

SUPPORTING INFORMATION FOR

One-pot synthesis of chroman-4-one-2-carboxamides

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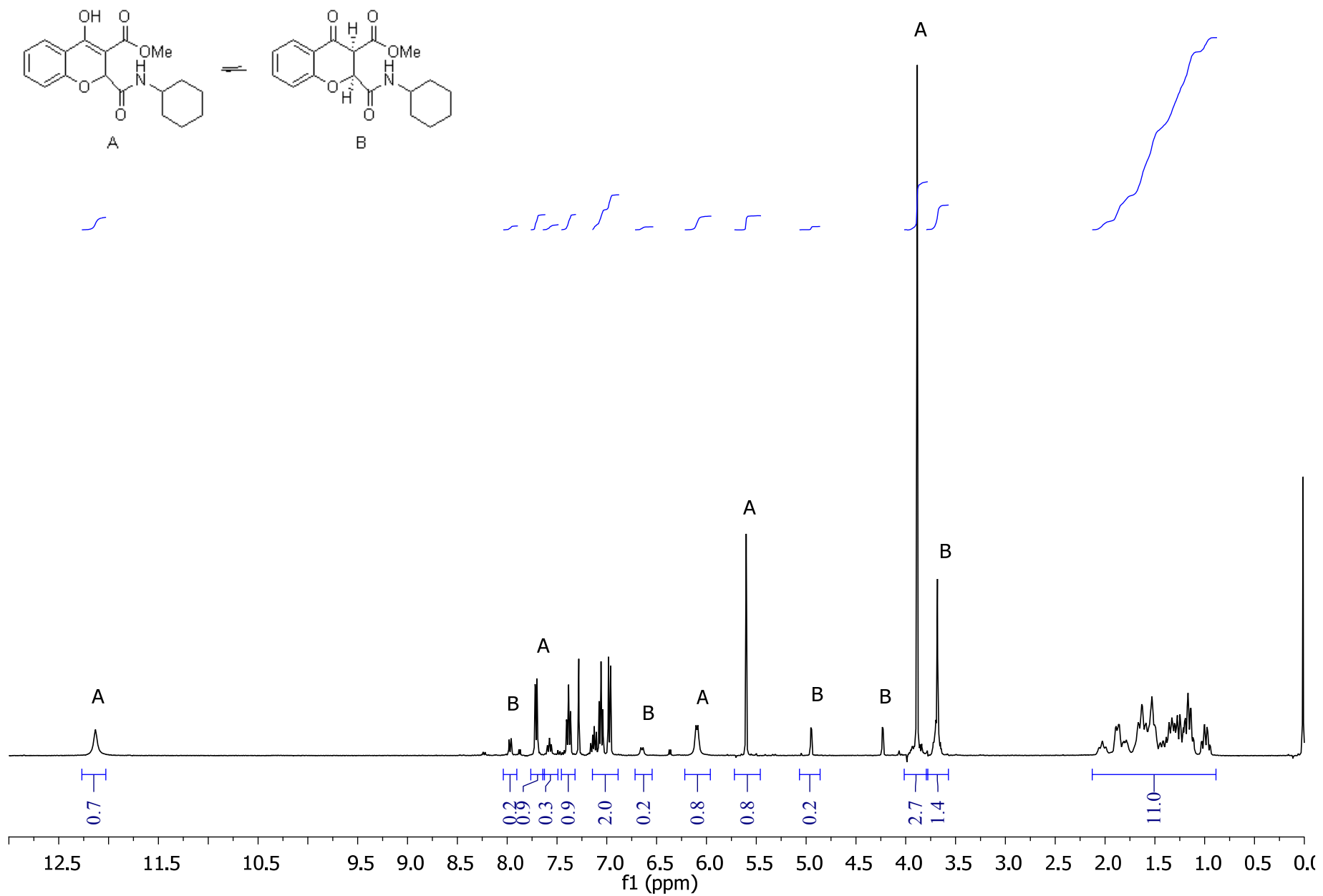
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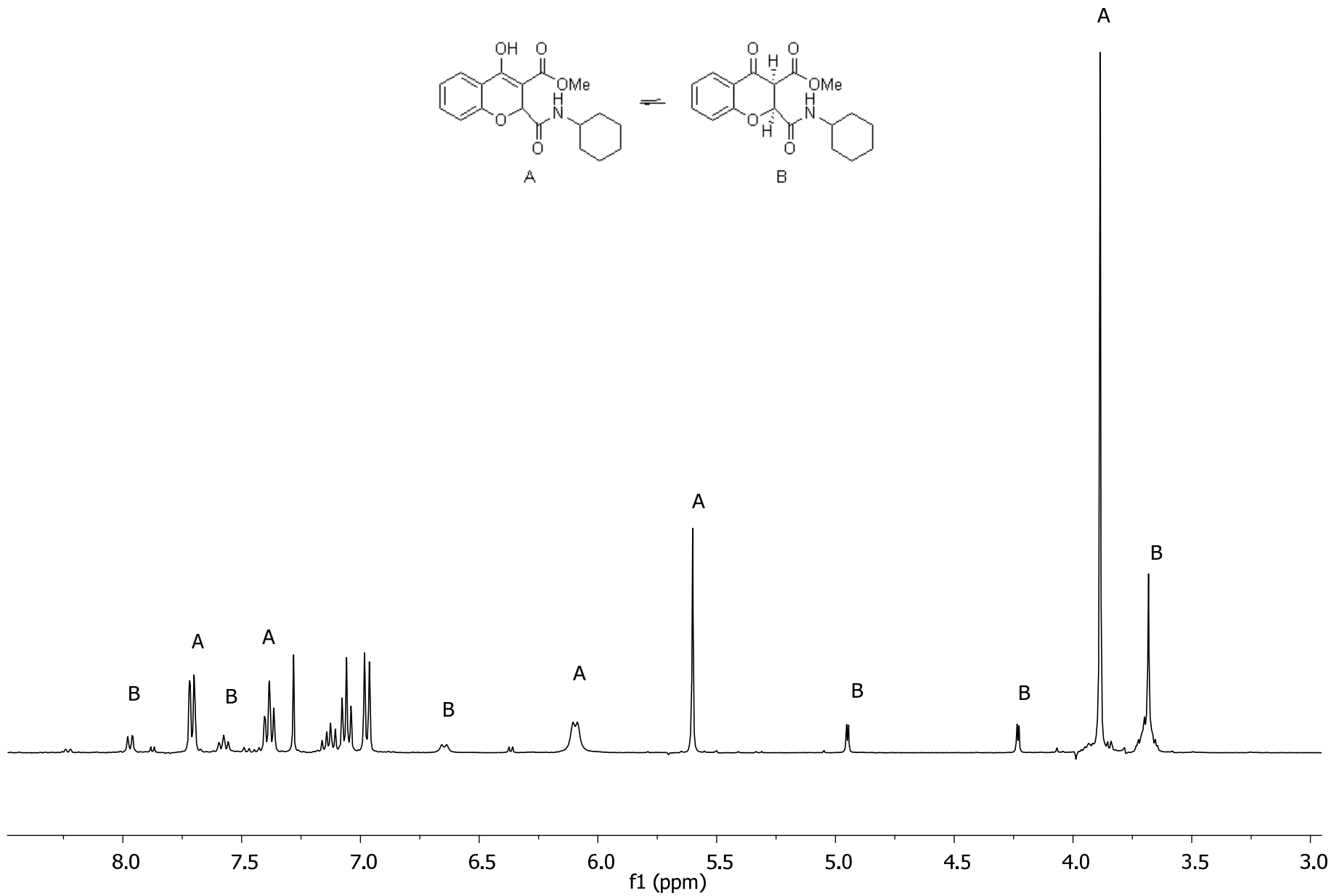
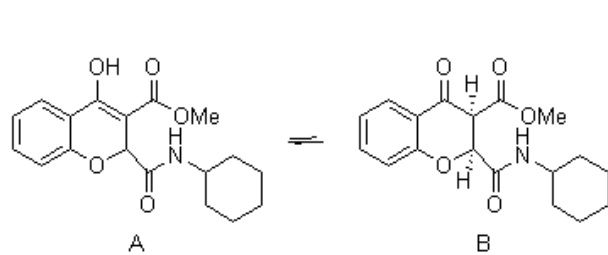
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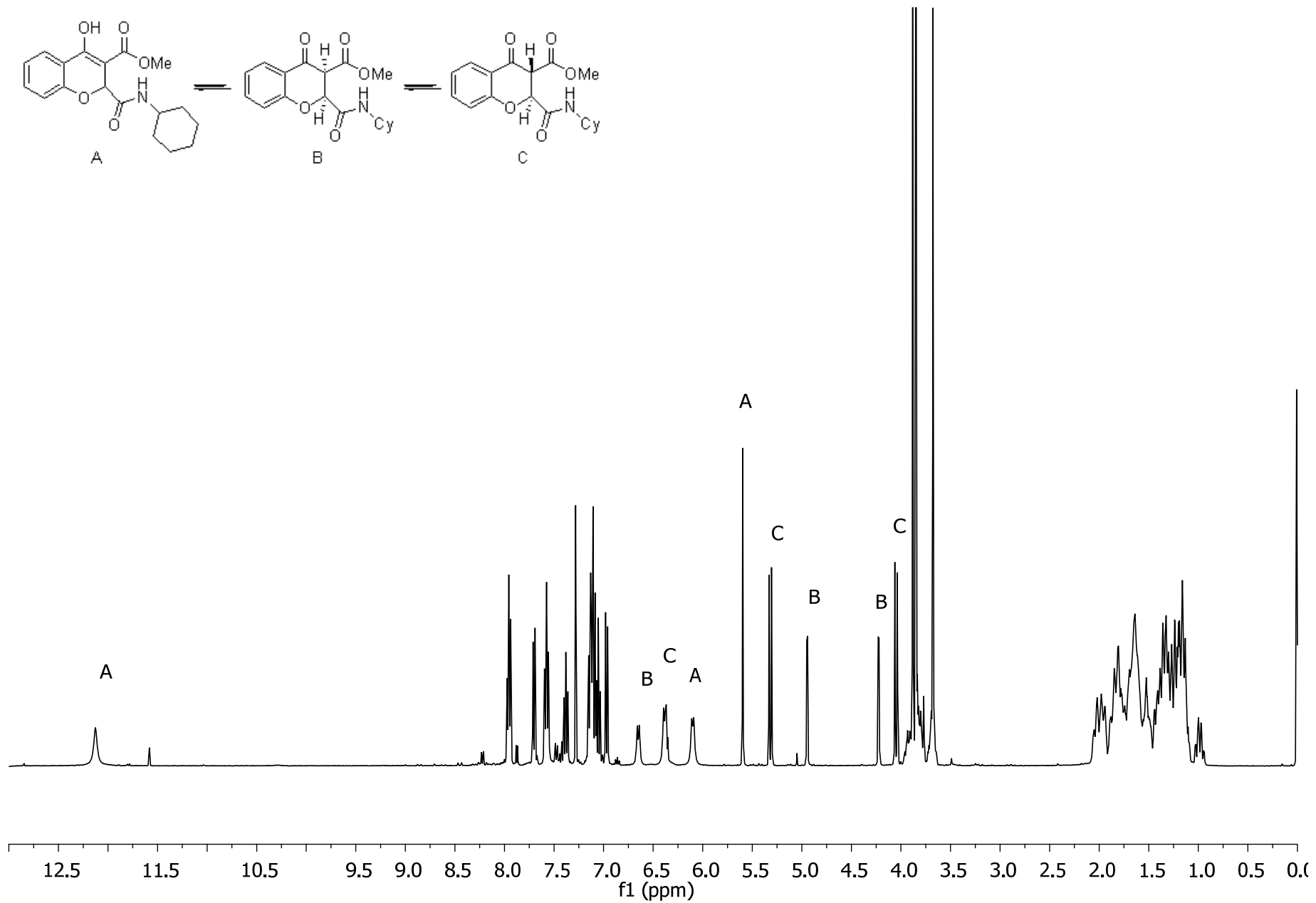
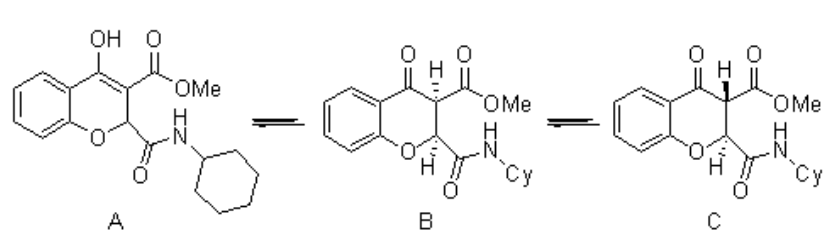
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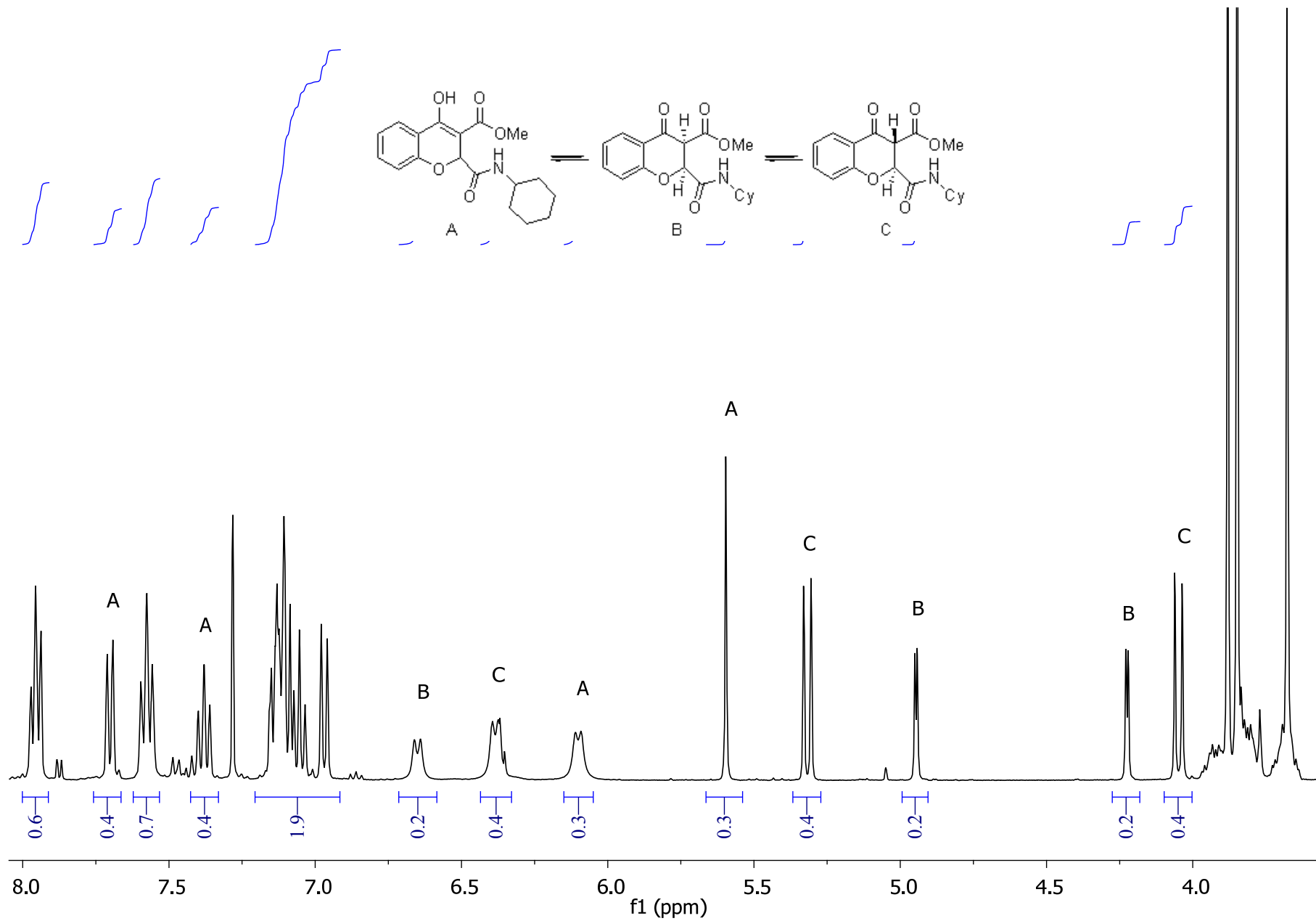
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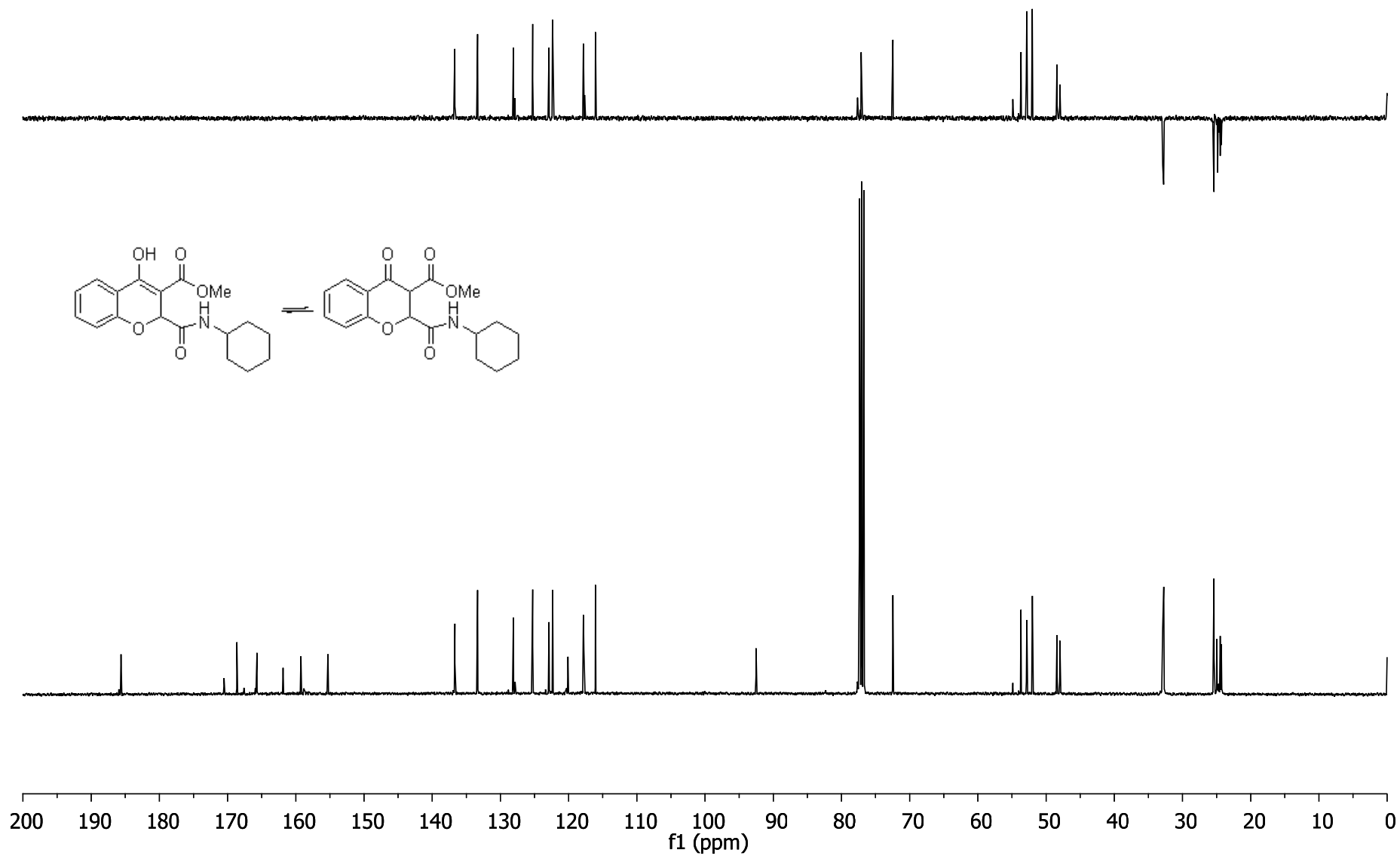
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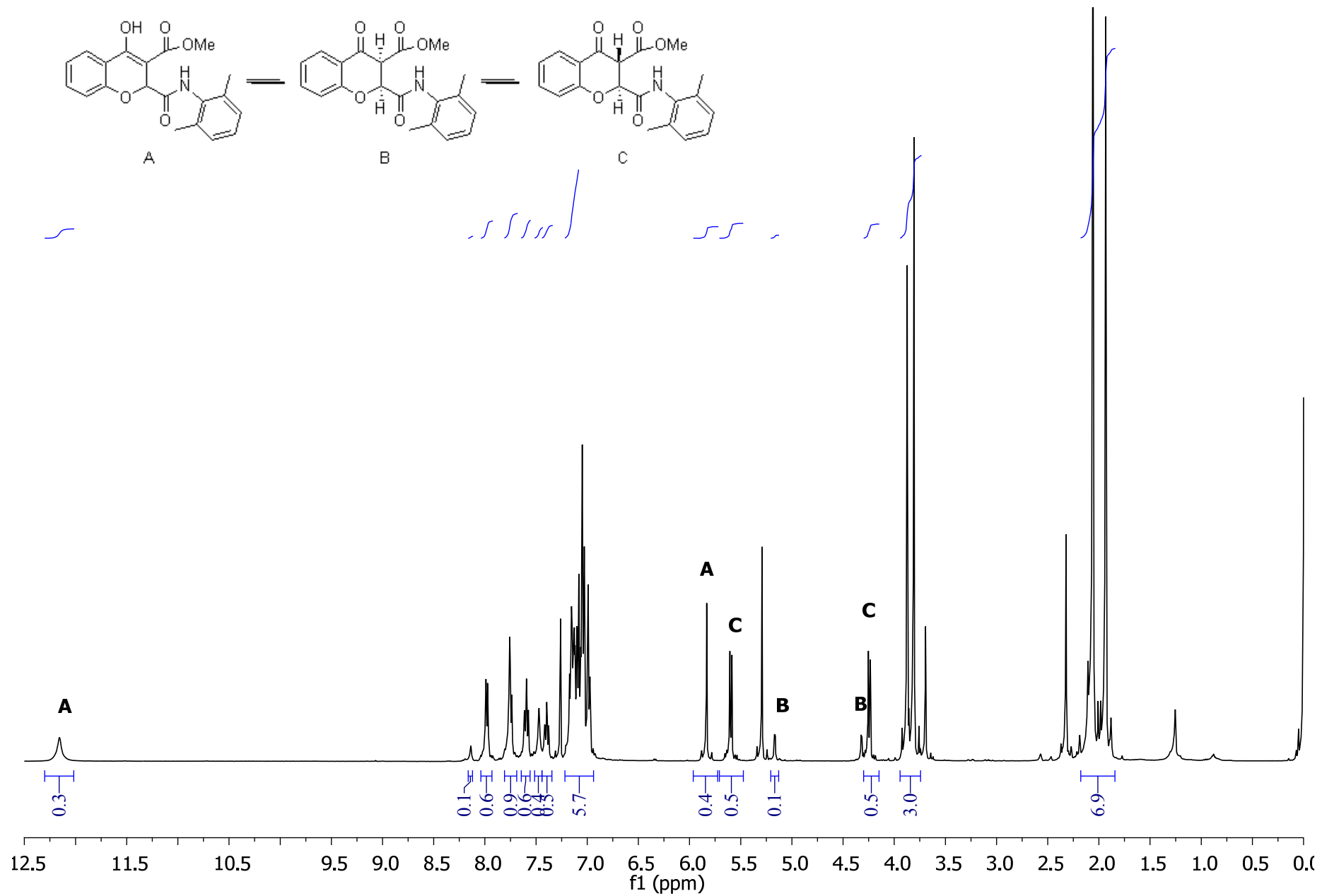


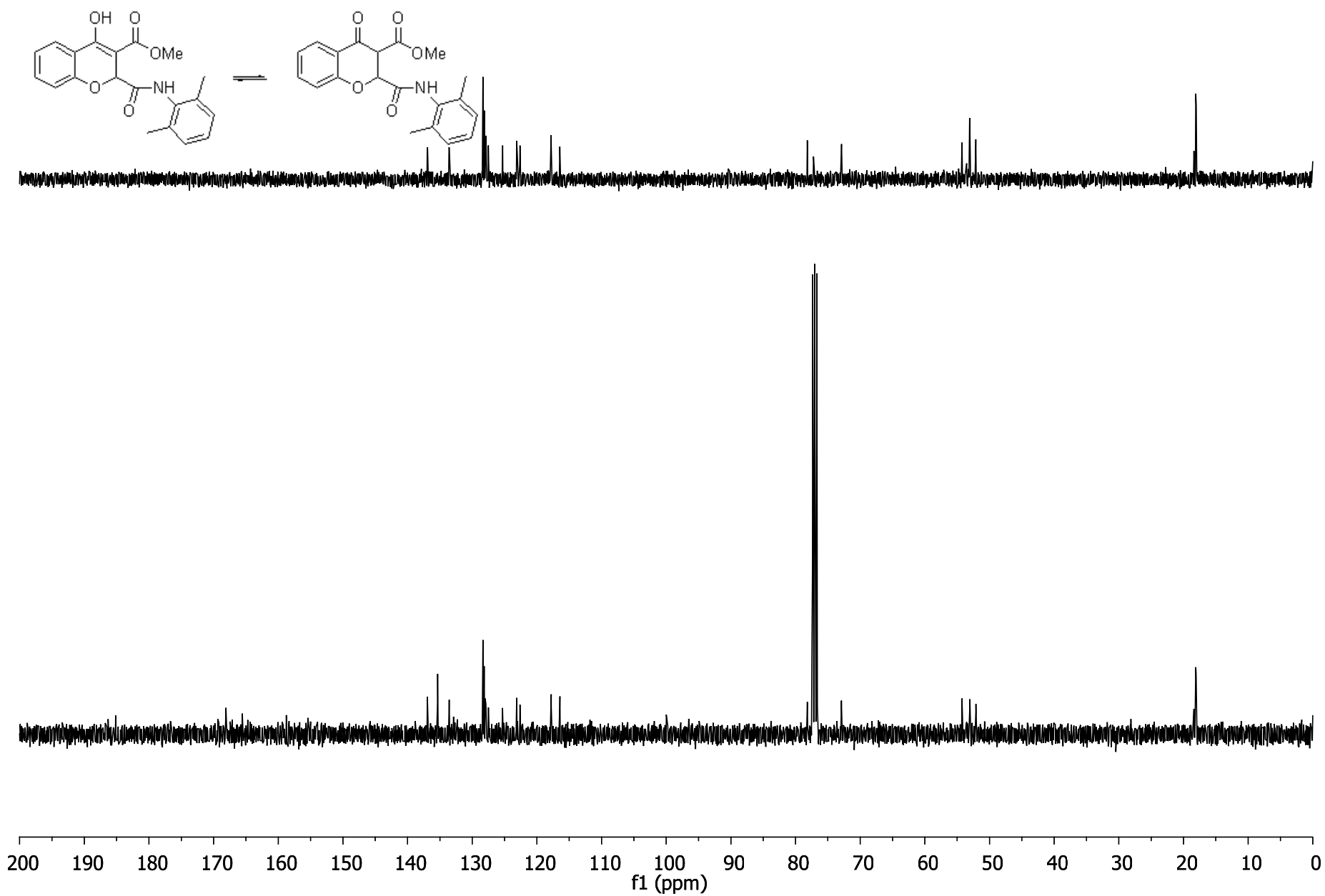


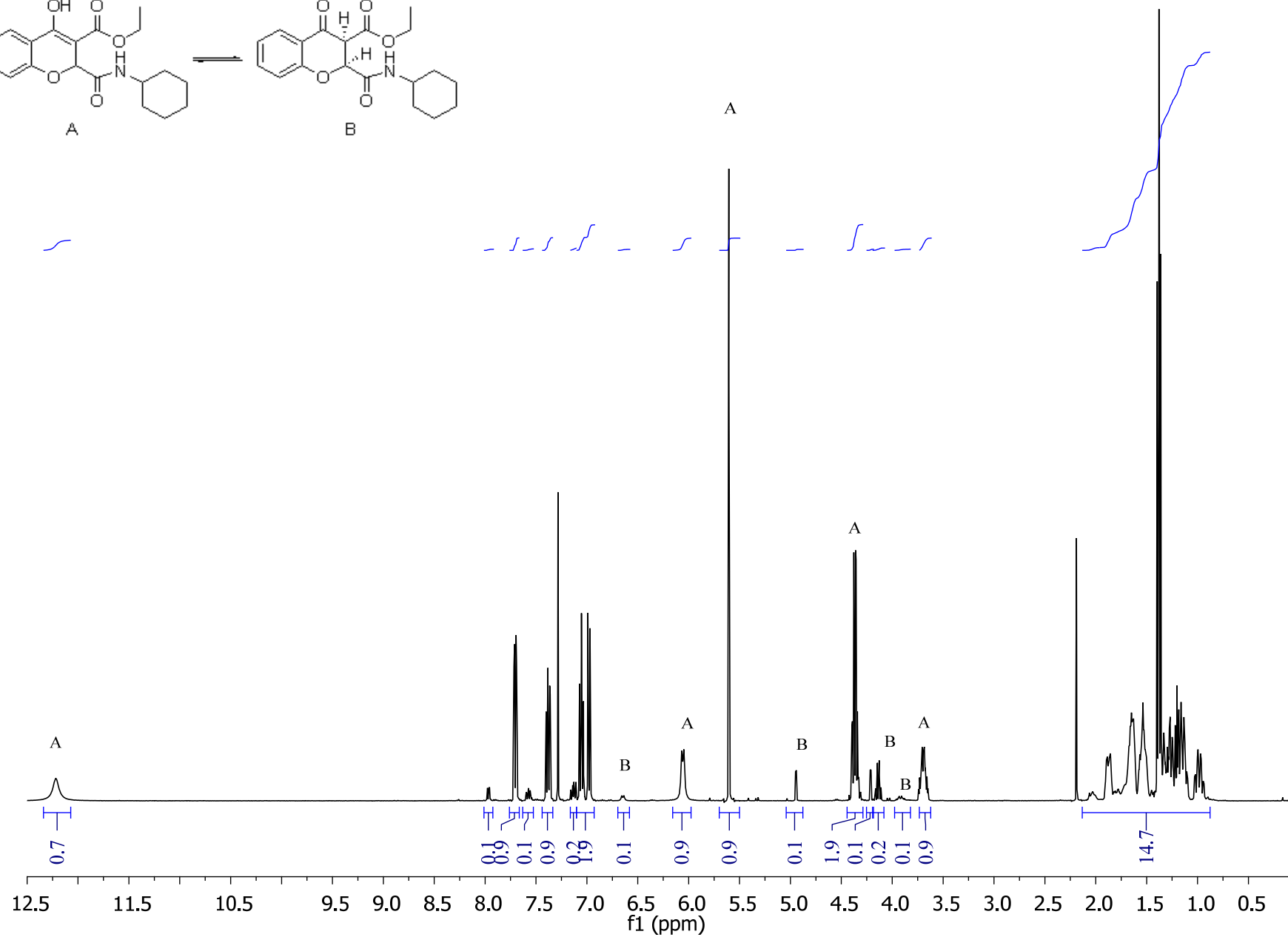
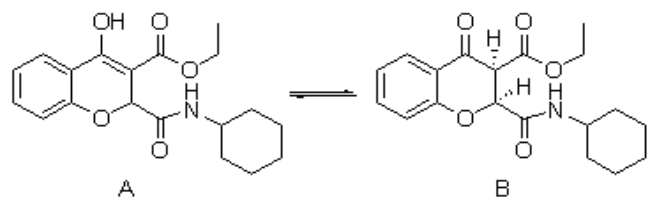


