

## Supporting Information

### Metal Free C-H Functionalization of Pyrrolidine to Pyrrolinium-based Room Temperature Ionic Liquid Crystals

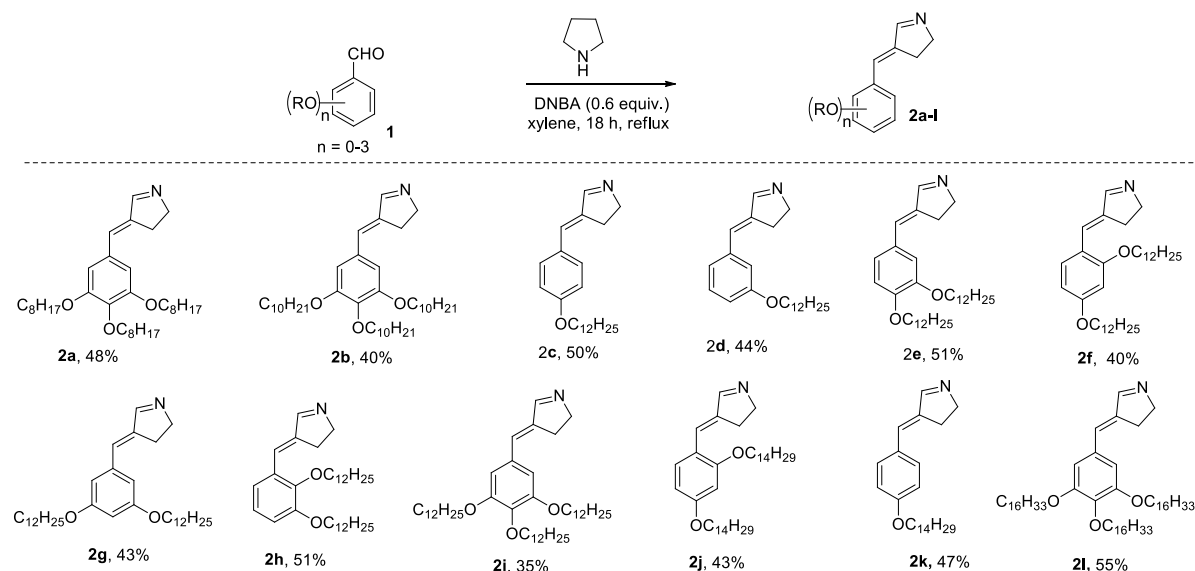
Sumana Mandal,<sup>a</sup> Ravindra Kumar Gupta,<sup>a</sup> <sup>Ψ</sup>Suraj Kumar Pathak,<sup>a,Ψ</sup> D. S. Shankar Rao,<sup>b</sup> S. Krishna Prasad,<sup>b</sup> Achalkumar Ammathnadu Sudhakar\* and Chandan K. Jana\*

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India.

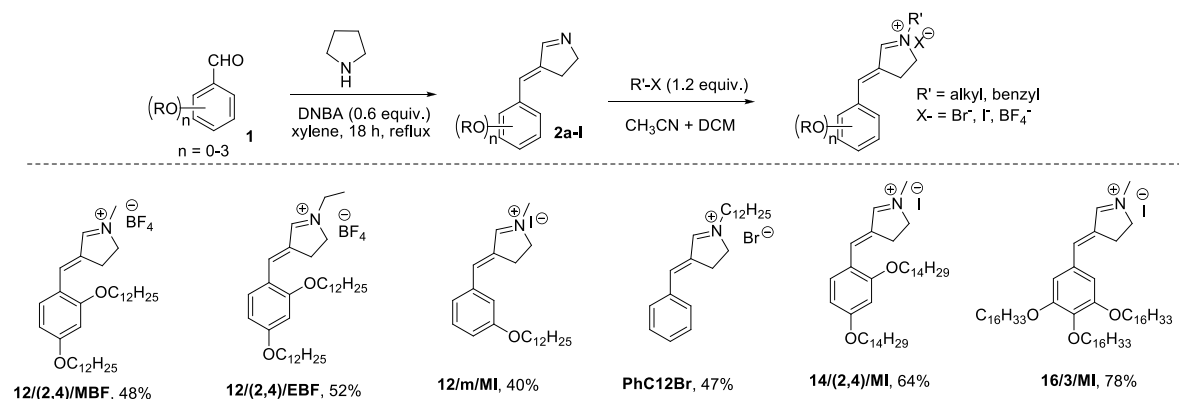
<sup>b</sup>Centre for Nano and Soft Matter Sciences (CeNS), P. B. No. 1329, Prof. U. R. Rao Road, Jalahalli, Bengaluru, 560 013, Karnataka, India

