

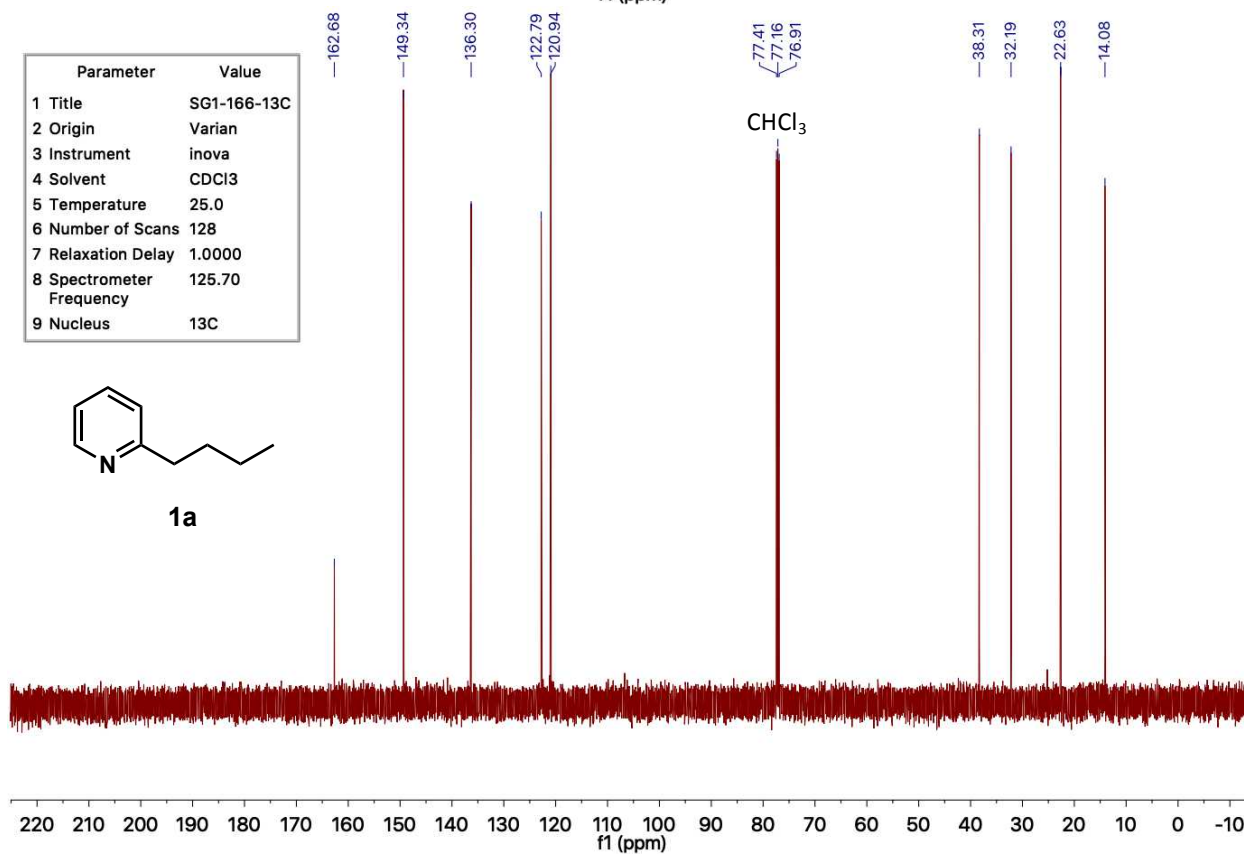
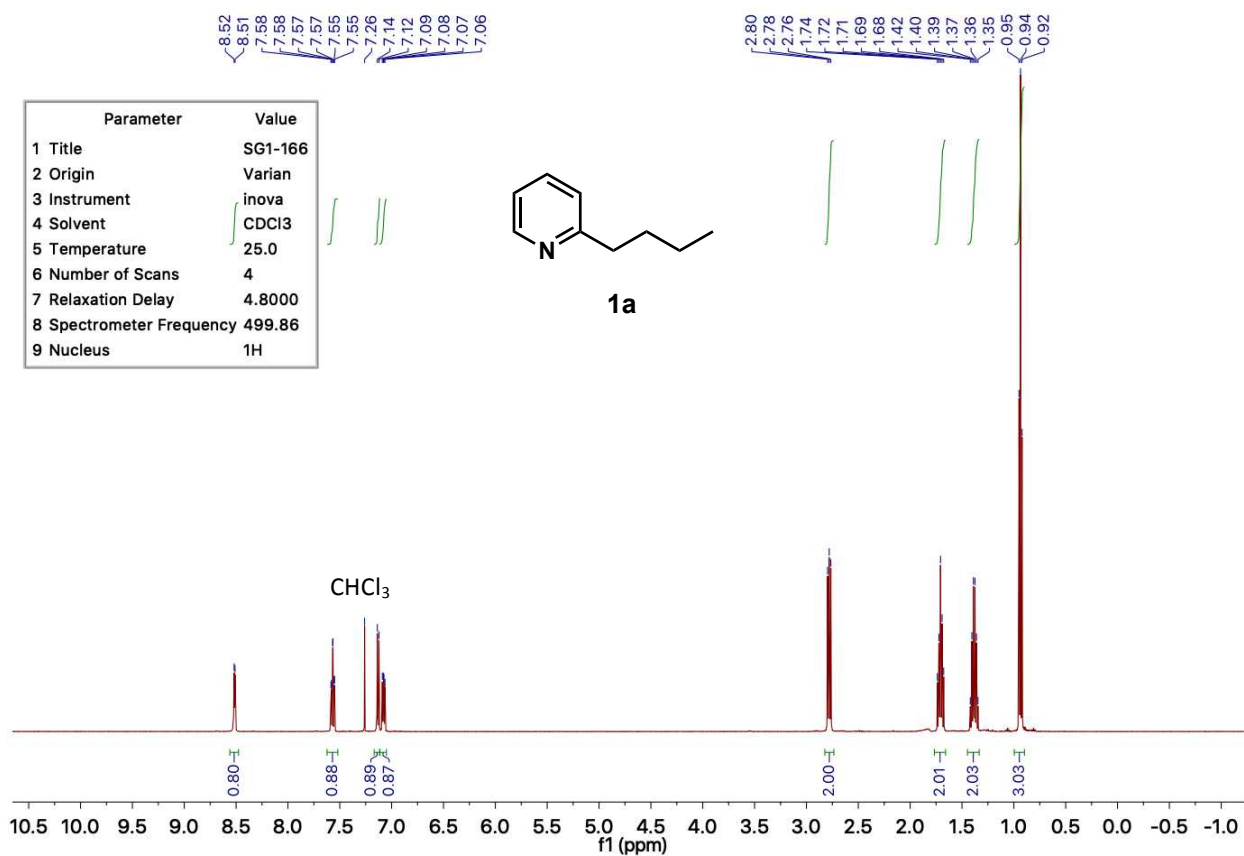
Enantioselective Alkylation of 2-Alkyl Pyridines Controlled by Organolithium Aggregation

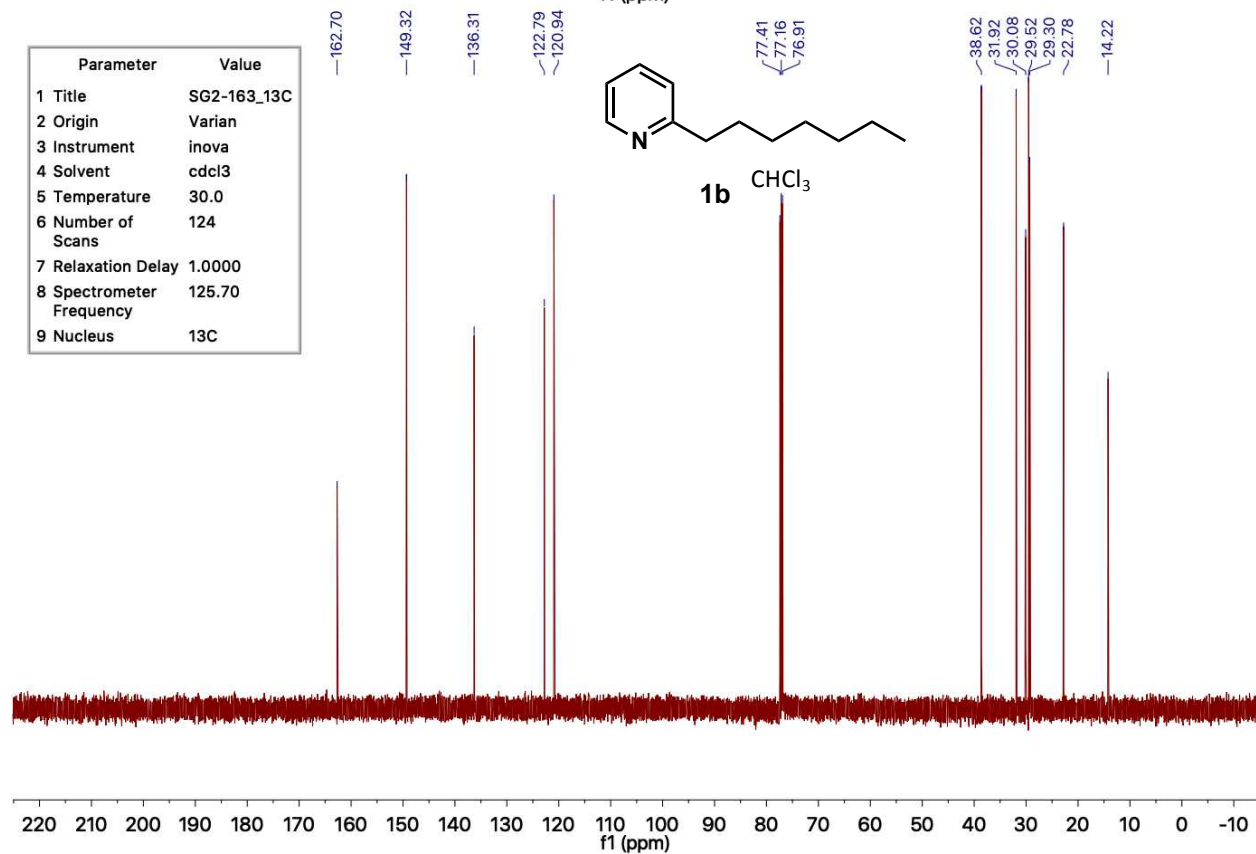
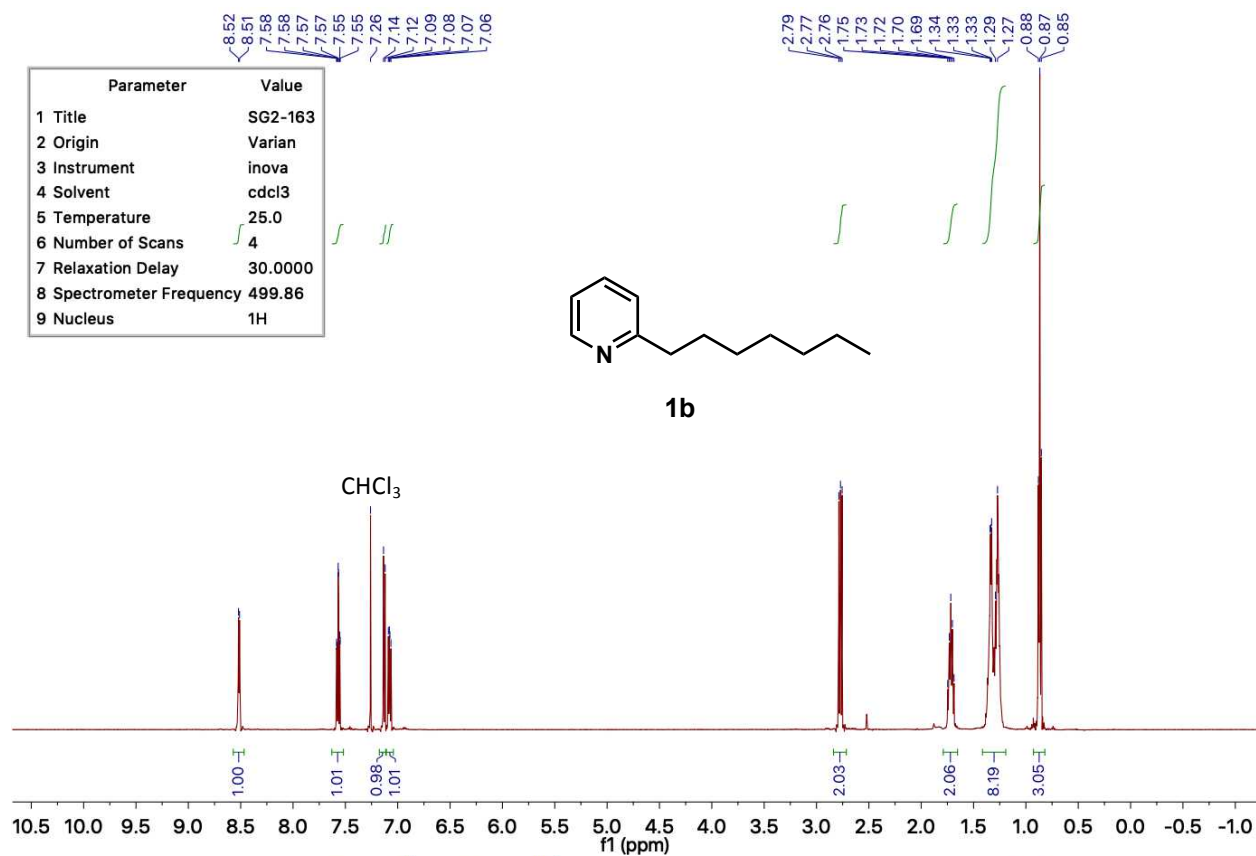
Joshua J. Gladfelder,[†] Santanu Ghosh,[†] Maša Podunavac,[†] Andrew W. Cook,[†] Yun Ma,[†] Ryan A. Woltornist,[‡] Ivan Keresztes,[‡] Trevor W. Hayton,^{*,†} David B. Collum,^{*,‡} Armen Zakarian^{*,†}

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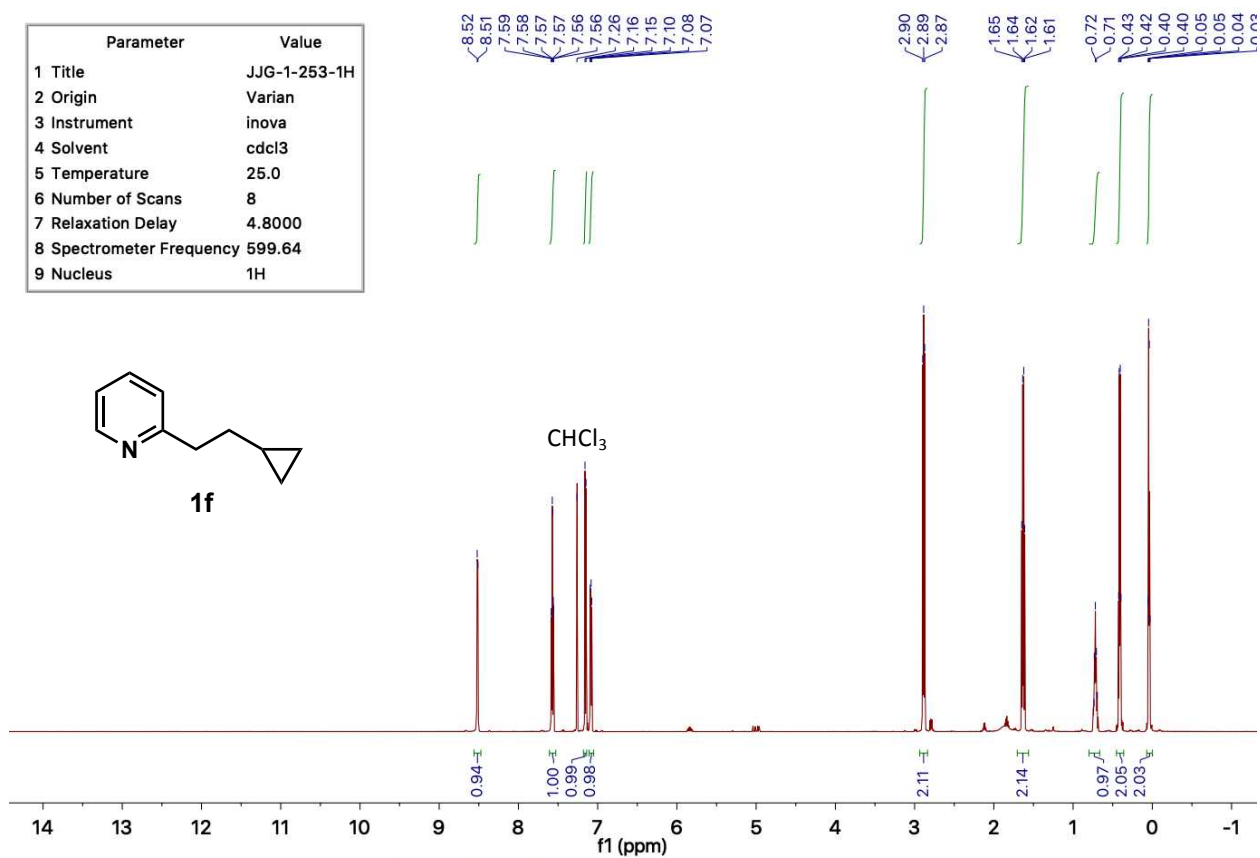
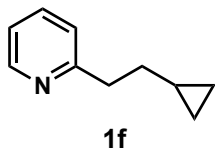
[‡]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

Supplementary Information II

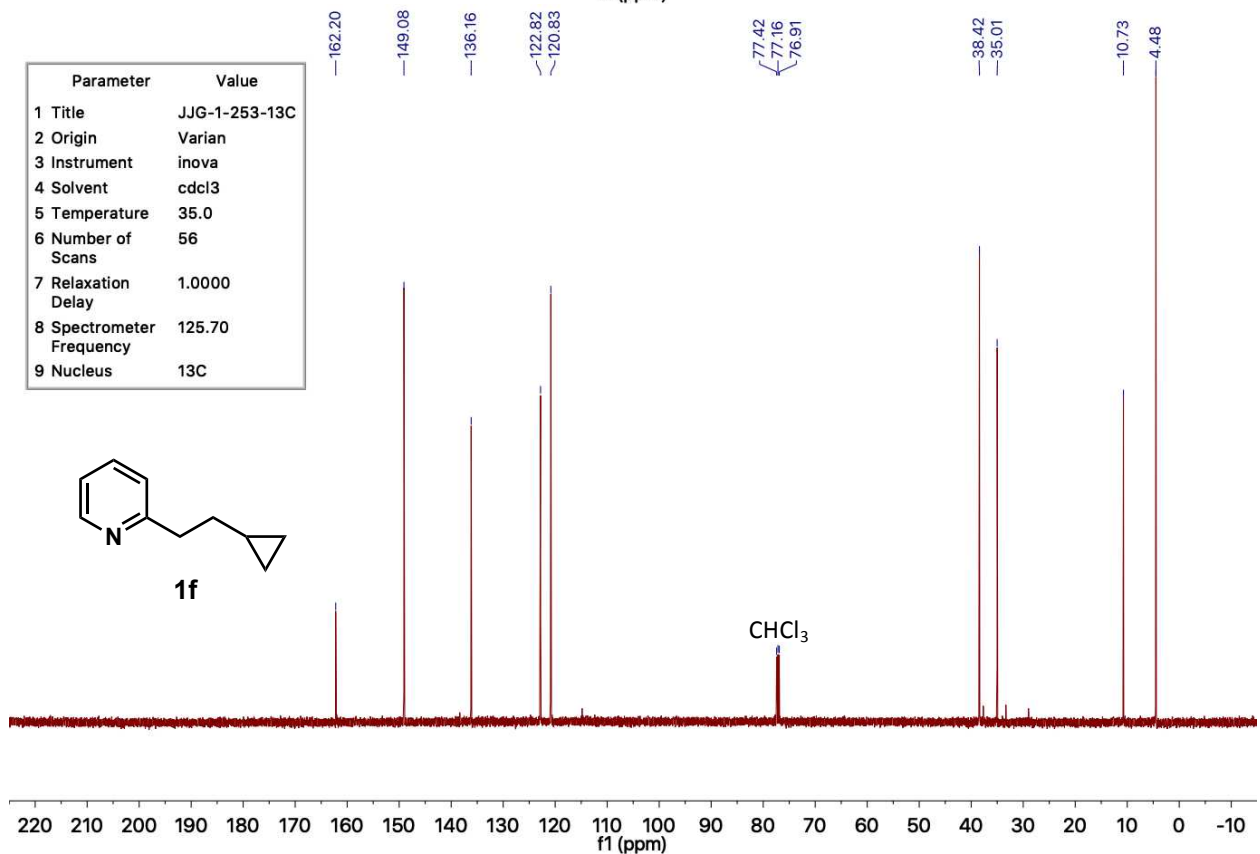
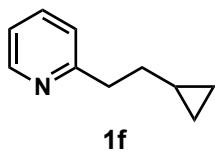


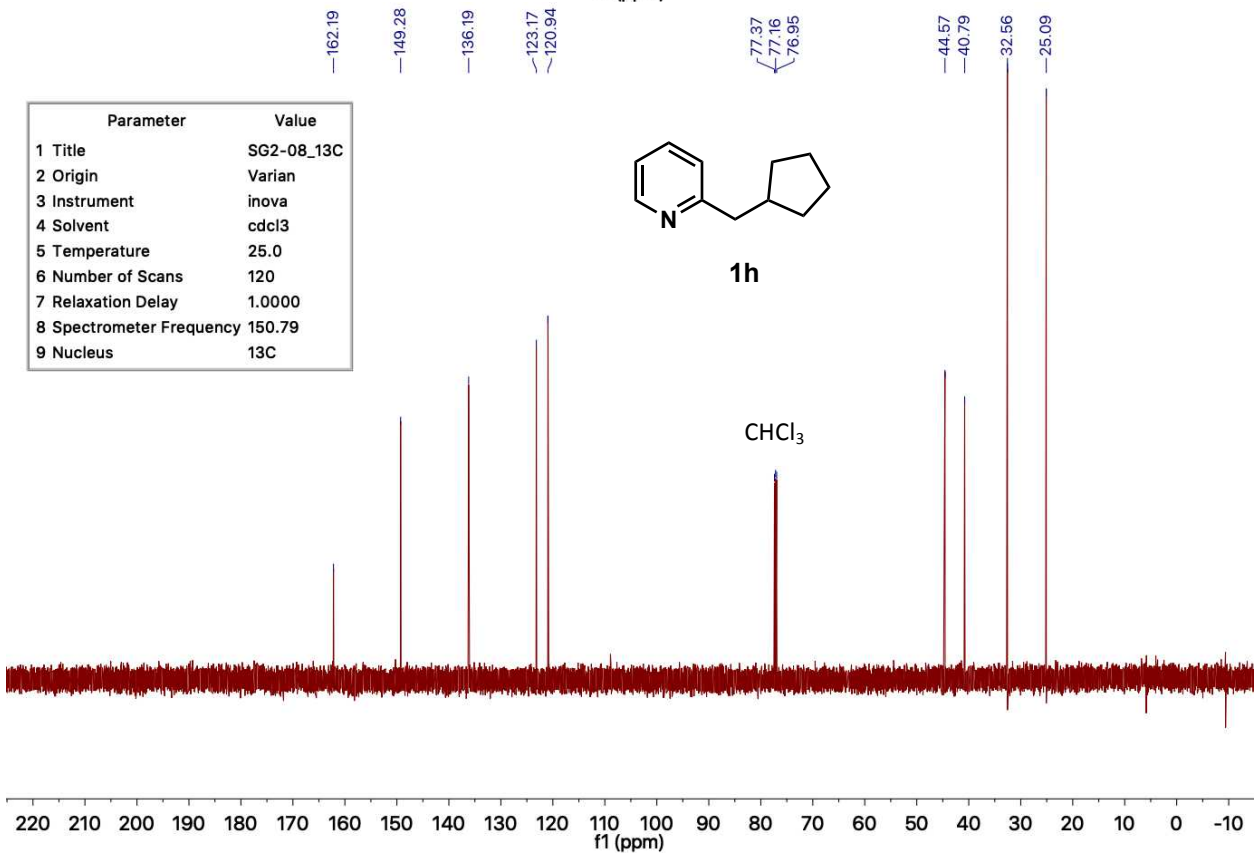
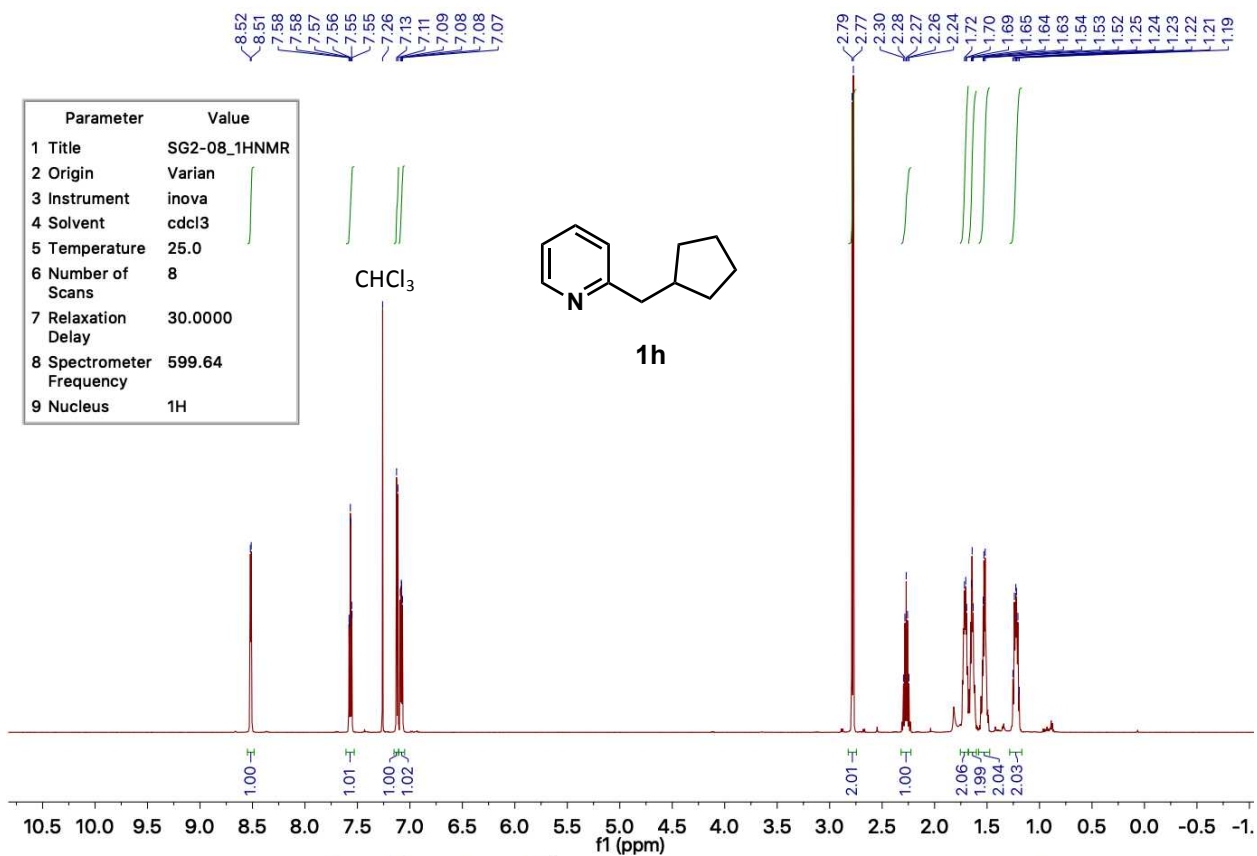


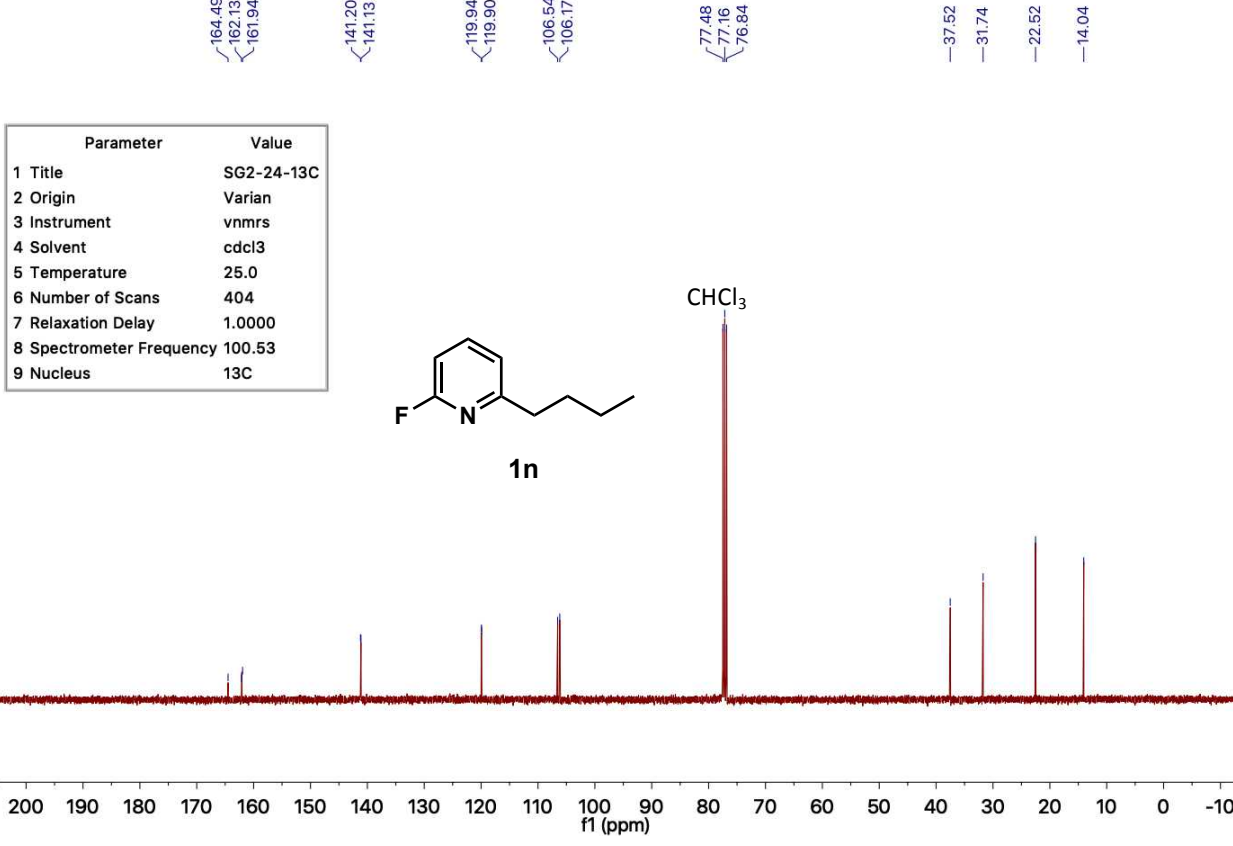
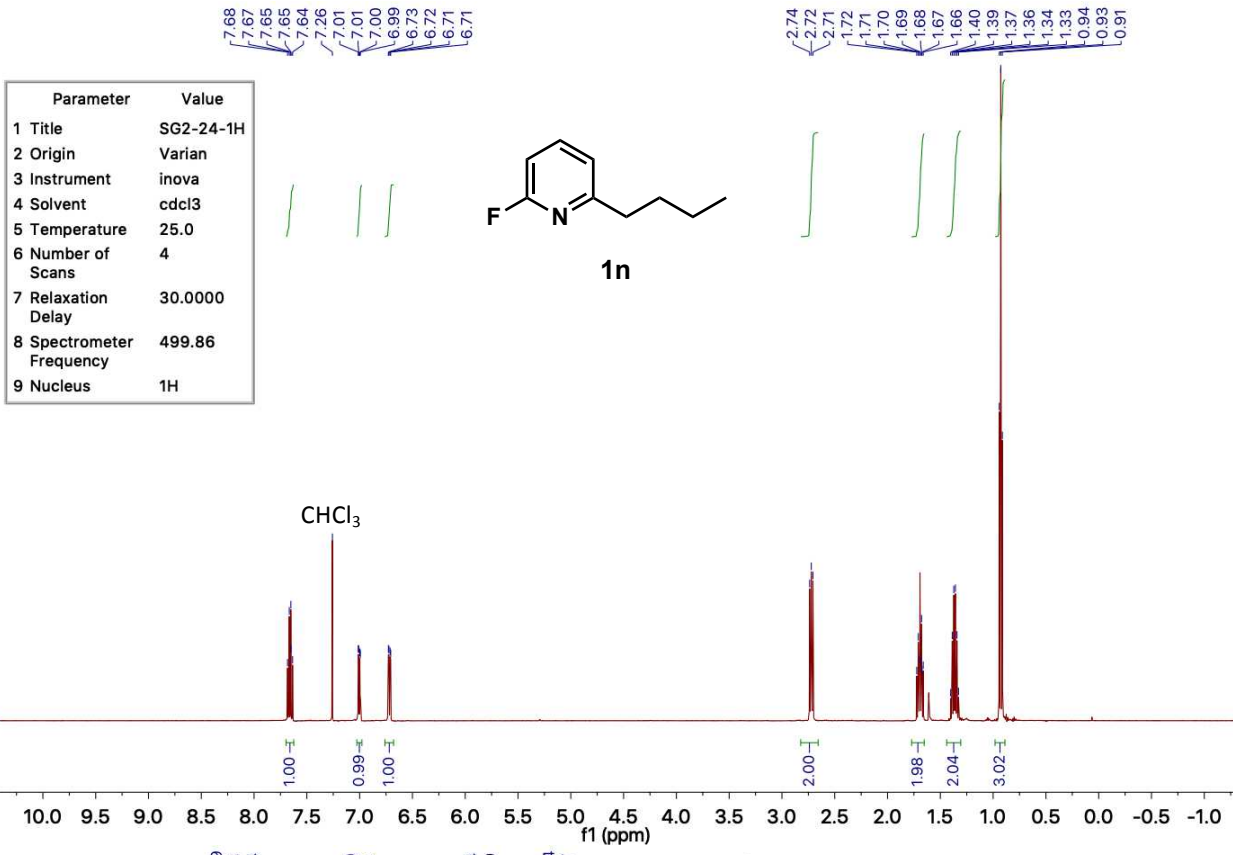
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3 Instrument	inova
4 Solvent	cdcl3
5 Temperature	25.0
6 Number of Scans	8
7 Relaxation Delay	4.8000
8 Spectrometer Frequency	599.64
9 Nucleus	¹ H



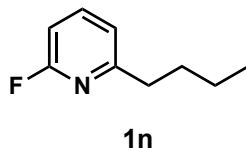
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2 Origin	Varian
3 Instrument	inova
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8 Spectrometer Frequency	125.70
9 Nucleus	¹³ C



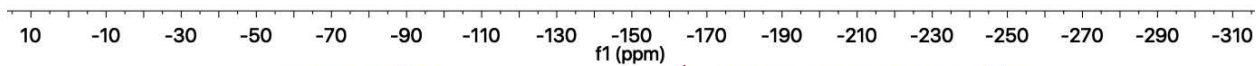




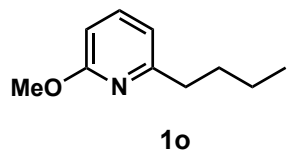
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2 Origin	Varian
3 Instrument	vnms
4 Solvent	cdcl3
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8 Spectrometer Frequency	376.11
9 Nucleus	19F



-67.92
-67.94



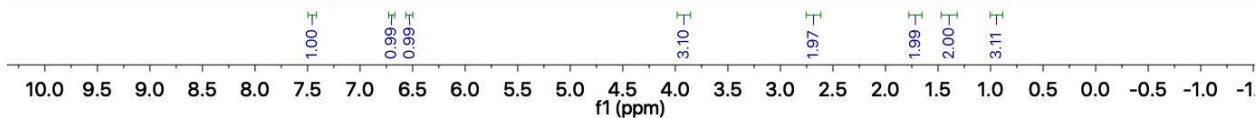
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8 Spectrometer Frequency	399.78
9 Nucleus	1H

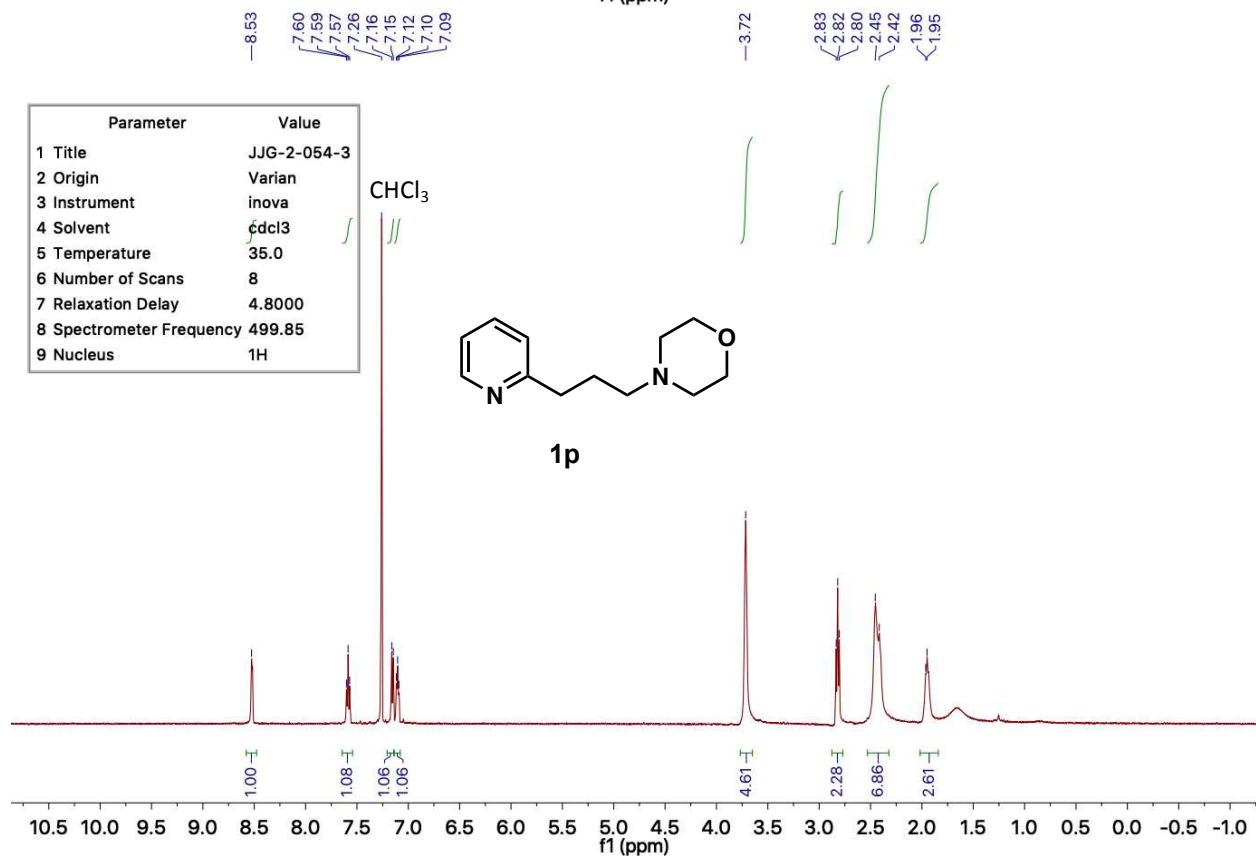
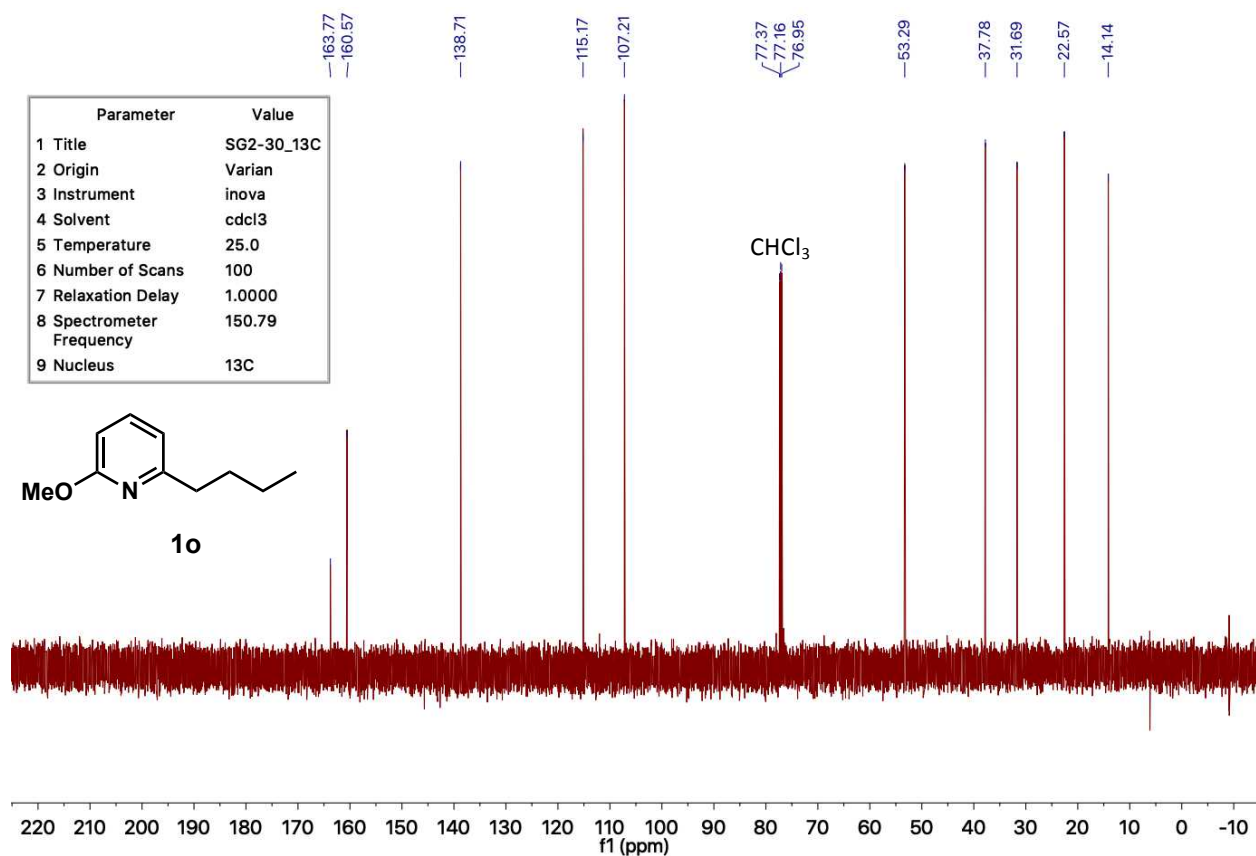


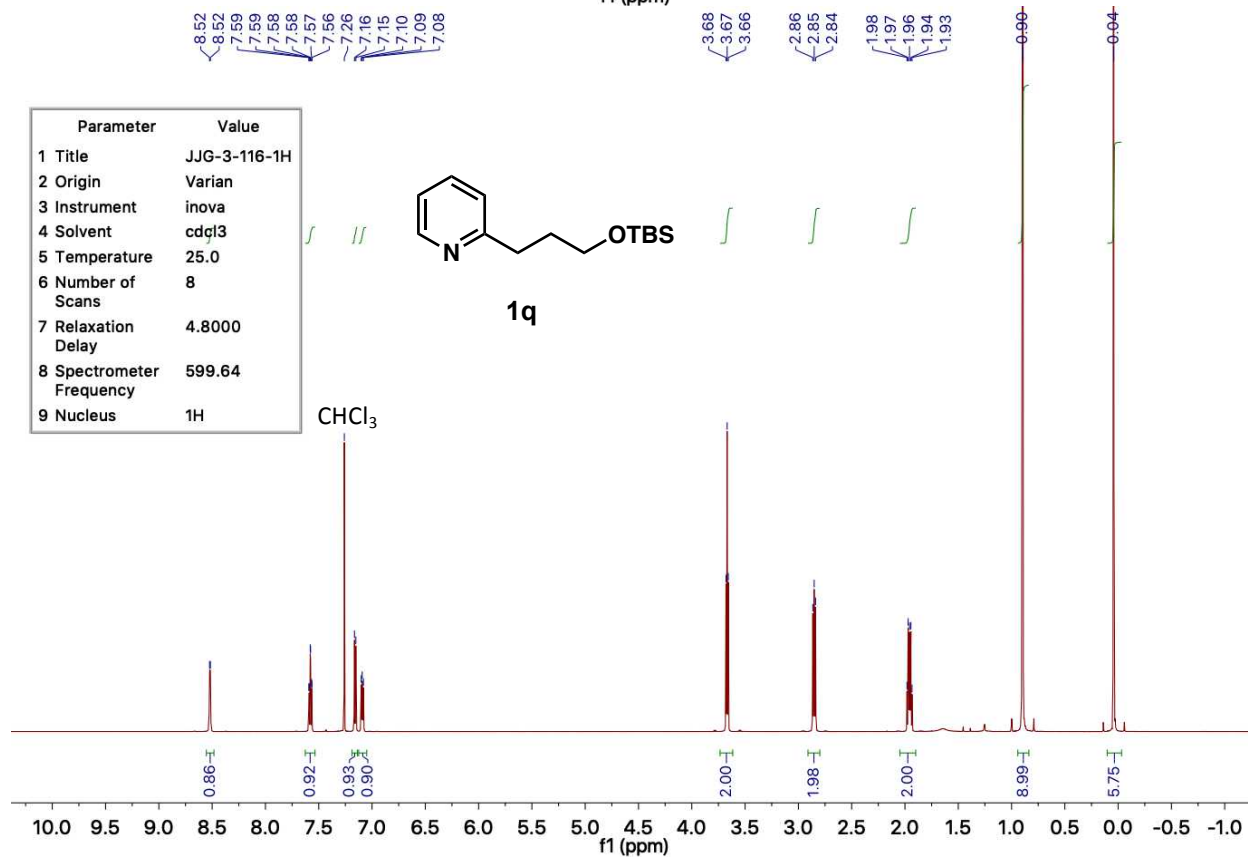
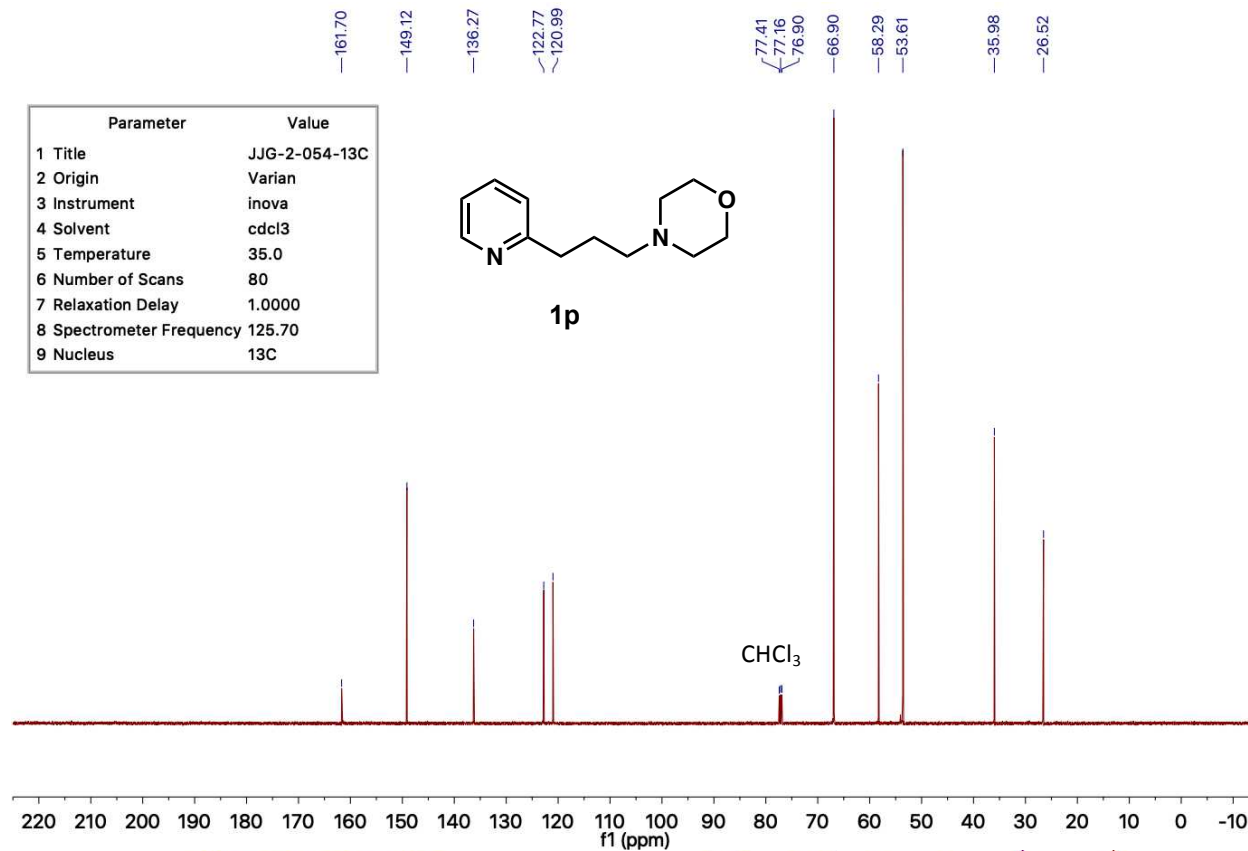
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7.45
7.43
7.26
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6.68
6.54
6.52