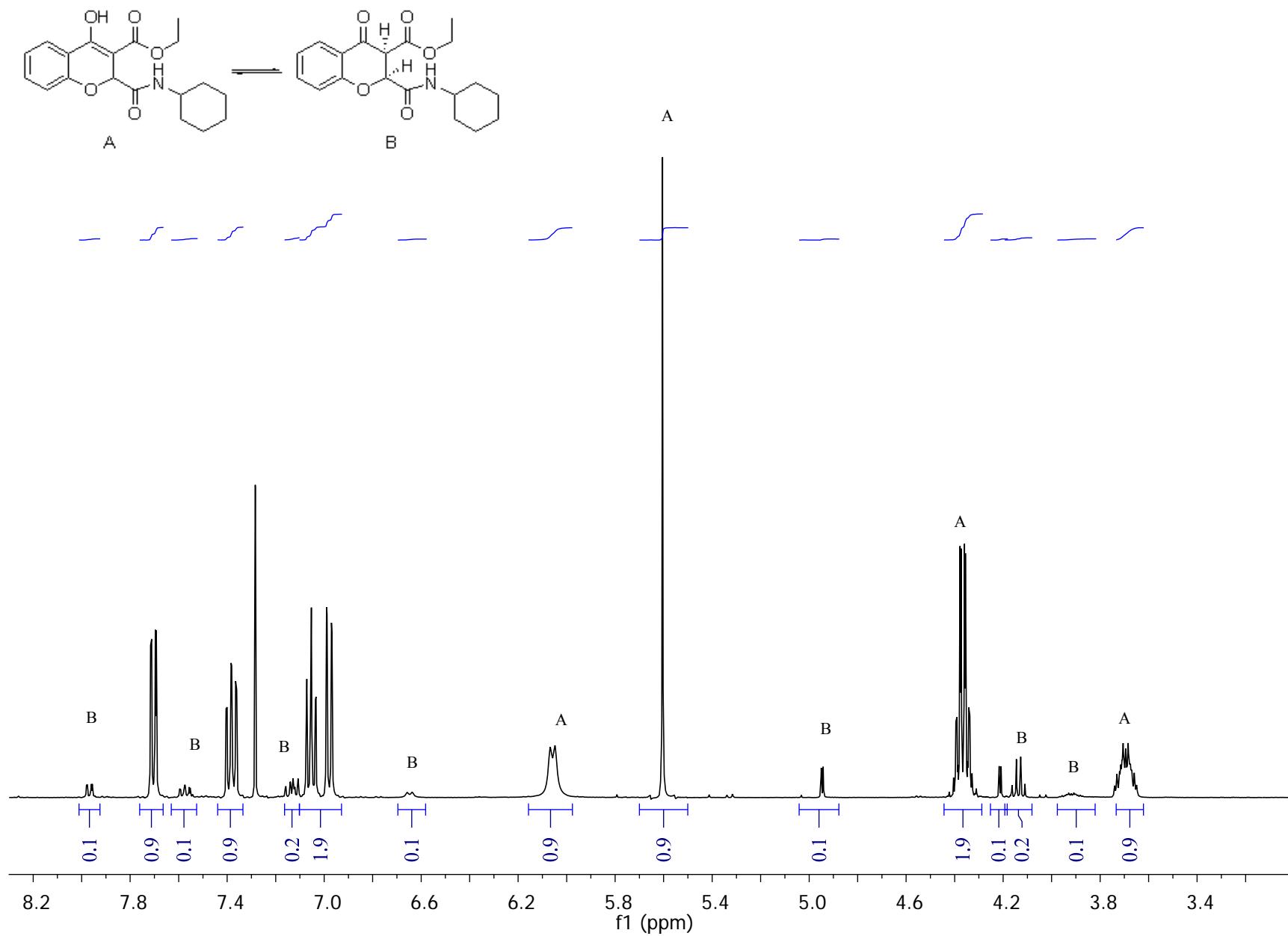


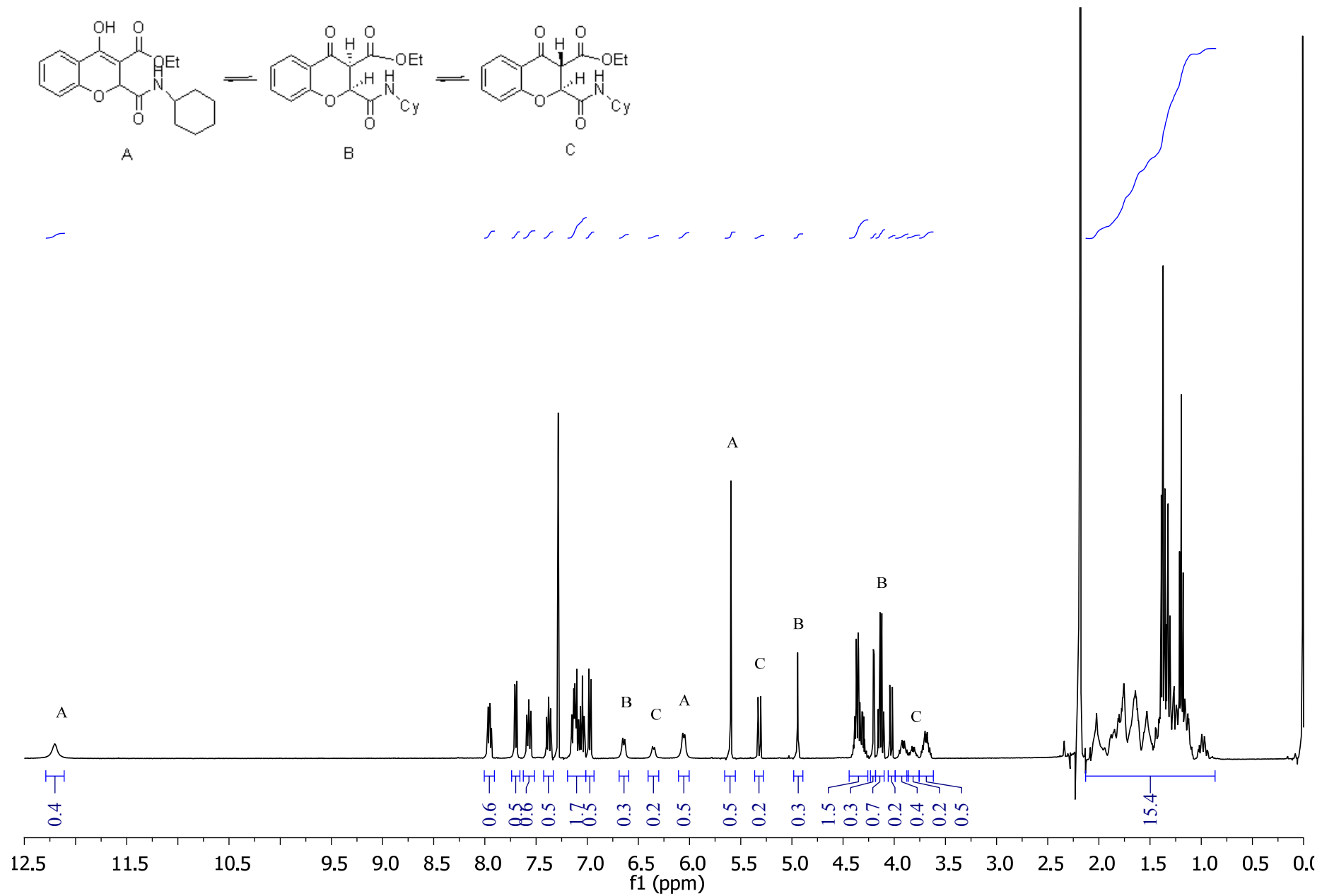


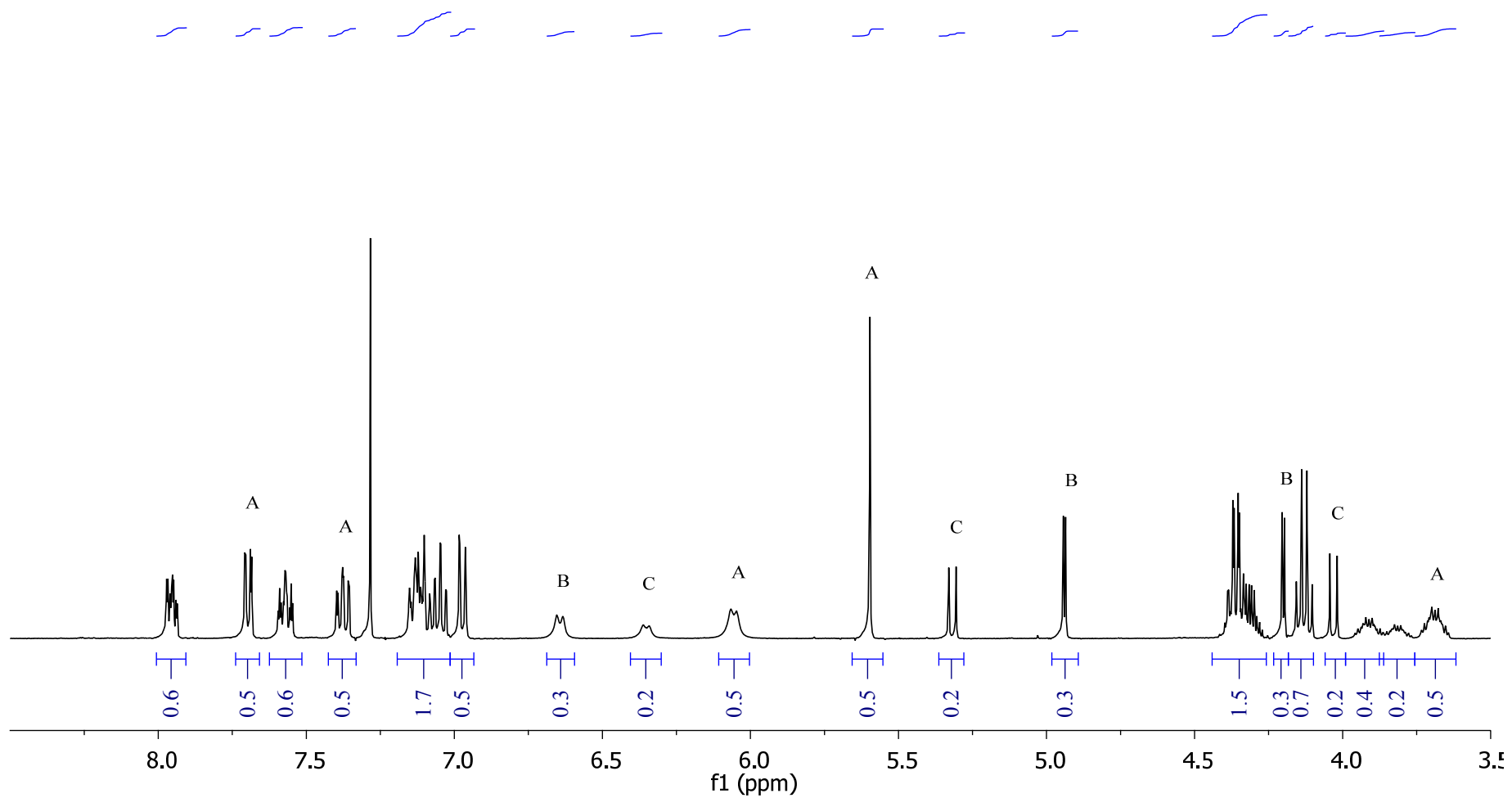
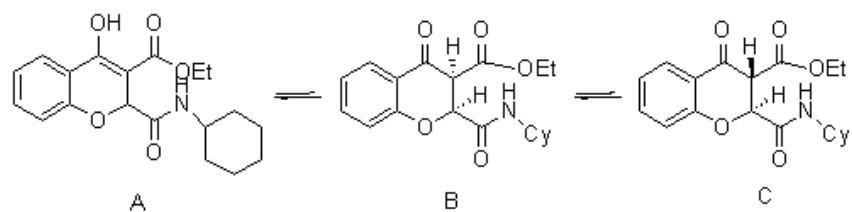


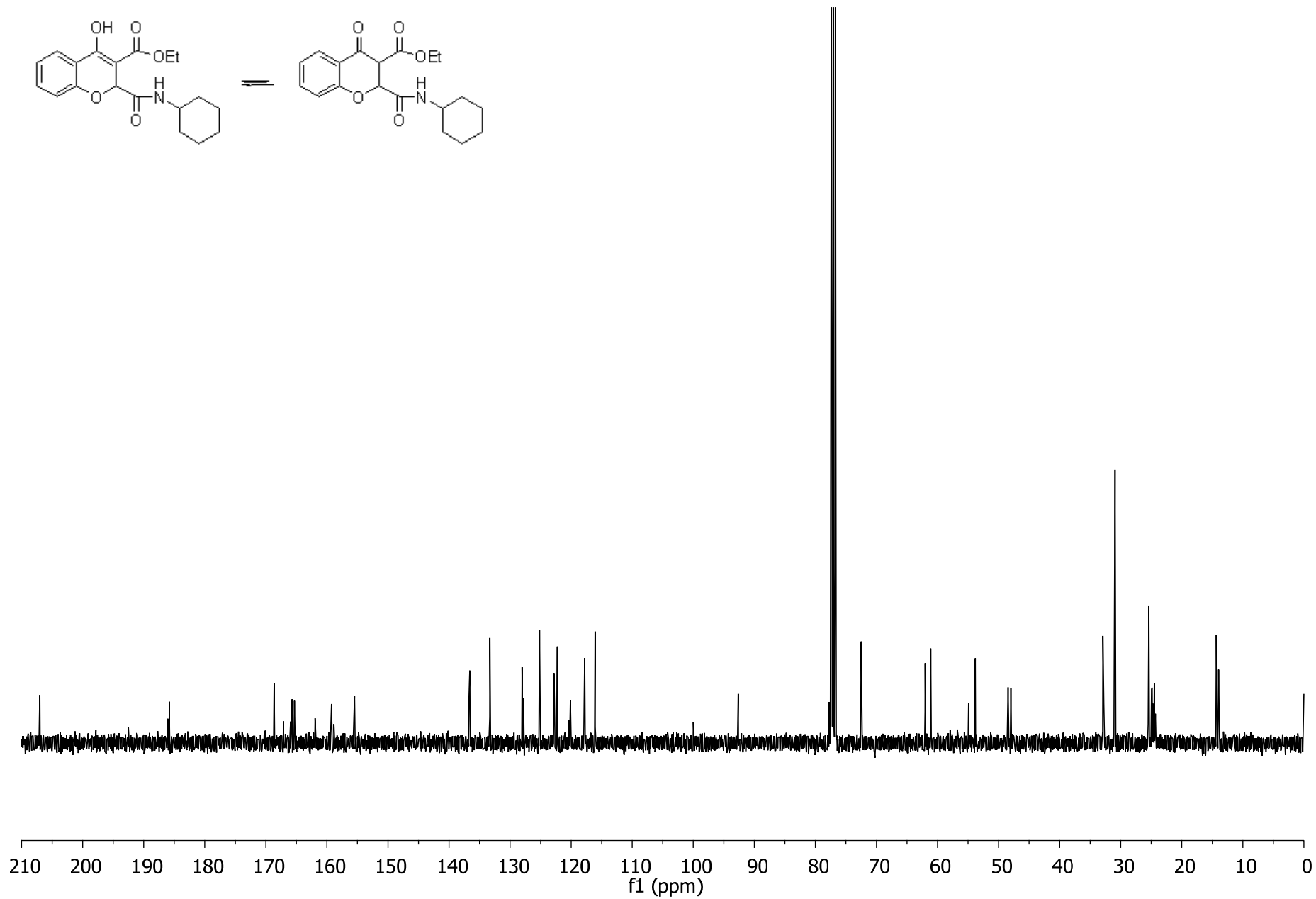
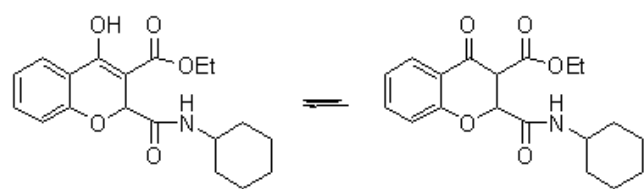


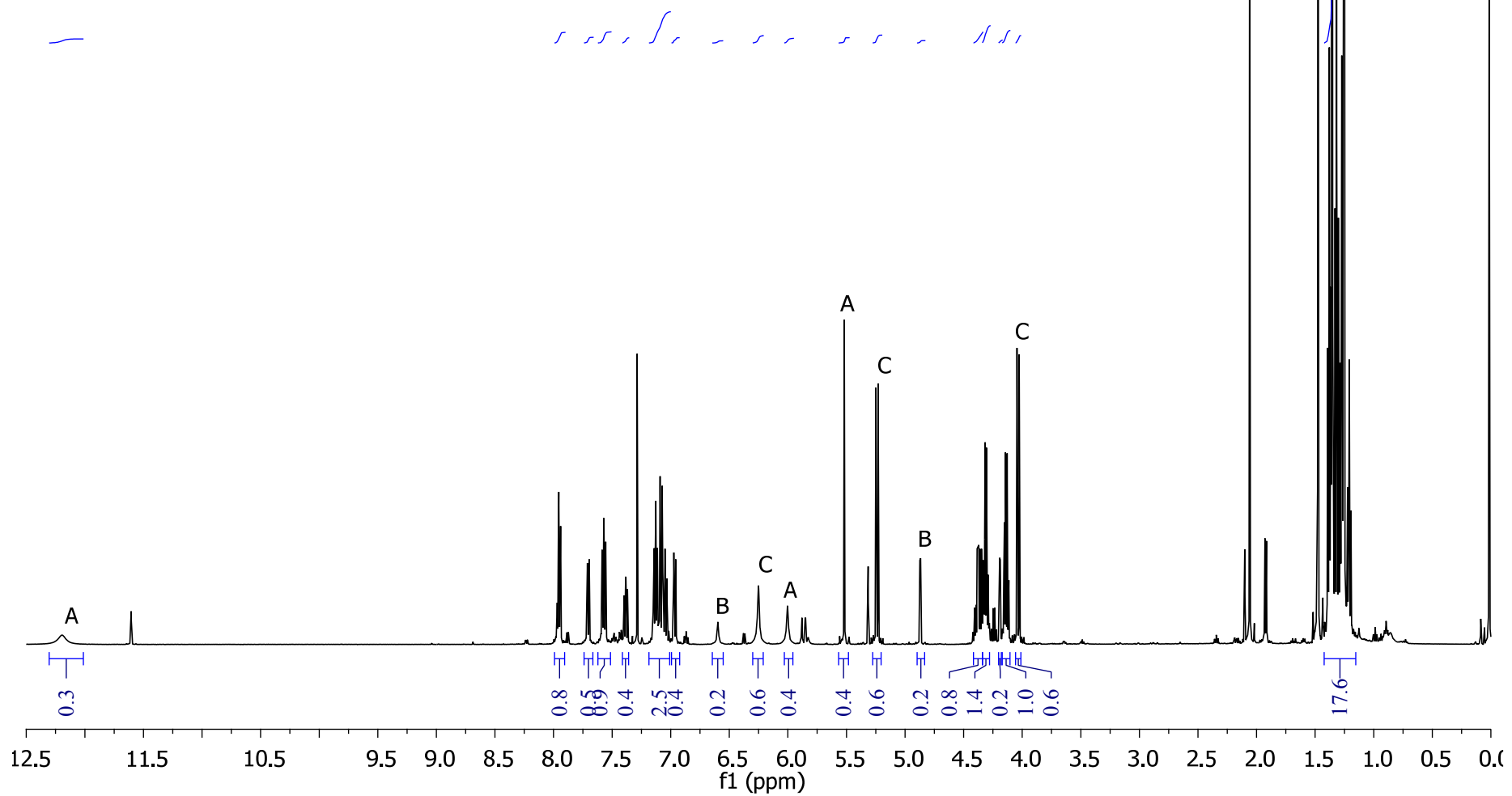
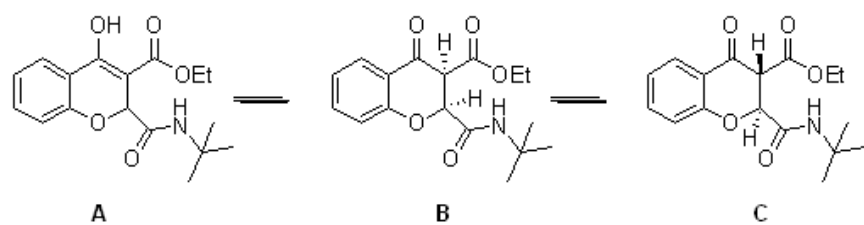


