

Supporting Information for Publication

Nitrile Stabilized Synthesis of Pyrrolidine and Piperidine Derivatives via Tandem Alkynyl aza Prins-Ritter Reactions

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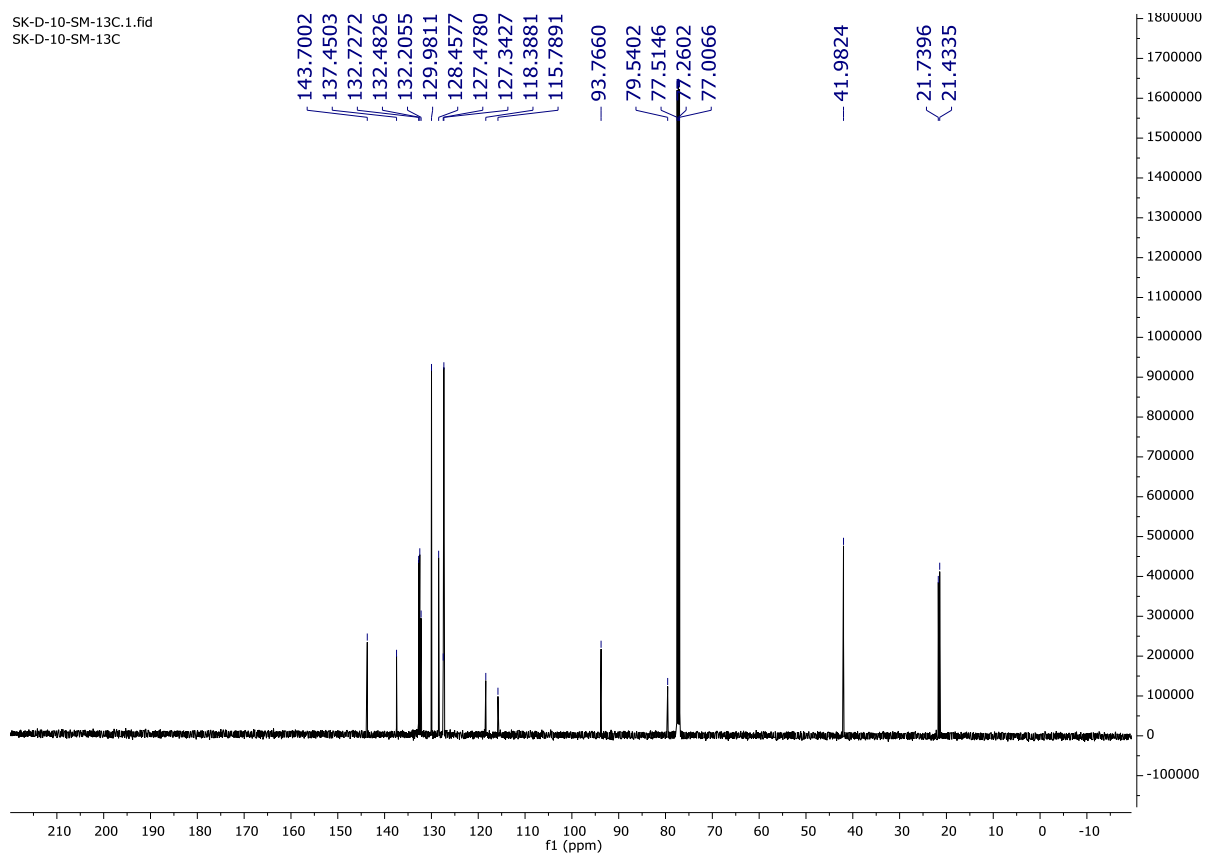
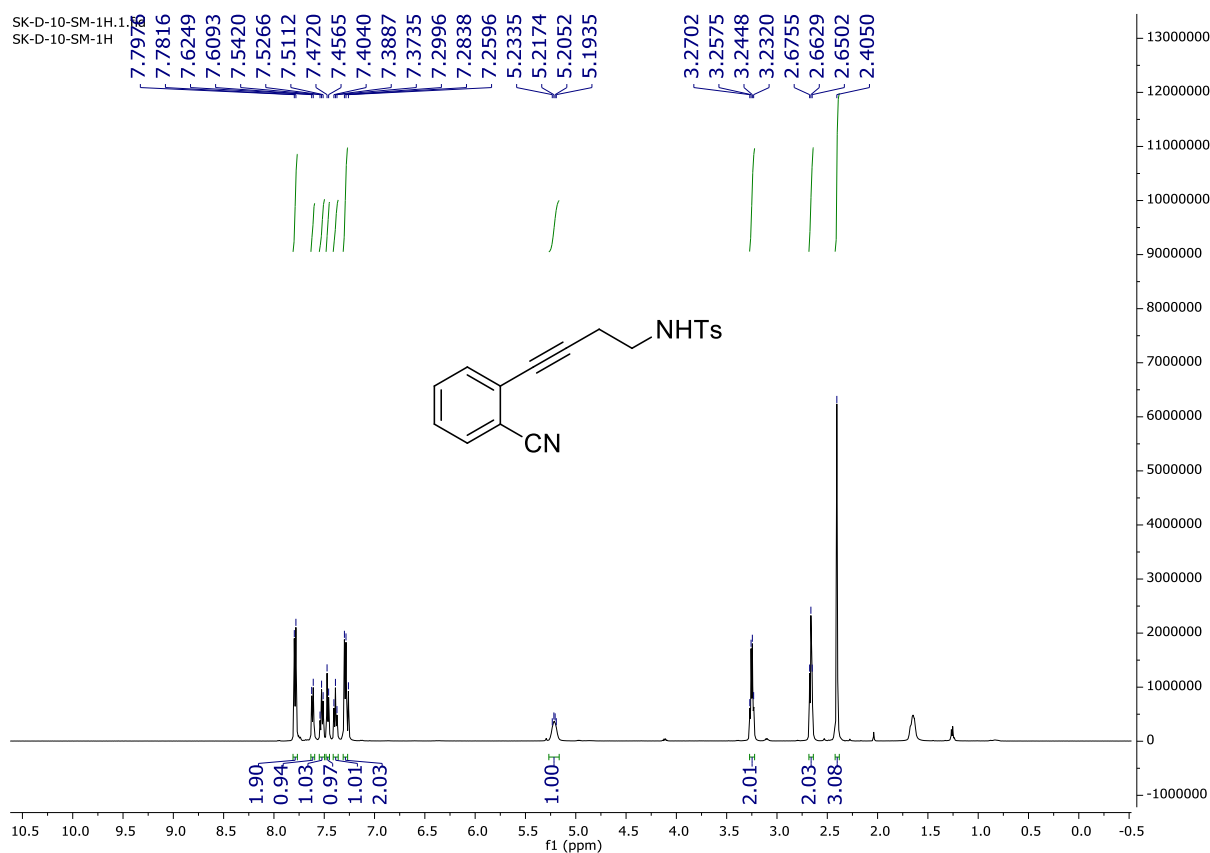
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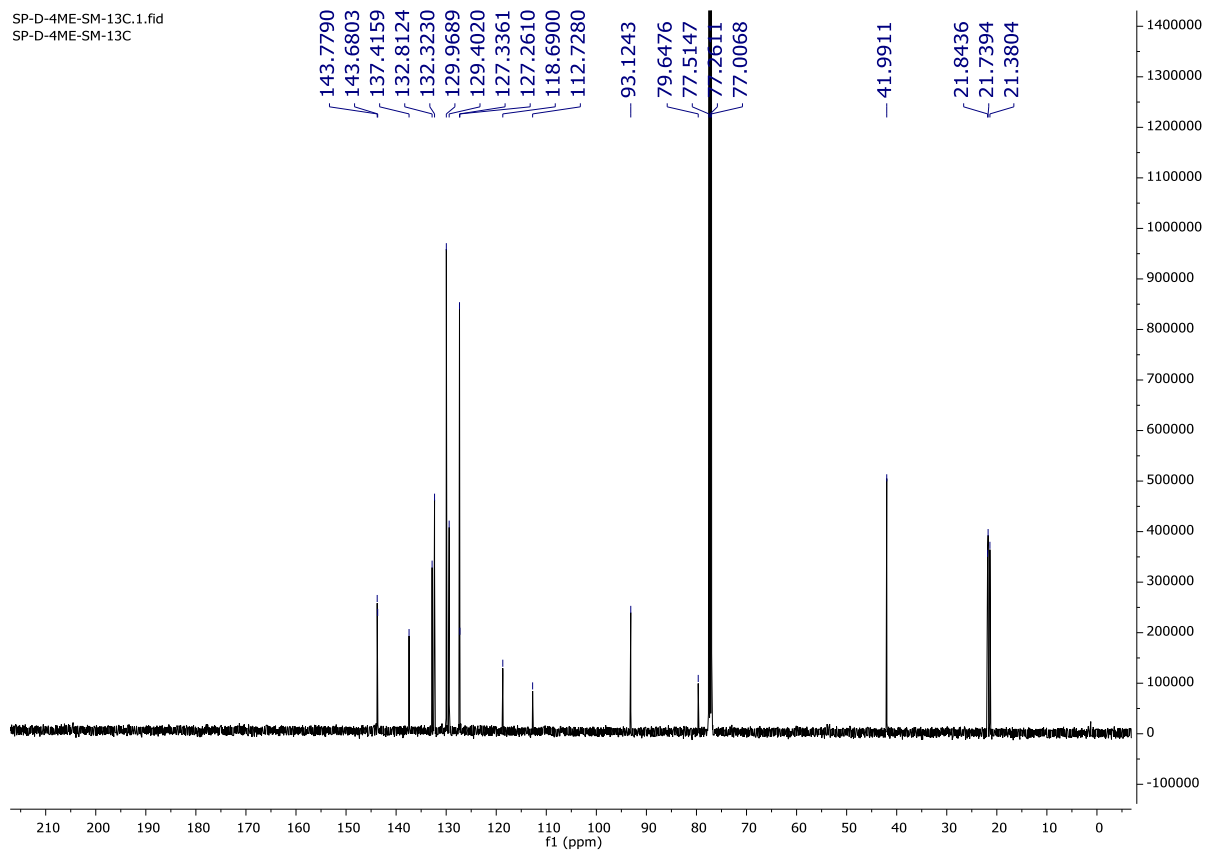
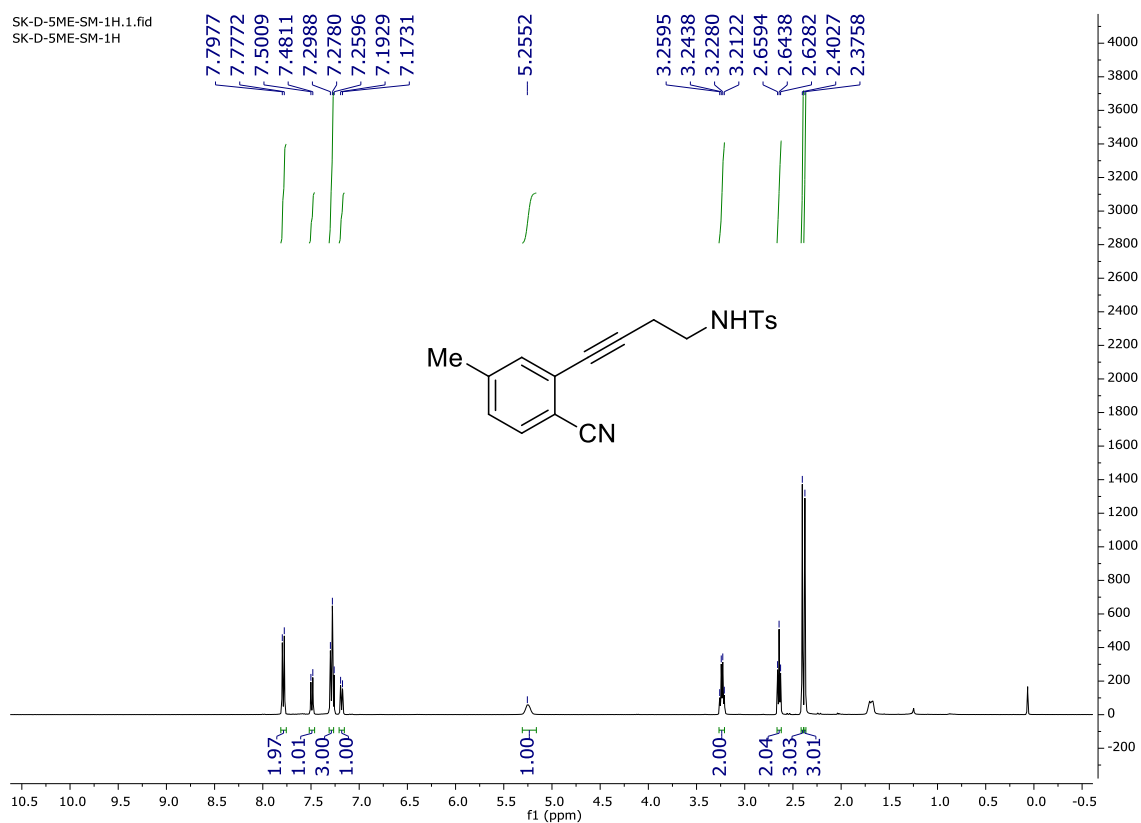
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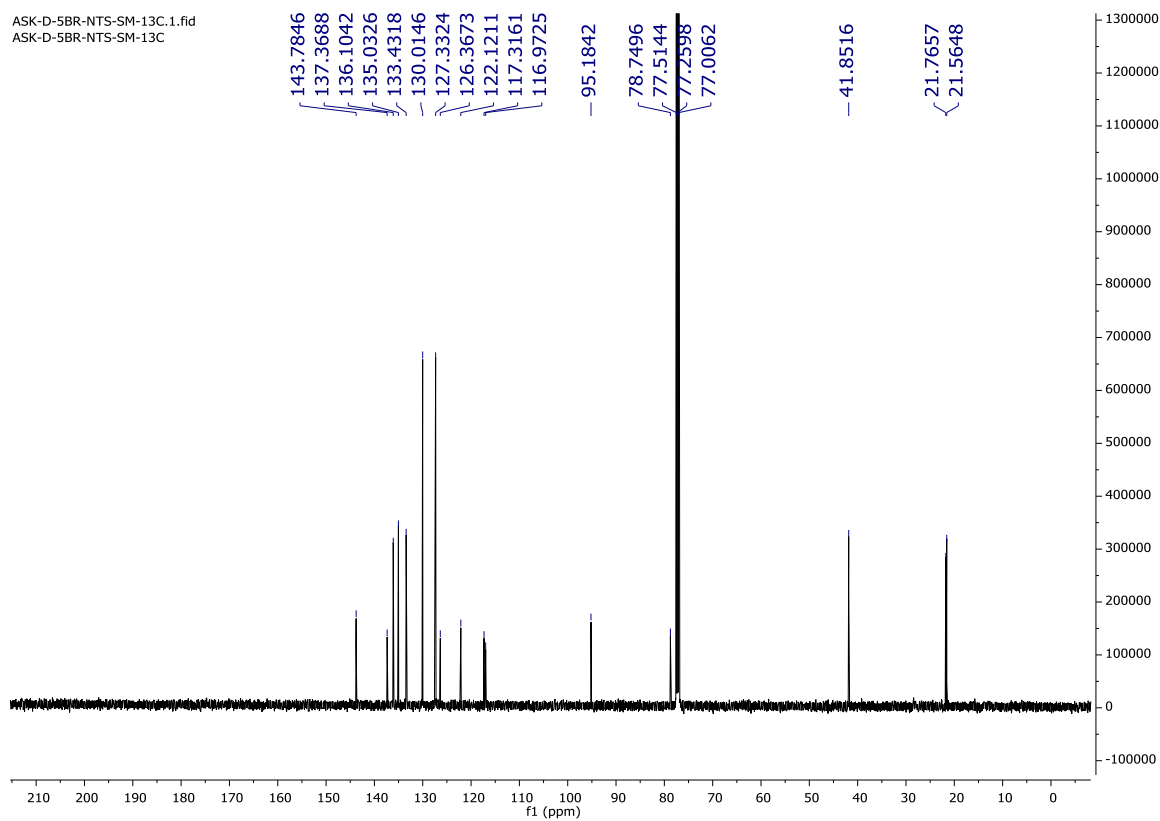
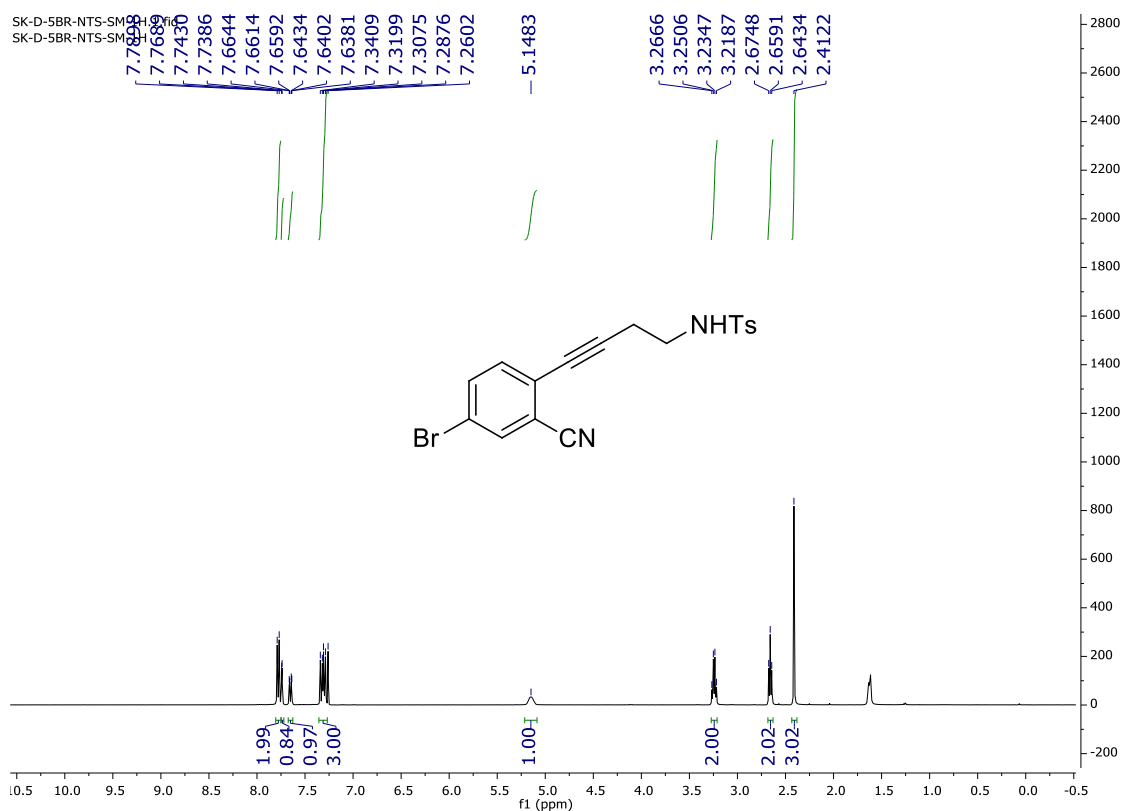
^1H (500 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) spectra of **1a**



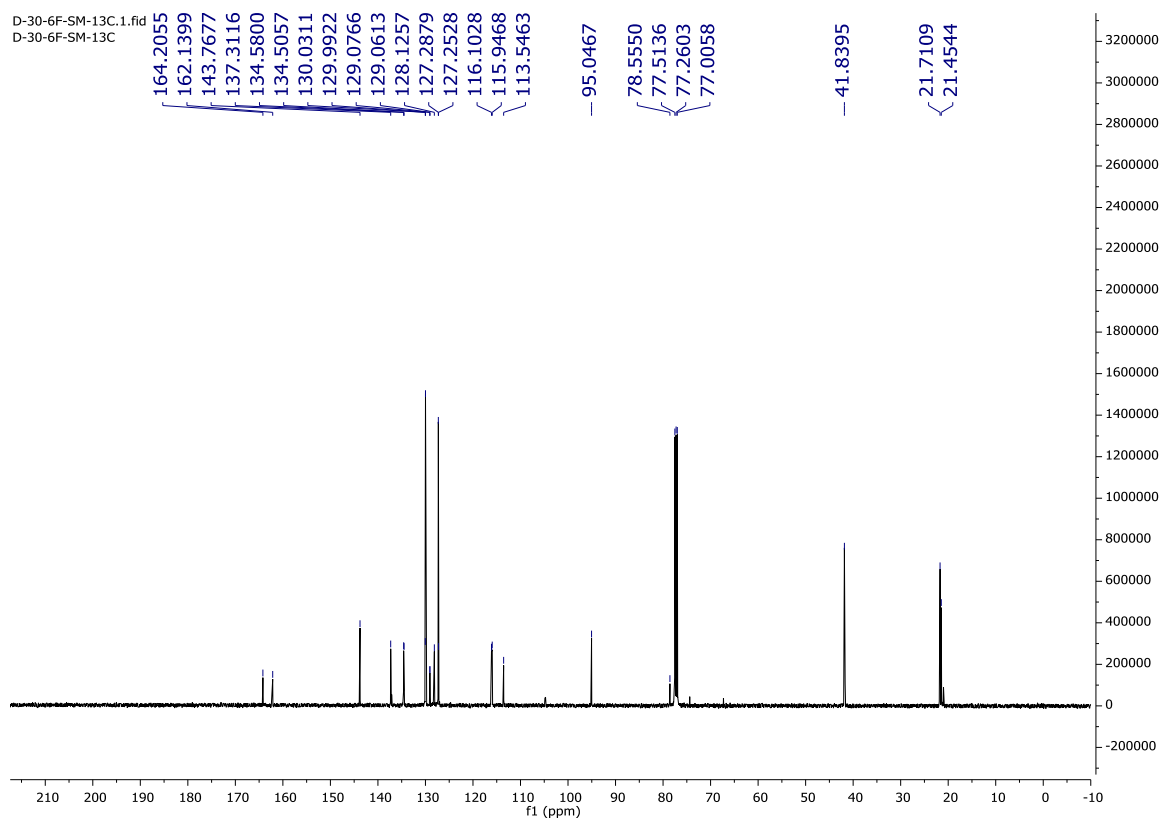
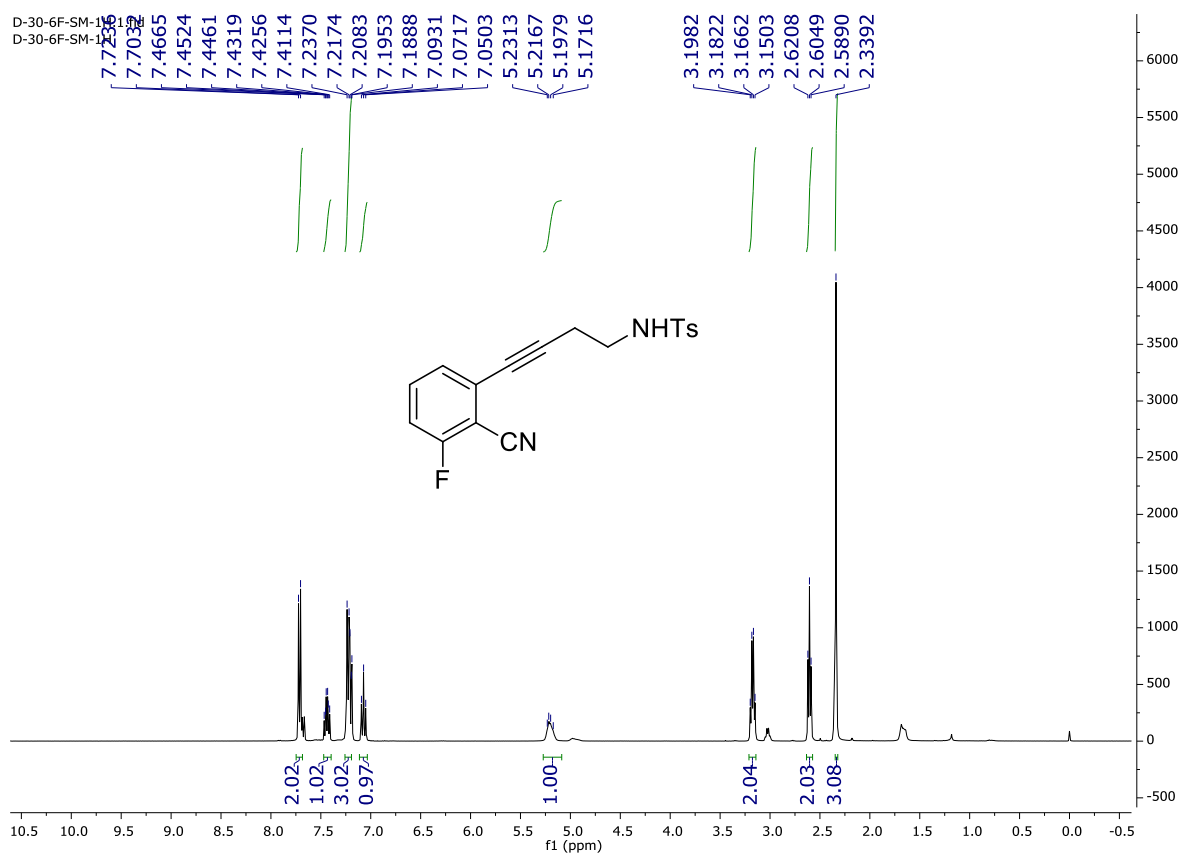
^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) spectra of **1b**



^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) spectra of **1c**

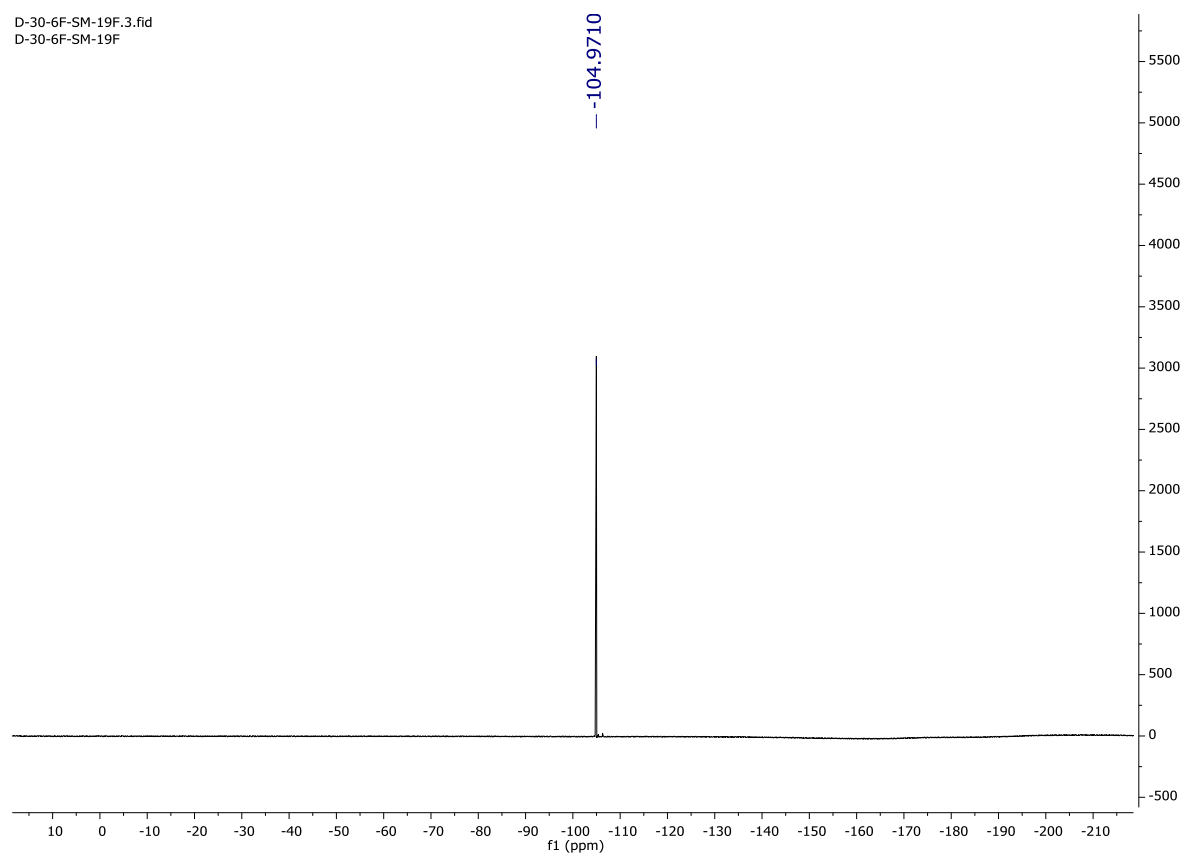


^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) spectra of **1d**

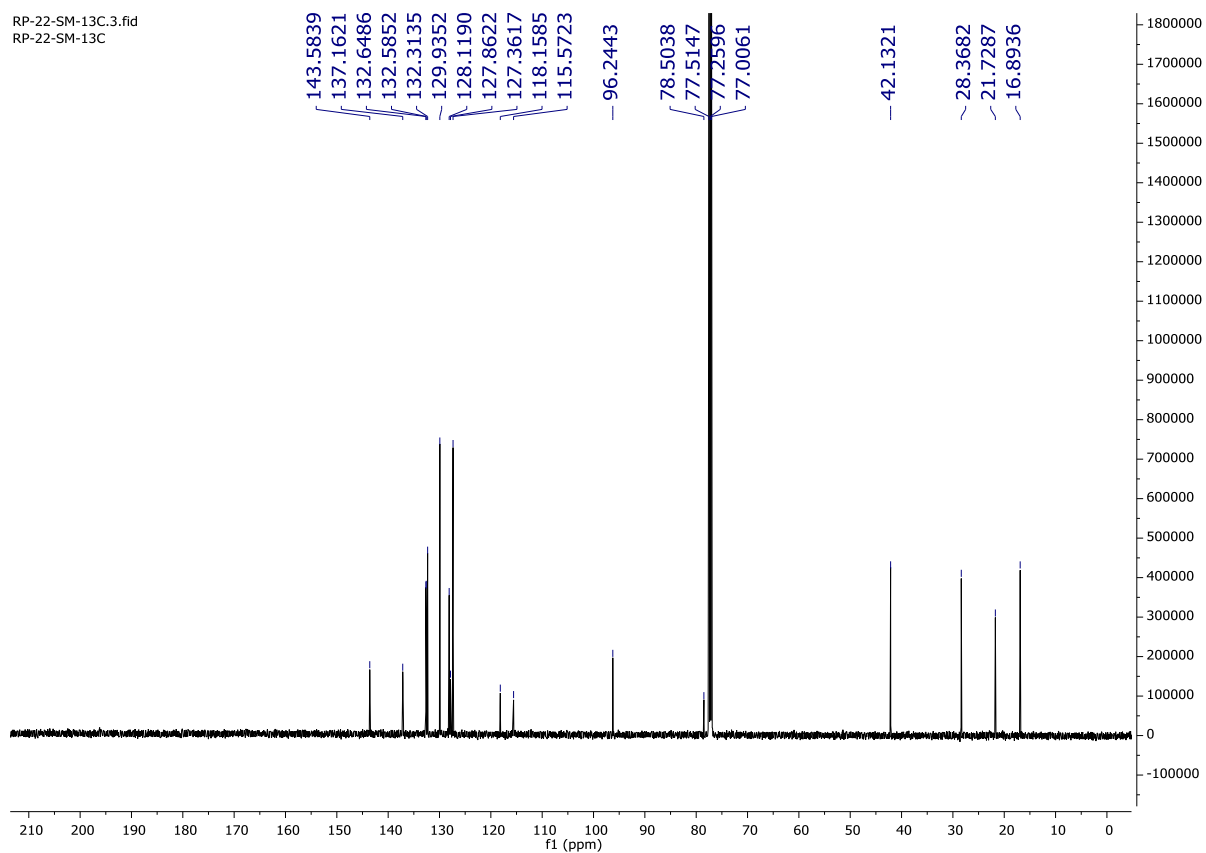
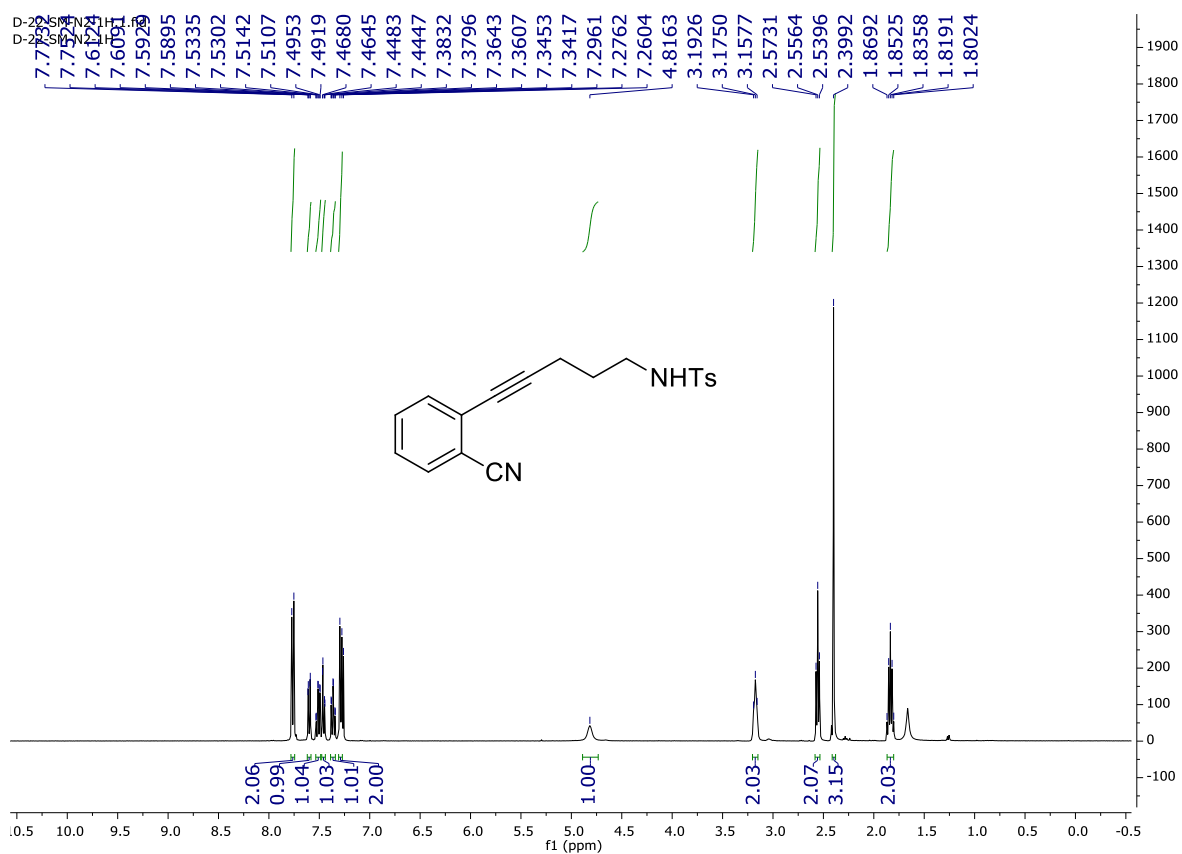