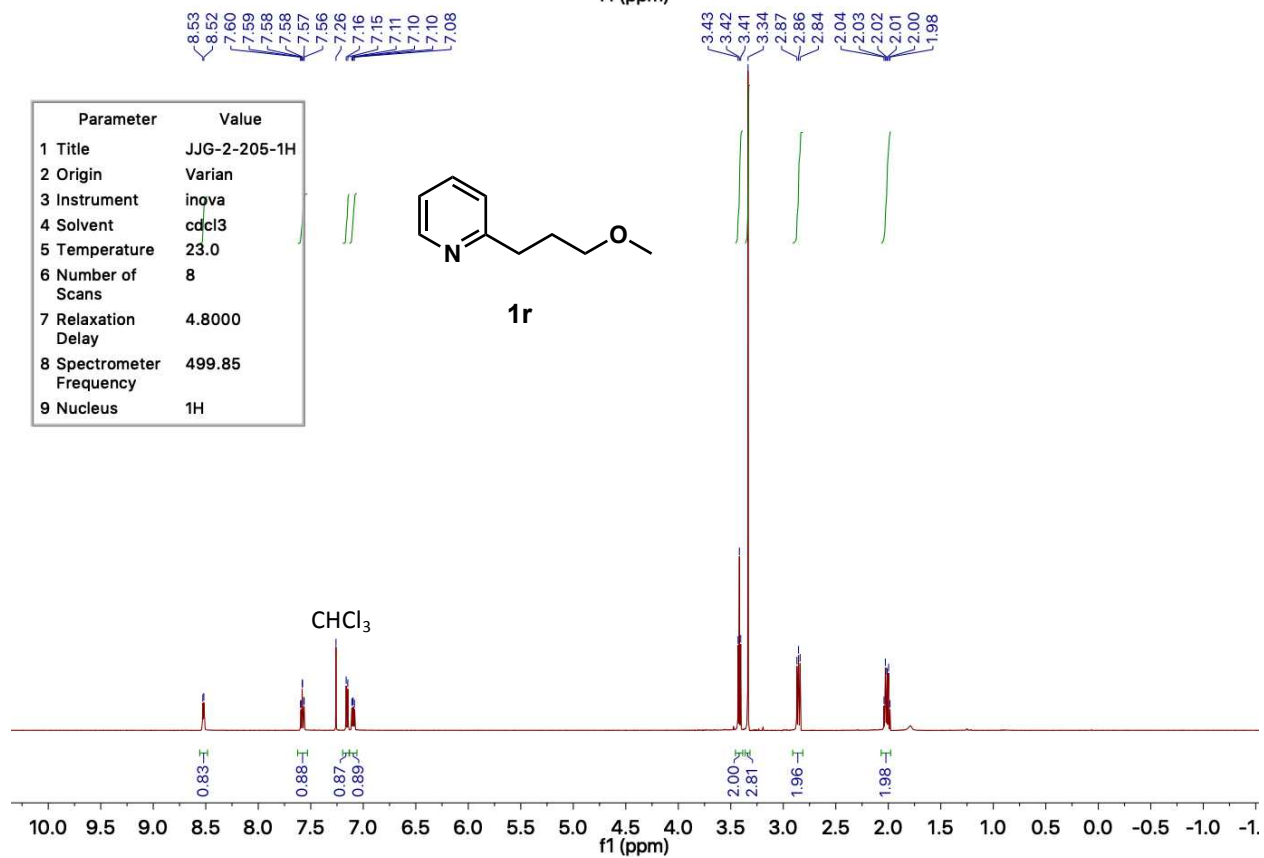
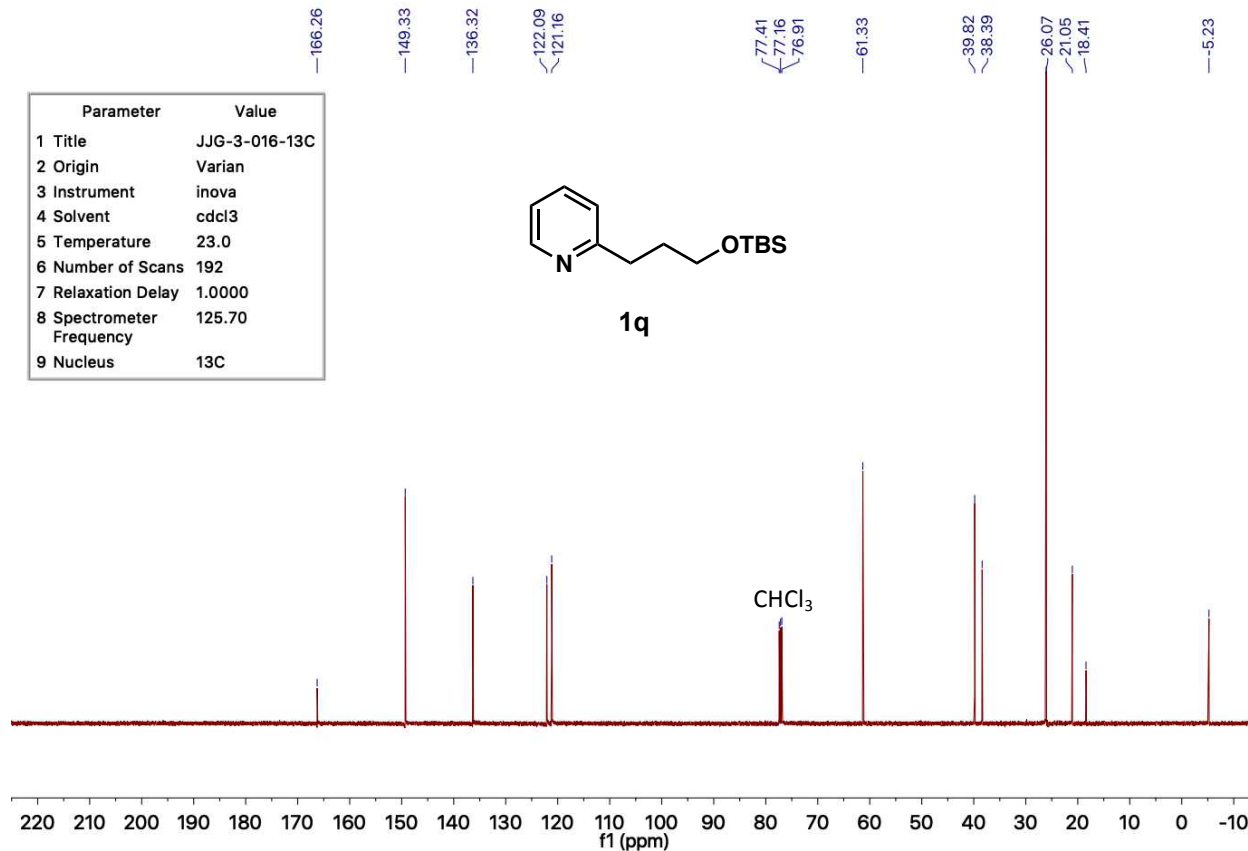
3.92
2.70
2.68
1.74
1.72
1.70
1.68
1.66
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1.40
1.38
1.37
1.35
1.33
0.96
0.94

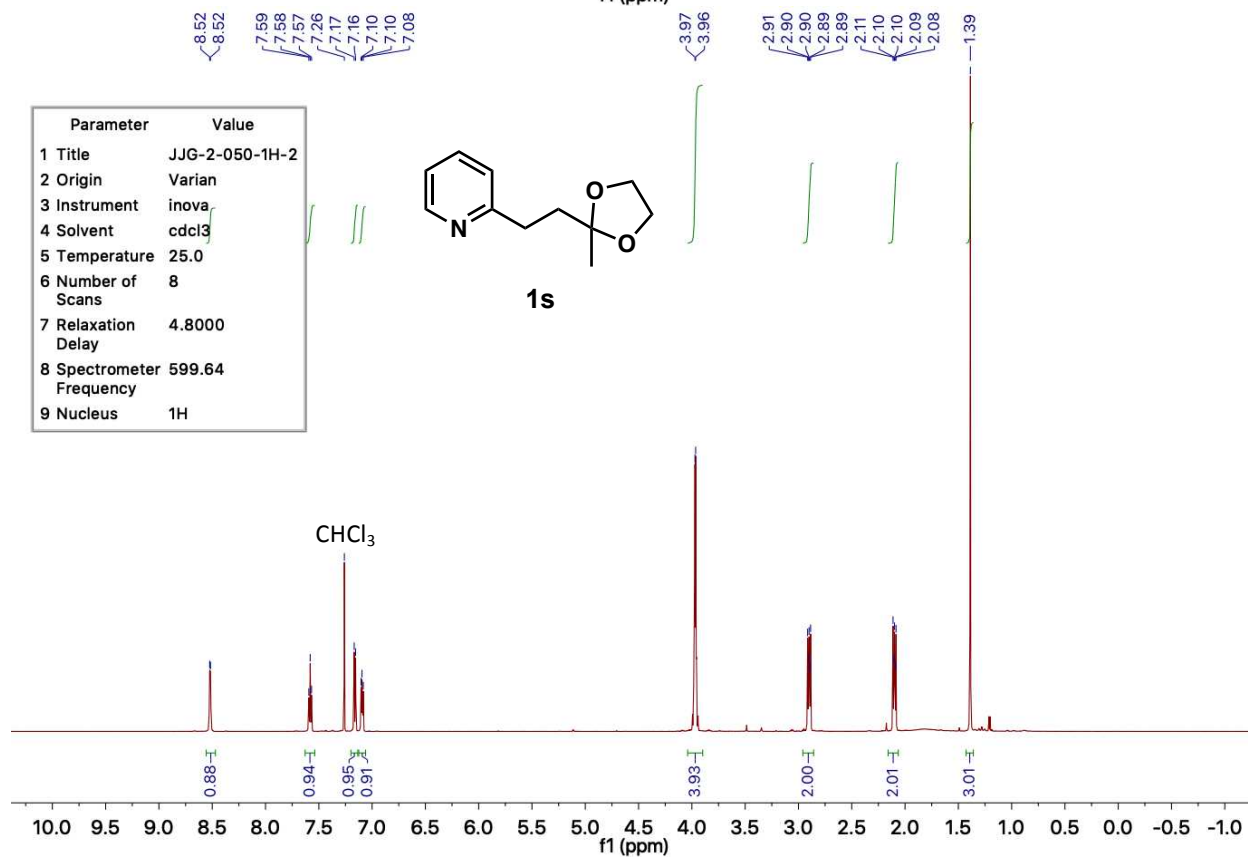
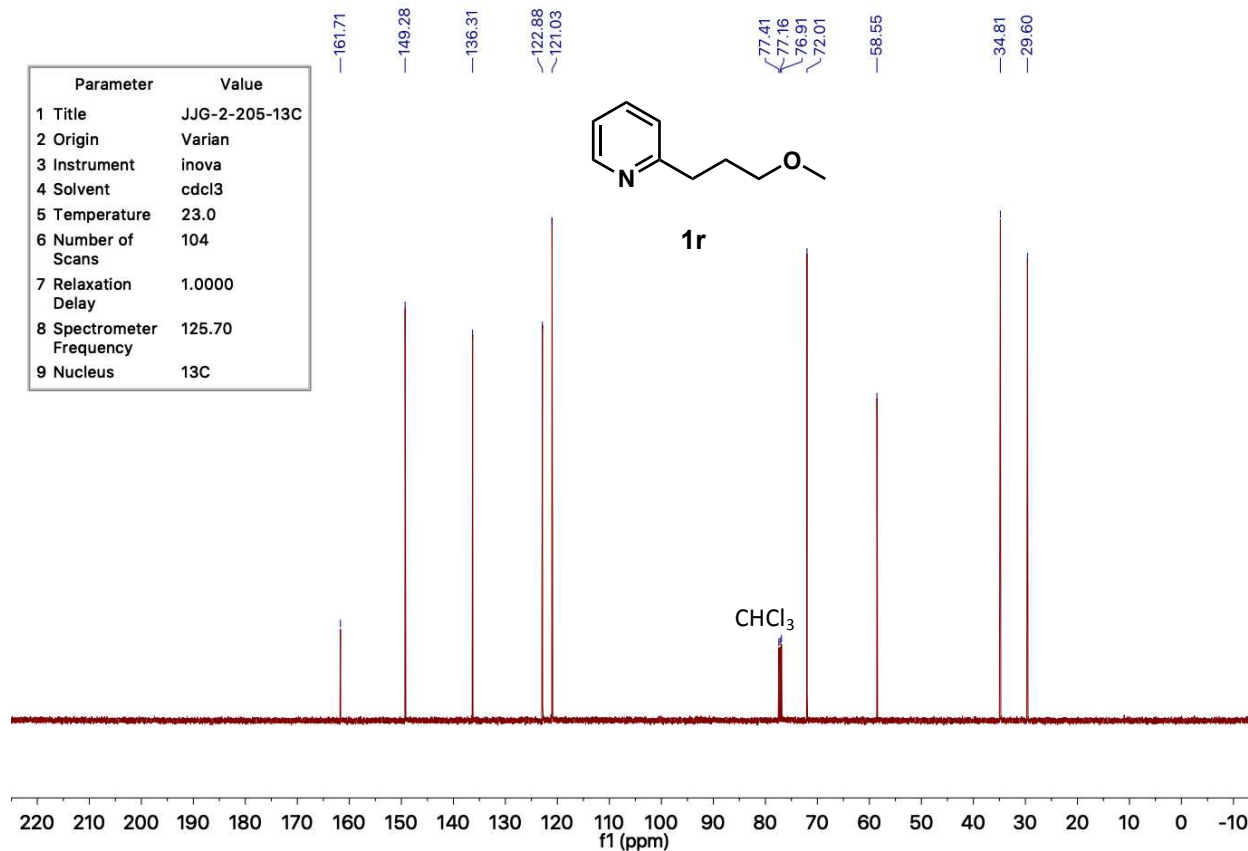
CHCl₃

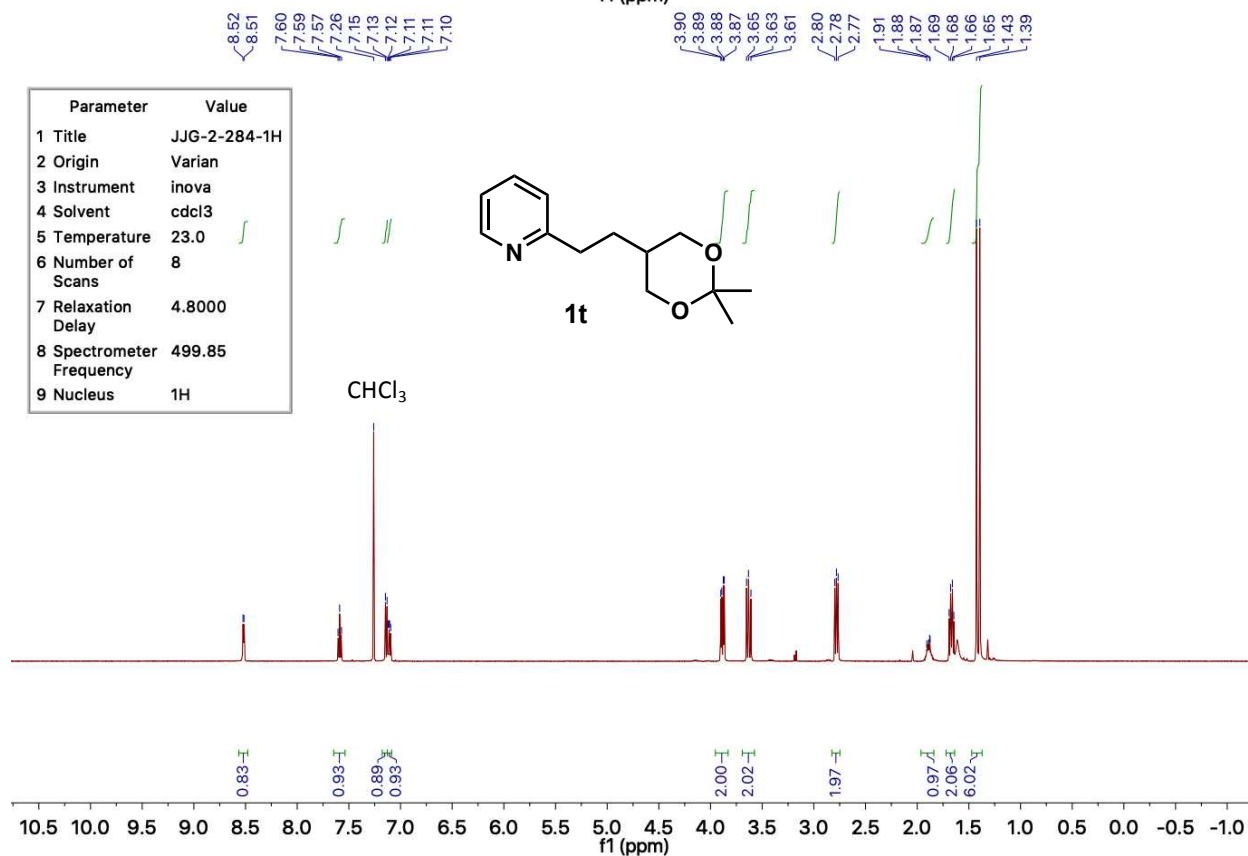
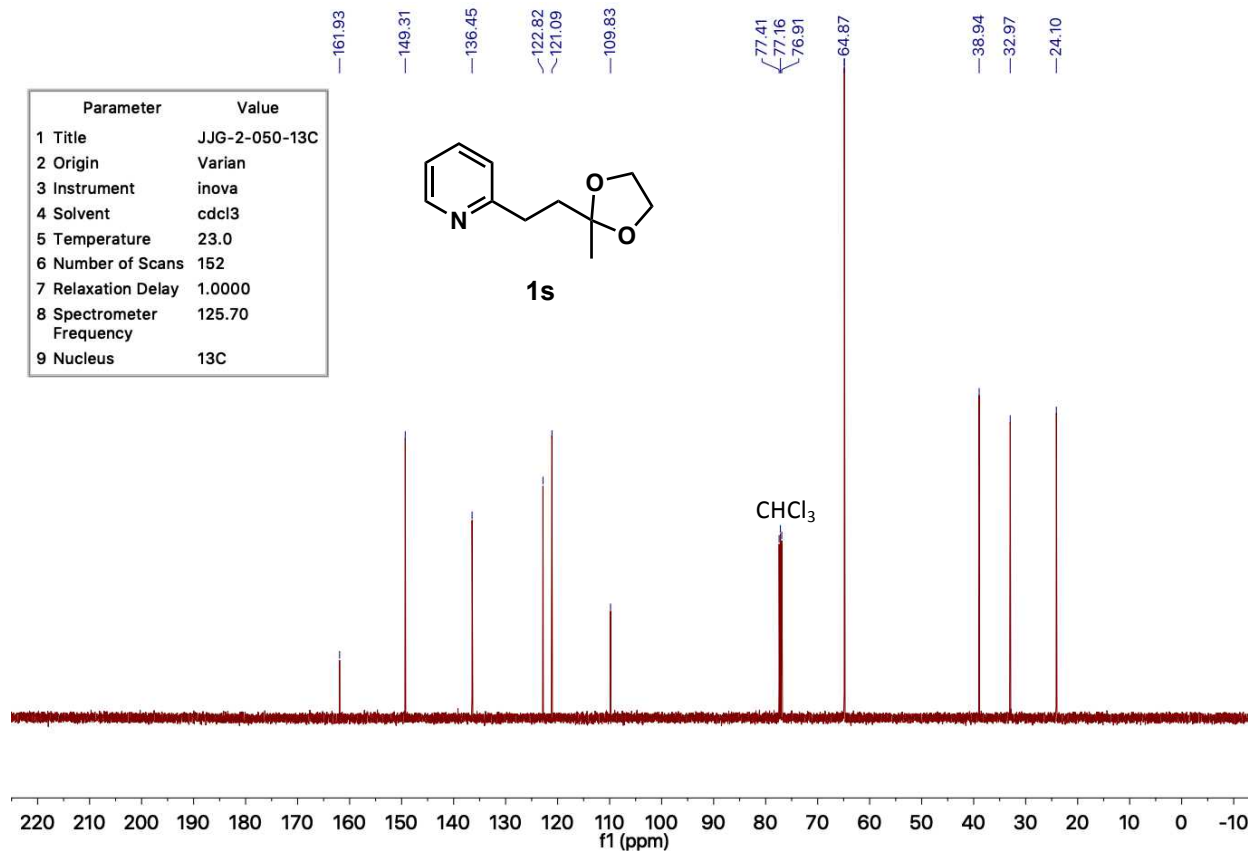




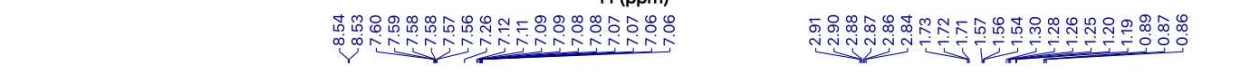
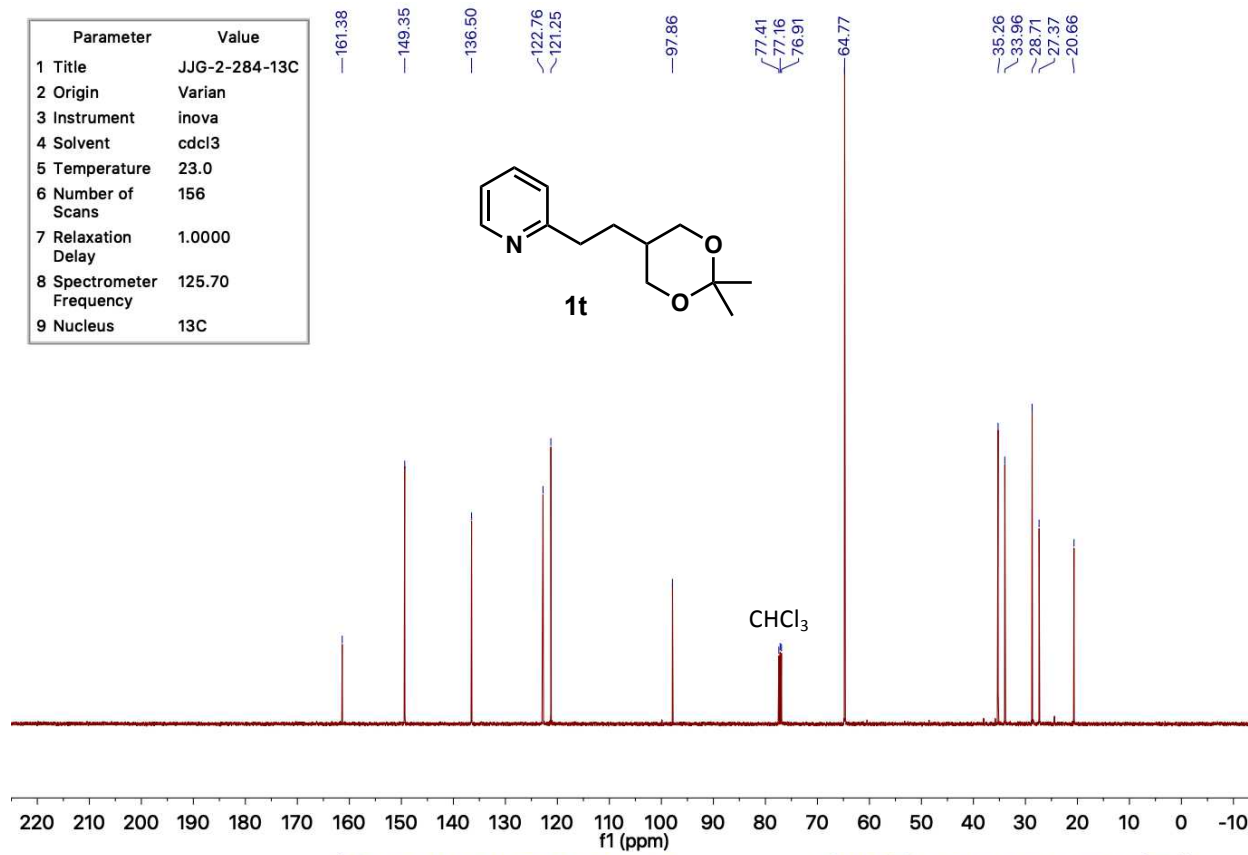




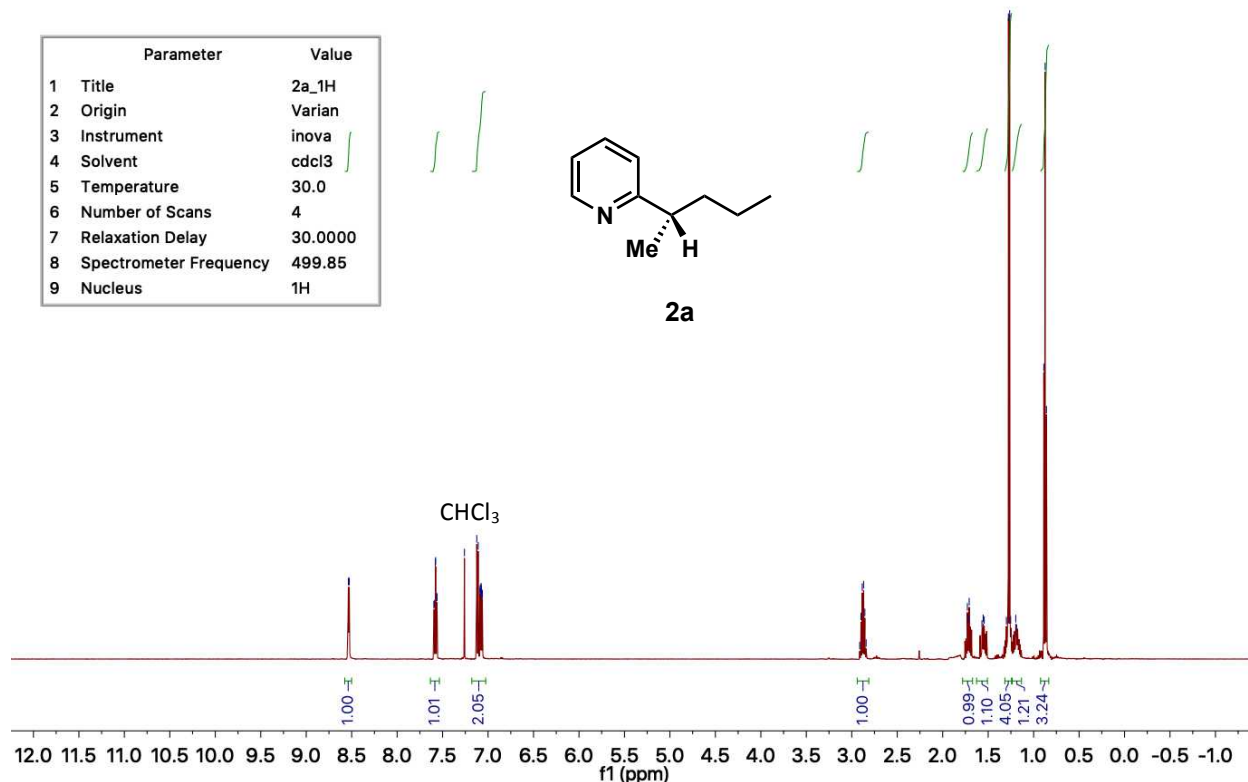


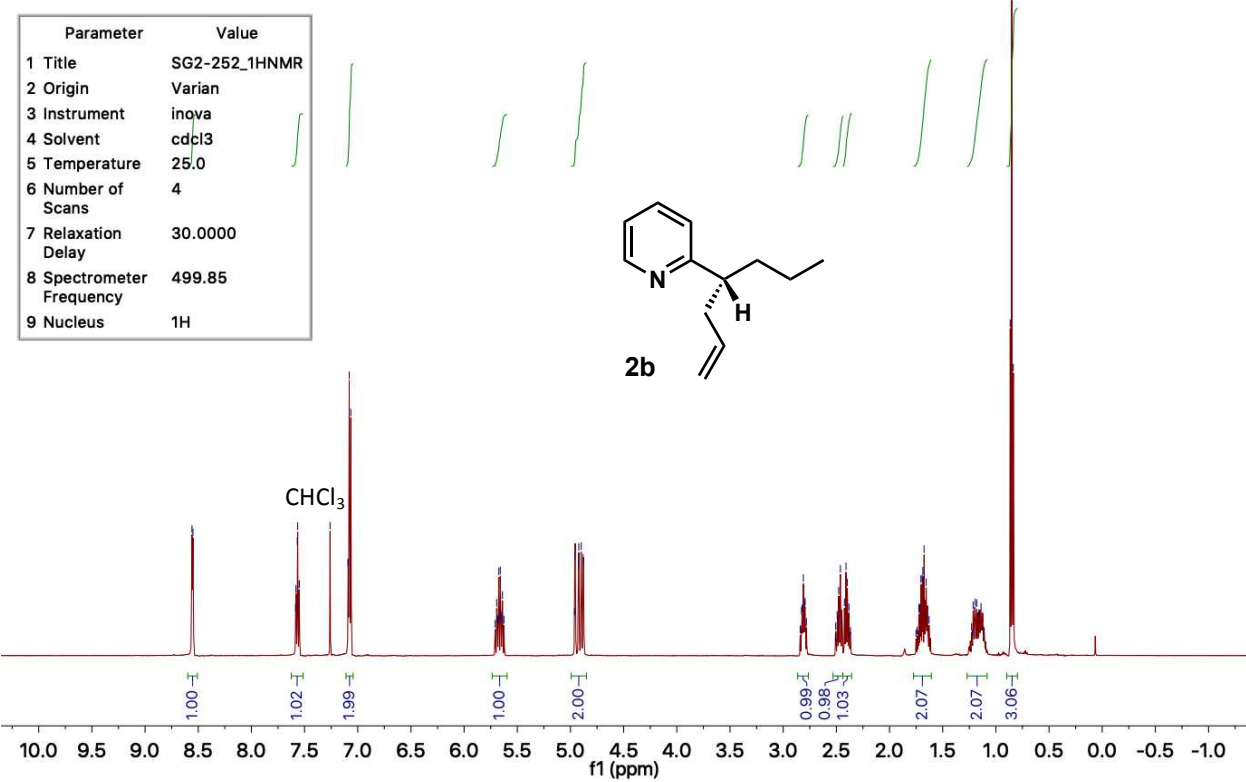
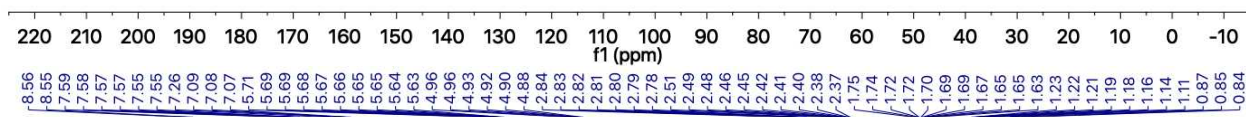
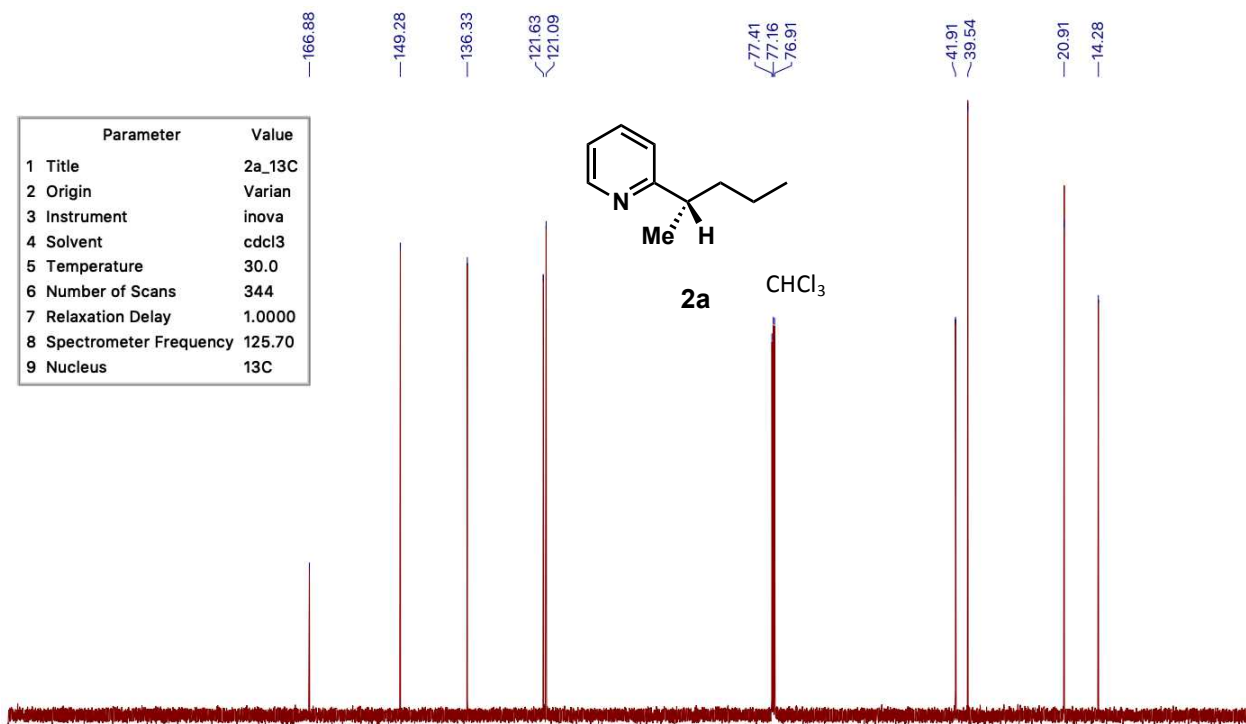


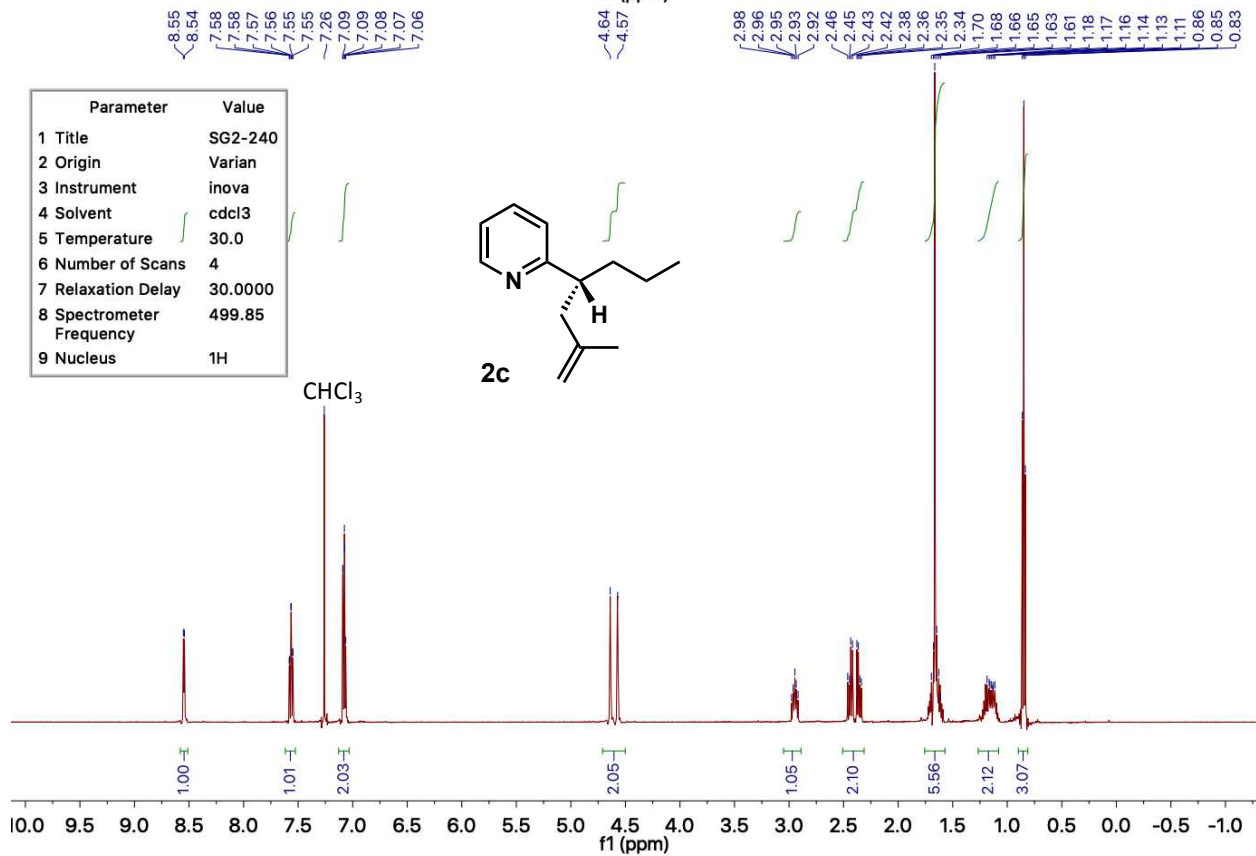
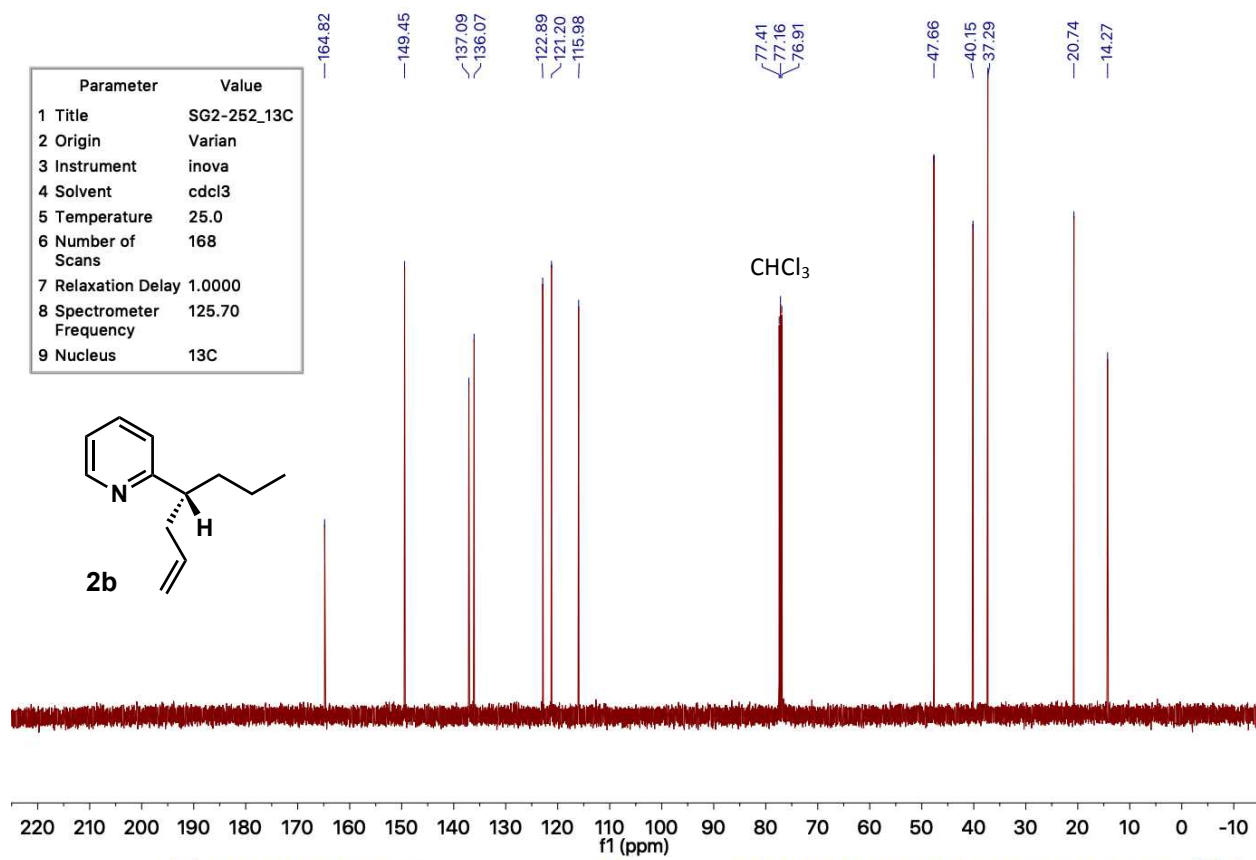
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8 Spectrometer Frequency	125.70
9 Nucleus	13C

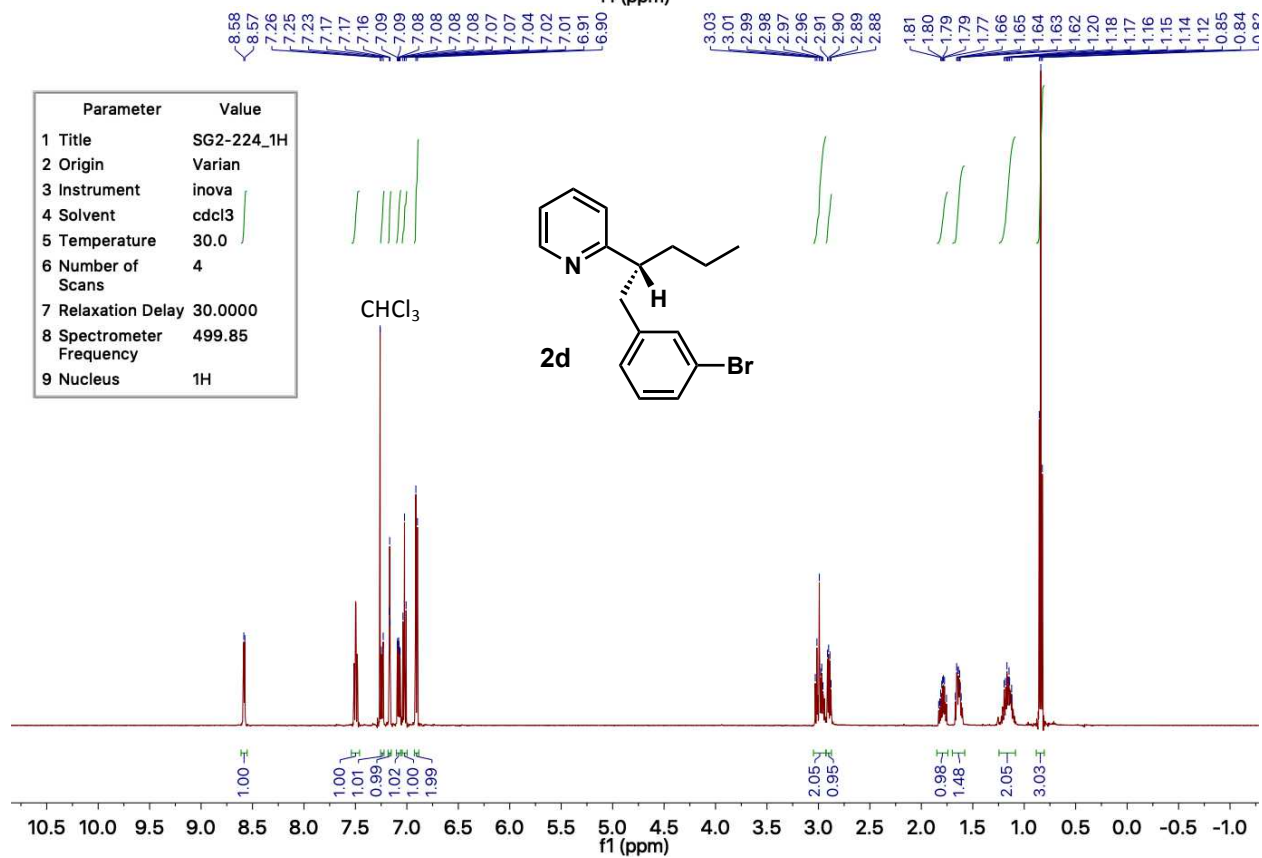
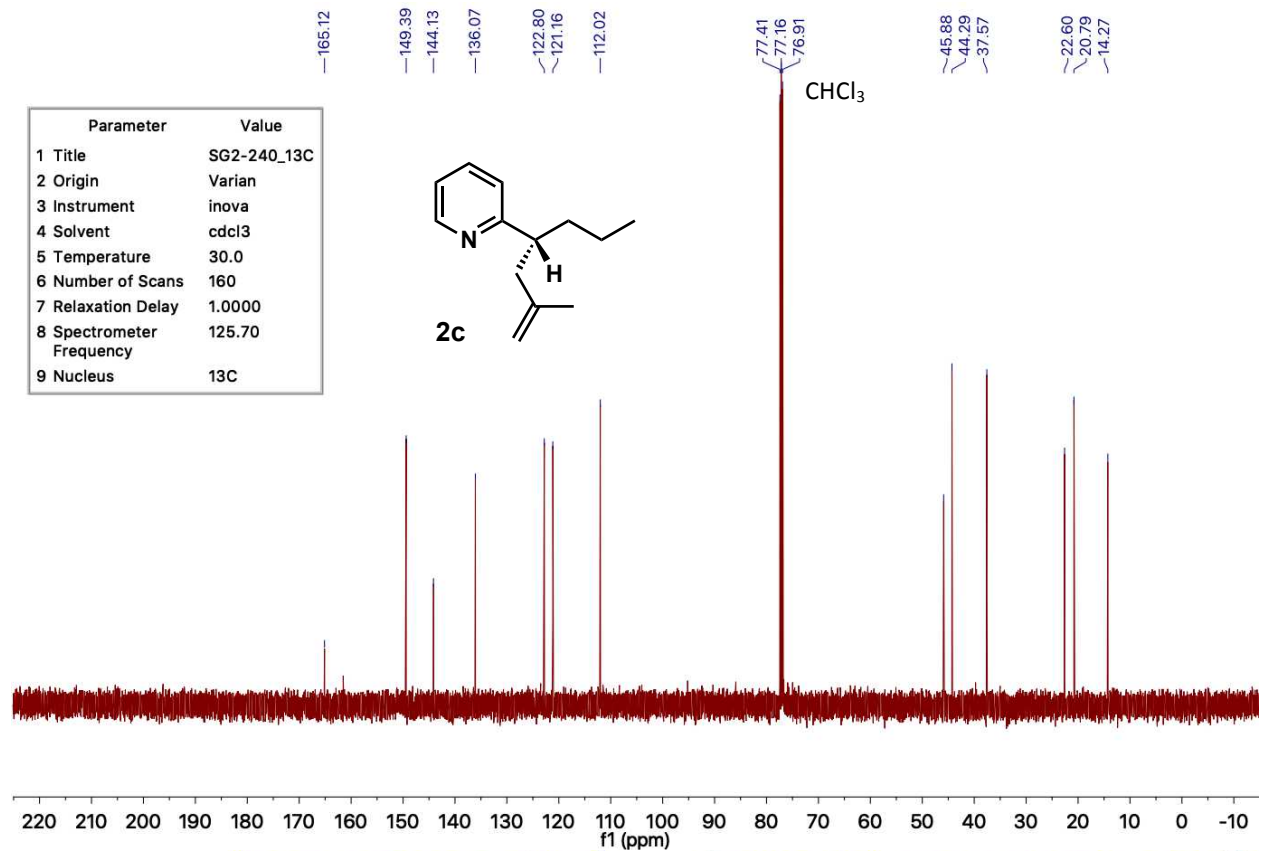