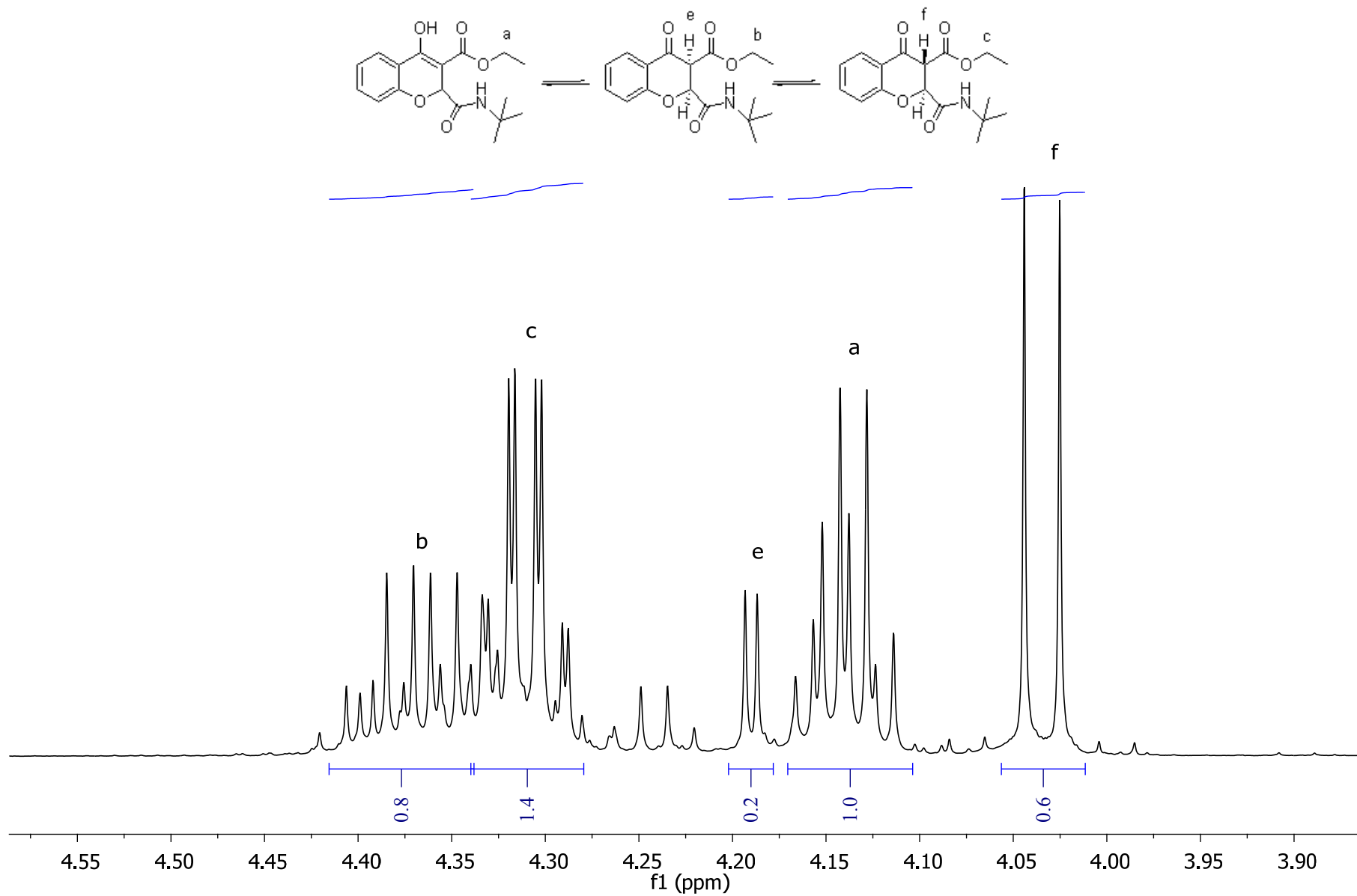


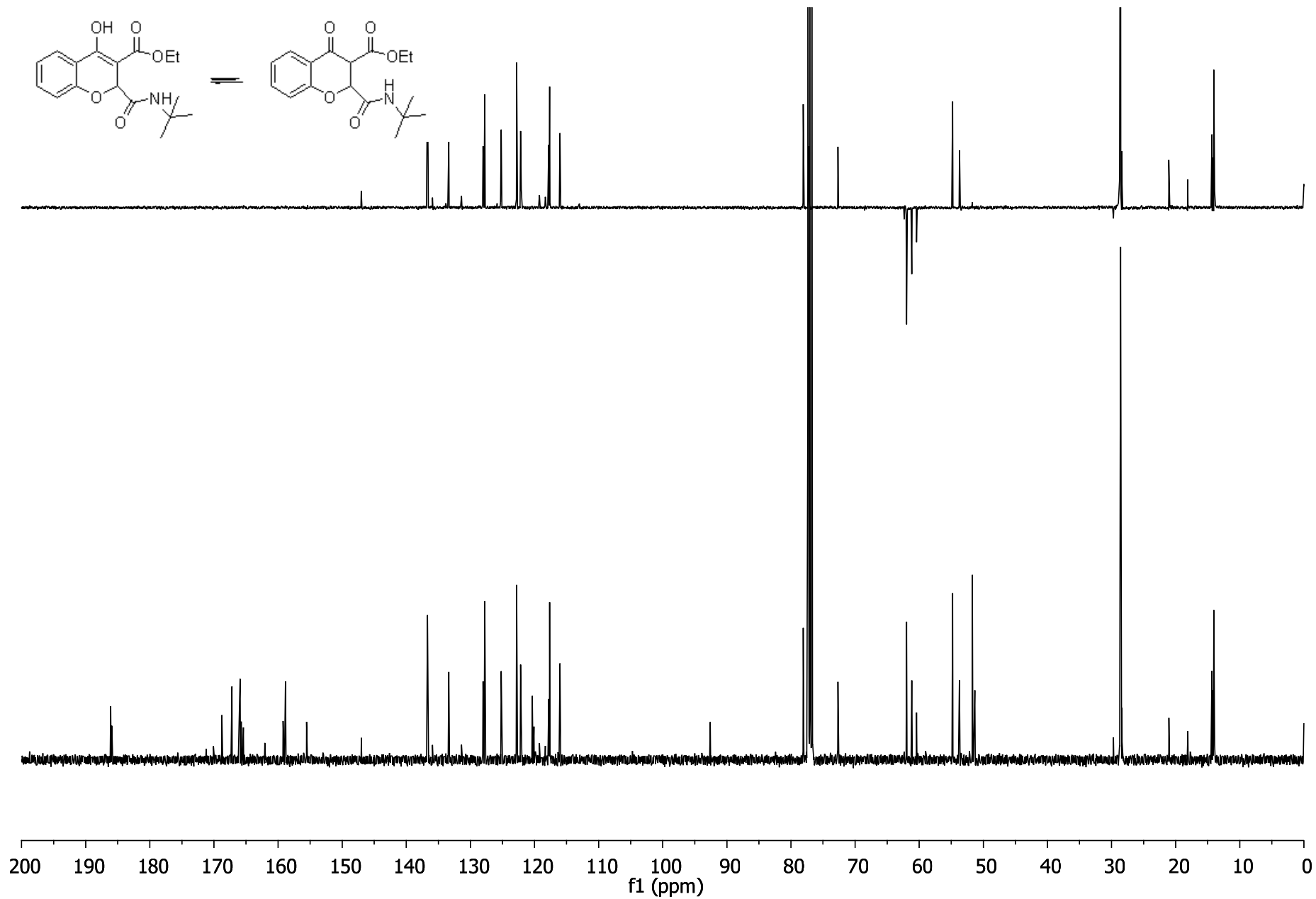


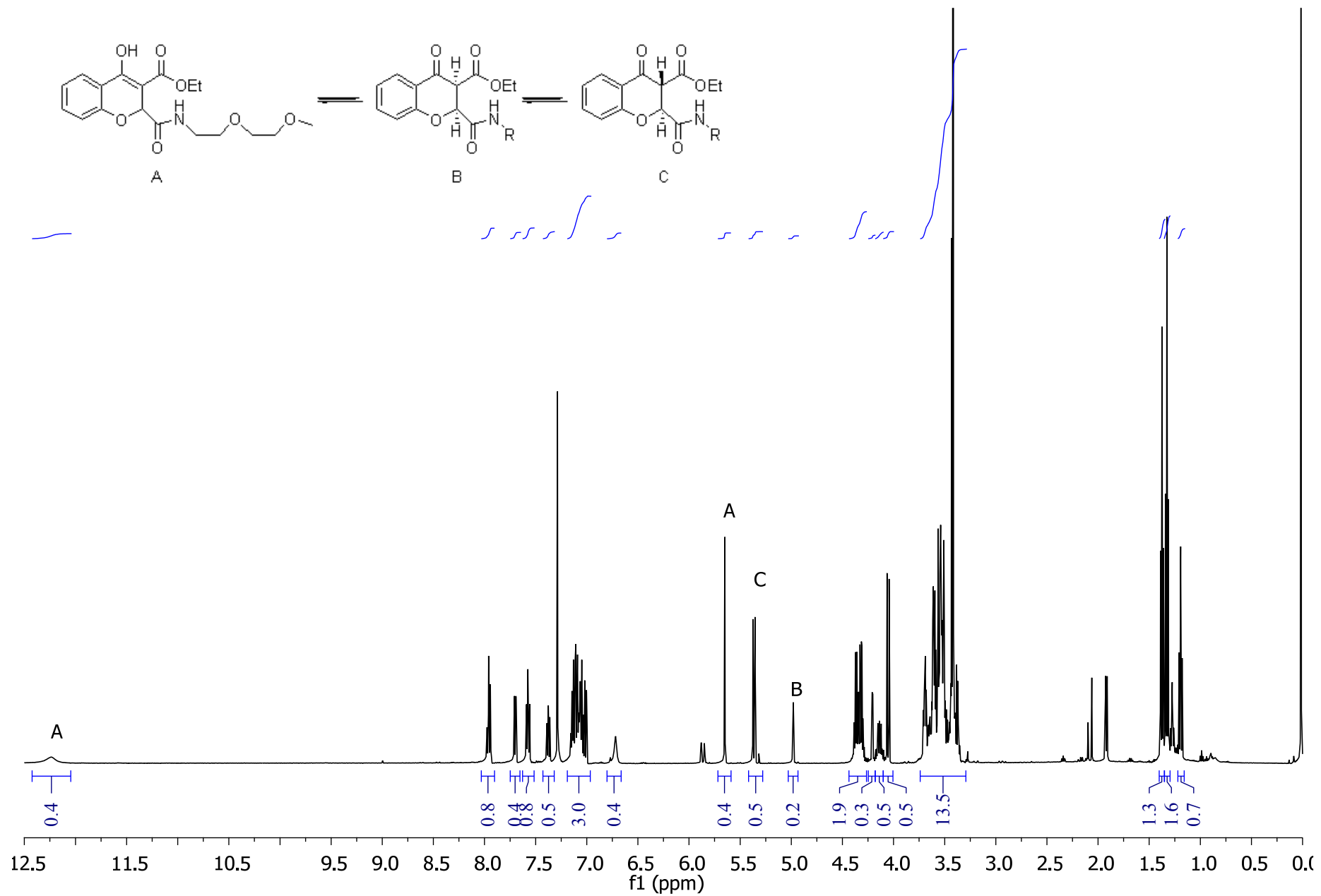


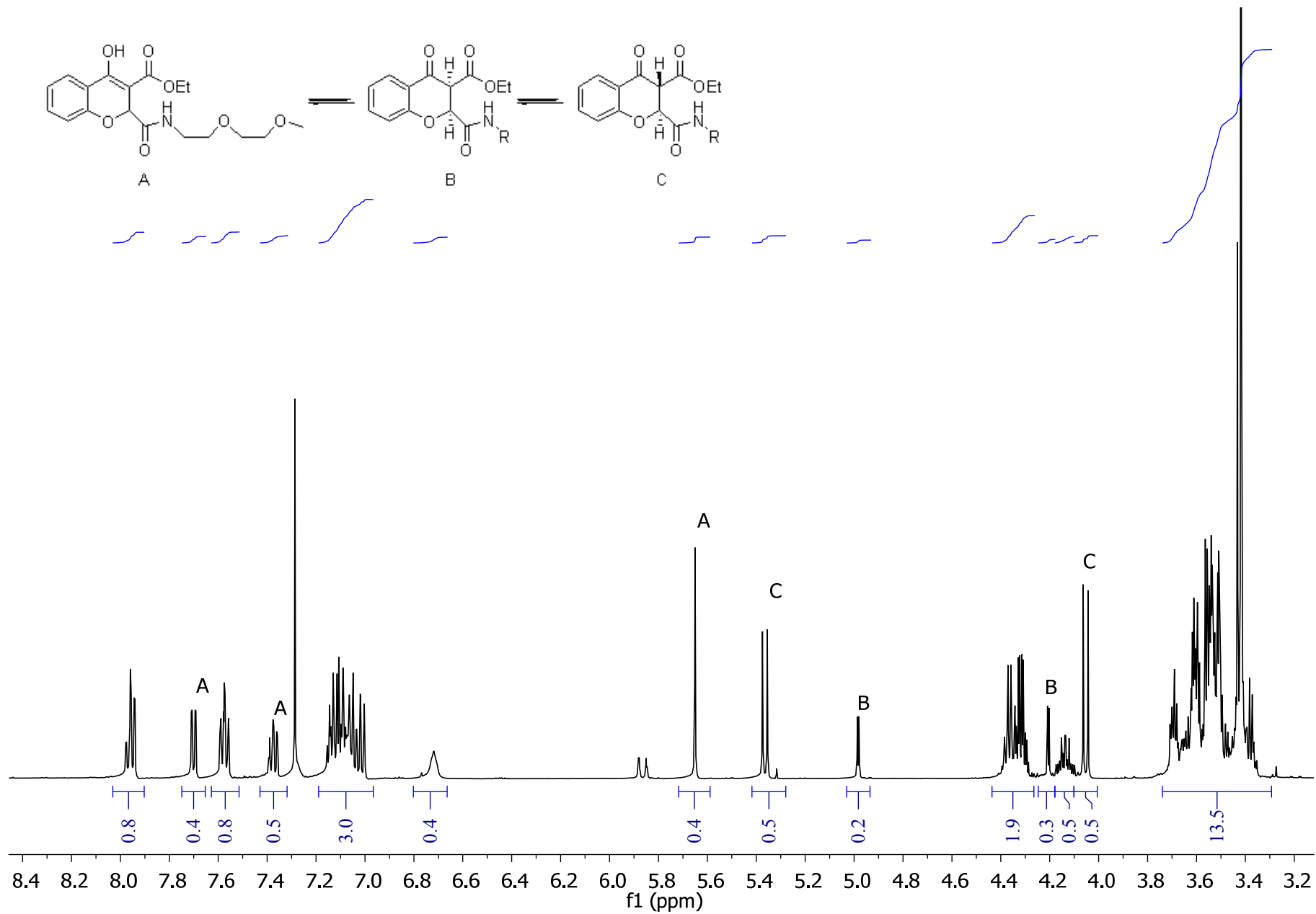


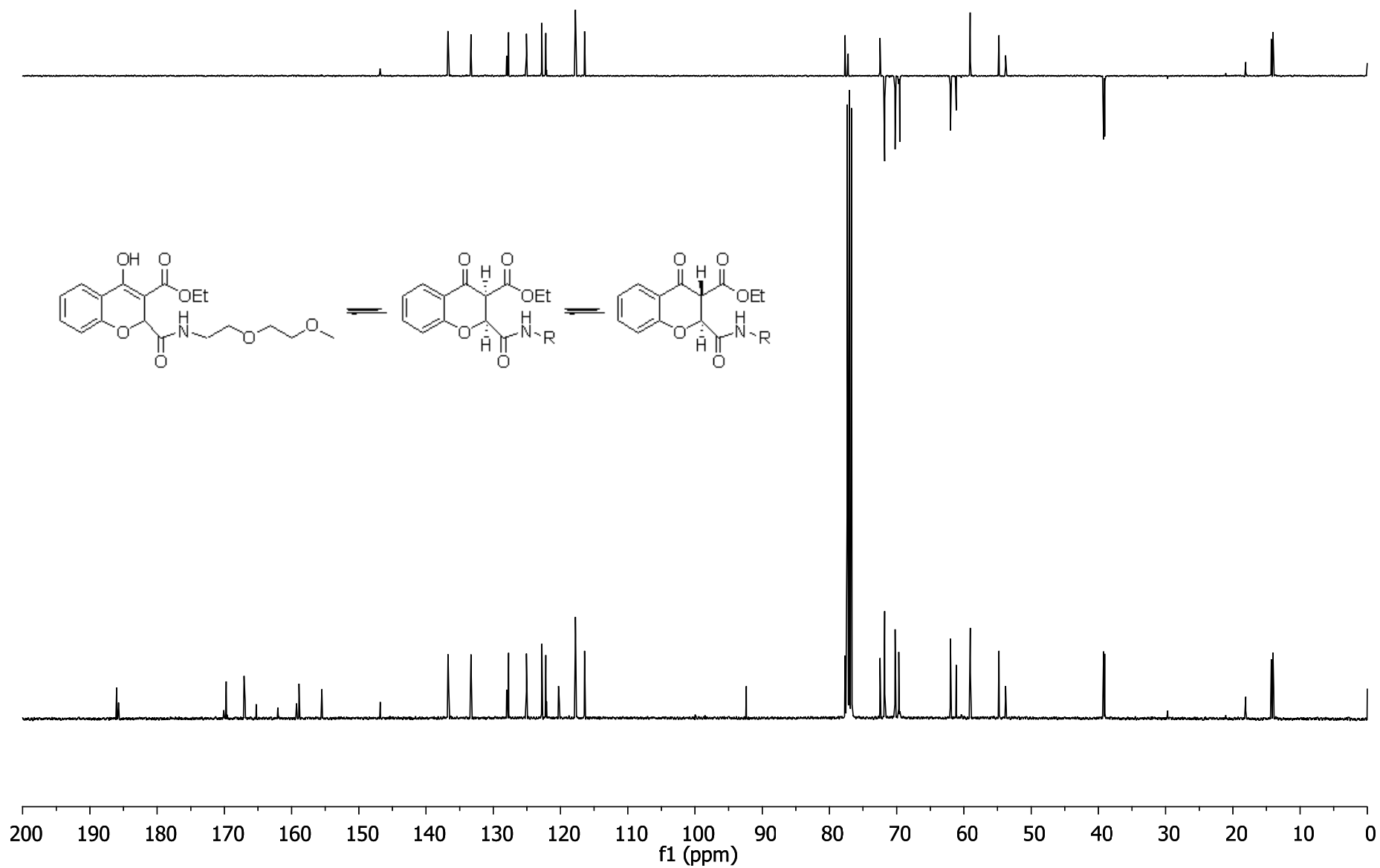


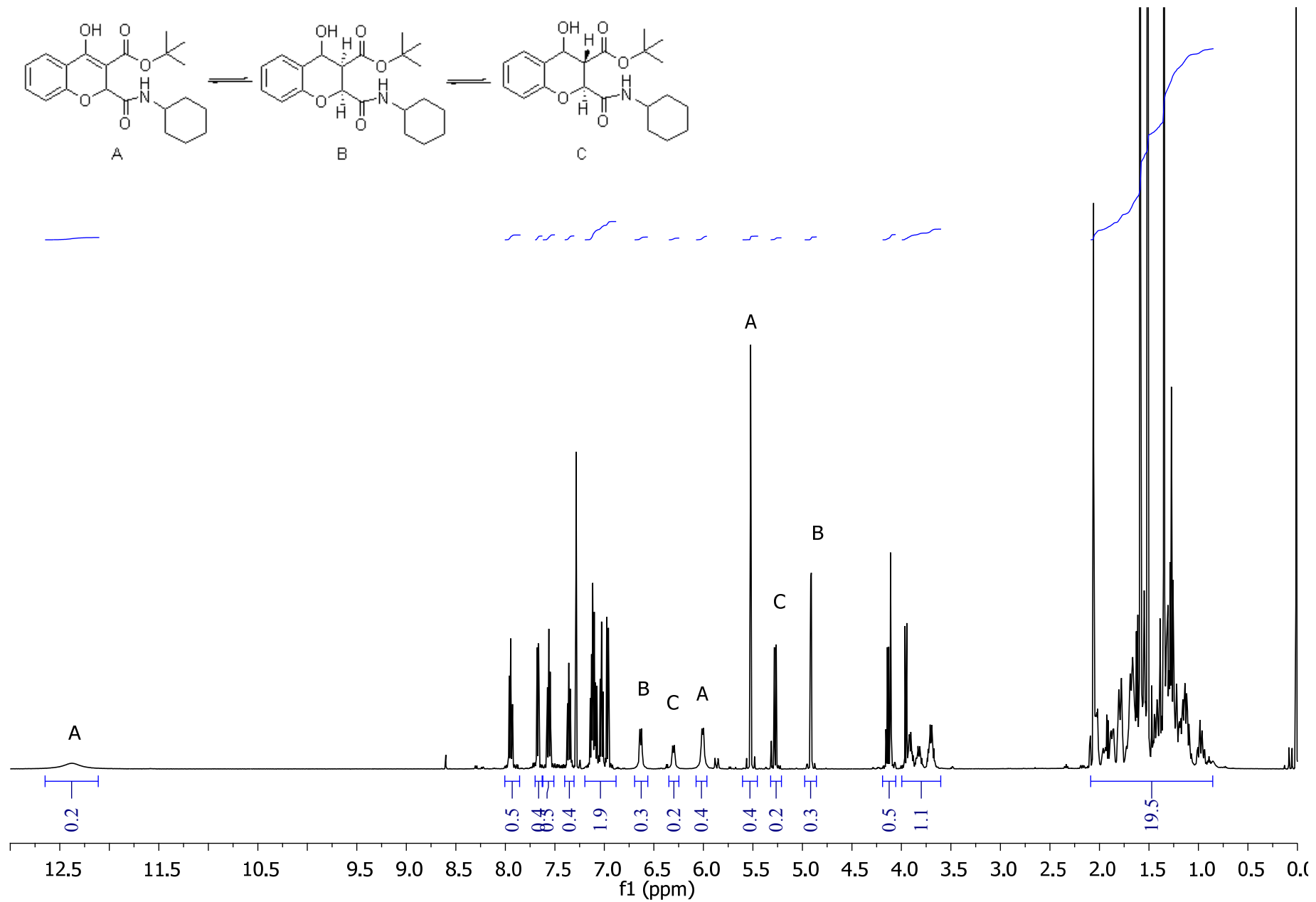


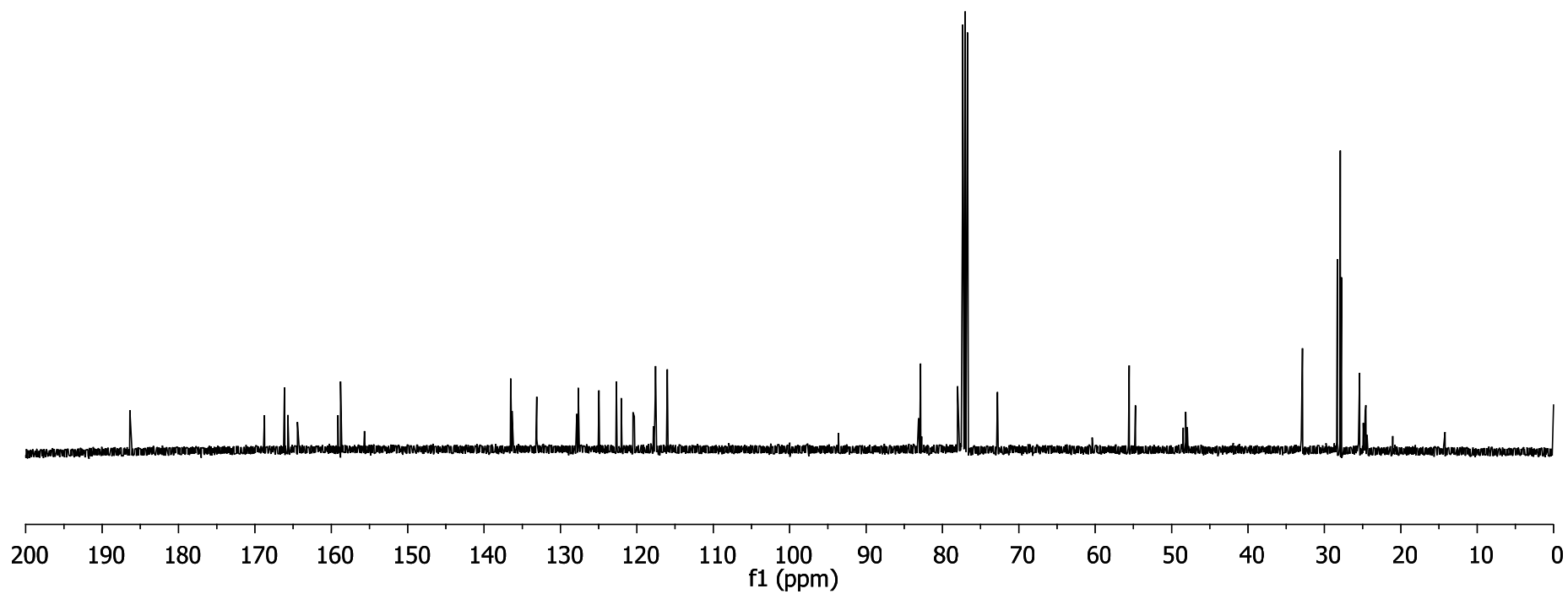
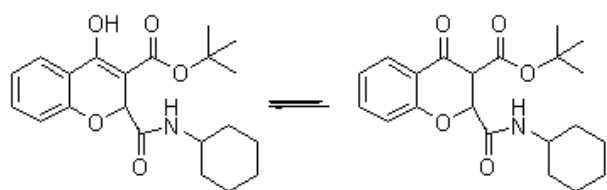
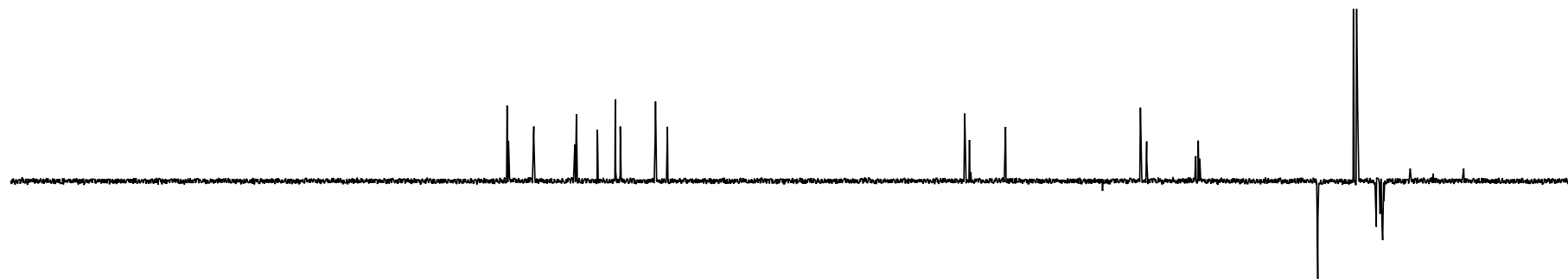


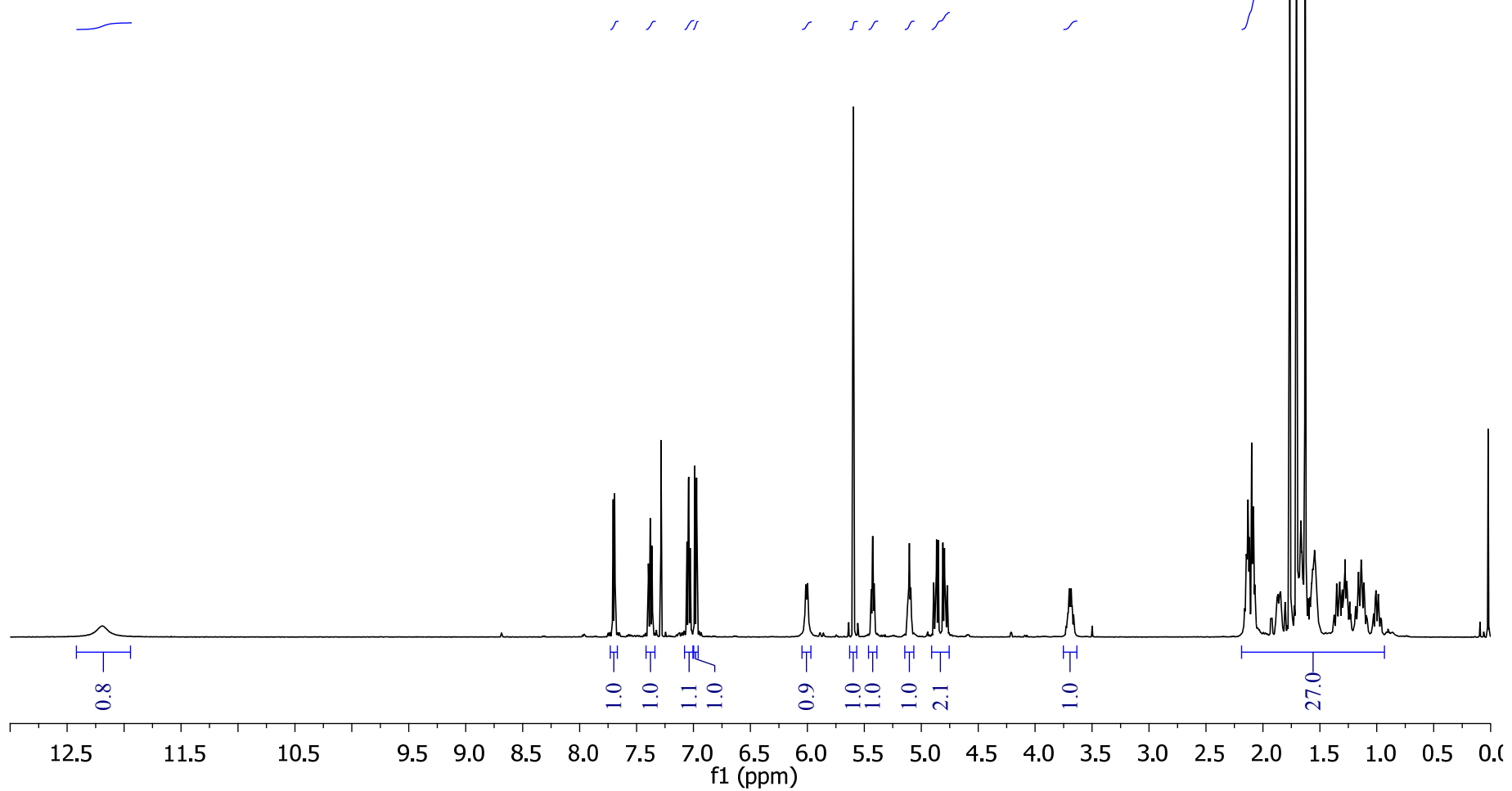
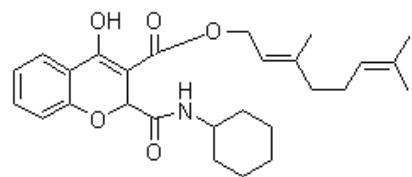


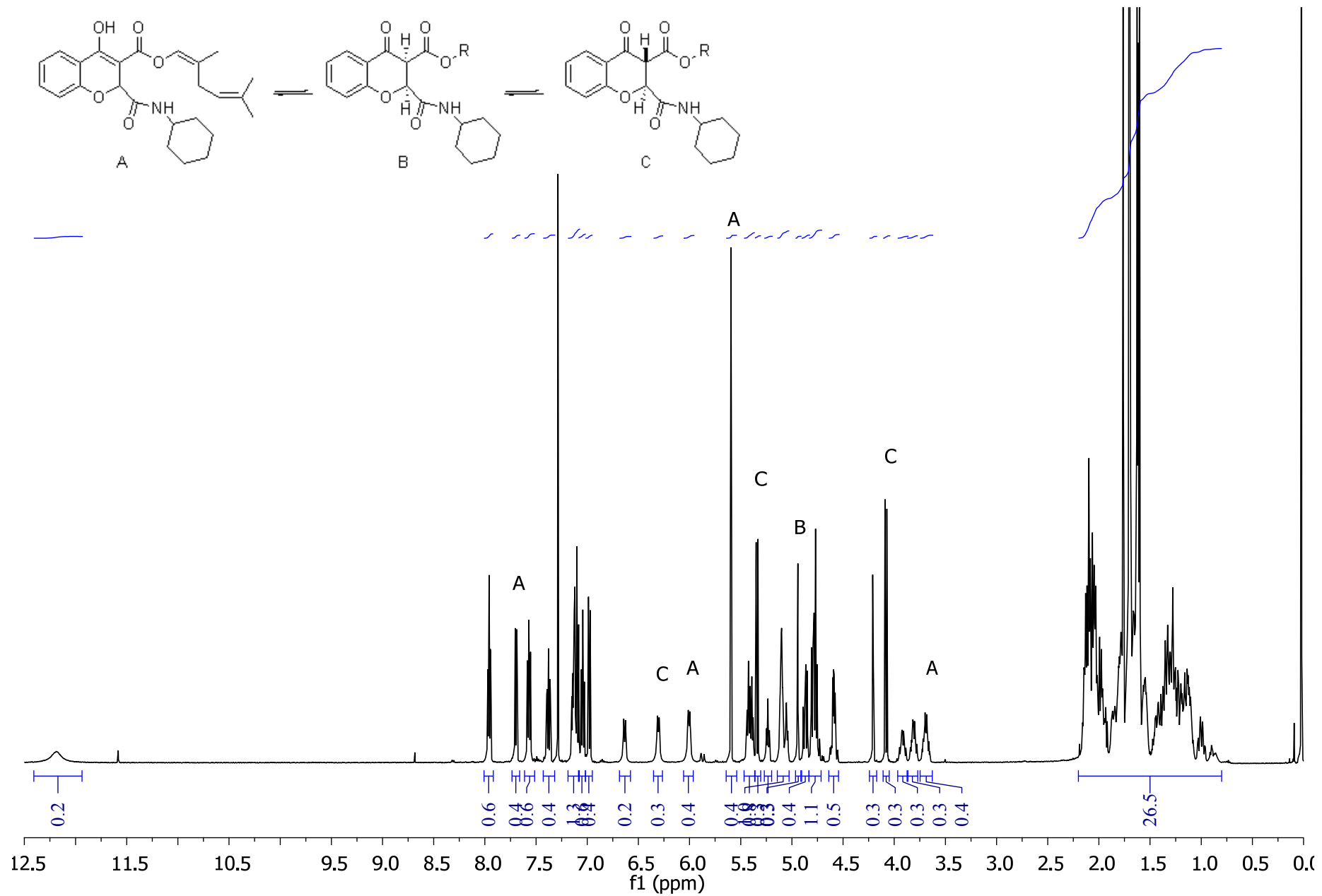


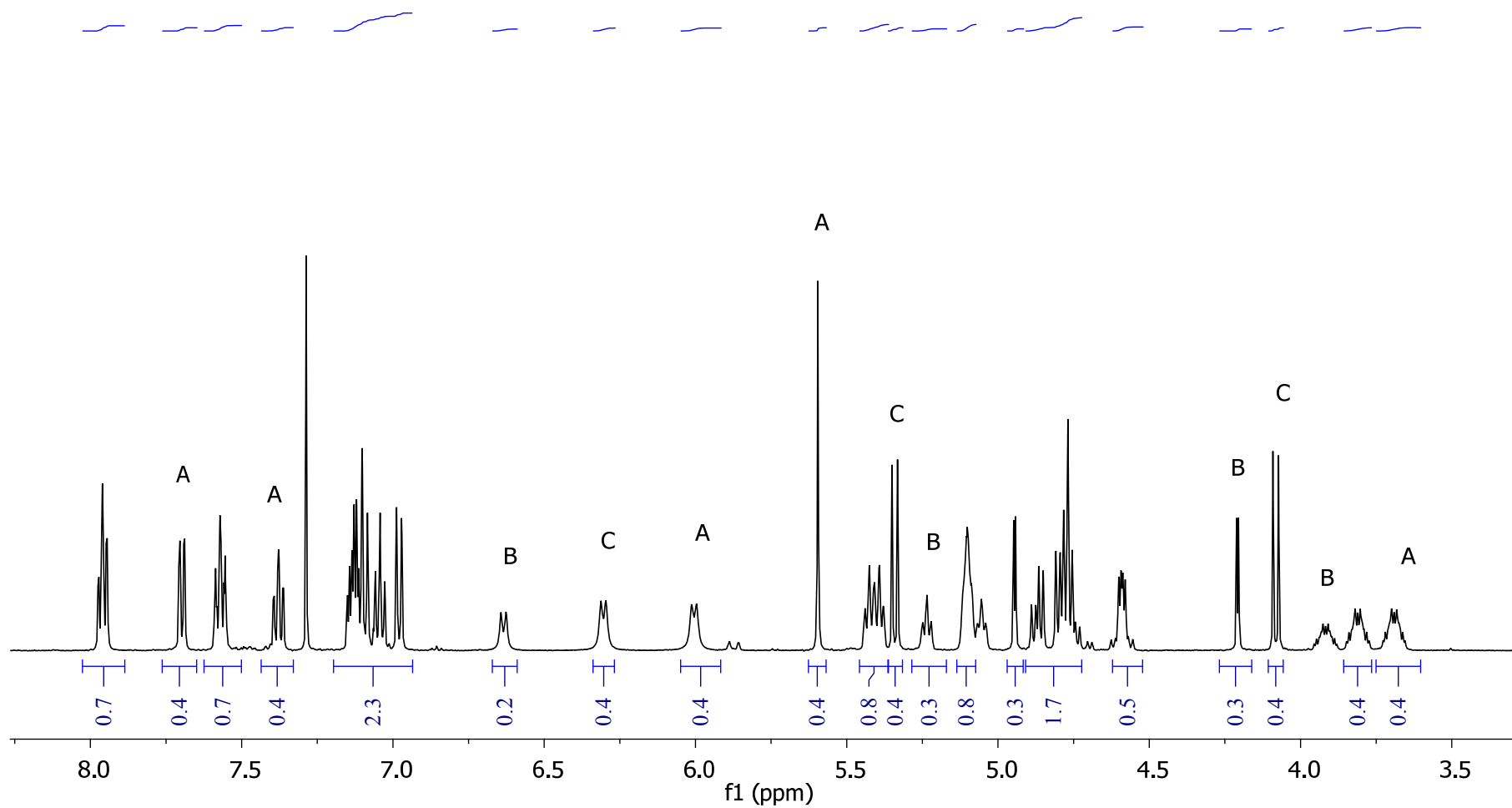
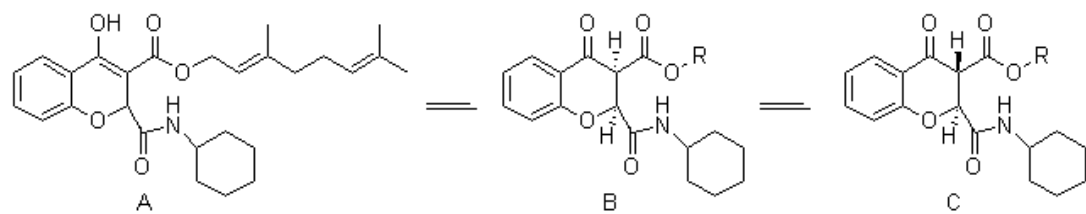


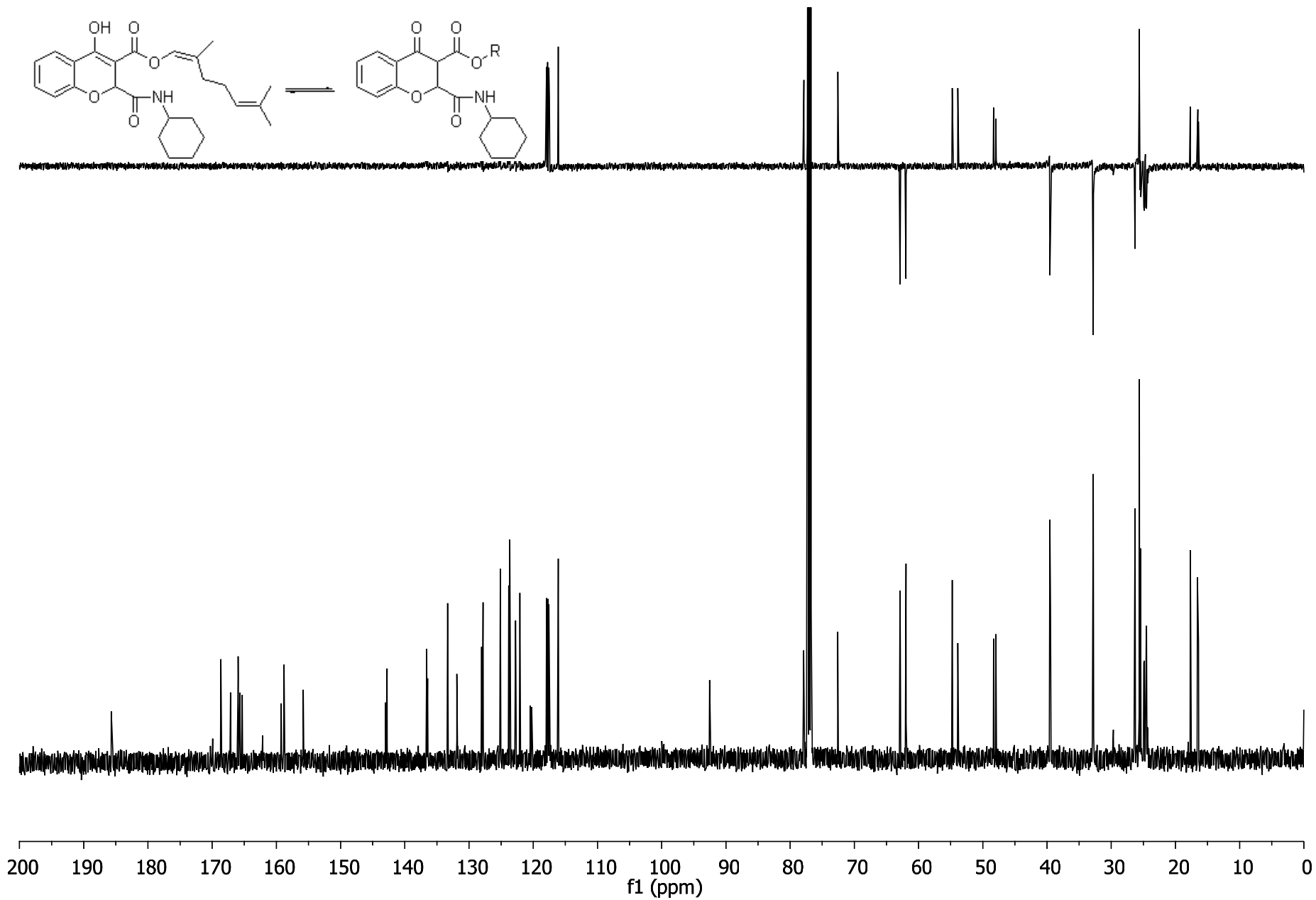


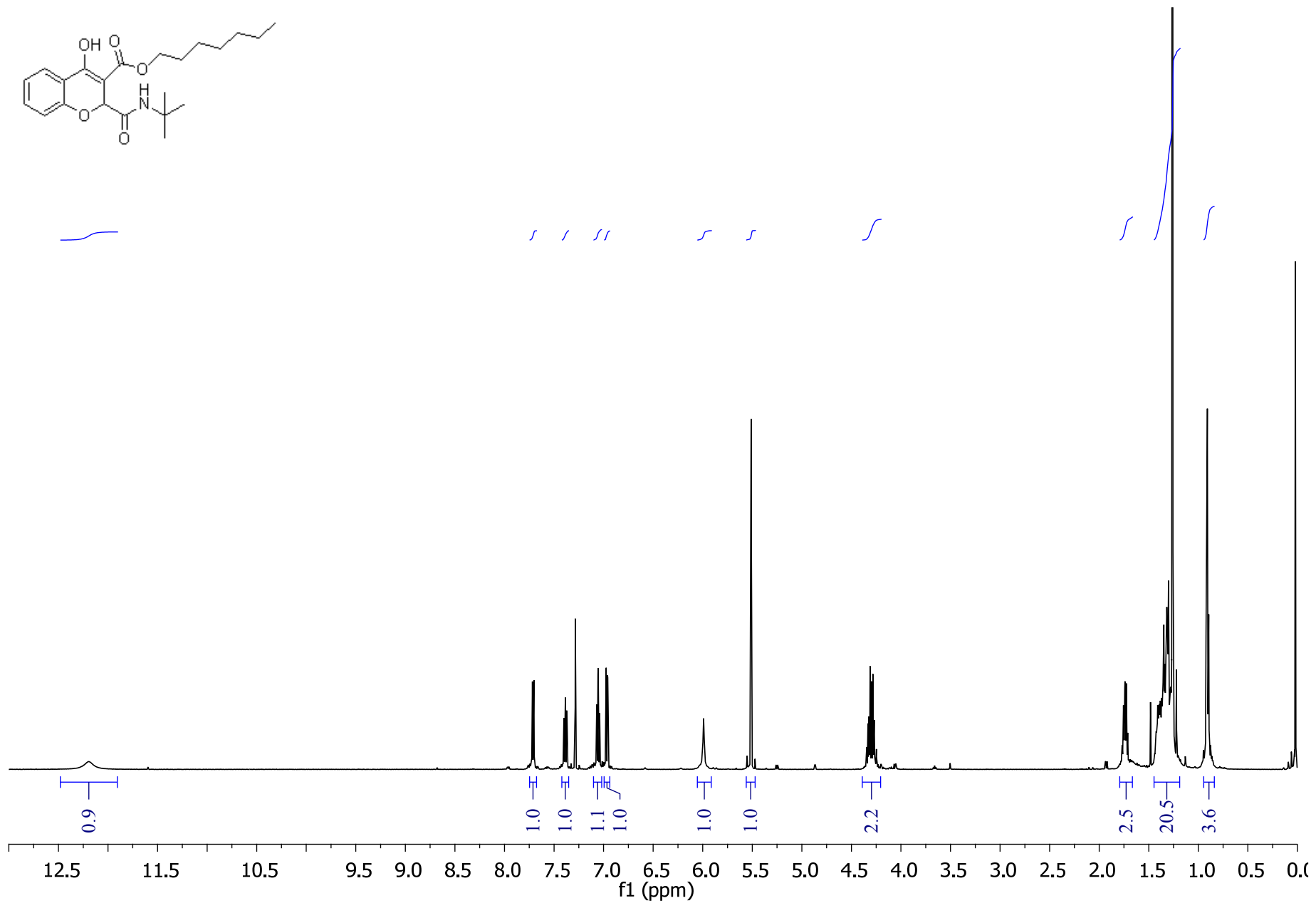
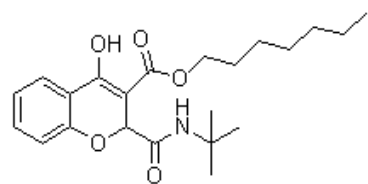


