

# Supporting Information for Synthesis of Functionalizable and Degradable Polymers by ROMP

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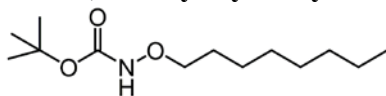
### Materials and General Information.

All commercially available reagents were purchased from Sigma-Aldrich (St. Louis, MO). Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Methanol was distilled over magnesium filings. Dichloromethane and triethylamine were distilled over calcium hydride. Dimethylsulfoxide (DMSO), *N,N*-dimethyl formamide (DMF), diethyl ether, hexanes, and ethyl acetate (EtOAc) were used as received. Deionized (milliQ) water and PD-10 Desalting Columns (GE Healthcare; Little Chalfont, UK) were used to purify water soluble polymers. All reactions were run under an inert atmosphere of N<sub>2</sub> unless otherwise specified. Reactions were stirred using Teflon coated magnetic stir bars. All glassware and stir bars were stored in oven before use. Cold baths were prepared using water/ice (0 °C) or ethylene glycol/CO<sub>2</sub> (-10 °C).

Analytical thin layer chromatography (TLC) was carried out on E. Merck (Darmstadt) TLC plates pre-coated with silica gel 60 F254 (250 μm layer thickness). Analyte visualization was accomplished using a UV lamp and by charring with potassium permanganate stain (Fischer, 1.5 g in 300 mL water with 6.5% K<sub>2</sub>CO<sub>3</sub> (w/v) and 5 mL 5% NaOH (w/v)). Flash column chromatography was performed on SiliaFlash<sup>®</sup> P60 (Silicycle; Quebec City, Canada; 40-63 μm particle size).

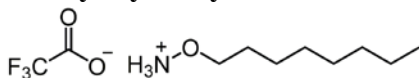
<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AC-300 MHz spectrometer (for small molecules) or Varian Inova-500 MHz spectrometer (for polymers). Chemical shifts are reported relative to tetramethylsilane or residual solvent peaks in parts per million (CHCl<sub>3</sub>: <sup>1</sup>H: δ 7.26, <sup>13</sup>C: δ 77.23). Peak multiplicity is reported as singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of doublet of triplets (ddt), triplet (t), doublet of triplets (dt), quartet (quart), pentet (pent), multiplet (m), AB quartet (ABX<sub>2</sub>). When visible, the degree of polymerization (DP) was based upon integration of the phenyl protons at the chain end relative to the polymer olefin protons. High resolution electrospray ionization mass spectra (HRESI-MS) were obtained on a Micromass LCT mass spectrometer. Room temperature GPC-SEC analysis (Viscotek GPC max) was performed on 300 x 7.5 mm PolyPor 5 μm mixed columns from Polymer Laboratories. Data was analyzed using OmniSEC software (Viscotek Inc.). Polymers were eluted with THF (1.0 mL/min, 40 °C) to determine M<sub>n</sub>, M<sub>w</sub>, and polydispersity index (M<sub>w</sub>/M<sub>n</sub>). Columns were calibrated with 10 narrow polystyrene standards (Polymer Laboratories S-M2-10 kit). UV-Vis absorption spectra were obtained on a Varian Cary 50-Scan UV-Visible Spectrophotometer and fluorescence emission spectra were obtained on a Hitachi F-4500 Fluorescence Spectrophotometer. All optical measurements were taken in a quartz cuvette and samples were prepared to a concentration of 80 μM chromophore, unless otherwise noted.

### ***N*-Boc, *O*-octyl hydroxylamine (**S1**)**



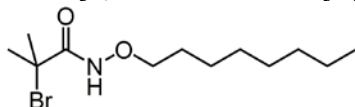
To a stirring solution of *N*-Boc hydroxylamine (1.40 g, 10.6 mmol) in 7.0 mL DMF was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.6 mL, 10.6 mmol) followed by 3.5 mL DMF. Then 1-bromooctane (1.6 mL, 9.5 mmol) was added to the solution followed by 3.5 mL DMF. The reaction was stirred at rt for 2 h, then 0.8 mL DMF was added to the reaction and the solution was moved to an oil bath and stirred at 50 °C. After 20 h, dichloromethane (90 mL) was added to the reaction and the solution was washed with 3 x 22 mL 15% aqueous citric acid solution. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (5 → 15% EtOAc/hexanes). **S1** was obtained as an oil (1.01 g, 43%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.12 (s, 1H), 3.86 (t, *J* = 6.7 Hz, 2H), 1.63 (pent, *J* = 7.0 Hz, 2H), 1.50 (s, 9H), 1.43-1.21 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): δ 156.9, 81.6, 77.0, 31.8, 29.4, 29.2, 28.2, 28.0, 25.9, 22.7, 14.1. HRESI-MS calcd for C<sub>11</sub>H<sub>27</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 263.2330; found 263.2324.

### ***O*-octyl hydroxylamine trifluoroacetate salt (**1a**)**



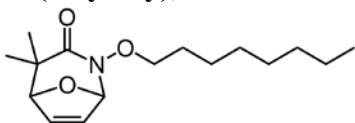
To a stirring solution of **S1** (1.01 g, 4.1 mmol) in dichloromethane (20 mL) at 0 °C was added trifluoroacetic acid (10.0 mL). Stirring continued for 1 h at 0 °C. The volatile compounds were removed under reduced pressure and the excess acid was removed by azeotrope with toluene (3 x 20 mL). **1a** was obtained as a clear oil (1.01 g, quant.), which was carried on without further purification. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 11.00-9.50 (broad s, 3H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.66 (pent, *J* = 7.0 Hz, 2H), 1.50-1.12 (m, 10H), 0.90 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): δ 162.8 (q, *J* = 36.7 Hz), 116.1 (q, *J* = 290.5 Hz), 76.0, 31.7, 29.1, 29.1, 27.5, 25.4, 22.6, 14.0. HRESI-MS calcd for C<sub>8</sub>H<sub>20</sub>NO [M-TFA]<sup>+</sup> 146.1540; found 146.1537.

### ***O*-octyl, α-bromoisobutyryl hydroxamic ester (**2a**)**



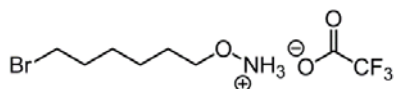
To a stirring solution of **1a** (1.06 g, 4.1 mmol) in dichloromethane (15.5 mL) at 0 °C was added triethylamine (0.4 mL, 4.2 mmol) in one portion followed by α-bromoisobutyryl bromide (0.5 mL, 4.1 mmol) dropwise. Stirring continued for 15 min at 0 °C. Pyridine (0.5 mL, 4.7 mmol) was added and the reaction was allowed to slowly warm to rt. After 20 h, the reaction was diluted with dichloromethane (15 mL) and washed with H<sub>2</sub>O (2 x 15 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (5 → 10% EtOAc/hexanes). **2a** was obtained as an oil (710 mg, 59%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.22 (s, 1H), 3.96 (t, *J* = 6.7 Hz, 2H), 1.99 (s, 6H), 1.70 (pent, *J* = 7.0 Hz, 2H), 1.55-1.20 (m, 10H), 0.91 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.7, 76.9, 59.7, 32.5, 31.8, 29.4, 29.2, 28.0, 25.8, 22.7, 14.1. HRESI-MS calcd for C<sub>12</sub>H<sub>24</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup> 311.1329; found 311.1318.

### *N*-(octyloxy), 8-oxo-2-azabicyclo[3.2.1]oct-6-en-3-one (**3a**)



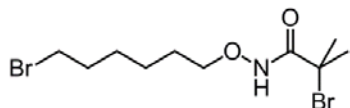
To a stirring solution of **2a** (705 mg, 2.4 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol and furan [1:1 (v/v) 0.25 M] at 0 °C was added triethylamine (0.68 mL, 4.8 mmol) dropwise over 5 min. Stirring continued at 0 °C for 5 min, then the reaction was allowed to warm to rt over 25 min. The volatile compounds were removed under reduced pressure and the residue was purified by flash column chromatography (7 → 15% EtOAc/hexanes). Compound **3a** was obtained as a light yellow oil (443 mg, 66%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 6.73 (broad d, *J* = 5.5 Hz, 1H), 6.49 (broad d, *J* = 5.5 Hz, 1H), 5.49 (broad s, 1H), 4.52 (broad s, 1H), 3.93 (ABX<sub>2</sub>, *J*<sub>AB</sub> = 9.2 Hz, *J*<sub>AX</sub> = 6.7 Hz, *J*<sub>BX</sub> = 7.3 Hz, 2H), 1.73-1.60 (m, 2H), 1.50 (s, 3H), 1.45-1.20 (m, 10H), 1.06 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): δ 175.9, 135.5, 134.7, 90.8, 87.4, 75.9, 49.0, 31.8, 29.4, 29.2, 28.2, 27.0, 25.9, 22.7, 19.8, 14.1. HRESI-MS calcd for C<sub>16</sub>H<sub>27</sub>NO<sub>3</sub> [M+H]<sup>+</sup> = 282.2064; found 282.2075.

### *O*-(6-bromohexyl) hydroxylamine trifluoroacetate salt (**1b**)



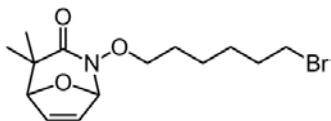
To a stirring solution of *N*-Boc-*O*-(6-bromohexyl) hydroxylamine<sup>[1]</sup> (954 mg, 3.22 mmol) in dichloromethane (16 mL) at 0 °C was added trifluoroacetic acid (8.0 mL). Stirring continued for 1 h at 0 °C. The volatile compounds were removed under reduced pressure and the excess acid was removed by azeotrope with toluene (3 x 20 mL). **1b** was obtained as a clear oil (998 mg, quant.), which was carried on without further purification. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 10.41 (broad s, 3H), 4.05 (broad t, *J* = 6.2 Hz, 2H), 3.40 (t, *J* = 7.0 Hz, 2H), 1.85 (pent, *J* = 6.7 Hz, 2H), 1.68 (broad pent, *J* = 6.3 Hz, 2H), 1.51-1.33 (m, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ 33.7, 32.6, 27.8, 27.6, 24.2. HRESI-MS calcd for C<sub>6</sub>H<sub>15</sub>BrNO [M+H]<sup>+</sup> 196.0332; found 196.0332.

### *O*-(6-bromohexyl), α-bromoisobutyryl hydroxamic ester (**2b**)



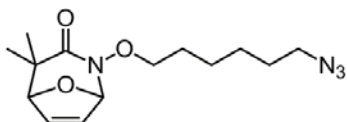
To a stirring solution of **1b** (945 mg, 3.05 mmol) in dichloromethane (11.5 mL) at 0 °C was added triethylamine (0.38 mL, 3.1 mmol) in one portion followed by α-bromoisobutyryl bromide (0.37 mL, 3.05 mmol) dropwise. Stirring continued for 15 min at 0 °C. Pyridine (0.29 mL, 3.45 mmol) was added and the reaction was allowed to slowly warm to rt. After 20 h, the reaction was diluted with dichloromethane (12 mL) and washed with H<sub>2</sub>O (2 x 12 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20% EtOAc/hexanes). **2b** was obtained as a light yellow oil (600 mg, 57%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 9.59 (broad s, 1H), 3.95 (t, *J* = 6.7 Hz, 2H), 3.42 (t, *J* = 6.8 Hz, 2H), 1.97 (s, 6H), 1.87 (pent, *J* = 7.0 Hz, 2H), 1.68 (pent, *J* = 6.9 Hz, 2H), 1.53-1.38 (m, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ 169.5, 76.2, 58.6, 33.8, 32.5, 32.1, 27.8, 27.7, 24.9. HRESI-MS calcd for C<sub>10</sub>H<sub>19</sub>Br<sub>2</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 343.9856; found 343.9851.

### *N*-(6-bromohexyloxy)-8-oxo-2-azabicyclo[3.2.1]oct-6-en-3-one (**3b**)



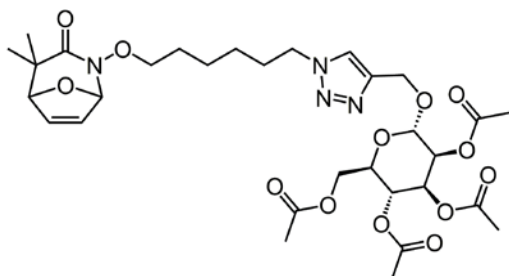
To a stirring solution of **2b** (665 mg, 1.93 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol and furan [1:1 (v/v) 0.25 M] at 0 °C was added triethylamine (0.46 mL, 3.85 mmol) dropwise over 5 min. Stirring continued at 0 °C for 5 min, then the reaction was allowed to warm to rt over 40 min. The volatile compounds were removed under reduced pressure and the residue was purified by flash column chromatography (20% EtOAc/hexanes). Compound **3b** was obtained as a light yellow oil (406 mg, 63%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.73 (dd, *J* = 6.0, 1.0 Hz, 1H), 6.48 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.48 (d, *J* = 1.0 Hz, 1H), 4.51 (d, *J* = 1.8 Hz, 1H), 3.92 (ABX<sub>2</sub>, *J*<sub>AB</sub> = 9.6 Hz, *J*<sub>AX</sub> = *J*<sub>BX</sub> = 6.8 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.87 (broad pent, *J* = 6.8 Hz, 2H), 1.67 (m, 2H), 1.49 (s, 3H), 1.46 (m, 4H), 1.05 (s, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ 175.6, 135.4, 134.7, 90.7, 87.3, 75.4, 48.9, 33.8, 32.6, 28.0, 27.9, 26.9, 25.1, 19.8. HRESI-MS calcd for C<sub>14</sub>H<sub>22</sub>BrNO<sub>3</sub> [M+H]<sup>+</sup> = 332.0856; found 332.0840.

### *N*-(6-azidohexyloxy)-8-oxo-2-azabicyclo[3.2.1]oct-6-en-3-one (**3c**)



To a stirring solution of **3b** (100 mg, 0.302 mmol) in DMF (10 mL) was added sodium azide (98 mg, 1.51 mmol). The solution was allowed to stir at 65 °C over night. After cooling to rt, the solution was diluted with water (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed under reduced pressure to afford **3c** as a clear oil (73 mg, 83%). Intermediate **3c** was taken on immediately without further purification, as it was found to be unstable. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.70 (dd, *J* = 5.8, 1.0 Hz, 1H), 6.49 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.47 (d, *J* = 1.1 Hz, 1H), 4.50 (d, *J* = 1.6 Hz, 1H), 3.92 (ABX<sub>2</sub>, *J*<sub>AX</sub> = *J*<sub>BX</sub> = 6.7 Hz, *J*<sub>AB</sub> = 9.2 Hz, 2H), 3.27 (t, *J* = 7.0 Hz, 2H), 1.71-1.56 (m, 4H), 1.48 (s, 3H), 1.48-1.39 (m, 4H), 1.04 (s, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ 175.4, 135.3, 134.6, 90.6, 87.1, 75.3, 51.2, 48.8, 28.5, 27.9, 26.7, 26.3, 25.3, 19.6. HRESI-MS calcd for C<sub>14</sub>H<sub>22</sub>N<sub>4</sub>O<sub>3</sub> [M+H]<sup>+</sup> 295.1765; found 295.1758.

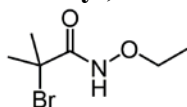
### *N*-(6-(4-(methoxy $\alpha$ -D-mannose-2,3,4,6-tetraacetate)triazole)hexyloxy)-8-oxo-2-azabicyclo[3.2.1]oct-6-en-3-one (**6**)



To a stirring solution of **3c** (37 mg, 0.126 mmol) and 1-propargyl- $\alpha$ -D-mannose-2,3,4,6-tetraacetate (49 mg, 0.126 mmol)<sup>[2]</sup> in toluene (0.25 mL) was added tris(triphenylphosphine) copper(I) bromide (2.7 mg, 0.0063 mmol)<sup>[3]</sup>. The reaction was allowed to stir at room temperature over night.

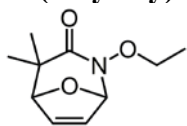
The reaction was then directly loaded onto a silica flash chromatography column for purification (60 → 90% EtOAc/hexanes). Compound **6** was isolated as an oil (55 mg, 64%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.60 (s, 1H), 6.72 (dd, *J* = 6.2, 1.0 Hz, 1H), 6.49 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.47 (d, *J* = 1.0 Hz, 1H), 5.36-5.24 (m, 3H), 4.96 (d, *J* = 1.4 Hz, 1H), 4.85 (d, *J* = 12.1 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.51 (d, *J* = 1.9 Hz, 1H), 4.37 (t, *J* = 7.4 Hz, 2H), 4.30 (dd, *J* = 12.4, 5.4 Hz, 1H), 4.13-4.06 (m, 3H), 3.96 (ABX<sub>2</sub>, *J*<sub>AB</sub> = 9.6, *J*<sub>AX</sub> = *J*<sub>BX</sub> = 6.6 Hz, 2H), 2.16 (s, 3H), 2.12 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 2.00-1.90 (m, 2H), 1.71-1.60 (m, 2H), 1.53-1.34 (m, 6H), 1.05 (s, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ 175.9, 170.8, 170.2, 170.0, 169.9, 143.6, 135.6, 134.9, 122.9, 97.0, 90.8, 87.5, 75.5, 69.6, 69.2, 68.8, 66.2, 62.3, 61.3, 50.4, 49.1, 30.3, 28.1, 27.0, 26.4, 25.4, 21.0, 20.9, 20.8, 20.8, 19.9. HRESI-MS calcd for C<sub>31</sub>H<sub>44</sub>N<sub>4</sub>O<sub>13</sub> [M+H]<sup>+</sup> 681.2978; found 681.2986.

### *O*-ethyl, α-bromoisobutyryl hydroxamic ester (**2d**)



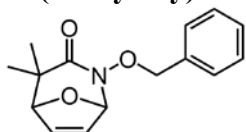
To a stirring solution of *O*-ethyl hydroxylamine hydrochloride (700 mg, 7.2 mmol) in dichloromethane (30 mL) at 0 °C was added triethylamine (1.00 mL, 7.2 mmol) in one portion followed by α-bromoisobutyryl bromide (0.89 mL, 7.2 mmol) dropwise. Stirring continued for 15 min at 0 °C. Pyridine (0.67 mL, 8.3 mmol) was added and the reaction was allowed to slowly warm to rt. After 20 h, the reaction was diluted with dichloromethane (30 mL) and washed with H<sub>2</sub>O (2 x 30 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (25% EtOAc/hexanes). **2d** was obtained as a light yellow oil (1.24 mg, 81%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 9.10 (broad s, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 1.90 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): δ 169.8, 72.3, 59.8, 32.5, 13.4. HRESI-MS calcd for C<sub>6</sub>H<sub>12</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup> 210.0125; found 210.0127.

### *N*-(ethyloxy)-8-oxo-2-azabicyclo[3.2.1]oct-6-en-3-one (**3d**)



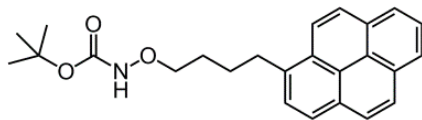
To a stirring solution of **2d** (1.17 g, 5.5 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol and furan [1:1 (v/v) 0.25 M] at 0 °C was added triethylamine (1.6 mL, 11.1 mmol) dropwise over 5 min. Stirring continued at 0 °C for 5 min, then the reaction was allowed to warm to rt over 25 min. The volatile compounds were removed under reduced pressure and the residue was purified by flash column chromatography (25% EtOAc/hexanes). Compound **3d** was obtained as an oil (720 mg, 69%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 6.66 (broad d, *J* = 6.6 Hz, 1H), 6.42 (broad d, *J* = 6.4 Hz, 1H), 5.41 (s, 1H), 4.44 (s, 1H), 3.93 (m, 2H), 1.45 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.98 (s, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): δ 175.8, 135.5, 134.7, 90.9, 87.4, 71.8, 49.0, 26.9, 19.8, 13.8. HRESI-MS calcd for C<sub>10</sub>H<sub>15</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 198.1125; found 198.1130.

### *N*-(benzyloxy)-8-oxo-2-azabicyclo[3.2.1]oct-6-en-3-one (**3e**)



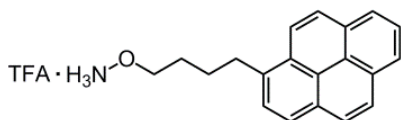
Compound **3e** was synthesized as previously reported in ref. 29.

### ***N*-Boc, *O*-(4-pyrenylbutyl) hydroxylamine (**S2**)**



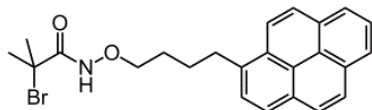
To a stirring solution of 4-(1-pyrenyl)butyl methanesulfonate<sup>[4]</sup> (415 mg, 1.18 mmol) and *N*-Boc hydroxylamine (235 mg, 1.77 mmol) in DMF (1.3 mL) was added DBU (0.26 mL, 1.77 mmol) in DMF (0.65 mL). The reaction was allowed to stir for 20 h at 50 °C. The reaction was then concentrated and the residue was purified on a flash chromatography column (20% EtOAc/Hexanes). **S2** was isolated as an oil (236 mg, 51%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.19 (dd, *J* = 9.3 Hz, 1H), 8.12-8.06 (m, 2H), 8.05-8.00 (m, 2H), 7.98-7.88 (m, 3H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.21 (broad s, 1H), 3.86 (t, *J* = 6.6 Hz, 2H), 3.30 (t, *J* = 7.4 Hz, 2H), 1.96-1.82 (m, 4H), 1.82-1.68 (m, 4H), 1.44 (s, 9H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ 157.1, 136.6, 131.5, 131.0, 129.9, 128.7, 127.6, 127.3, 127.3, 126.7, 125.9, 125.2, 125.1, 124.9, 124.9, 124.8, 123.5, 81.7, 76.6, 33.3, 28.3, 28.2, 27.7. HRESI-MS calcd for C<sub>25</sub>H<sub>31</sub>NO<sub>3</sub> [M+NH<sub>4</sub>]<sup>+</sup> 407.2333; found 407.2348.

### ***O*-(4-pyrenylbutyl) hydroxylamine trifluoroacetate salt, **1f**.**



To a stirring solution of **S2** (117 mg, 0.30 mmol) in dichloromethane (1.5 mL) at 0 °C was added trifluoroacetic acid (0.75 mL). Stirring continued for 1 h at 0 °C. The volatile compounds were removed under reduced pressure and the excess acid was removed by azeotropeing with toluene (3 x 20 mL). **1f** was obtained as an oil (121 mg, quant.), which was carried on without further purification. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 10.09 (broad s, 3H), 8.00-7.50 (m, 8H), 7.35 (d, *J* = 8.1 Hz, 1H), 3.92 (broad t, *J* = 5.5 Hz, 2H), 2.82 (broad t, *J* = 7.0 Hz, 2H), 1.70-1.30 (m, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): δ 135.8, 131.5, 130.9, 129.9, 129.3, 128.5, 127.5, 127.3, 126.9, 126.7, 125.7, 125.6, 125.0, 125.0, 124.8, 123.1, 75.9, 32.6, 27.5, 27.3. HRESI-MS calcd for C<sub>20</sub>H<sub>20</sub>NO [M-TFA]<sup>+</sup> 290.1540; found 290.1532.

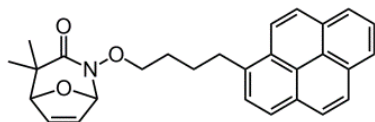
### ***O*-(4-pyrenylbutyl), α-bromoisobutyryl hydroxamic ester (**2f**)**



To a stirring solution of **1f** (120 mg, 0.30 mmol) in dichloromethane (1.05 mL) at 0 °C was added triethylamine (38 μL, 0.30 mmol) in one portion followed by α-bromo isobutyryl bromide (36 μL, 0.30 mmol) dropwise. Stirring continued for 15 min at 0 °C. Pyridine (30 μL, 0.35 mmol) was added and the reaction was allowed to slowly warm to rt. After 20 h, the reaction was diluted with dichloromethane (5 mL) and washed with H<sub>2</sub>O (2 x 4 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20% EtOAc/hexanes). **2f** was obtained as an oil (68 mg, 53%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 9.14 (broad s, 1H), 8.23 (d, *J* = 9.1 Hz, 1H), 8.16-8.10 (m, 2H), 8.00-7.91 (m, 3H), 7.82- (d, *J* = 7.7 Hz, 1H), 3.94 (t, *J* = 6.6 Hz, 2H), 3.35 (t, *J* = 7.4 Hz,

2H), 2.04-1.86 (m, 8H), 1.86-1.74 (m, 2H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  169.9, 136.5, 131.6, 131.1, 130.0, 128.8, 127.7, 127.5, 126.8, 126.0, 125.2, 125.2, 125.0, 125.0, 124.9, 123.5, 76.7, 59.6, 33.3, 32.5, 28.0. ESI-MS calcd for  $\text{C}_{48}\text{H}_{53}\text{BrN}_2\text{O}_4$   $[\text{2M-HBr}]^+$  calcd 795.7; found 796.4. **2d** was found to dimerize upon ionization, eliminating 1 eq of HBr.

### *N*-(4-pyrenylbutyloxy)-8-oxo-2-azabicyclo[3.2.1]oct-6-en-3-one (**3f**)

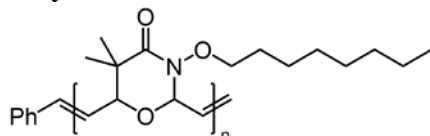


To a stirring solution of **2f** (120 mg, 0.28 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol and furan [1:1 (v/v) 0.25 M] at 0 °C was added triethylamine (73  $\mu\text{L}$ , 0.59 mmol) dropwise over 5 min. Stirring continued at 0 °C for 5 min, then the reaction was allowed to warm to rt over 40 min. The volatile compounds were removed under reduced pressure and the residue was purified by flash column chromatography (20% EtOAc/hexanes). Compound **3f** was obtained as an orange solid (96 mg, 82%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.25 (d,  $J = 9.0$  Hz, 1H), 8.18-8.11 (m, 2H), 8.11-8.05 (m, 2H), 8.02-7.93 (m, 3H), 7.84 (d,  $J = 7.8$  Hz, 1H), 6.65 (dd,  $J = 5.8, 0.9$  Hz, 1H), 6.43 (dd,  $J = 6.1, 1.8$  Hz, 1H), 5.42 (d,  $J = 1.1$  Hz, 1H), 4.46 (d,  $J = 1.7$  Hz, 1H), 3.98 (ABX<sub>2</sub>,  $J_{AB} = 9.3$  Hz,  $J_{AX} = J_{BX} = 6.5$  Hz, 2H), 3.36 (t,  $J = 7.6$  Hz, 2H), 2.05-1.72 (m, 4H), 1.47 (s, 3H), 1.03 (s, 3H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  175.9, 136.7, 135.6, 134.9, 131.7, 131.1, 130.0, 128.9, 127.7, 127.5, 127.5, 126.8, 126.0, 125.3, 125.3, 125.1, 125.0, 124.9, 123.6, 91.0, 87.6, 75.7, 49.2, 33.4, 28.5, 28.3, 27.1, 20.0. HRESI-MS calcd for  $\text{C}_{28}\text{H}_{27}\text{NO}_3$   $[\text{M+H}]^+$  426.2064; found 426.2063.

### General Procedure: Synthesis of Polymers by ROMP

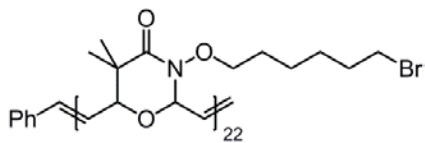
To a stirring solution of initiator **11** or **5**<sup>[5]</sup> in either chloroform or THF (0.1 mL) and under an atmosphere of argon was added monomer (0.20 mmol) in either chloroform or THF (0.1 mL). The reaction was allowed to stir for the time and temperature specified in Table 1. The reaction was quenched with ethyl vinyl ether (100  $\mu\text{L}$ ) and the solution was allowed to stir over night at rt. The reaction mixture was triturated using Et<sub>2</sub>O or MeOH (30 mL) and the resulting solid was isolated via centrifugation.

### Polymer 4a



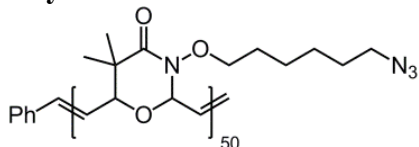
Polymers **4a** were synthesized following the general procedure using monomer **3a**. Polymer was collected by trituration into MeOH.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  6.25-5.60 (m, 2H), 5.50-5.20 (m, 1H), 4.35-3.55 (m, 3H), 1.75-1.00 (m, 18H), 1.90-1.80 (broad t,  $J = 6.7$  Hz, 3H).

### Polymer 4b



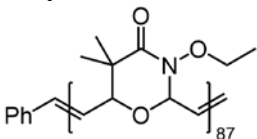
Polymers **4b** were synthesized following the general procedure using monomer **3b**. Polymer was collected by trituration into cold MeOH.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.50-7.30 (m, 0.18 H), 7.00-6.80 (m, 0.04H), 6.20-5.70 (m, 2H, olefin), 5.45-5.25 (m, 1H), 4.30-3.70 (m, 3H), 3.40 (broad t,  $J=6.1$  Hz, 2H), 1.85 (broad s, 2H), 1.70-1.35 (m, 6H), 1.30-1.05 (m, 6H).