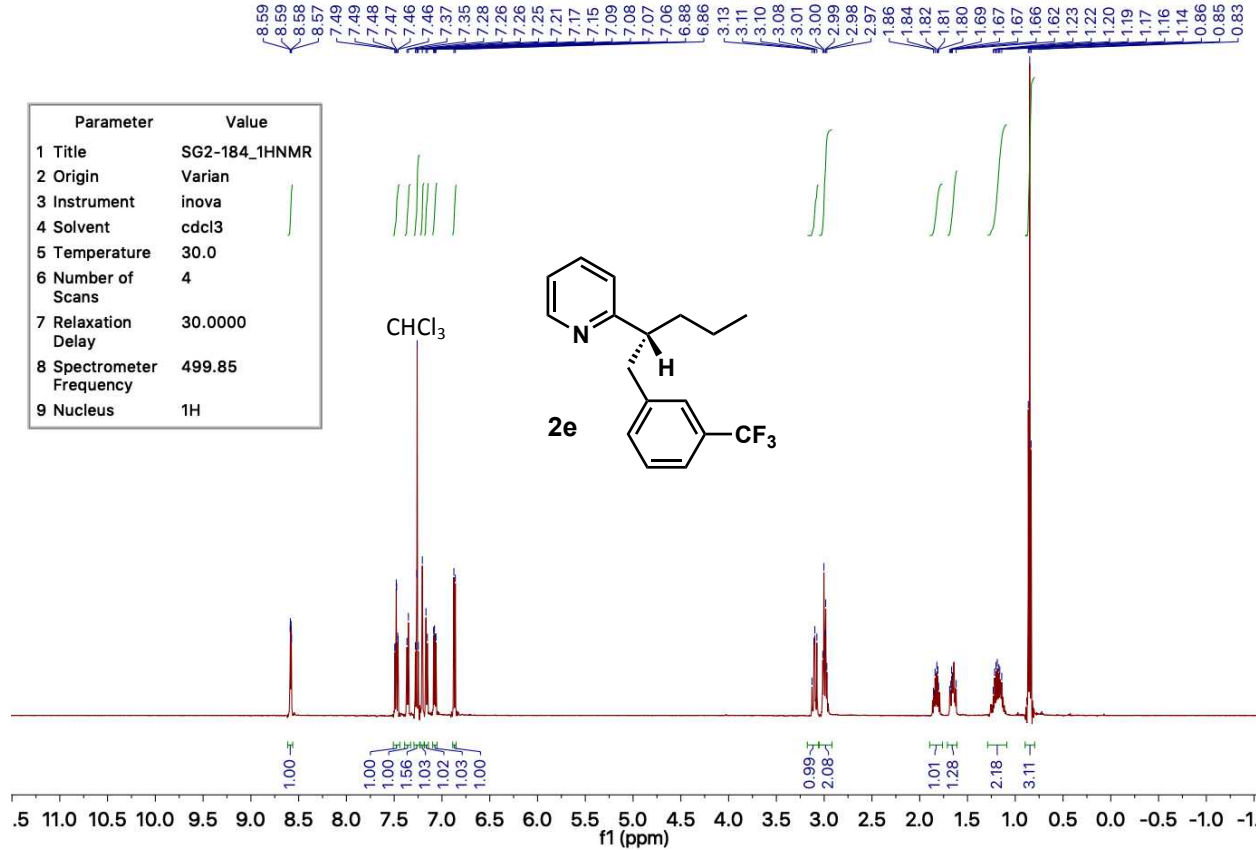
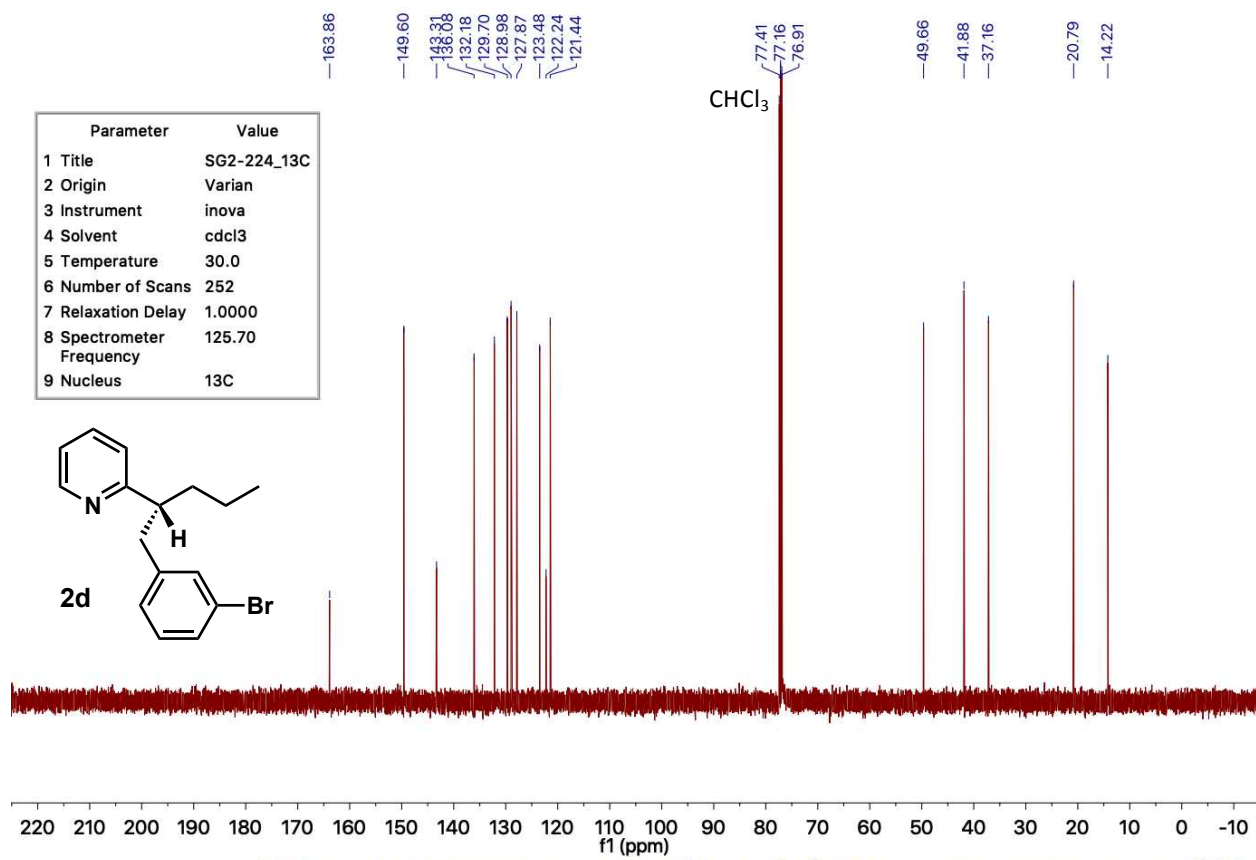
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5 Temperature	30.0
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8 Spectrometer Frequency	499.85
9 Nucleus	1H

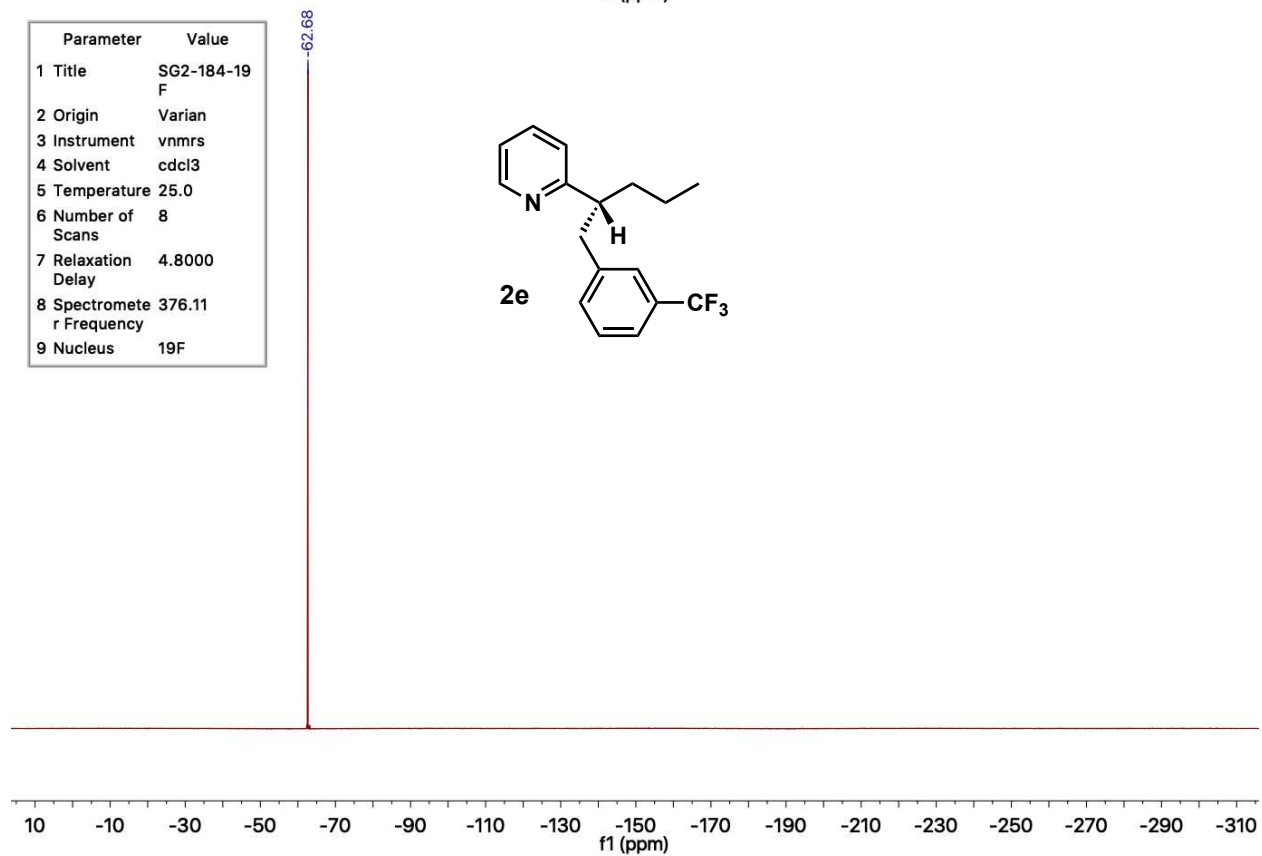
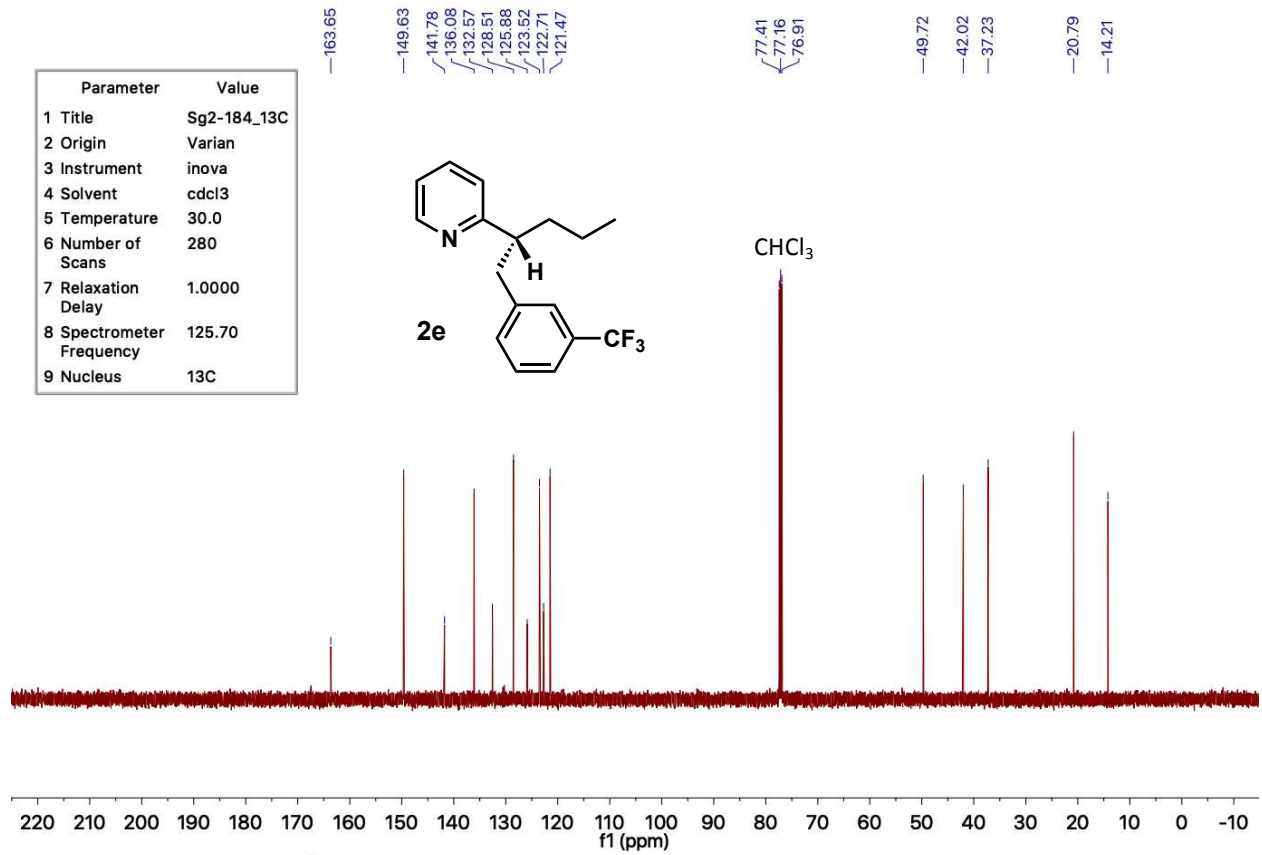


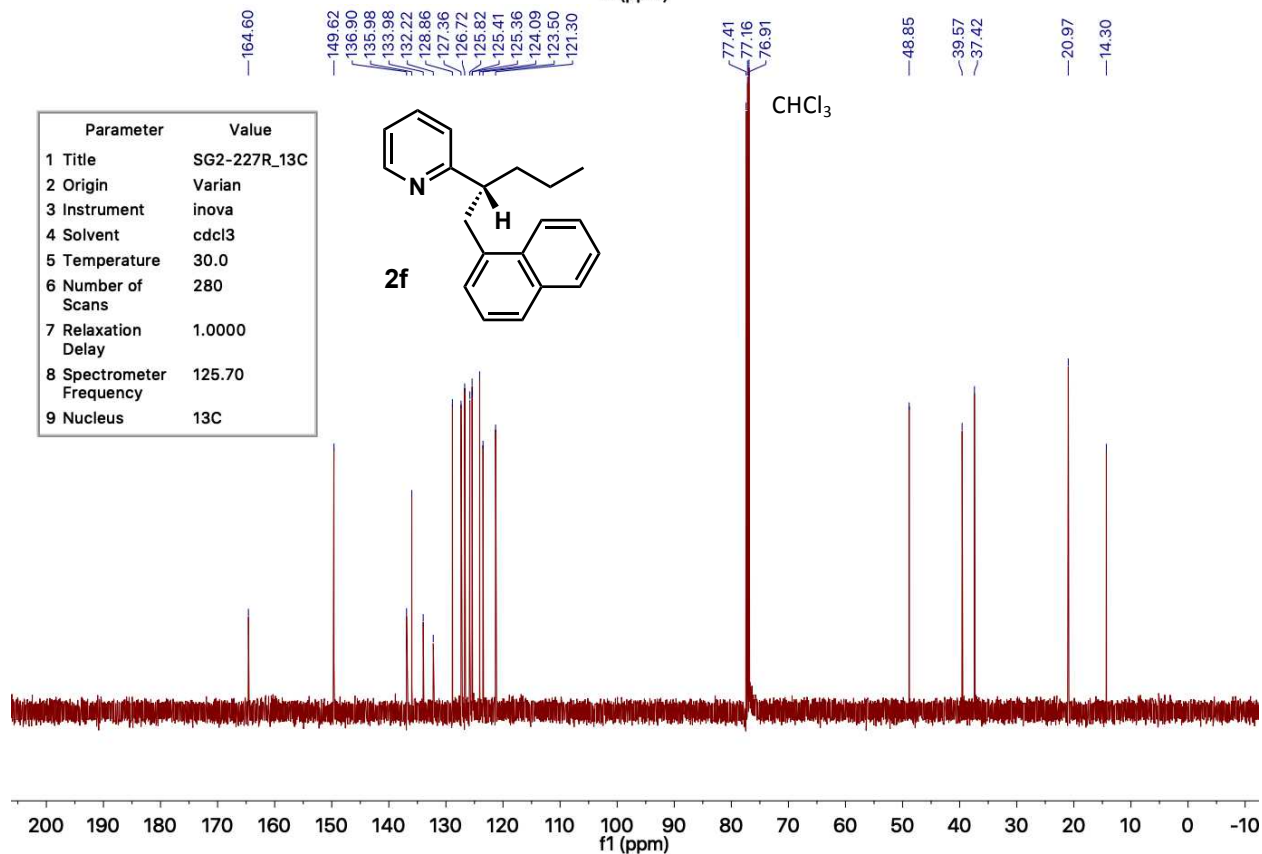
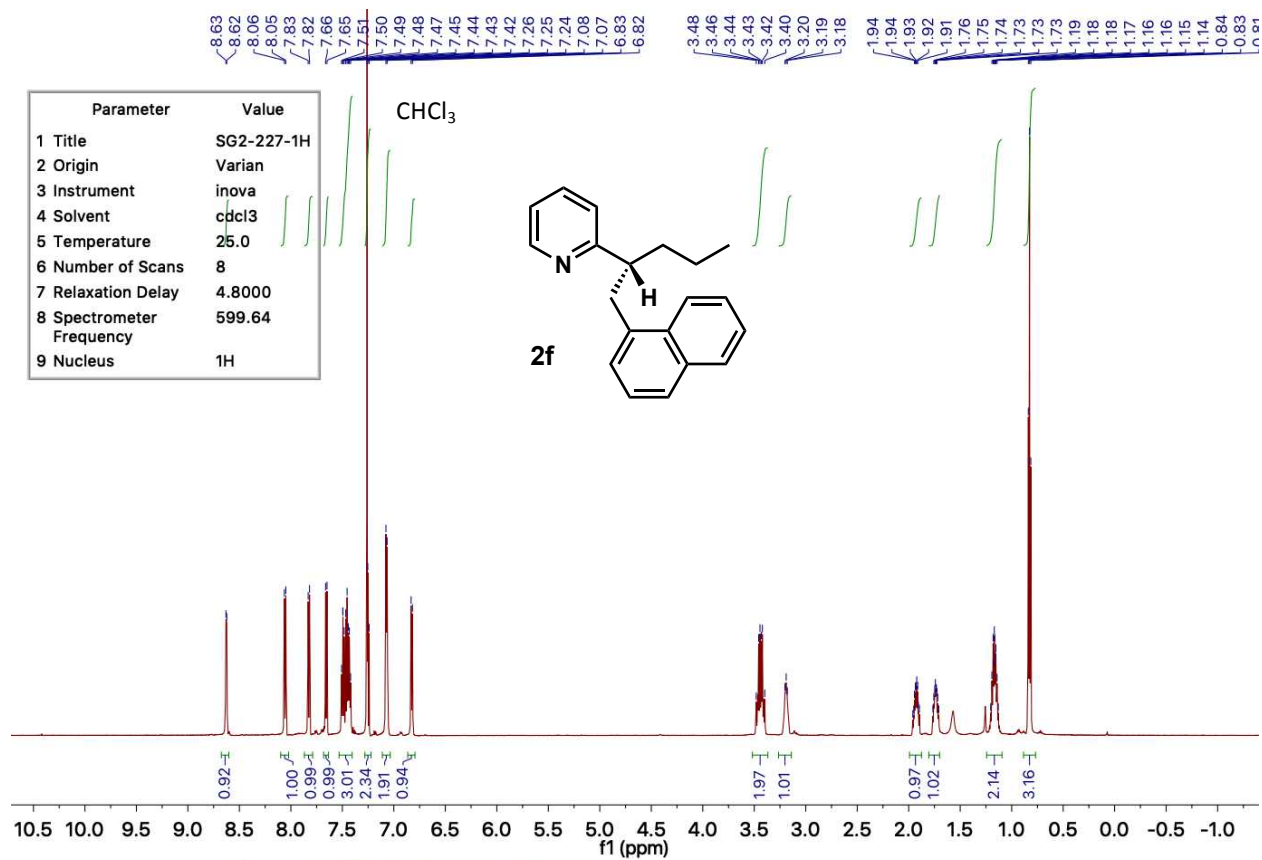


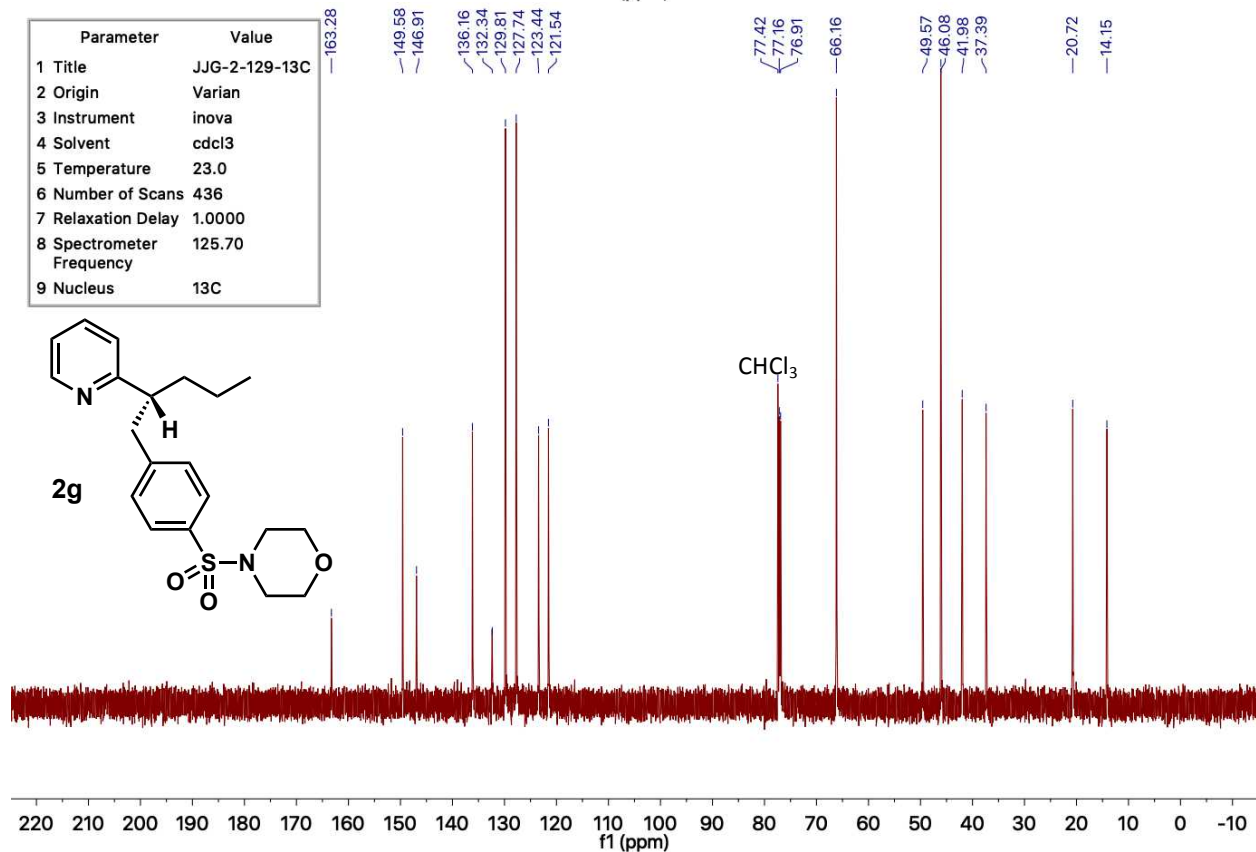
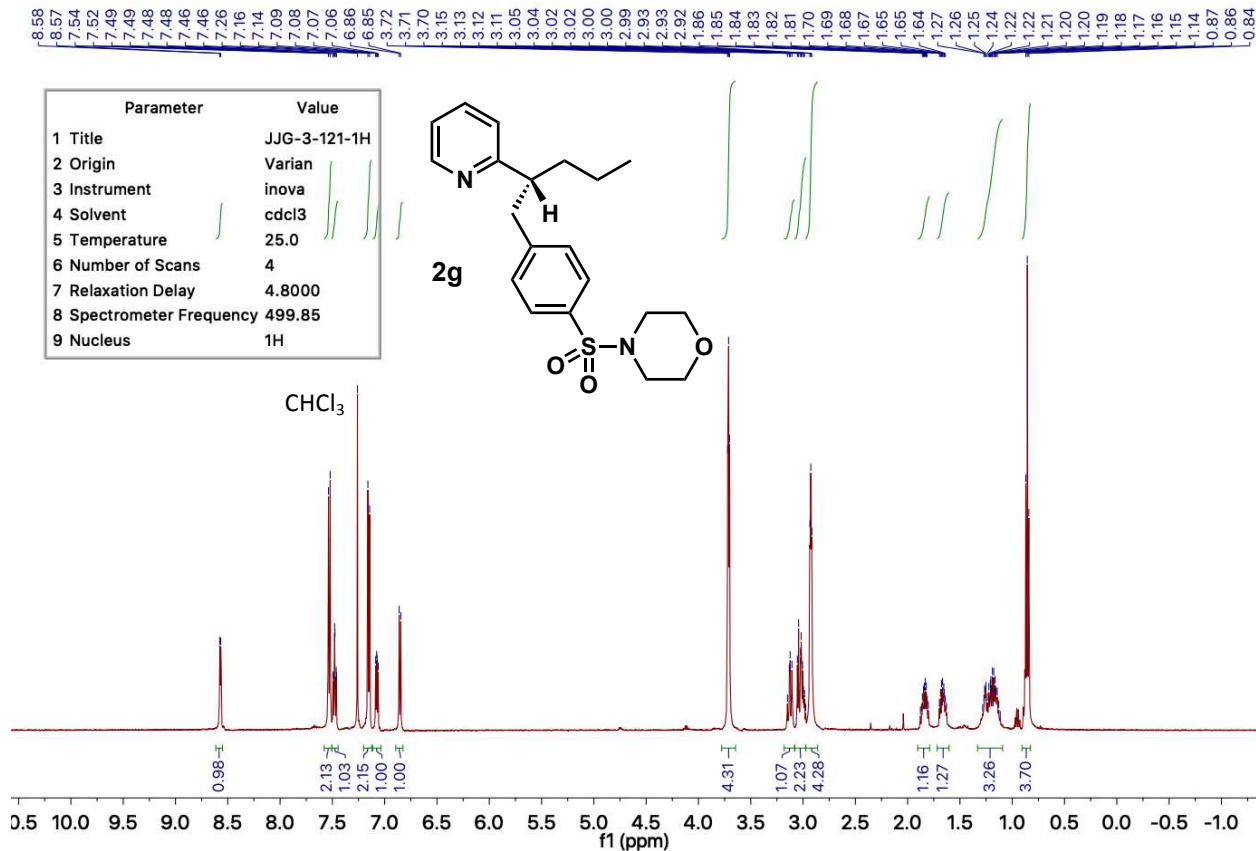


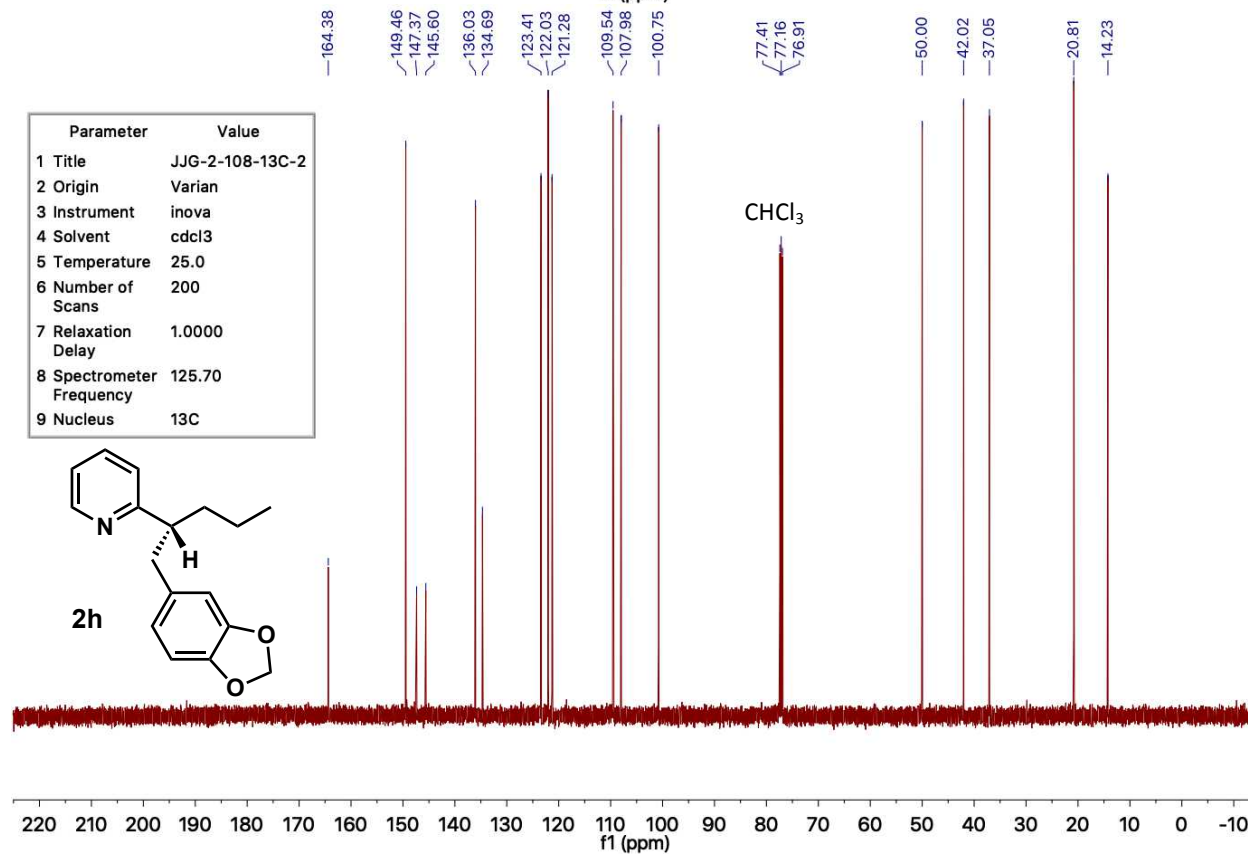
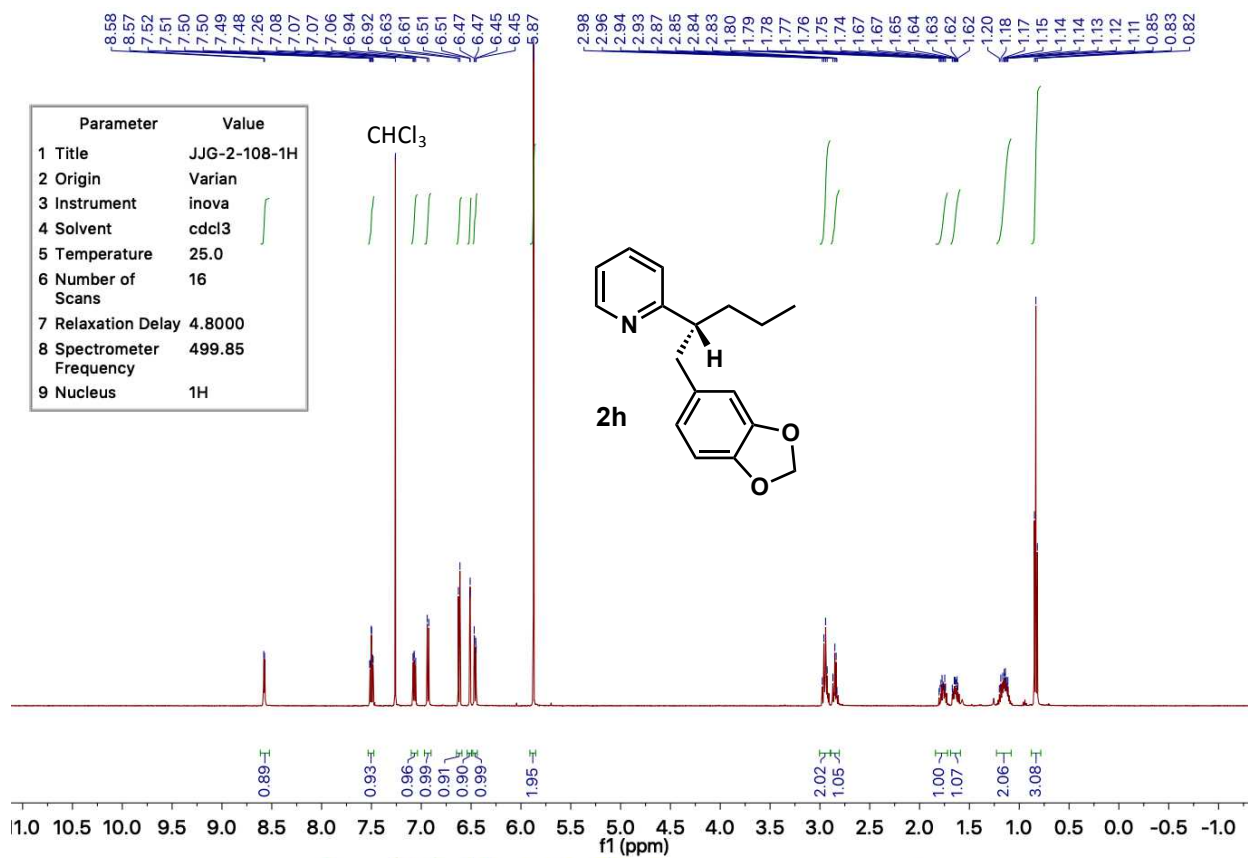


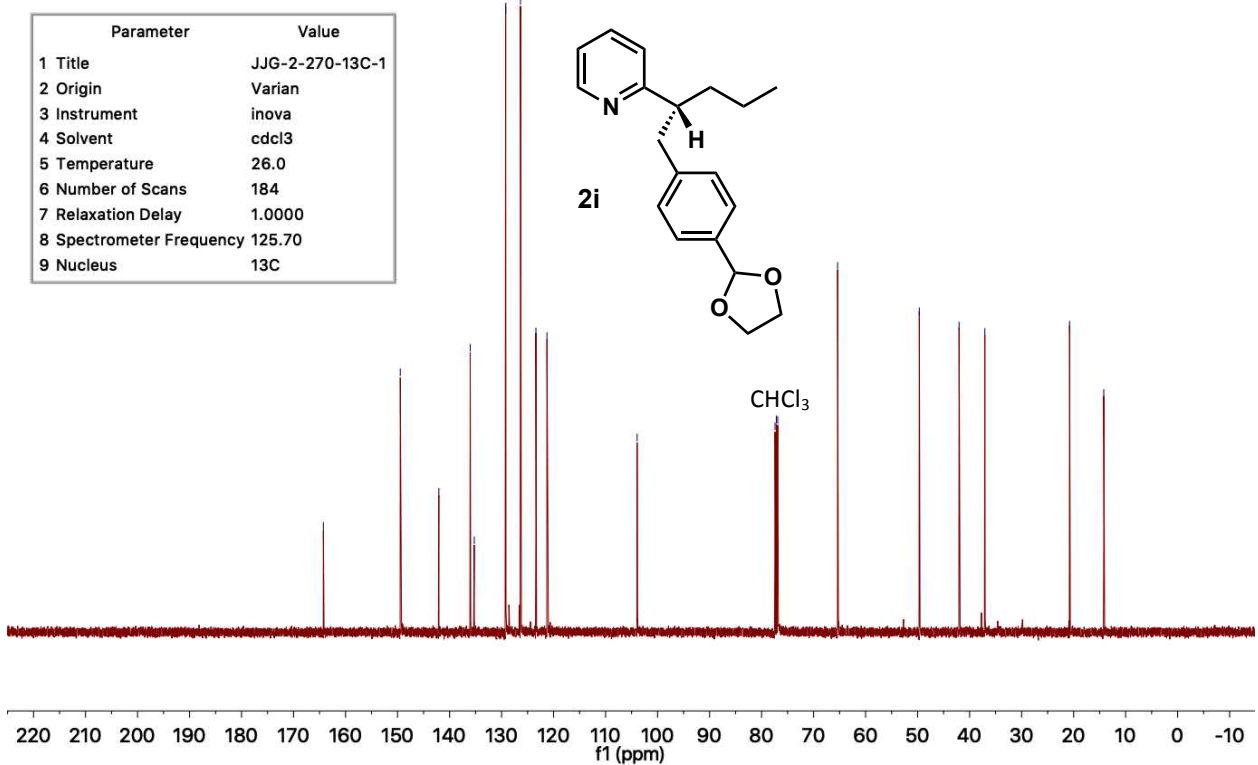
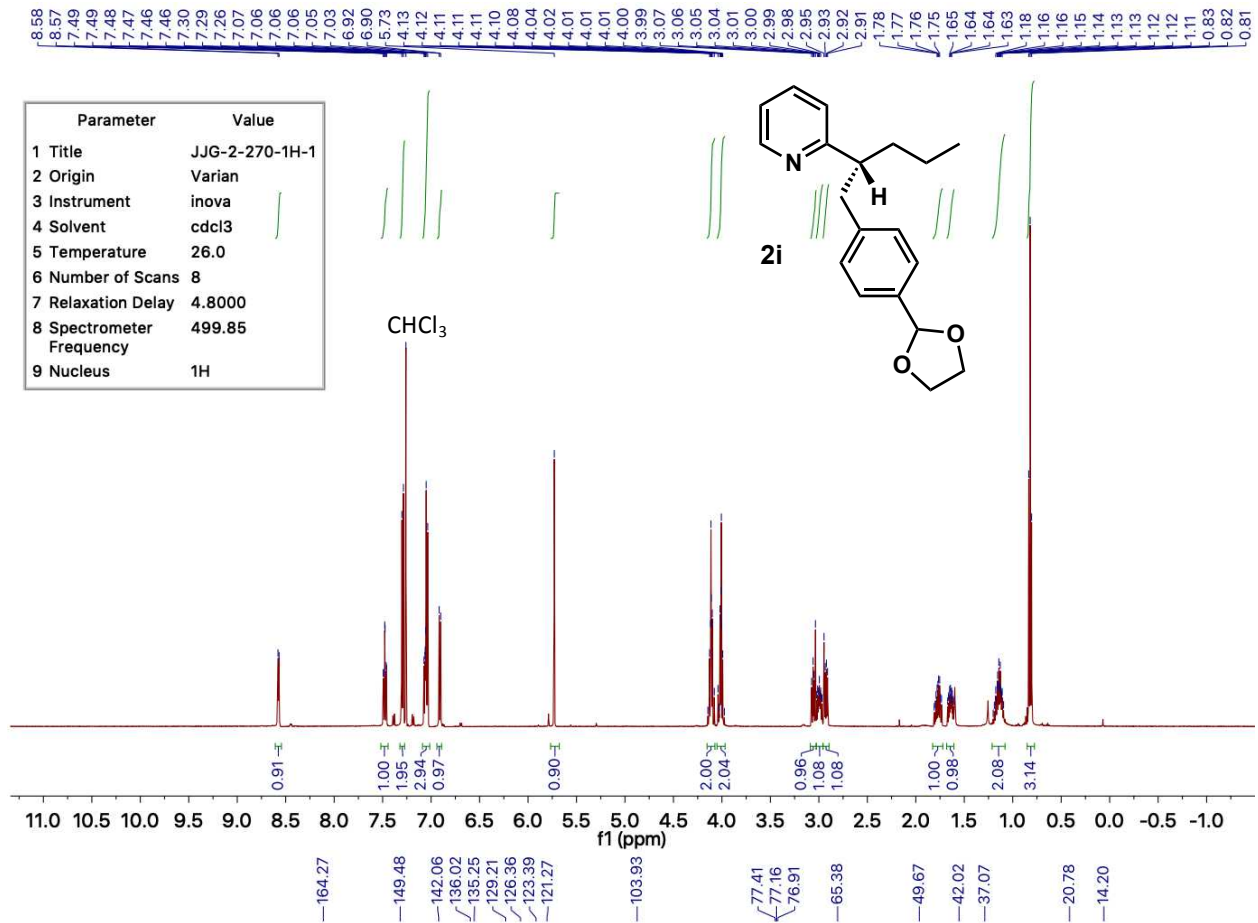


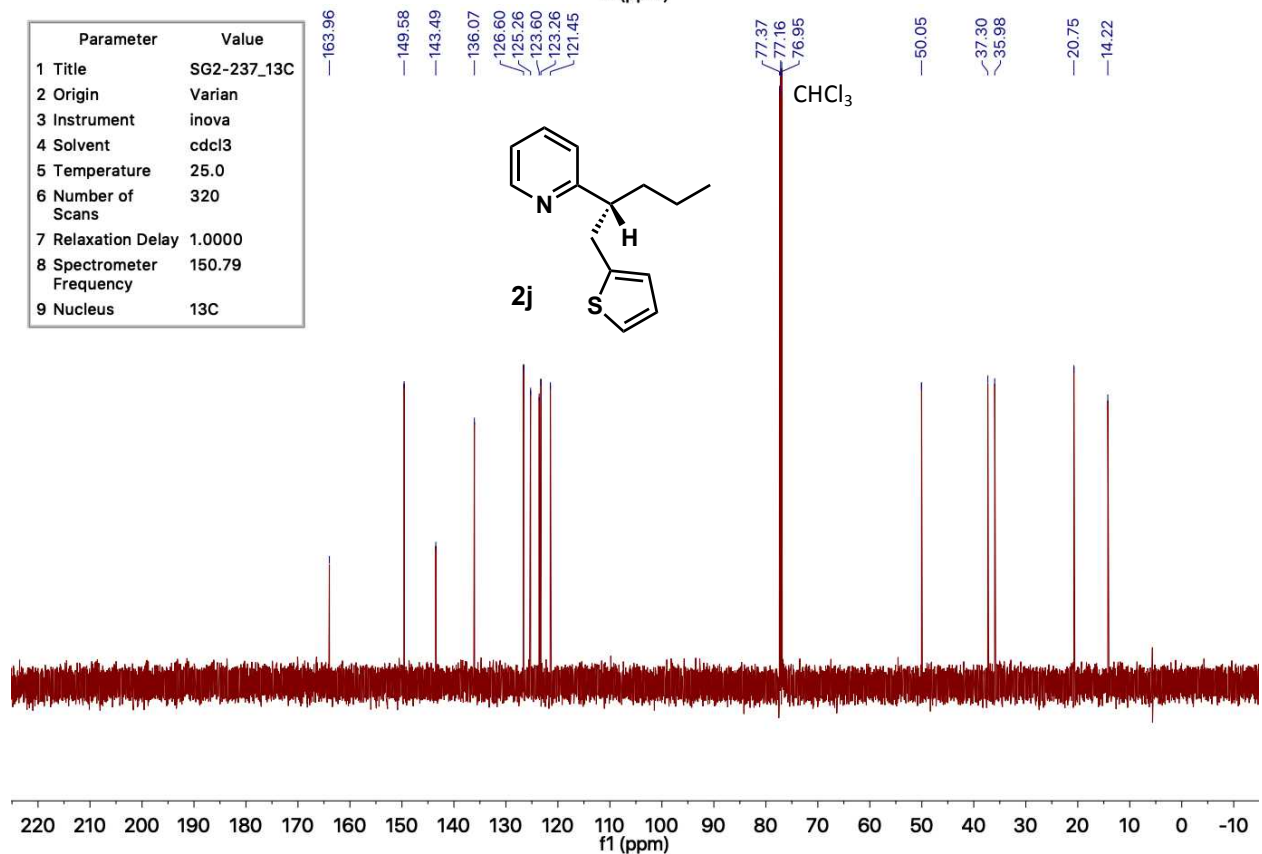
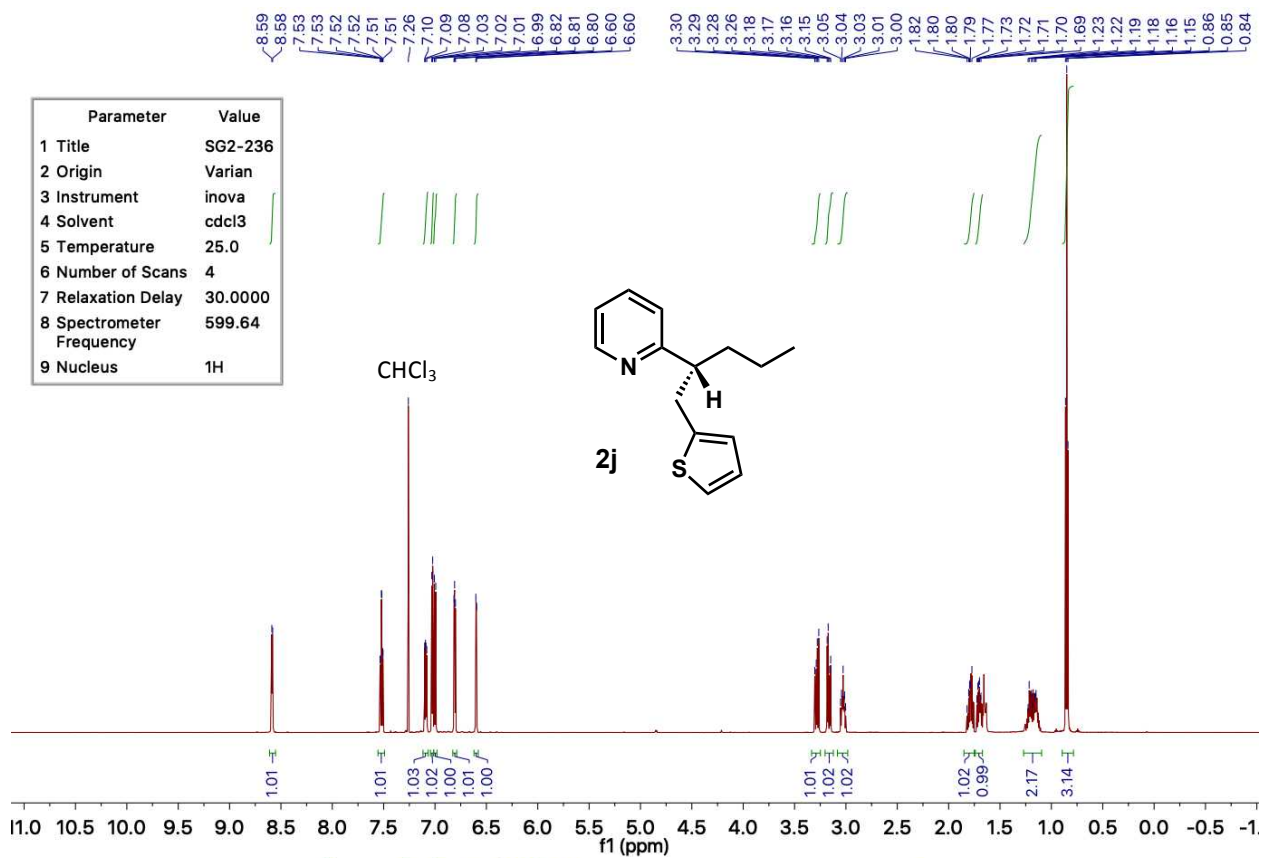


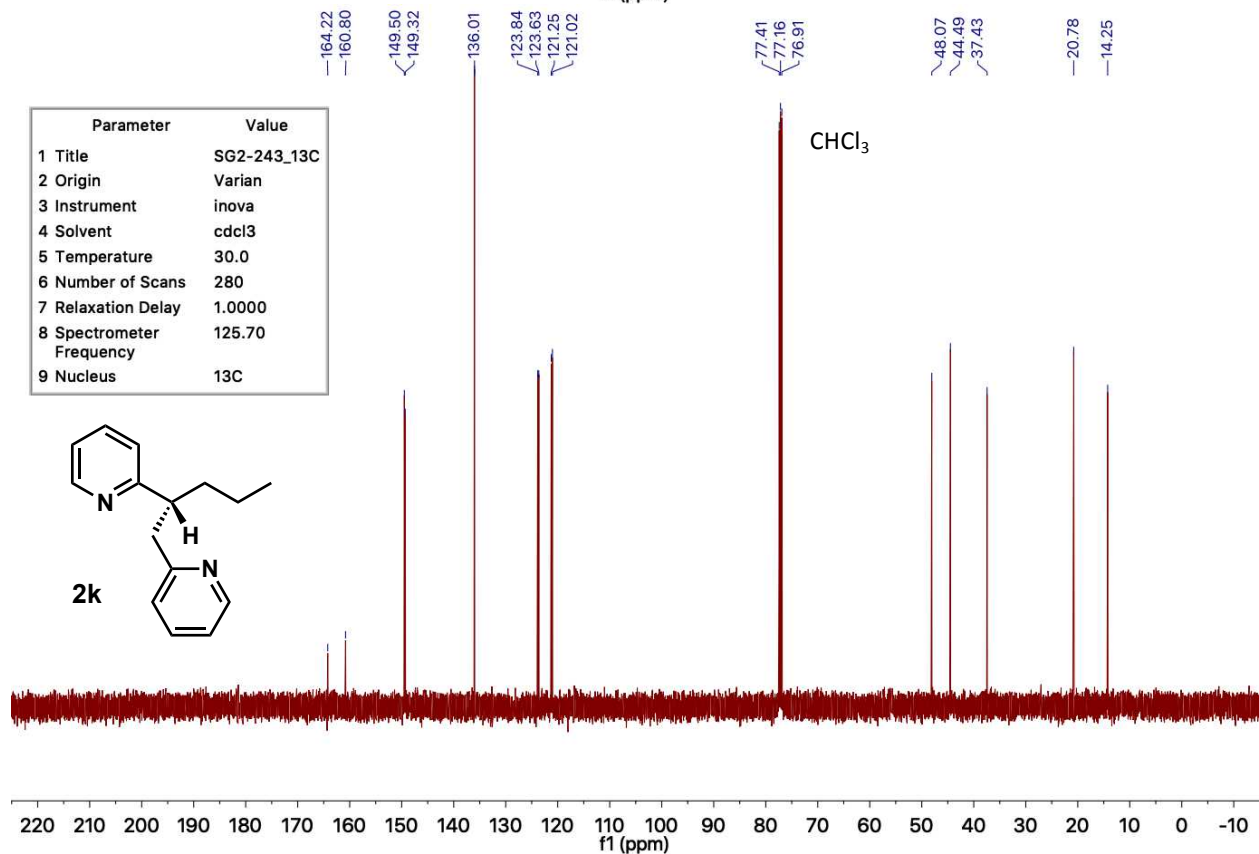
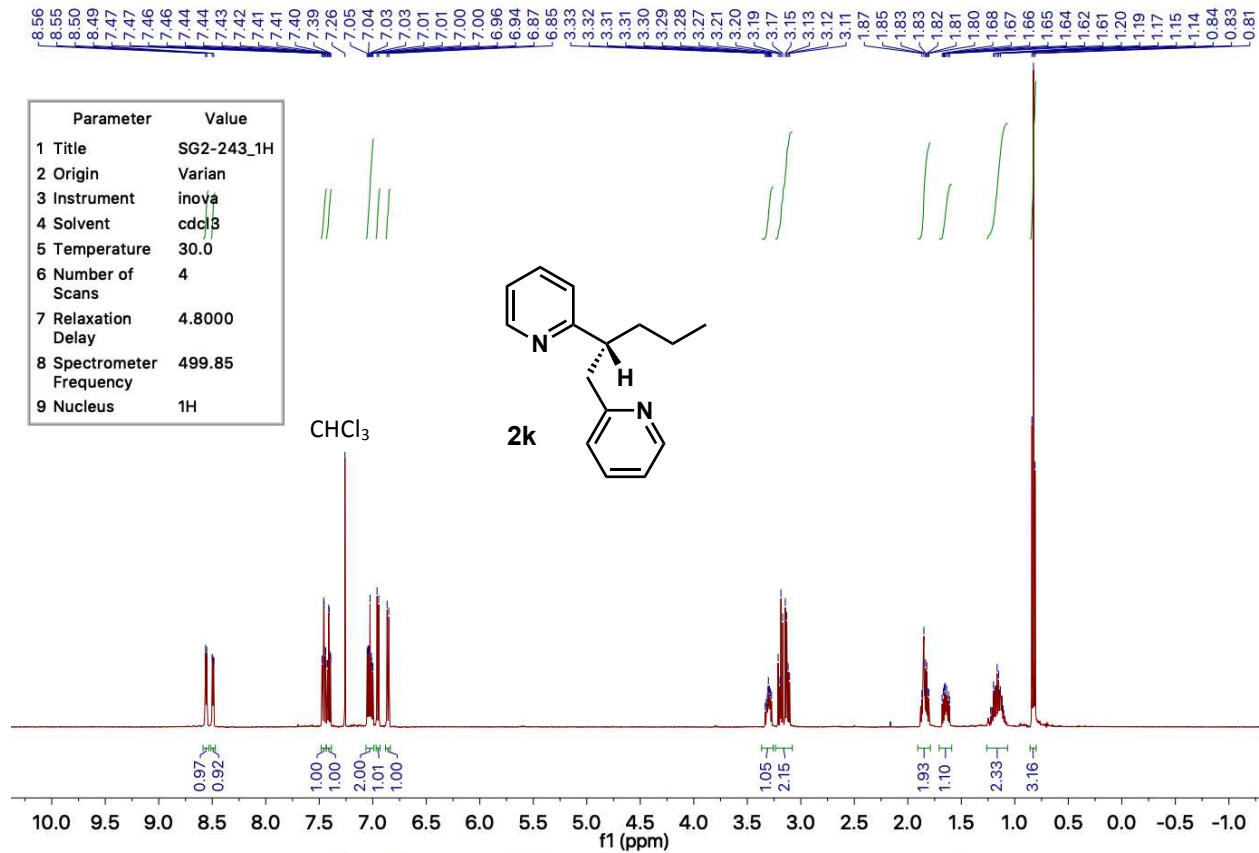


