

## Supplementary Material

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

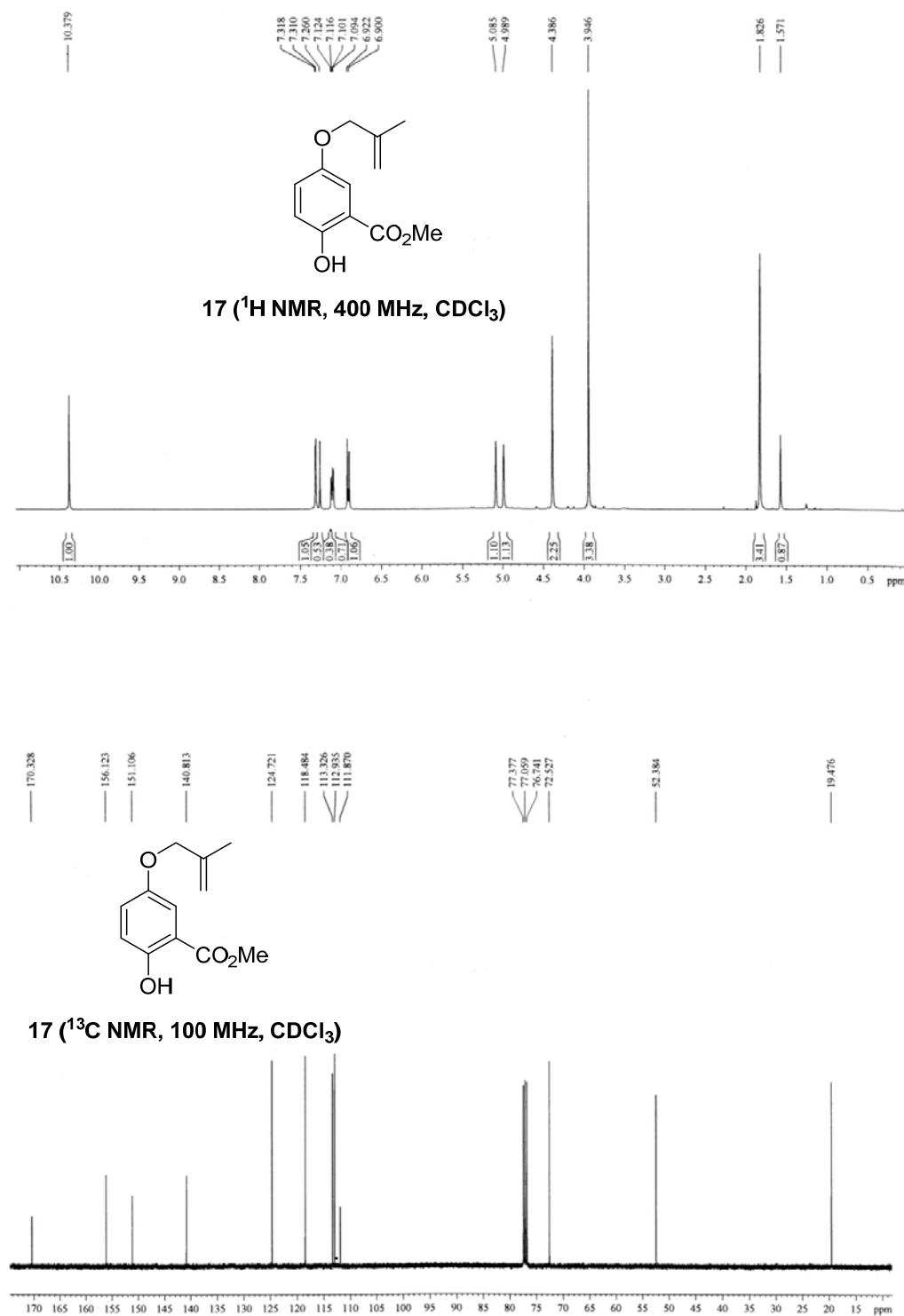
Shyam Basak, Sutapa Ray and Dipakranjan Mal<sup>\*</sup>

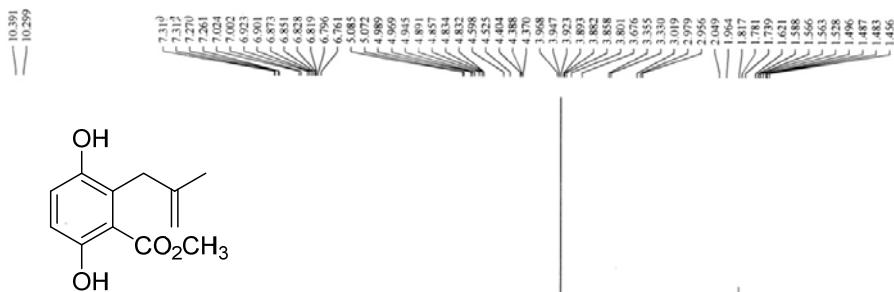
*Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302,  
India*

*E-mail: [dmal@chem.iitkgp.ernet.in](mailto:dmal@chem.iitkgp.ernet.in)*

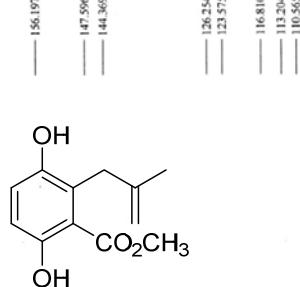
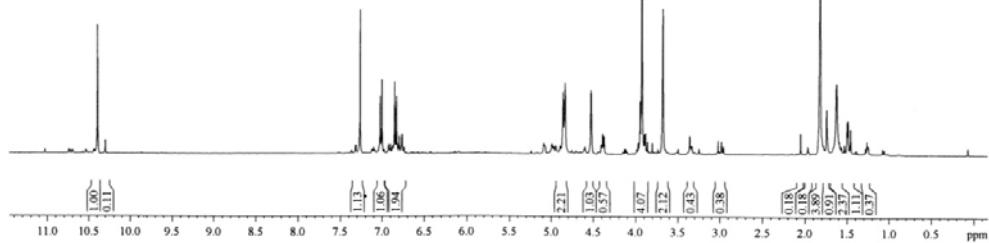
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Spectra	S2
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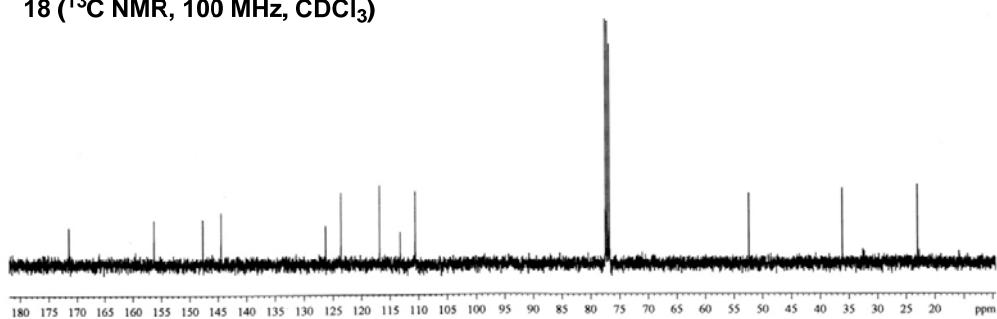
**<sup>1</sup>H, <sup>13</sup>C NMR spectra of synthesized compounds:**

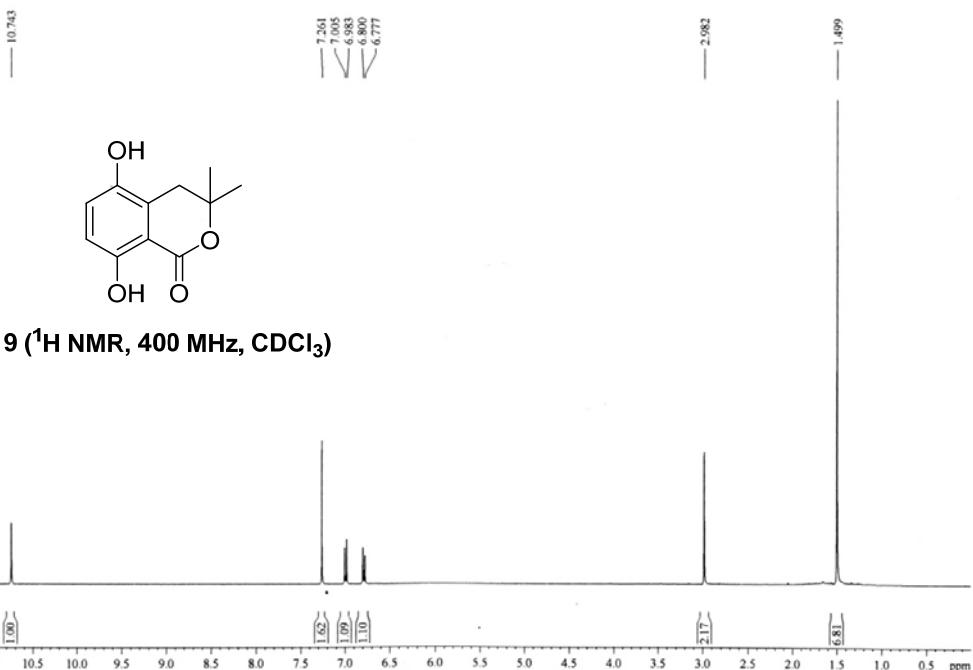
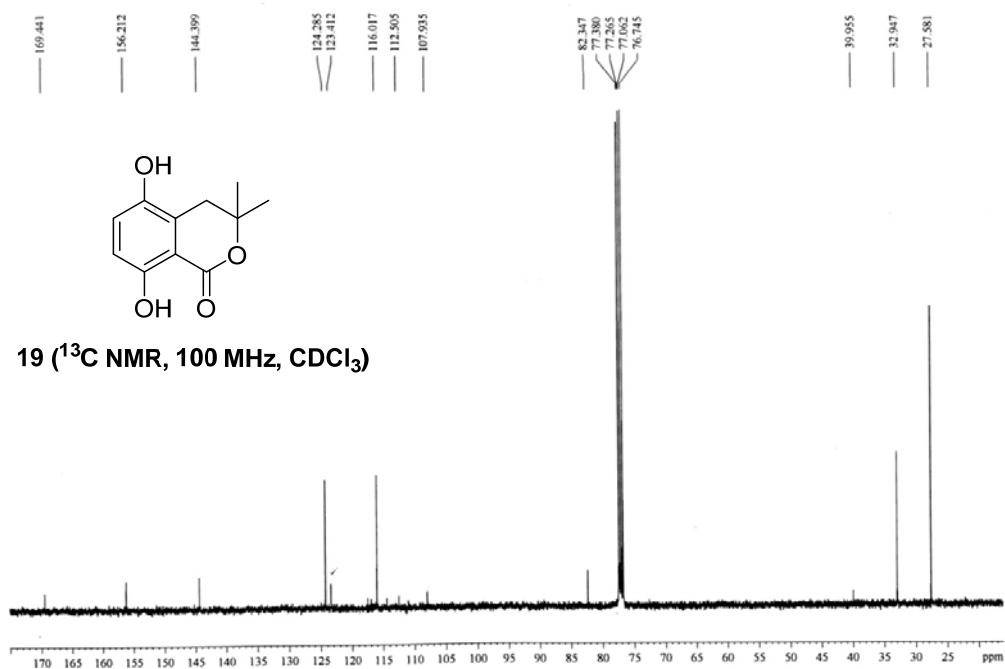


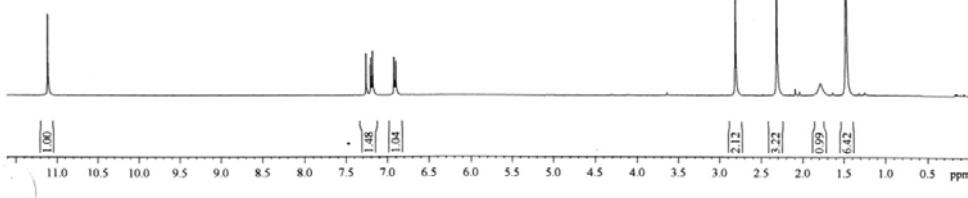
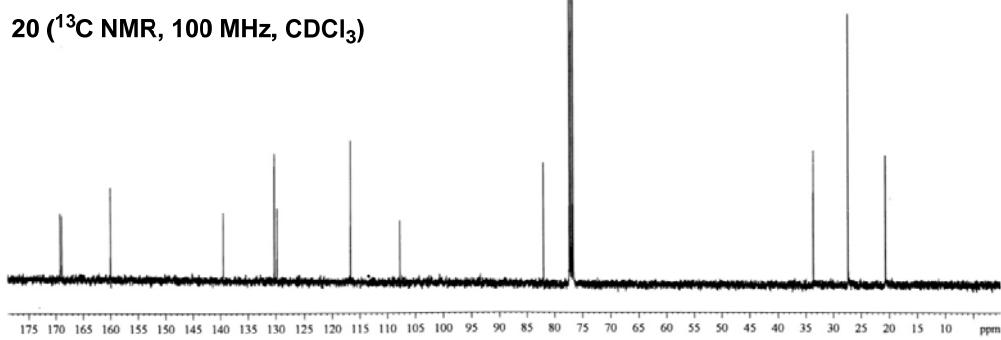
18 ( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )

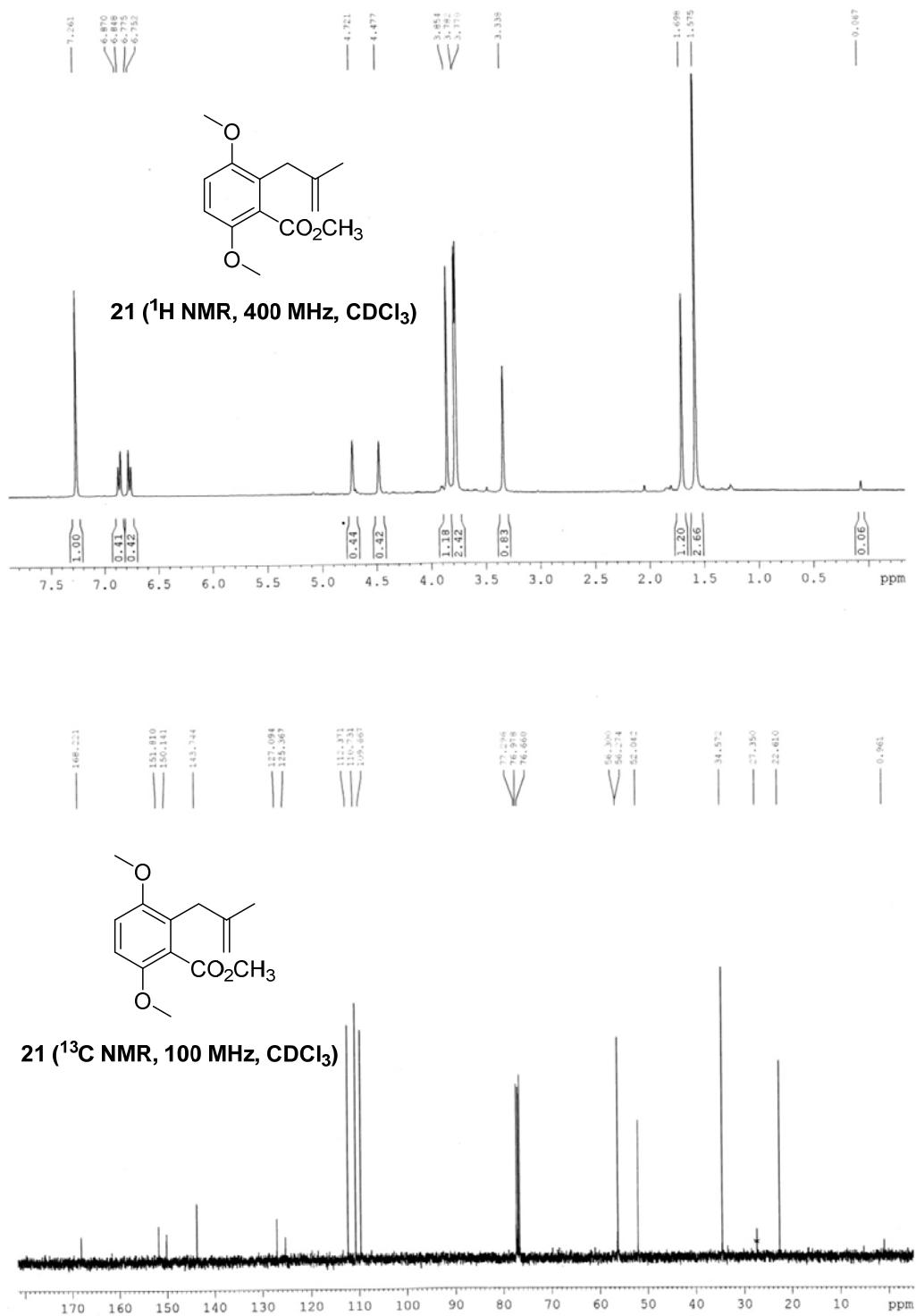


18 ( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )

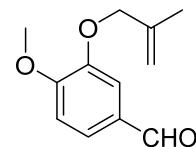


19 (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)19 (<sup>13</sup>C NMR, 100 MHz, CDCl<sub>3</sub>)

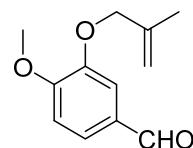
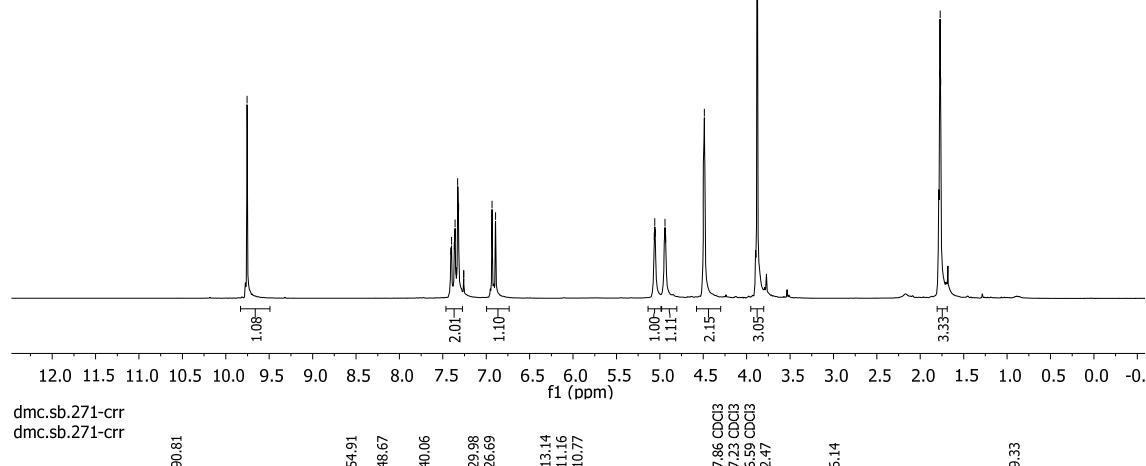
**20 ( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )****20 ( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )**



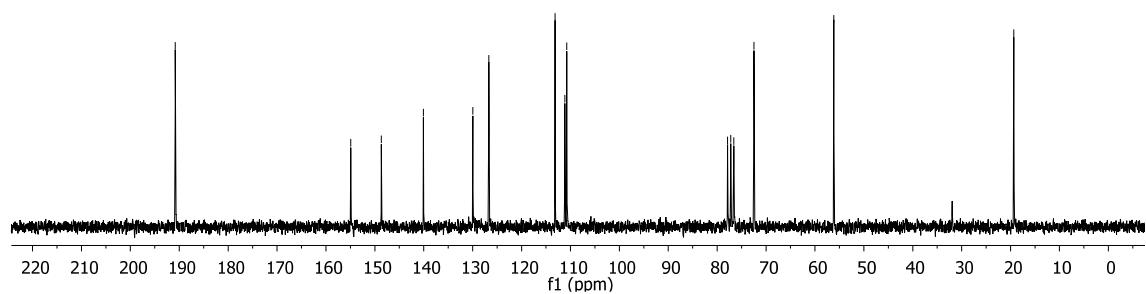
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dm.sb.271-crr

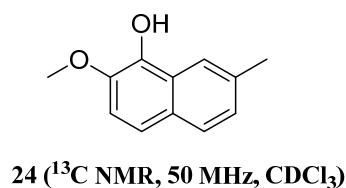
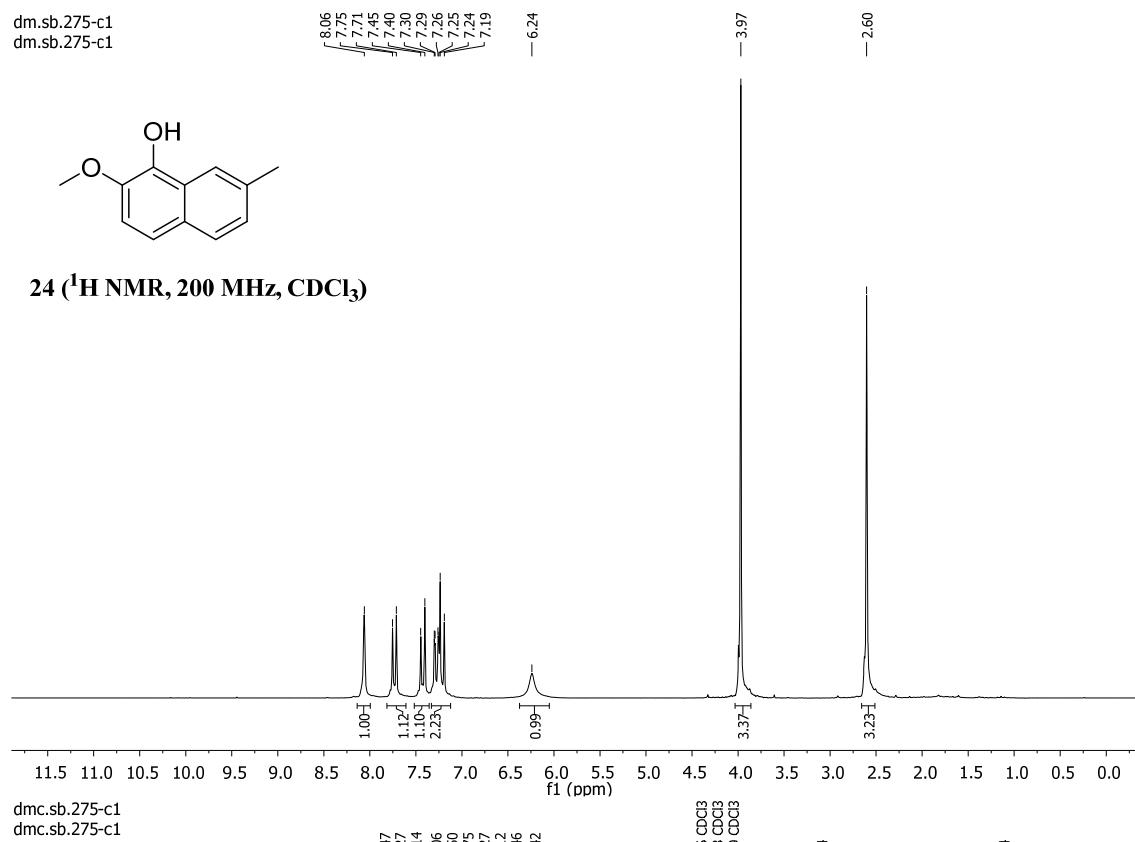


23 ( $^1\text{H}$  NMR, 200 MHz,  $\text{CDCl}_3$ )



23 ( $^{13}\text{C}$  NMR, 50 MHz,  $\text{CDCl}_3$ )

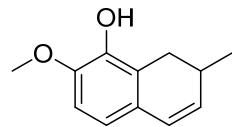




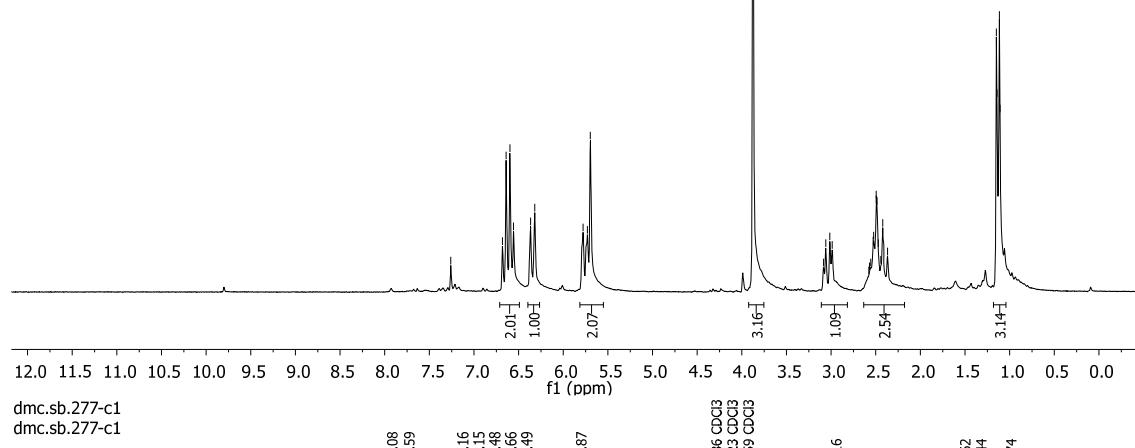
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dm.sb.277-c1

