H, ^{13}C NMR spectra of synthesized compounds:

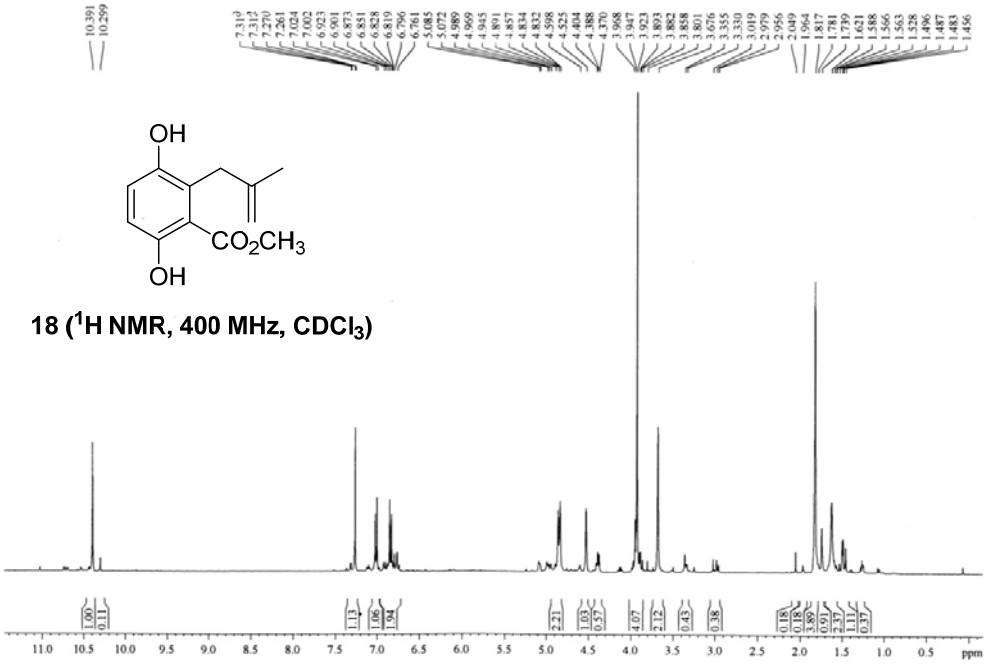


17 (^{1}H NMR, 400 MHz, $CDCl_3$)

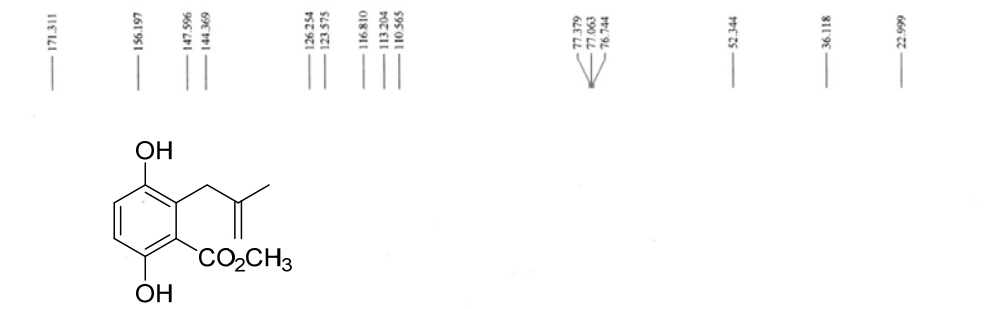


17 (^{13}C NMR, 100 MHz, $CDCl_3$)

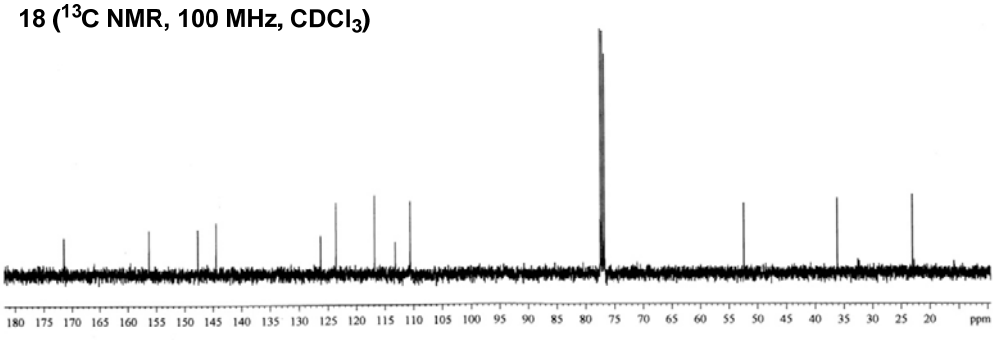
©ARKAT USA, Inc



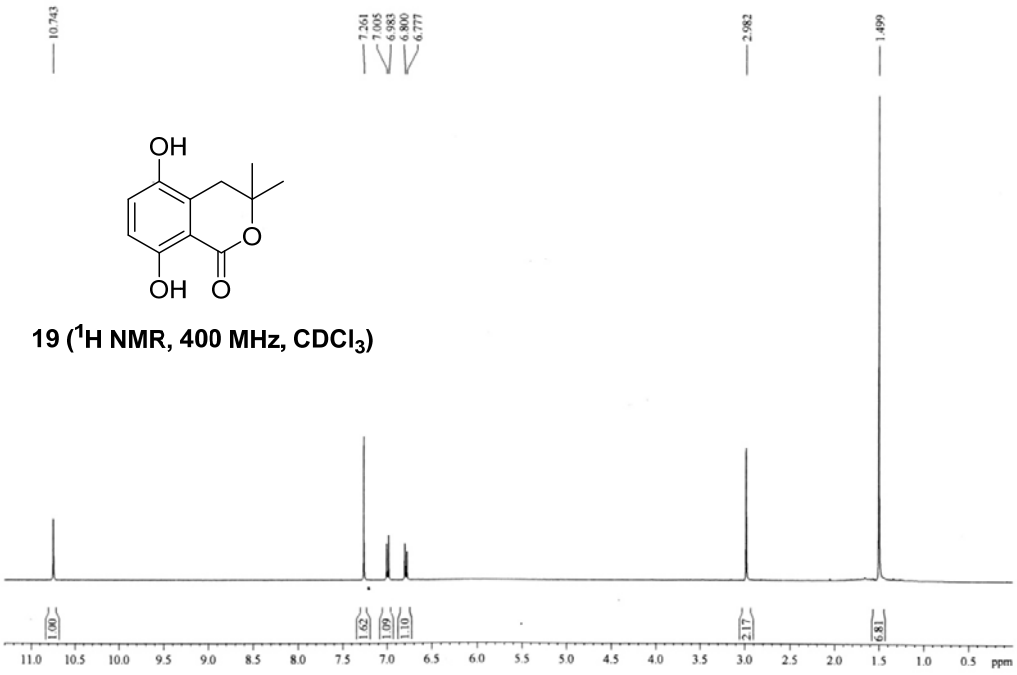
18 (^{1}H NMR, 400 MHz, $CDCl_3$)



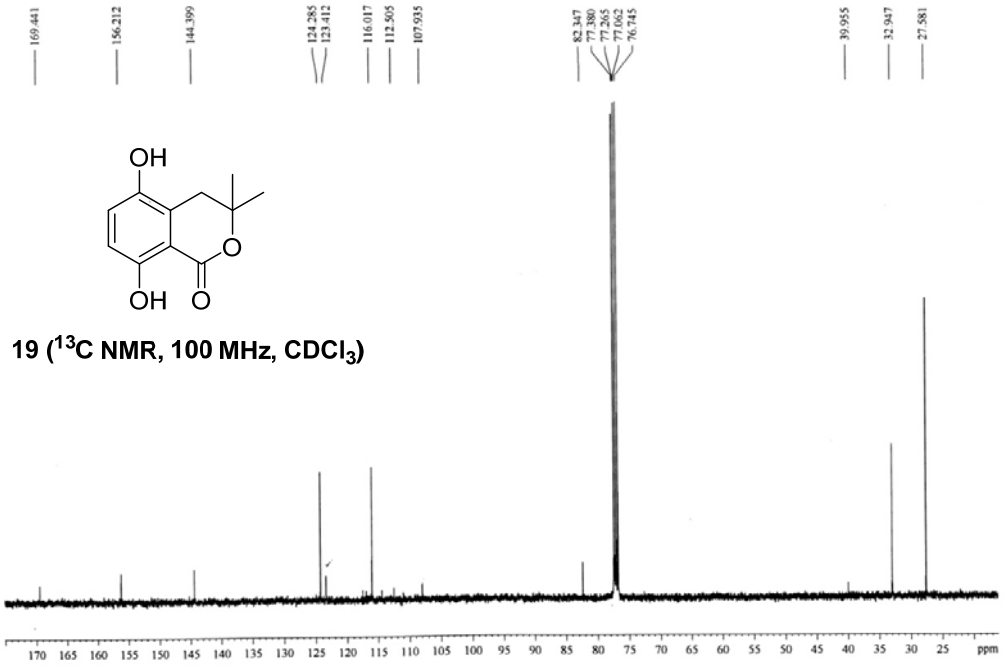
18 (^{13}C NMR, 100 MHz, $CDCl_3$)



©ARKAT USA, Inc

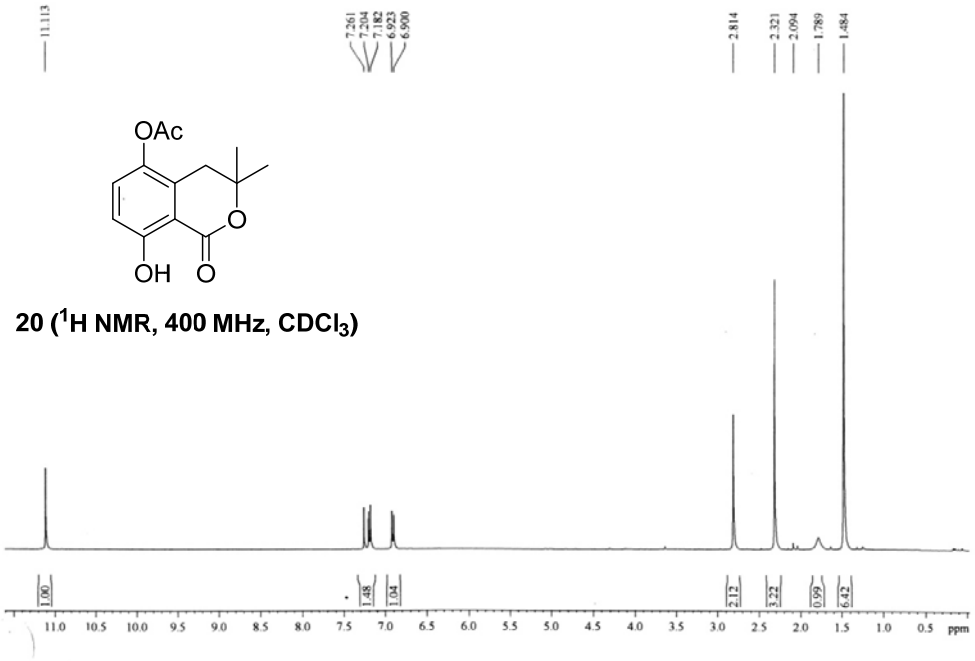


19 (^{1}H NMR, 400 MHz, $CDCl_3$)

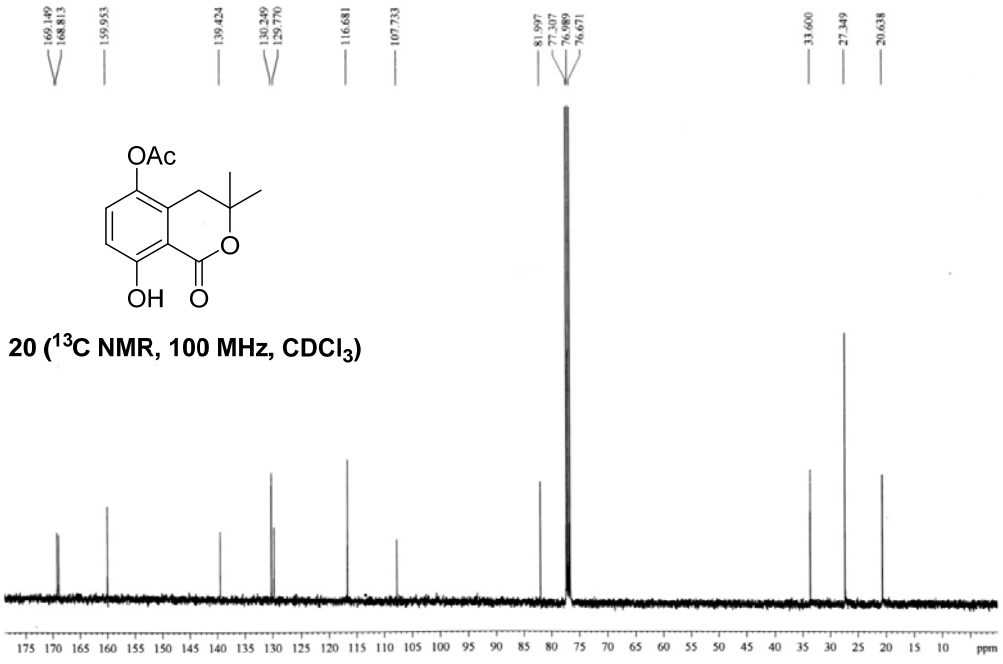


19 (^{13}C NMR, 100 MHz, $CDCl_3$)

©ARKAT USA, Inc

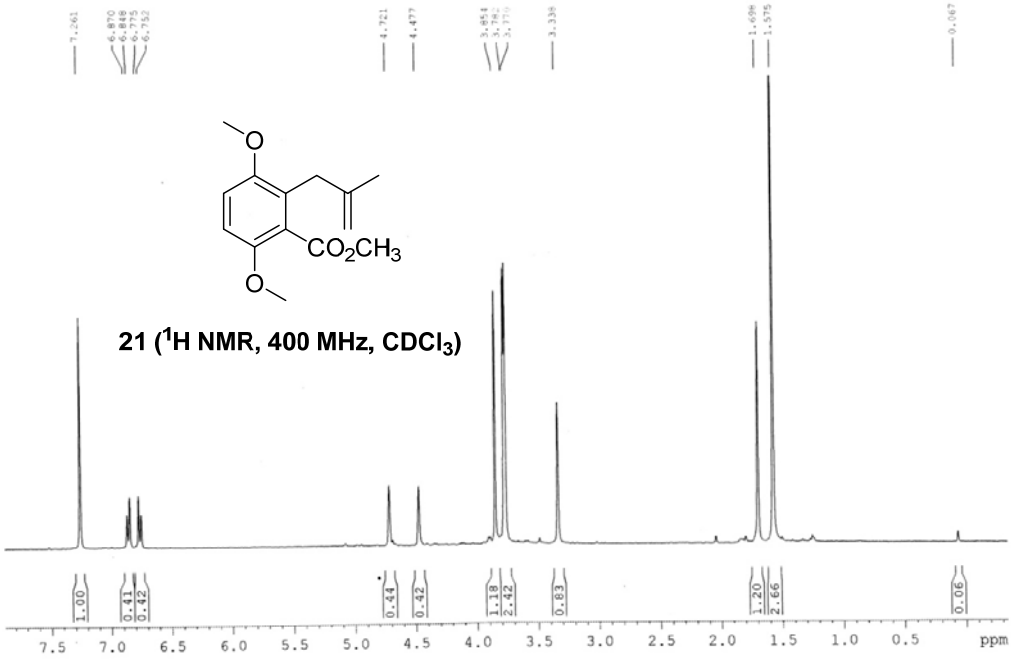


20 (^{1}H NMR, 400 MHz, $CDCl_3$)

