

Supplementary Materials

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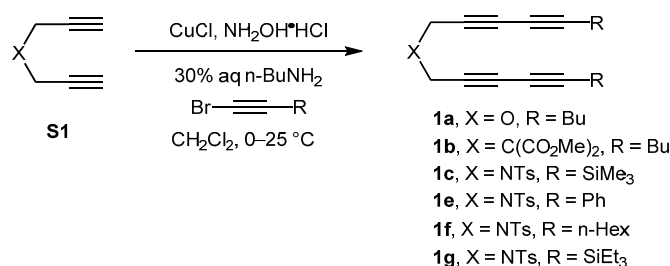
1. General Information

Reactions were carried out in oven-dried glassware unless otherwise noted. Compounds were purchased from Aldrich or Acros or TCI America or Oakwood Chemicals unless otherwise noted. Toluene, acetonitrile and dichloromethane were distilled over calcium hydride (CaH_2) under nitrogen atmosphere. THF was distilled over sodium-benzophenone ketyl under nitrogen atmosphere. Column chromatography was performed using silica gel 60 Å (32–63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck precoated silica gel 60 (particle size 0.040–0.063 mm). ^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker AV-500 spectrometer. ^{19}F -NMR spectrum was recorded in Varian Mercury-Vx-300 spectrometer.

2. Preparation of Substrates

1,3-*bis*-Diyne were prepared following the multistep procedure described below.

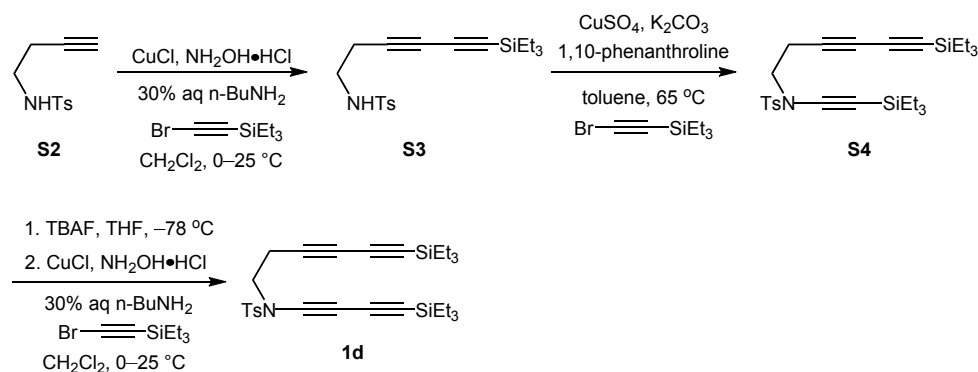
2.1. Symmetrical 1,3-*bis*-Diyne



General Procedure for the Cadiot–Chodkiewicz Reaction

In a two-neck round-bottom flask containing CuCl (1.2 mmol, 0.6 equiv.) was added 30% aqueous *n*-BuNH₂ solution (4 mL/mmol of diyne) under nitrogen flow. A pinch of NH₂OH·HCl was added until a blue color disappeared. A solution of diyne (2.0 mmol, 1 equiv.) in dichloromethane was added at 0 °C to the flask and the solution became yellow. A solution of alkynyl bromide (5.0 mmol, 2.5 equiv.) in dichloromethane was added drop wise at 0 °C. The reaction mixture was stirred at room temperature until completion of the reaction monitored by TLC. The nitrogen flow was removed and the biphasic reaction mixture was transferred to a separatory funnel. Dichloromethane layer was separated and dried over anhydrous MgSO₄. After filtration, the organic layer was concentrated and the crude material was purified by column chromatography to get pure tetraynes.

2.2. Unsymmetrical 1,3-bis-diyne 1d



2.2.1. Procedure for the Synthesis of S3

In a two-neck round-bottomed flask containing CuCl (0.6 mmol, 0.3 equiv) was added 30% aqueous $n\text{-BuNH}_2$ solution (2 mL/mmol of **S2**) under nitrogen flow. A pinch of $\text{NH}_2\text{OH}\cdot\text{HCl}$ was added until a blue color disappeared. A solution of the terminal alkyne **S2** (2.0 mmol, 1.0 equiv.) in dichloromethane was added at $0\text{ }^\circ\text{C}$ to the flask and the solution became yellow. A solution of alkynyl bromide (2.4 mmol, 1.2 equiv.) in dichloromethane was added drop wise at $0\text{ }^\circ\text{C}$. The reaction mixture was stirred at room temperature until completion of the reaction monitored by TLC. The nitrogen flow was removed and the biphasic reaction mixture was transferred to a separatory funnel. Dichloromethane layer was separated and dried over anhydrous MgSO_4 . After filtration, the organic layer was concentrated and the crude material was purified by column chromatography (Hex–EtOAc, 10:1 to 5:1) to get pure **S3** (90% yield).

2.2.2. Procedure for the Synthesis of S4

A mixture of **S3** (1.5 mmol, 1.0 equiv.), $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (0.15 mmol, 10 mol %), 1,10-phenanthroline (0.3 mmol, 20 mol %), K_2CO_3 (3.0 mmol, 2.0 equiv.) and (bromoethynyl)triethylsilane (2.3 mmol, 1.5 equiv.) in dry toluene (10 mL) was stirred at $65\text{ }^\circ\text{C}$ for overnight. After completion, the reaction mixture was cooled down to room temperature and filtered through a small pad of silica gel. The filtrate was concentrated under reduced pressure and the crude was purified by column chromatography (Hex–EtOAc, 20:1 to 10:1) to get pure **S4** (82% yield).

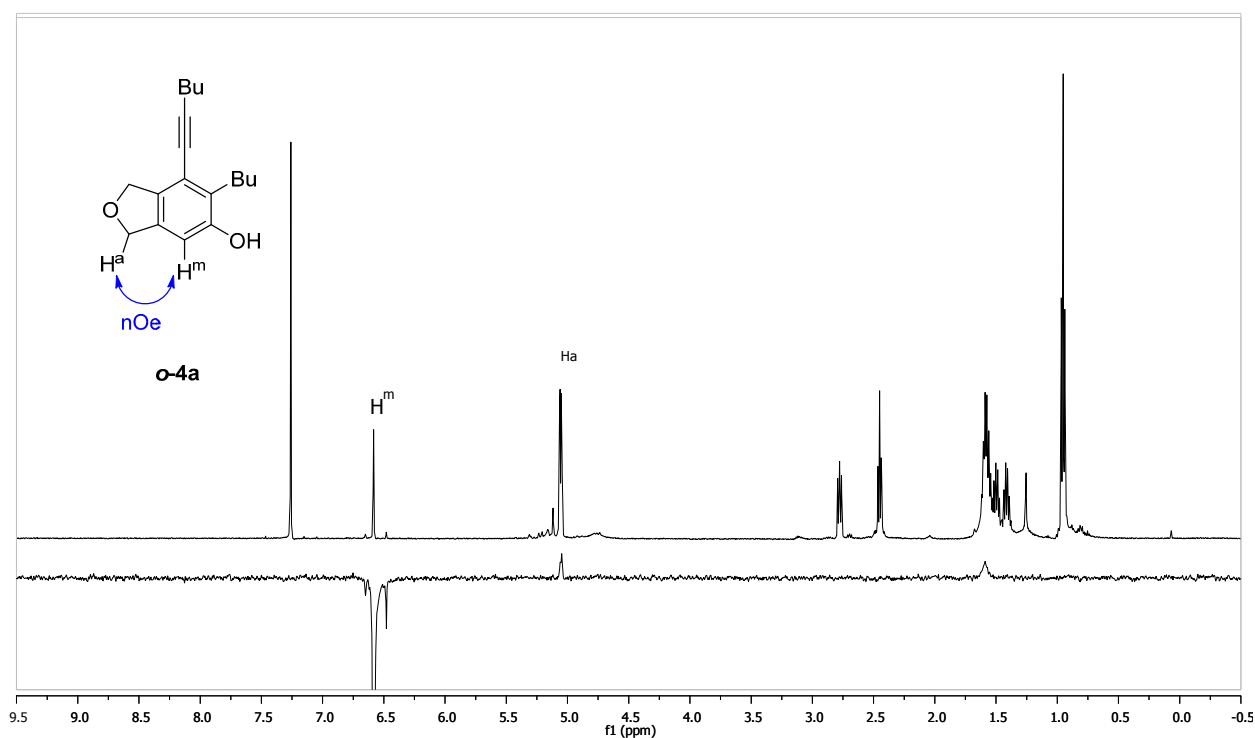
2.2.3. Procedure for the Synthesis of 1d

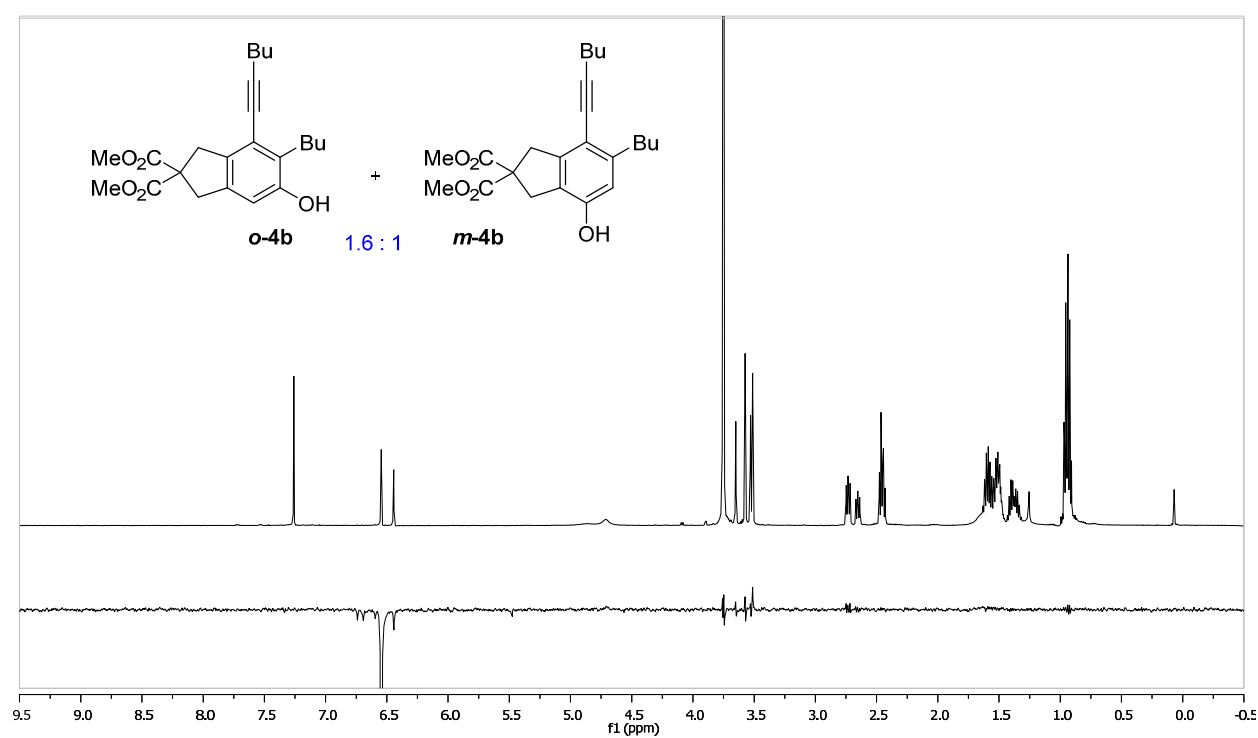
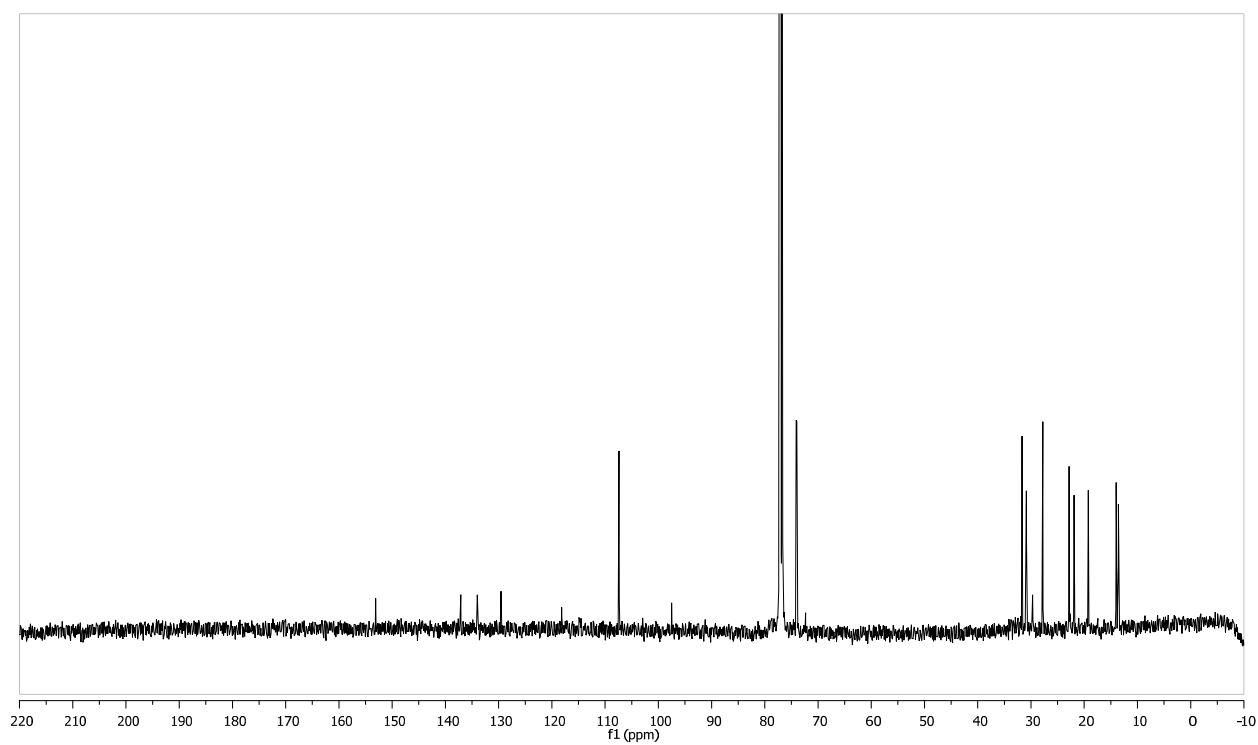
To a stirred solution of **S4** (1.0 mmol, 1 equiv.) in THF at $-78\text{ }^\circ\text{C}$, was added TBAF (1.1 mmol, 1.1 equiv.) slowly. After completion of the reaction (usually within a couple of minutes, monitored by TLC) the reaction mixture was diluted with ethyl acetate, transferred in a separatory funnel, washed successively with water and brine. The organic layer was separated, dried over anhydrous MgSO_4 , filtered, concentrated under reduced pressure and the crude triyne with terminal alkyne was used for the next step.

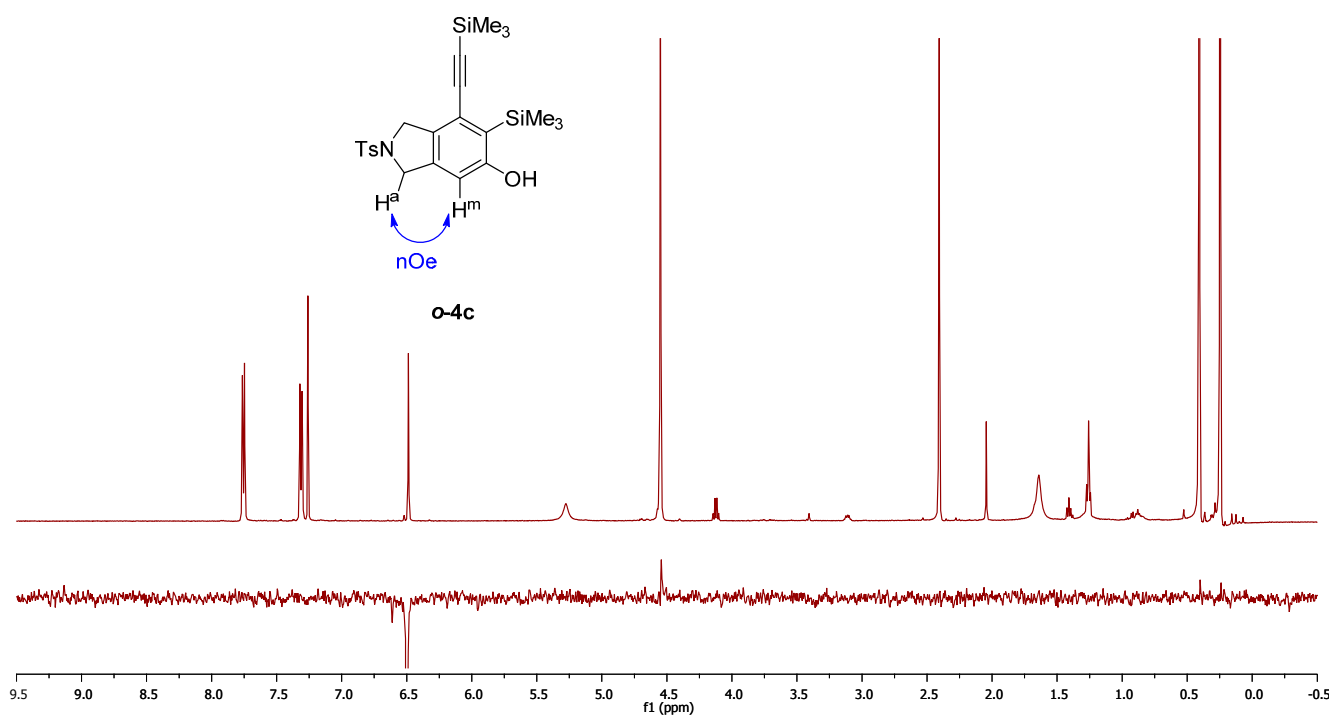
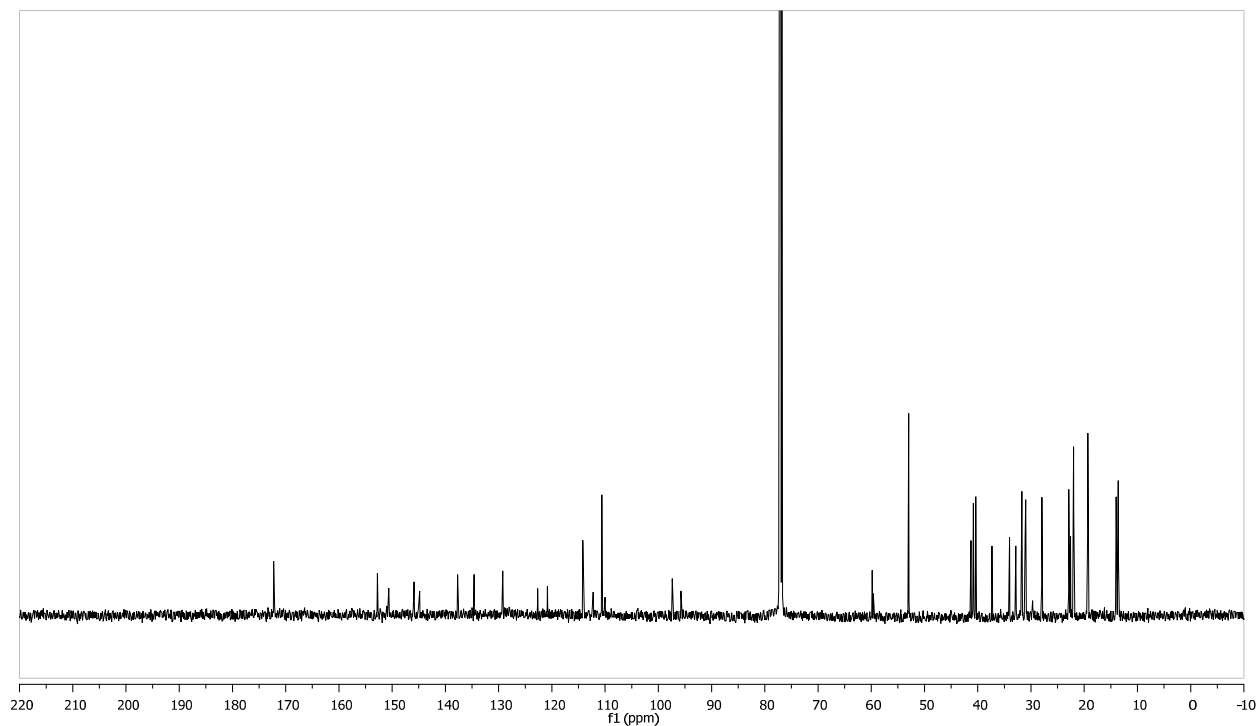
In a two-neck round-bottomed flask containing CuCl (0.3 mmol, 0.3 equiv.) was added 30% aqueous $n\text{-BuNH}_2$ solution (2 mL/mmol of the terminal alkyne) under nitrogen flow. A pinch of $\text{NH}_2\text{OH}\cdot\text{HCl}$ was added until a blue color disappeared. A solution of the crude alkyne (roughly 1.0 mmol) in