-7.26  
6.68  
6.64  
6.60  
6.56  
6.37  
6.32  
5.78  
5.73  
5.70

-3.88  
3.09  
3.06  
3.01  
2.99  
2.53  
2.52  
2.50  
2.49  
2.48  
2.47  
2.45  
2.42  
2.41  
1.14  
1.12  
1.11



**25 (<sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>)**



dmc.sb.277-c1  
dmc.sb.277-c1

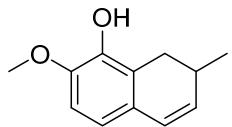
-146.08  
-142.39

-107.87

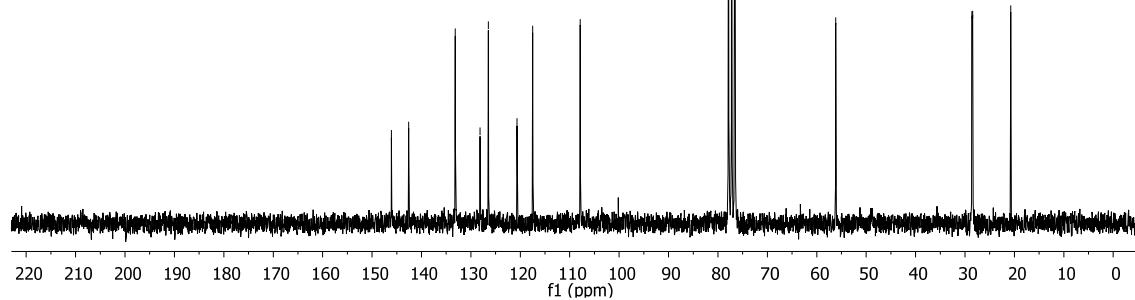
~77.86 CDCl<sub>3</sub>  
~77.23 CDCl<sub>3</sub>  
~76.59 CDCl<sub>3</sub>

-56.16

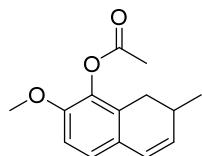
~28.62  
~28.44  
-20.74



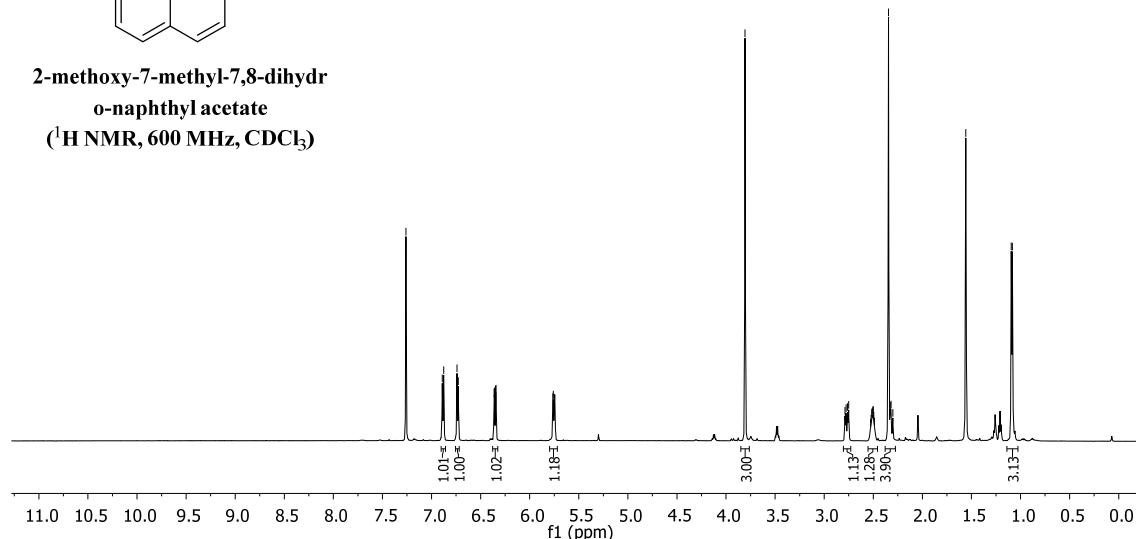
**25 (<sup>13</sup>C NMR, 50 MHz, CDCl<sub>3</sub>)**



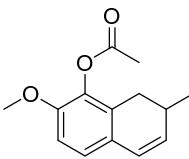
D Mal  
dm /sb / 277-cl-acetate - 1h



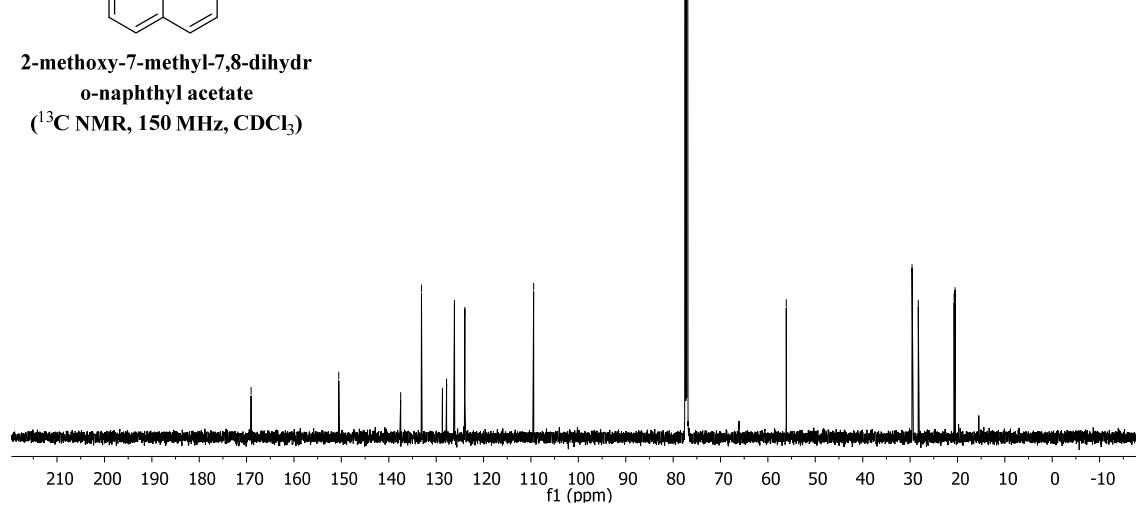
**2-methoxy-7-methyl-7,8-dihydro  
o-naphthyl acetate**  
( $^1\text{H}$  NMR, 600 MHz,  $\text{CDCl}_3$ )



D Mal  
dm /sb / 277-cl-acetate - 13c

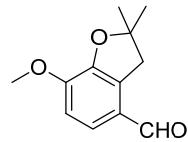


**2-methoxy-7-methyl-7,8-dihydro  
o-naphthyl acetate**  
( $^{13}\text{C}$  NMR, 150 MHz,  $\text{CDCl}_3$ )

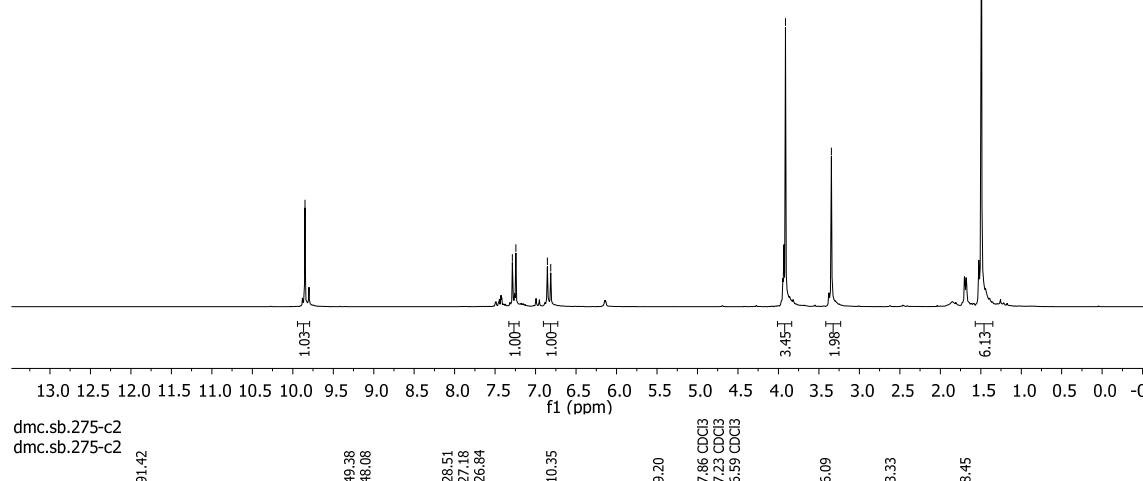


dm.sb.275-c2  
dm.sb.275-c2

— 9.85  
— 7.29  
— 7.24  
— 6.85  
— 6.81



**26 (<sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>)**



— 191.42

— 149.38  
— 148.98

— 128.51  
— 127.18  
— 126.94

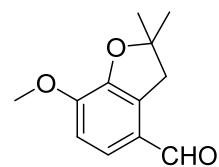
— 110.35

— 89.20  
— 77.86 CDCl<sub>3</sub>  
— 77.22 CDCl<sub>3</sub>  
— 76.59 CDCl<sub>3</sub>

