

ELECTRONIC SUPPORTING INFORMATION (ESI)

**BENT BOND (τ) AND THE ANTIPERIPLANAR HYPOTHESIS, AND THE
REACTIVITY AT THE ANOMERIC CENTER IN PYRANOSIDES**

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General information

The following document includes general experimental conditions and detailed protocols for the synthesis of new compounds along with the isolation and spectroscopic information for the lasts. Transformation requiring inert and anhydrous conditions were carried out within a nitrogen atmosphere with dry solvents and oven dried/flame dried glassware. THF was distilled over sodium and benzophenone. DCM and CH₃CN were distilled over CaH₂. Et₂O and toluene were obtained dried from a Vacuum Atmosphere Inc. Solvent Purification System. All commercially available reagents were used as received without further purification. Thin-layer chromatography analysis of reaction mixtures were performed using Silicycle Silia plate TLC alumina backed and analysed using UV light and/or by staining with either potassium permanganate, cerium ammonium molybdate (CAM) or *p*-anysaldehyde. Flash column chromatography purification was carried out on Silicycle silia gel 60 Å, 230–400 mesh. NMR spectroscopic data for ¹H, ¹³C, ¹⁹F and NOESY 1D were recorded at ambient temperature in neutralised CDCl₃ using Agilent DD2 500, Bruker 300 MHz and Varian Inova 400 spectrometers. High-resolution mass spectra were obtained on a LC/MS–TOF Agilent 6210 using electrospray ionization (ESI). Infrared spectra were obtained using a Aminco Bowman Adrid Zone infrared spectrometer with a NaCl crystal matrix. Melting point values were determined using a Stanford Research System OptiMelt capillary melting point apparatus and are uncorrected.

Kinetic control experiment

The kinetic pathway of the glycosylation reactions studied were confirmed using control experiment based on the method reported by Woerpel.⁸ These experiments are valuable in the context of the O-glycosylation, whereas anomerization cannot occur in the case of C-glycosylation. Purified compounds from previous nucleophilic addition were resubmitted to the reaction conditions in the presence of a different donor. As shown in Fig. S-1, compound **1(CIEtO)** submitted with **3(SPh)** and TFE as nucleophile did not undergo anomerization as the initial anomeric ratio was found to be the same in the crude mixture at 65 α :35 β . No incorporation of 2-chloroethanol was observed on donor **3** as only **1(CIEtO)** and **3(TFE)** were observed. Also, in order to verify that the ratio observed at first was not already the outcome of a thermodynamic equilibrium, pure **β -2(TFE)** (entry 4) has been submitted to the O-glycosylation conditions. ¹H NMR and F¹⁹ NMR showed no incorporation of TFE in donor **1** and pure **β -2(TFE)** was again observed, thus, confirming the kinetic pathway.

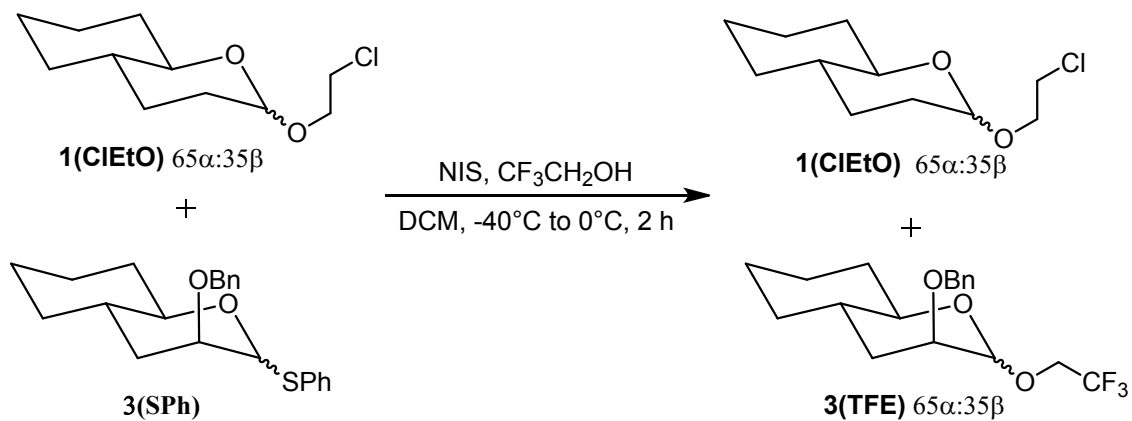


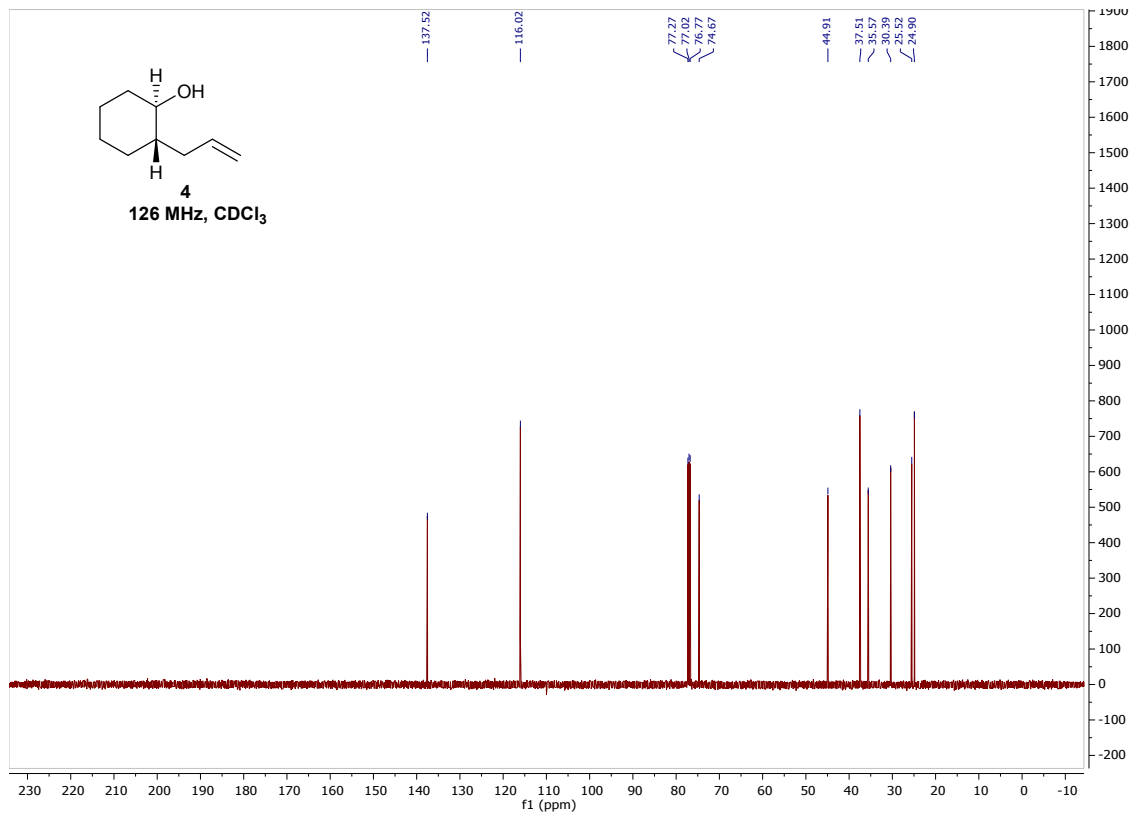
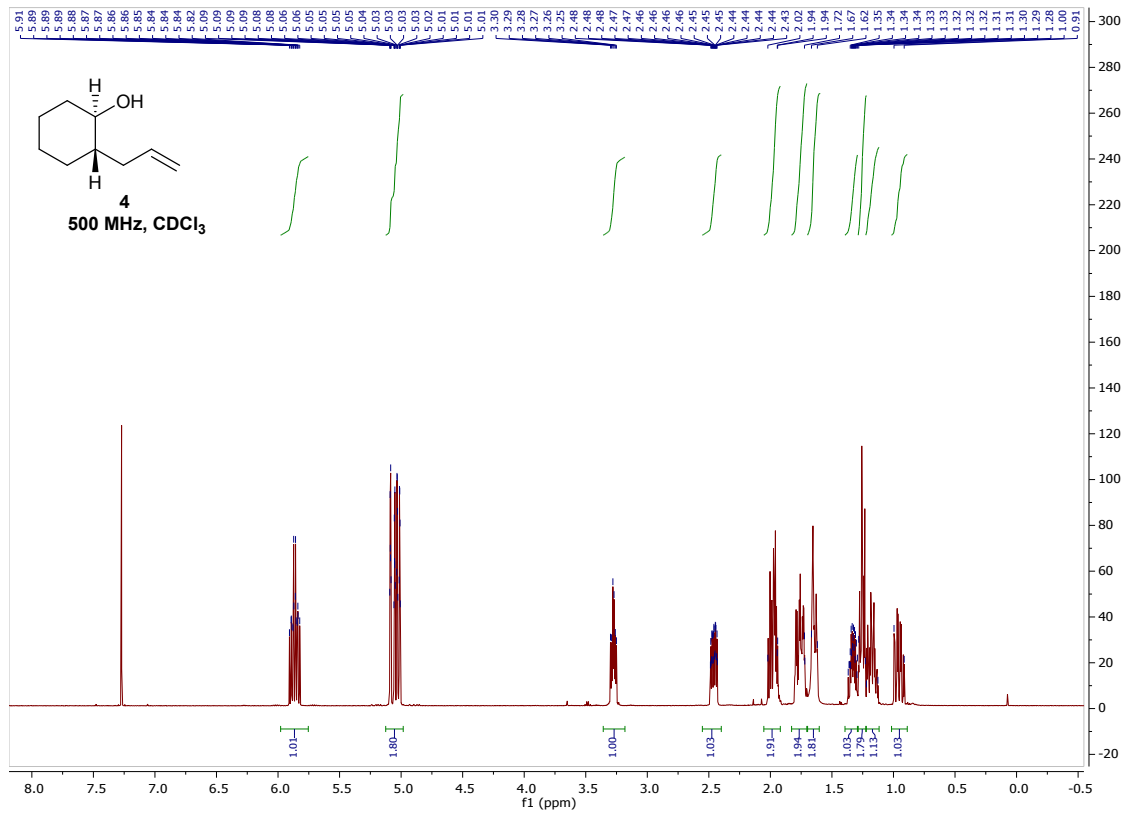
Fig. S1 Kinetic control experiments.

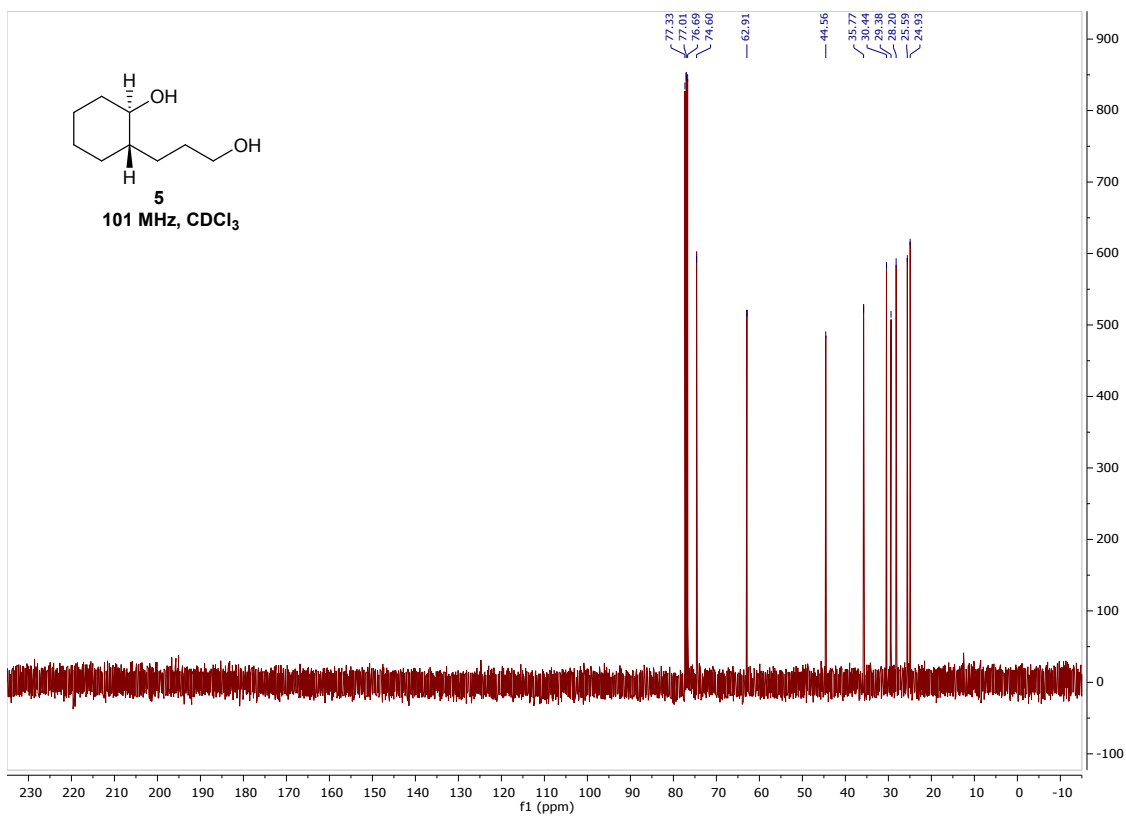
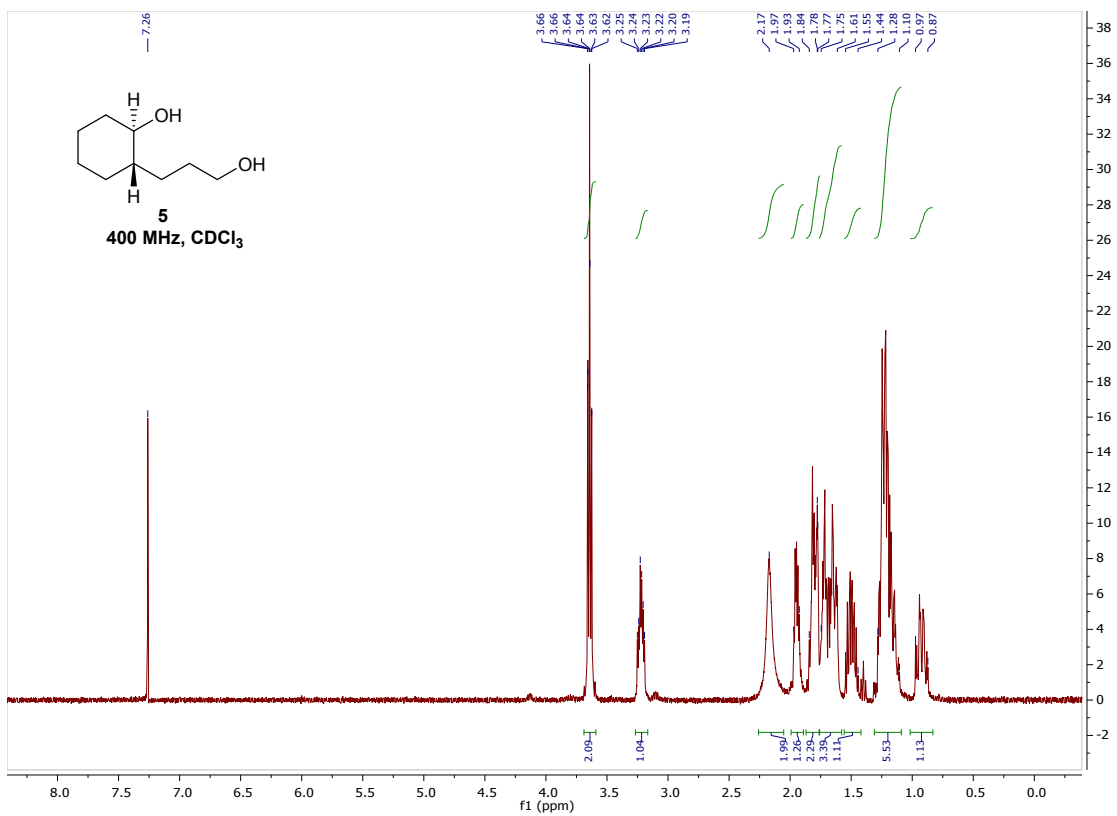
Entry	Compound	Donor	Initial ratio ($\alpha:\beta$)	Observed ^a ($\alpha:\beta$)	Incorporation product
1	1(CIEtOH)	3(SPh)	65:35	65:35	None
2^b	2(TFE)	1(SPh)	65:35	65:35	None
3^b	3(TFE)	1(SPh)	70:30	75:25	None
4^b	β -2(TFE)	1(SPh)	0:100	0:100	None

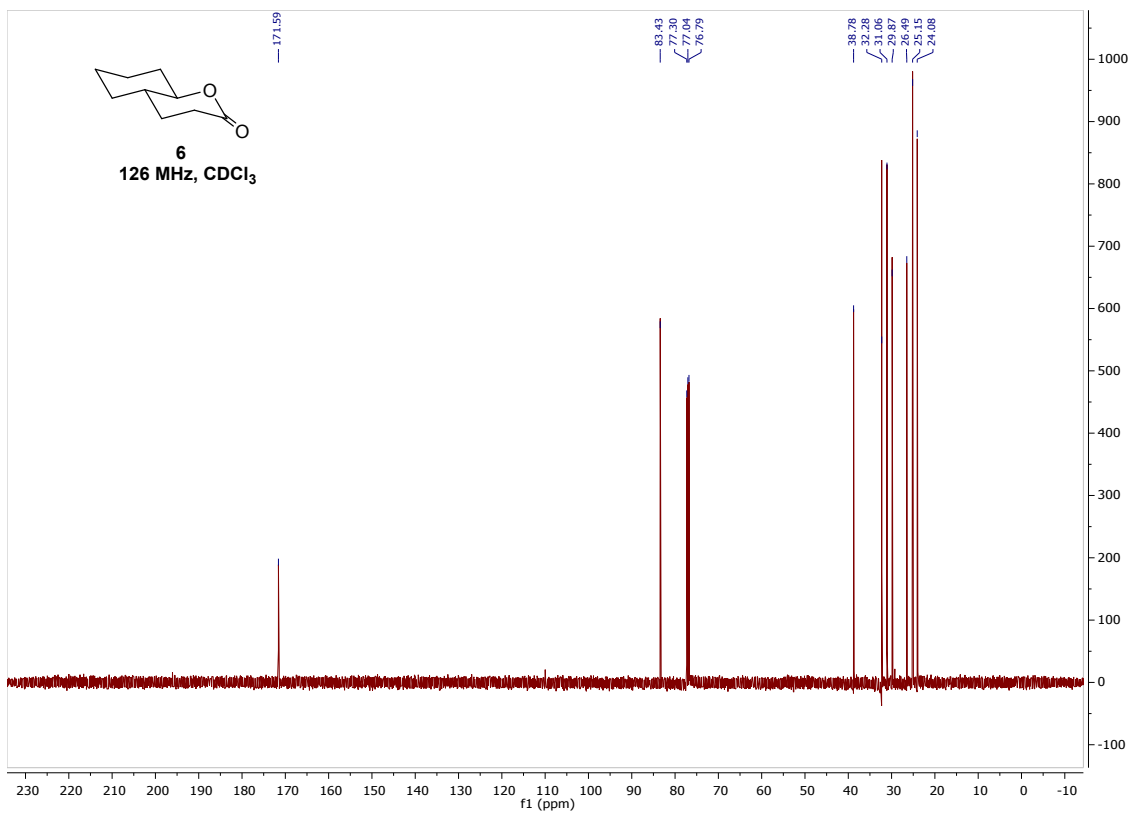
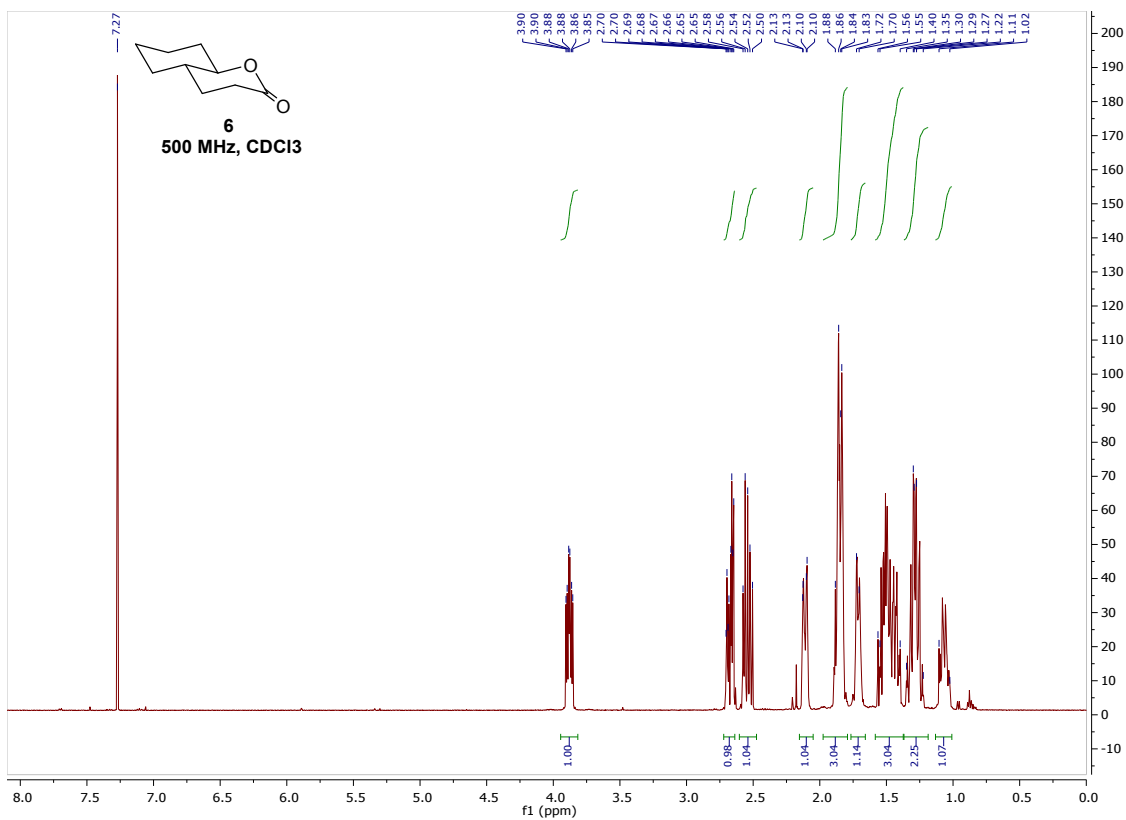
^aDetermined by ^1H NMR and ^{19}F NMR of the crude mixtures; ^bEthanol was used as nucleophile

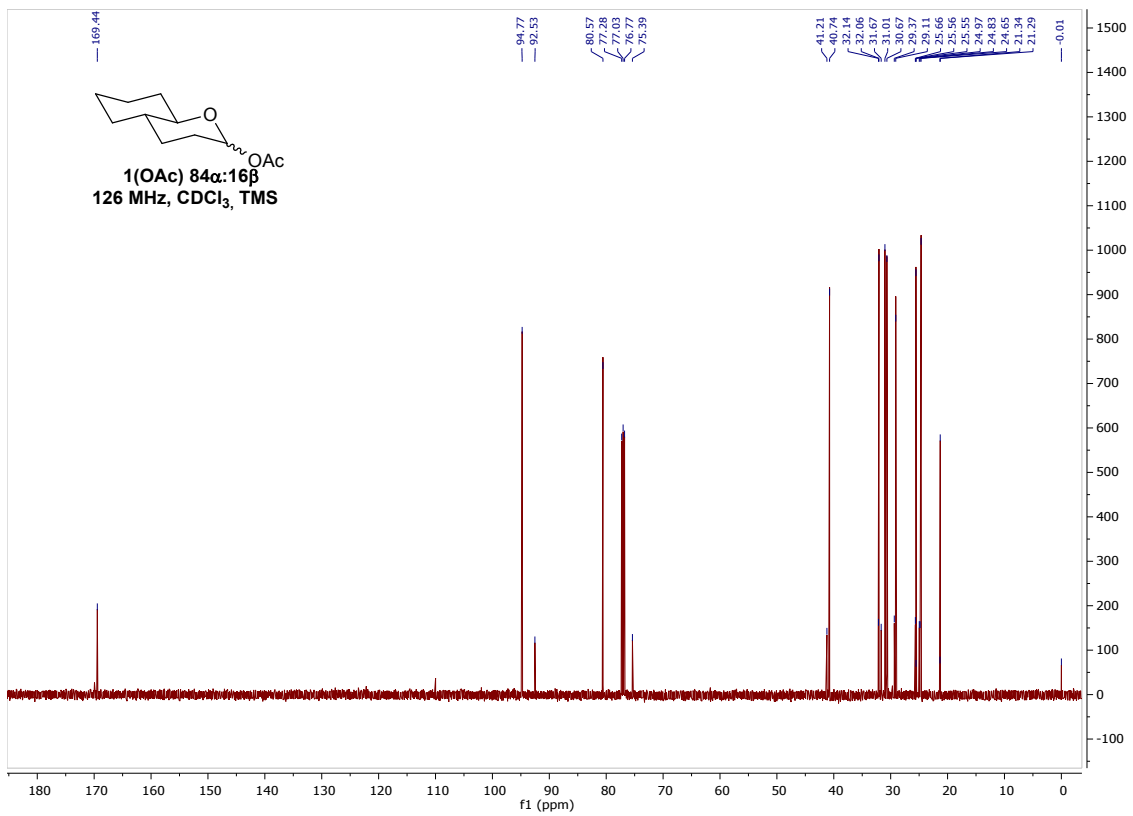
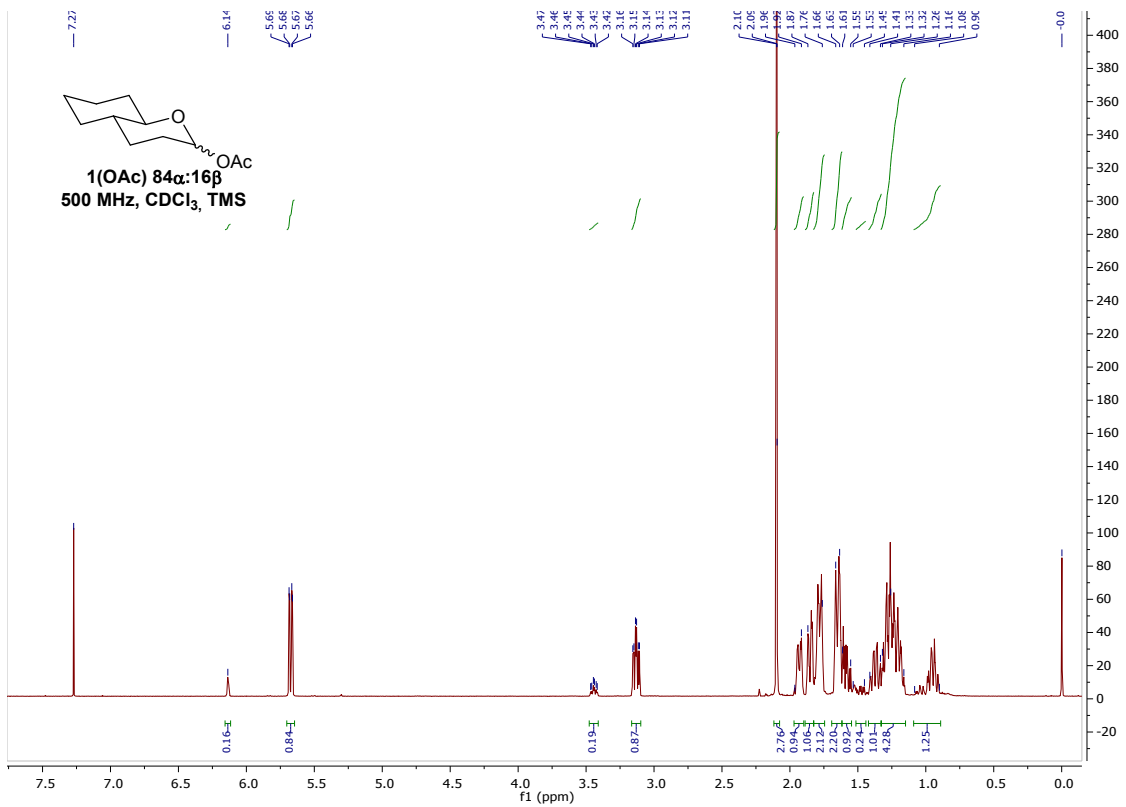
Table S1 Kinetic control experiments.

