

Synthesis of Vinyl Chlorides *via* Triphosgene-Pyridine Activation of Ketones

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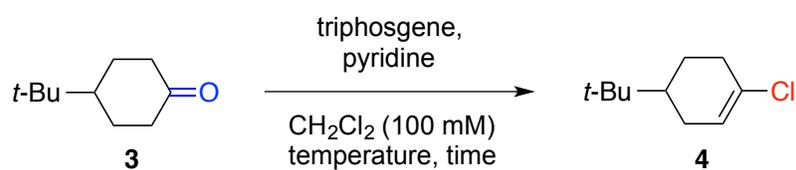
SUPPORTING INFORMATION

1. GC-MS studies.....S-2
2. ¹H and ¹³C NMR Spectra and X-ray DataS-19

Reaction Optimization Study

The following optimization studies were conducted on a Thermo Scientific Trace 1310 Gas Chromatography with sampler type AS 1310. The column used for this system was a Thermo Scientific TG-5MS 5% phenyl methyl siloxane (model number 26098-1420), which was 30 meters in length. The column had an internal diameter of 250 μm . Oven, inlet, and detector temperatures were set to 250 $^{\circ}\text{C}$, and helium was used as the inert carrier gas.

Table S-1. Optimization Study^(a)

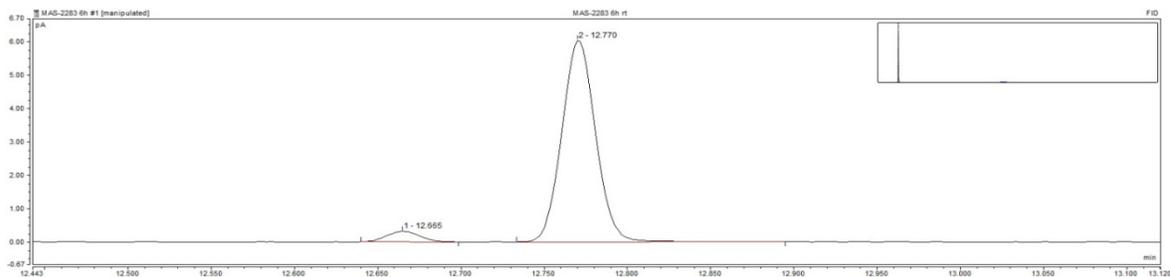


entry	equiv of triphosgene	equiv of pyridine	6hr (%)		24hr (%)		48hr (%)	
			rt	reflux	rt	reflux	rt	reflux
1	0.5	1.0	5	5	14	16	23	20
2	0.5	2.0	9	9	31	39	50	61
3	0.5	3.0	12	15	40	53	58	80
4	0.5	4.0	16	19	50	65	71	80
5	1.0	1.0	8	10	22	27	28	31
6	1.0	2.0	17	19	39	54	57	77
7	1.0	3.0	20	24	56	75	77	94
8	1.0	4.0	26	32	68	90	87	97

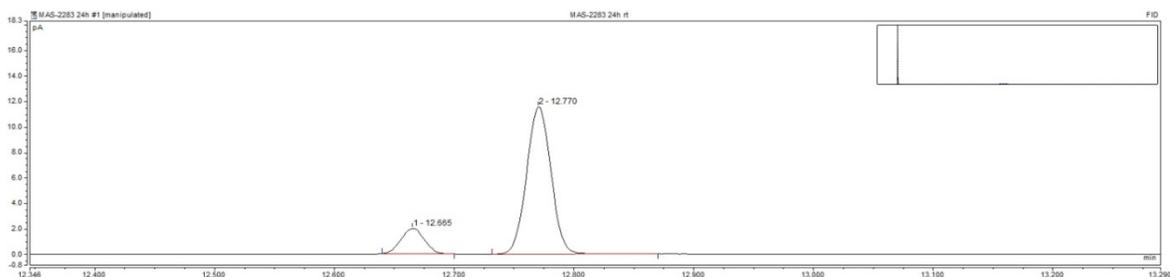
(a) Yields were determined by GC analysis of the crude mixtures assuming that these two compounds elicited identical GC responses.

Table S-1, Entry 1, Room Temperature

Triphosgene (0.5 equiv), pyridine (1.0 equiv), room temperature, 6 hours



Triphosgene (0.5 equiv), pyridine (1.0 equiv), room temperature, 24 hours



Triphosgene (0.5 equiv), pyridine (1.0 equiv), room temperature, 24 hours

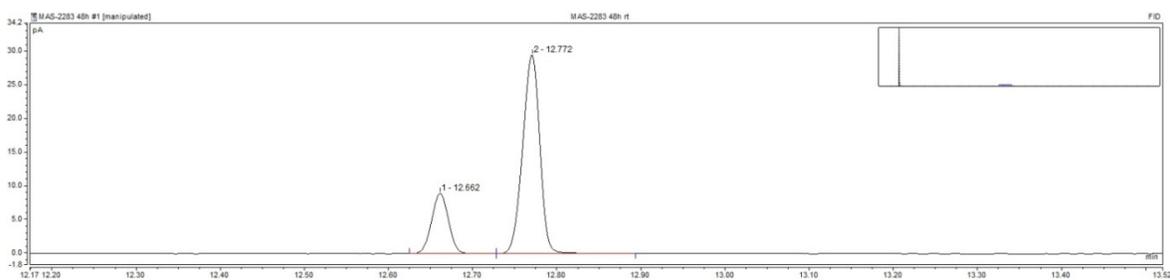
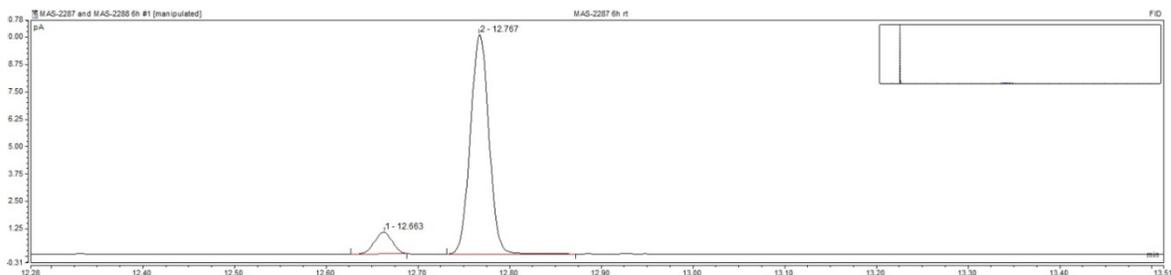
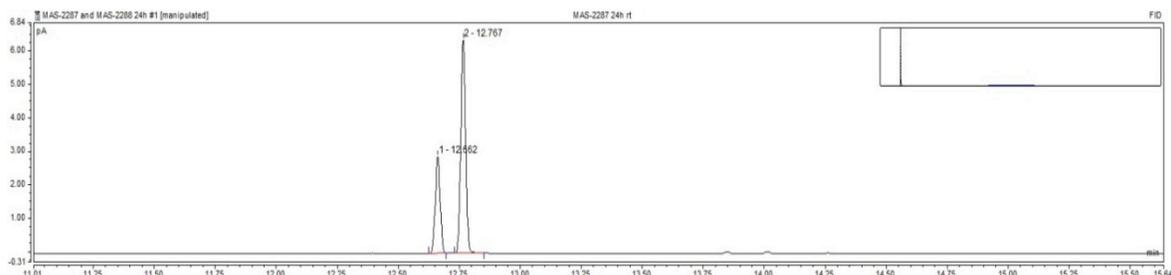


Table S-1, Entry 2, Room Temperature

Triphosgene (0.5 equiv), pyridine (2.0 equiv), room temperature, 6 hours



Triphosgene (0.5 equiv), pyridine (2.0 equiv), room temperature, 24 hours



Triphosgene (0.5 equiv), pyridine (2.0 equiv), room temperature, 48 hours

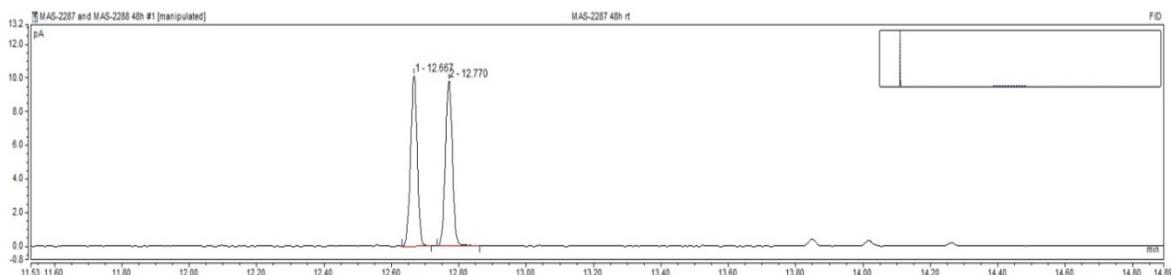
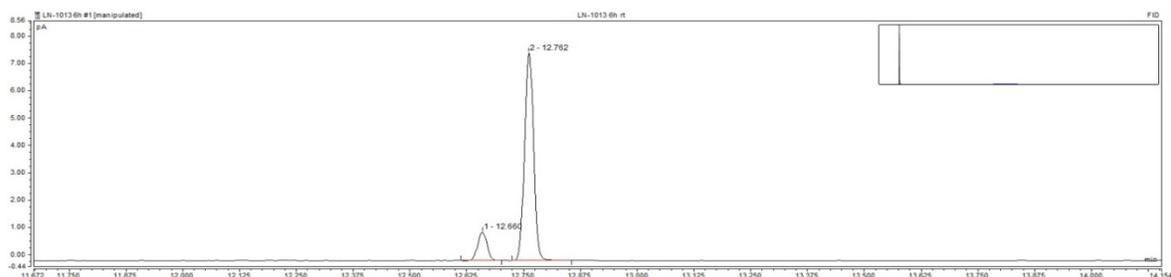
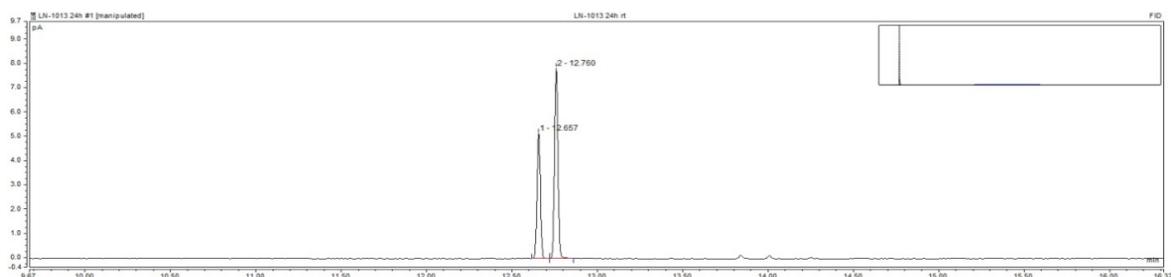


Table S-1, Entry 3, Room Temperature

Triphosgene (0.5 equiv), pyridine (3.0 equiv), room temperature, 6 hours



Triphosgene (0.5 equiv), pyridine (3.0 equiv), room temperature, 24 hours



Triphosgene (0.5 equiv), pyridine (3.0 equiv), room temperature, 48 hours

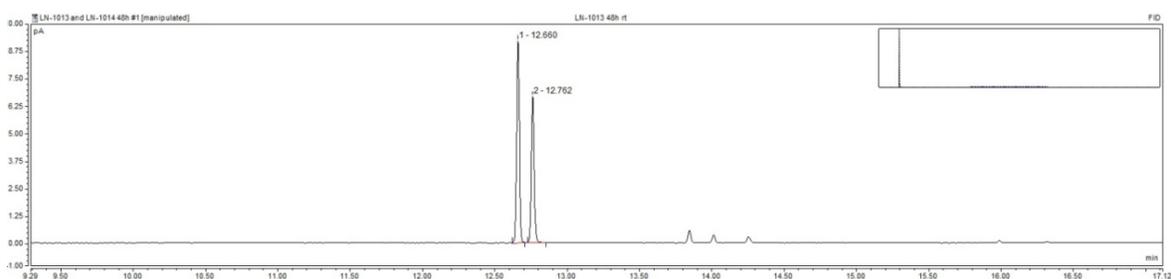
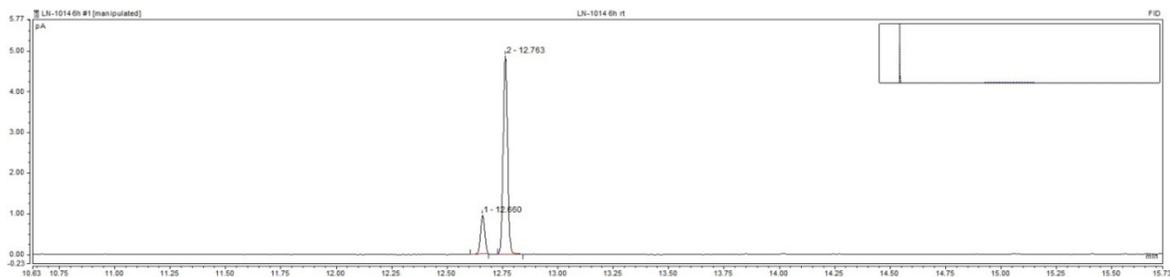
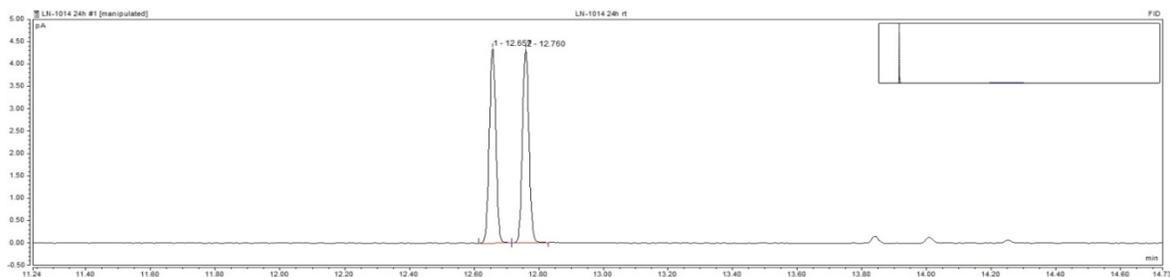


Table S-1, Entry 4, Room Temperature

Triphosgene (0.5 equiv), pyridine (4.0 equiv), room temperature, 6 hours



Triphosgene (0.5 equiv), pyridine (4.0 equiv), room temperature, 24 hours



Triphosgene (0.5 equiv), pyridine (4.0 equiv), room temperature, 48 hours

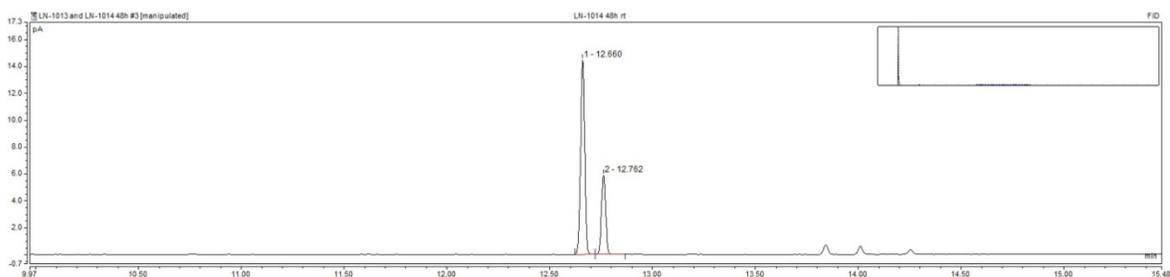
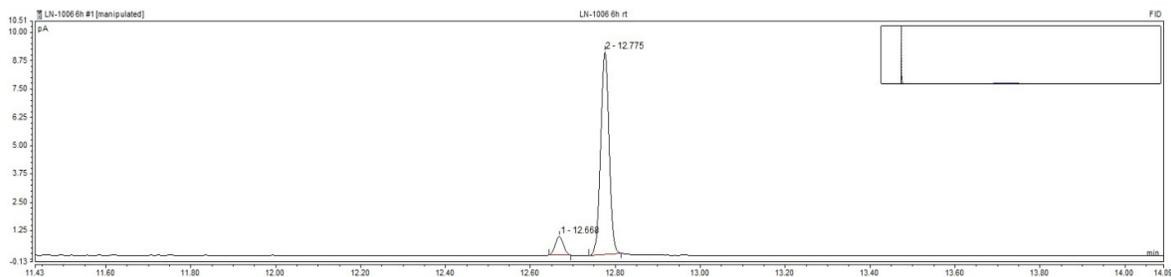
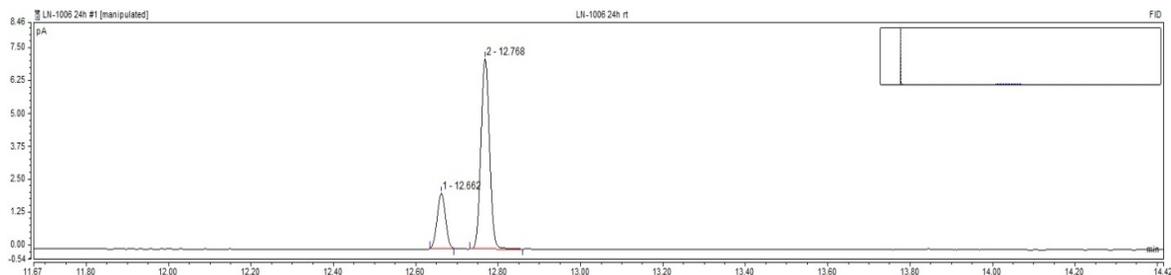


Table S-1, Entry 5, Room Temperature

Triphosgene (1.0 equiv), pyridine (1.0 equiv), room temperature, 6 hours



Triphosgene (1.0 equiv), pyridine (1.0 equiv), room temperature, 24 hours



Triphosgene (1.0 equiv), pyridine (1.0 equiv), room temperature, 48 hours

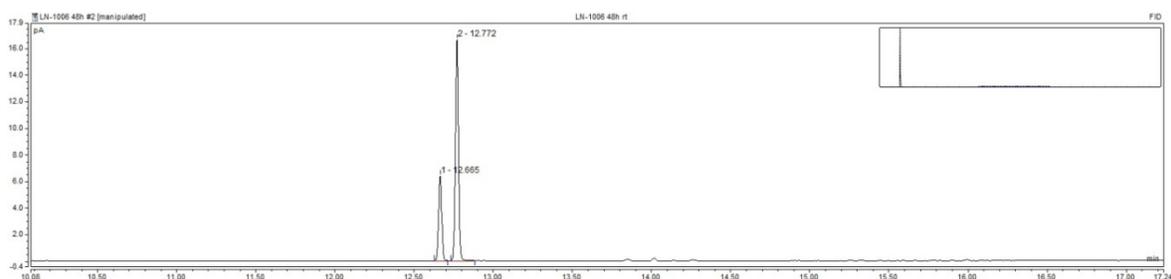
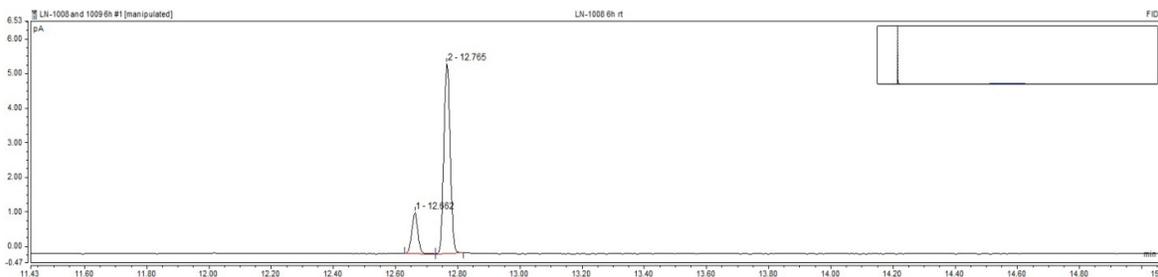
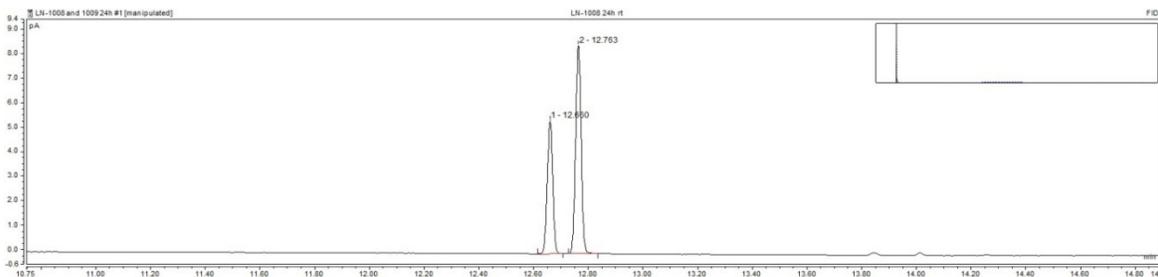


Table S-1, Entry 6, Room Temperature

Triphosgene (1.0 equiv), pyridine (2.0 equiv), room temperature, 6 hours



Triphosgene (1.0 equiv), pyridine (2.0 equiv), room temperature, 24 hours



Triphosgene (1.0 equiv), pyridine (2.0 equiv), room temperature, 48 hours

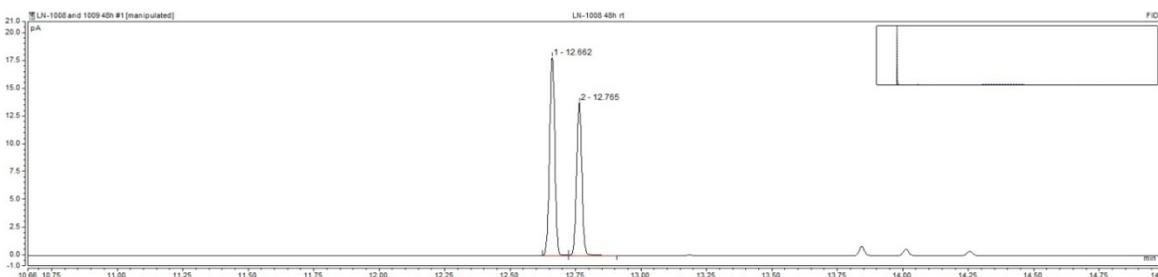
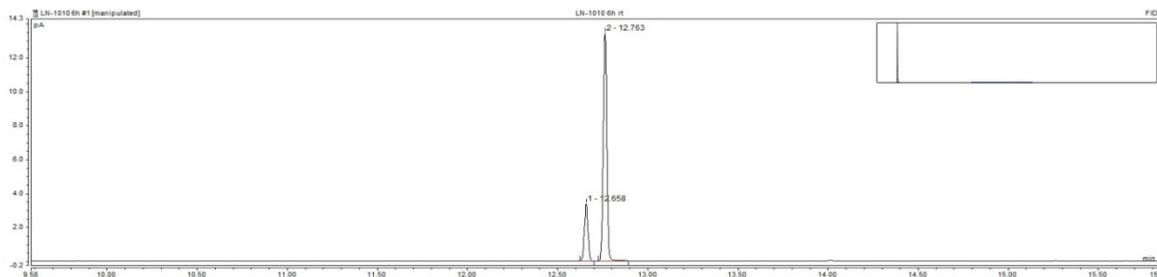
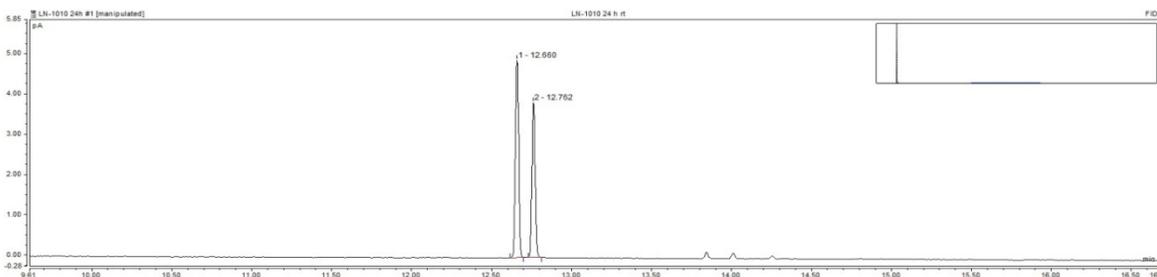


