

# **Hg(OAc)<sub>2</sub>•0.1Sc(OTf)<sub>3</sub>-Catalyzed Cycloisomerization of 2-(4-Pentynyl)-furan**

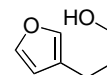
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Experimental Part	2-9
<sup>1</sup> H and <sup>13</sup> C NMR	10-55

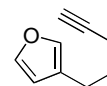
### 3-(3-Furanyl)propan-1-ol

This compound was prepared following the reported procedure. [Uenishi, J.; Kawahama, R.; Yonemitsu, O. *J. Org. Chem.* **1997**, 62, 1691-1701.]



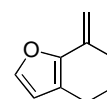
### 3-(4-Pentynyl)furan (1)

To a stirred solution of 3-(3-furanyl)propan-1-ol (2.7 g, 19.3 mmol) and Et<sub>3</sub>N (3.17 mL, 22.8 mmol) in DMSO (25 mL) was added a solution of C<sub>5</sub>H<sub>5</sub>N•SO<sub>3</sub> complex (3.6 g, 22.8 mmol) in DMSO (25 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. After the addition of saturated NH<sub>4</sub>Cl, organic materials were extracted with ether, and to the dried and concentrated extract dissolved in MeOH (160 mL) was added K<sub>2</sub>CO<sub>3</sub> (5.28 g, 38.3 mmol) and dimethyl-1-diazo-2-oxopropylphosphonate (4.4 g, 31.9 mmol). The mixture was stirred for 2 h at room temperature. After addition of brine, organic materials were extracted with Et<sub>2</sub>O. Dried and concentrated extract was subjected to column chromatography on silica gel using pentane as an eluent to give 3-(4-pentynyl)furan (**1**) (1.19 g, 46%) as a colorless oil. [*cf* Muller, S.; Liepold, B.; Roth, G. J.; Bestmann, H. J. *Synlett*, **1996**, 521-522.] FT IR (neat)  $\nu_{\max}$  3299, 3133, 3111, 2943, 2863, 2117 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz in CDCl<sub>3</sub>)  $\delta$  1.77 (2H, m), 1.98 (1H, t, *J* = 2.7 Hz), 2.22 (2H, dt, *J* = 6.8 Hz, 2.7 Hz), 2.55 (2H, t, *J* = 6.8 Hz), 6.28 (1H, br s), 7.24 (1H, br s), 7.35 (1H, t, *J* = 1.7 Hz); <sup>13</sup>C NMR (50 MHz in CDCl<sub>3</sub>)  $\delta$  17.70, 23.50, 28.61, 68.66, 83.95, 110.83, 123.95, 139.00, 142.73; MS (CI) *m/z* 135 (M<sup>+</sup>+H); HRMS (CI) *m/z* calcd for C<sub>9</sub>H<sub>11</sub>O (M<sup>+</sup>+H) 135.0810, found 135.0801.



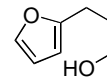
### 7-Methylene-4,5,6,7-tetrahydrobenzofuran (2)

To a stirred solution of 3-(4-pentynyl)furan (**1**) (500 mg, 37.9 mmol) in CH<sub>3</sub>CN (15 mL) was added Hg(OTf)<sub>2</sub>•3TMU complex (3.79mL, 0.1 M solution in CH<sub>3</sub>CN) at -20 °C and the mixture was stirred for 20 min at the same temperature. After addition of saturated NaHCO<sub>3</sub>, the organic materials were extracted with Et<sub>2</sub>O, and the dried and concentrated material was subjected to column chromatography on silica gel using pentane as an eluent to give 7-methylene-4,5,6,7-tetrahydrobenzofuran (**2**) in 81% yield (base on the NMR using naphthalene as the internal standard) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3091, 2934, 2849 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz in CDCl<sub>3</sub>)  $\delta$  1.83 (2H, m), 2.47 (2H, m), 2.54 (2H, t, *J* = 6.1 Hz), 4.74 (1H, br s), 5.21 (1H, br s), 6.25 (1H, d, *J* = 1.9 Hz), 7.28 (1H, d, *J* = 1.9 Hz); <sup>13</sup>C NMR (50 MHz in CDCl<sub>3</sub>)  $\delta$  22.91, 24.17, 31.52, 102.91, 111.04, 121.42, 134.58, 141.51, 149.89; MS (CI) *m/z* 135 (M<sup>+</sup>+H); HRMS (CI) *m/z* calcd for C<sub>9</sub>H<sub>11</sub>O (M<sup>+</sup>+H) 135.0810, found 135.0836.



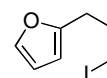
### 3-(2-Furanyl)propan-1-ol

3-(2-Furanyl)propan-1-ol (11.5 g, 91.2 mmol) was prepared from 2-furaldehyde (11.0 g, 115 mmol) according to the procedure described for 3-(3-furanyl)propan-1-ol as a colorless oil. [cf Uenishi, J.; Kawahama, R.; Yonemitsu, O. *J. Org. Chem.* **1997**, 62, 1691-1701]. FT IR (neat)  $\nu_{\max}$  3345, 2945, 2877, 1597, 1508  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  1.91 (2H, m), 2.74 (2H, t,  $J = 7.3$  Hz), 3.69 (2H, t,  $J = 6.3$  Hz), 6.01 (1H, m), 6.29 (1H, dd,  $J = 3.2$  Hz, 2.0 Hz), 7.31 (1H, dd,  $J = 2.0$  Hz, 0.73 Hz);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  24.09, 30.69, 61.46, 104.79, 109.95, 140.71, 155.46; MS (CI)  $m/z$  127 ( $\text{M}^+ + \text{H}$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_7\text{H}_{11}\text{O}_2$  ( $\text{M}^+ + \text{H}$ ) 235.9698, found 235.9705.



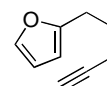
### 2-(3-Iodopropyl)furan

To a stirred solution of 3-(2-furanyl)-1-propanol (10 g, 79.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (260 mL) were added  $\text{Et}_3\text{N}$  (22.3 mL, 158 mmol), DMAP (4.9 g, 40.1 mmol) and *p*-toluenesulfonyl chloride (18.3 g, 96.0 mmol) at 0 °C and the mixture was stirred for 10 min at 0 °C and then at room temperature for 2 h. After addition of brine, organic materials were extracted with  $\text{CH}_2\text{Cl}_2$ . Dried and concentrated extract was purified by a column chromatography on silica gel using hexane as an eluent to give 3-(2-furanyl)propyl 4-methylbenzenesulfonate (19.0 g, 85 %). 3-(2-Furanyl)propyl 4-methylbenzenesulfonate (19.0 g, 67.9 mmol) was dissolved in DMF (200 mL), and to this was added NaI (12.2 g, 81.5 mmol) at 70 °C, and the mixture was stirred for 2 h at the same temperature under argon atmosphere. After addition of saturated  $\text{Na}_2\text{S}_2\text{O}_3$  and saturated  $\text{NaHCO}_3$ , organic materials were extracted with pentane. Dried and concentrated extract was subjected to column chromatography on silica gel using pentane as an eluent to give 2-(3-iodopropyl)furan (12.2 g, 76%) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3146, 3114, 3005, 2927, 2848, 1597, 1506  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  2.14 (2H, m), 2.76 (2H, t,  $J = 7.1$  Hz), 3.20 (2H, t,  $J = 6.8$  Hz), 6.05 (1H, m), 6.29 (1H, dd,  $J = 3.2$  Hz, 2.0 Hz), 7.31 (1H, dd,  $J = 2.0$  Hz, 0.73 Hz);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  26.28, 29.32 (2C), 103.51, 107.91, 139.00, 151.77; MS (CI)  $m/z$  236 ( $\text{M}^+$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_7\text{H}_9\text{OI}$  ( $\text{M}^+$ ) 235.9698, found 235.9705.



### 2-(4-Pentynyl)furan (3)

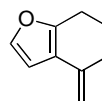
To a stirred solution of propargyltrimethylsilane (1.25 g, 12.8 mmol) in THF (21 mL) was added *n*-BuLi (1.6 M in hexane solution 7.7 mL) at 0 °C and the mixture was stirred for 30 min. To this was added a solution of 2-(3-iodopropyl)furan (2.00 g, 8.50 mmol) in HMPA (8 mL) at 0 °C, and the mixture was allowed to stir for 10 min at 0 °C. After addition of saturated  $\text{NH}_4\text{Cl}$ , organic materials were extracted with  $\text{Et}_2\text{O}$ . To the dried and concentrated extract dissolved in THF (28 mL) was added a solution of TBAF (1.0 M in THF 15 mL), and the mixture was stirred for 10 min at room temperature. After addition of  $\text{H}_2\text{O}$ , organic materials were extracted with pentane. Dried and



concentrated extract was subjected to column chromatography on silica gel using pentane as an eluent to give 2-(4-pentynyl)furan (**3**) (1.5 g, 87%) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3300, 3147, 3115, 2948, 2912, 2869, 2843, 2117  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  1.87 (2H, m), 1.98 (1H, t,  $J = 2.7$  Hz), 2.24 (2H, dt,  $J = 6.8$  Hz, 2.7 Hz), 2.76 (2H, t,  $J = 6.8$  Hz), 6.02 (1H, m), 6.28 (1H, dd,  $J = 3.2$  Hz, 2.0 Hz), 7.31 (1H, dd,  $J = 2.0$  Hz, 0.98 Hz);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  17.75, 26.76, 26.83, 68.77, 83.72, 105.23, 110.05, 140.93, 155.08; MS (CI)  $m/z$  135 ( $\text{M}^+\text{+H}$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_9\text{H}_{11}\text{O}$  ( $\text{M}^+\text{+H}$ ) 135.0810, found 135.0780.

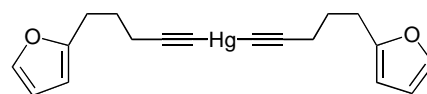
#### 4-Methylene-4,5,6,7-tetrahydrobenzofuran (**4**)

To a stirred solution of 2-(4-pentynyl)furan (**3**) (402 mg, 3.00 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was added  $\text{Hg}(\text{OAc})_2$  (15 mL, 0.01 M solution in  $\text{CH}_3\text{CN}$ ) and  $\text{Sc}(\text{OTf})_3$  (1.5 mL, 0.01 M solution in  $\text{CH}_3\text{CN}$ ), and the mixture was stirred for 20 min at 25 °C. After addition of saturated  $\text{NaHCO}_3$ , the organic materials were extracted with  $\text{Et}_2\text{O}$ . Dried and concentrated extract was subjected to column chromatography on silica gel using pentane as an eluent to give 4-methylene-4,5,6,7-tetrahydrobenzofuran (**4**) in 80% yield (base on the NMR using naphthalene as the internal standard) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3147, 3119, 3081, 2934, 2847, 1648  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  1.91 (2H, m), 2.41 (2H, m), 2.68 (2H, t,  $J = 6.3$  Hz), 4.77 (1H, br d,  $J = 1.7$  Hz), 4.99 (1H, d,  $J = 1.4$  Hz), 6.47 (1H, d,  $J = 1.9$  Hz), 7.24 (1H, d,  $J = 1.9$  Hz);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  23.38, 31.33 (2C), 104.82, 106.37, 119.22, 138.46, 141.17, 153.30; MS (CI)  $m/z$  135 ( $\text{M}^+\text{+H}$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_9\text{H}_{11}\text{O}$  ( $\text{M}^+\text{+H}$ ) 135.0809, found 135.0799.



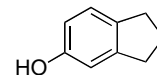
#### Bis[5-(2-furanyl)-1-pentynyl]mercury (**5**)

To a stirred solution of 2-(4-pentynyl)furan (**3**) (402 mg, 3.00 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was added  $\text{Hg}(\text{OAc})_2$  (15 mL, 0.01 M solution in  $\text{CH}_3\text{CN}$ ) at room temperature (25 °C). The mixture was stirred for 20 min at 25 °C. After the addition of saturated  $\text{NaHCO}_3$ , organic materials were extracted with  $\text{Et}_2\text{O}$ . Dried and concentrated extract was subjected to column chromatography on silica gel using hexane and ethyl acetate (5:1) as an eluent to give a small amount of bis[5-(2-furanyl)-1-pentynyl]mercury (**5**) as a colorless oil and recovery starting material **3** (90%). FT IR (neat)  $\nu_{\max}$  2942, 2903, 2866, 2159  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz in  $\text{CDCl}_3$ )  $\delta$  1.87 (2H, m), 2.31 (2H, t,  $J = 6.6$  Hz), 2.76 (2H, t,  $J = 6.6$  Hz), 6.01 (1H, m), 6.28 (1H, dd,  $J = 3.0$ , 1.8 Hz), 7.30 (1H, dd,  $J = 1.8$ , 0.9 Hz);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  18.83, 26.98, 27.24, 105.26, 107.34, 110.14, 111.32, 140.94, 155.24; MS (CI)  $m/z$  469 ( $\text{M}^+\text{+1}$ ), 266 (42), 133 (100); HRMS (CI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{18}\text{HgO}_2$  ( $\text{M}^+\text{+1}$ ) 469.1092, found 469.1082.



### 5-Hydroxy-2, 3-dihydro-1*H*-indene (6)

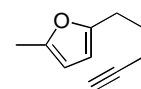
To a stirred solution of 2-(4-pentynyl)furan (**3**) (50 mg, 0.373 mmol) in acetone (1 mL) was added PtCl<sub>2</sub> (4.69 mg, 1.86 μmol), and the mixture was stirred at reflux for 10 h.



After the addition of H<sub>2</sub>O, organic materials were extracted with Et<sub>2</sub>O. Dried and concentrated extract was subjected to column chromatography on silica gel using hexane and ethyl acetate (6:1) as an eluent to give a 10:1 mixture of 5-hydroxy-2, 3-dihydro-1*H*-indene (**6**) and an unidentified product in 72% yield as a colorless oil. FT IR (neat)  $\nu_{\max}$  3344, 2951, 2844 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz in CDCl<sub>3</sub>)  $\delta$  2.06 (2H, m), 2.83 (4H, m), 6.60 (1H, dd,  $J$  = 8.1 Hz, 2.4 Hz), 6.71 (1H, br s), 7.06 (1H, d,  $J$  = 8.1 Hz); <sup>13</sup>C NMR (75 MHz in CDCl<sub>3</sub>)  $\delta$  25.81, 31.91, 33.00, 111.41, 112.99, 124.88, 136.27, 146.02, 154.07; MS (CI)  $m/z$  135 (M<sup>+</sup>+H), 134 (M<sup>+</sup>), 103 (8); HRMS (CI)  $m/z$  calcd for C<sub>9</sub>H<sub>10</sub>O (M<sup>+</sup>) 134.0732, found 134.0718.

### 2-Methyl-5-(4-pentynyl)furan (**13**)

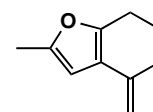
Compound (**13**) was prepared from 5-methyl-2-furaldehyde according to the procedure described for 2-(4-pentynyl)furan (**3**) as a colorless oil.



FT IR (neat)  $\nu_{\max}$  3301, 3104, 2948, 2922, 2869, 2843, 2118 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz in CDCl<sub>3</sub>)  $\delta$  1.56 (2H, m), 1.97 (1H, t,  $J$  = 2.6 Hz), 2.24 (2H, dt,  $J$  = 7.0 Hz, 2.6 Hz), 2.25 (3H, d,  $J$  = 0.74 Hz), 2.69 (2H, t,  $J$  = 7.3 Hz), 5.84 (1H, m), 5.88 (1H, d,  $J$  = 3.3 Hz); <sup>13</sup>C NMR (50 MHz in CDCl<sub>3</sub>)  $\delta$  13.31, 17.69, 26.83, 26.93, 68.64, 83.85, 105.80, 105.86, 150.40, 153.29; MS (CI)  $m/z$  148 (M<sup>+</sup>); HRMS (CI)  $m/z$  calcd for C<sub>10</sub>H<sub>12</sub>O (M<sup>+</sup>) 148.0888, found 148.0868.

### 2-Methyl-4-methylene-4,5,6,7-tetrahydrobenzofuran (**14**)

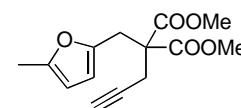
Compound **14** was prepared from 2-methyl-5-(4-pentynyl)furan (**13**) according to the procedure described for 4-methylene-4,5,6,7-tetrahydrobenzofuran (**4**).



FT IR (neat)  $\nu_{\max}$  3080, 2934, 2846 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz in CDCl<sub>3</sub>)  $\delta$  1.89 (2H, m), 2.26 (3H, br s), 2.36 (2H, m), 2.64 (2H, t,  $J$  = 6.2 Hz), 4.72 (1H, br s), 4.91 (1H, d,  $J$  = 1.1 Hz), 6.06 (1H, d,  $J$  = 1.1 Hz); <sup>13</sup>C NMR (50 MHz in CDCl<sub>3</sub>)  $\delta$  13.54, 23.33, 23.49, 31.32, 102.18, 104.22, 120.02, 138.80, 150.83, 151.72; MS (CI)  $m/z$  148 (M<sup>+</sup>); HRMS (CI)  $m/z$  calcd for C<sub>10</sub>H<sub>12</sub>O (M<sup>+</sup>) 148.0888, found 148.0872.

### Dimethyl 2-[(5-methyl-2-furanyl)methyl]-2-(2-propynyl)propanedioate (**15**)

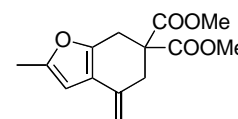
To a stirred suspension of NaH (211 mg, 8.81 mmol) in DMF (20 mL) was dropwise added dimethyl 2-(2-propynyl)malonate (1.0 g, 5.87 mmol), and the mixture was stirred for 30 min 0°C. To this was added 2-(bromomethyl)-5-methylfuran (1.03 g, 5.90



mmol), and the mixture was stirred for 90 min at 0 °C. After addition of H<sub>2</sub>O, organic materials were extracted with ether, and the dried and concentrated extract was subjected to column chromatography on silica gel using hexane and ethyl acetate (25:1) as an eluent to give dimethyl 2-[(5-methyl-2-furanyl)methyl]-2-(2-propynyl)-propanedioate (**15**) (600 mg, 38 %) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3291, 3105, 3003, 2954, 2925, 2844, 2122, 1758 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz in CDCl<sub>3</sub>)  $\delta$  2.06 (1H, t,  $J$  = 2.7 Hz), 2.20 (3H, d,  $J$  = 0.48 Hz), 2.77 (2H, d,  $J$  = 2.7 Hz), 3.39 (2H, s), 3.77 (6H, s), 5.84 (1H, m), 6.01 (1H, d,  $J$  = 3.2 Hz); <sup>13</sup>C NMR (50 MHz in CDCl<sub>3</sub>)  $\delta$  13.23, 22.46, 30.74, 52.66, 56.71, 71.49, 78.80, 106.06, 109.44, 147.86, 151.60, 169.83; MS (CI)  $m/z$  265 (M<sup>+</sup>+H); HRMS (CI)  $m/z$  calcd for C<sub>14</sub>H<sub>17</sub>O<sub>5</sub> (M<sup>+</sup>+H) 265.1076, found 265.1071.

