

# Supporting Information

## **Topochemical Polymerization of a Diarylbutadiyne Derivative in the Gel and Solid States**

**Jules Roméo Néabo, Késhia Imelda Sika Tohoundjona, and Jean-Francois Morin**

Département de Chimie et Centre de recherche sur les matériaux avancés (CERMA),  
Université Laval, Pavillon Alexandre-Vachon, 1045 Avenue de la Médecine, Québec,  
Canada G1V 0A6. Fax: 418 6567916; Tel: 4186562131 poste 2812; E-mail: Jean-  
Francois.Morin@chm.ulaval.ca

### Table of Content

- 1- General**
- 2- Synthetic procedures and NMR data**
- 3- NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectra**
- 4- Table S1: Gelation properties of compound 1 in organic solvents**
- 5- Figure S1: Toluene and o-DCB based gels**
- 6- Figure S2: DSC of 10 mg/mL of o-DCB-based gel**
- 7- Figure S3: XRD spectra of toluene-based gel and compound 1 in MeOH**
- 8- Figure S4: FT-Raman of compounds 1 and P1**
- 9- Figure S5: Thermochromism behavior of P1: drop-cast film at (a) 20 °C and (b) > 100 °C.**

## 1- General

Chemical reagents were purchased from Sigma-Aldrich Co. Canada, Alfa Aesar Co., TCI America Co. or Oakwood Products Inc. and were used as received. Solvents used for organic synthesis were obtained from Fisher Scientific (except THF from Sigma-Aldrich Co. Canada) and purified with a Solvent Purifier System (SPS) (Vacuum Atmosphere Co., Hawthorne, USA). Other solvents were obtained from Fisher Scientific and were used as received. Tetrahydrofuran (THF) and triethylamine ( $\text{Et}_3\text{N}$ ) used for Sonogashira reactions were degassed 30 minutes prior to use. All anhydrous and air sensitive reactions were performed in oven-dried glassware under positive argon pressure. Analytical thin-layer chromatographies were performed with silica gel 60 F<sub>254</sub>, 0.25 mm pre-coated TLC plates (Silicycle, Québec, Canada). Compounds were visualized using 254 nm and/or 365 nm UV wavelength and/or aqueous sulfuric acid solution of ammonium heptamolybdate tetrahydrate (10 g/100 mL  $\text{H}_2\text{SO}_4$  + 900 mL  $\text{H}_2\text{O}$ ). Flash column chromatographies were performed on 230-400 mesh silica gel R10030B (Silicycle, Québec, Canada).

## Apparatus

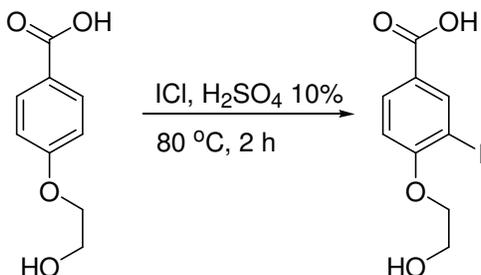
Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz ( $^1\text{H}$ ) and 100 MHz ( $^{13}\text{C}$ ). High-resolution mass spectra (HRMS) were recorded with an Agilent 6210 Time-of-Flight (TOF) LC-MS apparatus equipped with an ESI or APPI ion source (Agilent Technologies, Toronto, Canada). FT-IR was recorded in ATR mode on Infrared spectrometer (Thermo-Nicolet Magne 850) equipped with temperature Golden Gate. UV-visible absorption spectra were recorded on a Varian diode-array spectrophotometer (model Cary 500) using 3-mm path length quartz cells. Fluorescence spectroscopy was performed using fluorescence spectrophotometer (Model Cary eclipse) coupled with a Carry temperature controller. DSC and TGA measurements were done on a Mettler Toledo (DSC 823<sup>e</sup> and TGA/SDTA851<sup>e</sup>). Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6360 LV. X-ray diffraction was recorded on Siemens X-Rays Diffractometer (Model

D5000).

**Gelation test:** To test the gelation properties of compound **1** in a given solvent, we proceeded as follow: in a vial, compound **1** was dissolved in a solvent. After dissolution by sonication, the vial was sealed and heated until a clear solution was obtained. The clear solution was allowed to cool down at room temperature. The stability of the gel was confirmed by tube inversion.

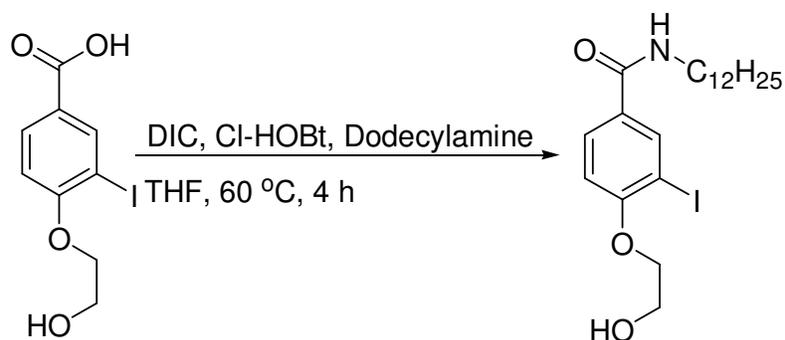
**SEM imaging:** the gel obtained in toluene was deposited on a stainless steel substrate and allowed to dry for 3-4 days. Then, gold particles were sputtered on dried gel prior to imaging.

## 2- Synthetic procedures and NMR data

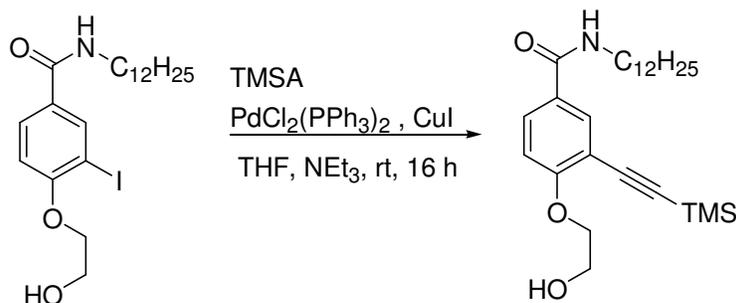


**Compound 3.** In a 100 mL round-bottom flask equipped with a magnetic stir bar, 4-(2-hydroxyethoxy)-benzoic acid (2.10 g, 11.5 mmol) and iodine monochloride (5.61 g, 34.6 mmol) were added to a 10% sulfuric acid aqueous solution (60 mL) at 0 °C. After the addition, the mixture was refluxed for 16 hours. The mixture was then cooled at room temperature and the precipitate formed was filtered under vacuum. The solid was washed with a sodium sulphite aqueous solution followed by distilled water. Triturating in toluene provides 3.44 g of compound **2** as a white solid (97%). (Diamond ATR):  $\nu$  3257, 1671  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, ppm): 8.14 (d,  $J$  = 1.9 Hz, 1H); 8.00 (dd,  $J$  = 1.9 Hz,  $J$  = 8.6 Hz, 1H); 7.02 (d,  $J$  = 8.6 Hz, 1H); 4.19 (t,  $J$  = 4.8 Hz, 2H); 3.94 (t,  $J$  = 4.8 Hz, 2H). <sup>13</sup>C NMR (400 MHz, CD<sub>3</sub>OD, ppm): 161.52;

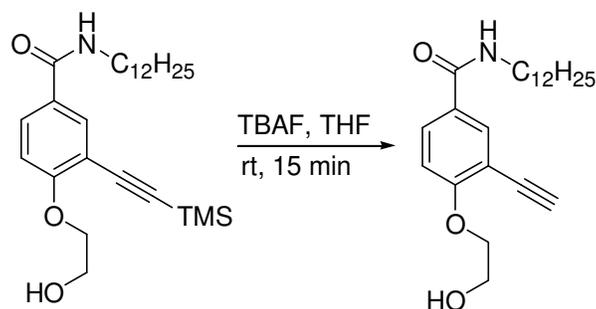
141.02; 131.63; 122.16; 111.27; 110.00; 85.02; 71.68; 60.02. HRMS: Calculated for  $C_9H_9IO_4$ : 306.9473  $[M-H]^-$ ; Found: 306.9468.



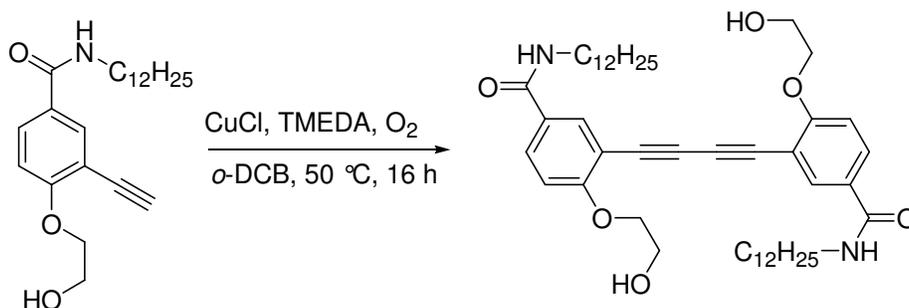
**Compound 4a.** In a 50 mL two-necked round-bottom flask with a magnetic stir bar, compound **3** (2.00 g, 6.49 mmol) and 6-Chloro-1-hydroxybenzotriazole (Cl-HOBt) (1.03 g, 6.10 mmol) were dissolved in degassed THF (35 mL) and the solution was heated at 60 °C under argon atmosphere. Then, *N,N*-diisopropylcarbodiimide (DIC) (1.02 mL, 6.49 mmol) was added dropwise over 10 minutes. After an additional 30 min of stirring, dodecylamine (1.14 g, 6.10 mmol) was added and the mixture was stirred for 3 hours. The mixture was then cooled at room temperature and the solution was filtered under vacuum. Aqueous acetic acid solution (10%) was added to the filtrate and the resulting mixture was extracted with  $CH_2Cl_2$  and the combined organic layers were washed successively with distilled water and brine. The organic layer was dried using  $Na_2SO_4$  and the solvent was removed under vacuum. The crude material was purified by column chromatography (silica gel, hexanes/acetone 7:3 as eluent) to provide 3.03 g of compound **3** as a white solid (84%). (Diamond ATR):  $\nu$  3373, 3337, 2918, 2850, 1609  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ , ppm): 8.14 (d,  $J = 1.9$  Hz, 1H); 7.74 (dd,  $J = 1.9$  Hz,  $J = 8.6$  Hz, 1H); 6.81 (d,  $J = 8.6$  Hz, 1H); 6.10 (s, 1H); 4.16 (t,  $J = 4.3$  Hz, 2H); 4.02 (m, 2H); 3.41 (m, 2H); 2.35 (t,  $J = 6.5$  Hz, 1H); 1.60 (m, 2H); 1.33-1.12 (m, 18H); 0.87 (t,  $J = 6.4$  Hz, 3H).  $^{13}C$  NMR (400 MHz,  $CDCl_3$ , ppm): 165.79; 159.52; 138.24; 129.71; 129.14; 111.79; 86.68; 71.06; 61.36; 40.47; 32.15; 29.90; 29.89; 29.87; 29.84; 29.79; 29.59; 29.57; 27.25; 22.93; 14.38. HRMS: Calculated for  $C_{23}H_{34}NIO_3$ : 475.1583  $[M-H]^-$ ; Found: 475.1501.