### Polymer 4c



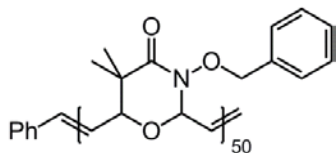
Polymer **4b** (5 mg) and sodium azide (5 mg, 5 equiv with respect to bromine) were taken up in 1.0 mL DMF. The reaction was stirred at 65 °C overnight. The reaction was allowed to cool and the solvent was removed under reduced pressure. The residue was taken up in 2.0 mL of dichloromethane and the solution was separated from the insoluble material. The solvent was removed under reduced pressure to afford polymer **4c**.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.60-7.40 (m, 0.10H), 6.20-5.75 (m, 2H), 5.50-5.25 (m, 1H), 4.30-3.70 (m, 3H), 3.26 (broad t, 2H), 1.75-1.00 (m, 16H).

### Polymer 4d



Polymers **4d** were synthesized following the general procedure using monomer **3d**. Polymer was collected by trituration into  $\text{Et}_2\text{O}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  6.30-5.60 (m, 2H), 5.60-5.10 (m, 1H), 4.70-3.50 (m, 3H), 1.50-0.90 (m, 9H).

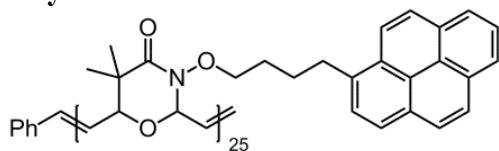
### Polymer 4e



Polymers **4e** were synthesized following the general procedure using monomer **3e** in a 1:1 THF: $\text{CHCl}_3$  solution. Polymer was collected by trituration into  $\text{Et}_2\text{O}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.50-7.20 (broad s, 5H), 6.10-5.60 (m, 2H), 5.20-4.60 (m, 3H), 4.15-3.90 (broad d, 1H), 1.35-1.00 (broad s, 6H). See Table S2 for representative  $M_n$  and PDI values.

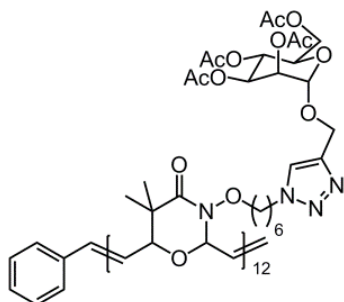


### Polymer 4f



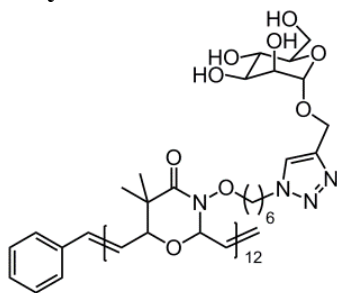
Polymer **4f** was prepared following the general procedure using monomer **3f**. Polymer was collected via trituration into Et<sub>2</sub>O. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.40-7.40 (m, 9.1H), 6.00-2.80 (m, 7H), 1.90-1.30 (m, 5H), 1.30-0.50 (m, 6H).

### Polymer 7



Polymer **7** was synthesized following the general procedure using monomer **6**. Collect polymer by trituration into Et<sub>2</sub>O. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.62 (broad s, 1H), 7.50-7.43 (m, 0.18H), 7.40-7.30 (m, 0.21H), 6.20-5.70 (m, 2H), 5.50-5.15 (m, 4H), 4.96 (broad s, 1H), 4.85 (broad d, 1H), 4.68 (broad d, 1H), 4.50-4.00 (m, 6H), 4.00-3.75 (m, 2H), 2.15 (broad s, 3H), 2.11 (broad s, 3H), 2.04 (broad s, 3H), 1.98 (broad s, 3H), 2.00-1.90 (m, 2H), 1.50-0.80 (m, 14H).

### Polymer 8



To a stirring solution of polymer **7** (7.0 mg) dissolved in DMSO (1.0 mL) was added a solution of sodium methoxide in methanol (50 μL, 0.5 M). The solution was allowed to stir at rt for 45 min and then directly loaded onto a PD-10 desalting column to remove the DMSO and methoxide. The water was removed by lyophilization to obtain polymer **8** as an off white solid (5.0 mg). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 500 MHz): δ 8.15 (s, 1H), 7.59 (s, 0.13H), 7.36 (s, 0.21H), 6.20-5.60 (m, 2H), 5.00-4.20 (m, 10H), 4.10-3.70 (m, 5H), 1.83 (s, 2H), 1.80-1.00 (m, 16H).

entry	[ <b>3e</b> ] <sub>o</sub> /[ <b>11</b> ] <sup>[a]</sup>	time (h)	conv (%) <sup>[b]</sup>	Yield <sup>[c],[d]</sup>	M <sub>n</sub> <sup>theo</sup> (g/mol)	M <sub>n</sub> <sup>GPC</sup> <sup>[e]</sup> (g/mol)	PDI (M <sub>n</sub> /M <sub>w</sub> )
1	10/1	1	41	73	1100	13800	1.7
2	10/1	3	66	76	1700	11700	1.8
3	10/1	7	92	72	2400	9400	2.0
4	10/1	13	92	83	2400	8800	2.1
5	10/1	20	97	76	2500	2600	2.6

[a] [**3e**]<sub>o</sub> = 1M in CHCl<sub>3</sub>, 20 °C. [b] based off of <sup>1</sup>H-NMR integrations of monomer olefin signals to polymer olefin signals. [c] isolated. [d] theoretical yield based off of monomer conversion. [e] calibrated with polystyrene standards, eluted in THF.

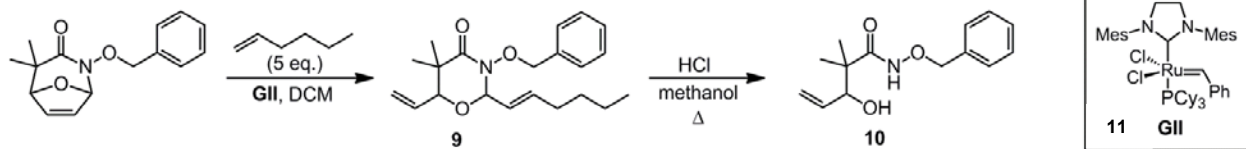
**Table S1.** Evidence for backbiting during the polymerization of oxazinone monomers using catalyst **11** in the non-oxygenated solvent CHCl<sub>3</sub>. There is a concomitant increase in PDI and decrease in M<sub>n</sub> as the polymerization progresses. In addition, these values continue to erode even after the starting material has been consumed.

entry	[ <b>3e</b> ] <sub>o</sub> /[ <b>5</b> ] <sup>[a]</sup>	solvent	Temp (°C)	time (h)	conv (%) <sup>[b]</sup>	yield <sup>[c],[d]</sup>	M <sub>n</sub> <sup>theo</sup> (g/mol)	M <sub>n</sub> <sup>GPC</sup> (g/mol) <sup>[e]</sup>	PDI (M <sub>n</sub> /M <sub>w</sub> )
1	10/1 <sup>[f]</sup>	CHCl <sub>3</sub>	20	7	92	72	2400	9400	2.0
2	100/1 <sup>[f]</sup>	CHCl <sub>3</sub>	40	28	71 <sup>[g]</sup>	49	18400	11200	1.7
3	100/1	THF	20	2	80	n/a	20700	20500	3.3
4	25/1	THF:CHCl <sub>3</sub> <sup>[h]</sup>	-10 → rt	3	85	79	5500	8500	1.5
5	50/1	THF:CHCl <sub>3</sub> <sup>[h]</sup>	-10 → rt	5	78	85	10100	11300	1.7
6	100/1	THF:CHCl <sub>3</sub> <sup>[h]</sup>	-10 → rt	7	64	60	16700	18900	2.1
7	100/1	THF:CHCl <sub>3</sub> <sup>[h]</sup>	-10 → rt	25	65	60	16900	19000	2.2
8	200/1	THF:CHCl <sub>3</sub> <sup>[h]</sup>	-10 → rt	7	57	66	29600	28500	2.1

[a] [**3e**]<sub>o</sub> = 1M. [b] based off of <sup>1</sup>H-NMR integrations of monomer olefin signals to polymer olefin signals. [c] isolated. [d] theoretical yield based off of monomer conversion. [e] calibrated with polystyrene standards, eluted in THF. [f] using catalyst **11** [g] additional 15-20% cyclic dimer. [h] 1:1 (v/v).

**Table S2.** Polymerization of monomer **3e** using ROMP. It was found that the optimized polymerization conditions for monomer **3a** (i.e. 1M in THF, **5**, rt) did not work efficiently for monomer **3e**. Better polymerization conditions for this monomer were found to be: 1M in 1:1 THF:CHCl<sub>3</sub>, **5**, -10 °C warming to rt. Although backbiting was mitigated using these reaction conditions [polymer M<sub>n</sub> and PDI does not erode over long reaction times (entry 6 and 7)], the observed polymer dispersities remained high. The reason this monomer is less well behaved is still under further investigation. However, we posit that the growing polymer chain of **4e** is less soluble in neat THF than the other polymers. This solubility discrepancy leads to increased PDIs as the growing chain-end randomly exists in and out of solution.

### Characterization of the Decomposition Products from the Ring-Opening of an *N*-alkoxy-1,3-oxazin-2-one “1-mer”:



### 3-benzyloxy-5,5-dimethyl-2-(1'-pentenyl)-6-vinyl-1,3-oxazin-4-one (**9**)

To a stirring solution of **3e** (100 mg, 0.388 mmol) in dichloromethane (1.0 mL) was added 1-hexene (0.24 mL, 1.95 mmol) and then **11** (33 mg, 0.0388 mmol) in dichloromethane (0.3 mL). The reaction was allowed to stir at room temperature for 1.45 h and was then quenched by the addition of ethyl vinyl ether (150  $\mu$ L). The solution was allowed to stir for an additional hour. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (5  $\rightarrow$  18% EtOAc/hexanes). The product was isolated as a red oil (59 mg, 44%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.45-7.30 (m, 5H), 5.95 (dt,  $J$  = 15.5, 7.0 Hz, 1H), 5.79 (ddd,  $J$  = 17.4, 10.5, 6.5 Hz, 1H), 5.49 (ddt,  $J$  = 15.5, 7.8, 1.5 Hz, 1H), 5.32 (dt,  $J$  = 17.5, 1.5 Hz, 1H), 5.30 (dt,  $J$  = 10.5, 1.5 Hz, 1H), 5.08 (d,  $J$  = 7.8 Hz, 1H), 4.90 (AB quartet,  $J_{AB}$  = 9.5 Hz, 2H), 3.96 (broad d,  $J$  = 6.0 Hz, 1H), 2.12 (broad quart,  $J$  = 6.8 Hz, 2H), 1.49-1.31 (m, 4H), 1.23 (s, 3H), 1.14 (s, 3H), 0.91 (t,  $J$  = 7.2 Hz, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  173.4, 139.7, 135.3, 132.2, 129.8, 128.9, 128.5, 125.5, 119.4, 91.5, 82.7, 77.3, 45.0, 31.98, 30.9, 22.5, 21.0, 20.7, 14.9. HRESI-MS calcd for C<sub>21</sub>H<sub>29</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 344.2; observed 344.2. The regiochemistry of **9** was determined by the coupling between signals at  $\delta$  5.49 to  $\delta$  5.08 and coupling between signals at  $\delta$  5.79 to  $\delta$  3.96. NMR spectrum showed that is single isomer was isolated.

### Decomposition of **9**

To a stirring solution of **9** (20 mg) in methanol (0.50 mL) was added 1 mL of a 2.27 M HCl solution in methanol. The solution was allowed to stir at 45 °C over night.<sup>[6]</sup> The solution was neutralized by elution through a plug of Aberlite<sup>®</sup> IRA 400(OH) basic resin and the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (the column was packed with 10% EtOAc/hexanes and eluted with a gradient to 20% EtOAc/hexanes). A low R<sub>f</sub> fraction was isolated to afford a clear oil characterized as **10**. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.85 (s, 1H, NH), 7.60-7.25 (m, 5H), 5.82 (ddd,  $J$  = 17.1, 10.3, 6.8 Hz, 1H), 5.28 (dt,  $J$  = 17.2, 1.0 Hz, 1H), 5.23 (dd, 10.3, 1.0 Hz, 1H), 4.91 (s, 2H), 3.99 (broad d,  $J$  = 6.9 Hz, 1H), 1.21 (s, 3H), 1.08 (s, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  174.7, 136.1, 135.3, 129.3, 128.8, 128.6, 118.5, 78.6, 78.0, 45.0, 23.8, 20.4. HRESI-MS calcd for C<sub>14</sub>H<sub>19</sub>NO<sub>3</sub> [M+Na]<sup>+</sup> 272.1288; observed 272.1266.

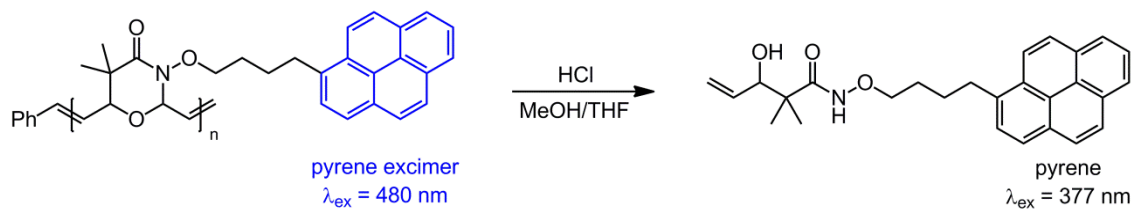
### Monitoring the Acidic Degradation of the ROMP Derived Polymers:

A stock solution of HCl in methanol (2.27 M) underwent four 10x dilutions to afford methanol solutions with [H<sup>+</sup>] between 2.27 M and 0.27  $\mu$ M. Polymer (2.4 mg) was taken up in THF (0.75 mL) and allowed to dissolve over 1 h. The polymer solution was passed through a syringe driven filter (Millex<sup>®</sup> - GV, PVDF – 0.22  $\mu$ m) and an initial M<sub>n</sub> reading was acquired by GPC. Acidic methanol solution (0.25 mL) was added to the polymer solution and degradation at each [H<sup>+</sup>] concentration was monitored by analyzing aliquots of solution (100  $\mu$ L) over 48 h by GPC.

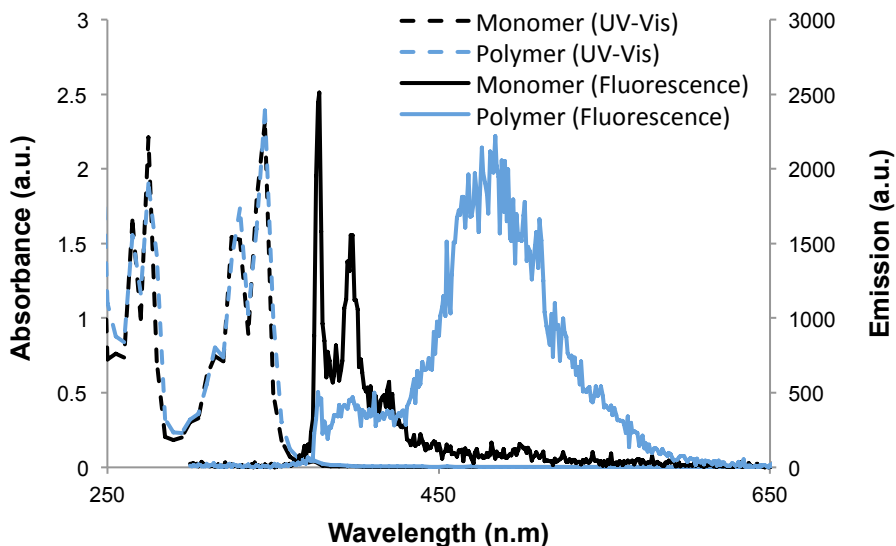
### Monitoring the Basic Degradation of the ROMP Derived Polymers:

A commercially available stock solution of sodium methoxide in methanol (0.50 M) underwent four 10x dilutions to afford methanol solutions with  $[\text{OMe}]$  between 0.5 M and 0.05  $\mu\text{M}$ . Polymer (2.4 mg) was taken up in THF (0.75 mL) and allowed to dissolve over 1 h. The polymer solution was passed through a syringe driven filter (Millex<sup>®</sup> - GV, PVDF – 0.22  $\mu\text{m}$ ) and an initial  $M_n$  reading was acquired by GPC. Basic methanol solution (0.25 mL) was added to the polymer solution and degradation was monitored at each  $[\text{OMe}]$  concentration by analyzing aliquots of solution (100  $\mu\text{L}$ ) over 48 h by GPC.

### Monitoring the Degradation of Polymer 4d via Pyrene Fluorescence:



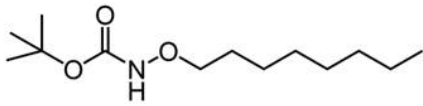
Polymer **4d** (2.4 mg) was taken up in THF (0.75 mL) and allowed to dissolve over 1 h. The polymer solution was passed through a syringe driven filter (Millex<sup>®</sup> - GV, PVDF – 0.22  $\mu\text{m}$ ) and then acidified methanol (0.25 mL, 2.27 M) was added to the solution. The solution was allowed to stir at room temperature. Periodically, aliquots of the solution (14.3  $\mu\text{L}$ ) were drawn and diluted with THF (1.0 mL). The fluorescence emission spectrum of the sample was taken ( $\lambda_{\text{ex}} = 250 \text{ nm}$ ) and the ratio of pyrene exciplex emission ( $\lambda_{\text{em}} = 480 \text{ nm}$ ) to monomeric pyrene emission ( $\lambda_{\text{em}} = 377 \text{ nm}$ ) was calculated. Decomposition was monitored by following this ratio over time (see Figure 3).



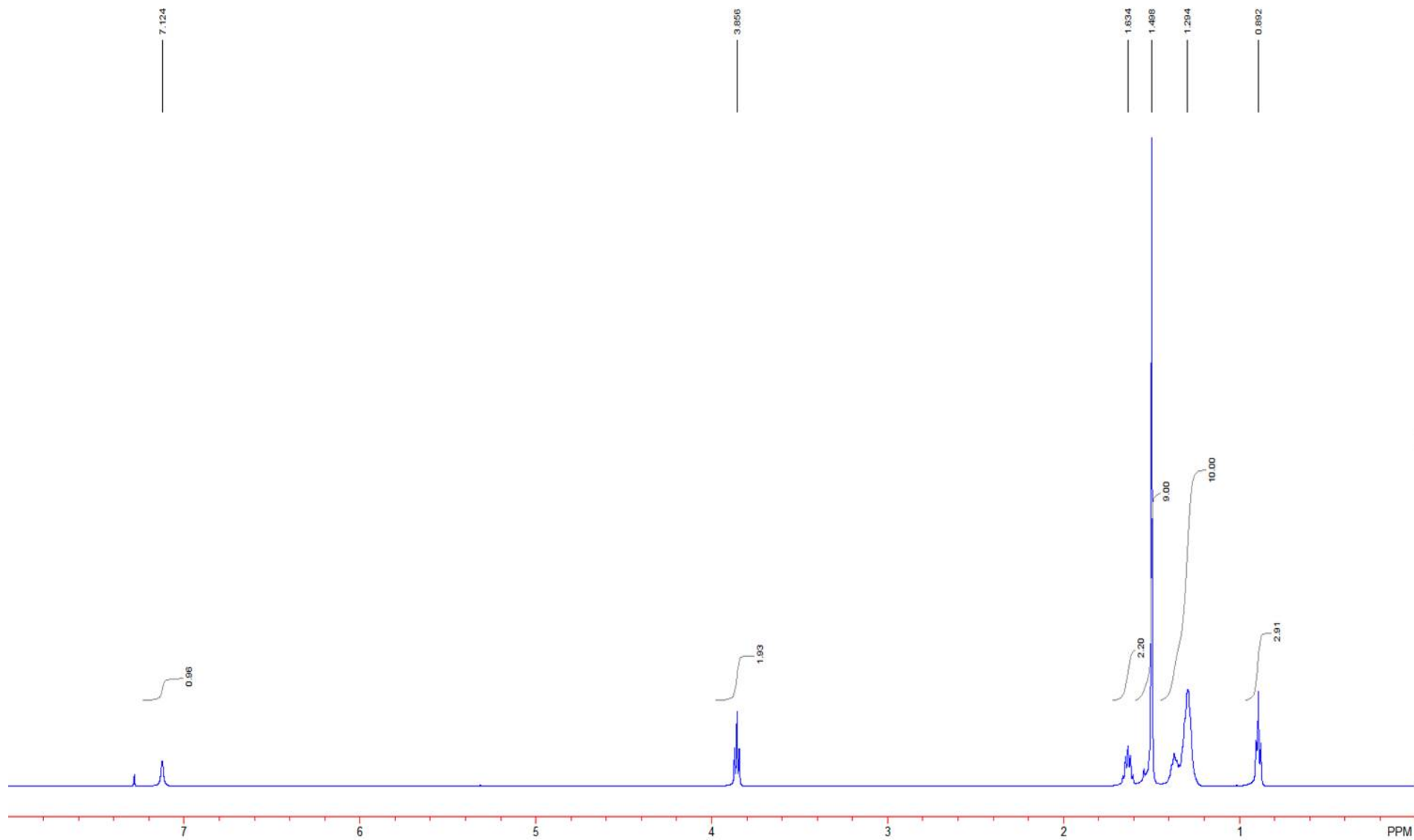
**Figure S1.** Optical properties of monomer **3f** and polymer **4f**. UV-Vis absorbance spectra are identical indicating that the ground state of pyrene is not changed upon polymerization of **3f**. There is a red shift in fluorescence emission spectra upon polymerization characteristic of pyrene excimer formation (see ref. 47). As the polymer degrades, free pyrene is released from polymer **4f** decreasing the number of molecules engaged in exciplex formation.  $\lambda_{\text{ex}} = 250 \text{ nm}$ .  $[\text{em}(480 \text{ nm})/\text{em}(377 \text{ nm})]_{\text{monomer}} = 0.038$ ,  $[\text{Em}(480 \text{ nm})/\text{Em}(377 \text{ nm})]_{\text{polymer}} = 3.5$ .

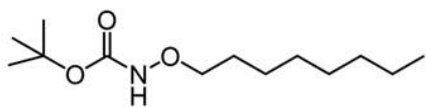
## References

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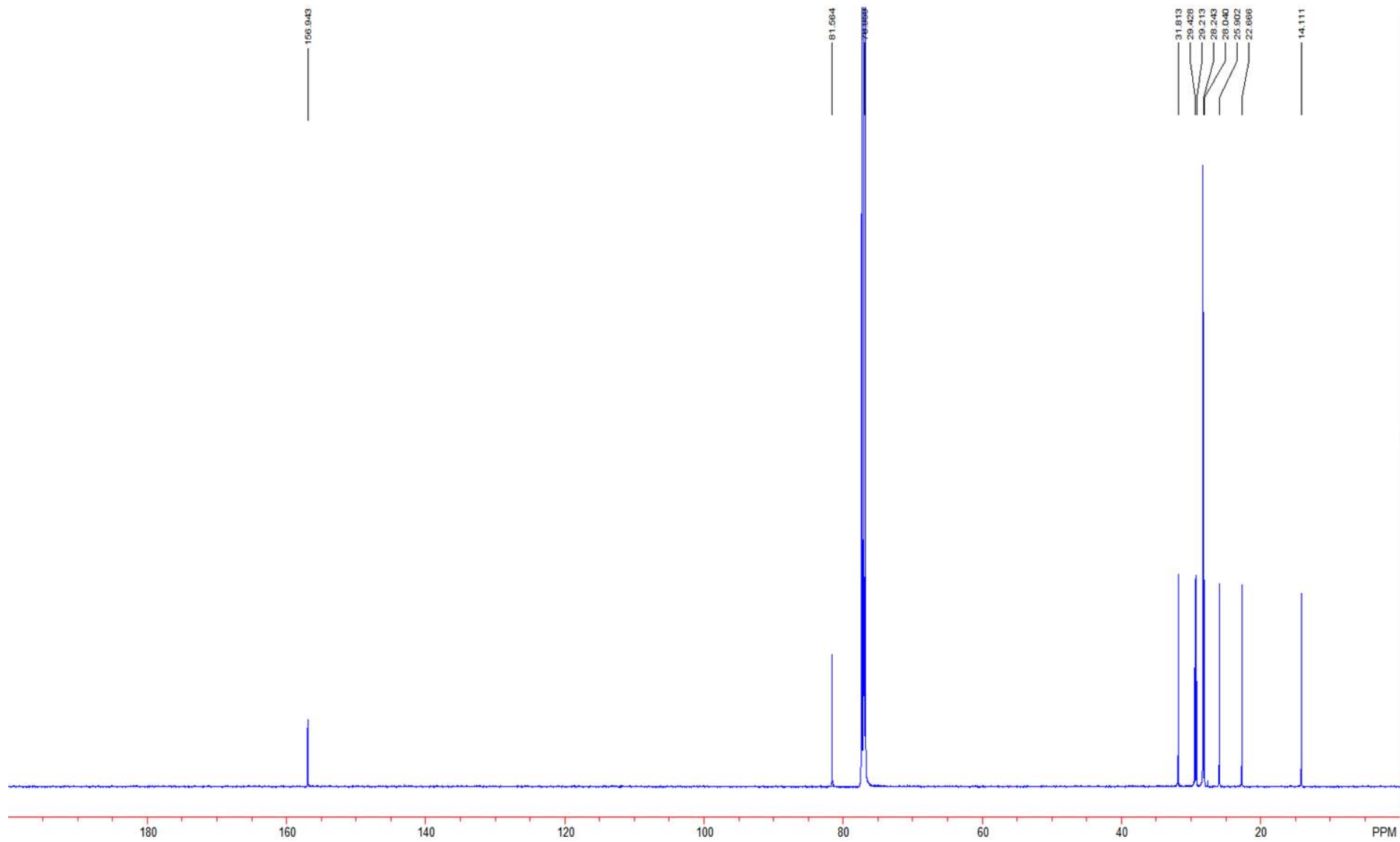


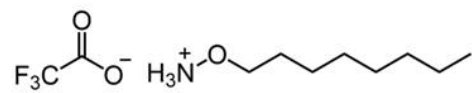
**S1**  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz)



