

# Synthesis of Fused Tricyclic Systems by Rearrangement of Furan-Substituted Vinyl Cyclopropanes

Verena Klaus, Stéphane Wittmann, Hans M. Senn and J. Stephen Clark\*

*WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow,  
University Avenue, Glasgow G12 8QQ, United Kingdom*

\* Corresponding author: [stephen.clark@glasgow.ac.uk](mailto:stephen.clark@glasgow.ac.uk)

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## Computational Information

All calculations were performed with the programme Gaussian 09<sup>1</sup> at the density-functional level of theory. The M06-2X exchange-correlation functional<sup>2</sup> was used throughout, which yields reliable reaction energies and barriers for main-group chemistry<sup>3,4</sup> and is able to account for dispersive interactions; it was recently applied with good success to calculate the thermochemistry of [3,3]-rearrangements in 1,2-arylvinylcyclopropanes.<sup>5</sup> M06-2X is a hybrid meta-GGA with 54% global exact-exchange admixture. All reported results were obtained with the def2-TZVP basis set.<sup>6</sup> Structures were freely optimised to default tolerances and stationary points characterised by the presence of zero (minima) or one (transition states) negative eigenvalues in the analytically computed Hessian. Suitable starting structures for transition-state optimisations were obtained from scans along the C<sup>1</sup>–C<sup>6</sup> distance; transition states were verified to be connected to the respective minima by following the IRC. Gibbs free energies were calculated using the standard ideal-gas/rigid-rotor/harmonic-oscillator (RRHO) approximation. For the reactions under study, the RRHO is expected to perform well, given the rigidity of the structures, the intramolecular nature of the reactions, and the focus on relative differences (*i.e.*,  $\Delta\Delta G$  values) between highly similar cases. Solvent effects were not taken into account in the calculations, which is justified given the low polarity of the experimentally used solvents (toluene or benzene). Images were created with Jmol.<sup>7</sup>

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<http://www.jmol.org/>.

## Absolute energies

Calculated with M06-2X/def2-TZVP. Finite-temperature contributions for  $T = 313.15$  K,  $p = 100$  kPa. For TS structures, the frequency of the transition mode is also indicated.

	$E / E_h$	$G / E_h$	$E_{ZPV} / E_h$	$S / (\text{cal mol}^{-1})$	$\nu^\ddagger / \text{cm}^{-1}$
<b>E-25</b>	-772.10113	-771.82911	0.32485	148.0	
<b>29</b>	-772.10995	-771.82936	0.32791	133.8	
<b>TS E</b>	-772.05987	-771.78184	0.32474	132.8	460i
<b>Z-29</b>	-772.09939	-771.82534	0.32530	144.2	
<b>epi-29</b>	-772.10232	-771.82143	0.32797	133.1	
<b>TS Z</b>	-772.05319	-771.77513	0.32484	132.9	460i

## Cartesian coordinates of stationary points

In Xmol xyz format.

### Reactant E-25

```

C -0.423056 2.427349 0.775380
C 0.936438 2.295869 0.204625
C 1.375152 0.982178 -0.450101
C 2.001997 1.450042 0.830976
H 1.276177 3.182940 -0.318545
C -0.872438 1.881419 1.898464
C -2.278904 2.002911 2.392571
H -0.198715 1.295046 2.516552
H -1.116272 3.011017 0.174005
H -2.882099 2.610388 1.717768
H -2.309119 2.457464 3.385386
H -2.745288 1.018690 2.479530
C 2.413121 1.109353 -1.557598
C 0.446542 -0.148063 -0.473049
H 1.770020 0.947815 1.760223
C 3.443846 1.821049 0.539122
O -0.373988 -0.235586 -1.567585
C 0.164628 -1.155641 0.376209
C -0.896850 -1.915890 -0.222914
C -1.181326 -1.303918 -1.411199
H 0.631040 -1.365701 1.323493
C -1.492755 -3.114494 0.389569
C -2.126927 -1.555740 -2.532278
C 3.491196 2.042246 -0.982438
H 4.087355 0.984718 0.821397
H 3.778345 2.697920 1.095586
H 4.476507 1.836942 -1.398859
H 3.259073 3.080646 -1.219480
H 1.989840 1.480620 -2.492104
H 2.828056 0.117364 -1.752894

```

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H	-3.127712	-1.778383	-2.168118
H	-1.798825	-2.393500	-3.151064
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C	-2.601741	-3.834820	-0.339707
H	-2.309226	-4.074176	-1.362753
H	-3.488456	-3.199366	-0.387832
H	-2.841358	-4.745952	0.201900

### Reactant Z-25

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C	0.717498	2.008934	0.423975
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C	1.806547	1.102478	0.928915
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C	0.211714	-0.322349	-0.532578
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C	-2.322502	-1.509228	-2.773673
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H	3.010604	2.971673	-0.924161
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H	-3.325007	-1.784430	-2.452984
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H	-1.853504	2.423801	2.703870
H	-1.449645	1.621551	0.520925

### Product 29

C	0.112490	1.751301	1.941675
C	1.386243	1.983688	1.635953
C	1.615419	0.730035	-0.576039
C	2.297769	1.256979	0.674760
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C	-1.914926	1.410332	0.554650
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H	2.757008	0.426617	1.224567
C	3.410785	2.166519	0.102597
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H	-1.039185	-2.717096	-2.880973
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**Product epi-29**

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**Transition state E**

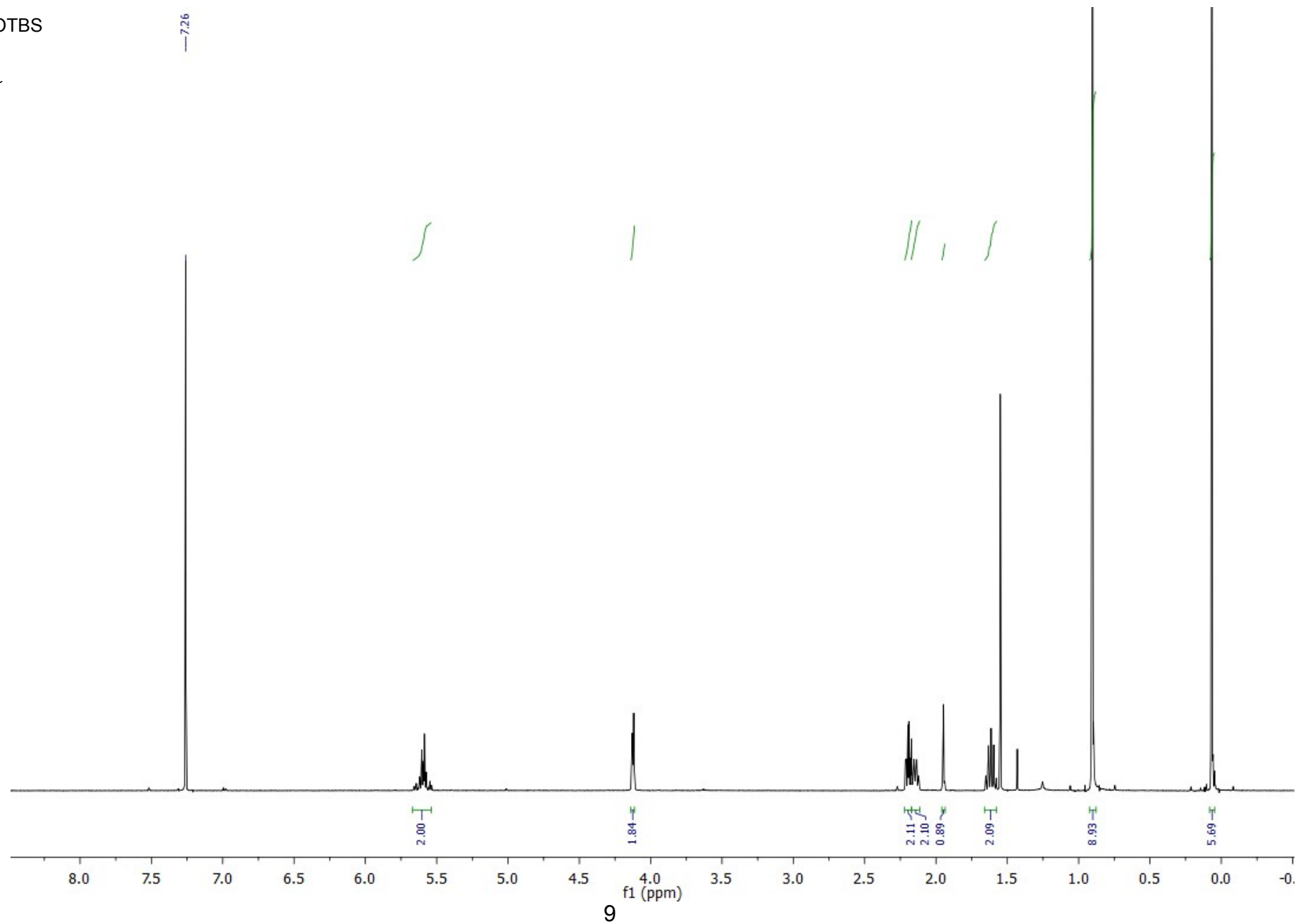
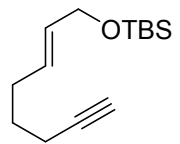
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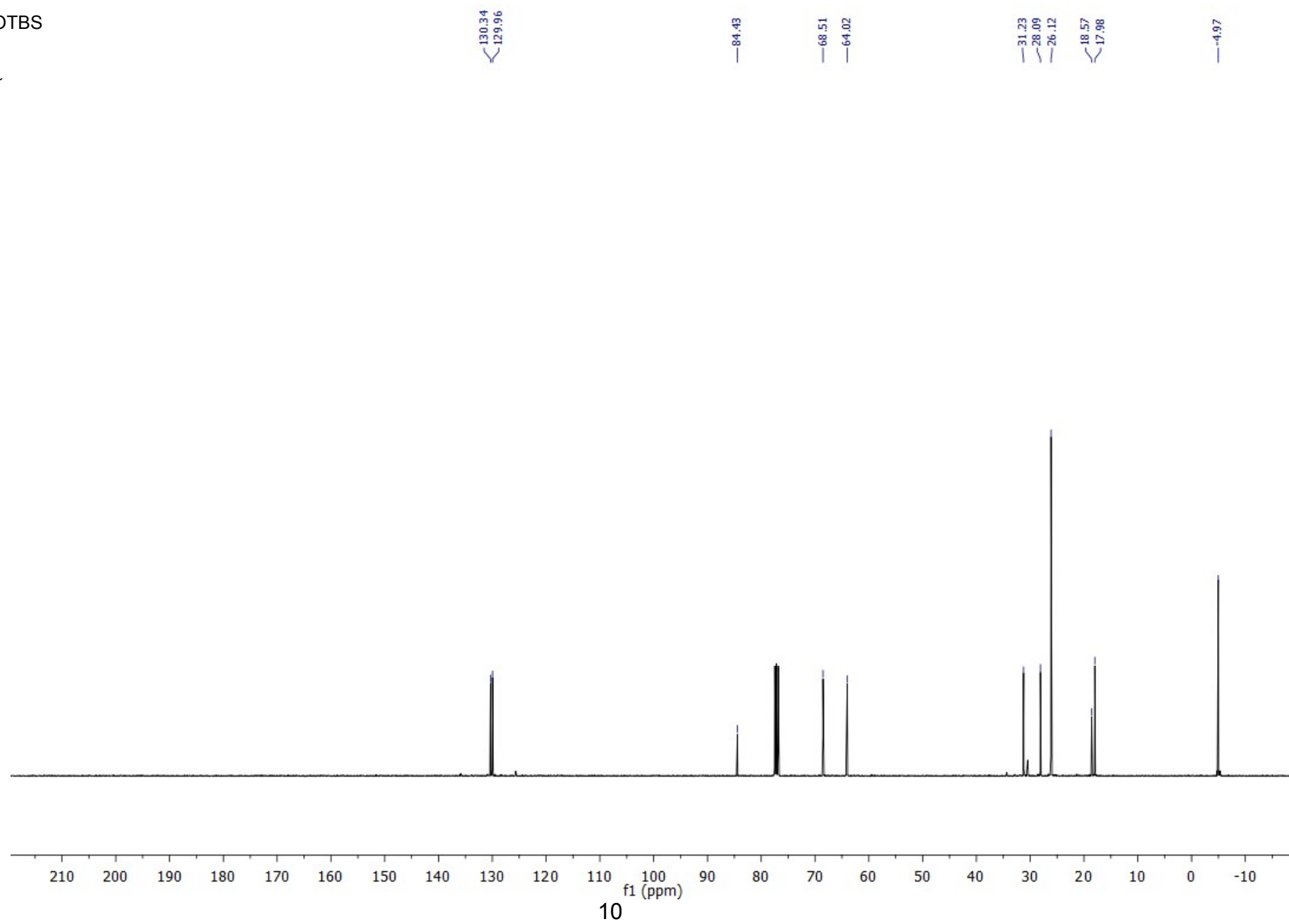
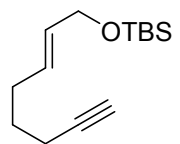
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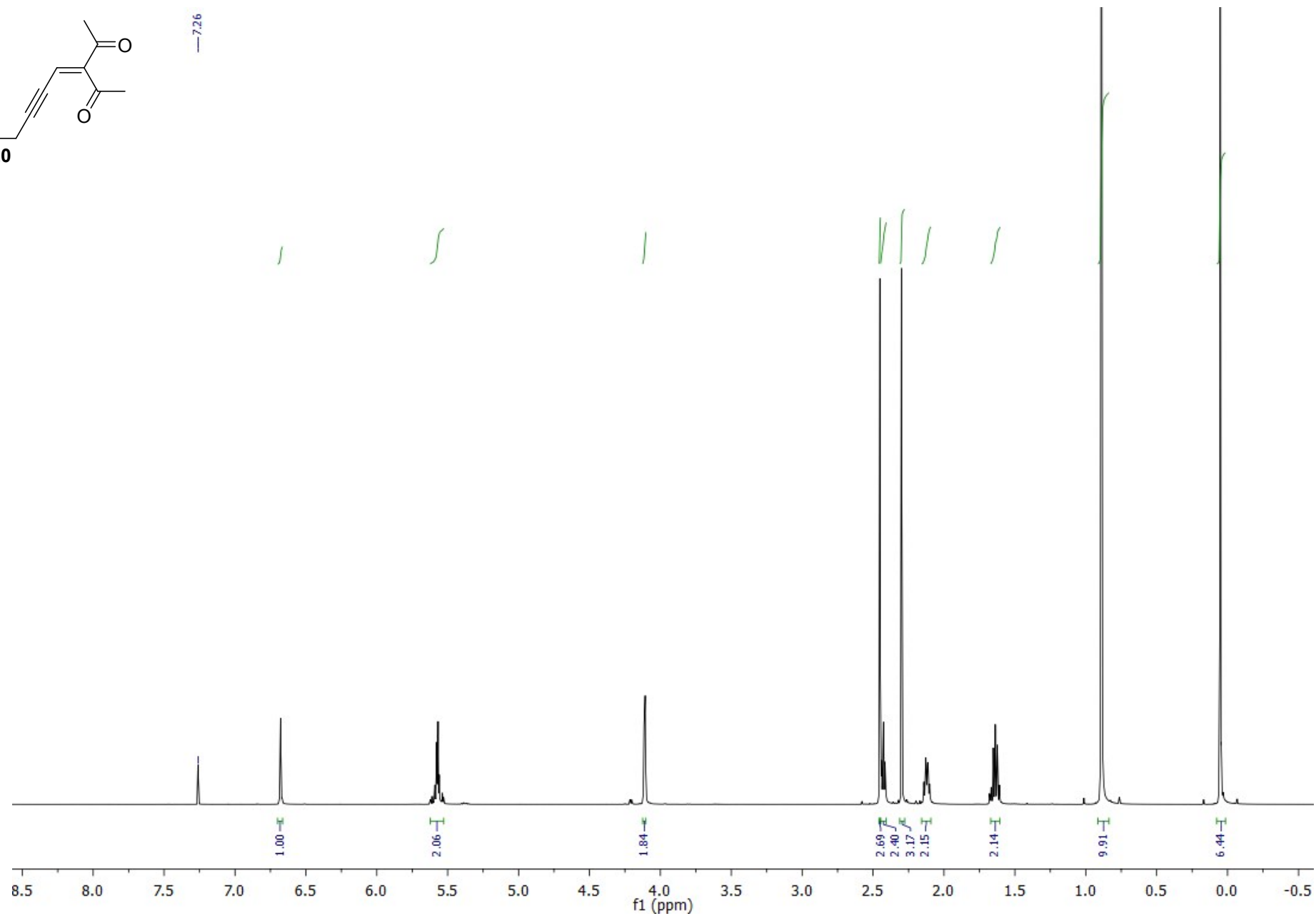
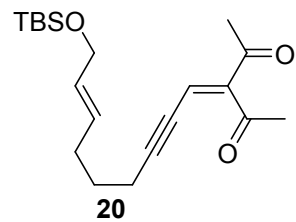
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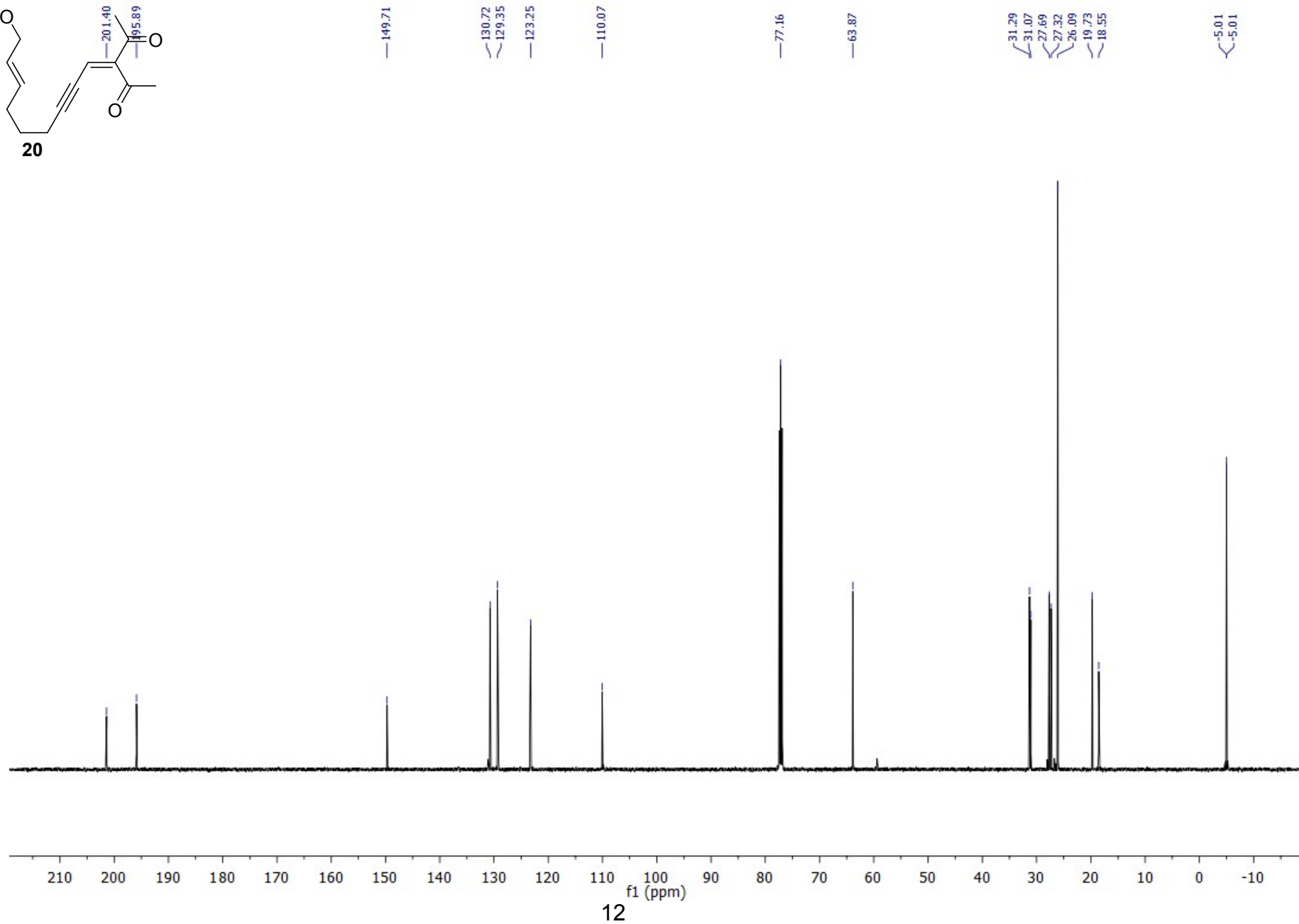
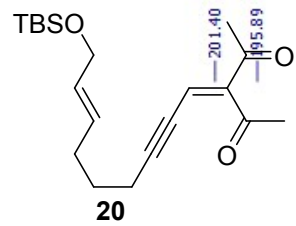
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H	-2.396916	-3.237962	-0.796441
O	-1.716679	-3.365583	3.526741
C	-2.732156	-4.348468	1.625118
H	-2.259620	-4.983224	0.875447
H	-3.479698	-3.731644	1.121414
H	-3.228418	-4.959567	2.374562
C	0.062051	-0.525757	4.588119
H	1.147864	-0.479212	4.640855
H	-0.268123	-1.525661	4.872590
H	-0.320552	0.176221	5.333473
H	-1.566645	-0.329213	3.181304
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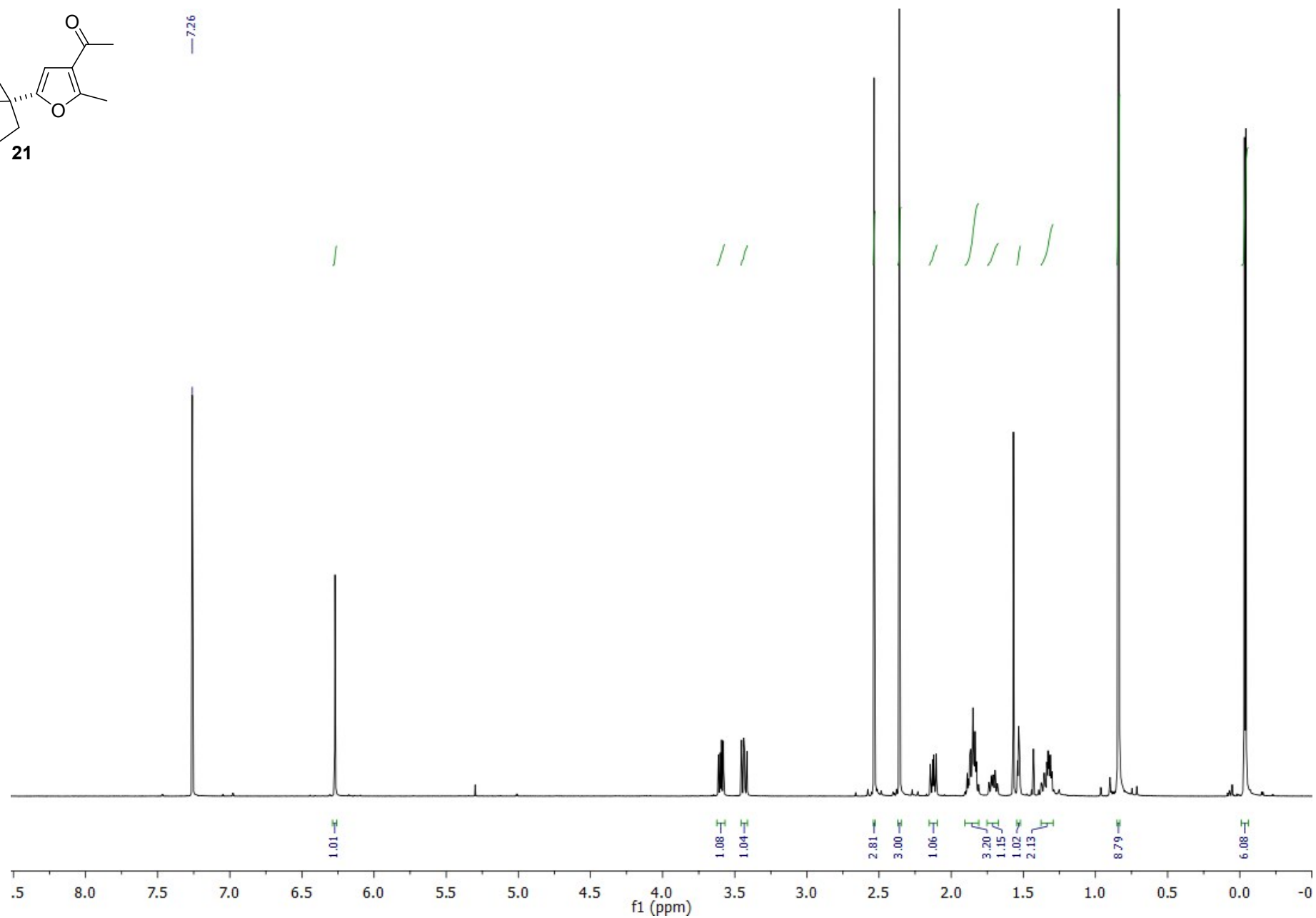
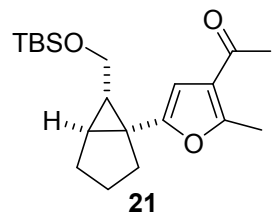