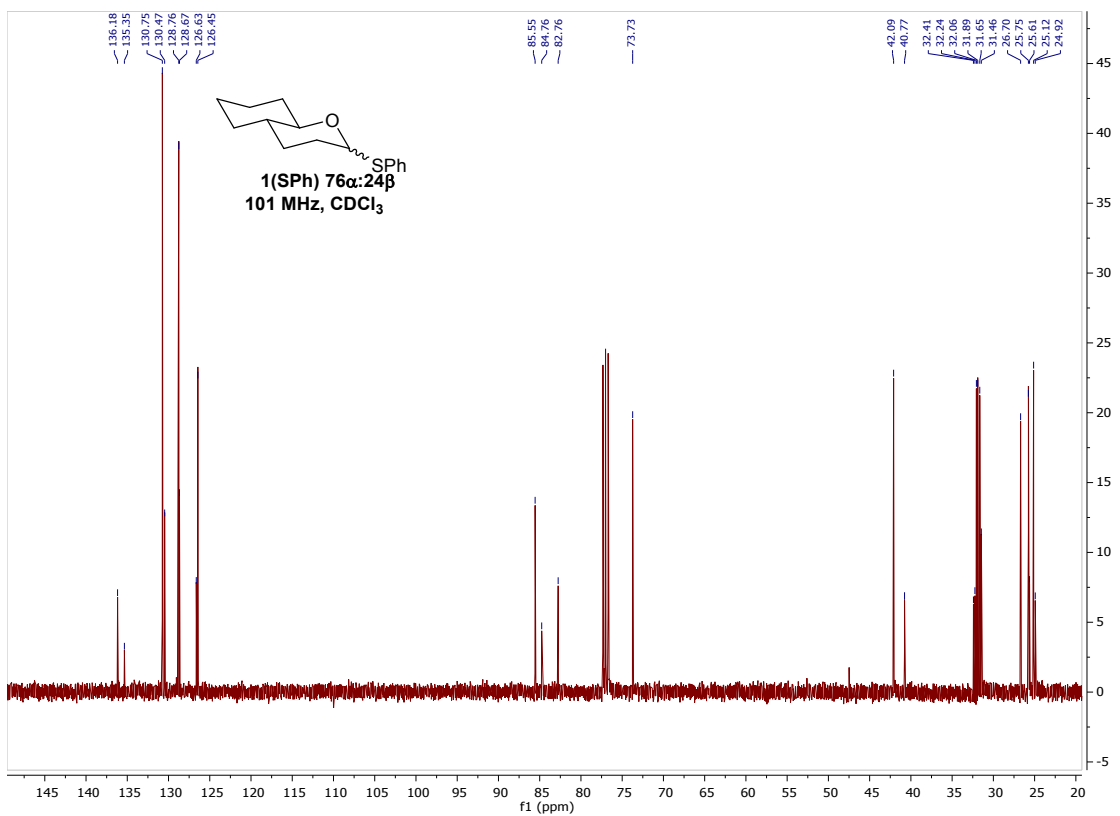
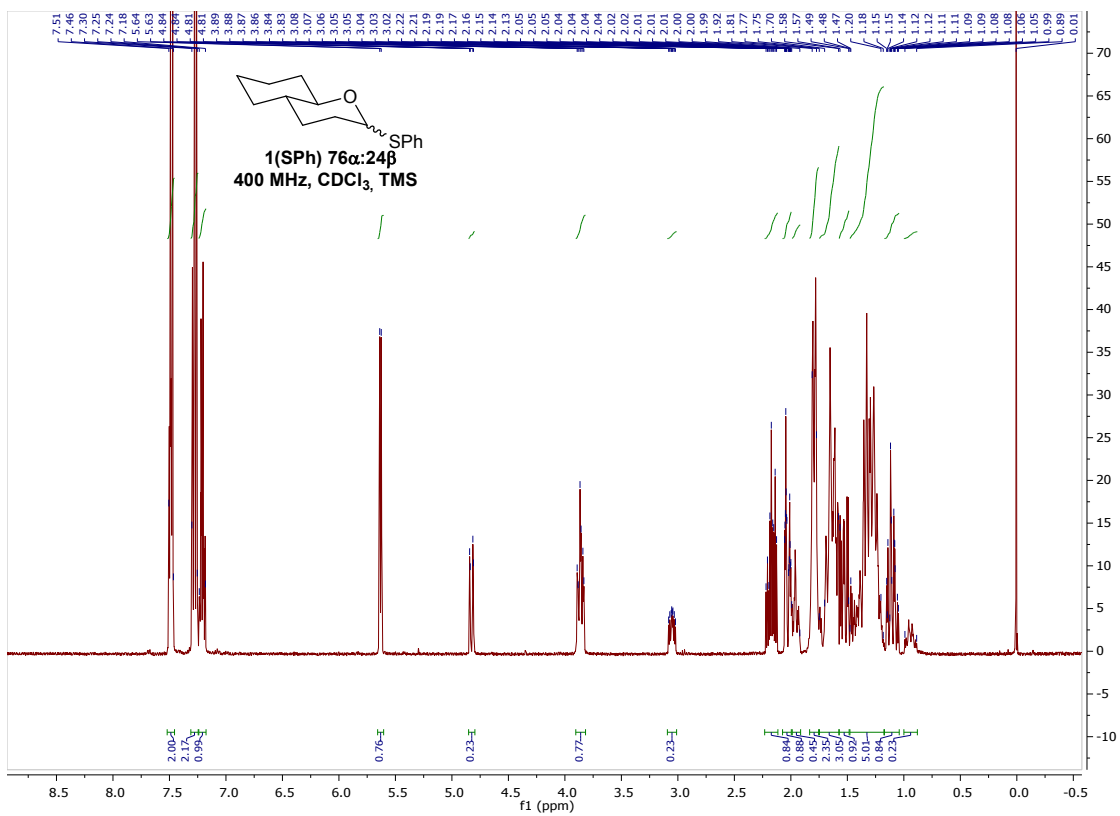
NMR spectra of purified compounds

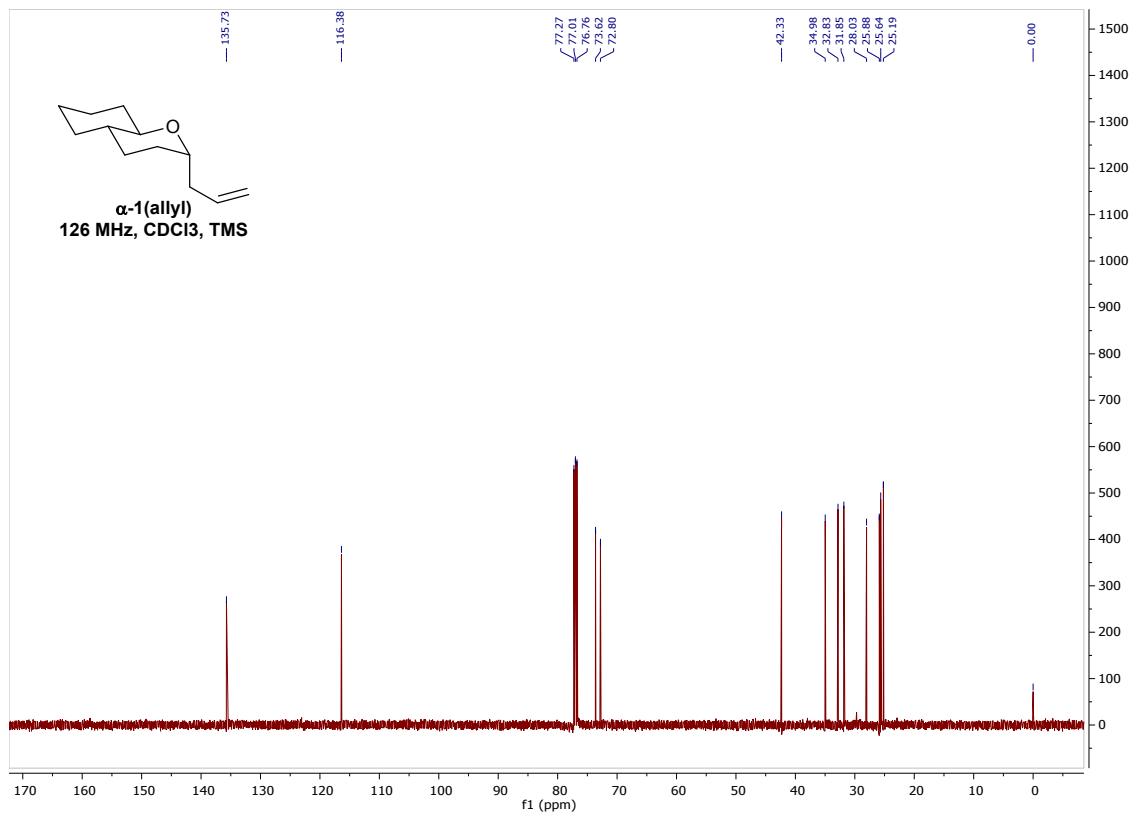
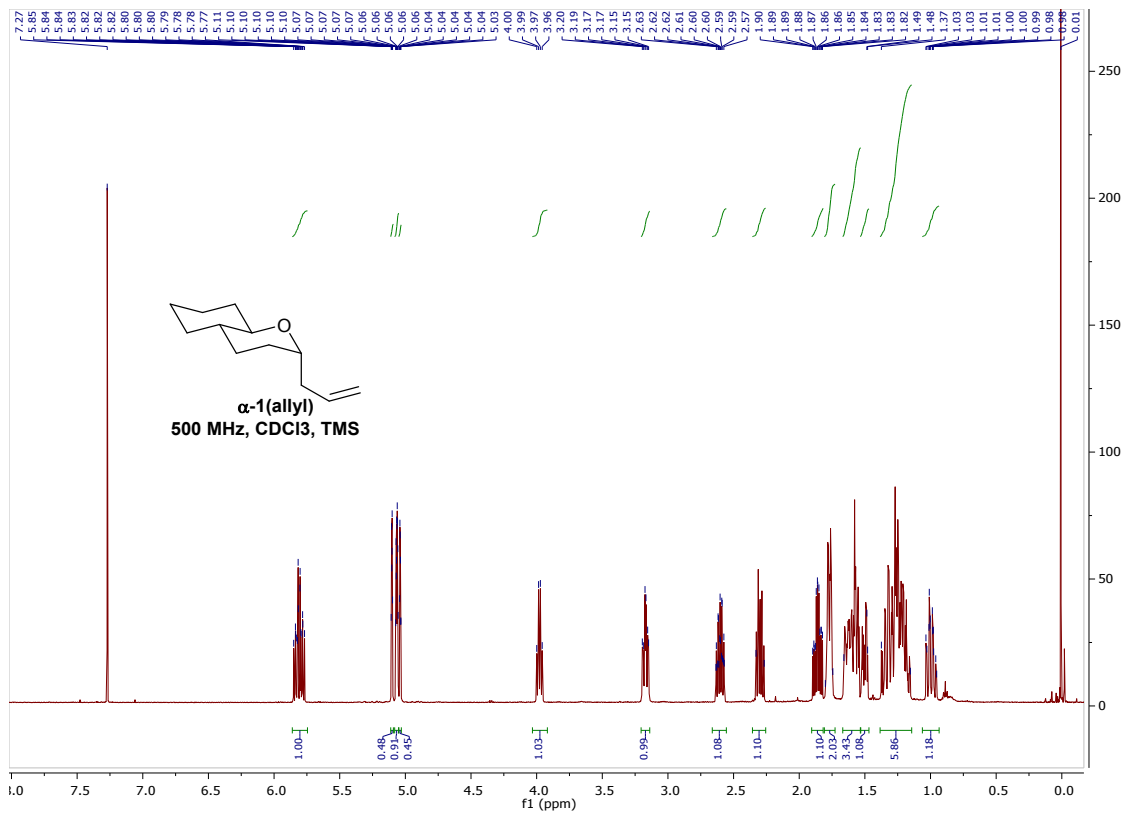


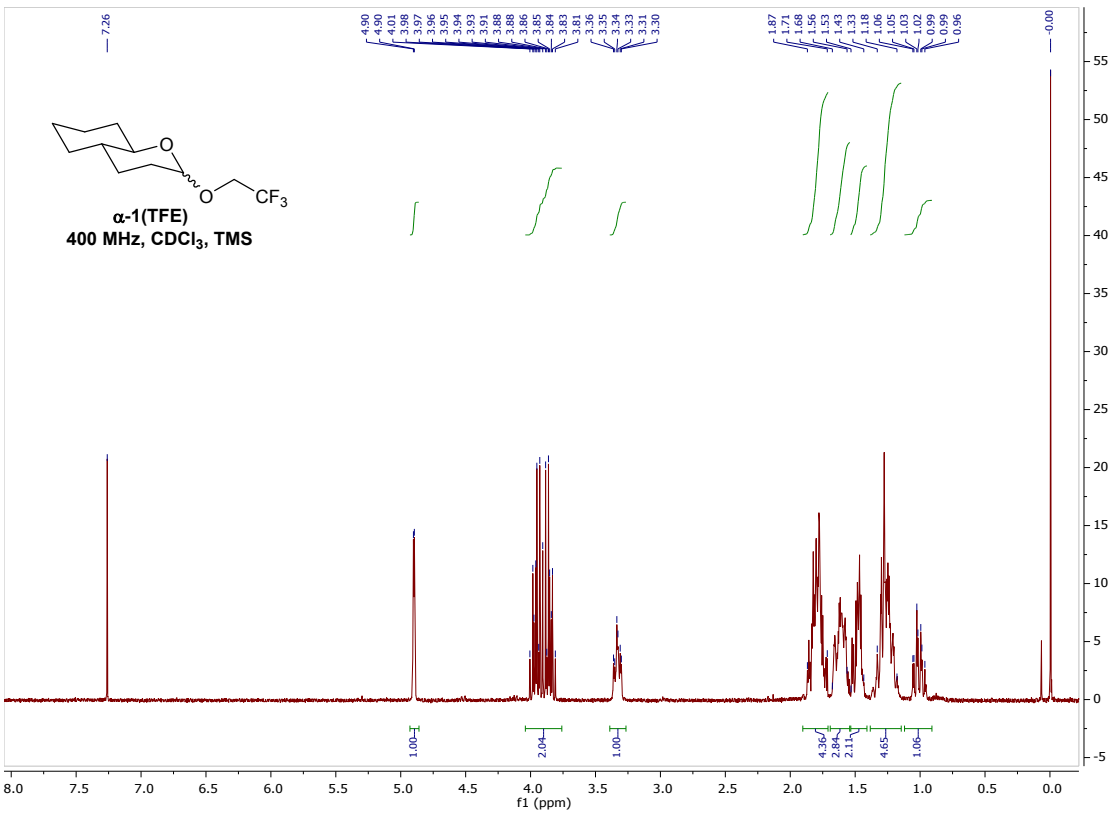
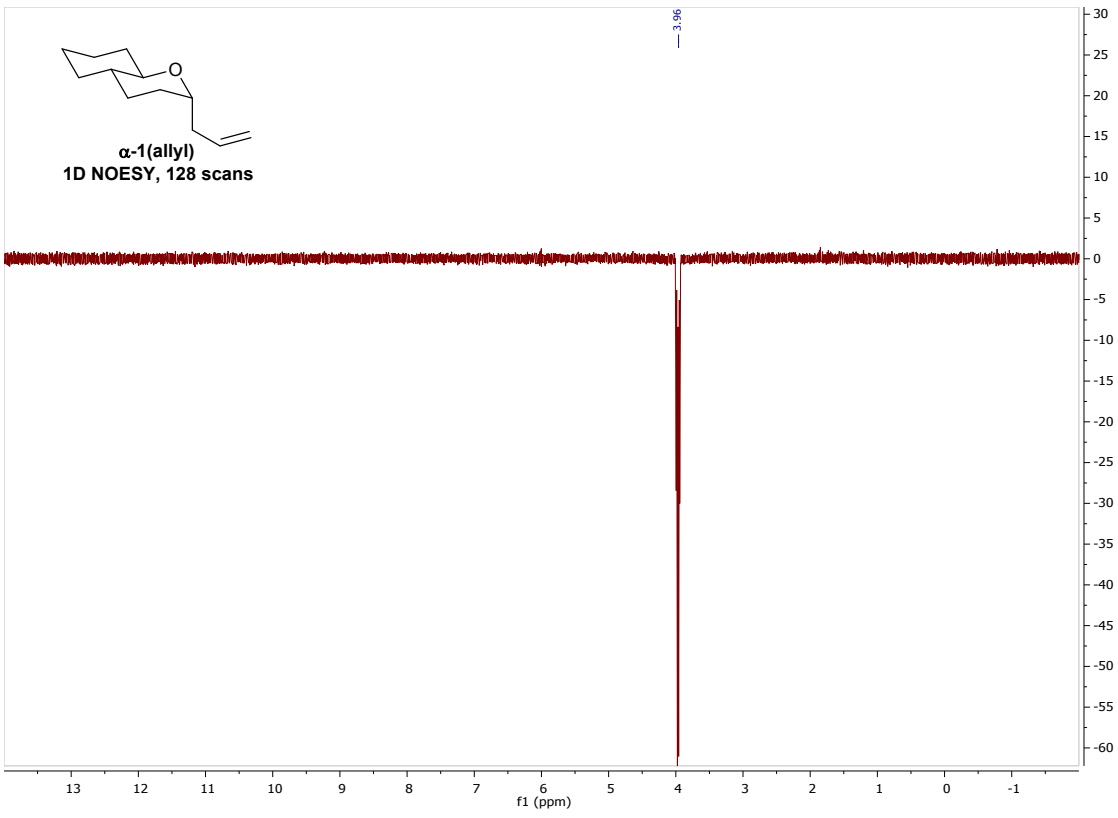


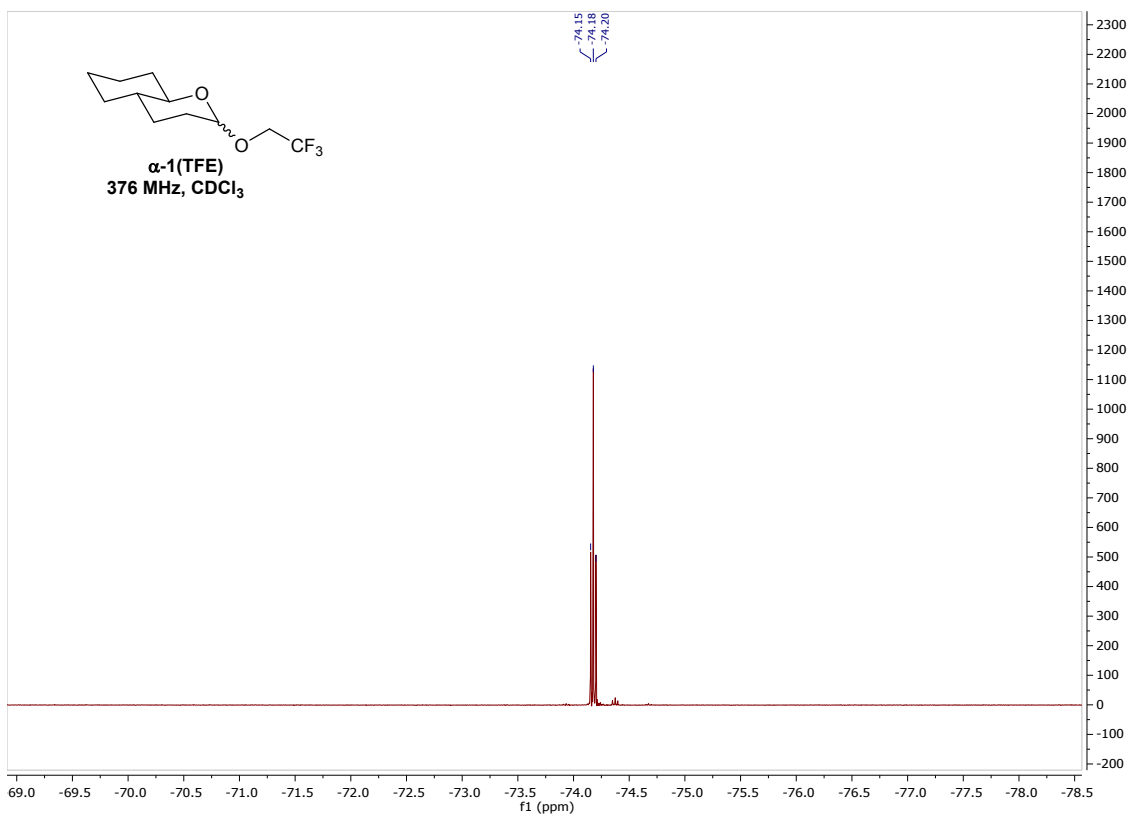
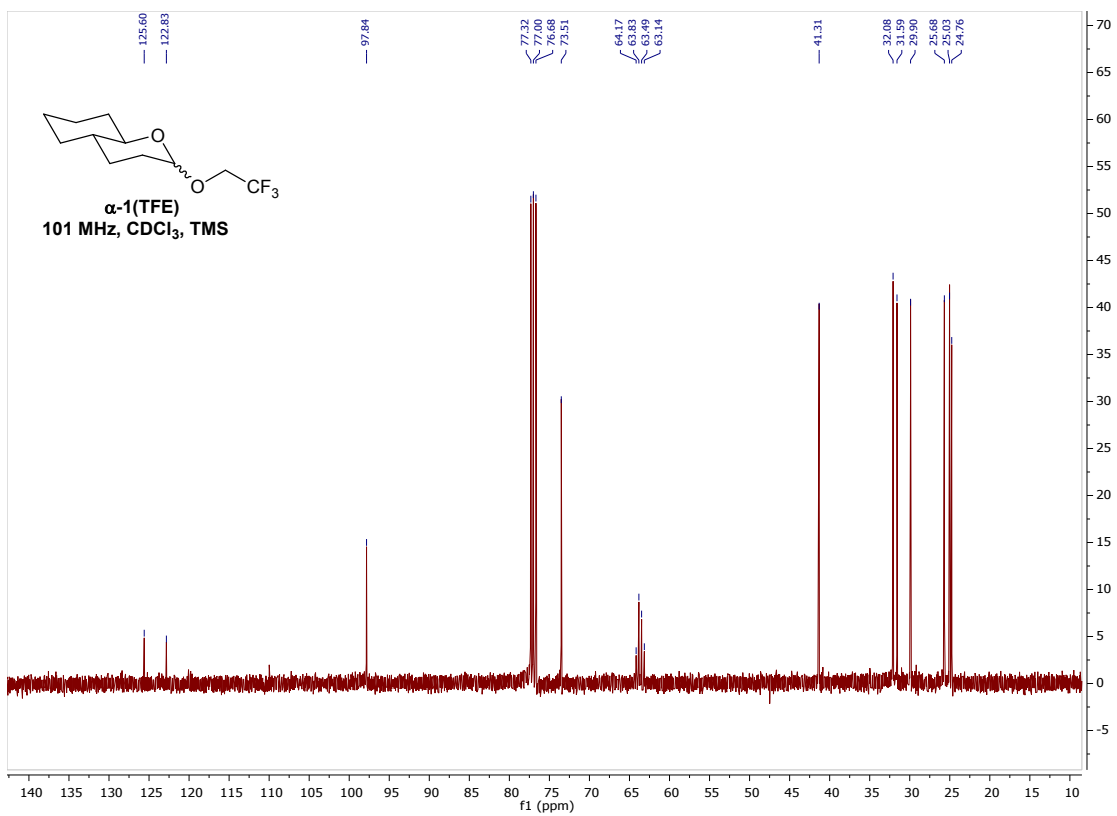


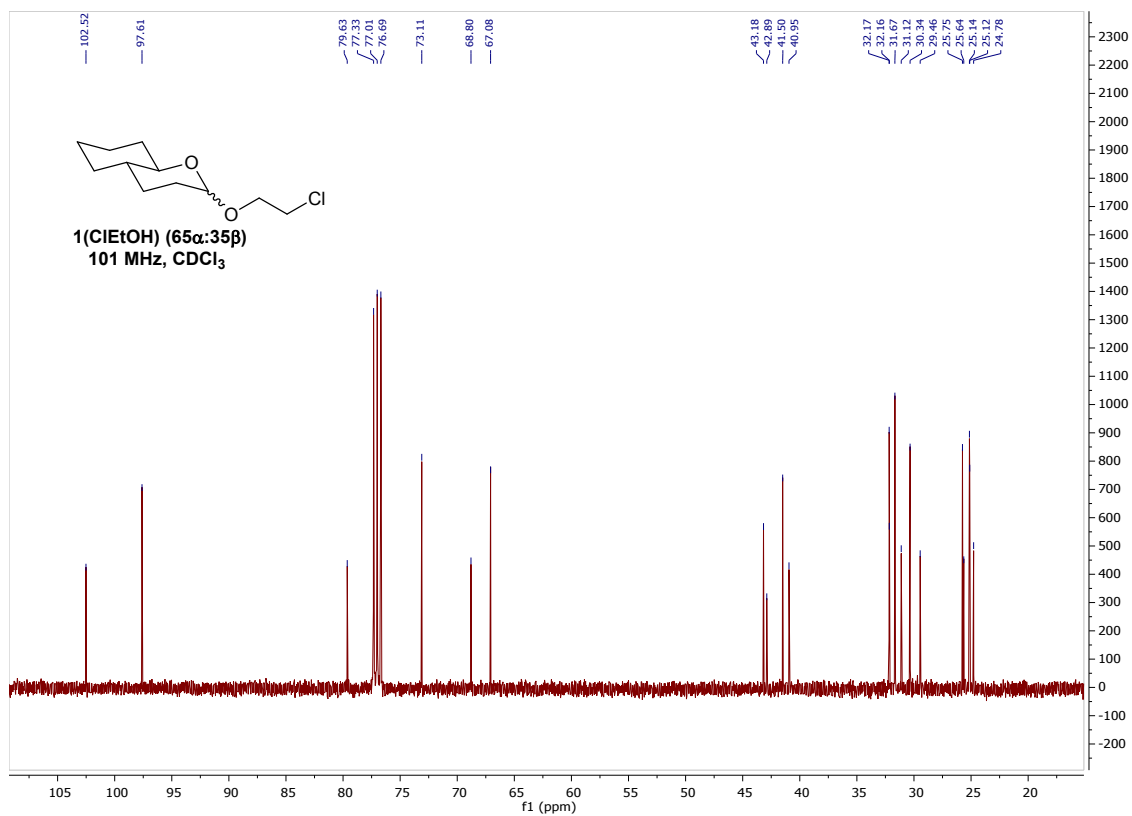
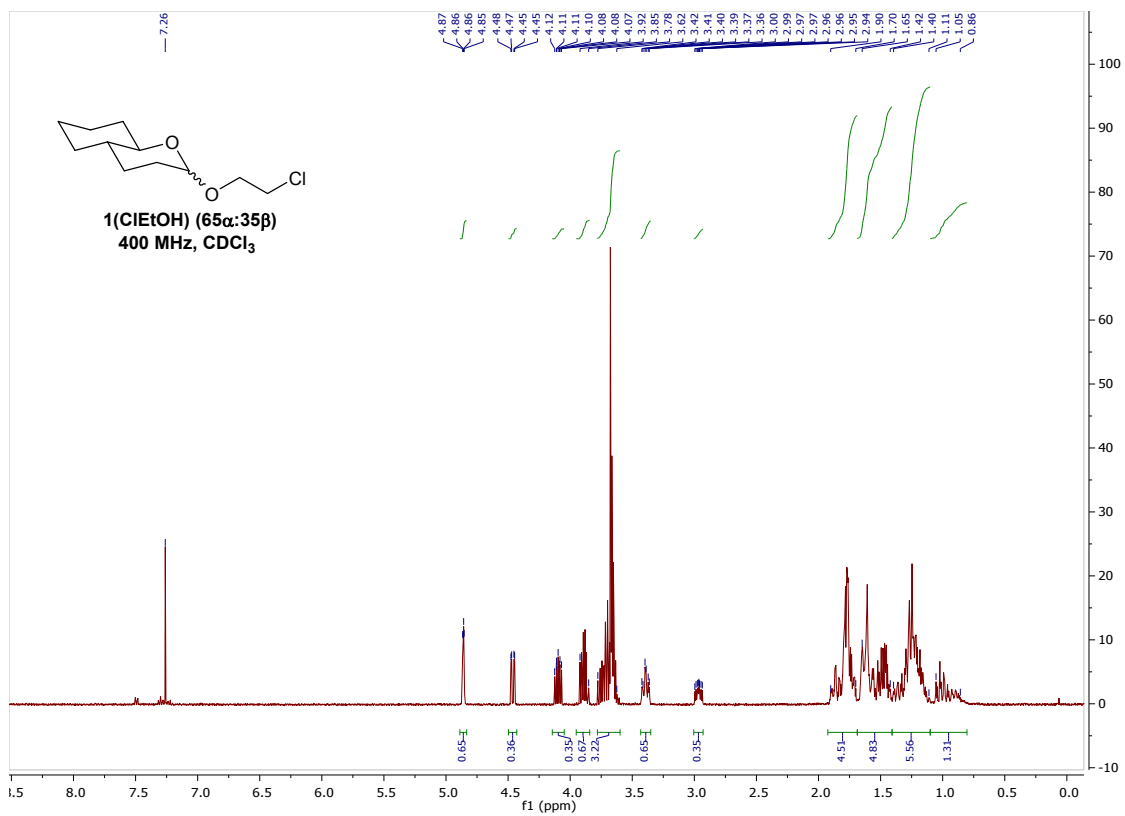


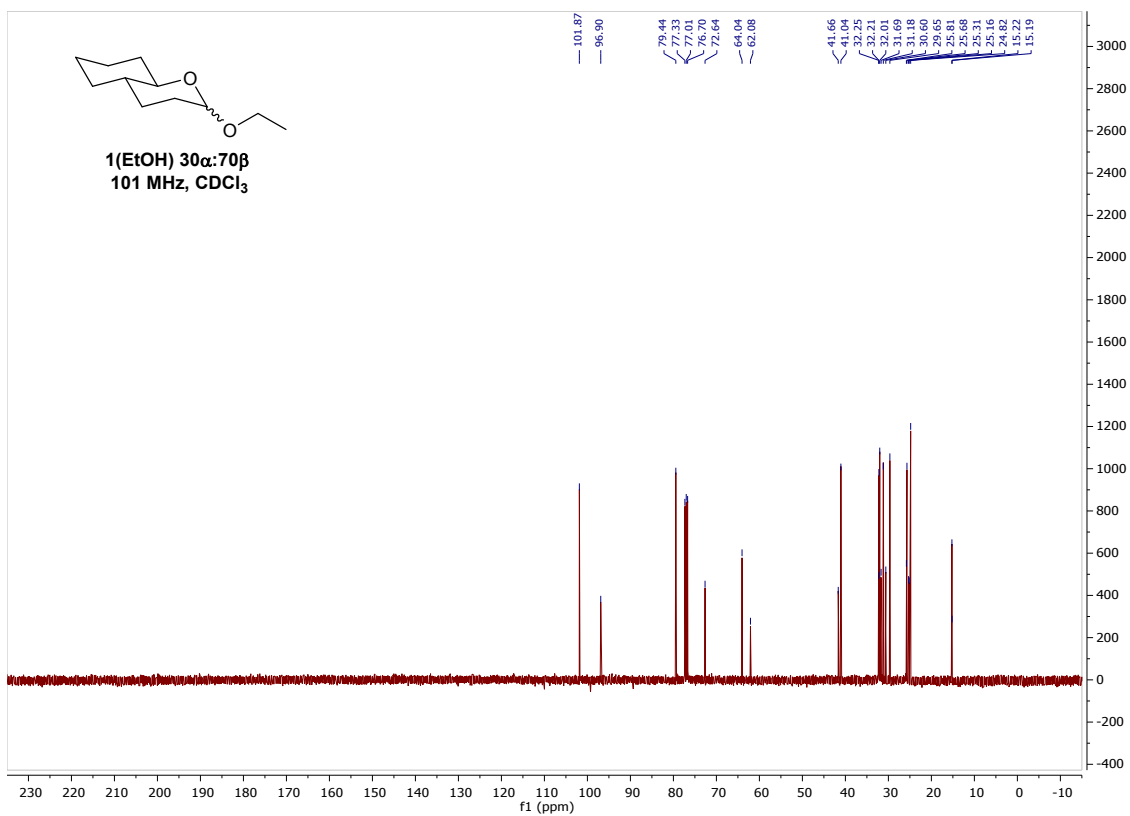
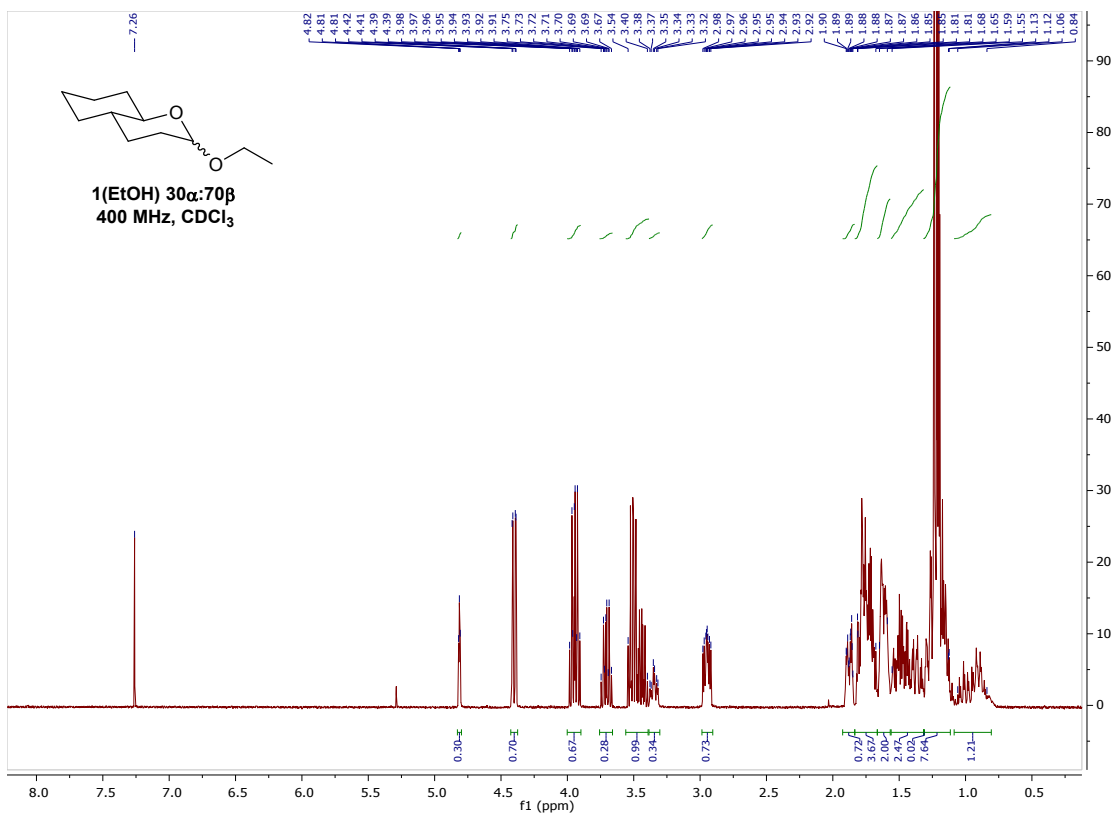