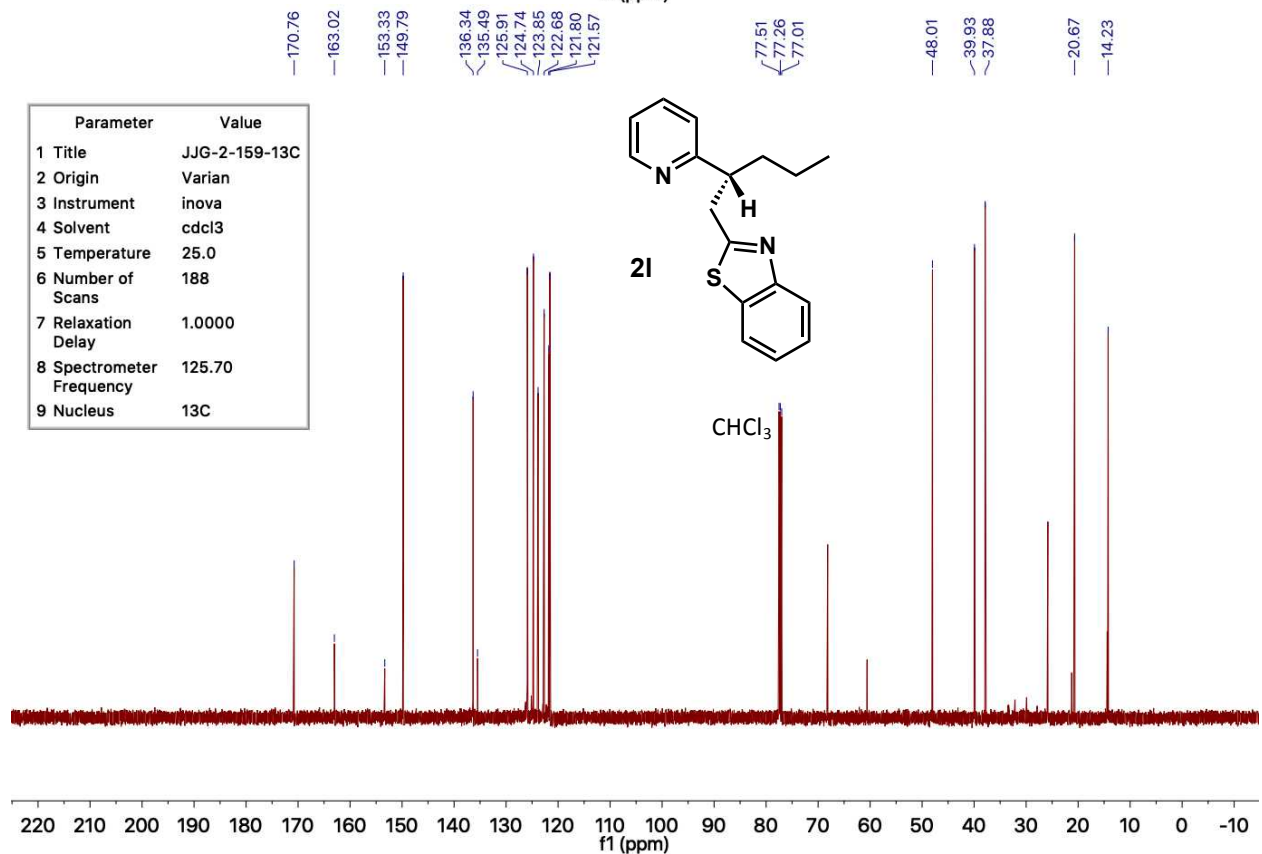
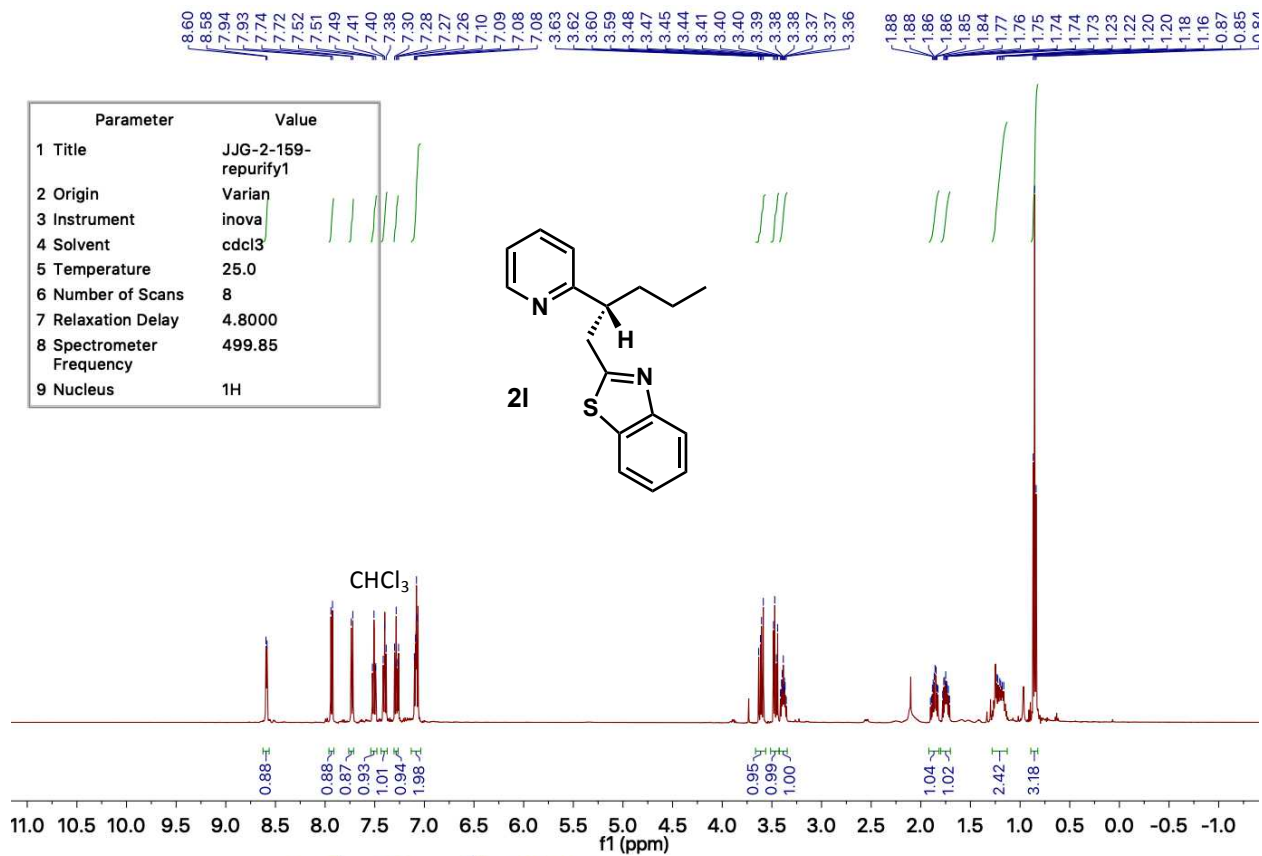


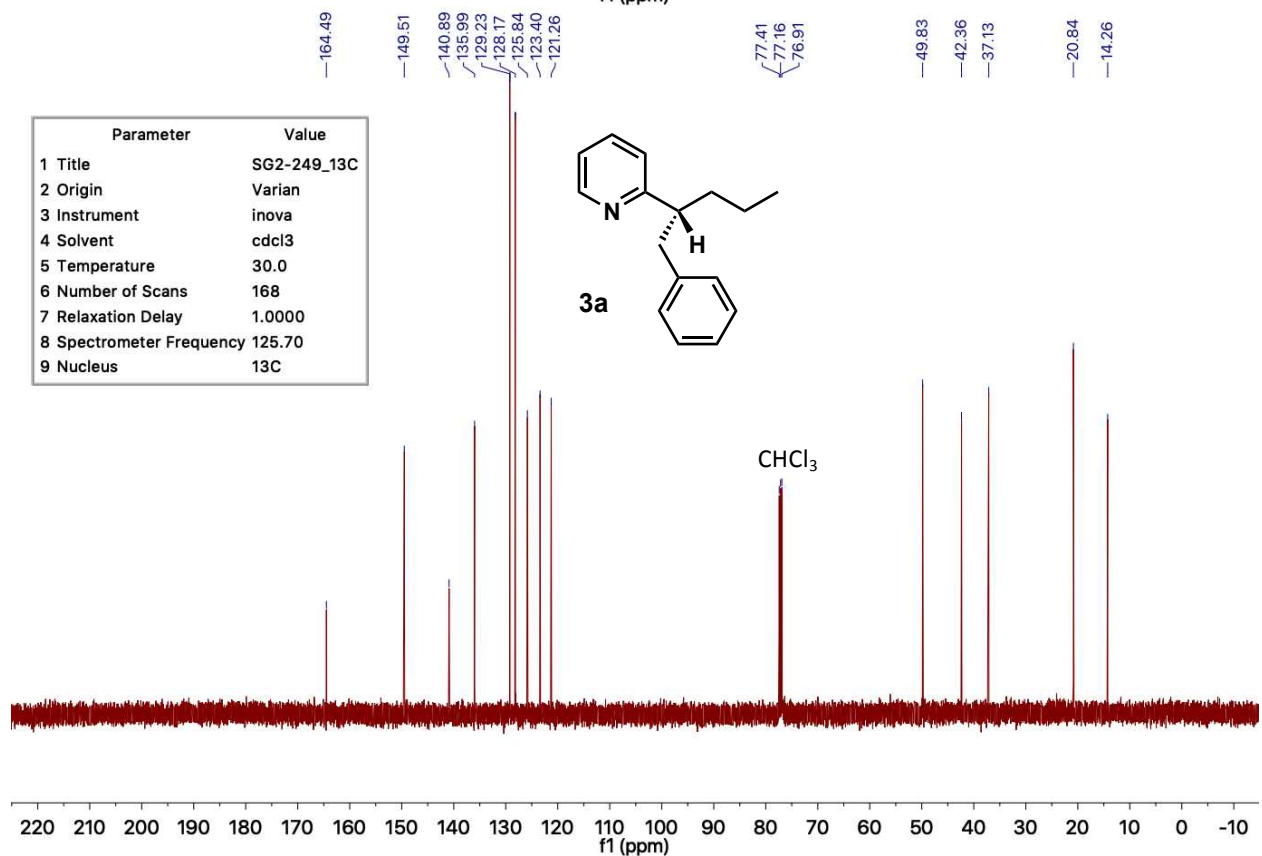
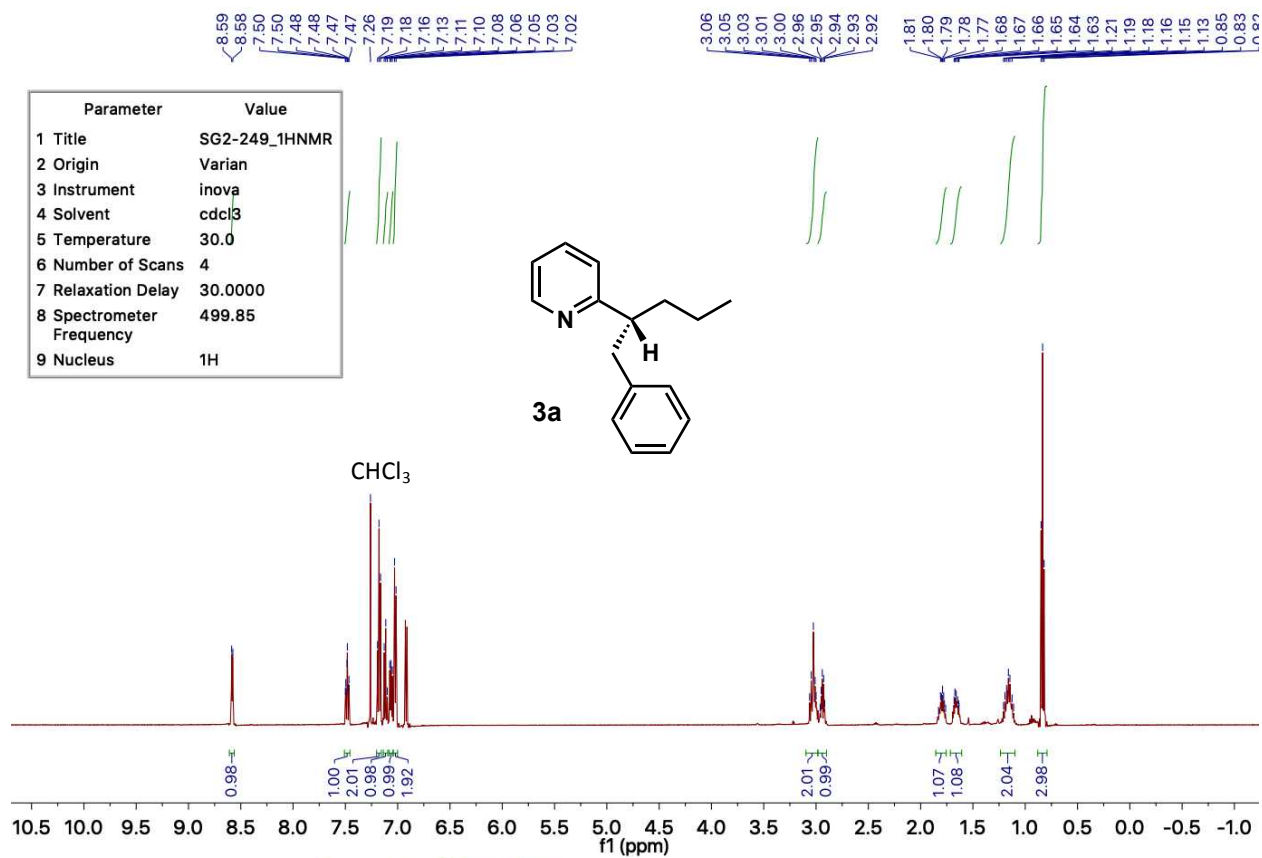


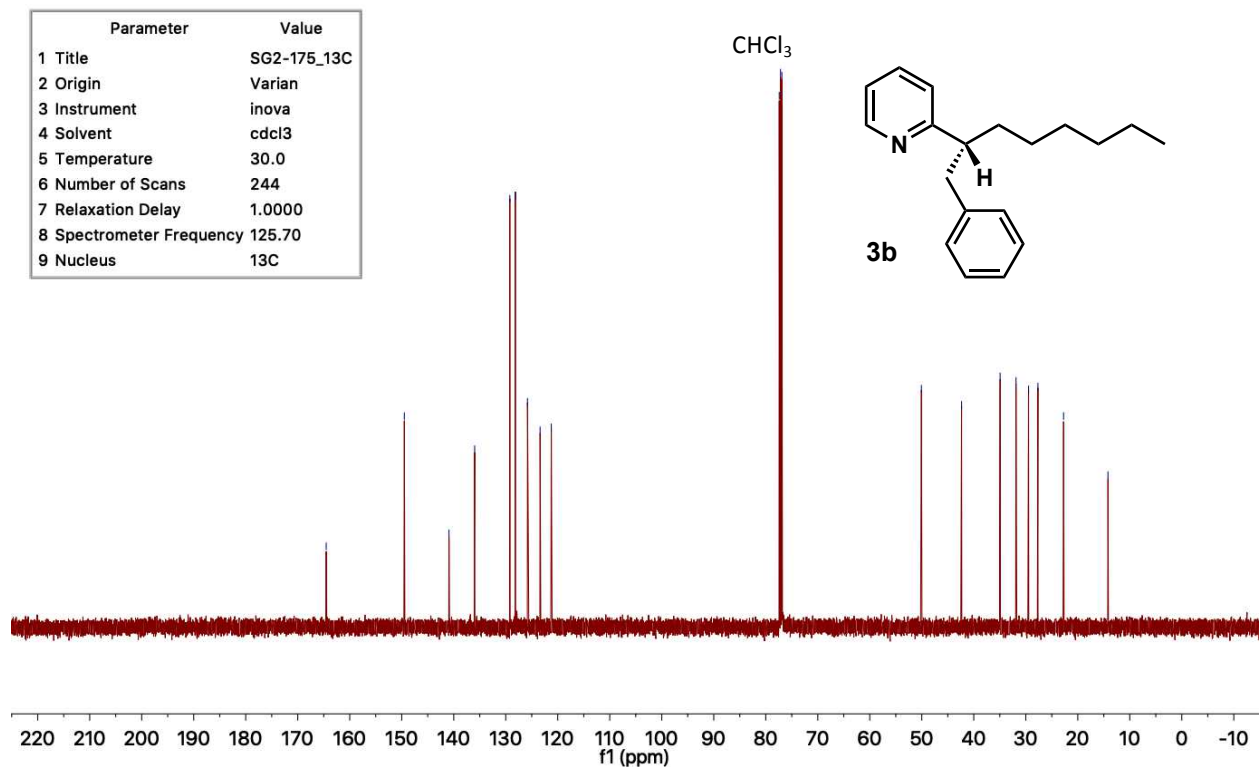
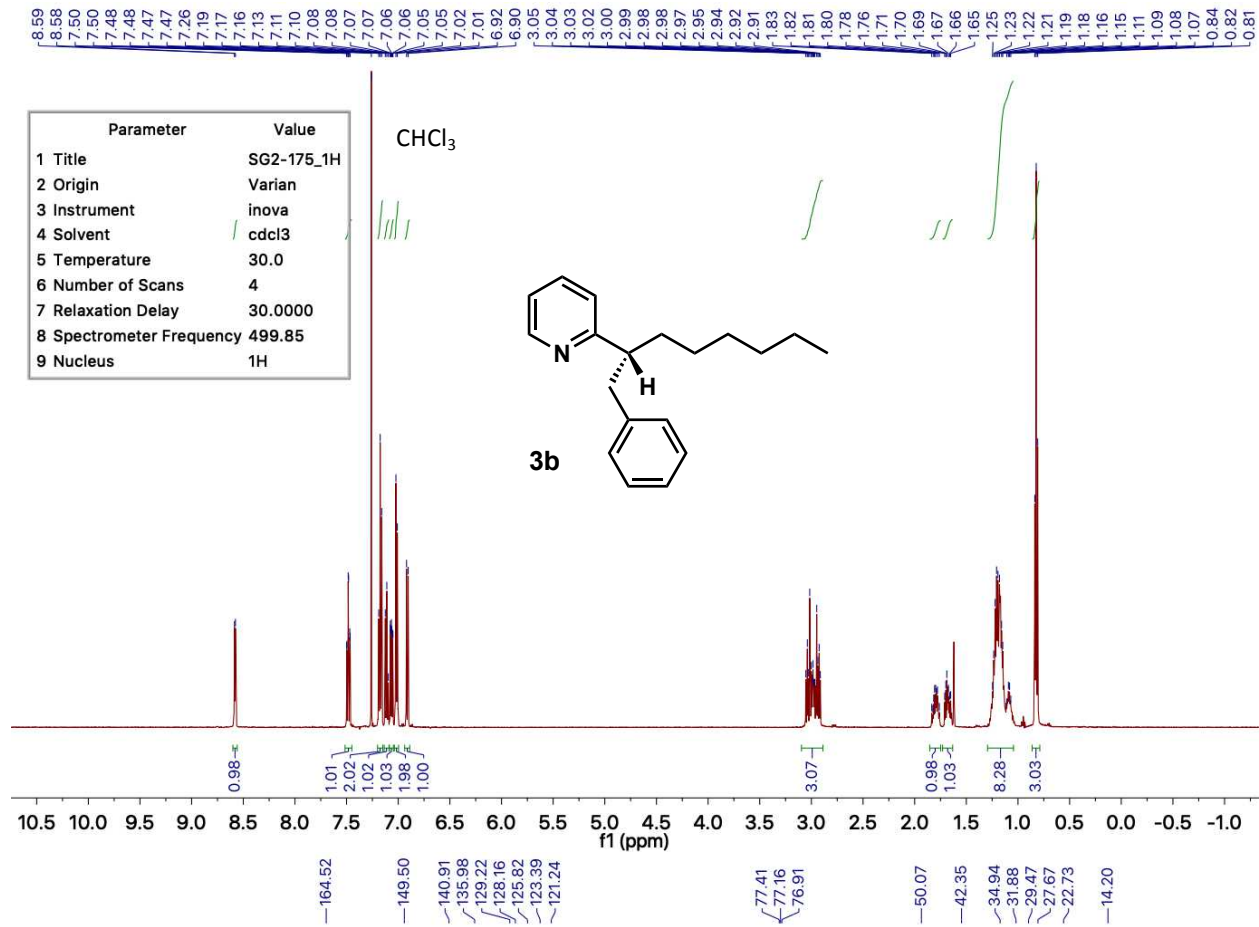


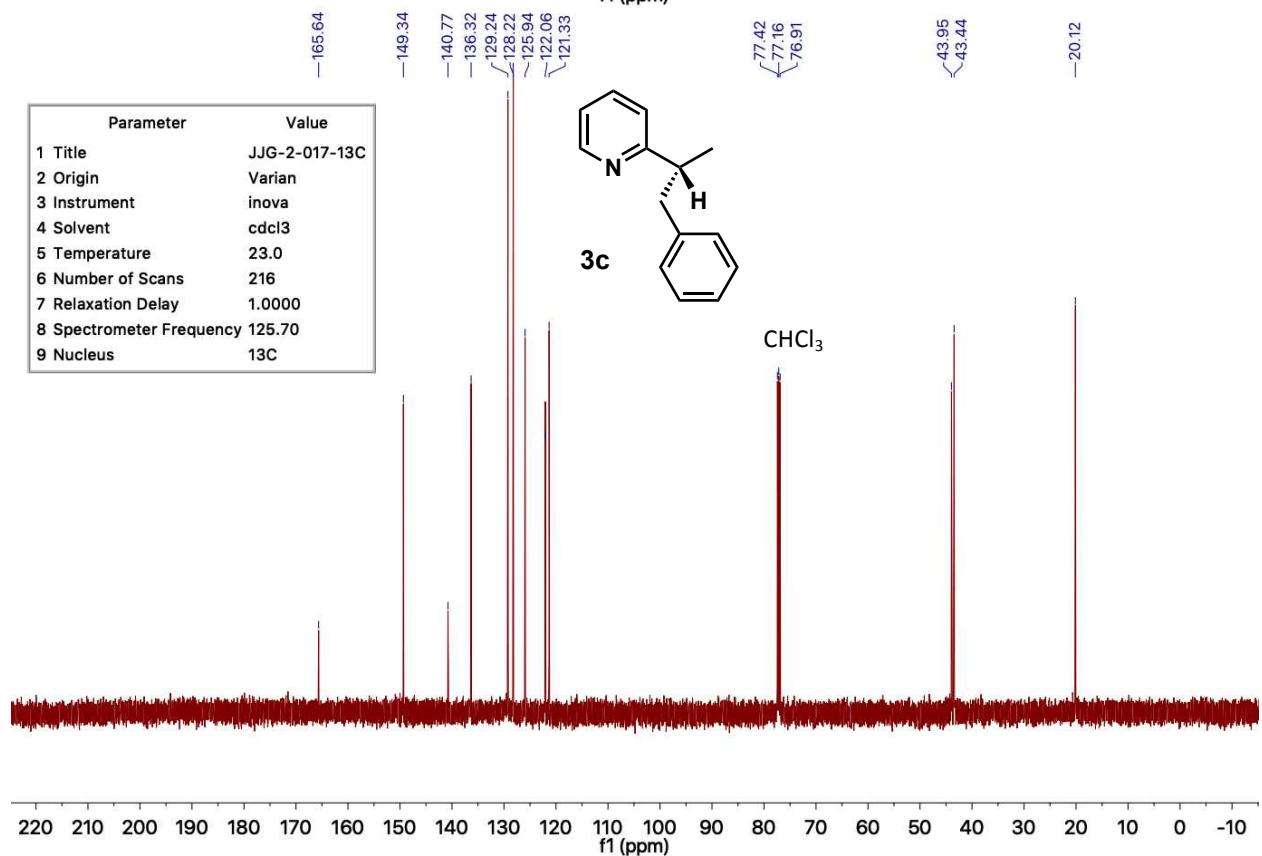
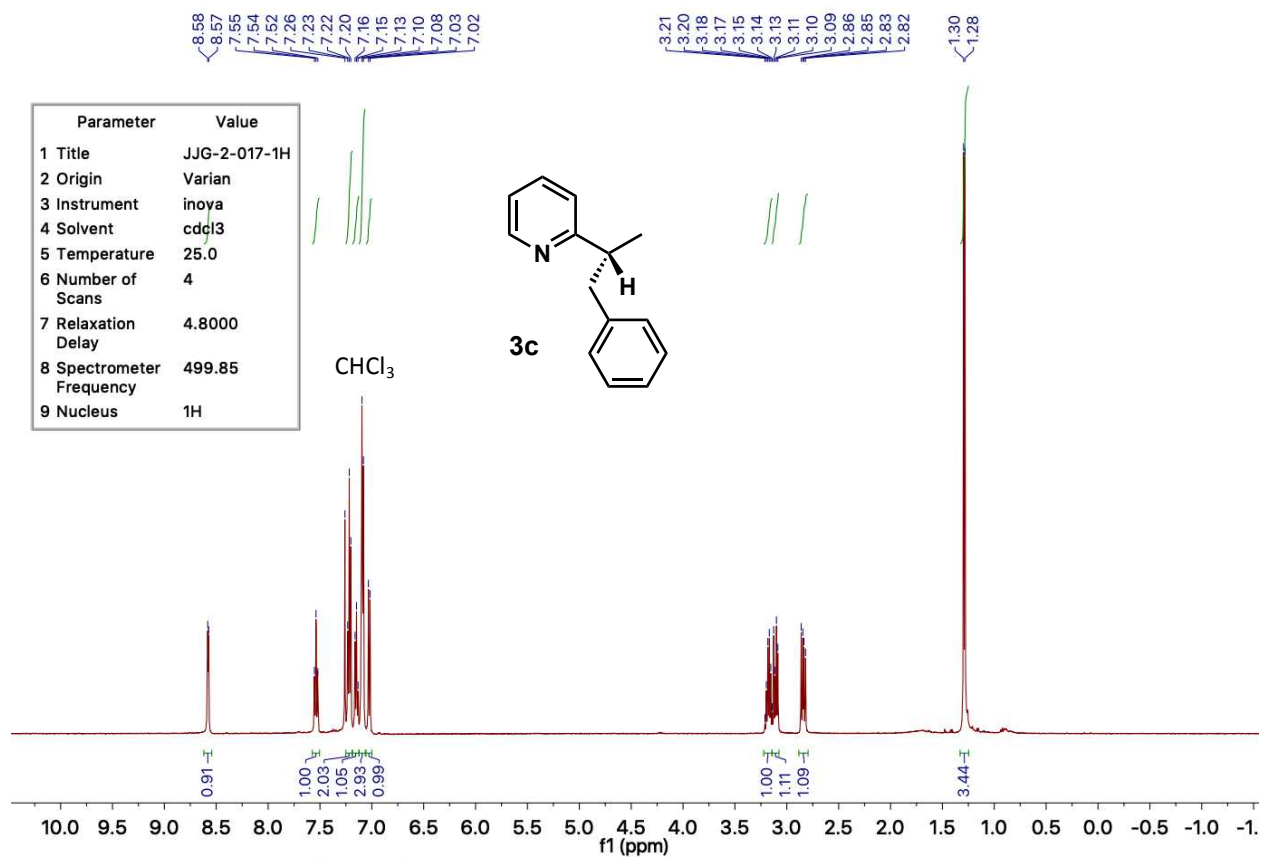


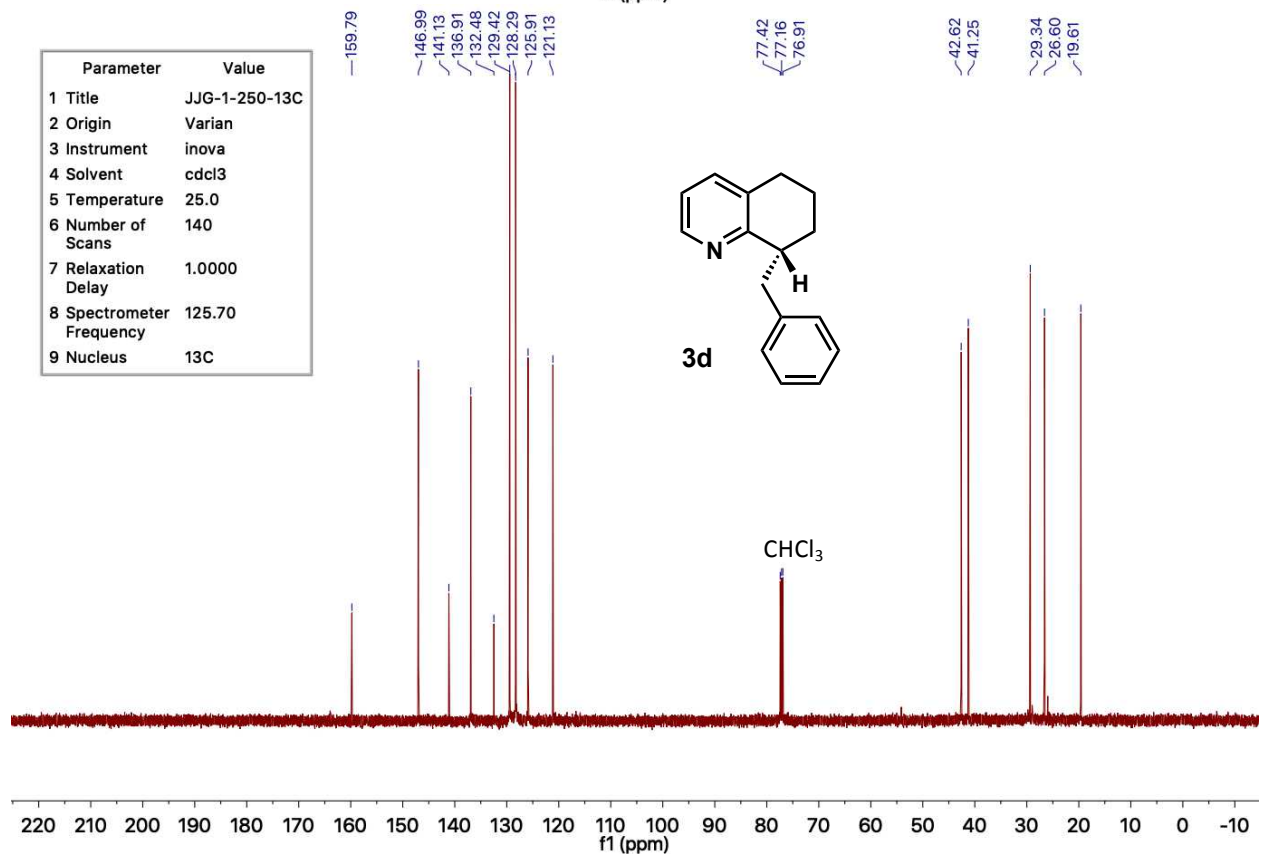
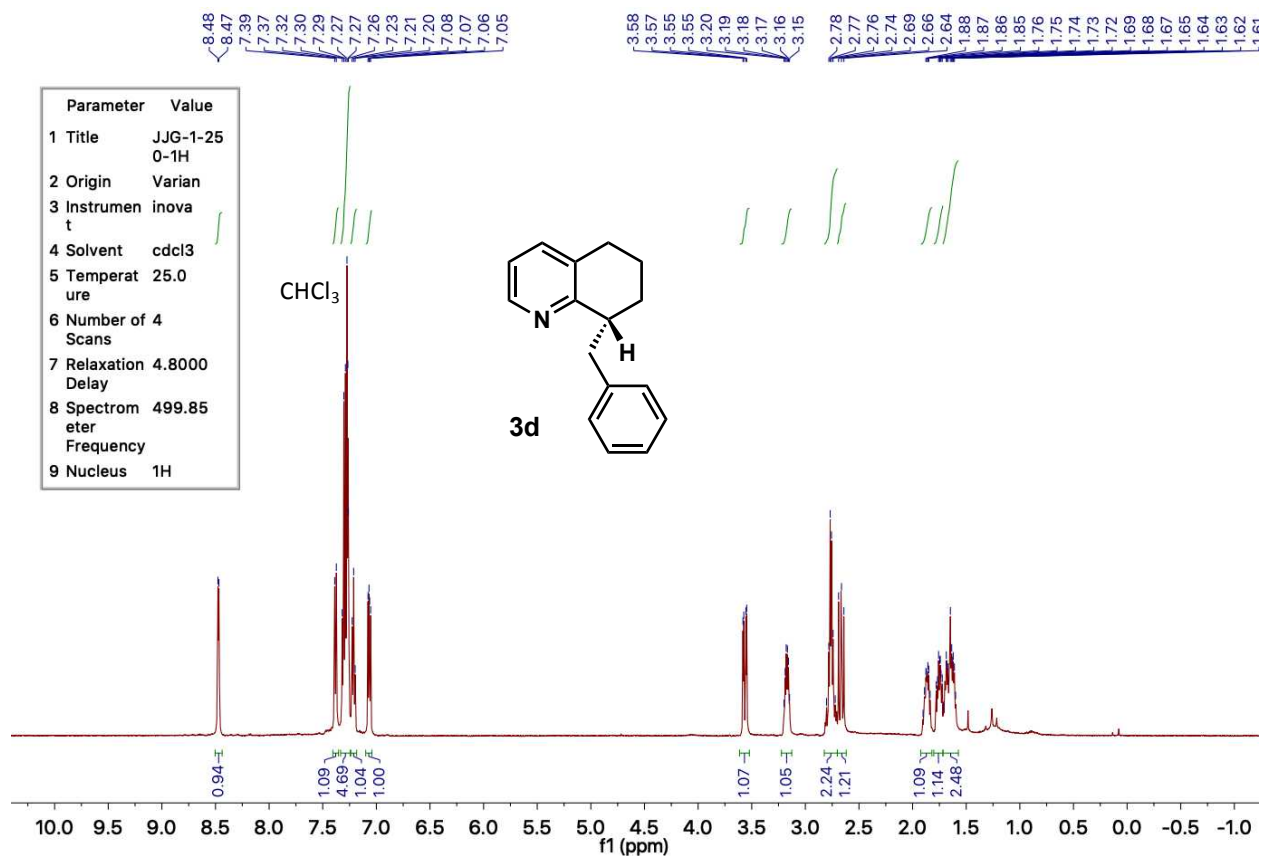


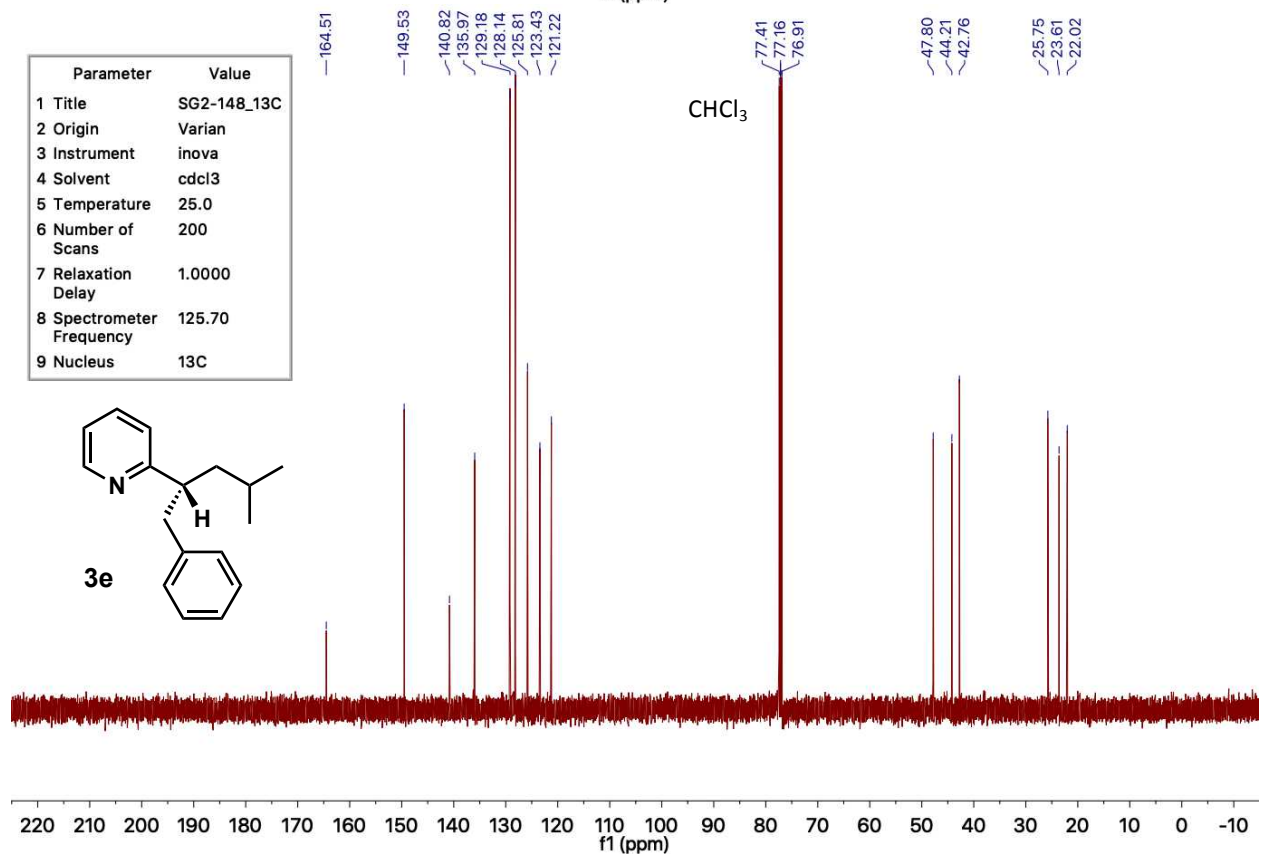
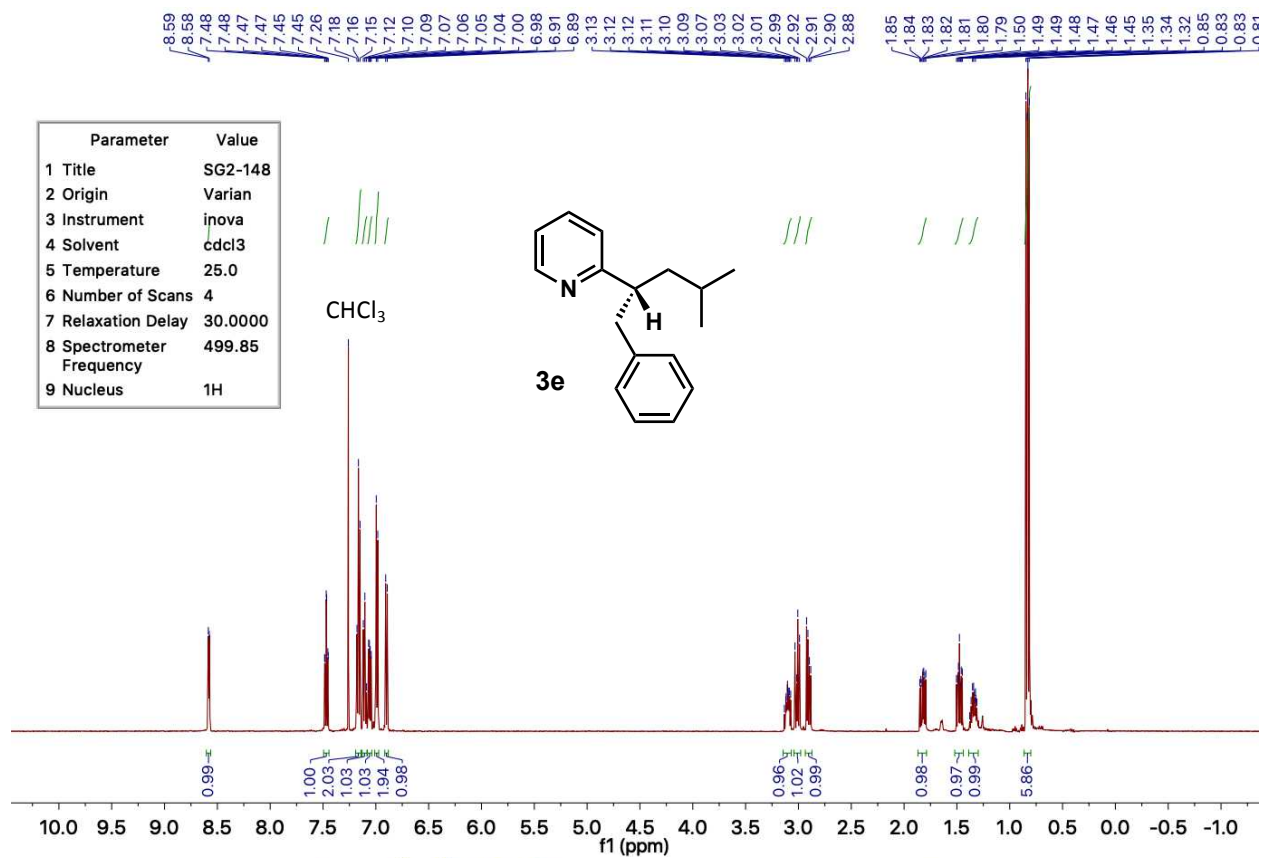


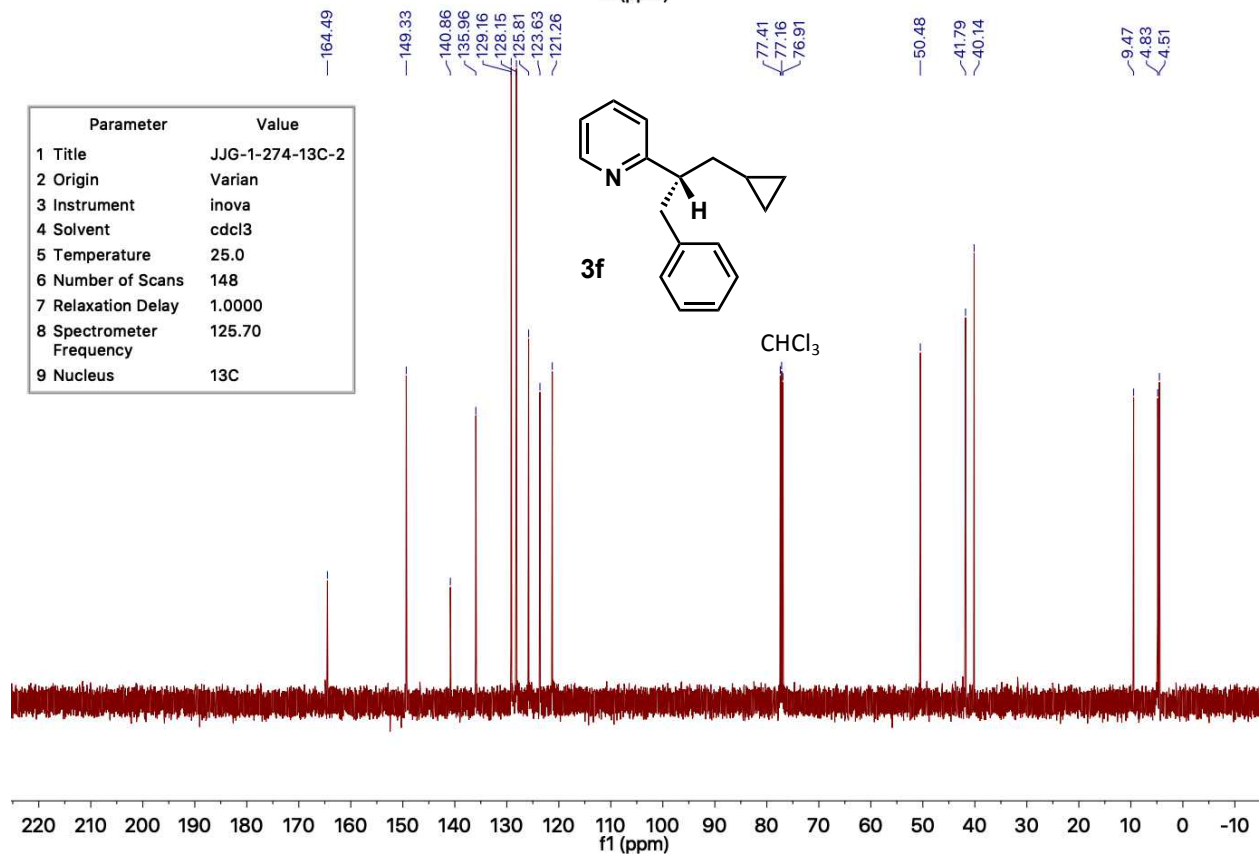
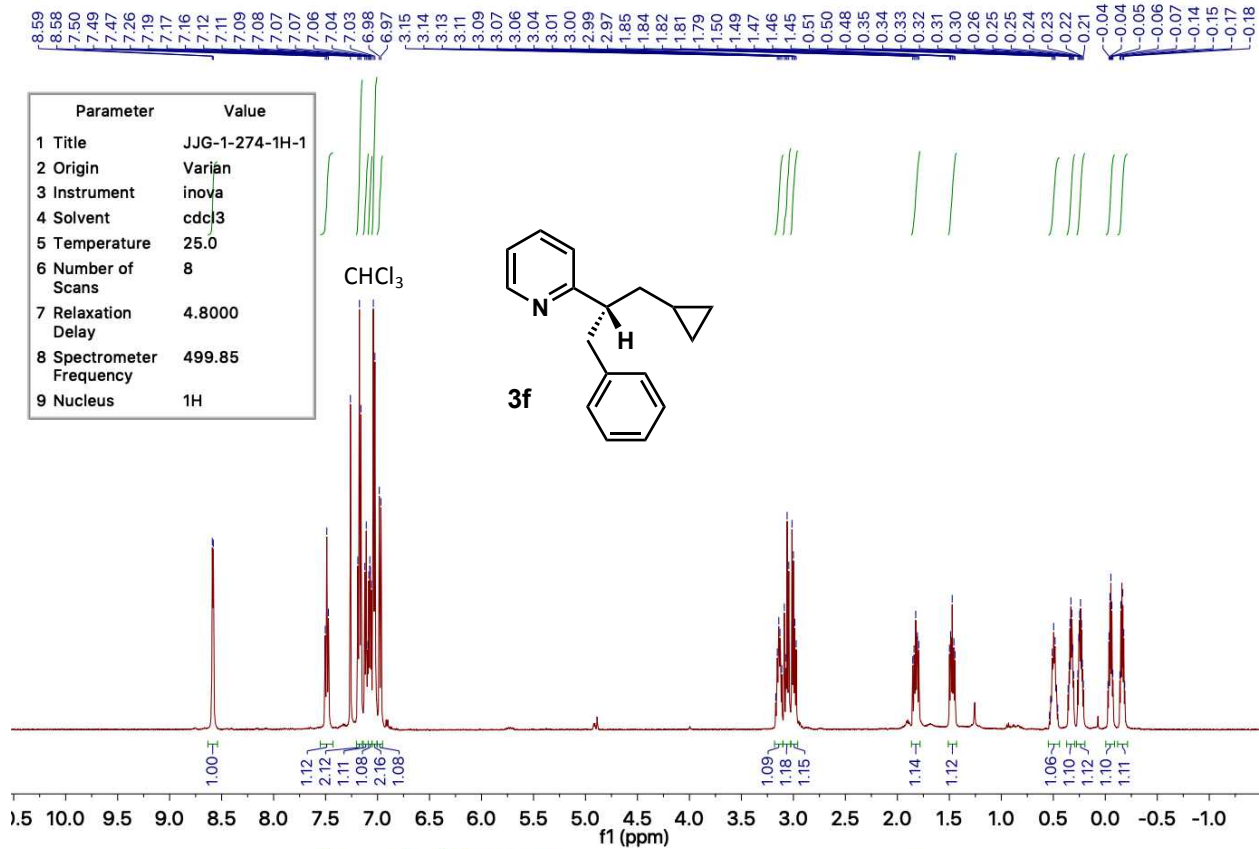