Table S-1, Entry 7, Room Temperature

Triphosgene (1.0 equiv), pyridine (3.0 equiv), room temperature, 6 hours



Triphosgene (1.0 equiv), pyridine (3.0 equiv), room temperature, 24 hours



Triphosgene (1.0 equiv), pyridine (3.0 equiv), room temperature, 48 hours

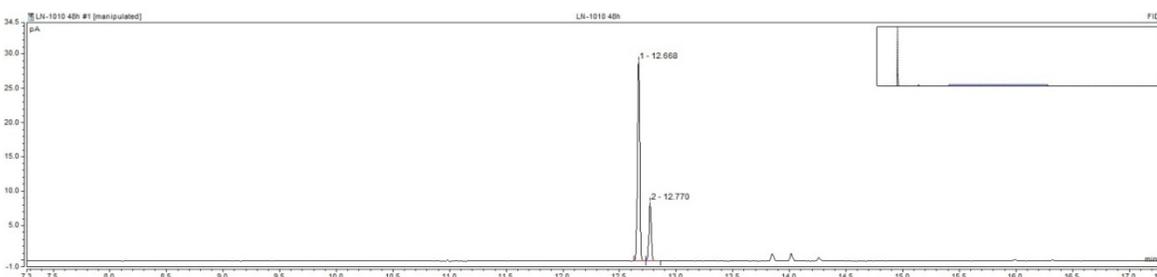
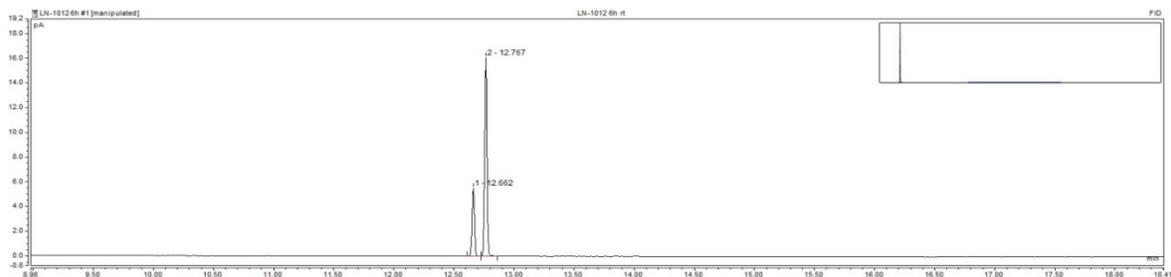
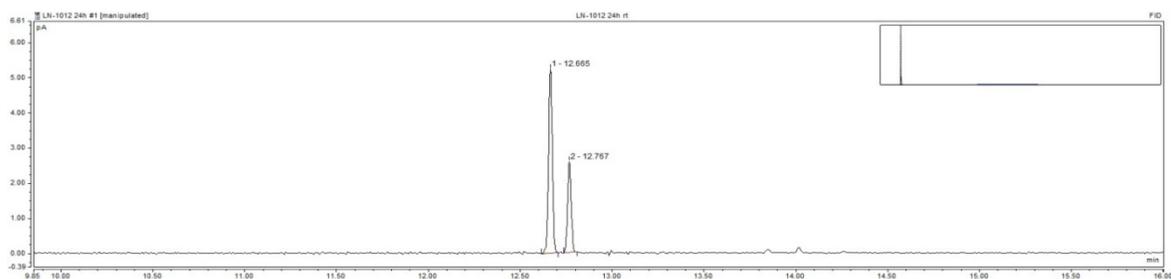


Table S-1, Entry 8, Room Temperature

Triphosgene (1.0 equiv), pyridine (4.0 equiv), room temperature, 6 hours



Triphosgene (1.0 equiv), pyridine (4.0 equiv), room temperature, 24 hours



Triphosgene (1.0 equiv), pyridine (4.0 equiv), room temperature, 24 hours

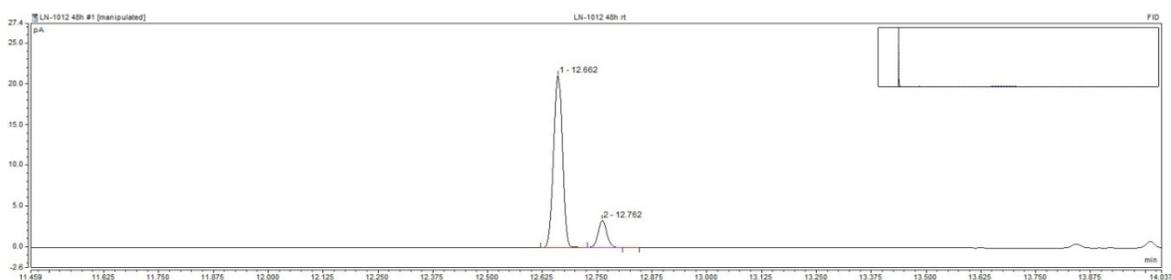
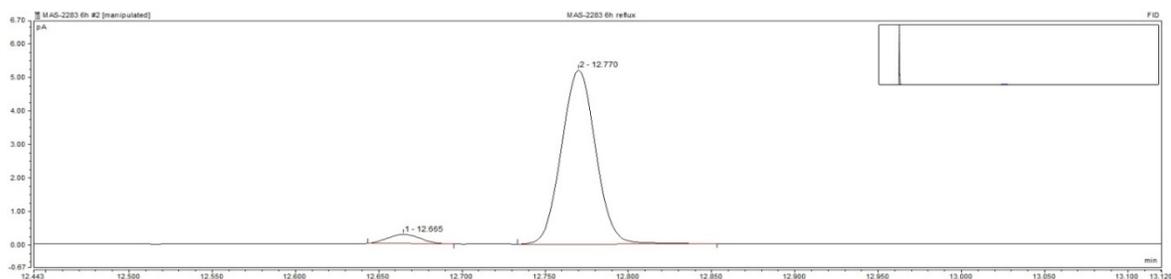
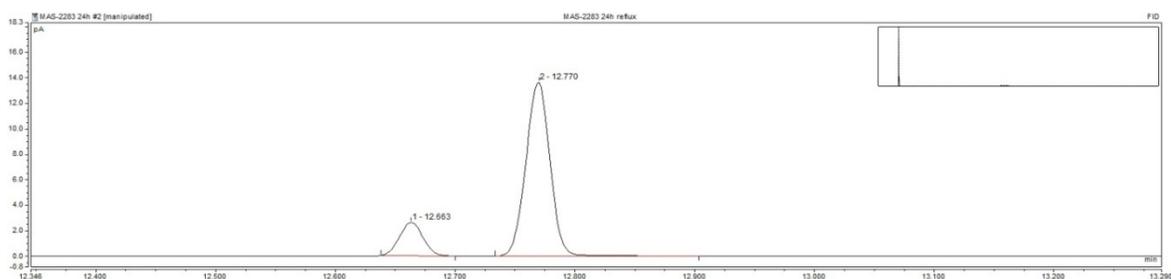


Table S-1, Entry 1, Reflux

Triphosgene (0.5 equiv), pyridine (1.0 equiv), reflux, 6 hours



Triphosgene (0.5 equiv), pyridine (1.0 equiv), reflux, 24 hours



Triphosgene (0.5 equiv), pyridine (1.0 equiv), reflux, 48 hours

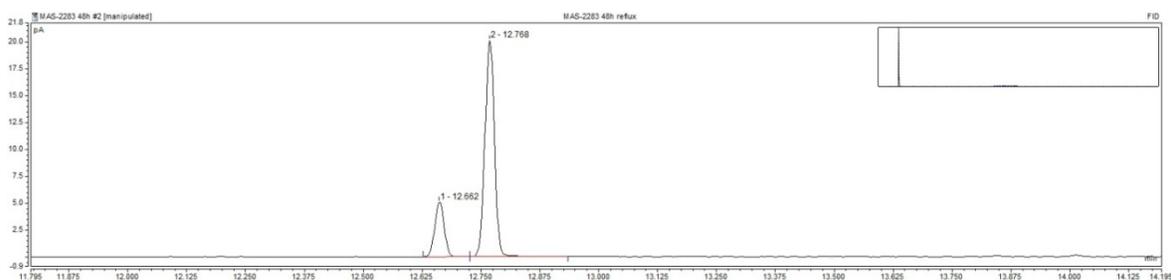
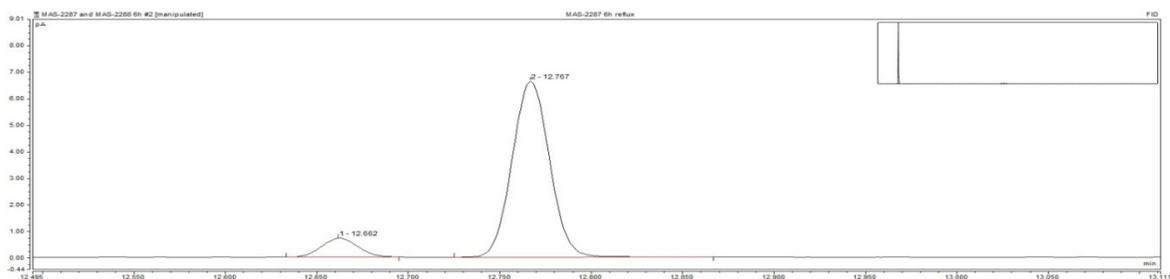
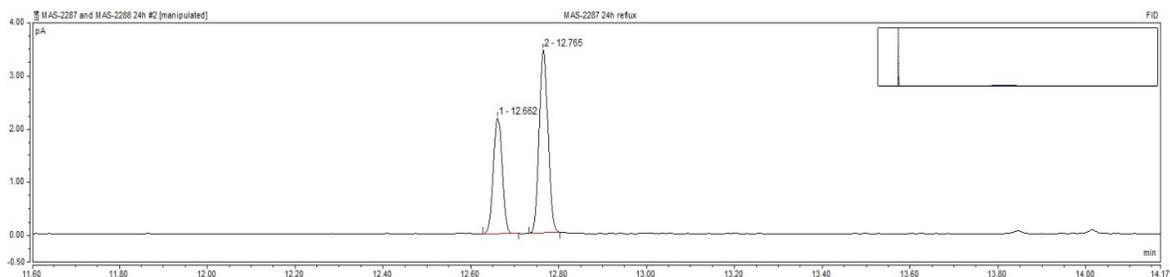


Table S-1, Entry 2, Reflux

Triphosgene (0.5 equiv), pyridine (2.0 equiv), reflux, 6 hours



Triphosgene (0.5 equiv), pyridine (2.0 equiv), reflux, 24 hours



Triphosgene (0.5 equiv), pyridine (2.0 equiv), reflux, 48 hours

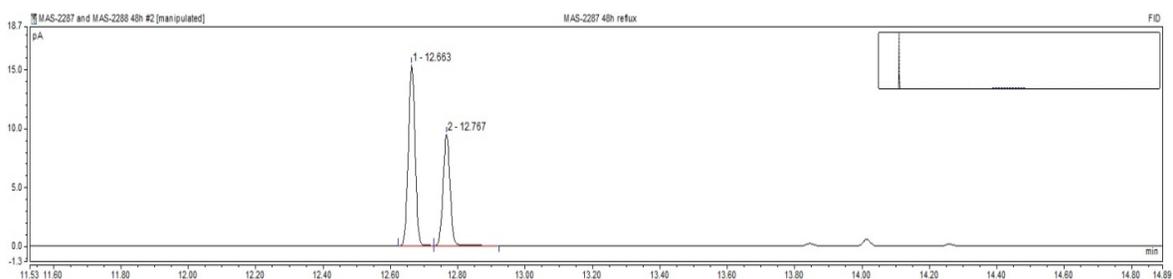
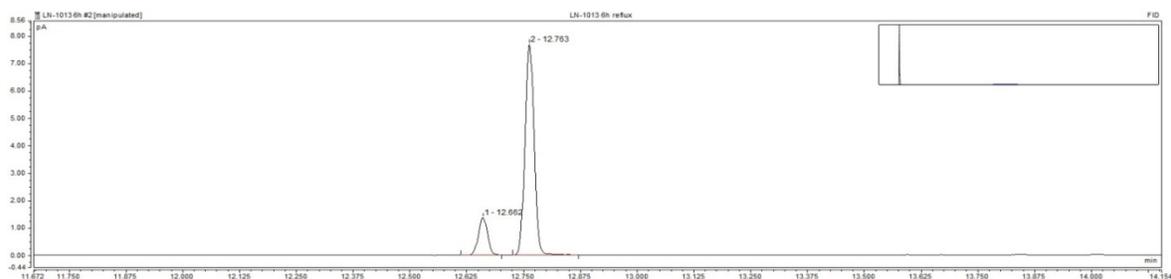
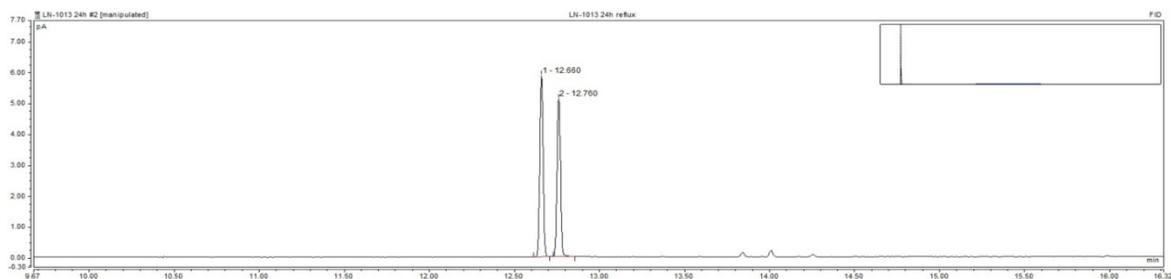


Table S-1, Entry 3, Reflux

Triphosgene (0.5 equiv), pyridine (3.0 equiv), reflux, 6 hours



Triphosgene (0.5 equiv), pyridine (3.0 equiv), reflux, 24 hours



Triphosgene (0.5 equiv), pyridine (3.0 equiv), reflux, 48 hours

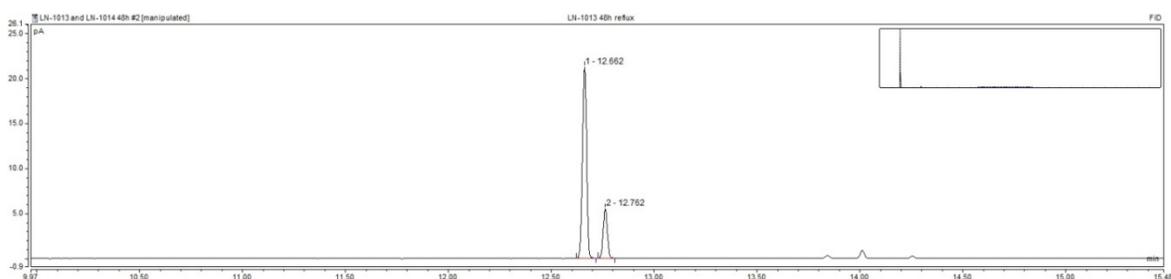
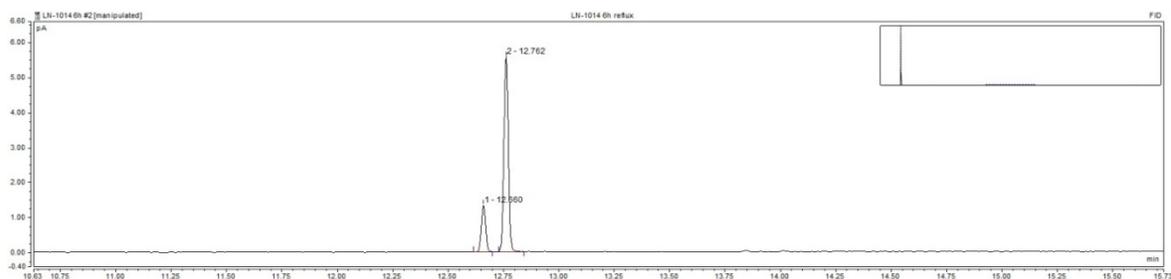
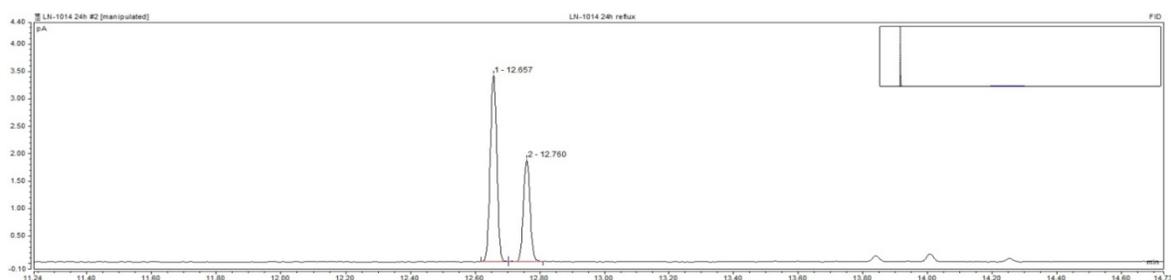


Table S-1, Entry 4, Reflux

Triphosgene (0.5 equiv), pyridine (4.0 equiv), reflux, 6 hours



Triphosgene (0.5 equiv), pyridine (4.0 equiv), reflux, 24 hours



Triphosgene (0.5 equiv), pyridine (4.0 equiv), reflux, 48 hours

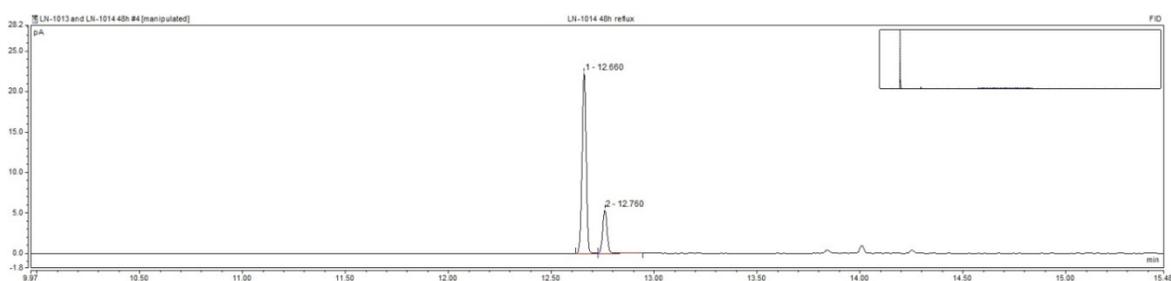
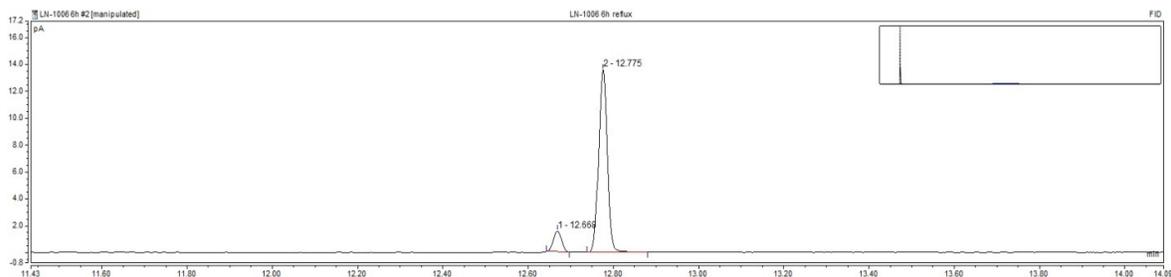
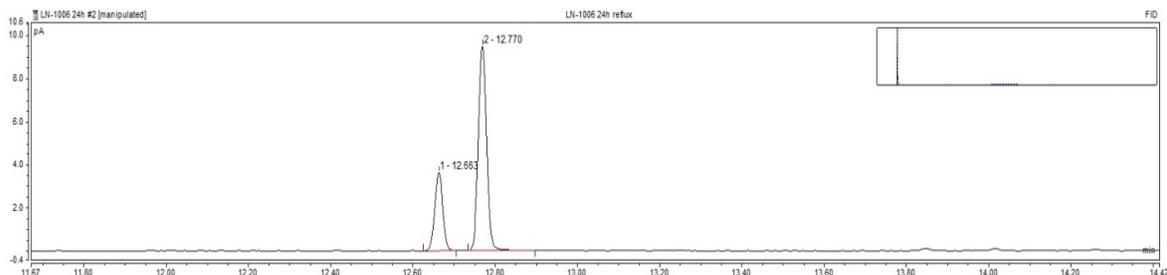


Table S-1, Entry 5, Reflux

Triphosgene (1.0 equiv), pyridine (1.0 equiv), reflux, 6 hours



Triphosgene (1.0 equiv), pyridine (1.0 equiv), reflux, 24 hours



Triphosgene (1.0 equiv), pyridine (1.0 equiv), reflux, 48 hours

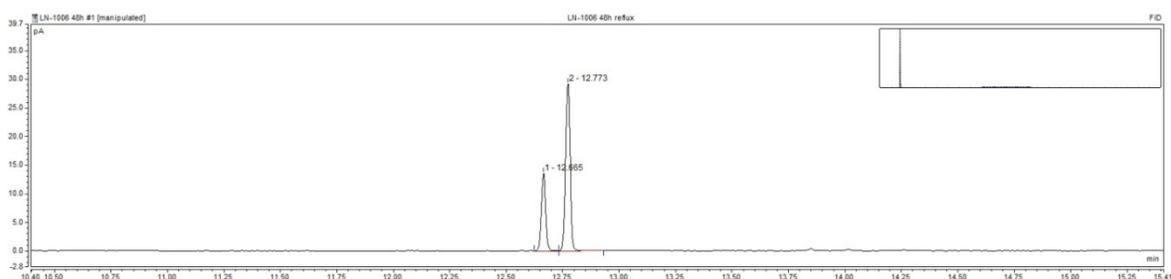
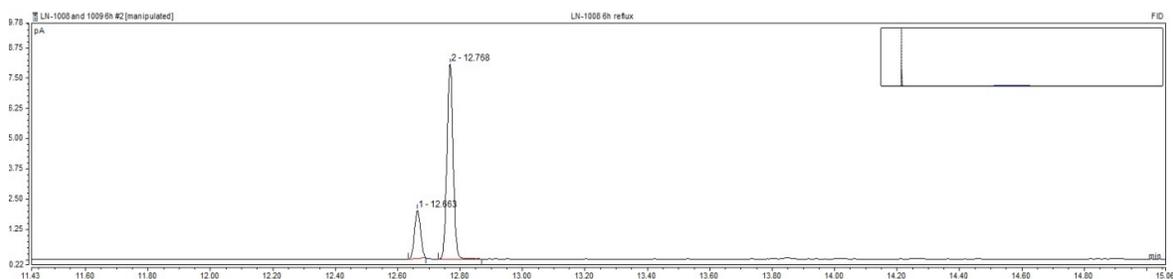
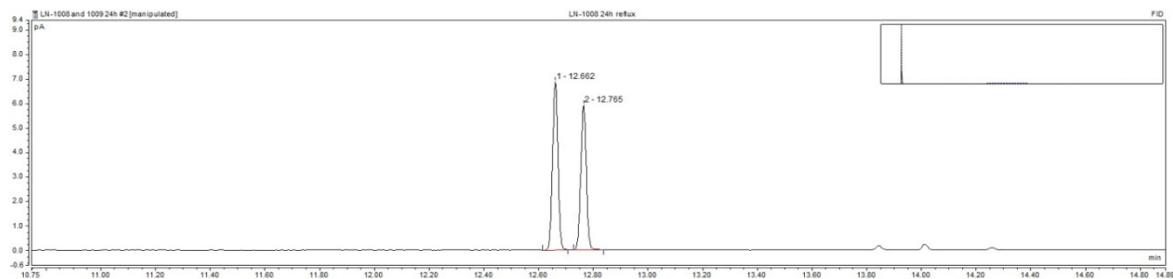


Table S-1, Entry 6, Reflux

Triphosgene (1.0 equiv), pyridine (2.0 equiv), reflux, 6 hours



Triphosgene (1.0 equiv), pyridine (2.0 equiv), reflux, 24 hours



Triphosgene (1.0 equiv), pyridine (2.0 equiv), reflux, 48 hours

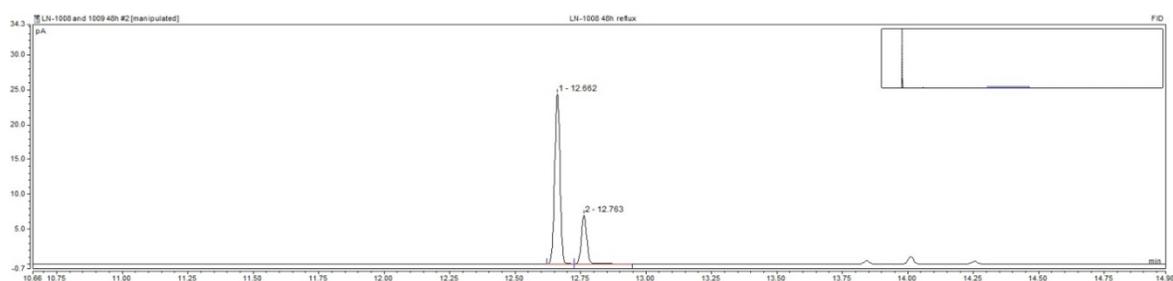
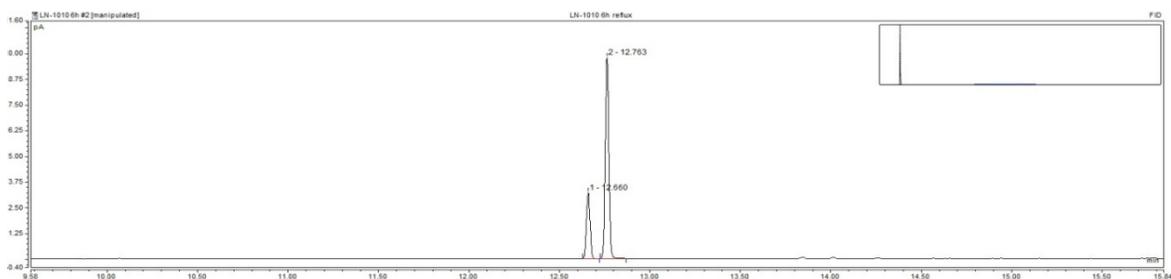
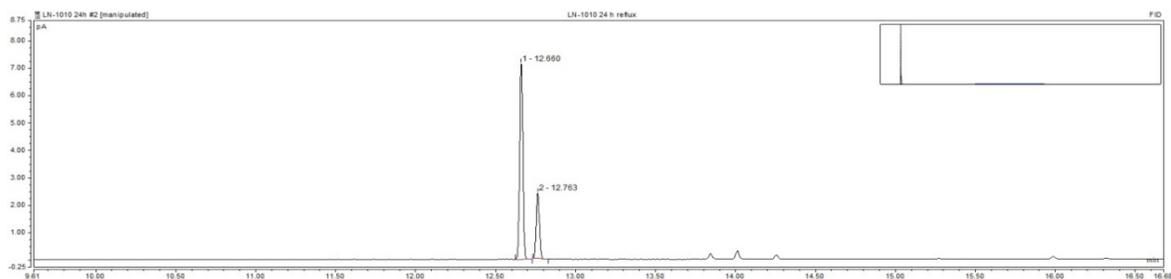


