

## Supporting information

### **Ag(I)-catalyzed rapid access to 2-amino-4-methylenethiazolines with potential application in bioconjugation chemistry**

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## 1. X-ray crystal structure analysis

The crystallographic data for compounds **2a** and **3e** have been deposited in Cambridge Crystallographic Data Centre (CCDC) with deposition Numbers of 2068592 and 2068587, respectively. These data can be obtained free of charge from CCDC via <https://www.ccdc.cam.ac.uk/structures/>.

Table S1 Crystal data and structure refinement for compound **2a**.

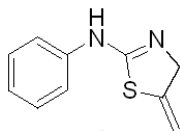
Identification code	2a
Empirical formula	C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> S
Formula weight	190.26
Temperature/K	190.0
Crystal system	triclinic
Space group	P-1
a/Å	8.4613(5)
b/Å	11.5857(7)
c/Å	20.5398(13)
α/°	105.707(4)
β/°	100.475(4)
γ/°	90.015(4)
Volume/Å <sup>3</sup>	1903.4(2)
Z	8
ρ <sub>calc</sub> /cm <sup>3</sup>	1.328
μ/mm <sup>-1</sup>	1.720
F(000)	800.0
Crystal size/mm <sup>3</sup>	0.12 × 0.1 × 0.1
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	3.96 to 121.466
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 14, -26 ≤ l ≤ 26
Reflections collected	23108
Independent reflections	8548 [R <sub>int</sub> = 0.0761, R <sub>sigma</sub> = 0.1039]
Data/restraints/parameters	8548/0/469
Goodness-of-fit on F <sup>2</sup>	1.045
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0625, wR <sub>2</sub> = 0.1331
Final R indexes [all data]	R <sub>1</sub> = 0.1374, wR <sub>2</sub> = 0.1614
Largest diff. peak/hole / e Å <sup>-3</sup>	0.41/-0.37

Table S2 Crystal data and structure refinement for compound **3e**.

Identification code	3e
Empirical formula	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> S
Formula weight	196.31
Temperature/K	190.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	16.845(2)
b/Å	7.2075(11)
c/Å	9.0263(13)
α/°	90
β/°	104.890(6)
γ/°	90
Volume/Å <sup>3</sup>	1059.1(3)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.231
μ/mm <sup>-1</sup>	1.547
F(000)	424.0
Crystal size/mm <sup>3</sup>	0.12 × 0.1 × 0.1
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	11.682 to 123.988
Index ranges	-18 ≤ h ≤ 21, -6 ≤ k ≤ 9, -11 ≤ l ≤ 8
Reflections collected	7889
Independent reflections	2450 [R <sub>int</sub> = 0.0445, R <sub>sigma</sub> = 0.0442]
Data/restraints/parameters	2450/0/118
Goodness-of-fit on F <sup>2</sup>	1.121
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0454, wR <sub>2</sub> = 0.1238
Final R indexes [all data]	R <sub>1</sub> = 0.0536, wR <sub>2</sub> = 0.1306
Largest diff. peak/hole / e Å <sup>-3</sup>	0.28/-0.46

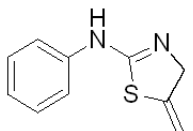
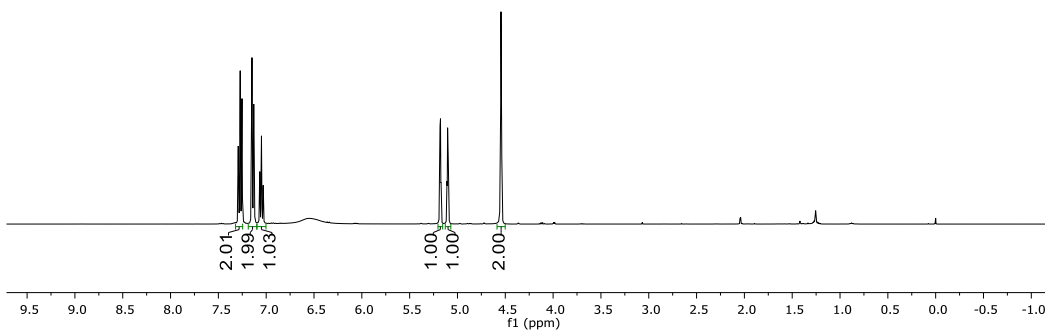
## 2. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds

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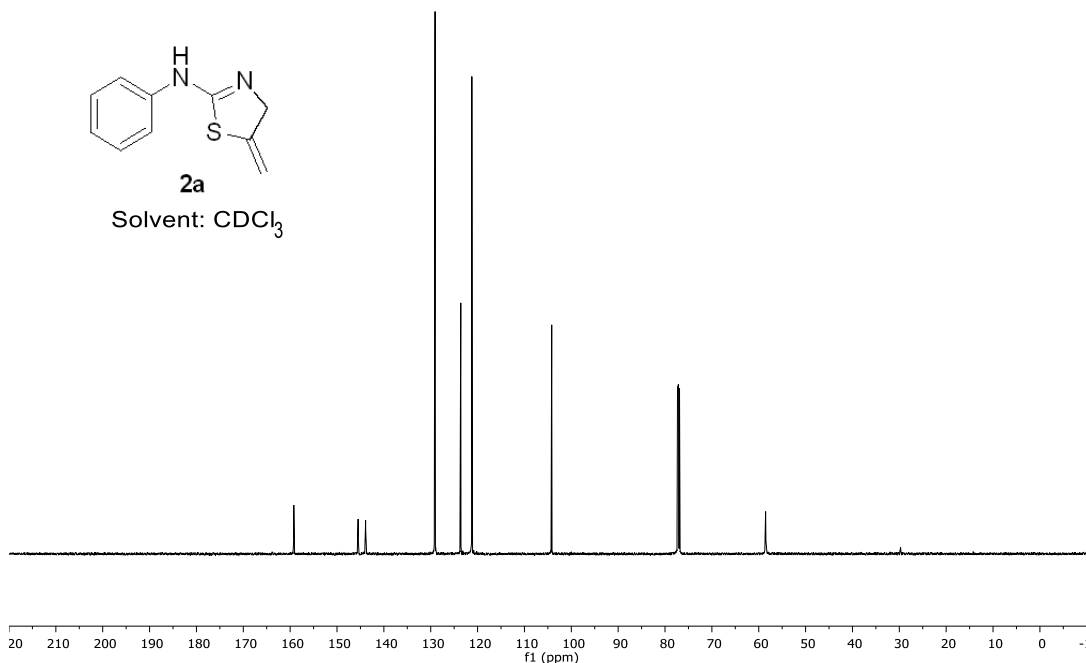
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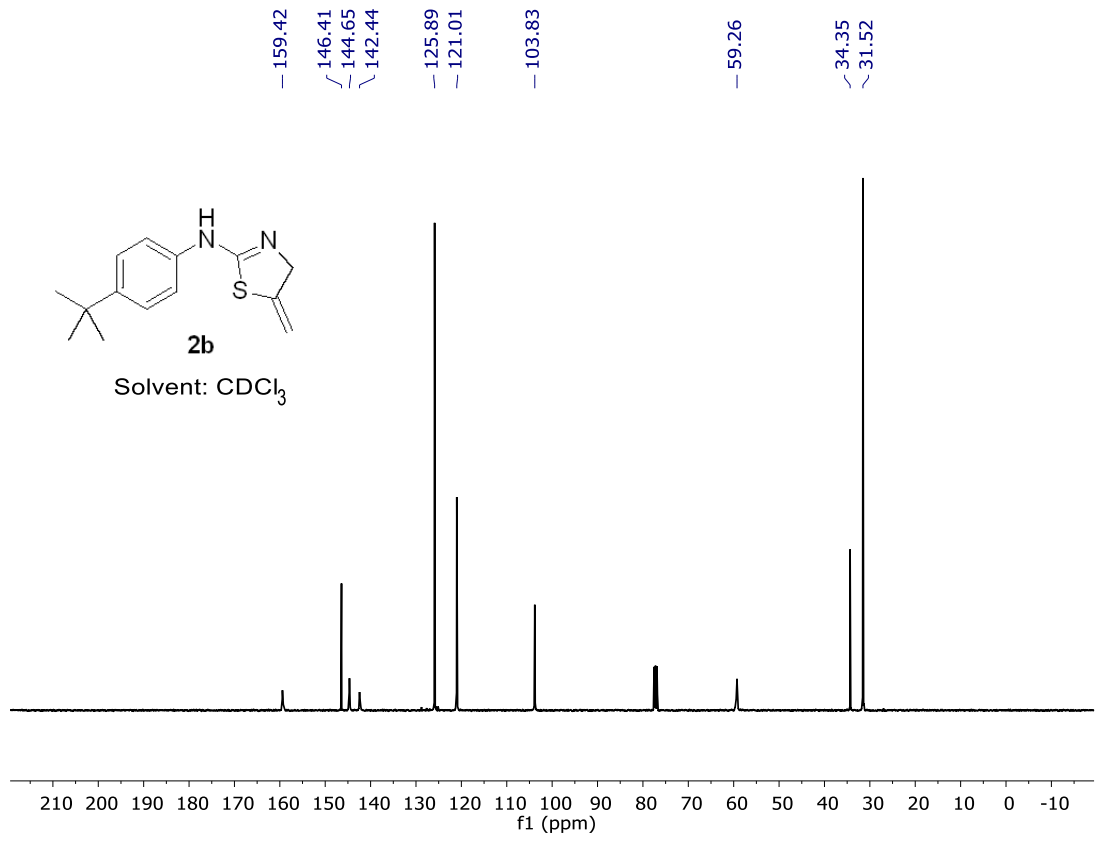
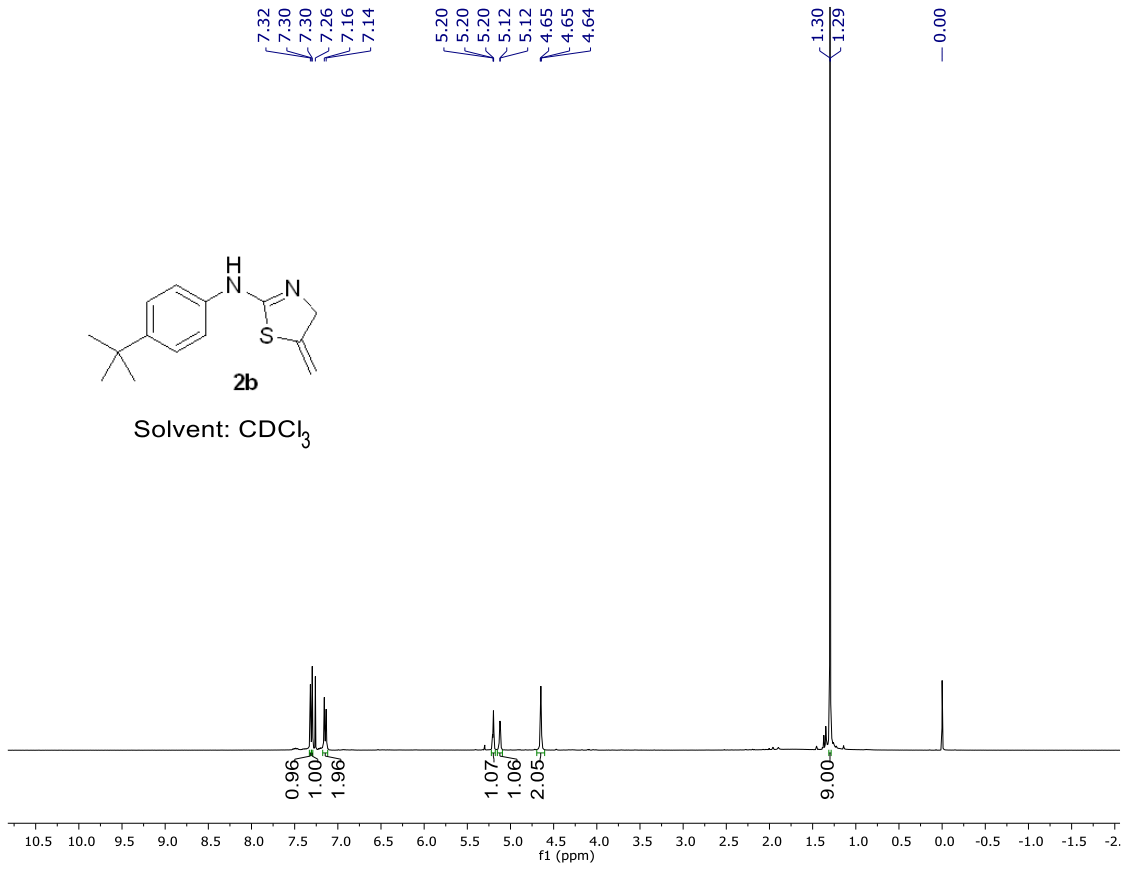
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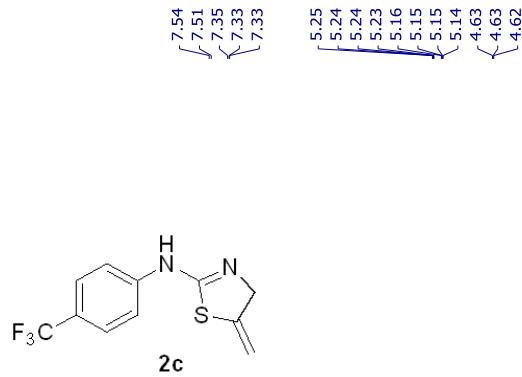


