Supporting Information

Stereospecific Hydrogenolysis of Benzylic Alcohols over Pd/C

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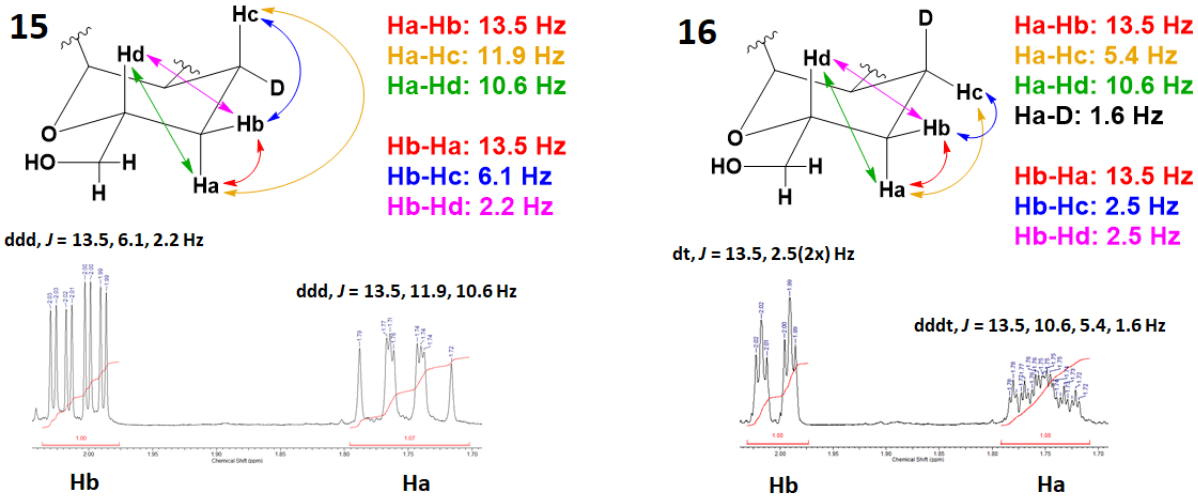
I. Structural assignment of *cis* and *trans* chromanes 15 and 16

The following coupling constants were found for chromanes **15** and **16**, and were assigned as described below.



Geminal ^{2}J coupling constants between two protons are larger than vicinal ^{3}J coupling constants. For vicinal coupling constants, the size of the coupling varies depending on whether the protons are axial or equatorial: the vicinal coupling is largest between two axial protons (Hax-Hax), smaller for an axial-equatorial coupling (Hax-Heq), and smallest for an equatorial-equatorial coupling (Heq-Heq).

The -CH_2OH moiety in **15** and **16** is expected to be in the equatorial position to minimize steric hindrance. The deuterium atom at the benzylic carbon is positioned either equatorially (**15**) or axially (**16**).

On the ^{1}H-NMR spectra of **15** and **16**, the geminal coupling constants for methylene protons Ha and Hb are identical at 13.5 Hz. The vicinal coupling constants of methylene protons Ha and Hb to protons Hc and Hd allowed us to assign chromane **15** as *cis* and chromane **16** as *trans*.

cis-Chromane **15**

Vicinal ax-ax coupling: large ax-ax couplings of 11.9 and 10.6 Hz were measured between Ha and Hc and Ha and Hd, respectively.

Vicinal ax-eq coupling: smaller ax-eq couplings of 6.1 Hz for Hb-Hc and 2.2 Hz for Hb-Hd were measured. While 2.2 Hz seems much lower than 6.1 Hz, we found a similar value for the Hb-Hd coupling in chromane **16**.

There are no eq-eq couplings for chromane **15**.

trans-Chromane **16**

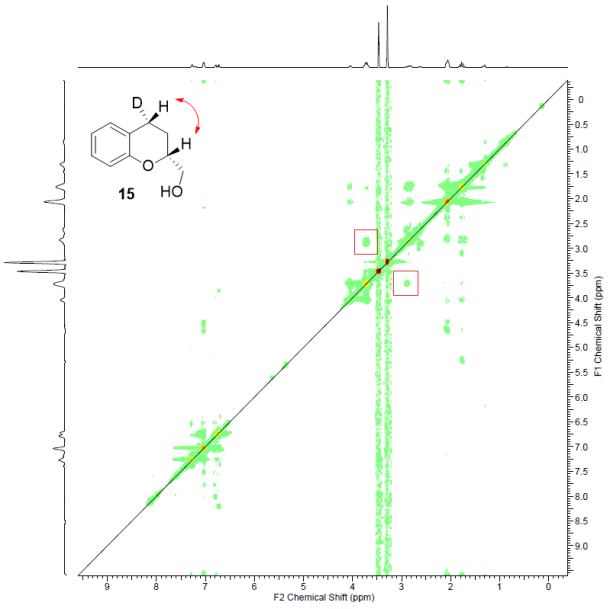
Vicinal ax-ax coupling: a large ax-ax coupling of 10.6 Hz was measured between Ha and Hd. The deuterium atom also showed a small $^{3}J_{HD}$ ax-ax coupling of 1.6 Hz to Ha. This is close to known values in the literature.[1] When the deuterium is axial, as is the case for chromane **16**, its ax-ax coupling to Ha

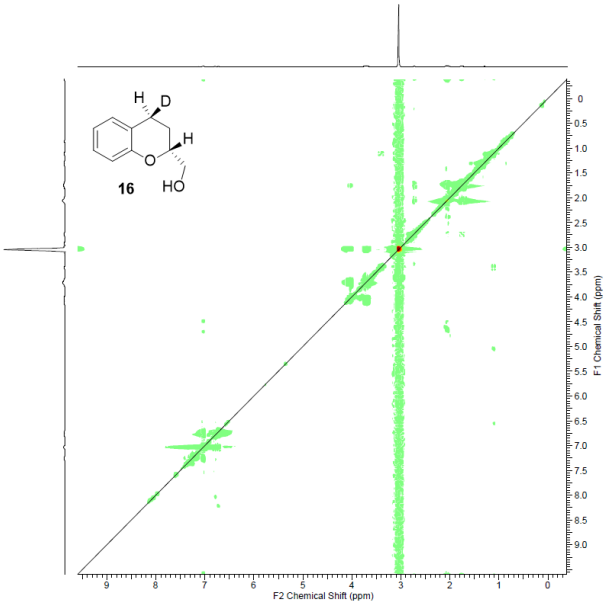
is large enough to be resolved on the ^{1}H-NMR spectrum. For chromane **15**, the ax-eq coupling of equatorial deuterium to Ha is too small and cannot be observed on the ^{1}H-NMR spectrum.

Vicinal ax-eq coupling: couplings of 5.4 Hz for Ha-Hc and 2.5 Hz for Hb-Hd were measured.

Vicinal eq-eq coupling: a value of 2.5 Hz was obtained for Hb-Hc eq-eq coupling. This is identical to the Hb-Hd ax-eq coupling constant, and results in the *dt* pattern observed for proton Hb in chromane **16**.

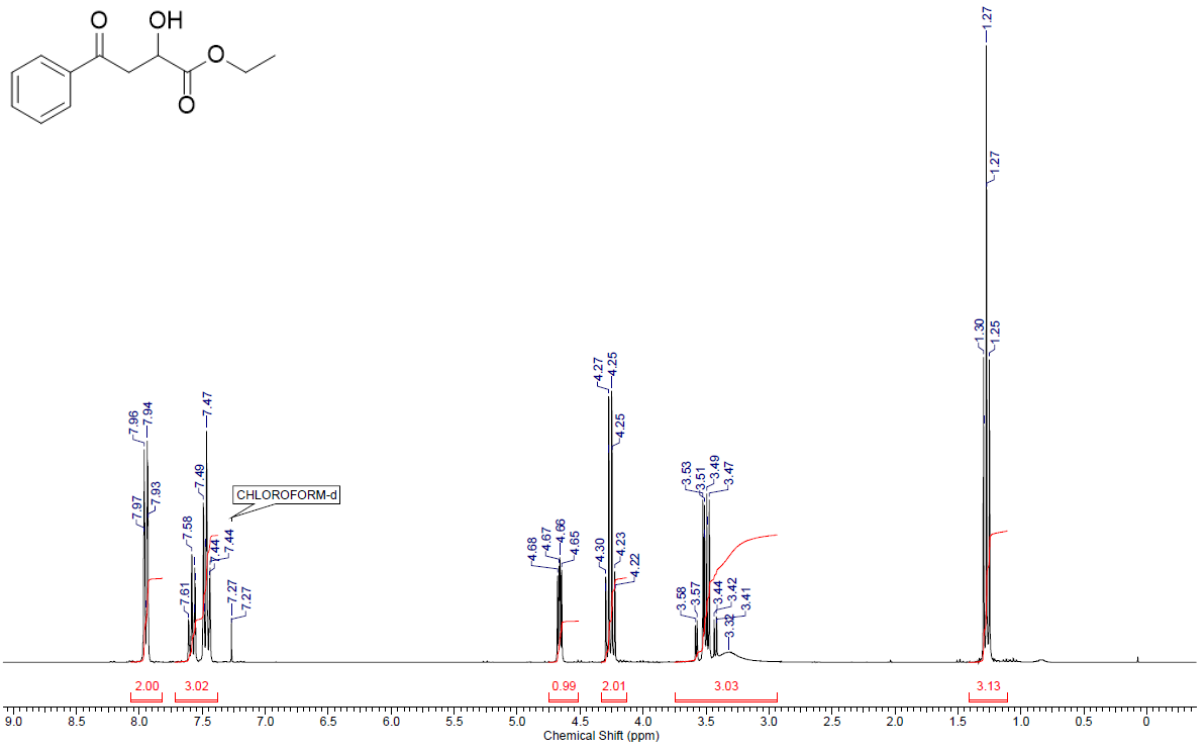
ROESY experiments (see below) showed an interaction between Hc and Hd for chromane **15**, and no interaction between Hc and Hd for chromane **16**.