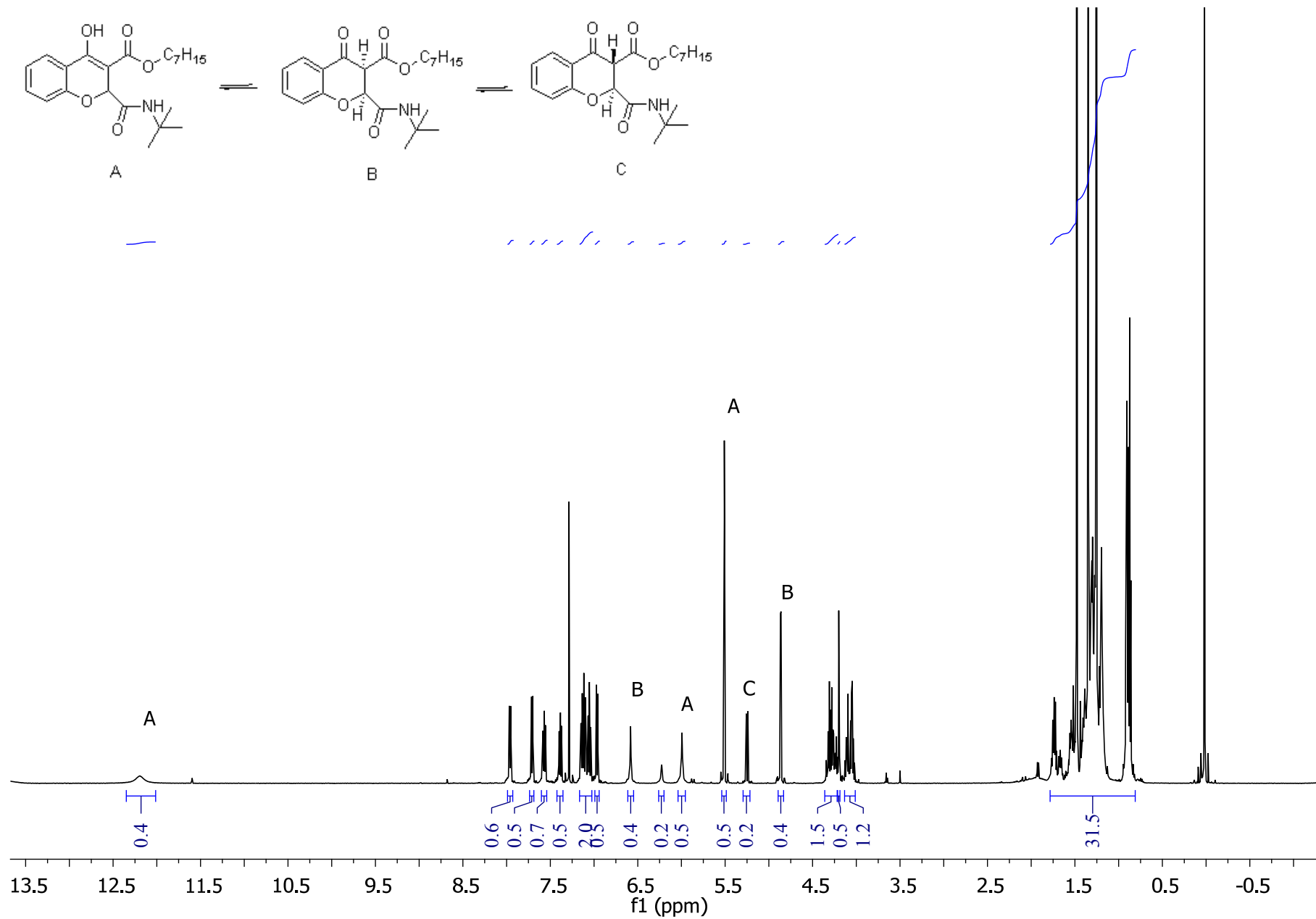


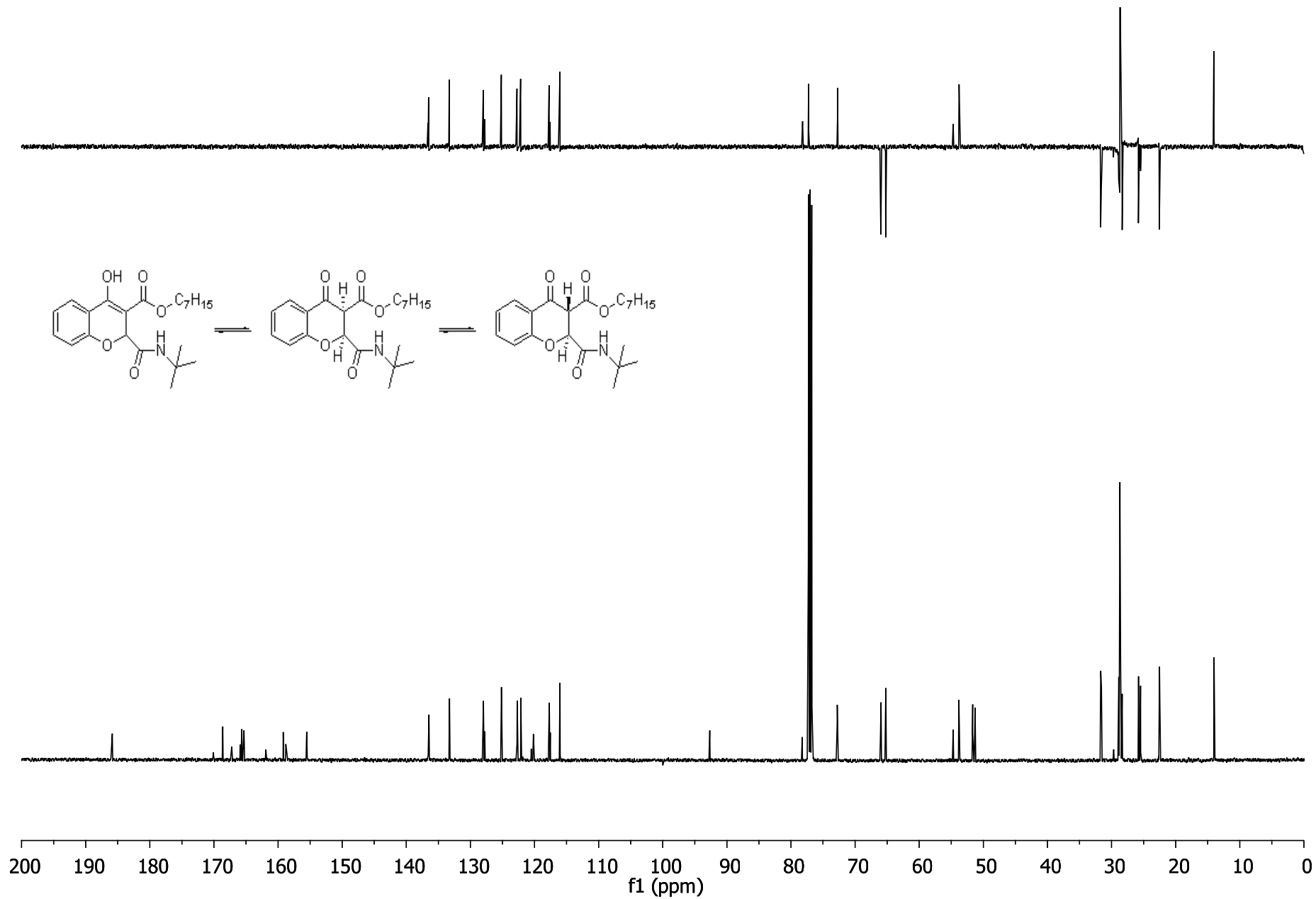


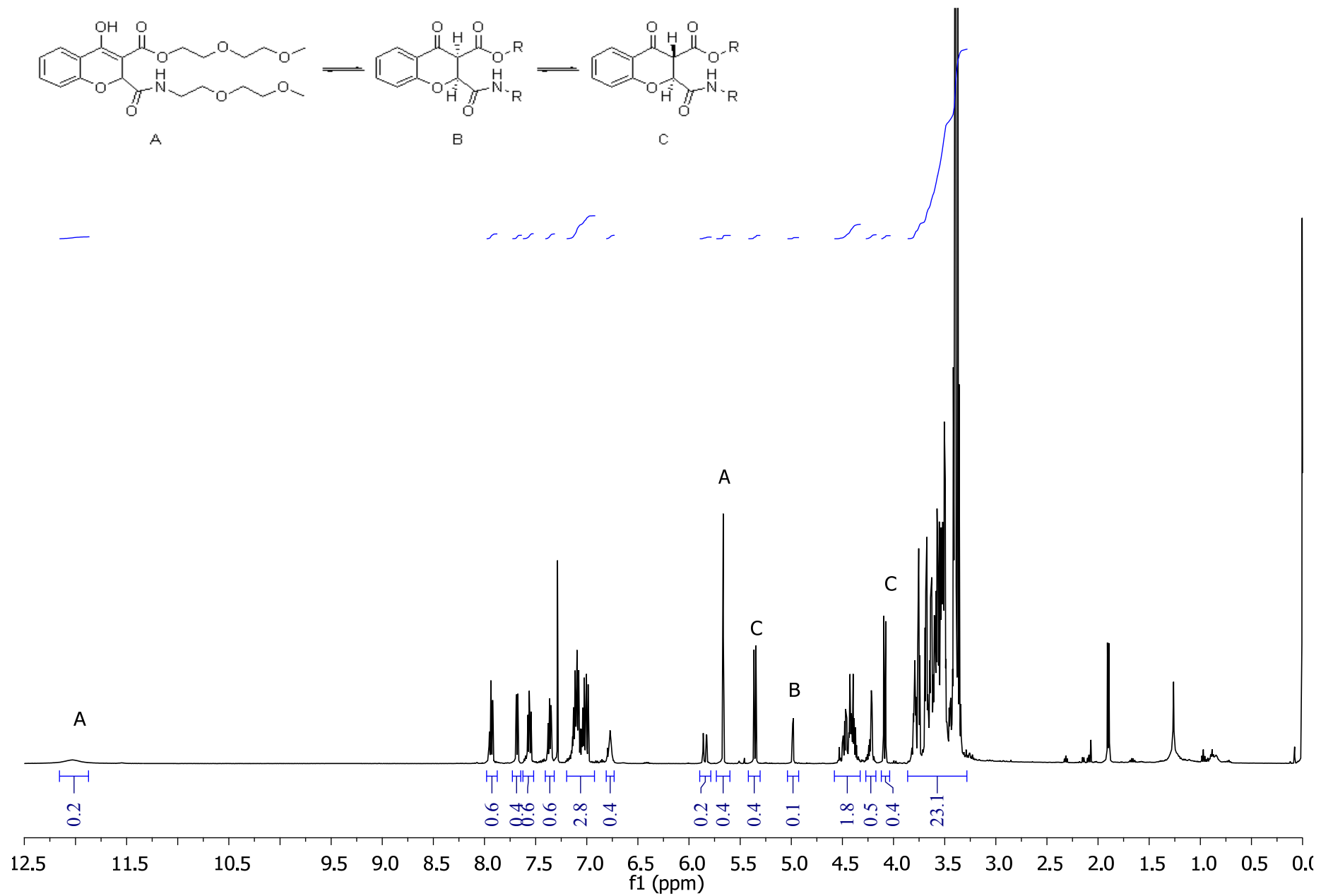


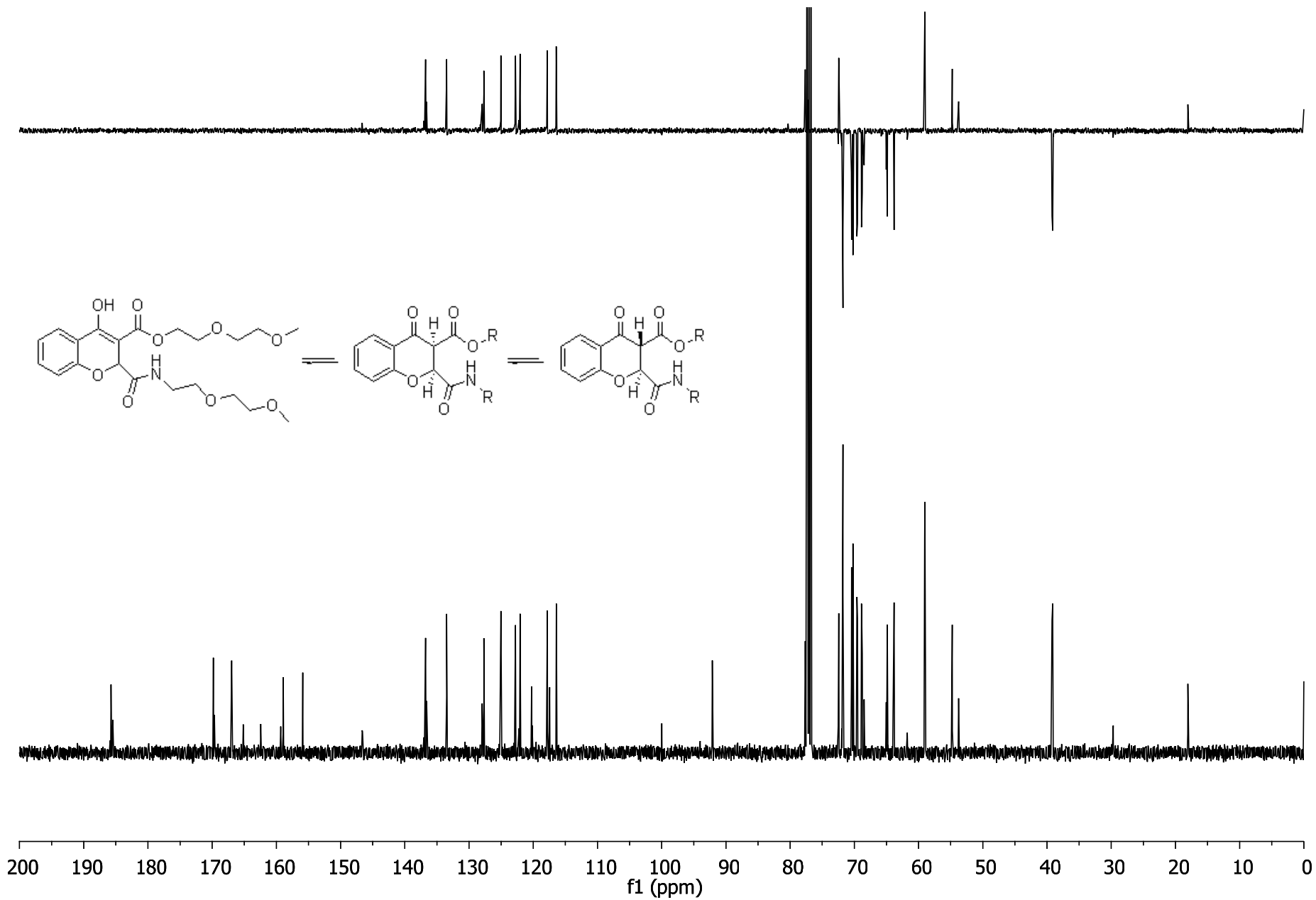


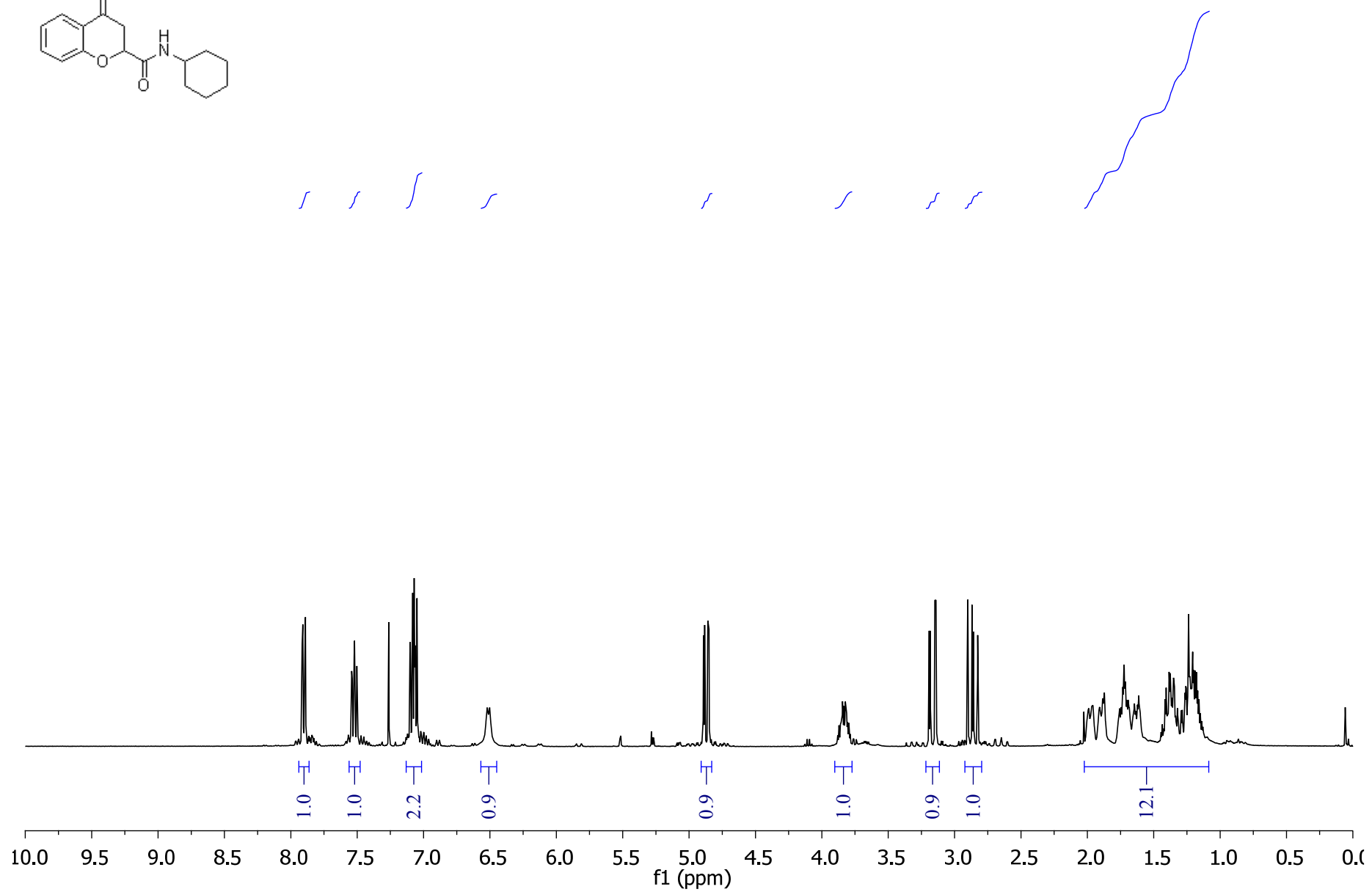
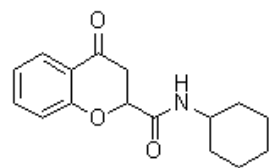


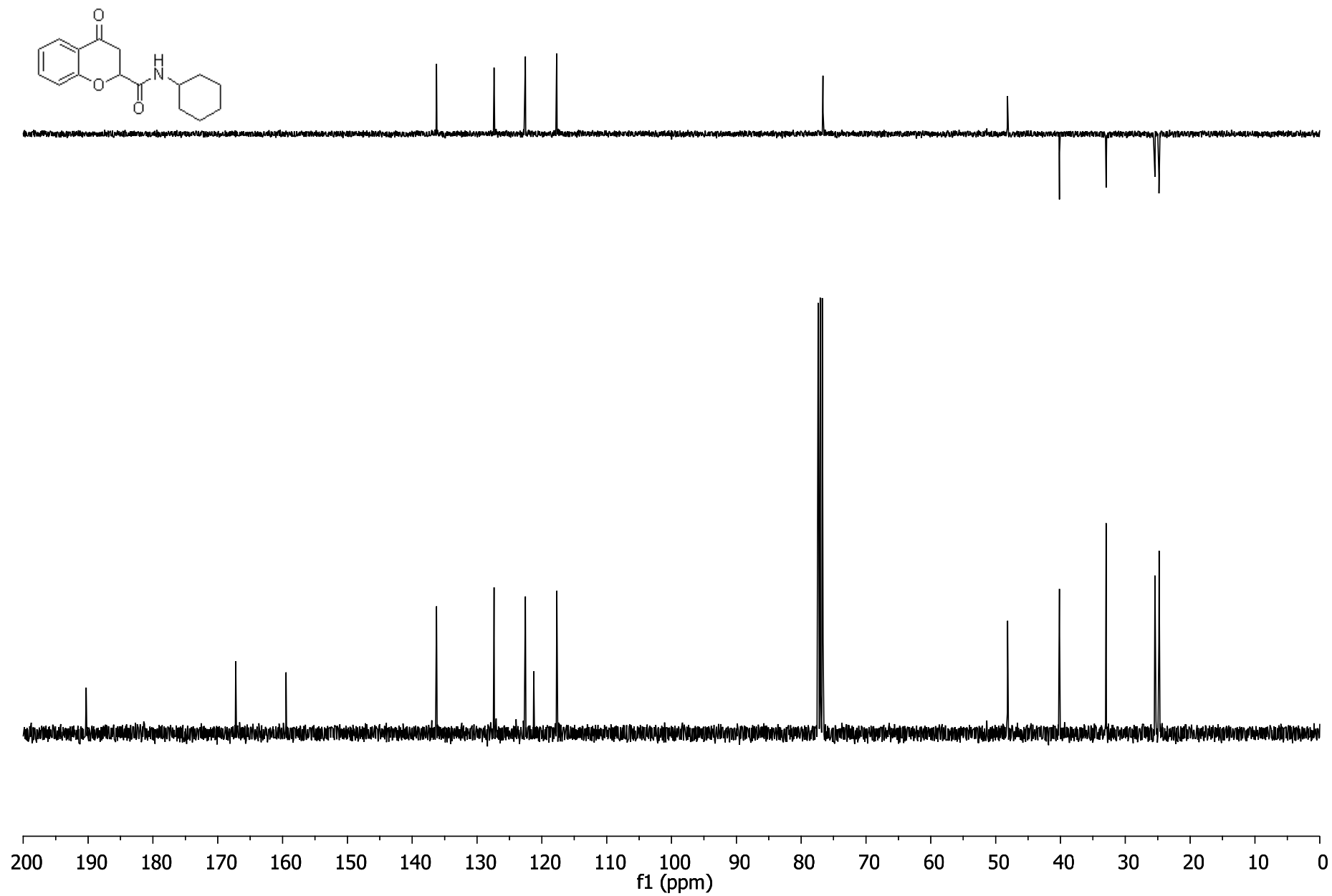


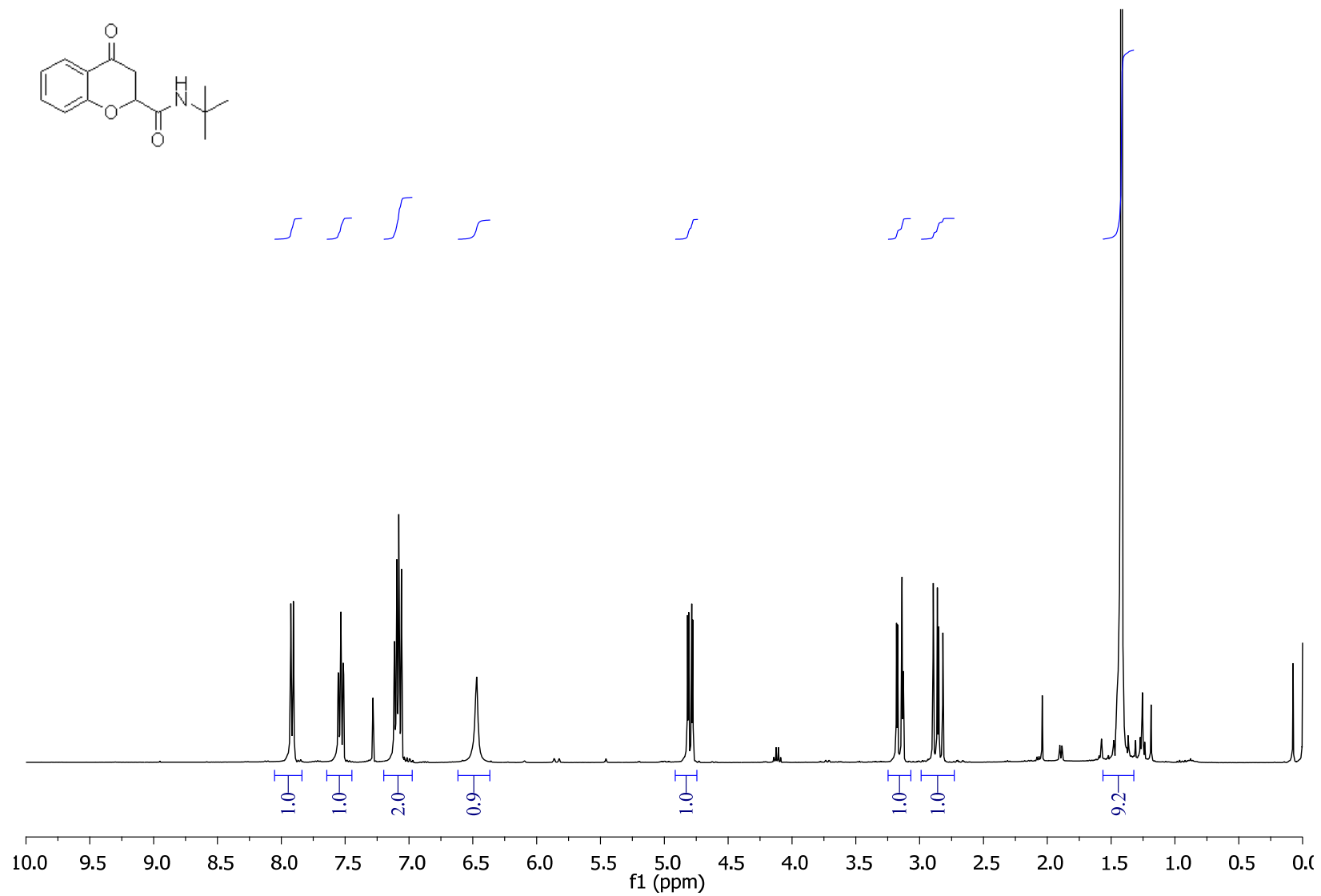


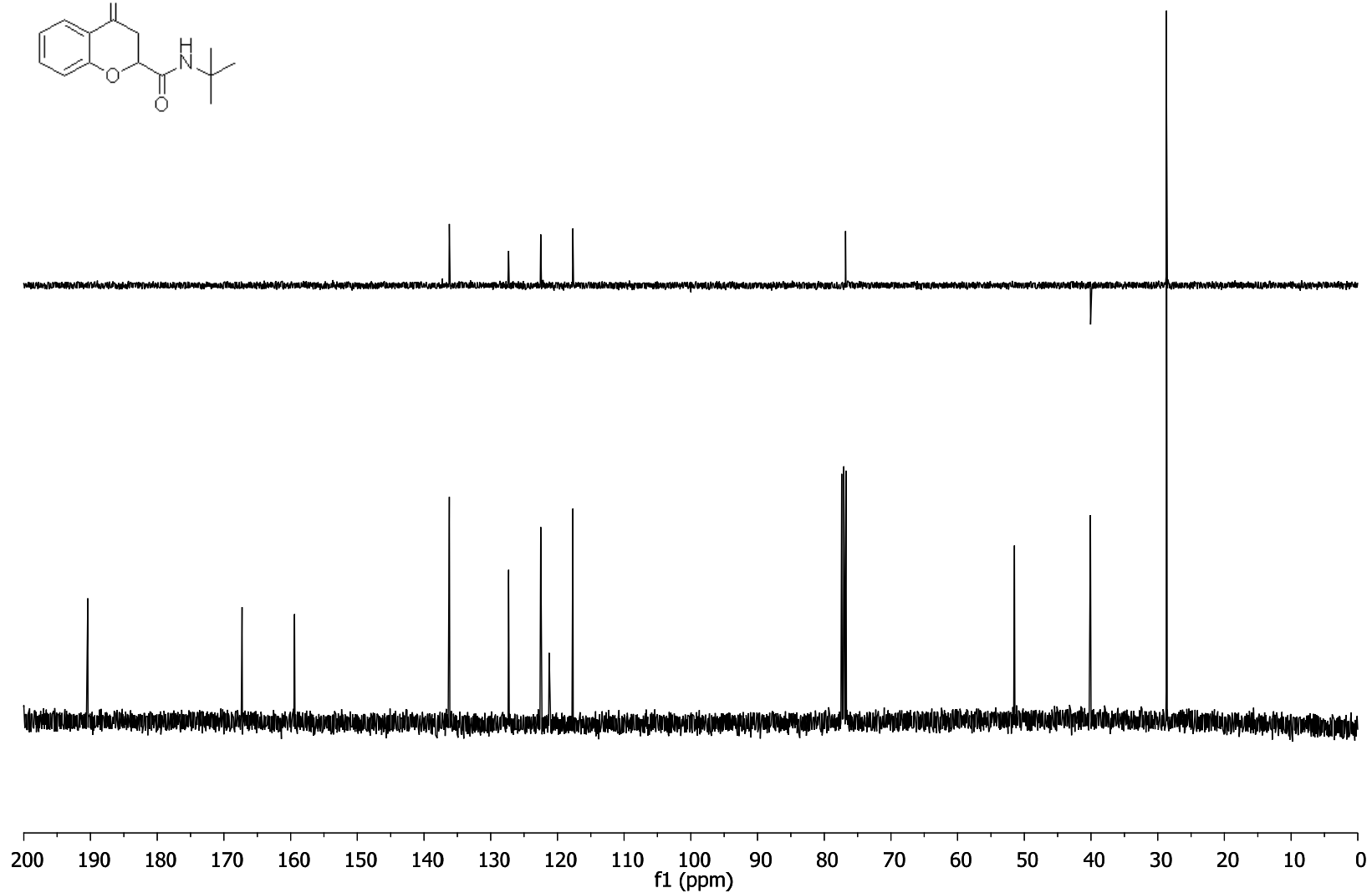
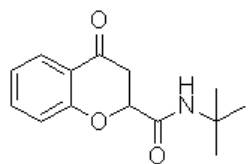