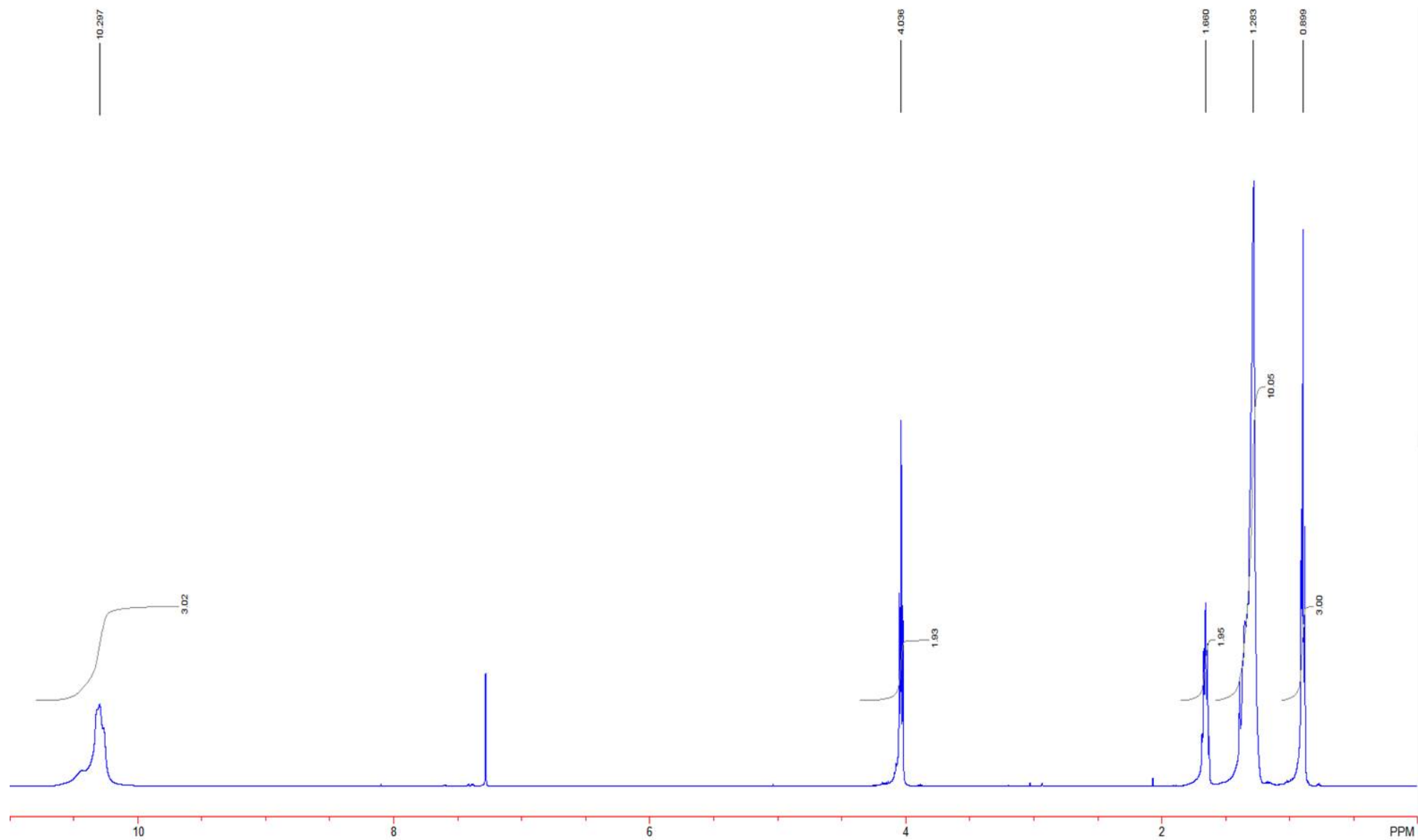


**S1**  
 $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz)

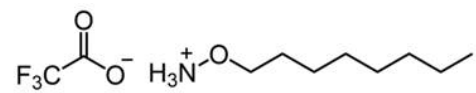




**1a**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)

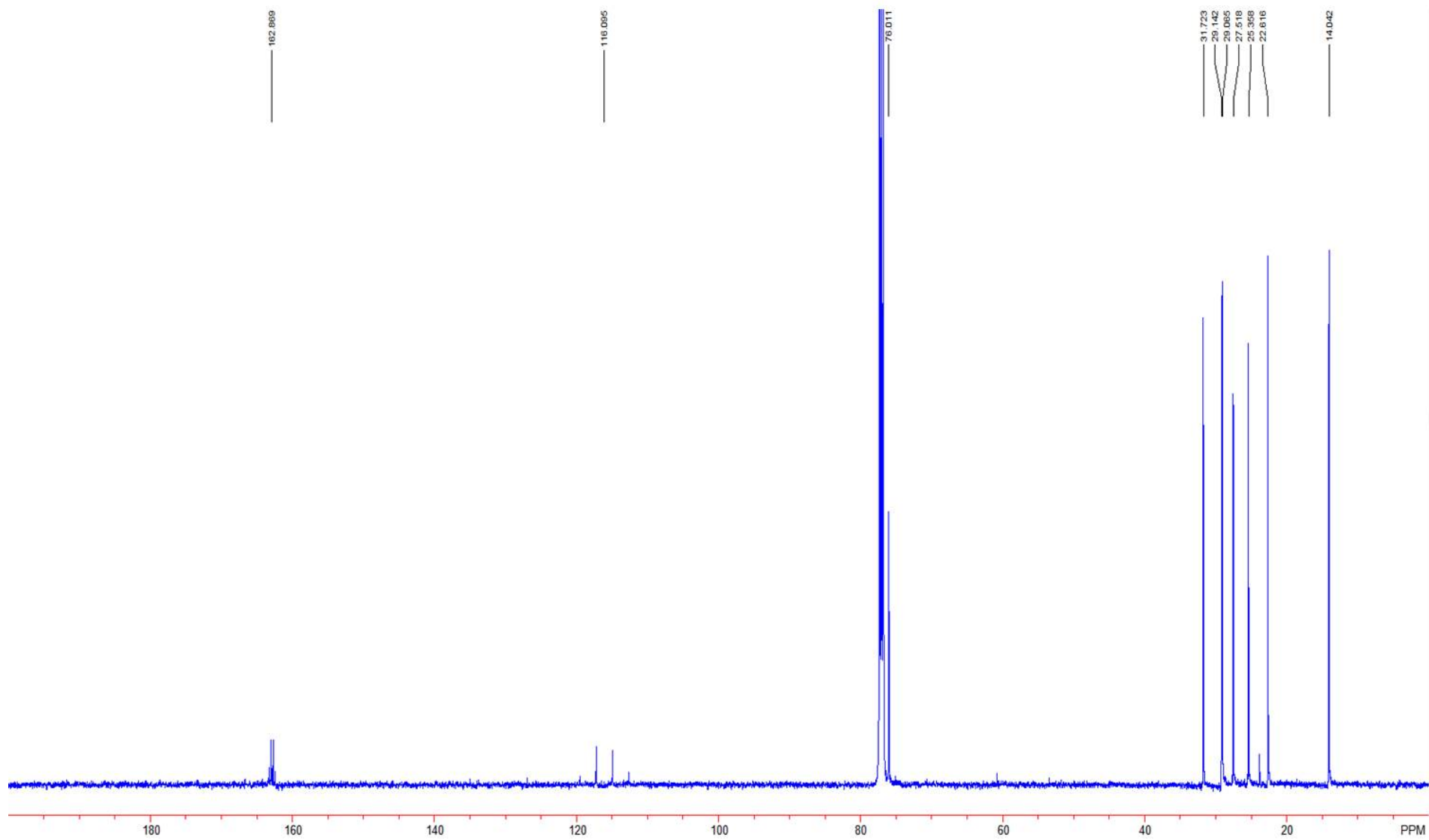


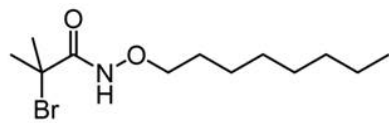




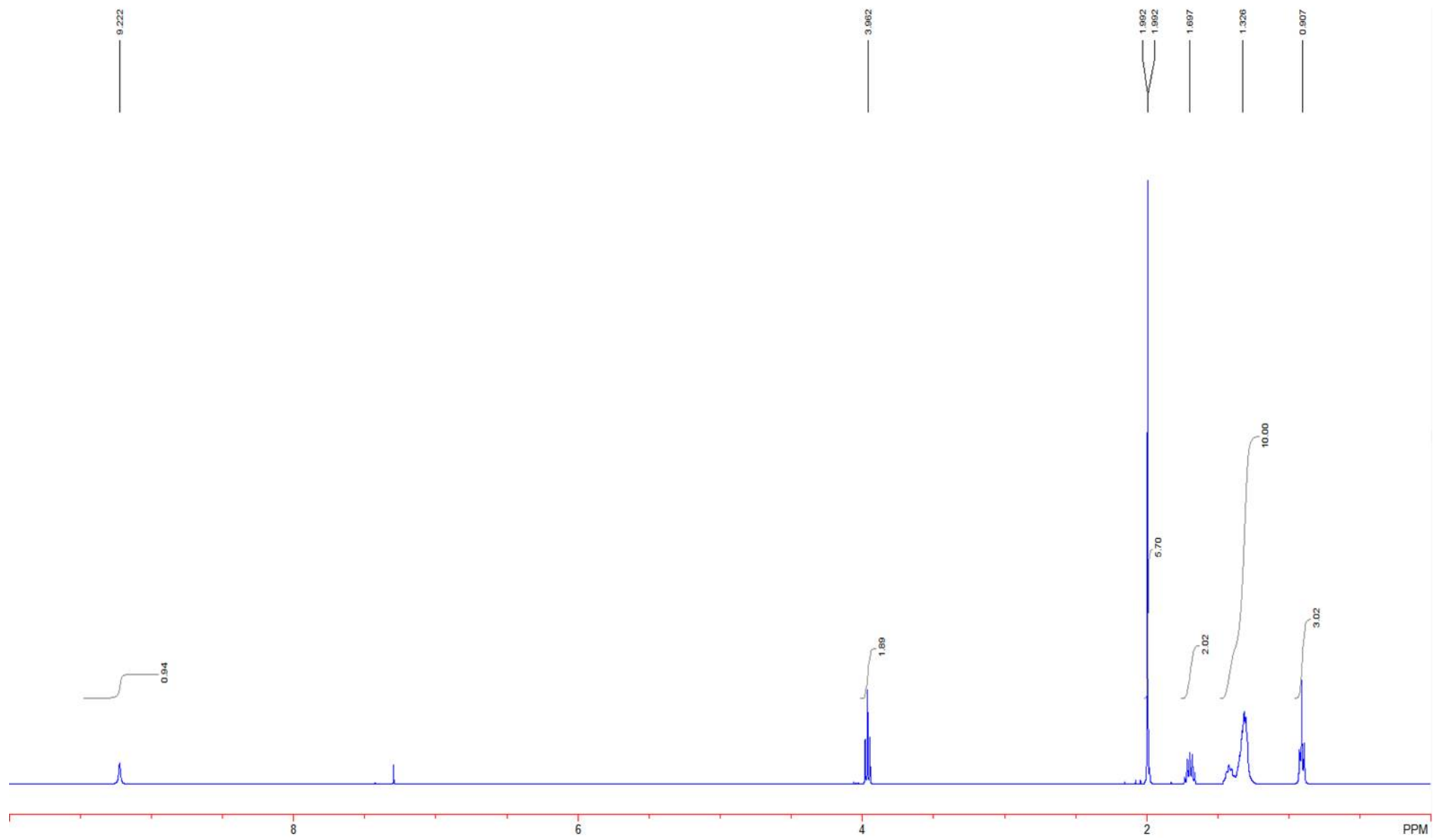
**1a**

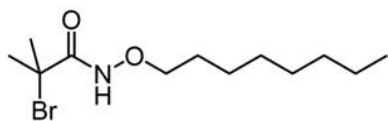
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125 MHz)



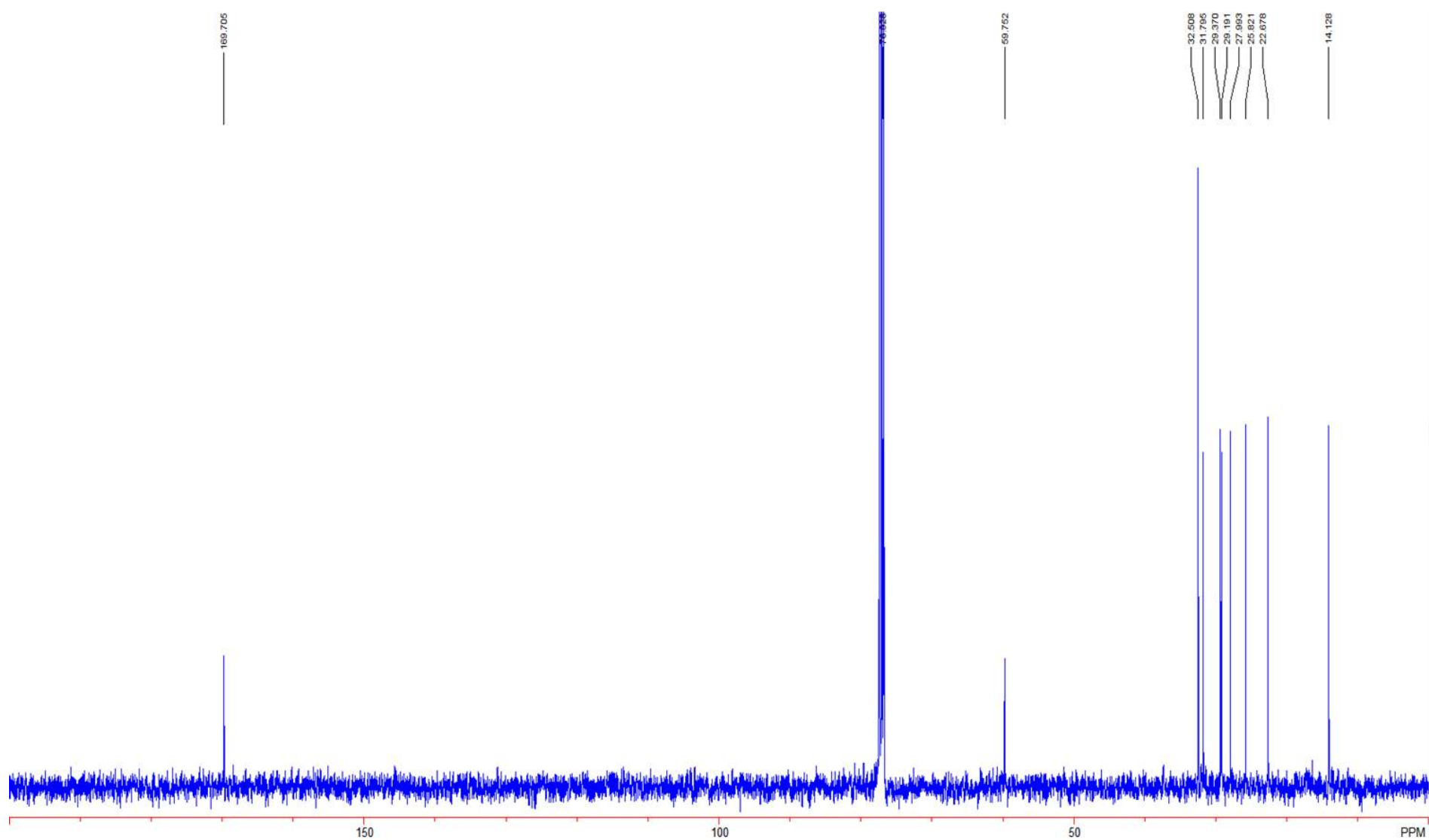


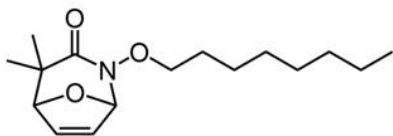
**2a**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)



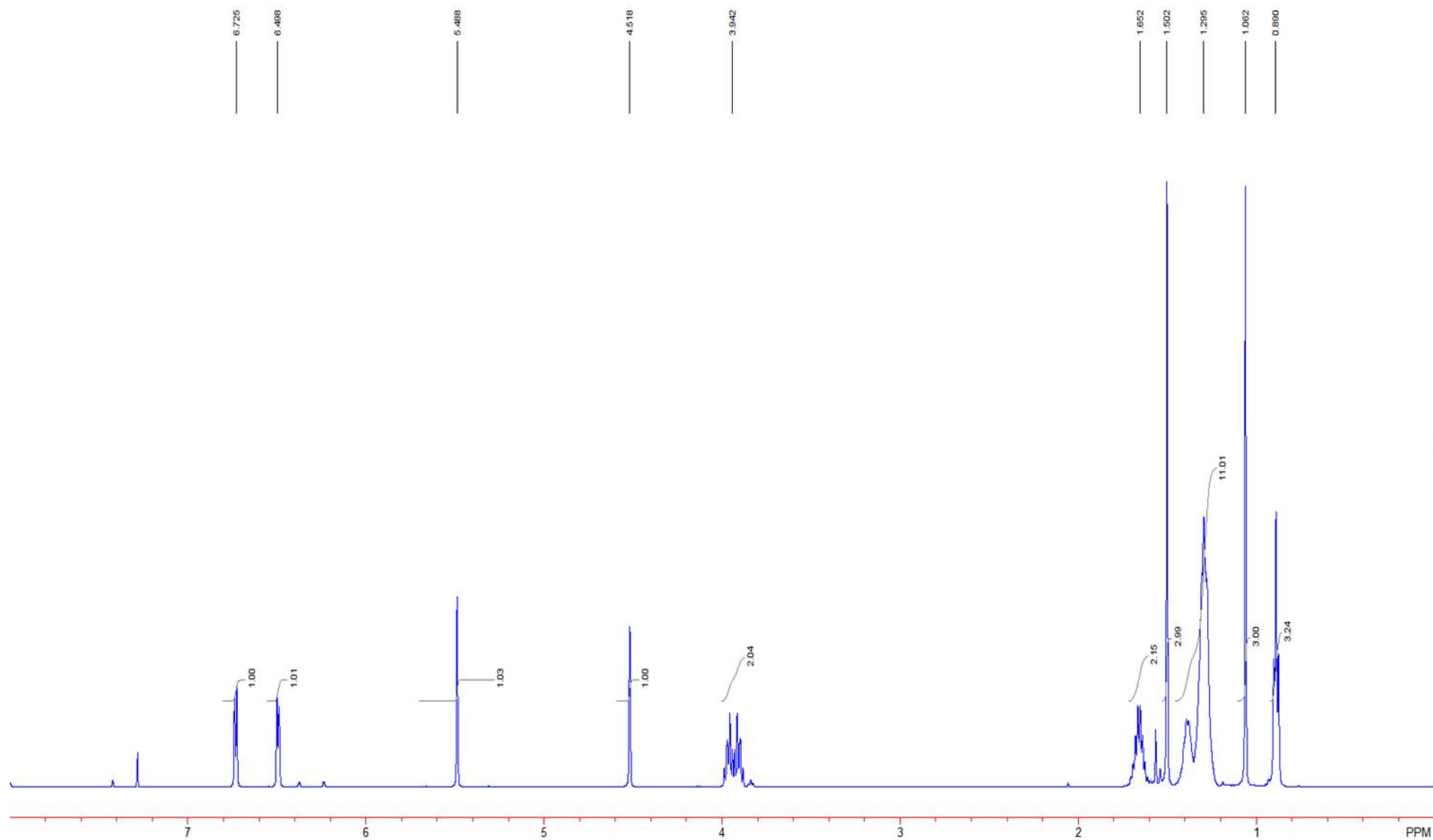


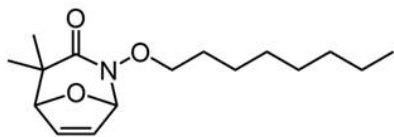
**2a**  
 $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)



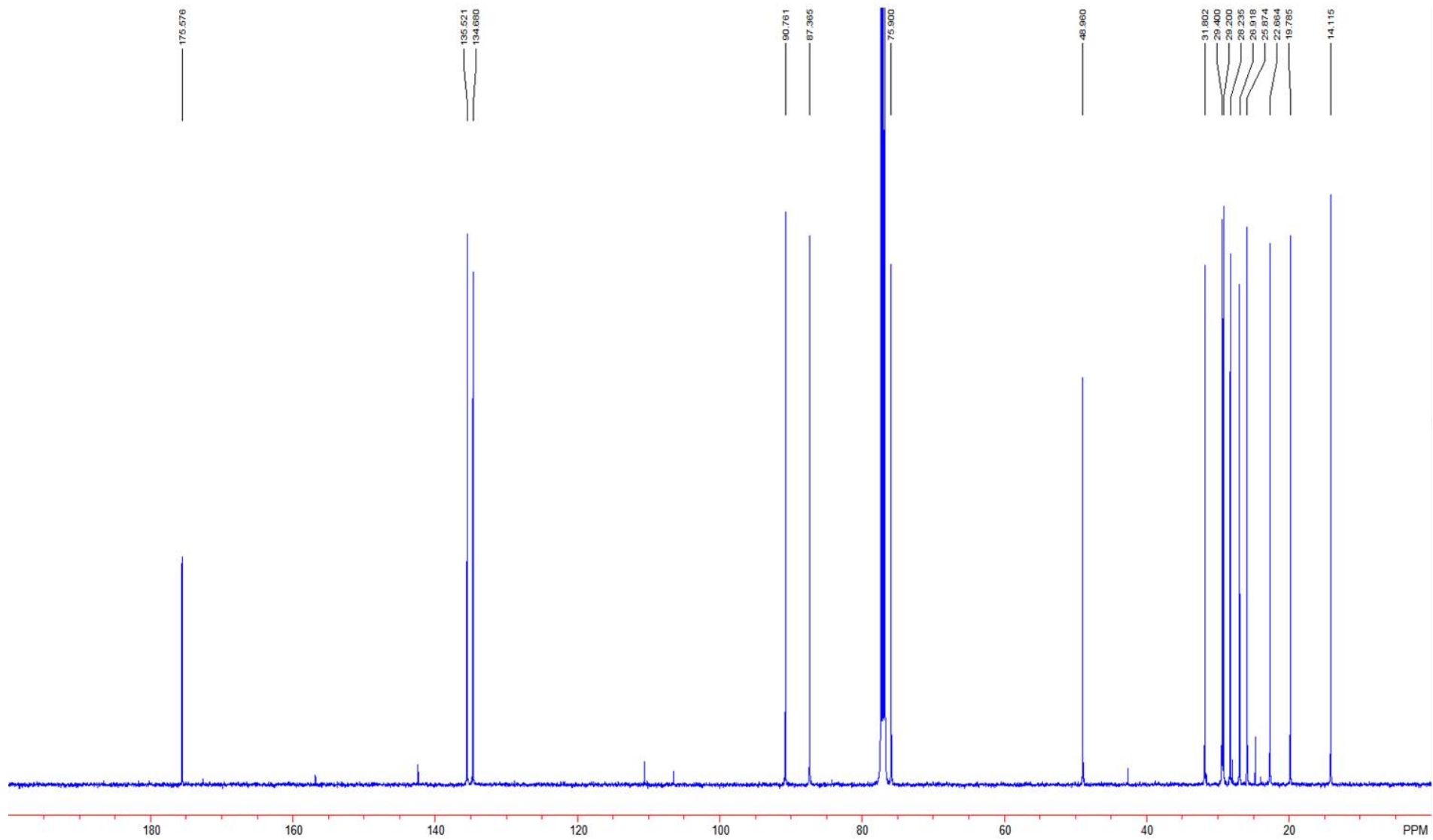


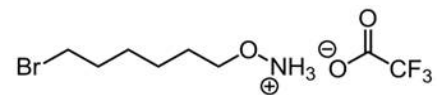
**3a**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)



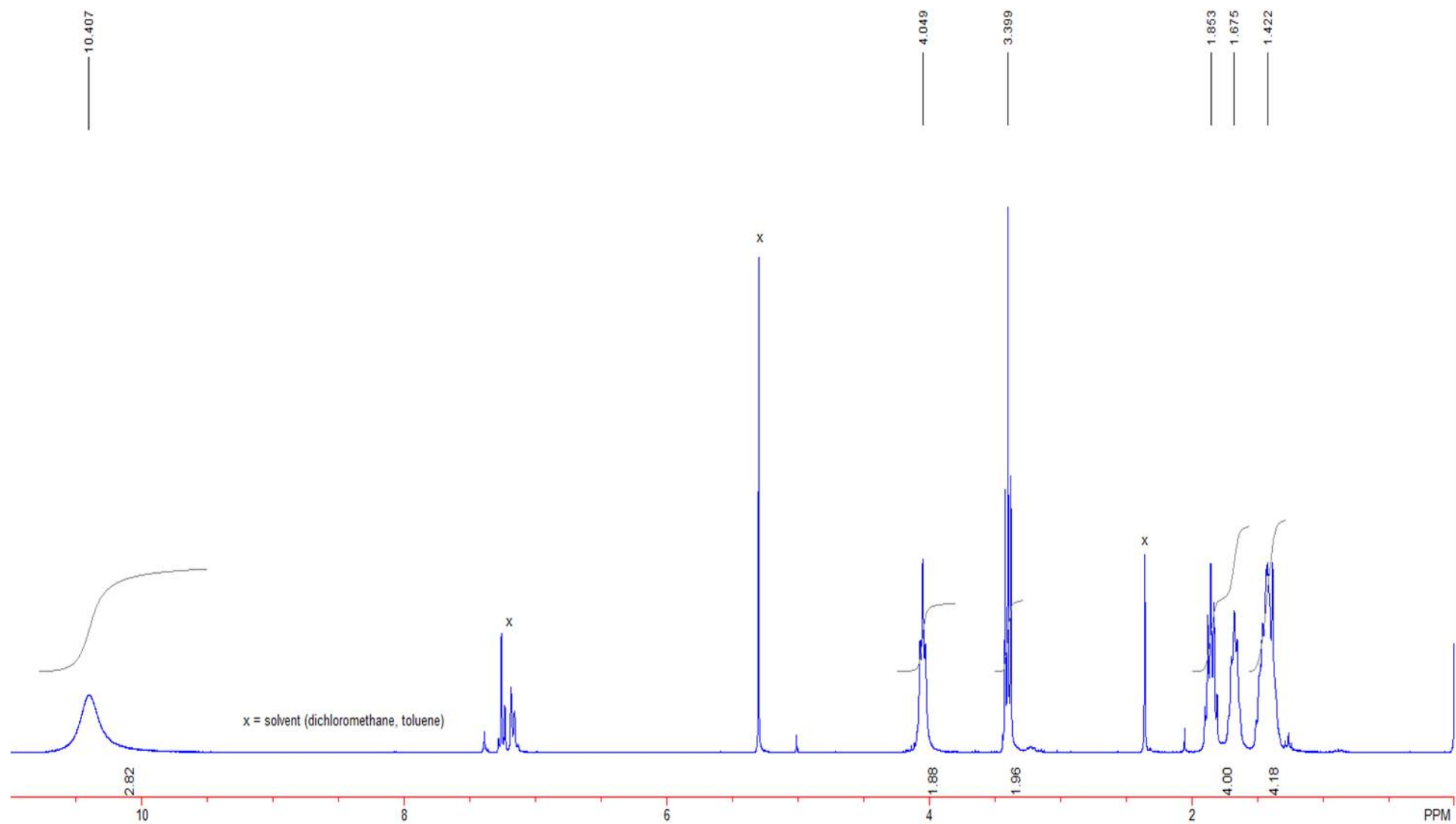


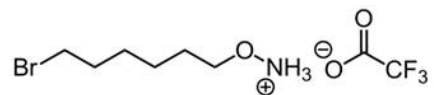
**3a**  
 $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125 MHz)



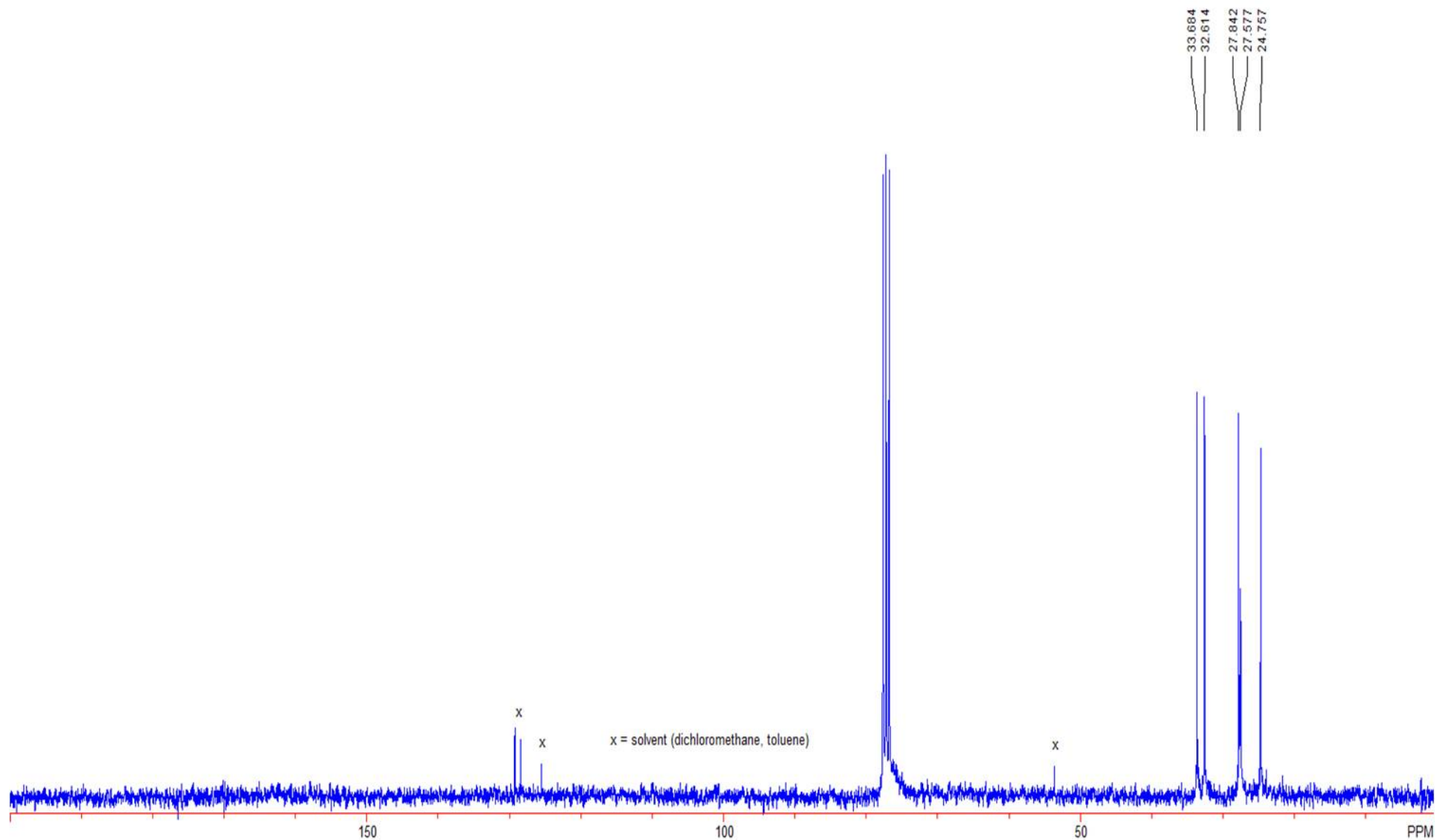


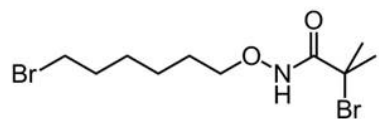
**1b**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz)