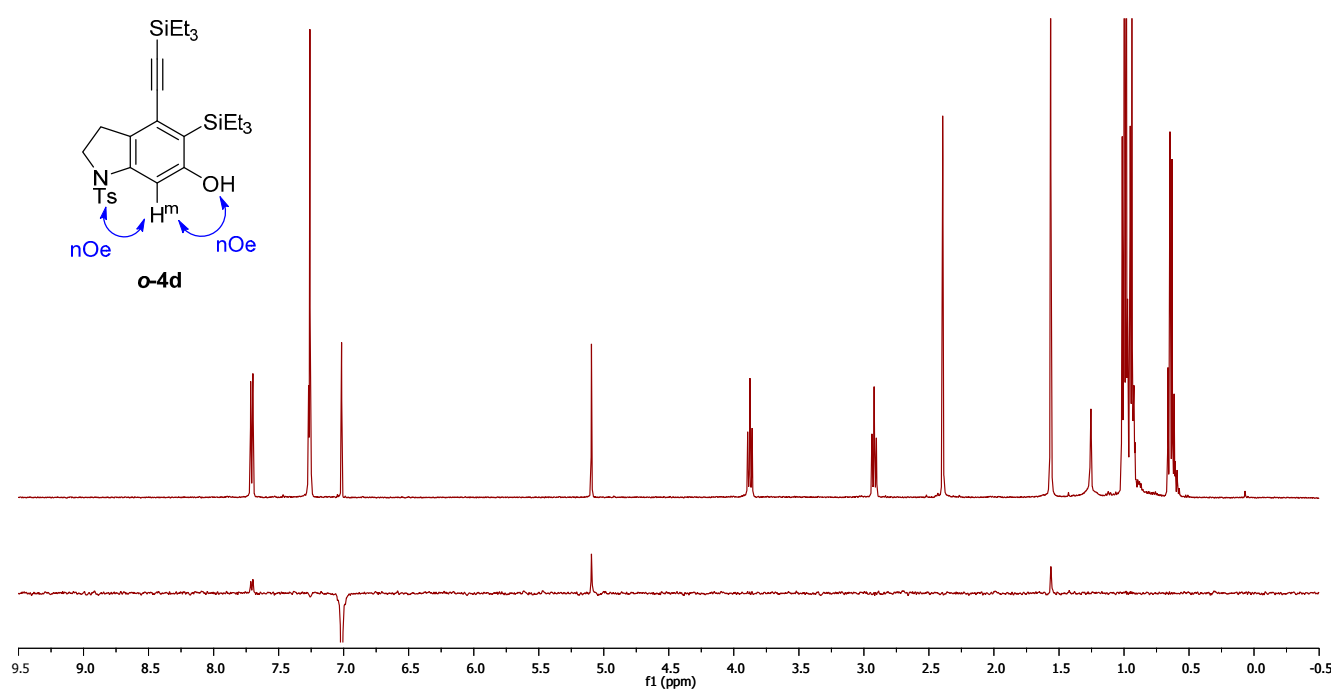
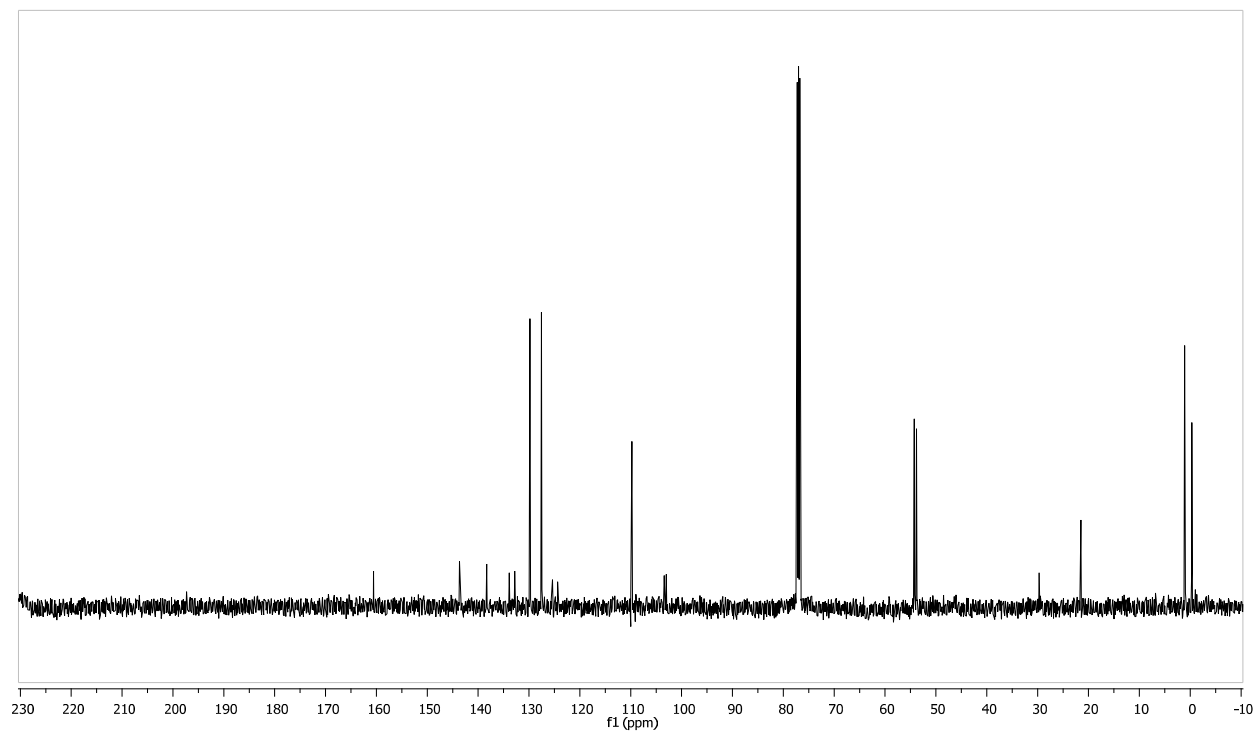
dichloromethane was added at 0 °C to the flask and the solution became yellow. A solution of alkynyl bromide (1.2 mmol, 1.2 equiv.) in dichloromethane was added drop wise at 0 °C. The reaction mixture was stirred until completion of the reaction monitored by TLC. The nitrogen flow was removed and the biphasic reaction mixture was transferred to a separatory funnel. Dichloromethane layer was separated and dried over anhydrous MgSO₄. After filtration, the organic layer was concentrated and the crude material was purified by column chromatography (Hex–EtOAc, 20:1 to 10:1) to get pure **1d** (88% yield, 2 steps).

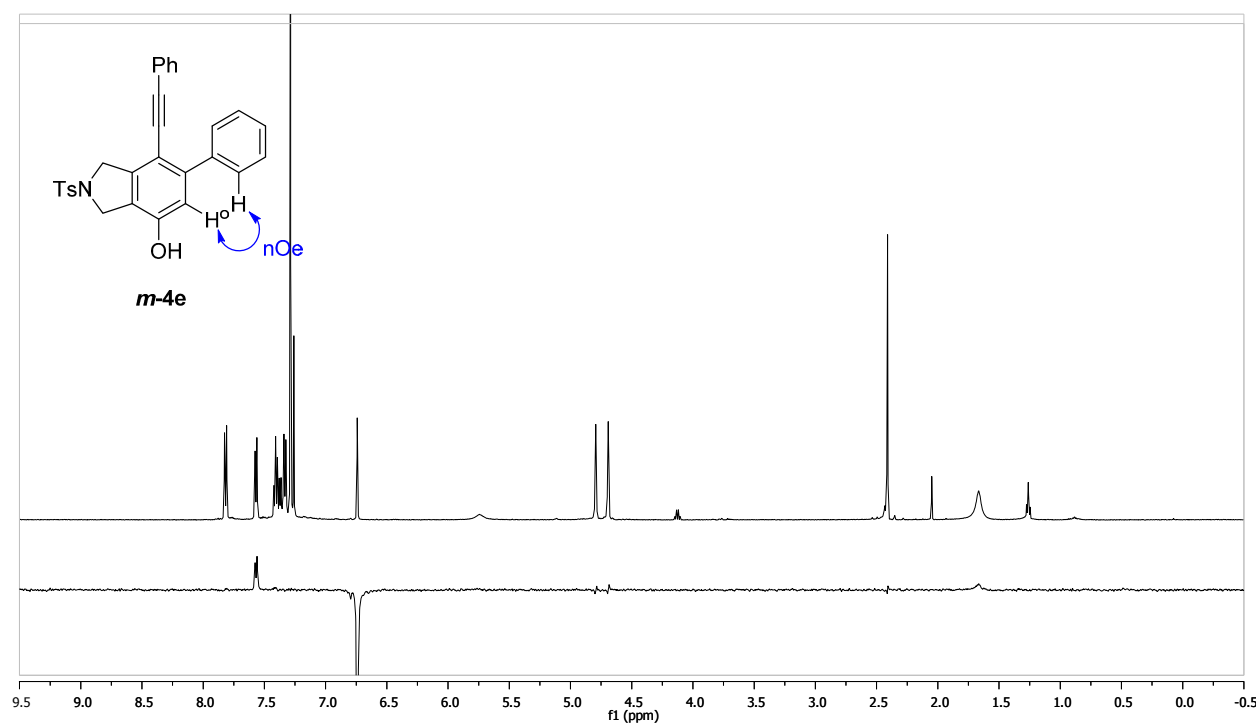
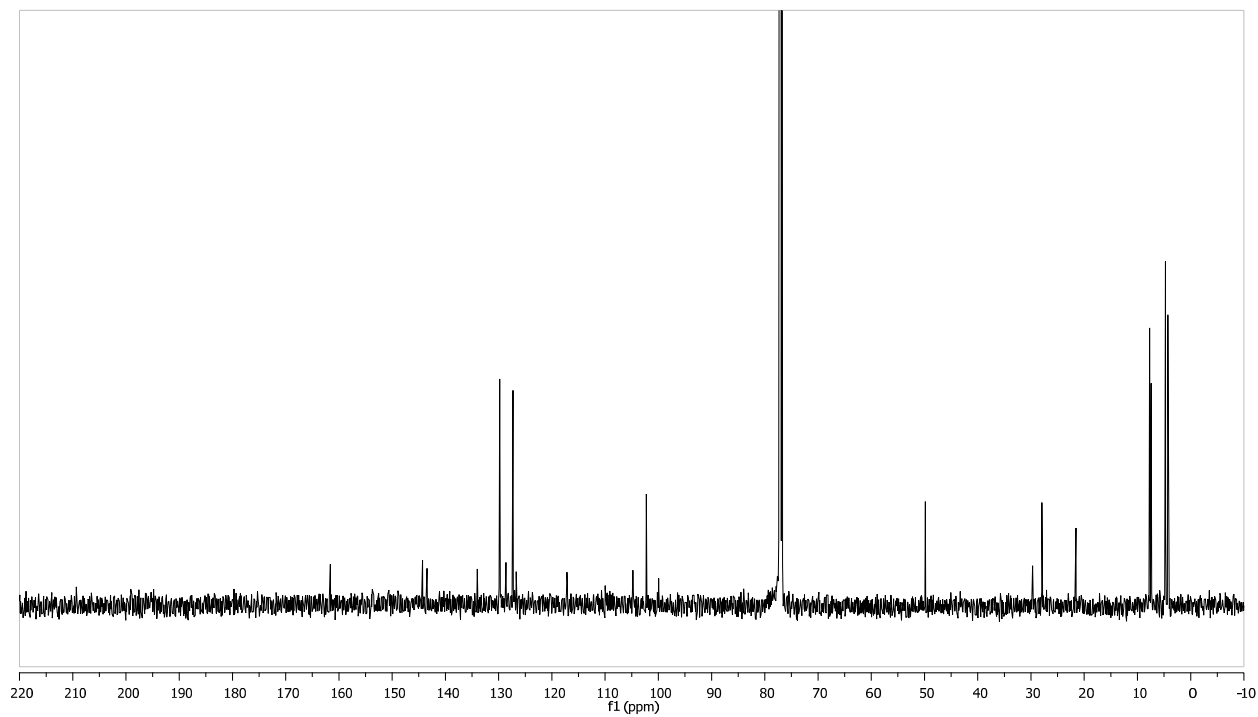
NMR Spectra of the Products

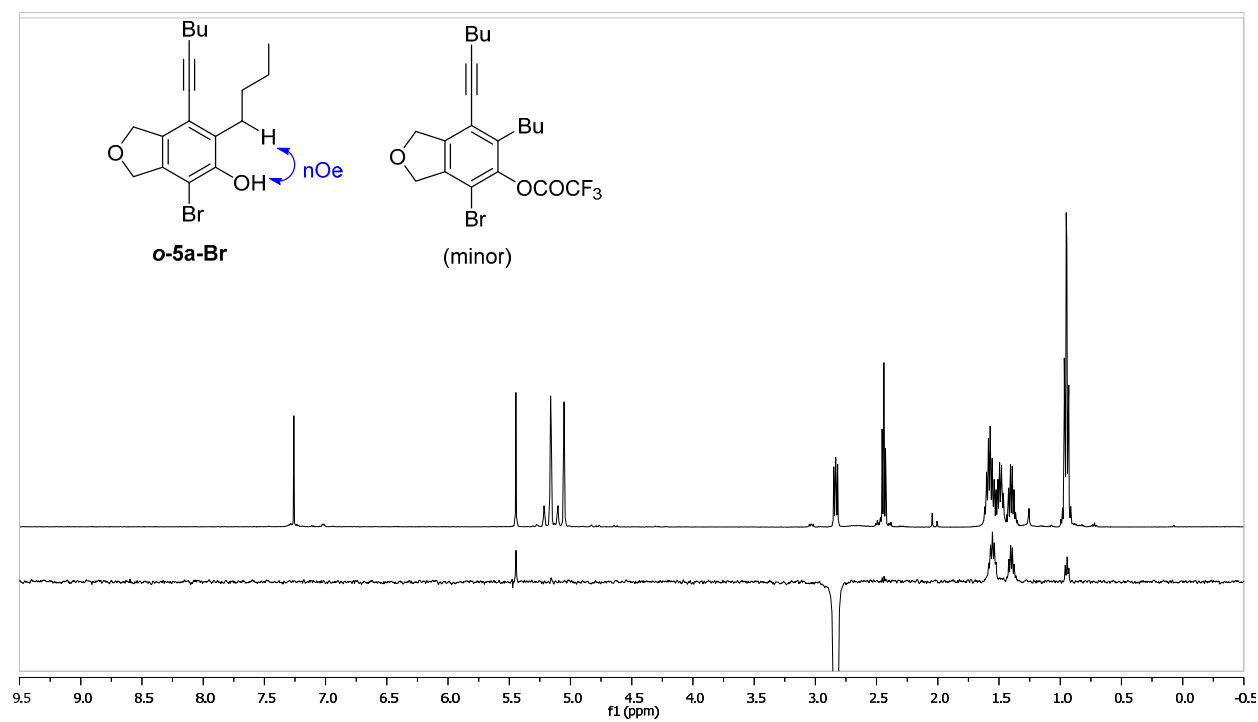
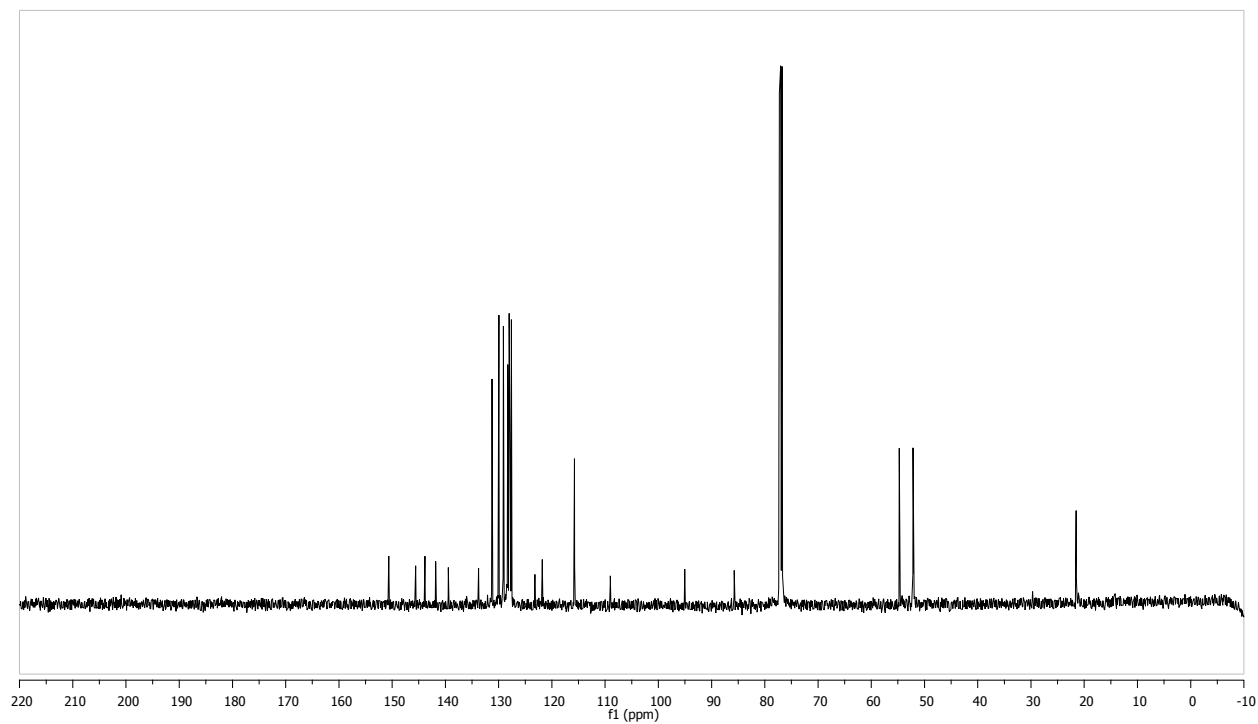