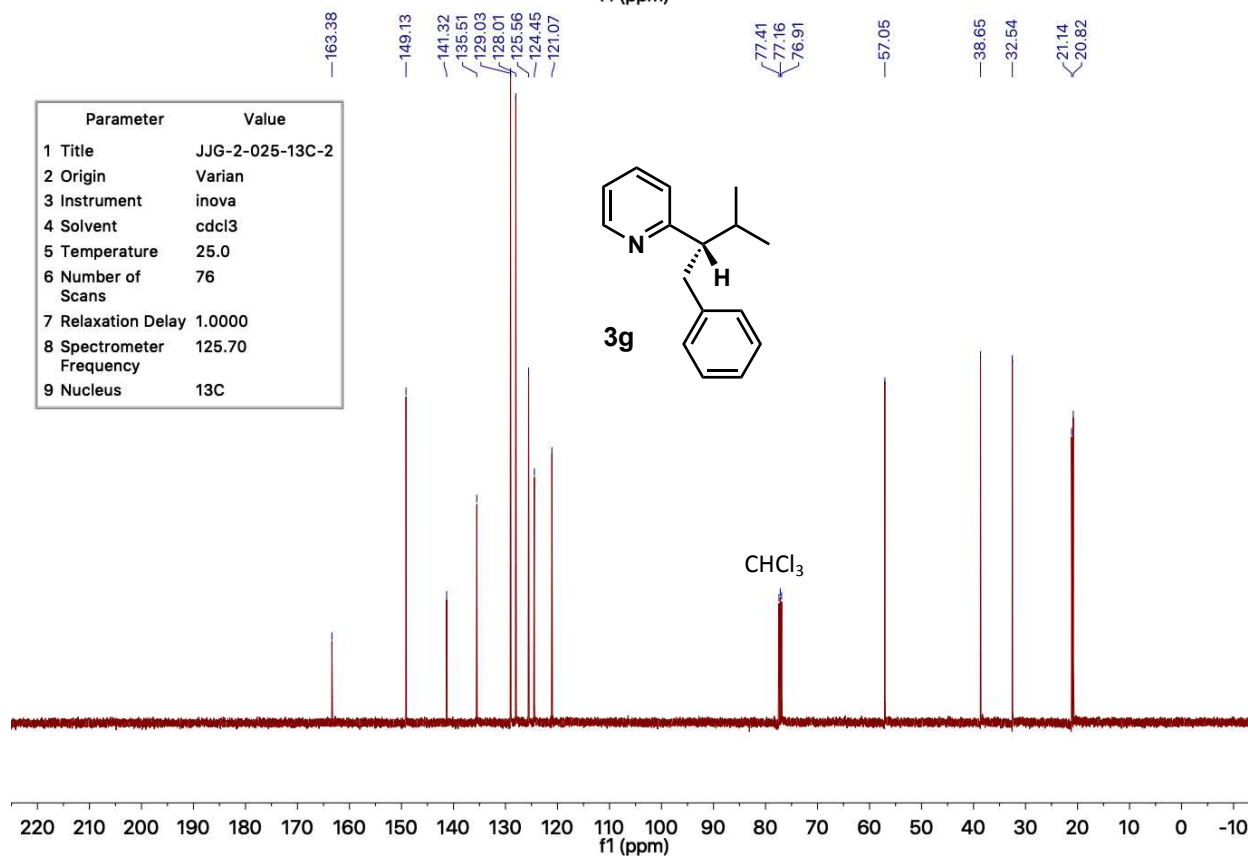
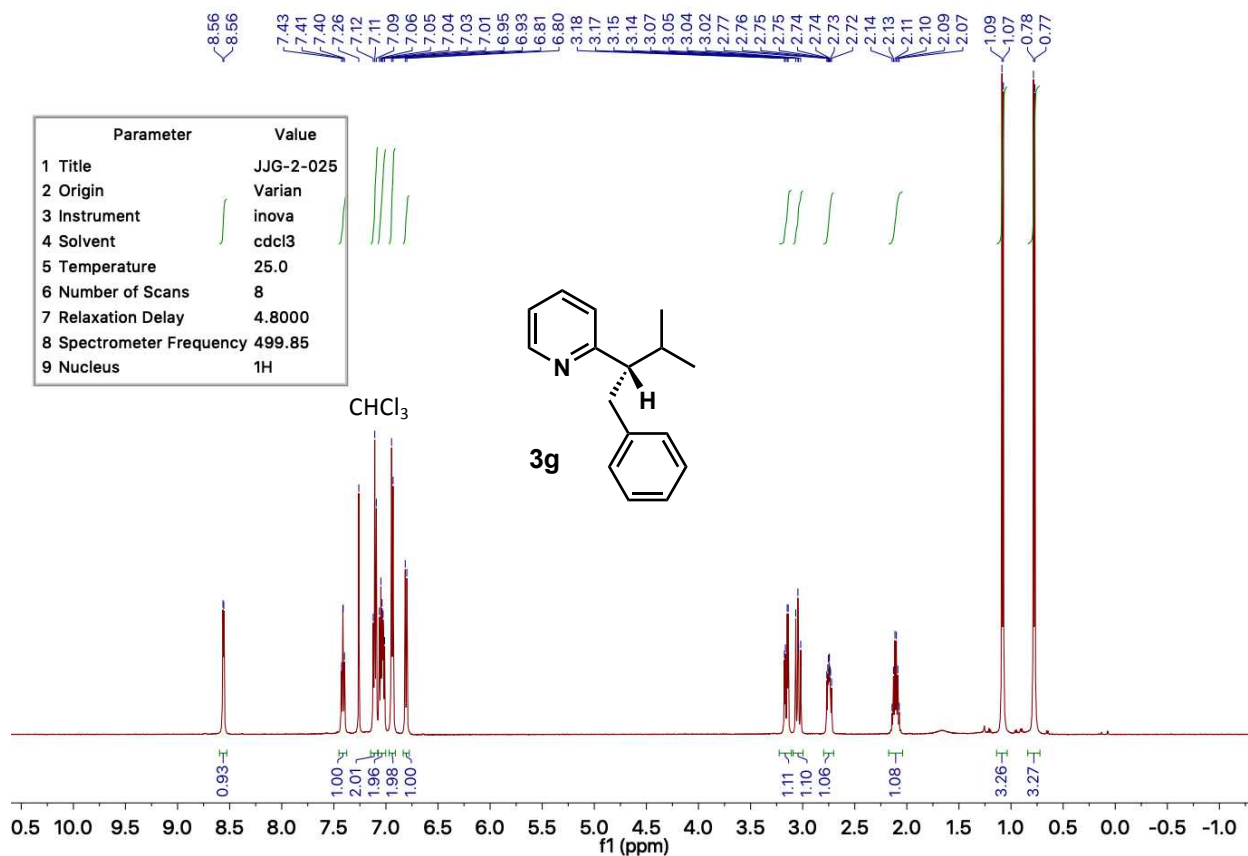


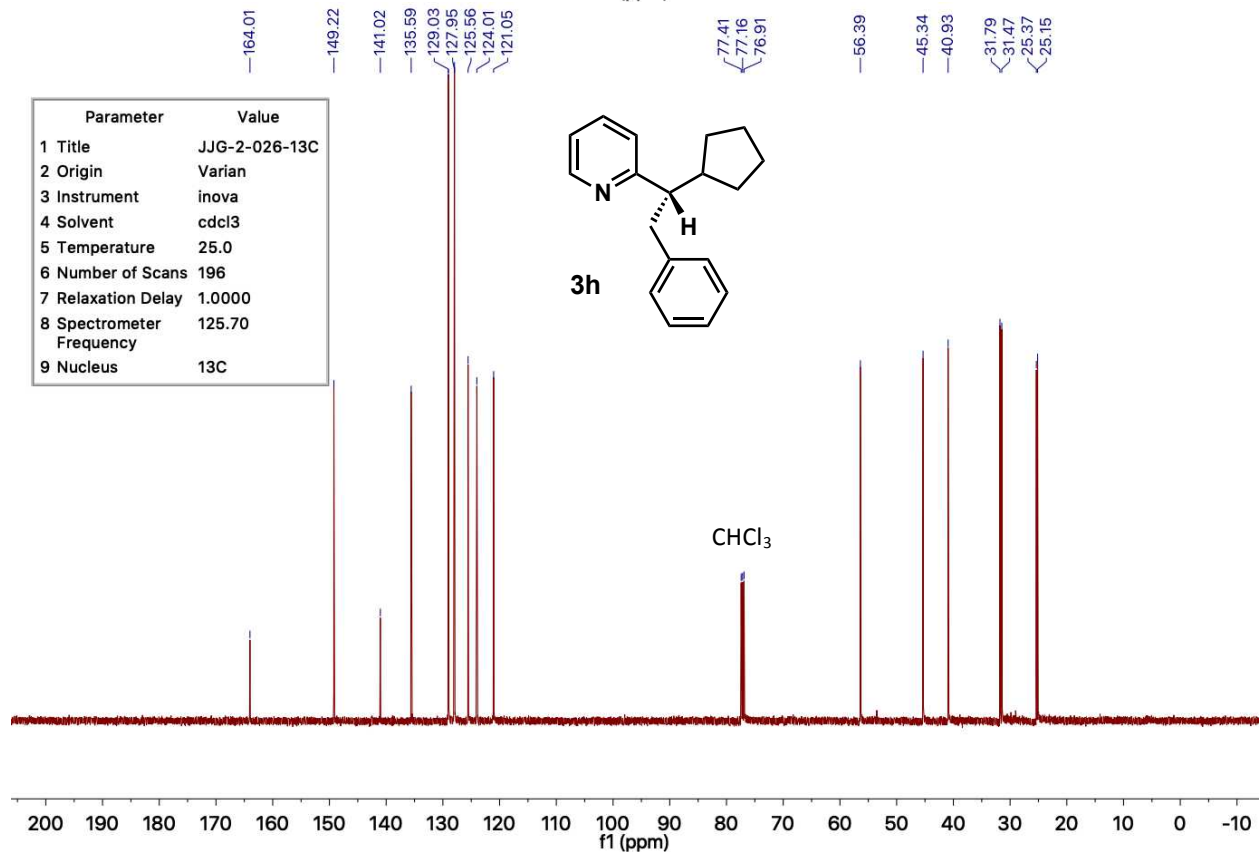
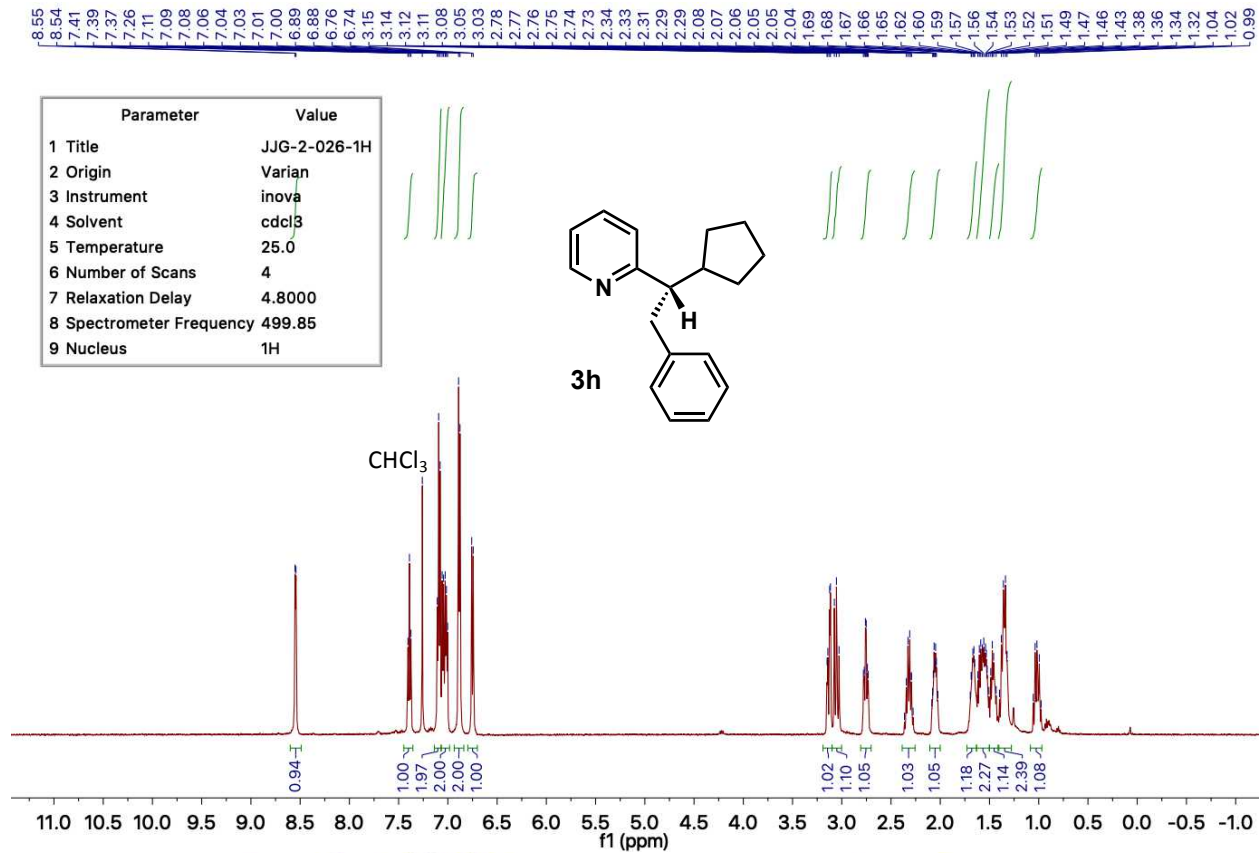


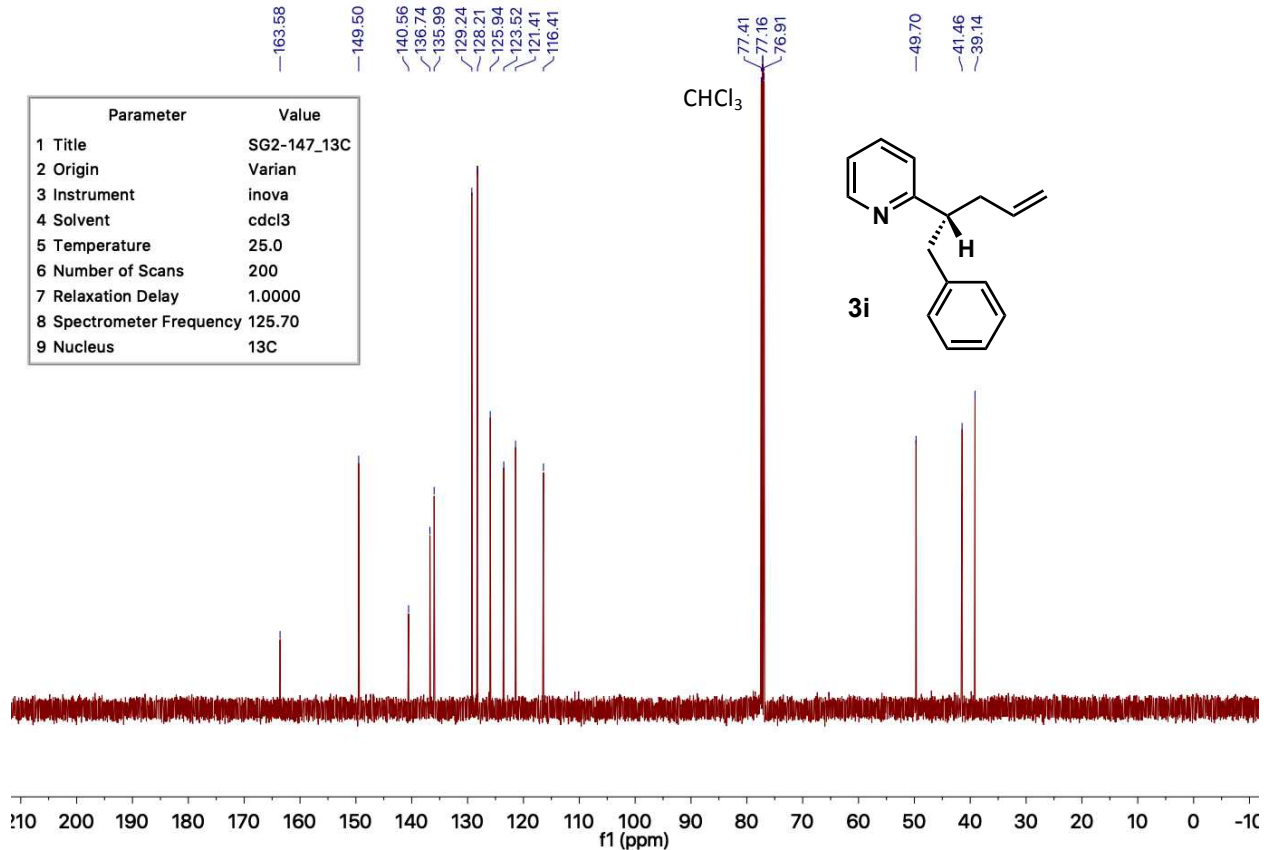
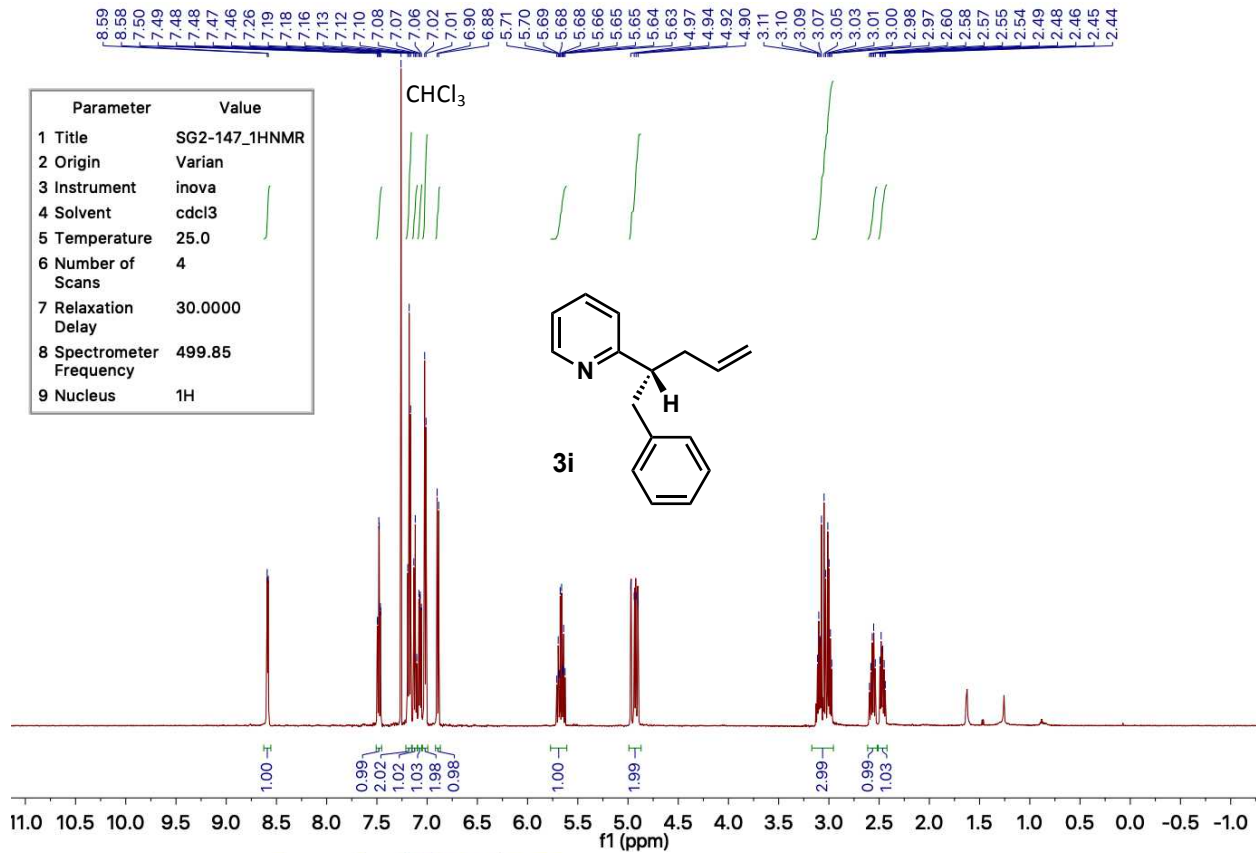


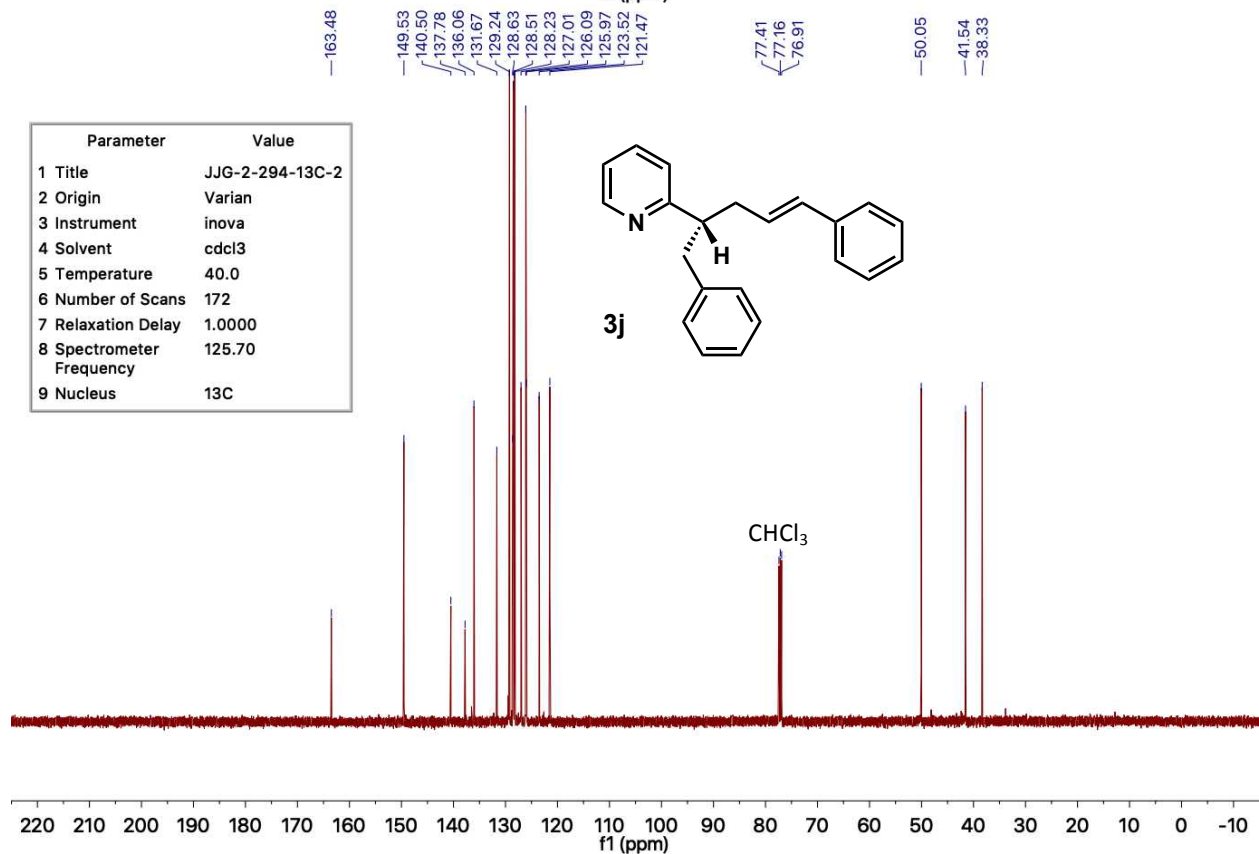
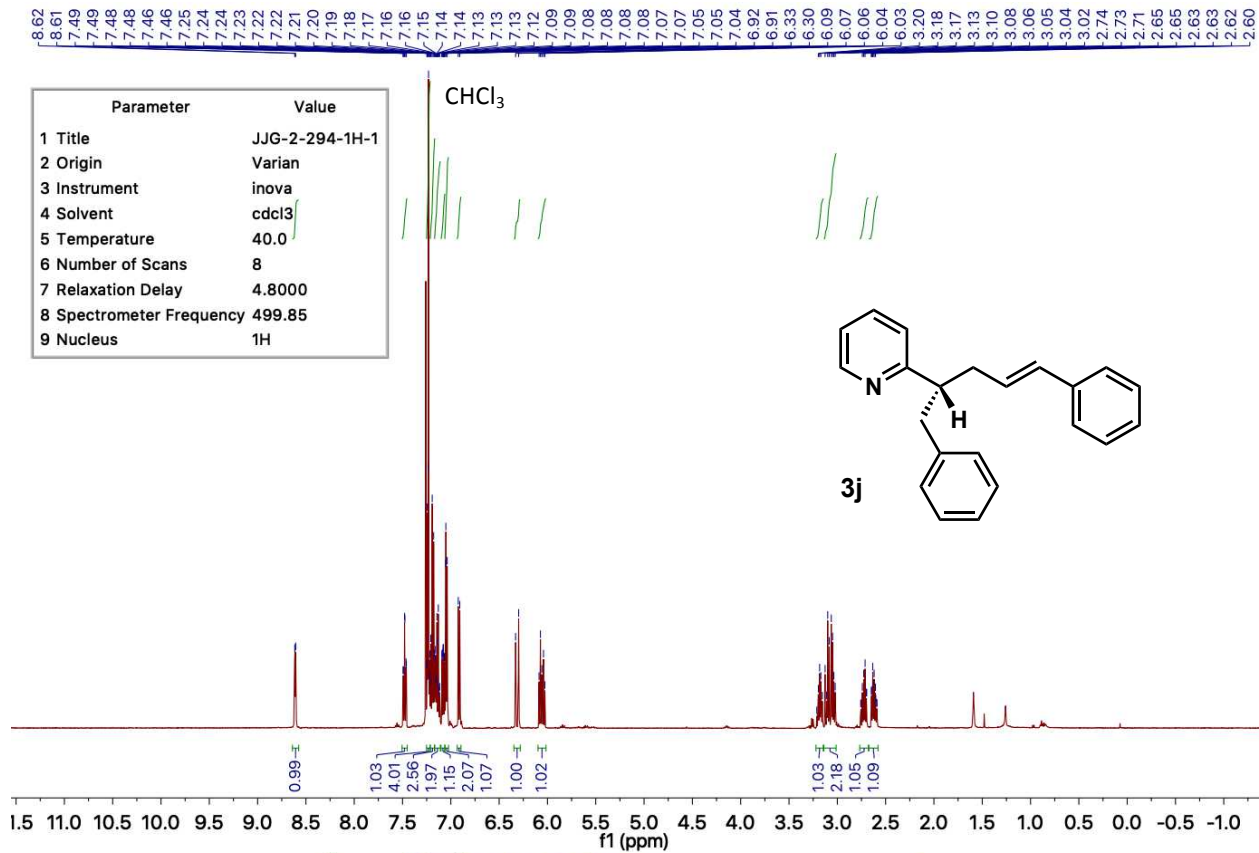


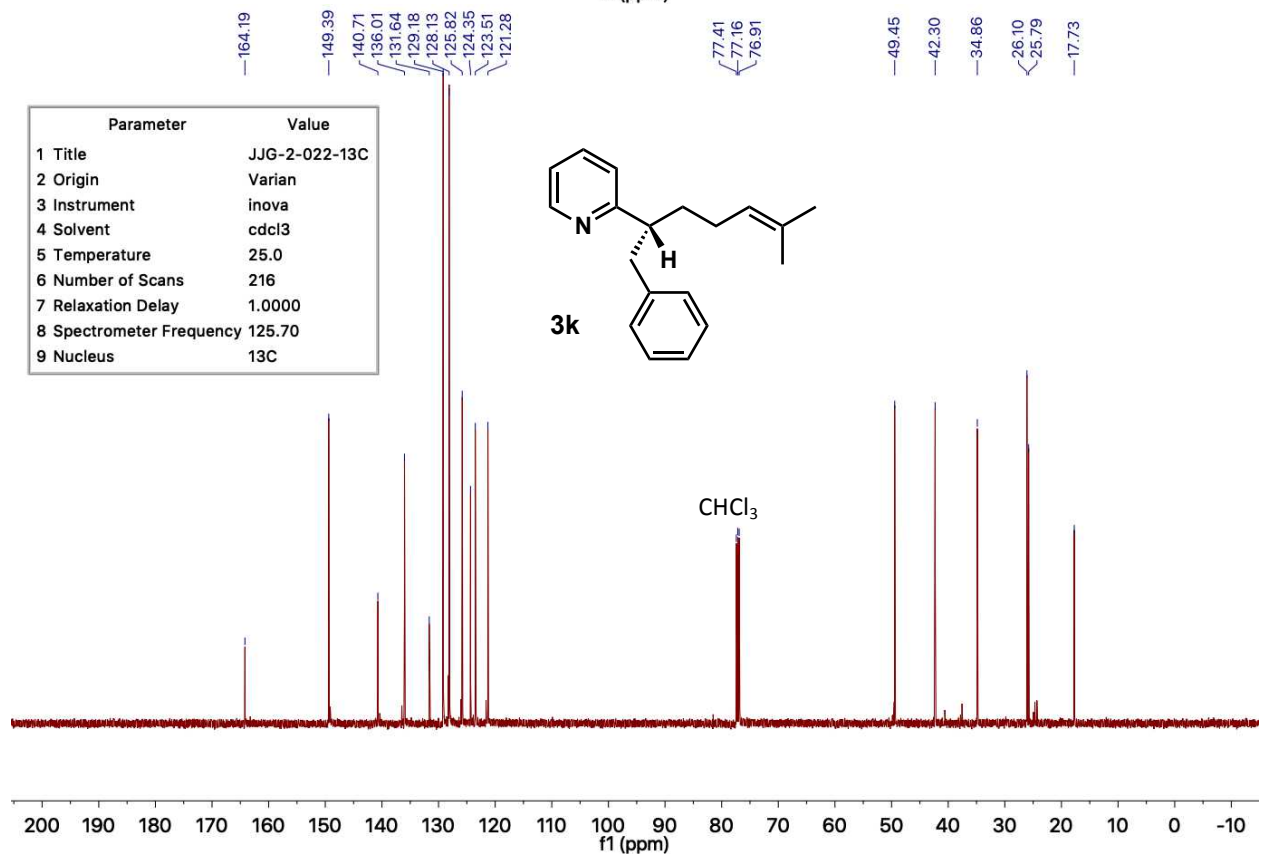
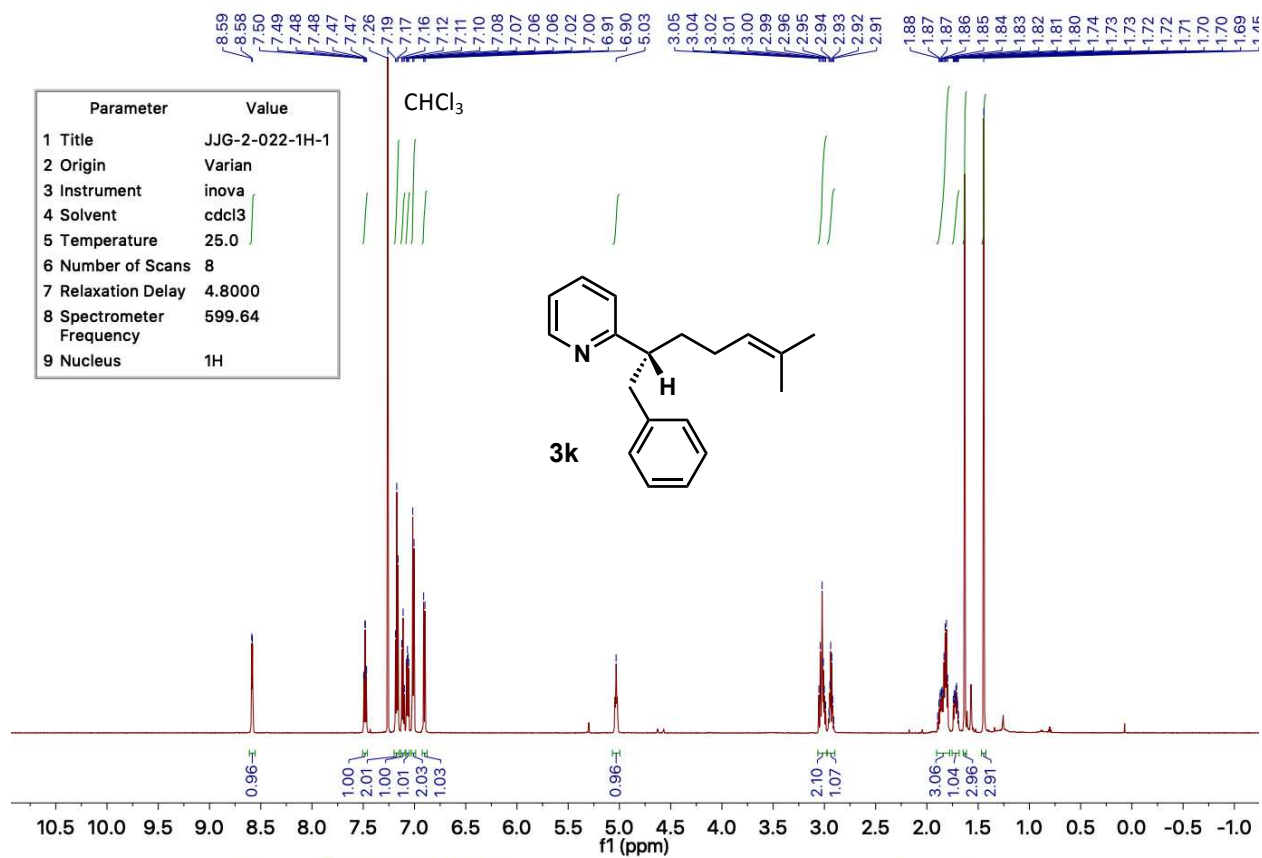


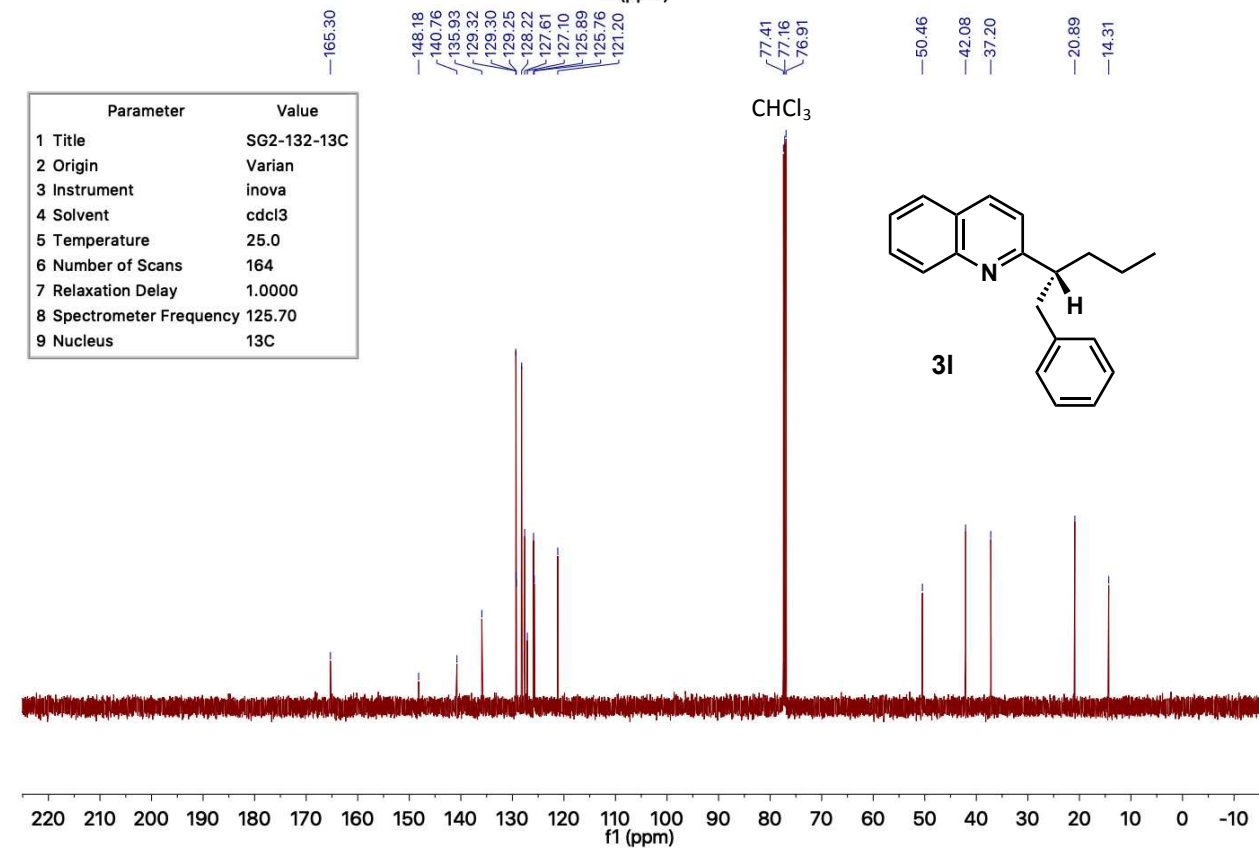
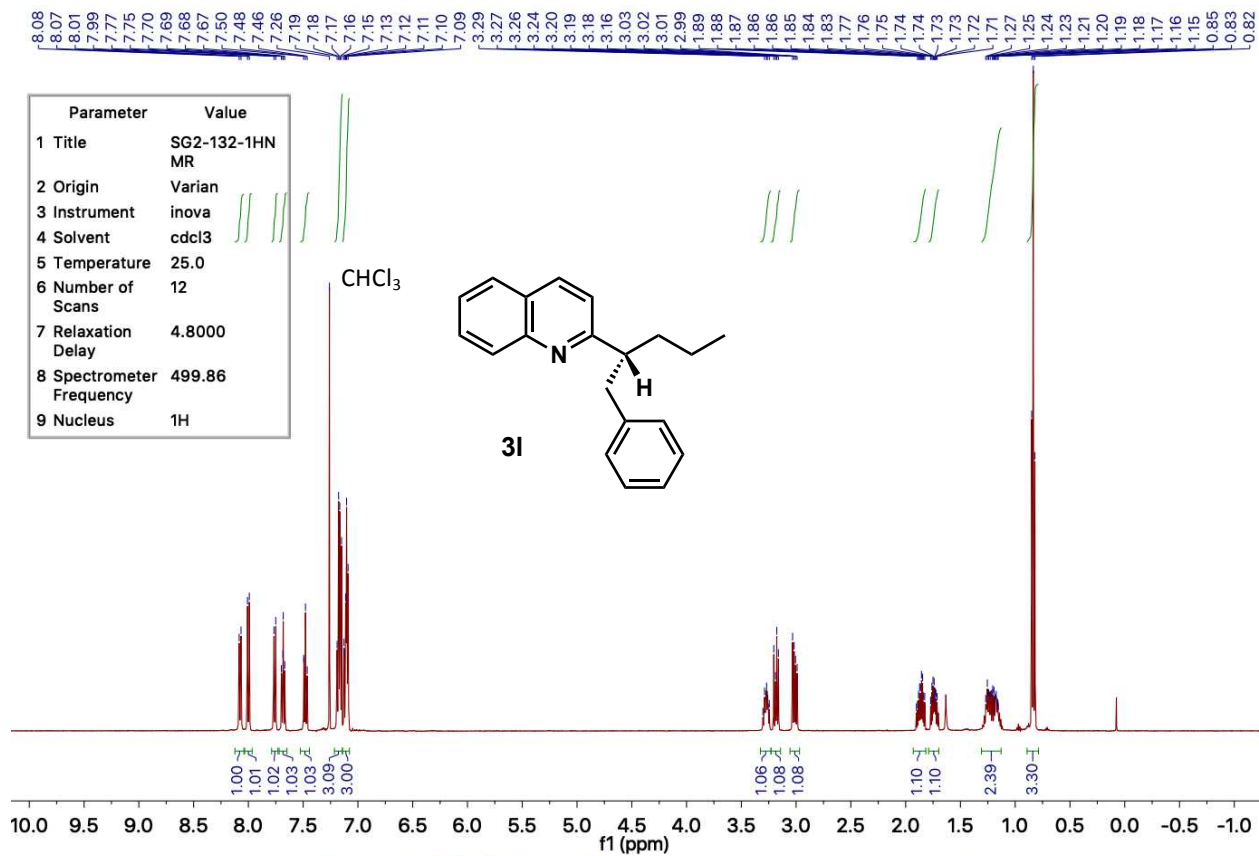


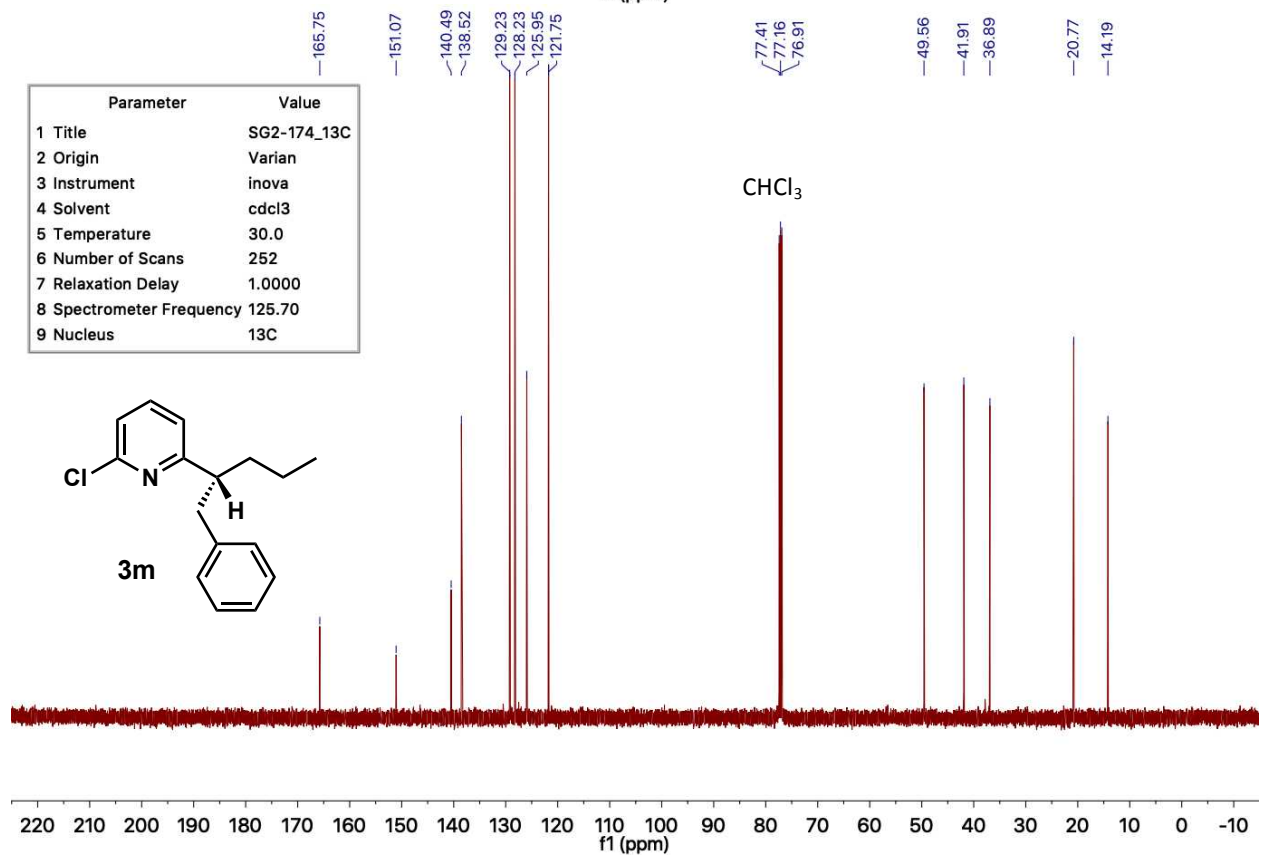
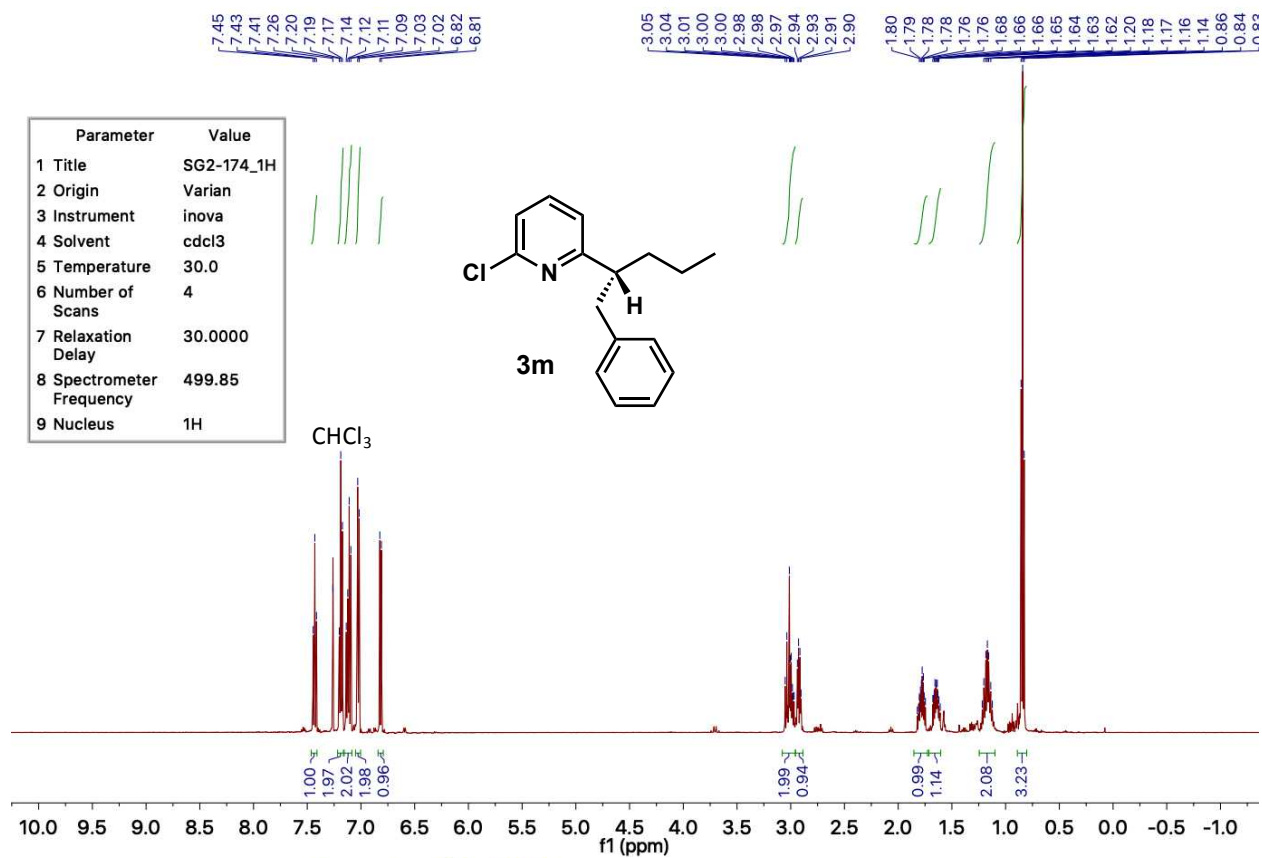