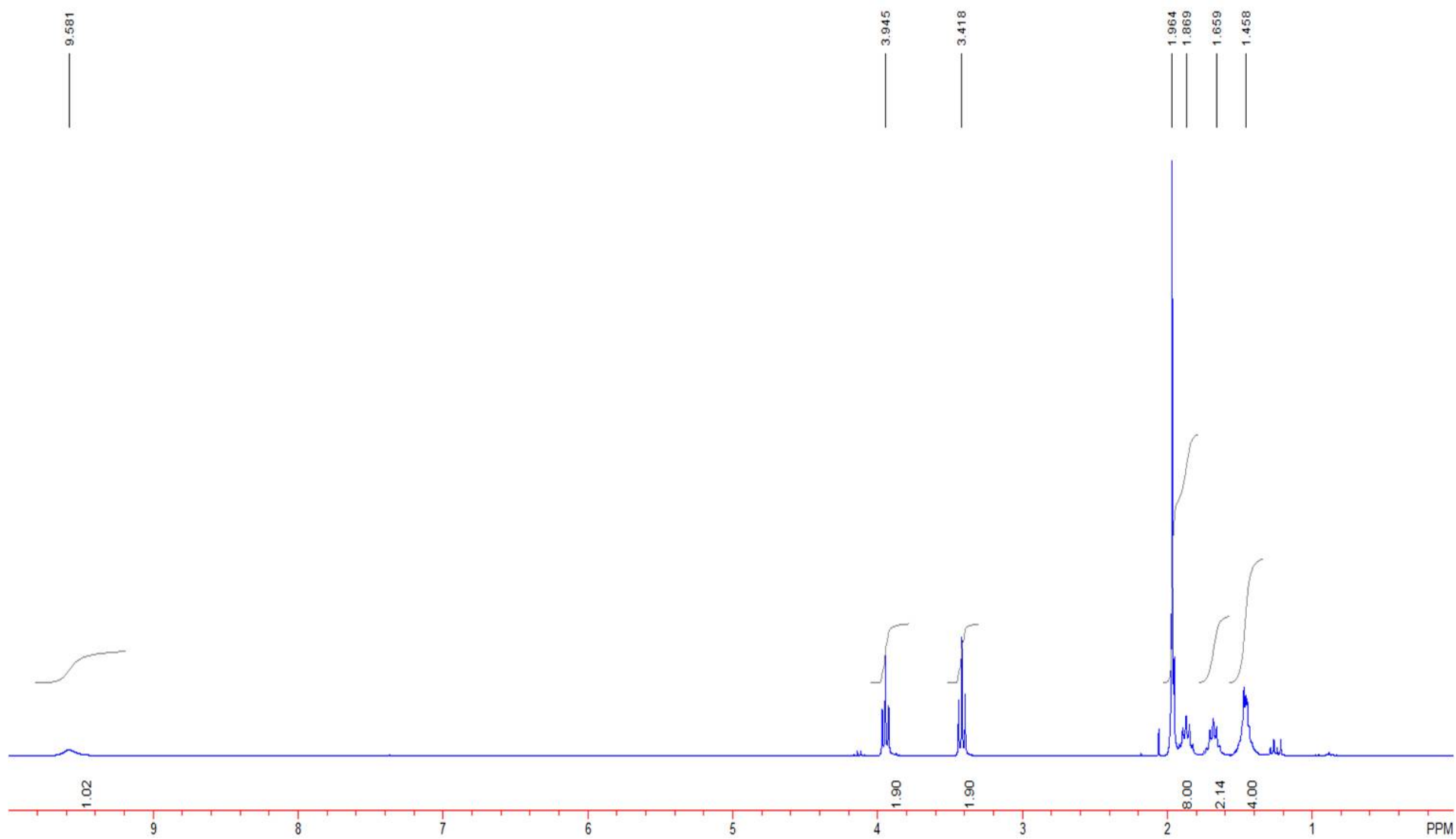


**1b**  
 $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz)

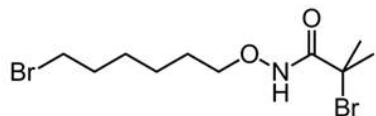




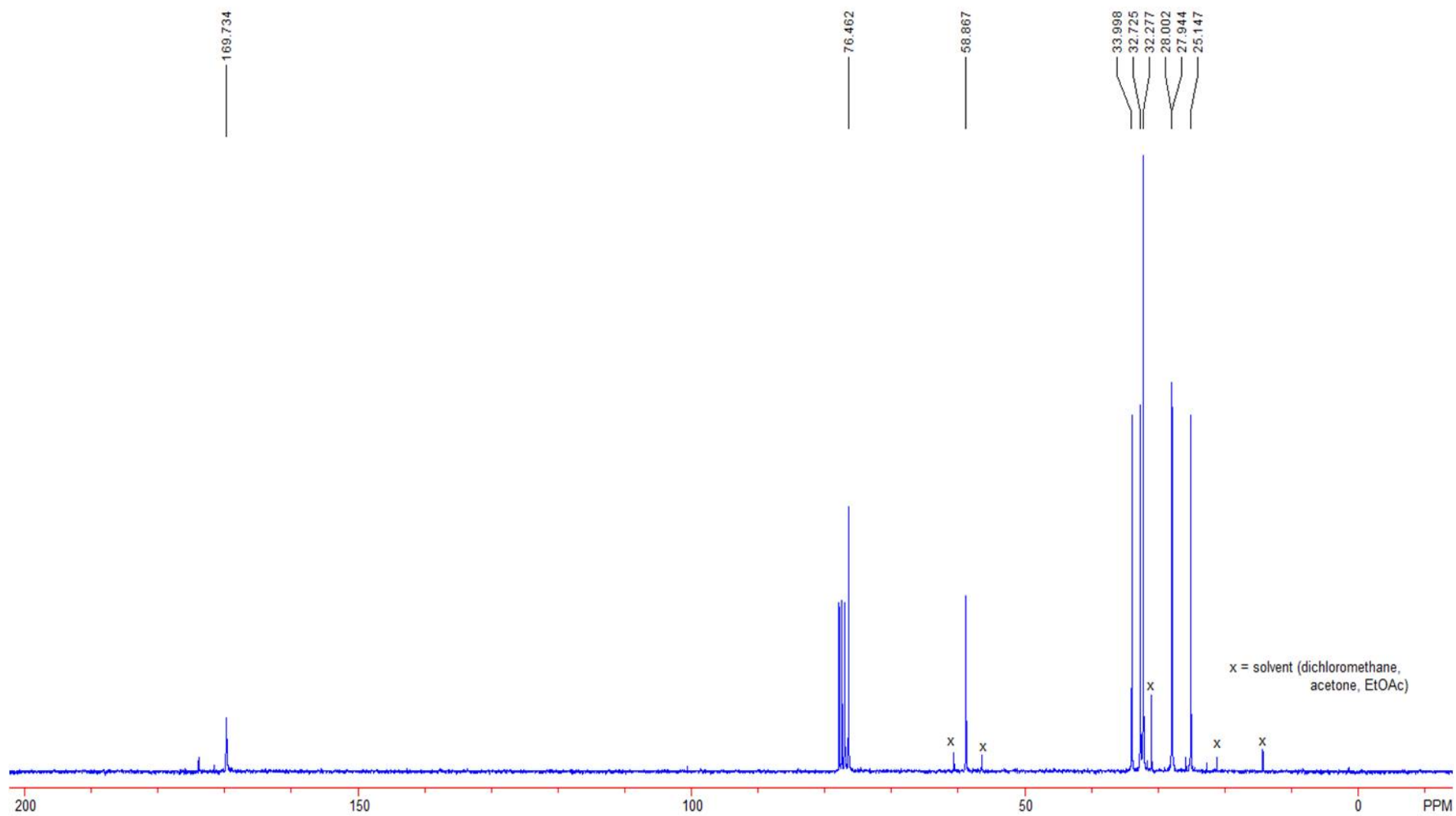
**2b**  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)

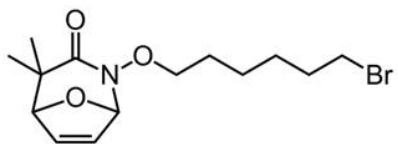




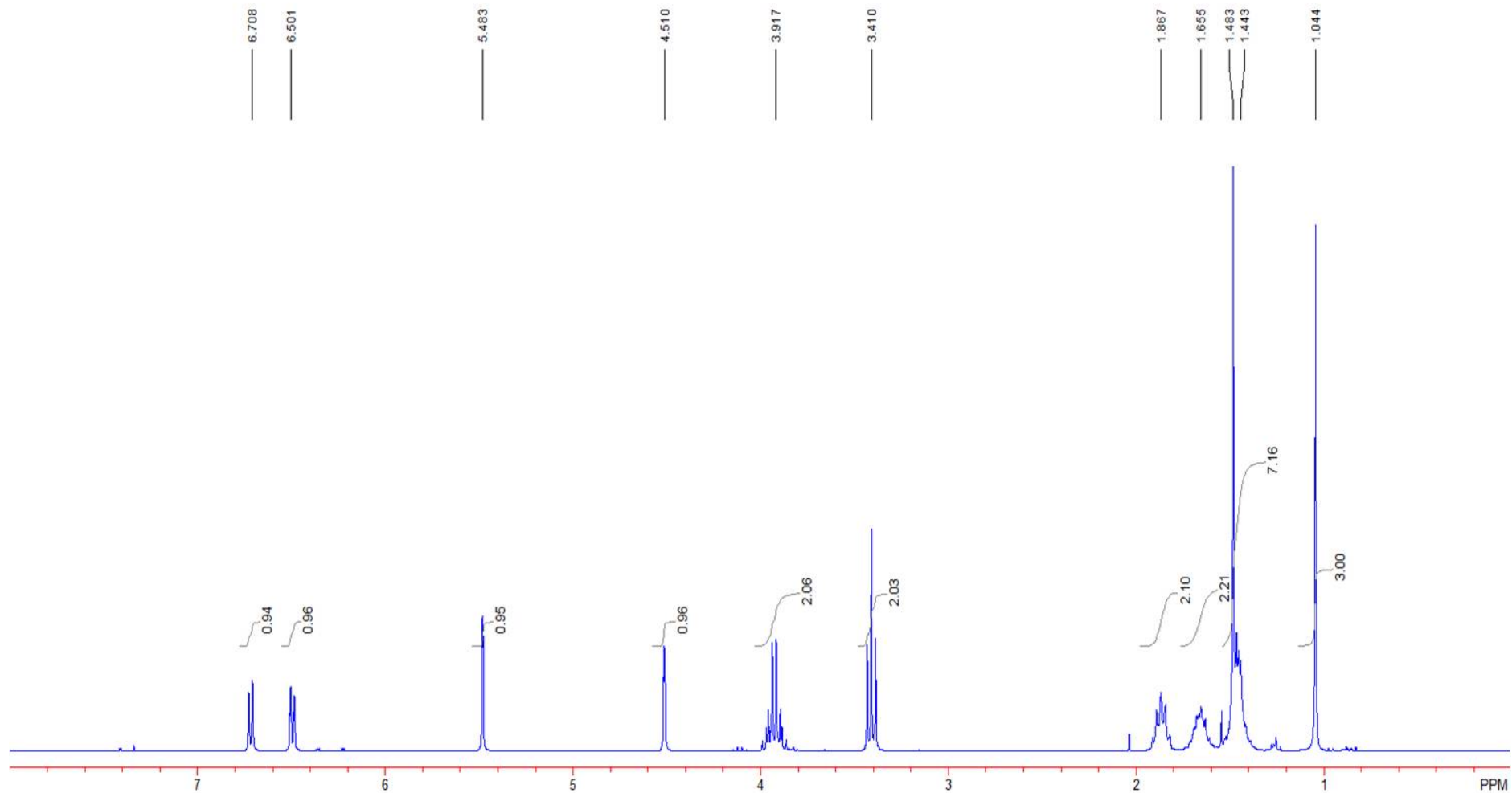


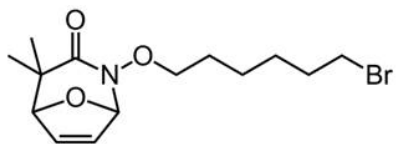
**2b**  
 $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz)



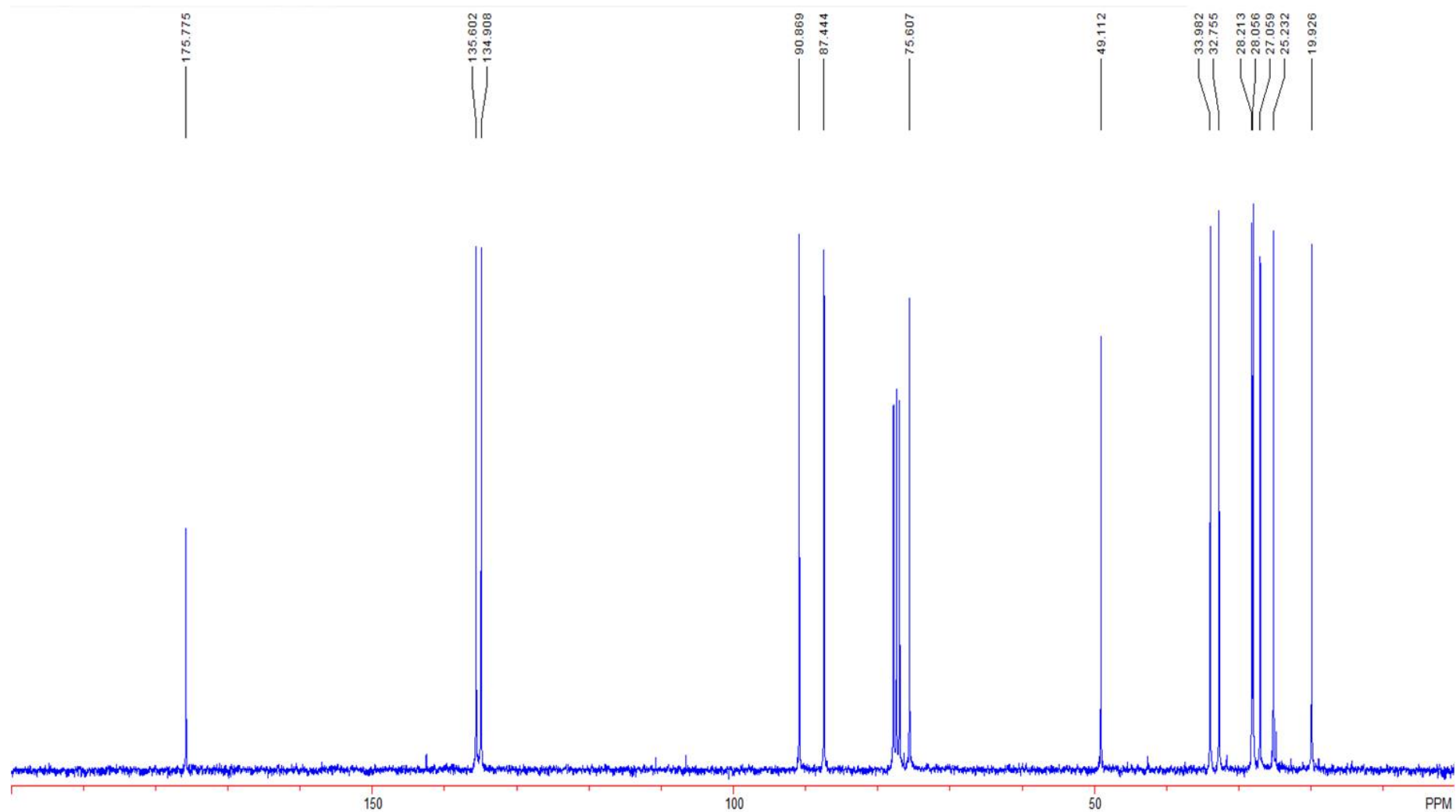


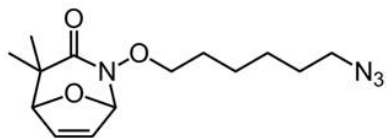
**3b**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz)



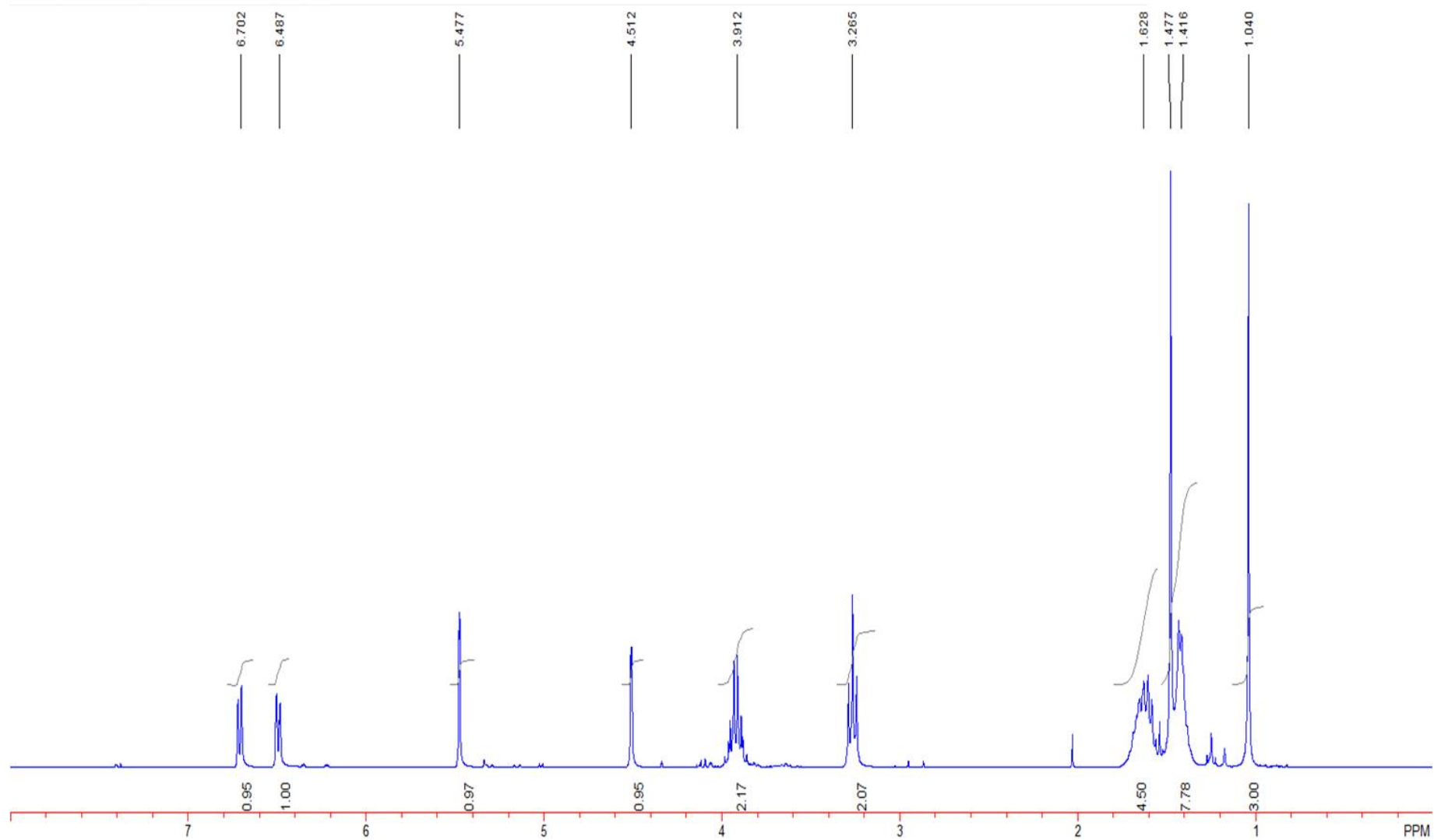


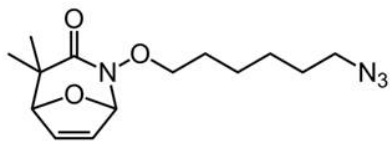
**3b**  
 $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz)



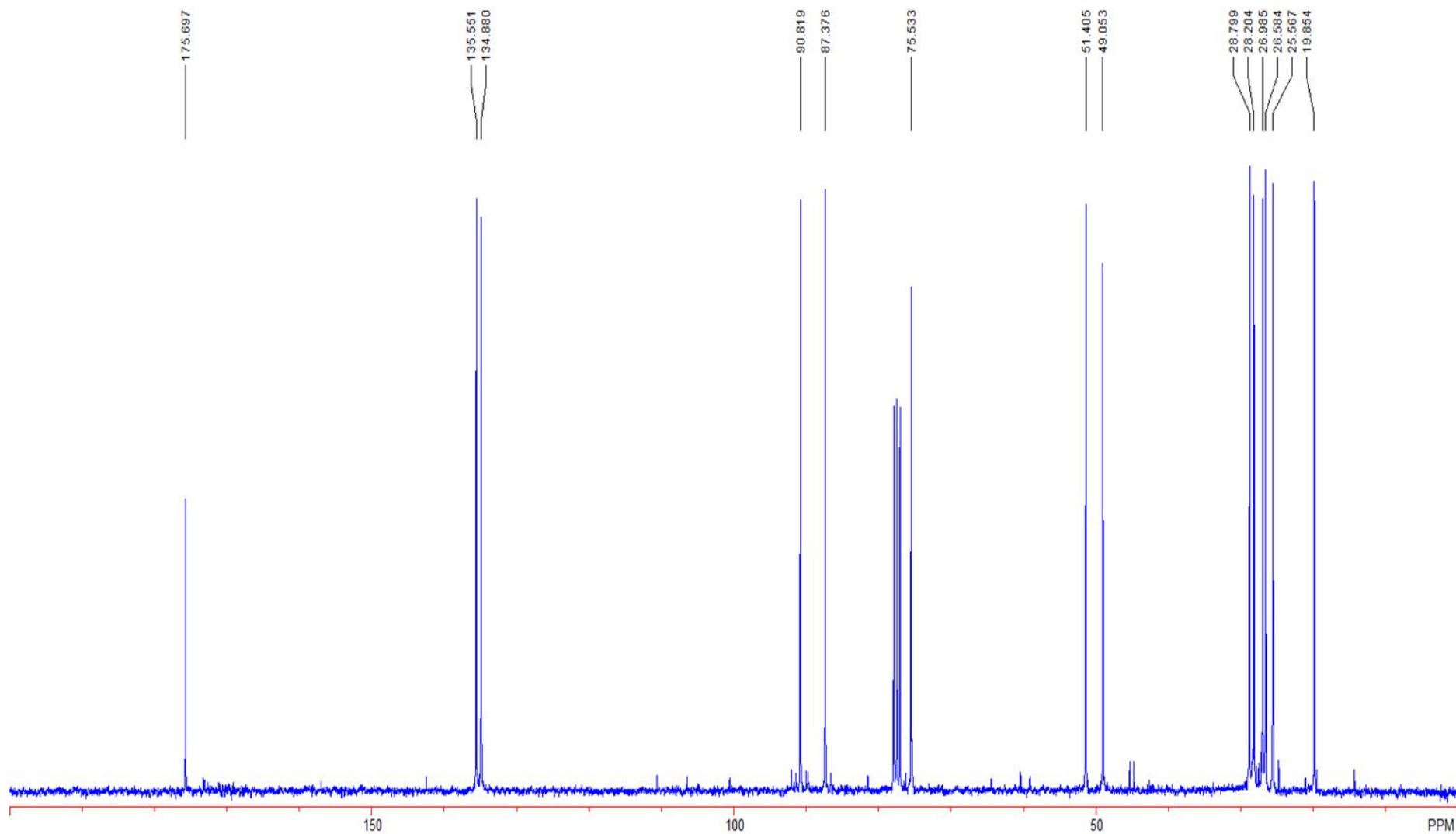


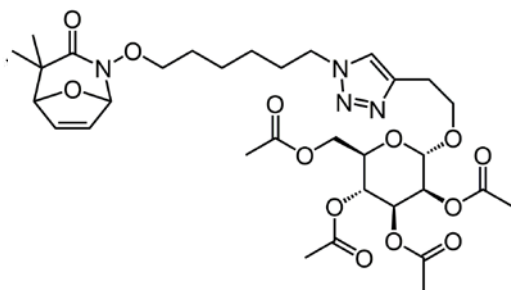
**3c**  
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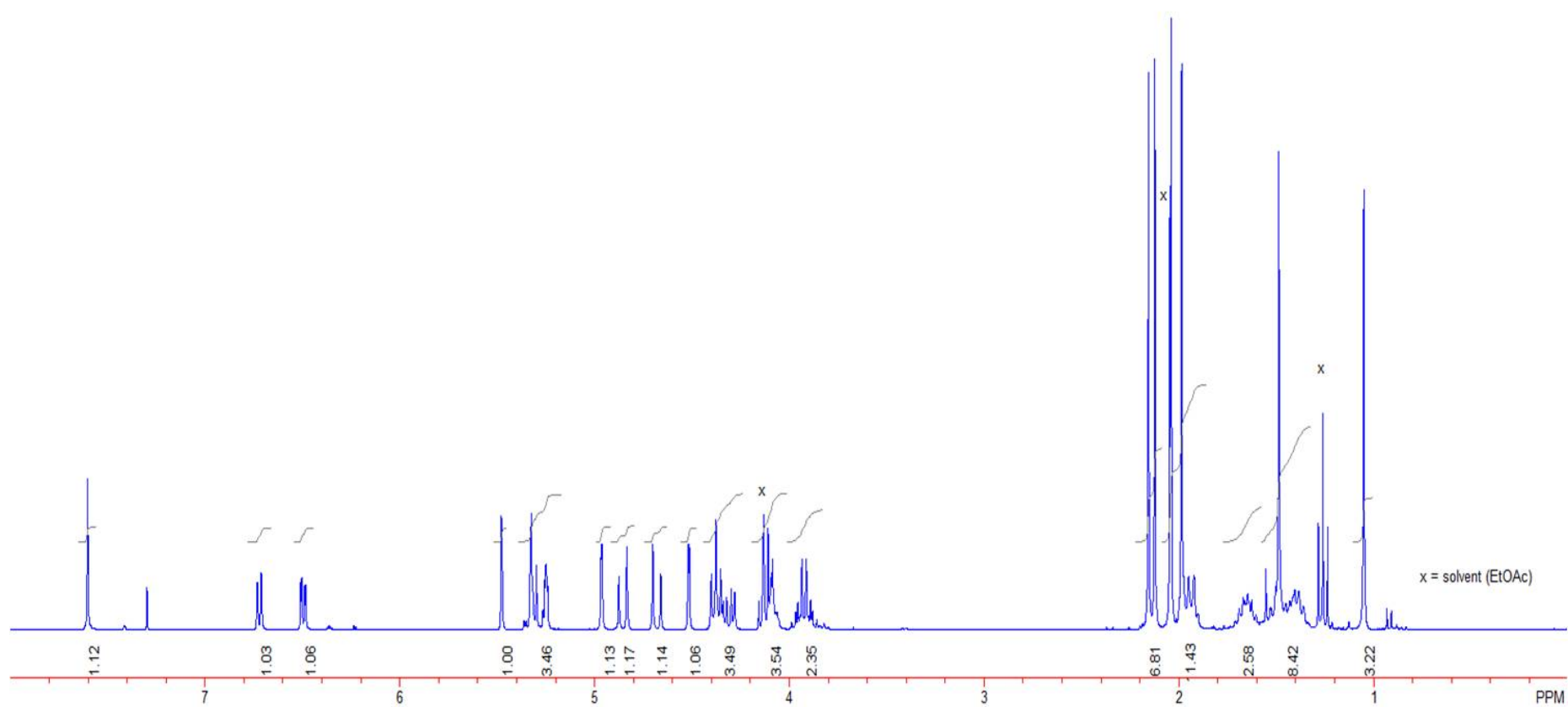
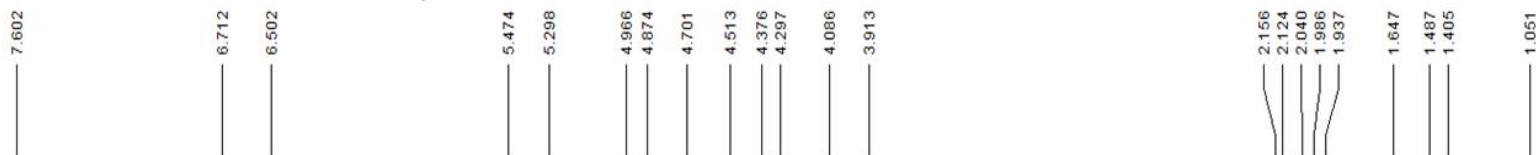


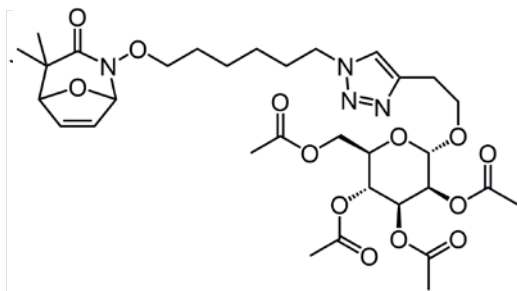
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 $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz)



