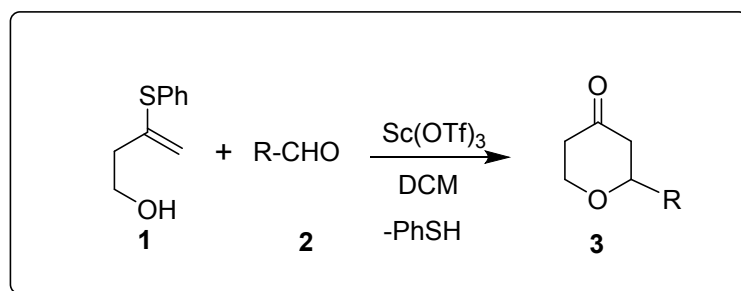


Supporting Information for

**A novel self-terminated Prins strategy for the synthesis of tetrahydropyran-4-one derivatives and their behavior in Fisher indole synthesis**

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## 1. Experimental Section

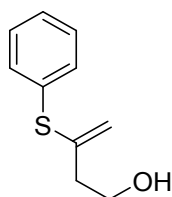
IR spectra were measured with a Thermo Nicolet Nexus 670 spectrometer.  $^1\text{H-NMR}$  spectra were measured with Bruker-400 and Bruker Avance 700 spectrometer. All signals are expressed as ppm downfield from tetramethylsilane used as an internal standard ( $\delta$  value).  $^{13}\text{C}$  NMR spectra were recorded on the instruments operating at 75 MHz or 125 MHz with  $\text{CDCl}_3$  as a solvent with internal standard ( $\delta$  77.0). Mass spectra were taken with Finnigan MAT1020B or JEOL. Column chromatography was performed using E. Merck 100-200, mesh silica gel.

### *Typical procedure*

To a mixture of (3-(phenylthio)but-3-en-1-ol (0.5 mmol) and aldehyde/ketone (0.6 mmol) in anhydrous DCM (5 mL) was added  $\text{Sc}(\text{OTf})_3$  (5 mol%) at 0 °C. The resulting mixture was allowed to stir at room temperature for the specified time. After completion of the reaction, the reaction mixture was quenched with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2x5 mL). The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The resulting crude product was purified by silica gel column chromatography (100-200 mesh) using ethyl acetate/hexane gradient mixture to afford the pure product **3**.

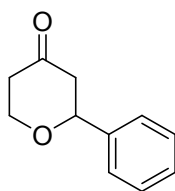
## 2. Characterization data of products

### 3-(Phenylthio)but-3-en-1-ol (1)



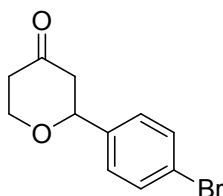
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.41-7.45 (m, 2H), 7.25-7.36 (m, 3H), 5.24 (s, 1H), 5.00 (s, 1H), 3.77 (t,  $J = 6.2$  Hz, 2H), 2.48 (t,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 142.1, 133.1, 132.4, 129.1, 127.9, 115.0, 60.7, 39.5; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3369, 2927, 1609, 1583, 1475, 1439, 1144, 1046, 846, 748, 691; ESI-HRMS calcd for  $\text{C}_{10}\text{H}_{13}\text{OS}$  ( $\text{M}+\text{H}$ ) $^+$  181.0682, found 181.0684.

**2-Phenyldihydro-2H-pyran-4(3H)-one (3a):**



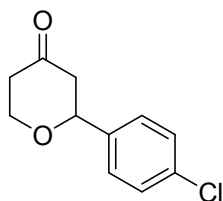
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.25-7.29 (m, 3H), 7.19-7.22 (m, 2H), 4.53 (dd,  $J = 8.5, 5.8$  Hz, 1H), 4.32 (ddd,  $J = 11.6, 7.5, 1.5$  Hz, 1H), 3.73 (td,  $J = 23.8, 2.9$  Hz, 1H), 2.57-2.65 (m, 1H), 2.52-2.55 (m, 2H), 2.32 (dt,  $J = 14.6, 1.4$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 206.2, 140.5, 128.6, 128.0, 125.5, 79.7, 66.6, 49.8, 42.1; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3419, 2974, 2930, 1721, 1453, 1350, 1254, 1156, 1144, 1057, 755, 699; ESI-HRMS calcd for:  $\text{C}_{11}\text{H}_{13}\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$  177.0910, found 177.0912.

**2-(4-Bromophenyl)tetrahydro-4H-pyran-4-one (3b):**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.51 (d,  $J = 8.5$  Hz, 2H), 7.25 (d,  $J = 8.5$  Hz, 2H), 4.61 (dd,  $J = 11.0, 3.0$  Hz, 1H), 4.43 (ddd,  $J = 11.6, 7.3, 1.4$  Hz, 1H), 3.84 (td,  $J = 23.9, 2.9$  Hz, 1H), 2.68-2.76 (m, 1H), 2.54-2.66 (m, 2H), 2.42-2.46 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 205.7, 139.6, 131.7, 127.2, 121.9, 79.0, 66.7, 49.8, 42.0; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3419, 2968, 2858, 1719, 1369, 1247, 1152, 1057, 1025, 756, 699; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{12}\text{BrO}_2$  ( $\text{M}+\text{H}$ ) $^+$  255.0015, found 255.0016.

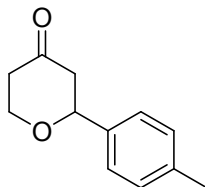
**2-(4-Chlorophenyl)tetrahydro-4H-pyran-4-one (3c):**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.22-7.41 (m, 4H), 4.62 (d,  $J = 7.9$  Hz, 1H), 4.43 (t,  $J = 8.4$  Hz, 1H), 3.83 (t,  $J = 11.3$  Hz, 1H), 2.35-2.82 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 205.7, 139.0, 133.7, 128.7, 126.9, 78.9, 66.6, 49.8, 42.0; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3418, 2863, 2822, 2856, 1719, 1461,

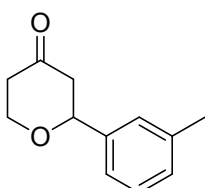
1367, 1367, 1245, 1165,1077, 1029, 778, 700; ESI-HRMS calcd for C<sub>11</sub>H<sub>11</sub>ClO<sub>2</sub> (M+H)<sup>+</sup> 211.0526, found 211.03338.

**2-(*p*-Tolyl)dihydro-2*H*-pyran-4(3*H*)-one (3d):**



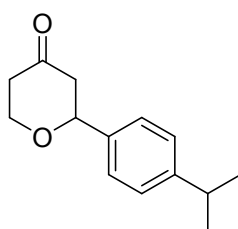
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ ppm): 7.24 (d, *J*=8.0 Hz, 2H), 7.19 (d, *J*=7.8, Hz, 2H), 4.16 (dd, *J*=9.1, 4.8 Hz, 1H), 4.42 (ddd, *J*=11.4, 7.3, 1.5 Hz, 1H), 3.83 (td, *J*=12.2, 2.8 Hz, 1H), 2.67-2.77 (m, 1H), 2.60-2.66 (m, 1H), 2.40-2.44 (m, 1H), 2.35 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ ppm): 206.4, 137.6, 129.2, 125.6, 79.7, 66.2, 49.9, 42.1, 21.0; IR (neat)  $\nu_{\max}$ /cm<sup>-1</sup>: 2963, 2922, 2856, 1717, 1367, 1245, 1077, 778, 700; ESI-HRMS calcd for C<sub>12</sub>H<sub>15</sub>O<sub>2</sub> (M+H)<sup>+</sup> 191.1072 found 191.1066.

**2-(*m*-Tolyl)tetrahydro-4*H*-pyran-4-one (3e):**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ ppm): 7.27 (t, *J*=5.5 Hz, 1H), 7.20 (s, 1H), 7.11-7.18 (m, 2H), 4.61 (dd, *J*=7.9, 6.2 Hz, 1H), 4.44 (ddd, *J*=11.5, 7.4, 1.3 Hz, 1H), 3.84 (td, *J*=11.7, 2.8 Hz, 1H), 2.59-2.80 (m, 3H), 2.39-2.47 (m, 1H), 2.37 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ ppm): 206.4, 140.5, 138.4, 128.9, 128.6, 126.3, 122.7, 79.9, 66.8, 49.9, 42.2, 21.4; IR (neat)  $\nu_{\max}$ /cm<sup>-1</sup>: 3418, 2922, 2856, 1719, 1607, 1367, 1245, 1165, 1077, 778, 700; ESI-HRMS calcd for C<sub>12</sub>H<sub>15</sub>O<sub>2</sub> (M+H)<sup>+</sup> 191.1067 found 191.1068.

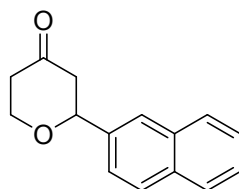
**2-(4-Isopropylphenyl)dihydro-2*H*-pyran-4(3*H*)-one (3f):**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ ppm): 7.29, (d, *J*=8.1 Hz, 2H), 7.24, (d, *J*=8.1 Hz, 2H), 4.61 (dd, *J*=9.9, 4.0 Hz, 1H), 4.41 (dd, *J*=11.4, 7.3 Hz, 1H), 3.79-3.86 (m, 1H), 2.91 (sep, *J*=6.9 Hz, 1H),

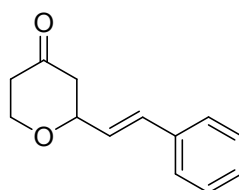
2.61-2.75 (m, 3H), 2.42 (d,  $J = 14.6$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 206.4, 148.9, 137.8, 126.6, 125.7, 79.7, 66.6, 49.7, 42.1, 33.8, 29.6, 23.8; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3420, 2961, 2926, 2857, 1720, 1463, 1367, 1248, 1152, 1024, 829. ESI-HRMS calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$  219.1380, found 219.1381.

**2-(Naphthalen-2-yl)dihydro-2H-pyran-4(3H)-one (3g):**



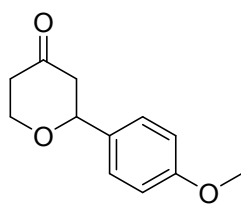
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 8.02 (d,  $J = 8.4$  Hz, 1H), 7.89 (dd,  $J = 7.9, 1.5$  Hz, 1H), 7.83 (d,  $J = 8.2$  Hz, 1H), 7.66 (d,  $J = 7.2$  Hz, 1H), 7.55 (dd,  $J = 8.2, 1.5$  Hz, 1H), 7.50 (d,  $J = 7.2$  Hz, 1H), 5.40 (dd,  $J = 10.2, 3.8$  Hz, 1H), 4.50 (ddd,  $J = 11.7, 7.3, 2.0$  Hz, 1H), 4.00 (td,  $J = 23.5, 3.0$  Hz, 1H), 2.78-2.90 (m, 3H), 2.51-2.56 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 206.6, 135.9, 133.7, 129.9, 128.9, 128.7, 126.3, 125.7, 125.4, 123.1, 122.8, 76.9, 66.7, 49.1, 42.3; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3398, 2891, 1701, 1594, 1255, 1063, 1008, 793, 773. ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$  227.1066, found 227.1070.

**(E)-2-Styryldihydro-2H-pyran-4(3H)-one (3h):**



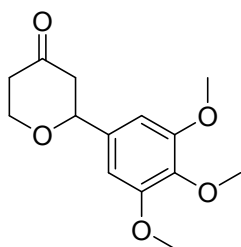
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.39 (dd,  $J = 8.7, 1.5$  Hz, 2H), 7.33 (t,  $J = 7.5$  Hz, 2H), 7.24-7.28 (m, 1H), 6.65 (d,  $J = 16.0$  Hz, 1H), 6.23 (dd,  $J = 16.0, 5.9$  Hz, 1H), 4.37 (ddd,  $J = 11.4, 7.2, 1.7$  Hz, 1H), 4.29-4.34 (m, 1H), 3.79 (td,  $J = 23.6, 3.0$  Hz, 1H), 2.62-2.69 (m, 1H), 2.50-2.59 (m, 2H), 2.37-2.43 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 206.1, 136.0, 131.6, 128.5, 127.9, 126.5, 78.1, 66.3, 48.1, 42.1; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3420, 3026, 2962, 2921, 2852, 1718, 1366, 1246, 1079, 749. ESI-HRMS calcd for:  $\text{C}_{13}\text{H}_{13}\text{O}_2$  ( $\text{M}-\text{H}$ ) $^+$  201.0908 found 201.0910.

**2-(4-Methoxyphenyl)dihydro-2H-pyran-4(3H)-one (3i)**



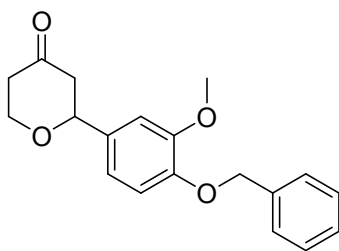
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.25-7.34 (m, 2H), 6.91 (d,  $J = 9.0$  Hz, 2H), 4.60 (dd,  $J = 9.8, 4.5$  Hz, 1H), 4.35-4.45 (m, 1H), 3.77-3.88 (m, 4H), 2.60-2.79 (m, 3H), 2.38-2.47 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 206.5, 159.4, 137.0, 132.7, 127.0, 114.0, 79.5, 66.7, 55.3, 49.9, 42.1. IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2984, 2881, 1740, 1594, 1378, 1255, 773; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{15}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  207.1021, found 207.1013.

**2-(3,4,5-Trimethoxyphenyl)dihydro-2H-pyran-4(3H)-one (3j):**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.60 (s, 2H), 4.59 (t,  $J = 7.0$  Hz, 1H), 4.44 (dd,  $J = 11.6, 7.5$  Hz, 1H), 3.88 (s, 6H), 3.84 (s, 3H), 3.84 (td,  $J = 23.8, 2.9$  Hz, 1H), 2.70-2.77 (m, 1H), 2.65 (d,  $J = 7.3$  Hz, 1H), 2.44 (d,  $J = 14.6$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 206.1, 153.4, 137.7, 136.1, 102.6, 79.9, 66.7, 60.8, 56.1, 50.0, 42.0. IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3389, 2947, 2857, 1714, 1524, 1460, 1369, 1234, 1129, 1061, 708. ESI-HRMS calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_5$  ( $\text{M}+\text{H}$ ) $^+$  267.1227, found 267.1228.

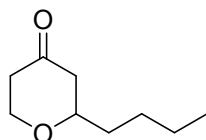
**2-(4-(Benzyloxy)-3-methoxyphenyl)dihydro-2H-pyran-4(3H)-one (3k):**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.25-7.47 (m, 5H), 6.96 (s, 1H), 6.83 (dd,  $J = 18.1, 8.3$  Hz, 2H), 5.15 (s, 2H), 4.57 (dd,  $J = 9.0, 5.3$  Hz, 1H), 4.40 (dd,  $J = 11.3, 7.5$  Hz, 1H), 3.91 (s, 3H), 3.81 (td,  $J = 24.2, 2.3$  Hz, 1H), 2.59-2.77 (m, 3H), 2.41 (d,  $J = 14.3$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 206.4, 149.8, 148.0, 137.0, 133.7, 128.5, 127.8, 127.2, 118.0, 114.0, 109.5, 79.6, 71.0, 66.3,

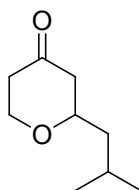
56.0, 49.9, 42.1; IR (neat)  $\nu_{\max}/\text{cm}^{-1}$ : 3420, 2961, 2926, 2857, 1720, 1463, 1367, 1248, 1152, 1086, 1024, 829. ESI-HRMS calcd for  $\text{C}_{19}\text{H}_{21}\text{O}_4$  ( $\text{M}+\text{H}$ )<sup>+</sup> 313.1434, found 313.1435.

### 2-Butyltetrahydro-4H-pyran-4-one (3l)



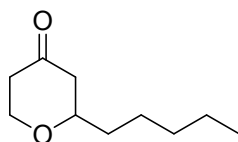
<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 4.29 (dd,  $J = 11.4, 7.3$  Hz, 1H), 3.65 (td,  $J = 11.6, 2.9$  Hz, 1H), 3.54-3.60(m, 1H), 2.54-2.64 (m, 1H), 2.40 (d,  $J = 14.3$  Hz, 1H), 2.25-2.35 (m, 2H), 1.61-1.72 (m, 1H), 1.29-1.58 (m, 6H), 0.91 (t,  $J = 7.2$  Hz, 3H); <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 207.3, 78.0, 66.4, 48.3, 42.2, 36.0, 27.2, 22.5, 13.9; IR (neat)  $\nu_{\max}/\text{cm}^{-1}$ : 3444, 2956, 2926, 1716, 1584, 1464, 1361, 1150, 739, 691; ESI-HRMS calcd for  $\text{C}_9\text{H}_{15}\text{O}_2$  ( $\text{M}-\text{H}$ )<sup>+</sup> 155.1066, found 155.1065.

### 2-Isobutyldihydro-2H-pyran-4(3H)-one (3m)



<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 4.29 (ddd,  $J = 11.5, 7.5, 1.3$  Hz, 1H), 3.59-3.72 (m, 2H), 2.52-2.66(m, 1H), 2.16-2.43 (m, 3H), 1.73-1.90 (m, 1H), 1.57-1.70 (m, 1H), 1.20-1.35 (m, 1H), 0.92 (dd,  $J = 6.6, 5.8$  Hz, 6H); <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 207.1, 76.3, 66.5, 48.8, 45.4, 42.2, 24.2, 23.0, 22.1; IR (neat)  $\nu_{\max}/\text{cm}^{-1}$ : 3425, 2958, 2928, 2868, 1721, 1468, 1376, 1250, 1161, 1087, 769; ESI HRMS calcd for  $\text{C}_9\text{H}_{17}\text{O}_2$  ( $\text{M}-\text{H}$ )<sup>+</sup> 157.1224, found 157.12234.

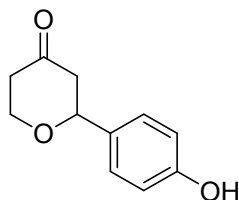
### 2-Pentyldihydro-2H-pyran-4(3H)-one (3n):



<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 4.26 (ddd,  $J = 11.6, 7.5, 1.4$  Hz, 1H), 3.63 (td,  $J = 23.8, 2.9$  Hz, 1H), 3.52-3.57 (m, 1H), 2.52-2.60 (m, 1H), 2.37 (dt,  $J = 14.3, 2.4$  Hz, 1H), 2.23-2.32 (m, 2H), 1.60-1.67 (m, 1H), 1.38-1.52 (m, 2H), 1.22-1.35 (m, 6H), 0.87 (t,  $J = 7.0$  Hz, 3H); <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 207.1, 78.1, 66.4, 48.3, 42.2, 36.2, 31.6, 24.7, 22.4, 13.9; IR (neat)  $\nu_{\max}/\text{cm}^{-1}$ : 3422,

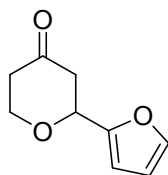
2929, 2857, 1718, 1463, 1378, 1219, 1087, 770. ESI-HRMS calcd for C<sub>10</sub>H<sub>19</sub>O<sub>2</sub> (M+H)<sup>+</sup> 171.1379, found 171.1382.

**2-(4-hydroxyphenyl)dihydro-2H-pyran-4(3H)-one (3o):**



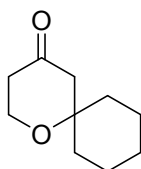
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ ppm): 7.24 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.48 (br s, 1H, -OH), 4.59 (dd, *J* = 9.6, 4.3 Hz, 1H), 4.40 (dd, *J* = 11.5, 7.4 Hz, 1H), 3.83 (td, *J* = 23.8, 3.0 Hz, 1H), 2.58-2.78 (m, 3H), 2.43 (dt, *J* = 14.5, 1.1 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ ppm): 207.0, 155.7, 132.5, 127.3, 115.4, 79.5, 66.5, 49.7, 42.1; IR (neat) ν<sub>max</sub>/cm<sup>-1</sup>: 3241, 2925, 2855, 1698, 1517, 1460, 1367, 1263, 1150, 823. ESI-HRMS calcd for C<sub>11</sub>H<sub>13</sub>O<sub>3</sub> (M+H)<sup>+</sup> 193.0859, found 193.0862.

**2-(Furan-2-yl)dihydro-2H-pyran-4(3H)-one (3p):**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ ppm): 7.43 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.36 (dd, *J* = 3.2, 1.7 Hz, 1H), 6.33 (dt, *J* = 3.4, 0.7 Hz, 1H), 4.82 (dd, *J* = 10.0, 3.8 Hz, 1H), 4.19-4.27 (m, 1H), 3.81-3.90 (m, 1H), 2.88 (ddd, *J* = 14.7, 9.8, 1.1 Hz, 1H), 2.59-2.73 (m, 2H), 2.42-2.50 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ ppm): 205.5, 152.1, 142.9, 110.2, 108.2, 72.2, 65.5, 45.3, 42.0; IR (neat) ν<sub>max</sub>/cm<sup>-1</sup>: 3121, 2925, 2854, 1725, 1462, 1261, 1078, 1018, 800. ESI-HRMS calcd for: C<sub>9</sub>H<sub>11</sub>O<sub>3</sub> (M+H)<sup>+</sup> 167.0703, found 167.0705

**1-Oxaspiro[5.5]undecan-4-one (3q):**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ ppm): 3.92-3.98 (m, 2H), 2.37-2.42 (m, 2H), 2.30 (s, 2H), 1.68-1.77 (m, 2H), 1.48-1.62 (m, 3H), 1.16-1.45 (m, 5H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ ppm): 207.6, 76.6,

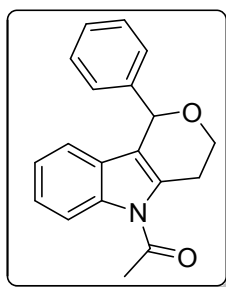


59.8, 52.9, 41.7, 35.0, 25.2, 21.1; IR (neat)  $\nu_{\max}/\text{cm}^{-1}$ : 3419, 2931, 2858, 1718, 1446, 1374, 13.8, 1263, 1075, 962, 746; ESI HRMS calcd for  $\text{C}_{10}\text{H}_{17}\text{O}_2$  (M-H)<sup>+</sup> 169.1223, found 167.10661

### Experimental procedure for the Fischer indole product

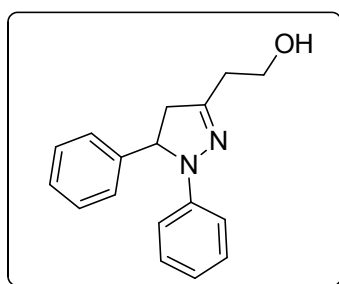
Phenylhydrazine hydrochloride (0.25 g, 1.62 mmol) and 2-substituted tetrahydropyran-4-one (, 0.14g, 1.62 mmol) were added to glacial acetic acid (2 g, 0.03 mol) and the mixture was refluxed for 6h with stirring. The mixture was then cooled and neutralized with 1 M NaOH, then diluted with water (100 mL) and extracted with  $\text{CHCl}_3$  (3 × 100 mL). Following the drying of the organic layer over  $\text{Na}_2\text{SO}_4$ , the solvent was removed under vacuum and the residue was passed through a short plug of silica gel to afford the pure product.