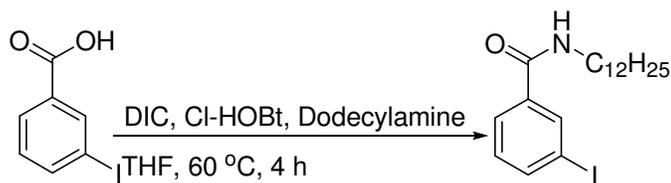
**Compound 5a.** In a 50 ml oven-dried round-bottom flask equipped with stir bar, compound **4a** (3.03 mg, 6.37 mmol) was dissolved in anhydrous and degassed THF (32 mL) under argon atmosphere. PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (17.7 mg, 0.02 mmol), CuI (4.8 mg, 0.02 mmol) and triethylamine (0.15 mL, 2.52 mmol) were added to the solution. The flask was filled and recharged with argon 4 times. Then, tetramethylsilylacetylene (TMSA) (0.15 mL, 0.94 mmol) was added dropwise and the mixture was continuously stirred overnight at room temperature. Ethyl acetate was then added and the resulting mixture was washed with aqueous NH<sub>4</sub>Cl. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered under vacuum and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (silica gel, hexanes/acetone 7:3 as eluent) to provide 2.05 g (73%) of compound **4** as brown oil. (Diamond ATR):  $\nu$  3308, 3235, 2914, 2848, 2152, 1628 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.77 (d, *J* = 2.2 Hz, 1H); 7.76 (dd, *J* = 2.2 Hz, *J* = 9.4 Hz, 1H); 6.91 (d, *J* = 9.4 Hz, 1H), 6.00 (s, 1H); 4.18 (t, *J* = 4.4 Hz, 2H); 3.98 (m, 2H); 3.42 (m, 2H); 2.30 (t, *J* = 6.3 Hz, 1H) 1.60 (m, 2H); 1.34-1.26 (m, 18H); 0.88 (t, *J* = 6.3 Hz, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm): 166.34; 161.84; 132.07; 129.74; 128.01; 113.36; 112.77; 100.31; 100.23; 70.80; 61.41; 40.41; 32.16; 29.95; 29.89; 29.88; 29.85; 29.80; 29.75; 29.59; 27.30; 22.94; 13.38; 0.18. HRMS: Calculated for C<sub>23</sub>H<sub>43</sub>O<sub>3</sub>NSi: 444.2939 [M-H]<sup>-</sup>; Found: 444.2941.



**Compound 6a.** In a 50 mL round-bottom flask equipped with a magnetic stir bar, compound **5a** (2.05 g, 5.6 mmol) was dissolved in THF (28 mL). Then, tetrabutylammonium fluoride (TBAF) (0.1 M in THF, 5.6 mL) was added dropwise and the reaction was stirred for 15 min. Ethyl acetate was added and the resulting mixture was washed with water. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered under vacuum and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (silica gel, hexanes/acetone 7:3 as eluent) to provide 1.58 g of compound **5** as white solid (93%). (Diamond ATR):  $\nu$  3453, 3266, 2918, 2852, 1613  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm): 7.82 (d,  $J = 2.1$  Hz, 1H); 7.76 (dd,  $J = 2.1$  Hz,  $J = 8.6$  Hz, 1H); 6.91 (d,  $J = 8.6$  Hz, 1H), 6.10 (s, 1H); 4.18 (t,  $J = 4.4$  Hz, 2H); 4.00 (m, 2H); 3.42 (m, 2H); 3.30 (s, 1H); 2.40 (t,  $J = 6.38$  Hz, 1H) 1.60 (m, 2H); 1.33-1.25 (m, 18H); 0.87 (t,  $J = 6.38$  Hz, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm): 166.31; 162.00; 132.73; 129.89; 127.87; 112.27; 112.06; 86.68; 79.24; 70.65; 61.34; 40.41; 32.15; 29.90; 29.88; 29.86; 29.83; 29.78; 29.59; 29.57; 27.25; 22.92; 14.36. HRMS: Calculated for  $\text{C}_{23}\text{H}_{35}\text{O}_3\text{N}$ : 372.2544 [M-H] $^-$ ; Found: 372.2518.

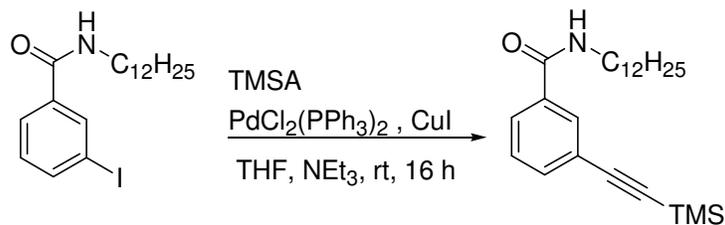


**Compound 1.** In a 50 mL round-bottom flask equipped with magnetic stir bar, CuCl (2.65 mg, 0.026 mmol) and tetramethylethylenediamine (TMEDA) (21  $\mu$ L, 0.093 mmol) were dissolved in *o*-dichlorobenzene (14 mL). The mixture was heated at 50  $^{\circ}$ C with a continuous stream of air bubbling through the solution. Then, compound **6a** (500 mg, 1.33 mmol) was added in portion and the mixture was stirred for an additional 16 hours at 50  $^{\circ}$ C before it was allowed to cool at room temperature. The greenish viscous solution was diluted in a mixture of methanol and water (8:2), allowing a white solid to precipitate. The precipitate was filtered under vacuum, washed with water and dried under vacuum to provide 425 mg of compound **1** as white solid (85%). (Diamond ATR):  $\nu$  3278, 2921, 2852, 1628  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ , ppm): 7.94 (d, 2H,  $J = 2.1$  Hz); 7.83 (dd, 2H,  $J = 2.1$  Hz,  $J = 8.8$  Hz); 7.11 (d, 2H,  $J = 8.8$  Hz), 4.19 (t, 4H,  $J = 4.6$  Hz); 3.93 (t, 4H,  $J = 4.6$  Hz); 3.31 (t, 4H,  $J = 6.9$  Hz); 1.58 (m, 4H); 1.32-1.125 (m, 36H); 0.85 (t, 6H,  $J = 6.4$  Hz).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ , ppm): 166.64; 164.83; 135.03; 132.28; 129.28; 113.54; 112.85; 80.19; 79.57; 72.88; 62.24; 41.62; 33.94; 31.88; 31.70; 31.68; 31.51; 31.38; 29.11; 24.63; 14.15. HRMS: Calculated for  $\text{C}_{46}\text{H}_{68}\text{O}_6\text{N}_2$ : 745.5150  $[\text{M}+\text{H}]^+$ ; Found: 745.5135.



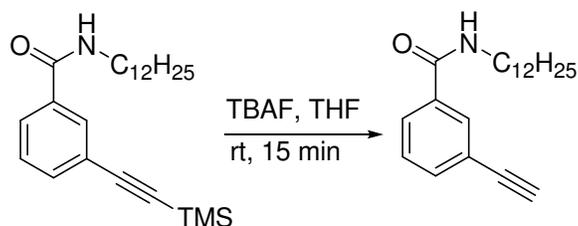
**Compound 4b.** In a 100 mL two-necked round-bottom flask equipped with a magnetic stir bar kept under argon atmosphere, 3-iodobenzoic acid (2.00 g, 8.06 mmol) and Cl-HOBt (1.50 g, 8.87 mmol) were dissolved in distilled THF (41 mL). The mixture was refluxed at 60  $^{\circ}$ C and DIC (1.26 mL, 8.06 mmol) was added. After 30 min, the temperature was slightly decreased and dodecylamine (1.64 g, 8.87 mmol) was added in portions over 10 min. The mixture was allowed to reflux overnight. After completion of the reaction, the mixture was cooled to room temperature and neutralized with 10 mL of diluted acetic acid solution. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  and the organic layer was successively washed with water and brine. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was

removed under vacuum. The crude material was then purified by column chromatography using hexanes/ethyl acetate 60:40 as eluent to yield 2.81 g (85%) of white solid. (Diamond ATR):  $\nu$  3311, 22181639  $\text{cm}^{-1}$   $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm) : 8.08 (s, 1H); 7.81 (d,  $J = 7.92$  Hz, 1H); 7.71 (d,  $J = 7.92$  Hz, 1H), 7.16 (t,  $J = 7.92$  Hz, 1H); 6.14 (s, 1H); 4.02 (m, 2H); 3.43 (m, 2H); 1.610 (m, 2H); 1.33-1.12 (m, 18H); 0.87 (t,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm) : 167.07; 140.42; 137.11; 136.12; 130.47; 126.31; 94.49; 40.50; 32.15; 29.88; 29.86; 29.84; 29.83; 29.77; 29.58; 29.55; 27.22; 22.93; 14.37. HRMS: Calculated for  $\text{C}_{19}\text{H}_{30}\text{INO}$ : 416.1445  $[\text{M}+\text{H}]^+$ ; Found: 416.1477.

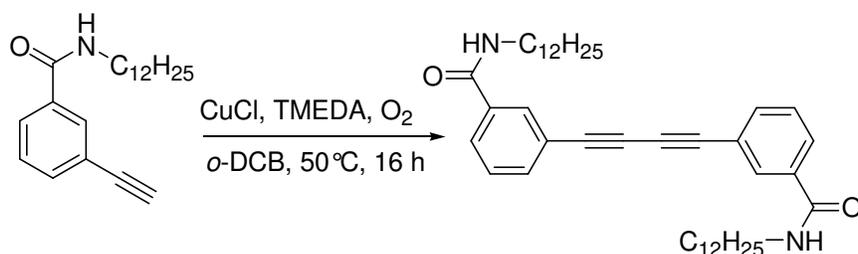


**Compound 5b.** In a 100 mL round-bottom flask equipped with a magnetic stir bar and kept under argon atmosphere, compound **4b** (2.00 g, 4.81 mmol) was dissolved in dry THF (24 mL) and triethylamine (2.68 mL) was added.  $\text{PdCl}_2(\text{PPh}_3)_2$  (136 mg, 0.19 mmol) and  $\text{CuI}$  (37 mg, 0.19 mmol) were added to the mixture and TMSA (1.17 mL) was added dropwise. The mixture was stirred overnight at room temperature. After completion of the reaction as shown by TLC, a solution of  $\text{NH}_4\text{Cl}$  (30 mL) was added and the mixture was extracted twice with 20 mL of ethyl acetate. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was removed under vacuum. The crude material was then purified by column chromatography using hexanes/acetate 80:20 as eluent to yield 1.80 g (97%) of a brownish oil. (Diamond ATR):  $\nu$  3262, 2915, 2848, 1637  $\text{cm}^{-1}$   $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm) : 7.80 (s, 1H); 7.73 (d,  $J = 7.61$  Hz, 1H); 7.57 (d,  $J = 7.61$  Hz, 1H), 7.37 (t,  $J = 7.61$  Hz, 1H); 6.09 (s, 1H); 4.02 (m, 2H); 3.43 (m, 2H); 1.610 (m, 2H); 1.34-1.26 (m, 18H); 0.87 (t,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm) : 166.88; 135.23; 134.75; 130.24; 128.86; 127.40; 123.77; 104.25; 95.65; 40.43; 32.15; 29.88; 29.86; 29.82; 29.78; 29.58; 29.56; 27.33;

22.92; 14.36. HRMS: Calculated for  $C_{24}H_{39}NOSi$ : 386.2874  $[M+H]^+$ ; Found: 386.2911.