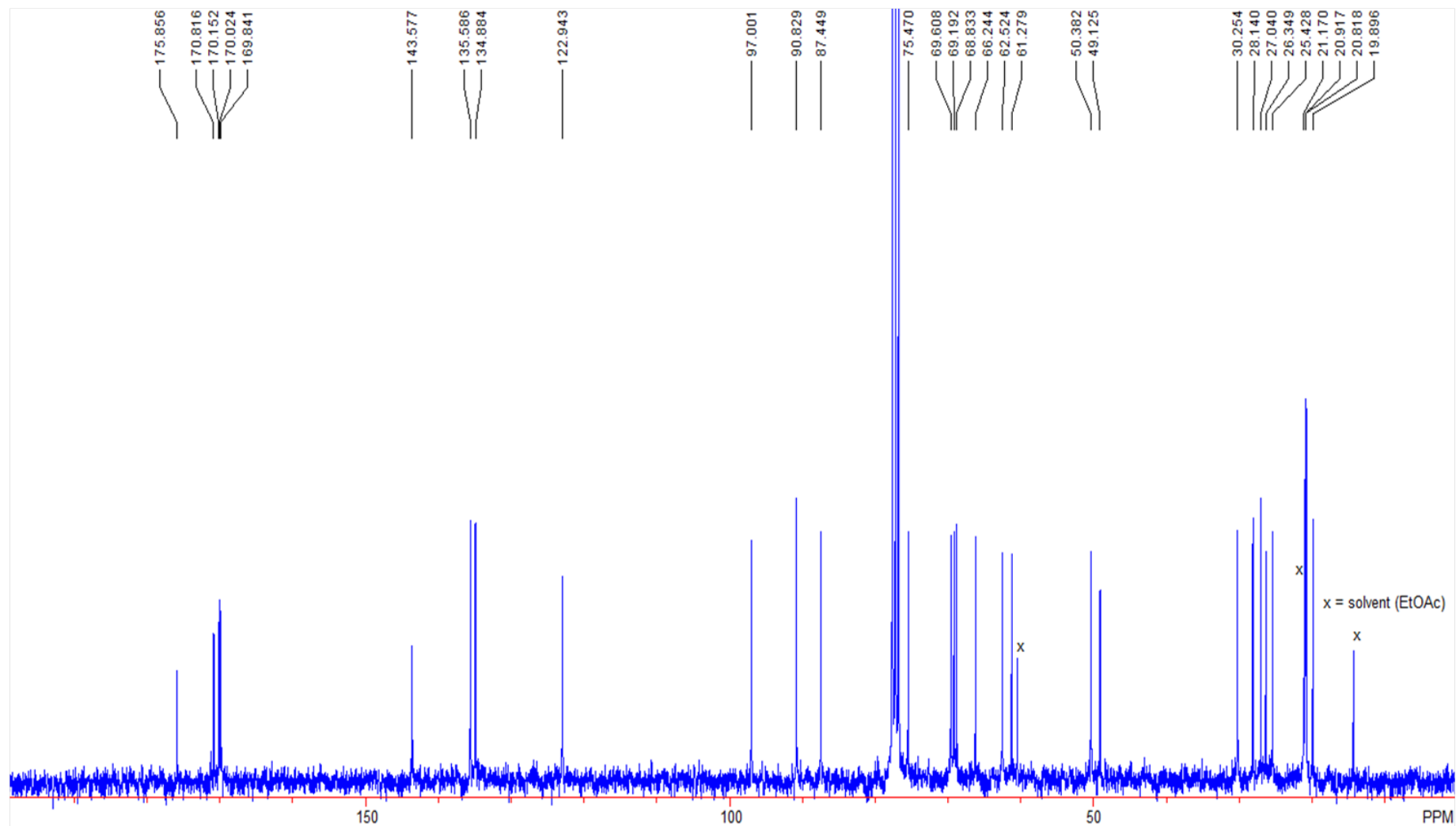


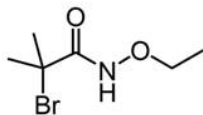
**6**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz)



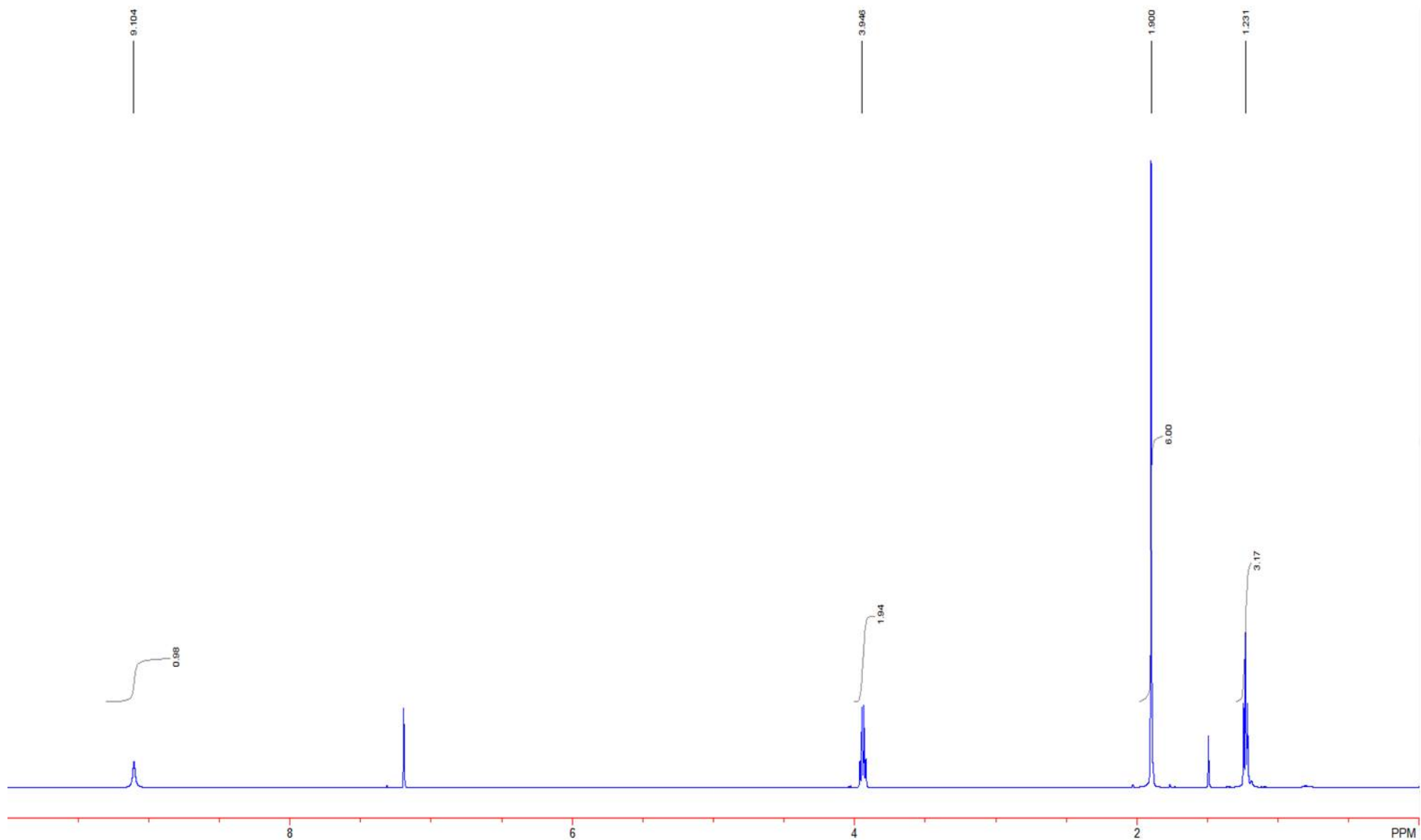


**6**  
 $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 75 MHz)

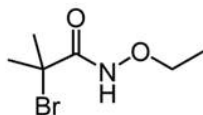




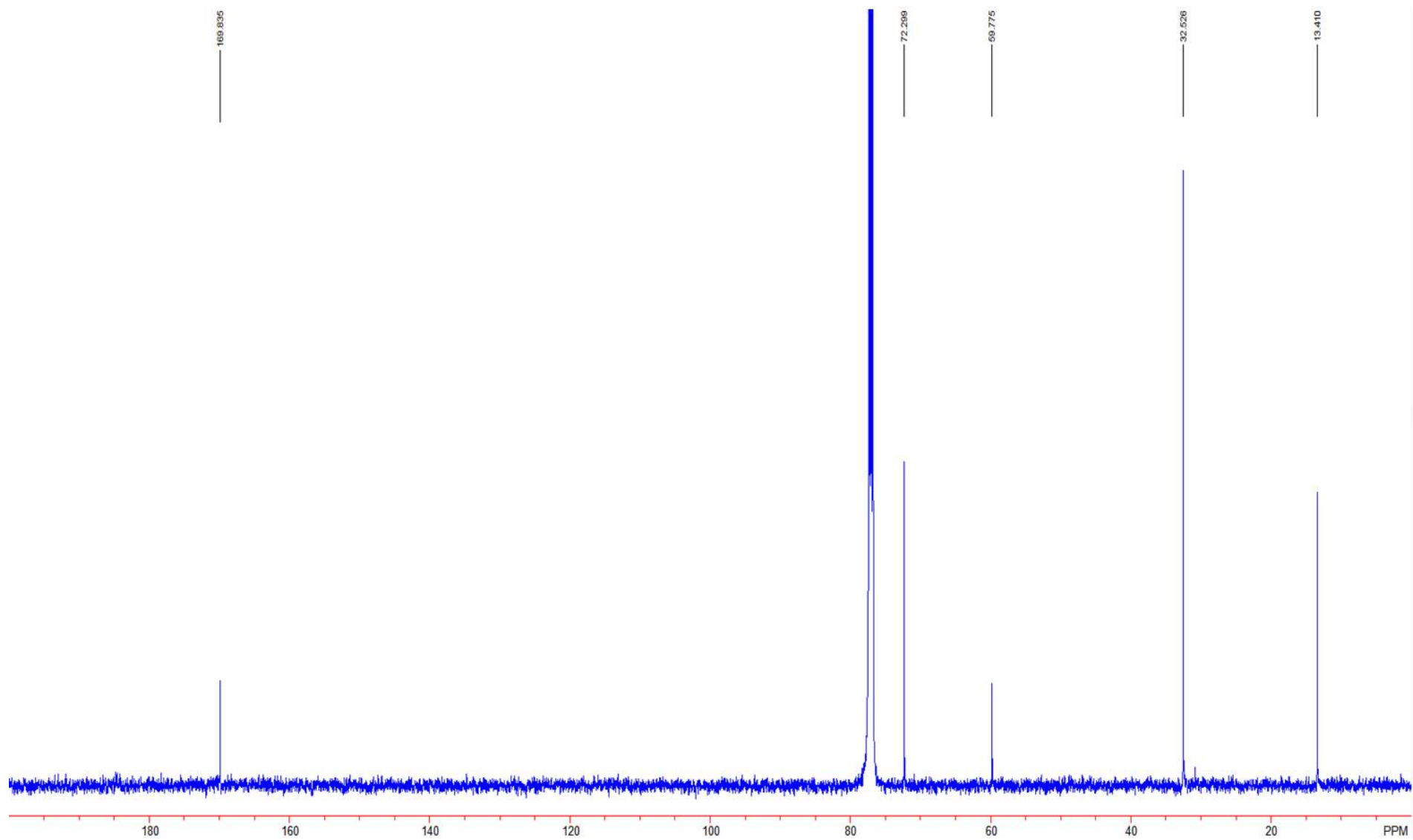
**2d**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)

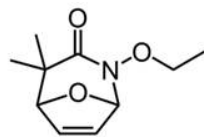




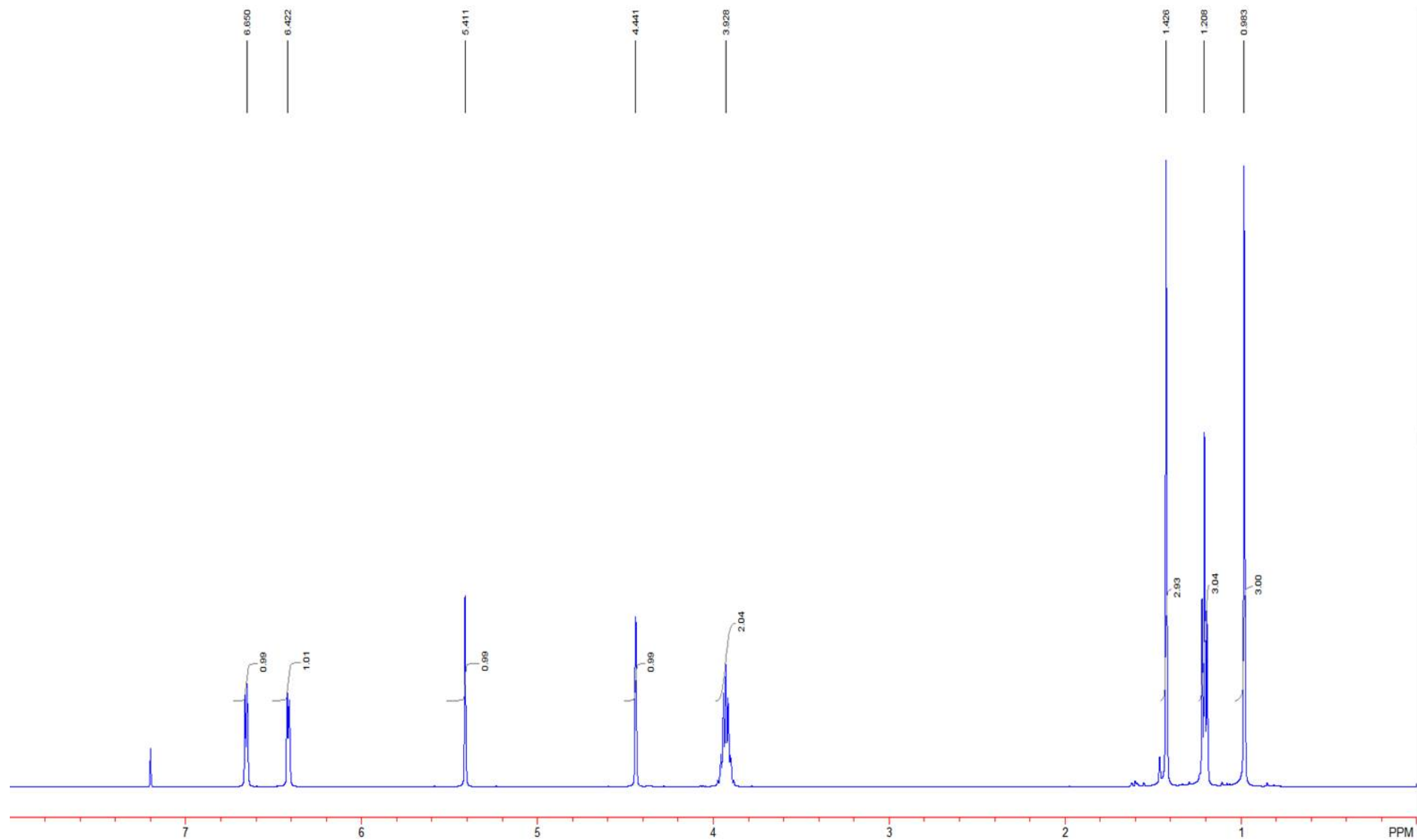


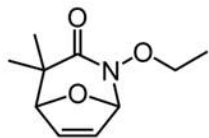
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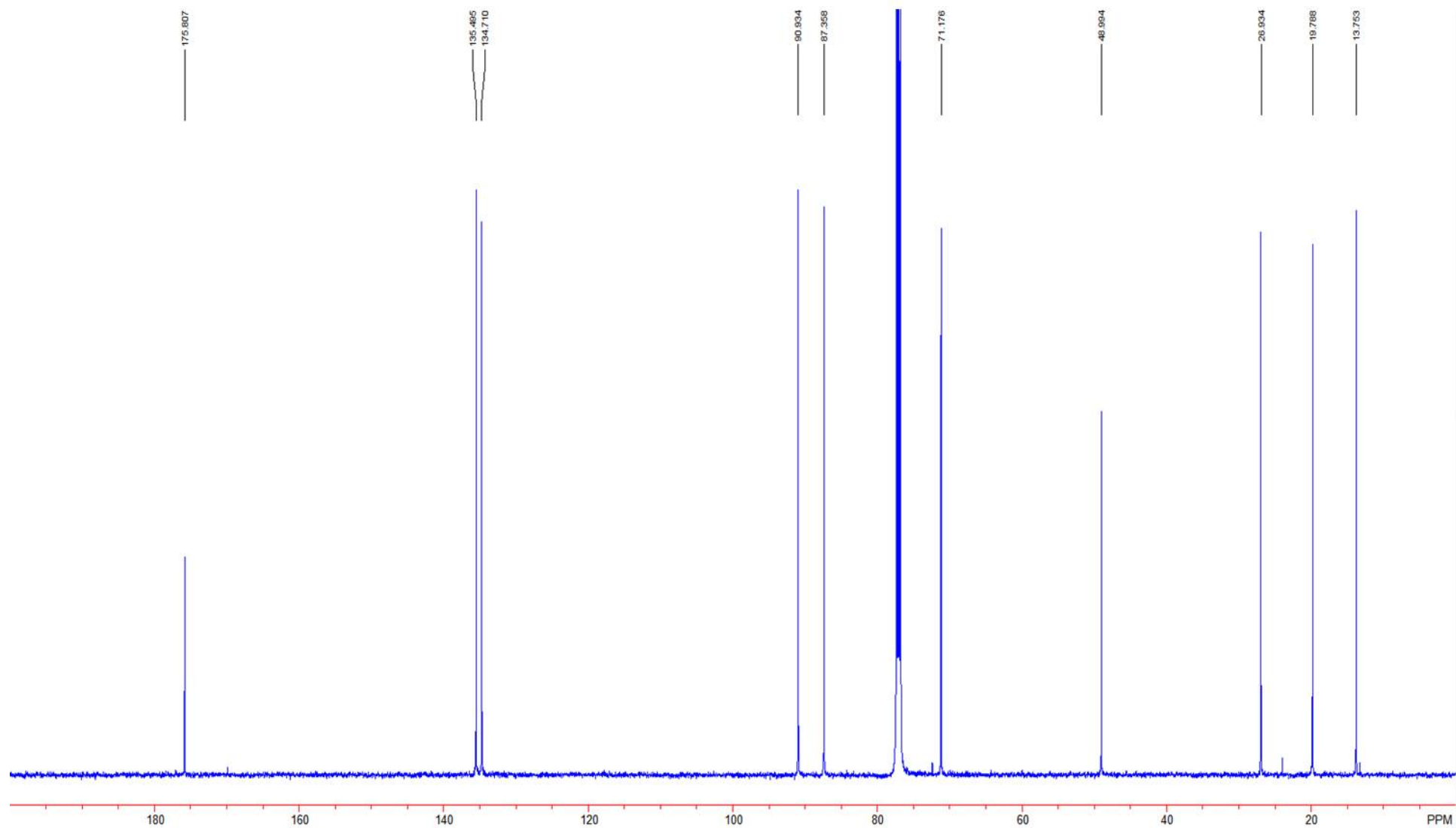


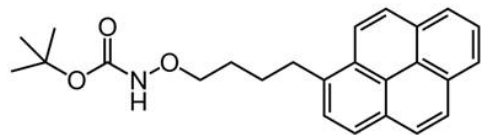
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 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)





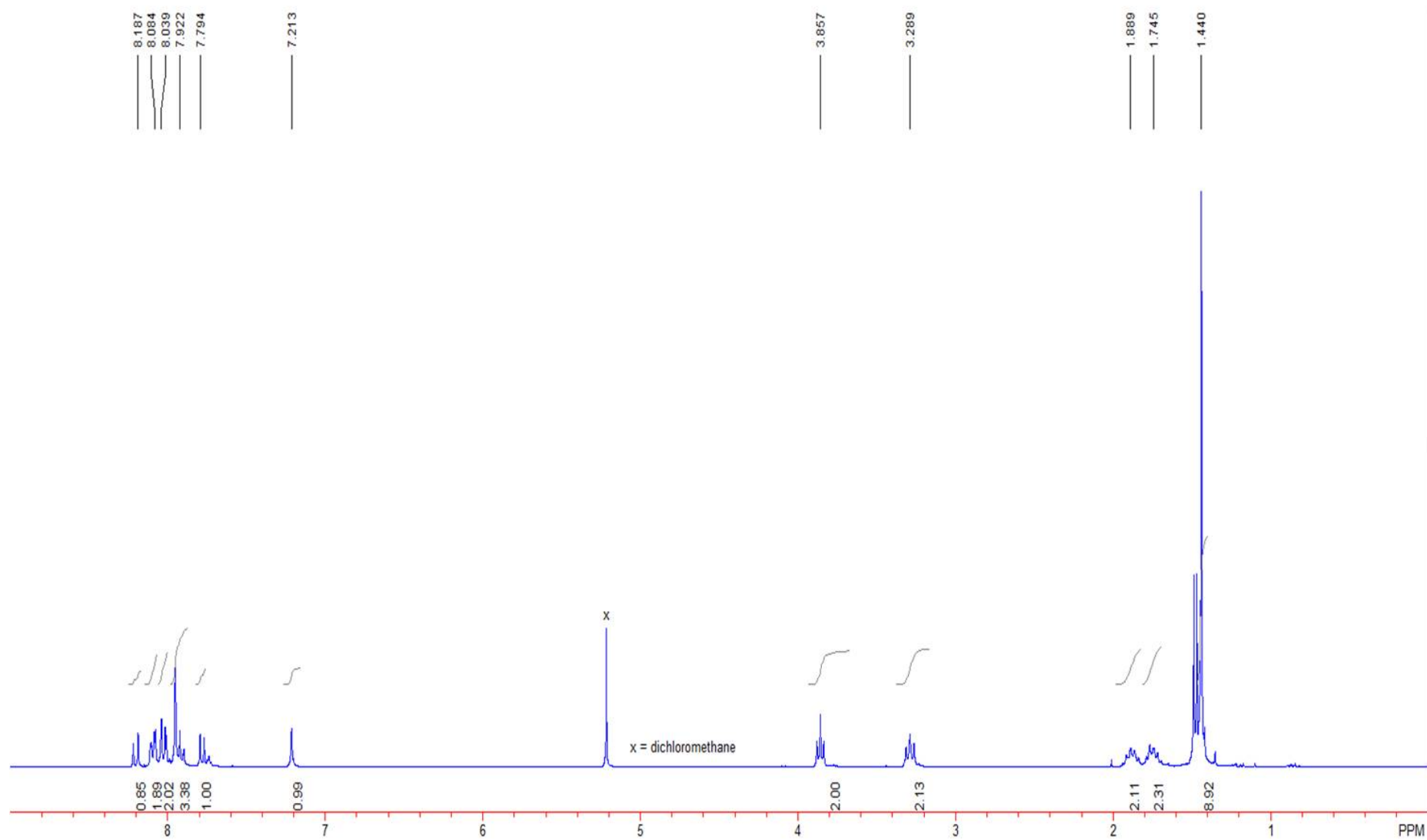
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 $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125 MHz)

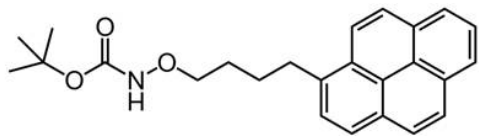




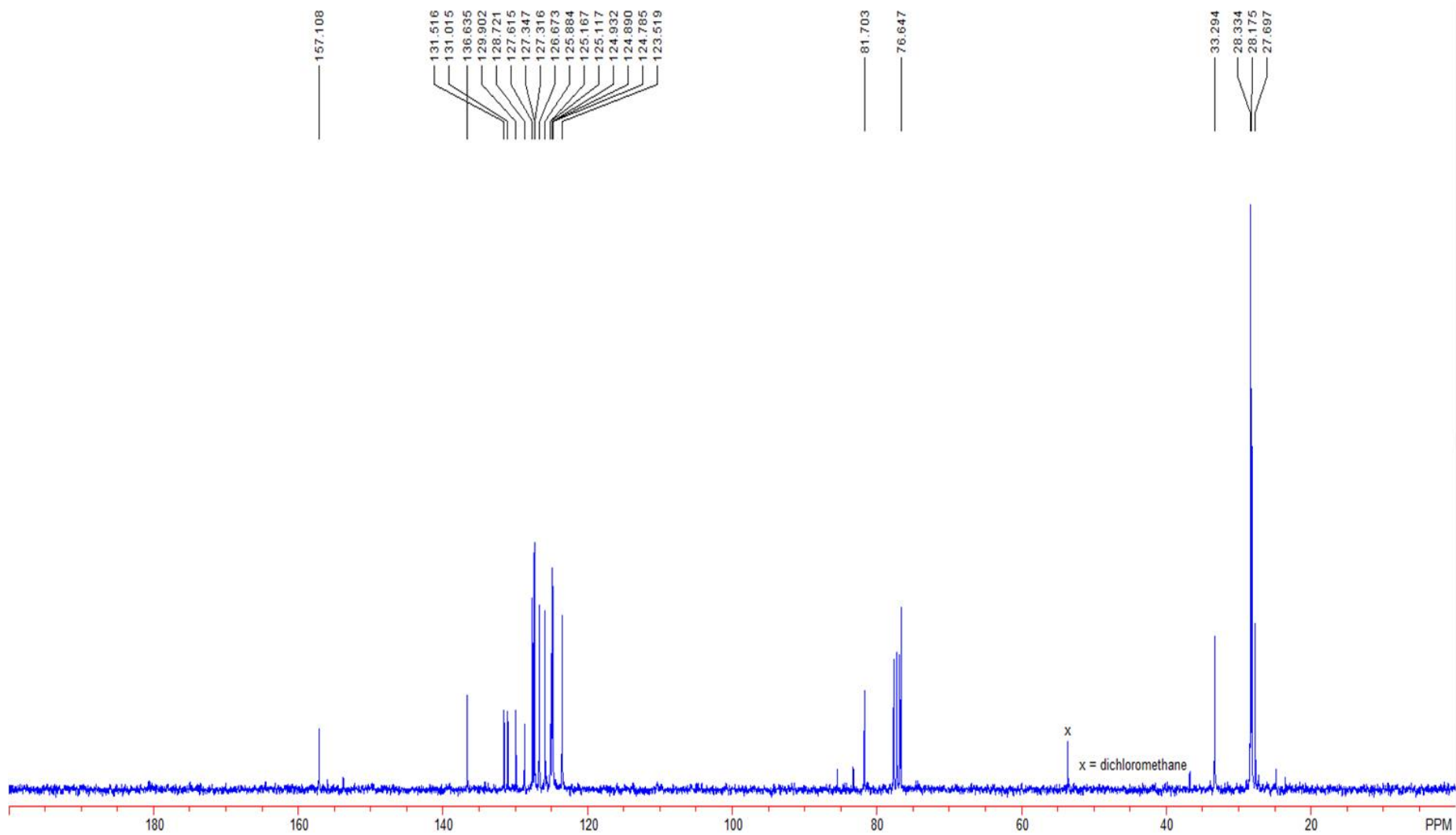
S2

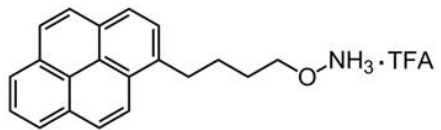
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300MHz)