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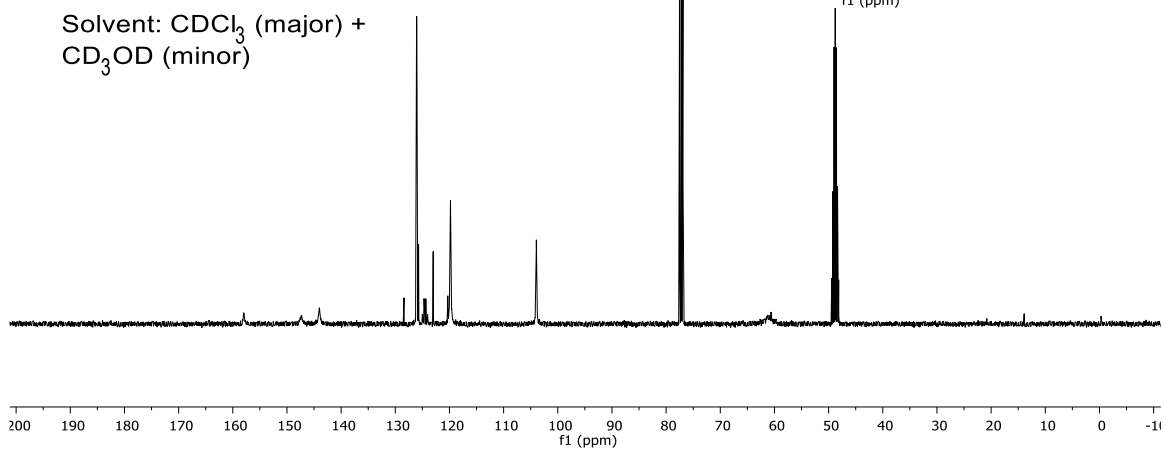
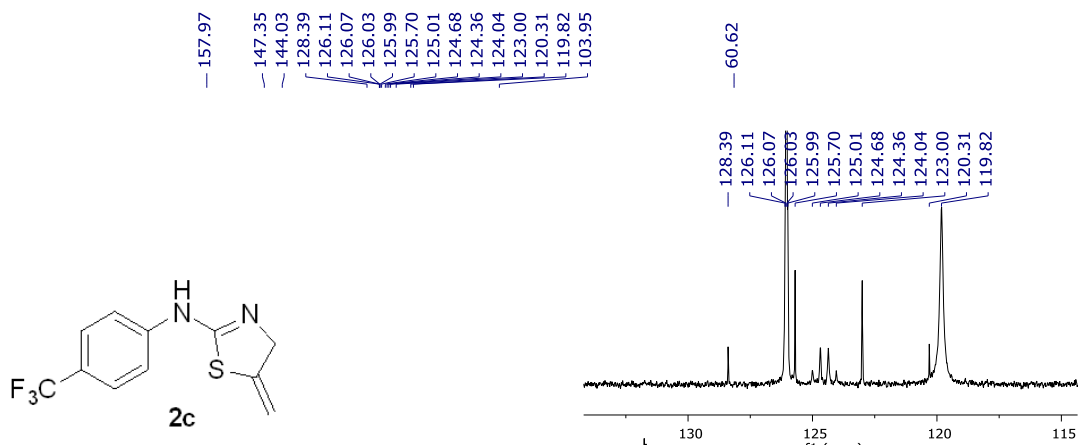
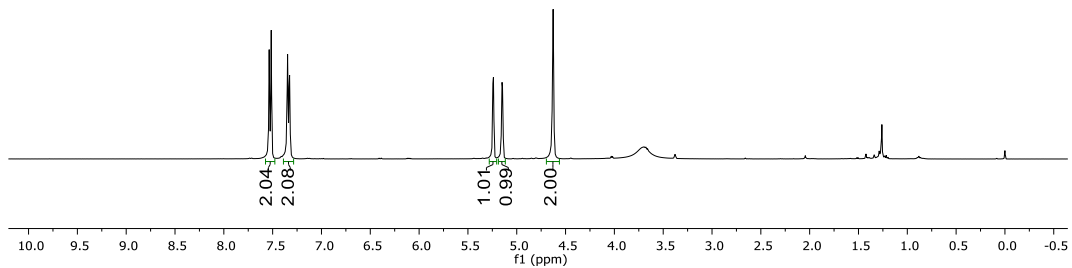
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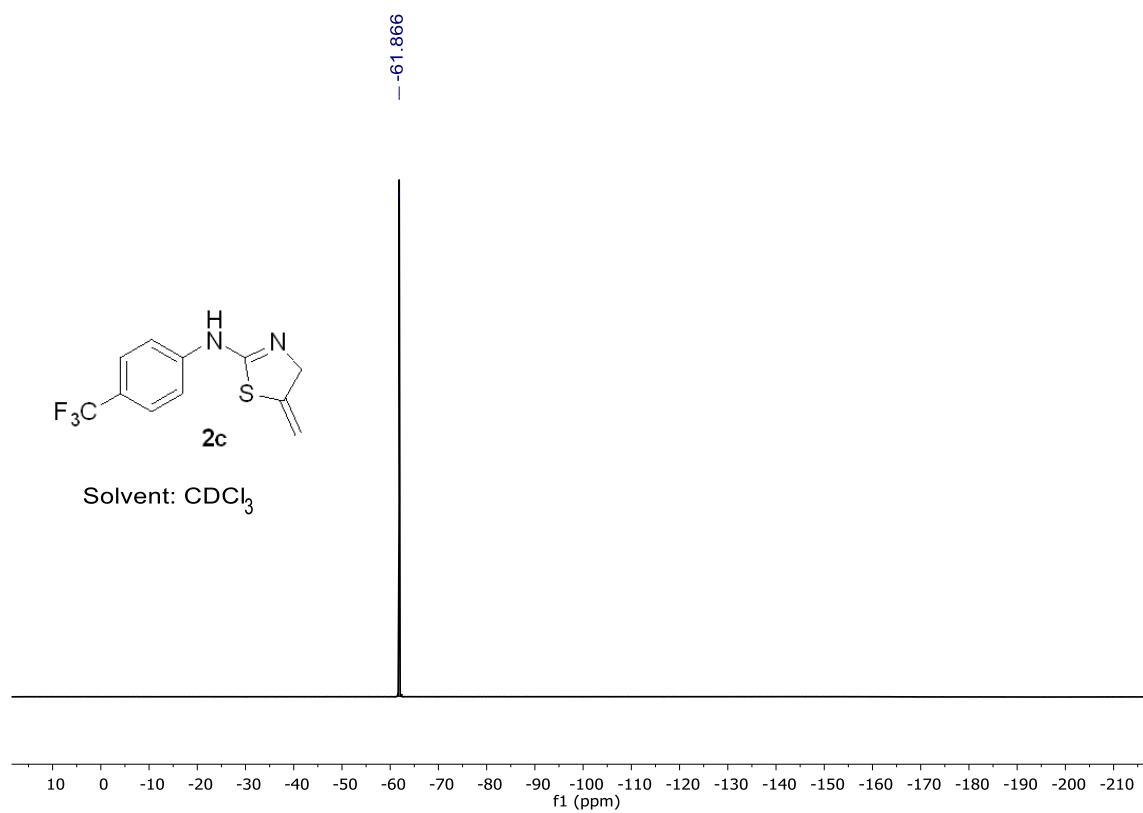
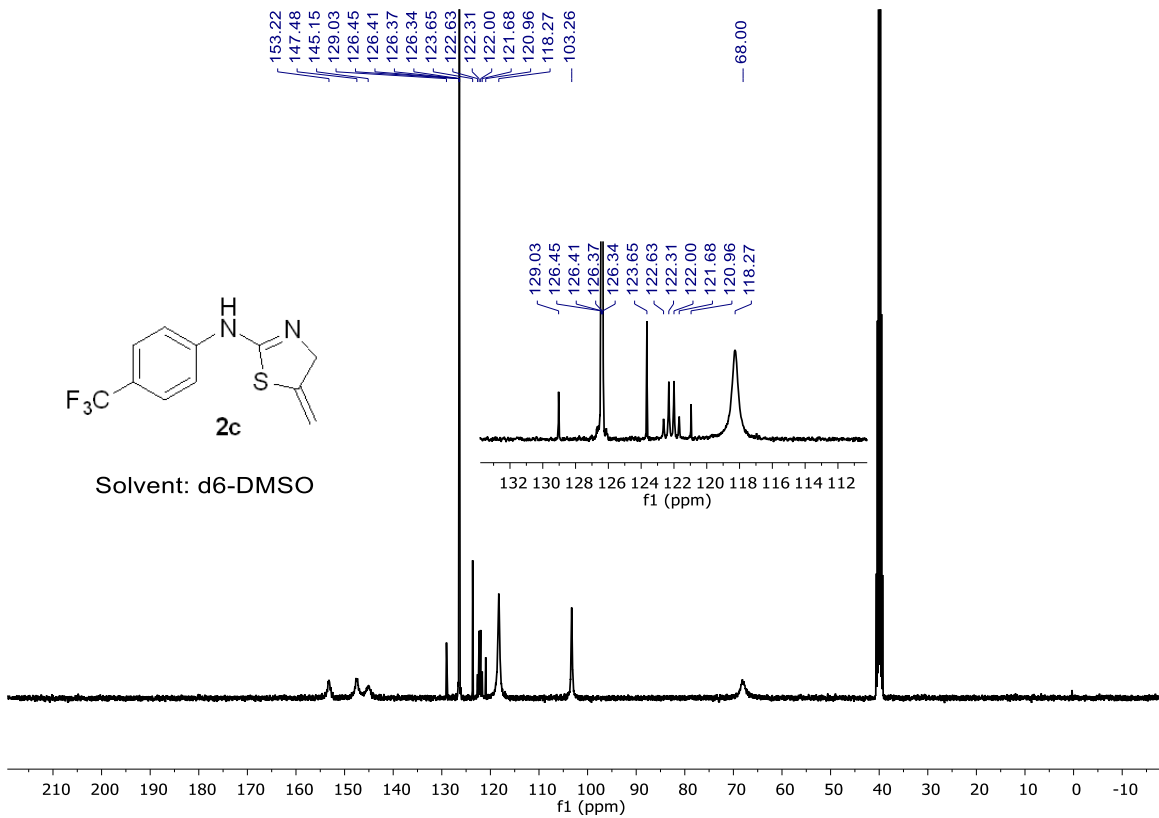