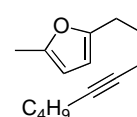
### Dimethyl 2-methyl-4-methylene-4,5-dihydrobenzofuran-6,6(7H)-dicarboxylate (**16**)

Compound **16** was prepared from dimethyl 2-[(5-methyl-2-furanyl)methyl]-2-(2-propynyl) propanedioate (**15**) according to the procedure described for 4-methylene-4,5,6,7-tetrahydrobenzo furan (**4**) as a colorless oil. FT IR (neat)  $\nu_{\max}$  2995, 2954, 2922, 2844, 1743 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz in CDCl<sub>3</sub>)  $\delta$  2.25 (3H, d,  $J$  = 1.0 Hz), 2.95 (2H, t,  $J$  = 1.2 Hz), 3.24 (2H, s), 3.72 (6H, s), 4.86 (1H, br s), 5.02 (1H, d,  $J$  = 1.2 Hz), 6.02 (1H, d,  $J$  = 1.0 Hz); <sup>13</sup>C NMR (50 MHz in CDCl<sub>3</sub>)  $\delta$  13.56, 29.42, 37.06, 52.95, 55.17, 102.07, 107.16, 119.51, 133.89, 147.94, 152.02, 170.76; MS (CI)  $m/z$  265 (M<sup>+</sup>+H); HRMS (CI)  $m/z$  calcd for C<sub>14</sub>H<sub>17</sub>O<sub>5</sub> (M<sup>+</sup>+H) 265.1076, found 265.1071.



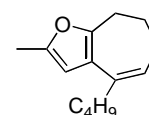
### 2-Methyl-5-(4-nonyl)furan (**17**)

Compound **17** was prepared from 2-(3-iodopropyl)-5-methylfuran and 1-hexyne according to the procedure described for 2-(4-pentynyl)furan (**3**) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3104, 2956, 2932, 2863, 1647, 1617, 1569 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz in CDCl<sub>3</sub>)  $\delta$  0.91 (3H, t,  $J$  = 7.3 Hz), 1.44 (4H, m), 1.79 (2H, m), 2.17 (4H, m), 2.25 (3H, s), 2.67 (2H, t,  $J$  = 7.7 Hz), 5.85 (2H, m); <sup>13</sup>C NMR (50 MHz in CDCl<sub>3</sub>)  $\delta$  13.51, 13.64, 18.29, 18.46, 21.96, 27.13, 27.67, 31.26, 79.42, 80.80, 105.63, 105.78, 150.28, 153.78; MS (CI)  $m/z$  205 (M<sup>+</sup>+H); HRMS (CI)  $m/z$  calcd for C<sub>14</sub>H<sub>21</sub>O (M<sup>+</sup>+H) 205.1593, found 205.1584.



### (Z)-4-Butyl-2-methyl-7,8-dihydro-6H-cyclohepta[b]furan (**18**)

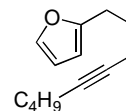
Compound **18** was prepared from 2-methyl-5-(4-nonyl)furan (**17**) according to the procedure described for 4-methylene-4,5,6,7-tetrahydrobenzofuran (**4**) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3111, 3055, 2958, 2930, 2860, 1709, 1644, 1577 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz in CDCl<sub>3</sub>)  $\delta$  0.91 (3H, t,  $J$  = 8.8 Hz), 1.34 (2H, m), 1.44 (2H, m), 1.83 (2H, m), 2.22 (2H, t,  $J$  = 7.9



Hz), 2.24 (3H, s), 2.26 (2H, m), 2.90 (2H, t,  $J = 6.6$  Hz), 5.53 (1H, t,  $J = 6.0$  Hz), 5.91 (1H, d,  $J = 0.82$ );  $^{13}\text{C}$  NMR (150 MHz in  $\text{CDCl}_3$ )  $\delta$  13.34, 14.00, 22.44, 22.85, 28.65, 29.97, 31.61, 36.56, 105.91, 120.14, 124.81, 131.98, 149.05, 151.74; MS (CI)  $m/z$  205 ( $\text{M}^+\text{H}$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{21}\text{O}$  ( $\text{M}^+\text{H}$ ) 205.1593, found 205.1580.

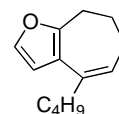
### 2-(4-nonyl)furan (19)

Compound **19** was prepared from 2-(3-iodopropyl)furan and 1-hexyne according to the procedure described for 2-(4-pentynyl)furan (**3**) as a colorless oil. FT IR (neat)  $\nu_{\text{max}}$  3146, 3114, 2958, 2933, 2863, 1597  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  0.91 (3H, t,  $J = 7.3$  Hz), 1.45 (4H, m), 1.81 (2H, m), 2.18 (4H, m), 2.73 (2H, t,  $J = 7.0$  Hz), 6.00 (1H, m), 6.27 (1H, dd,  $J = 3.3$  Hz, 1.8 Hz), 7.30 (1H, dd,  $J = 1.8$  Hz, 0.73 Hz);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  13.48, 18.12, 18.31, 21.83, 26.88, 27.44, 31.15, 79.20, 80.79, 105.01, 110.03, 140.86, 155.62; MS (CI)  $m/z$  190 ( $\text{M}^+$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{18}\text{O}$  ( $\text{M}^+$ ) 190.1358, found 190.1349.



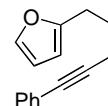
### (Z)-4-butyl-7,8-dihydro-6H-cyclohepta[b]furan (20)

Compound **20** was prepared from 2-(4-nonyl)furan (**19**) according to the procedure described for 4-methylene-4,5,6,7-tetrahydrobenzofuran (**4**) as a colorless oil. FT IR (neat)  $\nu_{\text{max}}$  3023, 2954, 2930, 2860, 1596, 1518  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  0.91 (3H, t,  $J = 7.3$  Hz), 1.39 (4H, m), 1.86 (2H, m), 2.28 (4H, m), 2.95 (2H, t,  $J = 6.6$  Hz), 5.58 (1H, t,  $J = 6.1$  Hz), 6.32 (1H, d,  $J = 2.0$  Hz), 7.24 (1H, d,  $J = 2.0$  Hz);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  14.02, 22.45, 22.72, 28.74, 29.97, 31.58, 36.56, 110.11, 119.53, 125.25, 131.66, 139.73, 153.57; MS (CI)  $m/z$  191 ( $\text{M}^+\text{H}$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{19}\text{O}$  ( $\text{M}^+\text{H}$ ) 191.1436, found 191.1461.



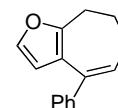
### 2-(5-Phenyl-4-pentynyl)furan (21)

Compound **21** was prepared from 2-(3-iodopropyl)furan and ethynylbenzene according to the procedure described for 2-(4-pentynyl)furan (**3**) as a colorless oil. FT IR (neat)  $\nu_{\text{max}}$  3142, 3114, 3080, 3055, 3033, 2941, 2906, 2867, 2839, 2225, 1950, 1879, 1804, 1750, 1716, 1670  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  1.95 (2H, m), 2.46 (2H, t,  $J = 7.3$  Hz), 2.81 (2H, t,  $J = 7.3$  Hz), 6.05 (1H, m), 6.29 (1H, dd,  $J = 2.9$  Hz, 1.8 Hz), 7.30 (3H, m), 7.39 (2H, m);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  18.72, 26.93, 27.04, 81.17, 89.42, 105.24, 110.11, 123.93, 127.59, 128.21 (2C), 131.58 (2C), 140.99, 155.33; MS (CI)  $m/z$  210 ( $\text{M}^+$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{O}$  ( $\text{M}^+$ ) 210.1045, found 210.1050.



### (Z)-4-Phenyl-7,8-dihydro-6H-cyclohepta[b]furan (22)

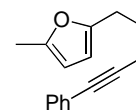
Compound **22** was prepared from 2-(5-phenyl-4-pentynyl)furan (**21**) according to the



procedure described for 4-methylene-4,5,6,7-tetrahydrobenzofuran (**4**) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3148, 3120, 3075, 3053, 3022, 2932, 2894, 2862, 2842, 1949, 1882, 1807, 1758, 1684, 1597  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  1.98 (2H, m), 2.44 (2H, dt,  $J = 6.6$  Hz, 4.4 Hz), 3.04 (2H, t,  $J = 6.6$  Hz), 5.89 (1H, t,  $J = 6.6$  Hz), 6.02 (1H, d,  $J = 2.2$  Hz), 7.20 (1H, d,  $J = 1.8$  Hz), 7.32 (5H, m);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  23.37, 28.63, 29.65, 112.10, 119.28, 126.81, 128.04 (2C), 128.21 (2C), 129.20, 134.82, 139.54, 143.07, 154.48; MS (CI)  $m/z$  211 ( $\text{M}^+\text{+H}$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{O}$  ( $\text{M}^+\text{+H}$ ) 211.1123, found 211.1102.

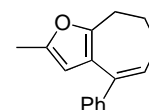
### 2-methyl-5-(5-phenyl-4-pentynyl)furan (**23**)

Compound **23** was prepared from 2-(3-iodopropyl)-5-methylfuran and ethynylbenzene according to the procedure described for 2-(4-pentynyl)furan (**3**) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3102, 3080, 3055, 3033, 3021, 2946, 2922, 2866, 2840, 2226, 1950, 1878, 1804, 1752, 1657, 1616, 1597, 1569  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  1.92 (2H, m), 2.26 (3H, s), 2.46 (2H, t,  $J = 6.8$  Hz), 2.75 (2H, t,  $J = 7.6$  Hz), 5.85 (1H, br d,  $J = 2.7$  Hz), 5.90 (1H, br d,  $J = 3.2$  Hz), 7.28 (3H, m), 7.39 (2H, m);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  13.47, 18.84, 27.14, 27.25, 81.10, 89.57, 105.83 (2C), 123.93, 127.53, 128.16 (2C), 131.53 (2C), 150.34, 153.41; MS (CI)  $m/z$  224 ( $\text{M}^+$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}$  ( $\text{M}^+$ ) 224.1202, found 224.1208.



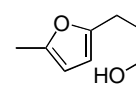
### (Z)-2-Methyl-4-phenyl-7,8-dihydro-6H-cyclohepta[b]furan (**24**)

Compound **24** was prepared from 2-methyl-5-(5-phenyl-4-pentynyl)furan (**23**) according to the procedure described for 4-methylene-4,5,6,7-tetrahydrobenzofuran (**4**) as a colorless oil. FT IR (neat)  $\nu_{\max}$  3076, 3054, 3024, 2932, 2889, 2866, 2842, 1949, 1882, 1808, 1755, 1677, 1630, 1598, 1576  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  1.95 (2H, m), 2.19 (3H, s), 2.41 (2H, m), 2.99 (2H, t,  $J = 6.6$  Hz), 5.59 (1H, d,  $J = 1.1$  Hz), 5.83 (1H, t,  $J = 6.2$  Hz), 7.31 (5H, m);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  13.14, 23.47, 28.59, 29.70, 107.92, 119.86, 126.68, 127.94 (2C), 128.20 (2C), 128.71, 135.13, 143.22, 148.88, 152.68; MS (CI)  $m/z$  224 ( $\text{M}^+$ ); HRMS (CI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{O}$  ( $\text{M}^+$ ) 224.1201, found 224.1188.



### 3-(5-methyl-2-furanyl)-1-propanol

3-(5-Methyl-2-furanyl)-1-propanol (12.3 g, 87.9 mmol) was prepared from 5-methyl-2-furaldehyde (11.0 g, 100 mmol) according to the procedure of 3-(3-furanyl)propan-1-ol. FT IR (neat)  $\nu_{\max}$  3358, 3105, 2946, 2922, 2880, 1617, 1570  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz in  $\text{CDCl}_3$ )  $\delta$  1.88 (2H, m), 2.25 (3H, s), 2.68 (2H, t,  $J = 7.6$  Hz), 3.69 (2H, t,  $J = 6.3$  Hz), 5.84 (1H, dd,  $J = 2.9$  Hz, 0.98 Hz), 5.88 (1H, d,  $J = 2.9$  Hz);  $^{13}\text{C}$  NMR (50 MHz in  $\text{CDCl}_3$ )  $\delta$  13.30,

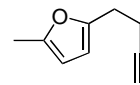


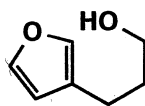


24.24, 30.93, 61.72, 105.45, 105.71, 150.18, 153.64; MS (CI)  $m/z$  141 ( $M^+ + H$ ); HRMS (CI)  $m/z$  calcd for  $C_8H_{13}O_2$  ( $M^+ + H$ ) 141.0915, found 141.0899.

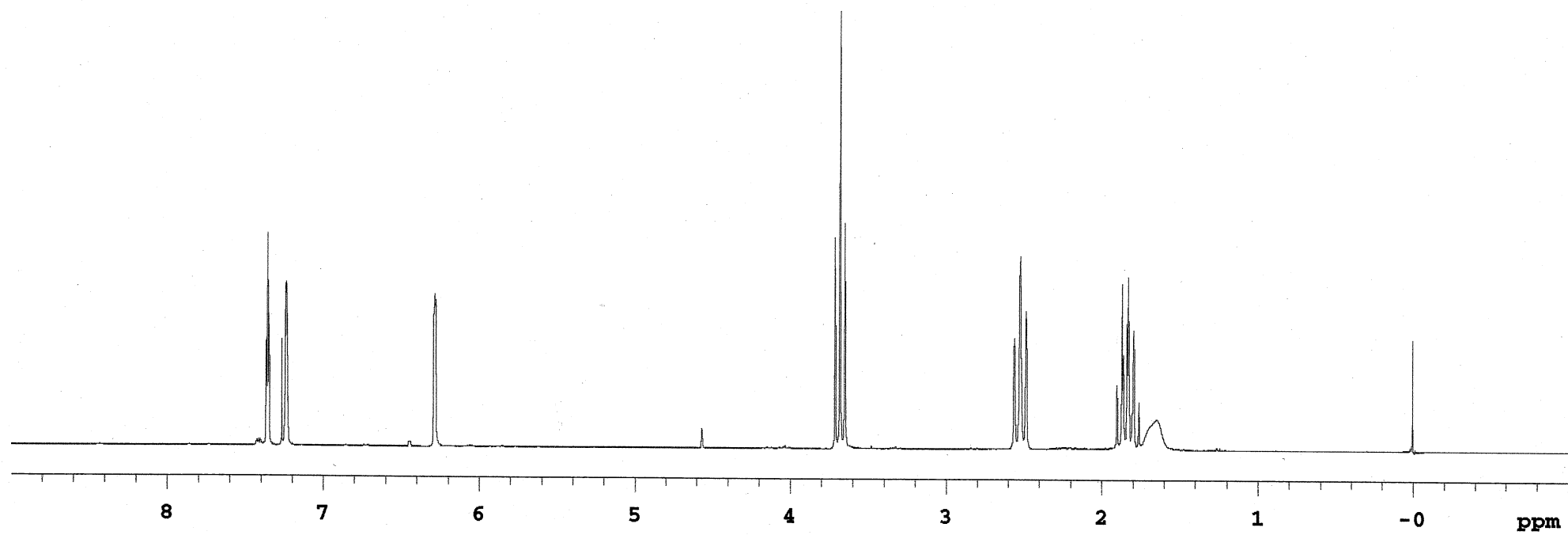
### 2-(3-butynyl)-5-methylfuran (**25**)

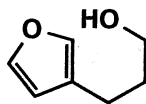
To a stirred solution of 3-(5-methyl-2-furanyl)-1-propanol (10 g, 71.3 mmol) and  $Et_3N$  (14.6 mL, 105 mmol) in DMSO (50 mL) was added a solution of  $C_5H_5N \cdot SO_3$  complex (16.7 g, 105 mmol) in DMSO (50 mL), and the mixture was stirred for 1 h at 0 °C. After the addition of saturated  $NH_4Cl$ , organic materials were extracted with ether, and to the dried and concentrated extract dissolved in  $CH_2Cl_2$  (300 mL) was added  $Et_3N$  (58 mL, 420 mmol), triphenylphosphine (73 g, 278 mmol) and  $CBr_4$  (33 g, 99.5 mmol) at -20 °C. The mixture was stirred for 20 min at -20 °C, and then warmed to room temperature. After addition of brine, the organic materials were extracted with ether. Insoluble materials were removed by the filtration through short path silica gel column. To the concentrated filtrate (4.90 g) was dissolved in THF (50 mL), and to this was added  $n-BuLi$  (1.6 M in hexane solution 21 mL) at -78 °C. The mixture was stirred for another 10 min at -78 °C, and warmed to room temperature. After addition of saturated  $NH_4Cl$ , organic materials were extracted with  $Et_2O$ . Dried and concentrated extract was subjected to column chromatography on silica gel using pentane as eluent to give 2-(3-butynyl)-5-methylfuran (**25**) (1.30 g, 58%) as a colorless oil. FT IR (neat)  $\nu_{max}$  3305, 3104, 2923, 2853, 2119, 1659, 1617, 1572  $cm^{-1}$ ;  $^1H$  NMR (200 MHz in  $CDCl_3$ )  $\delta$  1.98 (1H, t,  $J = 2.6$  Hz), 2.25 (3H, s), 2.50 (2H, dt,  $J = 7.3$  Hz, 2.6 Hz), 2.82 (2H, t,  $J = 7.3$  Hz), 5.86 (1H, dd,  $J = 2.9$  Hz, 1.1 Hz), 5.95 (1H, d,  $J = 2.9$  Hz);  $^{13}C$  NMR (50 MHz in  $CDCl_3$ )  $\delta$  13.30, 17.67, 27.37, 68.78, 83.33, 105.91, 106.20, 150.69, 152.20; MS (CI)  $m/z$  134 ( $M^+$ ); HRMS (CI)  $m/z$  calcd for  $C_9H_{10}O$  ( $M^+$ ) 134.0732, found 134.0728.