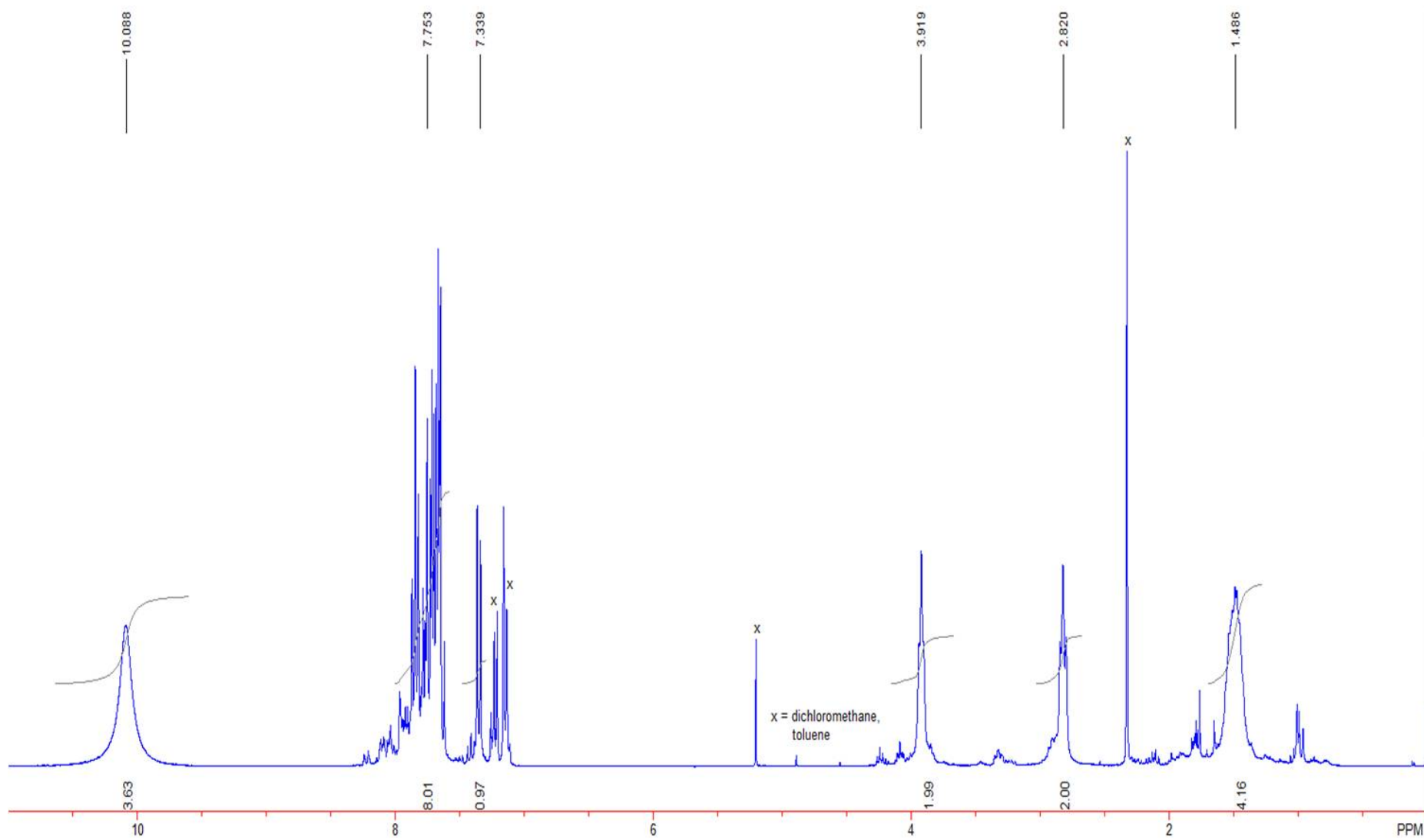
**S2**  
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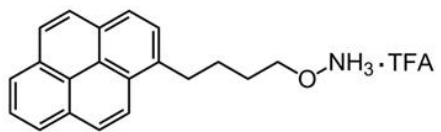




**1f**

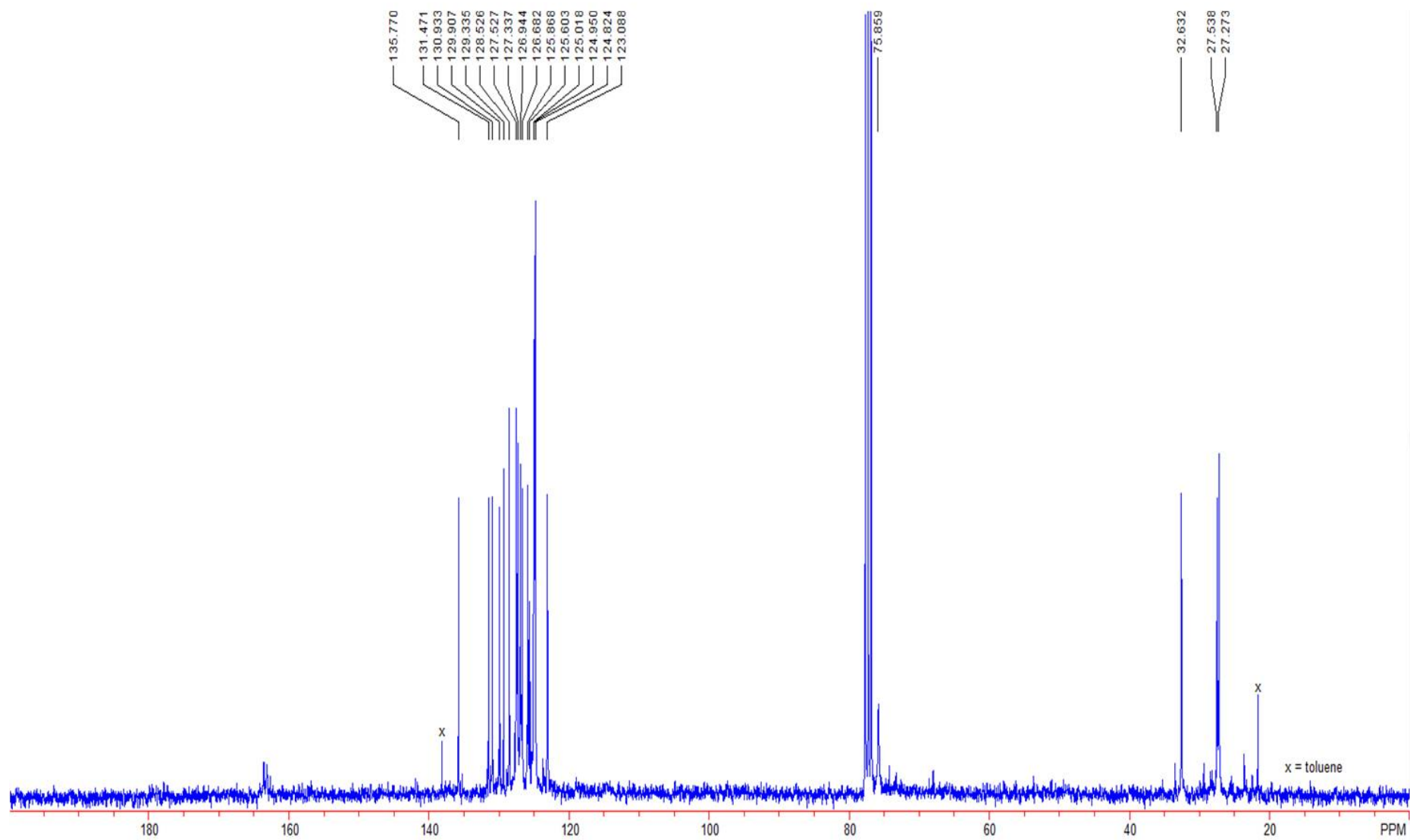
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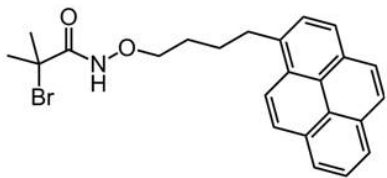




**1f**

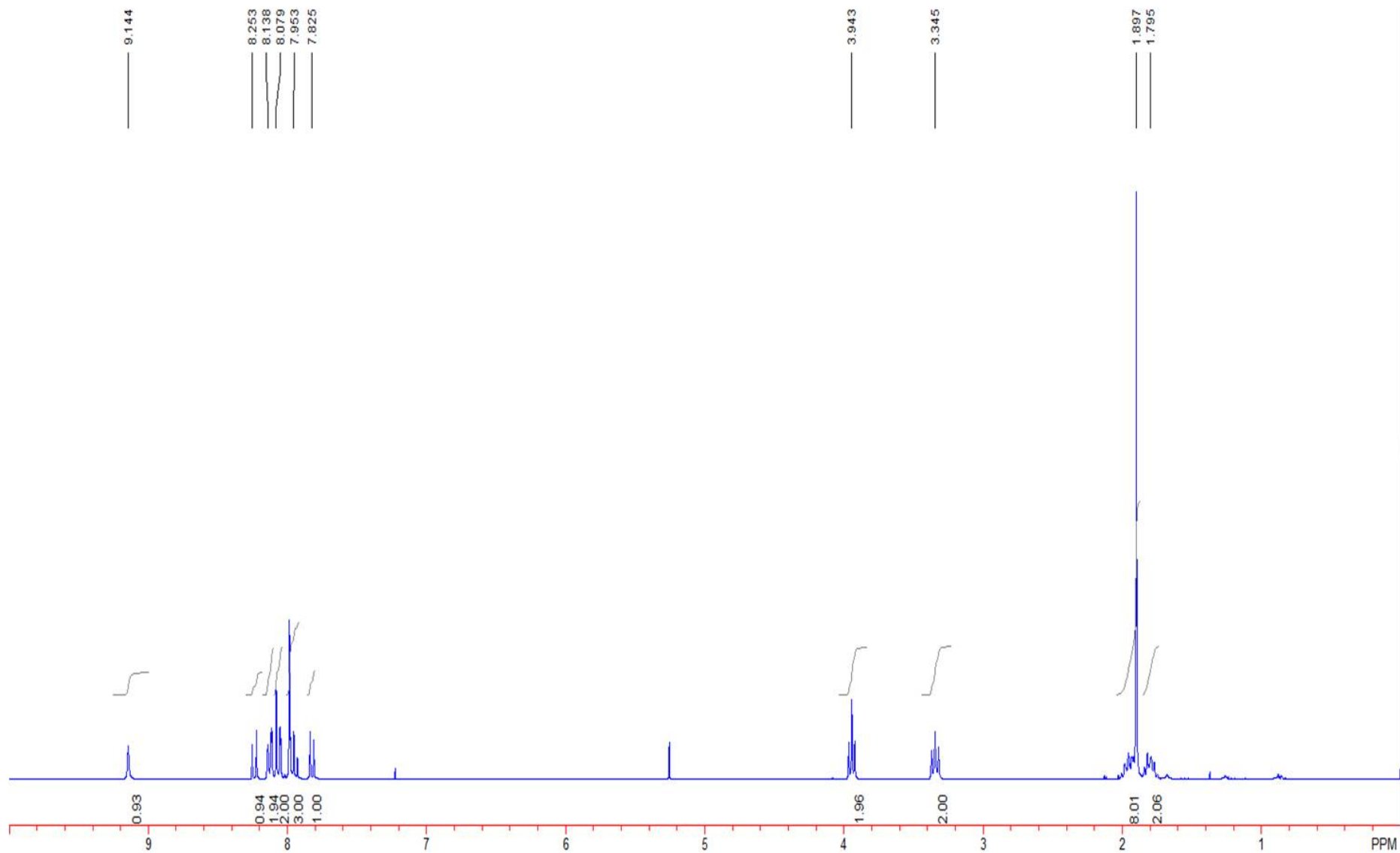
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 75 MHz)



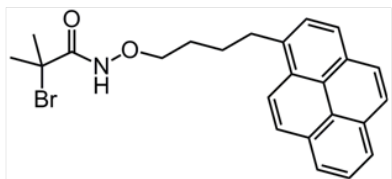


**2f**

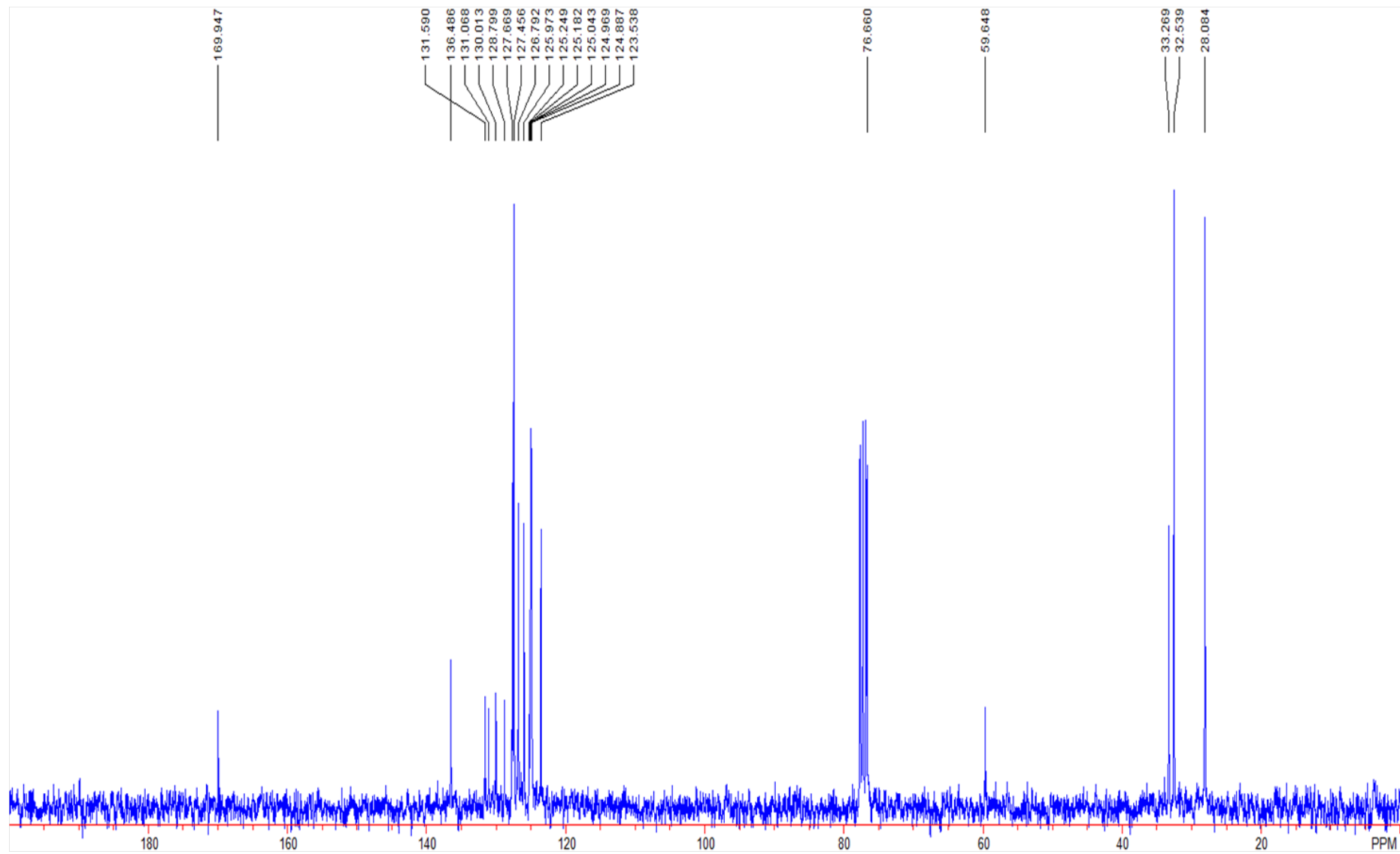
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz)

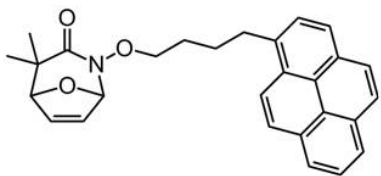






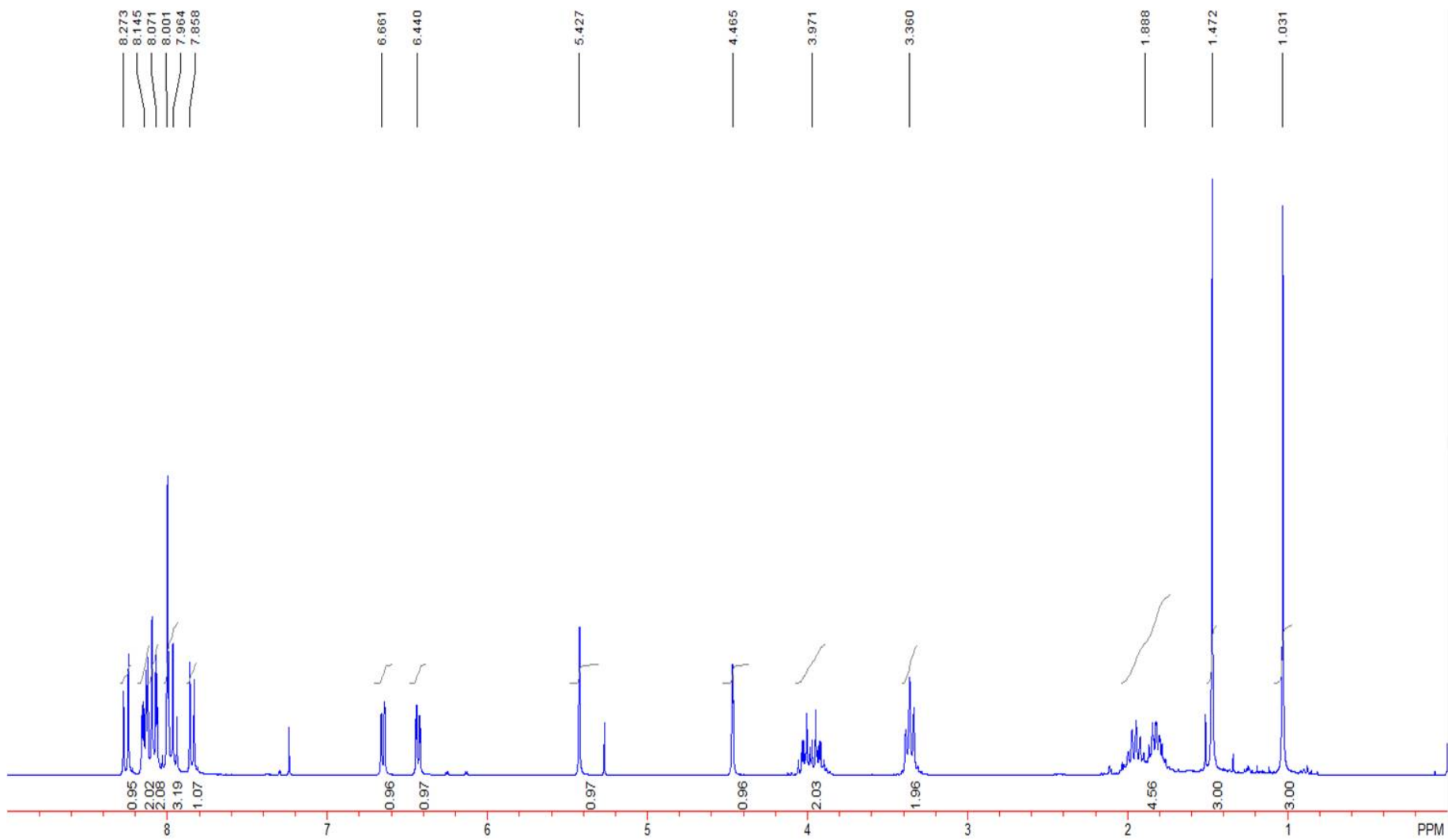
**2f**  
 $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz)

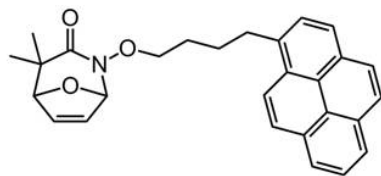




**3f**

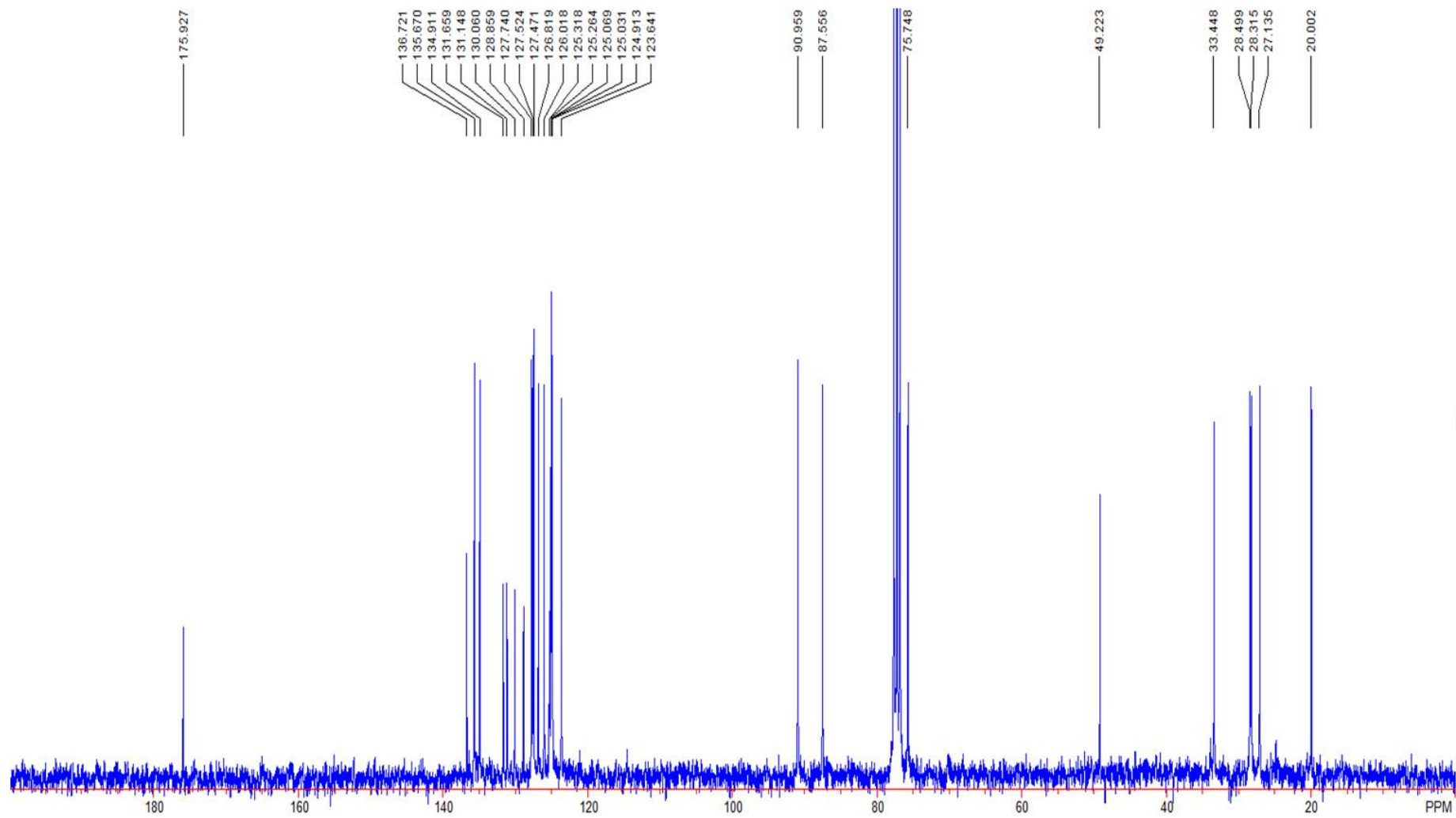
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300MHz)

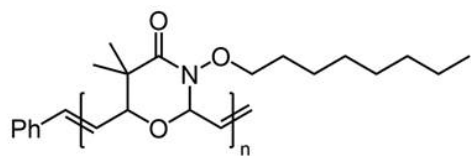




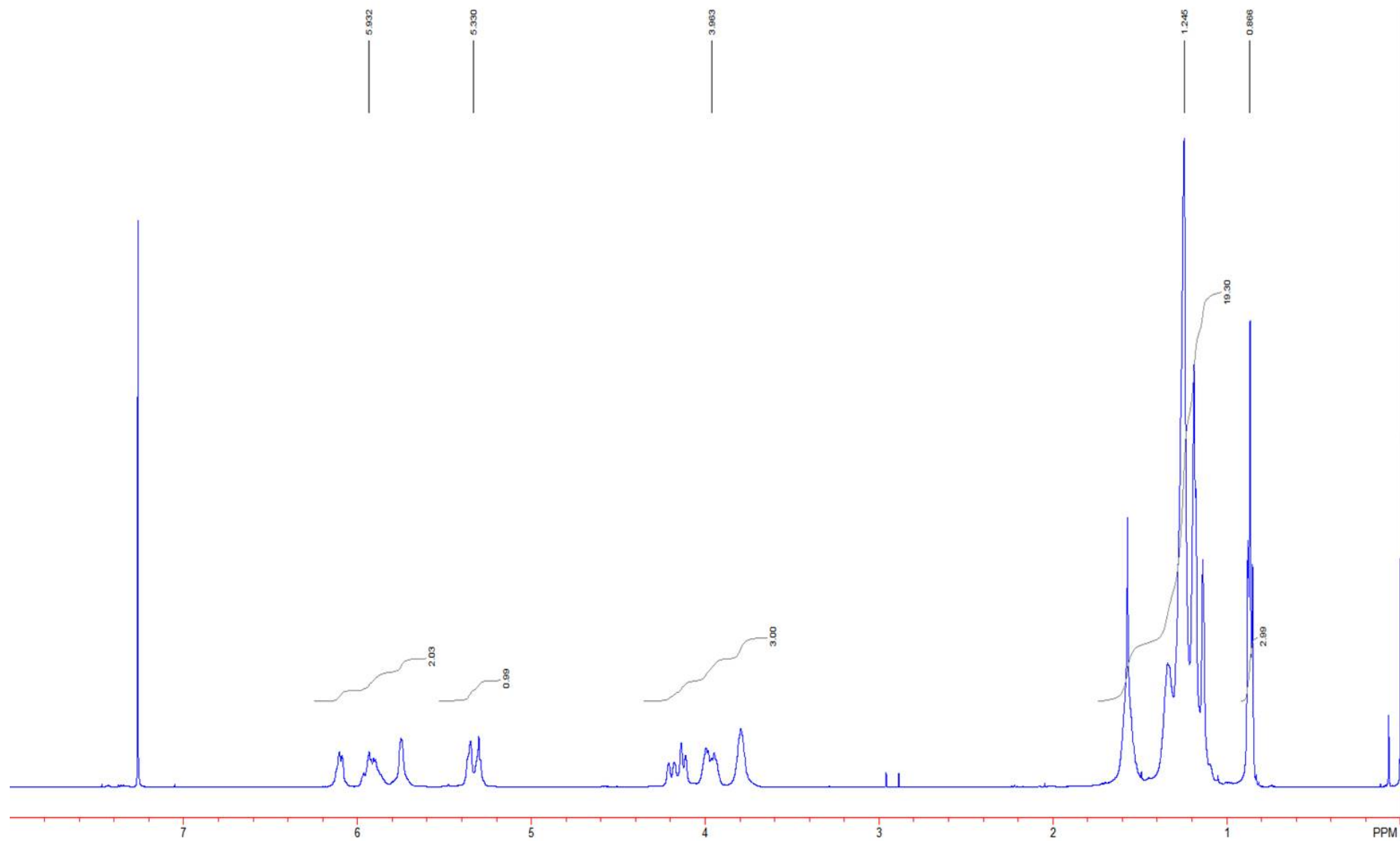
**3f**

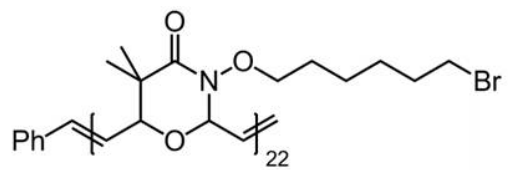
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 75 MHz)



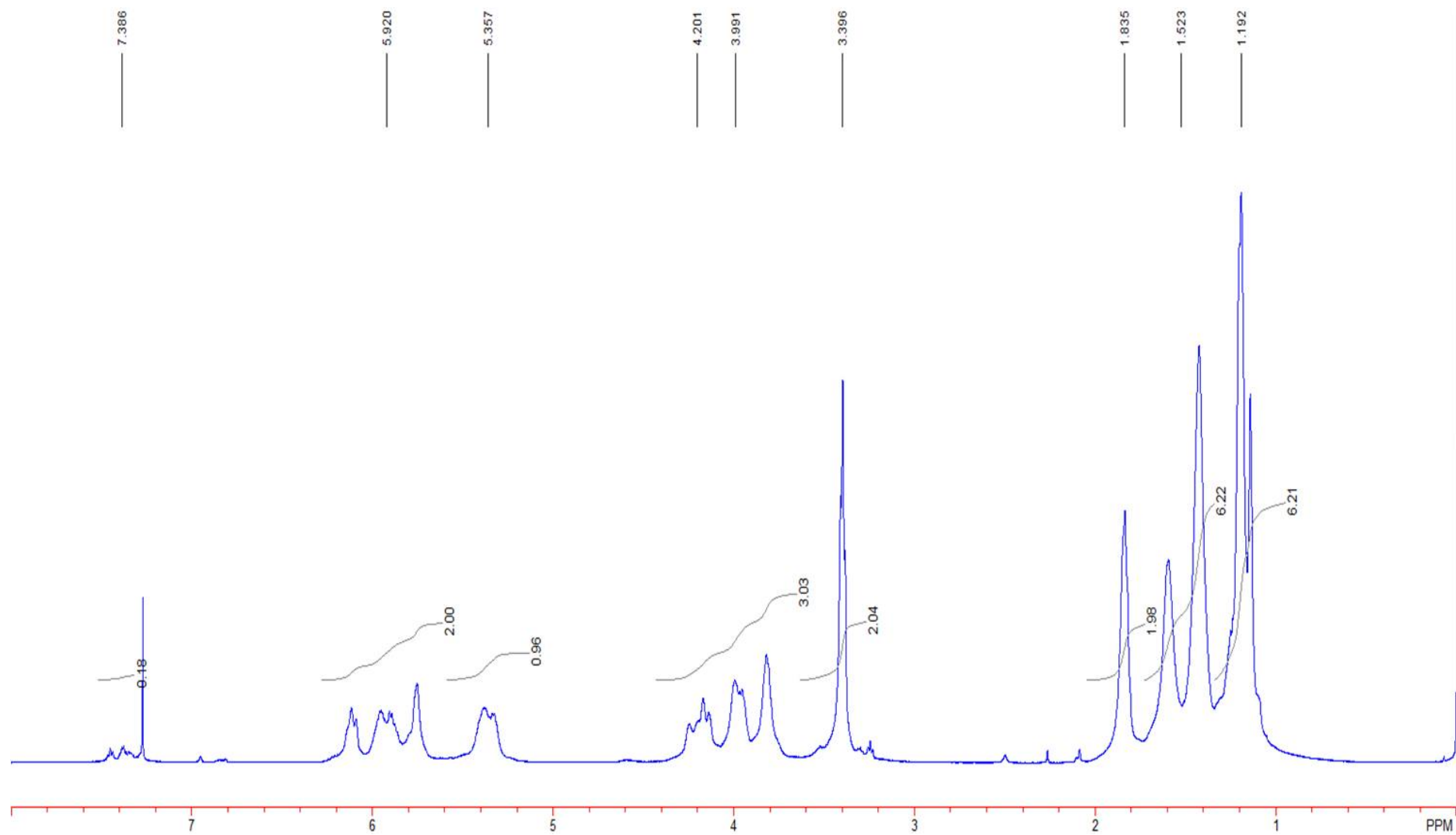


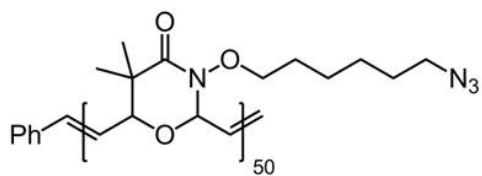
**4a**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)