E-mail: [achalkumar@iitg.ac.in](mailto:achalkumar@iitg.ac.in), [ckjana@iitg.ac.in](mailto:ckjana@iitg.ac.in)

<sup>Ψ</sup>Equal contribution

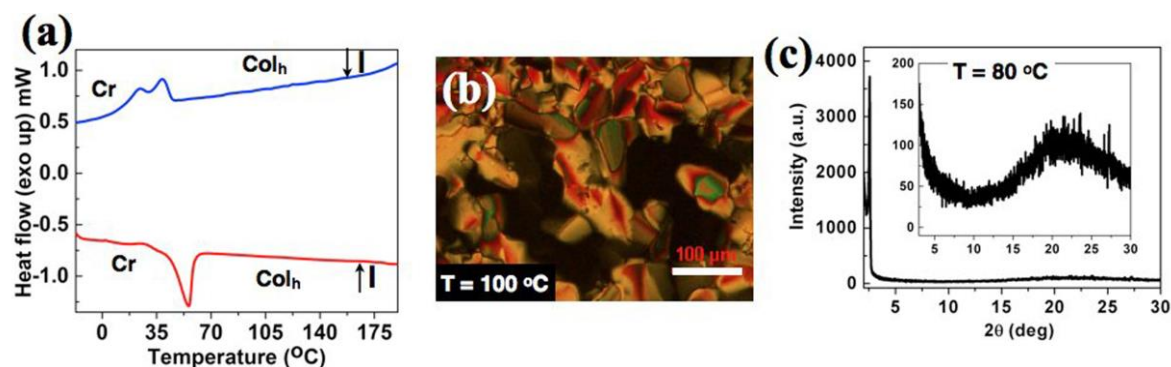


Scheme s1: Metal free direct C-H functionalization of pyrrolidine to pyrroline derivatives.