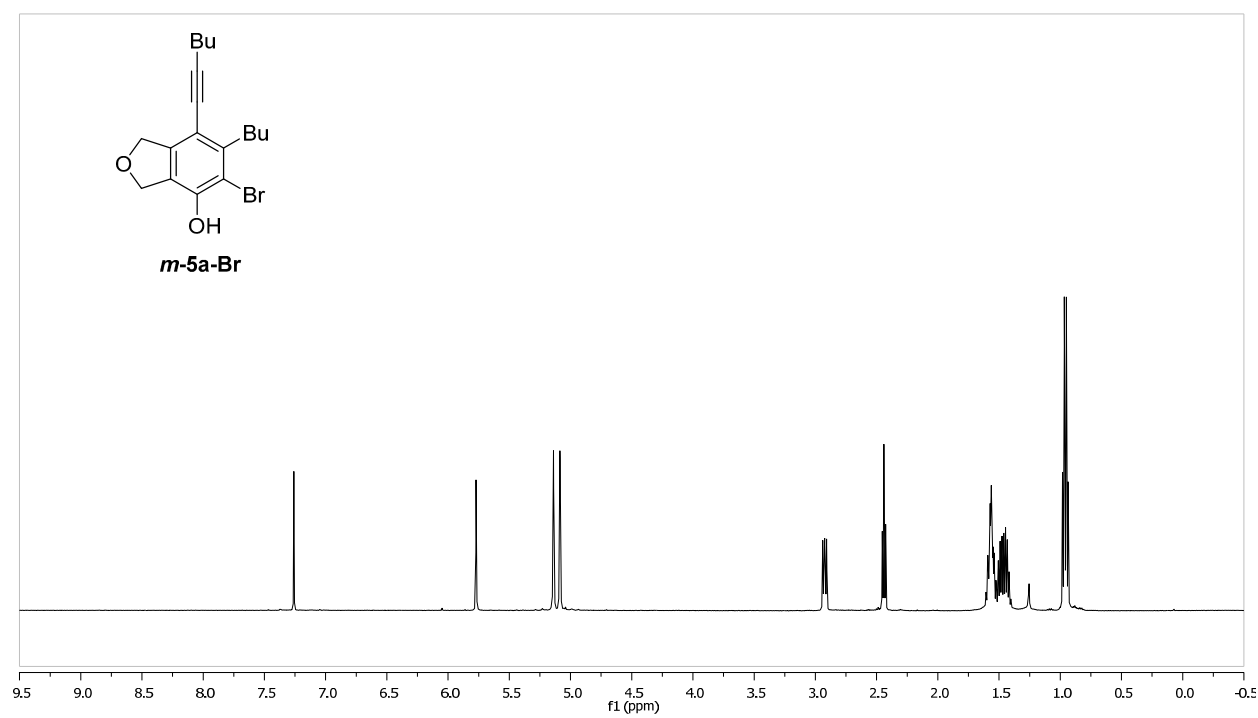
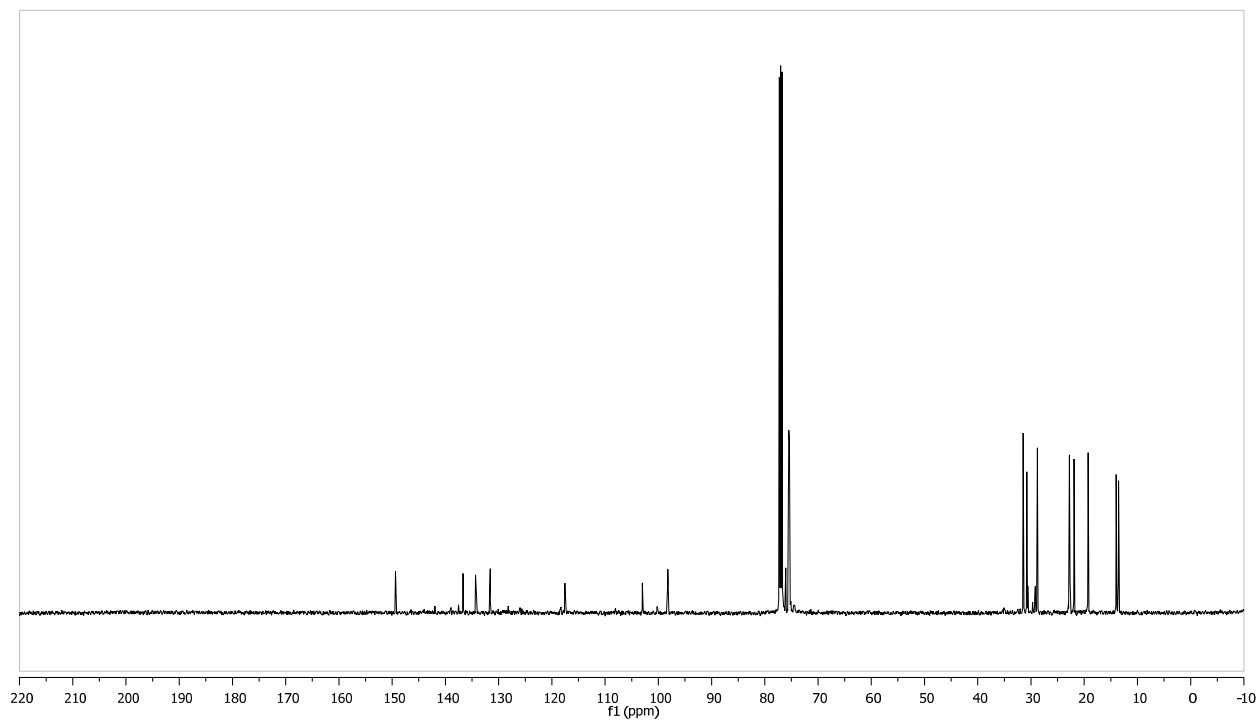


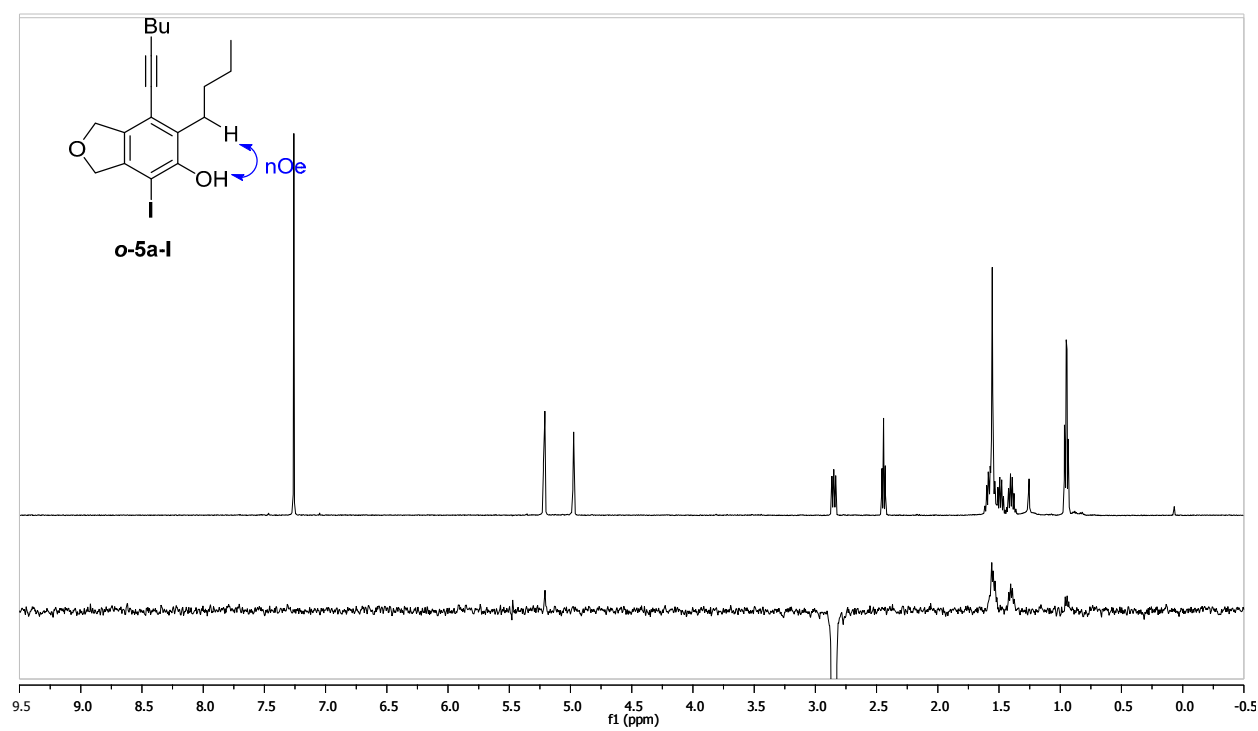
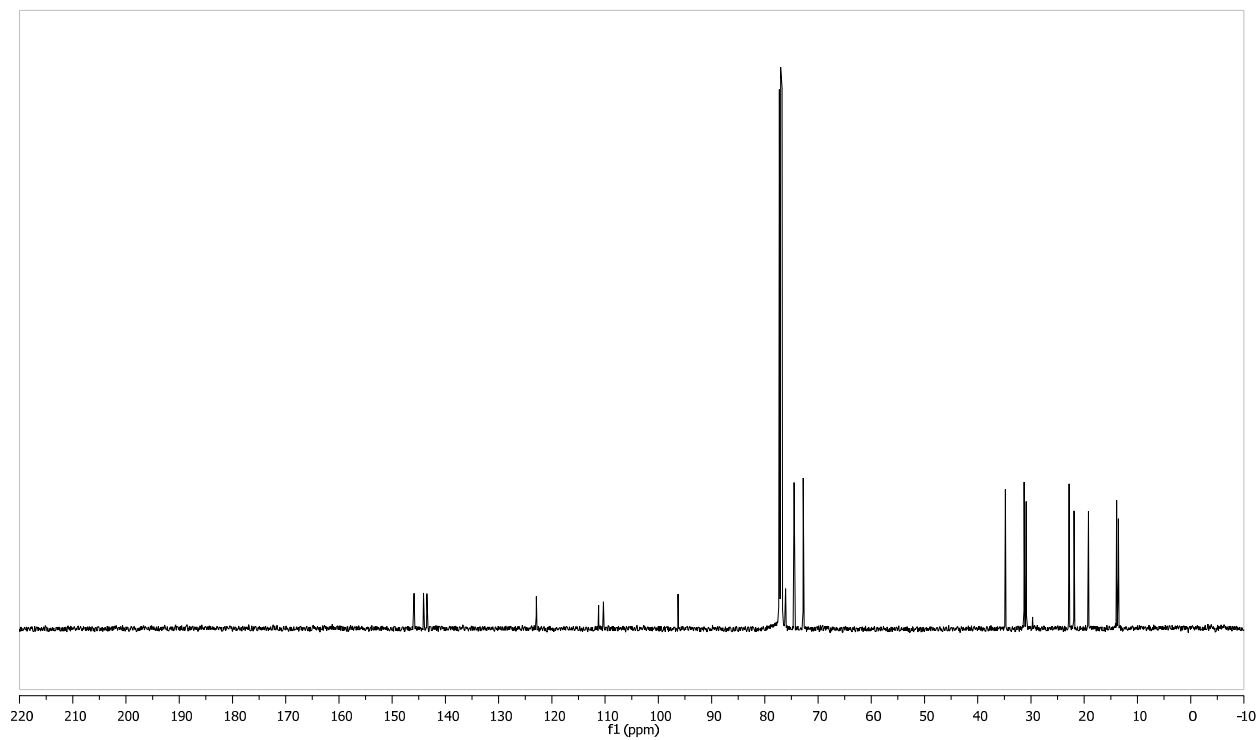


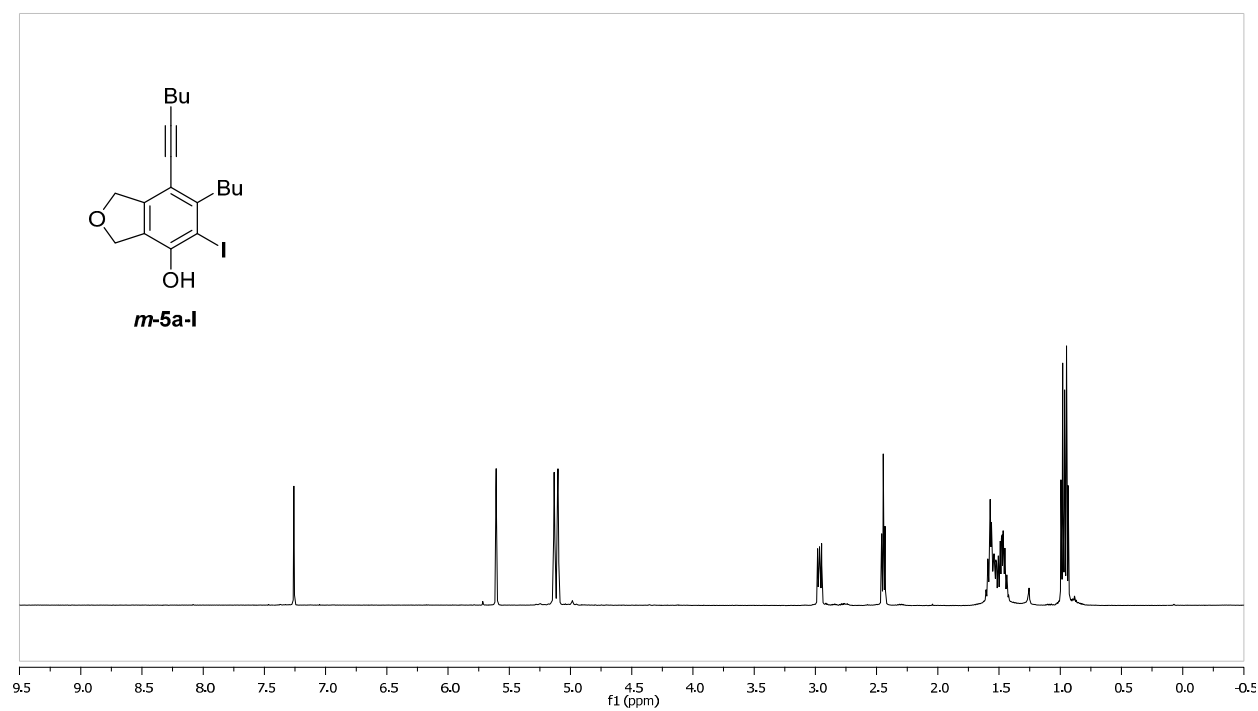
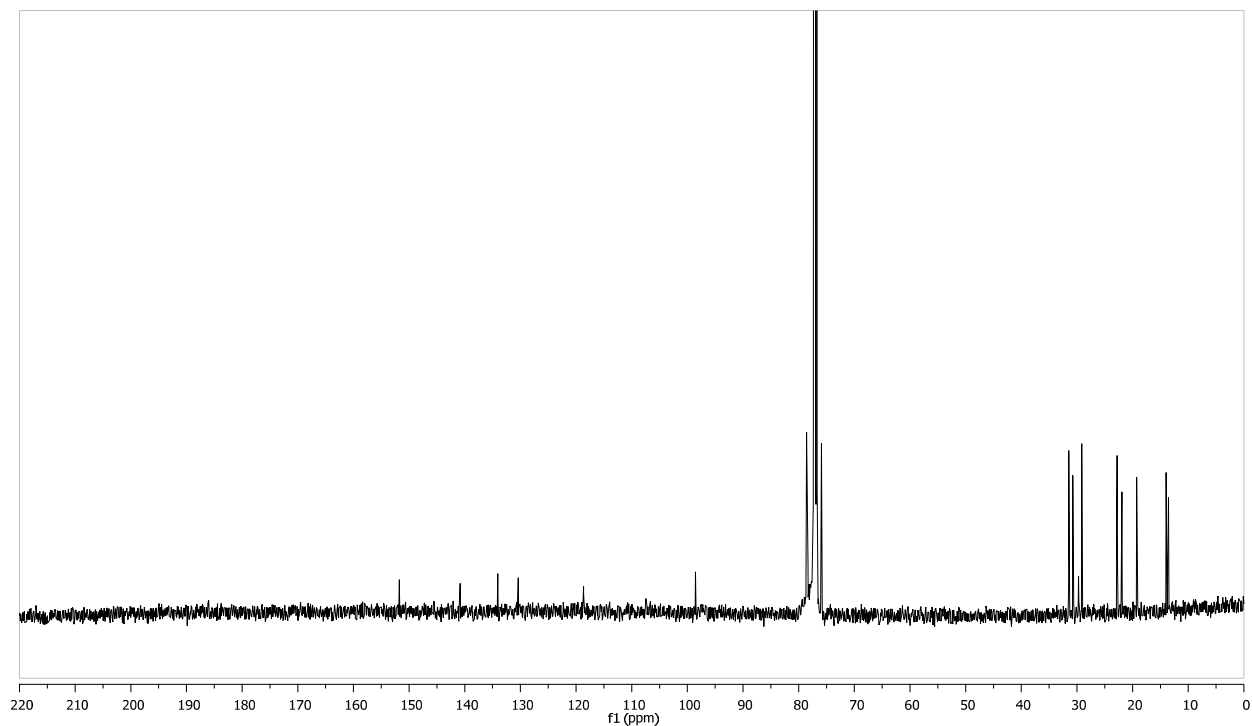