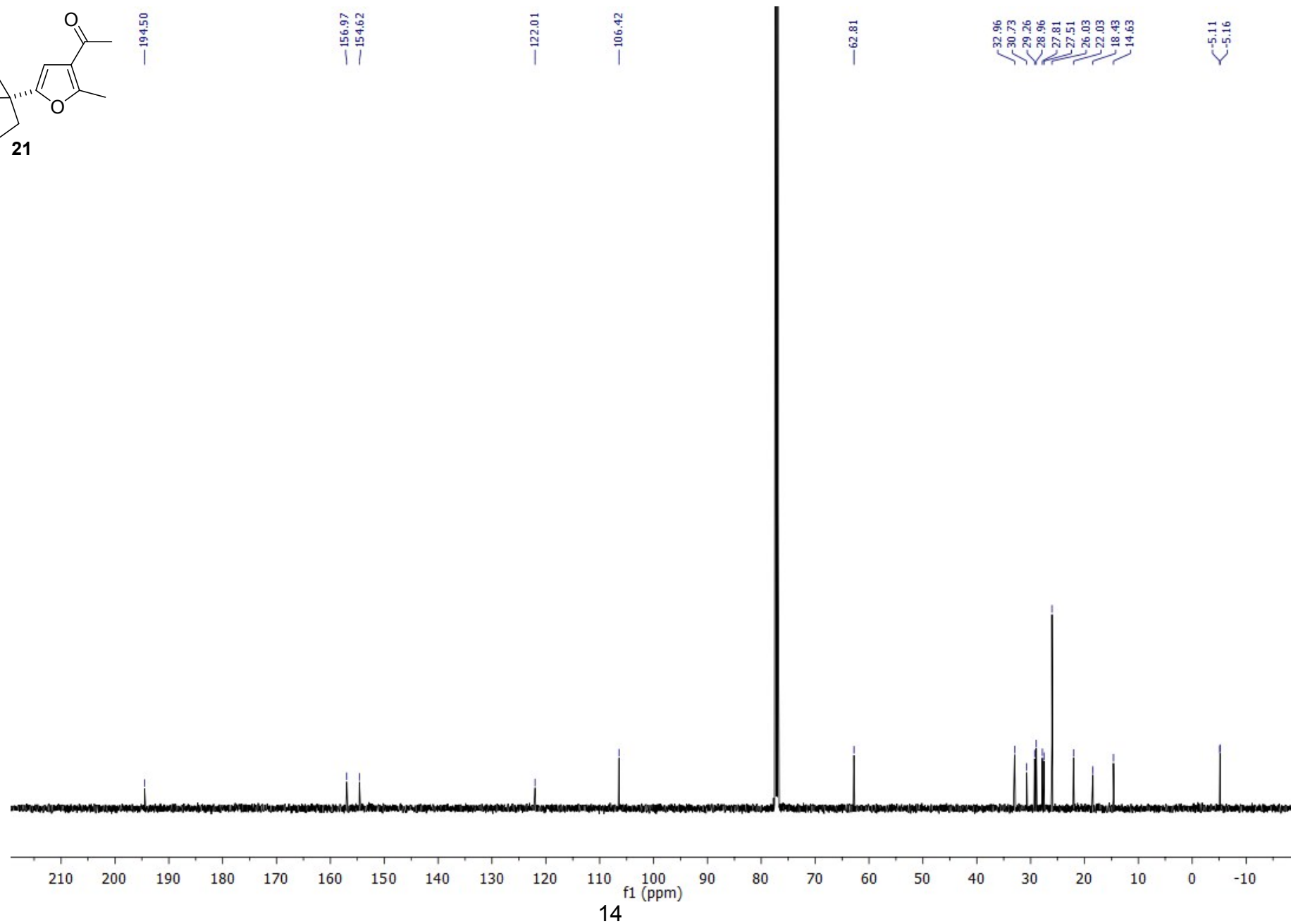
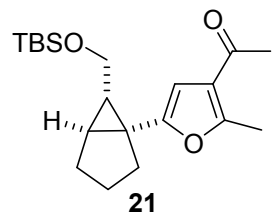