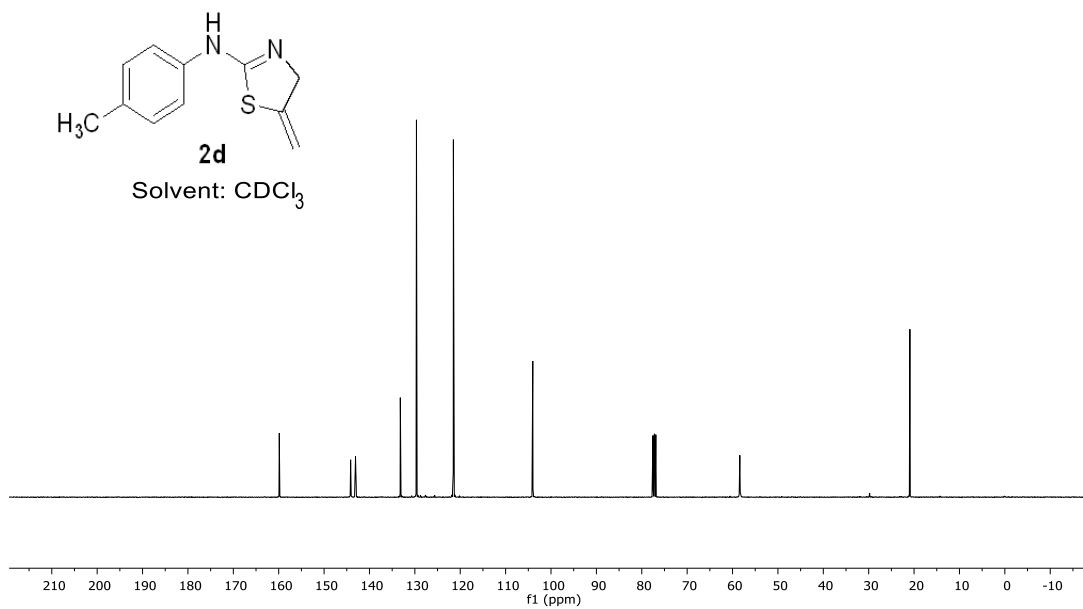
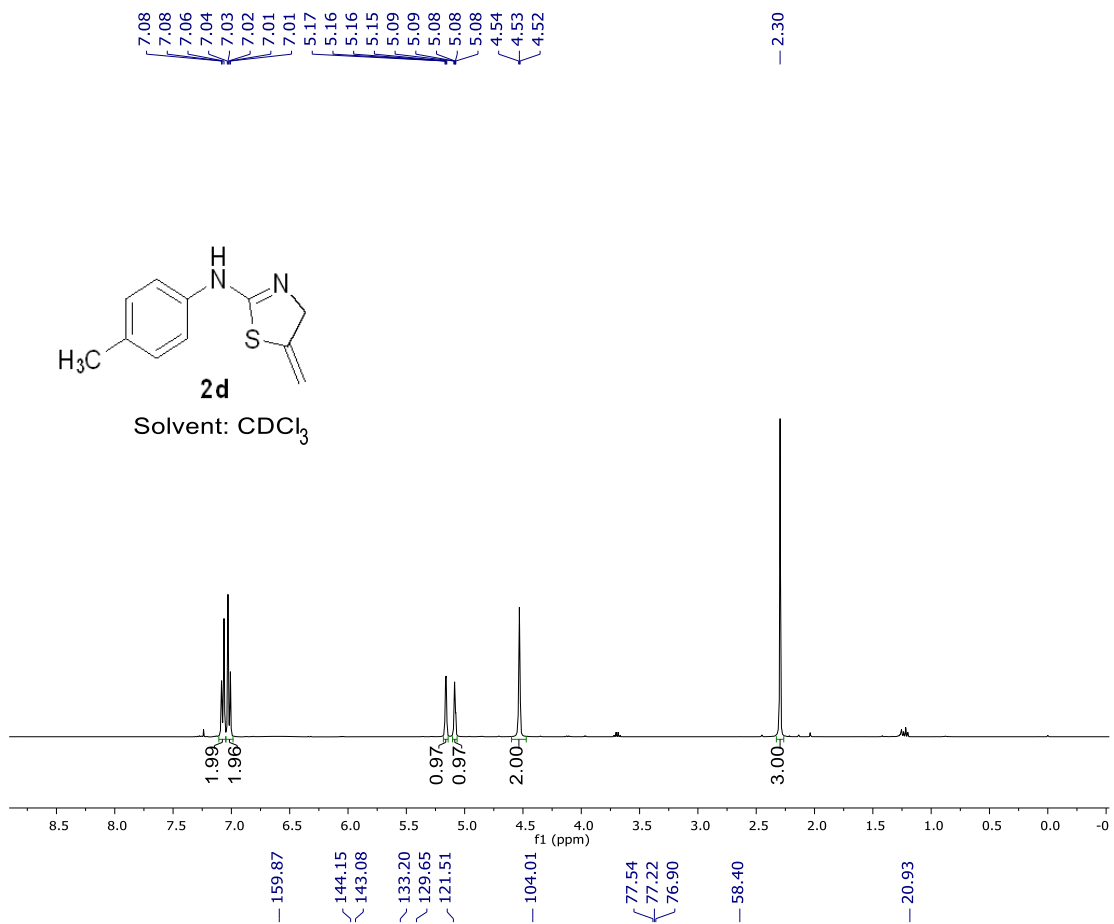




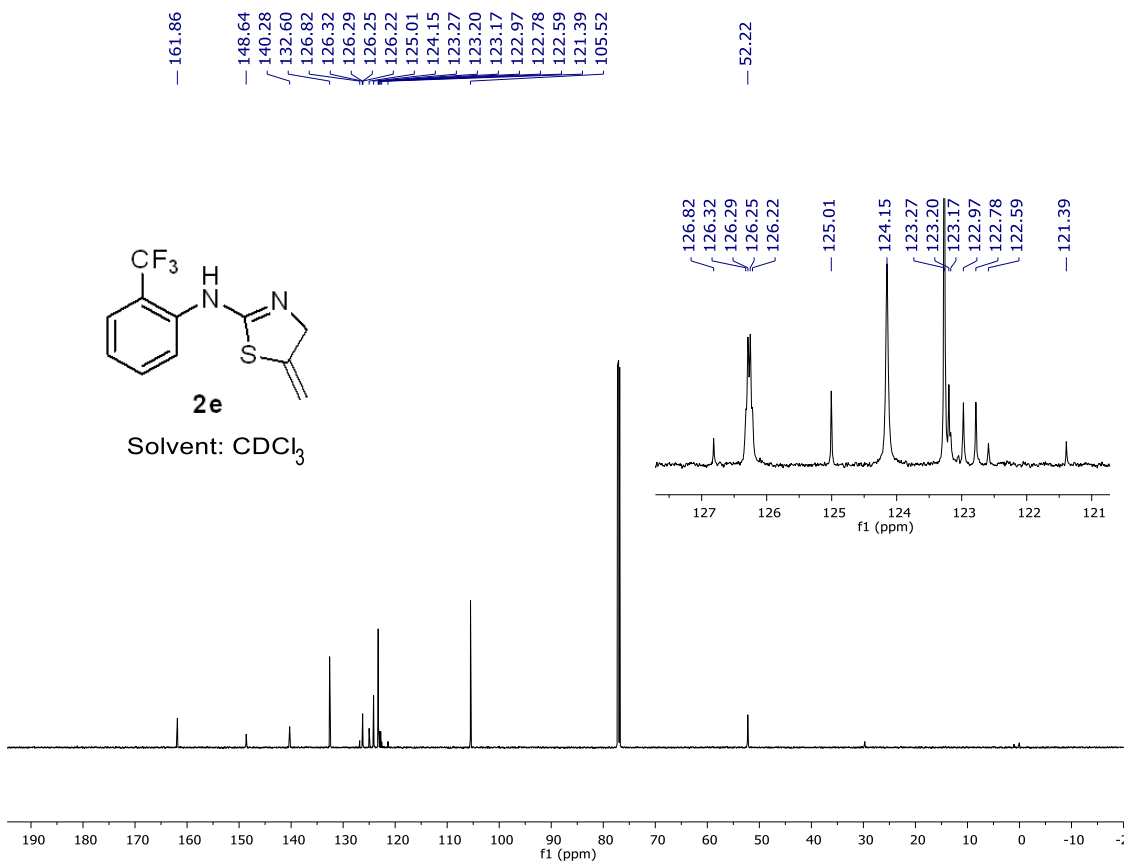
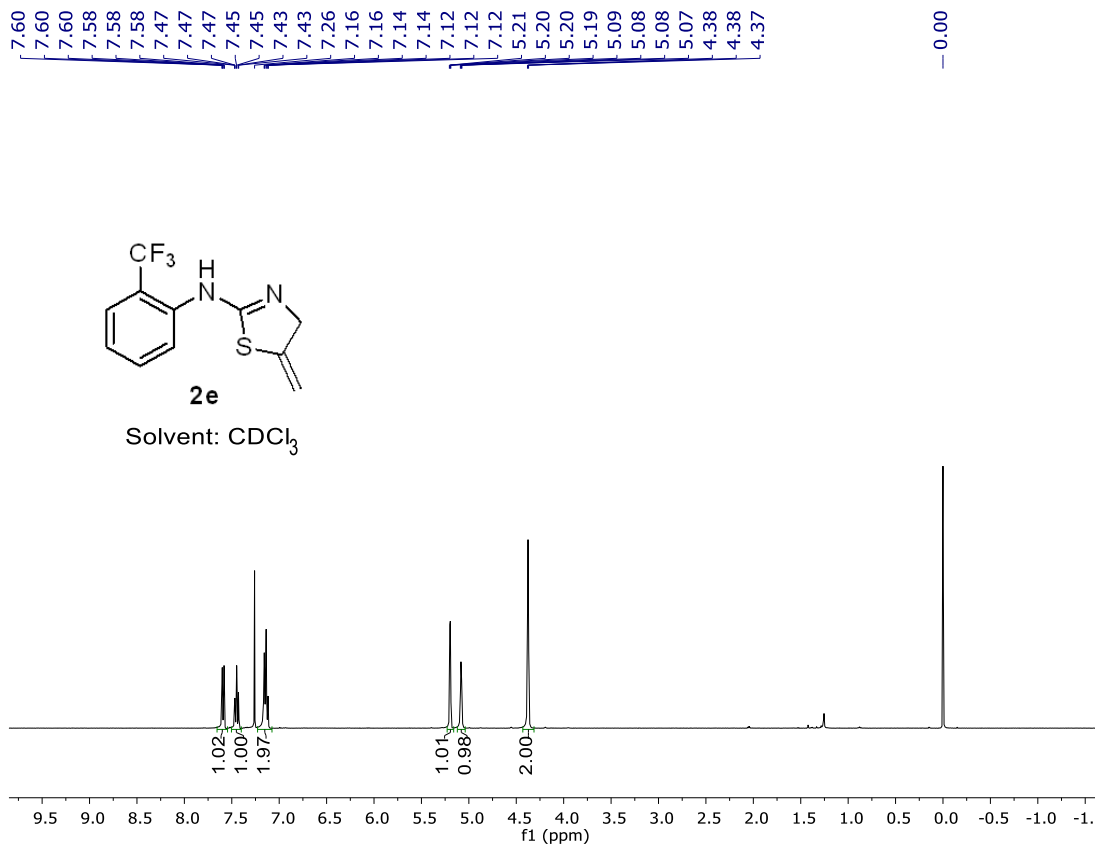
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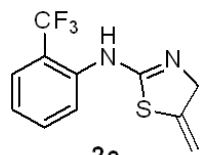






