

*Supporting Information*

# **H-Bonding-Driven Gel Formation of a Phenylacetylene Macrocycle**

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## 1. General procedure for new compounds

Solvents used for organic synthesis (tetrahydrofuran, methylene chloride, dimethylformamide) were dried and purified with a Solvent Purifier System (Vacuum Atmosphere Co., Hawthorne, USA). Other solvents were used as received. Tetrahydrofuran (THF) and triethylamine (TEA) used for Sonogashira reactions were degassed for 30 minutes prior to use. Pyridine used for Eglinton reactions was degassed for 30 minutes prior to use. All anhydrous and air sensitive reactions were performed in oven-dried glassware under positive argon pressure. Analytical thin-layer chromatography was performed with silica gel 60 F<sub>254</sub>, 0.25 mm pre-coated TLC plates. Preparative thin-layer chromatography was performed with 60 F<sub>254</sub>, 2000 µm pre-coated TLC plates. Compounds were visualized using 254 nm and/or 365 nm UV wavelength and/or aqueous sulphuric acid solution of ammonium heptamolybdate tetrahydrate (10 g/100 mL H<sub>2</sub>SO<sub>4</sub> + 900 mL H<sub>2</sub>O). Flash column chromatographies were performed on 230-400 mesh silica gel R10030B. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C). Signals are reported as m (multiplet), s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quadruplet) and br s (broad singlet) and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak. 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). IR spectra were recorded using a Nicolet Magna 850 Fourier transform infrared spectrometer (Thermo Scientific, Madison, WI) with a liquid nitrogen cooled narrow-band mercury cadmium telluride (MCT) detector and a Golden Gate ATR accessory (Spacac Ltd., London, UK). Each spectrum was obtained from 64 scans data resolution of 4 cm<sup>-1</sup>. Wavelengths are reported in cm<sup>-1</sup> and as s (strong), m (medium) and w (weak).

## 2. General procedure for gelation and gel characterization

### Apparatus

FT-IR spectra were recorded with a Nicolet Fourier transform spectrometer (Thermo-Nicolet, Madison, WI) equipped with a narrow-band mercury-cadmium-telluride detector and a germanium-coated KBr beamsplitter. X-rays diffraction spectra were recorded on Siemens X-ray diffractometer (Model D5000). DSC measurements were done on Mettler Toledo (DSC 823<sup>°</sup>) calibrated with ultrapure indium. SEM images were taken using JEOL JSM-6360 LV Scanning Electron Microscopy.

**SEM imaging:** Gel of **1** obtained in toluene (10 mg/mL) 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.

**FTIR:** Each spectrum is the result of an average of 128 interferograms at 2 cm<sup>-1</sup> resolution apodized with a Happ-Genzel function in the spectral range of 4000–650 cm<sup>-1</sup>. A 30 μL amount of the sample (gel **1** in decalin (10 mg/mL) was placed between CaF<sub>2</sub> windows Biocell<sup>TM</sup> (Biotools Inc., Jupiter, FL) manufactured with a calibrated path length of 5 μm. To prevent solvent evaporation during the course of long-term heating measurements, the sealing surface of the cell was lubricated with mineral oil. The spectra were corrected for the water vapor. The spectral region between 1700 and 1515 cm<sup>-1</sup> corresponding to the amide region was baseline-corrected using a quartic function. All data treatments were performed with GRAMS/AI 8.0 (ThermoGalactic, Salem, NH).

**XRD:** X-ray diffraction spectra were performed in a scan range of 1 to 40 θ for gel of **1** and for compound **1**. The sample of **1** was prepared as follow: compound **1** was dissolved in a minimum of freshly distilled THF and put on glass support. The solvent was let evaporated overnight and the X-ray diffractogram was taken on it. The sample of gel of **1**

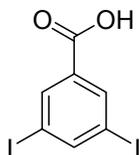
in cyclohexane (10 mg/mL) was prepared as follow: the gel of **1** was deposit on a glass substrate and let evaporated overnight and the X-ray diffractogram was taken on it.

**DSC:** DSC curves were registered at a scanning rate of 1 °C/min between -70 °C and -140 °C, followed by a scan between -140 °C and -70 °C under a nitrogen flow. The sample used was a gel of **1** in toluene (10 mg/mL).

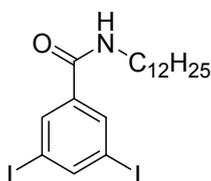
**Gelation test:** The gelation properties of compound **1** in a given solvent were achieved as followed: in a vial tube, compound **1** was mixed with a solvent. The vial sealed was heated until a clear solution was obtained. The clear solution was allowed to slowly cool down at room temperature and gelification appears after few minutes of cooling. The stability of the gel was confirmed by tube inversion. All tests were done for a concentration of 10 mg/mL.



#### 4. Experimental data for new compounds

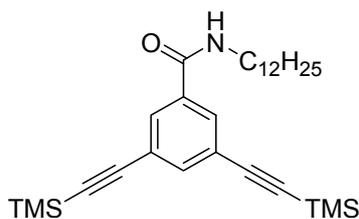


**Compound 5.** A 2 L erlenmeyer equipped with a mechanic stir was charged with 3,5-diaminobenzoic acid (6.00 g, 39.4 mmol) and H<sub>2</sub>SO<sub>4</sub> (60 mL). The reaction mixture was cooled to -5°C with an ethyleneglycol and CO<sub>2</sub> bath and NaNO<sub>2</sub> (6.53 g, 94.6 mmol) was slowly added. The mixture was stirred for an hour at -5°C before urea (497 mg, 8.28 mmol) and potassium iodide (65.5 g, 394 mmol) were added in small portions. The reaction mixture was stirred for an additional 2.5 hours at -5°C and then heated at 60°C for 30 minutes. After cooling to room temperature, the crude product was filtered under *vacuo* and the precipitate was dissolved in diethyl ether. The organic layer was then washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (3x), the aqueous phase is extracted with diethyl ether (3x), the organic phase is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure to afford The crude product is purified by flash chromatography on silica gel using EtOAc/Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> (0.2:5:95) as the eluent to afford compound **5** (6.85 g, 43% yield) as a light yellow amorphous powder. MP: >200 °C. <sup>1</sup>H NMR (ac-d<sub>6</sub>): 8.36 (t, *J* = 1.4 Hz, 1H), 8.33 (d, *J* = 1.4 Hz, 2H). <sup>13</sup>C NMR (ac-d<sub>6</sub>): 164.8, 149.9, 138.7, 135.0, 95.3. HRMS (ESI-TOF) *m/z* calcd for C<sub>7</sub>H<sub>4</sub>I<sub>2</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 373.8228, found 373.8229. FTIR (ATR): 2847br m, 2120s, 1684s, 1433s, 1272s, 873s, 763s.



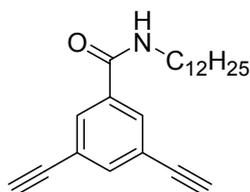
**Compound 6.** A 100 mL round bottom flask equipped with a magnetic stir bar was charged with compound **5** (2.50 g, 6.69 mmol), 1-Hydroxybenzotriazole (HOBt) (813

mg, 6.02 mmol) and THF (34 mL). The reaction mixture was heated to reflux and stirred for 30 minutes. *N,N'*-Diisopropylcarbodiimide (DIC) (1.04 mL, 6.68 mmol) and dodecylamine (1.86 g, 10.0 mmol) were then added and the reaction mixture was stirred overnight. After cooling to room temperature, the mixture was diluted with ethyl acetate. The organic layer was washed with water (3x), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using EtOAc/hexanes (12:88) as the eluent to afford compound **6** (2.98 g, 82% yield) as a white amorphous powder. MP: 92 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.14 (br s, 1H), 8.01 (d, *J* = 1.2 Hz, 2H), 6.24 (br s, 1H), 3.41 (q, *J* = 6.6 Hz, 2H), 1.59 (m, 2H), 1.29 (m, 18 H), 0.88 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 164.8, 147.9, 138.4, 135.5, 95.1, 40.7, 32.2, 30.2, 29.9 (2C), 29.8, 29.7, 29.6 (2C), 27.2, 22.9, 14.4. HRMS (ESI-TOF) *m/z* calcd for C<sub>19</sub>H<sub>29</sub>I<sub>2</sub>NO [M+H]<sup>+</sup>: 542.0411, found 542.0406; FTIR (ATR): 3283m, 2917m, 2851m, 2093m, 1628s, 1520s, 1295m, 856m.

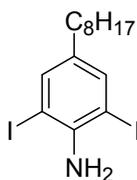


**Compound 7.** A 100 mL round bottom flask equipped with a magnetic stir bar was charged with compound **6** (2.50 g, 3.02 mmol), degassed THF (23 mL), degassed TEA (2.54 mL, 18.4 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (130 mg, 0.18 mmol), CuI (35 mg, 0.18 mmol) and trimethylsilylacetylene (1.92 mL, 13.8 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with NH<sub>4</sub>Cl (3x) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using EtOAc/hexanes (1:9) as the eluent to afford compound **7** (2.19 g, 98% yield) as dark orange oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.78 (d, *J* = 1.0 Hz, 2H), 7.64 (s, 1H), 6.56 (t, *J* = 5.4 Hz, 1H), 3.39 (q, *J* = 6.4 Hz, 2H), 1.57 (m, 2H), 1.25 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.24 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 166.4, 137.9, 135.7, 130.6, 124.3, 103.6, 96.5, 40.7, 32.4, 30.1 (3C), 30.0 (2C), 29.8 (2C), 27.4, 23.2, 14.6, 0.3. HRMS: (APPI-TOF) *m/z* calcd for

$C_{29}H_{47}NOSi_2$   $[M+H]^+$ : 482.3269, found 482.3268; FTIR (ATR): 3302w, 2923w, 2158w, 1637m, 1543m, 1248m, 981m, 839s.

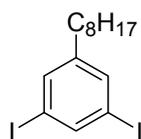


**Compound 8.** A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **7** (1.50 g, 3.11 mmol), KOH (700 mg, 12.4 mmol), THF (4.0 mL), MeOH (4.0 mL) and water (1.0 mL). The reaction mixture was stirred for 15 minutes, diluted with  $CH_2Cl_2$ , washed with 10% HCl (3x) and dried over  $Na_2SO_4$ . The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using EtOAc/hexanes (15:85) as the eluent to afford compound **8** (1.02 g, 97% yield) as a white amorphous powder. MP: 108 °C.  $^1H$  NMR ( $CDCl_3$ ): 7.83 (s, 2H), 7.69 (s, 1H), 6.17 (s, 1H), 3.43 (q,  $J = 6.5$  Hz, 2H), 3.14 (s, 2H), 1.60 (m, 2H), 1.26 (m, 18H), 0.88 (t,  $J = 7.0$  Hz, 3H).  $^{13}C$  NMR ( $CDCl_3$ ): 165.9, 138.1, 135.7, 130.9, 123.3, 81.9, 79.2, 40.5, 31.2, 29.9 (2C), 29.8 (2C), 29.7, 29.6, 29.5, 27.2, 22.9, 14.4. HRMS (APPI-TOF)  $m/z$  calcd for  $C_{23}H_{31}NO$   $[M+H]^+$ : 338.2478, found 338.2496; FTIR (ATR): 3286m, 2918s, 2850s, 1632s, 1537m, 890m.

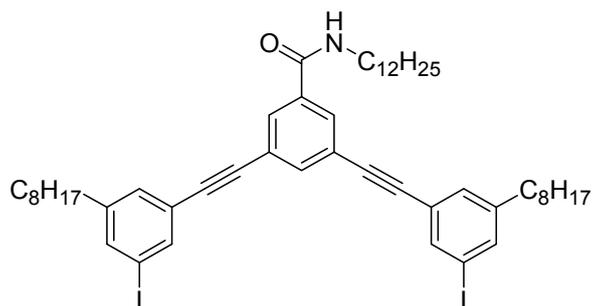


**Compound 3.** A 250 mL round bottom flask equipped with a magnetic stir bar was charged with 4-octylaniline (4.00 g, 19.5 mmol), pyridinium iodine monochloride (14.1 g, 58.4 mmol) and MeOH (78 mL). The reaction mixture was heated to reflux and stirred overnight. After cooling to room temperature, the mixture was diluted with  $CH_2Cl_2$ , washed with  $Na_2S_2O_3$  (3x), dried over  $Na_2SO_4$  and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel

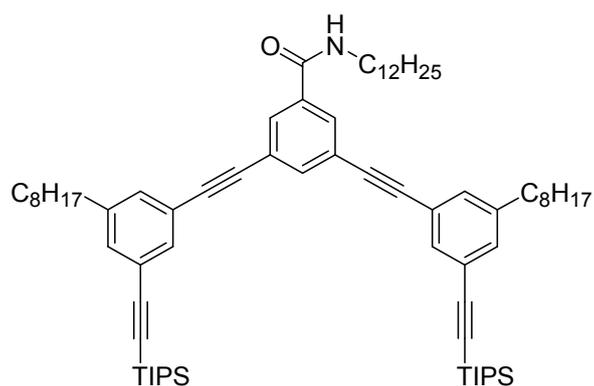
using hexanes to Et<sub>2</sub>O/hexanes (5:95) as eluents to afford compound **3** (7.76 g, 87% yield) as a white amorphous powder. MP: 79 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.45 (s, 2H), 4.45 (s, 2H), 2.40 (t, *J* = 7.6 Hz, 2H), 1.51 (m, 2H), 1.27 (br s, 10H), 0.88 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 144.1, 139.4, 136.5, 81.8, 34.2, 32.1, 31.7, 29.6, 29.5, 29.4, 22.9, 14.4. HRMS (ESI-TOF) *m/z* calcd for C<sub>14</sub>H<sub>21</sub>I<sub>2</sub>N [M+H]<sup>+</sup>: 457.9836, found 457.9843; FTIR (ATR): 2915s, 2848s, 1737m, 1462m, 1237m, 1020w.



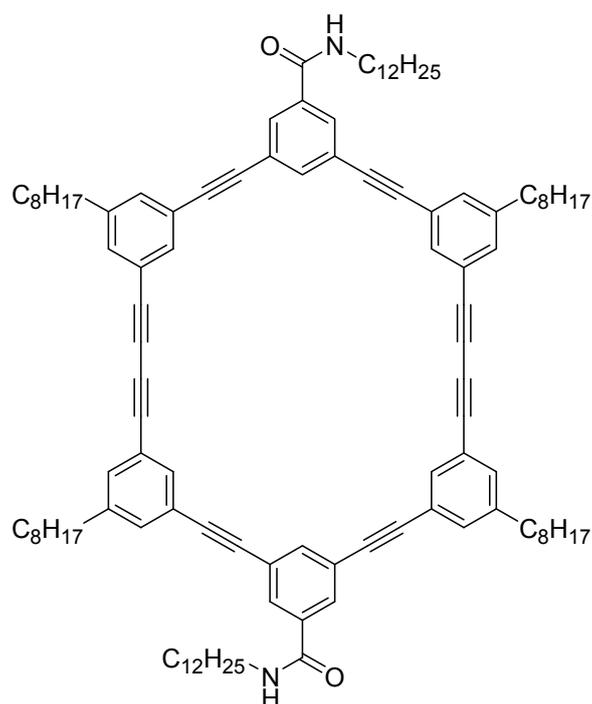
**Compound 4.** A 100 mL round bottom flask equipped with a magnetic stir bar was charged with compound **3** (5.00 g, 10.9 mmol) and H<sub>2</sub>SO<sub>4</sub> (18.0 mL). The mixture was cooled to -5 °C with an ethylene glycol/CO<sub>2</sub> bath before NaNO<sub>2</sub> (1.66 g, 24.1 mmol) was slowly added. After stirring for 2 hours, the reaction mixture was poured into cold water (75 mL) and filtered under vacuum. Another 1 L round bottom flask equipped with a magnetic stir bar and a dropping funnel was charged with copper sulfate pentahydrate (273 mg, 1.09 mmol) and EtOH (218 mL) and the resulting mixture was heated to reflux. The filtrate obtained in the first step was added to the refluxing mixture and stirred for 1 hour. After separation of an orange oil, the reaction mixture was cooled to room temperature, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to afford compound **4** (4.82 g, 98% yield) as orange oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.83 (s, 1H), 7.46 (s, 2H), 2.45 (t, *J* = 7.8 Hz, 2H), 1.53 (m, 2H), 1.26 (br s, 10H), 0.87 (t, *J* = 6.3 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 147.2, 142.3, 136.8, 94.9, 35.2, 31.9, 31.1, 29.4, 29.3, 29.2, 22.8, 14.3. GC-MS *m/z* calcd for C<sub>14</sub>H<sub>20</sub>I<sub>2</sub> [M\*]: 441.97, found 441.94; FTIR (ATR): 2928m, 2853m, 1574m, 1539m, 1263w, 1097w. *Despite several attempts, HRMS data for 4 were not obtained in both ESI and APPI mode.*



**Compound 9.** A 50 mL round bottom flask equipped with a magnetic stir bar was charged with compound **4** (2.15 g, 4.86 mmol), degassed THF (16.0 mL), degassed DIPEA (2.26 mL, 12.9 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (46 mg, 0.06 mmol) and CuI (12 mg, 0.06 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 5 minutes before compound **8** (547 mg, 1.62 mmol) was added. The mixture was stirred overnight and after the disappearance of compound **8** by TLC, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with NH<sub>4</sub>Cl (3x) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using hexanes to EtOAc/hexanes (4:96) as the eluents to afford compound **9** (503 mg, 32% yield) as a white amorphous powder. MP: 86 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.84 (s, 2H), 7.73 (s, 1H), 7.69 (s, 2H), 7.52 (s, 2H), 7.29 (s, 2H), 6.28 (t, *J* = 5.2 Hz, 1H), 3.45 (q, *J* = 6.4 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 4H), 1.60 (m, 6H), 1.27 (m, 38H), 0.87 (m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 166.1, 145.5, 138.2, 137.7, 136.9, 135.8, 131.2, 130.0, 124.5, 124.1, 94.0, 89.7, 88.7, 40.6, 35.6, 32.2, 32.1, 31.4, 29.9, 29.8 (3C), 29.7, 29.6 (2C), 29.5, 29.4, 27.3, 22.9 (2C), 14.4. *Several peaks are missing since many of them merged.* HRMS (APPI-TOF) *m/z* calcd for C<sub>51</sub>H<sub>69</sub>I<sub>2</sub>NO [M+H]<sup>+</sup> : 966.3541, found 966.3576; FTIR (ATR): 2923m, 2852m, 1637w, 1592w, 1552w, 893w.

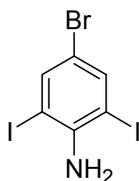


**Compound 10.** A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **9** (459 mg, 0.48 mmol), degassed THF (5.0 mL), degassed DIPEA (0.33 mL, 1.90 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (13 mg, 0.02 mmol), CuI (4.0 mg, 0.02 mmol) and triisopropylsilylacetylene (0.53 mL, 2.38 mmol). The reaction mixture was stirred overnight, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with NH<sub>4</sub>Cl and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using EtOAc/hexanes (8:92) as the eluent to afford compound **10** (447 mg, 88% yield) as slightly brownish oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.86 (s, 2H), 7.77 (s, 1H), 7.48 (s, 2H), 7.29 (s, 2H), 7.27 (s, 2H), 6.34 (t, *J* = 5.6 Hz, 1H), 3.45 (q, *J* = 6.5 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 4H), 1.61 (m, 6H), 1.28 (m, 38H), 1.14 (s, 42H), 0.88 (m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 166.2, 143.6, 137.0, 135.8, 132.9, 132.5, 131.8, 129.9, 124.3, 124.0, 122.8, 106.6, 91.2, 90.7, 88.1, 40.6, 35.8, 32.2, 32.1, 31.5, 29.9 (3C), 29.8, 29.7 (2C), 29.6, 29.5 (2C), 27.3, 22.9 (2C), 19.0, 18.9, 18.8, 14.4, 11.6. HRMS (APPI-TOF) *m/z* calcd for C<sub>73</sub>H<sub>111</sub>NOSi<sub>2</sub> [M+H]<sup>+</sup>: 1074.8277, found 1074.8248; FTIR (ATR): 3302w, 2923s, 2854m, 1638w, 1591w, 1544w, 1463w, 882w.

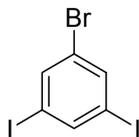


**Compound 1.** A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **10** (500 mg, 0.47 mmol), THF (9.0 mL) and TBAF (1.40 mL, 1.40 mmol). The reaction mixture was stirred for 15 minutes, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water (3x), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was then removed under reduced. A solution of the crude product (154 mg, 0.202 mmol) in degassed pyridine (4 mL) was added to a suspension of CuCl (811 mg, 8.19 mmol) and CuCl<sub>2</sub> (157 mg, 1.17 mmol) in degassed pyridine (17 mL) over 96 h at room temperature under a nitrogen atmosphere. After the completion of the addition, the mixture was allowed to stir for an additional 7 days and then poured in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and water (30 mL). The organic phase was extracted successively with water, 25% NH<sub>4</sub>OH, water, 10% acetic acid, water, 10% aqueous sodium hydroxide and brine. The organic layers were dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was first purified by flash chromatography on silica gel using CHCl<sub>3</sub>/hexanes (80:20) as the eluent followed by gel permeation chromatography on Bio-Beads<sup>®</sup> S-X3 beads using distilled THF as the eluent to afford compound **1** (40 mg, 26% yield) as a white amorphous powder. MP: 165-175 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.81 (s, 6H), 7.58 (s, 4H), 7.34 (s, 4H), 7.30 (s, 4H), 6.19 (m, 2H), 3.48 (q, *J* = 6.4 Hz, 4H), 2.59 (t, *J* = 7.2 Hz, S12

8H), 1.63 (m, 12H), 1.32 (m, 76H), 0.88 (m, 18H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 164.4, 144.2, 144.1, 136.5, 133.4, 132.4, 129.9, 123.6 (2C), 122.2, 122.1, 107.6, 89.5, 88.6, 80.7, 73.8, 39.9, 35.4, 32.1 (2C), 31.2, 29.9, 29.8, 29.6, 29.5, 29.4 (2C), 29.3, 29.1, 27.2, 24.9, 24.7, 24.5, 24.3, 24.1, 22.8, 13.7. HRMS (APPI-TOF)  $m/z$  calcd for  $\text{C}_{110}\text{H}_{138}\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$ : 1521.0865, found 1521.0871. FTIR (ATR): 3359m, 2617s, 2849s, 1631s, 1592m, 1544m, 1467m, 884m, 869m.

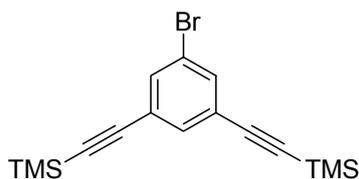


**Compound 11.** A 250 mL round bottom flask equipped with a magnetic stir bar was charged with 4-bromoaniline (6.00 g, 34.9 mmol), pyridinium iodine monochloride (25.3 g, 104.6 mmol) and MeOH (140 mL) and the resulting solution was heated to reflux. The reaction mixture was stirred overnight, cooled to room temperature and diluted with  $\text{CH}_2\text{Cl}_2$ . The mixture was washed with  $\text{Na}_2\text{S}_2\text{O}_3$ , dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using  $\text{Et}_2\text{O}$ /hexanes (5:95) as the eluent to afford compound **11** (10.9 g, 74% yield) as a white amorphous powder. MP: 132 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.73 (s, 2H), 4.63 (br s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 145.7, 141.04, 109.9, 81.1. HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_6\text{H}_4\text{BrI}_2\text{N}$   $[\text{M}+\text{H}]^+$ : 423.7689, found 423.7687. FTIR (ATR): 3392w, 3283m, 1602s, 1547m, 1435s, 860s.

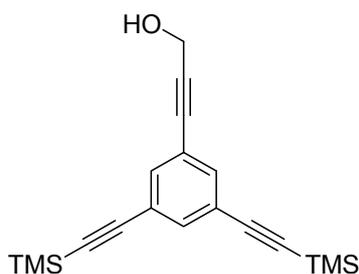


**Compound 12.** A 100 mL round bottom flask equipped with a magnetic stir bar was charged with compound **11** (8.00 g, 18.9 mmol) and  $\text{H}_2\text{SO}_4$  (32 mL). The mixture was cooled to -5 °C with an ethylene glycol/ $\text{CO}_2$  bath before  $\text{NaNO}_2$  (2.86 g, 41.5 mmol) was slowly added. After stirring for 2 hours, the reaction mixture was poured into cold water

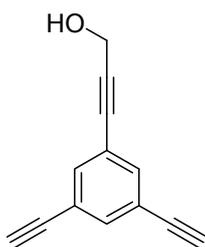
(75 mL) and filtered under *vacuo*. Another 1 L round bottom flask equipped with a magnetic stir bar and a dropping funnel was charged with copper sulfate pentahydrate (471 mg, 1.89 mmol) and EtOH (378 mL) and the resulting solution was heated to reflux. The filtrate was added to the refluxing mixture and stirred for 1 hour. The reaction mixture was cooled to room temperature and filtrated under *vacuo* to afford compound **12** (6.17 g, 80% yield) as a white amorphous powder. MP: 145 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.98 (s, 1H), 7.82 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 139.4, 139.3, 95.1. GC-MS *m/z* calcd for C<sub>6</sub>H<sub>3</sub>BrI<sub>2</sub> [M\*]: 407.75, found 407.95. FTIR (ATR): 1537m, 1393m, 1097m, 843m. *Despite several attempts, HRMS data for compound 12 was not obtained in both ESI and APPI mode.*



**Compound 13.** A 100 mL round bottom flask equipped with a magnetic stir bar was charged with compound **12** (4.00 g, 9.79 mmol), degassed THF (49 mL), degassed TEA (5.38 mL, 39.1 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (275 mg, 0.39 mmol), CuI (75 mg, 0.39 mmol) and trimethylsilylacetylene (2.84 mL, 20.5 mmol) under an argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with NH<sub>4</sub>Cl (3x) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using hexanes as the eluent to afford compound **13** (3.41 g, 98% yield) as colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.53 (s, 2H), 7.49 (s, 1H), 0.23 (s, 18 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 134.7, 134.2, 125.3, 121.9, 102.6, 96.8, 0.01. HRMS (APPI-TOF) *m/z* calcd for C<sub>16</sub>H<sub>21</sub>BrSi<sub>2</sub> [M+H]<sup>+</sup>: 349.0438, found 349.0454. FTIR (ATR): 2960m, 2160m, 1550m, 1249m, 842m.

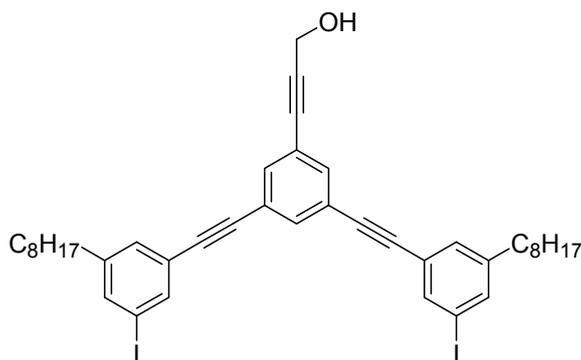


**Compound 14.** A 100 mL round bottom flask equipped with a magnetic stir bar was charged with compound **13** (2.20 g, 6.29 mmol), degassed TEA (21 mL), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (130 mg, 0.13 mmol), PPh<sub>3</sub> (118 mg, 1.89 mol), CuI (24 mg, 0.12 mmol) and propargyl alcohol (1.10 mL, 18.9 mmol) under a nitrogen atmosphere. The reaction mixture was heated at 50°C and stirred for 48 hours. The mixture was then diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with NH<sub>4</sub>Cl (3x), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using EtOAc/hexanes (15:85) as the eluent to afford compound **14** (1.54 g, 76% yield) as an orange oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.49 (s, 1H), 7.43 (s, 2H), 4.44 (s, 2H), 0.22 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 135.3, 134.8, 123.9, 123.4, 103.4, 95.9, 88.7, 84.0, 51.5, 0.06. HRMS (APPI-TOF) *m/z* calcd for C<sub>19</sub>H<sub>24</sub>OSi<sub>2</sub> [M+H]<sup>+</sup>: 325.1438, found 325.1445. FTIR (ATR): 2957m, 2898m, 2160w, 1733m, 1711m, 1250m, 1038m, 840s.

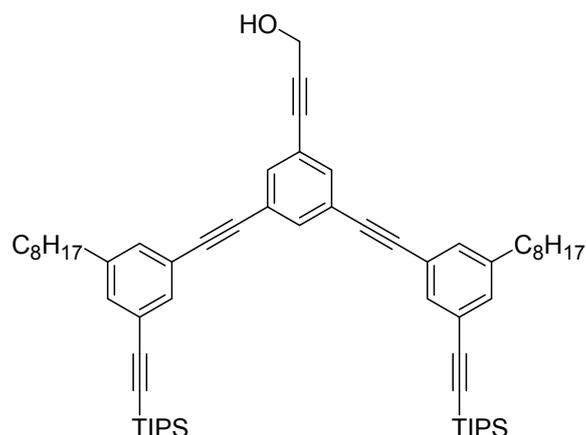


**Compound 15.** A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **14** (1.60 g, 4.93 mmol), KOH (1.10 g, 19.7 mmol), THF (6.0 mL), MeOH (6.0 mL) and water (1.0 mL). The reaction mixture was stirred for 15 minutes, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with 10% HCl (3x) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was purified by flash

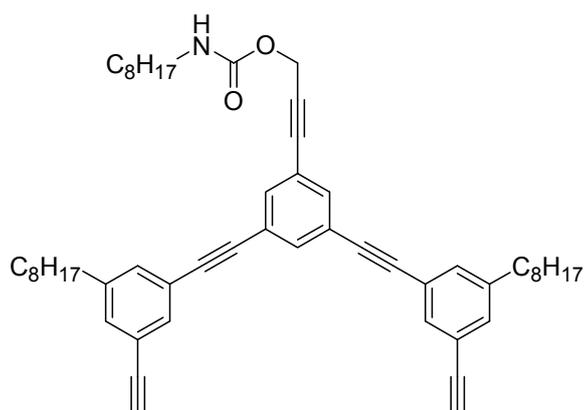
chromatography on silica gel using EtOAc/hexanes (15:85) as the eluent to afford compound **15** (880 mg, quantitative yield) as an orange oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.54 (s, 1H), 7.52 (s, 2H), 4.49 (d,  $J = 6.4$  Hz, 2H), 3.10 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 135.6, 135.5, 123.6, 123.1, 88.9, 83.9, 81.9, 78.8, 51.8. HRMS (APPI-TOF)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{O}$   $[\text{M}+\text{H}]^+$ : 181.0648, found 181.0652. FTIR (ATR): 3276m, 1579m, 1412w, 1000m, 877s.



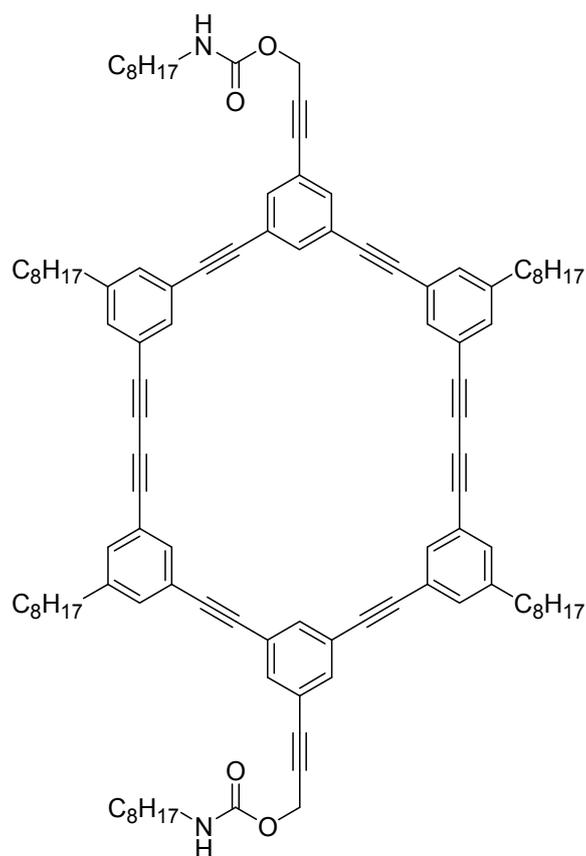
**Compound 16.** A 100 mL round bottom flask equipped with a magnetic stir bar was charged with compound **6** (5.88 g, 13.3 mmol), degassed THF (44 mL), degassed DIPEA (6.19 mL, 35.5 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (125 mg, 0.18 mmol), CuI (34 mg, 0.17 mmol) and compound **15** (800 mg, 4.44 mmol) and the resulting mixture was stirred overnight. After disappearance of compound **15** by TLC, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , washed with  $\text{NH}_4\text{Cl}$  (3x), dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexanes to EtOAc/hexanes (1:9) as the eluents to afford compound **16** (679 mg, 19% yield) as dark orange oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.68 (s, 2H), 7.59 (s, 1H), 7.52 (s, 4H), 7.29 (s, 2H), 4.50 (s, 2H), 2.53 (t,  $J = 7.6$  Hz, 4H), 1.59 (m, 4H), 1.28 (m, 20H), 0.88 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 145.4, 138.1, 137.7, 134.6, 134.5, 131.2, 124.6, 123.9, 123.6, 94.0, 89.5, 88.8, 88.6, 84.3, 51.8, 35.6, 32.1, 31.4, 29.6, 29.4, 22.9, 14.4. HRMS (APPI-TOF)  $m/z$  calcd for  $\text{C}_{41}\text{H}_{46}\text{I}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 809.1711, found 809.1702; FTIR (ATR): 3336w, 2922s, 2852s, 1591m, 1553m, 1442m, 1048w, 878m.



**Compound 17.** A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **16** (650 mg, 0.80 mmol), degassed THF (8.0 mL), degassed DIPEA (0.56 mL, 3.21 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (23 mg, 0.03 mmol), CuI (6 mg, 0.03 mmol) and triisopropylsilylacetylene (0.90 mL, 4.02 mmol). The reaction mixture was stirred overnight, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with NH<sub>4</sub>Cl, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using EtOAc/hexanes (1:9) as the eluent to afford compound **17** (584 mg, 80% yield) as orange oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.63 (s, 1H), 7.53 (s, 2H), 7.47 (s, 2H), 7.28 (s, 2H), 7.27 (s, 2H), 4.49 (s, 2H), 2.56 (t, *J* = 7.7 Hz, 4H), 1.61 (m, 4H), 1.29 (m, 20H), 1.13 (s, 42H), 0.88 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 143.6, 134.6, 134.4, 132.9, 132.5, 131.8, 124.2, 123.9, 123.9, 123.6, 122.9, 106.6, 91.2, 90.4, 88.7, 87.9, 84.3, 51.8, 35.8, 32.2, 31.5, 29.6, 29.5, 22.9, 18.9, 14.4, 11.6. HRMS (APPI-TOF) *m/z* calcd for C<sub>63</sub>H<sub>88</sub>OSi<sub>2</sub> [M+H]<sup>+</sup>: 917.6446, found 917.6476. FTIR (ATR): 3310w, 2923s, 2862s, 2152w, 1588s, 1462m, 1381w, 996w, 879s.



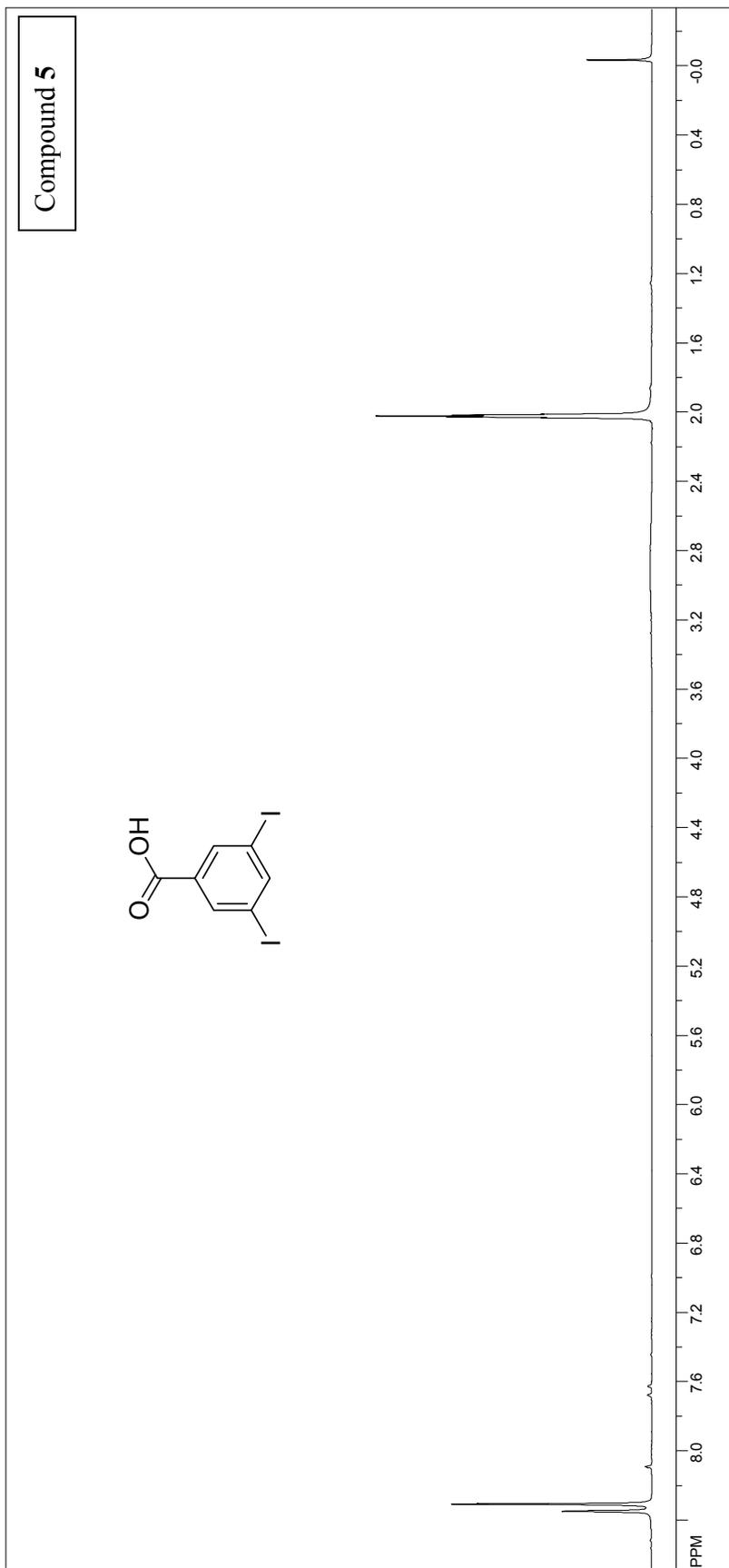
**Compound 19.** A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **17** (580 mg, 0.63 mmol), THF (12.0 mL) and TBAF (1.90 mL, 1.90 mmol). The reaction mixture was stirred for 15 minutes, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water (3x) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was charged in a 5 mL round bottom flask equipped with a magnetic stir bar containing octylisocyanate (48 μL, 0.273 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) and dibutyltin dilaureate (6 μL, 0.01 mmol). The reaction mixture was stirred overnight at room temperature, dilute with CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using hexanes to EtOAc/hexanes (15:85) as the eluents to afford compound **19** (58 mg, 35% yield) as a white amorphous powder. MP: 59 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.62 (s, 1H), 7.55 (s, 2H), 7.47 (s, 2H), 7.32 (s, 2H), 7.29 (s, 2H), 4.91 (s, 2H), 3.21 (q, *J*<sub>1</sub> = *J*<sub>2</sub> = 6.8 Hz, 2H), 3.08 (s, 2H), 2.58 (t, *J* = 7.5 Hz, 4H), 1.61 (m, 4H), 1.51 (m, 2H), 1.28 (br d, *J* = 10.9 Hz, 30H), 0.88 (m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 155.7, 143.7, 134.7, 134.6, 132.8, 132.7, 132.4, 124.1, 123.4, 123.0, 122.5, 90.2, 88.1, 85.3, 84.7, 83.2, 77.7, 53.2, 41.5, 35.7, 32.1, 32.0, 30.2, 29.7 (2C), 29.4, 26.9, 22.9, 14.4. HRMS (APPI-TOF) *m/z* calcd for C<sub>54</sub>H<sub>65</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 760.5088, found 760.5078. FTIR (ATR): 3299m, 3284m, 2917s, 2849s, 1690s, 1588m, 1466m, 1260s, 1148m, 1055m, 872s.