^{19}F (377 MHz, CDCl_3) spectrum of **1d**

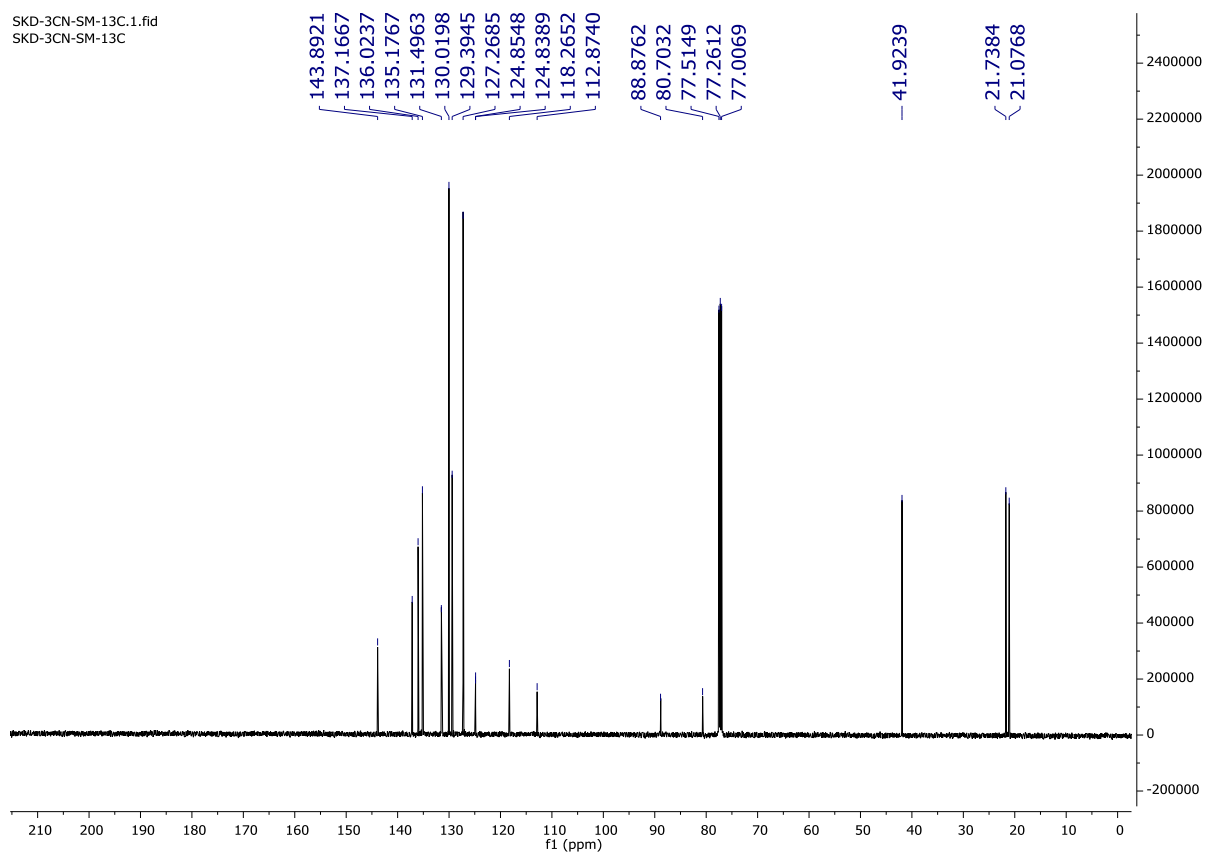
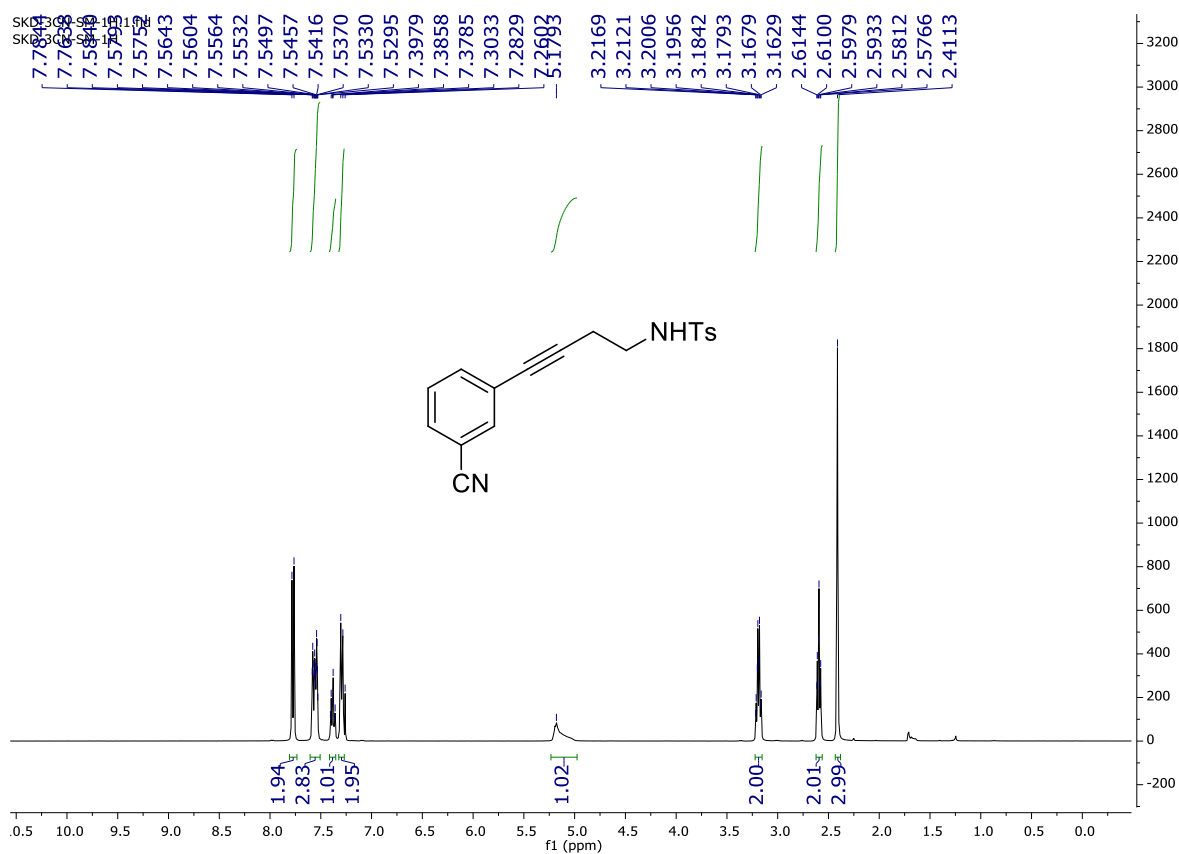
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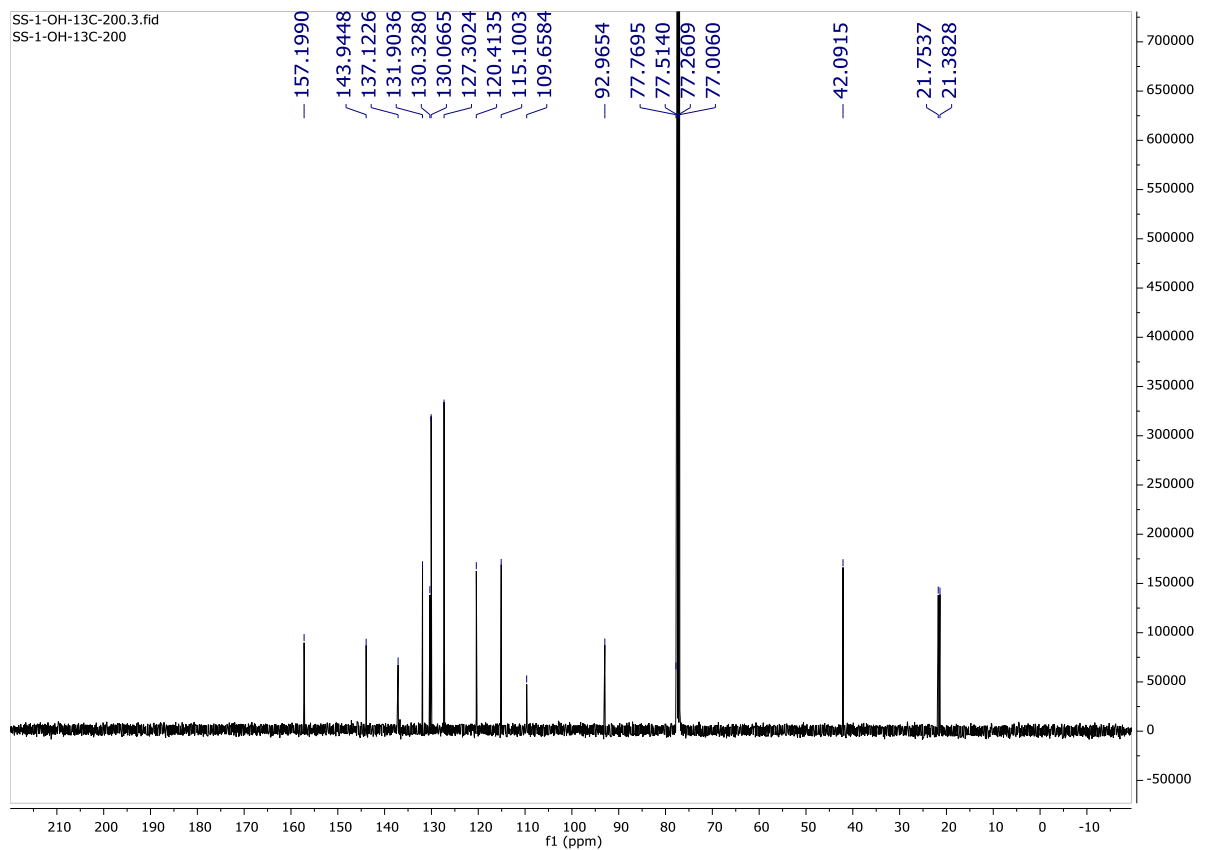
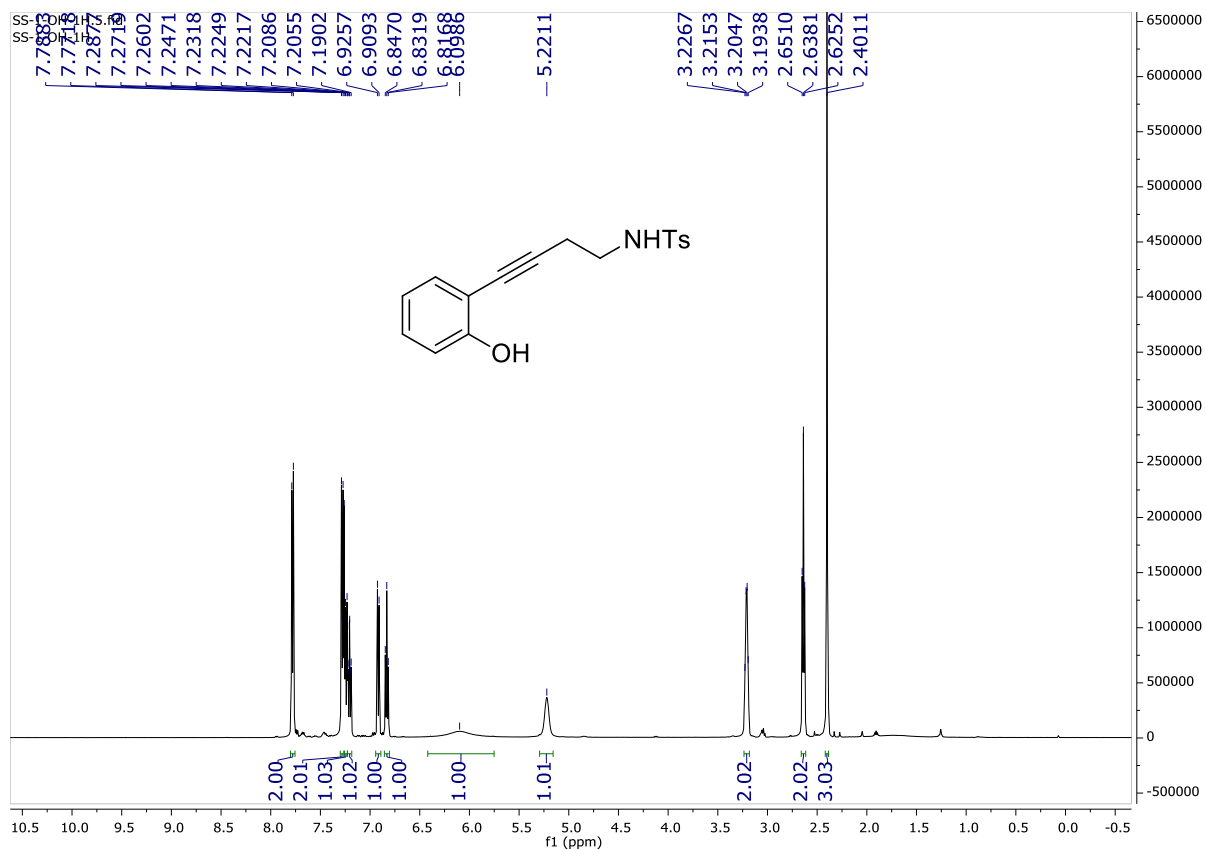
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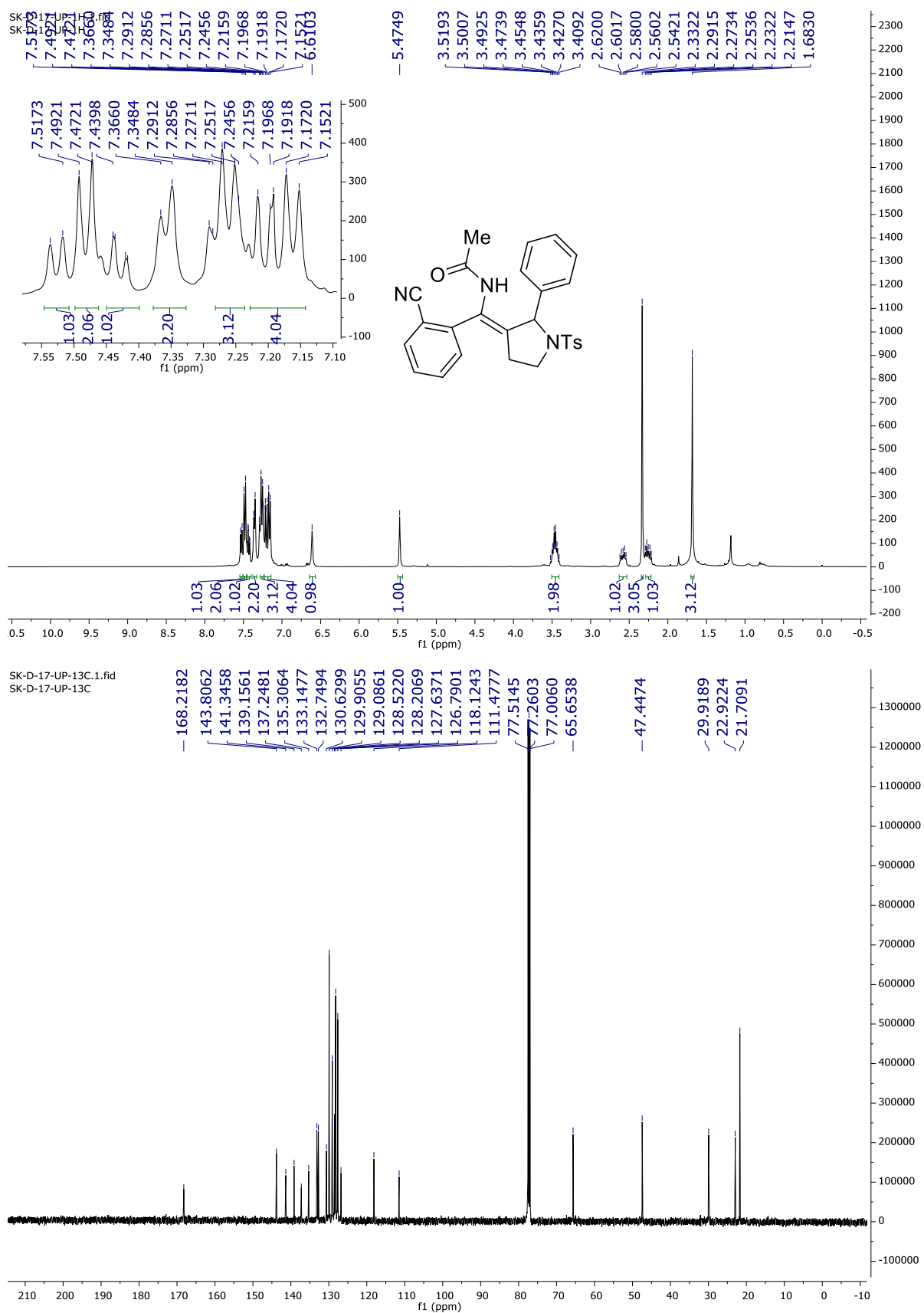
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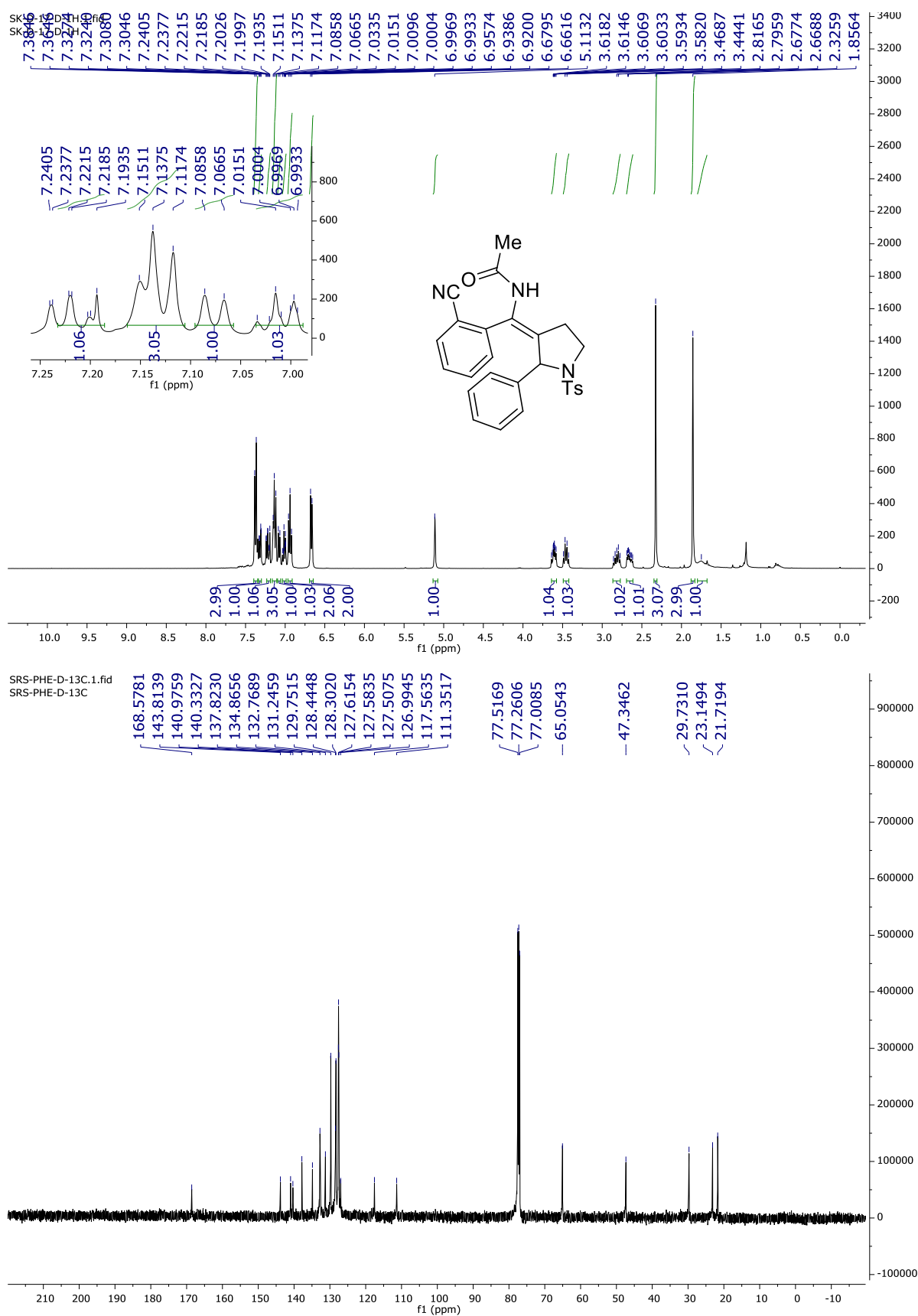
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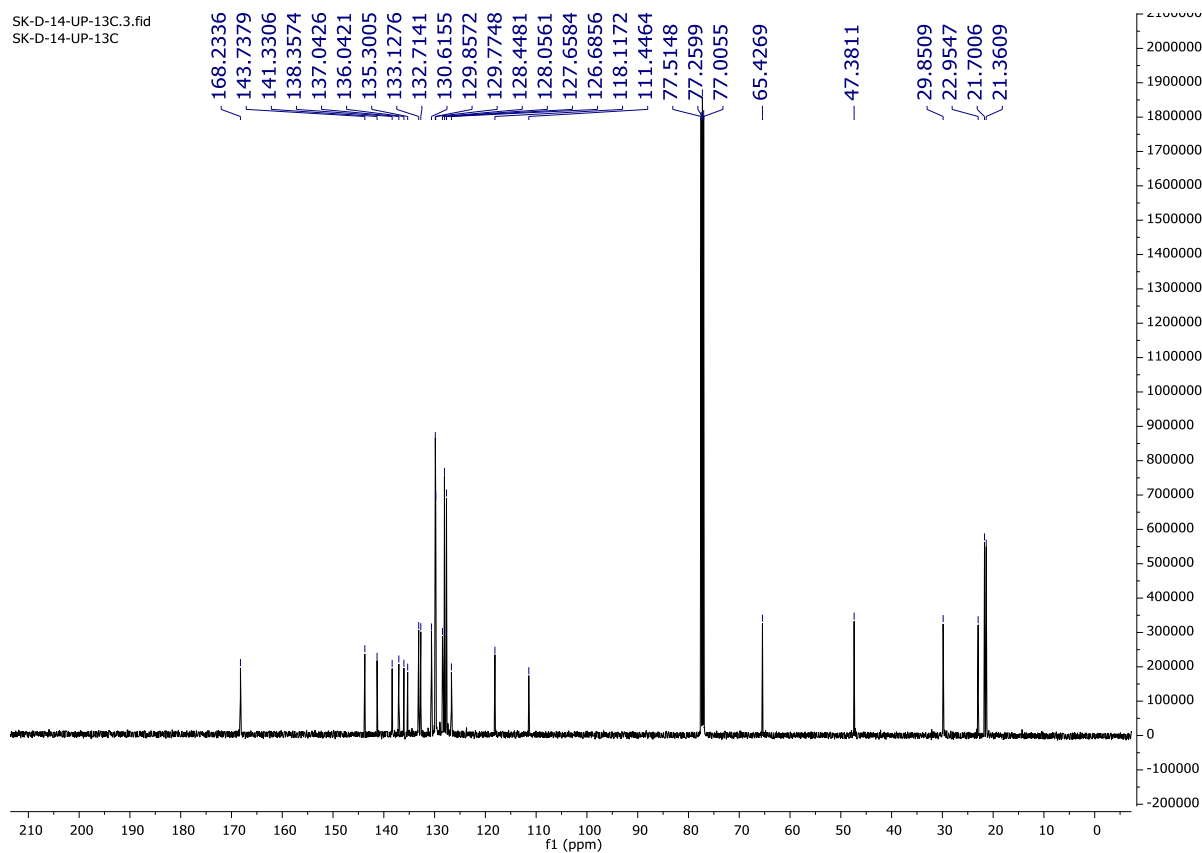
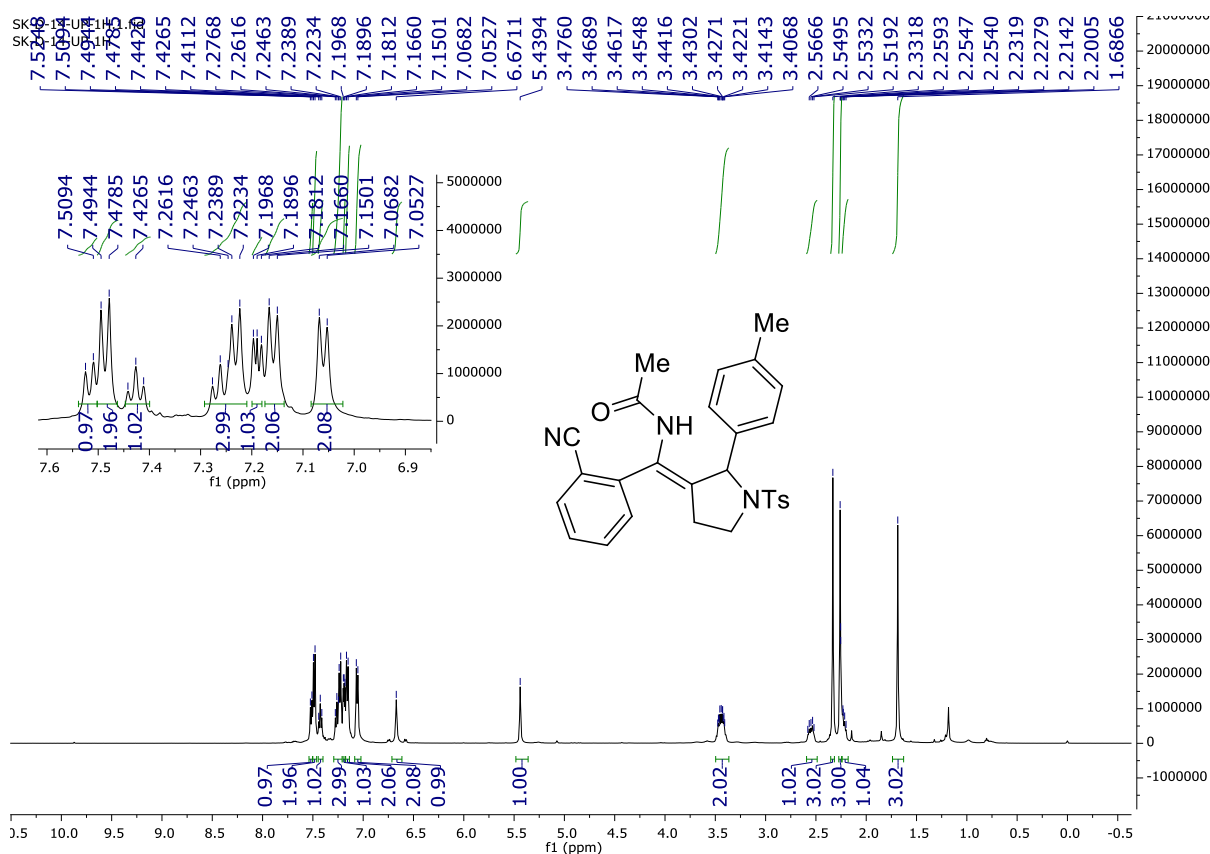
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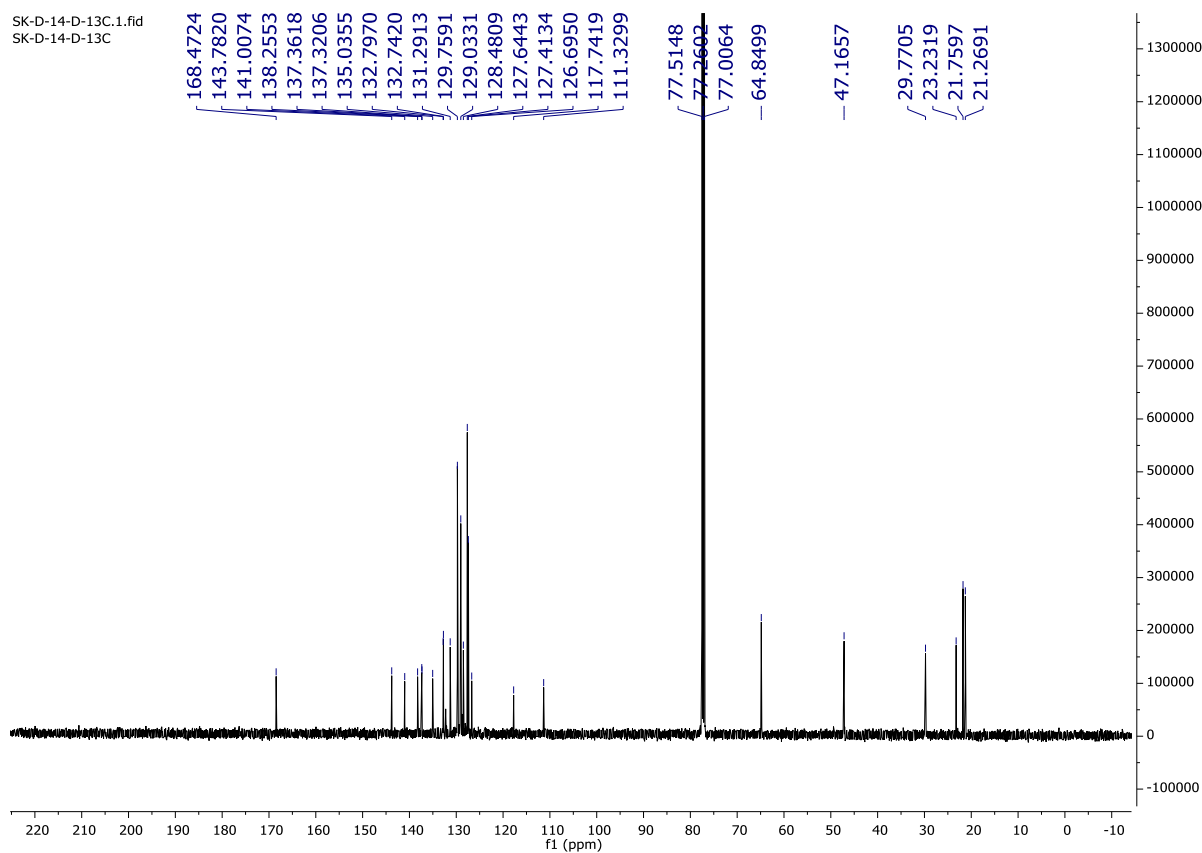
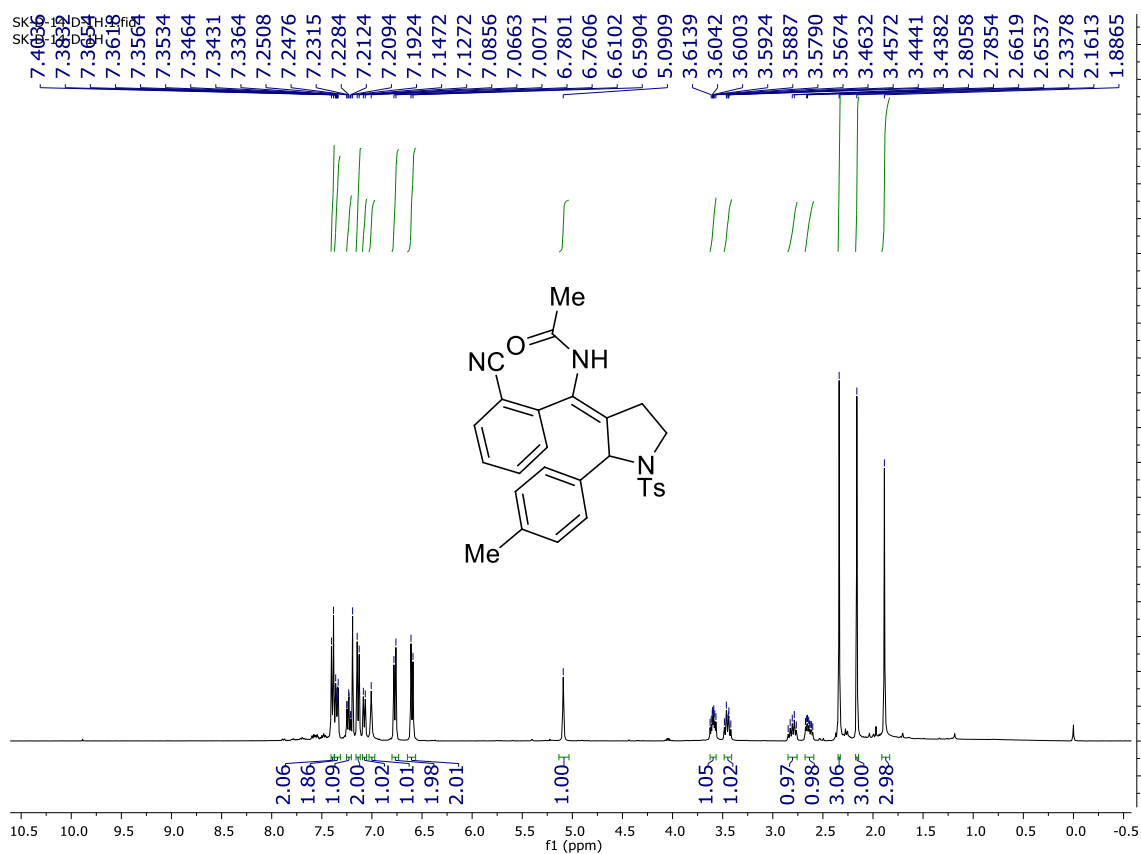
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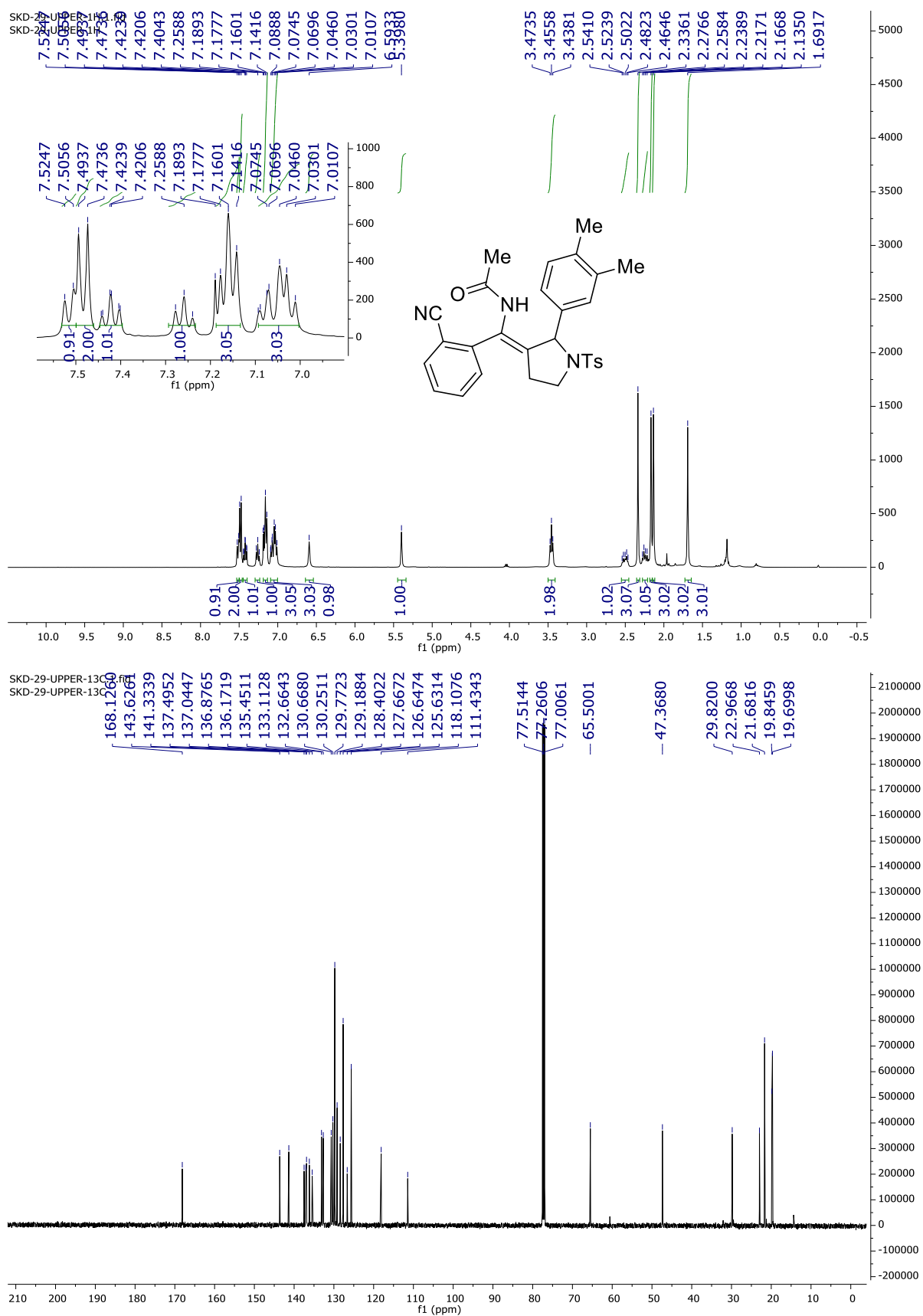
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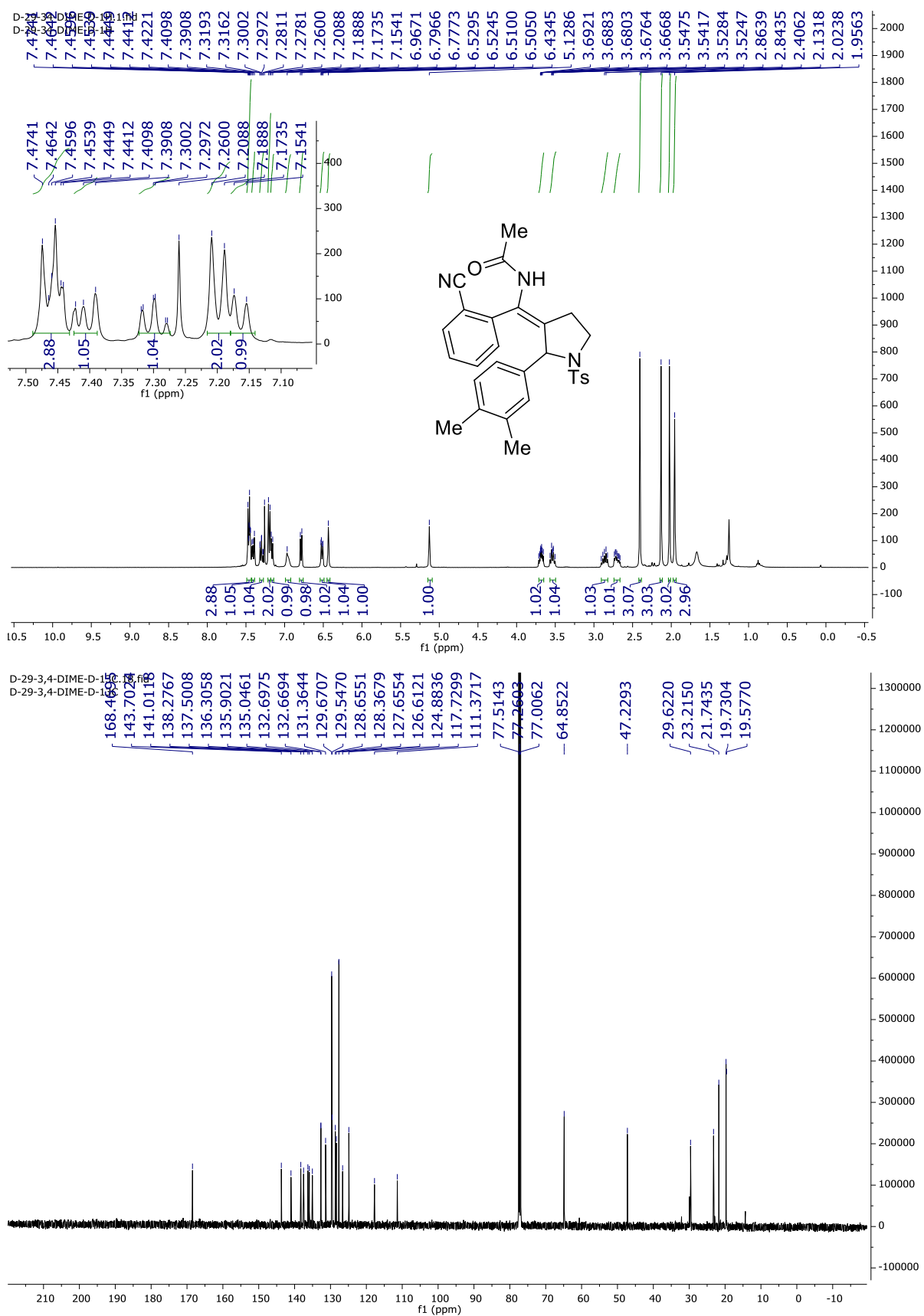
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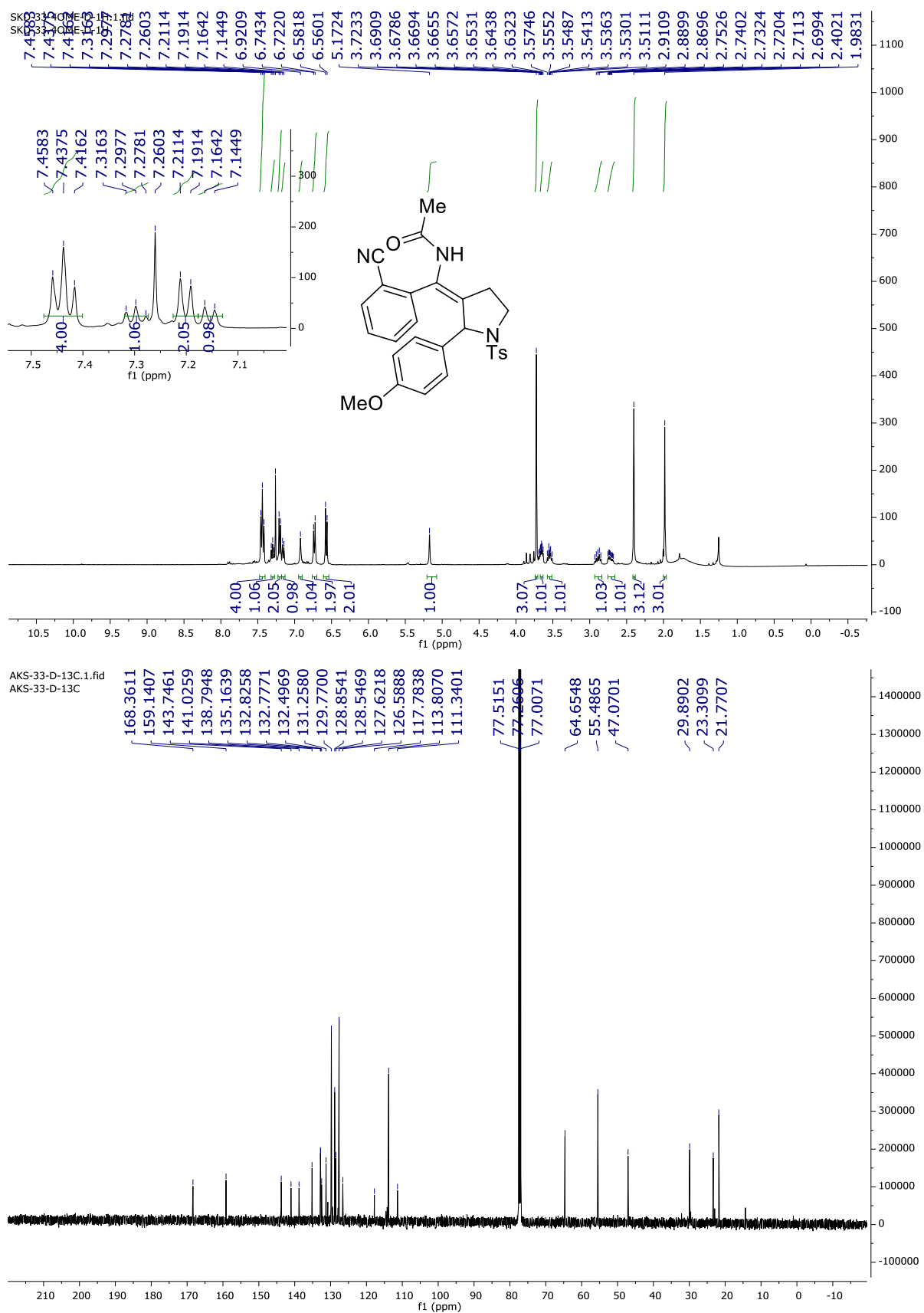