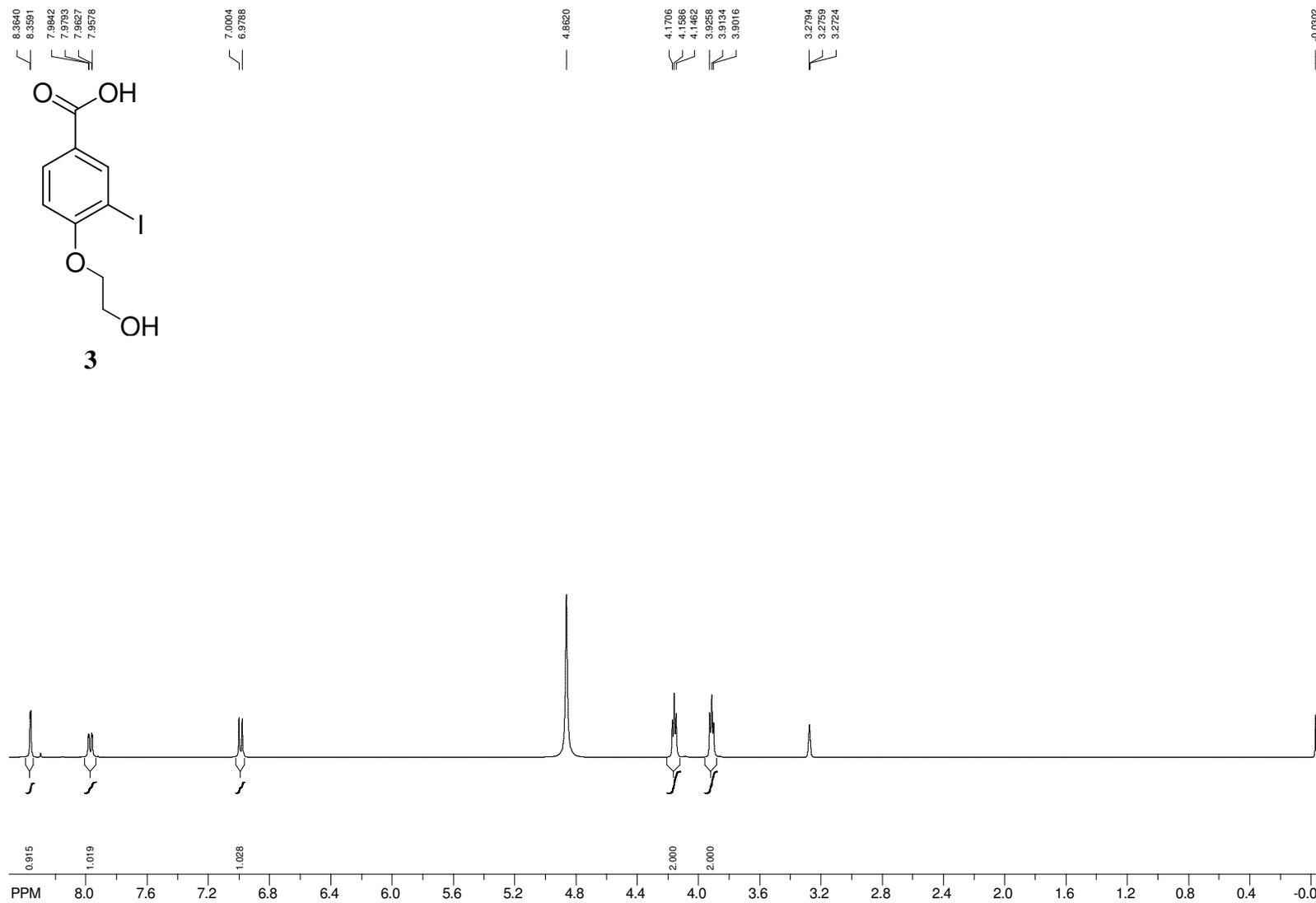
**Compound 6b.** In a 50 mL round-bottom flask equipped with magnetic stir bar, compound **5b** (1.80 g, 4.66 mmol), THF (24 mL) and TBAF were added successively. After 15 minutes, 30 mL of distilled water was added and the mixture was extracted twice with ethyl acetate (2 x 30 mL). The organic layer was dried over  $Na_2SO_4$  and the solvent was removed under vacuum. The crude material was then purified by column chromatography using hexanes/acetate 80:20 as eluent to provide 1.2 g (83%) of white solid. (Diamond ATR):  $\nu$  3327, 2915, 2848, 1637  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ , ppm) : 7.84 (s, 1H); 7.75 (d,  $J = 7.65$  Hz, 1H); 7.59 (d,  $J = 7.65$  Hz, 1H), 7.38 (t,  $J = 7.65$  Hz, 1H); 6.23 (s, 1H); 3.42 (m, 2H); 3.11 (s, 1H); 1.61 (m, 2H); 1.33-1.25 (m, 18H); 0.87 (t,  $J = 6.4$  Hz, 3H).  $^{13}C$  NMR (400 MHz,  $CDCl_3$ , ppm) : 166.838; 135.38; 134.94; 130.59; 128.91; 127.64; 122.78; 82.95; 78.39; 40.45; 32.15; 29.89; 29.87; 29.83; 29.79; 29.59; 29.57; 27.24; 22.93; 14.37 HRMS: Calculated for  $C_{21}H_{31}NO$ : 314.2478  $[M+H]^+$ ; Found: 314.2511.

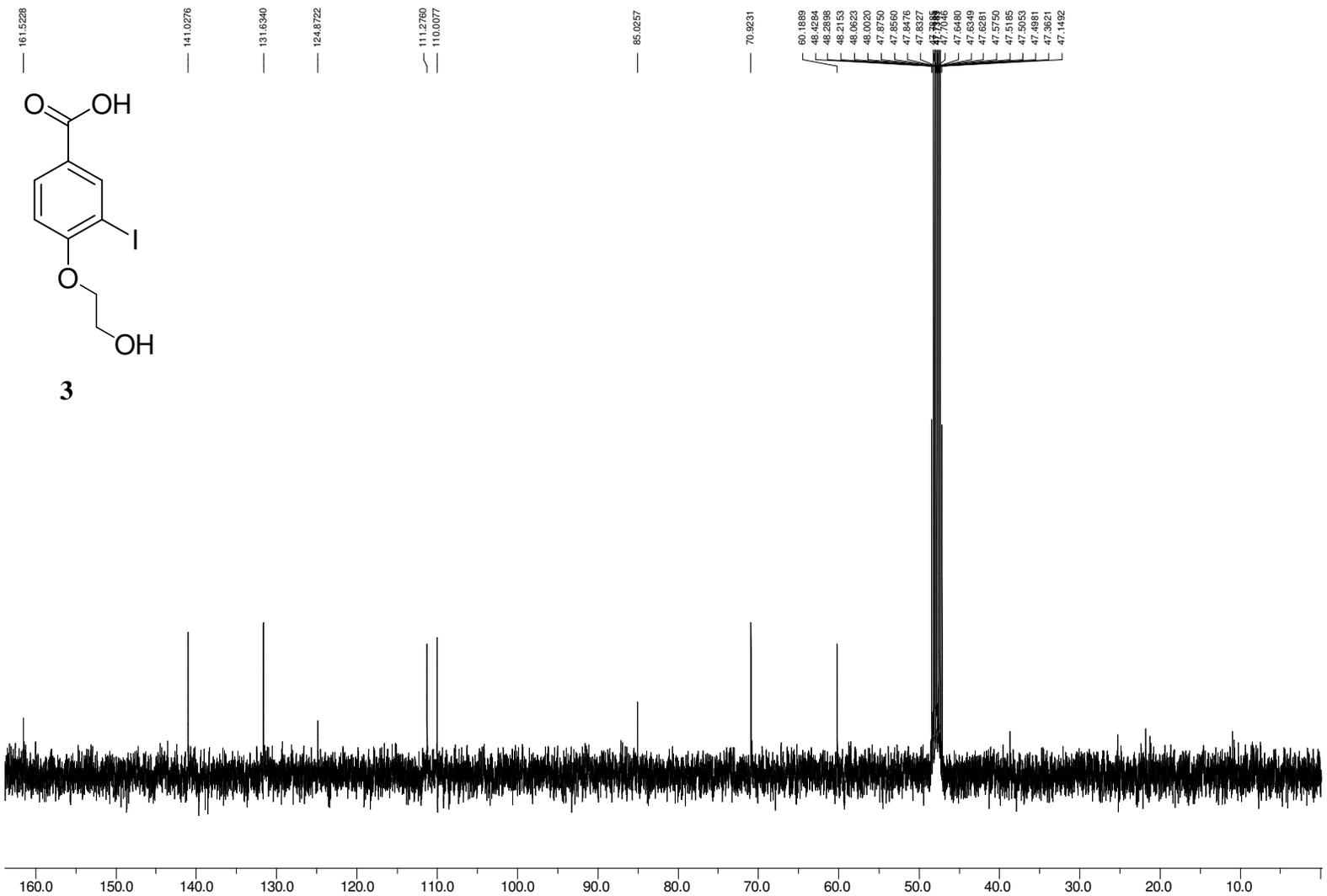


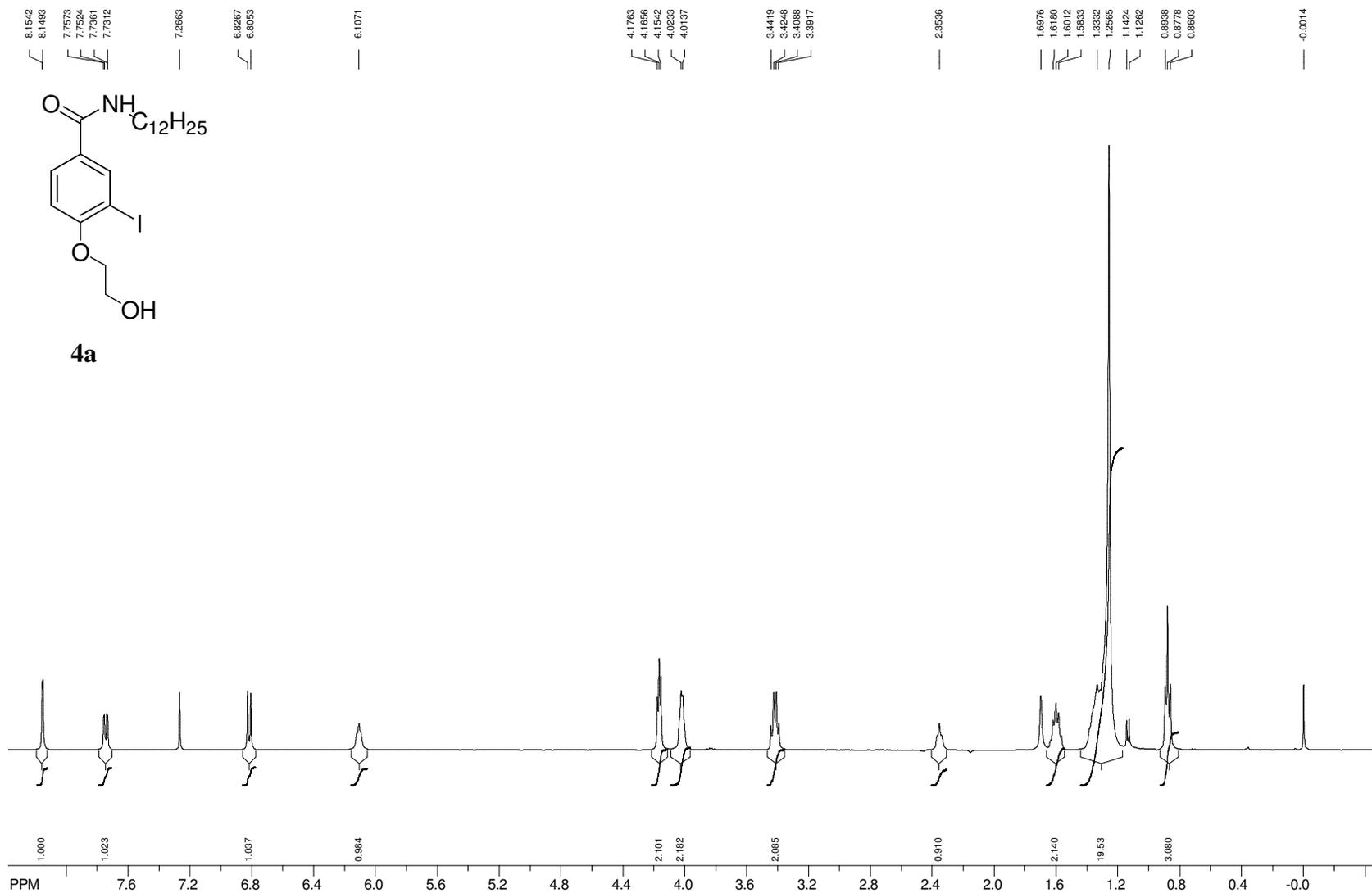
**Compound 2.** In a 50 mL round-bottom flask equipped with magnetic stir bar,  $CuCl$  (2.52 mg, 0.025 mmol) and TMEDA (20  $\mu L$ , 0.089 mmol) were dissolved in *o*-dichlorobenzene (13 mL). The mixture was heated at 50 °C with a continuous stream of air bubbling through the solution for 30 min. Then, compound **6b** (400 mg, 1.27

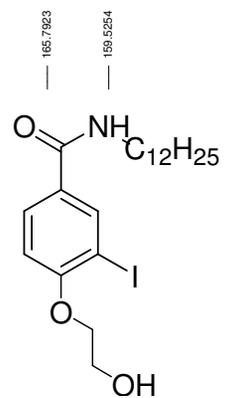
mmol) was added in portions and the mixture was stirred overnight in air. The mixture was poured in a mixture of methanol and water (8:2) allowing a white solid to precipitate. The precipitate was filtered under vacuum, washed with distilled water and dried under vacuum to provide 370 mg (93%) of white solid. This compound was not soluble in all the solvents tested. Consequently, the NMR and mass spectrometry data are not available. (Diamond ATR):  $\nu$  3315, 2921, 2848, 1628  $\text{cm}^{-1}$  HRMS: Calculated for  $\text{C}_{42}\text{H}_{60}\text{N}_2\text{O}_2$ : 625.4728  $[\text{M}+\text{H}]^+$ ; Found: 625.4774.