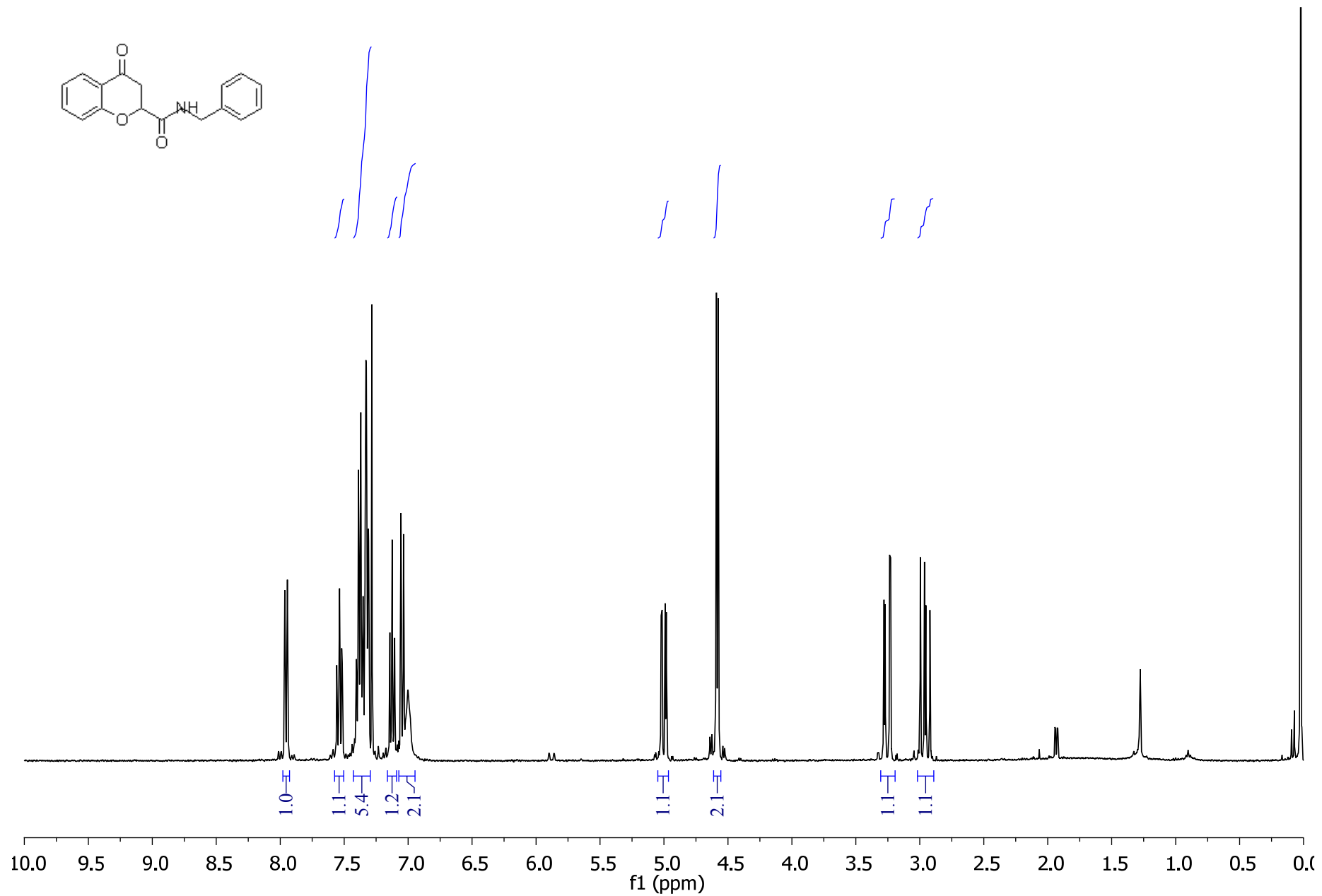


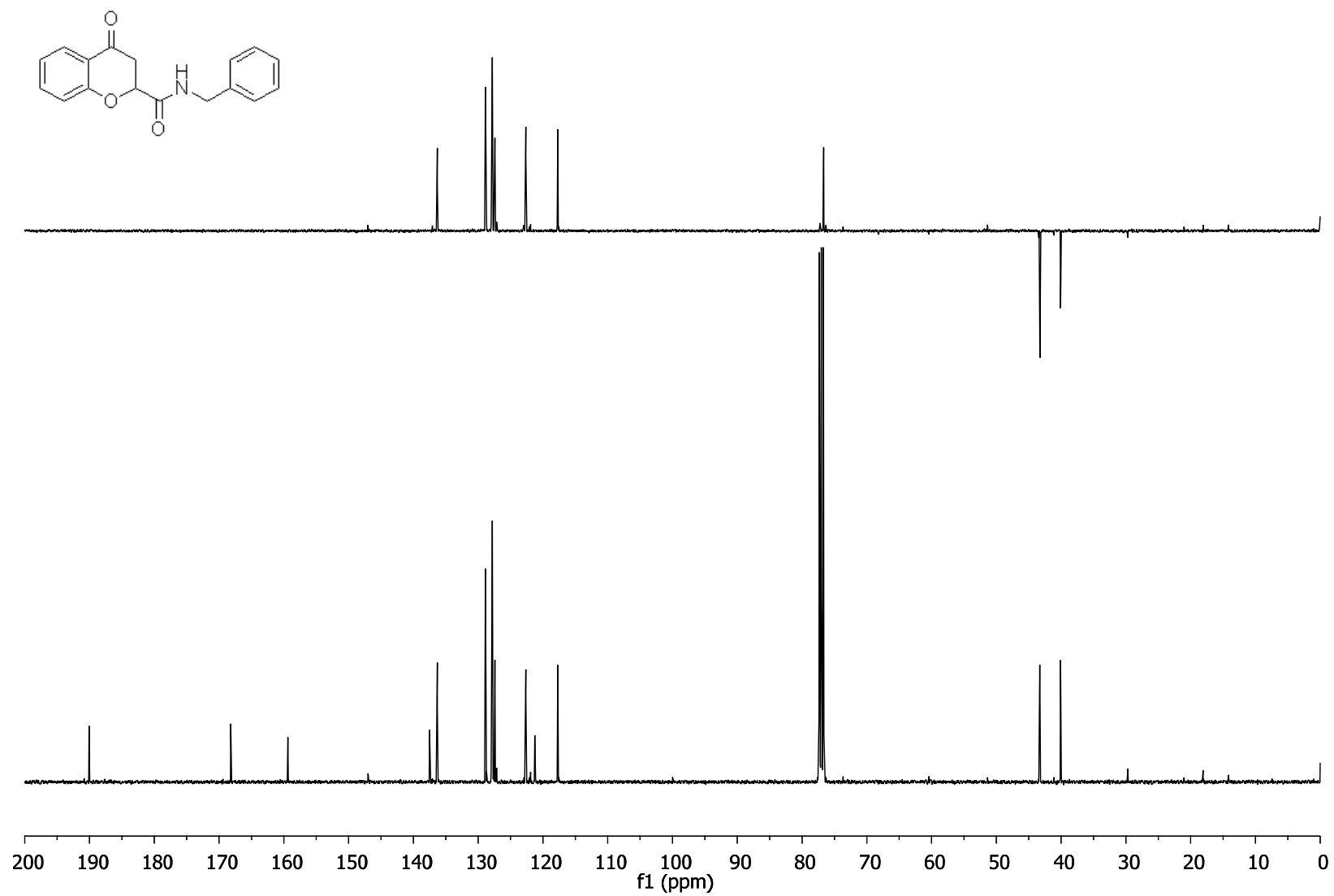


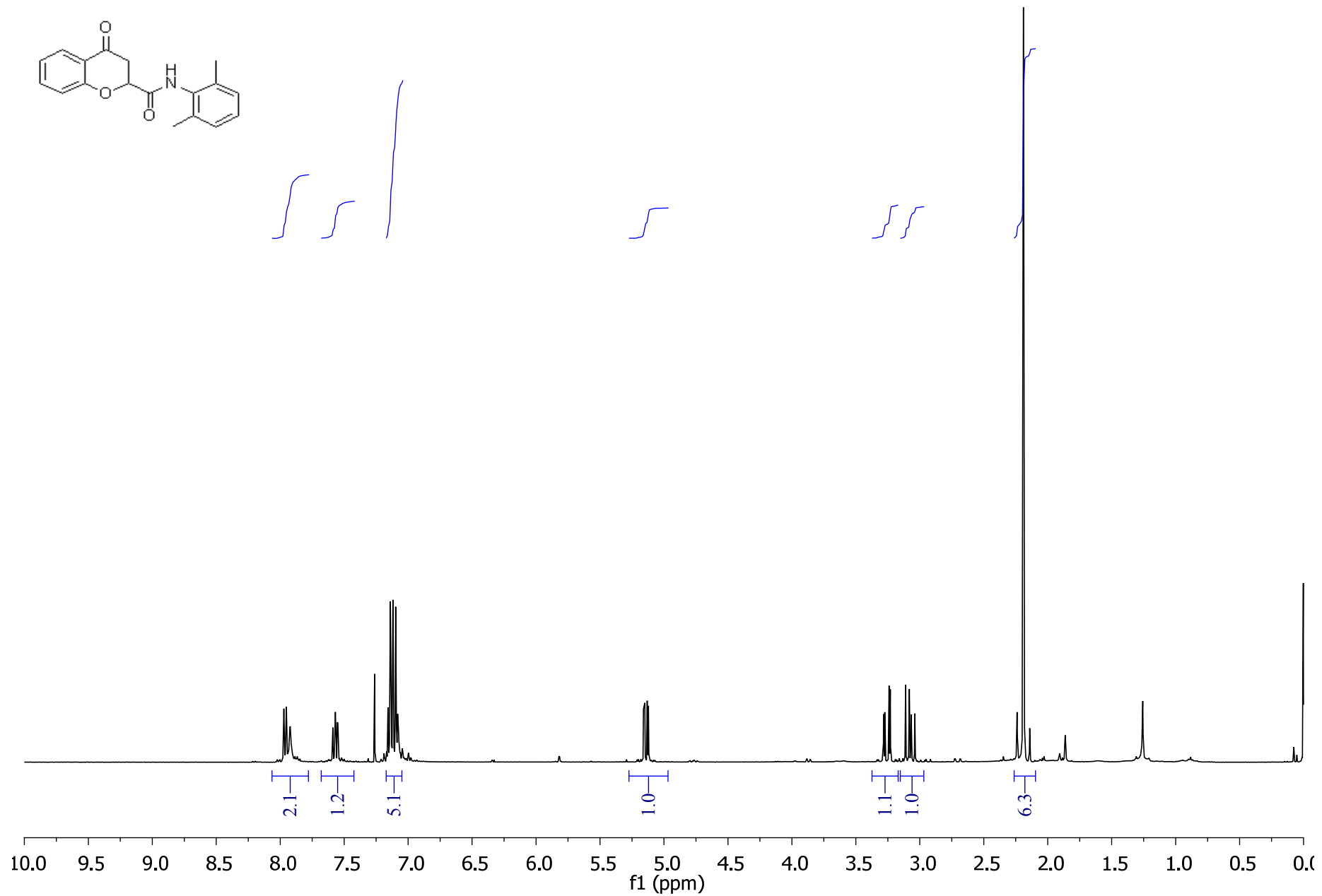


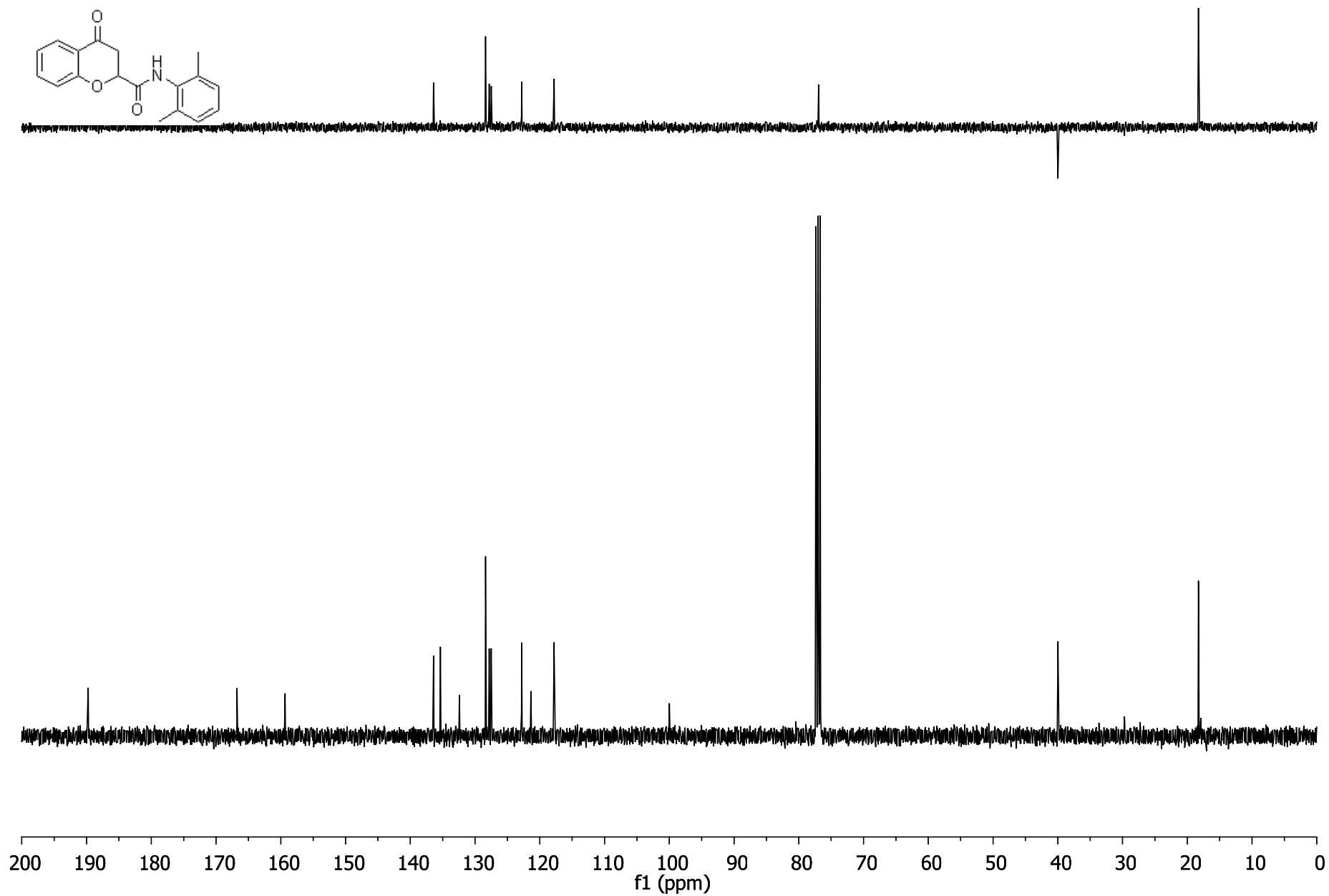


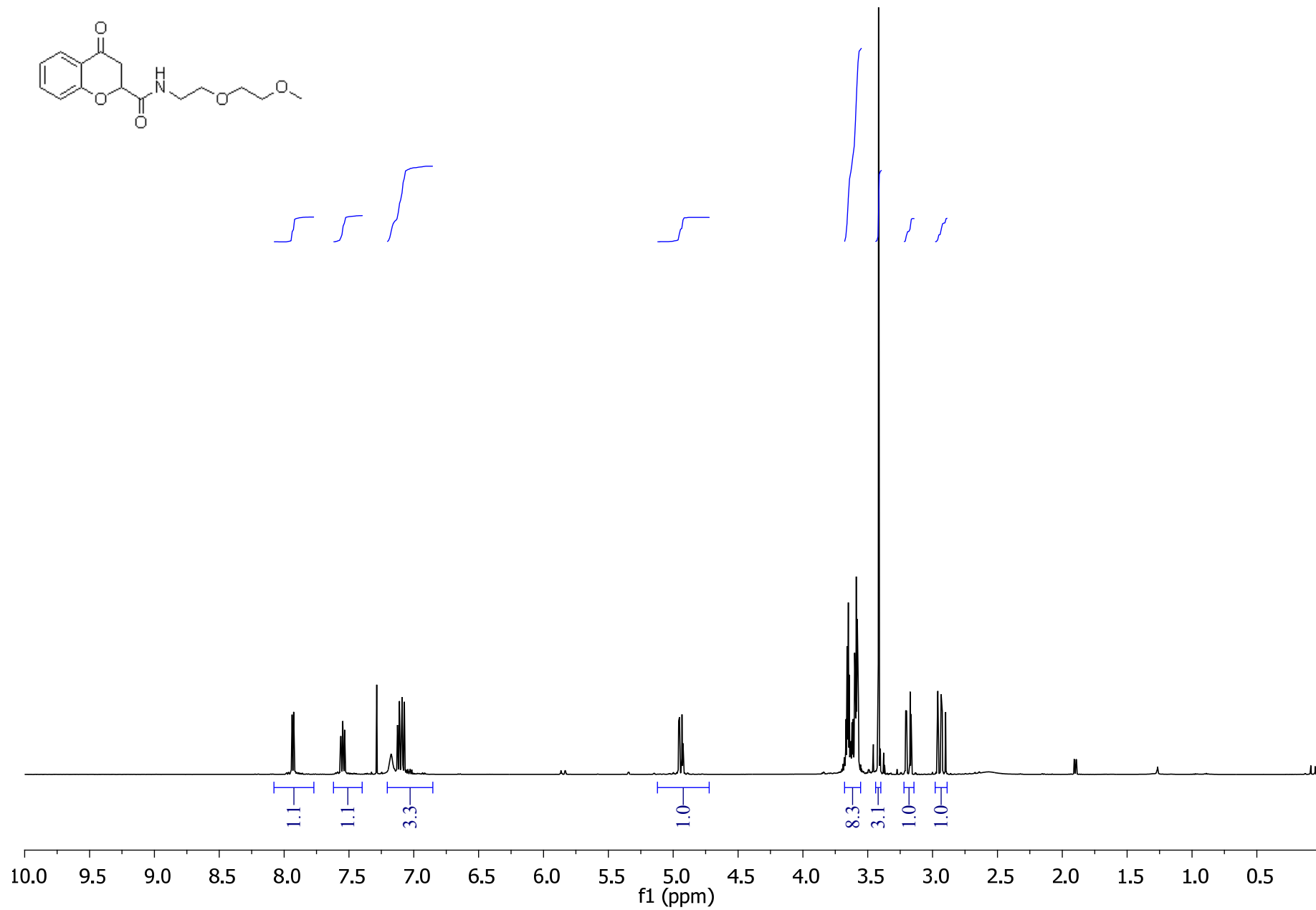


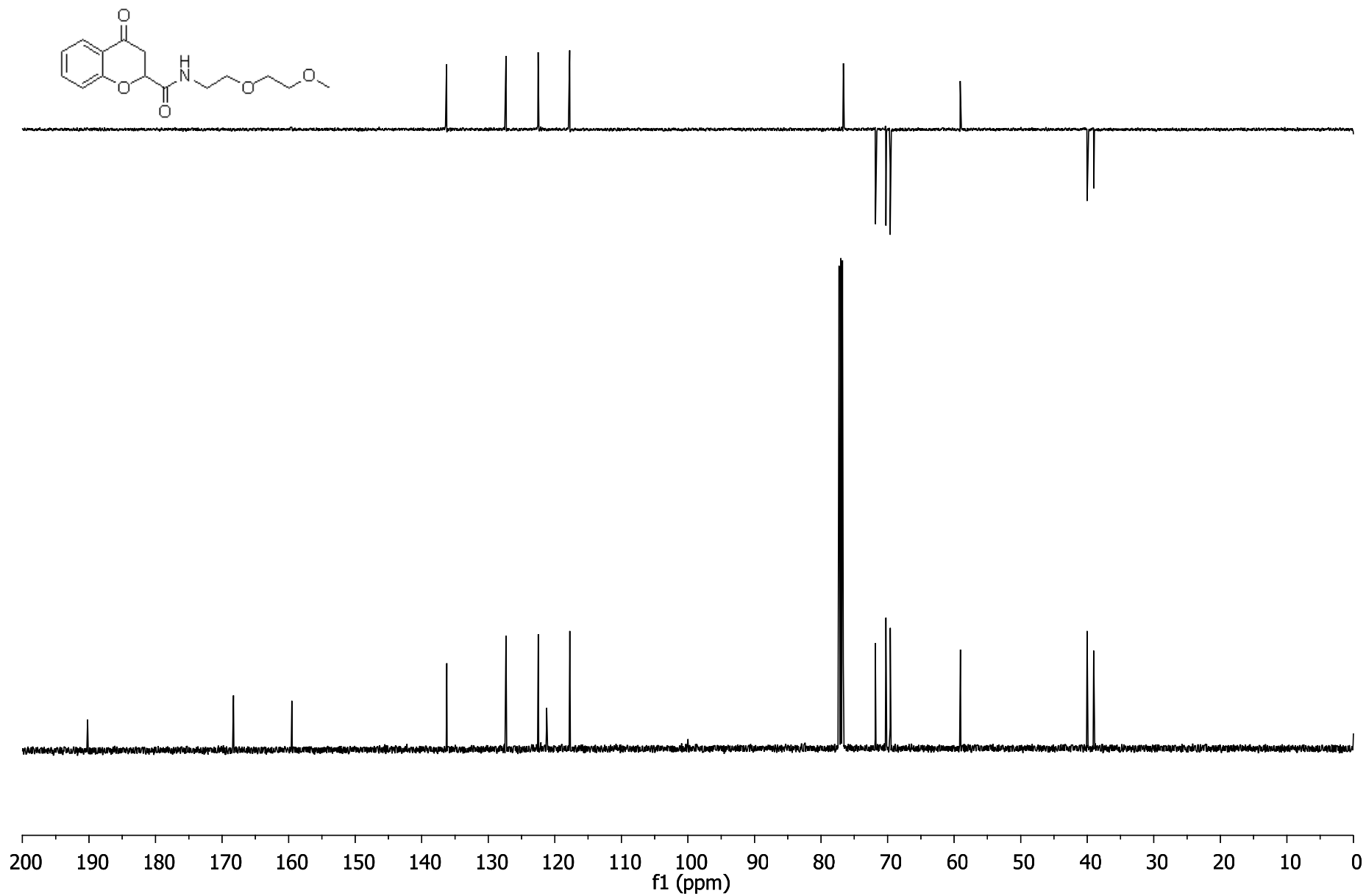


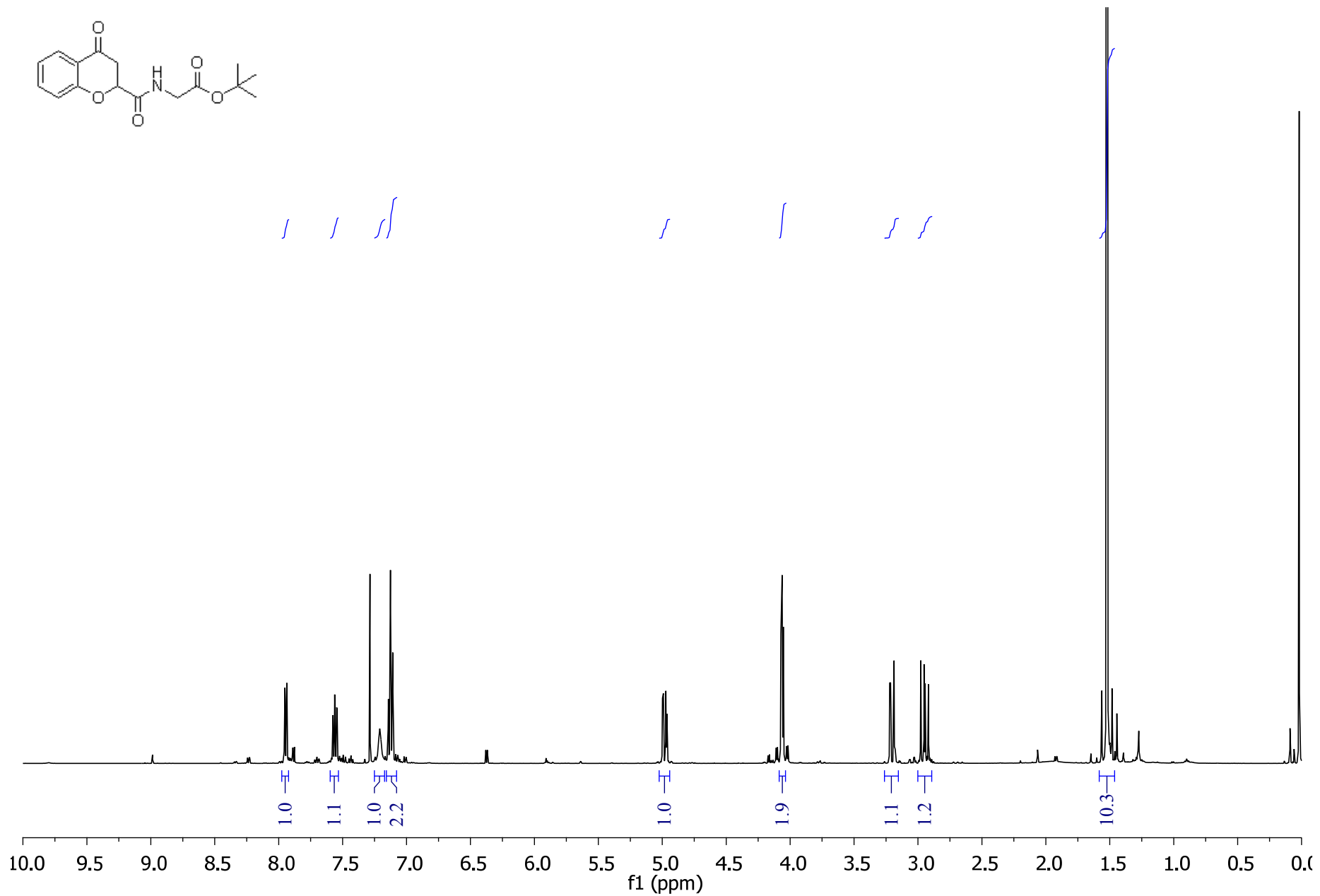
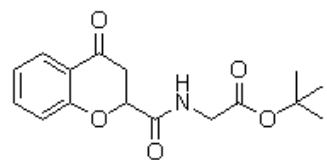


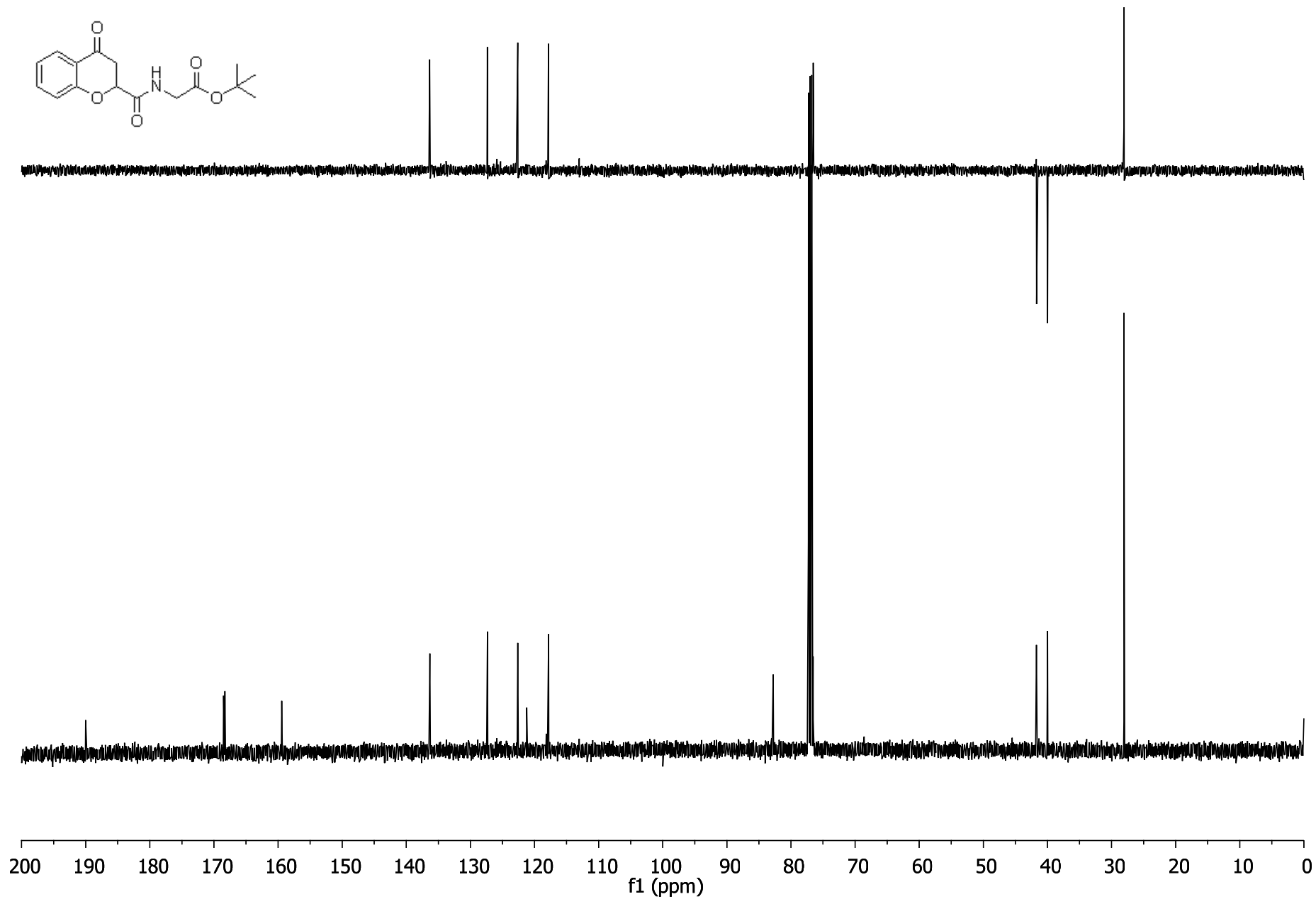


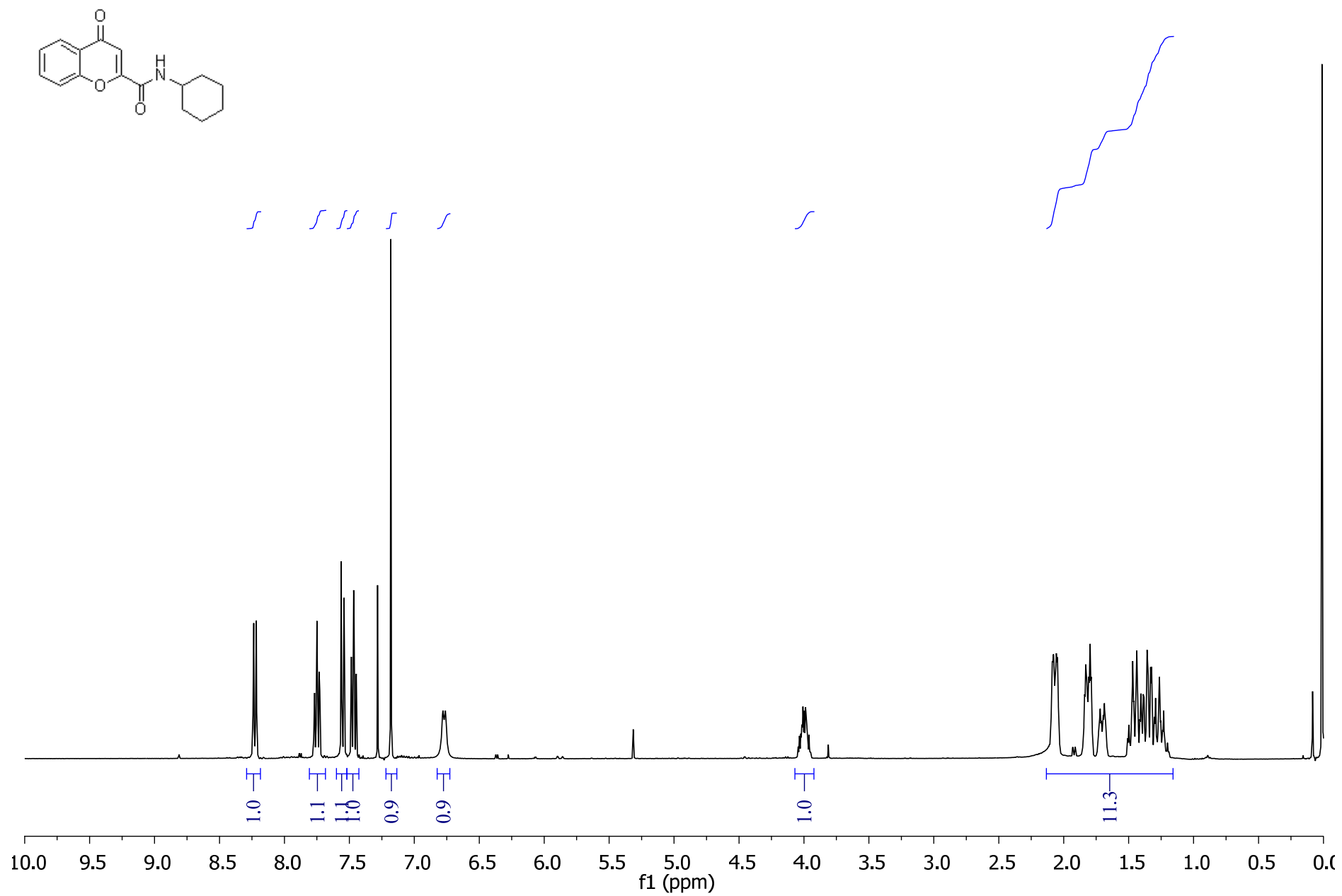


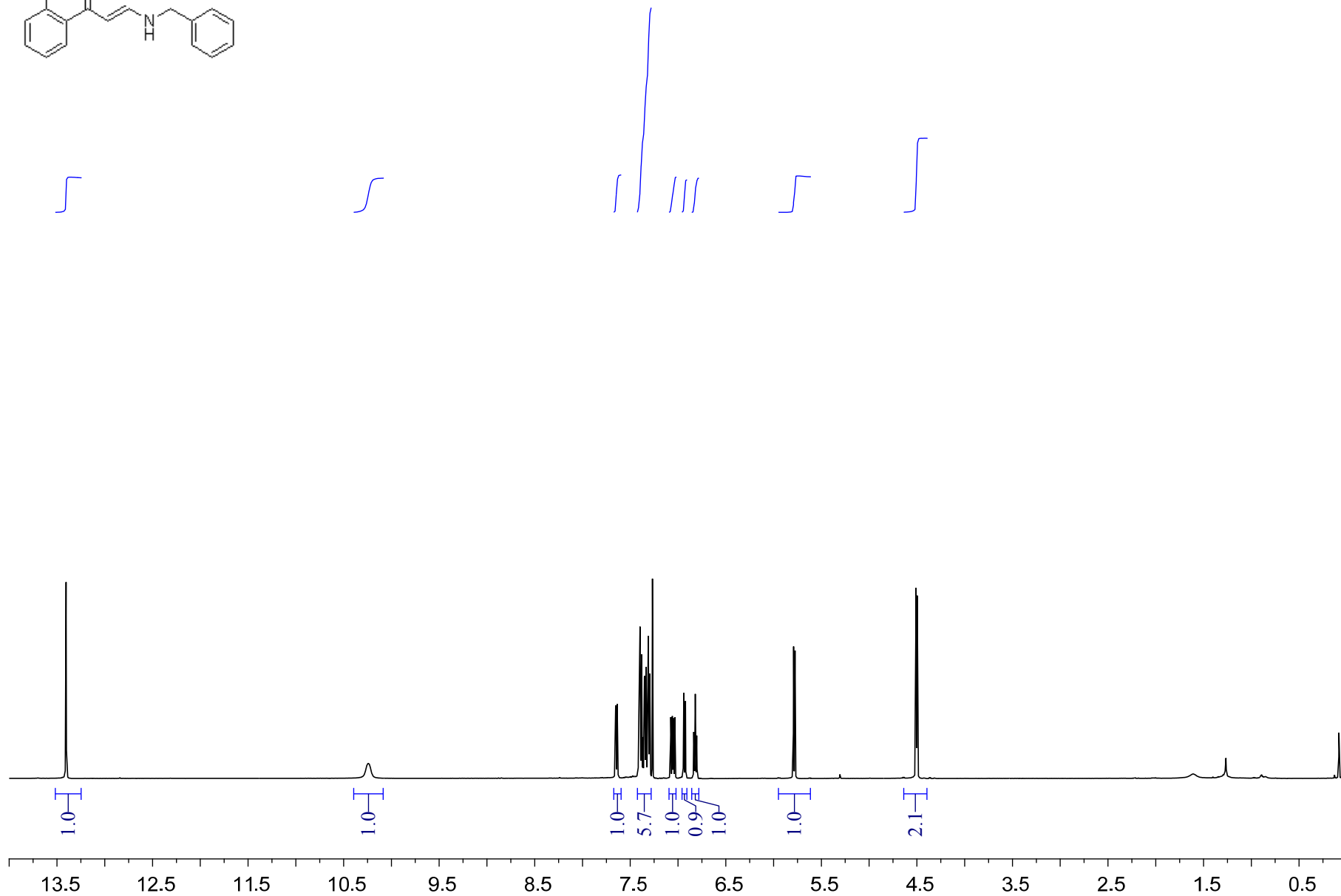
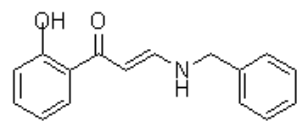