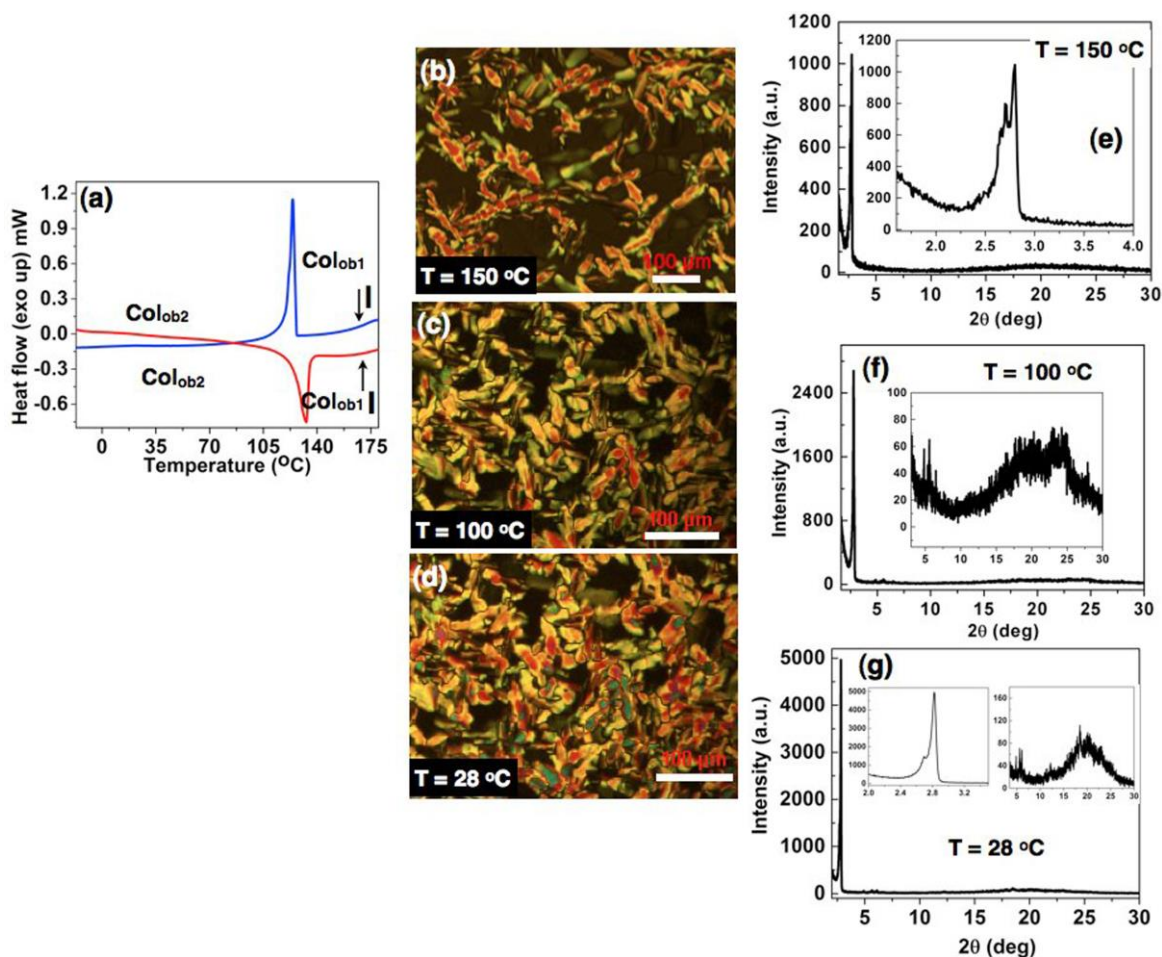


Scheme s2: Structures of additional pyrrolinium ions.