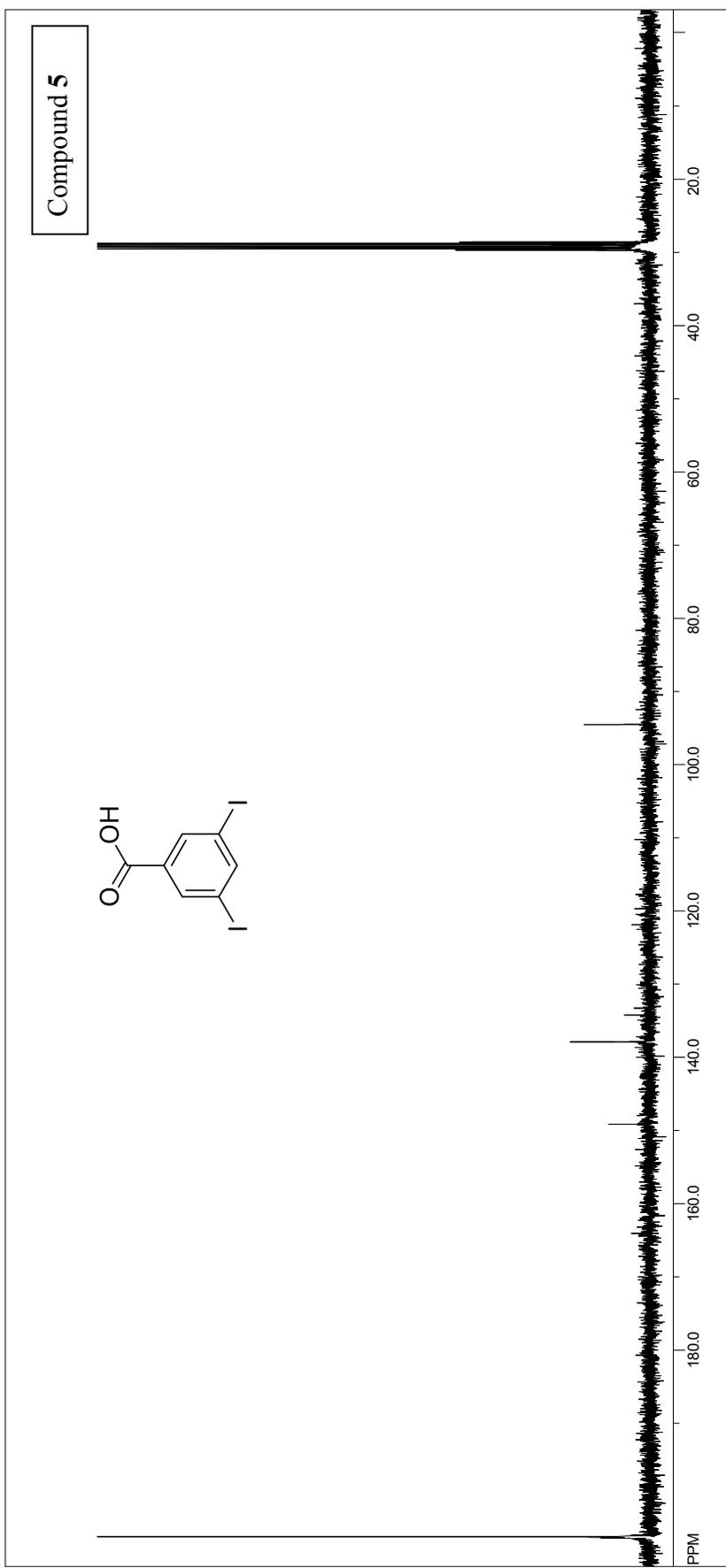


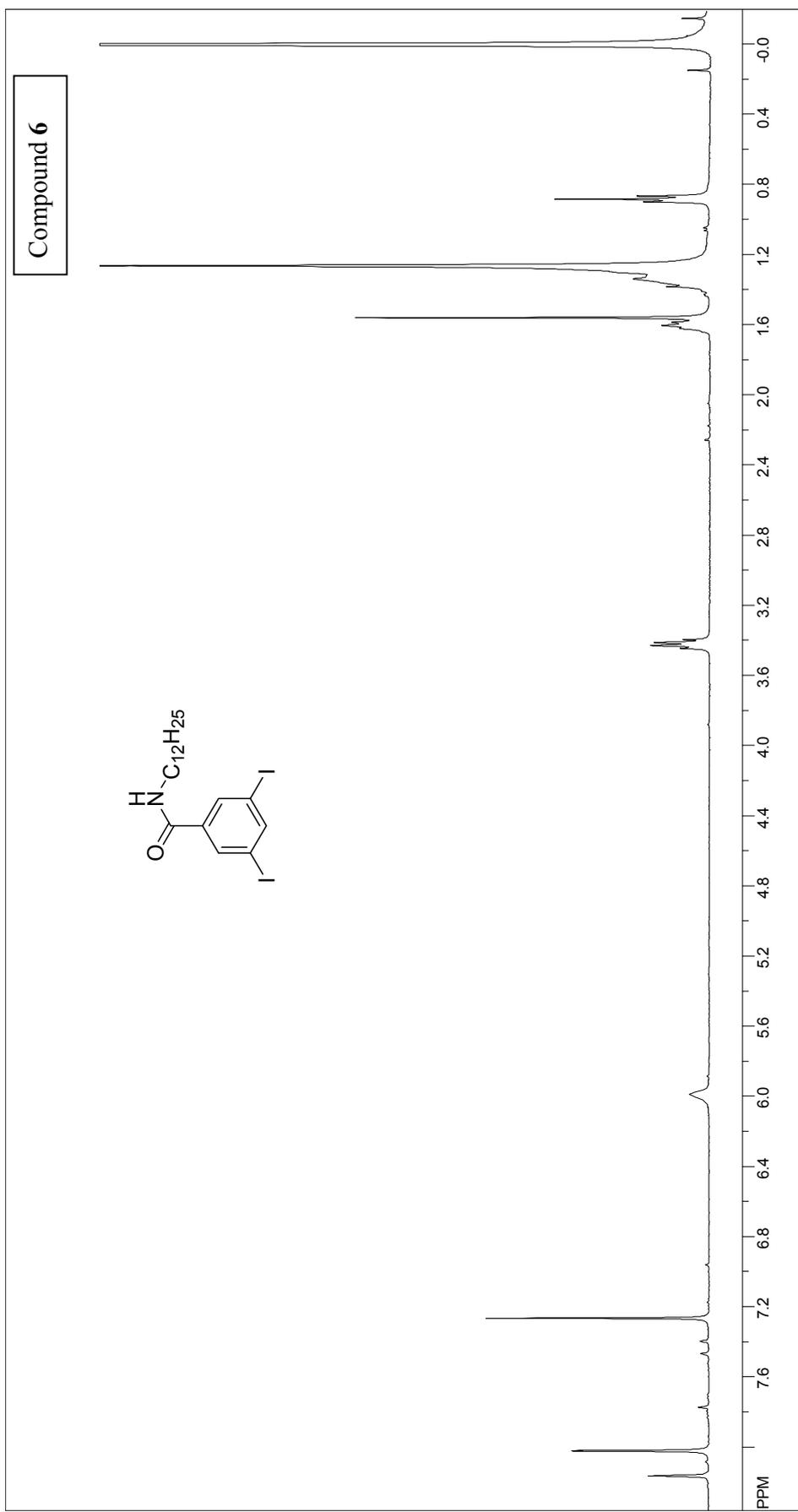
**Compound 2.** A 25 mL round bottom flask equipped with a magnetic stir bar was charged with CuCl (474 mg, 4.79 mmol), CuCl<sub>2</sub> (92 mg, 0.684 mmol) and degassed pyridine (10 mL). To this suspension was added a solution of compound **19** (52 mg, 0.0684 mmol) in degassed pyridine (3 mL) over 96 h at room temperature under a nitrogen atmosphere. After the completion of the addition, the mixture was allowed to stir for an additional 7 days and then poured in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and water (30 mL). The organic phase was extracted successively with water, 25% NH<sub>4</sub>OH, water, 10% acetic acid, water, 10% aqueous sodium hydroxide and brine. The organic layers were dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by preparative TLC on silica gel using CHCl<sub>3</sub>/hexanes (4:1) as the eluent to afford compound **2** (21 mg, 40% yield) as a white amorphous powder. MP: 135-145 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.68 (s, 2H), 7.58 (s, 4H), 7.55 (s, 4H), 7.33 (s, 4H), 7.31 (s, 4H), 4.92 (s, 4H), 4.81 (m, 2H), 3.22 (q, *J* = 6.4 Hz, 4H), 2.59 (t, *J* = 7.4 Hz, 8H), 1.53 (m, 12H), 1.3 (m, 60H), 0.89 (m, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 143.8, 134.3, 133.7, 132.7,

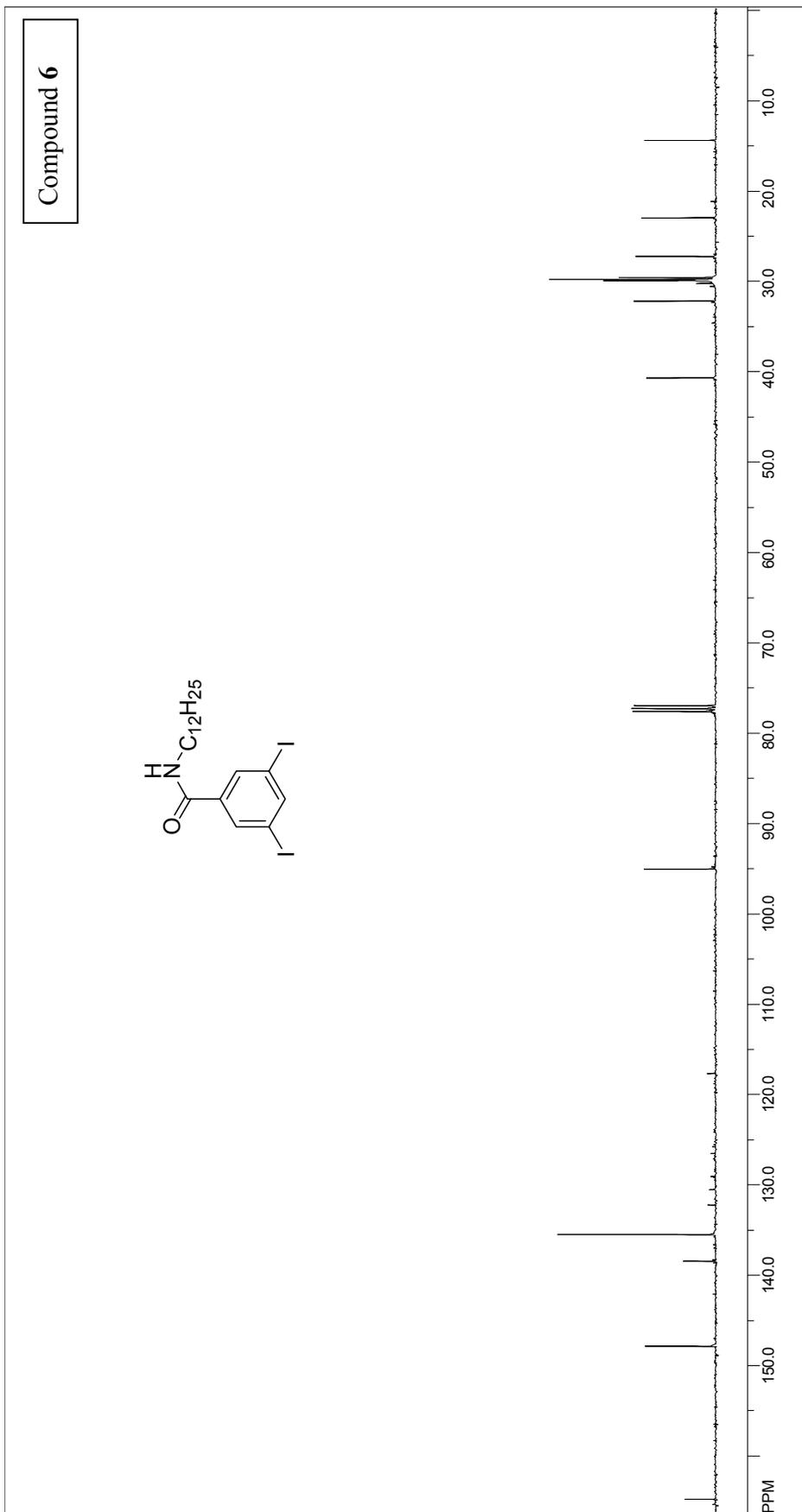
132.5, 131.1, 129.0, 124.0, 123.3, 122.2, 90.1, 88.4, 85.1, 84.8, 81.2, 74.6, 68.4, 53.3, 41.5, 38.9, 35.7, 32.1, 32.0, 31.3, 30.6, 30.1, 29.9 (2C), 29.7 (2C), 29.4, 29.2, 26.9 (2C), 23.9, 23.2, 22.9, 14.4, 11.2. HRMS (MALDI-TOF)  $m/z$  calcd for  $C_{54}H_{65}NO_2$   $[M+H]^+$ : 1514.9718, found 1514.9451. FTIR (ATR): 3309m, 2917s, 2849s, 1682s, 1589m, 1584m, 1546m, 1466m, 1442m, 1262s, 1140m, 1015m, 874s, 869s.

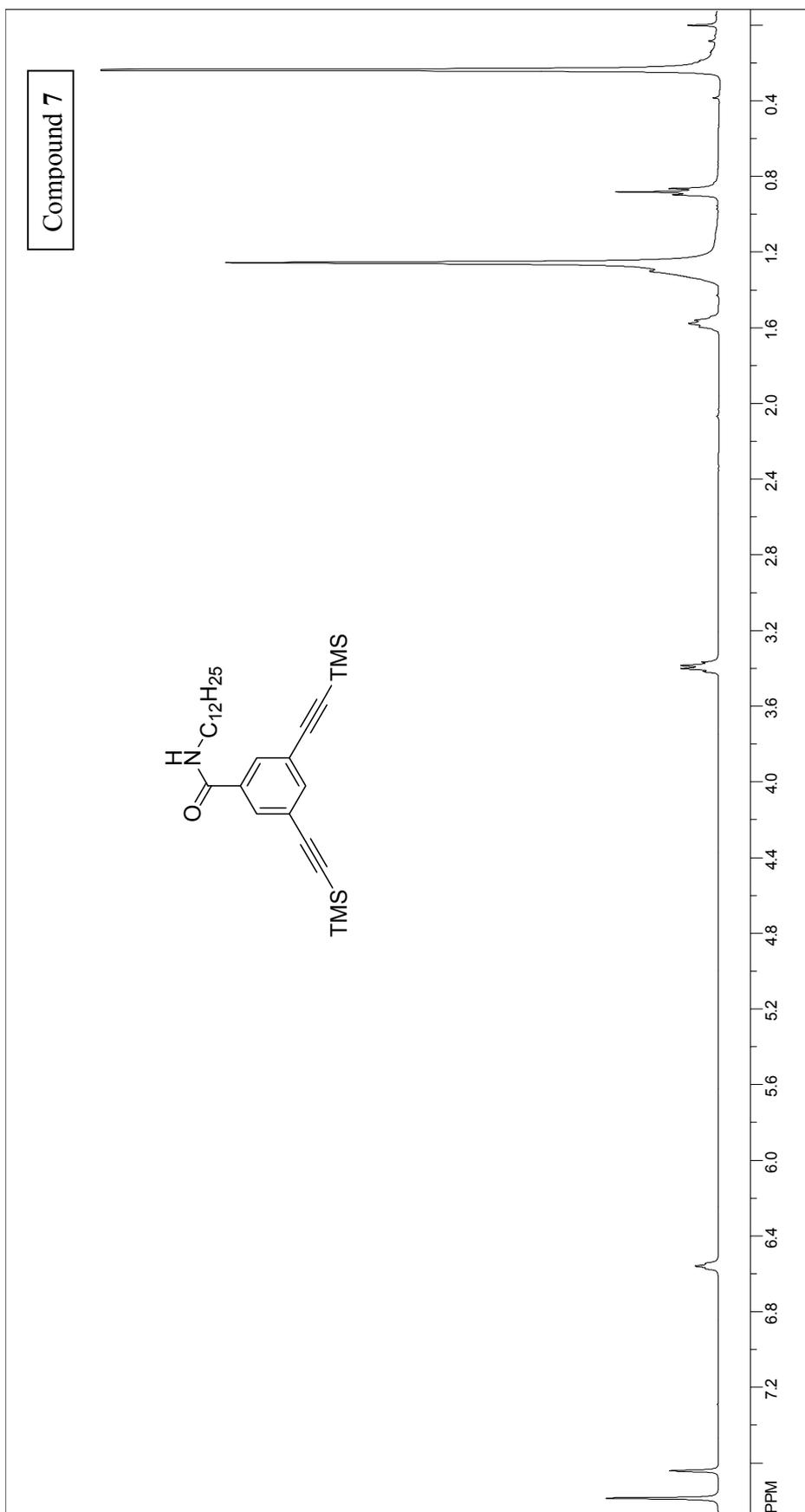
### 5. $^1\text{H}$ and $^{13}\text{C}$ NMR for new compounds