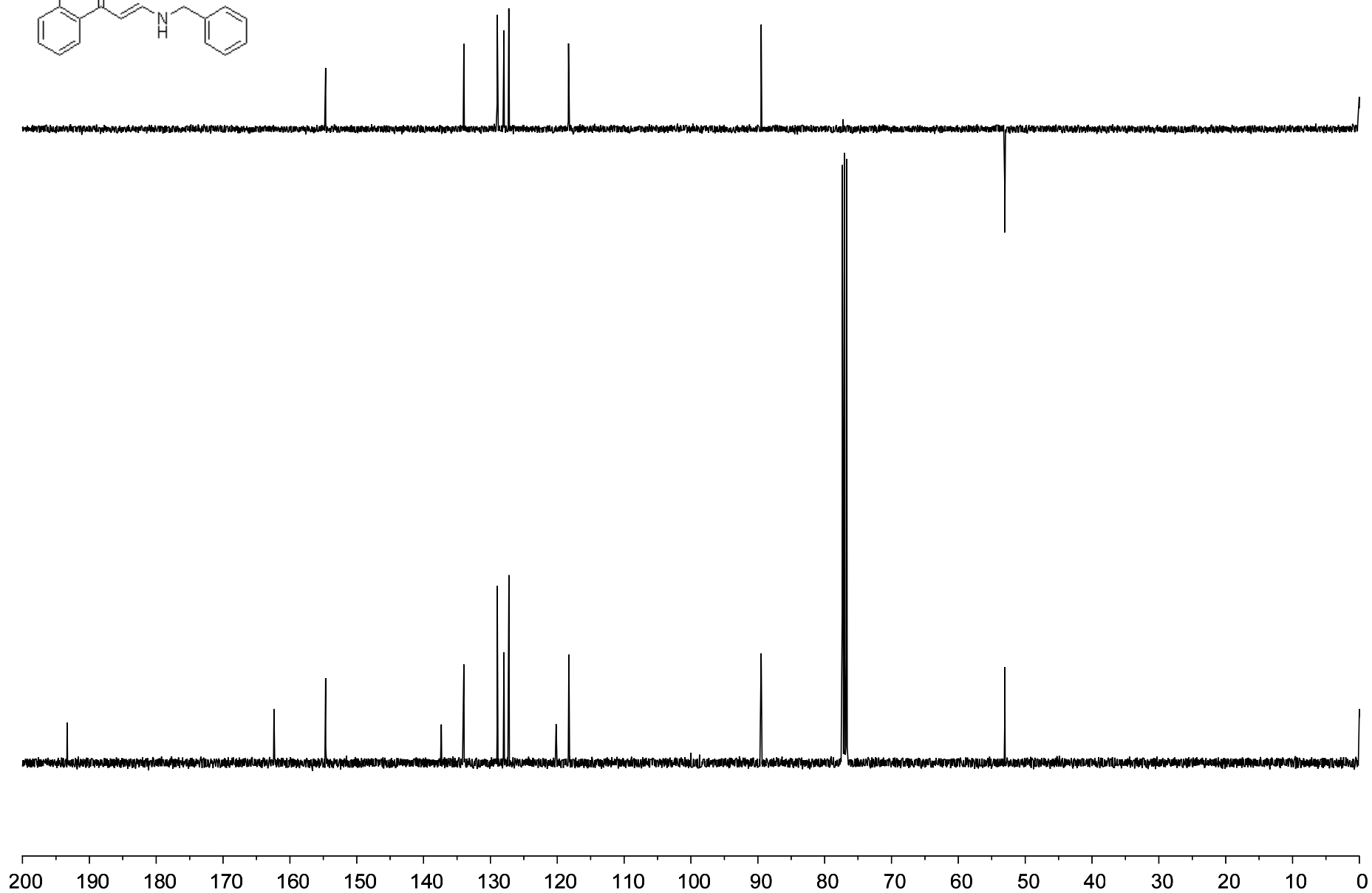
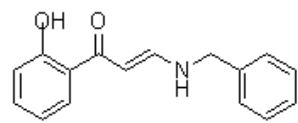


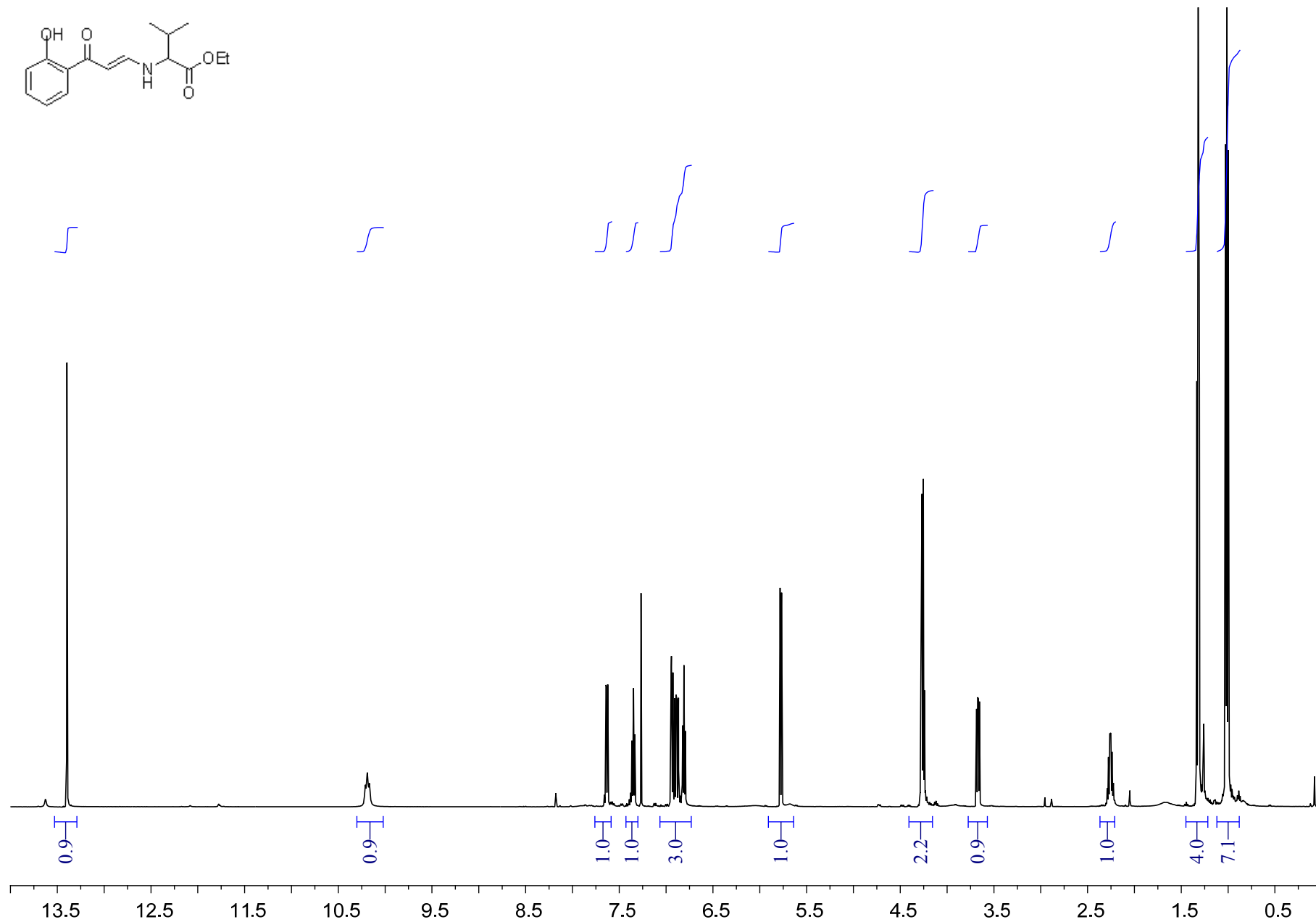
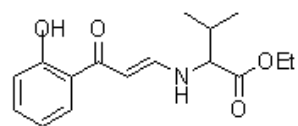


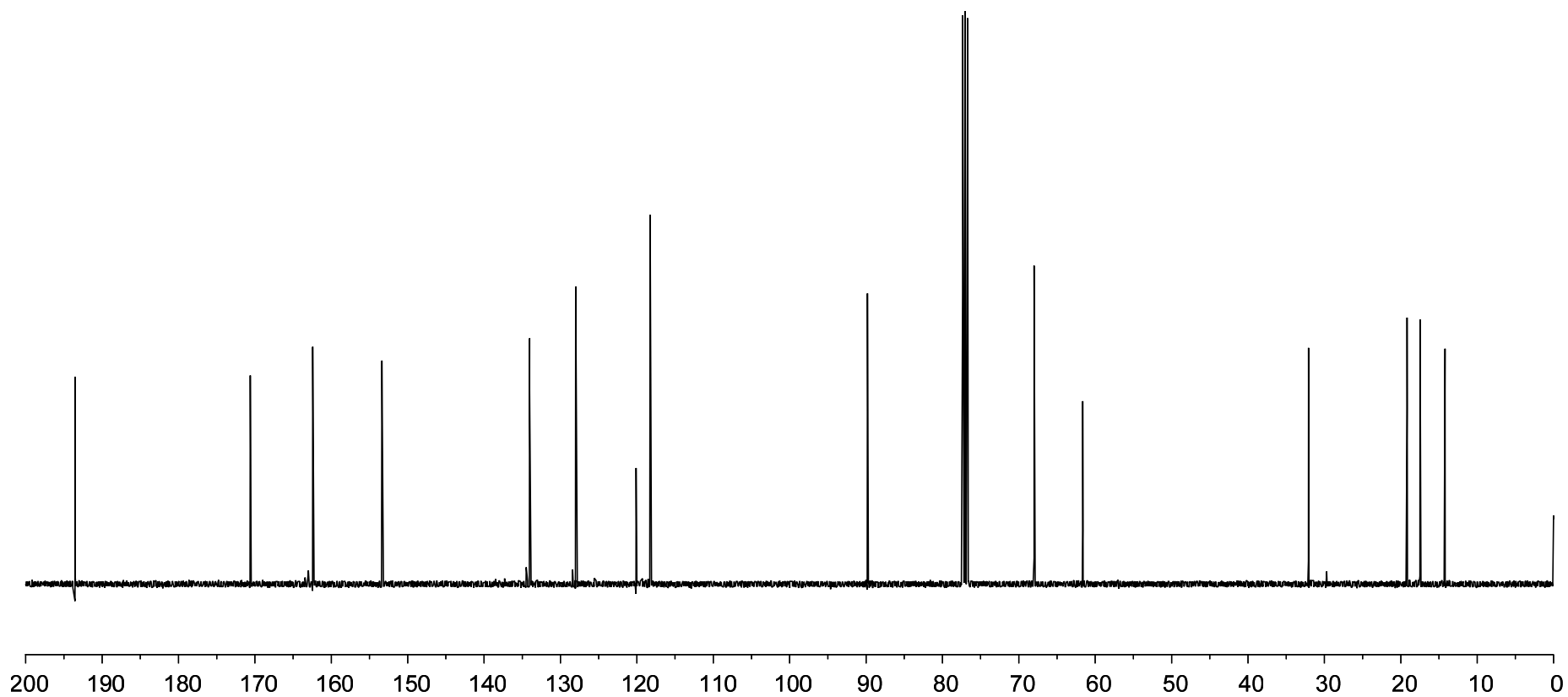
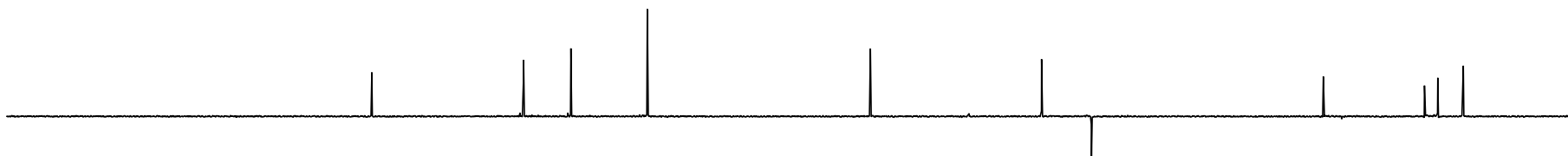
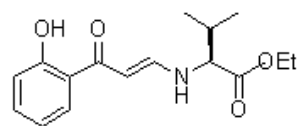


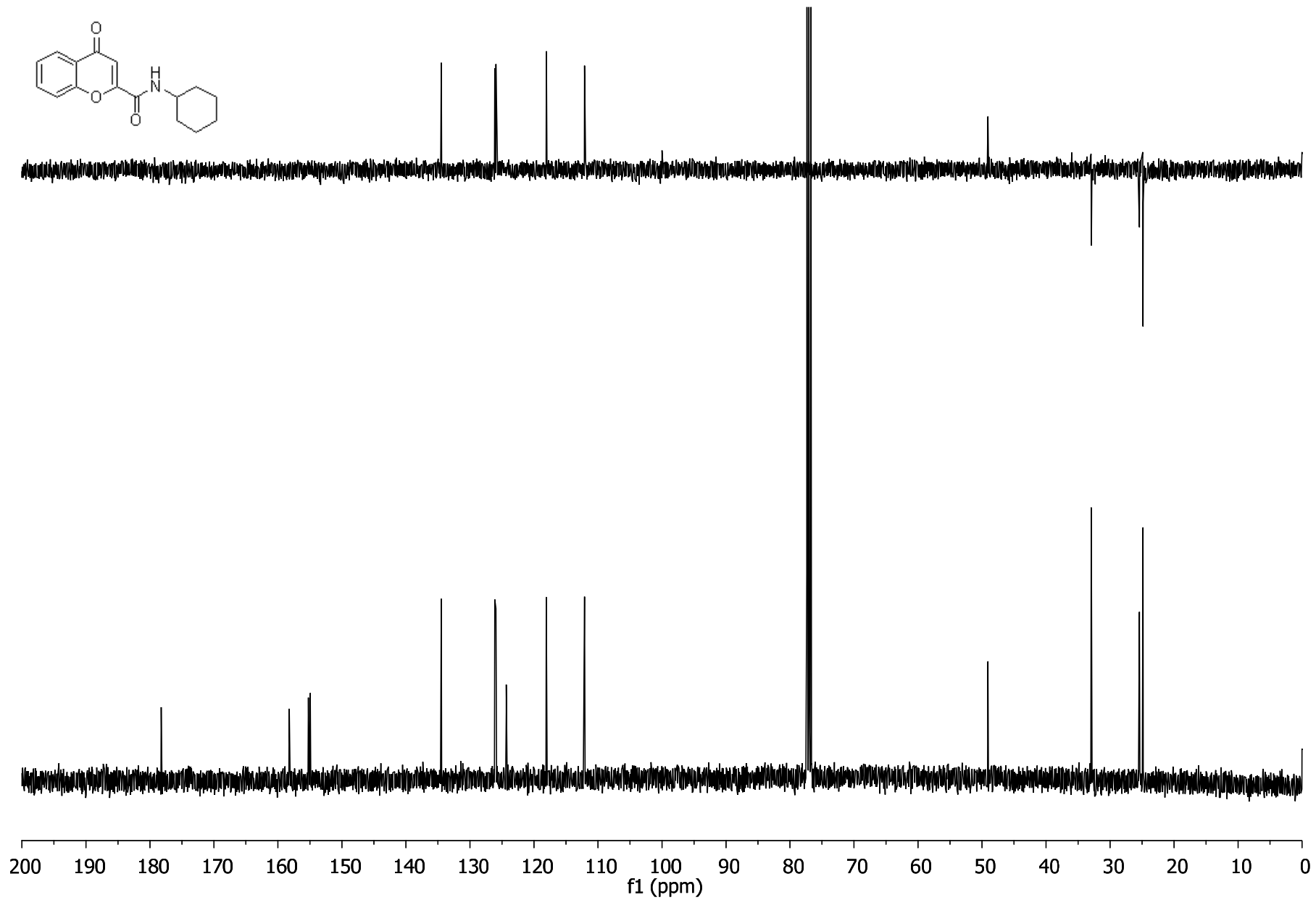


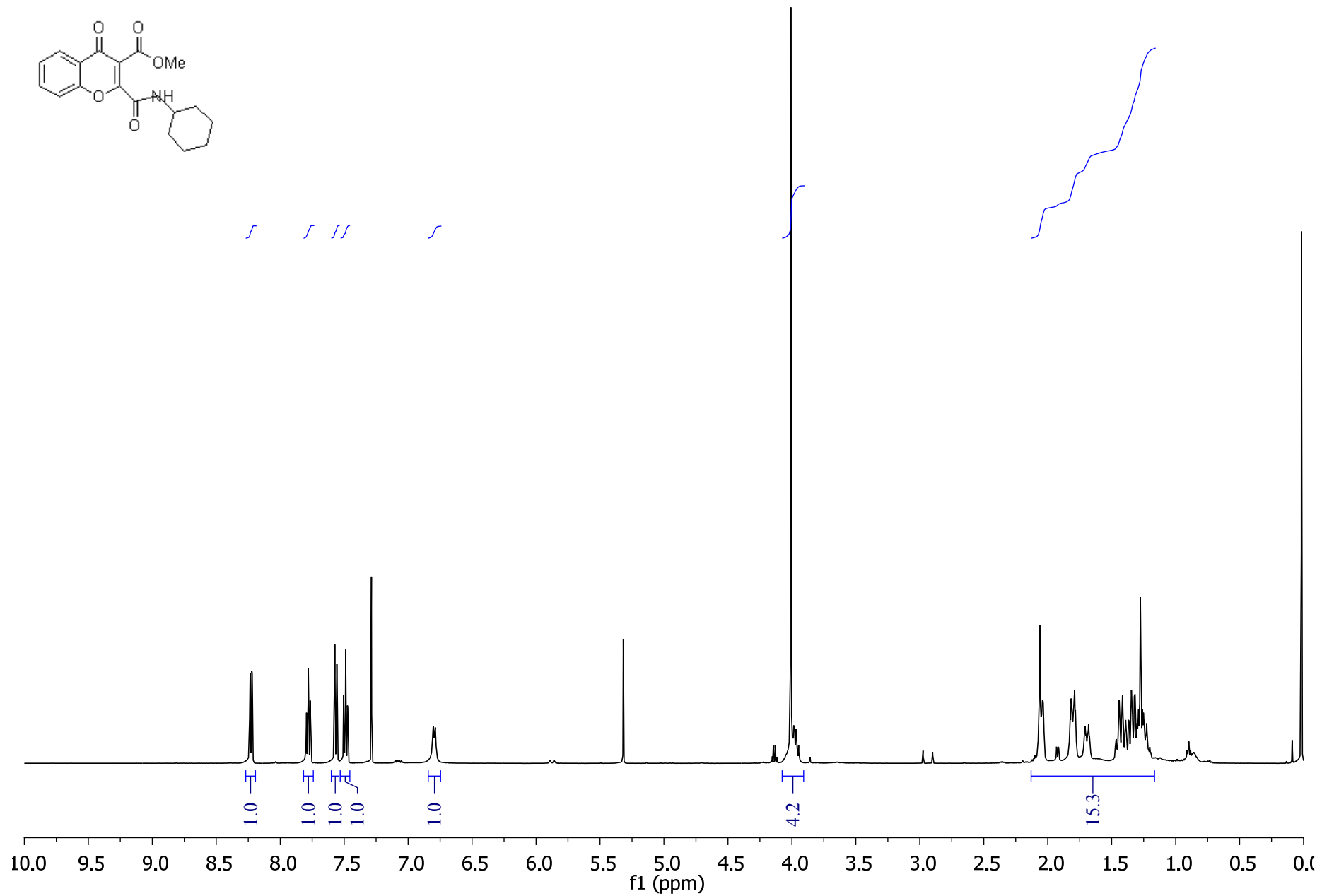


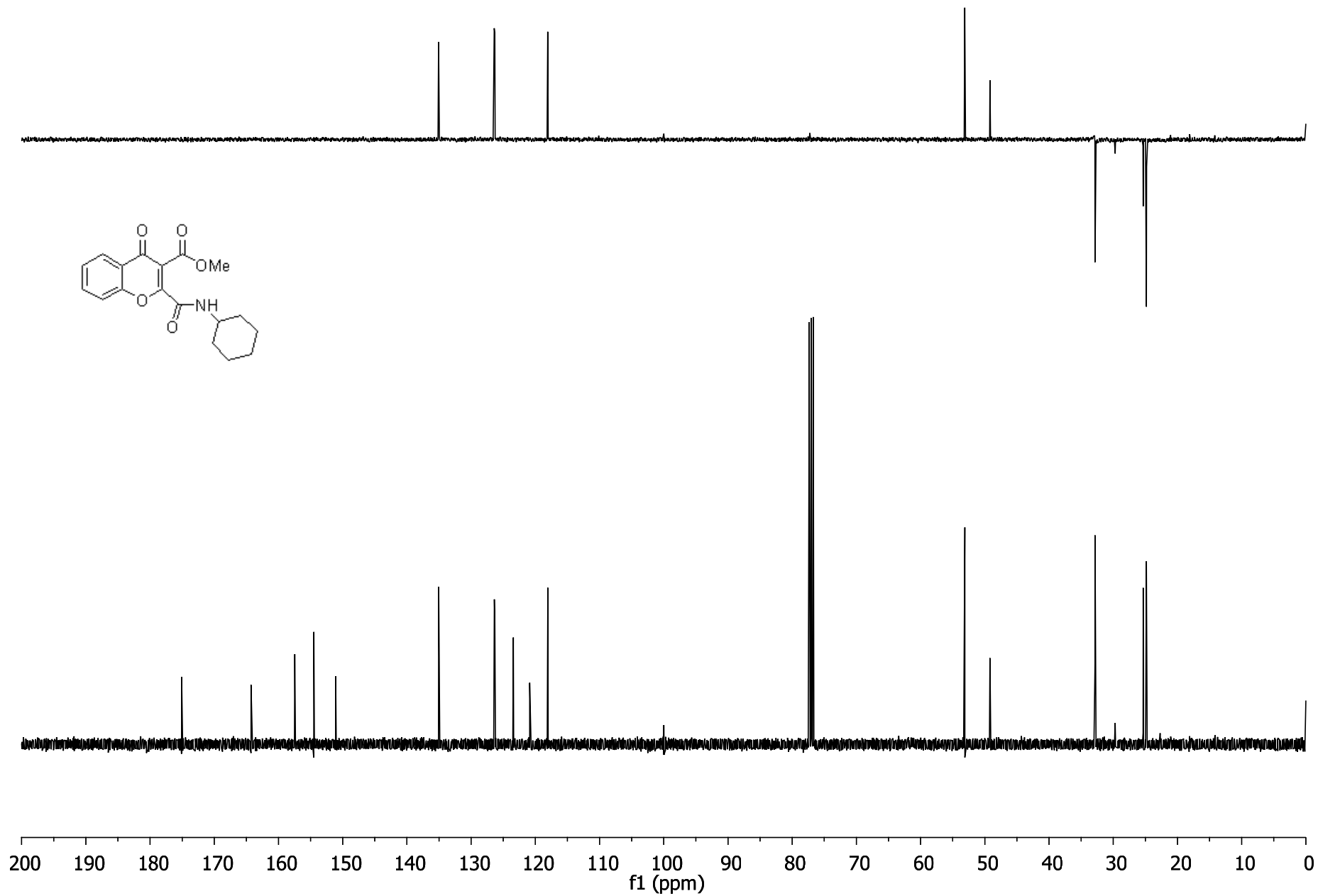


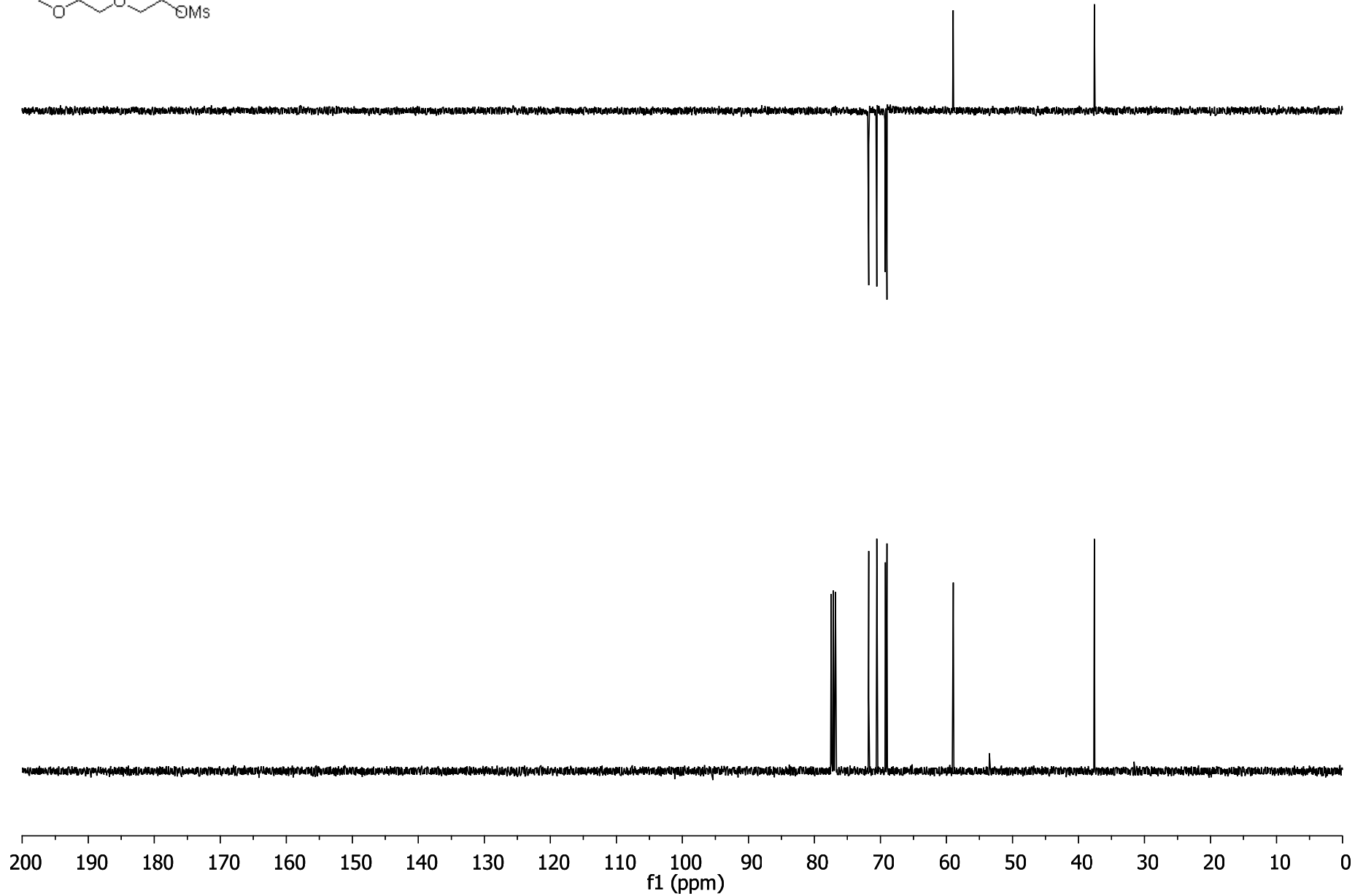
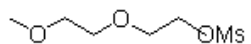