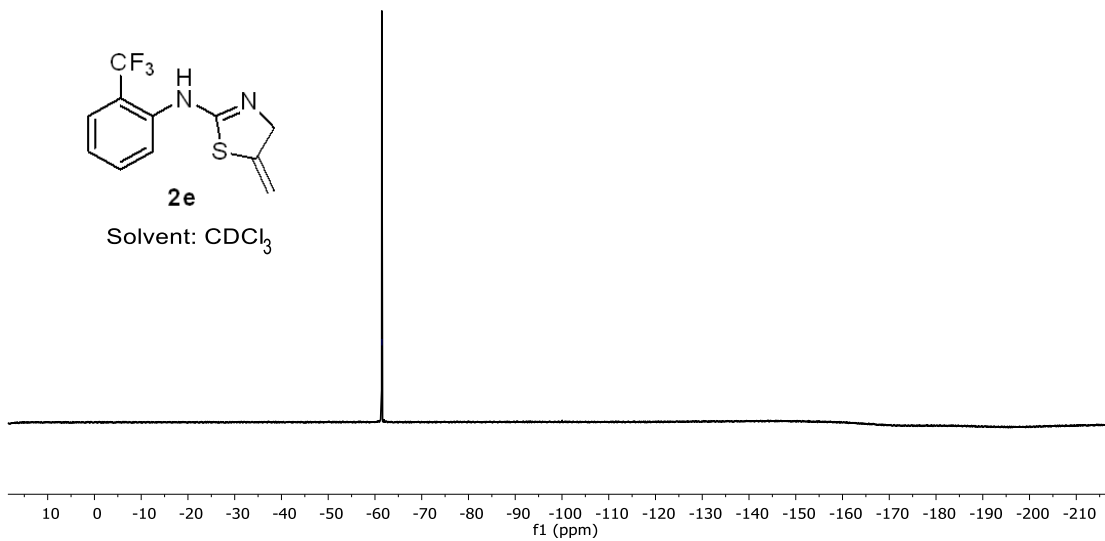


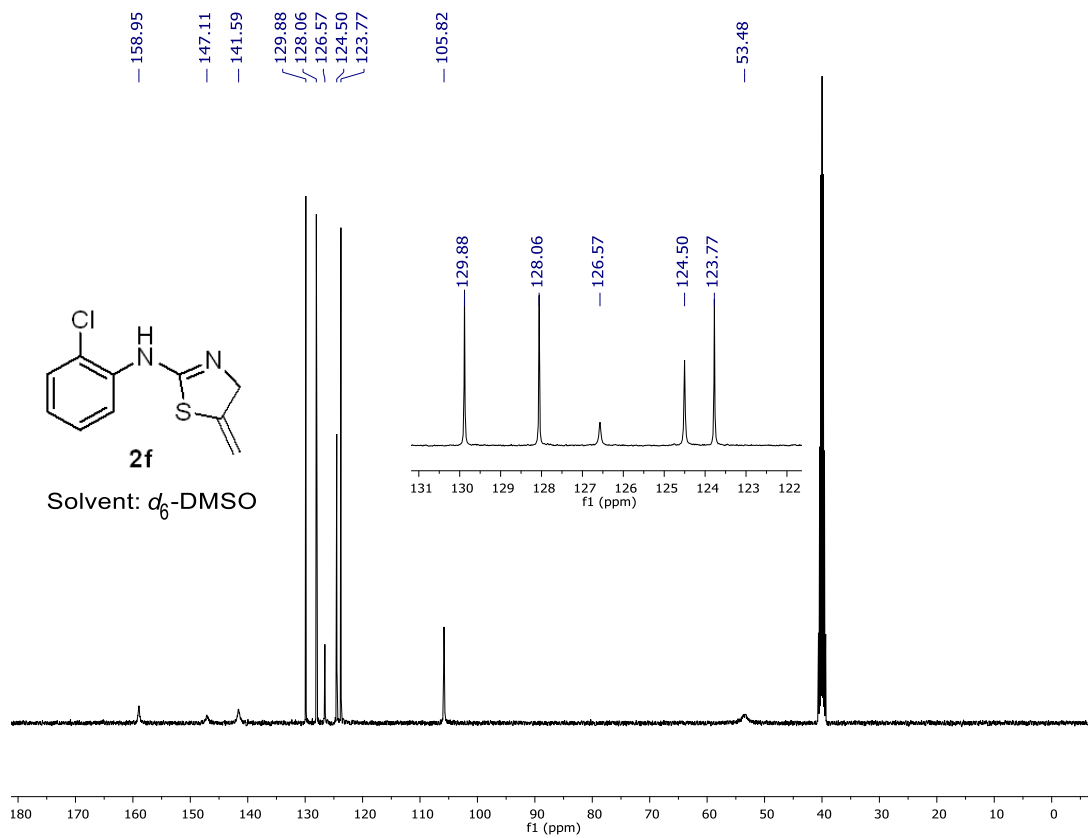
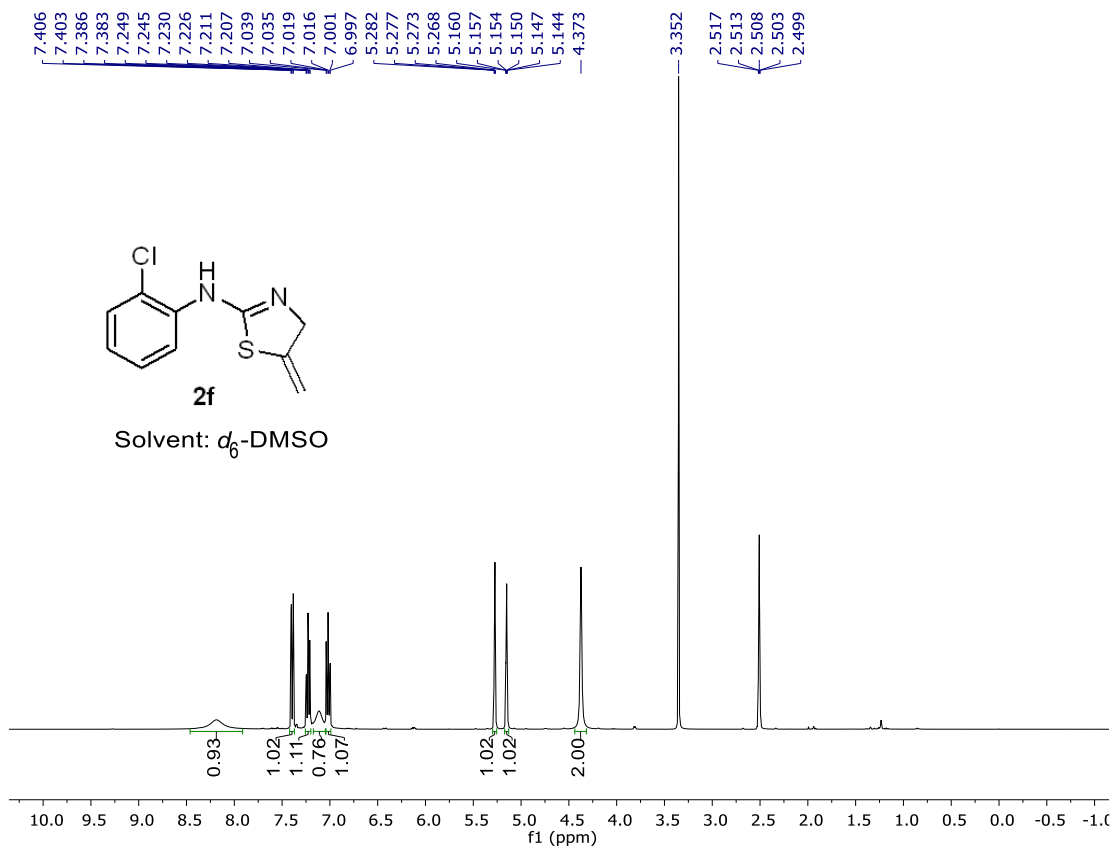
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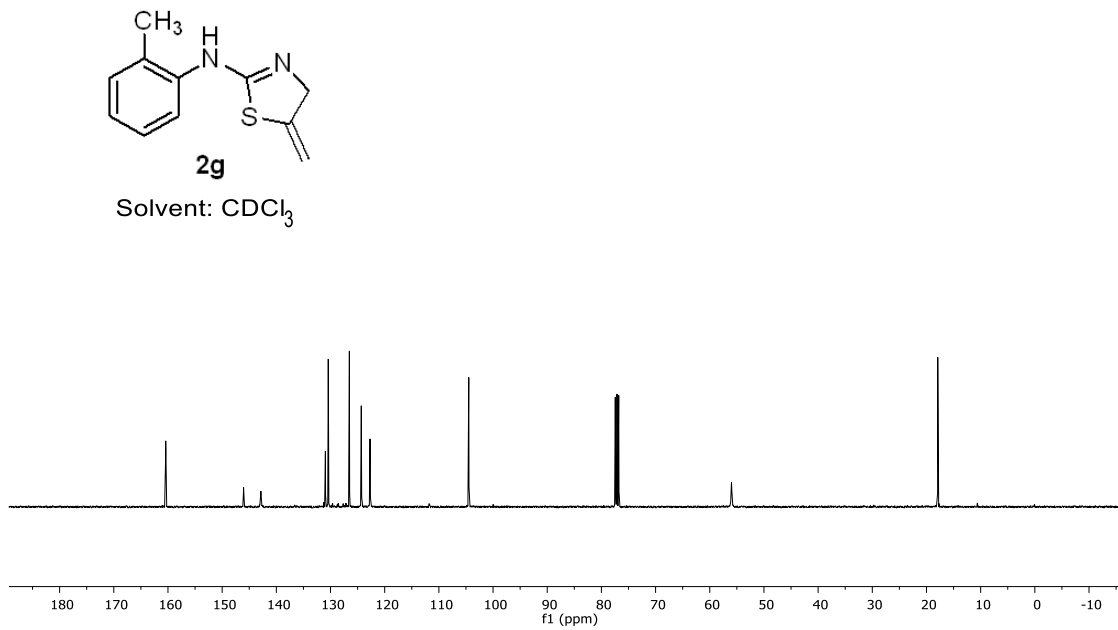
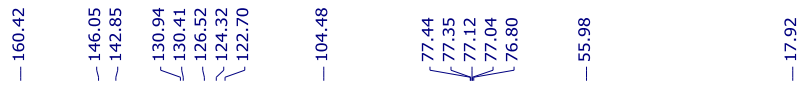
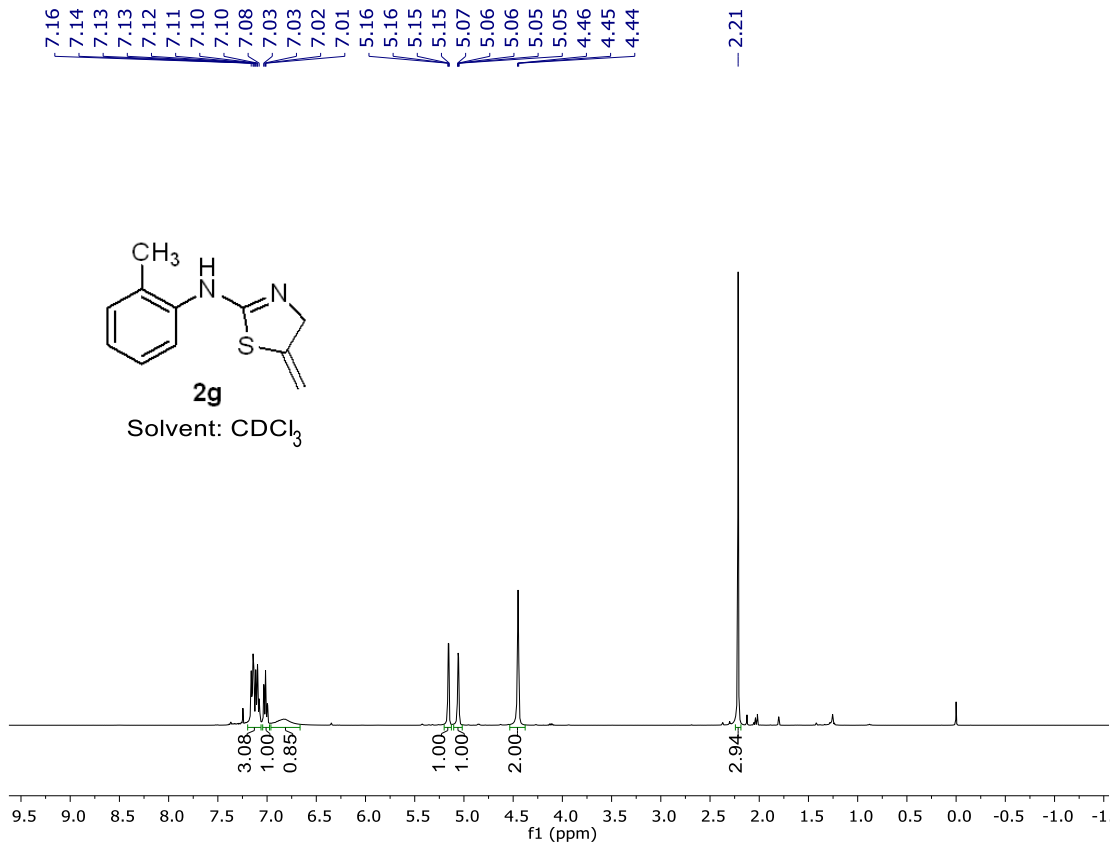