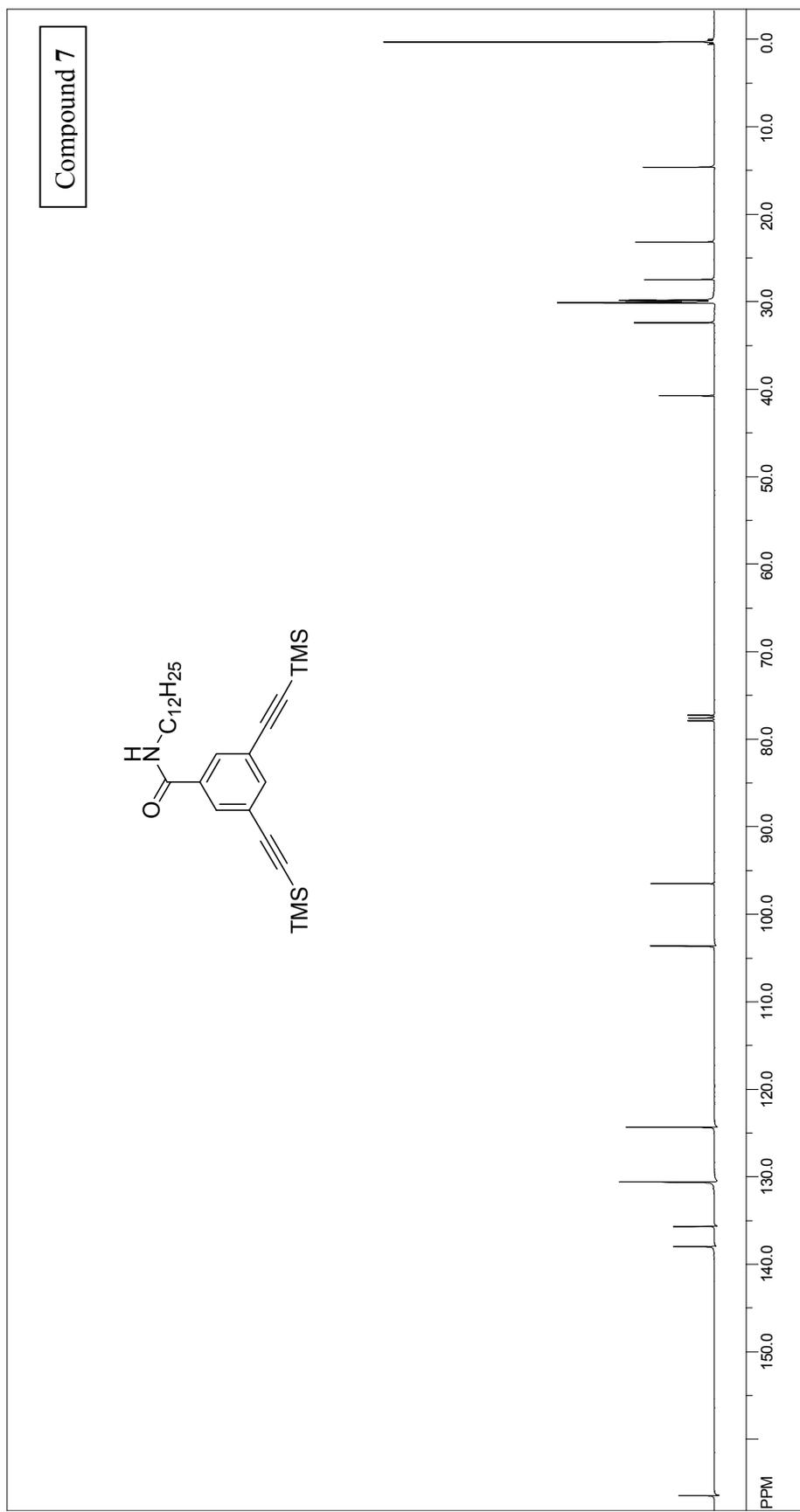


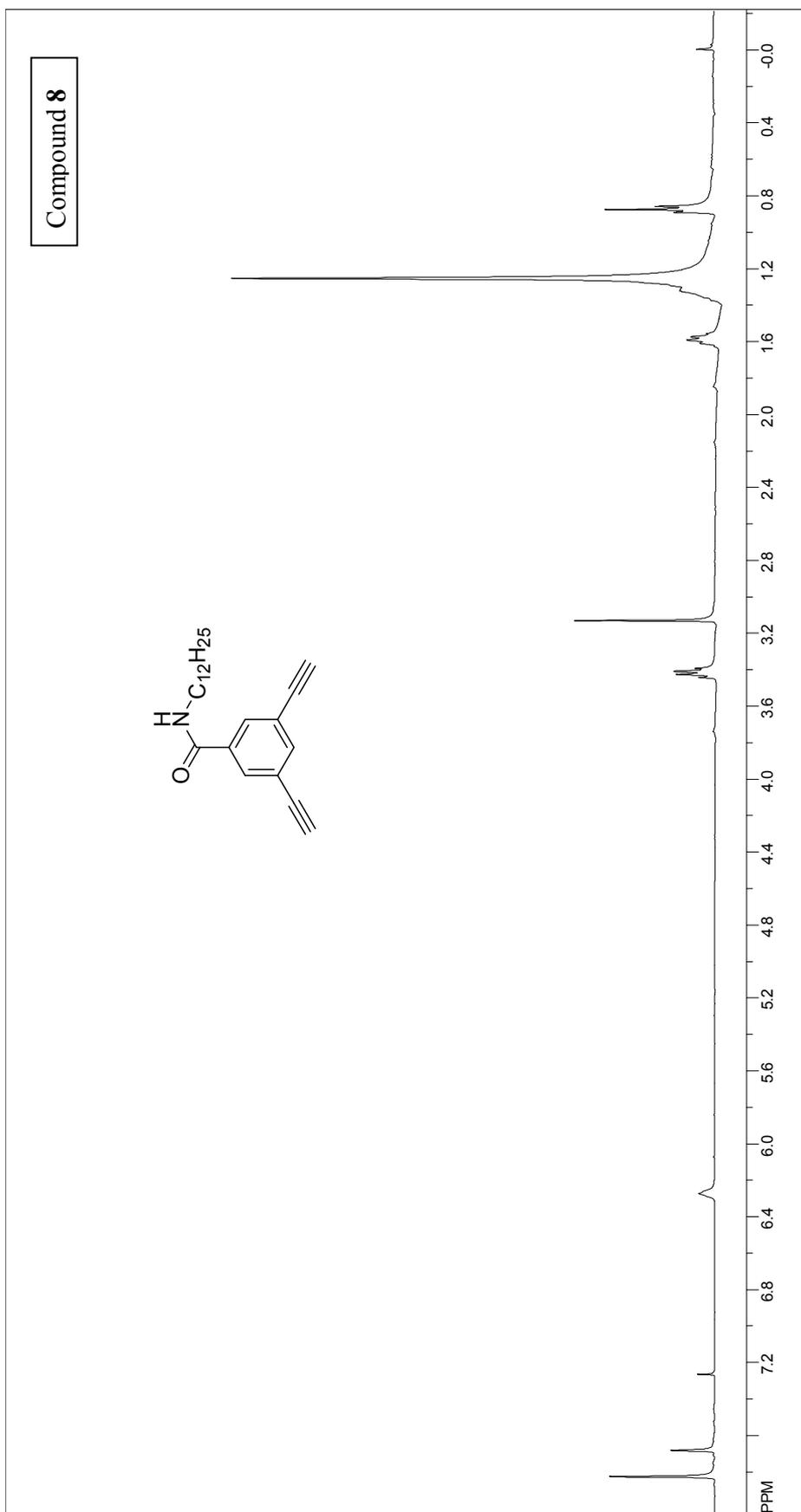


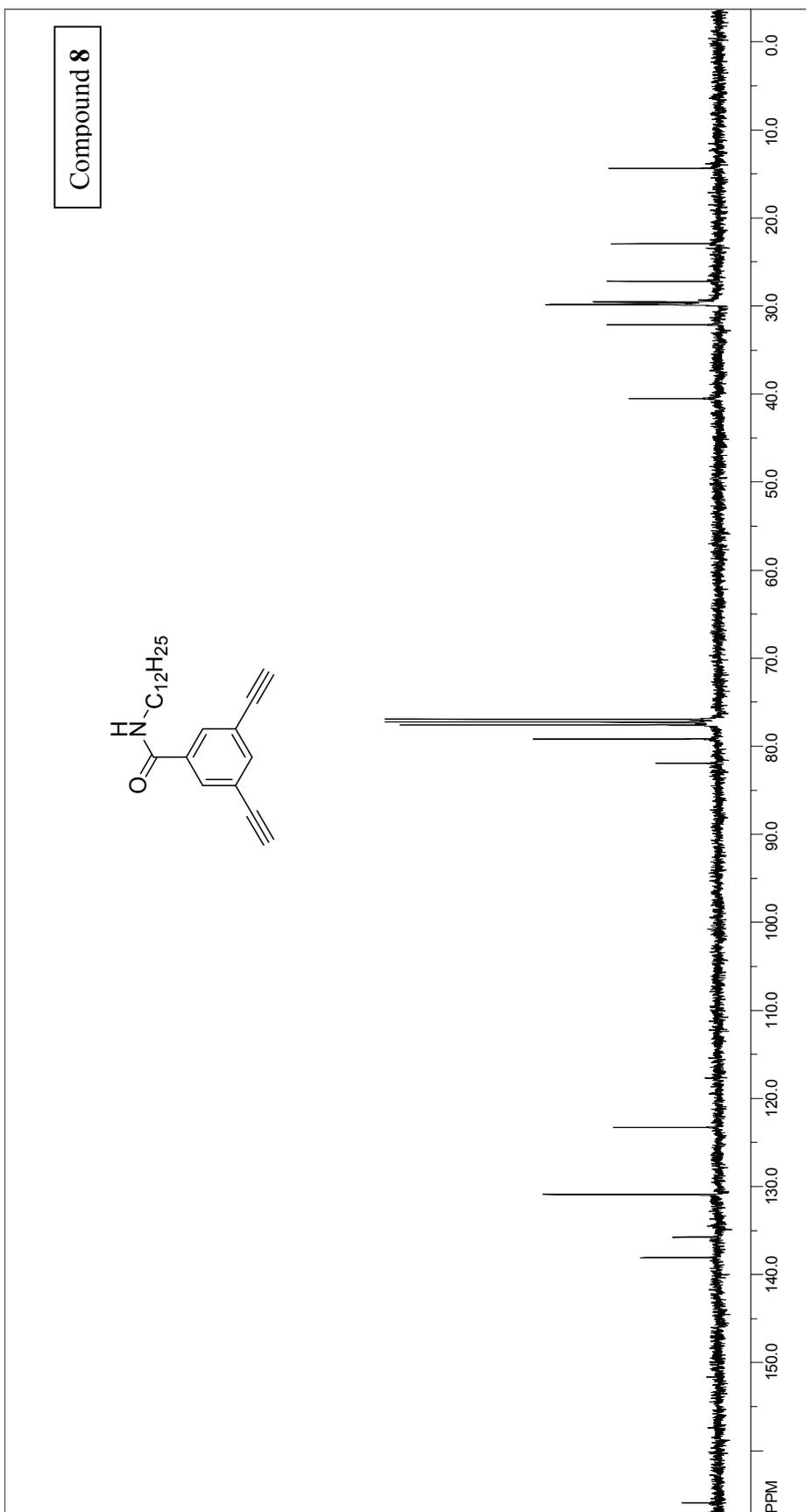


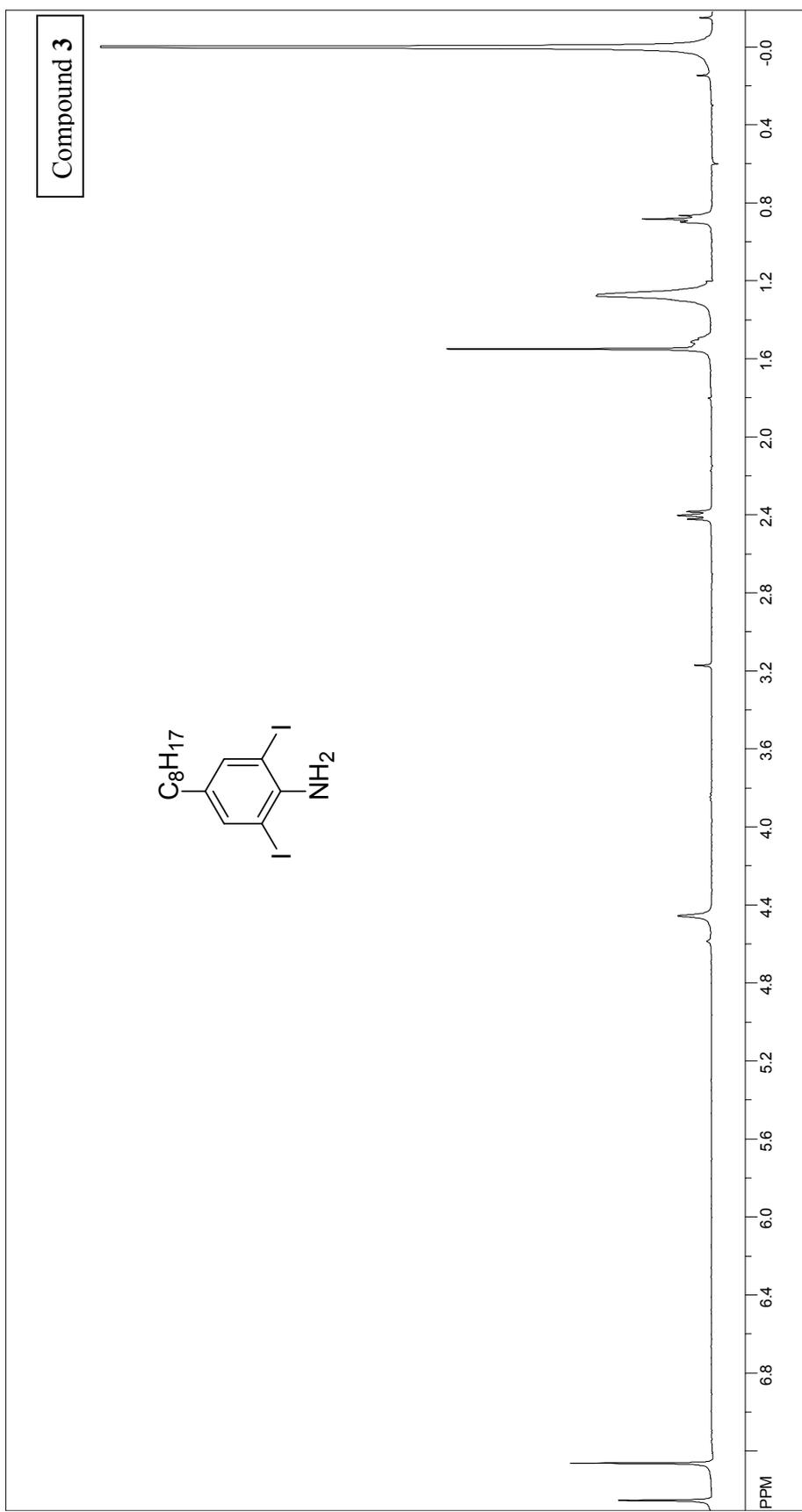


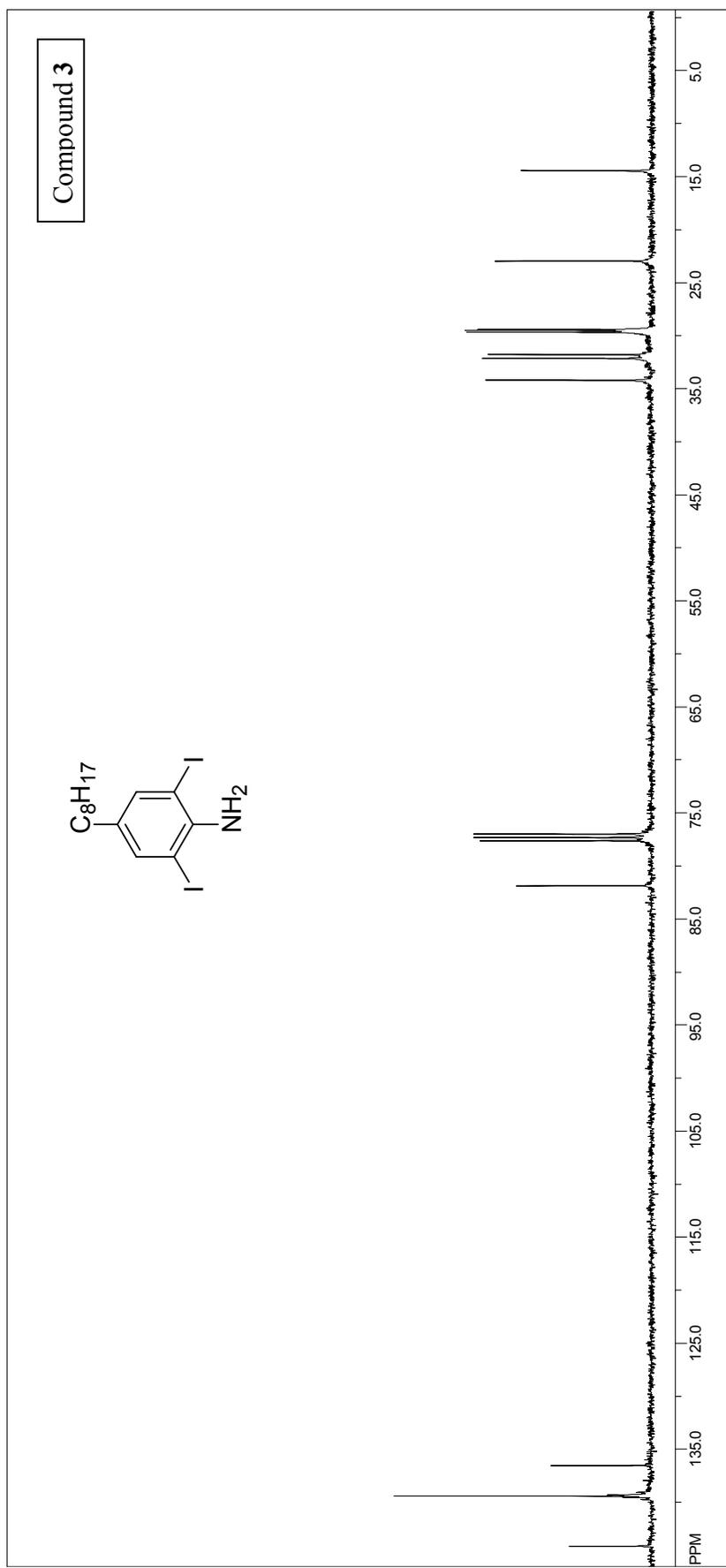


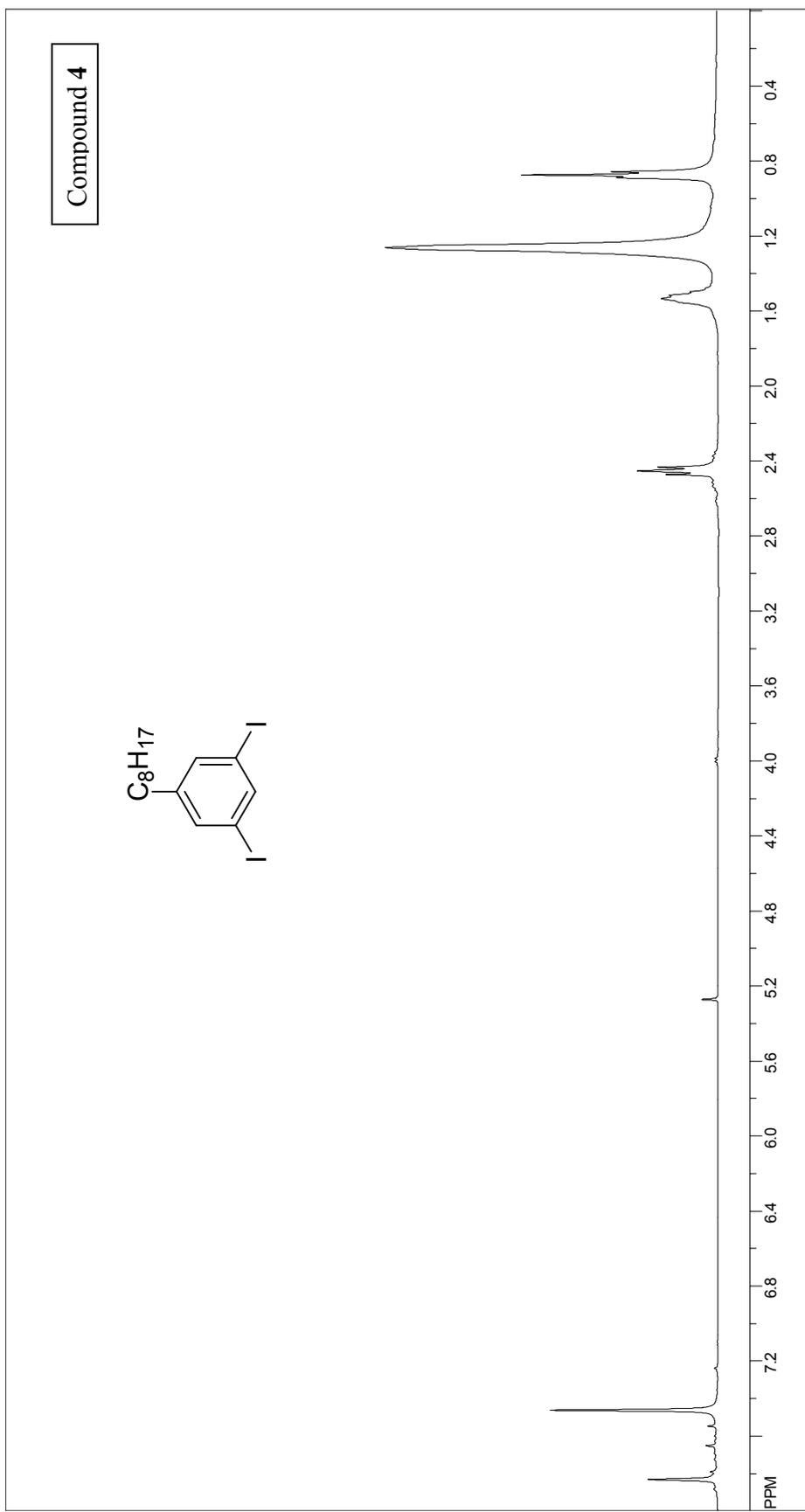


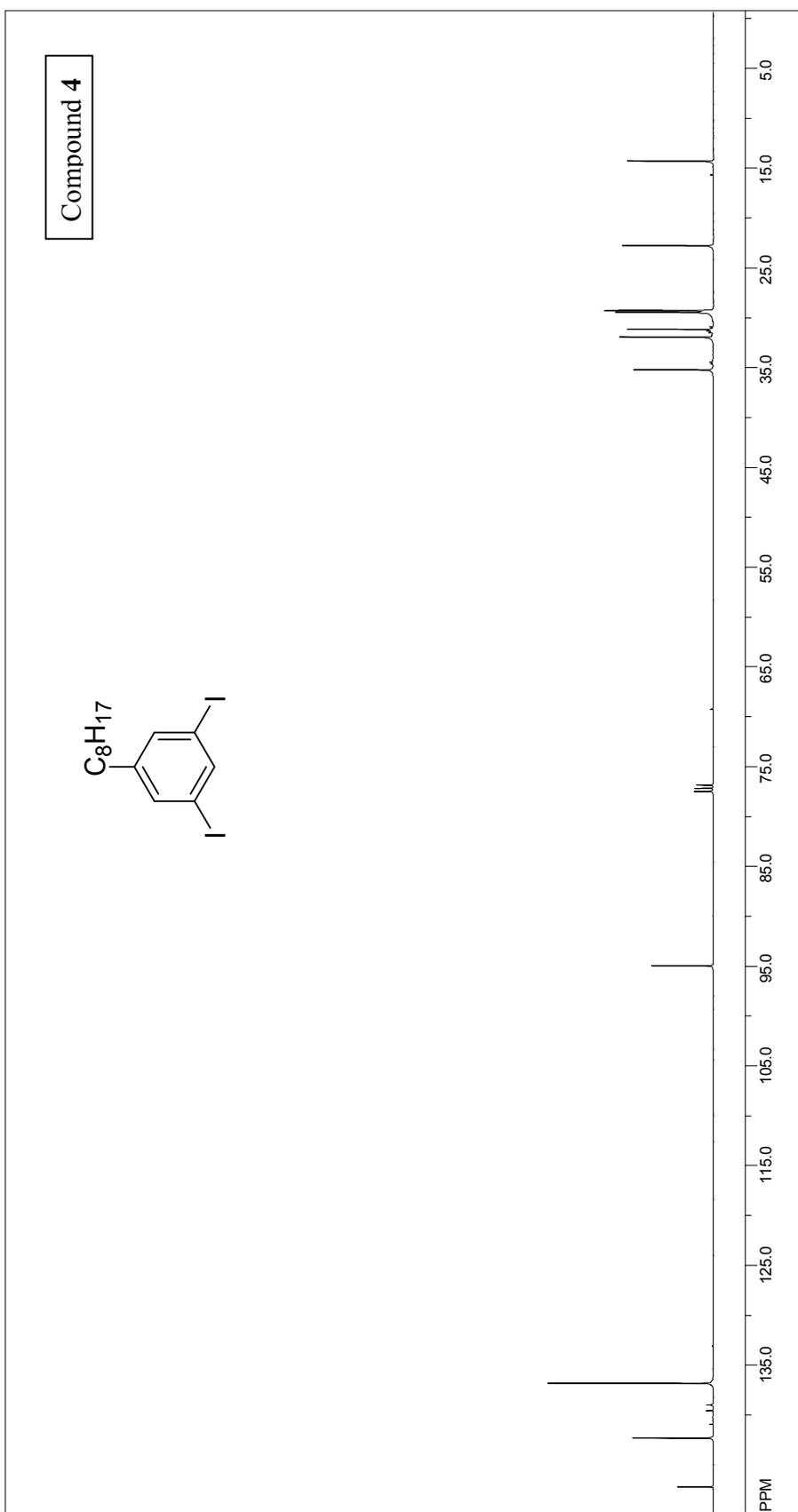