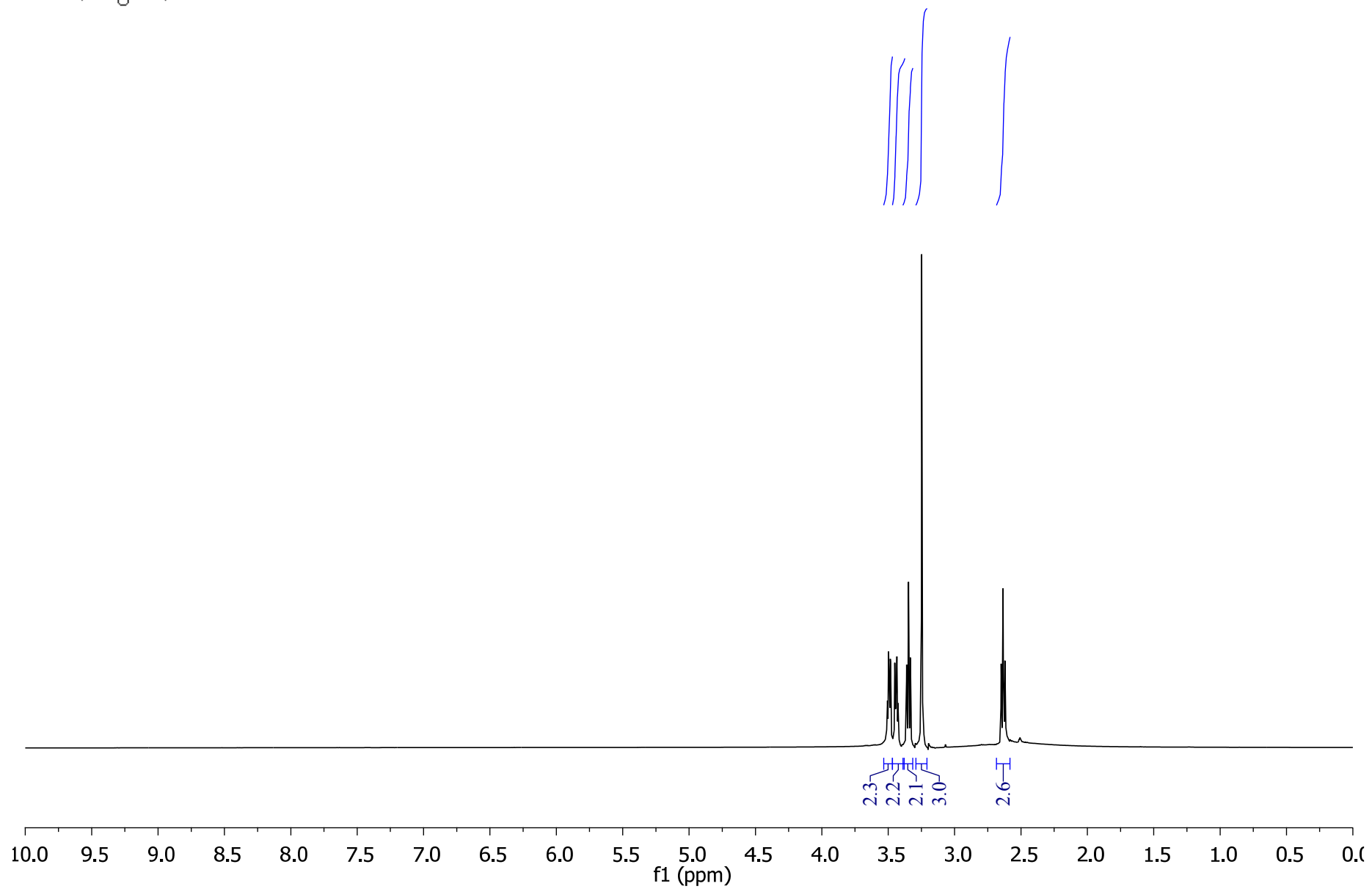
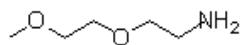


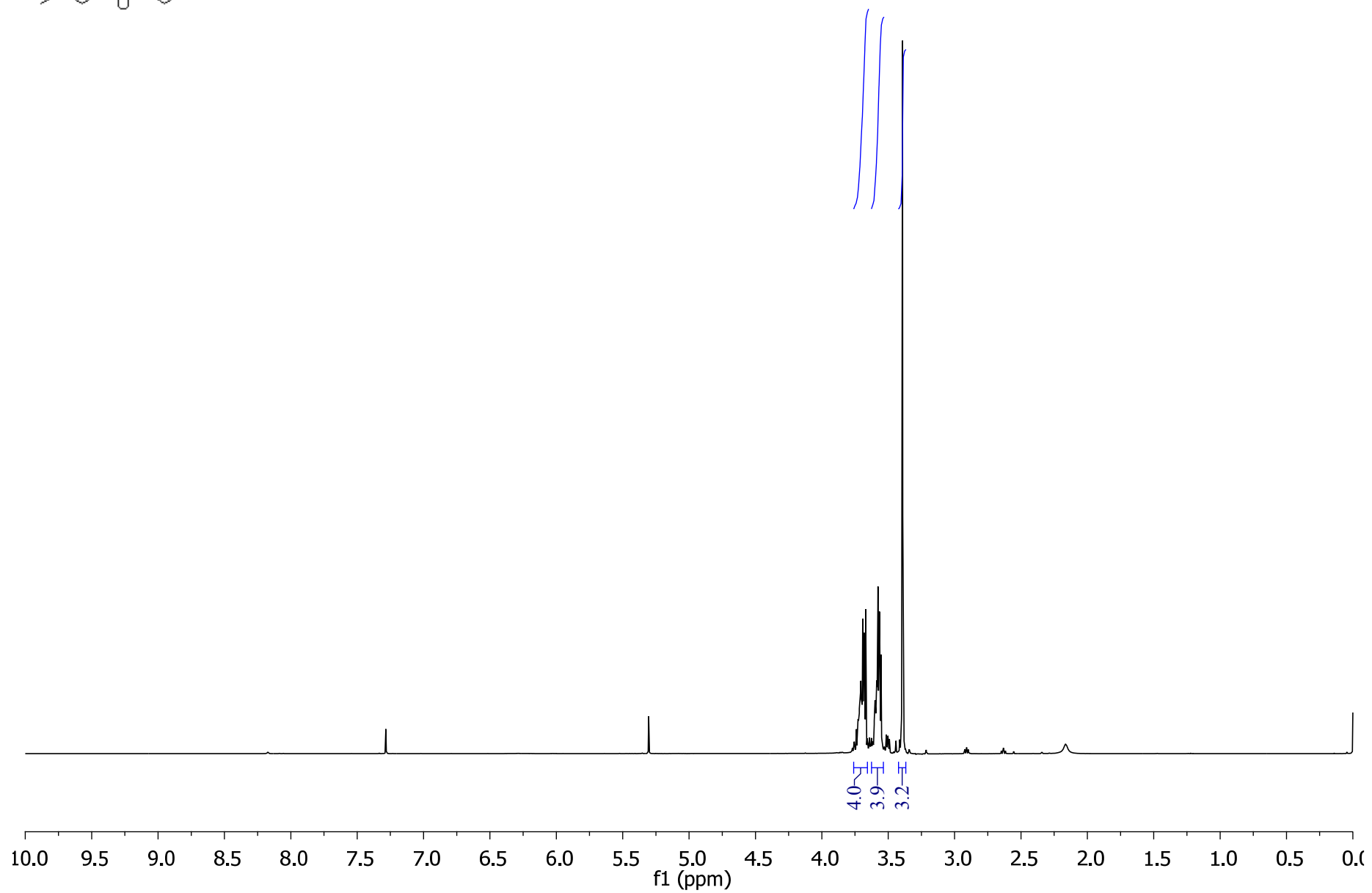
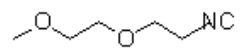












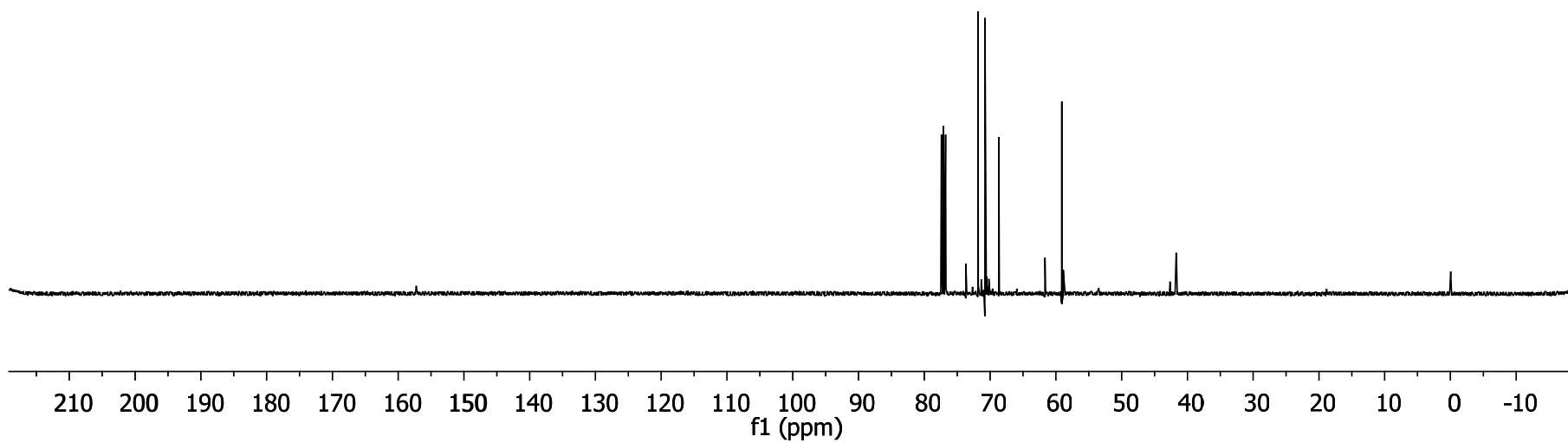
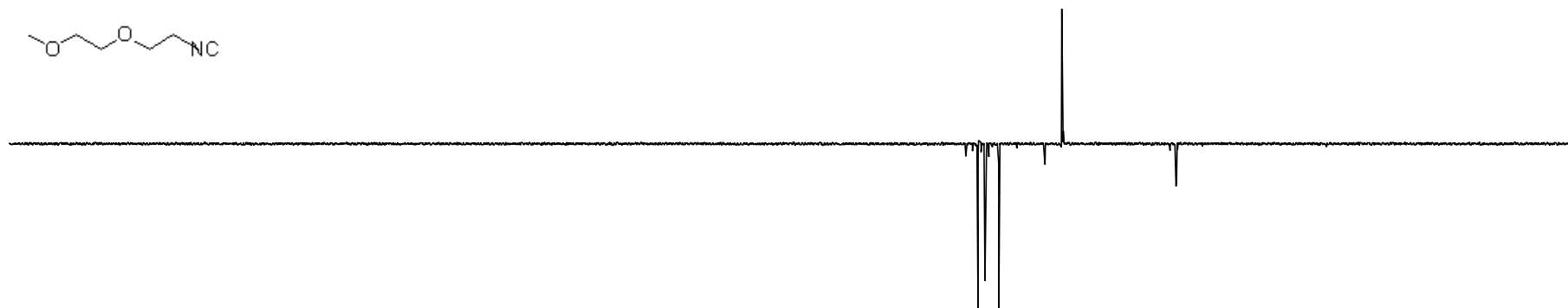
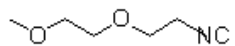


Table S1. Electronic energies and thermodynamic magnitudes of the critical structures involved in the reaction mechanisms found at the B3LYP/6-31G(d) theory level.

| Species | E (hartree) | H (hartree) | S (cal K ⁻¹ mol ⁻¹) | G (hartree) |
|---------------------------------------|----------------|----------------|---|----------------|
| P = 1 atm, T = 298.15 K | | | | |
| H₂O | -76.408953 | -76.384006 | 45.136 | -76.405452 |
| CH₃OH | -115.714405 | -115.658697 | 56.733 | -115.685652 |
| I | -818.308809 | -818.100564 | 113.891 | -818.154677 |
| I (H₂O) | -894.745898 | -894.510731 | 125.107 | -894.570173 |
| IIa | -818.315710 | -818.107760 | 115.304 | -818.162544 |
| IIa (H₂O) | -894.739603 | -894.503929 | 130.544 | -894.565955 |
| IIb | -818.322330 | -818.113804 | 114.042 | -818.167989 |
| IIb (H₂O) | -894.755337 | -894.519446 | 126.052 | -894.579337 |
| IIc | -818.324599 | -818.116548 | 116.658 | -818.171976 |
| IIc (H₂O) | -894.751409 | -894.515489 | 130.363 | -894.577428 |
| TSIIa-IIb | -894.694685 | -894.463691 | 120.746 | -894.521062 |
| TSI-IIb | -818.303761 | -818.100112 | 111.165 | -818.152930 |
| TSI-IIb (H₂O) | -894.742274 | -894.512725 | 121.624 | -894.570513 |
| TSIIb-IIc | -894.711196 | -894.480614 | 121.092 | -894.538149 |
| IIIa | -934.101260 | -933.833267 | 139.242 | -933.899425 |
| IIIb1 | -934.103022 | -933.834729 | 135.078 | -933.898909 |
| IIIb2 | -934.092008 | -933.825746 | 135.199 | -933.889984 |
| IIIc | -934.101424 | -933.833350 | 139.524 | -933.899642 |
| TSIIIb1-IIIb2 (H₂O) | -1010.50487 | -1010.21392 | 140.255 | -1010.28056 |
| TSIIIb1-IIIb2 | -934.091979 | -933.827773 | 133.222 | -933.891071 |
| TSIIIa-IIIb (H₂O) | -1010.47907 | -1010.18826 | 142.652 | -1010.25604 |
| TSIIIa-IIIb | -934.005191 | -933.742822 | 136.938 | -933.807885 |
| TSIIIb-IIIc (H₂O) | -1010.47663 | -1010.18604 | 141.338 | -1010.25319 |
| TSIIIb-IIIc | -933.999567 | -933.737277 | 136.955 | -933.802348 |

Table S2. Relative electronic energy (ΔE), enthalpy (ΔH), entropy contribution ($T\Delta S$) and Gibbs free energy in gas phase (ΔG_{gas}), in kcal mol⁻¹, of the critical structures located for the reaction at the B3LYP/6-31G(d) theory level.

| Species | ΔE | ΔH | $T\Delta S$ | ΔG_{gas} |
|---------------------------------------|------------|------------|-------------|------------------|
| P = 1 atm, T = 298.15 K | | | | |
| I (H₂O)* | -17.65 | -16.4156 | -10.1 | -6.3 |
| I | 0.0 | 0.0000 | 0.0 | 0.0 |
| IIa | -4.33 | -4.5153 | 0.4 | -4.9 |
| IIa (H₂O) | -13.71 | -12.15 | -8.5 | -3.7 |
| IIb | -8.48 | -8.3083 | 0.0 | -8.4 |
| IIb (H₂O) | -23.58 | -21.8845 | -9.8 | -12.1 |
| IIc | -9.91 | -10.0298 | 0.8 | -10.9 |
| IIc (H₂O) | -21.11 | -19.40 | -8.5 | -10.9 |
| TSIIa-IIb | 14.48 | 13.1024 | -11.4 | 24.5 |
| TSI-IIb | 3.17 | 0.2841 | -0.8 | 1.1 |
| TSI-IIb (H₂O) | -15.38 | -17.6672 | -11.2 | -6.5 |
| TSIIb-IIc | 4.12 | 2.4828 | -11.3 | 13.8 |
| IIIa | 0.1030 | 0.0522 | -0.1 | 0.1 |
| IIIb1 | -1.0030 | -0.8655 | -1.3 | 0.5 |
| IIIb2 | 5.9083 | 4.7713 | -1.3 | 6.1 |
| IIIc* | 0.0000 | 0.0000 | 0.0 | 0.0 |
| TSIIIb1-IIIb2 (H₂O) | 3.4502 | 2.1581 | -13.2 | 15.4 |
| TSIIIb1-IIIb2 | 5.9268 | 3.4996 | -1.9 | 5.4 |
| TSIIIa-IIIb (H₂O) | 19.6443 | 18.2569 | -12.5 | 30.8 |
| TSIIIa-IIIb | 60.3874 | 56.8074 | -0.8 | 57.6 |
| TSIIIb-IIIc (H₂O) | 21.1766 | 19.6518 | -12.9 | 32.6 |
| TSIIIb-IIIc | 63.9161 | 60.2866 | -0.8 | 61.1 |

* All energies are relatives to these both species **I (H₂O)** and **IIIc**.

Table S3. Single-point energies on the B3LYP/Basis of the B3LYP/6-31G* optimized structures located for the reaction pathways at different levels of theory.

| Species | B3LYP/ 6-31G* | B3LYP/ 6-31G** | B3LYP/ 6-31++G** | B3LYP/ 6-311++G** |
|---|------------------|-------------------|---------------------|----------------------|
| P = 1 atm. T = 298.15 K | | | | |
| H₂O | -76.408953 | -76.419710 | -76.434014 | -76.458420 |
| CH₃OH | -115.714405 | -115.723937 | -115.734838 | -115.764841 |
| I | -818.308809 | -818.326019 | -818.355803 | -818.534843 |
| I (H₂O) | -894.745898 | -894.774453 | -894.812170 | -895.014488 |
| IIa | -818.315710 | -818.3287765 | -818.357181 | -818.537155 |
| IIa (H₂O) | -894.739603 | -894.763385 | -894.800851 | -895.004658 |
| IIb | -818.322330 | -818.339512 | -818.369248 | -818.548514 |
| IIb (H₂O) | -894.755337 | -894.783323 | -894.821271 | -895.024036 |
| IIc | -818.3245998 | -818.337698 | -818.367142 | -818.546804 |
| IIc (H₂O) | -894.751409 | -894.775314 | -894.812519 | -895.015889 |
| TSIIa-IIb | -894.694685 | -894.721548 | -894.755302 | -894.957939 |
| TSI-IIb | -818.303761 | -818.322625 | -818.351556 | -818.529617 |
| TSI-IIb (H₂O) | -894.742274 | -894.772774 | -894.809835 | -895.010920 |
| TSIIb-IIc | -894.711196 | -894.738489 | -894.771786 | -894.973775 |
| IIIa | -934.101260 | -934.121818 | -934.157662 | -934.367956 |
| IIIb1 | -934.092008 | -934.117987 | -934.154042 | -934.362368 |
| IIIb2 | -934.103022 | -934.128019 | -934.164447 | -934.373619 |
| IIIc | -934.101424 | -934.121980 | -934.158211 | -934.368455 |
| TSIIIb1-IIIb2 (H₂O) | -1010.504879 | -1010.542059 | -1010.581937 | -1010.813718 |
| TSIIIb1-IIIb2 | -934.091979 | -934.118299 | -934.154348 | -934.362498 |
| TSIIIa-IIIb (H₂O) | -1010.479072 | -1010.513619 | -1010.553100 | -1010.785813 |
| TSIIIa-IIIb | -934.005191 | -934.029952 | -934.067473 | -934.276356 |
| TSIIIb-IIIc (H₂O) | -1010.476630 | -1010.511605 | -1010.551776 | -1010.784532 |
| TSIIIb-IIIc | -933.999567 | -934.024341 | -934.061777 | -934.270697 |

Table S4. Relative energies on the B3LYP/Basis for the reaction pathways at different levels of theory.

| Species | B3LYP/ 6-31G* | B3LYP/ 6-31G** | B3LYP/ 6-31++G** | B3LYP/ 6-311++G** |
|---------------------------------------|------------------|-------------------|---------------------|----------------------|
| P = 1 atm. T = 298.15 K | | | | |
| I (H₂O)* | -17.655 | -18.024 | -14.027 | -13.318 |
| I | 0.000 | 0.000 | 0.000 | 0.000 |
| IIa | -4.330 | -1.730 | -0.865 | -1.450 |
| IIa (H₂O) | -13.705 | -11.079 | -6.924 | -7.150 |
| IIb | -8.485 | -8.467 | -8.437 | -8.579 |
| IIb (H₂O) | -23.578 | -23.591 | -19.738 | -19.310 |
| IIc | -9.909 | -7.328 | -7.115 | -7.505 |
| IIc (H₂O) | -21.113 | -18.565 | -14.25 | -14.20 |
| TSIIa-IIb | 14.482 | 15.174 | 21.658 | 22.167 |
| TSI-IIb | 3.168 | 2.130 | 2.665 | 3.280 |
| TSI-IIb (H₂O) | -15.381 | -16.971 | -12.562 | -11.079 |
| TSIIb-IIc | 4.121 | 4.543 | 11.314 | 12.229 |
| IIIa | 0.103 | 0.102 | 0.345 | 0.313 |
| IIIb1 | -1.003 | -3.789 | -3.913 | -3.240 |
| IIIb2 | 5.908 | 2.506 | 2.616 | 3.820 |
| IIIc* | 0.000 | 0.000 | 0.000 | 0.000 |
| TSIIIb1-IIIb2 (H₂O) | 3.450 | -0.231 | 6.456 | 8.256 |
| TSIIIb1-IIIb2 | 5.927 | 2.310 | 2.424 | 3.738 |
| TSIIIa-IIIb (H₂O) | 19.644 | 17.615 | 24.551 | 25.767 |
| TSIIIa-IIIb | 60.387 | 57.749 | 56.939 | 57.793 |
| TSIIIb-IIIc (H₂O) | 21.177 | 18.879 | 25.382 | 26.571 |
| TSIIIb-IIIc | 63.916 | 61.270 | 60.513 | 61.344 |

* All energies are relative to these both species **I (H₂O)** and **IIIc**.

B3LYP/6-31G(d) optimized cartesian coordinates of the critical structures located in the present work.

CH₃OH

E = -115.714405144

| | | | |
|---|-----------|-----------|-----------|
| C | 0.662325 | -0.019545 | 0.000000 |
| H | 1.079718 | 0.991033 | -0.000001 |
| H | 1.036957 | -0.543658 | -0.893148 |
| H | 1.036957 | -0.543656 | 0.893149 |
| O | -0.749169 | 0.122497 | 0.000000 |
| H | -1.134236 | -0.766420 | 0.000000 |

H₂O

E = -76.4089533236

| | | | |
|---|----------|-----------|-----------|
| O | 0.000000 | 0.000000 | 0.119720 |
| H | 0.000000 | 0.761560 | -0.478879 |
| H | 0.000000 | -0.761560 | -0.478879 |

I

E = -818.308809299

| | | | |
|---|-----------|-----------|-----------|
| O | -0.012279 | -1.300645 | -0.154971 |
| C | -0.943808 | -0.484732 | 0.583149 |
| C | -0.653842 | 0.962626 | 0.436496 |
| C | 0.658294 | 1.497907 | 0.265492 |
| C | 1.698071 | 0.447381 | 0.168792 |
| C | 1.302468 | -0.892185 | -0.070427 |
| C | -1.756950 | 1.578694 | -0.073531 |
| O | -2.810057 | 0.766358 | -0.274137 |
| C | -2.380759 | -0.559615 | 0.025878 |
| C | 3.063013 | 0.765918 | 0.173966 |
| C | 4.025125 | -0.215086 | -0.031346 |
| C | 3.620320 | -1.533780 | -0.273480 |
| C | 2.270093 | -1.873841 | -0.299218 |
| N | -3.197602 | -1.485408 | -0.162548 |
| C | -2.822700 | -2.858263 | 0.132807 |
| O | 0.858577 | 2.714955 | 0.072876 |
| H | -1.824230 | -2.983771 | 0.569580 |
| H | 3.337997 | 1.804157 | 0.333869 |
| H | 1.945703 | -2.891504 | -0.491093 |
| H | -2.866802 | -3.434376 | -0.797994 |
| H | 4.364690 | -2.307365 | -0.441860 |
| H | 5.080537 | 0.039105 | -0.014640 |
| H | -3.573377 | -3.281706 | 0.808912 |
| H | -0.931380 | -0.847690 | 1.622456 |
| O | -1.870003 | 2.829599 | -0.442050 |
| H | -0.955786 | 3.208723 | -0.296611 |

I (H₂O)

E = -894.745897507

| | | | |
|---|-----------|-----------|-----------|
| O | 0.505036 | -1.523475 | -0.275572 |
| C | -0.585969 | -0.963241 | 0.472140 |
| C | -0.796894 | 0.499825 | 0.210397 |
| C | 0.358507 | 1.353057 | 0.187244 |
| C | 1.640752 | 0.594203 | 0.136183 |
| C | 1.655885 | -0.787409 | -0.154059 |
| C | -2.117251 | 0.660230 | -0.171942 |
| O | -2.787805 | -0.519983 | -0.254387 |
| C | -1.919638 | -1.575303 | 0.053804 |
| C | 2.864987 | 1.275167 | 0.230389 |
| C | 4.069823 | 0.609349 | 0.048478 |
| C | 4.063274 | -0.757864 | -0.258811 |
| C | 2.864585 | -1.456451 | -0.364788 |
| N | -2.360205 | -2.744592 | -0.026302 |
| C | -1.509372 | -3.872027 | 0.313772 |
| O | 0.385254 | 2.601139 | 0.143089 |
| H | -0.524189 | -3.608862 | 0.718041 |
| H | 2.833355 | 2.340791 | 0.432975 |
| H | 2.841426 | -2.516172 | -0.597786 |
| H | -1.359508 | -4.477832 | -0.587128 |
| H | 5.001335 | -1.284949 | -0.411093 |
| H | 5.010072 | 1.145963 | 0.132079 |
| H | -2.043068 | -4.499116 | 1.036484 |
| H | -0.385350 | -1.179617 | 1.534501 |
| O | -2.864242 | 1.666416 | -0.485238 |
| H | -2.451391 | 2.596776 | -0.300494 |
| H | -2.102024 | 4.240172 | 0.891906 |
| O | -1.852648 | 3.947714 | 0.001426 |
| H | -0.916109 | 3.603275 | 0.083251 |

IIa

E = -818.315709914

| | | | |
|---|-----------|-----------|-----------|
| O | 0.081212 | 1.305763 | 0.179249 |
| C | -0.857660 | 0.362726 | -0.306118 |
| C | -0.718742 | -0.983153 | 0.396038 |
| C | 0.622367 | -1.597899 | 0.018685 |
| C | 1.679115 | -0.542566 | -0.038427 |
| C | 1.374275 | 0.831893 | 0.098340 |
| C | -2.063845 | -1.625068 | 0.110329 |
| O | -2.964532 | -0.582551 | -0.084149 |
| C | -2.333740 | 0.671260 | -0.104369 |

| | | | |
|---|-----------|-----------|-----------|
| C | 3.027546 | -0.924989 | -0.145010 |
| C | 4.043538 | 0.018637 | -0.100187 |
| C | 3.720419 | 1.373769 | 0.057335 |
| C | 2.394402 | 1.784073 | 0.152155 |
| N | -3.043829 | 1.696724 | -0.007289 |
| C | -2.479229 | 3.033805 | -0.095990 |
| O | 0.830212 | -2.780206 | -0.159334 |
| H | -1.404287 | 3.075861 | -0.299292 |
| H | 3.240623 | -1.984575 | -0.247881 |
| H | 2.128655 | 2.831165 | 0.254662 |
| H | -2.681425 | 3.557243 | 0.845445 |
| H | 4.510203 | 2.118806 | 0.096914 |
| H | 5.081396 | -0.289600 | -0.179333 |
| H | -3.016889 | 3.576254 | -0.881656 |
| H | -0.684327 | 0.224192 | -1.387329 |
| O | -2.400593 | -2.769609 | 0.078218 |
| H | -0.688206 | -0.788533 | 1.480938 |

IIb

E = -818.322330496

| | | | |
|---|-----------|-----------|-----------|
| O | 0.000223 | -1.302335 | -0.161909 |
| C | -0.935179 | -0.475217 | 0.557999 |
| C | -0.667162 | 0.970849 | 0.359120 |
| C | 0.594020 | 1.440324 | 0.176871 |
| C | 1.674225 | 0.463021 | 0.145762 |
| C | 1.307557 | -0.890994 | -0.067353 |
| C | -1.865787 | 1.651476 | -0.048489 |
| O | -2.865981 | 0.708906 | -0.209251 |
| C | -2.375897 | -0.583347 | 0.026191 |
| C | 3.032715 | 0.810348 | 0.177940 |
| C | 4.013960 | -0.160466 | 0.013070 |
| C | 3.638966 | -1.490150 | -0.211765 |
| C | 2.295330 | -1.857131 | -0.259543 |
| N | -3.142065 | -1.554277 | -0.175996 |
| C | -2.694460 | -2.910789 | 0.087793 |
| O | 0.871639 | 2.719743 | -0.096324 |
| H | -1.698477 | -2.997189 | 0.540239 |
| H | 3.298971 | 1.852034 | 0.326361 |
| H | 1.993575 | -2.884076 | -0.437088 |
| H | -2.690226 | -3.466172 | -0.857116 |
| H | 4.401314 | -2.252340 | -0.347035 |
| H | 5.063671 | 0.113420 | 0.049406 |
| H | -3.430078 | -3.394781 | 0.739922 |
| H | -0.903165 | -0.793106 | 1.612672 |
| O | -2.026310 | 2.835307 | -0.282592 |
| H | 0.012582 | 3.201647 | -0.140355 |

IIb (H₂O)

E = -894.755336781

| | | | |
|---|-----------|-----------|-----------|
| O | 0.478045 | -1.546479 | -0.265428 |
| C | -0.612247 | -0.965472 | 0.467566 |
| C | -0.798007 | 0.495837 | 0.183768 |
| C | 0.331738 | 1.277918 | 0.096063 |
| C | 1.618707 | 0.566514 | 0.112776 |
| C | 1.634581 | -0.824987 | -0.136913 |
| C | -2.181547 | 0.716581 | -0.173334 |
| O | -2.819763 | -0.510577 | -0.239126 |
| C | -1.952984 | -1.560365 | 0.045653 |
| C | 2.842682 | 1.247794 | 0.218779 |
| C | 4.047347 | 0.569327 | 0.081399 |
| C | 4.042224 | -0.804184 | -0.191947 |
| C | 2.842867 | -1.502000 | -0.307462 |
| N | -2.384930 | -2.734646 | -0.044016 |
| C | -1.530008 | -3.861594 | 0.285700 |
| O | 0.431777 | 2.581352 | -0.082485 |
| H | -0.550228 | -3.601851 | 0.705684 |
| H | 2.823436 | 2.317492 | 0.396290 |
| H | 2.820456 | -2.566814 | -0.514882 |
| H | -1.365836 | -4.453478 | -0.622267 |
| H | 4.981400 | -1.337996 | -0.308342 |
| H | 4.987337 | 1.104364 | 0.174608 |
| H | -2.066301 | -4.503894 | 0.993250 |
| H | -0.426611 | -1.171238 | 1.535100 |
| O | -2.831526 | 1.719550 | -0.422147 |
| H | -2.330820 | 3.354505 | -0.140811 |
| H | -1.920314 | 4.263214 | 1.050495 |
| O | -1.701478 | 4.067896 | 0.126390 |
| H | -0.426569 | 3.112067 | 0.009062 |

IIc

E = -818.324599852

| | | | |
|---|-----------|-----------|-----------|
| O | -0.202887 | -1.176474 | -0.124060 |
| C | -1.066207 | -0.331294 | 0.653466 |
| C | -0.664458 | 1.141213 | 0.639542 |
| C | 0.836968 | 1.425000 | 0.672034 |
| C | 1.700378 | 0.302039 | 0.270641 |
| C | 1.143644 | -0.932679 | -0.110309 |
| C | -1.396309 | 1.686058 | -0.595456 |
| O | -2.444714 | 0.834153 | -0.874789 |
| C | -2.404588 | -0.311131 | -0.085293 |
| C | 3.097345 | 0.462533 | 0.232480 |
| C | 3.918789 | -0.574148 | -0.181641 |
| C | 3.345049 | -1.794711 | -0.569820 |
| C | 1.967467 | -1.980039 | -0.535368 |
| N | -3.377963 | -1.100560 | -0.117444 |
| C | -3.359073 | -2.332420 | 0.648088 |
| O | 1.252178 | 2.516364 | 1.018115 |

| | | | |
|---|-----------|-----------|-----------|
| H | -2.456095 | -2.502664 | 1.250873 |
| H | 3.500418 | 1.425606 | 0.529387 |
| H | 1.510679 | -2.919728 | -0.827871 |
| H | -3.466763 | -3.171335 | -0.048319 |
| H | 3.981525 | -2.611926 | -0.898029 |
| H | 4.995950 | -0.443035 | -0.211274 |
| H | -4.234516 | -2.348931 | 1.306764 |
| H | -1.144636 | -0.746322 | 1.663018 |
| O | -1.185327 | 2.676532 | -1.228495 |
| H | -1.108851 | 1.655118 | 1.501216 |

TSIIa-IIb

E = -894.694684549

Freq = -1180

| | | | |
|---|-----------|-----------|-----------|
| O | 0.261317 | 1.432828 | 0.389798 |
| C | -0.707950 | 0.732542 | -0.383353 |
| C | -0.733884 | -0.748133 | -0.099926 |
| C | 0.555571 | -1.393588 | -0.293319 |
| C | 1.695430 | -0.431477 | -0.265895 |
| C | 1.509832 | 0.907116 | 0.156489 |
| C | -2.098082 | -1.163416 | -0.431903 |
| O | -2.894573 | -0.033335 | -0.506162 |
| C | -2.163161 | 1.132548 | -0.223787 |
| C | 3.005357 | -0.895232 | -0.473295 |
| C | 4.097244 | -0.059102 | -0.286576 |
| C | 3.893447 | 1.256708 | 0.151890 |
| C | 2.608836 | 1.740258 | 0.378574 |
| N | -2.799589 | 2.181565 | 0.023910 |
| C | -2.115935 | 3.442120 | 0.266338 |
| O | 0.761646 | -2.625735 | -0.253142 |
| H | -1.025737 | 3.408227 | 0.169659 |
| H | 3.132350 | -1.932073 | -0.767792 |
| H | 2.434076 | 2.757669 | 0.713164 |
| H | -2.368627 | 3.785239 | 1.276210 |
| H | 4.744322 | 1.913056 | 0.312655 |
| H | 5.103680 | -0.426085 | -0.462891 |
| H | -2.517942 | 4.185961 | -0.430940 |
| H | -0.442717 | 0.897941 | -1.444576 |
| O | -2.604120 | -2.270705 | -0.489766 |
| H | -0.892852 | -1.564478 | 1.199127 |
| O | -0.993566 | -2.682219 | 1.626755 |
| H | -1.821345 | -2.937683 | 1.146456 |
| H | -0.273937 | -3.047463 | 1.010270 |