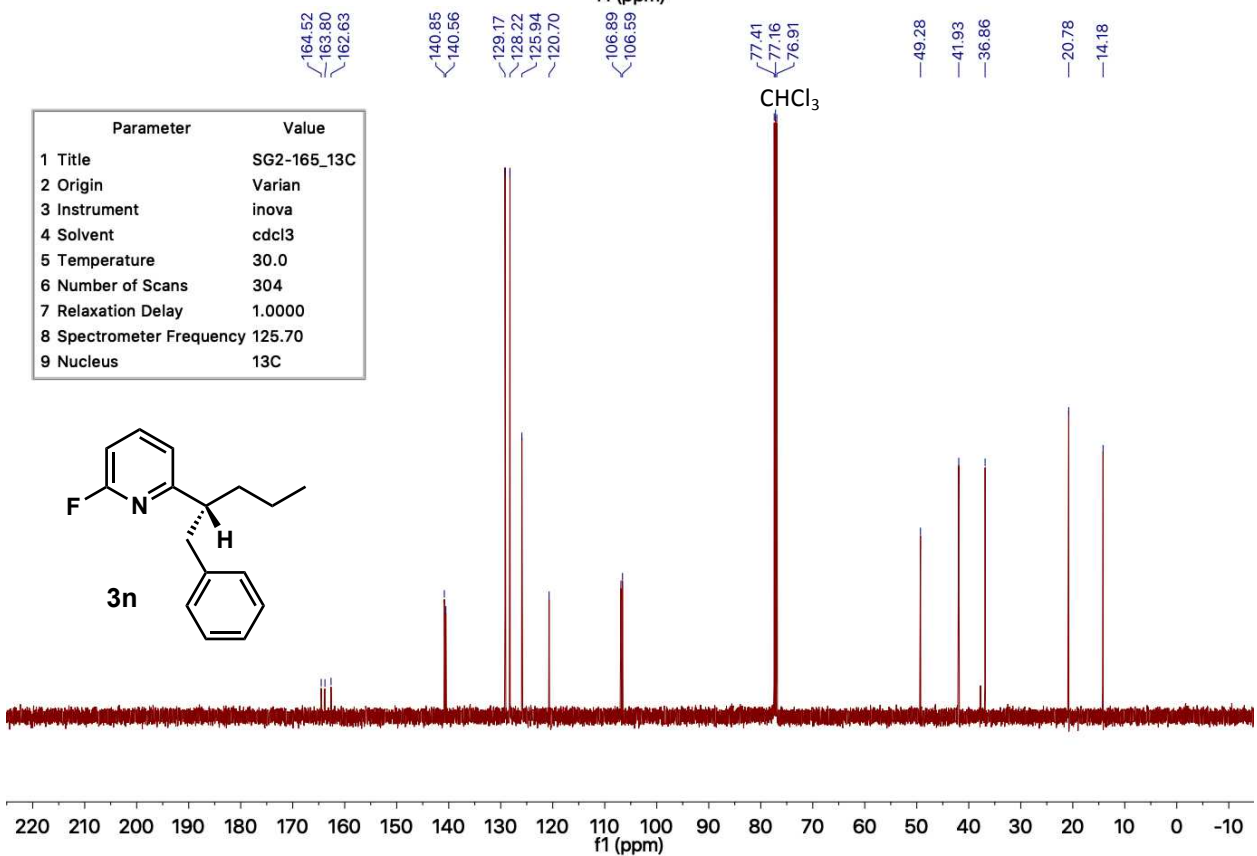
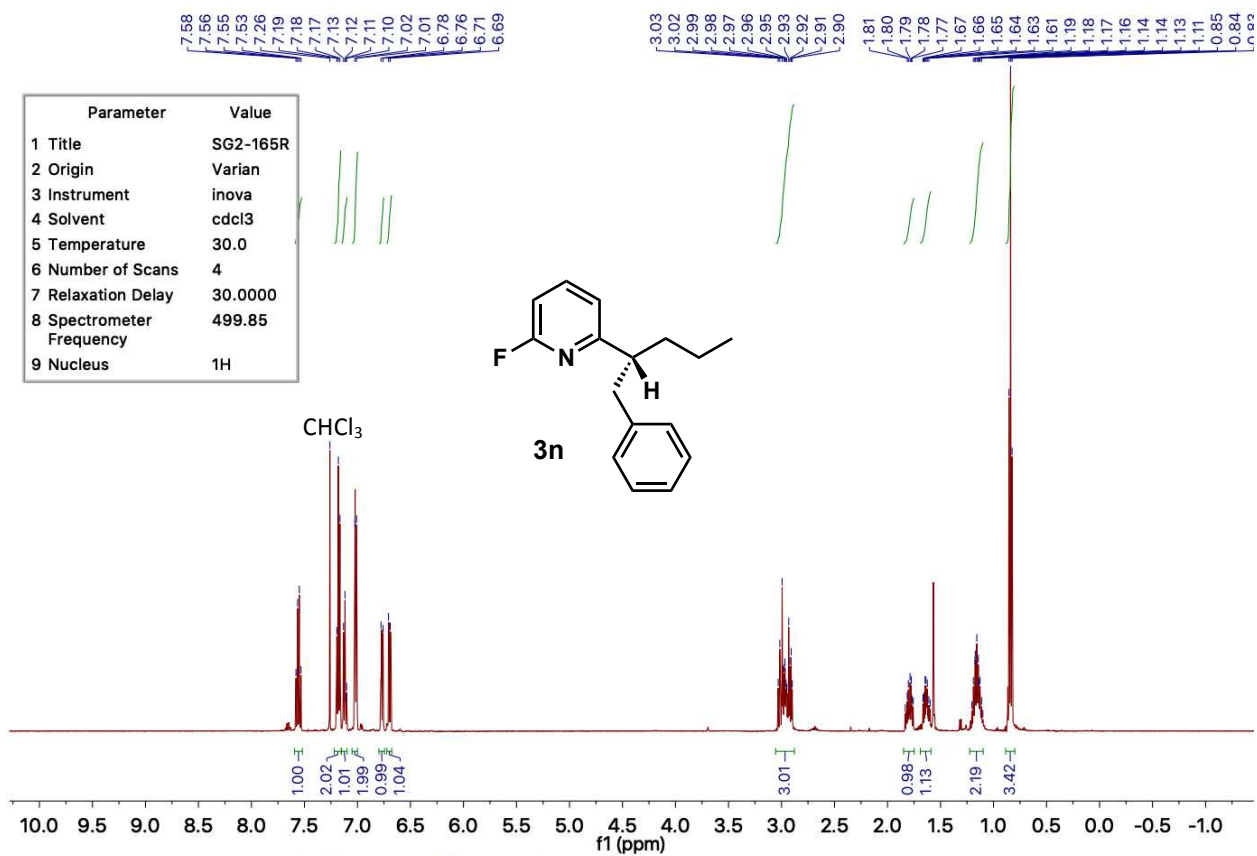




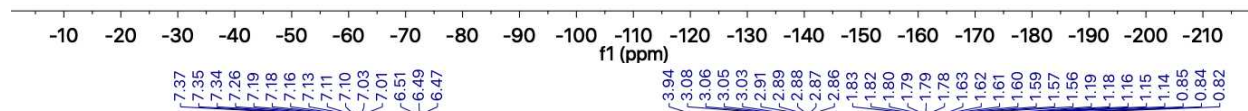
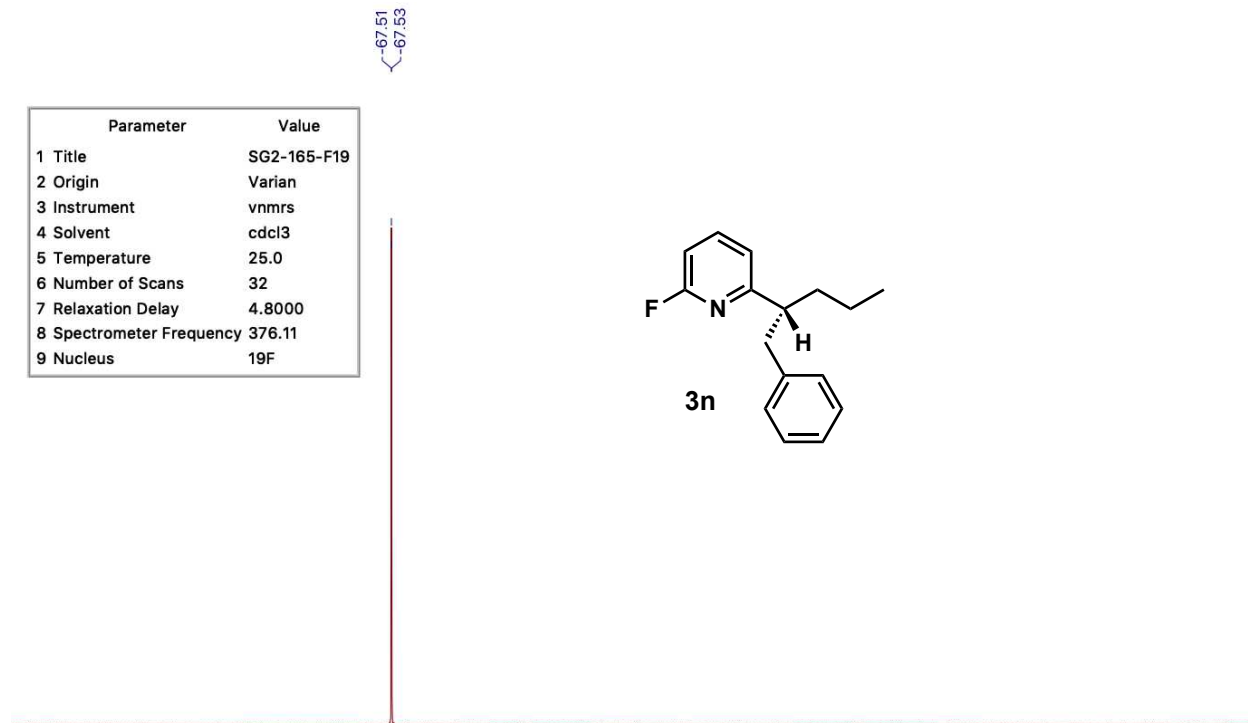
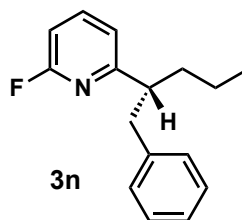




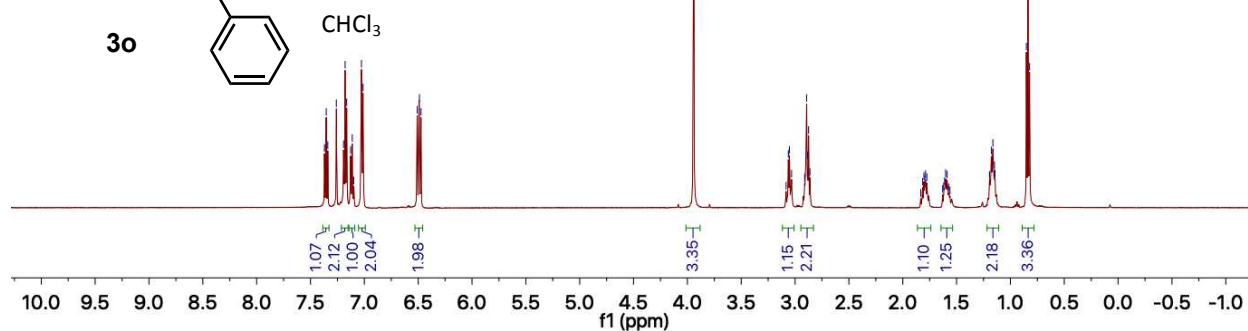
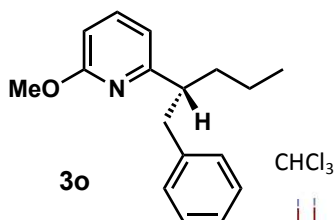


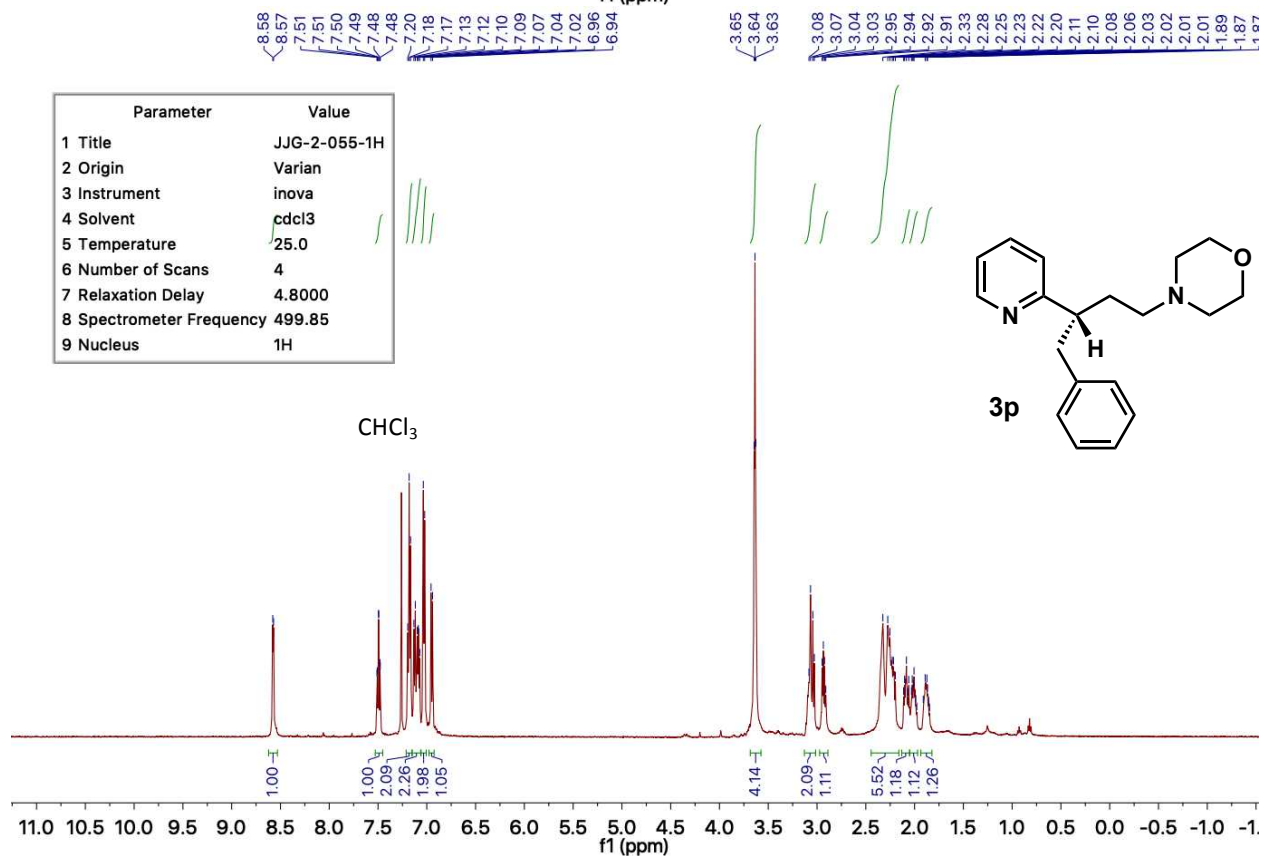
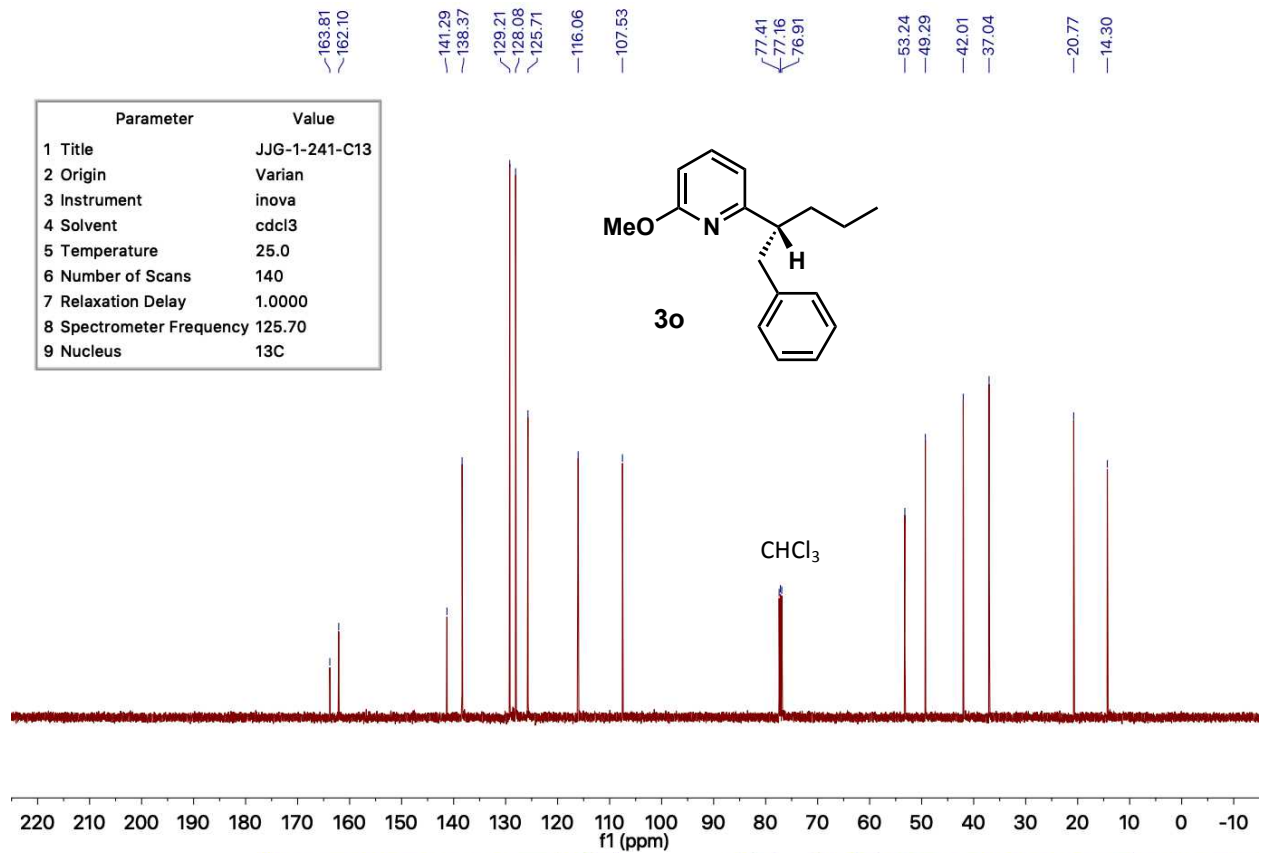


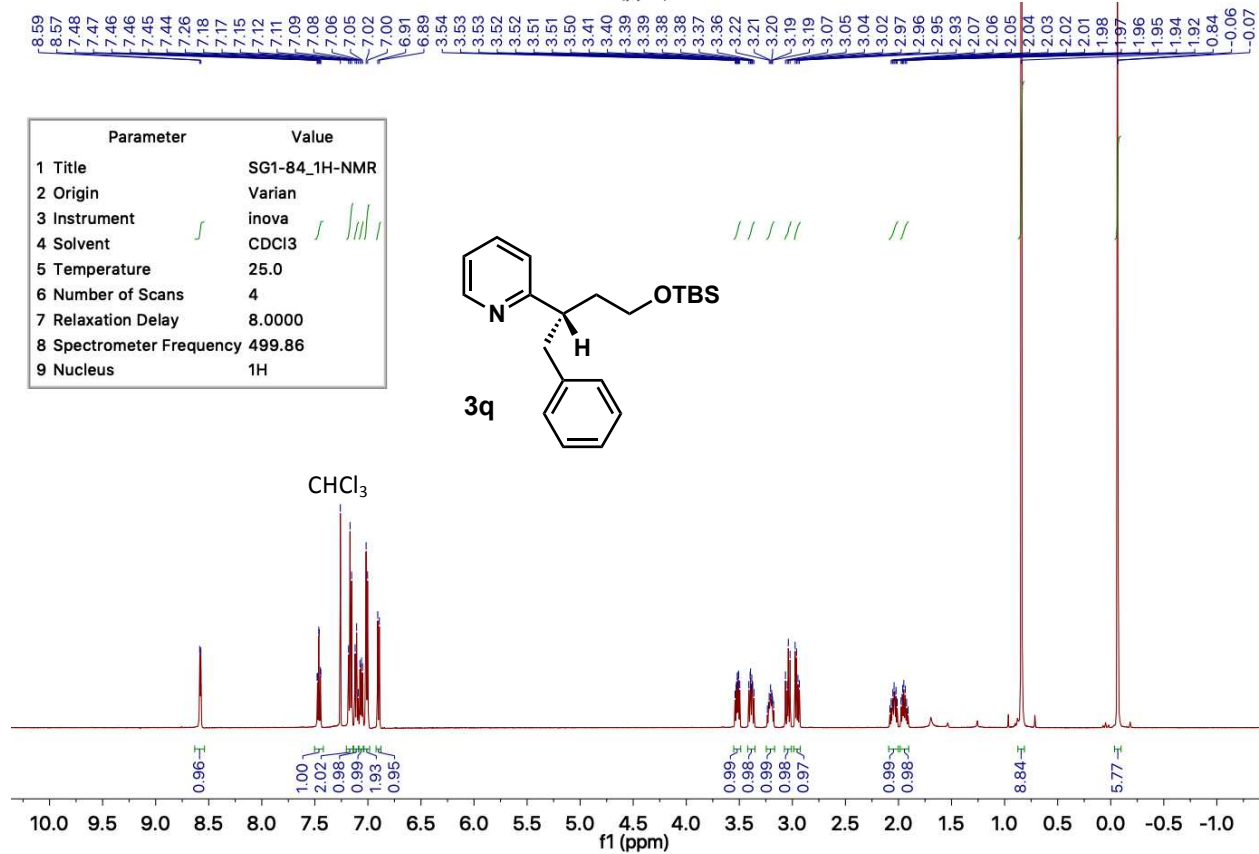
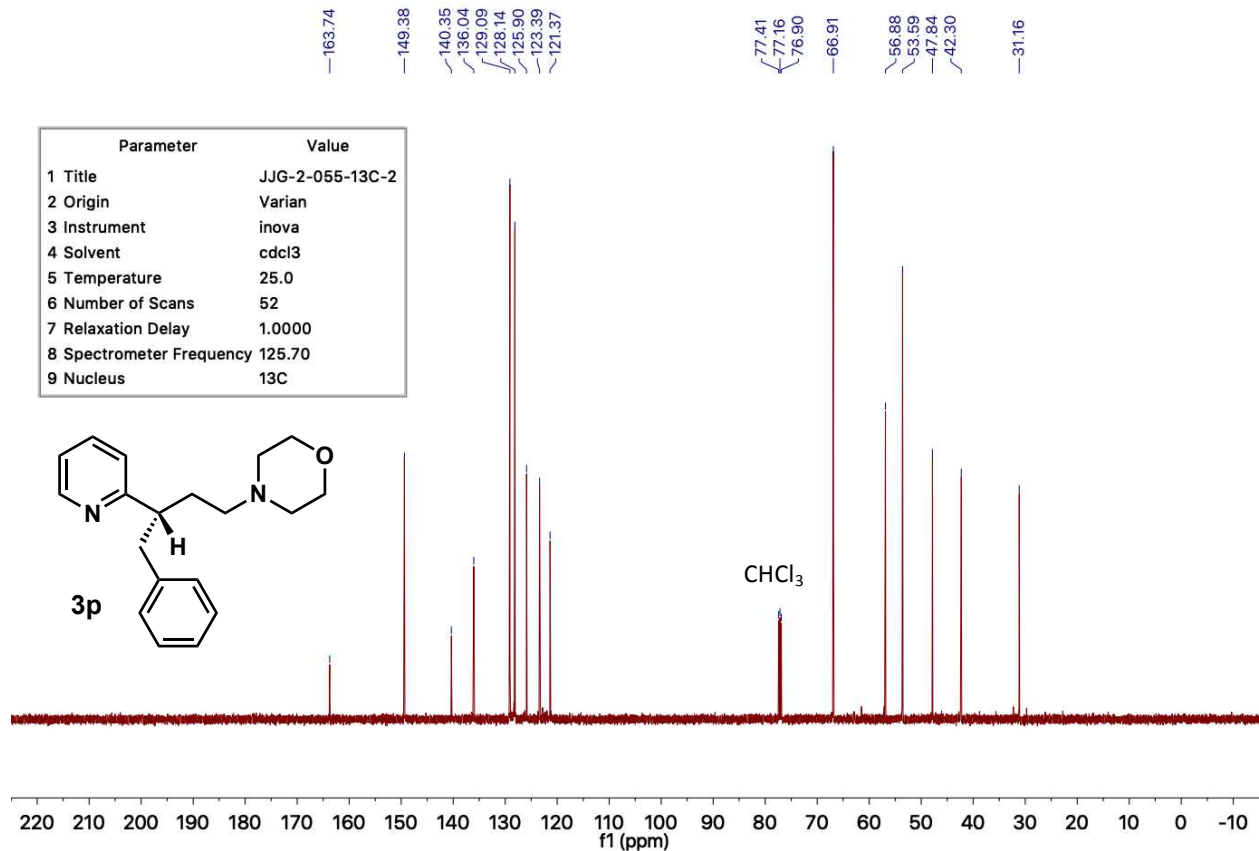
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3 Instrument	vnmrs
4 Solvent	cdcl3
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6 Number of Scans	32
7 Relaxation Delay	4.8000
8 Spectrometer Frequency	376.11
9 Nucleus	19F

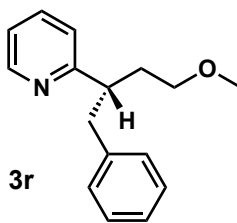
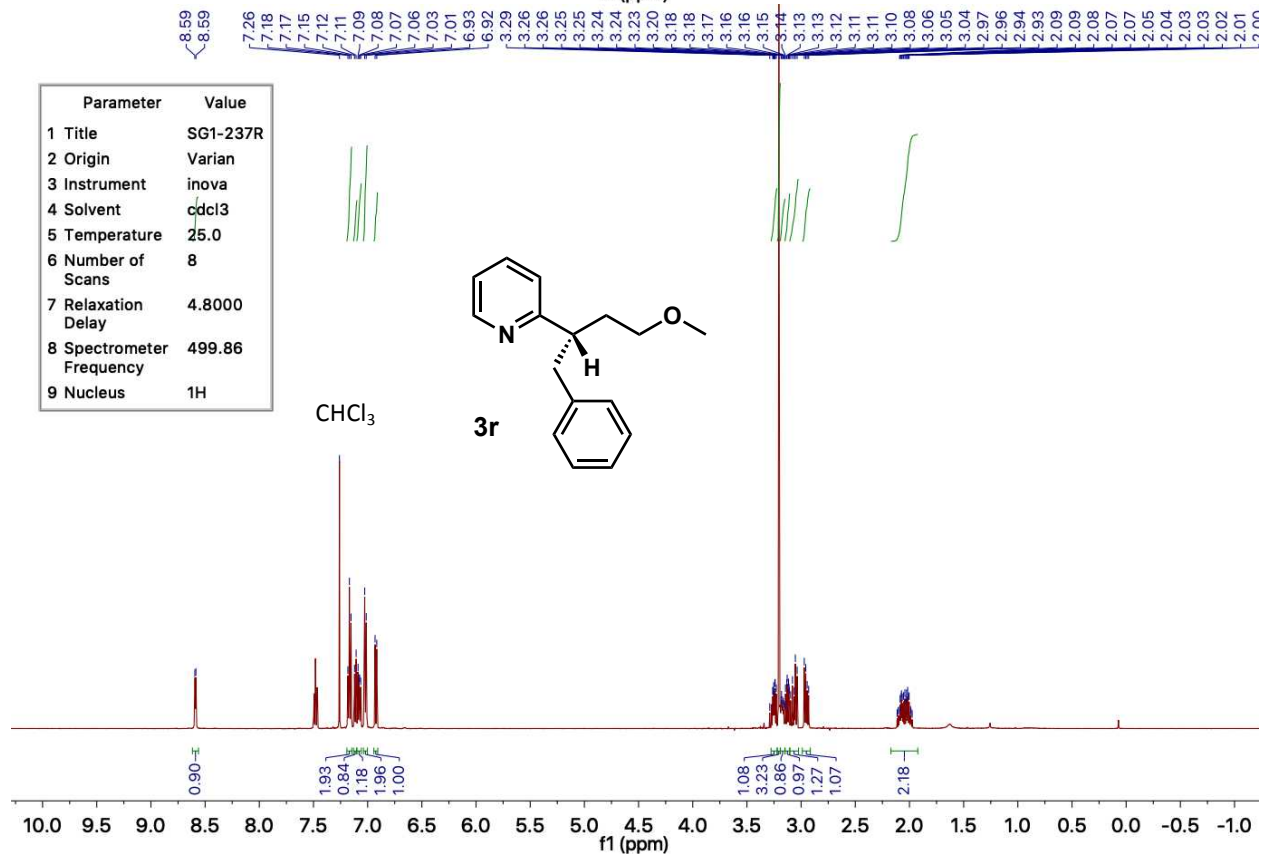
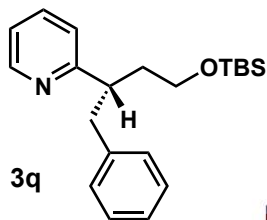
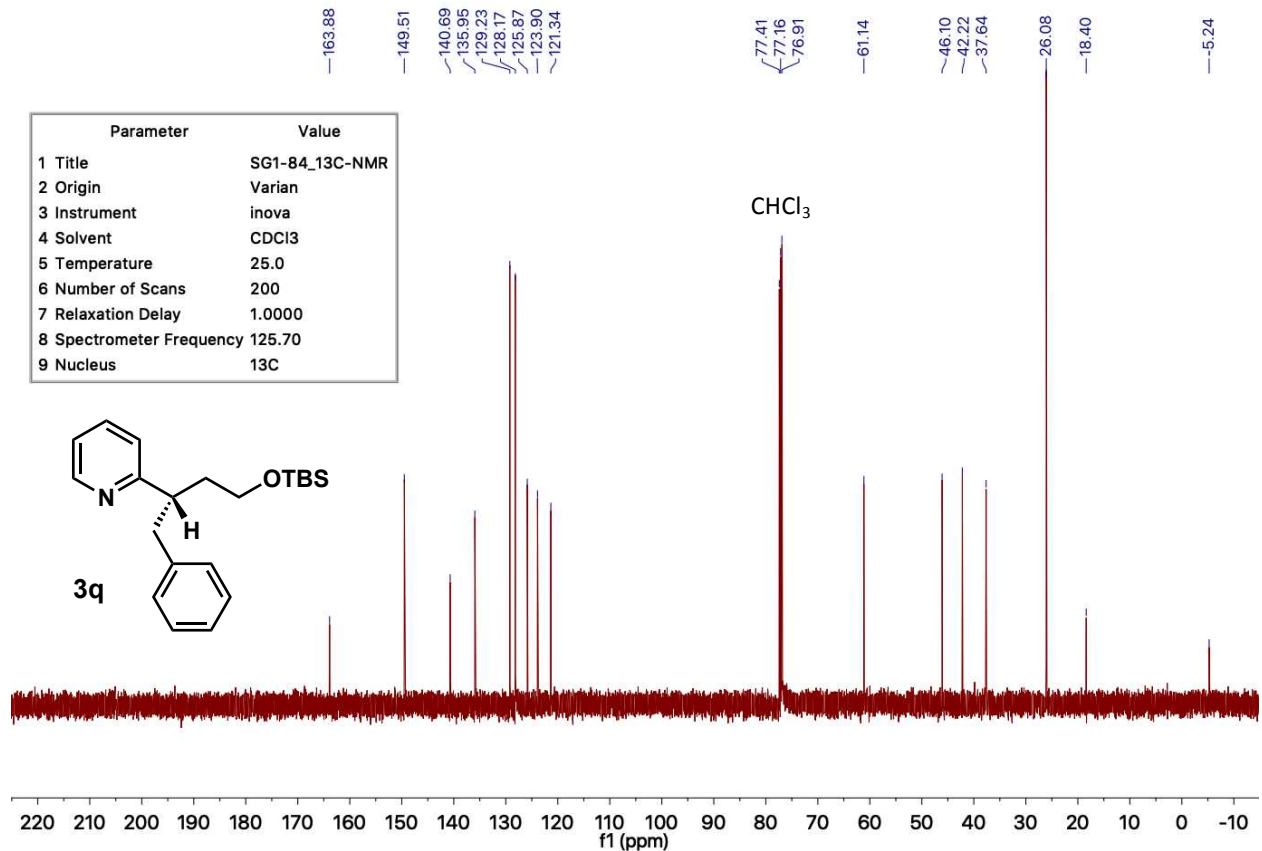


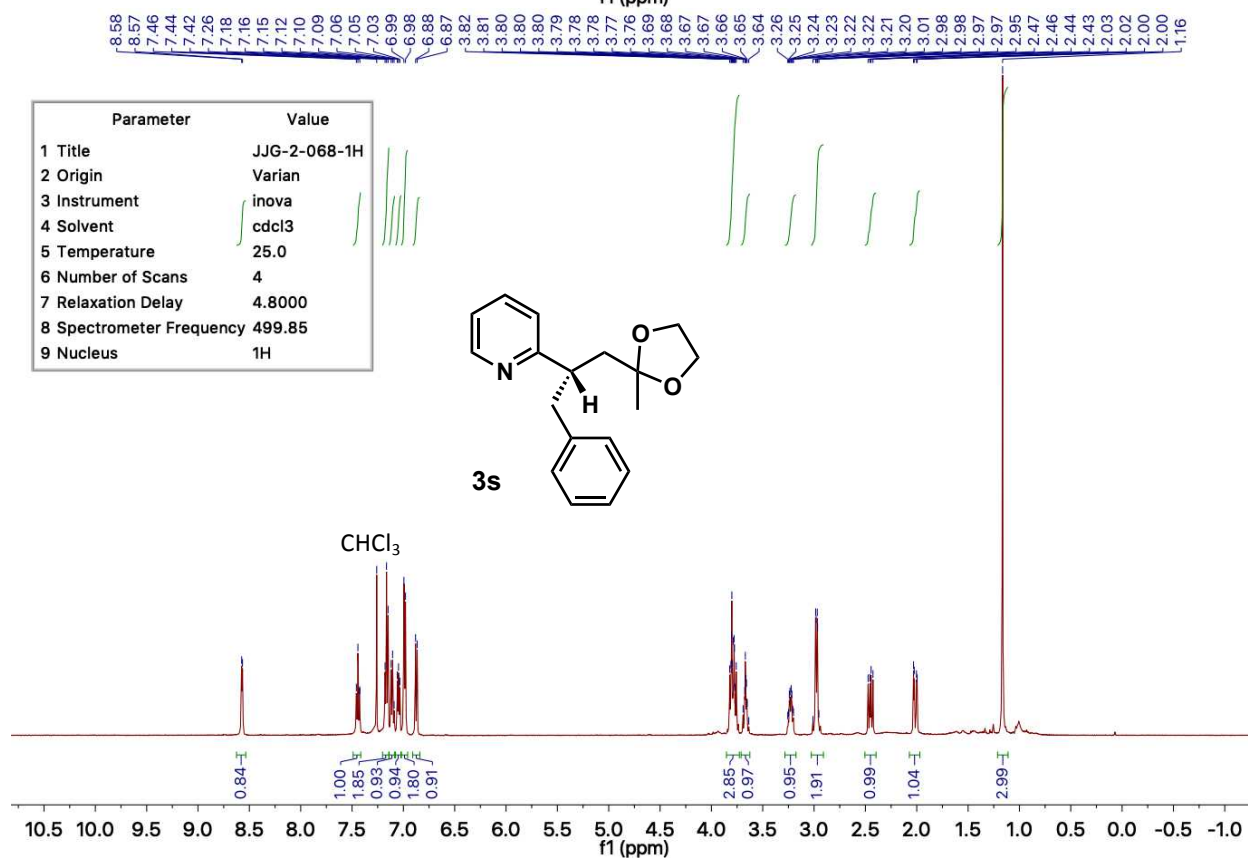
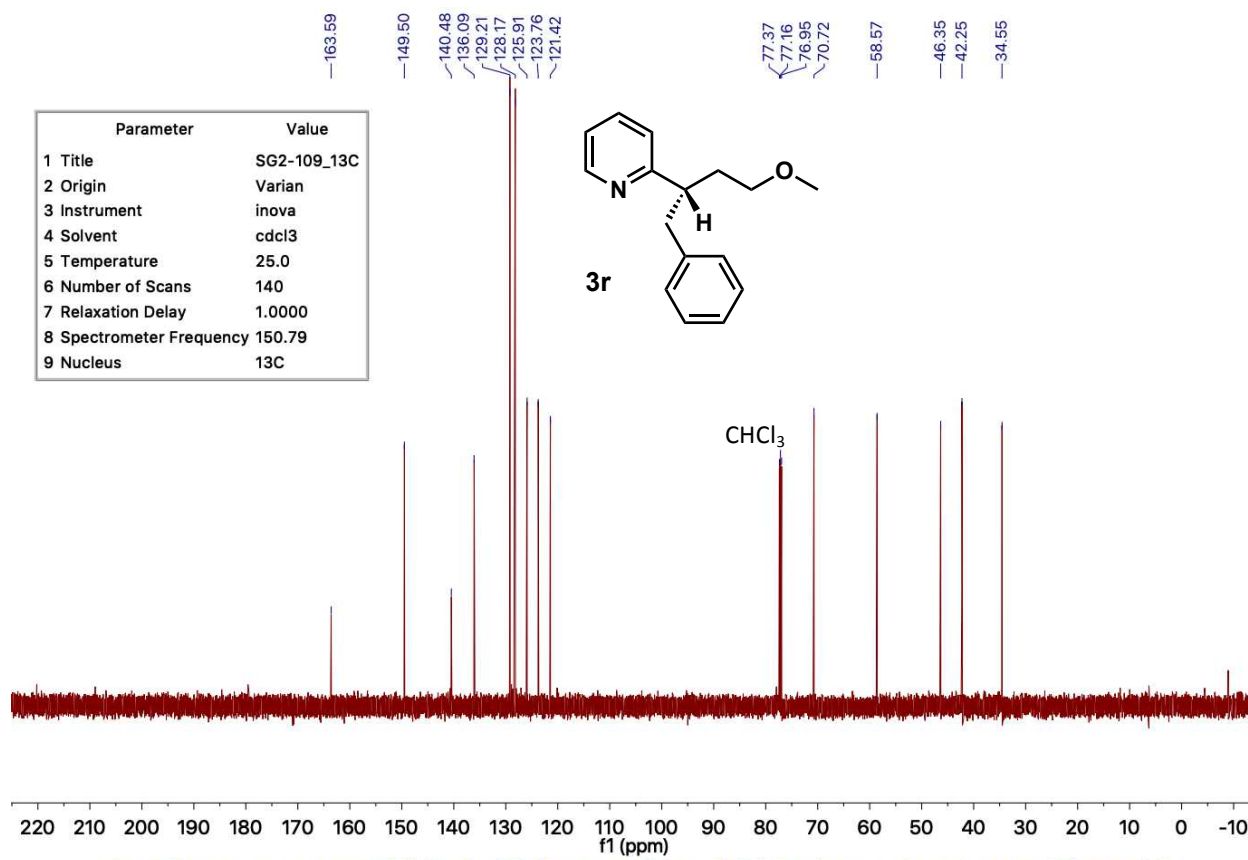
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2 Origin	Varian
3 Instrument	inova
4 Solvent	cdcl3
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7 Relaxation Delay	4.8000
8 Spectrometer Frequency	499.85
9 Nucleus	1H

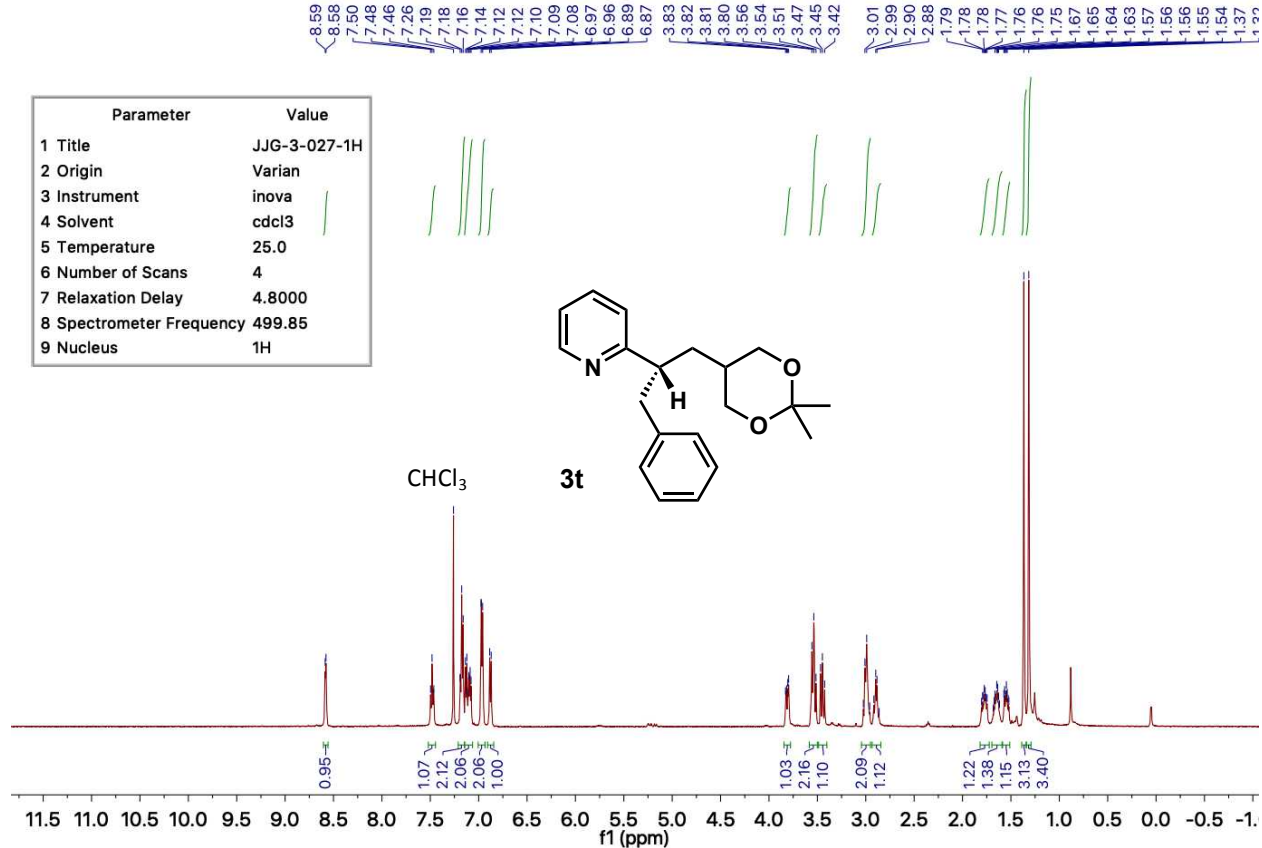
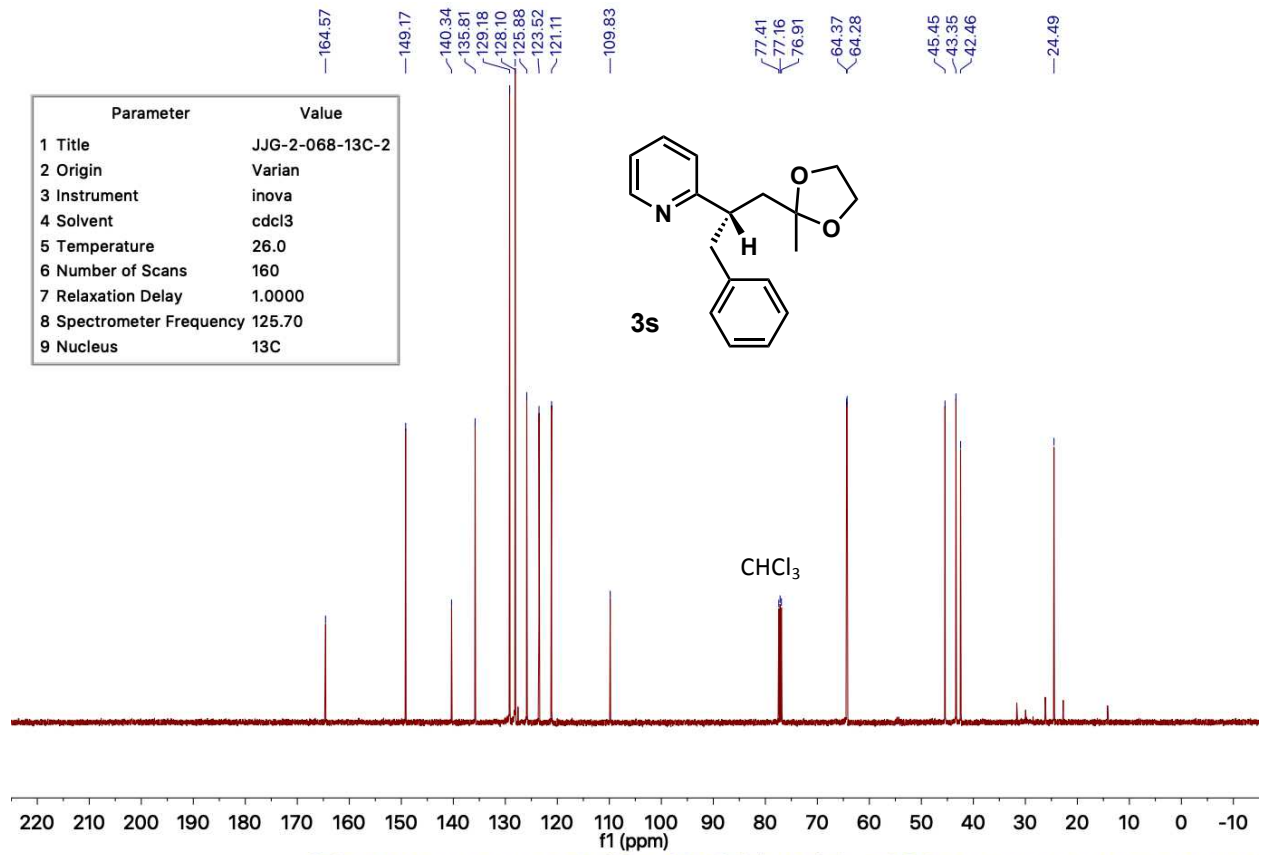


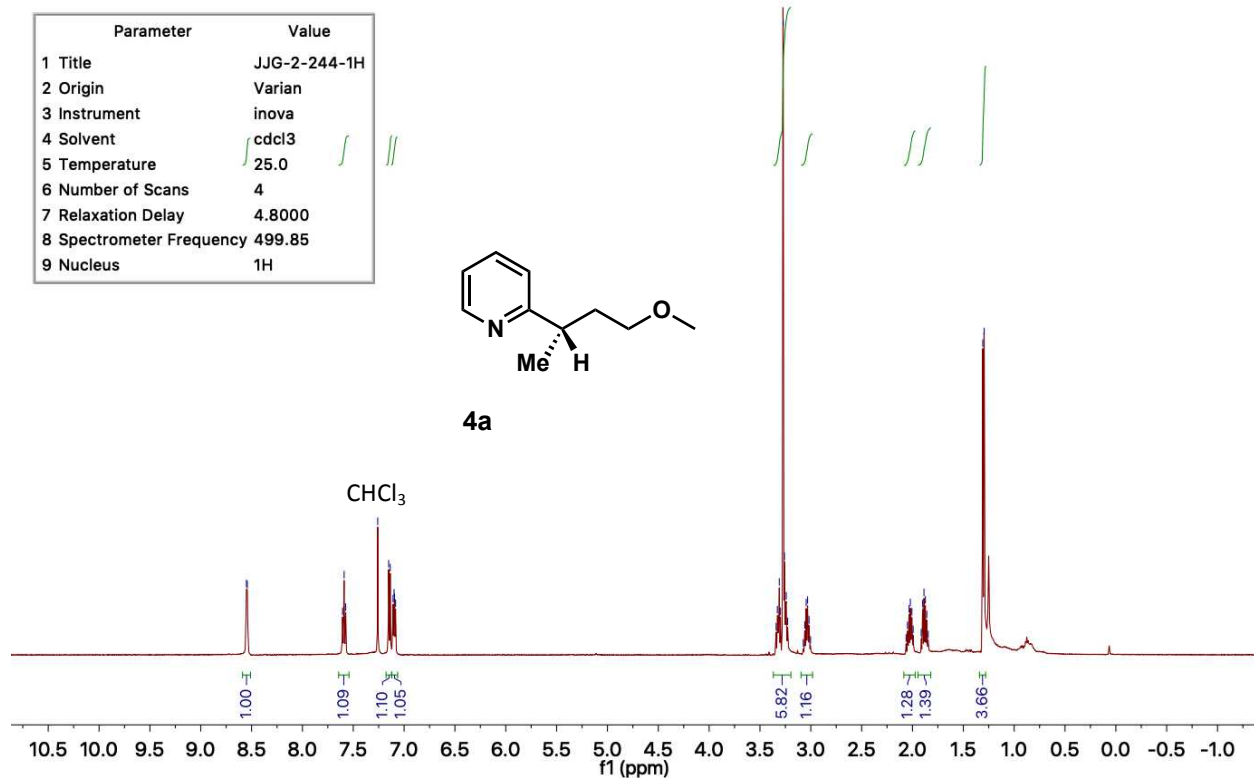
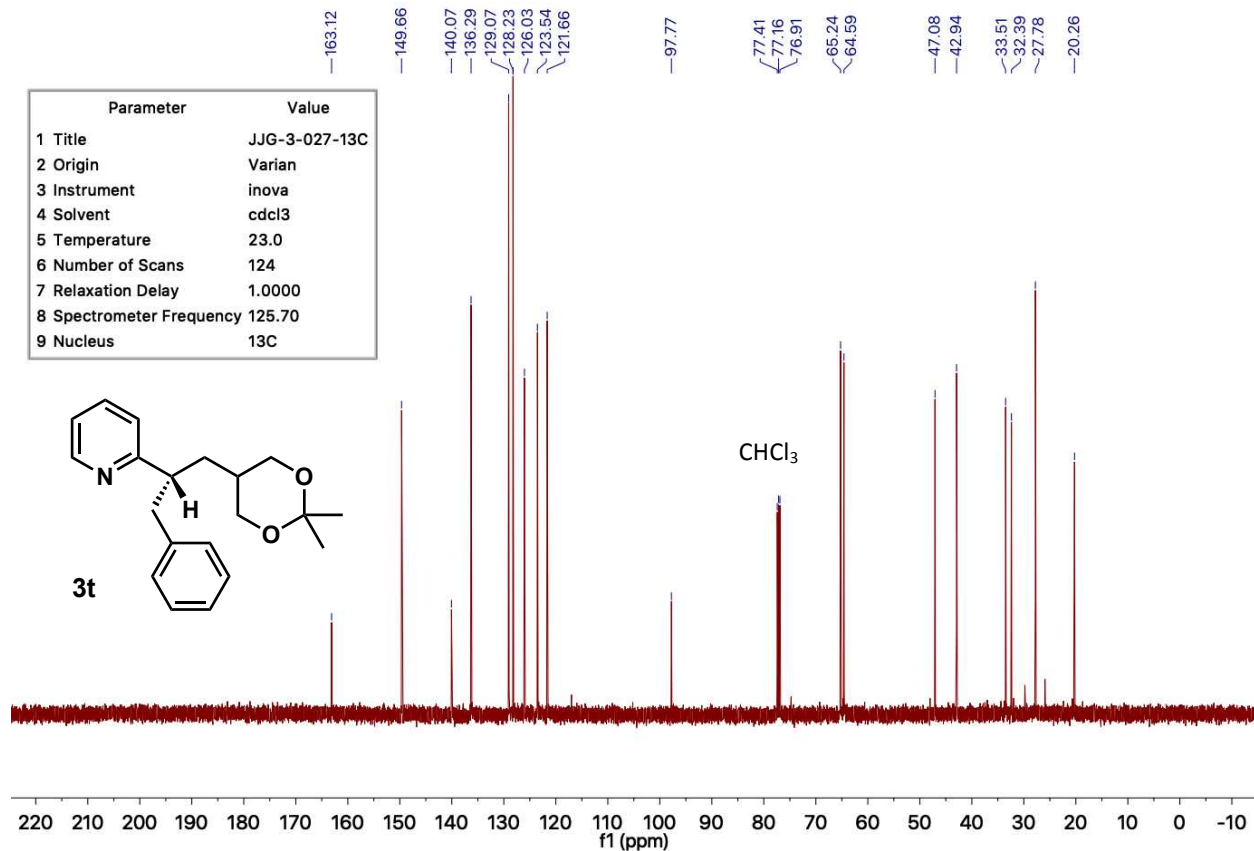


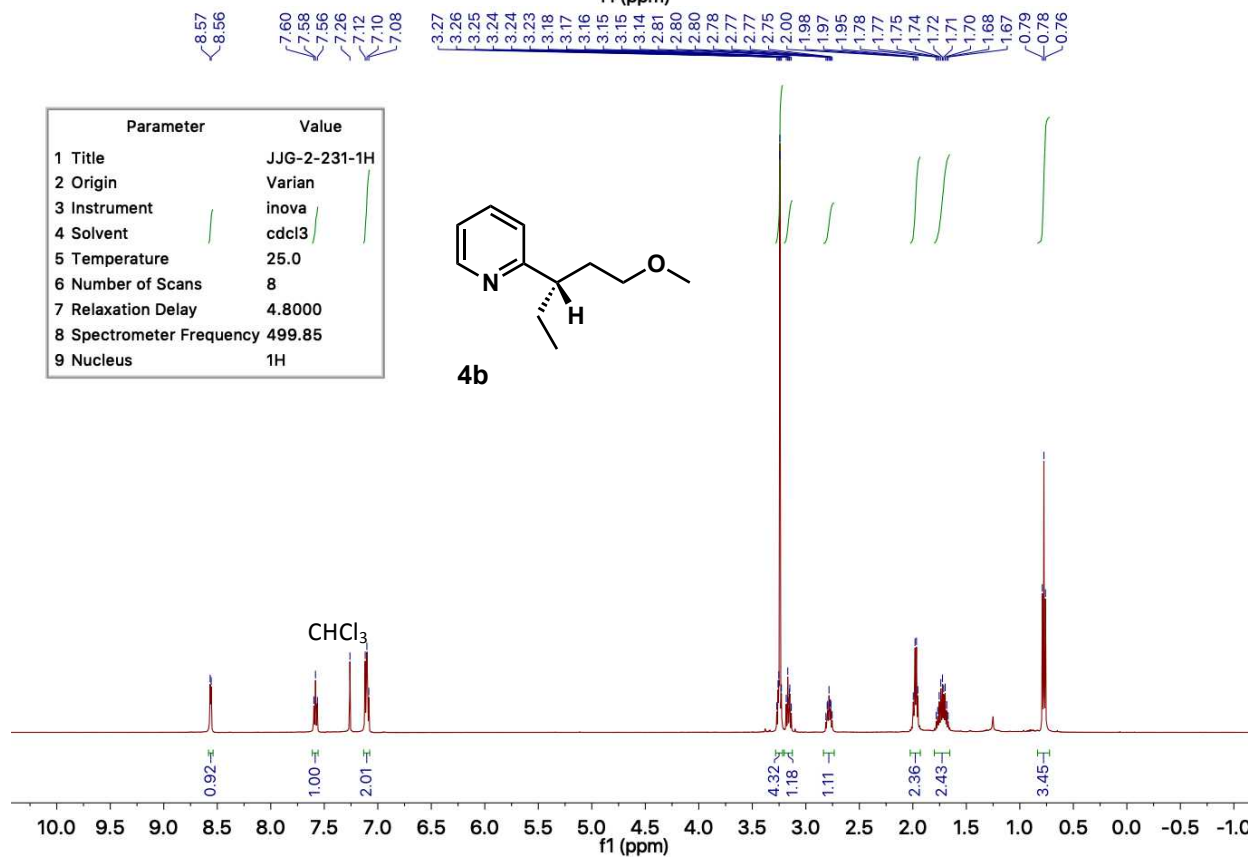
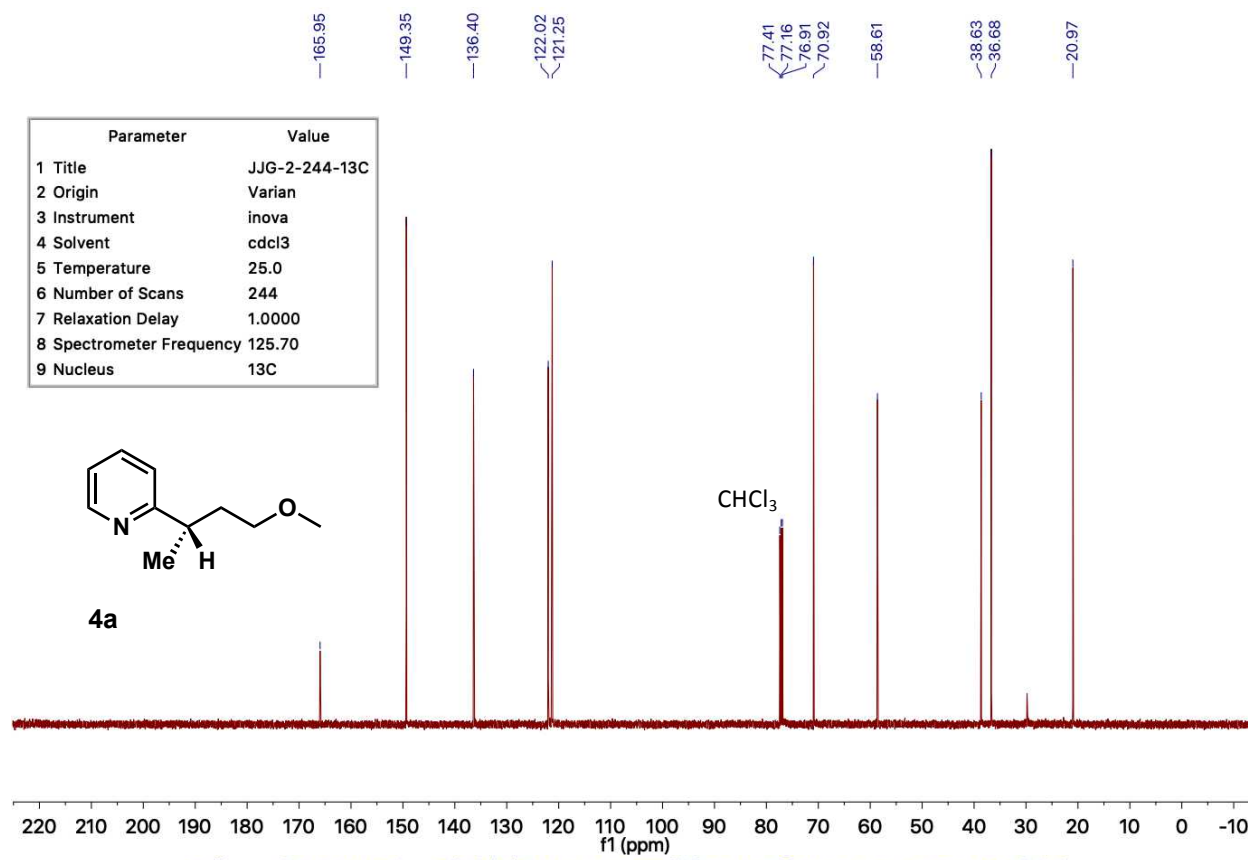




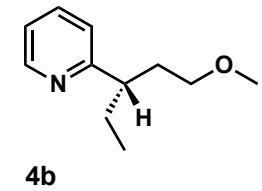
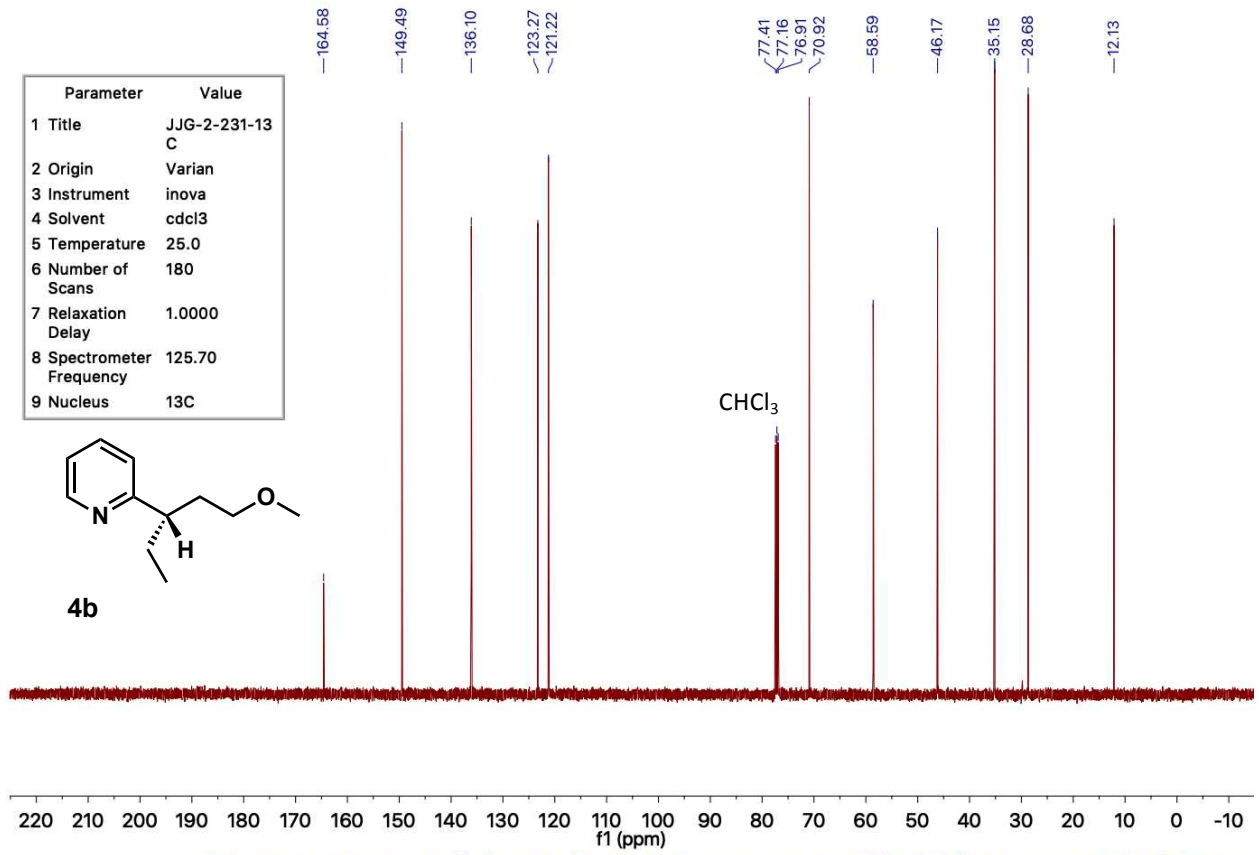




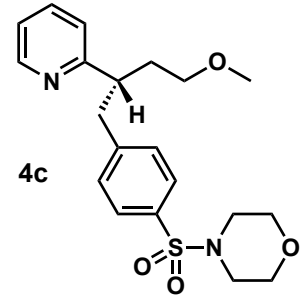
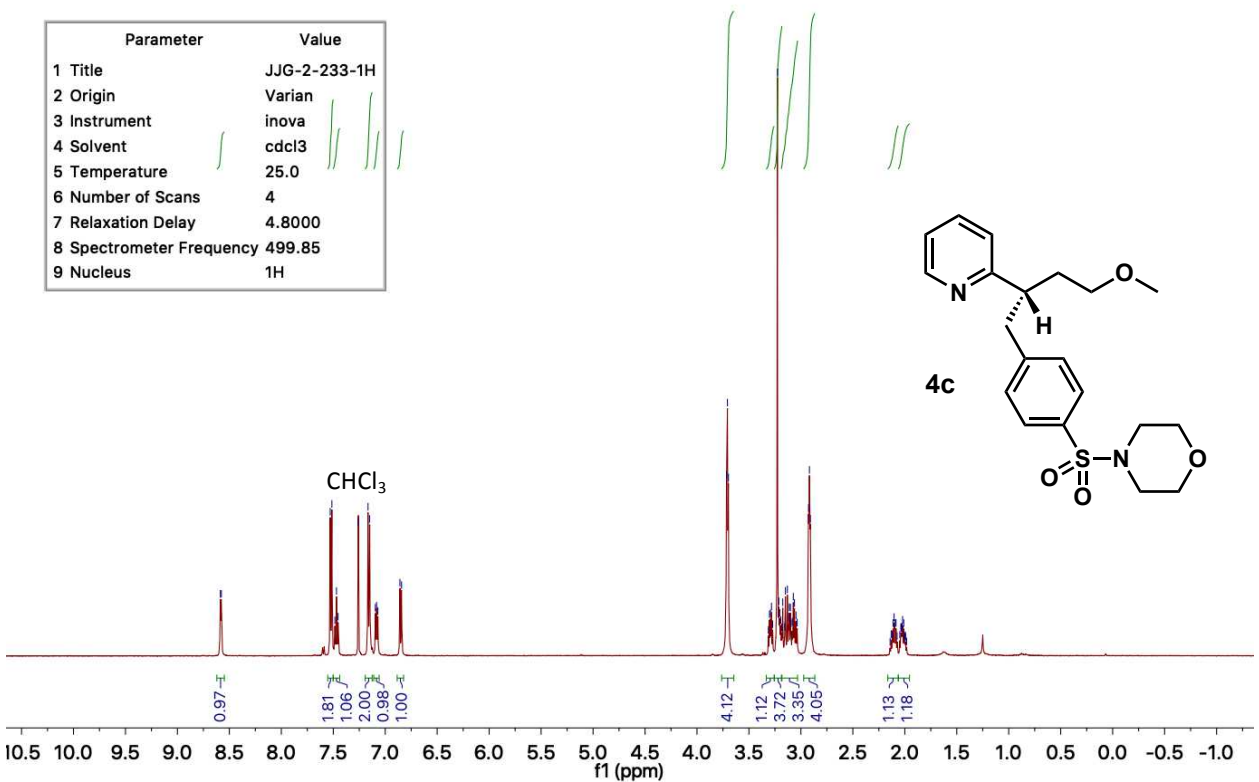


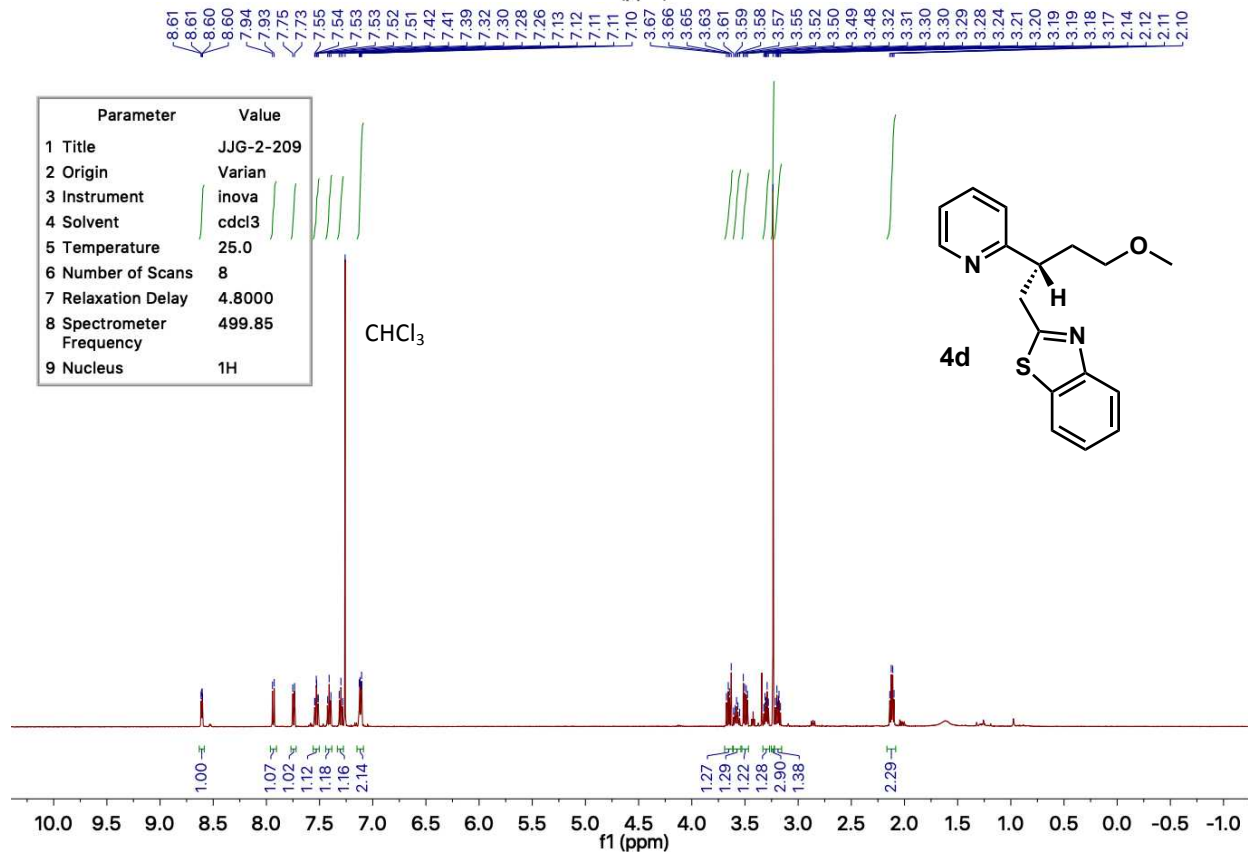
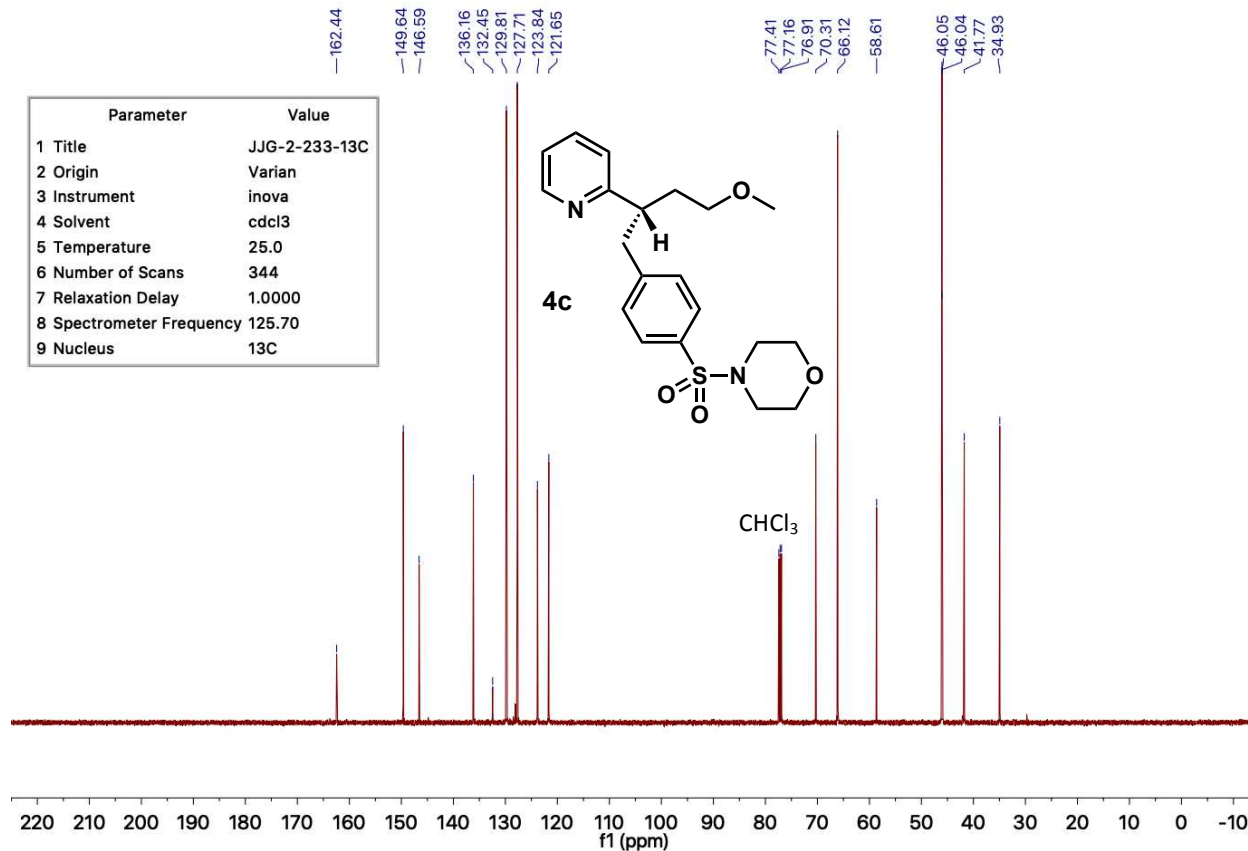


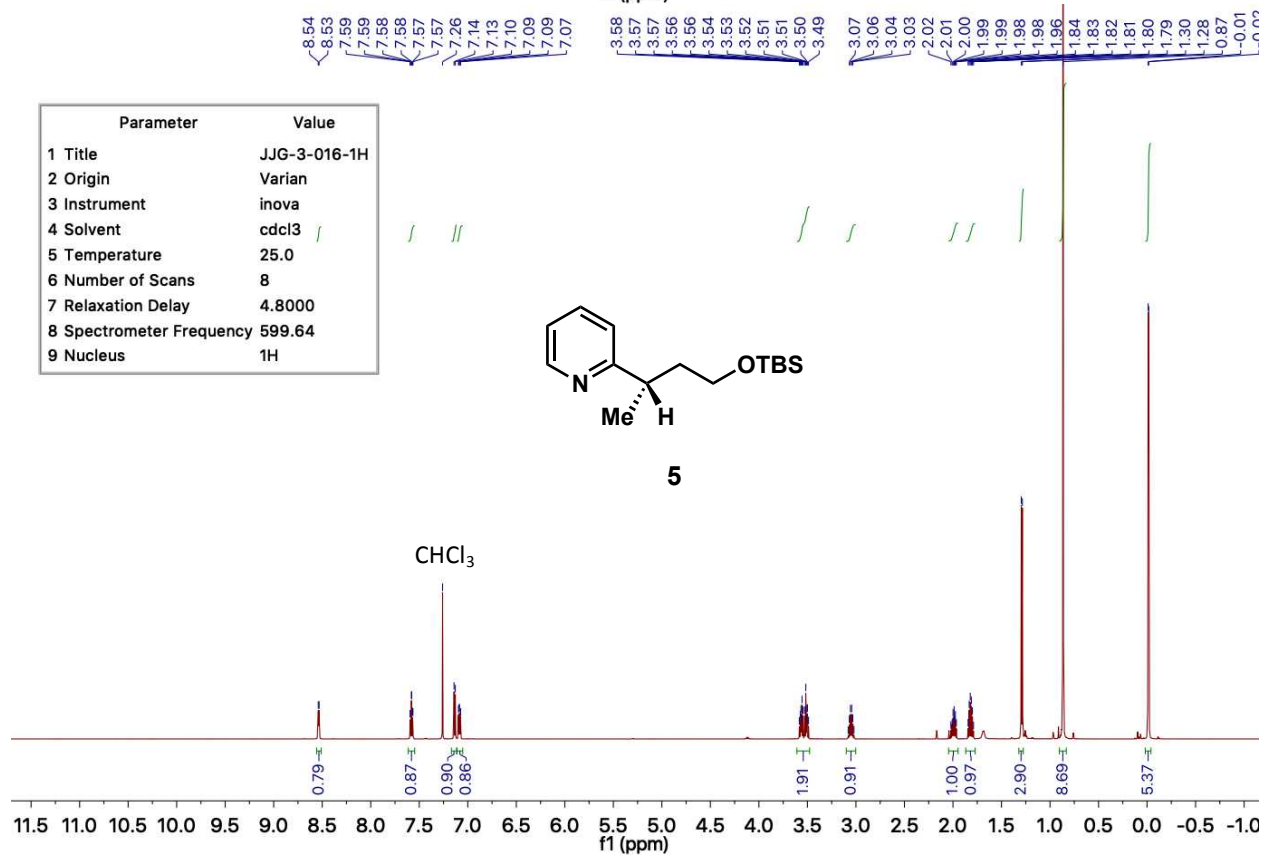
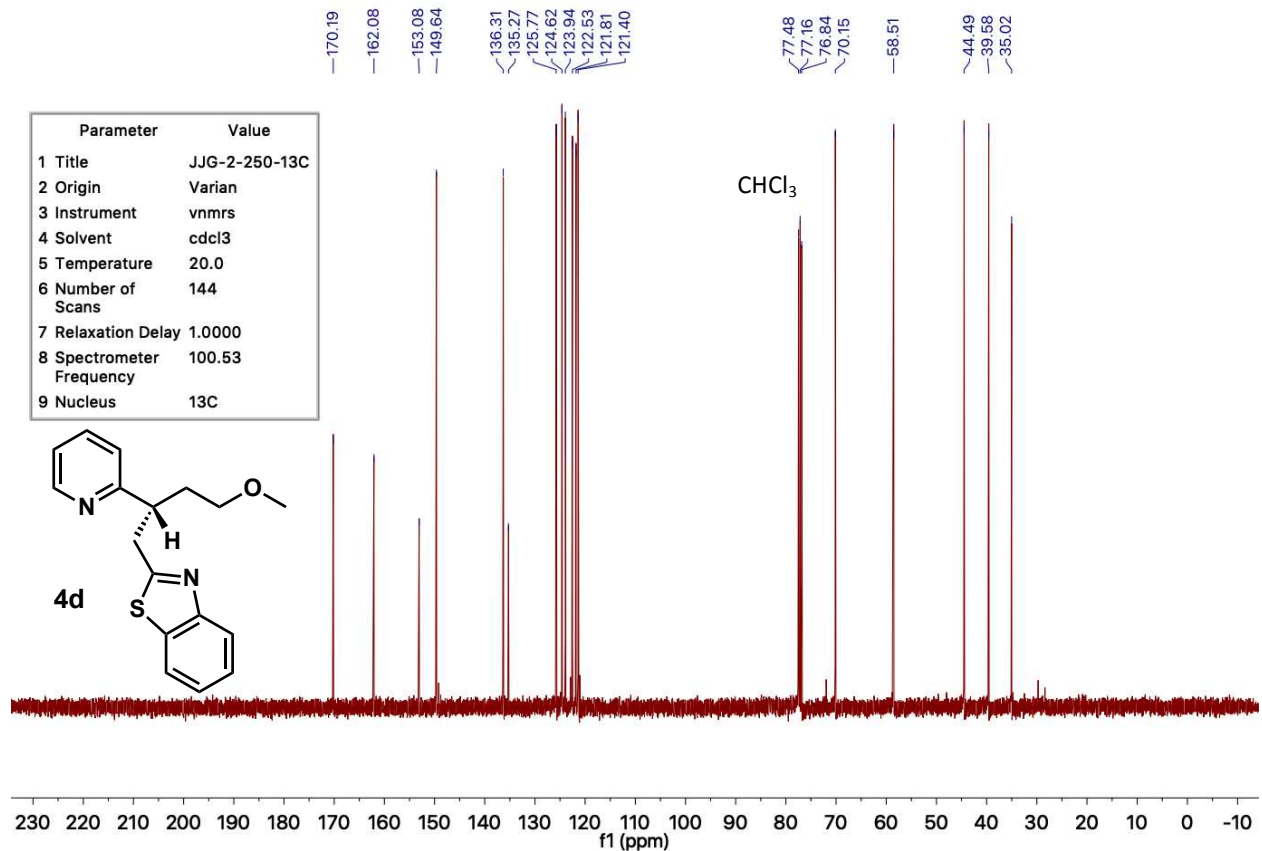
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3 Instrument	inova
4 Solvent	cdcl3
5 Temperature	25.0
6 Number of Scans	180
7 Relaxation Delay	1.0000
8 Spectrometer Frequency	125.70
9 Nucleus	13C

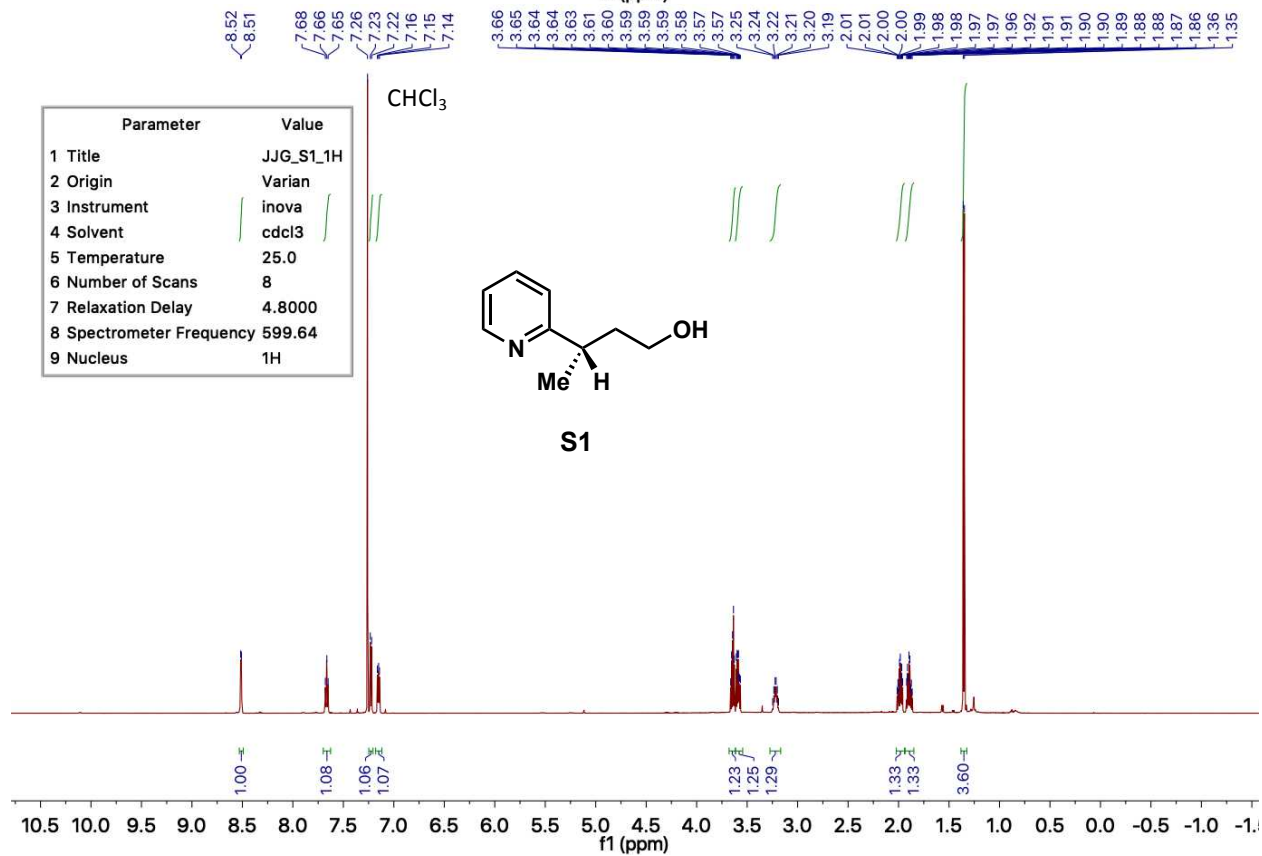
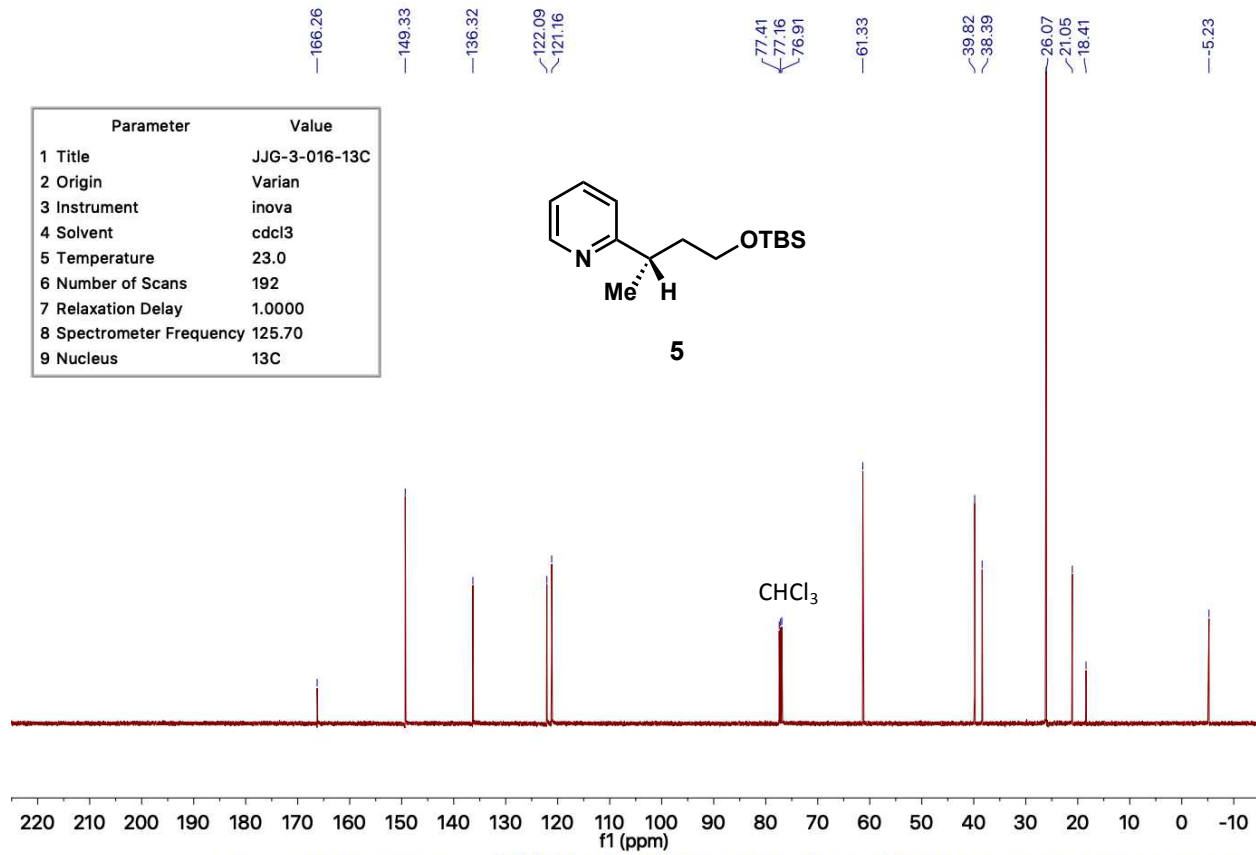


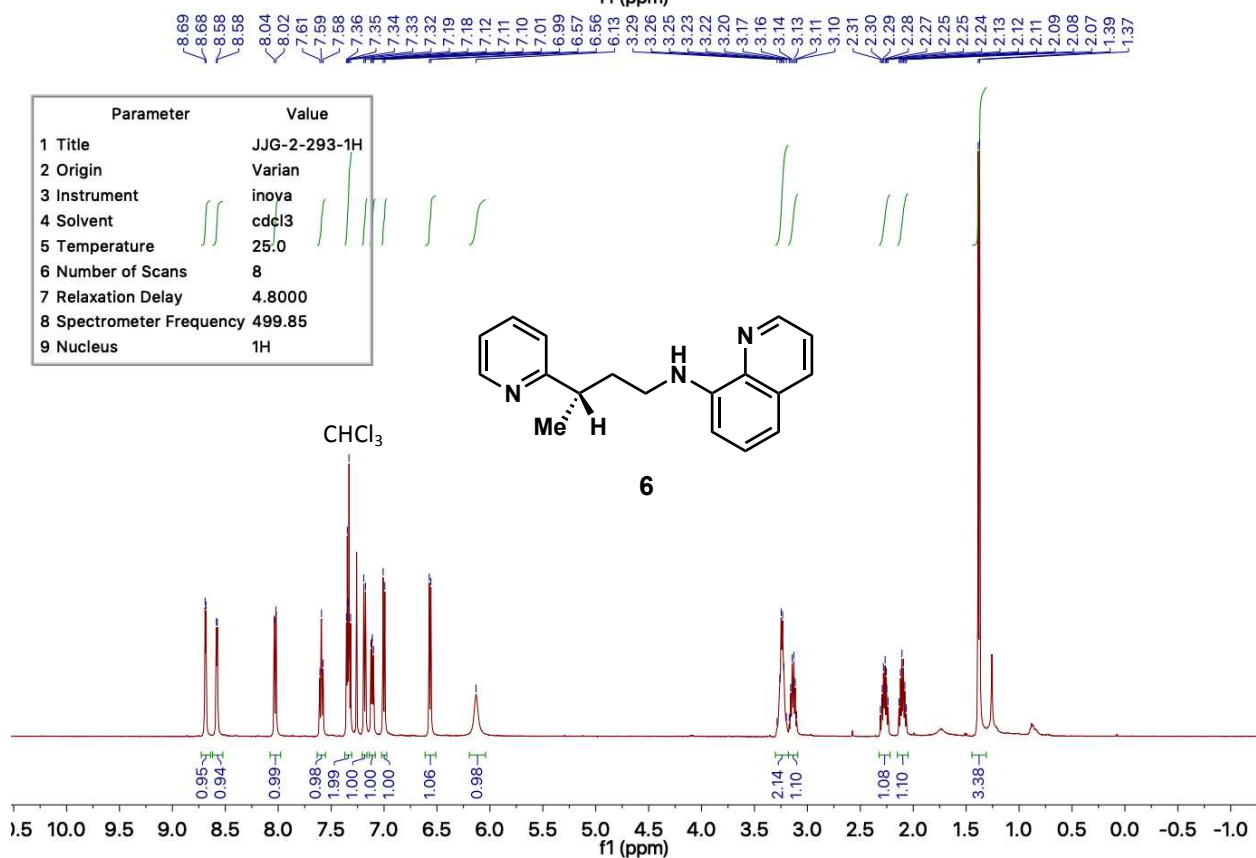
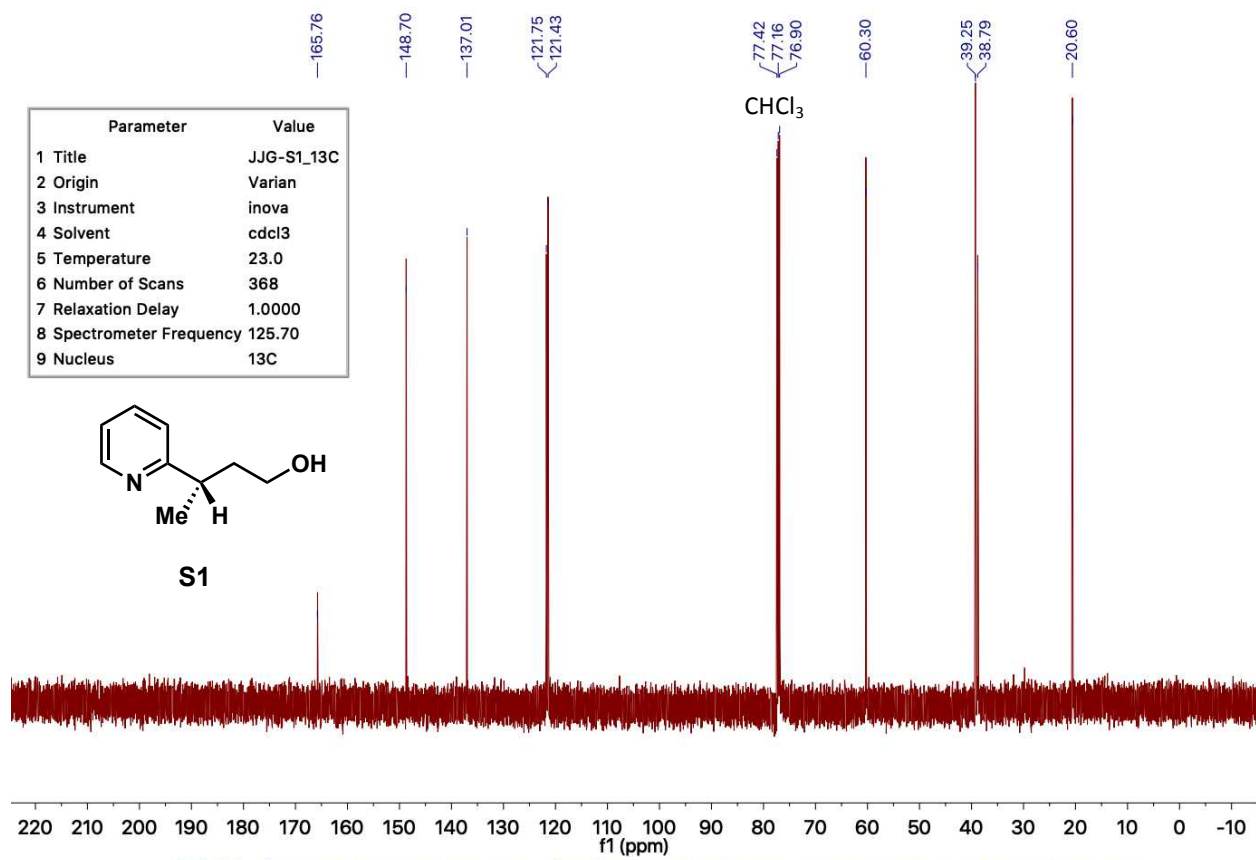
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3 Instrument	inova
4 Solvent	cdcl3
5 Temperature	25.0
6 Number of Scans	4
7 Relaxation Delay	4.8000
8 Spectrometer Frequency	499.85
9 Nucleus	1H



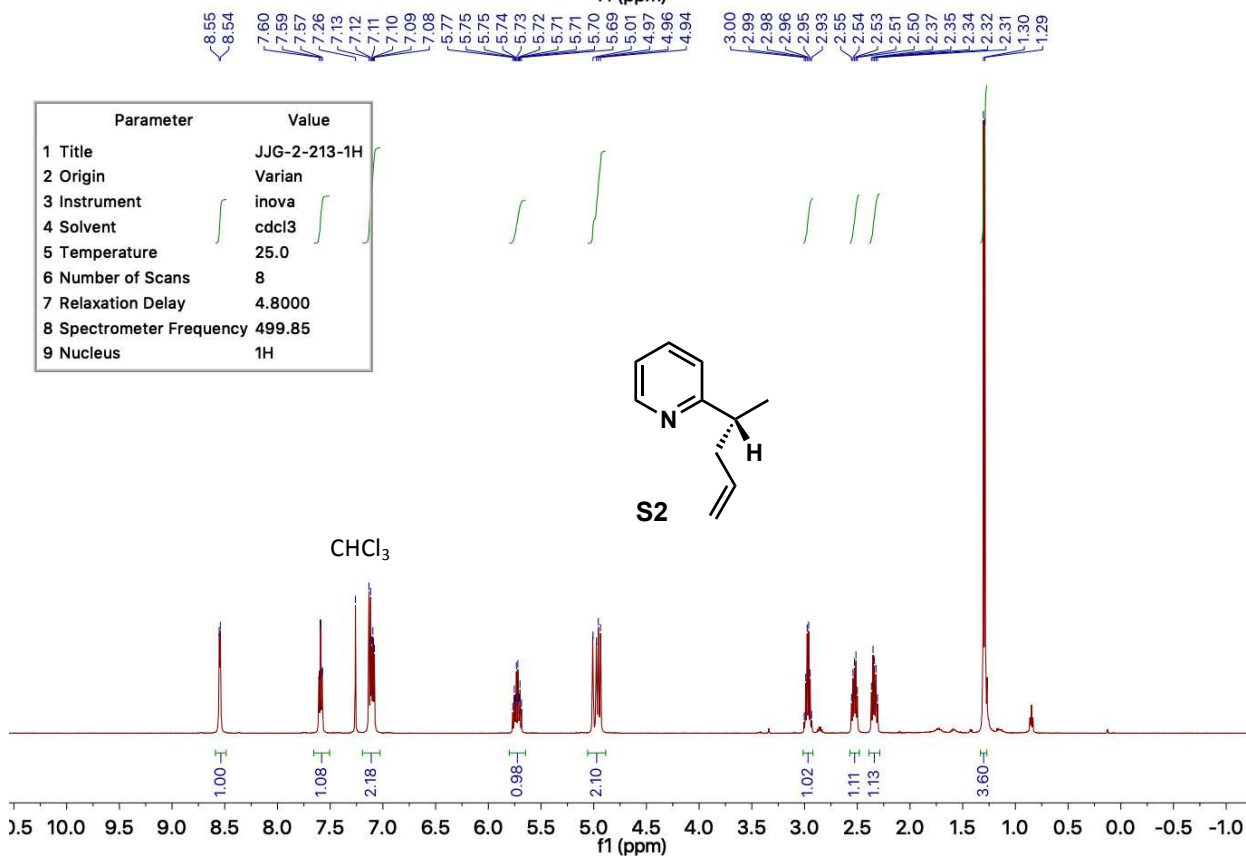
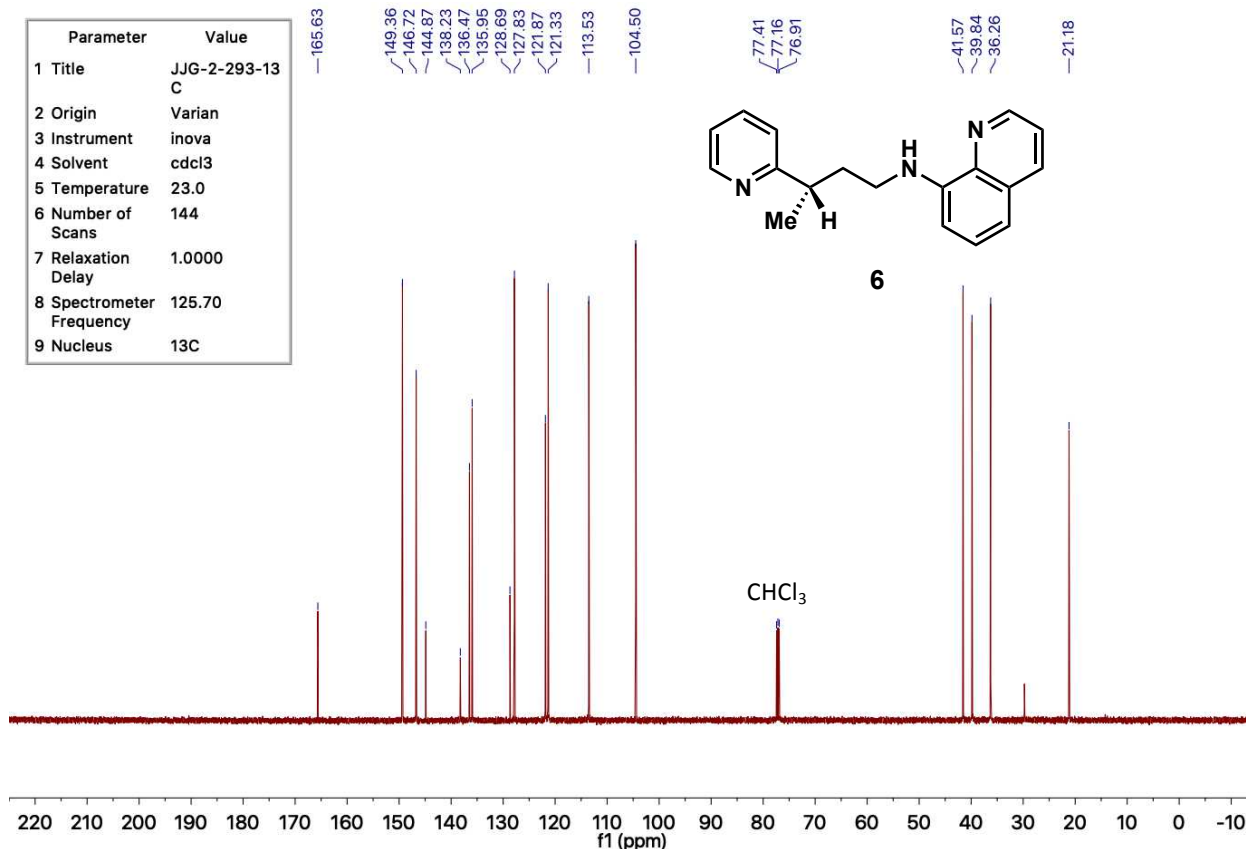


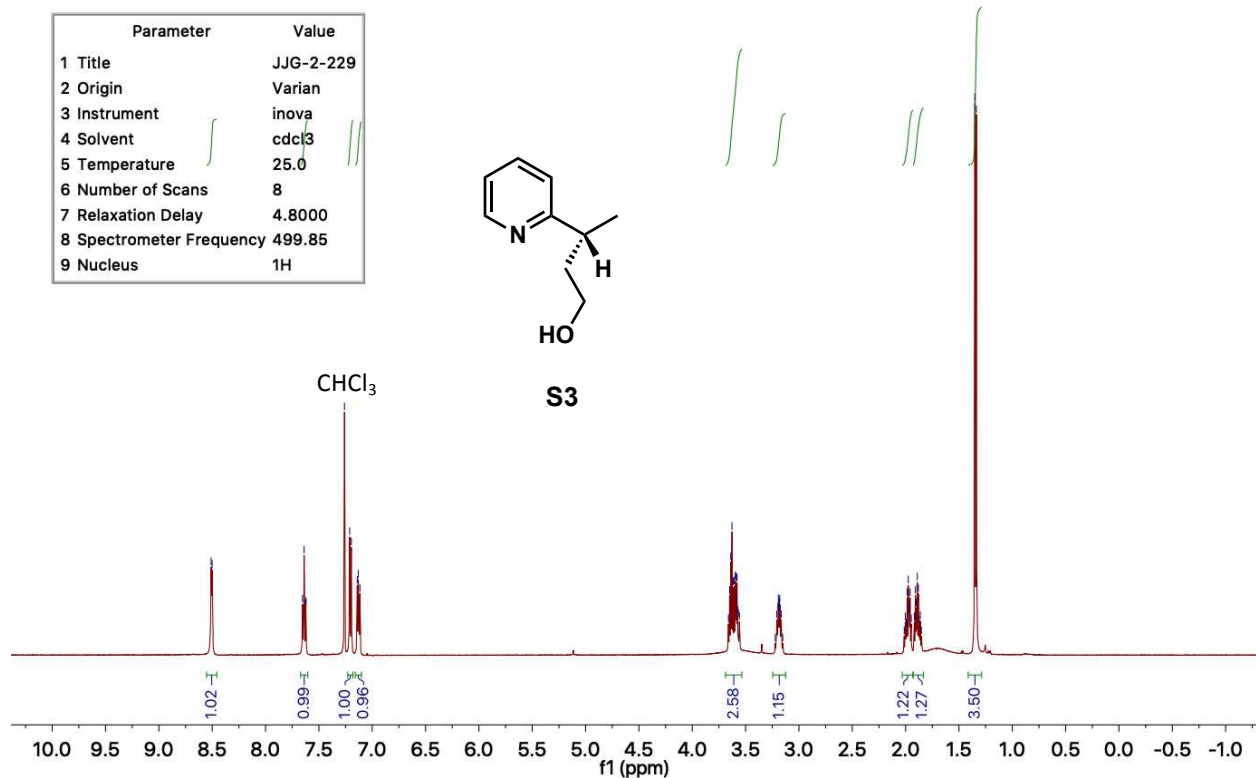
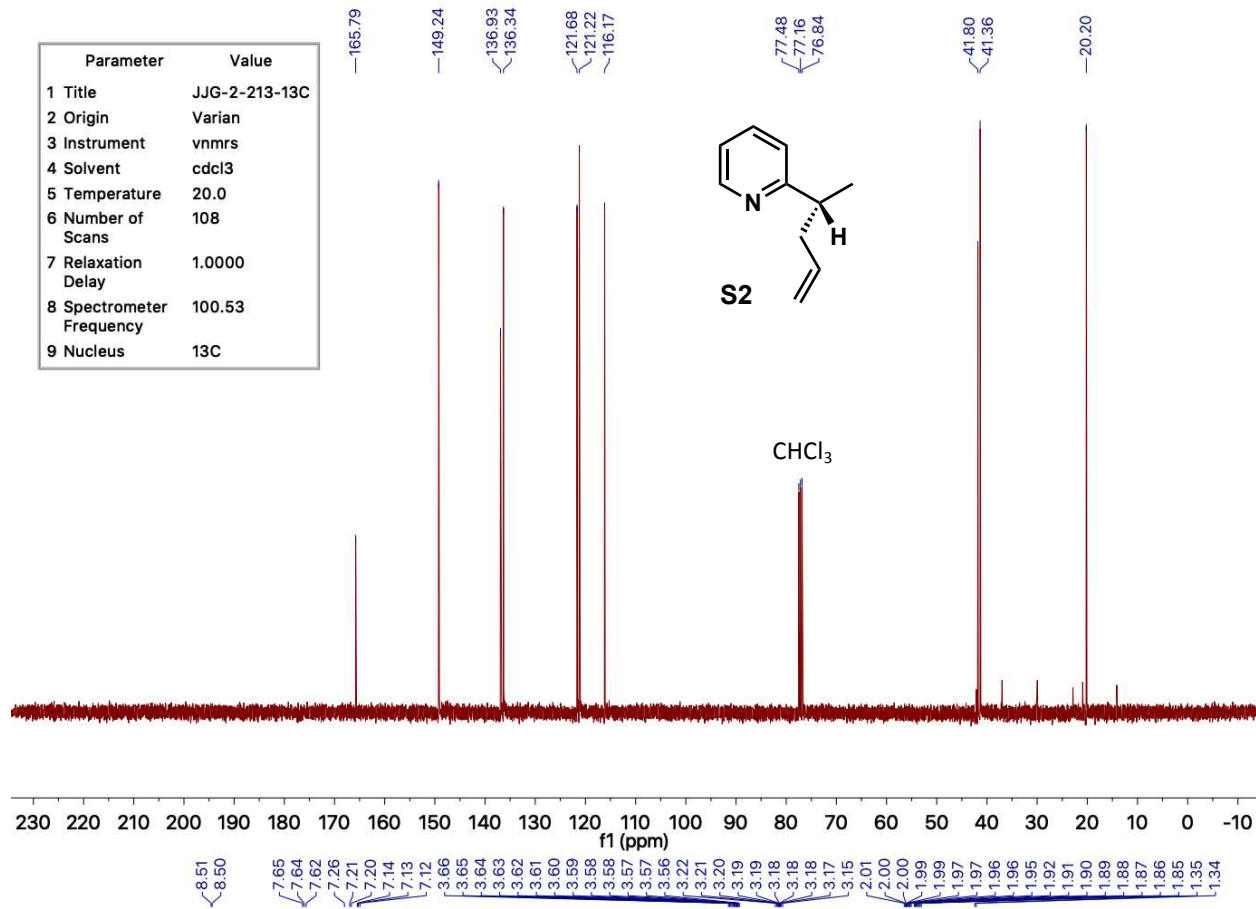


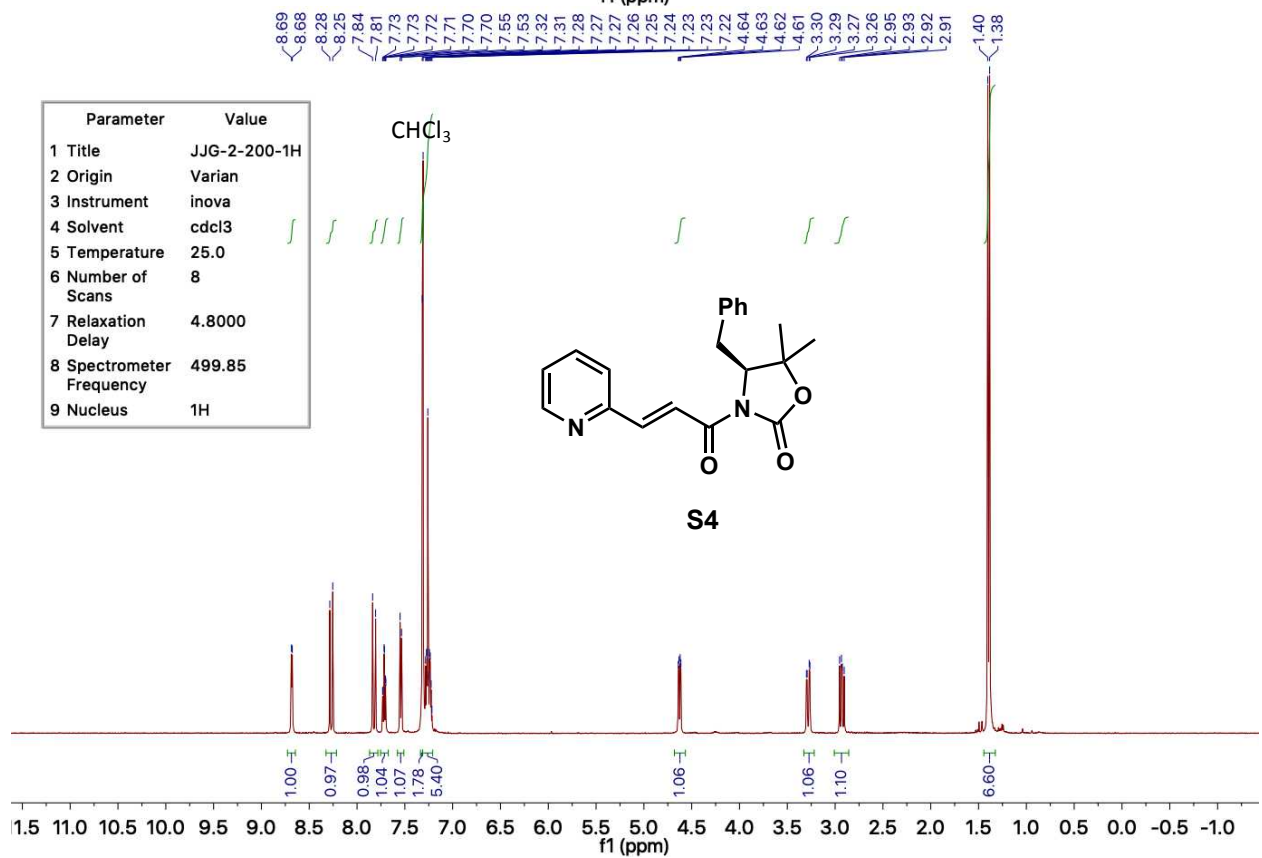
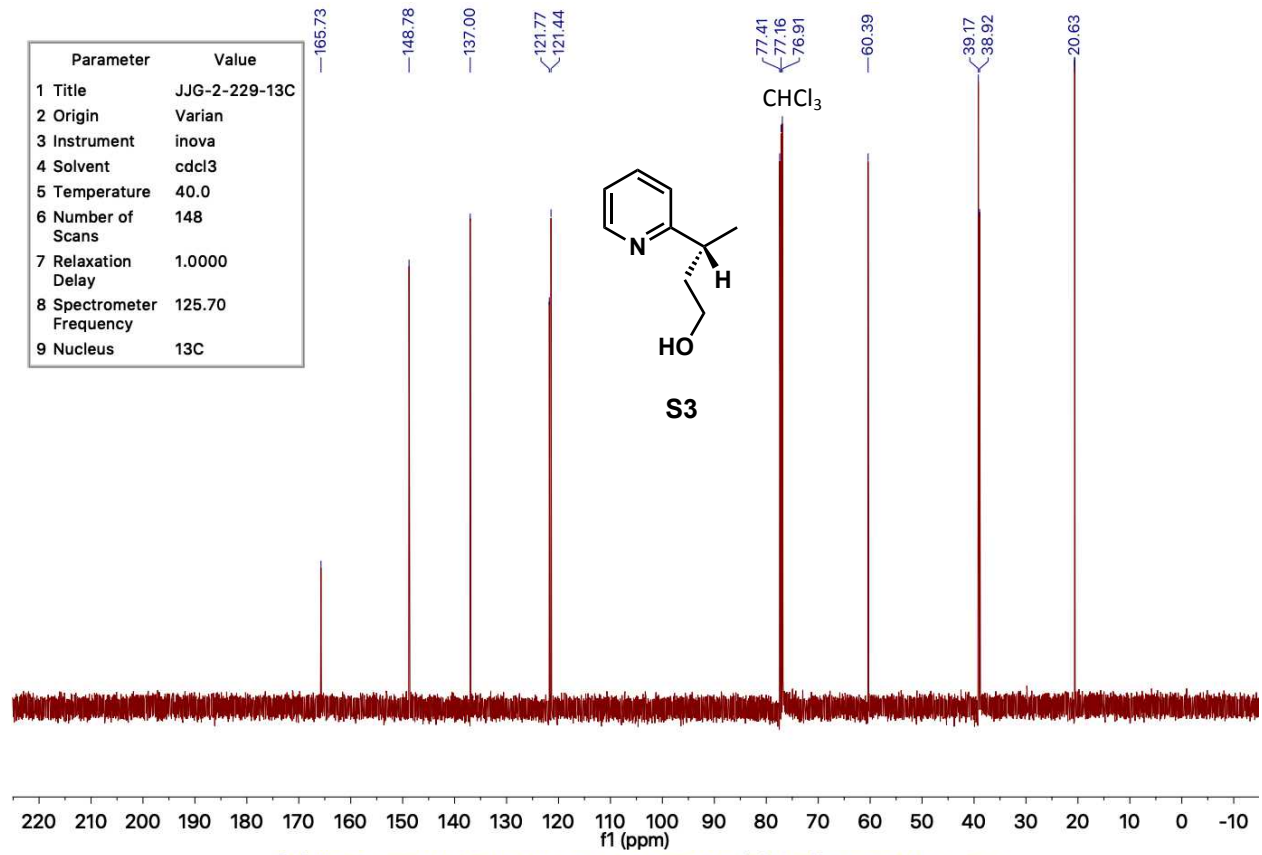


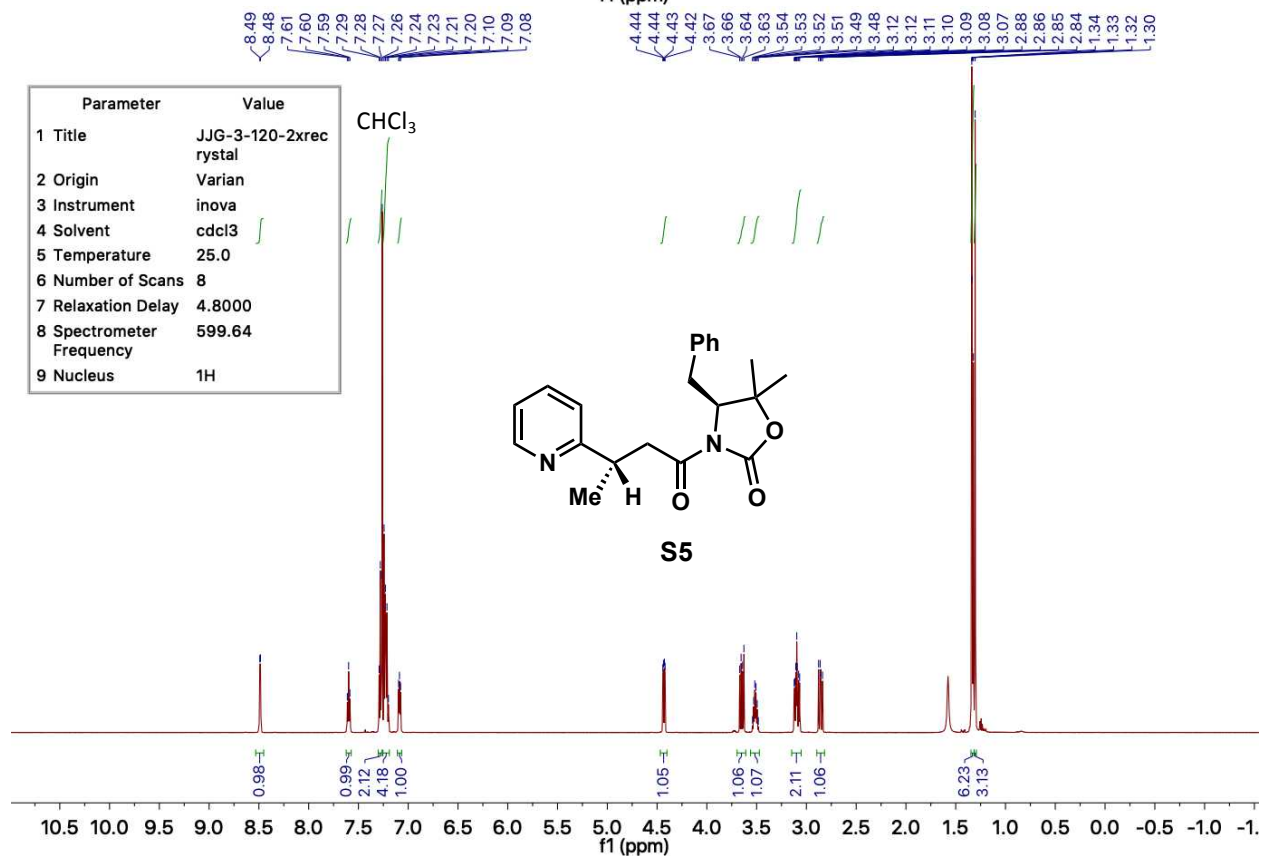
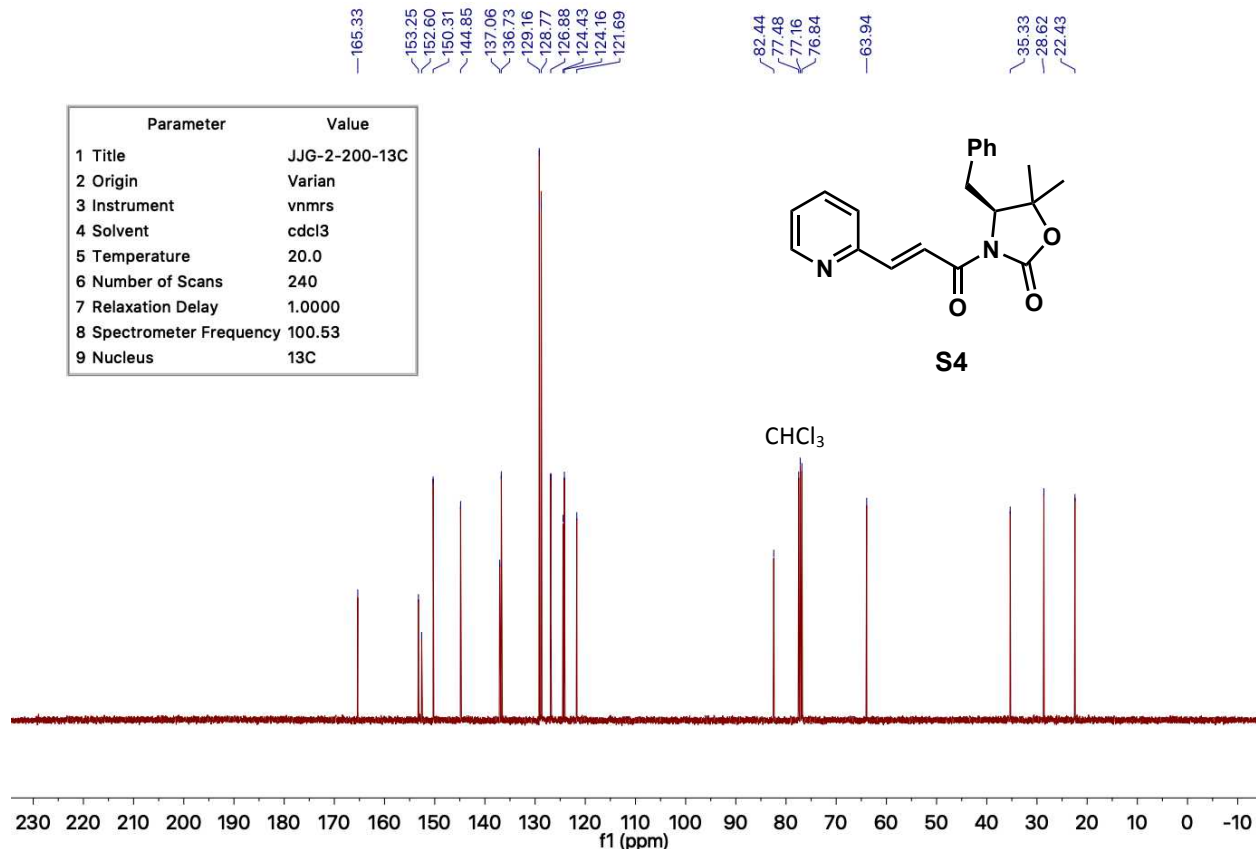


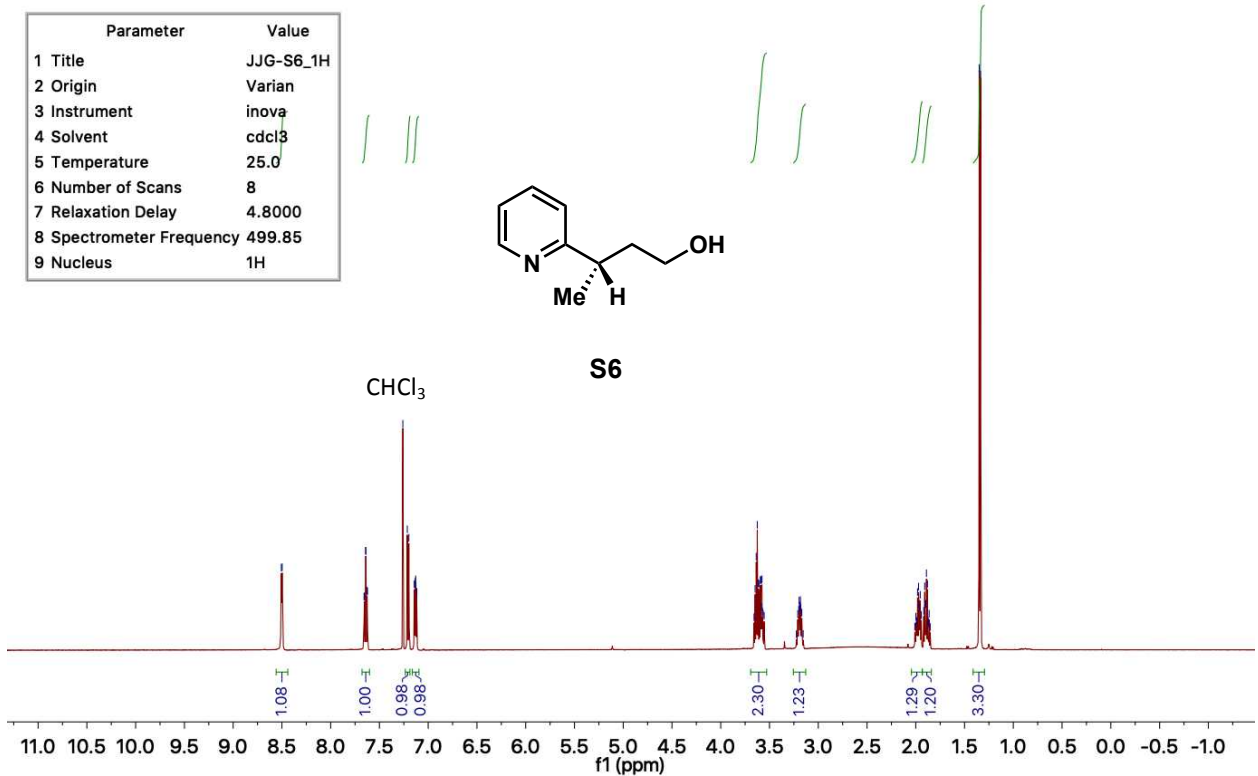
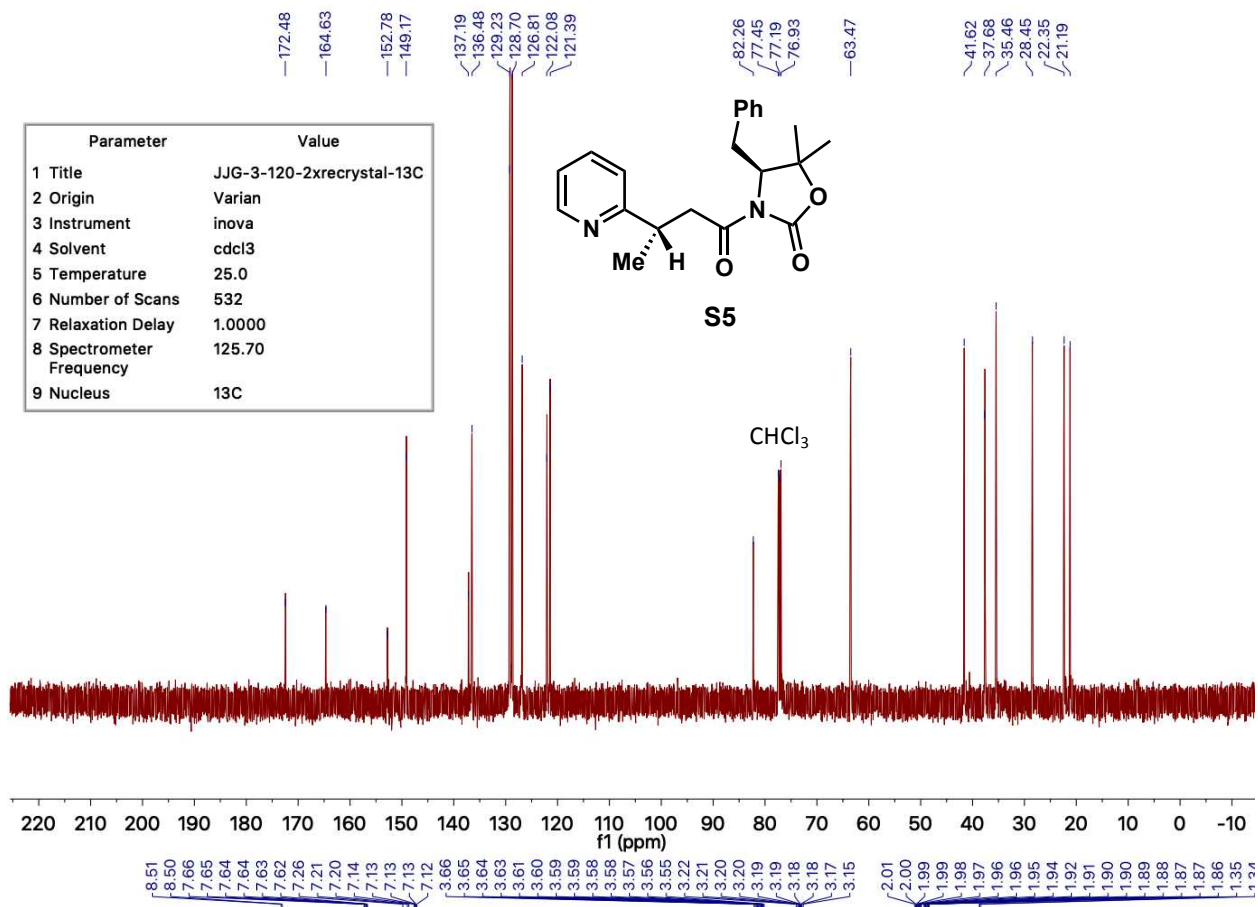
Parameter	Value
1 Title	JJG-2-293-13 C
2 Origin	Varian
3 Instrument	inova
4 Solvent	cdcl3
5 Temperature	23.0
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7 Relaxation Delay	1.0000
8 Spectrometer Frequency	125.70
9 Nucleus	13C

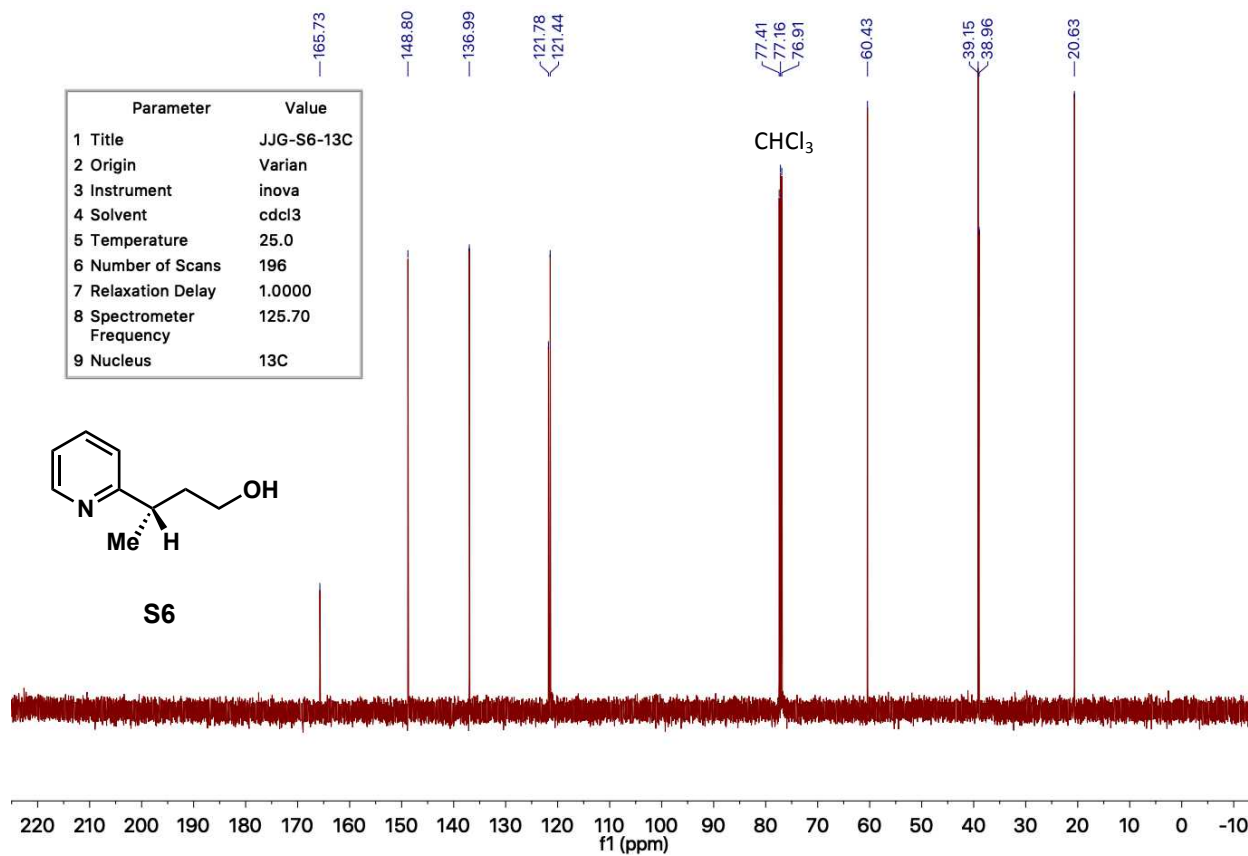












Copies of NMR spectra for aggregate (2-Py)(CH₂CH₂OMe)CHLi•(*R*)-Li¹DA•HMPA **1r**.

1D NMR [³¹P, ⁶Li] Spectroscopic Studies

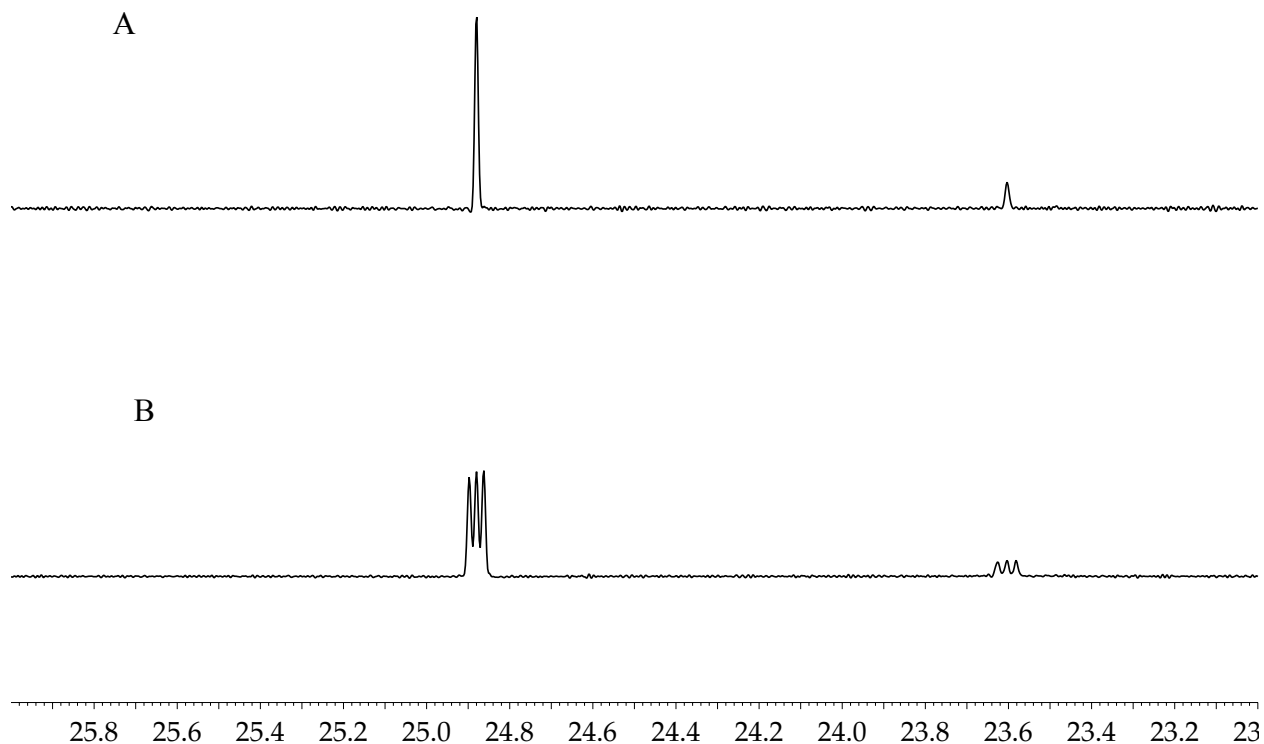


Figure S2-1. ³¹P NMR spectra (202.404 MHz, toluene-*d*₈) of 0.10 M **1r-Li** prepared from (*R*)-¹DA with 2.0 equiv [⁶Li]*n*-BuLi, 1.0 equiv **1r**, and 0.75 equiv HMPA recorded at -80 °C after aging at 0 °C for 40 mins: (A) with broad-band ⁶Li decoupling; (B) fully coupled. δ 24.88 (t, ²*J*_{P-Li} = 3.50), 23.61 (t, ²*J*_{P-Li} = 4.51).

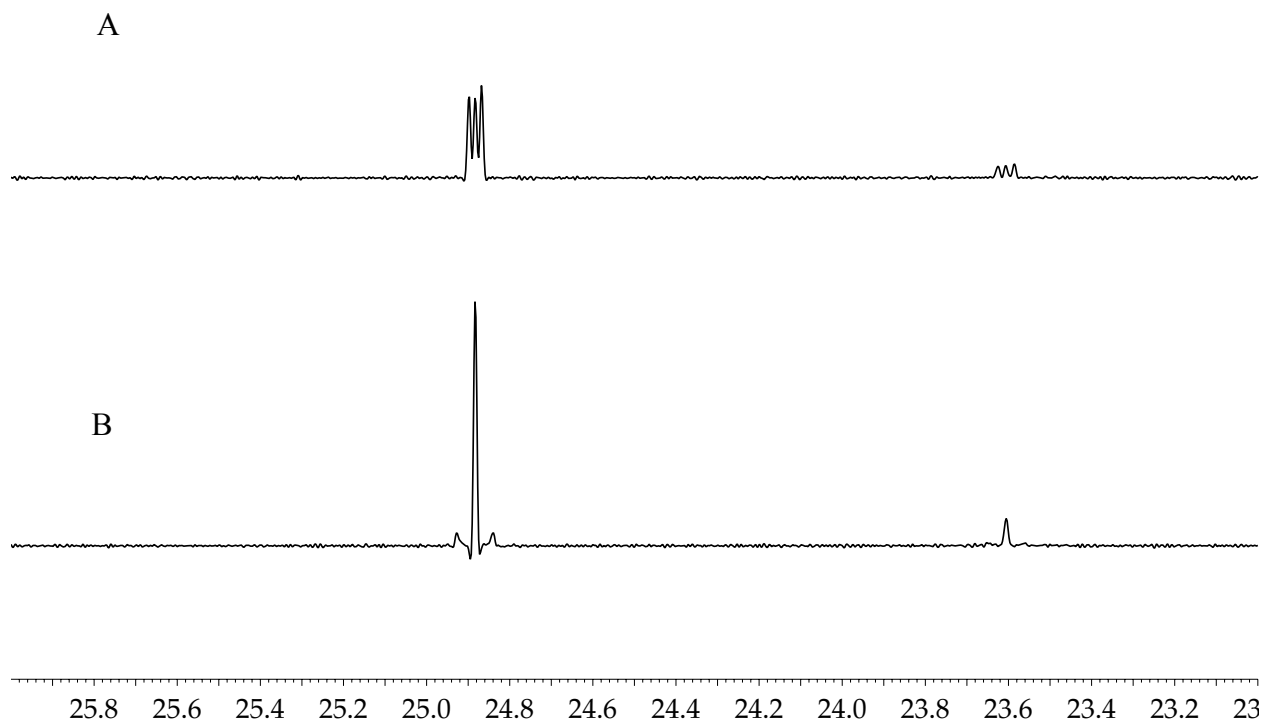


Figure S2-2. ^{31}P NMR spectra (202.404 MHz, toluene- d_8) of 0.10 M **1r-Li** prepared from (*R*)- ^1DA with 2.0 equiv $[\text{}^6\text{Li}]n\text{-BuLi}$, 1.0 equiv **1r**, and 0.75 equiv HMPA recorded at $-80\text{ }^\circ\text{C}$ after aging at $0\text{ }^\circ\text{C}$ for 40 mins: (A) with single frequency ^6Li decoupling 20 Hz off resonance from the ^6Li doublet at 2.48 ppm; (B) with single frequency ^6Li decoupling of the ^6Li doublet at 2.48 ppm.

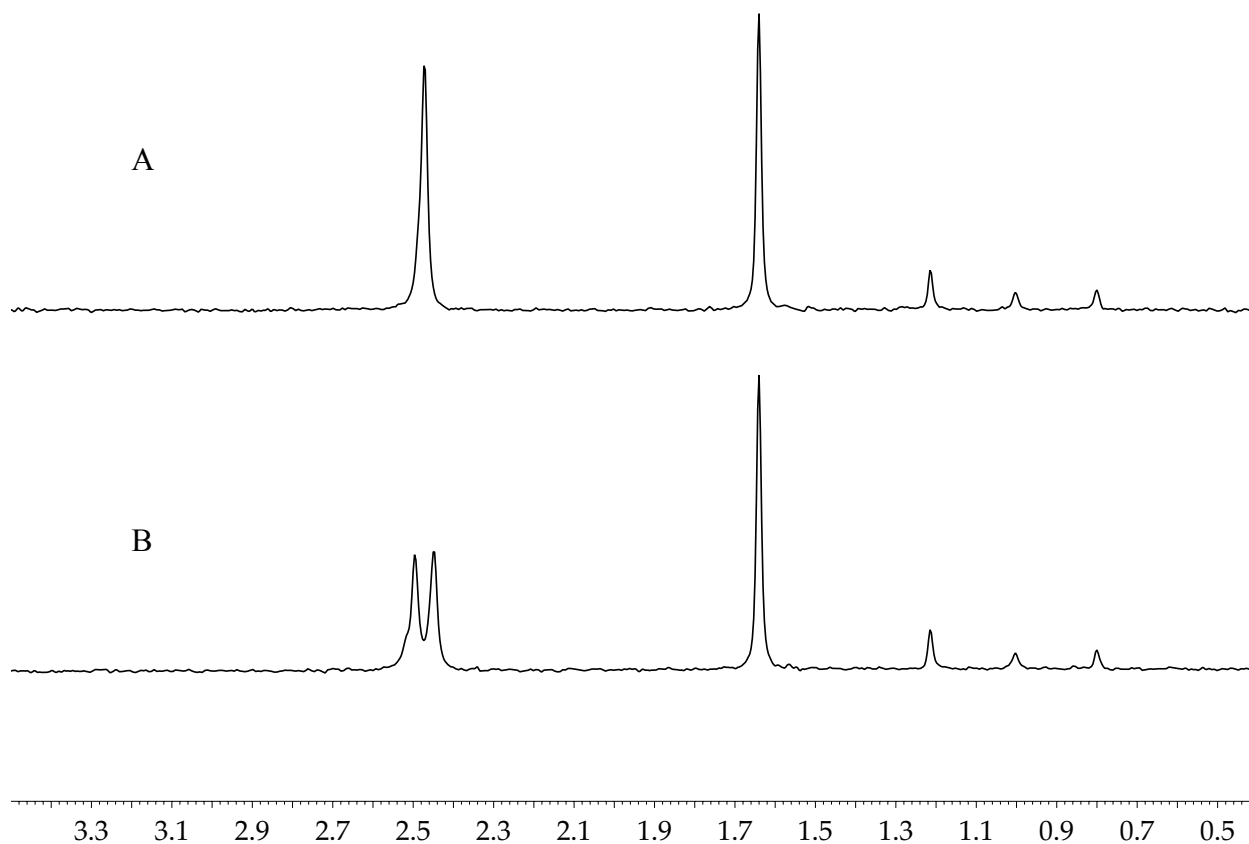


Figure S2-3. ${}^6\text{Li}$ NMR spectra (73.578 MHz, toluene- d_8) of 0.10 M **1r-Li** prepared from (*R*)- ${}^1\text{DA}$ with 2.0 equiv $[\text{}^6\text{Li}]n\text{-BuLi}$, 1.0 equiv **1r**, and 0.75 equiv HMPA recorded at $-80\text{ }^\circ\text{C}$ after aging at $0\text{ }^\circ\text{C}$ for 40 mins: (A) with broad-band ${}^{31}\text{P}$ decoupling; (B) fully coupled. δ 2.47 (d, ${}^2J_{\text{Li-P}}=3.50$), 1.64 (s).

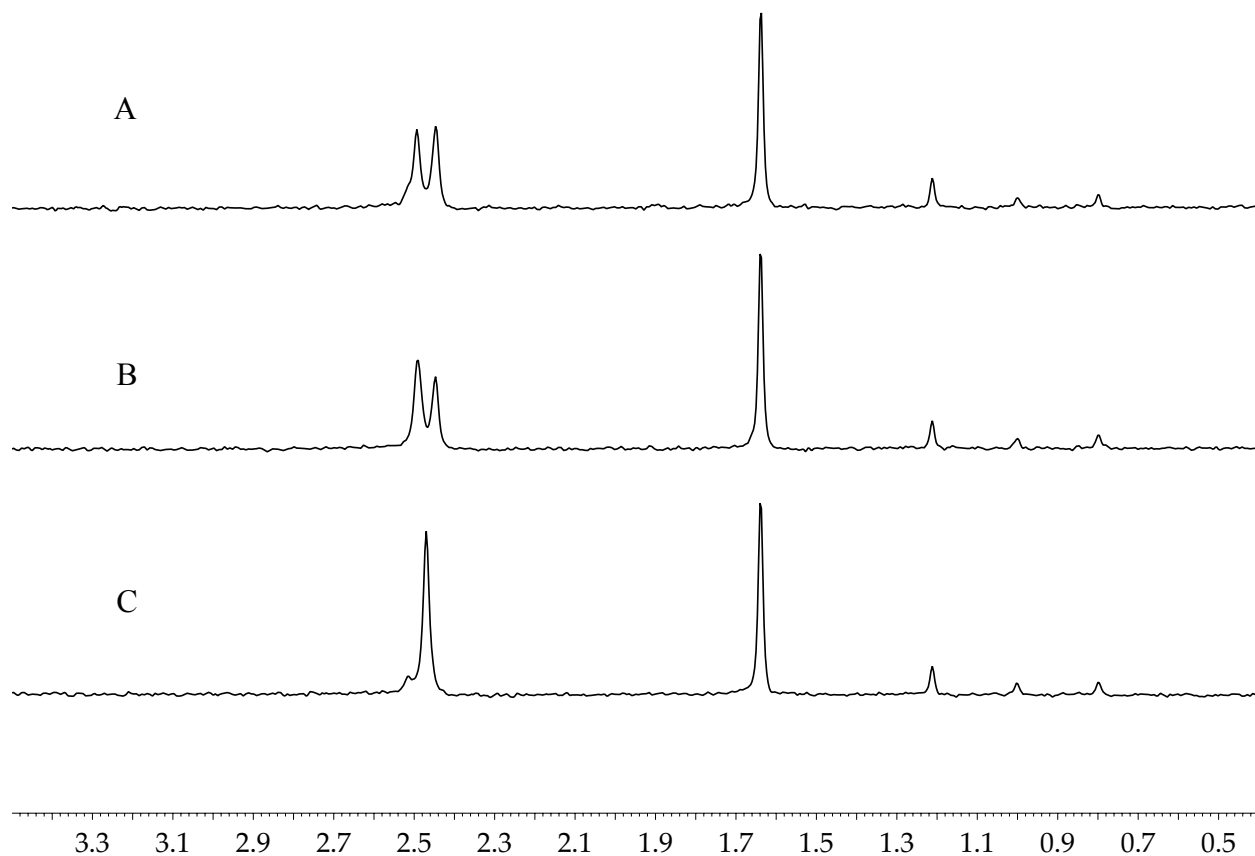


Figure S2-4. ^6Li NMR spectra (73.578 MHz, toluene- d_8) of 0.10 M **1r**-Li prepared from (*R*)- ^1DA with 2.0 equiv $[\text{}^6\text{Li}]n\text{-BuLi}$, 1.0 equiv **1r**, and 0.75 equiv HMPA recorded at $-80\text{ }^\circ\text{C}$ after aging at $0\text{ }^\circ\text{C}$ for 40 mins: (A) off-resonance decoupling; (B) on-resonance decoupling of the ^{31}P triplet at 23.61 ppm; (C) on-resonance decoupling of the ^{31}P triplet at 24.9 ppm.

Parameter	Value
Experiment	1D
Pulse Sequence	s2pul
Solvent	toluene
Temperature	-80.0
Number of Scans	16
Receiver Gain	0
Relaxation Delay	1.5000
Pulse Width	7.7500
Acquisition Time	5.2429
Nucleus	^1H
Spectrometer Frequency	499.92
Spectral Width	6250.0
Acquired Size	32768
Spectral Size	65536

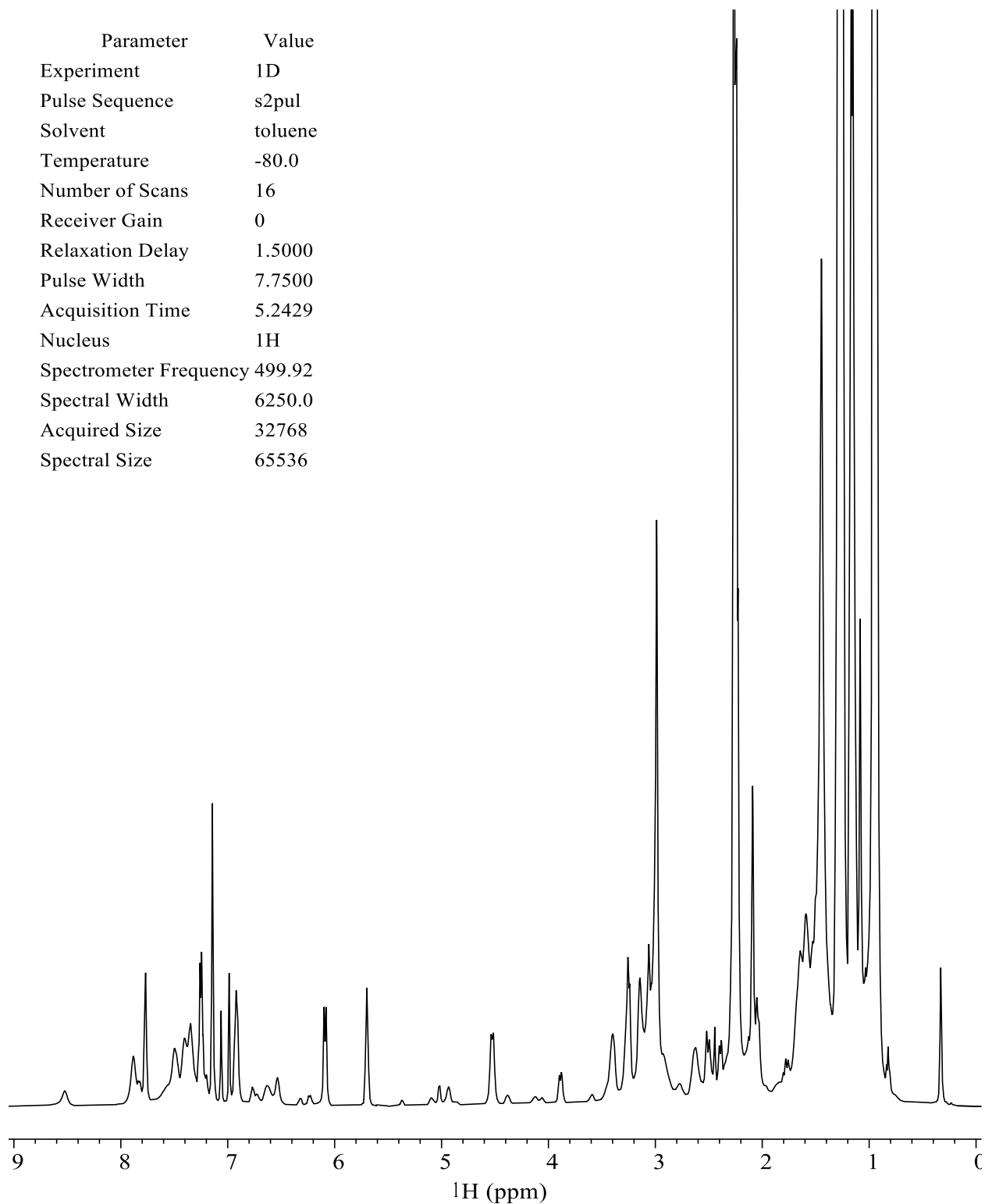


Figure S2-5. ^1H NMR spectrum (499.76 MHz, toluene- d_8) at $-80\text{ }^\circ\text{C}$ of a sample containing **1r-Li**.