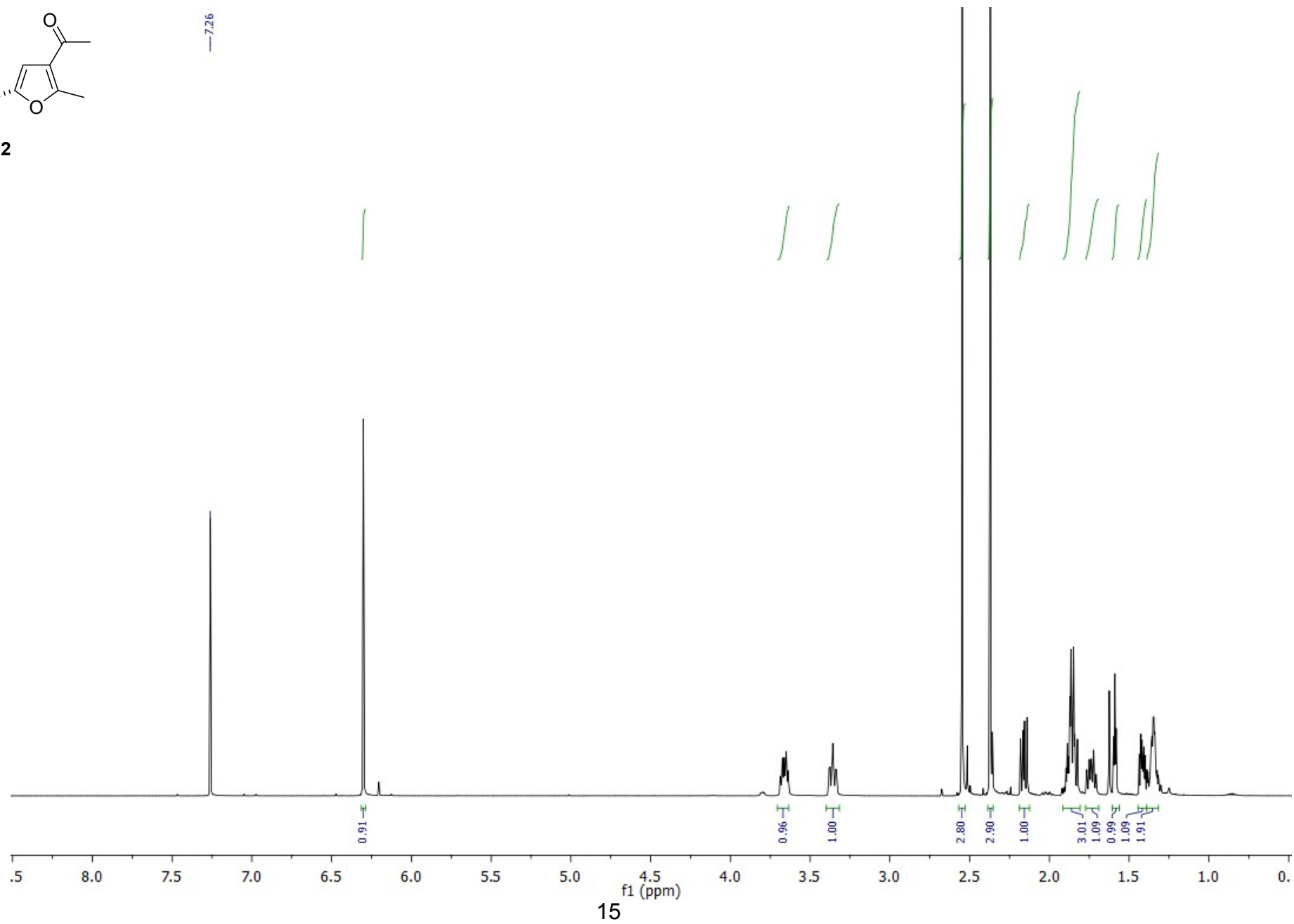
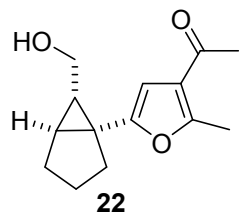


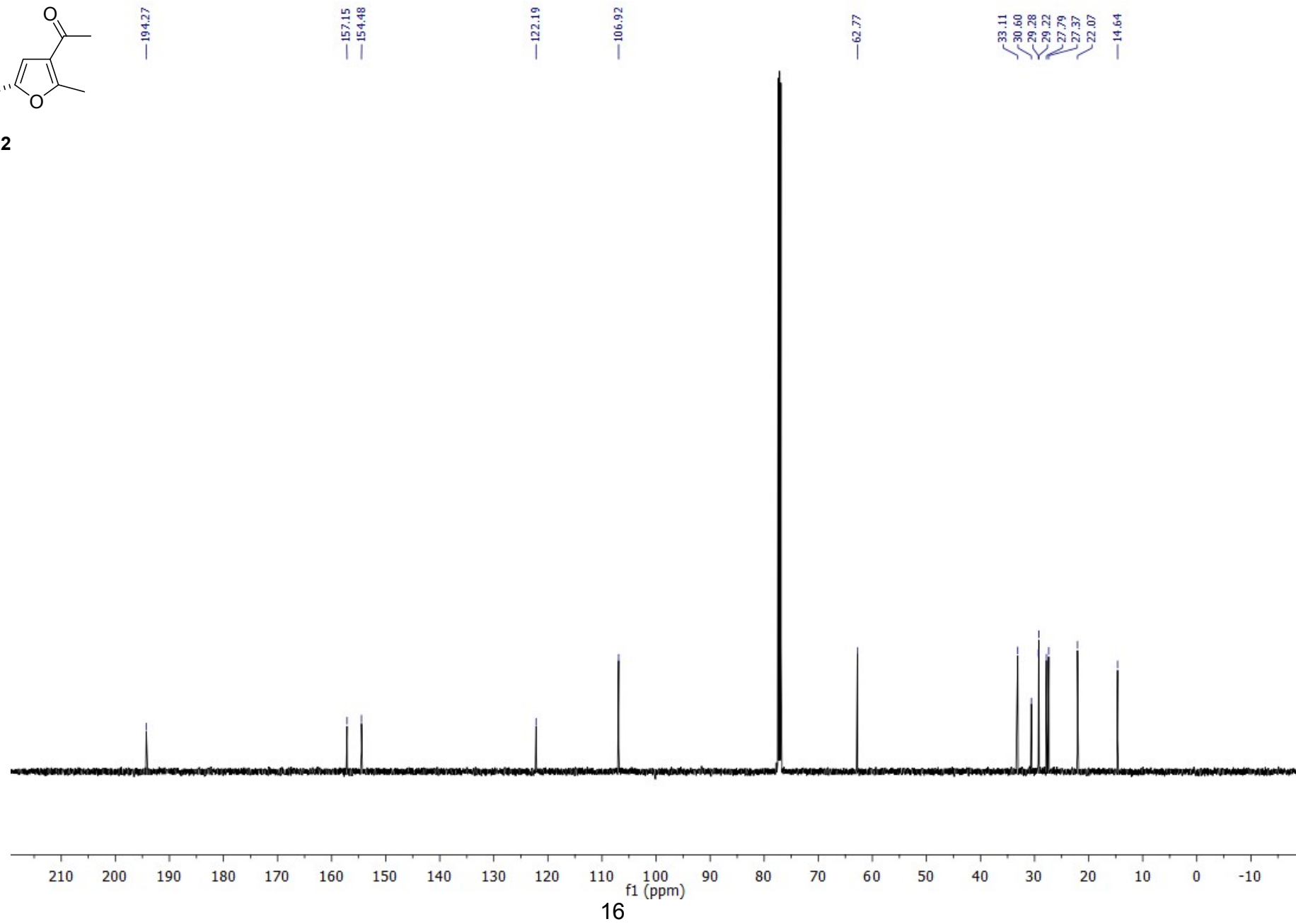
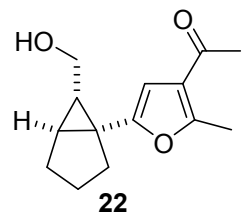




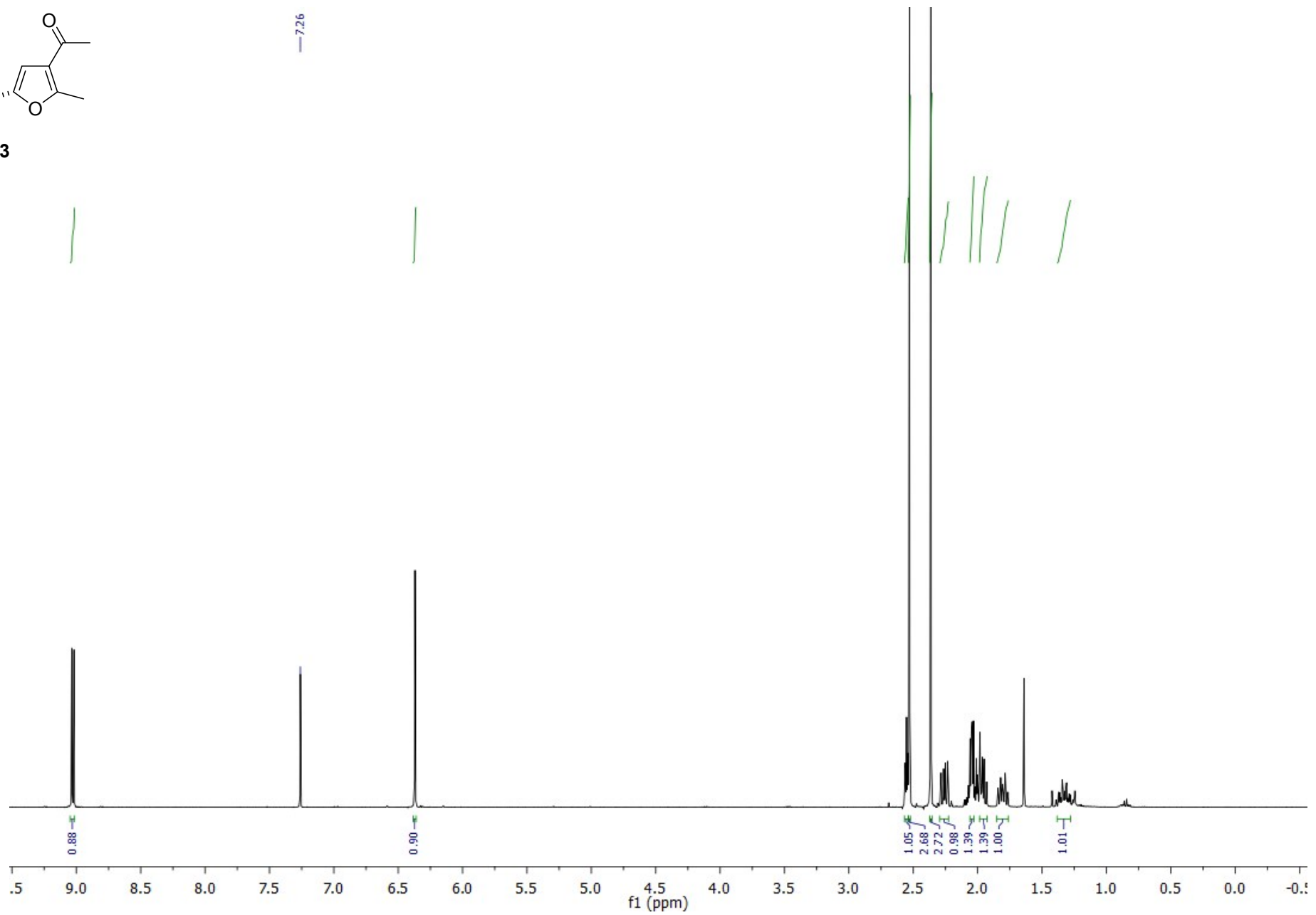
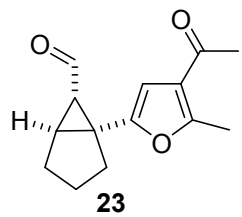


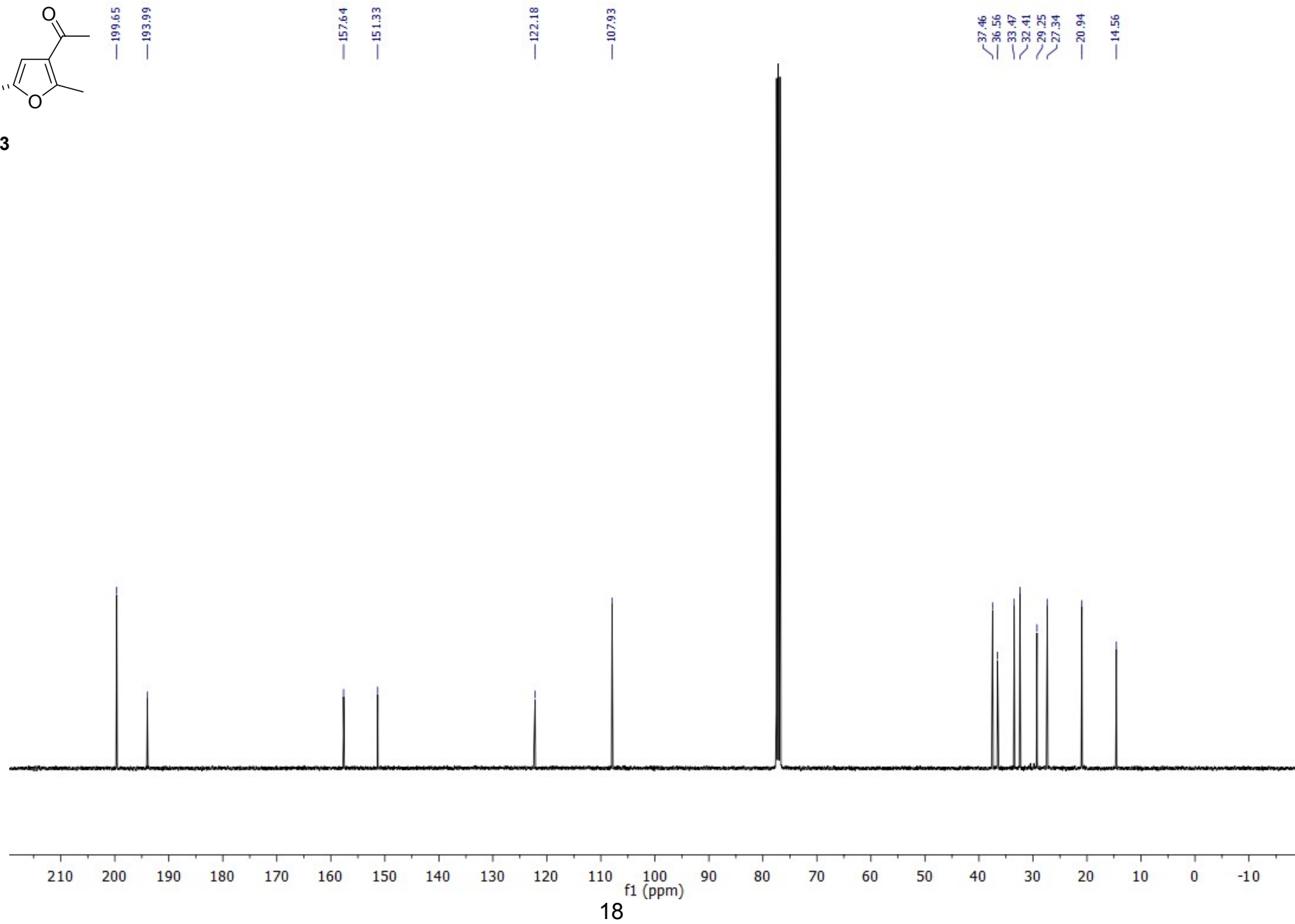
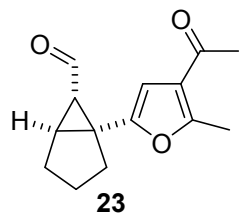