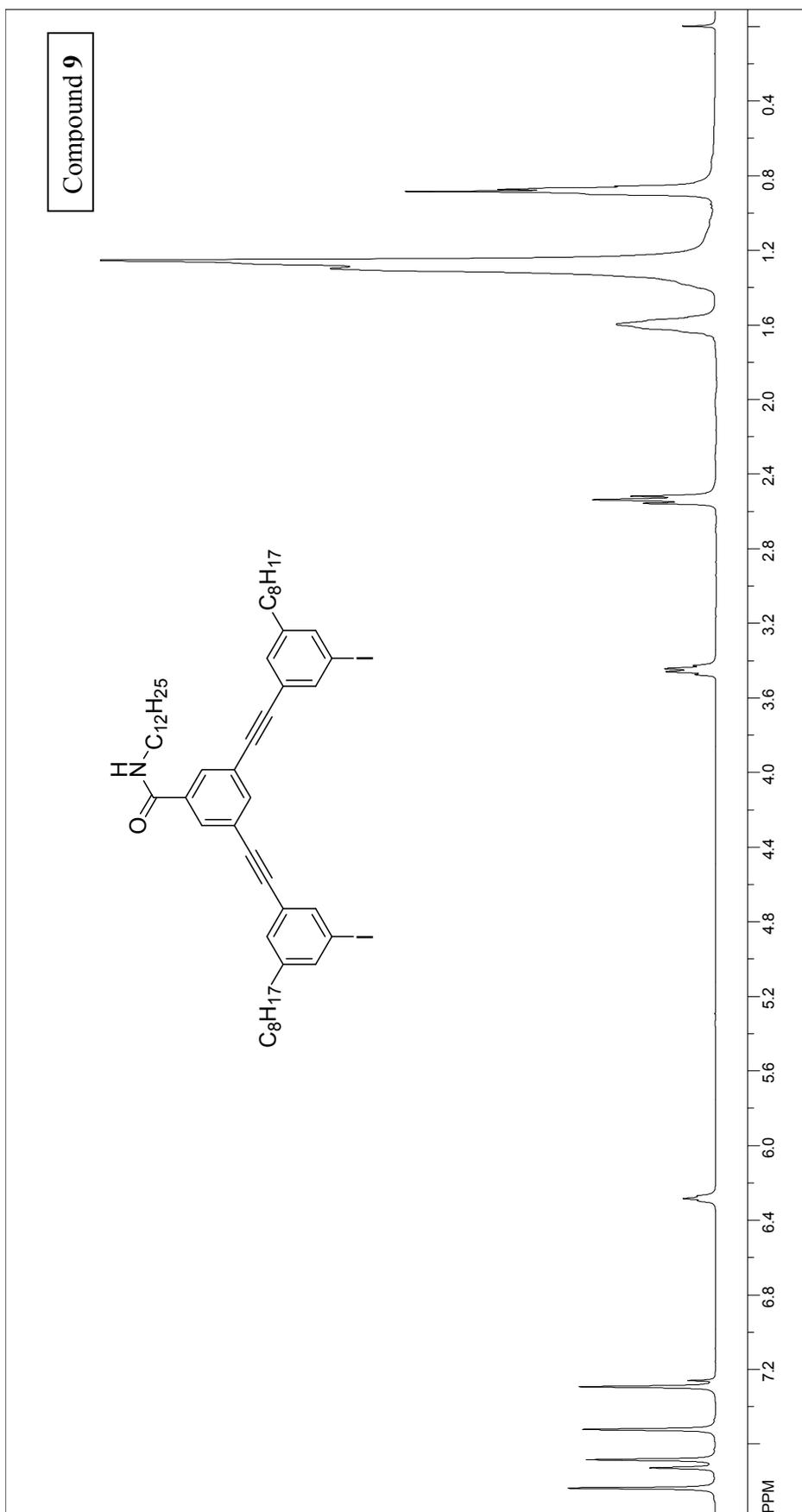


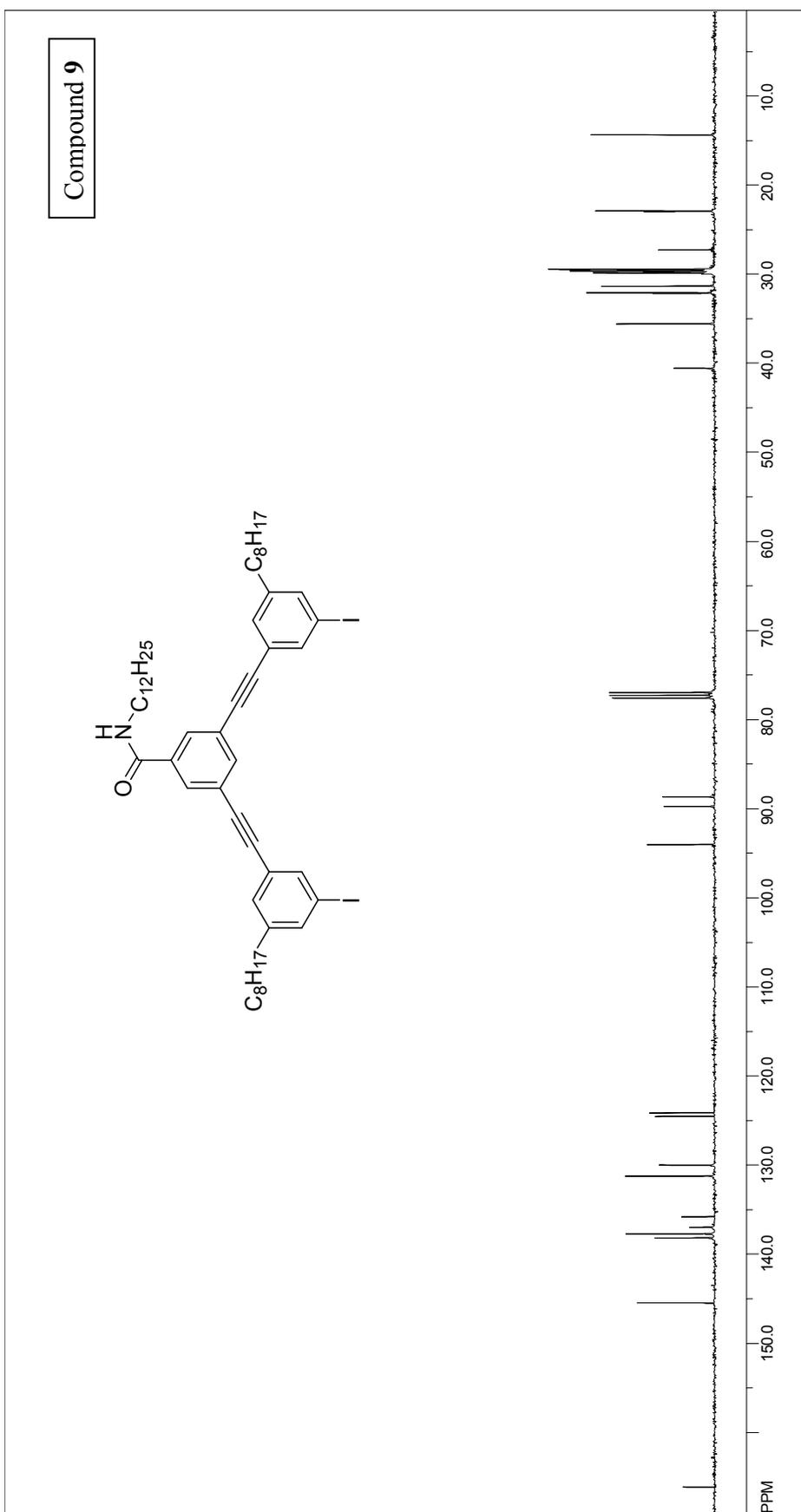


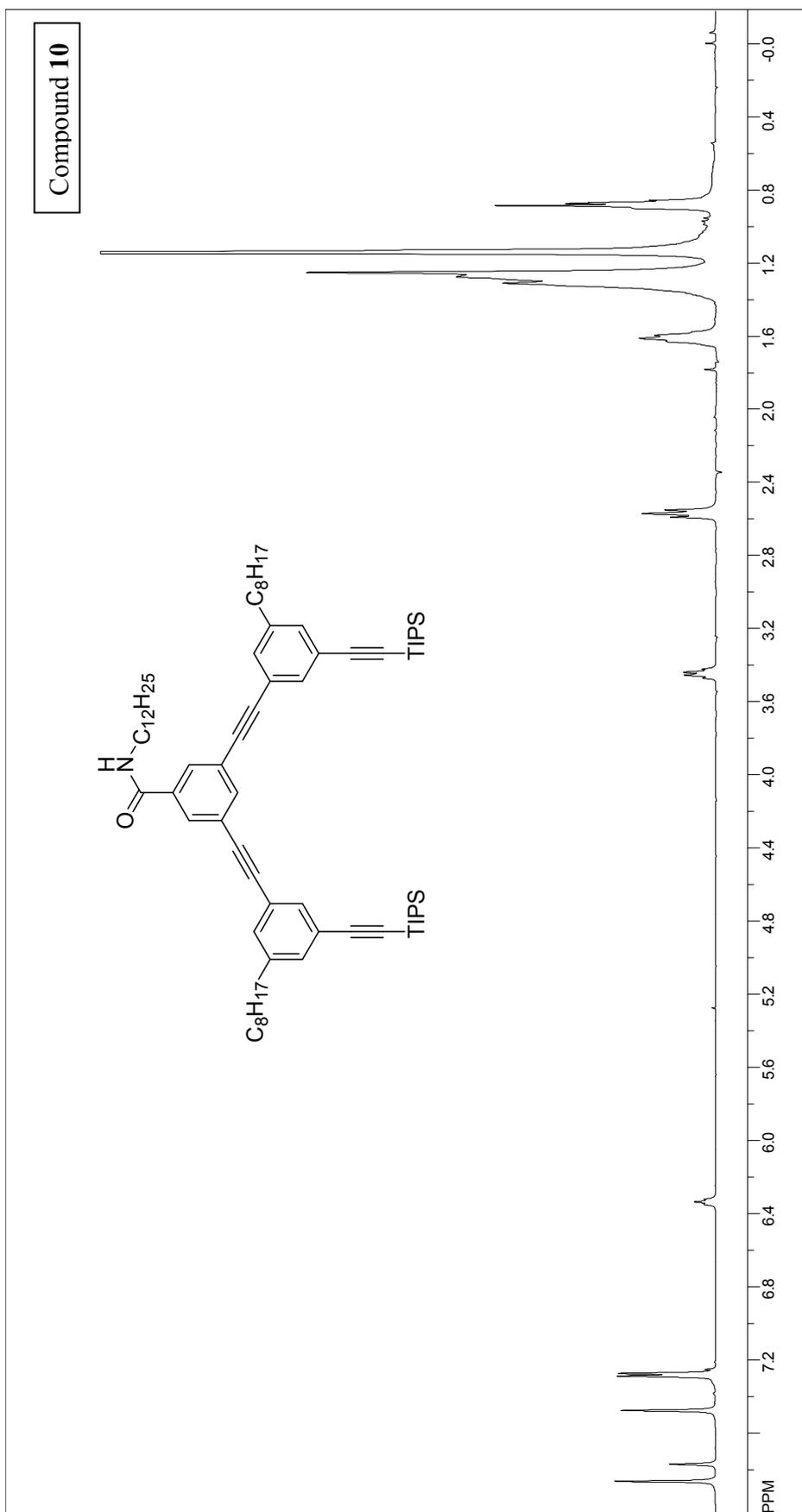


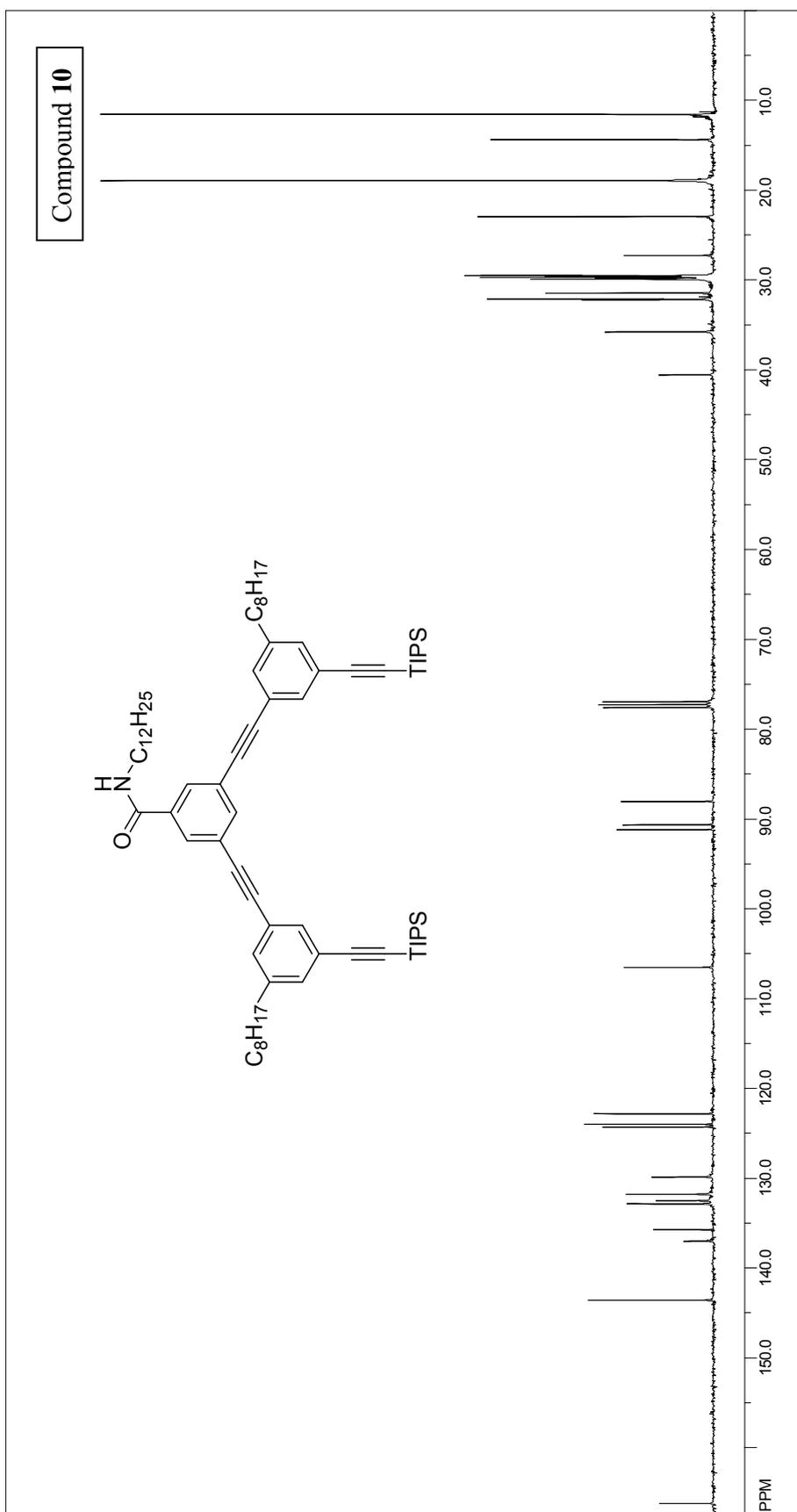


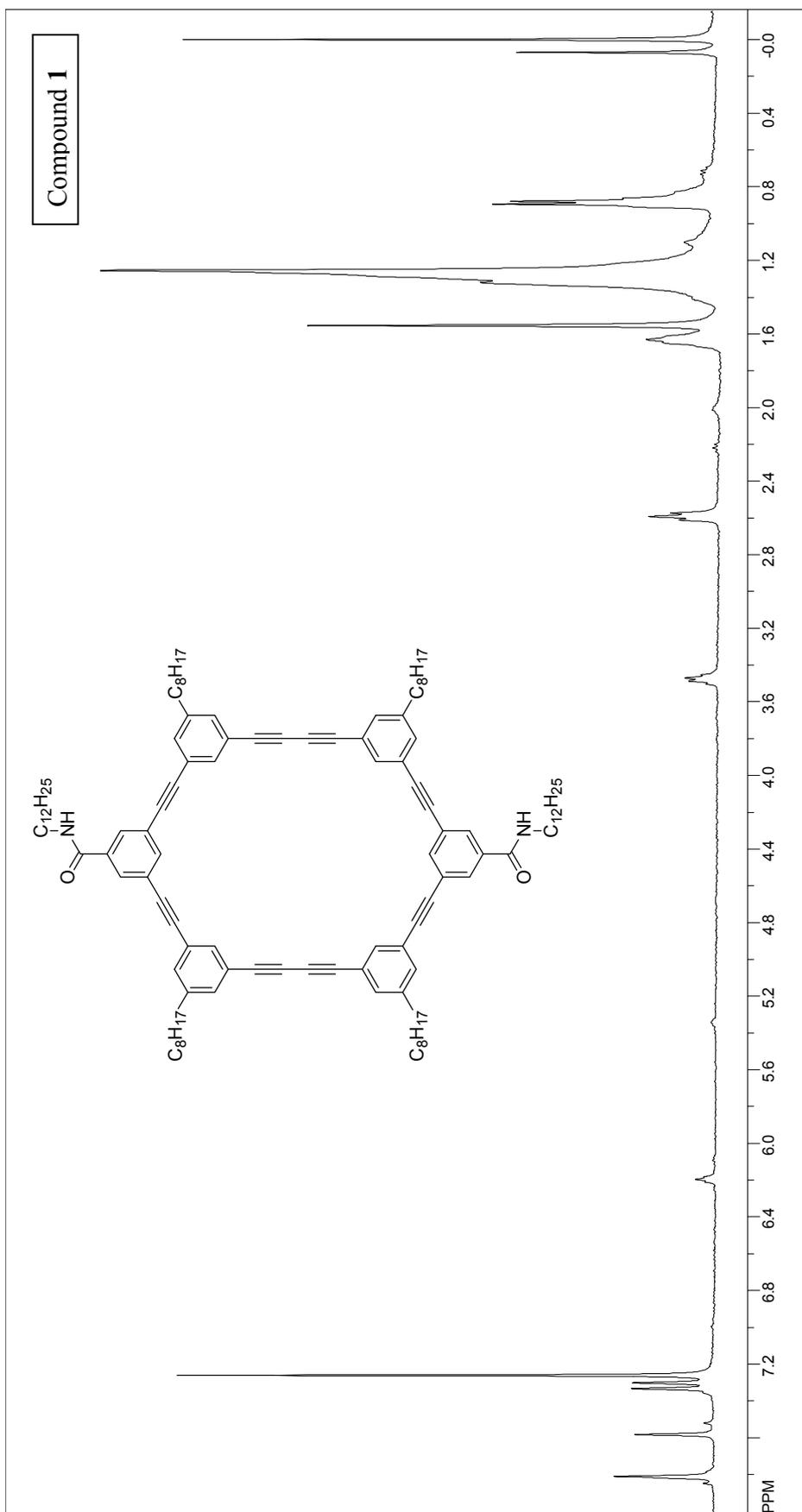


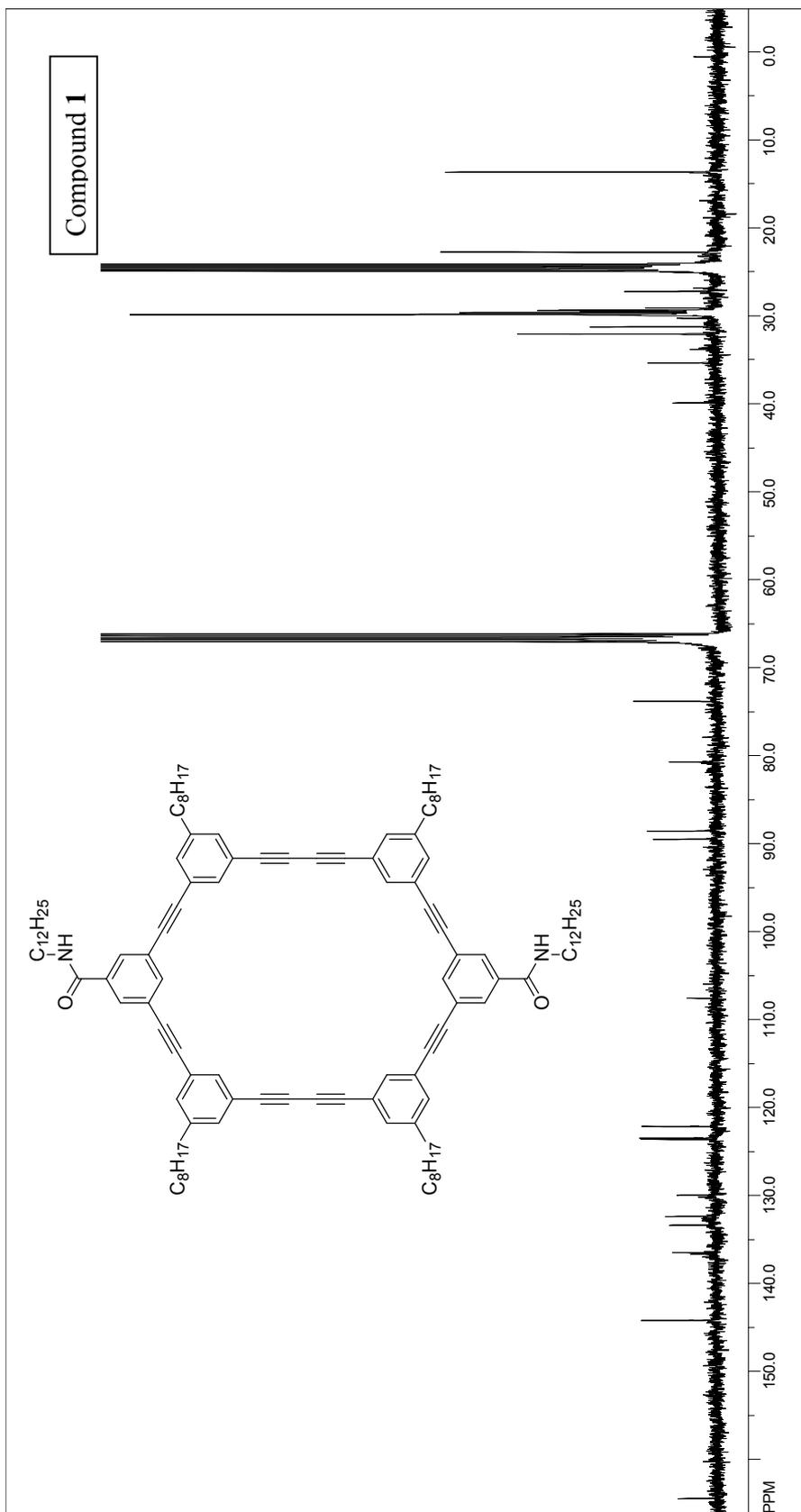




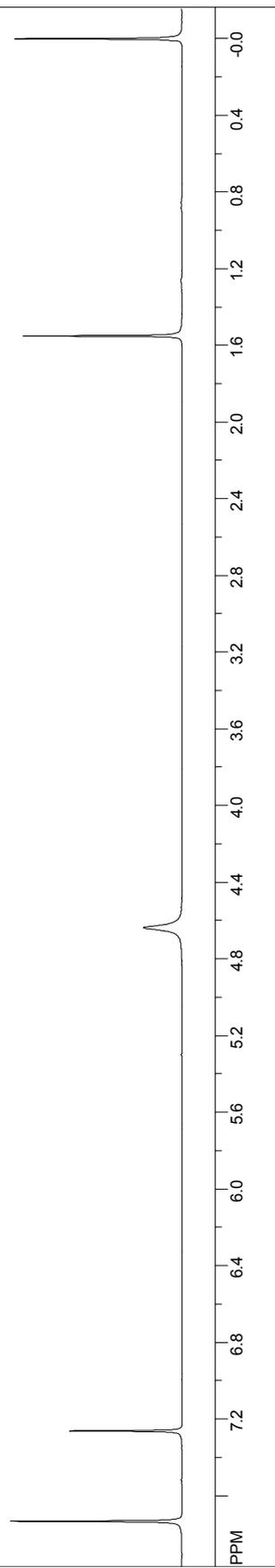
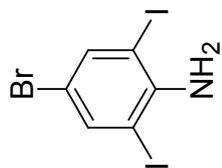