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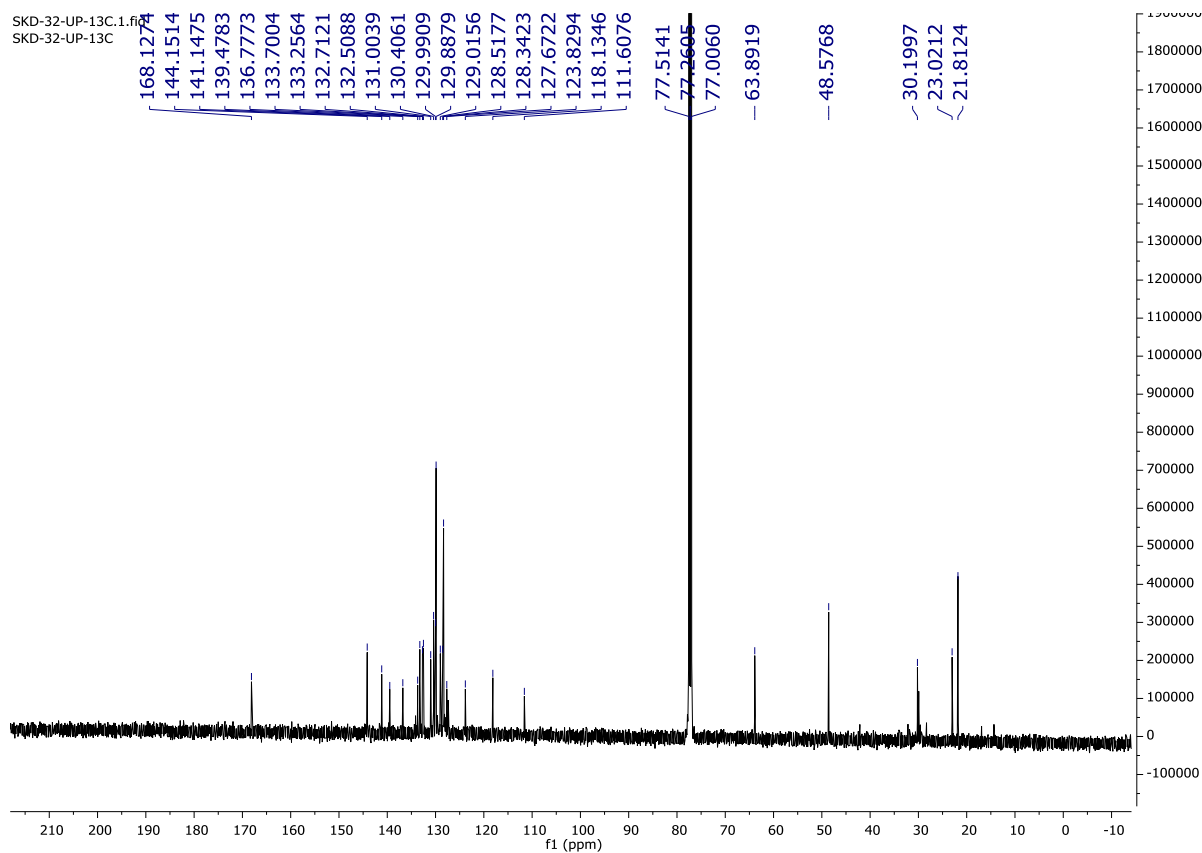
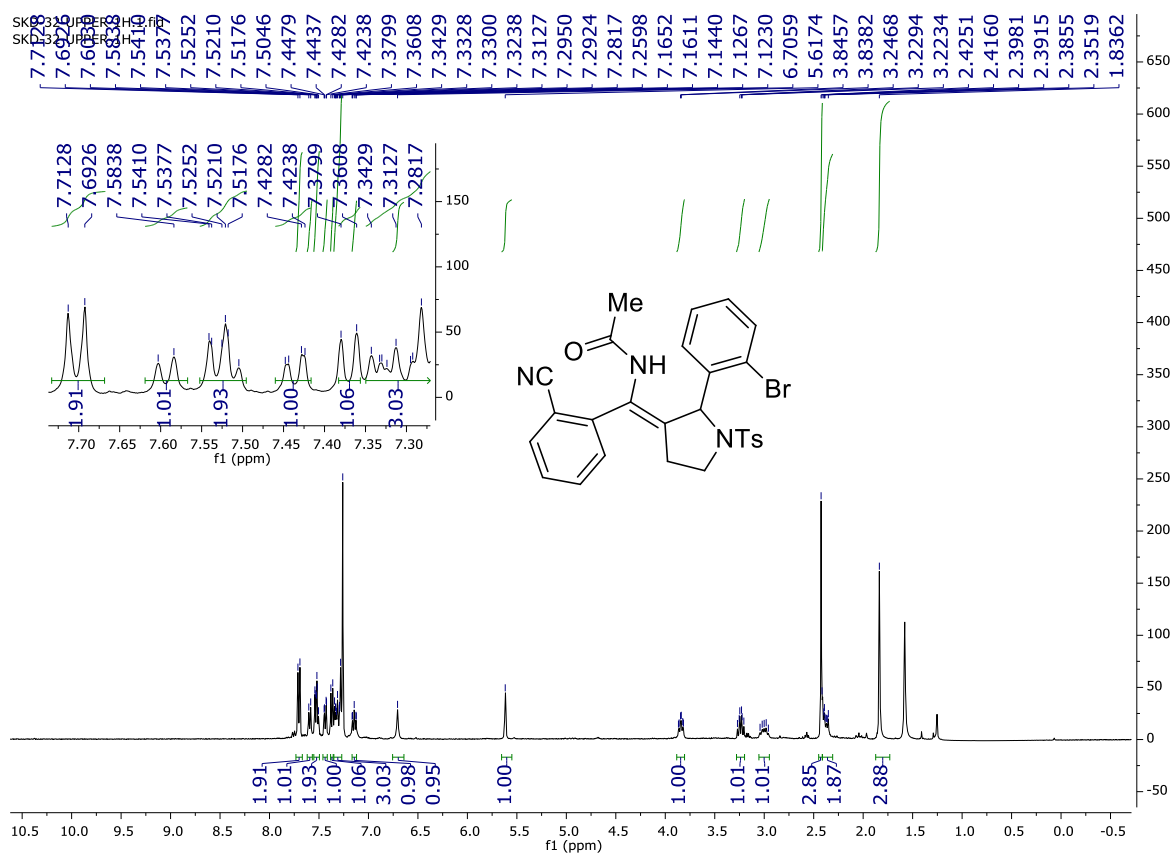
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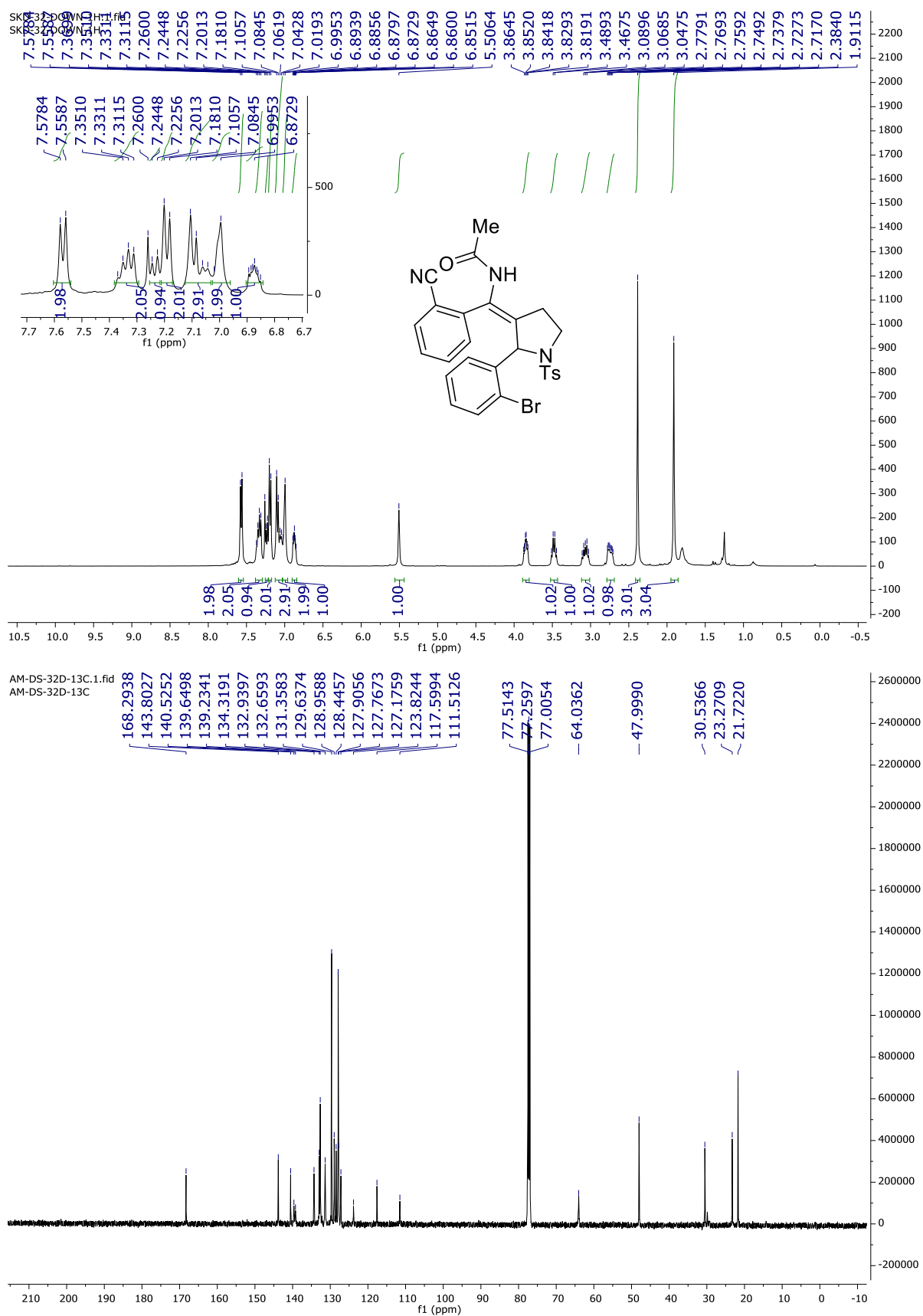
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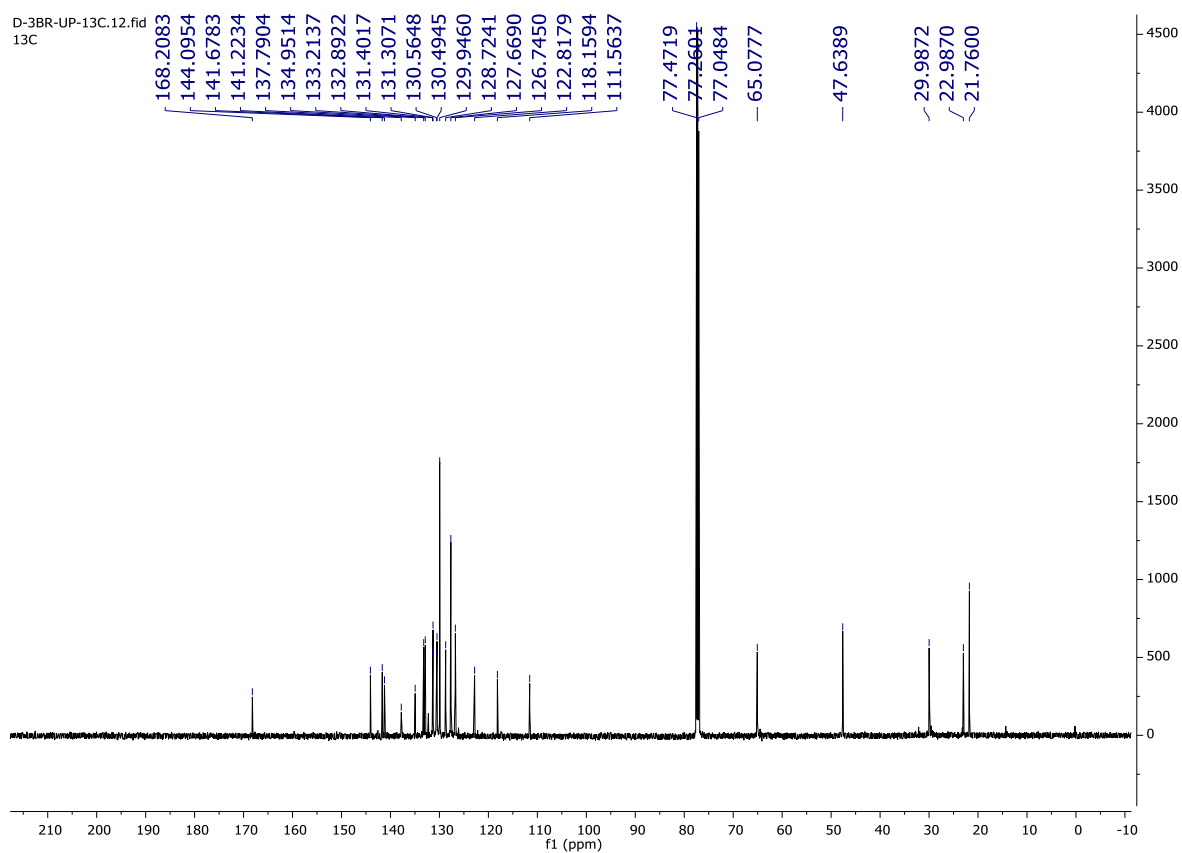
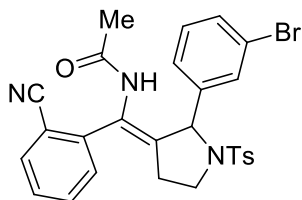
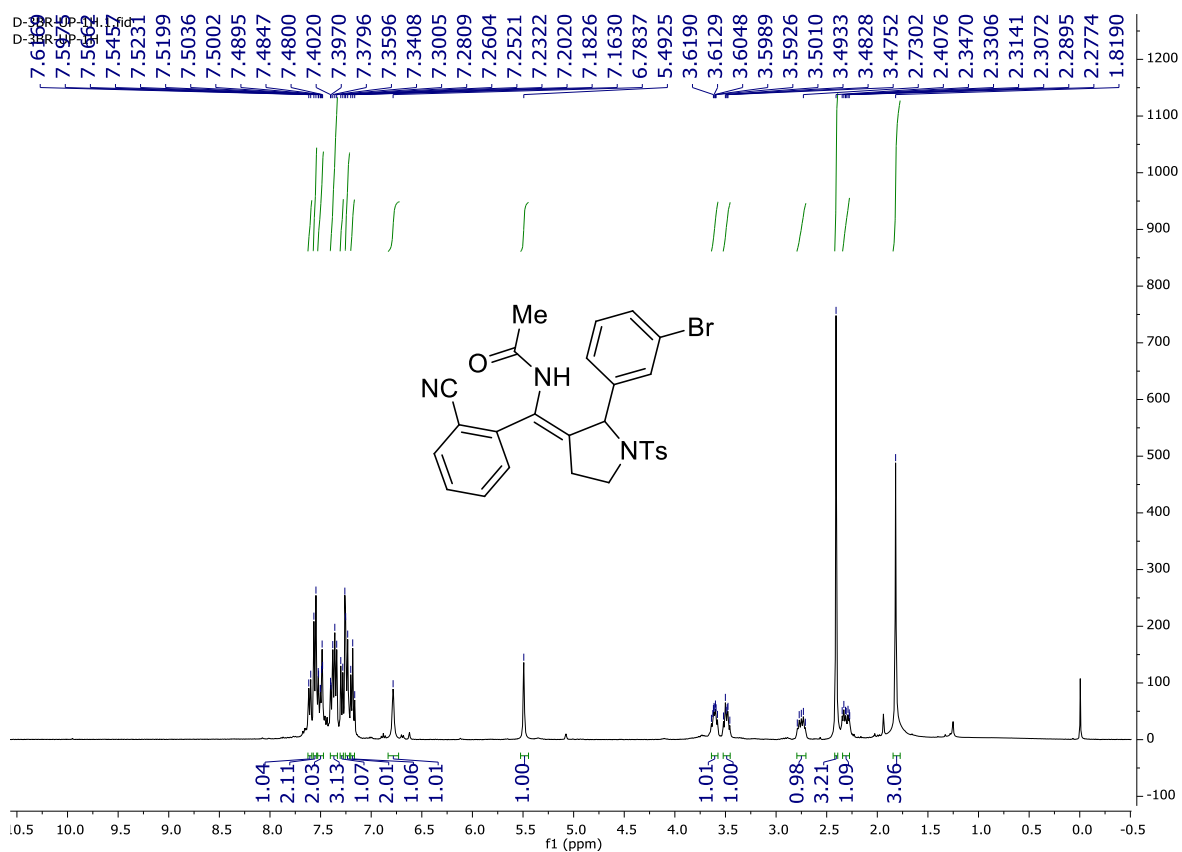
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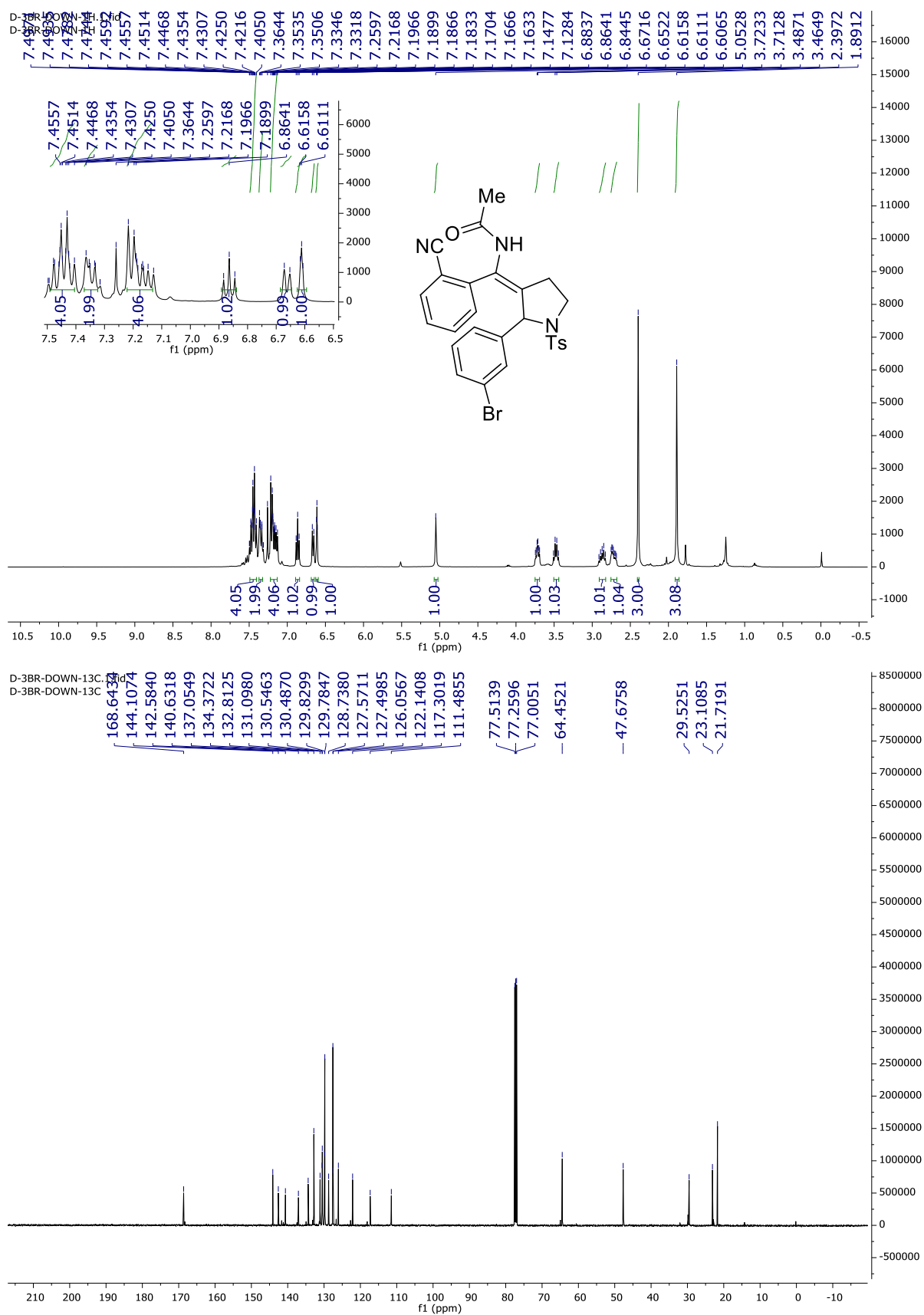
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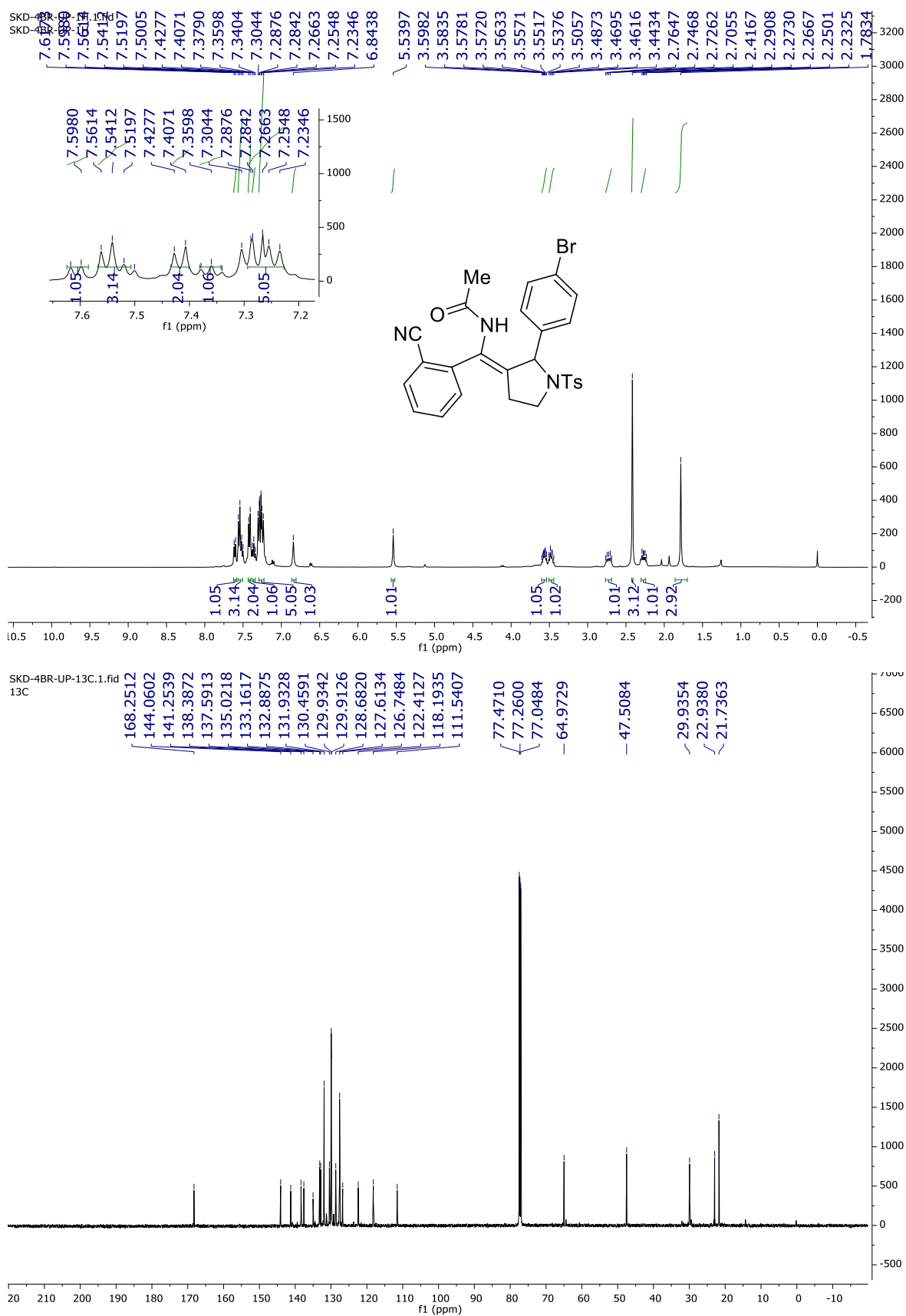
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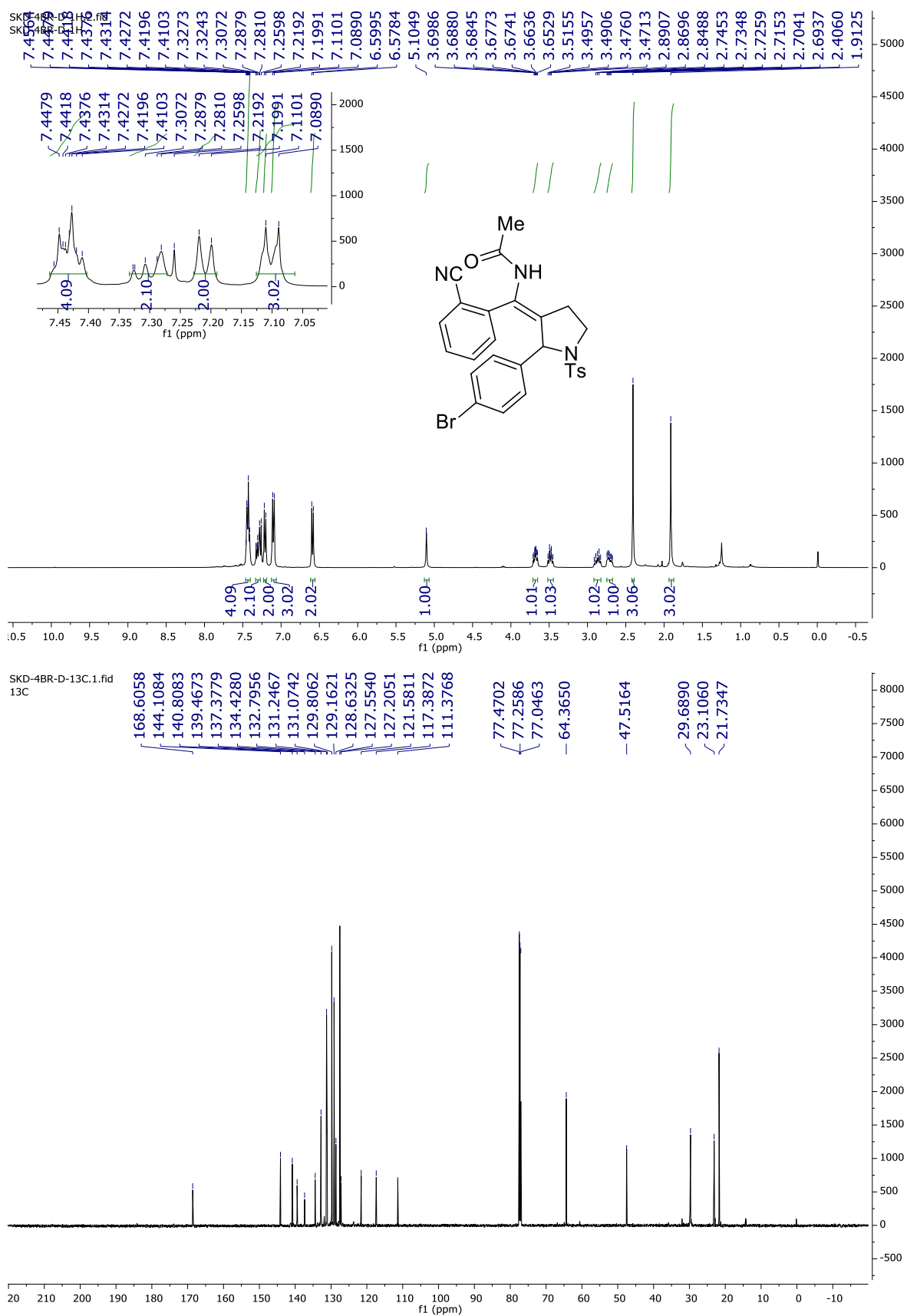
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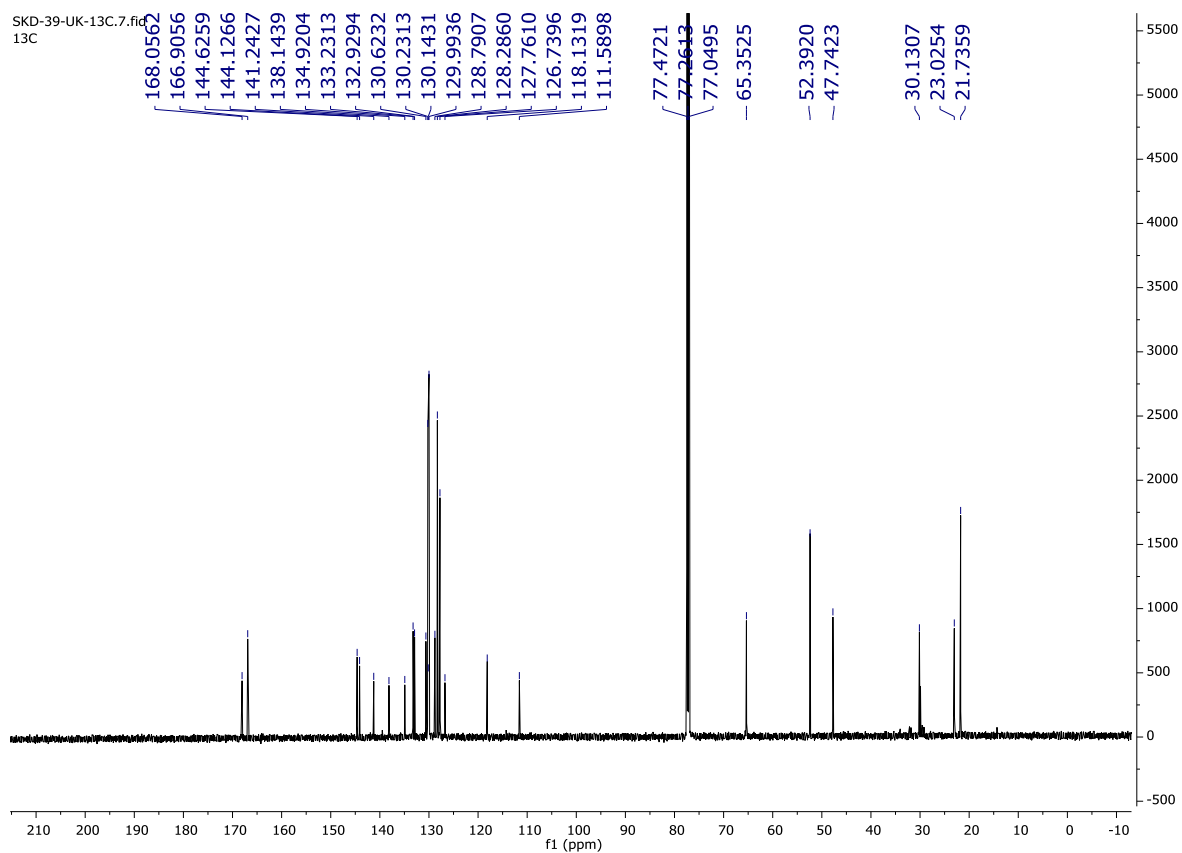
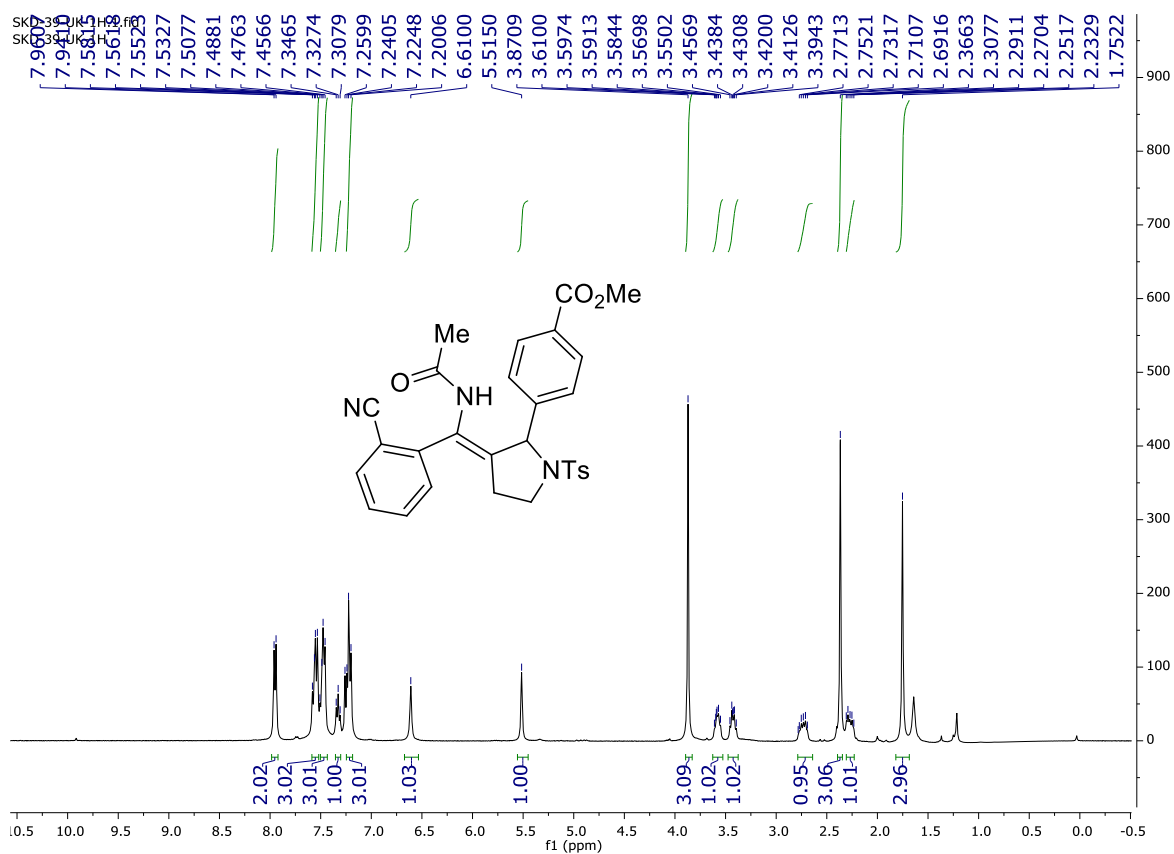
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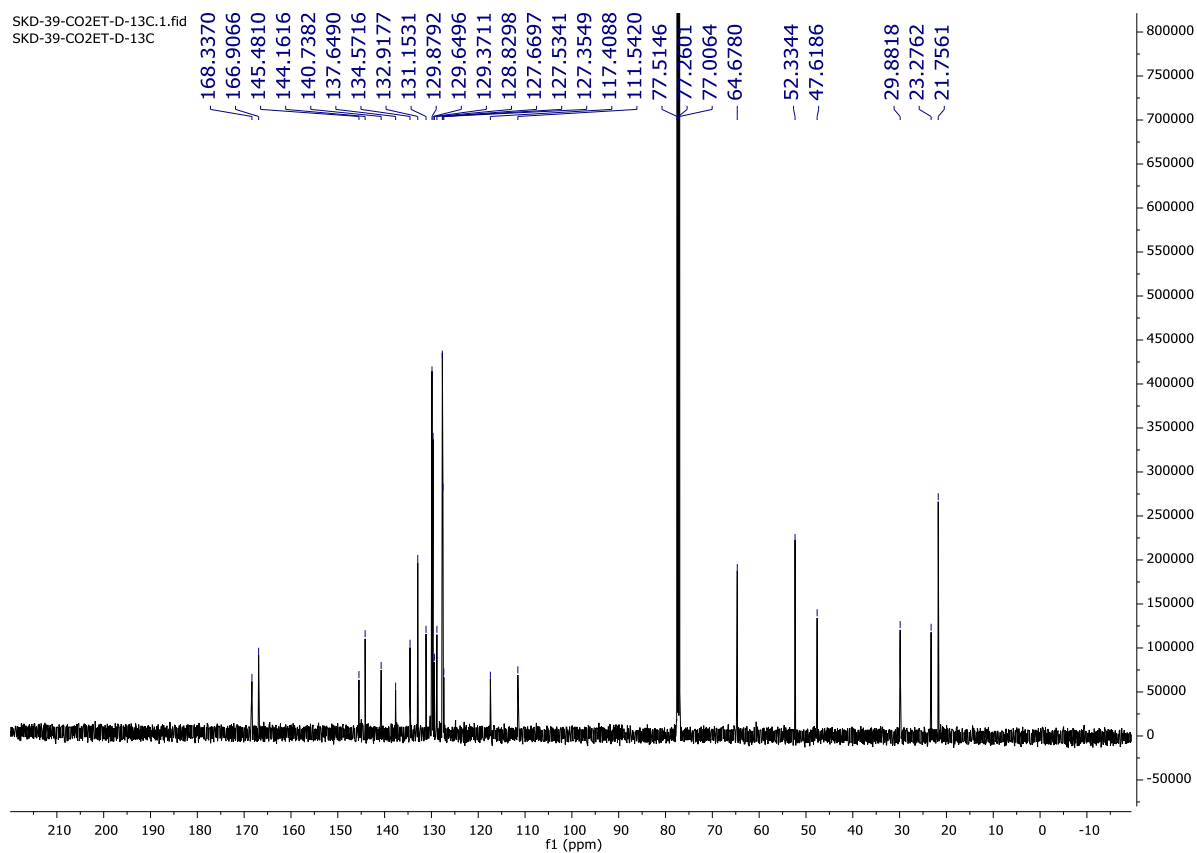
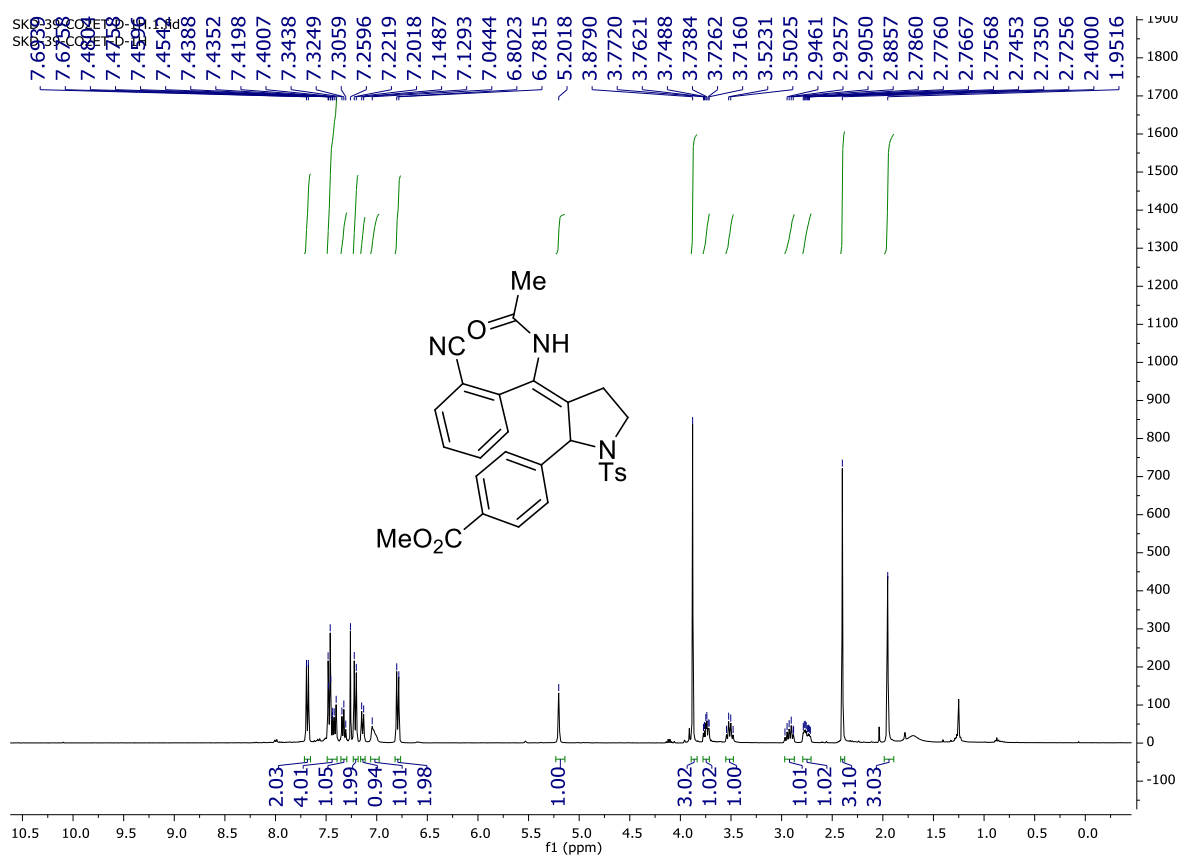
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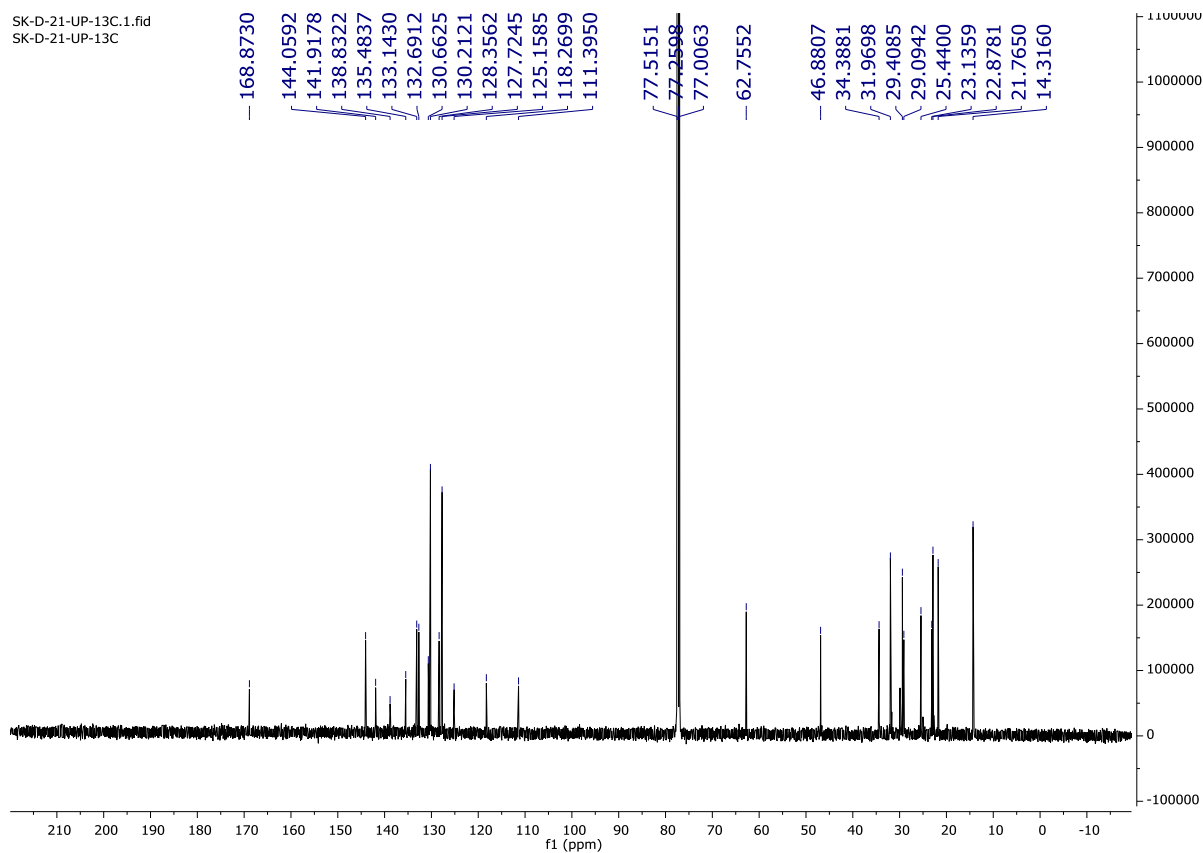