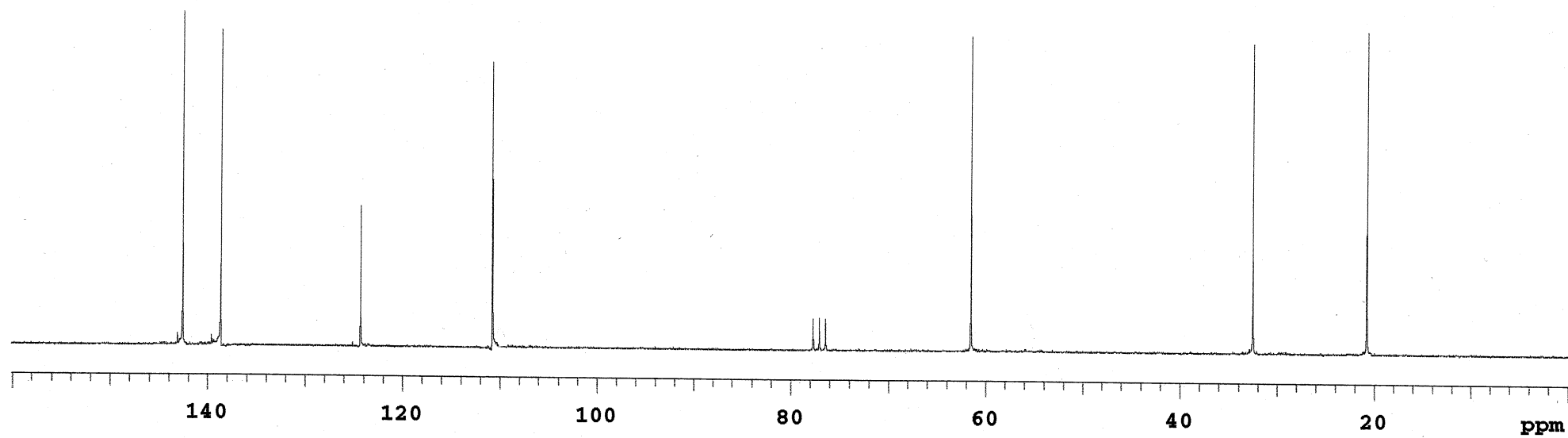


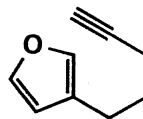
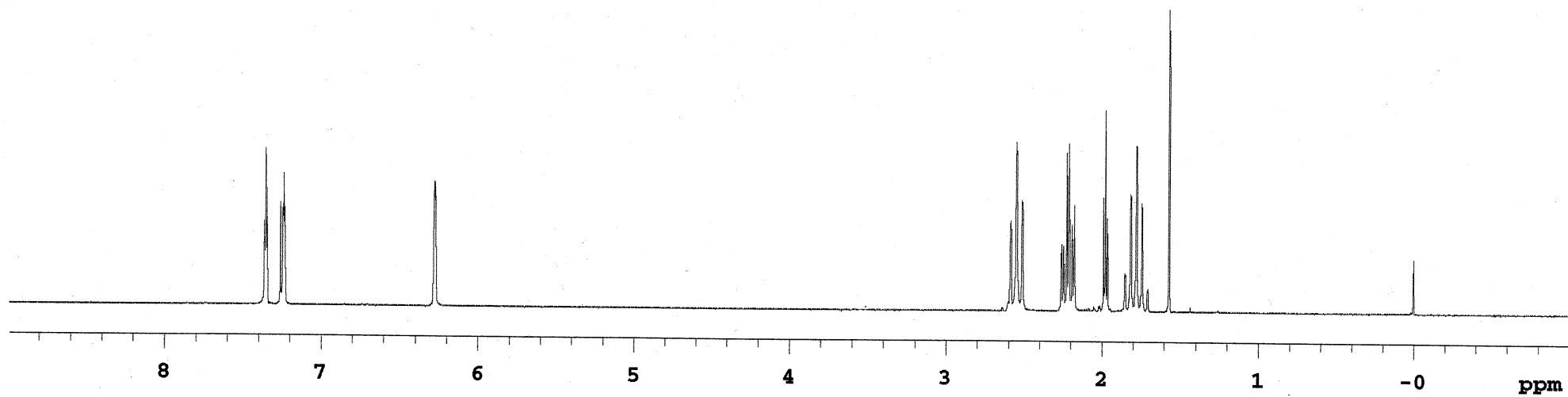
**3-(3-furanyl)propan-1-ol**

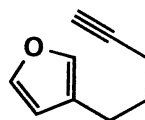
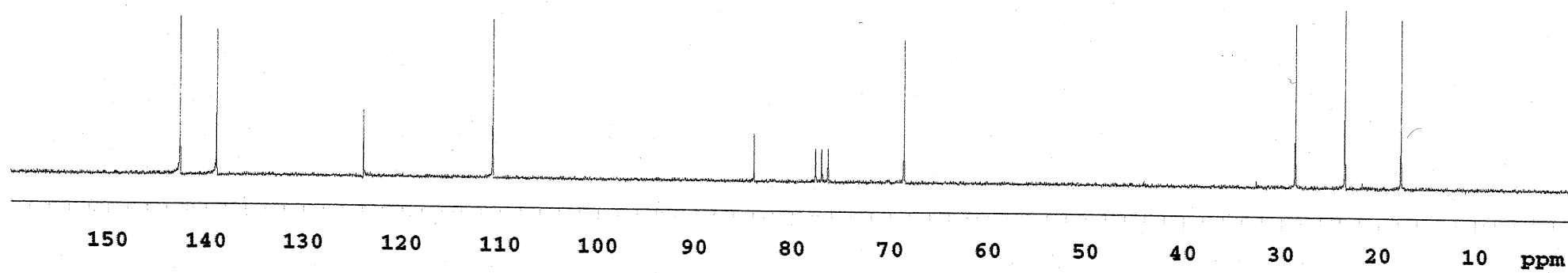


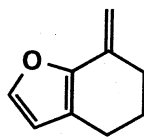
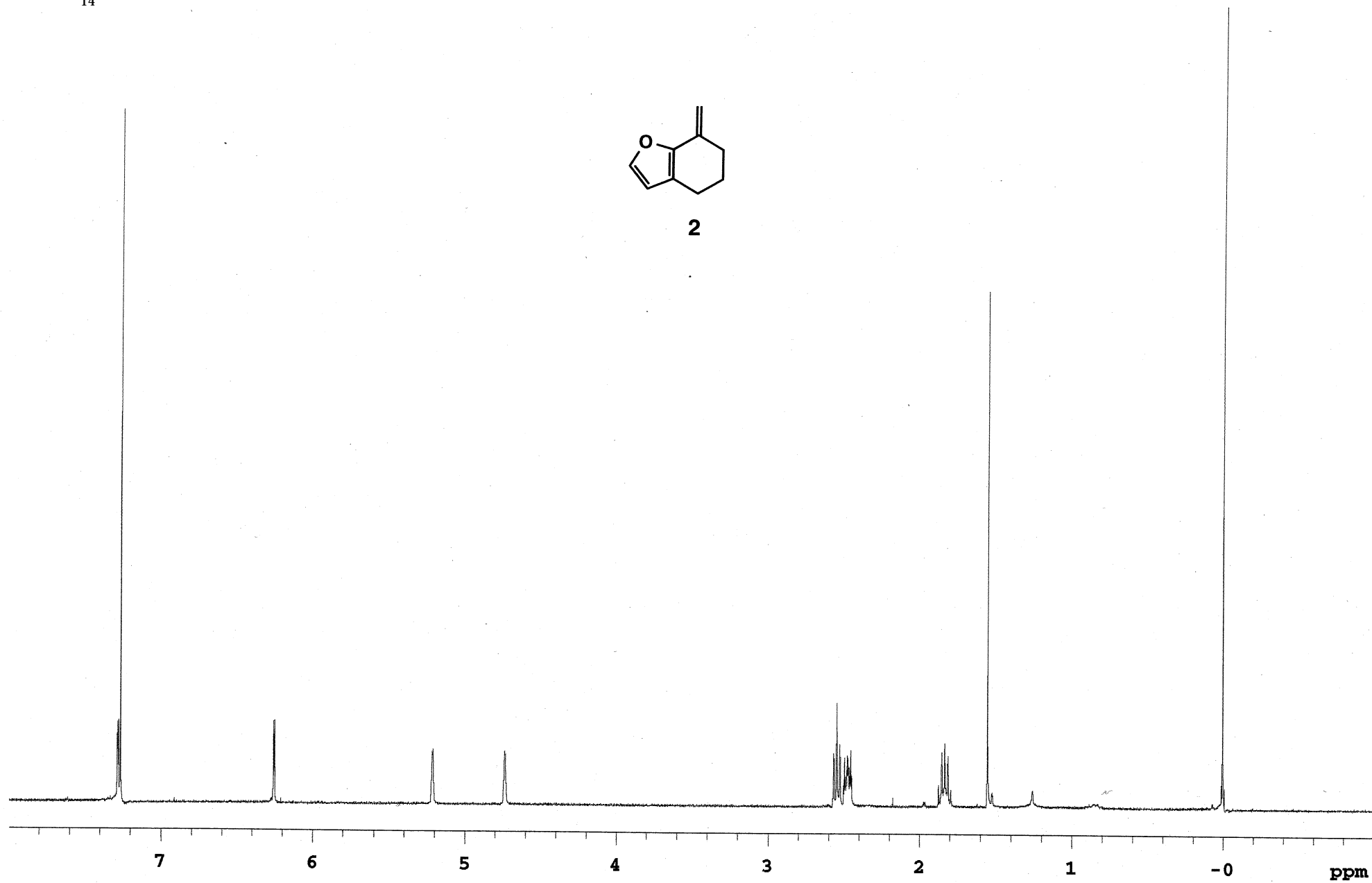


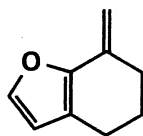
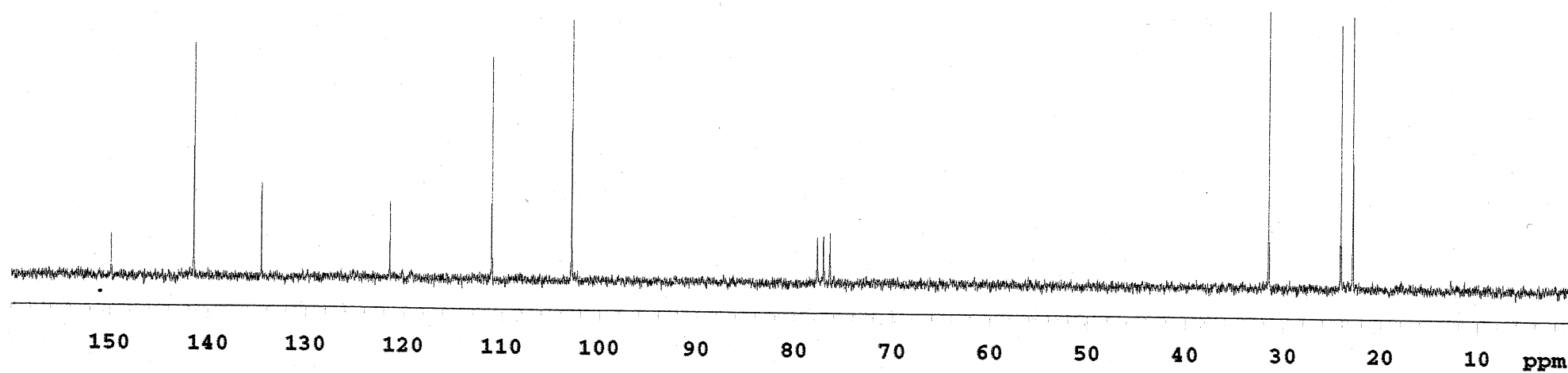
**3-(3-furanyl)propan-1-ol**

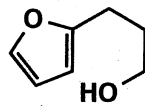


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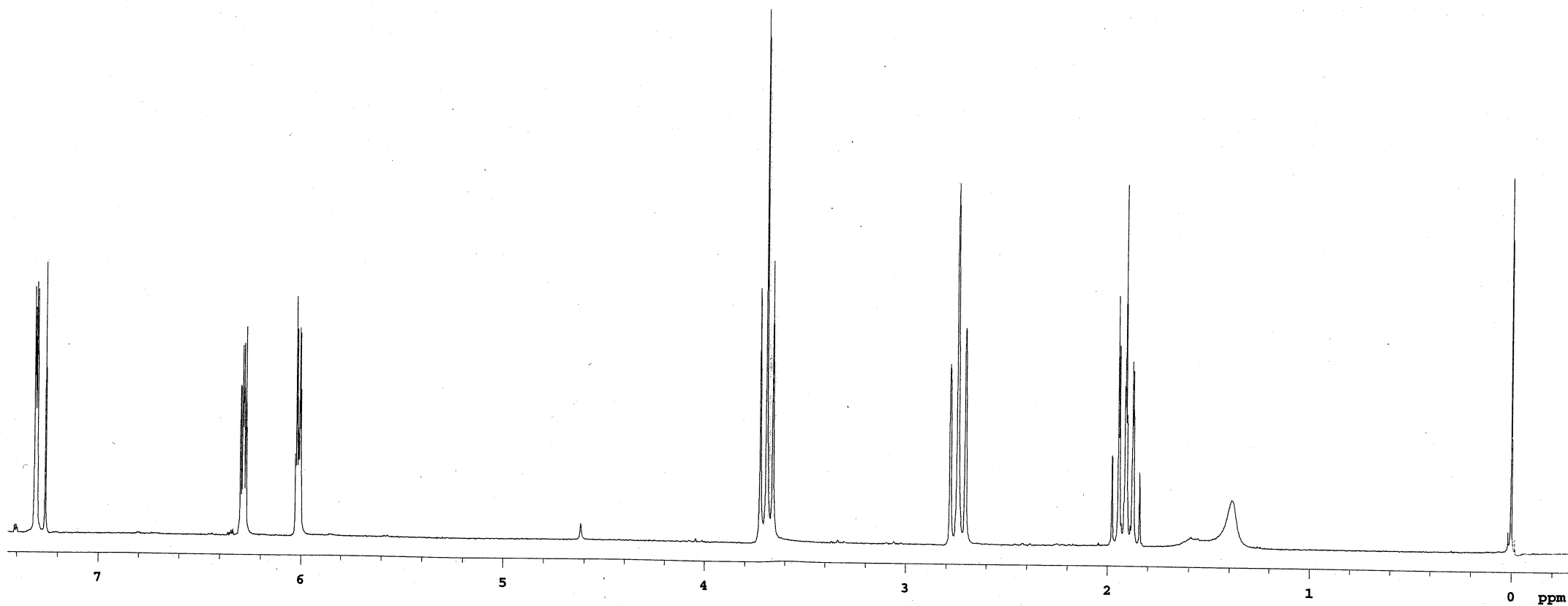
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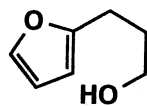
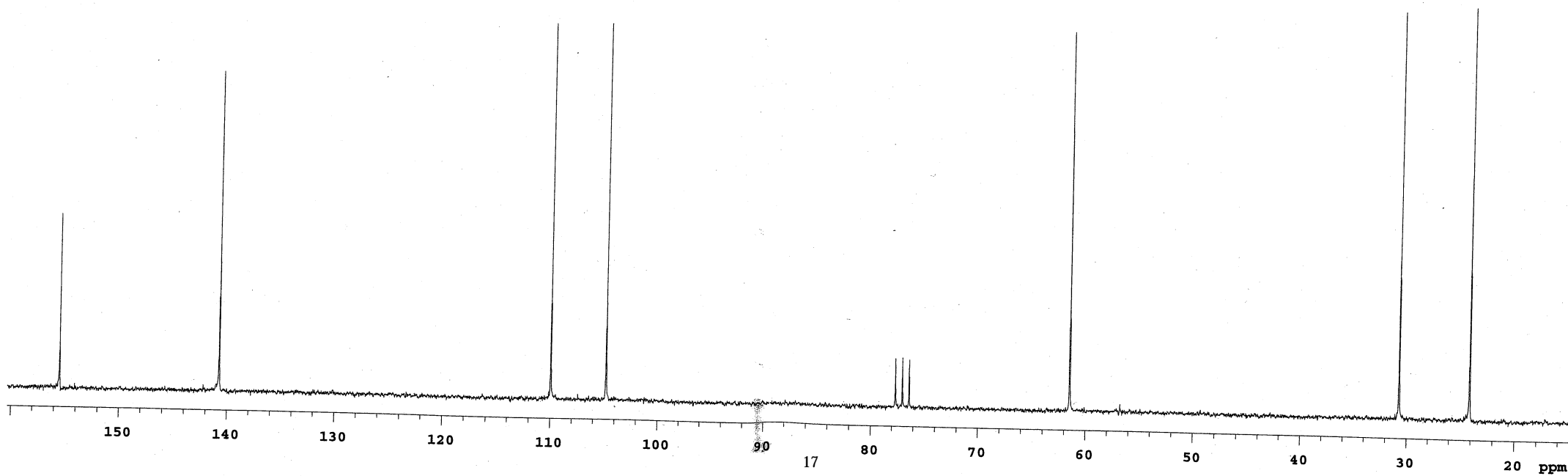
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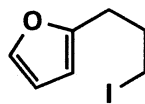
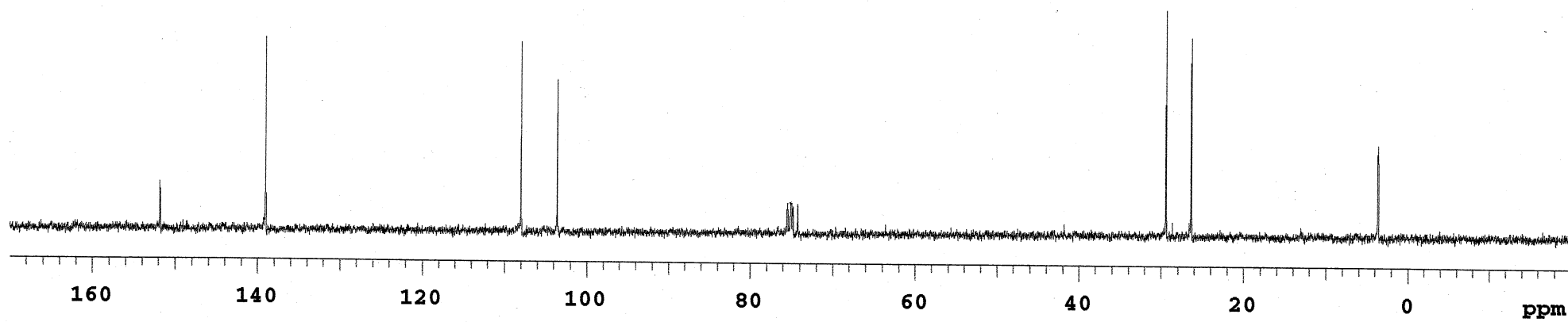
**3-(2-furanyl)propan-1-ol**

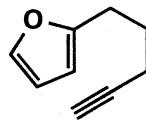
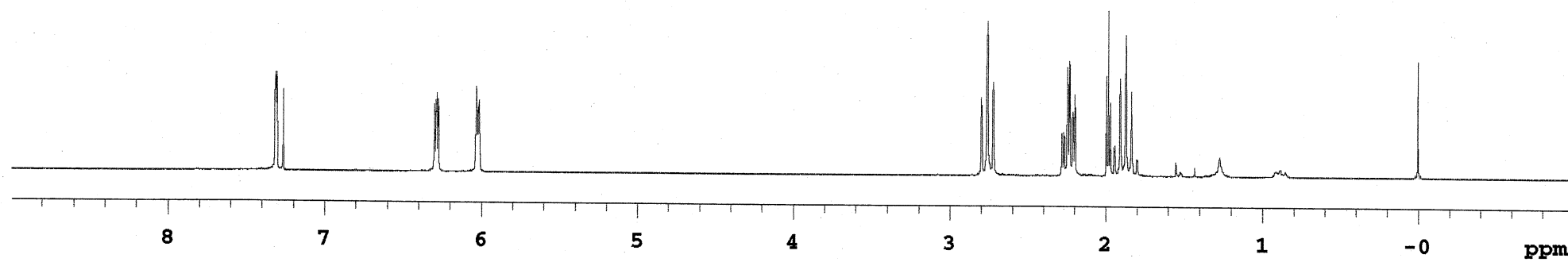


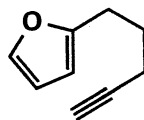
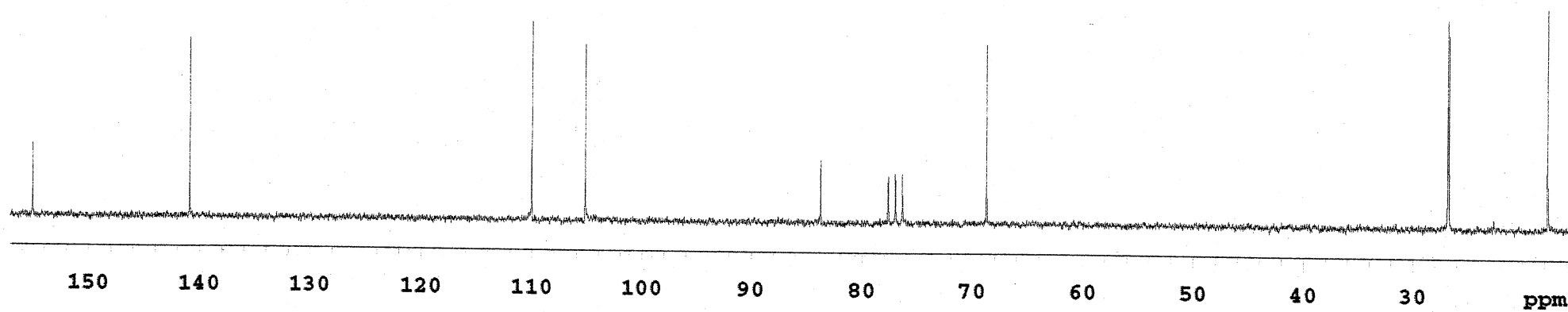