TSI-IIb

E = -818.303760609

Freq = -1212

| | | | |
|---|-----------|-----------|-----------|
| O | -0.035358 | -1.323318 | -0.093130 |
|---|-----------|-----------|-----------|

| | | | |
|---|-----------|-----------|-----------|
| C | -0.977782 | -0.502090 | 0.634132 |
| C | -0.642044 | 0.933696 | 0.543516 |
| C | 0.635514 | 1.436157 | 0.281451 |
| C | 1.690330 | 0.422358 | 0.184056 |
| C | 1.280625 | -0.920070 | -0.030043 |
| C | -1.694455 | 1.627126 | -0.037608 |
| O | -2.759277 | 0.841673 | -0.301190 |
| C | -2.393754 | -0.502303 | 0.007782 |
| C | 3.054871 | 0.739913 | 0.153265 |
| C | 4.008396 | -0.248434 | -0.059055 |
| C | 3.593324 | -1.568235 | -0.274163 |
| C | 2.241589 | -1.905219 | -0.268697 |
| N | -3.234856 | -1.395274 | -0.228512 |
| C | -2.924641 | -2.784320 | 0.064361 |
| O | 0.781531 | 2.669993 | -0.036670 |
| H | -1.948641 | -2.954430 | 0.536097 |
| H | 3.341521 | 1.777660 | 0.294084 |
| H | 1.911512 | -2.923806 | -0.444543 |
| H | -2.956650 | -3.348981 | -0.873930 |
| H | 4.331522 | -2.346498 | -0.447599 |
| H | 5.064618 | 0.001981 | -0.068525 |
| H | -3.715362 | -3.185300 | 0.707803 |
| H | -1.027404 | -0.907028 | 1.655649 |
| O | -1.626275 | 2.843266 | -0.408155 |
| H | -0.473929 | 3.028944 | -0.240285 |

TSI-IIb (H₂O)

E = --894.742274111

Freq = -942

| | | | |
|---|-----------|-----------|-----------|
| O | 0.432788 | -1.533541 | -0.280203 |
| C | -0.634005 | -0.925879 | 0.467451 |
| C | -0.782247 | 0.543177 | 0.204517 |
| C | 0.392614 | 1.328960 | 0.152333 |
| C | 1.647527 | 0.535862 | 0.132704 |
| C | 1.611640 | -0.847548 | -0.150576 |
| C | -2.123055 | 0.779461 | -0.157099 |
| O | -2.824711 | -0.392637 | -0.232682 |
| C | -1.993467 | -1.479191 | 0.052400 |
| C | 2.896322 | 1.169327 | 0.237105 |
| C | 4.075816 | 0.455007 | 0.071008 |
| C | 4.019079 | -0.911589 | -0.232538 |
| C | 2.794936 | -1.563217 | -0.349155 |
| N | -2.474559 | -2.632800 | -0.037822 |
| C | -1.661130 | -3.792782 | 0.284031 |
| O | 0.494845 | 2.592730 | 0.053230 |
| H | -0.670068 | -3.569629 | 0.697956 |
| H | 2.908066 | 2.236123 | 0.434017 |
| H | 2.732615 | -2.621778 | -0.579857 |
| H | -1.525289 | -4.386690 | -0.627134 |

| | | | |
|---|-----------|-----------|-----------|
| H | 4.937366 | -1.475365 | -0.373161 |
| H | 5.035243 | 0.954864 | 0.163436 |
| H | -2.217437 | -4.416329 | 0.992742 |
| H | -0.441996 | -1.152866 | 1.529567 |
| O | -2.790531 | 1.814616 | -0.424987 |
| H | -2.237417 | 2.891904 | -0.216423 |
| H | -1.809836 | 4.174300 | 0.902130 |
| O | -1.592627 | 3.854433 | 0.011167 |
| H | -0.611629 | 3.360736 | 0.056200 |

TSIIb-IIc

E = -894.711195991

Freq = -1090

| | | | |
|---|-----------|-----------|-----------|
| O | 0.210794 | -1.500903 | -0.059550 |
| C | -0.831828 | -0.699856 | 0.555836 |
| C | -0.749102 | 0.777715 | 0.270159 |
| C | 0.592484 | 1.352501 | 0.128503 |
| C | 1.713793 | 0.407128 | 0.075647 |
| C | 1.464412 | -0.974075 | -0.062735 |
| C | -1.825127 | 1.079019 | -0.689496 |
| O | -2.611380 | -0.040312 | -0.869522 |
| C | -2.145641 | -1.106759 | -0.111636 |
| C | 3.042949 | 0.868795 | 0.055704 |
| C | 4.097938 | -0.015435 | -0.106945 |
| C | 3.830869 | -1.384132 | -0.266186 |
| C | 2.527024 | -1.865975 | -0.248313 |
| N | -2.815084 | -2.168084 | -0.093004 |
| C | -2.356622 | -3.309826 | 0.676603 |
| O | 0.806155 | 2.590276 | 0.078325 |
| H | -1.454441 | -3.142347 | 1.280236 |
| H | 3.209051 | 1.936150 | 0.157675 |
| H | 2.307677 | -2.922264 | -0.363973 |
| H | -2.152639 | -4.134963 | -0.015441 |
| H | 4.652219 | -2.083221 | -0.398954 |
| H | 5.121159 | 0.346816 | -0.119140 |
| H | -3.170588 | -3.636698 | 1.333349 |
| H | -0.825566 | -0.949275 | 1.623830 |
| O | -2.139413 | 2.137950 | -1.200999 |
| H | -1.251429 | 1.969628 | 1.144262 |
| O | -1.335429 | 3.128595 | 1.199097 |
| H | -0.396751 | 3.224279 | 0.731507 |
| H | -1.945806 | 3.269032 | 0.436017 |

IIIa

E = -934.101259820

| | | | |
|---|-----------|-----------|-----------|
| C | 0.507421 | -0.596696 | -0.626767 |
| C | -0.807226 | -1.387660 | -0.487903 |
| C | -1.998620 | -0.582012 | -0.140956 |

| | | | |
|---|-----------|-----------|-----------|
| C | -1.883735 | 0.798407 | 0.098528 |
| C | 0.488478 | 0.622511 | 0.314028 |
| H | -3.334732 | -2.242705 | -0.296907 |
| C | -3.272000 | -1.175704 | -0.107426 |
| C | -3.019475 | 1.575375 | 0.345550 |
| C | -4.270123 | 0.966357 | 0.364684 |
| C | -4.402811 | -0.412826 | 0.144936 |
| H | -2.902034 | 2.638792 | 0.528026 |
| H | -5.151629 | 1.570746 | 0.560786 |
| H | -5.383975 | -0.876933 | 0.167814 |
| O | -0.675262 | 1.437184 | 0.081449 |
| O | -0.855152 | -2.586367 | -0.701053 |
| C | 1.703421 | -1.518100 | -0.401817 |
| O | 2.449347 | -1.896967 | -1.270799 |
| O | 1.776512 | -1.883328 | 0.892741 |
| C | 1.747950 | 1.486441 | 0.152260 |
| O | 2.850709 | 0.968733 | 0.293850 |
| N | 1.533698 | 2.791538 | -0.138145 |
| H | 0.574570 | 3.093870 | -0.232825 |
| C | 2.897464 | -2.718385 | 1.227045 |
| H | 2.871125 | -3.642439 | 0.644559 |
| H | 3.830555 | -2.186183 | 1.026045 |
| H | 2.796435 | -2.930604 | 2.291772 |
| H | 0.462894 | 0.269955 | 1.353048 |
| C | 2.618054 | 3.738945 | -0.325870 |
| H | 2.561454 | 4.551368 | 0.407728 |
| H | 3.555975 | 3.198703 | -0.191047 |
| H | 2.592551 | 4.168948 | -1.333688 |
| H | 0.568908 | -0.248241 | -1.665555 |

IIIb1

E = -934.103022

| | | | |
|---|-----------|-----------|-----------|
| C | 0.892952 | -0.630297 | 0.201439 |
| C | -0.086708 | -1.444287 | -0.305855 |
| C | -1.489084 | -1.079273 | -0.134623 |
| C | -1.792746 | -0.014516 | 0.735234 |
| C | 0.500818 | 0.708270 | 0.771238 |
| H | -2.291921 | -2.614133 | -1.397175 |
| C | -2.538346 | -1.793031 | -0.732580 |
| C | -3.119732 | 0.309520 | 1.020956 |
| C | -4.147696 | -0.410833 | 0.415527 |
| C | -3.861930 | -1.457808 | -0.468147 |
| H | -3.326769 | 1.119030 | 1.714195 |
| H | -5.179755 | -0.149798 | 0.633216 |
| H | -4.668403 | -2.011496 | -0.938968 |
| O | -0.813936 | 0.700035 | 1.371727 |
| O | 0.151318 | -2.604770 | -0.917341 |
| C | 2.279517 | -1.037204 | 0.093836 |
| O | 2.653501 | -2.063814 | -0.491193 |

| | | | |
|---|-----------|-----------|-----------|
| O | 3.144367 | -0.215820 | 0.713838 |
| C | 0.626228 | 1.840666 | -0.286176 |
| O | 1.514988 | 1.809261 | -1.126962 |
| N | -0.271263 | 2.850105 | -0.143015 |
| H | -0.971789 | 2.747006 | 0.577323 |
| C | 4.533047 | -0.561867 | 0.594885 |
| H | 4.723132 | -1.548753 | 1.024869 |
| H | 4.835797 | -0.562635 | -0.455092 |
| H | 5.070595 | 0.209042 | 1.147472 |
| H | 1.145773 | -2.696797 | -0.954058 |
| H | 1.172849 | 0.975317 | 1.591517 |
| C | -0.289727 | 4.013759 | -1.010055 |
| H | -0.150831 | 4.936561 | -0.434552 |
| H | 0.532705 | 3.906993 | -1.718934 |
| H | -1.233986 | 4.081197 | -1.563326 |

IIIb2

E = -934.092008

| | | | |
|---|-----------|-----------|-----------|
| C | 0.909243 | -0.582826 | 0.239924 |
| C | -0.047666 | -1.460989 | -0.336777 |
| C | -1.464346 | -1.105102 | -0.147327 |
| C | -1.798363 | -0.056300 | 0.728940 |
| C | 0.473588 | 0.740291 | 0.801896 |
| H | -2.207814 | -2.654206 | -1.415367 |
| C | -2.491676 | -1.843843 | -0.751690 |
| C | -3.137329 | 0.228632 | 1.011652 |
| C | -4.141598 | -0.515672 | 0.397967 |
| C | -3.824730 | -1.549676 | -0.492381 |
| H | -3.370175 | 1.026973 | 1.709889 |
| H | -5.181310 | -0.285321 | 0.614773 |
| H | -4.614803 | -2.122595 | -0.968254 |
| O | -0.851446 | 0.693654 | 1.375847 |
| O | 0.273691 | -2.531235 | -0.940644 |
| C | 2.249098 | -0.947905 | 0.143511 |
| O | 2.627793 | -2.038393 | -0.465804 |
| O | 3.186637 | -0.194466 | 0.703354 |
| C | 0.586256 | 1.884323 | -0.247217 |
| O | 1.524389 | 1.911880 | -1.032869 |
| N | -0.377791 | 2.836196 | -0.157200 |
| H | -1.107421 | 2.691176 | 0.525849 |
| C | 4.559779 | -0.579042 | 0.510885 |
| H | 4.746971 | -1.569662 | 0.932534 |
| H | 4.808603 | -0.579146 | -0.552896 |
| H | 5.140651 | 0.177824 | 1.037476 |
| H | 1.121214 | 1.032062 | 1.634823 |
| C | -0.415203 | 4.000856 | -1.022087 |
| H | -0.356830 | 4.927697 | -0.439121 |
| H | 0.447218 | 3.942363 | -1.687743 |
| H | -1.332237 | 4.018571 | -1.622763 |

| | | | |
|---|----------|-----------|-----------|
| H | 1.719639 | -2.467114 | -0.811644 |
|---|----------|-----------|-----------|

IIIc

E = -934.101423987

| | | | |
|---|-----------|-----------|-----------|
| C | -0.428949 | 0.803732 | 0.858824 |
| C | 1.075238 | 1.106305 | 1.010945 |
| C | 1.972254 | 0.099706 | 0.402811 |
| C | 1.453642 | -1.085649 | -0.153380 |
| C | -0.656114 | -0.711619 | 0.890084 |
| H | 3.728268 | 1.265676 | 0.756044 |
| C | 3.354291 | 0.345820 | 0.317290 |
| C | 2.299298 | -1.989693 | -0.806190 |
| C | 3.659717 | -1.716483 | -0.888845 |
| C | 4.197180 | -0.550810 | -0.321102 |
| H | 1.874648 | -2.895816 | -1.226112 |
| H | 4.312709 | -2.423253 | -1.393842 |
| H | 5.262451 | -0.352195 | -0.387286 |
| O | 0.132057 | -1.410391 | -0.085112 |
| O | 1.473699 | 2.115362 | 1.563528 |
| C | -0.976516 | 1.442996 | -0.418698 |
| O | -1.373871 | 0.831265 | -1.387047 |
| O | -0.957680 | 2.781167 | -0.323281 |
| C | -2.141849 | -1.065772 | 0.729556 |
| O | -2.958272 | -0.505831 | 1.453677 |
| N | -2.426318 | -2.028789 | -0.176087 |
| H | -1.681147 | -2.286302 | -0.808534 |
| C | -1.448444 | 3.492728 | -1.473984 |
| H | -0.850398 | 3.251476 | -2.356537 |
| H | -2.492364 | 3.231723 | -1.665389 |
| H | -1.354597 | 4.548758 | -1.221846 |
| H | -0.352569 | -1.073128 | 1.883775 |
| C | -3.793609 | -2.396369 | -0.499369 |
| H | -3.864852 | -3.476771 | -0.659072 |
| H | -4.426867 | -2.110737 | 0.341633 |
| H | -4.148253 | -1.877246 | -1.398766 |
| H | -0.947100 | 1.257413 | 1.706788 |

TSIIIb1-IIIb2 (H₂O)

E = -1010.50487910

Freq = -600

| | | | |
|---|-----------|-----------|-----------|
| C | 0.859371 | -0.487749 | -0.372132 |
| C | -0.050131 | -1.279320 | 0.381583 |
| C | -1.484438 | -1.056154 | 0.049525 |
| C | -1.874410 | -0.114268 | -0.920995 |
| C | 0.304998 | 0.813837 | -0.867868 |
| H | -2.157095 | -2.573747 | 1.388663 |
| C | -2.476516 | -1.852858 | 0.643421 |
| C | -3.210248 | -0.000644 | -1.314900 |
| C | -4.171981 | -0.810764 | -0.717848 |

| | | | |
|---|-----------|-----------|-----------|
| C | -3.809758 | -1.734785 | 0.270663 |
| H | -3.472960 | 0.726197 | -2.077706 |
| H | -5.211505 | -0.715371 | -1.020275 |
| H | -4.565241 | -2.360356 | 0.736784 |
| O | -0.973961 | 0.726252 | -1.522399 |
| O | 0.234697 | -2.152757 | 1.258017 |
| C | 2.256542 | -0.706855 | -0.494047 |
| O | 3.008241 | -1.365622 | 0.286981 |
| O | 2.825477 | -0.120647 | -1.570951 |
| C | 0.214610 | 1.798033 | 0.345736 |
| O | 0.938997 | 1.664552 | 1.339729 |
| N | -0.660154 | 2.812790 | 0.189579 |
| H | -1.246598 | 2.777010 | -0.633905 |
| C | 4.251979 | -0.229715 | -1.687146 |
| H | 4.550277 | -1.272498 | -1.820026 |
| H | 4.748190 | 0.172873 | -0.800106 |
| H | 4.511866 | 0.355390 | -2.570272 |
| H | 0.966493 | 1.269261 | -1.606721 |
| C | -0.897769 | 3.833866 | 1.196080 |
| H | -0.163064 | 3.695059 | 1.989790 |
| H | -1.905012 | 3.744972 | 1.619527 |
| H | -0.780774 | 4.834169 | 0.765384 |
| H | 1.685001 | 0.058288 | 2.221050 |
| O | 2.012429 | -0.855189 | 2.427357 |
| H | 1.210221 | -1.477595 | 2.158435 |
| H | 2.610738 | -1.131622 | 1.500027 |

TSIIIb1-IIIb2

E = -934.091979038

Freq = -337

| | | | |
|---|-----------|-----------|-----------|
| C | 0.907429 | -0.575942 | 0.243110 |
| C | -0.044334 | -1.453934 | -0.327049 |
| C | -1.461590 | -1.106862 | -0.146177 |
| C | -1.800516 | -0.055217 | 0.725338 |
| C | 0.470996 | 0.746543 | 0.804463 |
| H | -2.197895 | -2.662806 | -1.411291 |
| C | -2.484849 | -1.850776 | -0.751033 |
| C | -3.140873 | 0.227162 | 1.002821 |
| C | -4.141413 | -0.522170 | 0.388807 |
| C | -3.819417 | -1.558735 | -0.496535 |
| H | -3.378008 | 1.027438 | 1.697351 |
| H | -5.182336 | -0.293578 | 0.601538 |
| H | -4.606631 | -2.135401 | -0.972565 |
| O | -0.856942 | 0.698235 | 1.372954 |
| O | 0.286630 | -2.531317 | -0.926575 |
| C | 2.249532 | -0.951042 | 0.139840 |
| O | 2.607725 | -2.040697 | -0.468105 |
| O | 3.190206 | -0.198202 | 0.696029 |
| C | 0.587160 | 1.891367 | -0.243006 |

| | | | |
|---|-----------|-----------|-----------|
| O | 1.526886 | 1.918307 | -1.026754 |
| N | -0.376324 | 2.843965 | -0.154427 |
| H | -1.107302 | 2.699279 | 0.527267 |
| C | 4.560024 | -0.595264 | 0.504558 |
| H | 4.738225 | -1.586113 | 0.929530 |
| H | 4.807799 | -0.602320 | -0.559422 |
| H | 5.148048 | 0.158438 | 1.027764 |
| H | 1.655083 | -2.466201 | -0.807383 |
| H | 1.115141 | 1.037245 | 1.640559 |
| C | -0.410340 | 4.009793 | -1.017904 |
| H | -0.345619 | 4.935859 | -0.434325 |
| H | 0.449899 | 3.947723 | -1.686056 |
| H | -1.329042 | 4.032545 | -1.615789 |

TSIIIa-IIIb (H₂O)

E = -1010.47907208

Freq = -1105

| | | | |
|---|-----------|-----------|-----------|
| C | -1.050392 | -0.056172 | 0.148629 |
| C | -0.197948 | -1.023858 | 0.856400 |
| C | 1.175174 | -1.187734 | 0.335714 |
| C | 1.575451 | -0.538700 | -0.849209 |
| C | -0.283614 | 0.942201 | -0.679155 |
| H | 1.728367 | -2.587072 | 1.852748 |
| C | 2.059701 | -2.096843 | 0.943233 |
| C | 2.813845 | -0.831487 | -1.433178 |
| C | 3.665967 | -1.740680 | -0.816428 |
| C | 3.297807 | -2.371251 | 0.381400 |
| H | 3.088566 | -0.332358 | -2.357474 |
| H | 4.630302 | -1.956627 | -1.268835 |
| H | 3.972955 | -3.075226 | 0.858360 |
| O | 0.792749 | 0.381389 | -1.479059 |
| O | -0.572276 | -1.696370 | 1.844185 |
| C | -2.354543 | -0.521410 | -0.343738 |
| O | -3.203597 | -1.120302 | 0.326024 |
| O | -2.605985 | -0.175876 | -1.627882 |
| C | 0.256514 | 2.096330 | 0.206606 |
| O | -0.369342 | 2.464430 | 1.195768 |
| N | 1.392540 | 2.683929 | -0.243943 |
| H | 1.830853 | 2.275139 | -1.057089 |
| C | -3.920934 | -0.490877 | -2.113899 |
| H | -4.083722 | -1.571300 | -2.107922 |
| H | -4.686599 | -0.012625 | -1.497242 |
| H | -3.951645 | -0.104492 | -3.133301 |
| H | -1.662601 | -0.722909 | 2.560570 |
| H | -0.944895 | 1.399078 | -1.417205 |
| C | 2.019341 | 3.808276 | 0.426796 |
| H | 2.116081 | 4.664305 | -0.250983 |
| H | 1.382263 | 4.086902 | 1.267294 |
| H | 3.013980 | 3.541443 | 0.803335 |

| | | | |
|---|-----------|-----------|----------|
| H | -1.684219 | 0.457731 | 1.505560 |
| O | -2.269719 | 0.092550 | 2.445162 |
| H | -3.010323 | -0.342830 | 1.937166 |

TSIIIa-IIIb

E = -934.005190559

Freq = -1714

| | | | |
|---|-----------|-----------|-----------|
| C | -0.458990 | -0.638307 | 0.247563 |
| C | 0.746507 | -1.467078 | 0.201776 |
| C | 2.011602 | -0.688971 | 0.041084 |
| C | 1.986142 | 0.708882 | -0.088049 |
| C | -0.373511 | 0.692808 | -0.472119 |
| H | 3.241553 | -2.423711 | 0.158529 |
| C | 3.250076 | -1.343106 | 0.054471 |
| C | 3.171868 | 1.440810 | -0.185052 |
| C | 4.392056 | 0.769182 | -0.162767 |
| C | 4.436855 | -0.625767 | -0.048958 |
| H | 3.120117 | 2.520985 | -0.281606 |
| H | 5.314254 | 1.338722 | -0.242732 |
| H | 5.392214 | -1.142163 | -0.037019 |
| O | 0.809005 | 1.415672 | -0.093835 |
| O | 0.752687 | -2.693896 | 0.333944 |
| C | -1.721823 | -1.393274 | 0.189467 |
| O | -2.116493 | -1.632690 | 1.380379 |
| O | -2.324604 | -1.833671 | -0.868182 |
| C | -1.601688 | 1.556977 | -0.162205 |
| O | -2.717800 | 1.035241 | -0.149820 |
| N | -1.361309 | 2.869211 | 0.042598 |
| H | -0.390533 | 3.150579 | 0.074041 |
| C | -3.612596 | -2.472811 | -0.675744 |
| H | -3.494769 | -3.358197 | -0.048875 |
| H | -4.295089 | -1.759557 | -0.209586 |
| H | -3.949010 | -2.742446 | -1.675679 |
| H | -0.343670 | 0.568291 | -1.570858 |
| C | -2.407538 | 3.825661 | 0.356965 |
| H | -2.395455 | 4.661497 | -0.351323 |
| H | -3.364279 | 3.306915 | 0.284781 |
| H | -2.290156 | 4.220803 | 1.372920 |
| H | -1.152126 | -0.941470 | 1.630756 |

TSIIIb-IIIc (H₂O)

E = -1010.47663021

Freq = -812

| | | | |
|---|-----------|-----------|-----------|
| C | 0.284318 | 0.836615 | -0.383290 |
| C | -1.113428 | 1.276005 | -0.295894 |
| C | -2.125098 | 0.210342 | -0.135884 |
| C | -1.719977 | -1.115397 | 0.137316 |
| C | 0.386974 | -0.617411 | -0.775662 |
| H | -3.783344 | 1.552371 | -0.283922 |

| | | | |
|---|-----------|-----------|-----------|
| C | -3.494345 | 0.526127 | -0.081736 |
| C | -2.664039 | -2.083622 | 0.496563 |
| C | -4.011064 | -1.742023 | 0.547063 |
| C | -4.435072 | -0.438517 | 0.248111 |
| H | -2.325403 | -3.092397 | 0.710475 |
| H | -4.741719 | -2.501489 | 0.812687 |
| H | -5.490332 | -0.185713 | 0.285088 |
| O | -0.414846 | -1.493521 | 0.068799 |
| O | -1.475685 | 2.480729 | -0.323587 |
| C | 1.208986 | 1.376735 | 0.631519 |
| O | 1.450200 | 2.574842 | 0.827205 |
| O | 1.824648 | 0.424163 | 1.356382 |
| C | 1.820021 | -1.153608 | -0.878723 |
| O | 2.669059 | -0.502753 | -1.477962 |
| N | 2.016888 | -2.386273 | -0.349750 |
| H | 1.251975 | -2.790262 | 0.171971 |
| C | 2.875609 | 0.874224 | 2.228721 |
| H | 3.648839 | 1.394099 | 1.657790 |
| H | 2.477528 | 1.545479 | 2.993202 |
| H | 3.278226 | -0.031105 | 2.683946 |
| H | -0.346989 | 3.191799 | -1.102367 |
| H | -0.037426 | -0.723090 | -1.785746 |
| C | 3.308193 | -3.045952 | -0.372630 |
| H | 3.964496 | -2.464384 | -1.021773 |
| H | 3.752883 | -3.096208 | 0.629444 |
| H | 3.217503 | -4.063779 | -0.768205 |
| H | 0.654539 | 2.048675 | -1.424535 |
| O | 0.607510 | 3.161429 | -1.526574 |
| H | 1.147456 | 3.339681 | -0.696754 |

TSIIIb-IIIc

E = -933.999567239

Freq = -1760

| | | | |
|---|-----------|-----------|-----------|
| C | -0.375210 | -0.788291 | -0.550417 |
| C | 0.873979 | -1.473451 | -0.189128 |
| C | 2.070547 | -0.582494 | -0.103901 |
| C | 1.907456 | 0.795061 | 0.123340 |
| C | -0.309339 | 0.716134 | -0.697342 |
| H | 3.463907 | -2.192136 | -0.238068 |
| C | 3.363529 | -1.121027 | -0.091608 |
| C | 3.011272 | 1.616002 | 0.365572 |
| C | 4.288661 | 1.060136 | 0.359347 |
| C | 4.471242 | -0.308203 | 0.123137 |
| H | 2.853736 | 2.674453 | 0.548985 |
| H | 5.148621 | 1.700514 | 0.537226 |
| H | 5.470955 | -0.732619 | 0.120900 |
| O | 0.658195 | 1.363224 | 0.166470 |
| O | 0.957506 | -2.677551 | 0.063240 |
| C | -1.595778 | -1.477761 | -0.102364 |

| | | | |
|---|-----------|-----------|-----------|
| O | -1.947780 | -2.320695 | -0.992771 |
| O | -2.204225 | -1.346115 | 1.035705 |
| C | -1.672004 | 1.391190 | -0.493589 |
| O | -2.702387 | 0.825517 | -0.858870 |
| N | -1.623207 | 2.629319 | 0.045908 |
| H | -0.718908 | 2.948296 | 0.366783 |
| C | -3.450323 | -2.071003 | 1.202450 |
| H | -4.153079 | -1.752753 | 0.430000 |
| H | -3.264427 | -3.143966 | 1.132211 |
| H | -3.807481 | -1.799257 | 2.194674 |
| H | 0.009153 | 0.954882 | -1.724519 |
| C | -2.809457 | 3.425629 | 0.302062 |
| H | -2.732593 | 4.404758 | -0.183684 |
| H | -3.665351 | 2.888101 | -0.108139 |
| H | -2.961433 | 3.575636 | 1.377599 |
| H | -1.018576 | -1.777722 | -1.570869 |

Table S5. B3LYP/6-31G(d) optimized geometries of the species involved in the reaction mechanisms found for the reaction. Only the most relevant distances in angstroms are displayed.

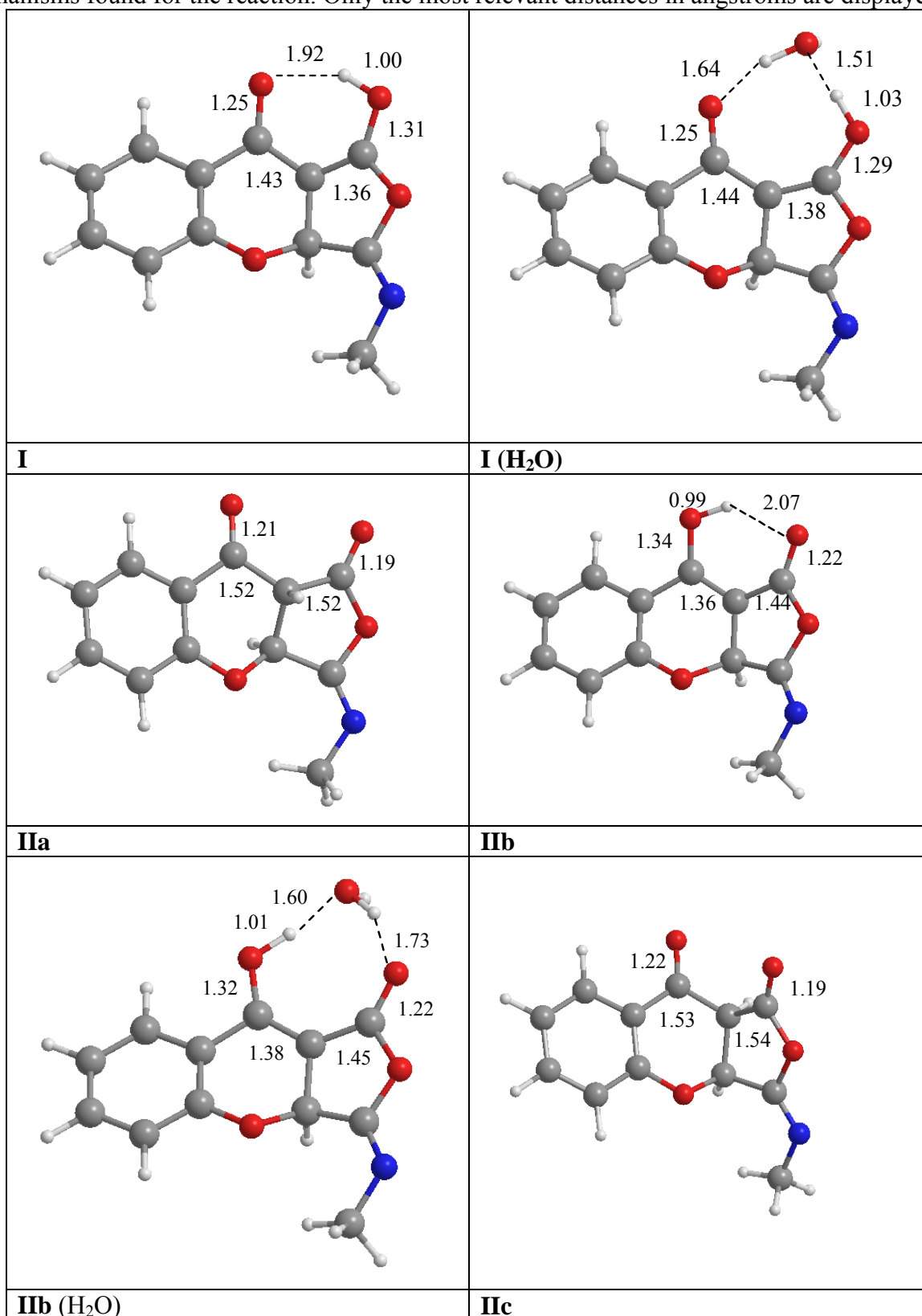


Table S3 (cont.)

| | |
|---|--|
| <p>Ball-and-stick model of transition state TSIIa-IIb. Bond lengths (Å): 1.25, 1.46, 1.46, 1.54, 1.20, 1.22.</p> | <p>Ball-and-stick model of transition state TSI-IIb. Bond lengths (Å): 1.28, 1.40, 1.39, 1.32, 1.18, 1.27.</p> |
| <p>TSIIa-IIb</p> | <p>TSI-IIb</p> |
| <p>Ball-and-stick model of transition state TSI-IIb (H₂O). Bond lengths (Å): 1.27, 1.41, 1.41, 1.23, 1.10, 1.18, 1.35.</p> | <p>Ball-and-stick model of transition state TSIIb-IIc. Bond lengths (Å): 1.26, 1.47, 1.47, 1.56, 1.16, 1.22.</p> |
| <p>TSI-IIb (H₂O)</p> | <p>TSIIb-IIc</p> |
| <p>Ball-and-stick model of product IIIa. Bond lengths (Å): 1.22, 1.54, 1.53, 1.21.</p> | <p>Ball-and-stick model of product IIIb1. Bond lengths (Å): 1.33, 1.37, 1.45, 1.00, 1.70, 1.24.</p> |
| <p>IIIa</p> | <p>IIIb1</p> |

Table S3 (cont.)

| | |
|--|-----------------------------|
| | |
| <p>IIIb2</p> | <p>IIIc</p> |
| | |
| <p>TSIIIb1-IIIb2 (H₂O)</p> | <p>TSIIIb1-IIIb2</p> |
| | |
| <p>TSIIIa-IIIb (H₂O)</p> | <p>TSIIIa-IIIb</p> |

Table S3 (cont.)