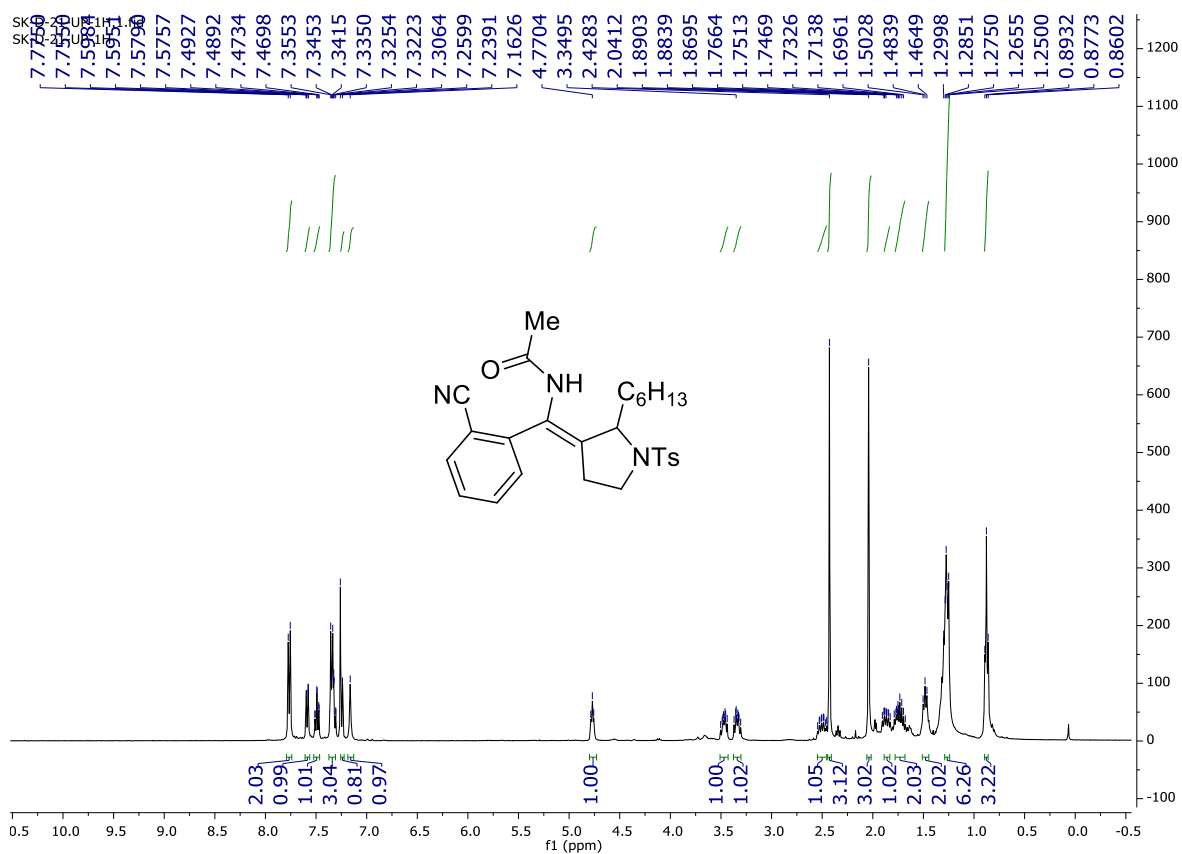
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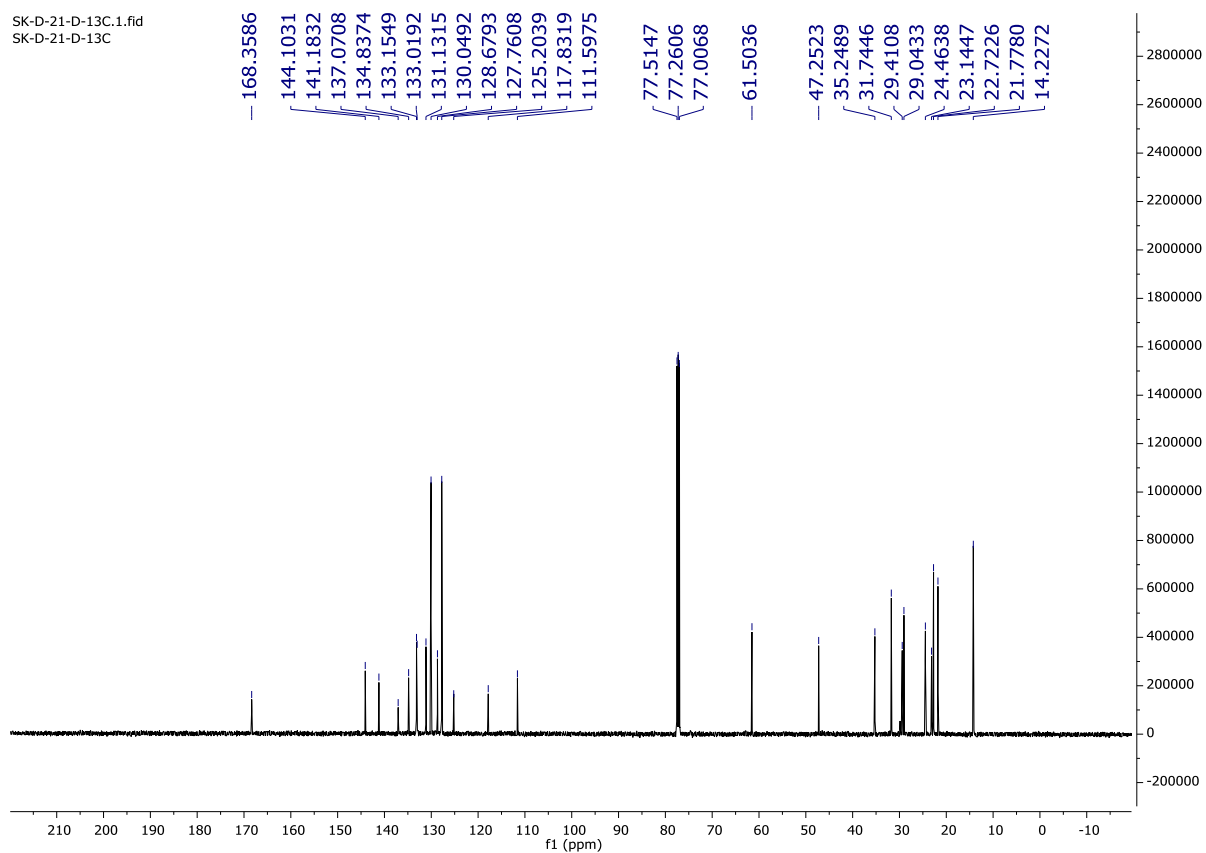
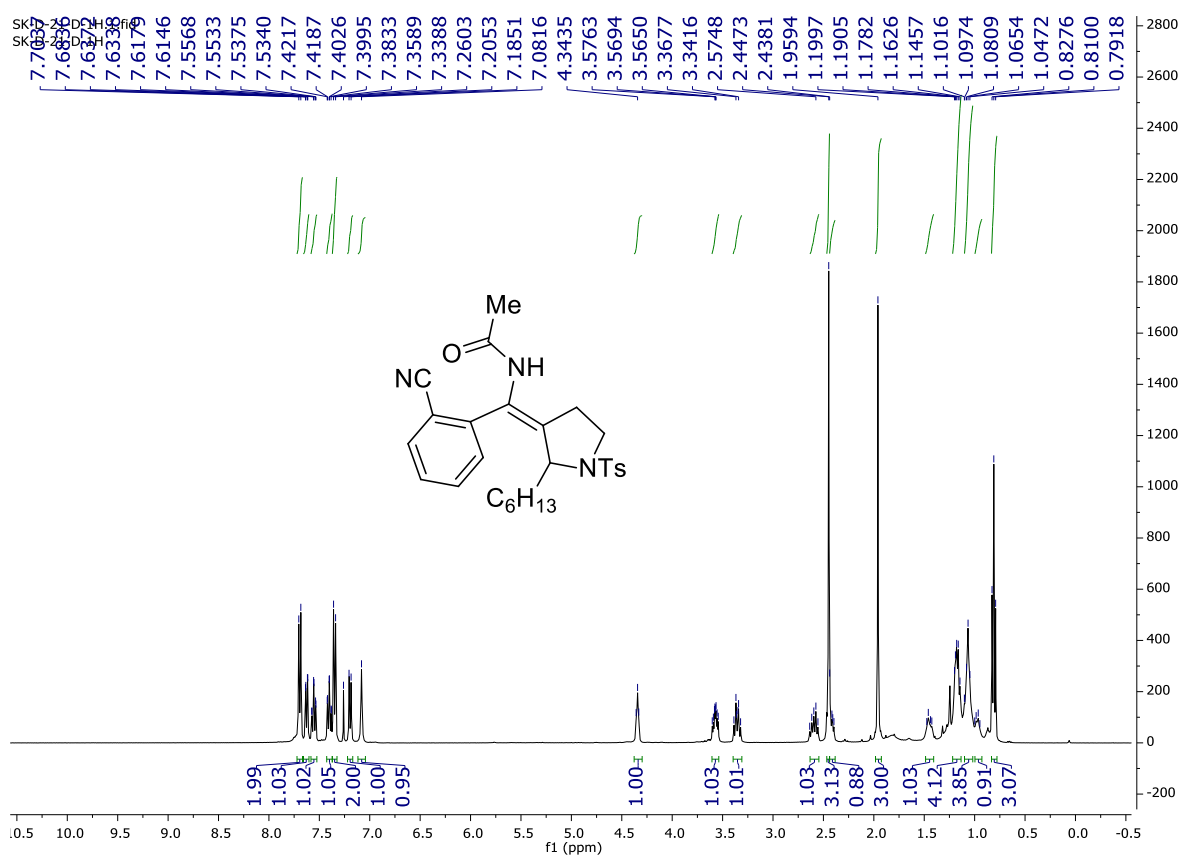
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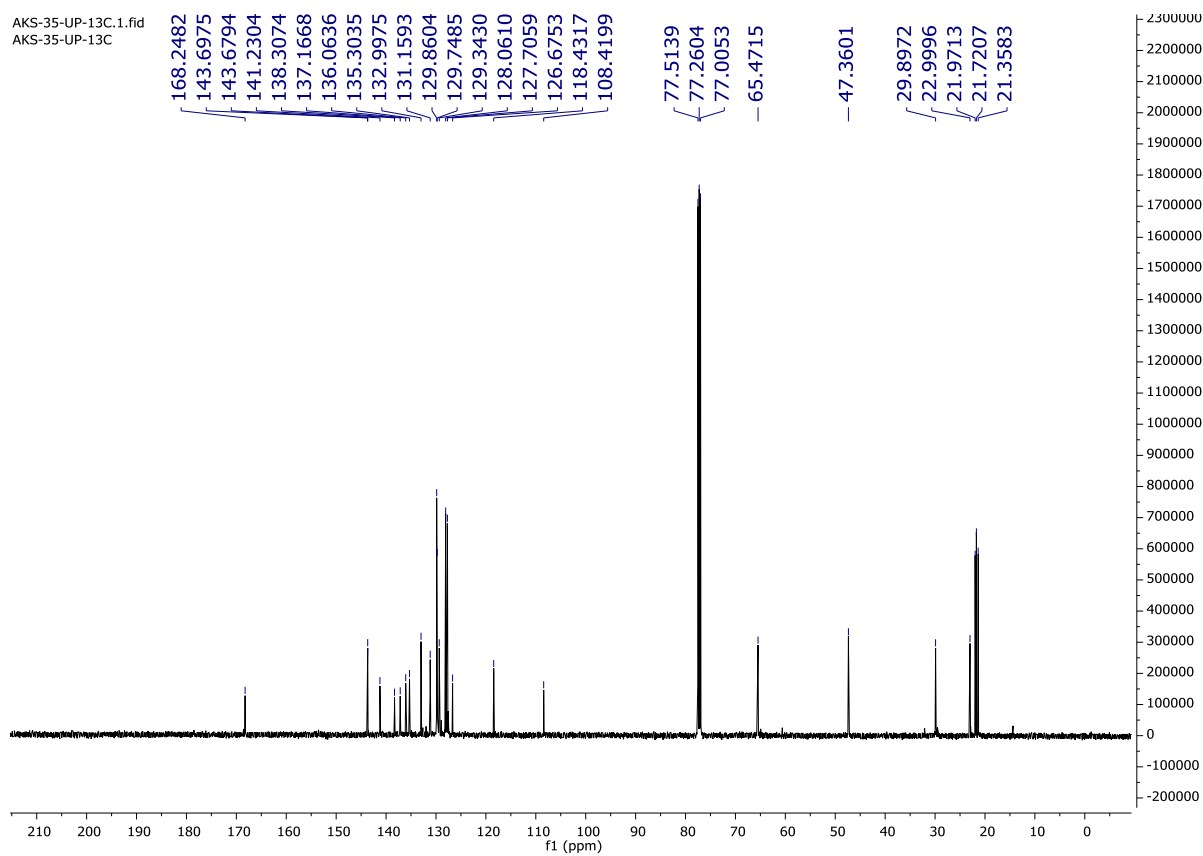
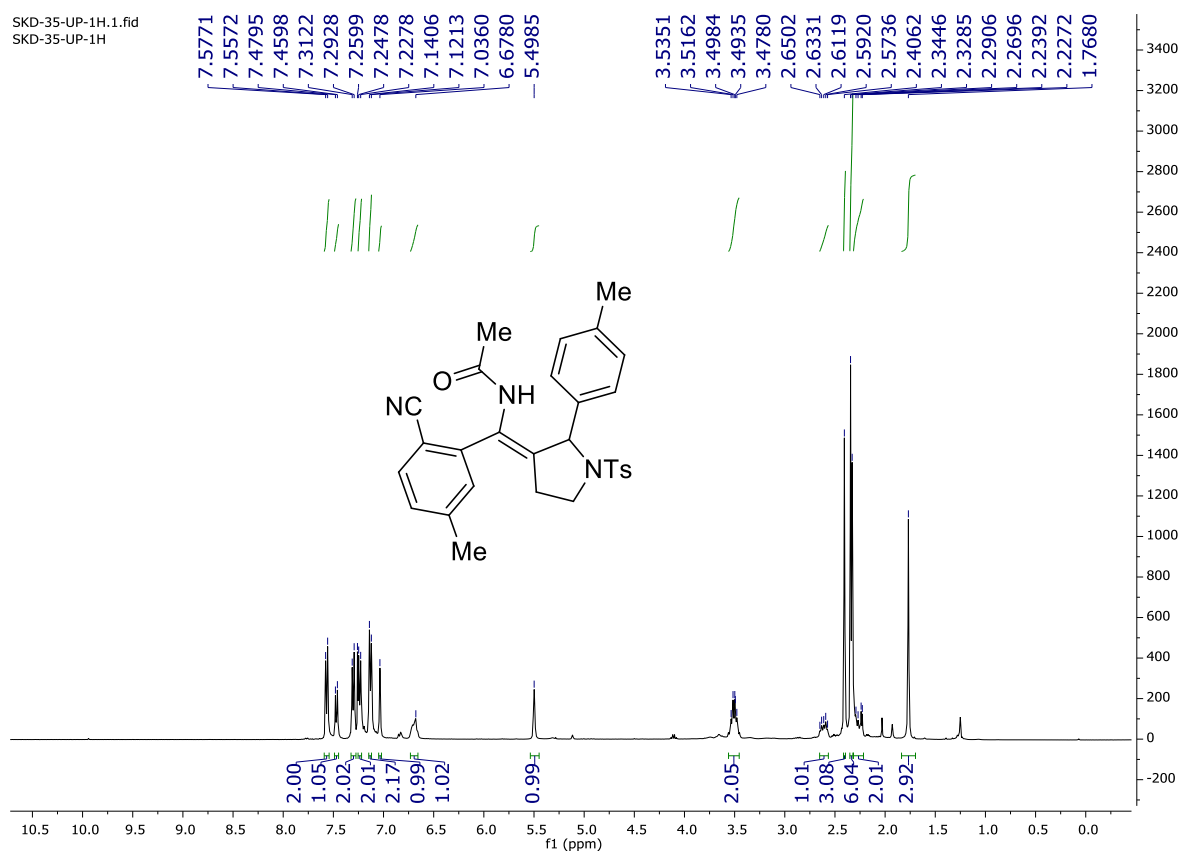
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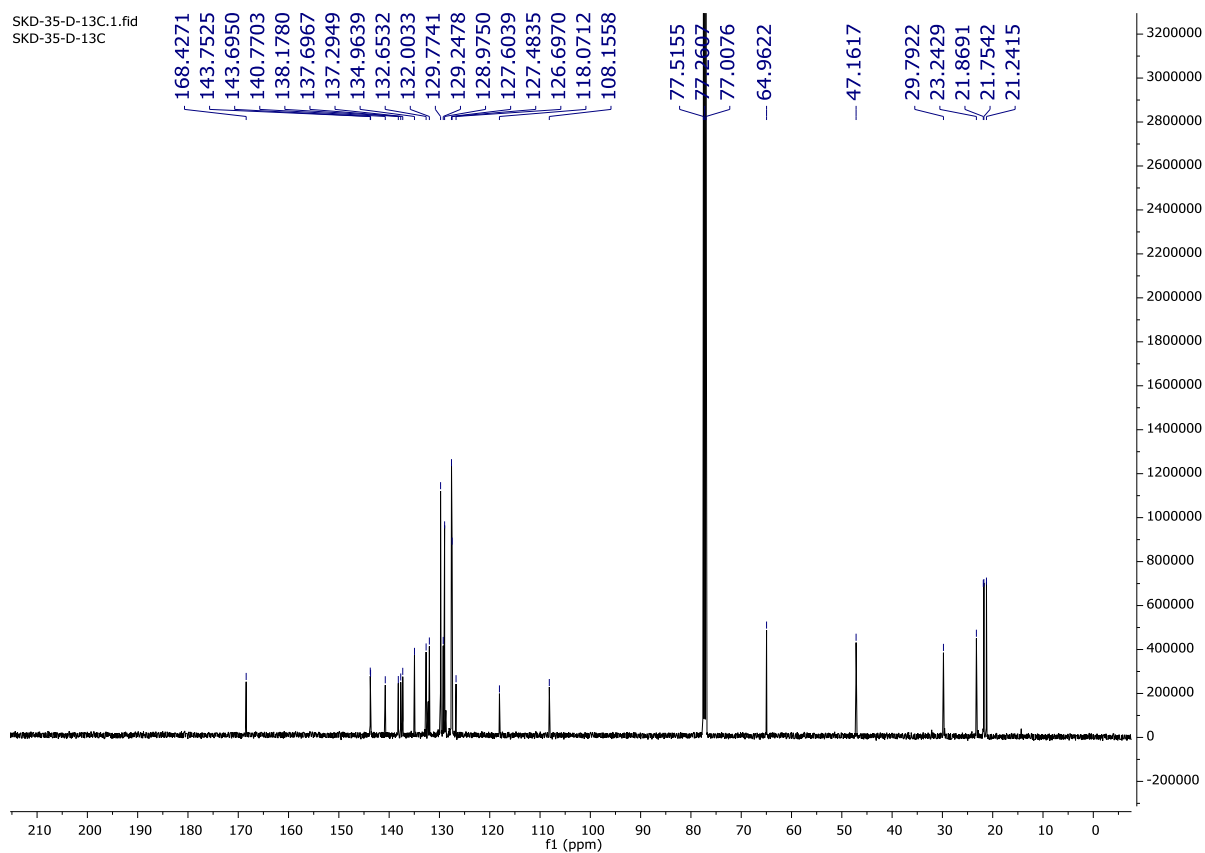
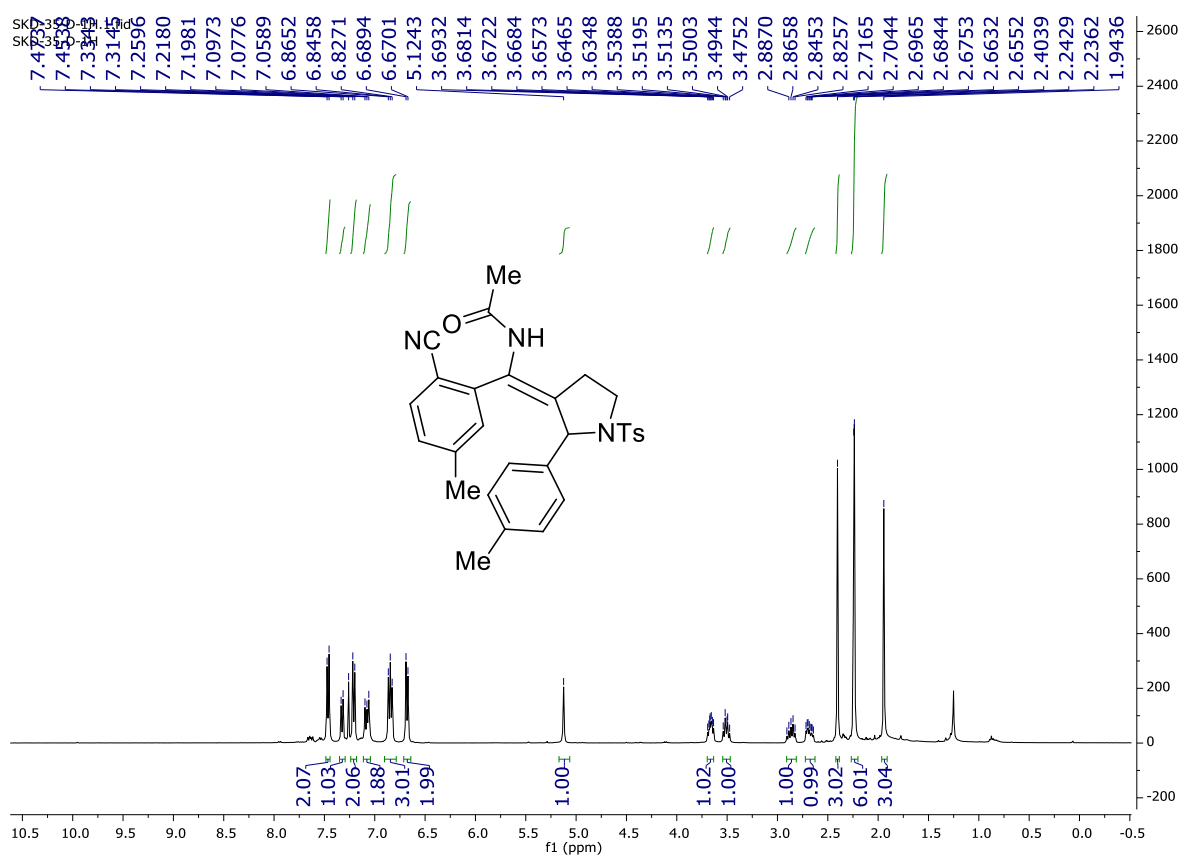
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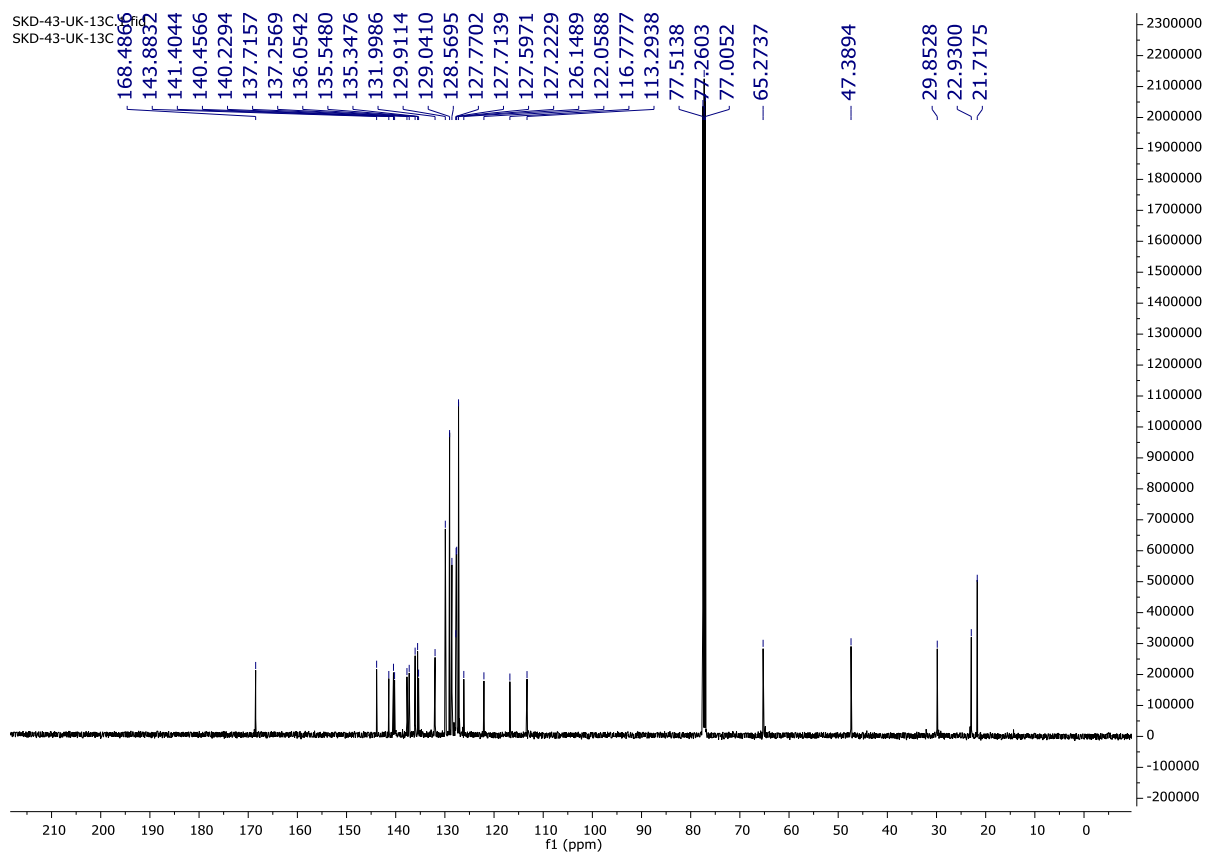
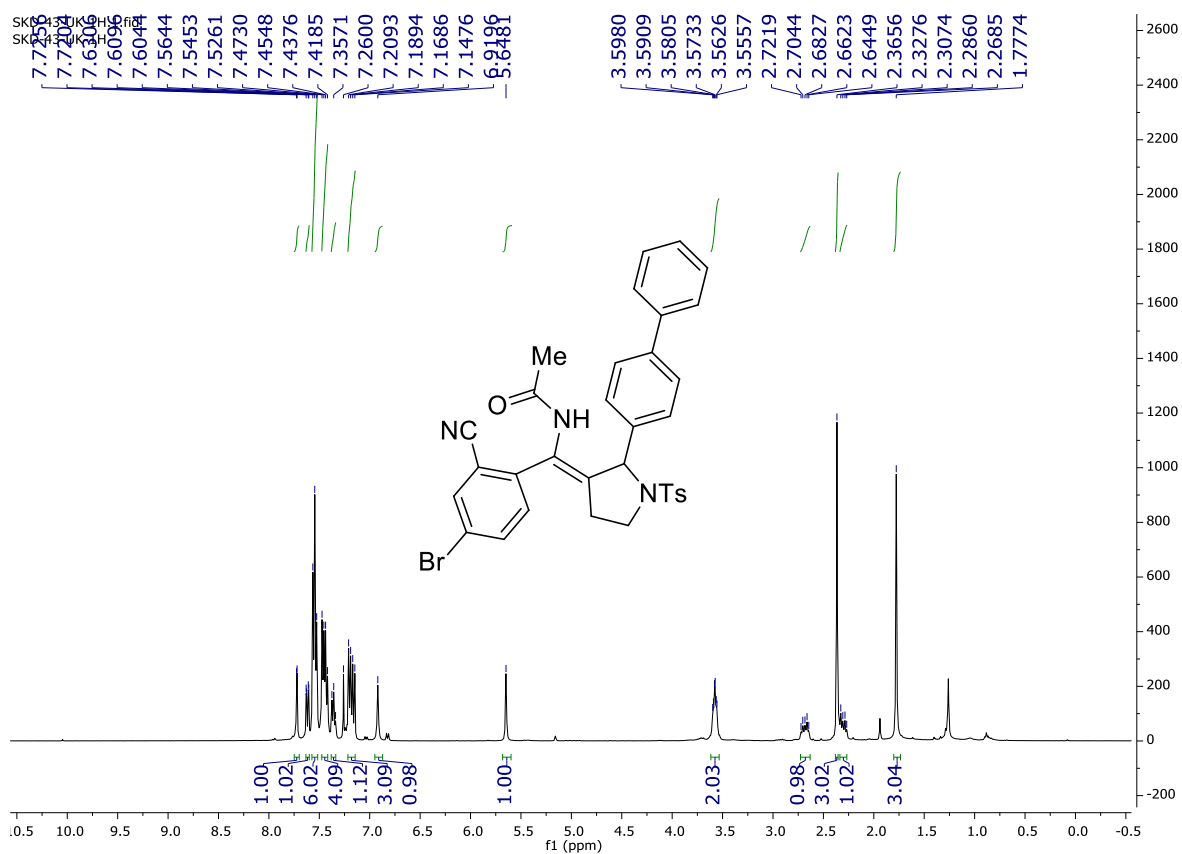
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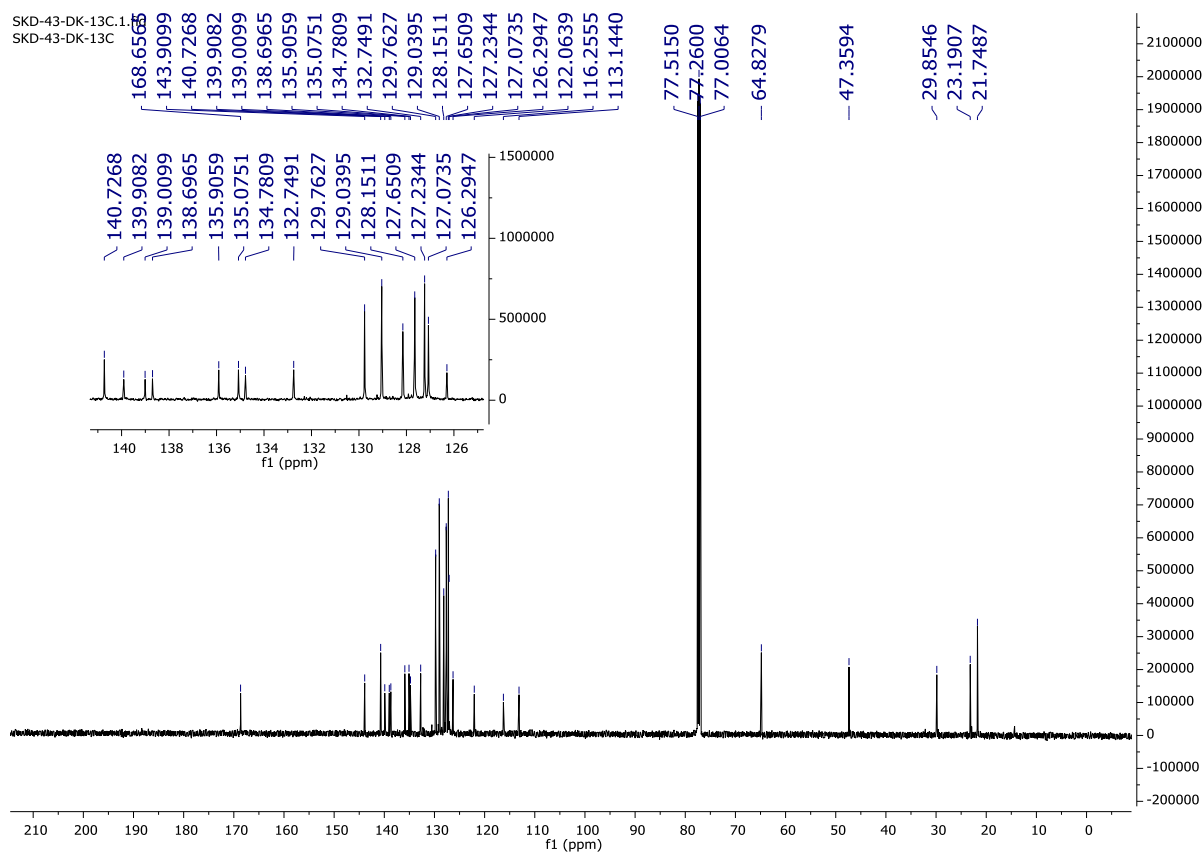
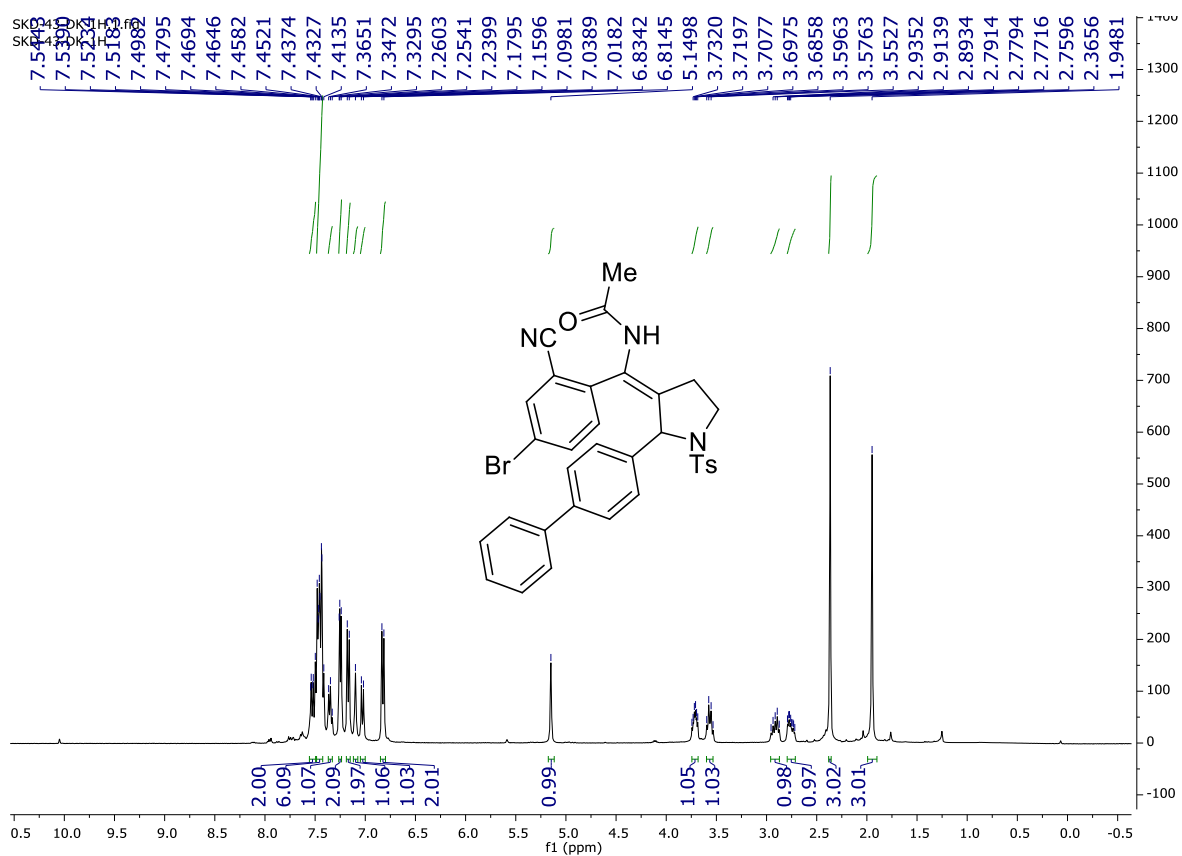
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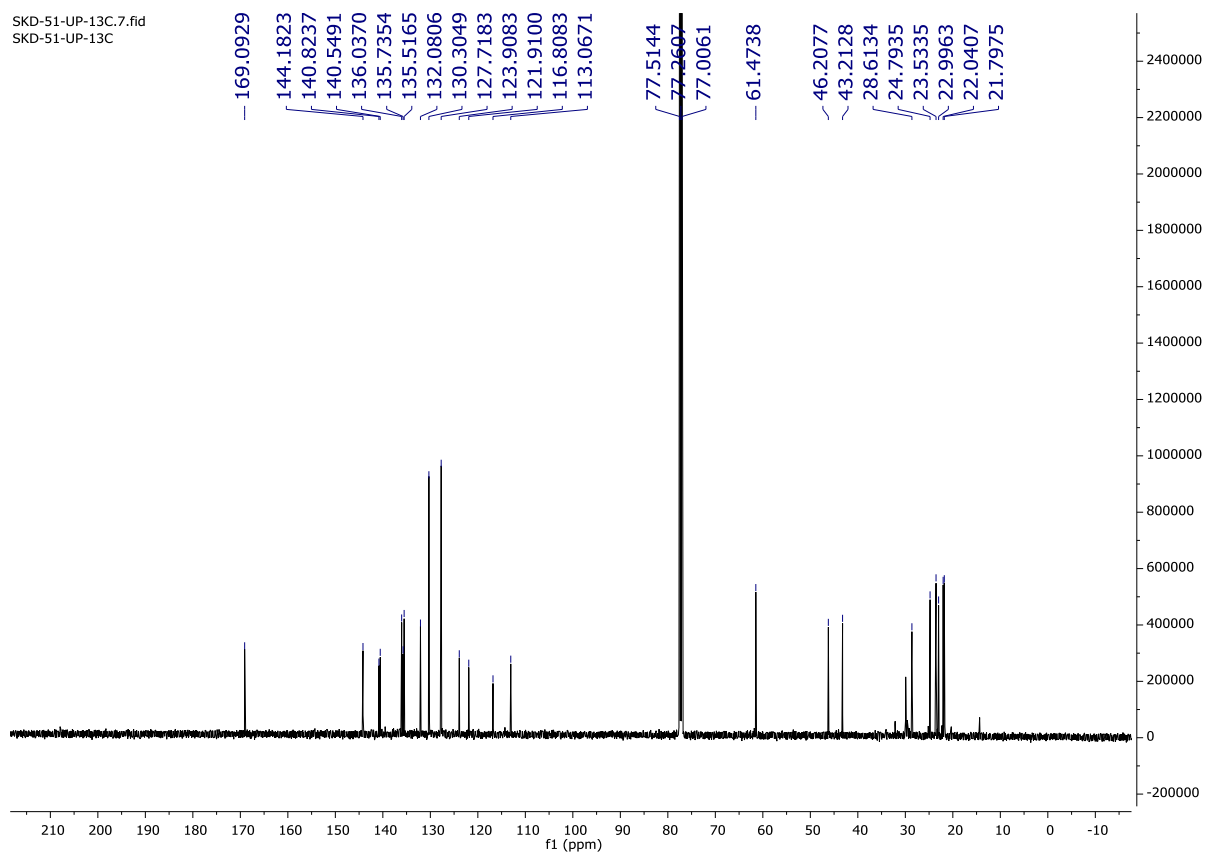
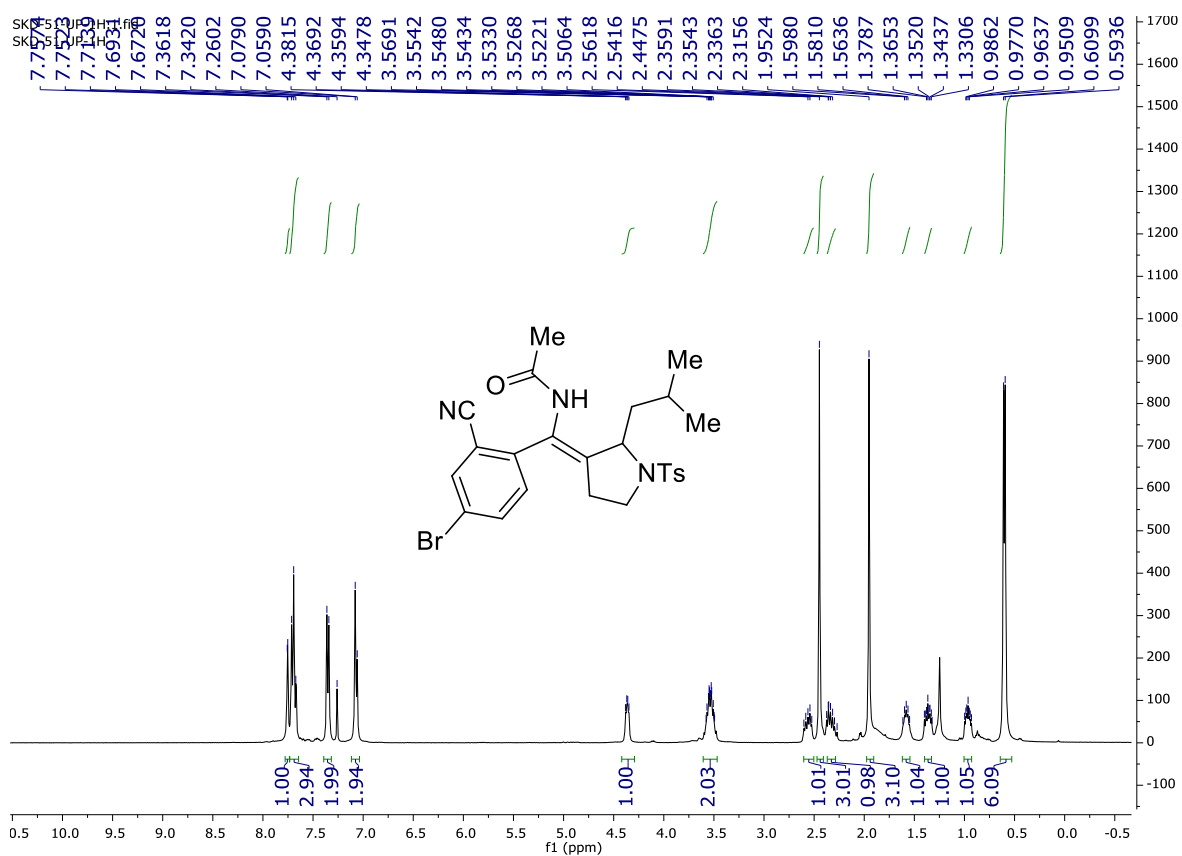
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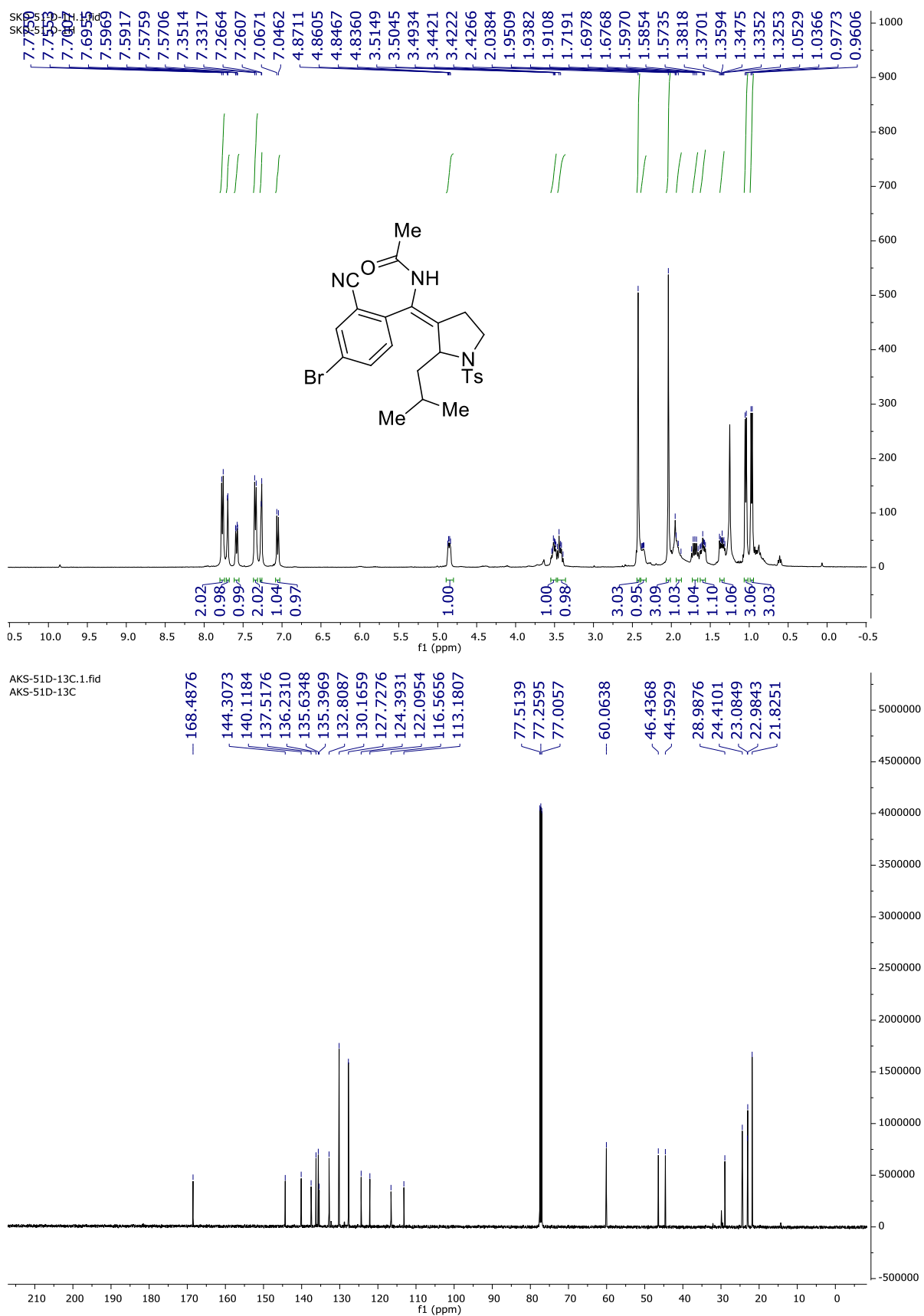
^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) NMR spectra of *E*-3ck