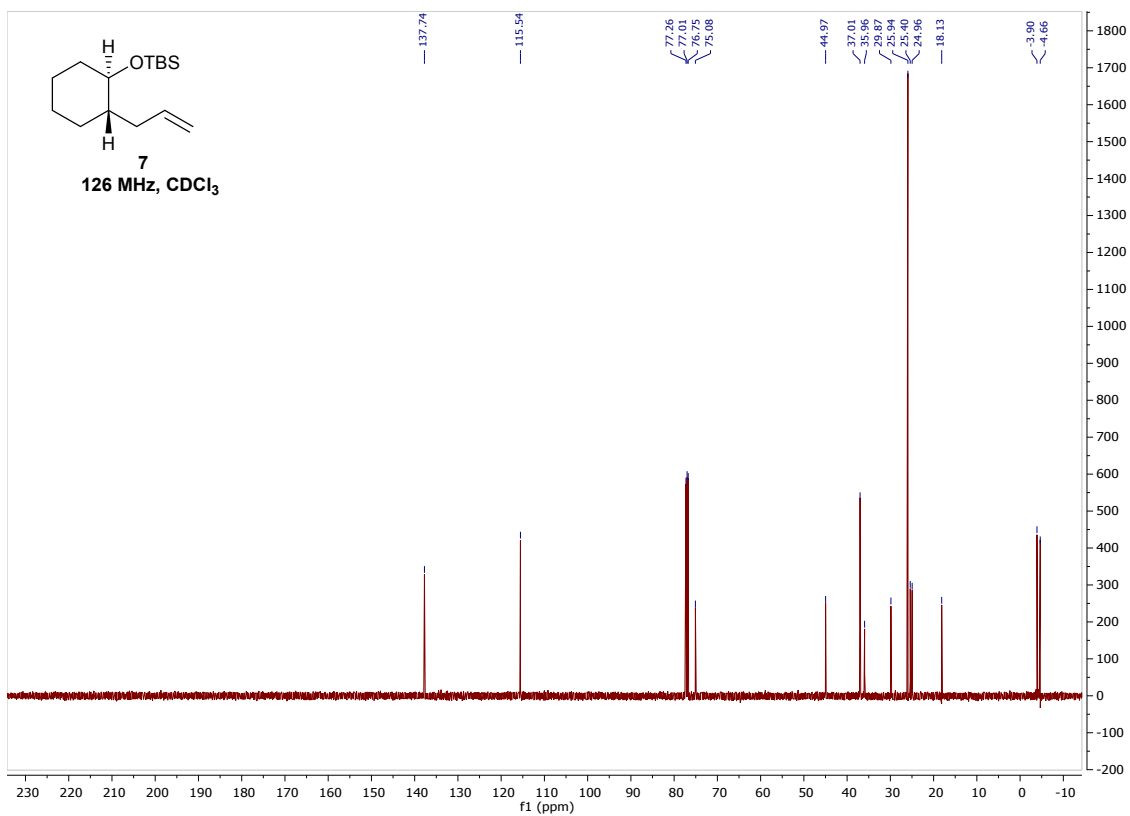
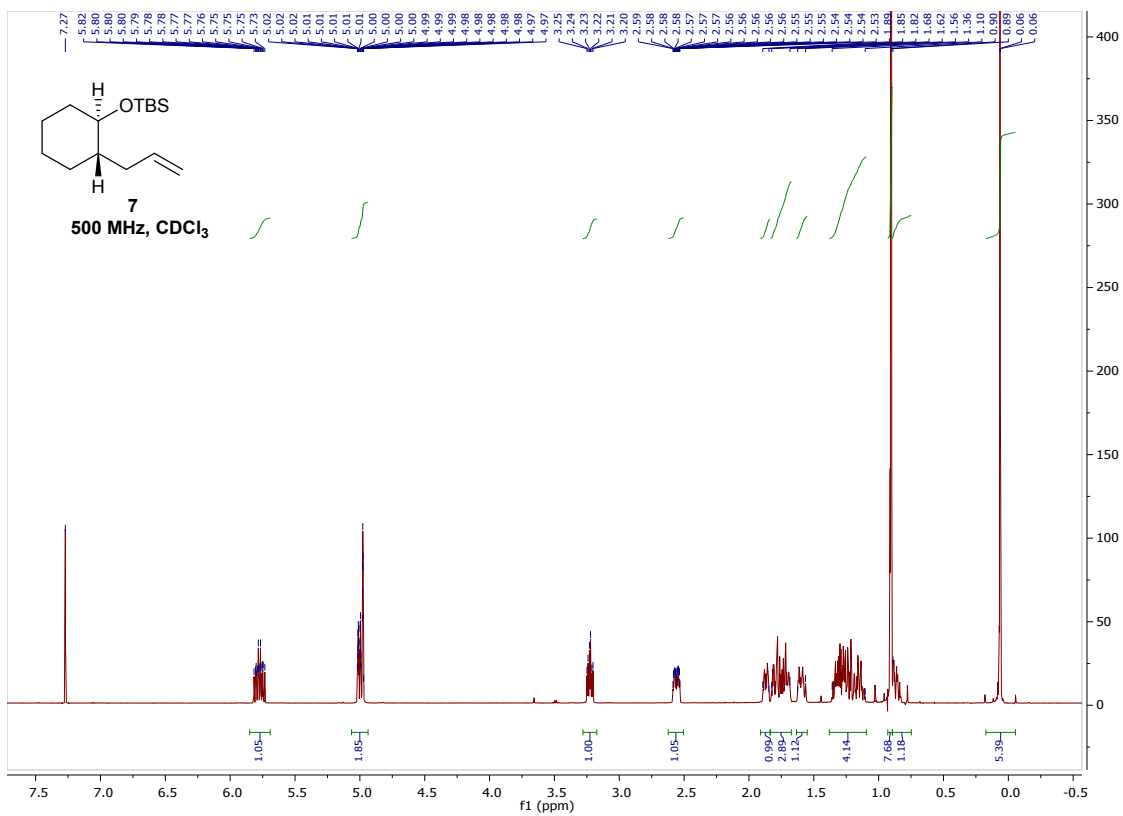


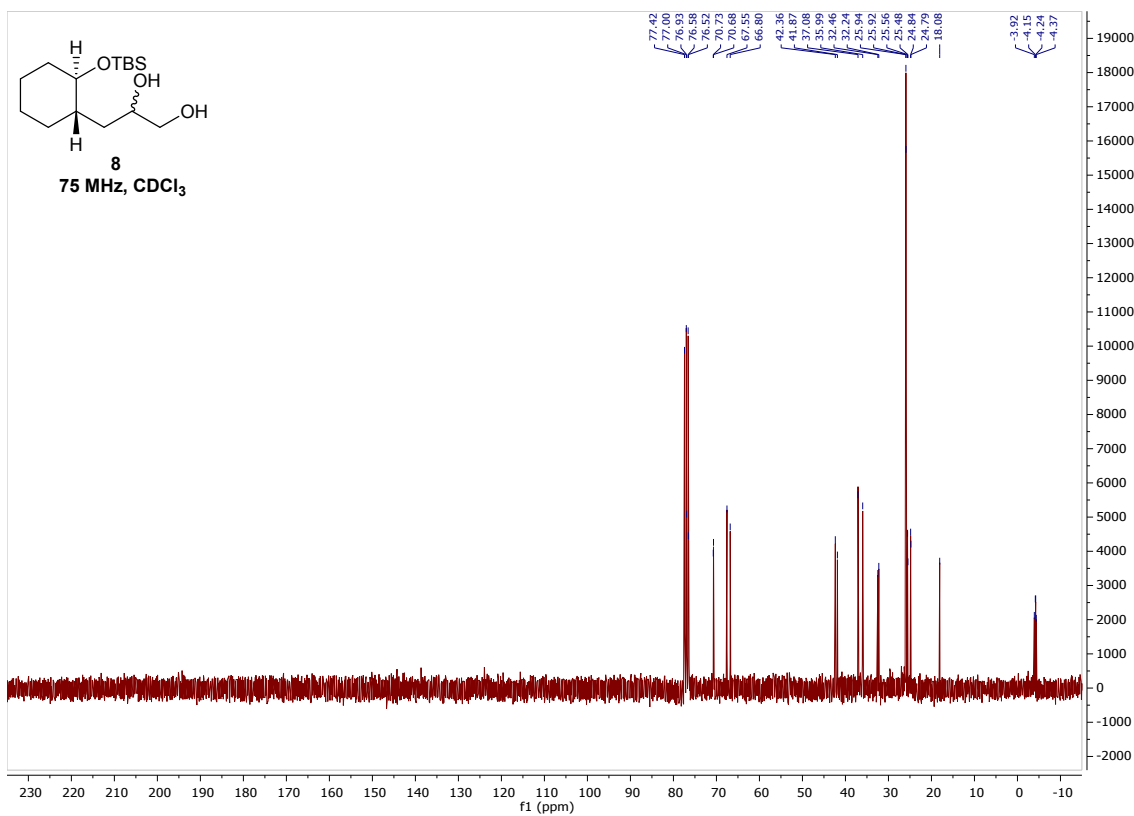
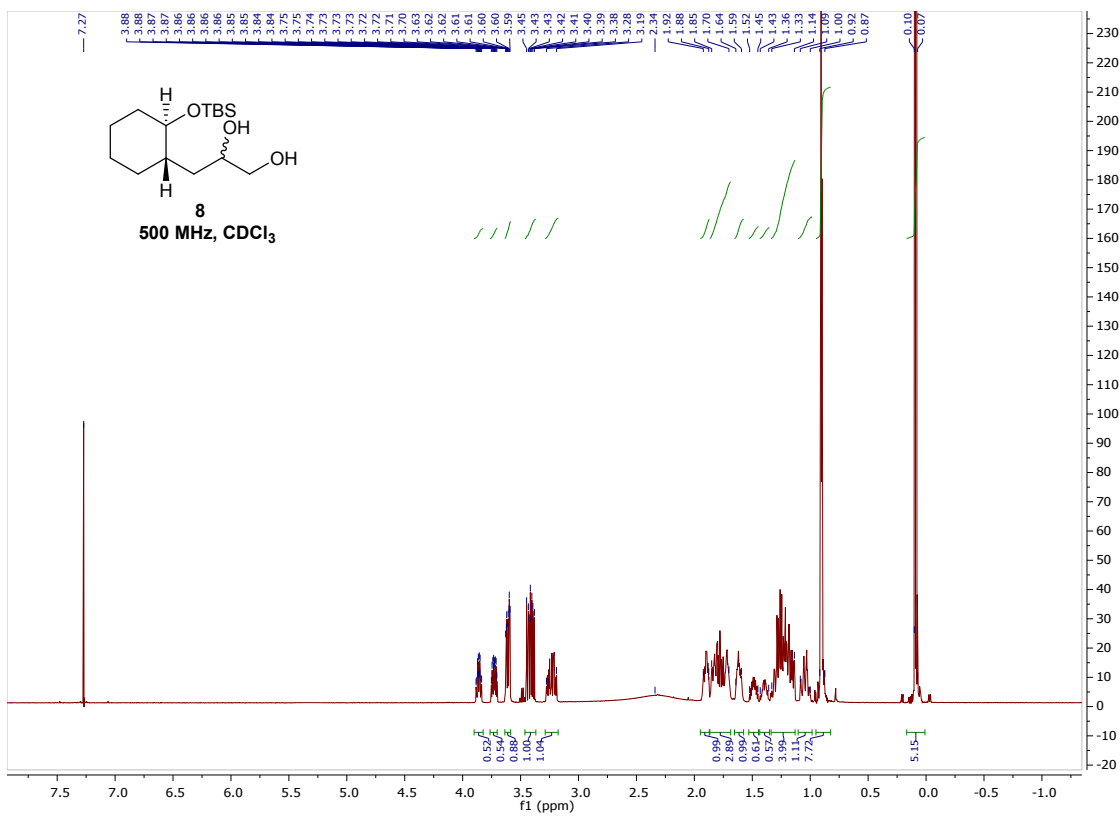


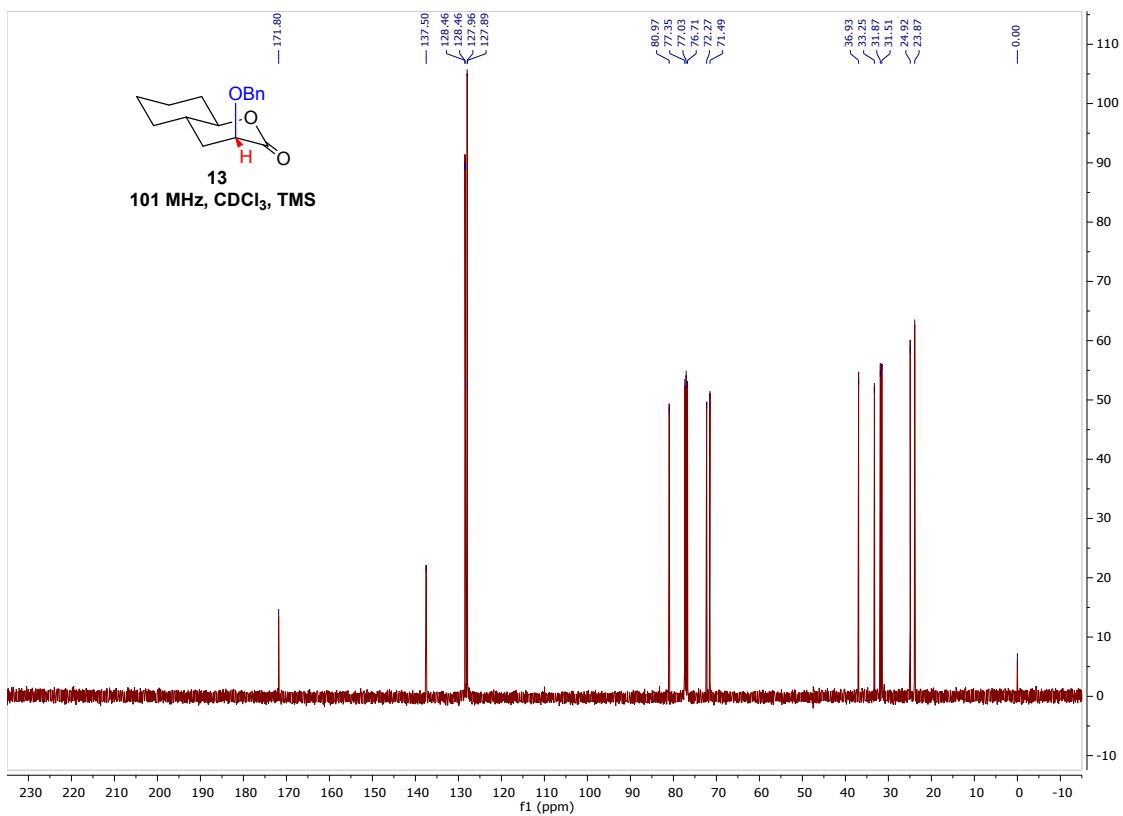
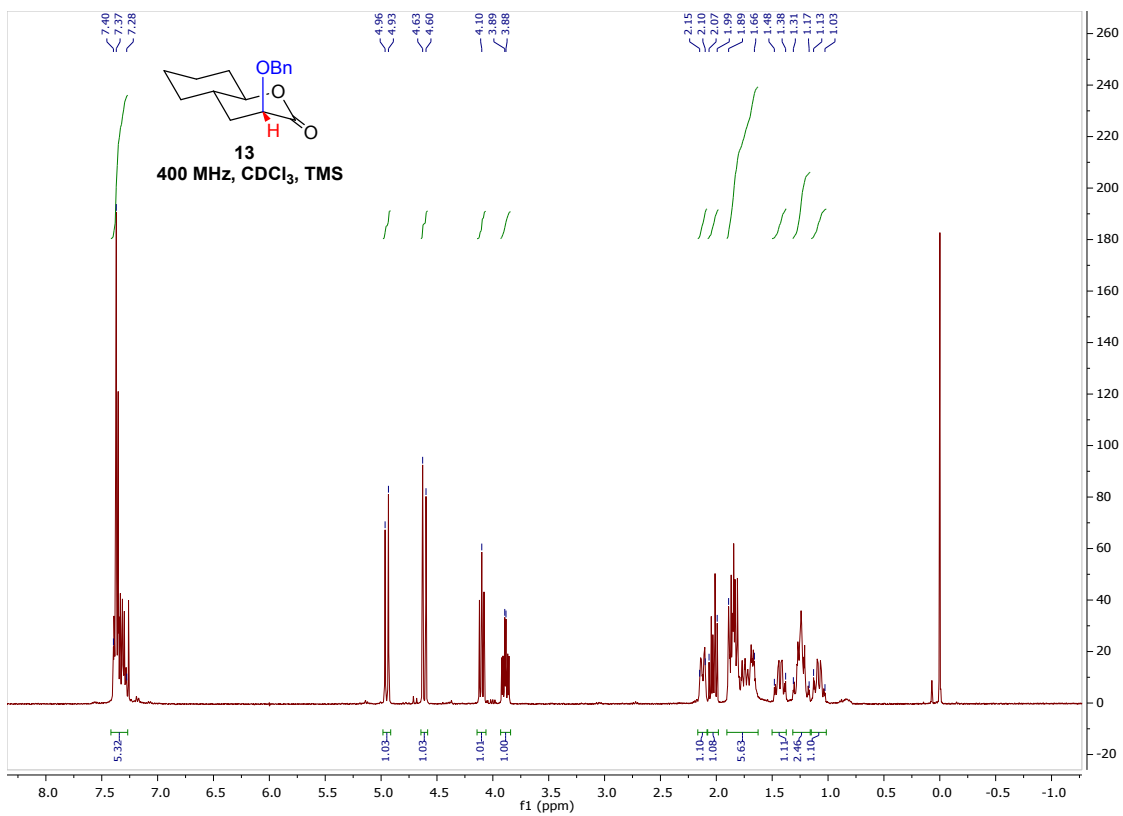


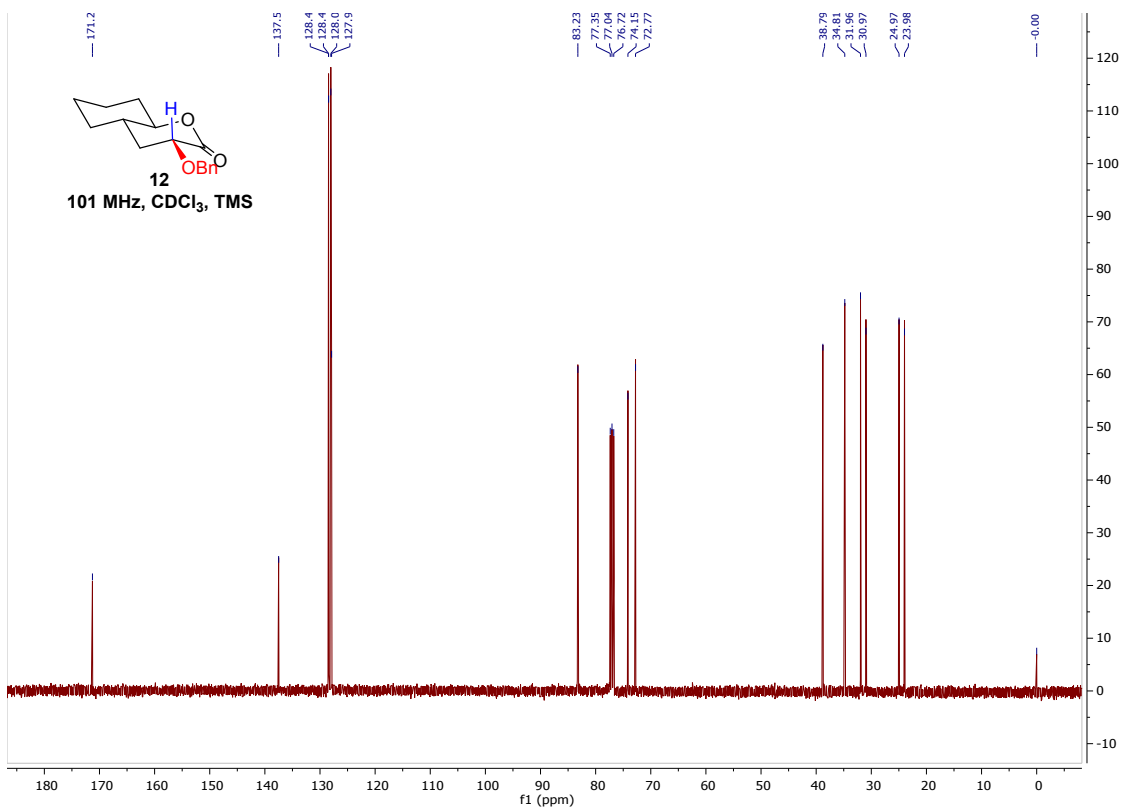
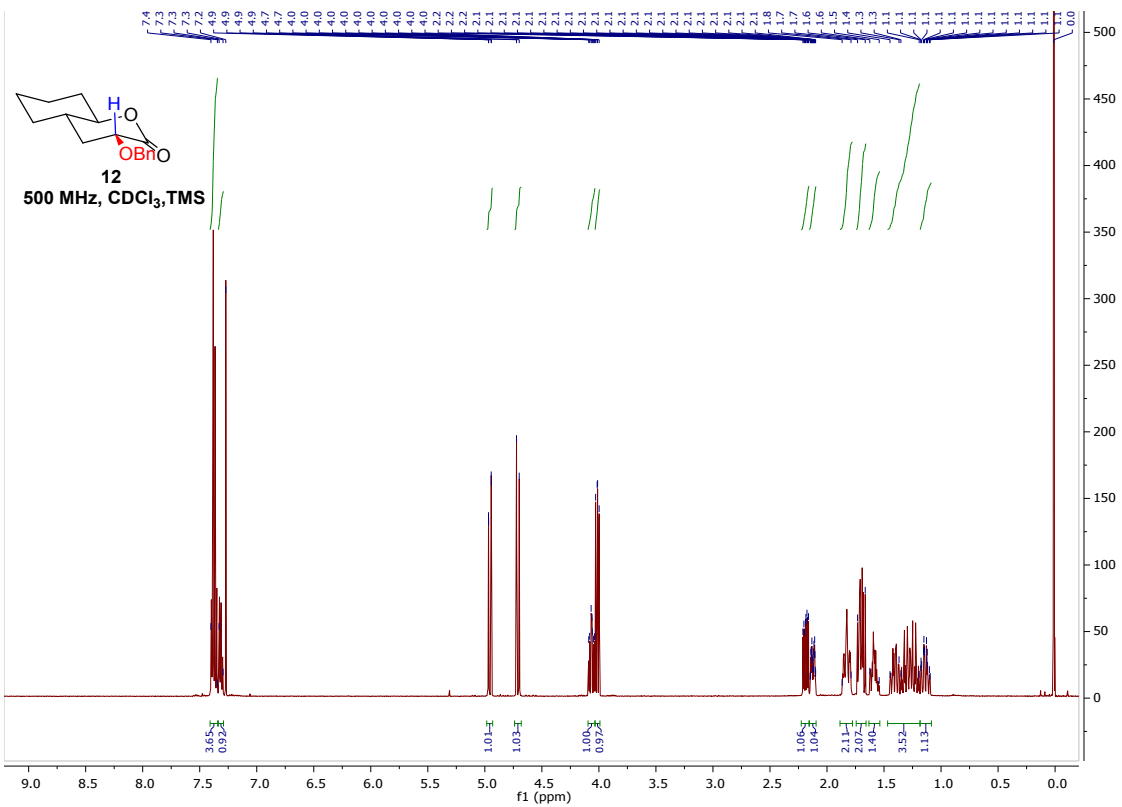


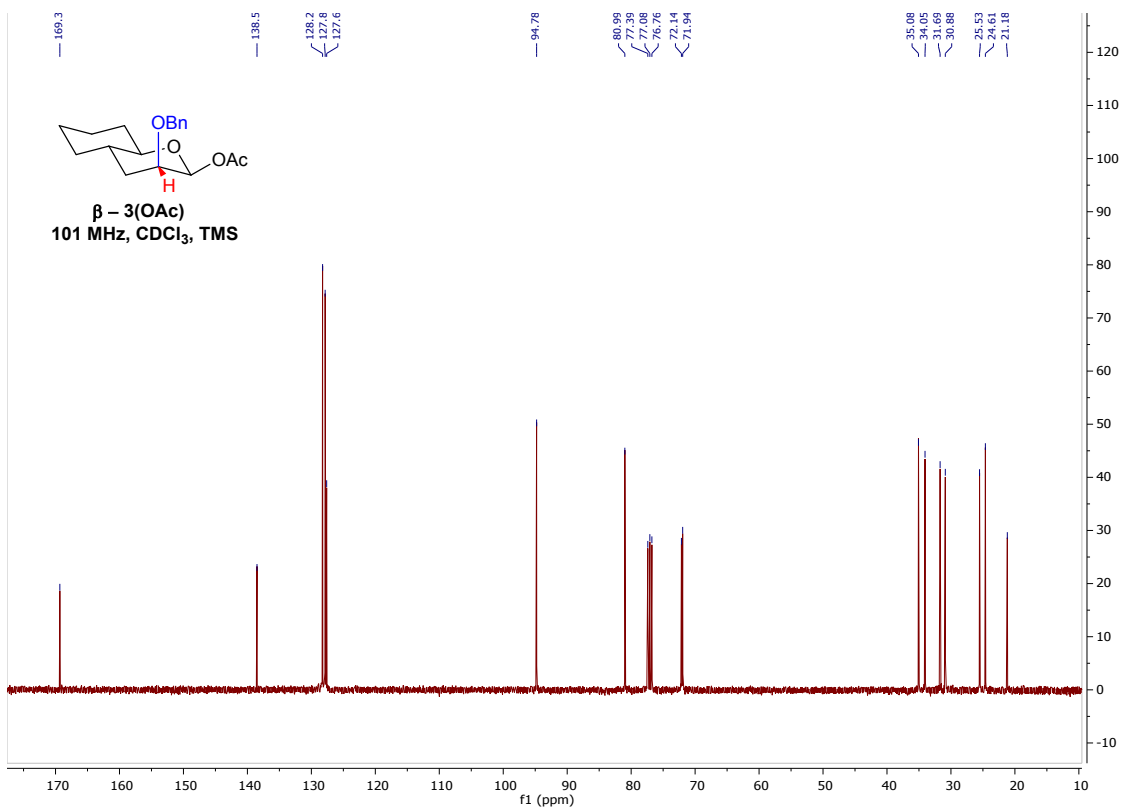
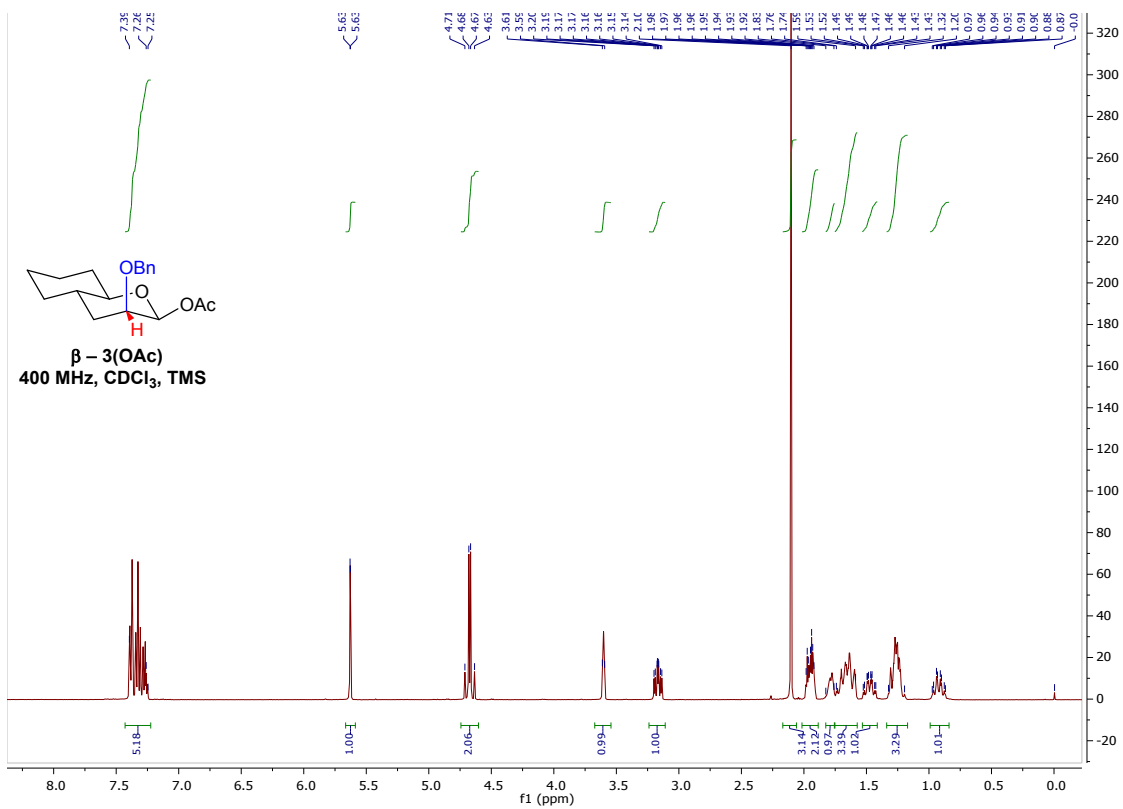