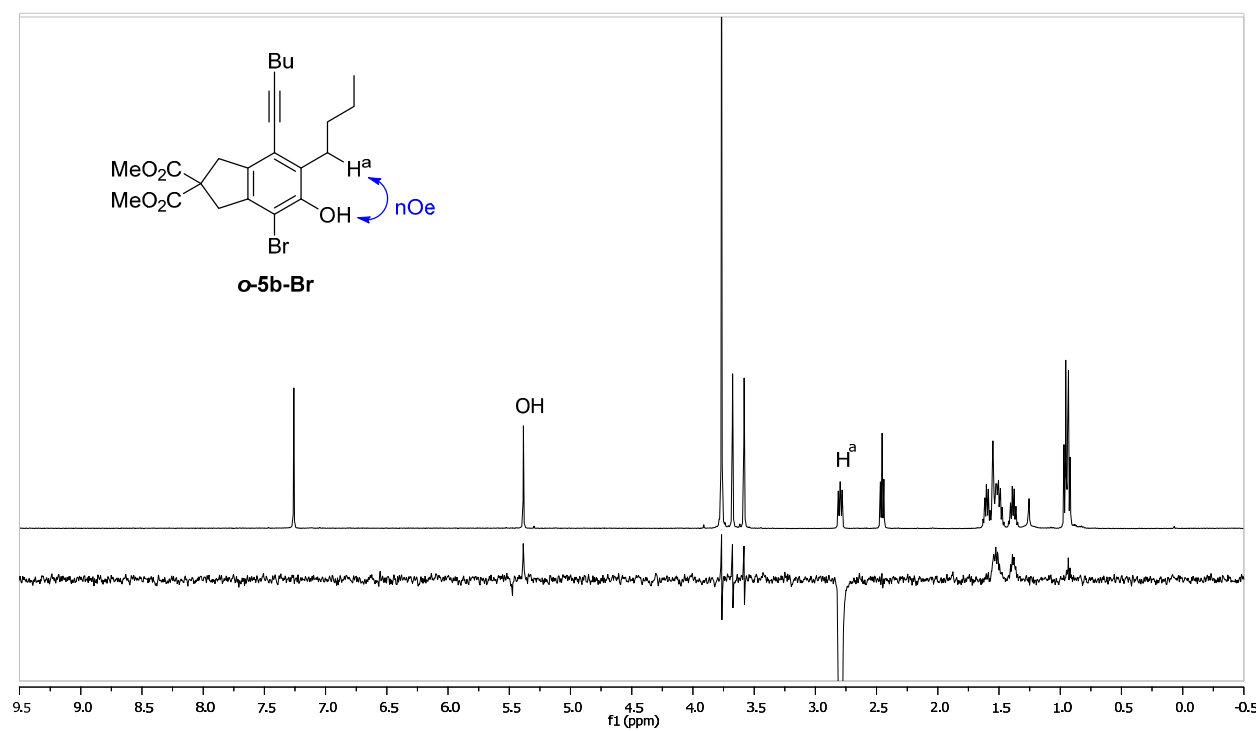
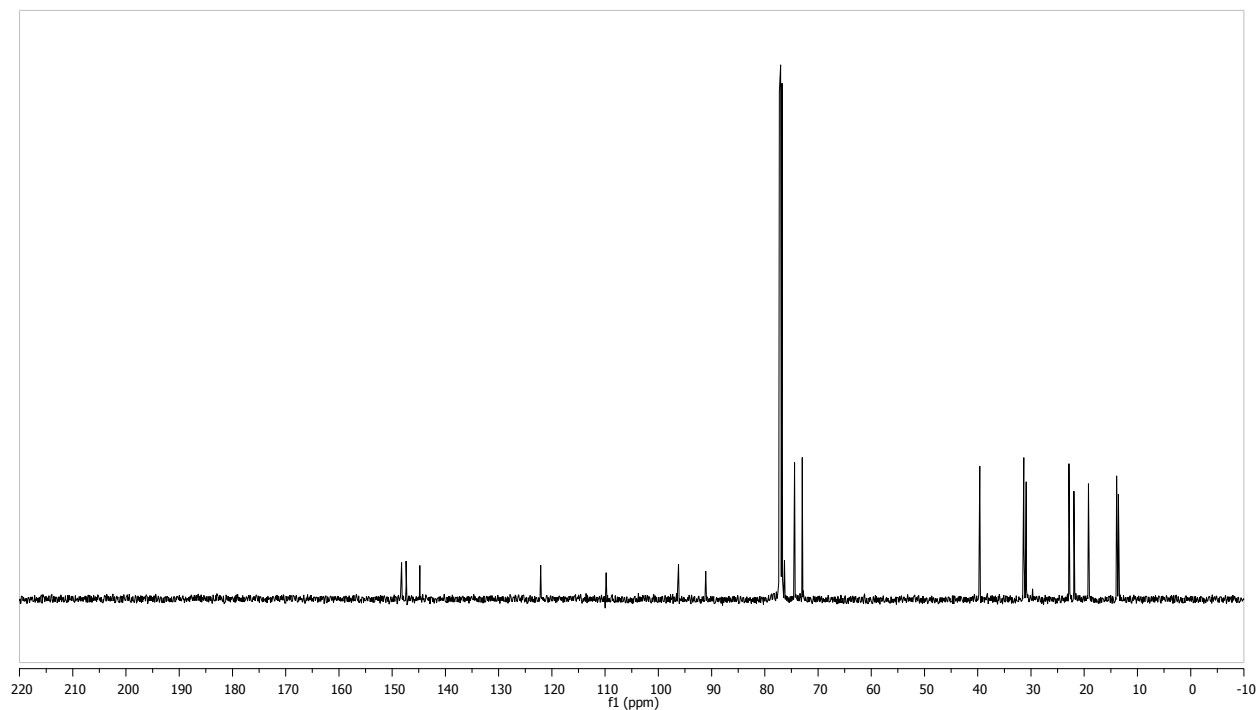


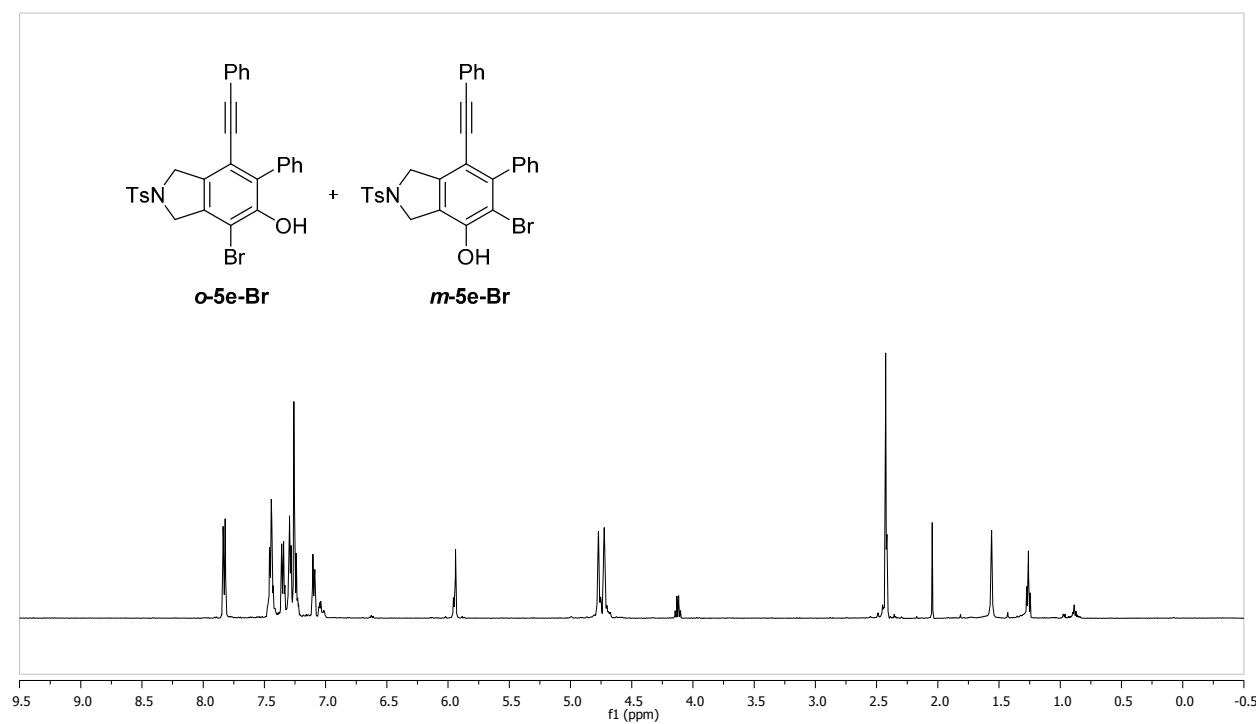
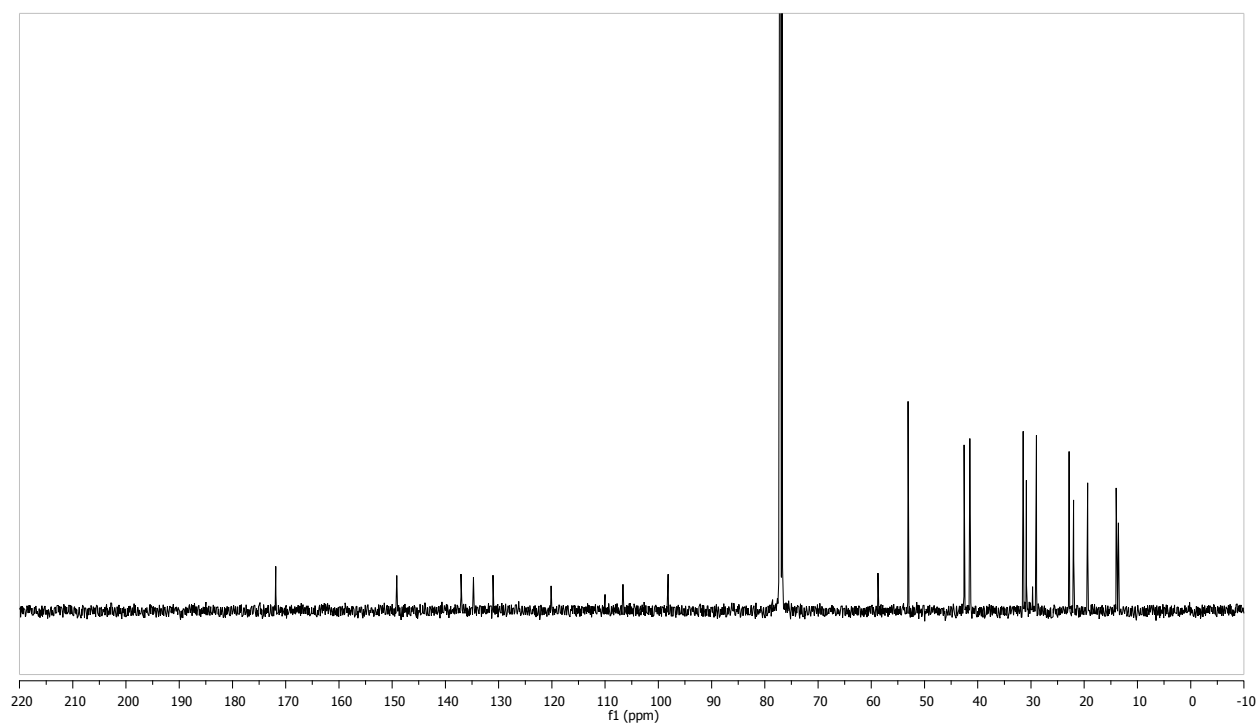


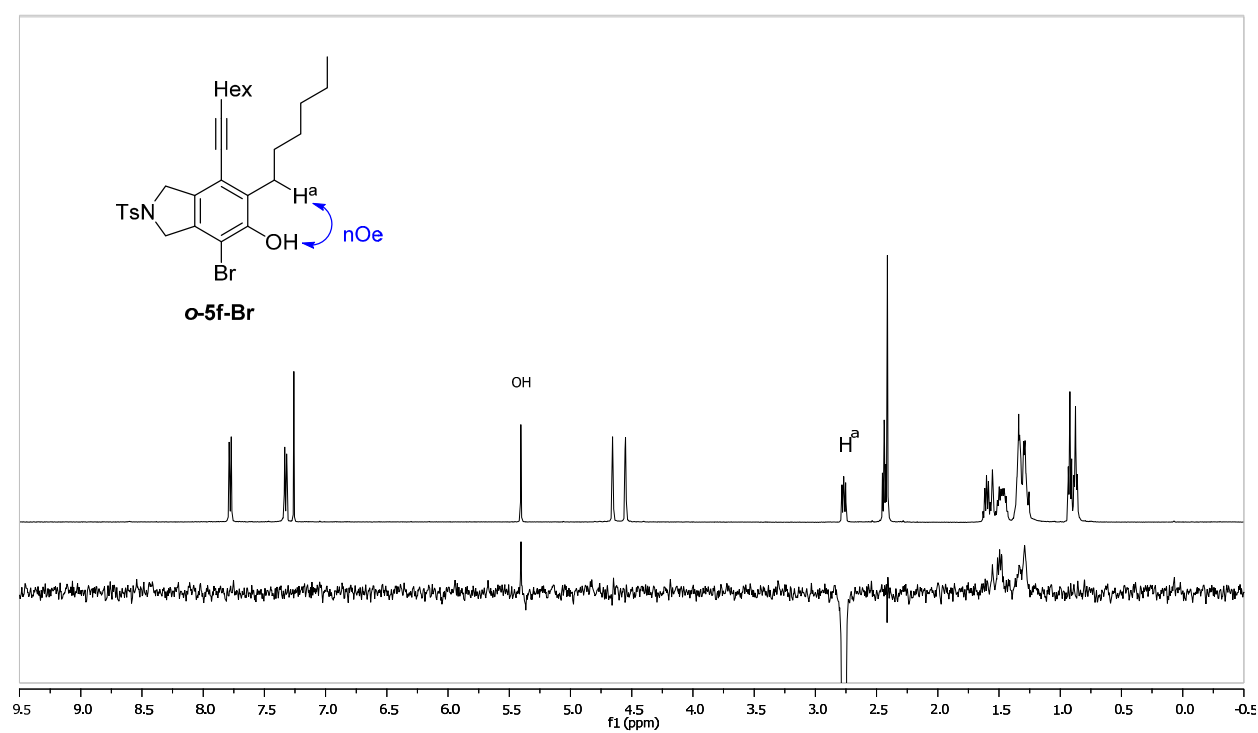
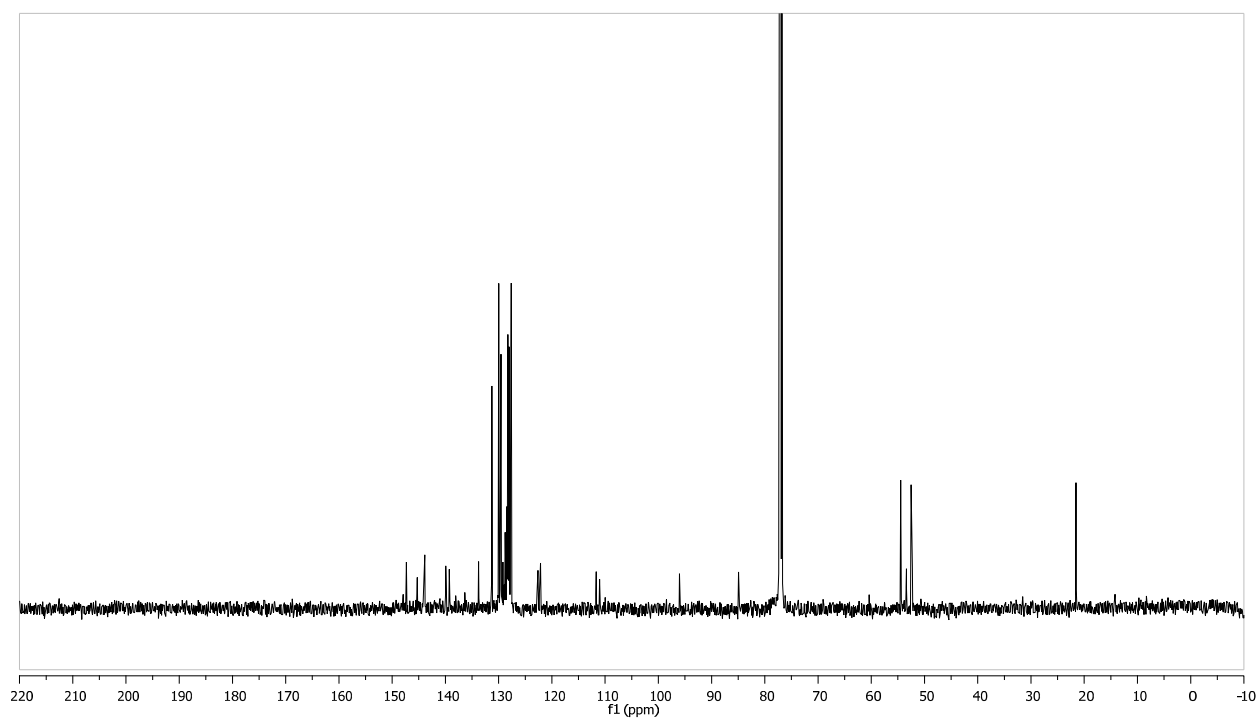