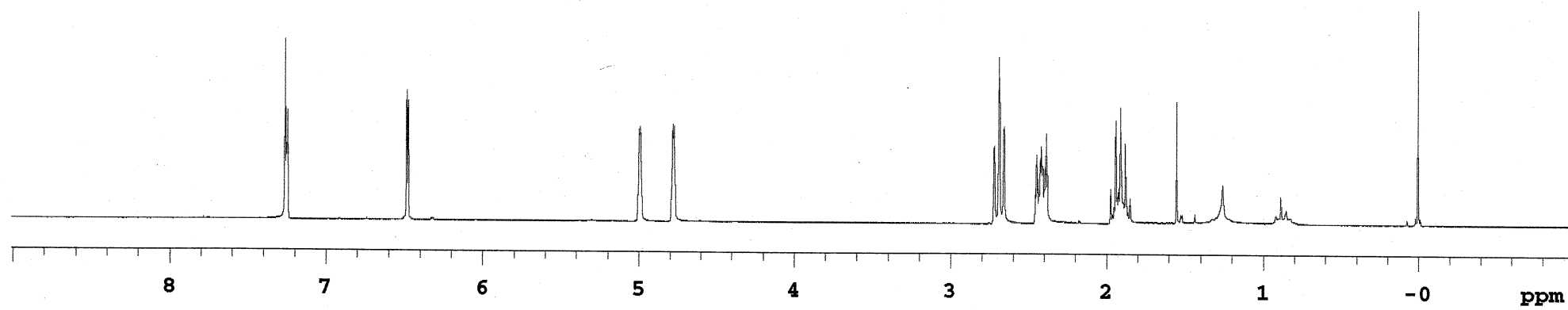
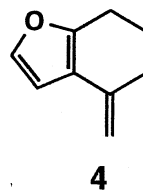
**3-(2-furanyl)propan-1-ol**

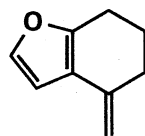


**2-(3-iodopropyl)furan**

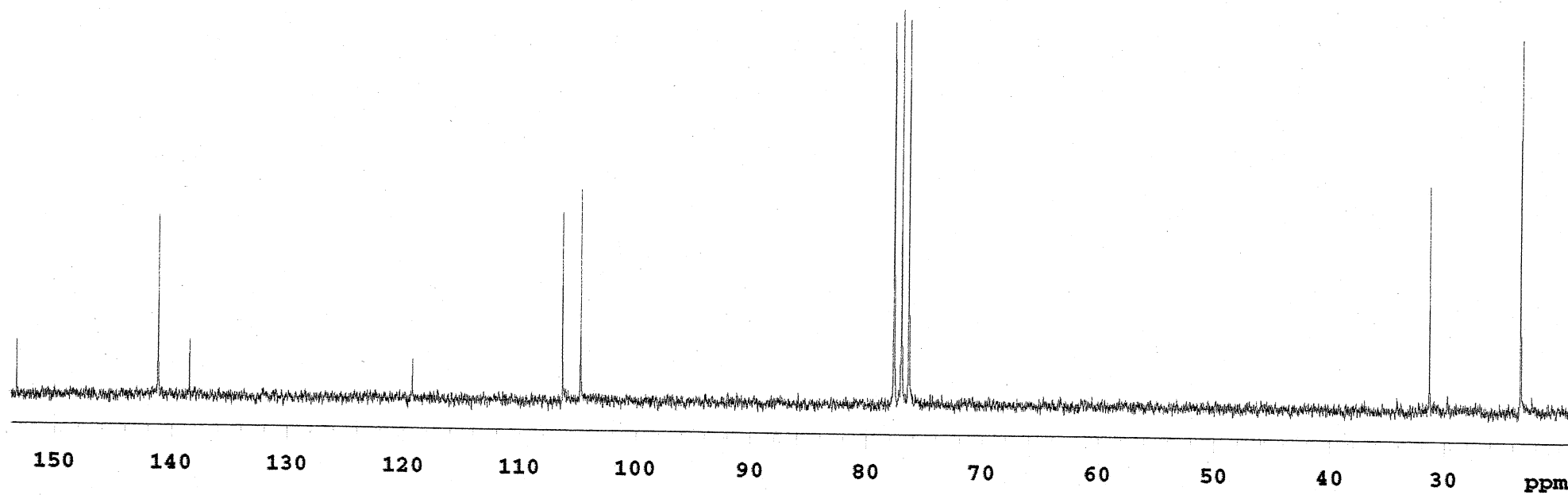
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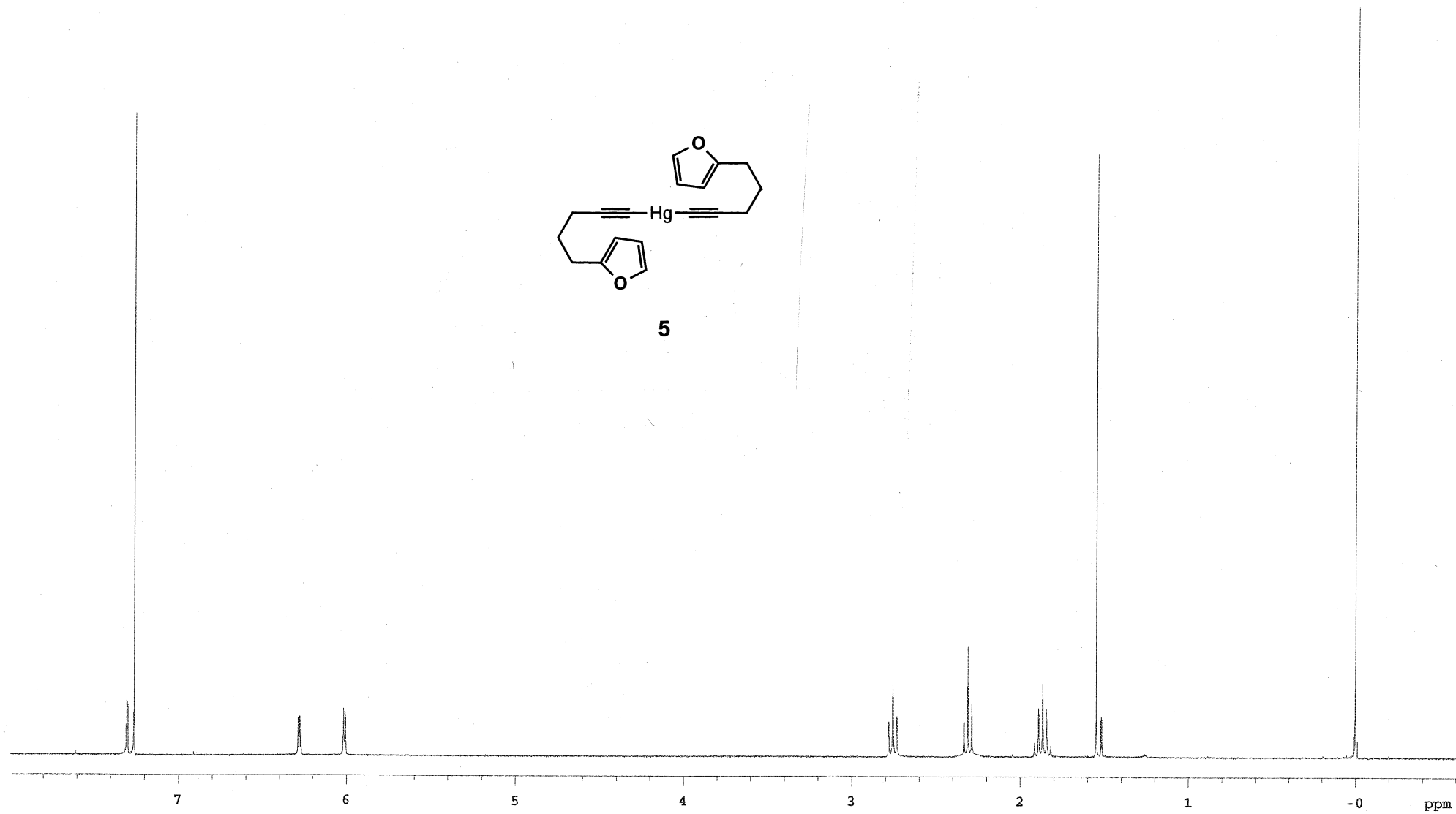
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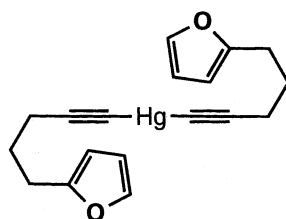
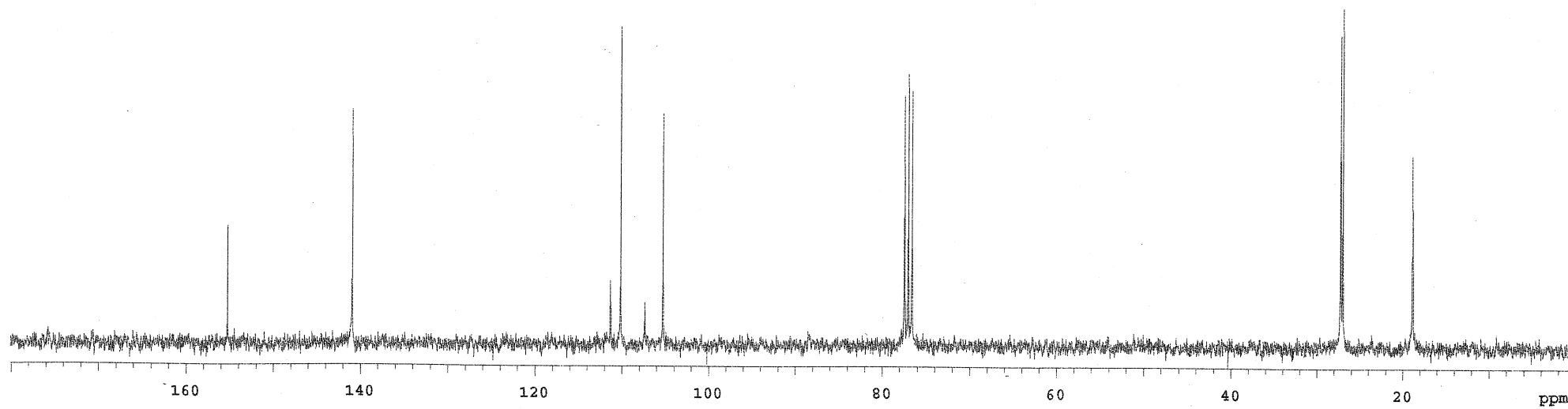


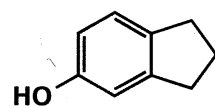
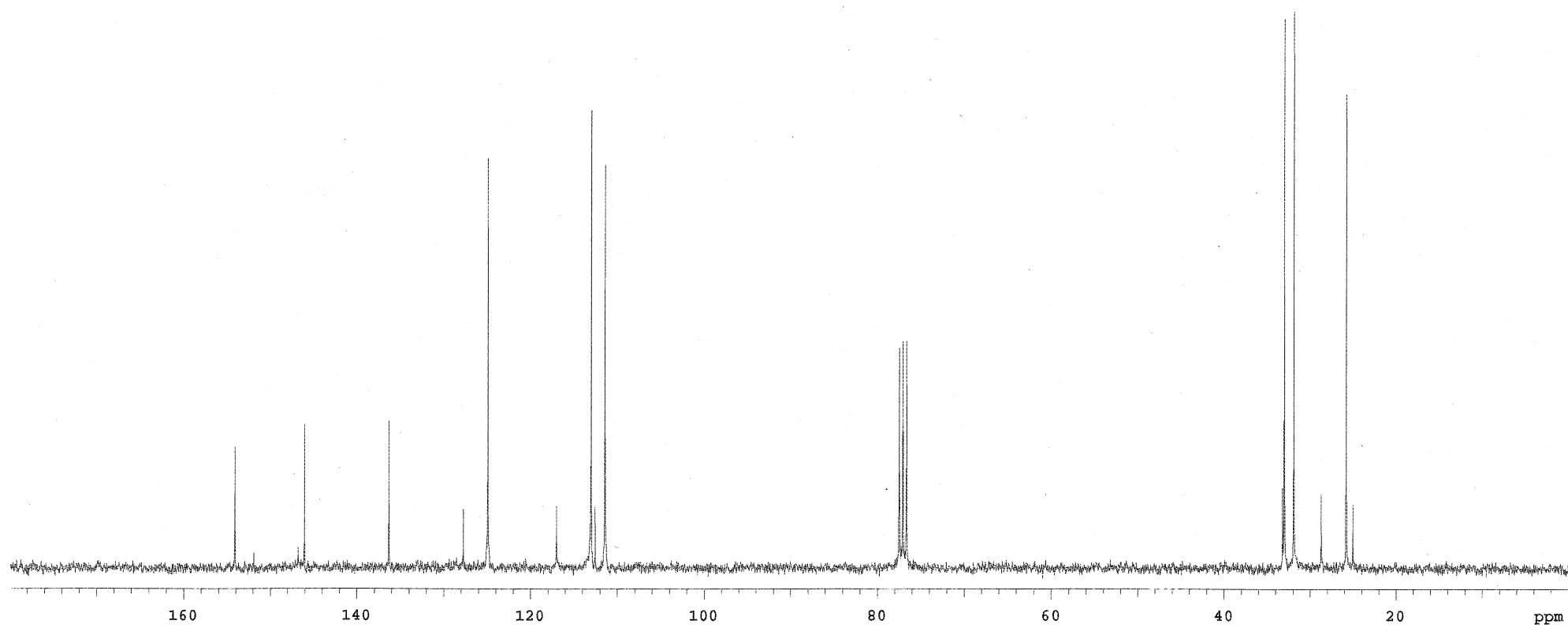
4

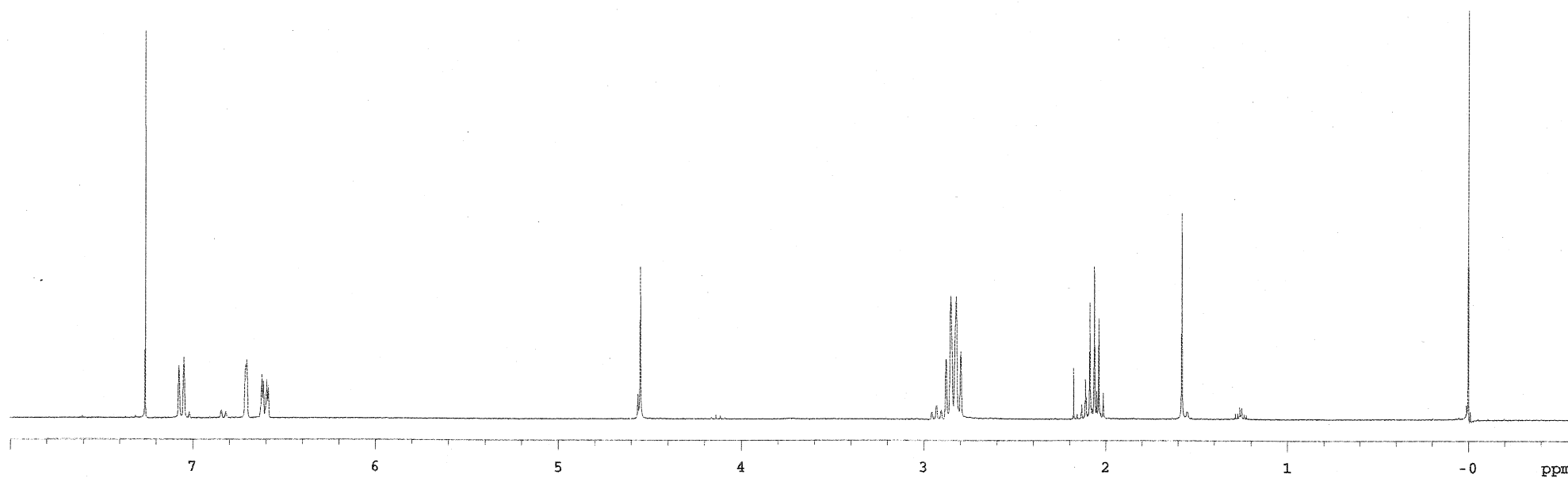
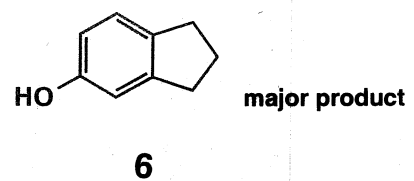


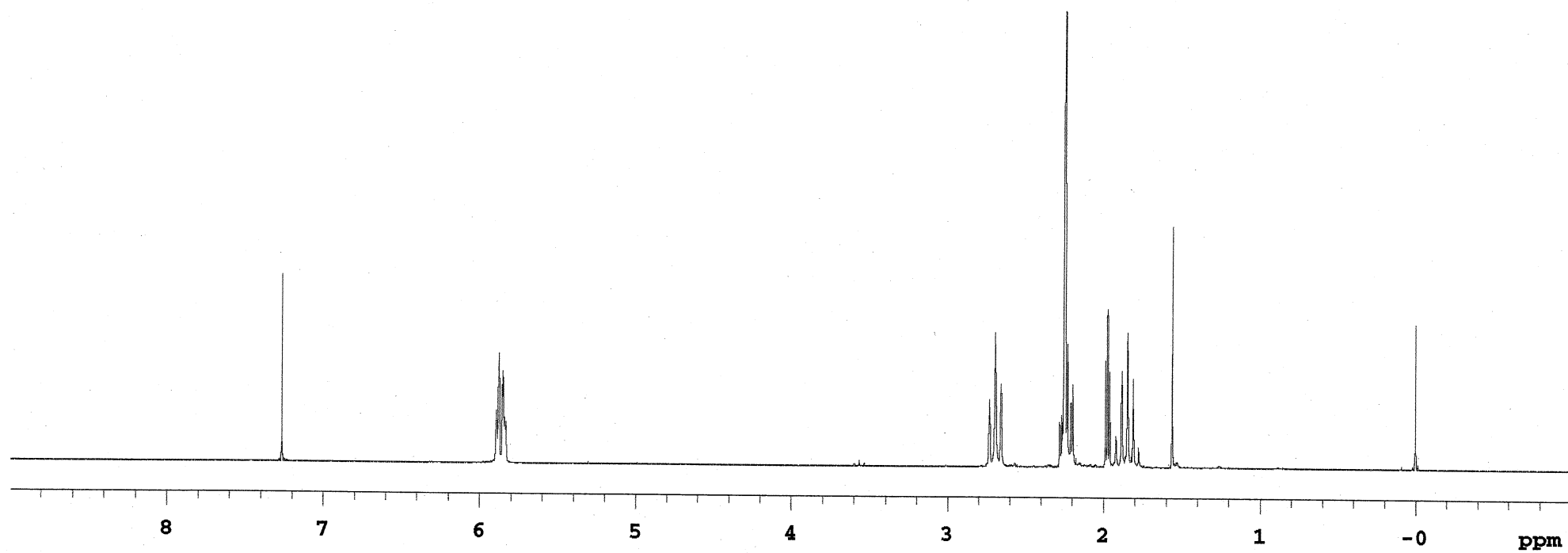
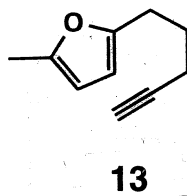