Table S-1, Entry 7, Reflux

Triphosgene (1.0 equiv), pyridine (3.0 equiv), reflux, 6 hours



Triphosgene (1.0 equiv), pyridine (3.0 equiv), reflux, 24 hours



Triphosgene (1.0 equiv), pyridine (3.0 equiv), reflux, 48 hours

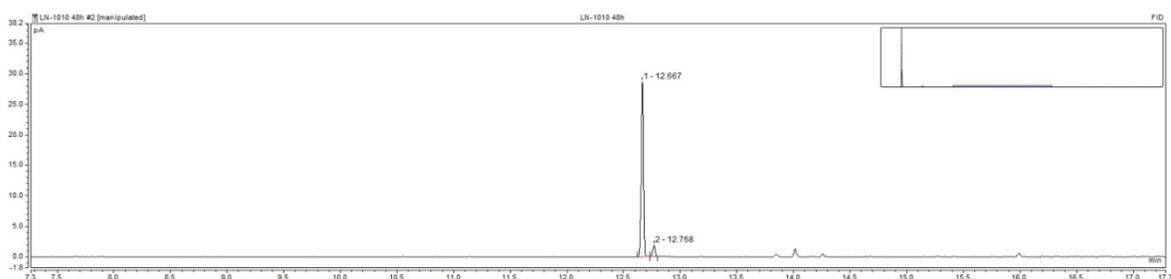
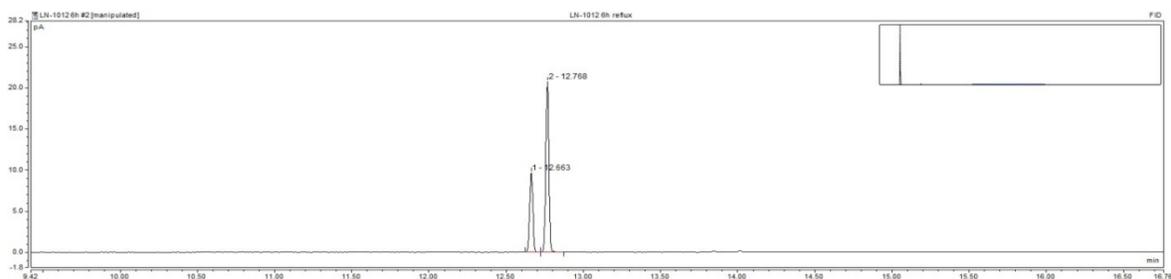
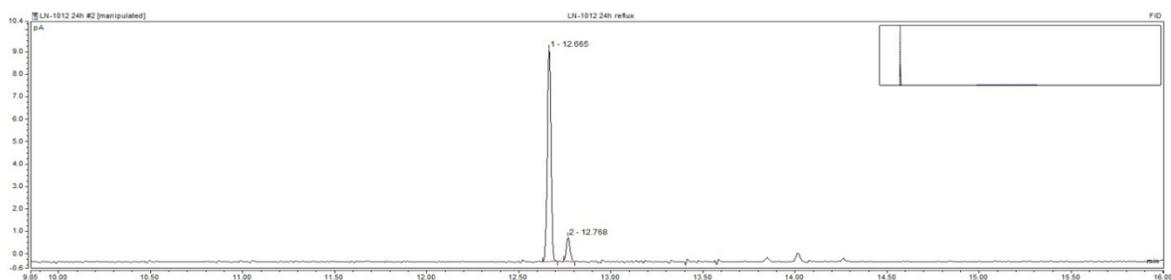


Table S-1, Entry 8, Reflux

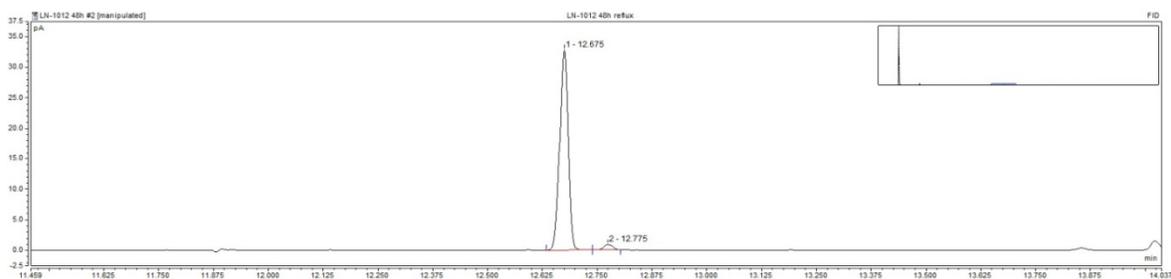
Triphosgene (1.0 equiv), pyridine (4.0 equiv), reflux, 6 hours

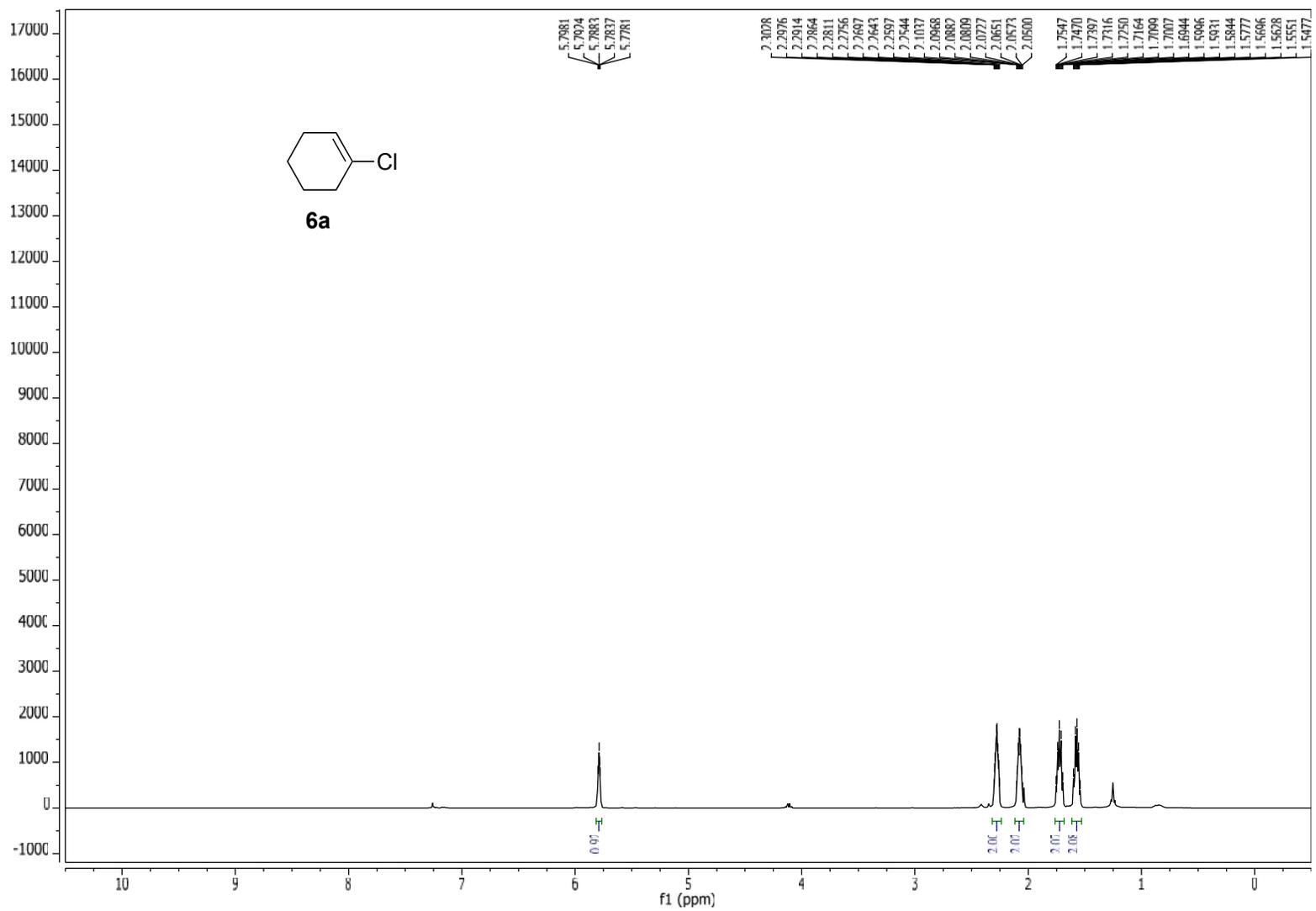


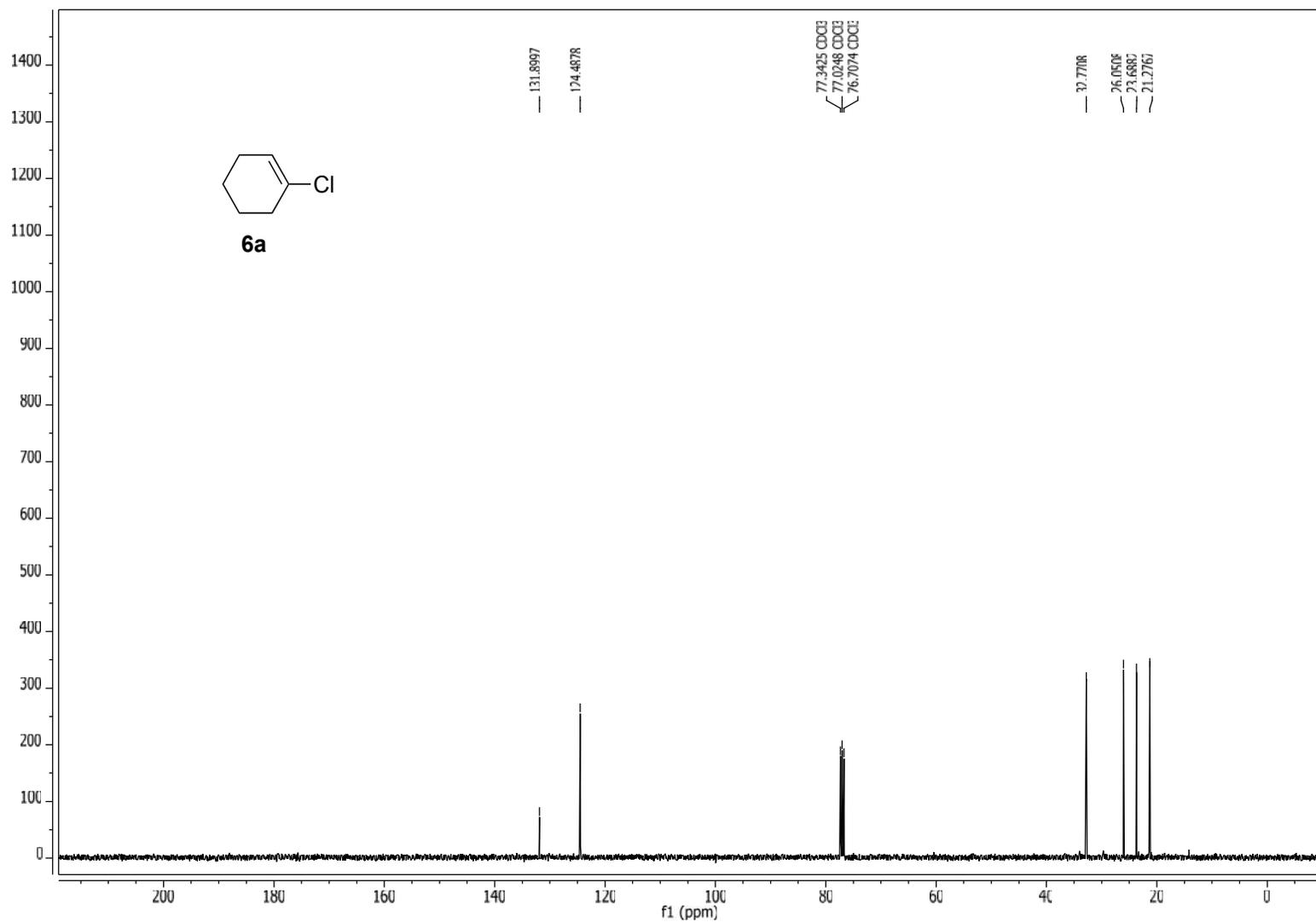
Triphosgene (1.0 equiv), pyridine (4.0 equiv), reflux, 24 hours



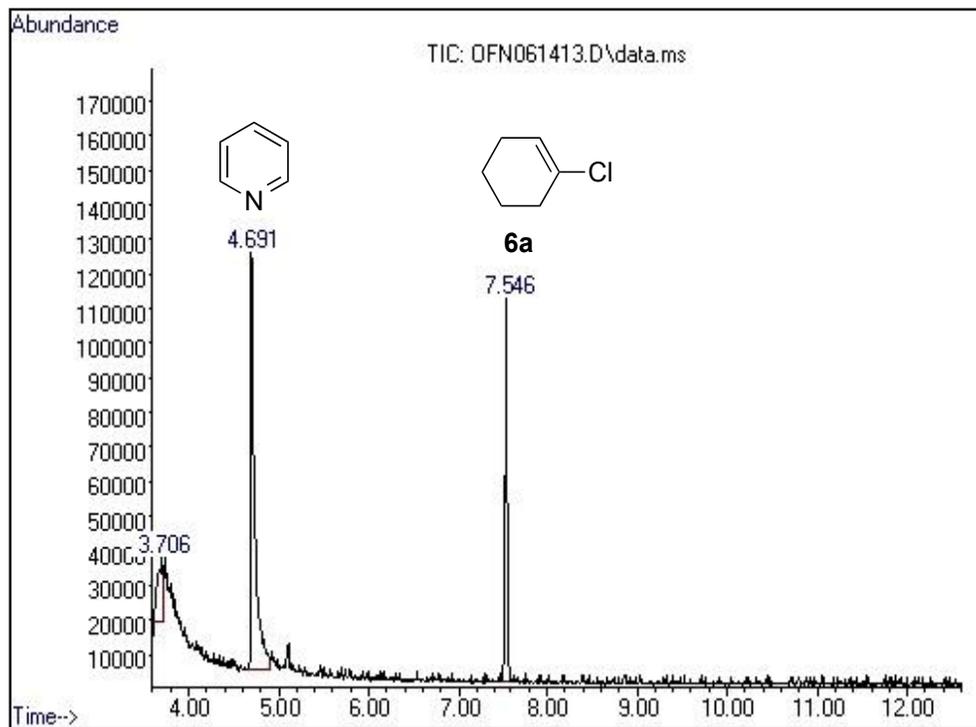
Triphosgene (1.0 equiv), pyridine (4.0 equiv), reflux, 48 hours



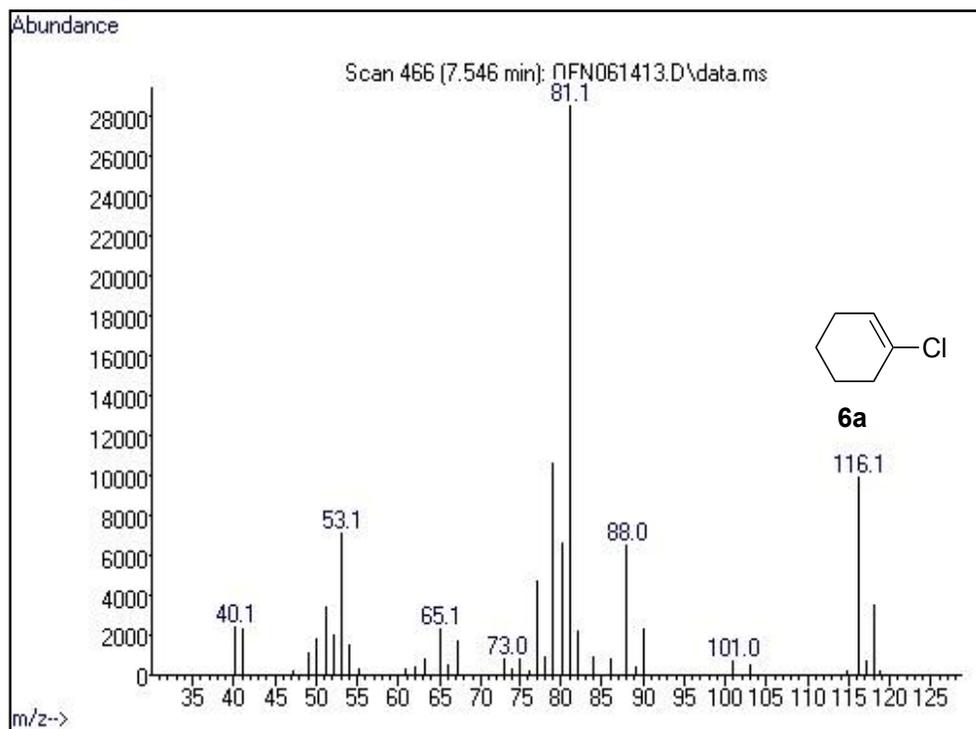


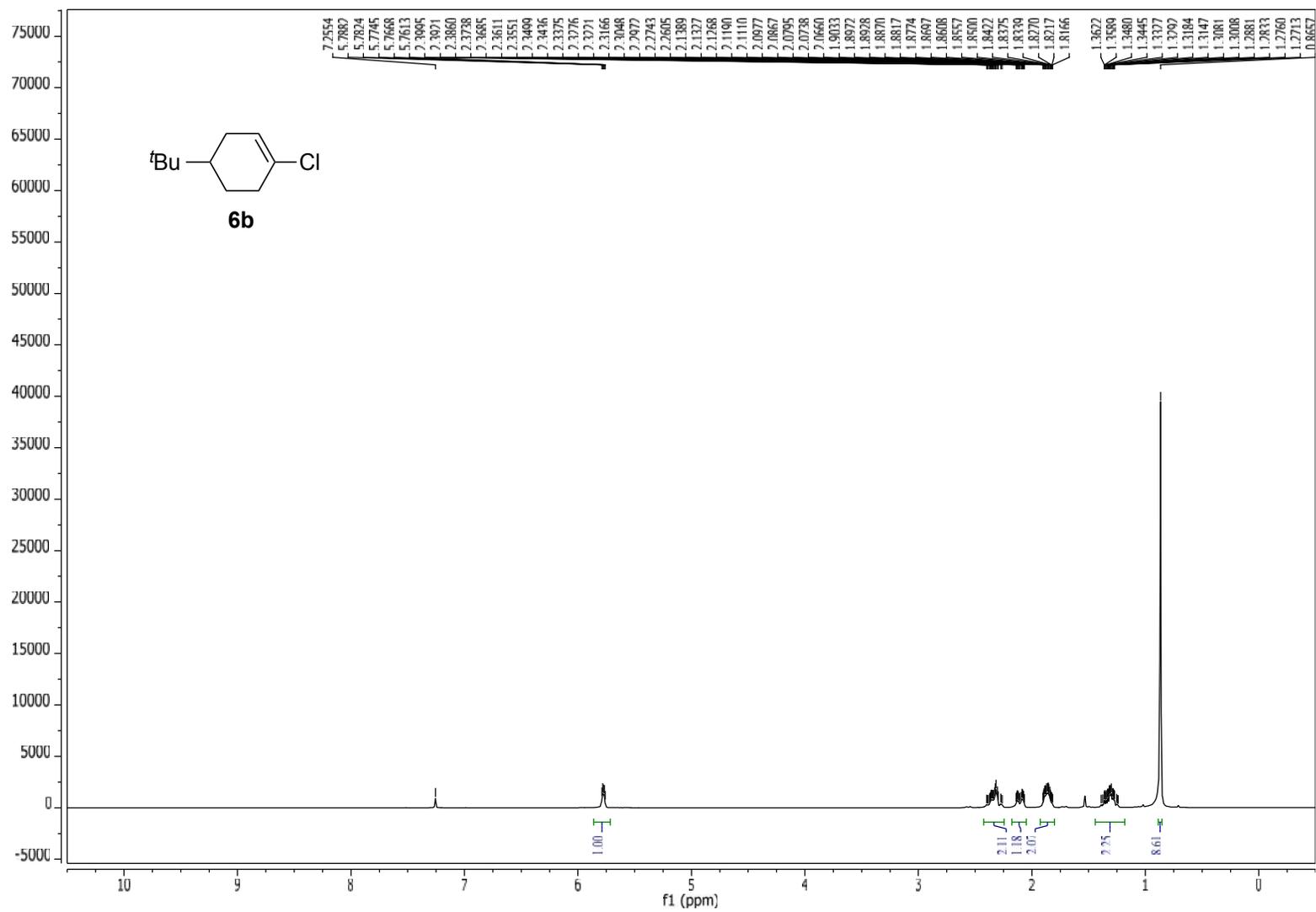


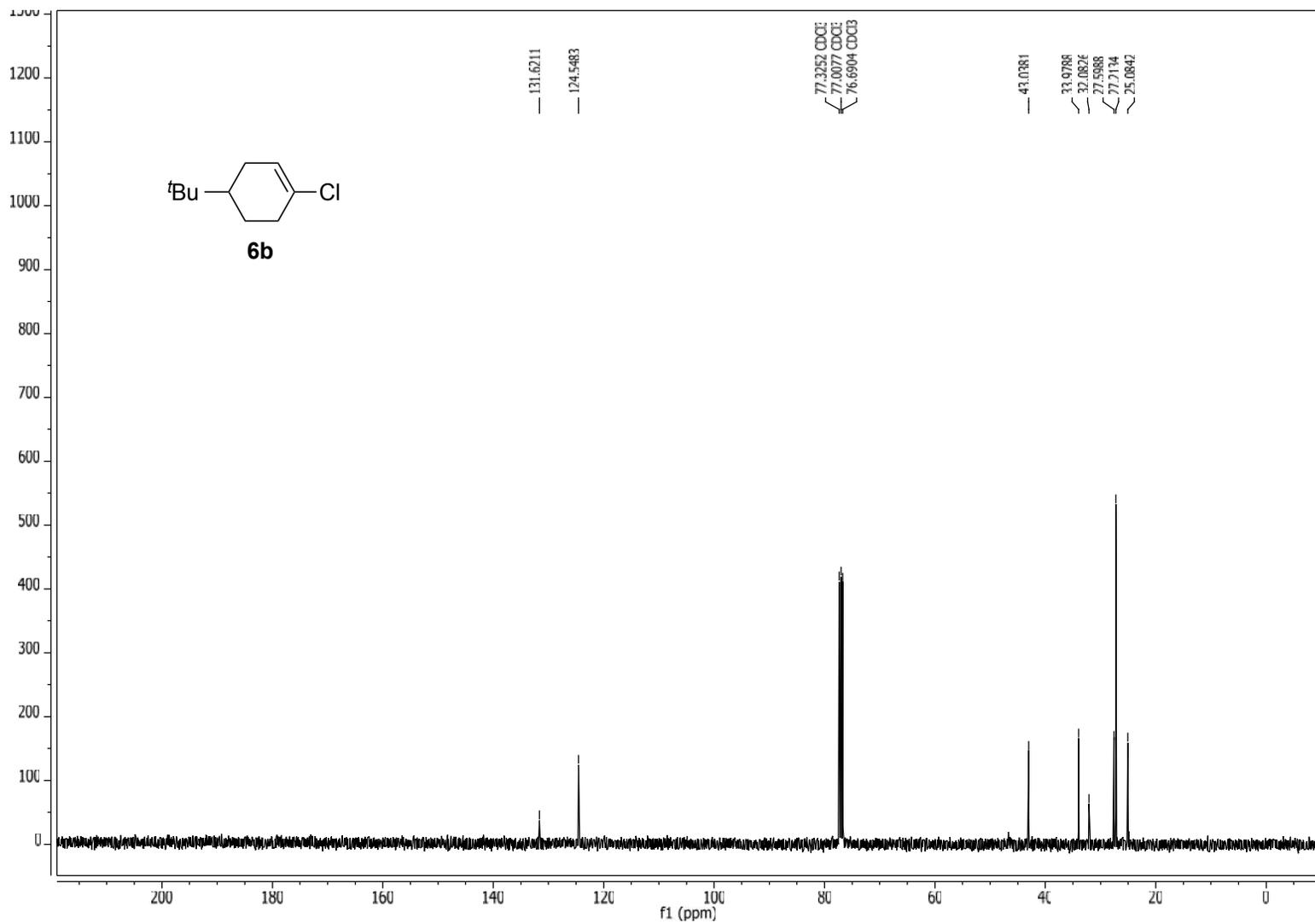
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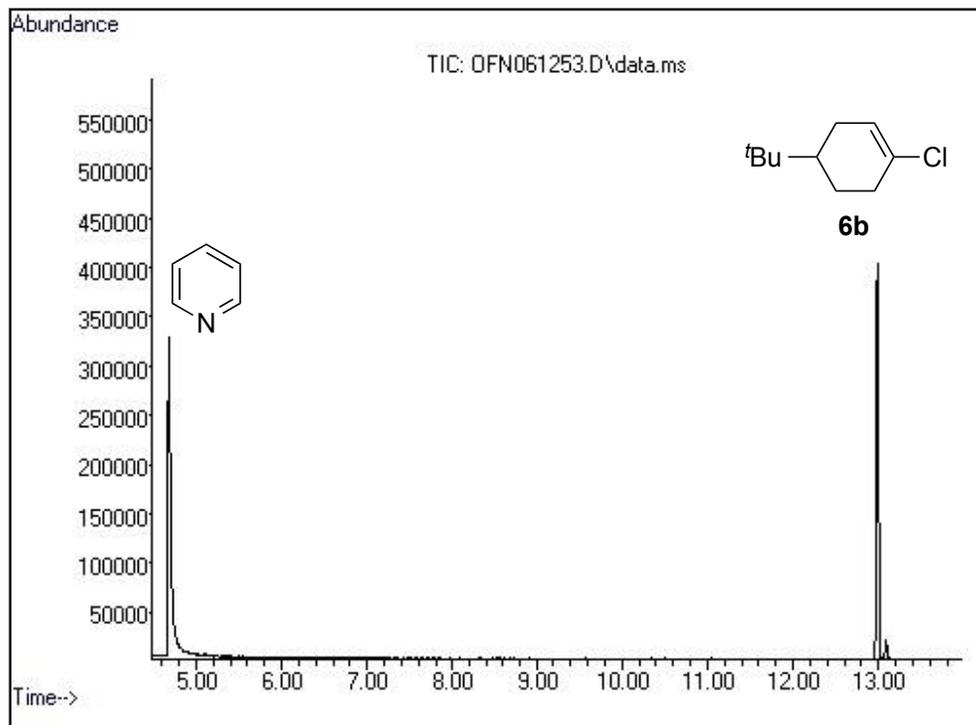
Product MS at 7.546 min:



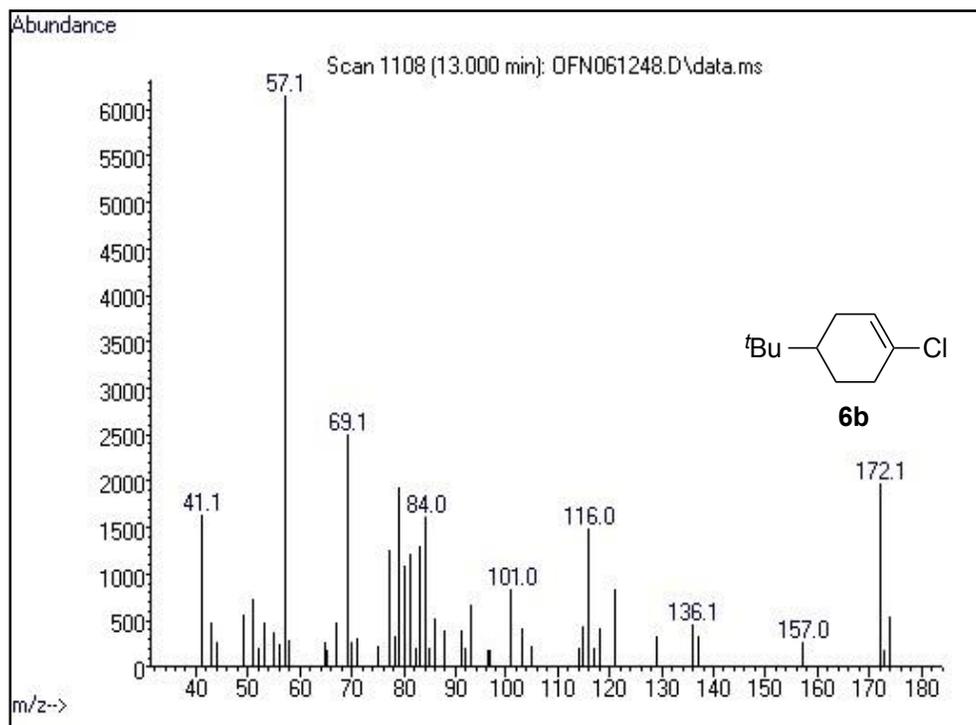


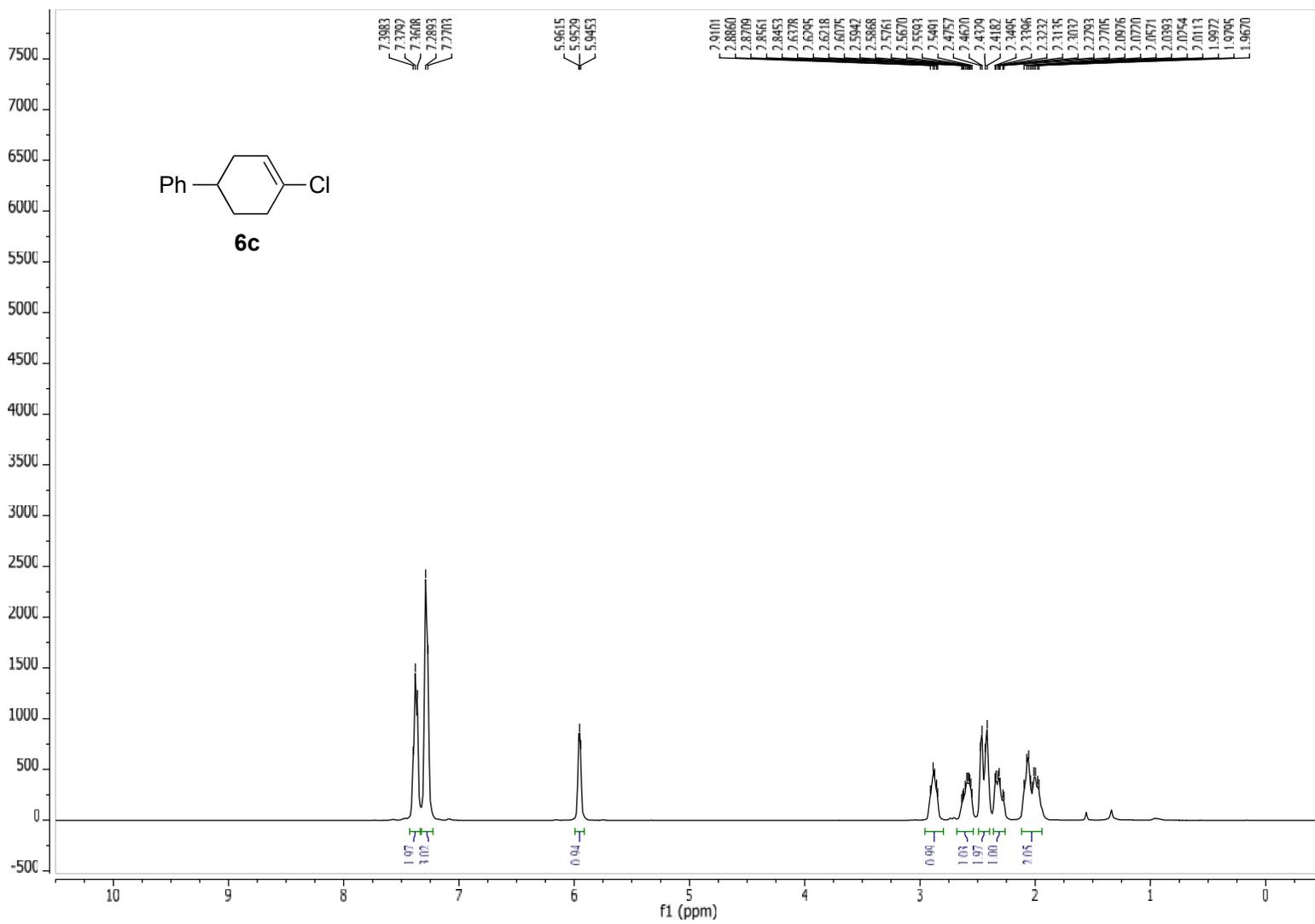


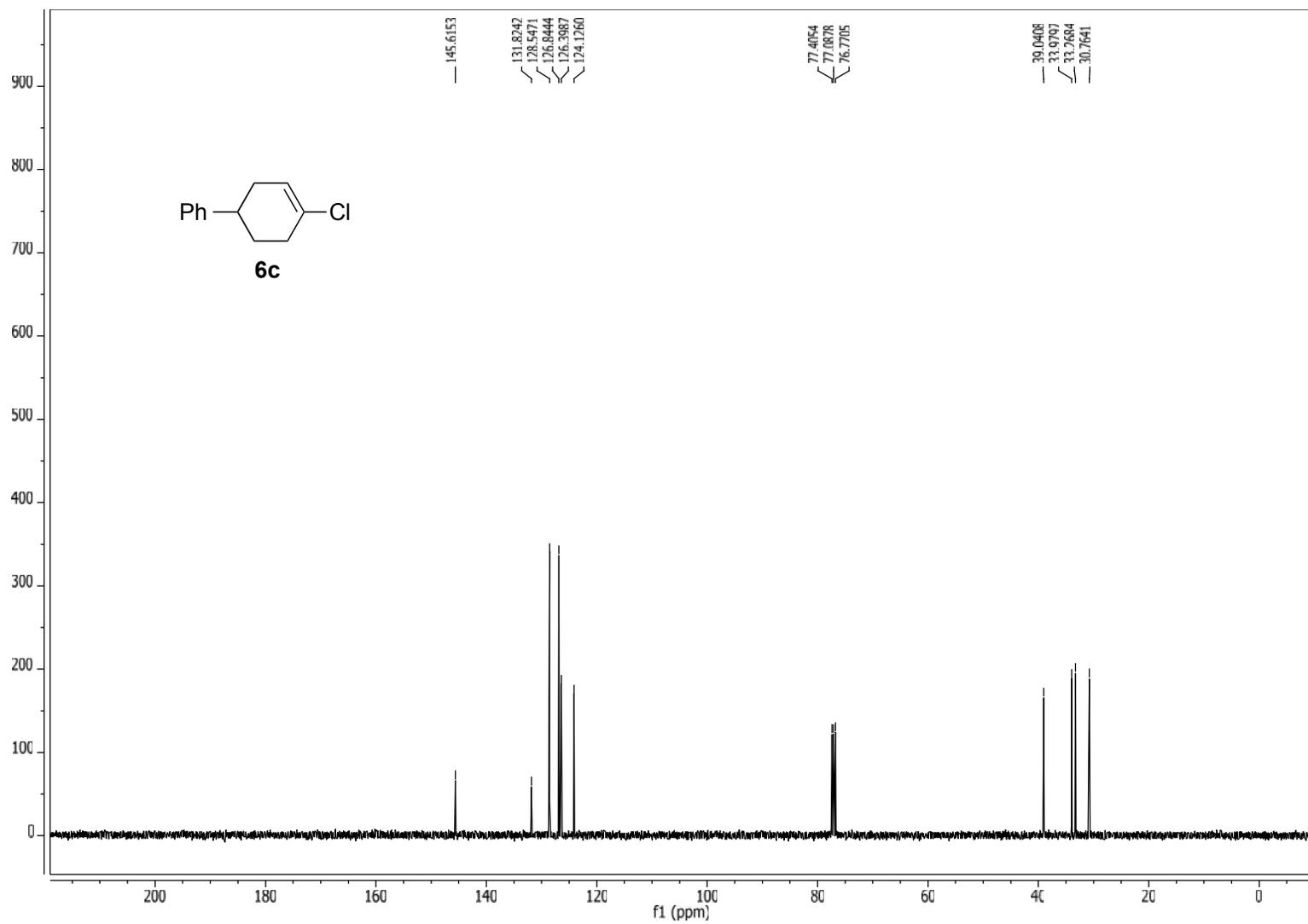
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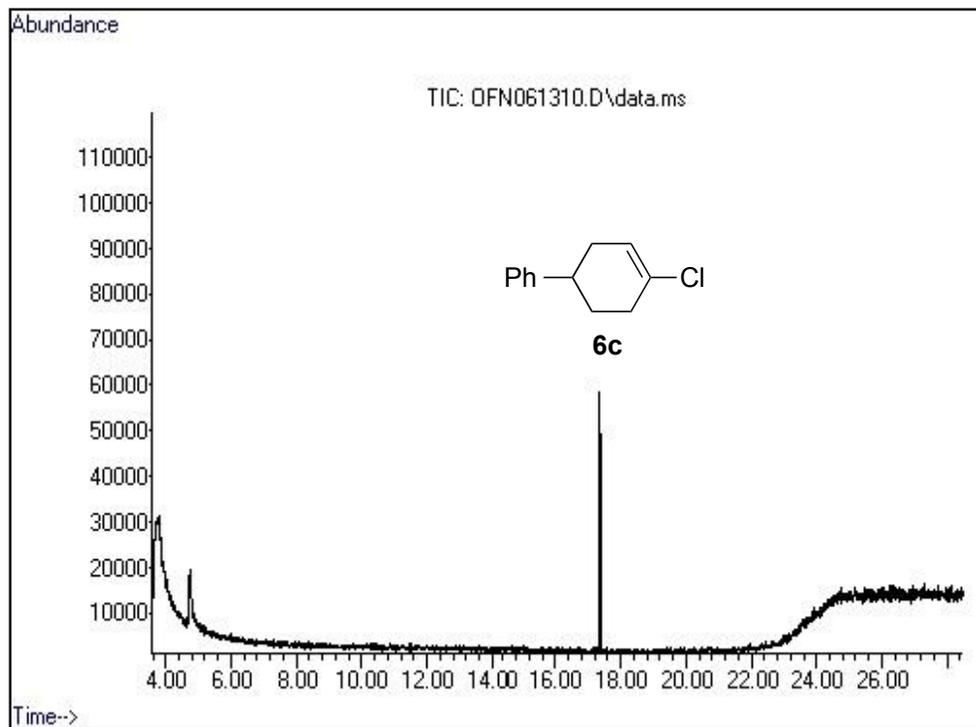
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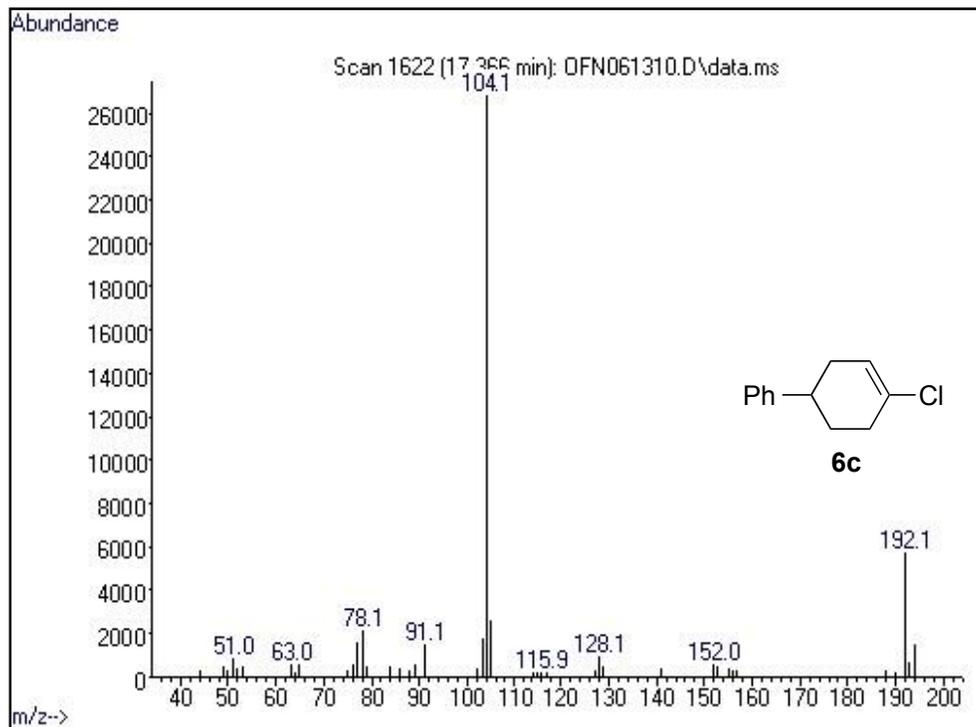


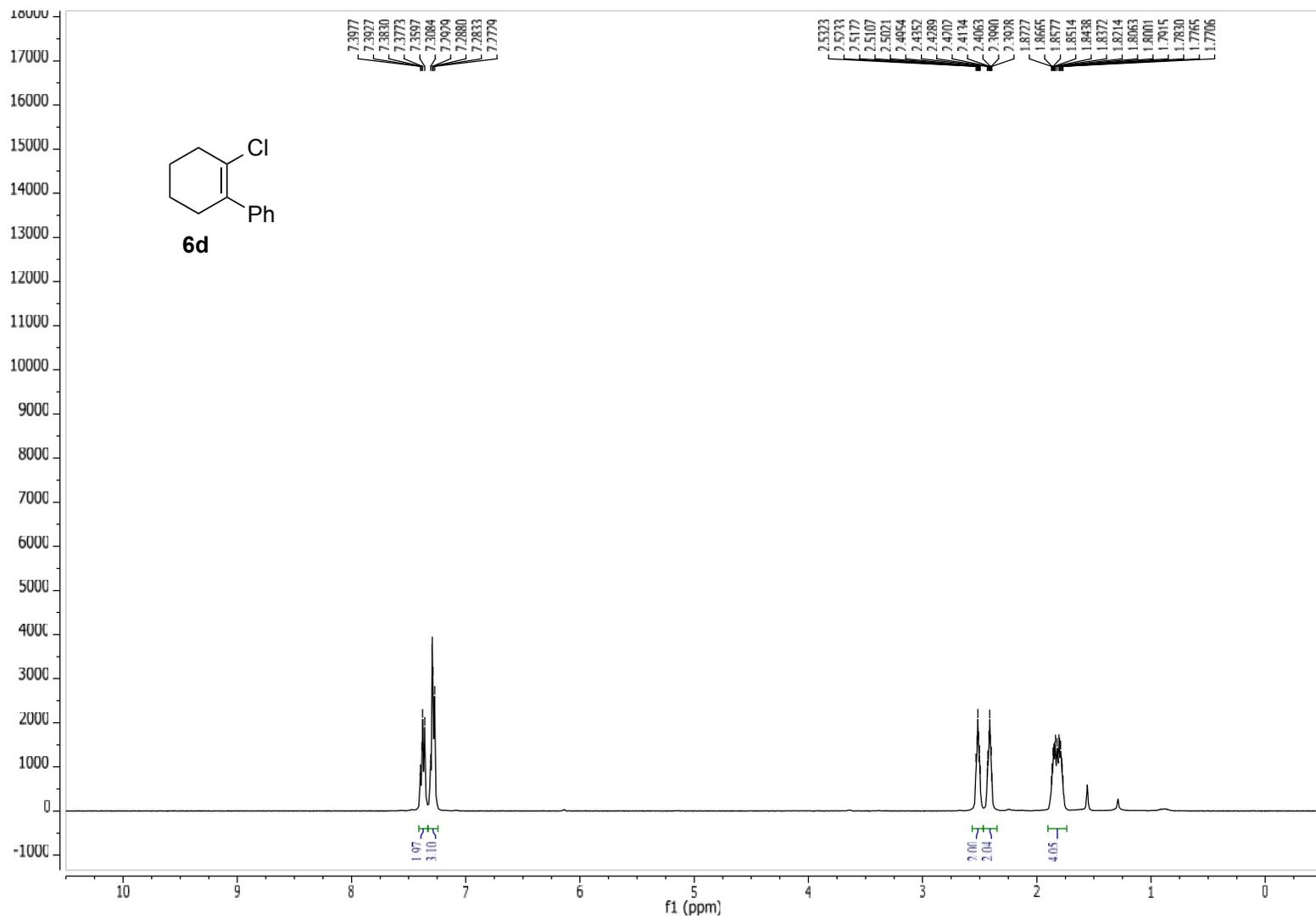


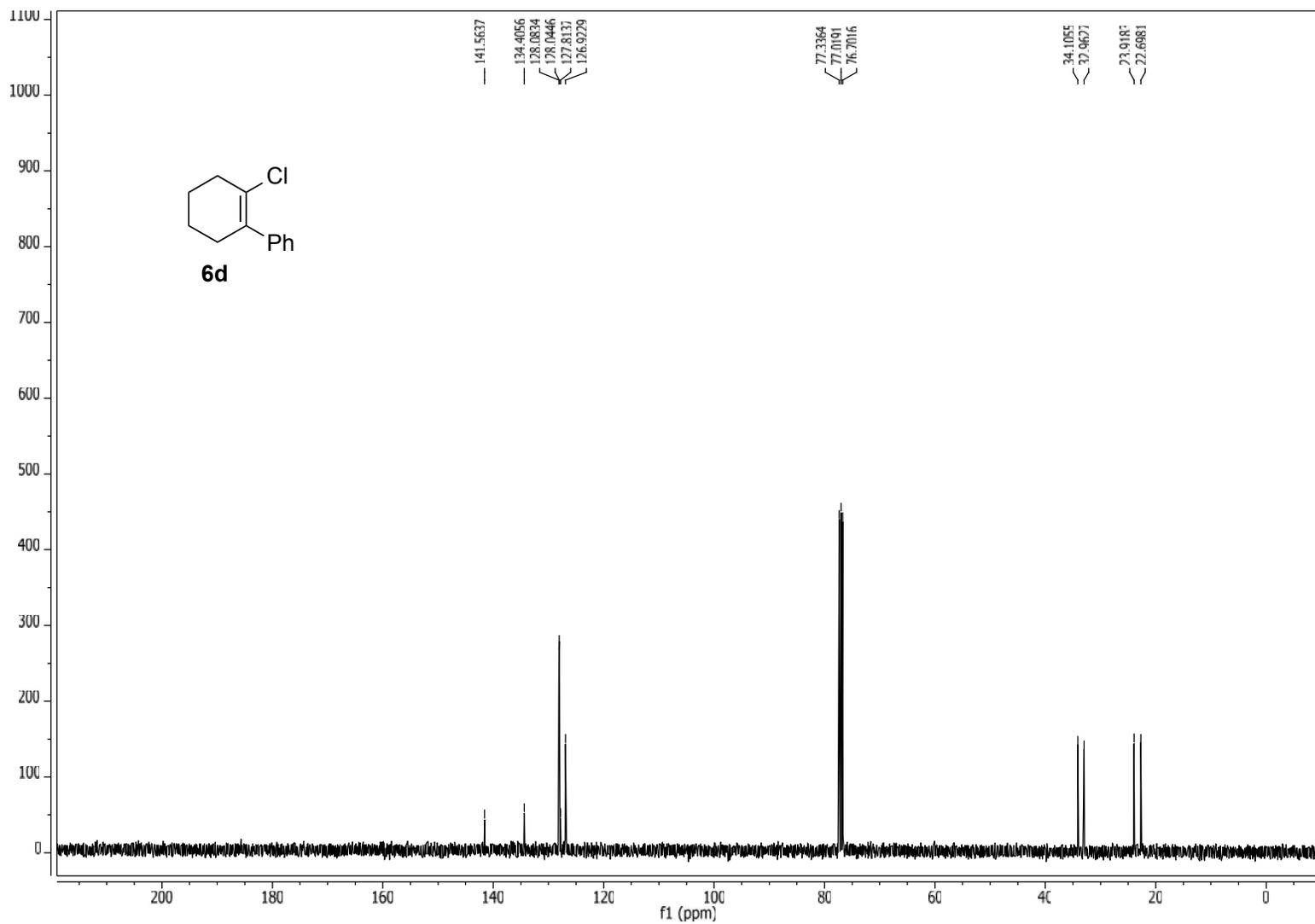
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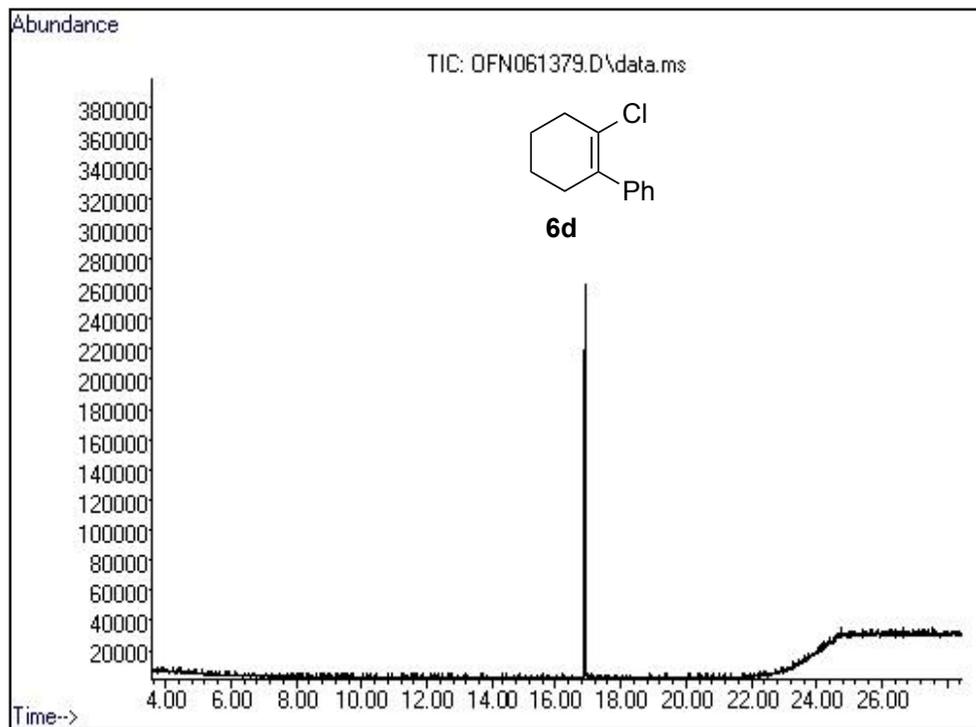
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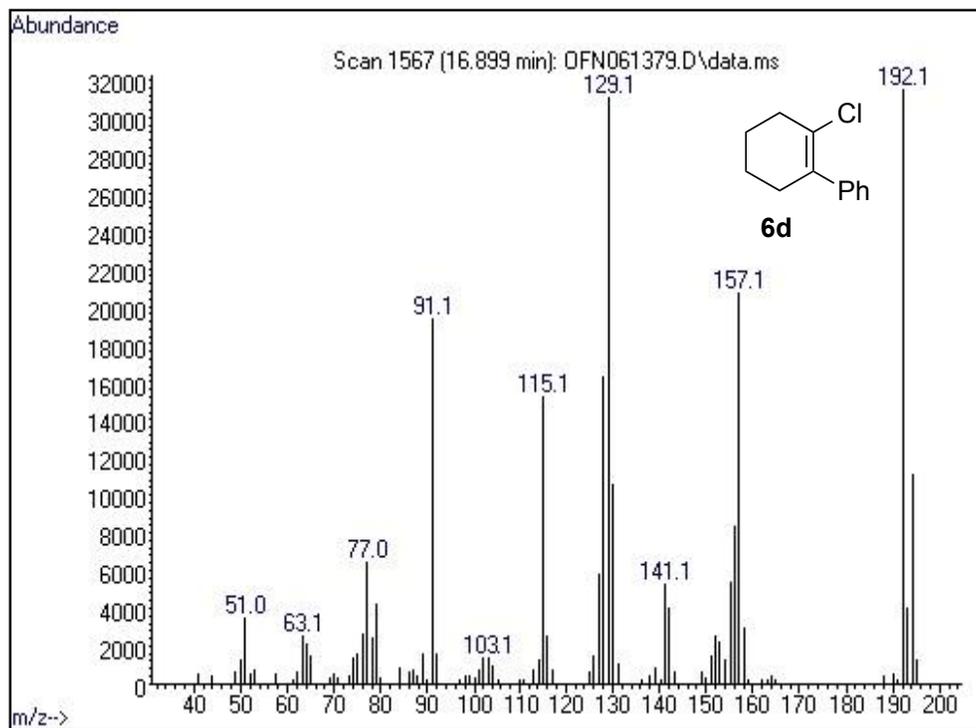