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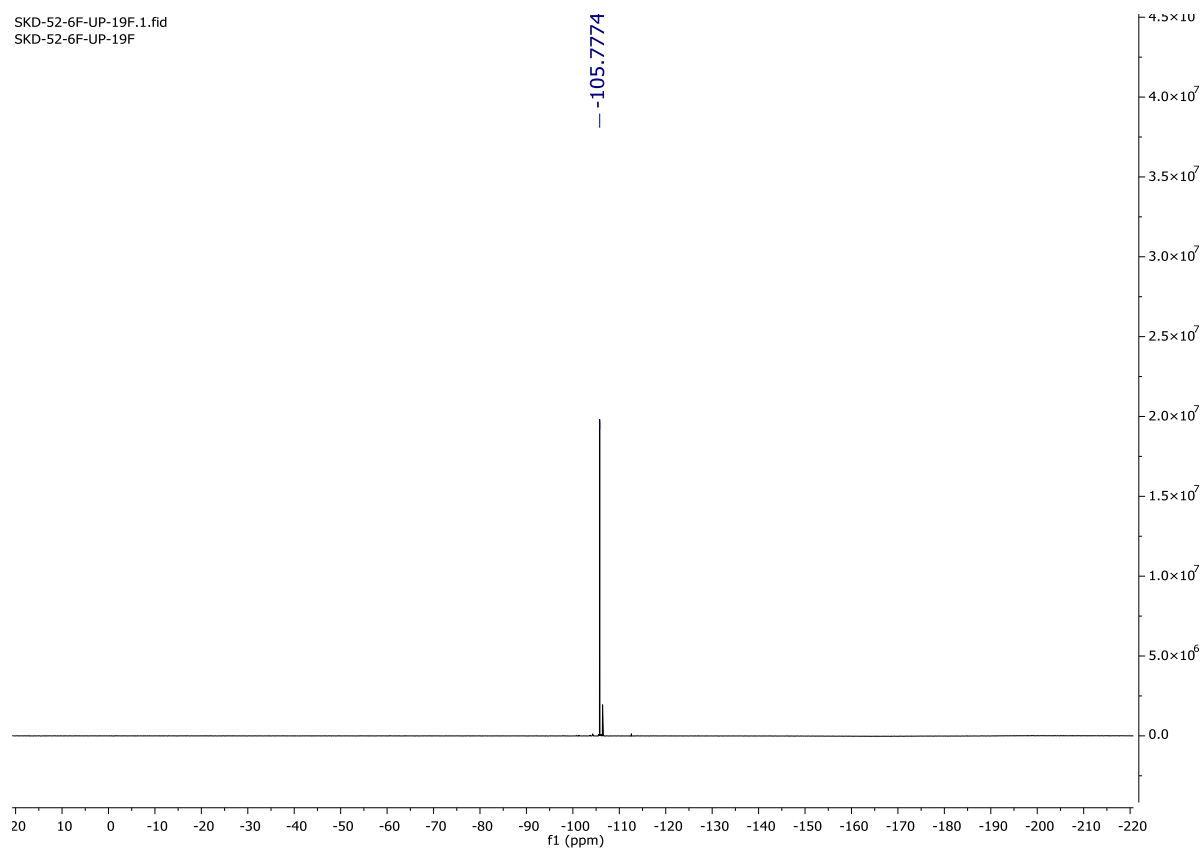


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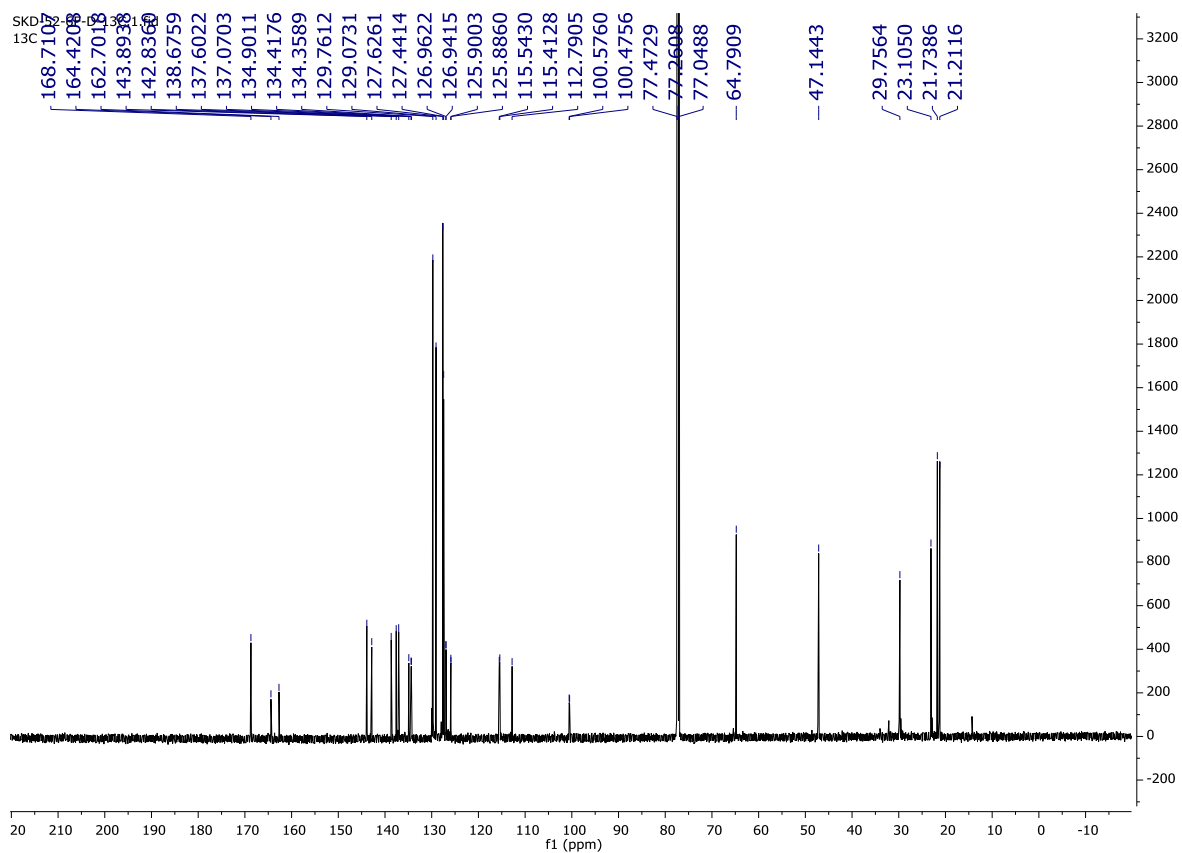
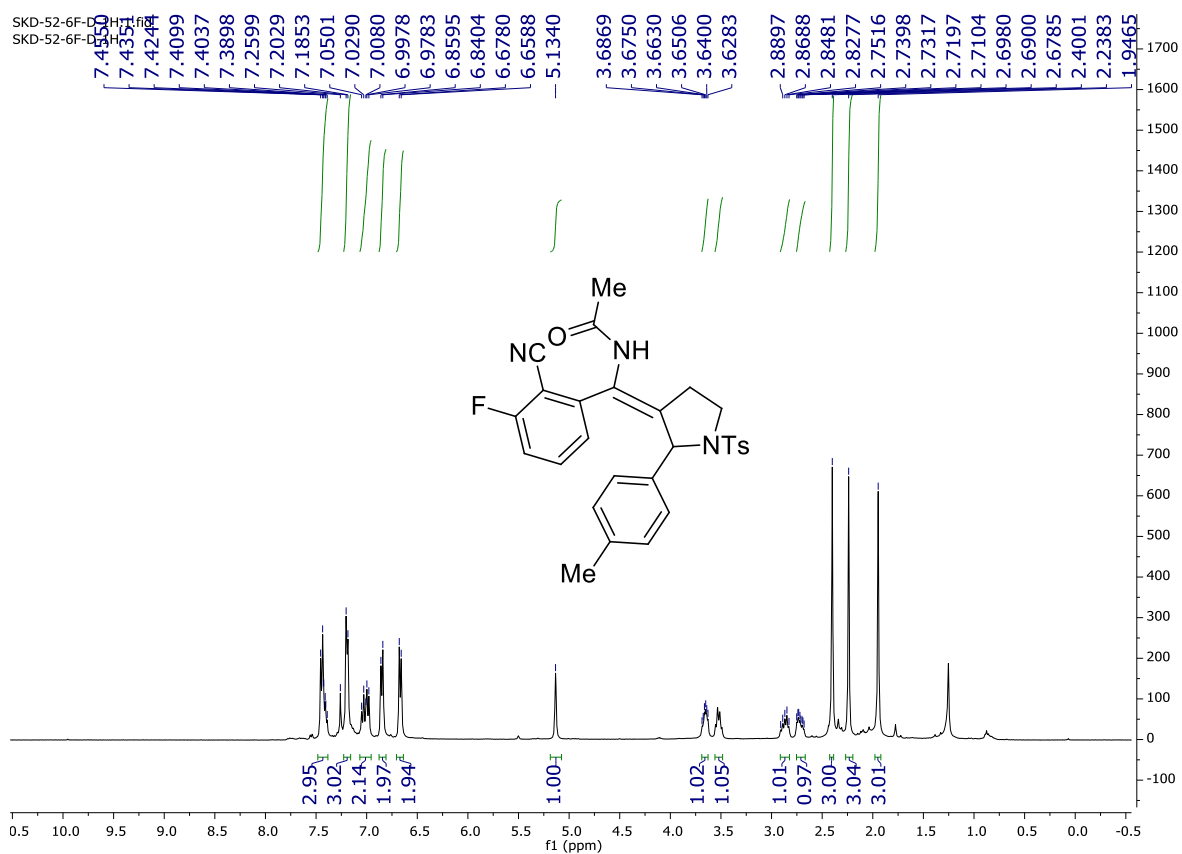


^{19}F (471 MHz, CDCl_3) NMR spectrum of **Z-3dc**

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SKD-52-6F-UP-19F

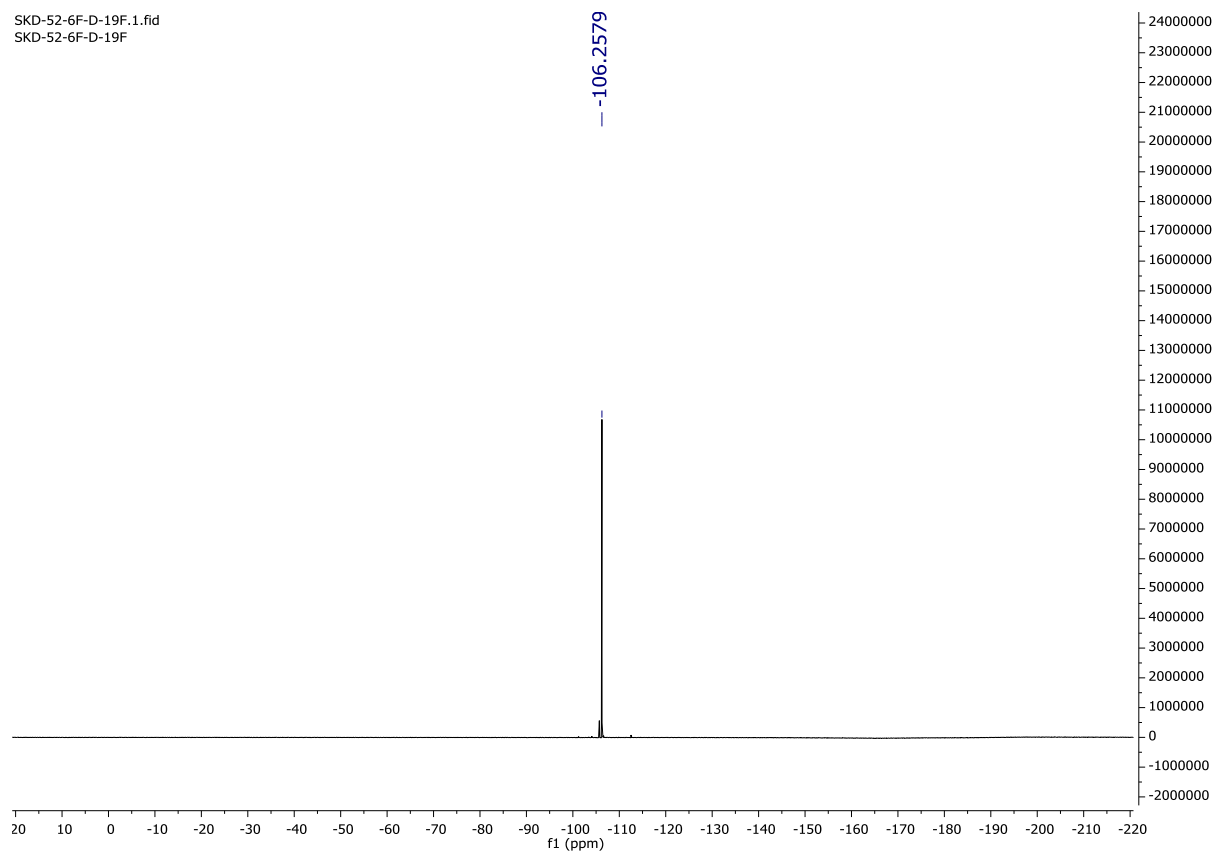


^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3) NMR spectra of *E*-3dc

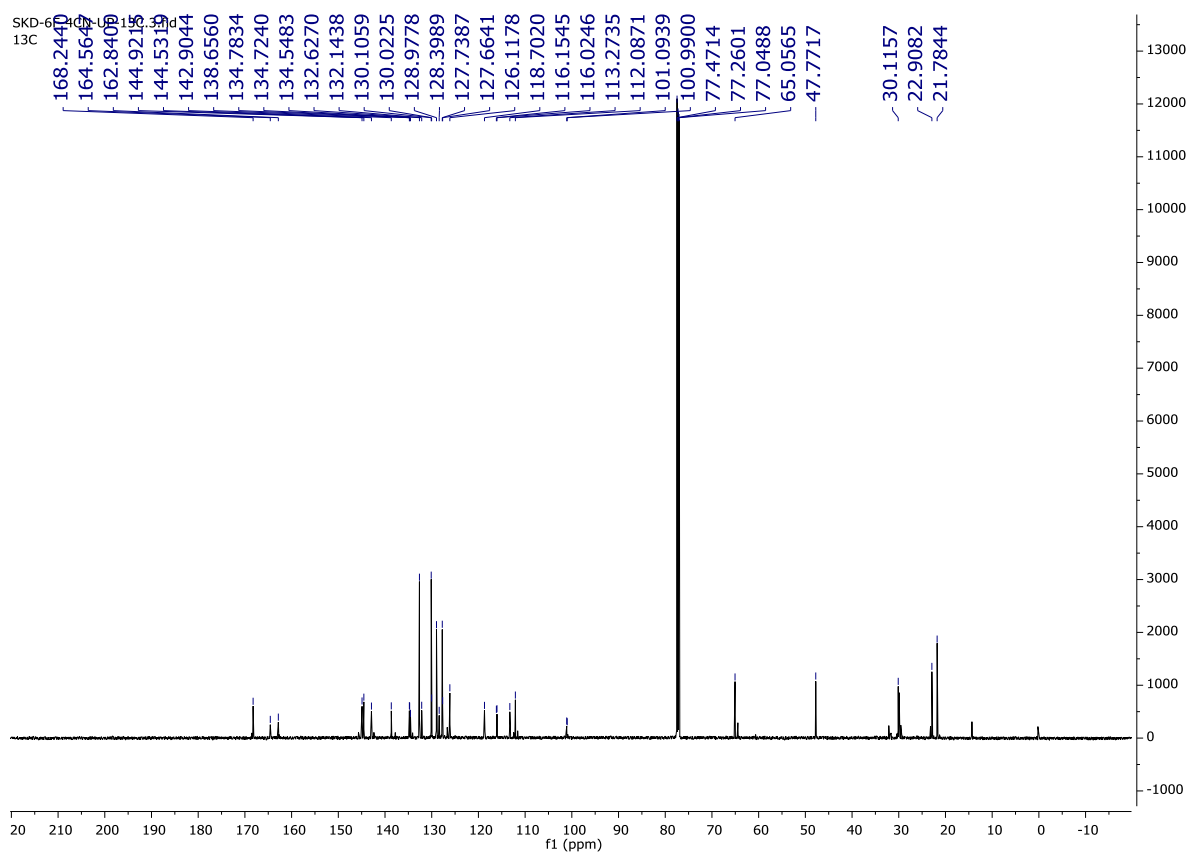
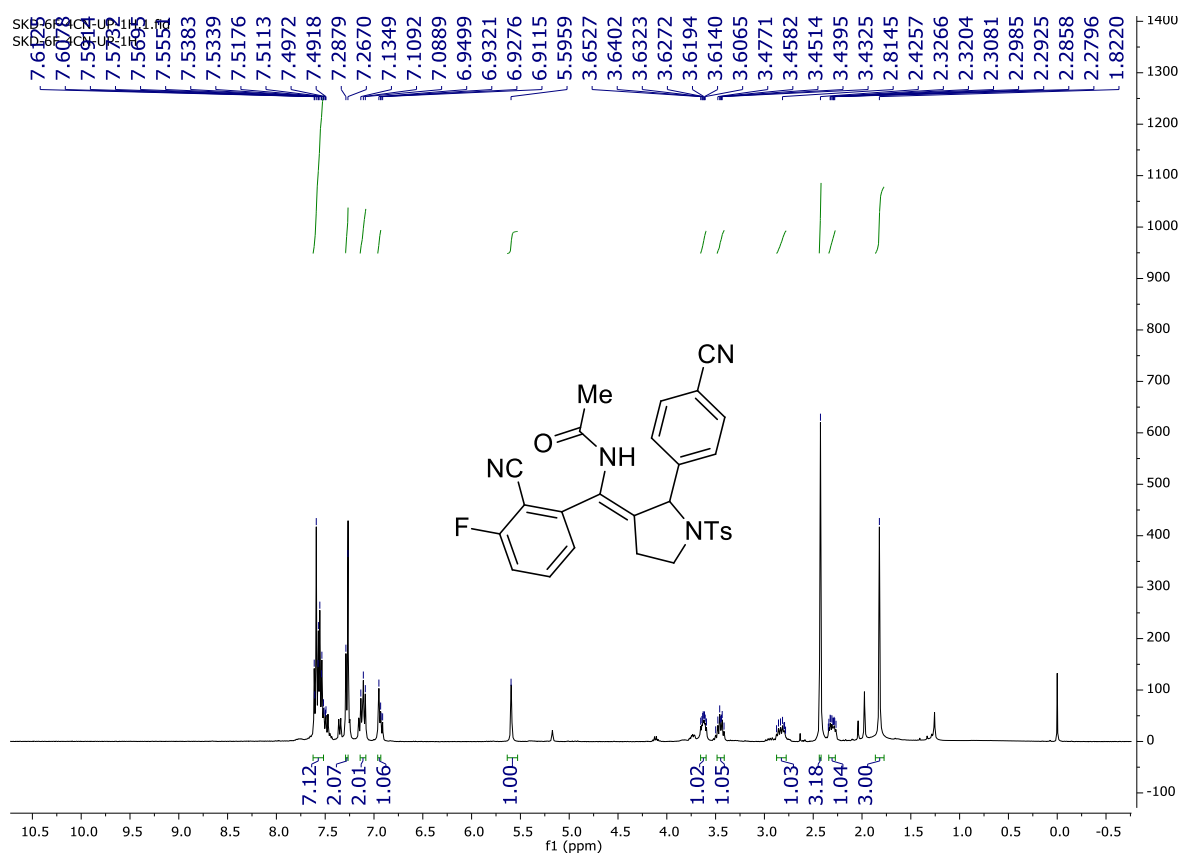


^{19}F (471 MHz, CDCl_3) NMR spectrum of *E*-3dc

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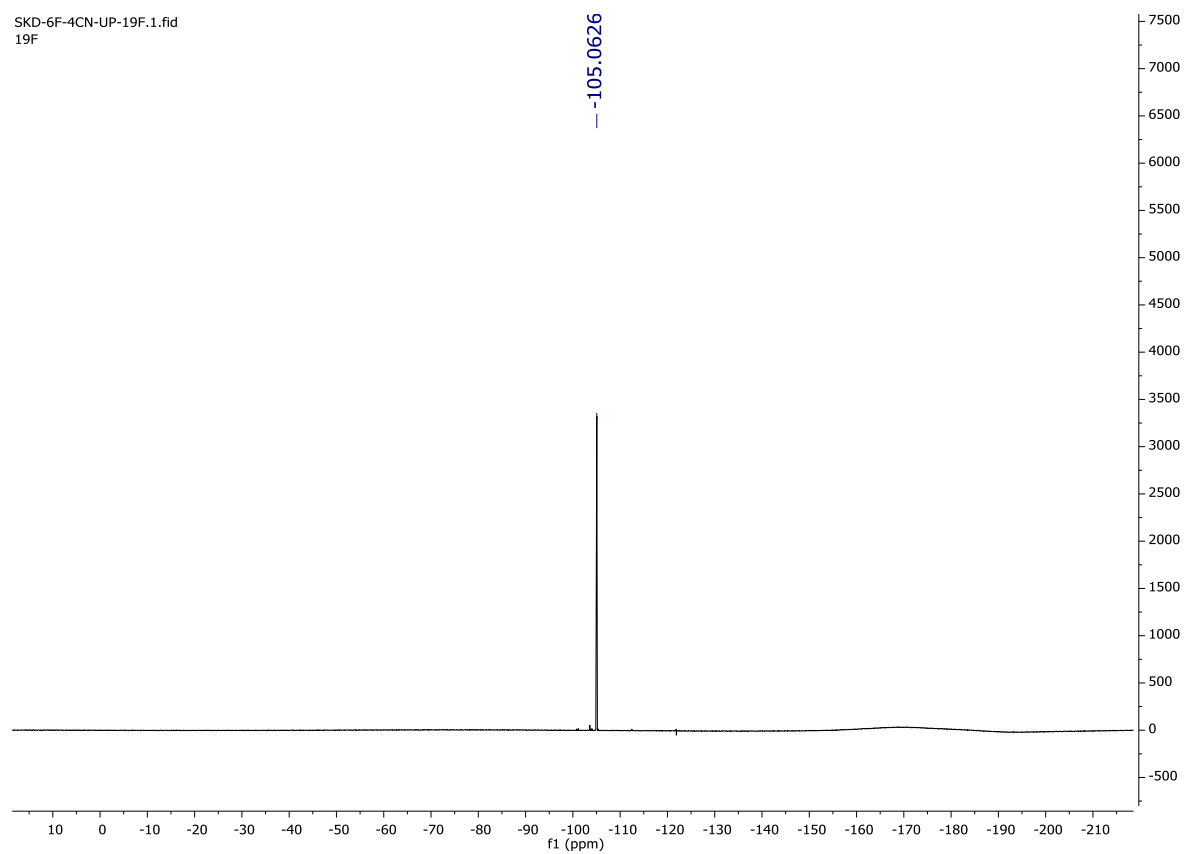


^1H (400 MHz, CDCl_3), ^{13}C { ^1H } (150 MHz, CDCl_3) NMR spectra of **Z-3dm**

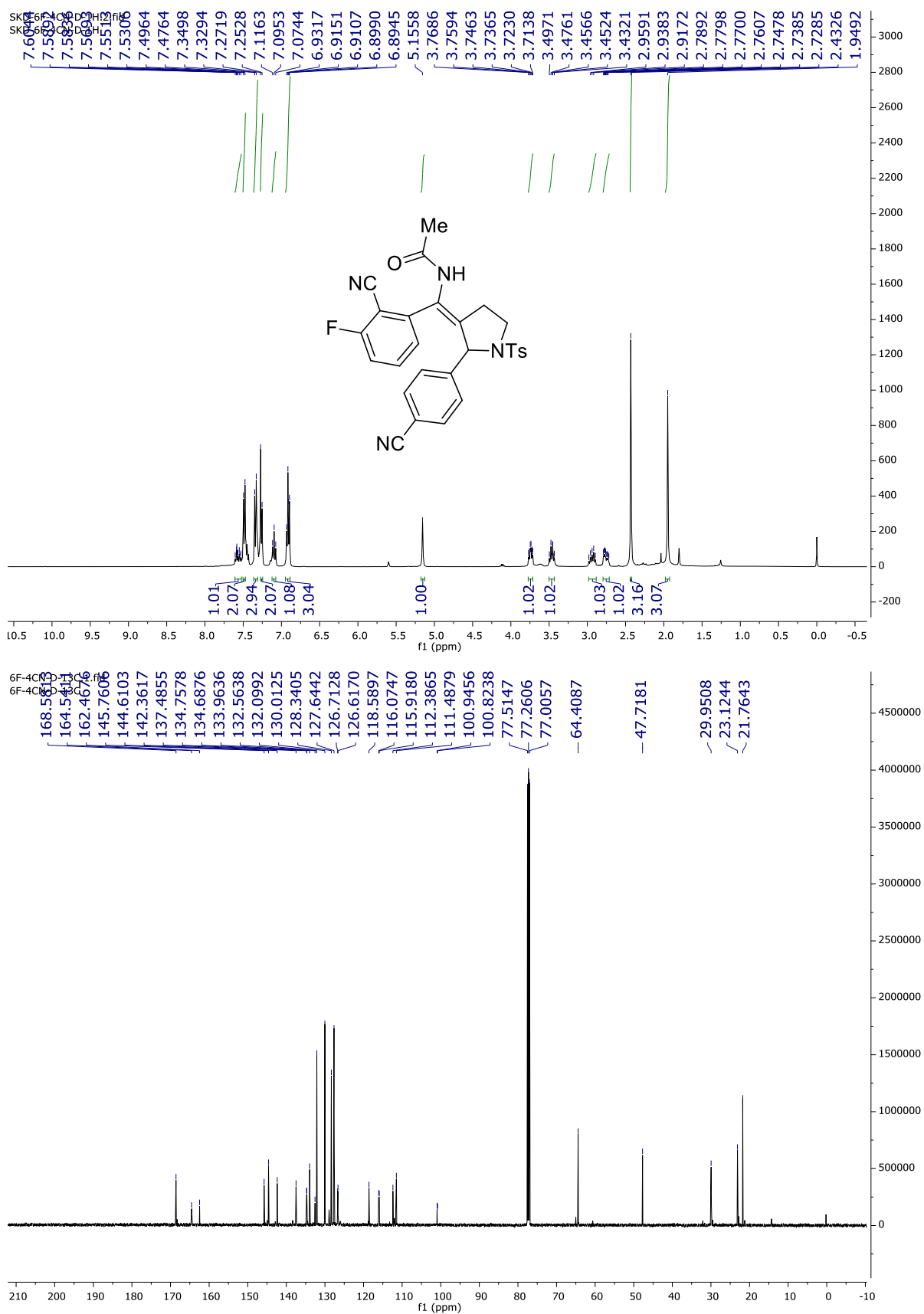


^{19}F (565 MHz, CDCl_3) NMR spectrum of **Z-3dm**

SKD-6F-4CN-UP-19F.1.fid
19F

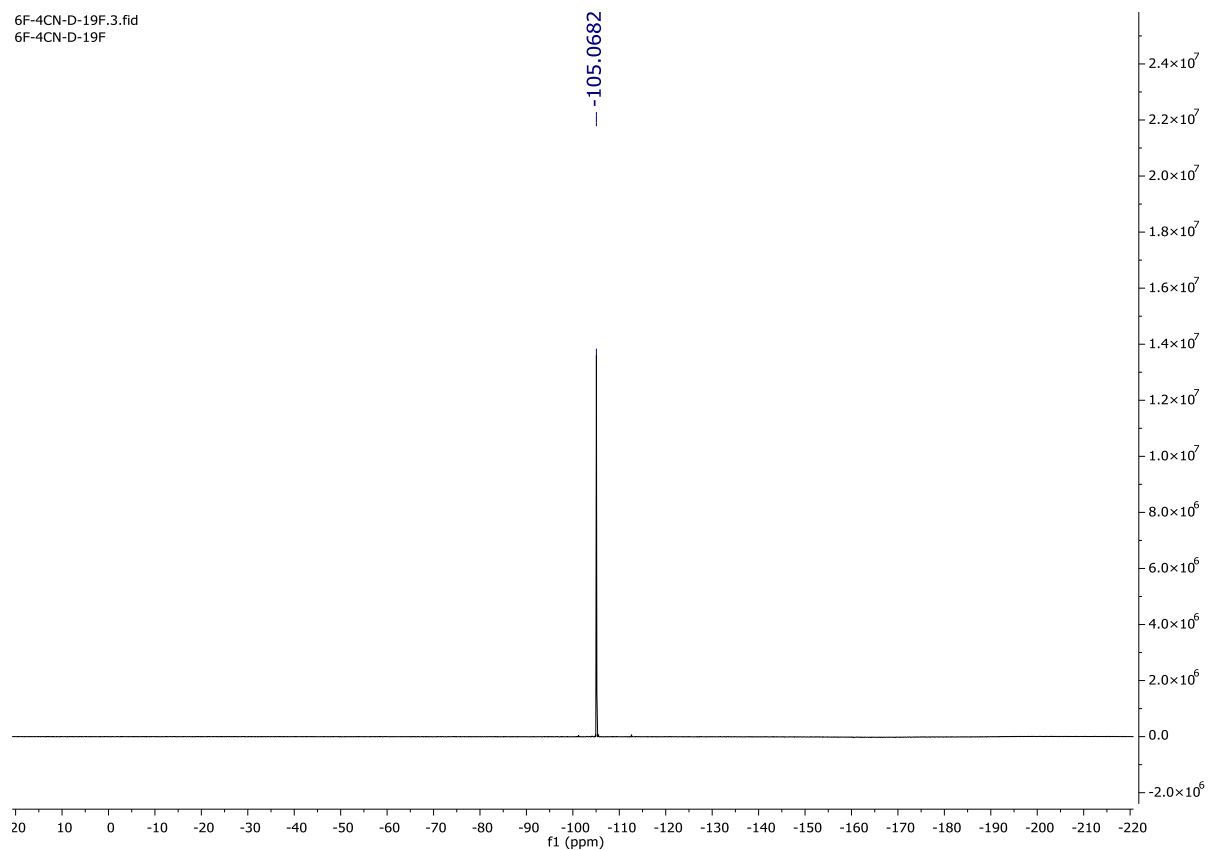


^1H (400 MHz, CDCl_3), $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) NMR spectra of *E*-3dm

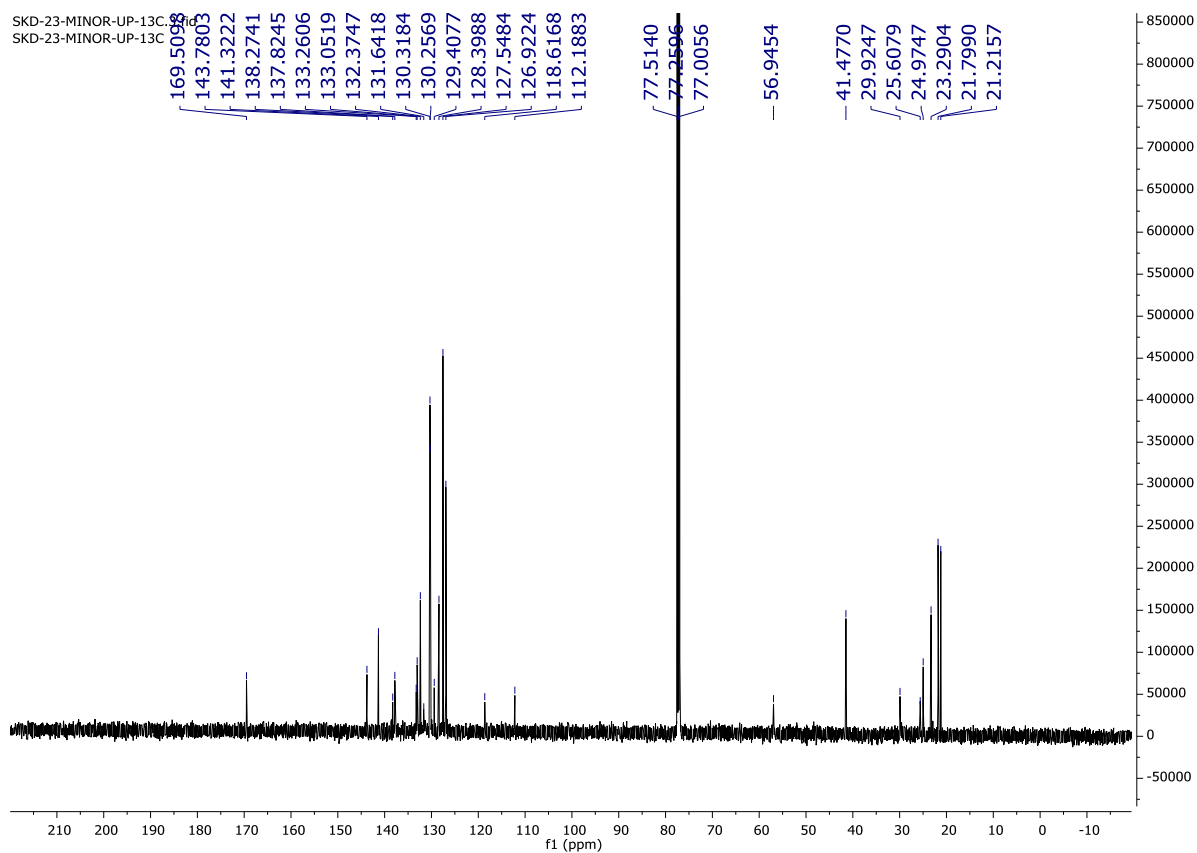
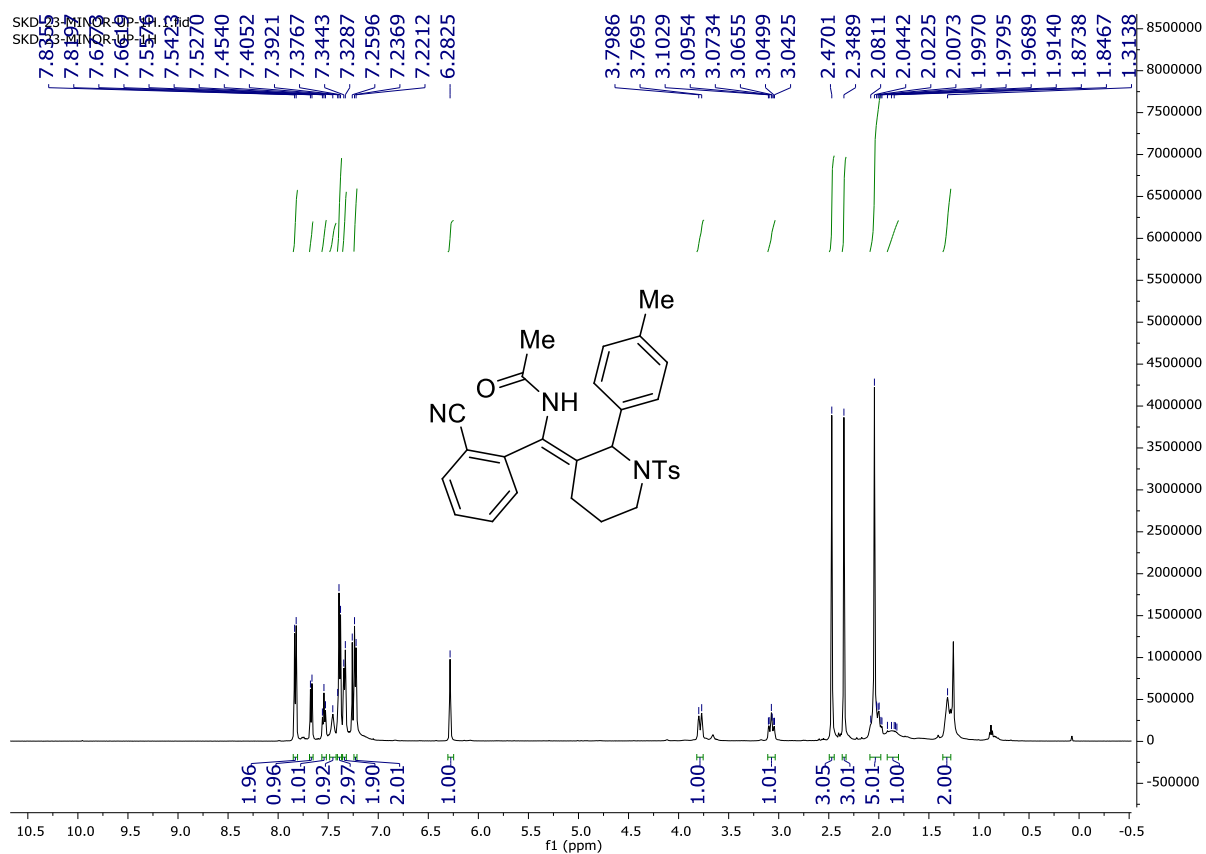


^{19}F (471 MHz, CDCl_3) NMR spectrum of *E*-3dm

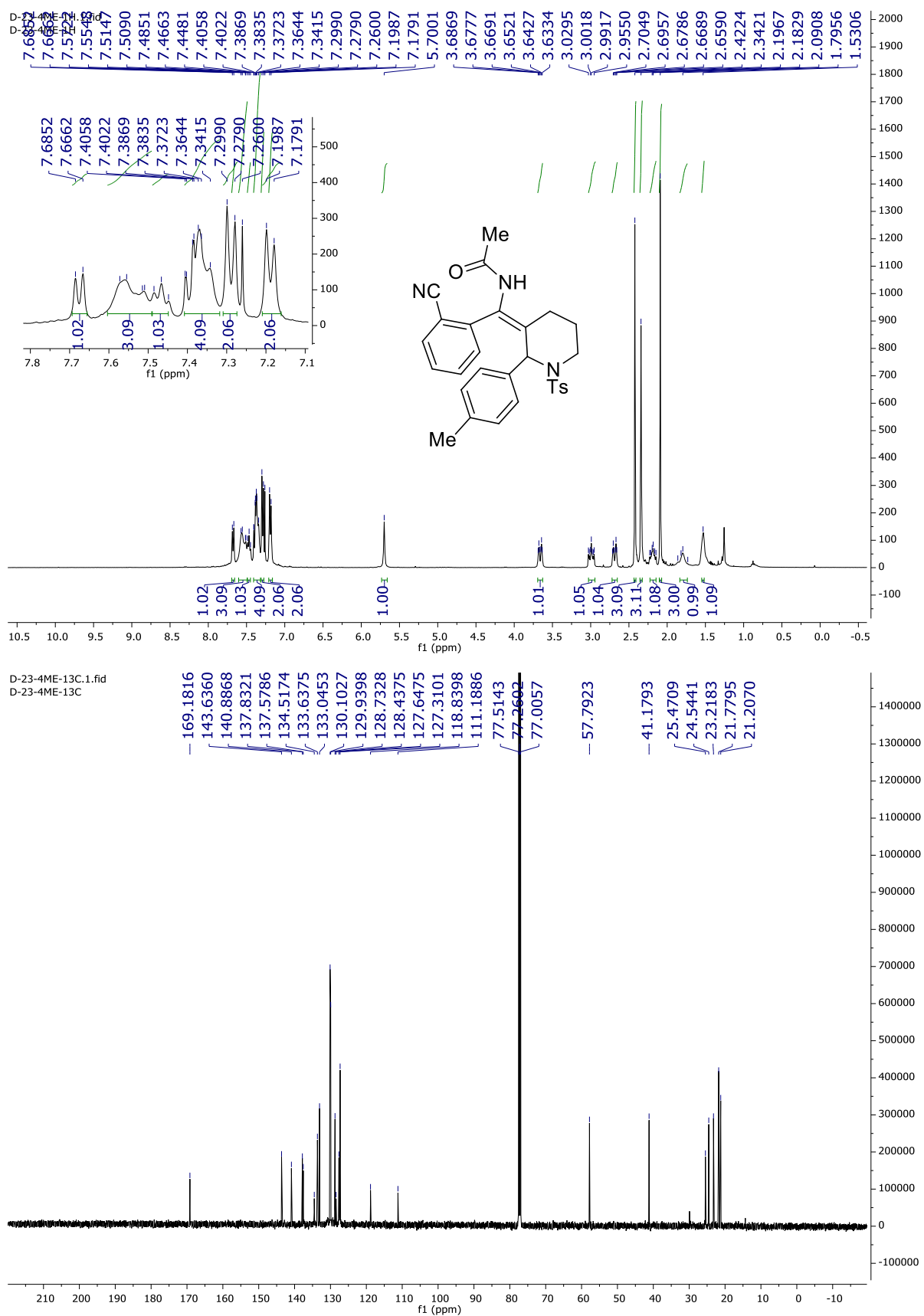
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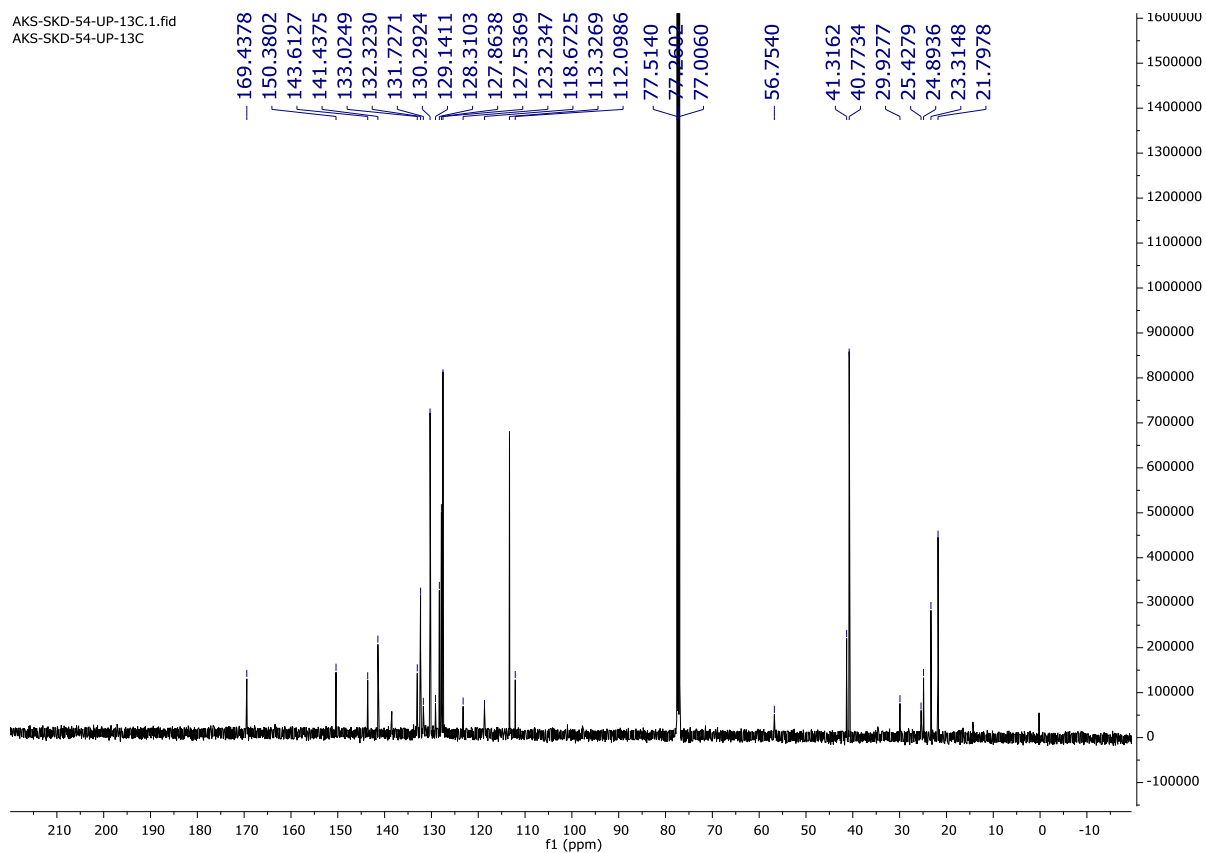
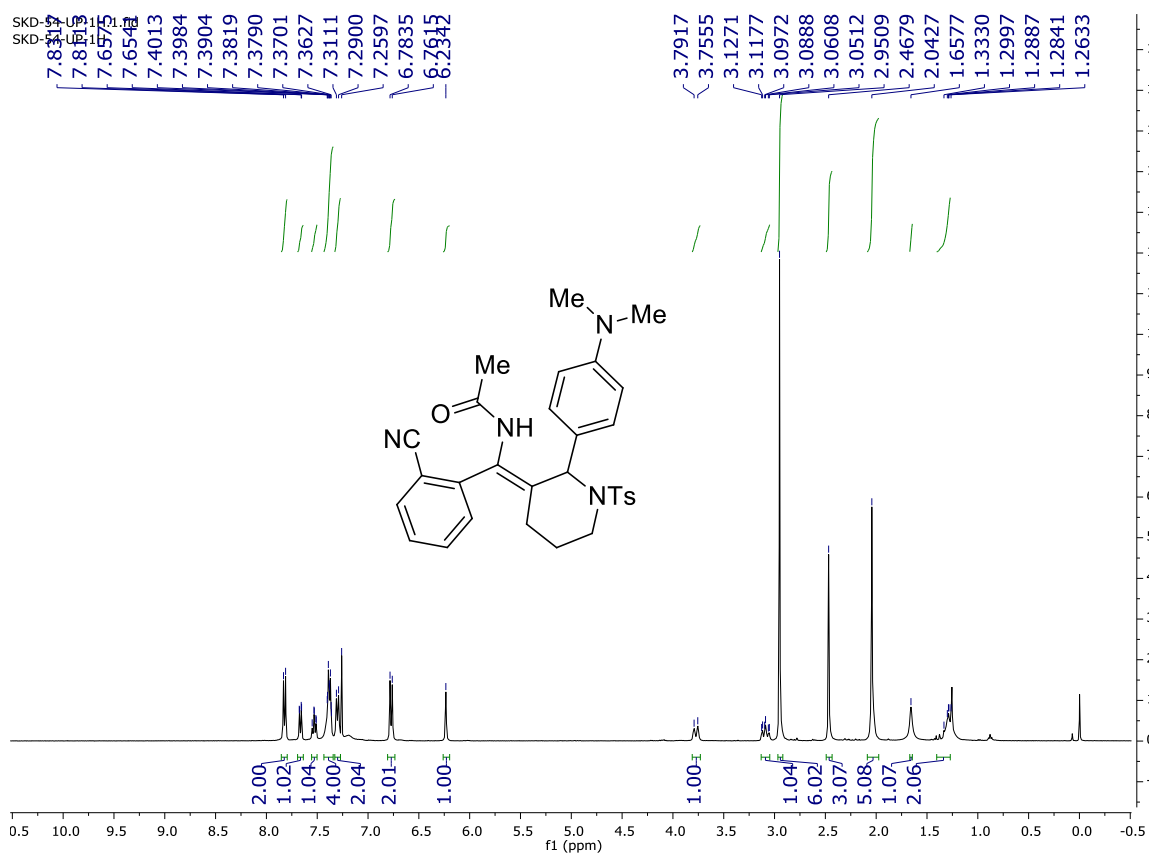
^1H (500 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) NMR spectra of **Z-4ec**



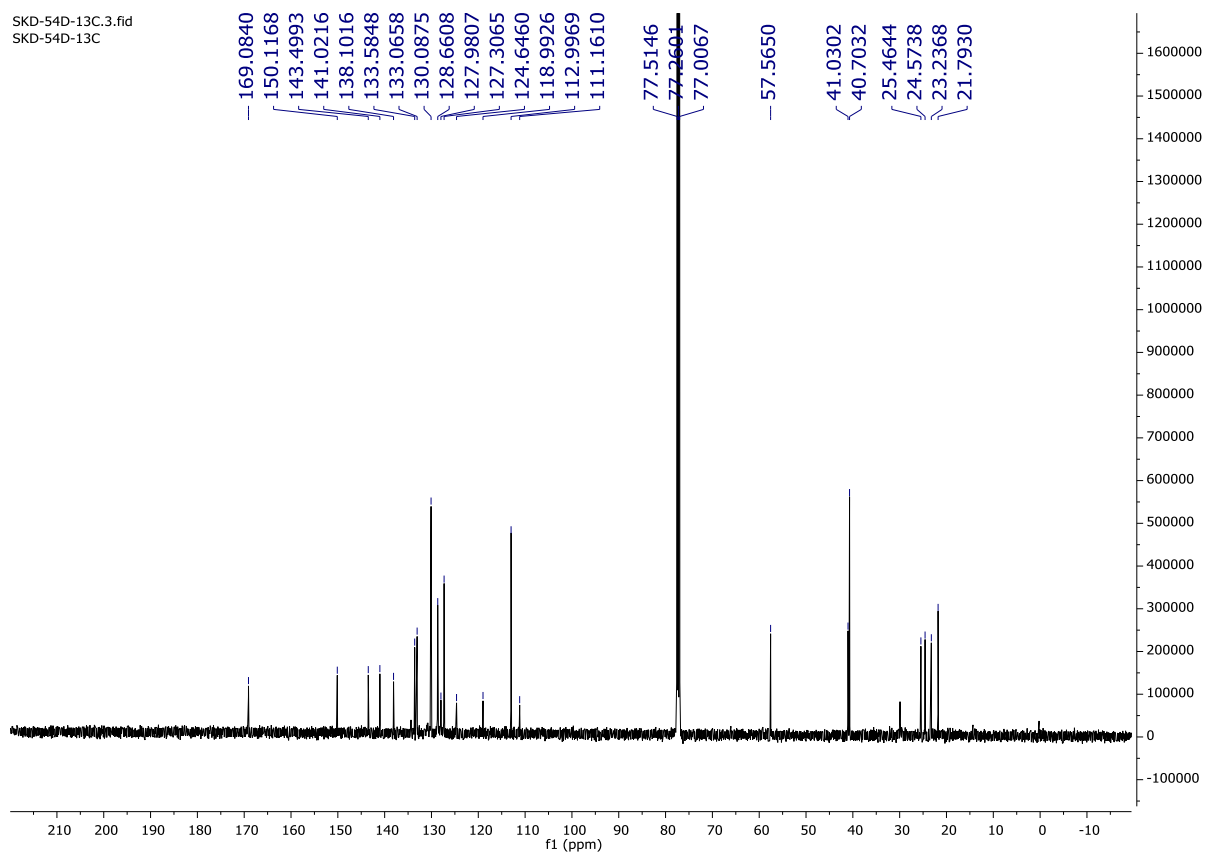
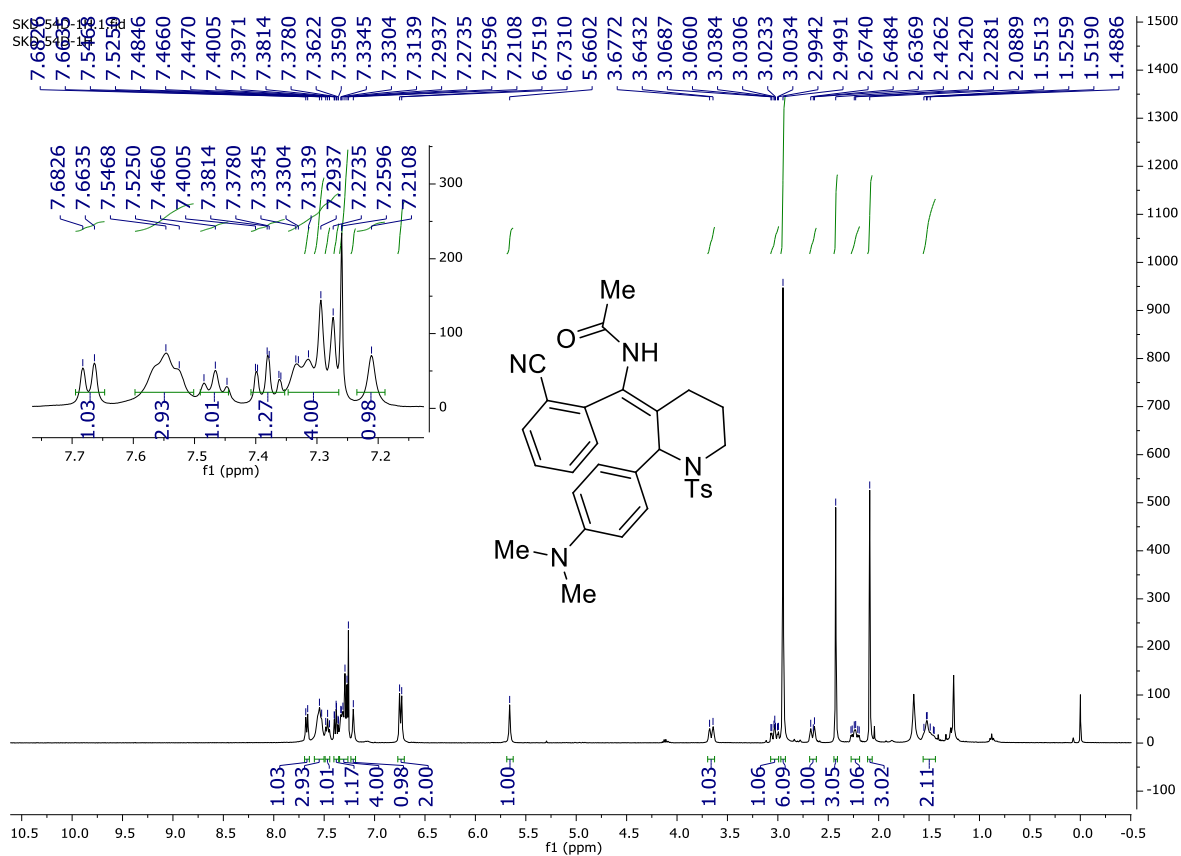
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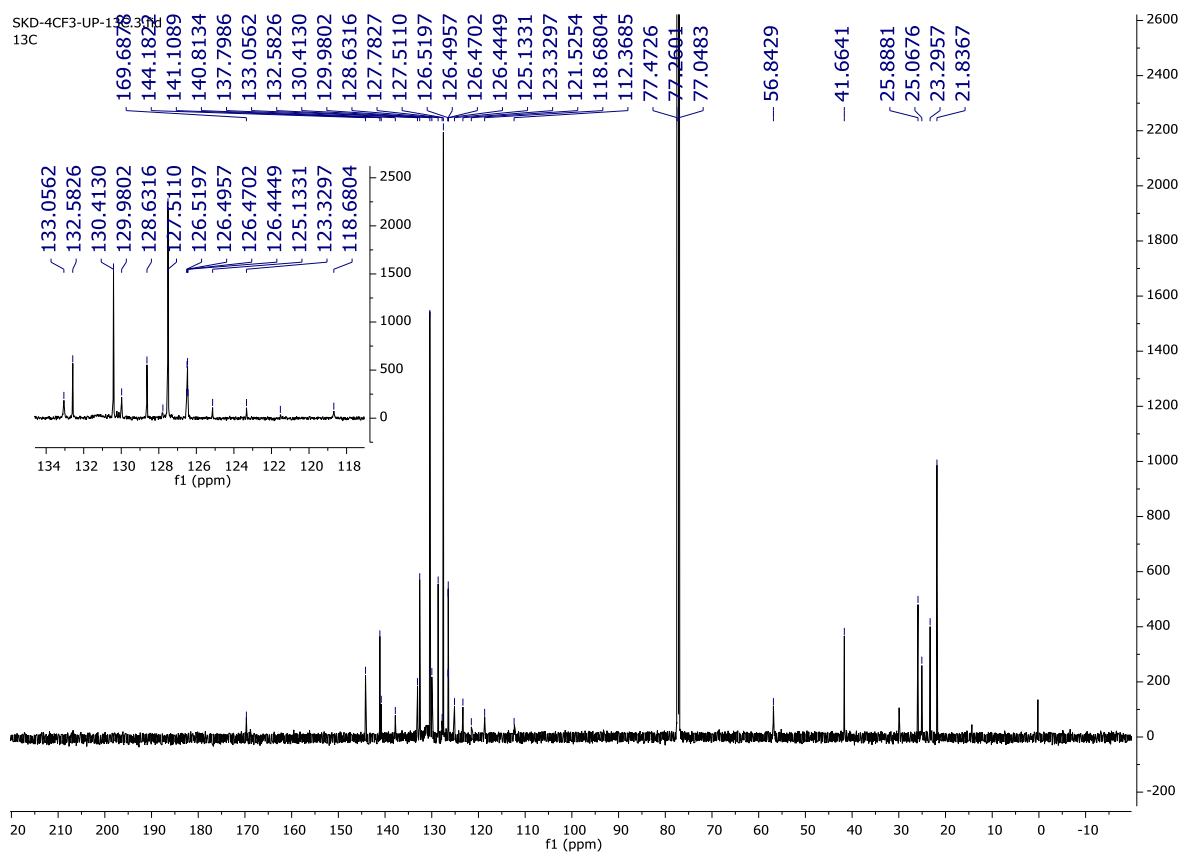
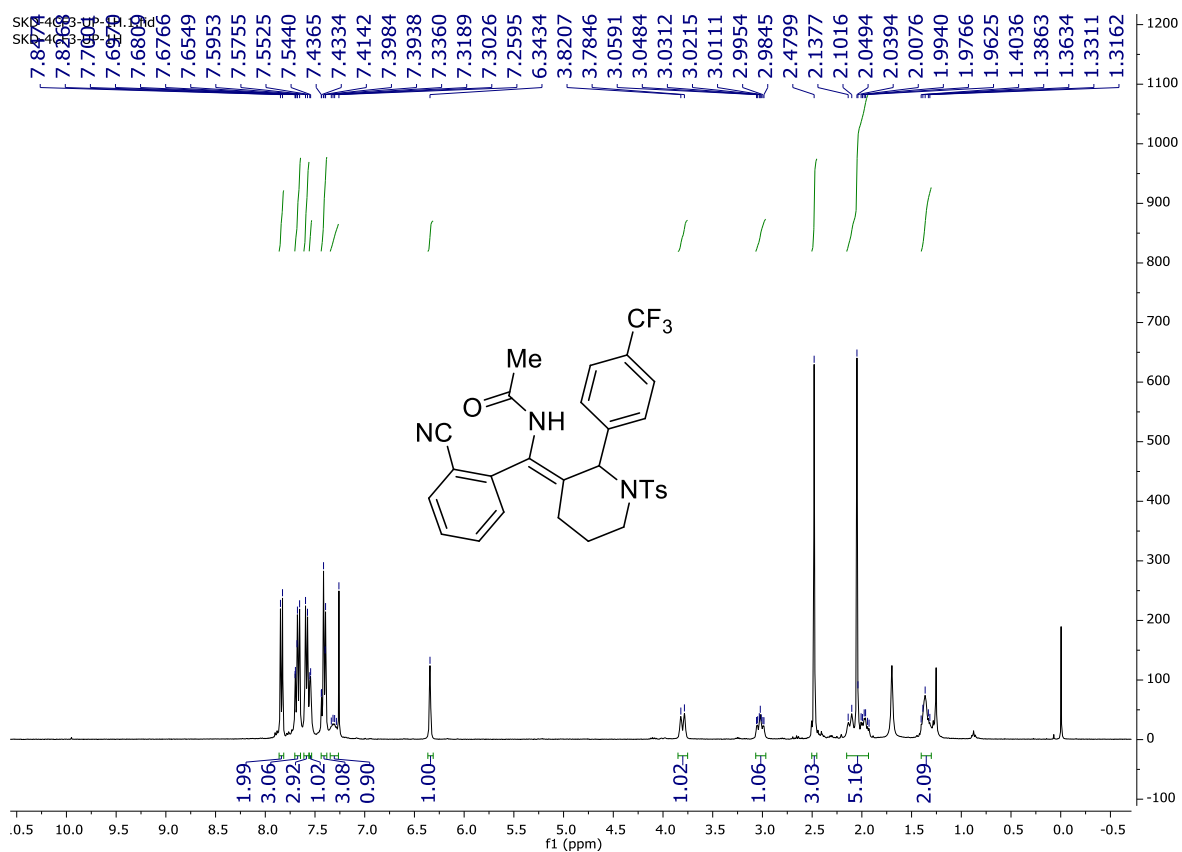
^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) NMR spectra of **Z-4en**



^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) NMR spectra of *E*-4en

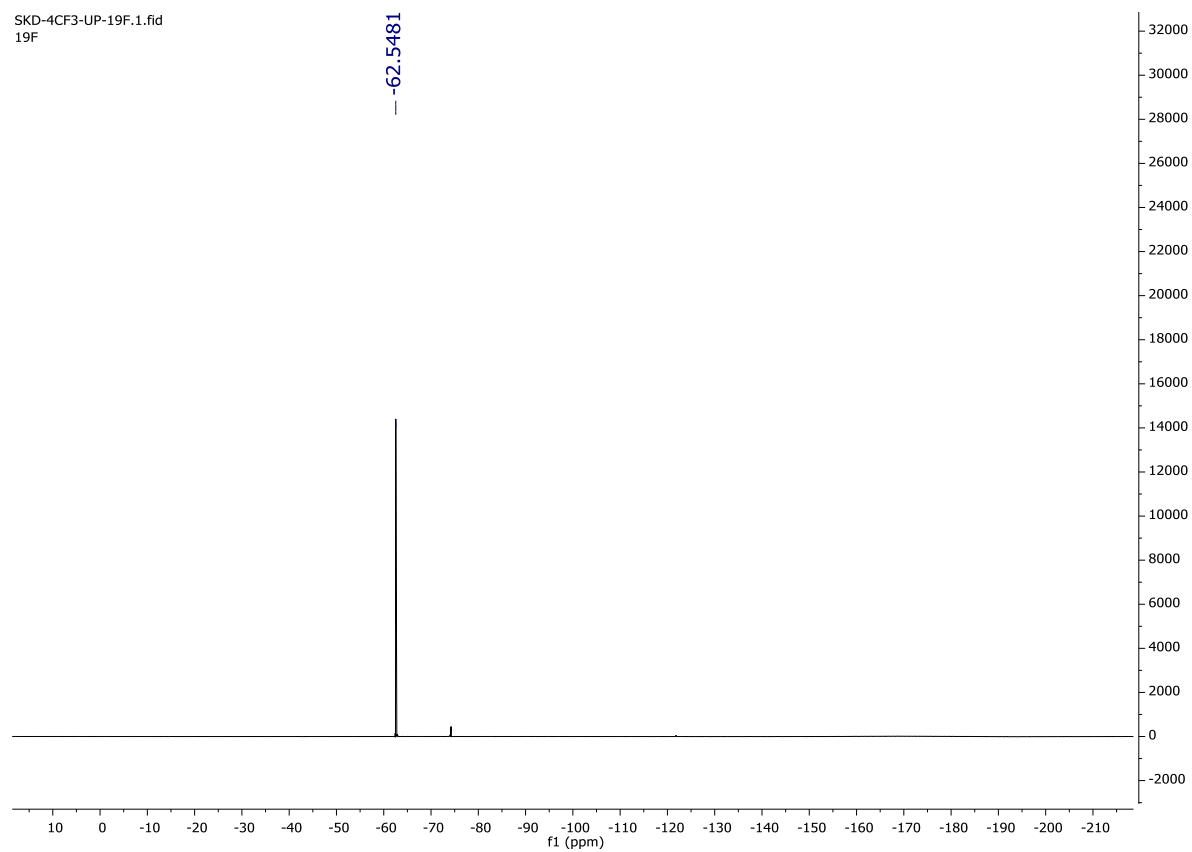


^1H (400 MHz, CDCl_3), ^{13}C (^1H) (150 MHz, CDCl_3) NMR spectra of **Z-4eo**

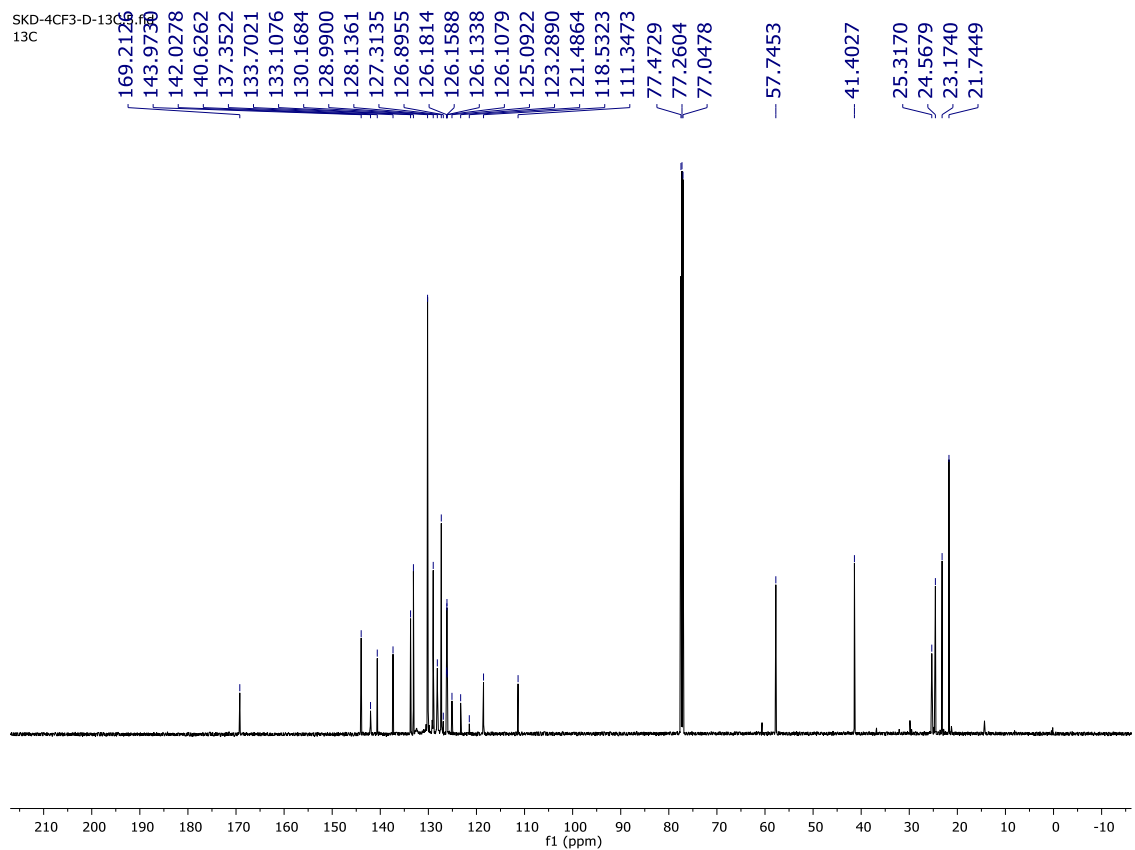
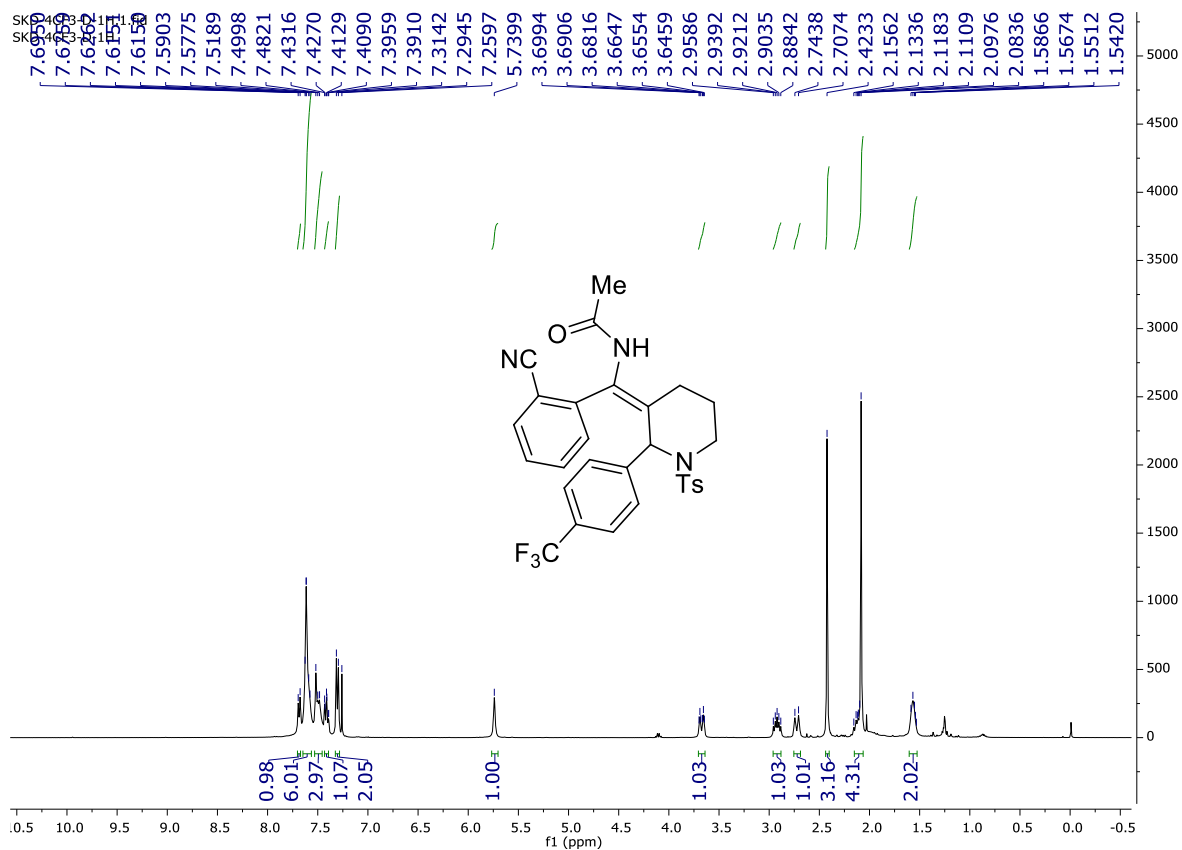