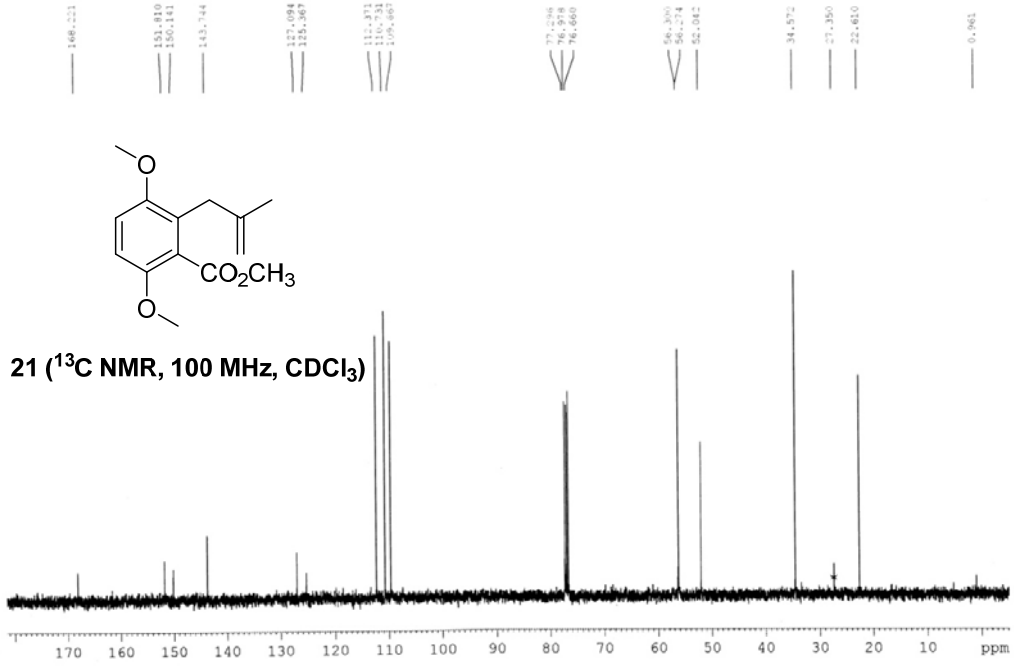


20 (^{13}C NMR, 100 MHz, $CDCl_3$)

©ARKAT USA, Inc

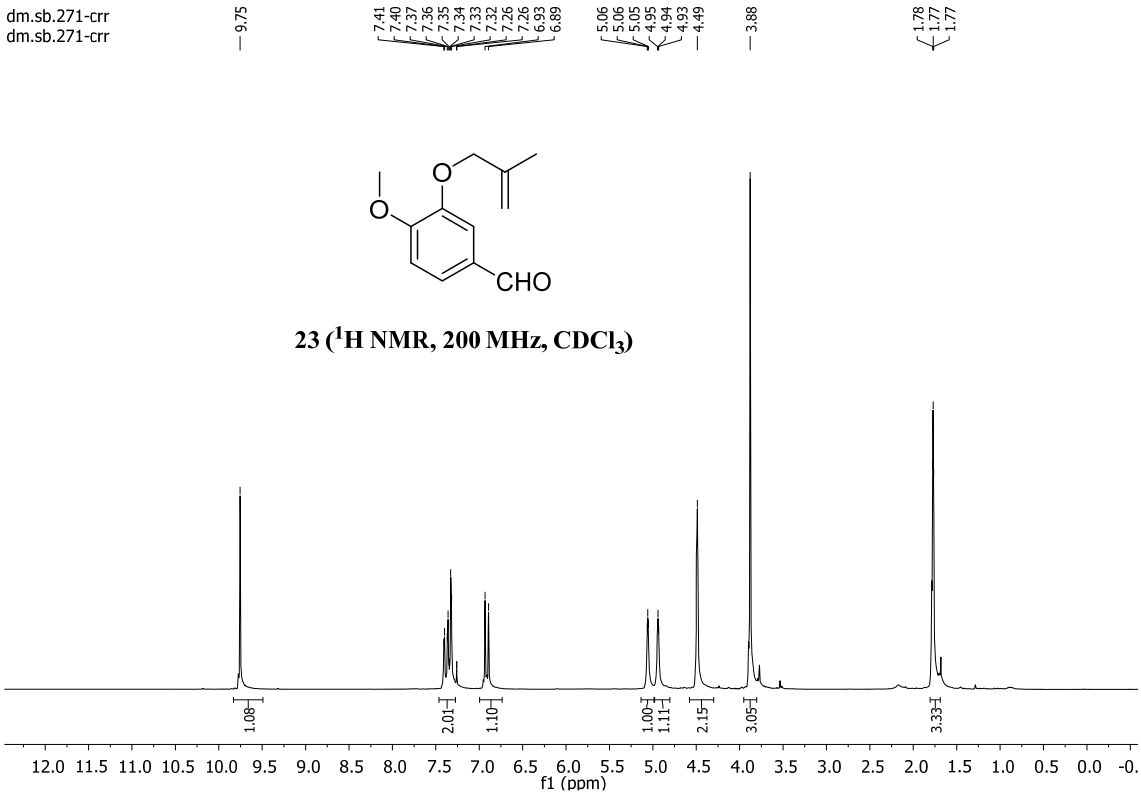


21 (^{1}H NMR, 400 MHz, $CDCl_3$)

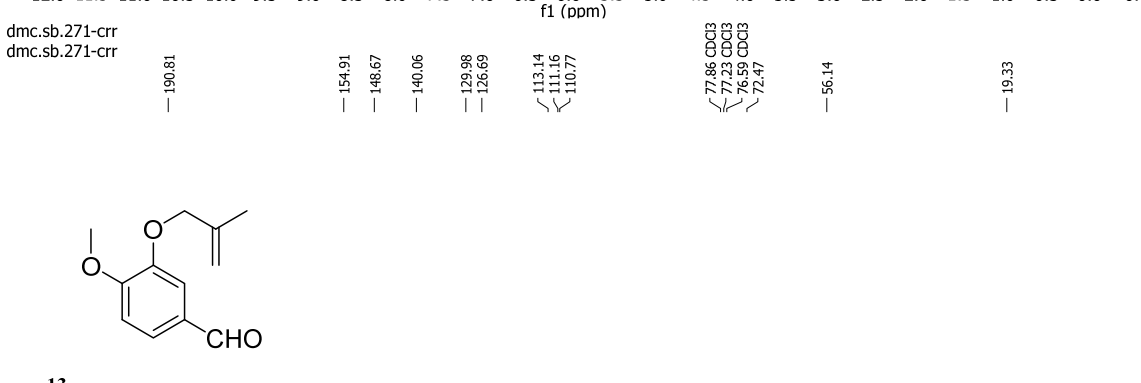


21 (^{13}C NMR, 100 MHz, $CDCl_3$)

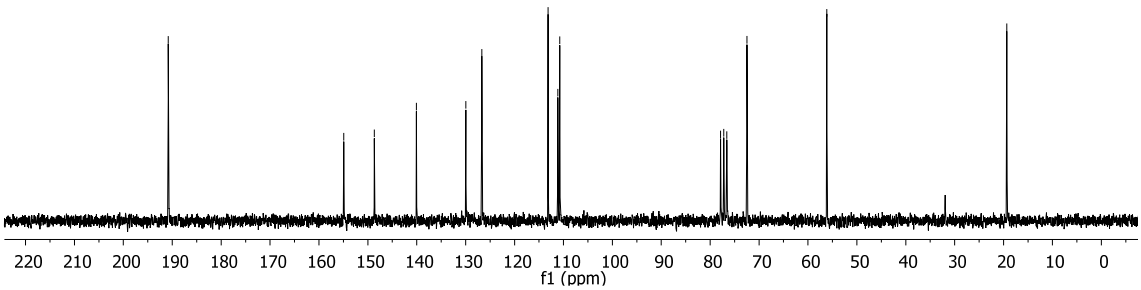
©ARKAT USA, Inc



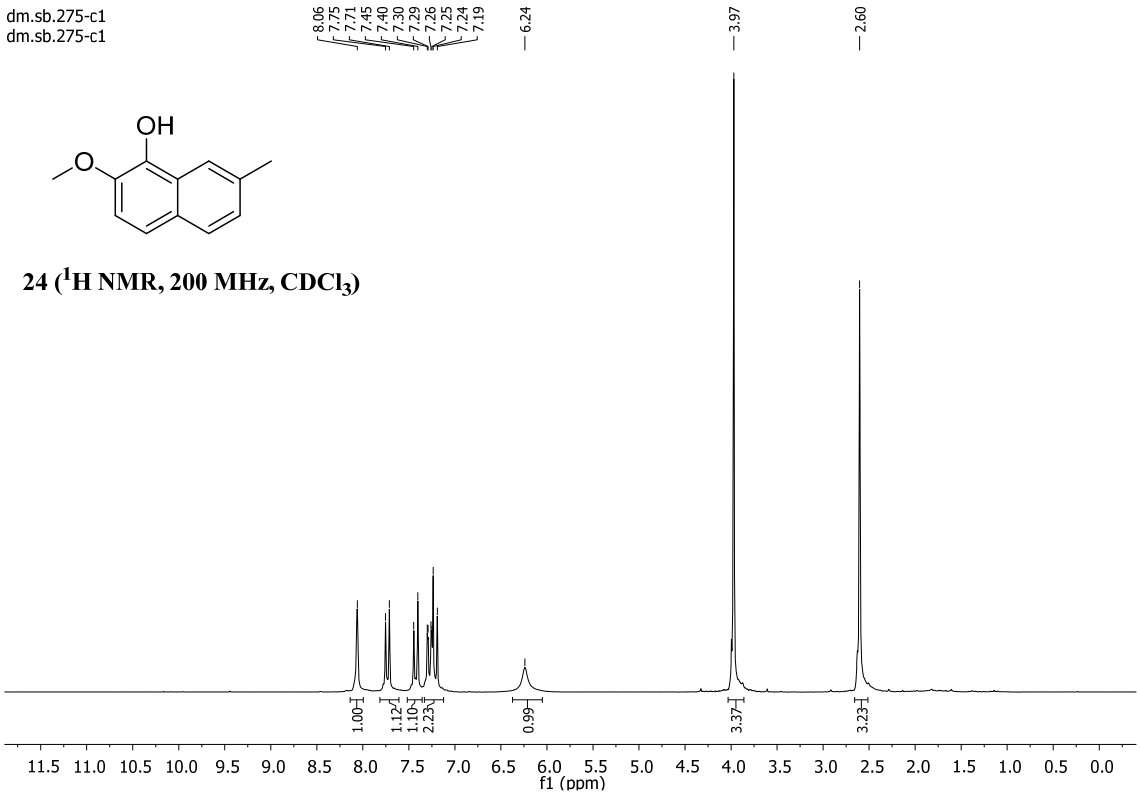
23 (^{1}H NMR, 200 MHz, $CDCl_3$)



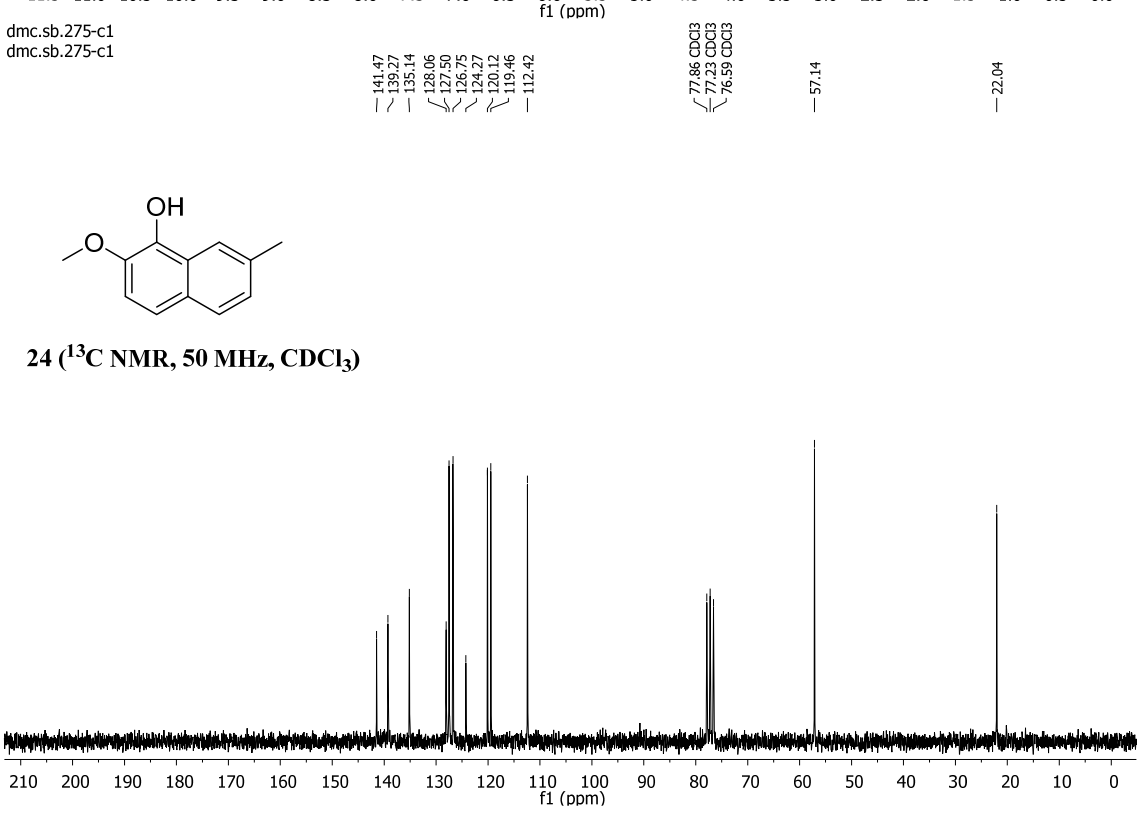
23 (^{13}C NMR, 50 MHz, $CDCl_3$)