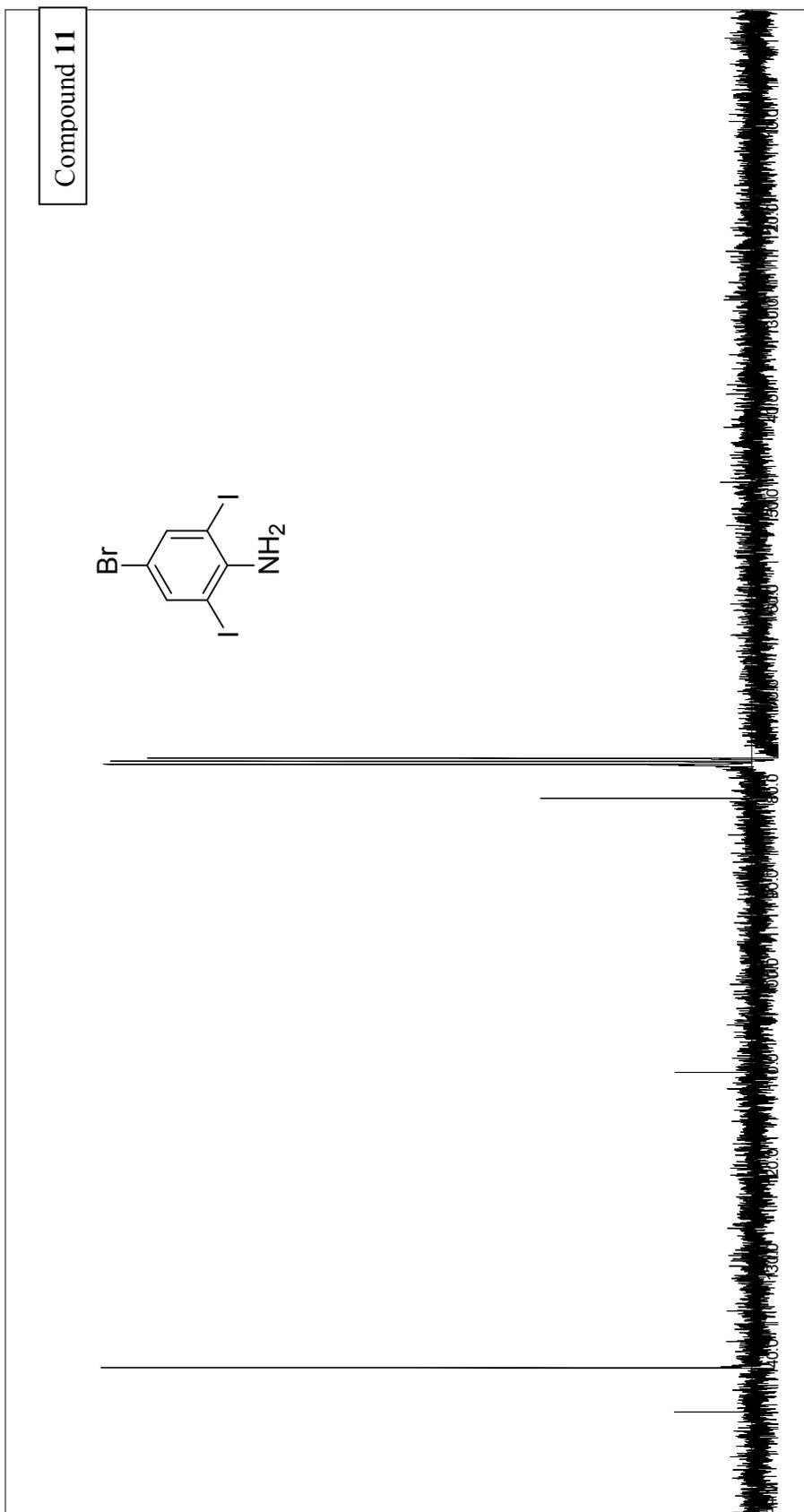


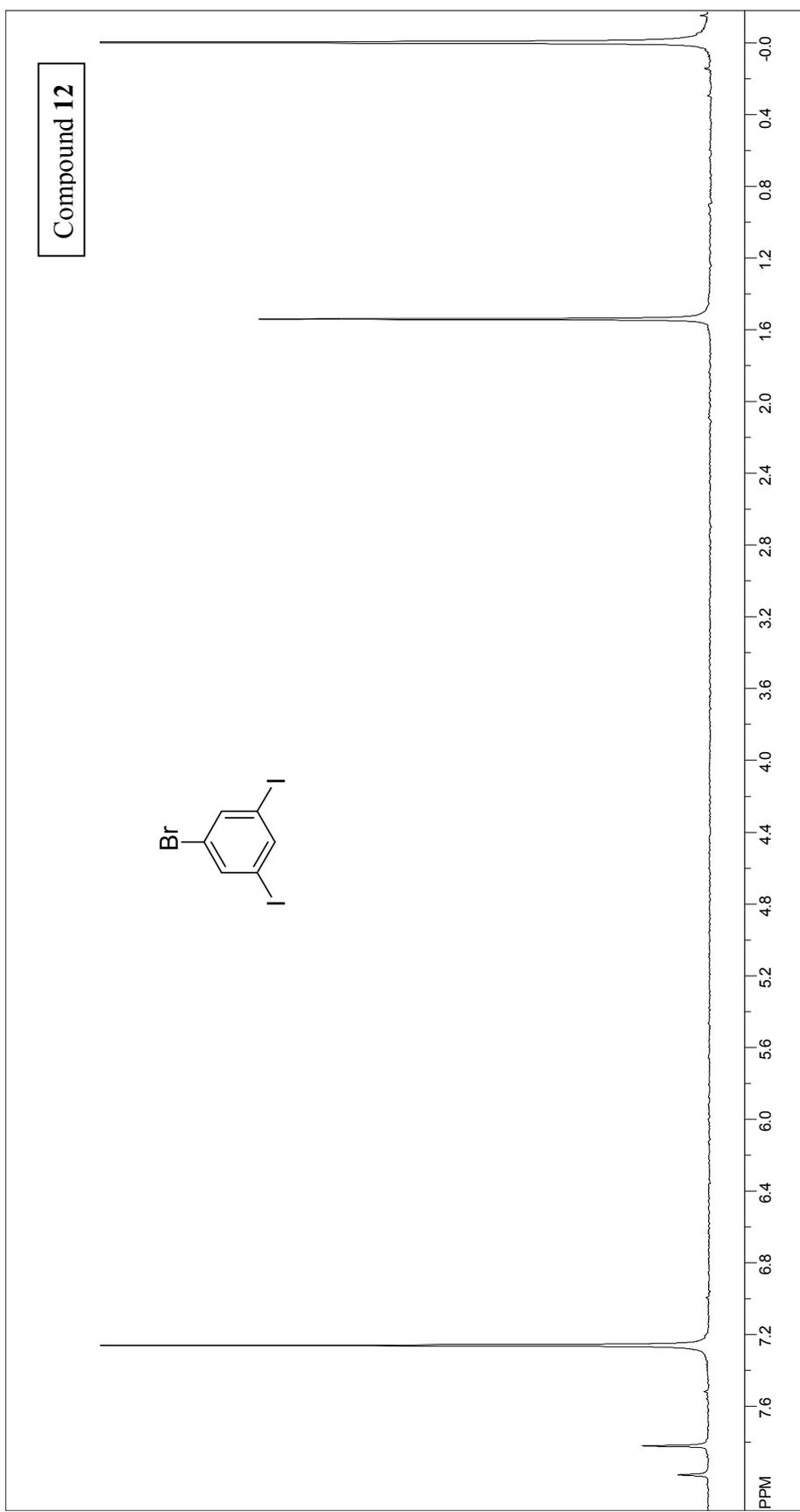


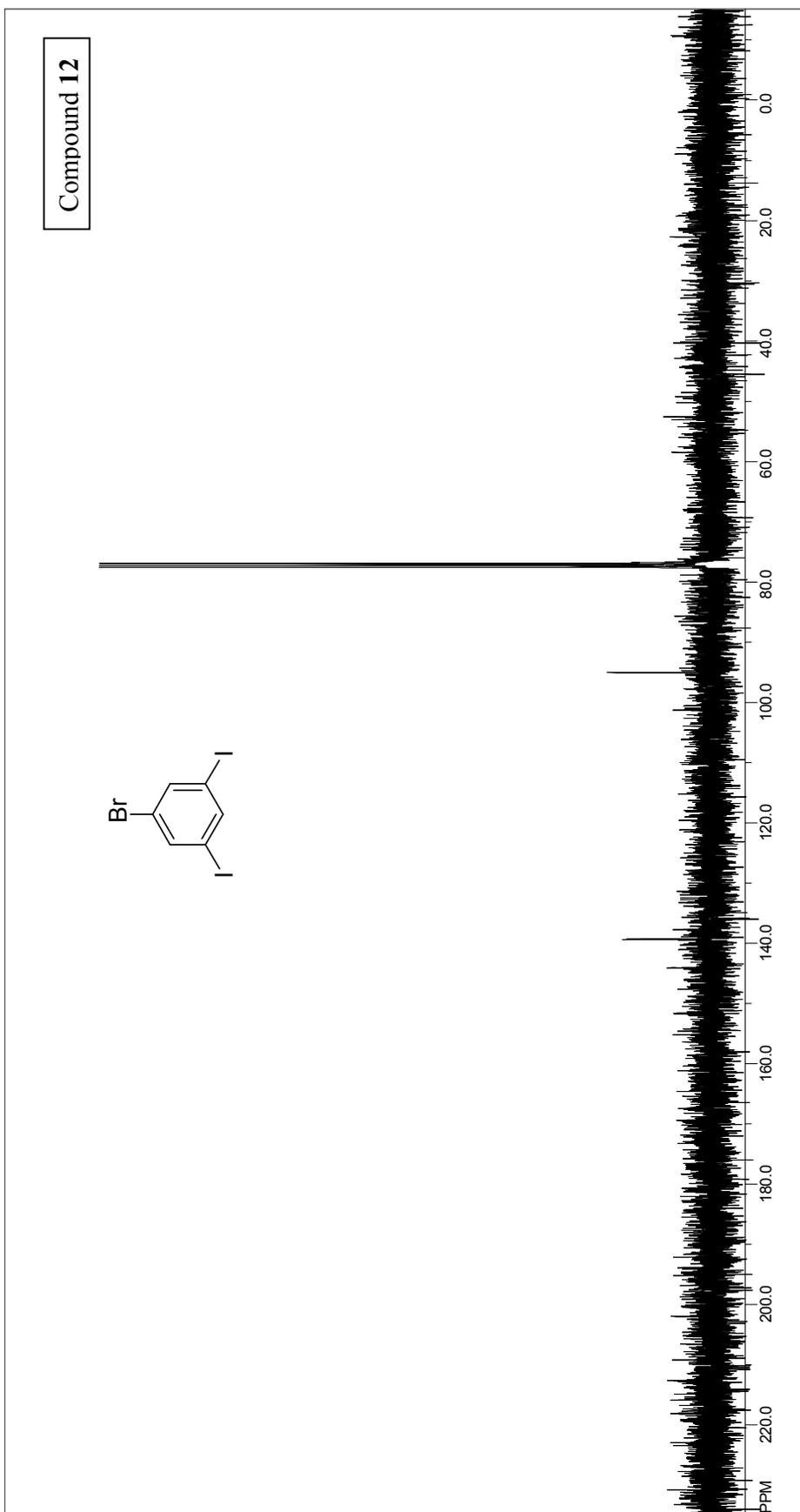


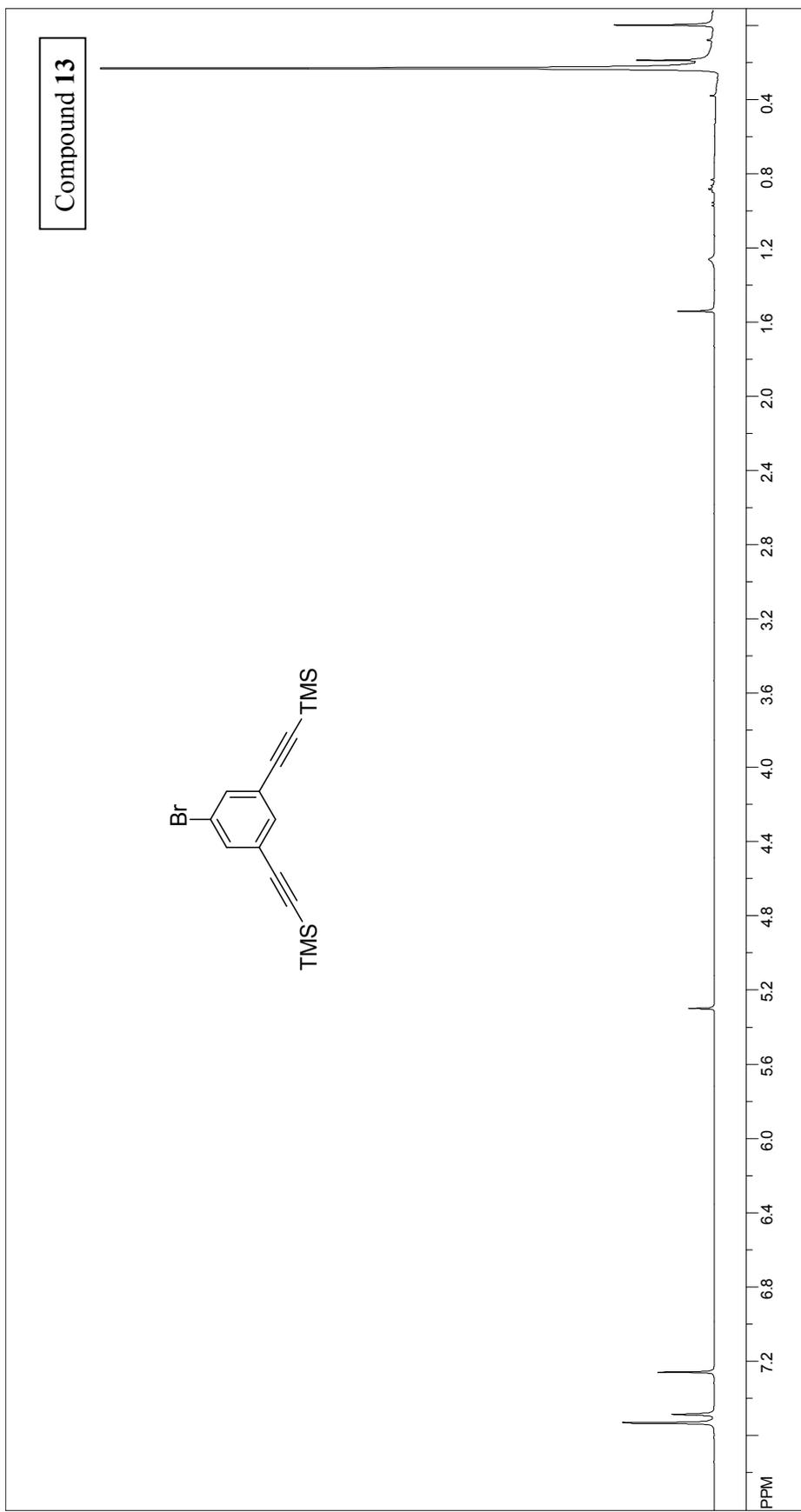
Compound **11**

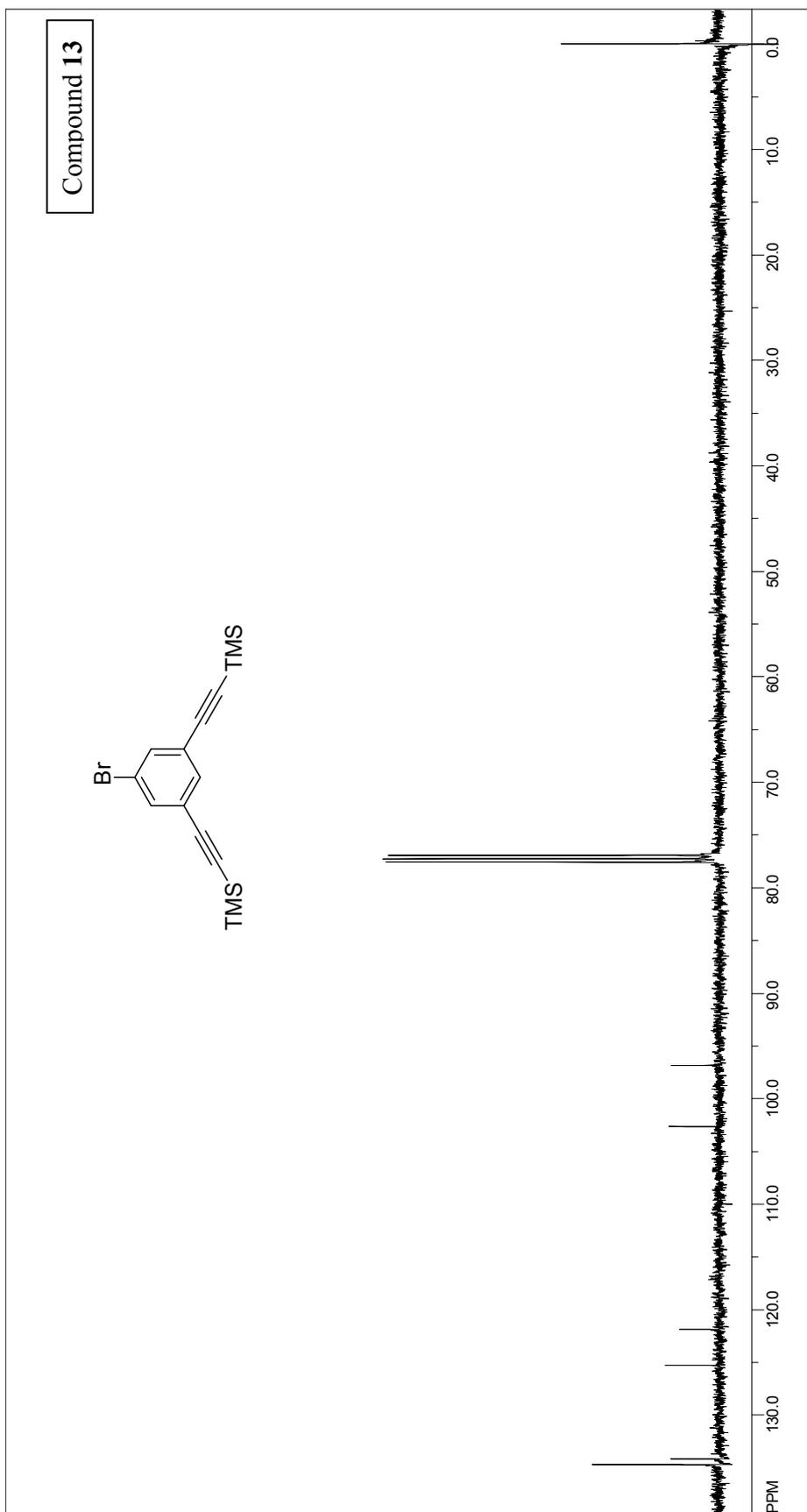


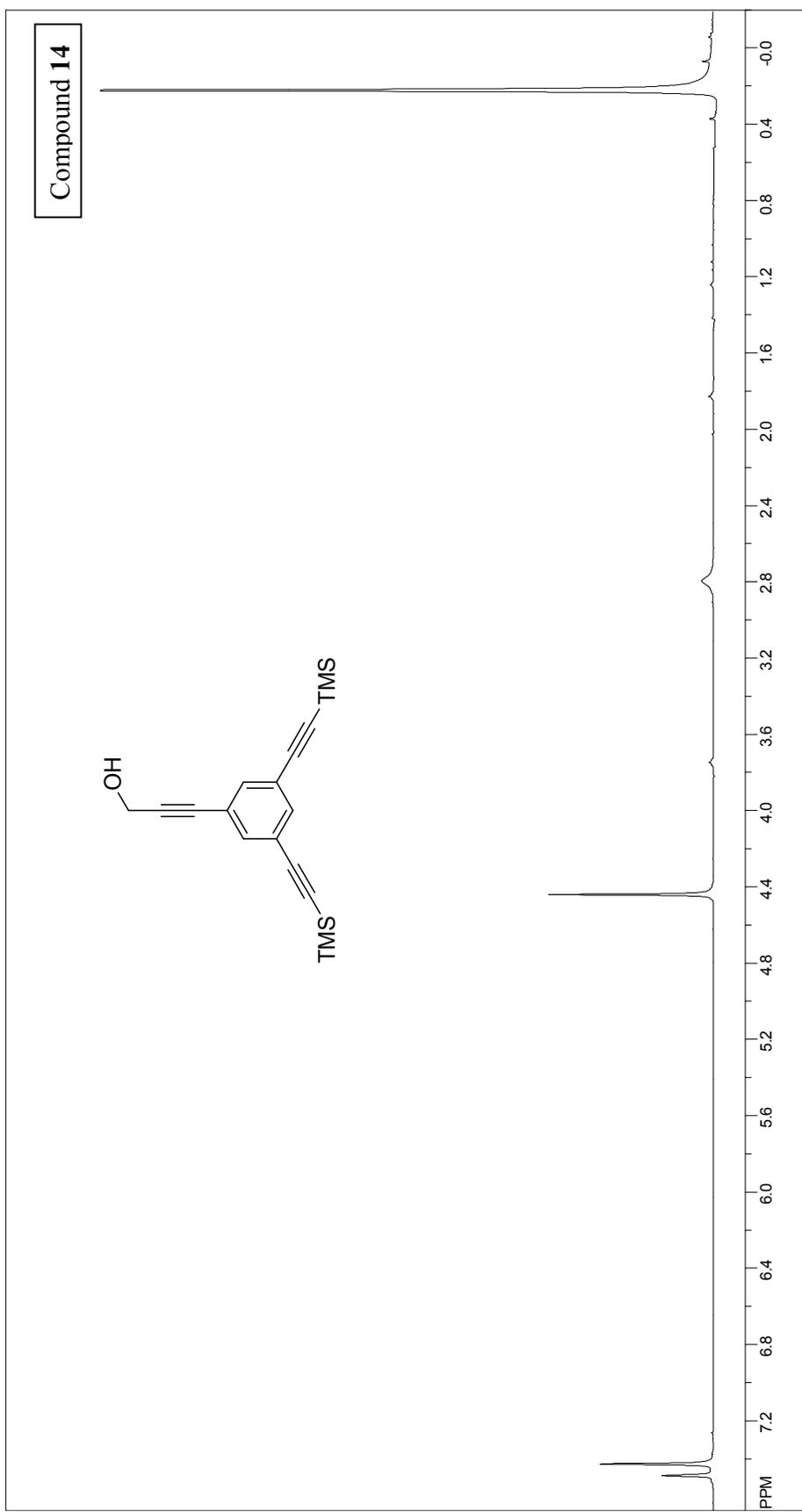


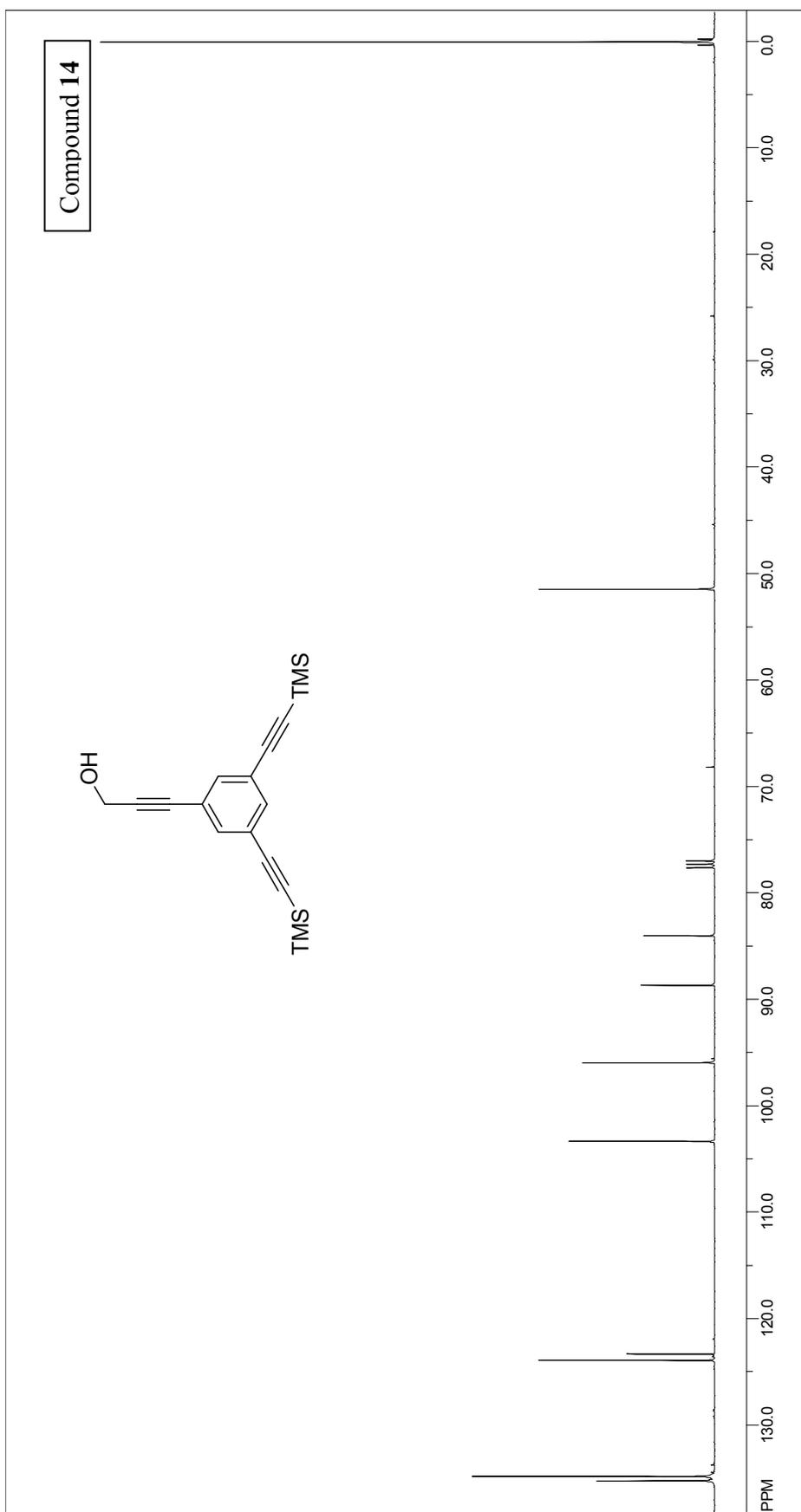




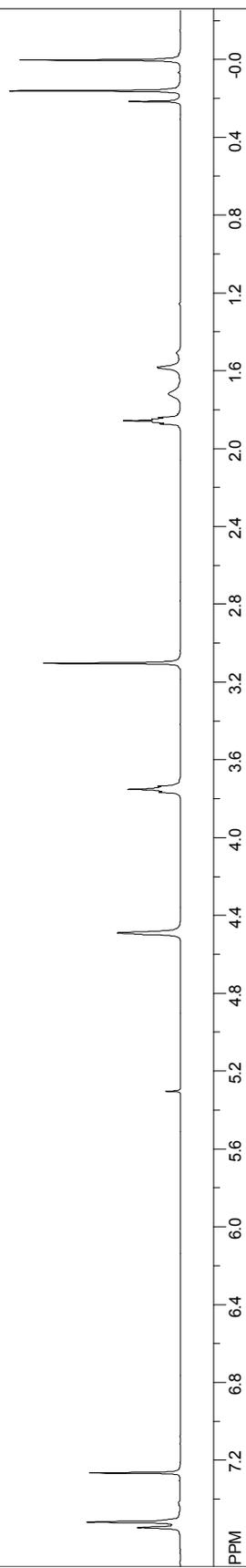
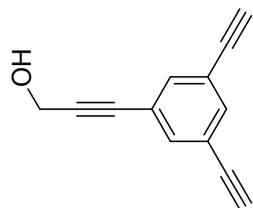




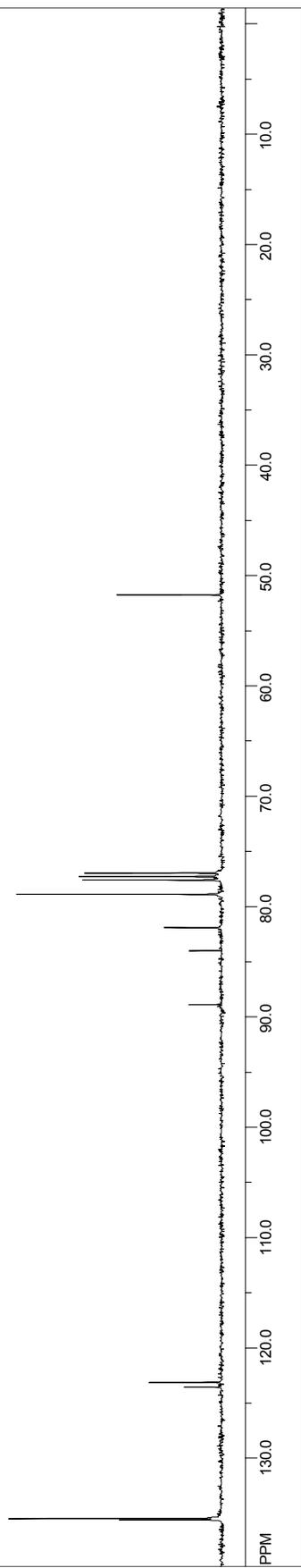
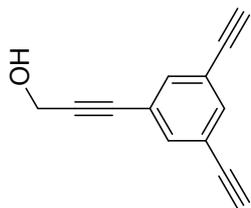




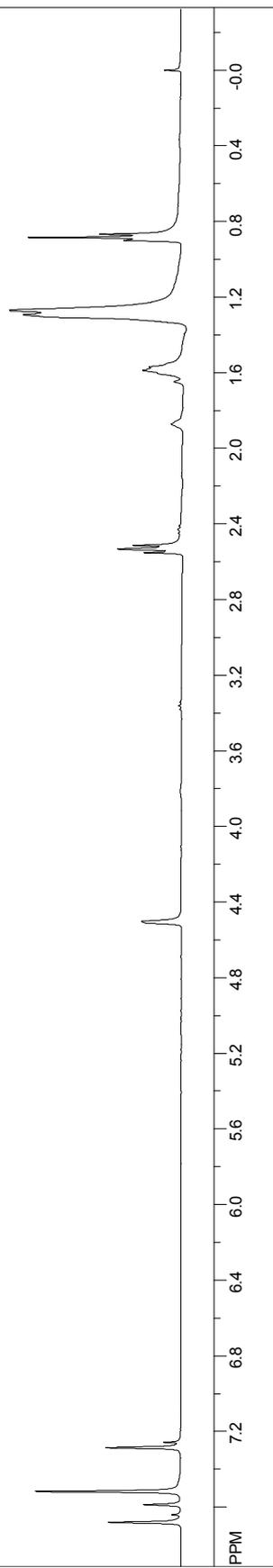
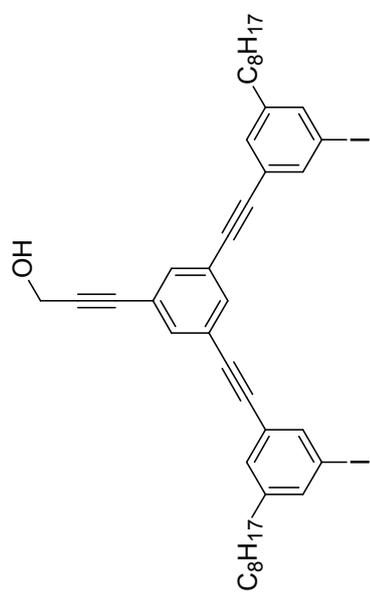
Compound **15**