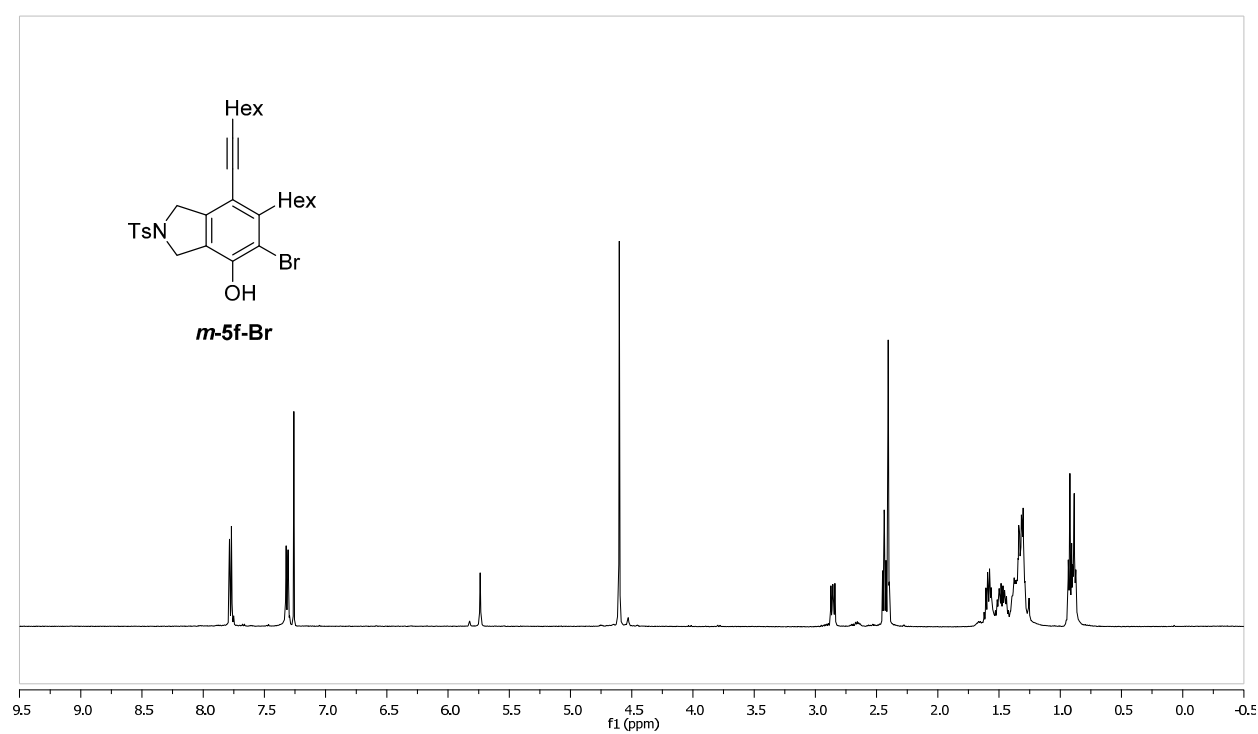
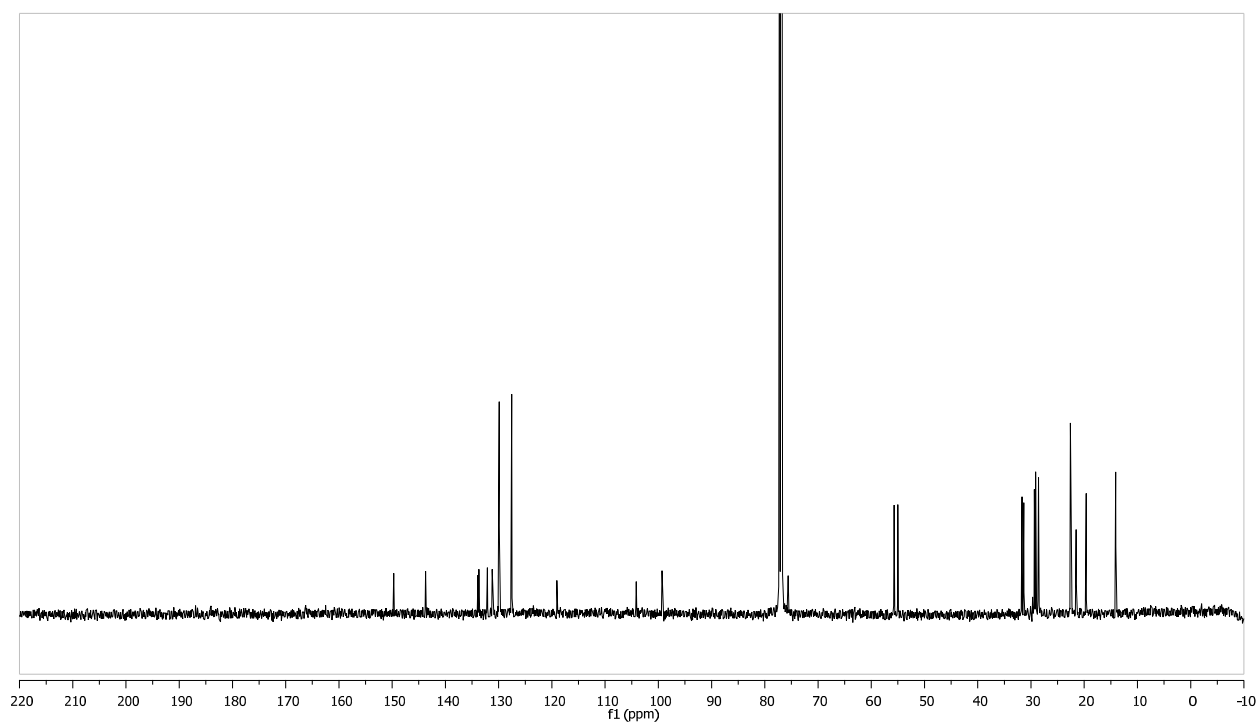


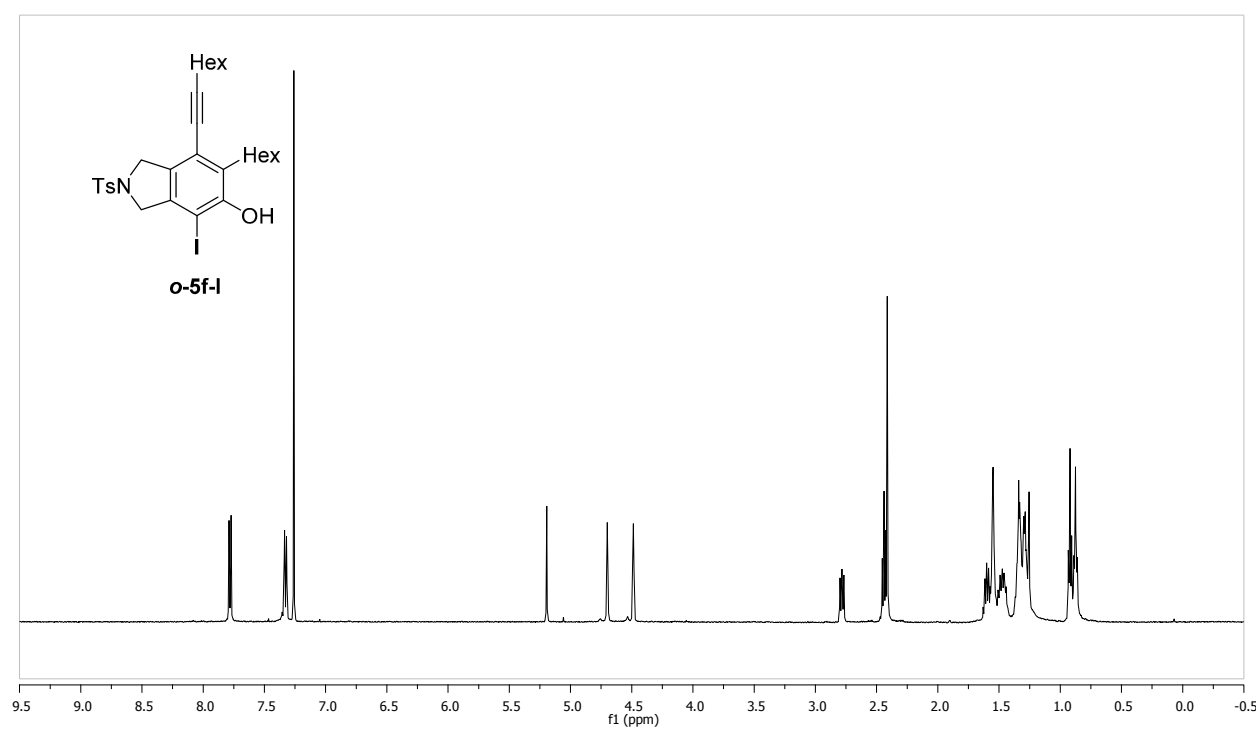
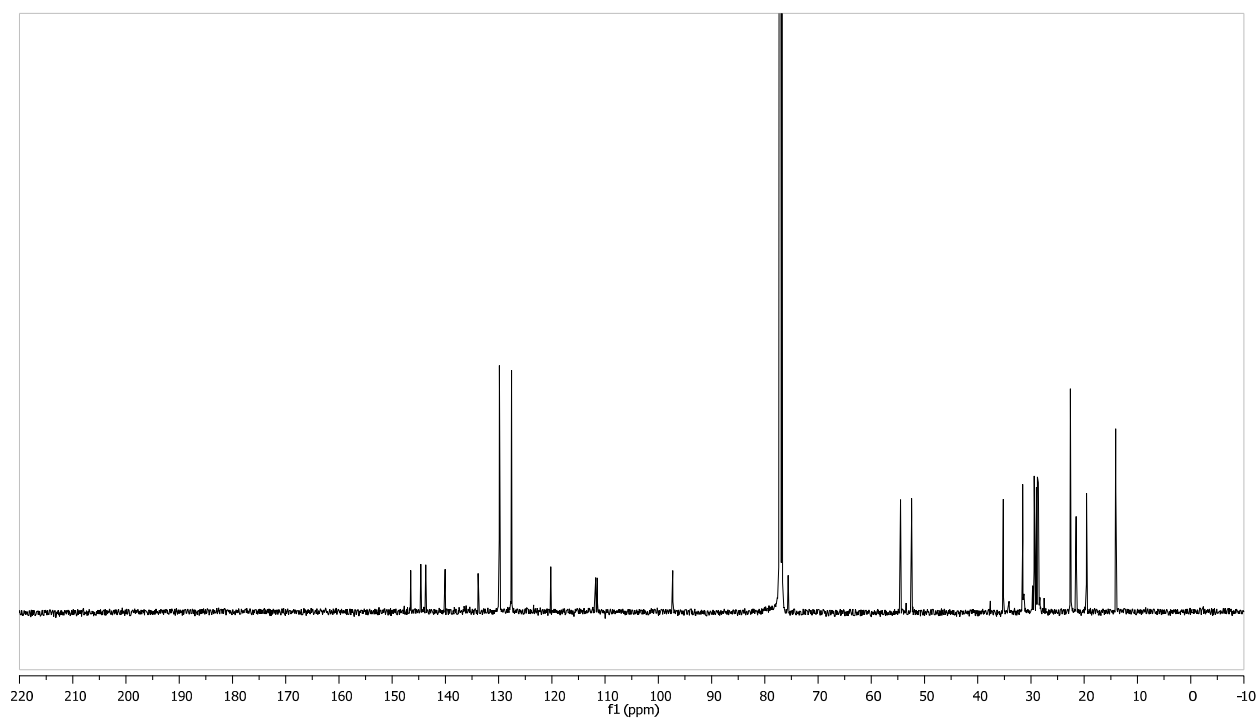


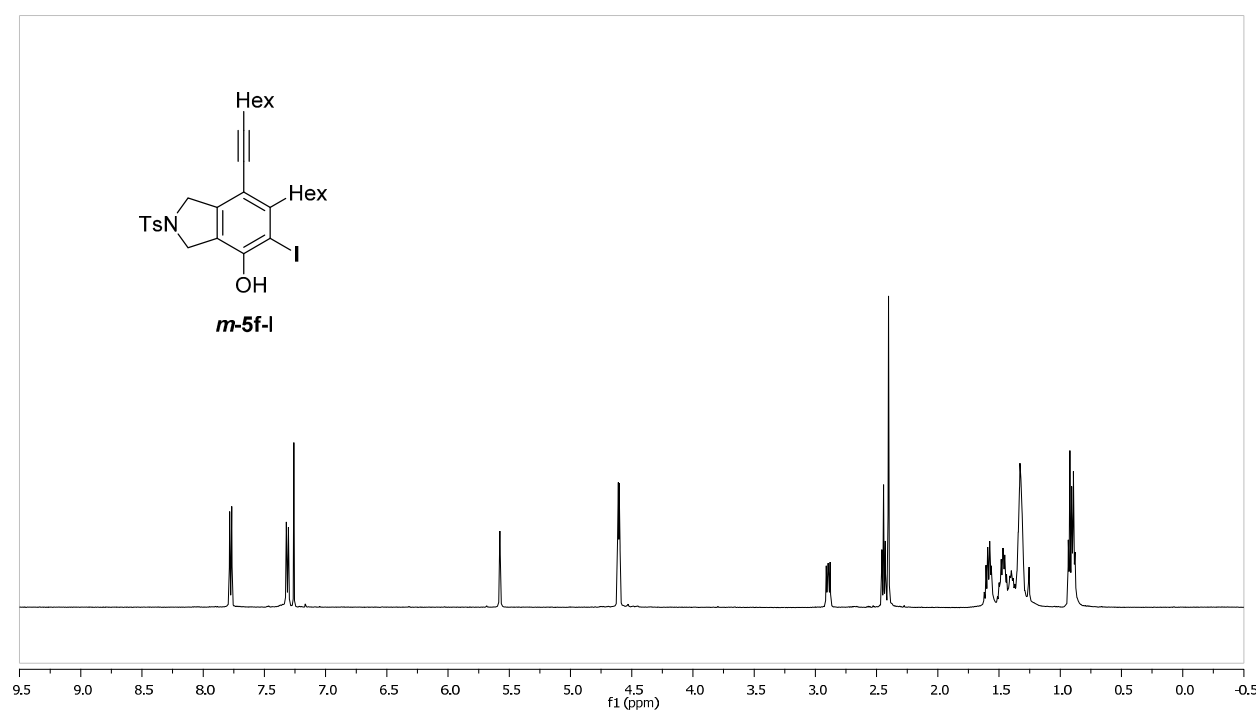
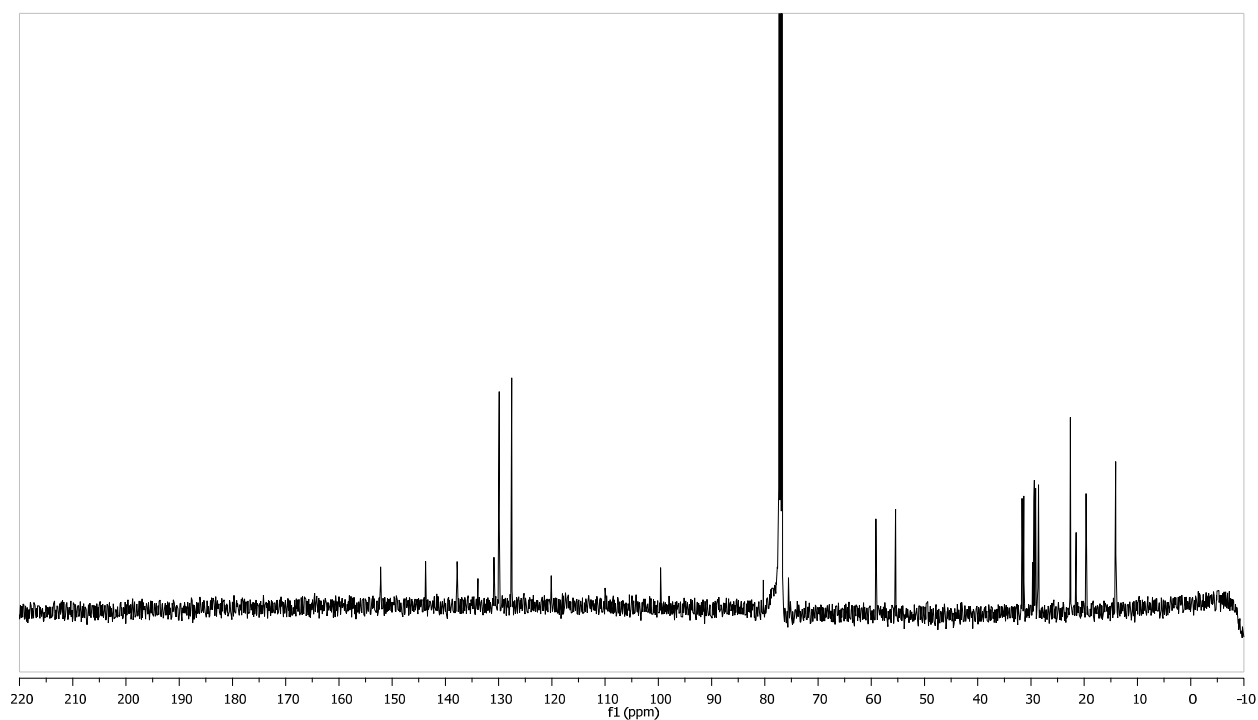


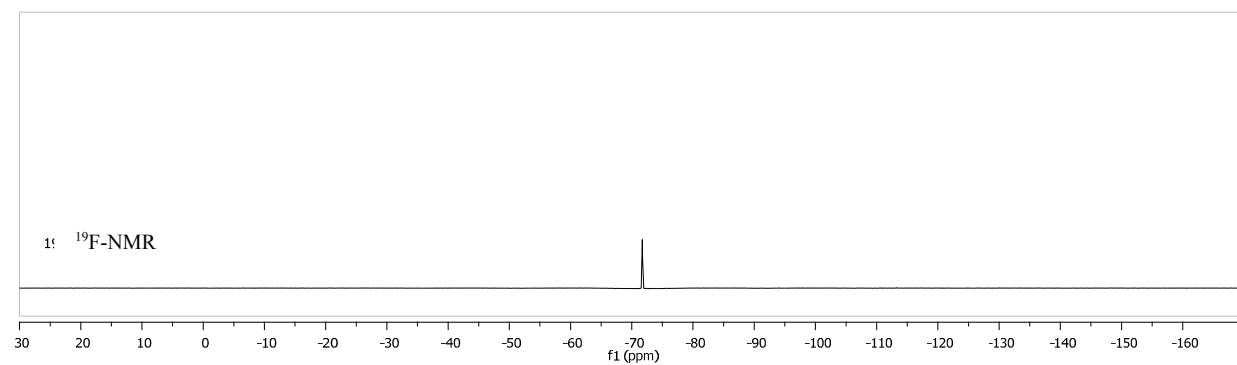
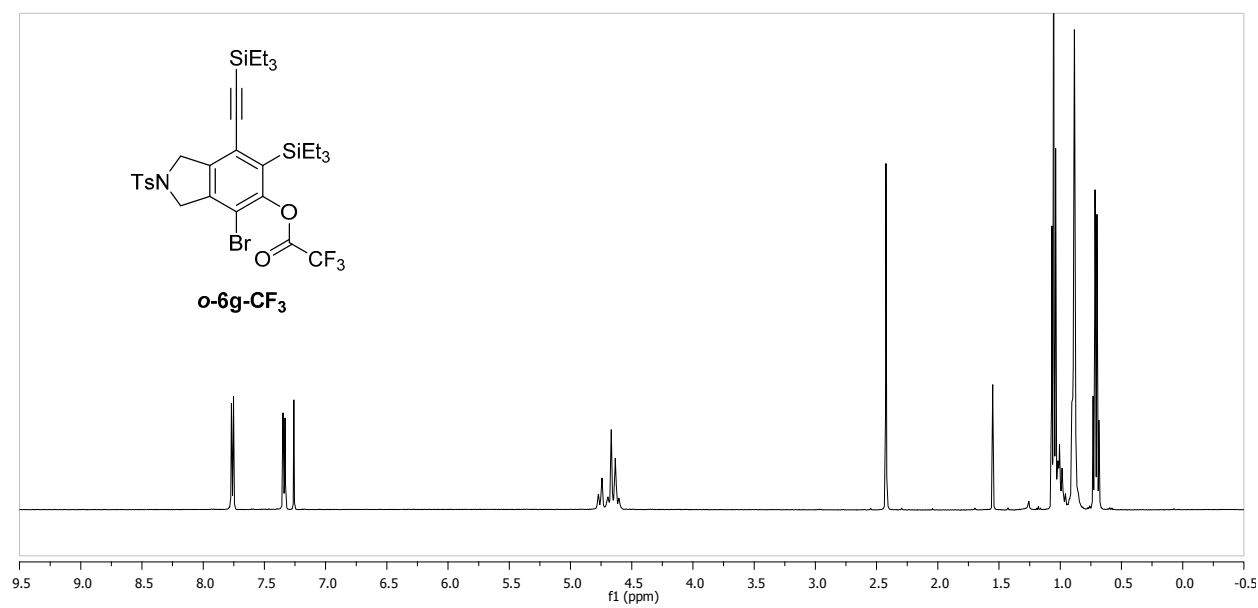
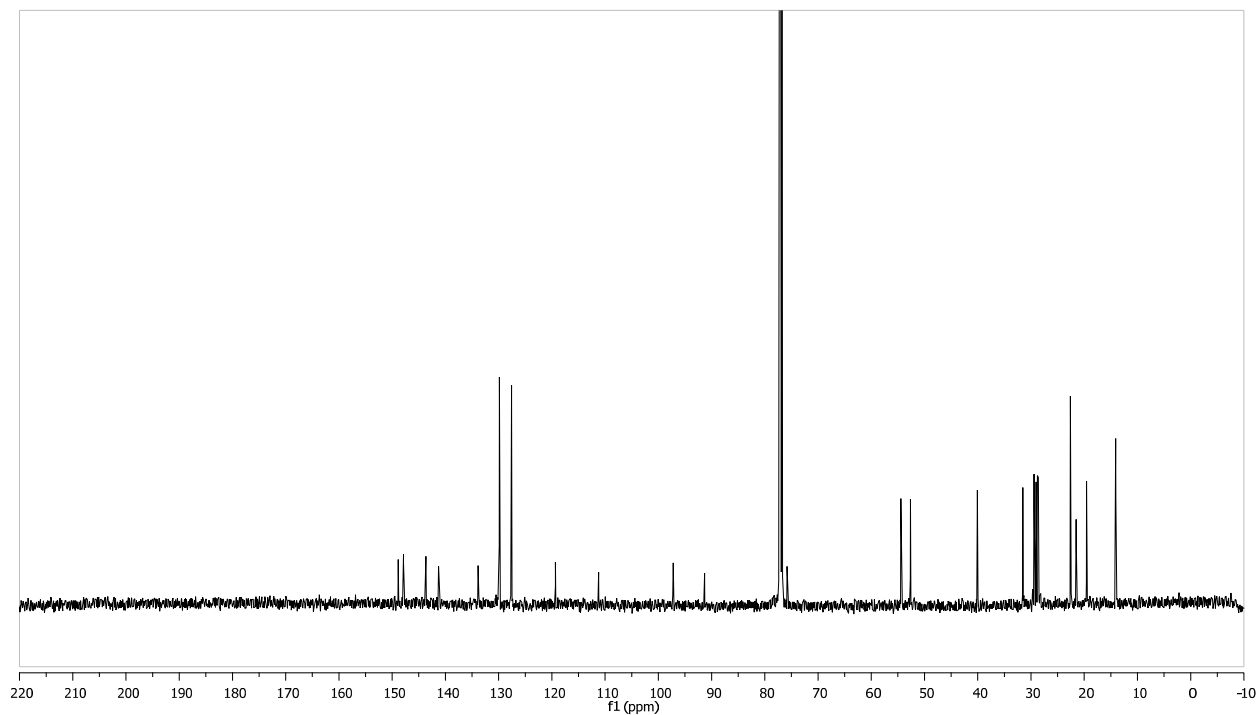