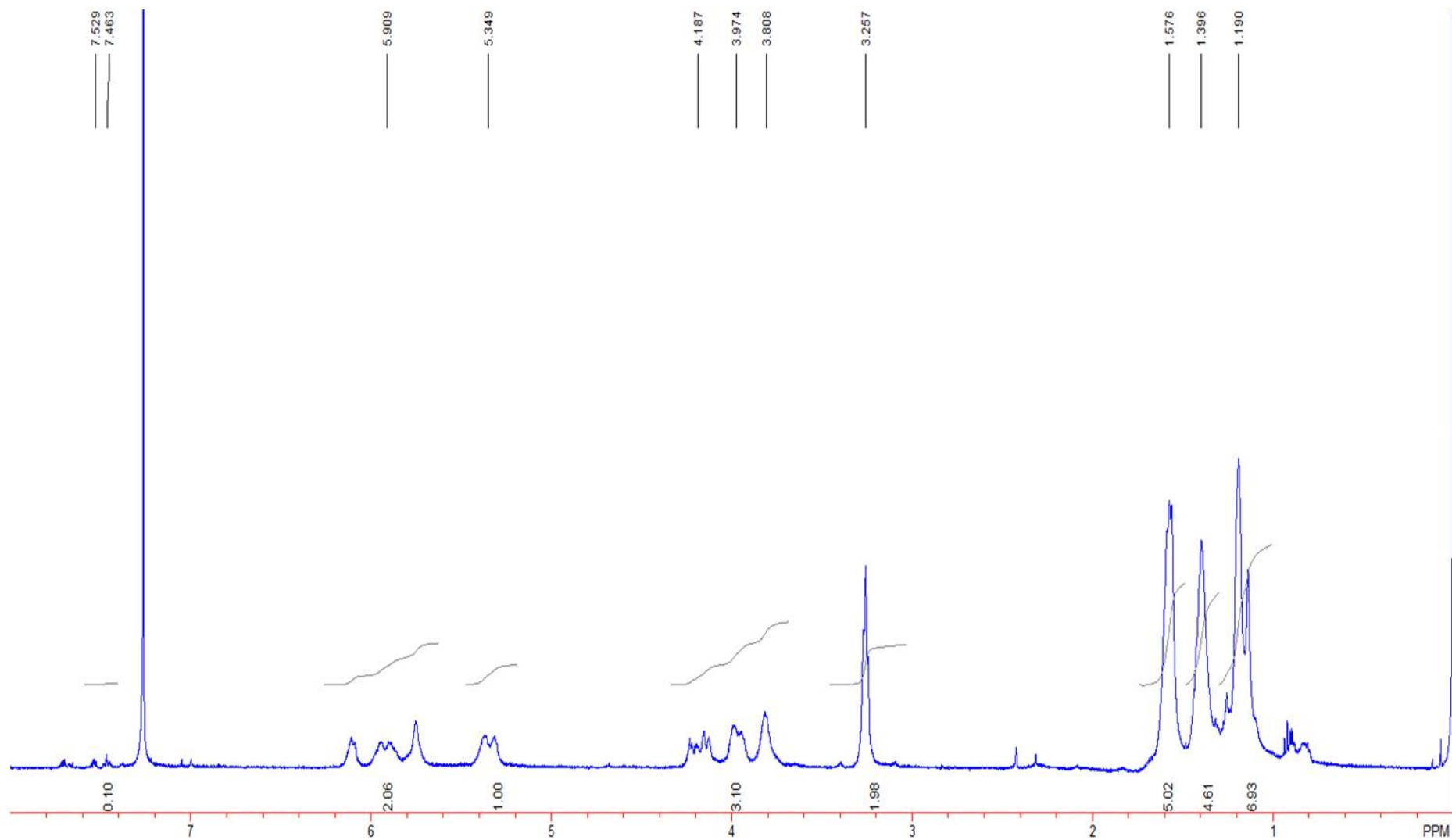


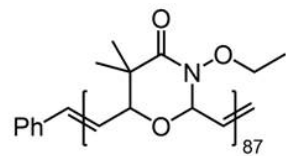
**4b**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)





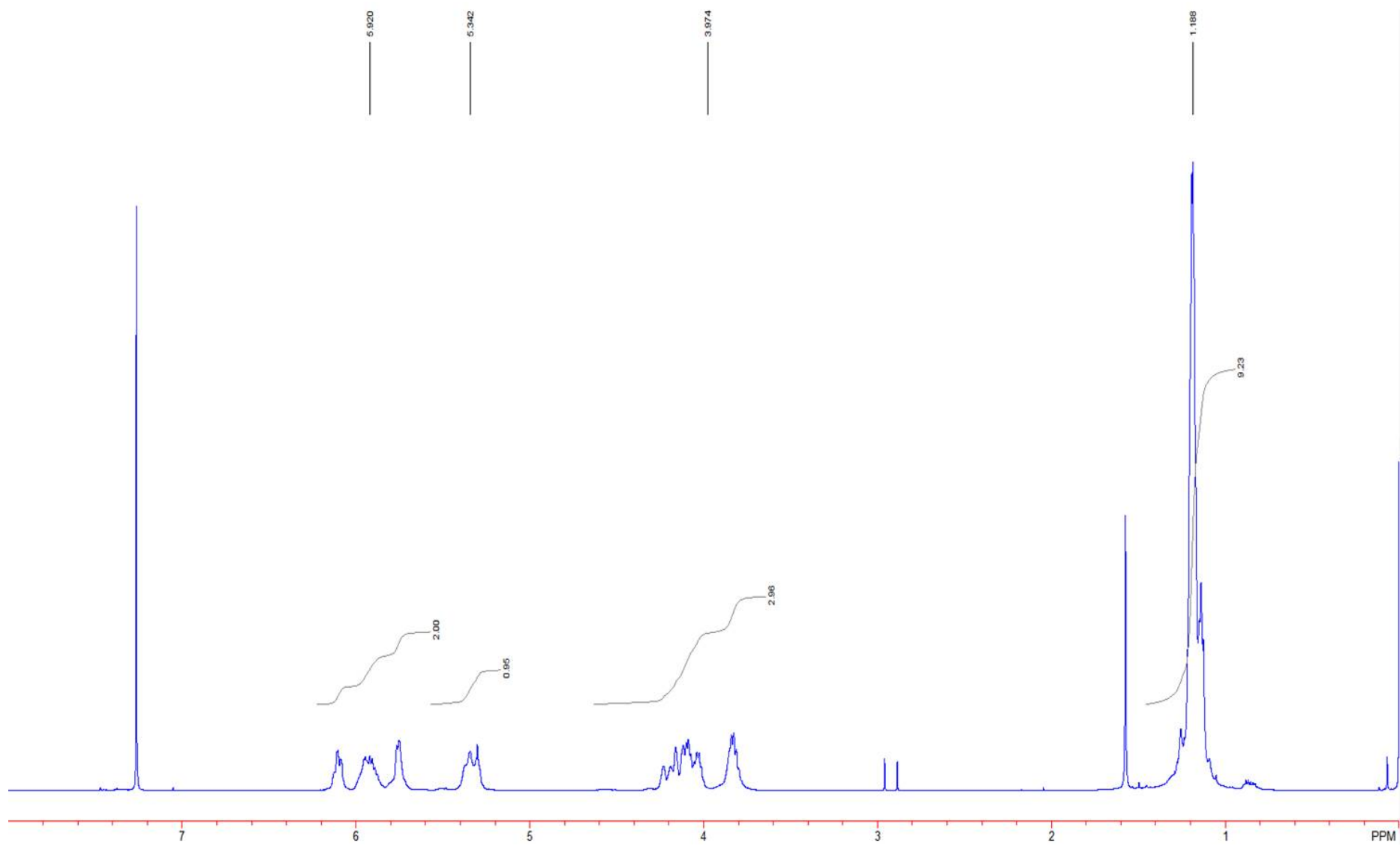
**4c**  
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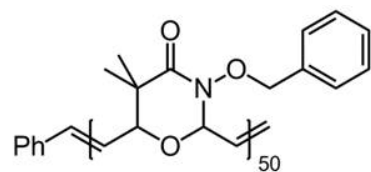




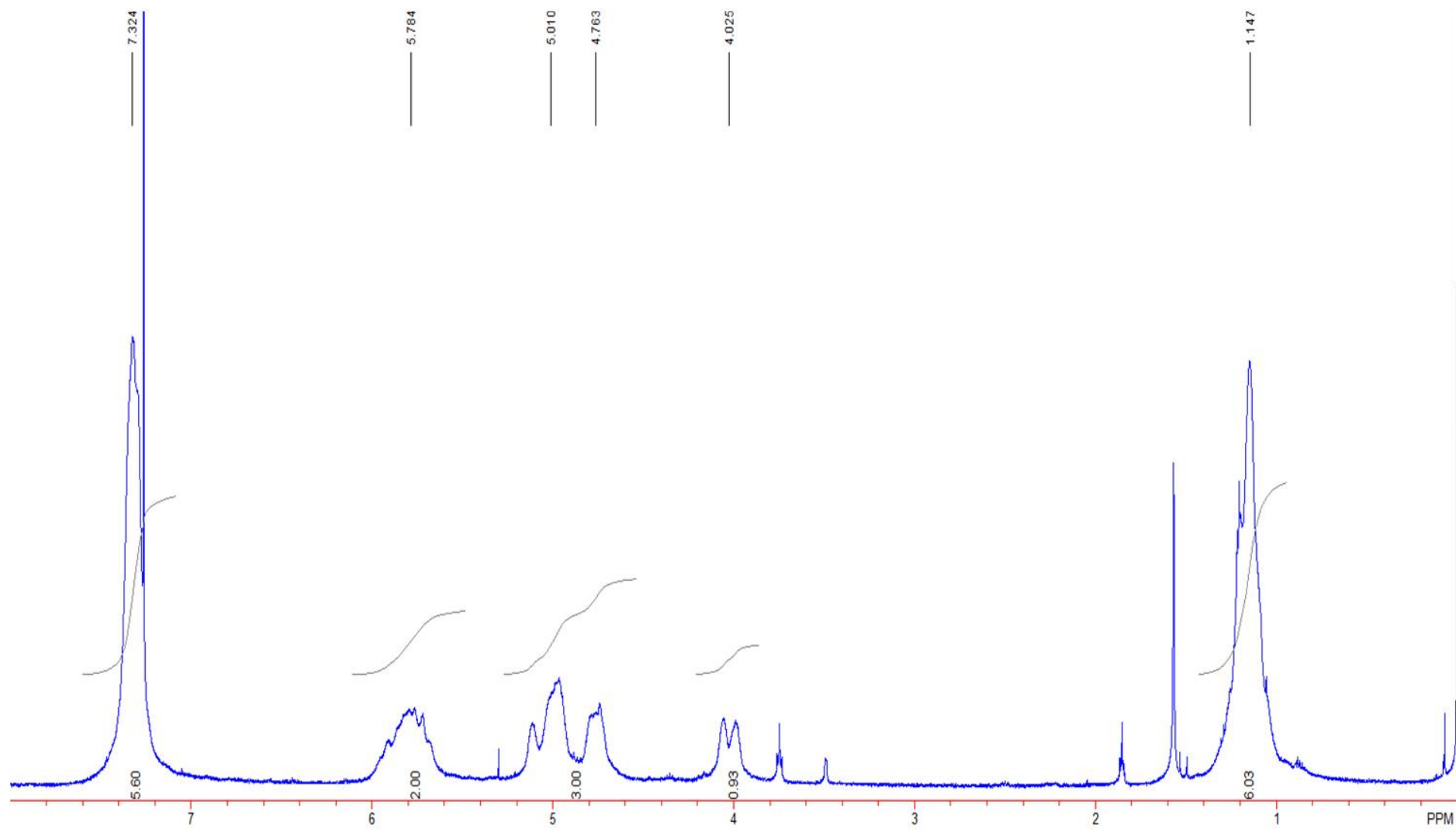
**4d**

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz)

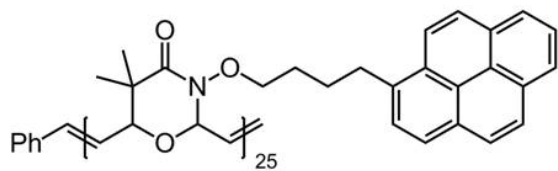




**4e**  
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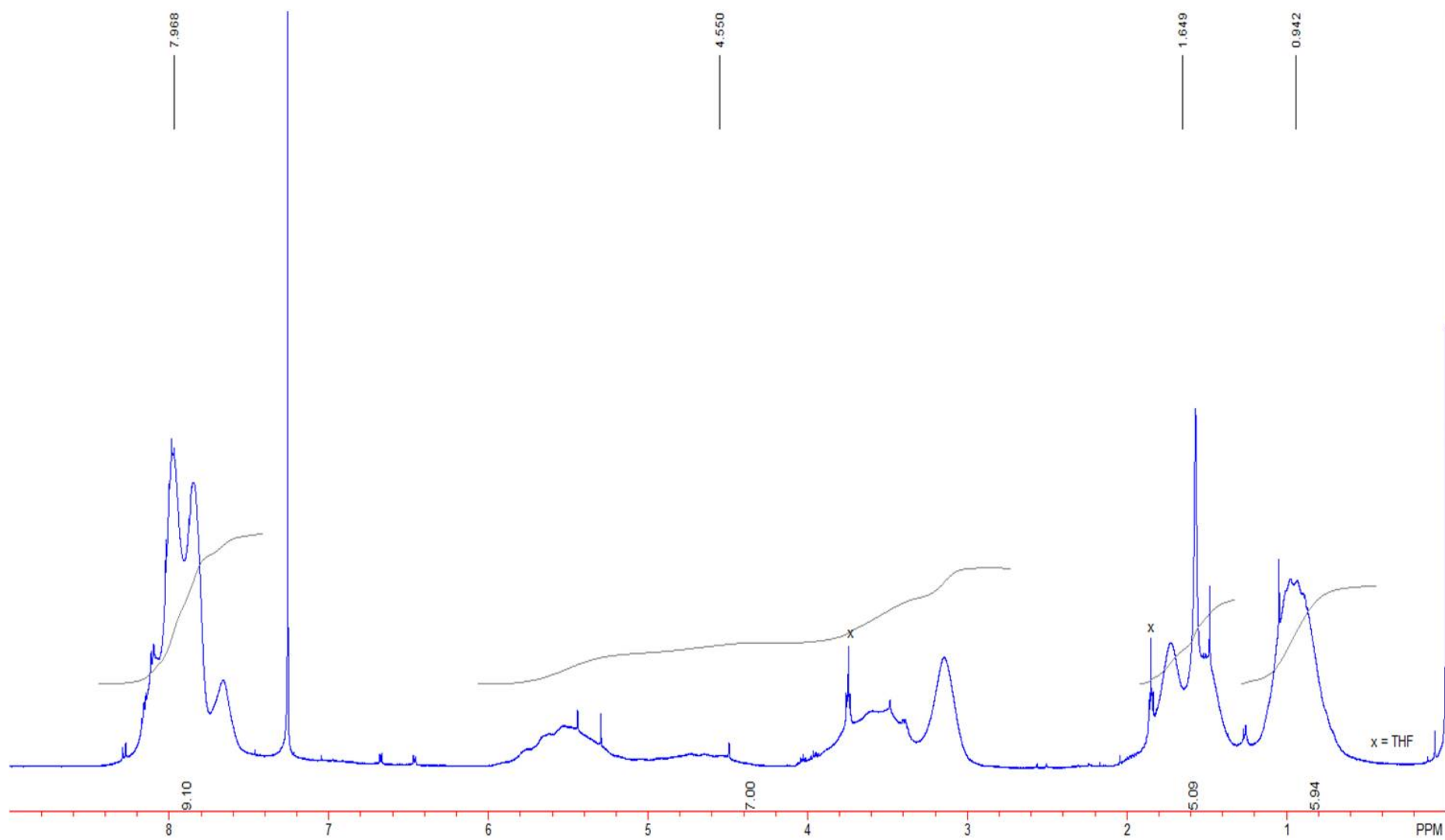






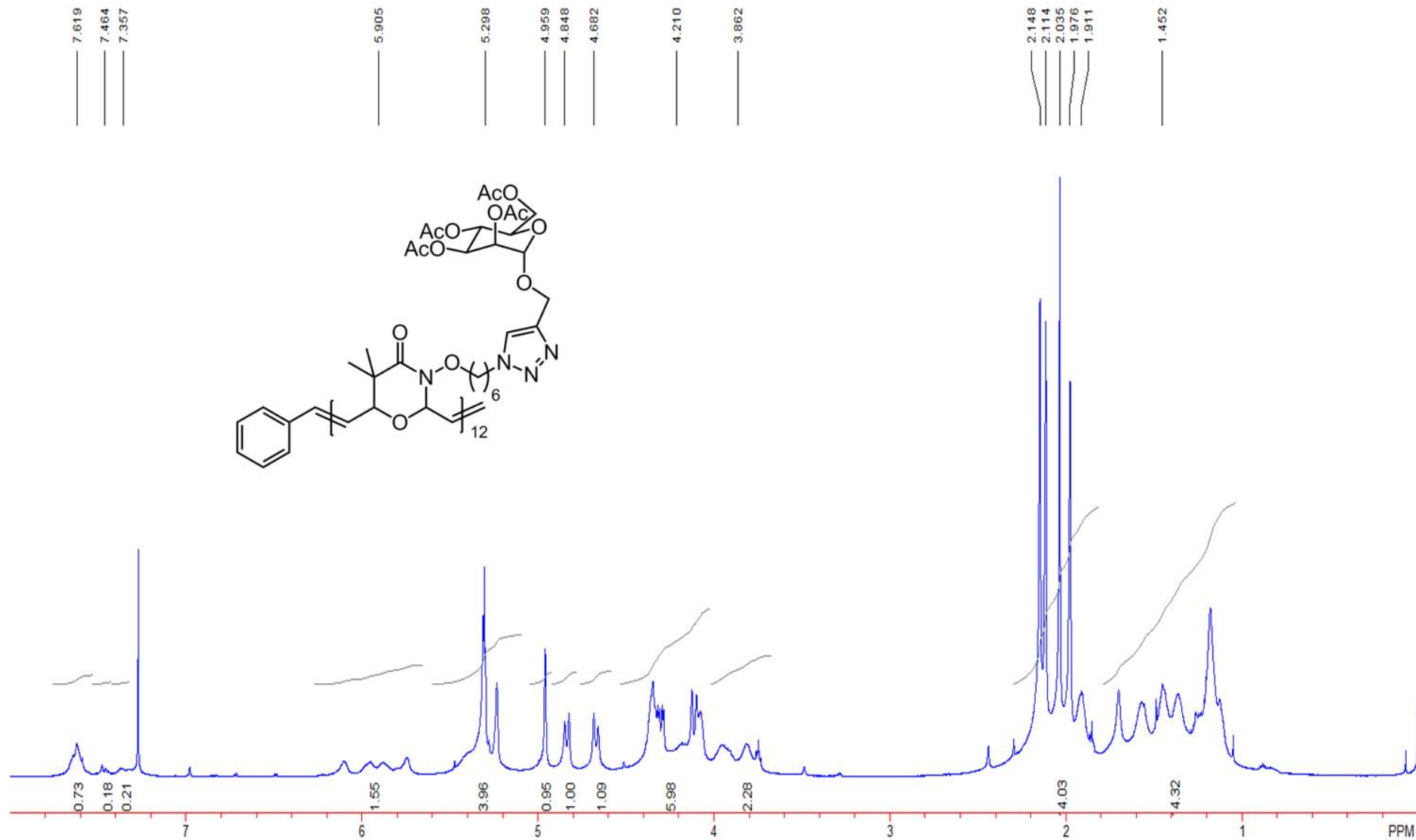
**4f**

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)



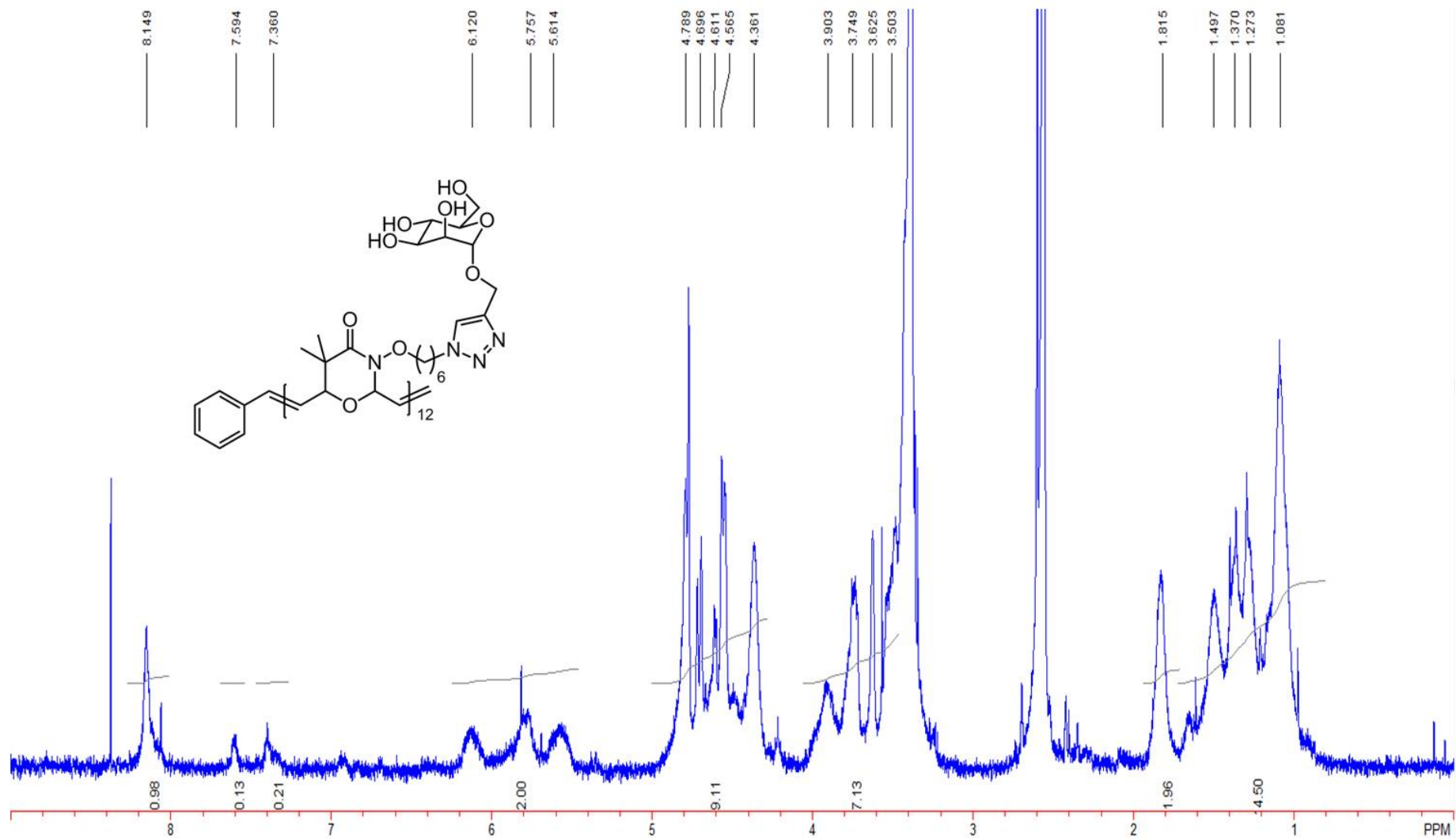
7

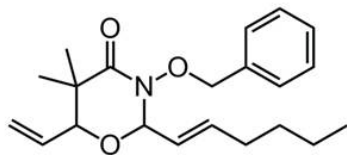
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)



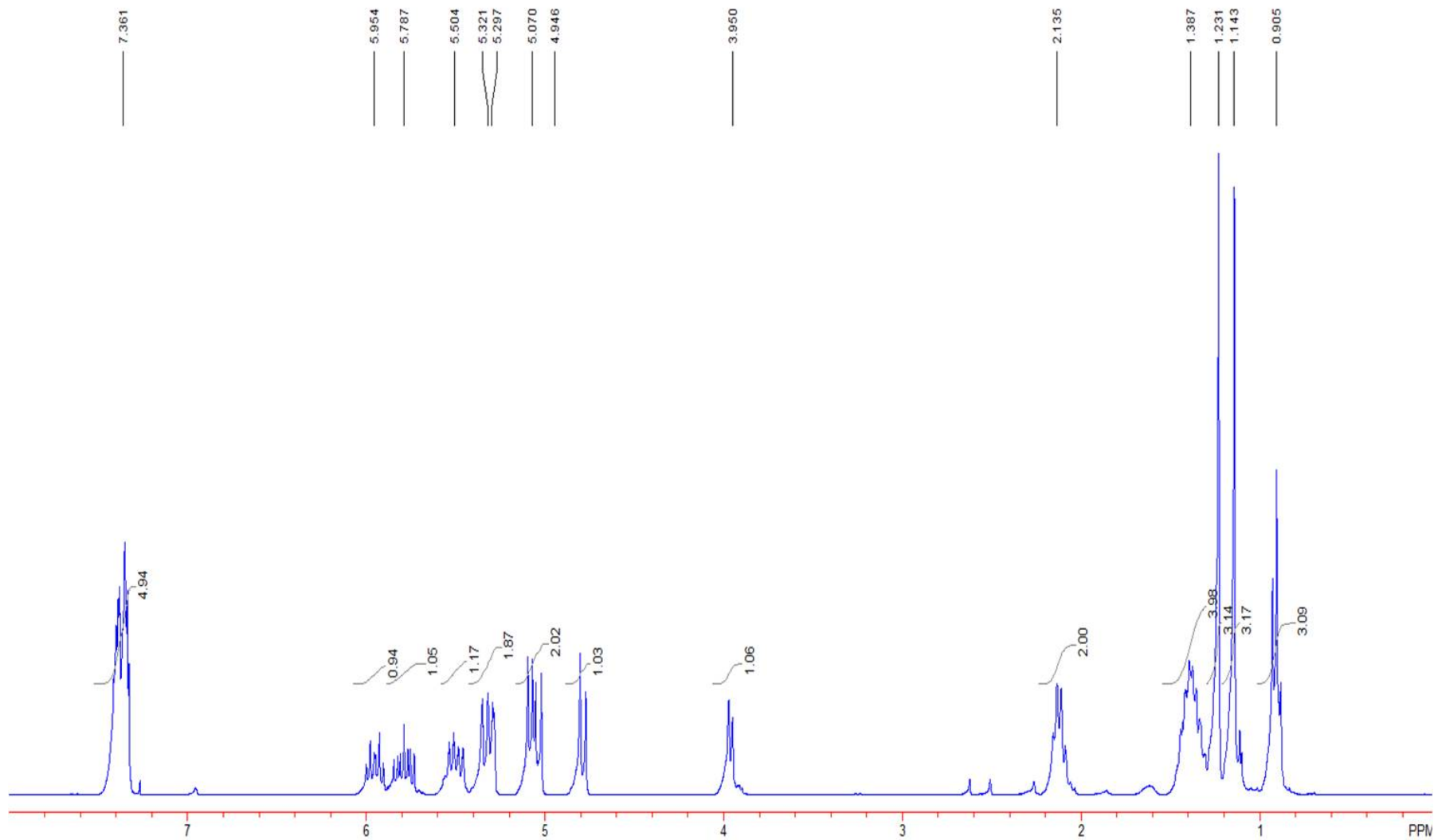
8

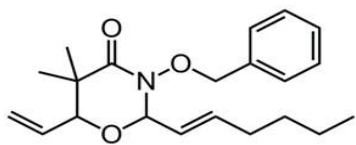
<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 500 MHz)