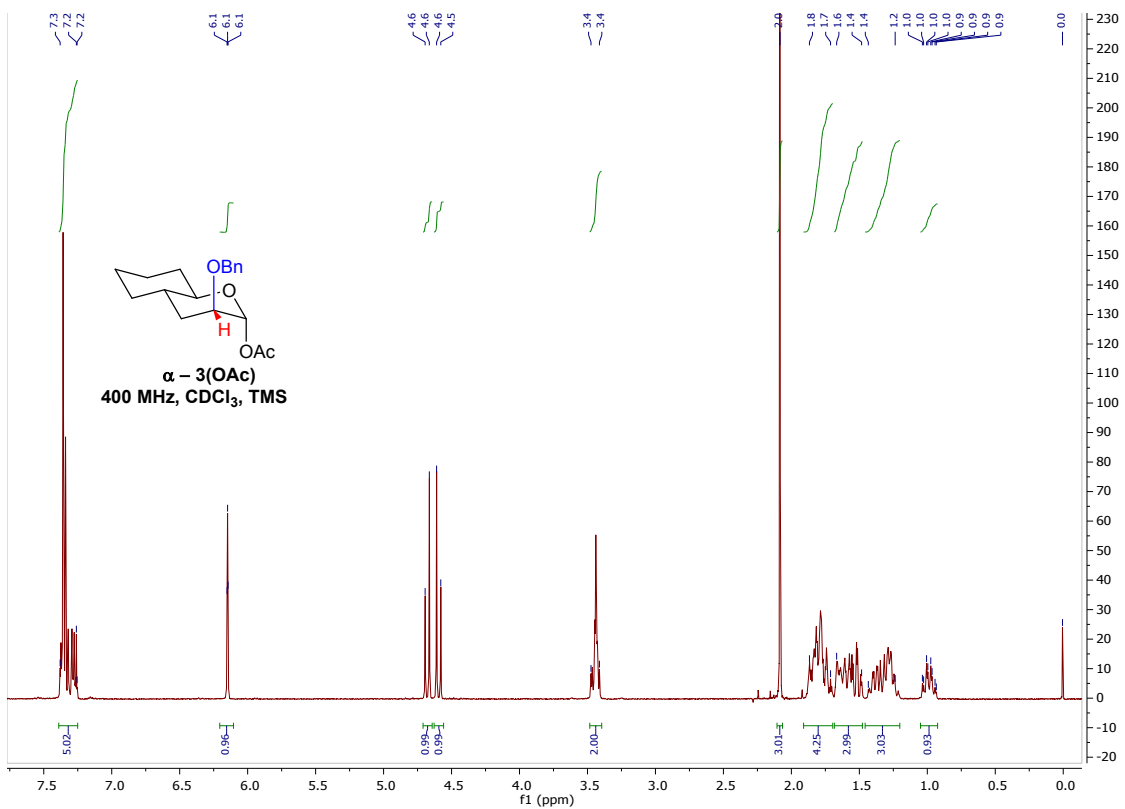
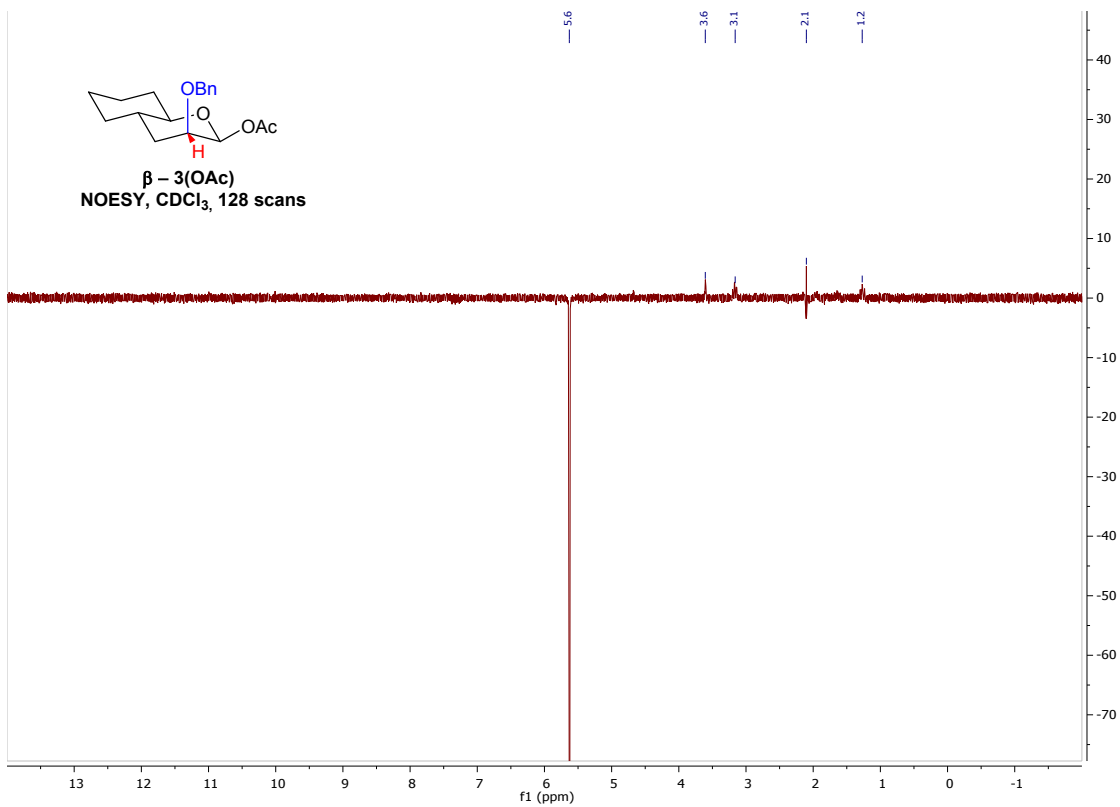


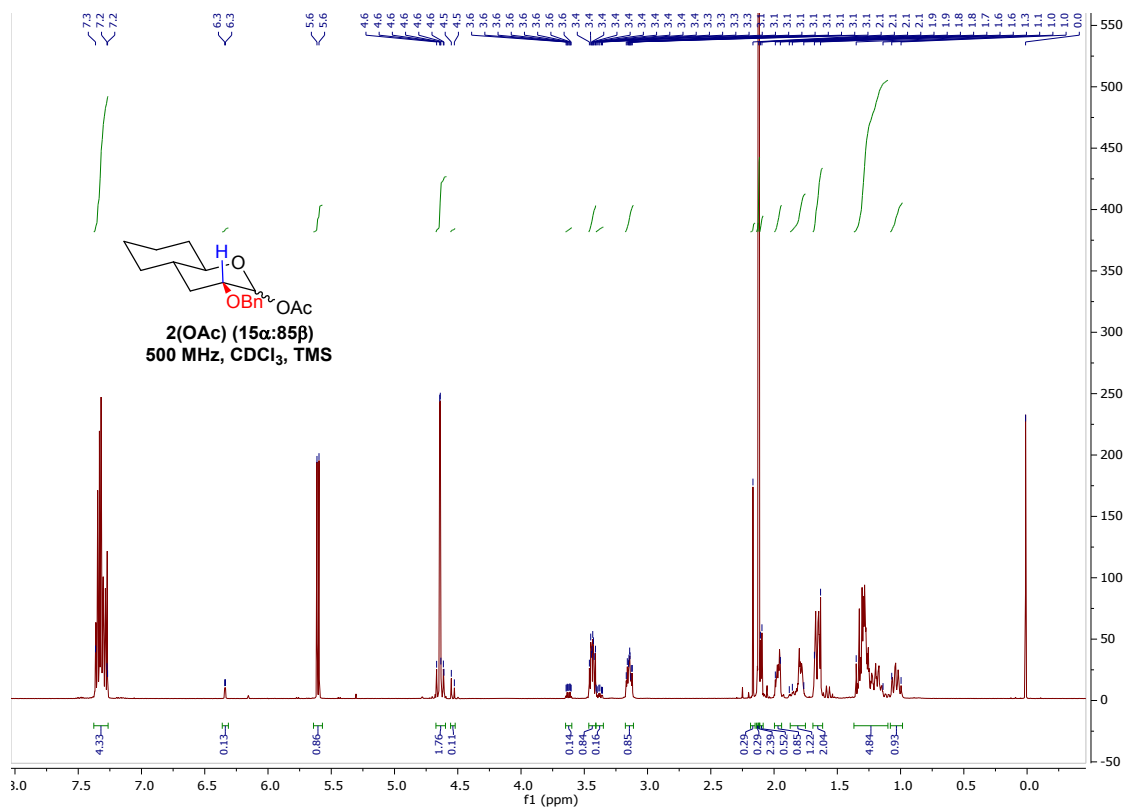
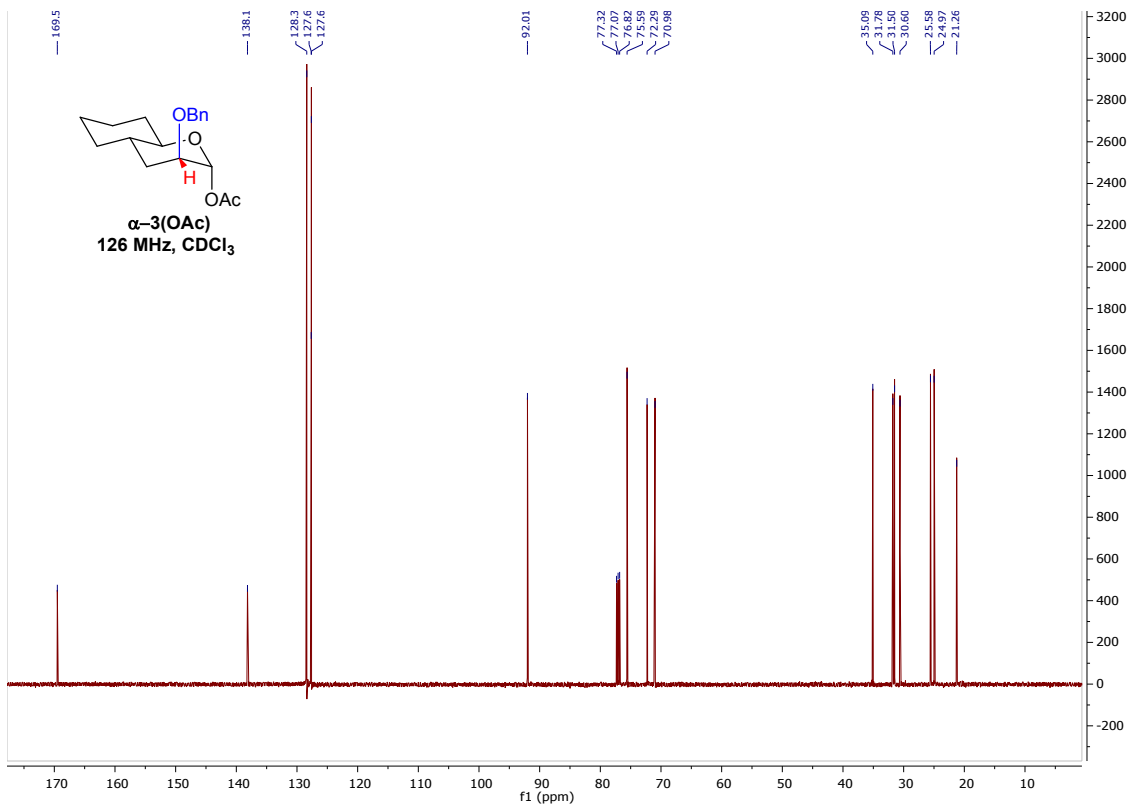


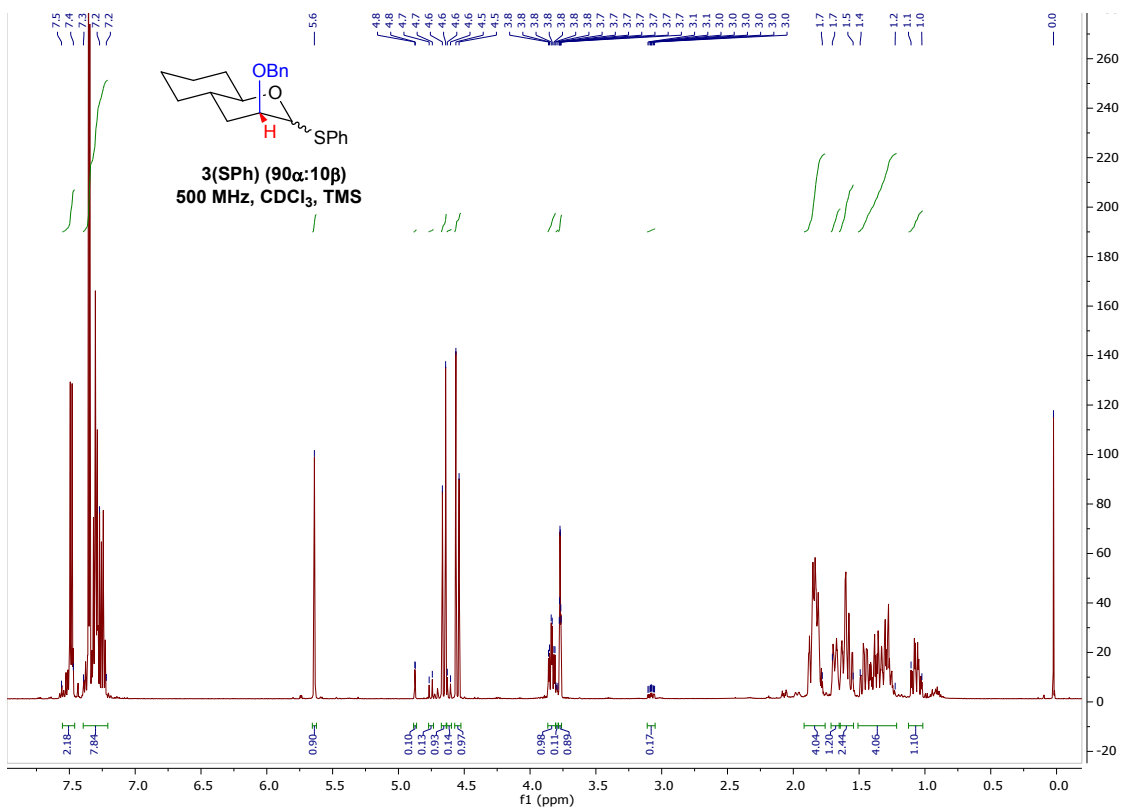
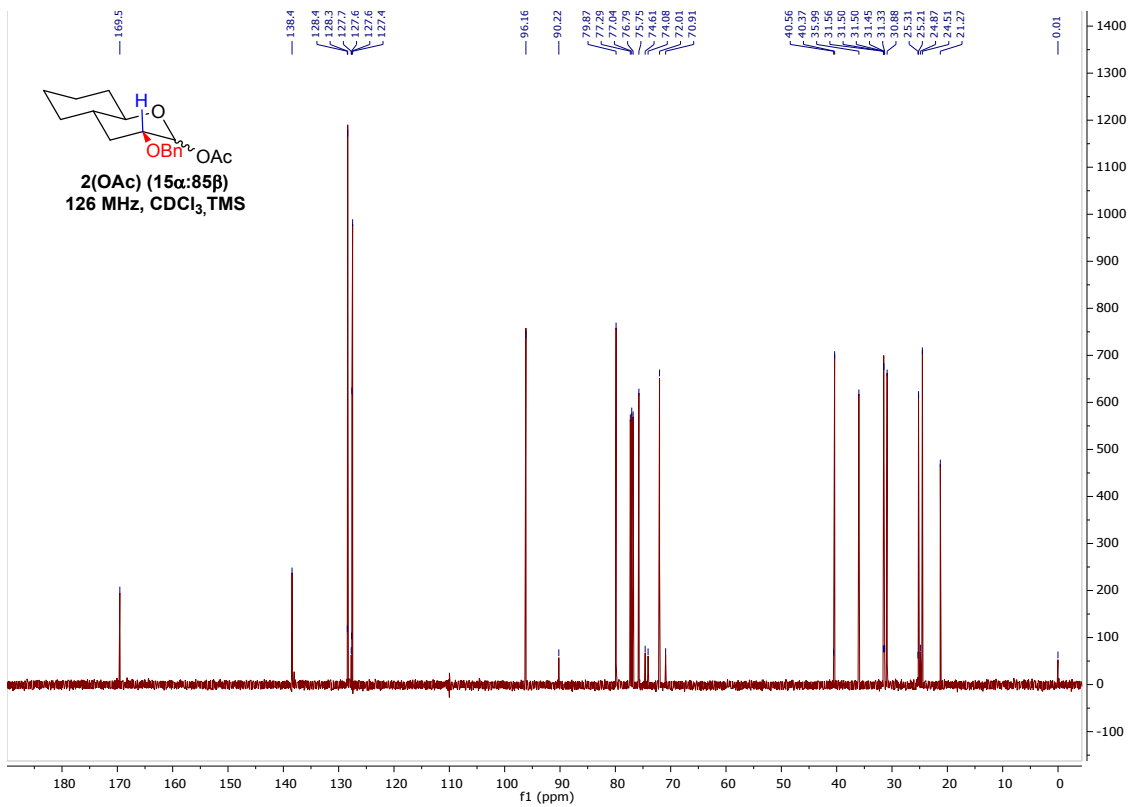


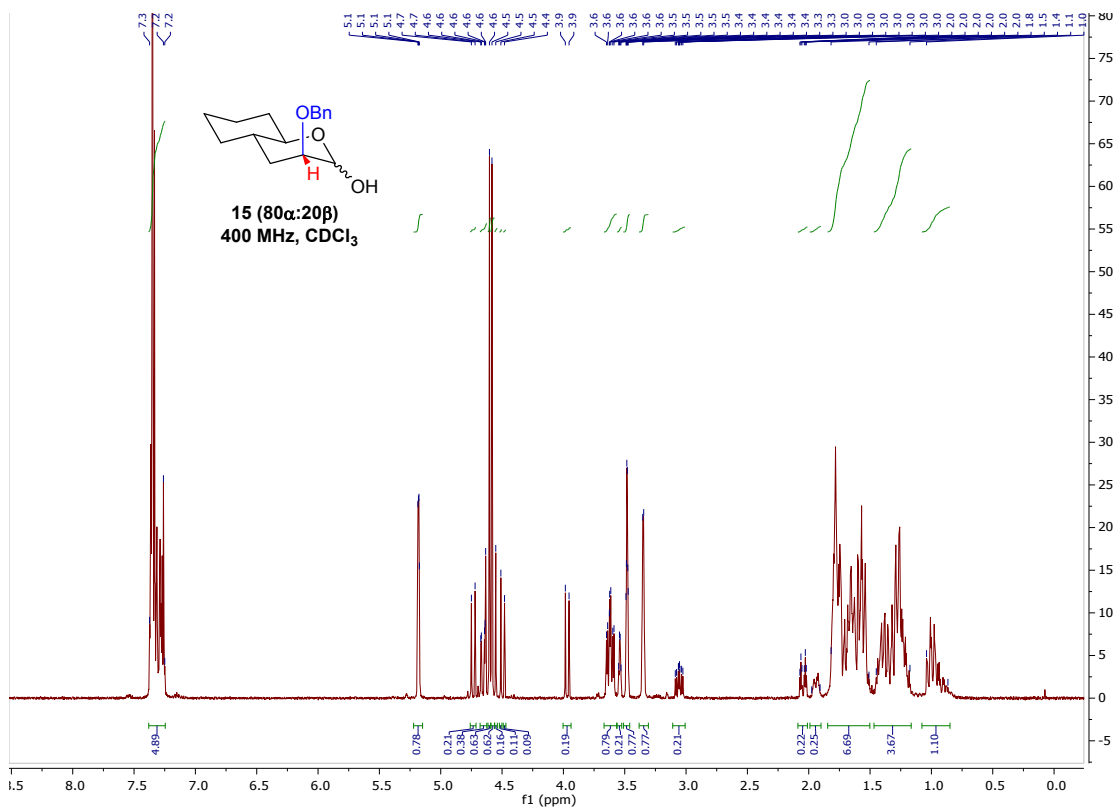
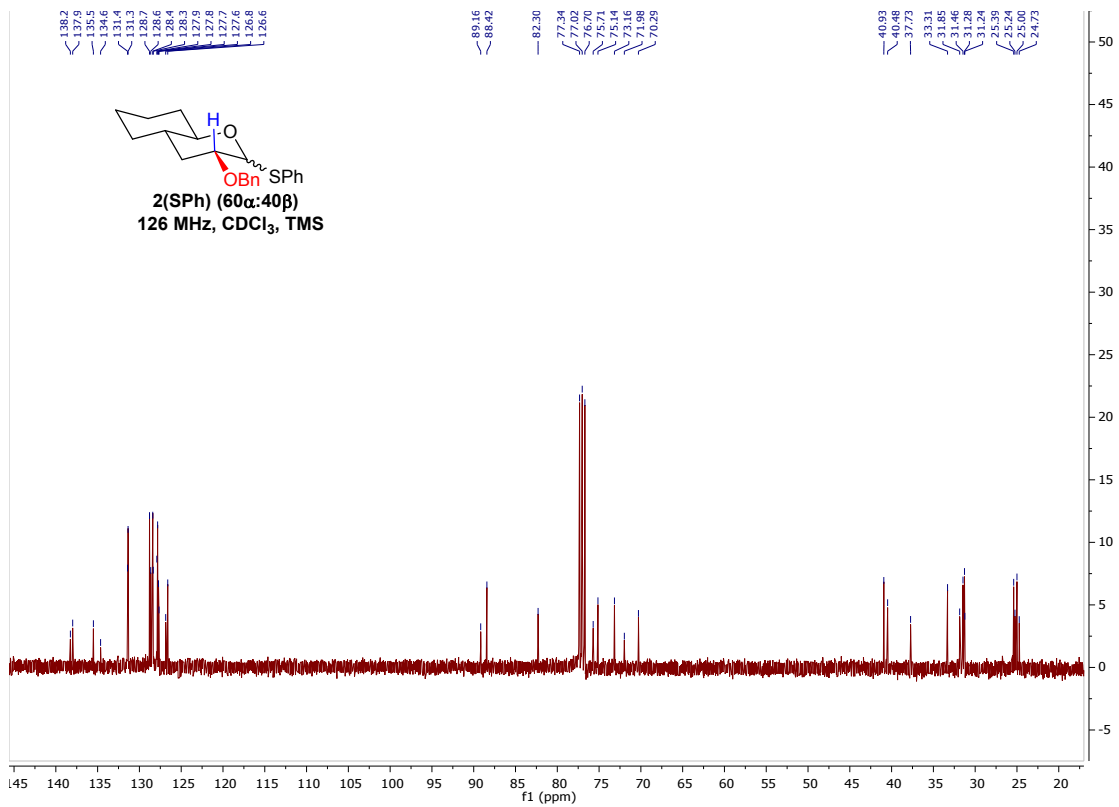


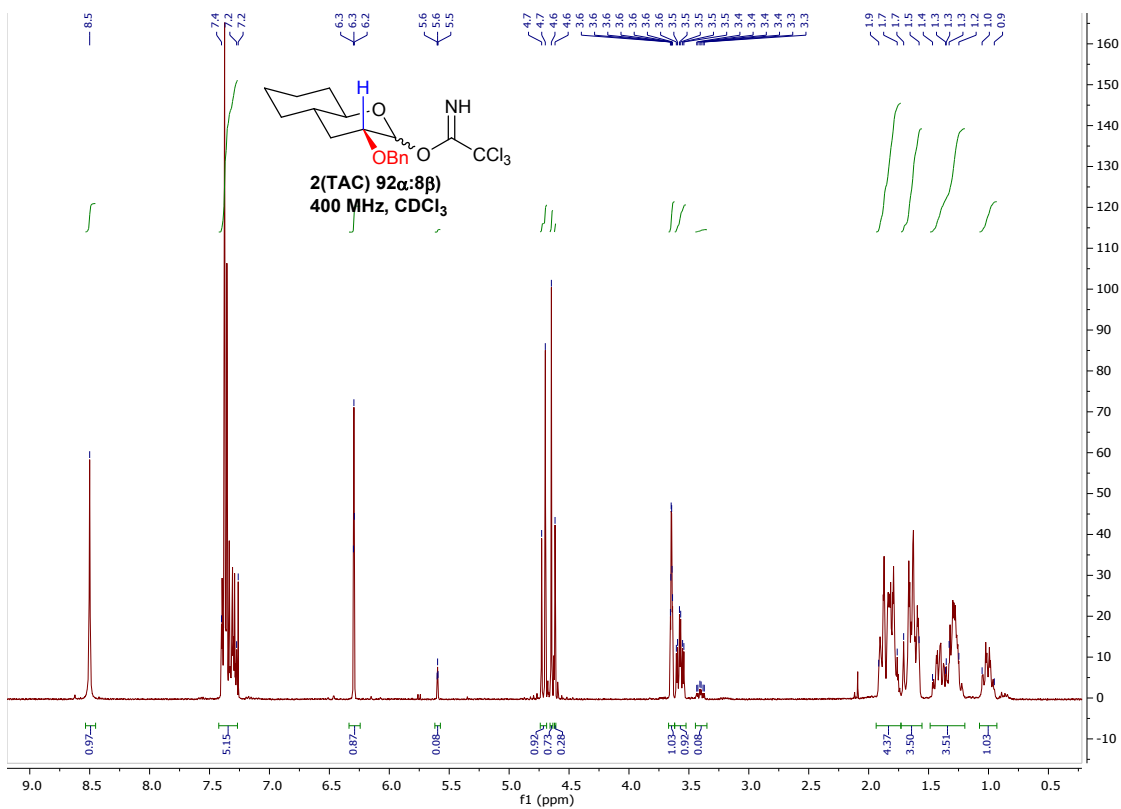
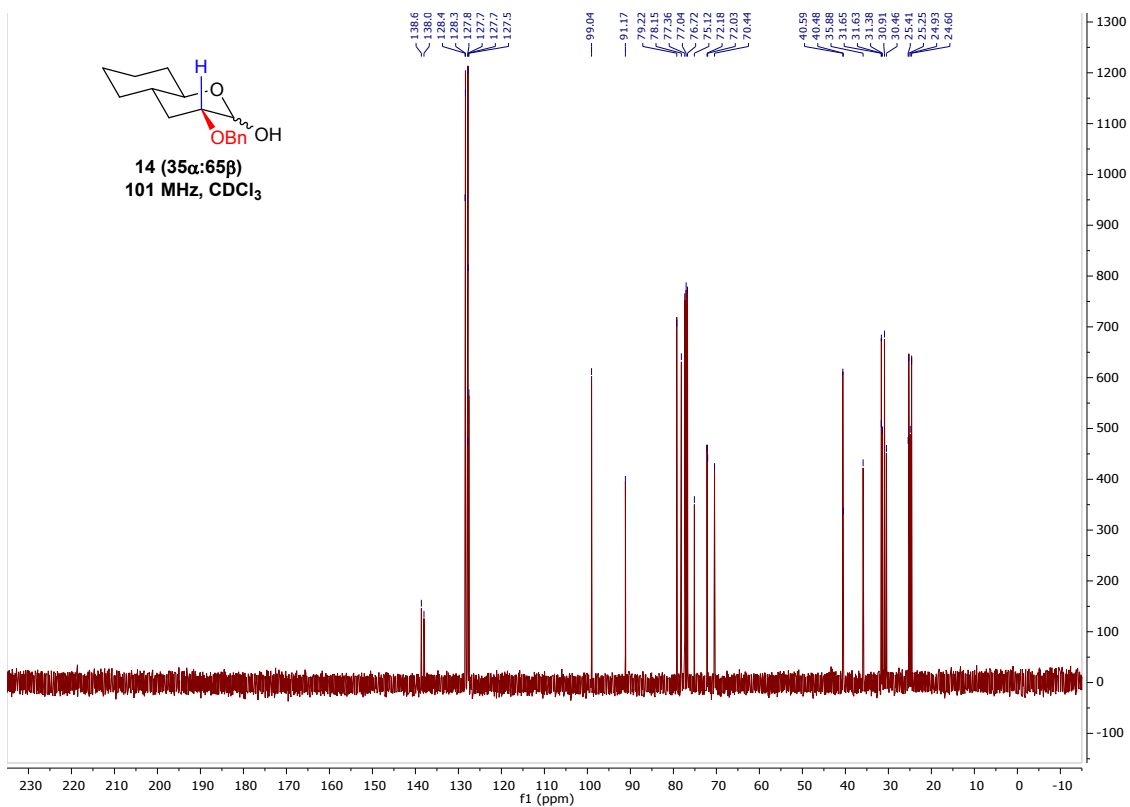


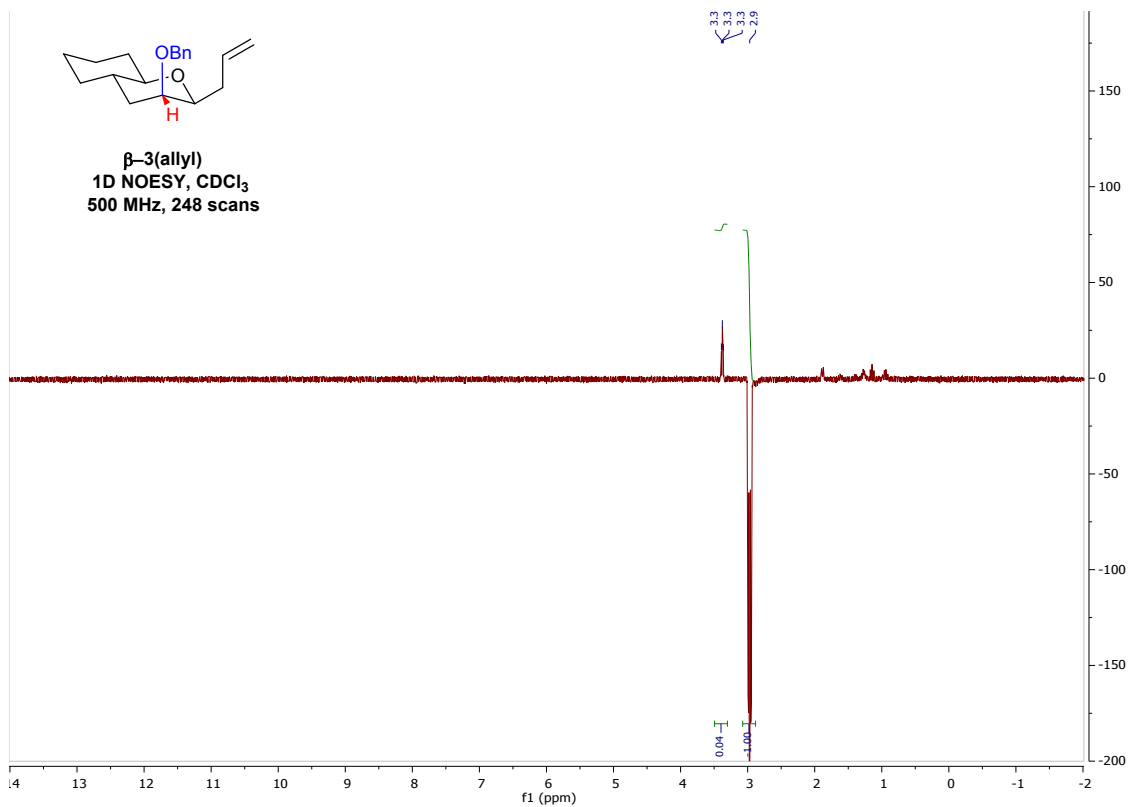
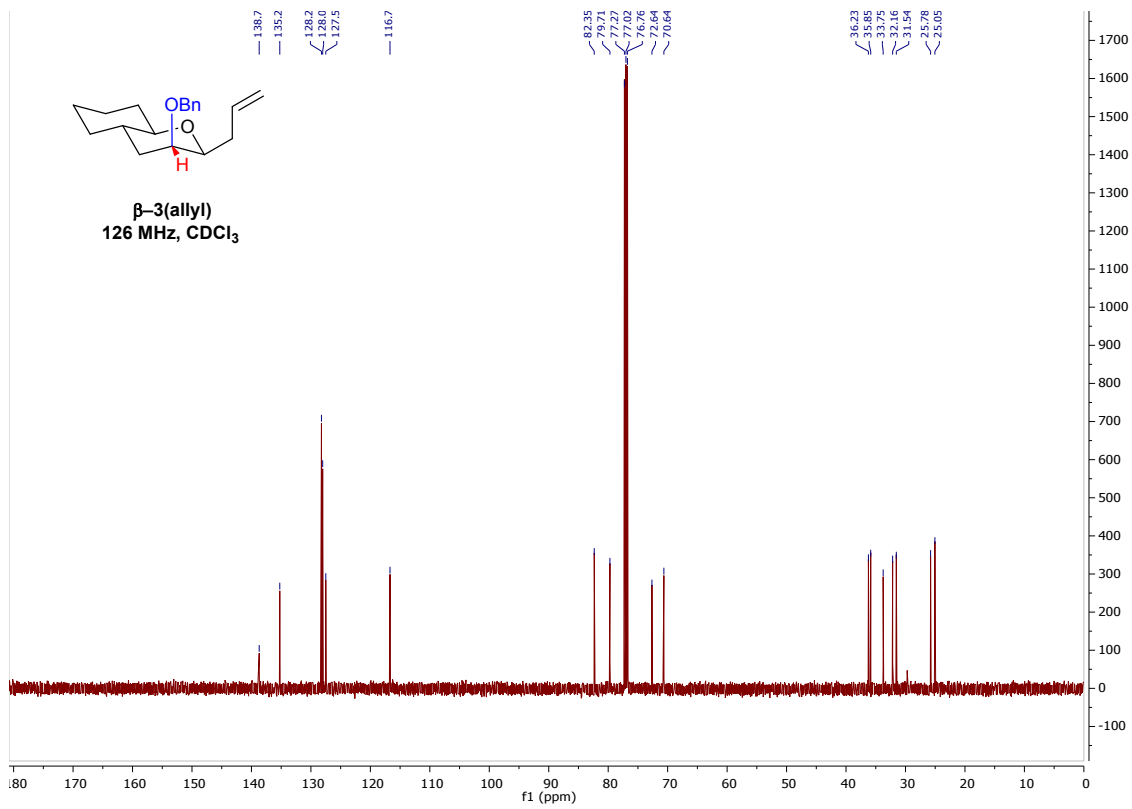