### 3- NMR spectra ( $^1\text{H}$ and $^{13}\text{C}$ )

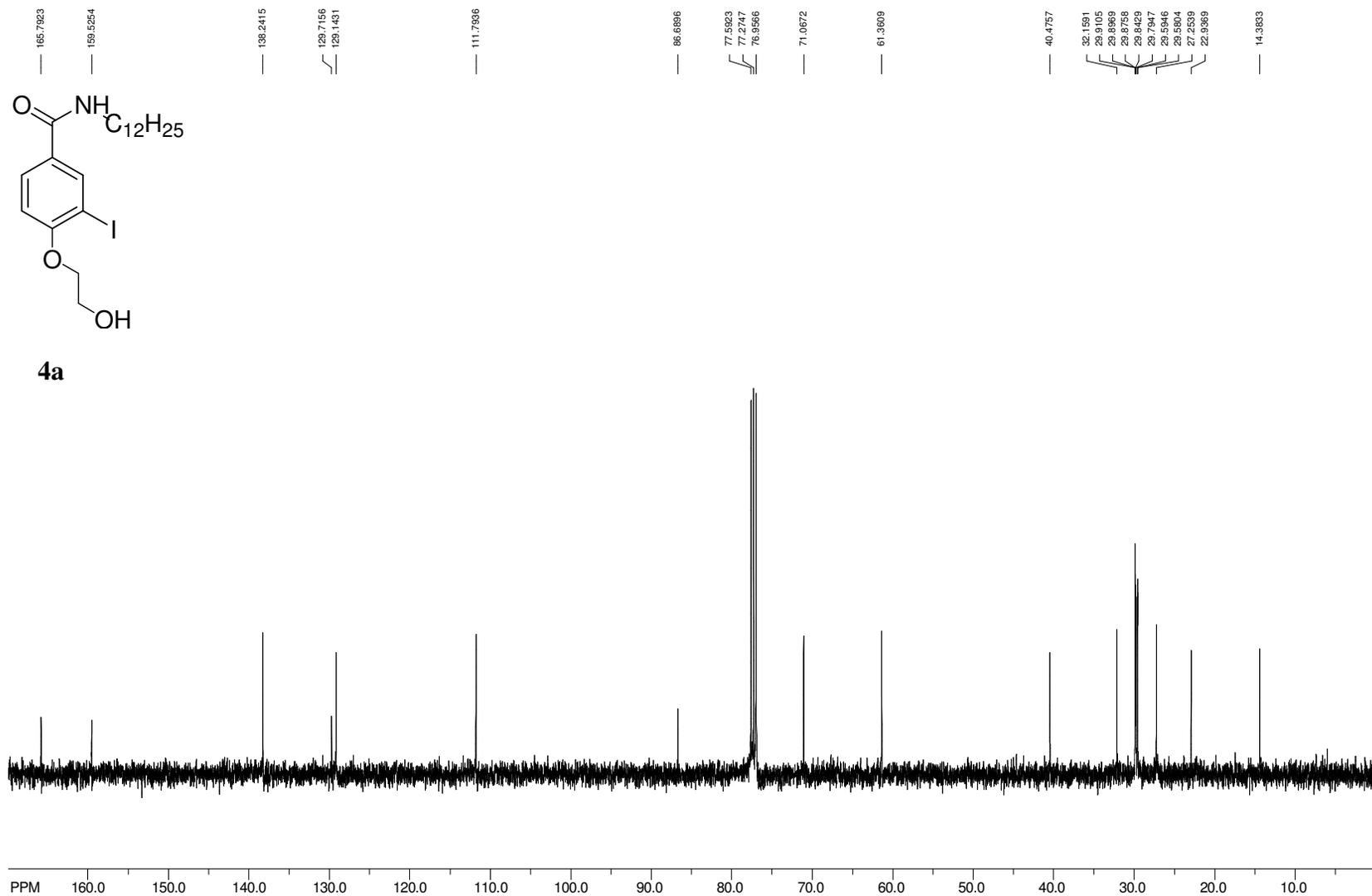


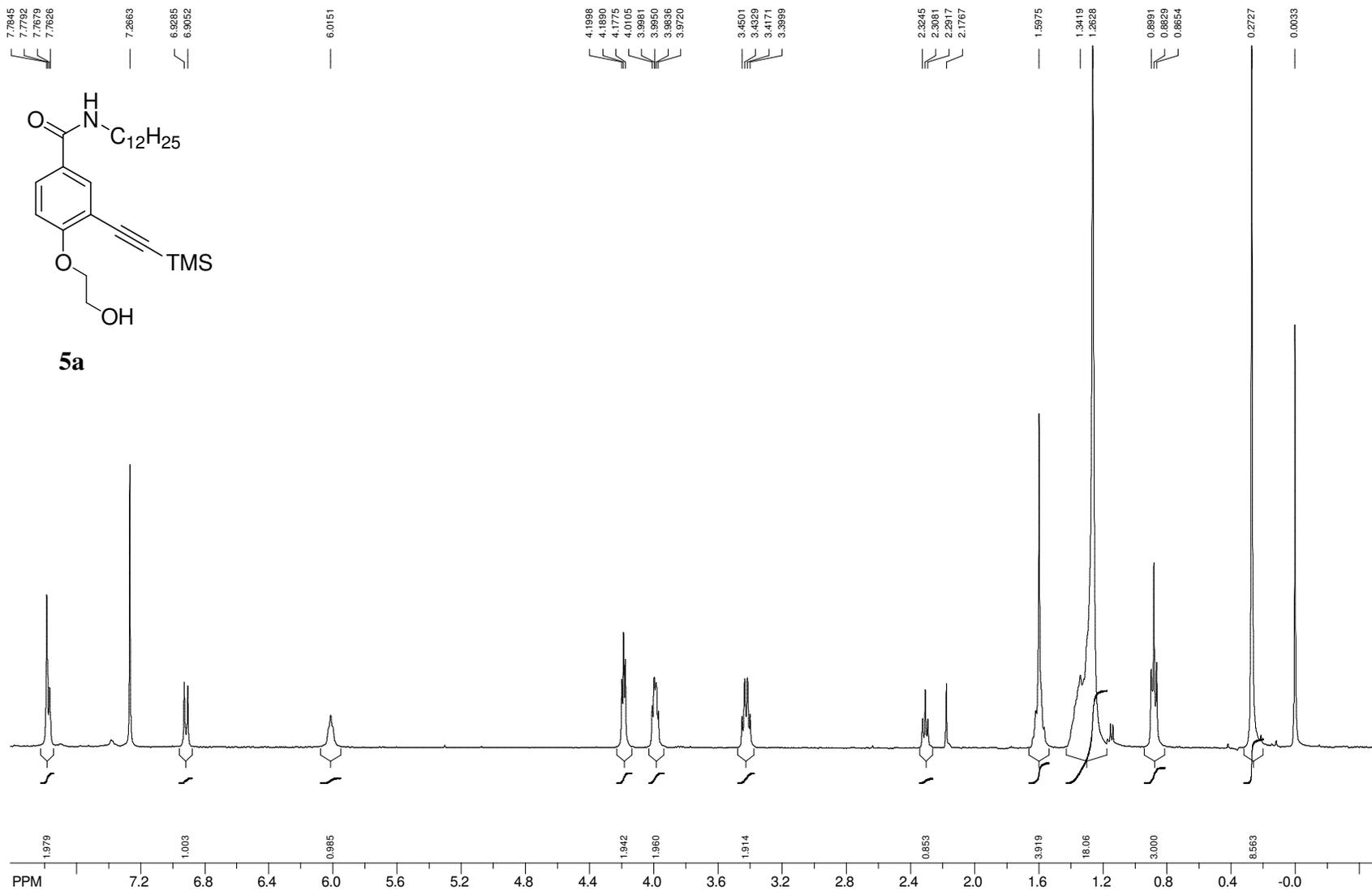


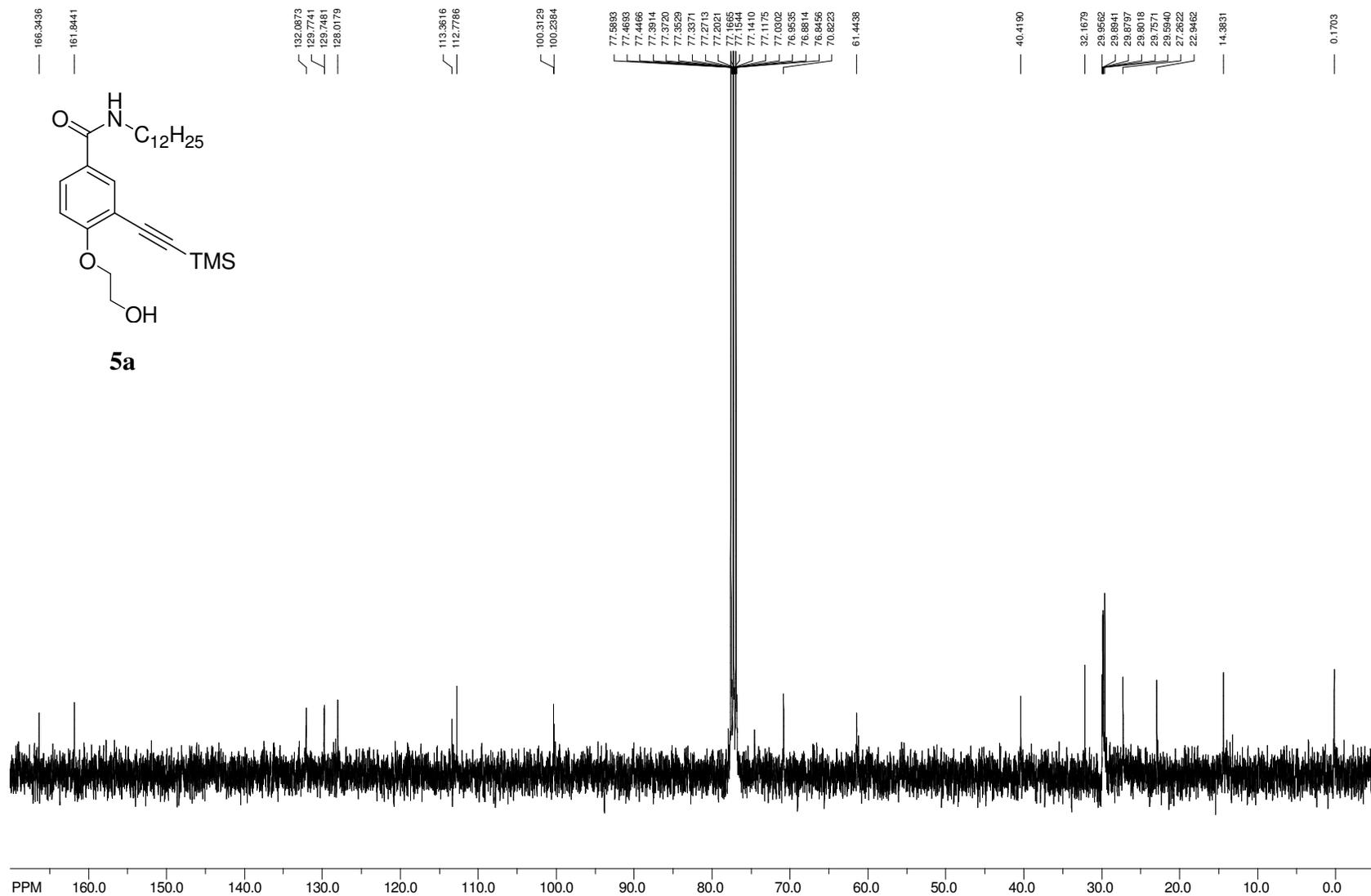


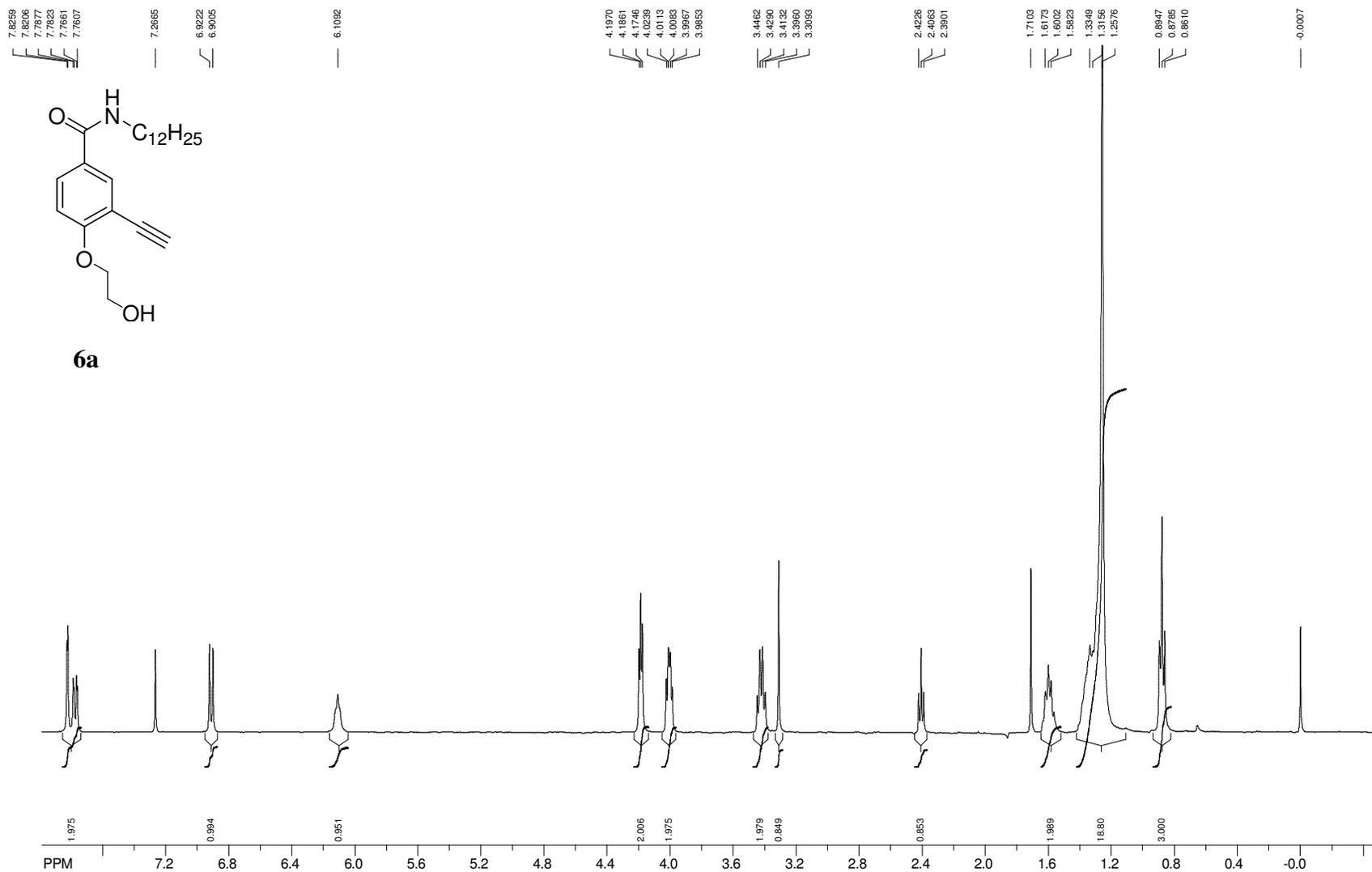


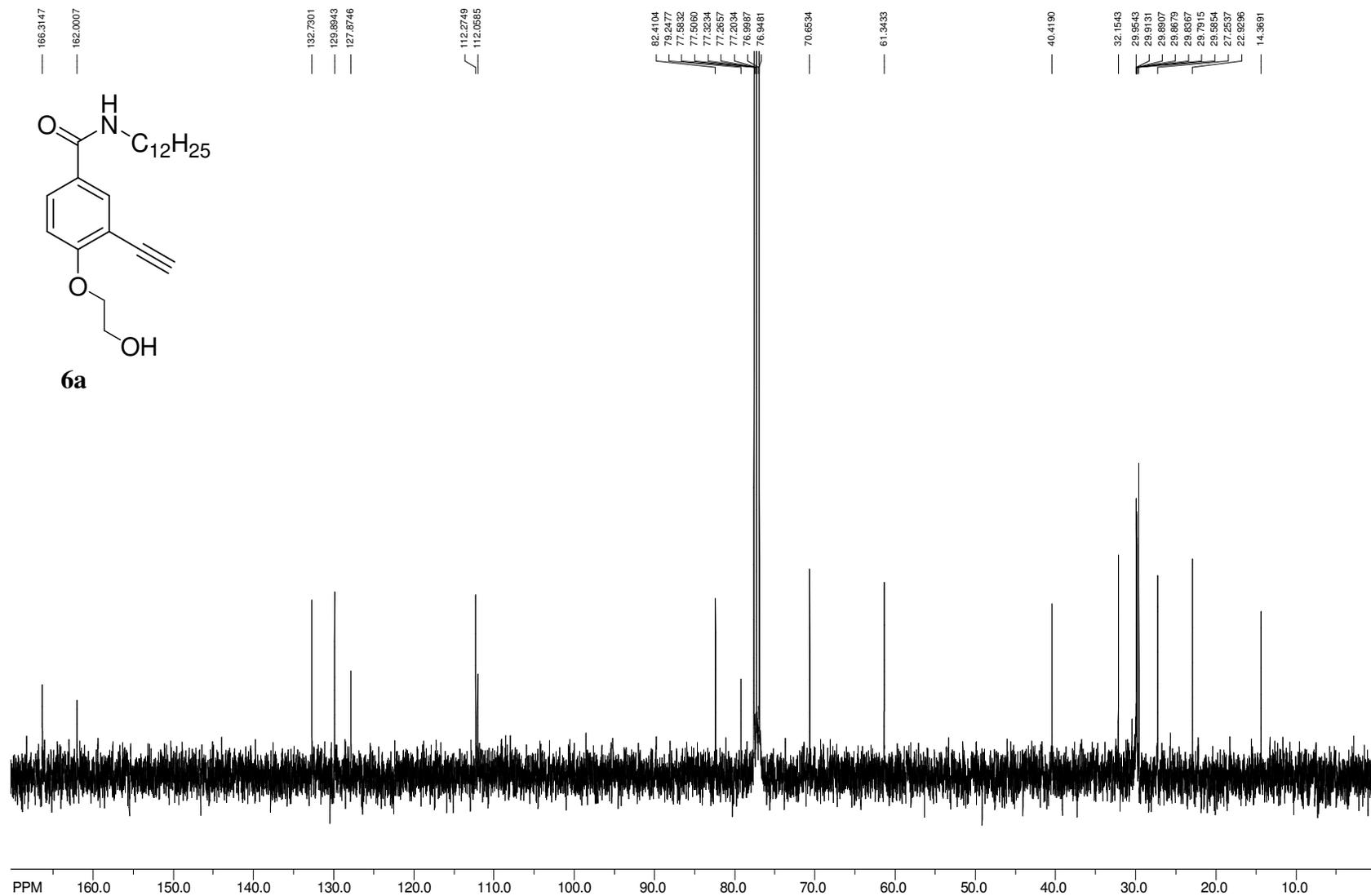
4a

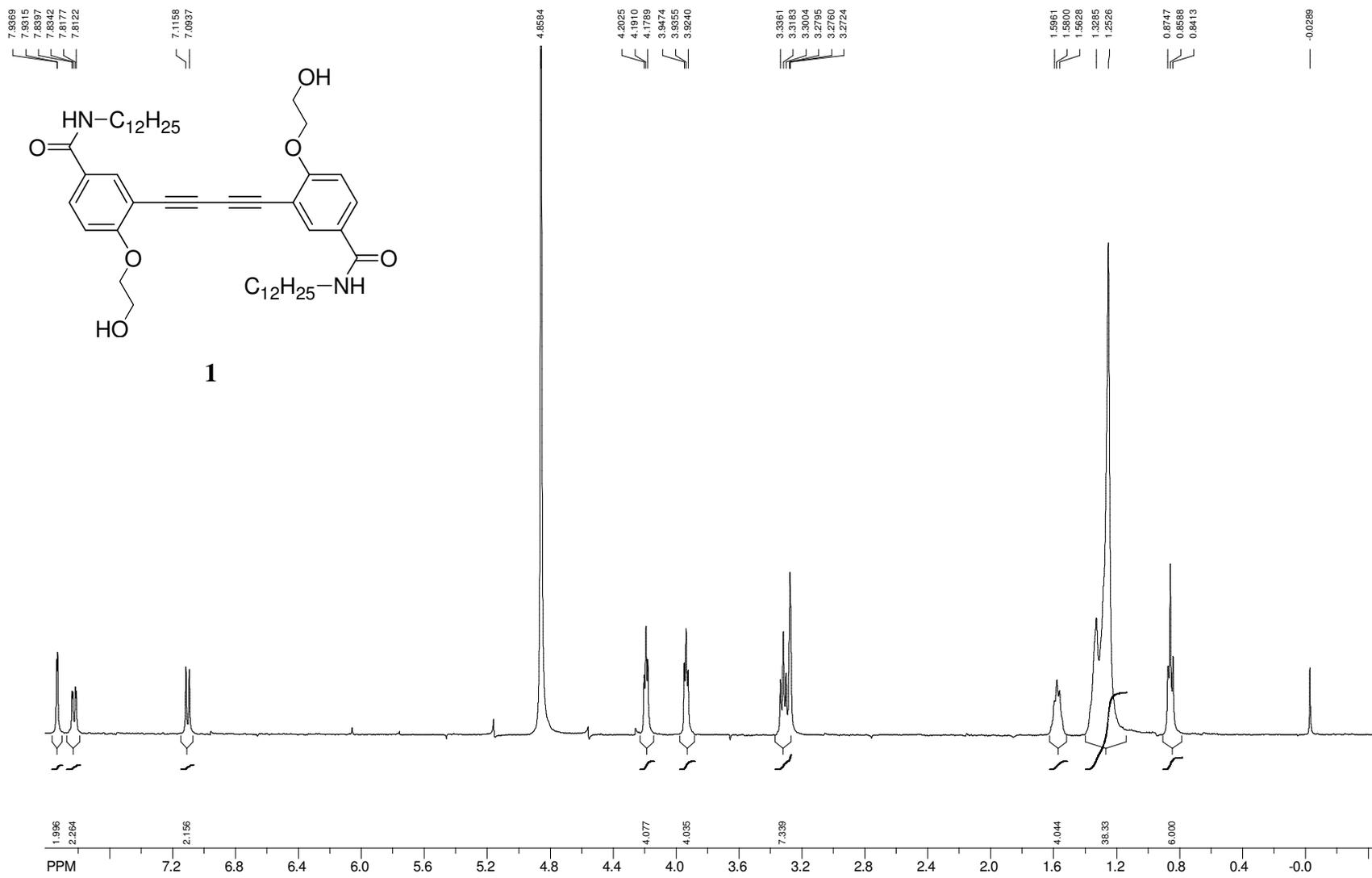


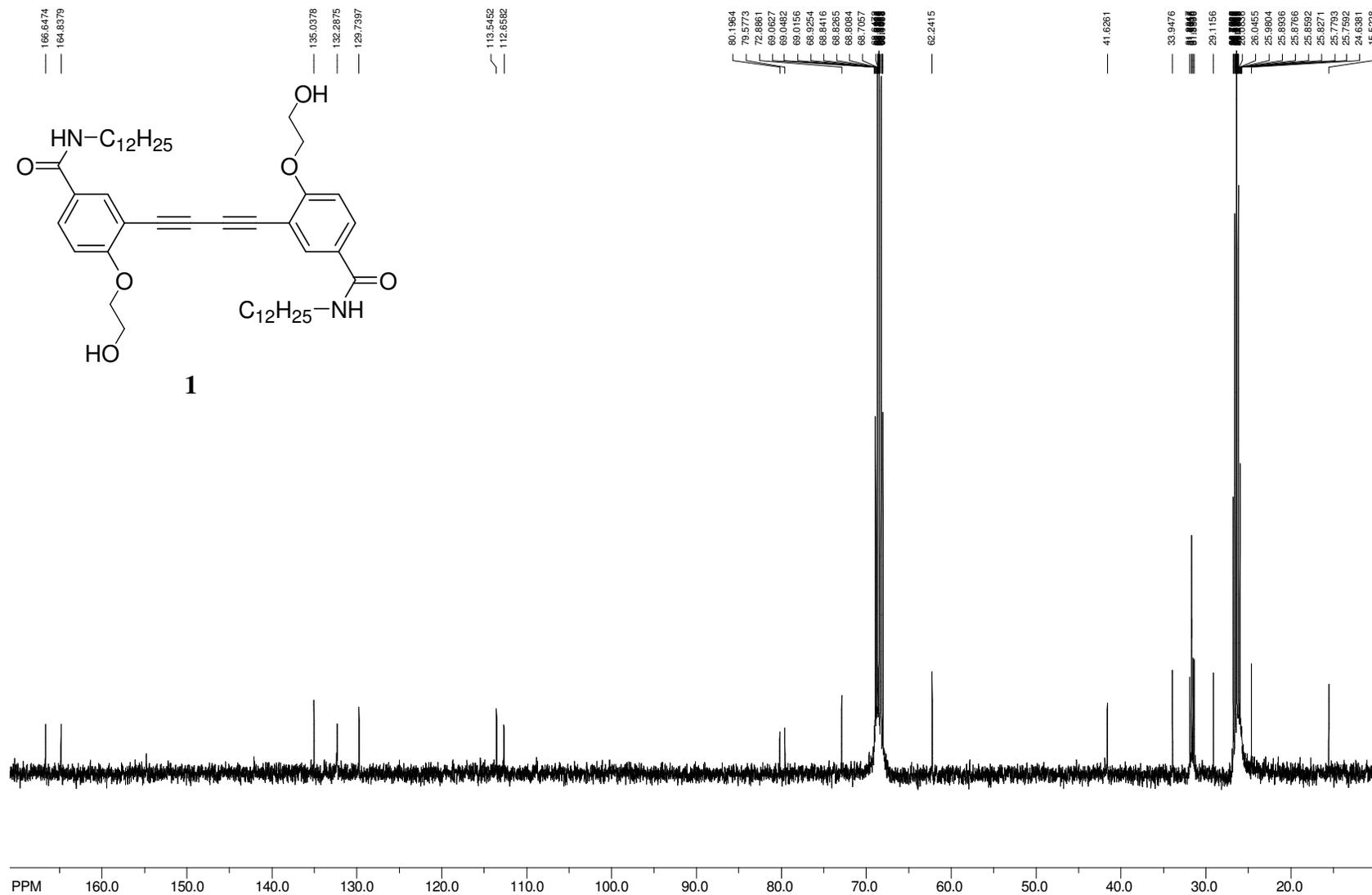