### 1-(1-Phenyl-3,4-dihydropyrano[4,3-b]indol-5(1*H*)-yl)ethanone 7a (major):



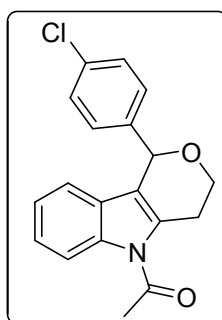
<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.24-7.37 (m, 7H), 7.13-7.16 (m, 2H), 6.38 (s, 1H), 4.42 (t,  $J$  = 6.8 Hz, 2H), 3.07 (t,  $J$  = 7.0 Hz, 2H), 2.09 (s, 3H); <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 171.1, 149.8, 143.8, 139.9, 130.5, 128.6, 128.4, 128.1, 127.2, 125.1, 107.0, 63.7, 29.6, 27.8. ppm; IR (neat)  $\nu_{\max}/\text{cm}^{-1}$ : 3449, 3059, 2925, 2854, 1738, 1597, 1502, 1239, 1035, 764, 696; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{17}\text{NO}_2$ : 291.1259 found : 291.1141.

### 2-(1,5-Diphenyl-4,5-dihydro-1*H*-pyrazol-3-yl)ethanol 8a (minor):



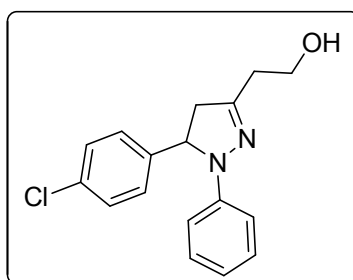
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.23-7.36 (m, 5H), 7.14 (t,  $J = 7.1$  Hz, 2H), 6.91 (d,  $J = 7.9$  Hz, 2H), 6.76 (t,  $J = 7.3$  Hz, 1H), 5.01 (dd,  $J = 11.5, 8.5$  Hz, 1H), 3.99 (t,  $J = 5.6$  Hz, 2H), 3.45 (dd,  $J = 17.5, 12.0$  Hz, 1H), 2.77 (dd,  $J = 17.5, 8.2$  Hz, 1H), 2.57 (t,  $J = 5.4$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 150.4, 145.7, 142.6, 129.0, 128.9, 127.5, 125.9, 118.9, 113.1, 64.2, 59.7, 47.1, 32.8 ppm; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3386, 2925, 1598, 1499, 1050, 751, 697; HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{19}\text{ON}_2 = 267.1491$ . found : 267.1483.

**1-(1-Phenyl-3,4-dihydropyrano[4,3-b]indol-5(1H)-yl)ethanone 7c (major):**



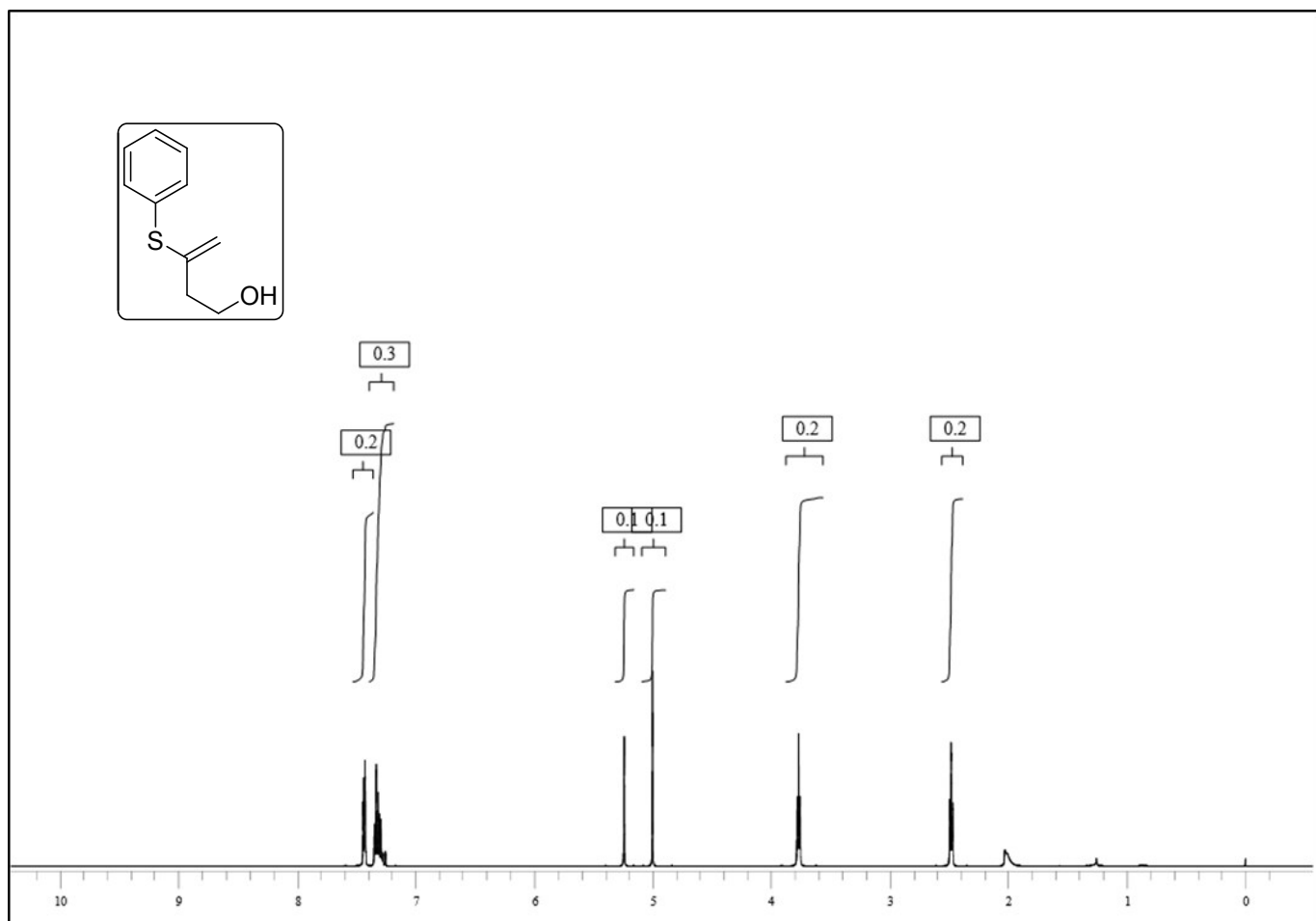
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.25-7.35 (m, 7H), 7.22 (dd,  $J = 5.4, 2.1$  Hz, 1H), 6.38 (s, 1H), 4.43 (t,  $J = 7.0$  Hz, 2H), 3.08 (t,  $J = 7.0$  Hz, 2H), 2.09 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 171.1, 149.9, 142.5, 139.7, 134.2, 129.8, 129.0, 128.7, 127.5, 125.1, 107.1, 63.6, 27.8, 21.1 ppm; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3420, 2907, 1702, 1597, 1500, 1323, 1163, 1091, 1063, 820, 743, 691  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{15}\text{ClNO}_2$ : 324.0797 found : 324.1431.

**2-(1,5-Diphenyl-4,5-dihydro-1H-pyrazol-3-yl)ethanol 8c (minor):**

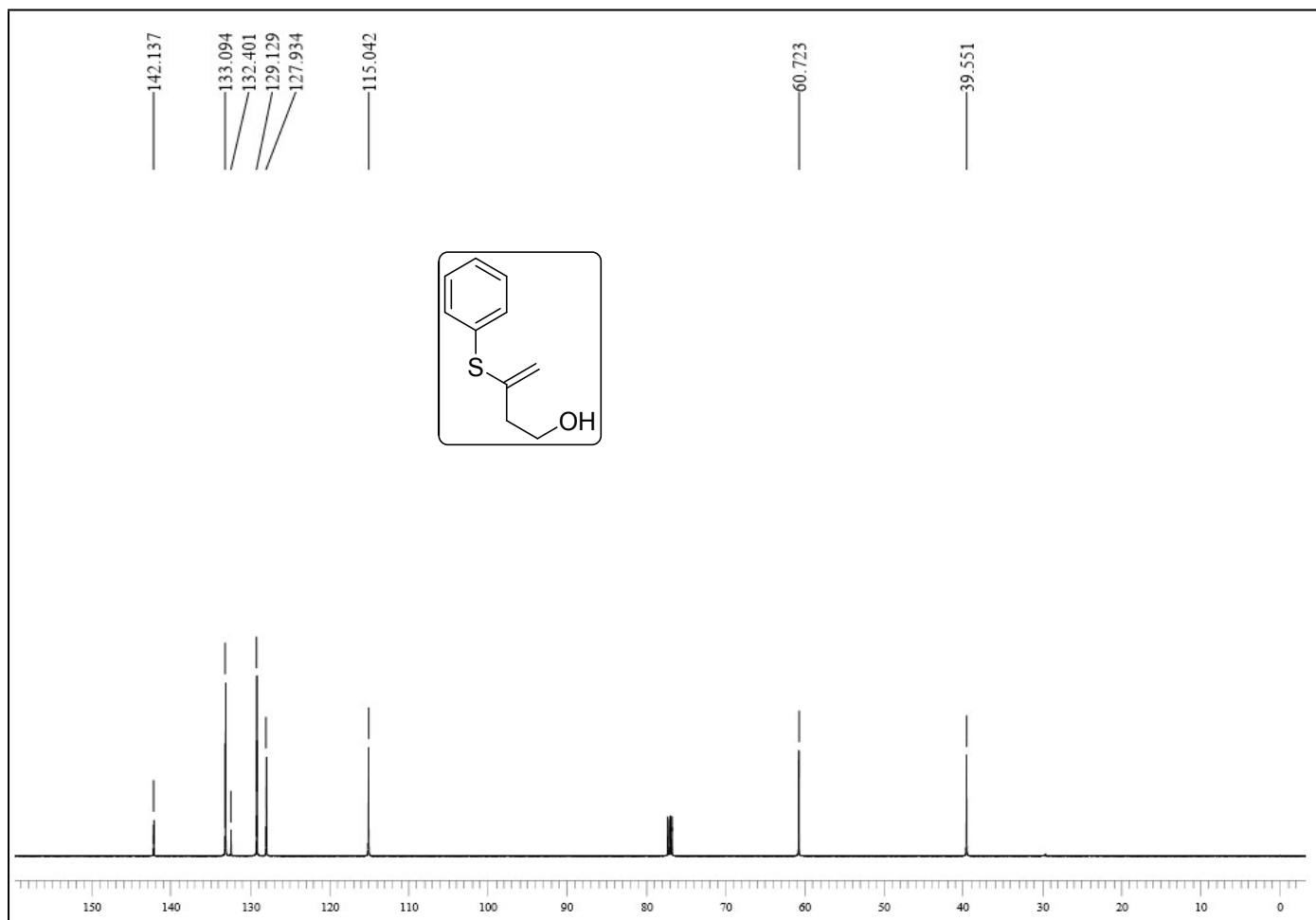


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.31 (d,  $J = 8.5$  Hz, 2H), 7.24 (d,  $J = 8.5$  Hz, 2H), 7.15 (td, d,  $J = 14.3, 1.9$  Hz, 2H), 6.88 (dd,  $J = 8.8, 1.0$  Hz, 2H), 6.78 (t,  $J = 7.3$  Hz, 1H), 4.99 (dd,  $J = 11.9, 8.2$  Hz, 1H), 3.99 (dd,  $J = 10.6, 5.3$  Hz, 2H), 3.46 (dd,  $J = 17.5, 12.0$  Hz, 1H), 2.74 (dd,  $J = 17.5, 8.2$  Hz, 1H), 2.58 (t,  $J = 5.4$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 150.4, 145.5, 141.1, 133.2, 129.2, 128.9, 127.3, 119.3, 113.9, 63.6, 59.7, 47.0, 32.8 ppm; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3450, 2927, 1602, 1462, 1429, 1366, 1153, 1034, 789. HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{18}\text{ON}_2\text{Cl} = 301.1108$  found : 301.1101.

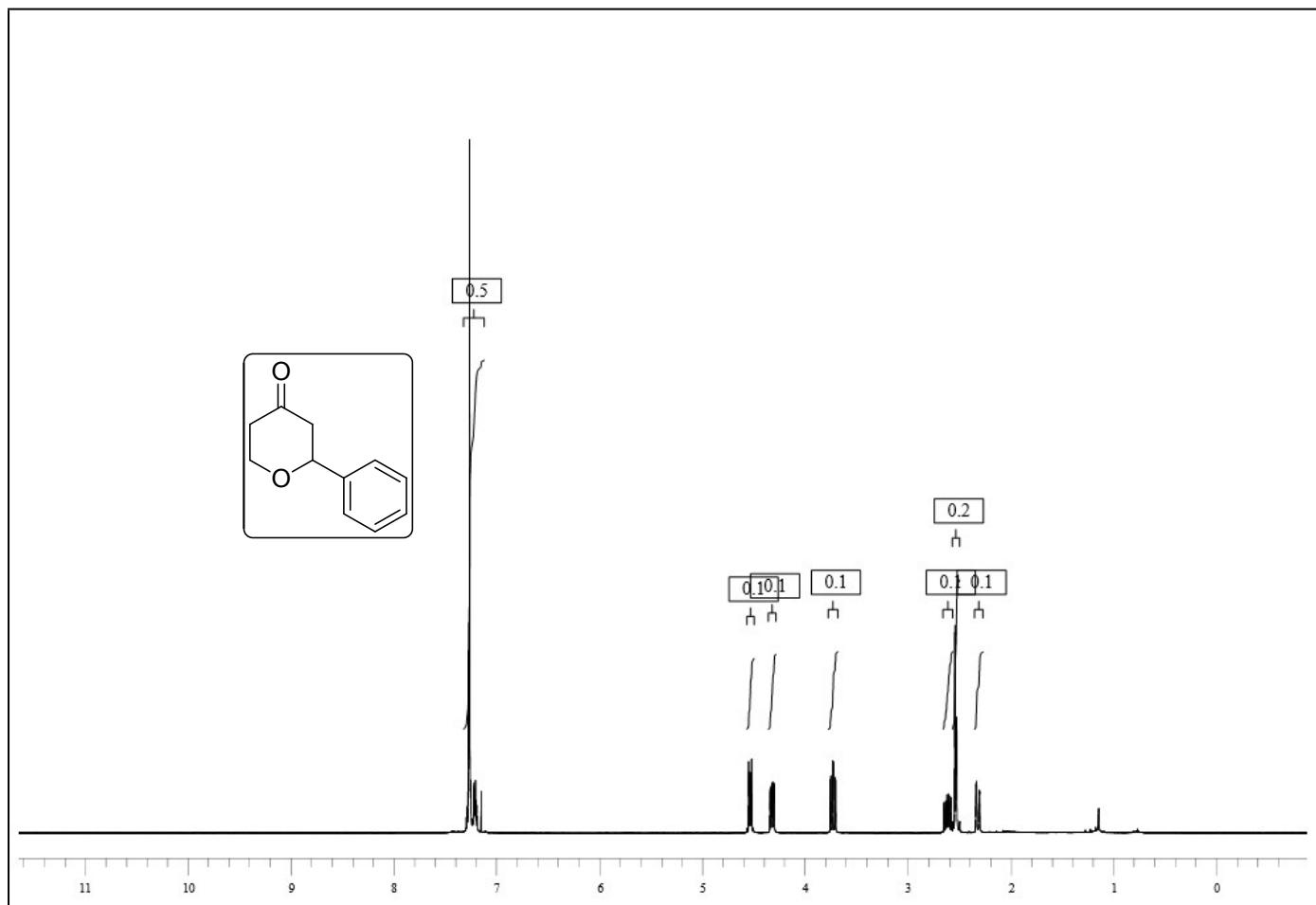
### 3. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products



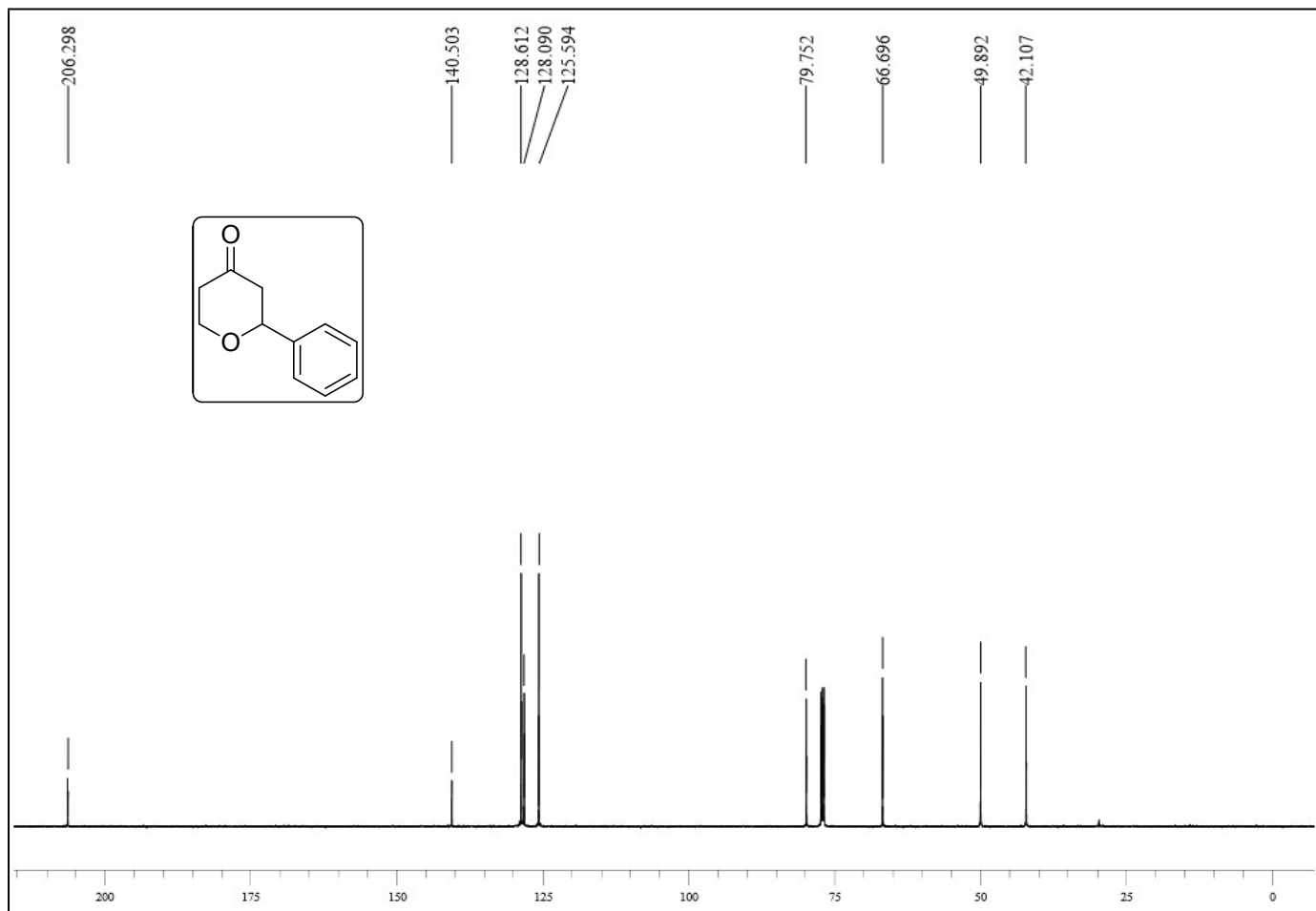
$^1\text{H}$  NMR spectrum of compound **1**



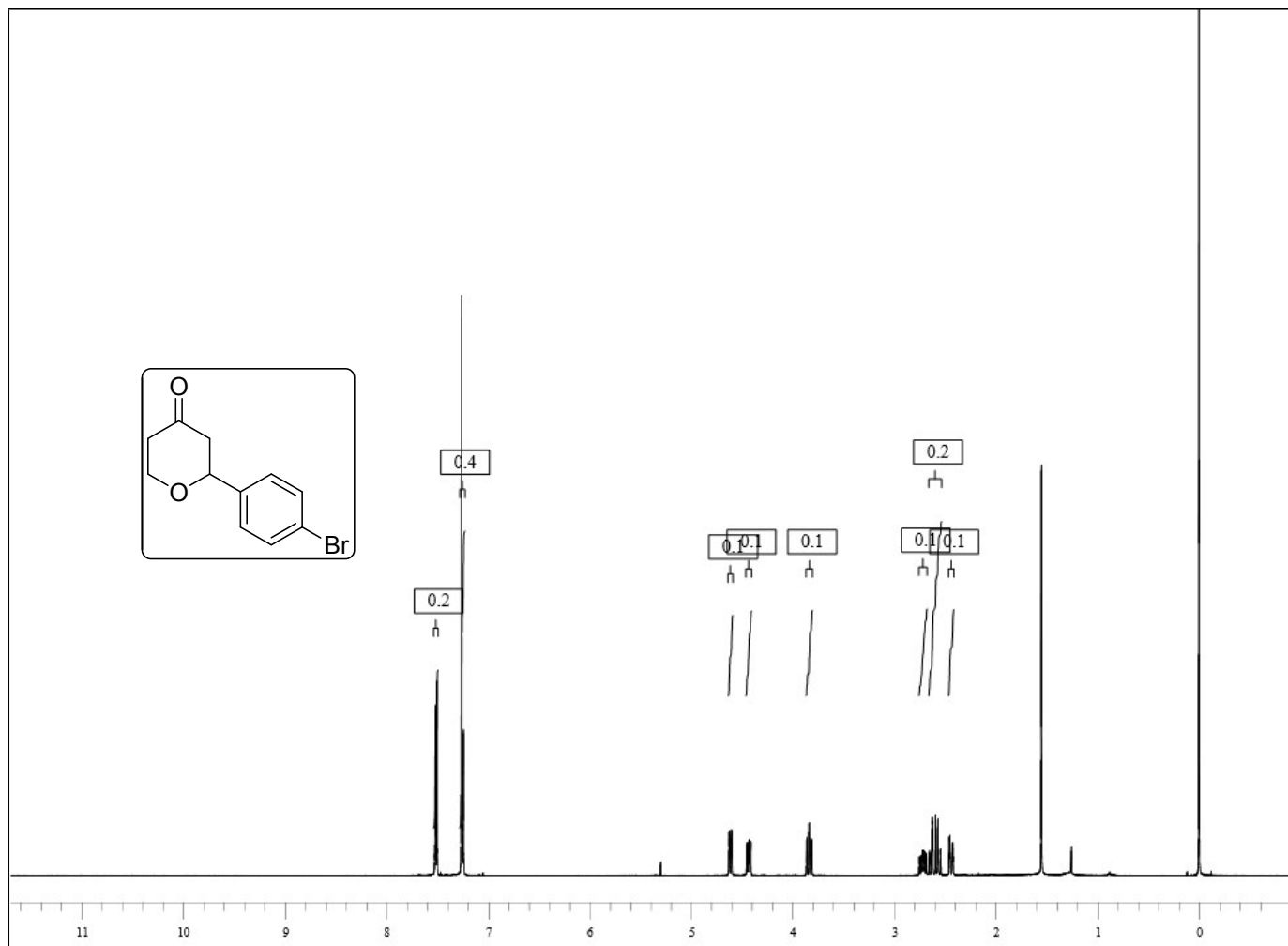
<sup>13</sup>C NMR spectrum of compound **1**