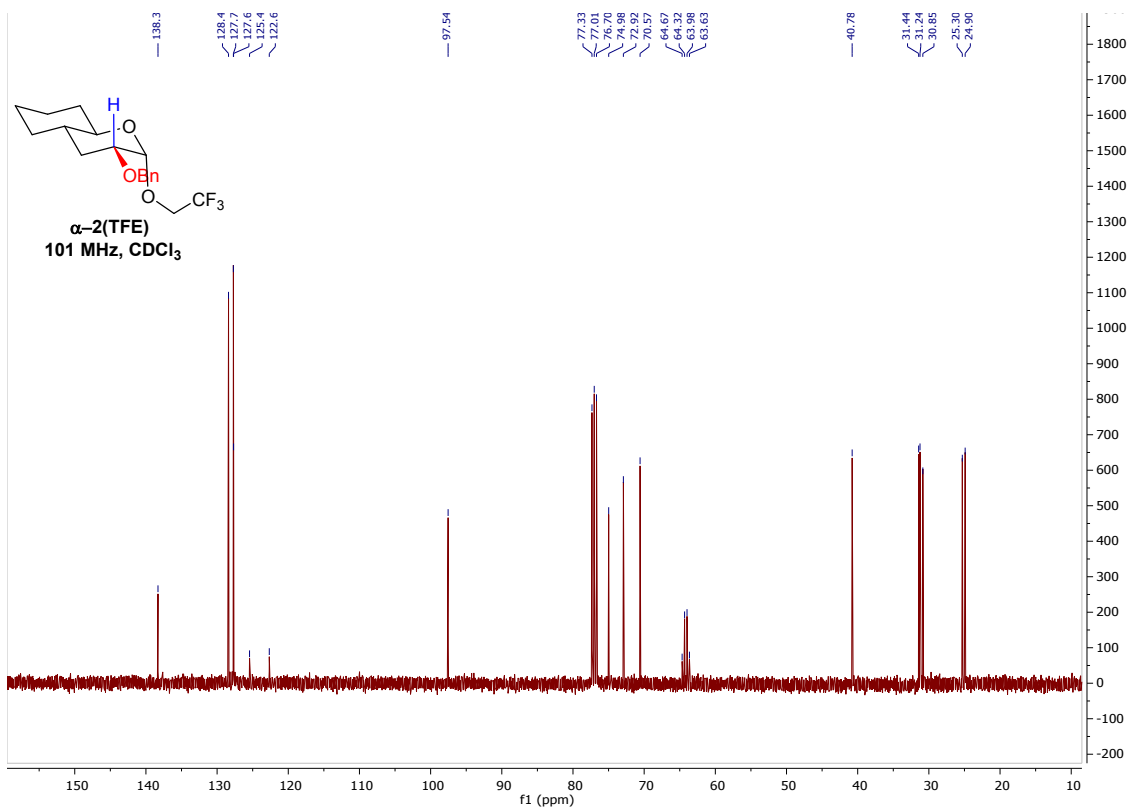
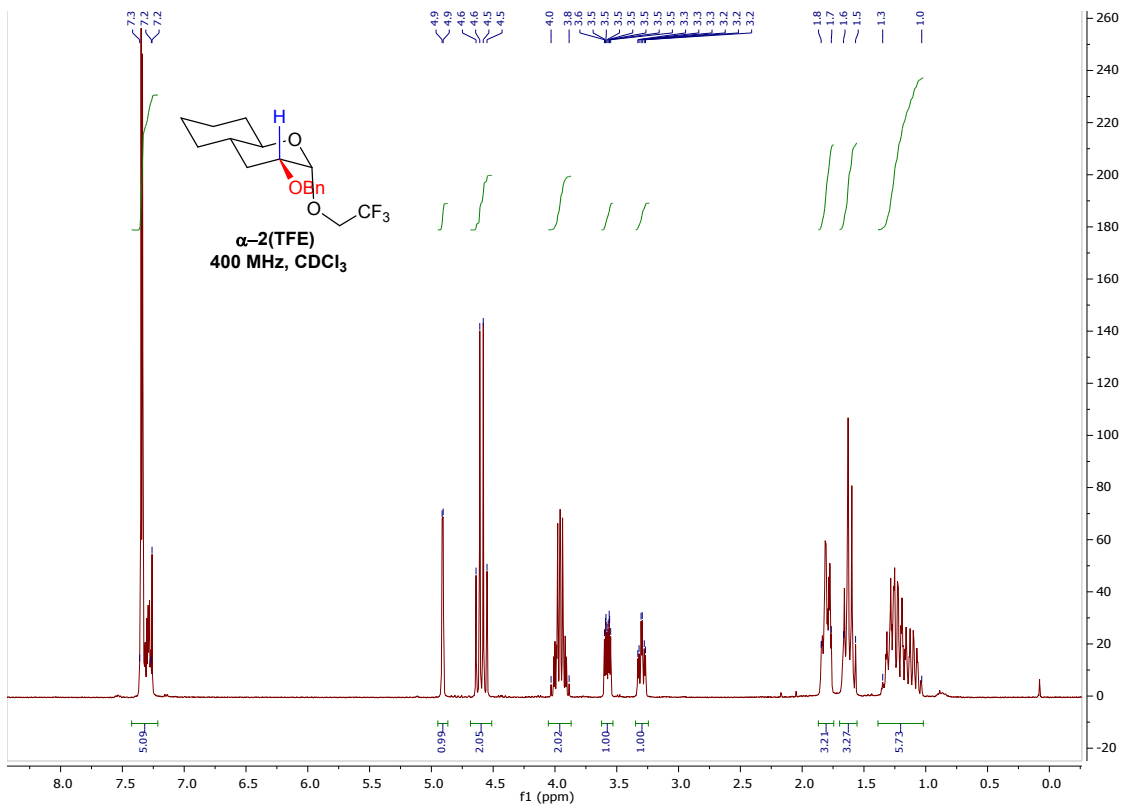


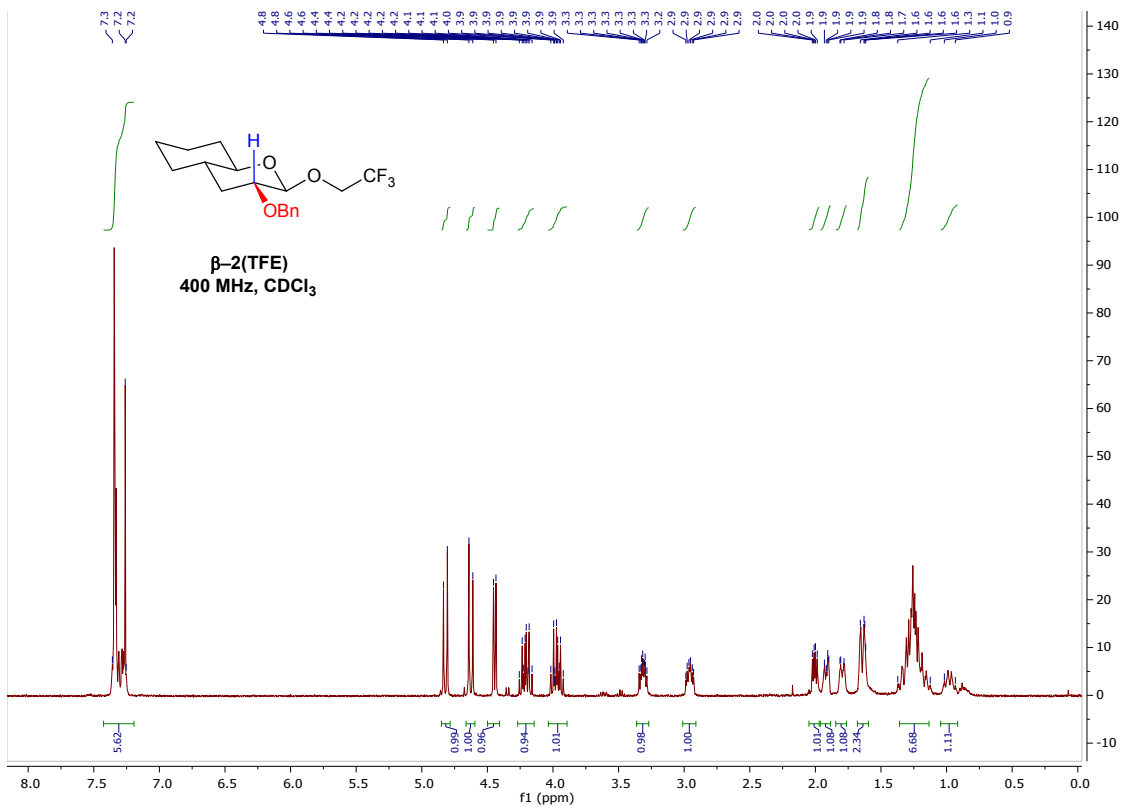
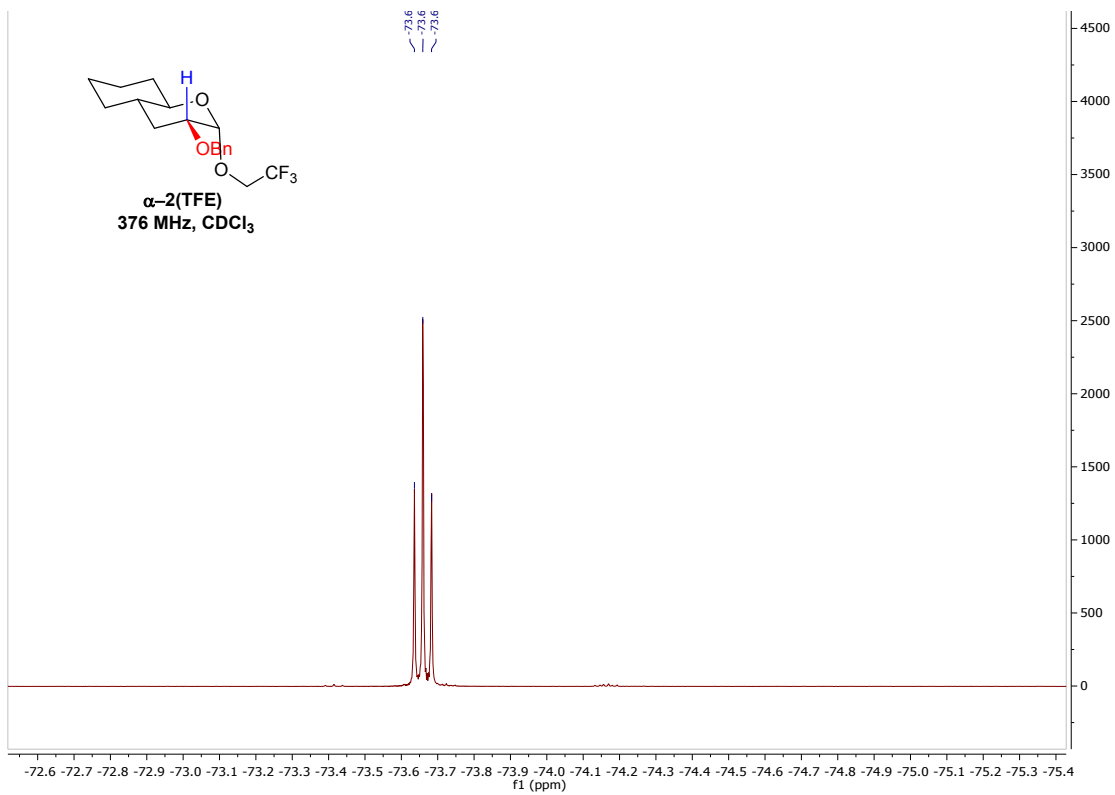


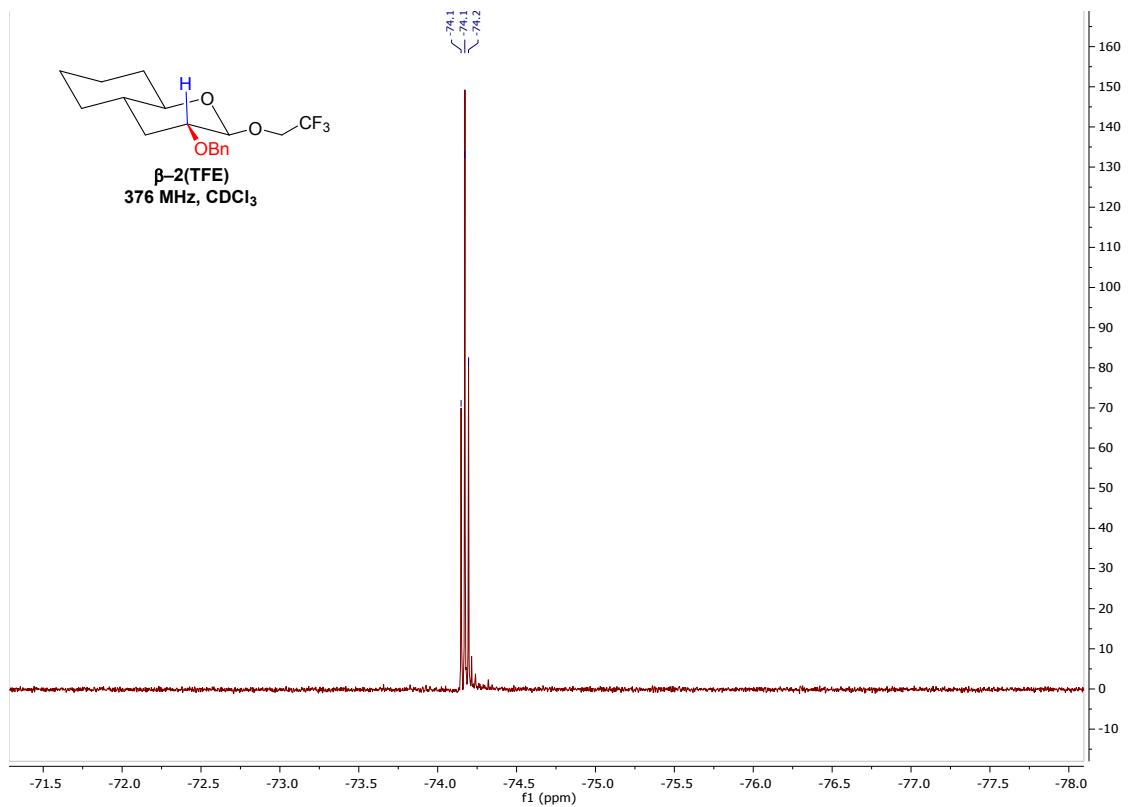
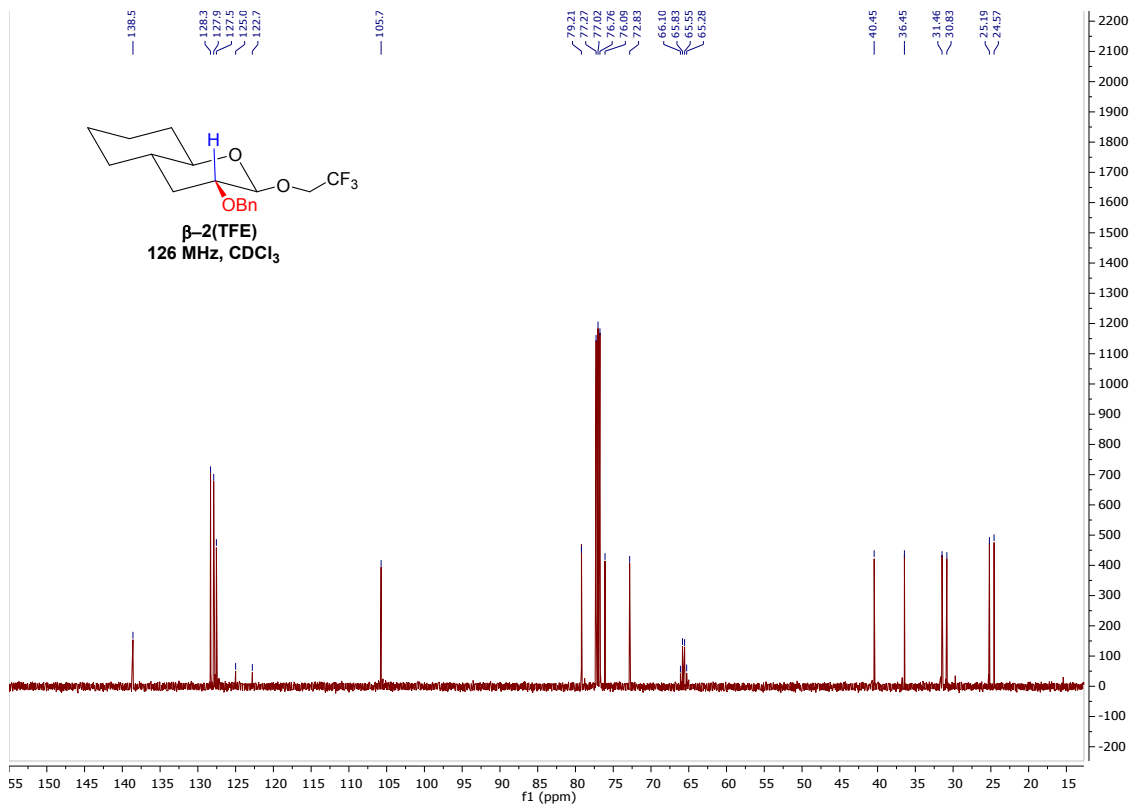


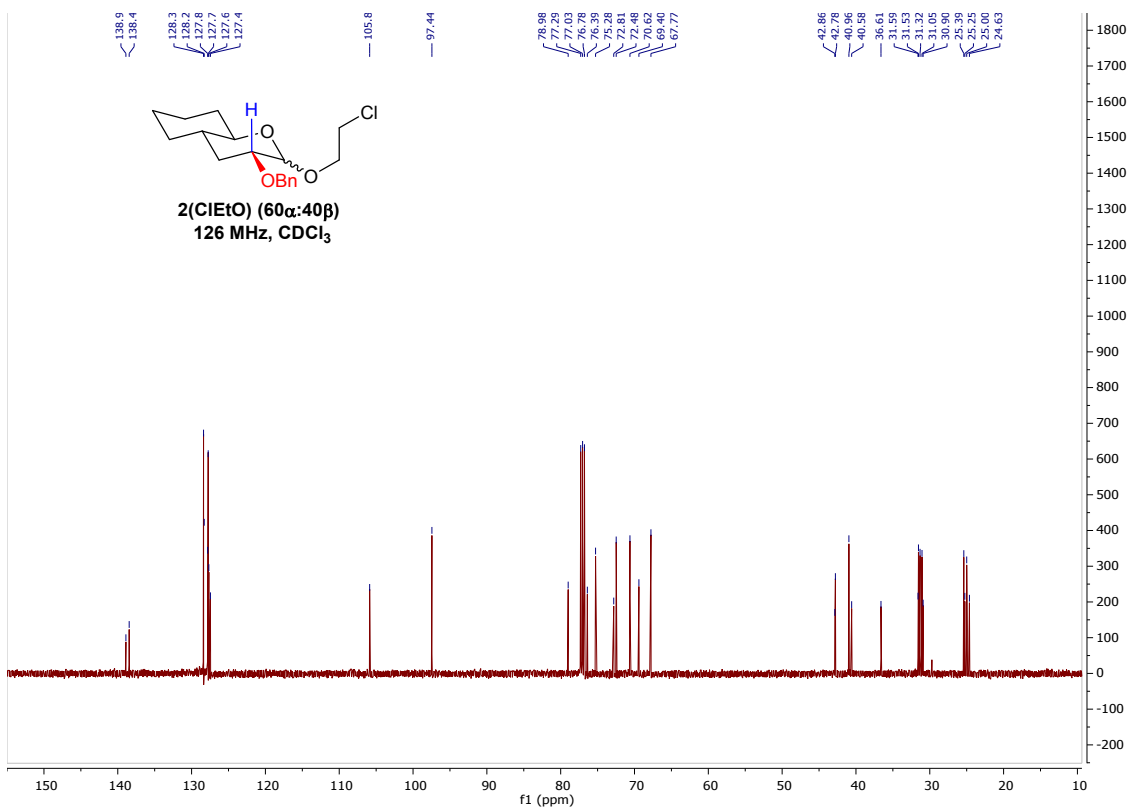
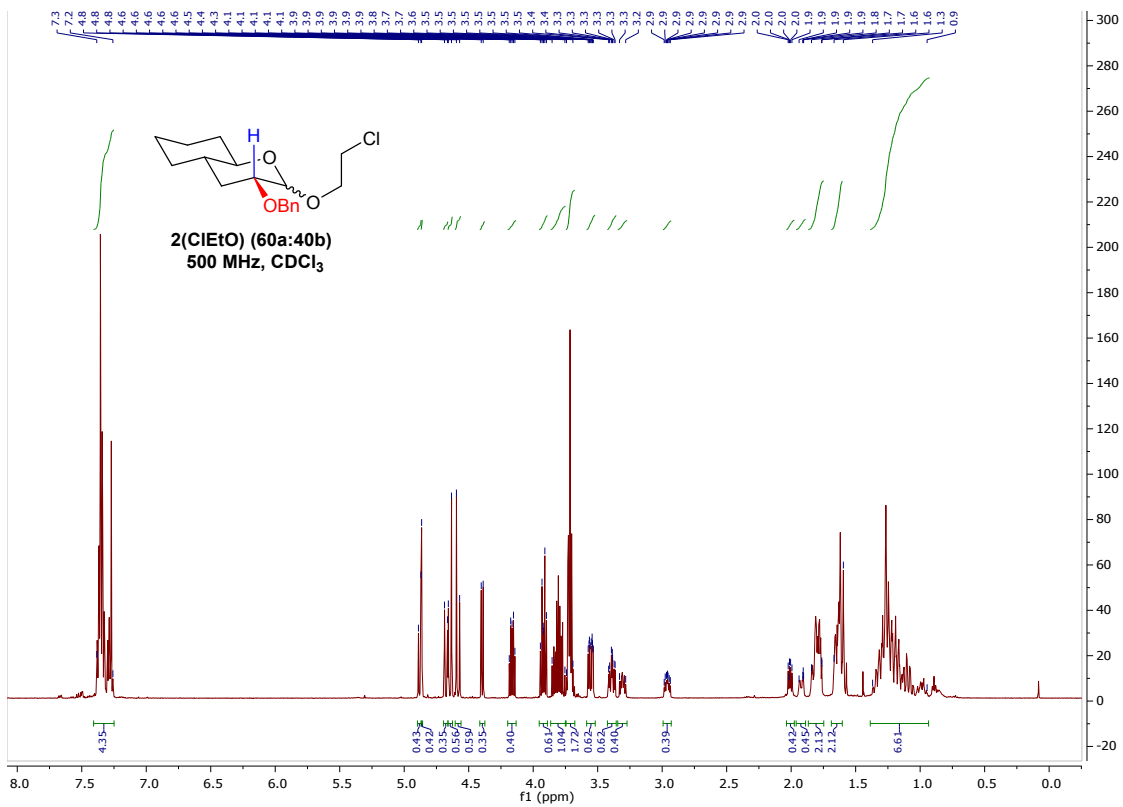


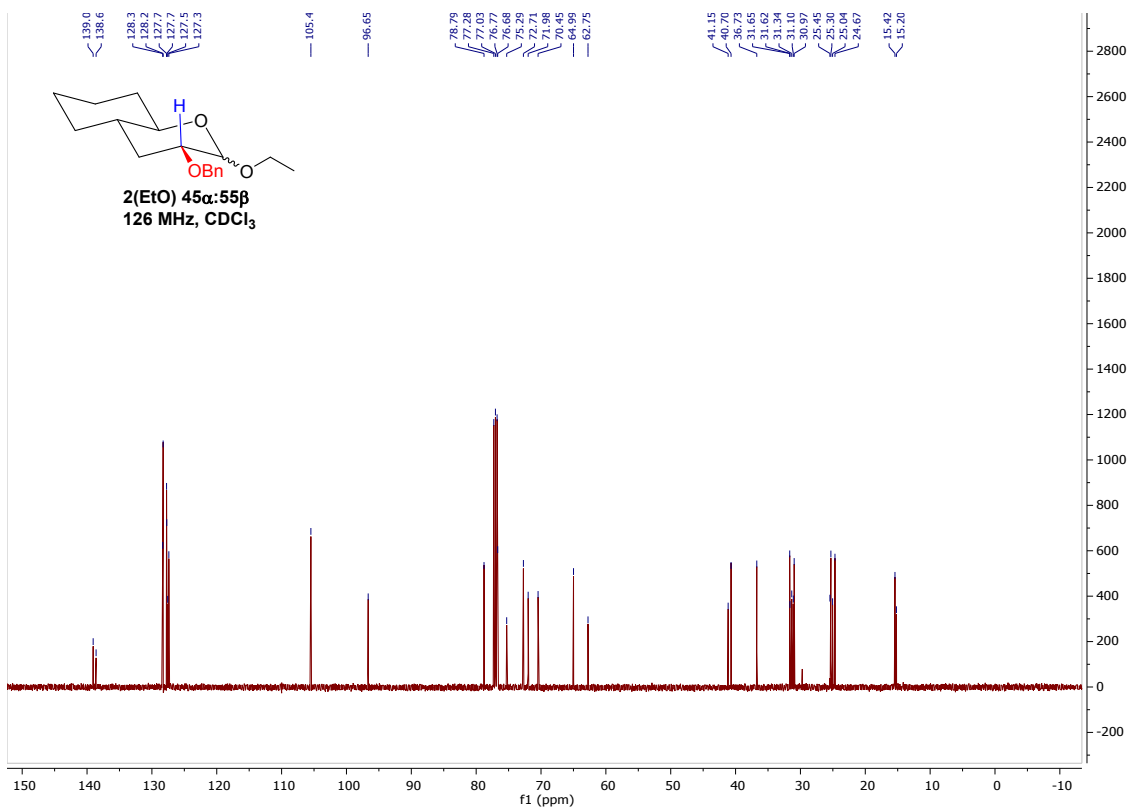
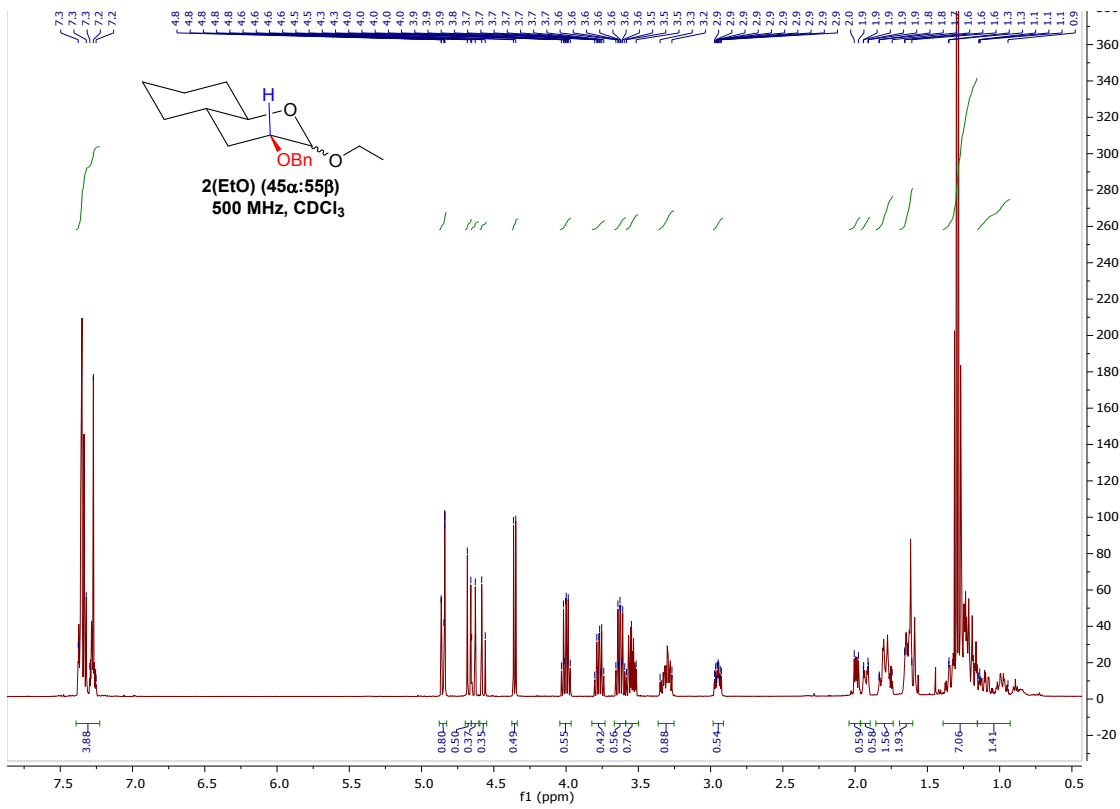