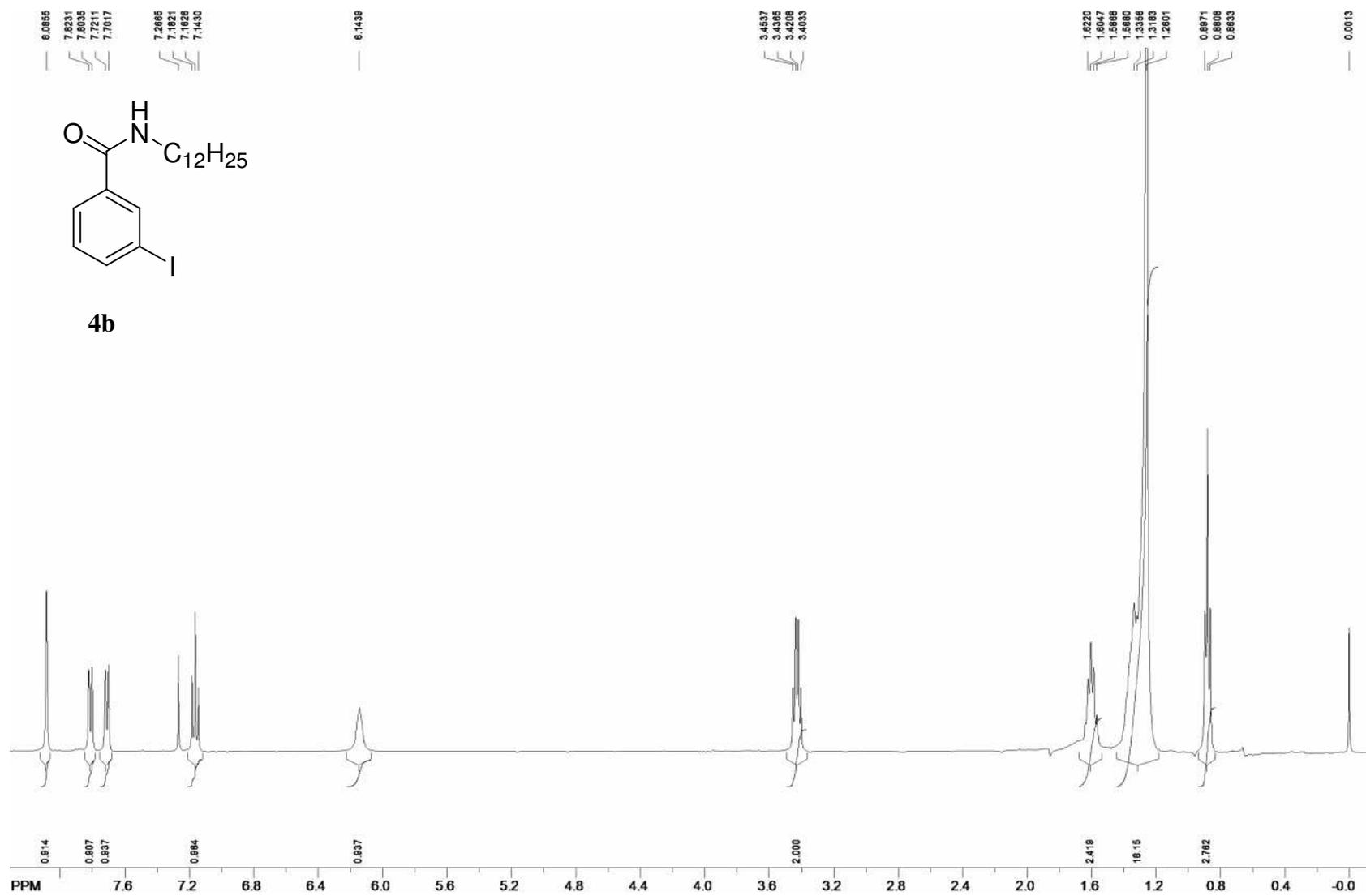


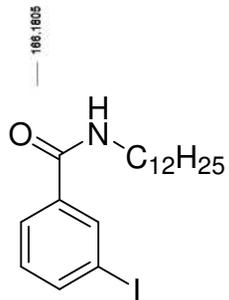




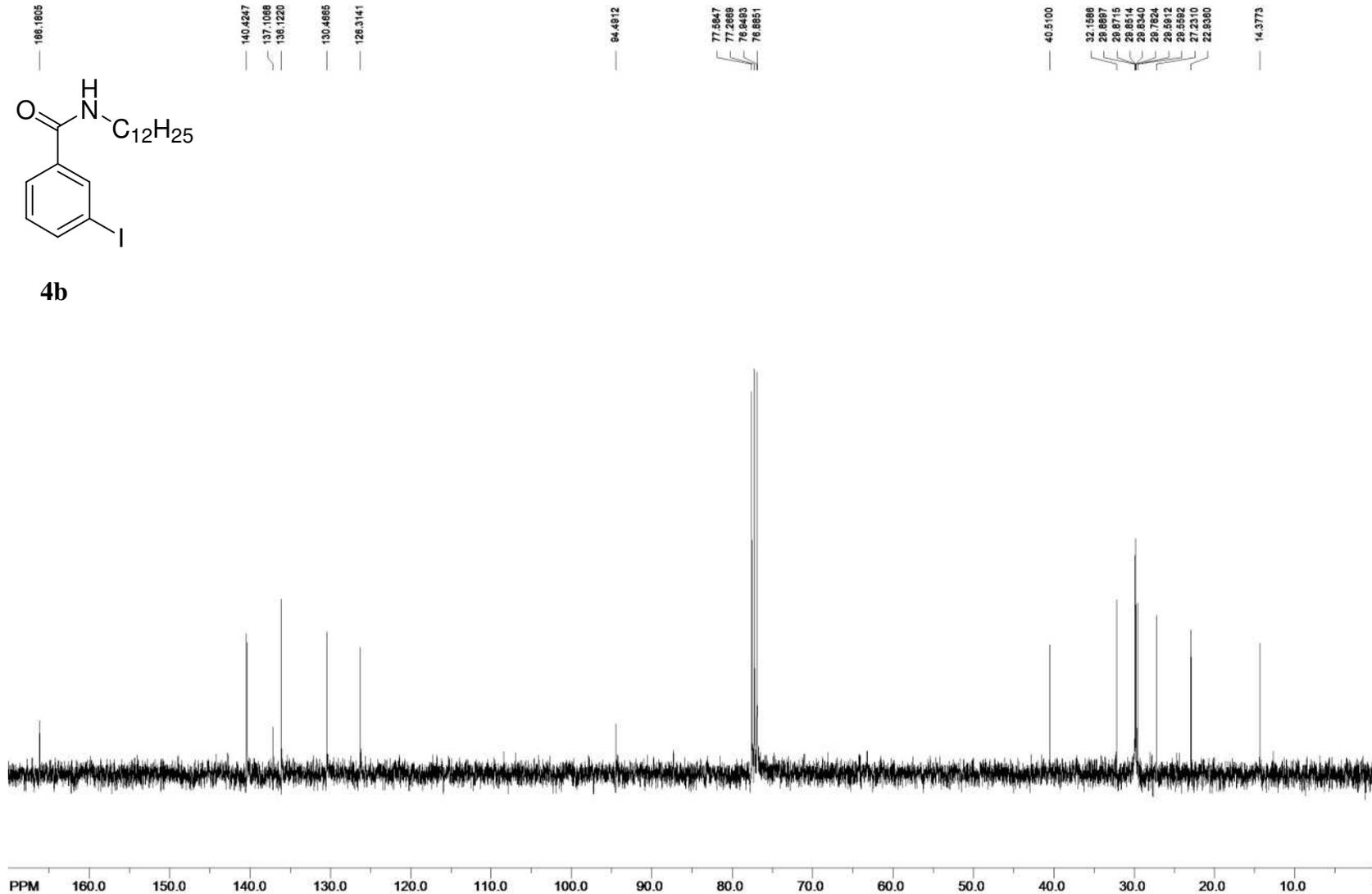


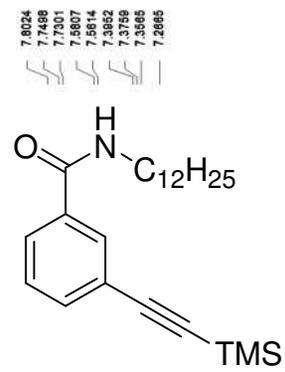




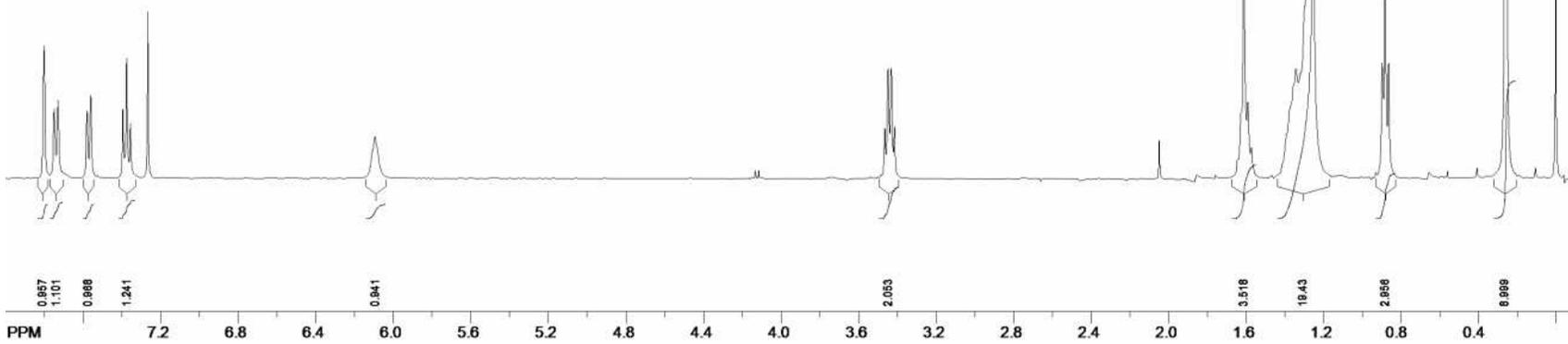


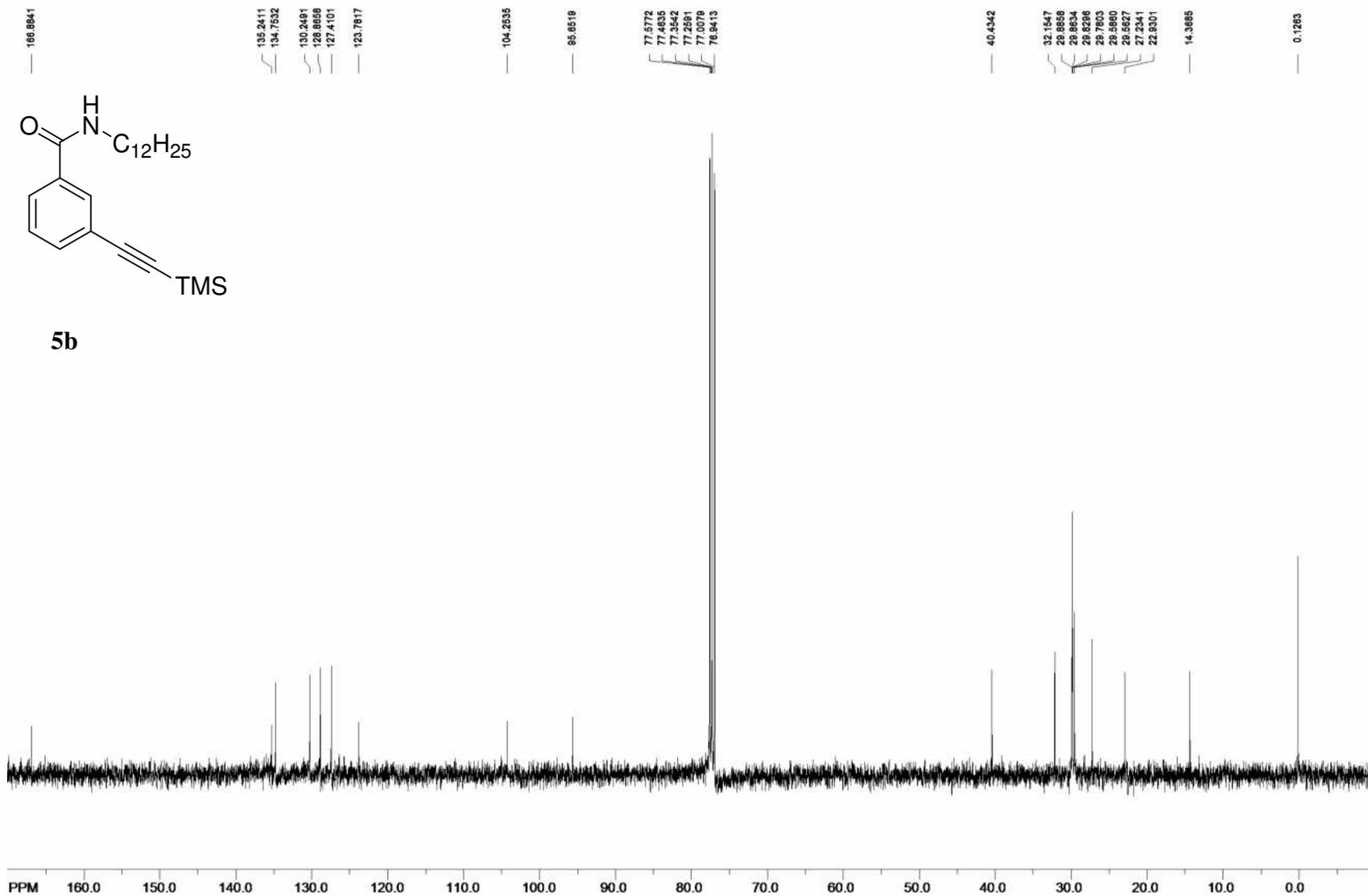
**4b**

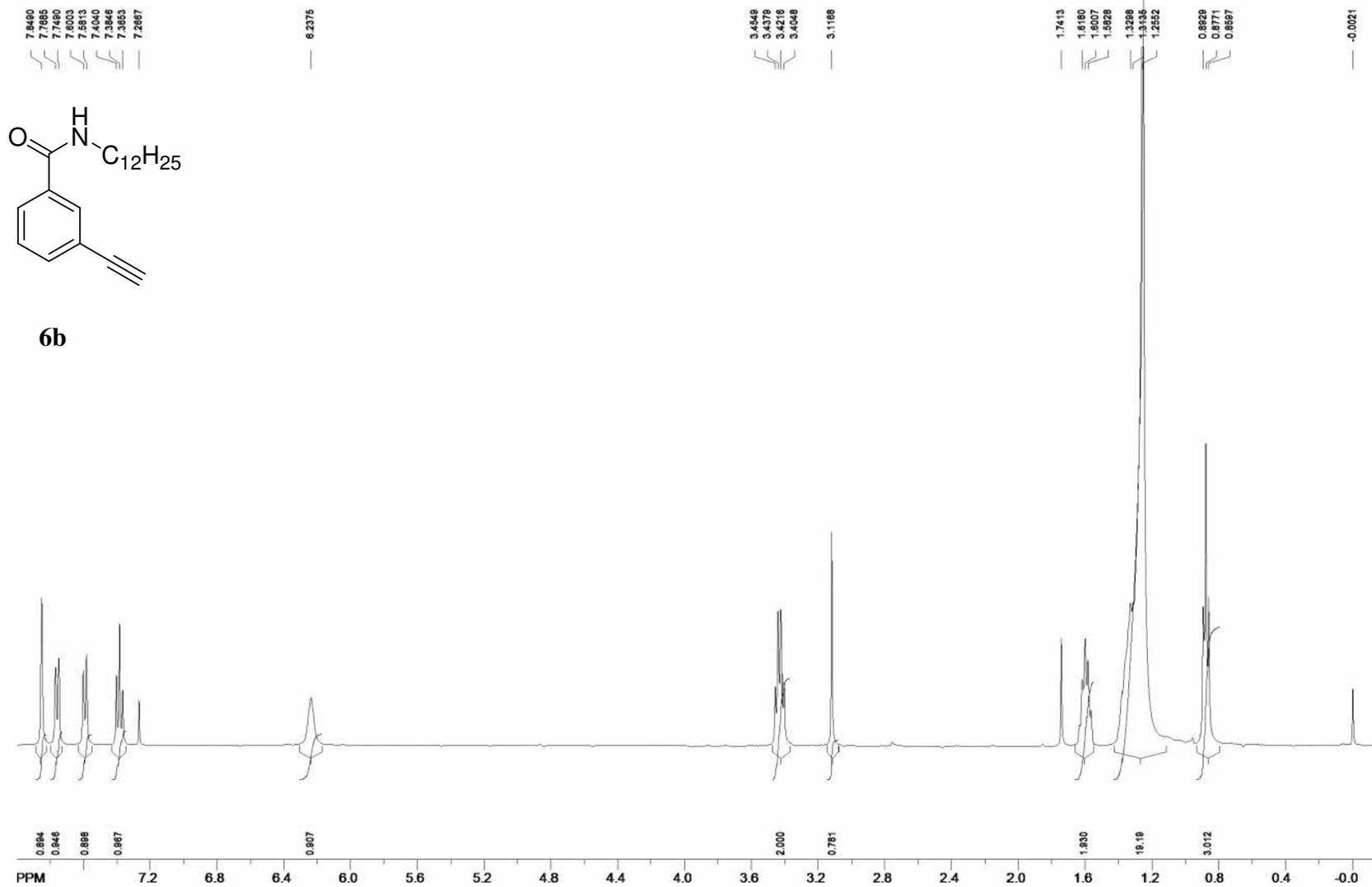


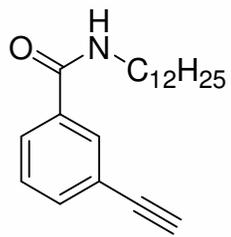


**5b**

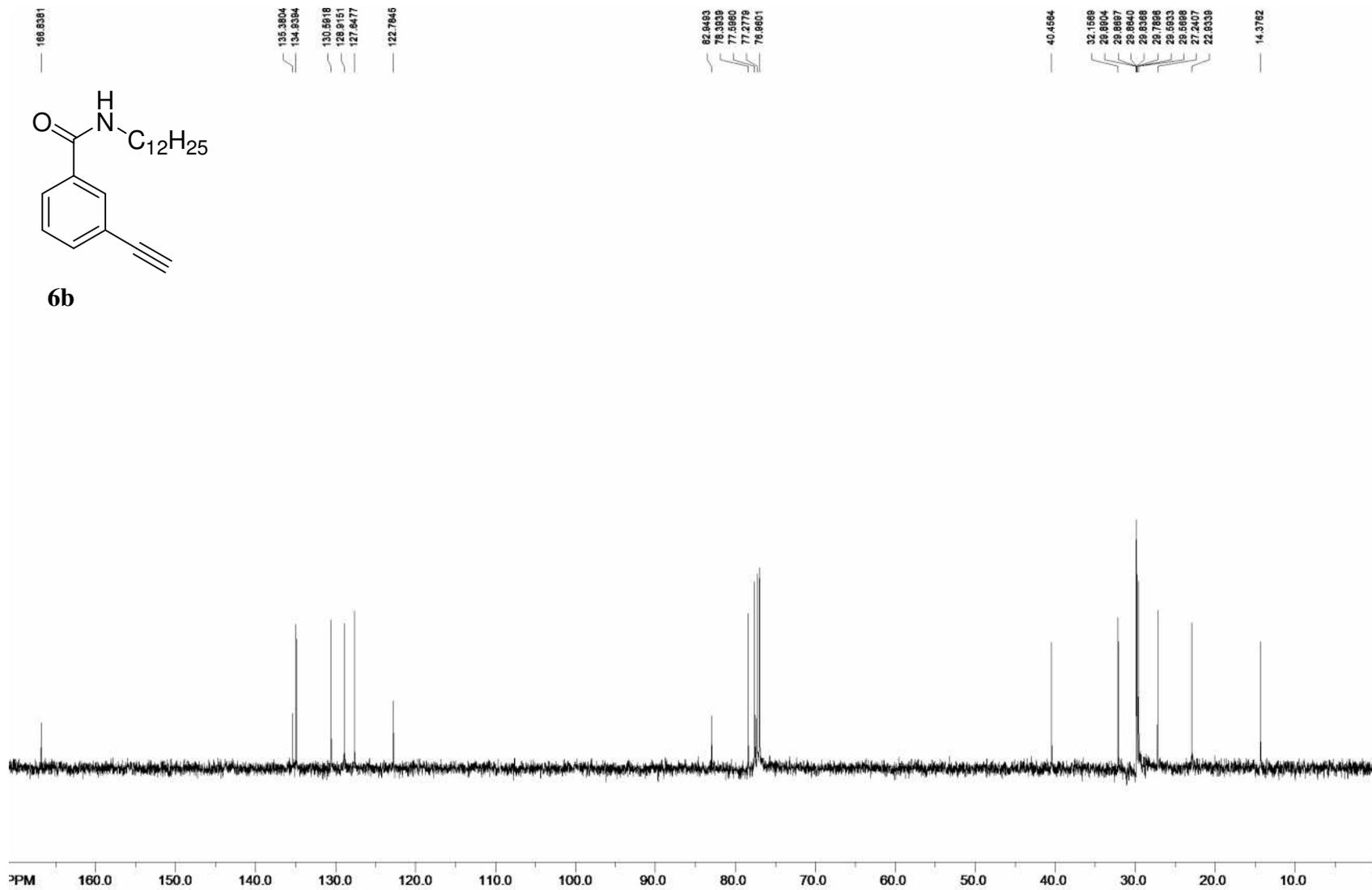