 ©ARKAT USA, Inc

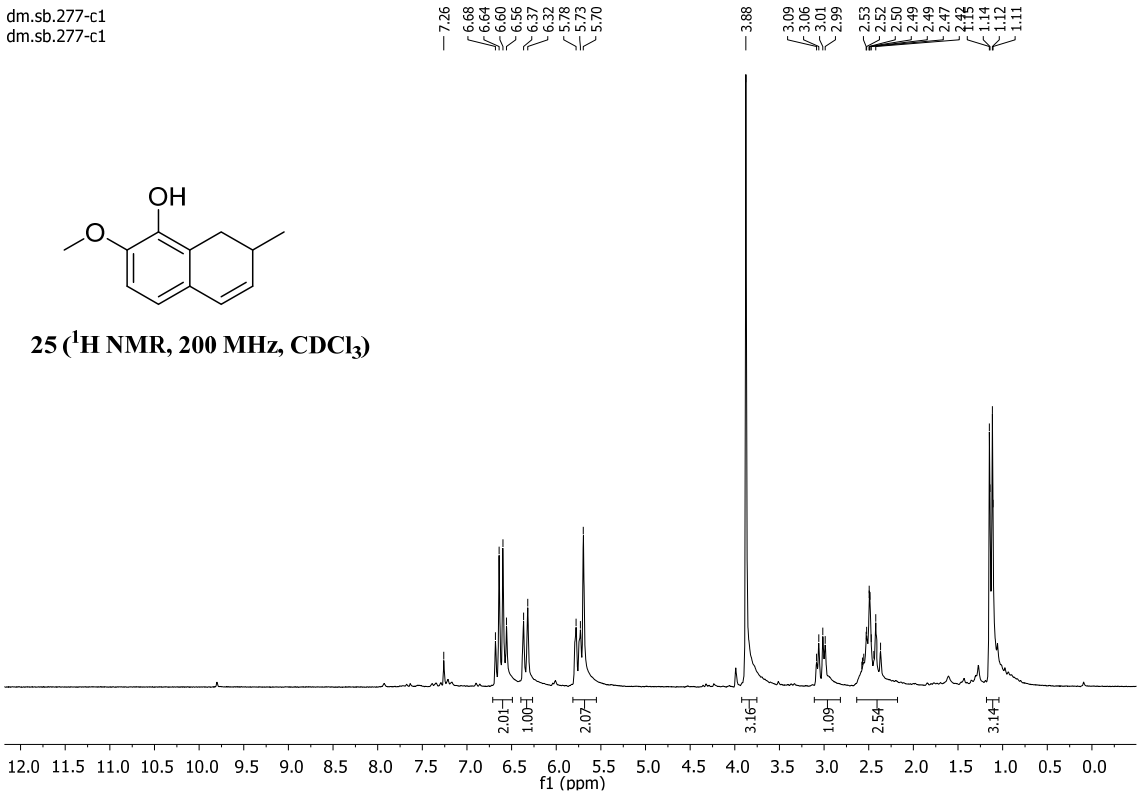


24 (^{1}H NMR, 200 MHz, $CDCl_3$)

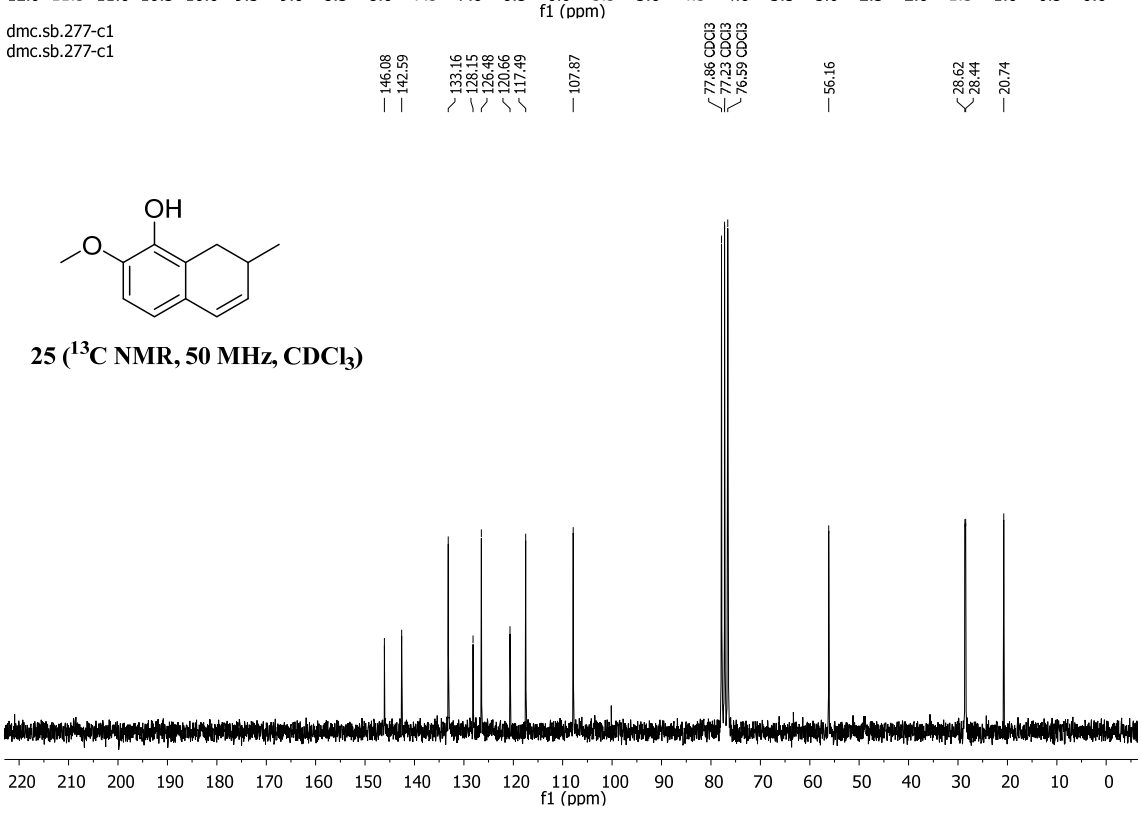


24 (^{13}C NMR, 50 MHz, $CDCl_3$)

©ARKAT USA, Inc

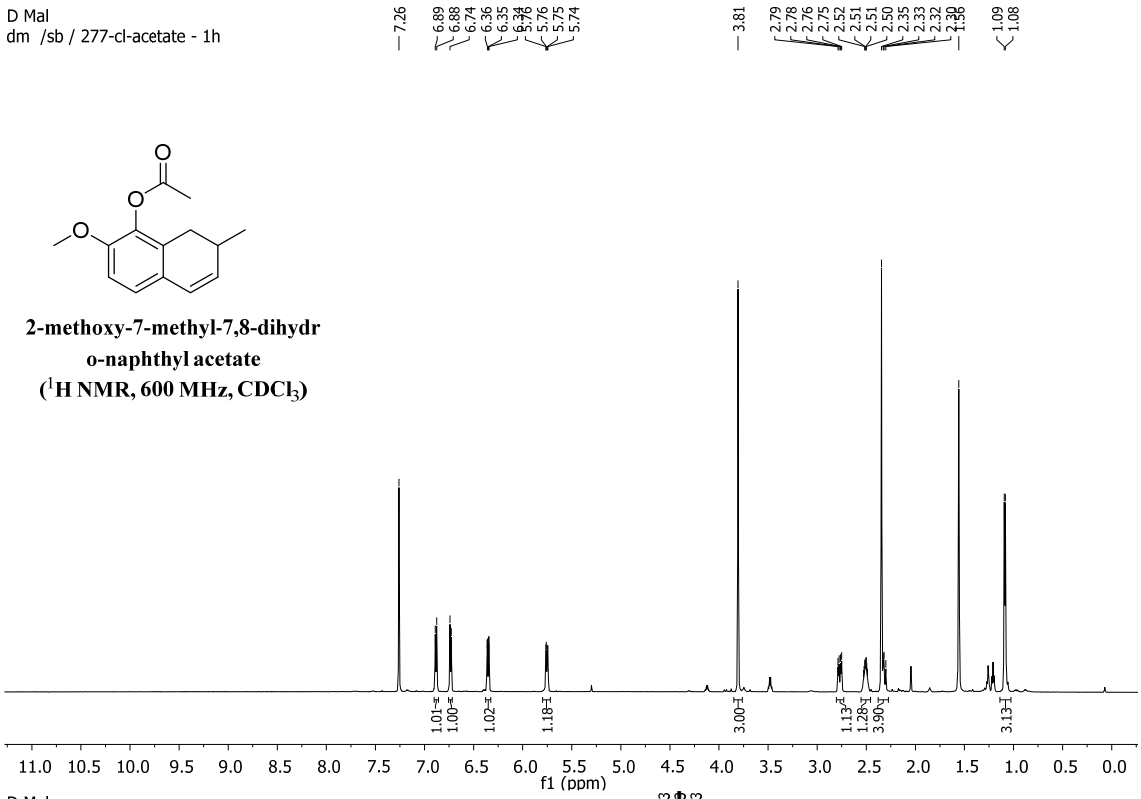


25 (^{1}H NMR, 200 MHz, $CDCl_3$)

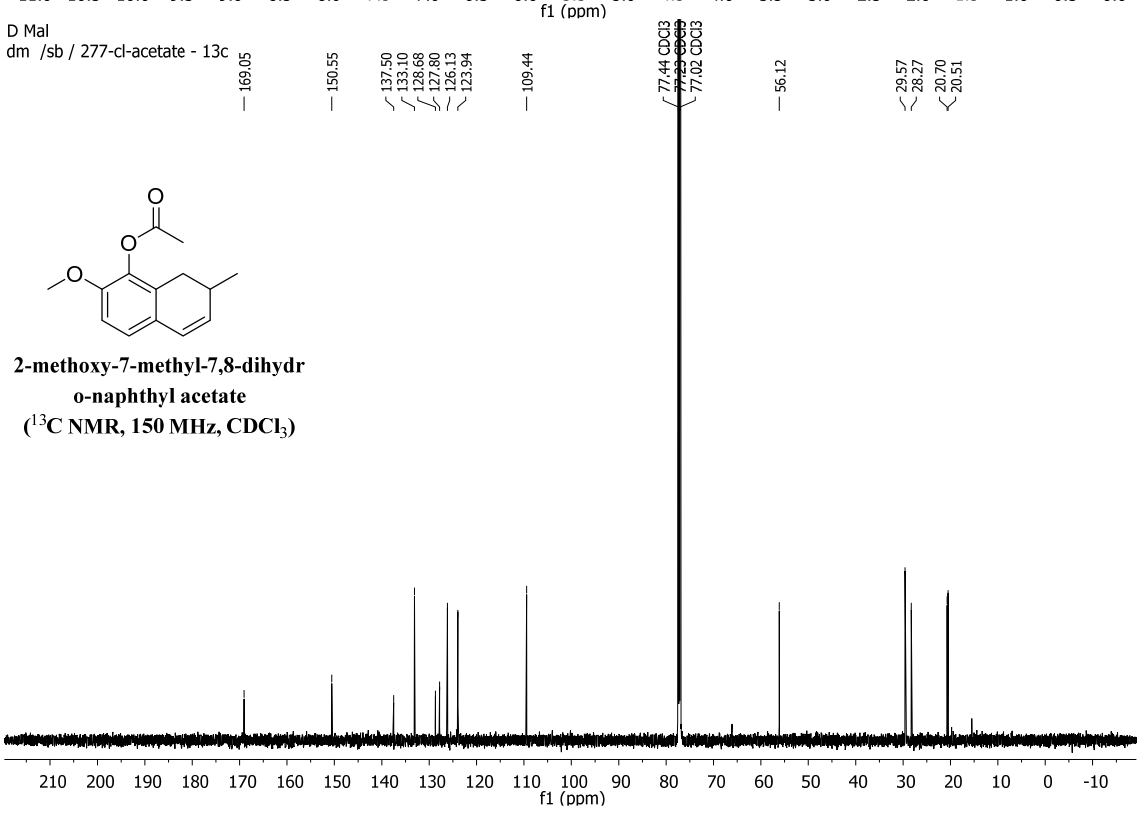


25 (^{13}C NMR, 50 MHz, $CDCl_3$)

©ARKAT USA, Inc

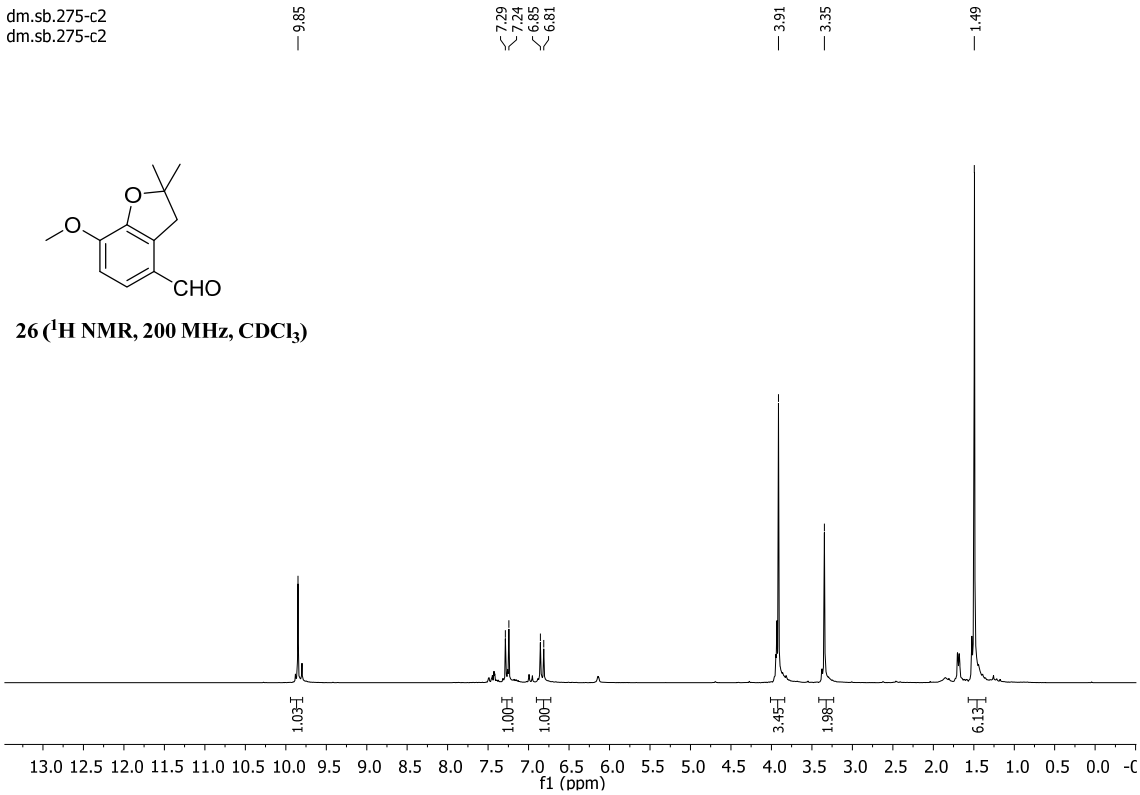


2-methoxy-7-methyl-7,8-dihydr o-naphthyl acetate (^{1}H NMR, 600 MHz, $CDCl_3$)