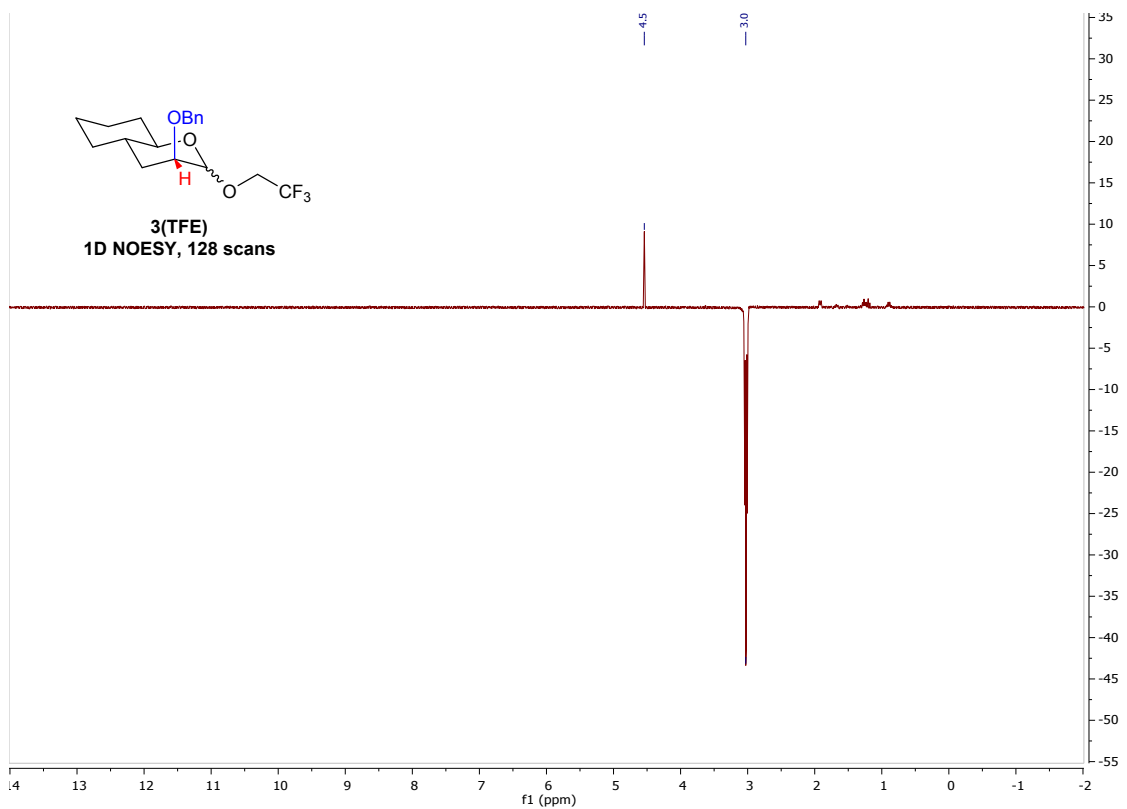
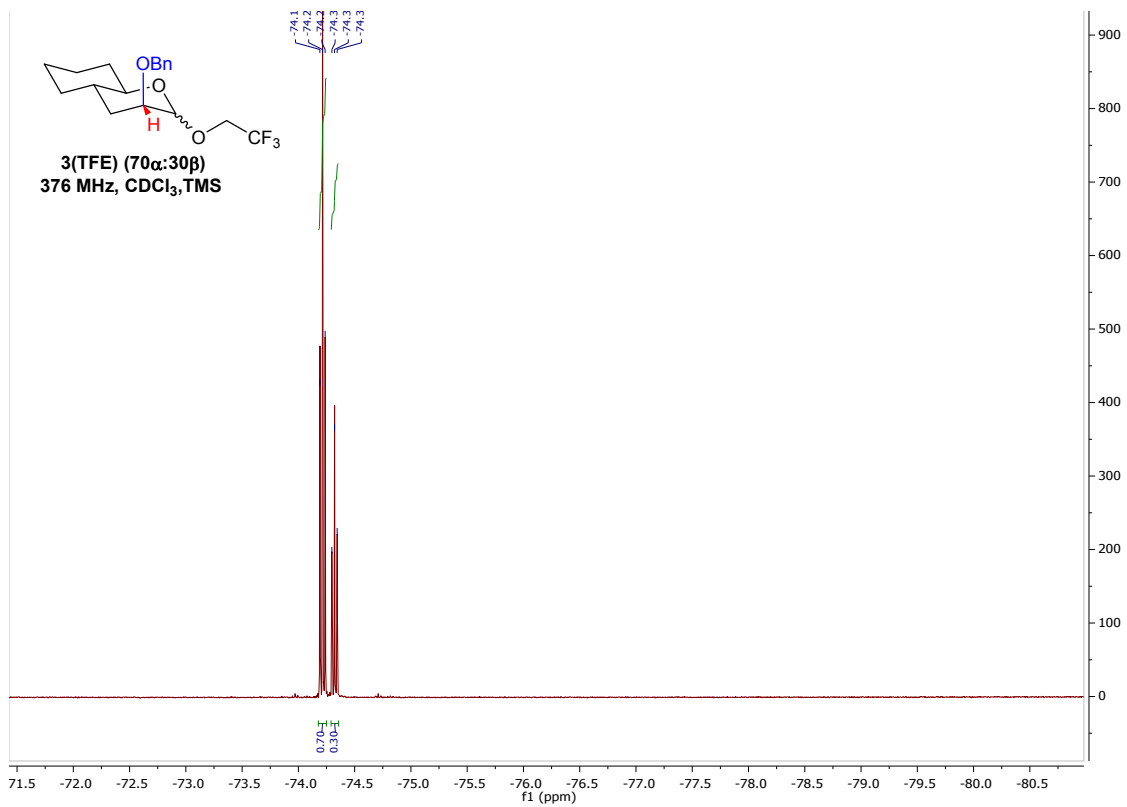




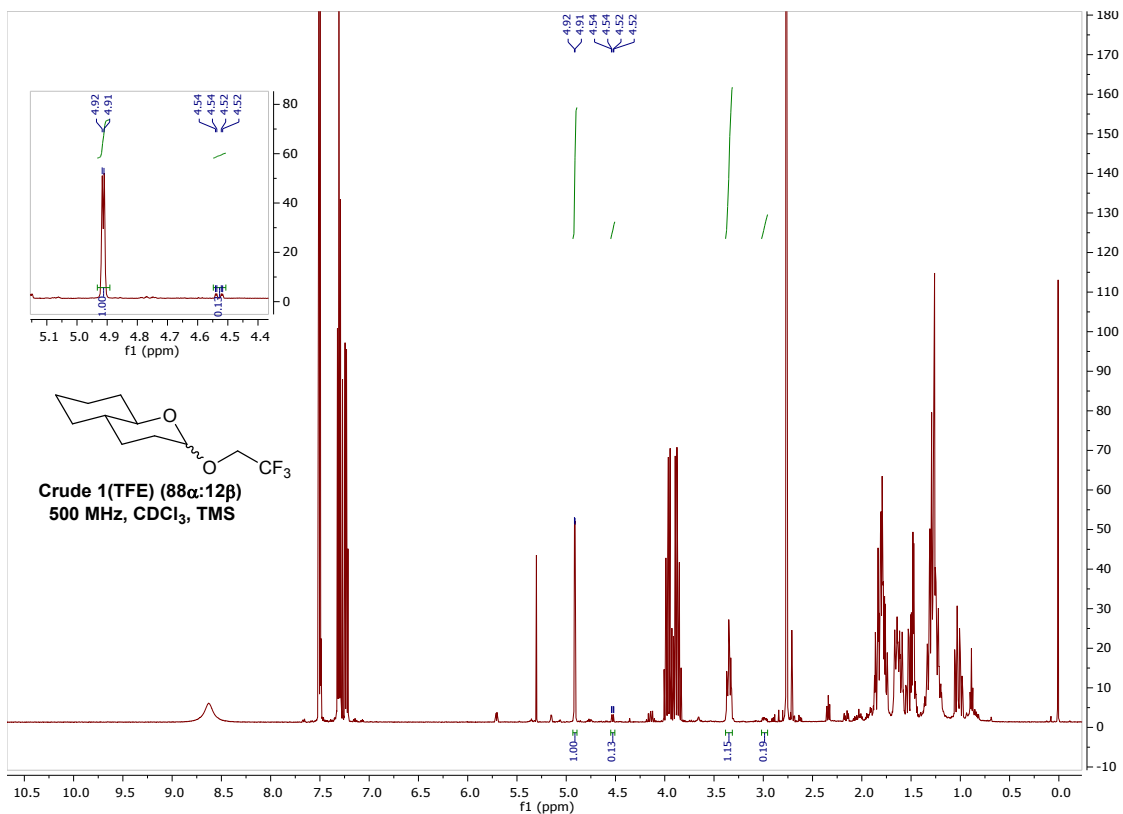
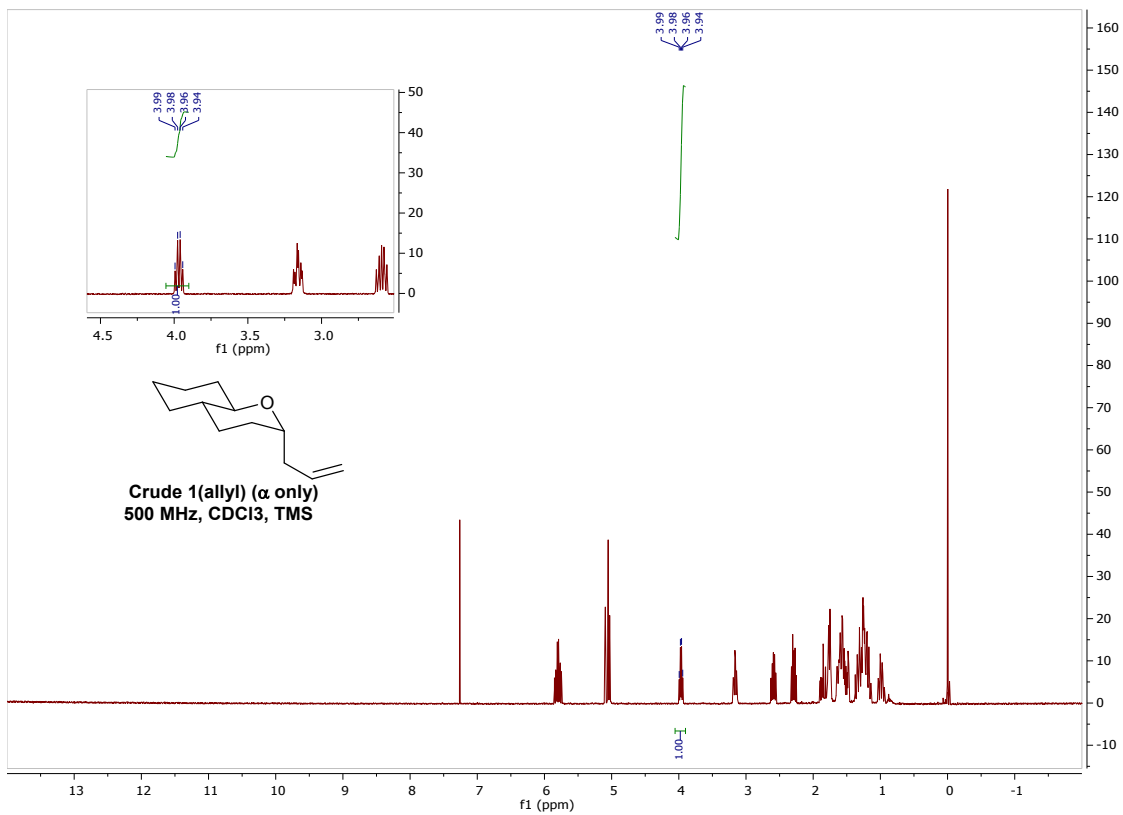


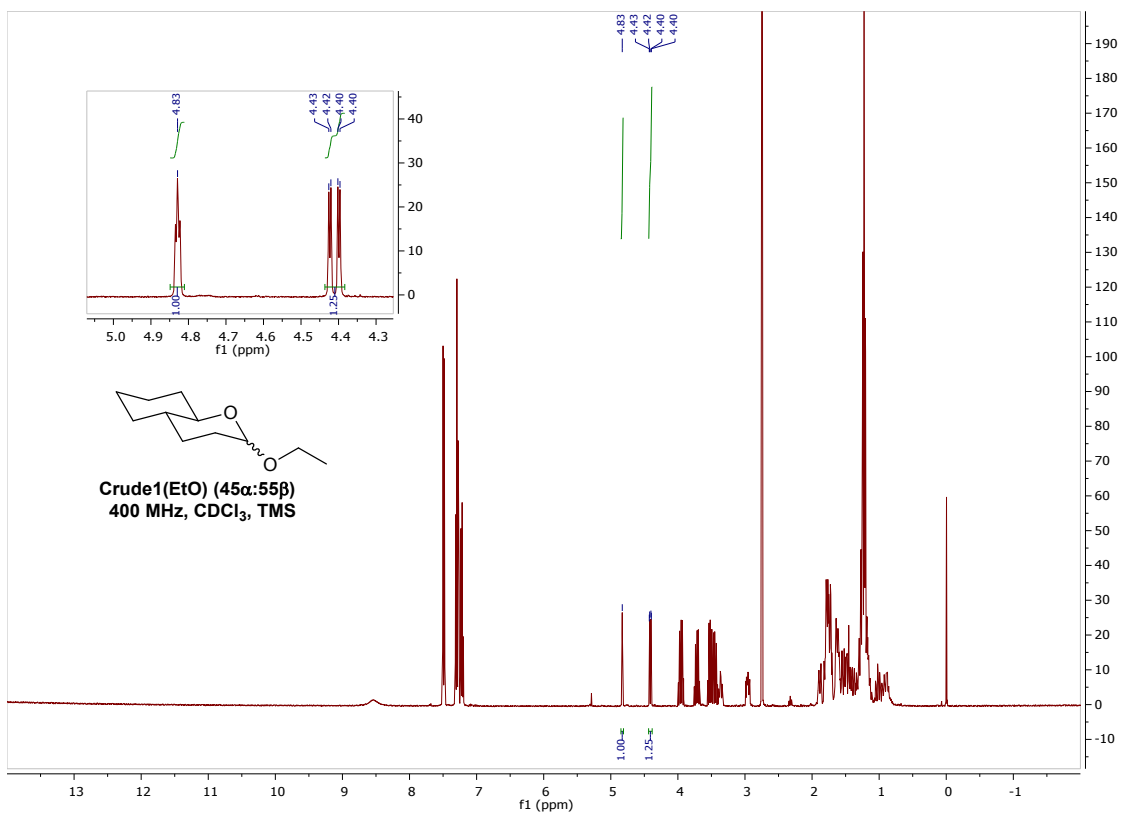
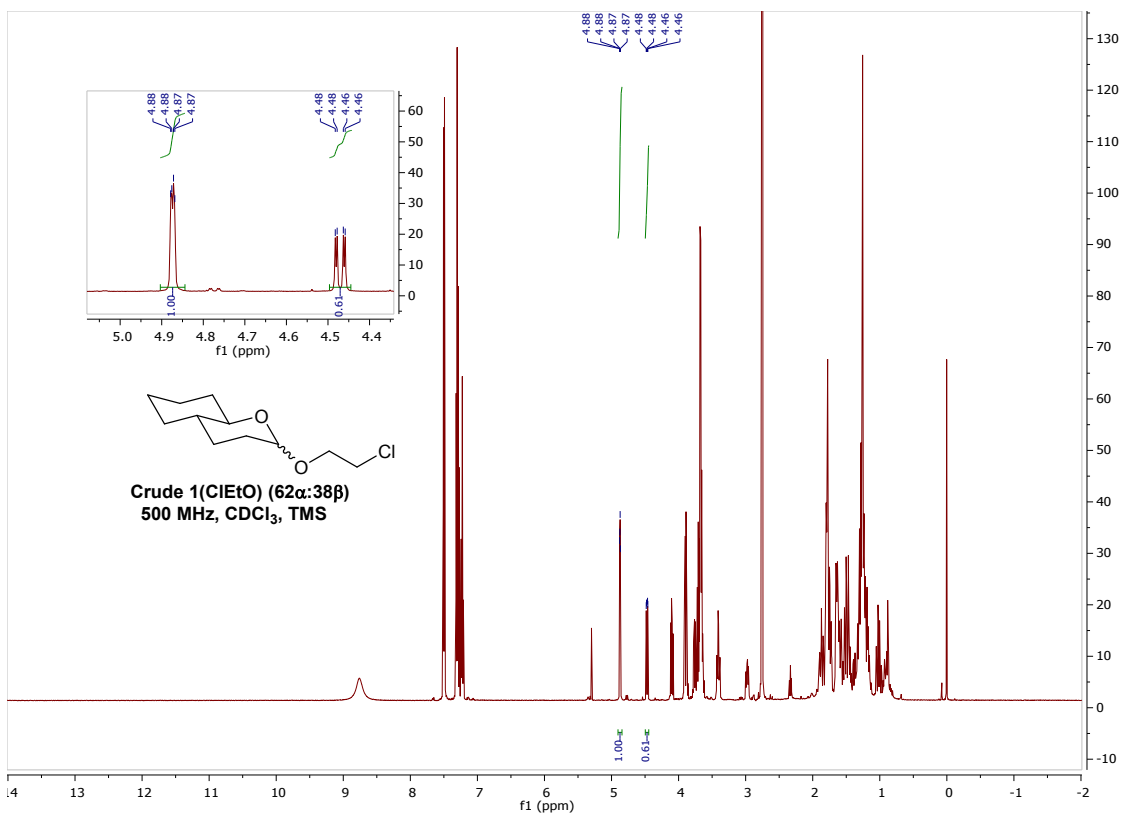


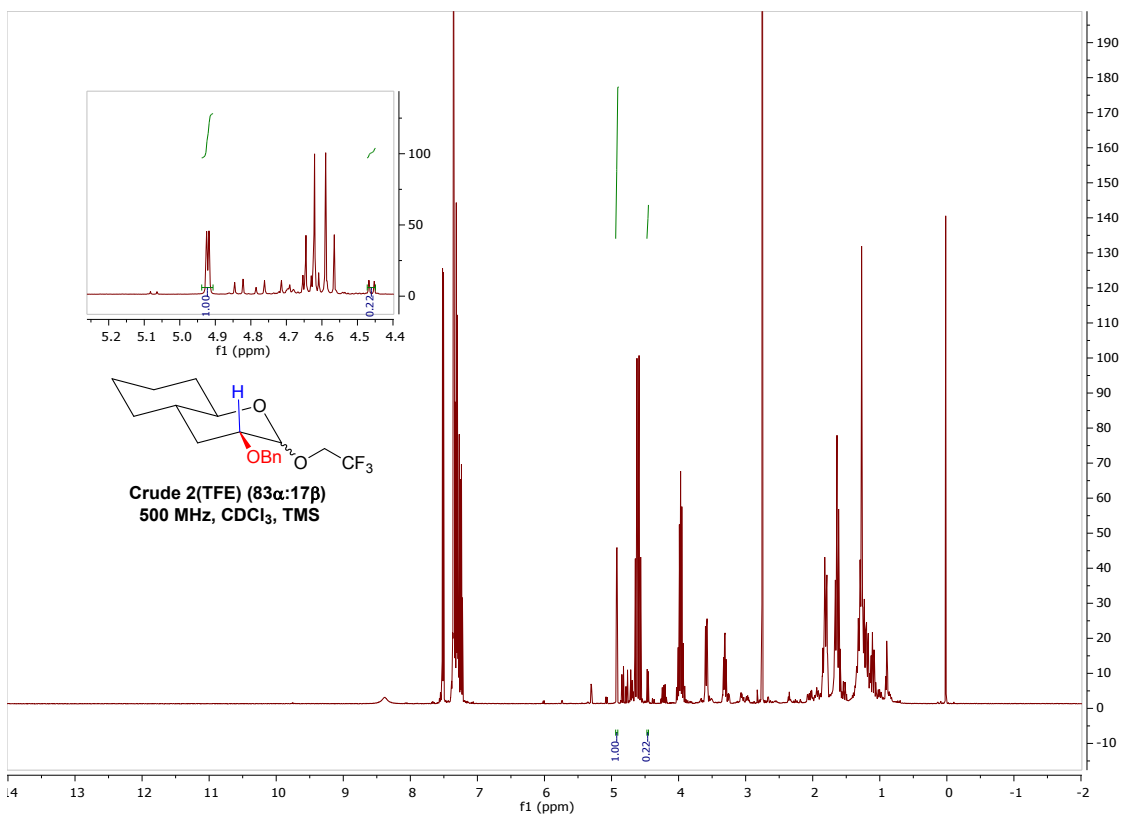
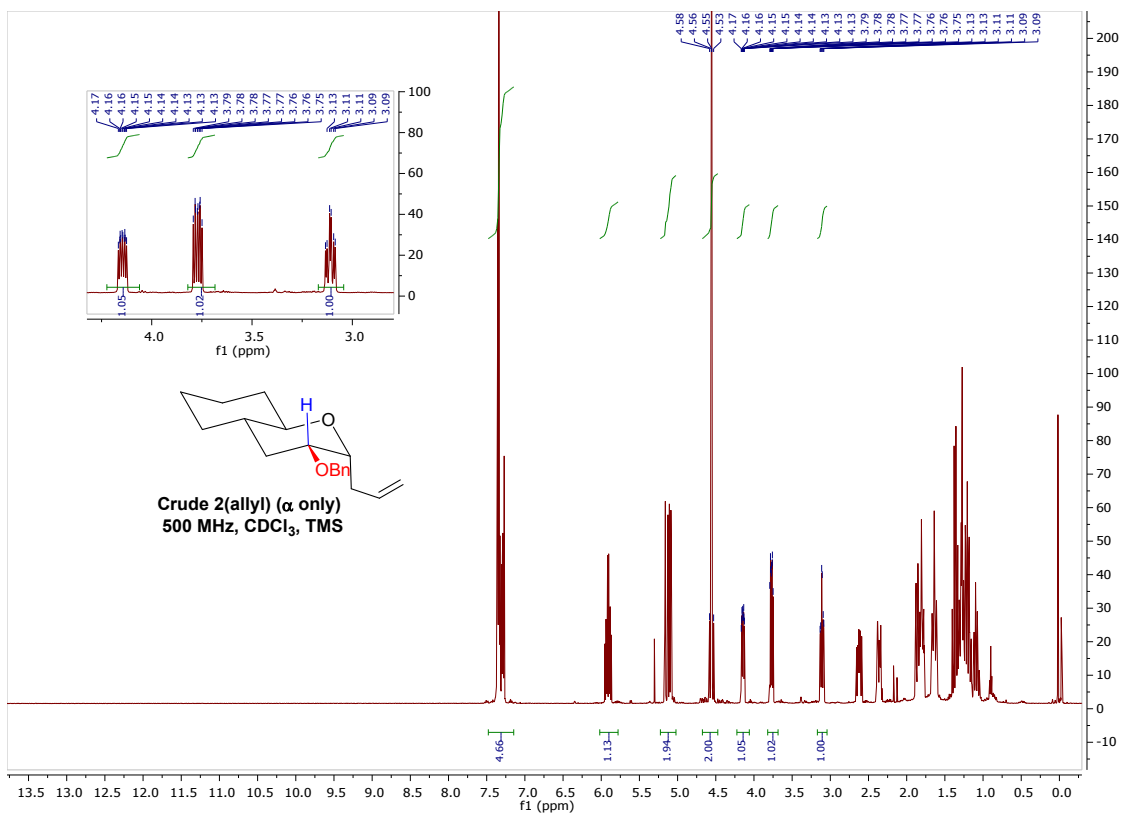


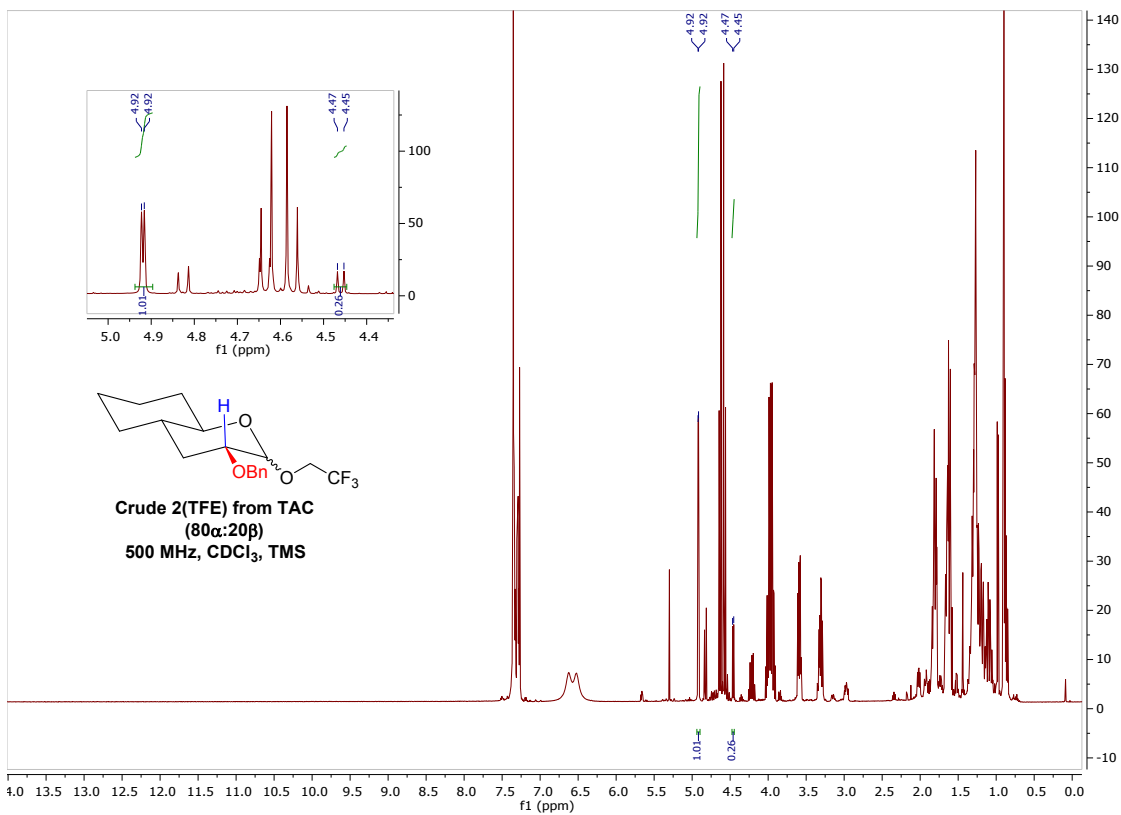
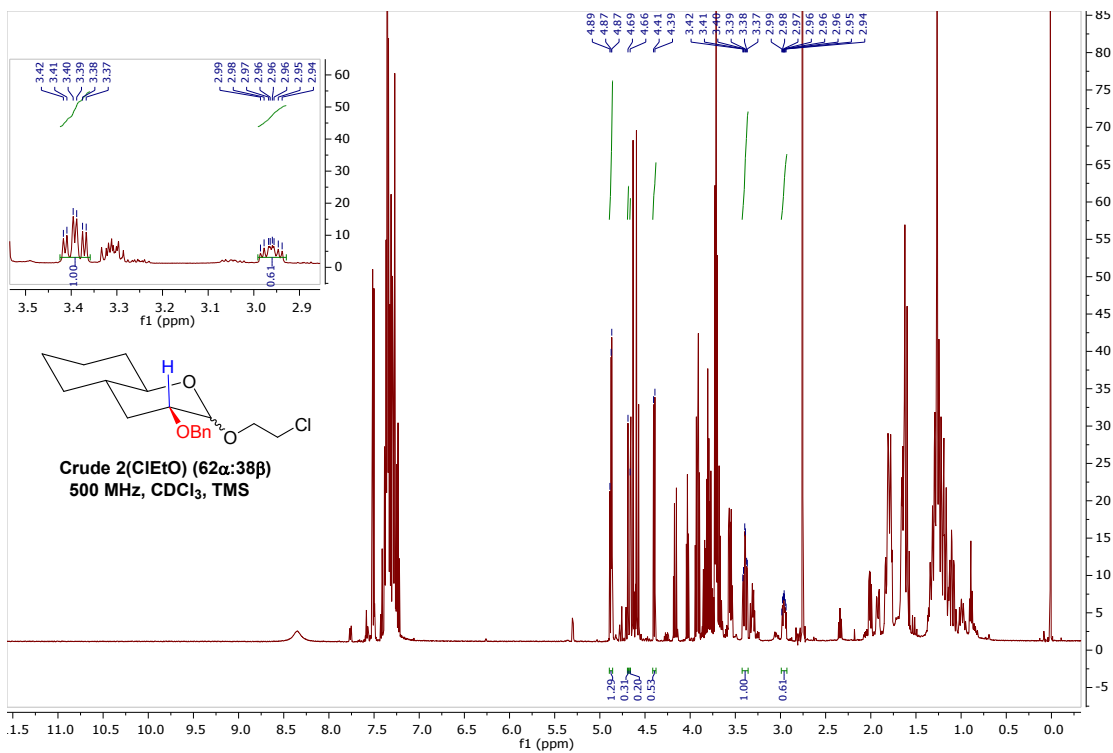


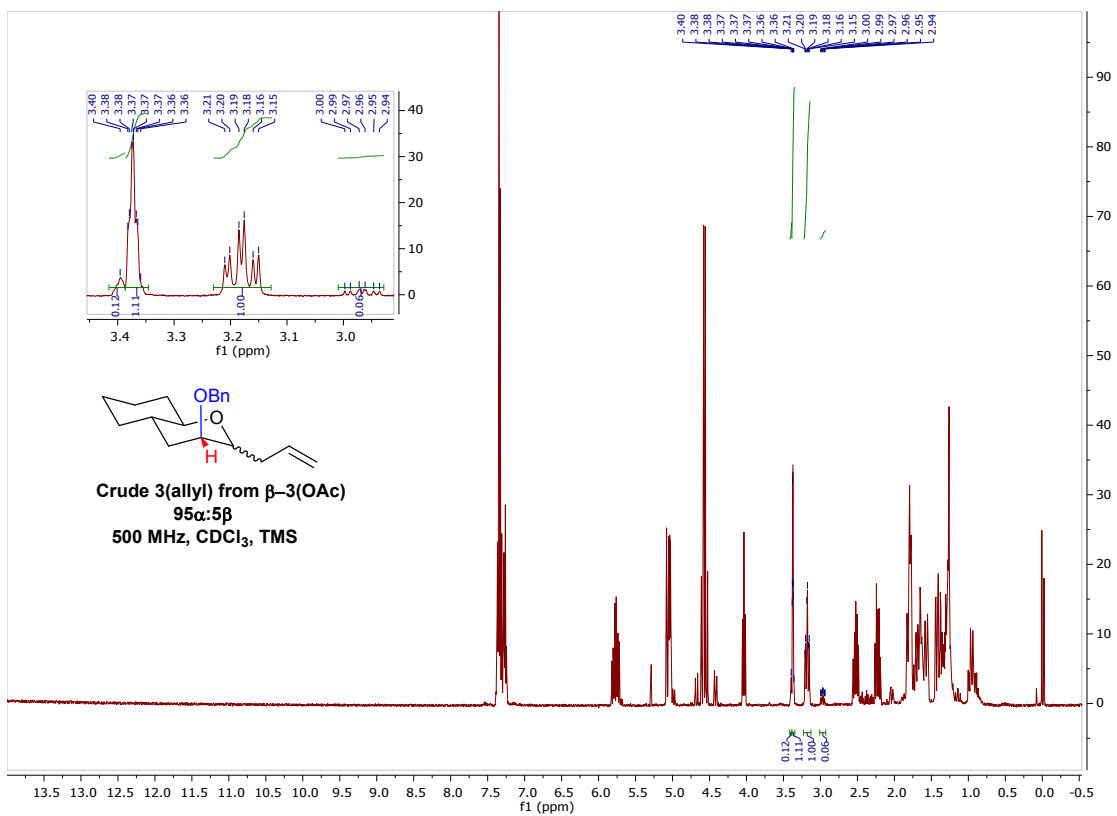
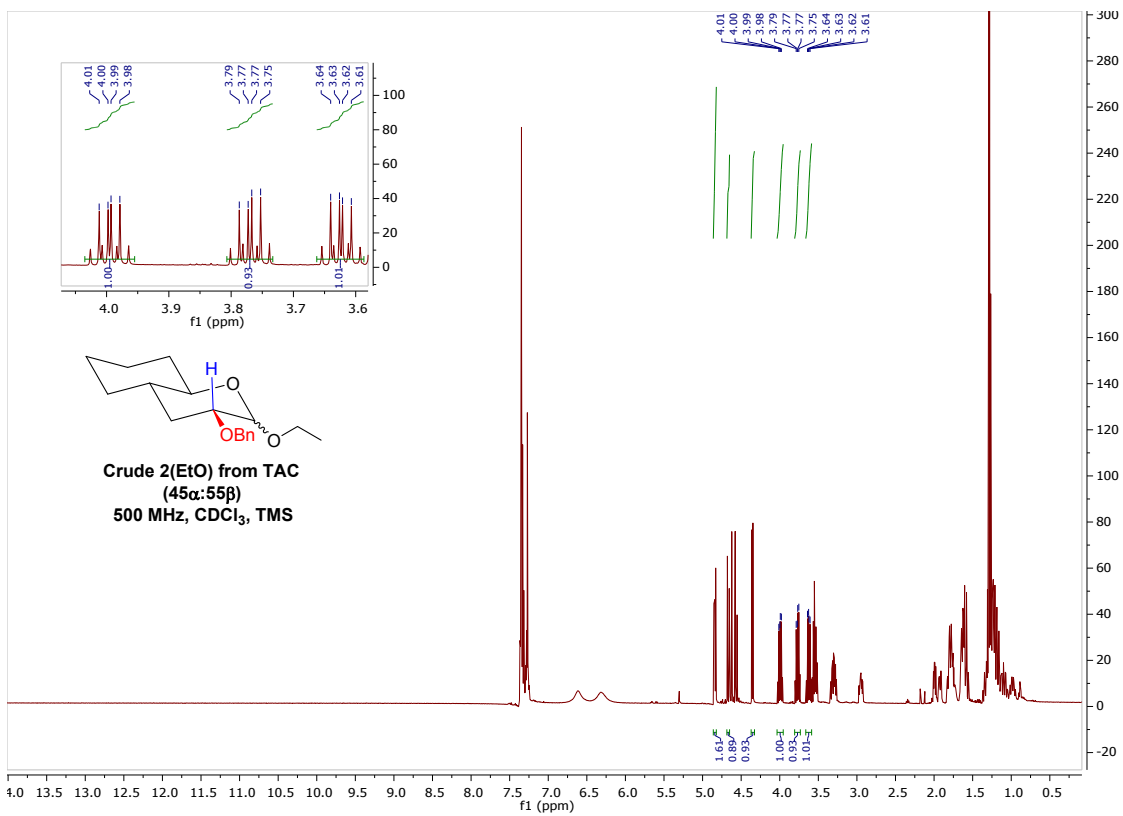
Crude ¹H NMR spectra from O and C-glycosylation in DCM