6b



4- **Table S1:** Gelation properties of compound **1**

<b>Solvent</b>	<b>Observations</b>	<b>Concentration</b>
<b>Toluene</b>	G	3 mg/mL
<b><i>o</i>-DCB</b>	G	5 mg/mL
<b>THF</b>	S	5 mg/mL
<b>MeOH</b>	S	5 mg/mL
<b>Acetone</b>	P	5 mg/mL
<b>DMSO</b>	S	5 mg/mL
<b>DMF</b>	V	5 mg/mL
<b>ACN</b>	P	5 mg/mL
<b>Cyclohexane</b>	I	5 mg/mL
<b>Benzene</b>	G	5 mg/mL
<b>1,4-Dioxane</b>	P	5 mg/mL

**G** = Gelification; **S** = Solution; **V** = Viscous; **I** = Insoluble; **P** = Precipitation

5- **Figure S1:** Toluene and *o*-DCB based gels

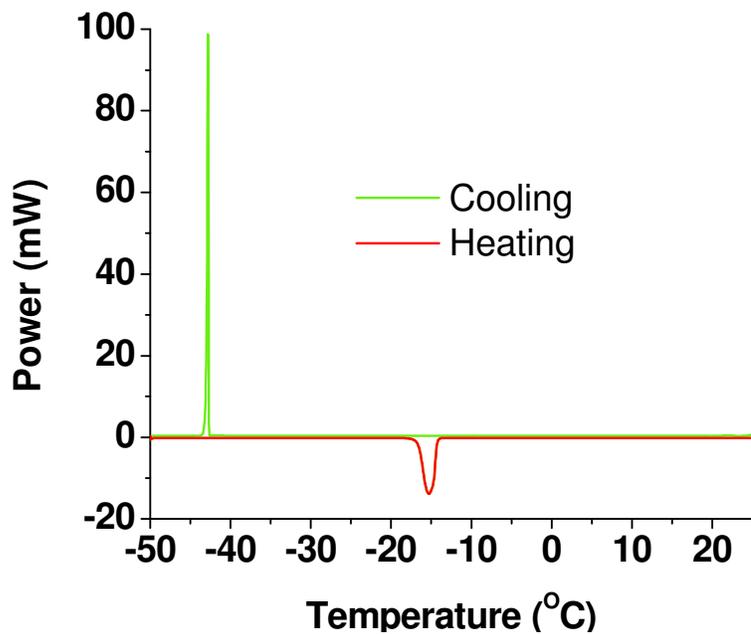


Toluene-based gel



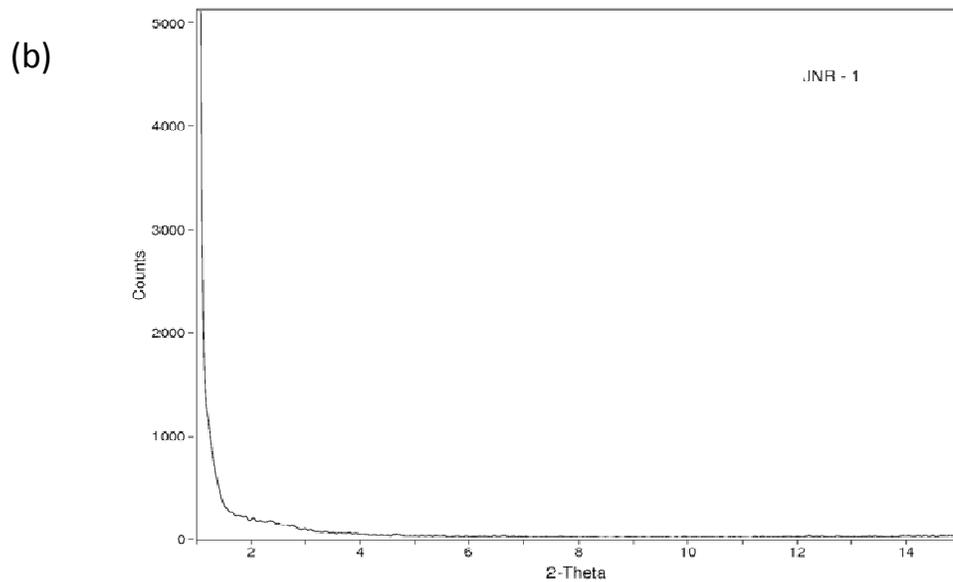
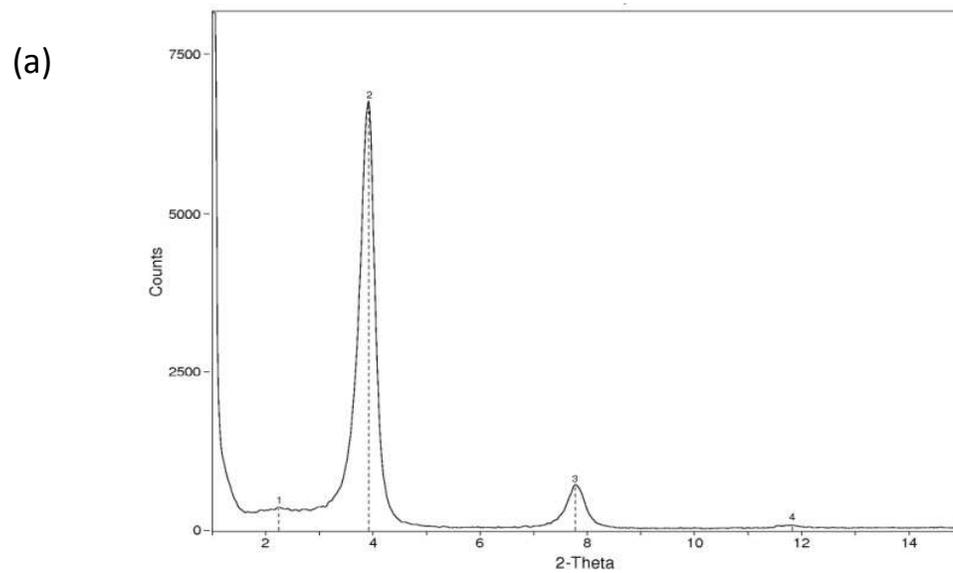
*o*-DCB-based gel

6- **Figure S2: DSC of 10 mg/mL of *o*-DCB-based gel**