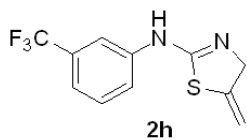
**2e**

Solvent: CDCl<sub>3</sub>

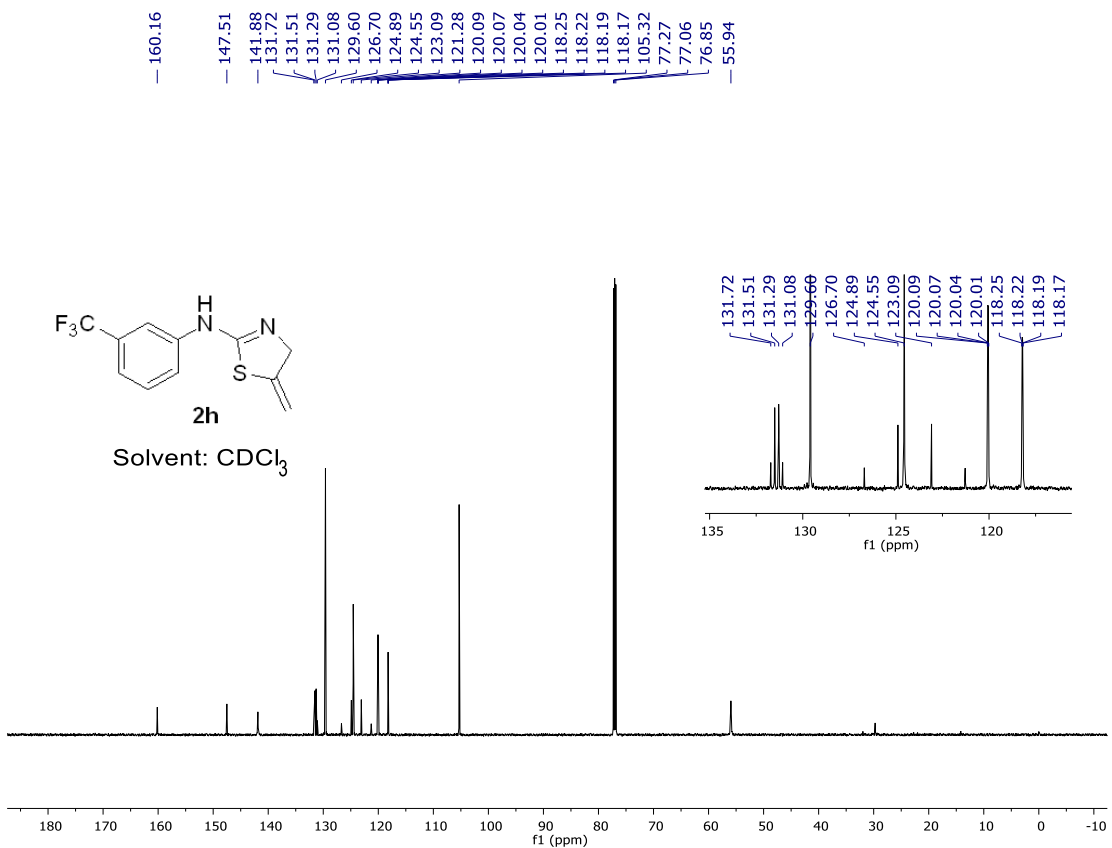
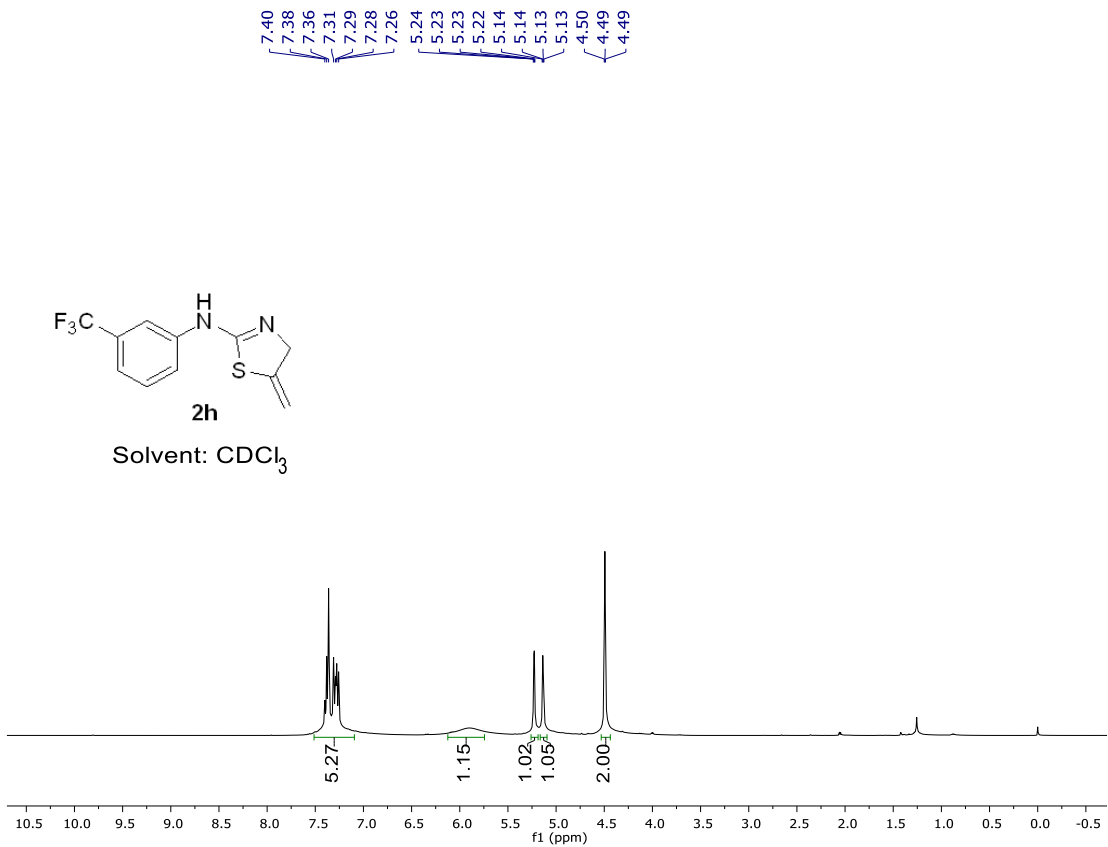