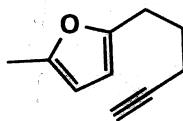
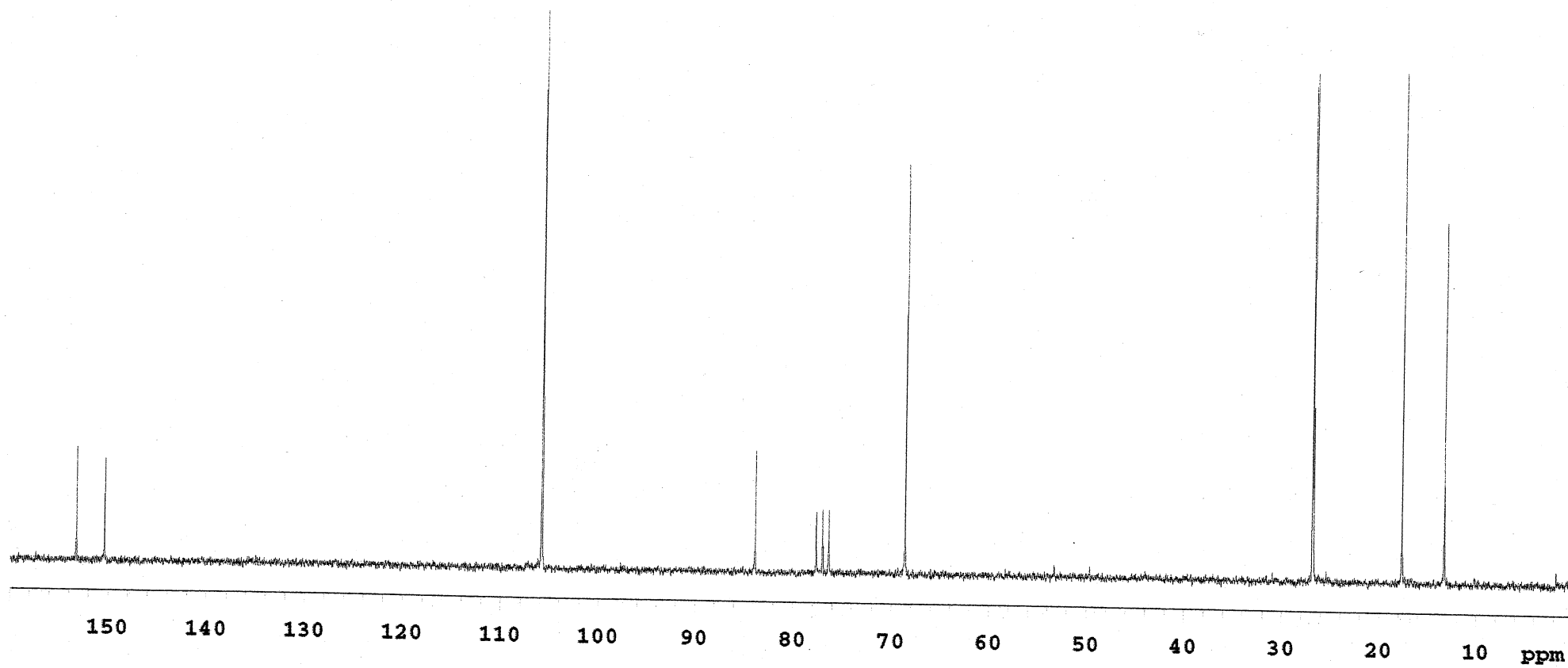


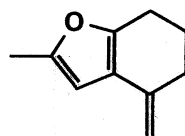
**5**

**6****major product**

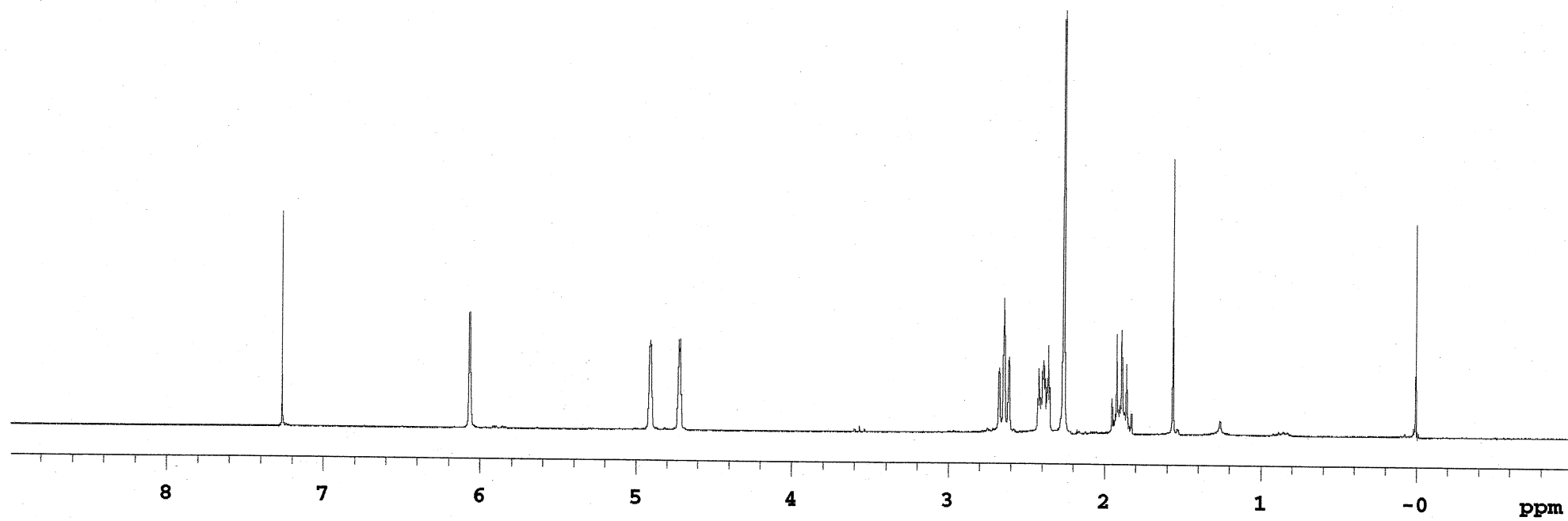


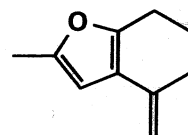


**13**

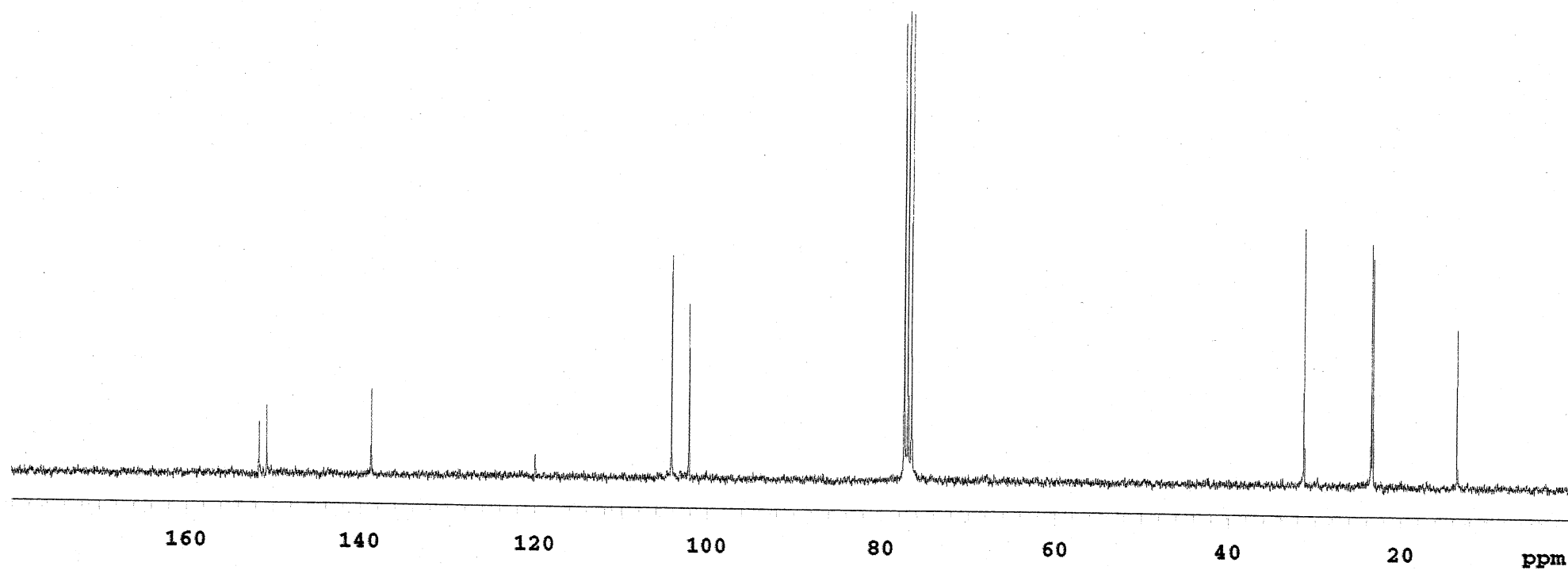


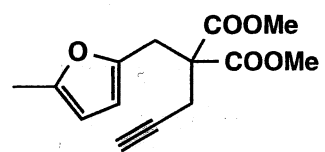
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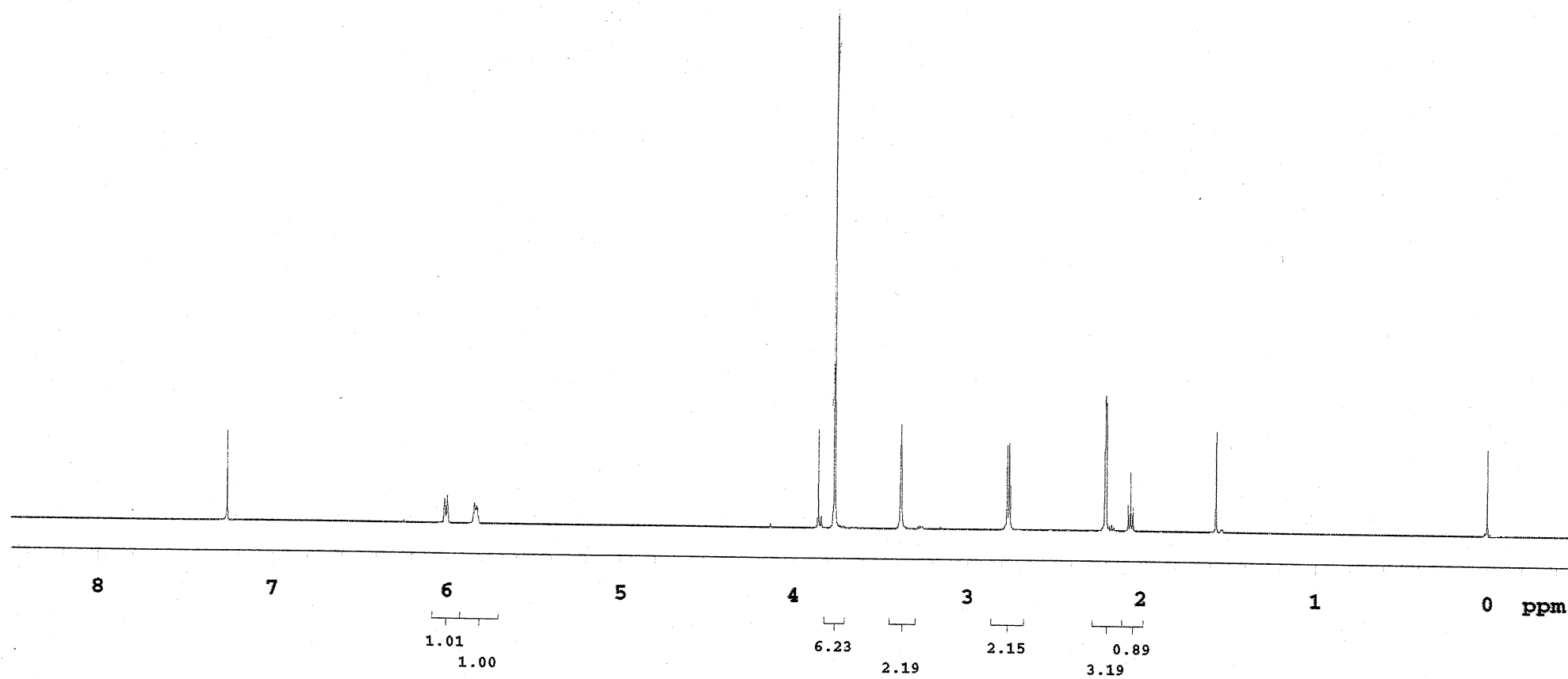


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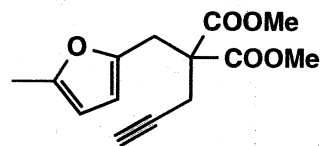




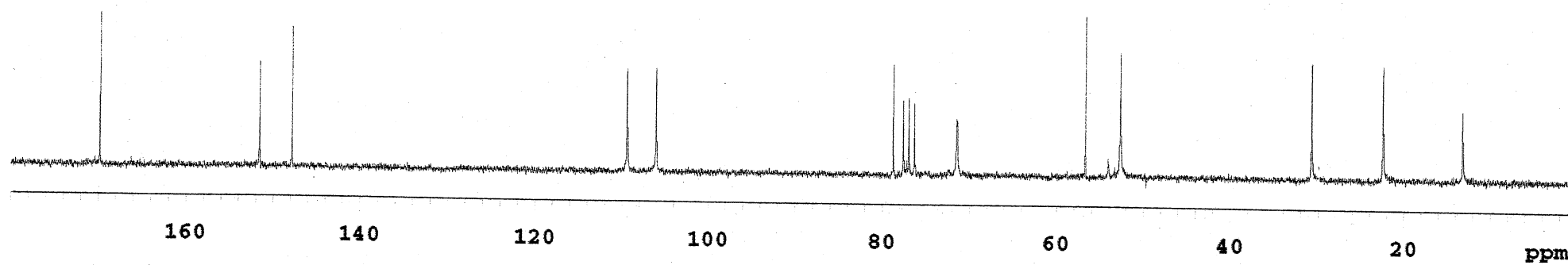
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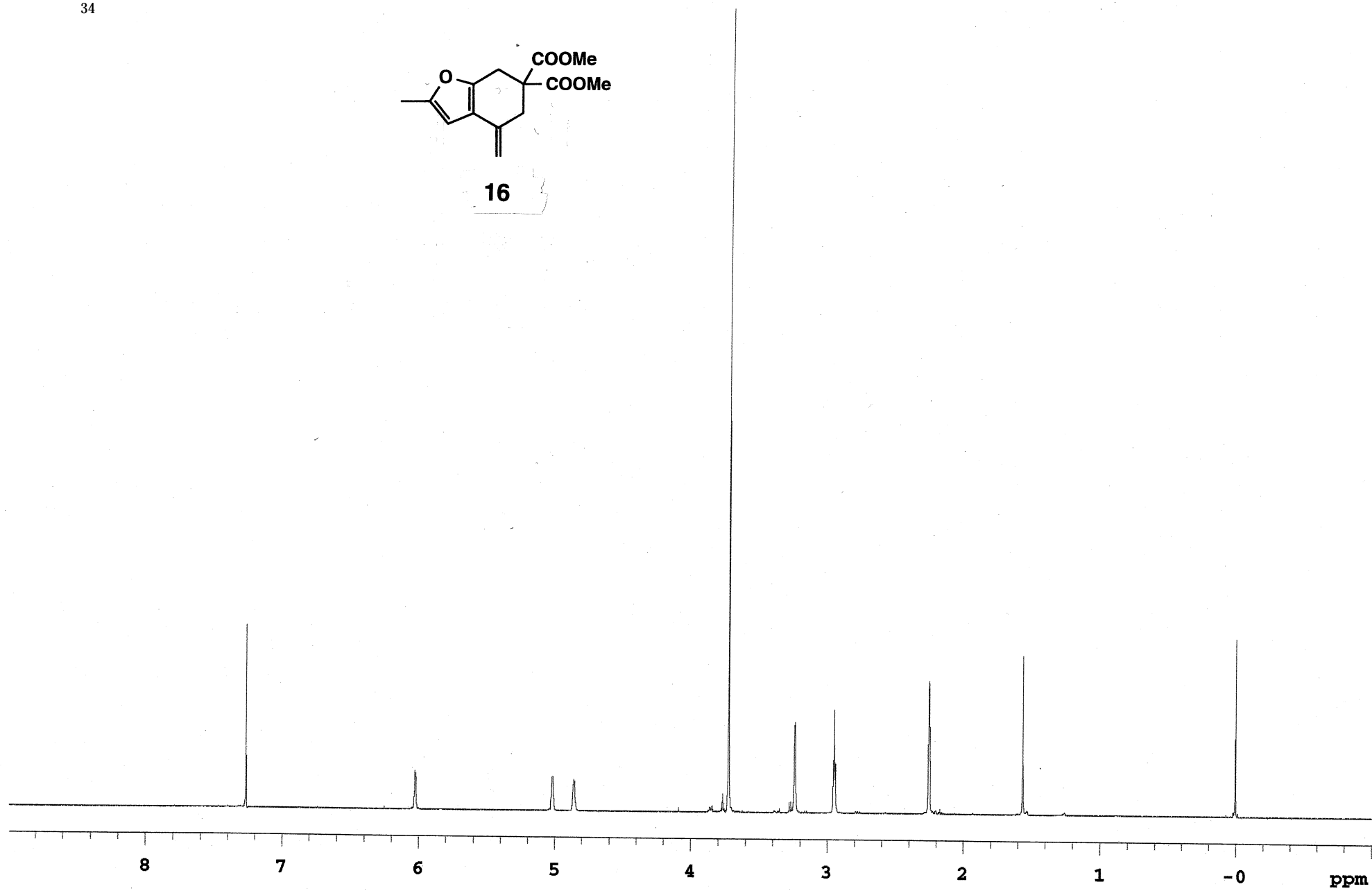
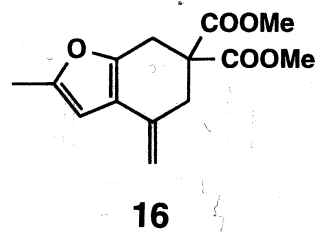


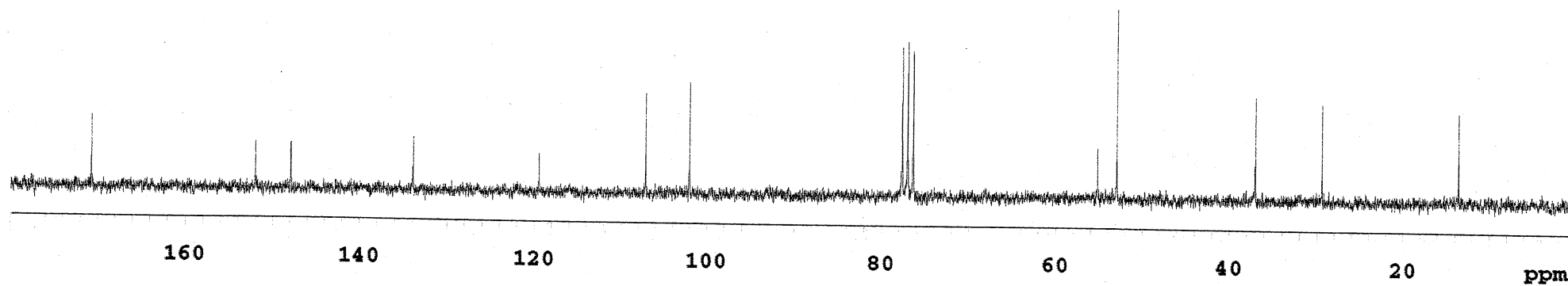
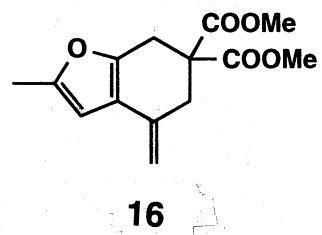