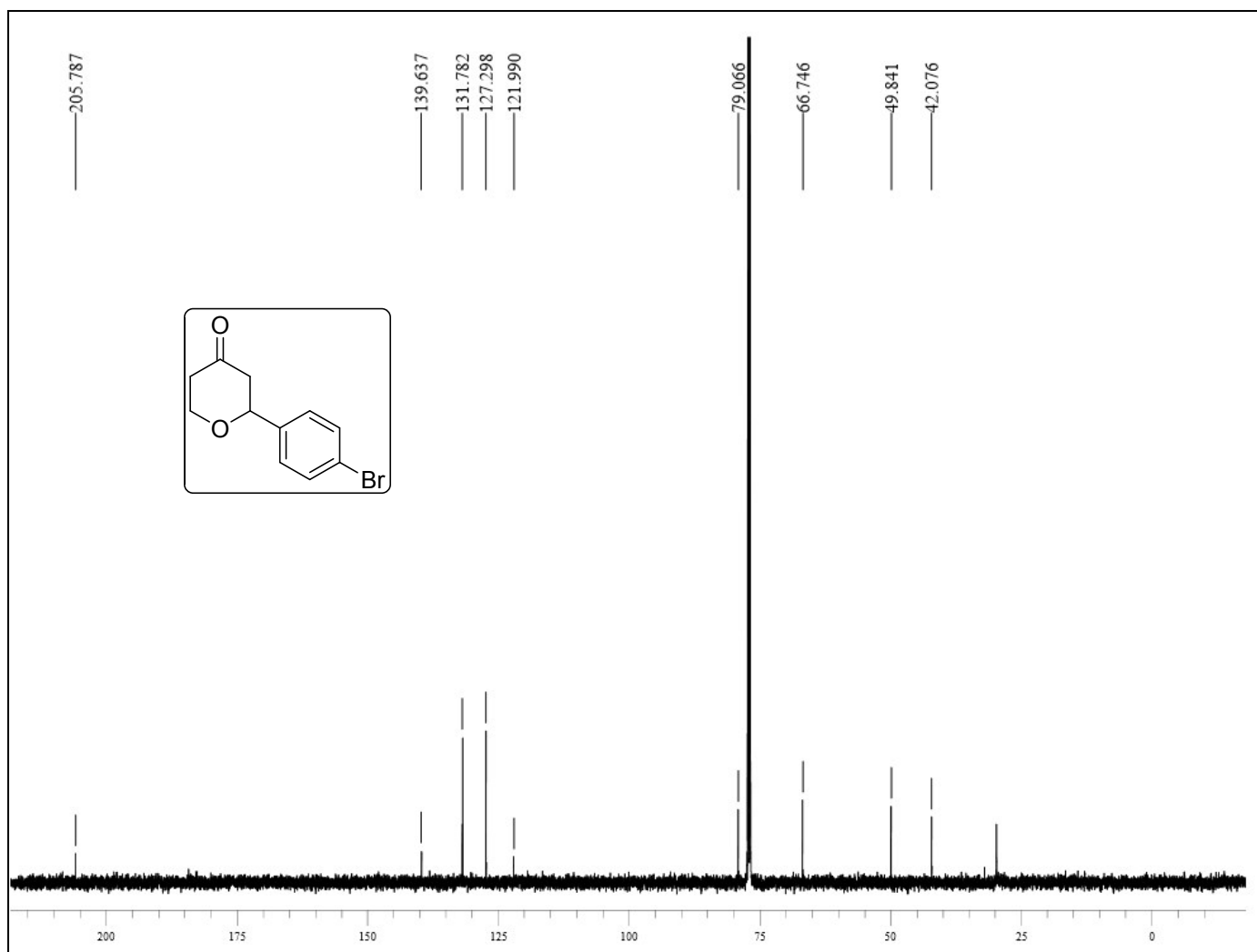
$^1\text{H}$  NMR spectrum of compound **3a**



$^{13}\text{C}$  NMR spectrum of compound **3a**

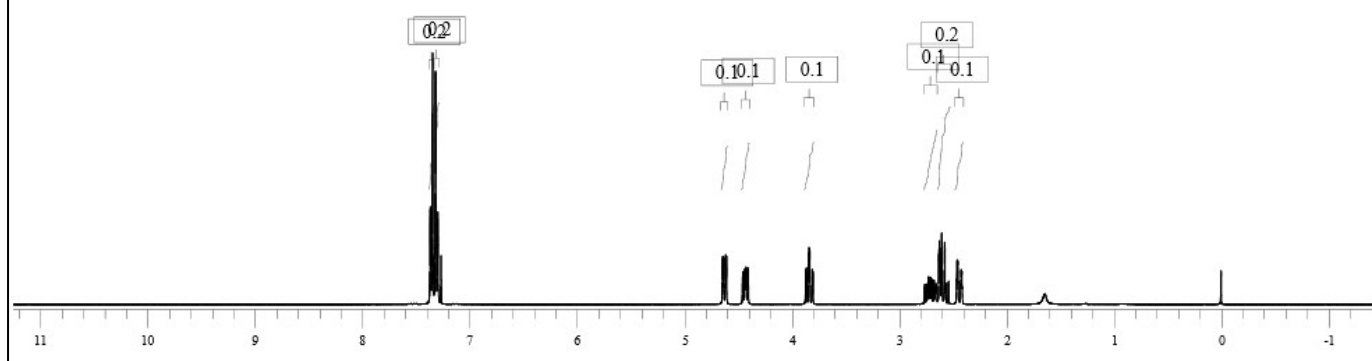
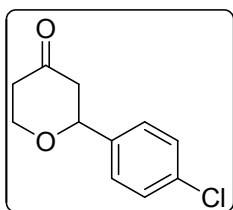


$^1\text{H}$  NMR spectrum of compound **3b**

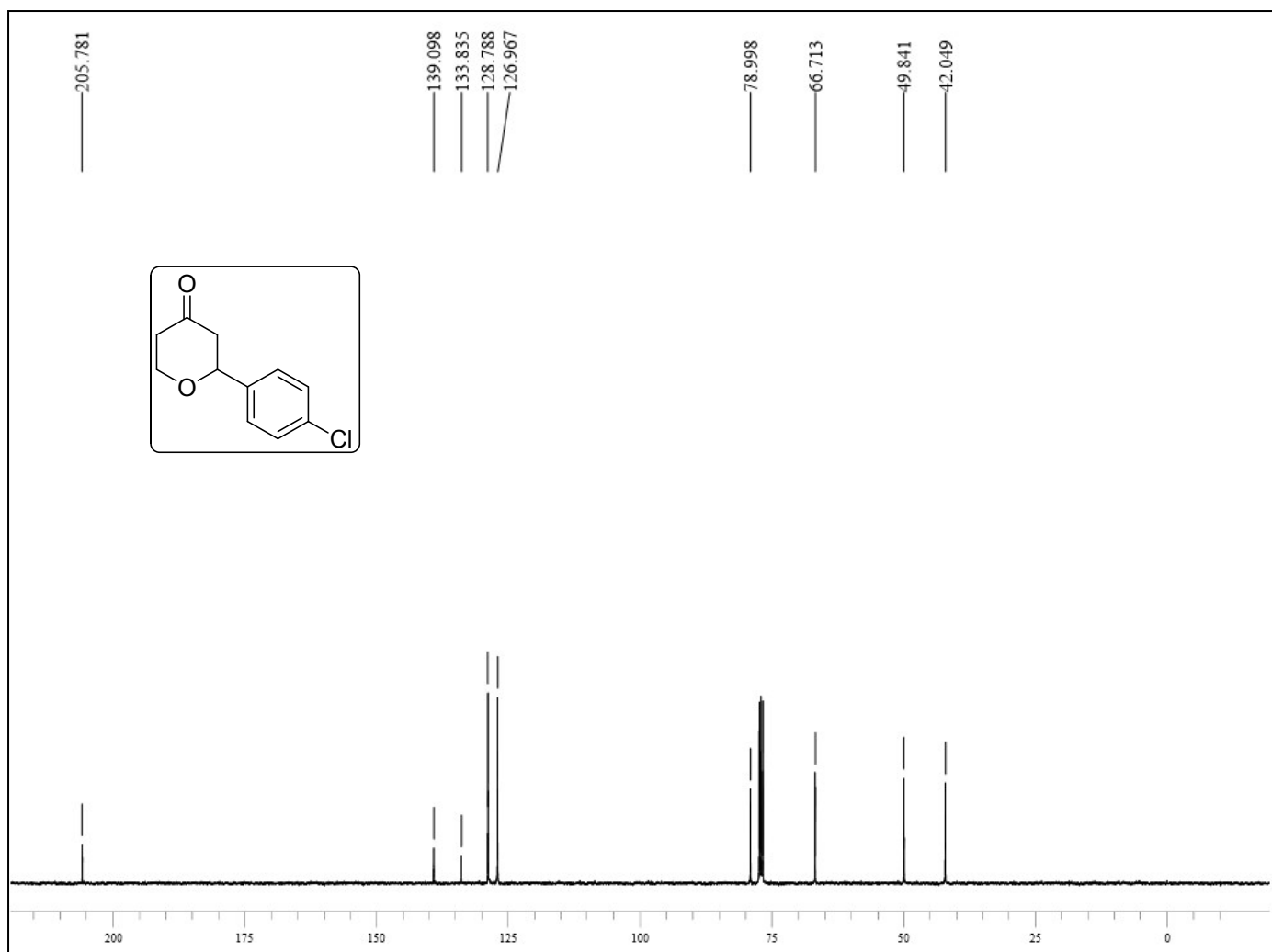


$^{13}\text{C}$  NMR spectrum of compound **3b**

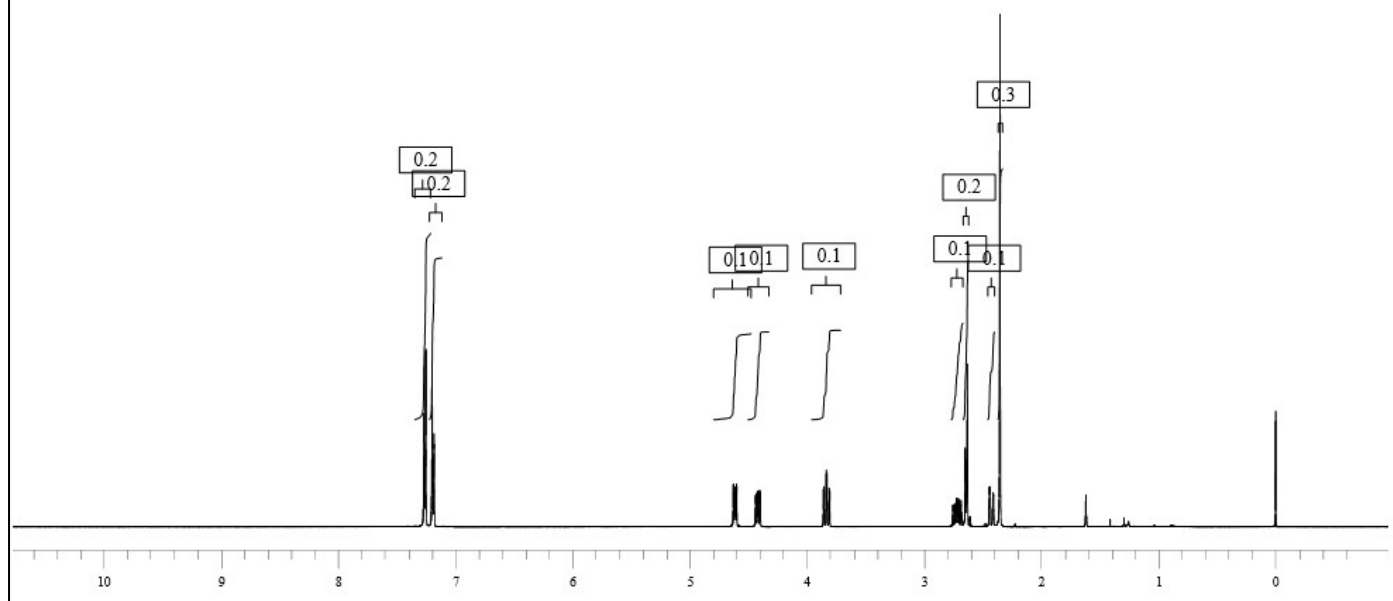
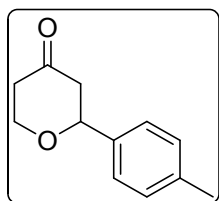




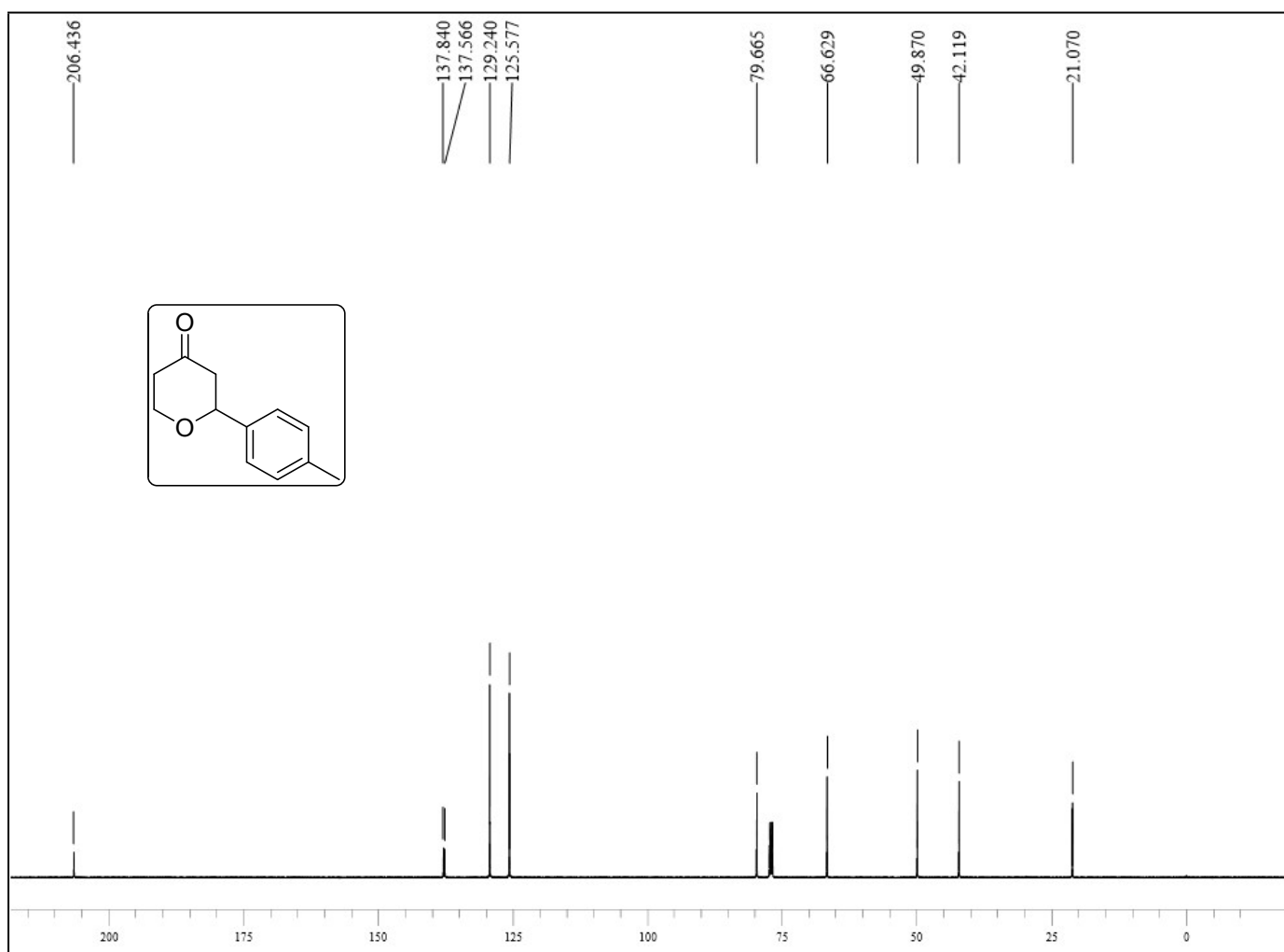
<sup>1</sup>H NMR spectrum of compound 3c

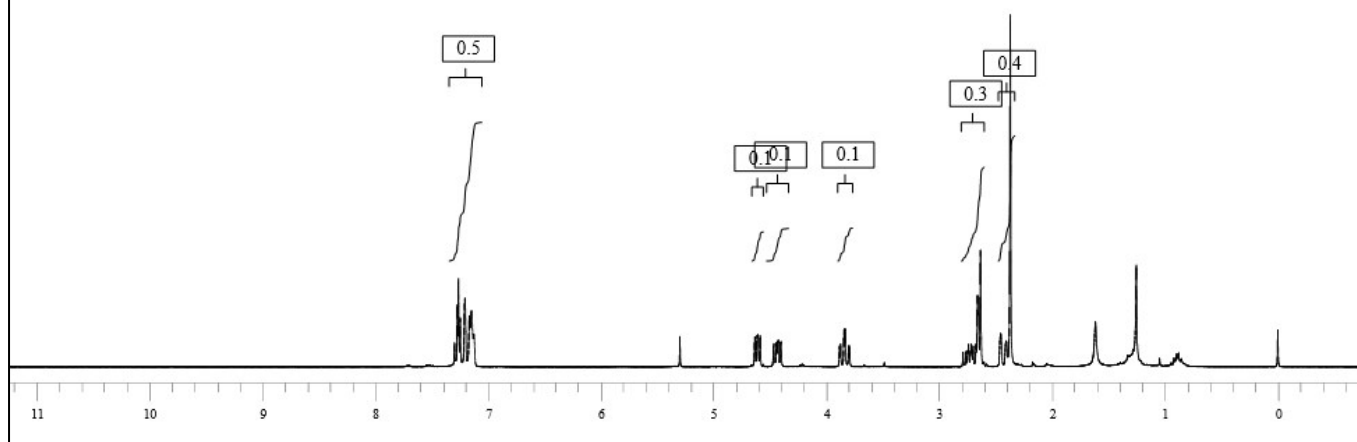
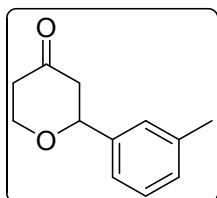


<sup>13</sup>C NMR spectrum of compound **3c**

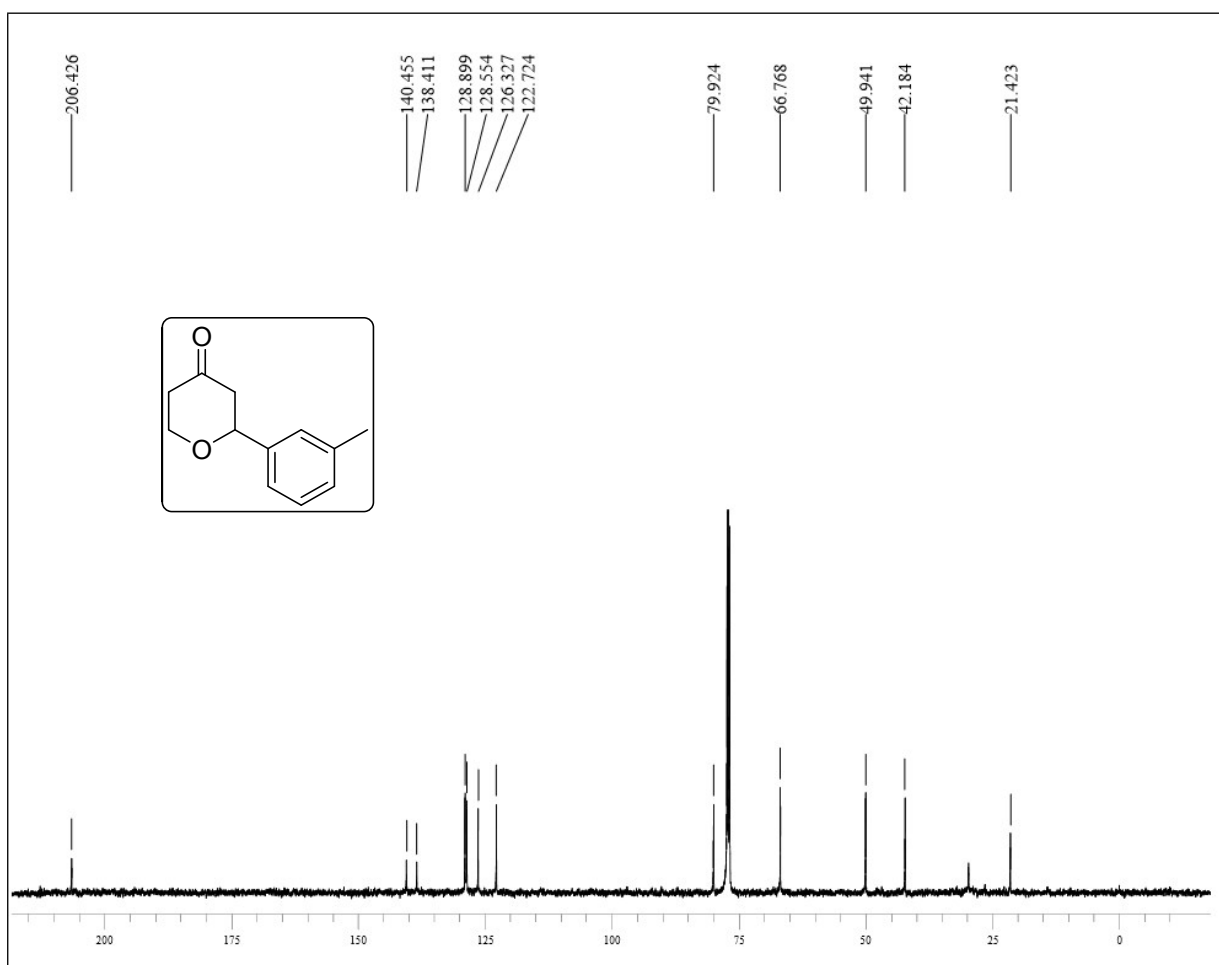


$^1\text{H}$  NMR spectrum of compound **3d**

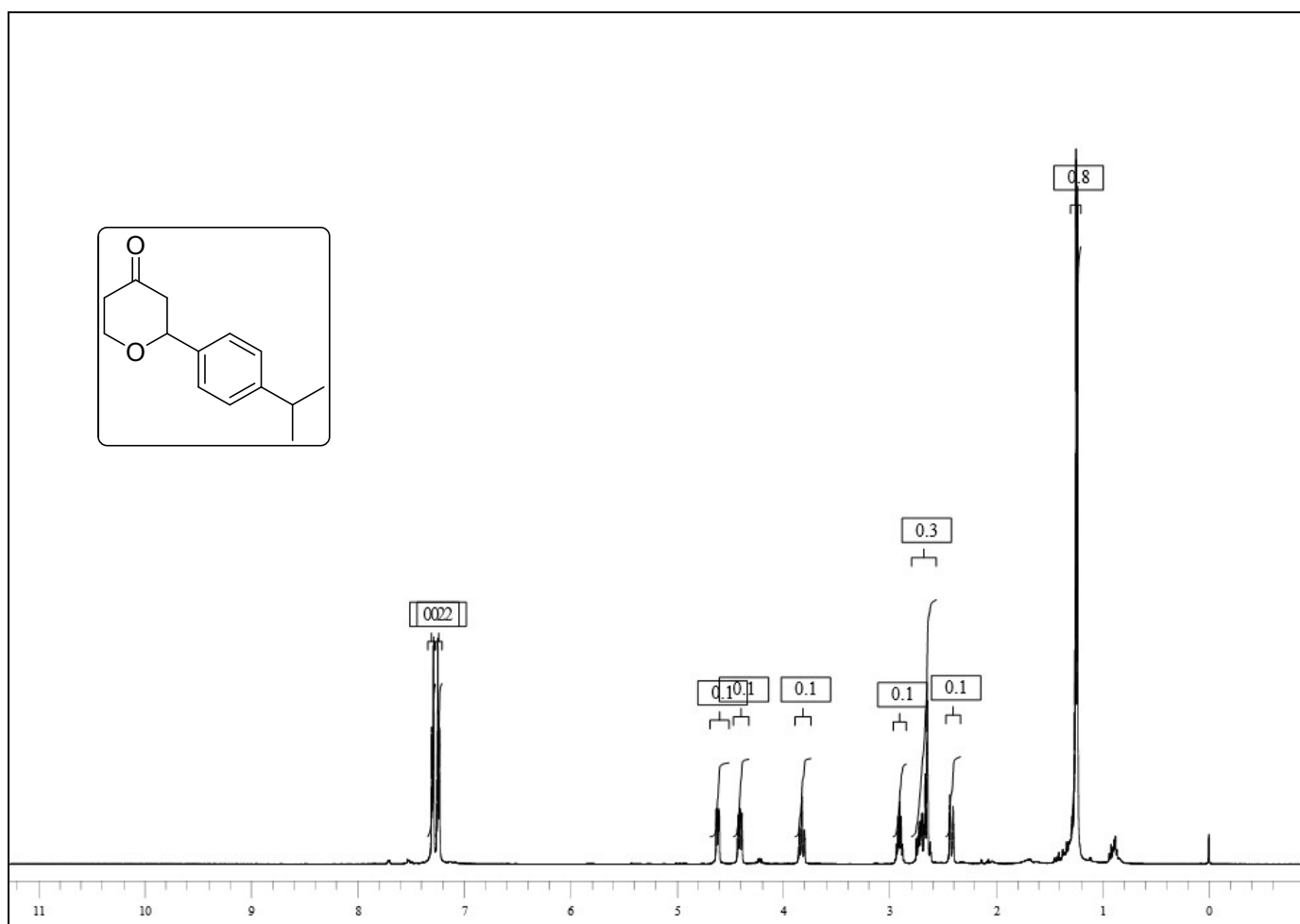




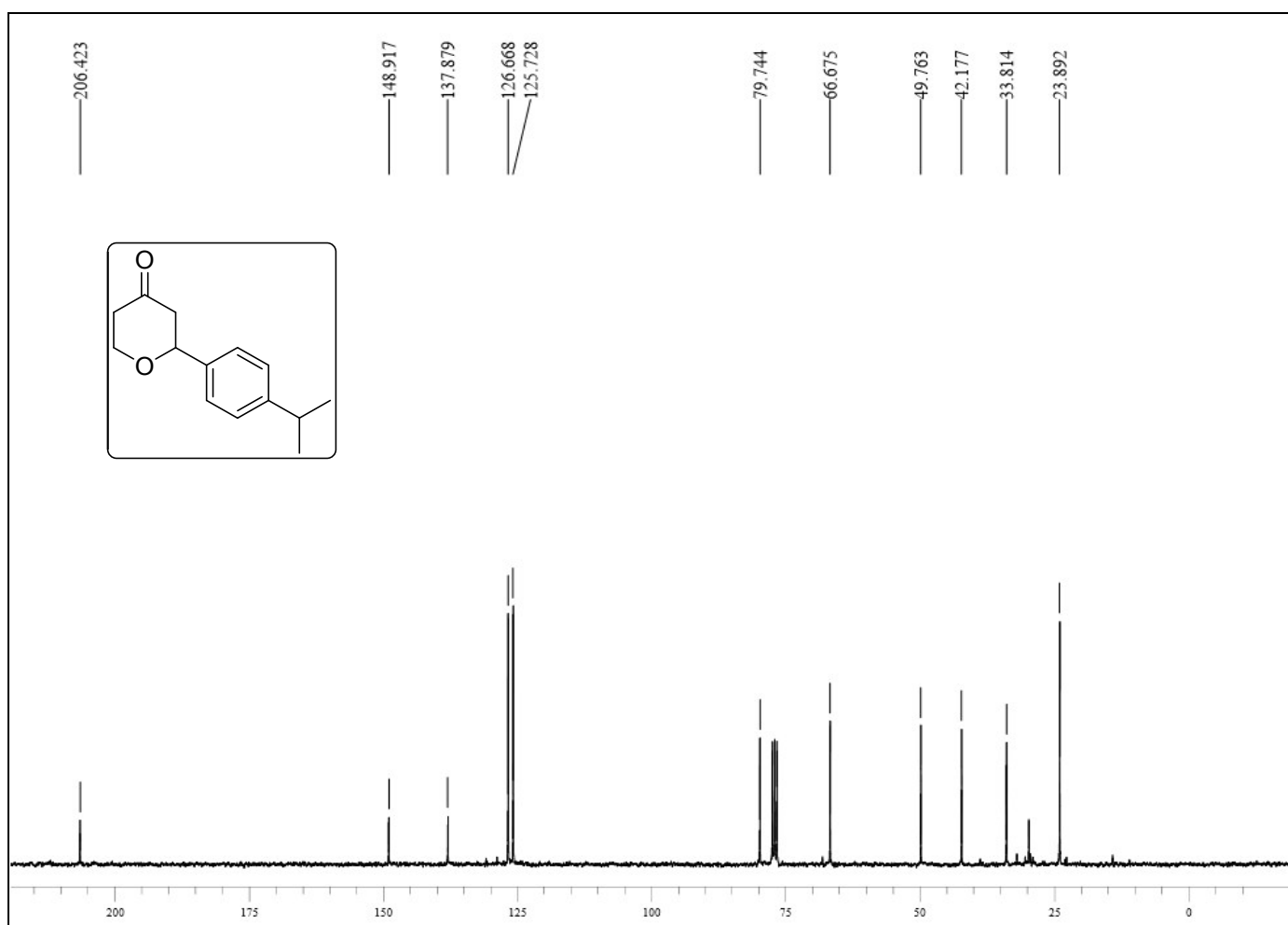
$^1\text{H}$  NMR spectrum of compound **3e**



<sup>13</sup>C NMR spectrum of compound **3e**

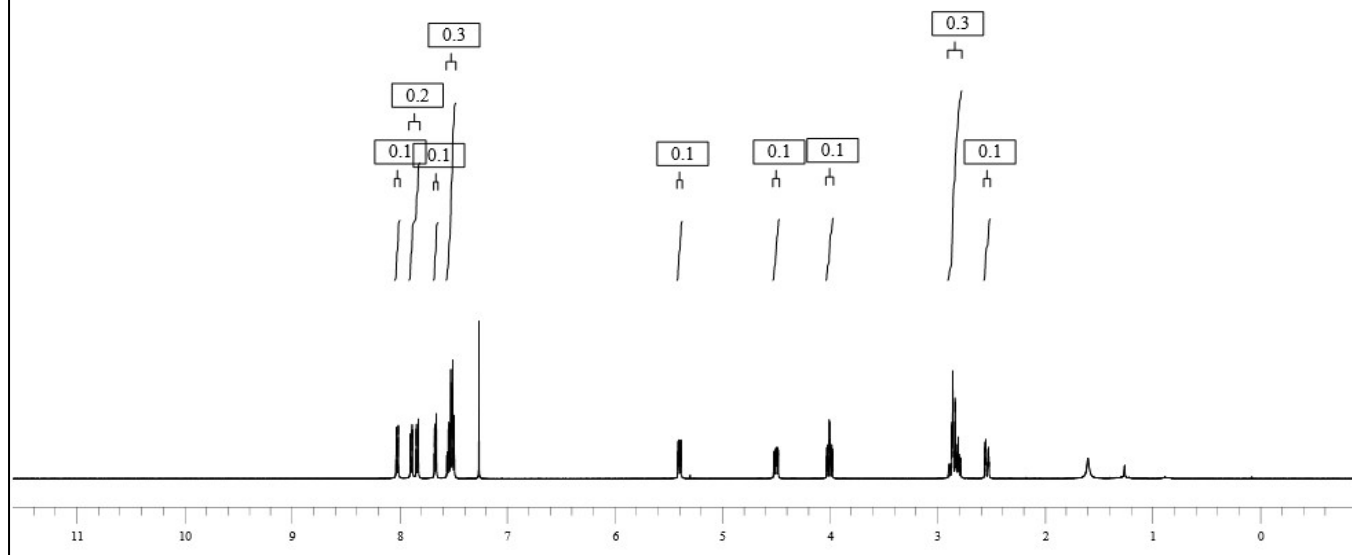
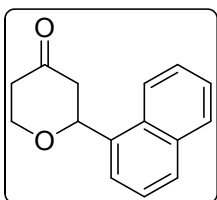


$^1\text{H}$  NMR spectrum of compound **3f**

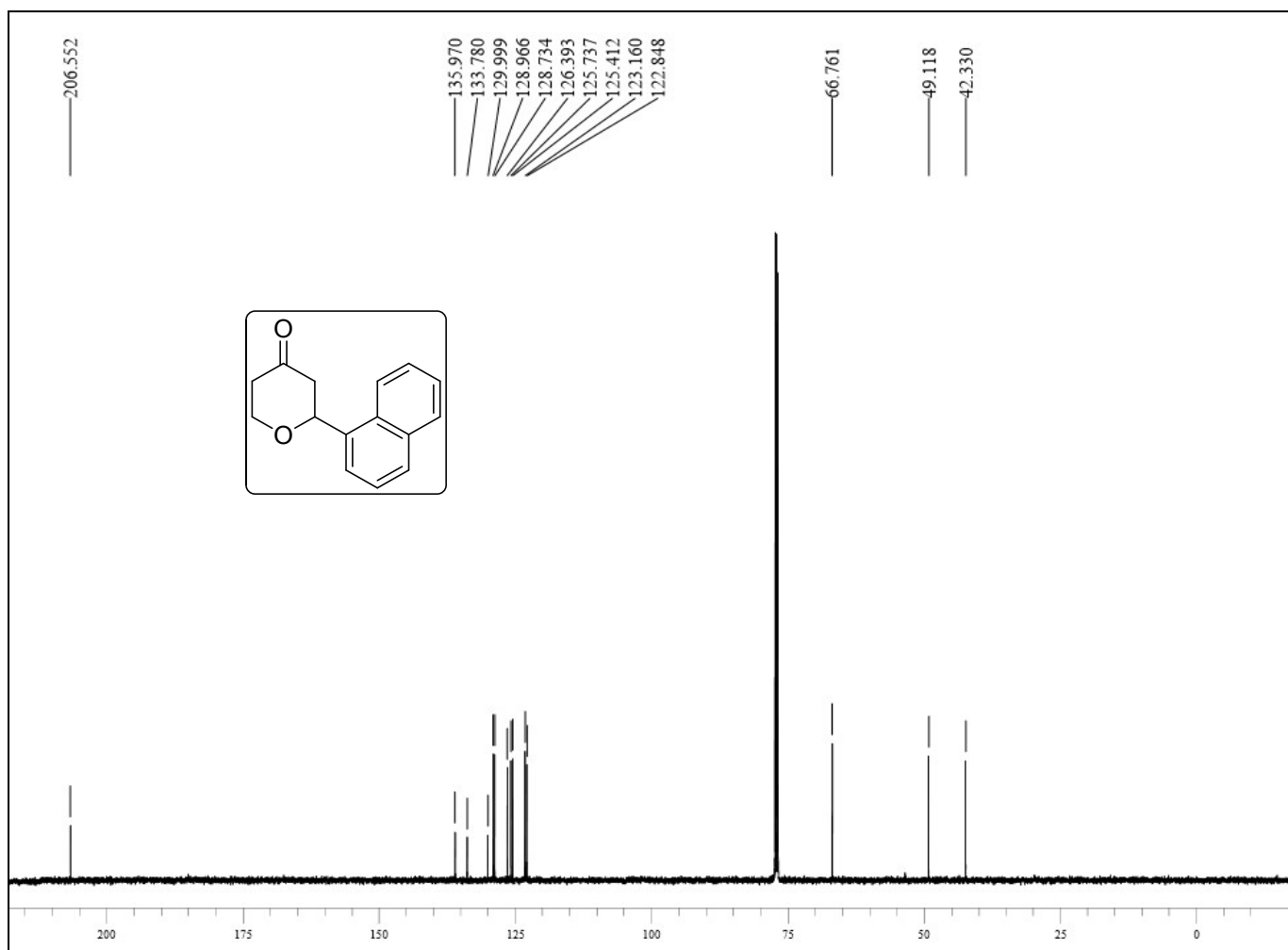


$^{13}\text{C}$  NMR spectrum of compound **3f**

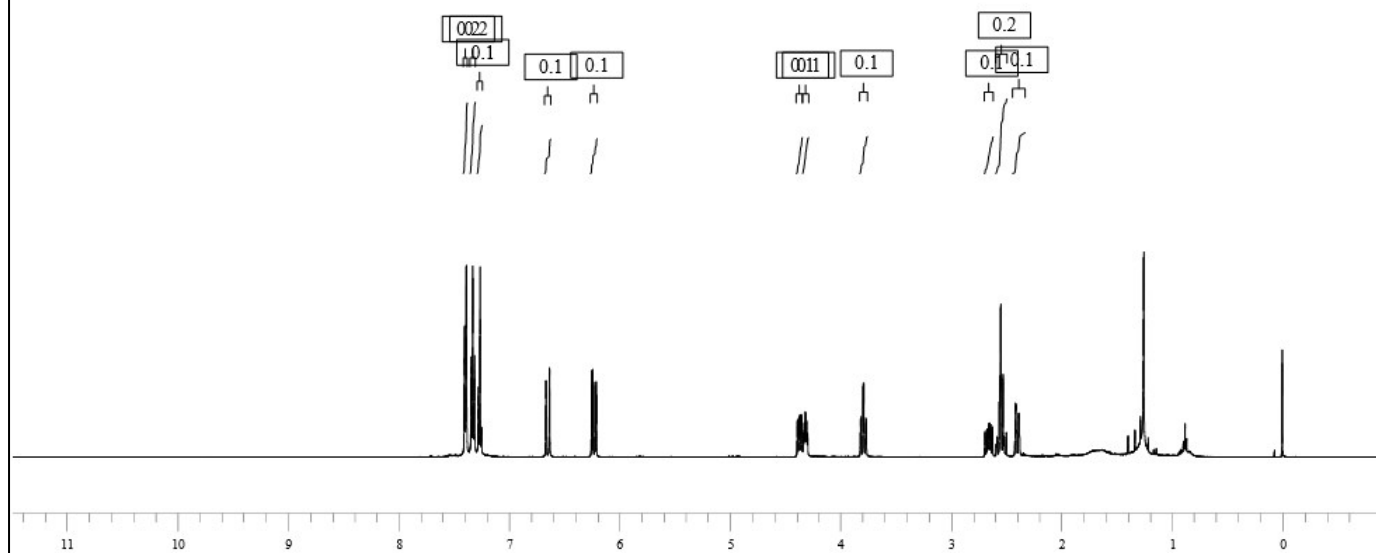
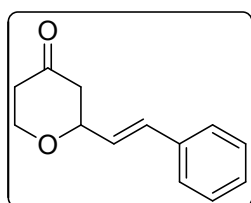




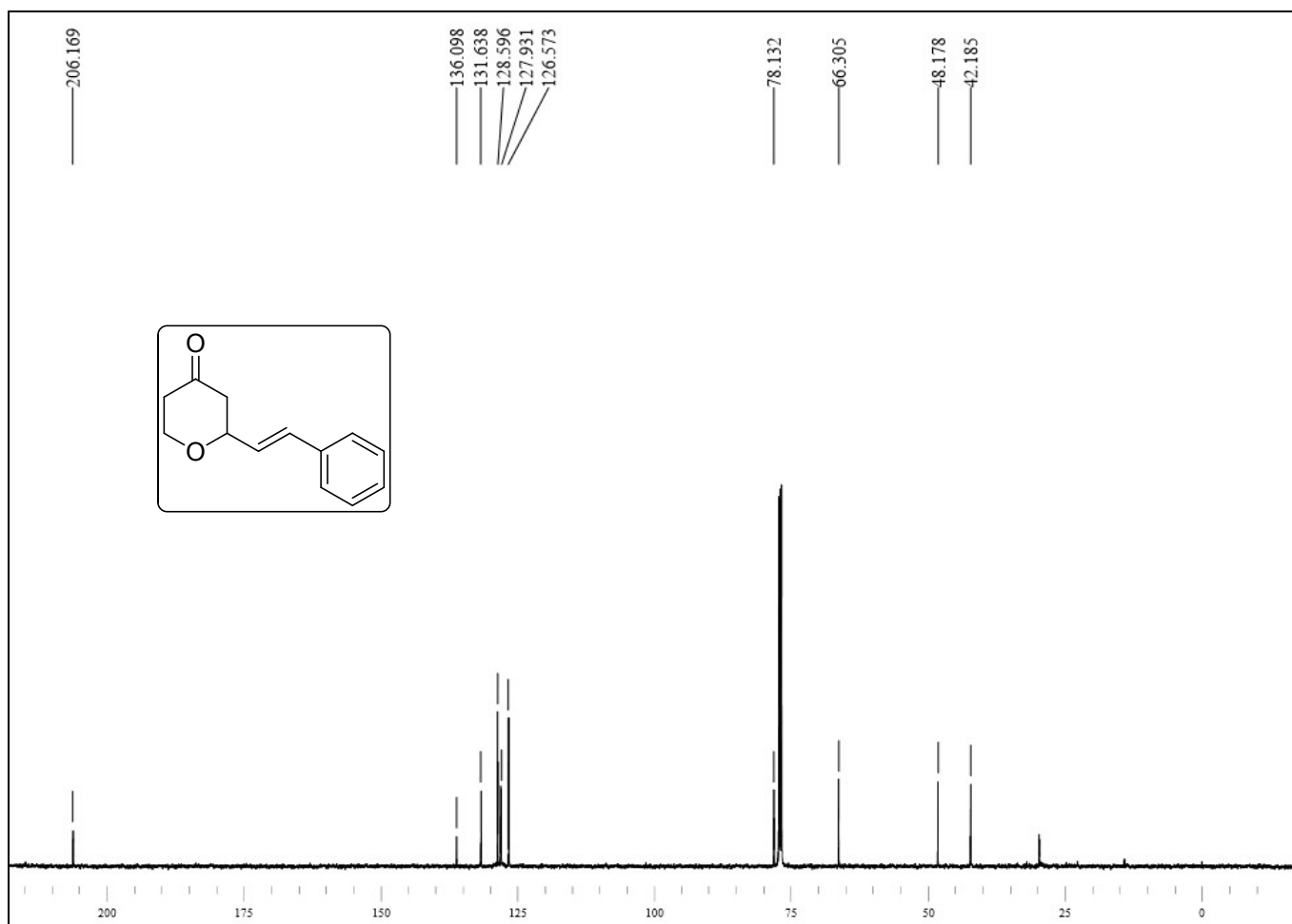
<sup>1</sup>H NMR spectrum of compound **3g**



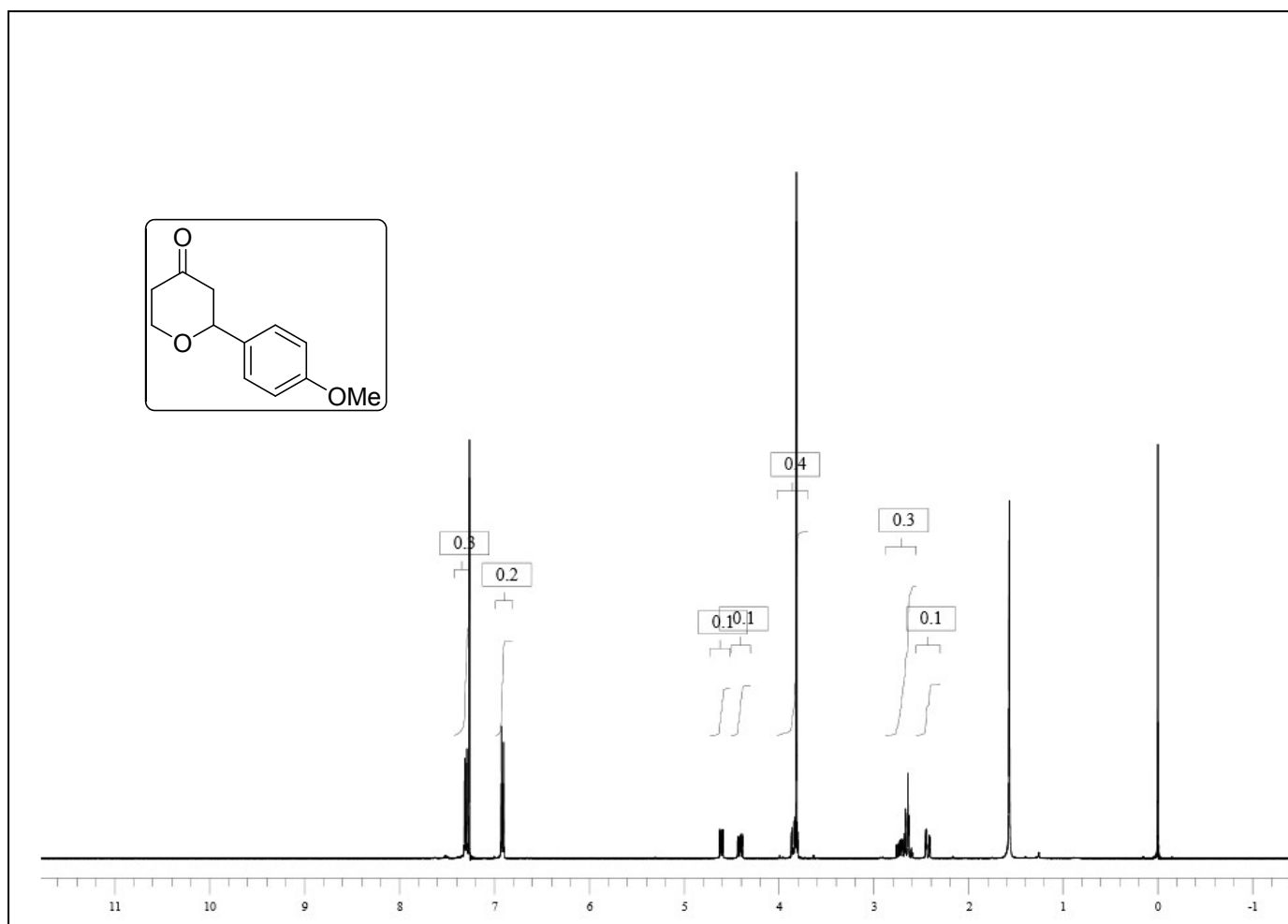
$^{13}\text{C}$  NMR spectrum of compound **3g**