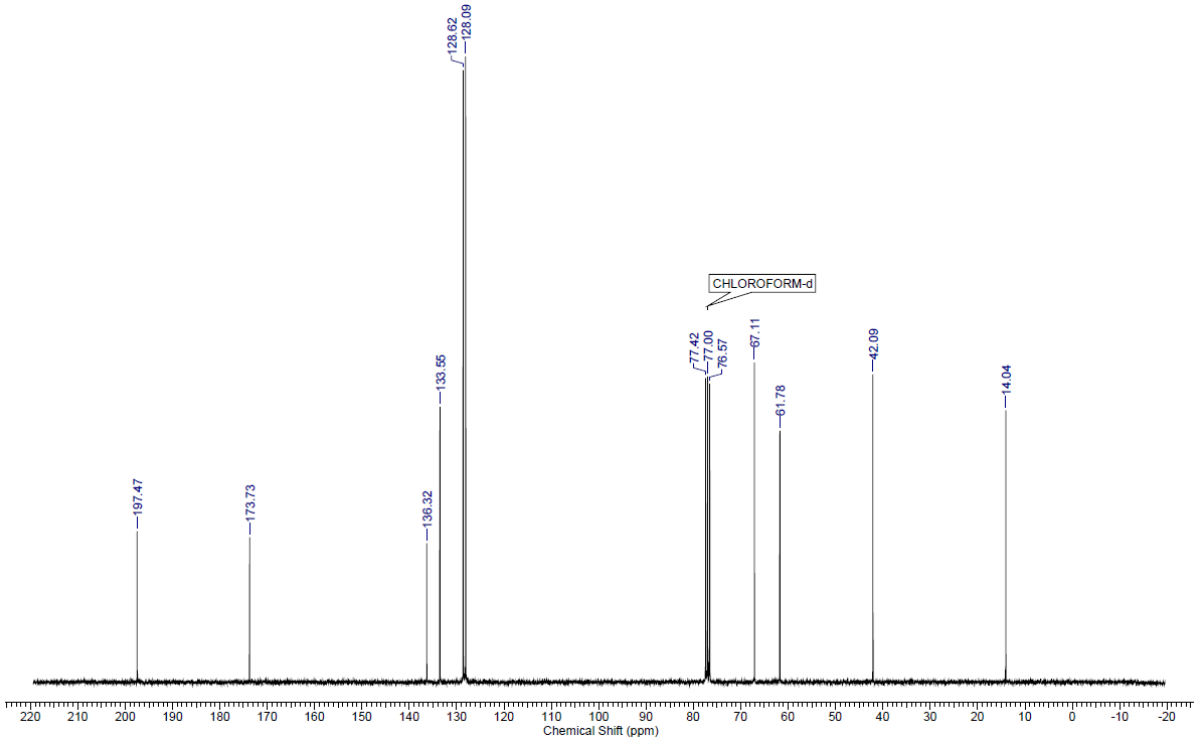


II. NMR Spectra

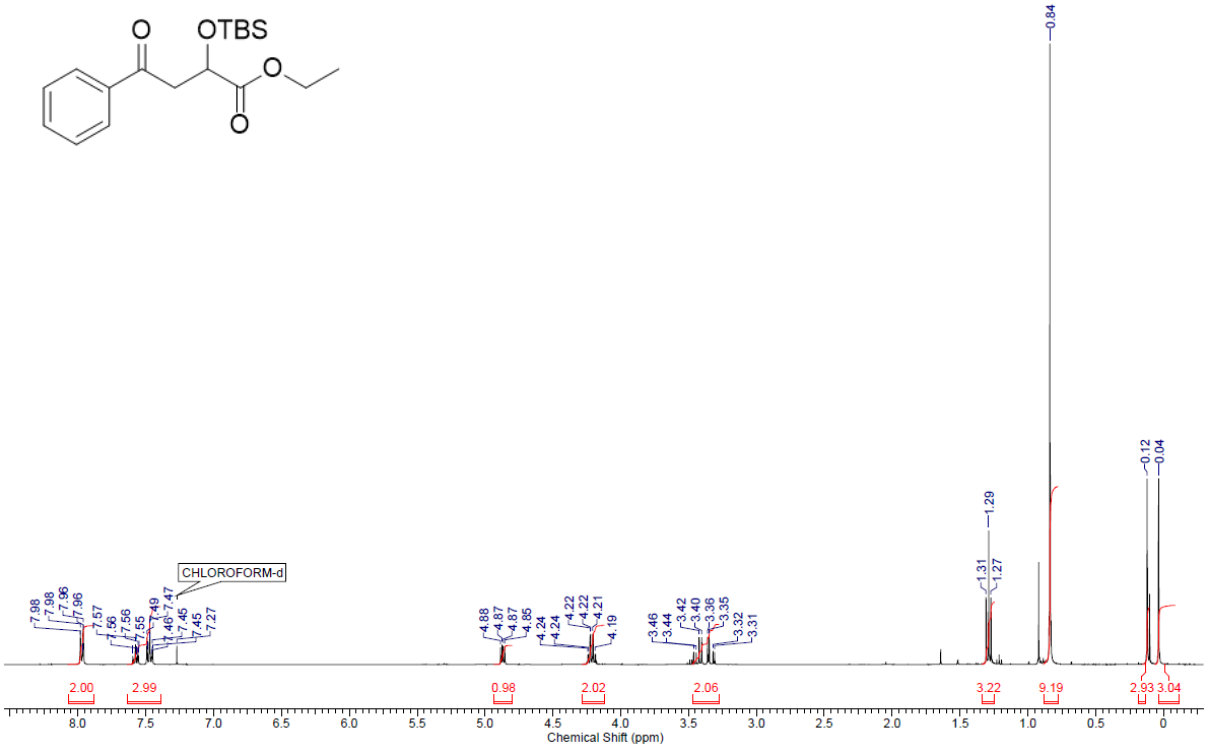
NMR spectra **5**. 300 MHz, $CDCl_3$



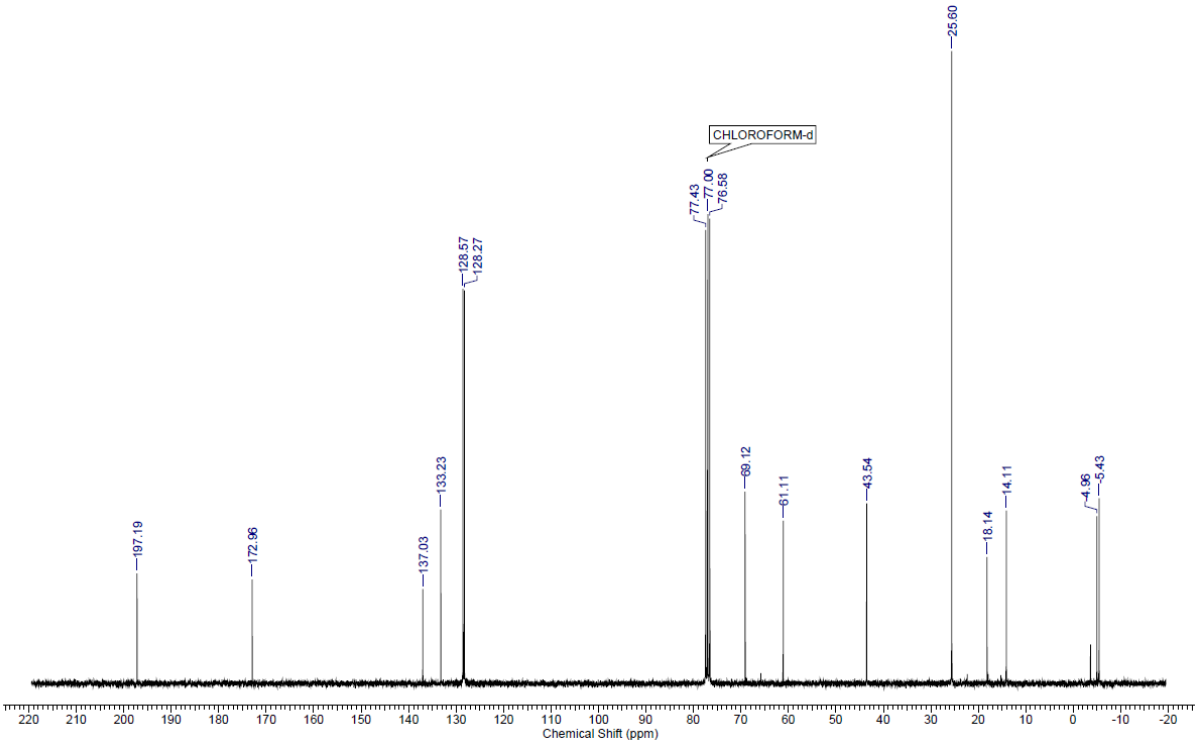
75 MHz, $CDCl_3$



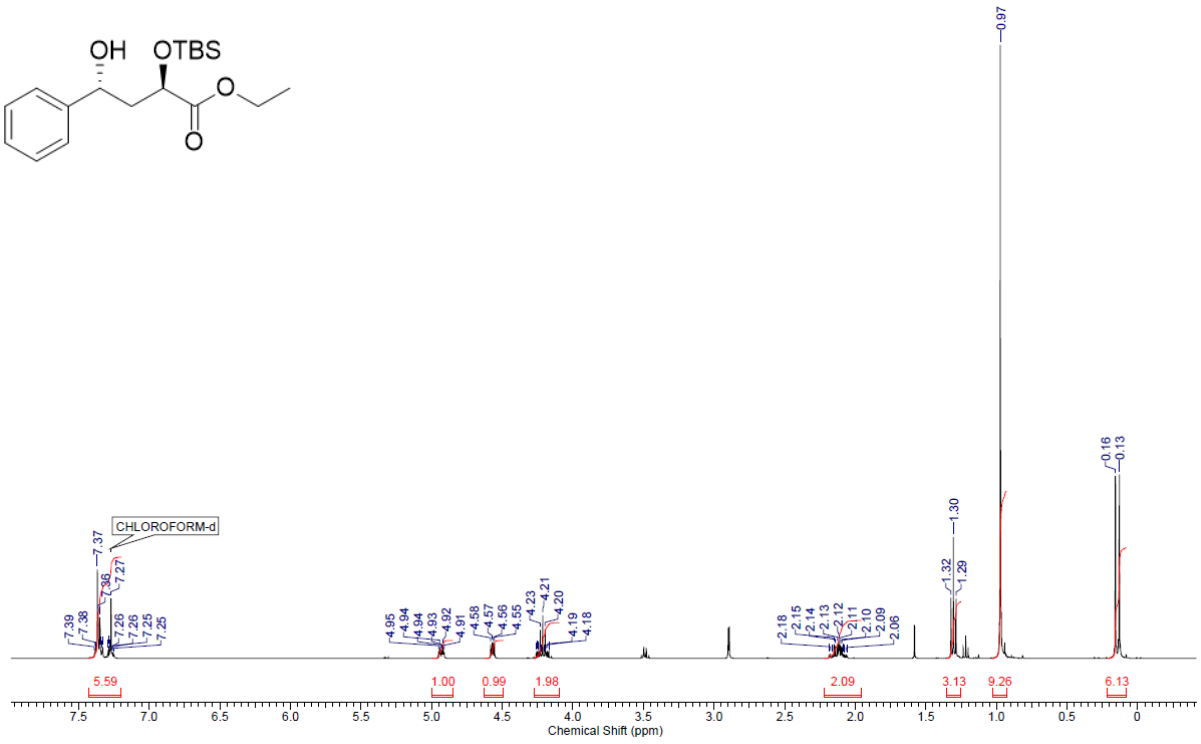
NMR Spectra **6**. 400 MHz, $CDCl_3$



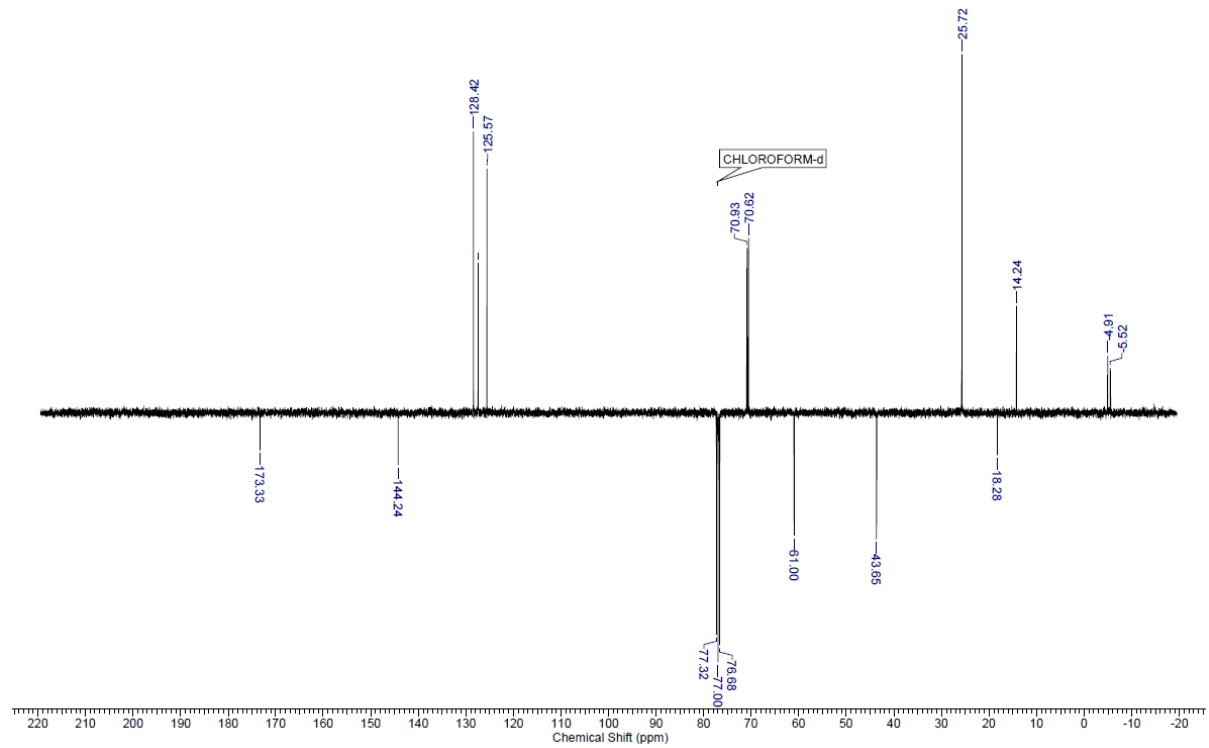
75 MHz, $CDCl_3$



NMR spectra **7**. 400 MHz, $CDCl_3$



101 MHz, $CDCl_3$



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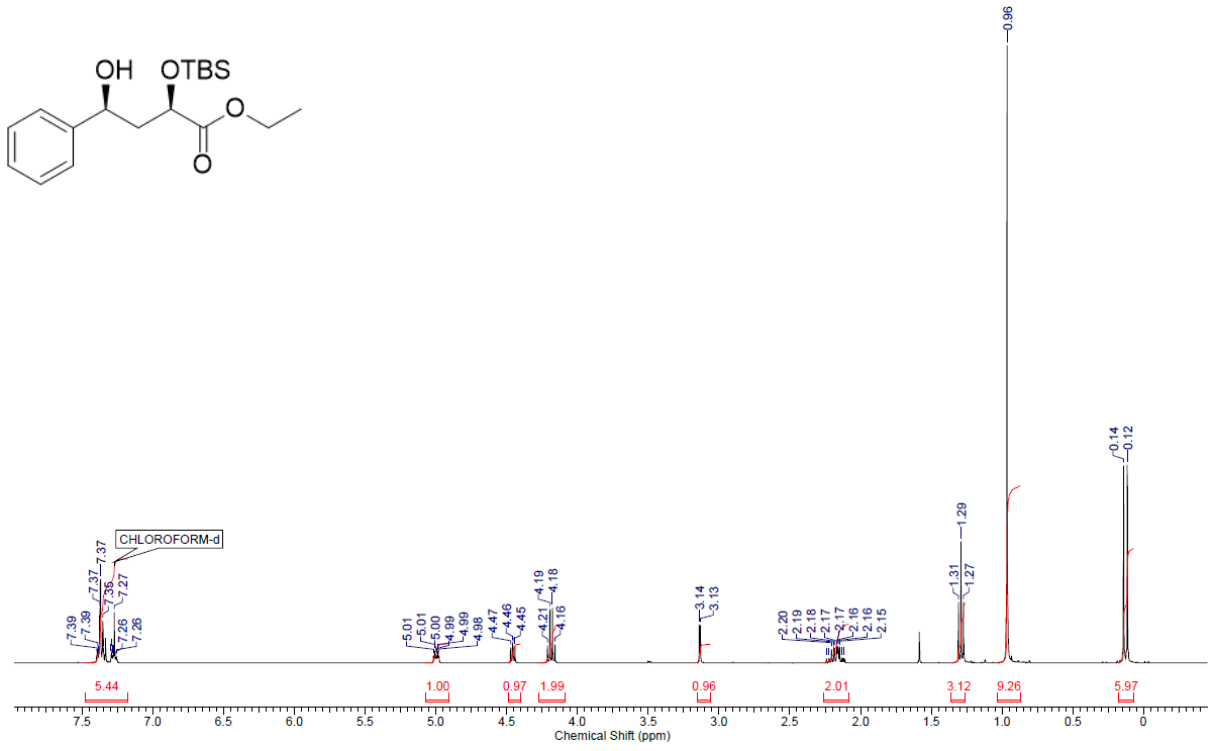
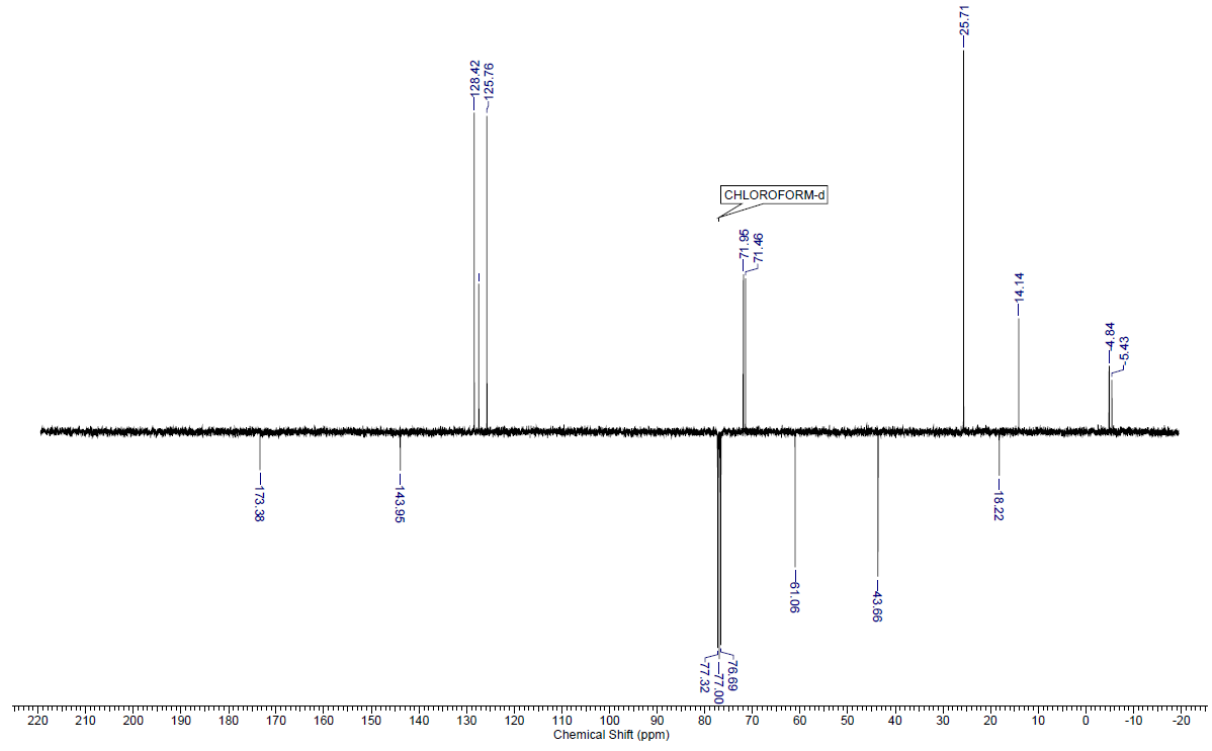
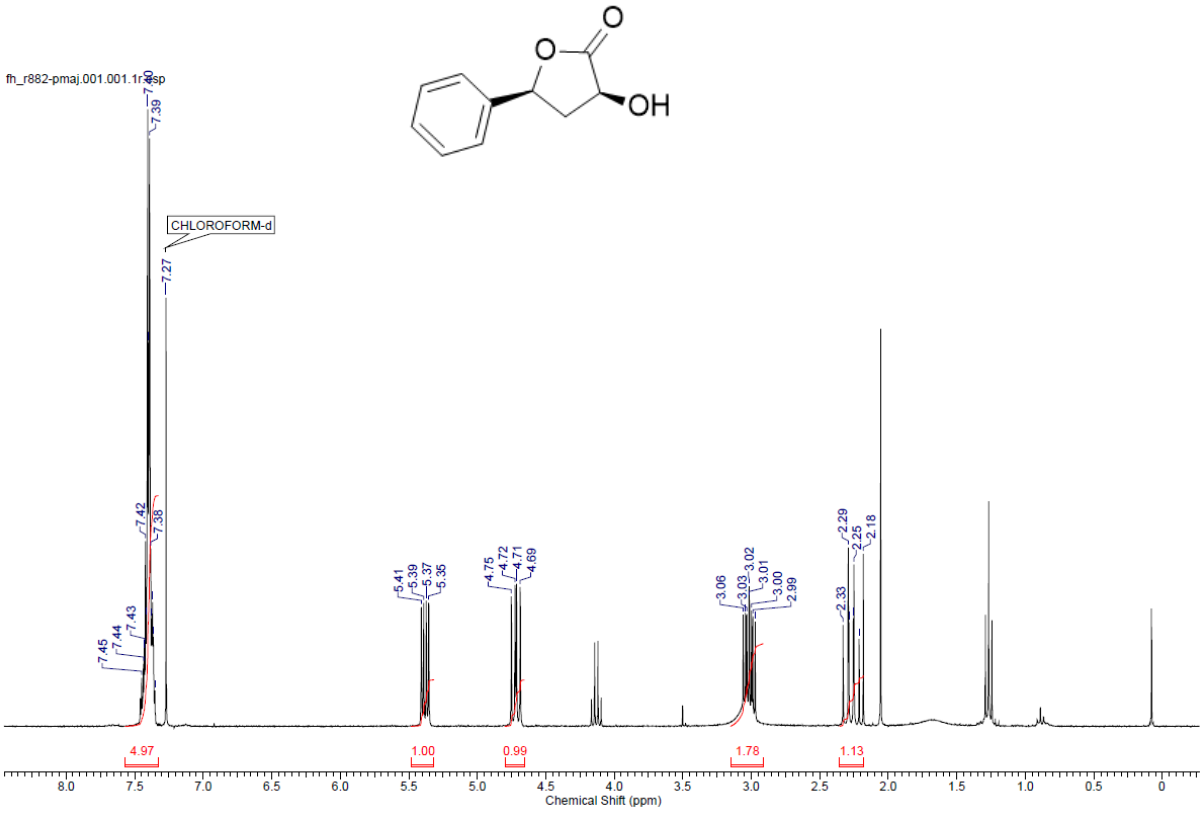