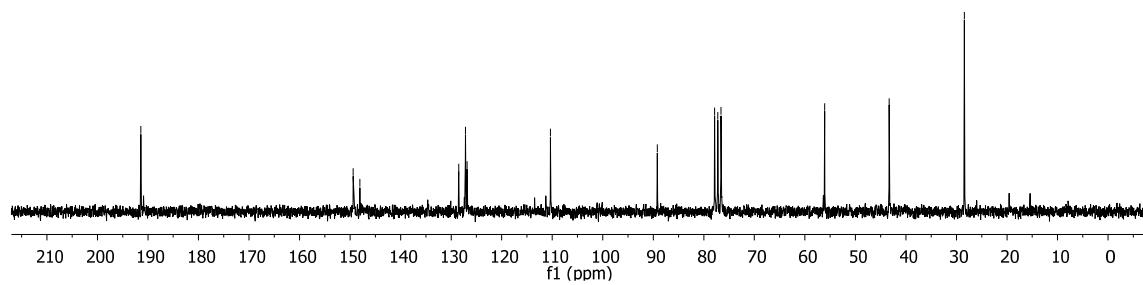
— 56.09

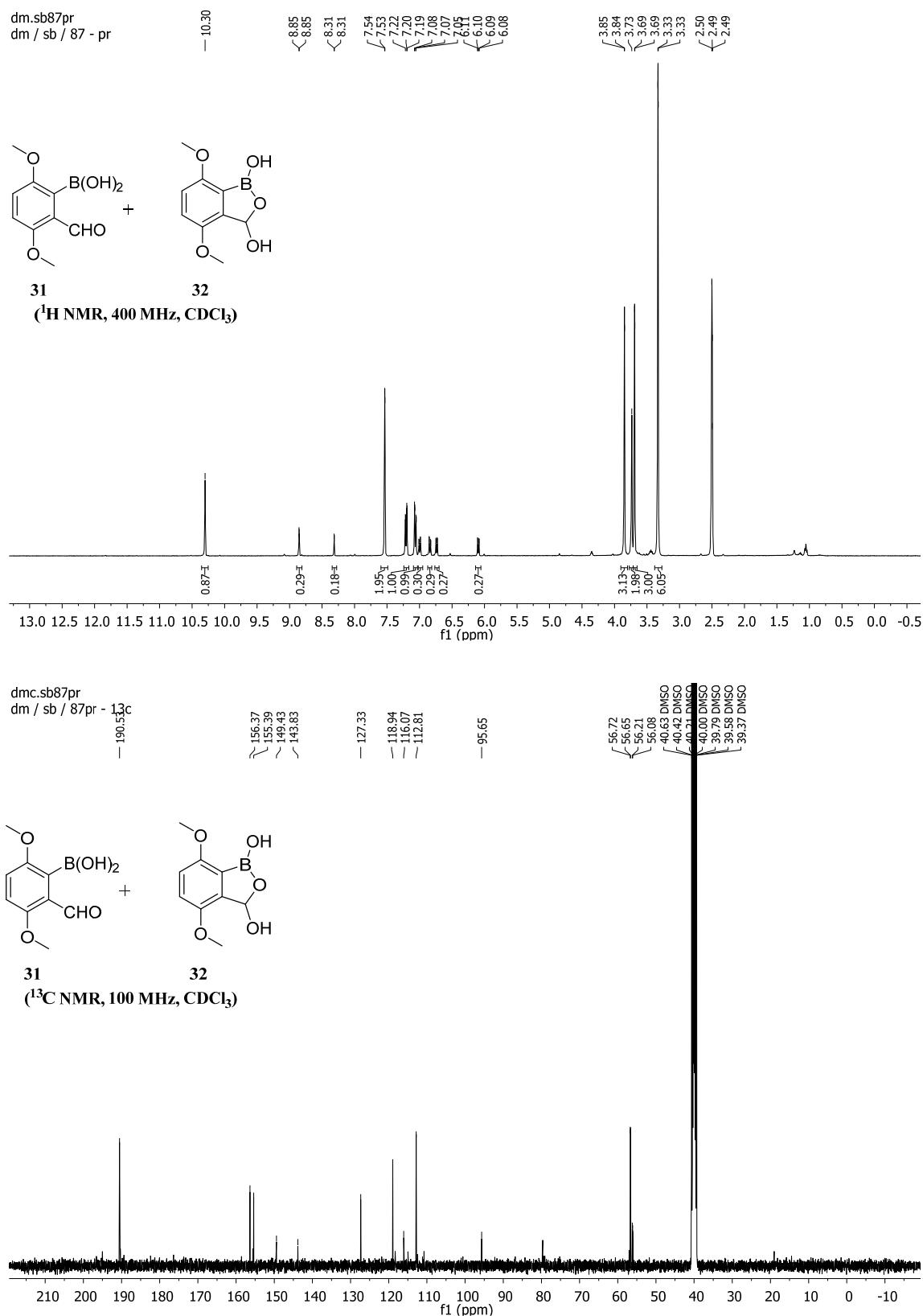
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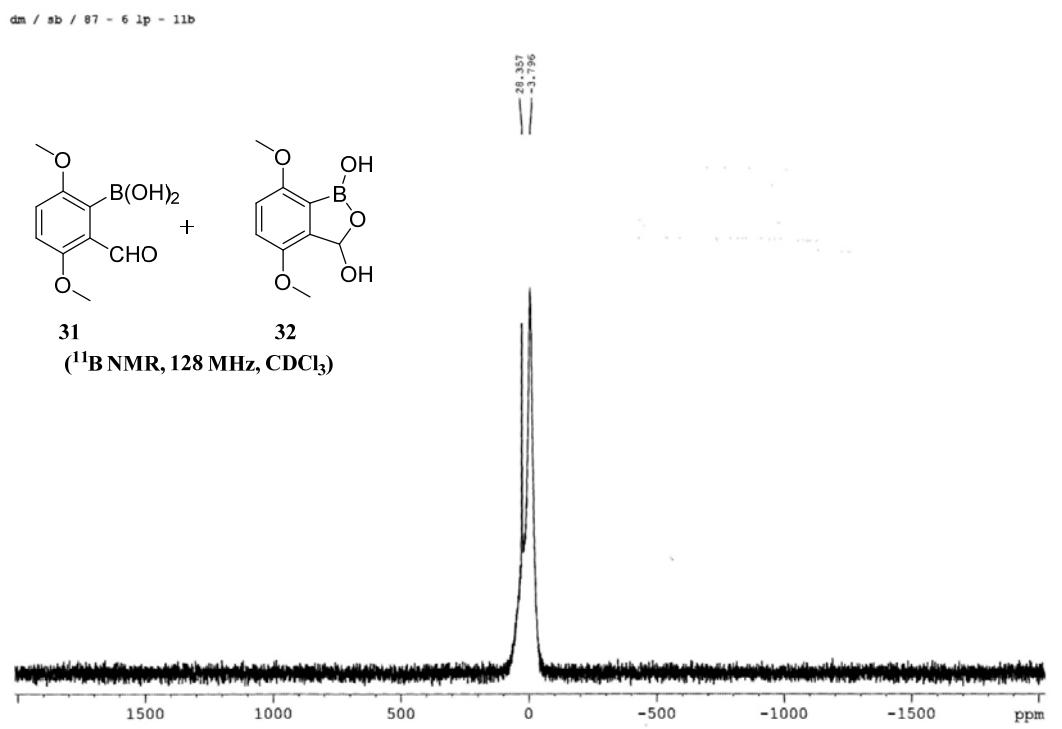
— 28.45



**26 (<sup>13</sup>C NMR, 50 MHz, CDCl<sub>3</sub>)**







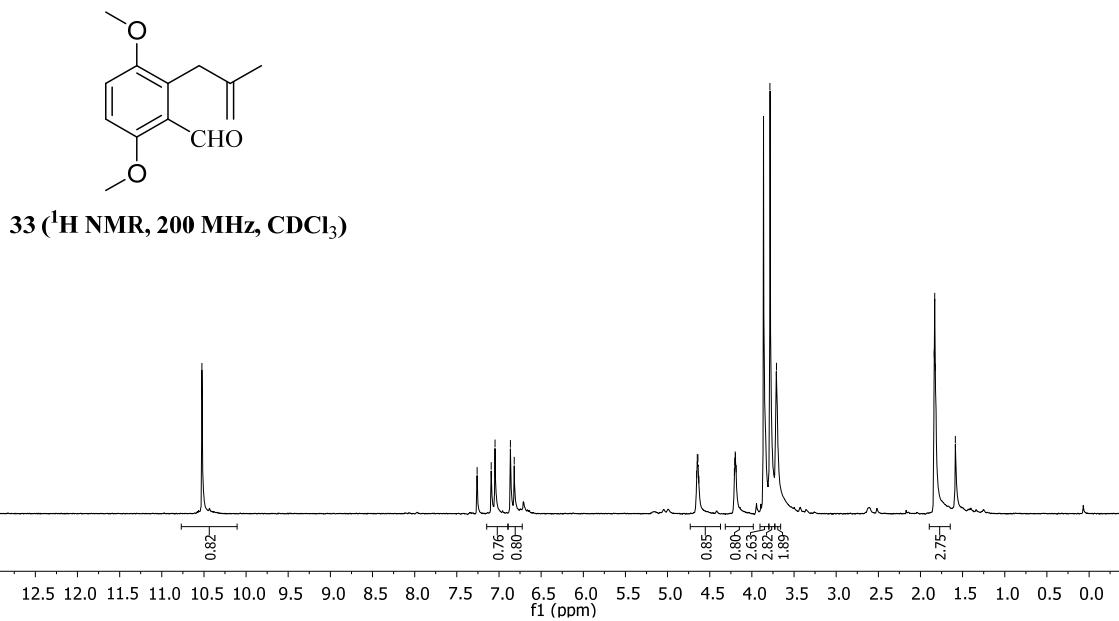
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dm, sb 161 2 Pr

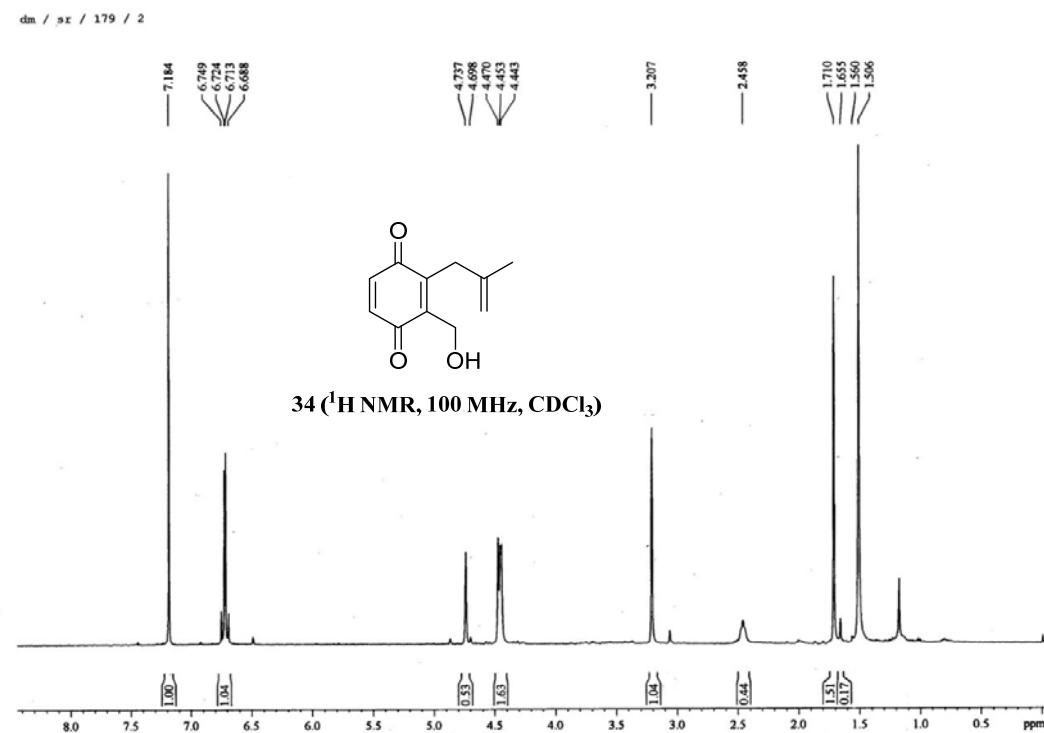
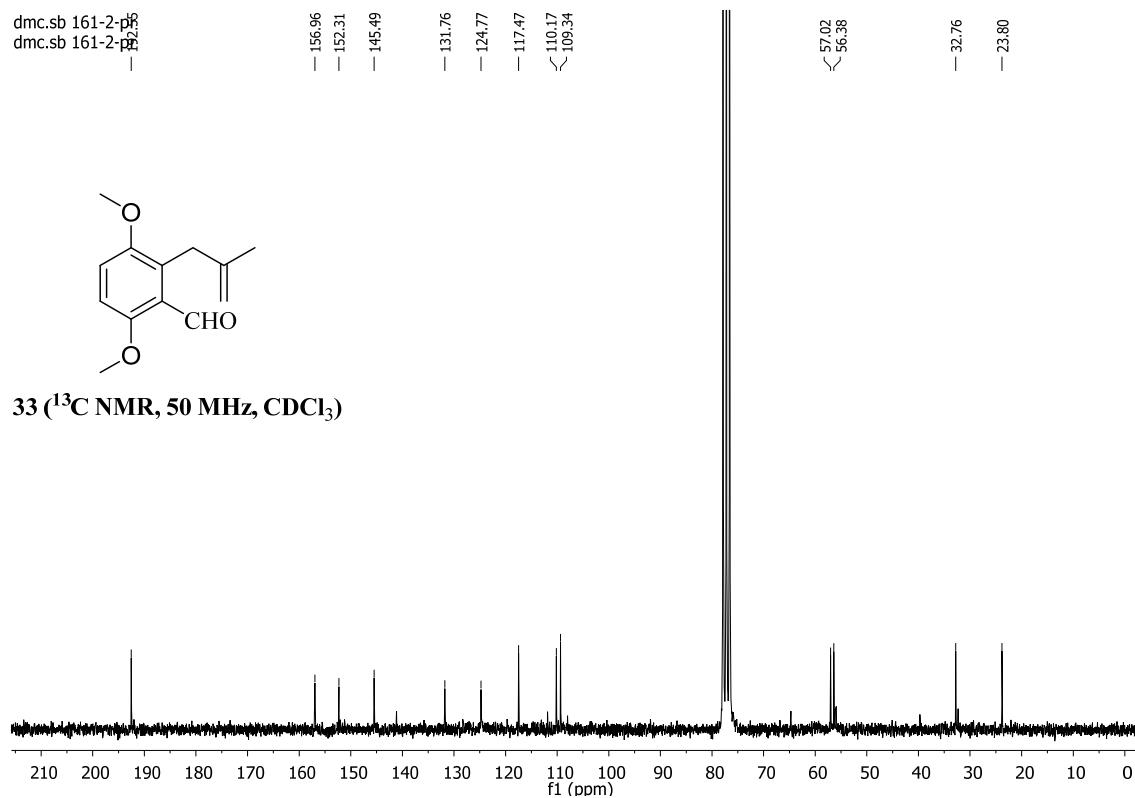
— 10.52