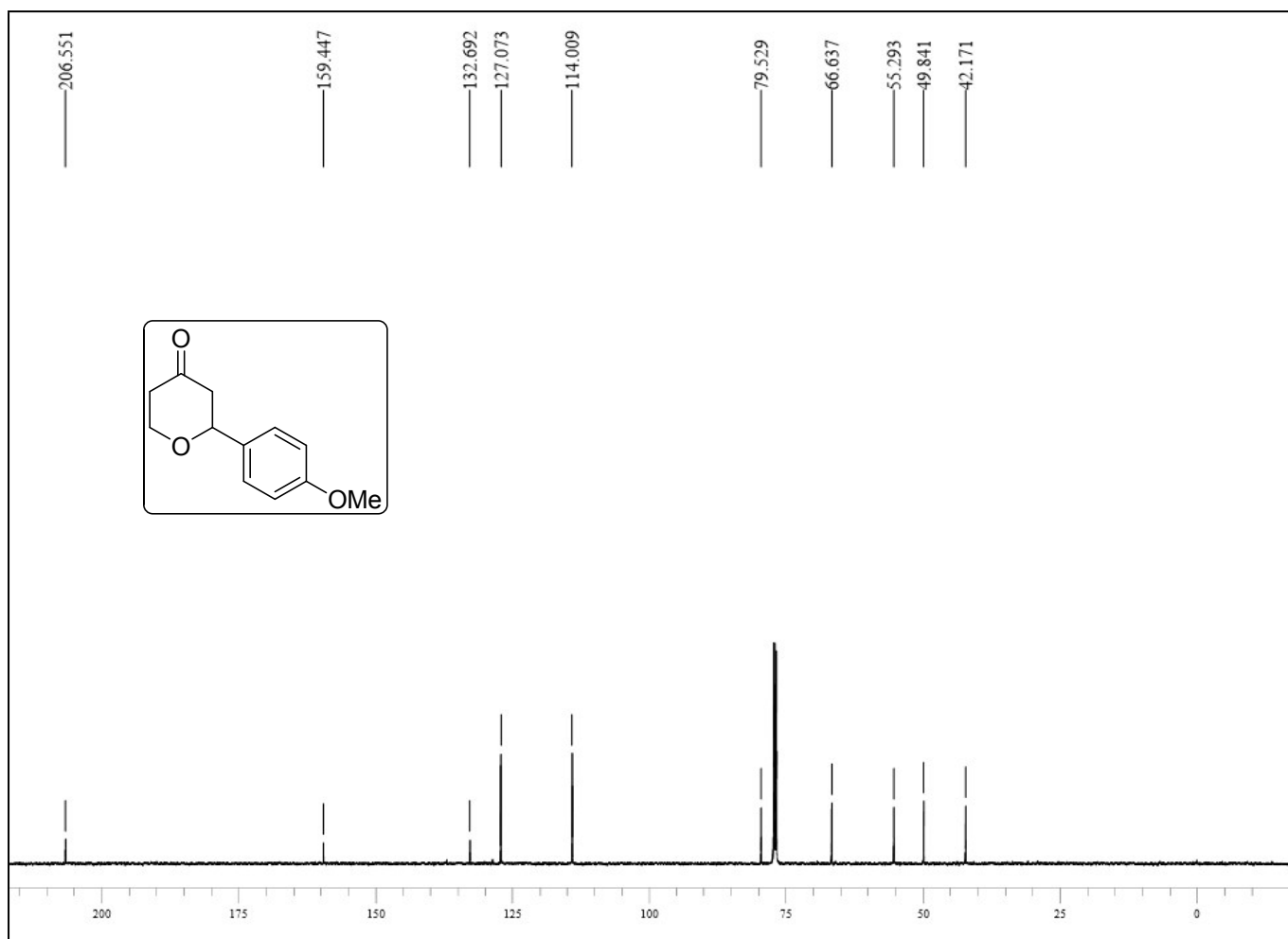
<sup>1</sup>H NMR spectrum of compound **3h**



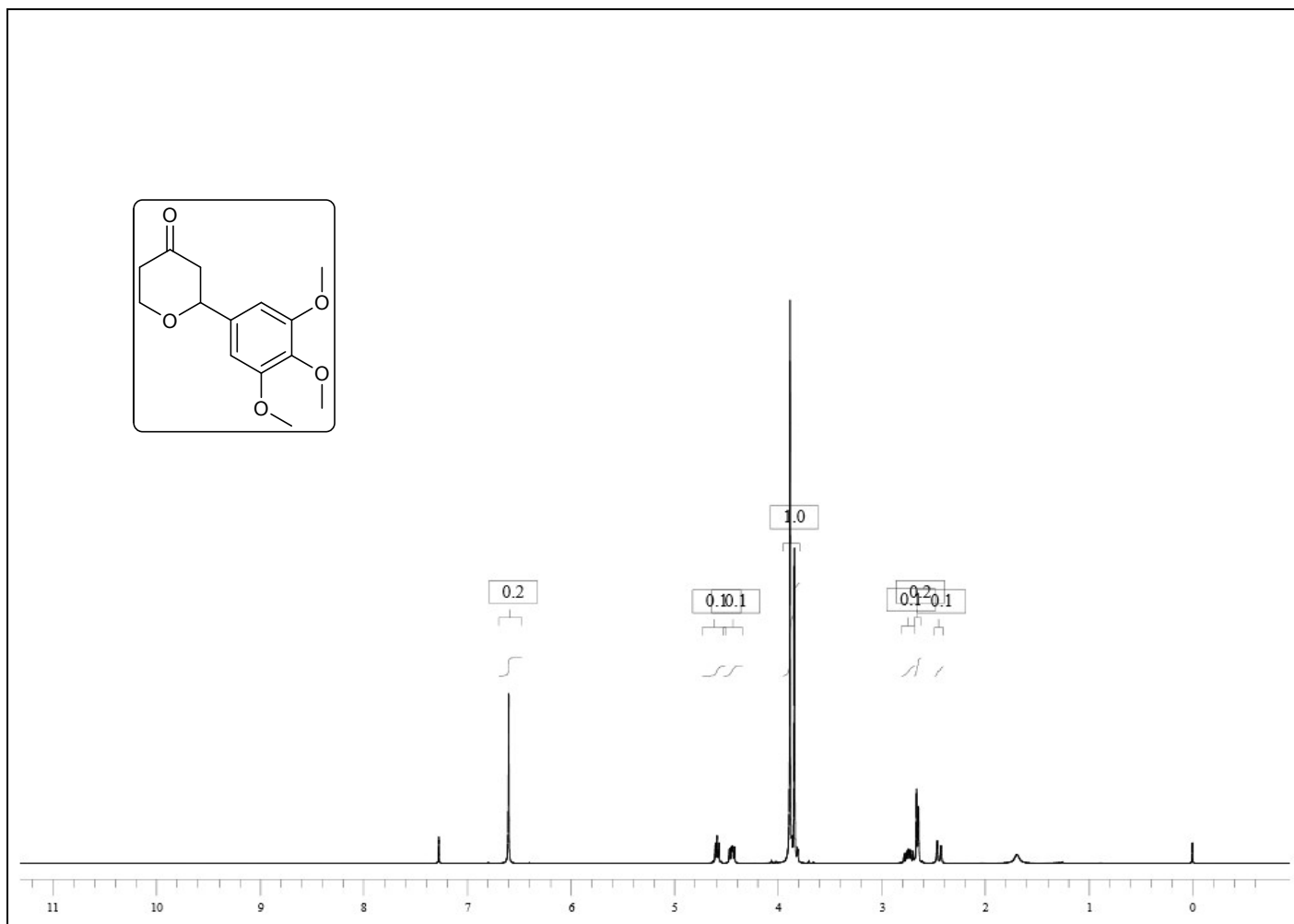
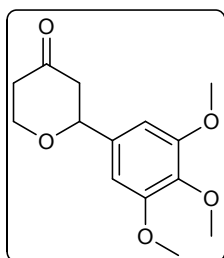
$^{13}\text{C}$  NMR spectrum of compound **3h**



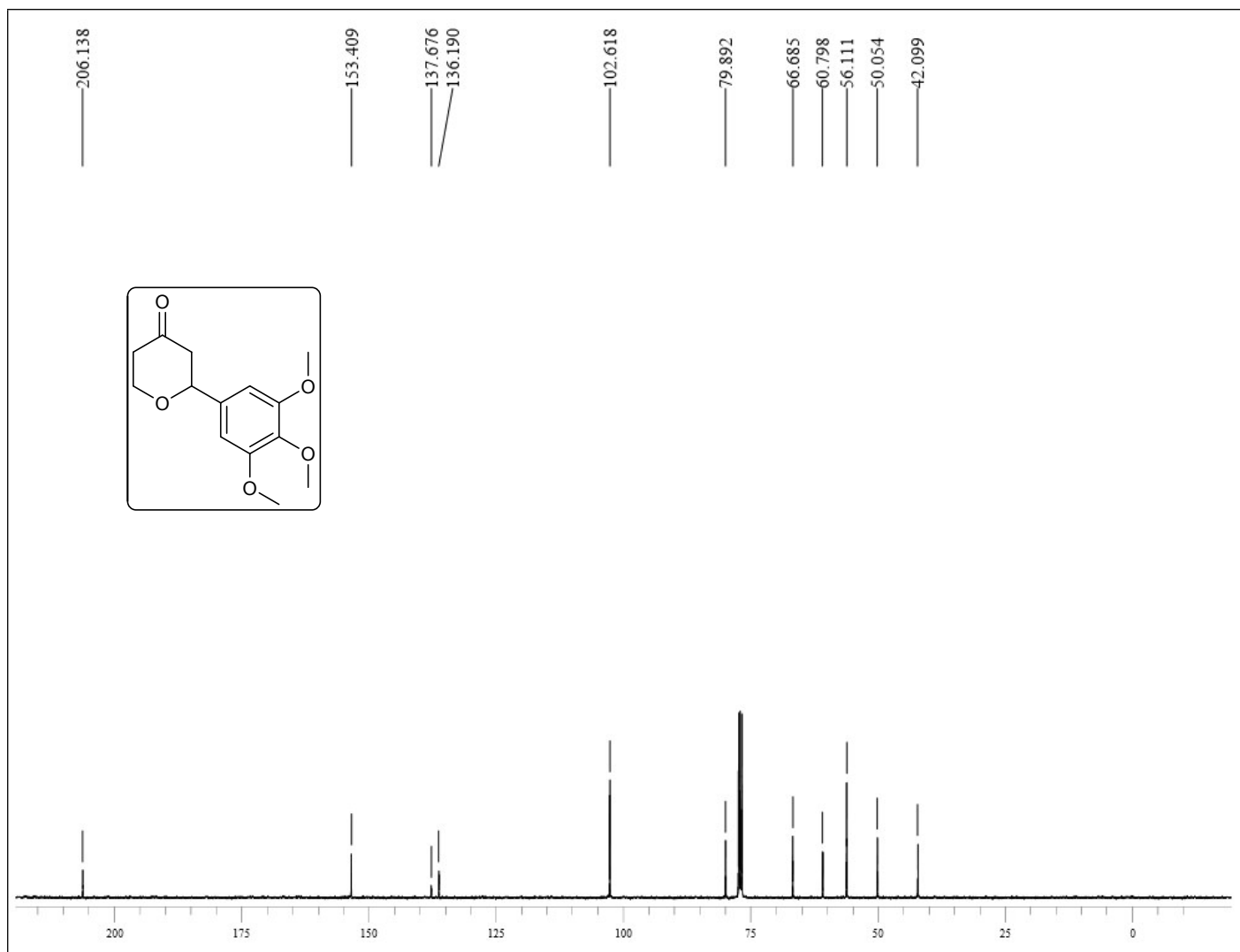
<sup>1</sup>H NMR spectrum of compound **3i**



$^{13}\text{C}$  NMR spectrum of compound **3i**

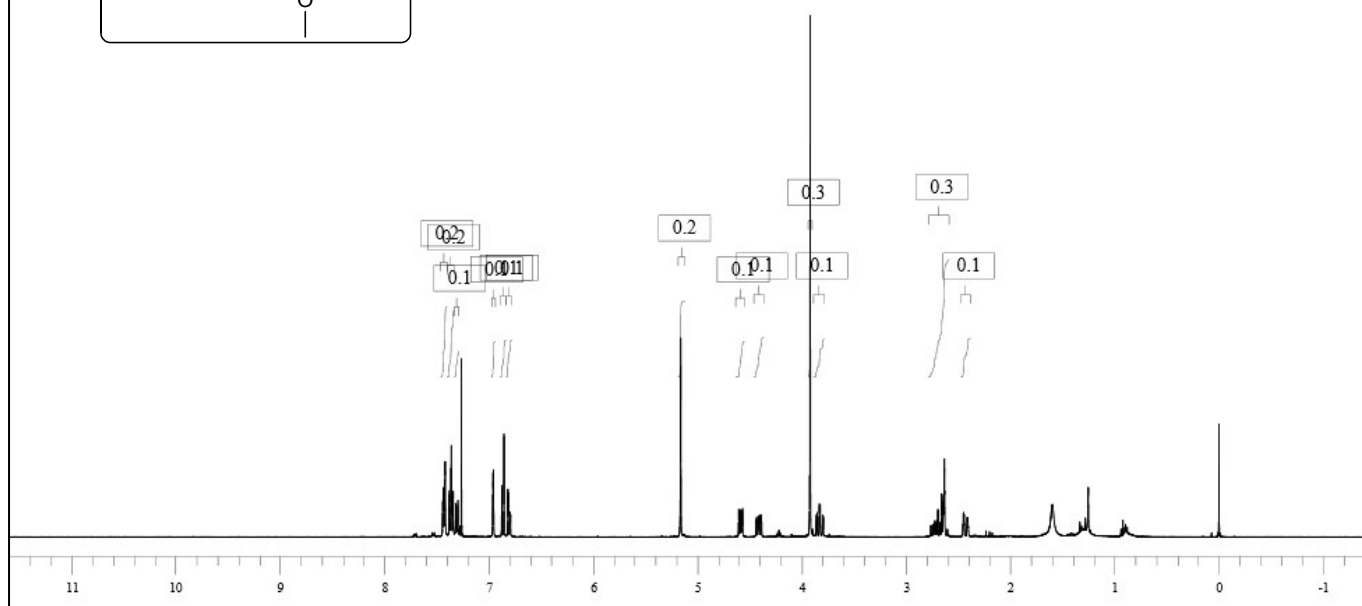
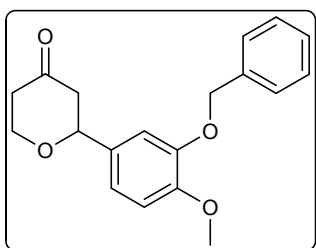


<sup>1</sup>H NMR spectrum of compound 3j

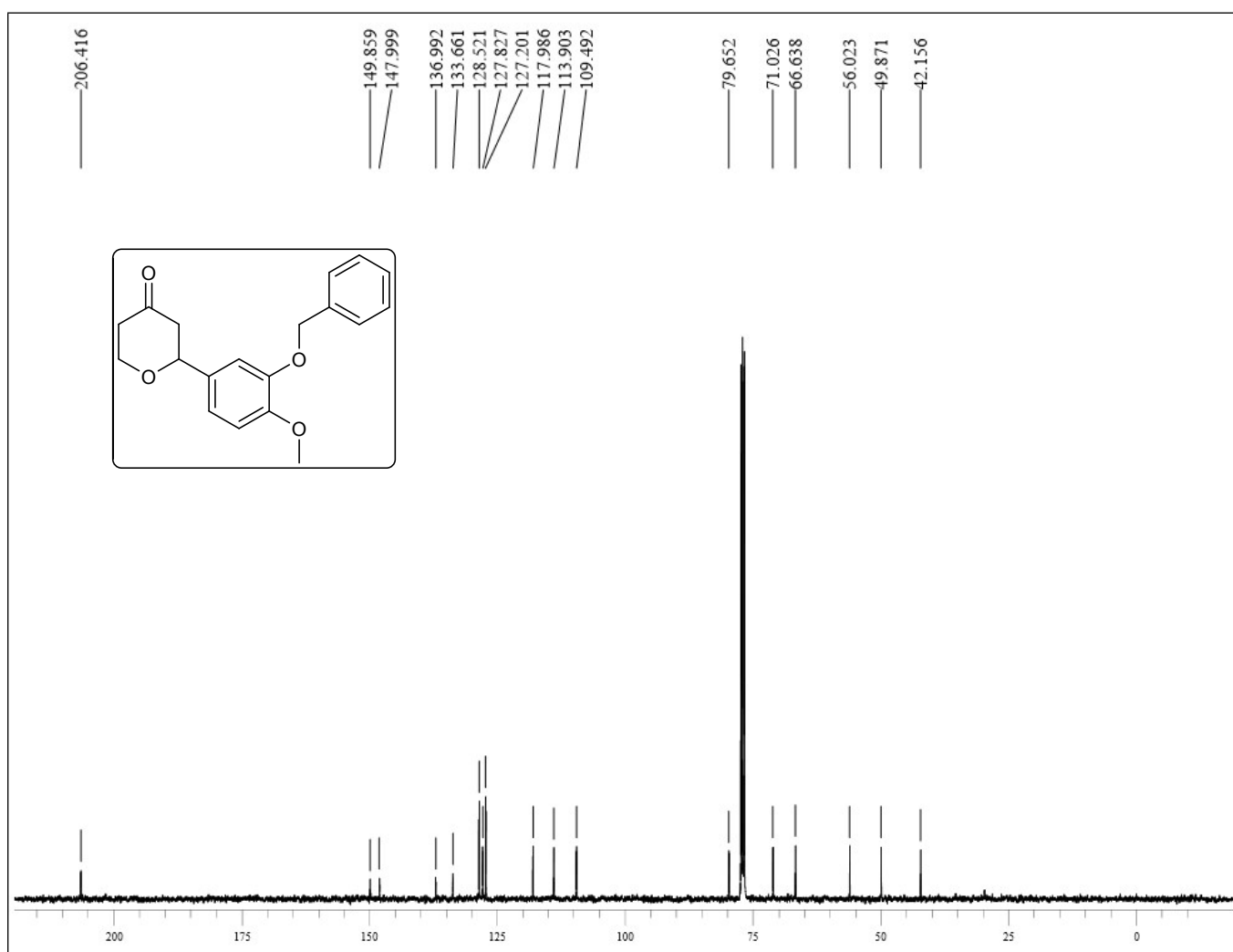


$^{13}\text{C}$  NMR spectrum of compound **3j**

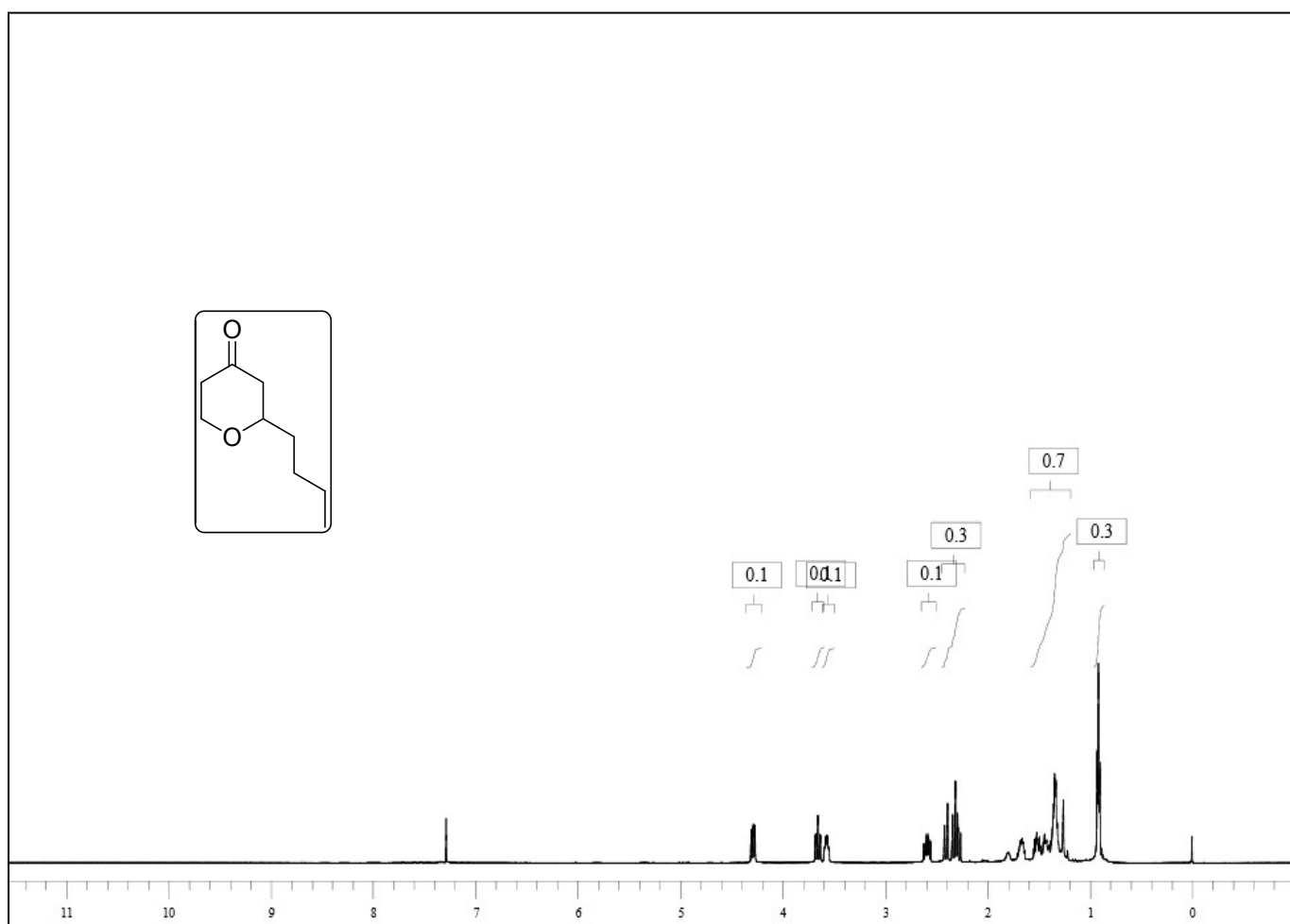
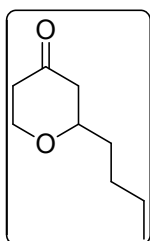




