

Electronic Supplementary Material (ESI) for Green Chemistry.

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## Supporting Information

### Switchable light vs acid-induced transformations of complex framework compounds at room temperature

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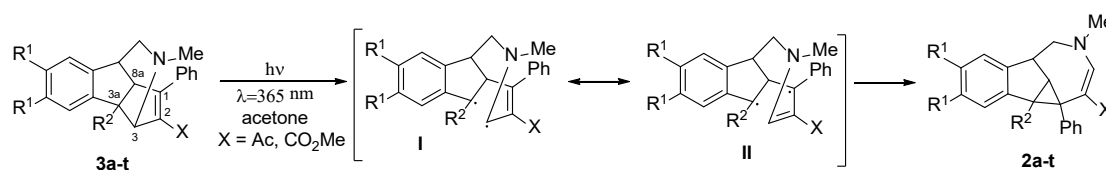
Email: [titov-aa@rudn.ru](mailto:titov-aa@rudn.ru); [rafael.luque@uco.es](mailto:rafael.luque@uco.es); [giovanni.talarico@unina.it](mailto:giovanni.talarico@unina.it)

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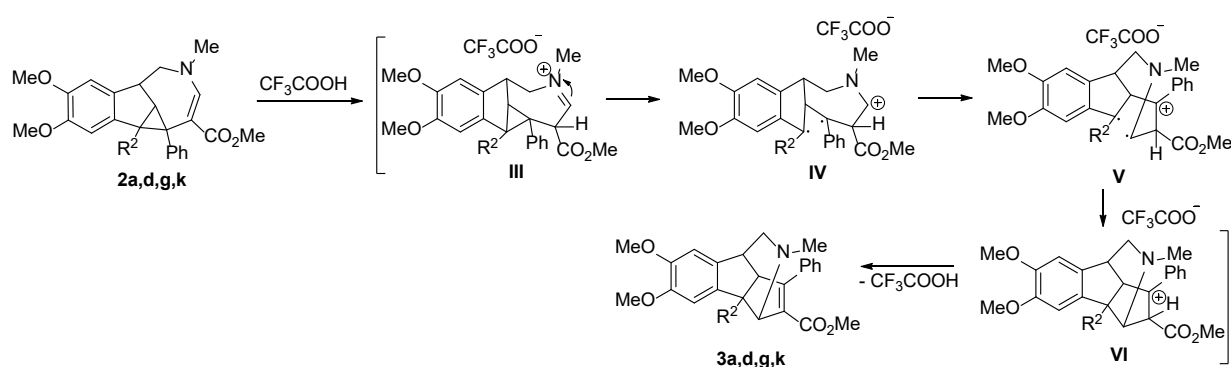
## 1. Proposed mechanisms of reactions.

Based on<sup>[1]</sup>, it can be suggested that, initially, under irradiation with UV at a wavelength of 365 nm, as a result of the cleavage of the C<sub>3</sub>–C<sub>3a</sub> bond, a biradical **I** is generated. Then it is isomerized into a biradical **II**, from which a cyclopropane ring is formed (**Scheme S1**).



**Scheme S1.** A proposed mechanism for the forward rearrangement of cyclopentenes **3** into vinylcyclopropanes **2**.

In a trifluoroacetic acid medium at room temperature, 2-azabenzo[*a*]cyclopropano[*cd*]azulenes **2a,d,g,k** are converted back to (epiminomethano)cyclopenta[*a*]indenes **3a,d,g,k** in 69-73% yields (**Scheme S2**). We assume that the first step of this transformation is the addition of a proton to the enamine fragment of the molecules of the cyclopropane derivatives **2a,d,g,k**, which leads to the formation of cation **III**, which undergoes transformation into a cation-biradical **IV**. Intermediate **IV** is isomerized to **V**, the recombination of which and subsequent elimination of the proton leads to the target products.



**Scheme S2.** A proposed mechanism for the reverse transformation of vinylcyclopropanes **2** into cyclopentenes **3** at room temperature.

Further, the proposed mechanisms reported in **Scheme S1** and **S2** was investigated in detail by using DFT calculations.

## 2. Computational Details

DFT static calculations have been performed with Gaussian09 and Gaussian16 set of programs<sup>[2]</sup> using the B3LYP functional of Becke and Perdew<sup>[3]</sup> for the closed shell systems and UB3LYP for the open shell systems. The geometry optimization has been described with the 6-31G(d) basis set and stationary points were characterized using vibrational analysis, and this analysis has been also used to calculate zero-point energies and thermal (enthalpy and entropy) corrections (298.15 K, 1 bar). Improved electronic energies has been obtained from single-point energy calculations using a 6-311G++(d,p) basis set, a solvation contribute (PCM model,<sup>[4]</sup> acetone for **3-2** and acetonitrile for **2-3** reactions, respectively) and dispersion corrections<sup>[5]</sup> (EmpiricalDispersion=GD3BJ in Gaussian package). These energies added to the 6-31G(d)-level thermal corrections are named  $\Delta G$ . It is well-known that open-shell systems place additional challenges to DFT, due to: (i) the spin-contamination problem; (ii) numerical instability in the exchange-correlation (XC) kernel; (iii) the single-determinant description of open-shell ground states can soon be inaccurate and energetically unstable.<sup>[6]</sup> Linear-response time-dependent density functional theory (TDDFT) along with multireference methods (i.e., complete active space self-consistent field or CASSCF, multireference configuration interaction or MRCI, complete active space with second-order perturbation theory or CASPT2) can provide more accurate results for activation energies. TDDFT, indeed, can partially overcome these well-known limitations with a reduced computational cost with respect to post-Hartree-Fock methods, since low lying triplet states can be obtained as linear combination of one particle excitations. On the other hand, electronic correlation and orbital relaxations are treated in a more accurate way with TDDFT with respect to converging an unrestricted DFT ground state triplet.<sup>[6,7]</sup> Thus, the electronic structures of triplet species for the transformation of **3a-2a** (Figure S1) and **3s-2s** (Figure S4) were corrected using the TDDFT within the linear-response framework.<sup>[8,9,10]</sup> These additional analysis on these triplet states were also made possible at TDDFT level relying on the recent development and implementation of analytic expressions for higher-order TDDFT properties using the most recent version of Gaussian electronic structure package G16.C01,<sup>[2]</sup> such as the TDDFT Hessians.<sup>[11,12]</sup>

### 3. Supplementary Figures

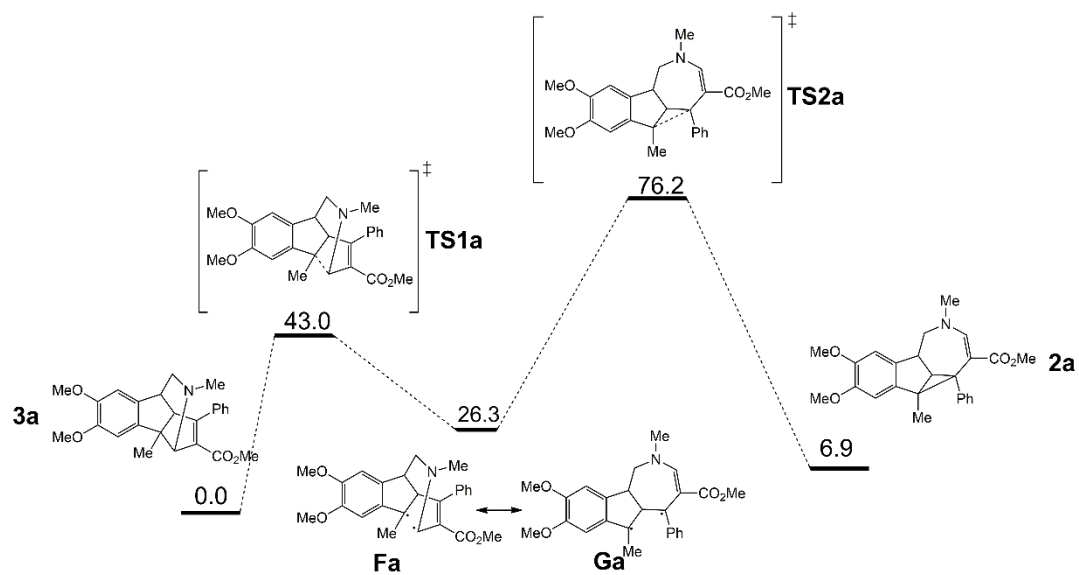


Figure S1. Gibbs energies (kcal/mol) for 3a-2a light-transformation obtained by DFT and TDDFT calculations.

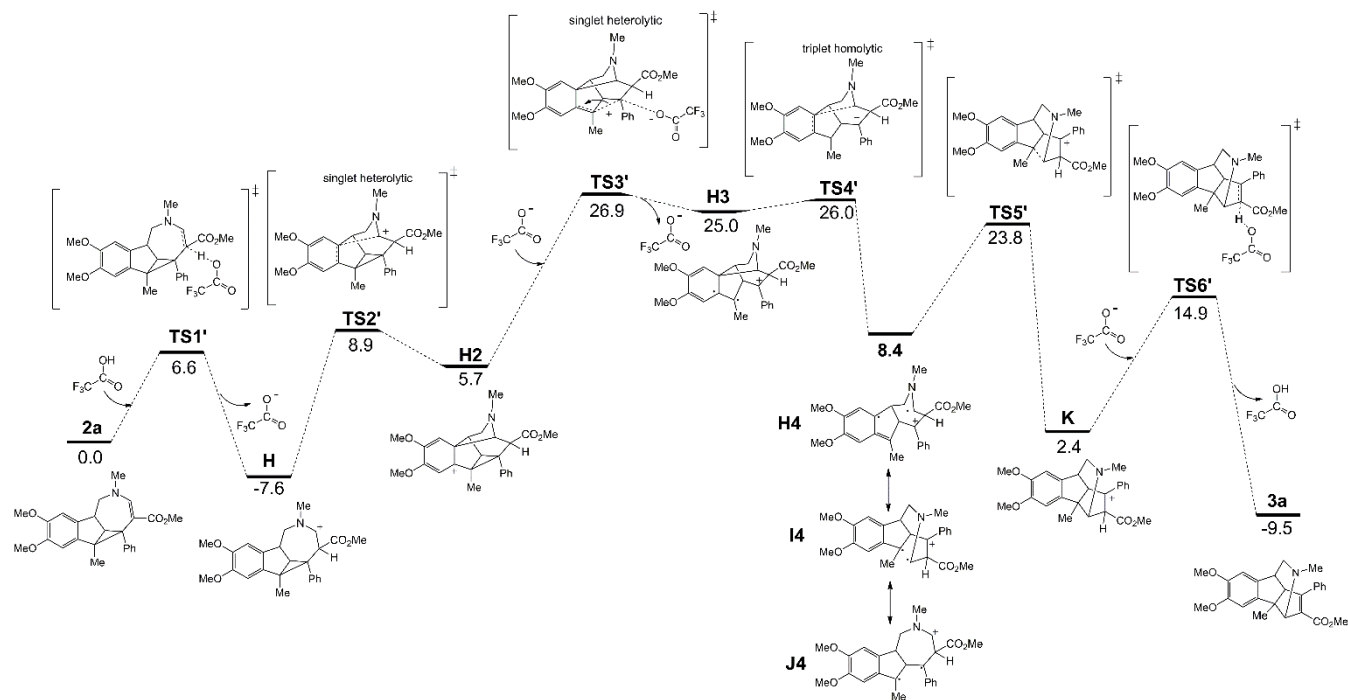
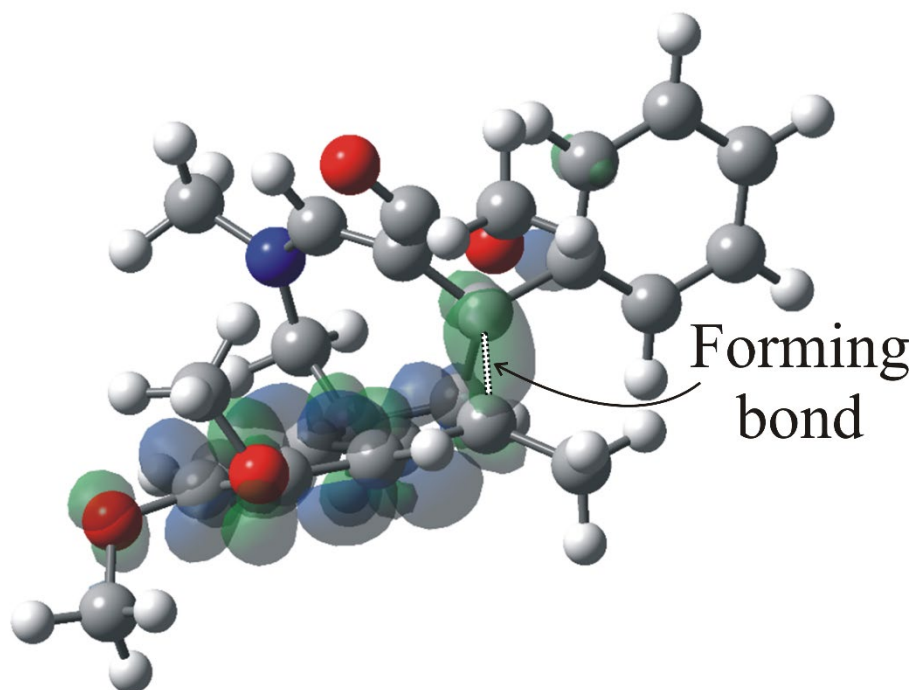
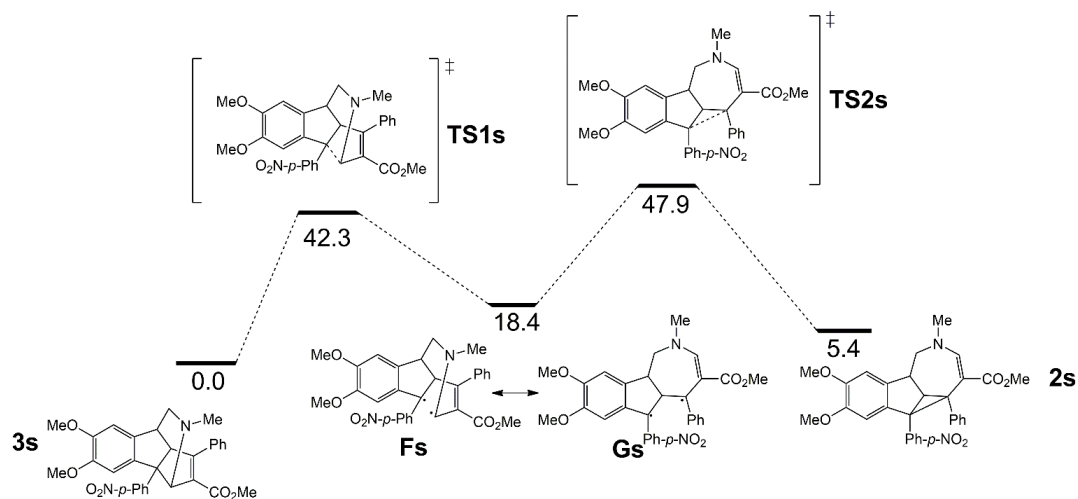


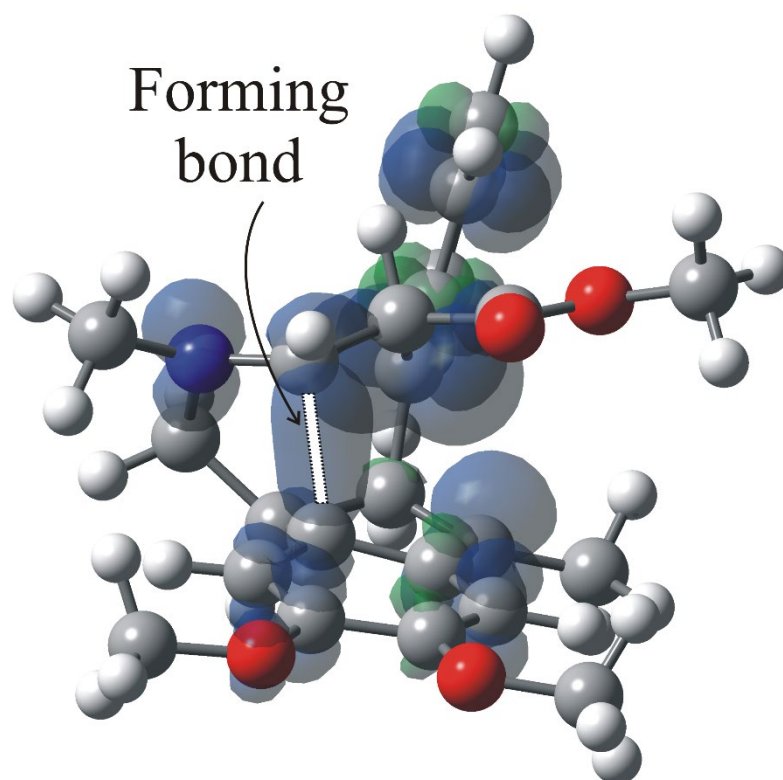
Figure S2. Gibbs energies (kcal/mol) for reaction path acid-catalyzed 2a-3a obtained by DFT calculations.



**Figure S3.** Spin density (difference between  $\alpha$  and  $\beta$  densities, green and blue as positive and negative, respectively) iso-surface of **TS2a**. Generalized spin density corresponding to the excited state energy calculated at TD-B3LYP/6-311++G(d,p) (implicit solvent) was employed.



**Figure S4.** Gibbs energies (kcal/mol) for **3s-2s** light-transformation obtained by DFT and TDDFT calculations.



**Figure S5.** Spin density (difference between  $\alpha$  and  $\beta$  densities, green and blue as positive and negative, respectively) iso-surface of TS4' reported in Figure S2. Spin density corresponding to the energy calculated for unrestricted triplet B3LYP/6-311++G(d,p) (implicit solvent) was employed.

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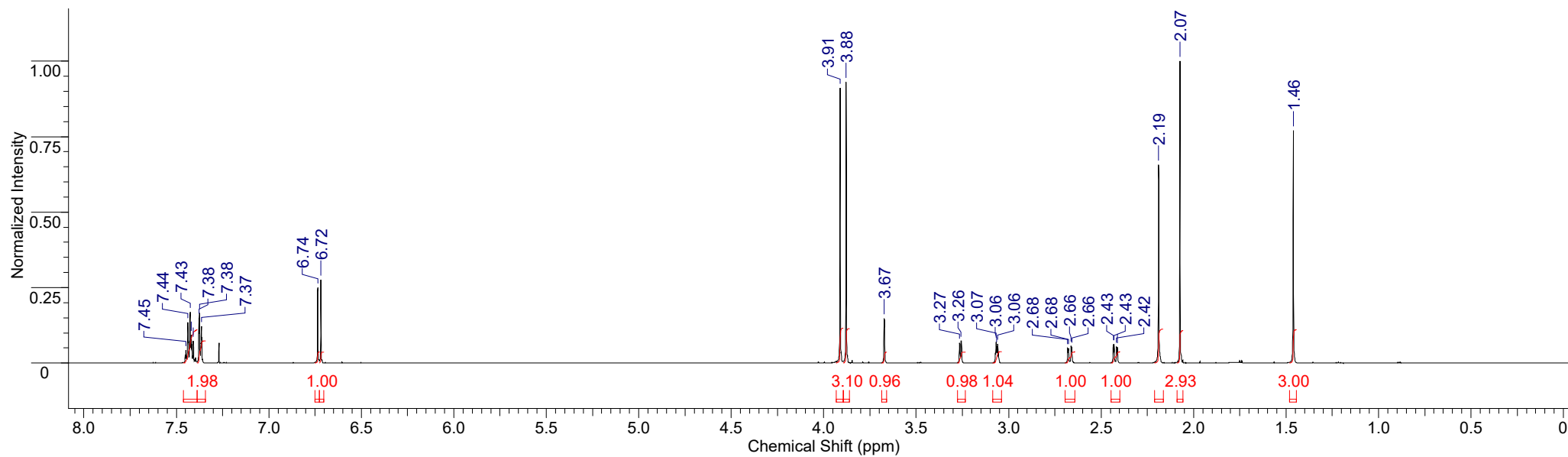
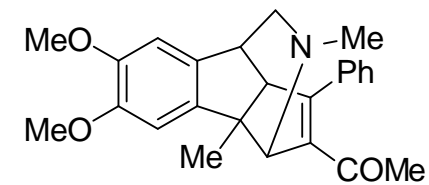


## 5. Appendix

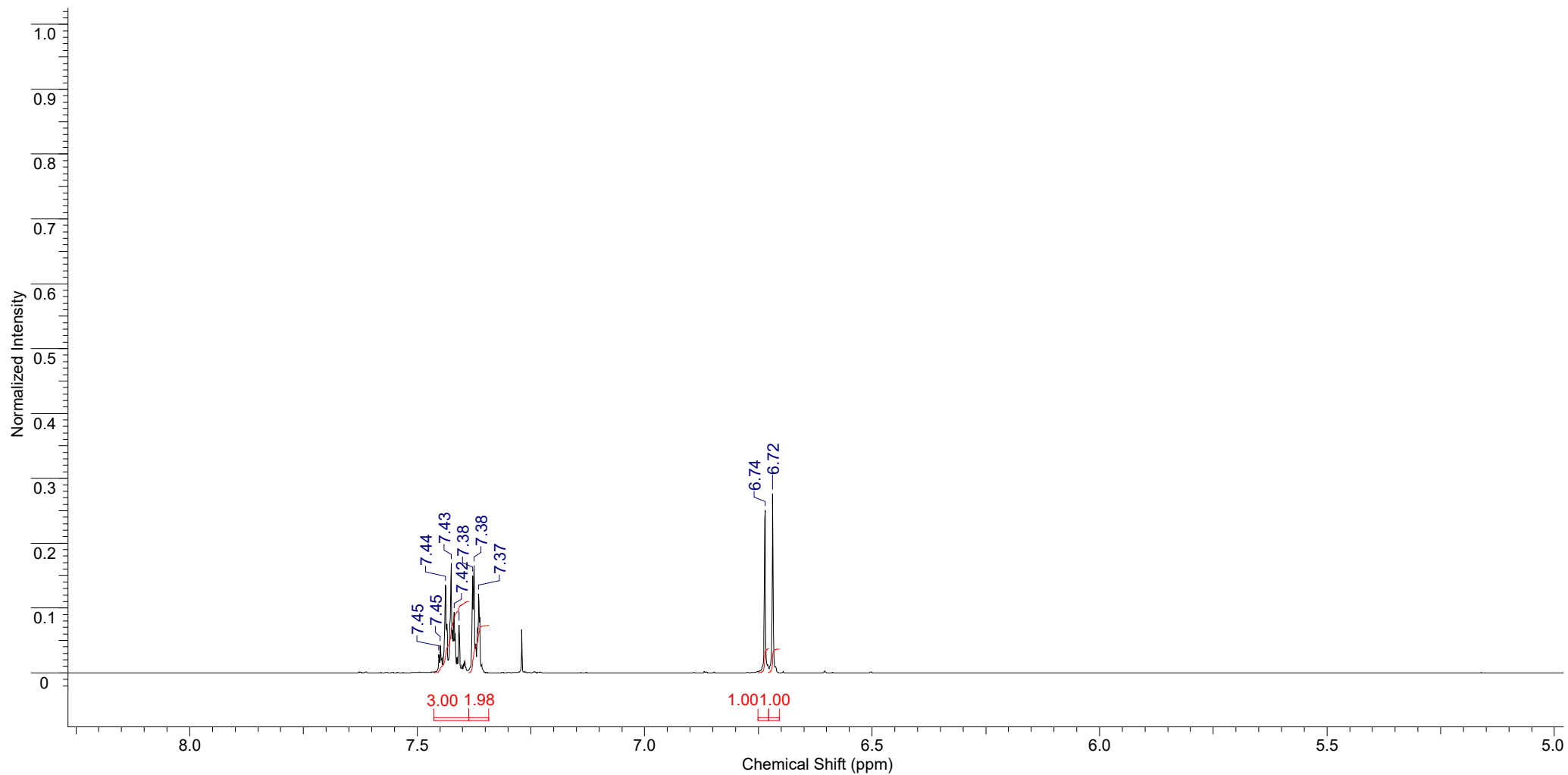
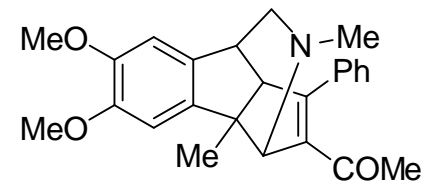
- Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra

1-[5,6-Dimethoxy-3a,10-dimethyl-1-phenyl-3,3a,8,8a-tetrahydro-3,8-(epiminomethano)cyclopenta[a]inden-2-yl]ethanone (3b)

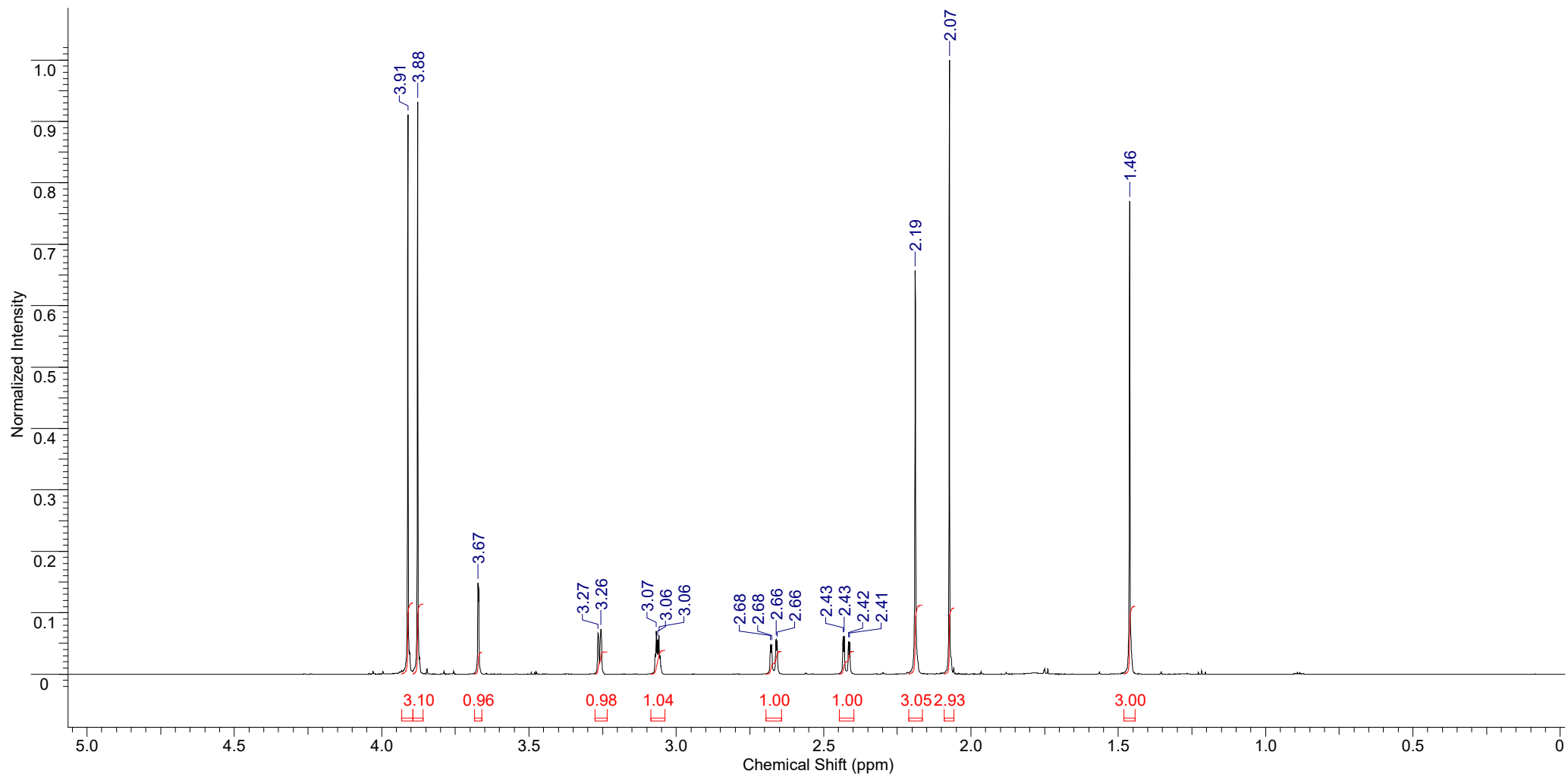
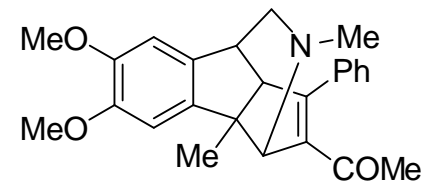
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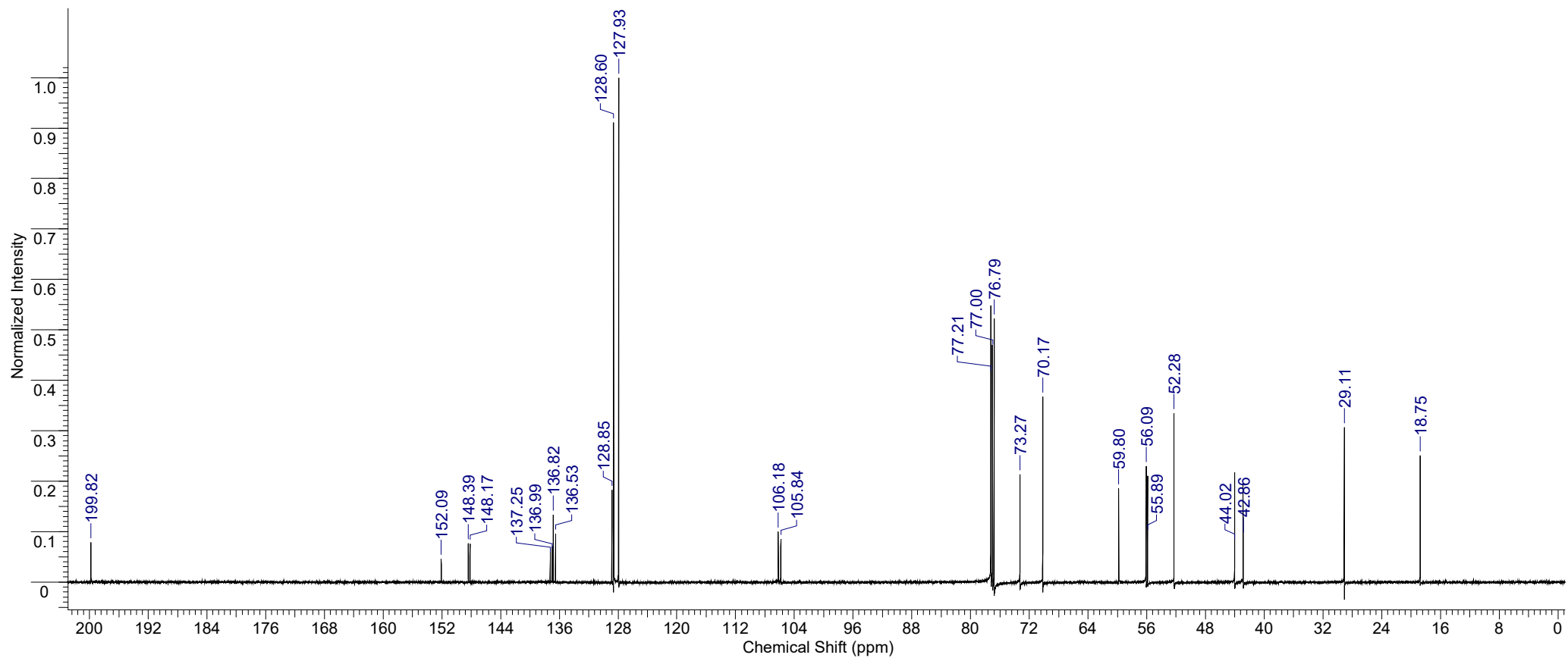
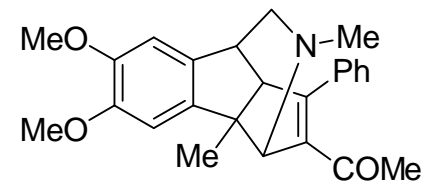
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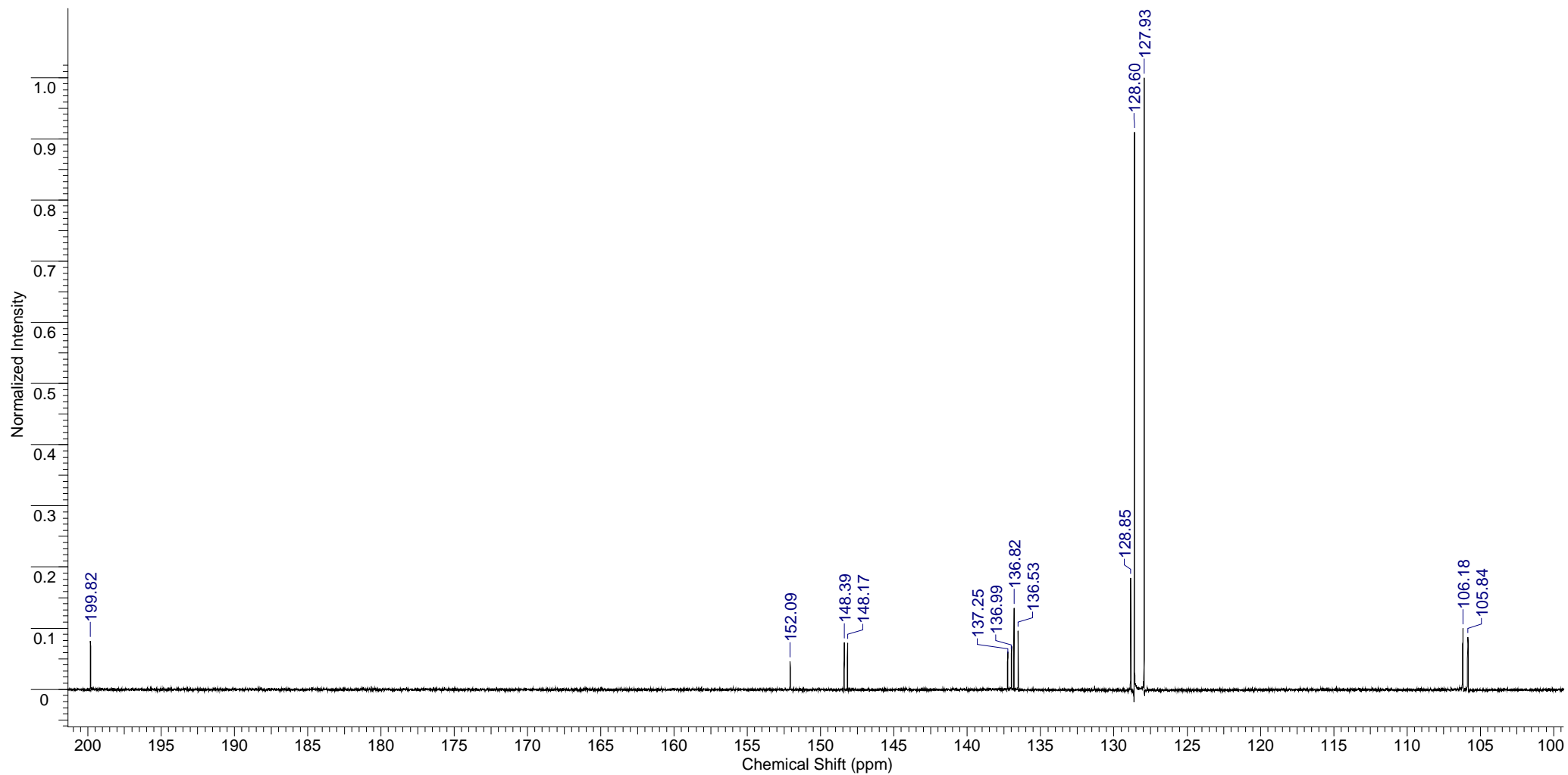
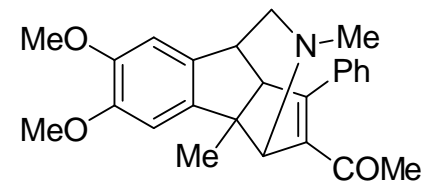
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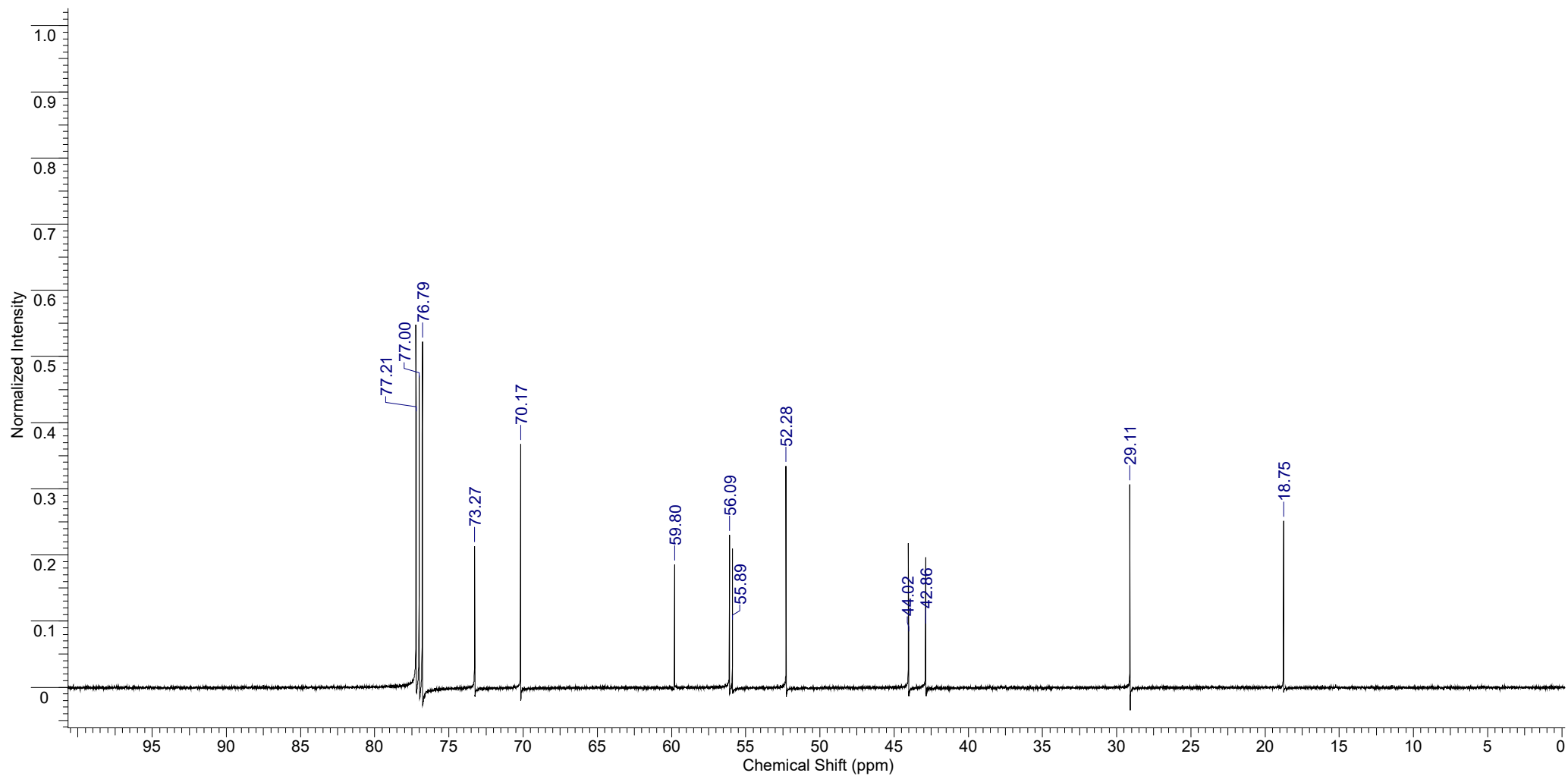
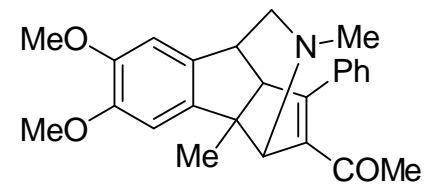
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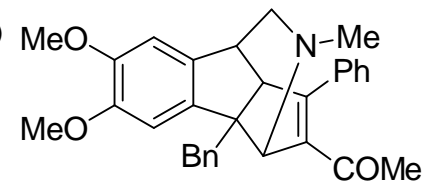
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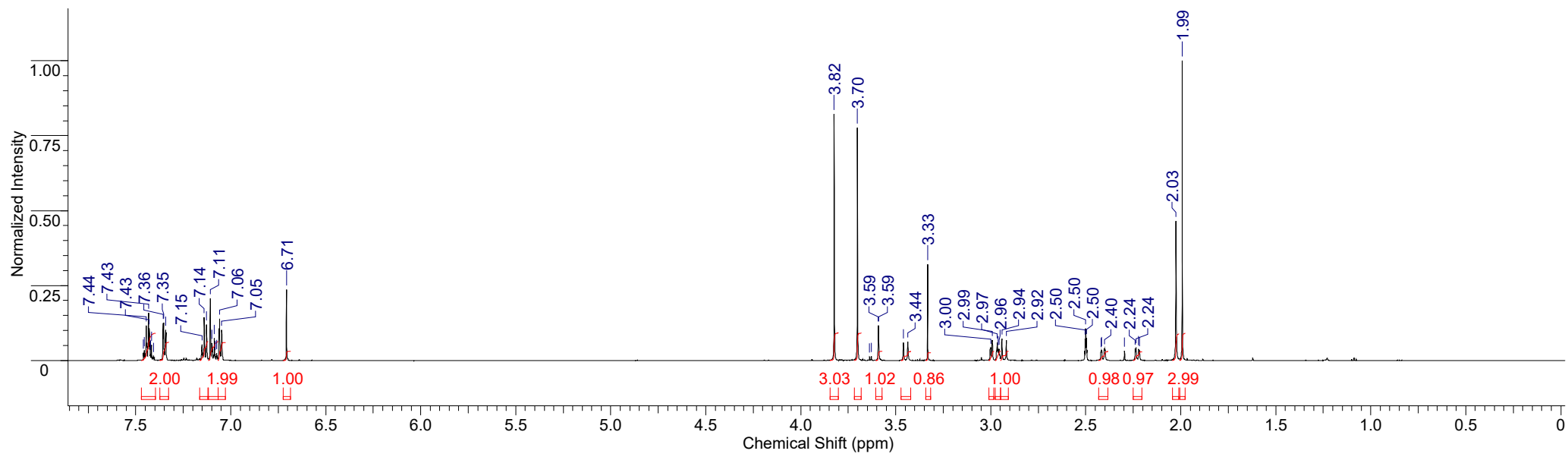
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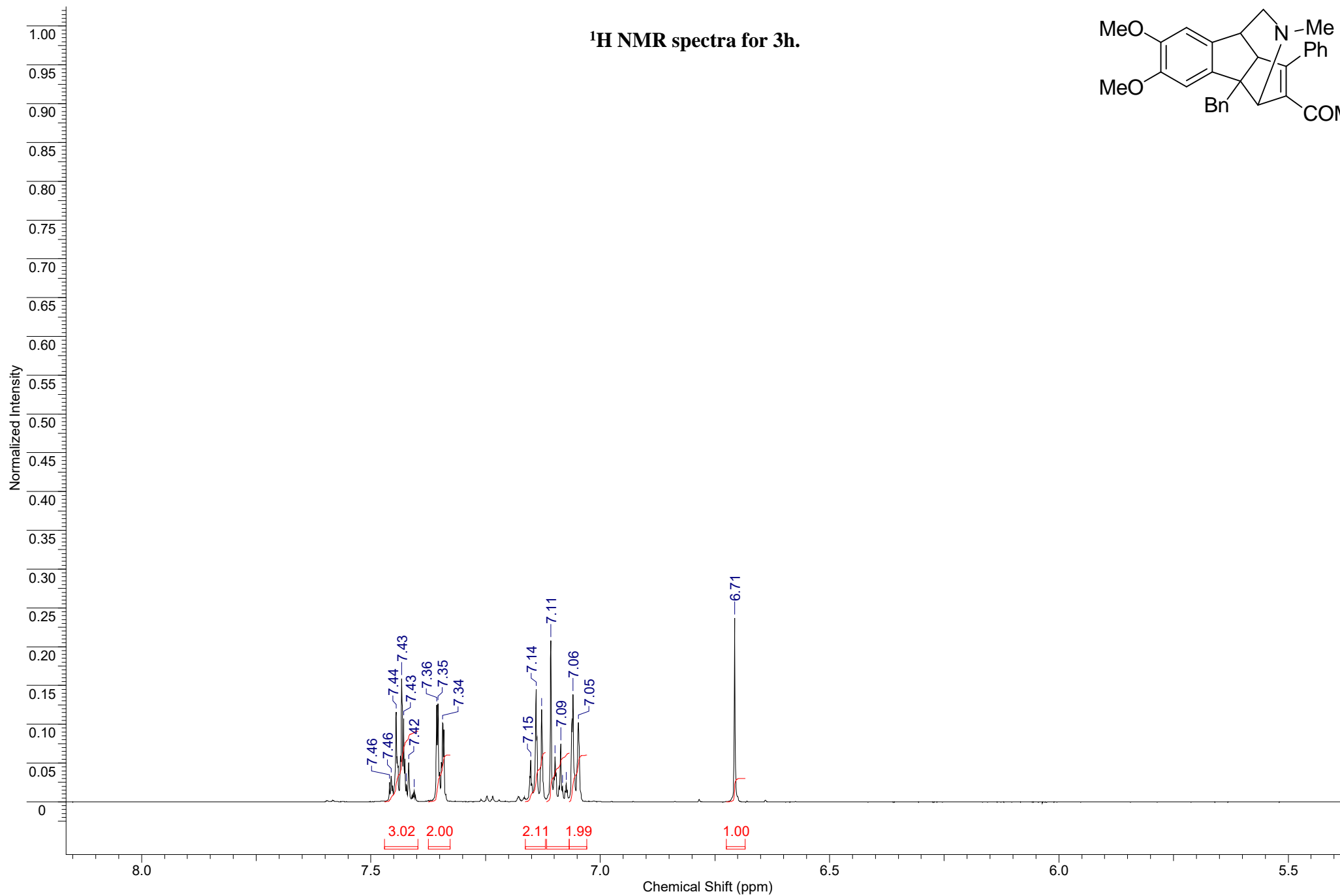
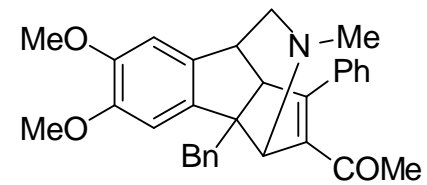


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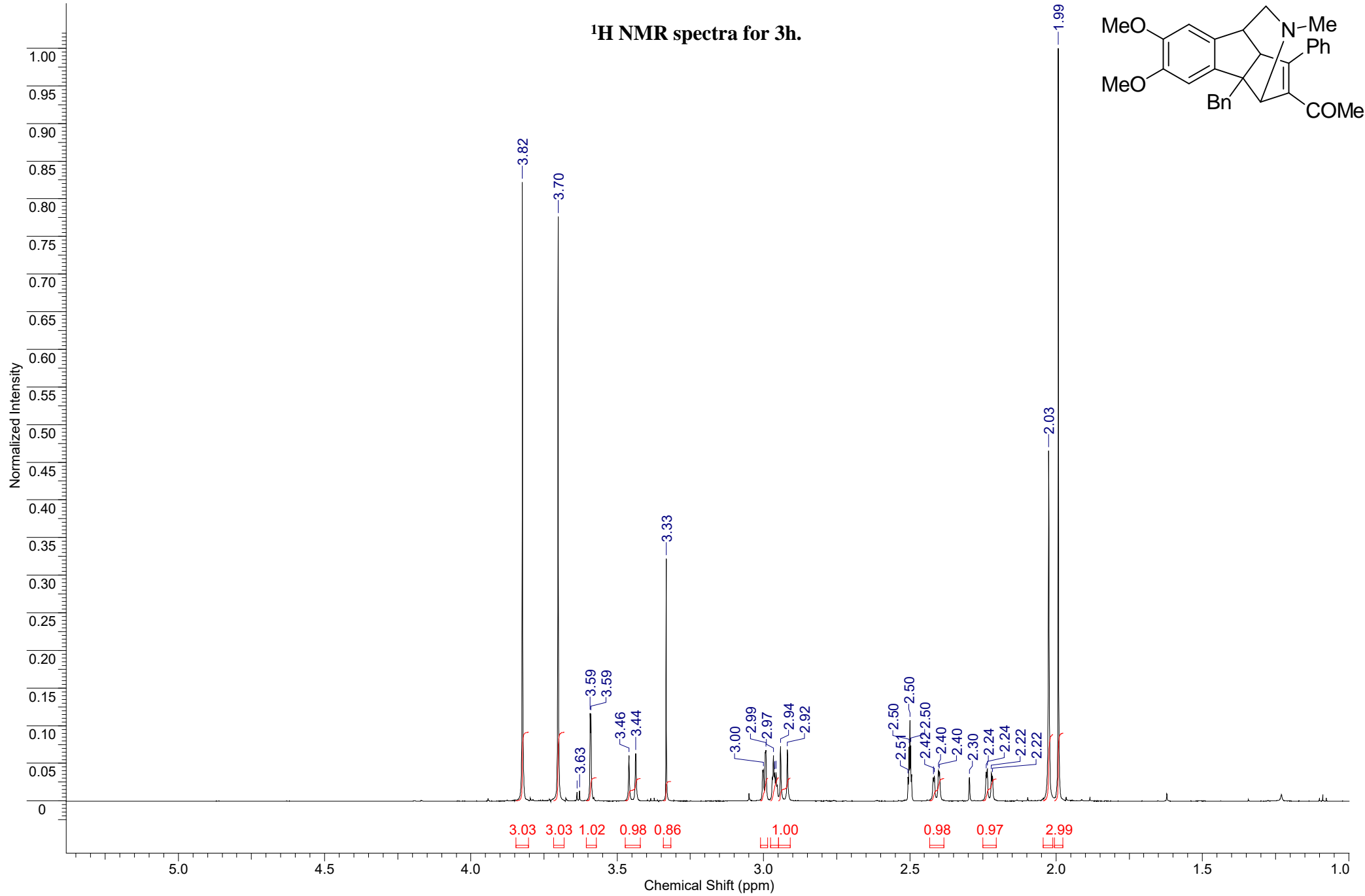
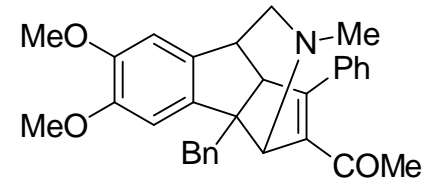




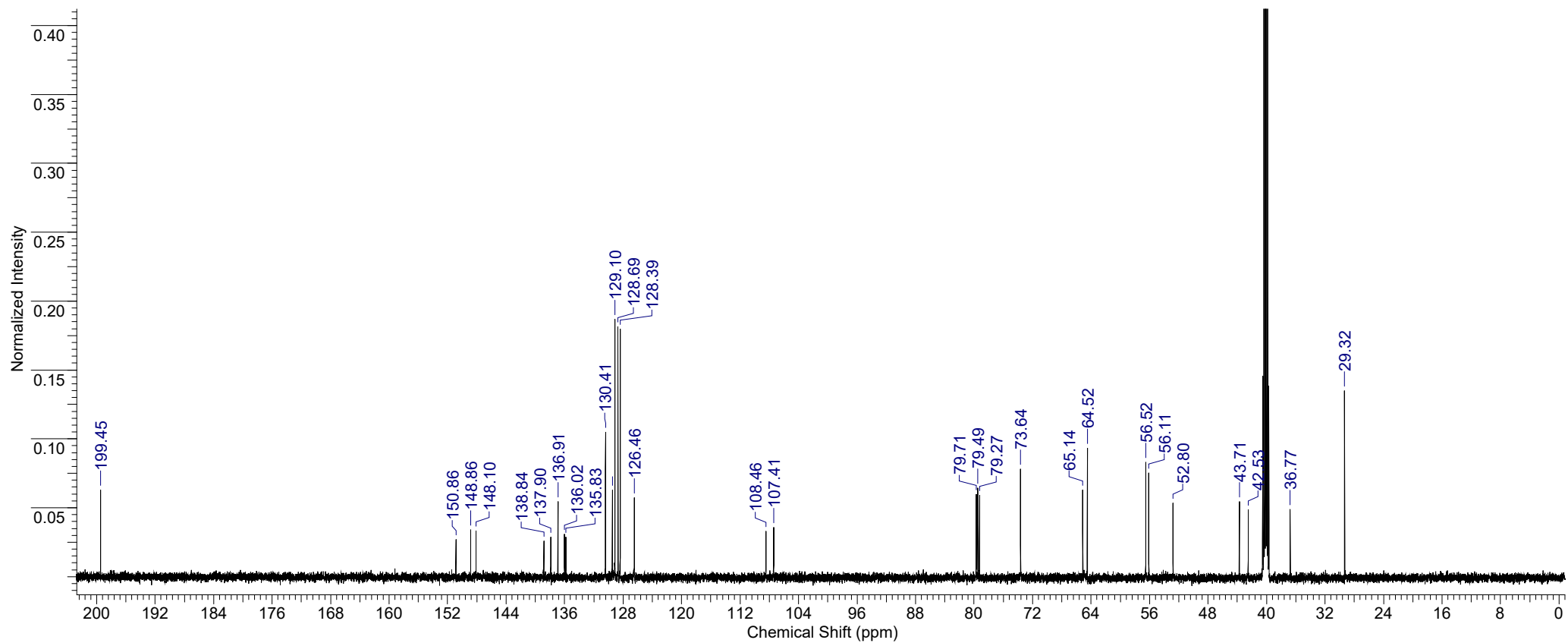
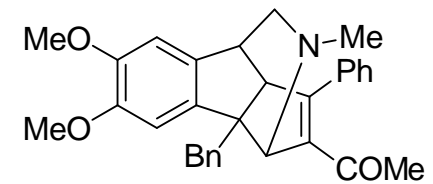
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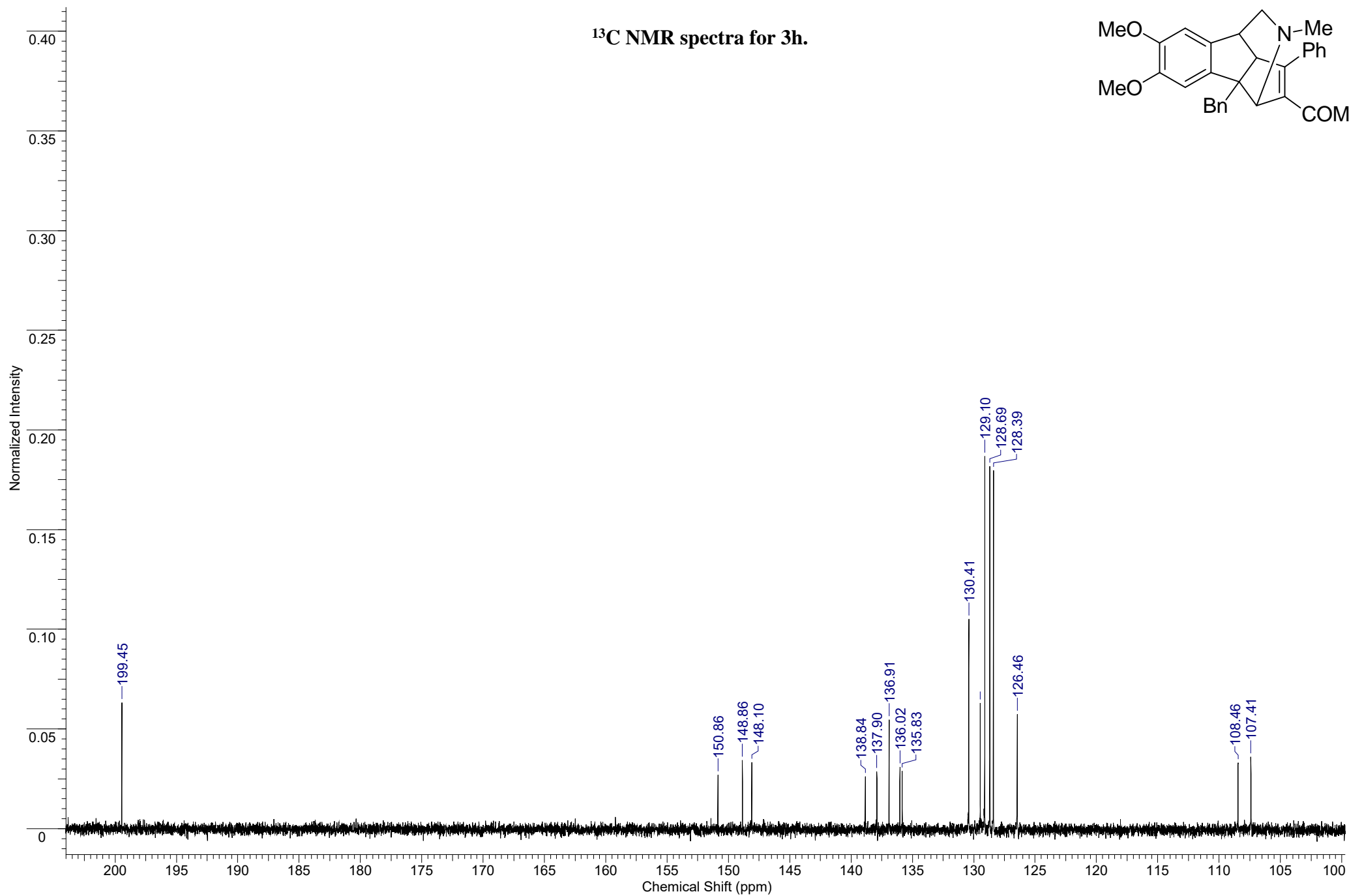
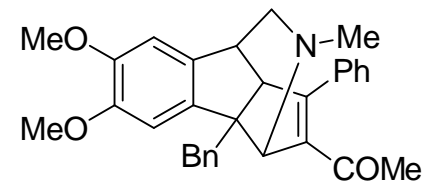
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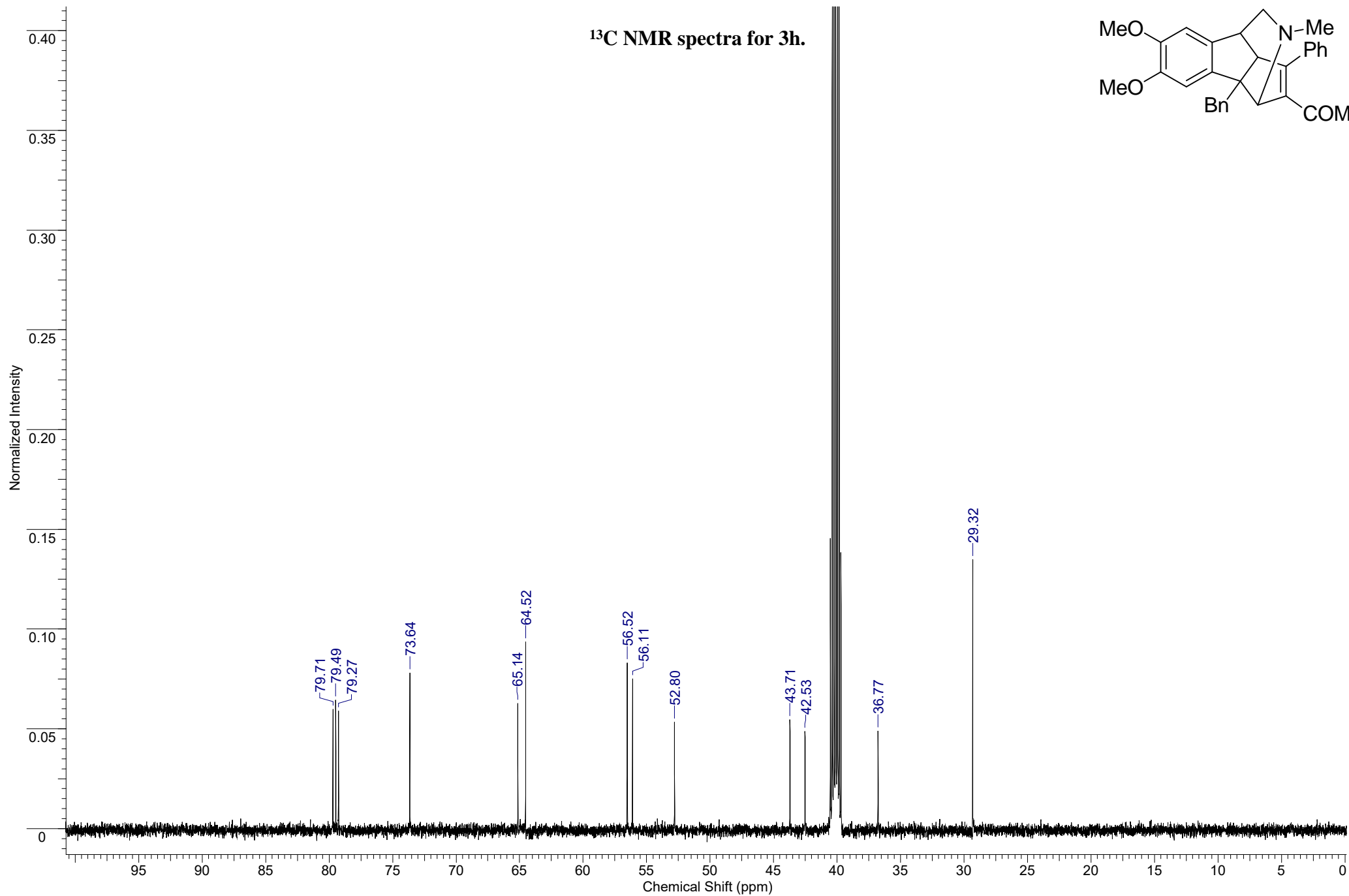
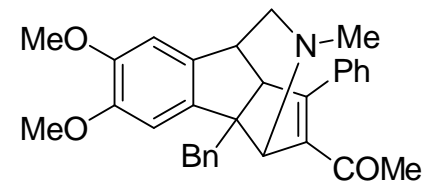
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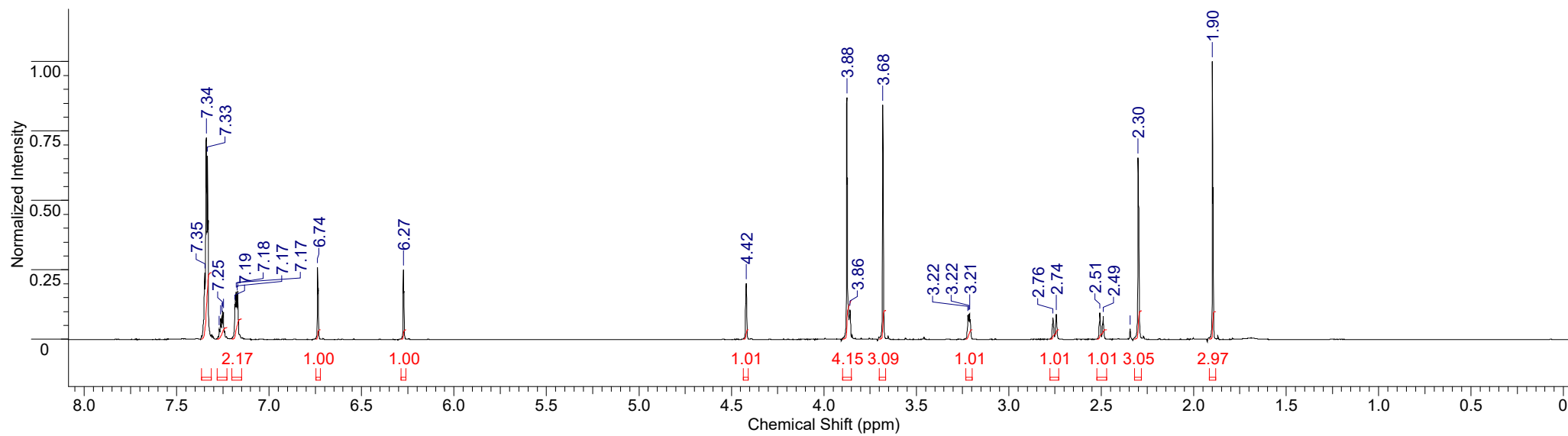
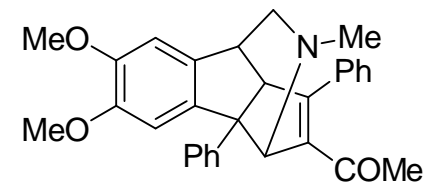


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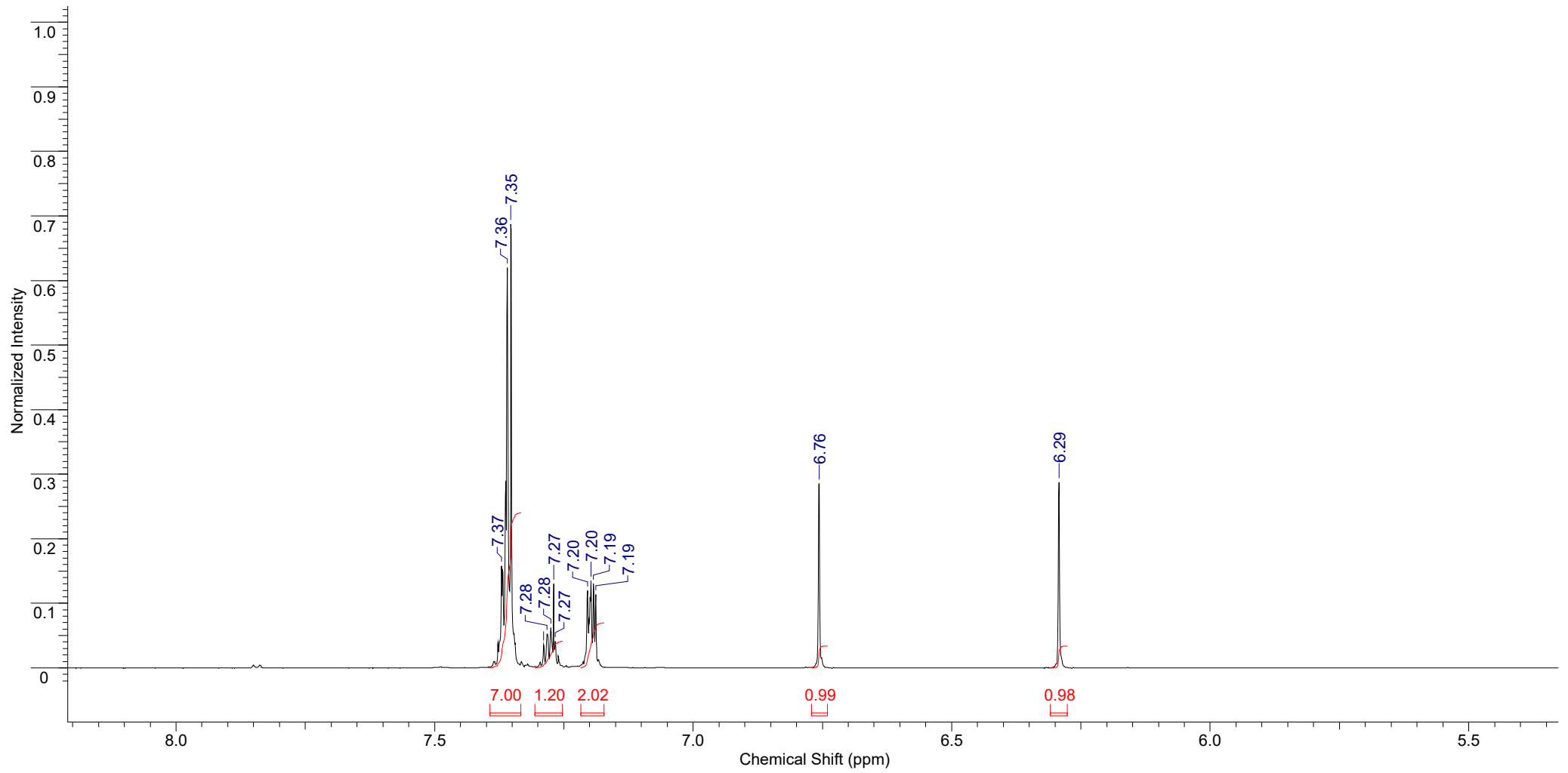
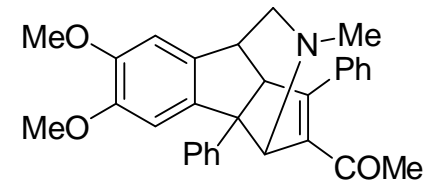


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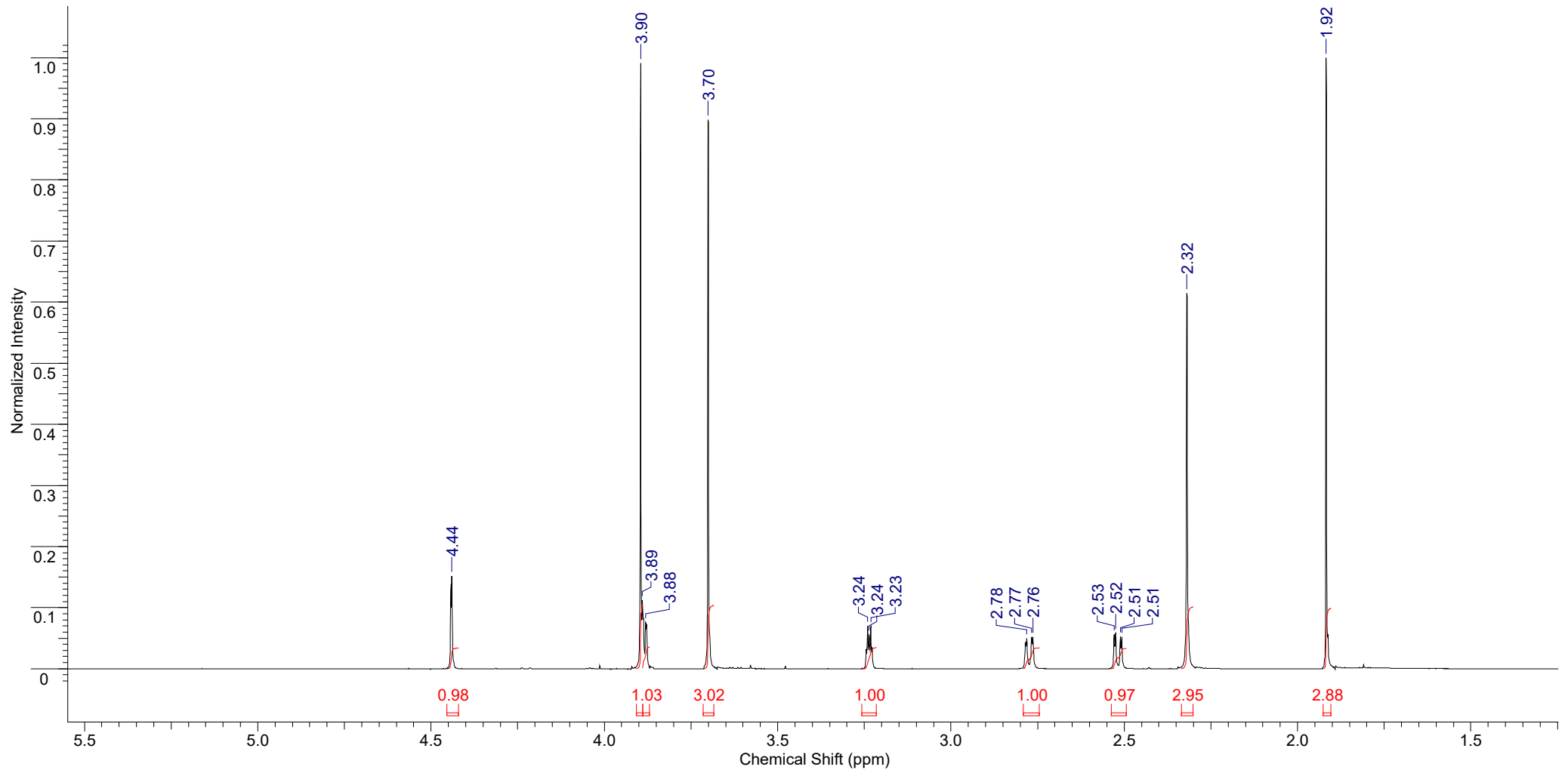
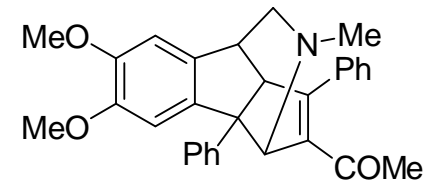
<sup>1</sup>H NMR spectra for 3k.



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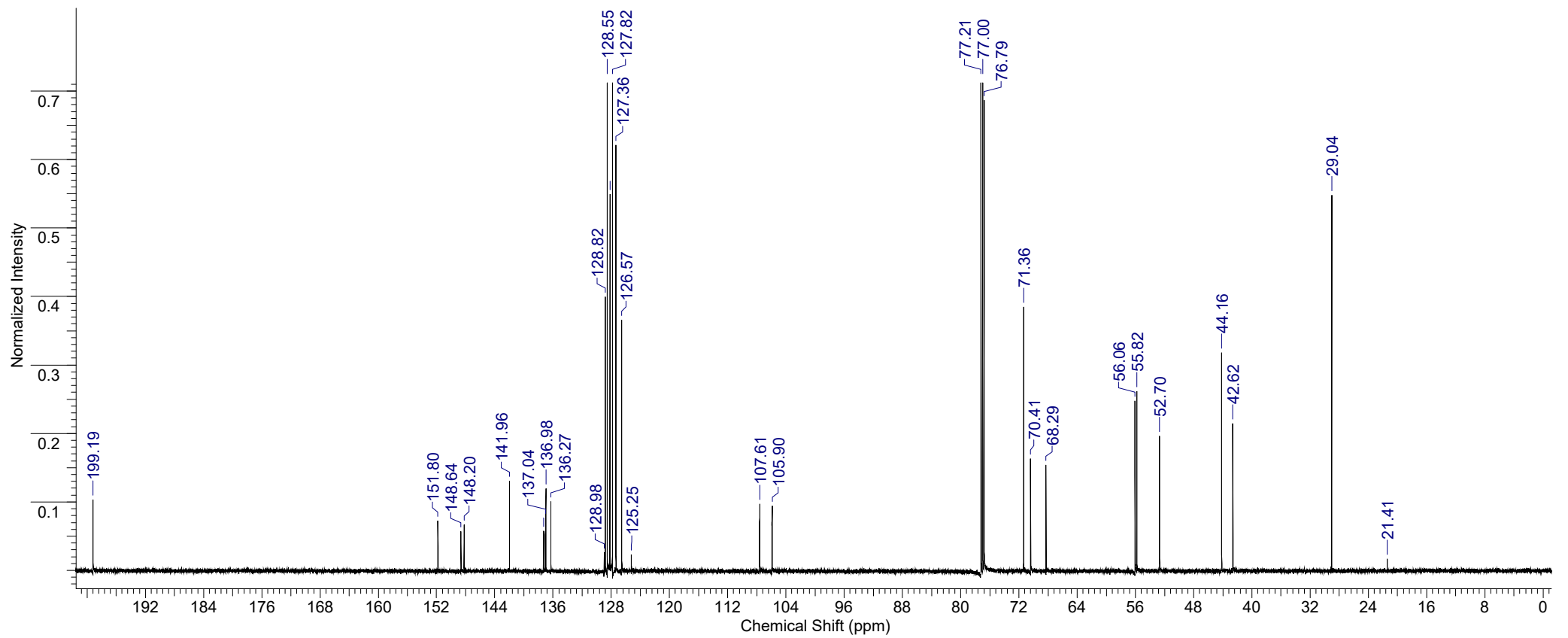
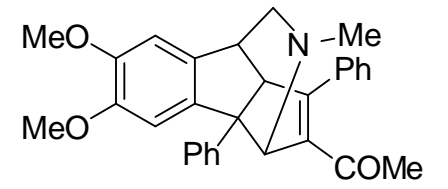


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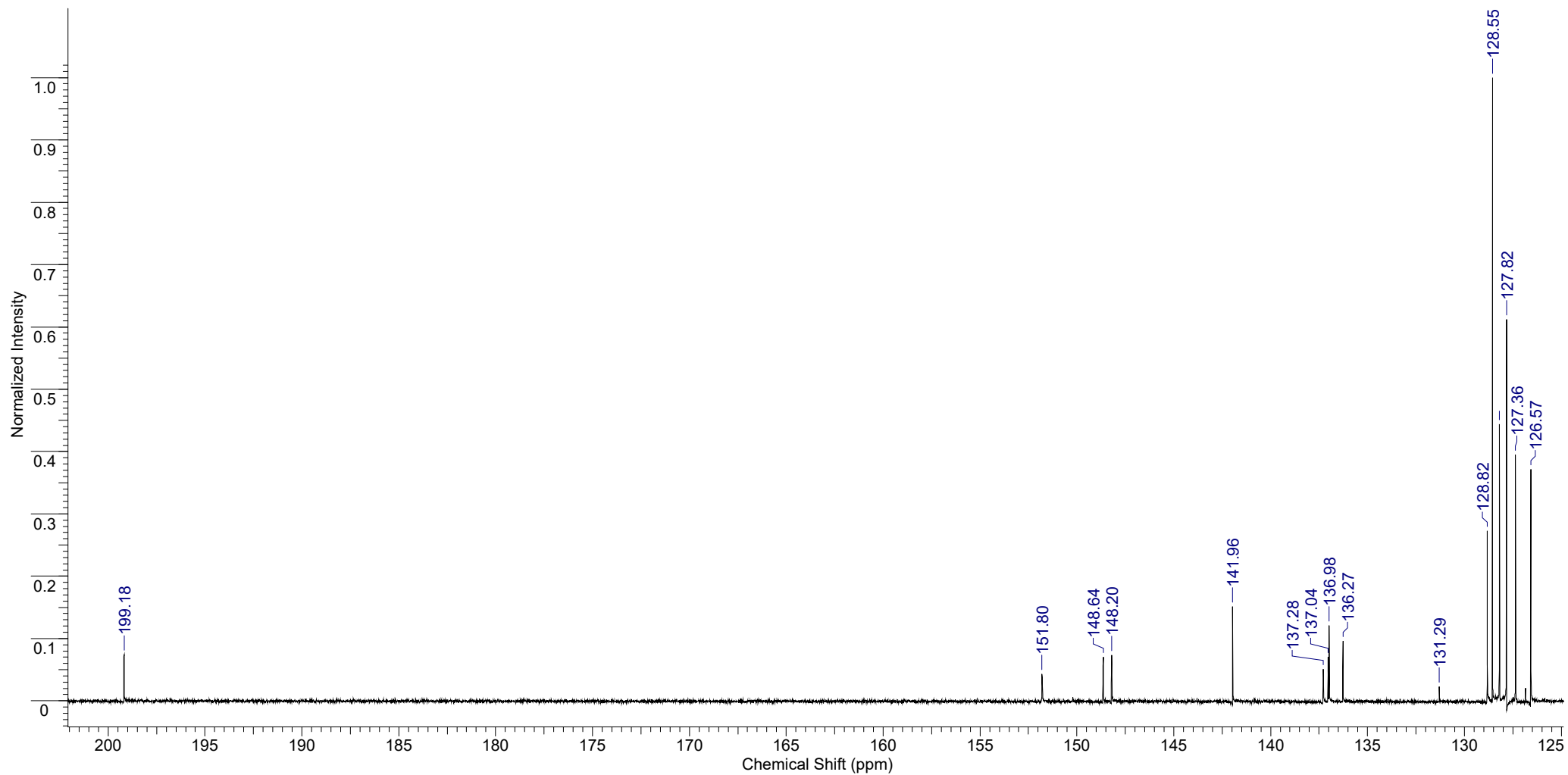
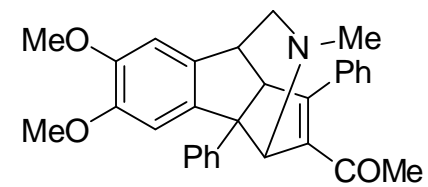




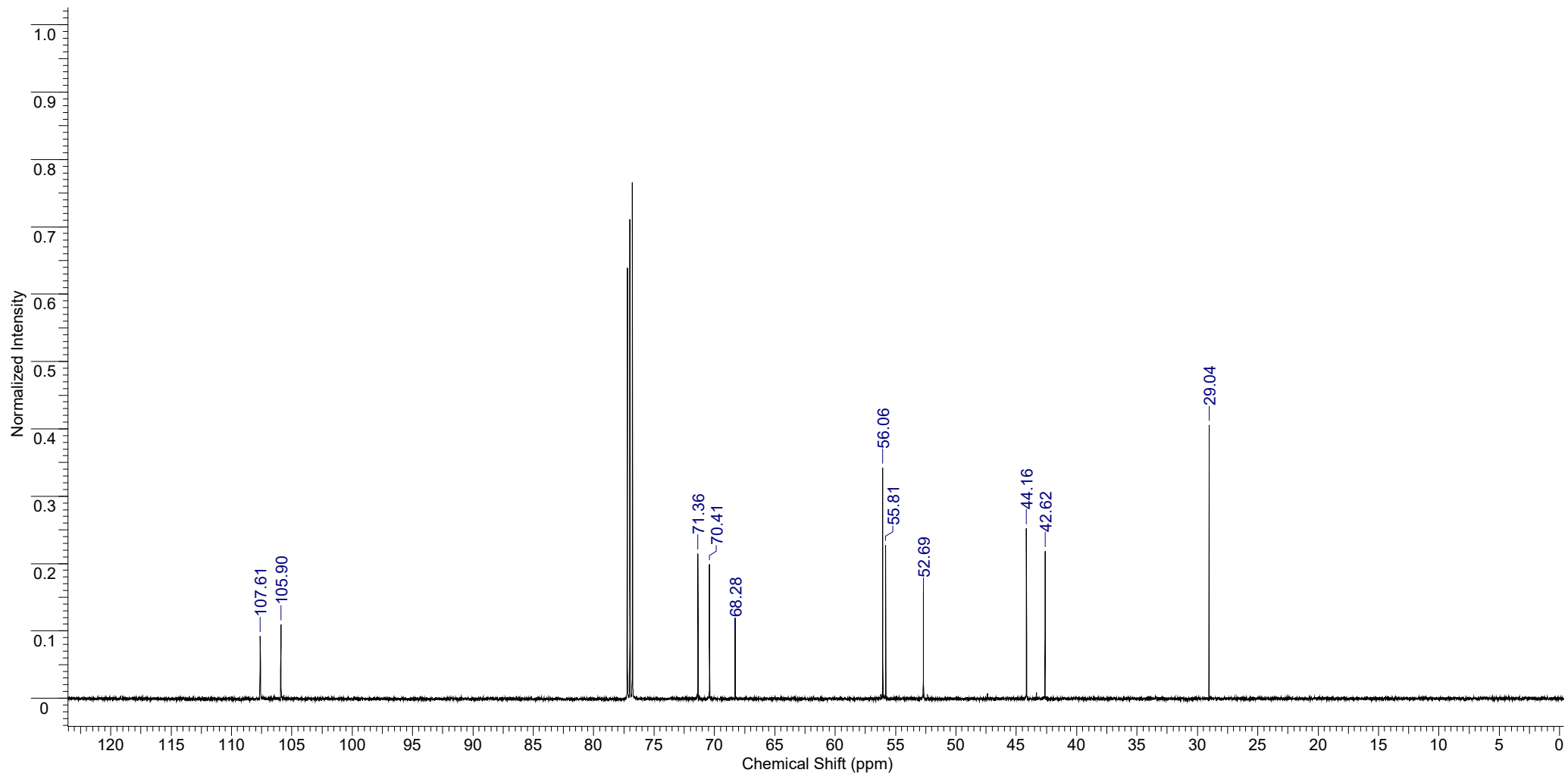
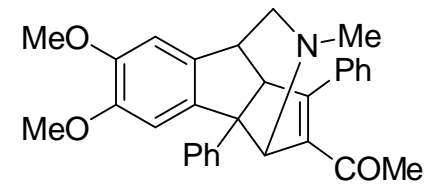
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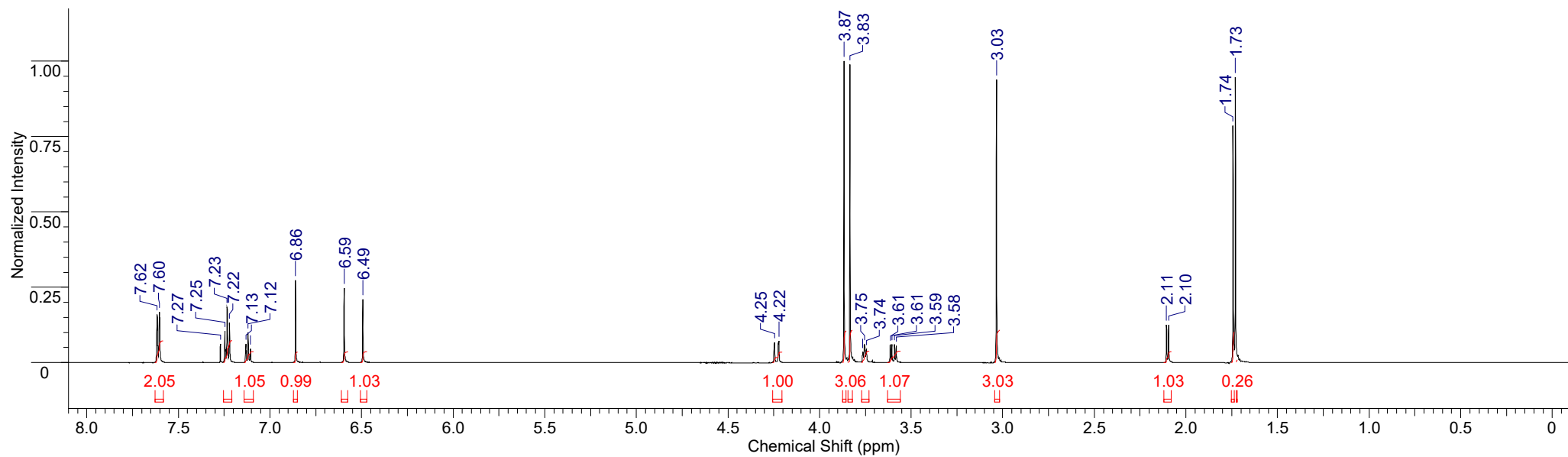
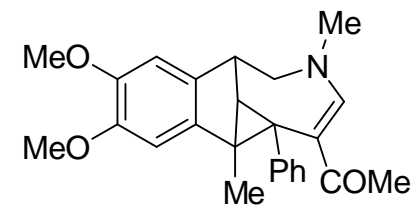


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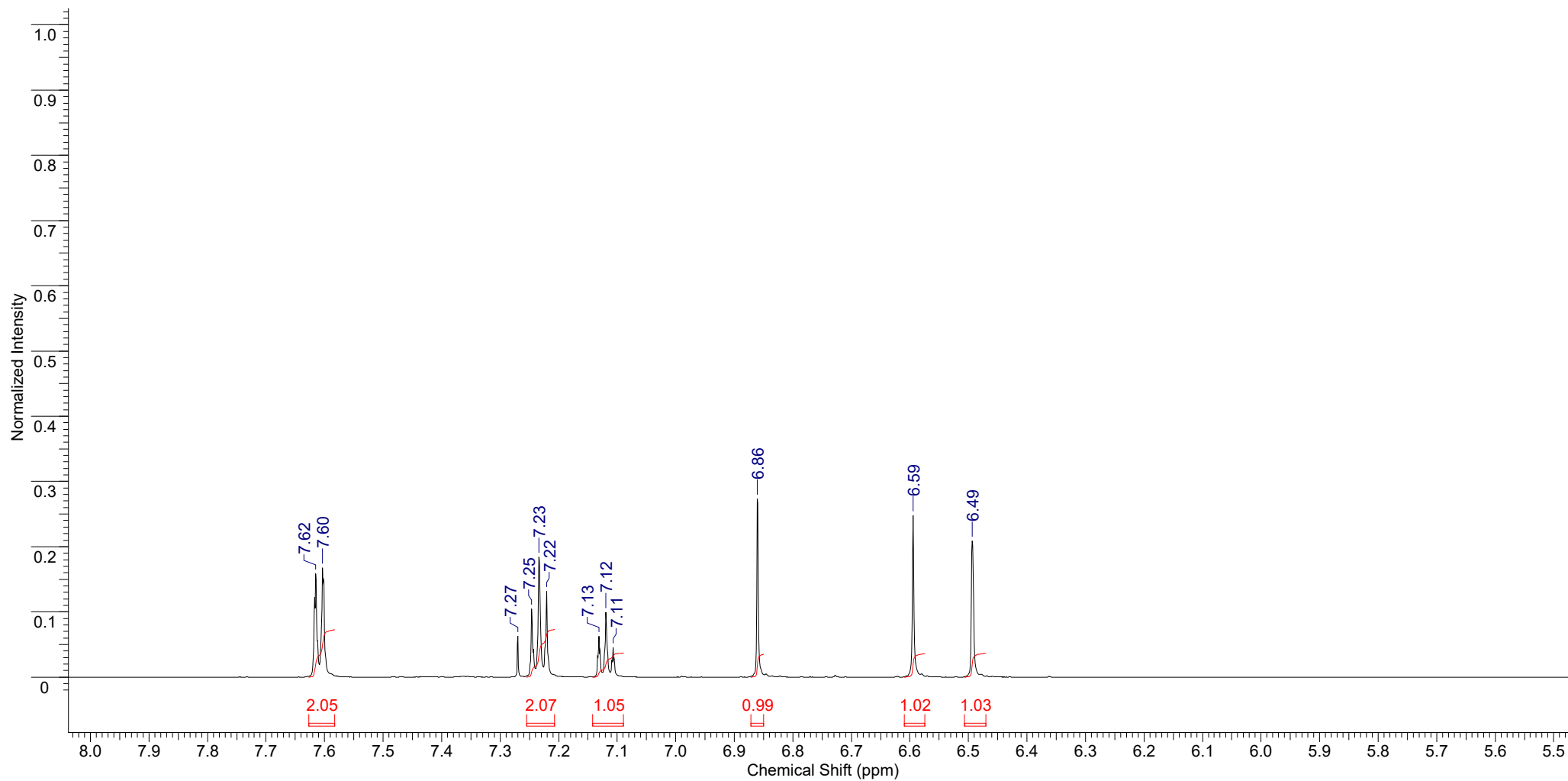
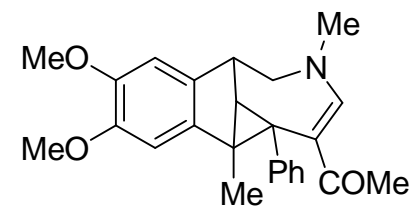


1-(6,7-Dimethoxy-2,4b-dimethyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[*a*]cyclopropa[*cd*]azulen-4-yl)ethanone (2b)

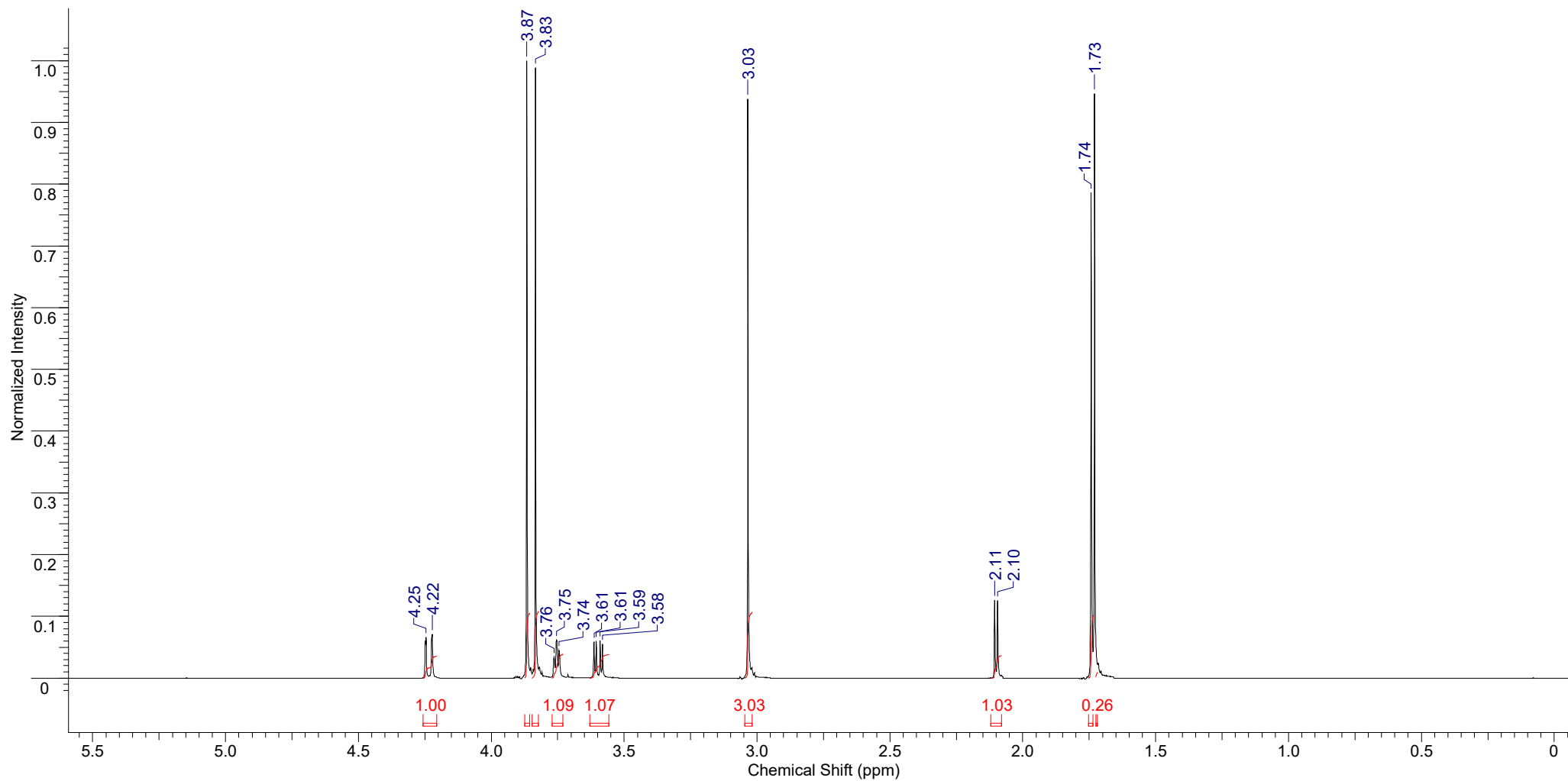
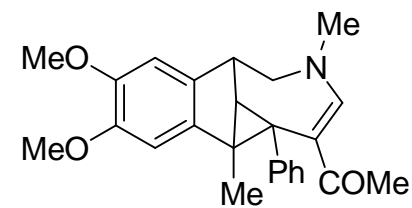
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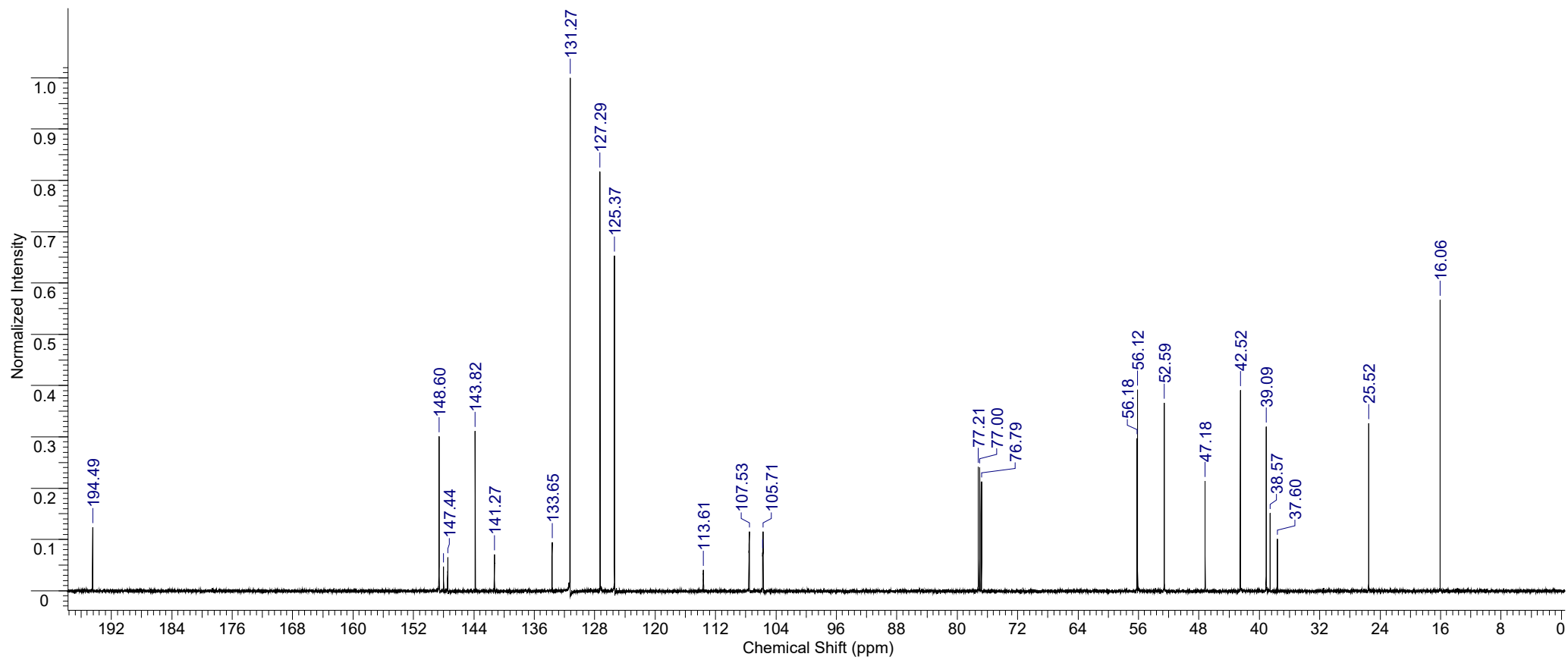
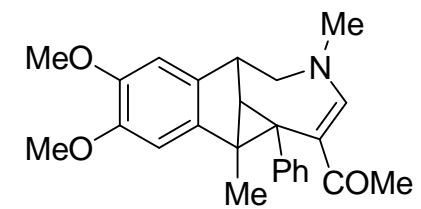
<sup>1</sup>H NMR spectra for 2b.



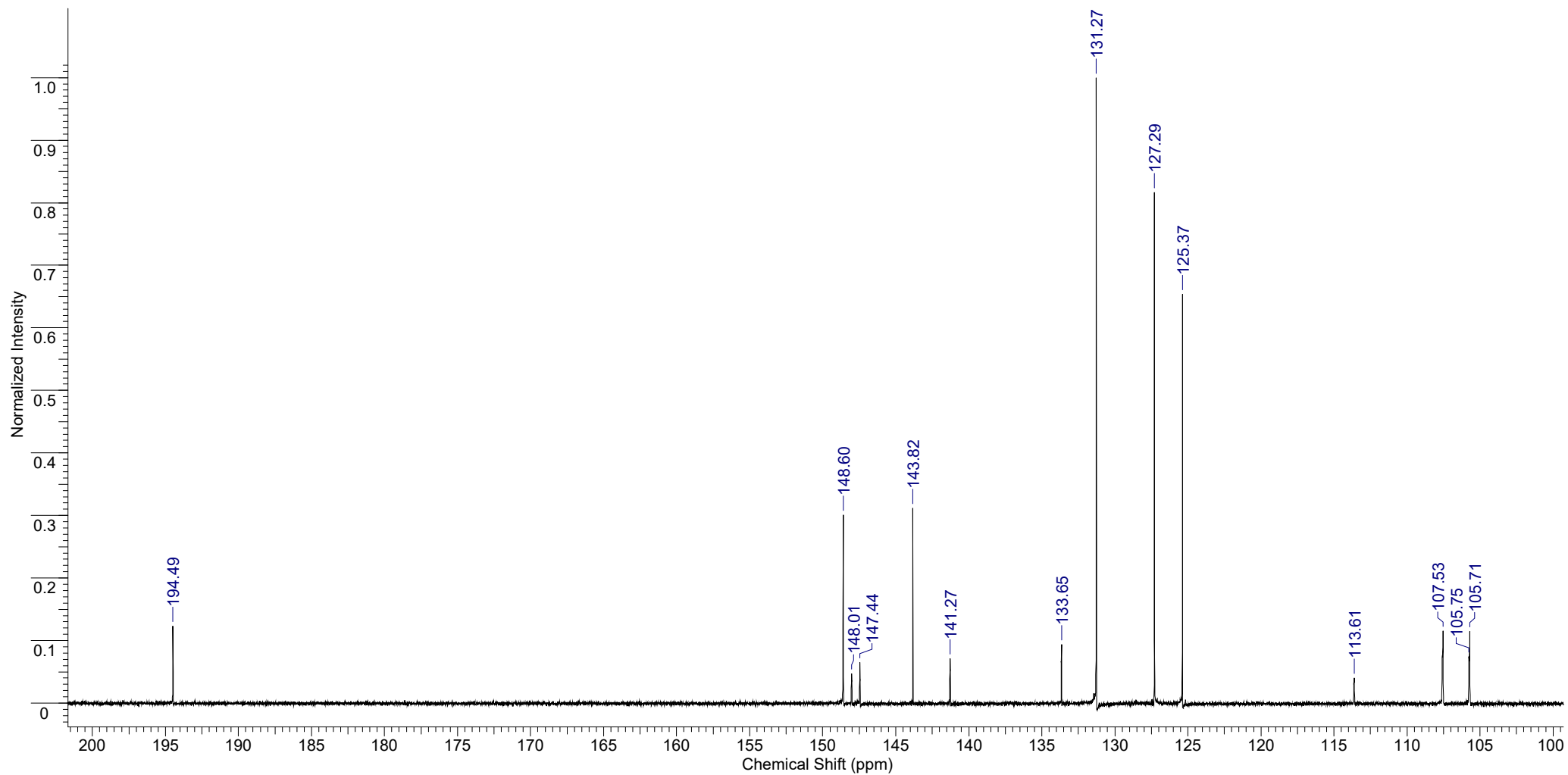
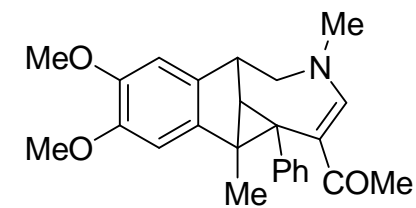
<sup>1</sup>H NMR spectra for 2b.



<sup>13</sup>C NMR spectra for 2b.

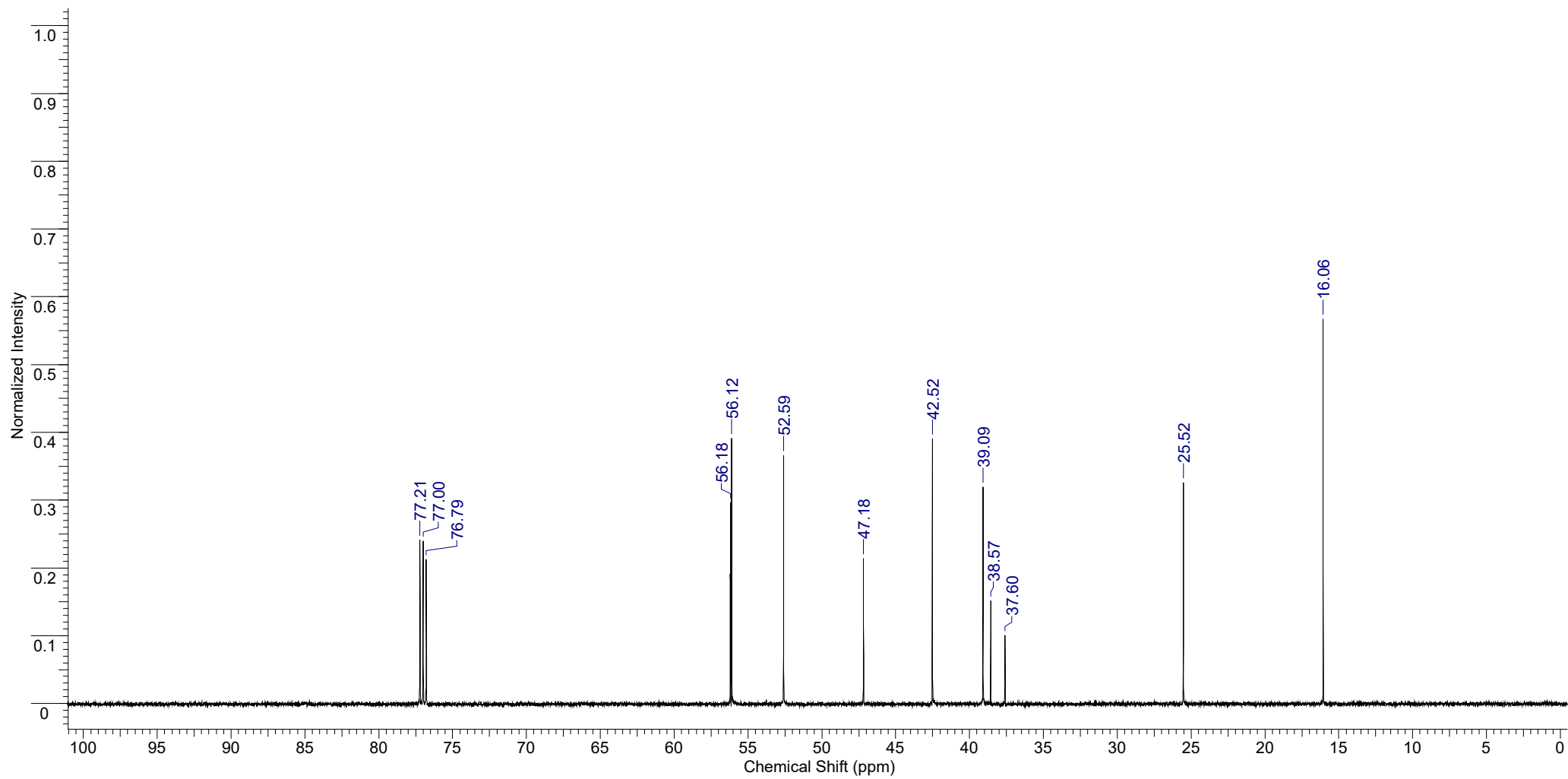
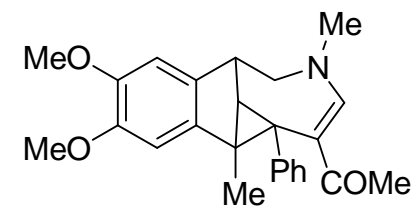


<sup>13</sup>C NMR spectra for 2b.



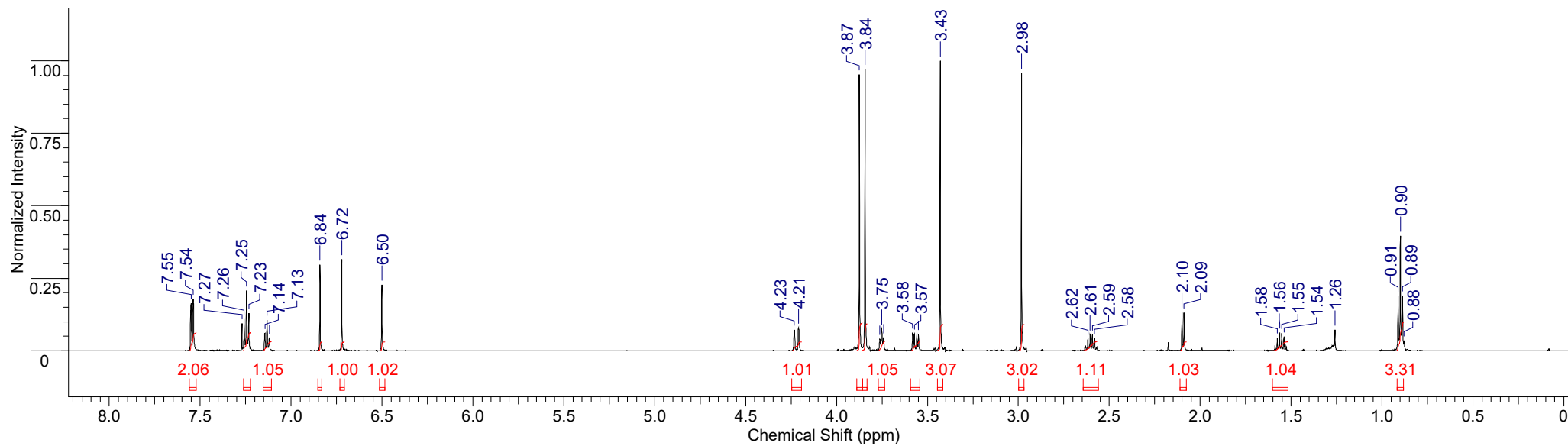
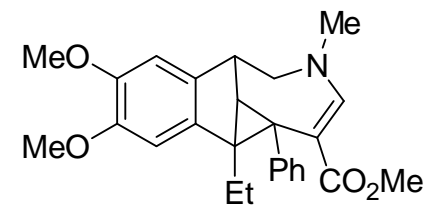


<sup>13</sup>C NMR spectra for 2b.

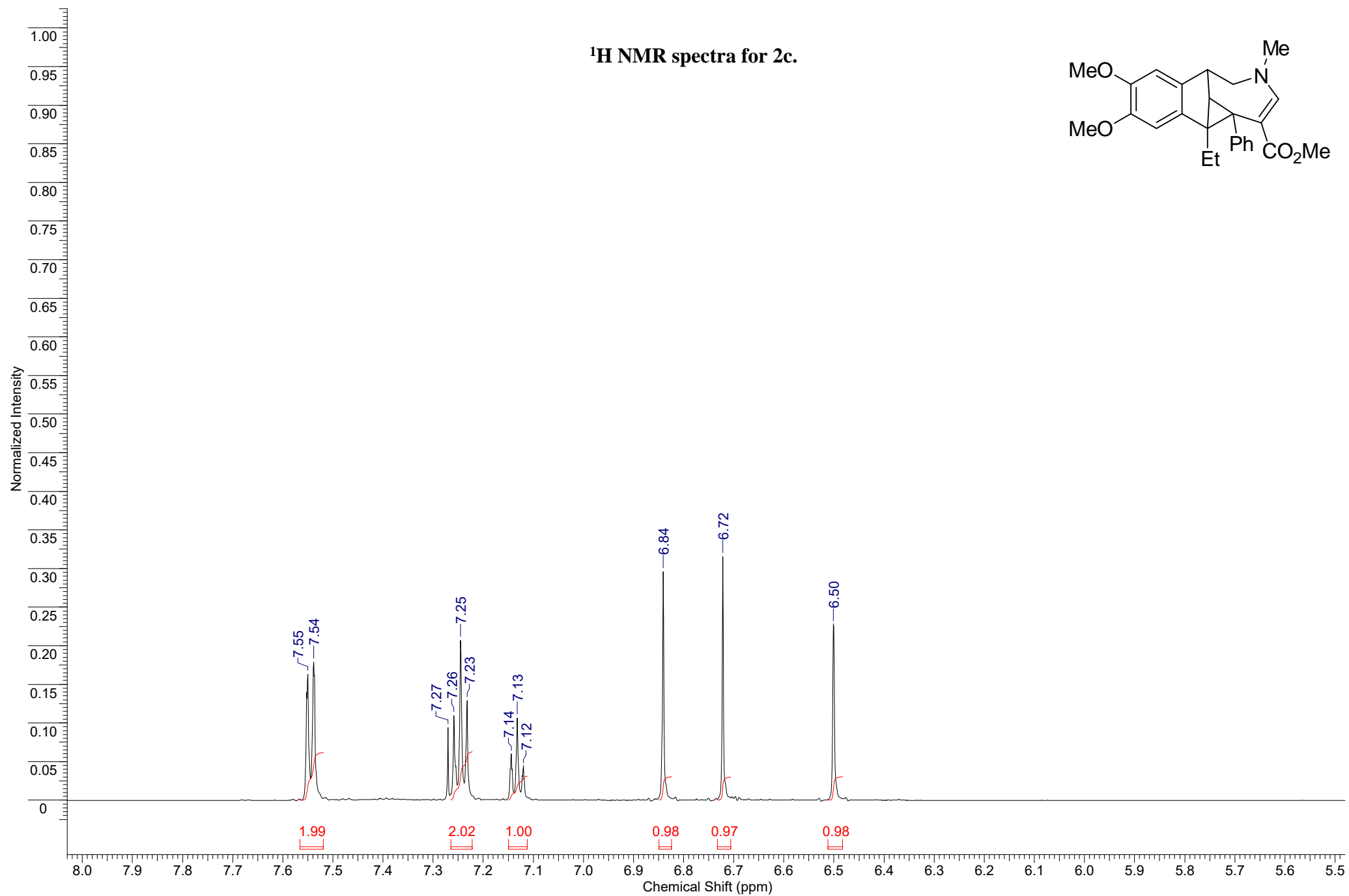
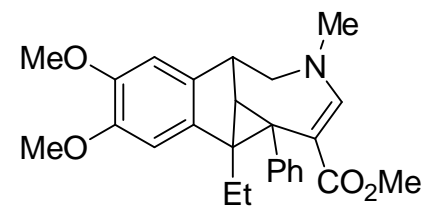


Methyl 4b-ethyl-6,7-dimethoxy-2-methyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzocyclopropa[cd]azulene-4-carboxylate (2c)

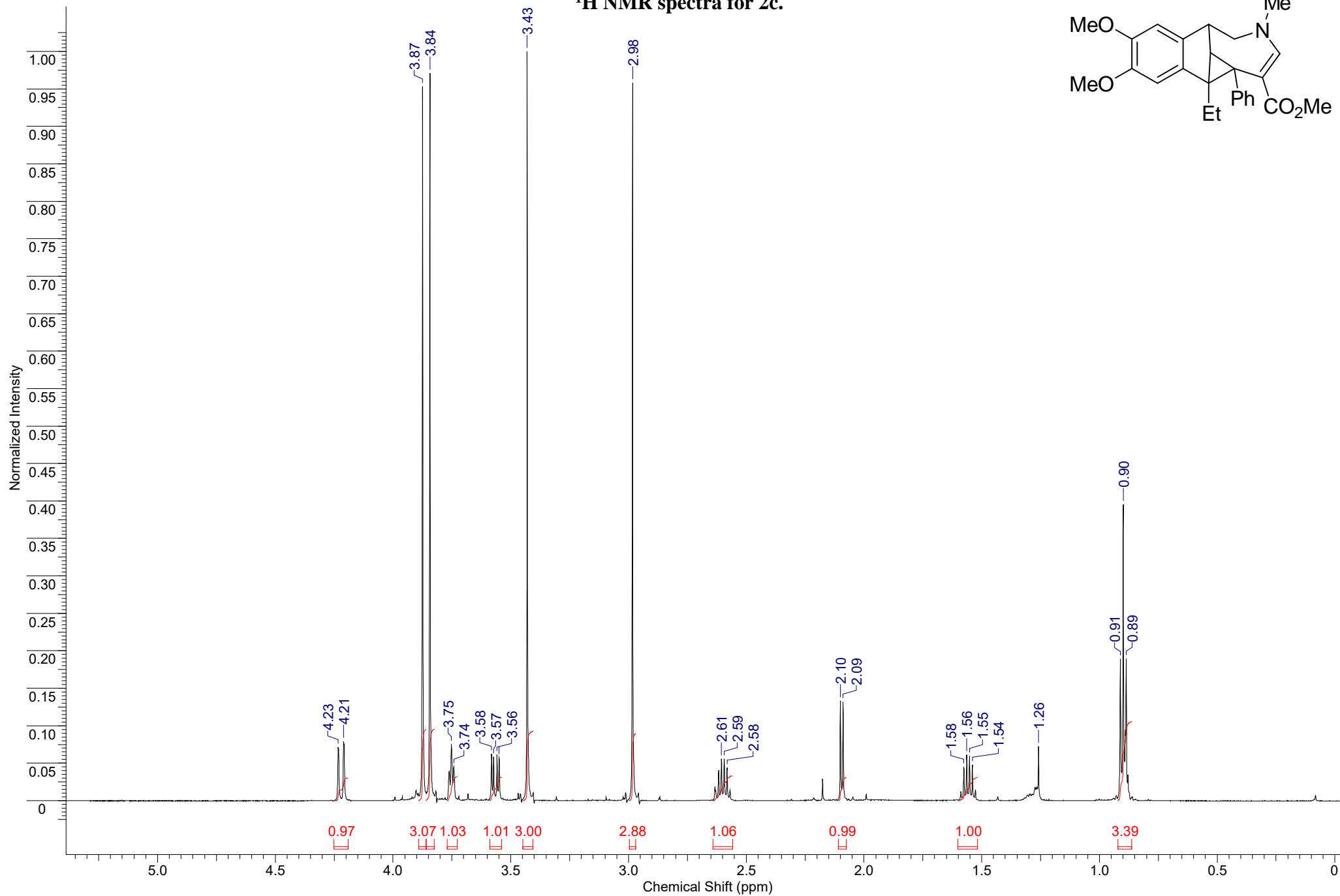
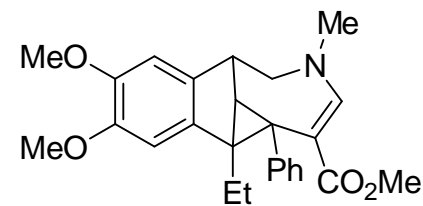
$^1\text{H}$  NMR spectra for 2c.



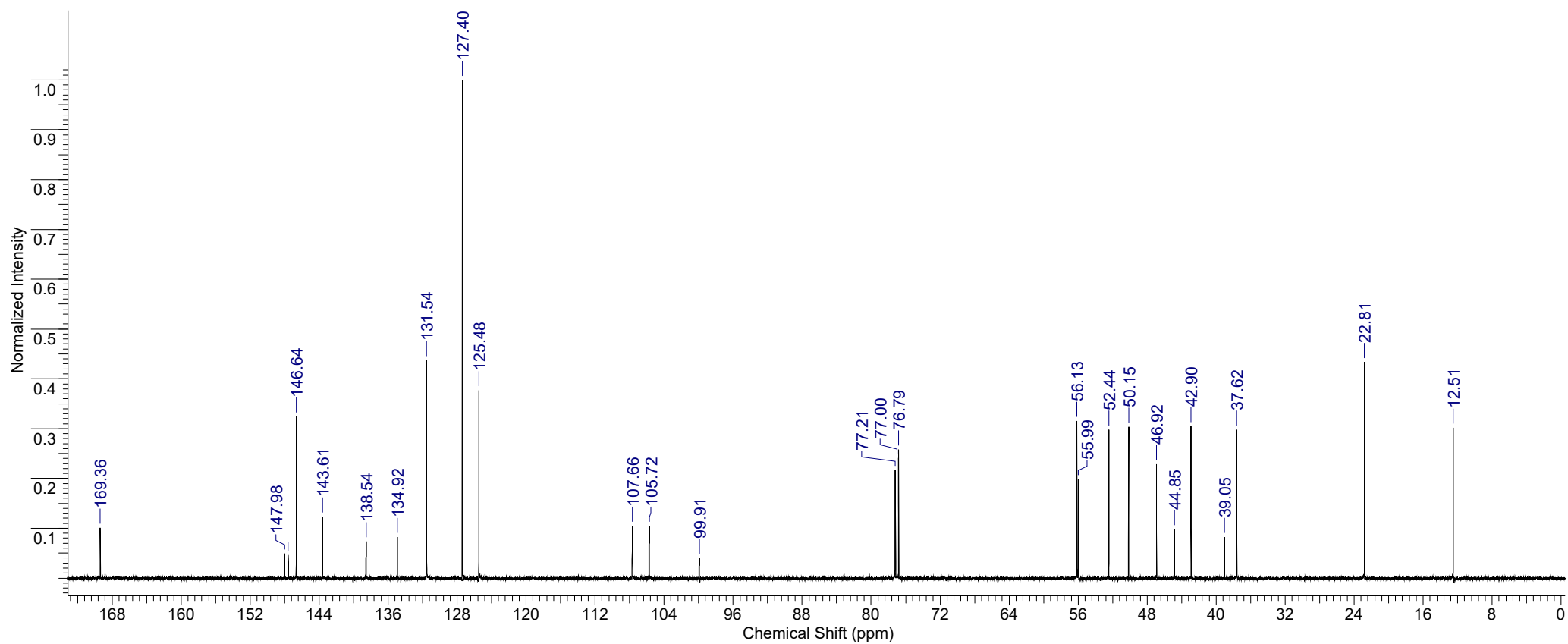
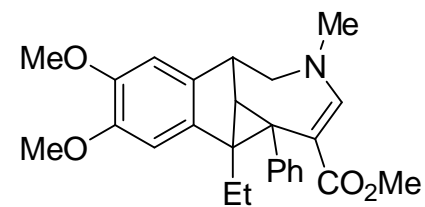
<sup>1</sup>H NMR spectra for 2c.



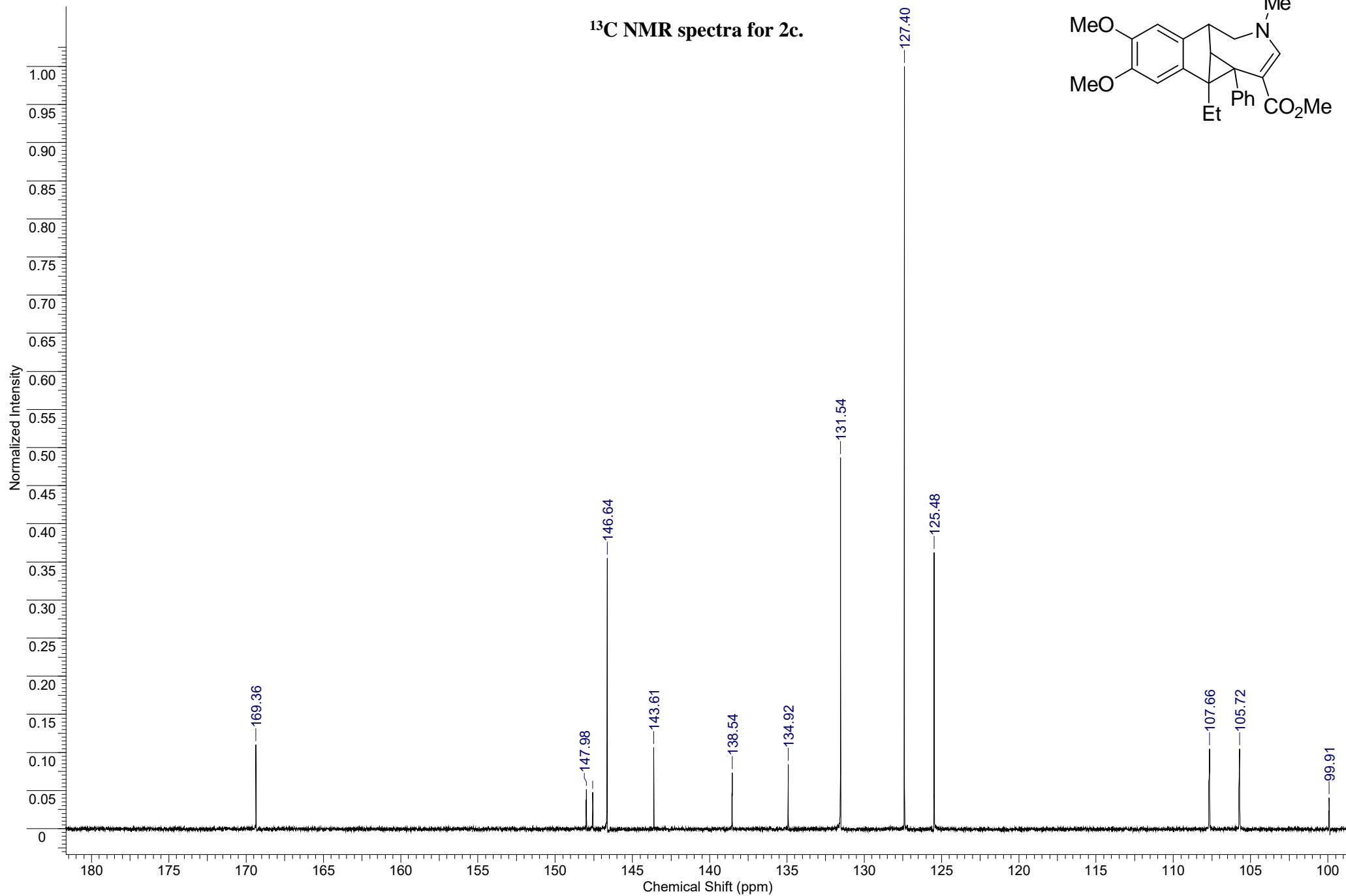
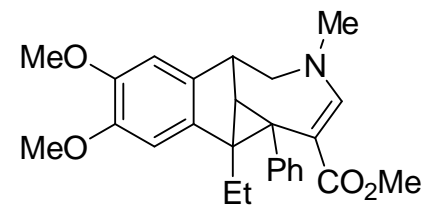
<sup>1</sup>H NMR spectra for 2c.



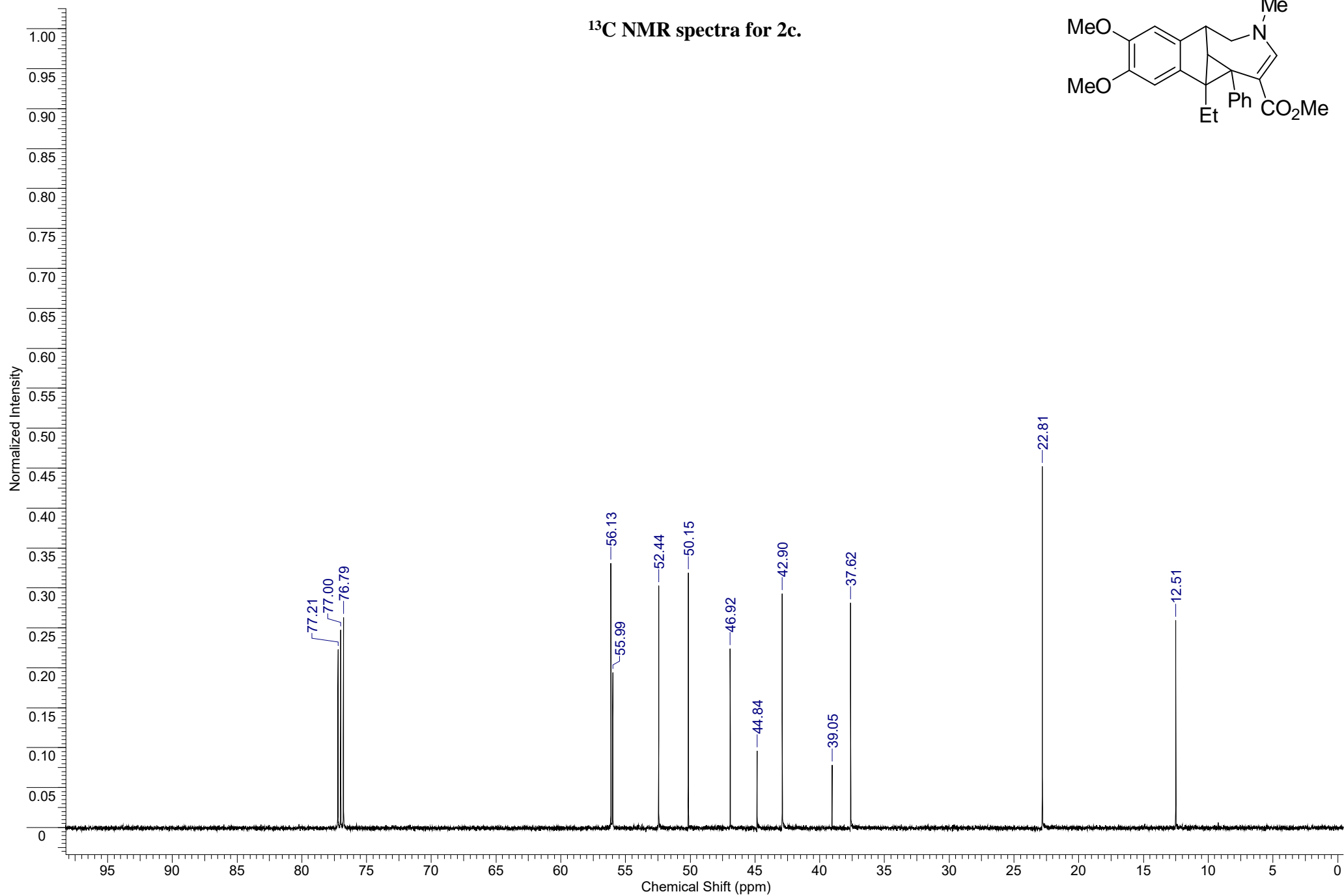
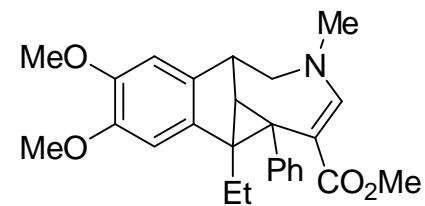
<sup>1</sup>H NMR spectra for 2c.



<sup>13</sup>C NMR spectra for 2c.

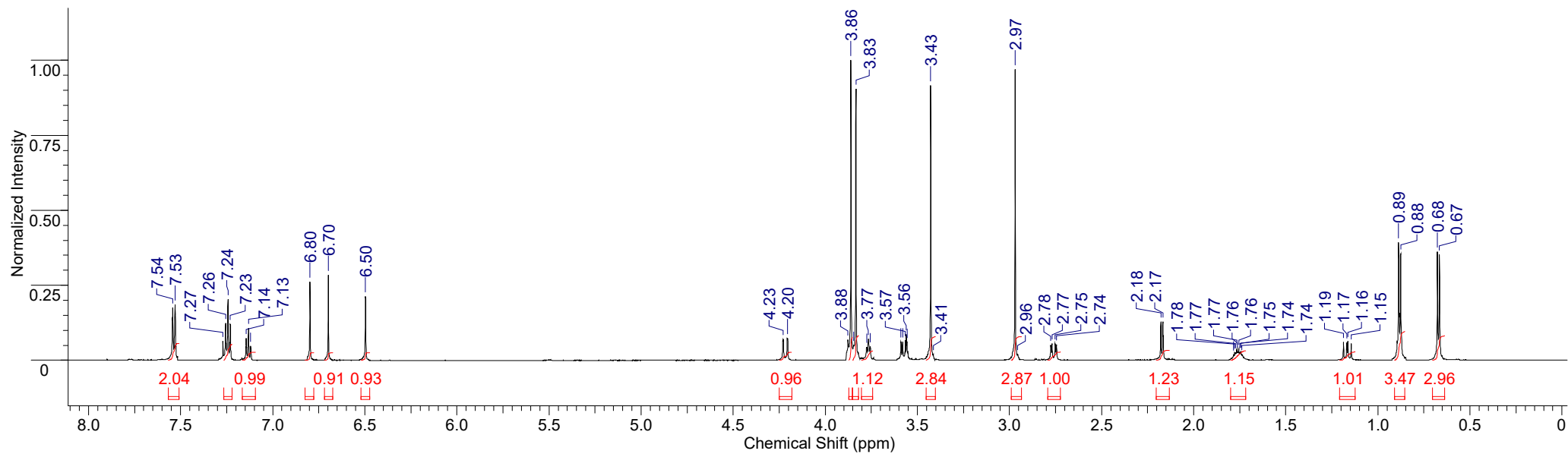
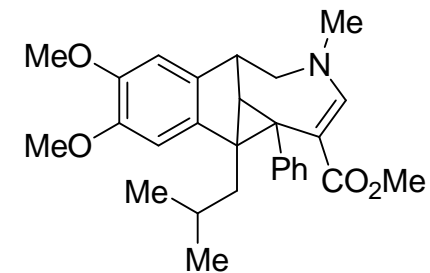


<sup>13</sup>C NMR spectra for 2c.



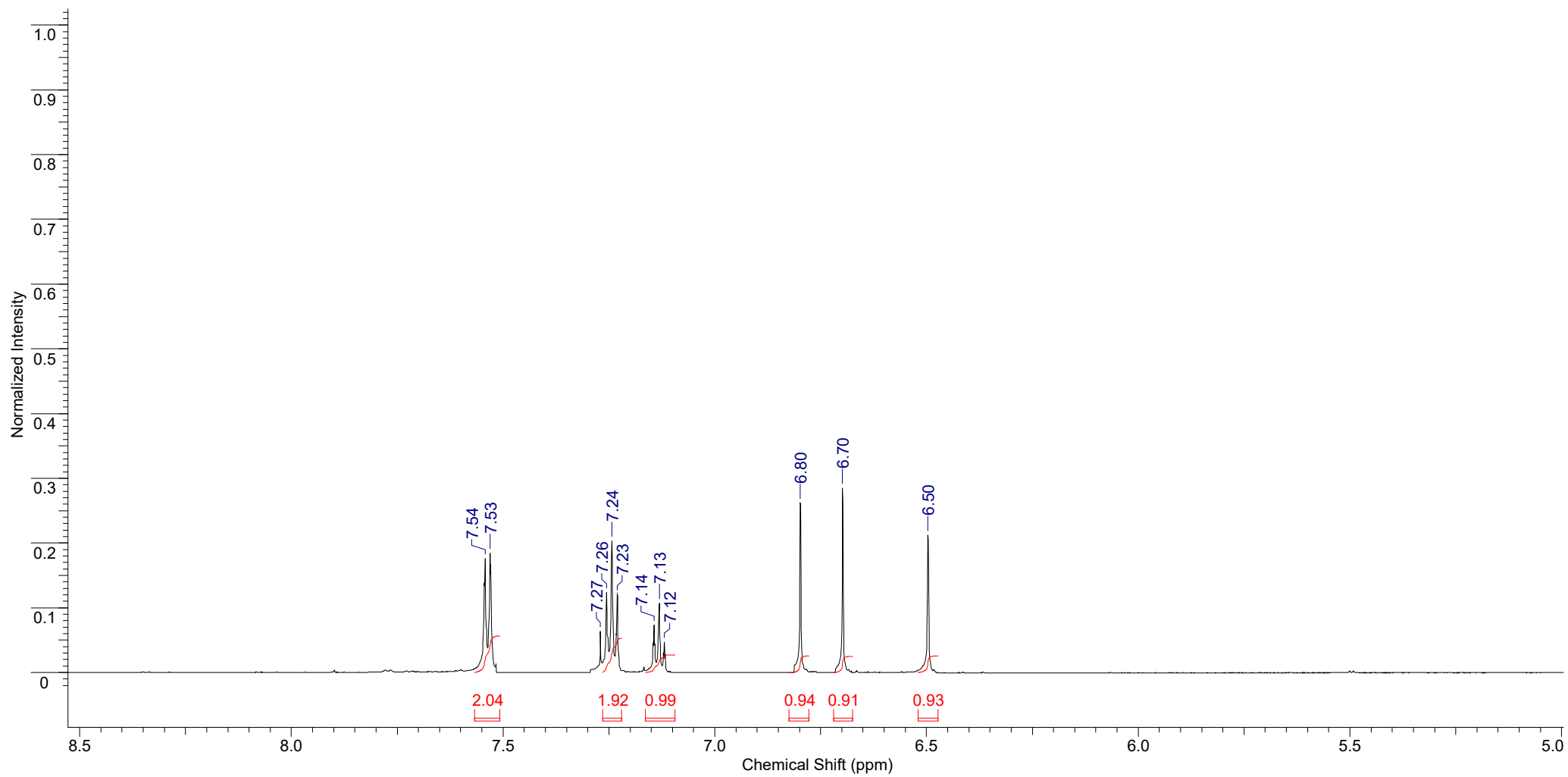
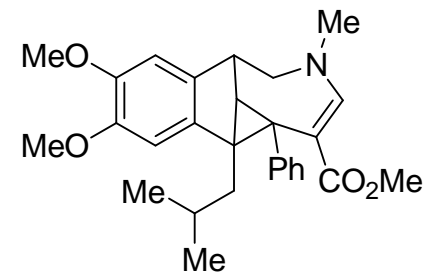
Methyl 6,7-dimethoxy-2-methyl-4b-(2-methylpropyl)-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzocyclopropa[cd]azulene-4-carboxylate (2e)

<sup>1</sup>H NMR spectra for 2e.

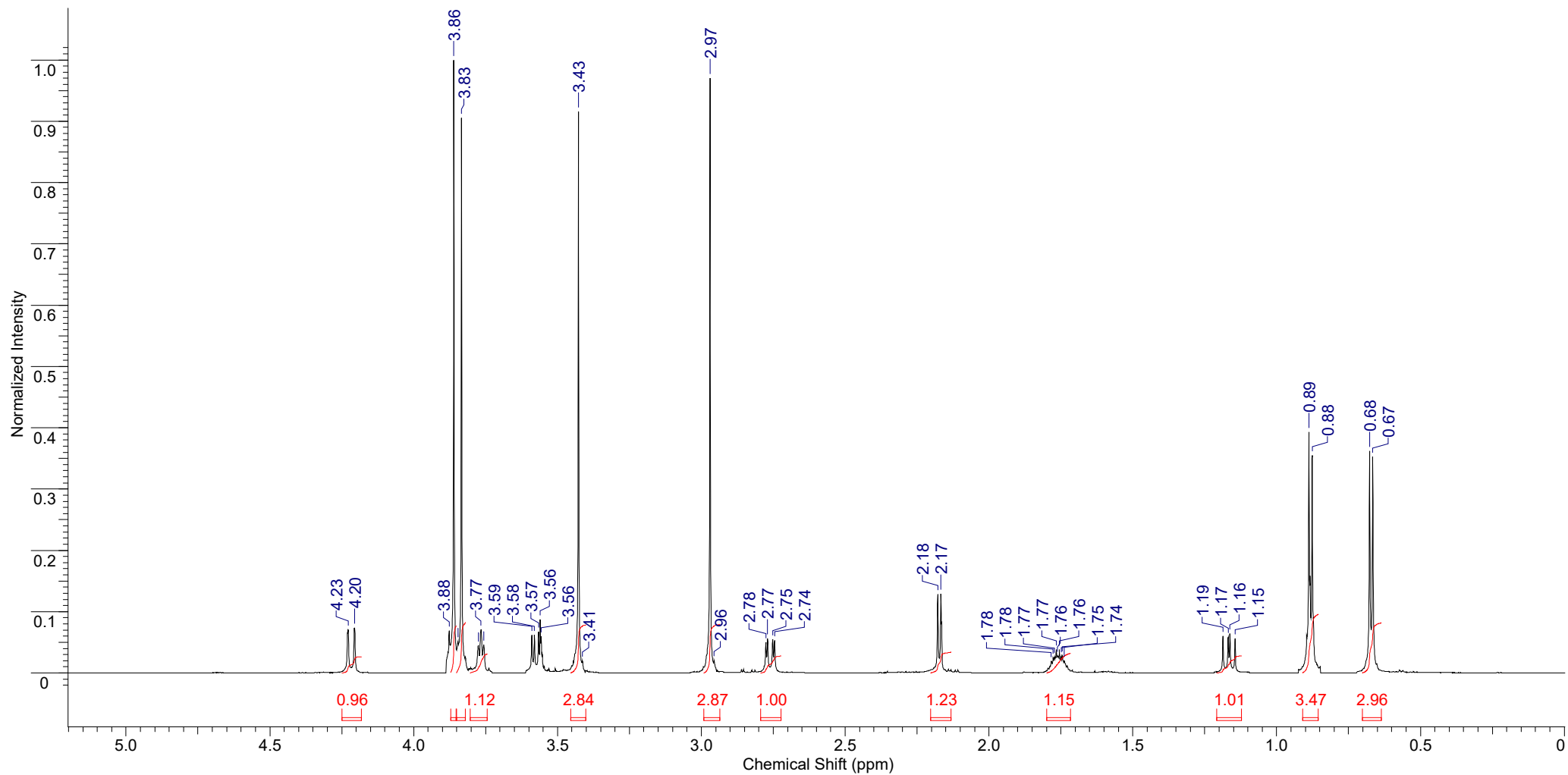
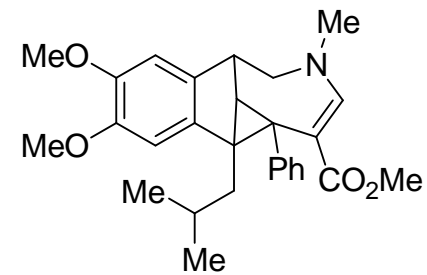




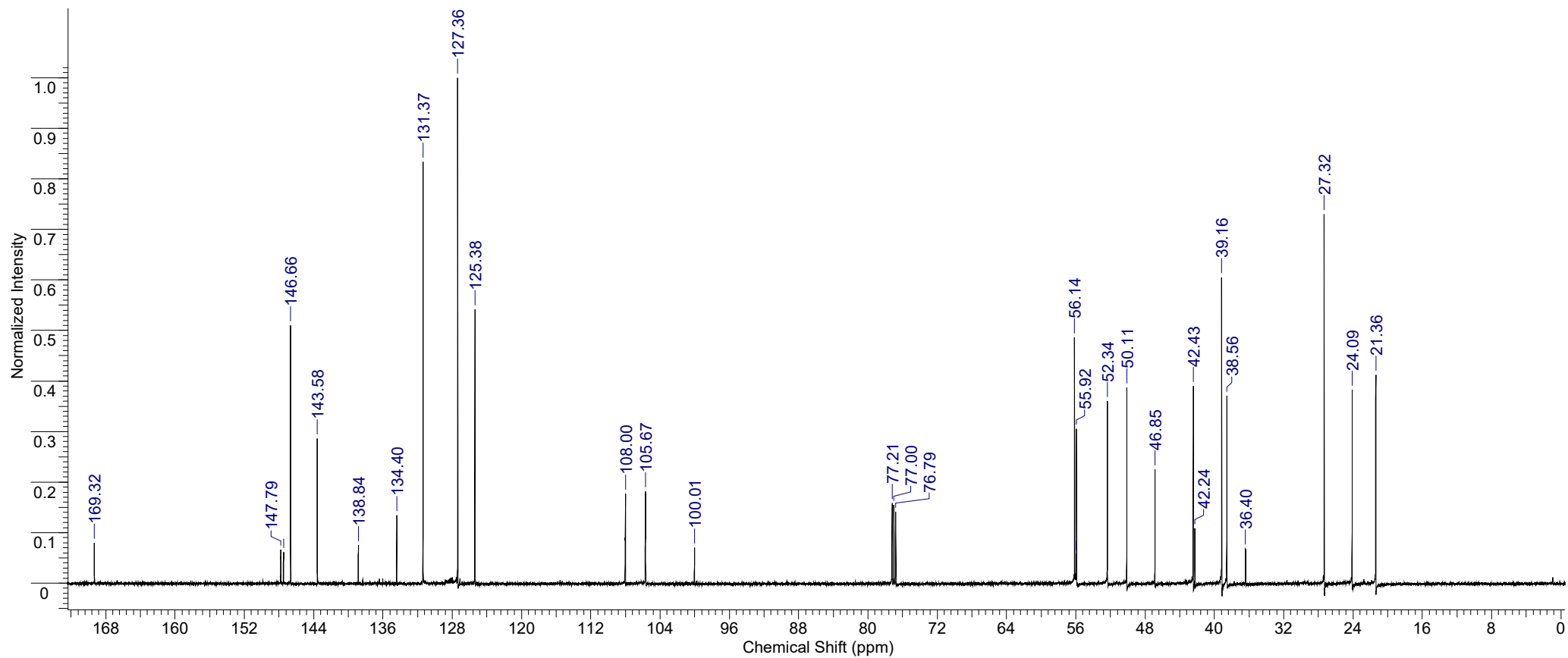
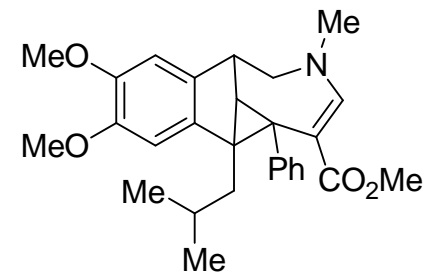
<sup>1</sup>H NMR spectra for 2e.



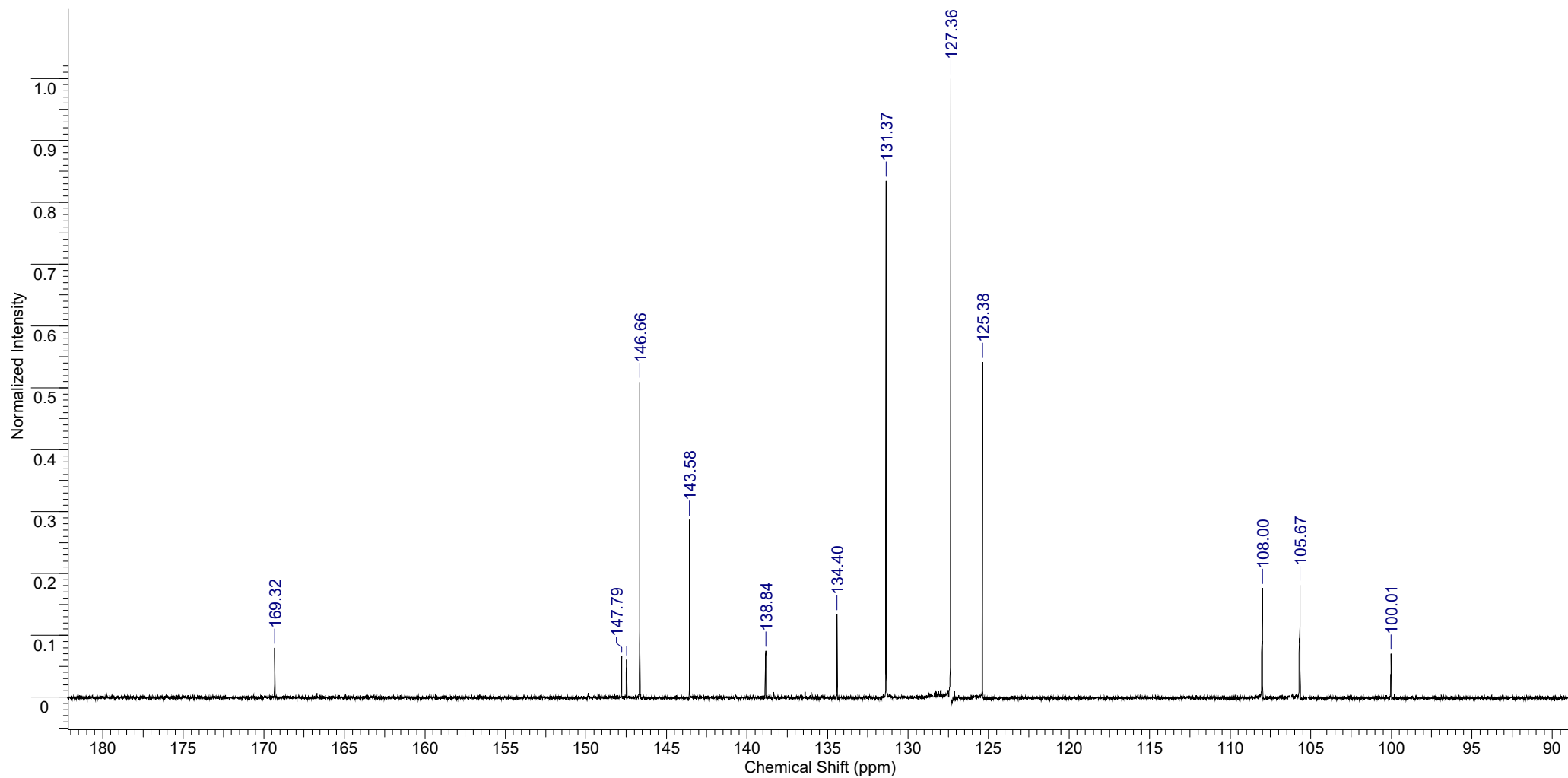
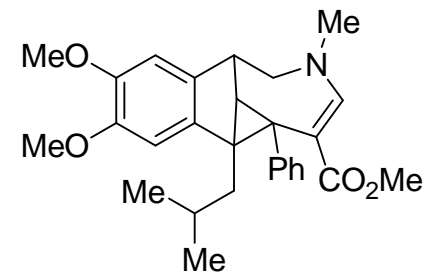
<sup>1</sup>H NMR spectra for 2e.



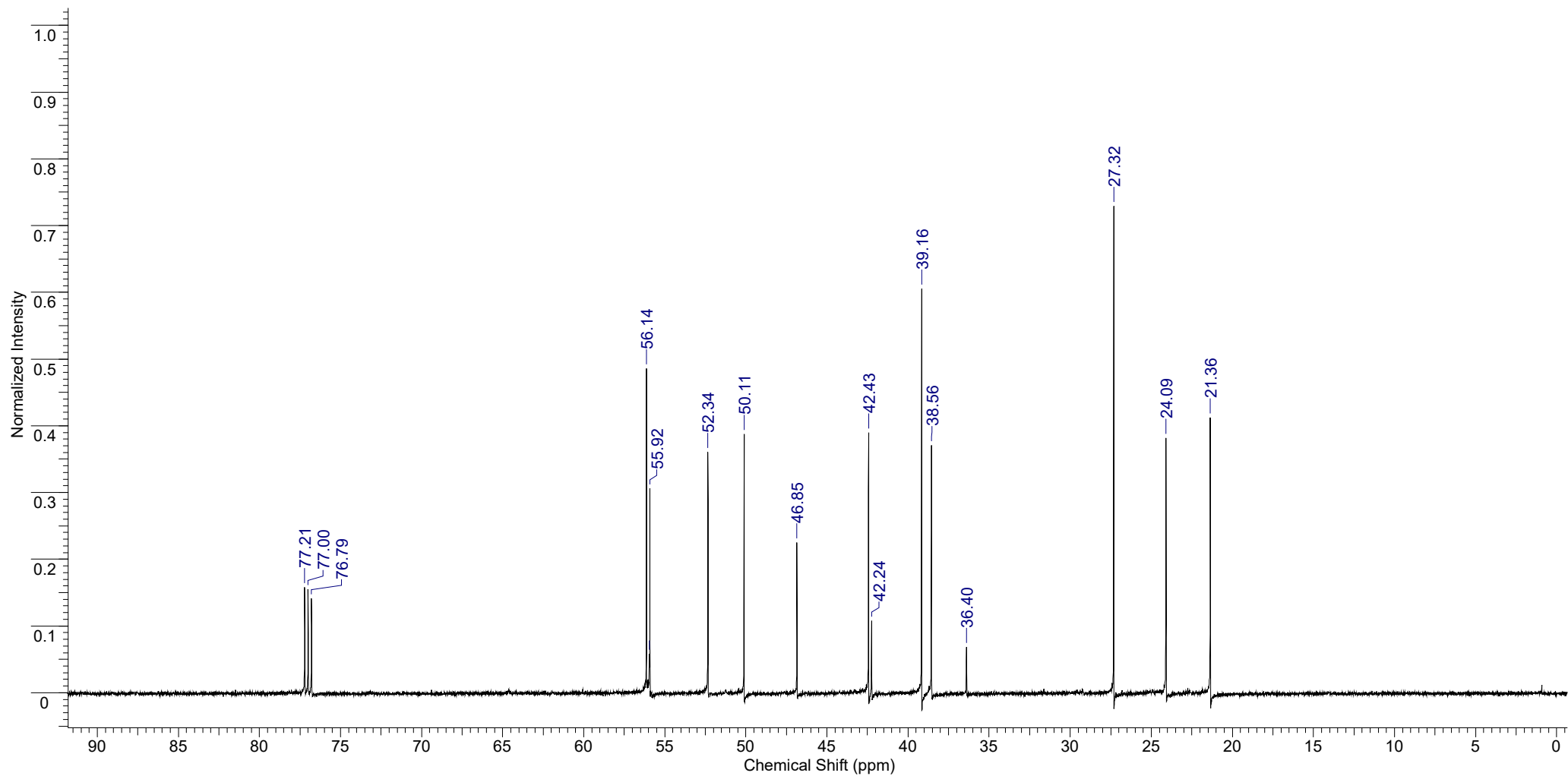
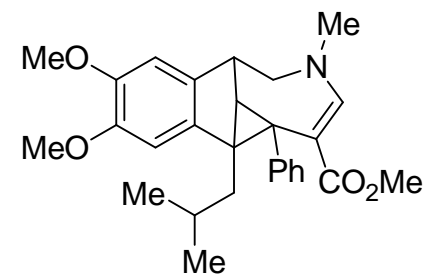
<sup>13</sup>C NMR spectra for 2e.



<sup>13</sup>C NMR spectra for 2e.

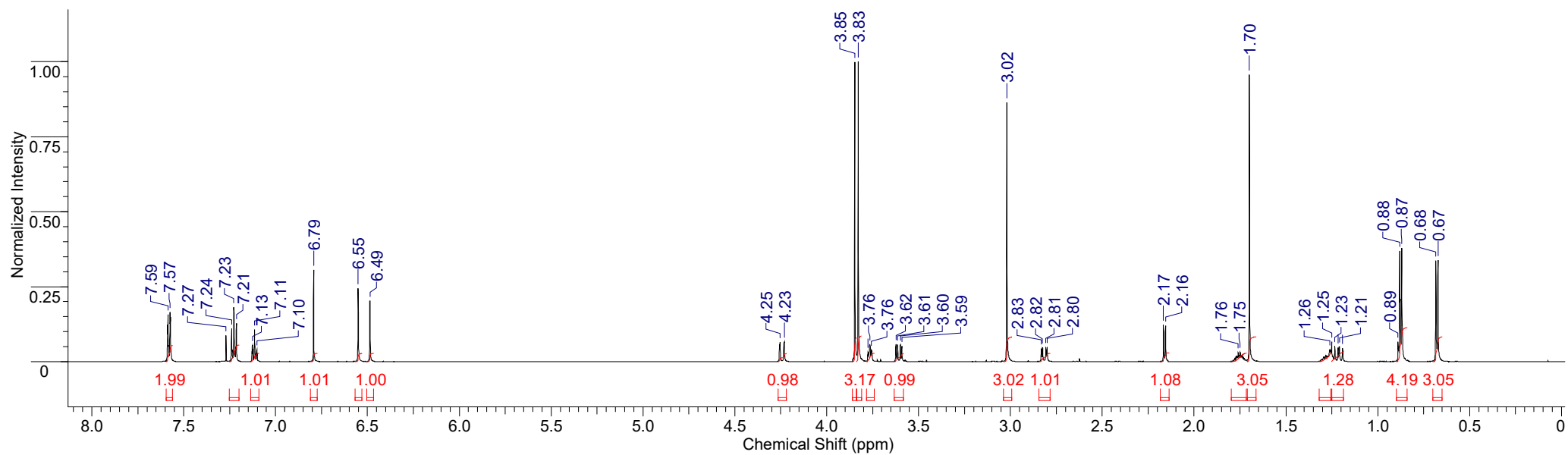
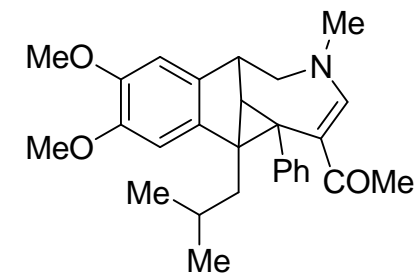


<sup>13</sup>C NMR spectra for 2e.

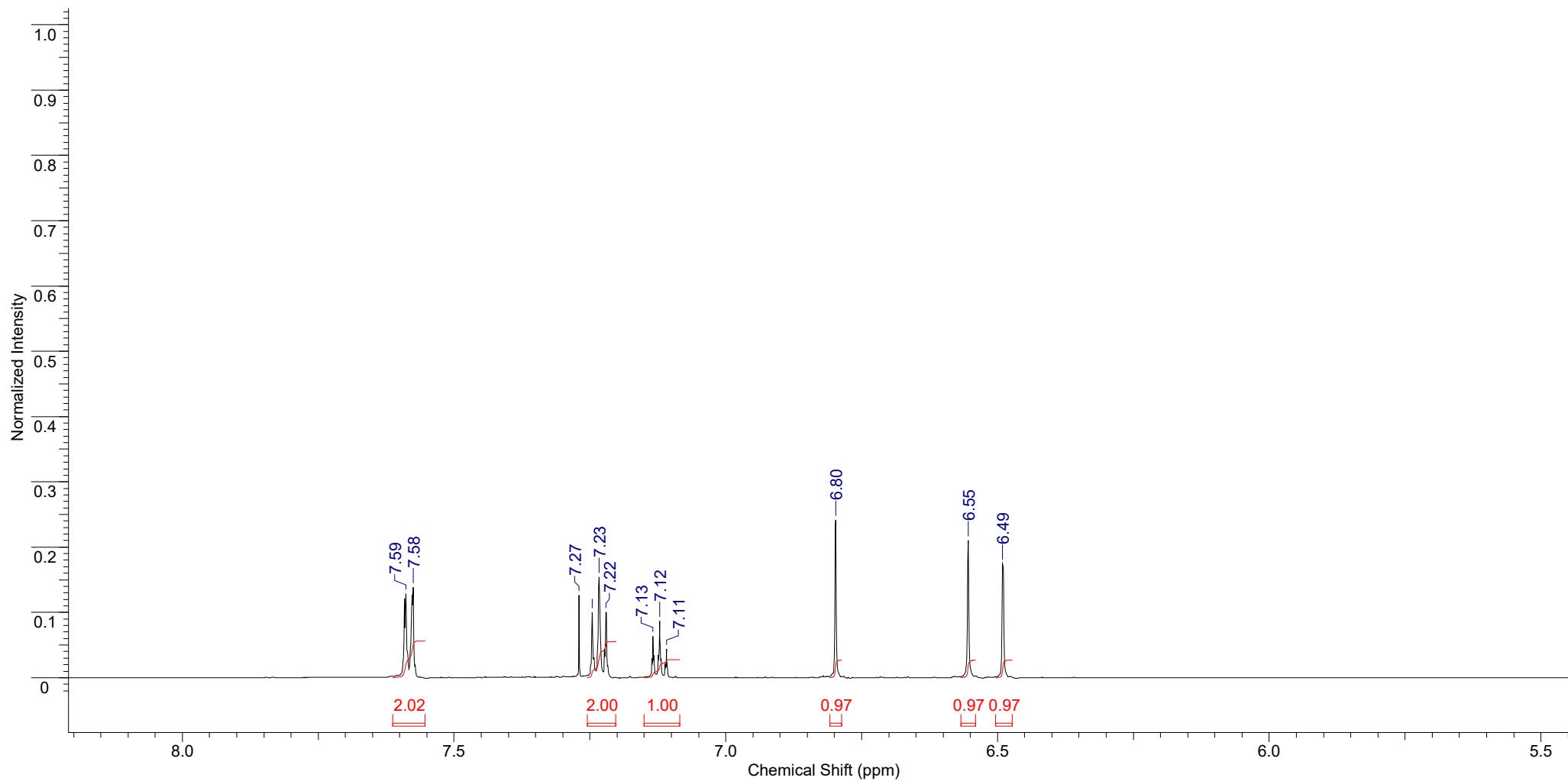
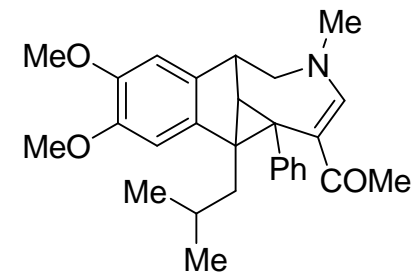


1-[6,7-dimethoxy-2-methyl-4b-(2-methylpropyl)-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzocyclopropa[cd]azulen-4-yl]ethanone (2f)

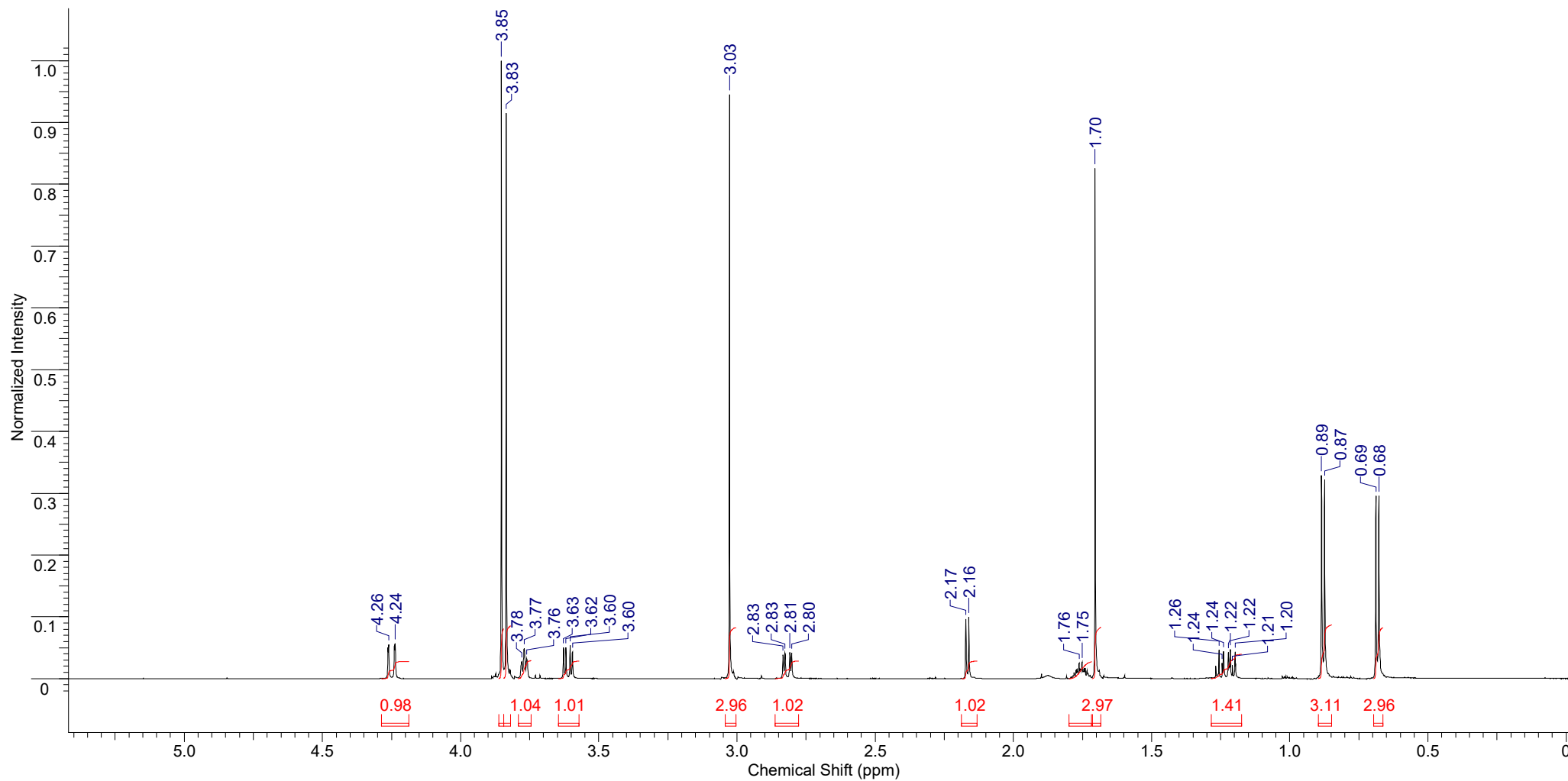
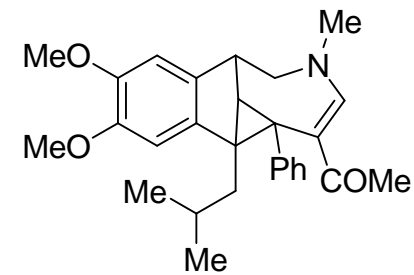
<sup>1</sup>H NMR spectra for 2f.



<sup>1</sup>H NMR spectra for 2f.

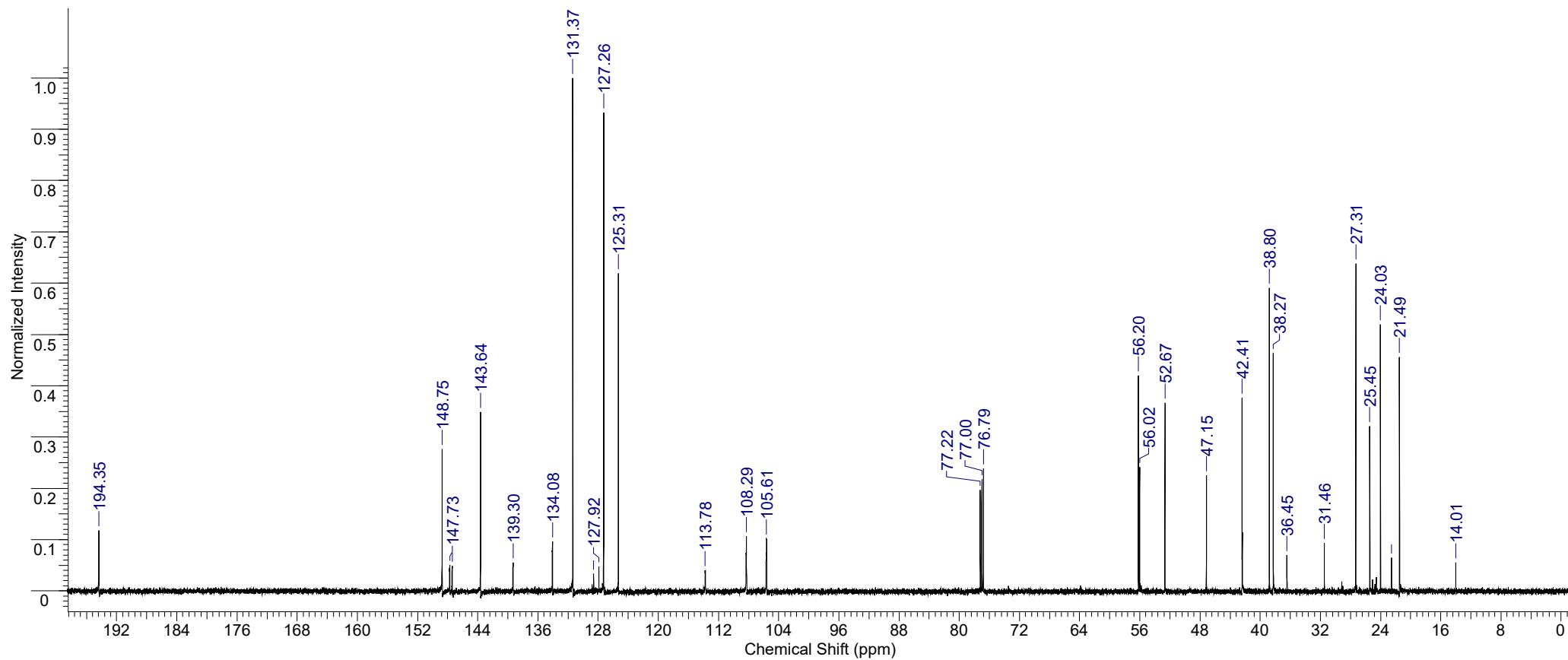
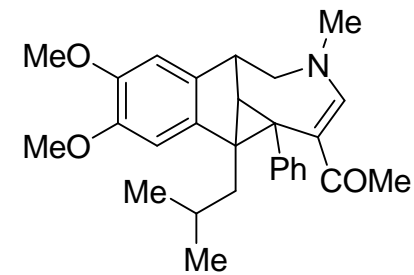


<sup>1</sup>H NMR spectra for 2f.

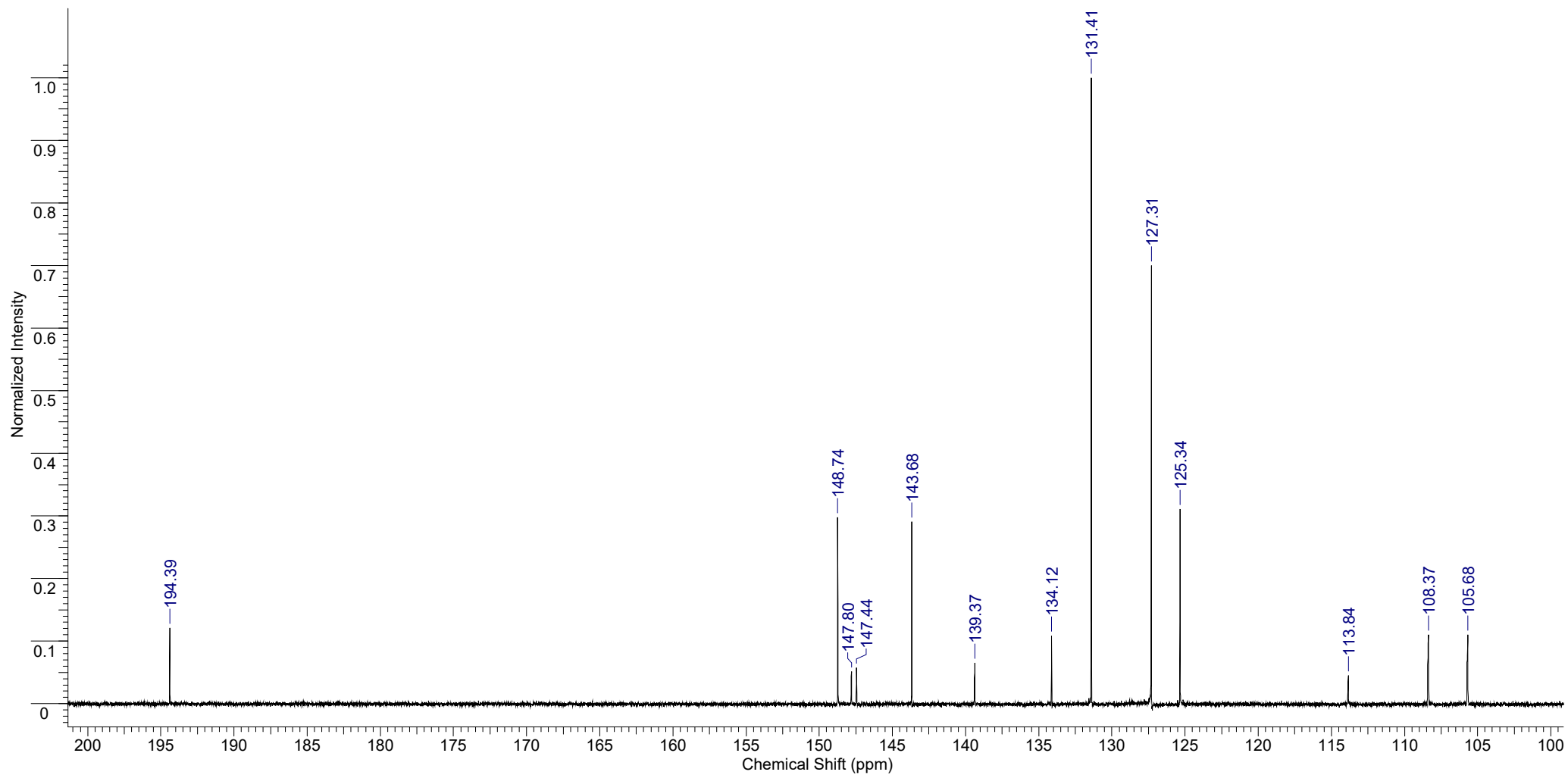
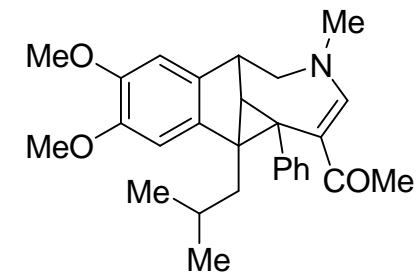




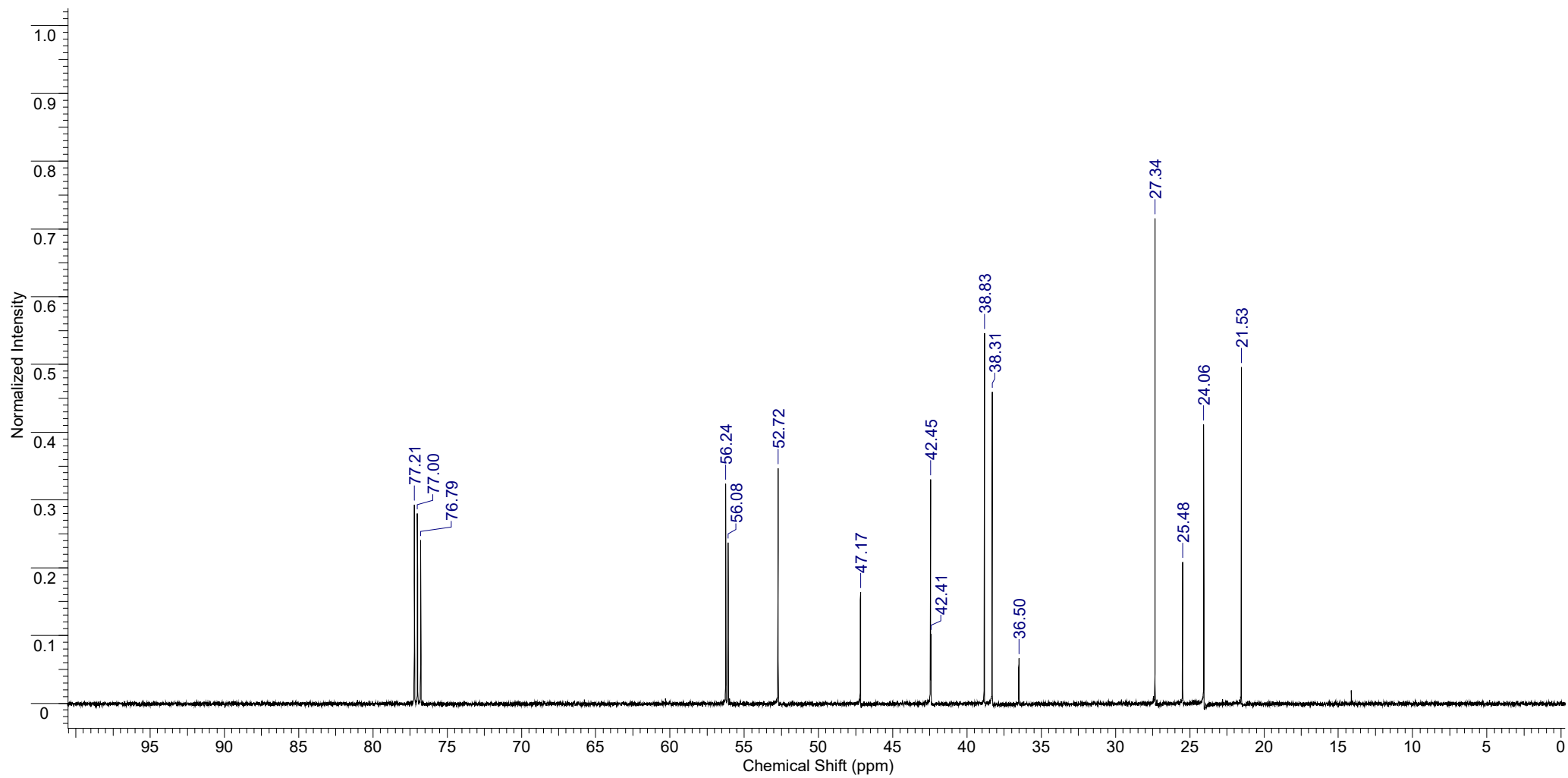
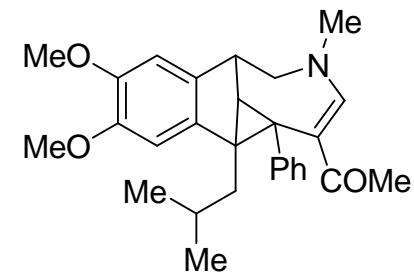
<sup>13</sup>C NMR spectra for 2f.



<sup>13</sup>C NMR spectra for 2f.

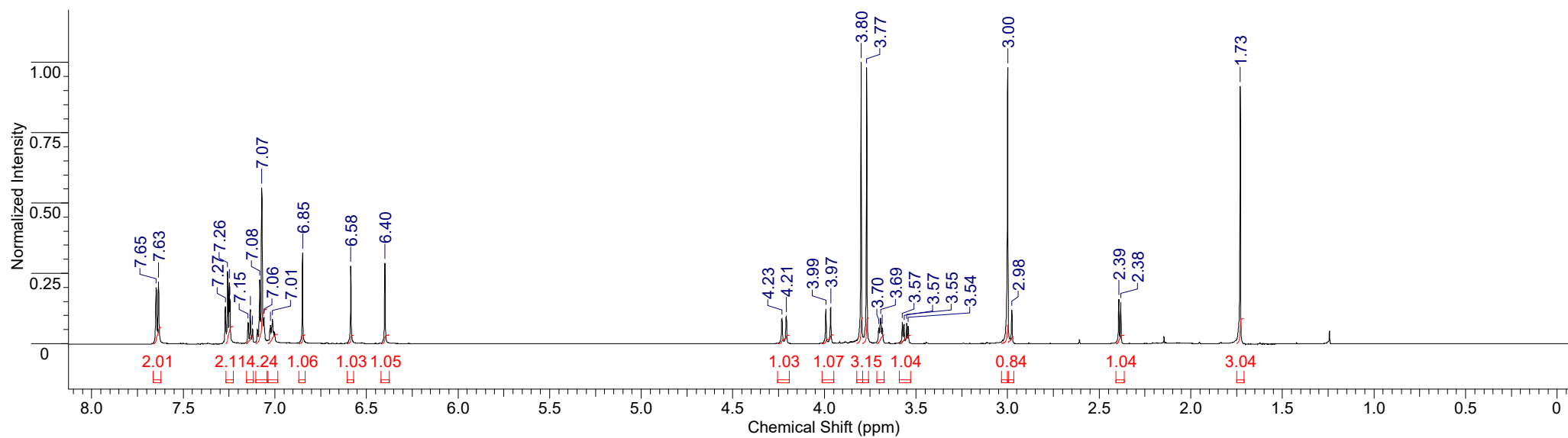
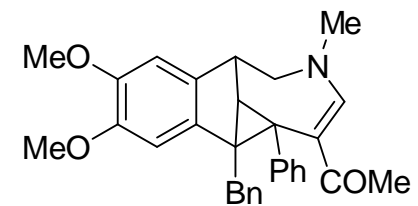


<sup>13</sup>C NMR spectra for 2f.

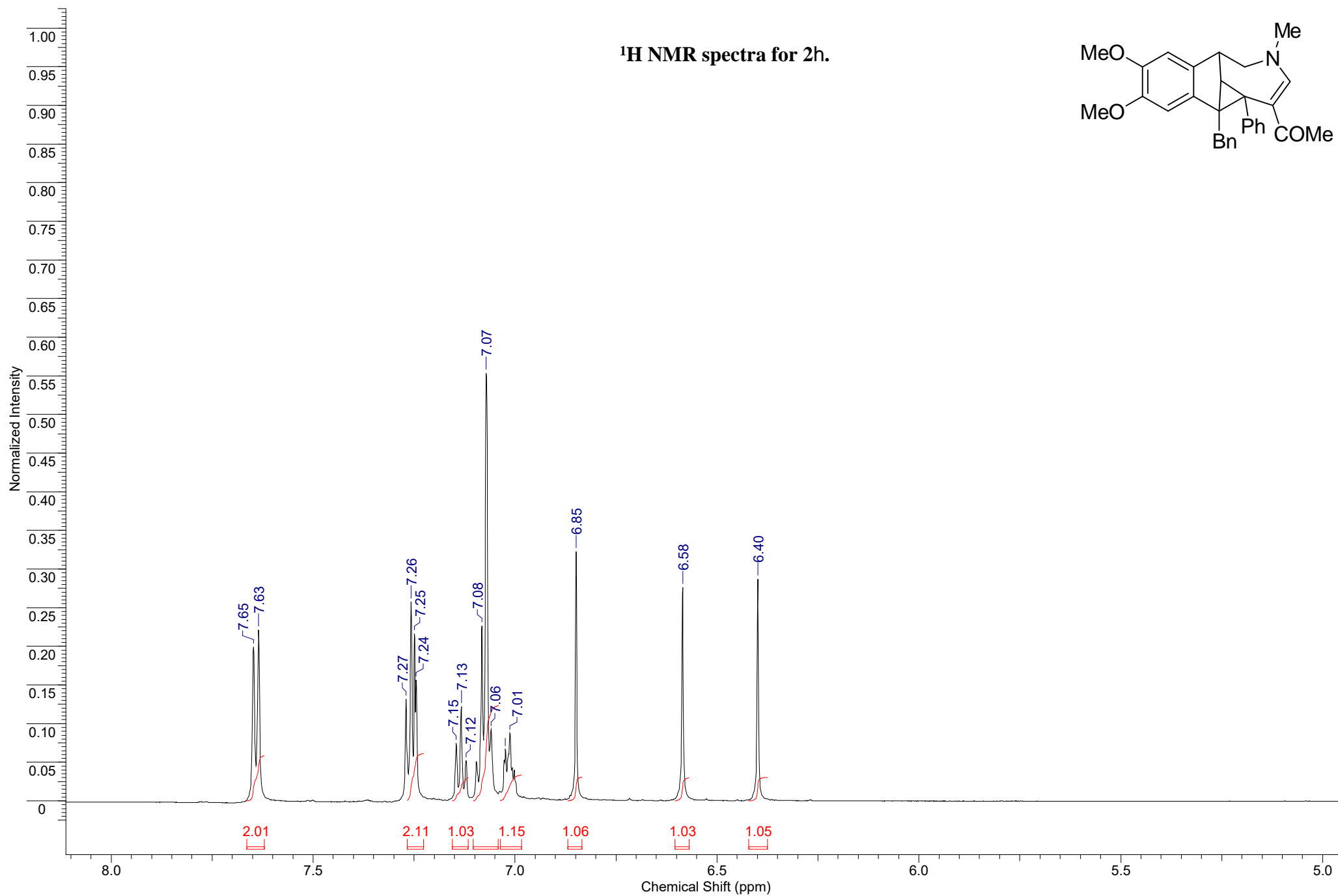
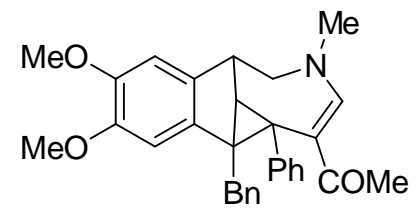


1-(4b-benzyl-6,7-dimethoxy-2-methyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzocyclopropa[cd]azulen-4-yl)ethanone (2h)

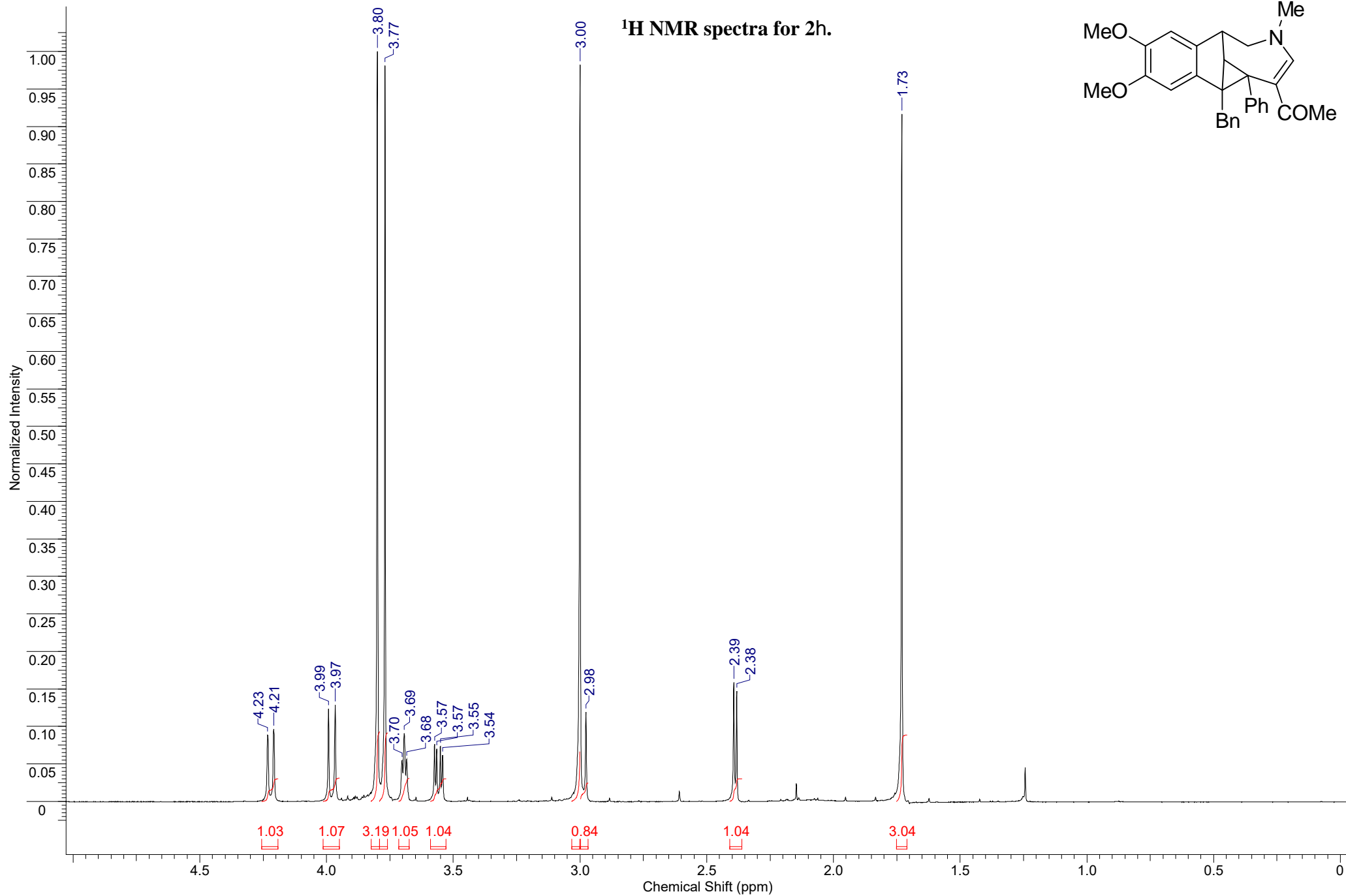
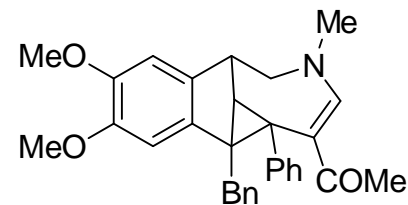
<sup>1</sup>H NMR spectra for 2h.



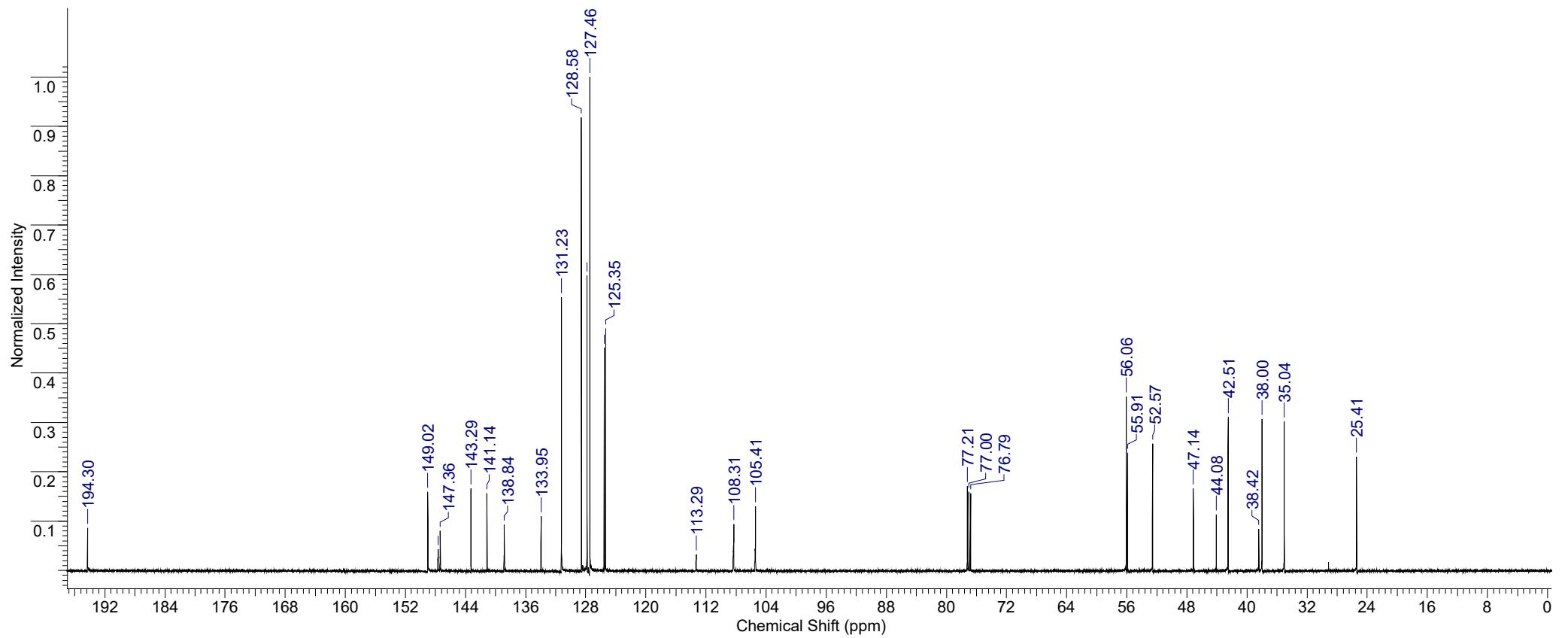
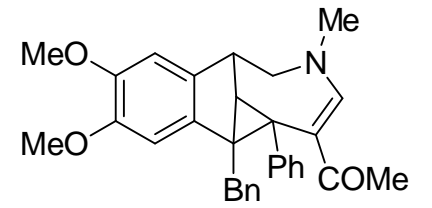
<sup>1</sup>H NMR spectra for 2h.



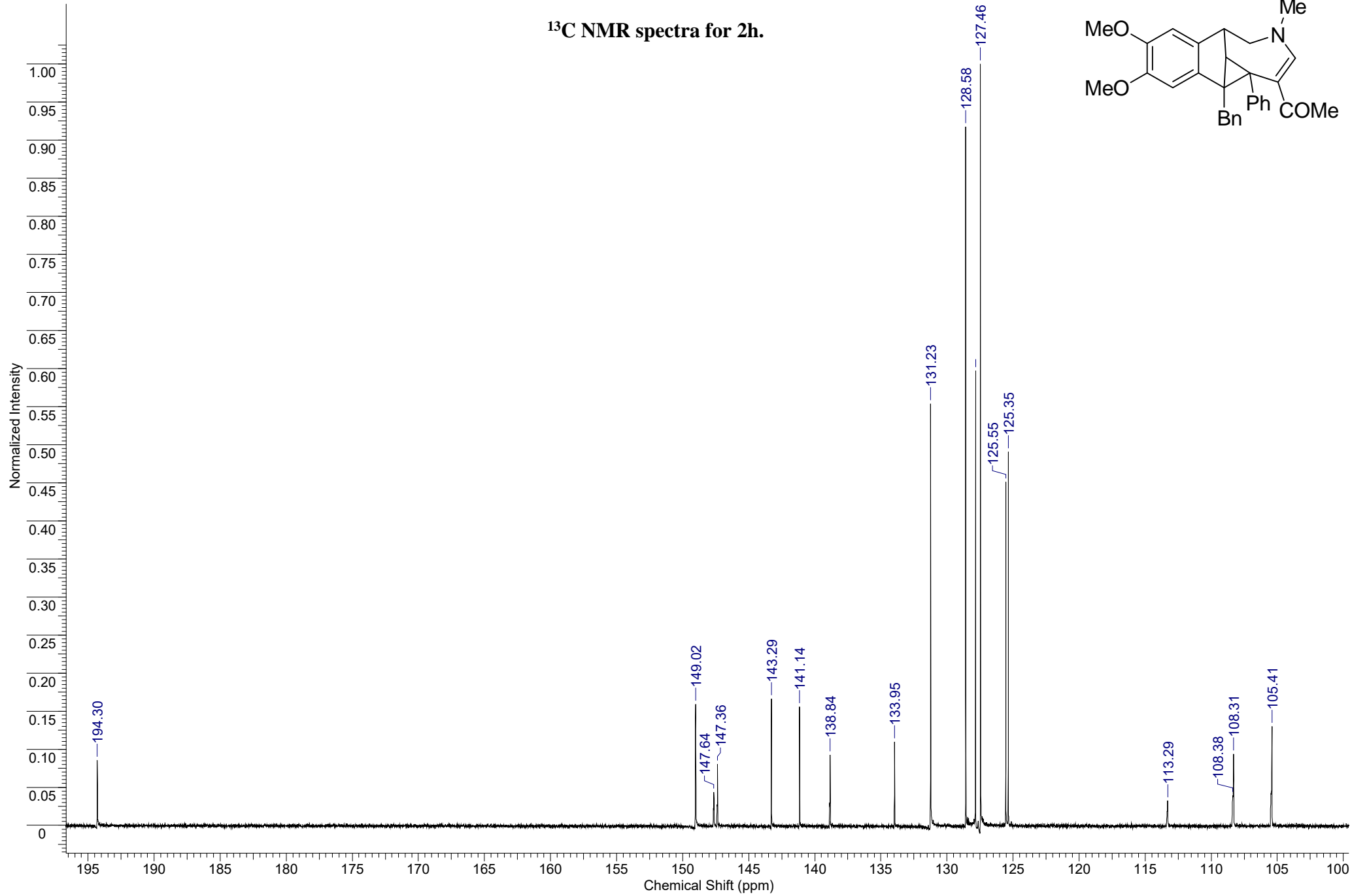
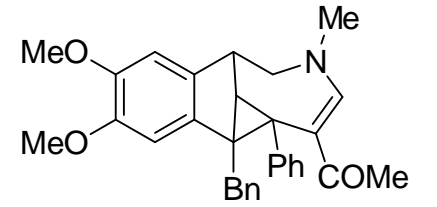
<sup>1</sup>H NMR spectra for 2h.



<sup>13</sup>C NMR spectra for 2h.

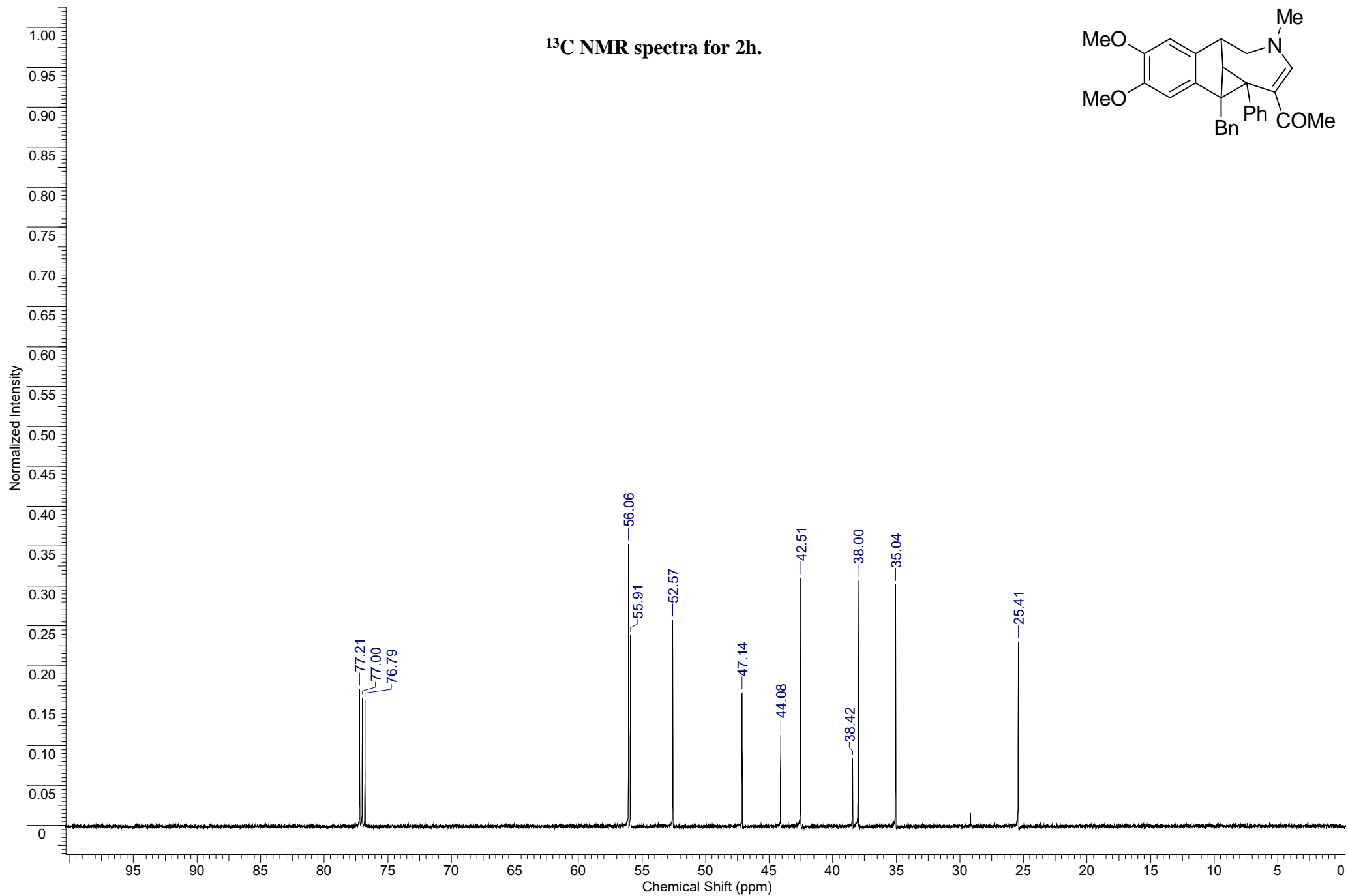
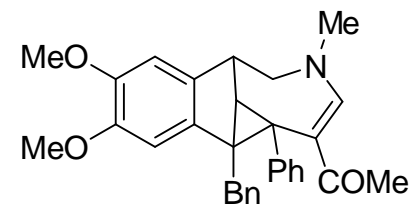


<sup>13</sup>C NMR spectra for 2h.



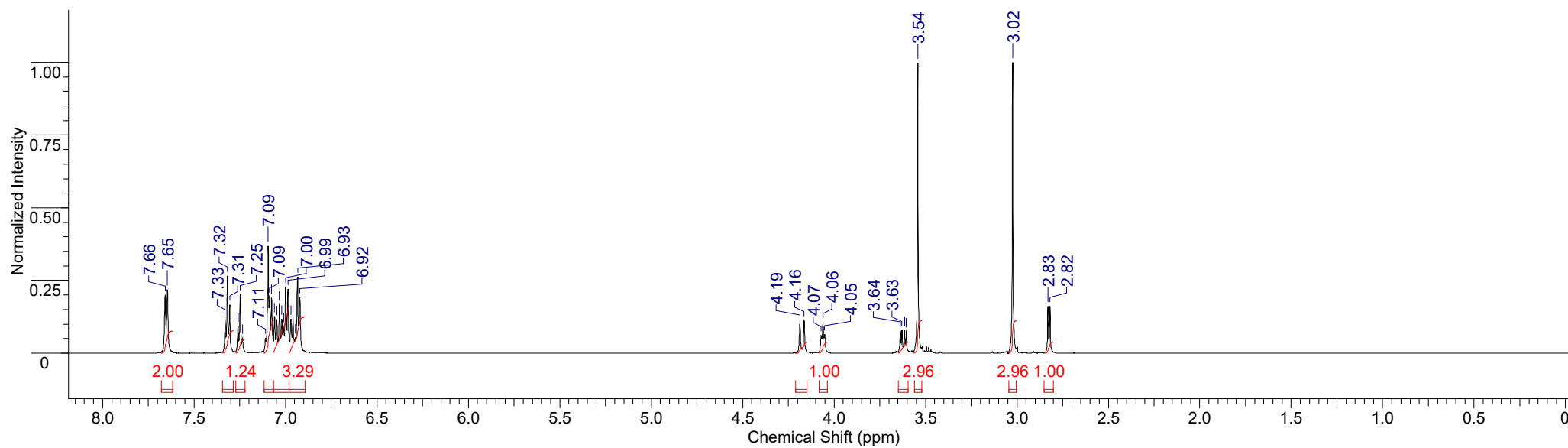
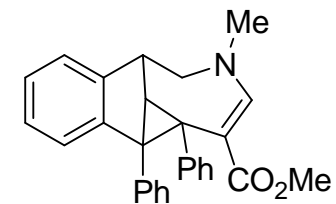


<sup>13</sup>C NMR spectra for 2h.

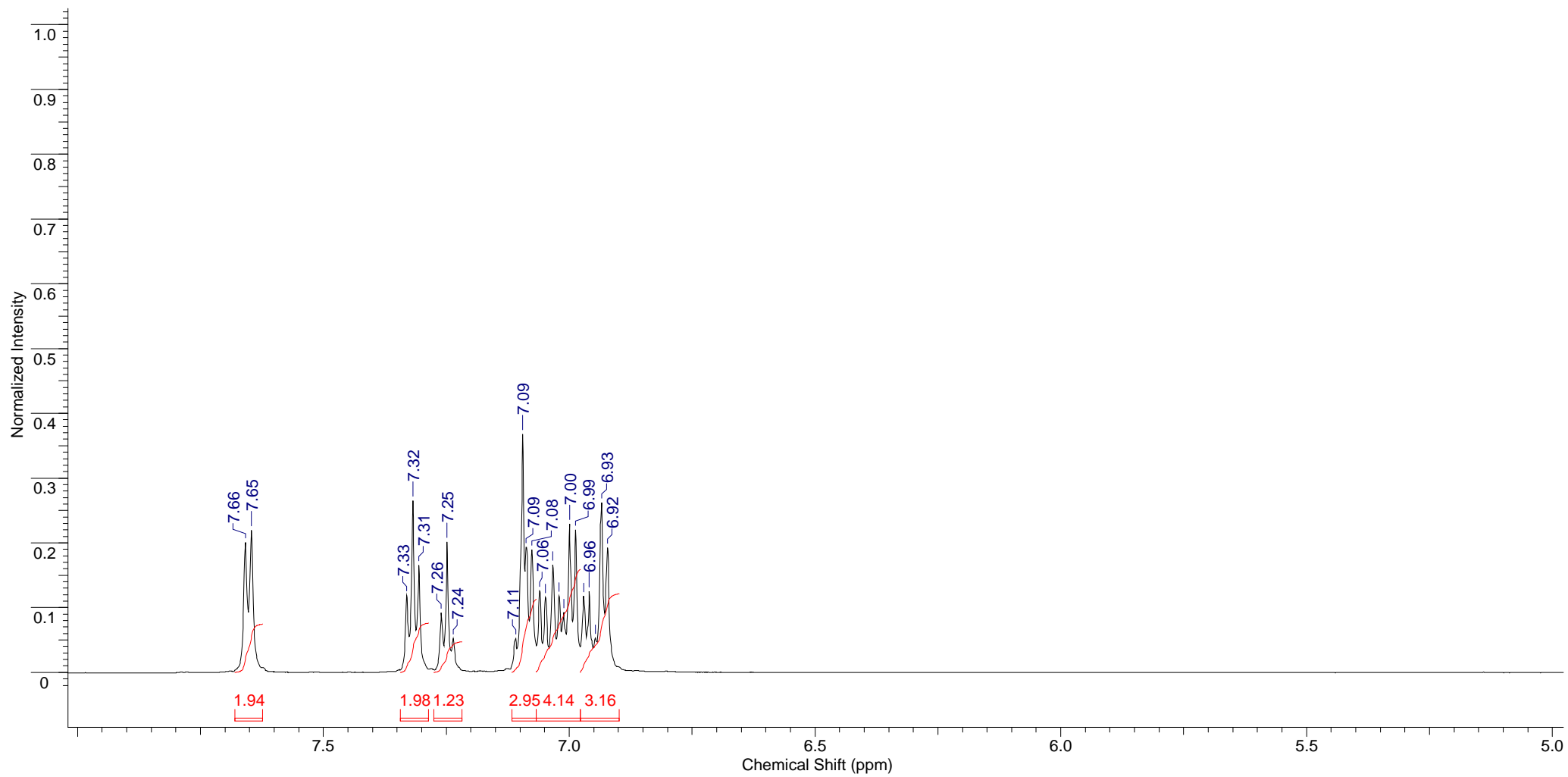
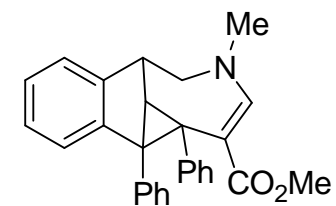


Methyl 2-methyl-4a,4b-diphenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[a]cyclopropa[cd]azulene-4-carboxylate (2i)

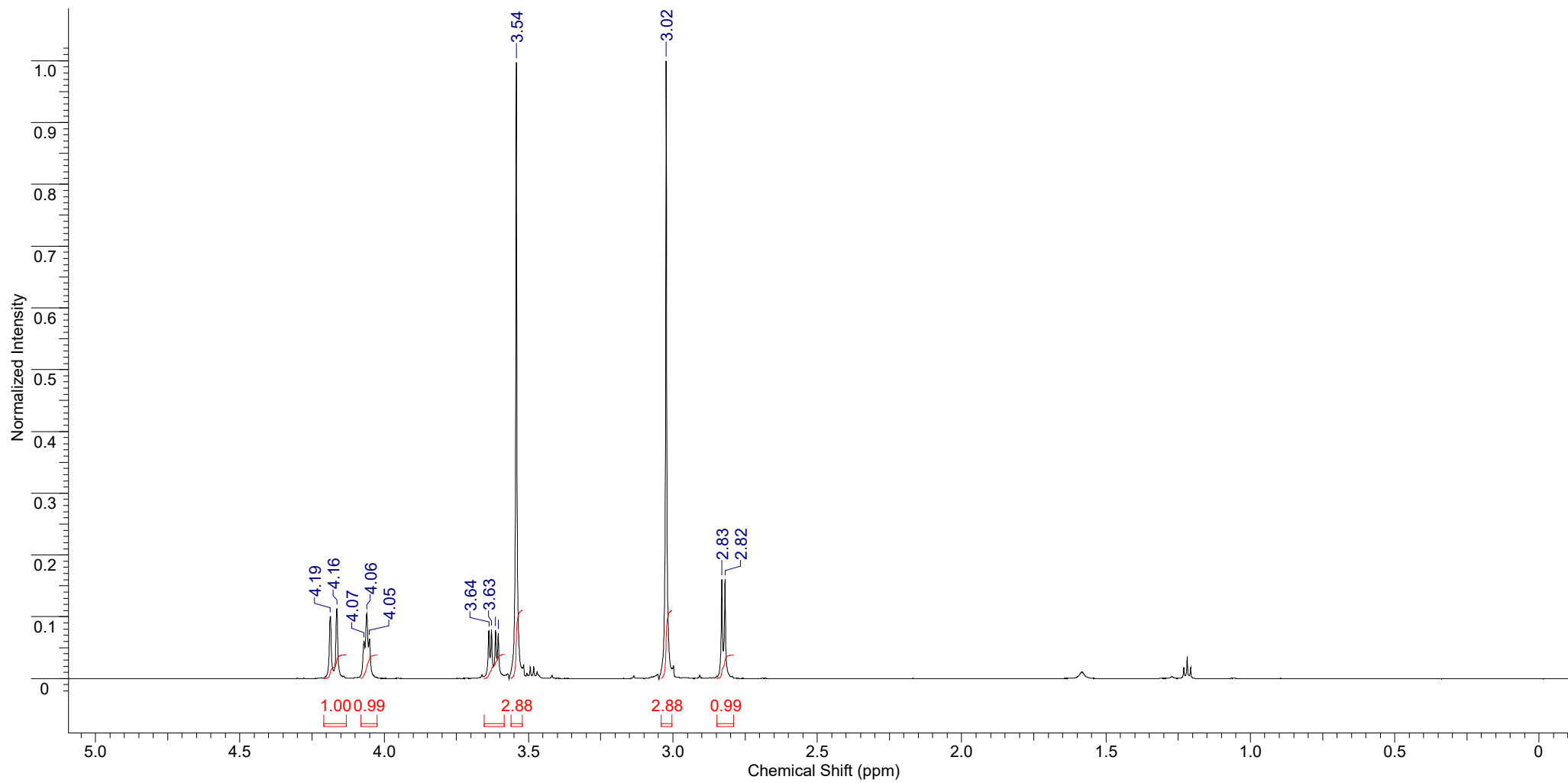
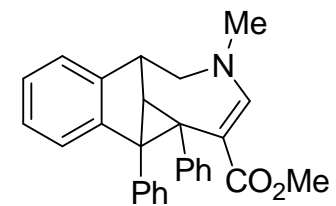
$^1\text{H}$  NMR spectra for 2i.



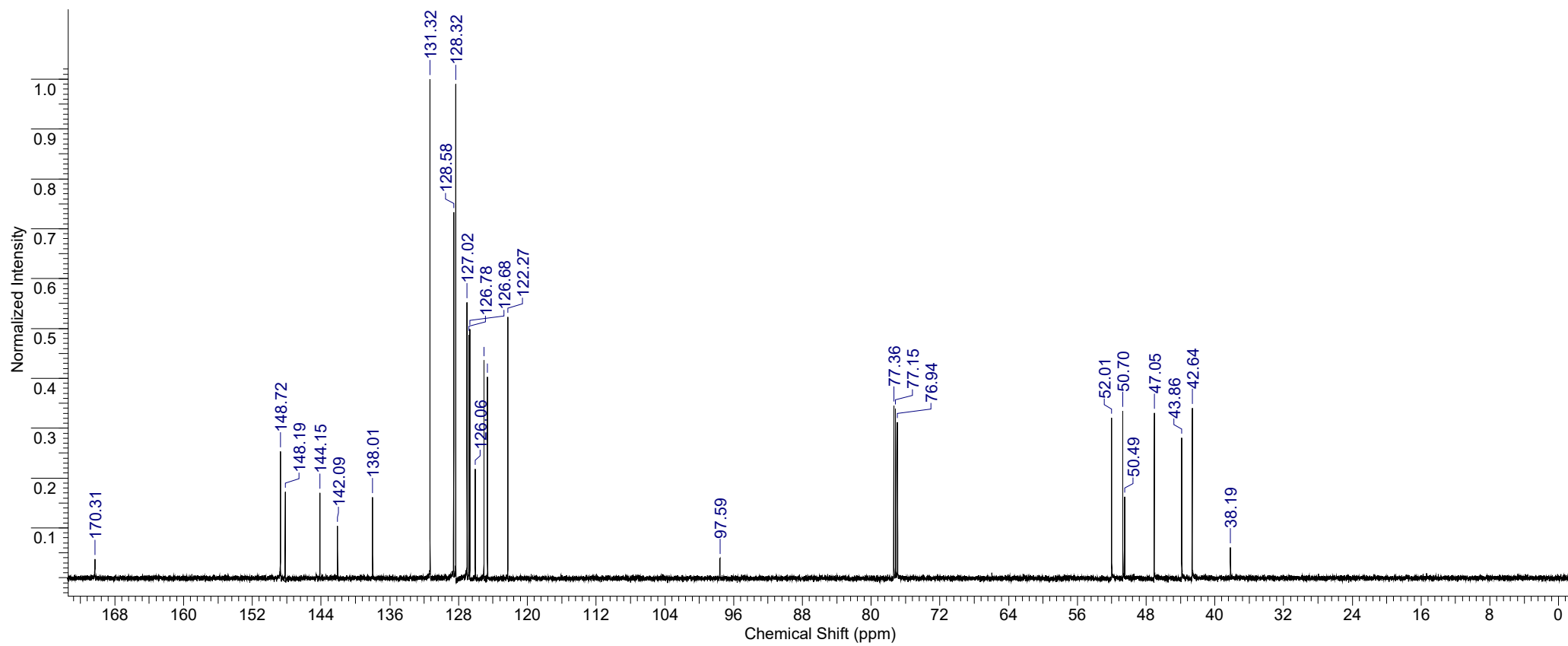
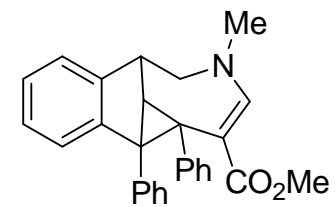
<sup>1</sup>H NMR spectra for 2i.



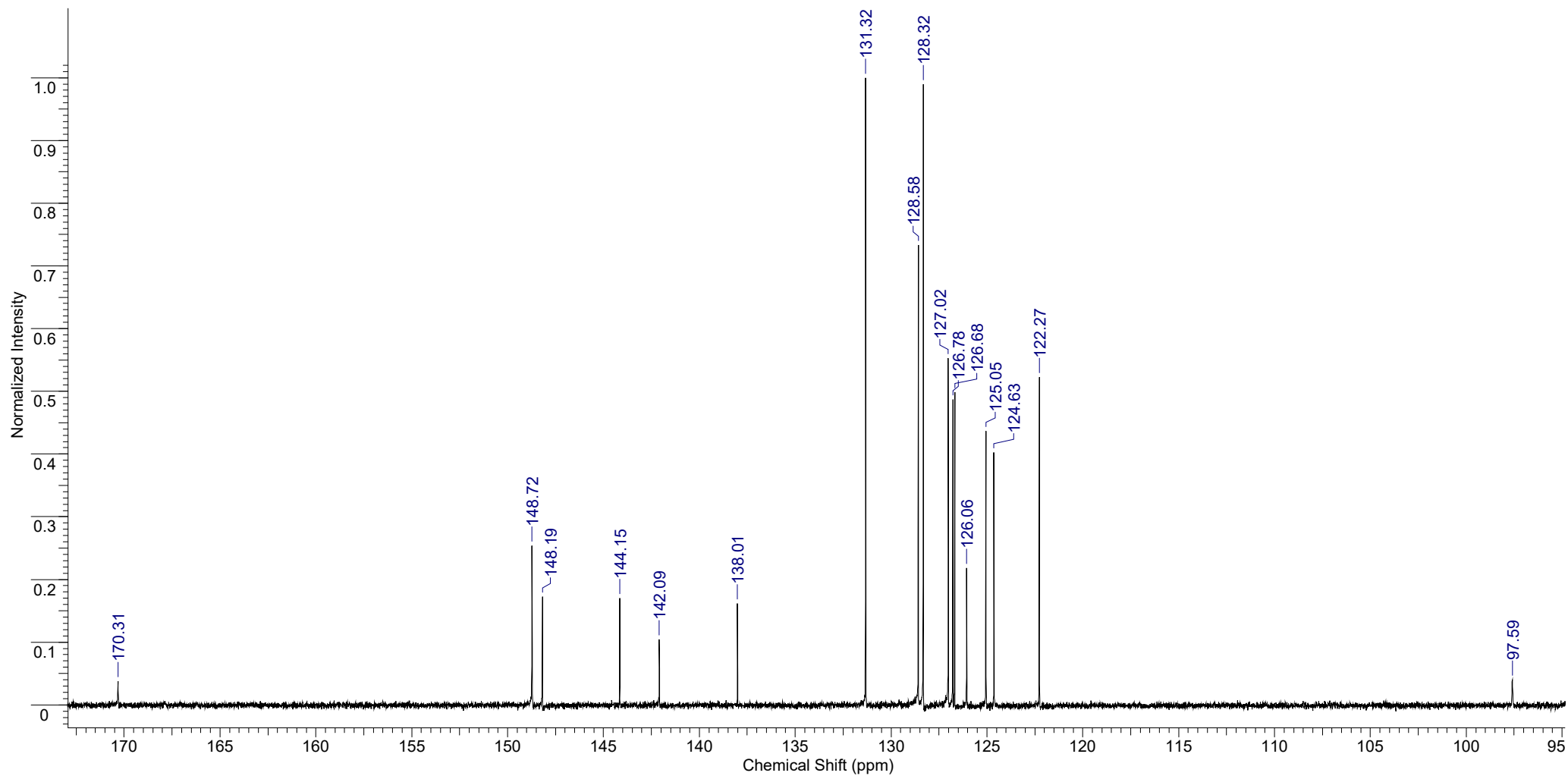
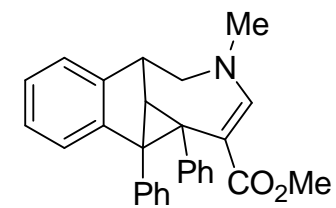
<sup>1</sup>H NMR spectra for 2i.



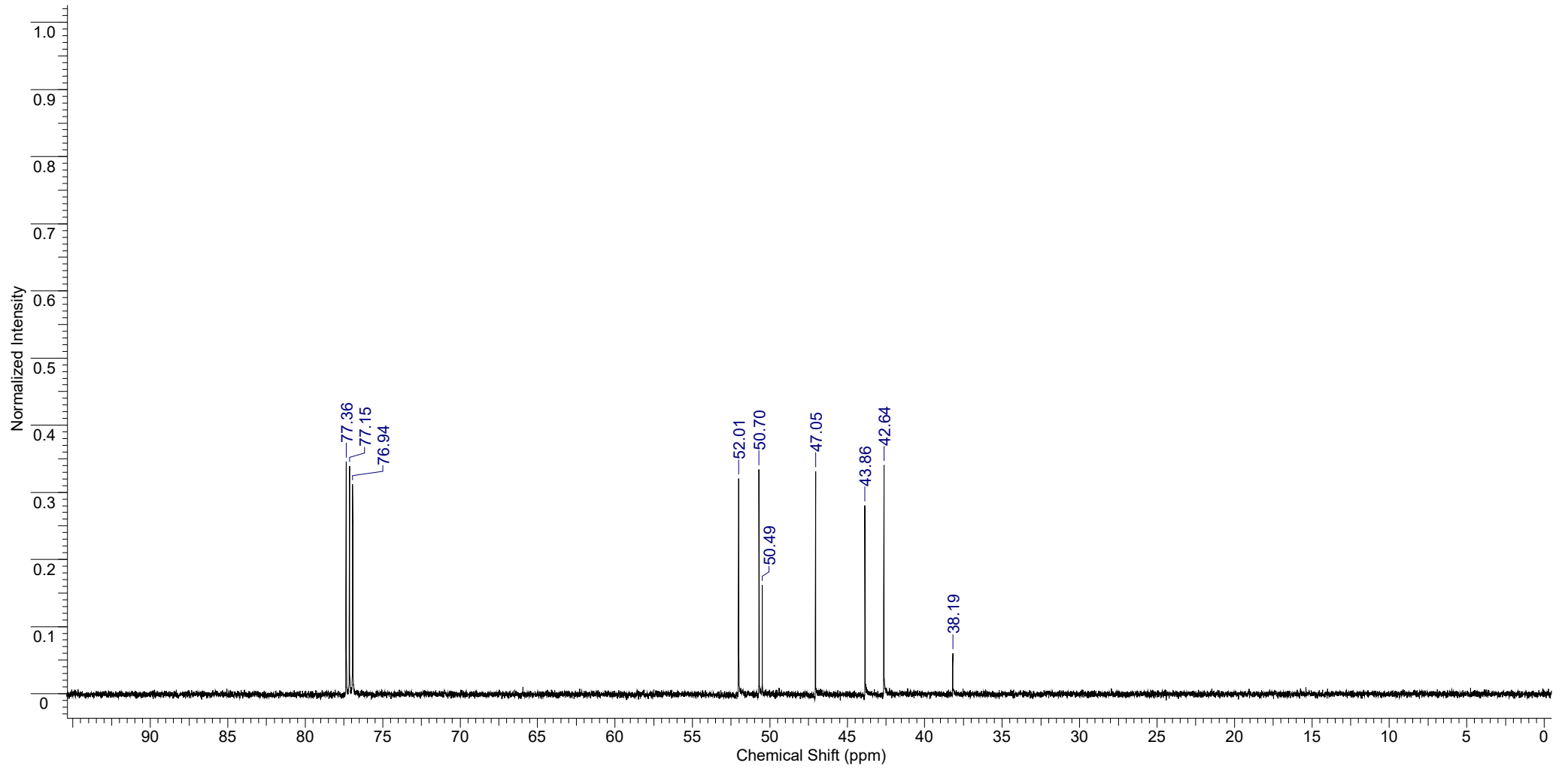
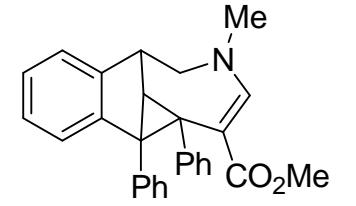
<sup>13</sup>C NMR spectra for 2i.



<sup>13</sup>C NMR spectra for 2i.

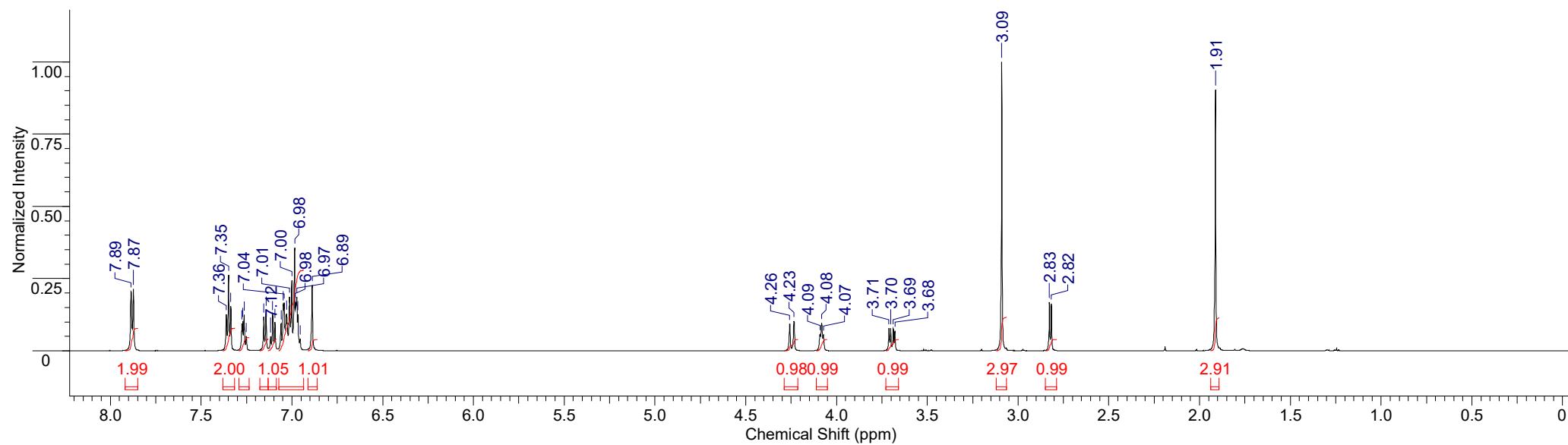
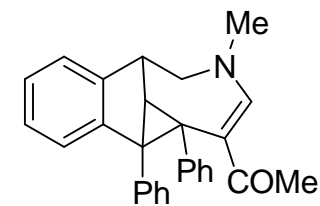


<sup>13</sup>C NMR spectra for 2i.



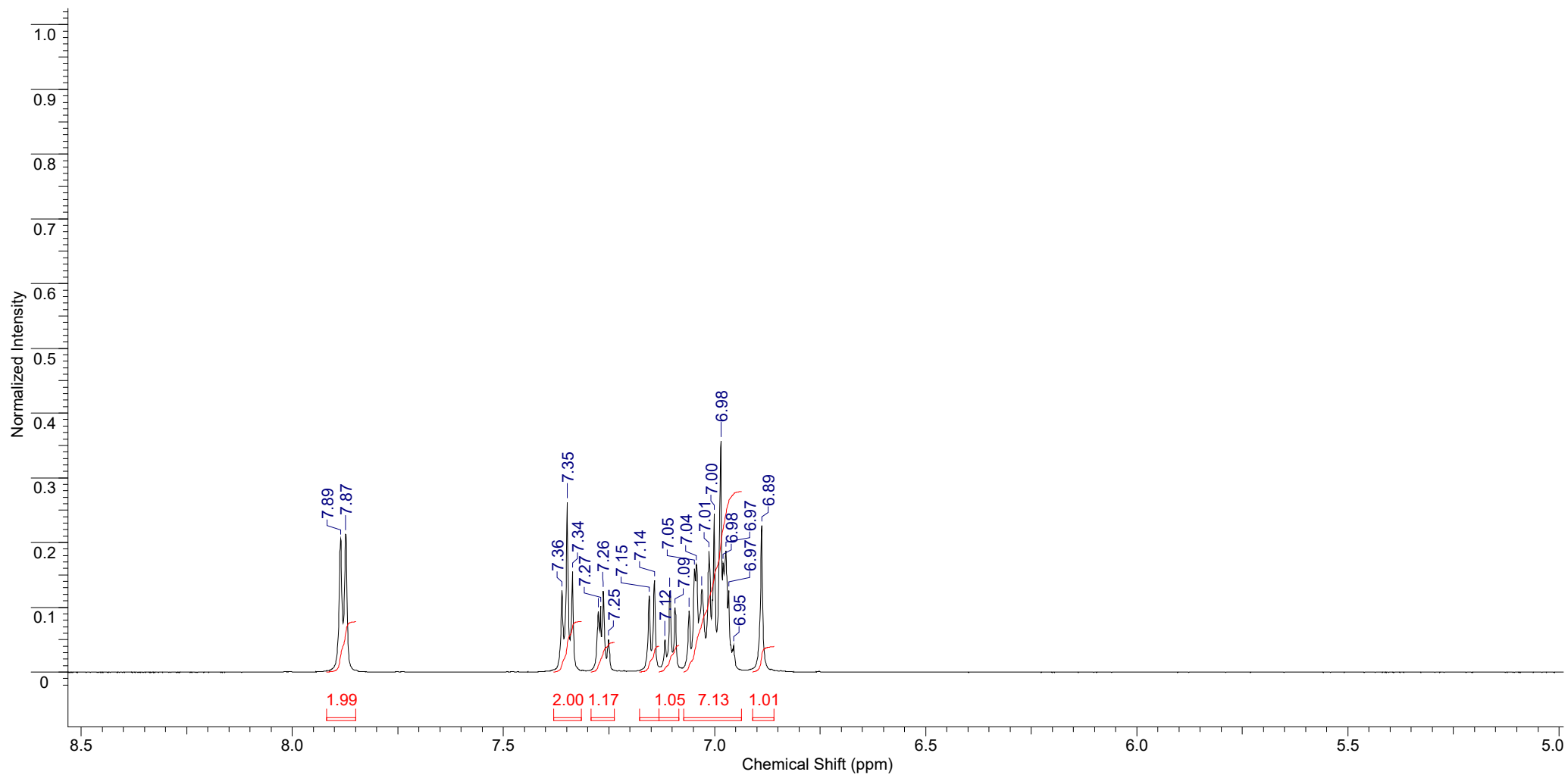
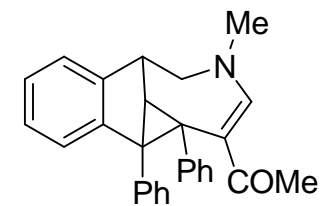
1-(2-Methyl-4a,4b-diphenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzocyclopropa[cd]azulen-4-yl)ethanone (2j)

<sup>1</sup>H NMR spectra for 2j.

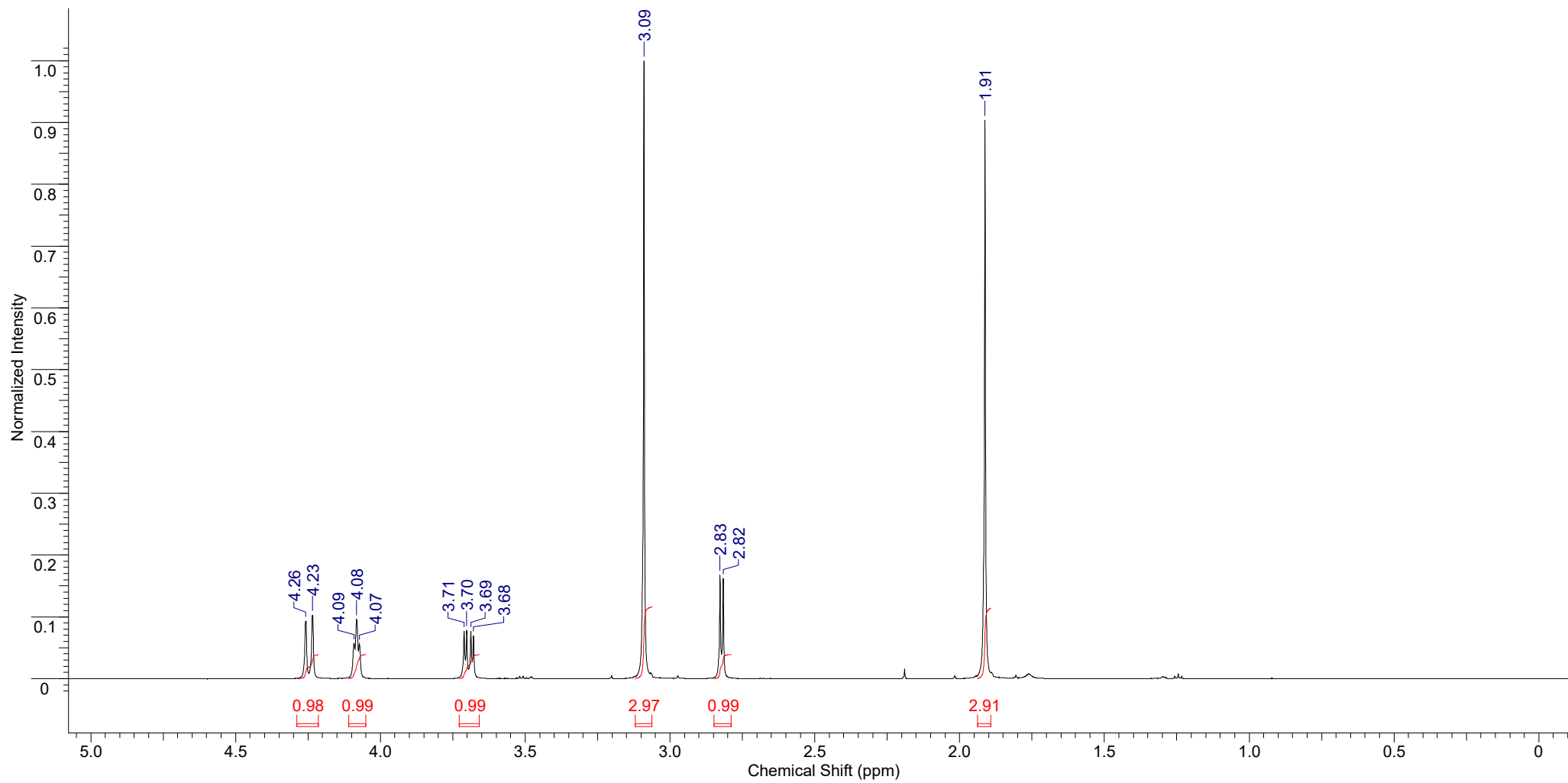
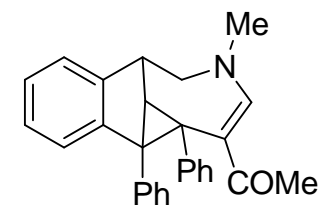




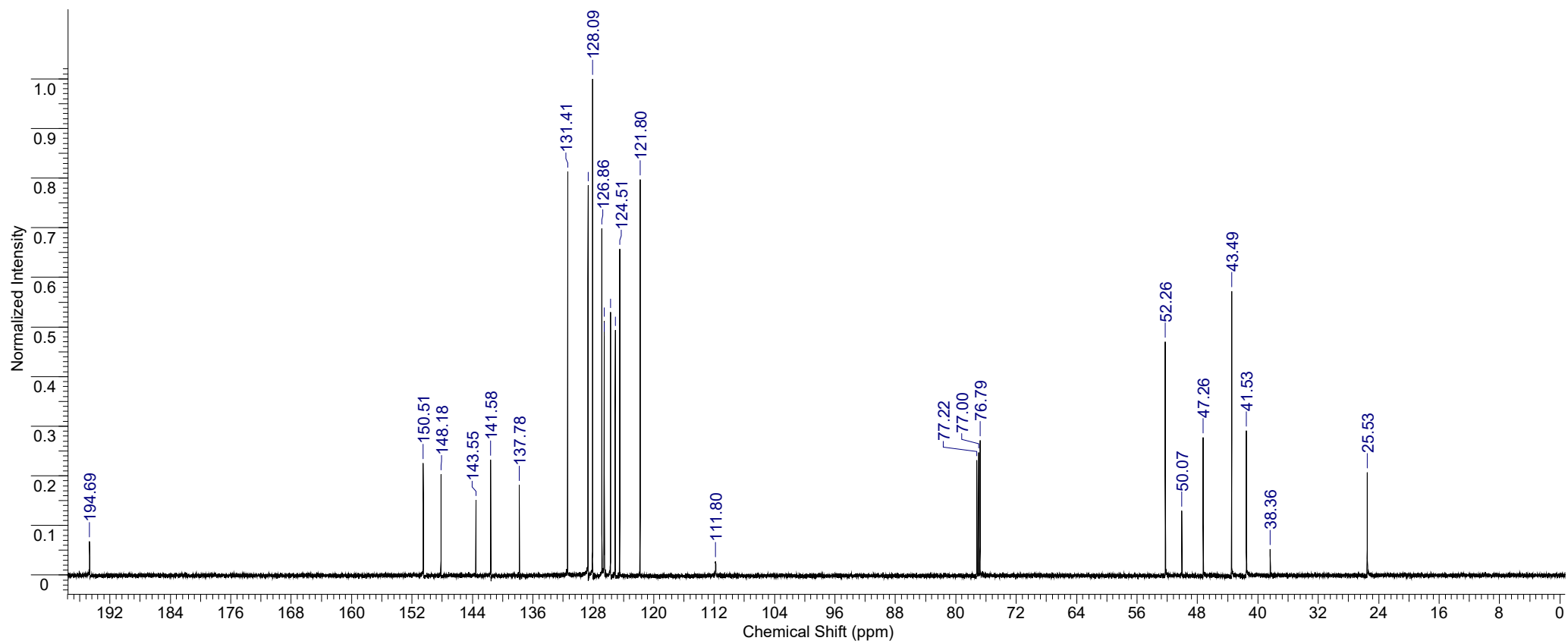
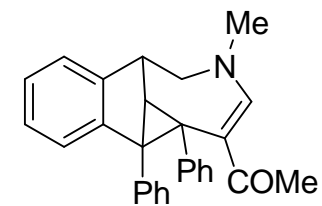
<sup>1</sup>H NMR spectra for 2j.



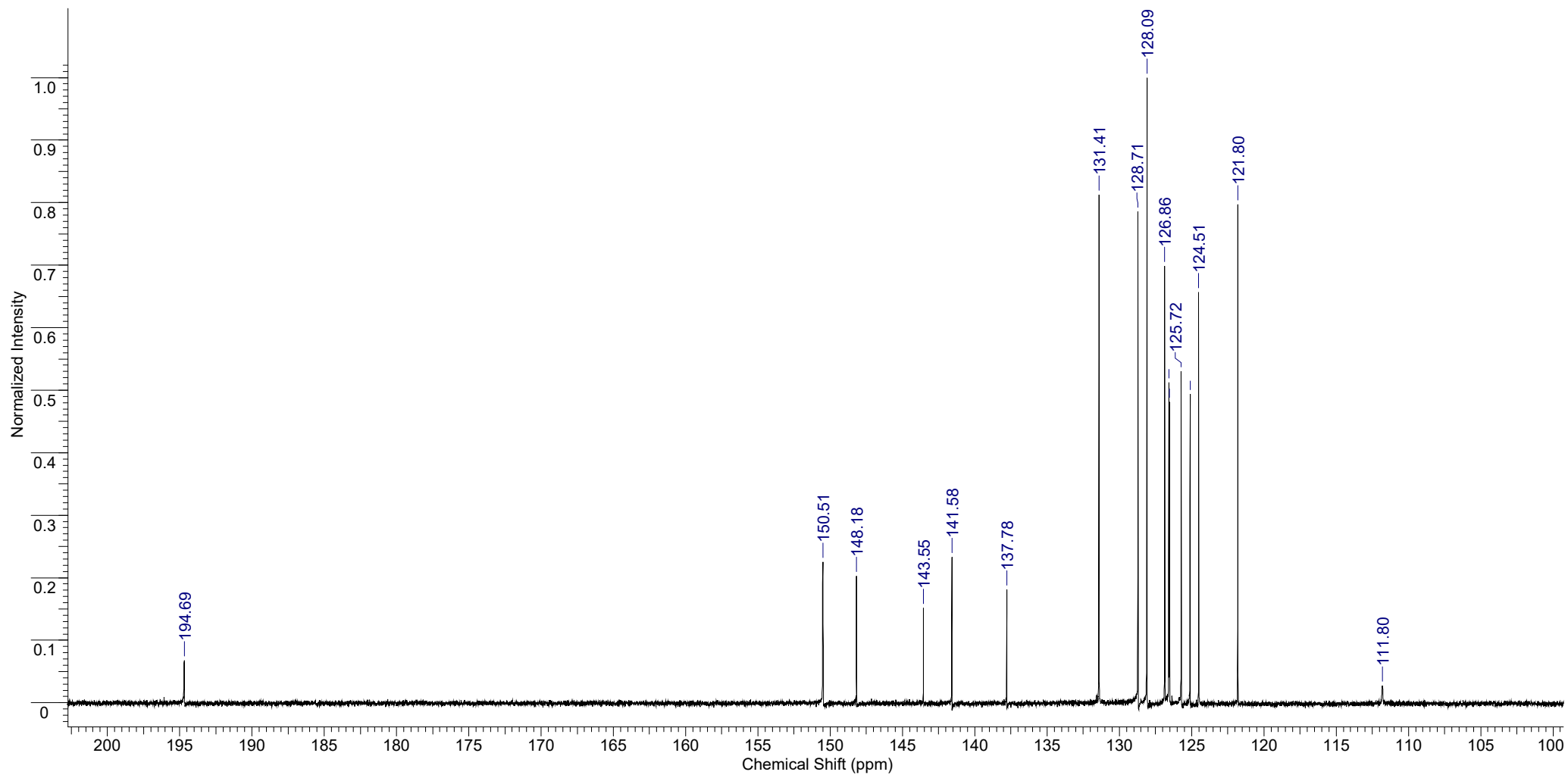
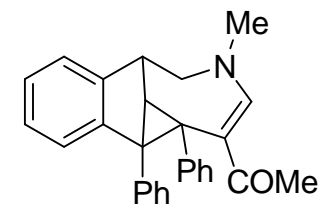
<sup>1</sup>H NMR spectra for 2j.



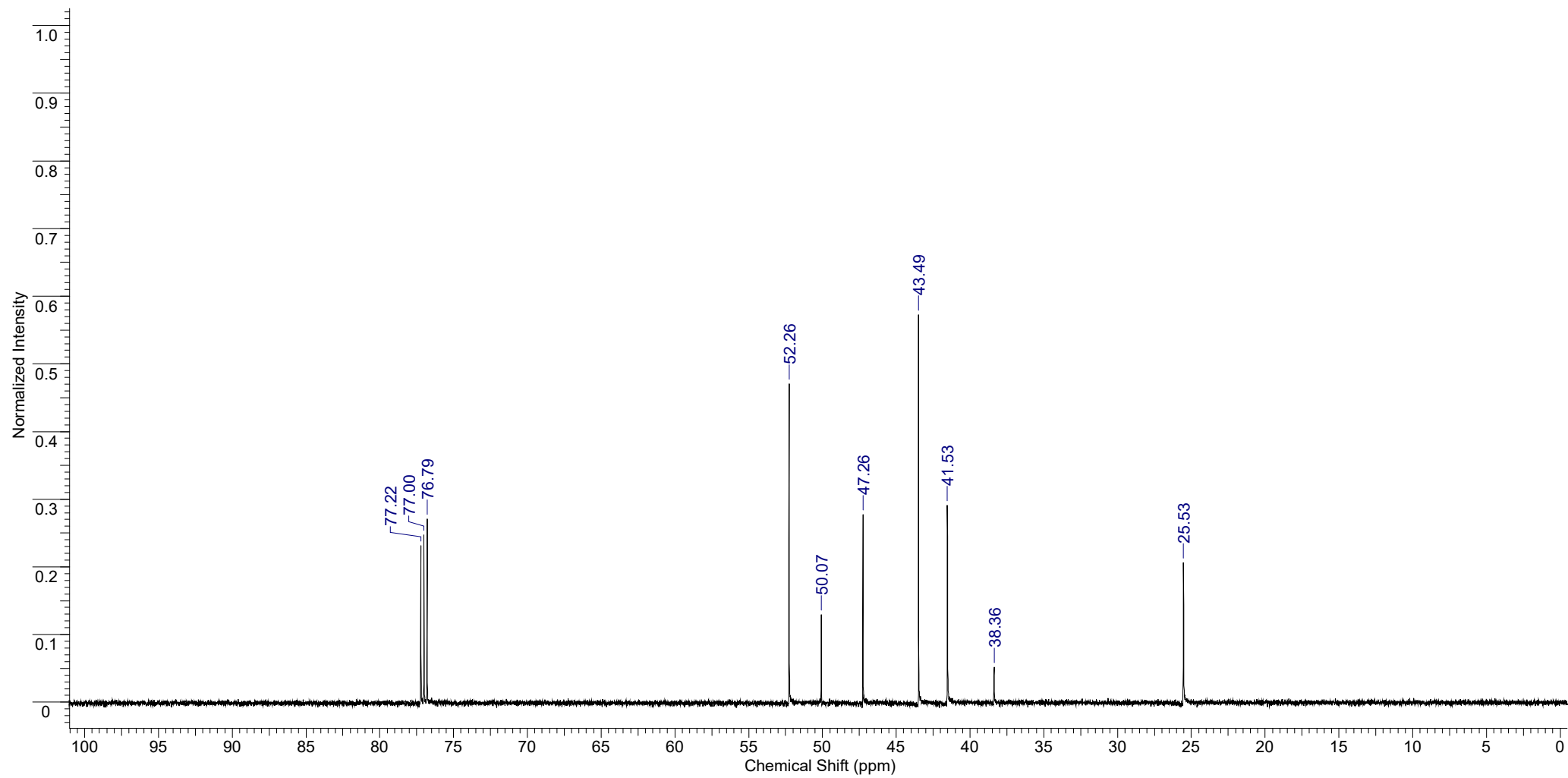
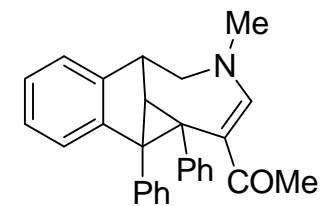
<sup>13</sup>C NMR spectra for 2j.



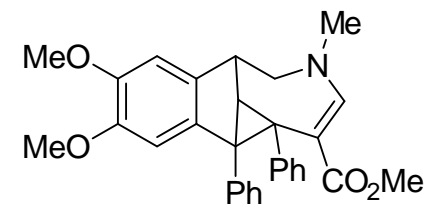
<sup>13</sup>C NMR spectra for 2j.



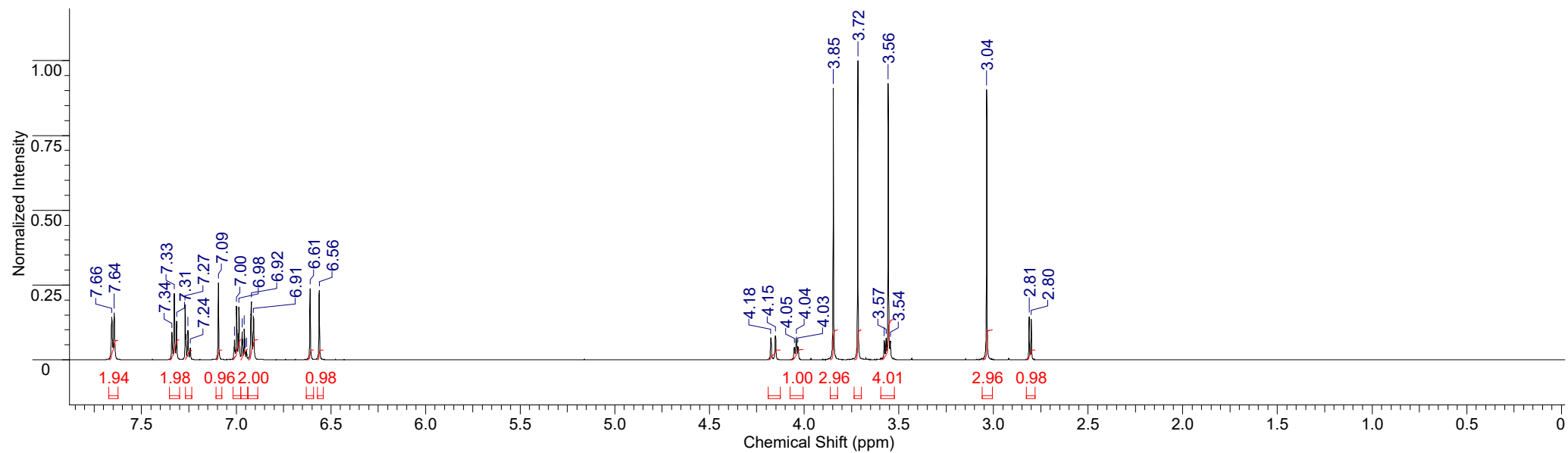
<sup>13</sup>C NMR spectra for 2j.



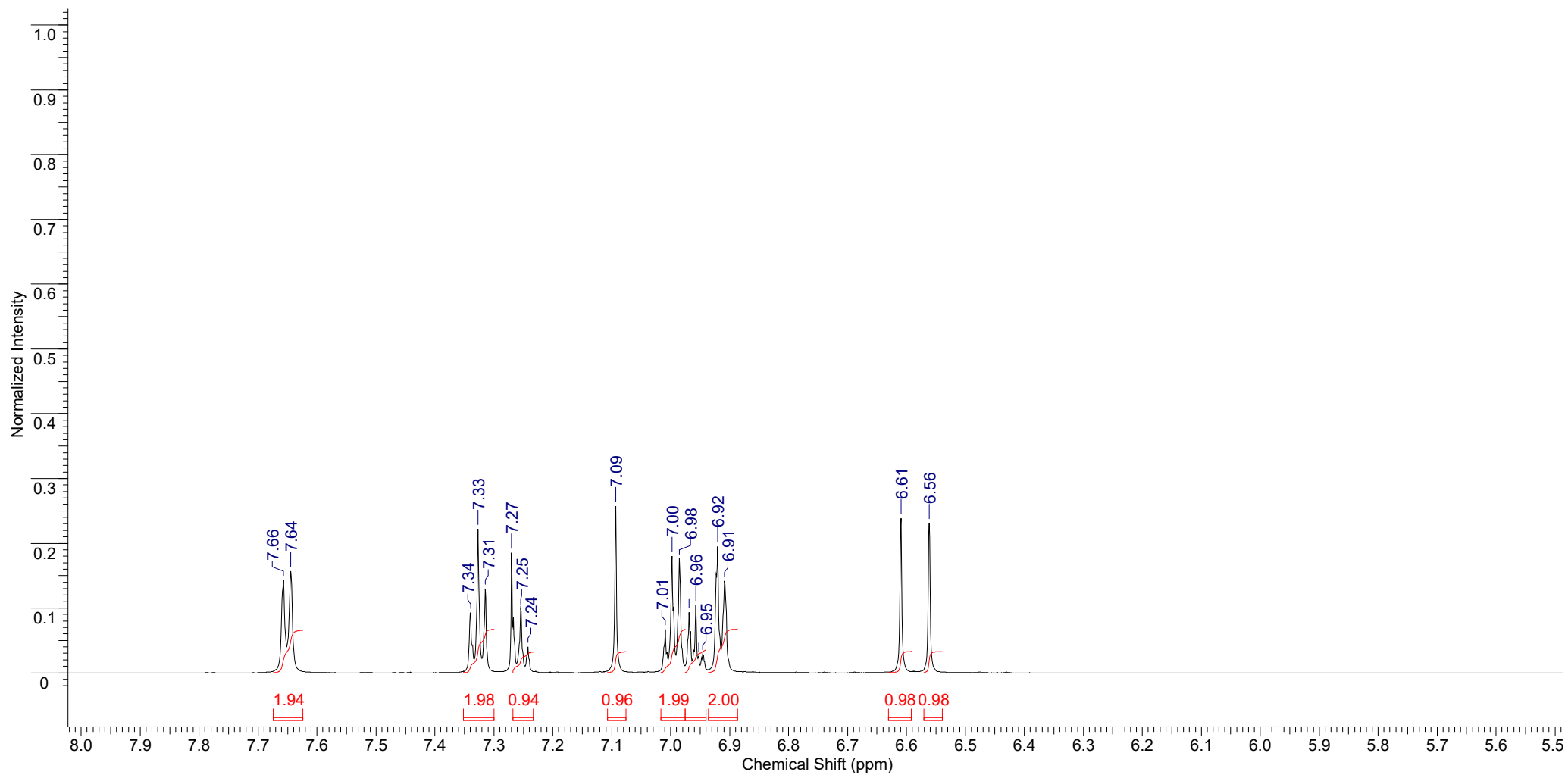
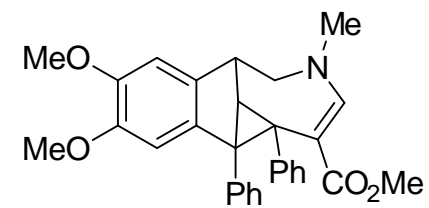
Methyl 6,7-dimethoxy-2-methyl-4a,4b-diphenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[a]cyclopropa[cd]azulene-4-carboxylate (2k)



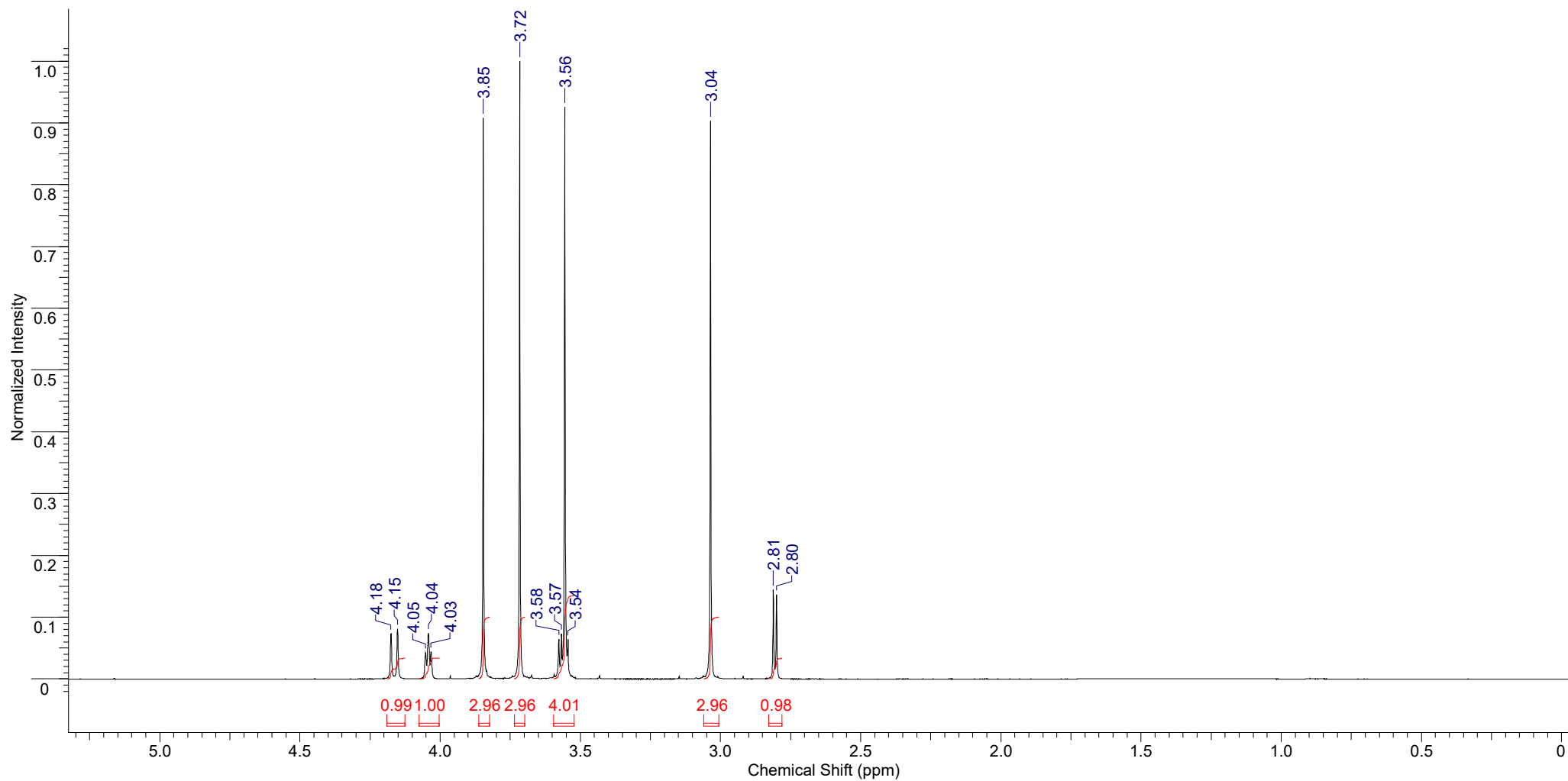
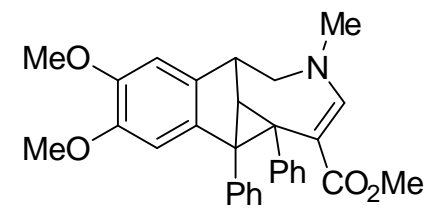
<sup>1</sup>H NMR spectra for 2k.



<sup>1</sup>H NMR spectra for 2k.

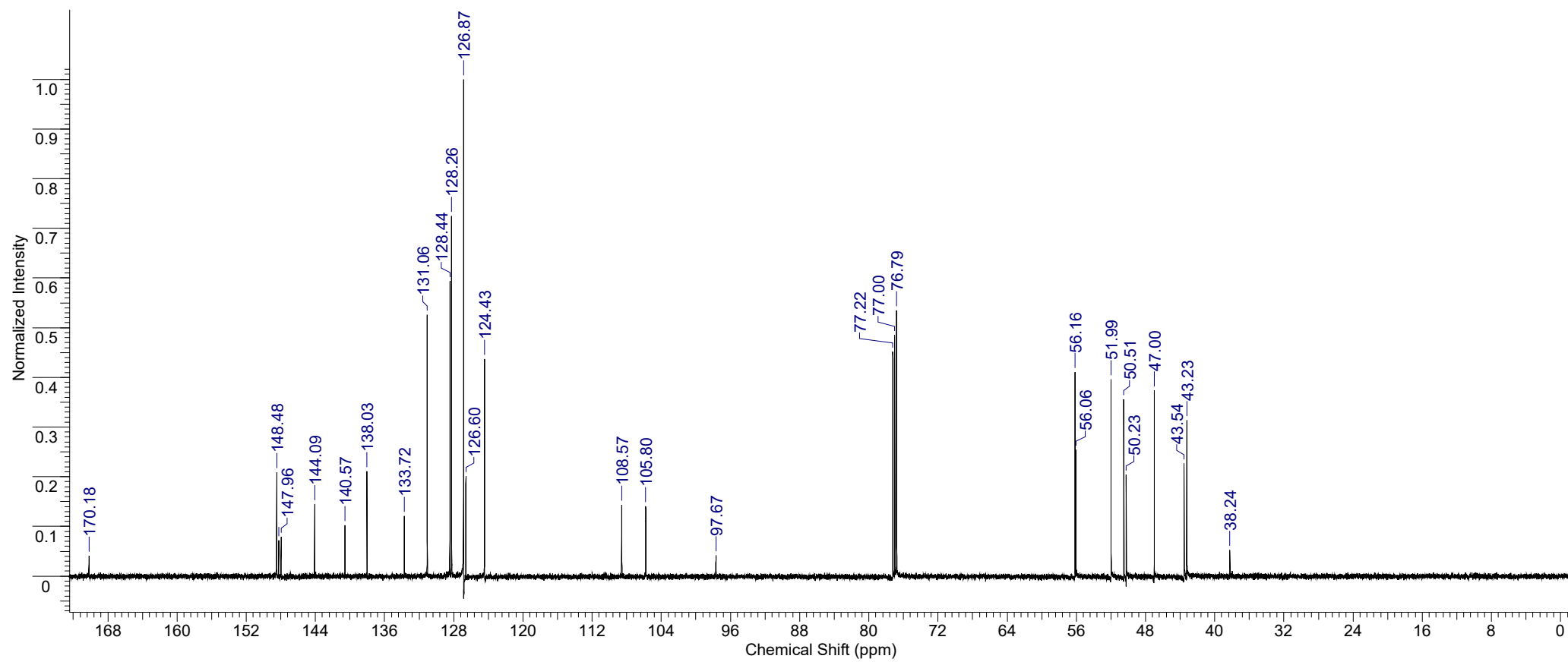
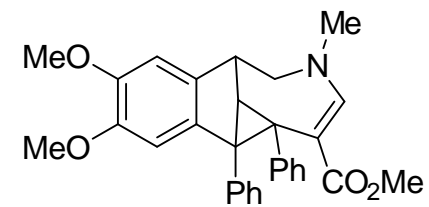


<sup>1</sup>H NMR spectra for 2k.

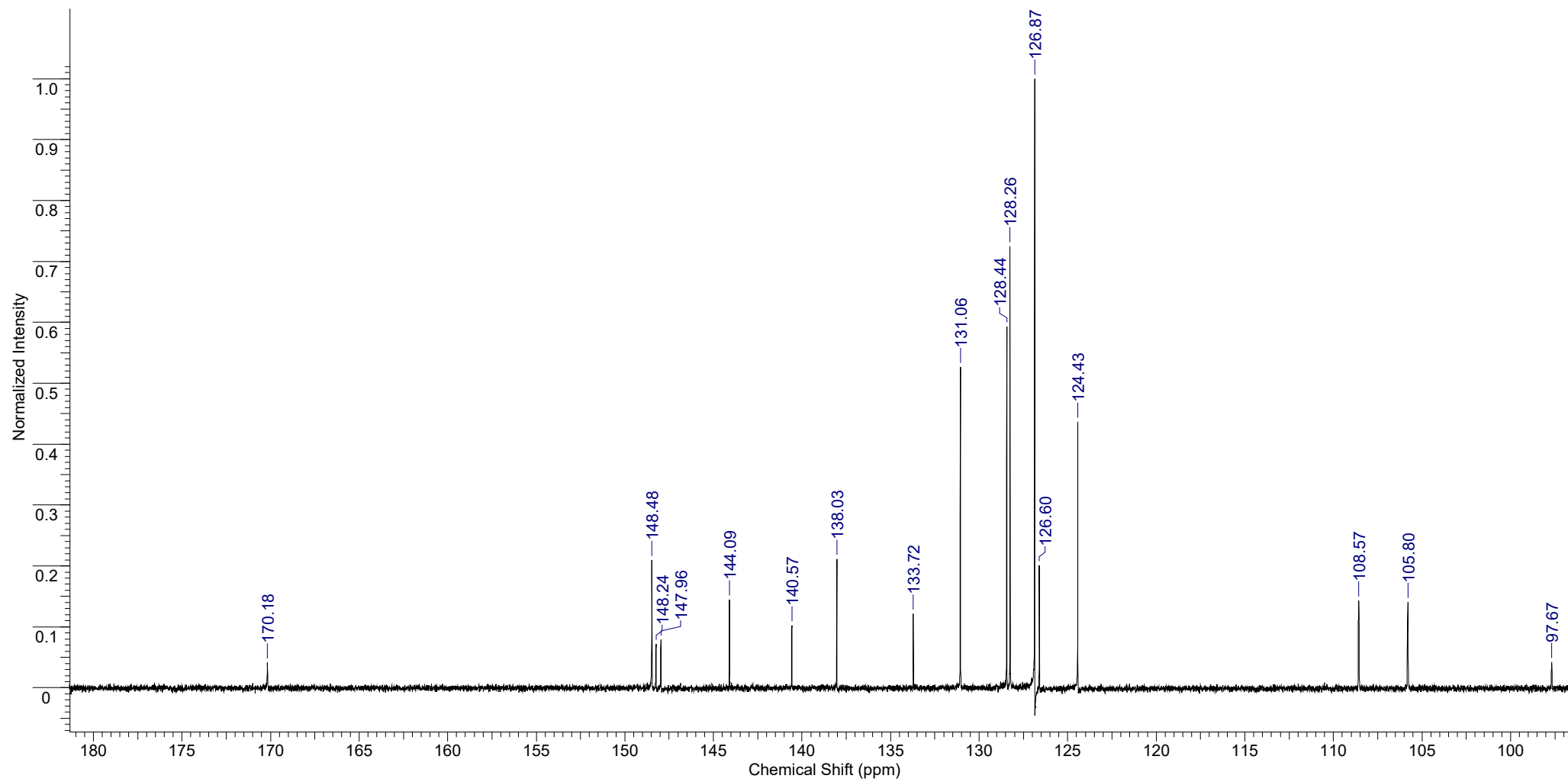
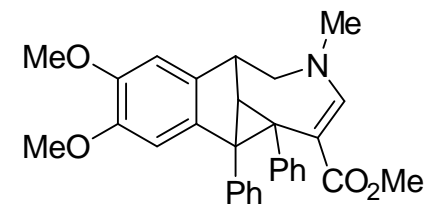




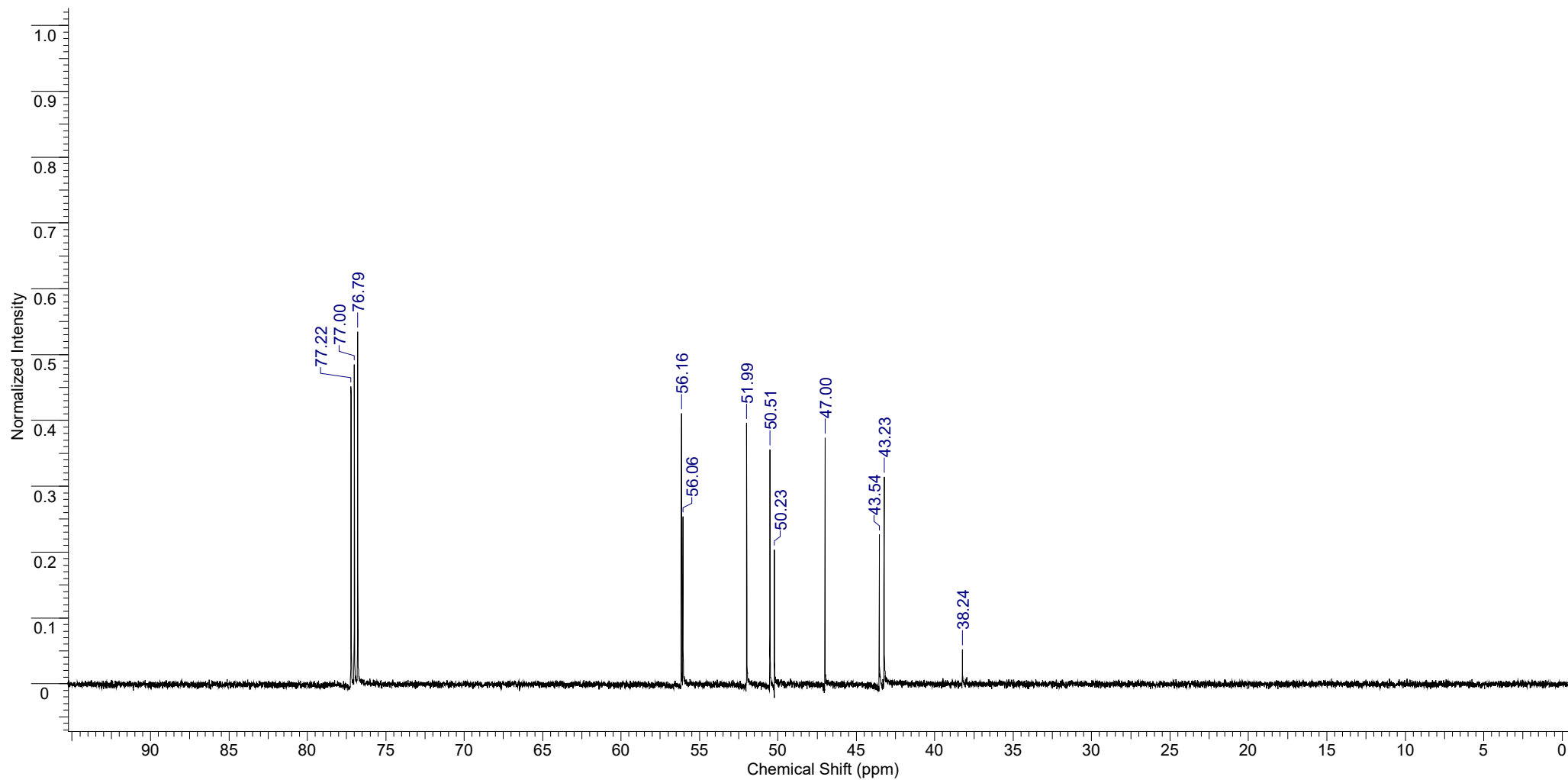
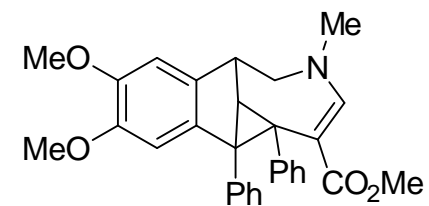
<sup>13</sup>C NMR spectra for 2k.



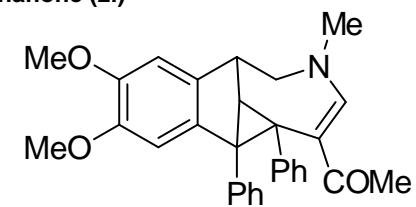
<sup>13</sup>C NMR spectra for 2k.



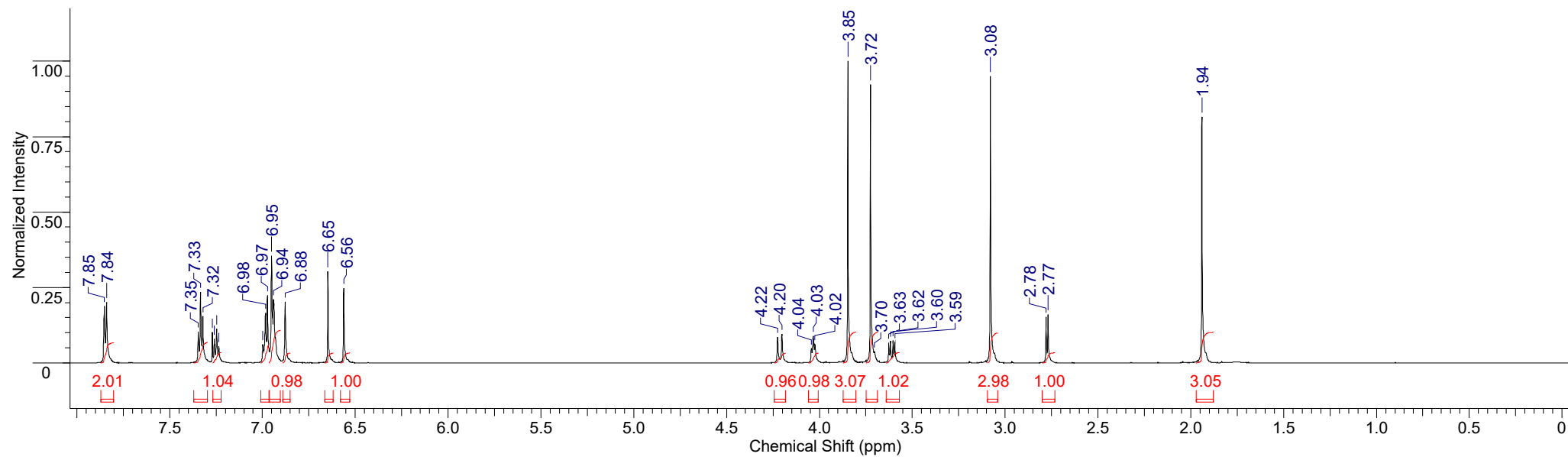
<sup>13</sup>C NMR spectra for 2k.



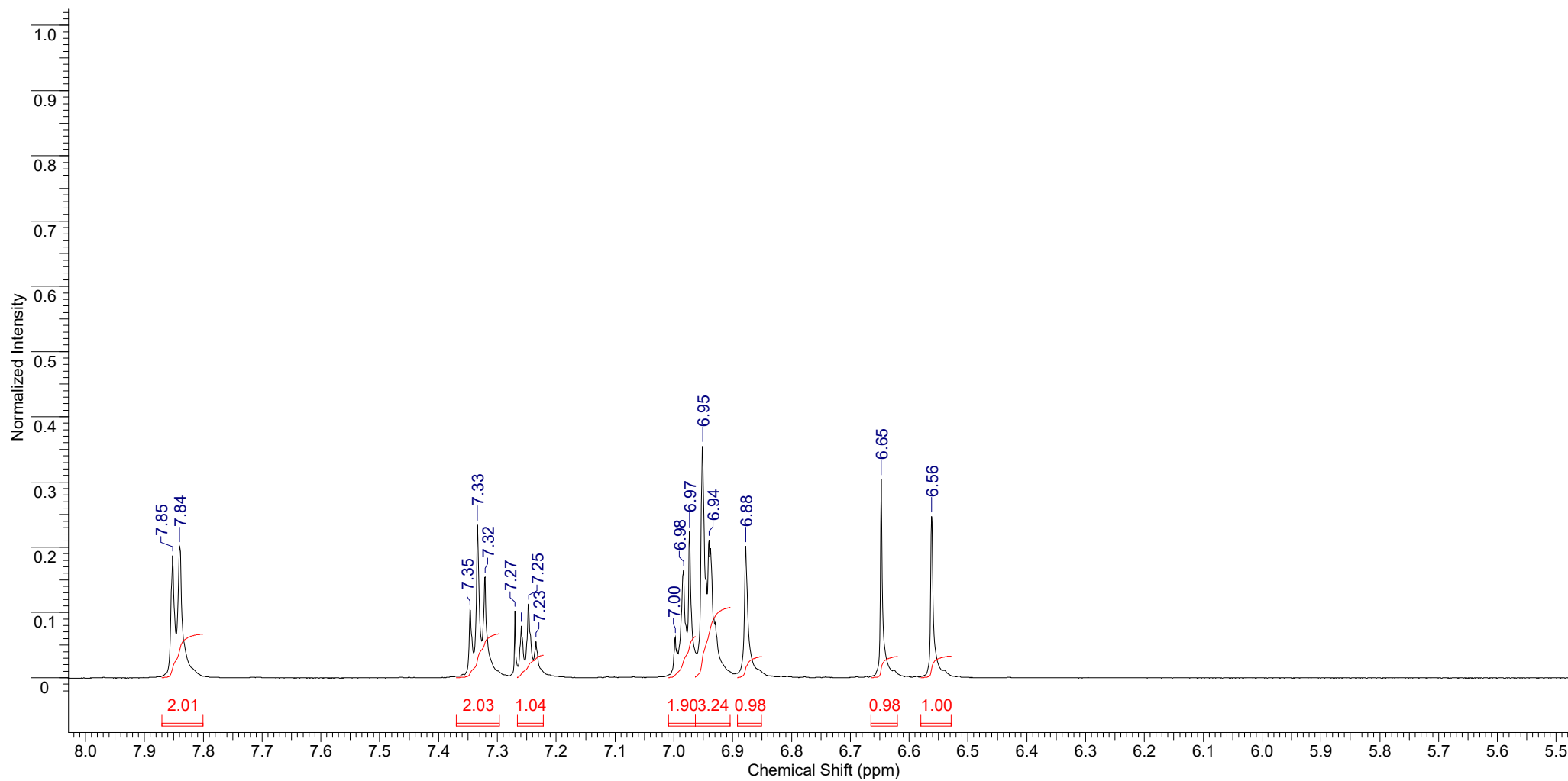
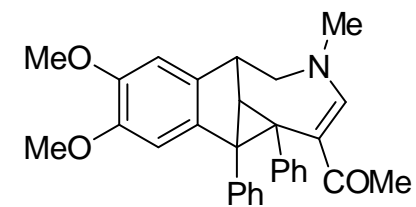
1-(6,7-Dimethoxy-2-methyl-4a,4b-diphenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[*a*]cyclopropa[*cd*]azulen-4-yl)ethanone (2l)



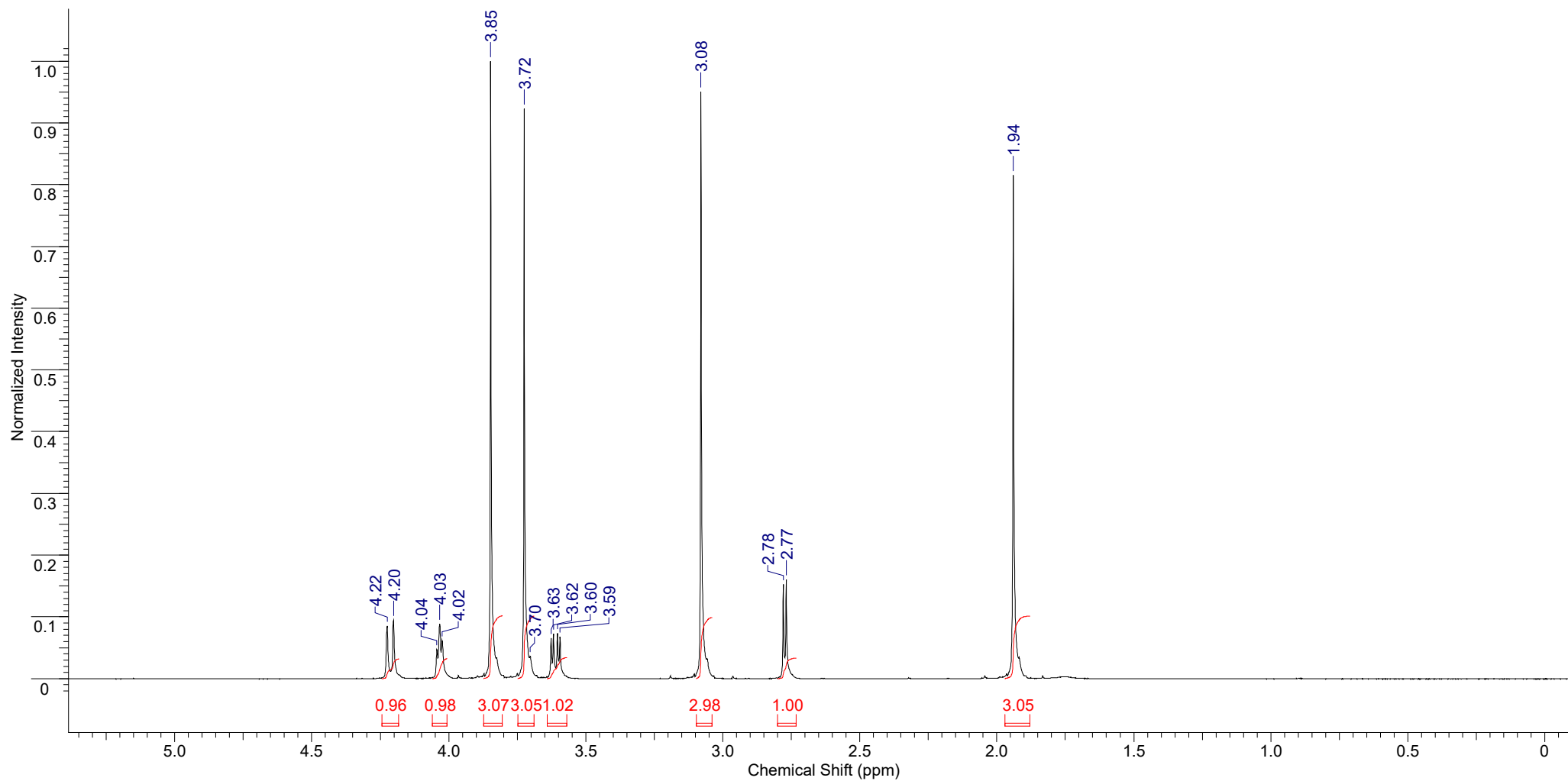
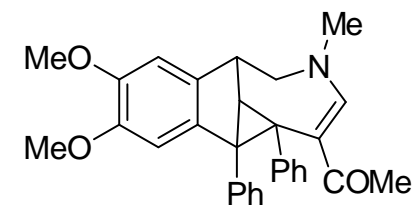
$^1\text{H}$  NMR spectra for 2l.



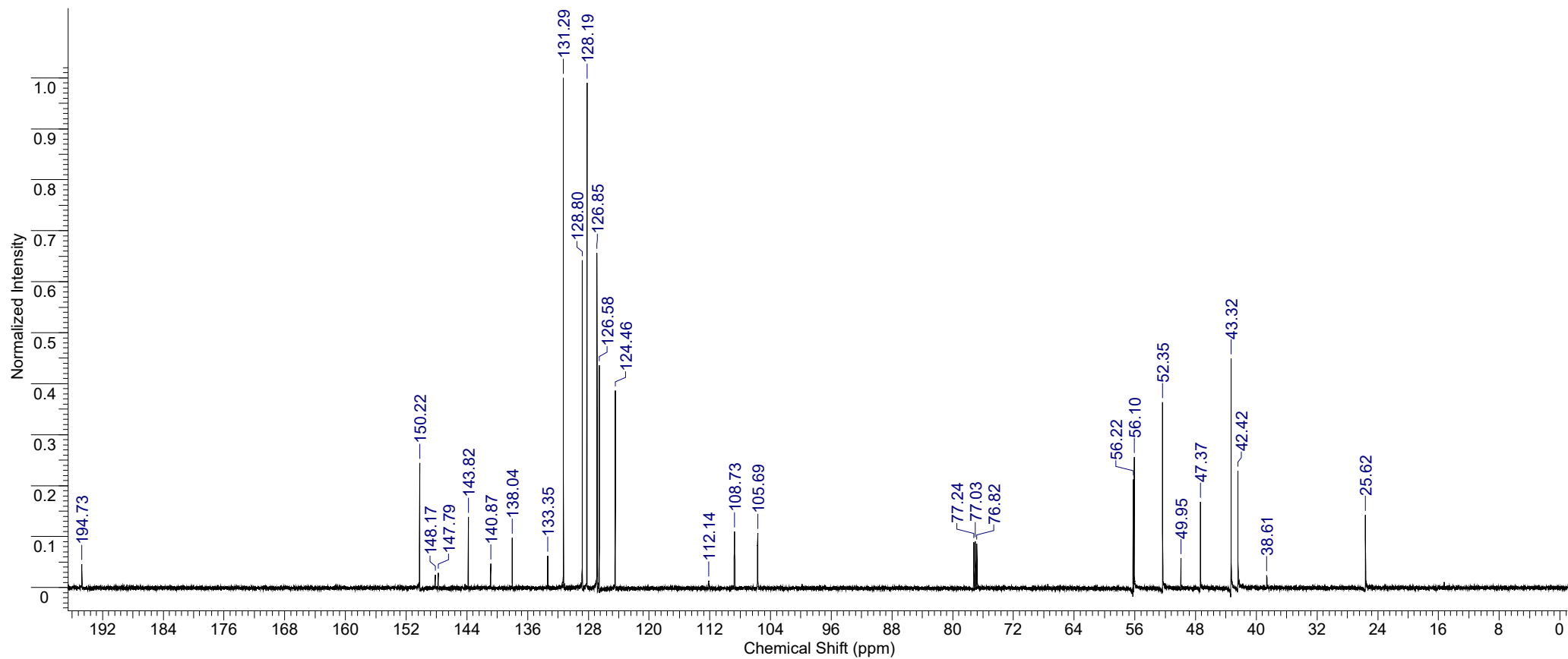
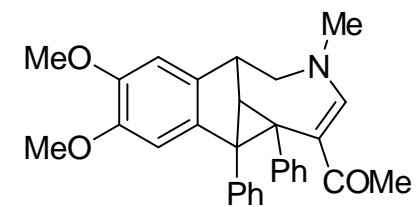
<sup>1</sup>H NMR spectra for 2l.



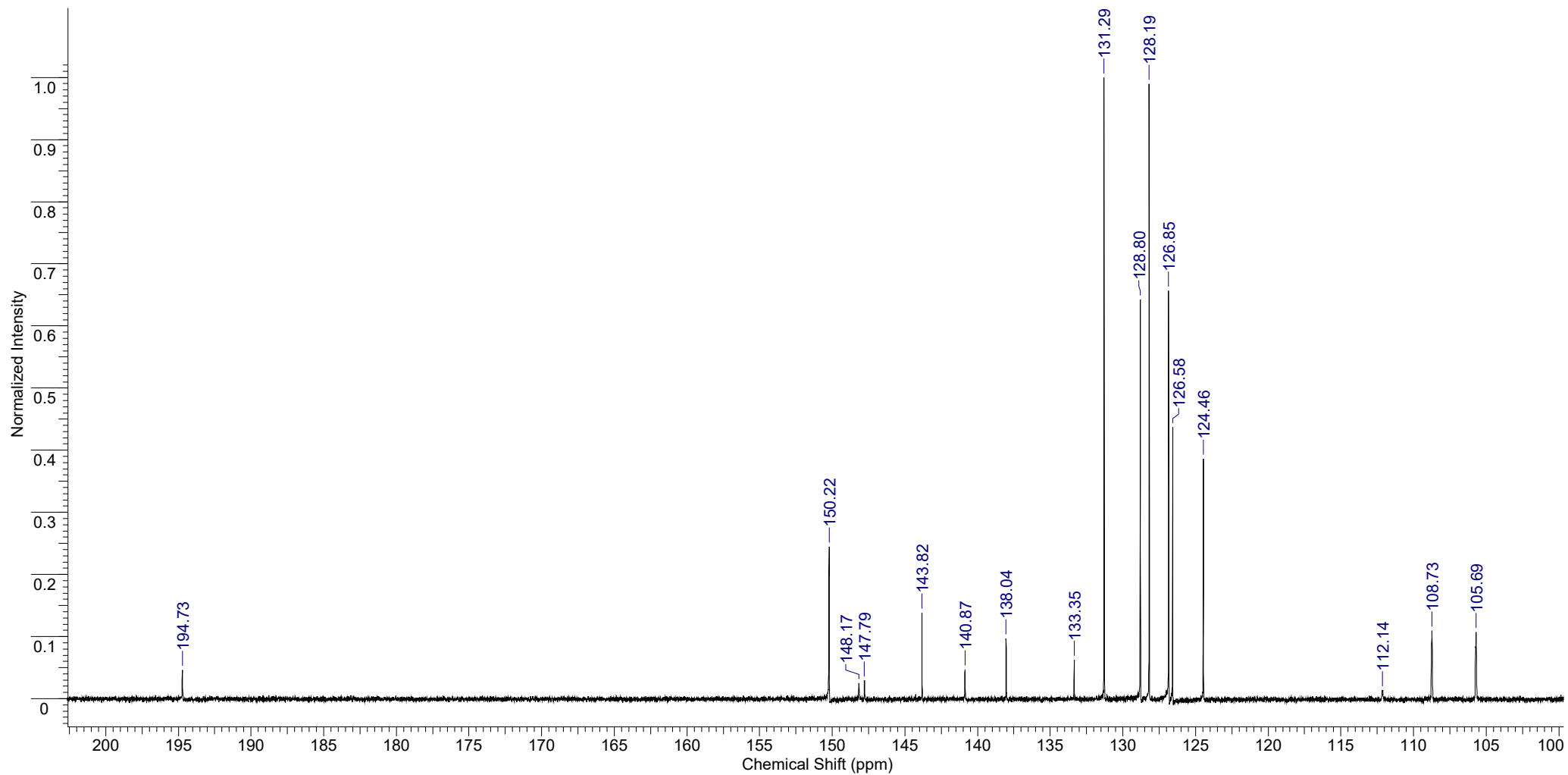
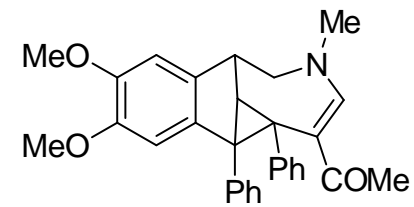
<sup>1</sup>H NMR spectra for 2l.



<sup>13</sup>C NMR spectra for 2l.

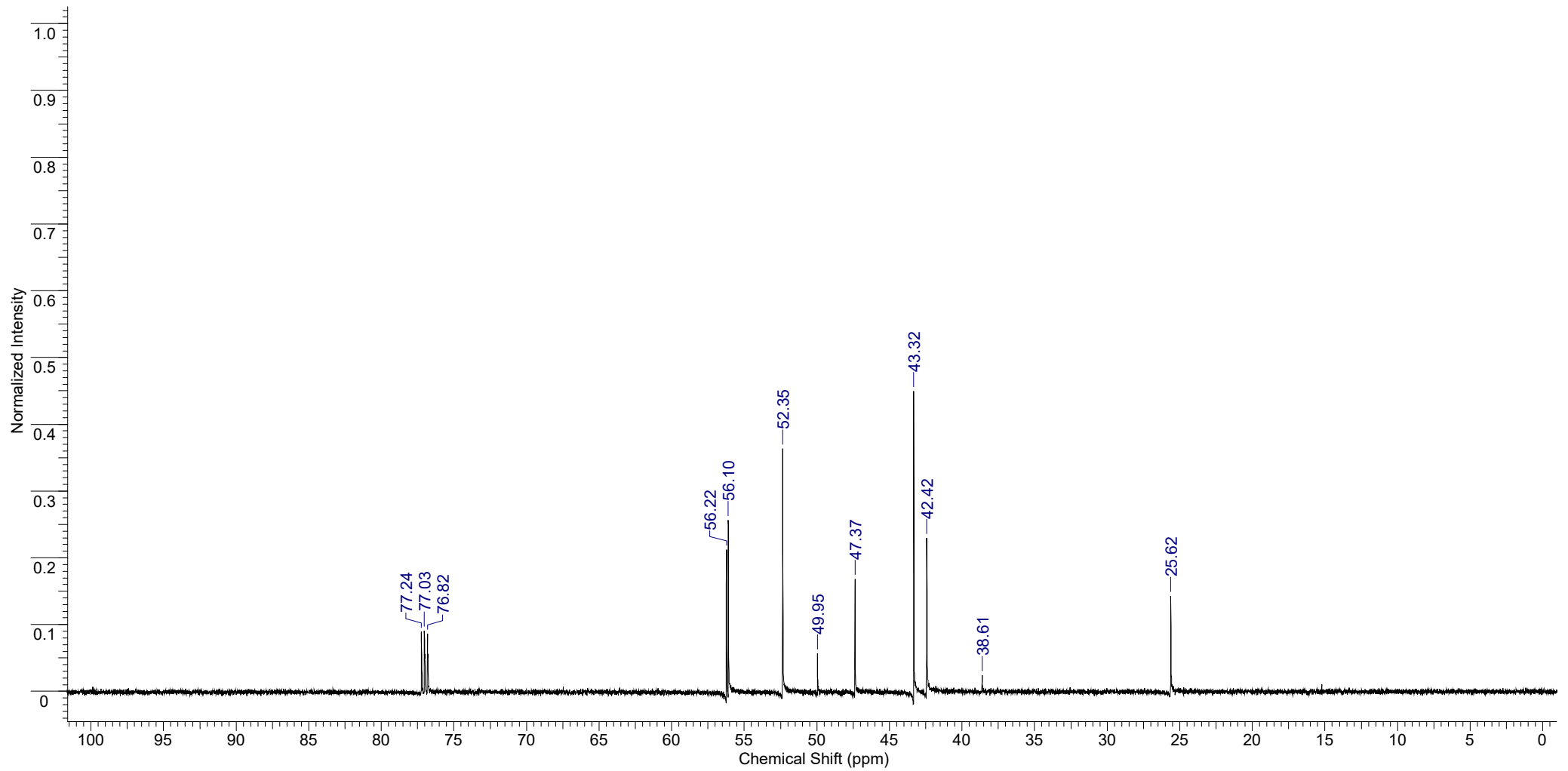
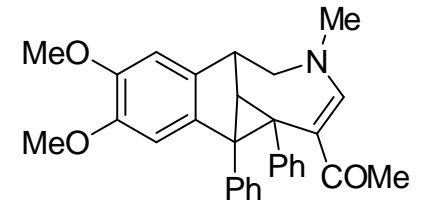


<sup>13</sup>C NMR spectra for 2l.



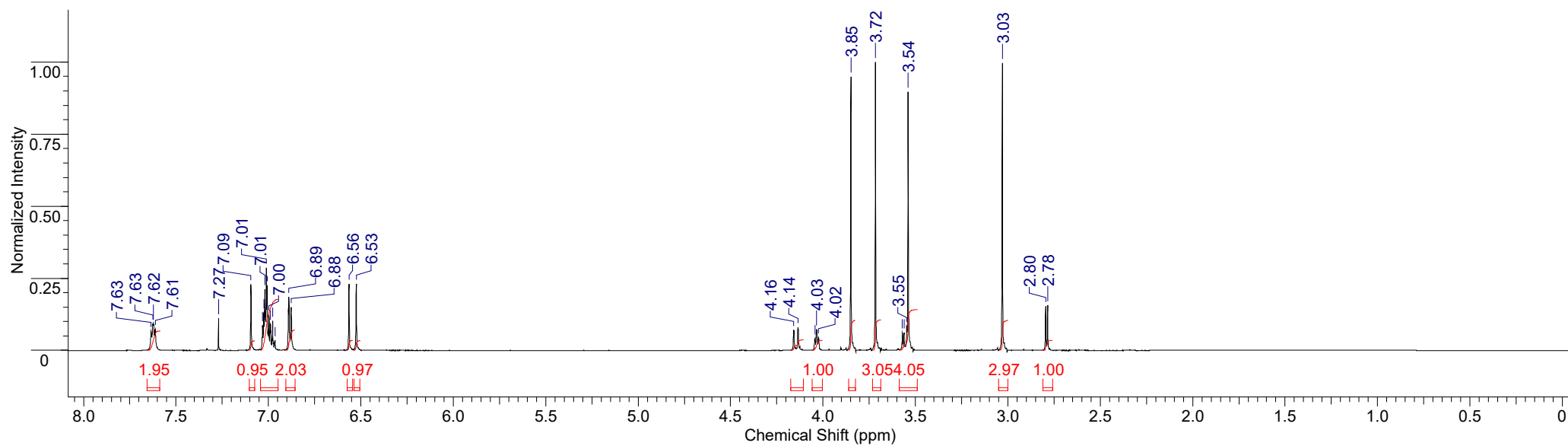
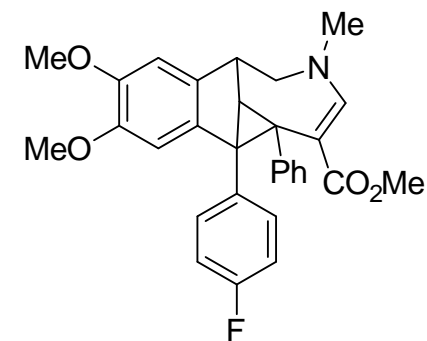


<sup>13</sup>C NMR spectra for 2l.

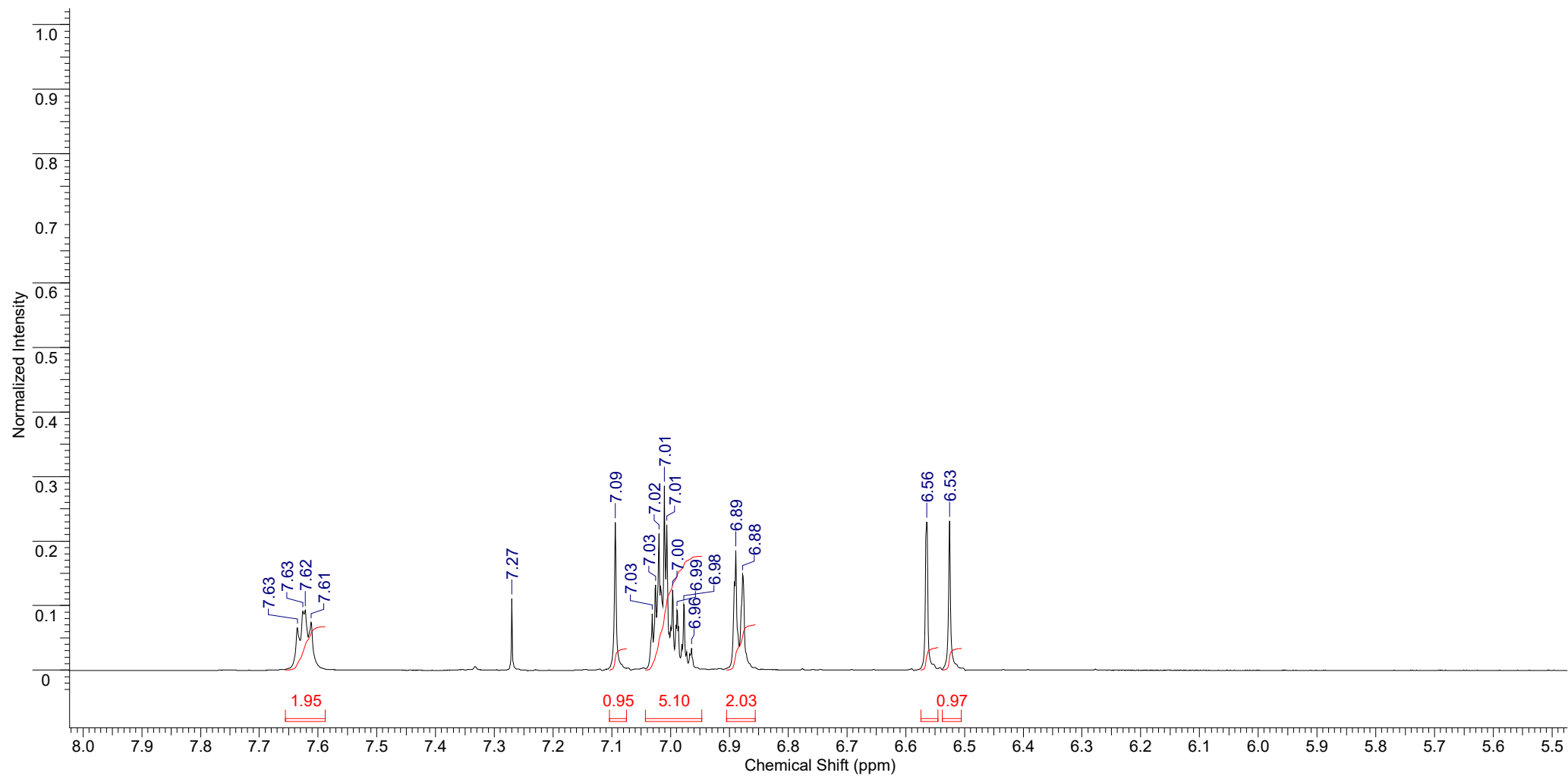
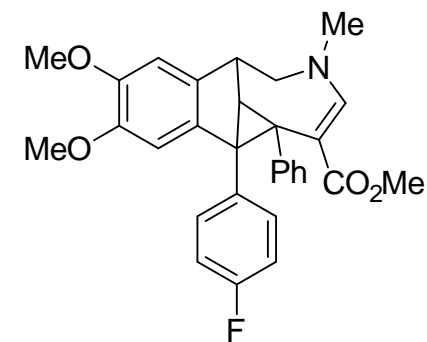


Methyl 4b-(4-fluorophenyl)-6,7-dimethoxy-2-methyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzocyclopropa[cd]azulene-4-carboxylate (2m)

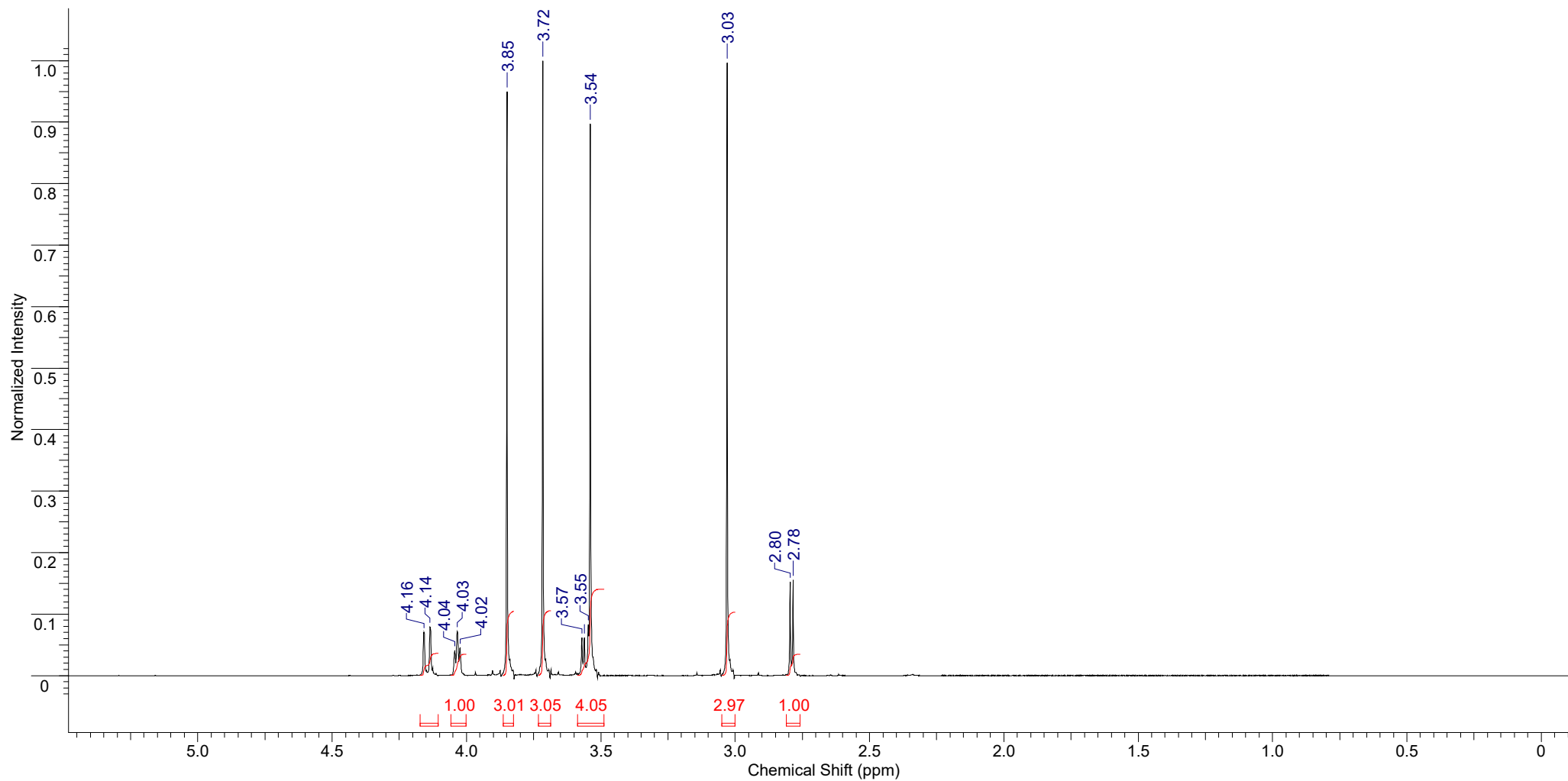
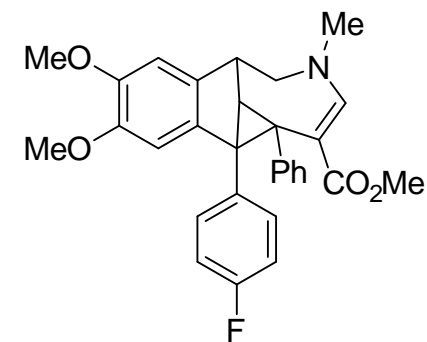
$^1\text{H}$  NMR spectra for 2m.



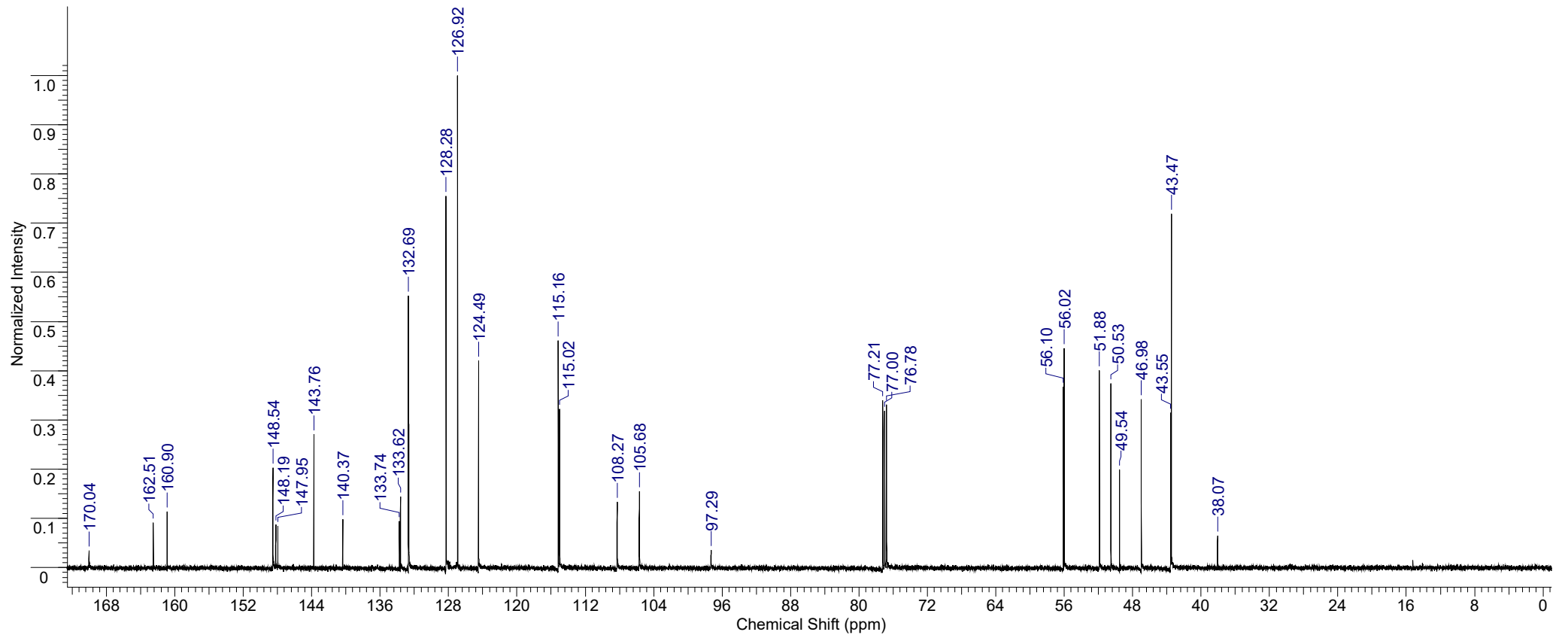
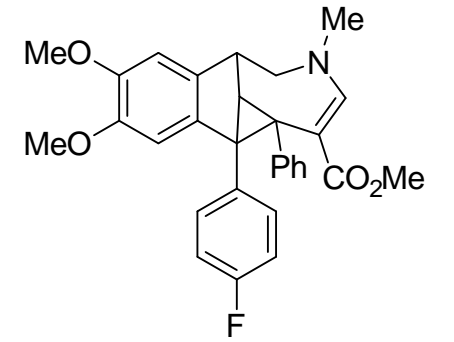
<sup>1</sup>H NMR spectra for 2m.



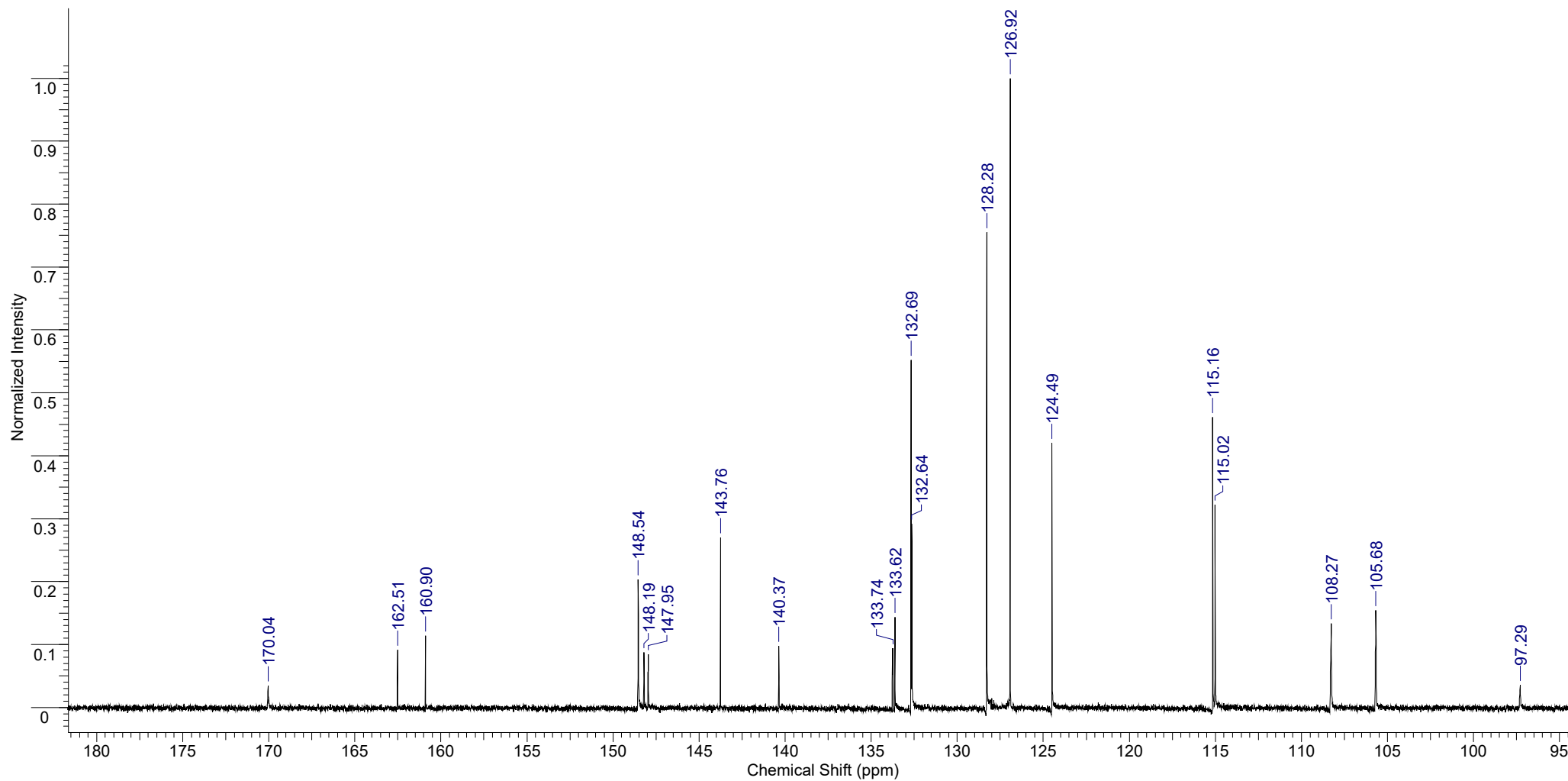
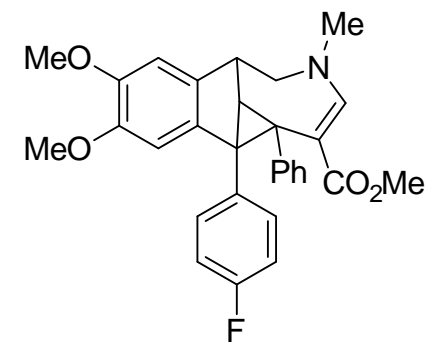
<sup>1</sup>H NMR spectra for 2m.



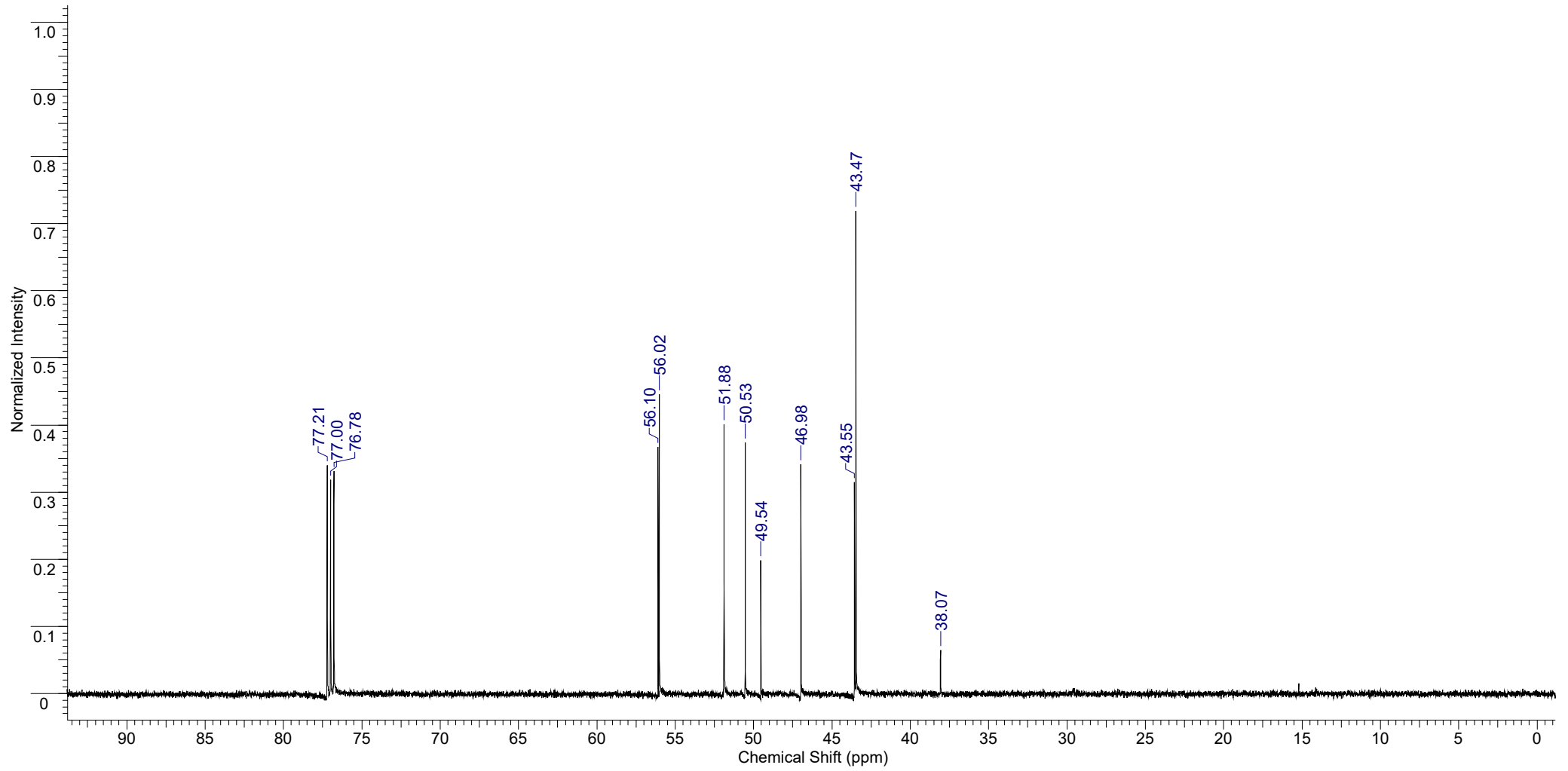
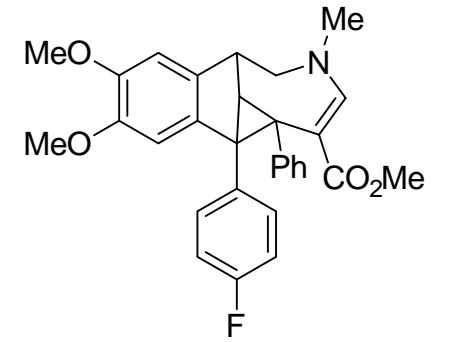
<sup>13</sup>C NMR spectra for 2m.



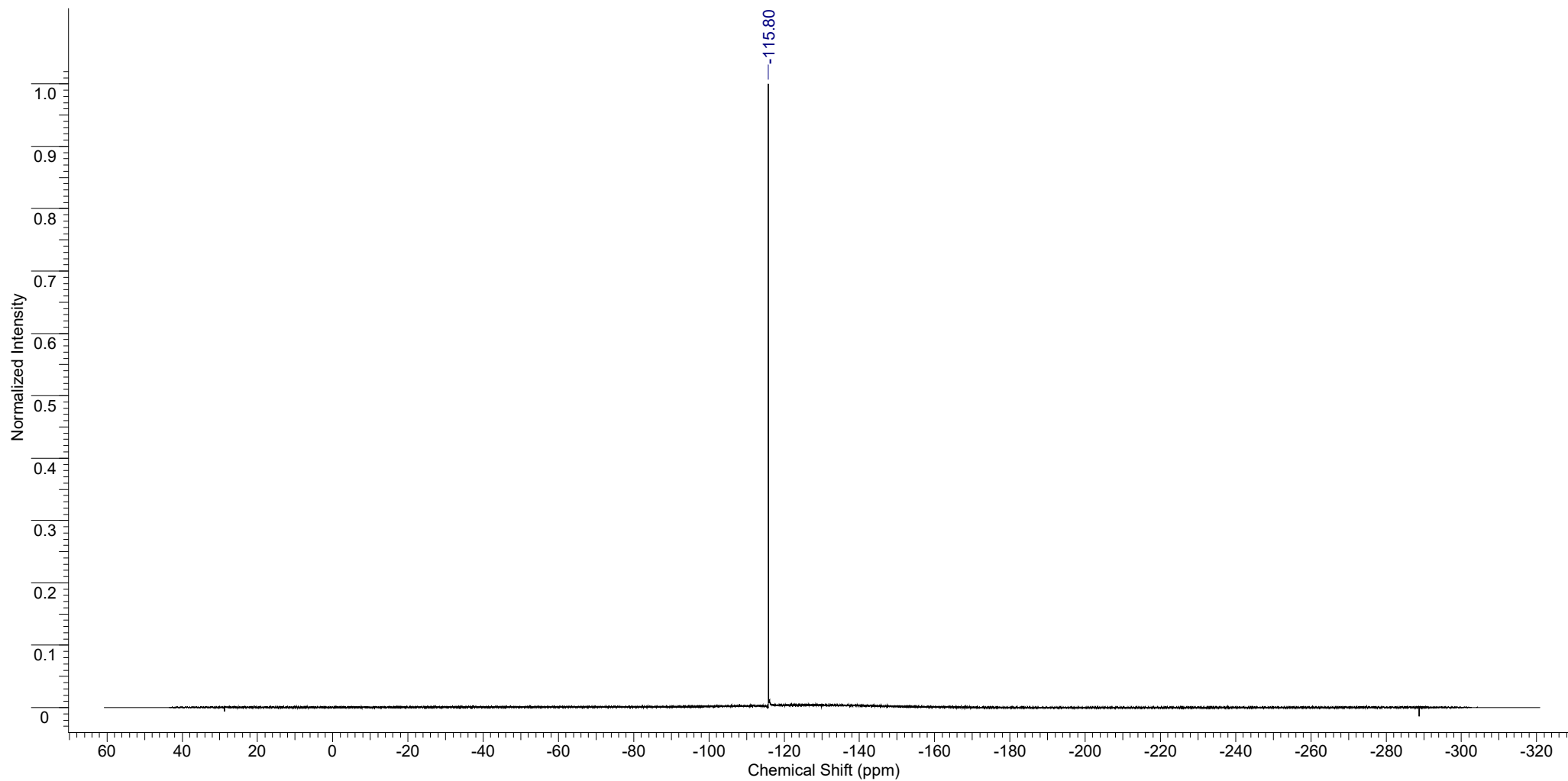
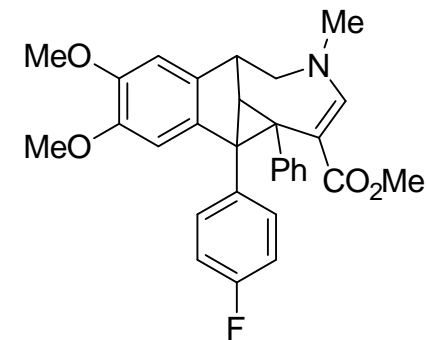
<sup>13</sup>C NMR spectra for 2m.



<sup>13</sup>C NMR spectra for 2m.

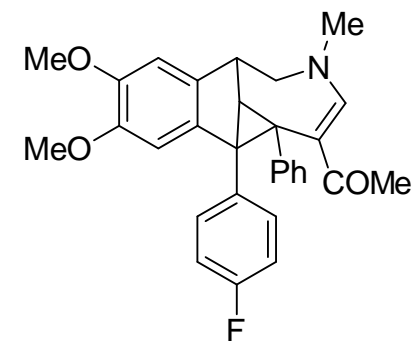


**<sup>19</sup>F NMR spectra for 2m.**

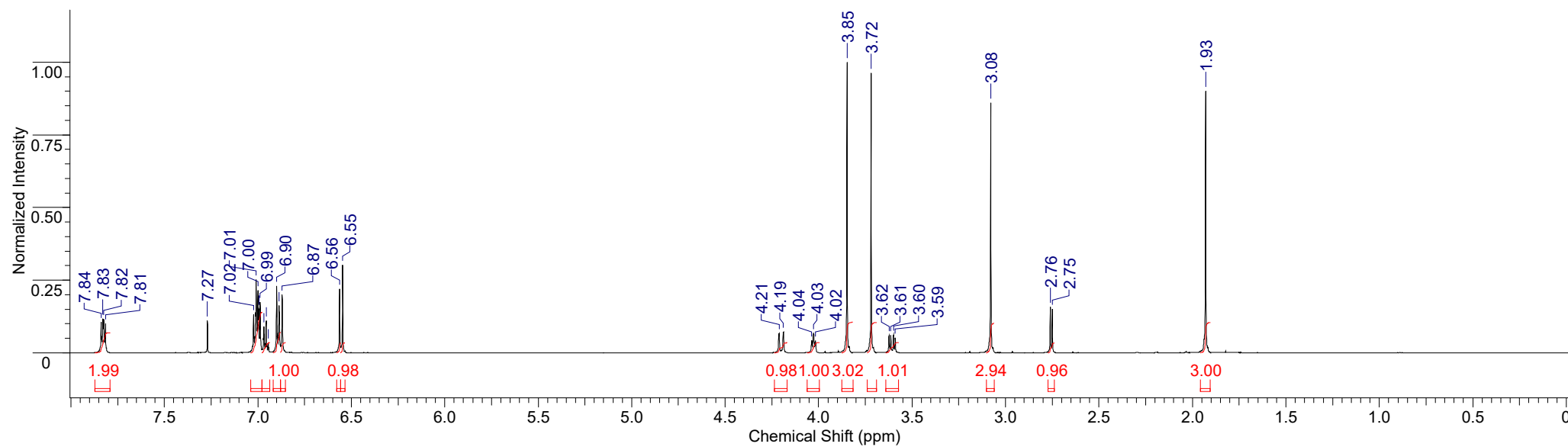




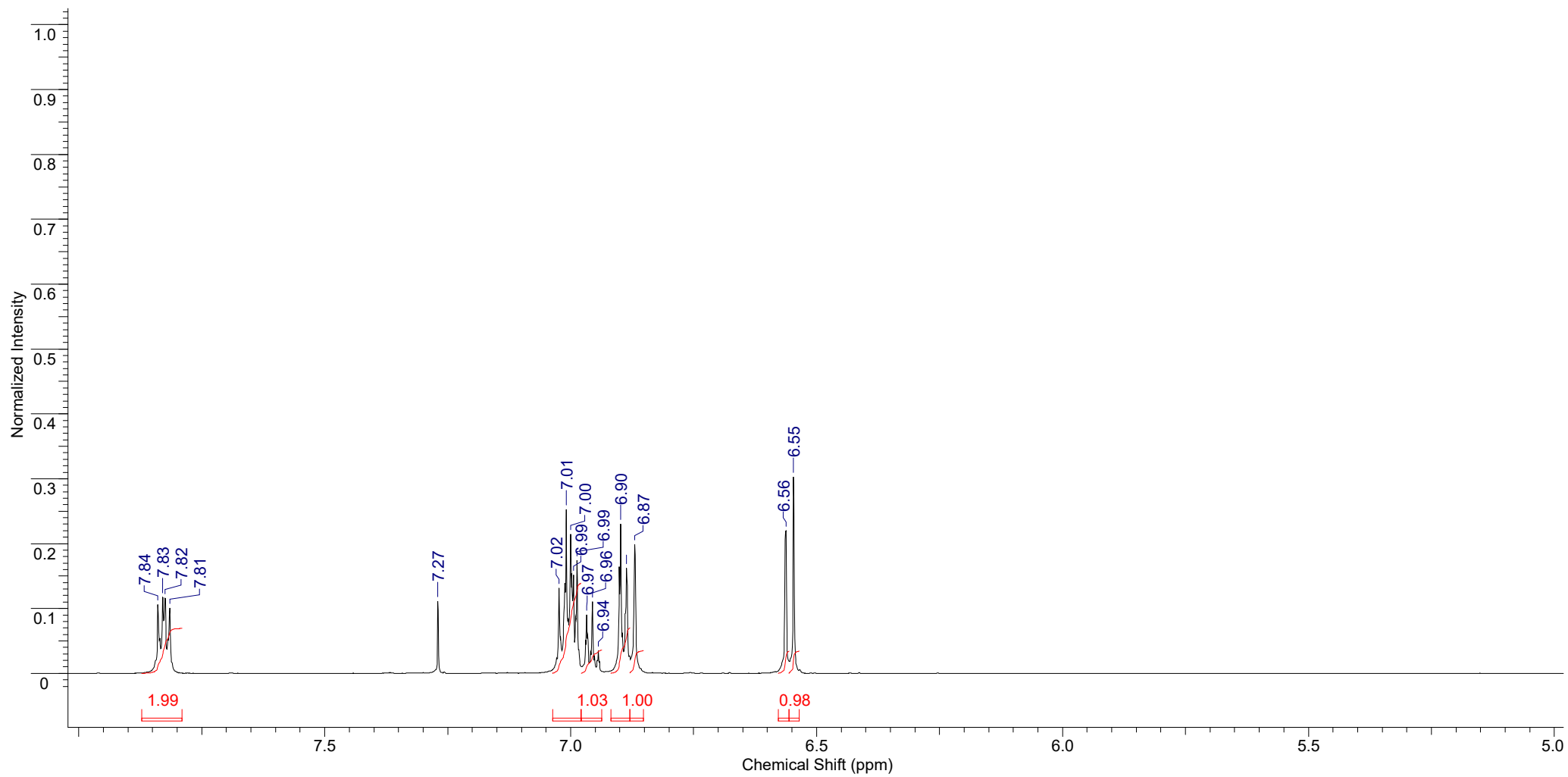
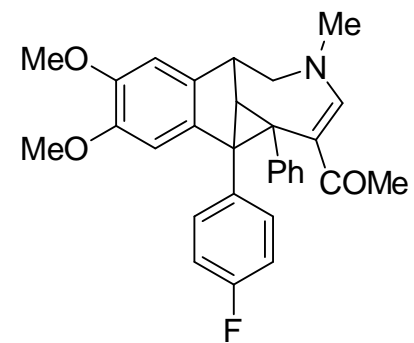
1-[4b-(4-Fluorophenyl)-6,7-dimethoxy-2-methyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzocyclopropa[cd]azulen-4-yl]ethanone (2n)



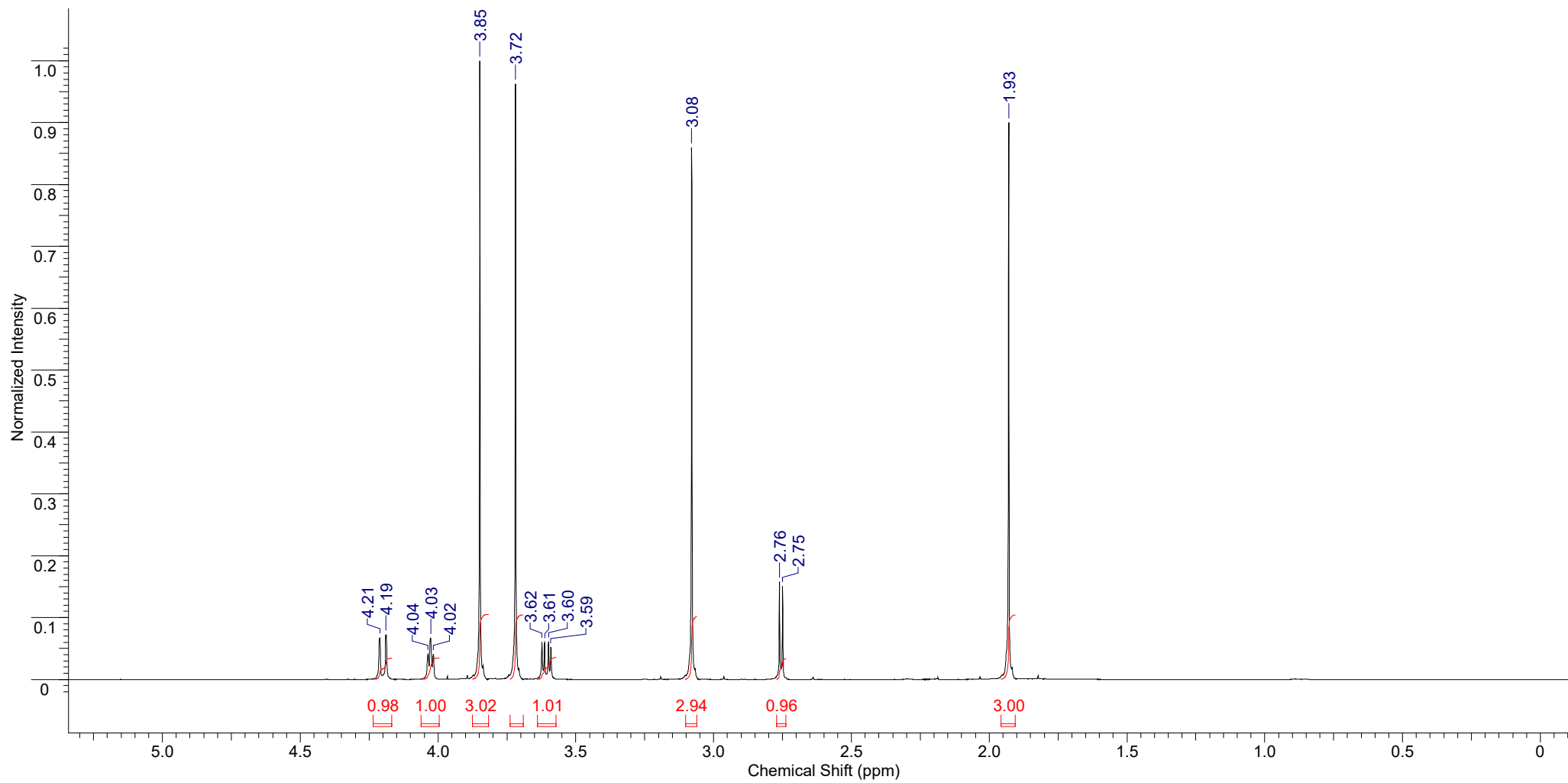
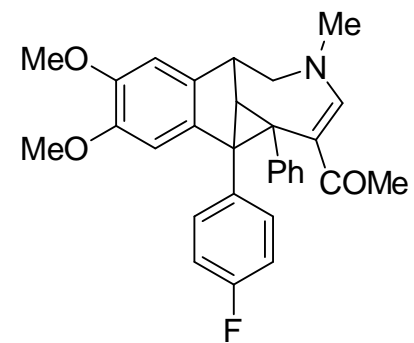
$^1\text{H}$  NMR spectra for 2n.



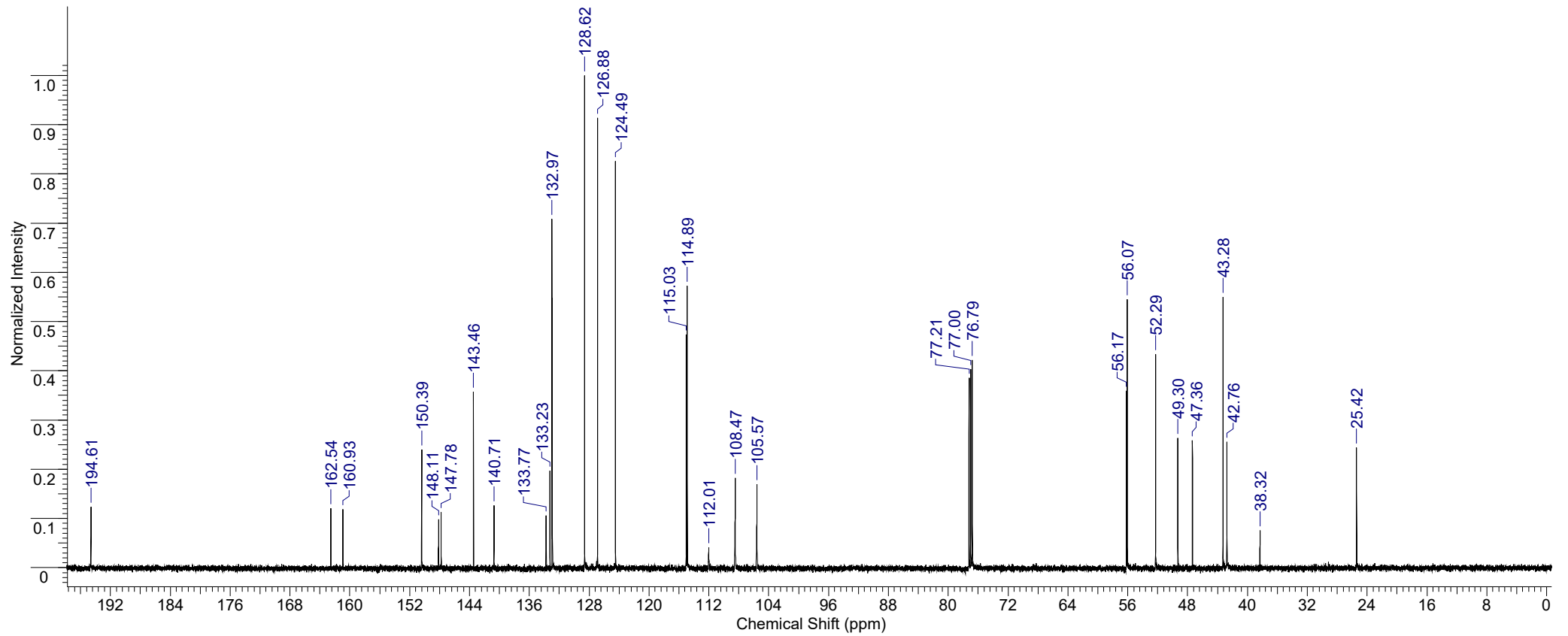
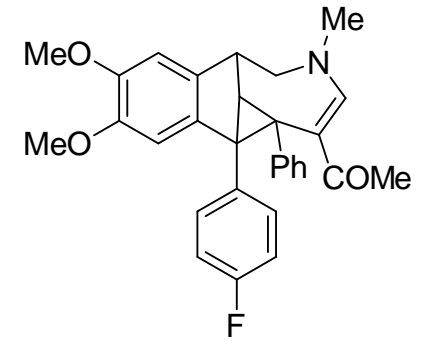
<sup>1</sup>H NMR spectra for 2n.



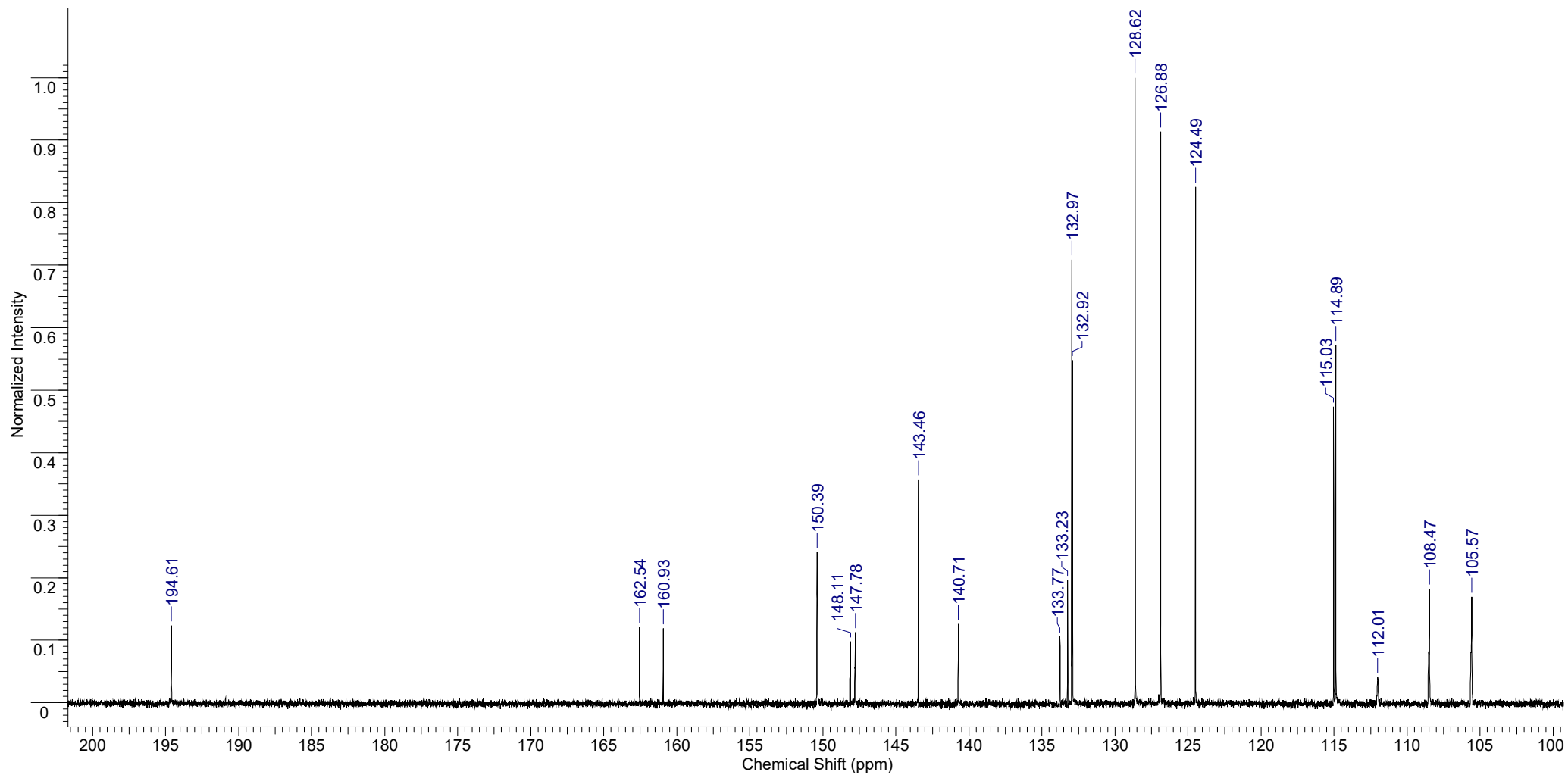
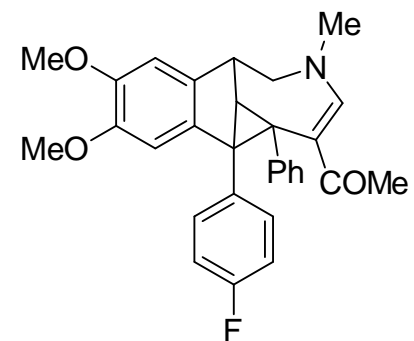
<sup>1</sup>H NMR spectra for 2n.



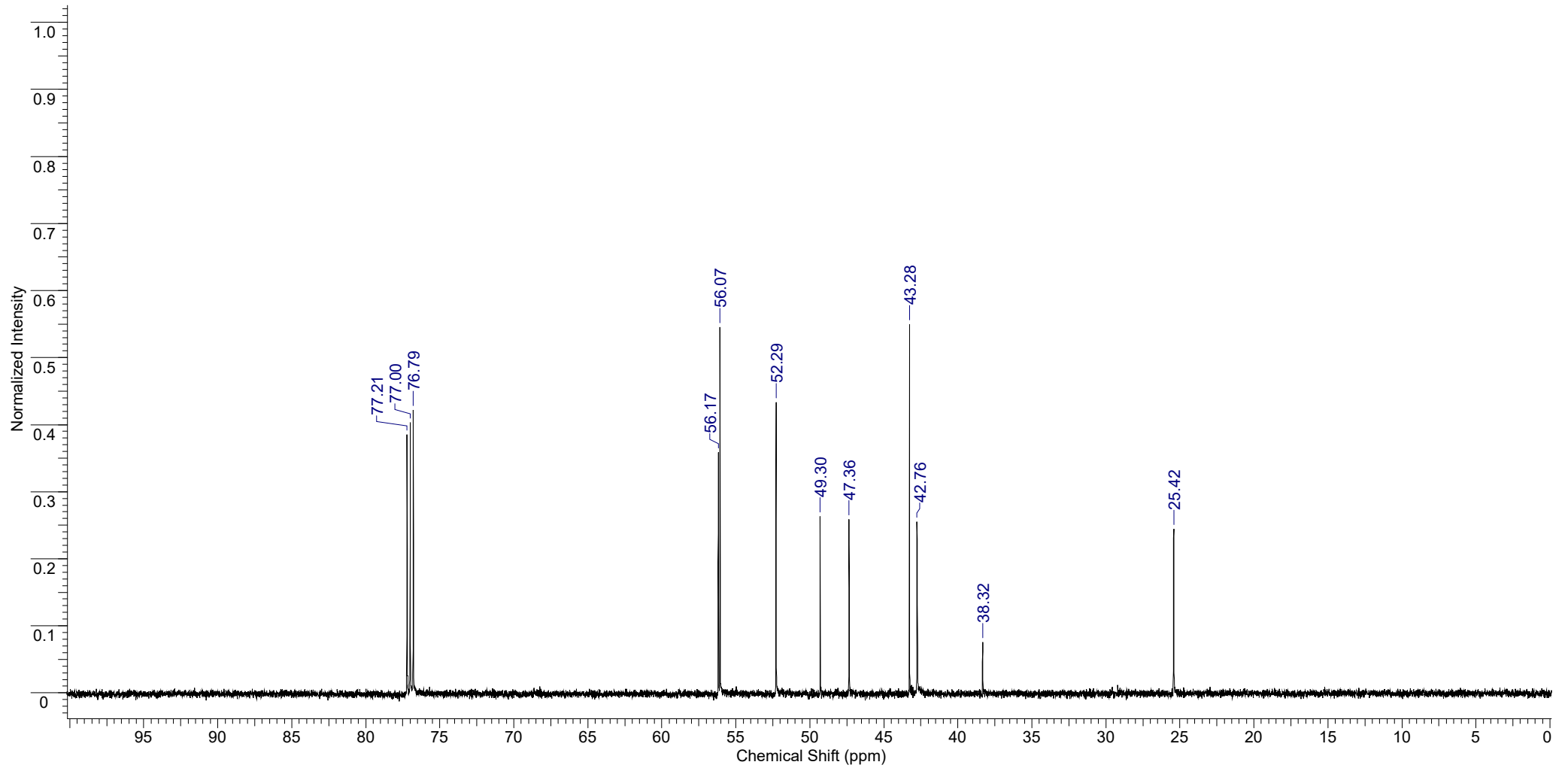
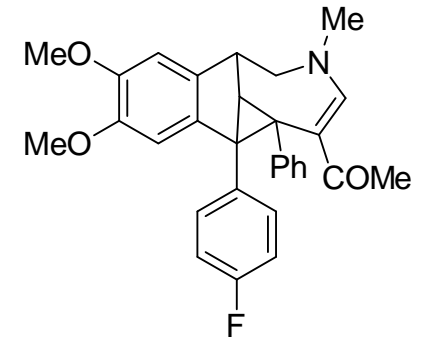
<sup>13</sup>C NMR spectra for 2n.



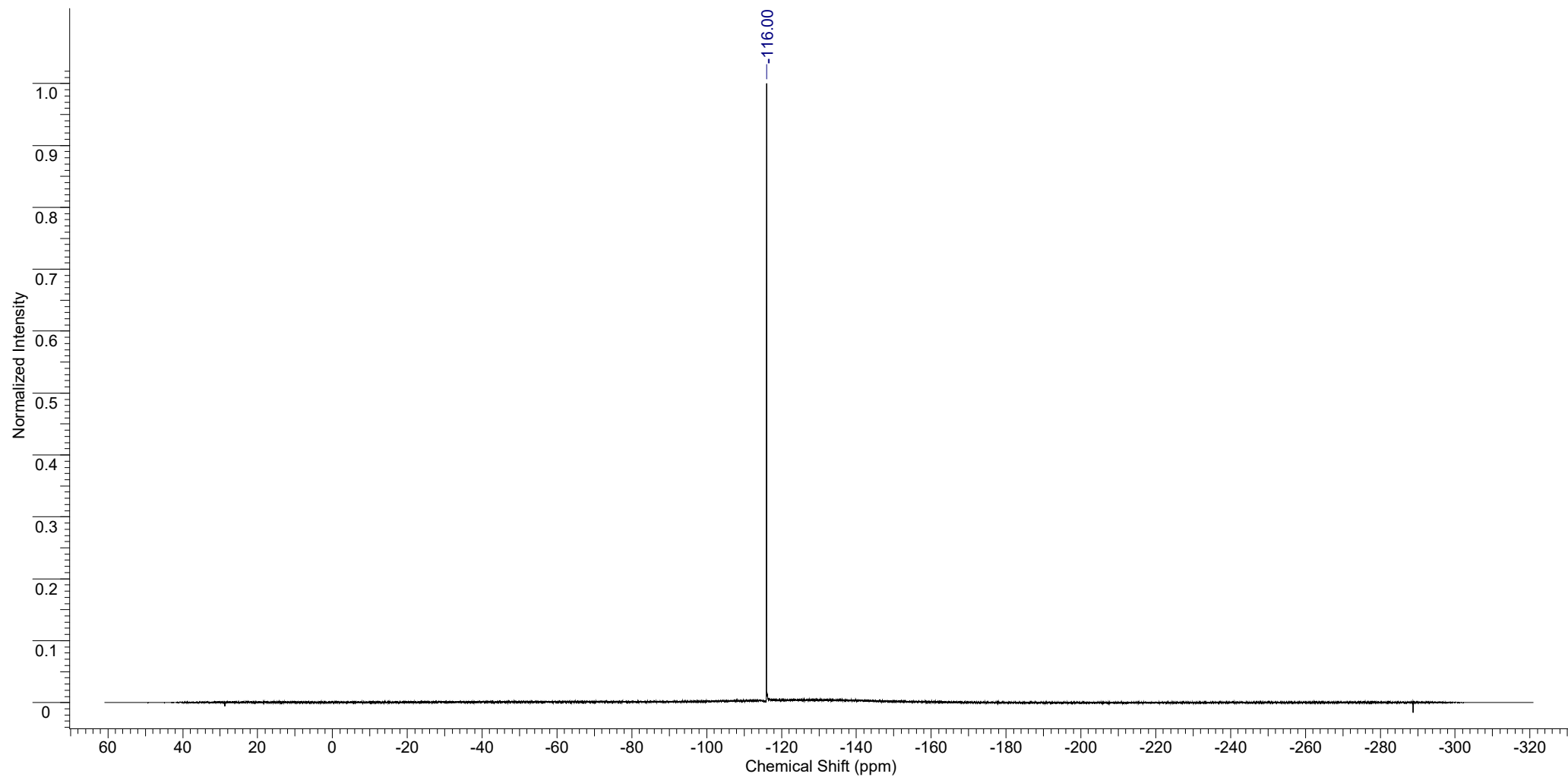
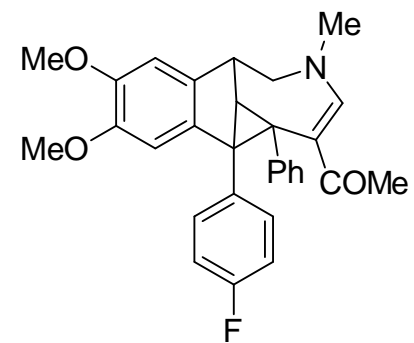
<sup>13</sup>C NMR spectra for 2n.



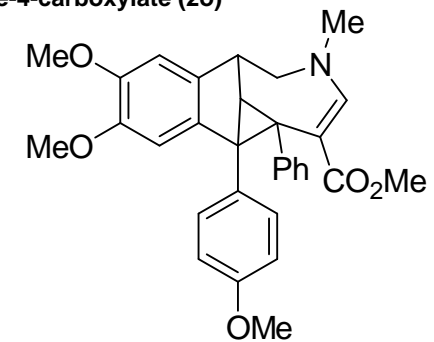
<sup>13</sup>C NMR spectra for 2n.



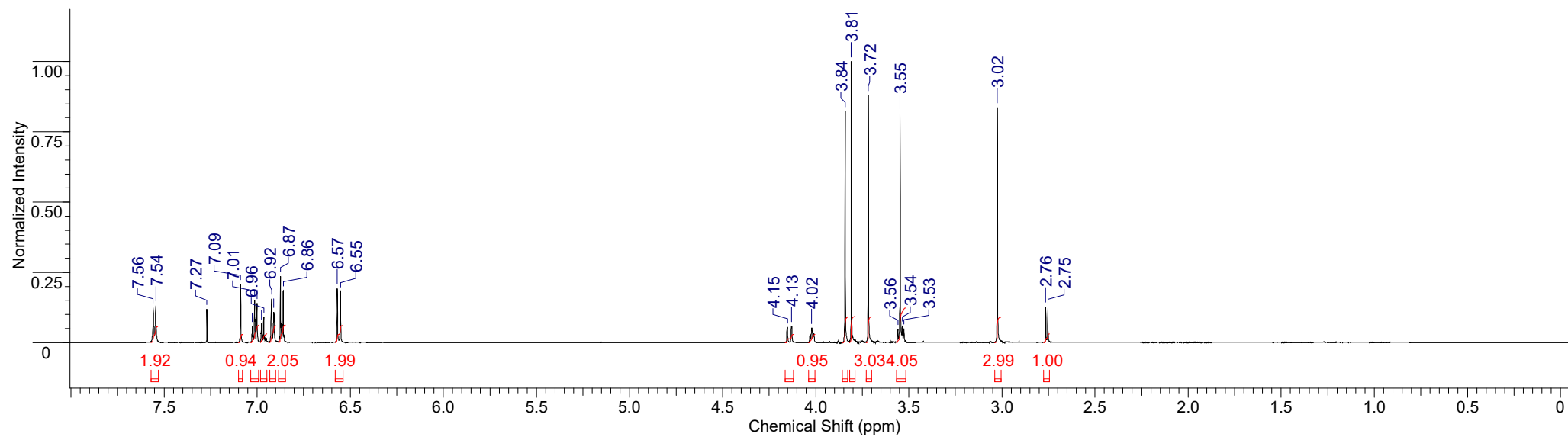
<sup>19</sup>F NMR spectra for 2n.



Methyl 6,7-dimethoxy-4b-(4-methoxyphenyl)-2-methyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[*a*]cyclopropa[*cd*]azulene-4-carboxylate (2o)

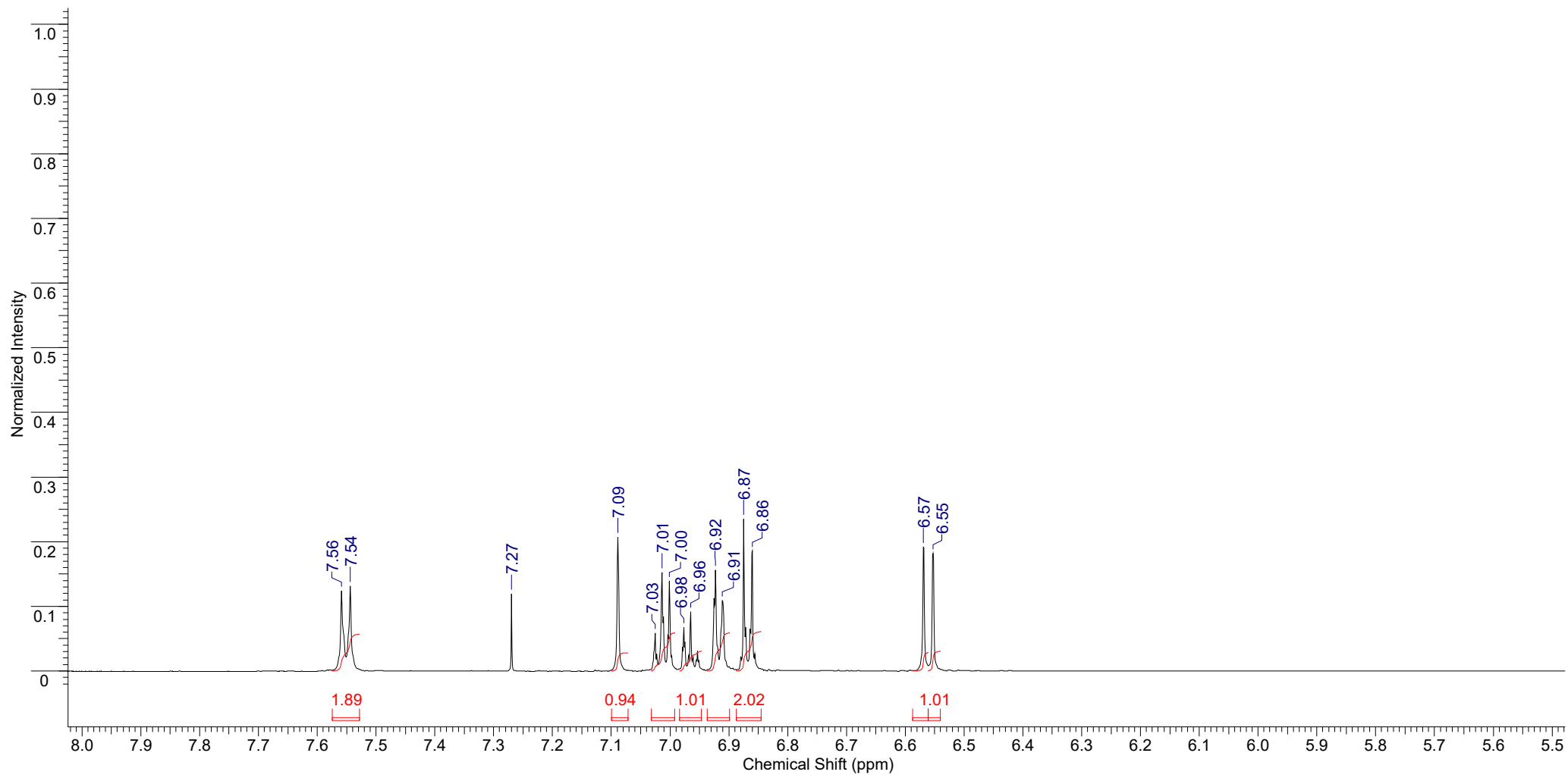
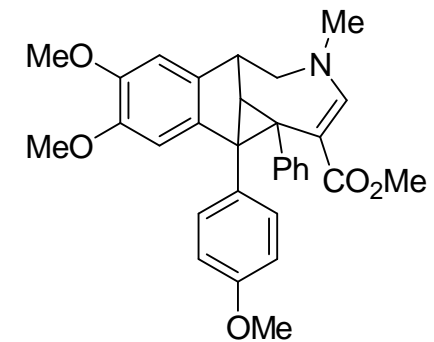


<sup>1</sup>H NMR spectra for 2o.

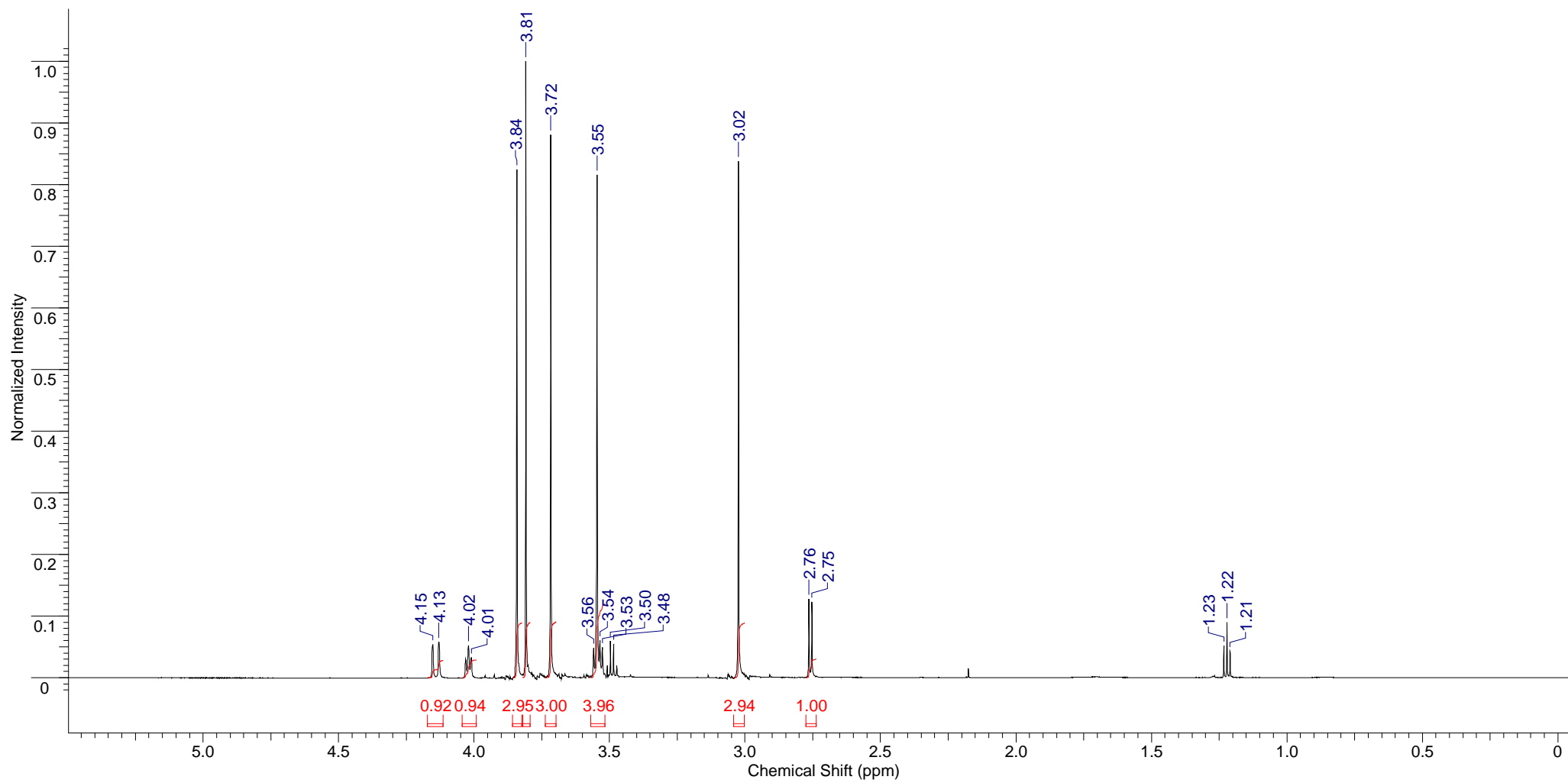
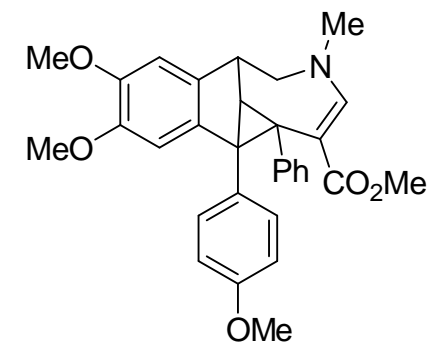




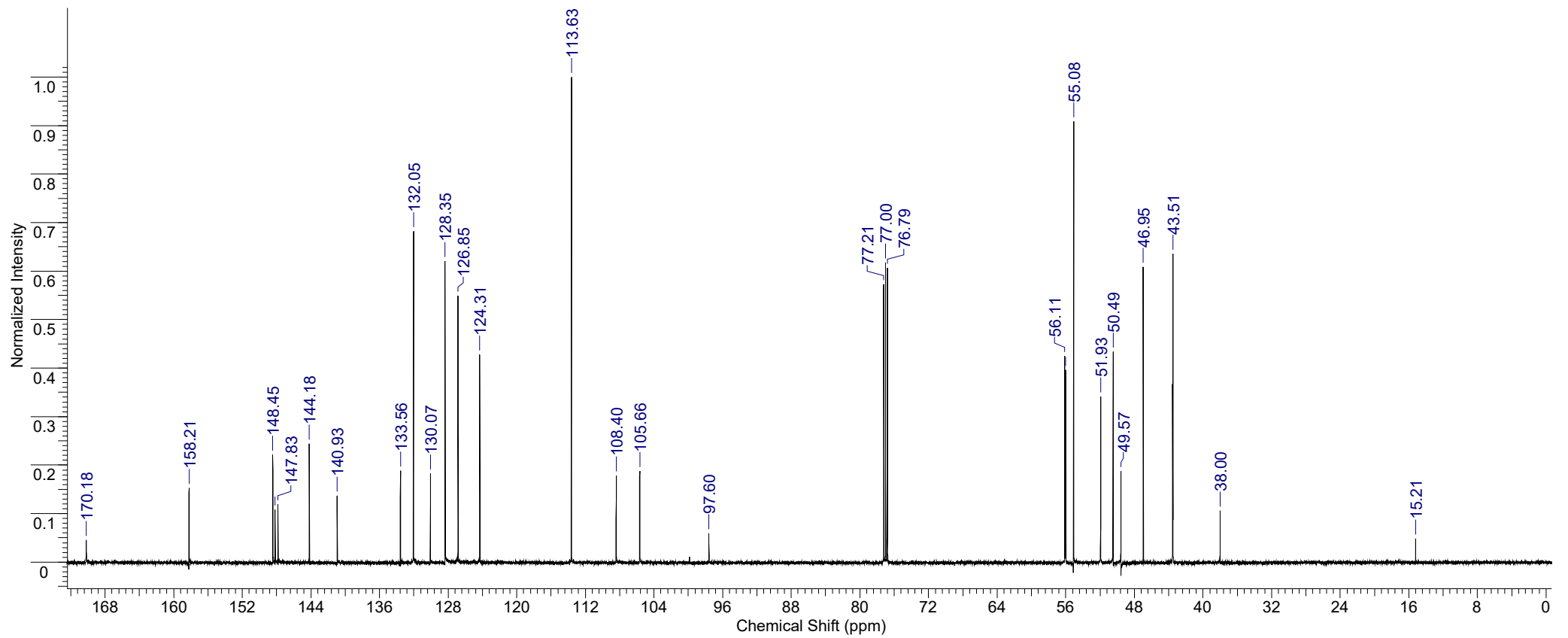
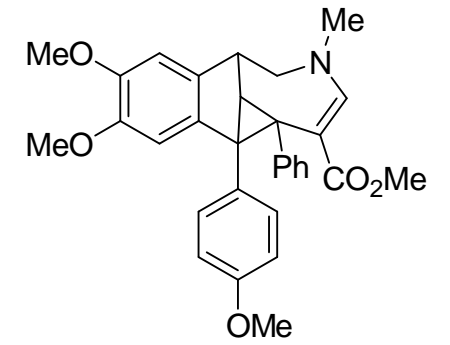
<sup>1</sup>H NMR spectra for 2o.



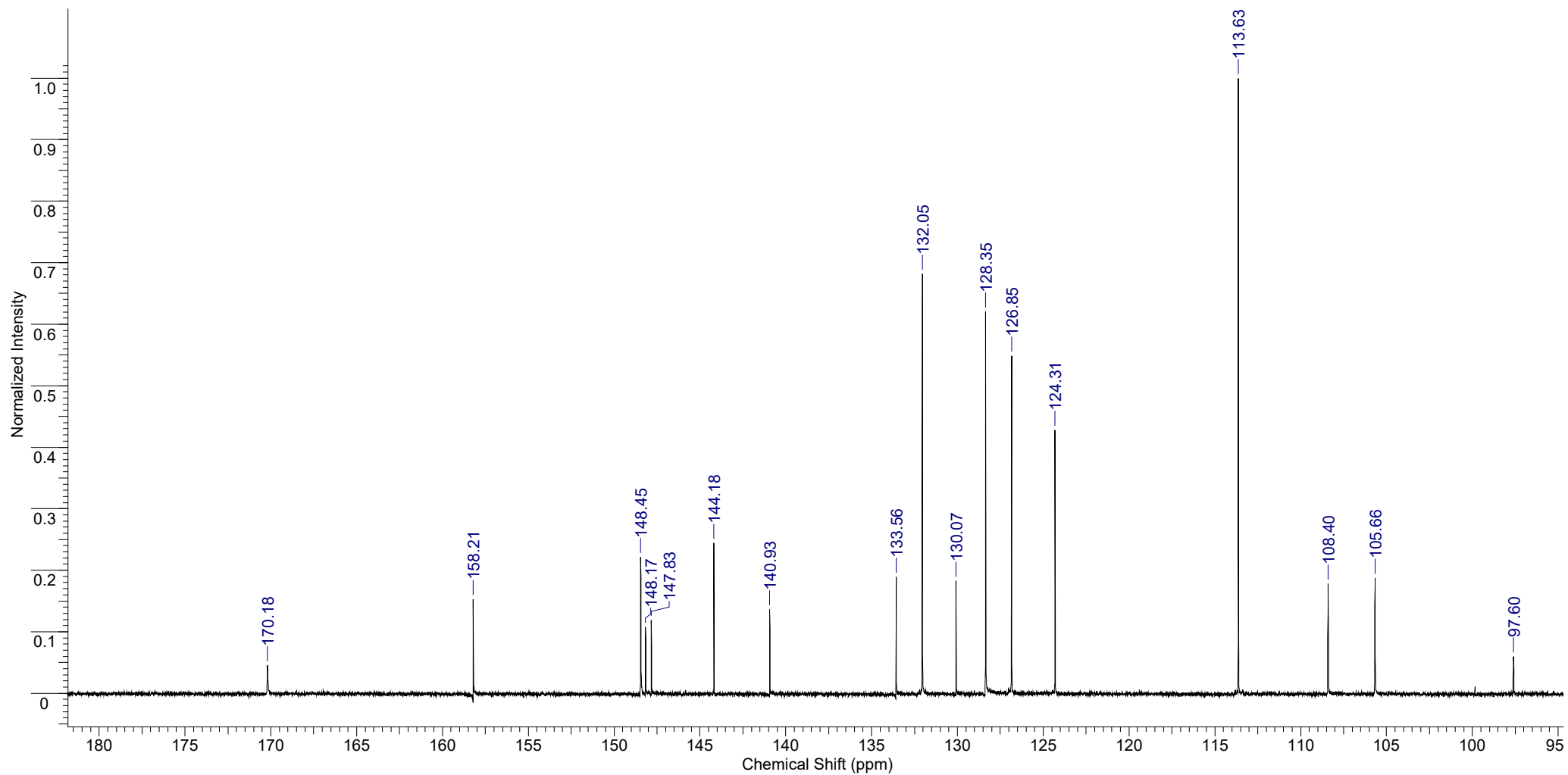
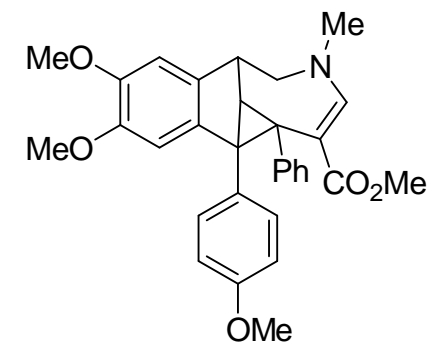
<sup>1</sup>H NMR spectra for 2o.



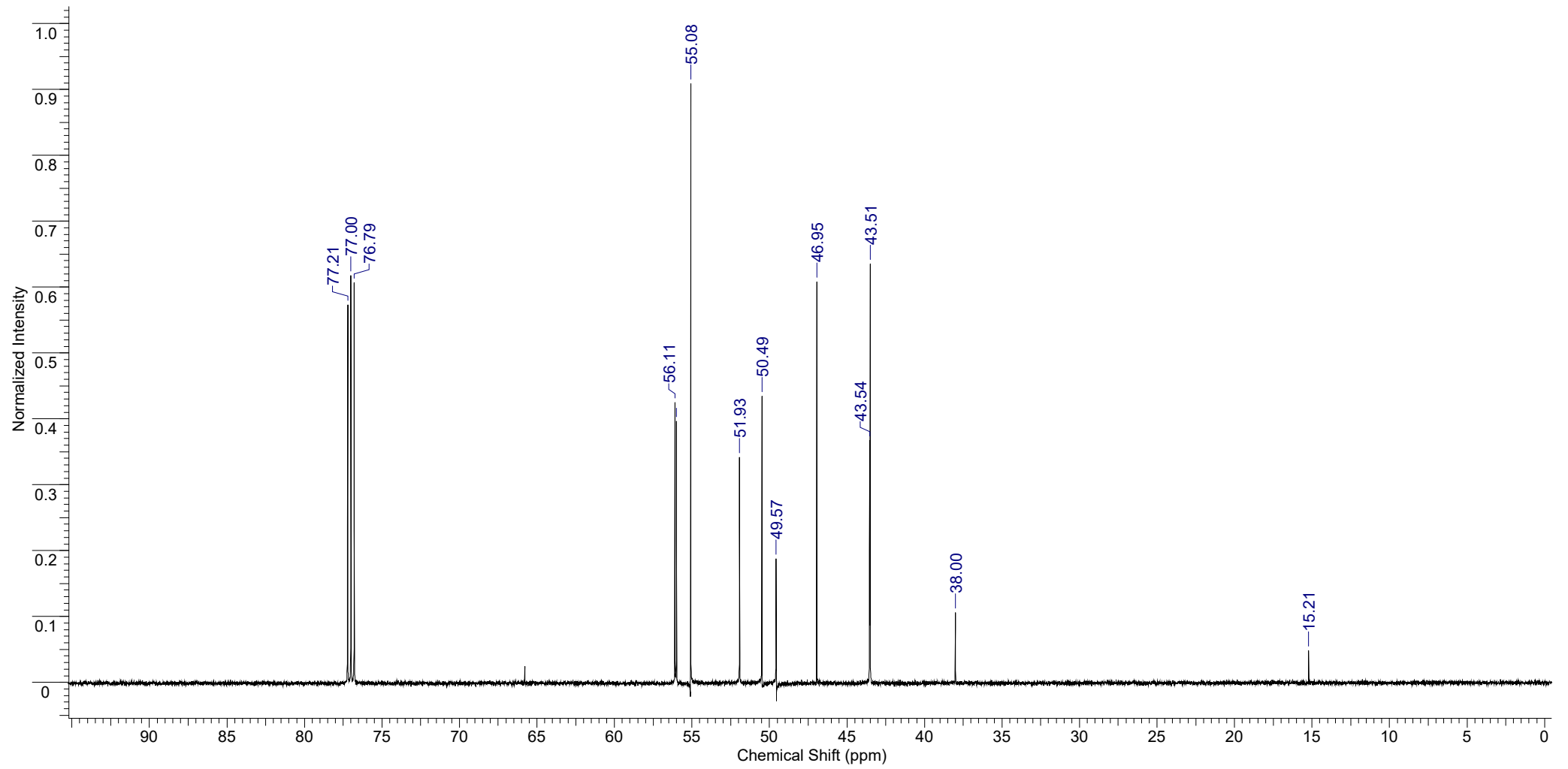
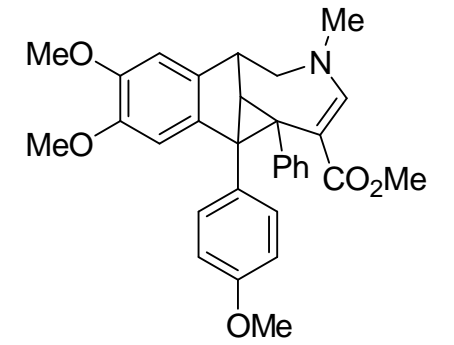
<sup>13</sup>C NMR spectra for 2o.



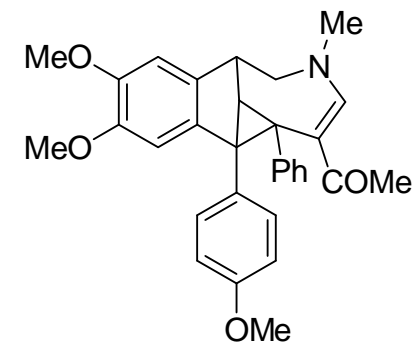
<sup>13</sup>C NMR spectra for 2o.



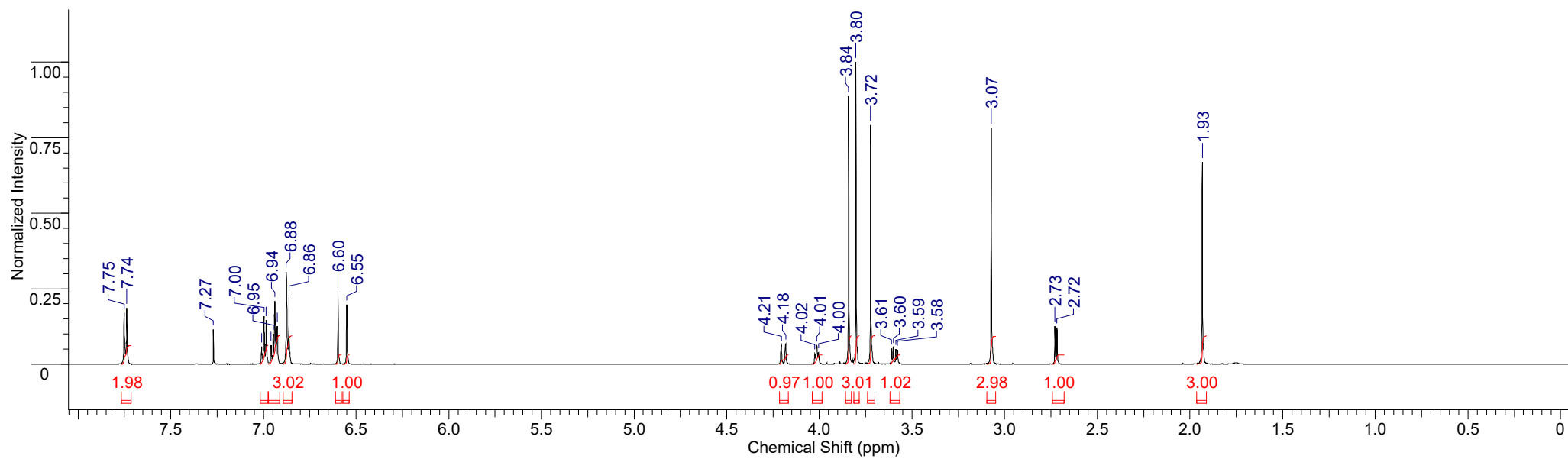
<sup>13</sup>C NMR spectra for 2o.



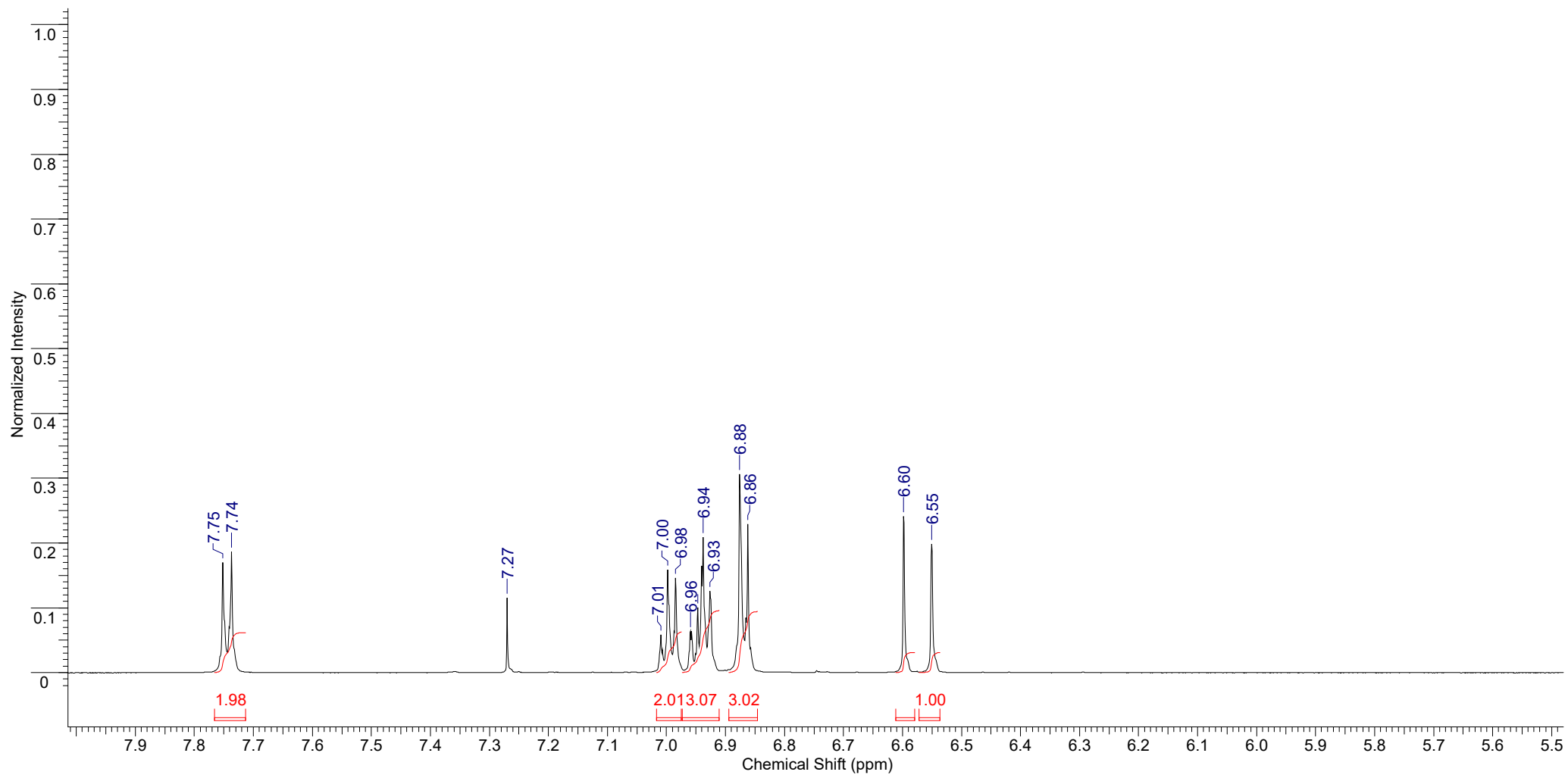
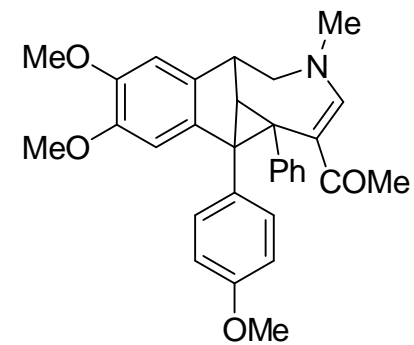
1-[6,7-Dimethoxy-4b-(4-methoxyphenyl)-2-methyl-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[*a*]cyclopropa[*cd*]azulen-4-yl]ethanone (2p)



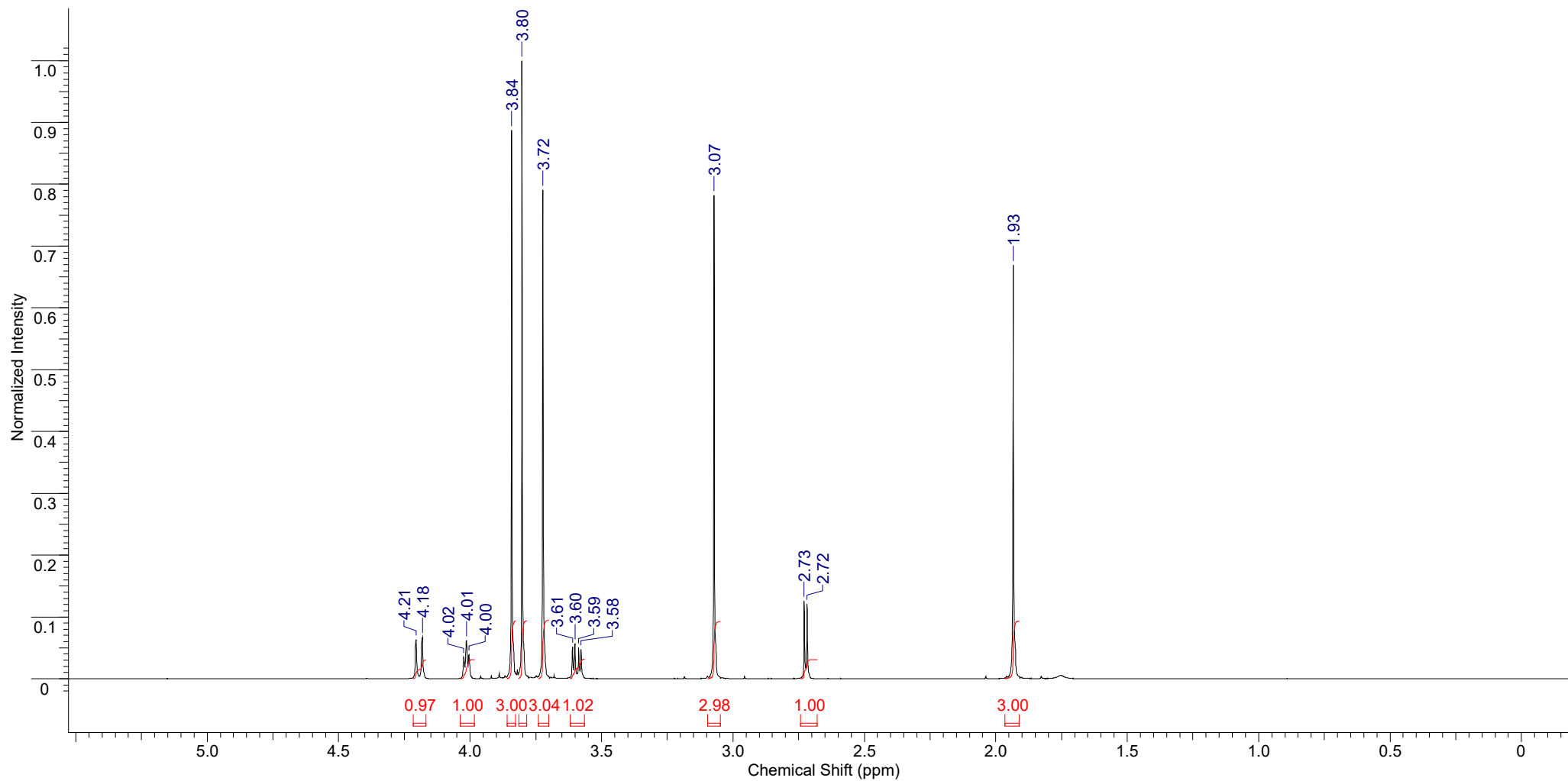
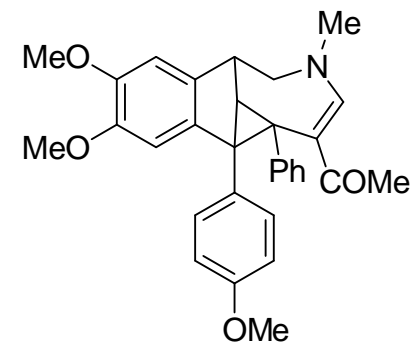
$^1\text{H}$  NMR spectra for 2p.



<sup>1</sup>H NMR spectra for 2p.

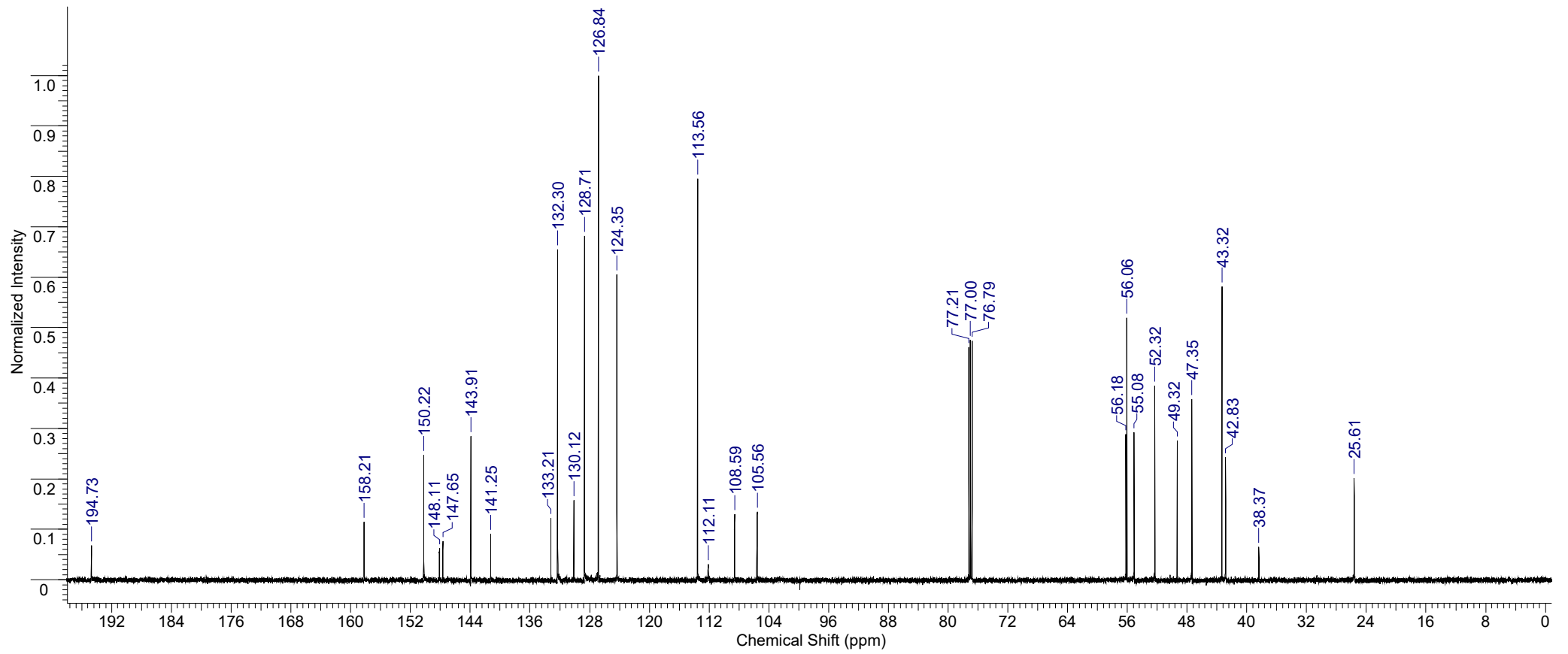
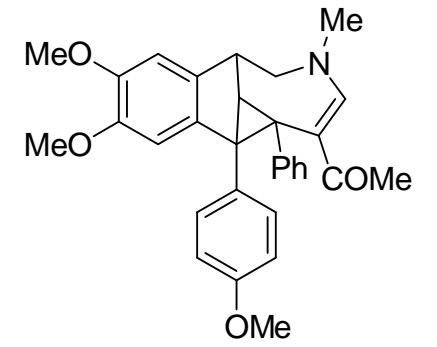


<sup>1</sup>H NMR spectra for 2p.

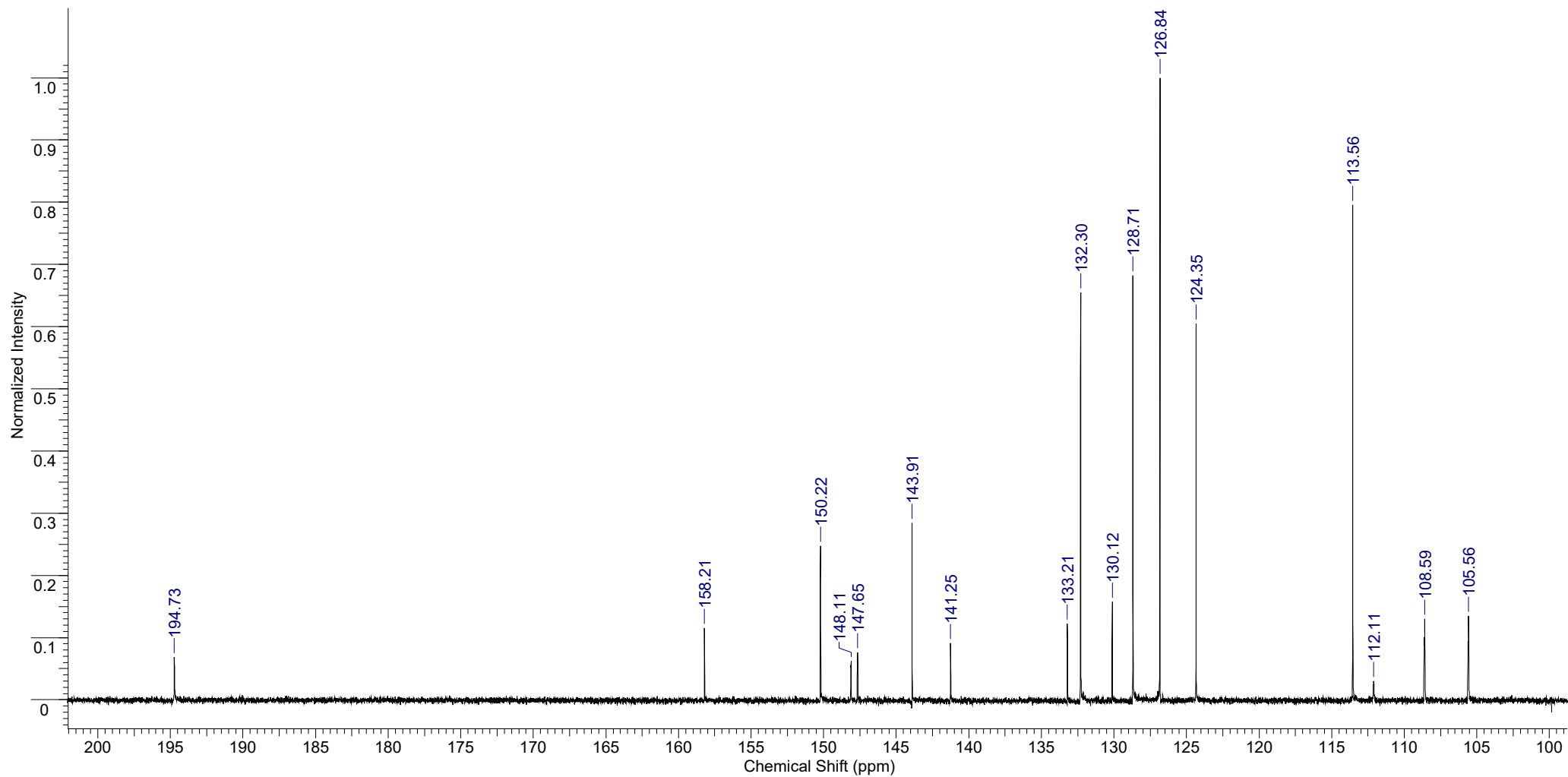
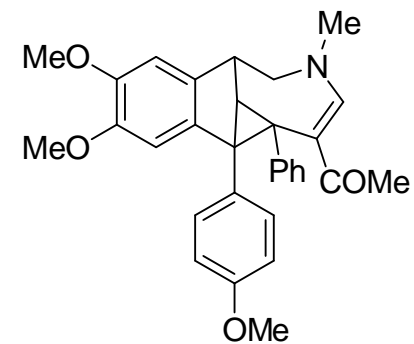




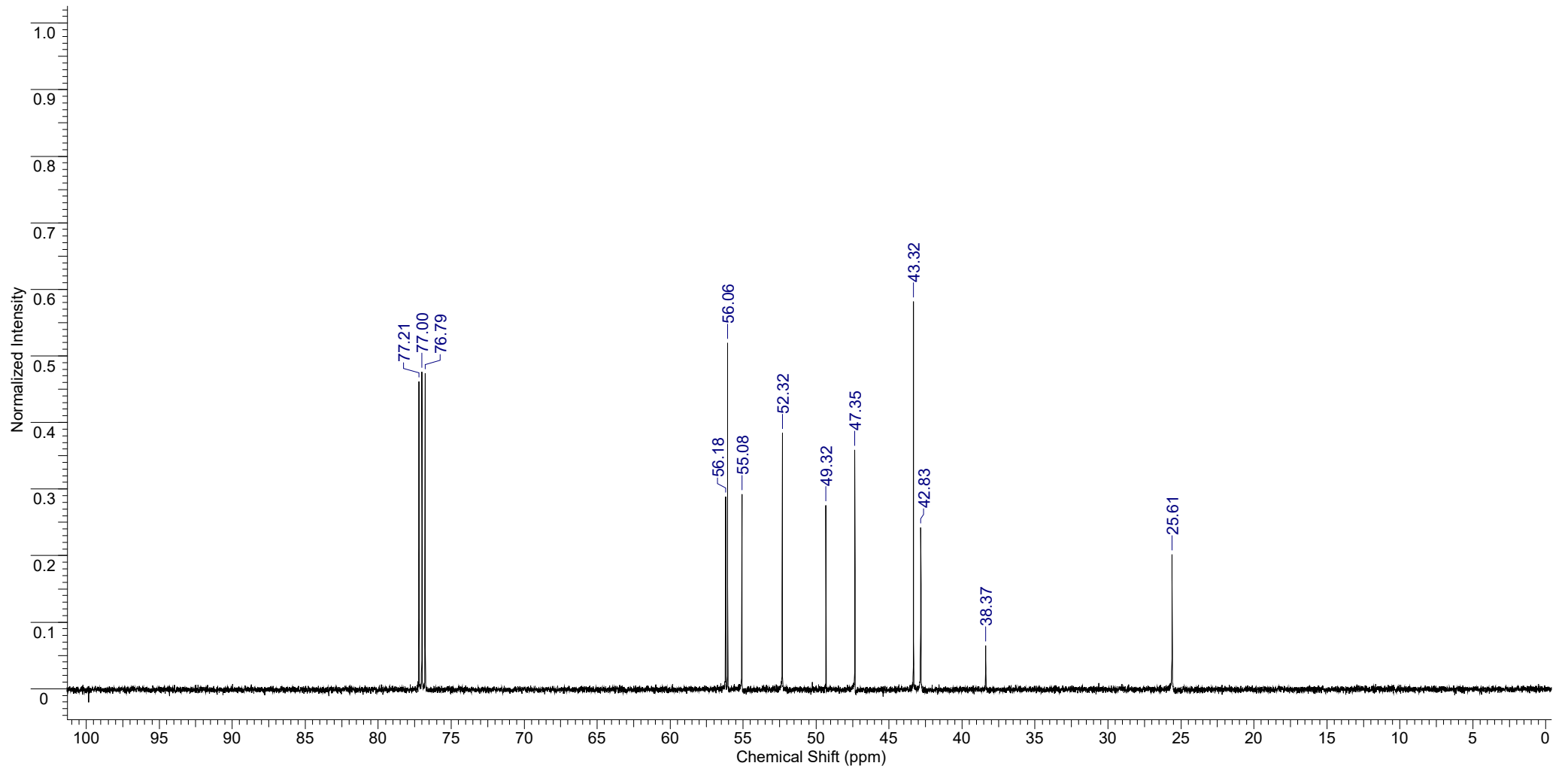
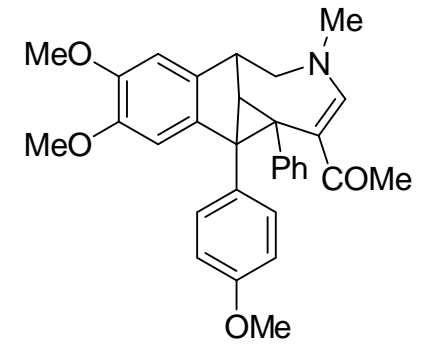
<sup>13</sup>C NMR spectra for 2p.



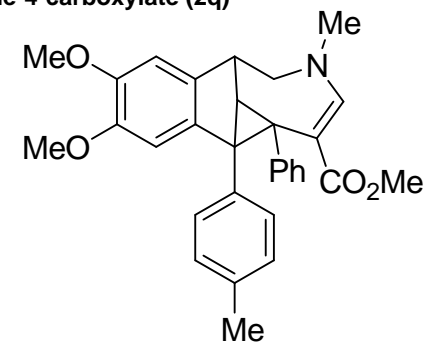
<sup>13</sup>C NMR spectra for 2p.



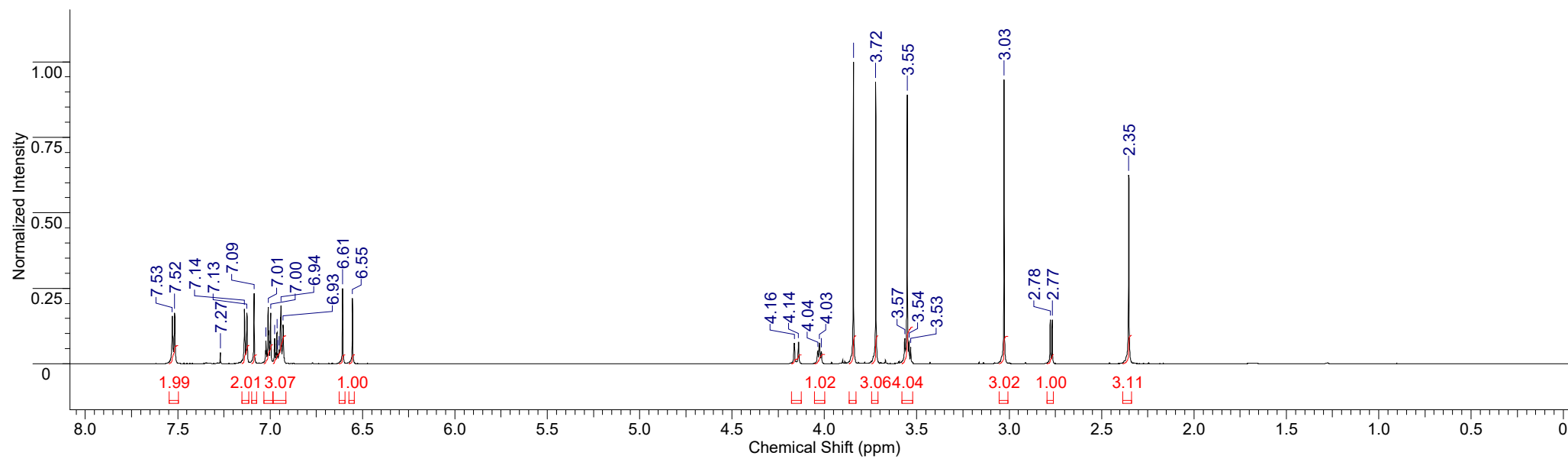
<sup>13</sup>C NMR spectra for 2p.



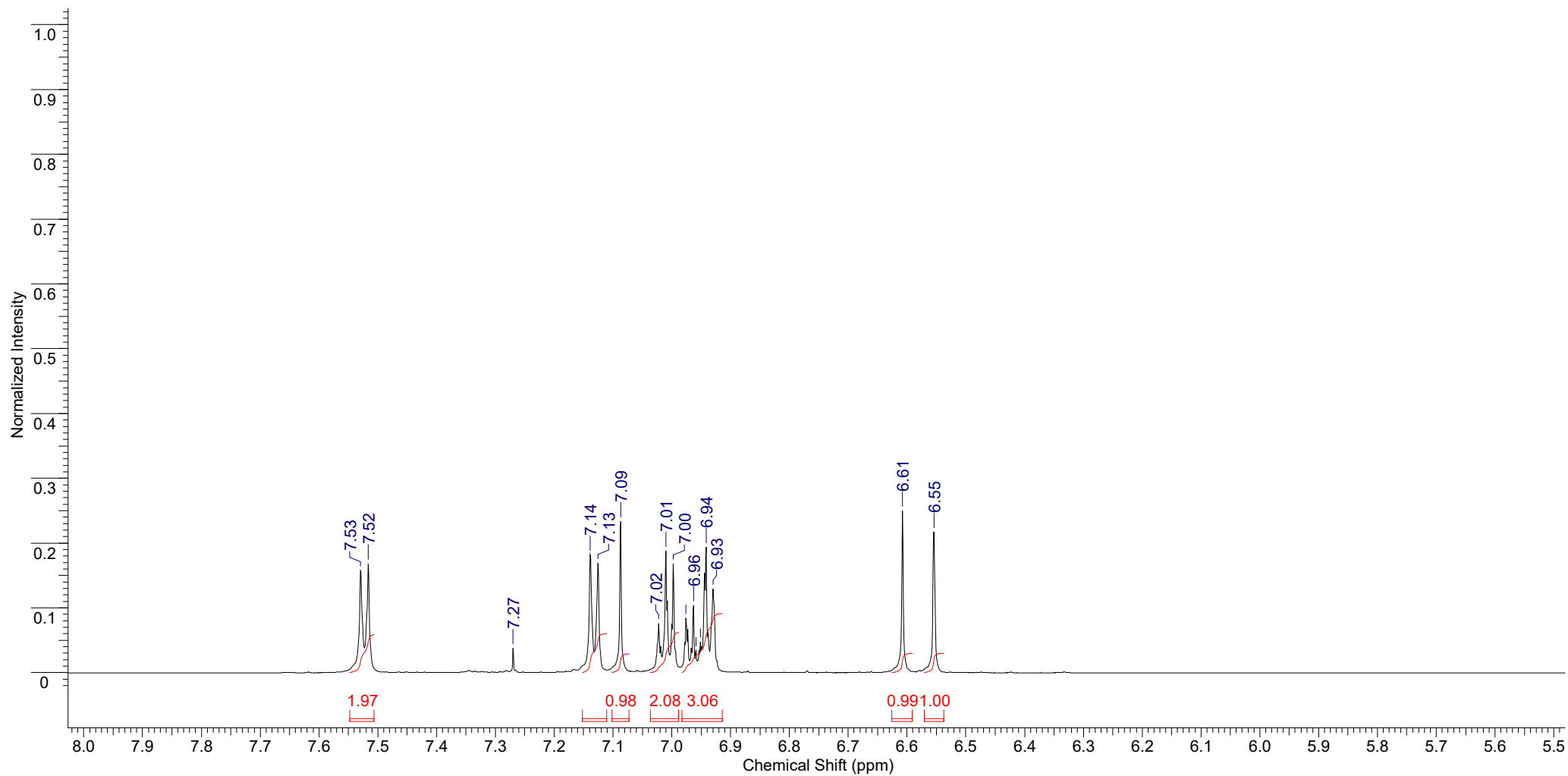
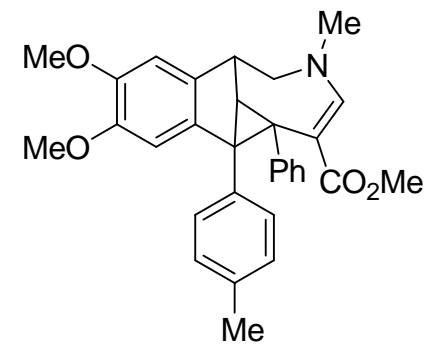
Methyl 6,7-dimethoxy-2-methyl-4b-(4-methylphenyl)-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[*a*]cyclopropa[*cd*]azulene-4-carboxylate (2q)



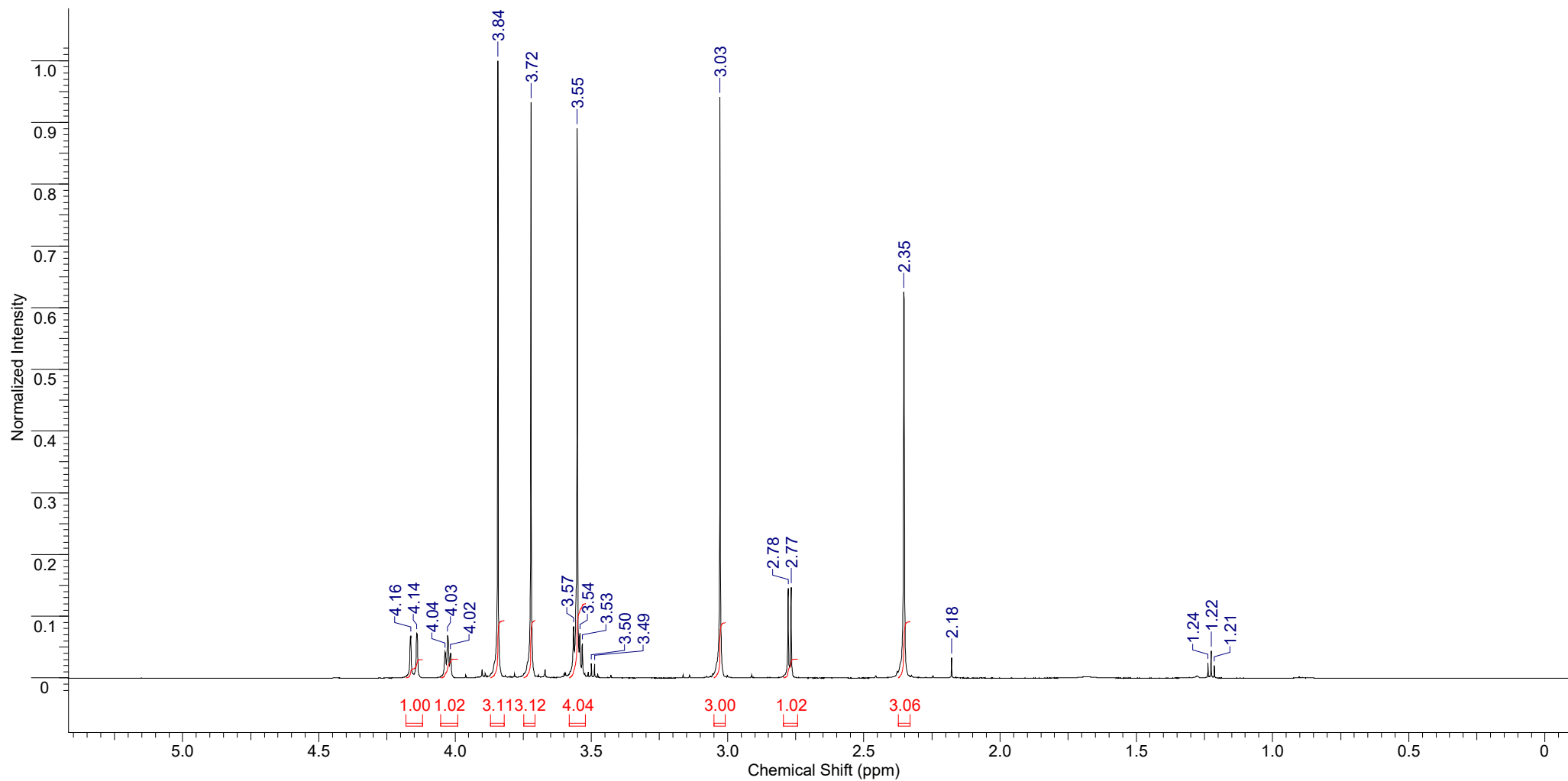
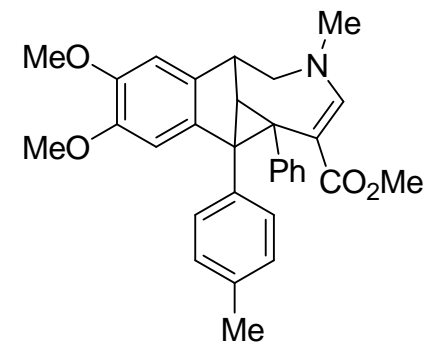
<sup>1</sup>H NMR spectra for 2q.



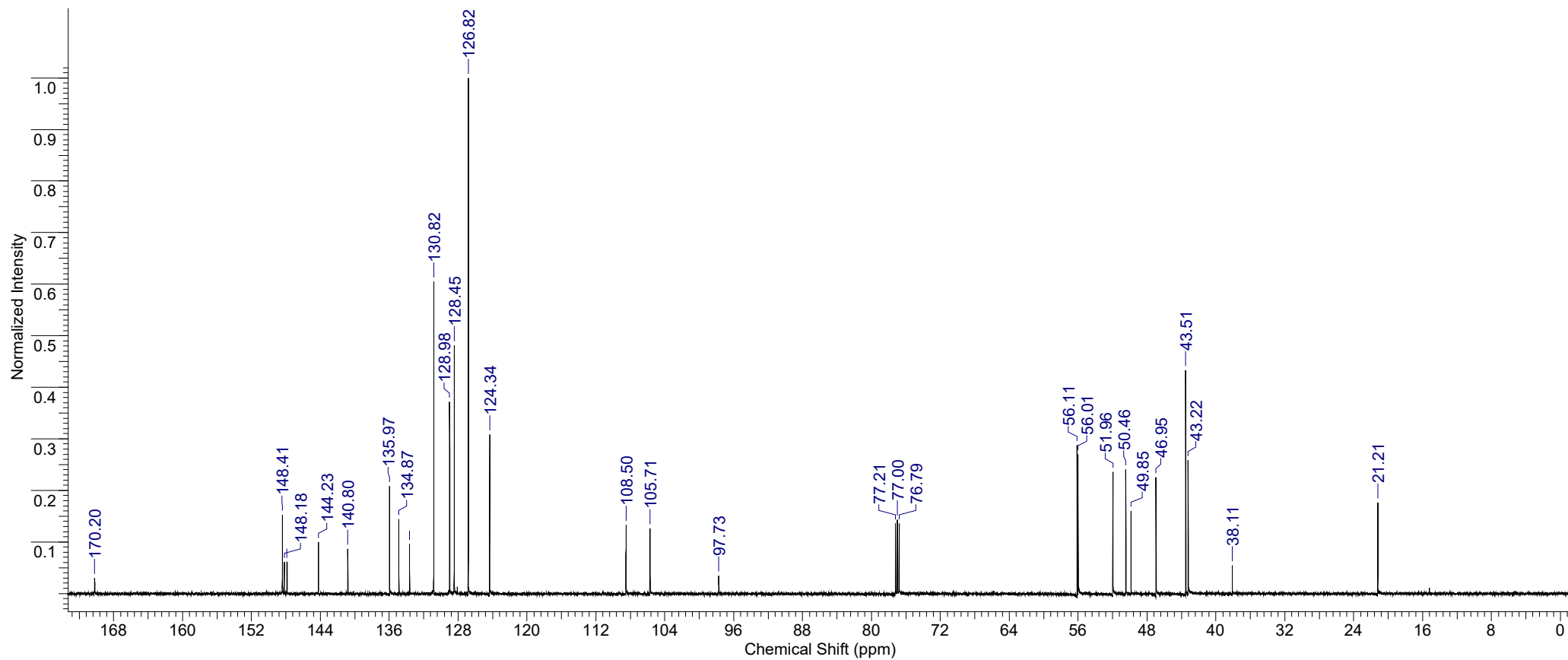
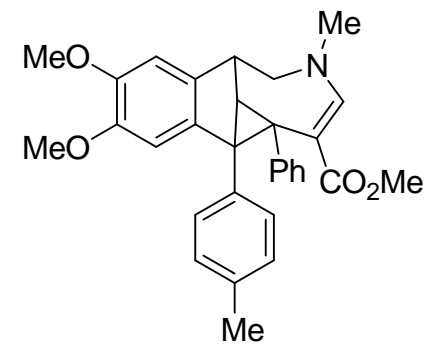
<sup>1</sup>H NMR spectra for 2q.



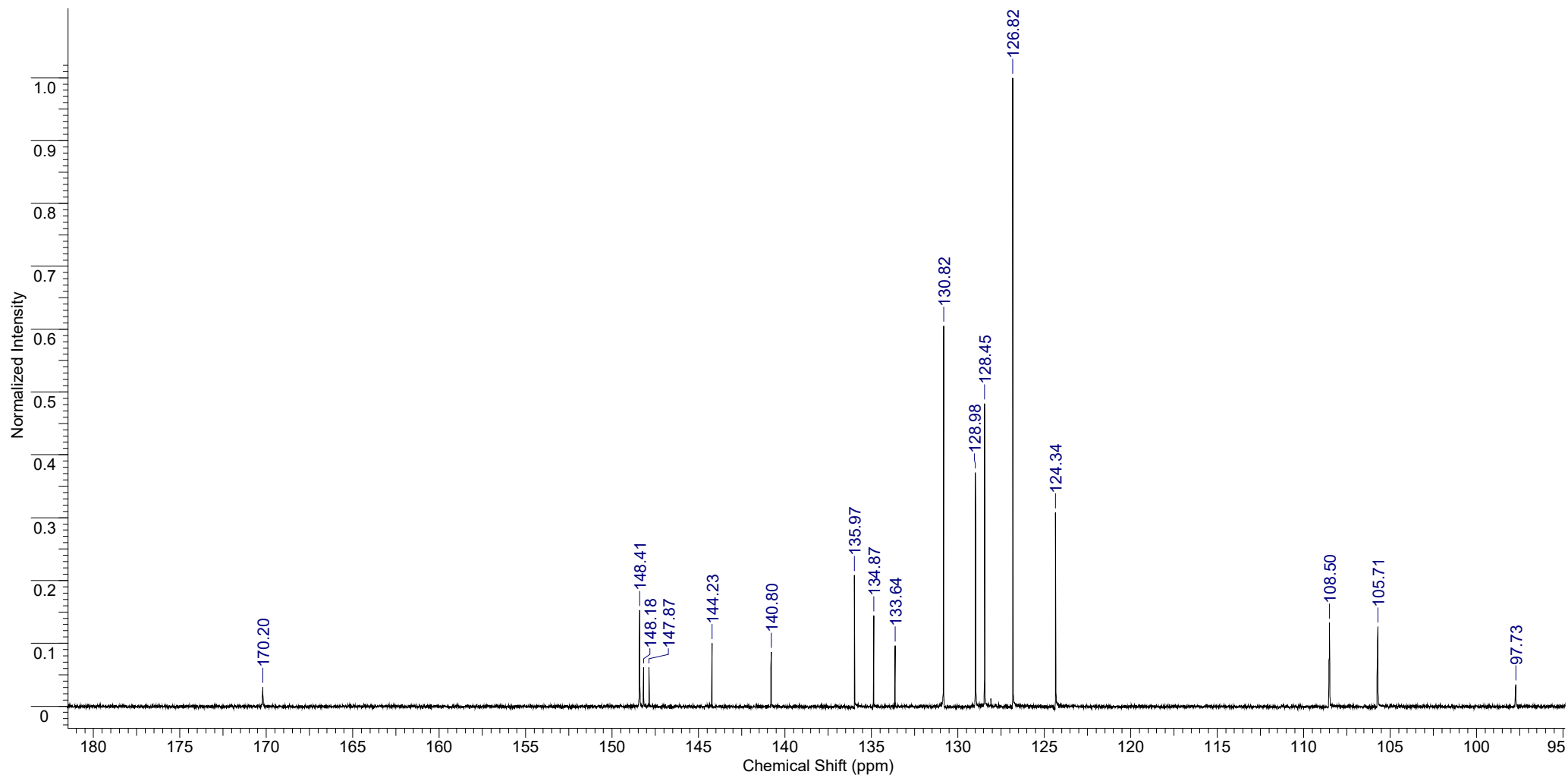
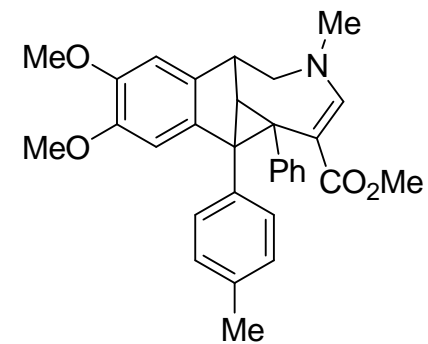
<sup>1</sup>H NMR spectra for 2q.



<sup>13</sup>C NMR spectra for 2q.

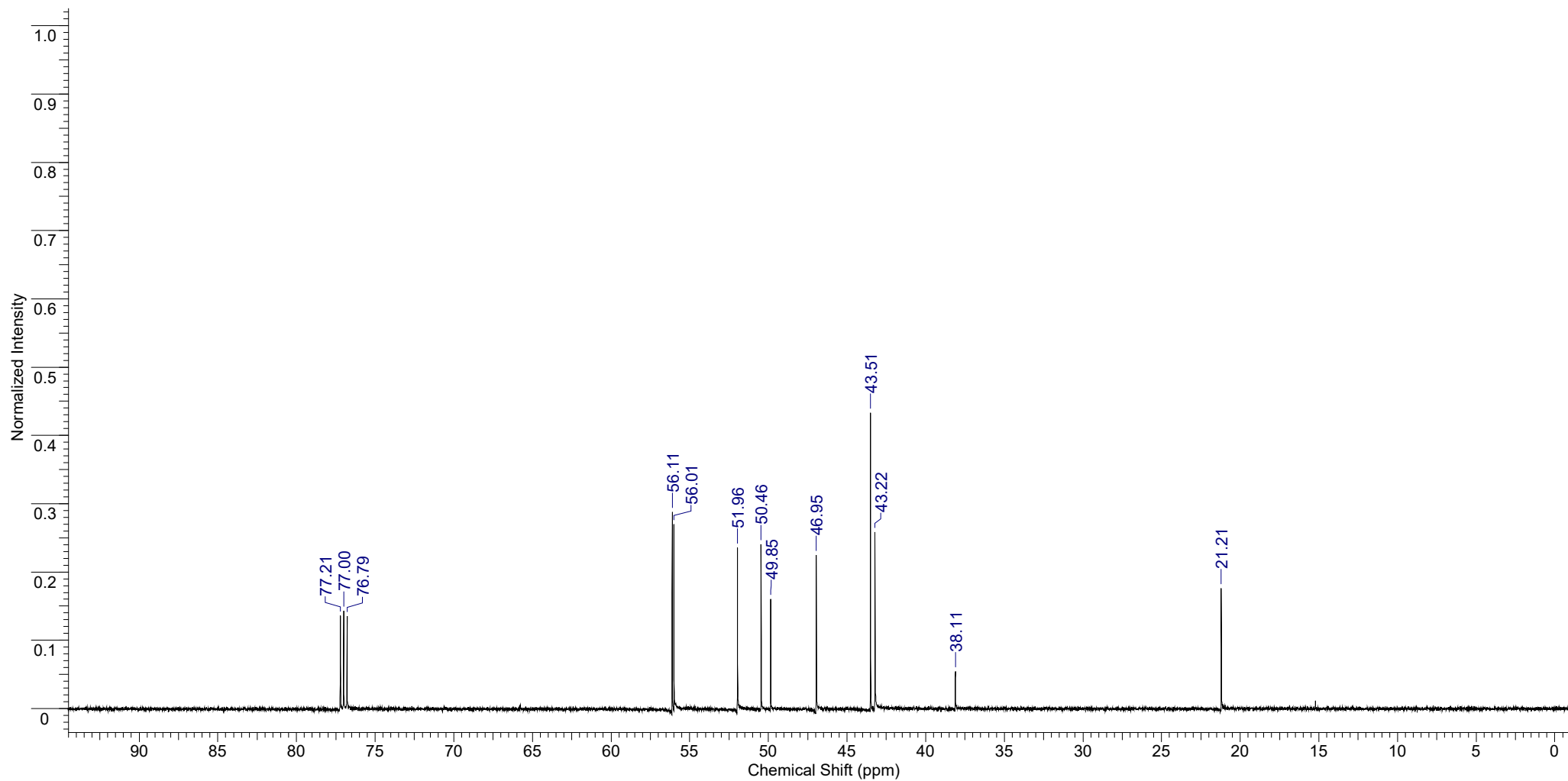
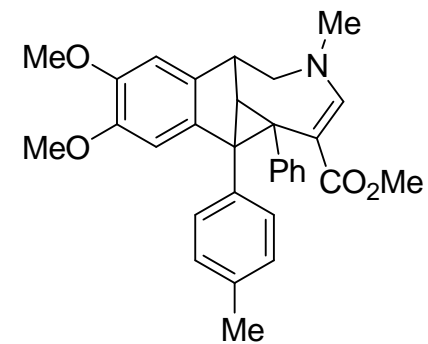


<sup>13</sup>C NMR spectra for 2q.

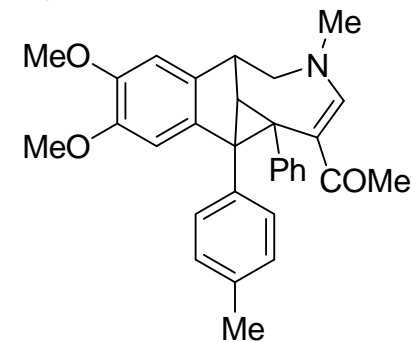




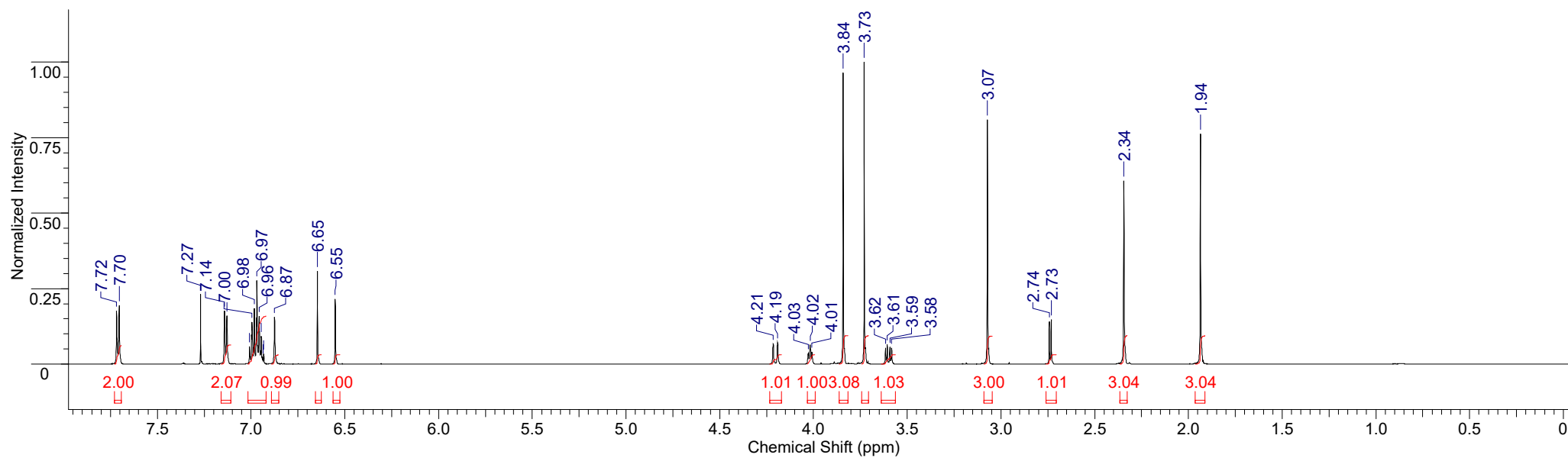
<sup>13</sup>C NMR spectra for 2q.



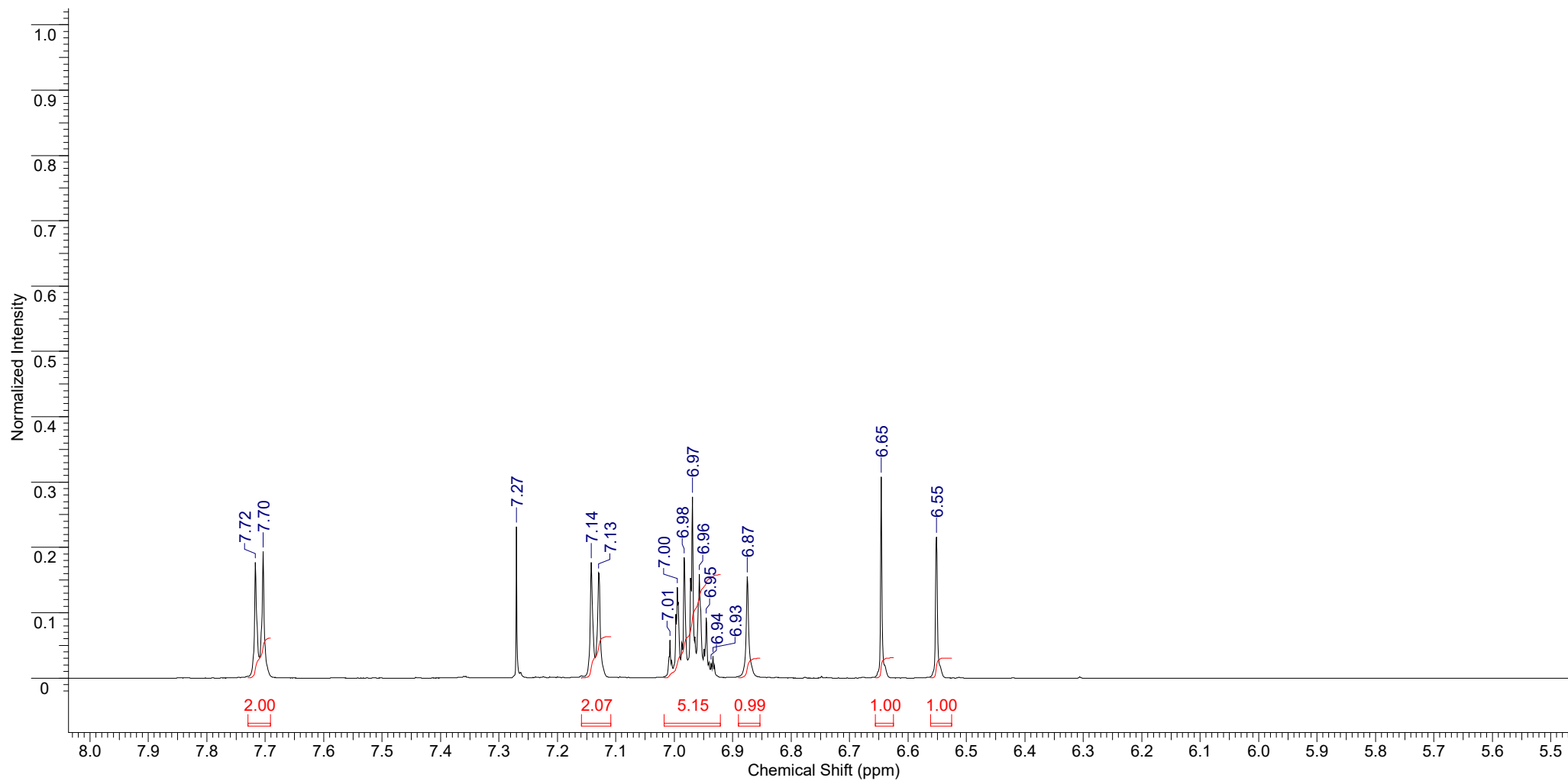
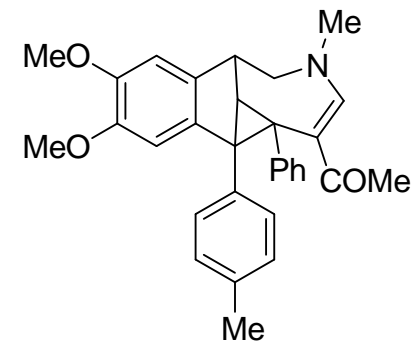
1-[6,7-Dimethoxy-2-methyl-4b-(4-methylphenyl)-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[*a*]cyclopropa[*cd*]azulen-4-yl]ethanone (2r)



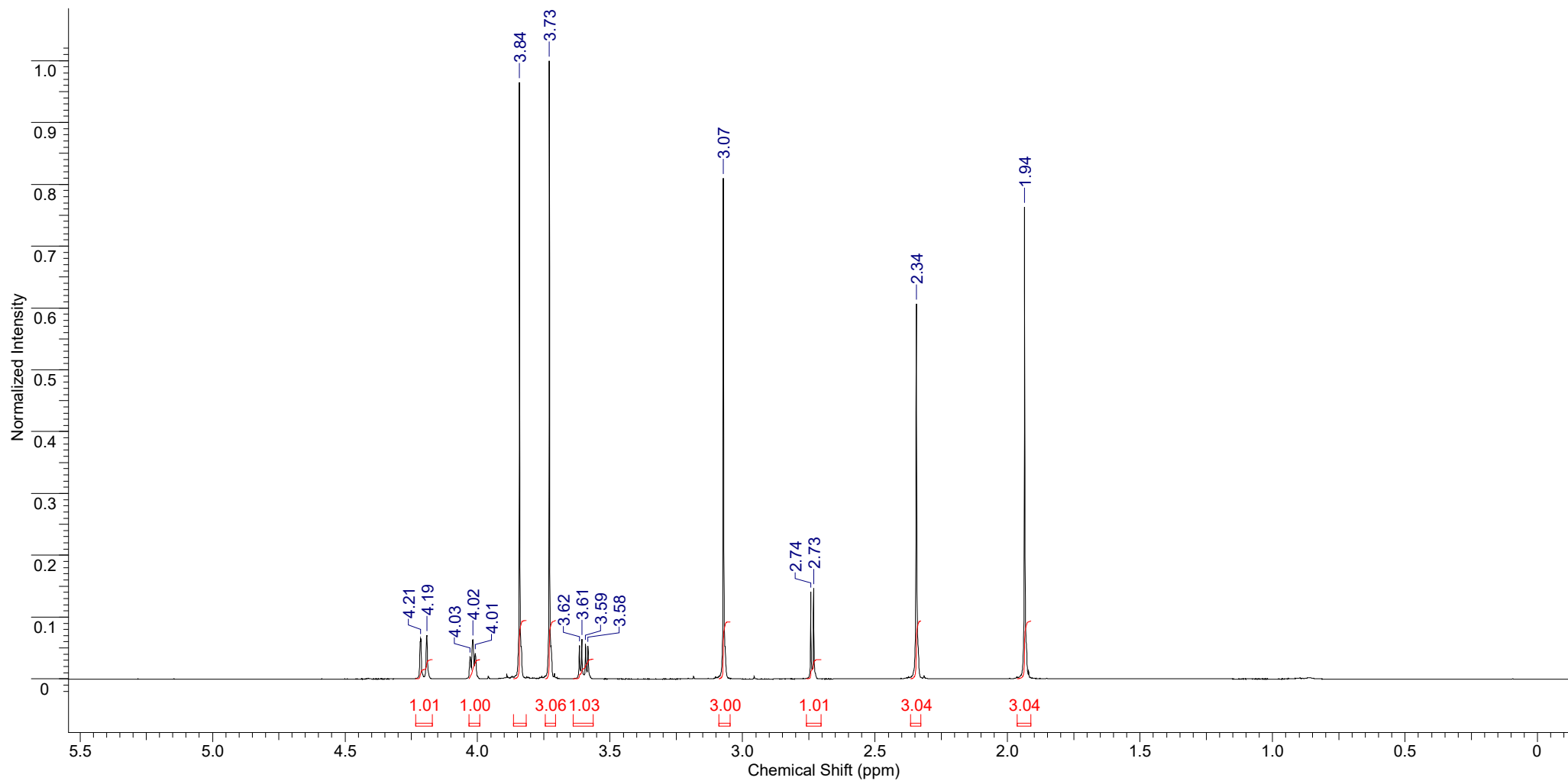
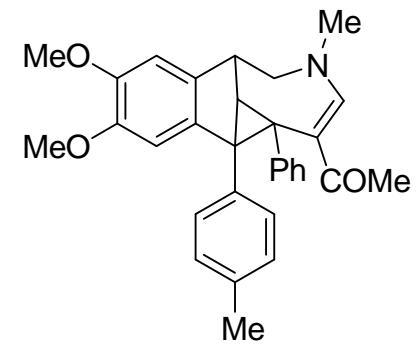
<sup>1</sup>H NMR spectra for 2r.



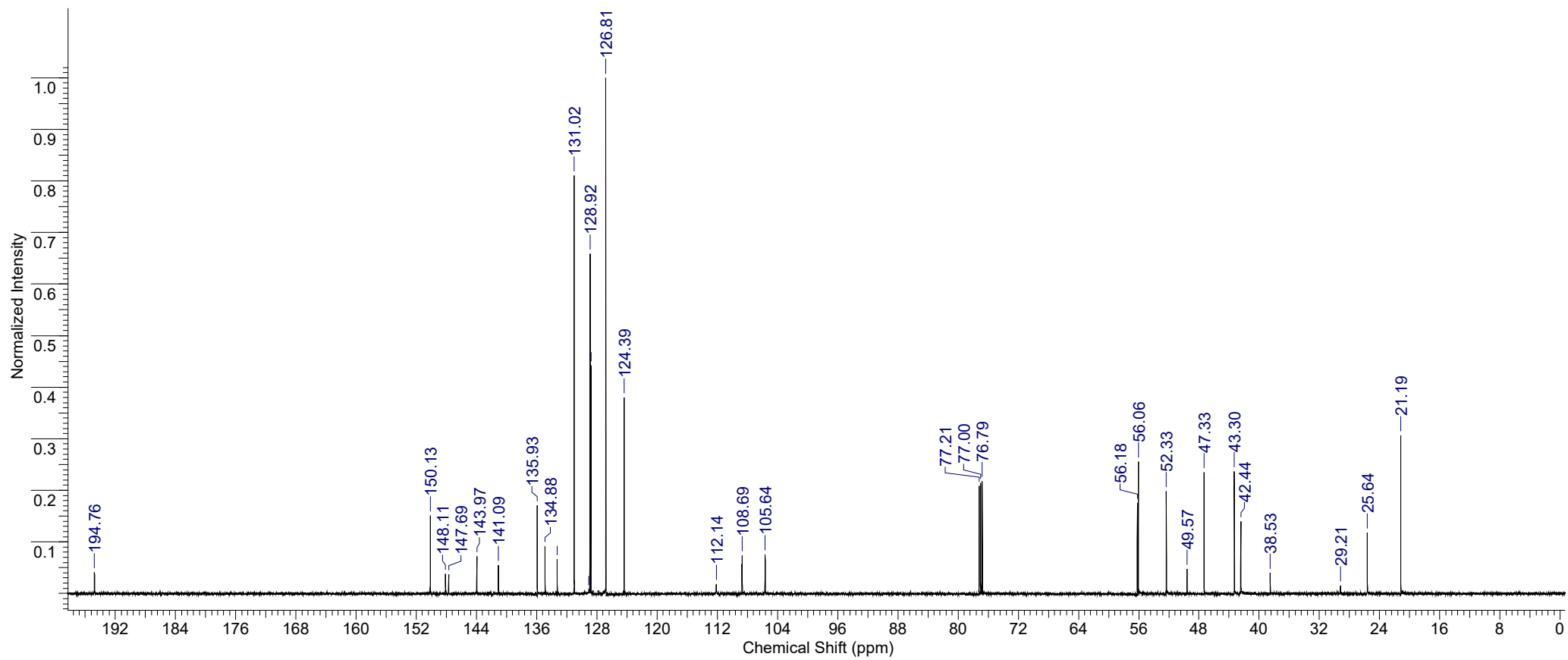
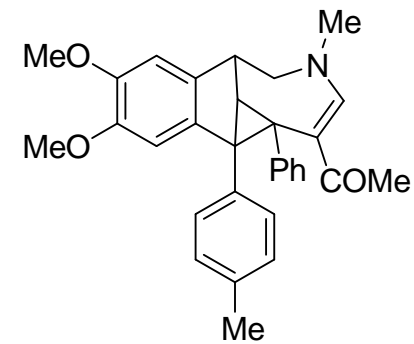
<sup>1</sup>H NMR spectra for 2r.



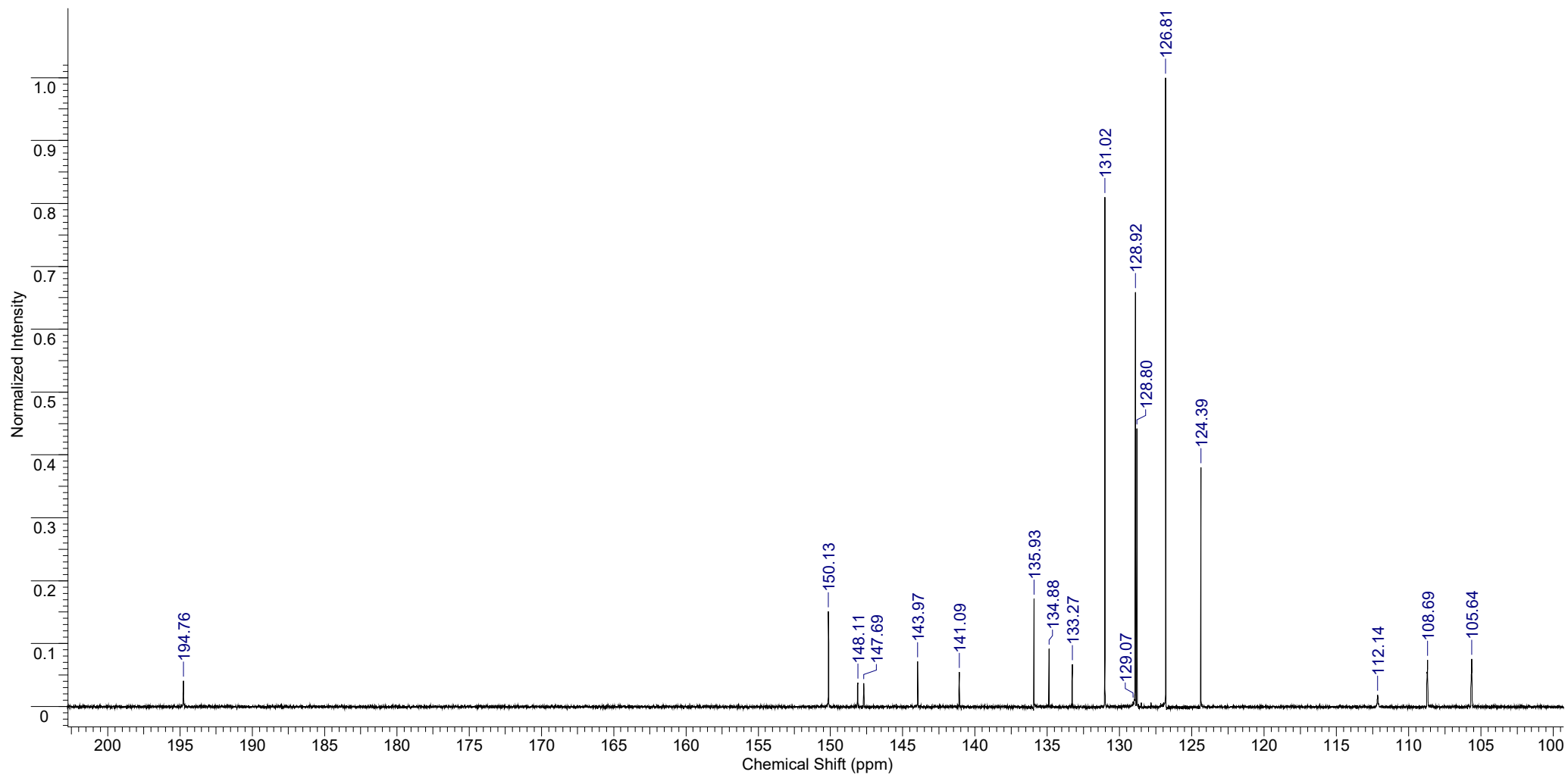
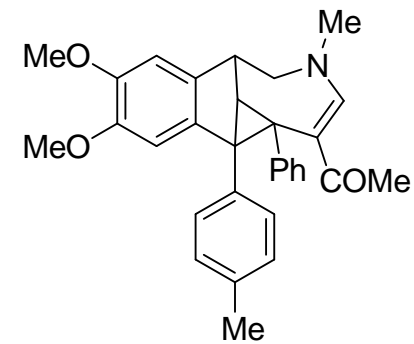
<sup>1</sup>H NMR spectra for 2r.



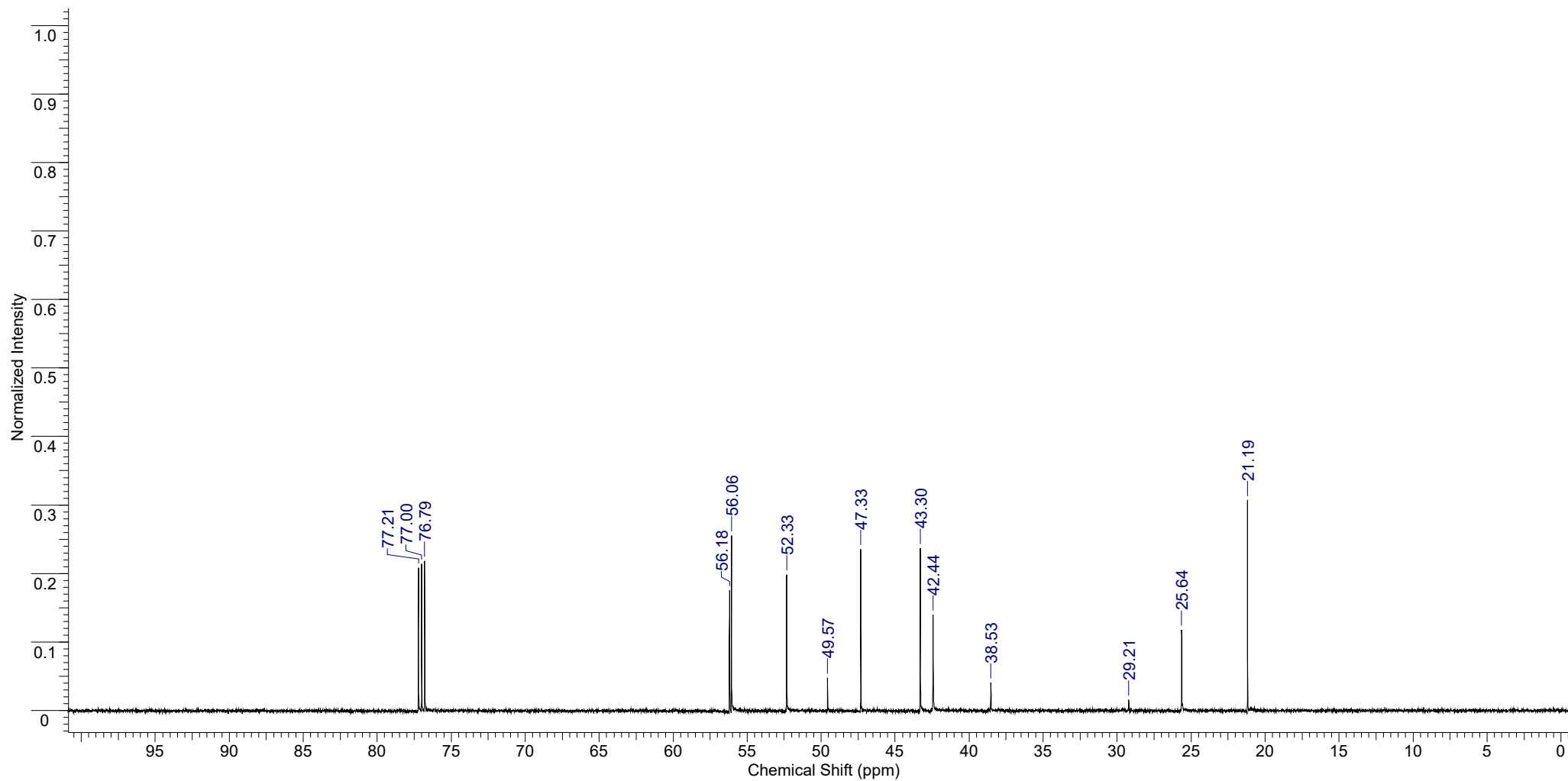
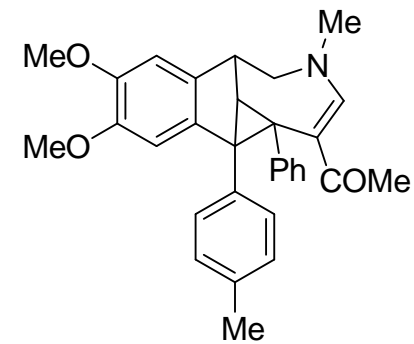
<sup>13</sup>C NMR spectra for 2r.



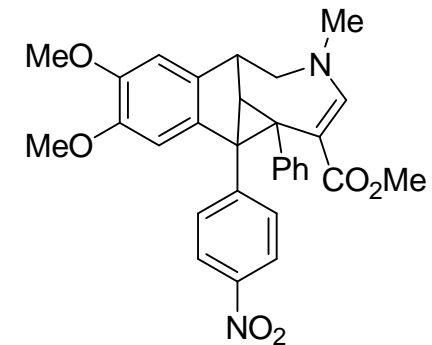
<sup>13</sup>C NMR spectra for 2r.



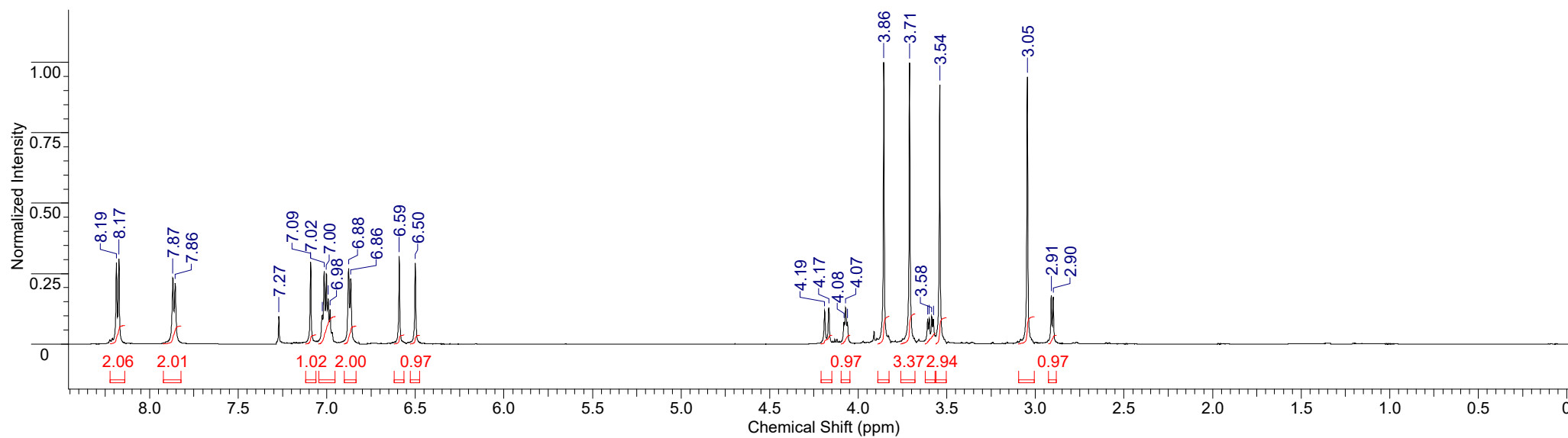
<sup>13</sup>C NMR spectra for 2r.



Methyl 6,7-dimethoxy-2-methyl-4b-(4-nitrophenyl)-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenzocyclopropa[cd]azulene-4-carboxylate (2s)

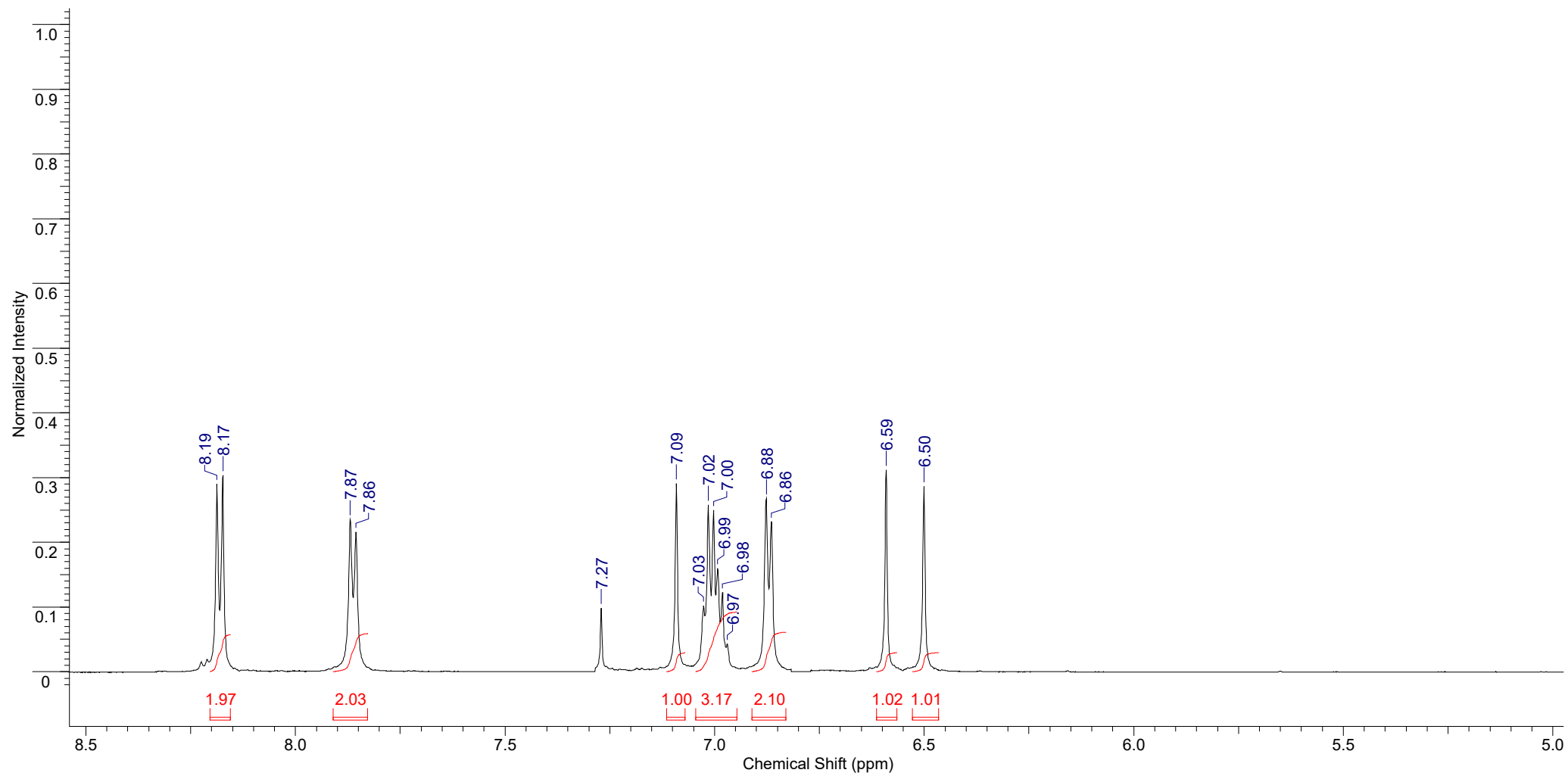
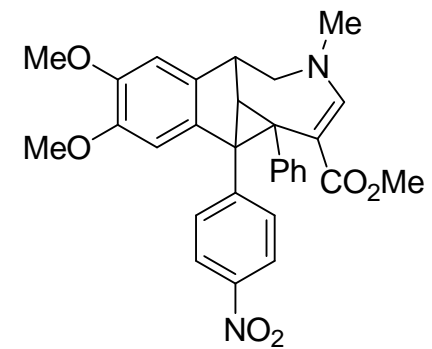


<sup>1</sup>H NMR spectra for 2s.

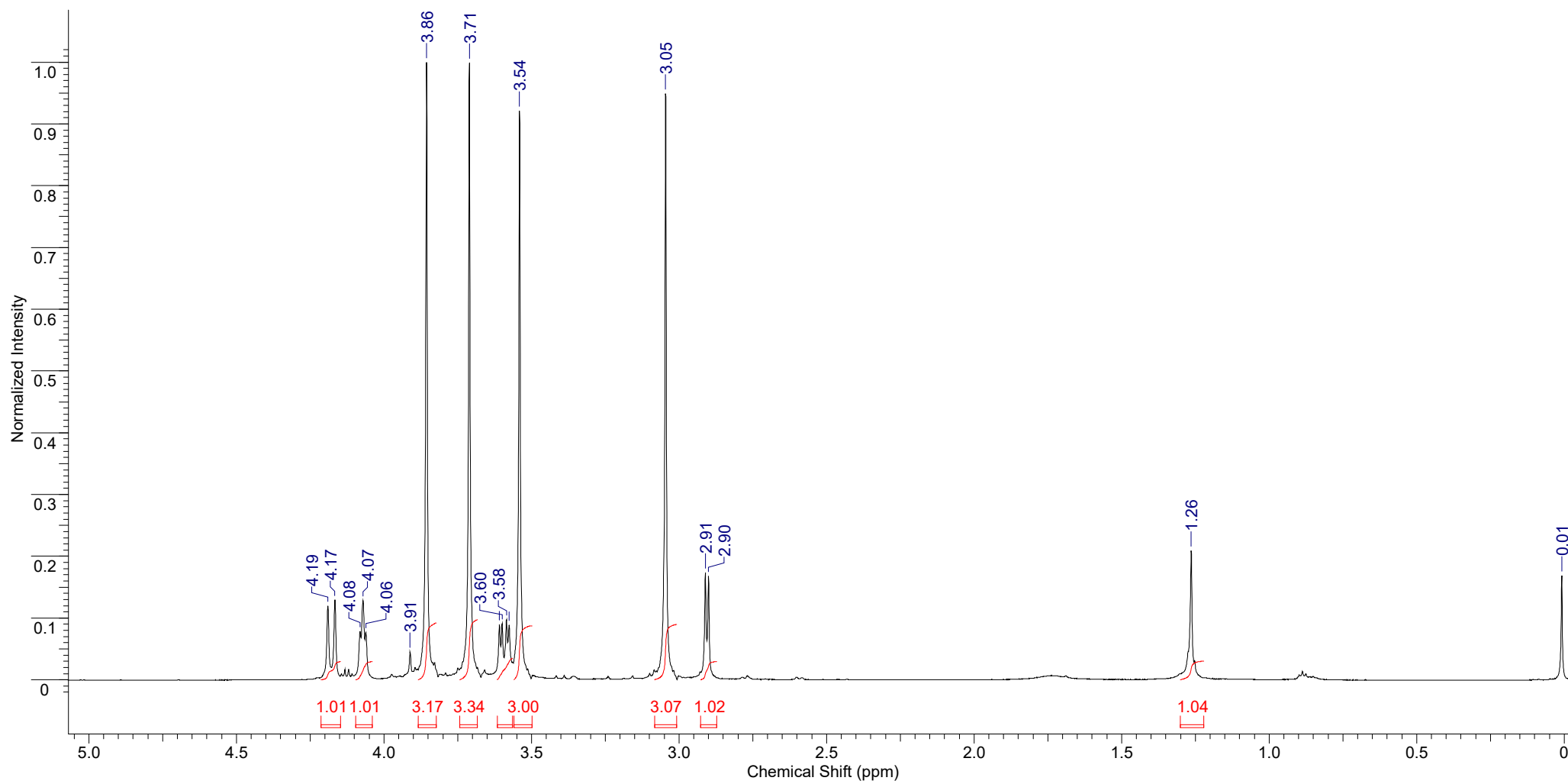
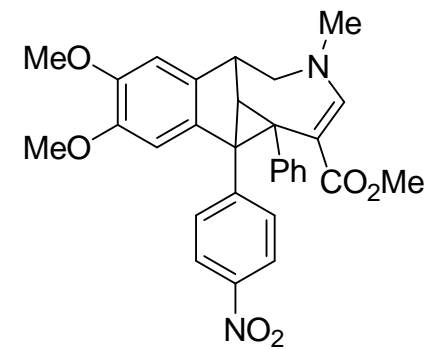




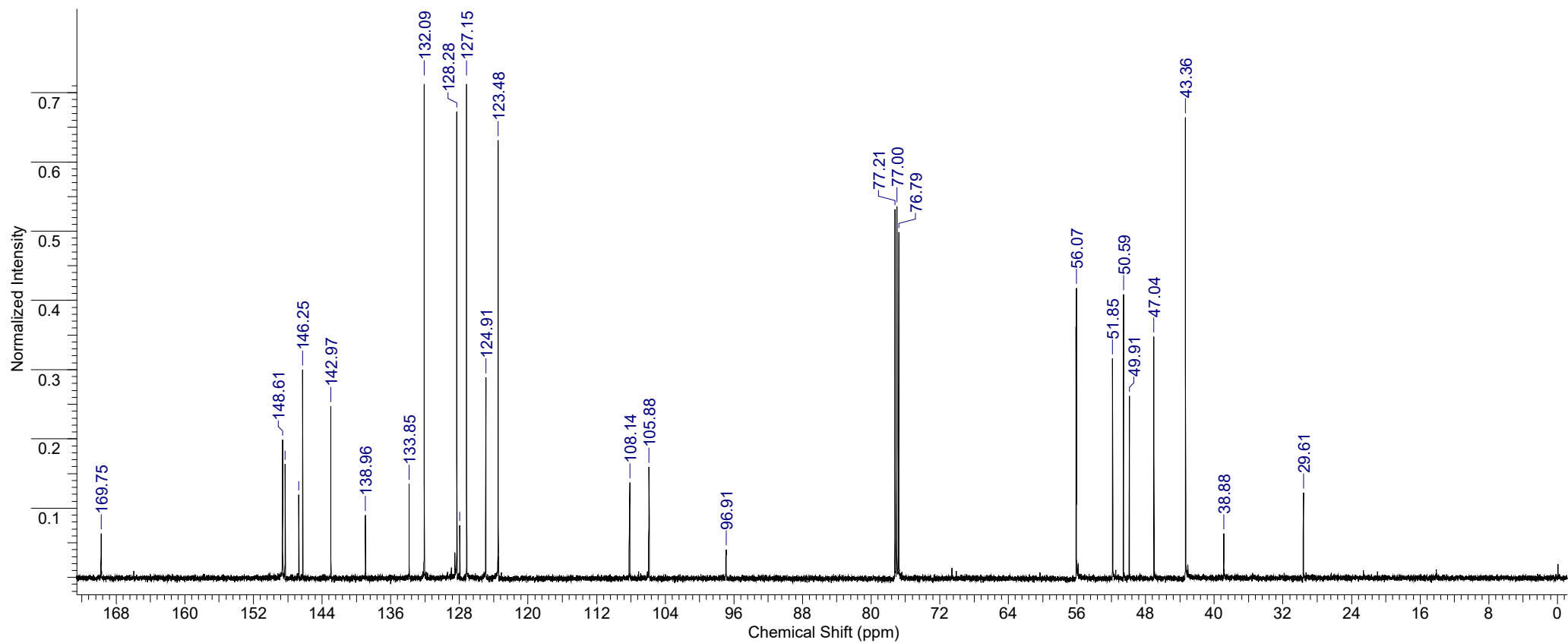
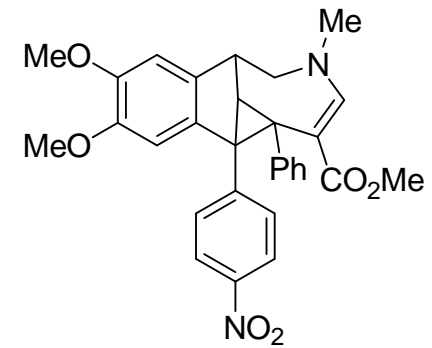
<sup>1</sup>H NMR spectra for 2s.



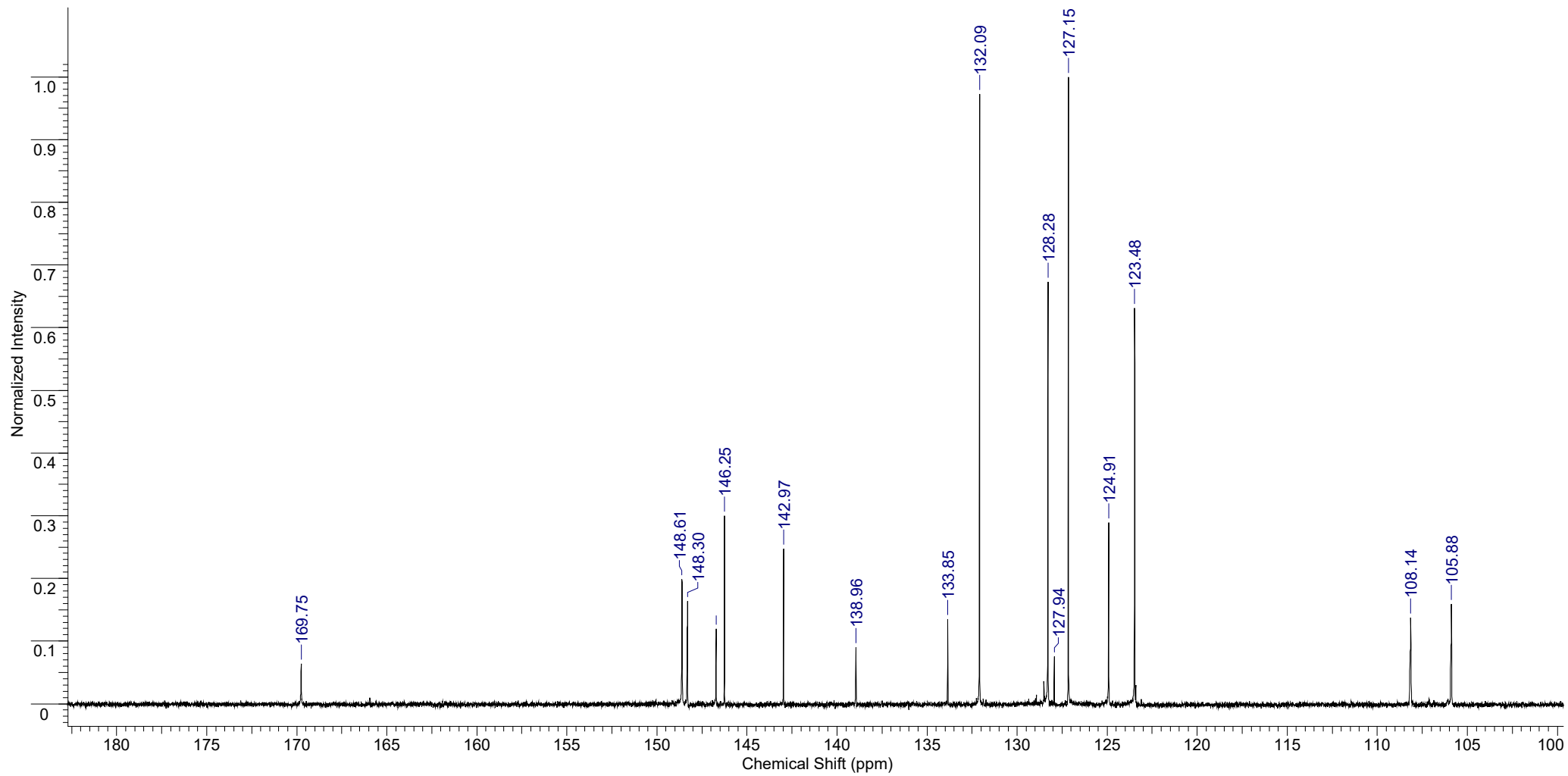
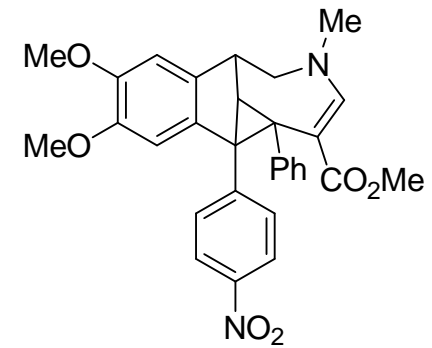
<sup>1</sup>H NMR spectra for 2s.



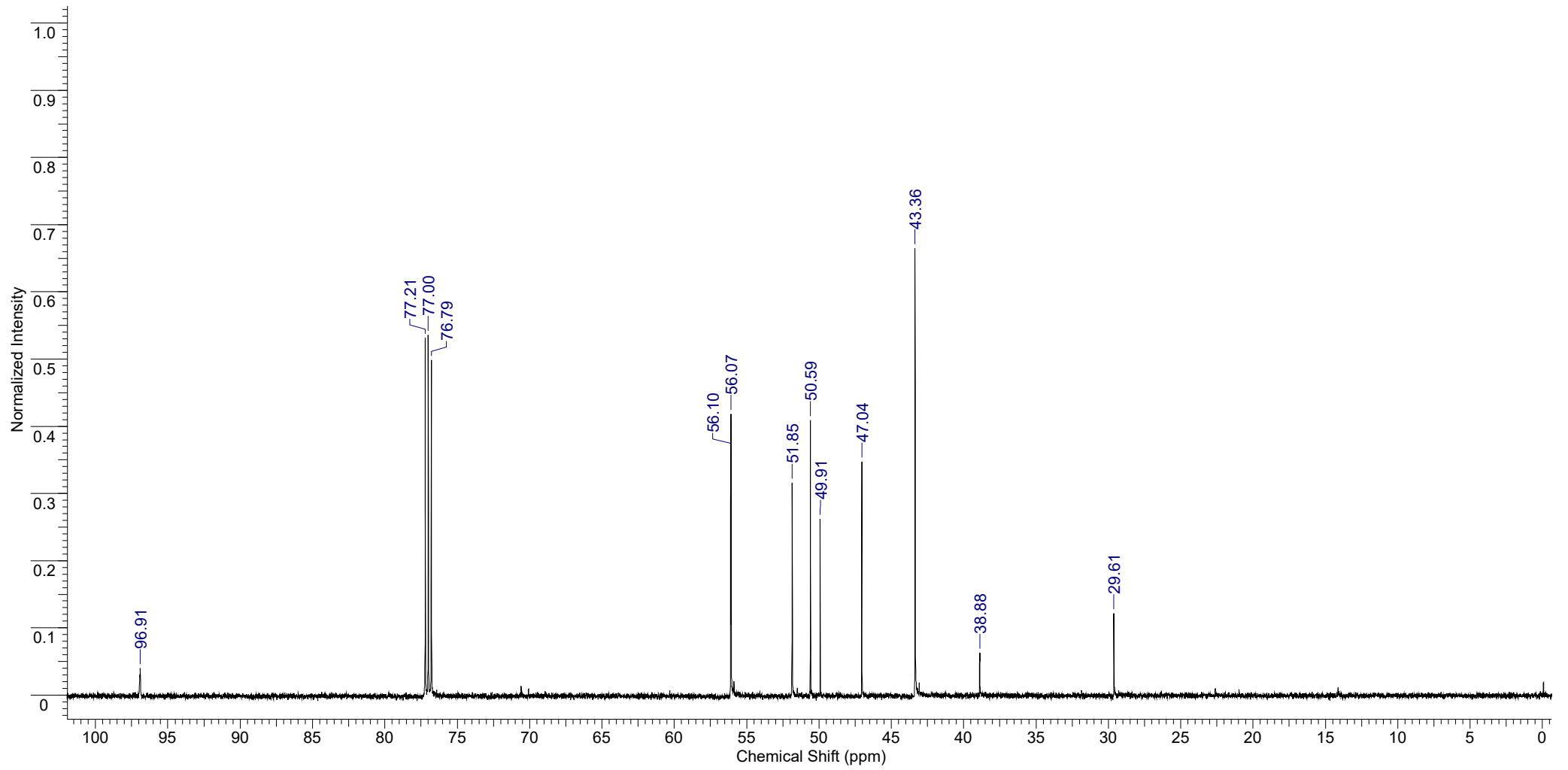
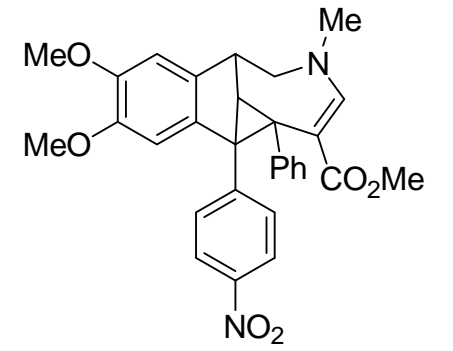
<sup>13</sup>C NMR spectra for 2s.



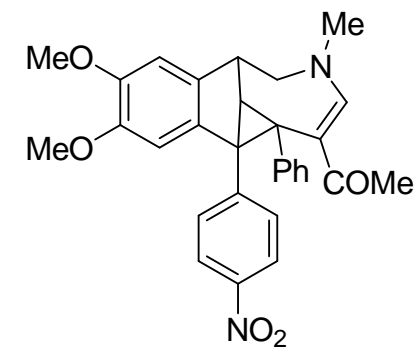
<sup>13</sup>C NMR spectra for 2s.



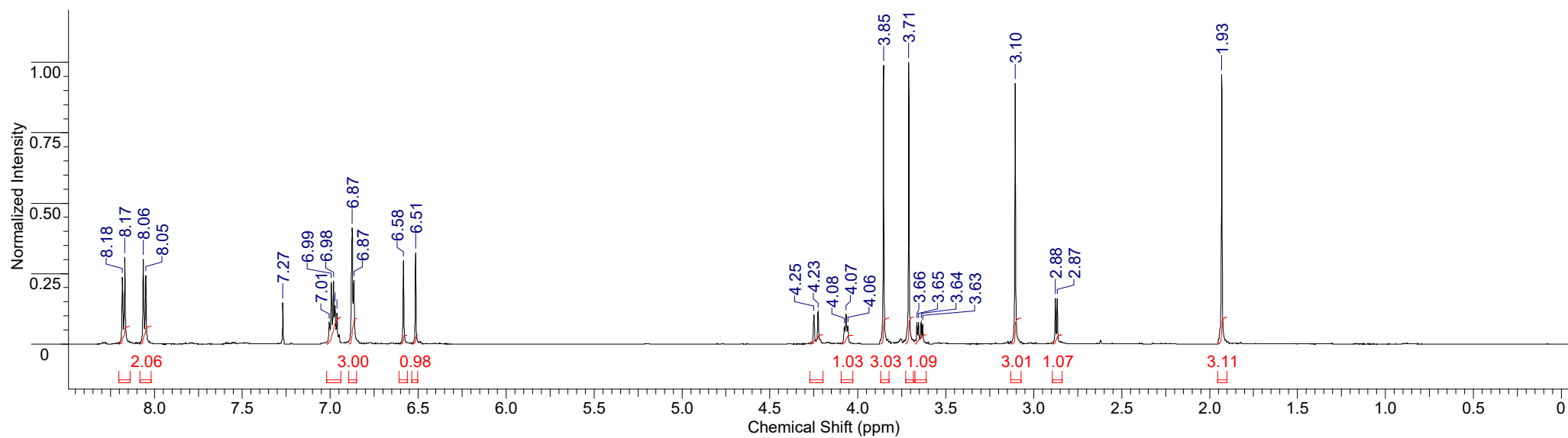
<sup>13</sup>C NMR spectra for 2s.



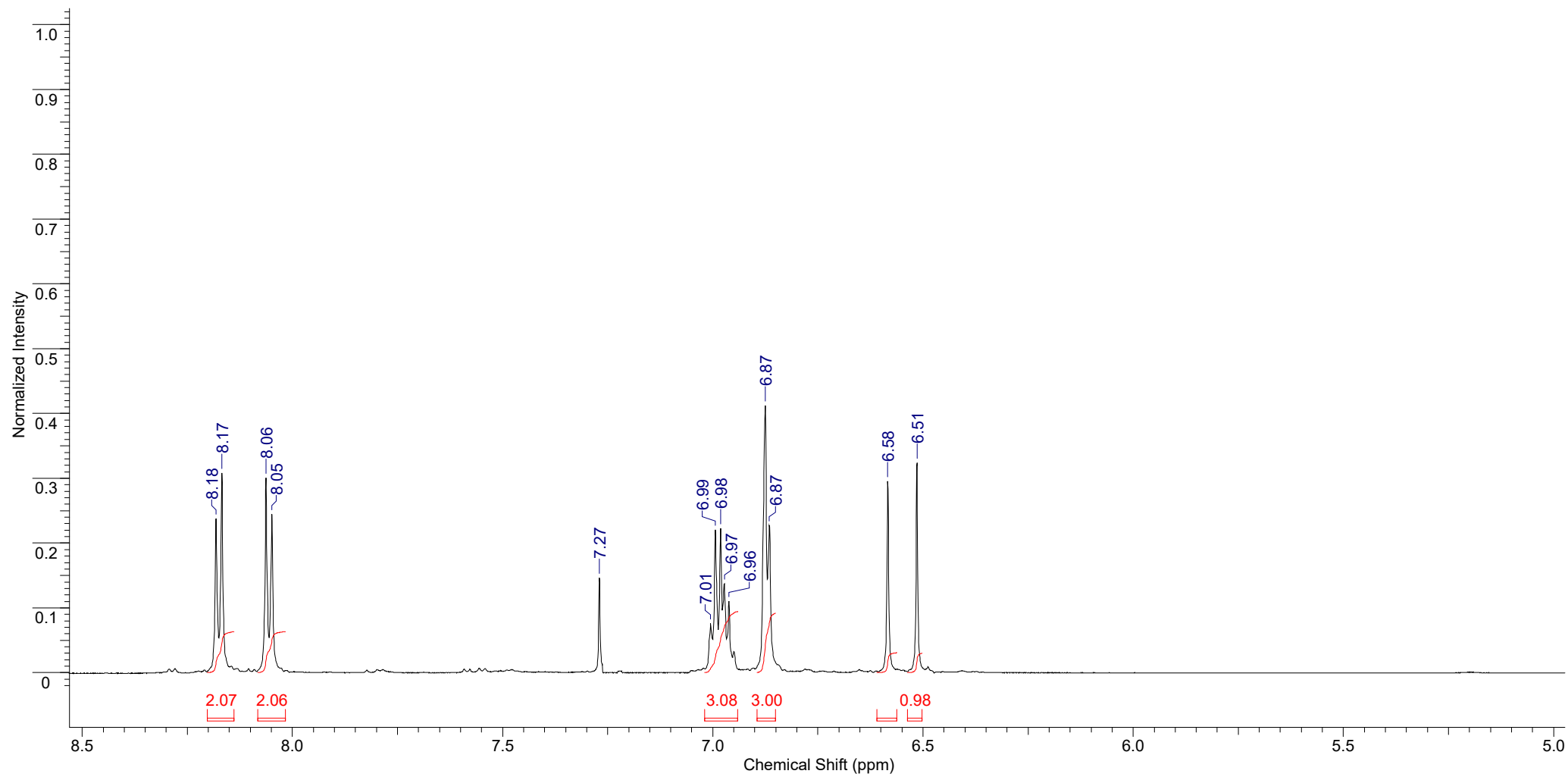
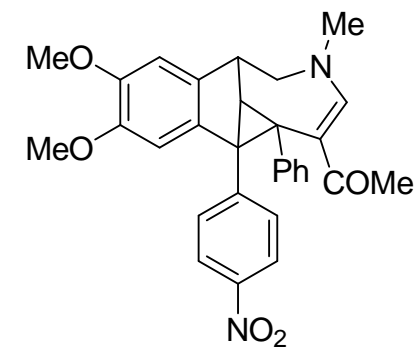
1-[6,7-Dimethoxy-2-methyl-4b-(4-nitrophenyl)-4a-phenyl-1,2,4a,4b,8b,8c-hexahydro-2-azabenz[a]cyclopropa[cd]azulen-4-yl]ethanone (2t)



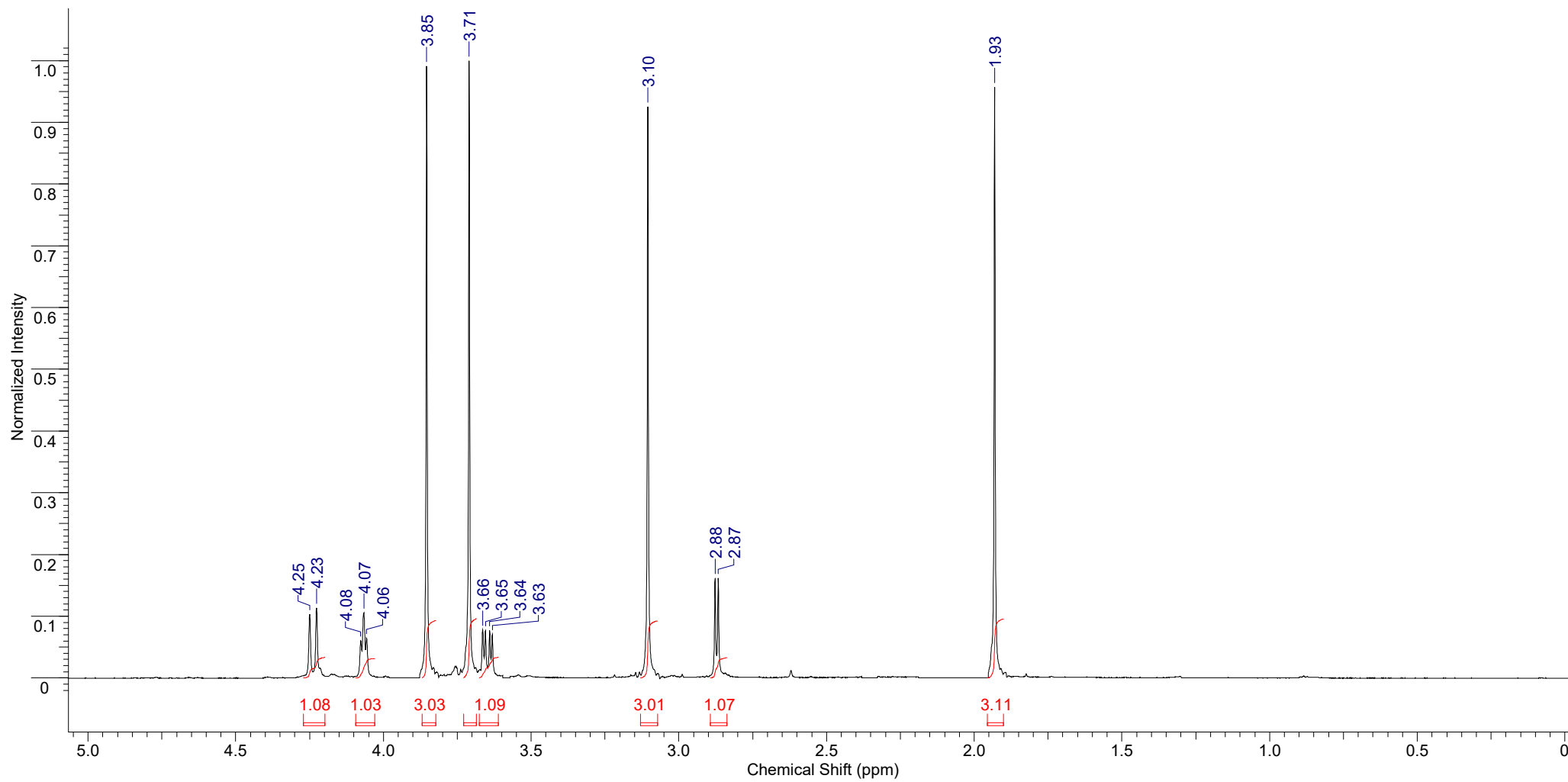
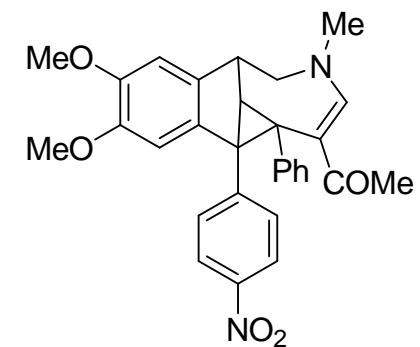
<sup>1</sup>H NMR spectra for 2t.



<sup>1</sup>H NMR spectra for 2t.

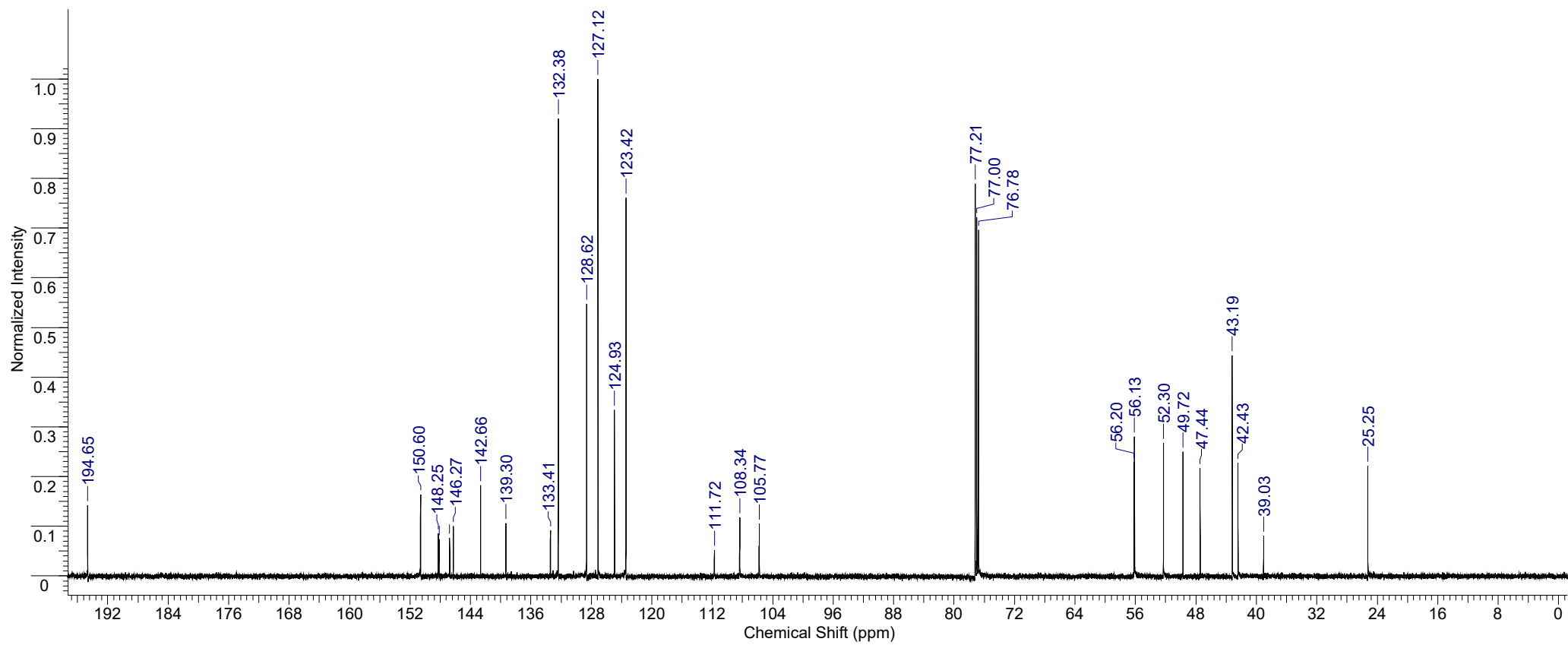
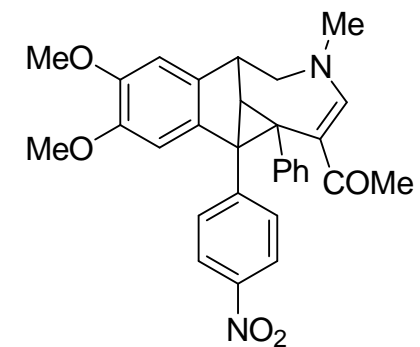


<sup>1</sup>H NMR spectra for 2t.

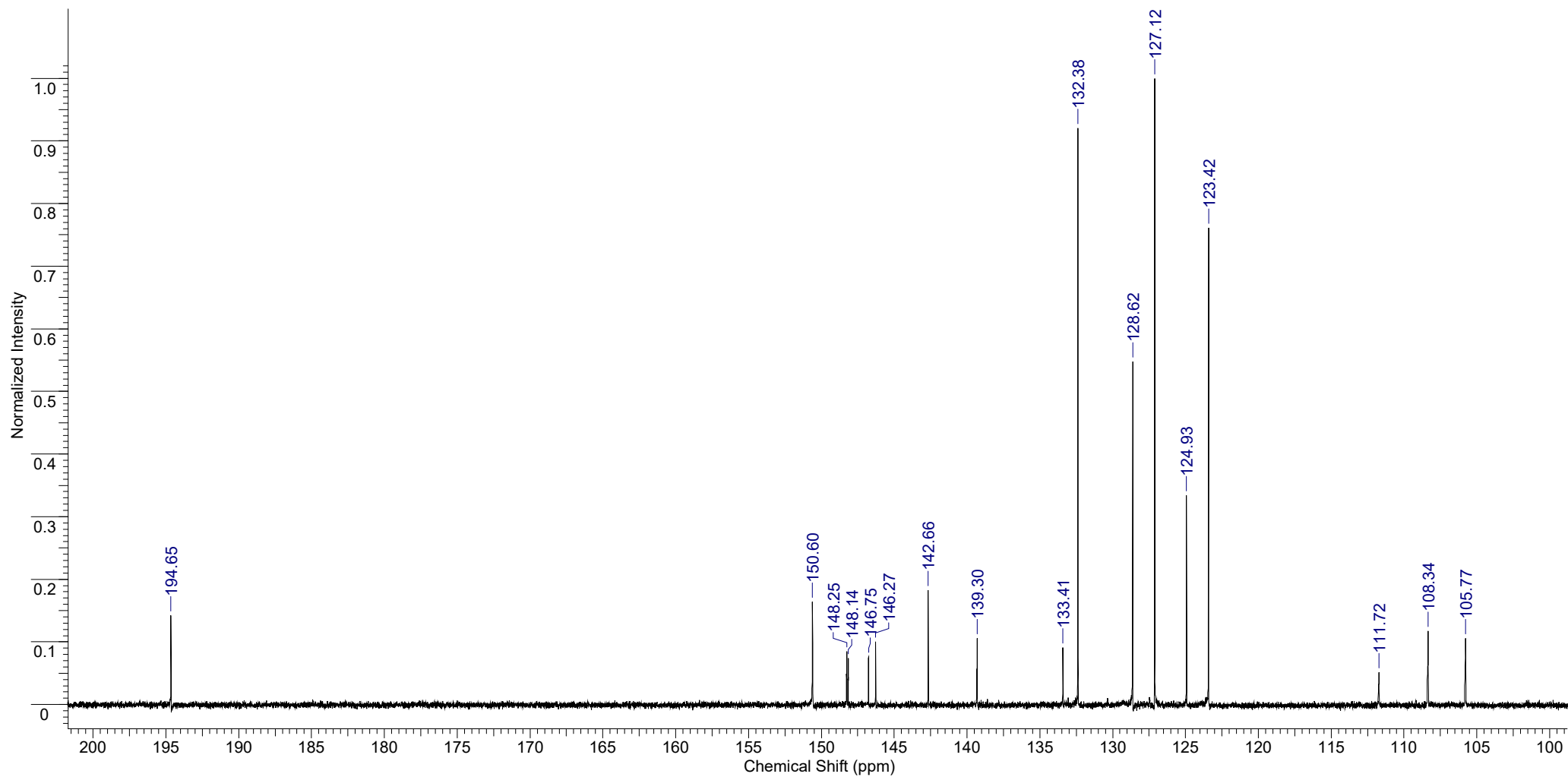
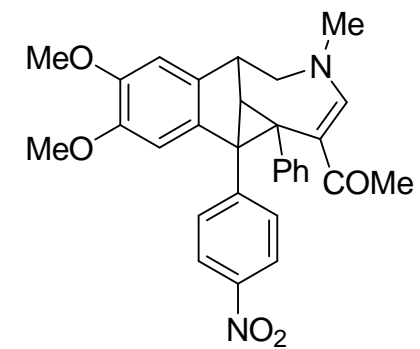




<sup>13</sup>C NMR spectra for 2t.



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<sup>13</sup>C NMR spectra for 2t.