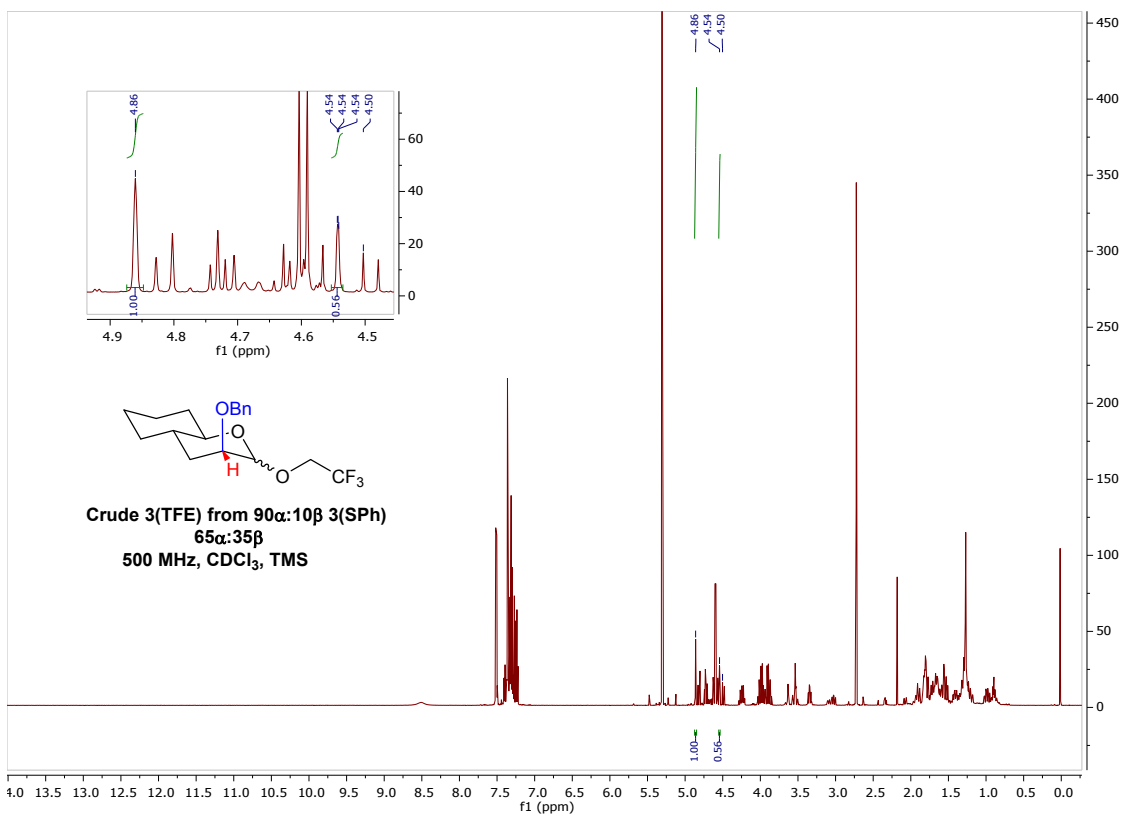
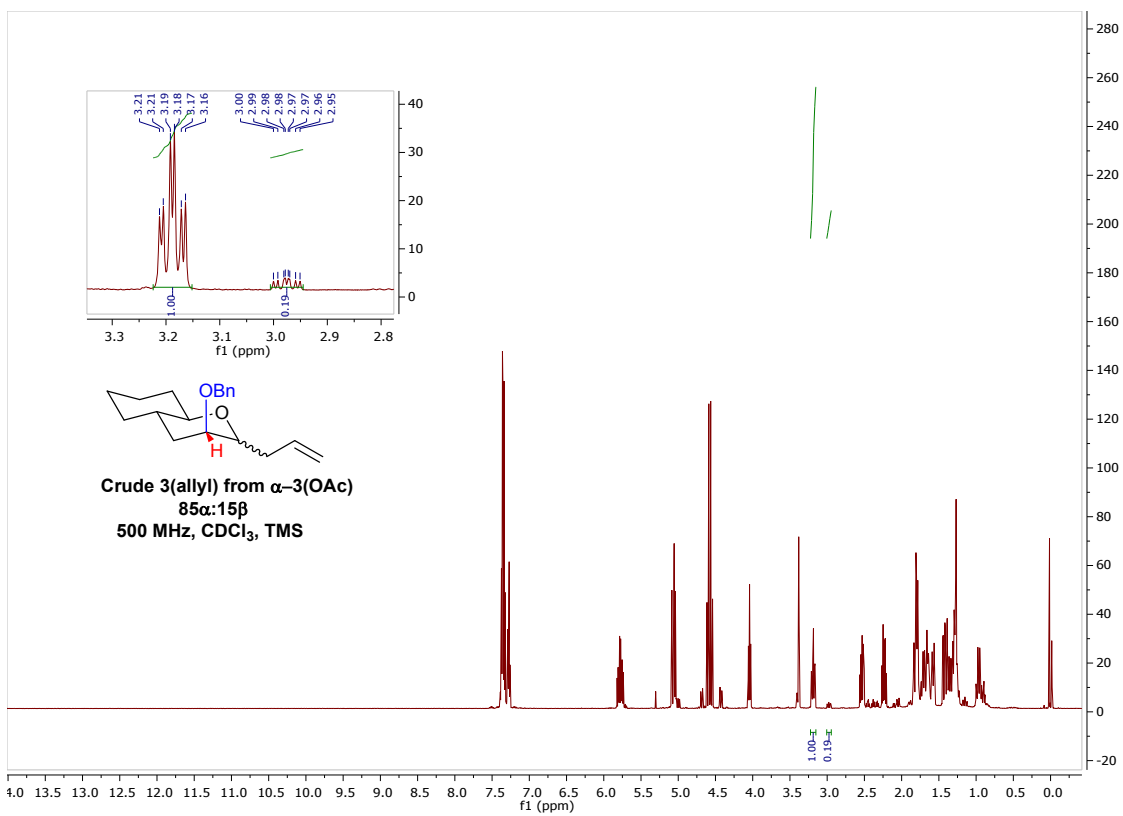


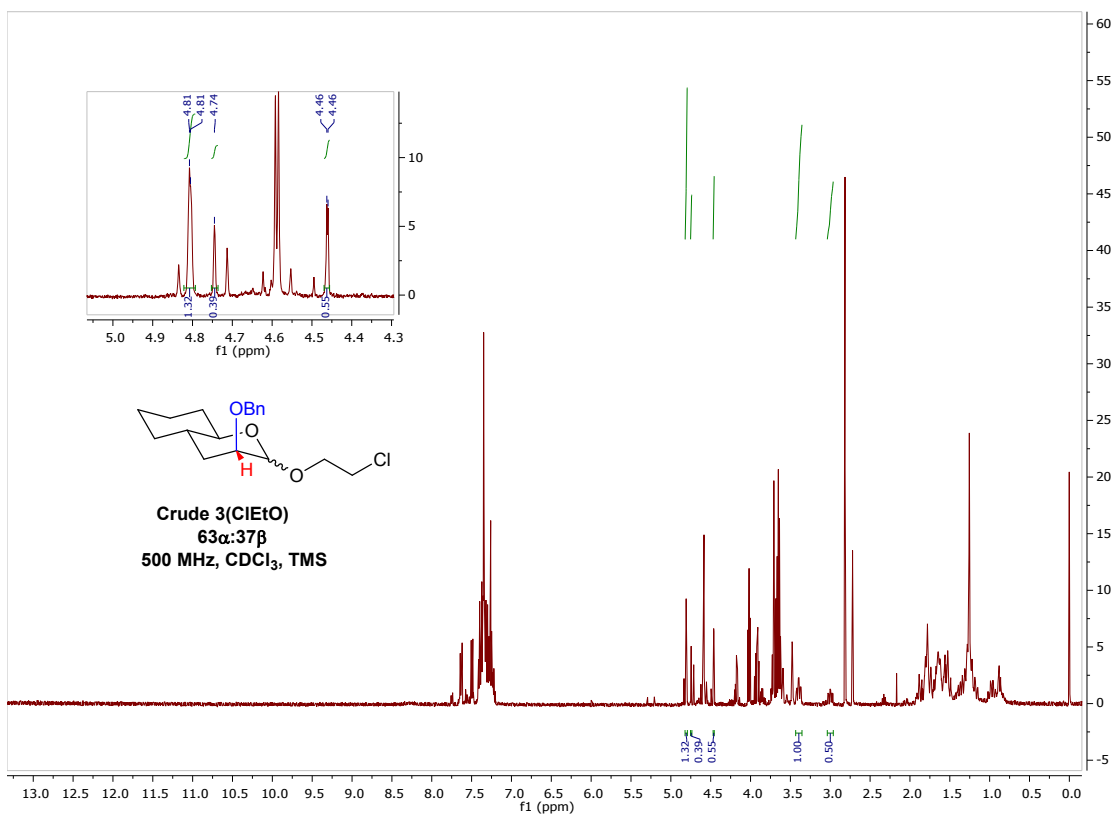
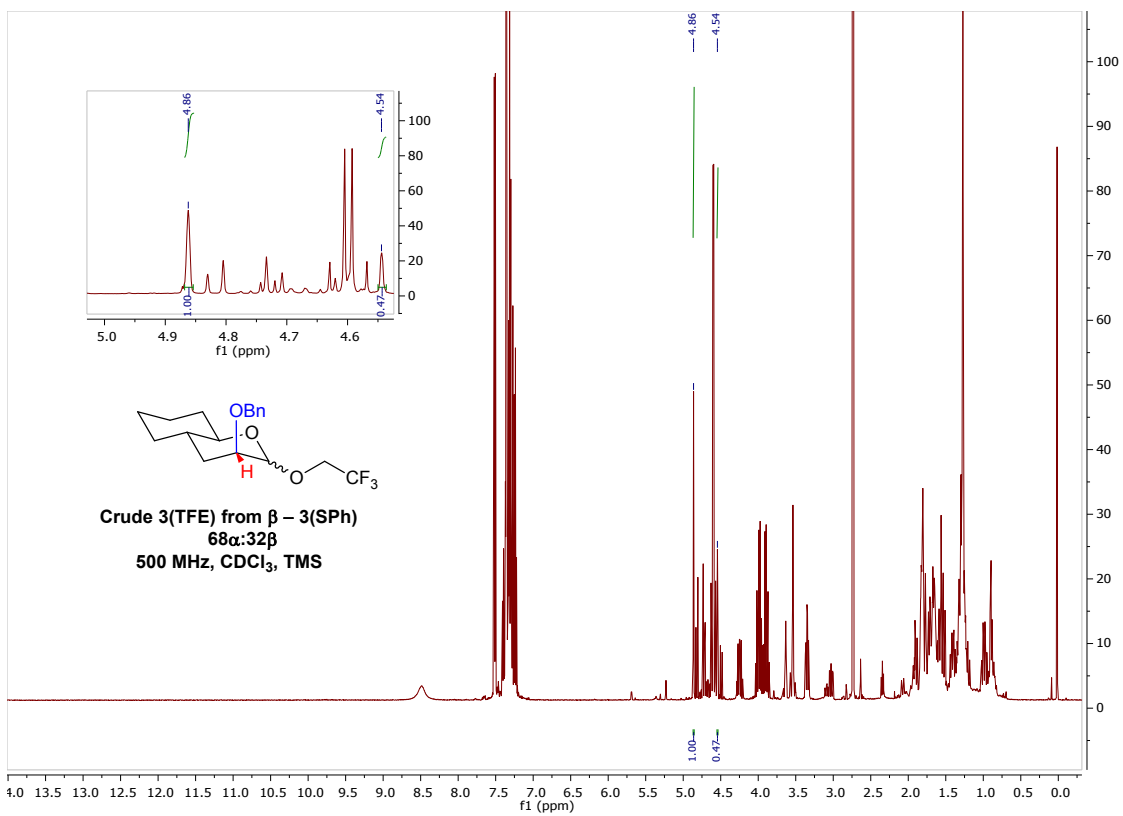


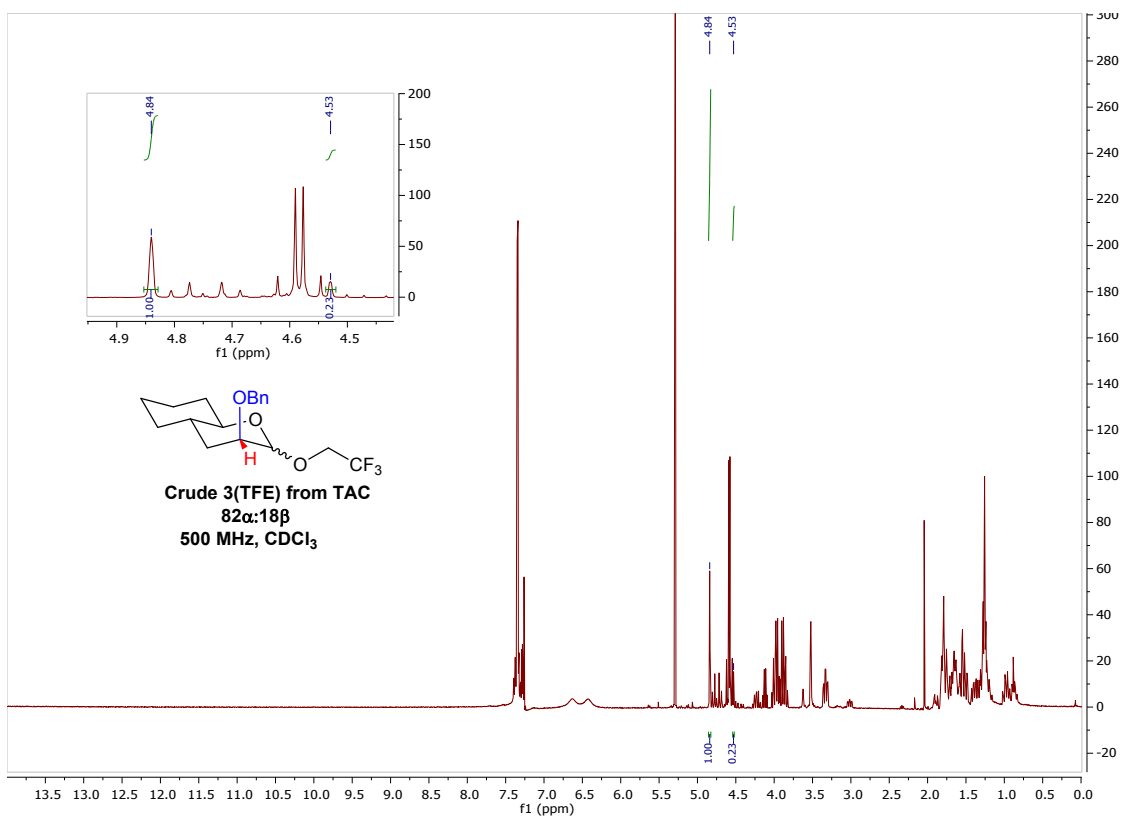
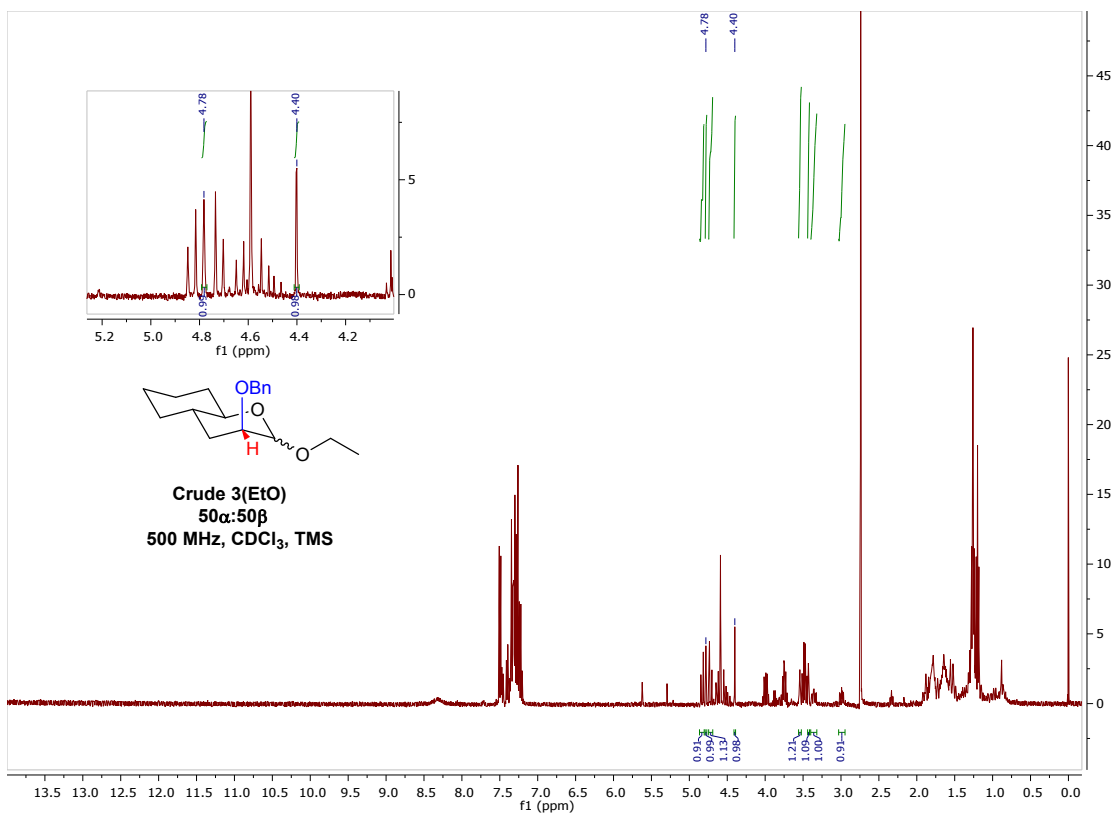


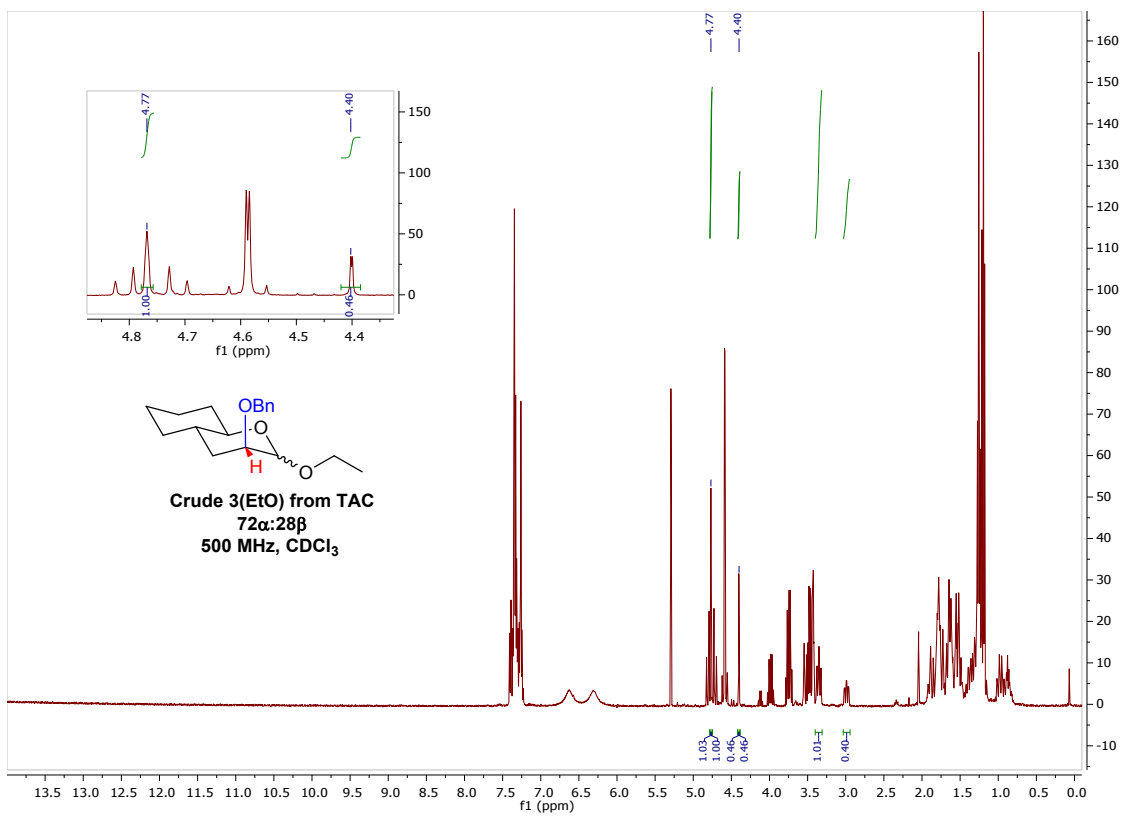




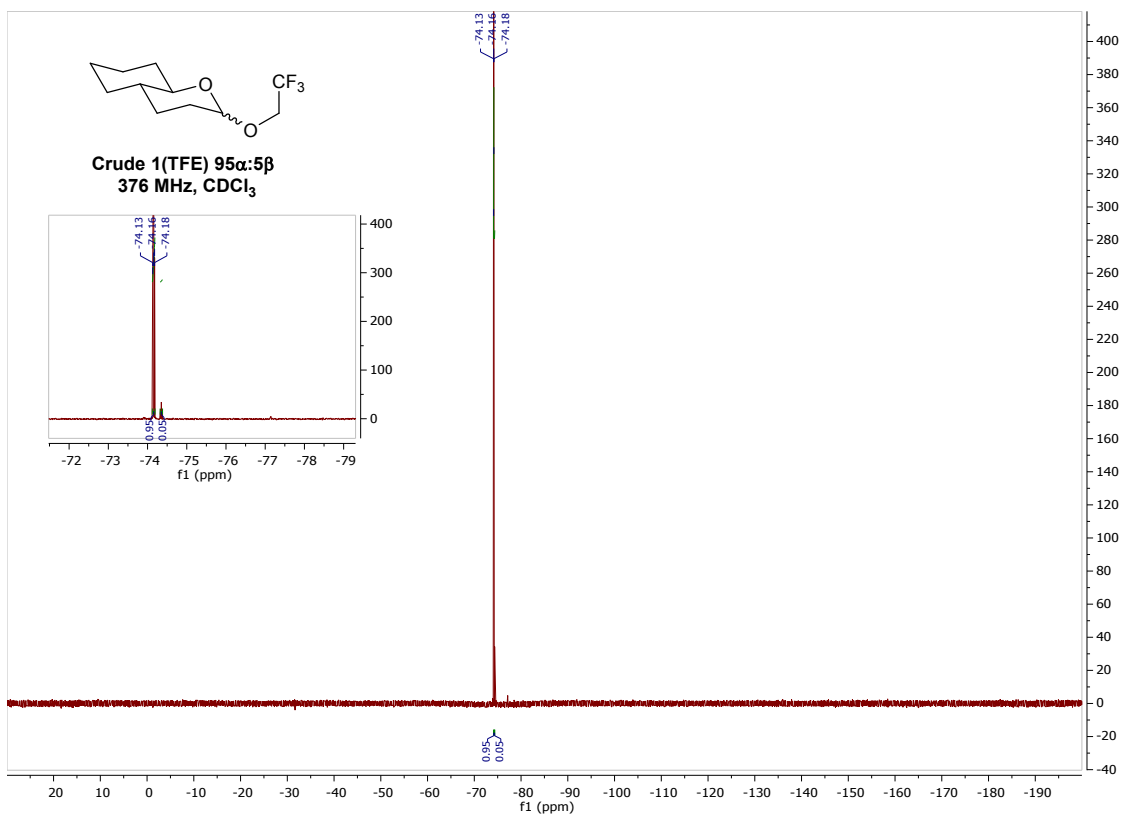
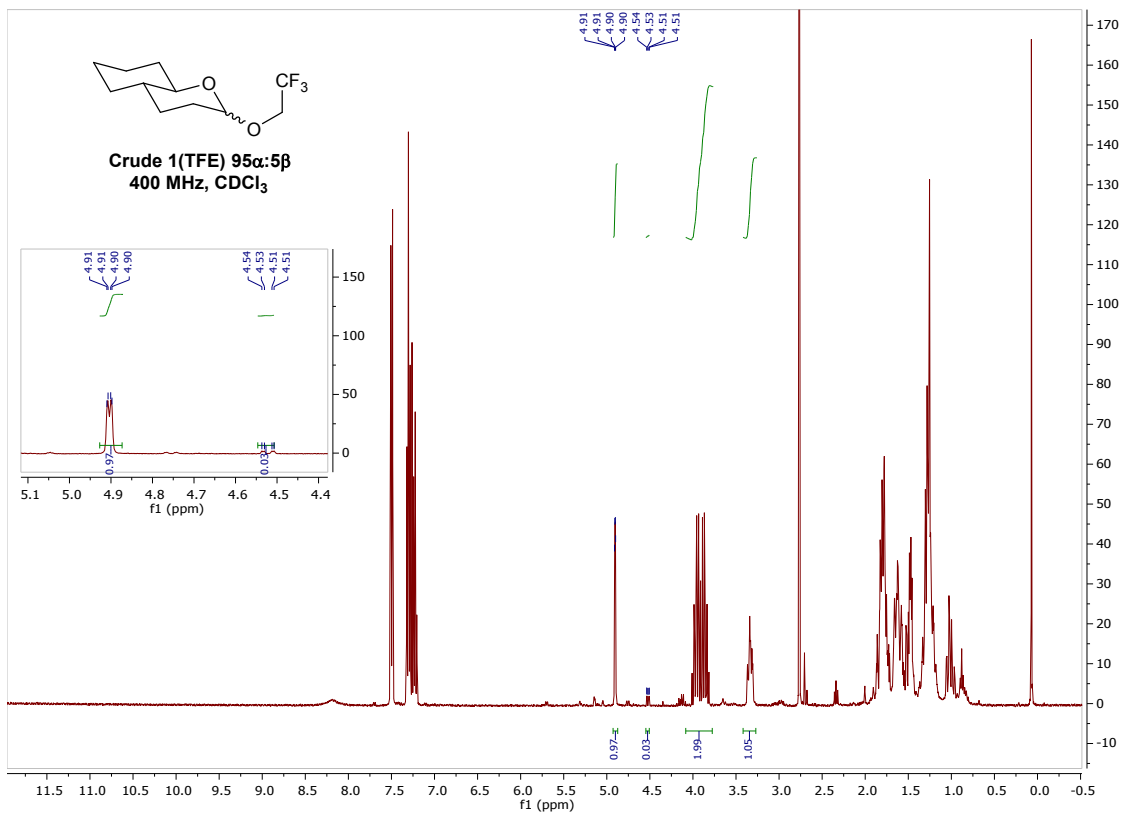


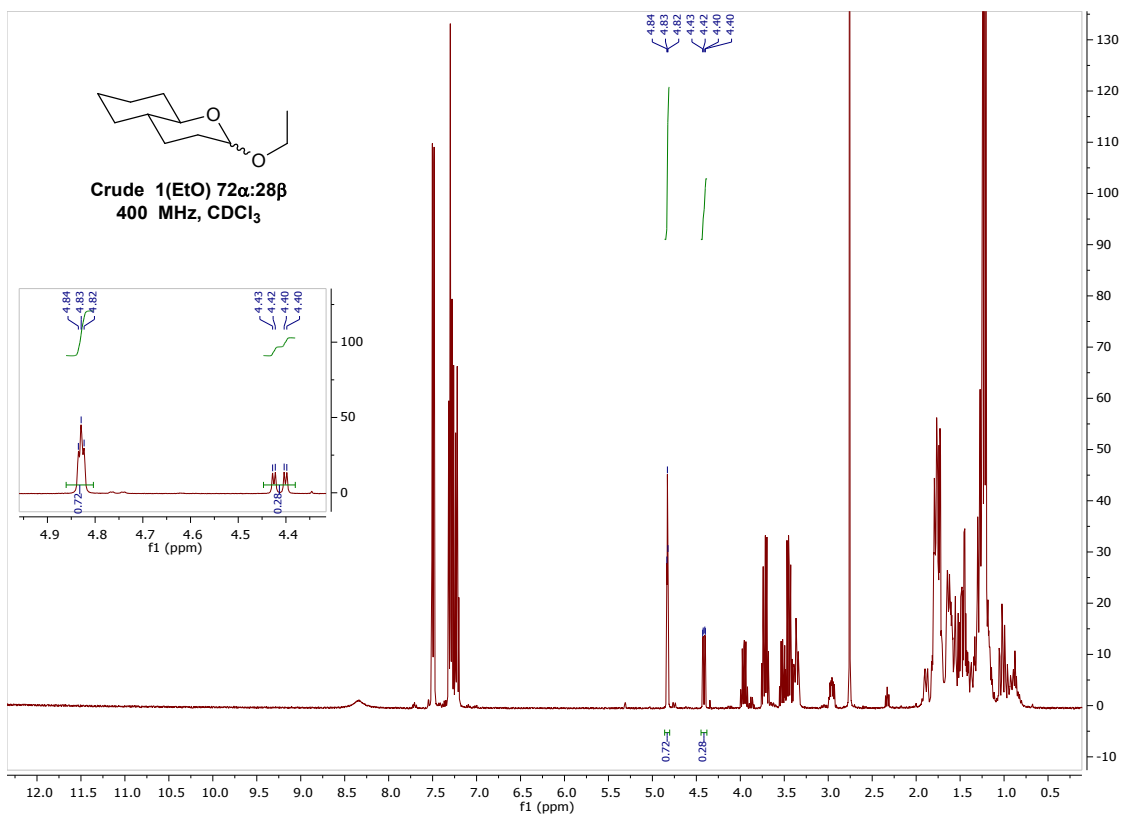
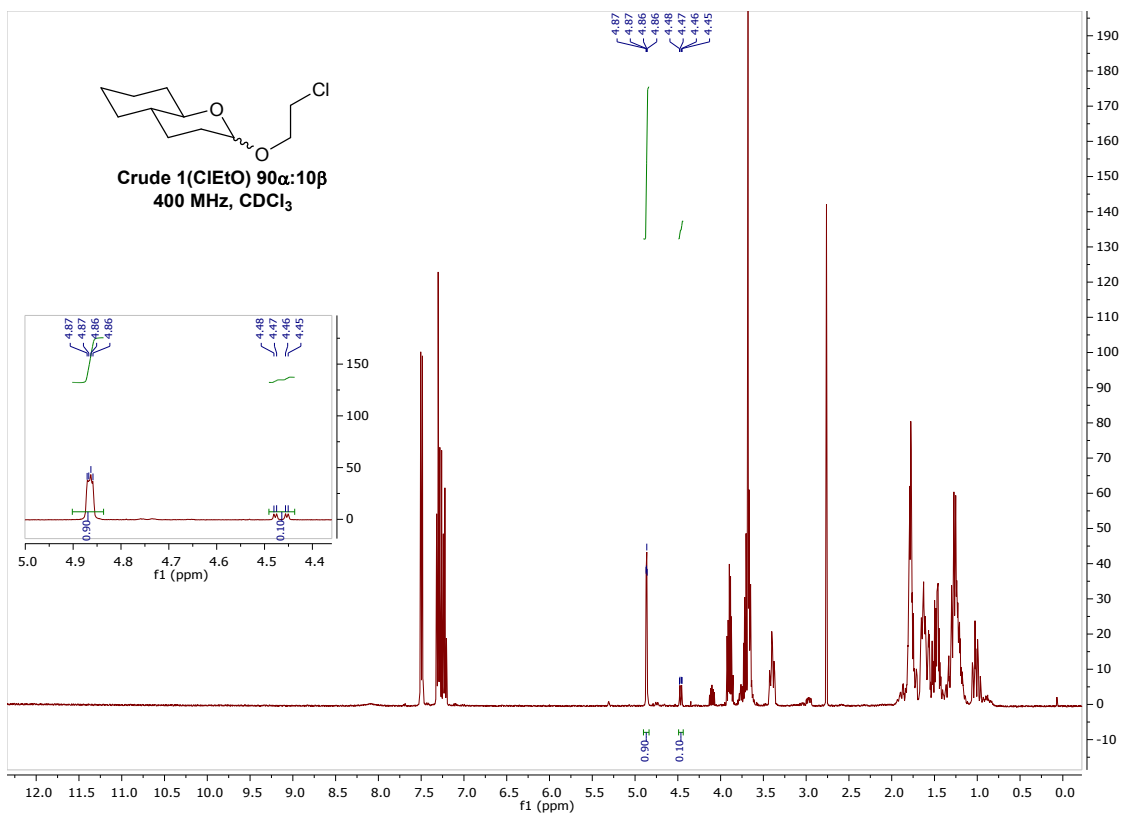