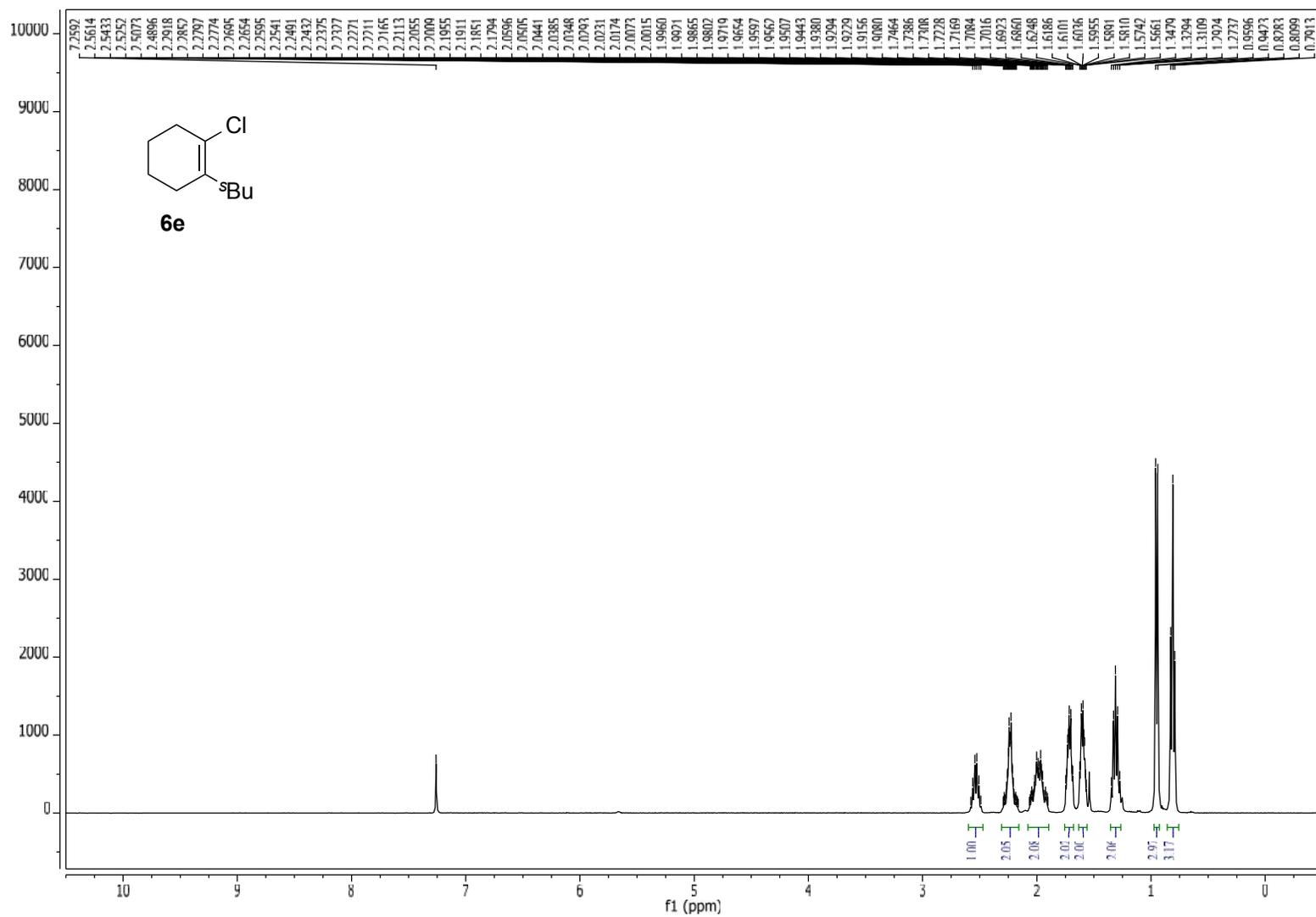


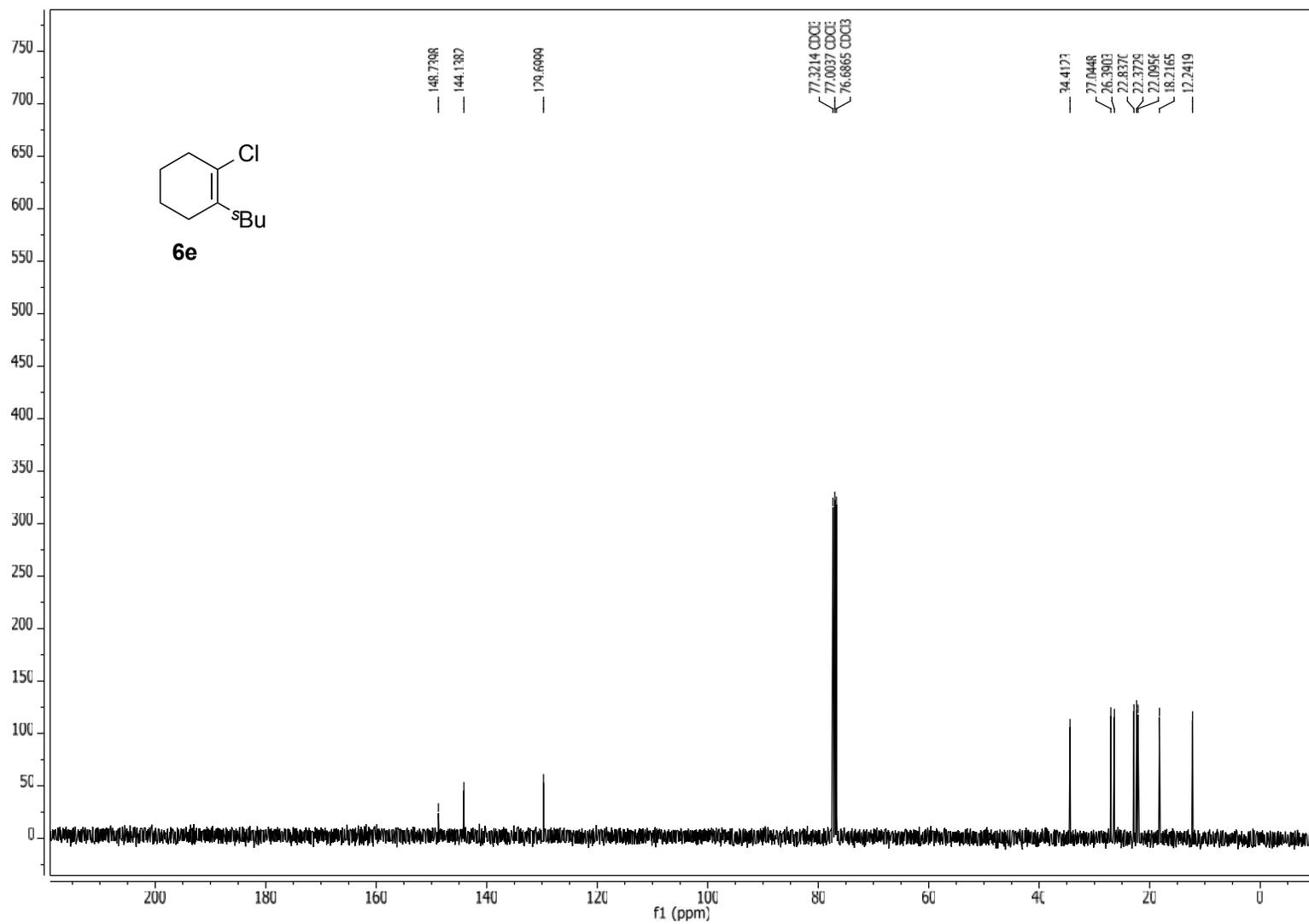
GC-MS:



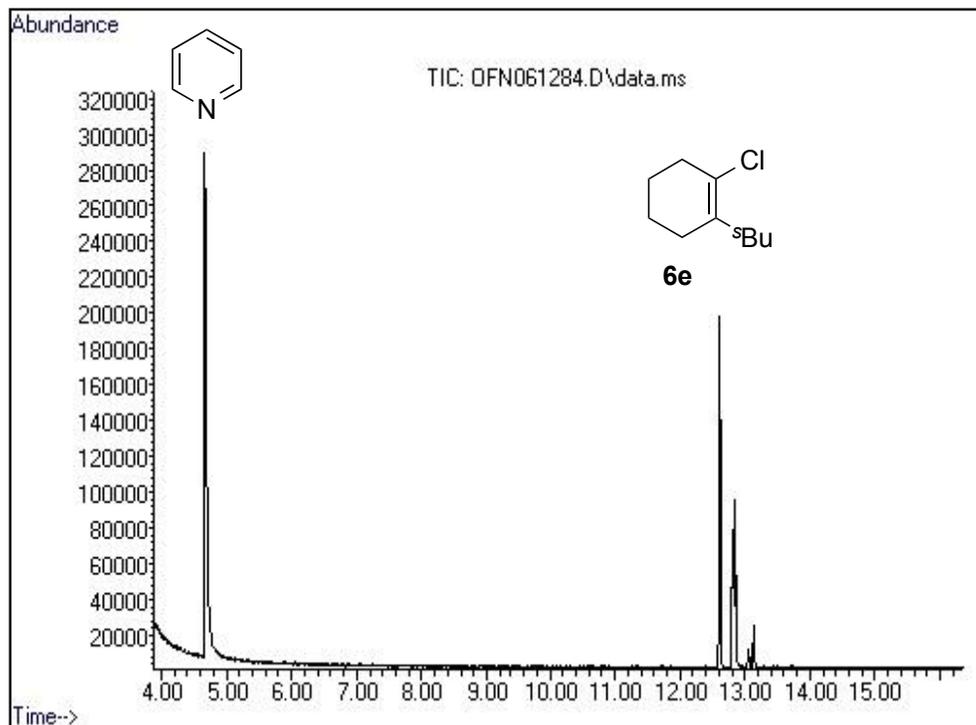
Product MS at 16.899 min:



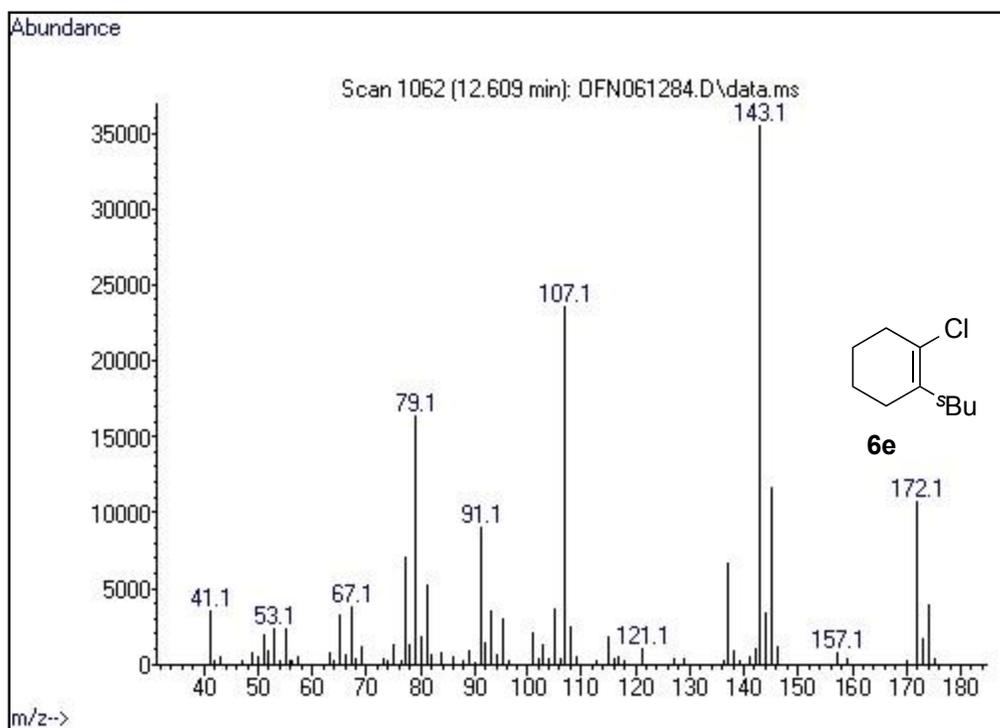


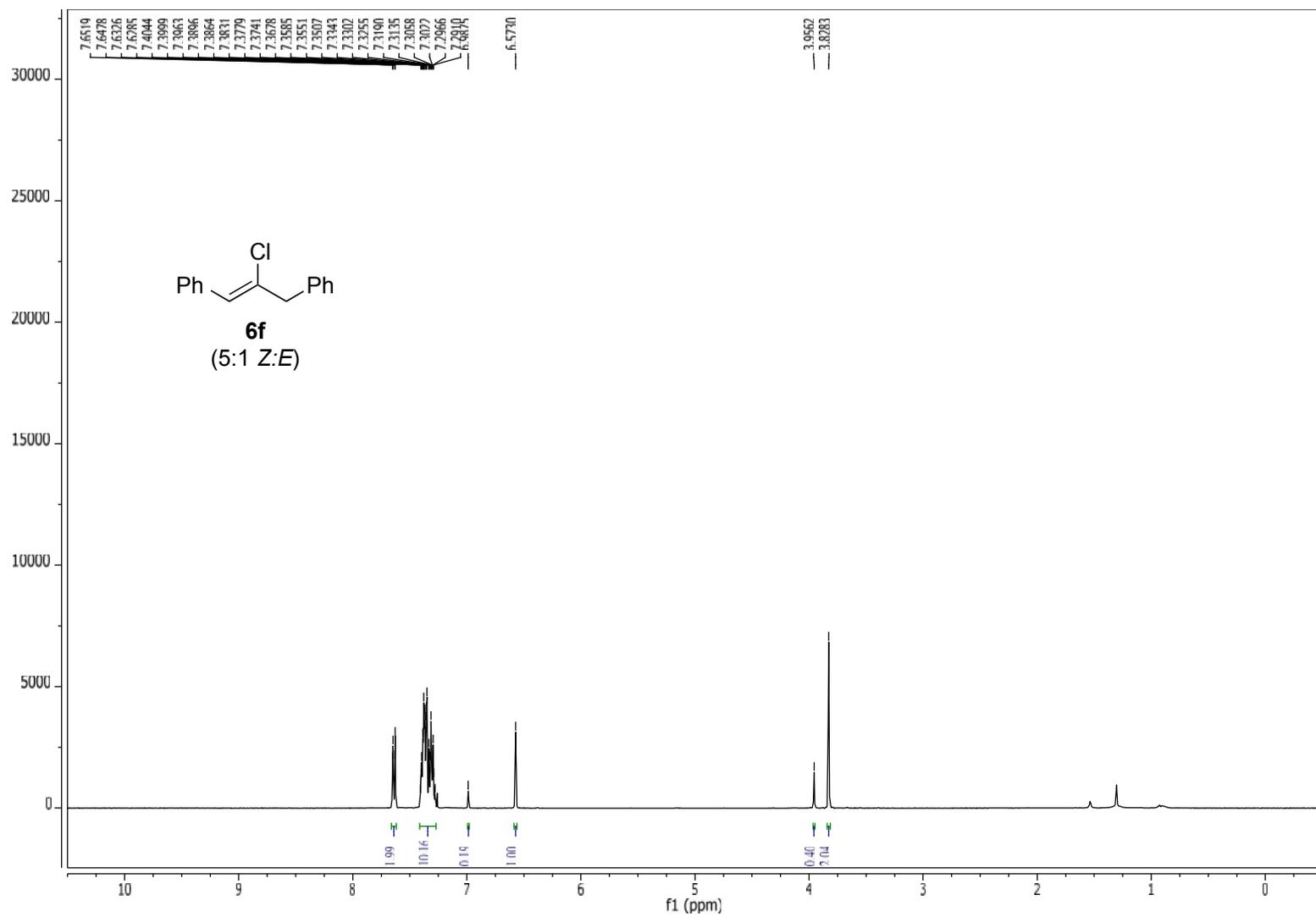


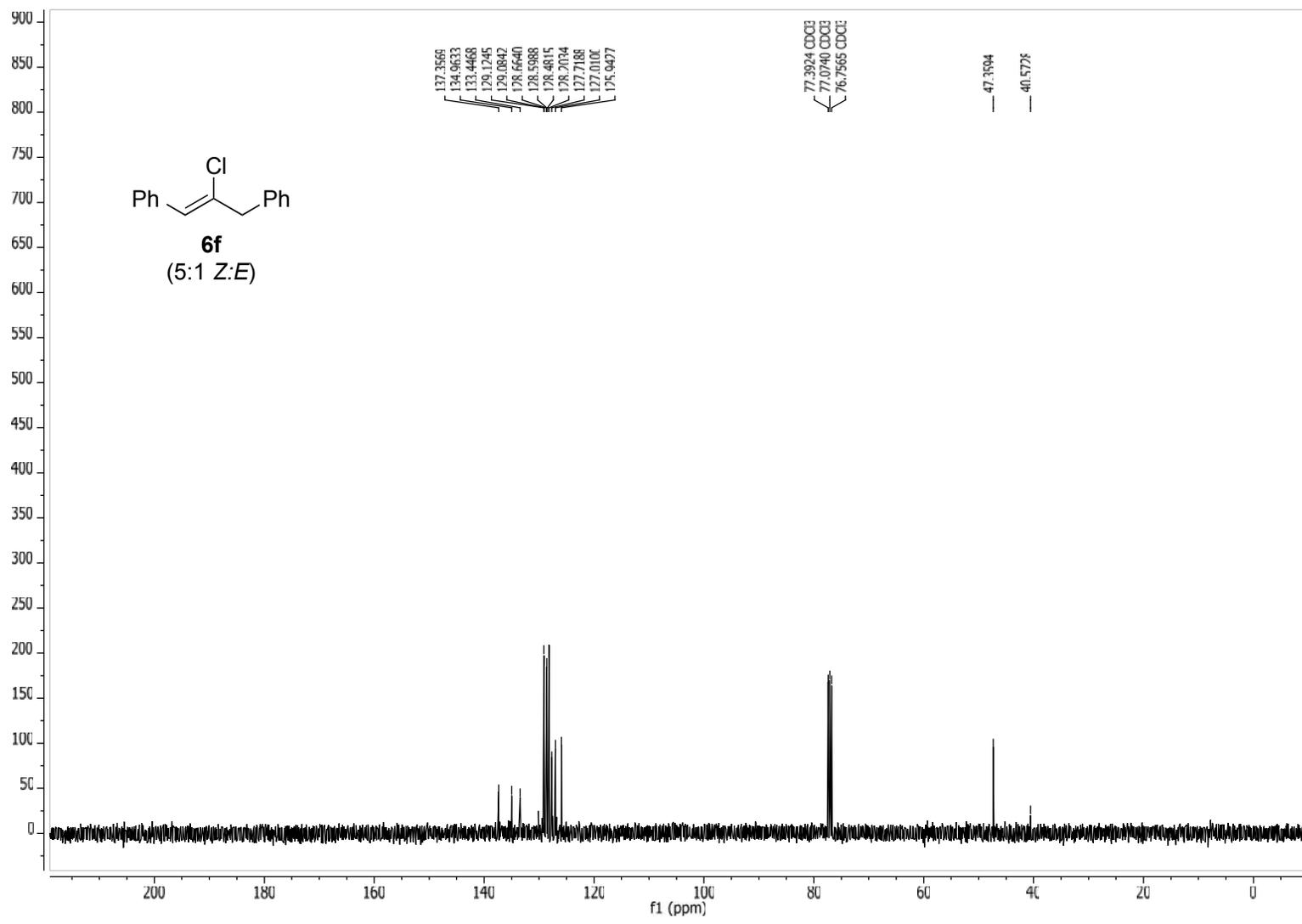
GC-MS:

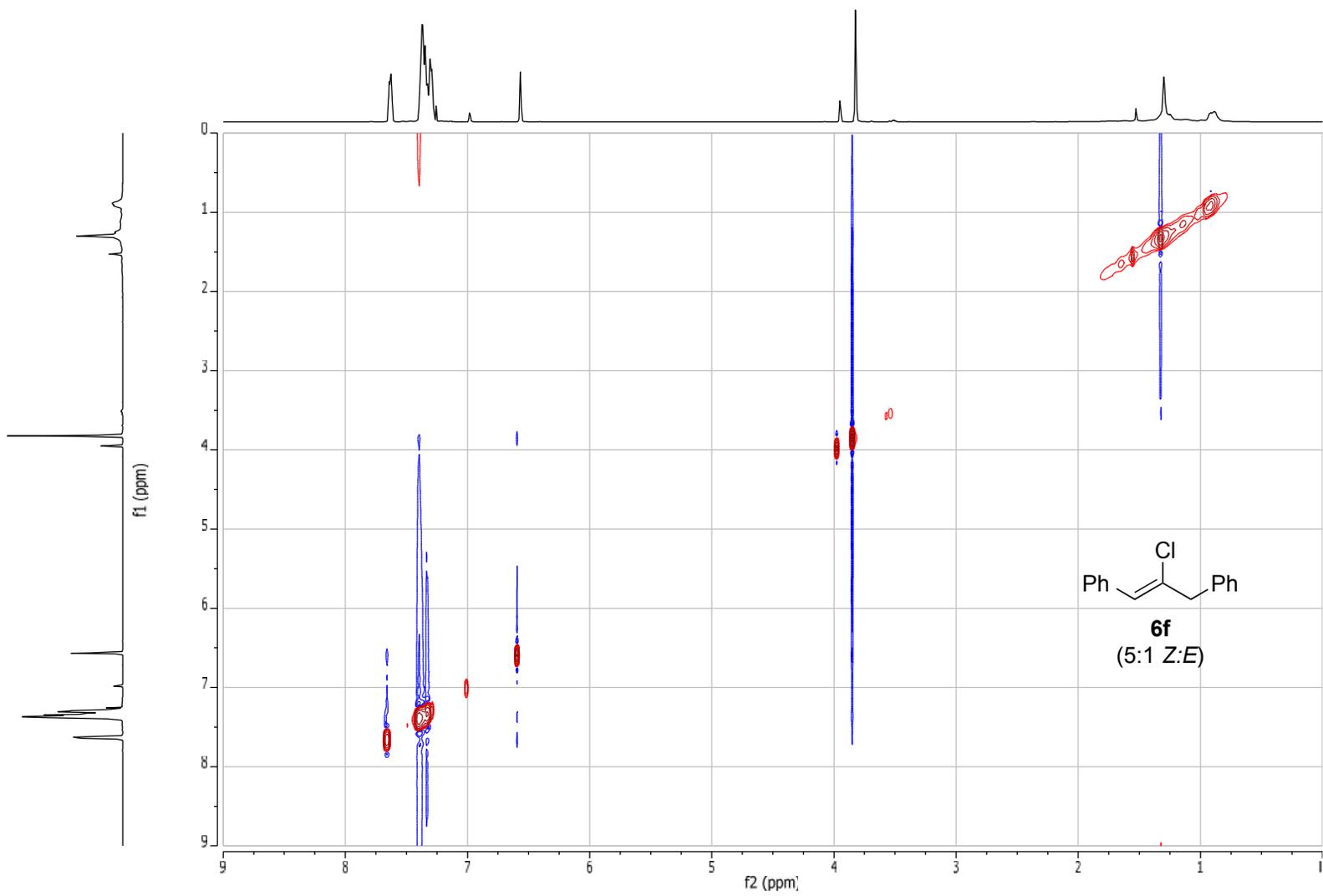


Major product MS at 12.609 min:

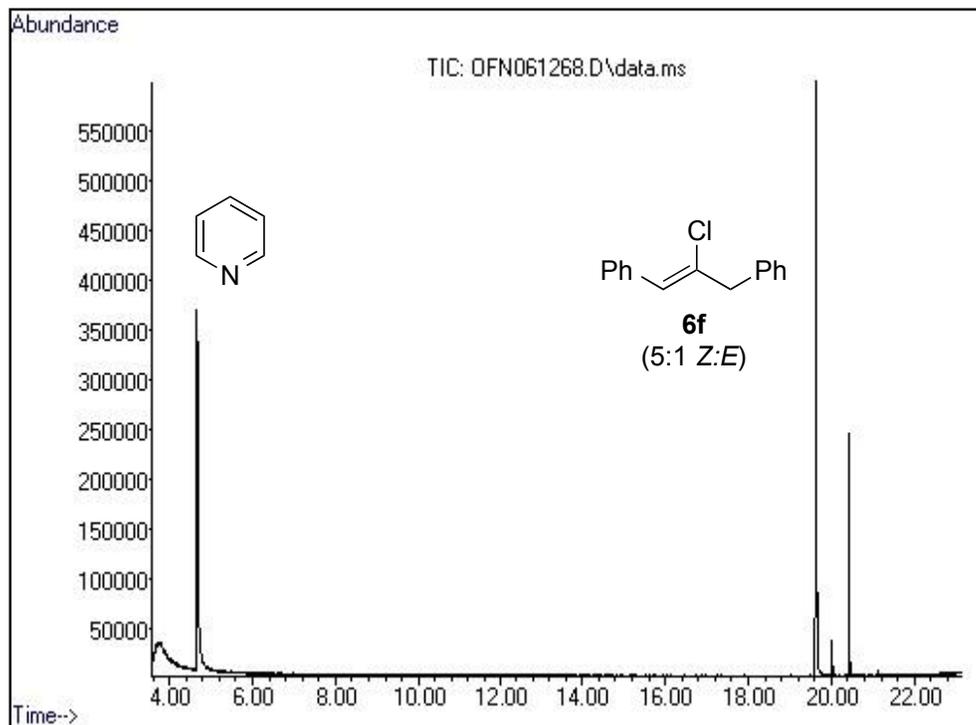




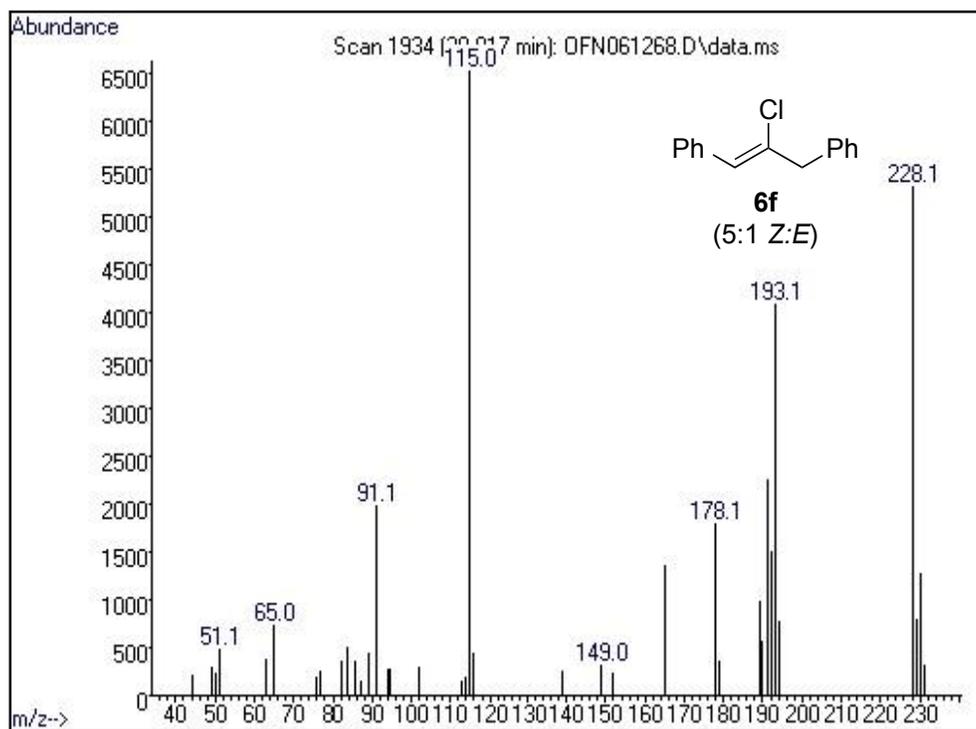




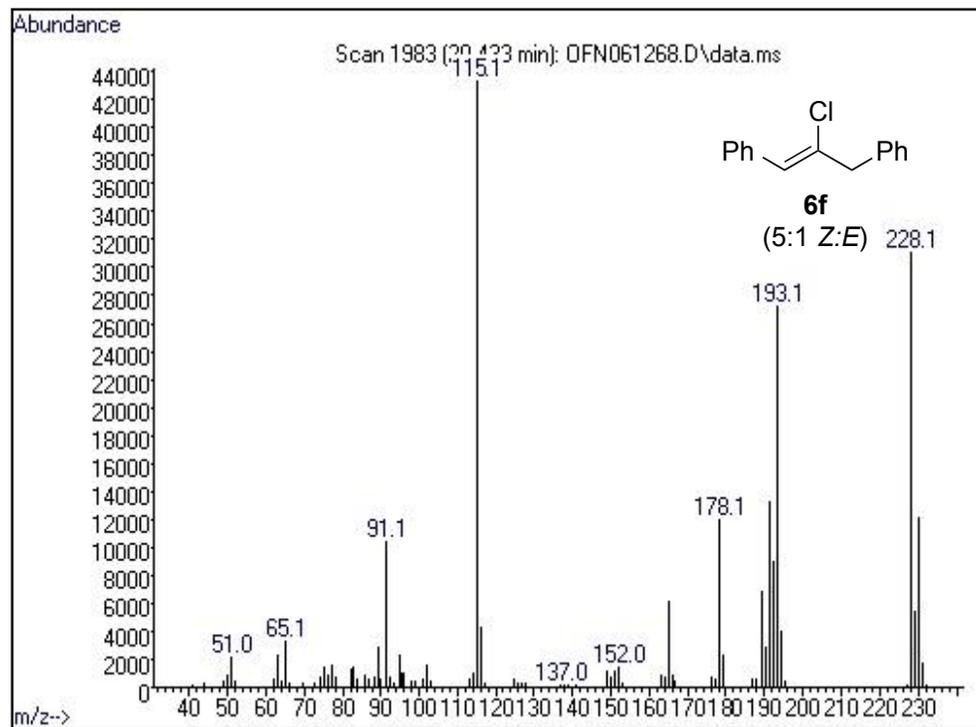
GC-MS:

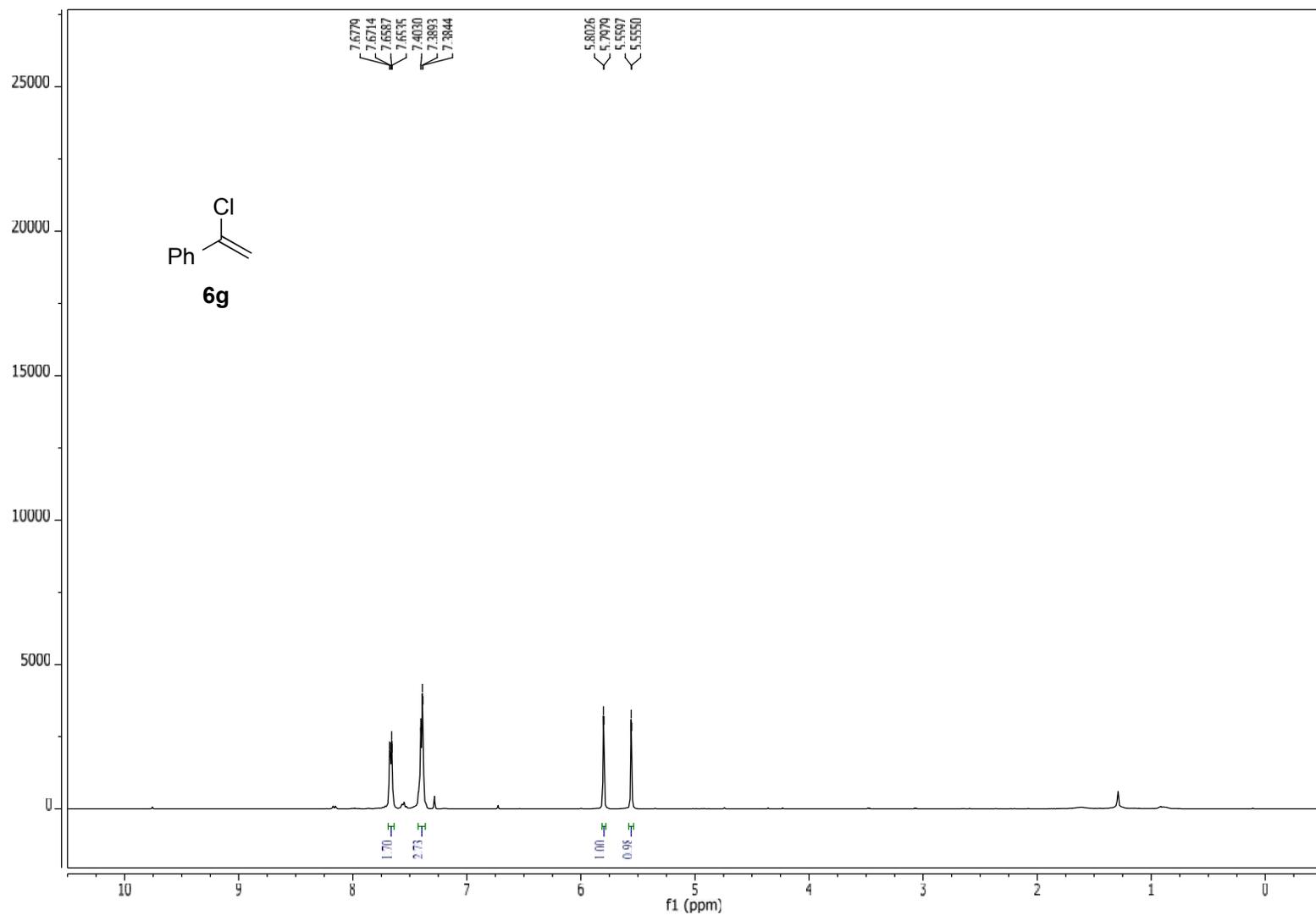


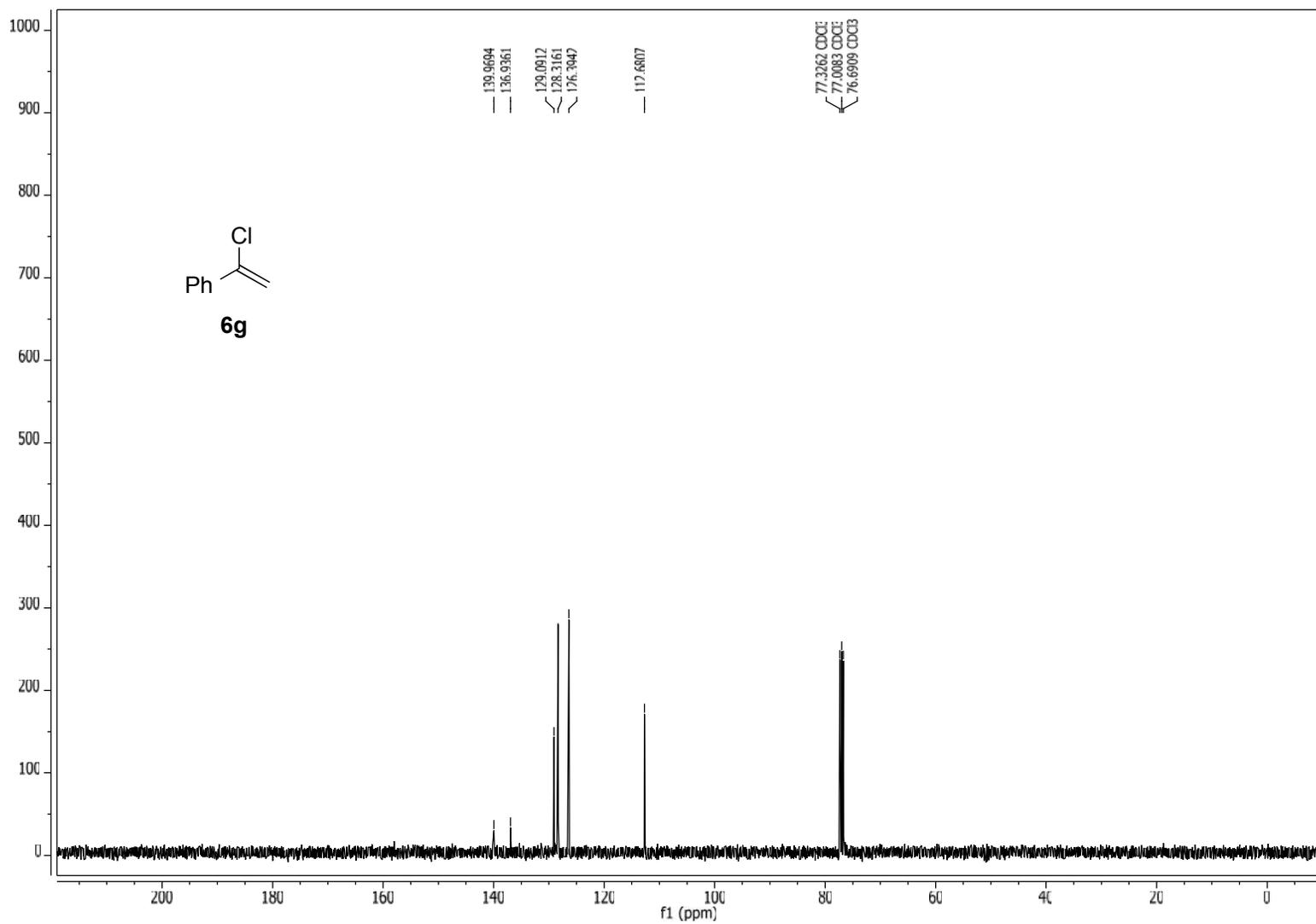
Major product MS at 20.017min:



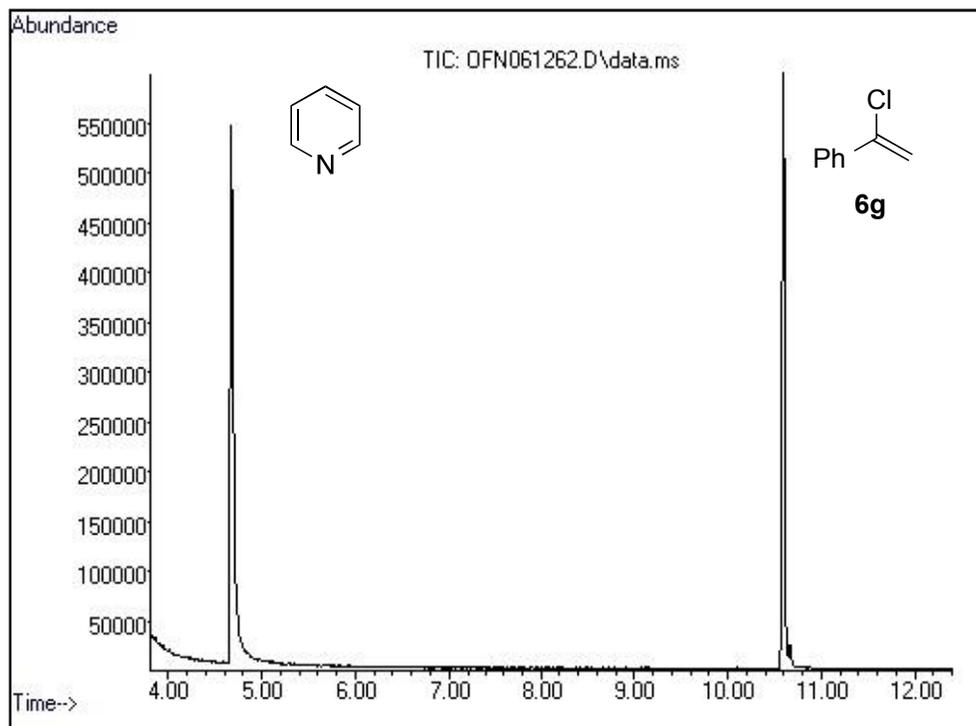
Minor product MS at 20.433 min:



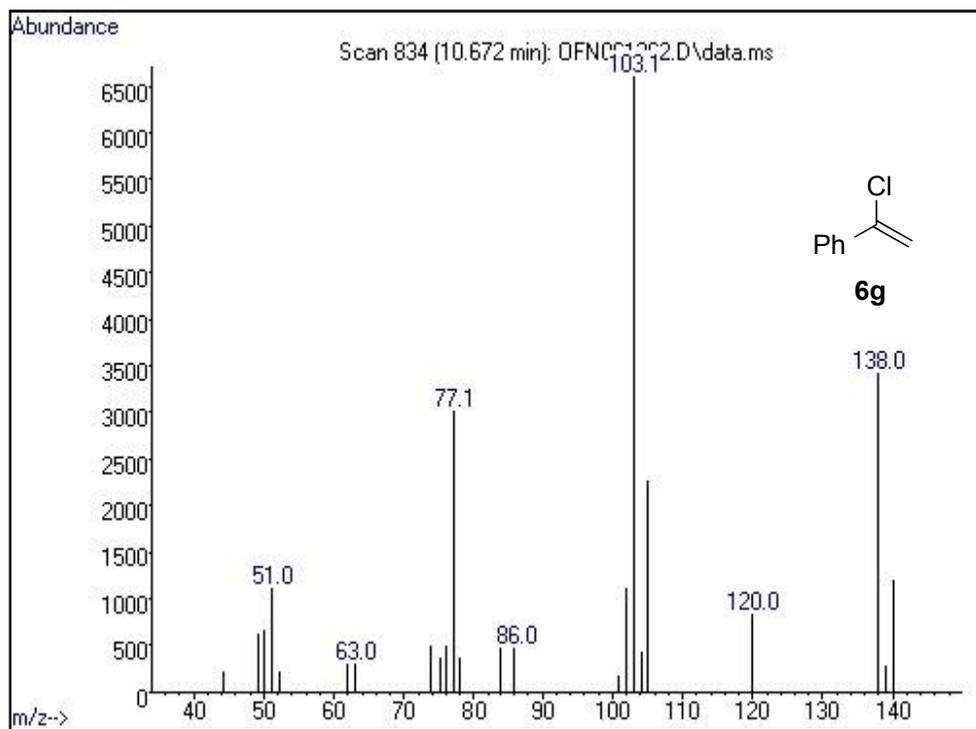


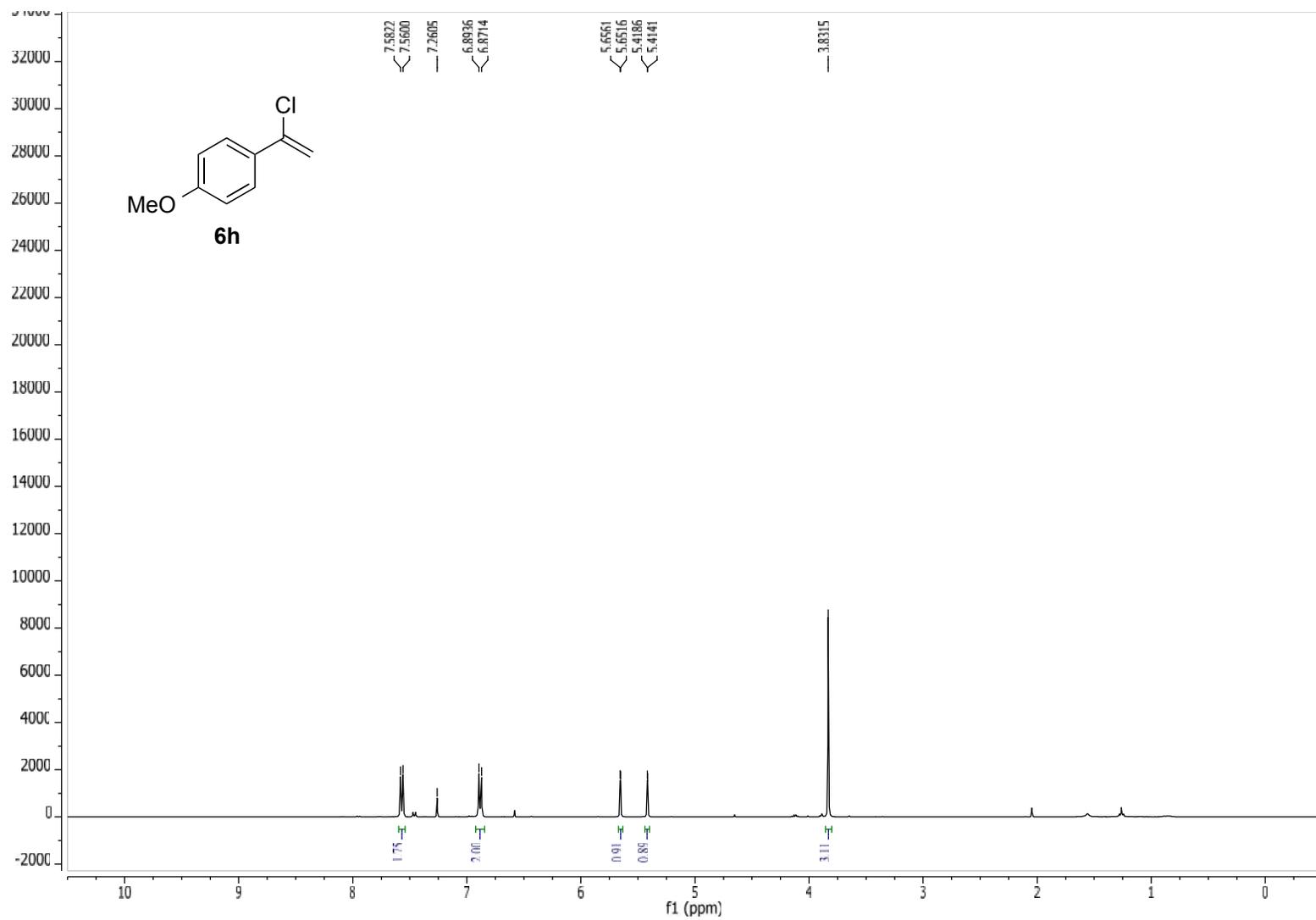


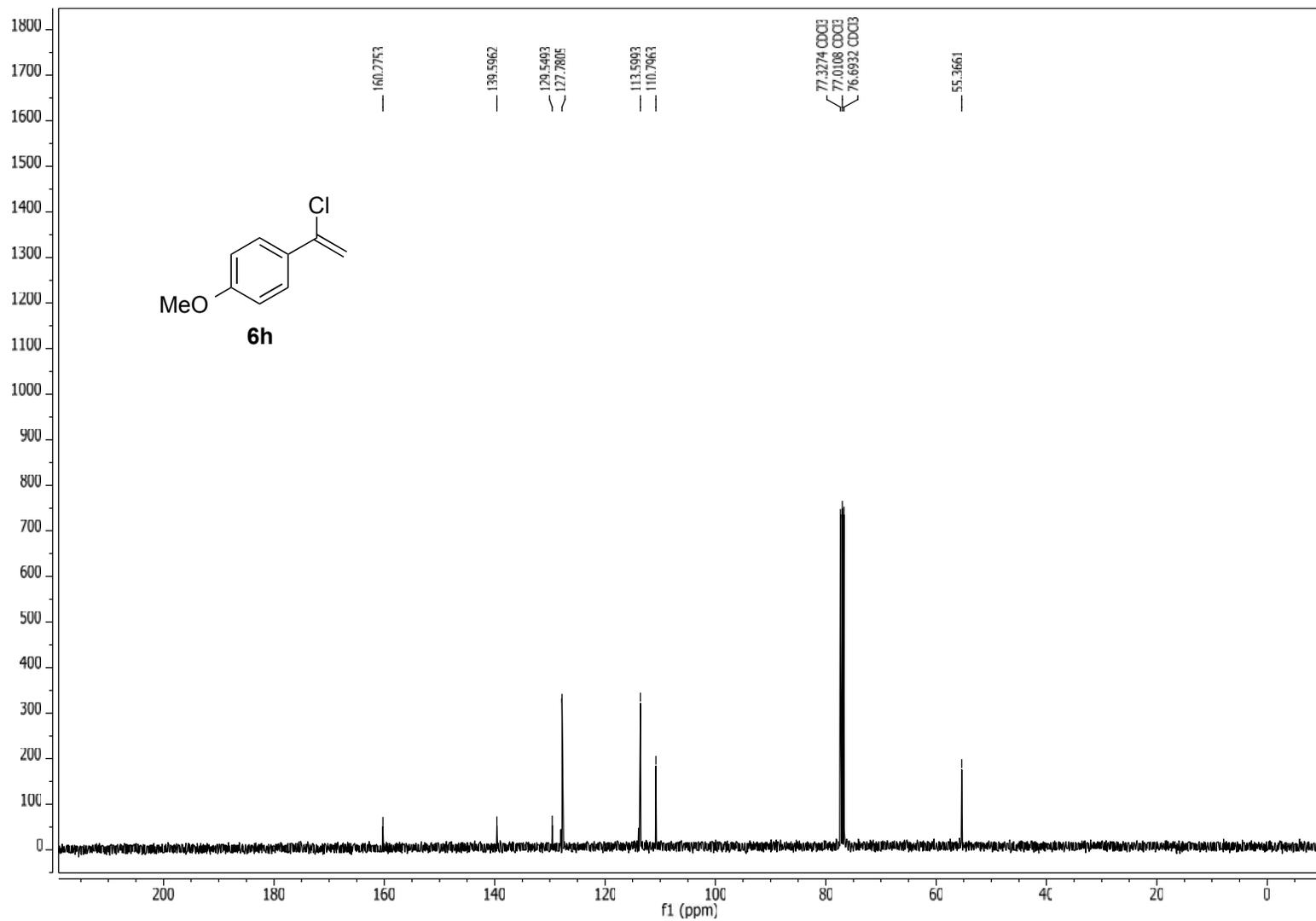
GC-MS:



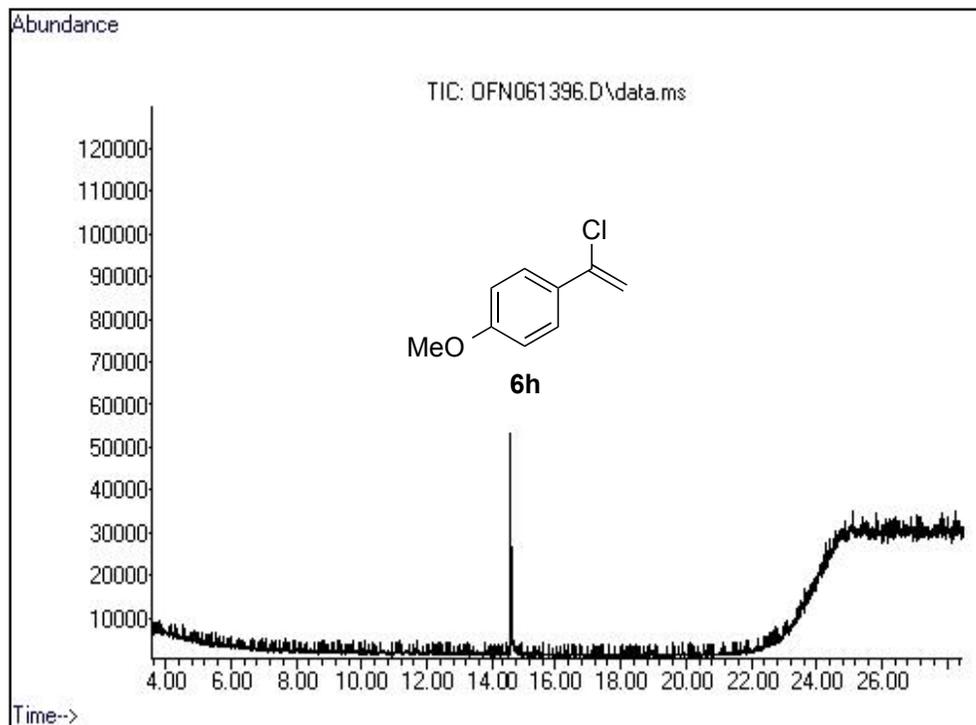
Product Peak at 10.672 min:



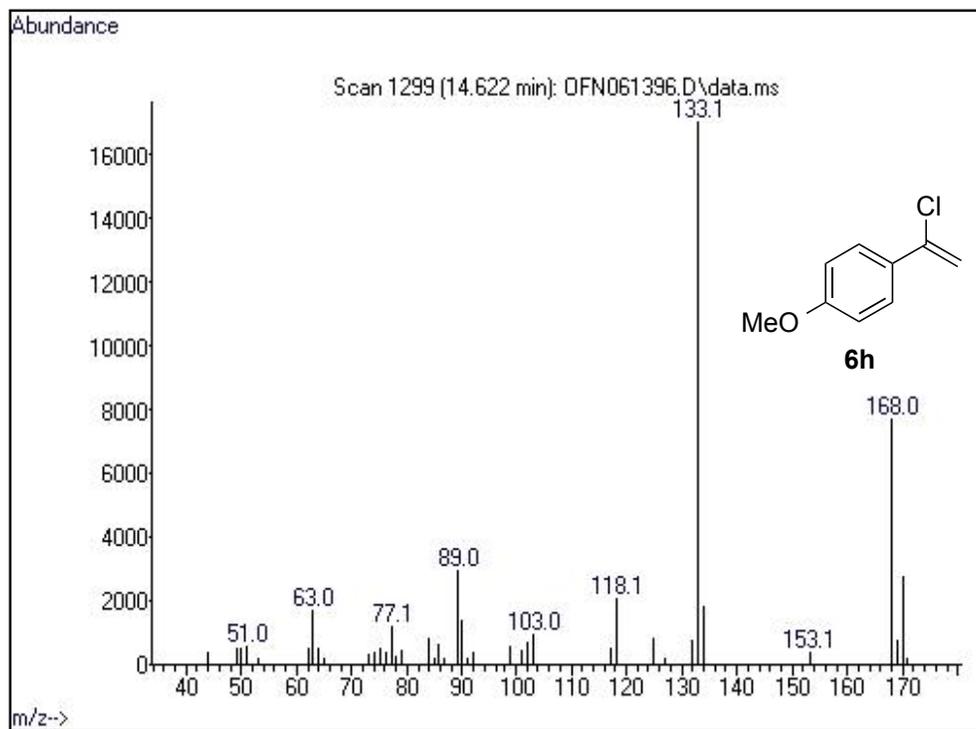


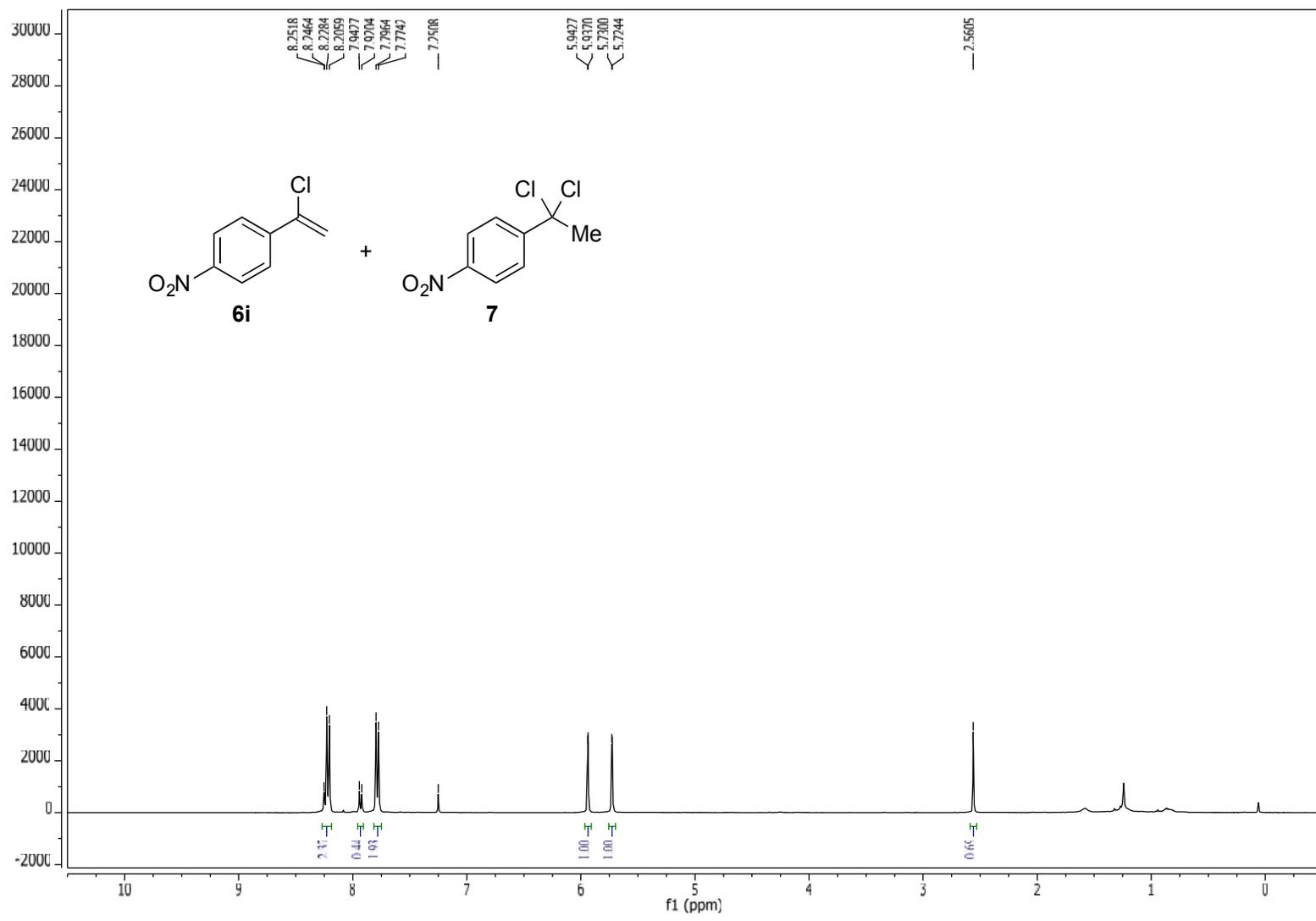


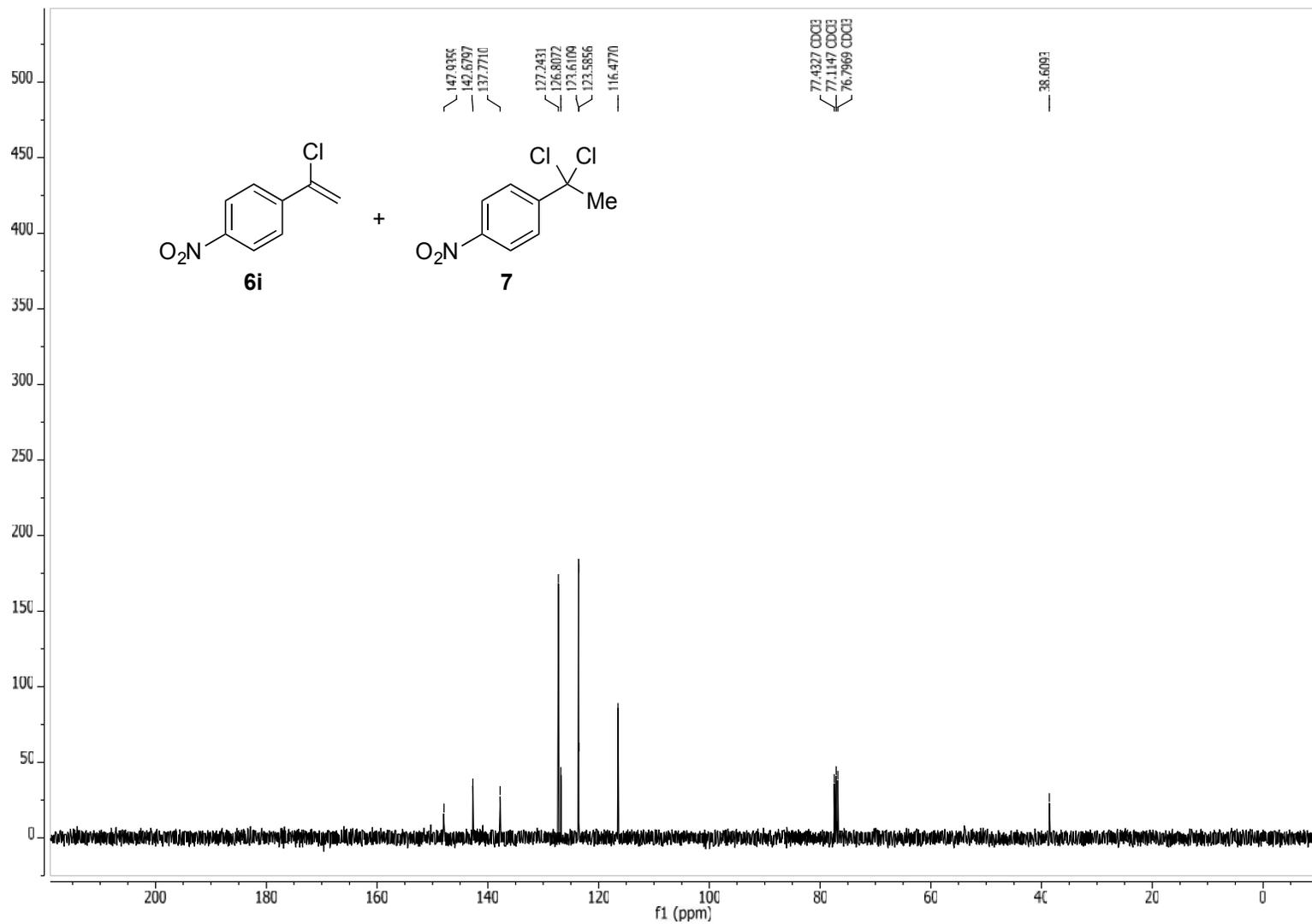
GC-MS:



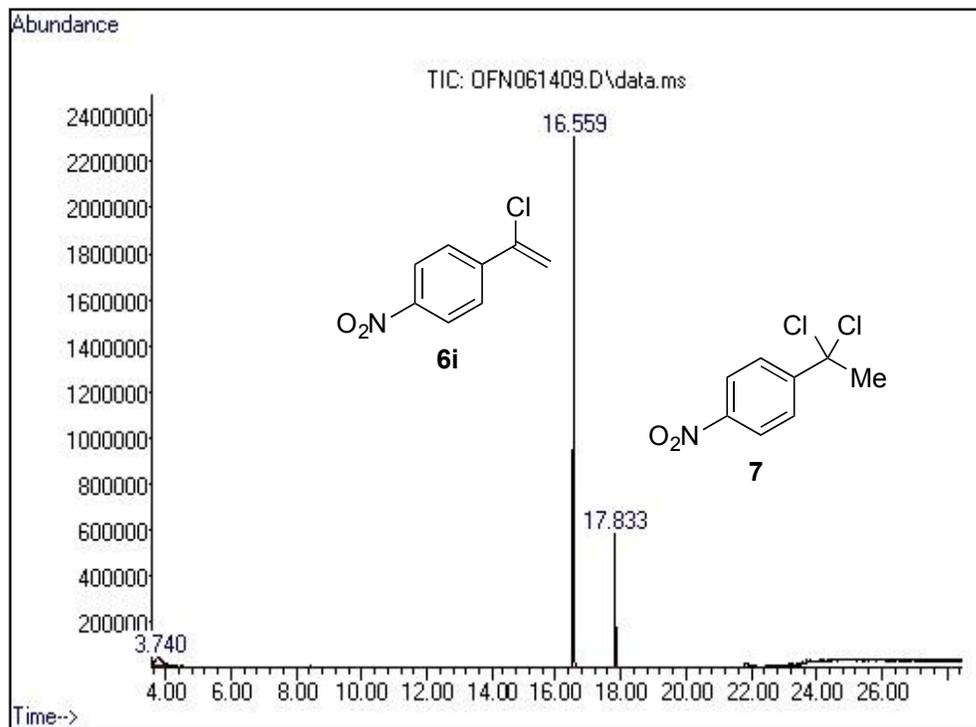
Product MS at 14.622 min:



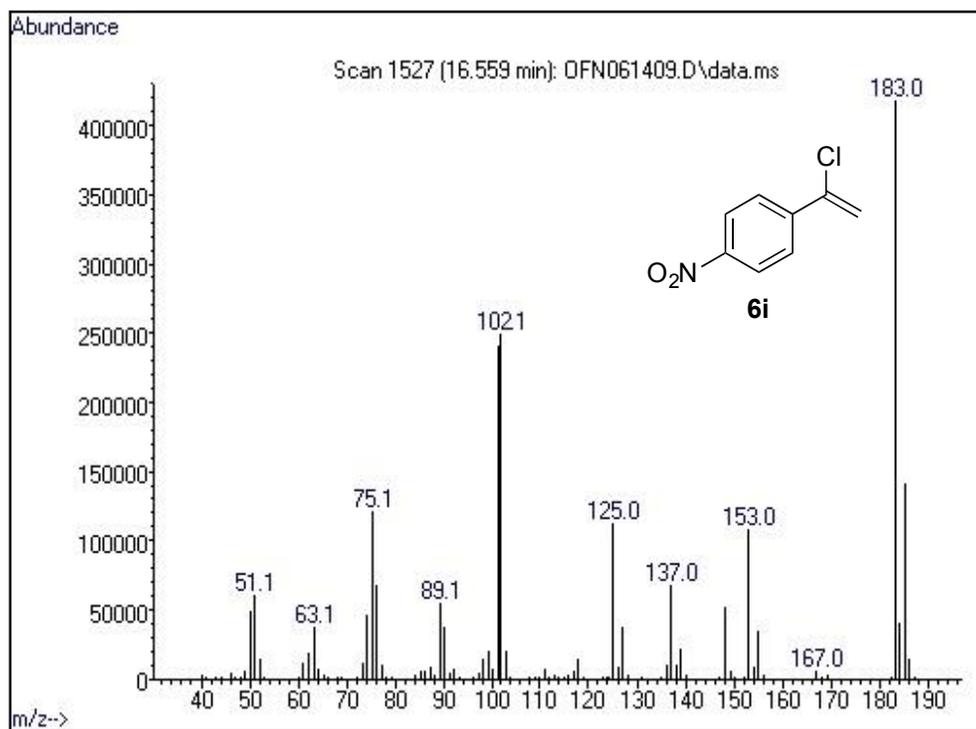




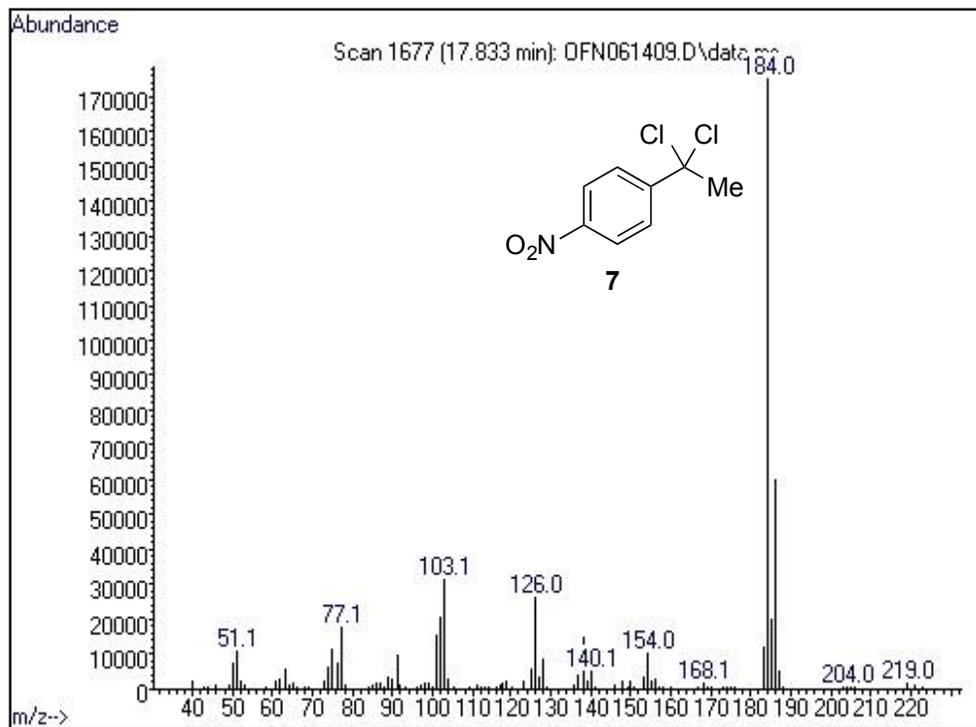
GC-MS:

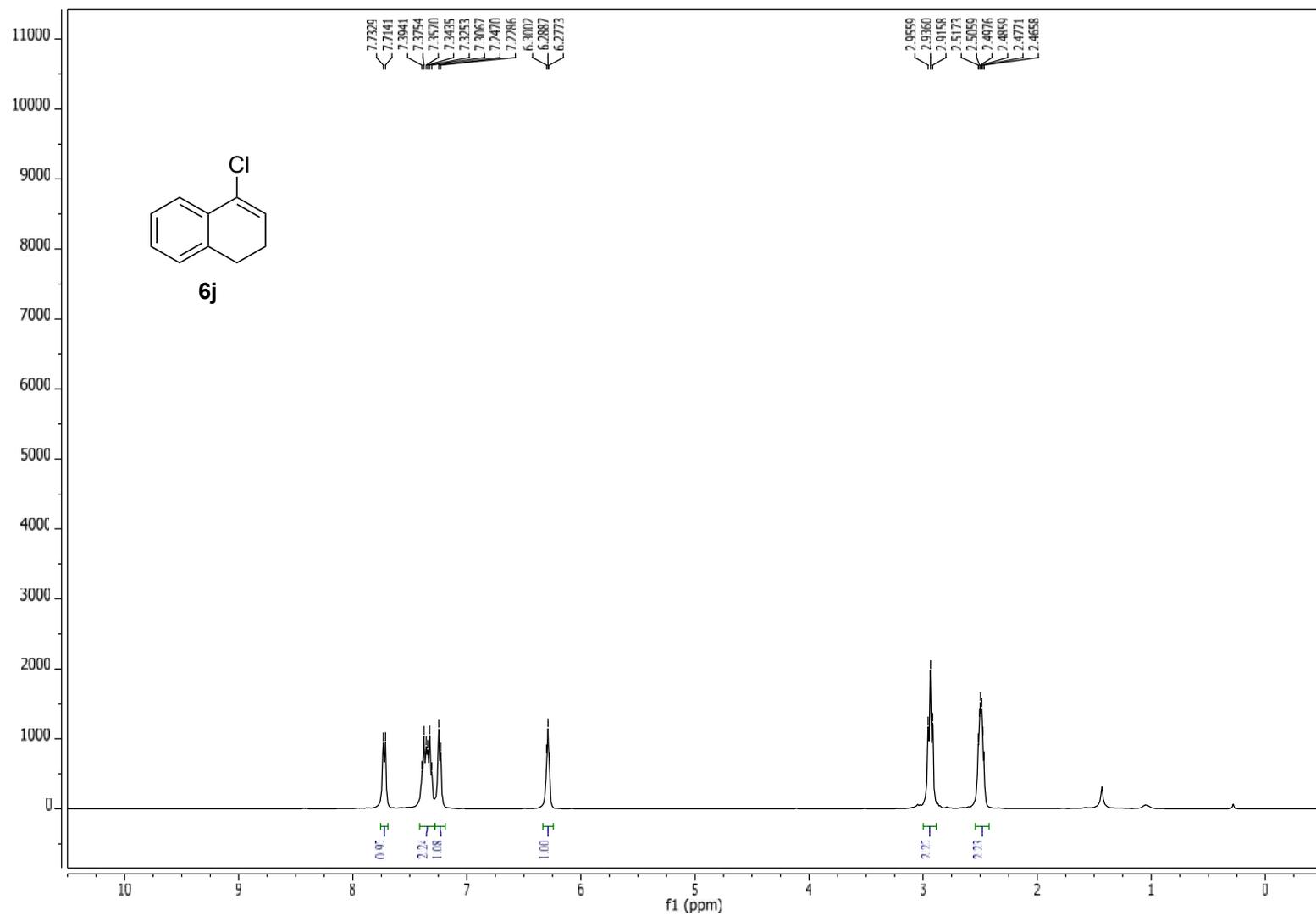


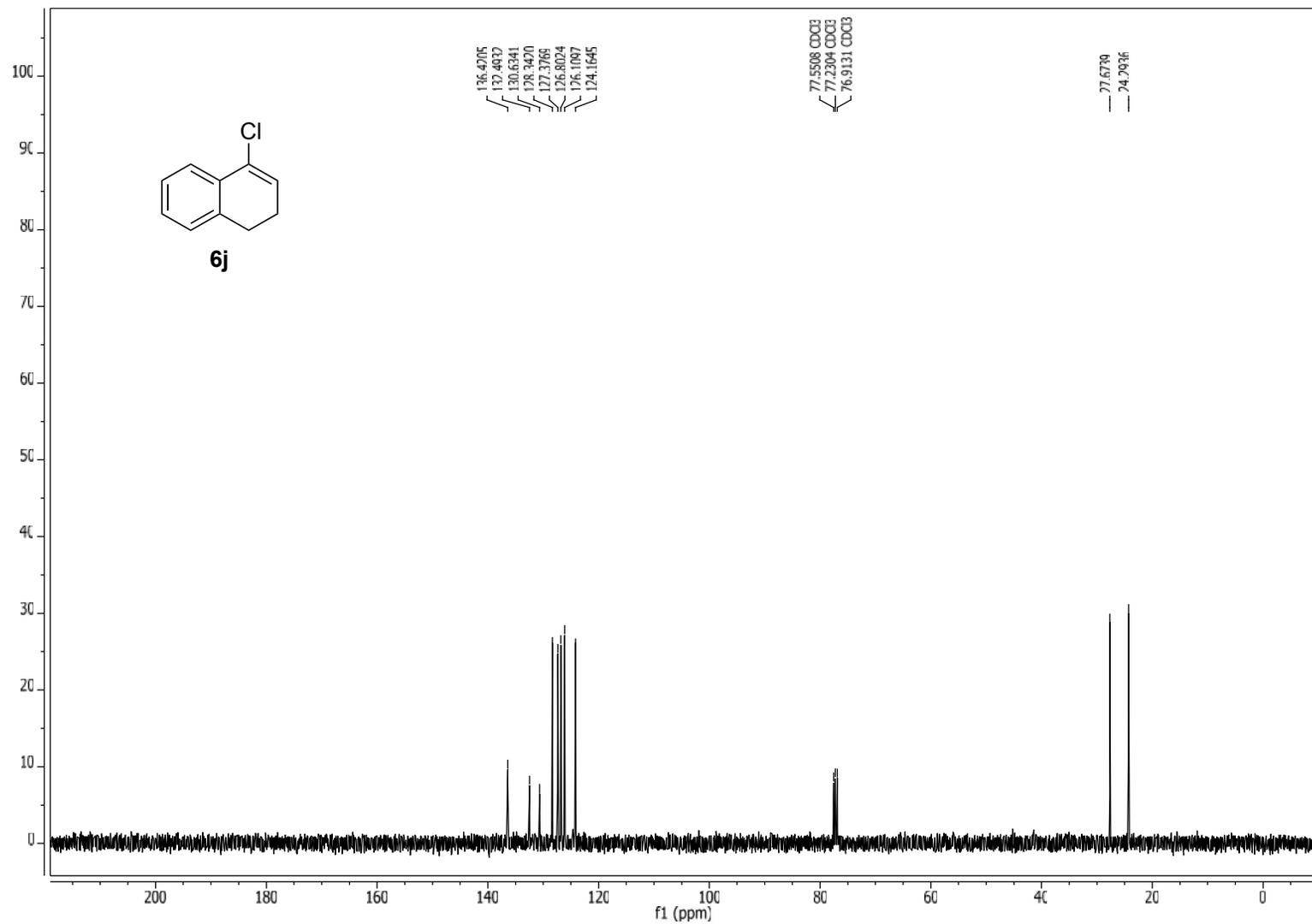
Major product MS at 16.559 min:



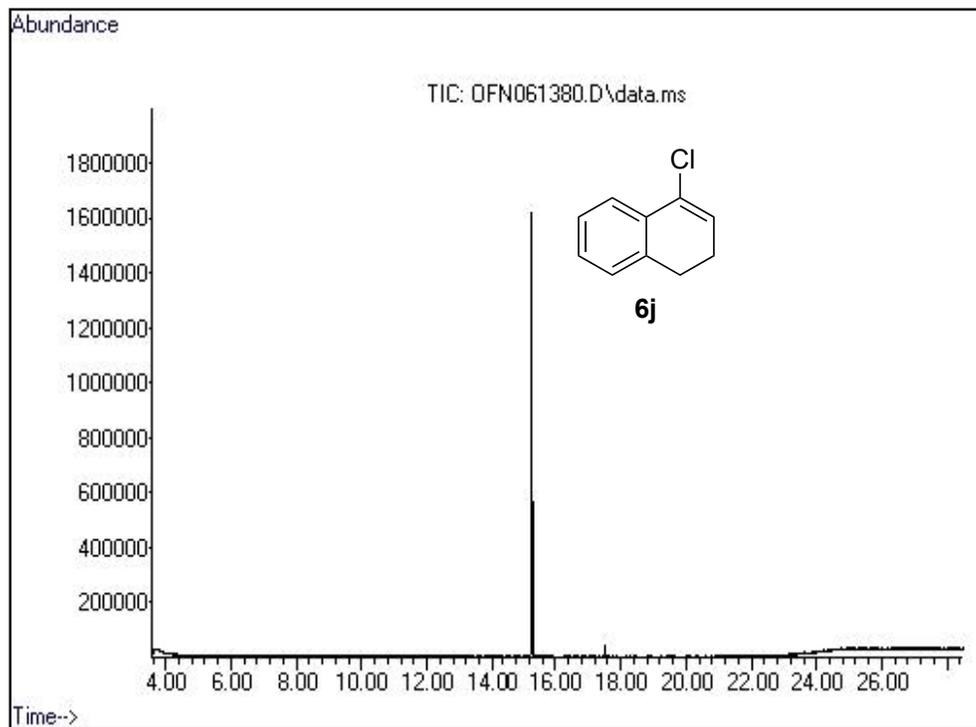
Minor product MS at 17.833 min:



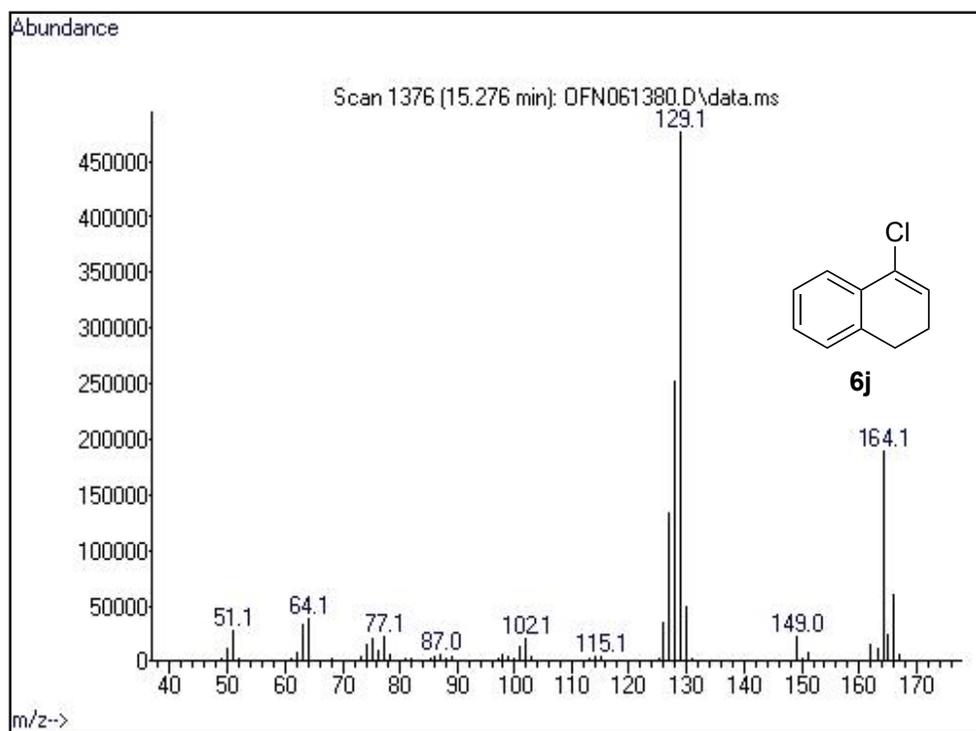


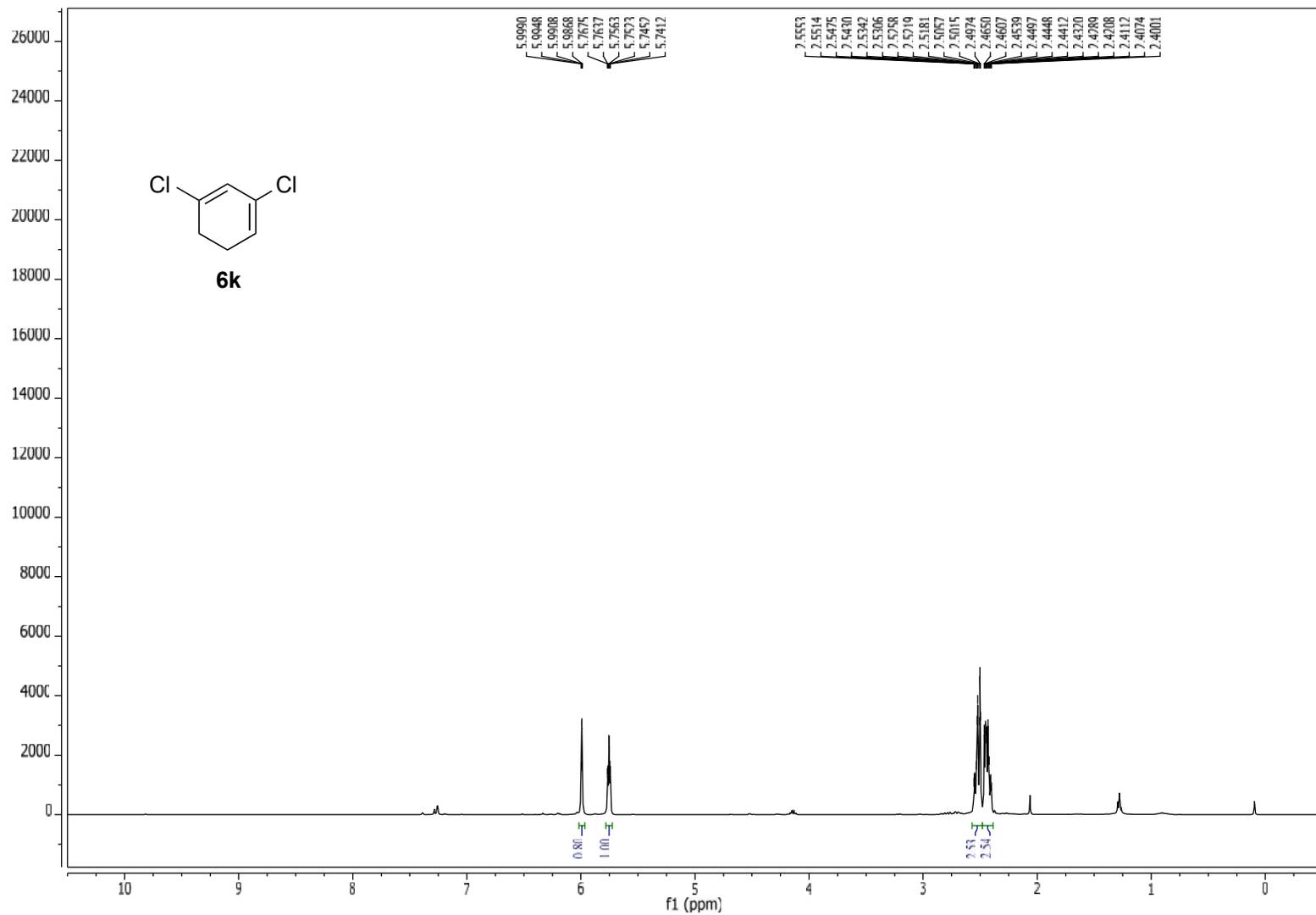


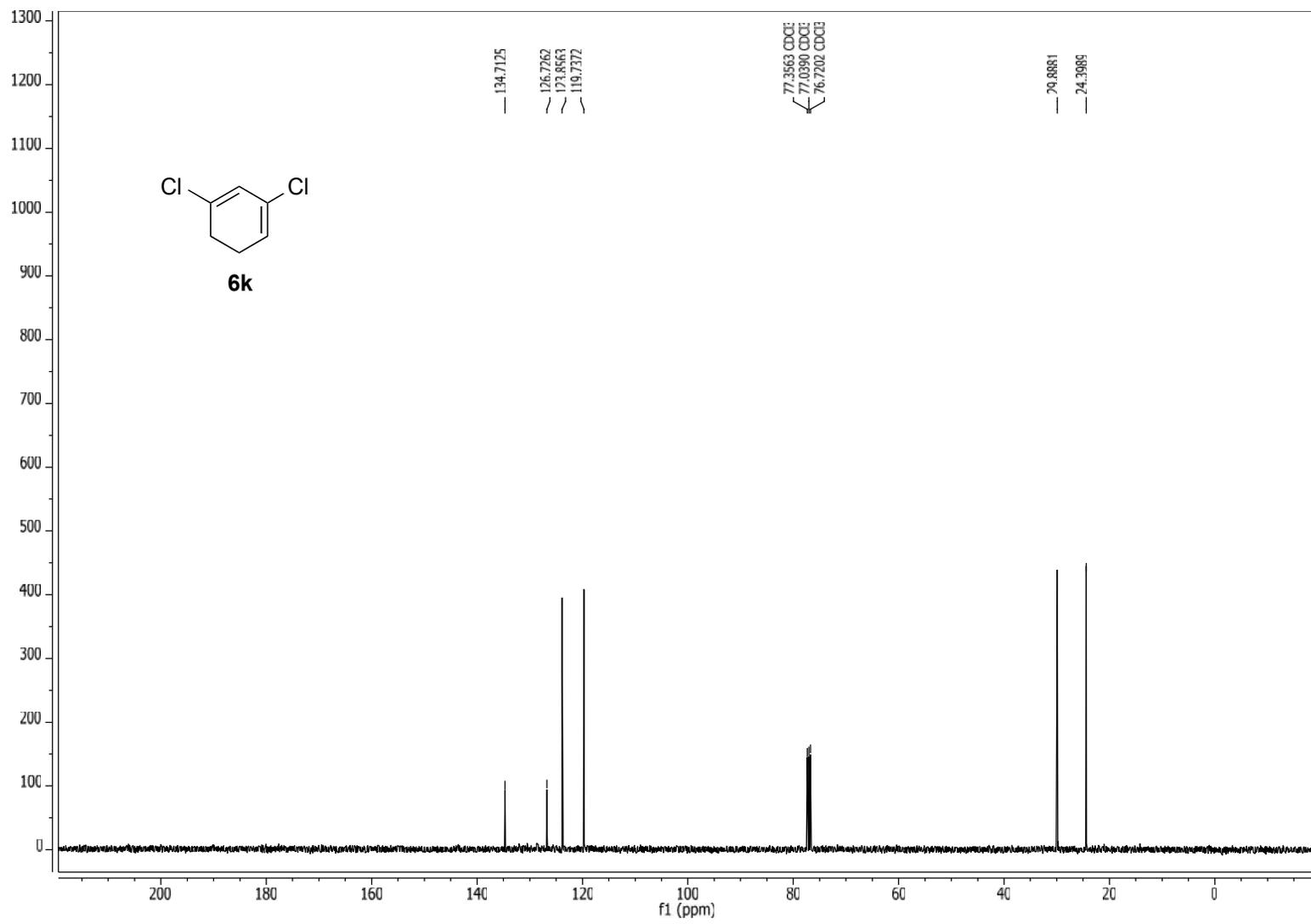
GC-MS:



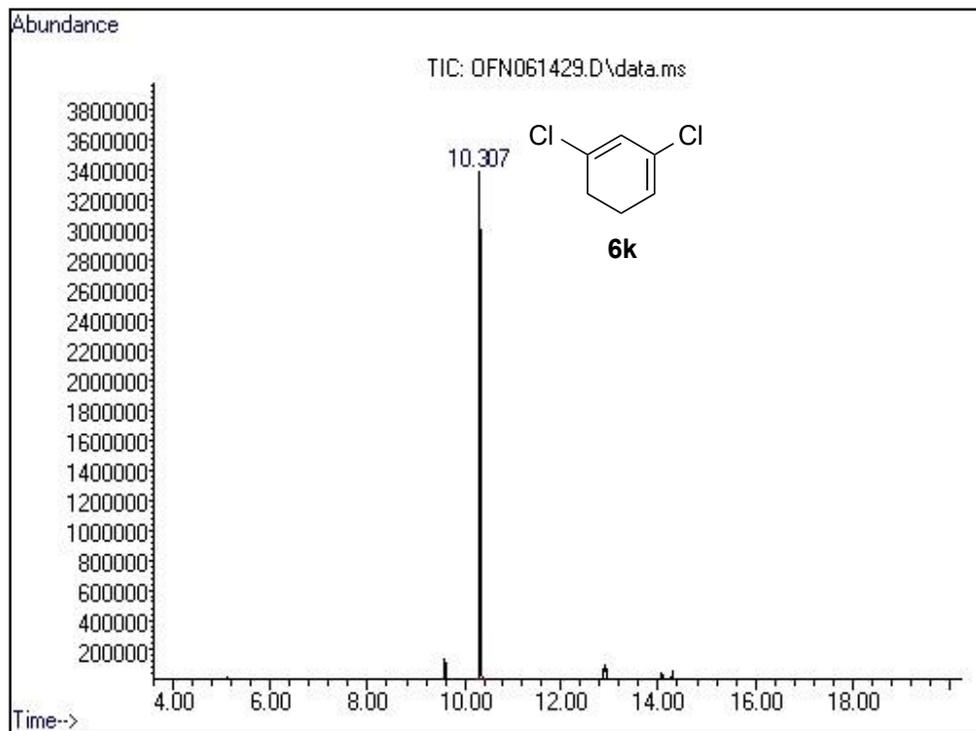
Product MS at 15.276 min:



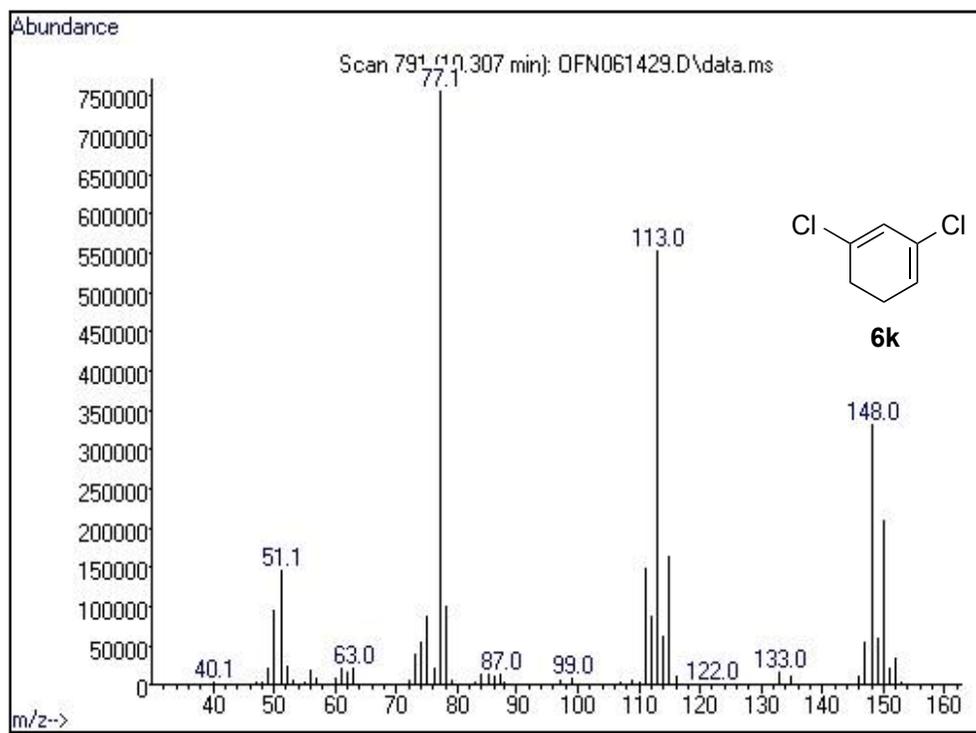


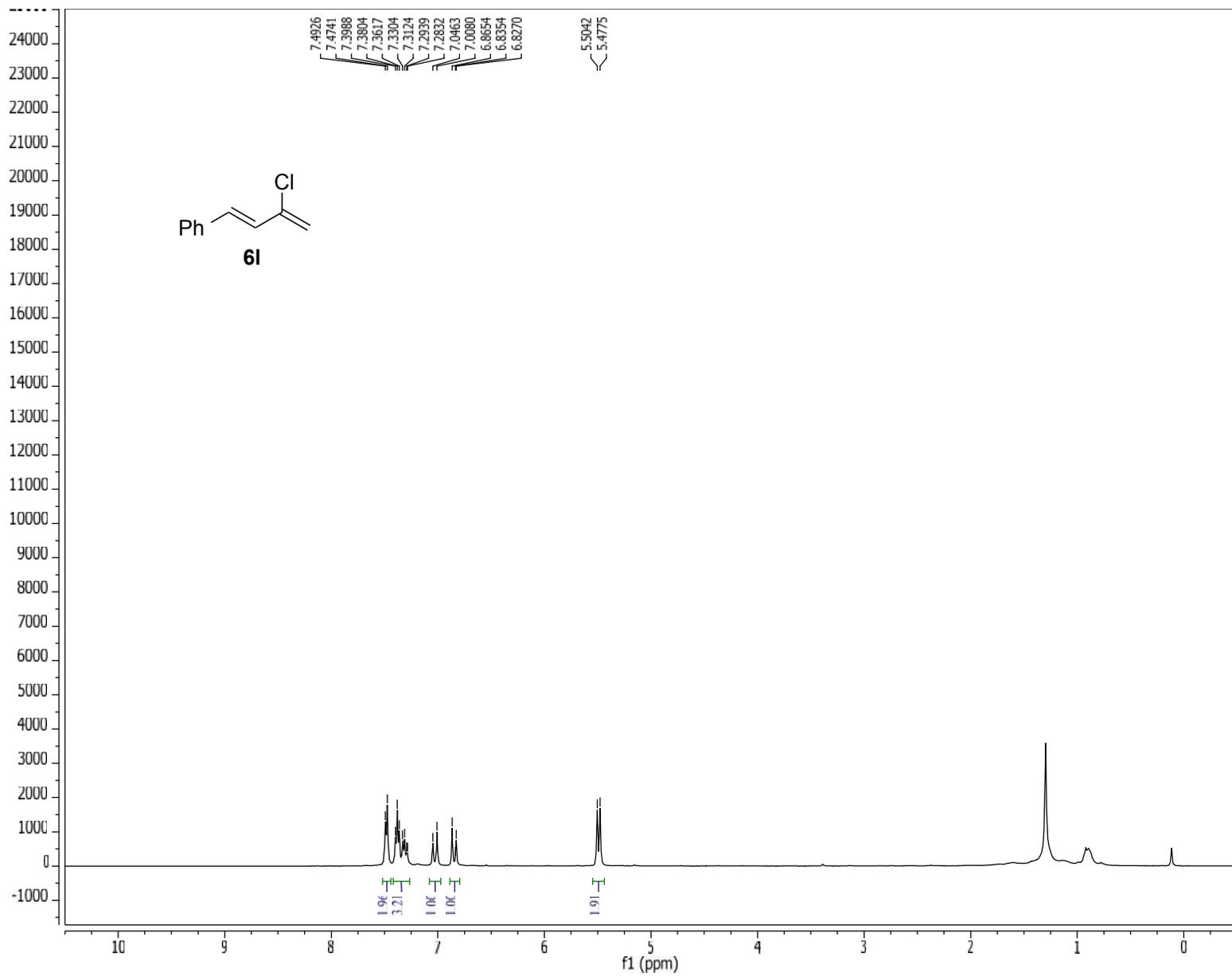


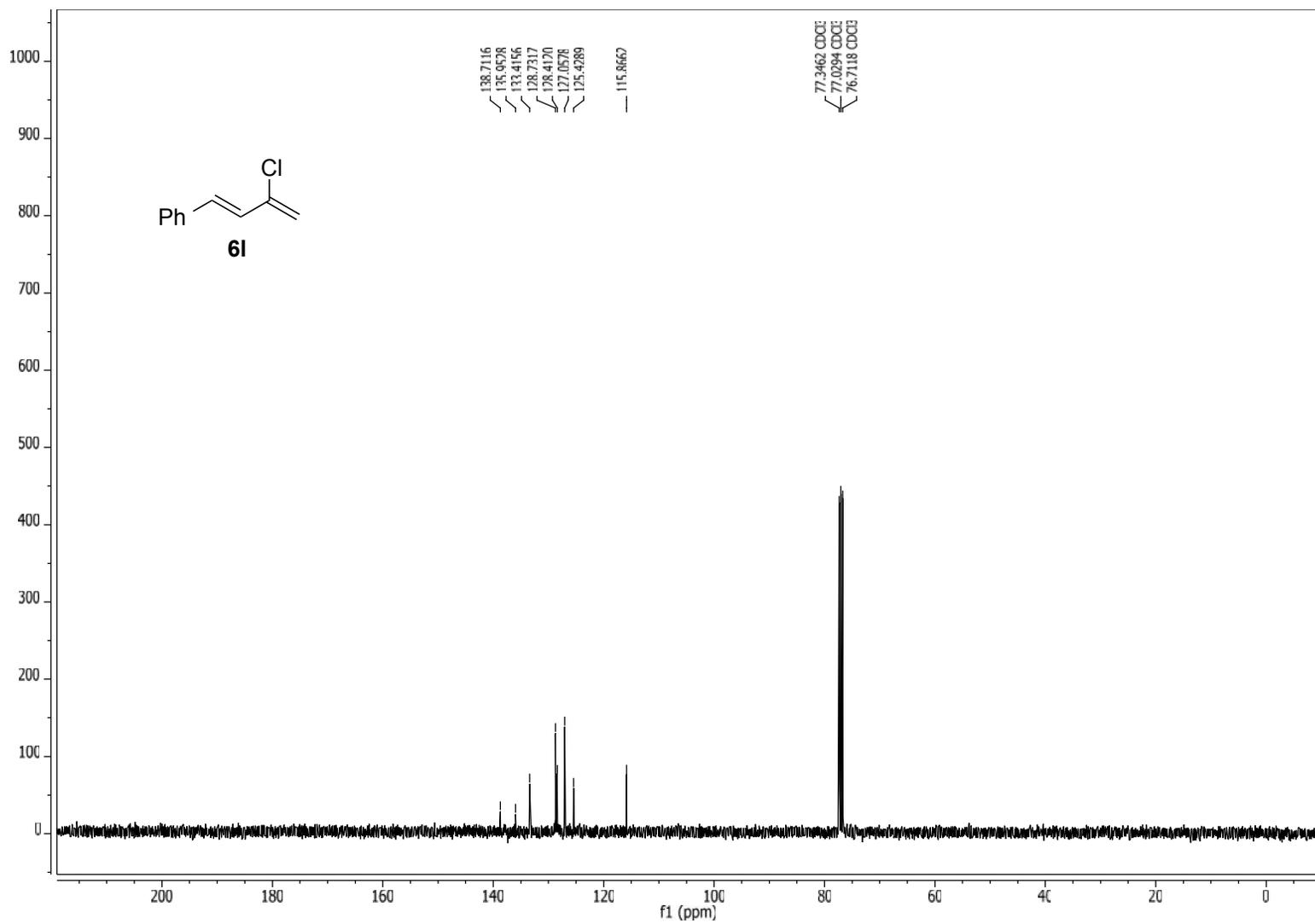
GC-MS:



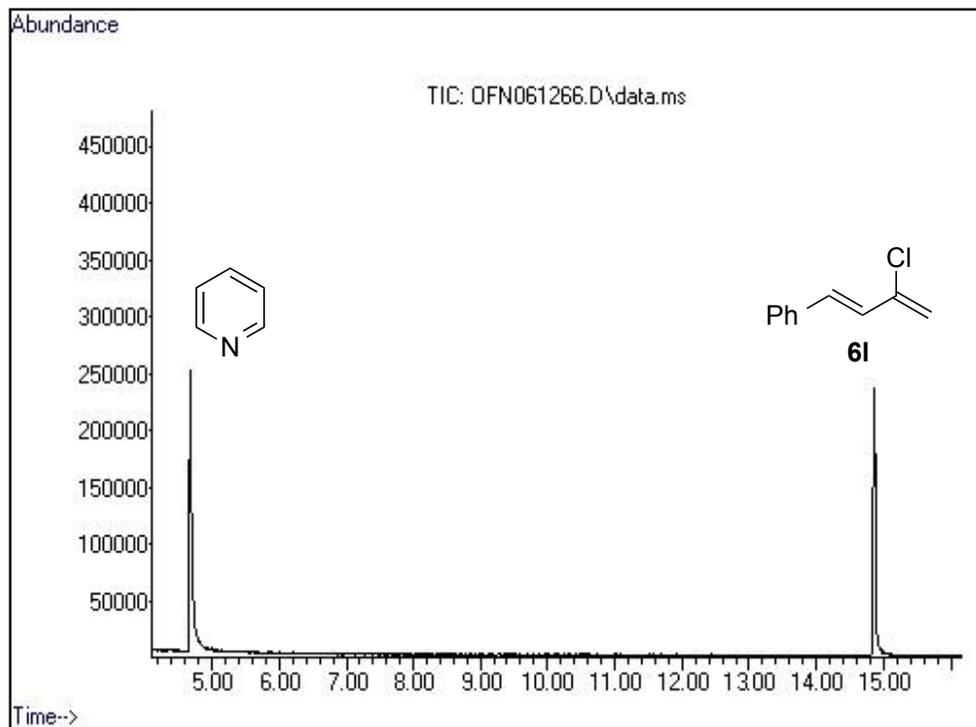
Product MS at 10.307 min:







GC-MS:



Product MS at 14.869 min:

