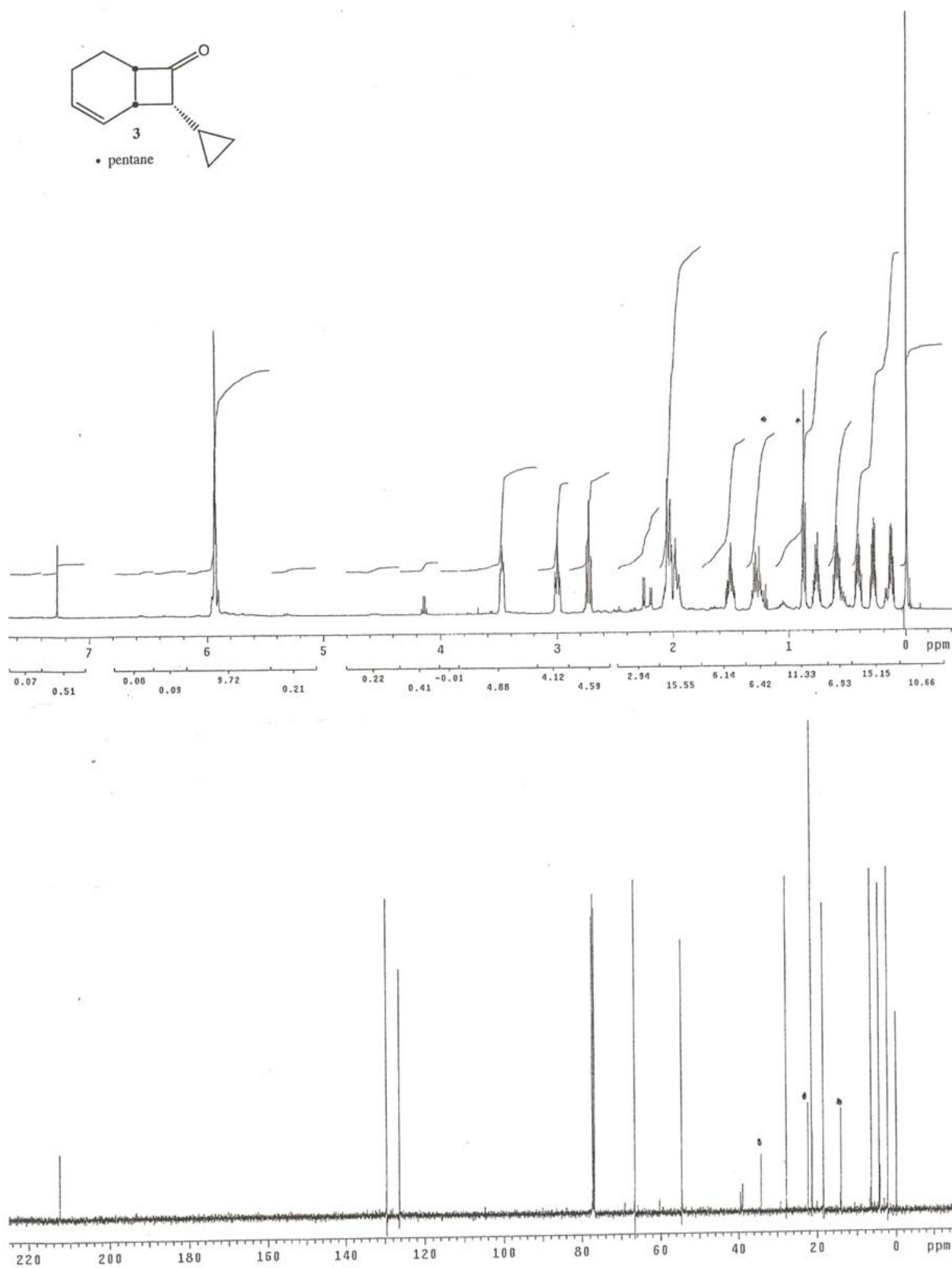
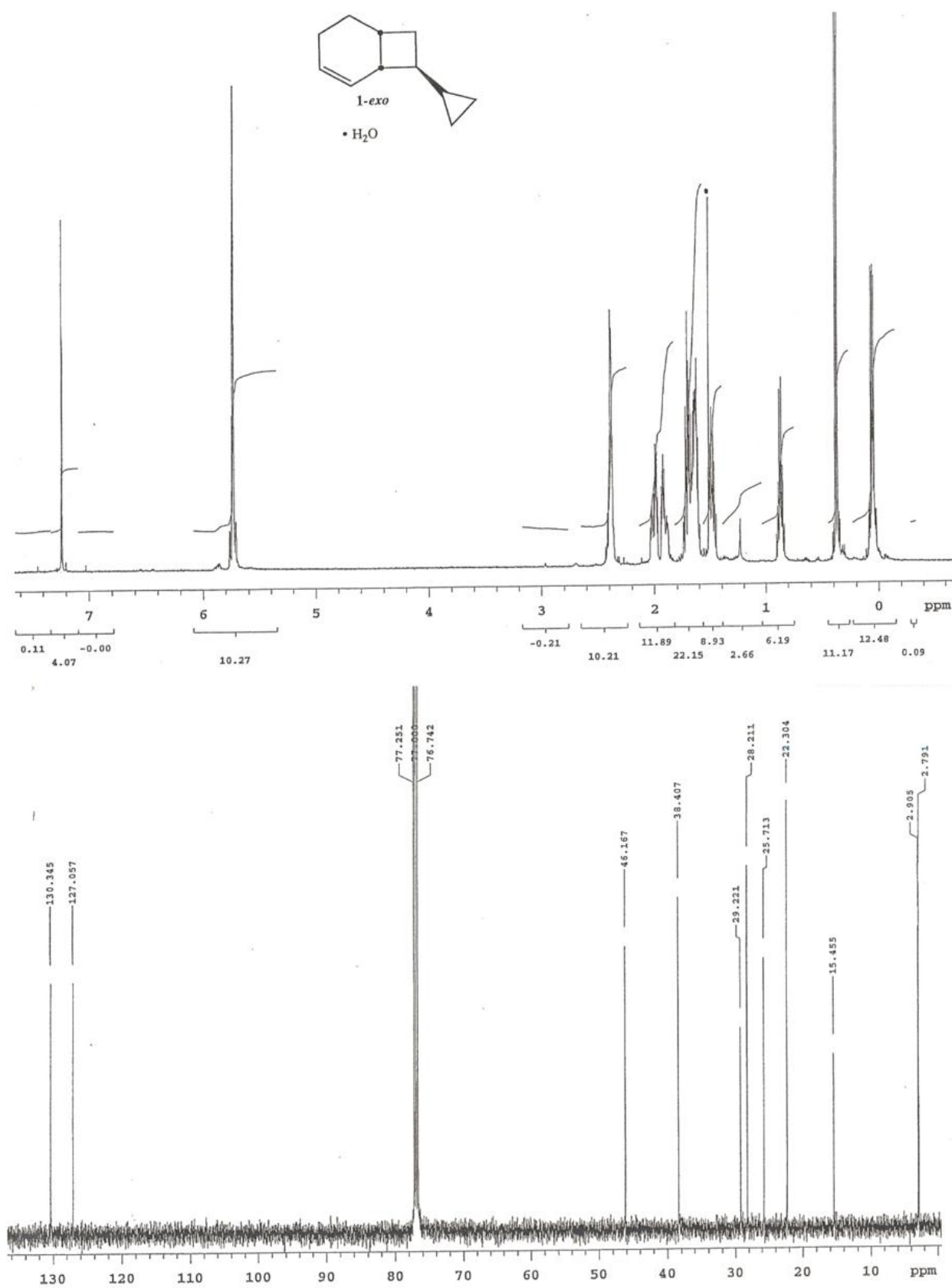
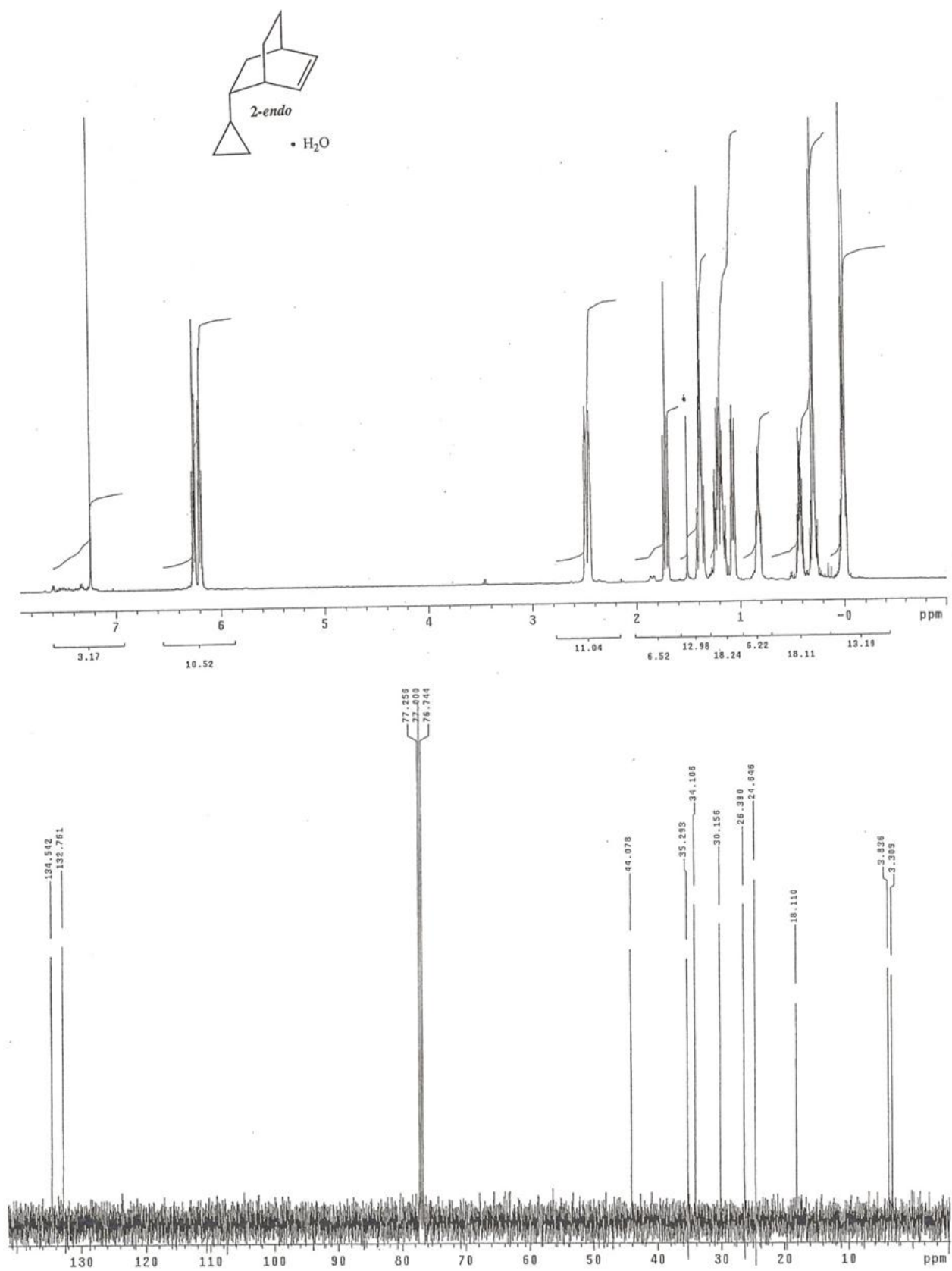


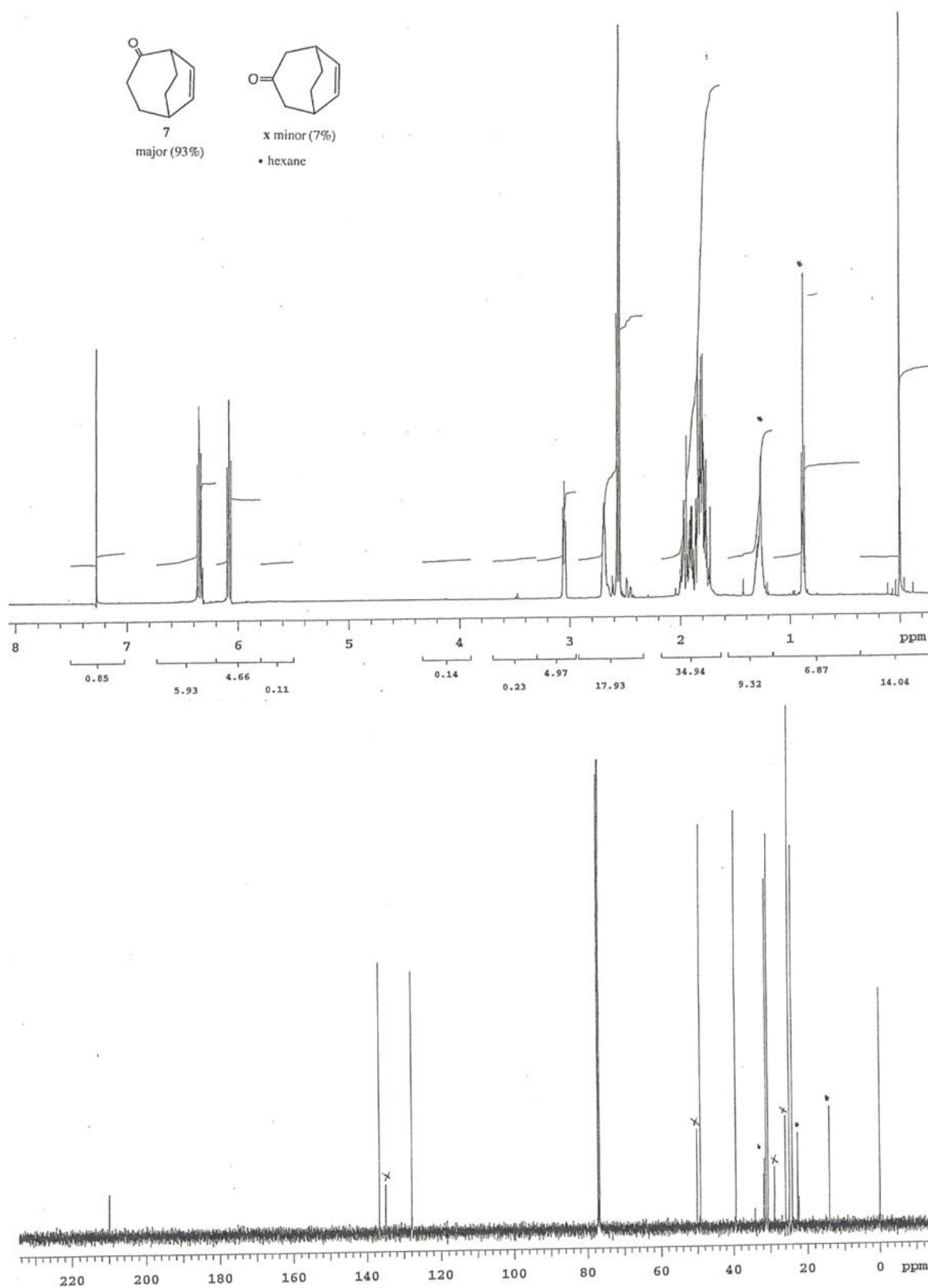
## Supplementary Materials

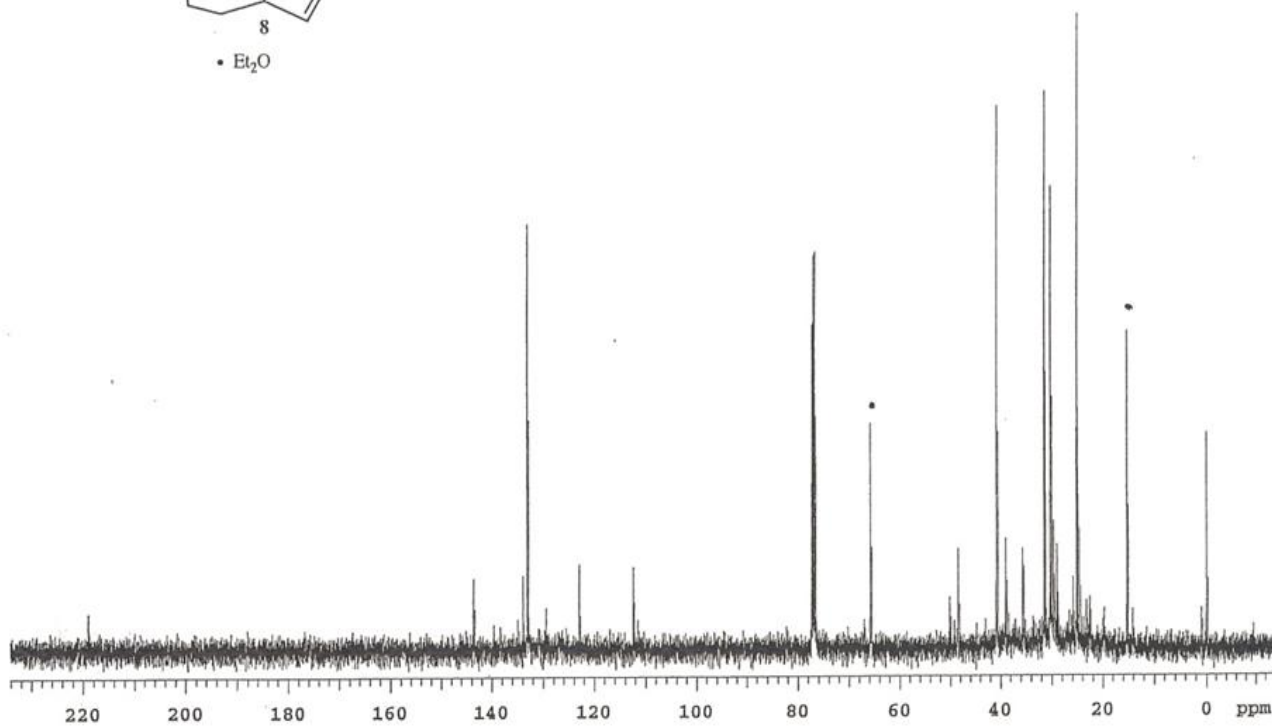
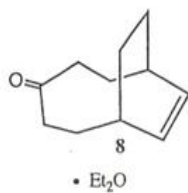
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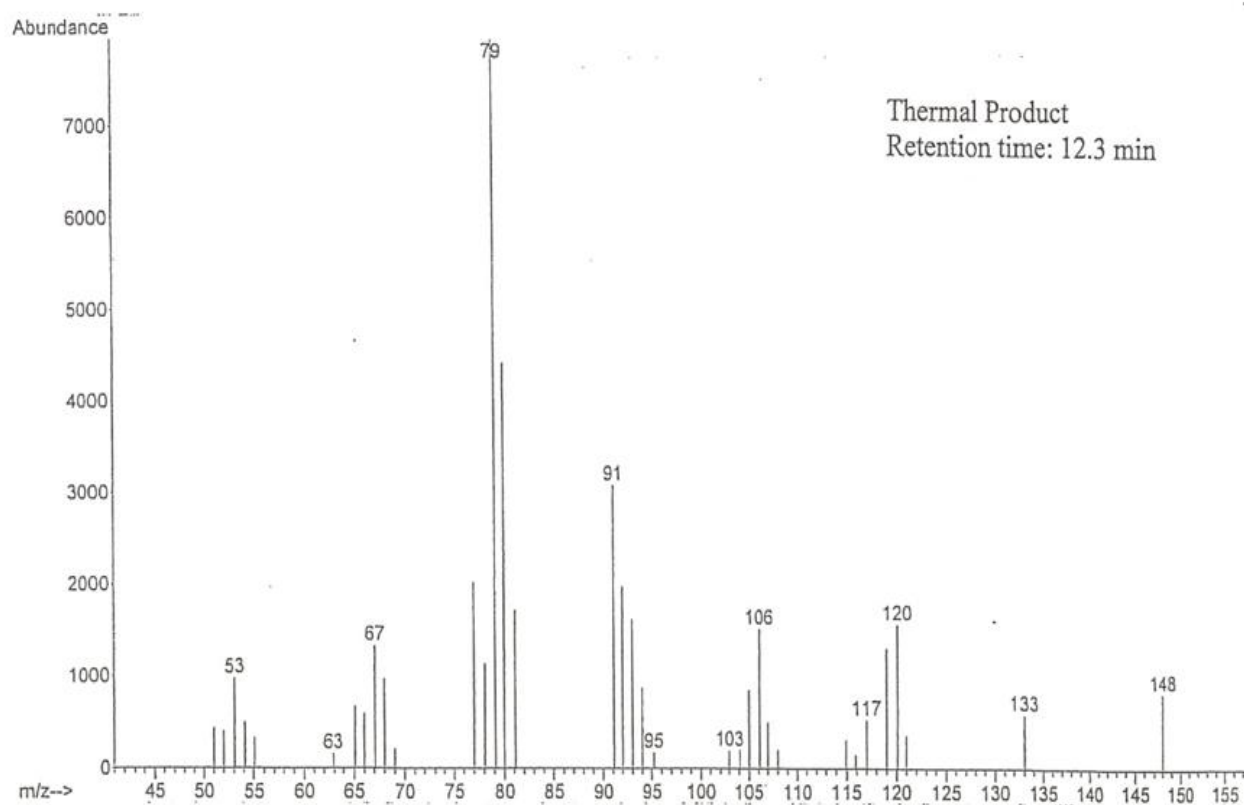
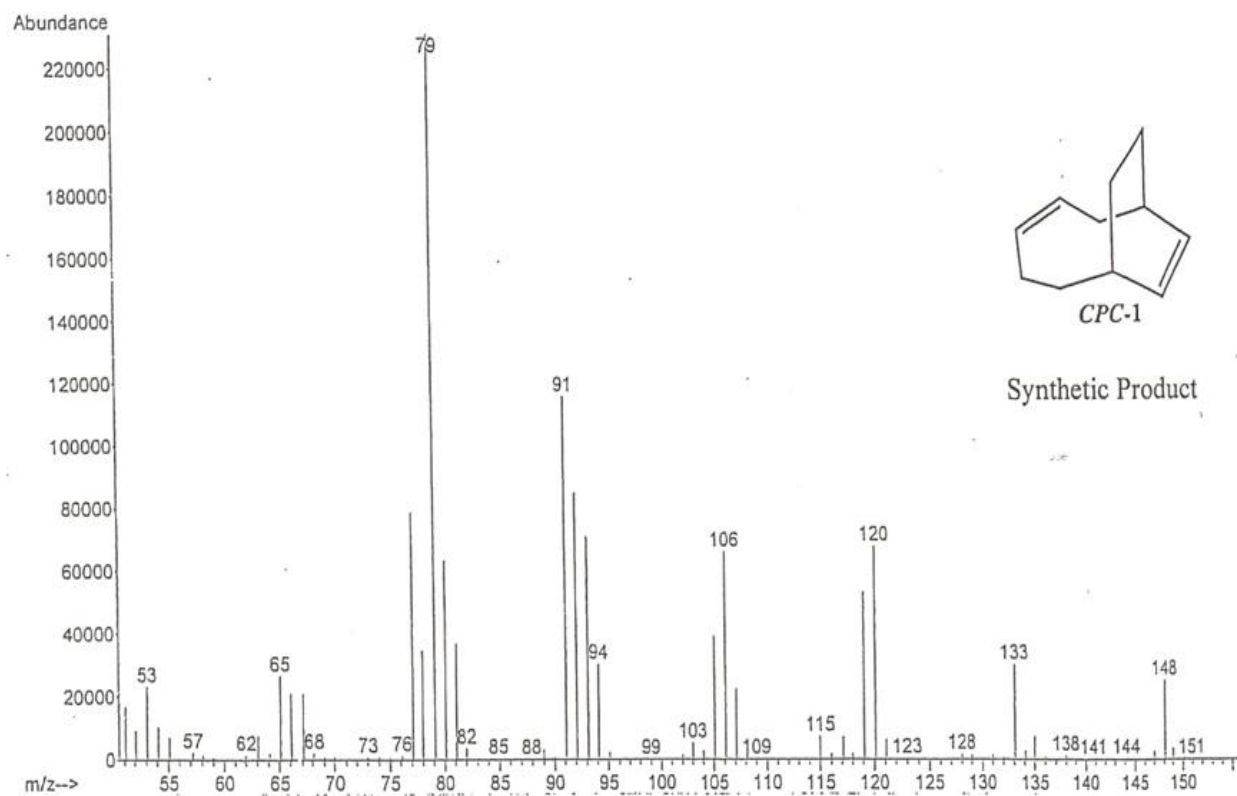
**Figure S1.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of *endo*-8-Cyclopropylbicyclo[4.2.0]oct-2-en-6-one (**3**).

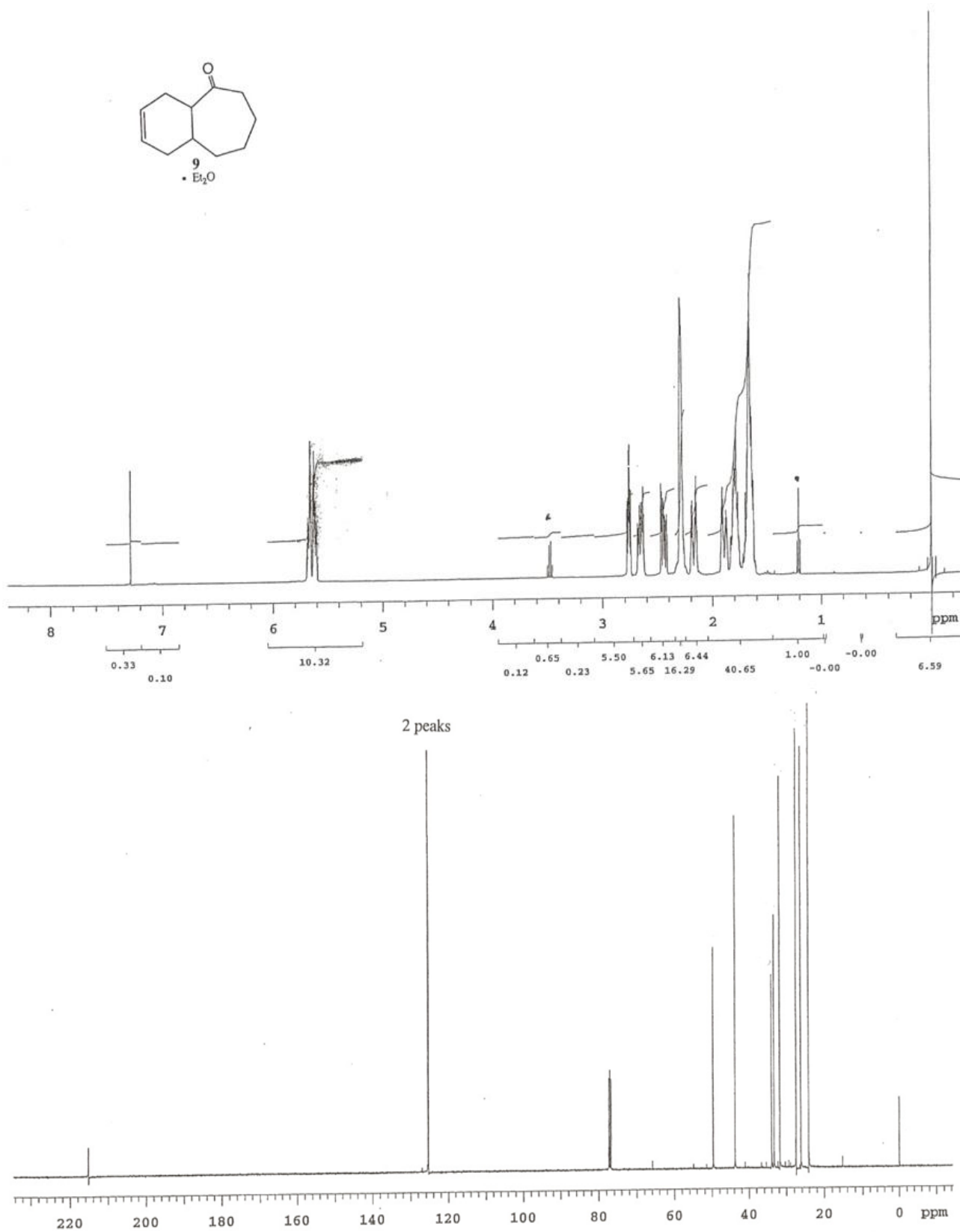
**Figure S2.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of *exo*-8-Cyclopropylbicyclo[4.2.0]oct-2-ene (**1-*exo***).

**Figure S3.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of *endo*-5-Cyclopropylbicyclo[2.2.2]oct-2-ene (**2-endo**).

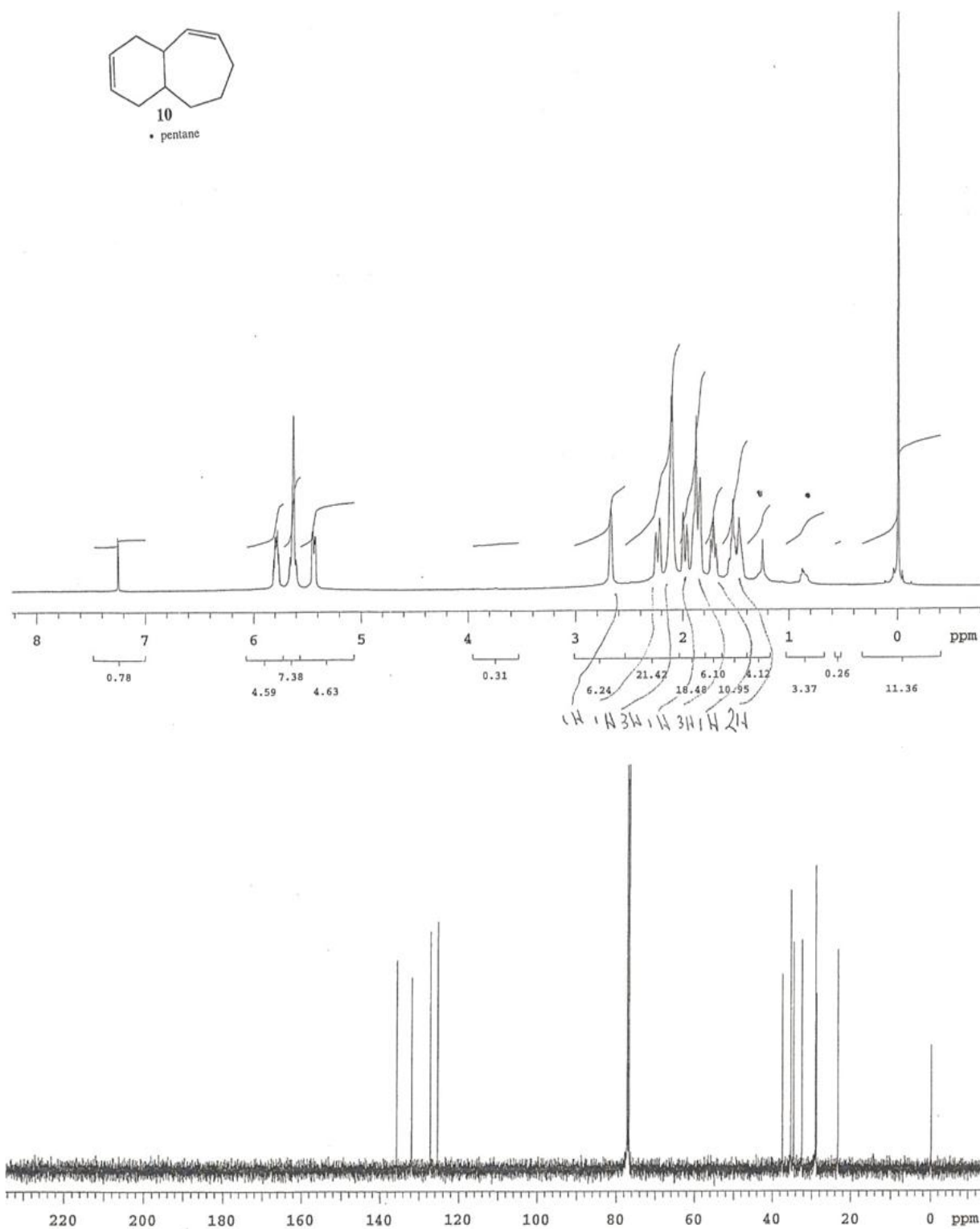
**Figure S4.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of Bicyclo[3.2.0]non-6-en-2-one (**7**).

**Figure S5.**  $^{13}\text{C}$ -NMR of Bicyclo[5.2.2]undec-8-en-4-one (**8**).

**Figure S6.** Mass Spectra of Bicyclo[5.2.2]undeca-3,8-diene (**CPC-1**).

**Figure S7.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of Bicyclo[5.4.0]undec-9-en-2-one (**9**).



**Figure S8.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of Bicyclo[5.4.0]undeca-2,9-diene (**10**).

**Table S1.** Time-dependent Concentration Kinetics for Compound **1-exo** @275 °C.

Time (h)	<b>2-endo</b> ( <i>sr</i> )	<b>2-exo</b> ( <i>si</i> )	<b>CPC-1</b>	<b>1-exo</b>	<b>1-endo</b>	fragments
0.0	0	0	0	1.00000	0	0
1.0	0.00953	0.01654	0*	0.86826	0.06619	0.03948
2.0	0.01750	0.03105	0.00335	0.76518	0.10194	0.08098
4.0	0.02805	0.05152	0.00622	0.57212	0.12505	0.21704
6.0	0.03942	0.07193	0.00930	0.47742	0.13000	0.27193
7.9	0.05084	0.09323	0.01161	0.42208	0.12870	0.29354
10.0	0.05955	0.10824	0.01444	0.34375	0.11278	0.36123
15.8	0.07450	0.13734	0.01745	0.21397	0.07333	0.48340
23.3	0.08815	0.15824	0.01898	0.11277	0.03944	0.58240
35.4	0.10271	0.17862	0.02137	0.05111	0.01719	0.62898

\* Value fell below integration threshold on the analytical GC recorder/integrator.

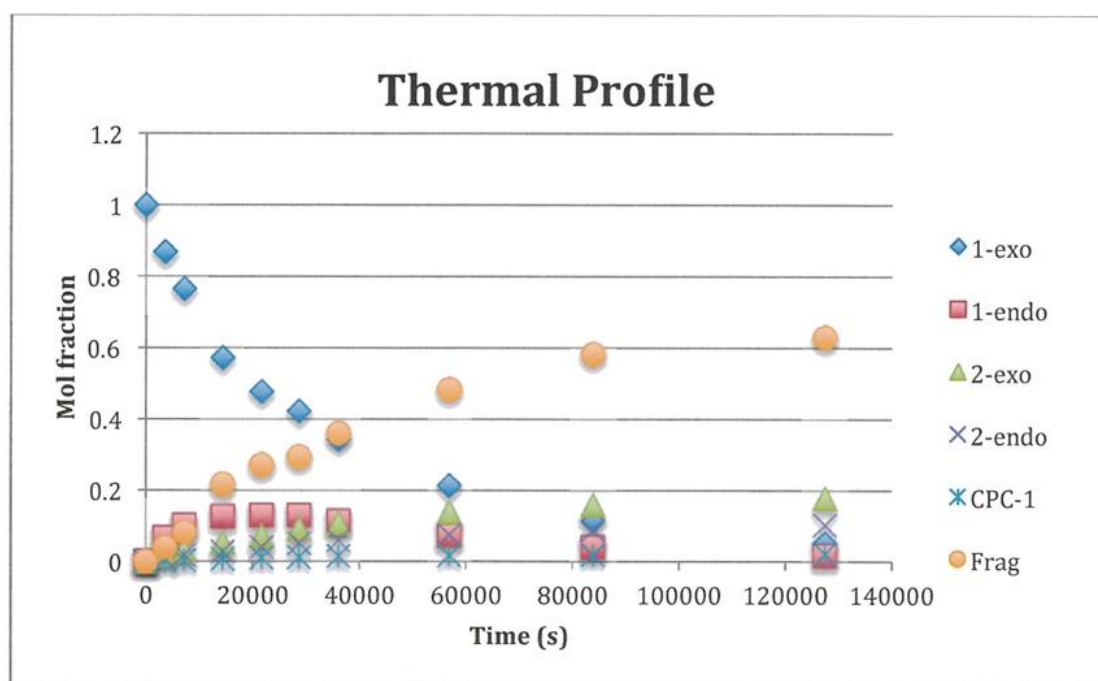
**Figure S9.** Concentration *versus* time plot for thermal reactions of **1-exo** @275 °C.

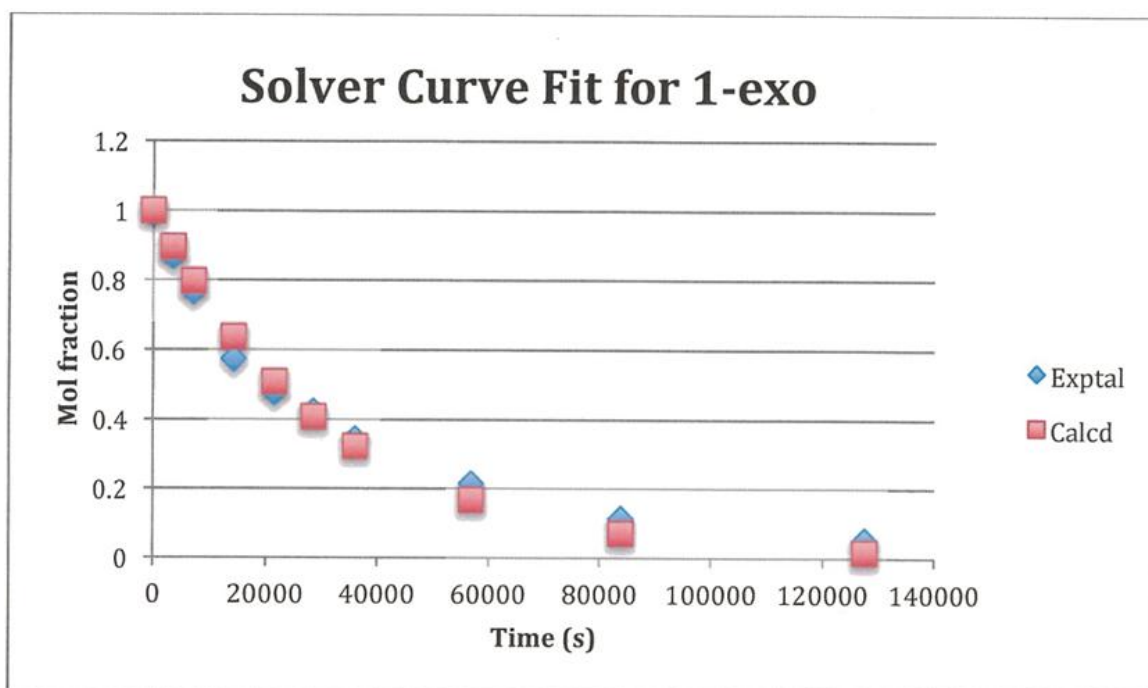
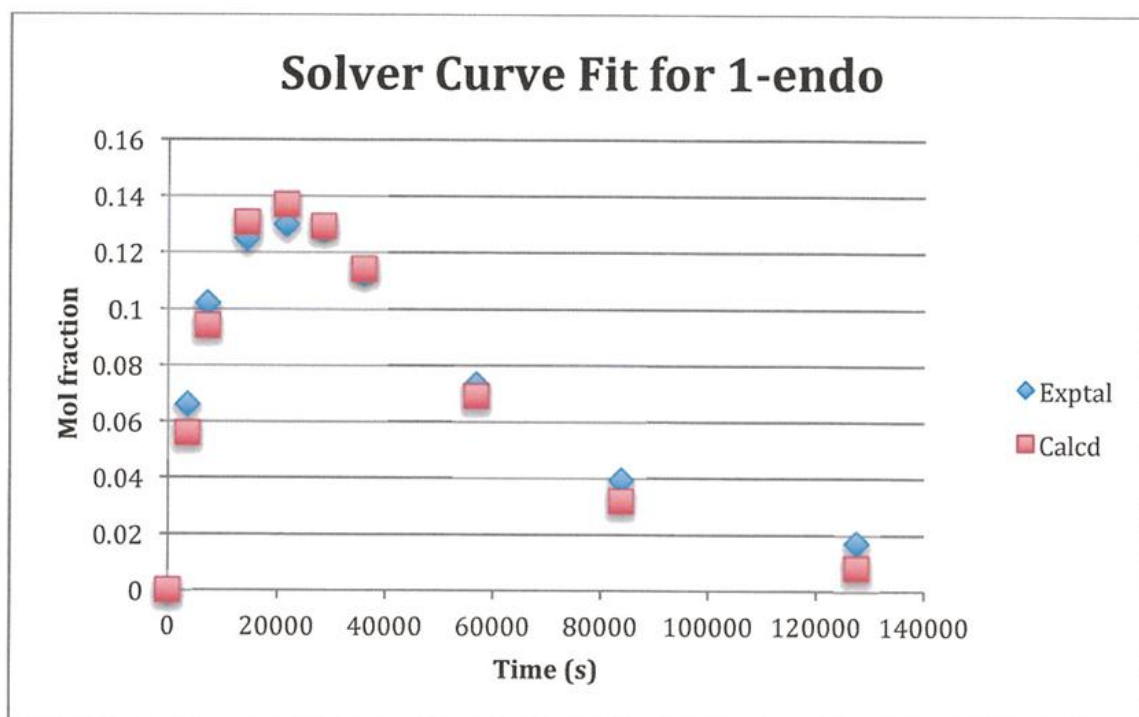
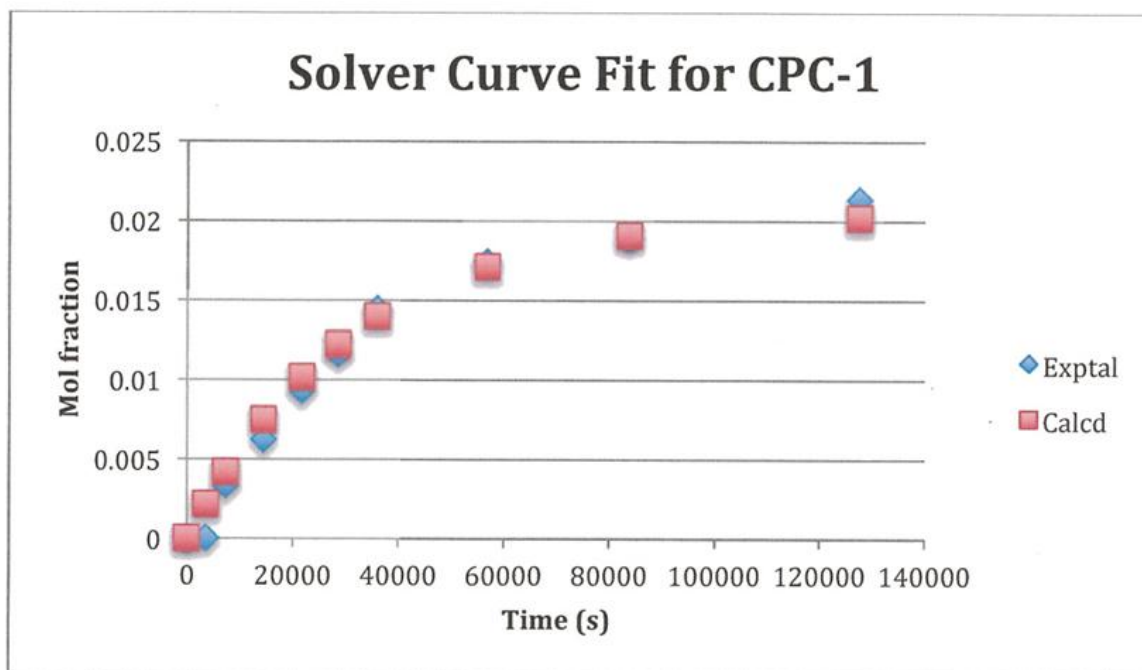
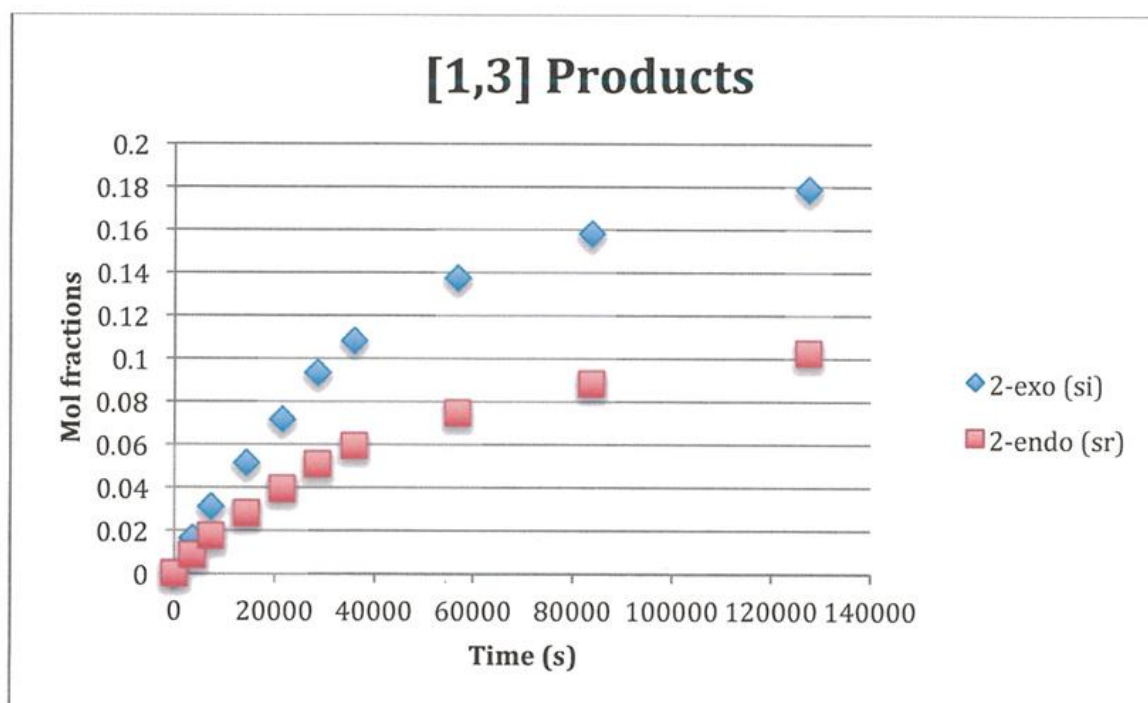
Figure S10. Solver Curve Fit for Compound 1-*exo*.Figure S11. Solver Curve Fit for Compound 1-*endo*.

Figure S12. Solver Curve Fit for Compound *CPC-1*.Figure S13. Concentration versus time plot for [1,3] thermal products (*2-exo* and *2-endo*).

**Figure S14.** Concentration *versus* time plot for fragmentation, both direct and indirect.