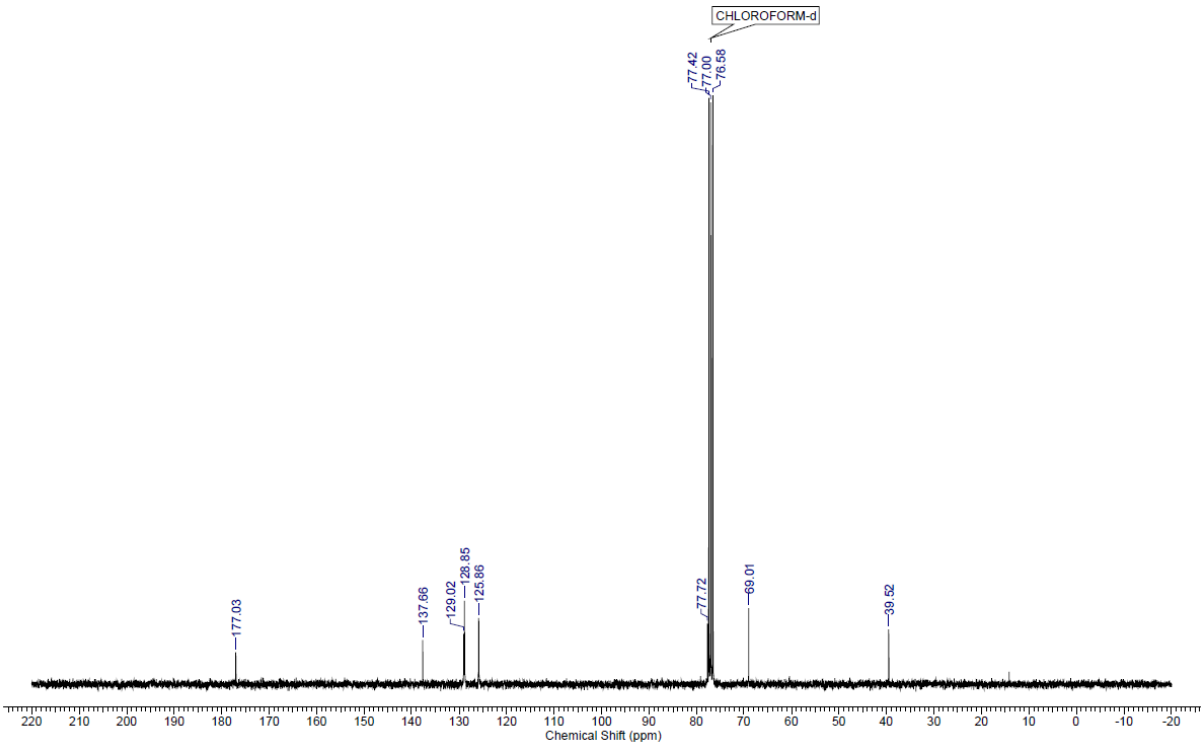
101 MHz, $CDCl_3$



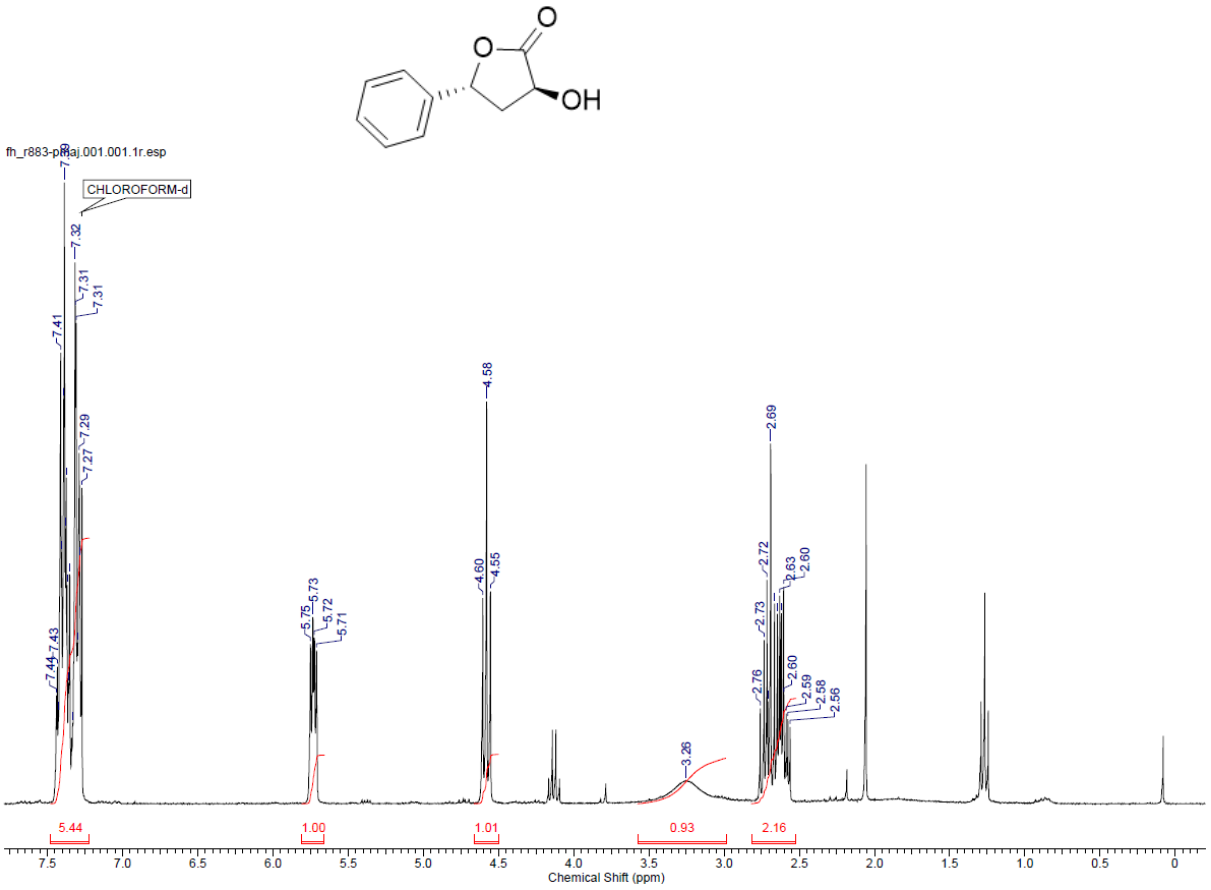
NMR Spectra **9**. 300 MHz, $CDCl_3$



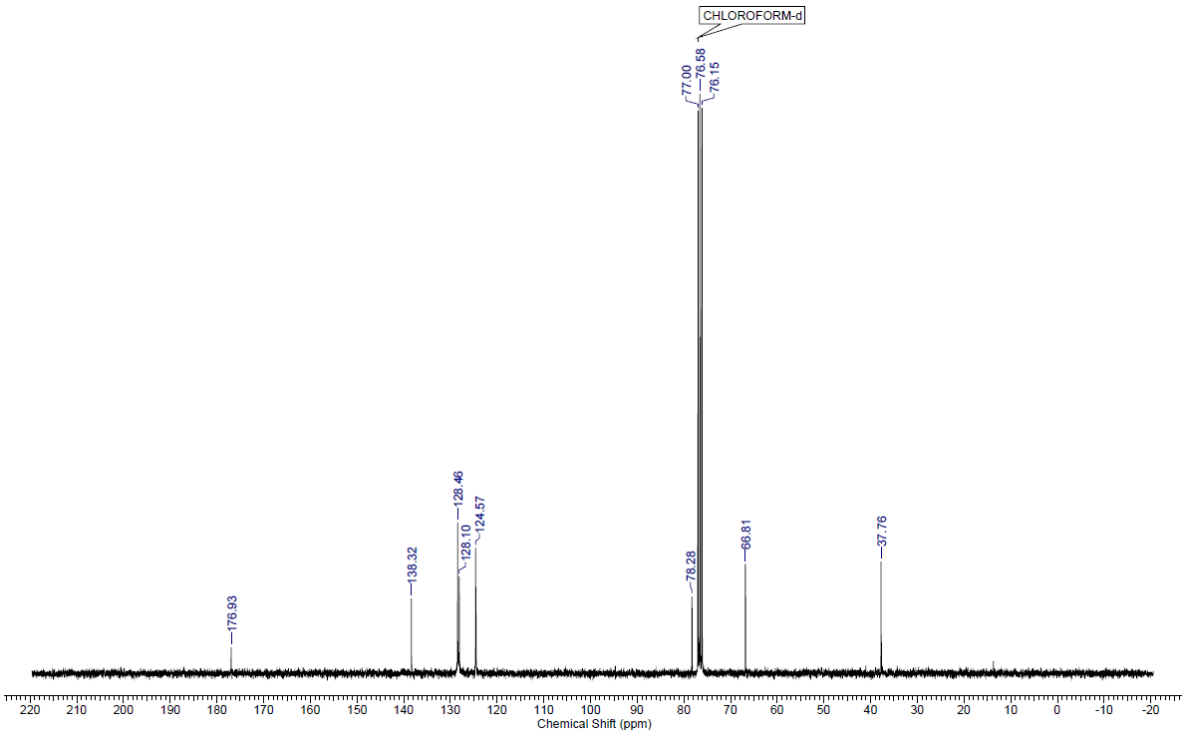
75 MHz, $CDCl_3$



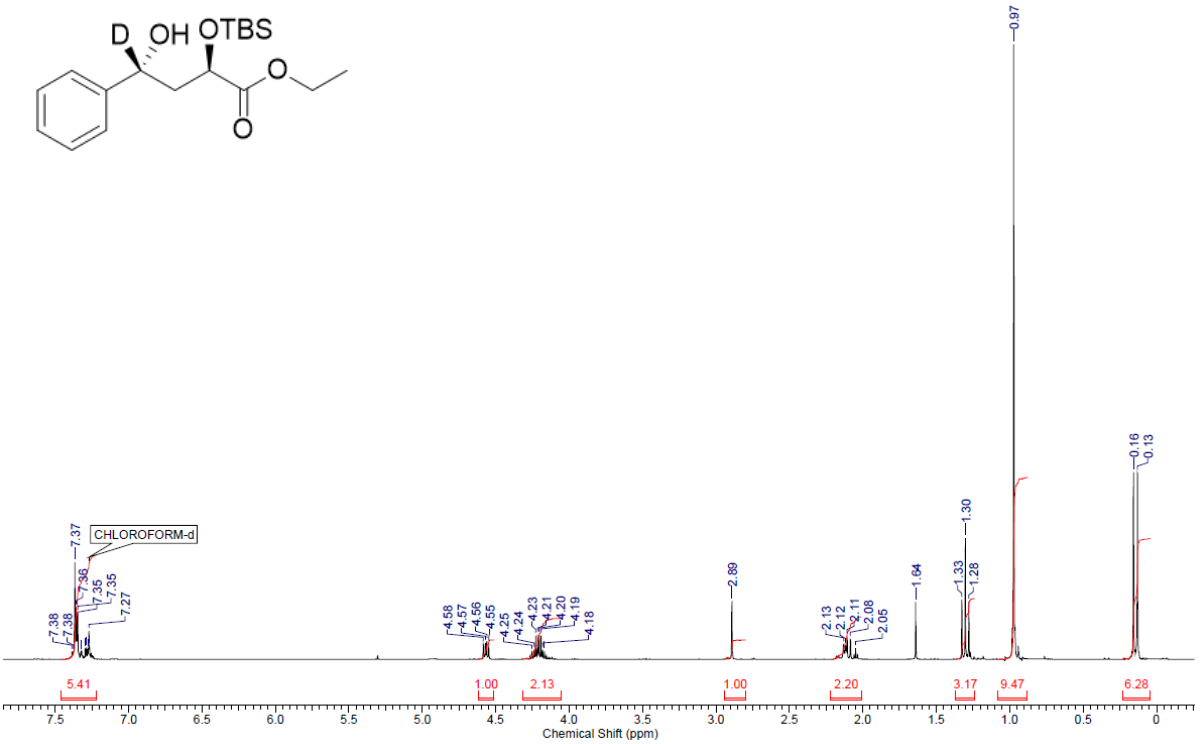
NMR Spectra **10**. 300 MHz, $CDCl_3$



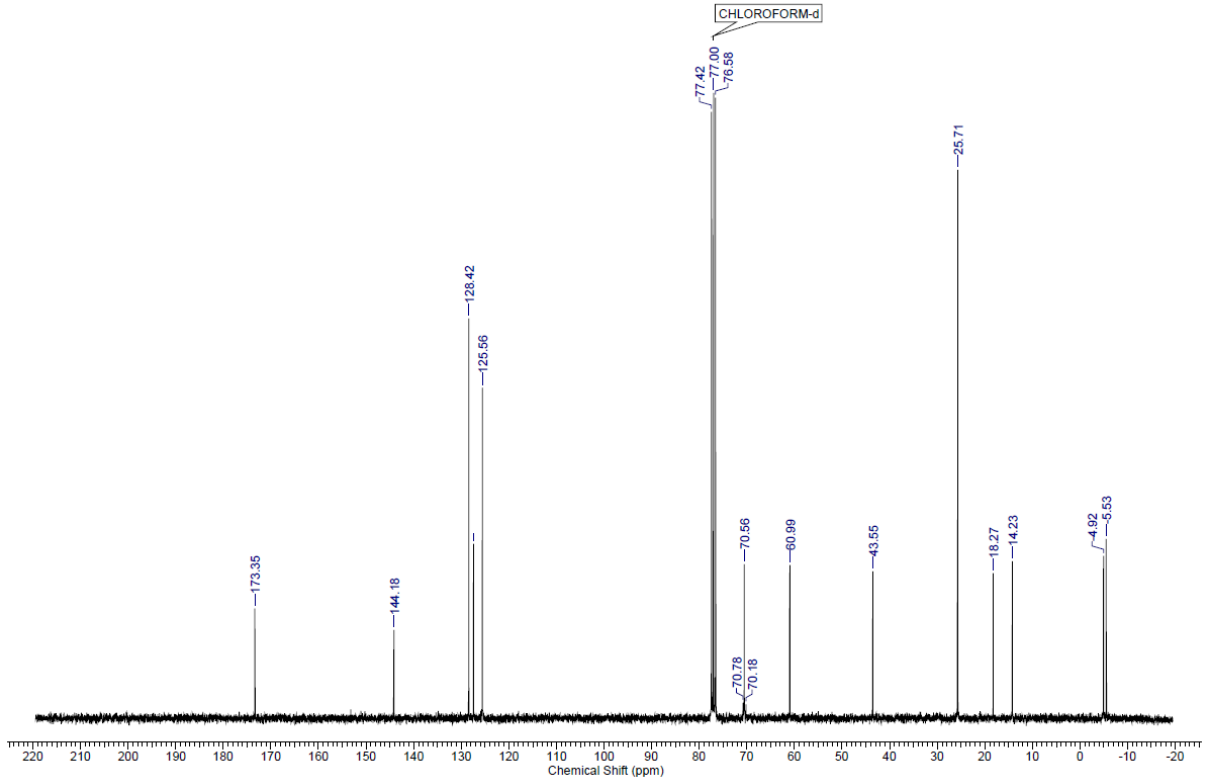
75 MHz, $CDCl_3$



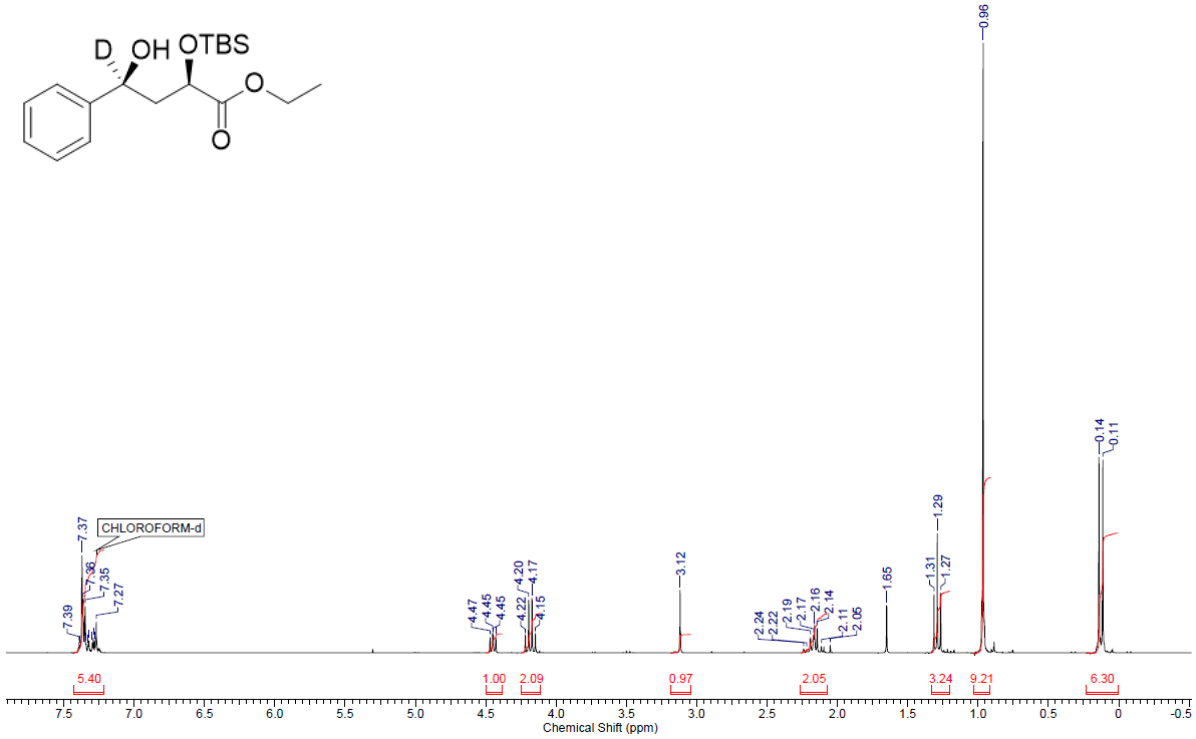
NMR Spectra **3**. 300 MHz, $CDCl_3$



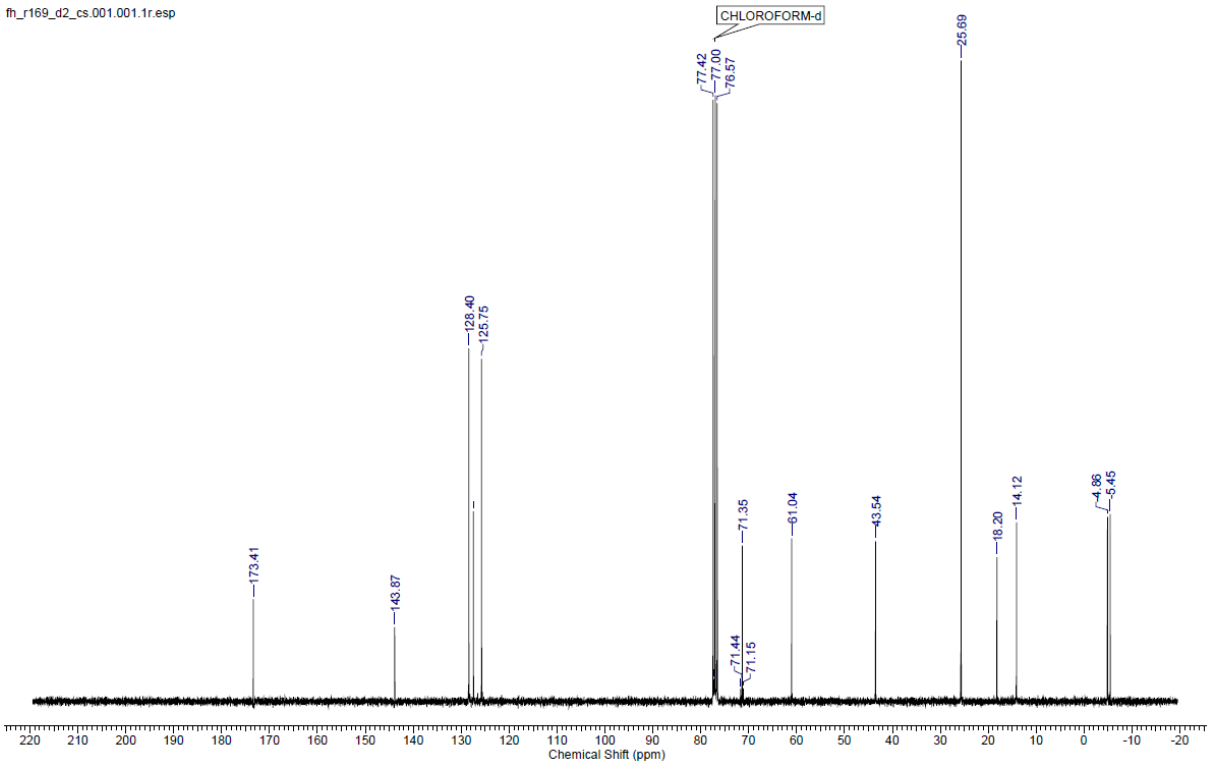
75 MHz, $CDCl_3$



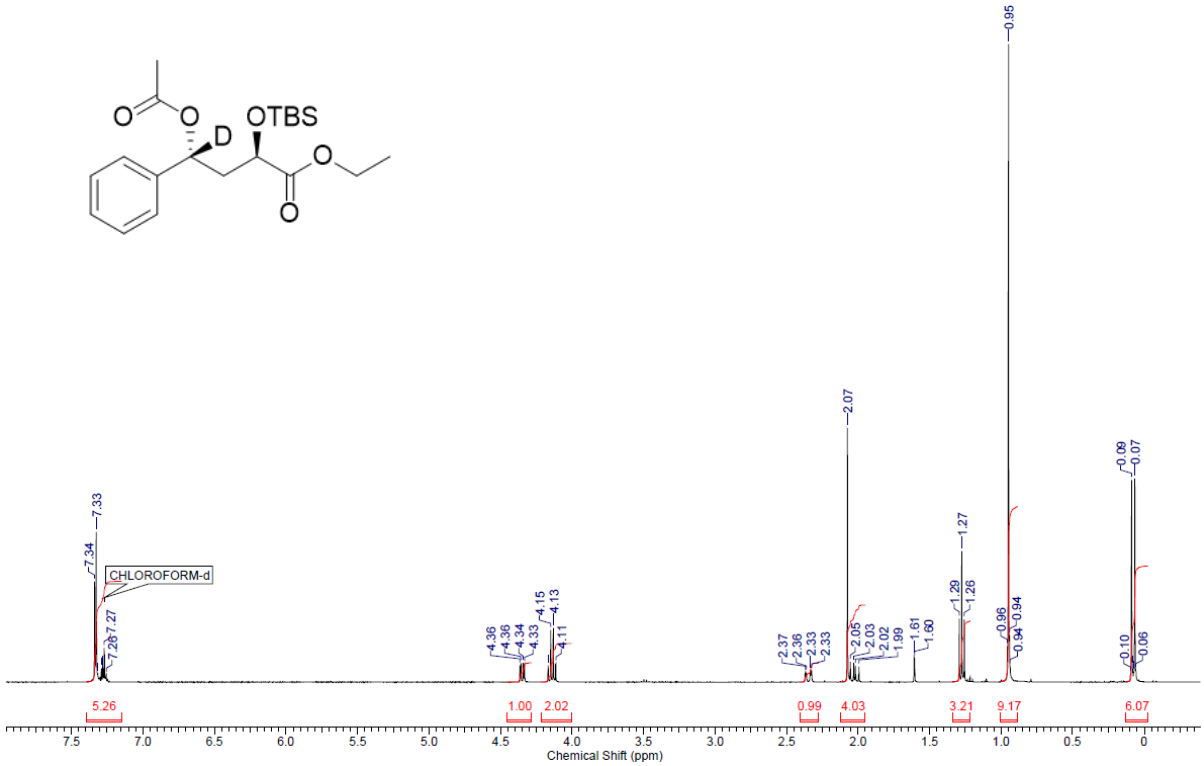
NMR Spectra **4**. 300 MHz, $CDCl_3$



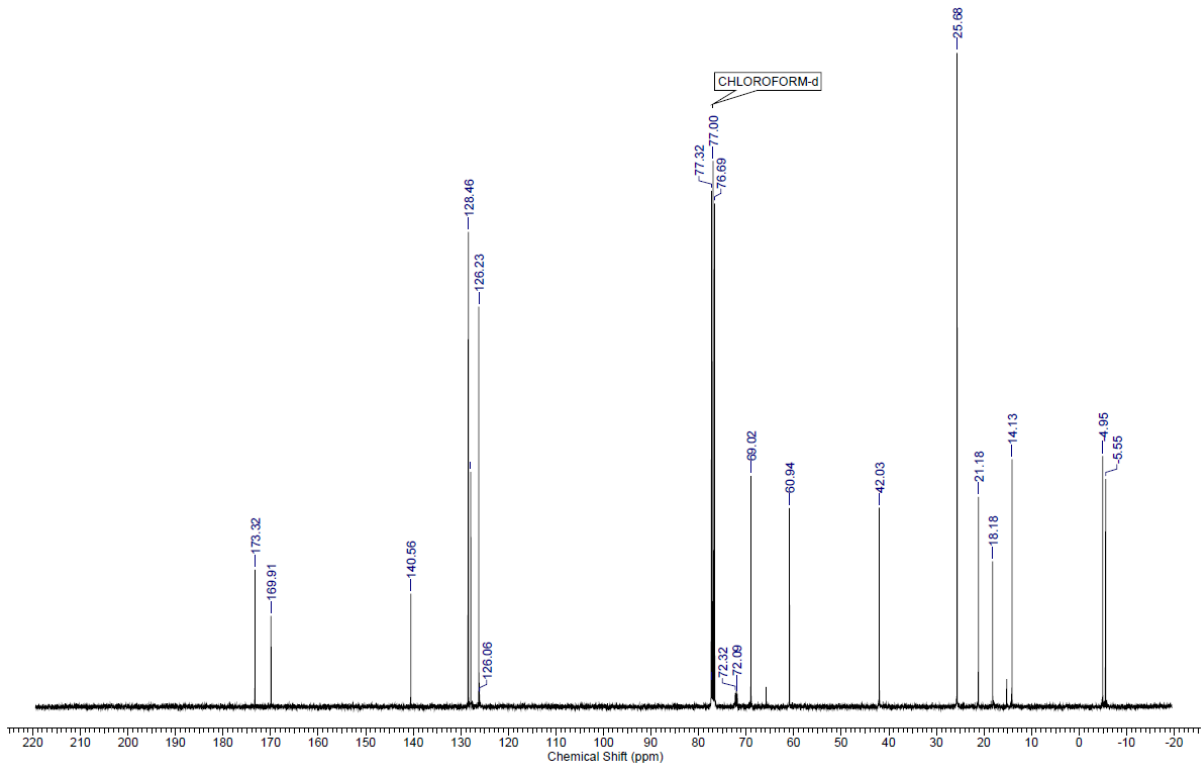
75 MHz, $CDCl_3$



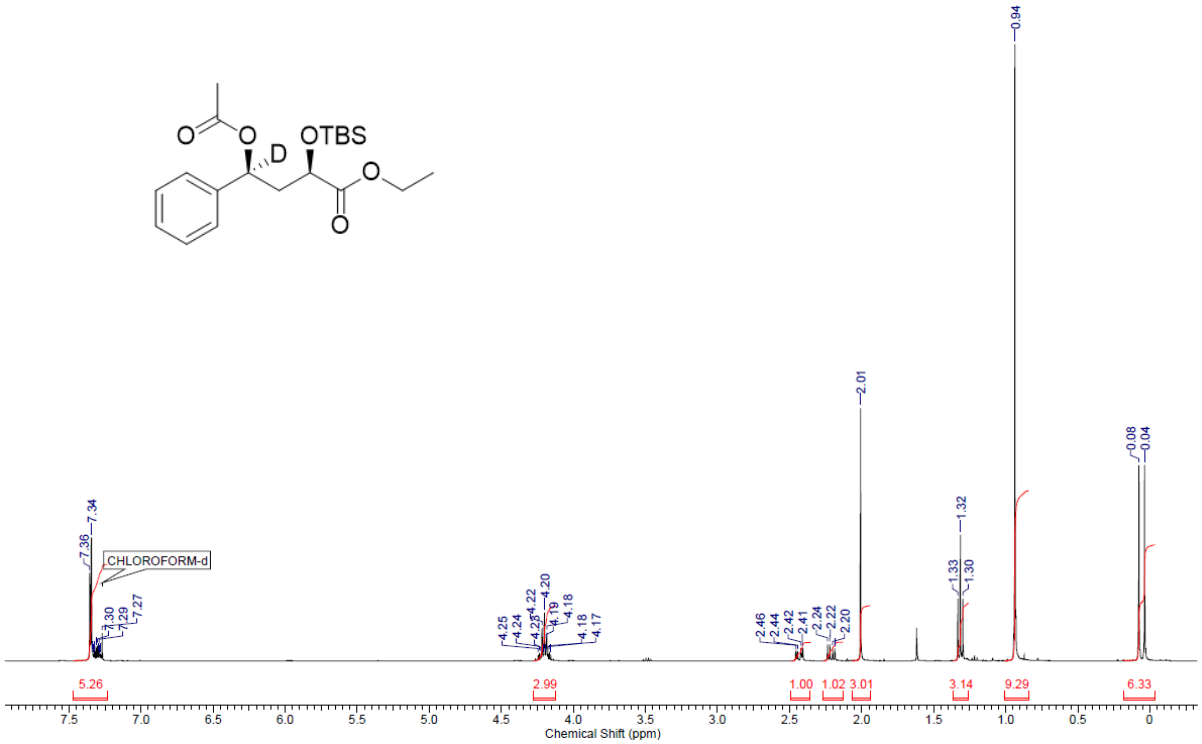
NMR Spectra **11**. 400 MHz, $CDCl_3$



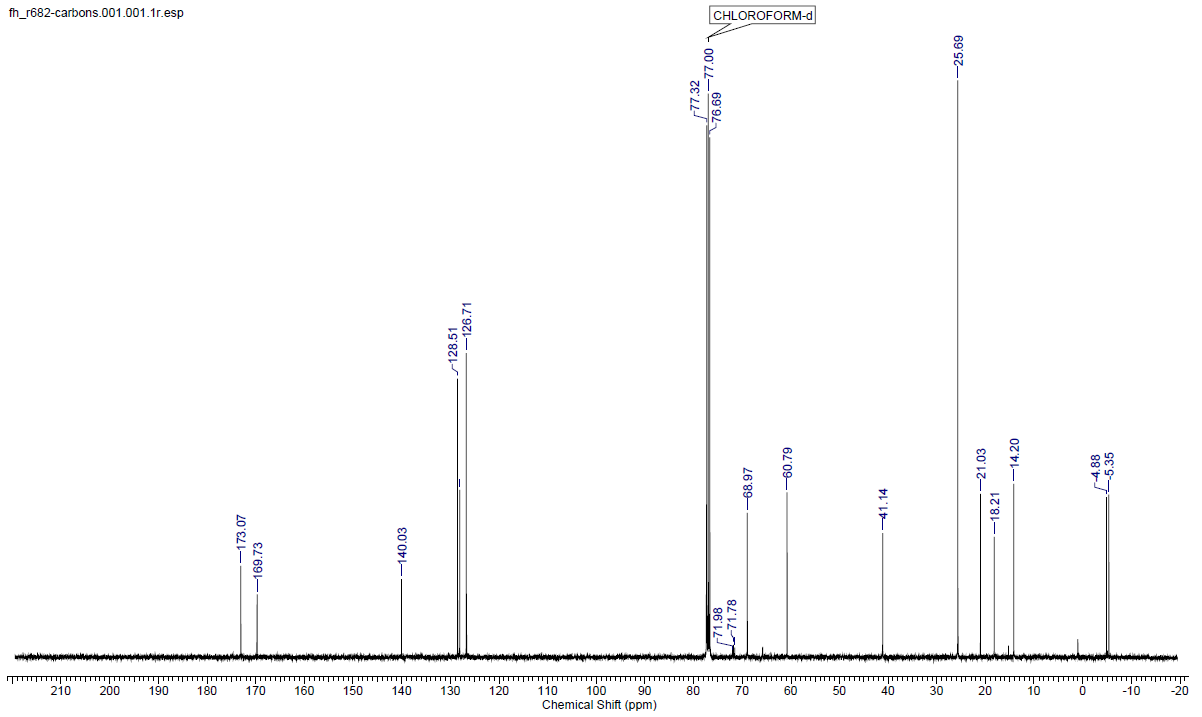
101 MHz, $CDCl_3$



NMR Spectra **12**. 400 MHz, $CDCl_3$



101 MHz, $CDCl_3$



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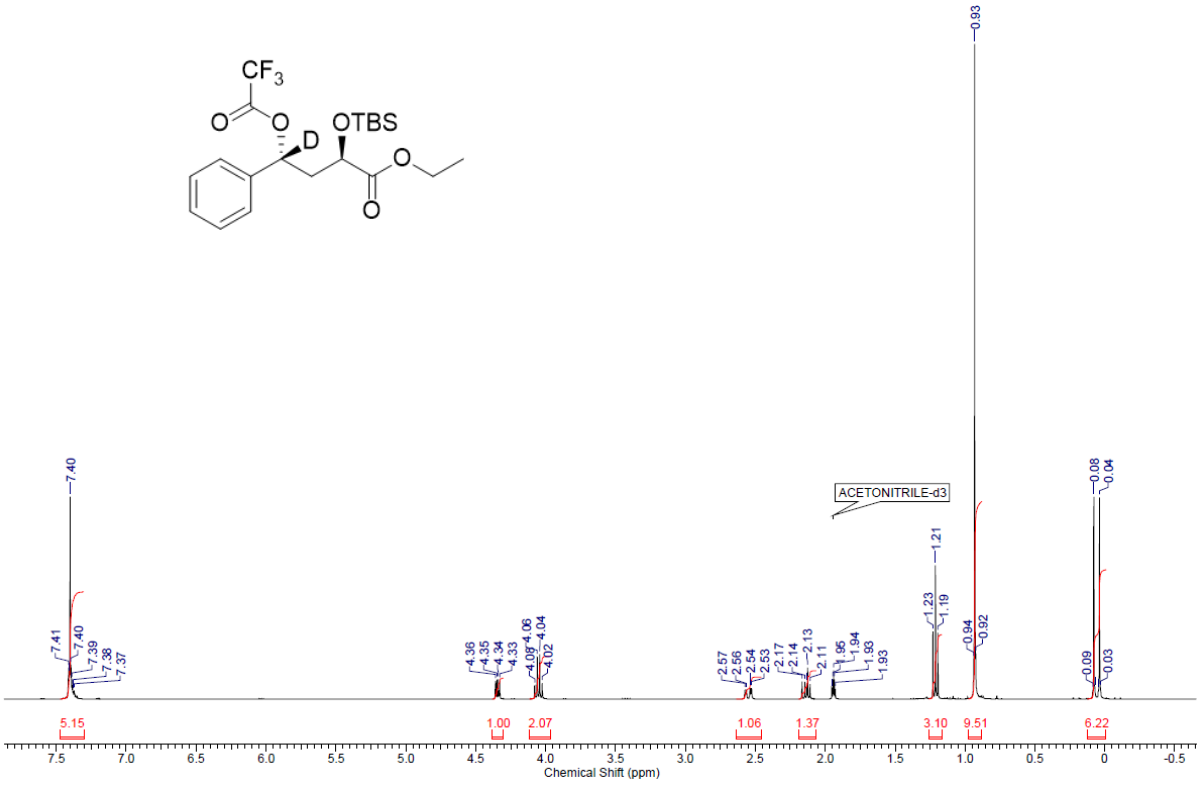
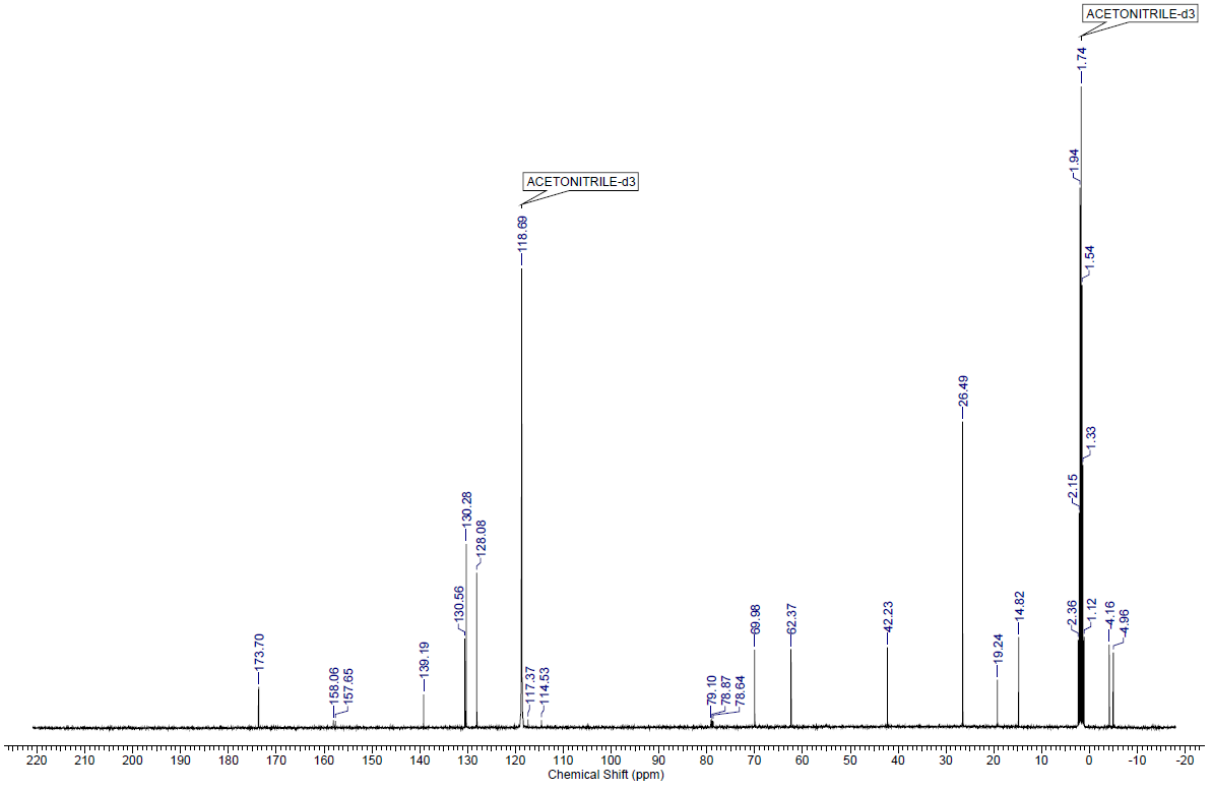


101 MHz, CD_3CN



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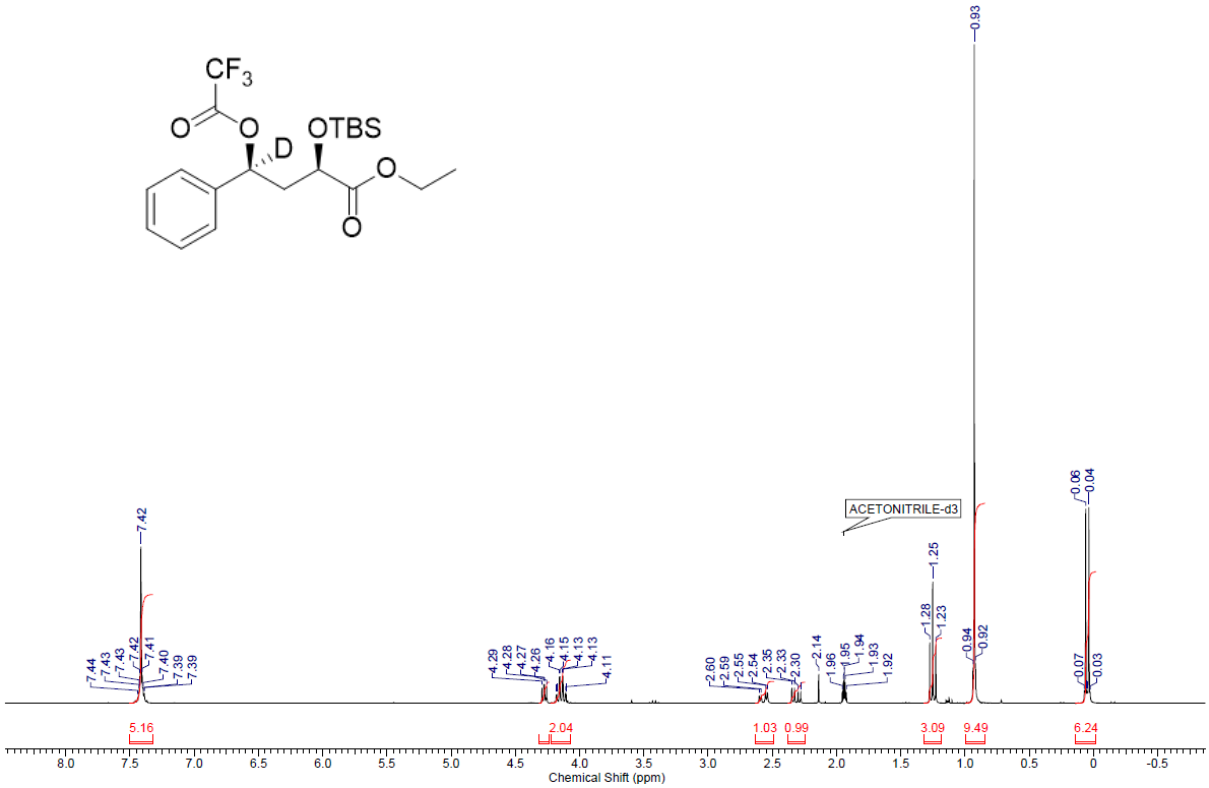
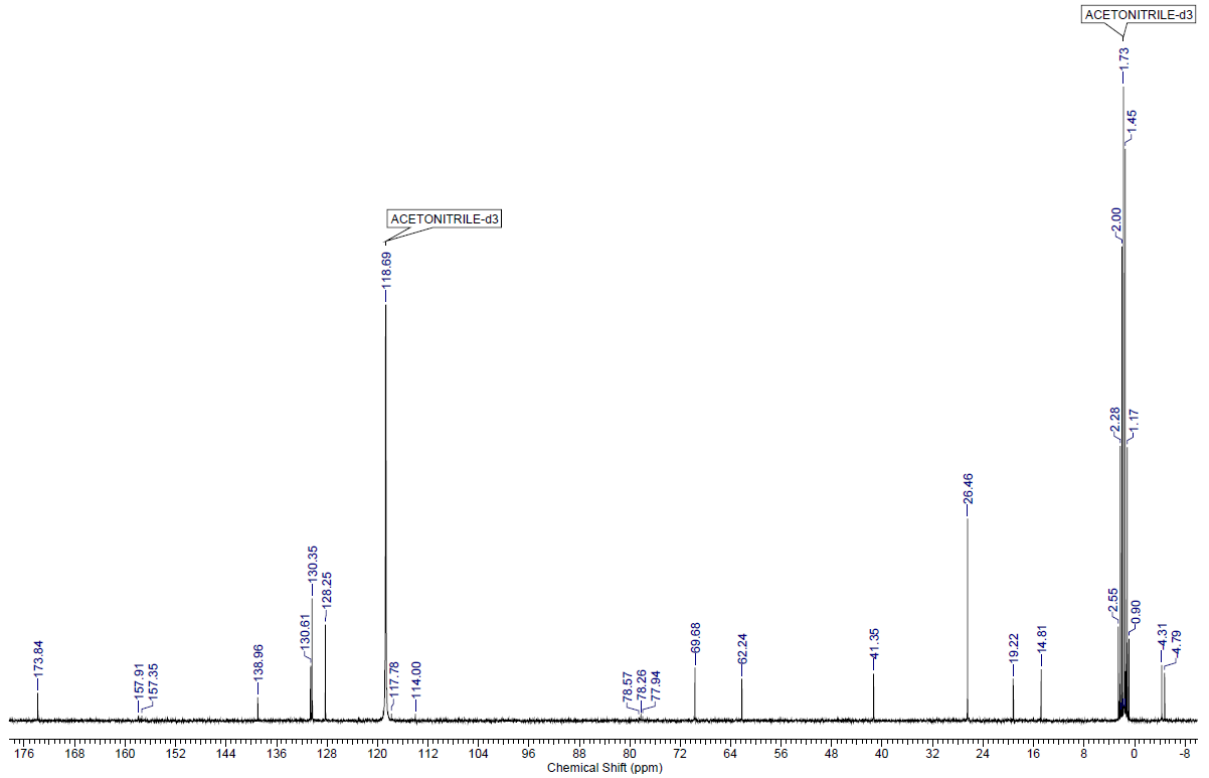
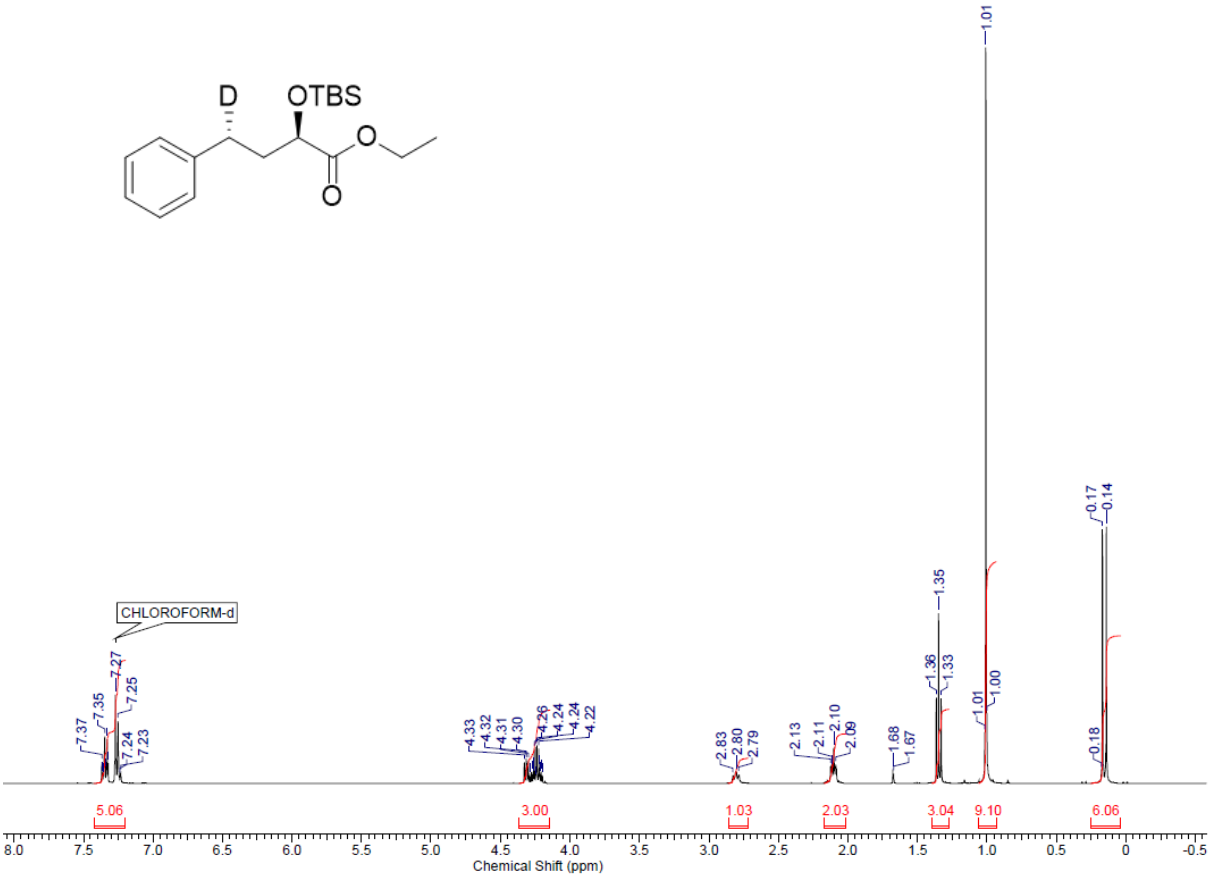