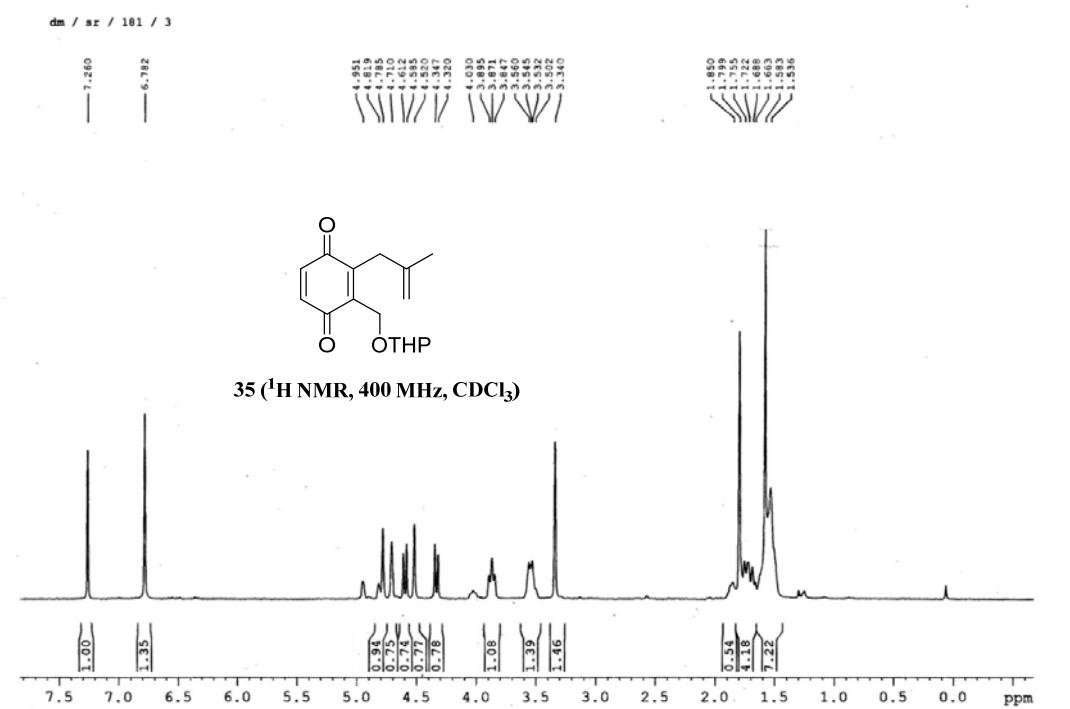
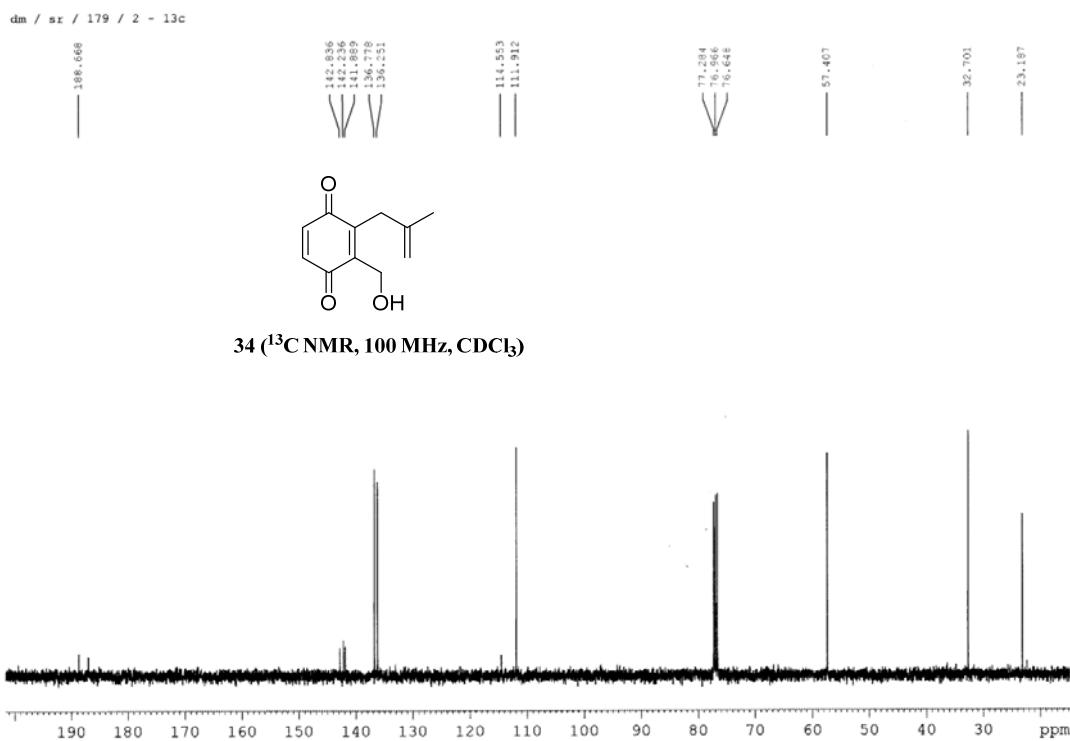
7.26  
7.09  
7.05  
6.86  
6.82

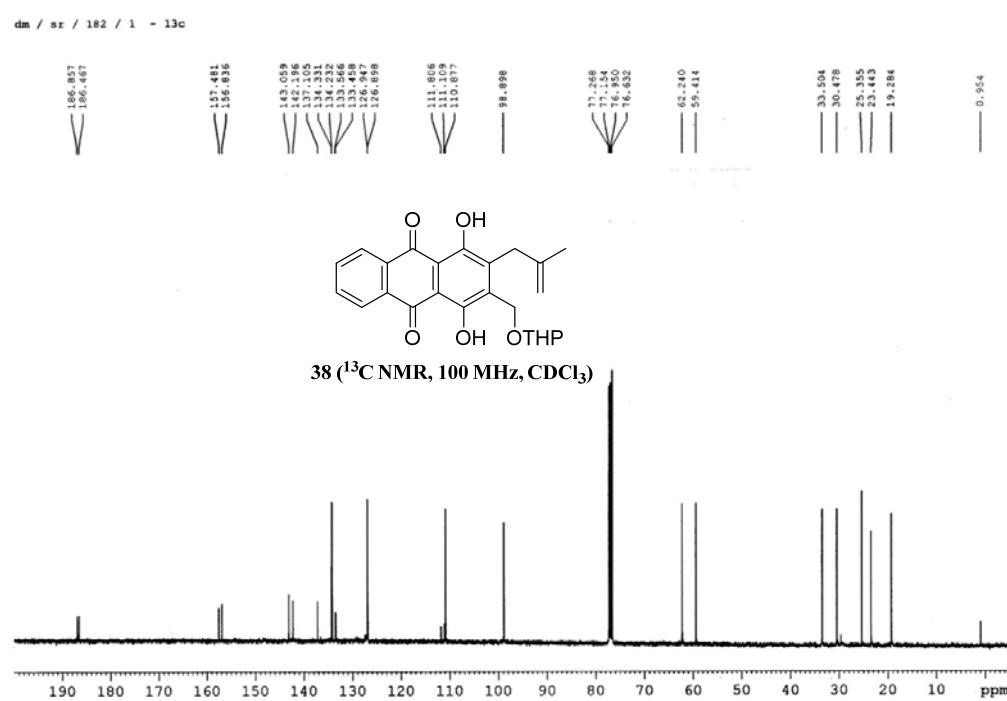
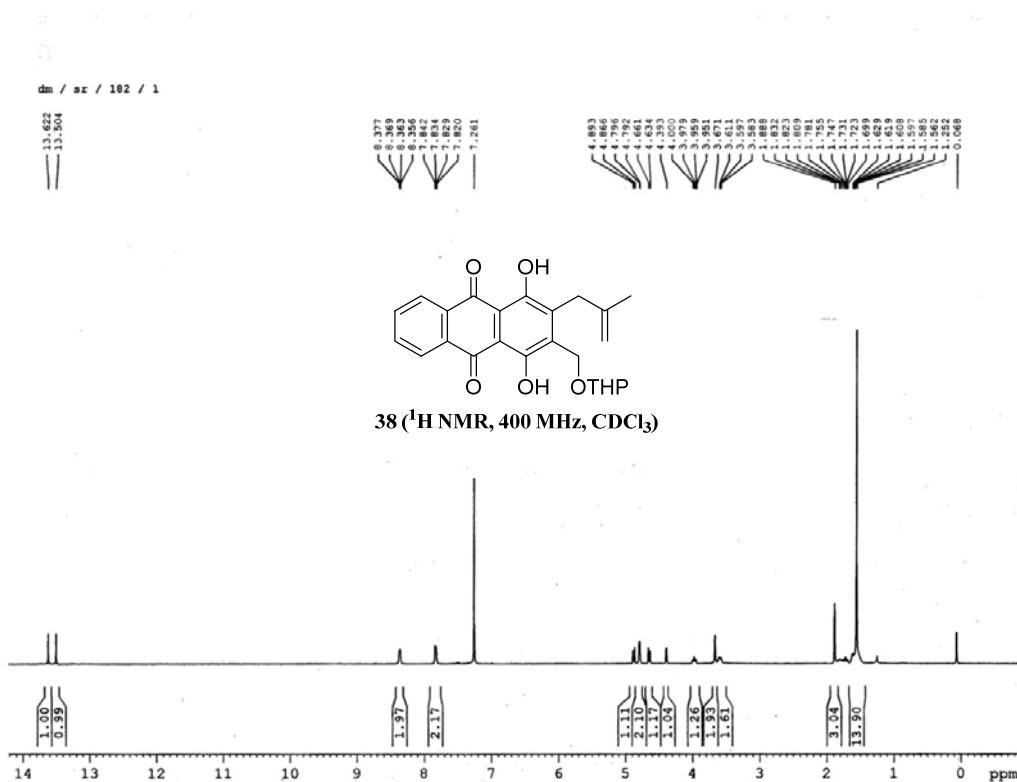
4.66  
4.65  
4.64  
4.63  
4.21  
4.20  
4.19  
4.19  
3.86  
3.79  
3.71

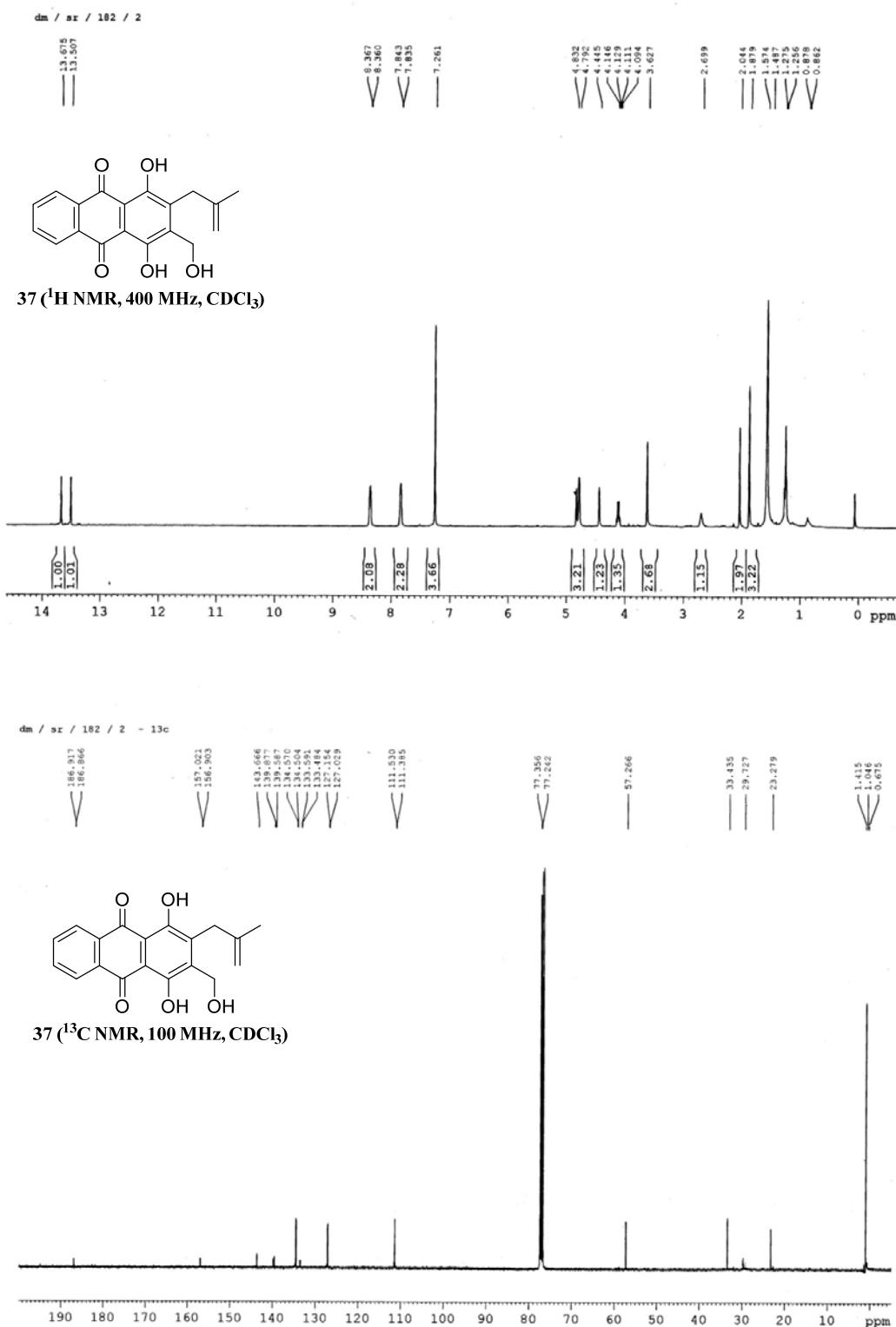
1.84  
1.83  
1.82  
1.59

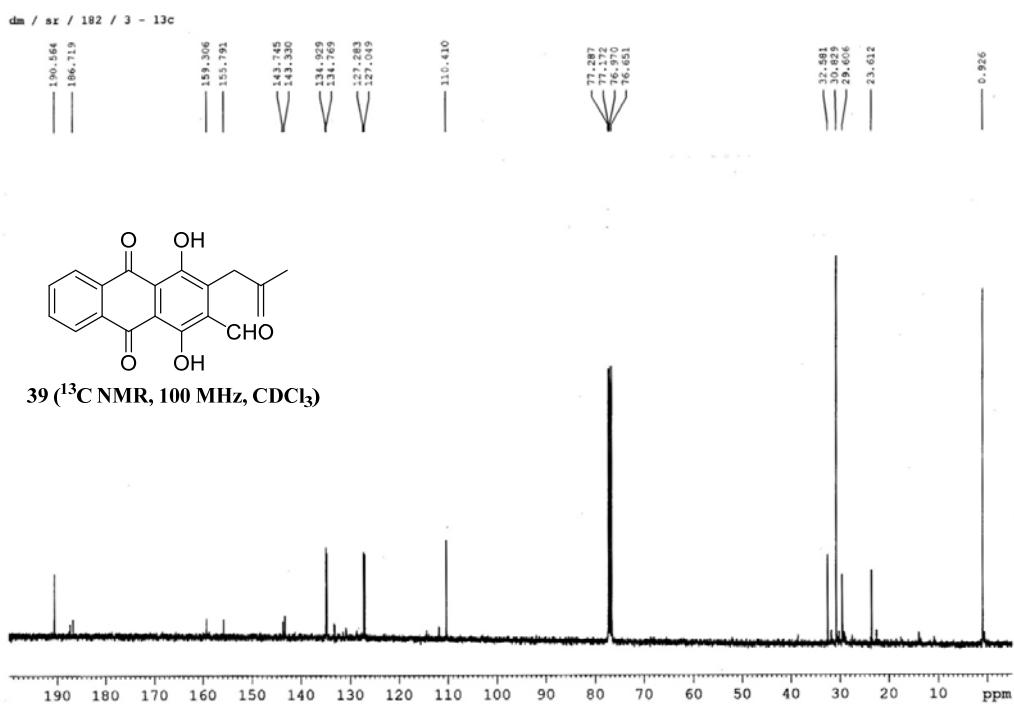
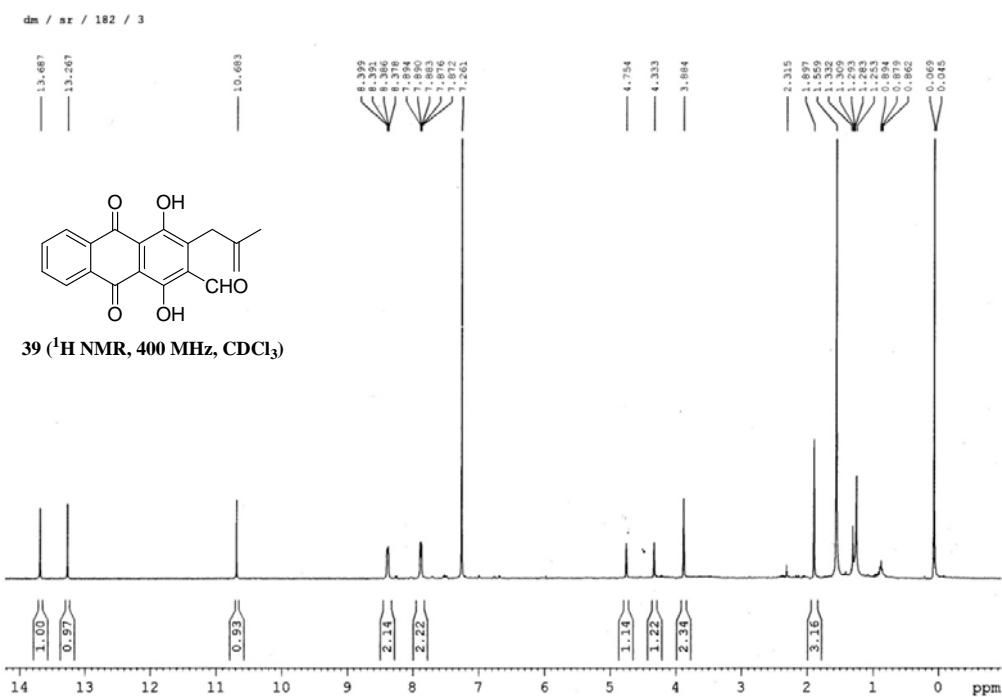


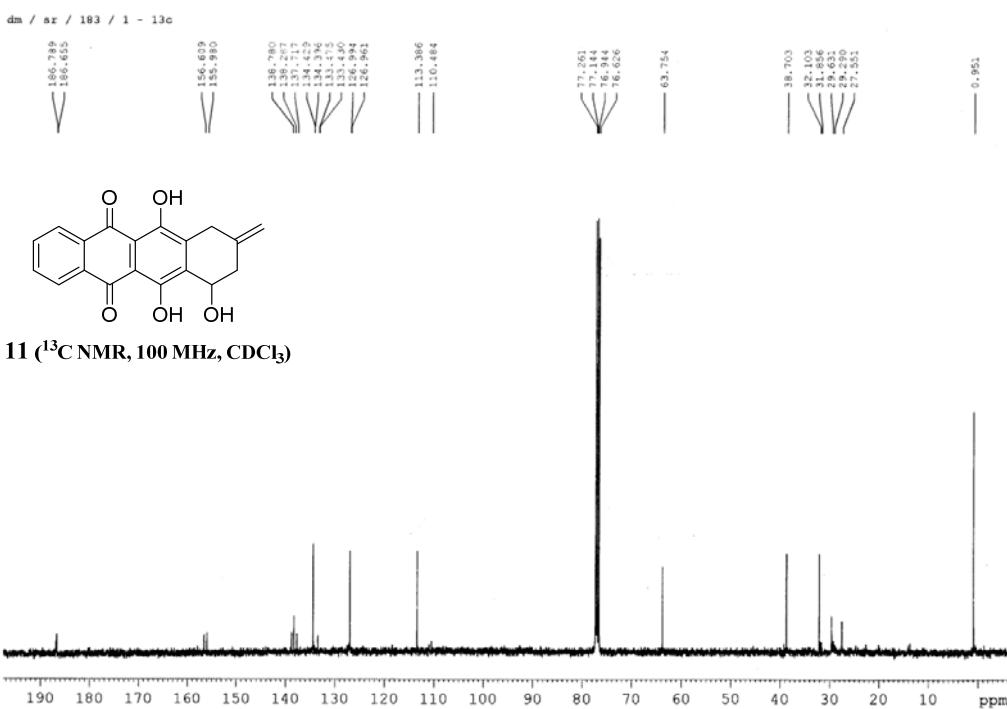
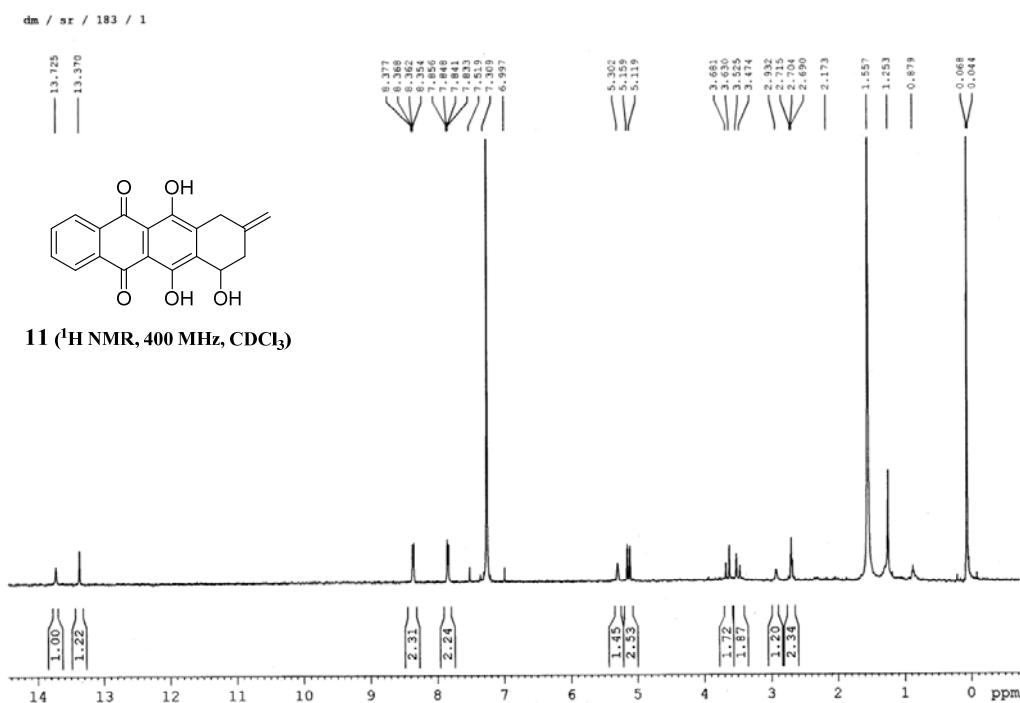