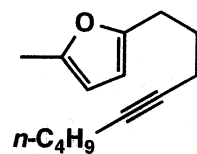


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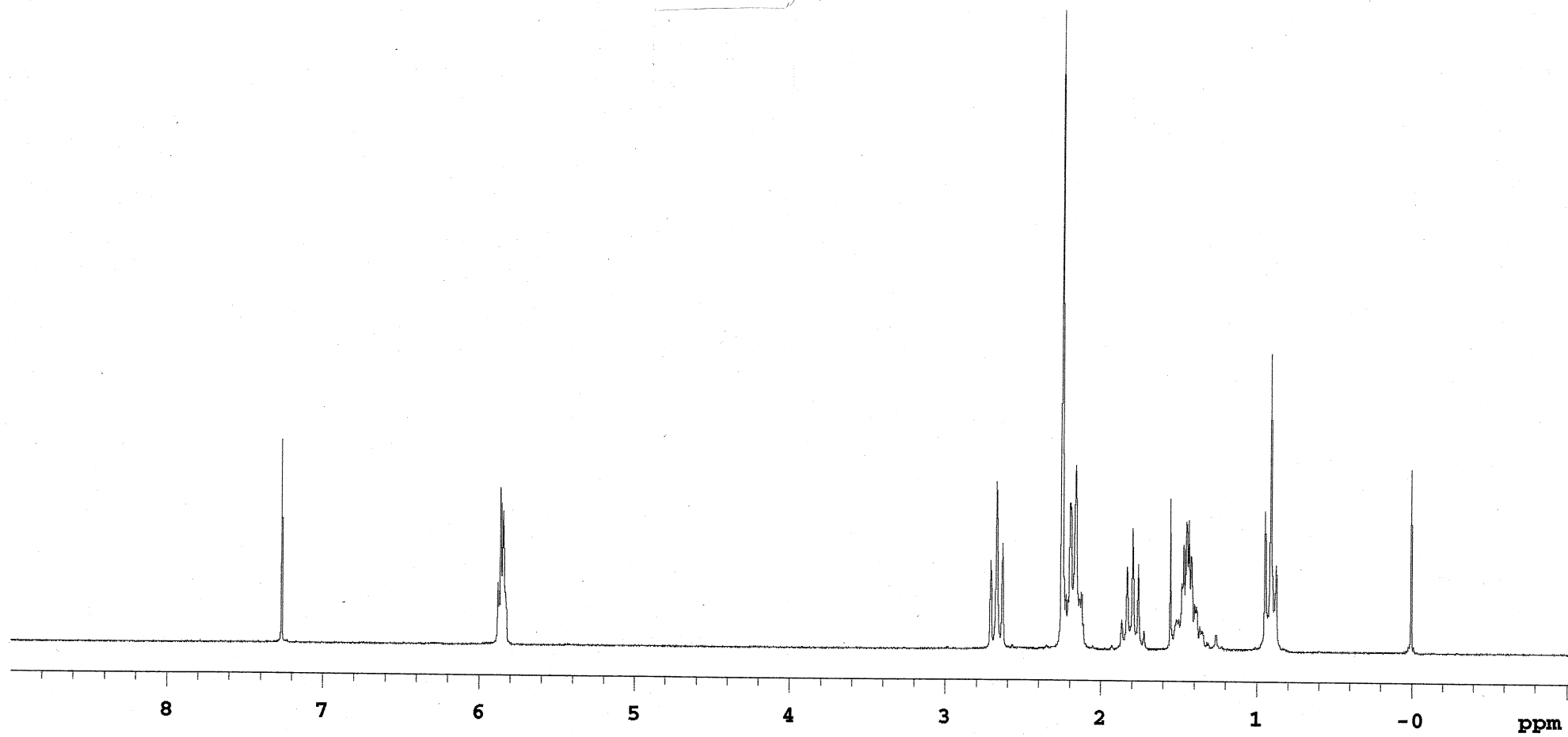


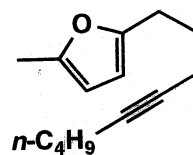




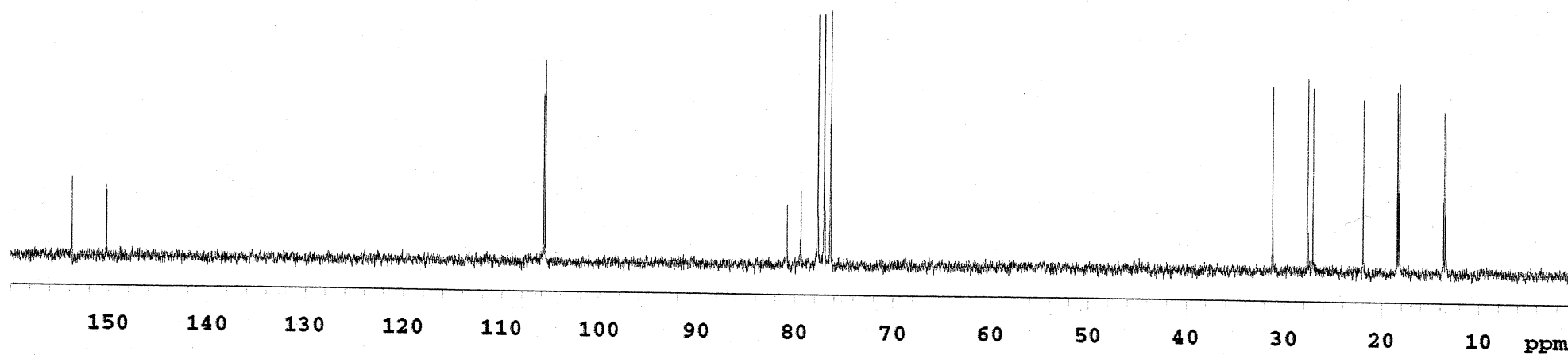


17





17



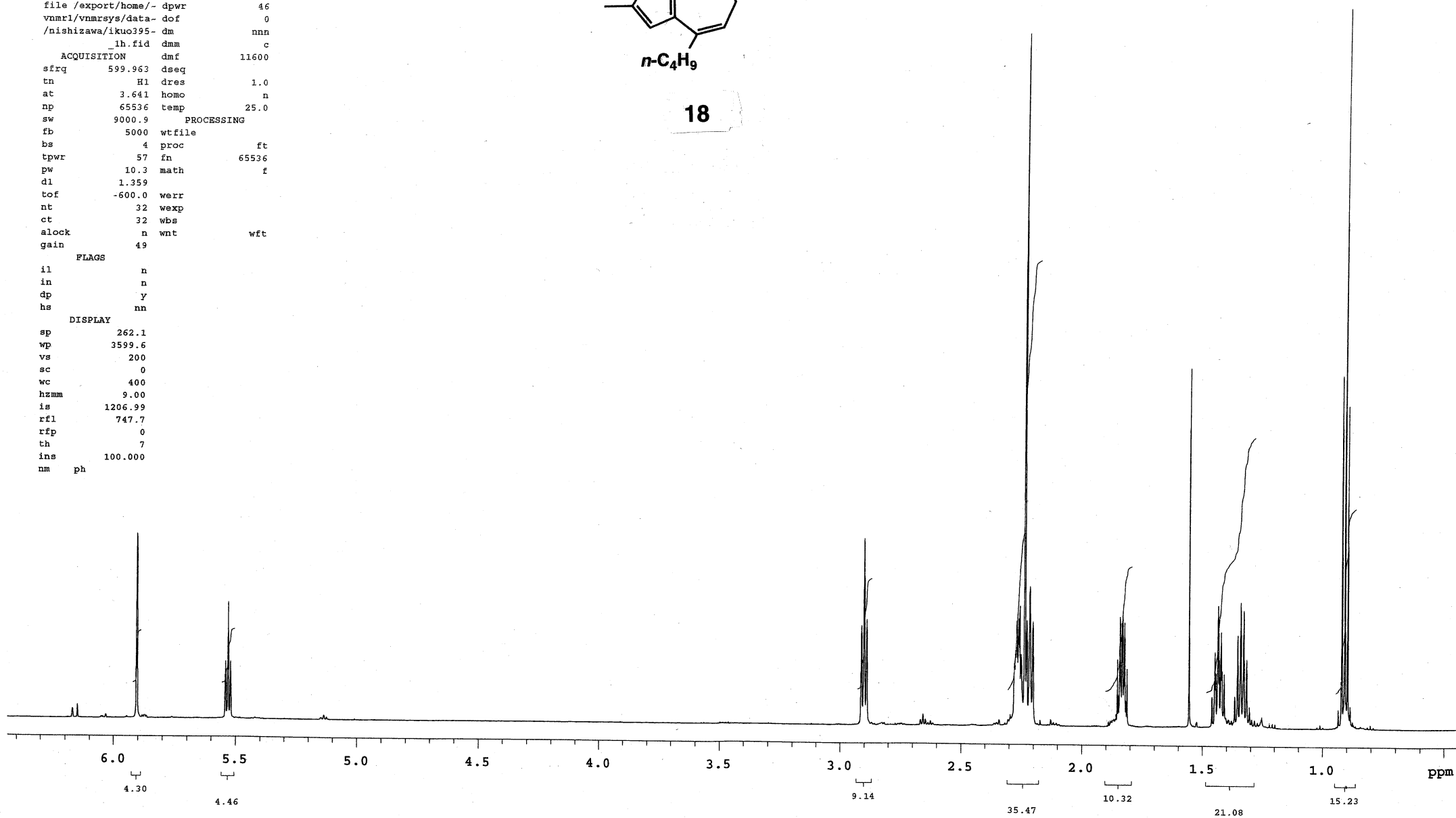
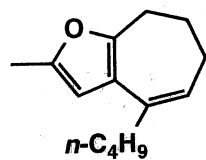
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DEC. & VT
solvent      CDCl3  dn      H1
file /export/home/- dpwr      46
vnmr1/vnmrSYS/data- dof      0
/nishizawa/ikuo395- dm      nnn
  _1h.fid  dmm      c
ACQUISITION  dmf      11600
sfrq      599.963 dseq
tn      H1 dres      1.0
at      3.641 homo      n
np      65536 temp      25.0
sw      9000.9
fb      5000 wtfile
bs      4 proc      ft
tpwr      57 fn      65536
pw      10.3 math      f
dl      1.359
tof      -600.0 werr
nt      32 wexp
ct      32 wbs
alock      n wnt      wft
gain      49

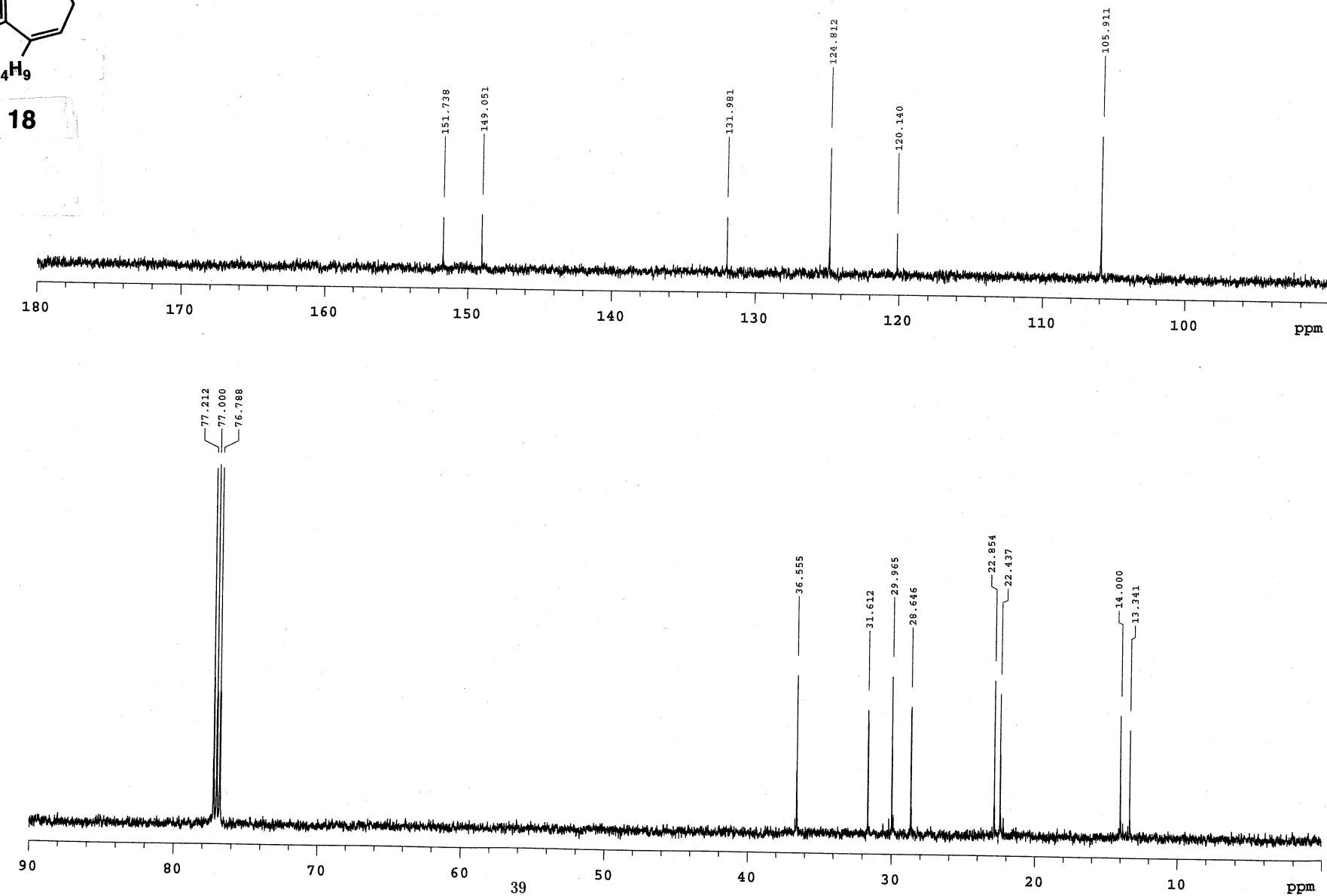
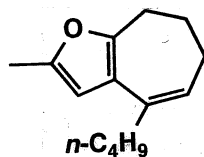
FLAGS
il      n
in      n
dp      Y
hs      nn

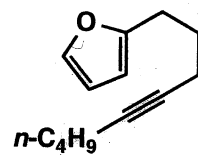
DISPLAY
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wp      3599.6
vs      200
sc      0
wc      400
hzmm      9.00
is      1206.99
rfl      747.7
rfp      0
th      7
ins      100.000
nm      ph

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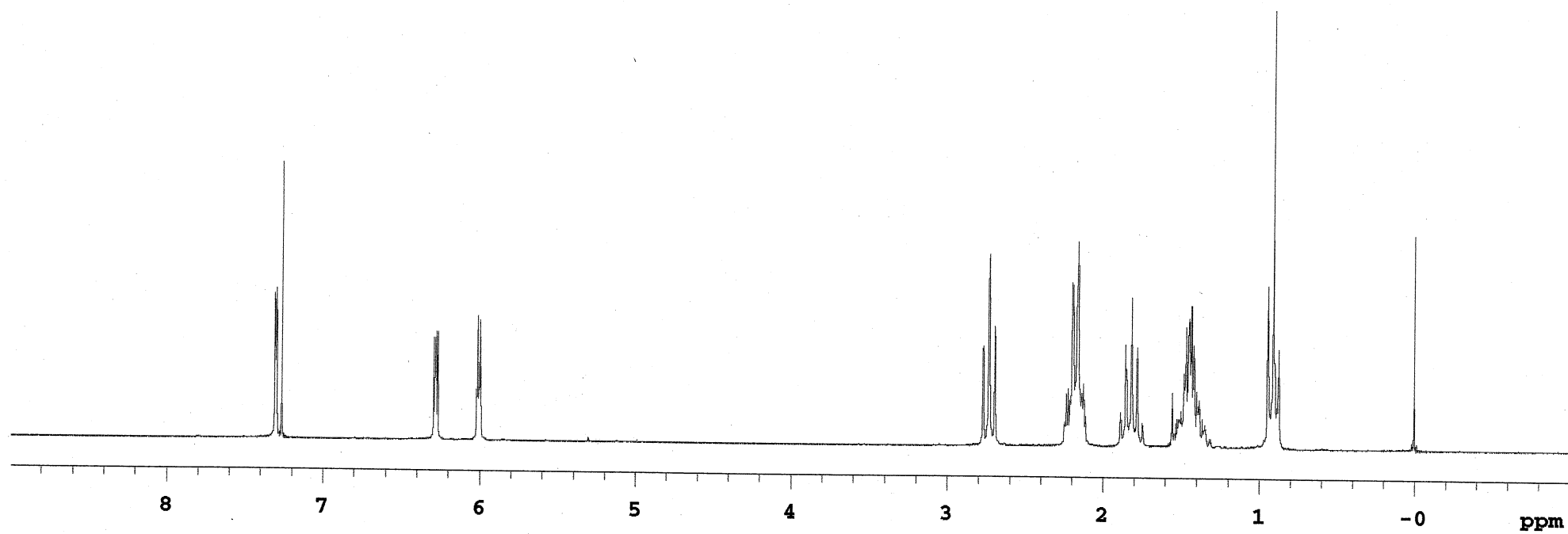


solvent CDCl<sub>3</sub>  
file /export/home/-  
vnmr1/vnmrSYS/data-  
/nishizawa/ikuo395-  
\_13c.fid  
ACQUISITION  
sfrq 150.877  
tn C13  
at 0.905  
np 65536  
sw 36199.1  
fb 20000  
bs 16  
tpwr 54  
pw 7.0  
dl 1.200  
tof 3384.3  
nt 65536  
ct 256  
alock n  
gain 56  
FLAGS  
il n  
in n  
dp Y  
hs nn  
DISPLAY  
sp 13577.1  
wp 13577.3  
vs 90  
sc 0  
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rfl 12525.6  
rfp 11616.2  
th 9  
ins 100.000  
nm ph