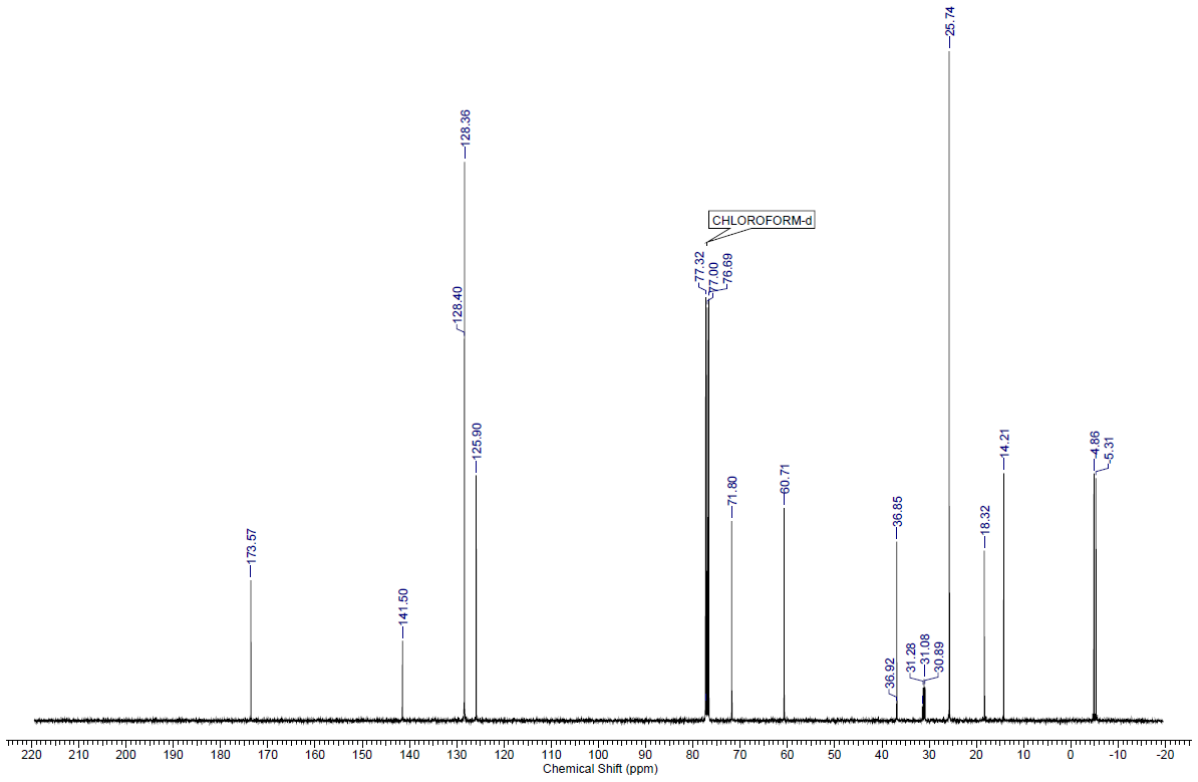
75 MHz, CD_3CN



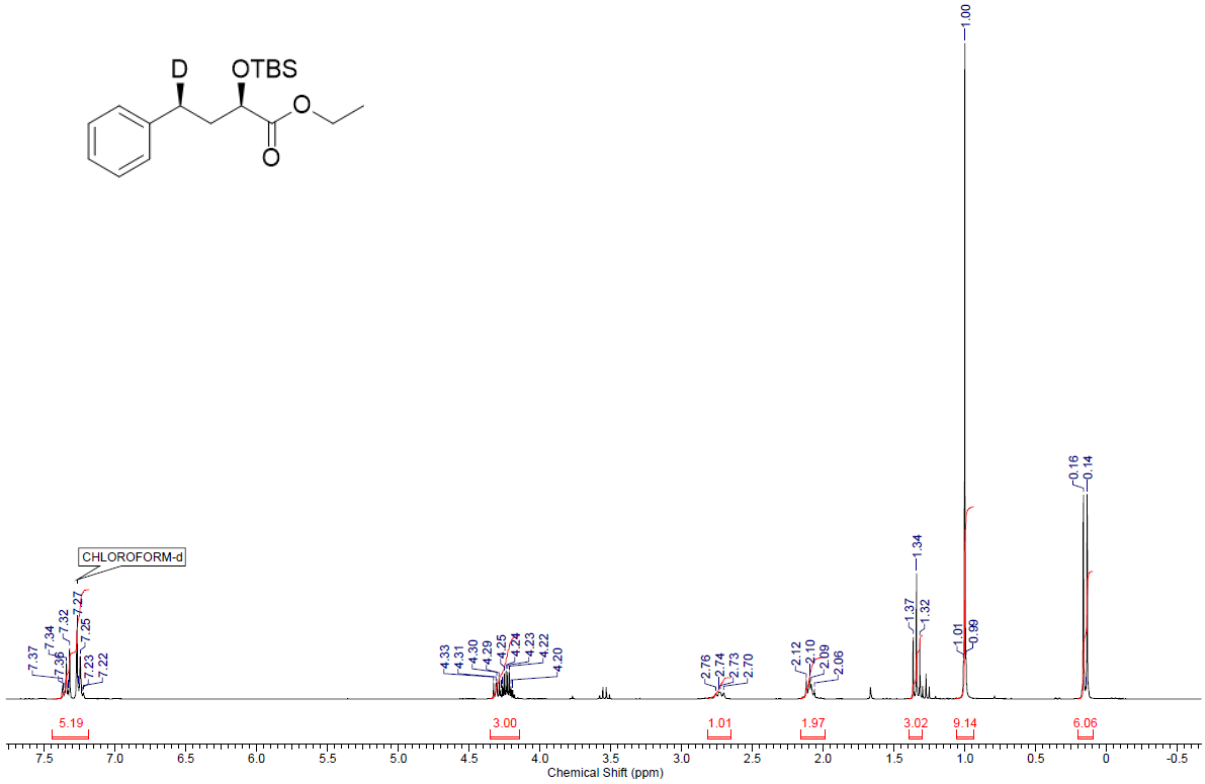
NMR Spectra **1**. 400 MHz, $CDCl_3$



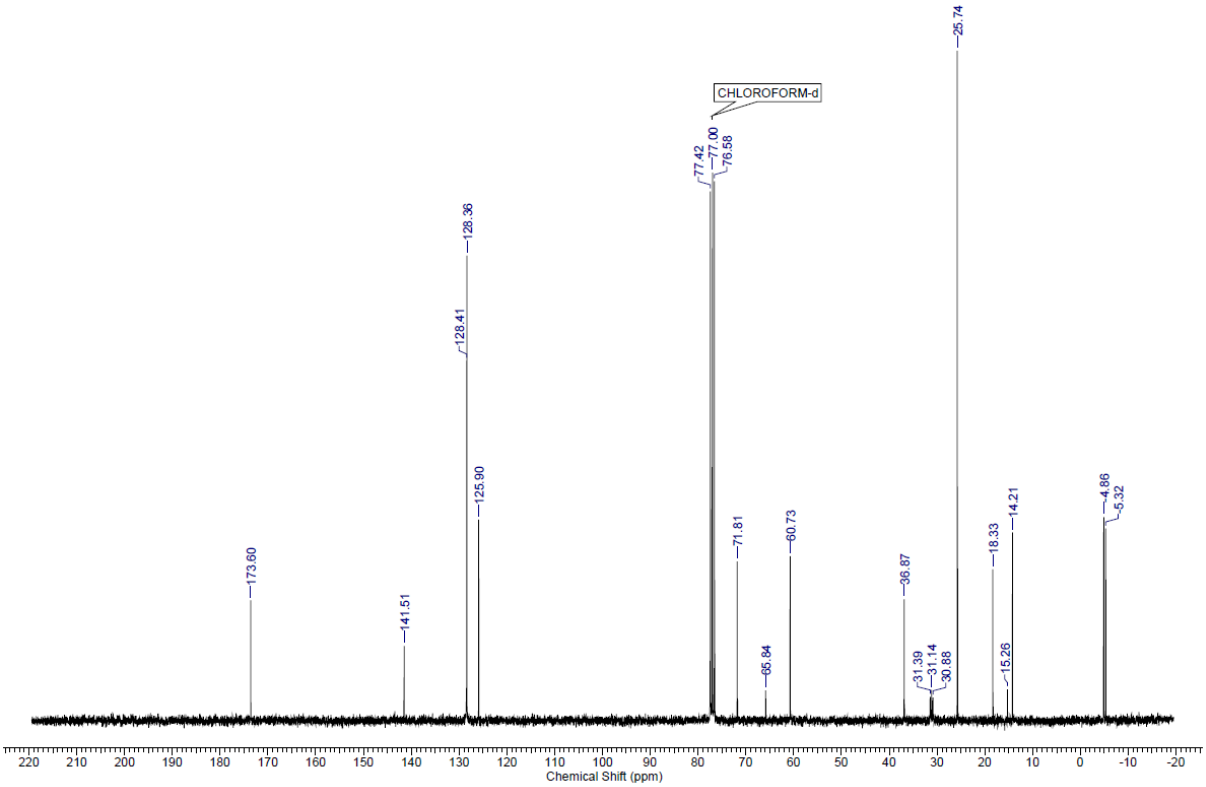
75 MHz, $CDCl_3$



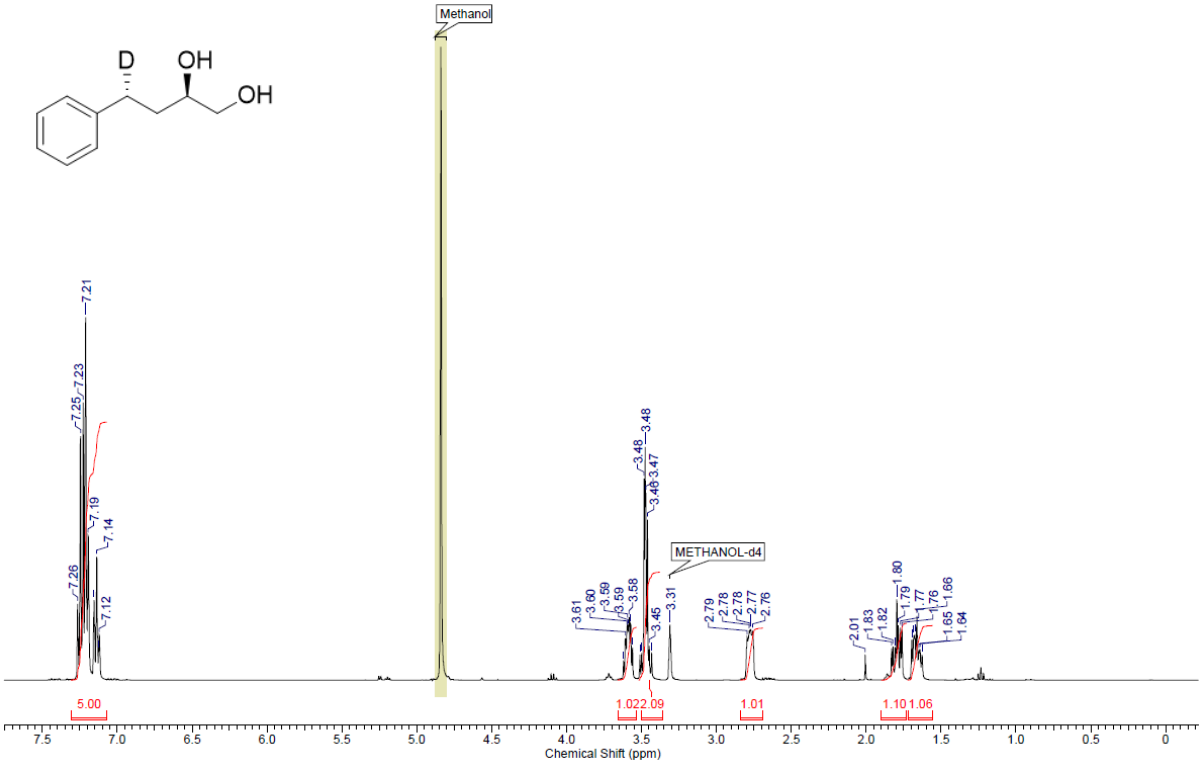
NMR Spectra **2**. 300 MHz, $CDCl_3$



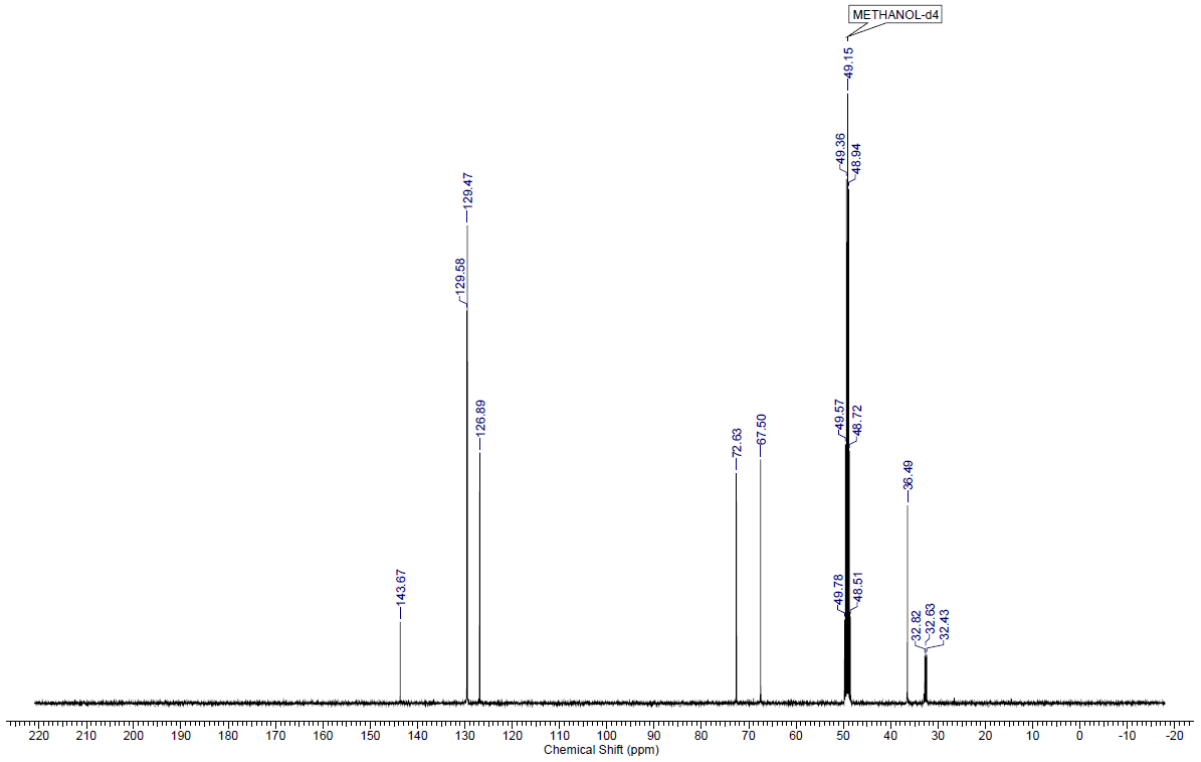
75 MHz, $CDCl_3$



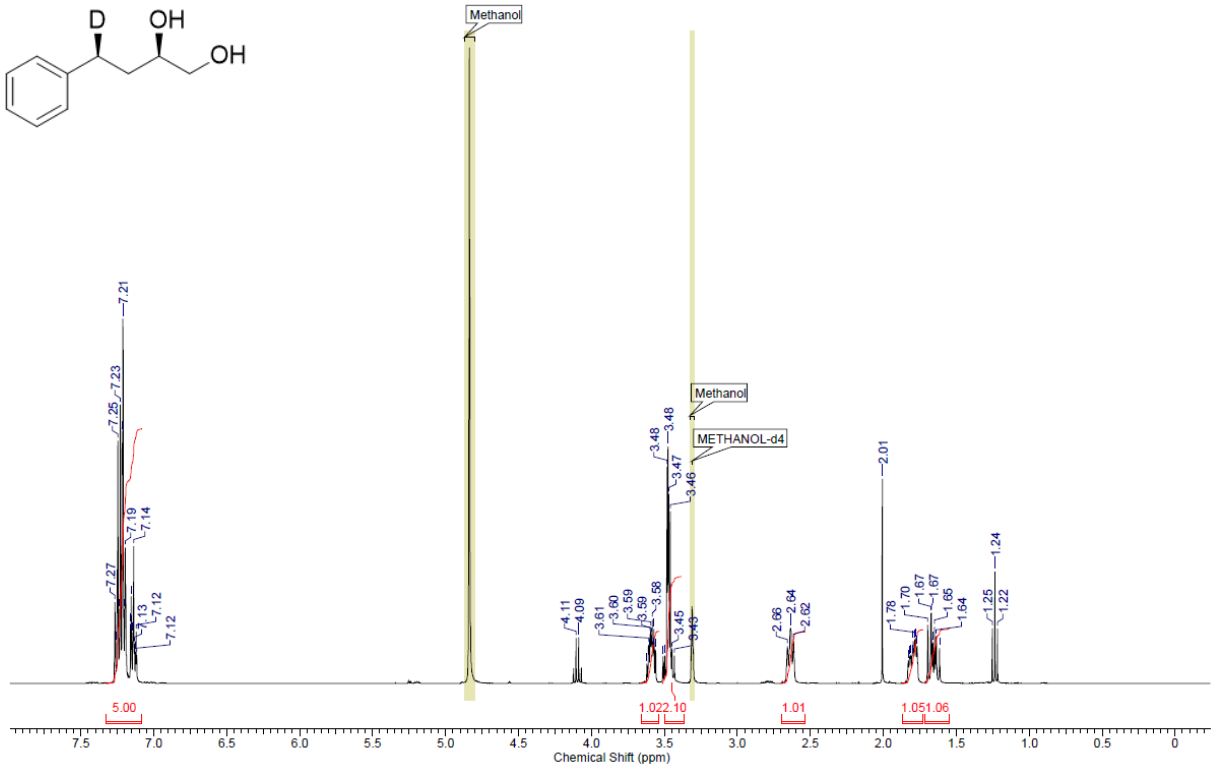
NMR Spectra **17**. 400 MHz, CD_3OD



101 MHz, CD_3OD



NMR Spectra **18**. 400 MHz, CD_3OD



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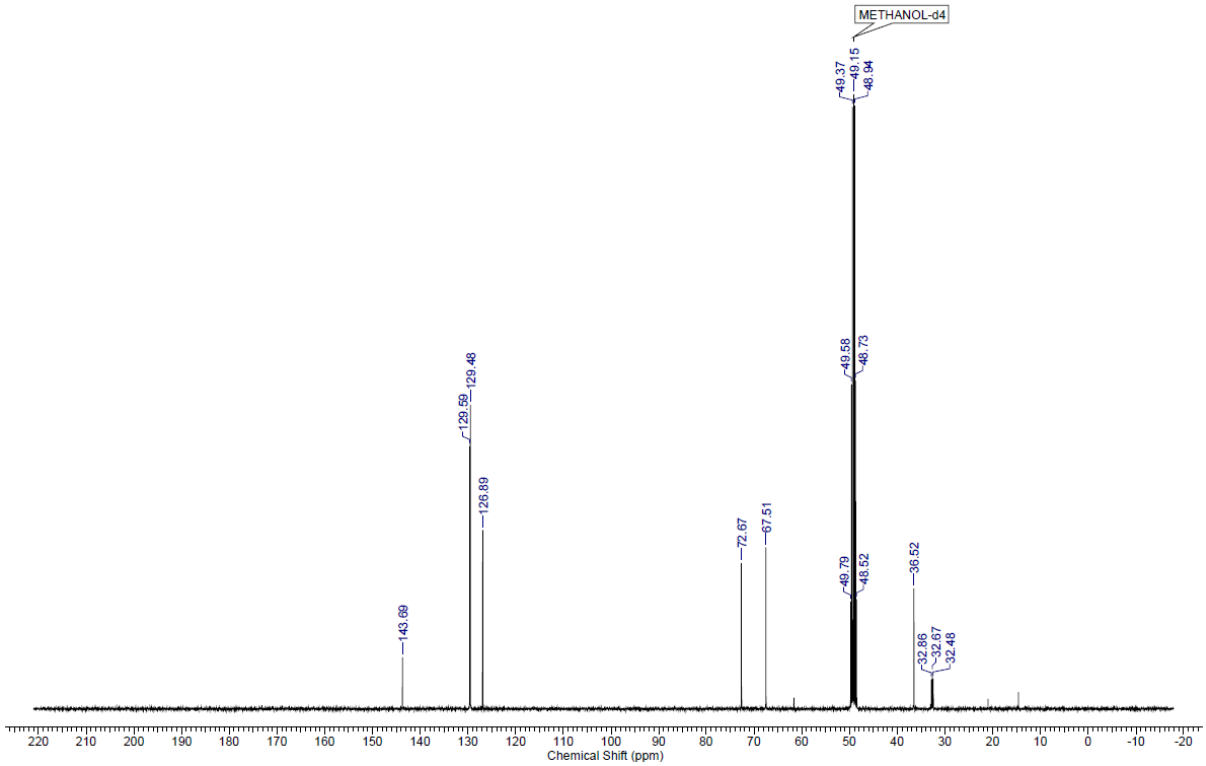
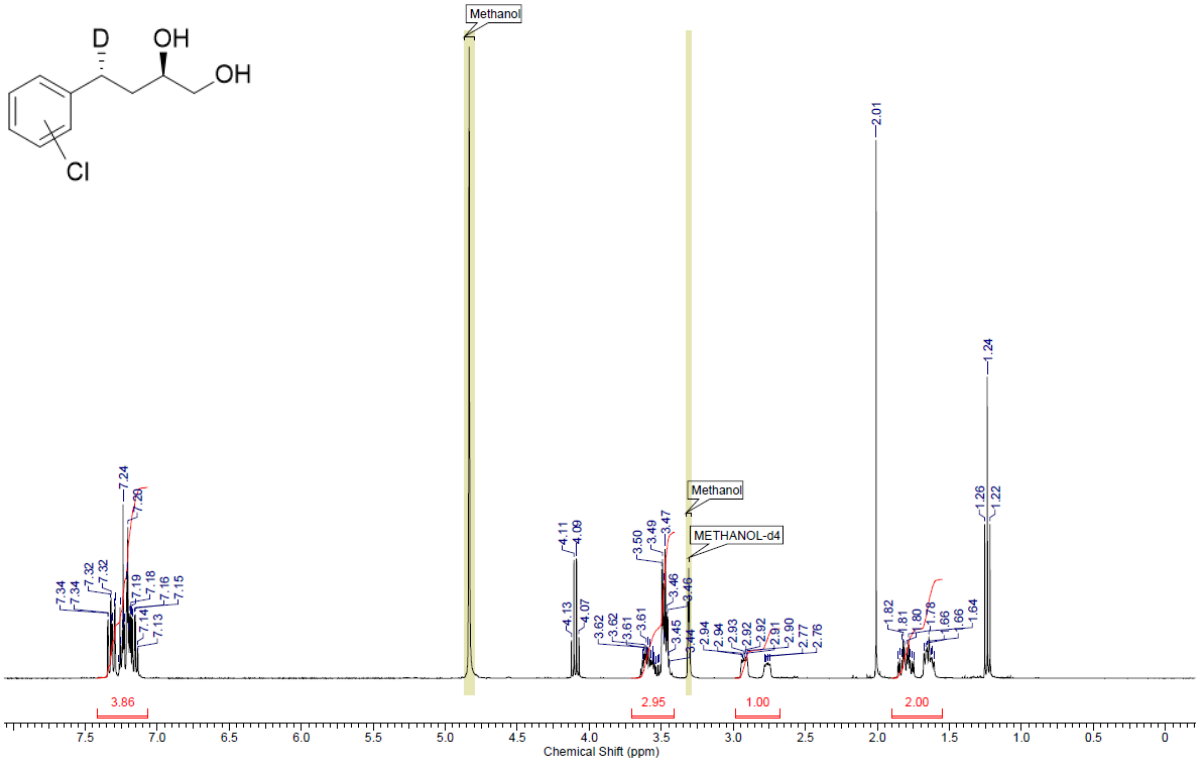


NMR Spectra **19**. 400 MHz, CD_3OD



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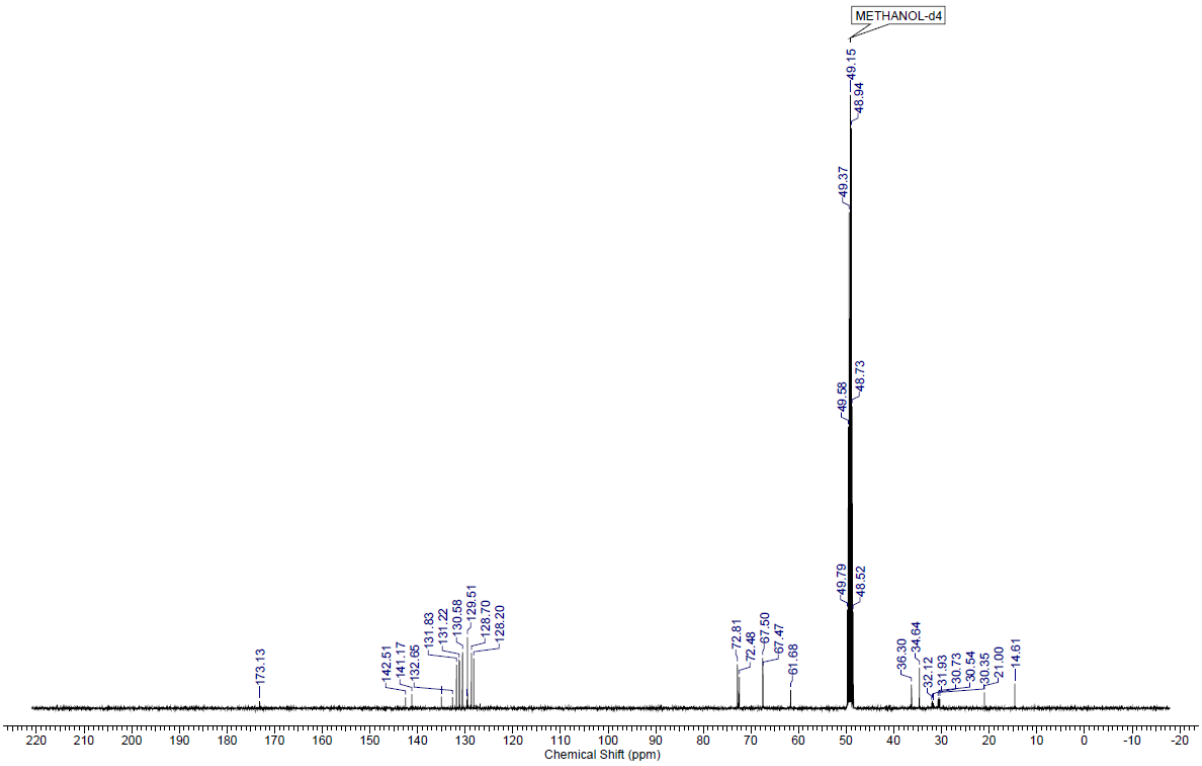
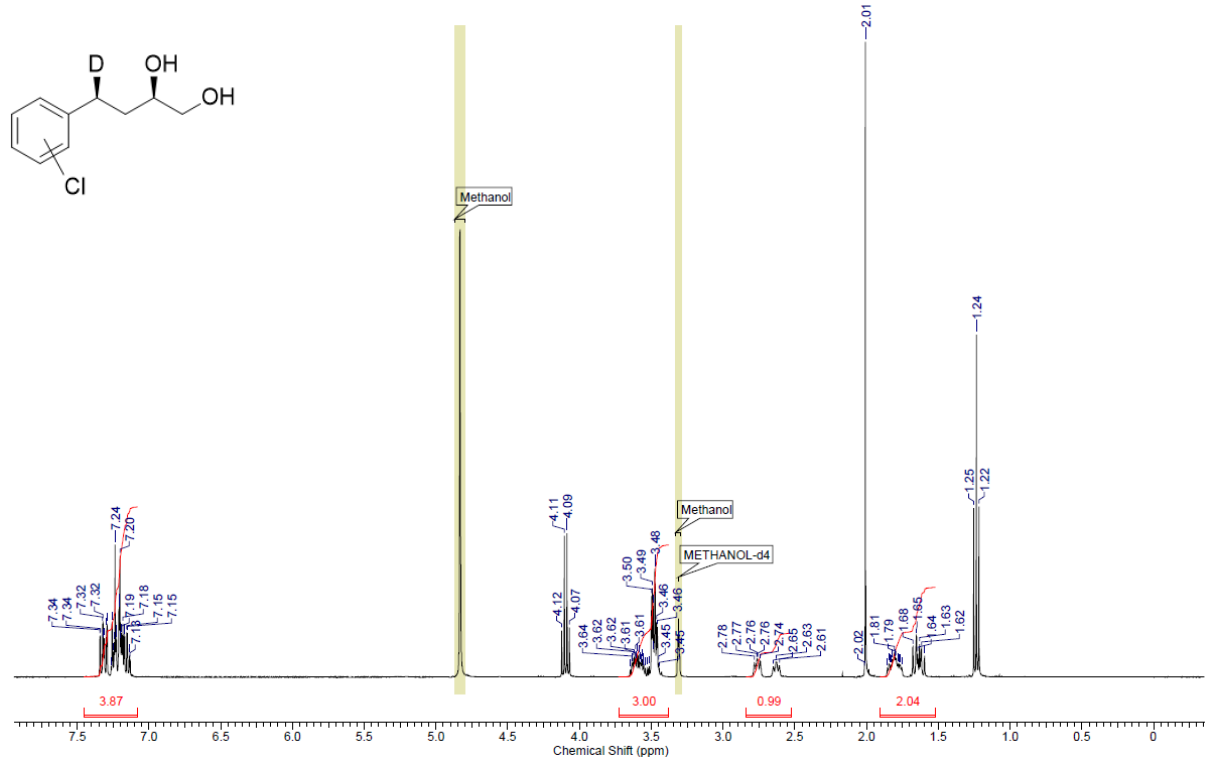
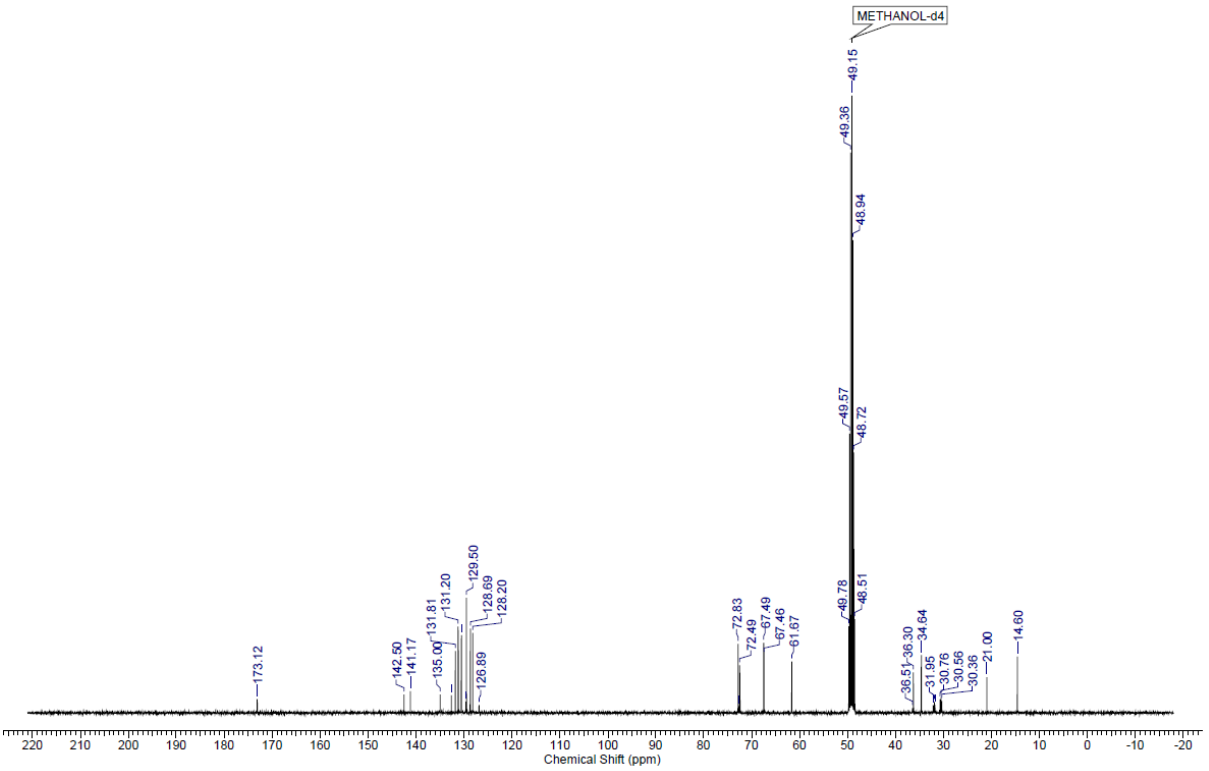