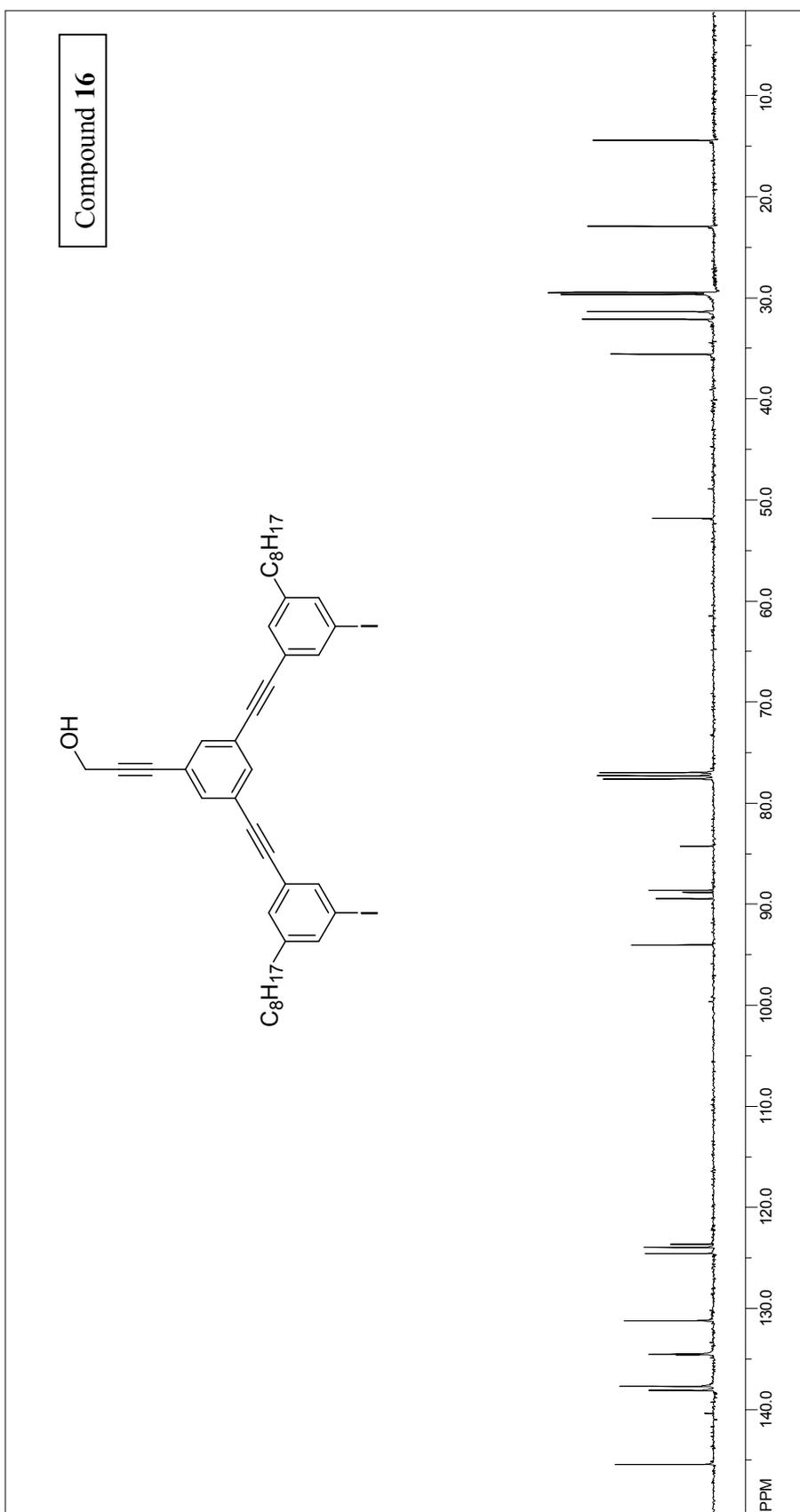


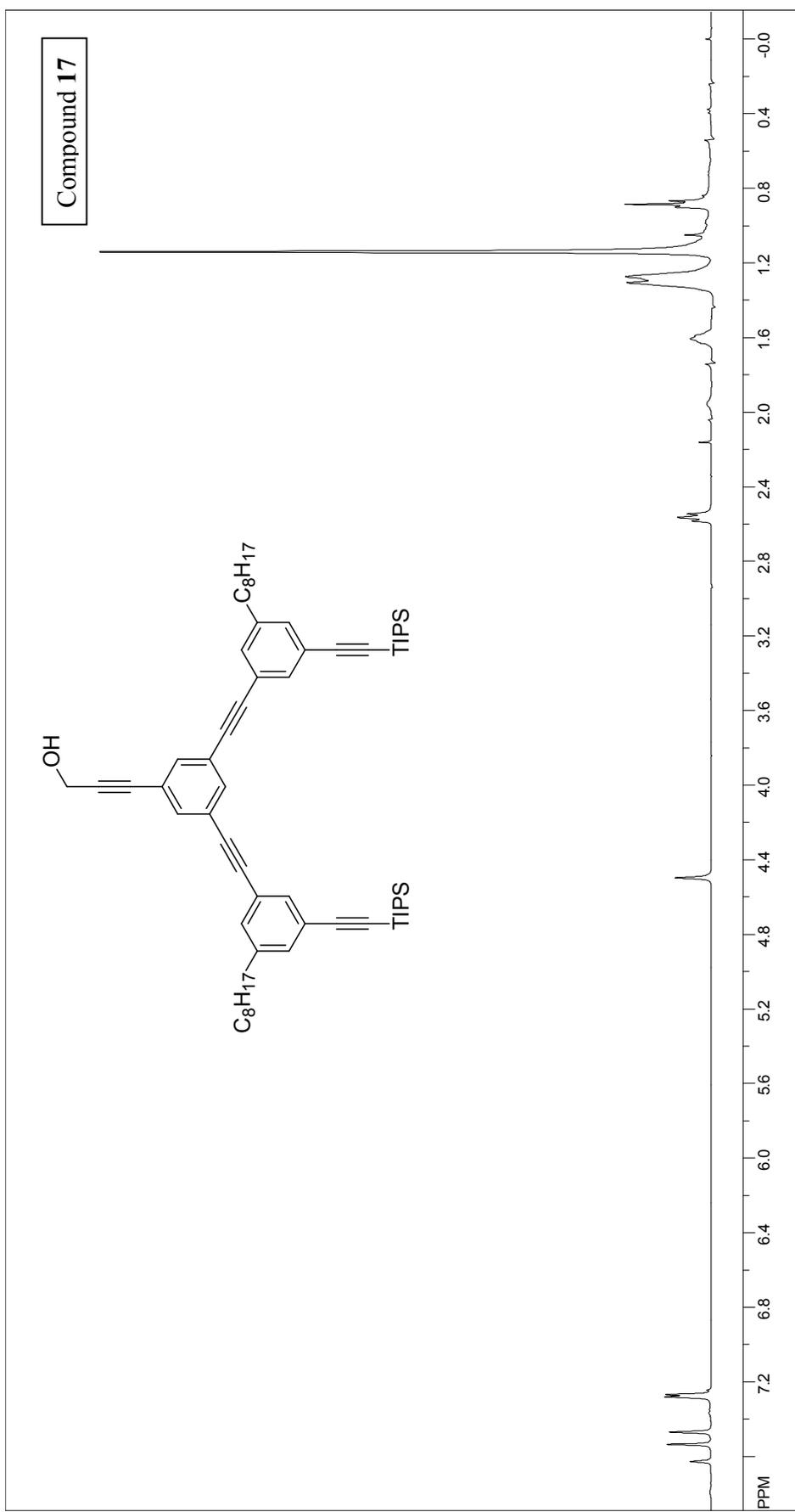
Compound 15

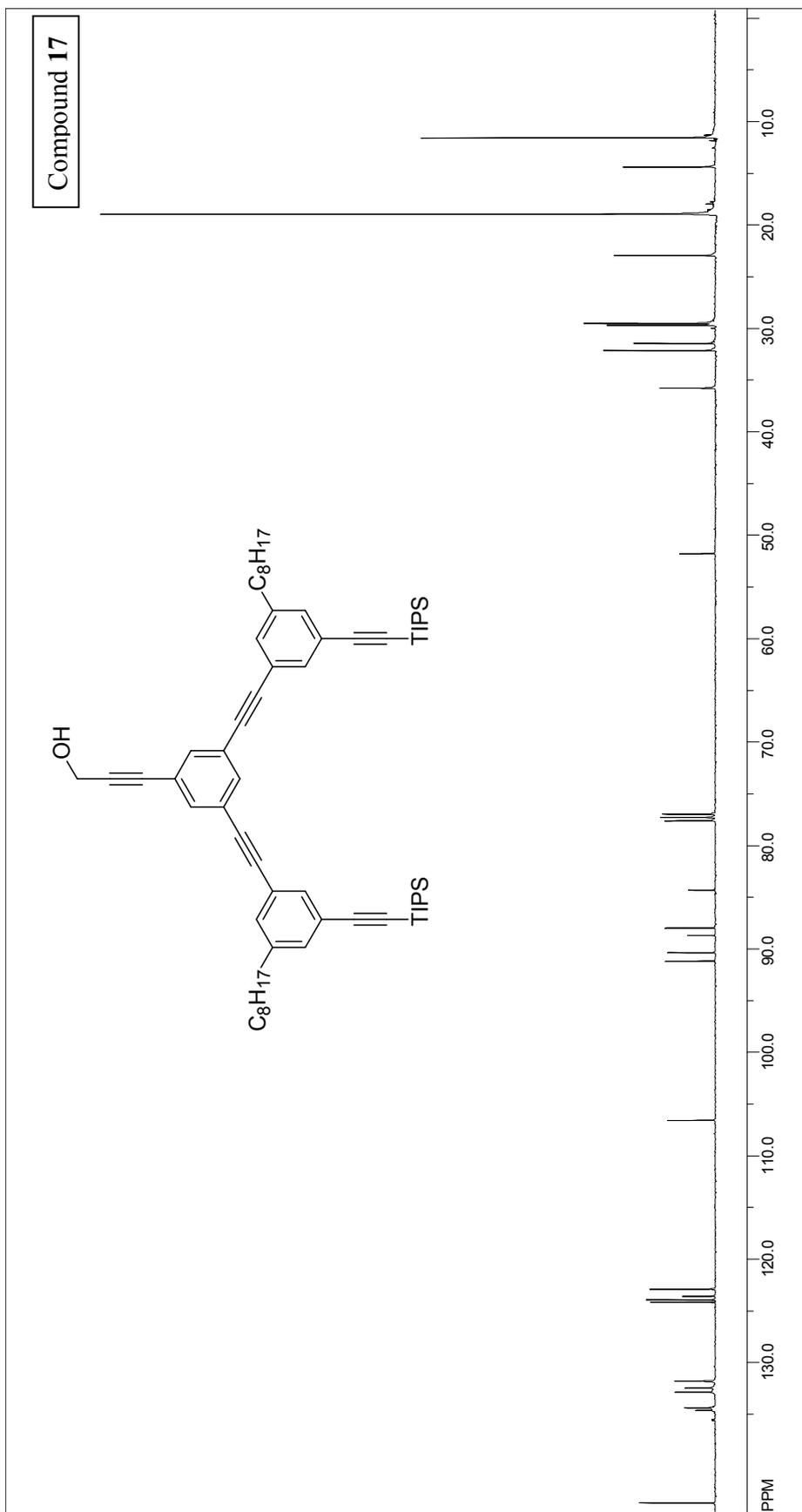


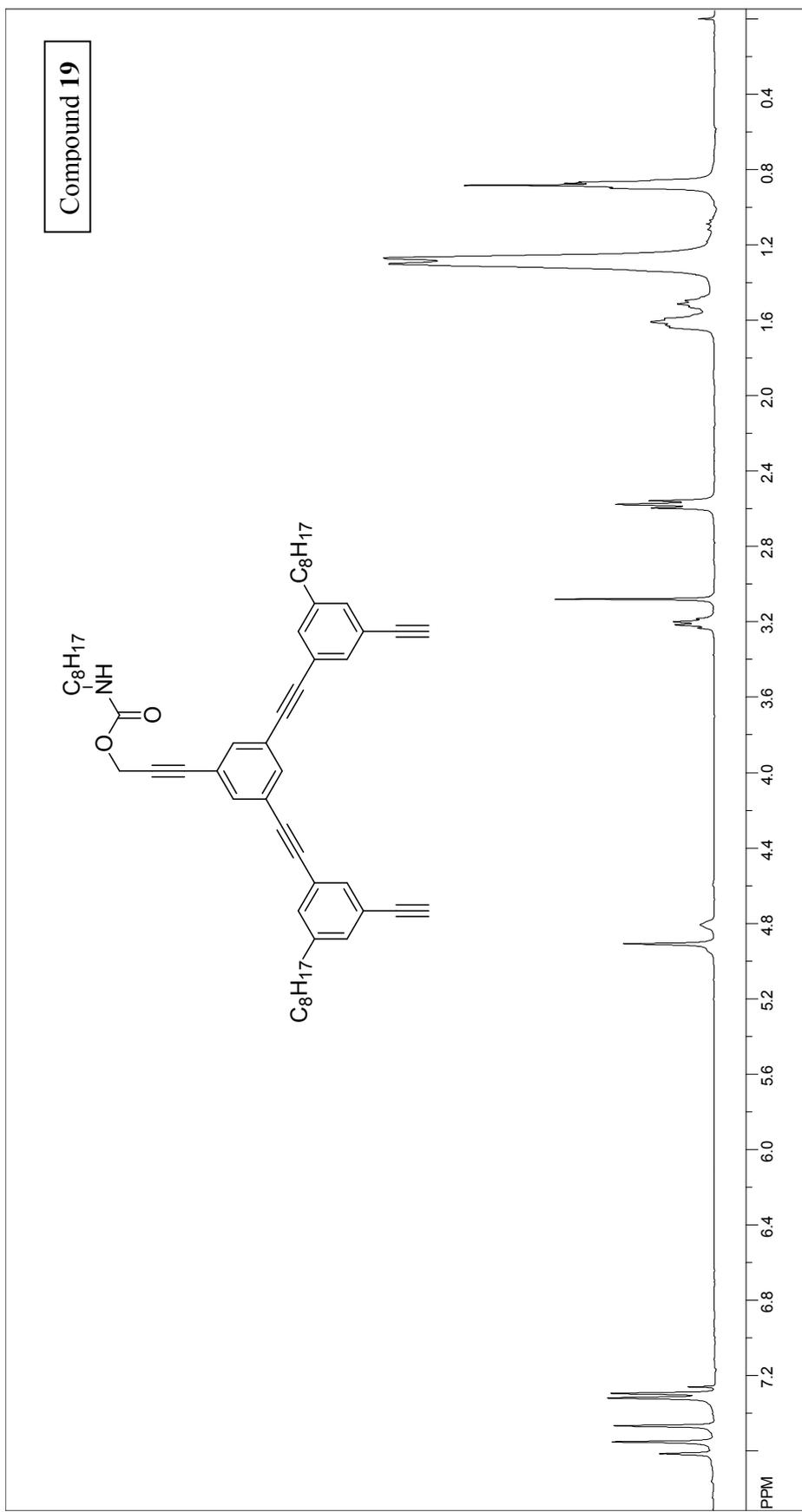
Compound 16

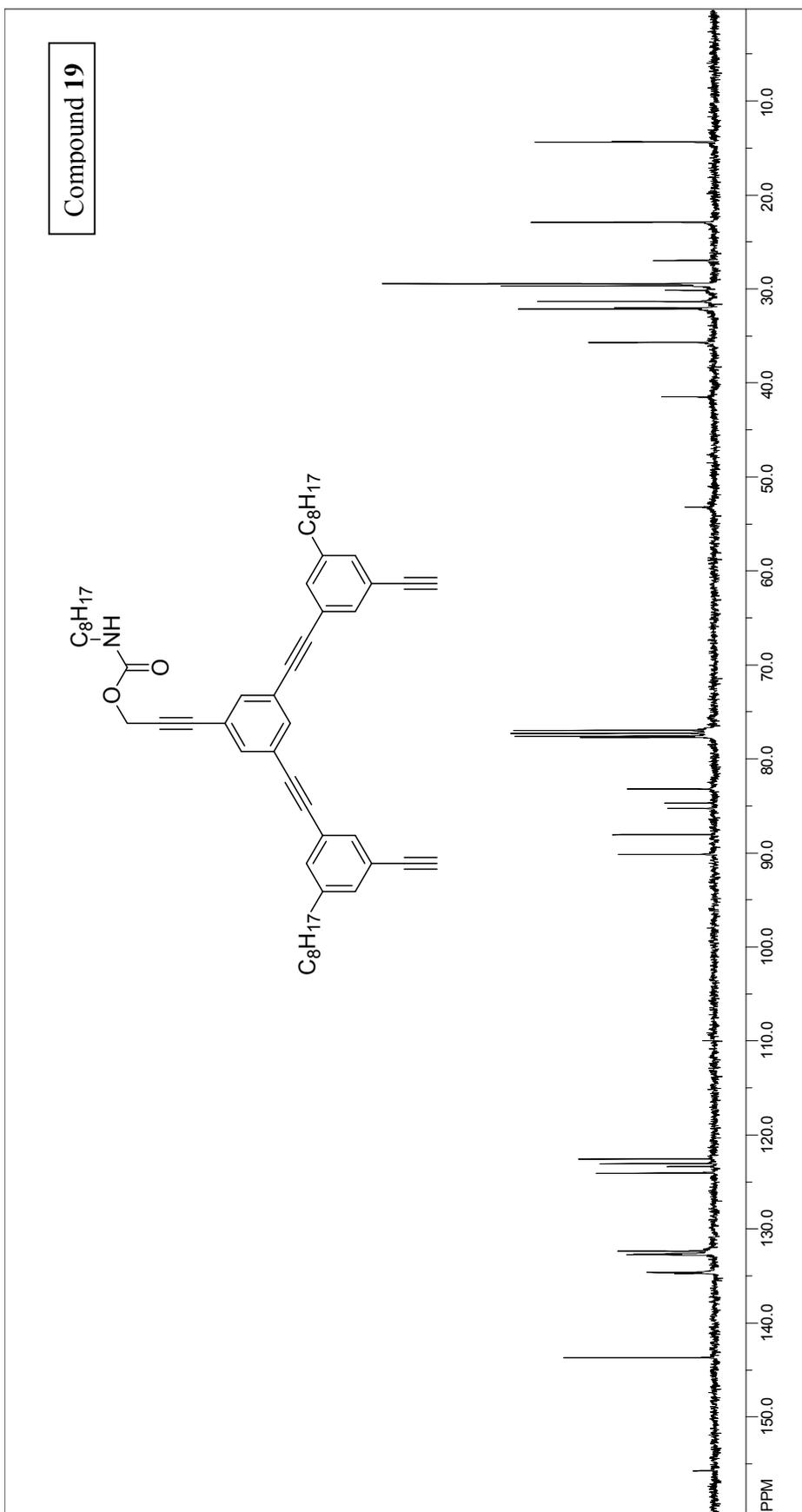


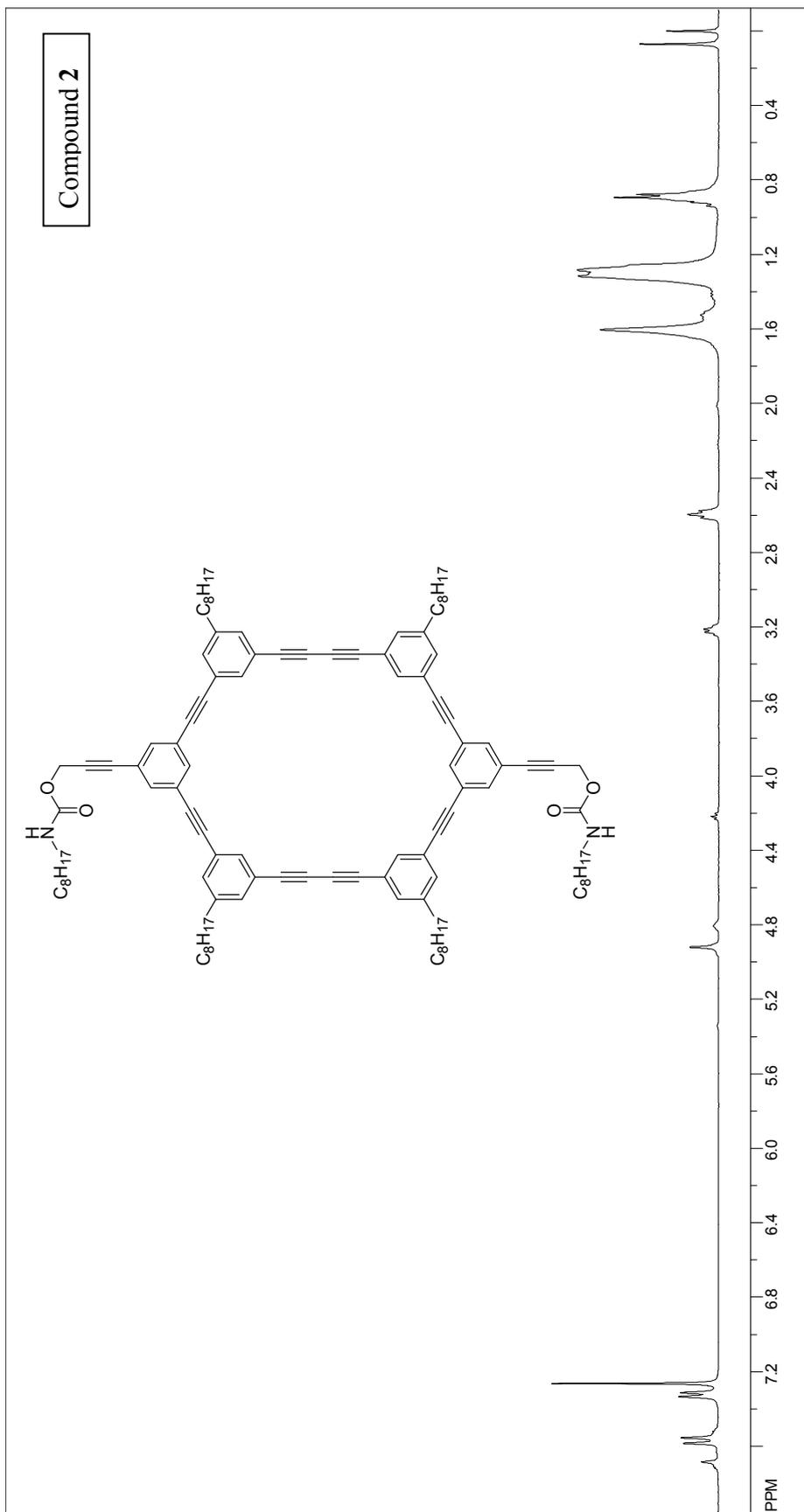


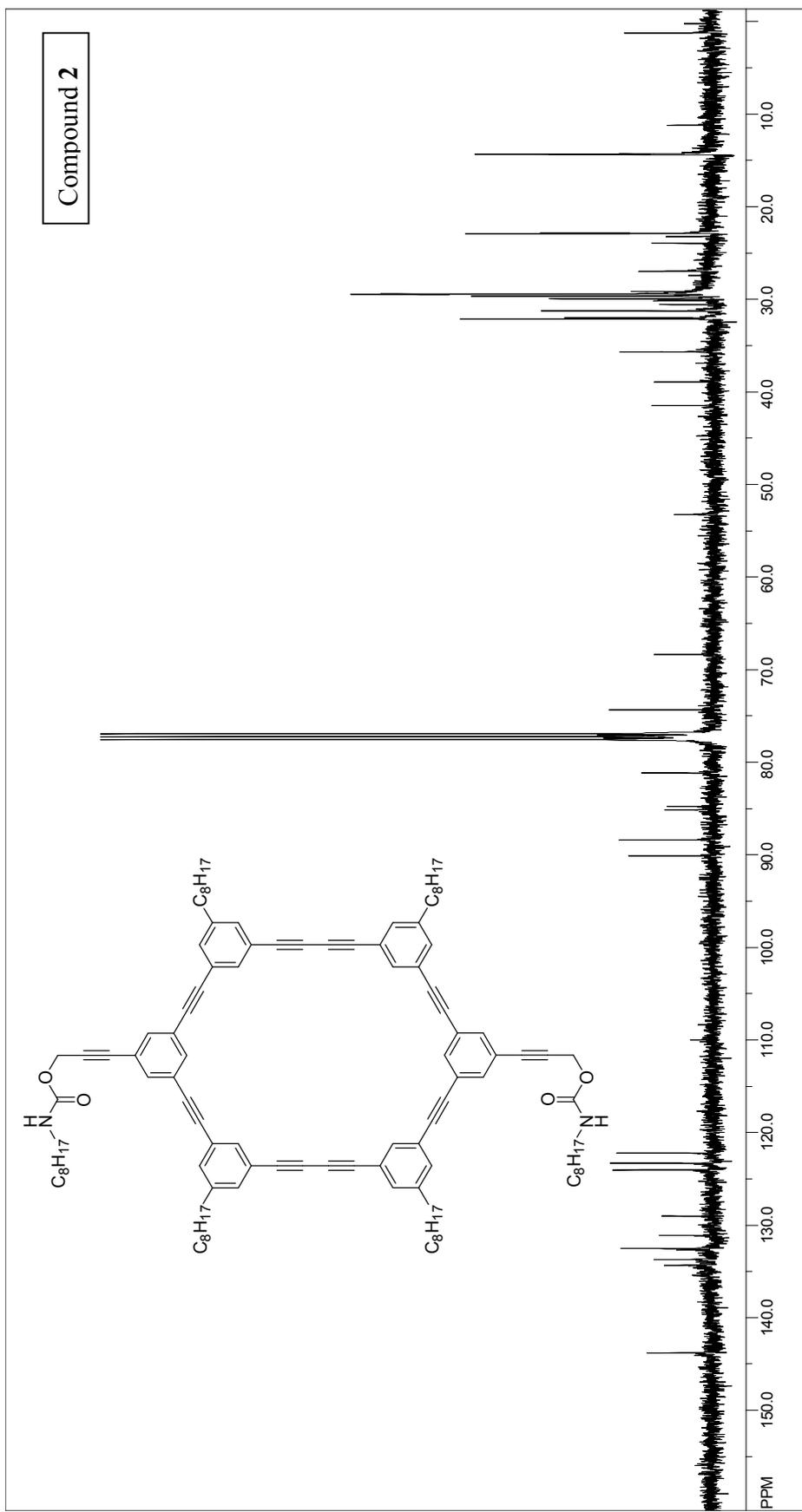












## 6. VT-FTIR spectrum of gel 1

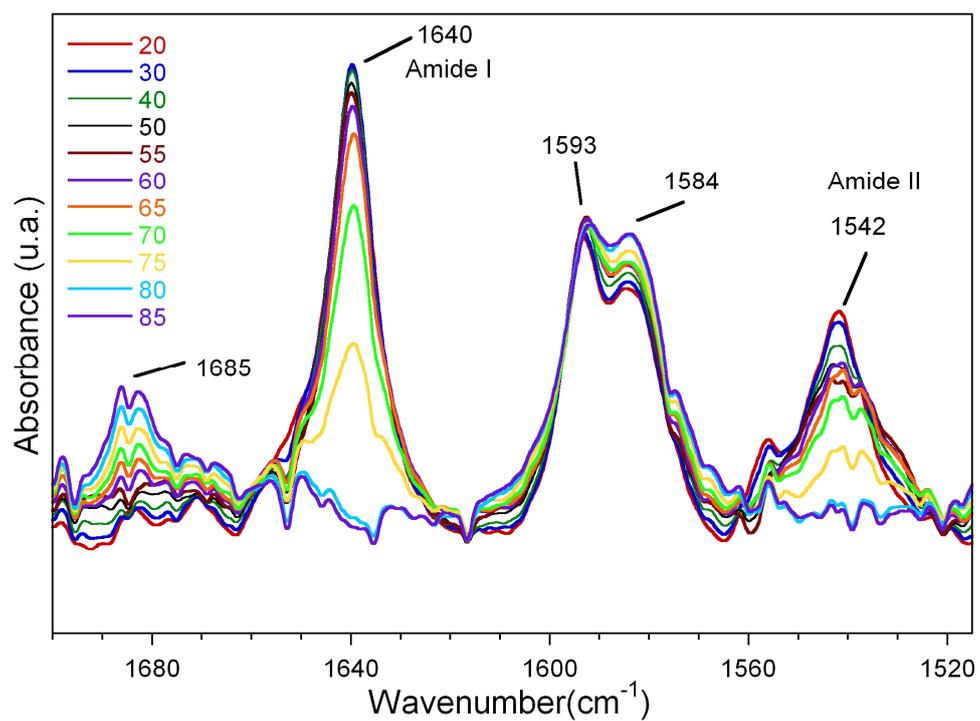