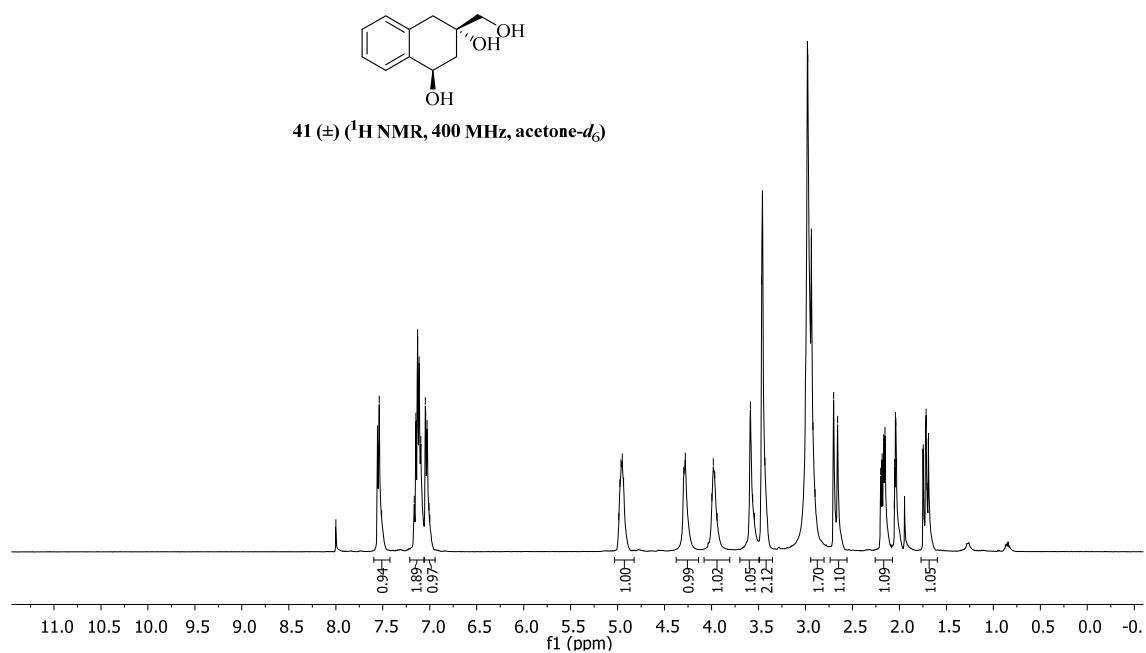
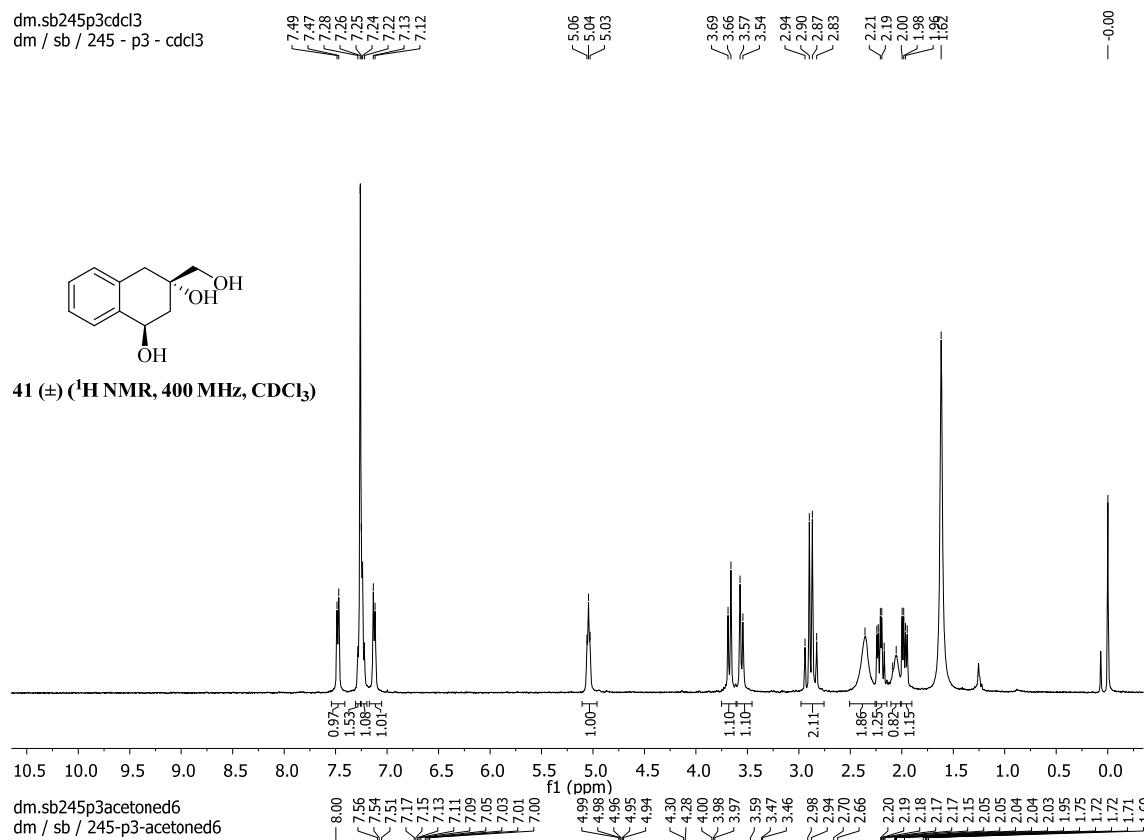


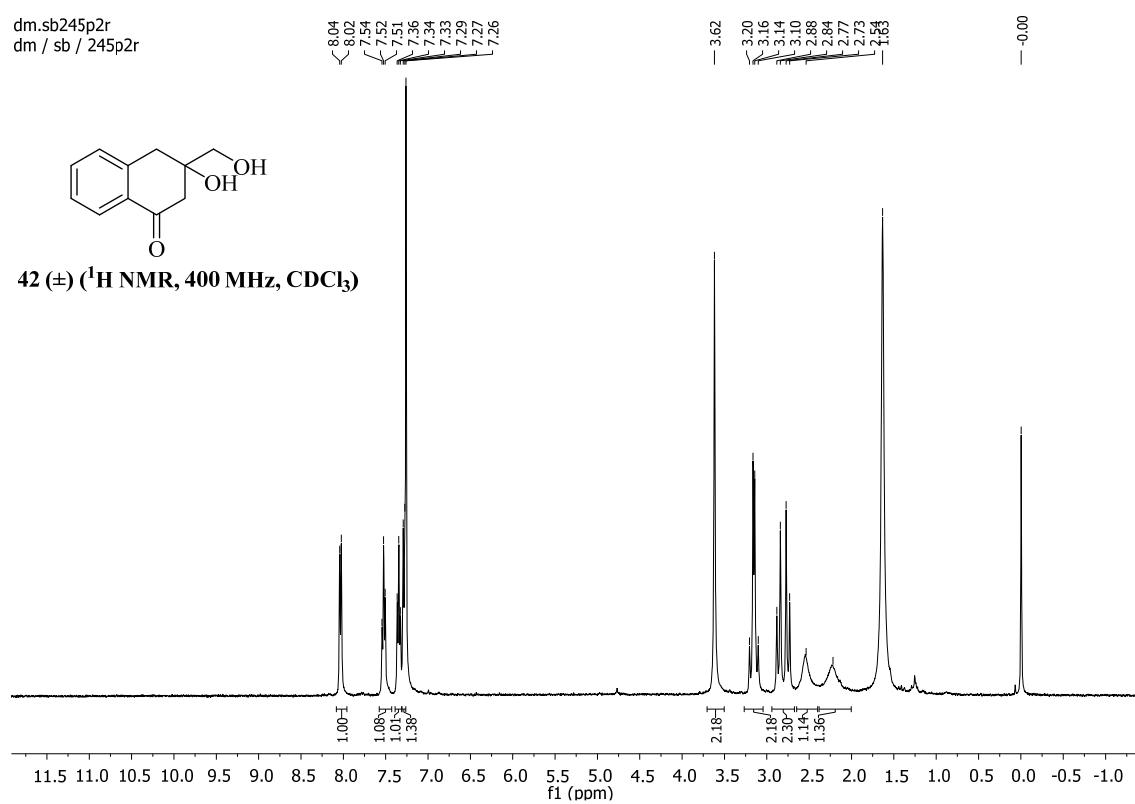
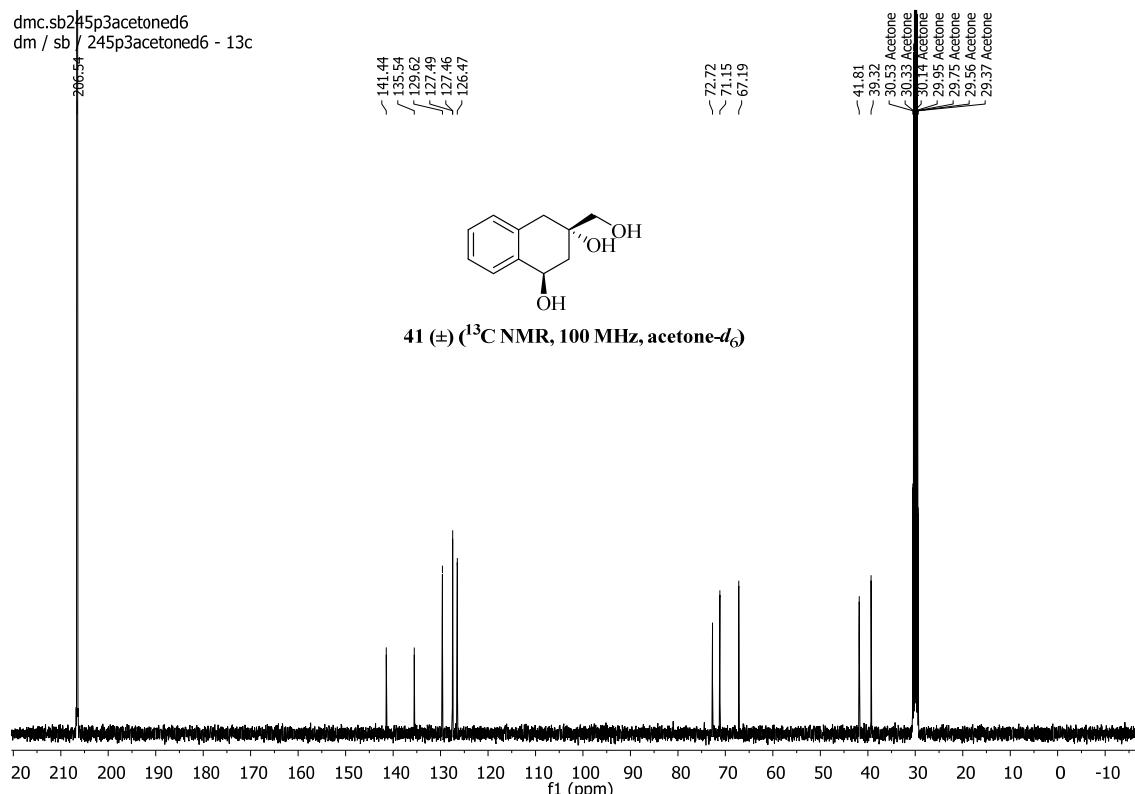


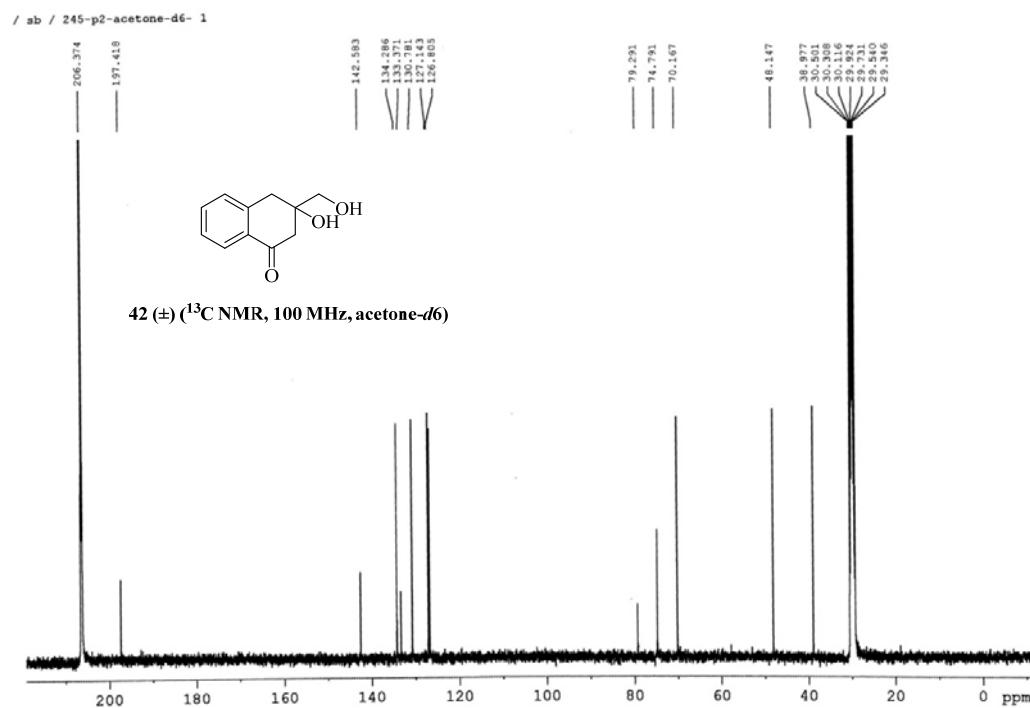
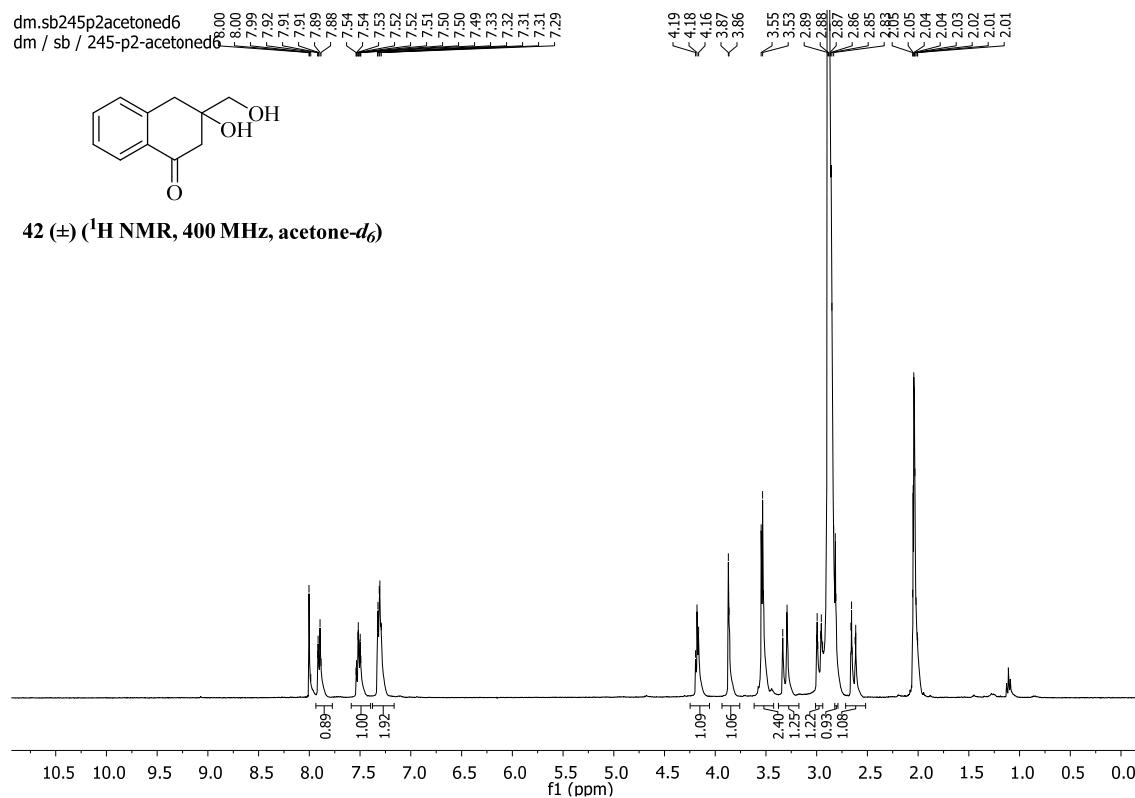