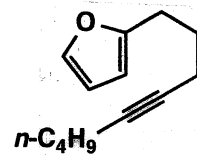




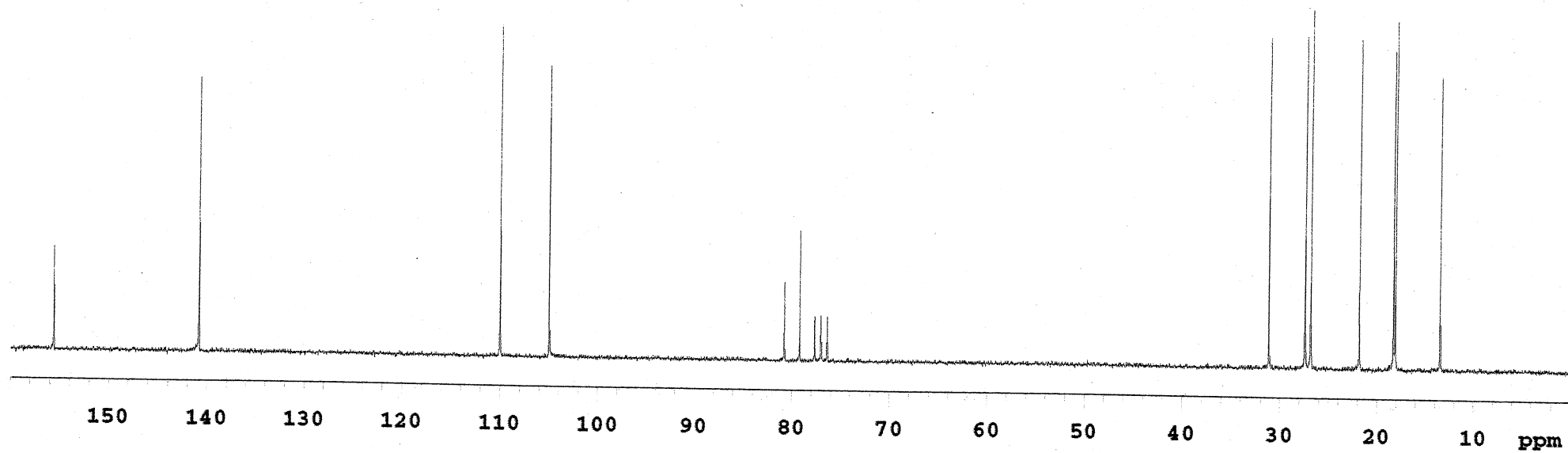
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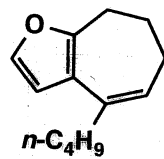




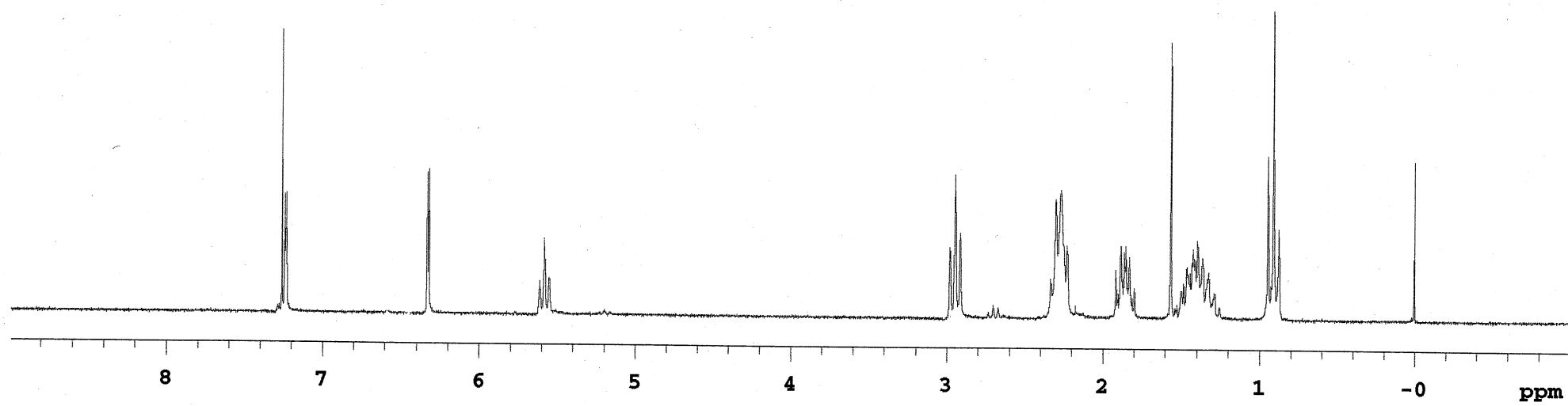


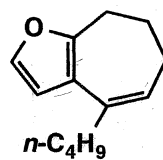
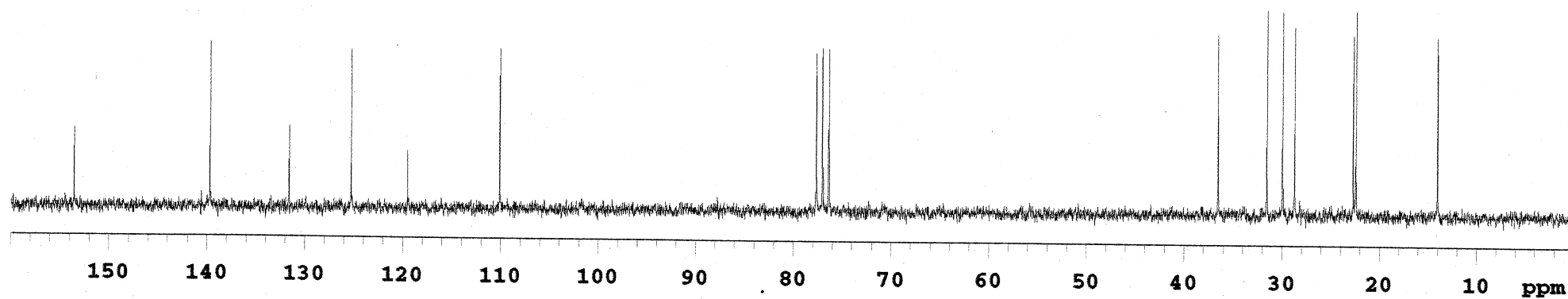
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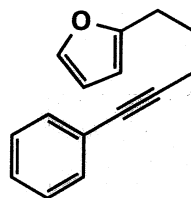
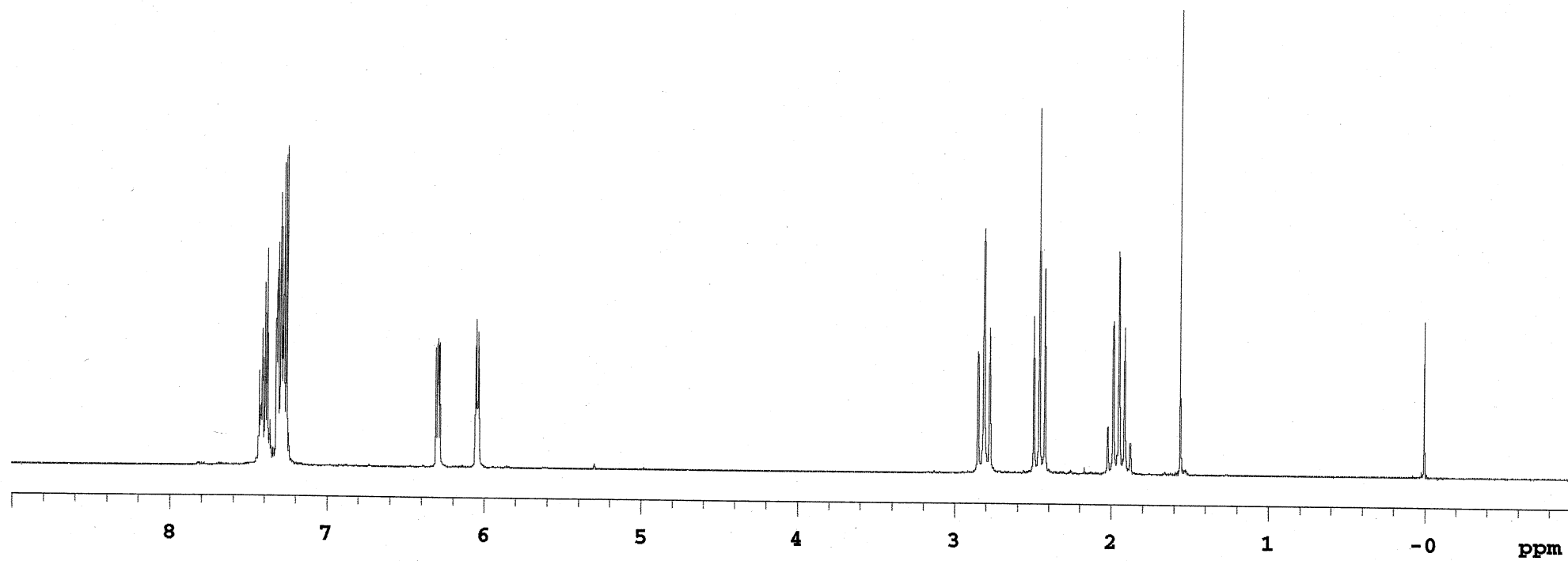




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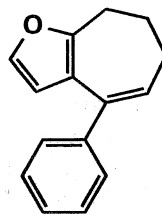


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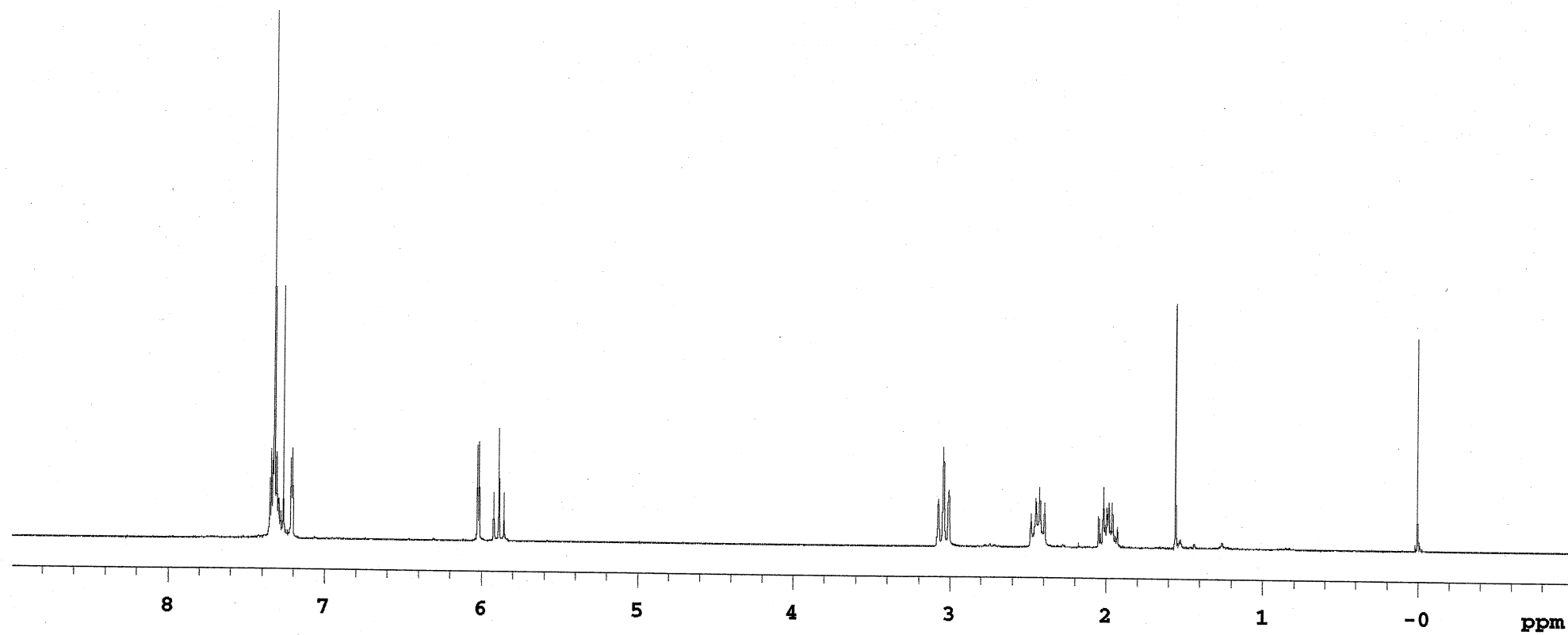
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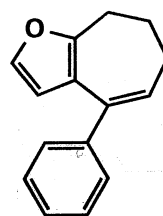
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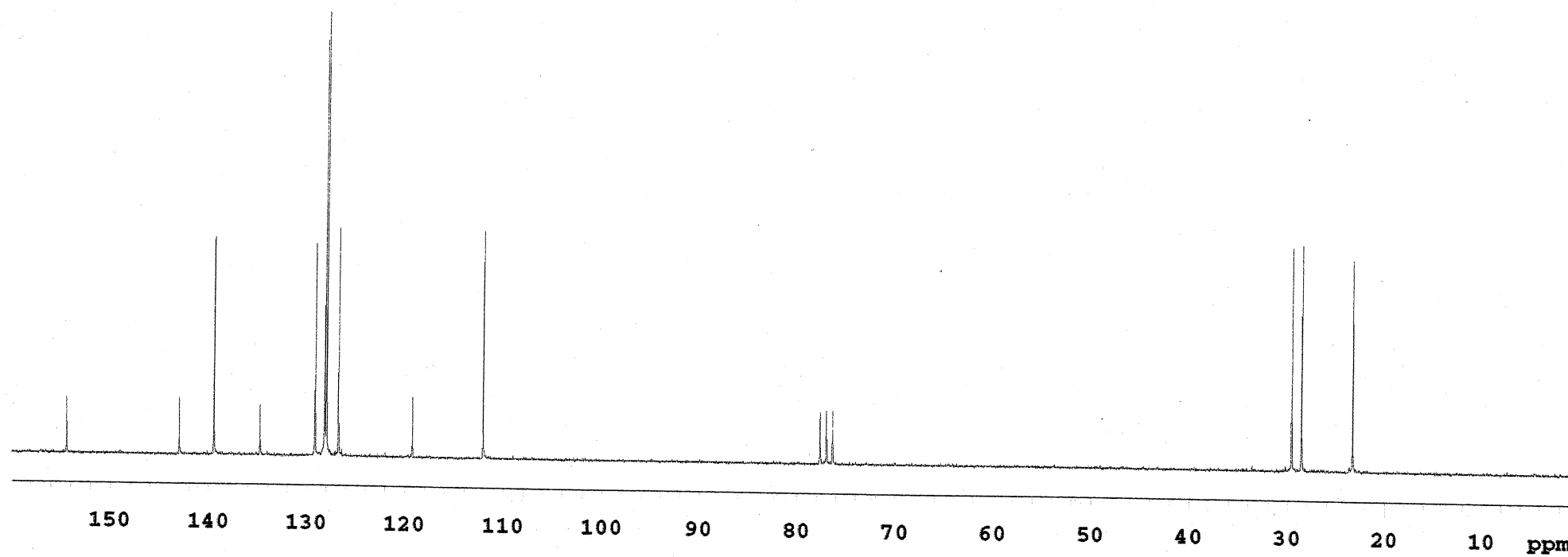


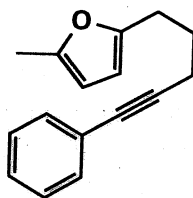
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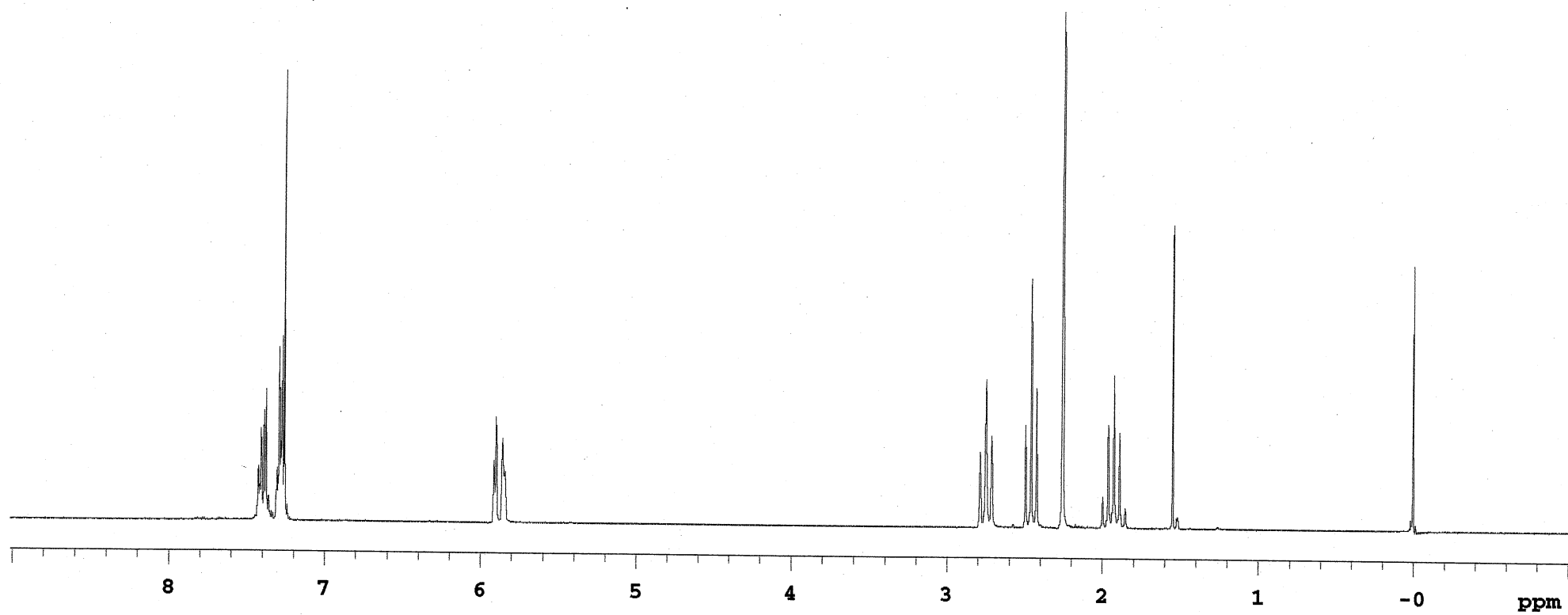


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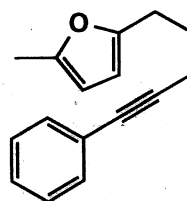




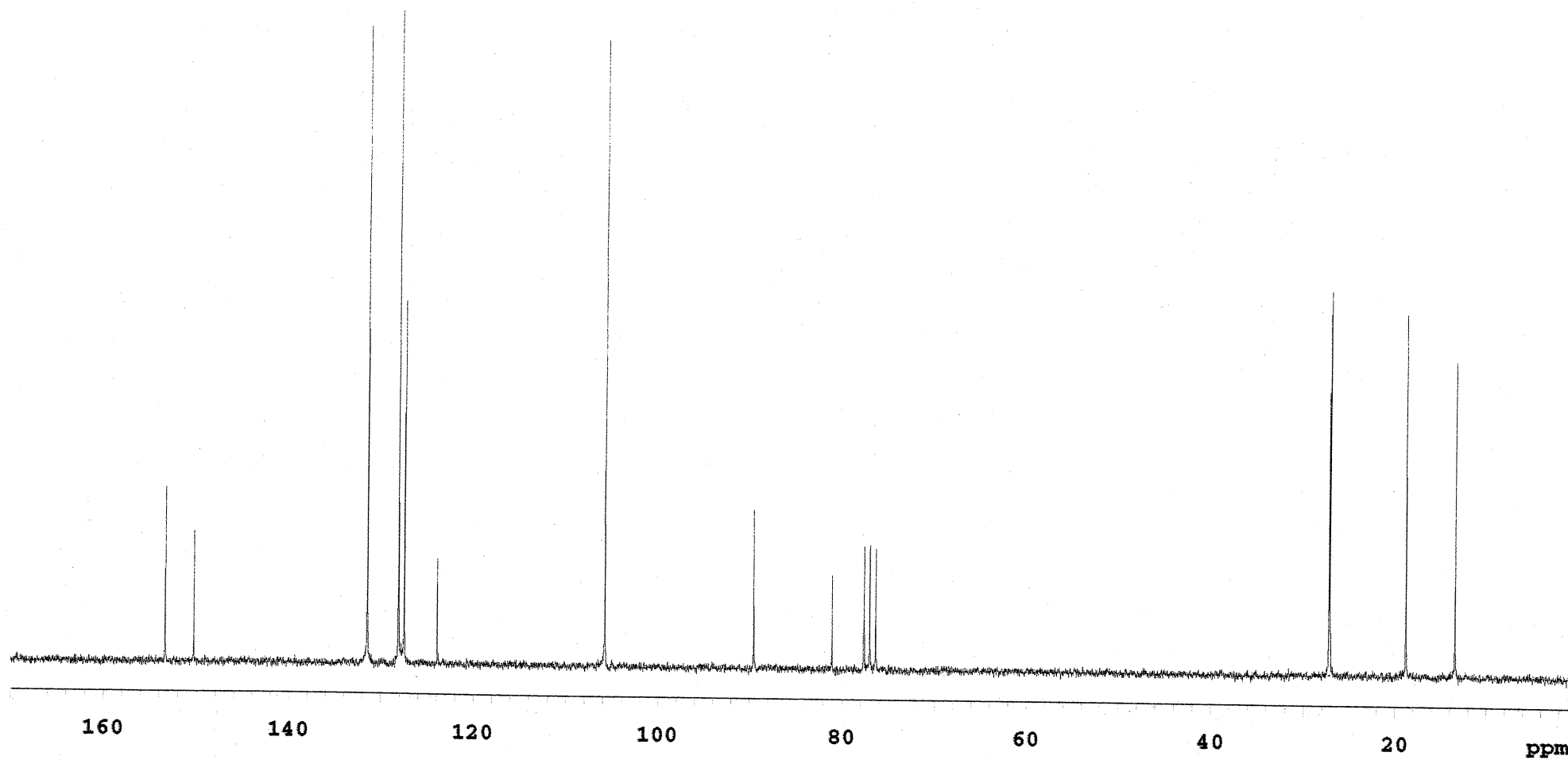
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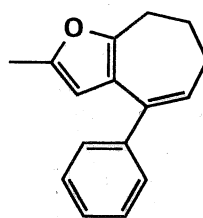