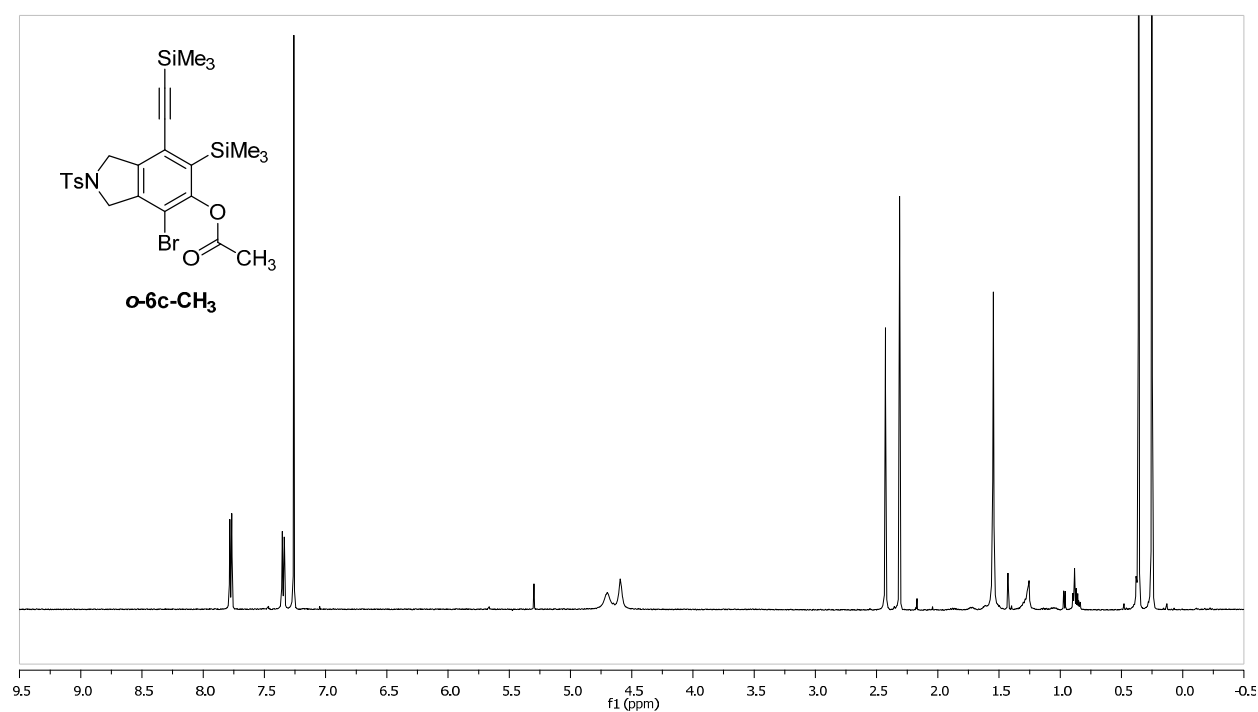
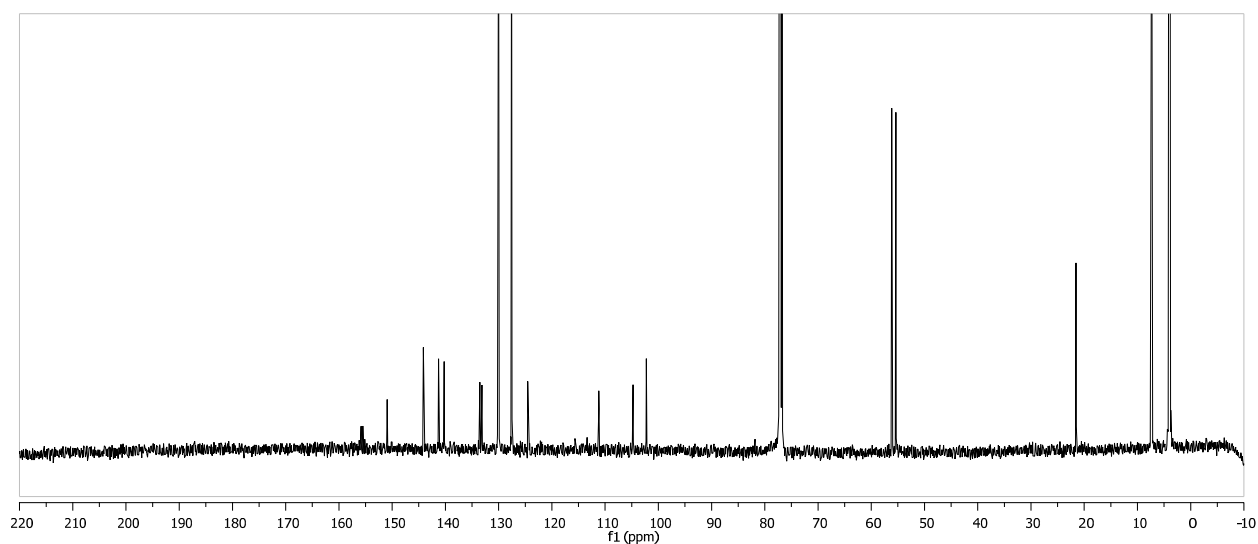


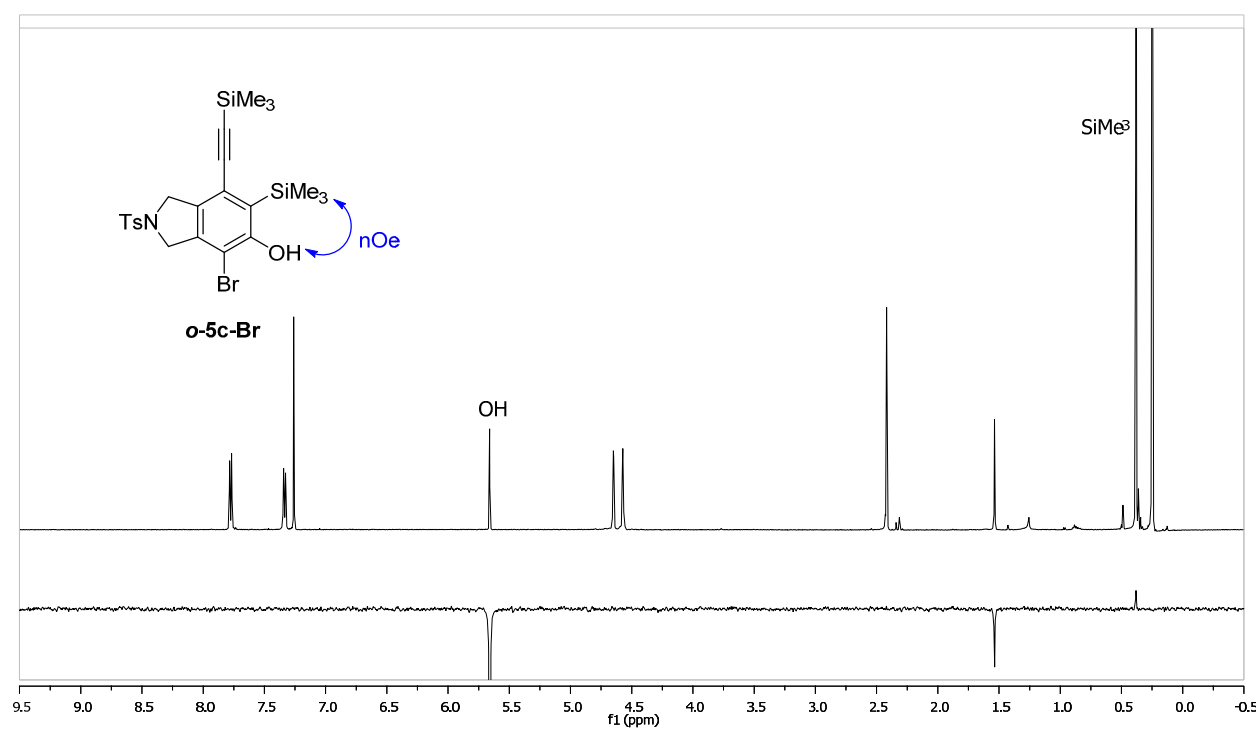
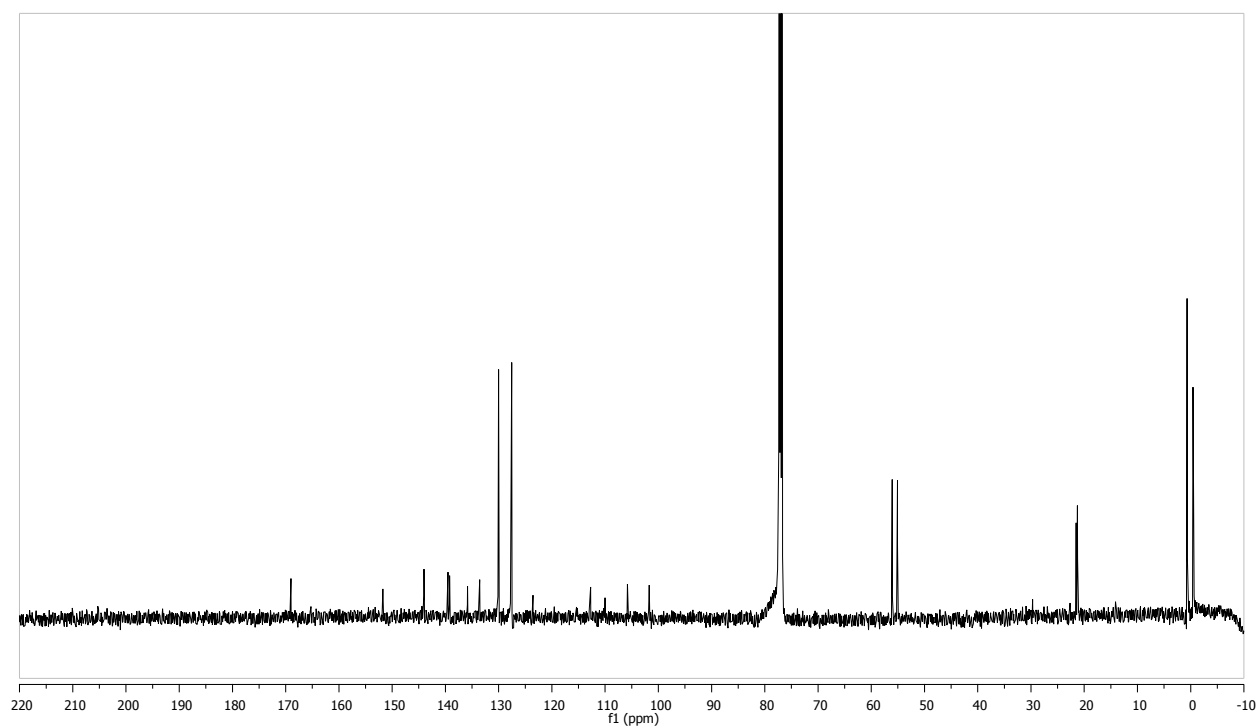


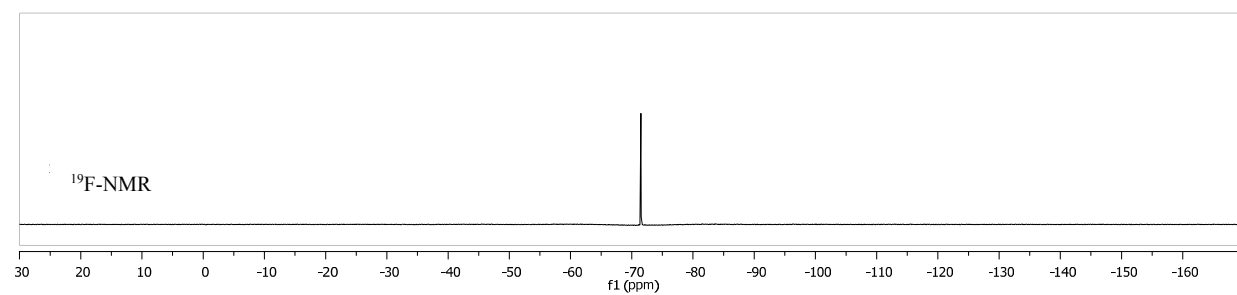
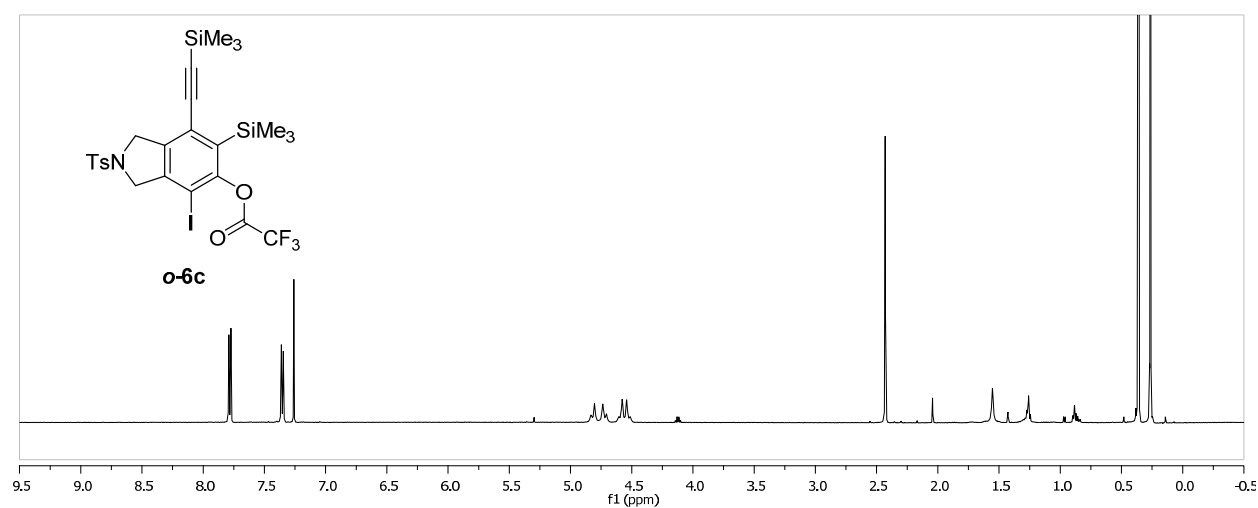
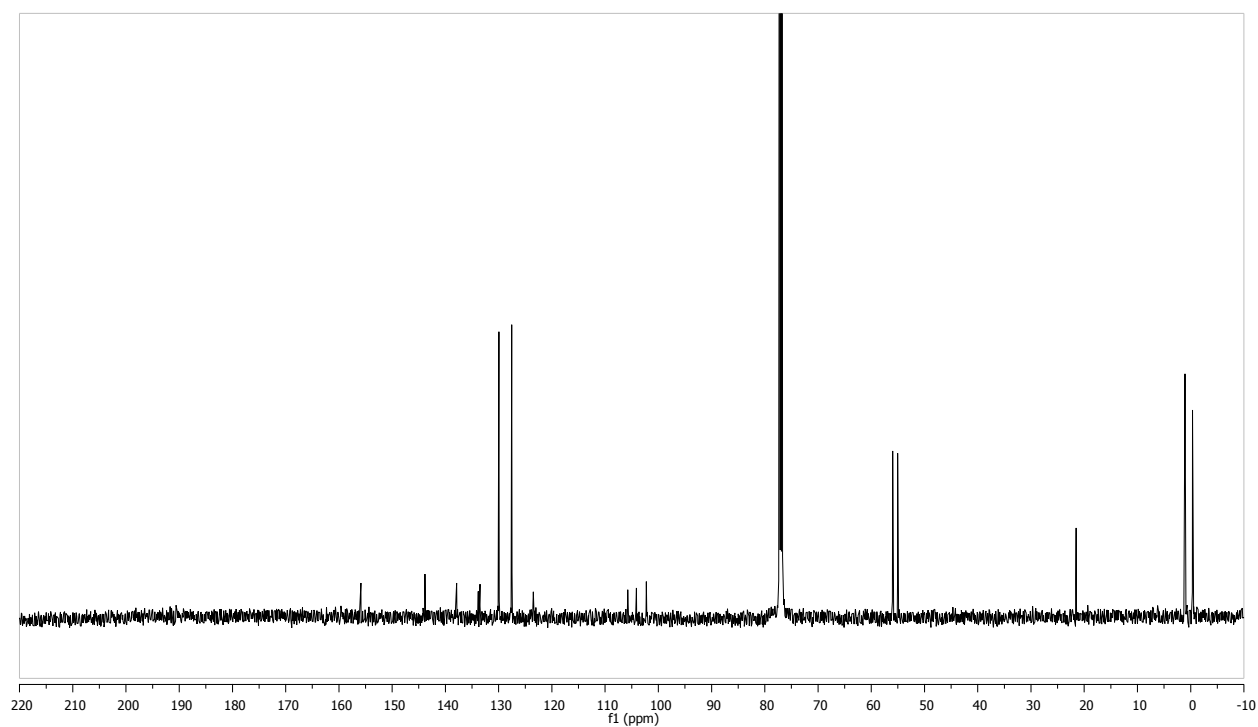