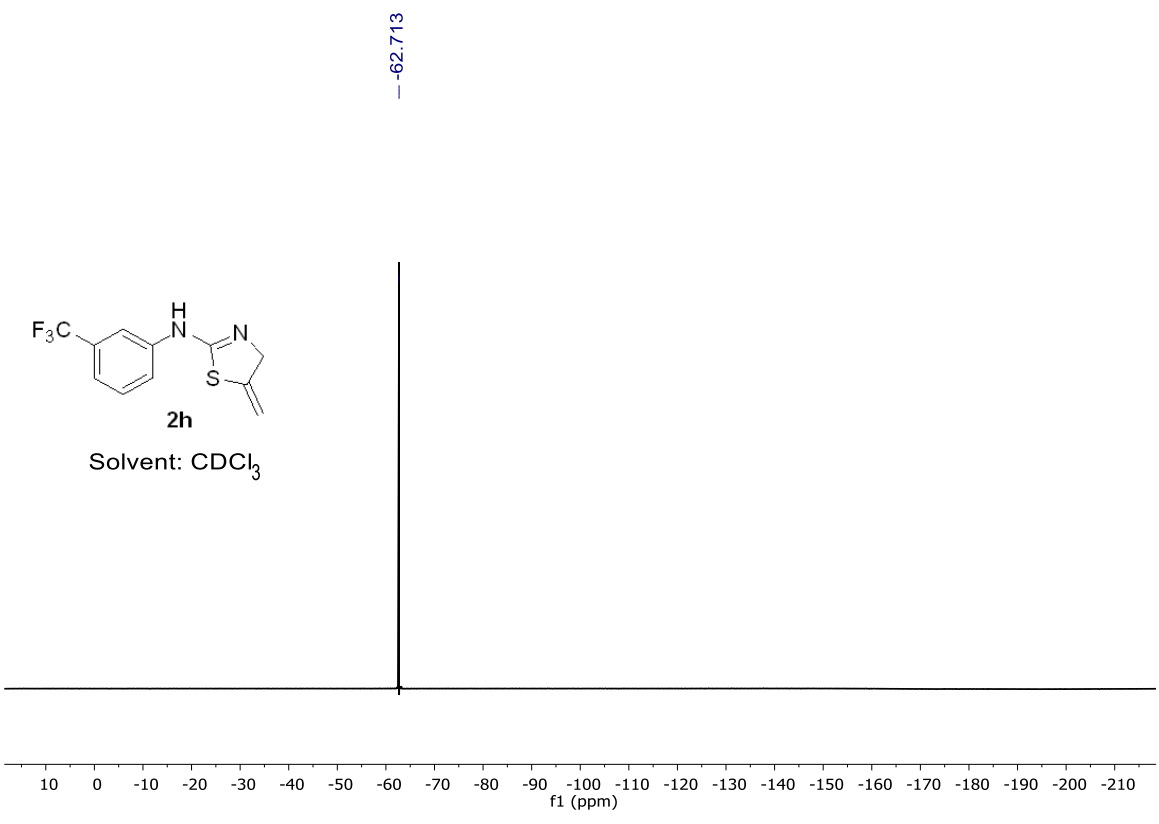






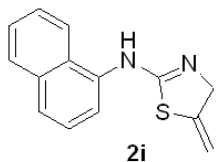
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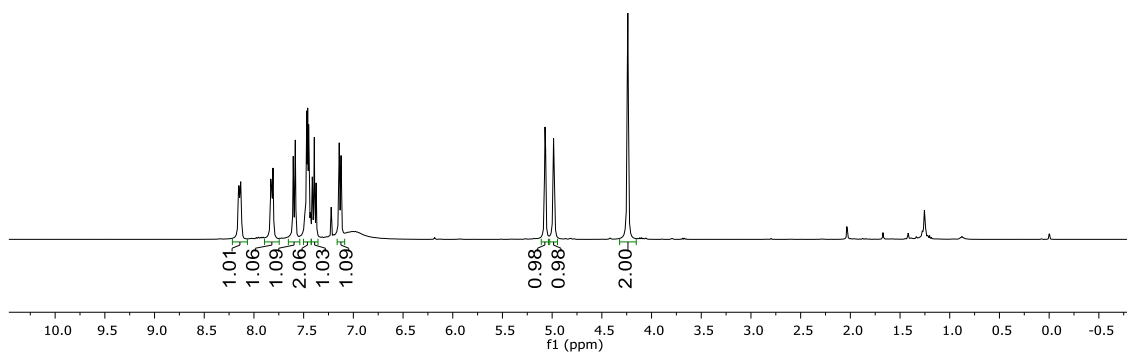


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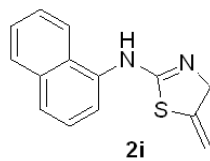
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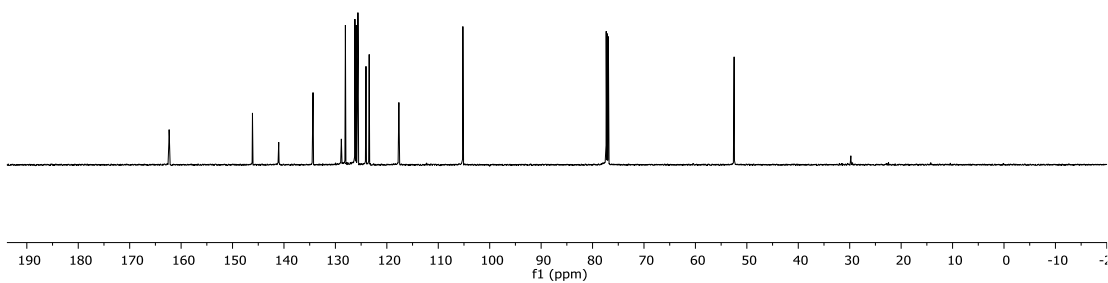
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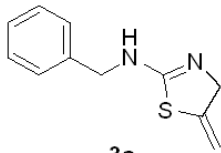
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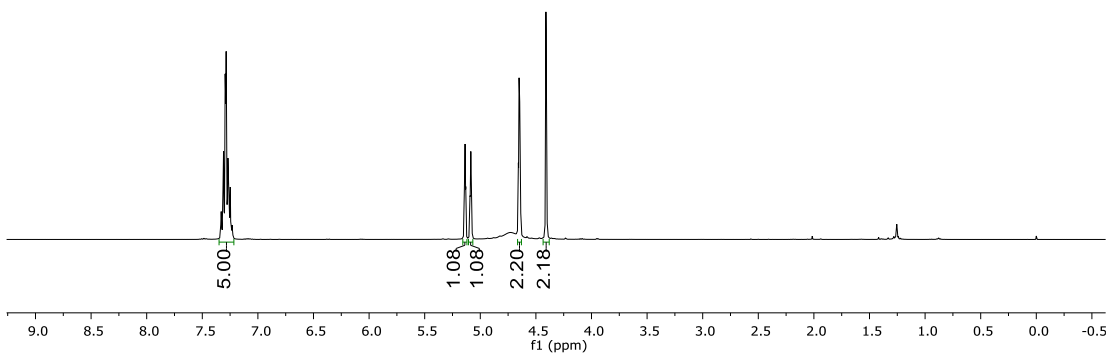


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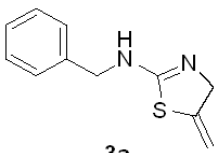


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Solvent: CDCl<sub>3</sub>

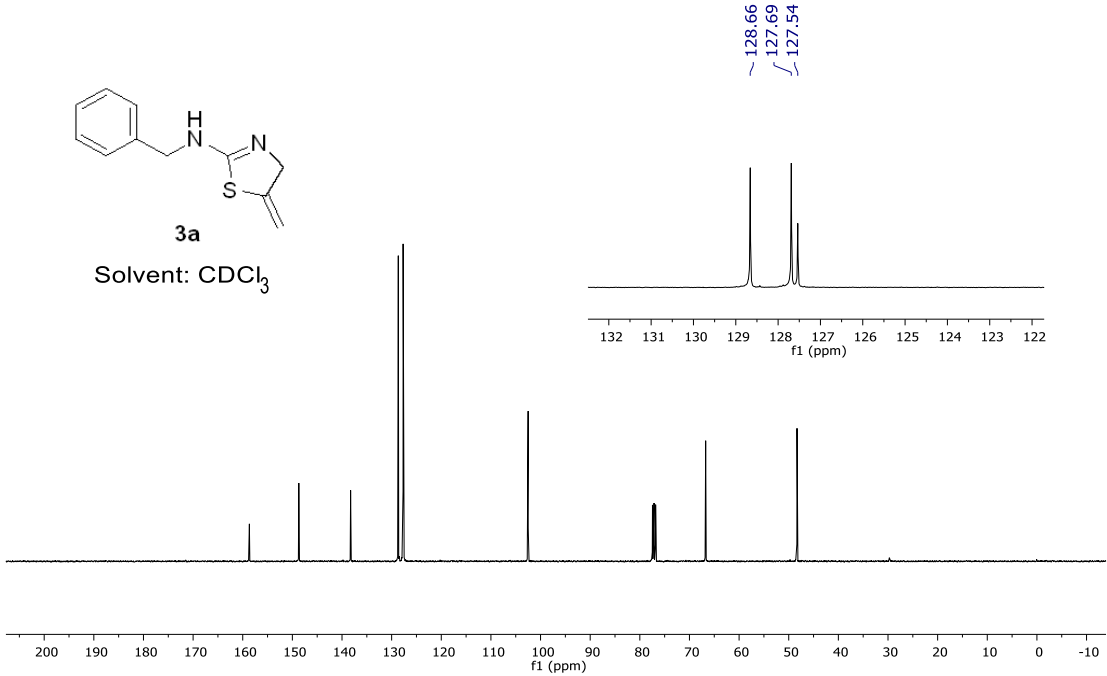


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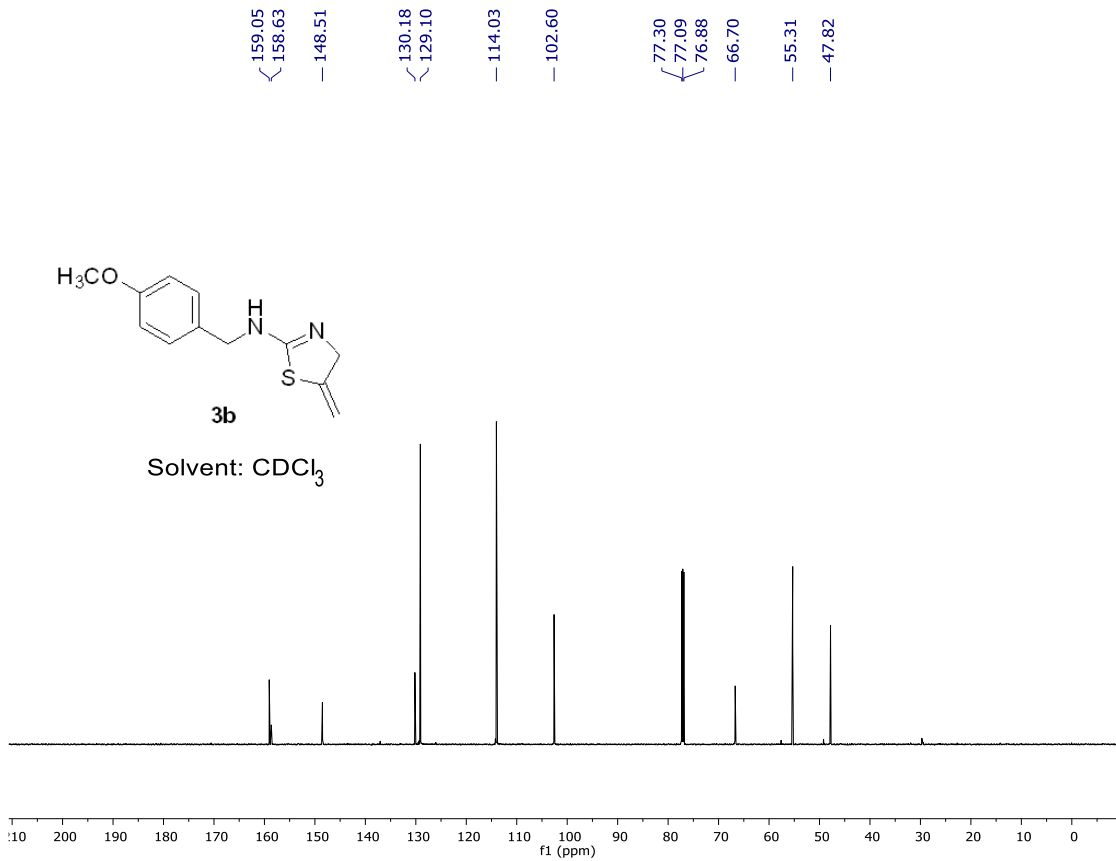
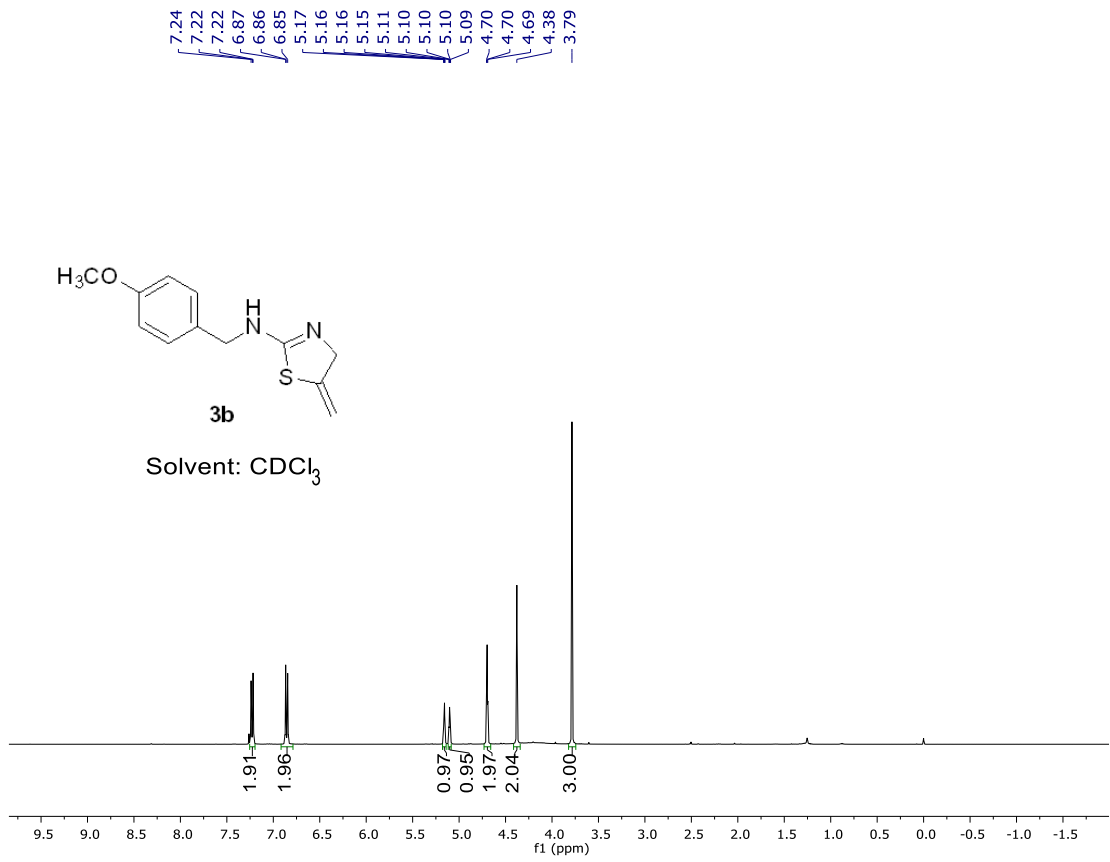


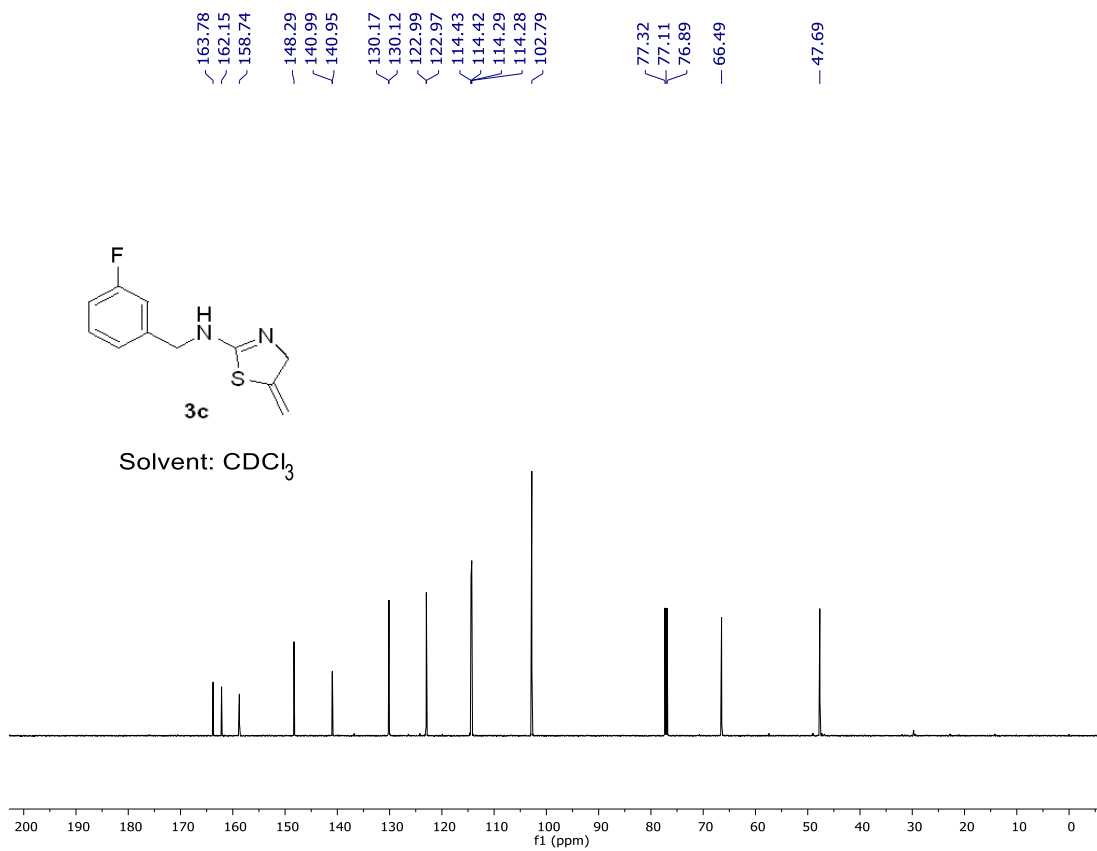
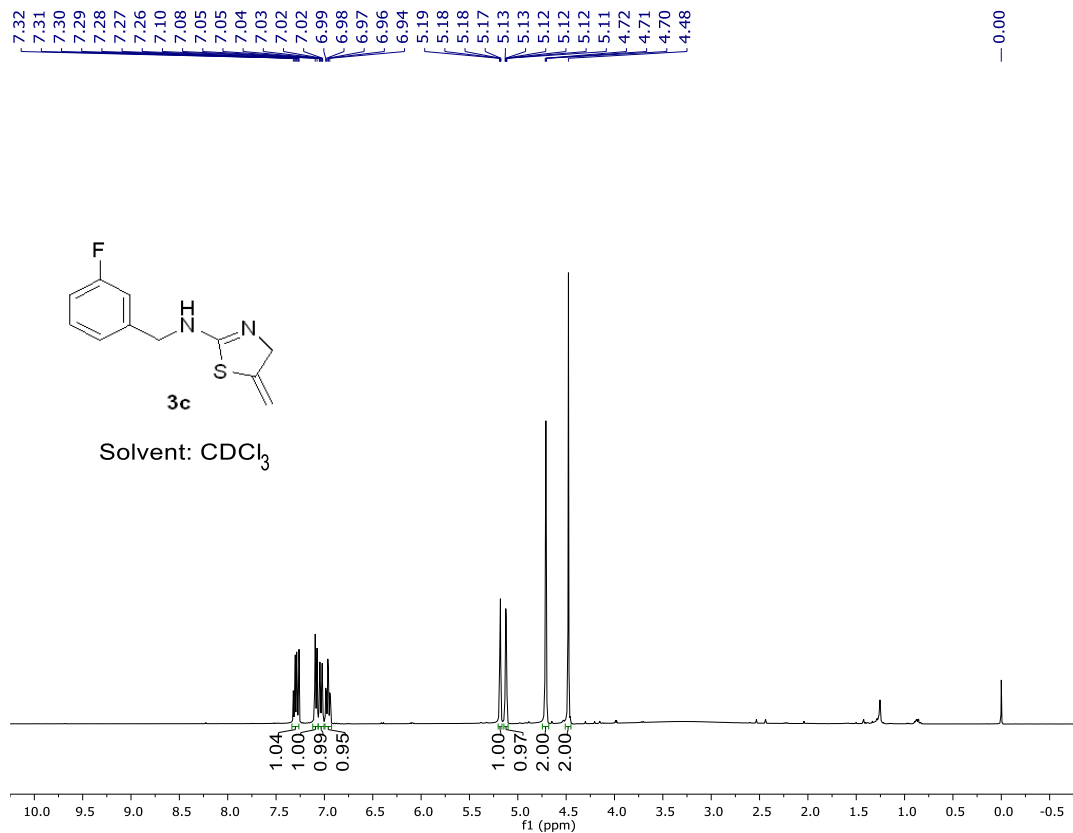
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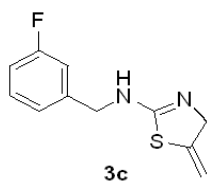
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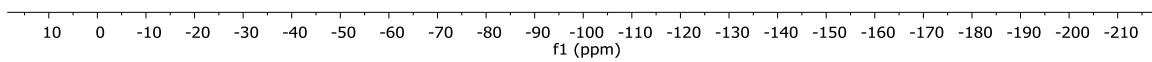




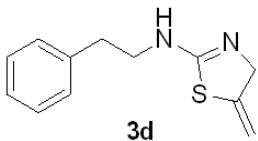


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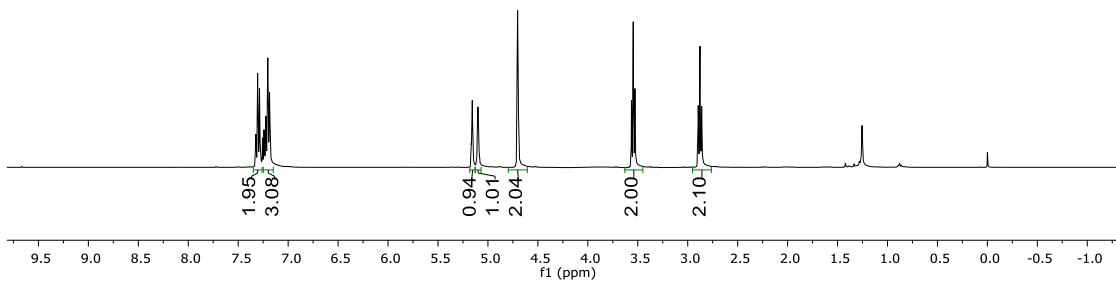
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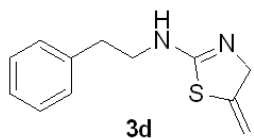
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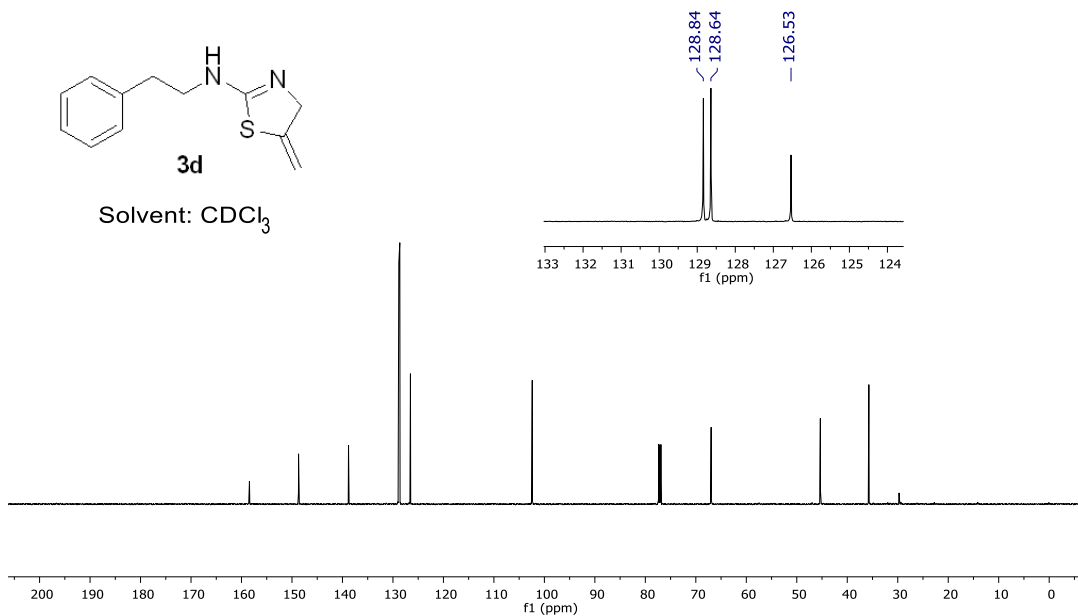
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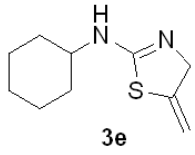
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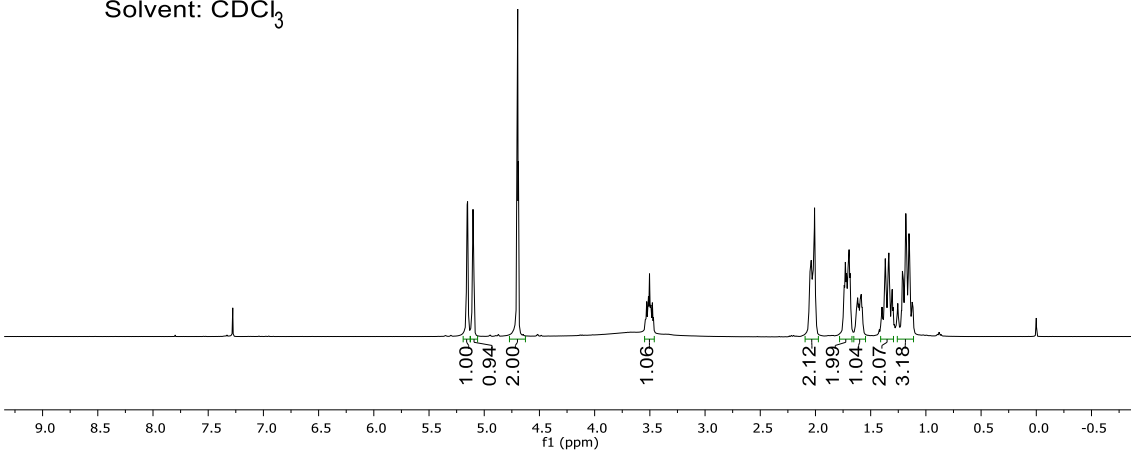
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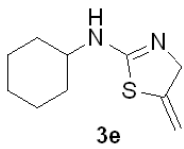
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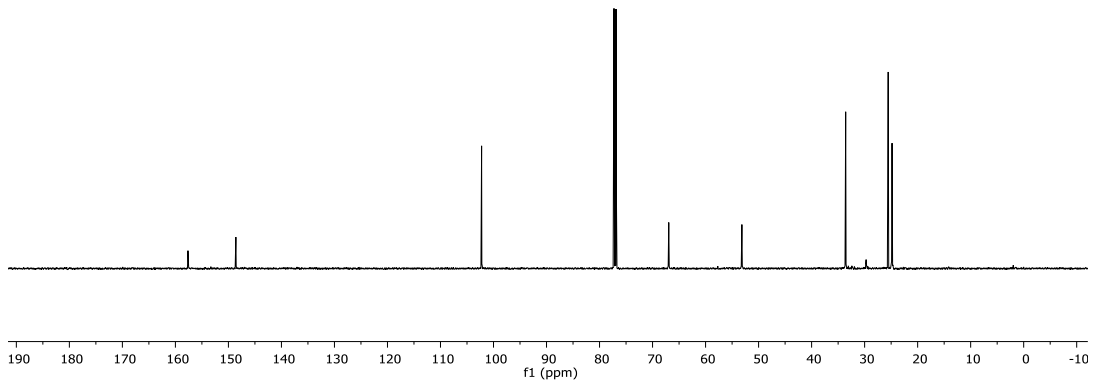
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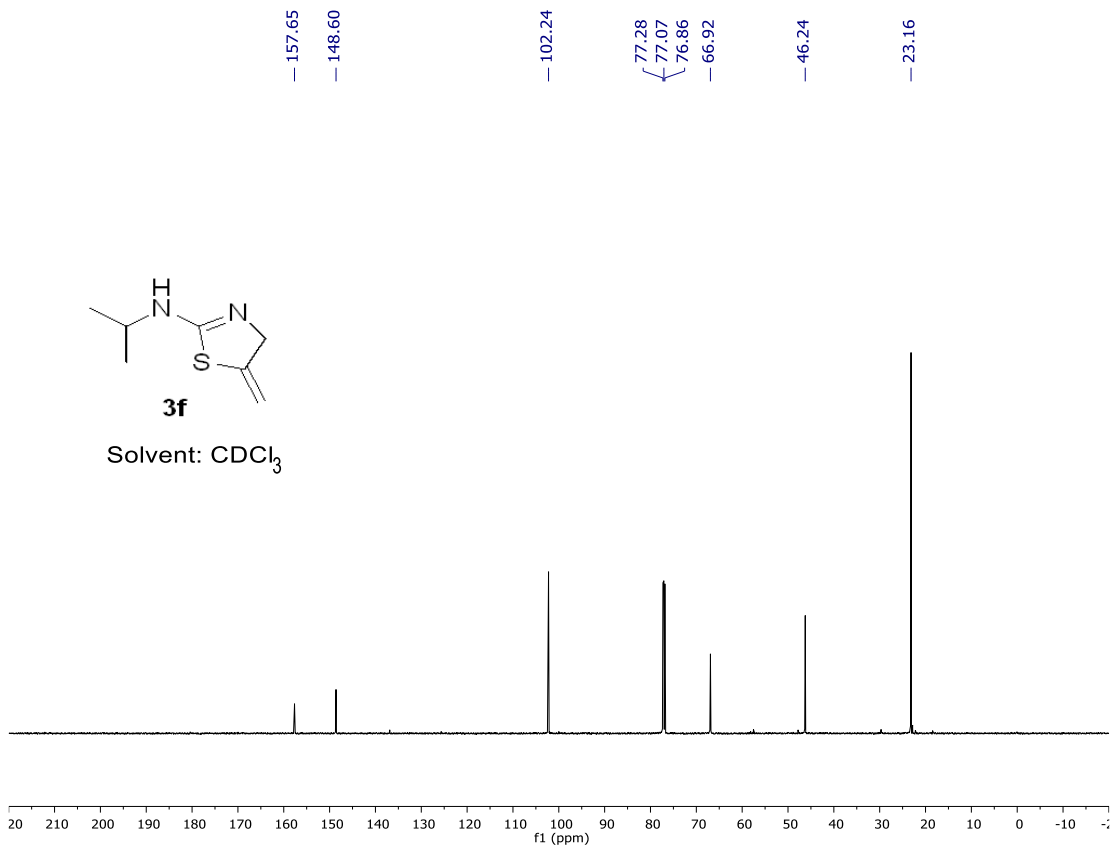
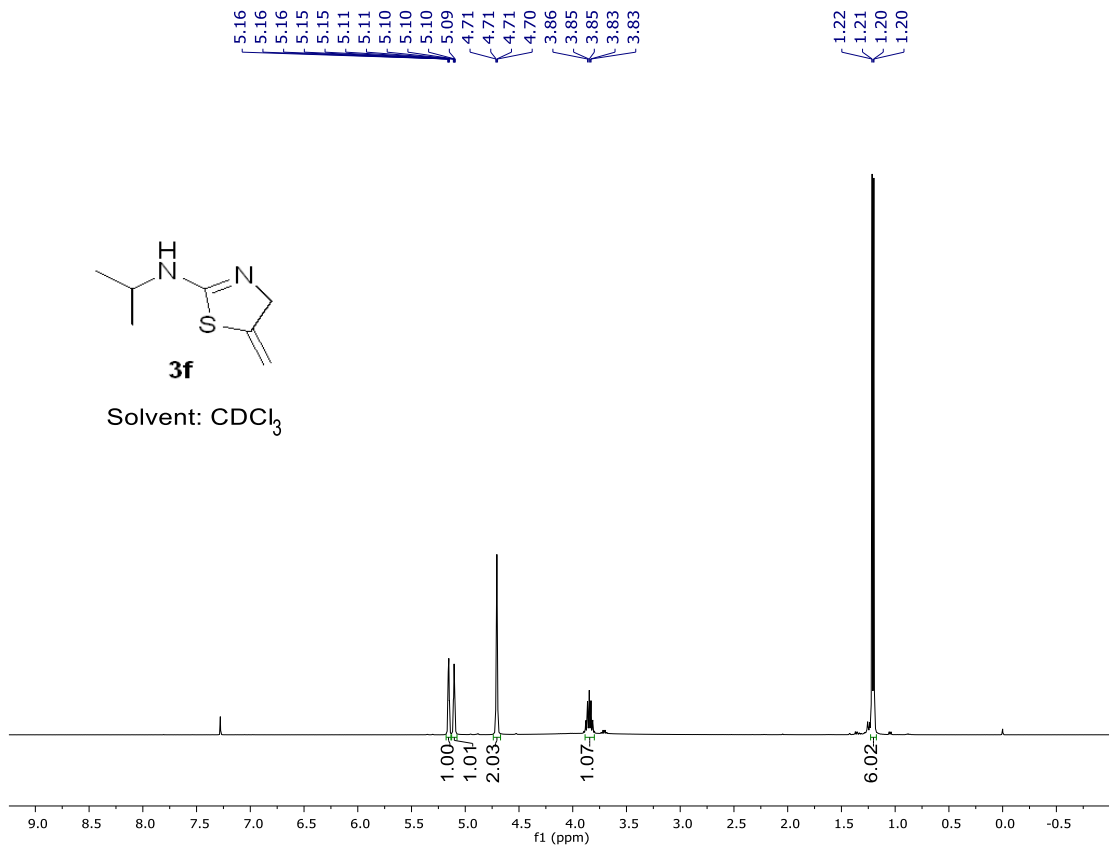


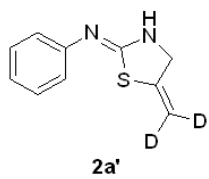
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24.83



Solvent: CDCl<sub>3</sub>







Solvent: CDCl<sub>3</sub>