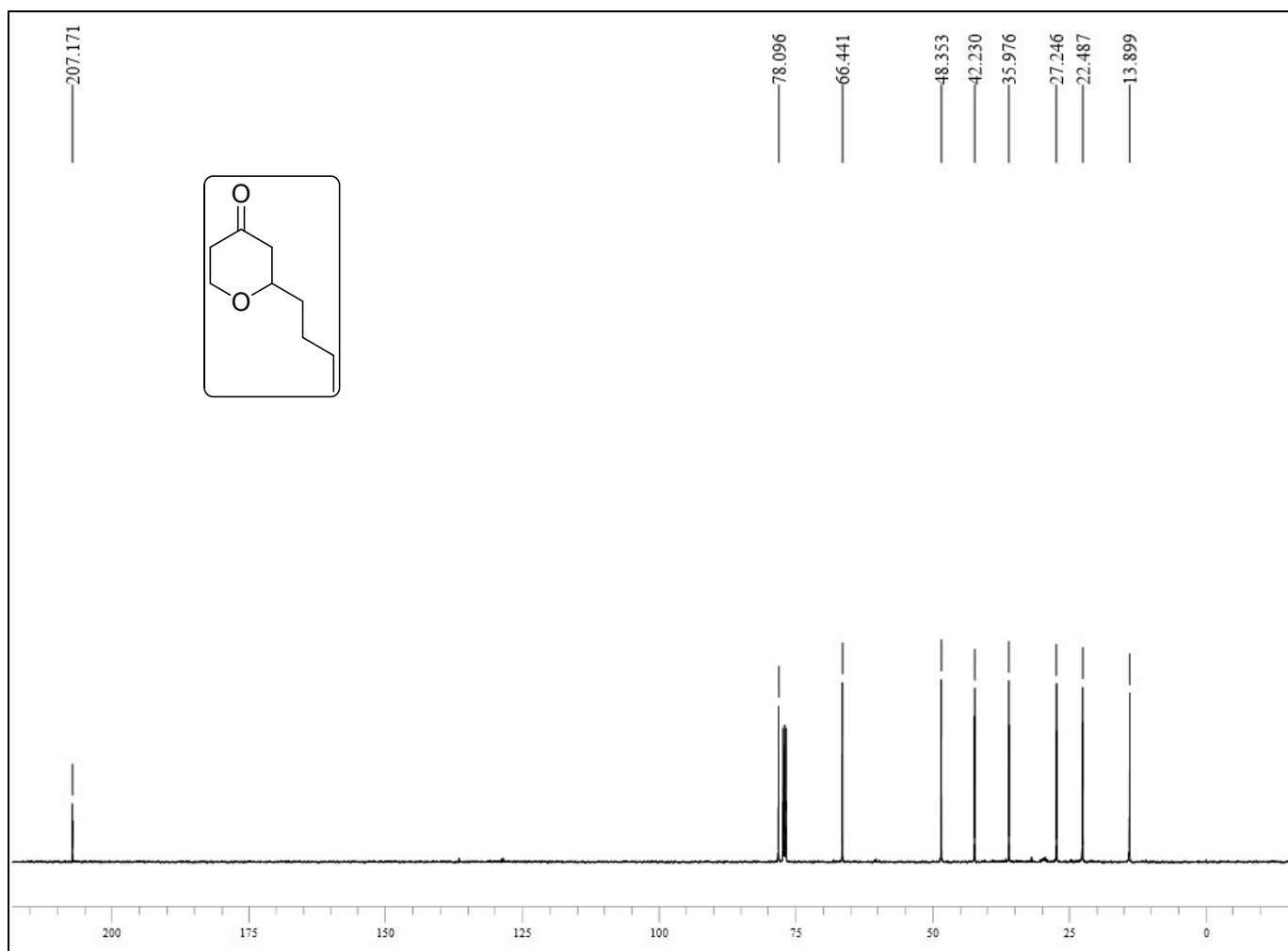
$^1\text{H}$  NMR spectrum of compound **3k**



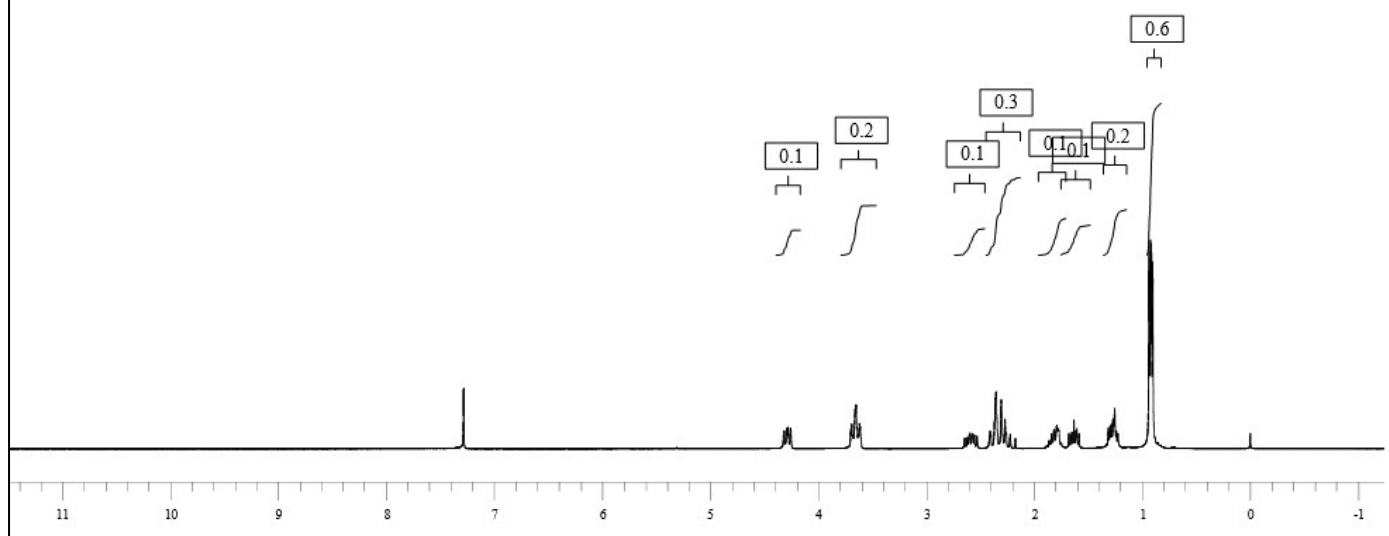
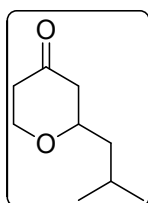
$^{13}\text{C}$  NMR spectrum of compound **3k**



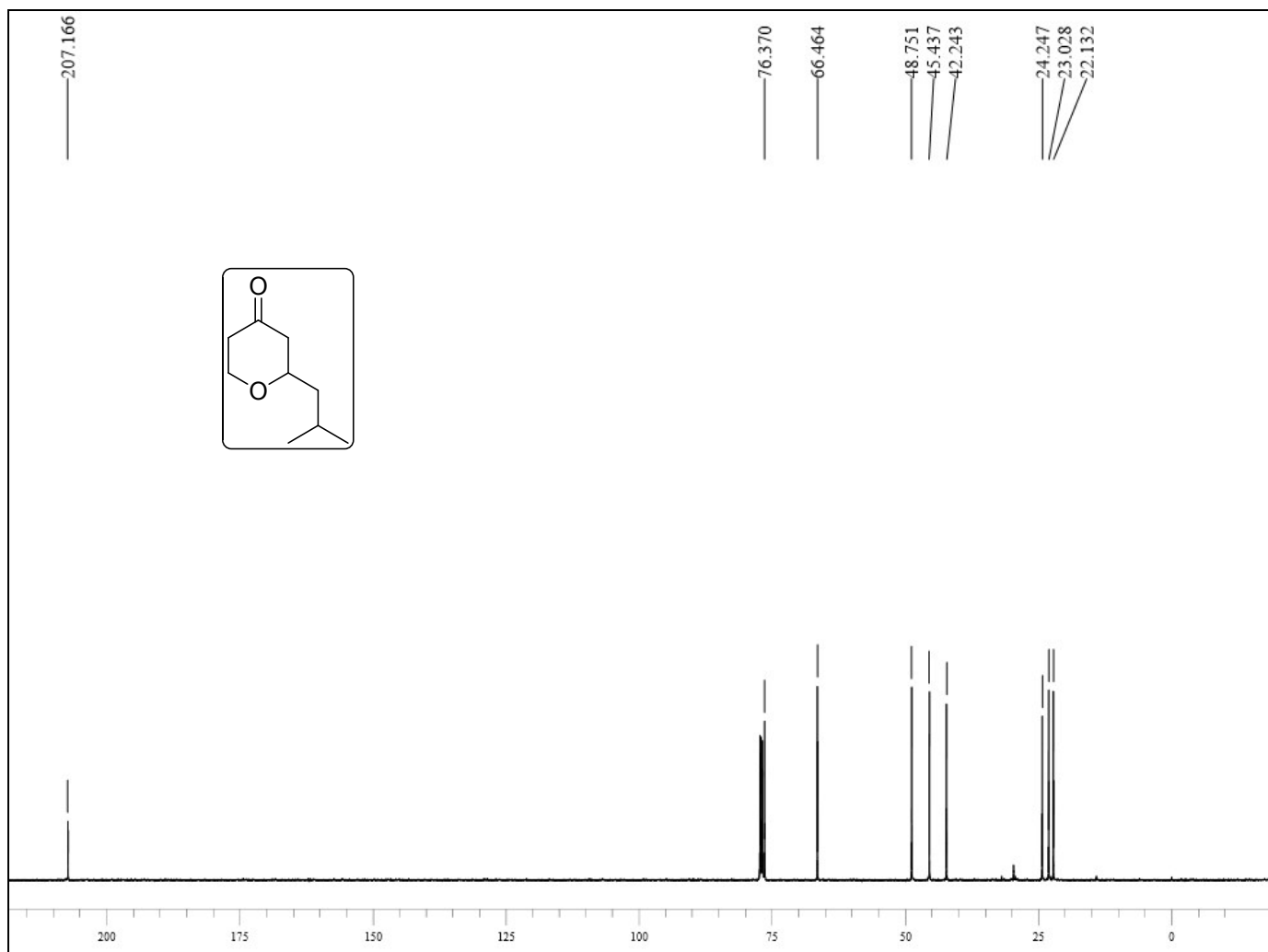
$^1\text{H}$  NMR spectrum of compound **31**



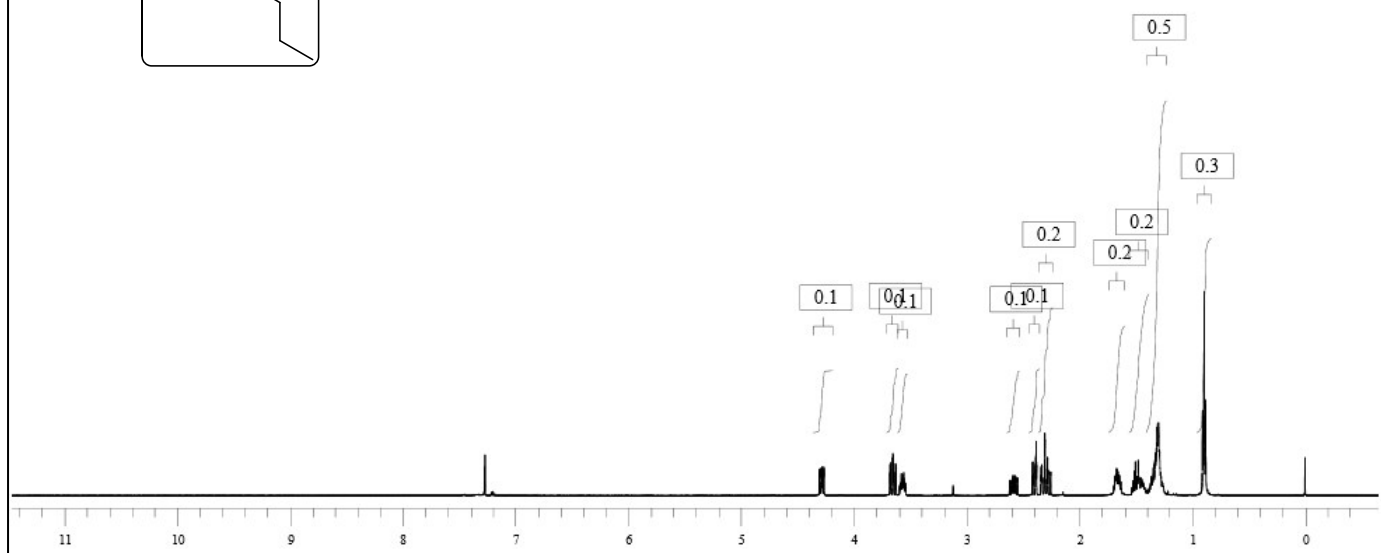
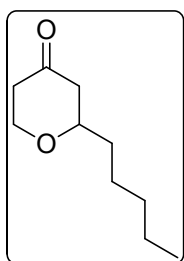
$^{13}\text{C}$  NMR spectrum of compound **31**



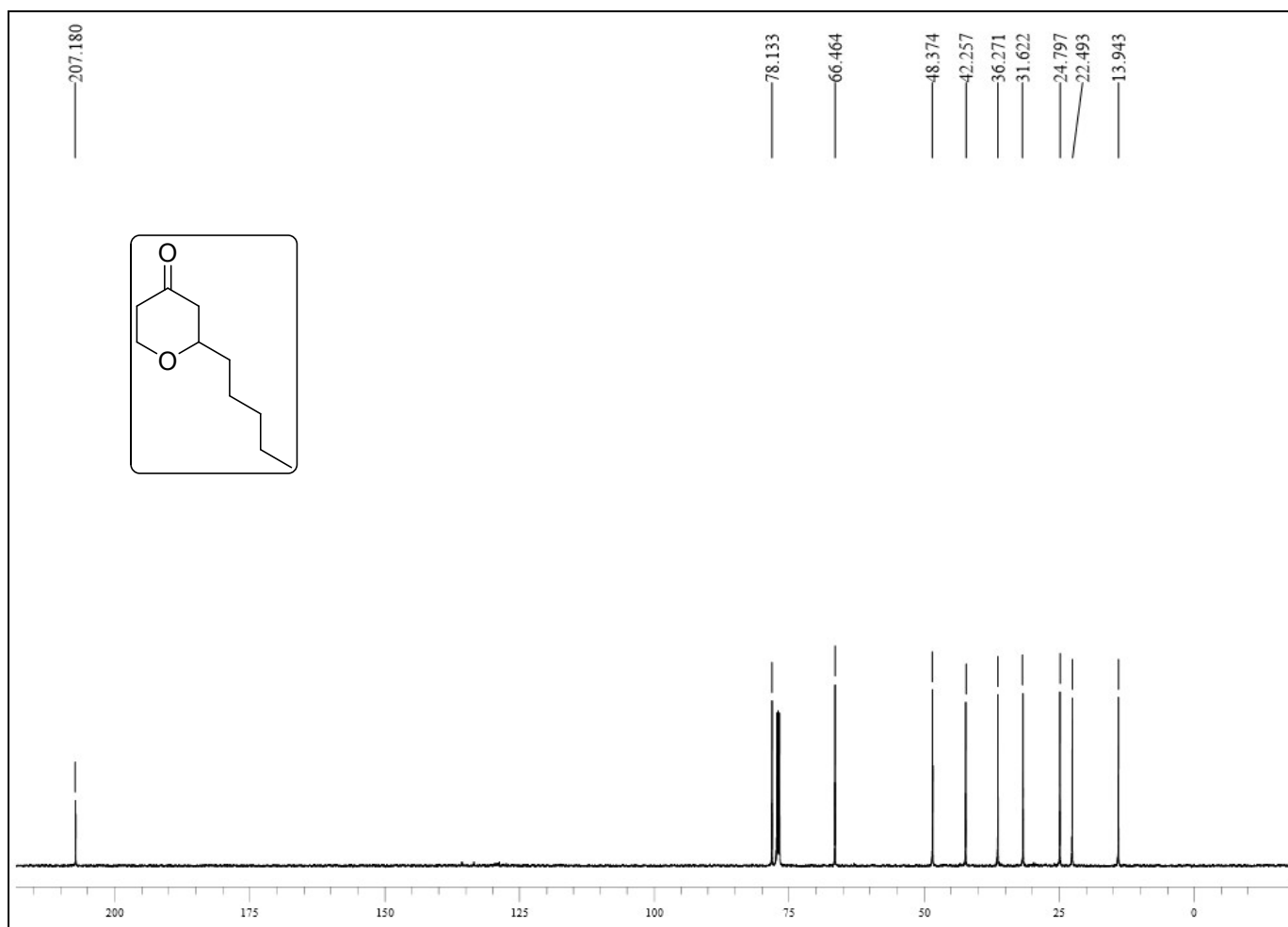
$^1\text{H}$  NMR spectrum of compound **3m**



$^{13}\text{C}$  NMR spectrum of compound **3m**

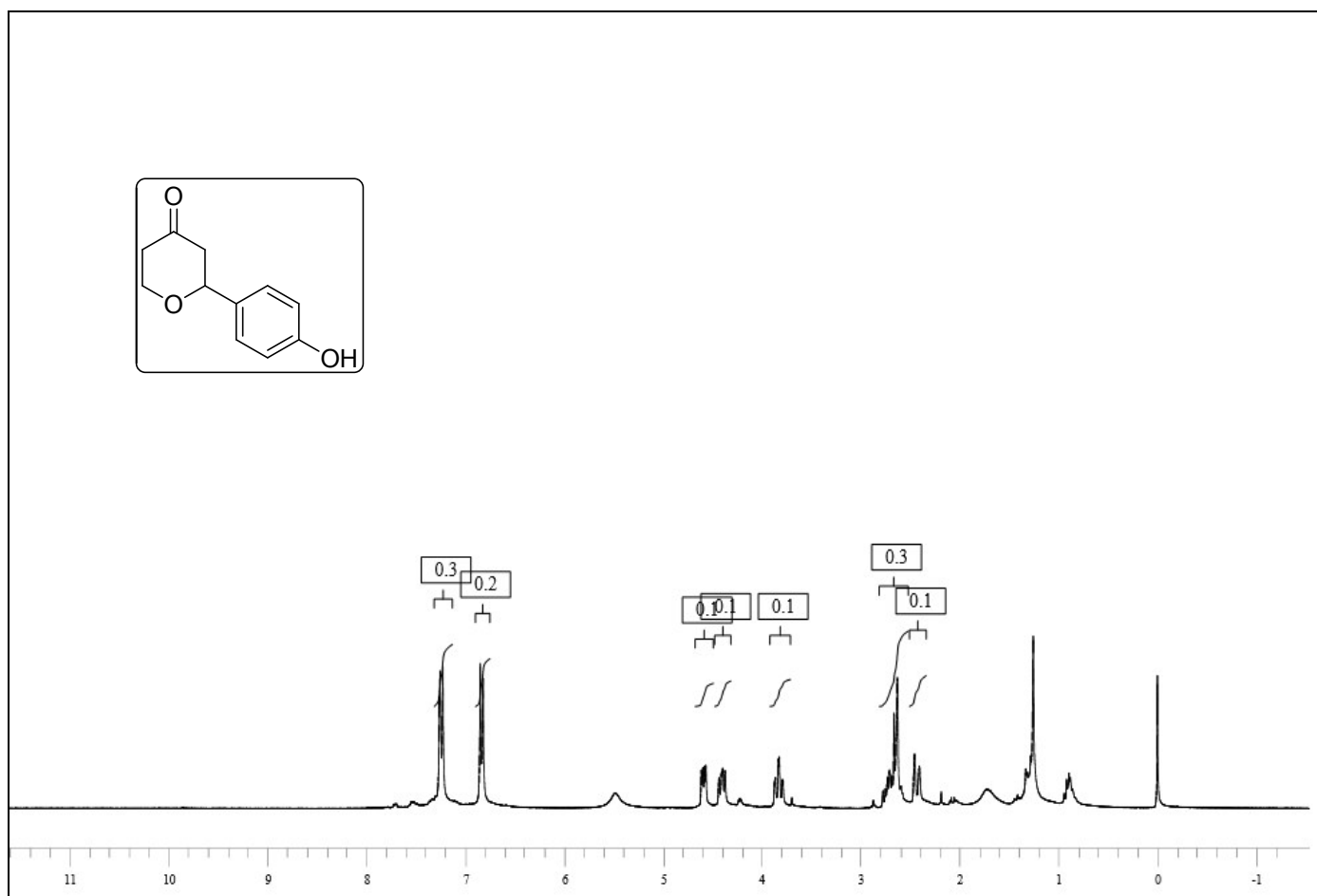
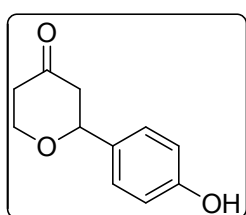