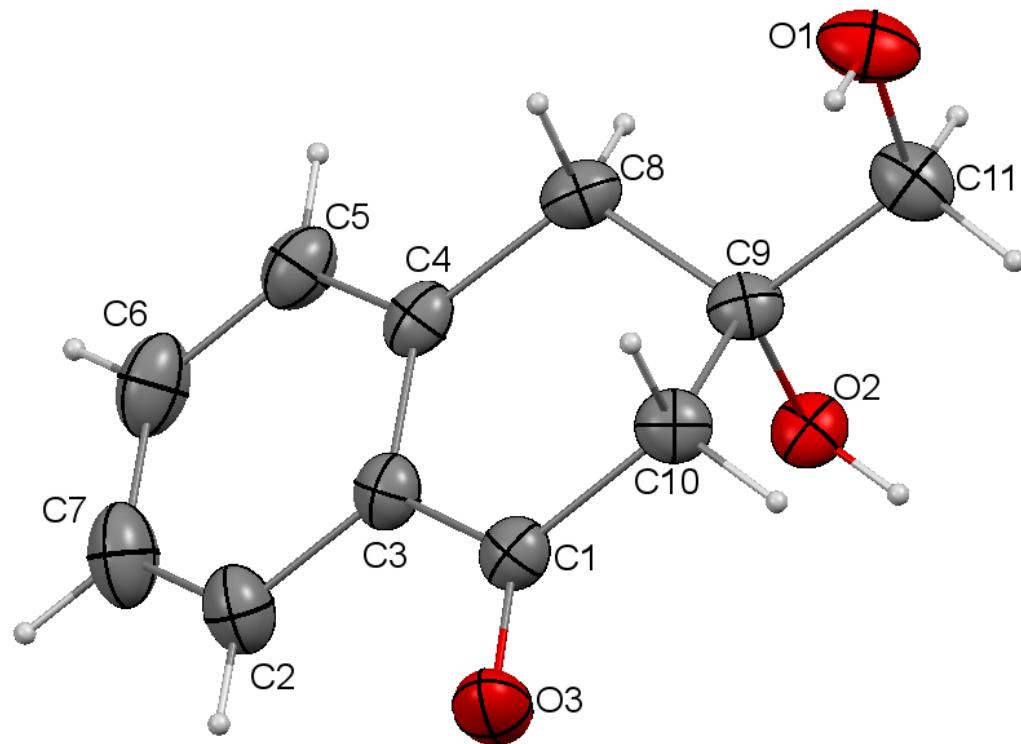






### X-ray Crystallography

Suitable single crystals of compound **42** for X-ray diffraction studies were obtained by slow evaporation of a solution of **42** in CHCl<sub>3</sub>. Single crystal X-ray diffraction data collections for the compound was performed at room temperature using Bruker-APEX-II CCD diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by SIR-92<sup>1</sup> or SHELXS-97 available in WinGX, which successfully located most of the non-hydrogen atoms. Subsequently, least square refinements were carried out on F<sup>2</sup> using SHELXL-97 (WinGX version)<sup>2,3</sup> 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.



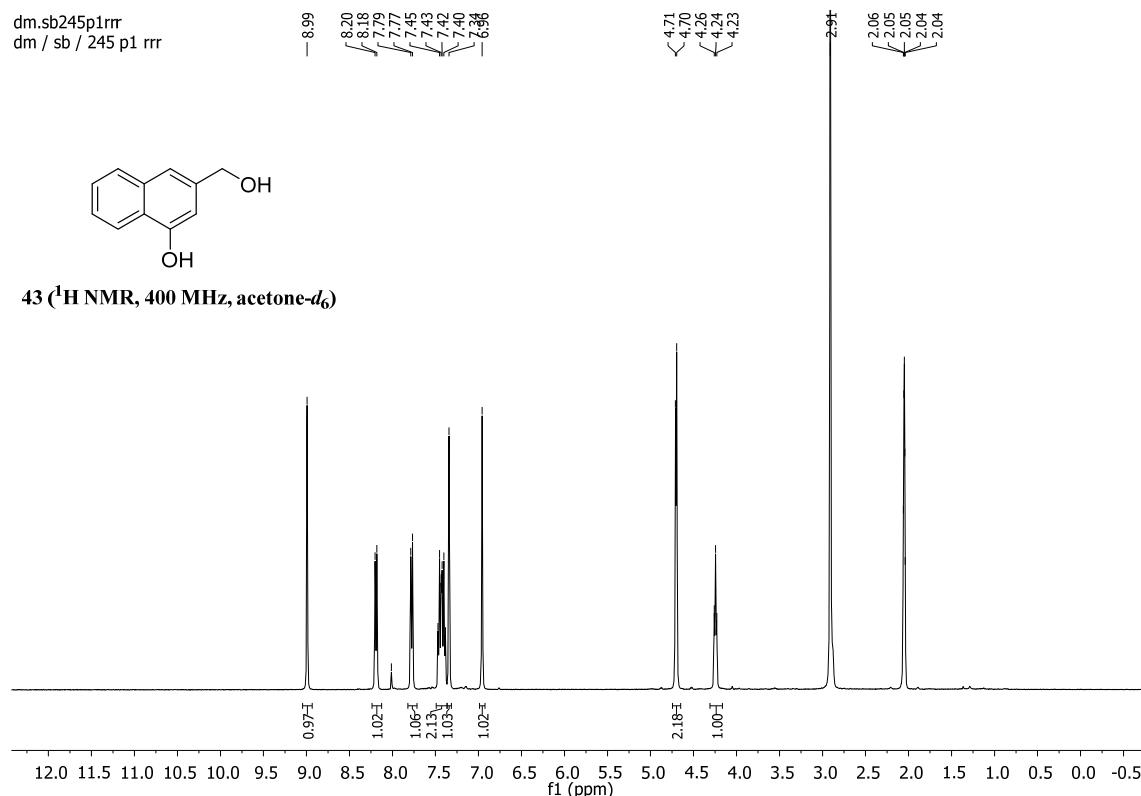
**Figure S42.** ORTEP diagram of **42** with 30% probability ellipsoids.

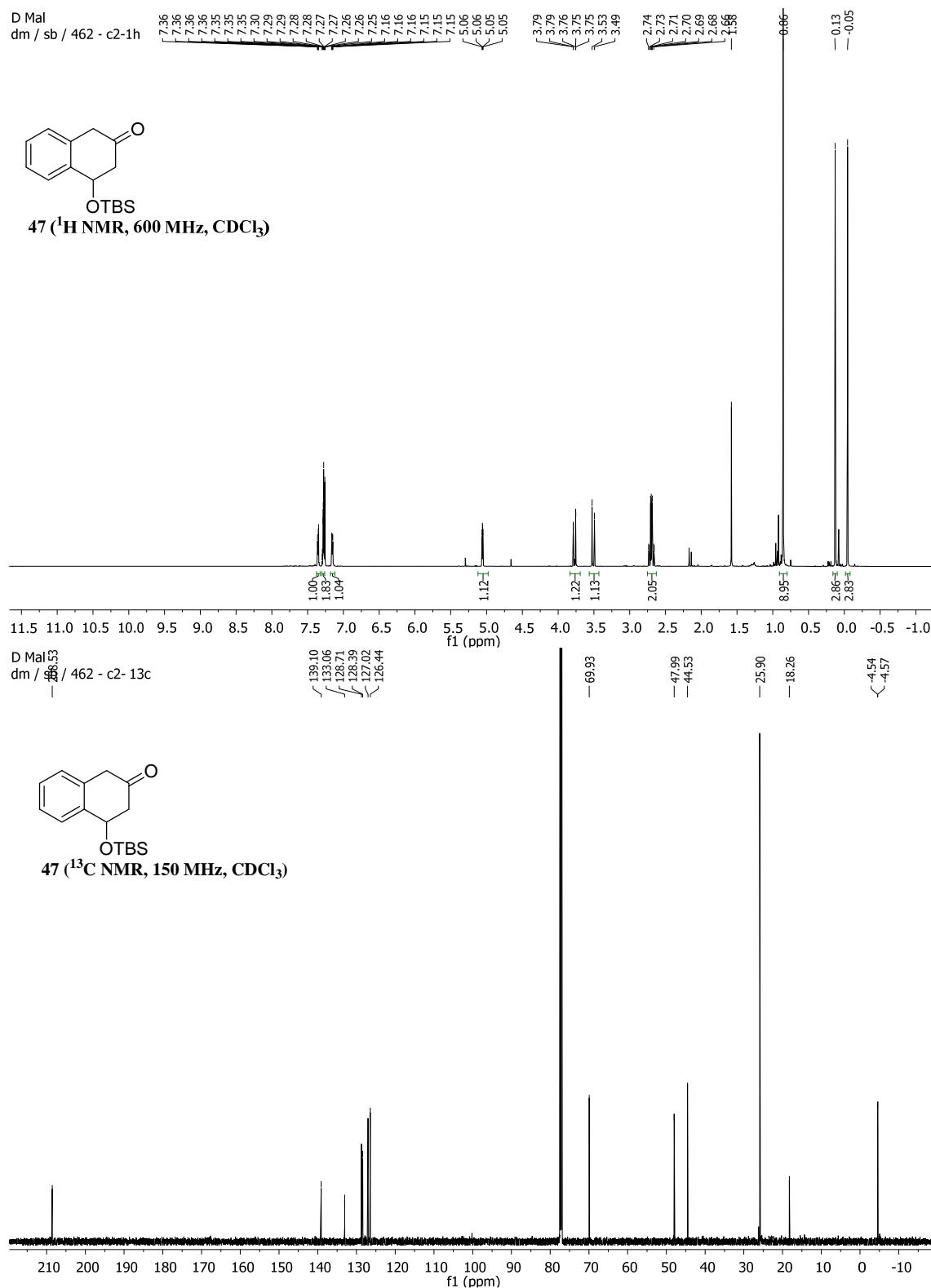
**Table S1.** Crystallographic Data for Compound **42****42**

<b>Empirical formula</b>	<b>C<sub>11</sub>H<sub>12</sub>O<sub>3</sub></b>
<b>Formula weight</b>	<b>192.21</b>
<b>Wavelength (Å)</b>	<b>0.71073</b>
<b>Temperature (K)</b>	<b>293(2)</b>
<b>Crystal system</b>	<b>Monoclinic</b>
<b>Color and shape</b>	<b>Dark Green, block</b>
<b>Space group</b>	<b>P2<sub>1</sub>/c</b>
<b>a/Å</b>	<b>5.2277(9)</b>
<b>b/Å</b>	<b>21.884(4)</b>
<b>c/Å</b>	<b>8.4573(15)</b>
<b>α/degree</b>	<b>90</b>
<b>β/degree</b>	<b>95.533(6)</b>
<b>γ/degree</b>	<b>90</b>
<b>Volume (Å<sup>3</sup>)</b>	<b>960.0(3)</b>
<b>Z</b>	<b>4</b>
<b>D<sub>calcd</sub>, g cm<sup>-3</sup></b>	<b>1.326</b>
<b>μ/mm<sup>-1</sup></b>	<b>0.096</b>
<b>F(000)</b>	<b>408</b>

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

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## 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.