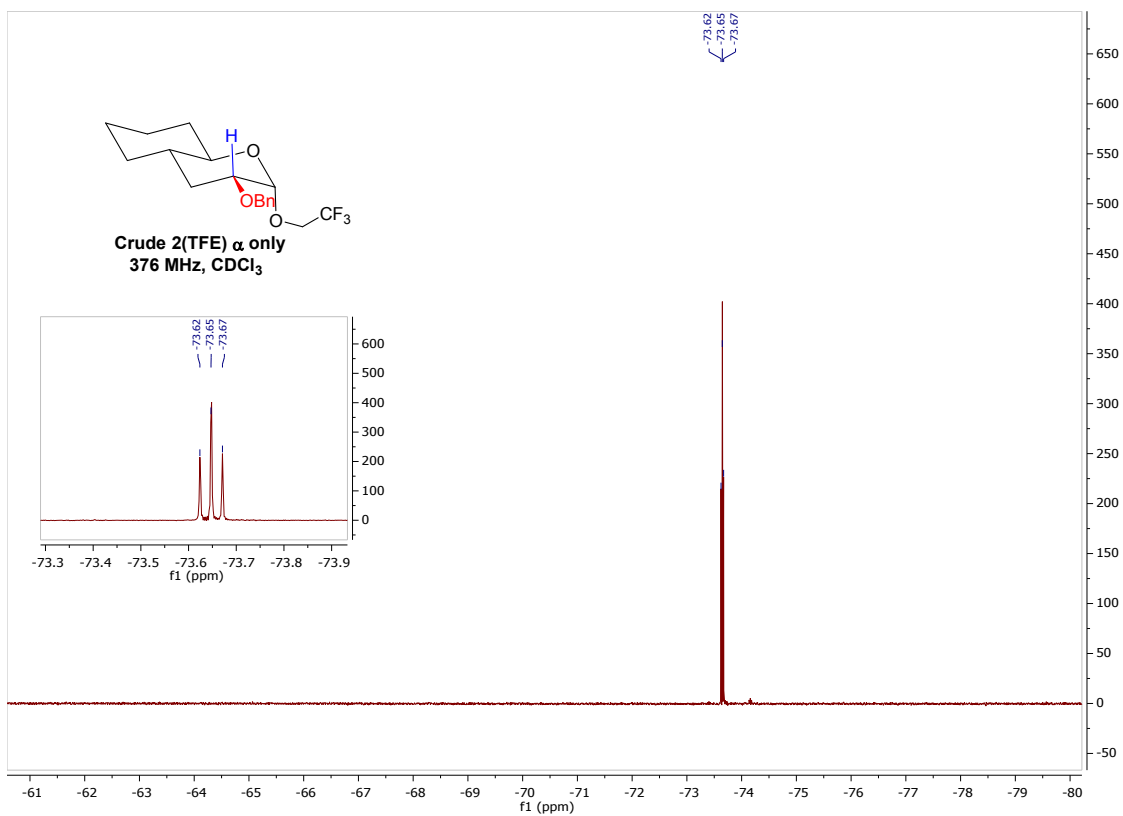
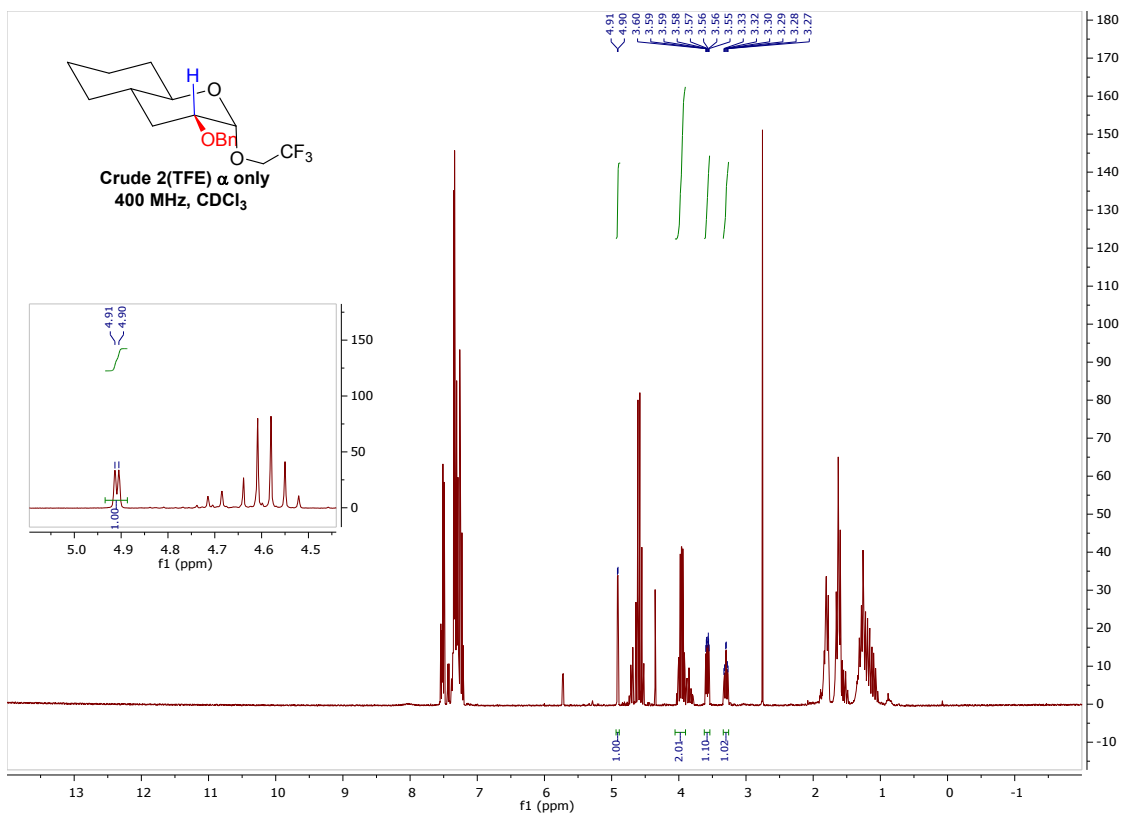


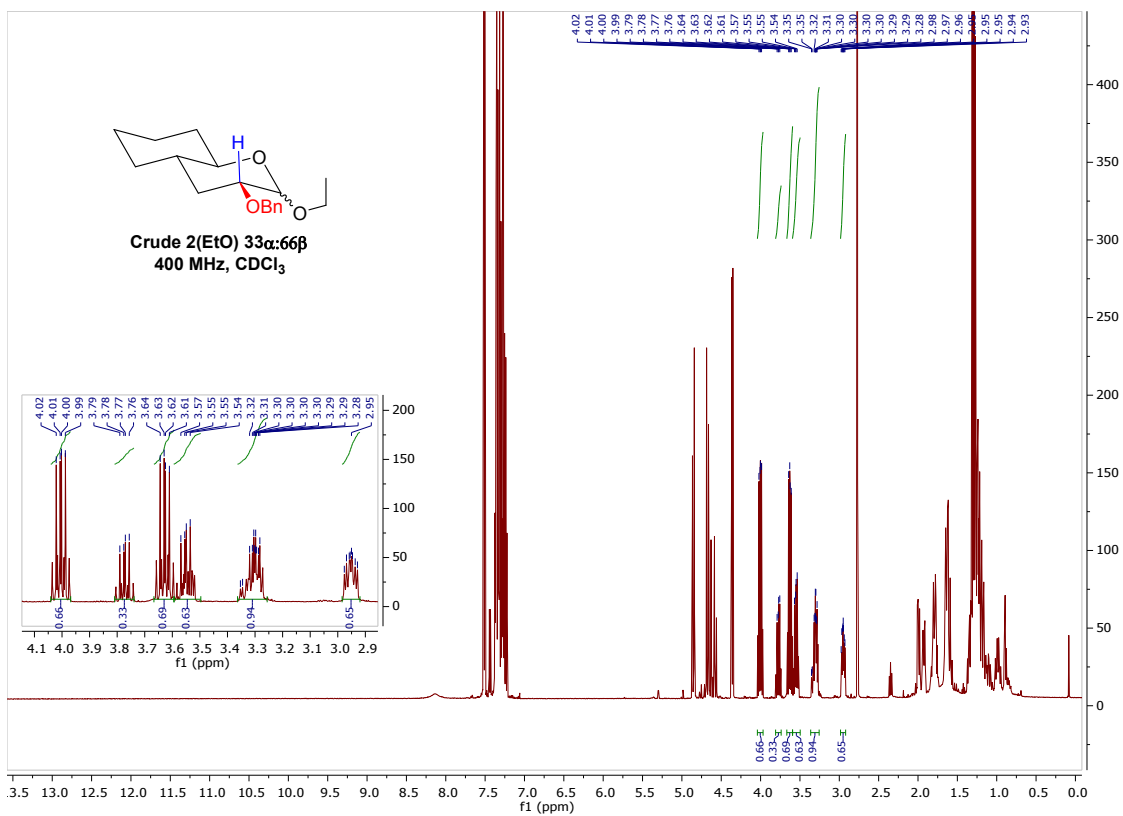
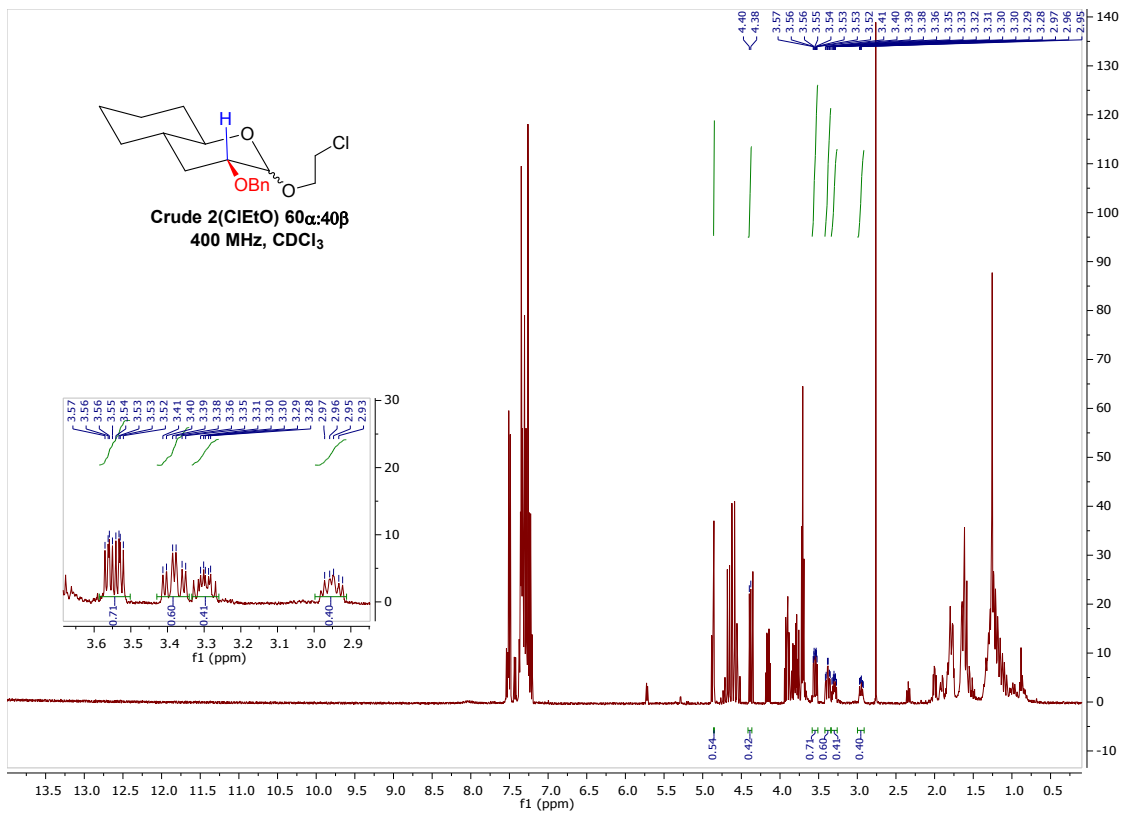


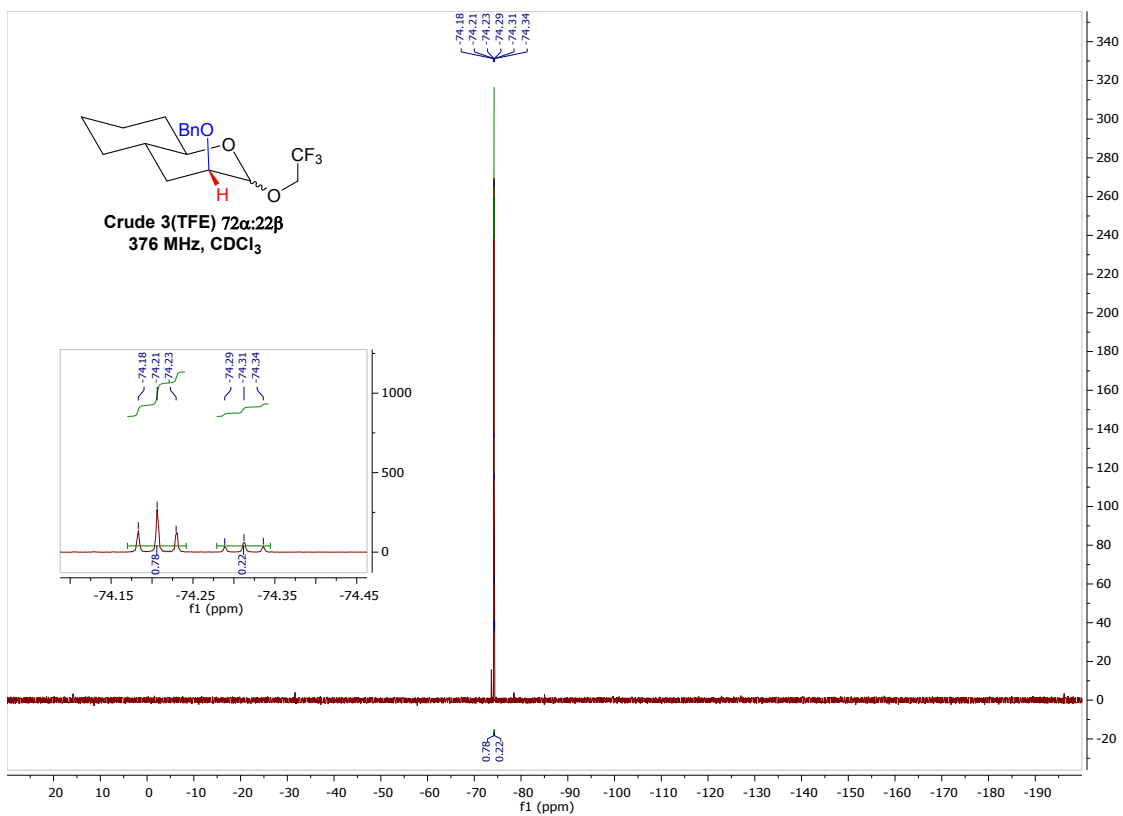
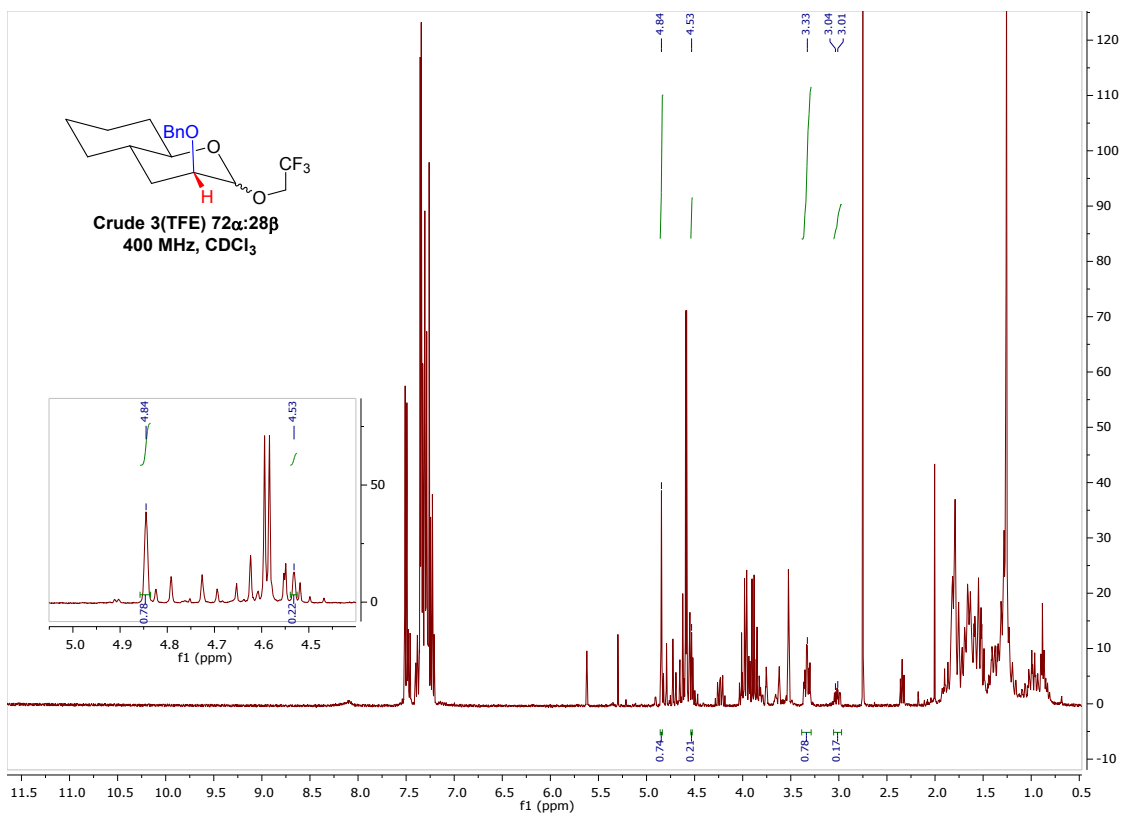
Crude ¹H NMR spectra from O-glycosylation in CH₃CN

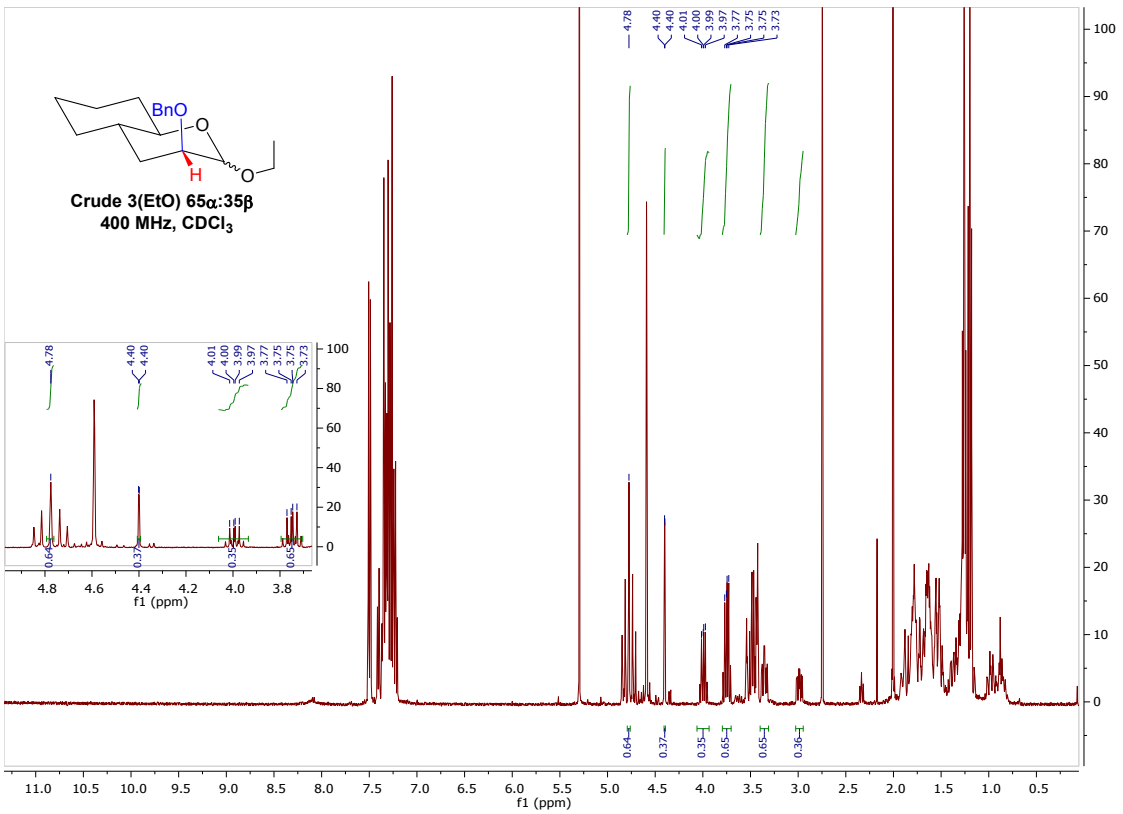
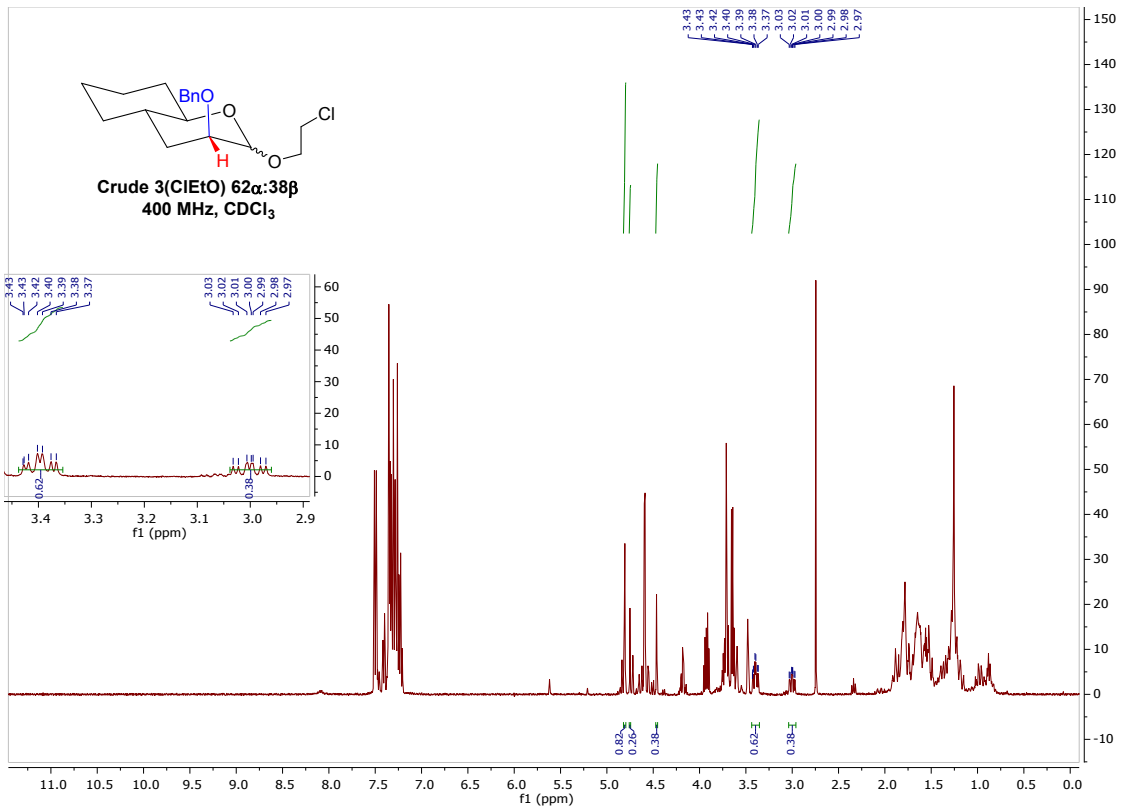


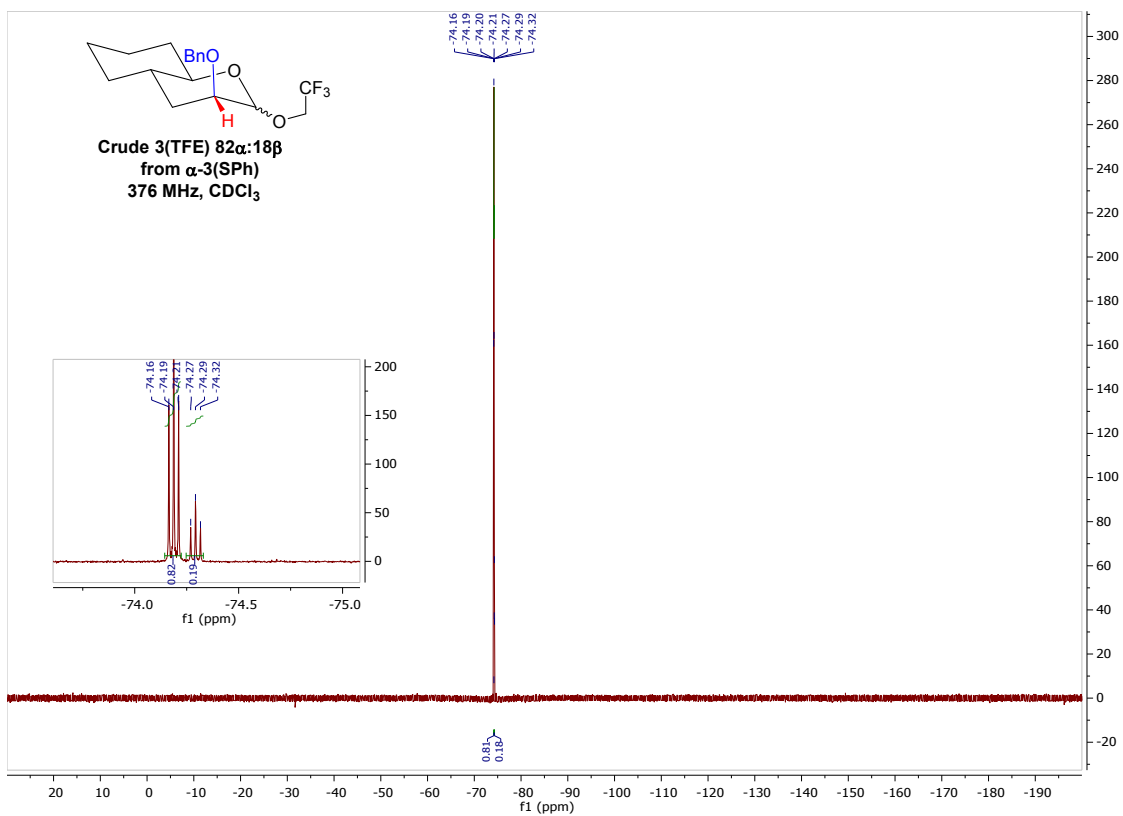
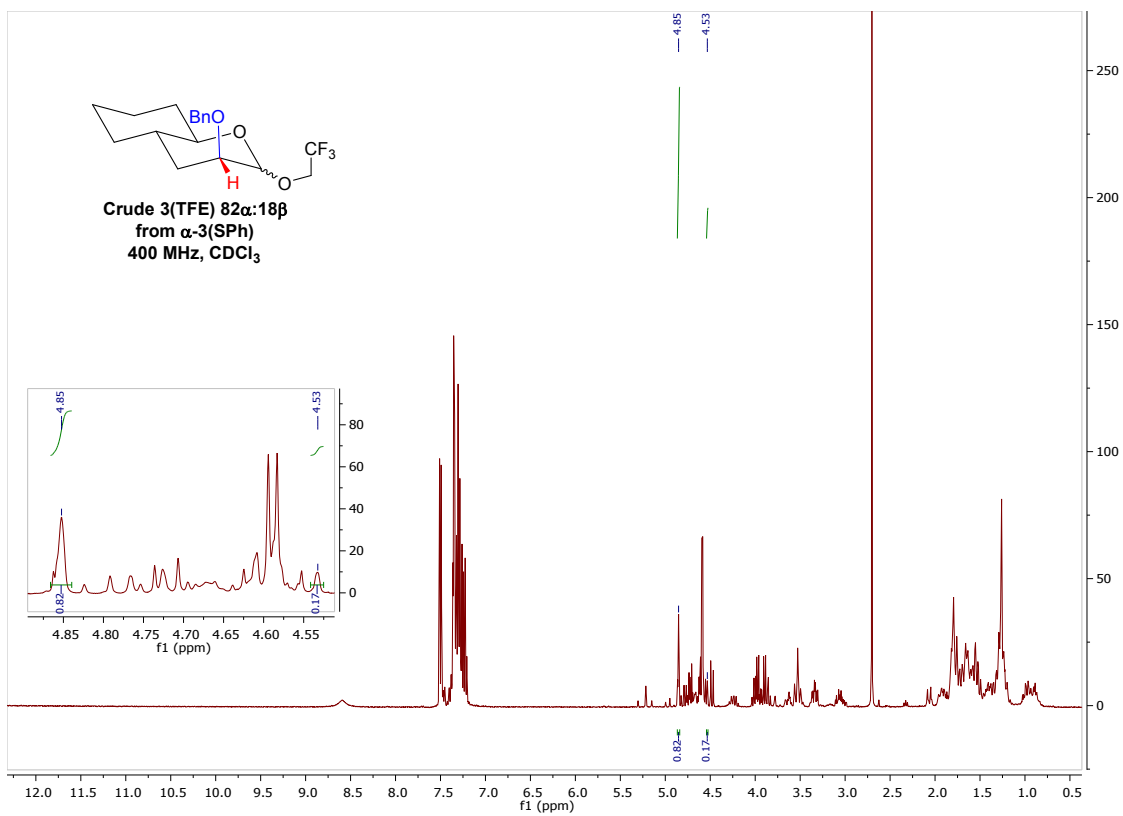












Crude ^1H NMR and ^{19}F NMR of kinetic control experiments