$^1\text{H}$  NMR spectrum of compound **3n**

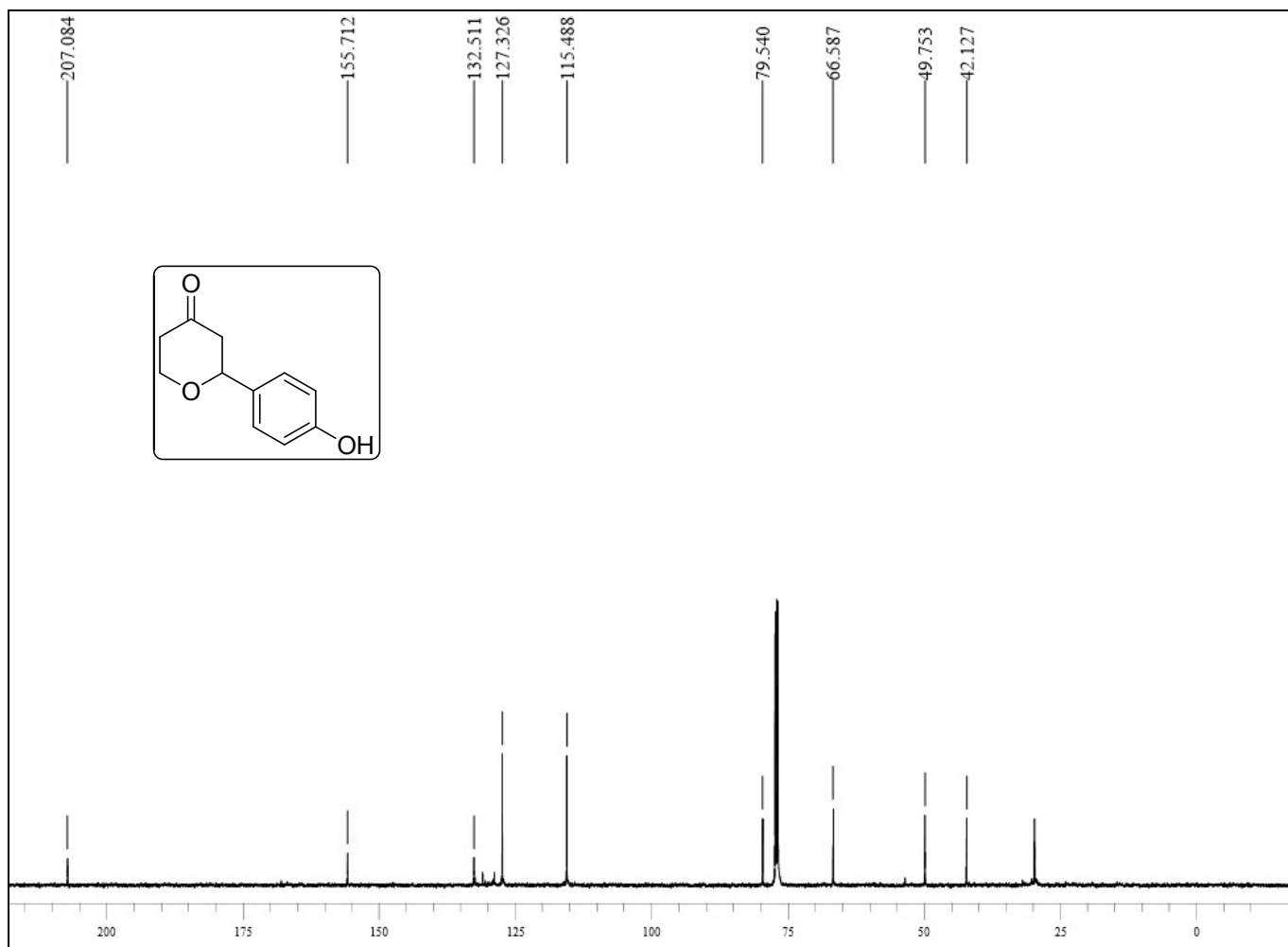


$^{13}\text{C}$  NMR spectrum of compound **3n**

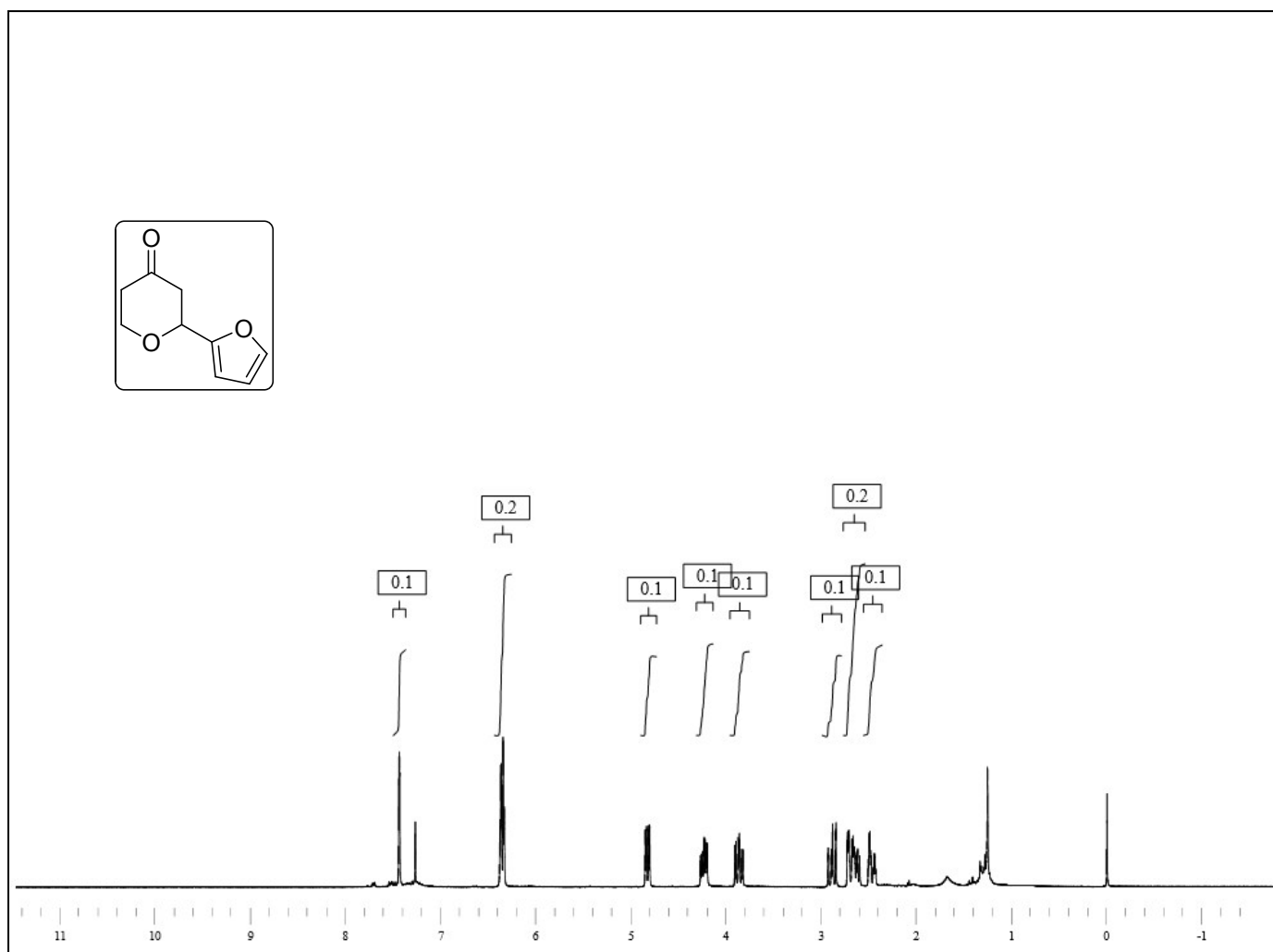
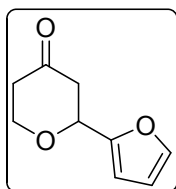




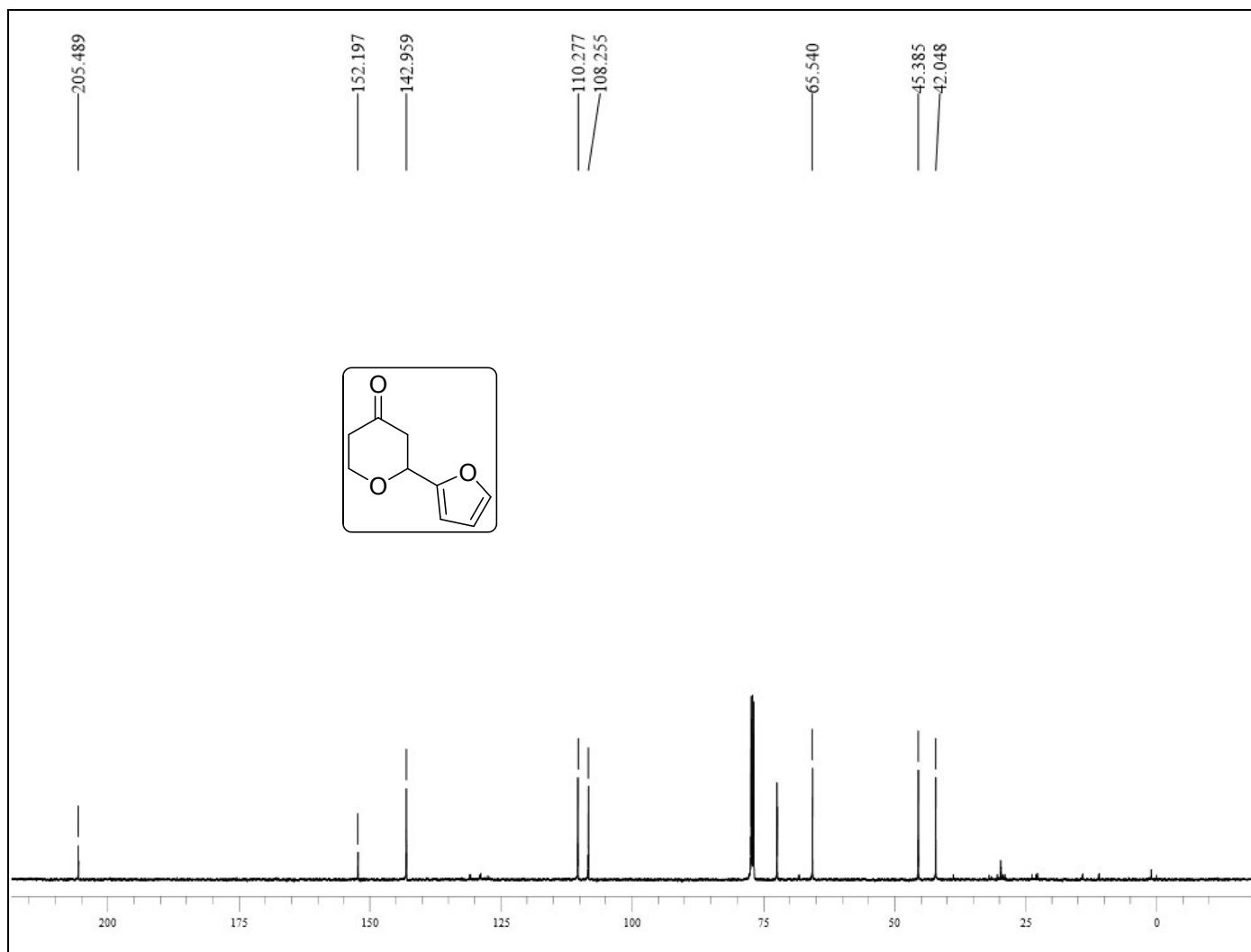
$^1\text{H}$  NMR spectrum of compound **3o**



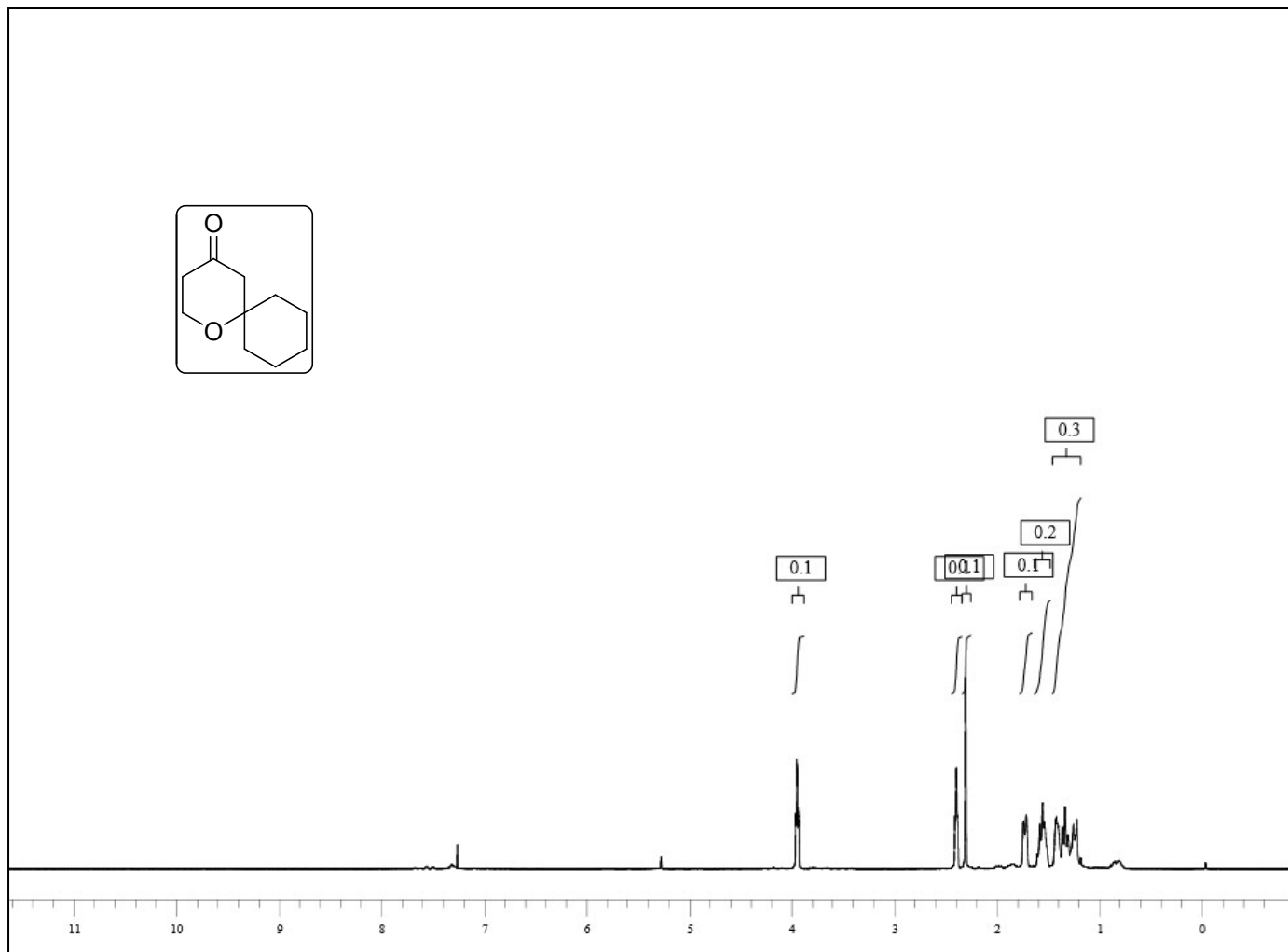
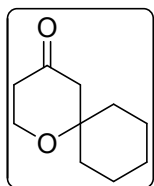
$^{13}\text{C}$  NMR spectrum of compound **3o**



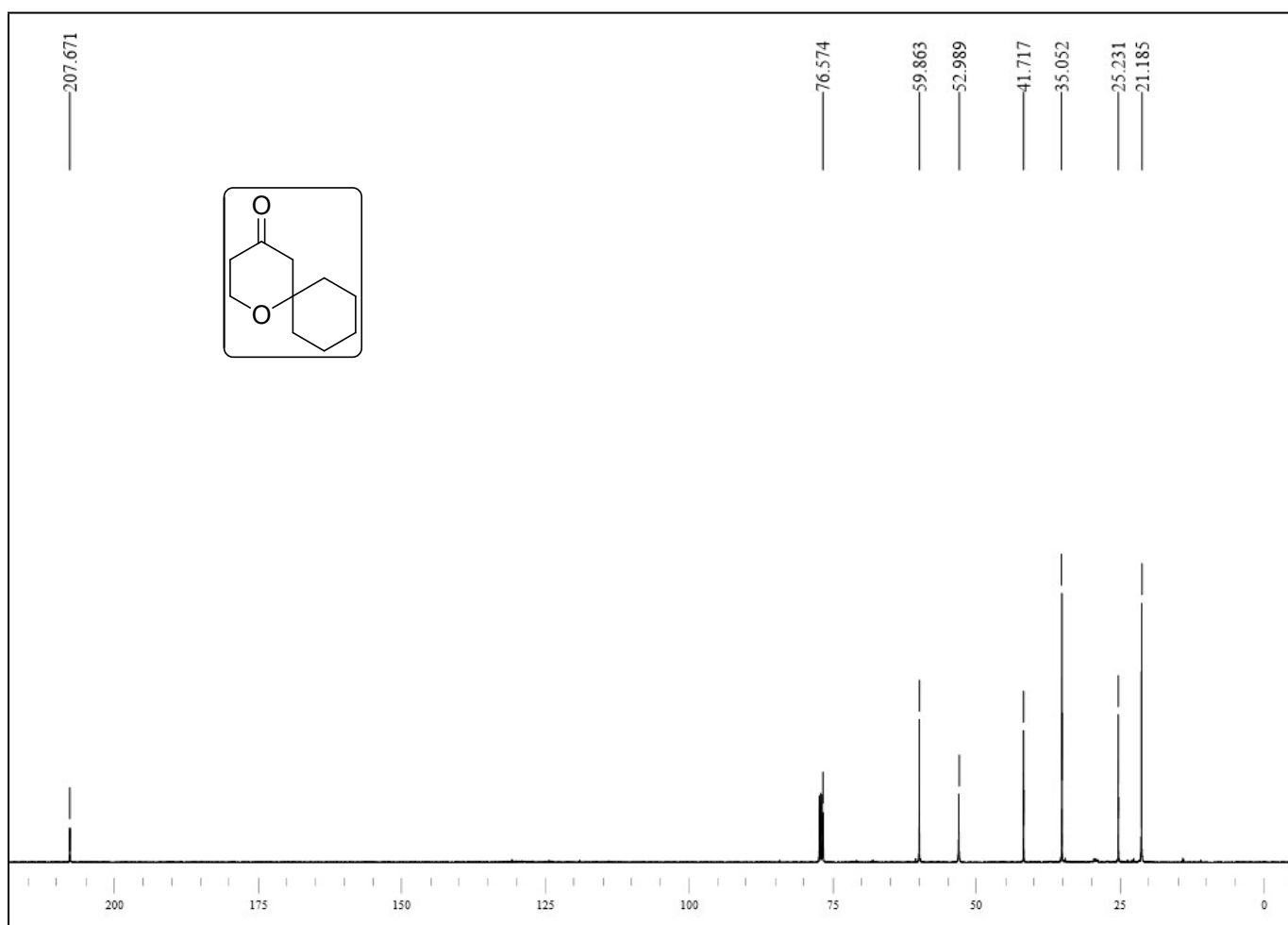
$^1\text{H}$  NMR spectrum of compound **3p**



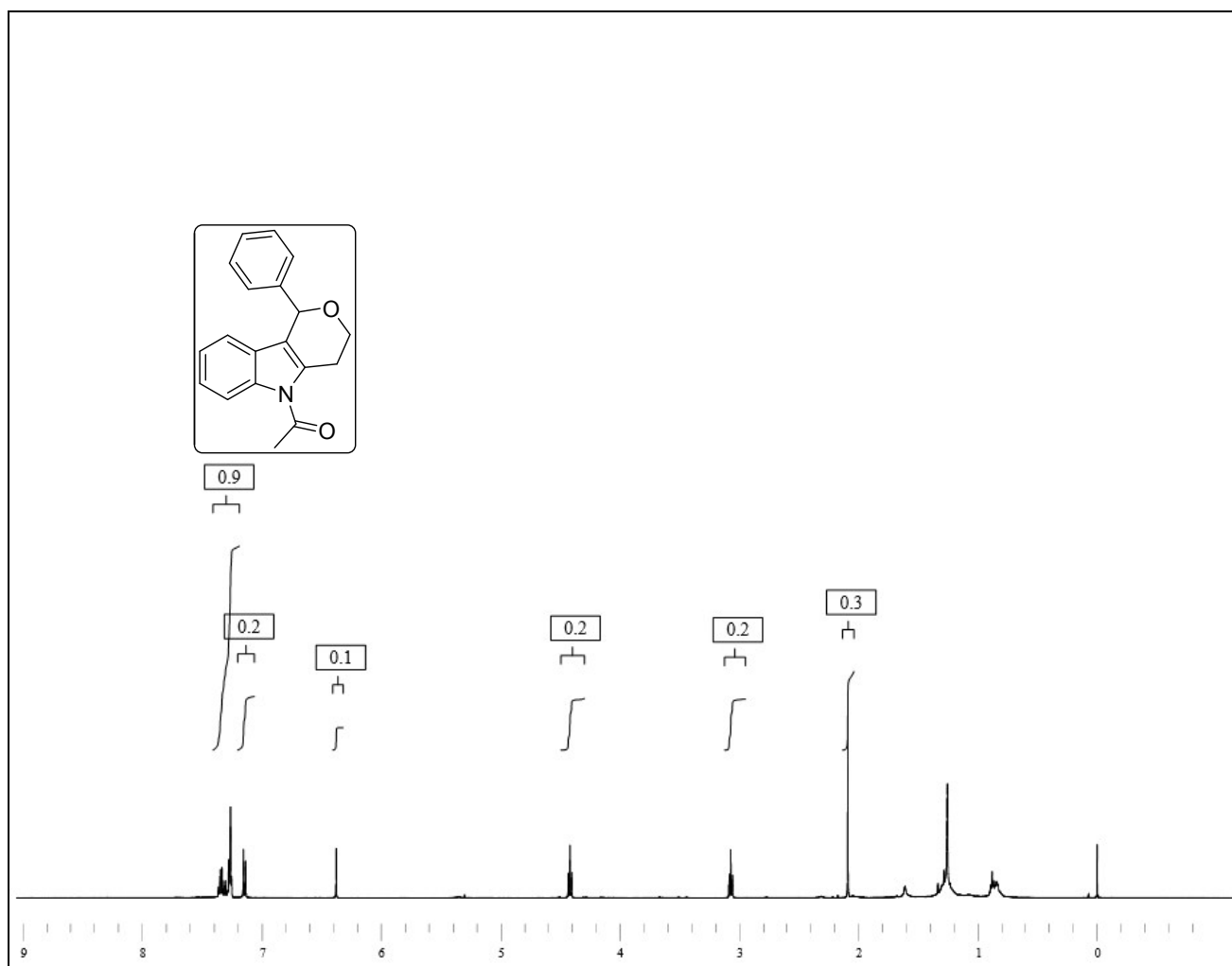
<sup>13</sup>C NMR spectrum of compound **3p**



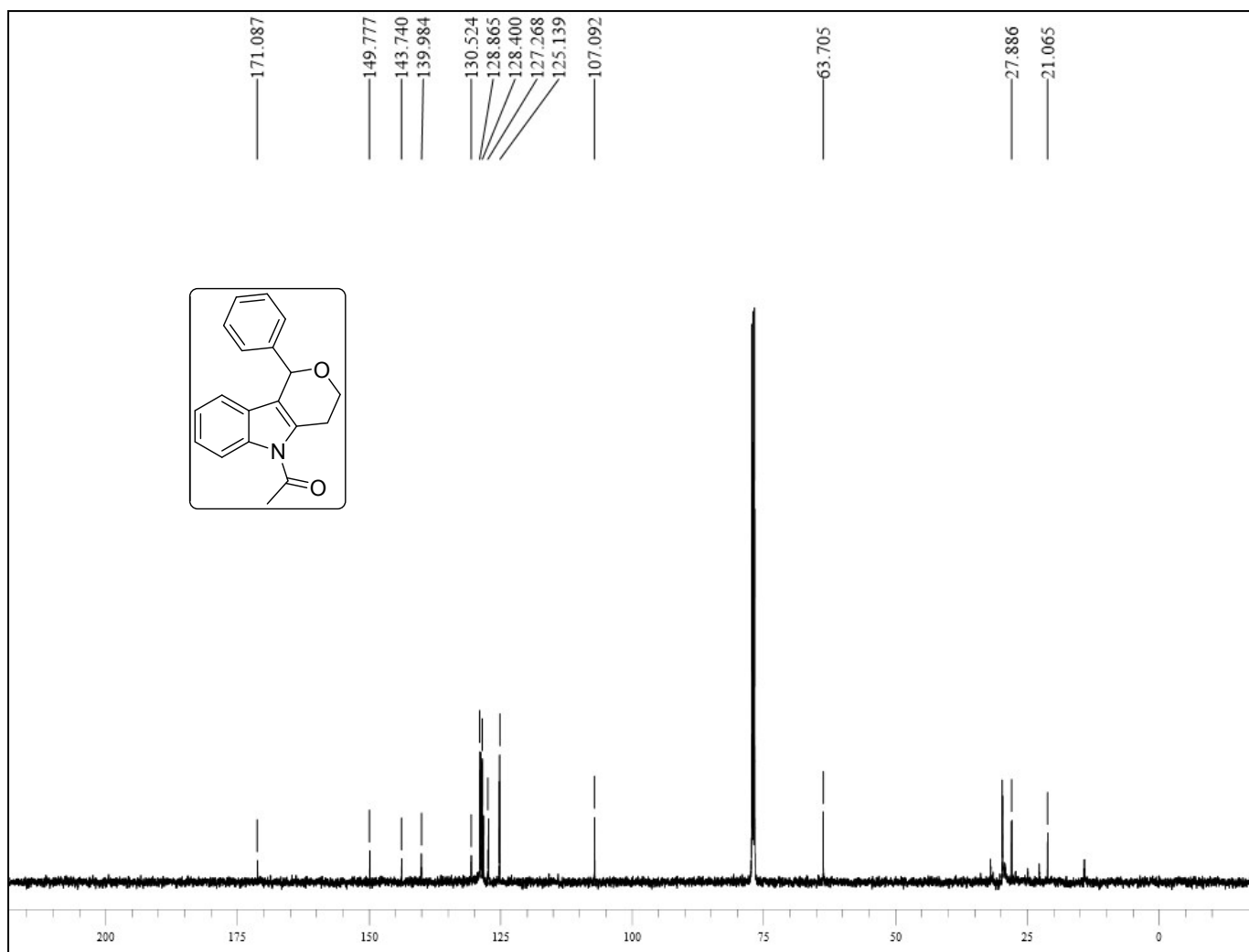
<sup>1</sup>H NMR spectrum of compound **3q**