^{19}F (565 MHz, CDCl_3) NMR spectrum of **Z-4eo**

SKD-4CF3-UP-19F.1.fid
19F

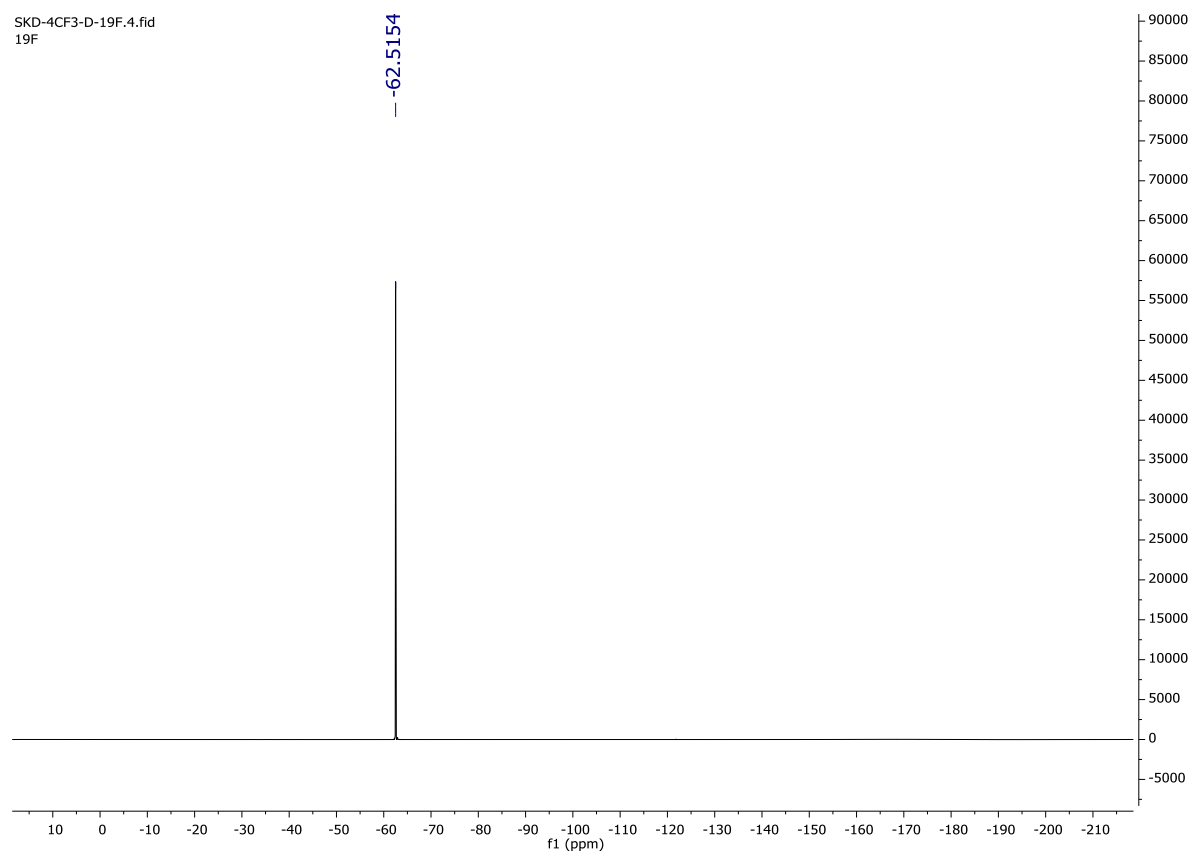


^1H (400 MHz, CDCl_3), $^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3) and ^{19}F NMR spectra of *E-4eo*

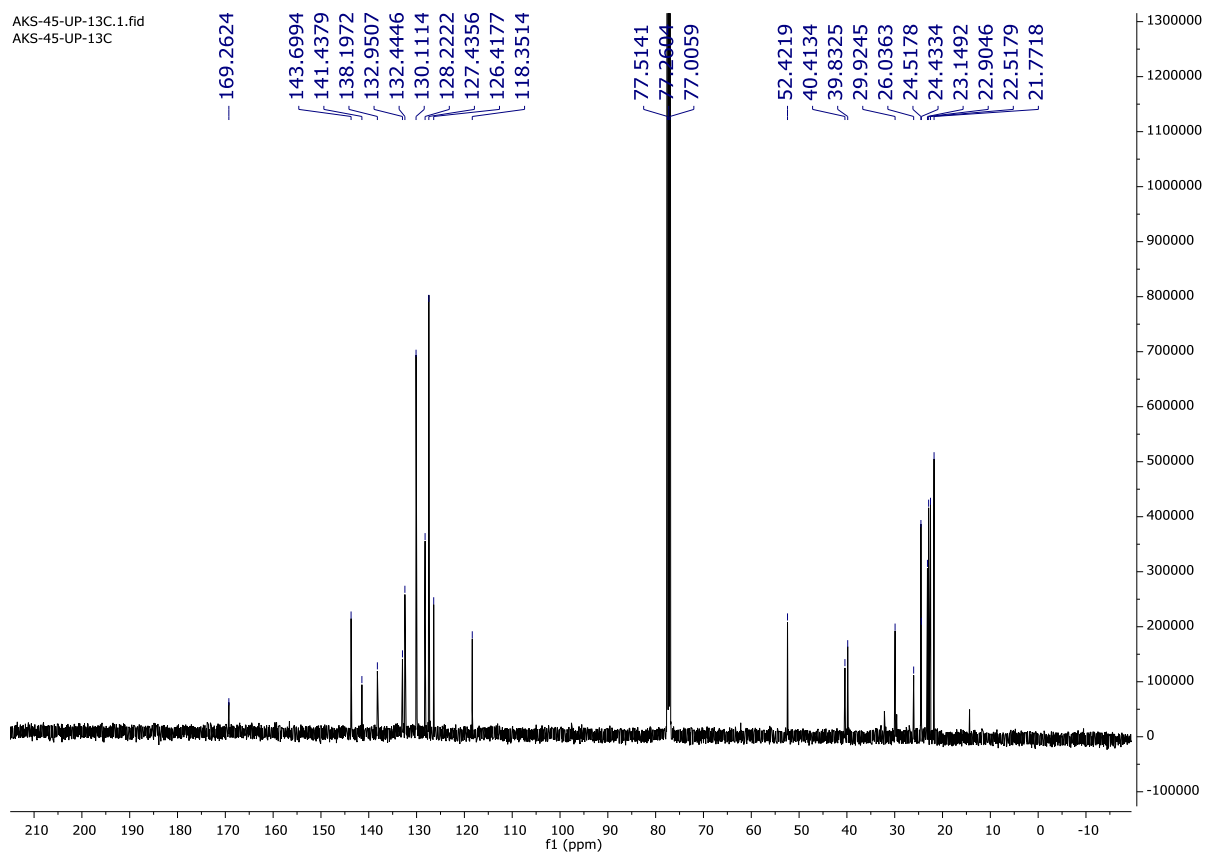
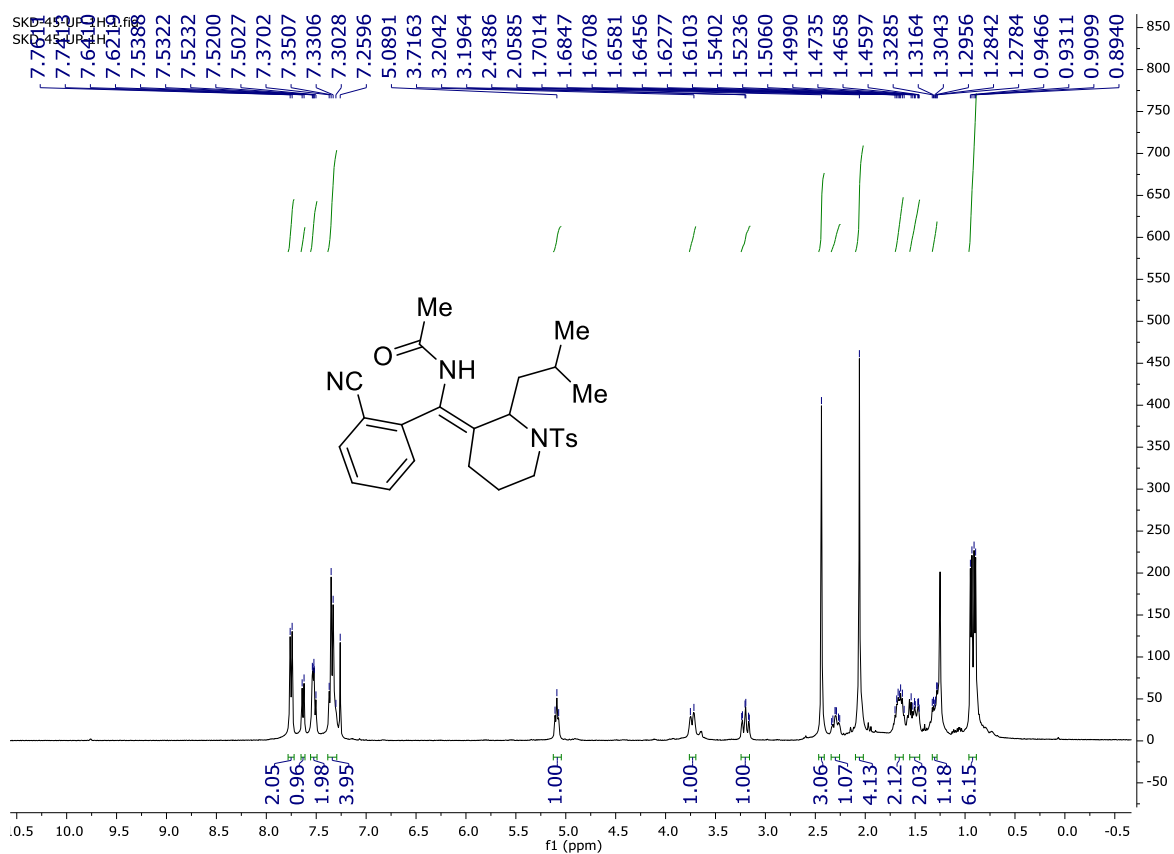


^{19}F (565 MHz, CDCl_3) NMR spectrum of *E*-4eo

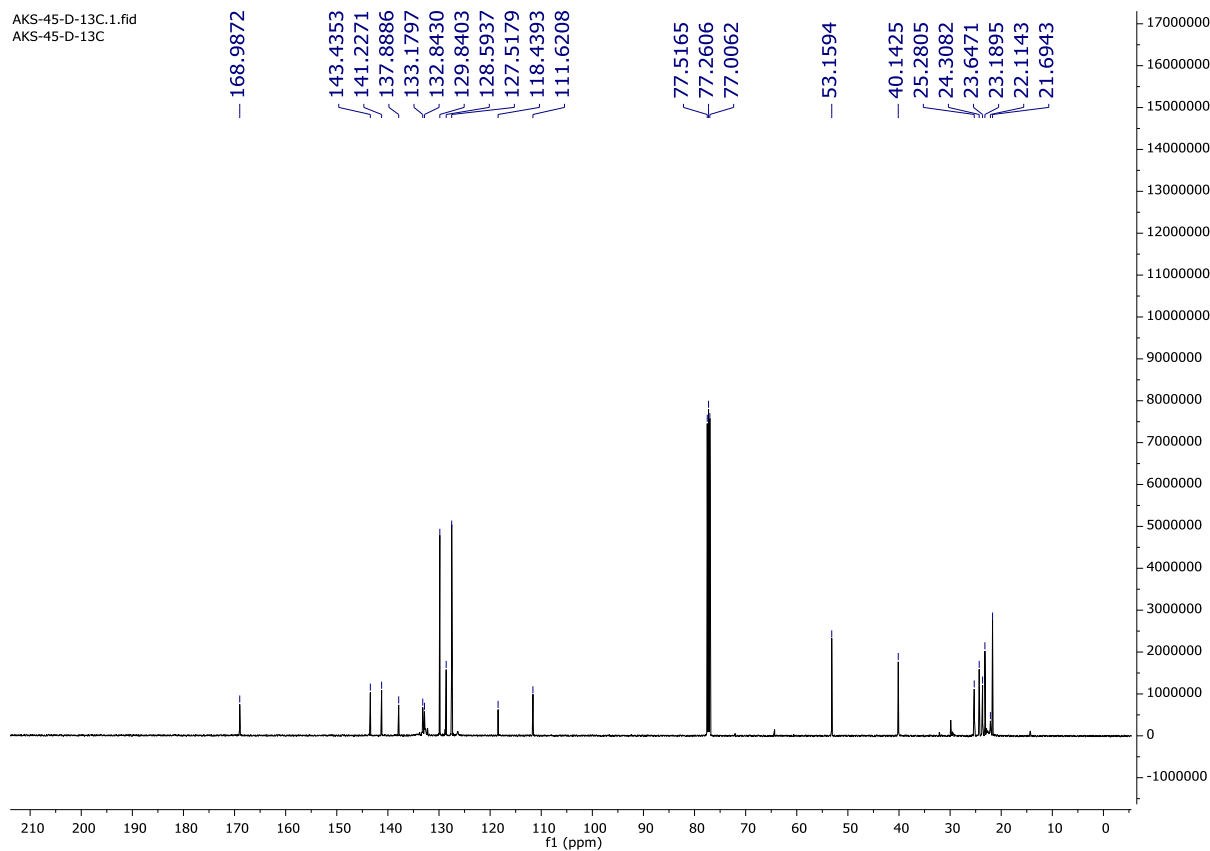
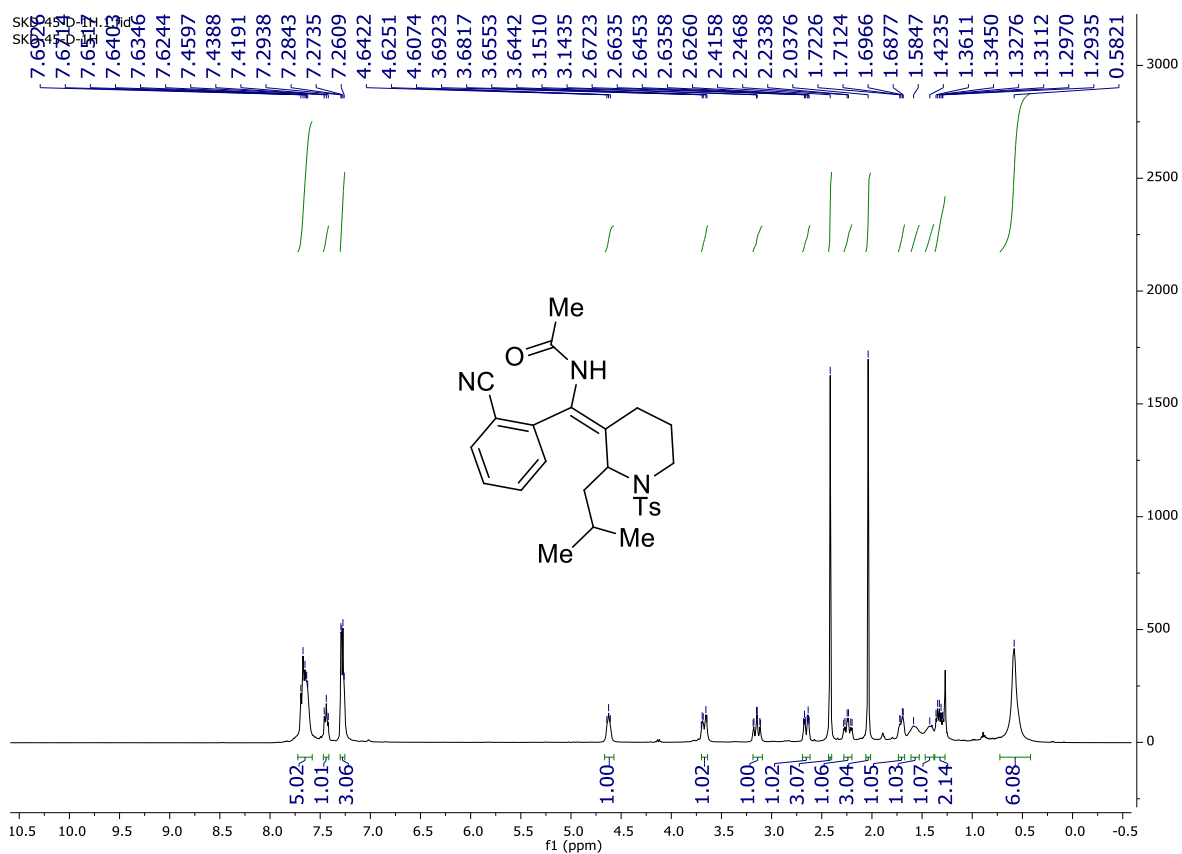
SKD-4CF3-D-19F.4.fid
19F



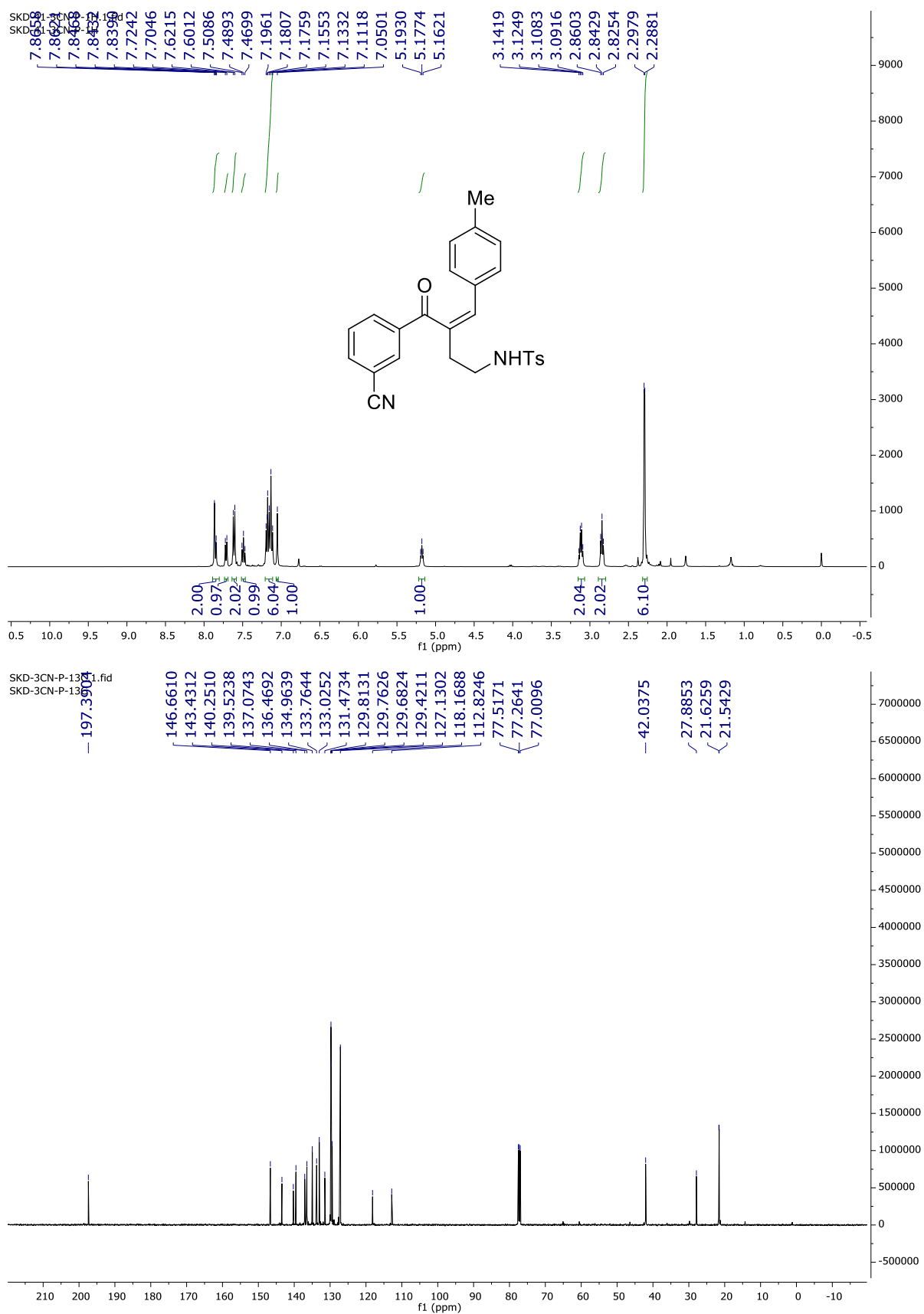
^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) NMR spectra of **Z-4eI**



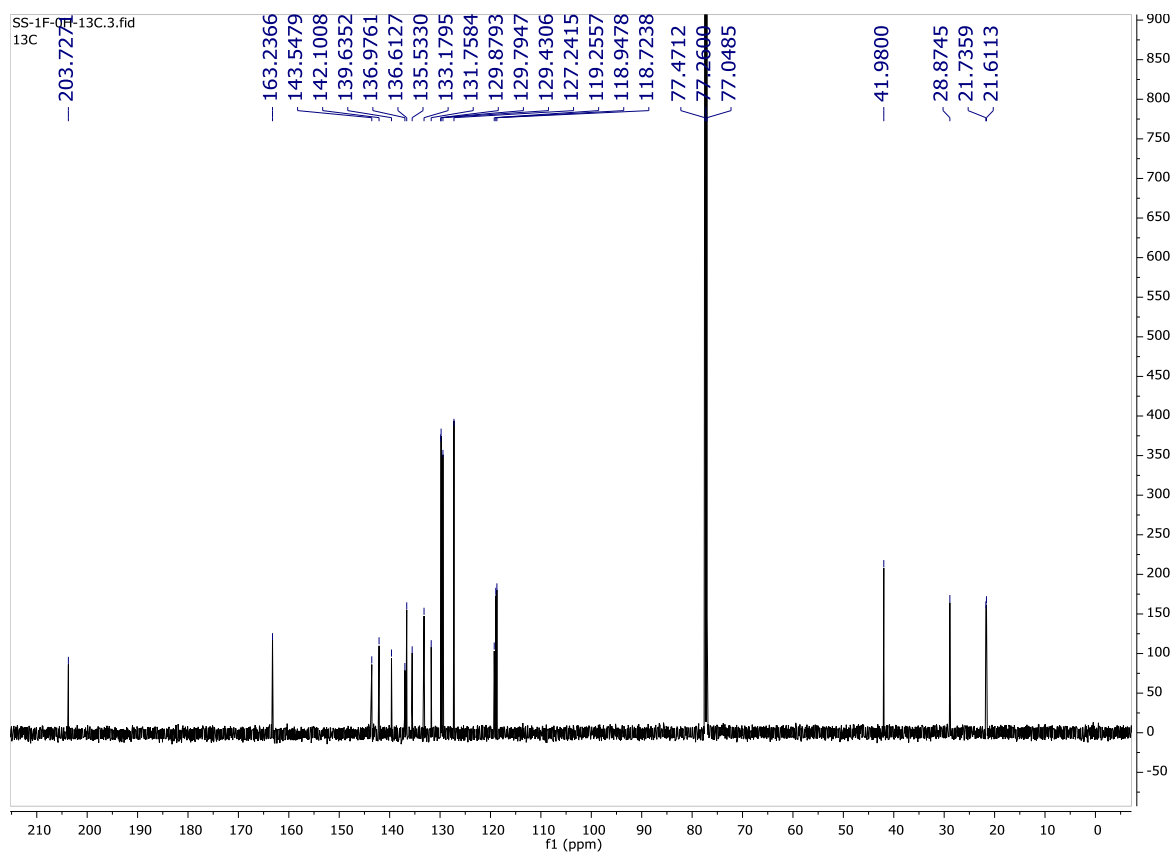
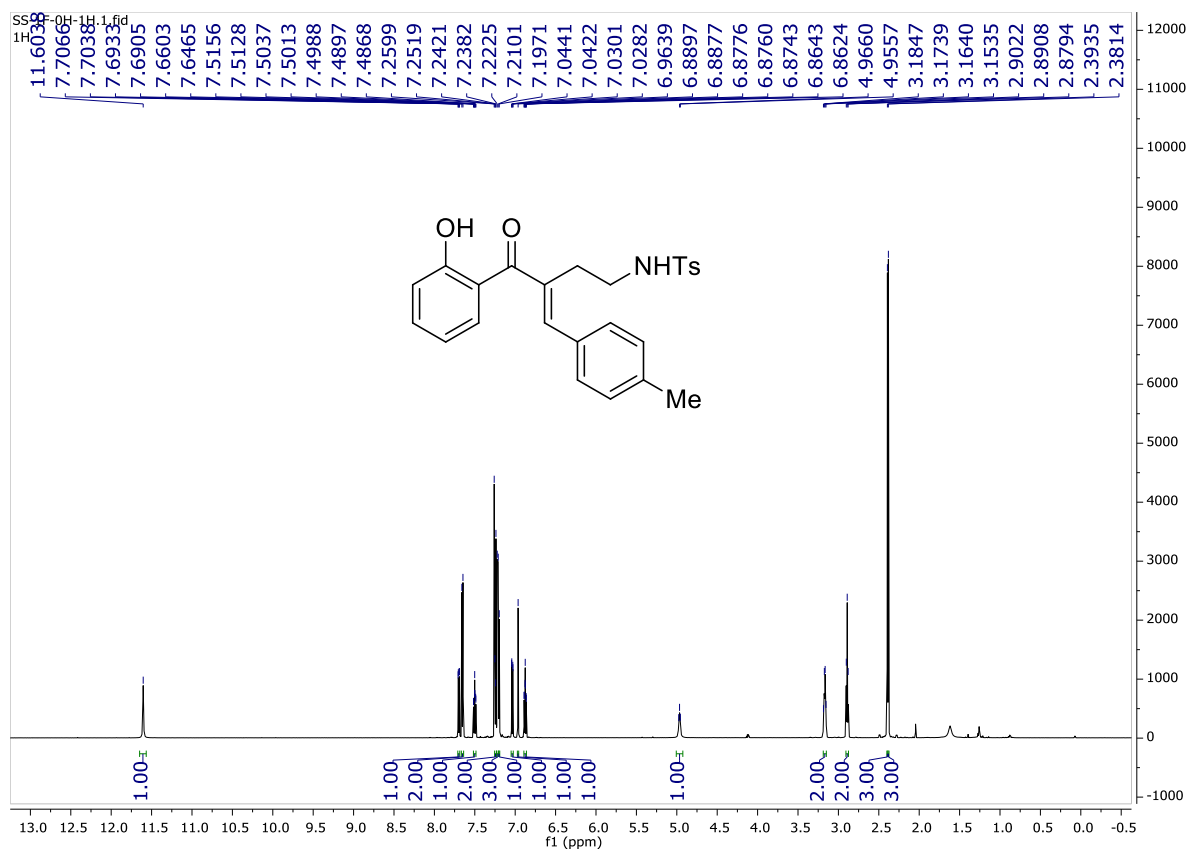
^1H (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) NMR spectra of *E*-4el



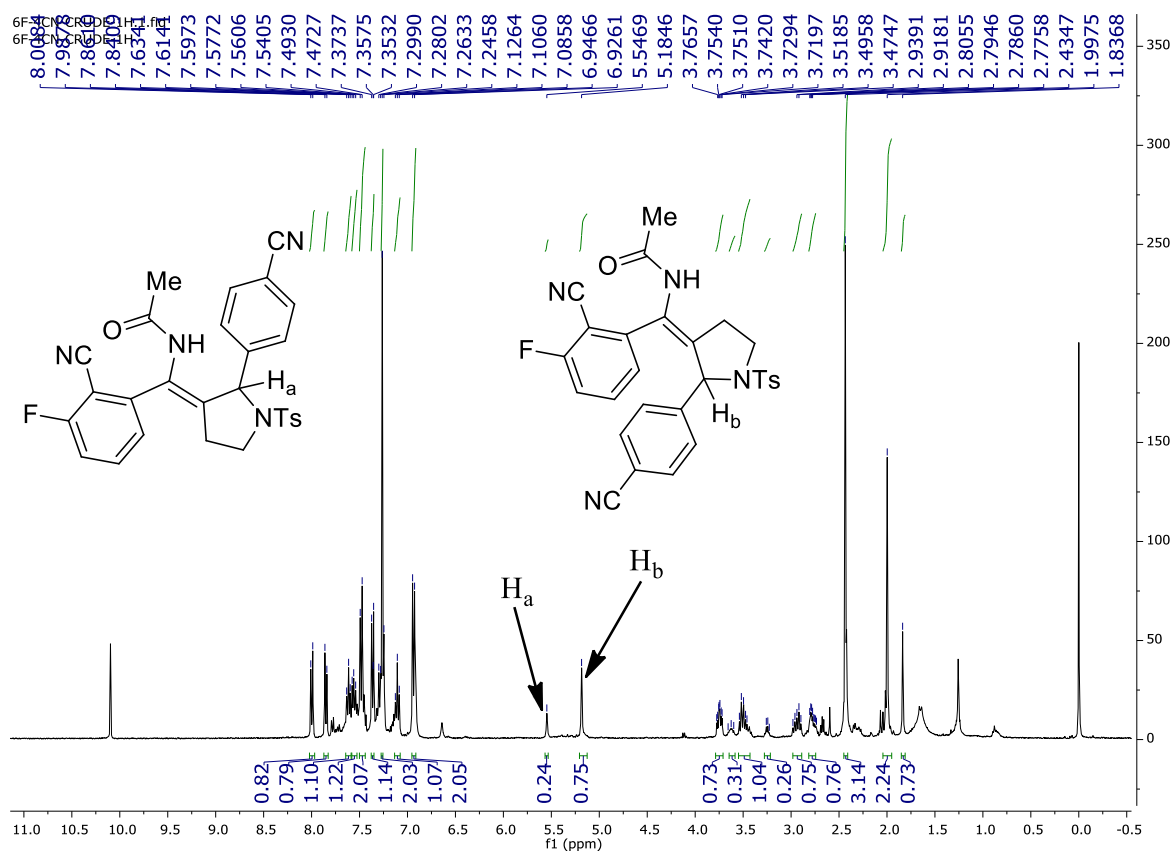
^1H (400 MHz, CDCl_3) and ^{13}C { ^1H } (125 MHz, CDCl_3) NMR spectra of **5fc**



^1H (600 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ (150 MHz, CDCl_3) NMR spectra of **5gc**



Crude ¹H (400 MHz, CDCl₃) NMR spectrum of 3dm



Single crystal X-ray diffraction:

1. Single crystals of compound ***E-3ad***, was obtained by slow evaporation of hexane and ethyl acetate solution (9:1). The Bruker SMART APEX-II CCD diffractometer was used to collect the intensity data. The instrument is equipped with a fine focus 1.75 kW sealed tube Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The data acquisition was done with the SMART software. The SAINT and XPREP software were implemented for data integration and reduction.¹ Multiscan empirical absorption corrections were employed to the data using the program SADABS.² Structures were solved by direct methods using SHELXS- 2016 and refined with full-matrix least-squares on F2 using SHELXL- 2016/6.³ Structural illustrations have been drawn with ORTEP-3 for Windows.⁴ The detailed data collection and structure refinement are summarized in Table S1, CCDC 2287207 (for ***E-3ad***), contained supplementary crystallographic data for this paper.

Reference:

- 1) SMART; SAINT; XPREP; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.
- 2) Sheldrick, G. M. SADABS: Software for Empirical Absorption Correction University of Gottingen, Institut fur Anorganische Chemieder Universitat: Gottingen, Germany, 1999.
- 3) Sheldrick, G. M. SHELXS-2014, Program for the crystal structure solution; University of Göttingen: Göttingen, Germany, 2014.
- 4) Farrugia, L. J. XRDIF: simulation of X-ray diffraction patterns, *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table S56: The crystal parameters of compound *E*-3ad

	CCDC 2287207
Formula	C ₂₉ H ₂₉ N ₃ O ₃ S
Formula weight	499.61
<i>T</i> /K	297(2)
Crystal system	monoclinic
Space group	'P 21/n'
<i>a</i> /Å	22.290(2)
<i>b</i> /Å	11.2327(11)
<i>c</i> /Å	22.560(2)
<i>α</i> /°	90
<i>β</i> /°	108.847(3)
<i>γ</i> /°	90
<i>V</i> /Å ³	5345.7(9)
<i>Z</i>	8
Abs. Coeff./mm ⁻¹	0.156
Abs. Correction	'none'
GOF on <i>F</i> ²	0.981
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0697 <i>wR</i> 2 = 0.1717
<i>R</i> indices [all data]	<i>R</i> 1 = 0.1219 <i>wR</i> 2 = 0.1972

Figure S57: ORTEP diagram of compound *E*-3ad with 30% probability