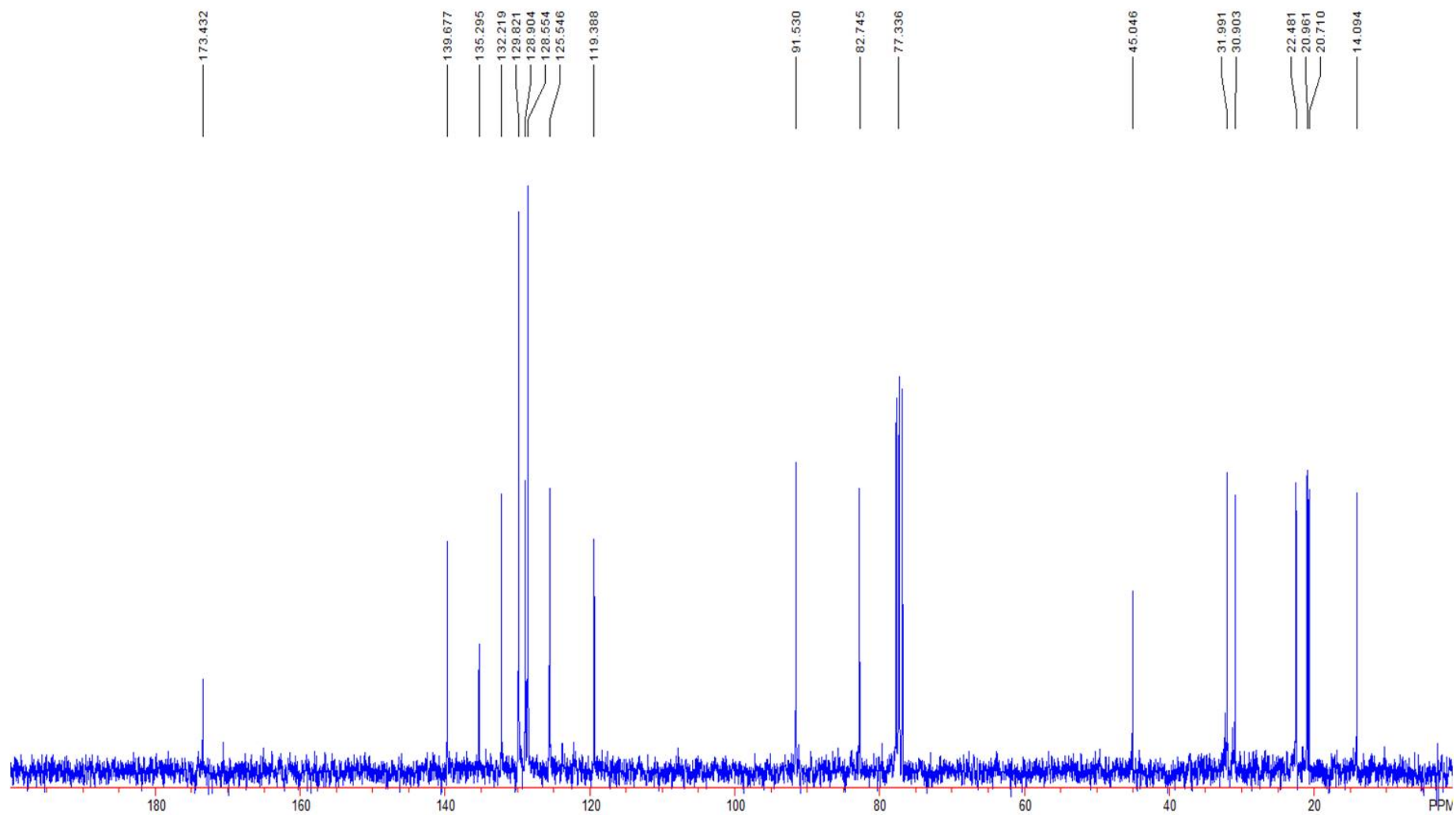
**9**  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)

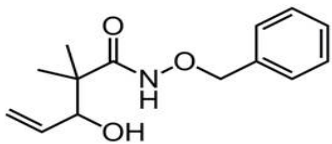




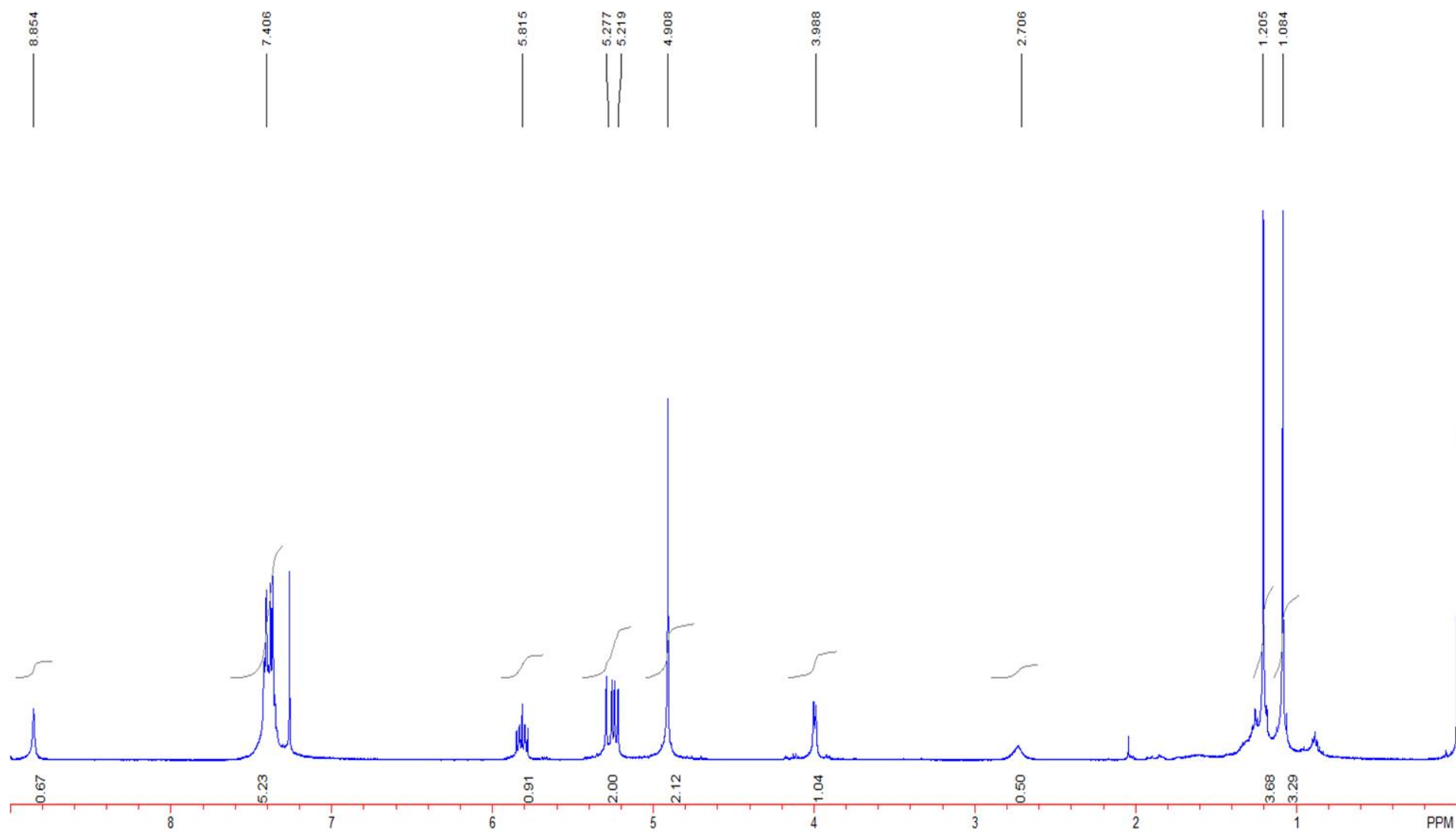
**9**

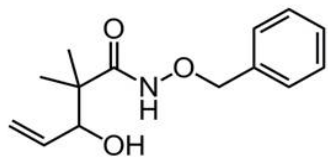
$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz)





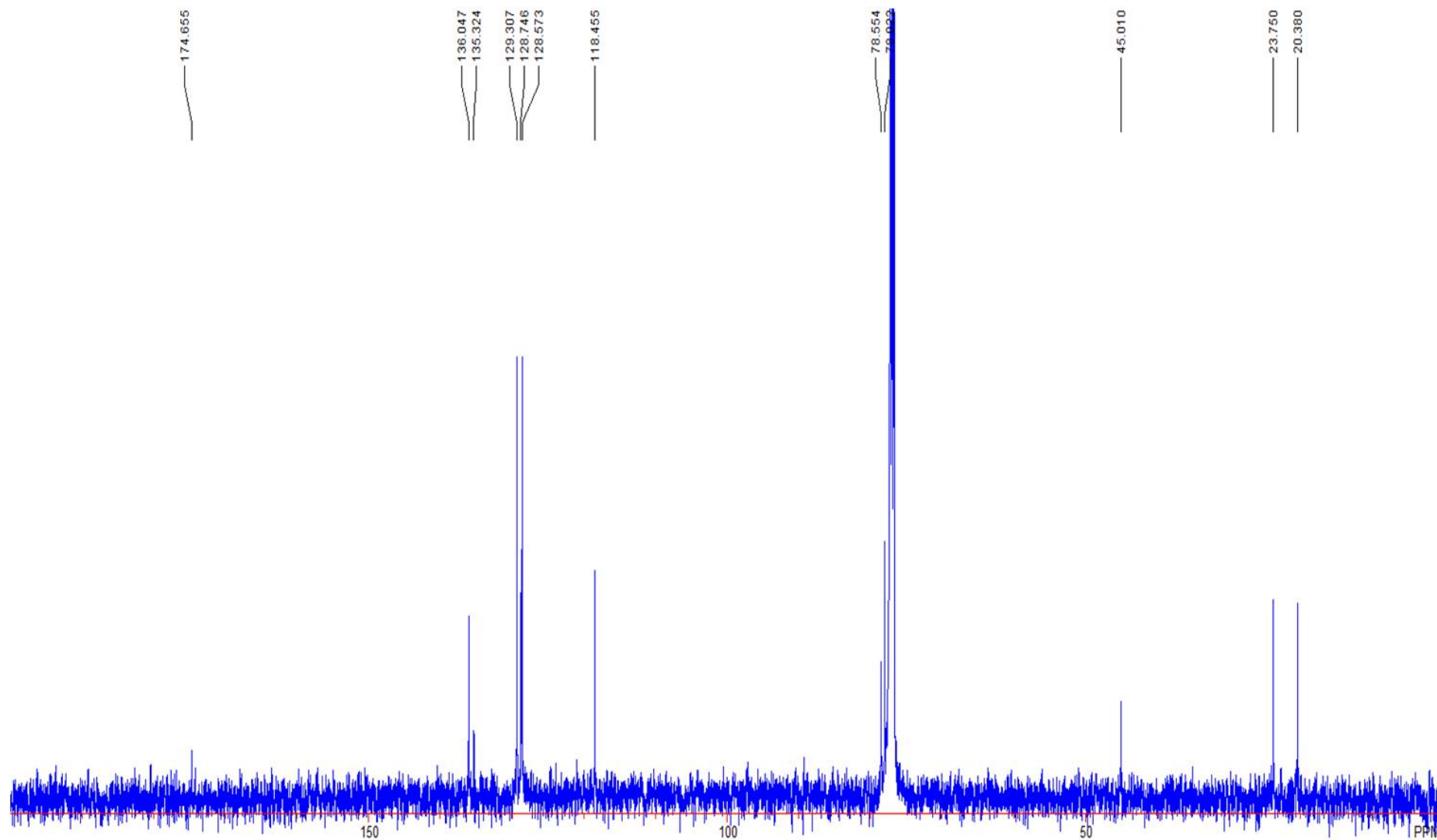
**10**  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz)

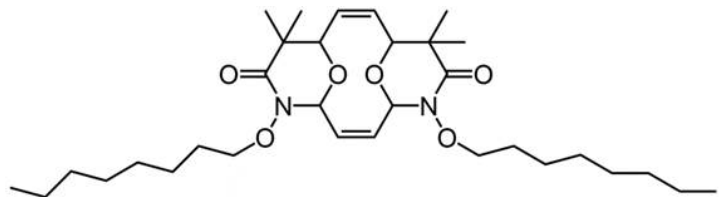




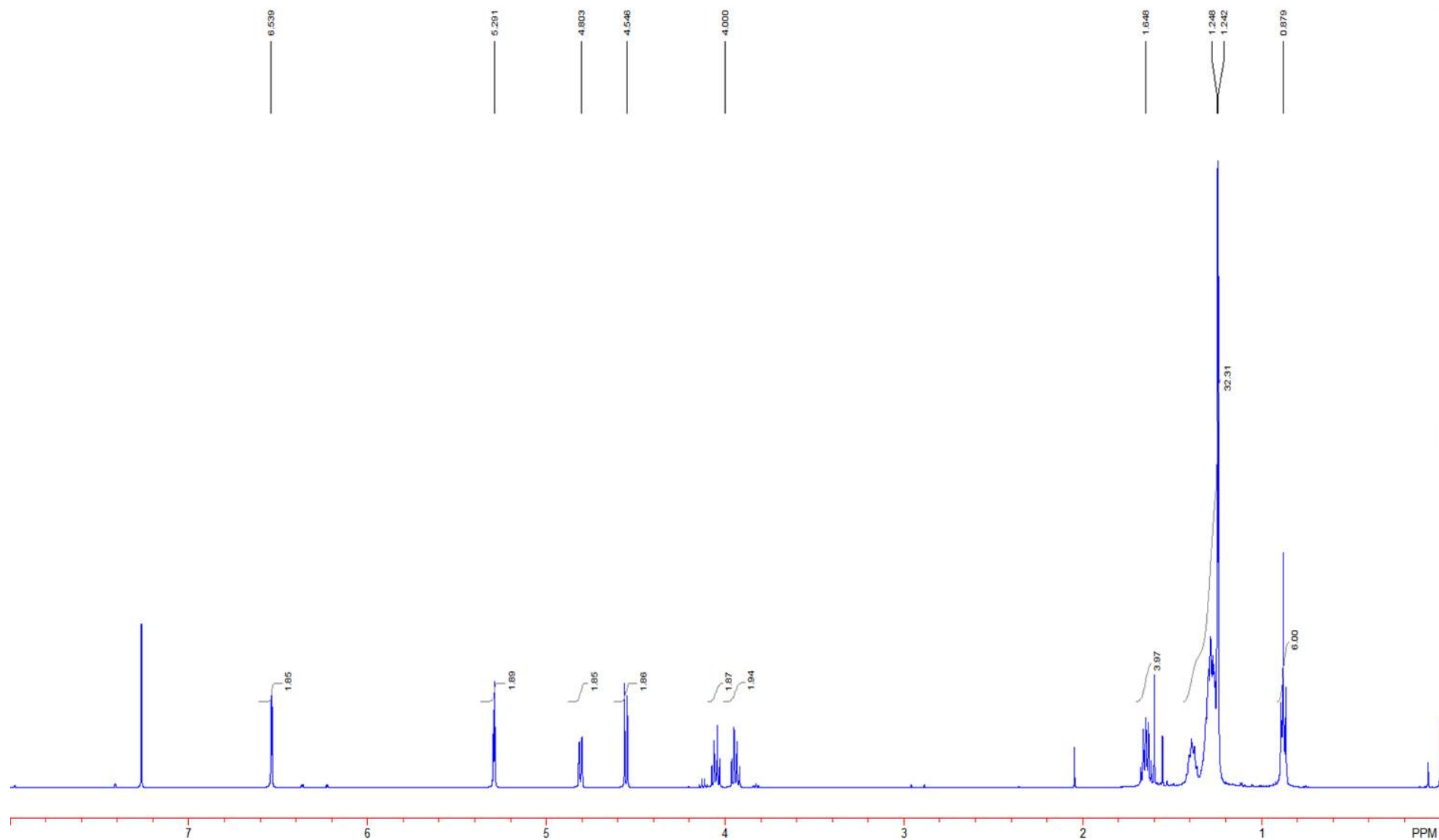
**10**

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125 MHz)

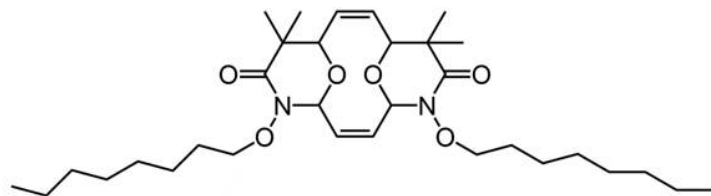




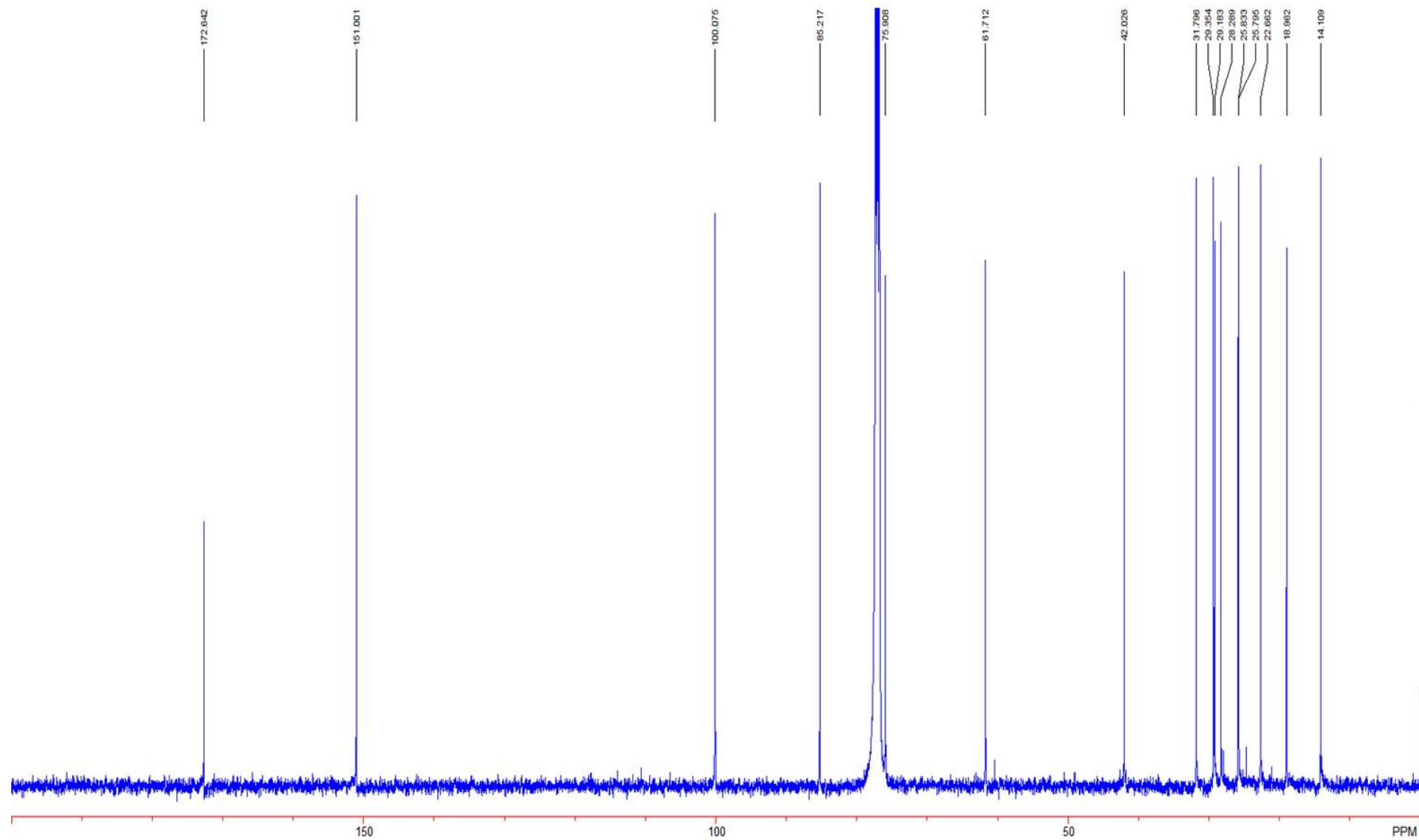
**cyclic dimer of 3a**  
 $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)

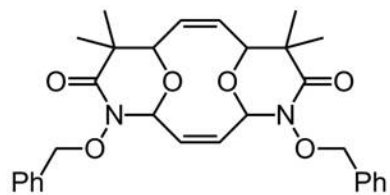






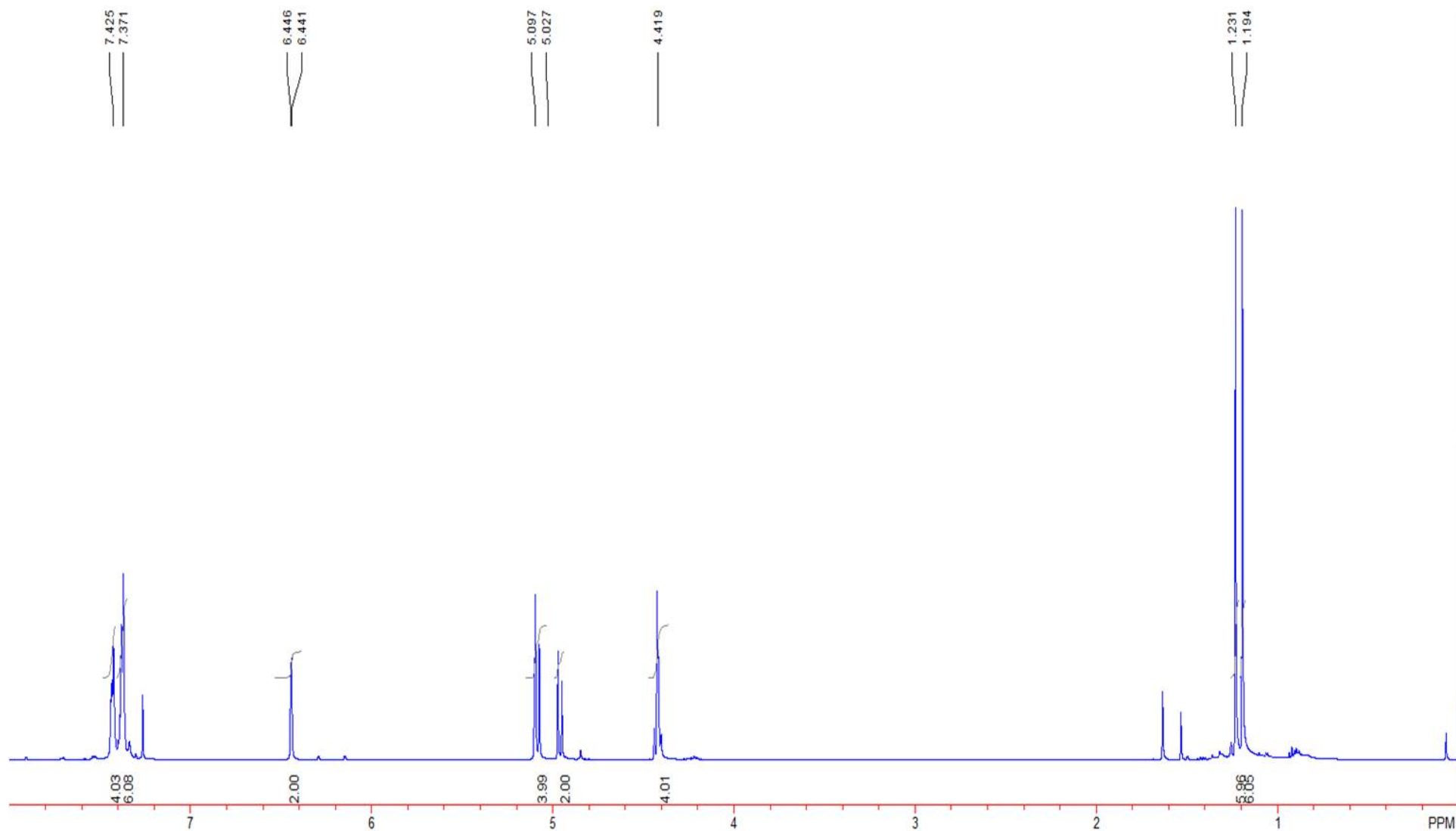
**cyclic dimer of 3a**  
 $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz)

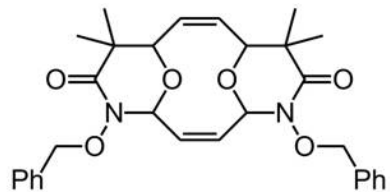




**cyclic dimer of 3e**

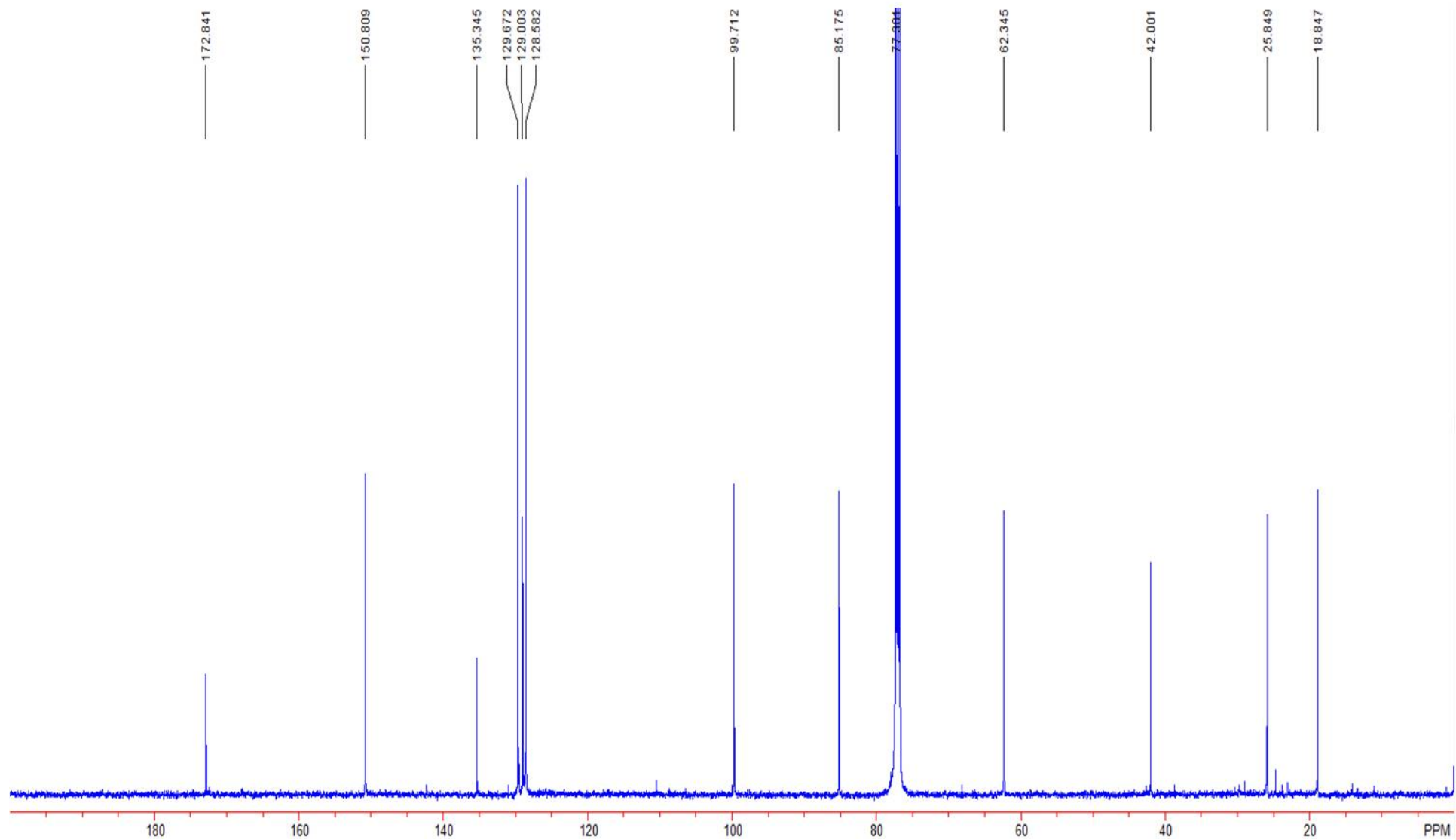
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz)

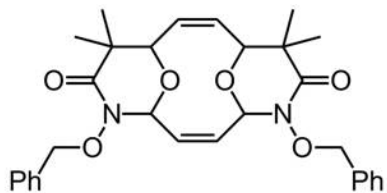




**cyclic dimer of 3e**

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz)





**cyclic dimer of 3e**

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125 MHz)