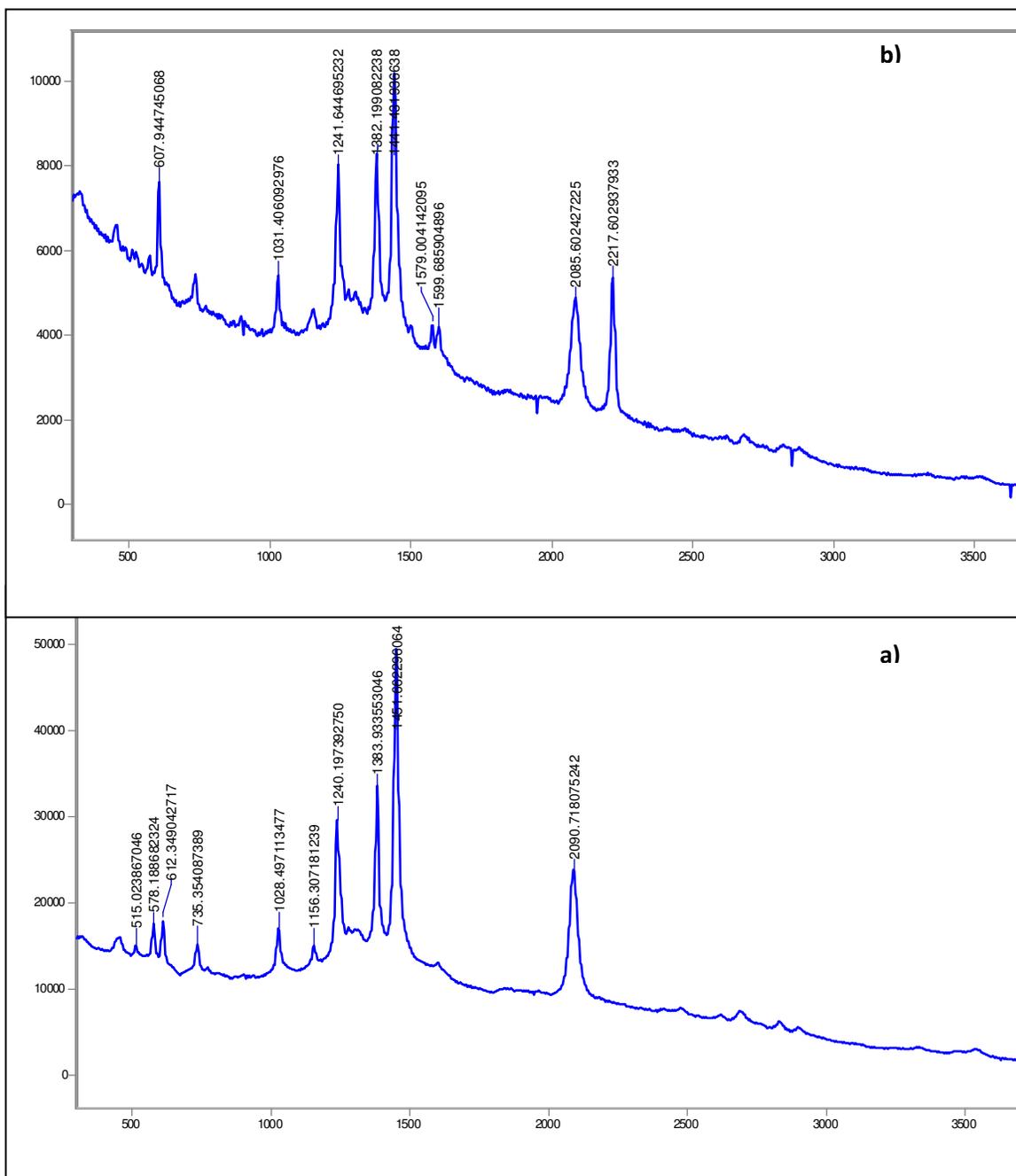


7- **Figure S3: XRD spectra of (a) dried toluene-based gel of**

compound **1** and (b) drop-cast film of compound **1** from MeOH solution



8- Figure S4: FT-Raman of (a) compounds **1** and (b) **P1**



- 9- **Figure S5:** Thermochromism behavior of **P1**: drop-cast film at (a) 20 °C and (b) > 100 °C.