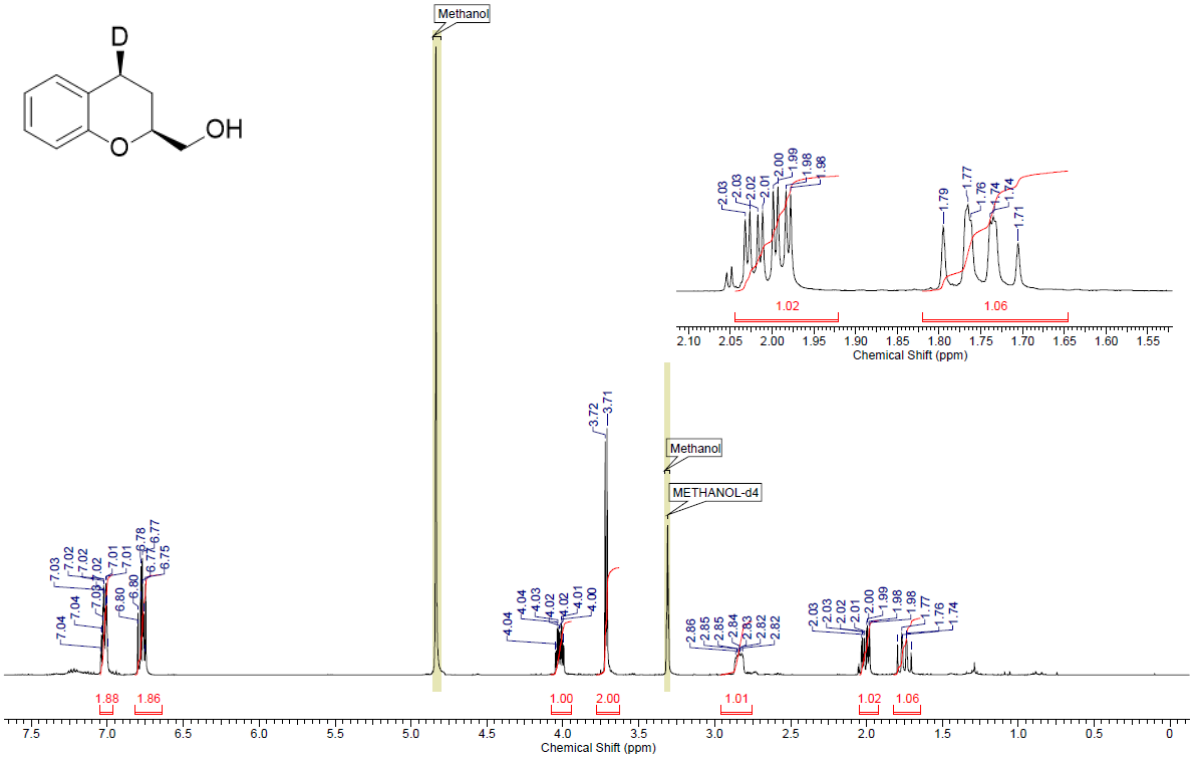
NMR Spectra **20**. 400 MHz, CD_3OD



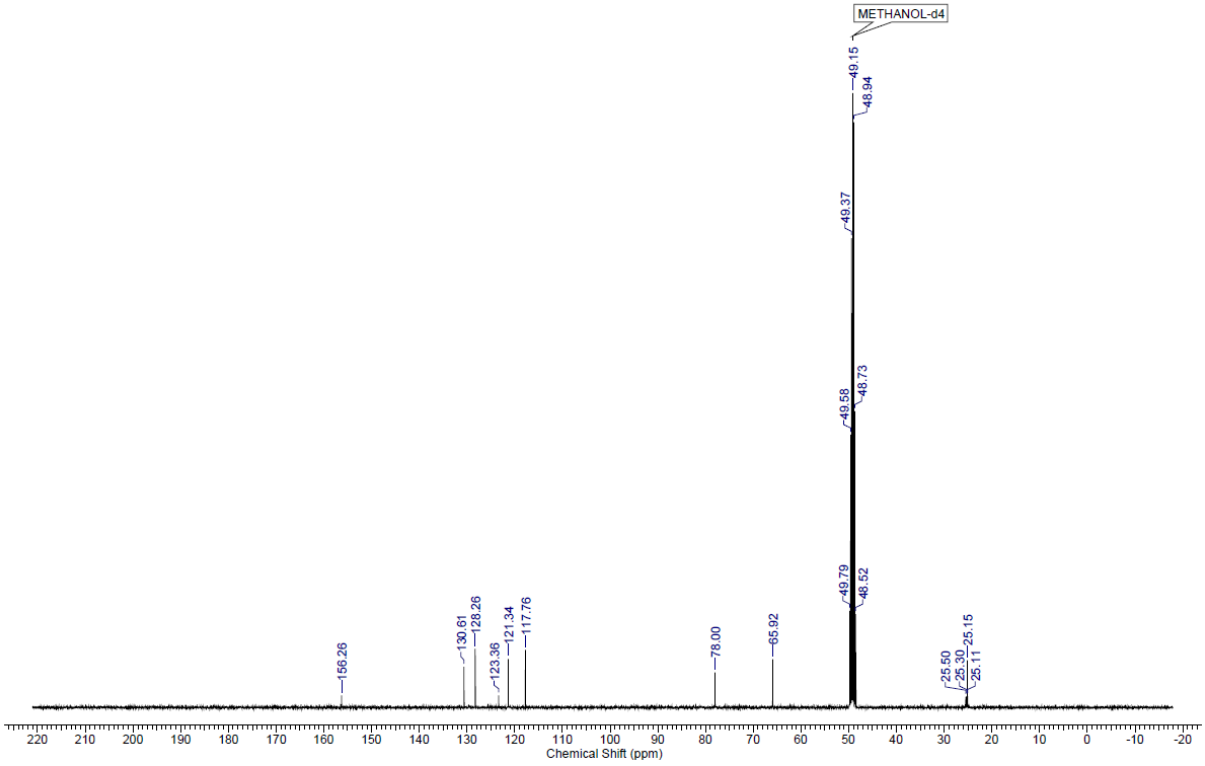
101 MHz, CD_3OD



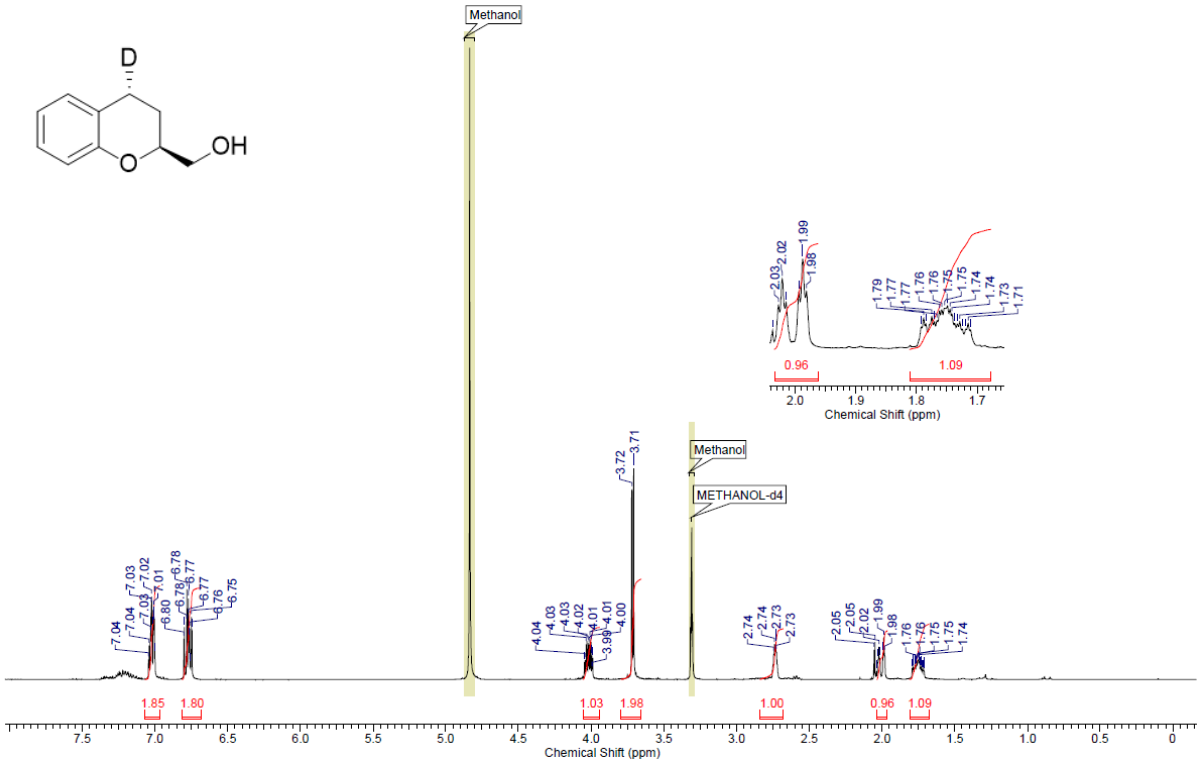
NMR Spectra **15**. 400 MHz, CD_3OD



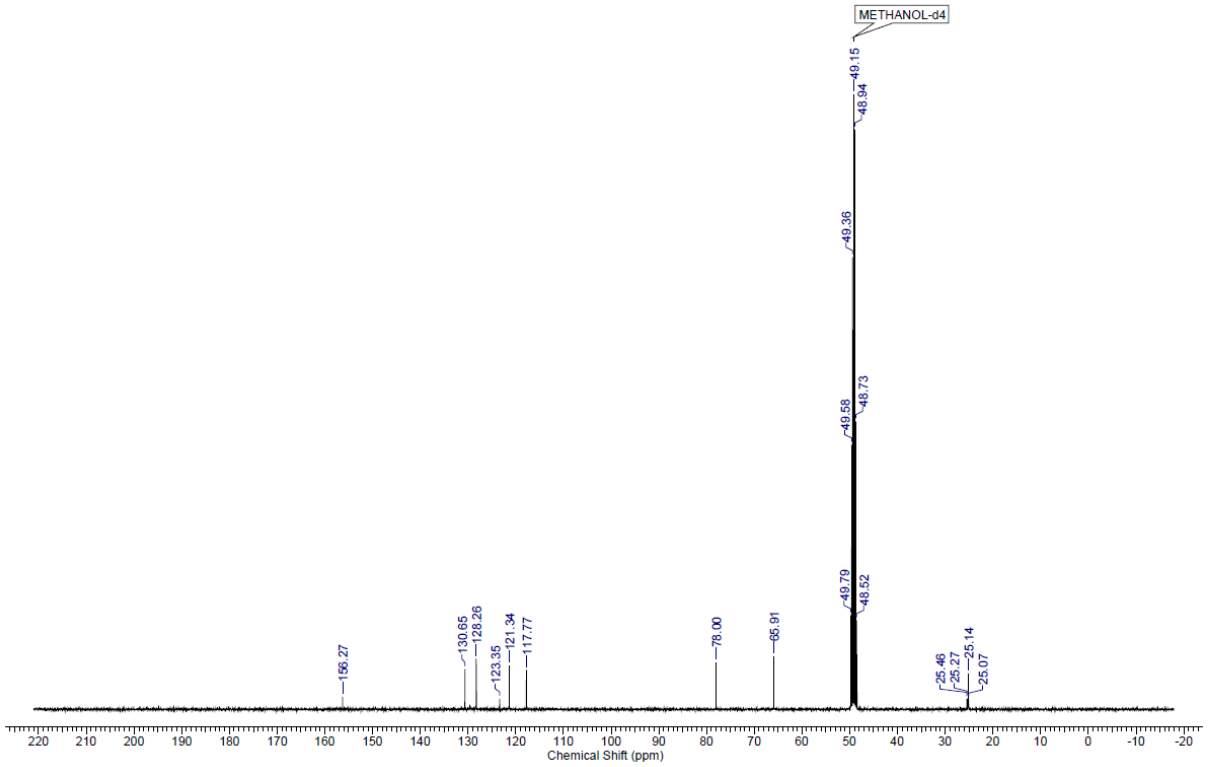
101 MHz, CD_3OD



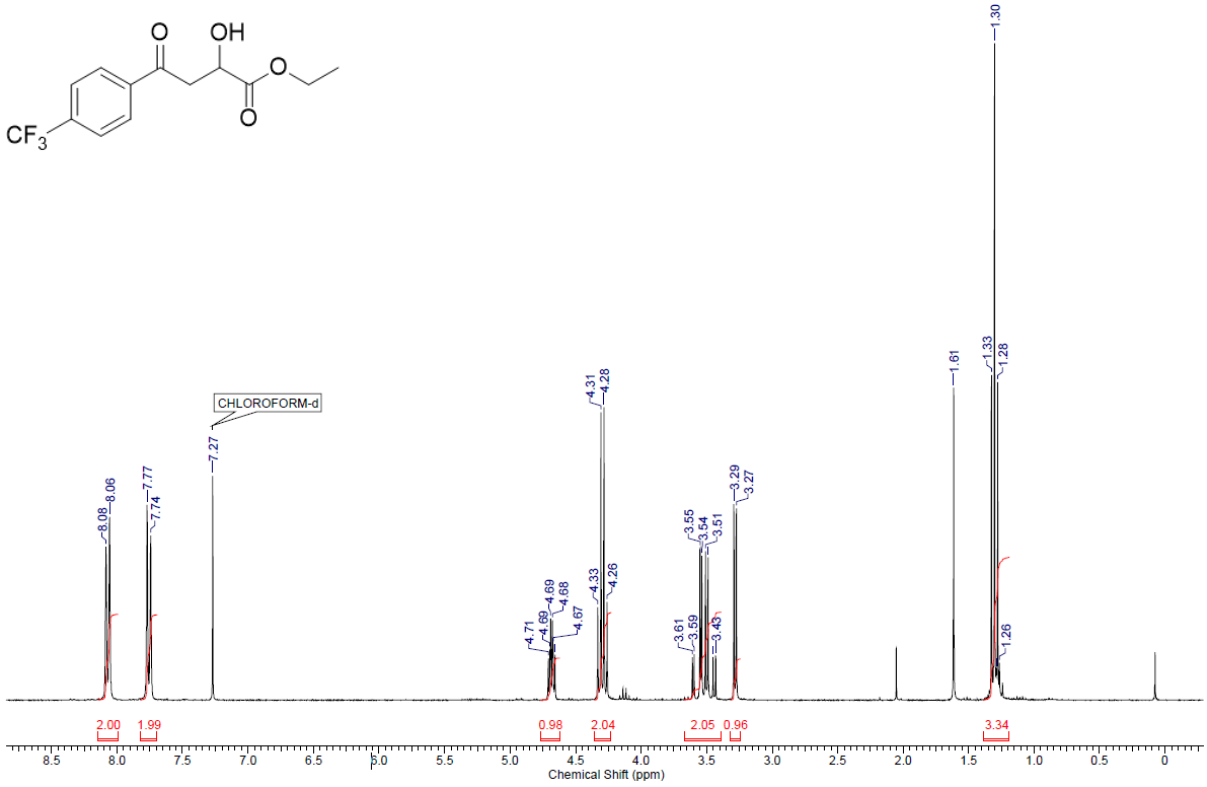
NMR Spectra **16**. 400 MHz, CD_3OD



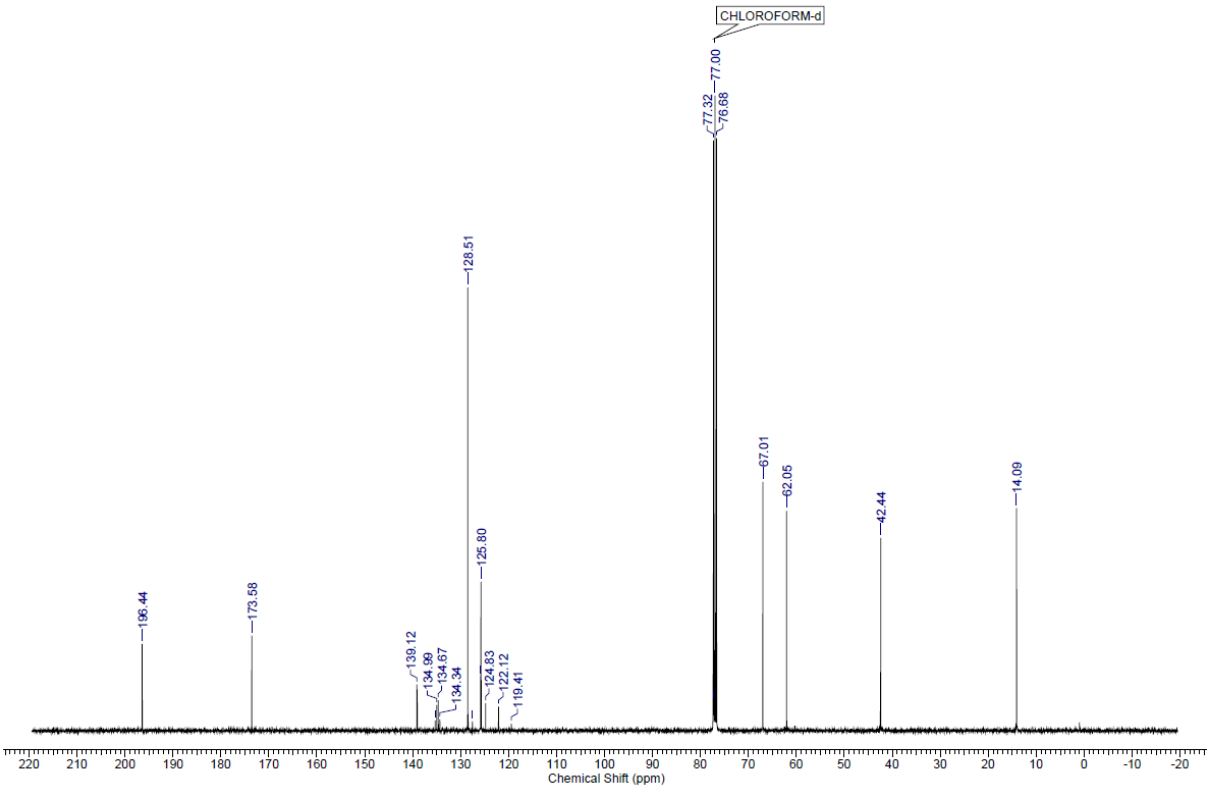
101 MHz, CD_3OD



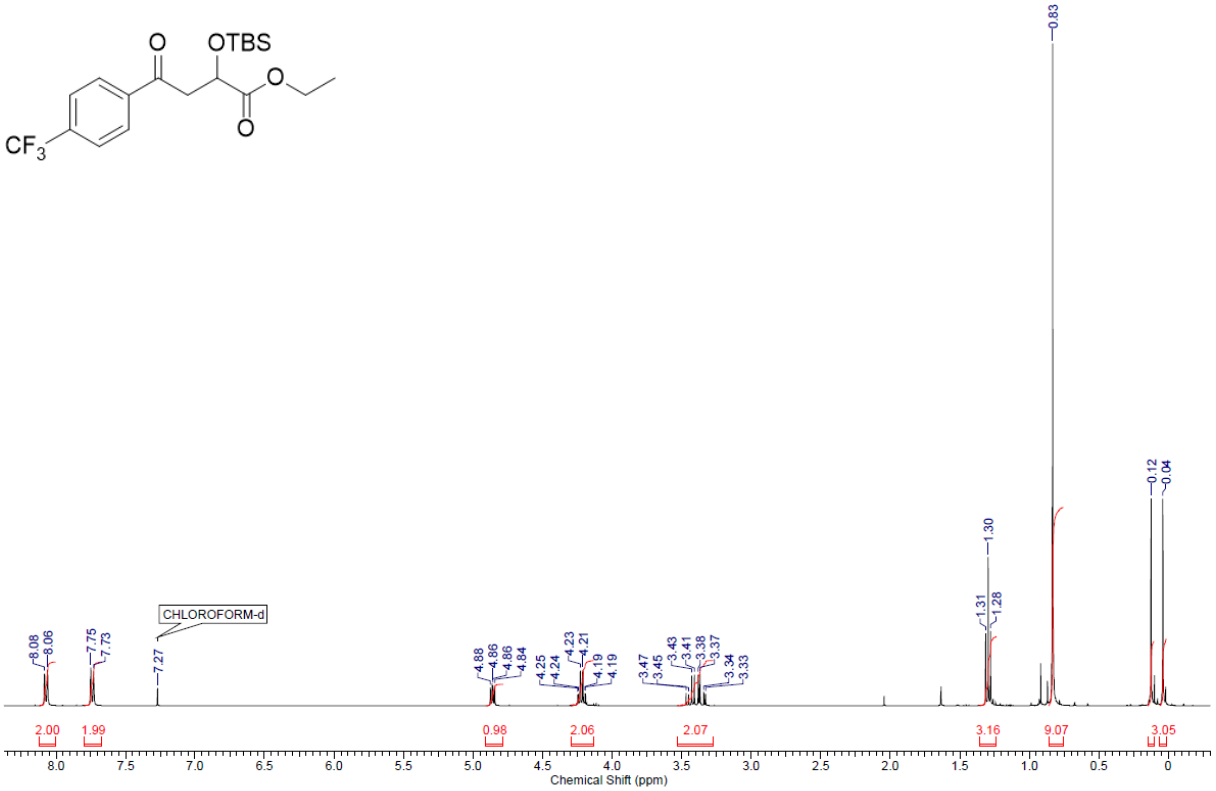
NMR Spectra **21**. 300 MHz, $CDCl_3$



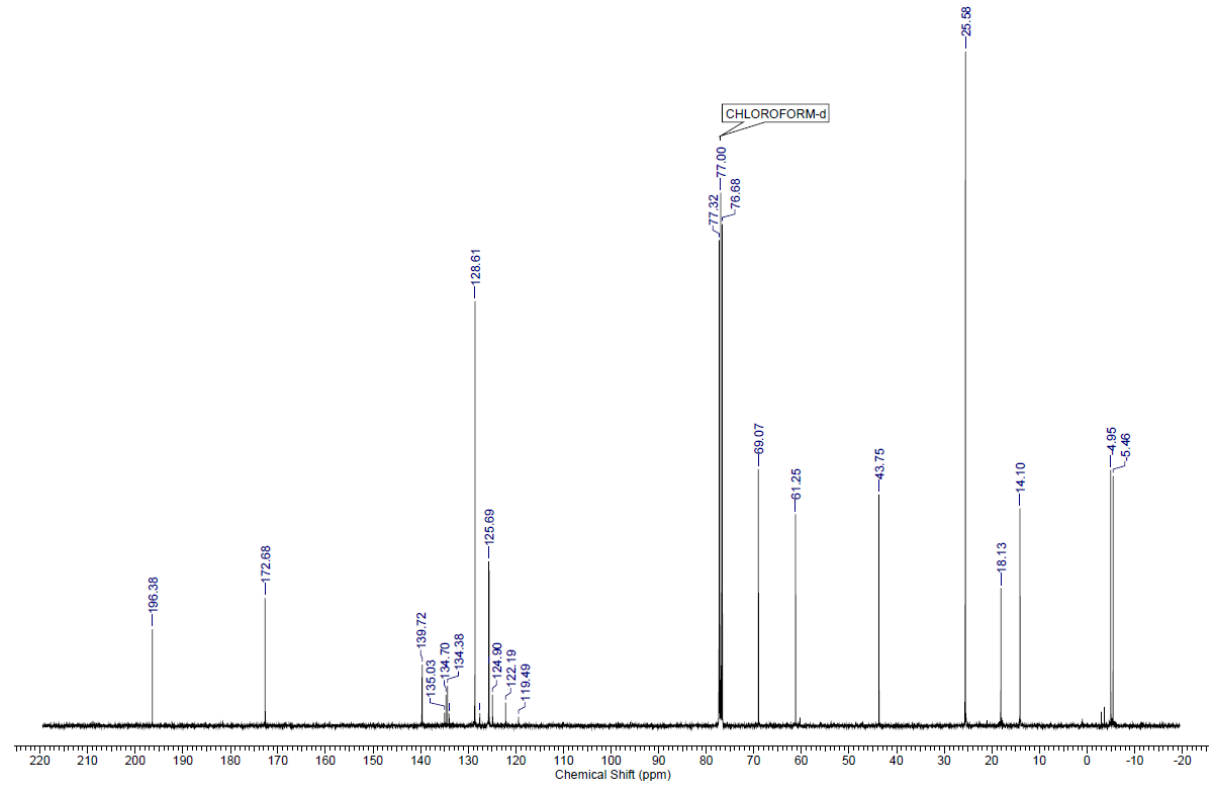
75 MHz, $CDCl_3$



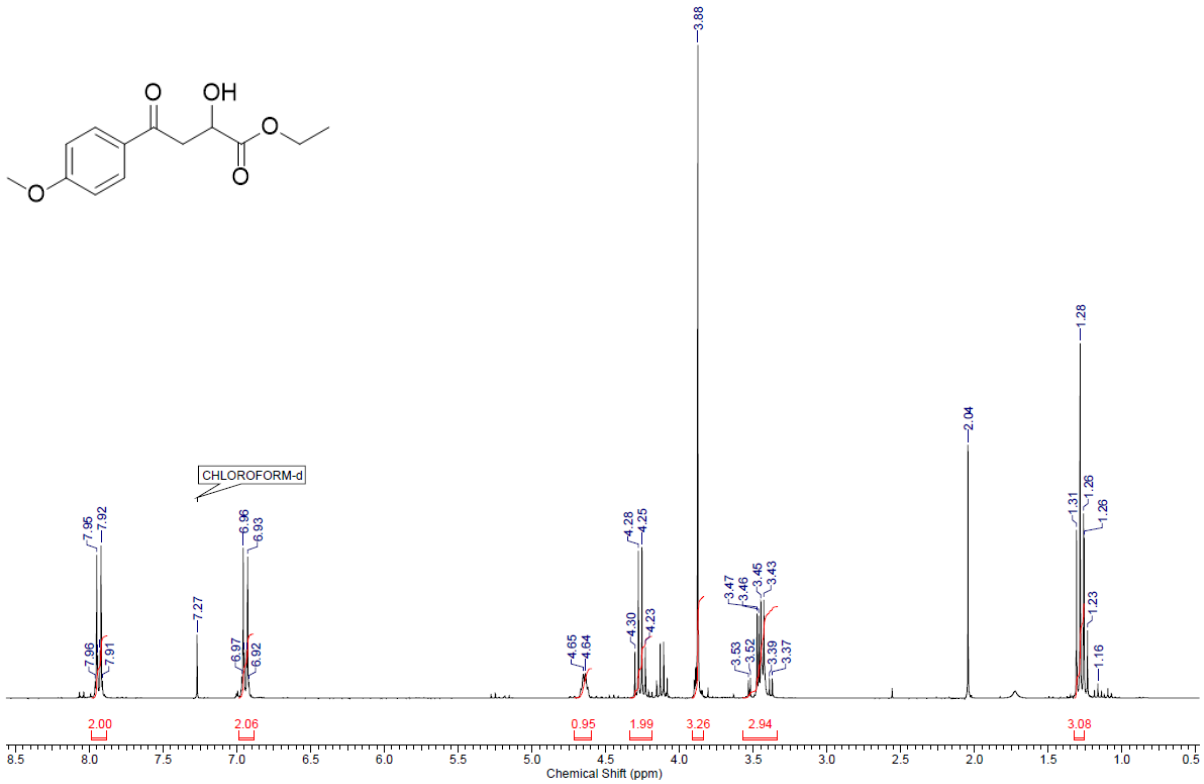
NMR Spectra **22**. 400 MHz, $CDCl_3$



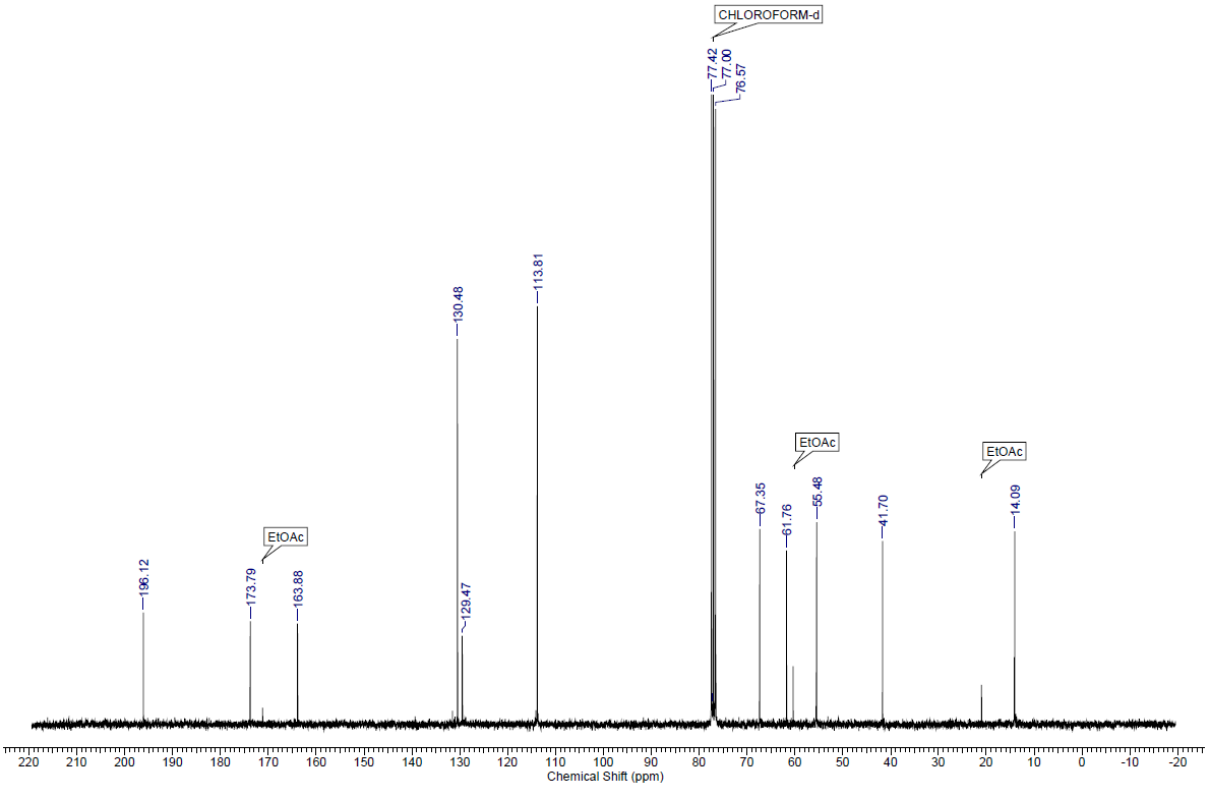
101 MHz, $CDCl_3$



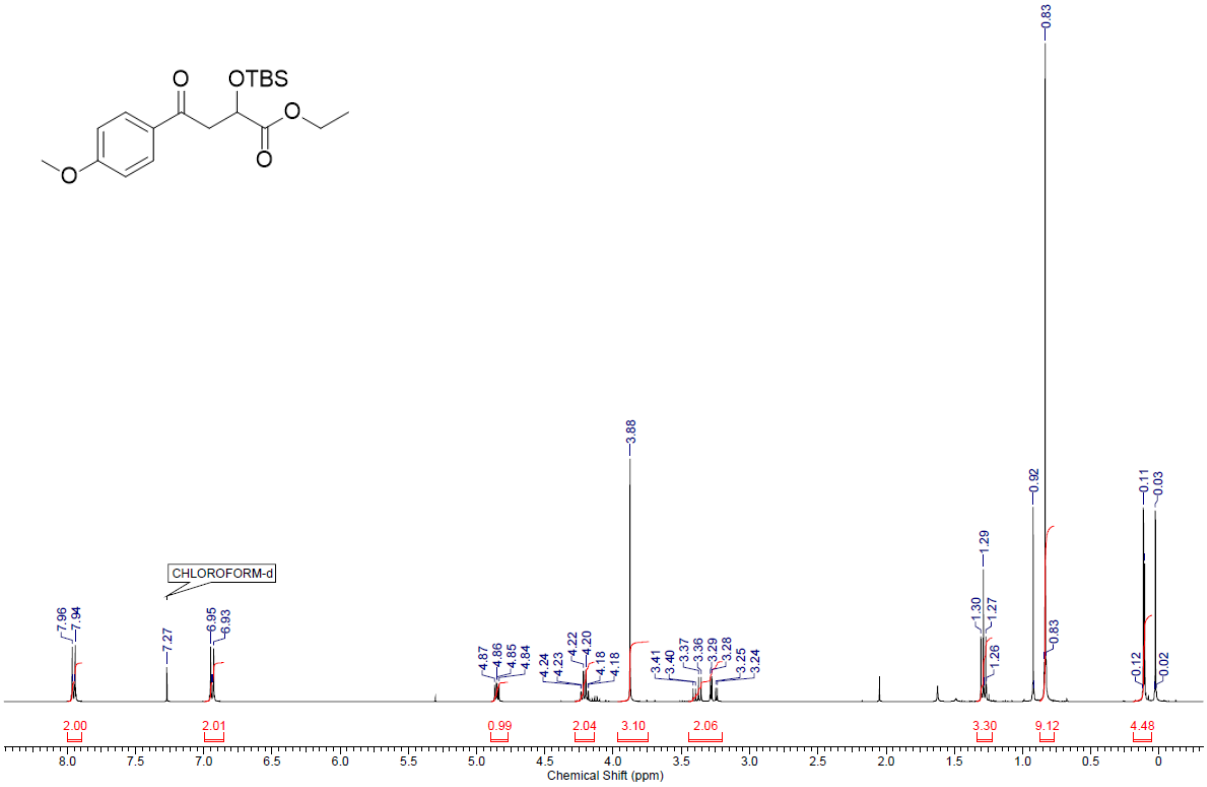
NMR Spectra **23**. 300 MHz, $CDCl_3$



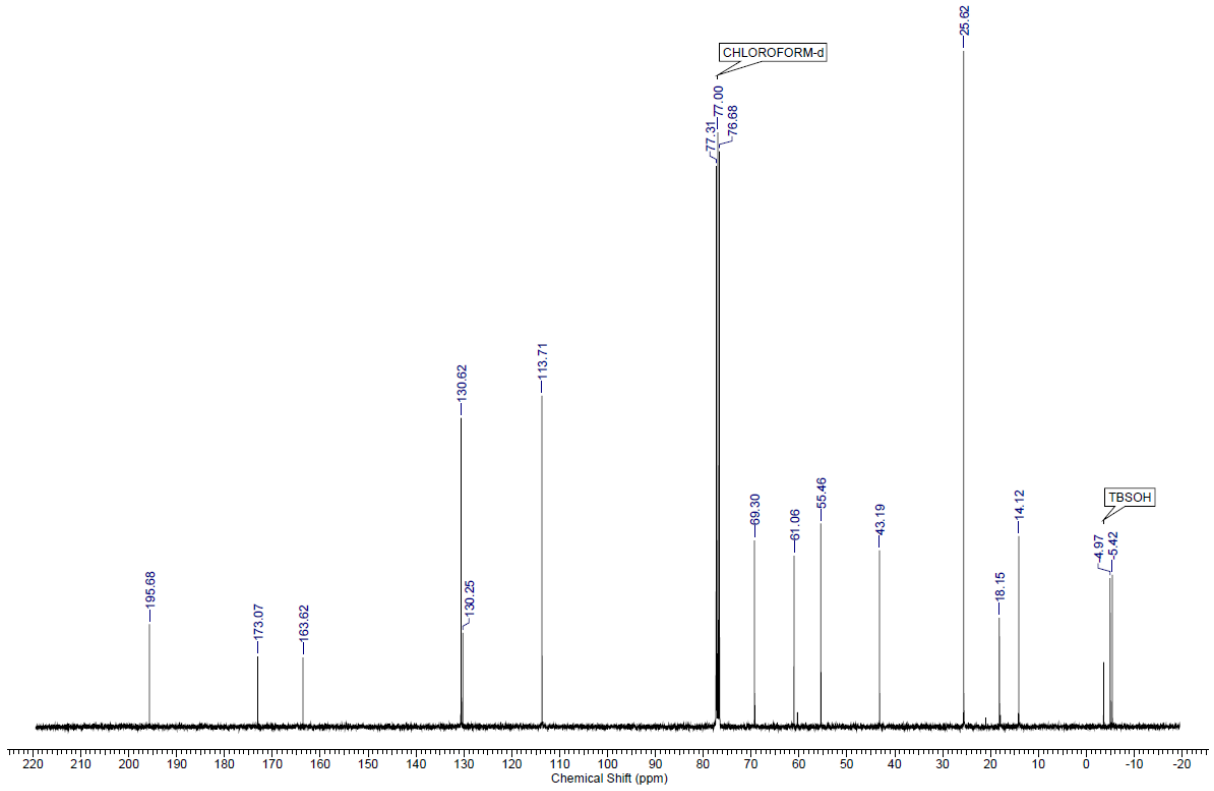
75 MHz, $CDCl_3$



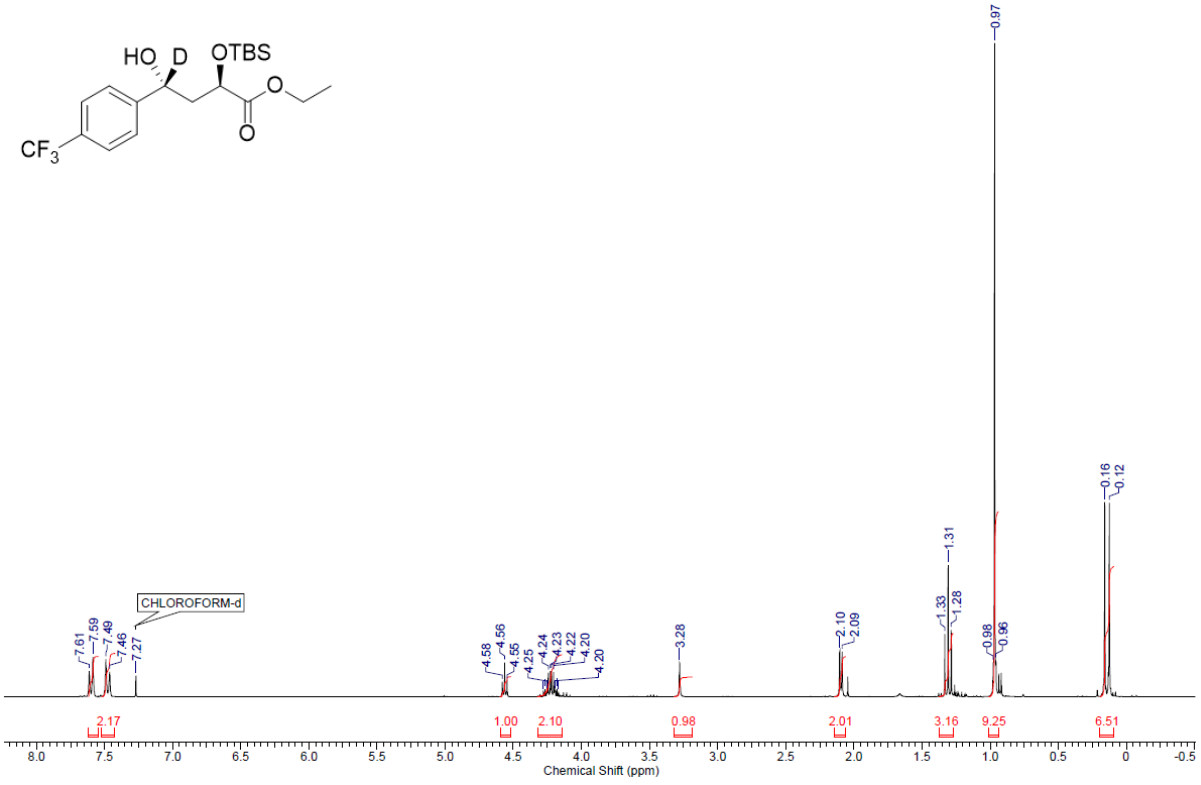
NMR Spectra **24**. 400 MHz, $CDCl_3$



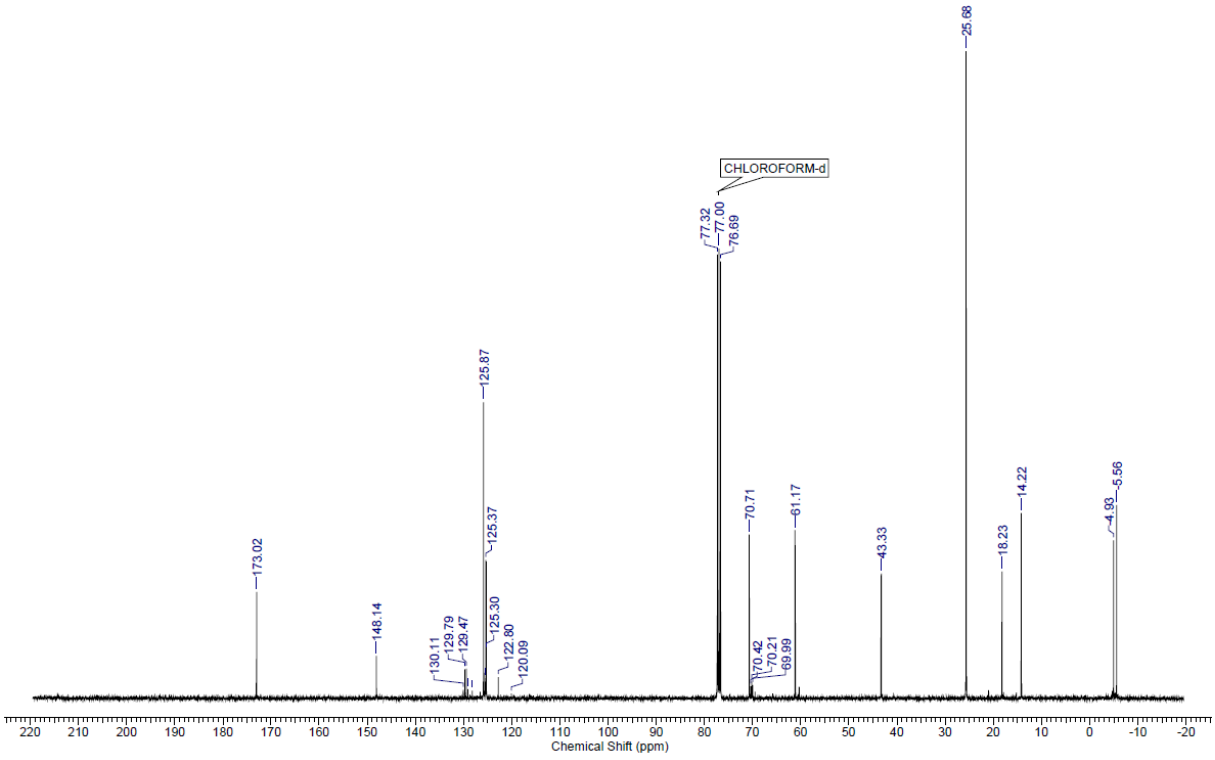
101 MHz, $CDCl_3$



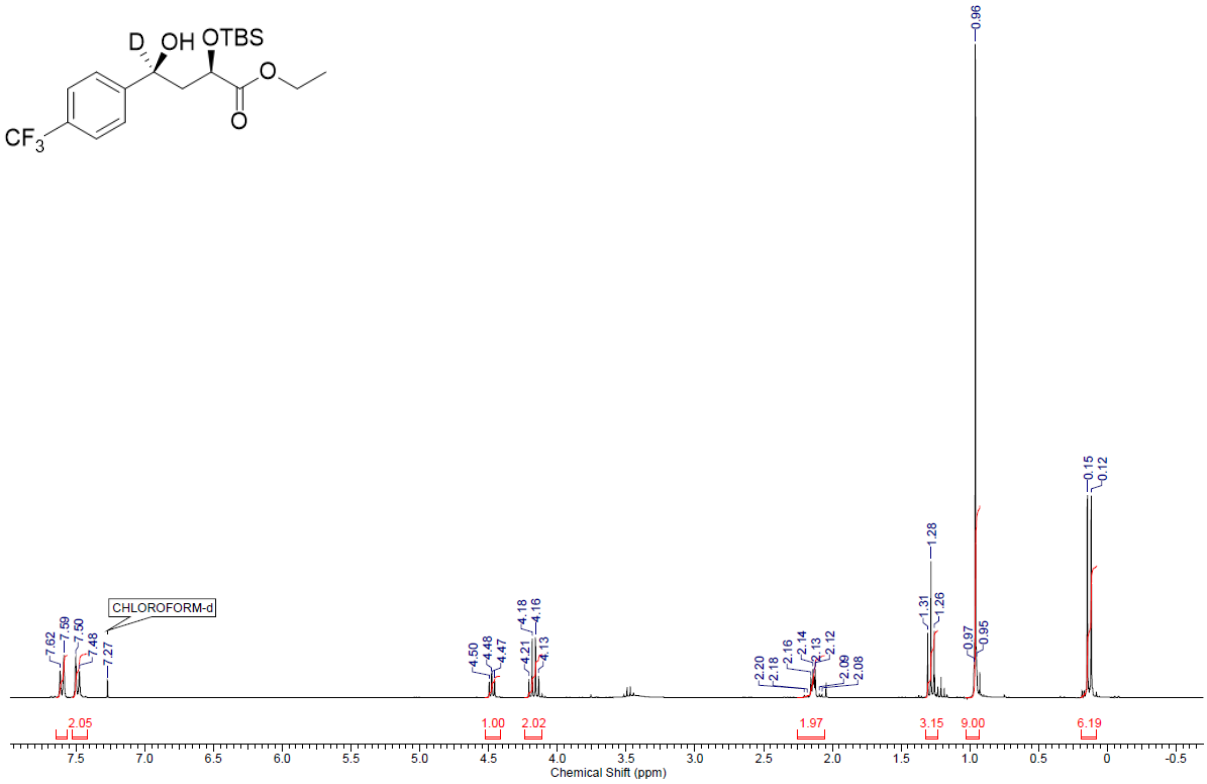
NMR Spectra **25**. 300 MHz, $CDCl_3$



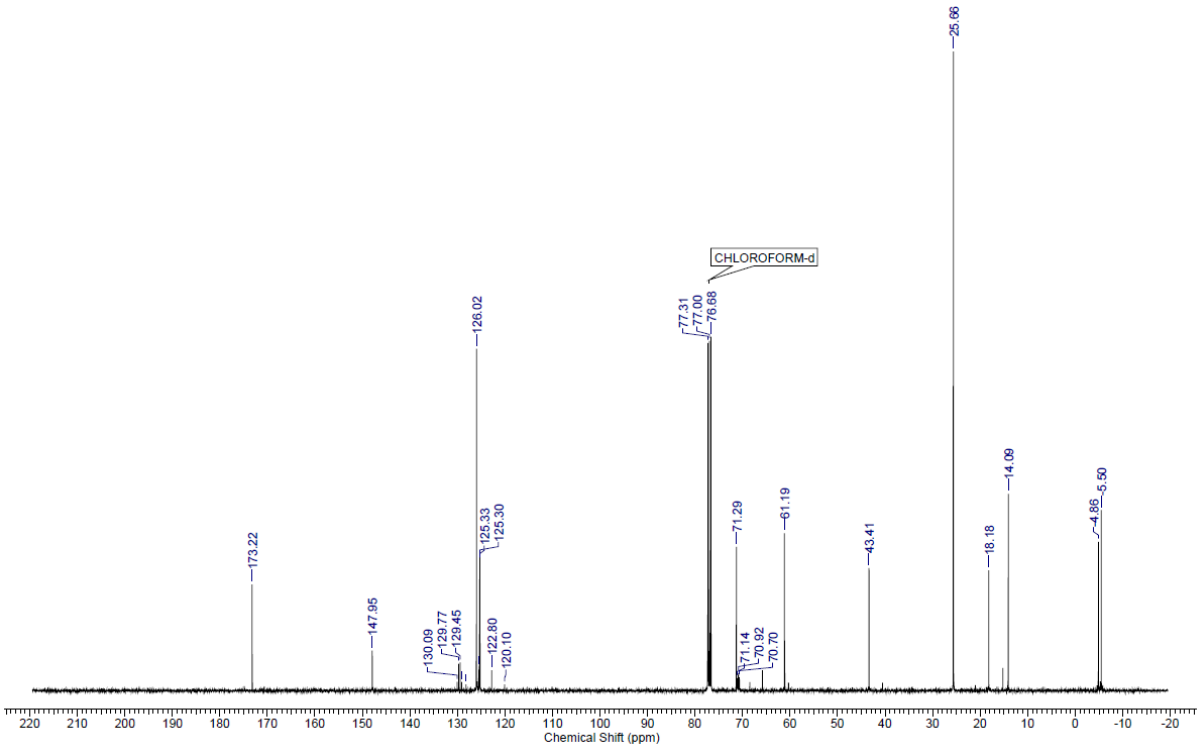
101 MHz, $CDCl_3$



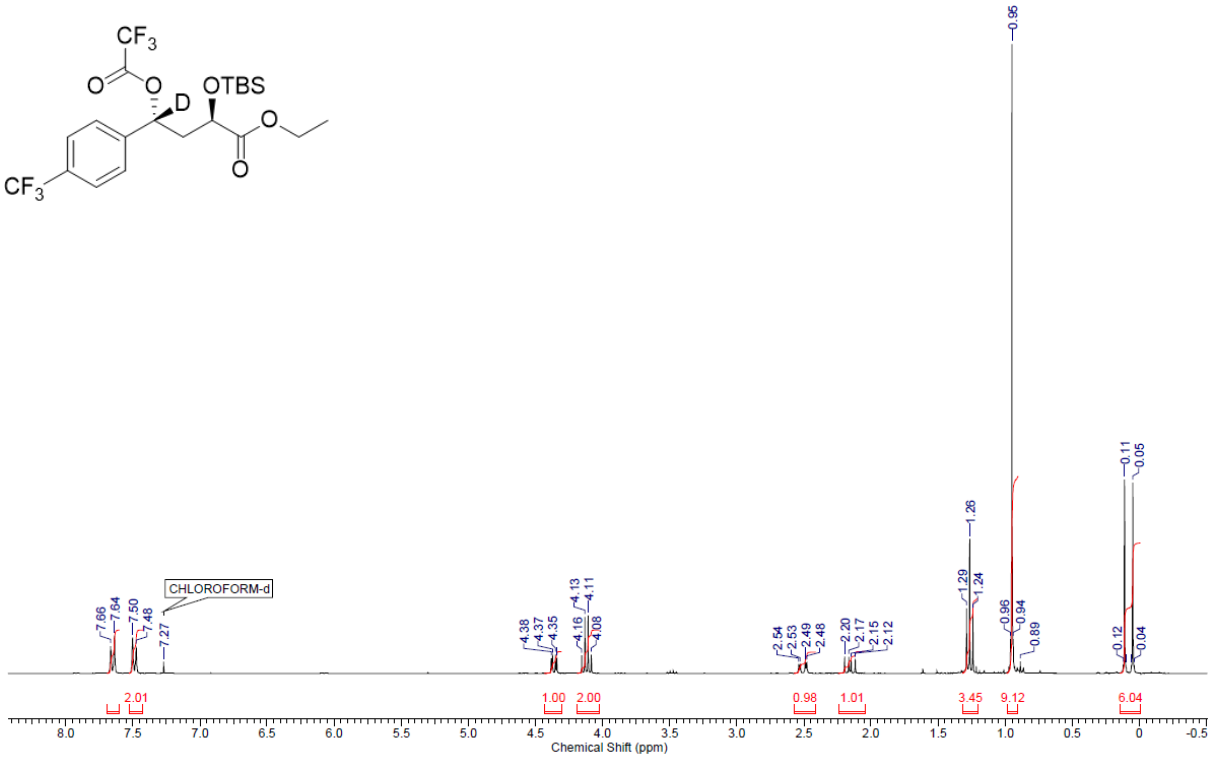
NMR Spectra **26**. 300 MHz, $CDCl_3$



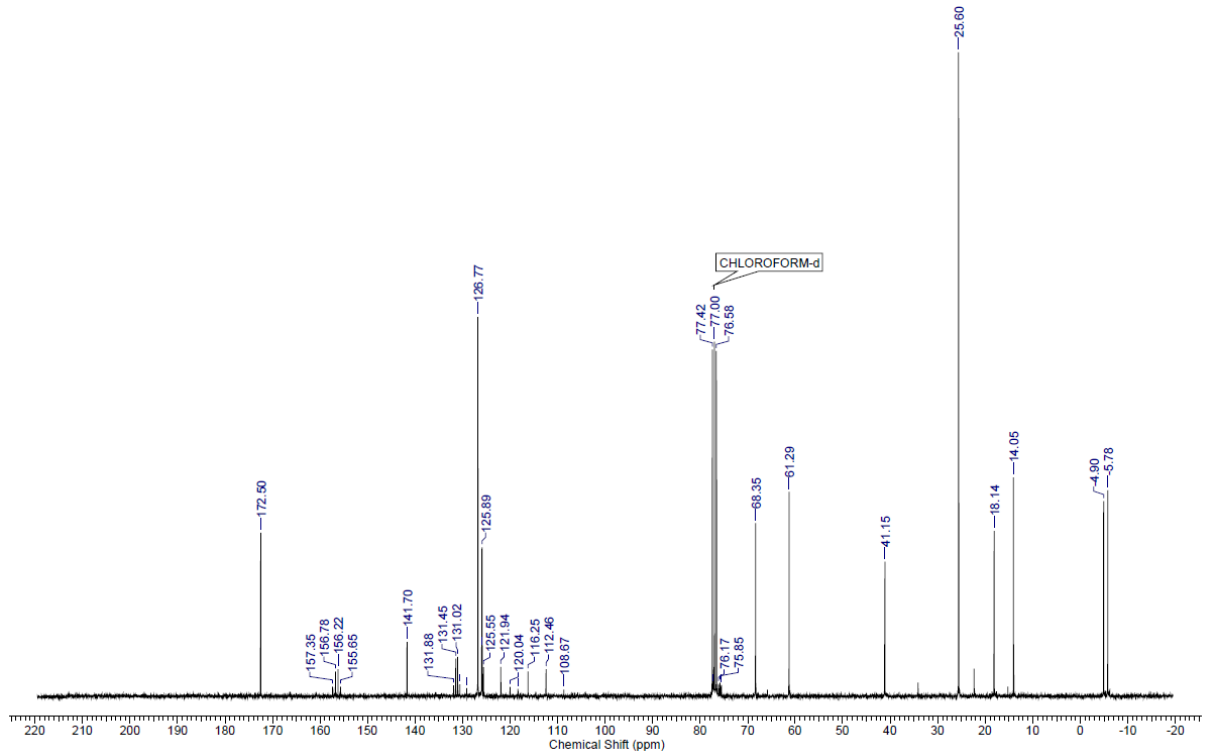
101 MHz, $CDCl_3$



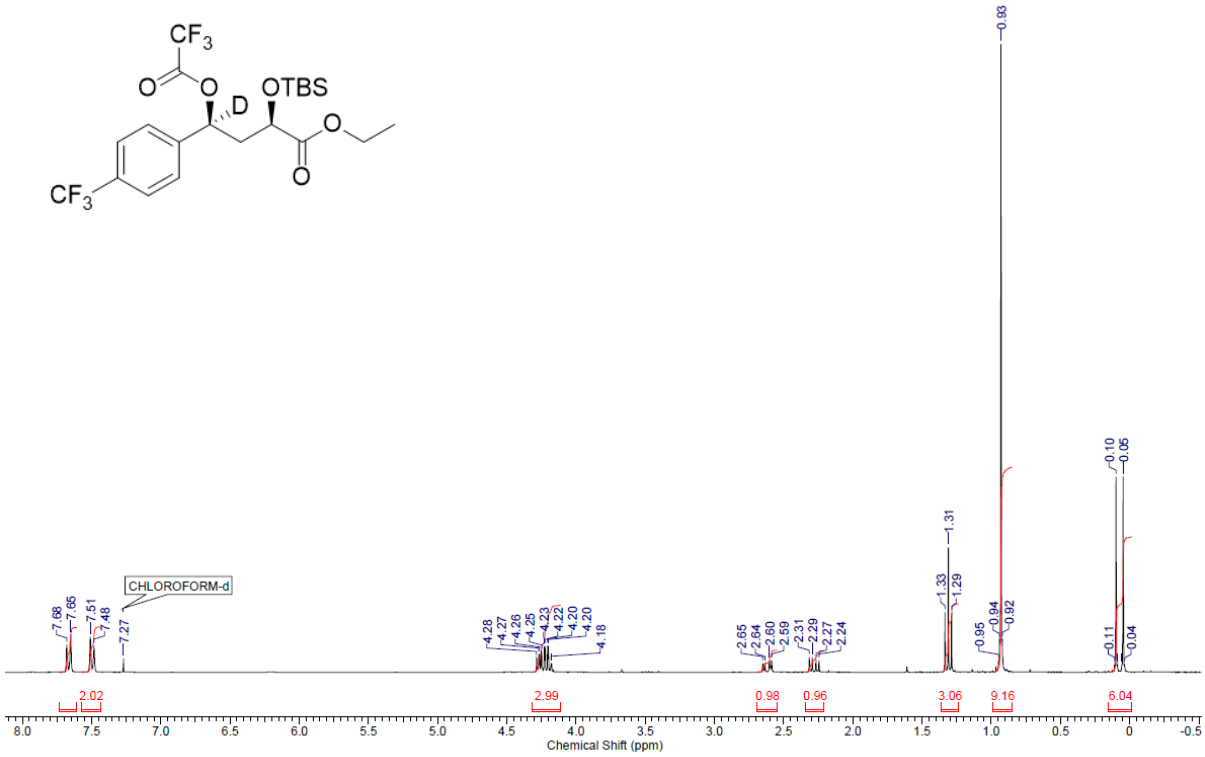
NMR Spectra **27**. 300 MHz, $CDCl_3$



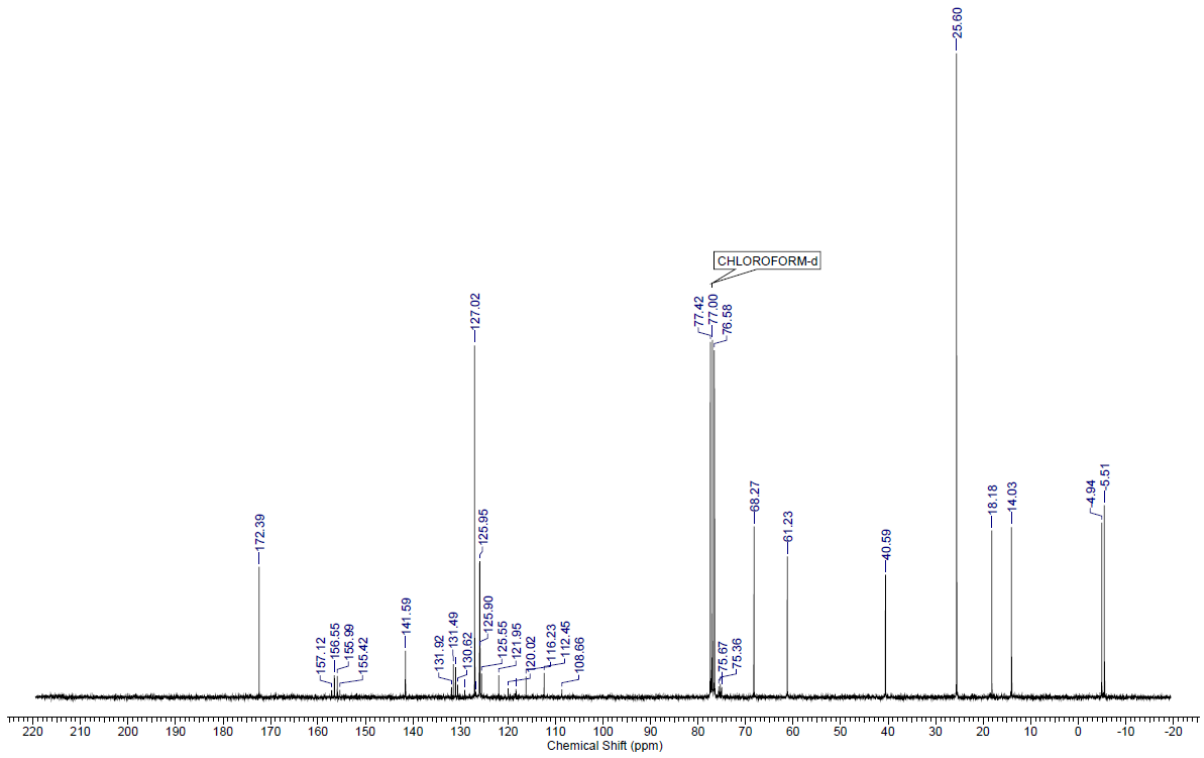
75 MHz, $CDCl_3$



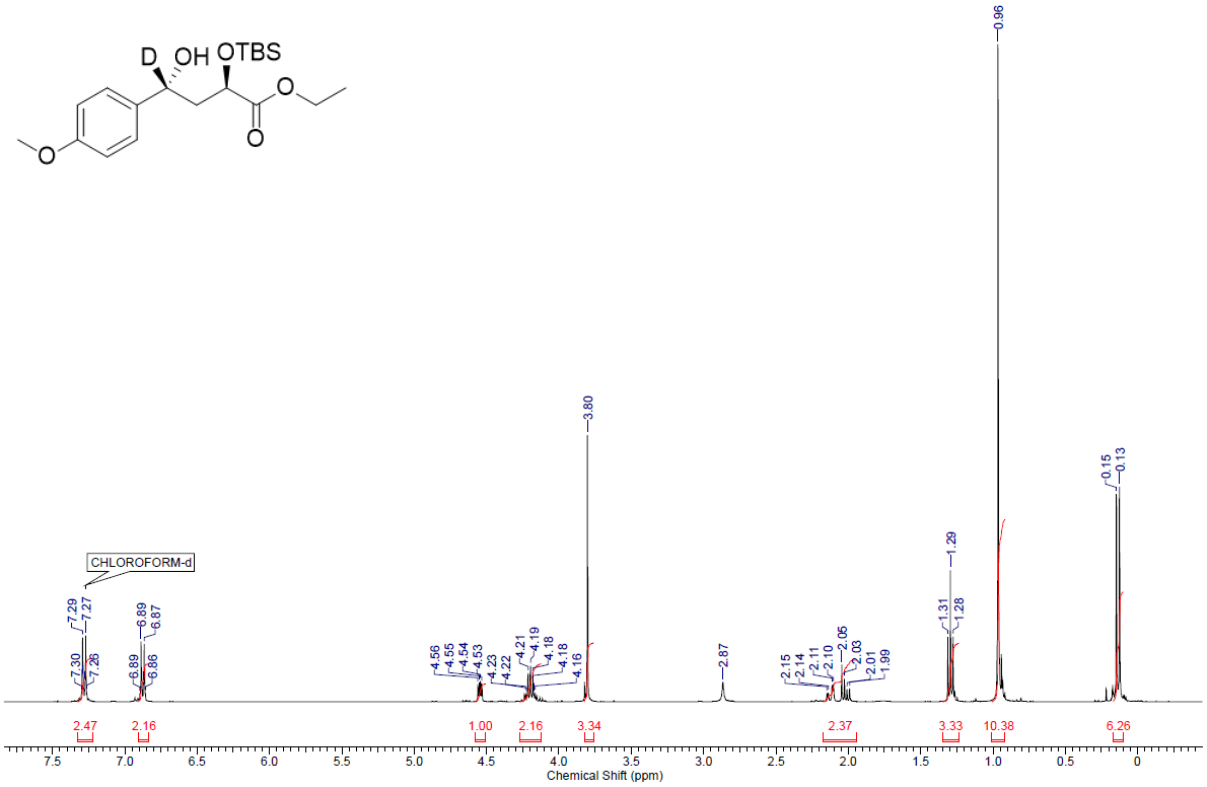
NMR Spectra **28**. 300 MHz, $CDCl_3$



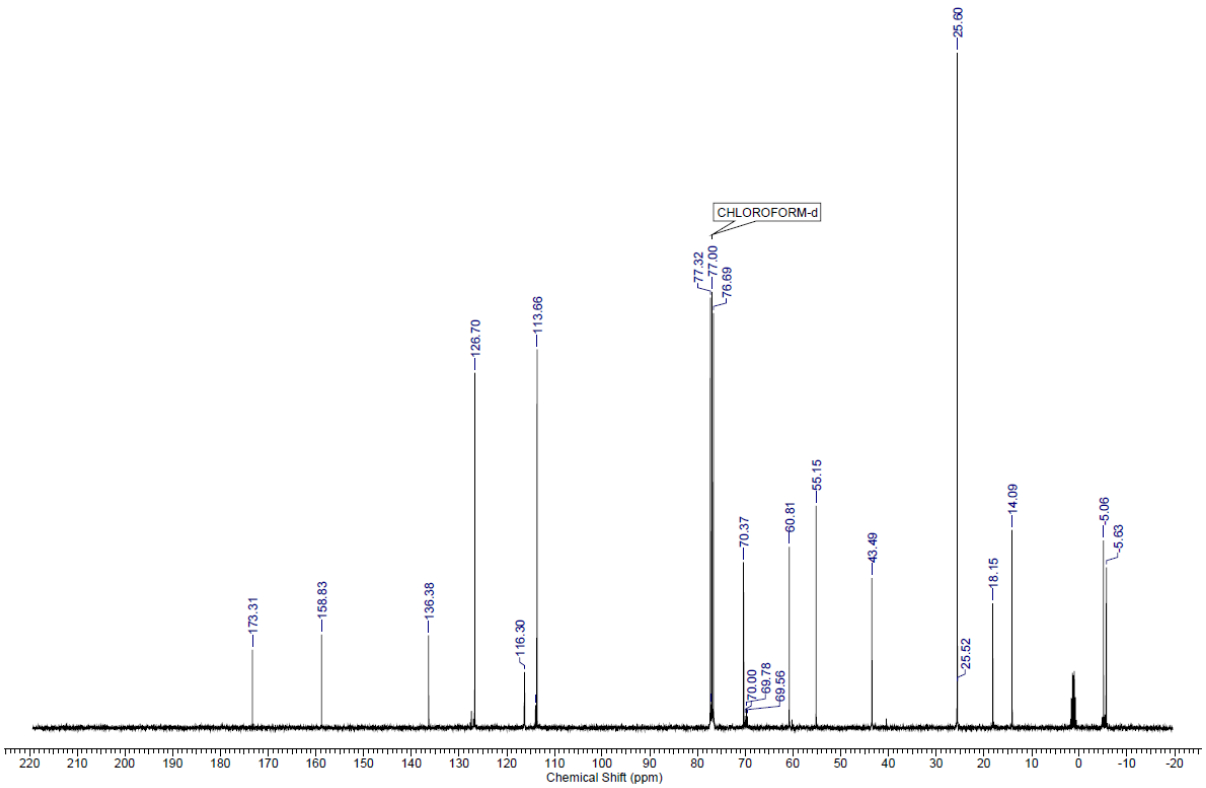
75 MHz, $CDCl_3$



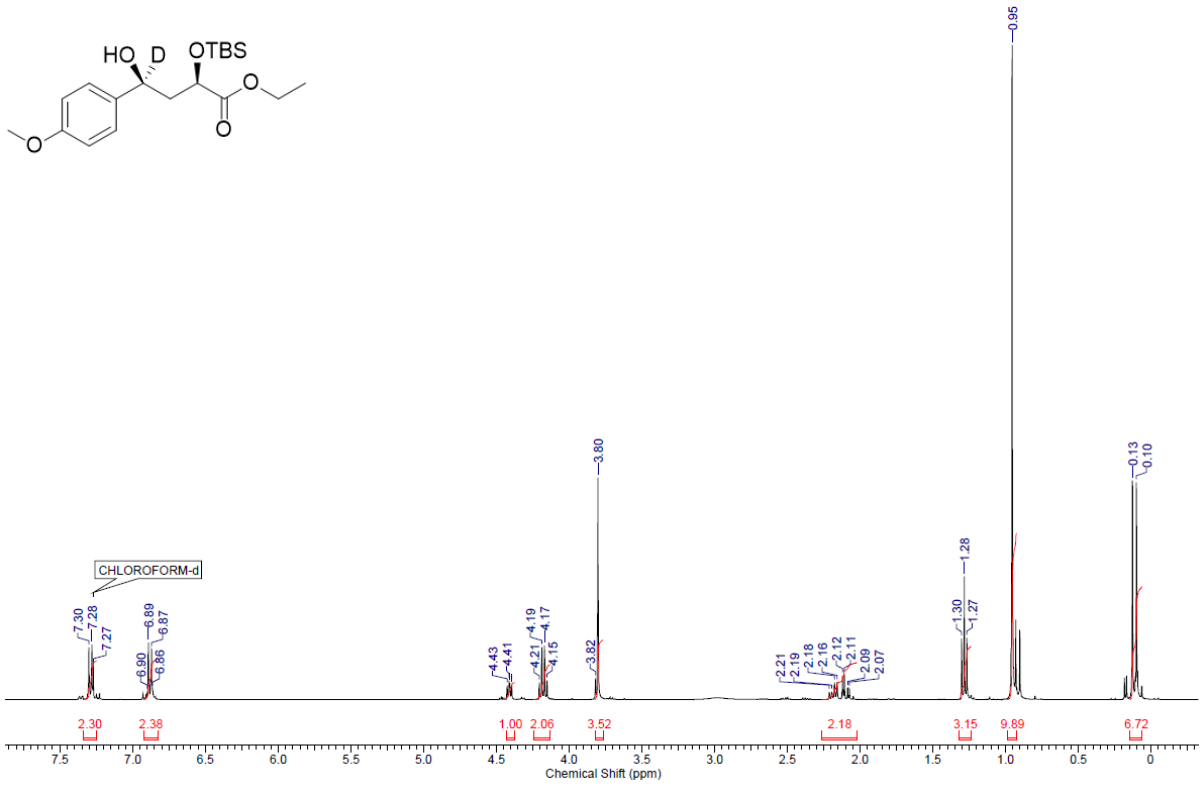
NMR Spectra **29**. 300 MHz, $CDCl_3$



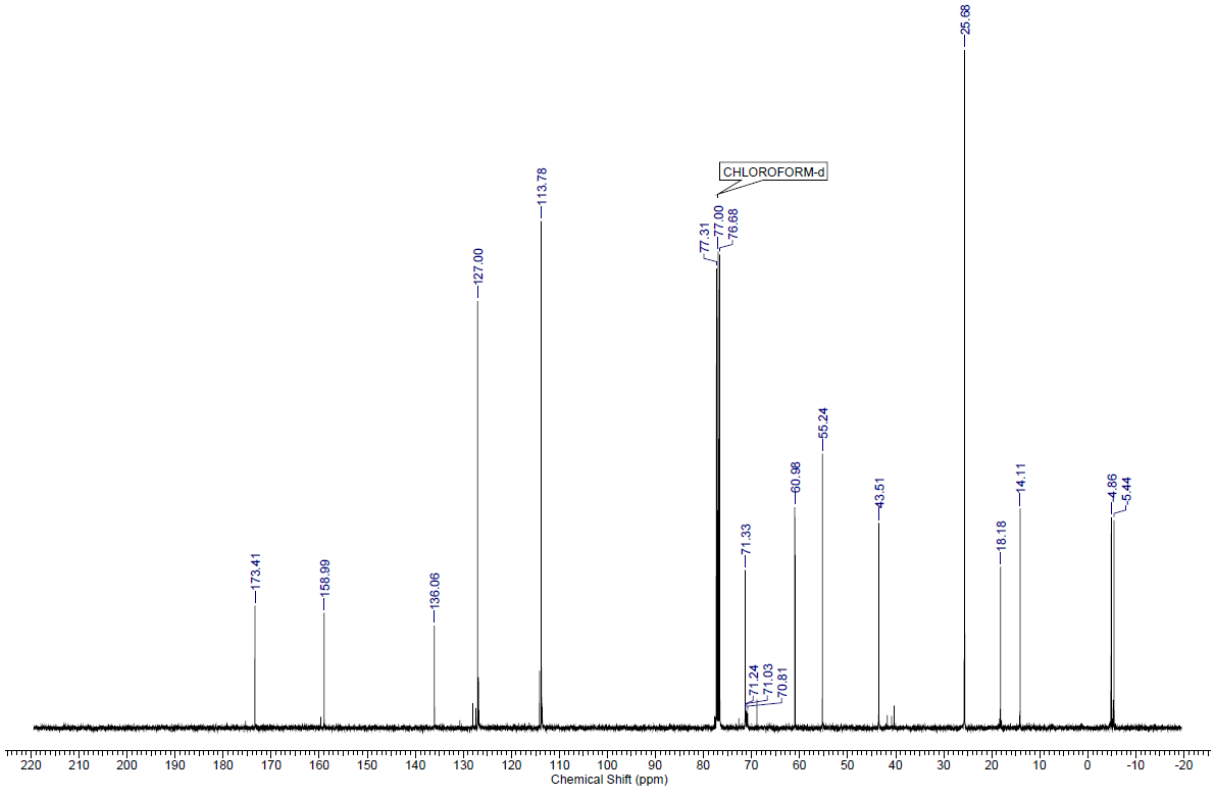
101 MHz, $CDCl_3$



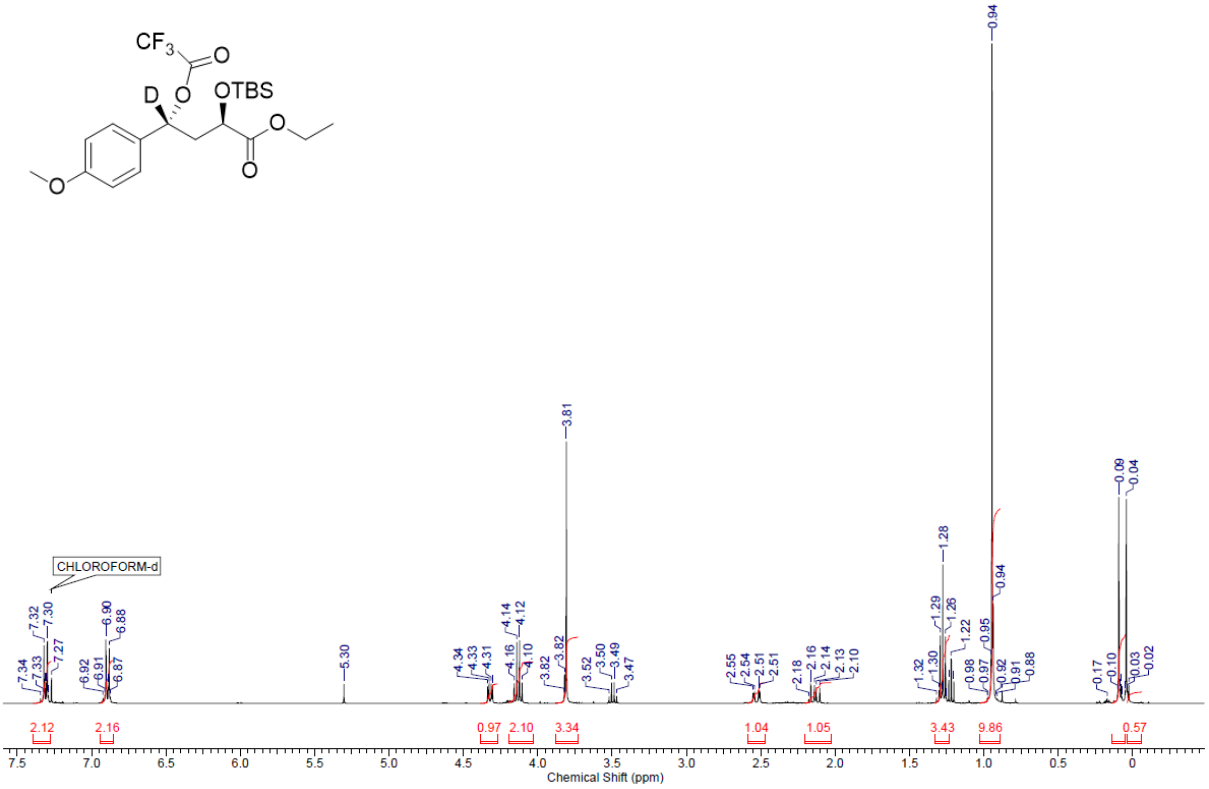
NMR Spectra **30**. 300 MHz, $CDCl_3$



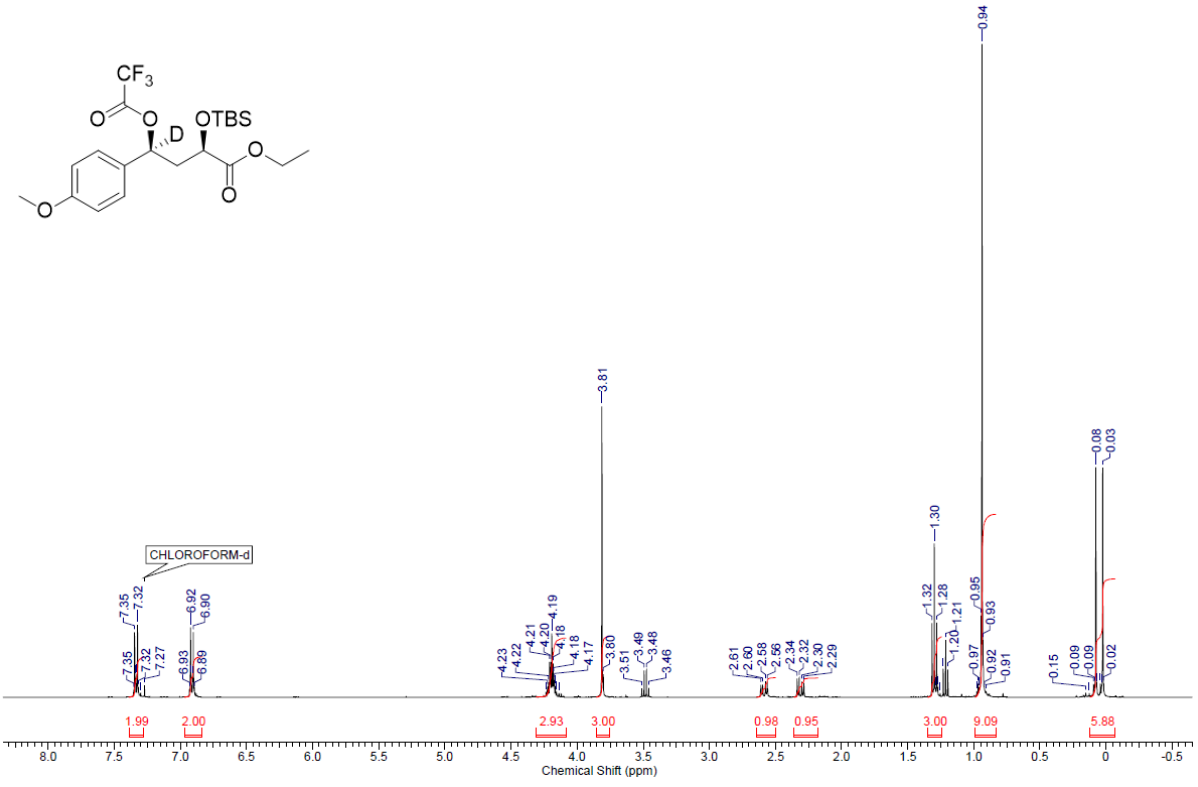