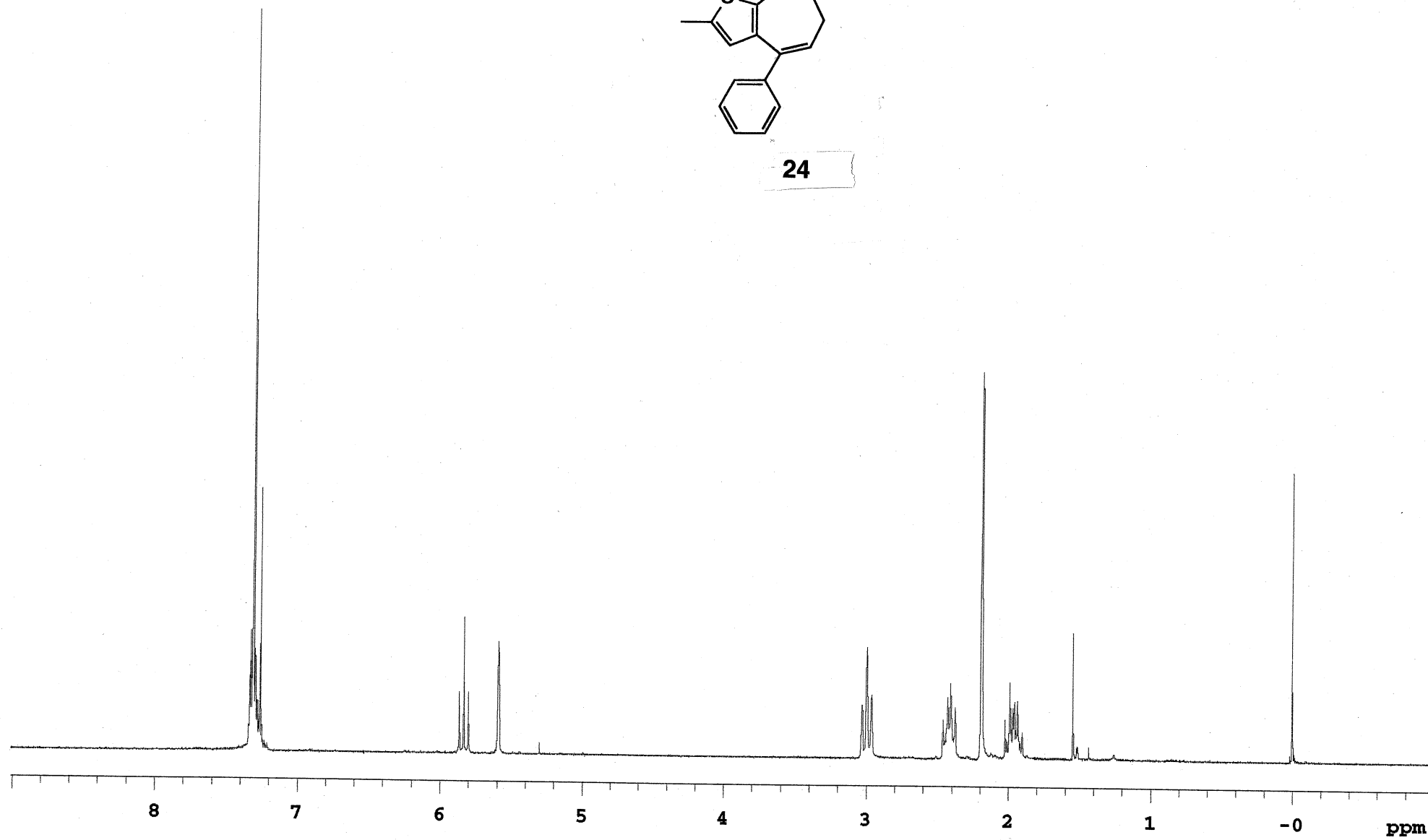


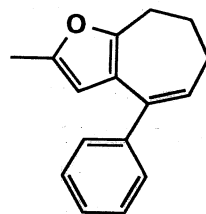
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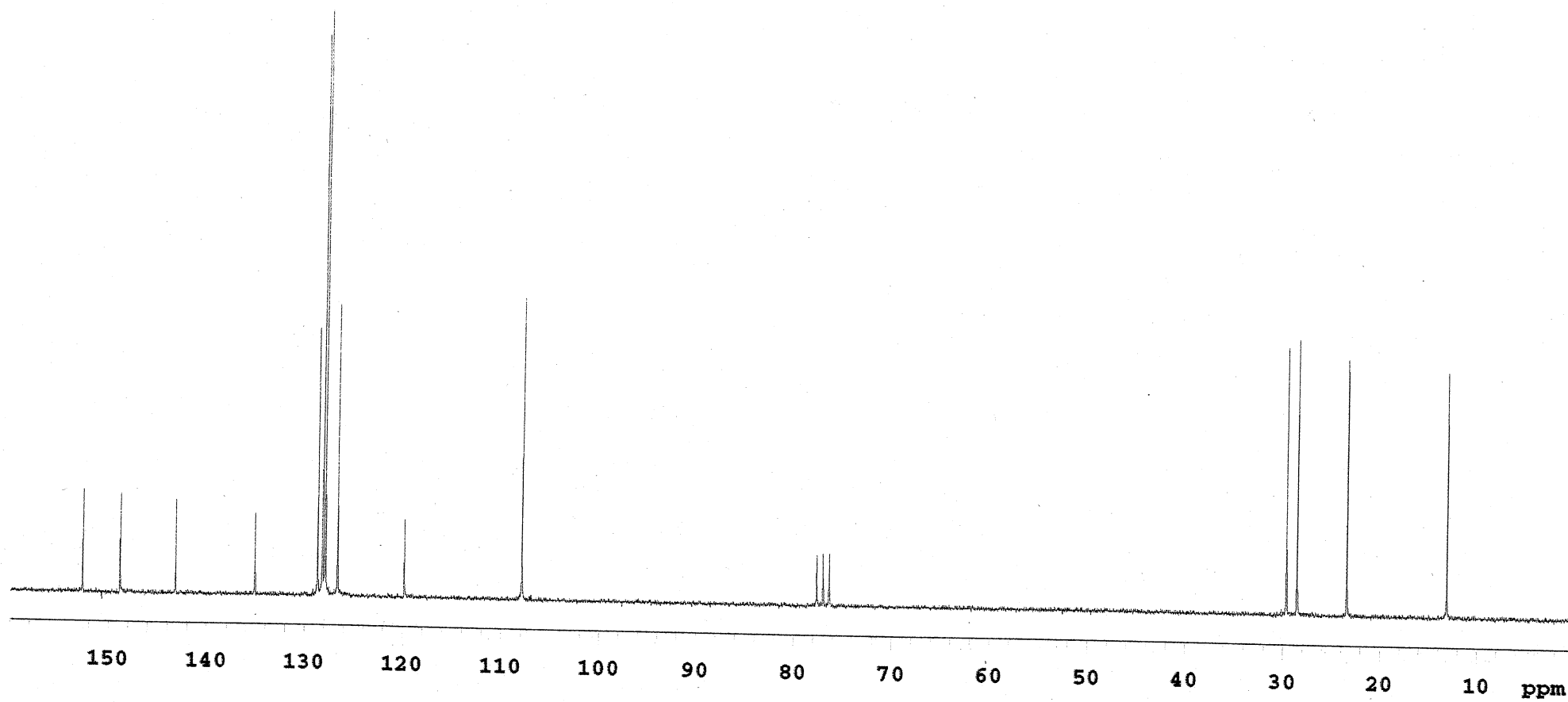


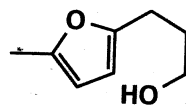
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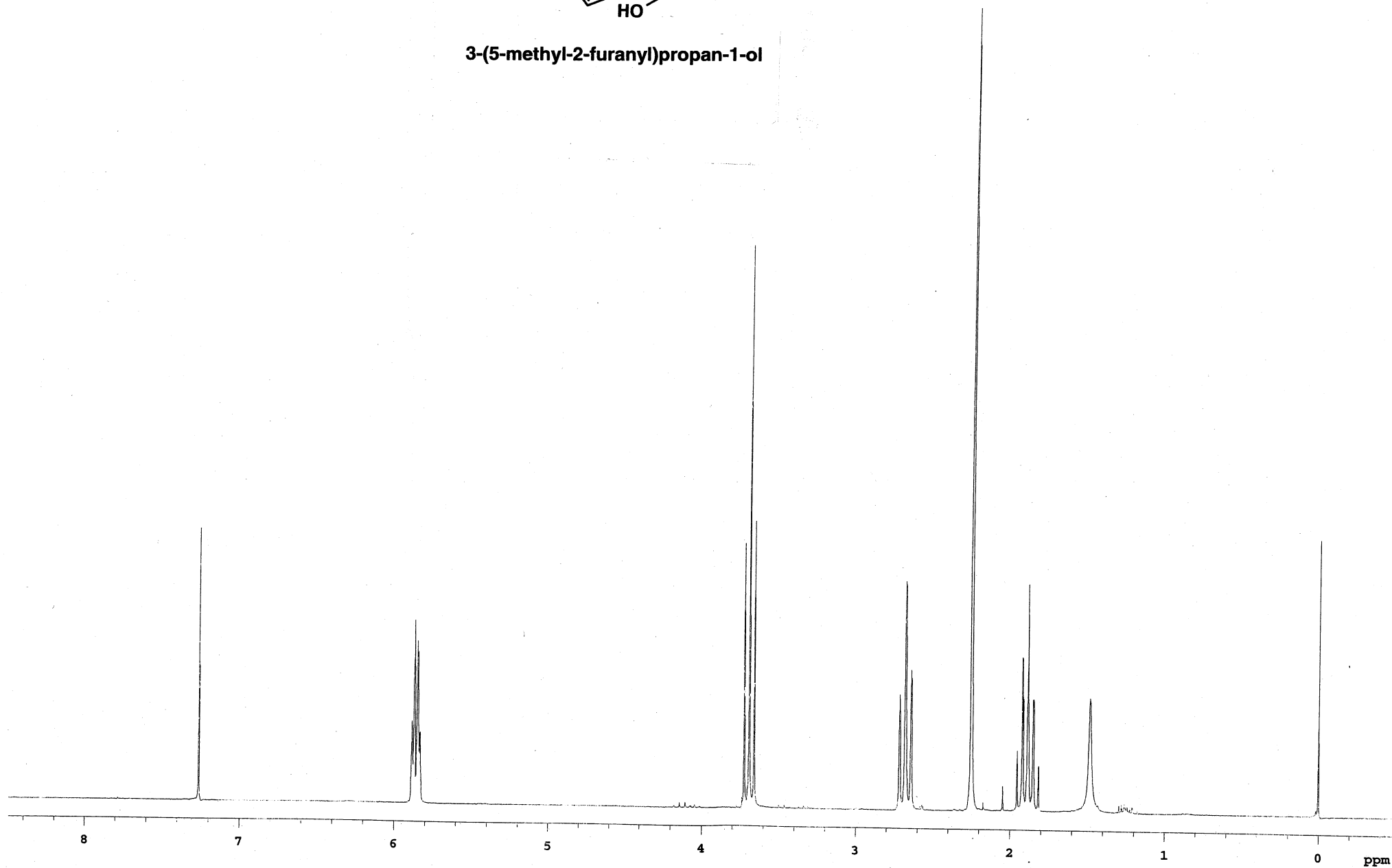


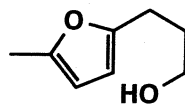
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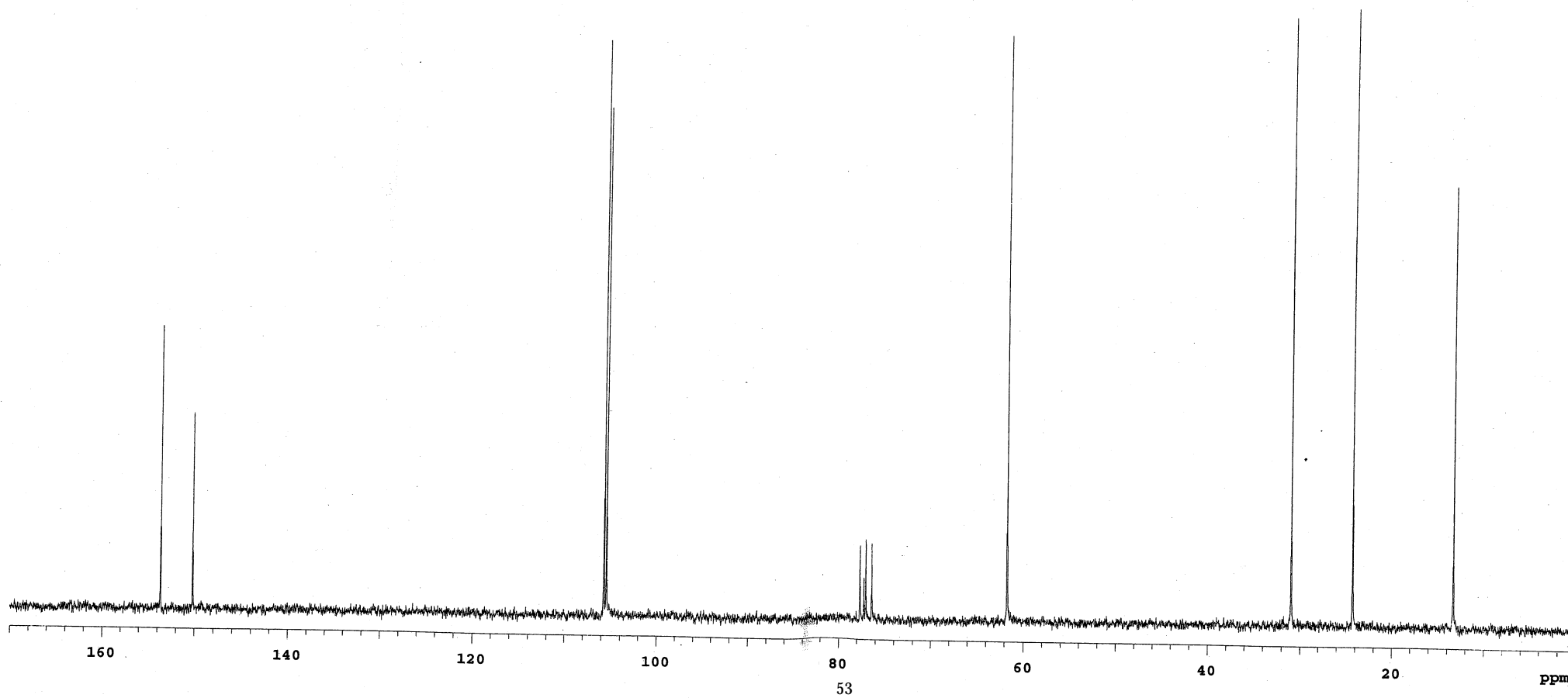


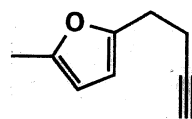
**3-(5-methyl-2-furanyl)propan-1-ol**



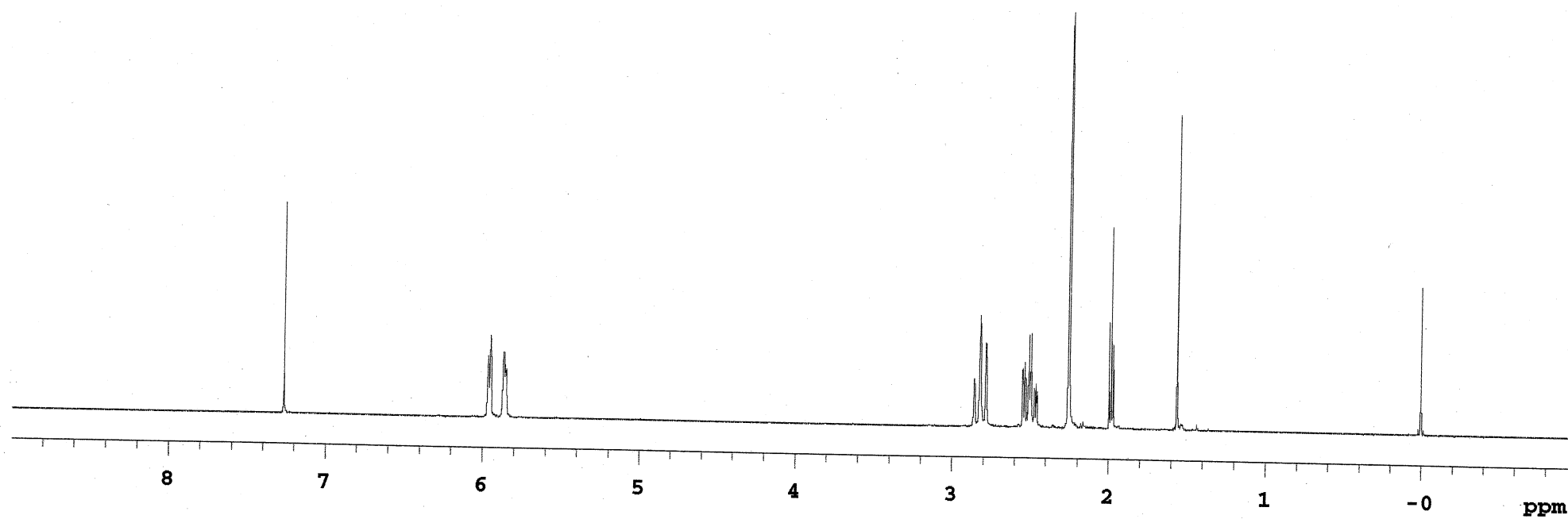


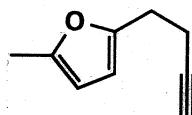
**3-(5-methyl-2-furanyl)propan-1-ol**





25





25