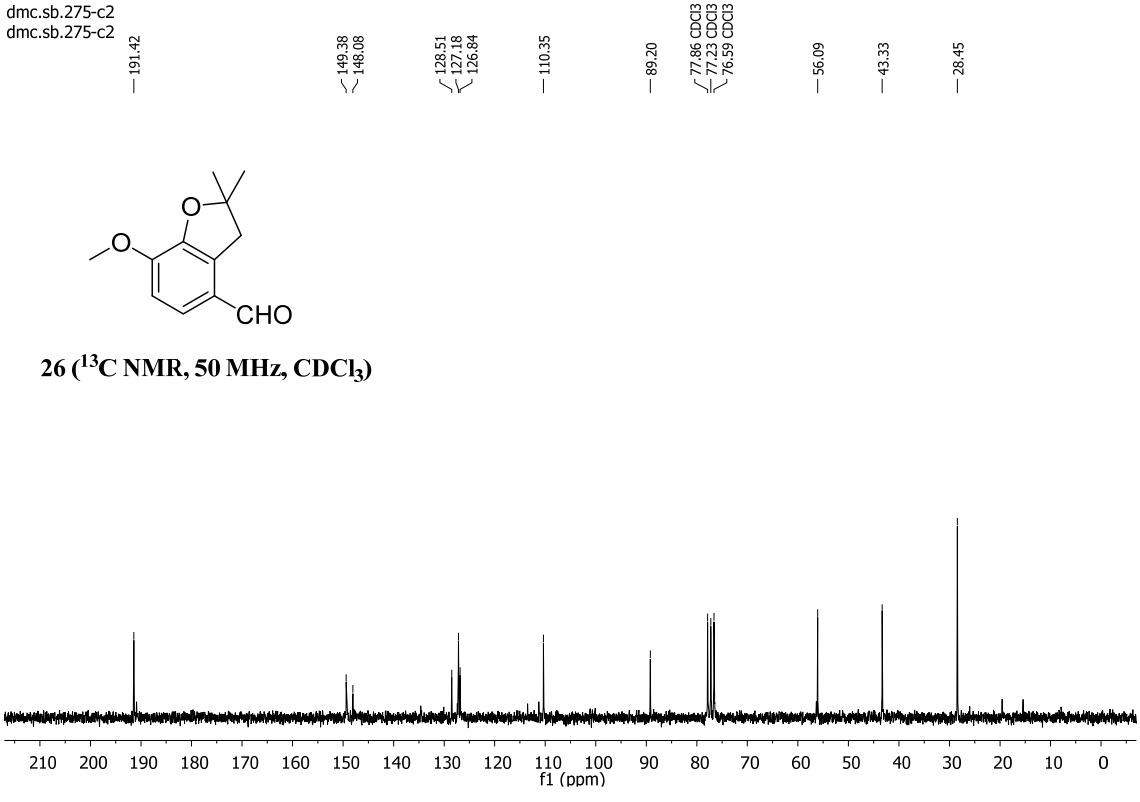


2-methoxy-7-methyl-7,8-dihydr o-naphthyl acetate (^{13}C NMR, 150 MHz, $CDCl_3$)

©ARKAT USA, Inc

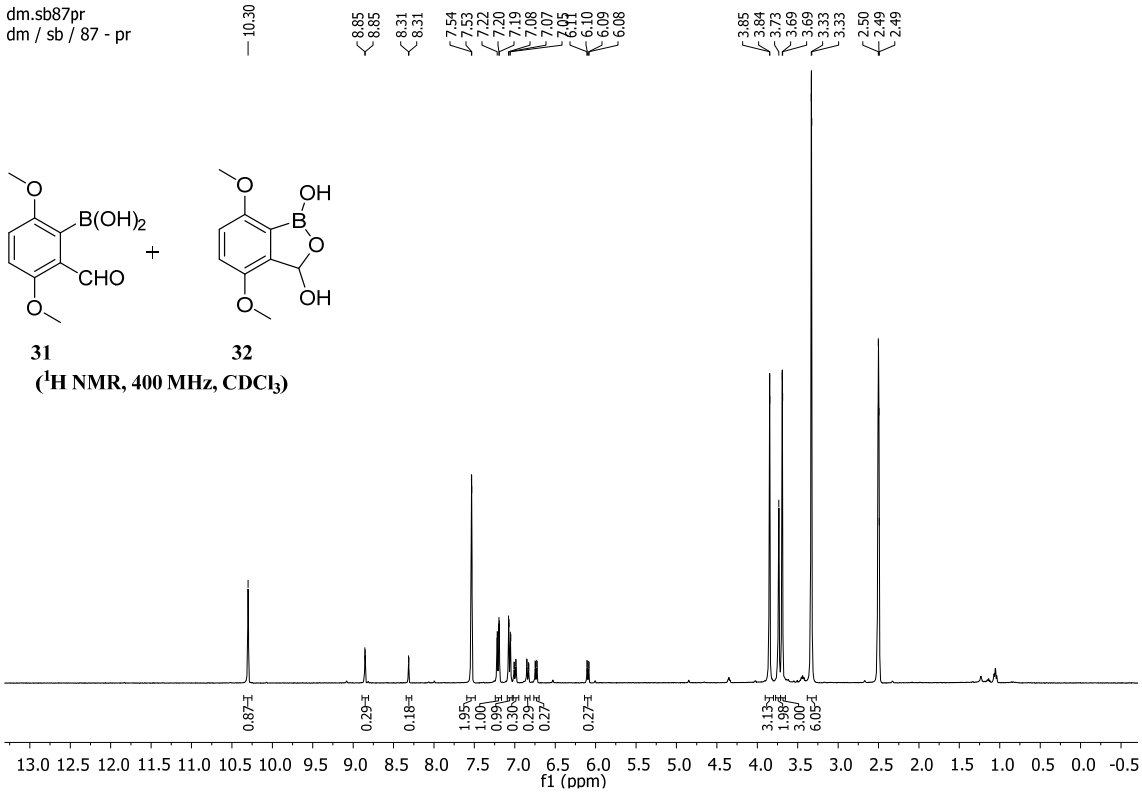


26 (^{1}H NMR, 200 MHz, $CDCl_3$)



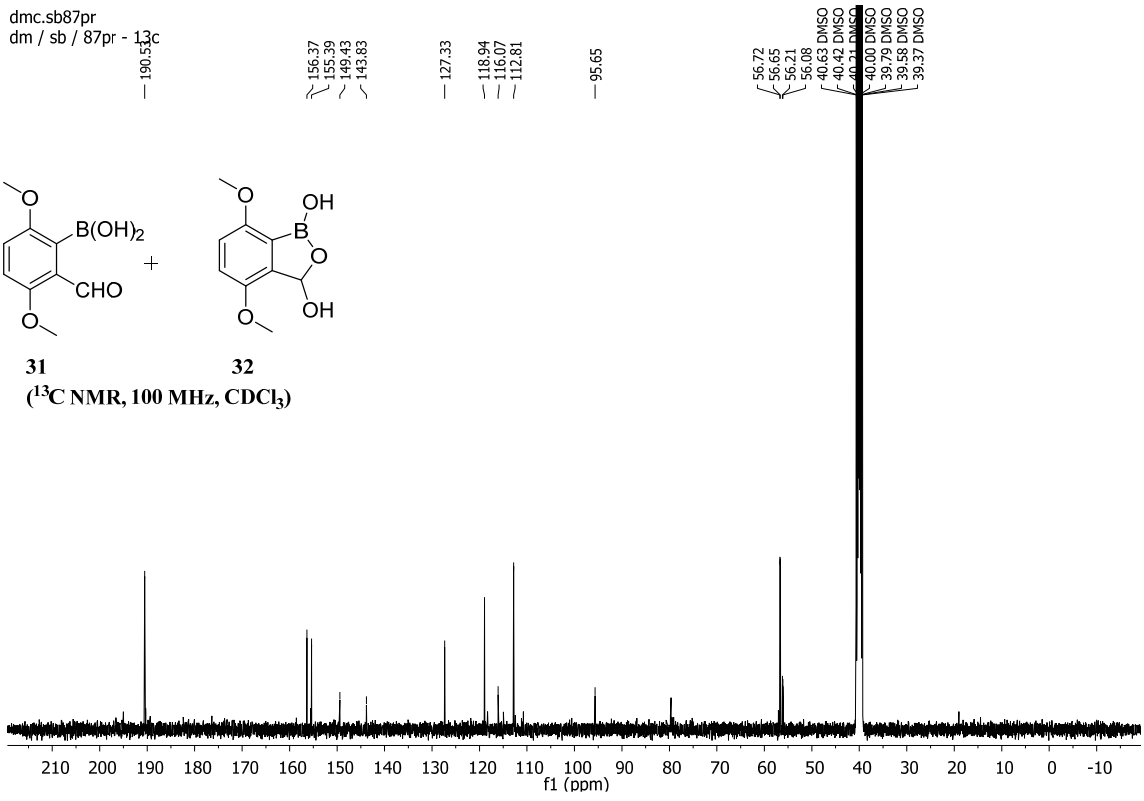
26 (^{13}C NMR, 50 MHz, $CDCl_3$)

©ARKAT USA, Inc



31 **32**

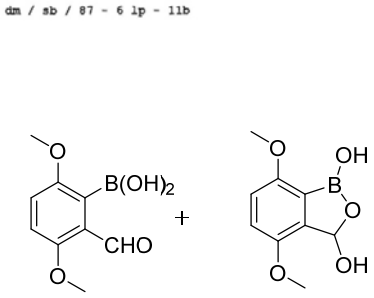
(^{1}H NMR, 400 MHz, $CDCl_3$)



31 **32**

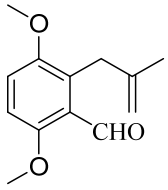
(^{13}C NMR, 100 MHz, $CDCl_3$)

©ARKAT USA, Inc

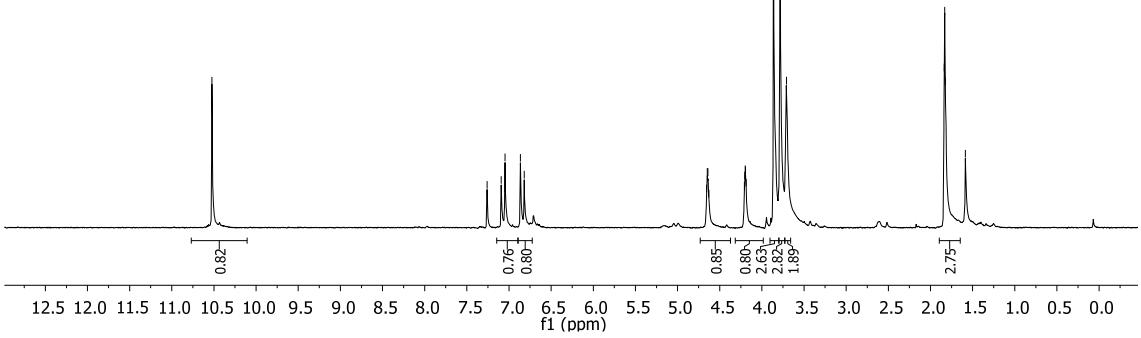


31 **32**

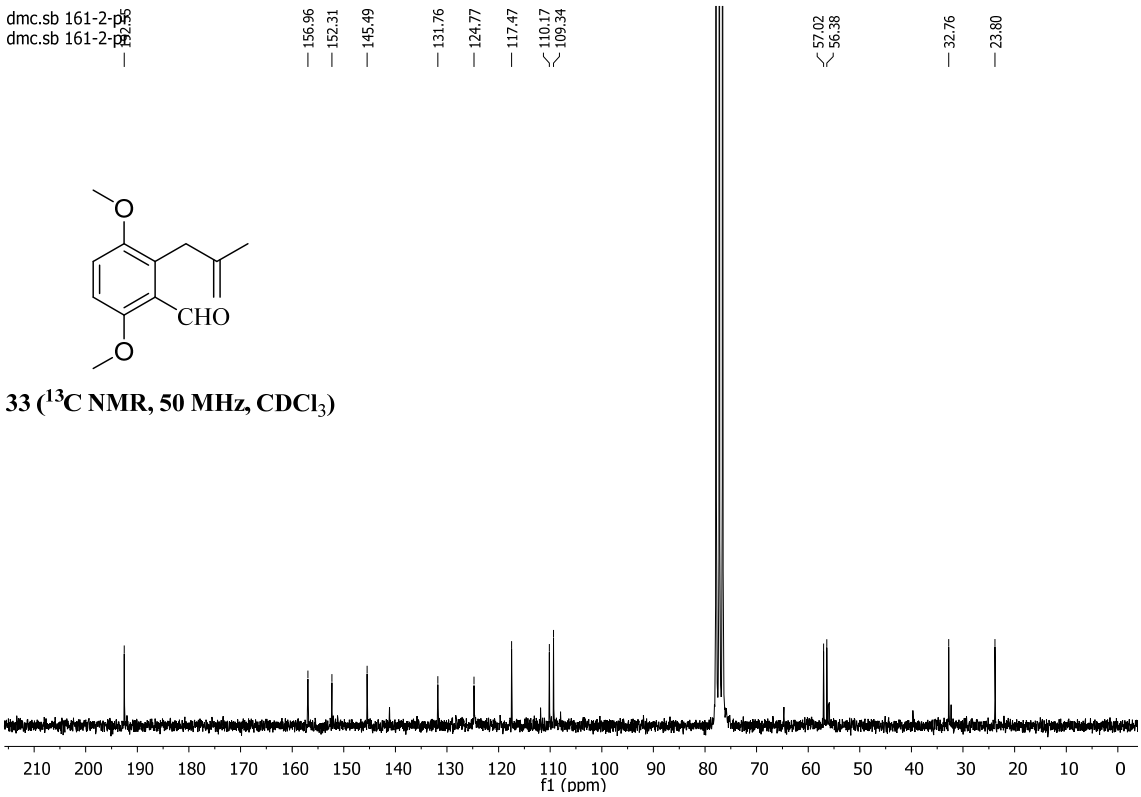
(^{11}B NMR, 128 MHz, $CDCl_3$)