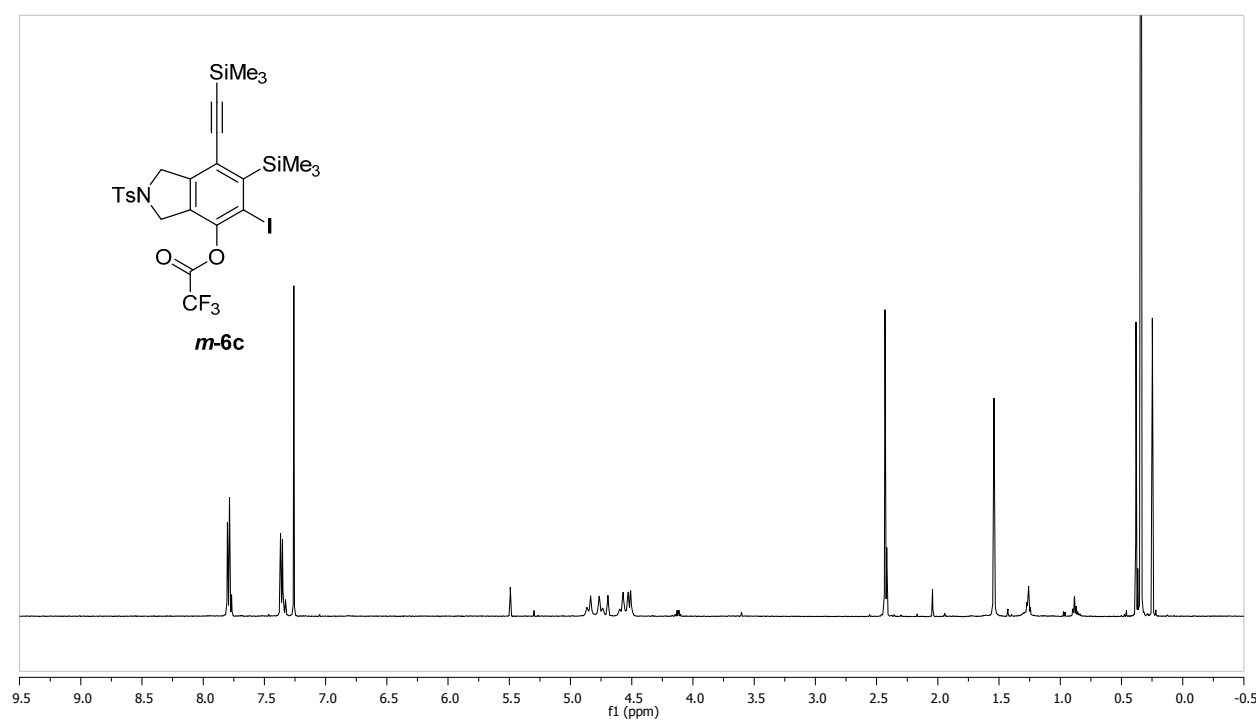
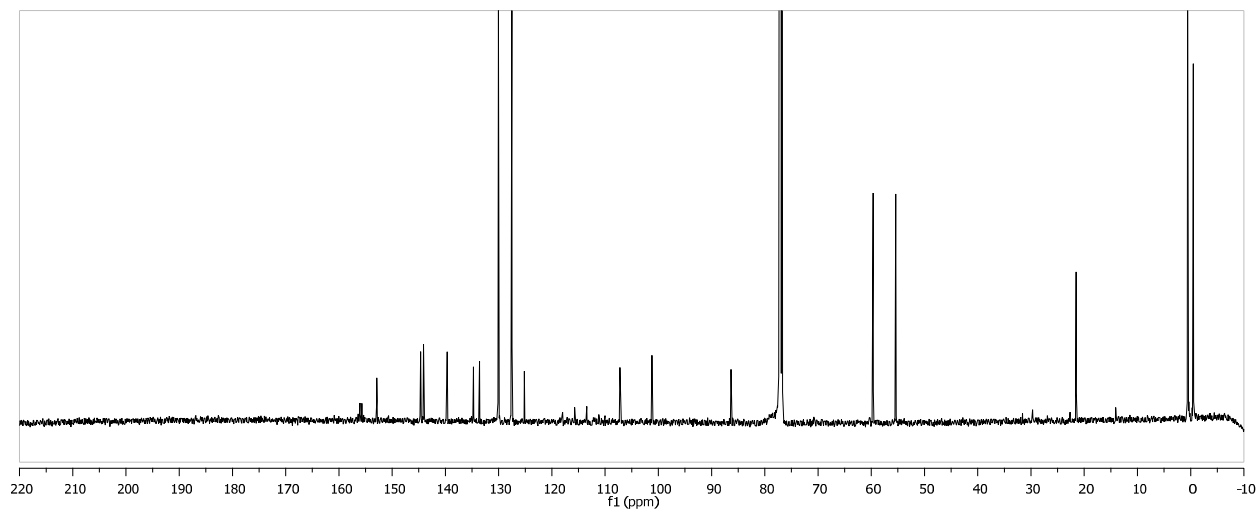


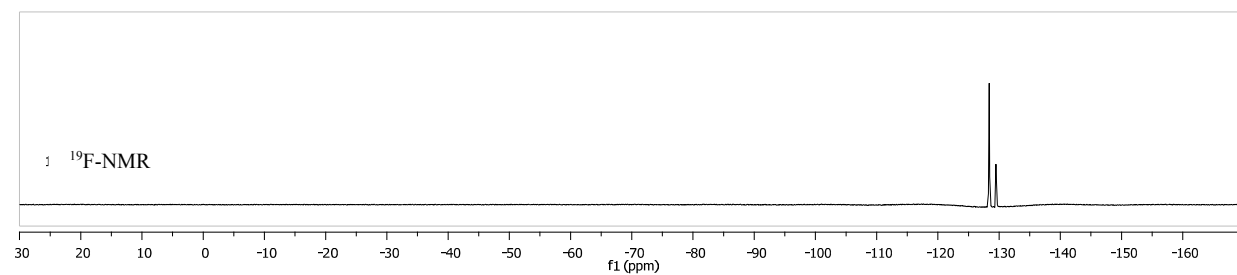
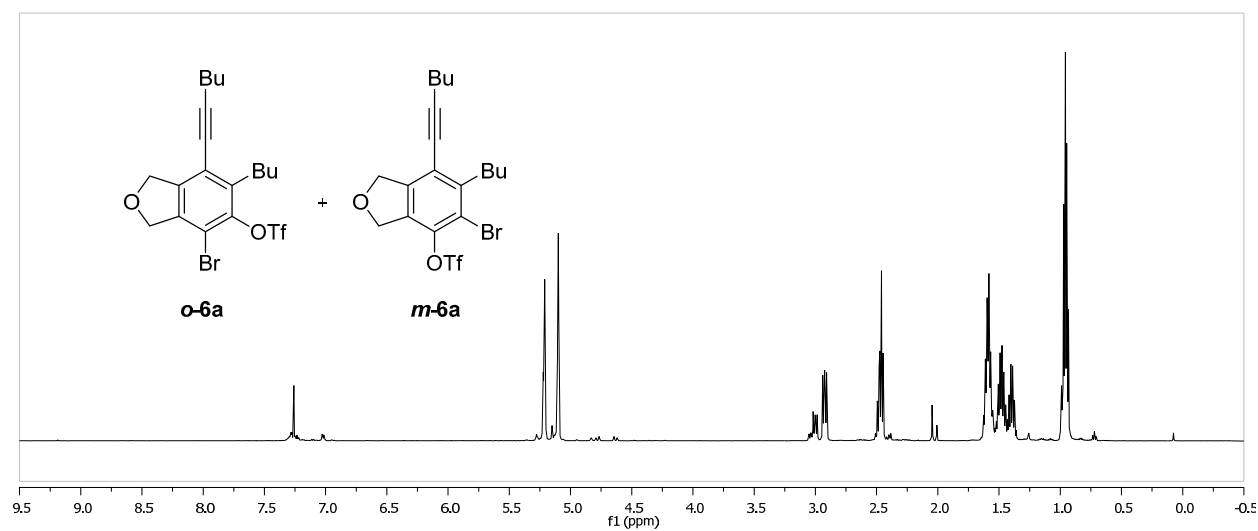
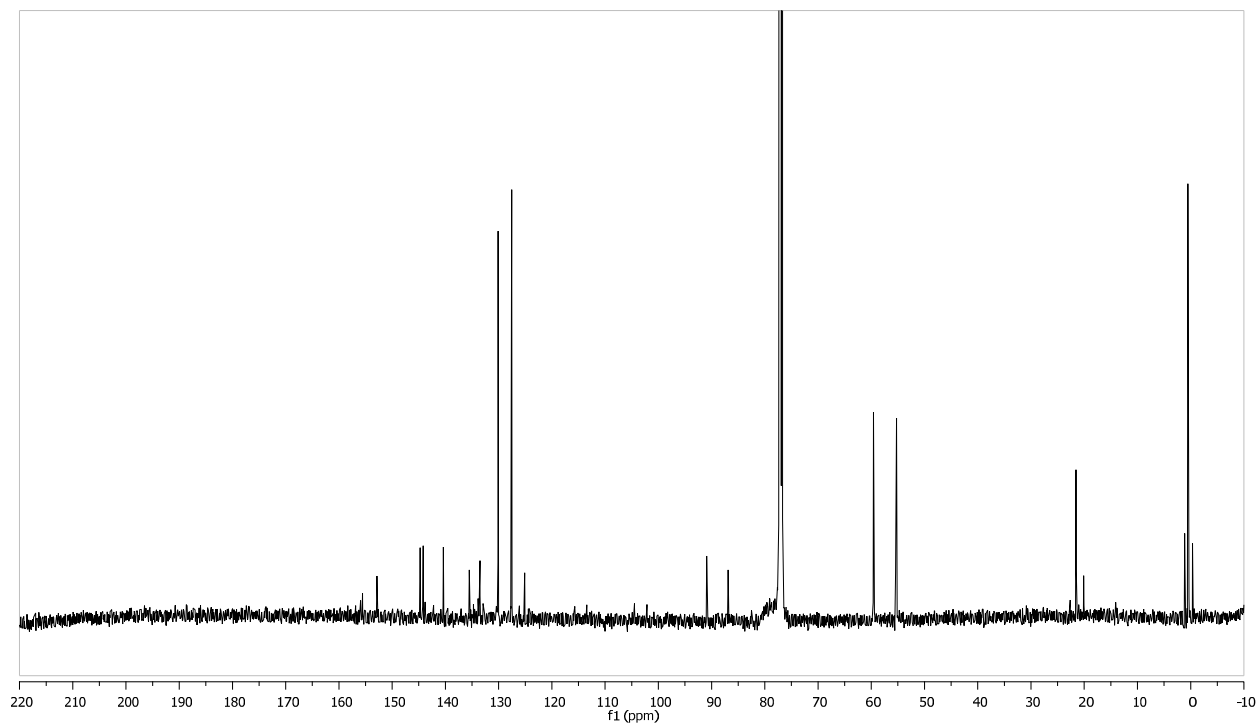


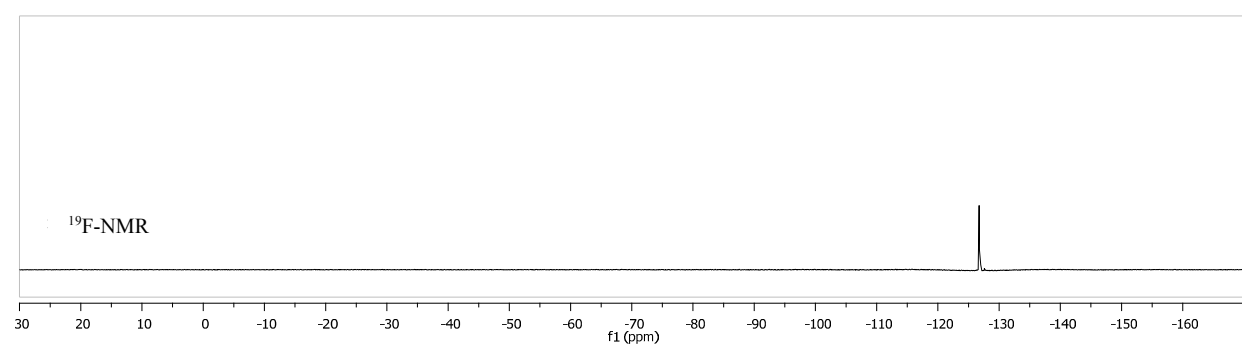
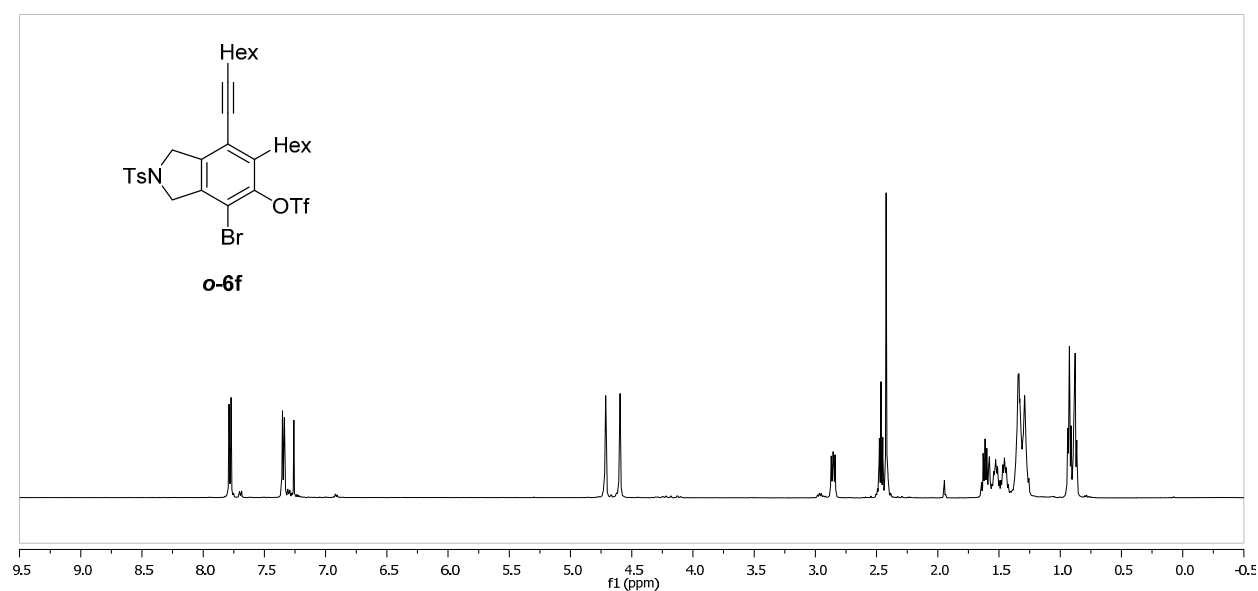
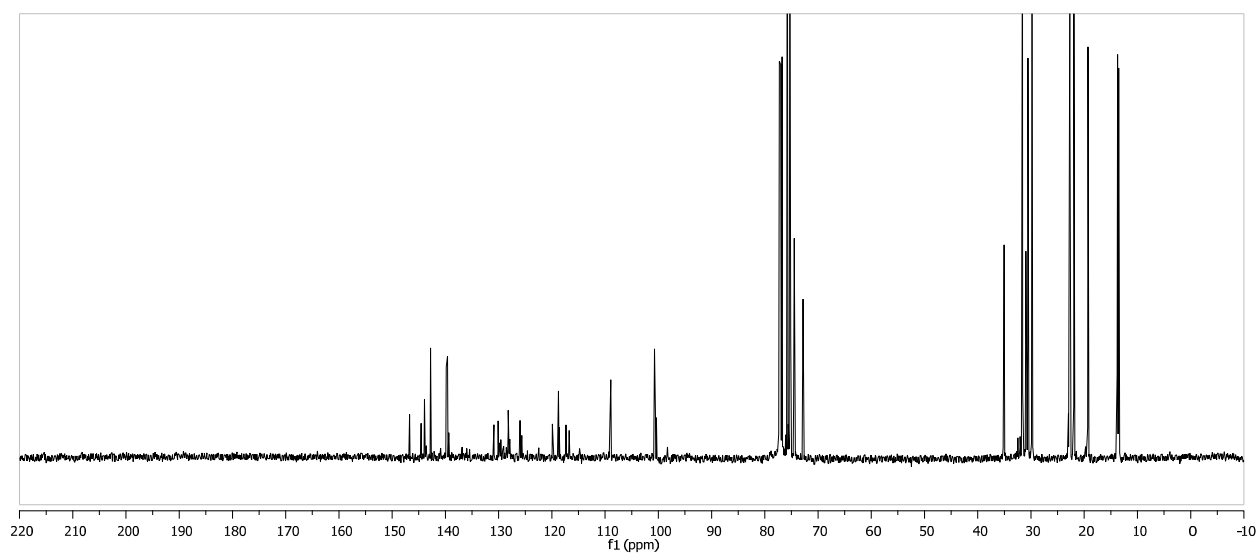