Figure S-1 : The infrared spectra of gel 1 in decalin as function of temperature.

## 7. X-Ray diffractions spectra of 1

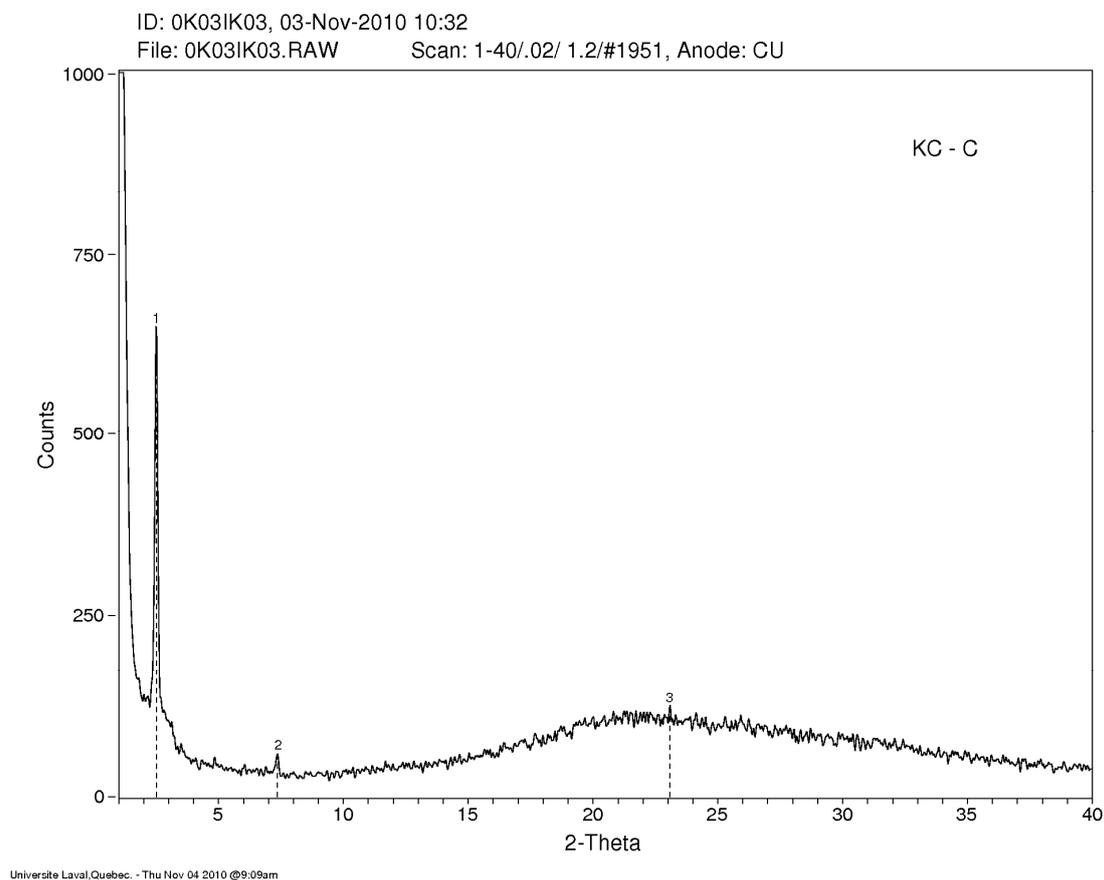


Figure S-2 : X-Ray diffraction spectrum of gel 1 in cyclohexane (10 mg/mL)

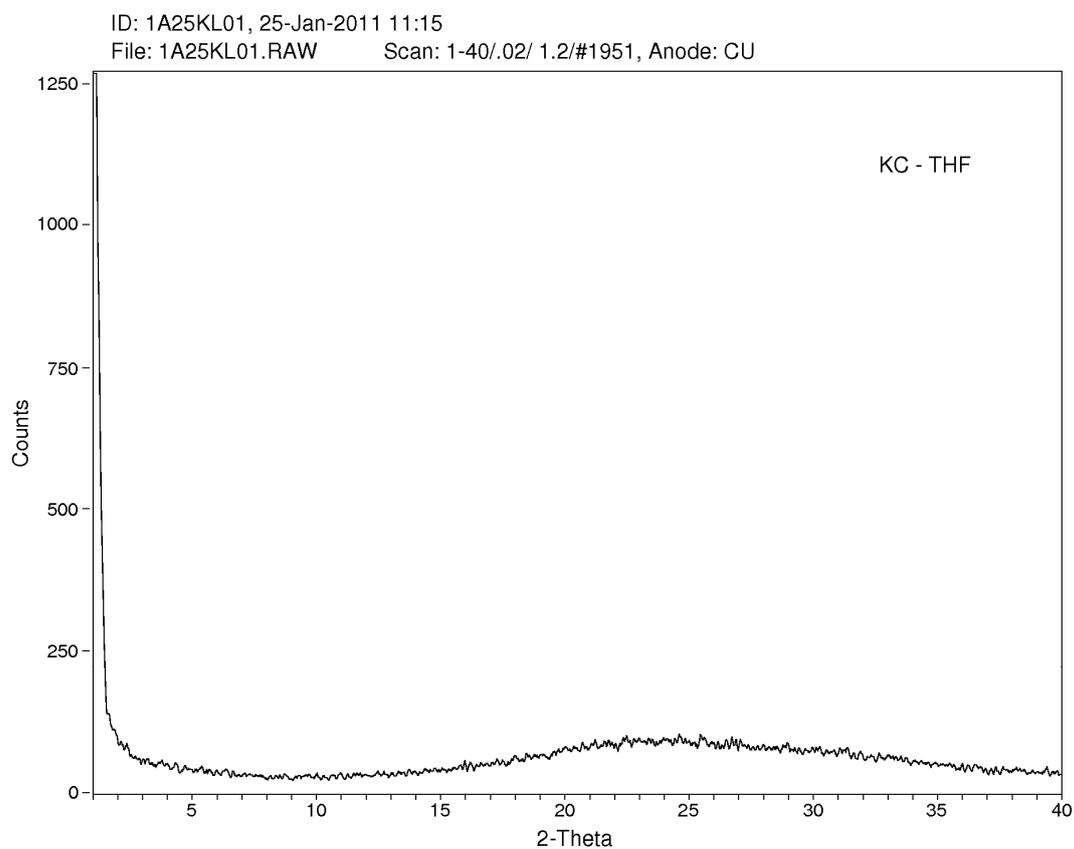


Figure S- 3: X-Ray diffraction spectrum of **1** in THF