$^{13}\text{C}$  NMR spectrum of compound **3q**

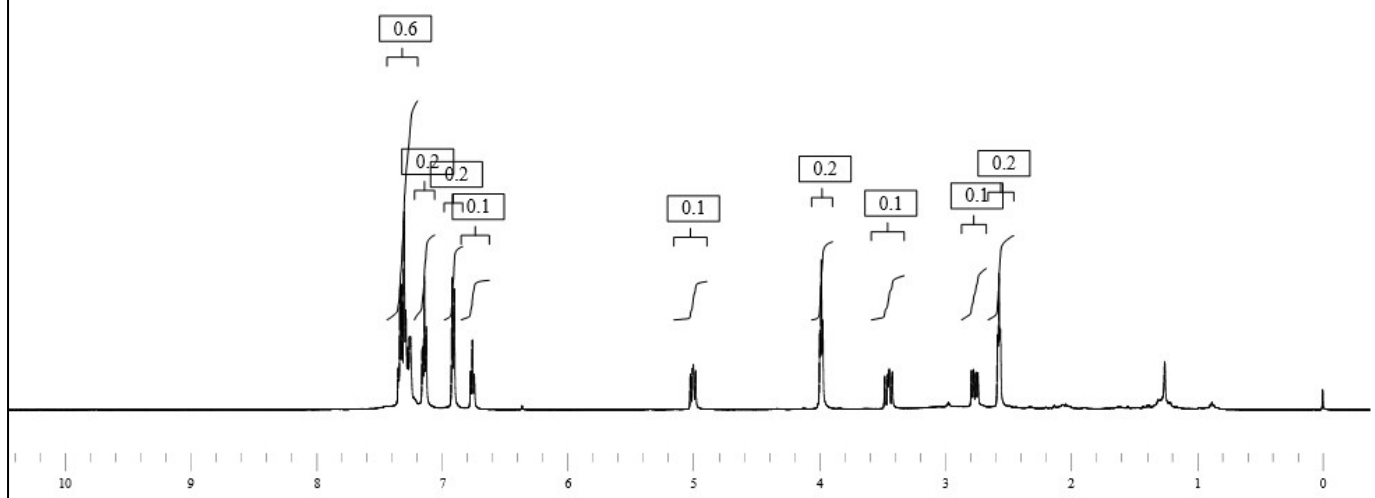
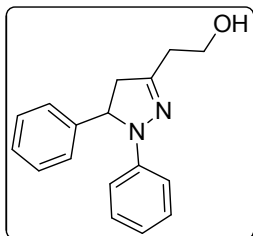


<sup>1</sup>H NMR spectrum of compound 7a (major)

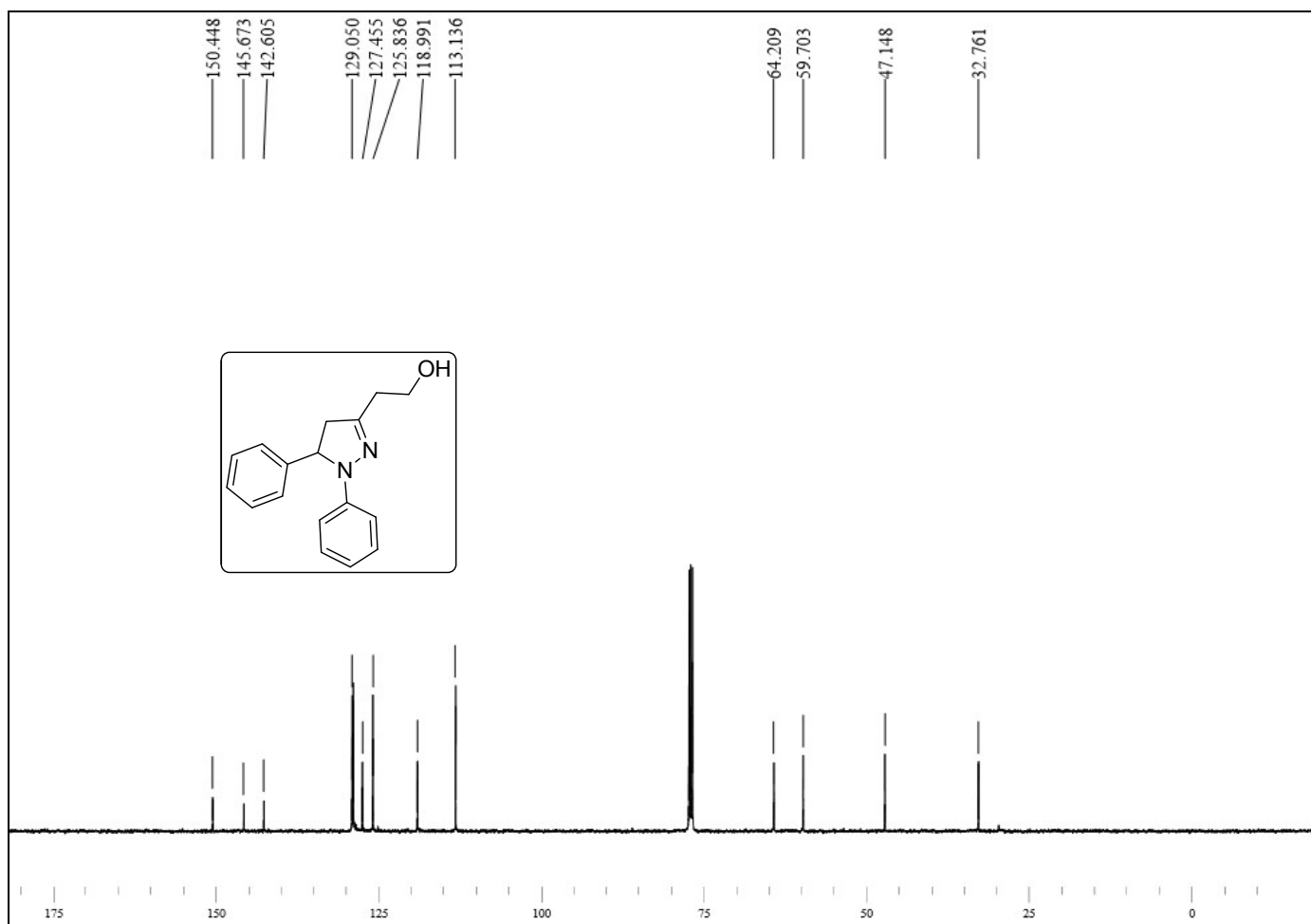


<sup>13</sup>C NMR spectrum of compound 7a (major)

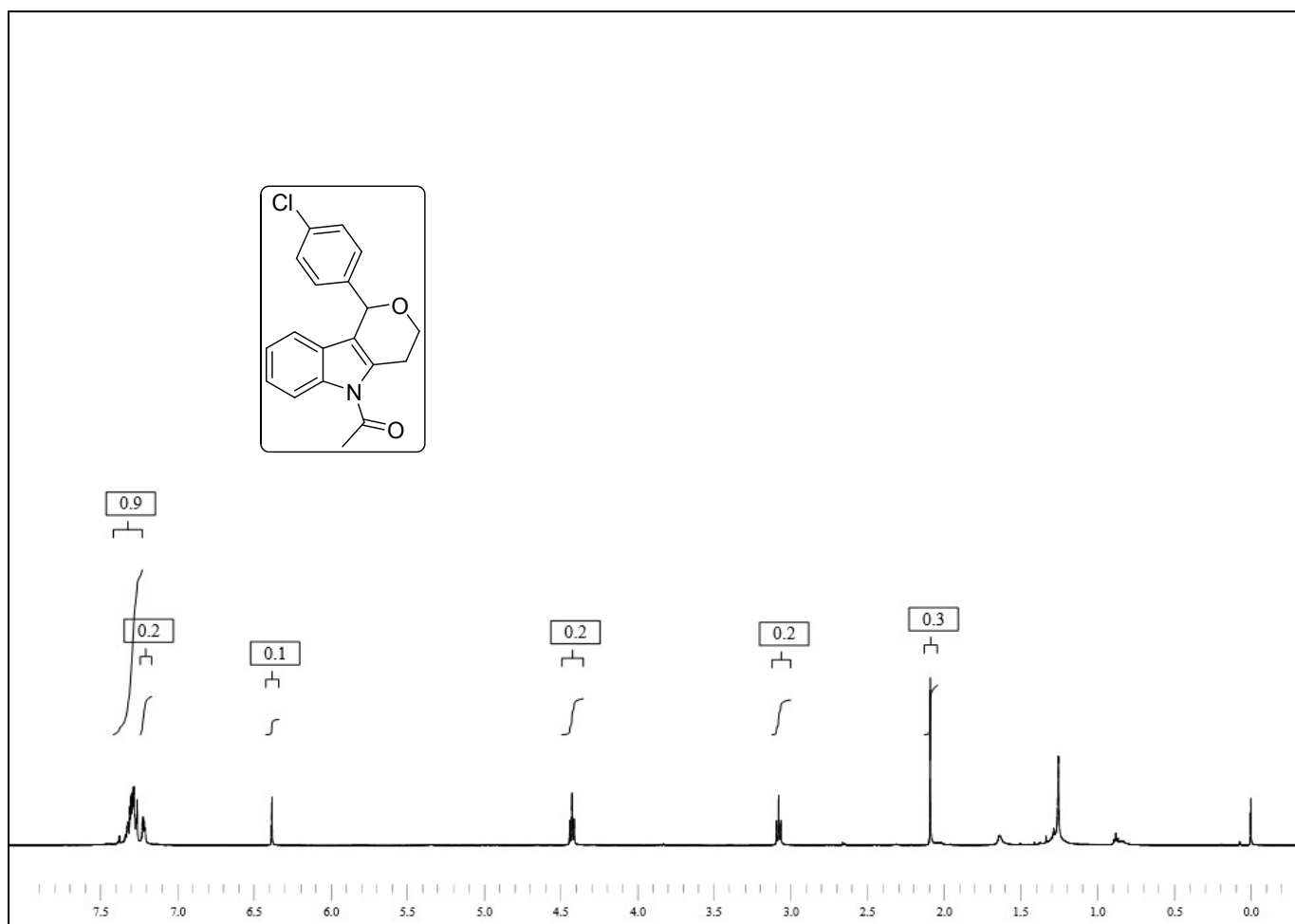




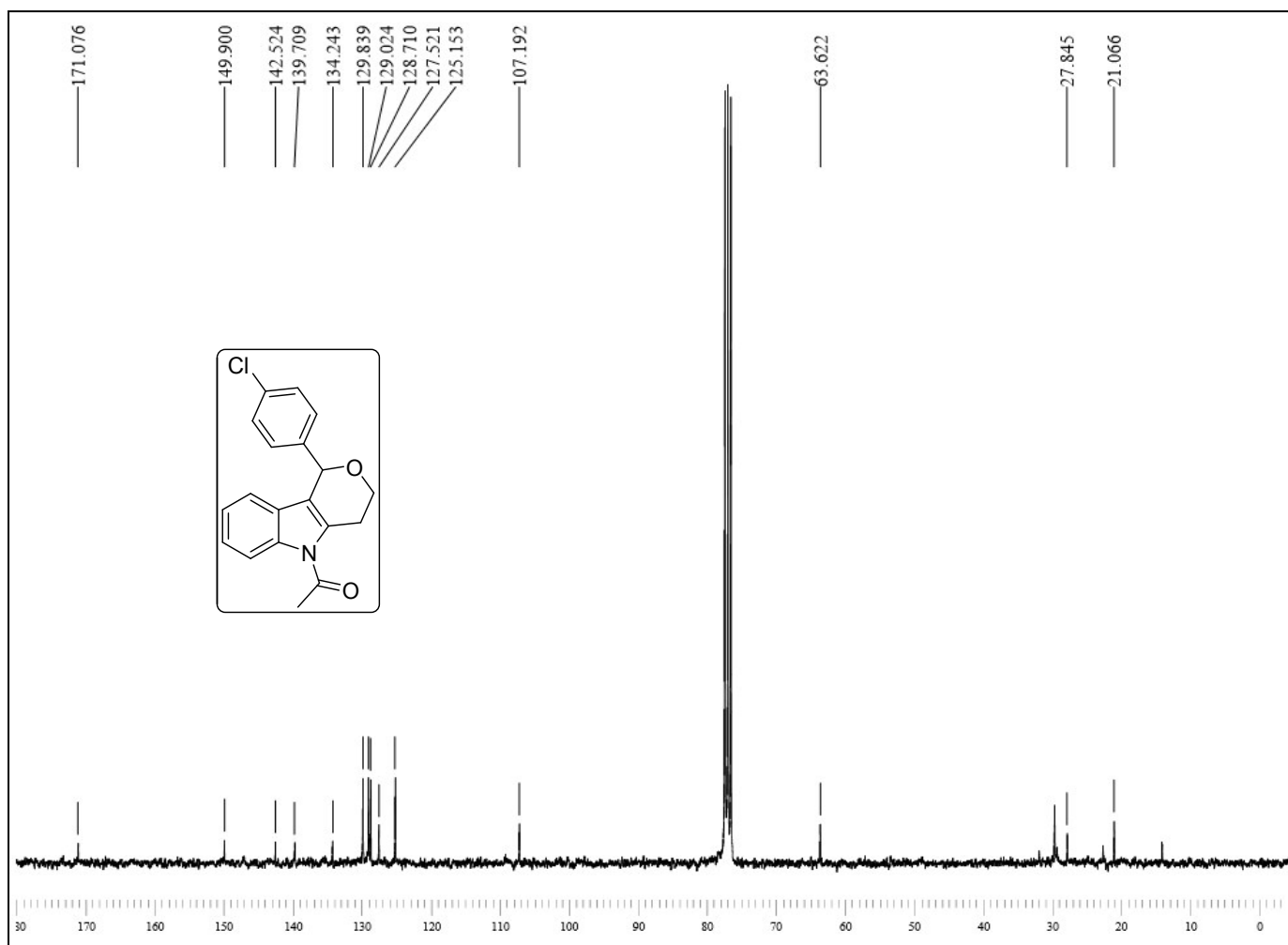
$^1\text{H}$  NMR spectrum of compound **8a (minor)**



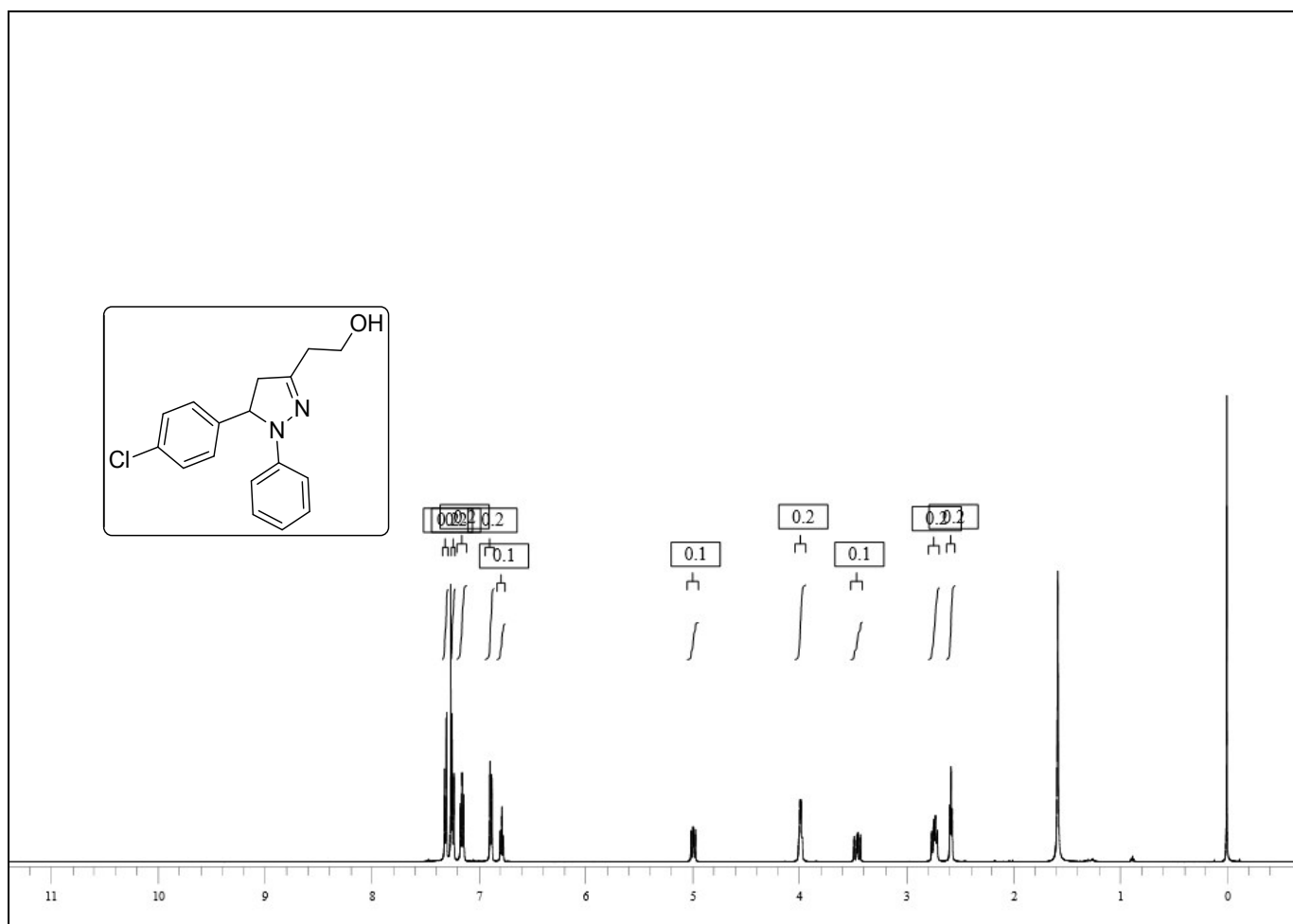
$^{13}\text{C}$  NMR spectrum of compound **8a (minor)**



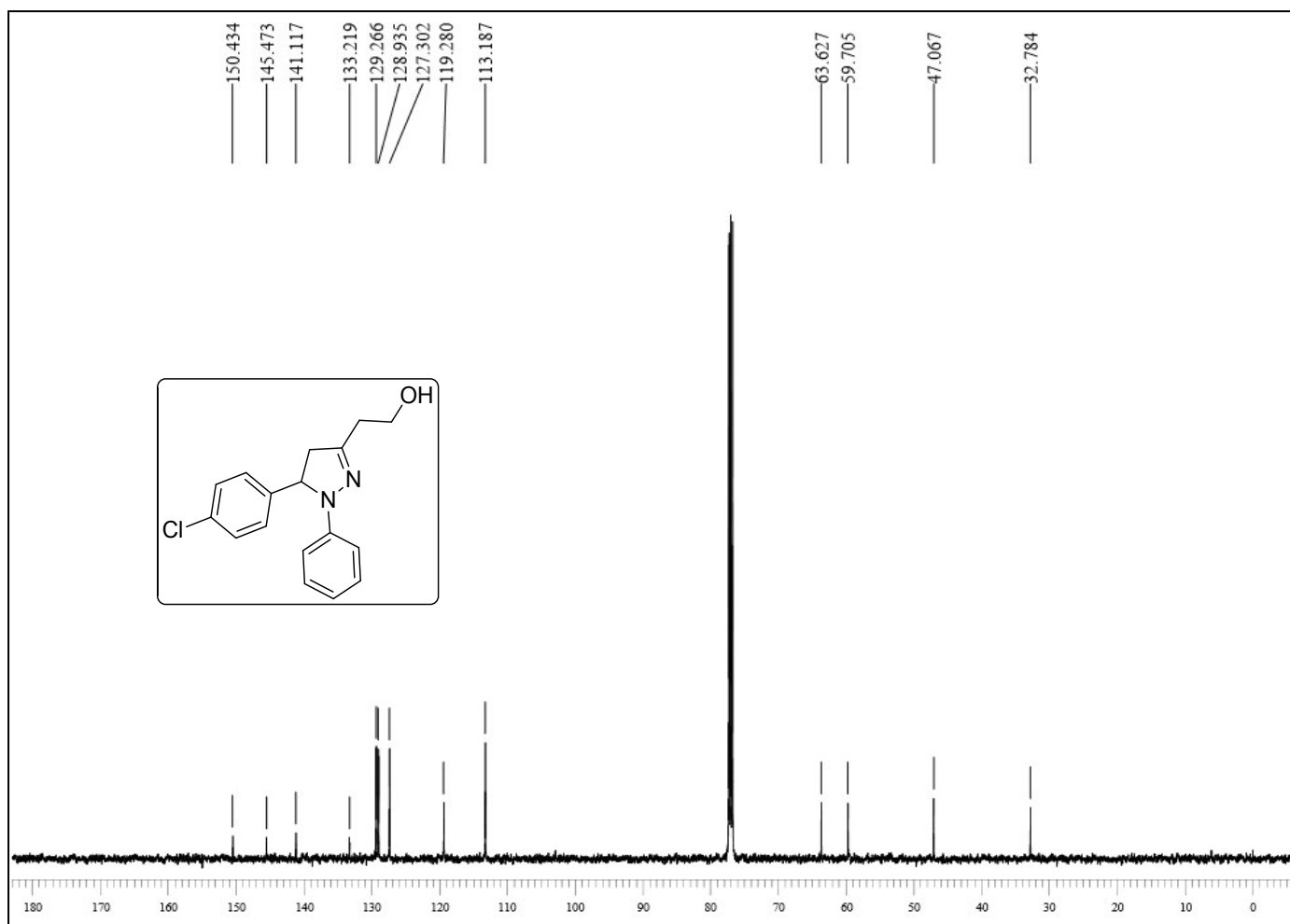
<sup>1</sup>H NMR spectrum of compound 7c (major)



<sup>13</sup>C NMR spectrum of compound 7c (major)



<sup>1</sup>H NMR spectrum of compound **8c** (minor)



<sup>13</sup>C NMR spectrum of compound **8c** (minor)

#### 4. X-ray Crystallography

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ) with  $\omega$ -scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data was accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. O-bound and C-bound H atoms were located in a difference density map but were positioned geometrically and included as riding atoms, with O-H distance = 0.82  $\text{\AA}$  and C—H distance = 0.93–0.97  $\text{\AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C and O})$  and  $1.2U_{\text{eq}}(\text{C})$  for the other H atoms. . The methyl groups were allowed to rotate but not to tip. Owing to the poor quality and diffraction ability of the crystal, the data set contains a large number of weak high-angle reflections, which accounts for the high K values in the analysis of variance. Hence, the SHEL command was used to cut off the weak high-angle reflections.

**Crystal Data for 8c:**  $\text{C}_{17}\text{H}_{17}\text{N}_2\text{OCl}$  ( $M=300.79$ ): triclinic, space group P-1 (no. 2),  $a = 5.479(3)\text{\AA}$ ,  $b = 7.926(4)\text{\AA}$ ,  $c = 18.296(9)\text{\AA}$ ,  $\alpha = 78.658(8)^\circ$ ,  $\beta = 86.196(8)^\circ$ ,  $\gamma = 79.757(8)^\circ$ ,  $V = 766.2(6)\text{\AA}^3$ ,  $Z = 2$ ,  $T = 294.15\text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.250\text{ mm}^{-1}$ ,  $D_{\text{calc}} = 1.3036\text{ g/mm}^3$ , 8327 reflections measured ( $4.54 \leq 2\Theta \leq 56.66$ ), 3488 unique ( $R_{\text{int}} = 0.0934$ ) which were used in all calculations. The final  $R_1$  was 0.1306 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.2288 (all data). CCDC 1440304 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.