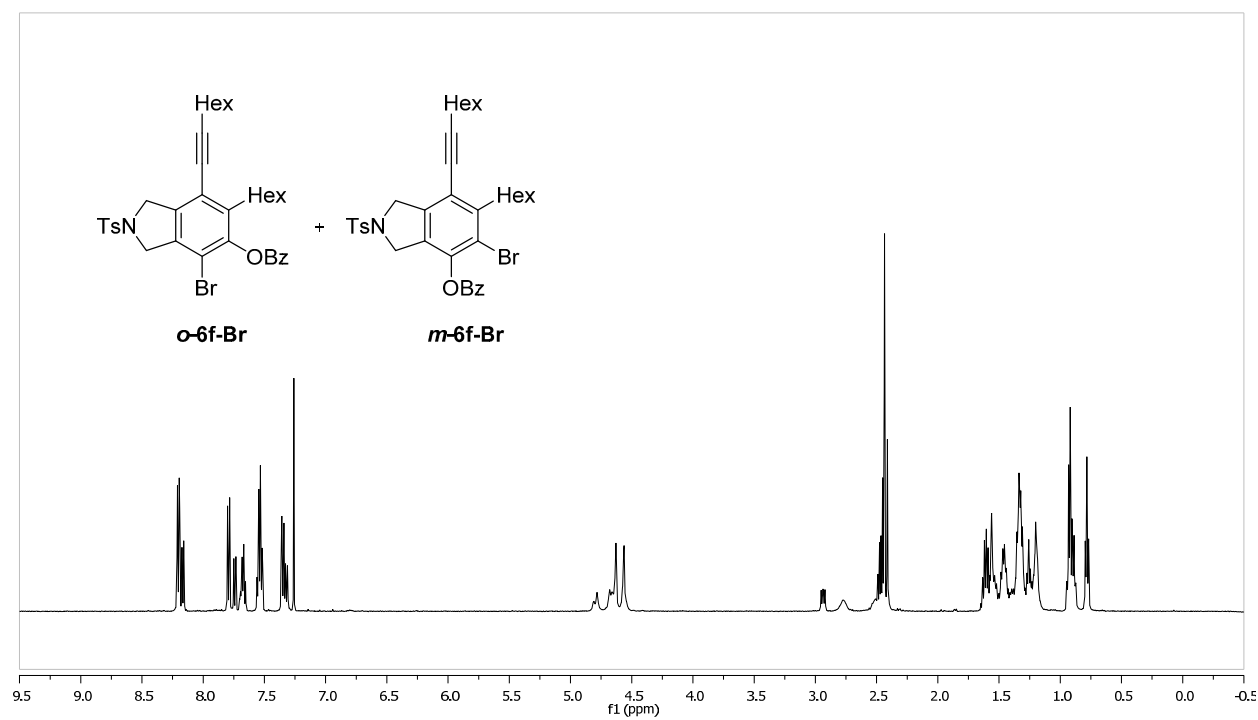
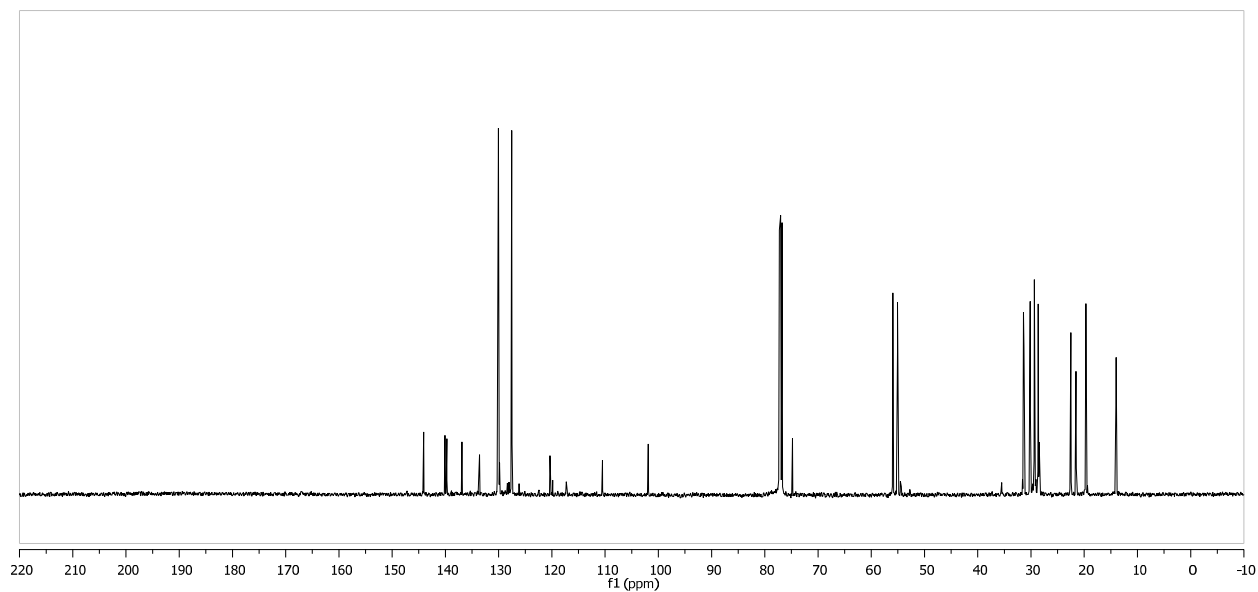


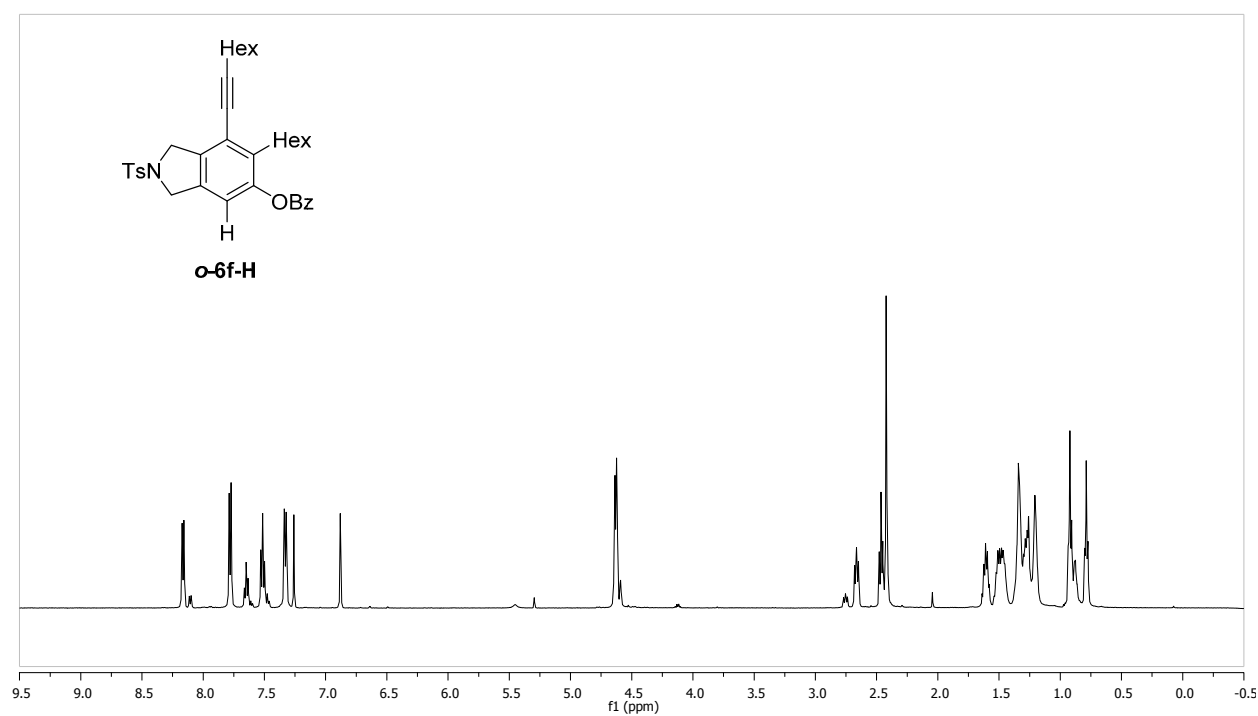
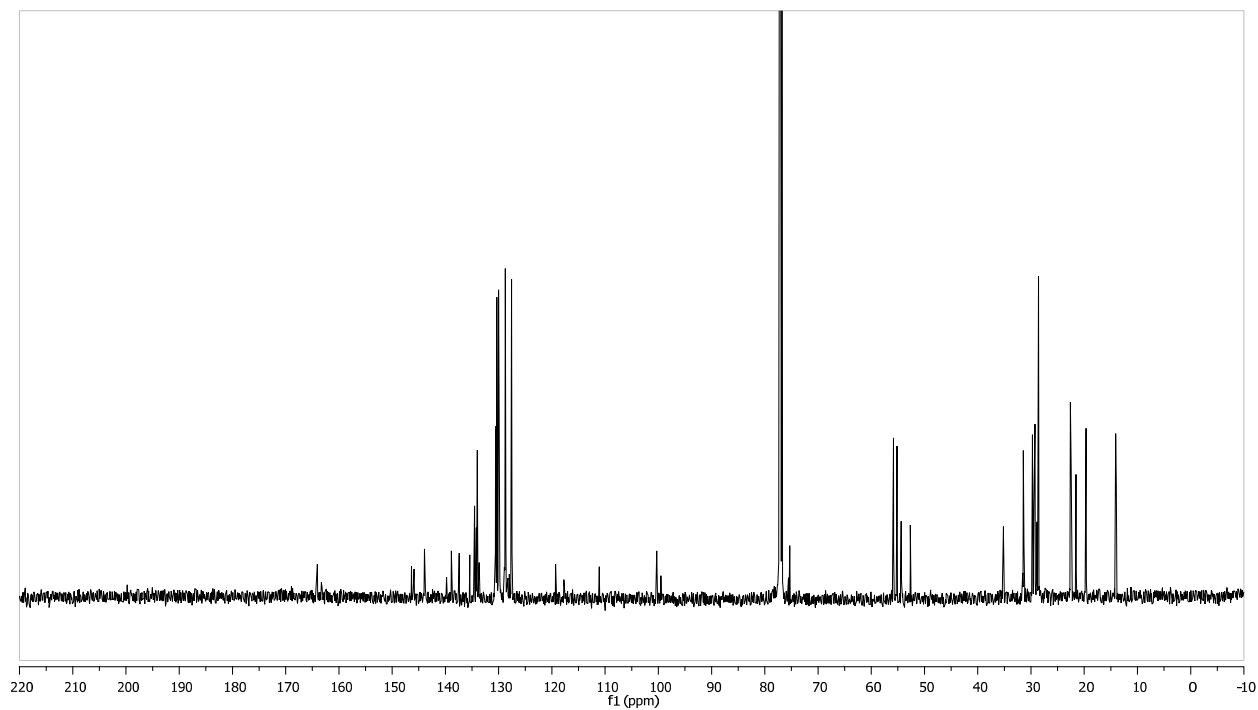


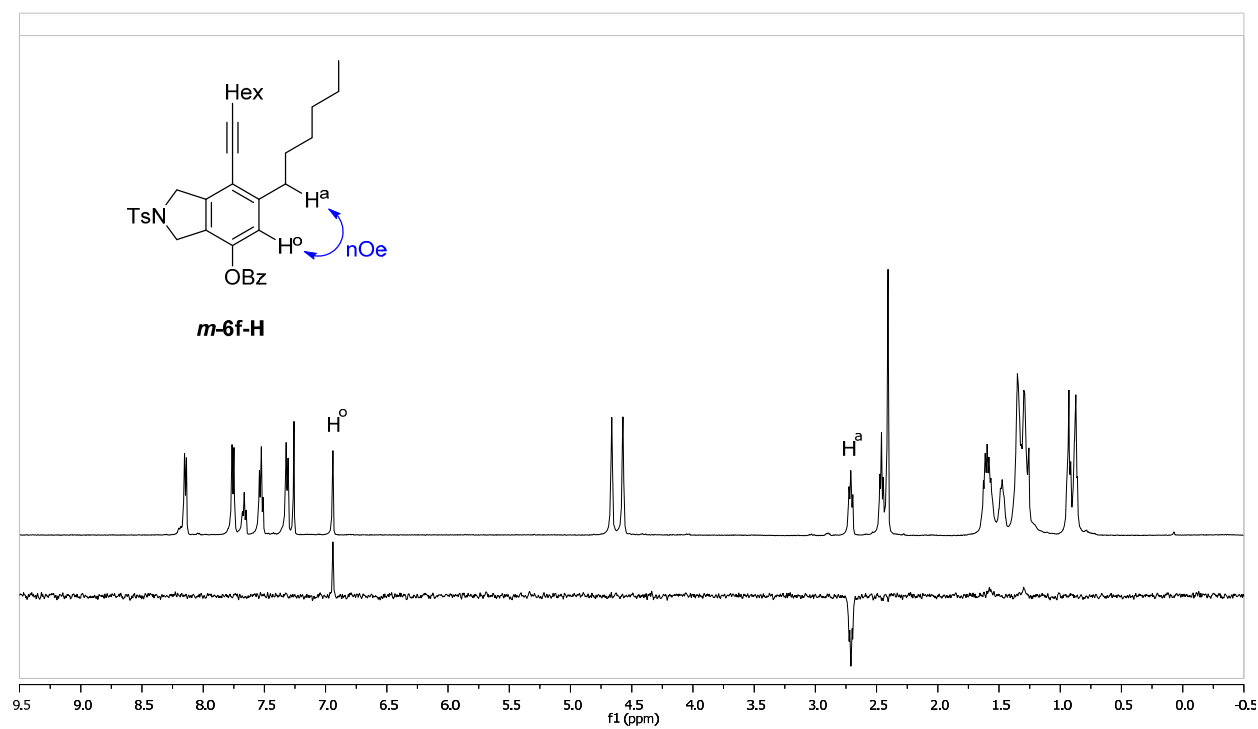
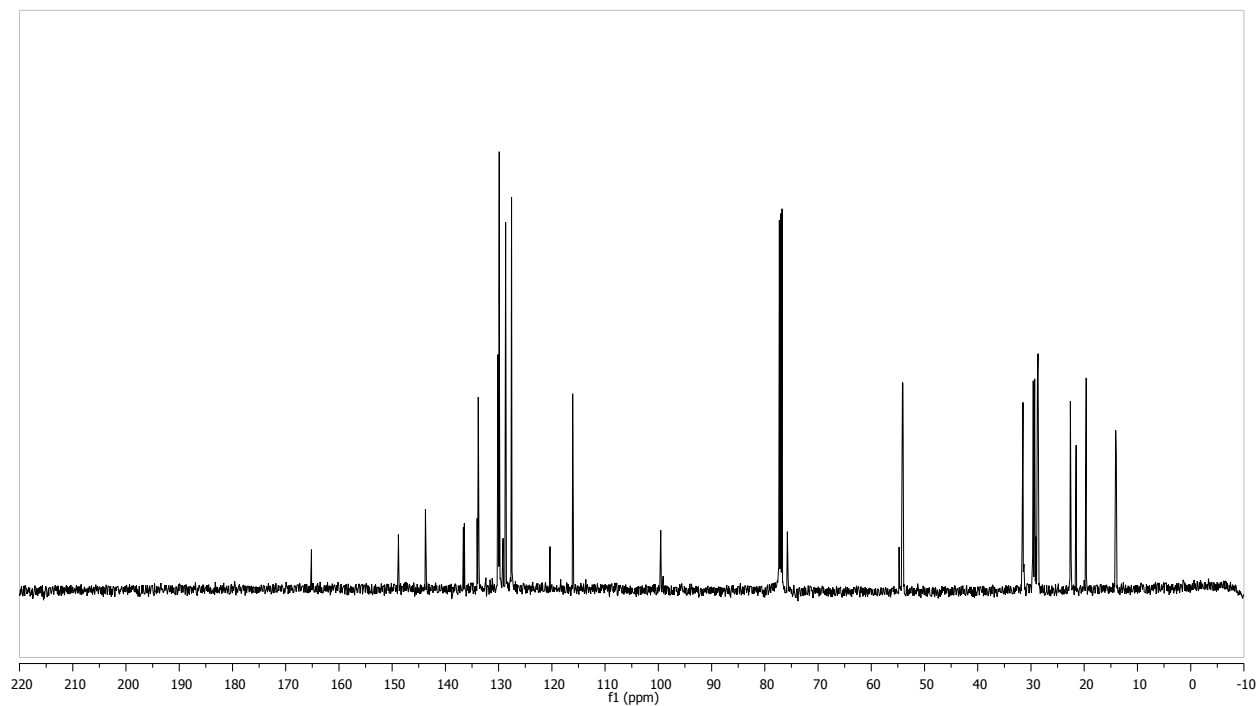


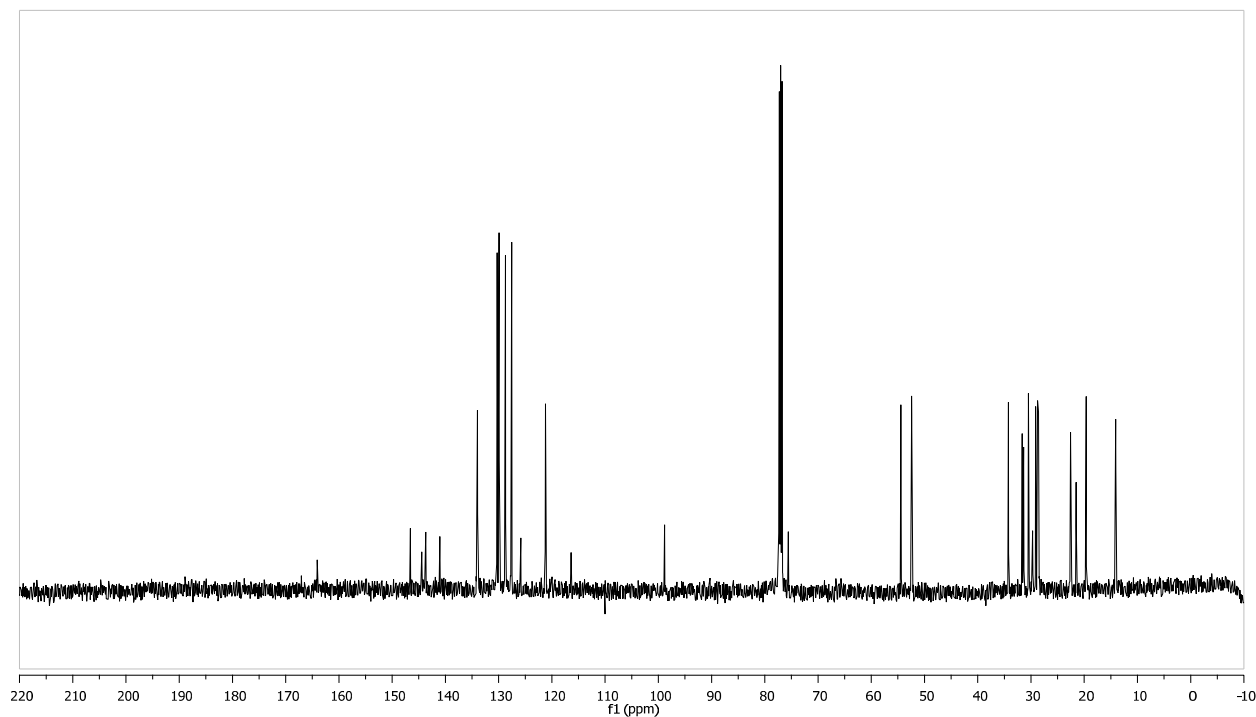






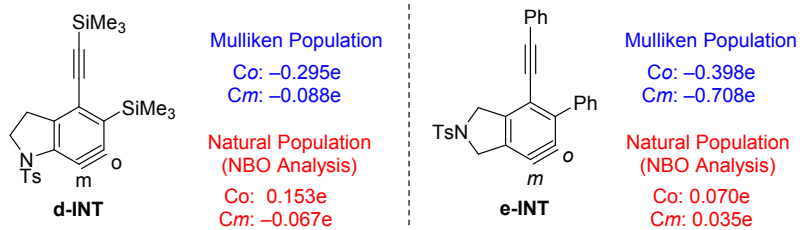






Mulliken Population Analysis

The observed regioselectivity for the reactions of **1d** and **1e** can be further confirmed by the Mulliken Population analysis (but less accurately by NBO analysis) of aryne intermediates **d-INT** and **e-INT**.



Optimization and population analysis were performed at the B3LYP/6-31+G(d) level of theory.