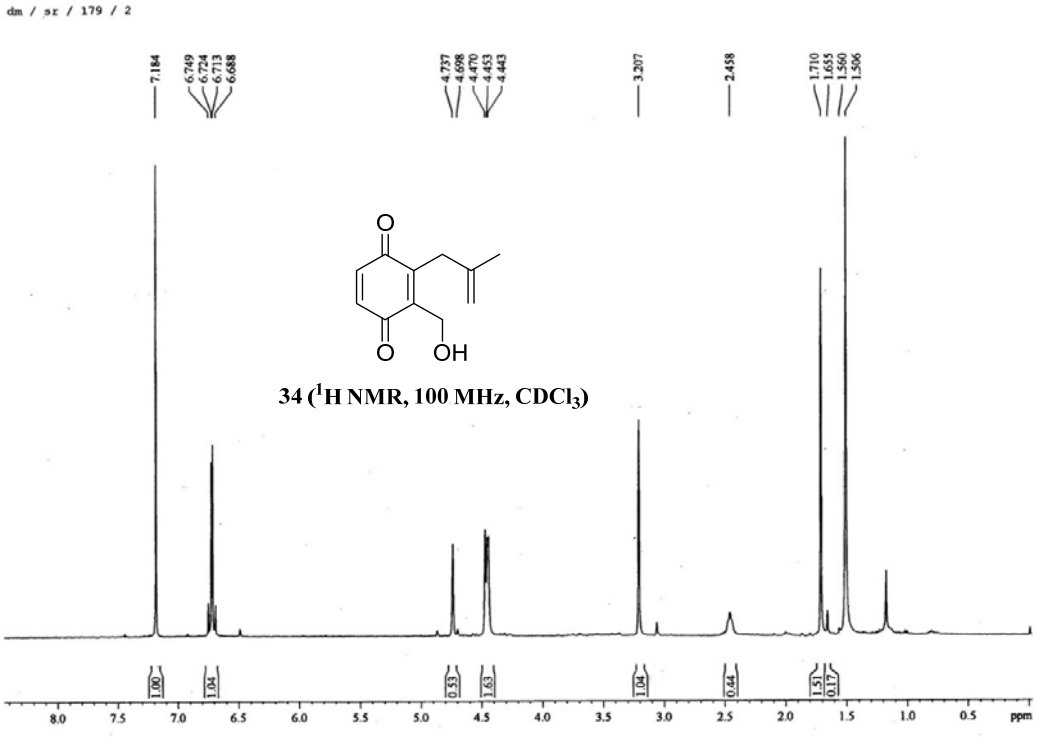
33 (^{1}H NMR, 200 MHz, $CDCl_3$)



©ARKAT USA, Inc

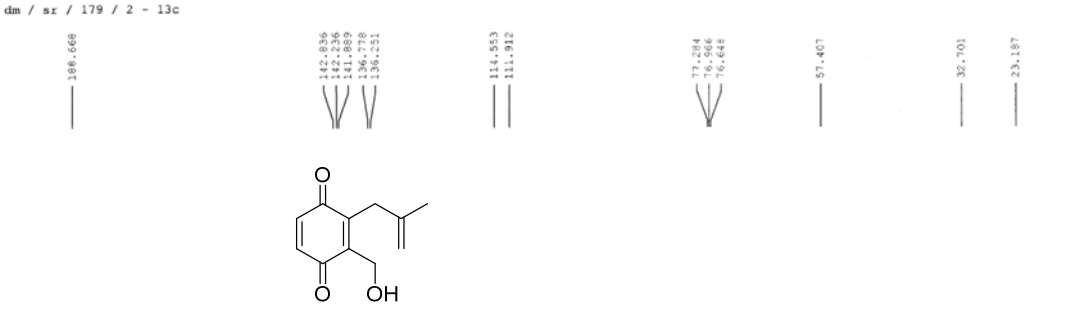


33 (^{13}C NMR, 50 MHz, $CDCl_3$)

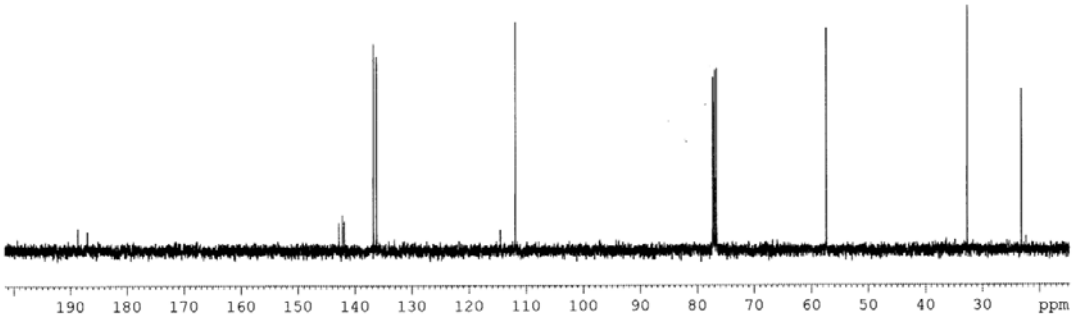


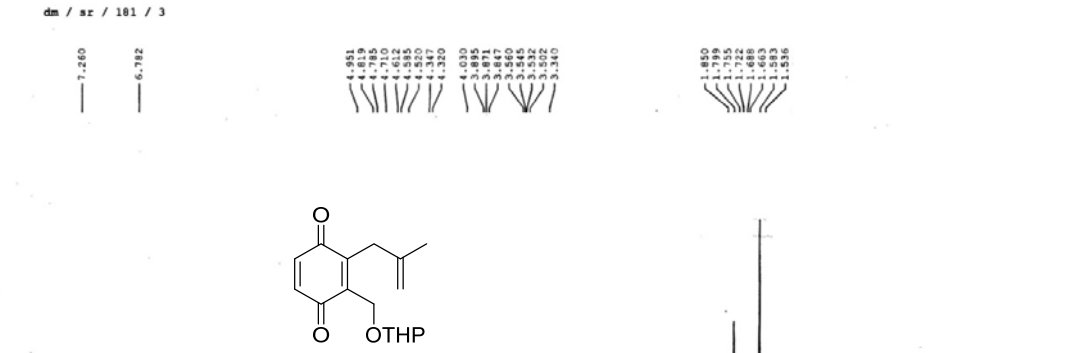
34 (^{1}H NMR, 100 MHz, $CDCl_3$)

©ARKAT USA, Inc



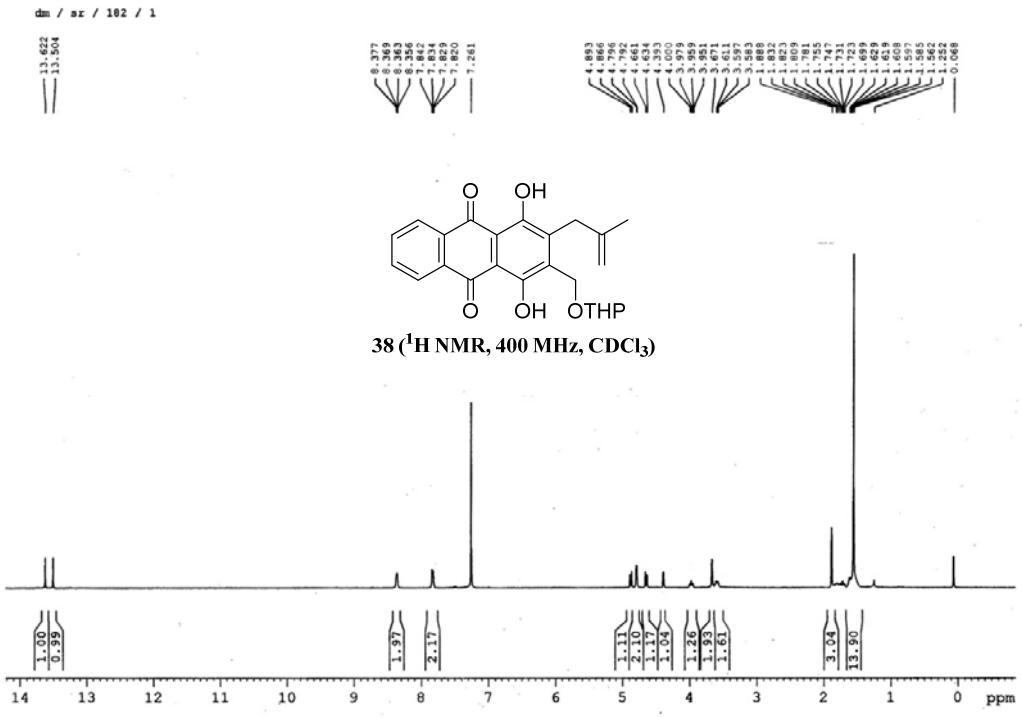
34 (^{13}C NMR, 100 MHz, $CDCl_3$)



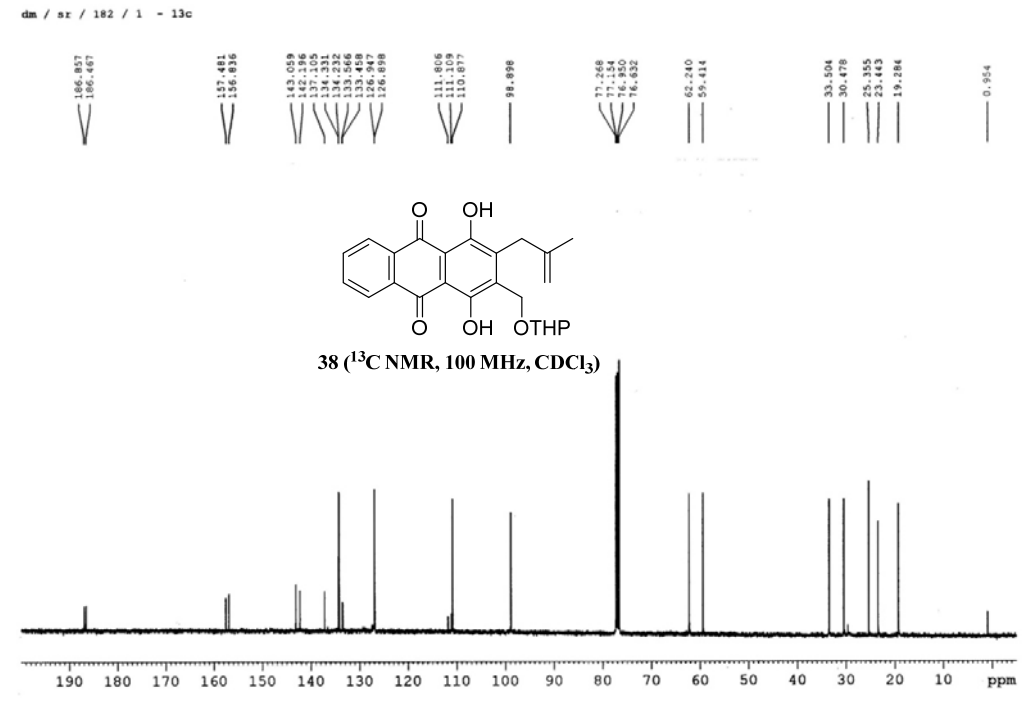


35 (^{1}H NMR, 400 MHz, $CDCl_3$)

©ARKAT USA, Inc

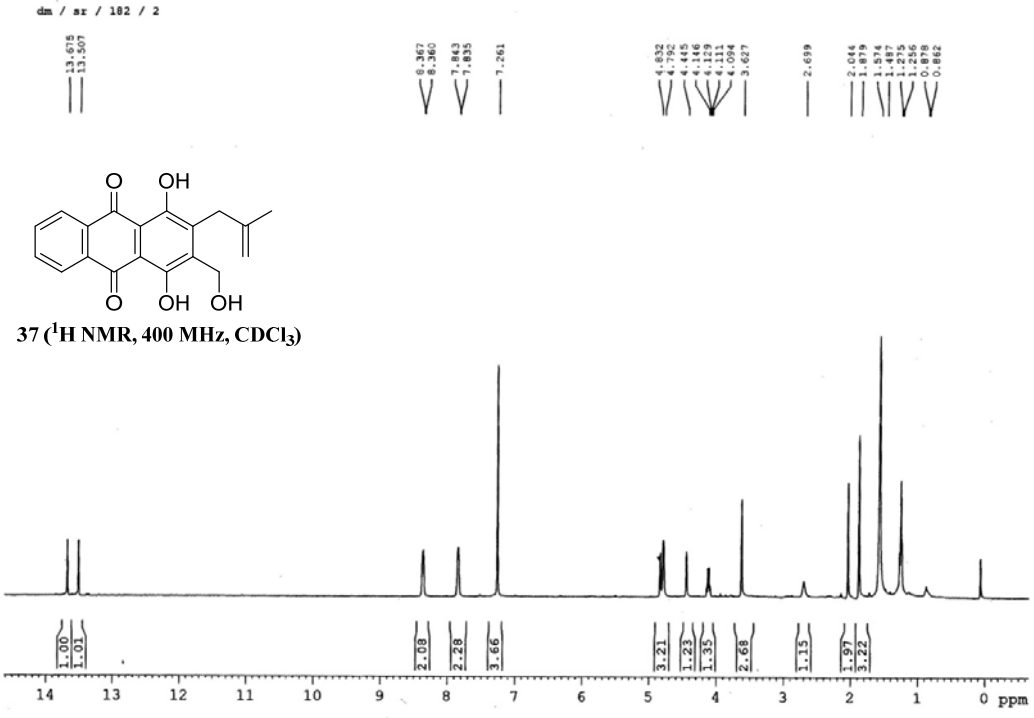


38 (^{1}H NMR, 400 MHz, $CDCl_3$)

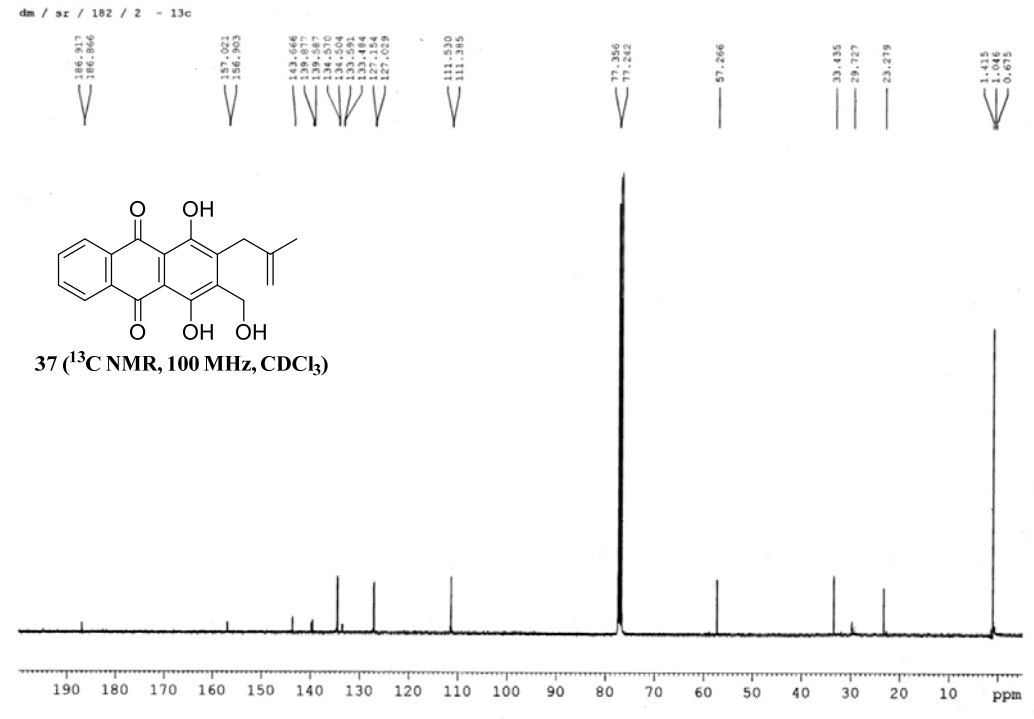


38 (^{13}C NMR, 100 MHz, $CDCl_3$)