101 MHz, $CDCl_3$



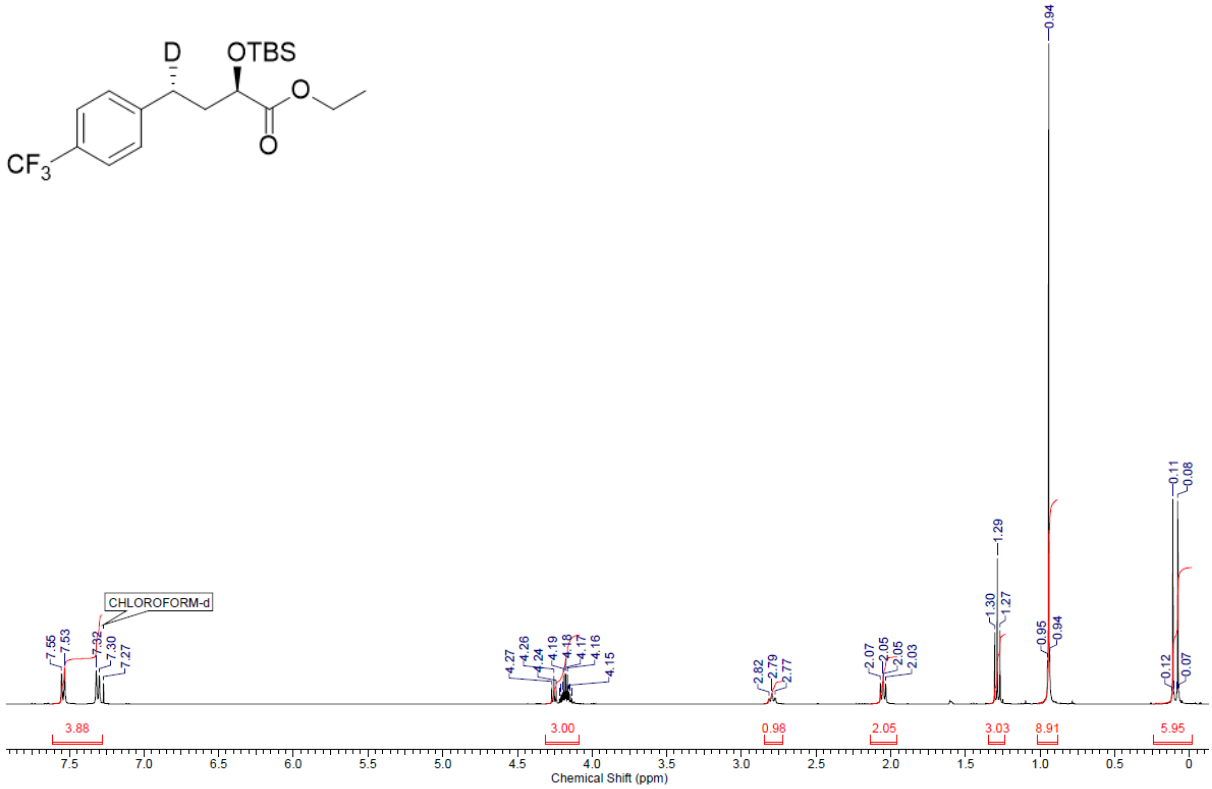
^{1}H-NMR Spectrum **31**. 400 MHz, $CDCl_3$



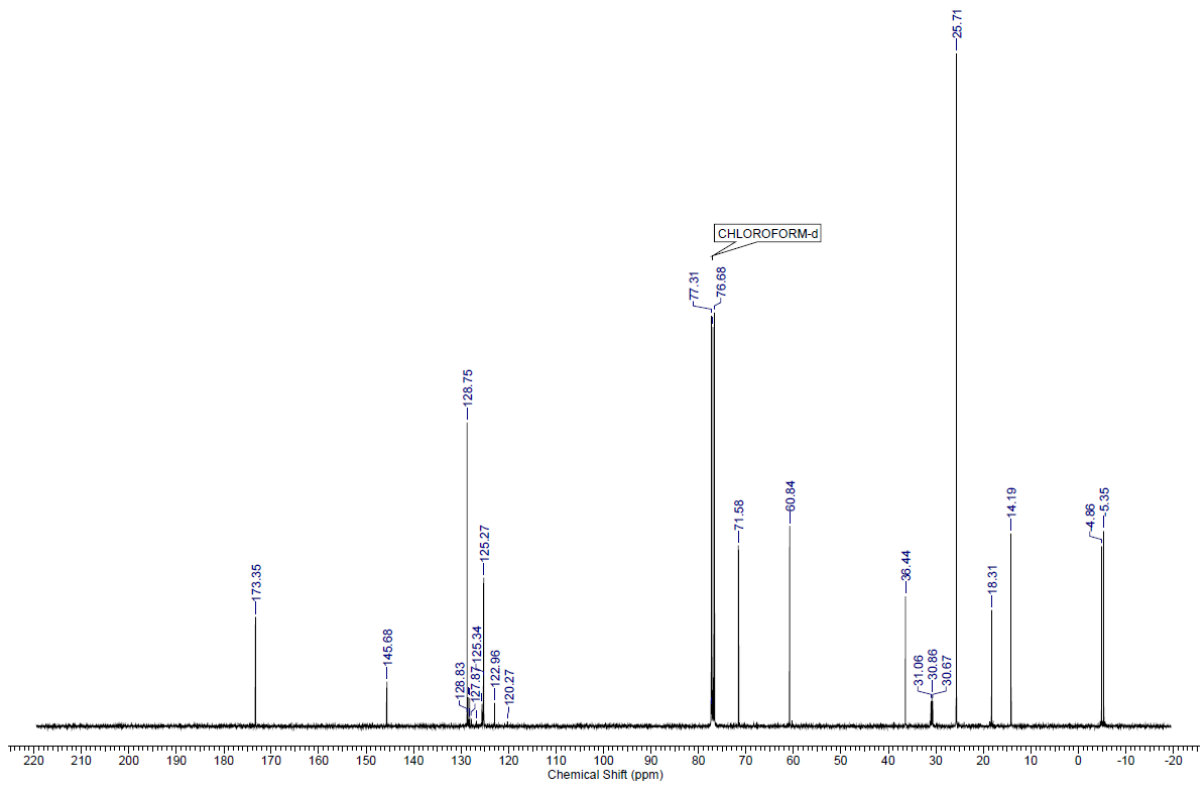
^{1}H-NMR Spectrum **32**. 400 MHz, $CDCl_3$



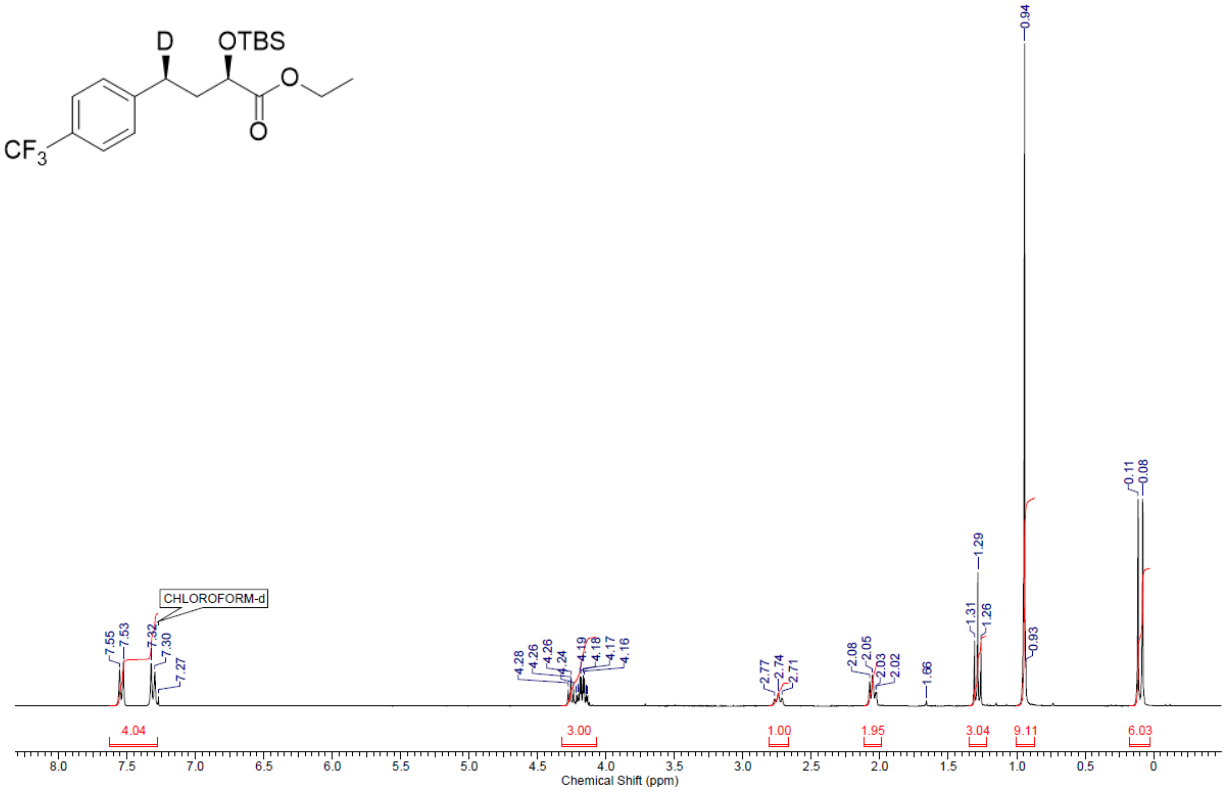
NMR Spectra **33**. 400 MHz, $CDCl_3$



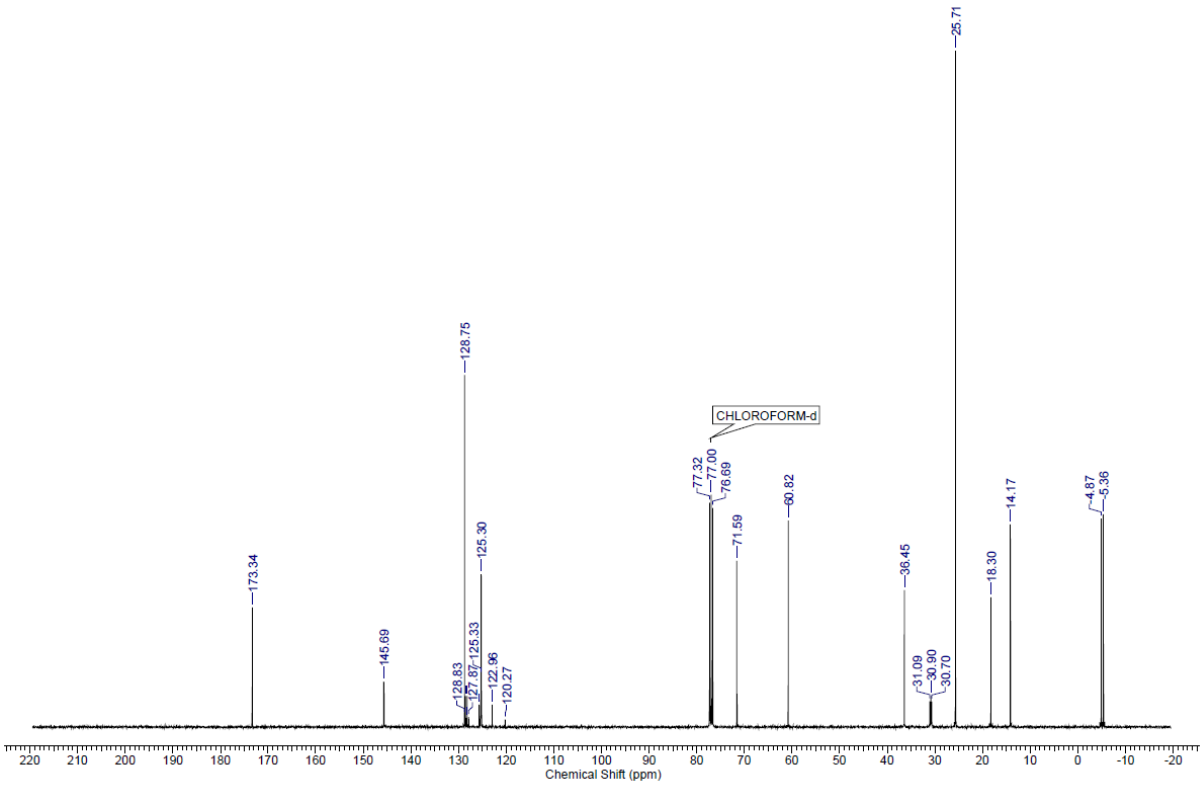
101 MHz, $CDCl_3$



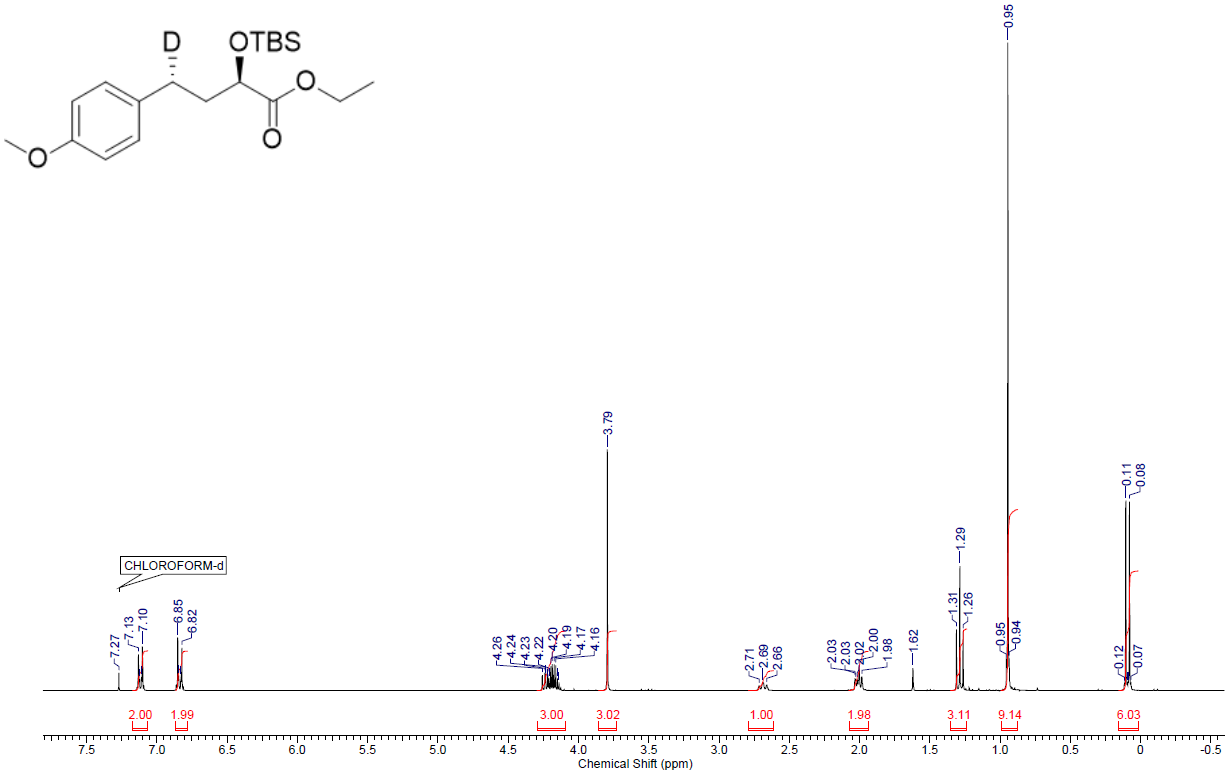
NMR Spectra **34**. 300 MHz, $CDCl_3$



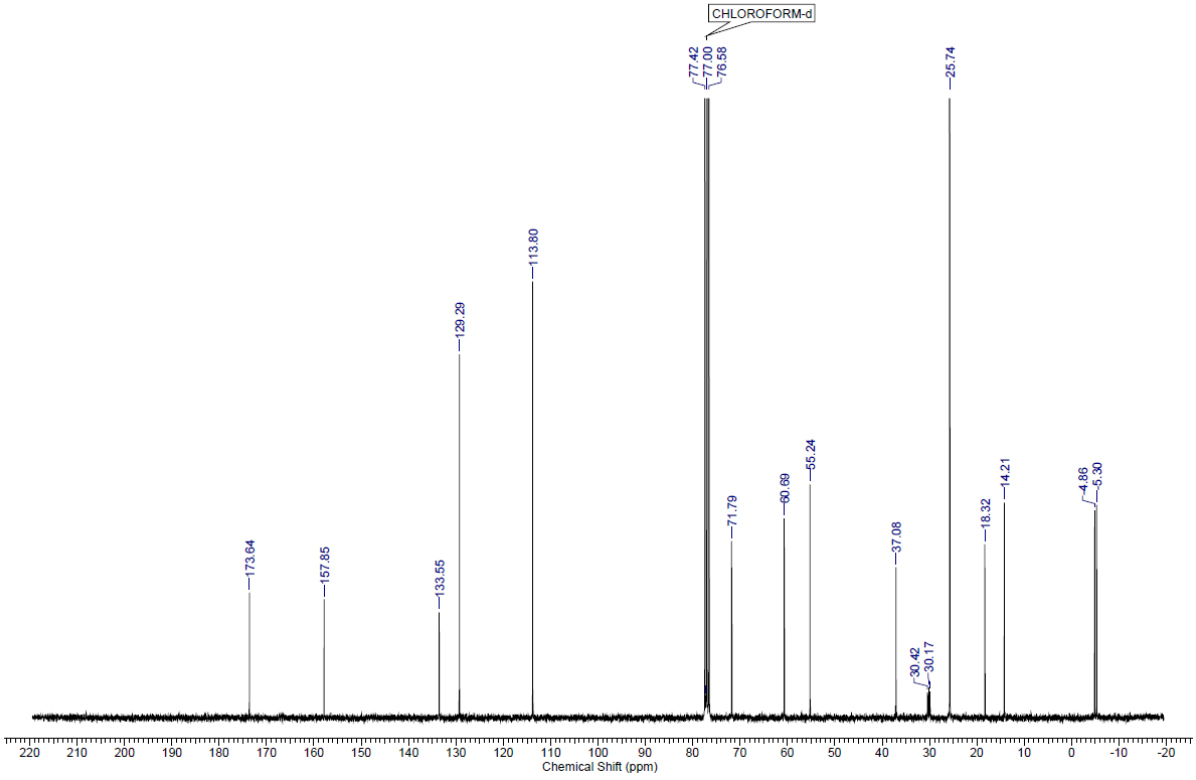
101 MHz, $CDCl_3$



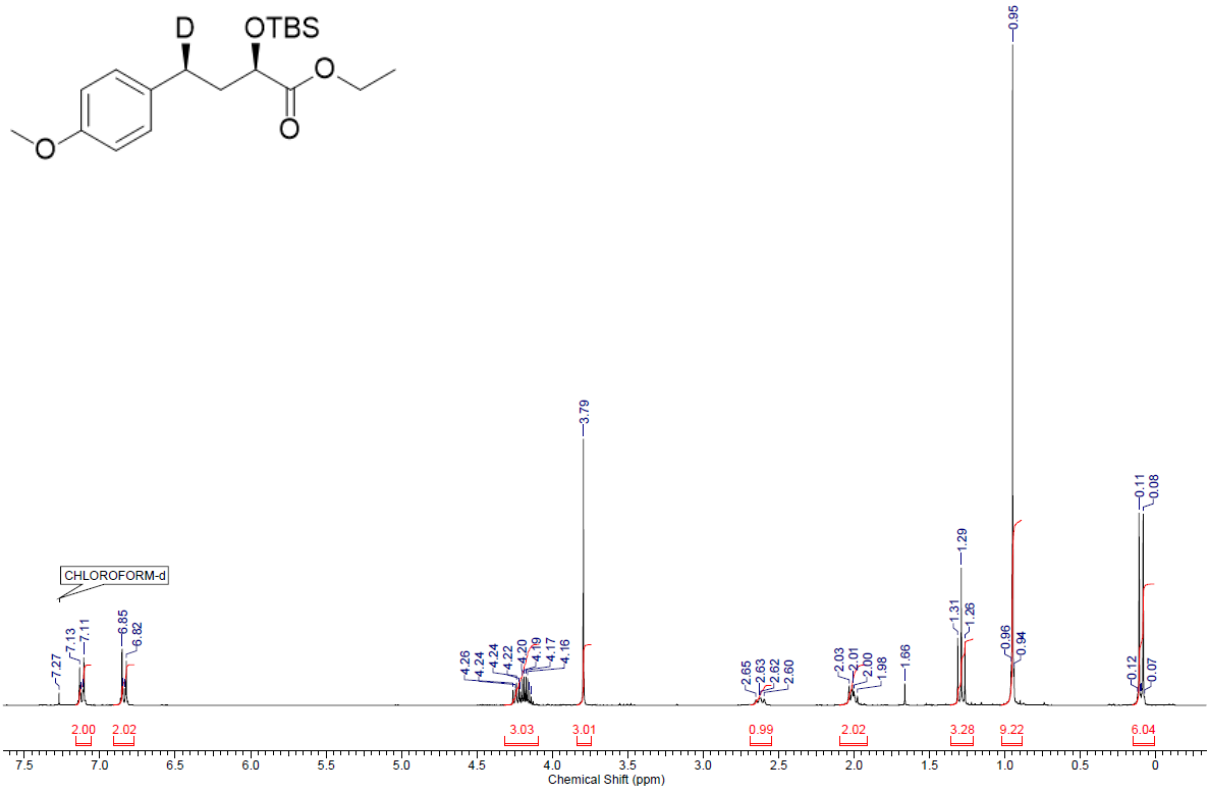
NMR Spectra **35**. 300 MHz, $CDCl_3$



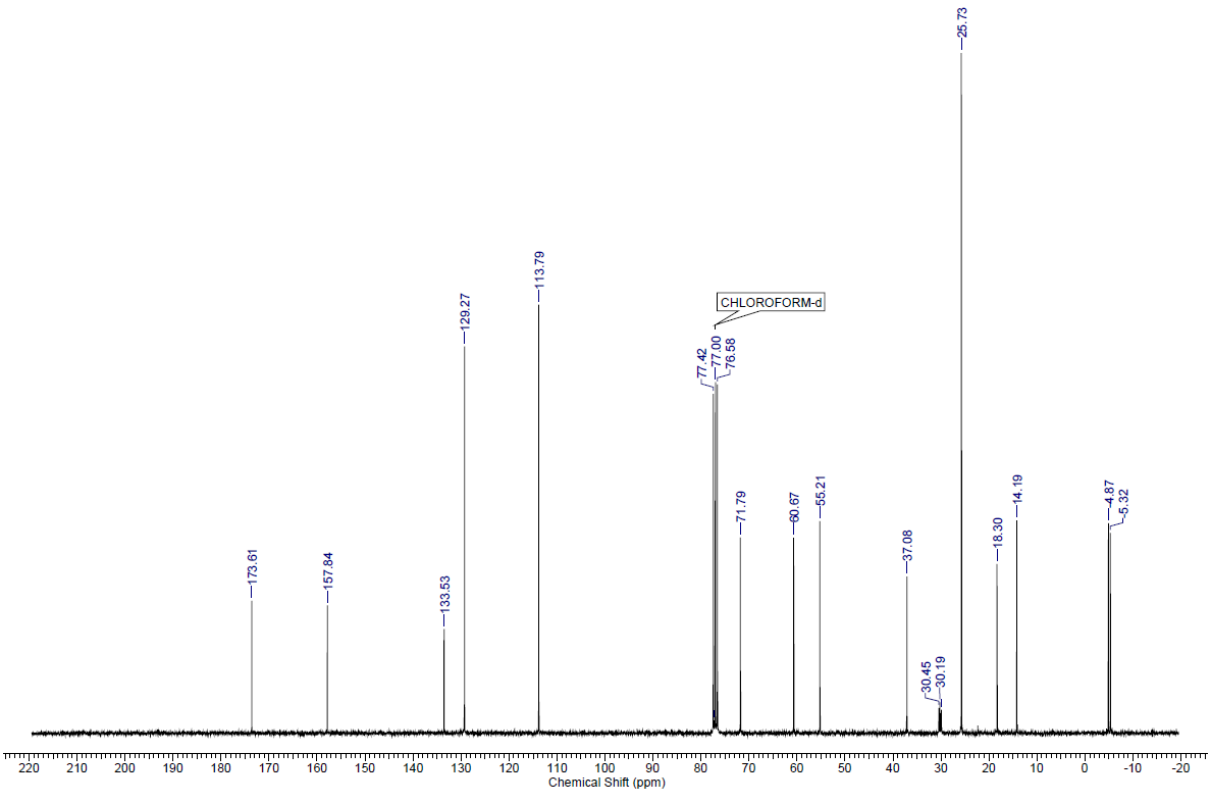
75 MHz, $CDCl_3$



NMR Spectra **36**.300 MHz, $CDCl_3$



75 MHz, $CDCl_3$



III. References

(1) Lewis, W. C.; Norcross, B. E. Average Geminal and Vicinal Proton—Deuterium Coupling Constants in Variously Deuterated Ethanol, Propanol-2, and Toluene. *J. Org. Chem.* **1965**, *30*, 2866–2867. 10.1021/jo01019a526