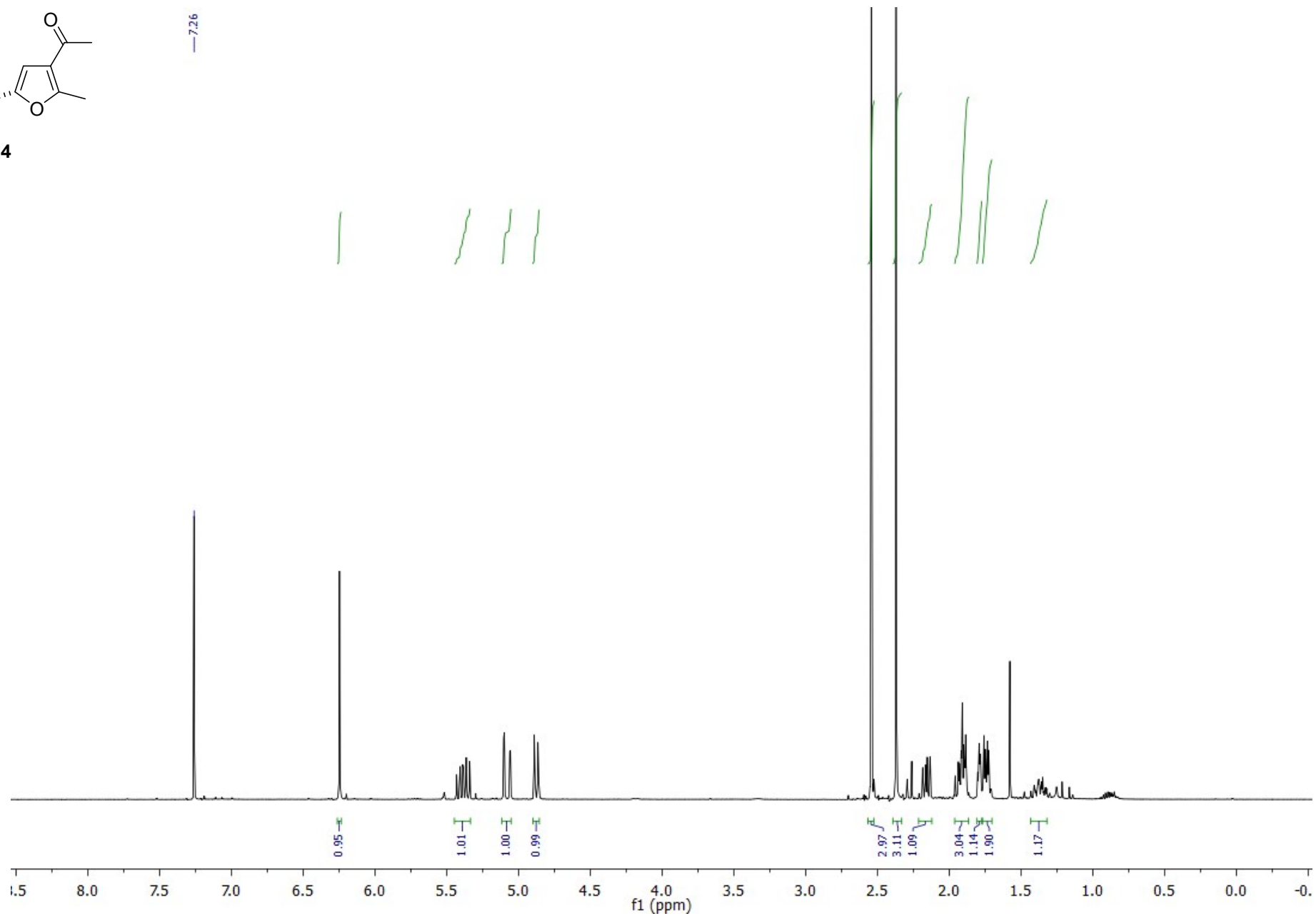
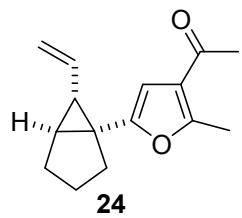


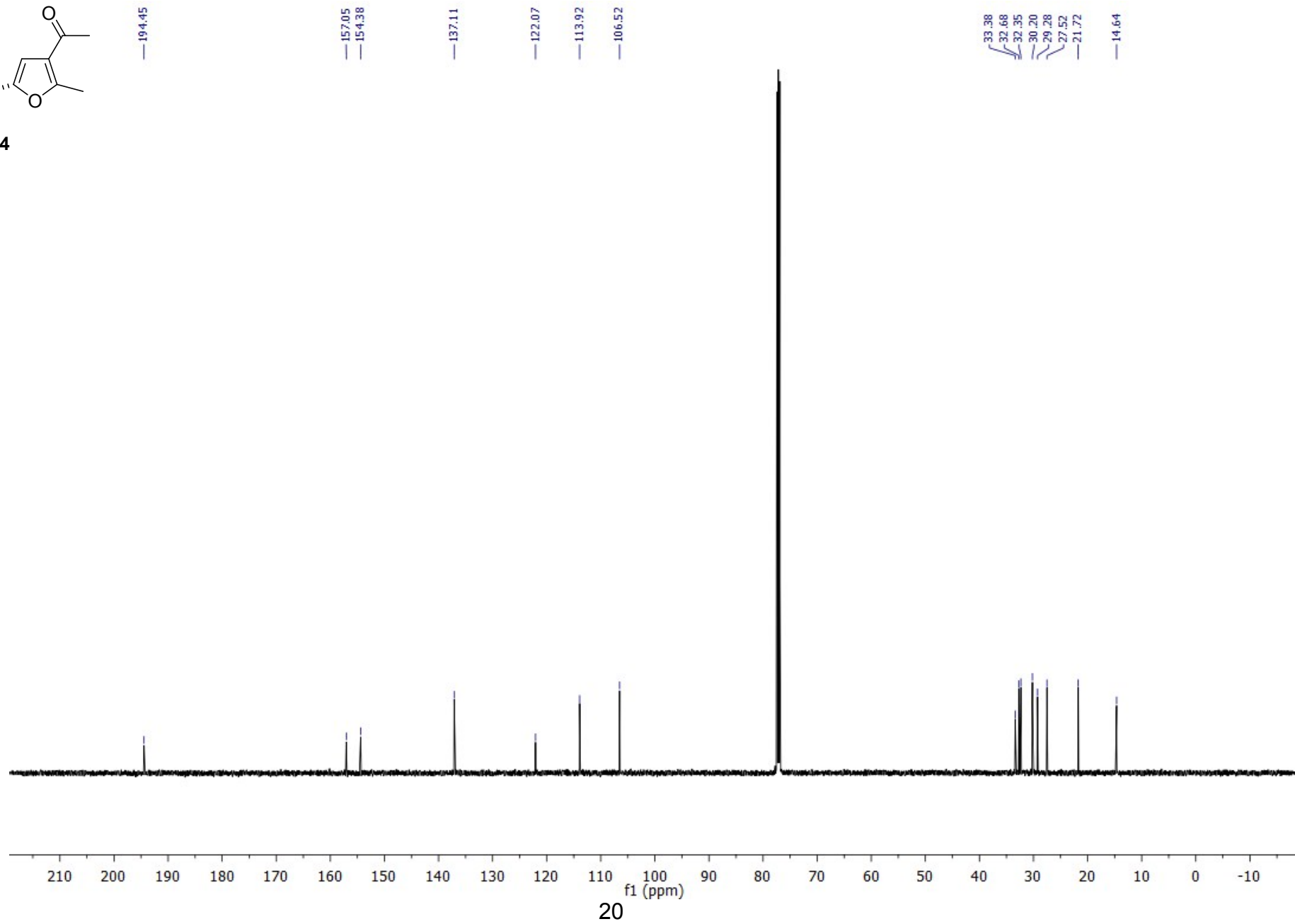
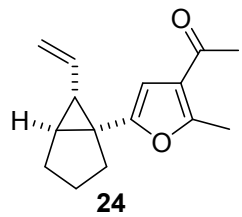


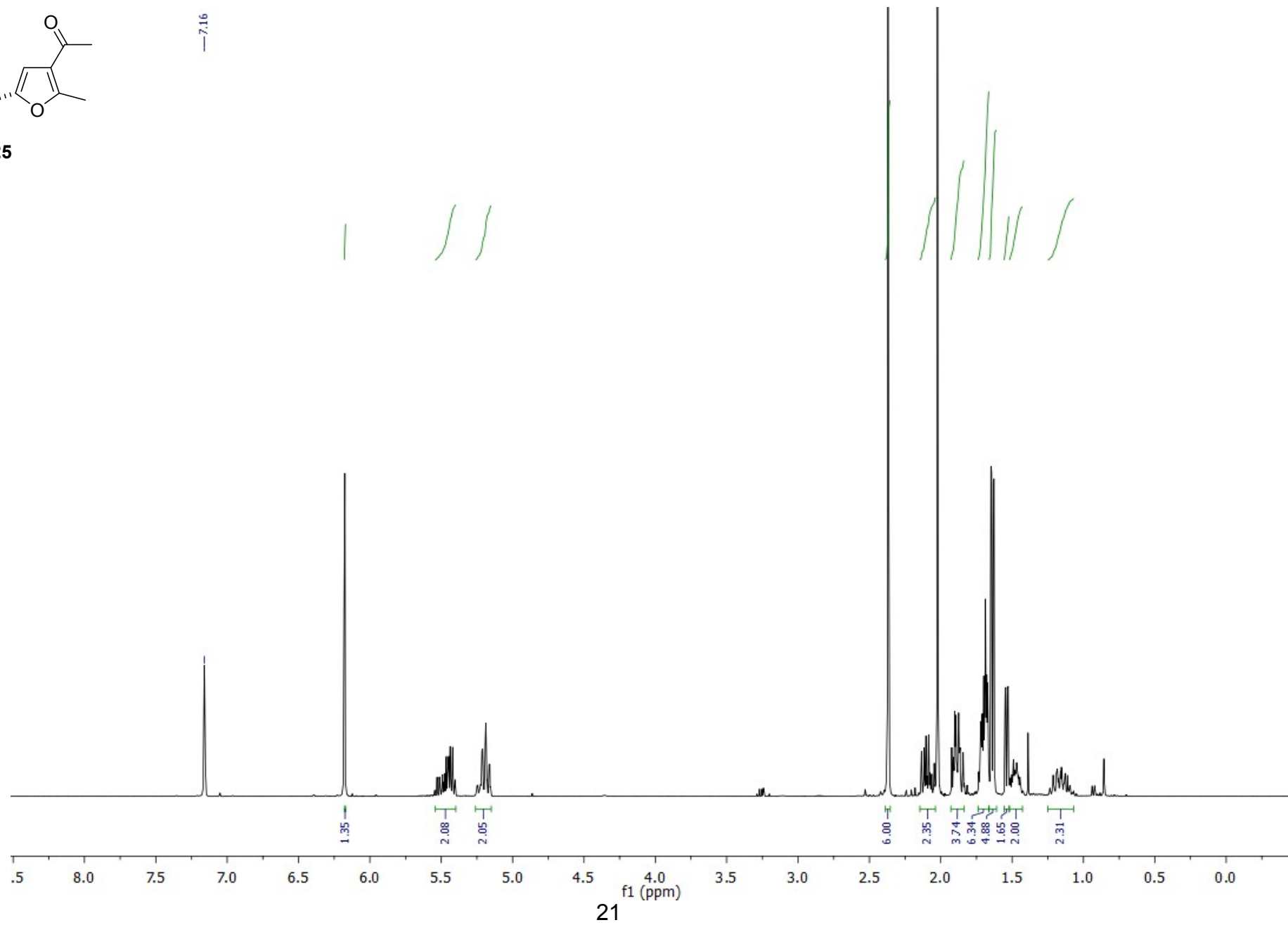
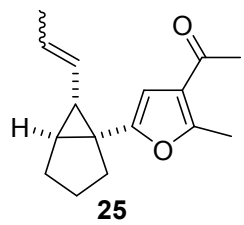


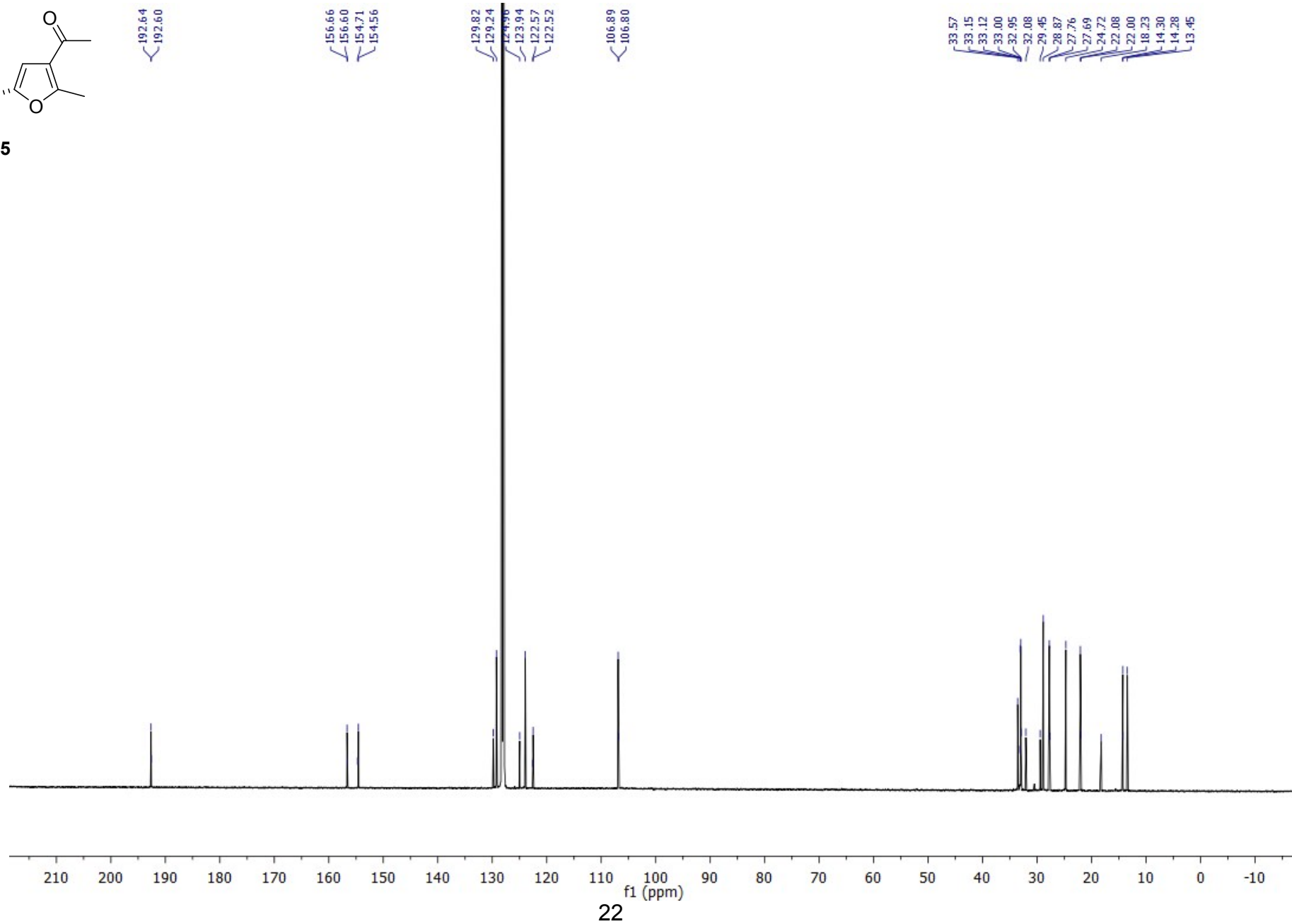
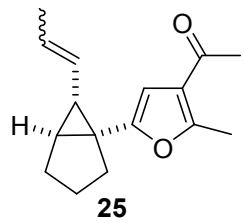


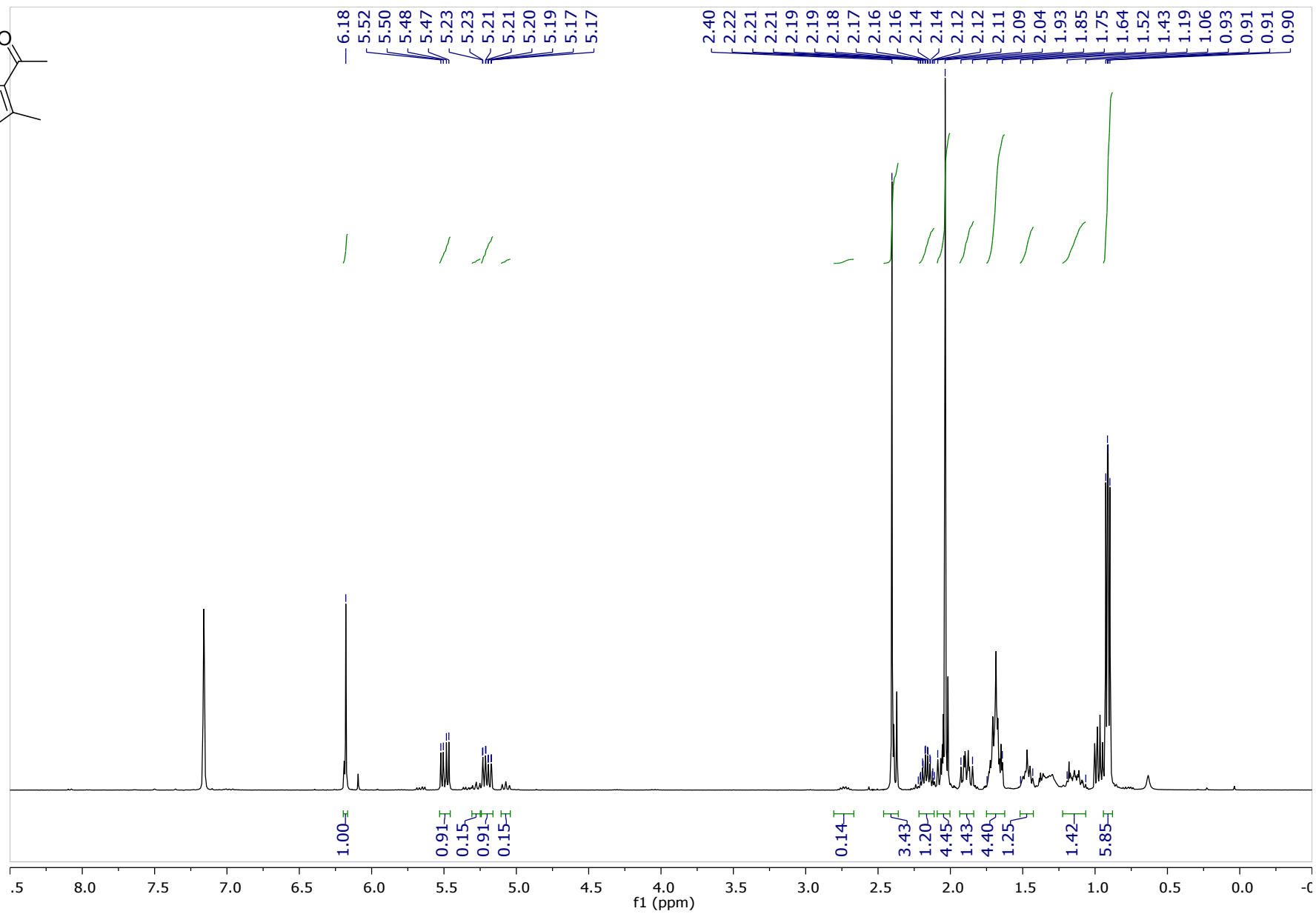
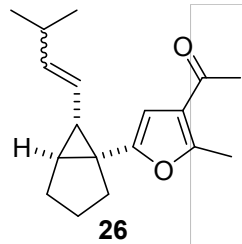


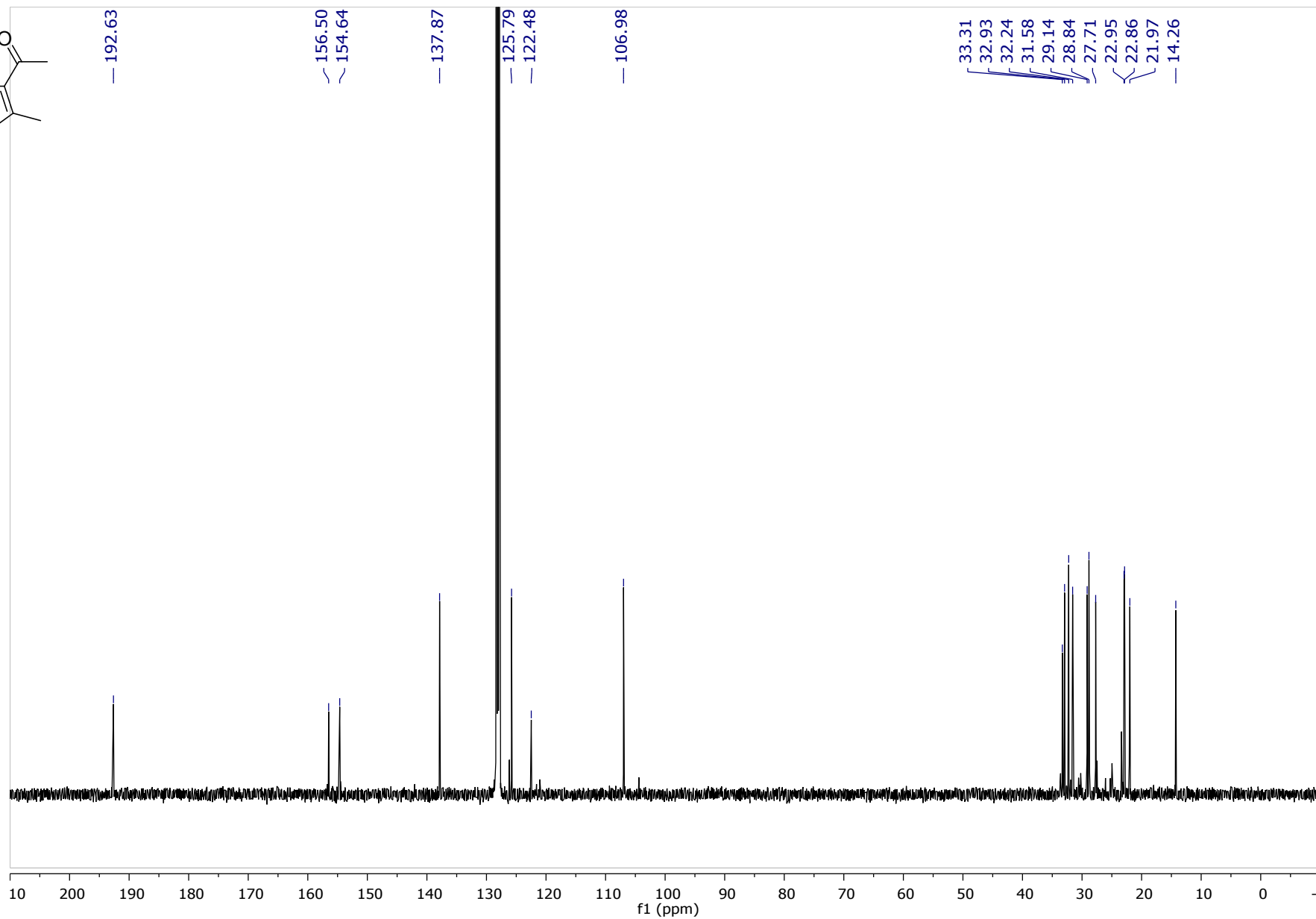
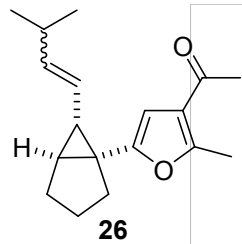




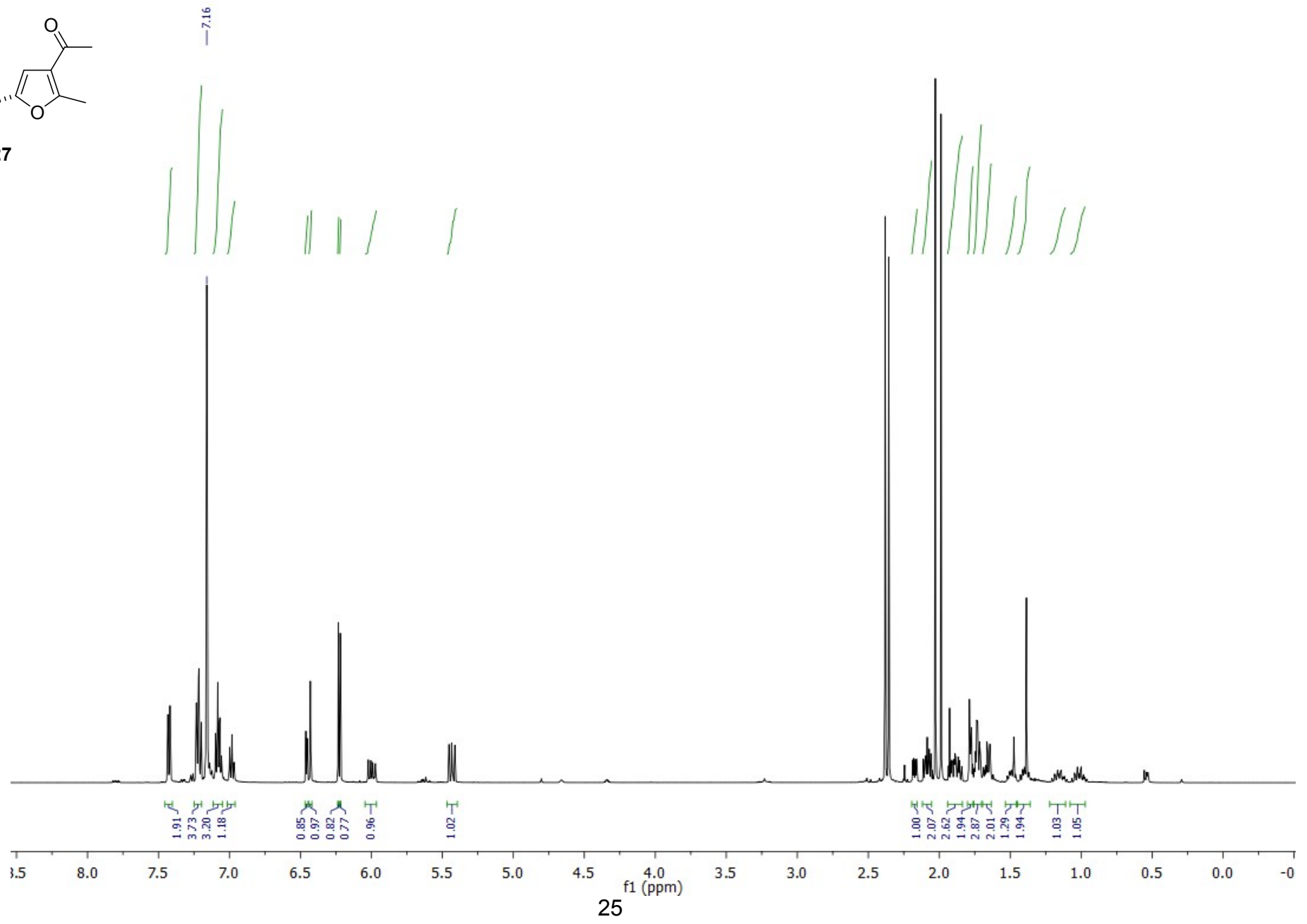
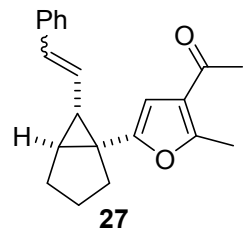


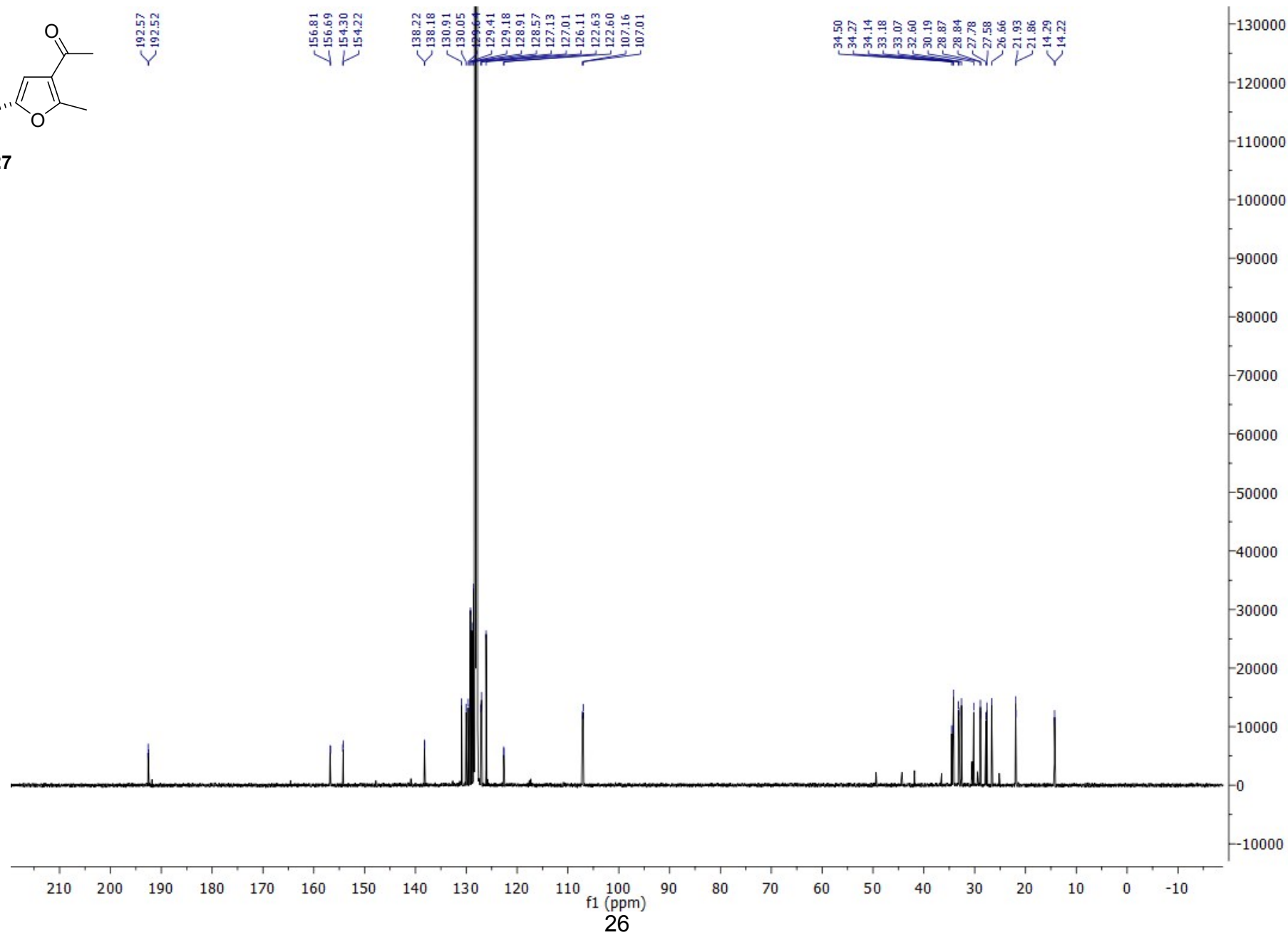
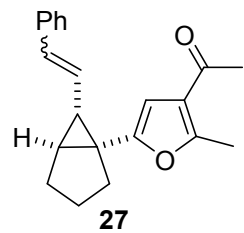


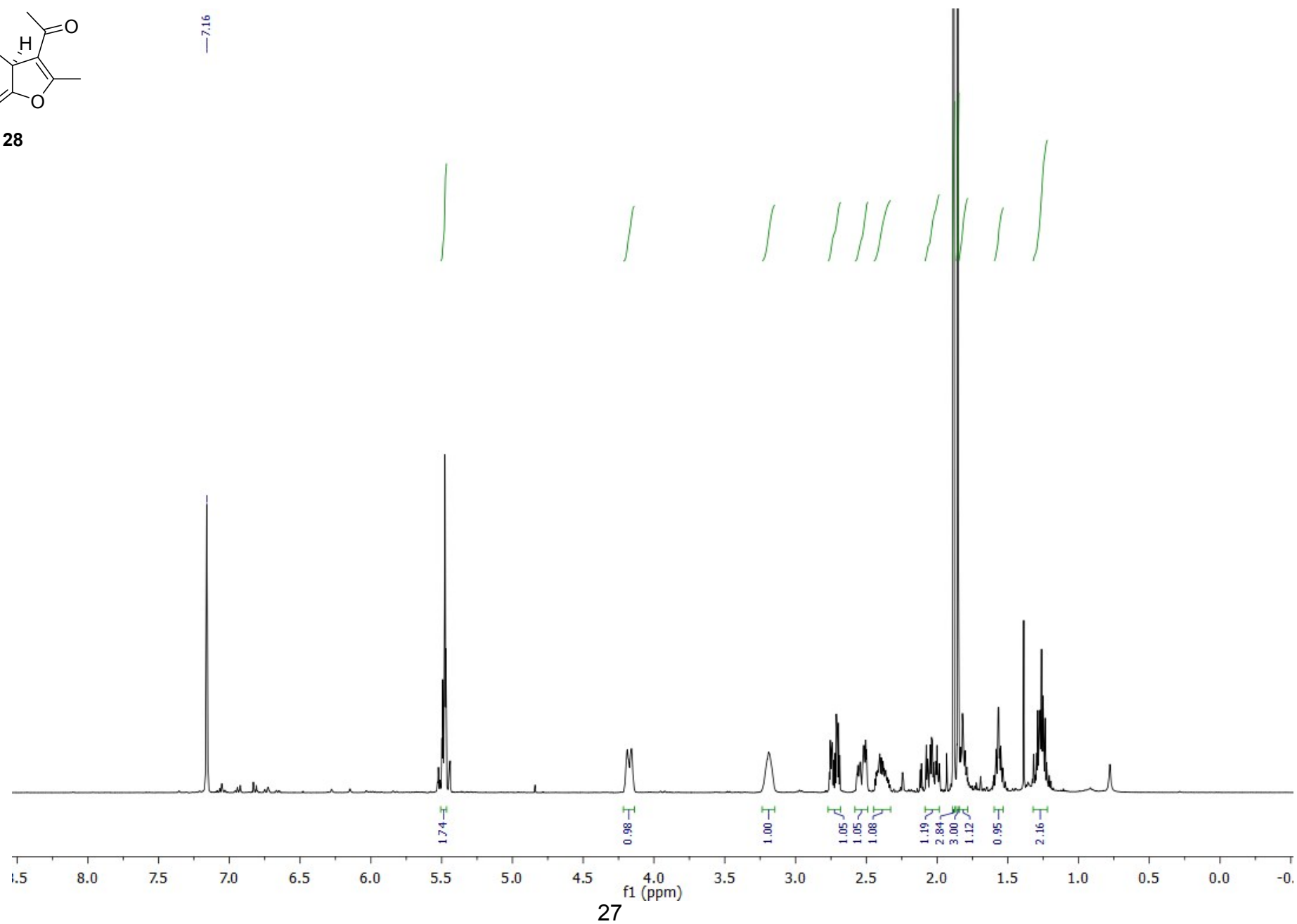
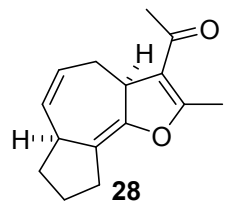


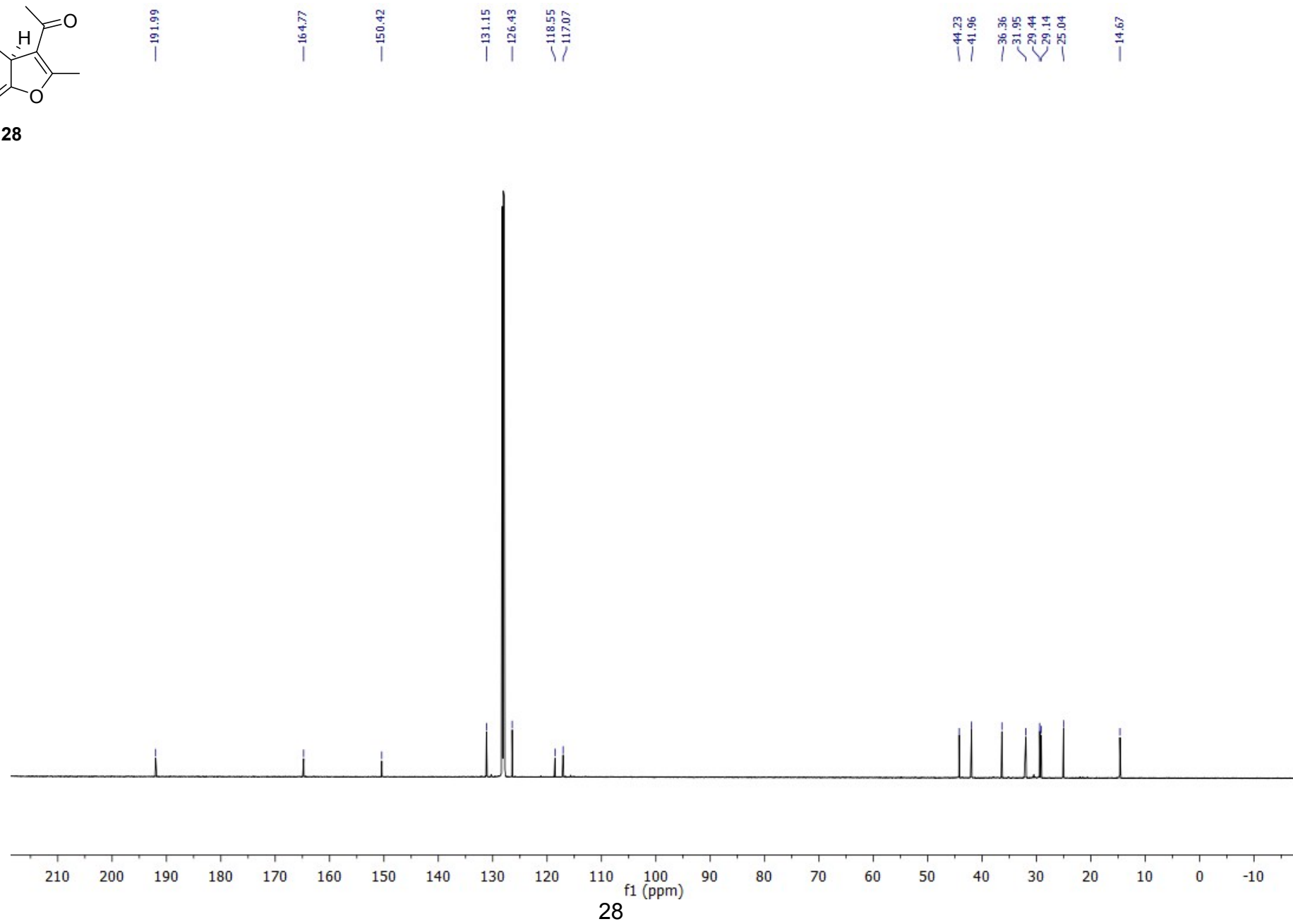
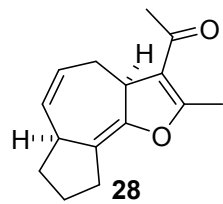


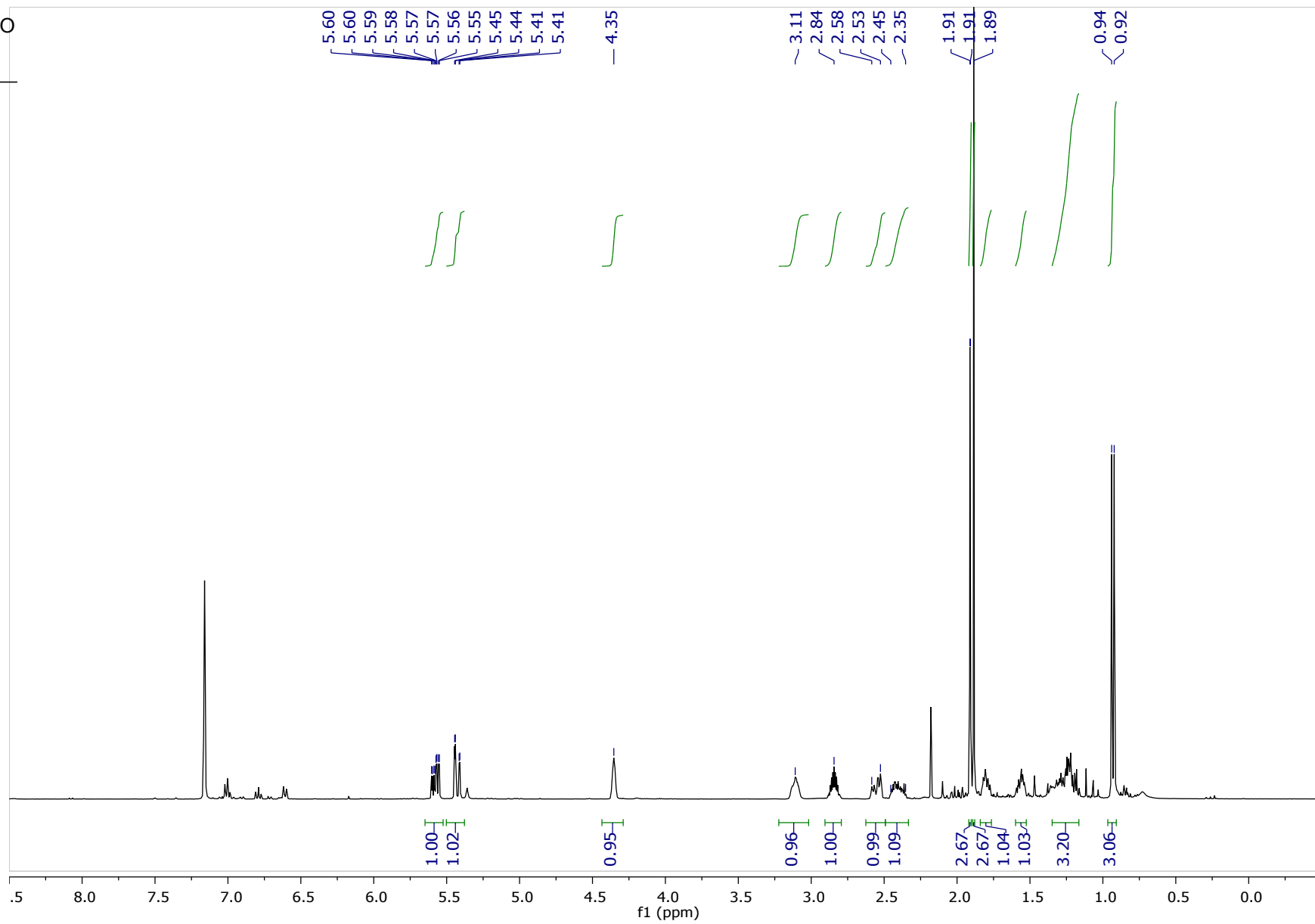
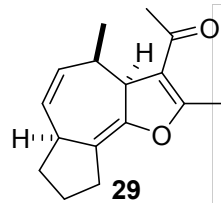


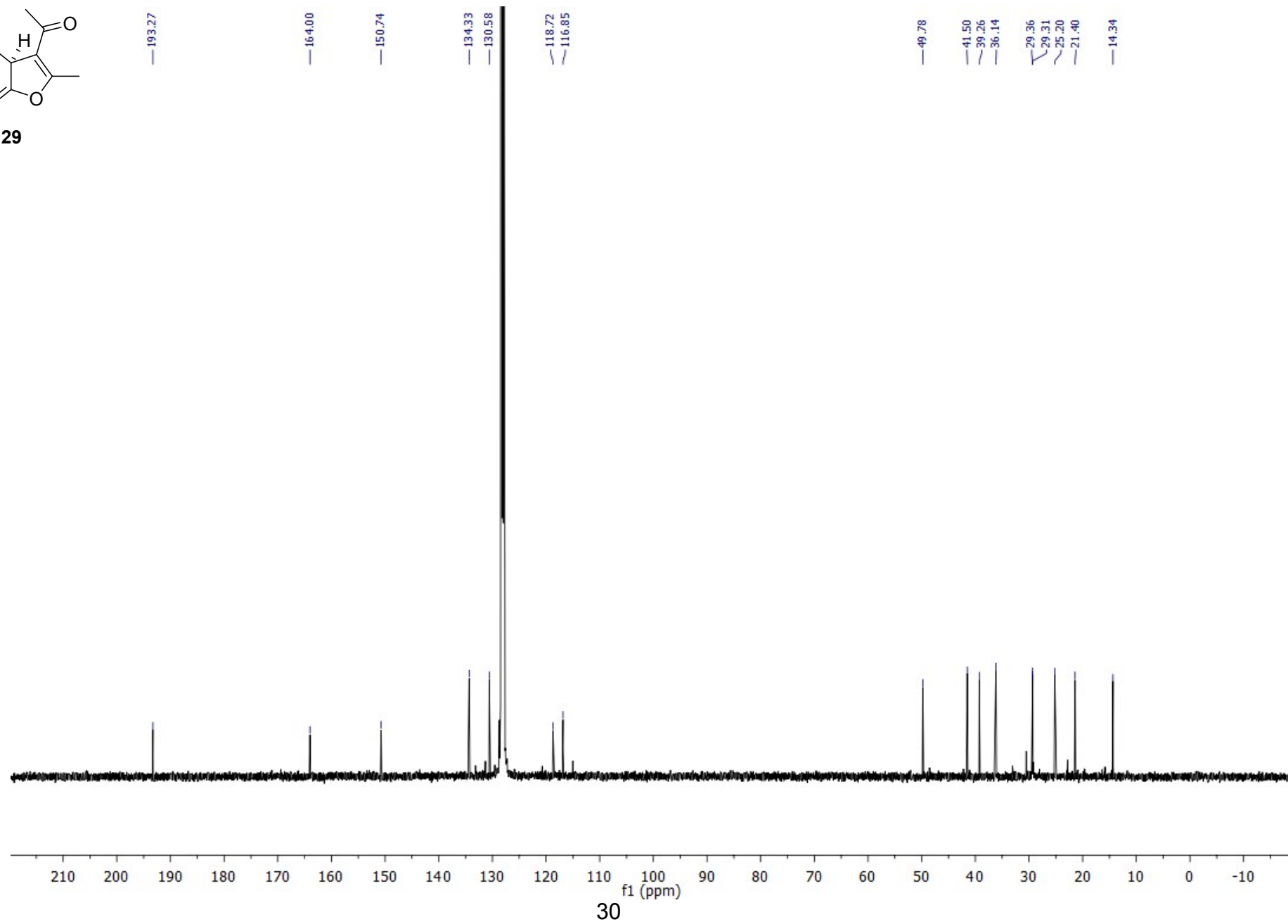
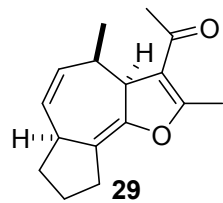


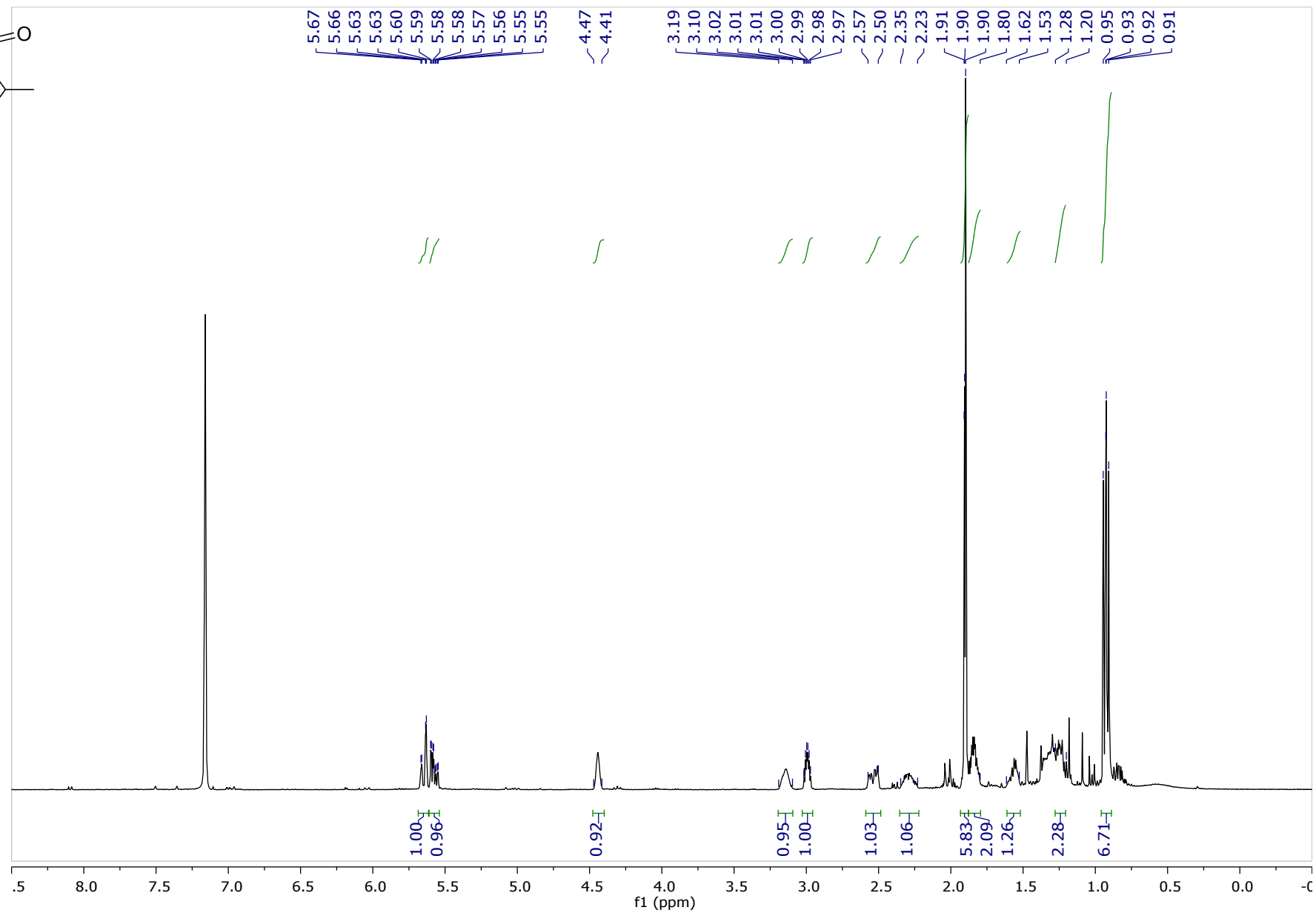
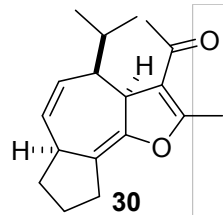


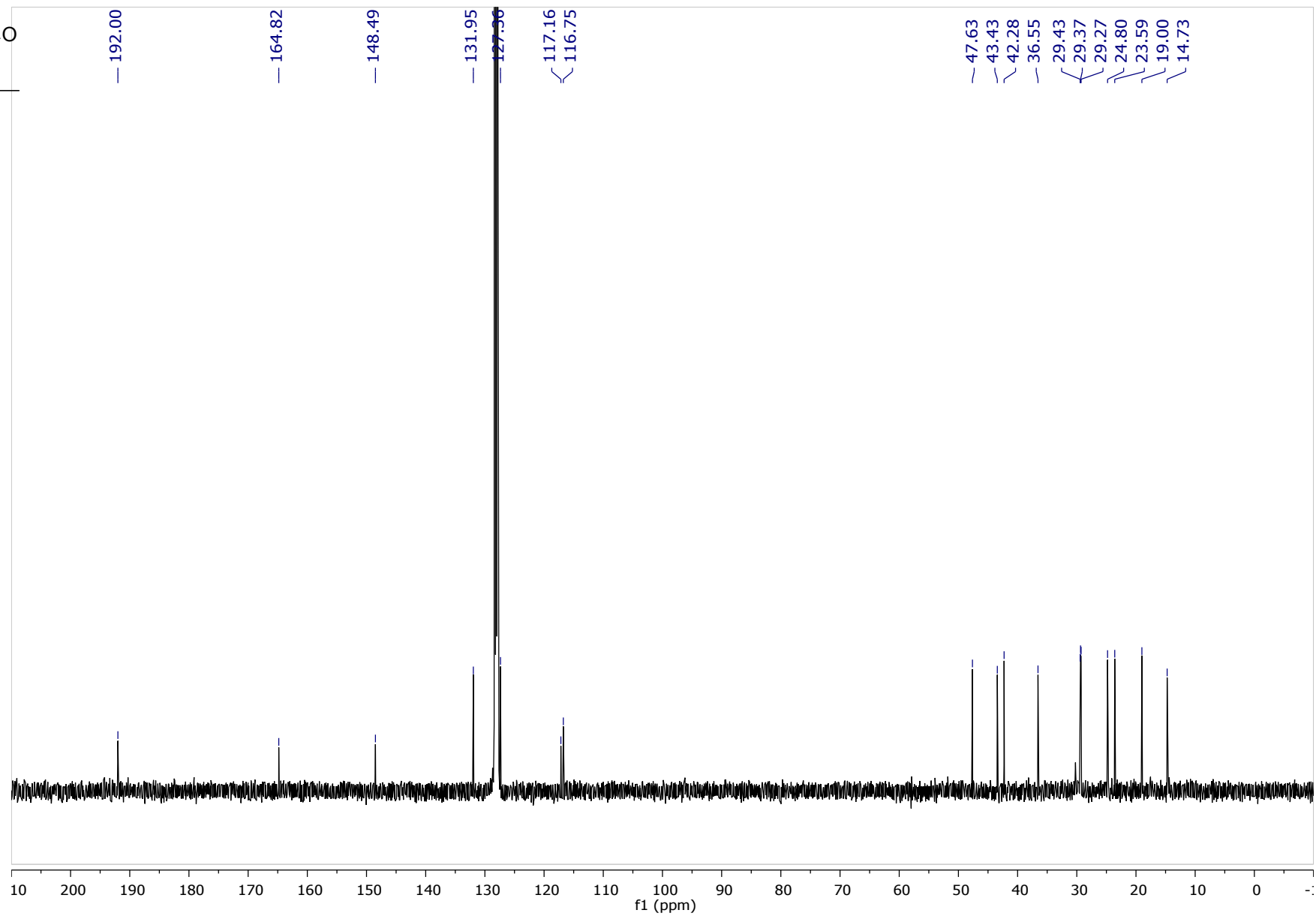
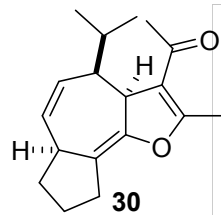




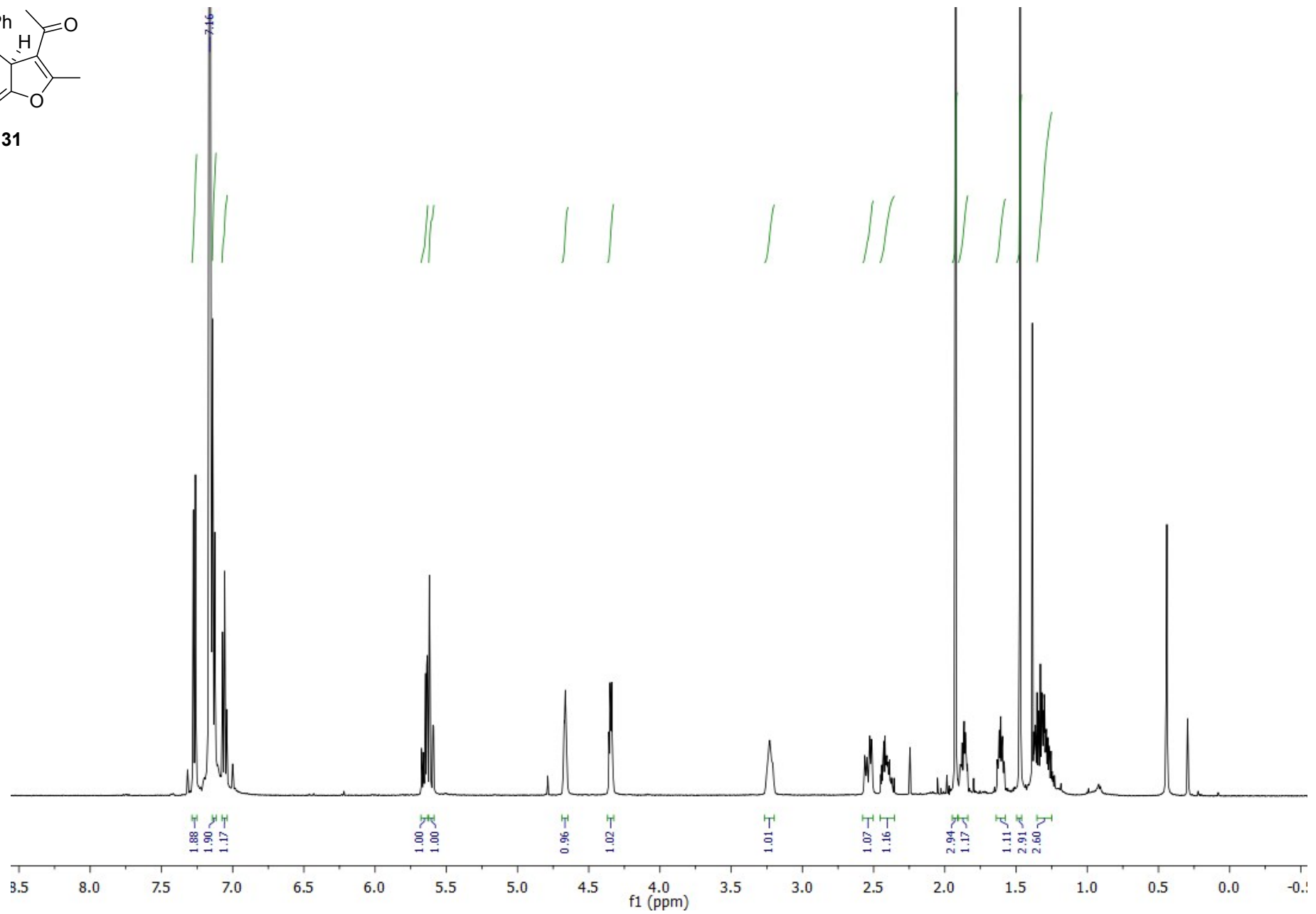
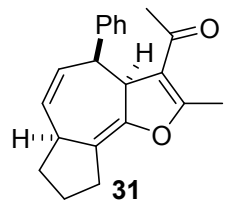


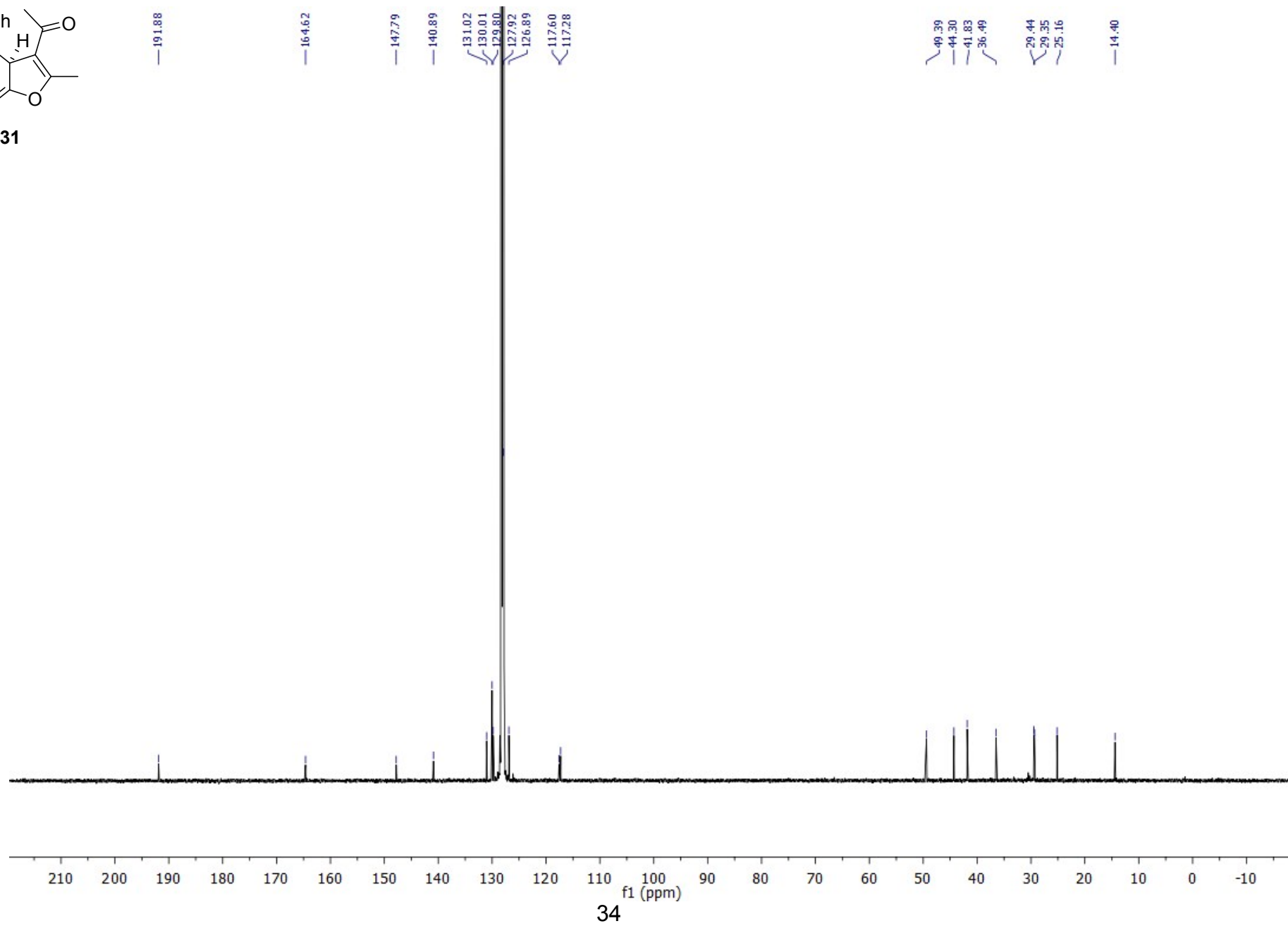
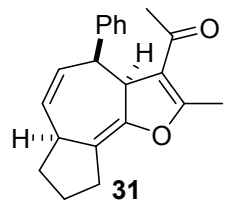


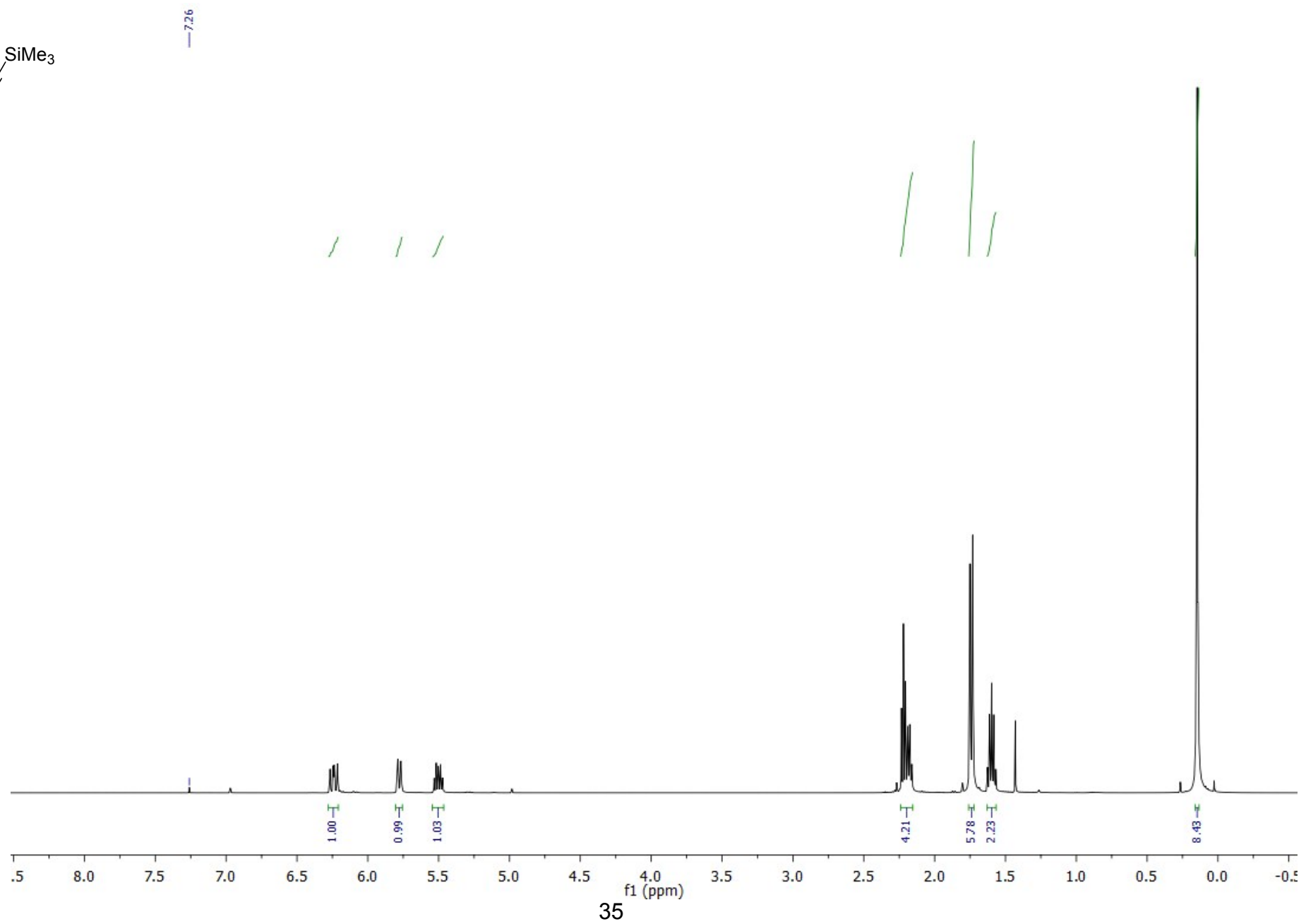
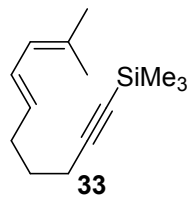


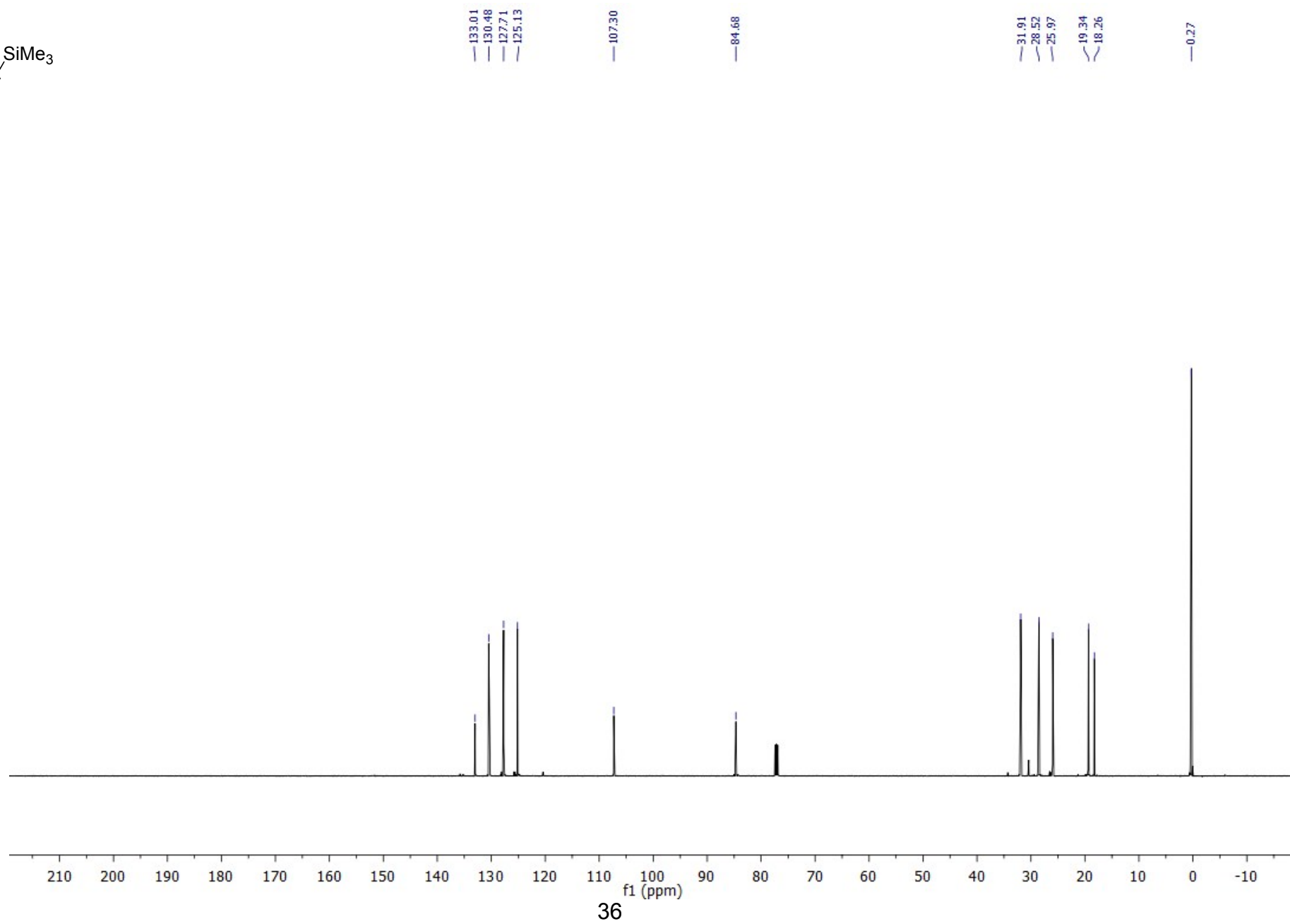
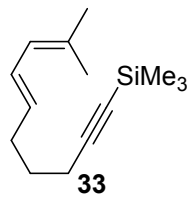


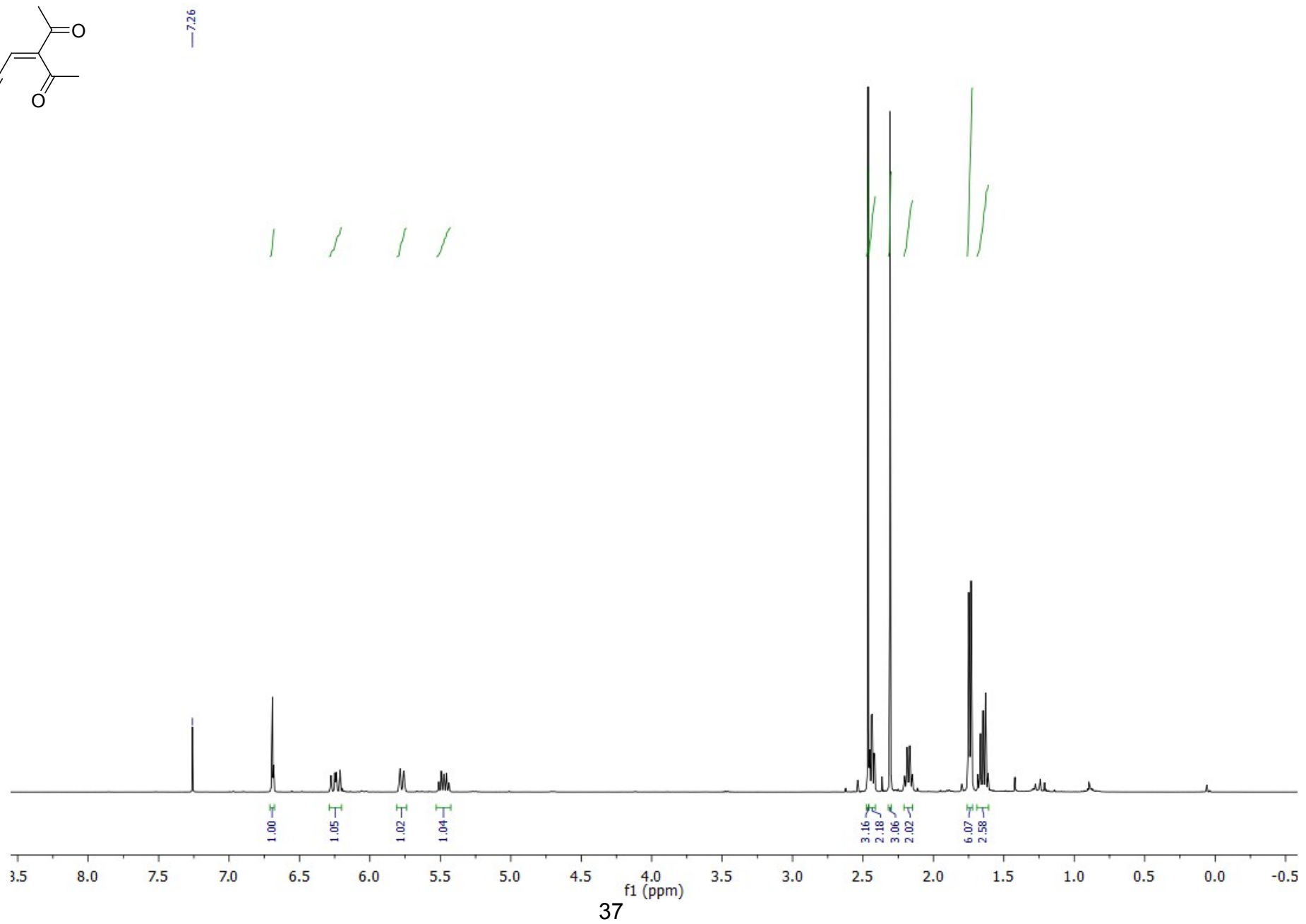
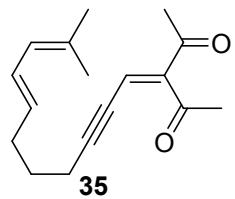


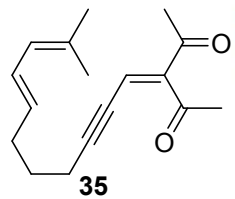












— 201.40

— 195.91

— 149.70

— 133.84

— 129.84

— 128.16

— 124.88

— 123.31

— 110.22

— 77.20

— 32.00

— 31.09

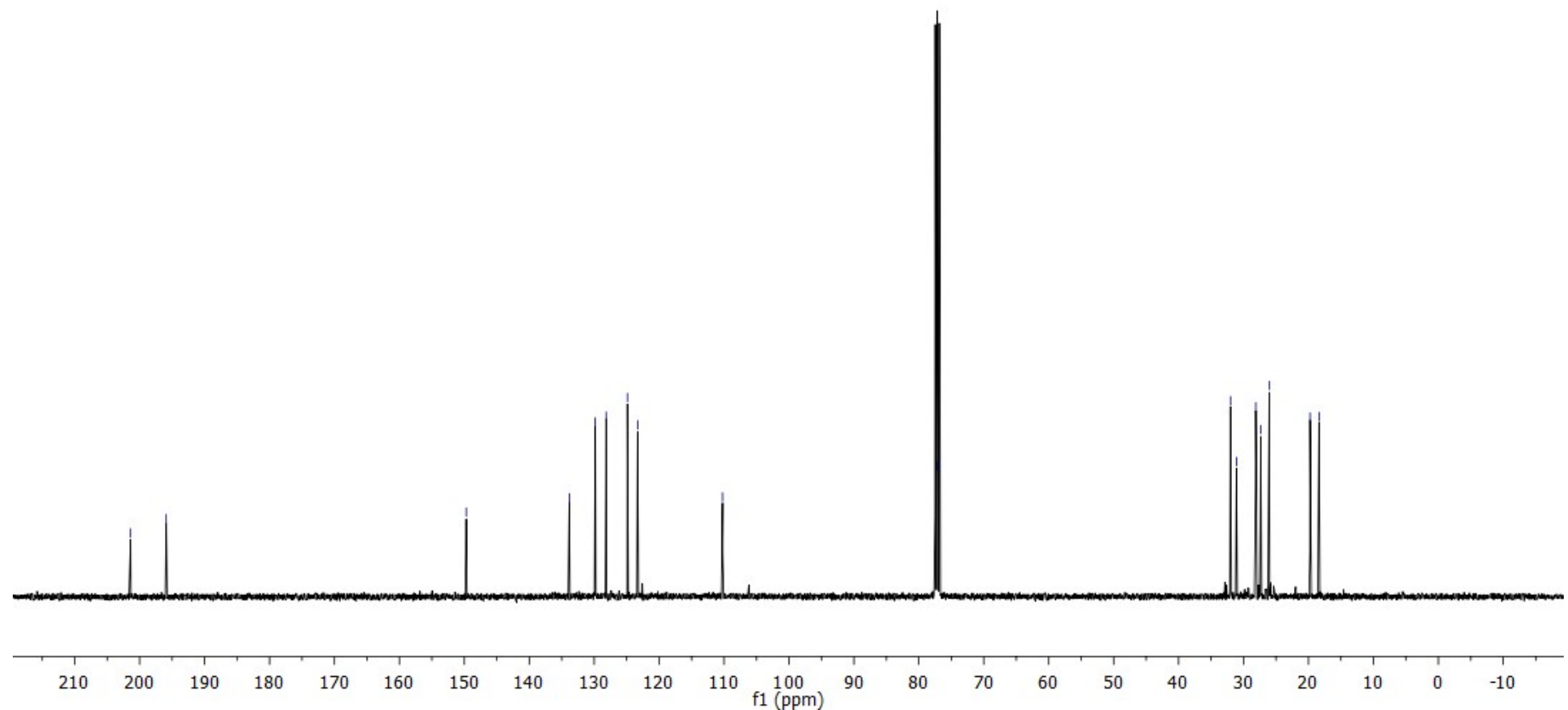
— 28.11

— 27.35

— 26.03

— 19.75

— 18.37



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