©ARKAT USA, Inc

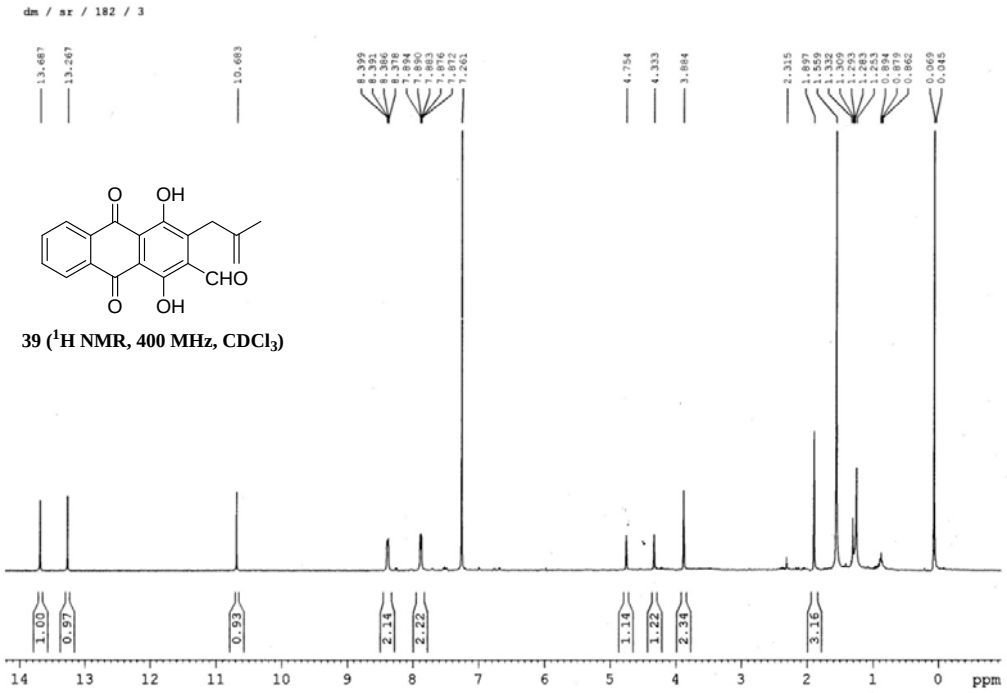


37 (^{1}H NMR, 400 MHz, $CDCl_3$)

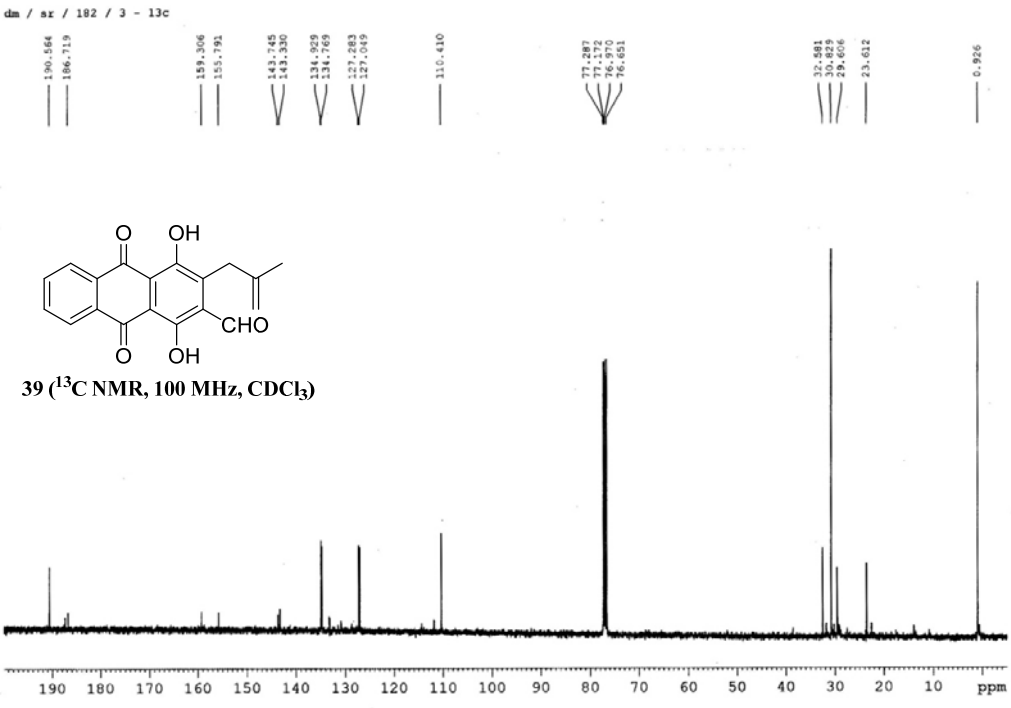


37 (^{13}C NMR, 100 MHz, $CDCl_3$)

©ARKAT USA, Inc

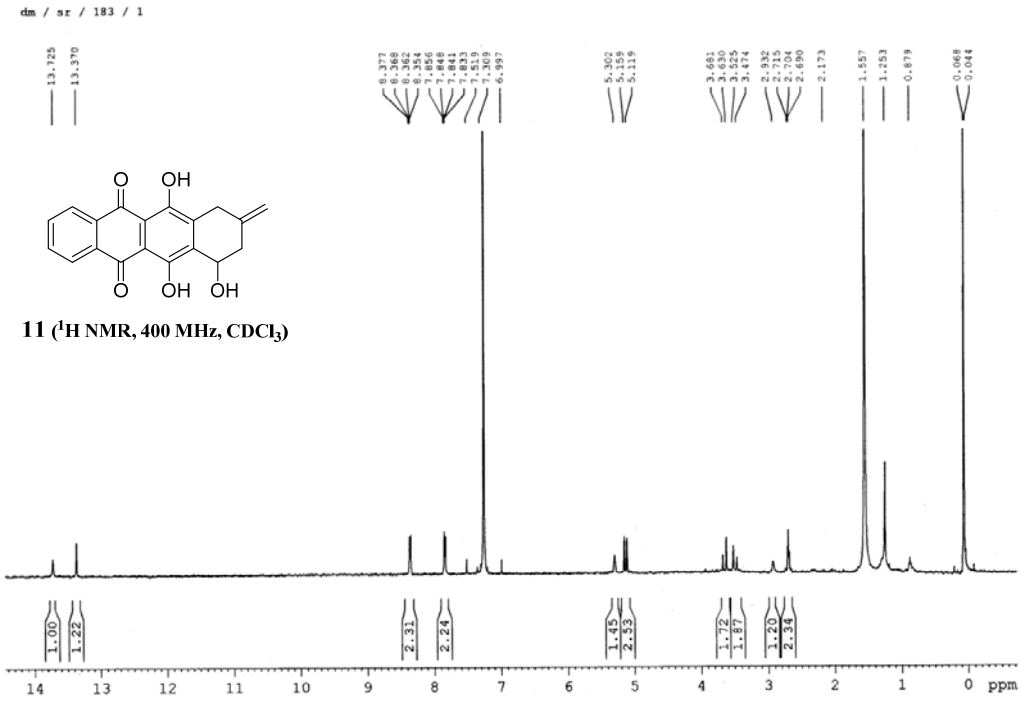


39 (^{1}H NMR, 400 MHz, $CDCl_3$)

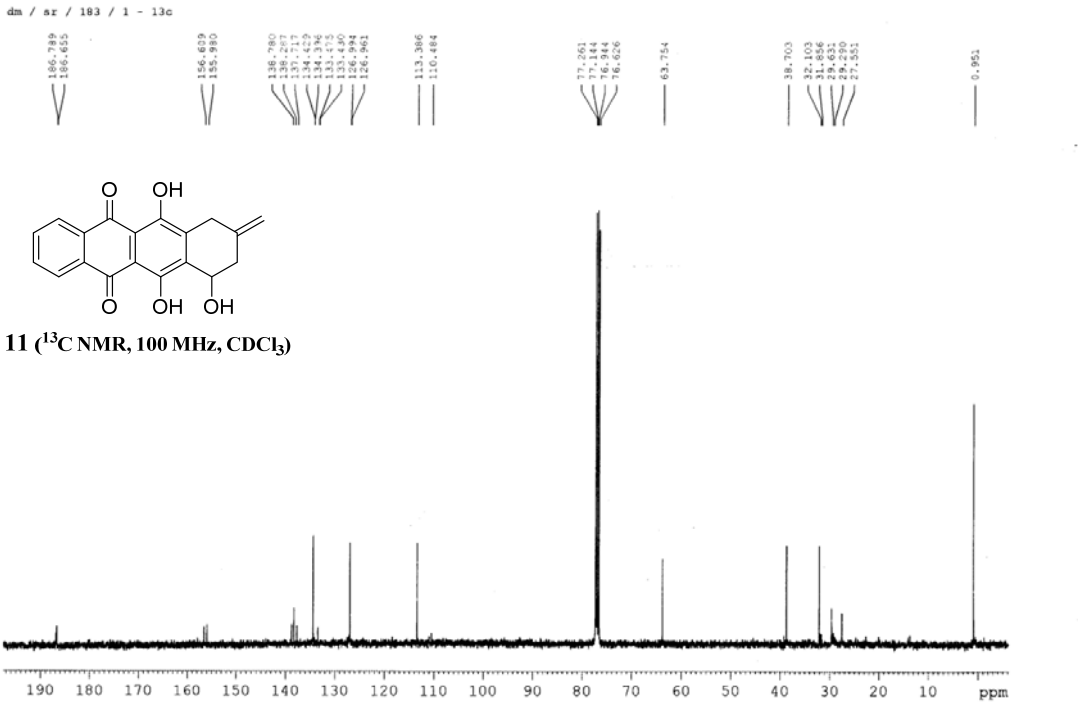


39 (^{13}C NMR, 100 MHz, $CDCl_3$)

©ARKAT USA, Inc

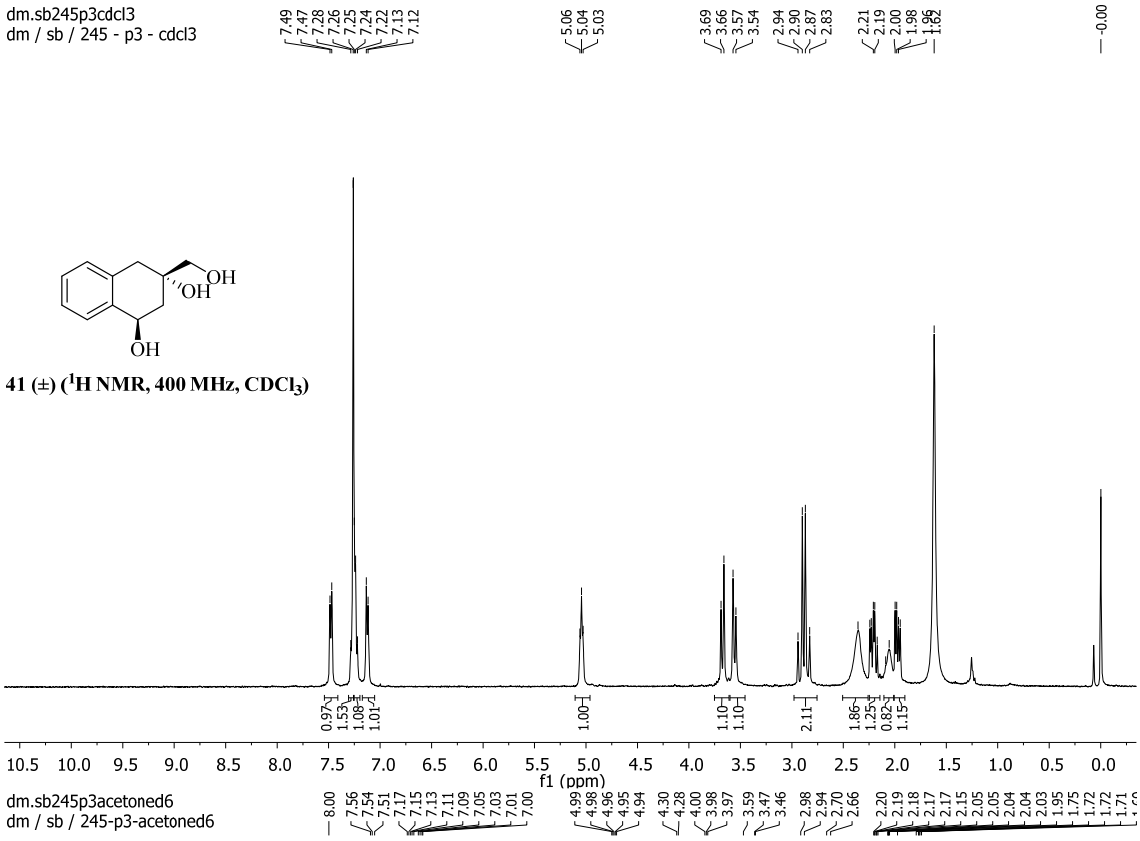


11 (**^{1}H NMR, 400 MHz, $CDCl_3$**)



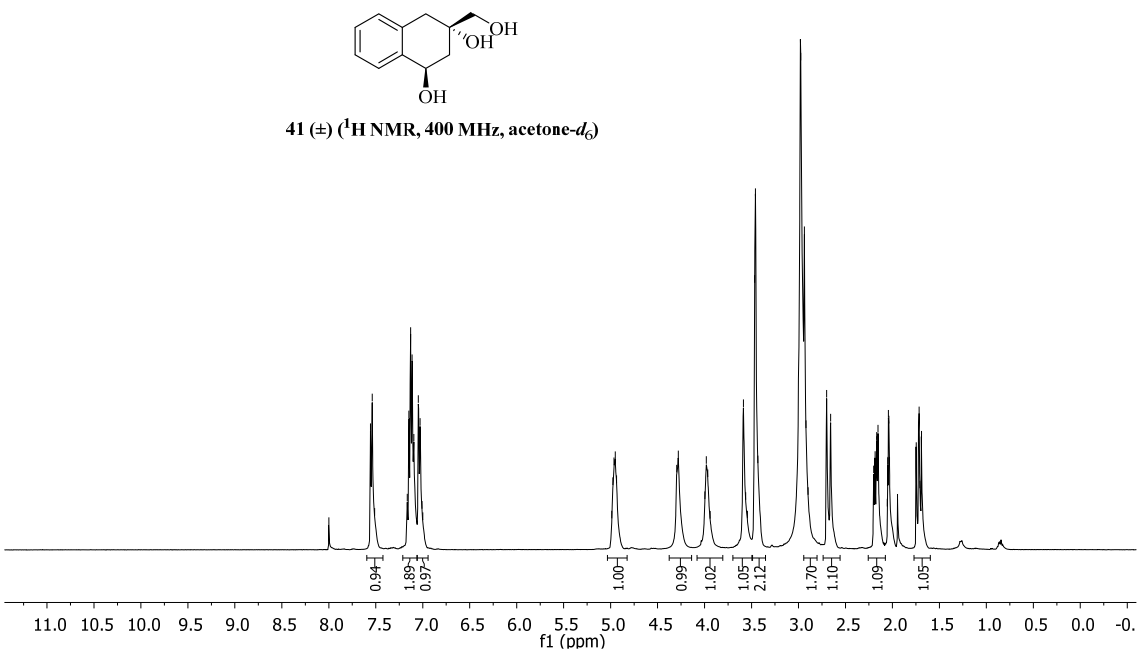
11 (**^{13}C NMR, 100 MHz, $CDCl_3$**)

©ARKAT USA, Inc

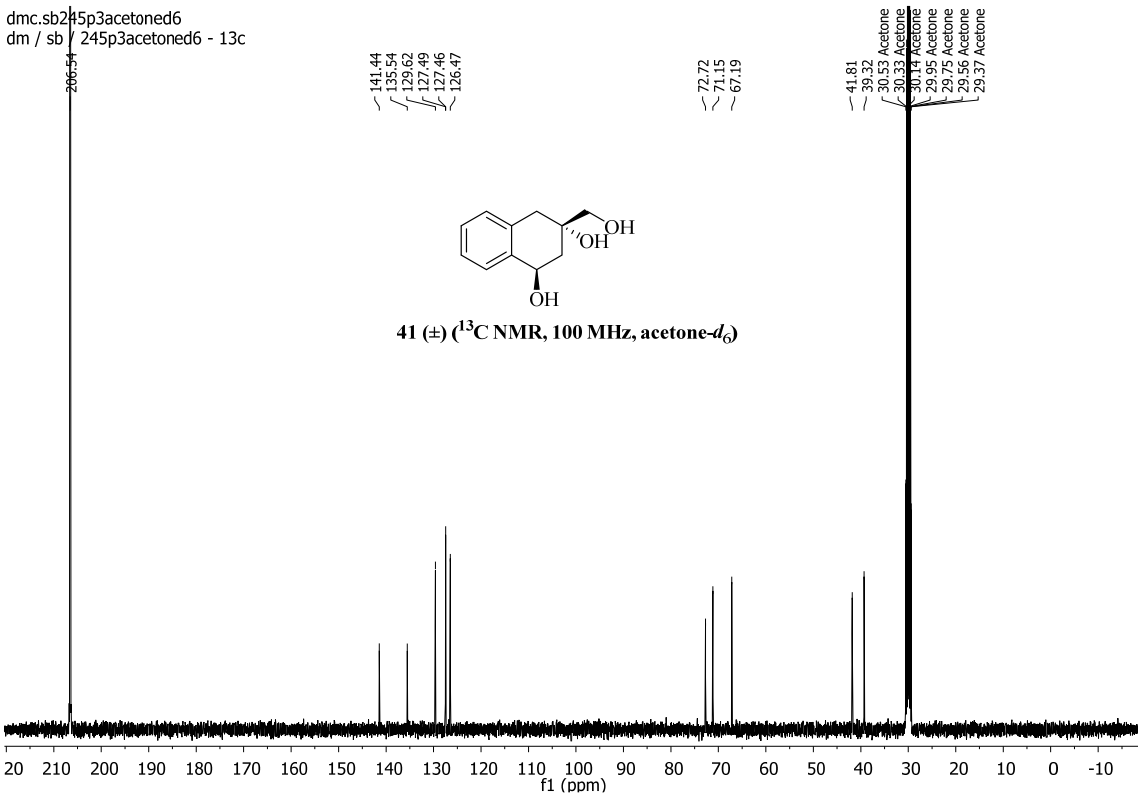


41 (±) (^{1}H NMR, 400 MHz, $CDCl_3$)

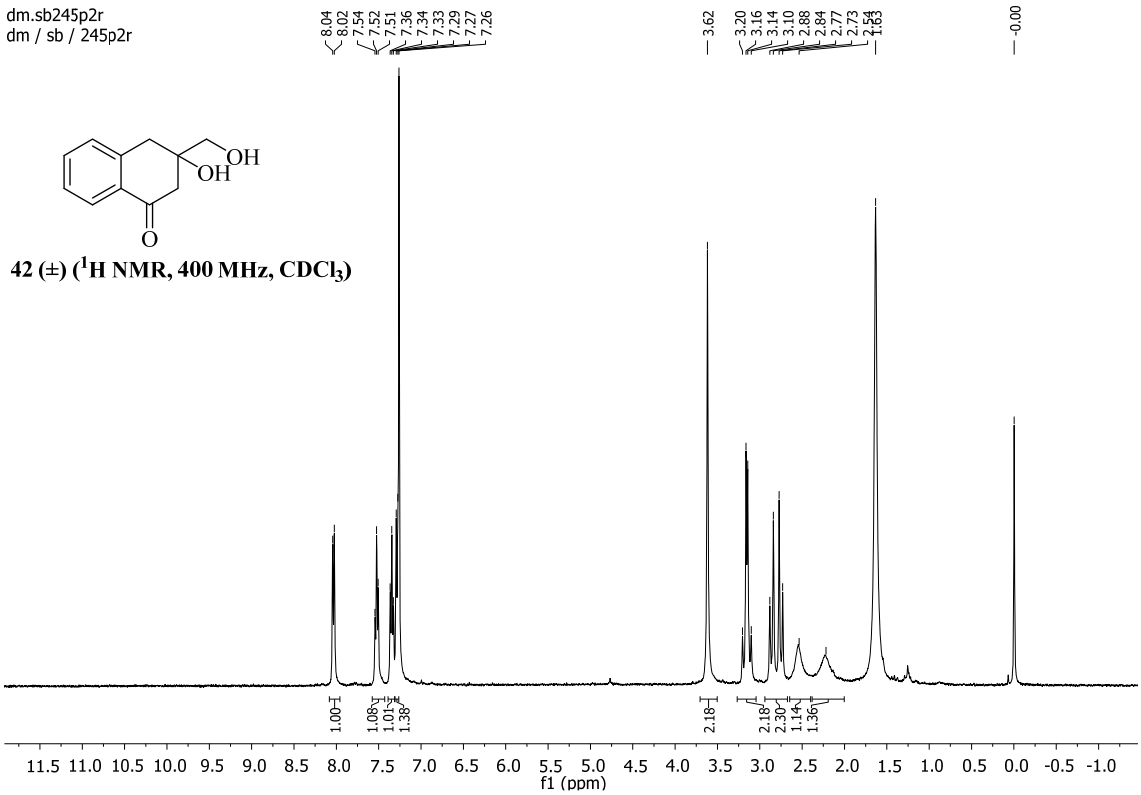
41 (±) (^{1}H NMR, 400 MHz, acetone-d_6)



 ©ARKAT USA, Inc

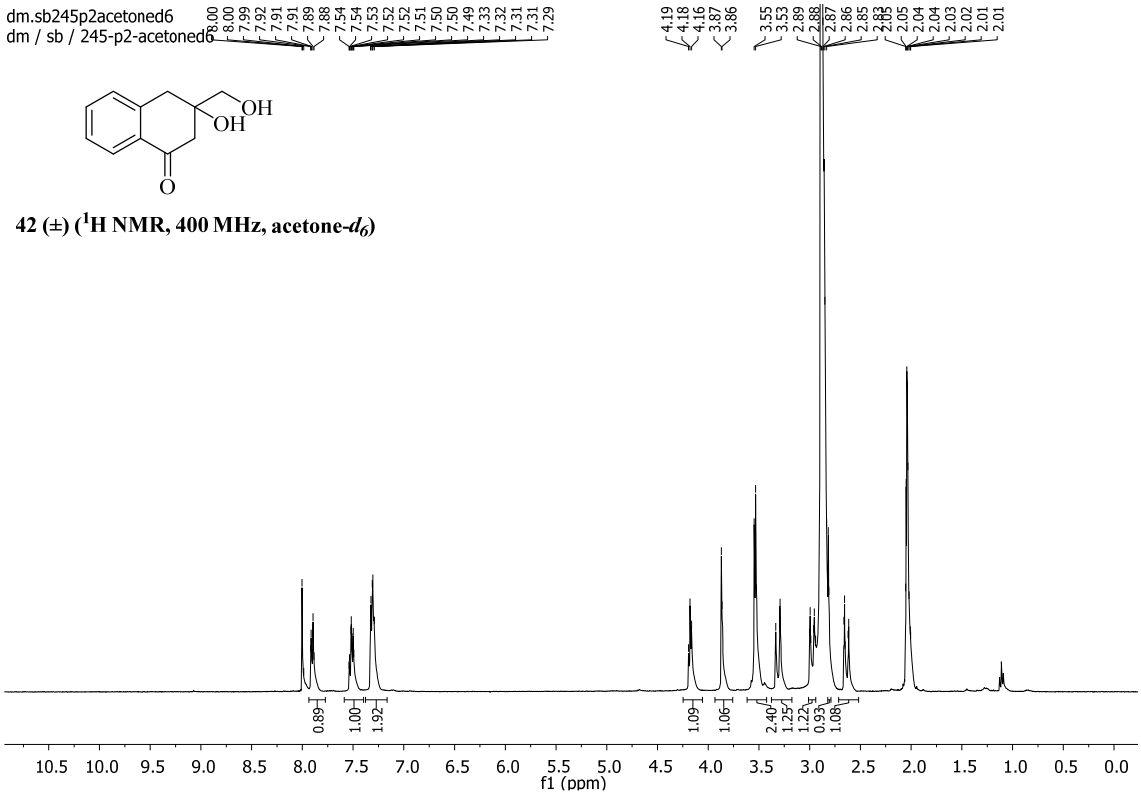


41 (±) (^{13}C NMR, 100 MHz, acetone-d_6)

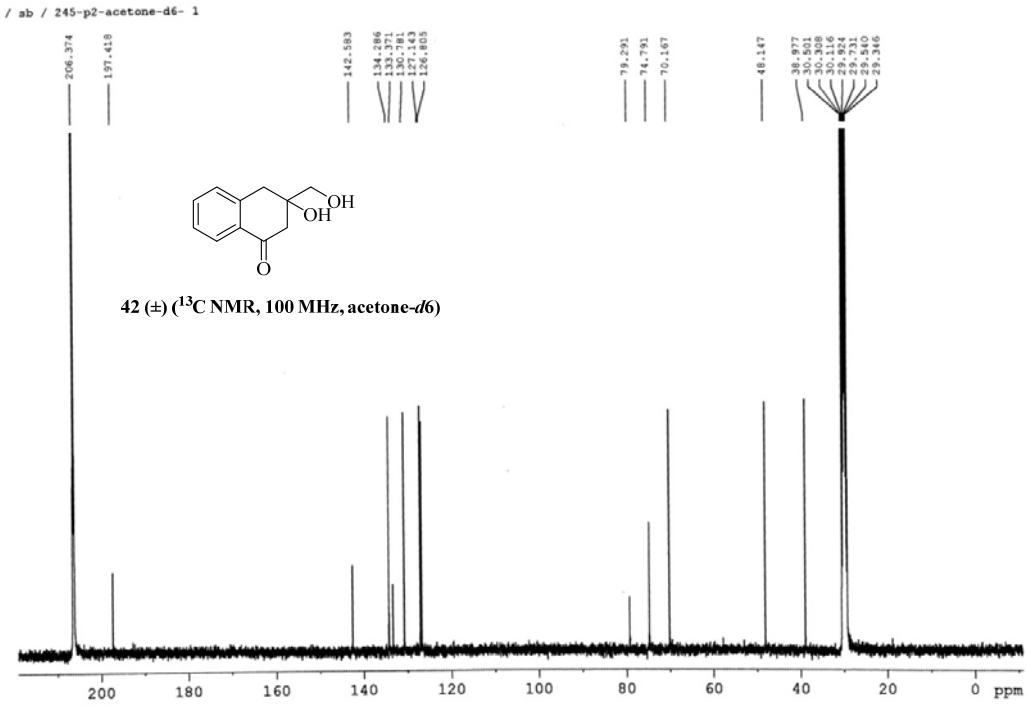


42 (±) (^{1}H NMR, 400 MHz, $CDCl_3$)

©ARKAT USA, Inc



42 (±) (^{1}H NMR, 400 MHz, acetone-d_6)



42 (±) (^{13}C NMR, 100 MHz, acetone-*d*6)

©ARKAT USA, Inc

X-ray Crystallography

Suitable single crystals of compound **42** for X-ray diffraction studies were obtained by slow evaporation of a solution of **42** in $CHCl_3$. Single crystal X-ray diffraction data collections for the compound was performed at room temperature using Bruker-APEX-II CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by SIR-92[1] or SHELXS-97 available in WinGX, which successfully located most of the non-hydrogen atoms. Subsequently, least square refinements were carried out on F^2 using SHELXL-97 (WinGX version)[2,3] to locate the remaining non-hydrogen atoms. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on calculated positions using riding models. These hydrogen atoms were located from the difference Fourier map and then refined isotropically with the thermal parameters equivalent to 1.2 times the thermal parameter value of the atom to which hydrogen atoms are bonded.

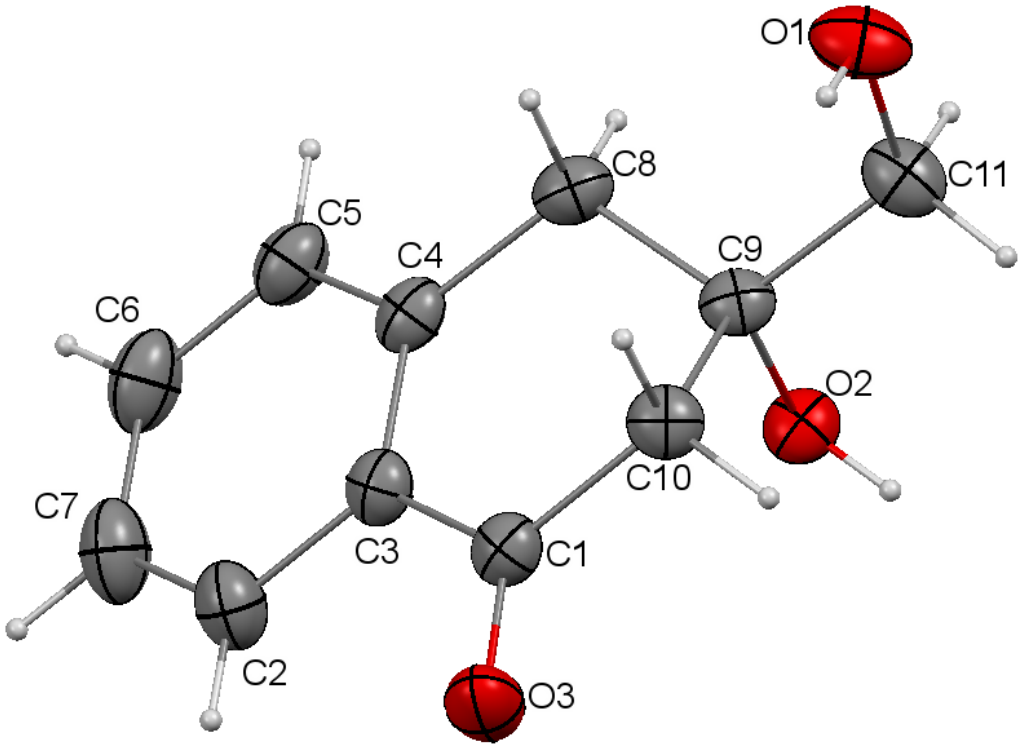


Figure S$_{42}$. ORTEP diagram of **42** with 30% probability ellipsoids.

©ARKAT USA, Inc

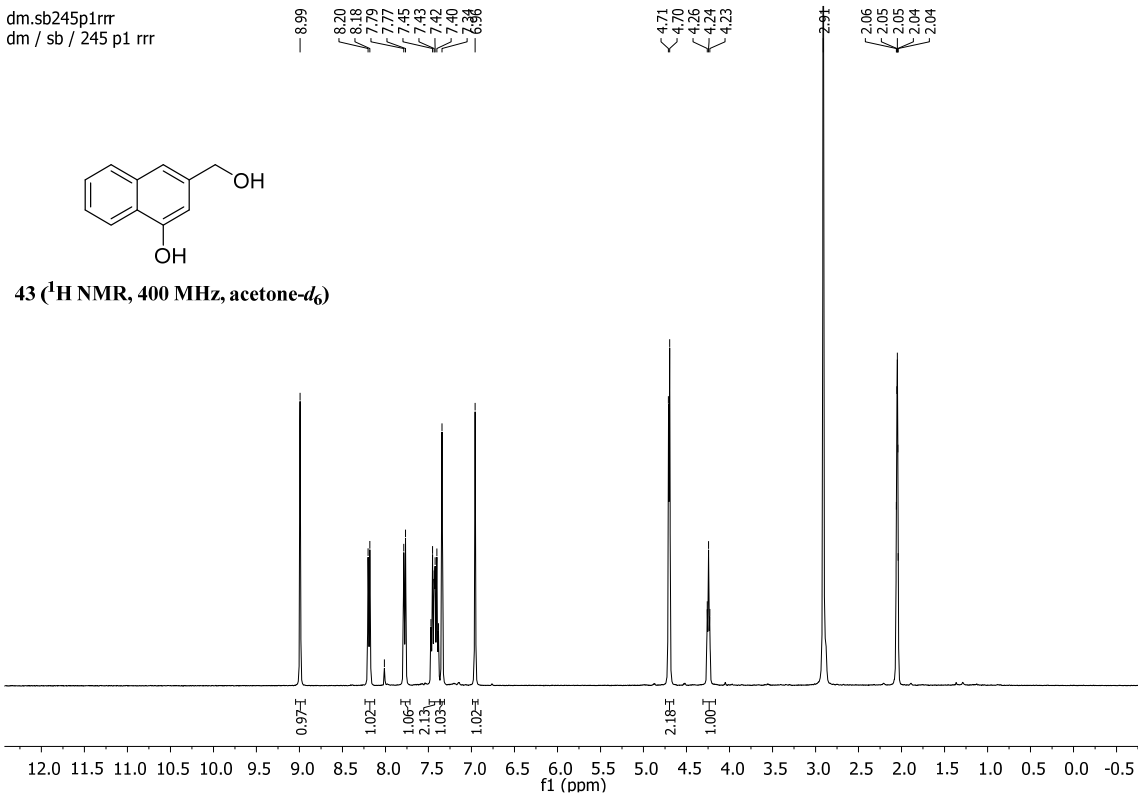
Table S1. Crystallographic Data for Compound **42**

	42
Empirical formula	**$C_{11}H_{12}O_3$**
Formula weight	**192.21**
Wavelength (Å)	**0.71073**
Temperature (K)	**293(2)**
Crystal system	**Monoclinic**
Color and shape	**Dark Green, block**
Space group	***P2₁/c***
***a*/Å**	**5.2277(9)**
***b*/Å**	**21.884(4)**
***c*/Å**	**8.4573(15)**
***α*/degree**	**90**
***β*/degree**	**95.533(6)**
***γ*/degree**	**90**
Volume (Å^3)	**960.0(3)**
Z	**4**
D_{calcd}, g cm^{-3}	**1.326**
***μ*/mm^{-1}**	**0.096**
***F*(000)**	**408**

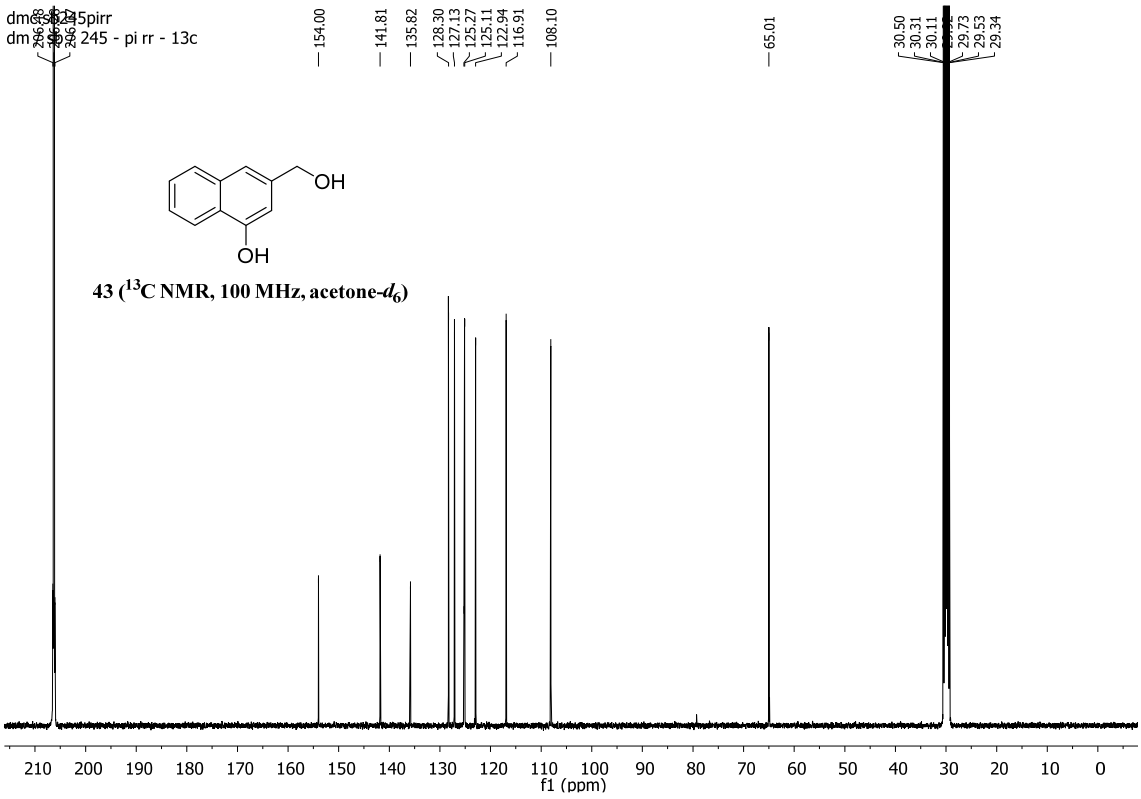
©ARKAT USA, Inc

Crystal size/mm	**0.23×0.17×0.13**
θ range (degree)	**1.86 to 26.52**
Limiting indices	**–6<=h<=6, –26<=k<=27, –10<=l<=10**
Total/ unique no. of reflns.	**12183/ 1994**
R_{int}	**0.0940**
Data / restr./ params.	**1994 / 0 / 127**
GOF (F^2)	**0.691**
R1*, *wR2	**0.0629, 0.1832**
R indices (all data) *R1*, *wR2*	**0.1359, 0.2739**
Largest different peak and hole (e Å^{-3})	**0.188 and –0.189**

©ARKAT USA, Inc

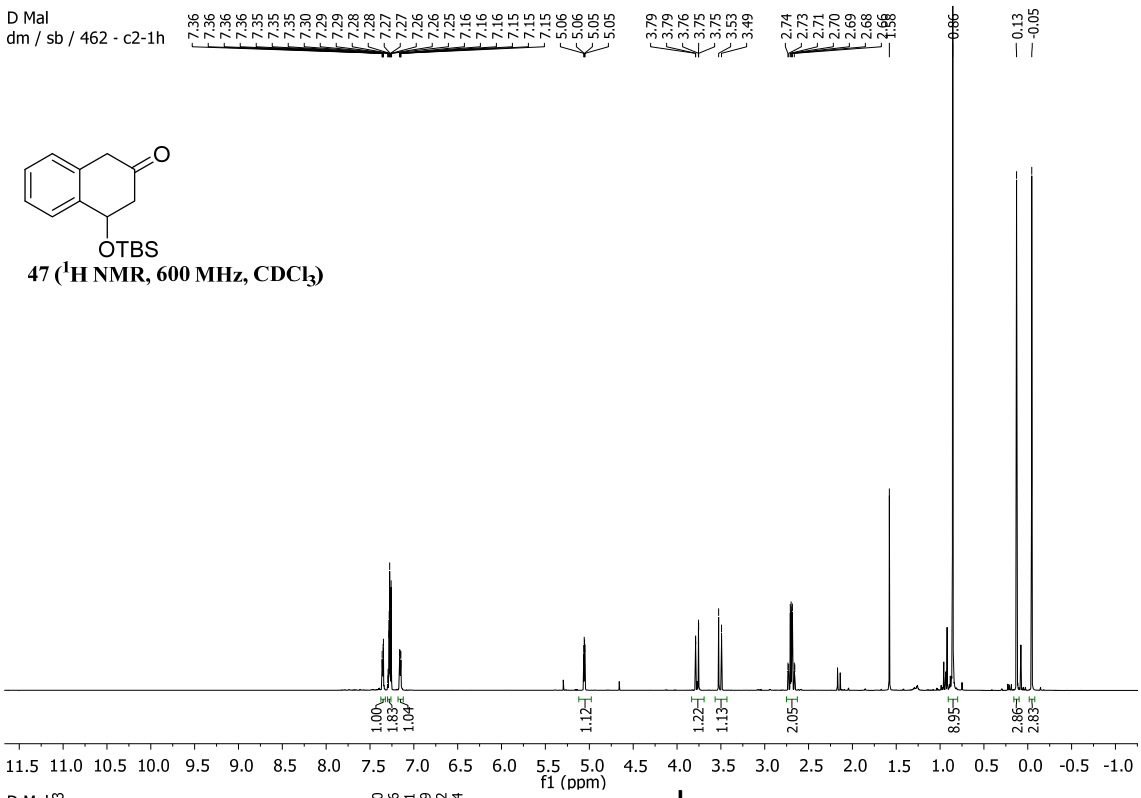


43 (^{1}H NMR, 400 MHz, acetone-d_6)

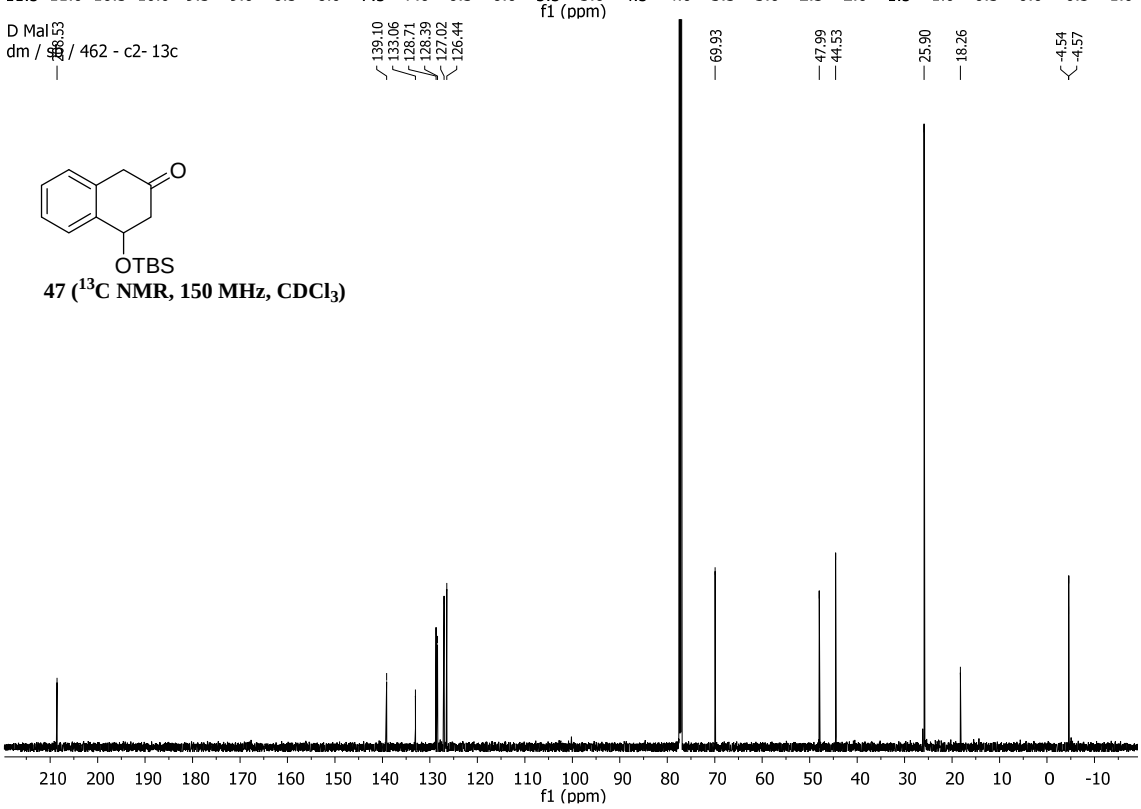


43 (^{13}C NMR, 100 MHz, acetone-d_6)

©ARKAT USA, Inc



47 (^{1}H NMR, 600 MHz, $CDCl_3$)



47 (^{13}C NMR, 150 MHz, $CDCl_3$)

©ARKAT USA, Inc

References

1. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst.* **1993**, *26*, 343.

2. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

3. Farrugia, L. *J. Appl. Crystallogr.* **1999**, *32*, 837.

 ©ARKAT USA, Inc