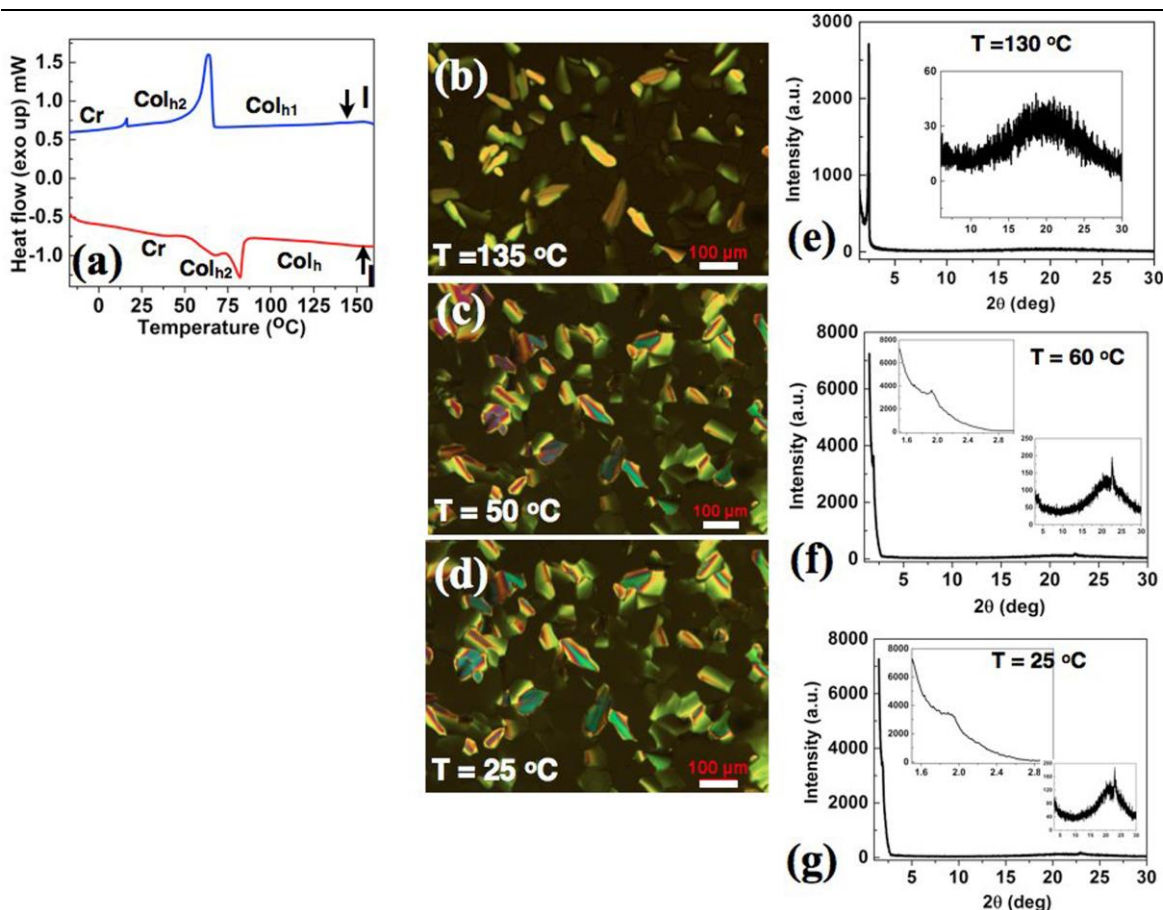
## 1. Mesomorphic behavior



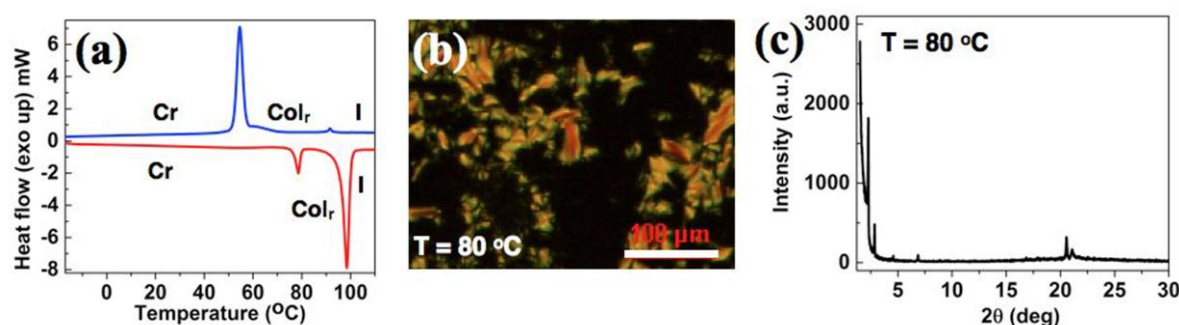
**Figure S1.** DSC scans of compound **10/3/MI** in the first cooling and second heating scans (a); POM image obtained for compound **10/3/MI** at 100 °C in  $Col_h$  phase (b); XRD profile of compound **10/3/MI** depicting the intensity vs  $2\theta$  obtained in  $Col_h$  phase at 80 °C (c). Scale bar corresponds to 100  $\mu m$ .



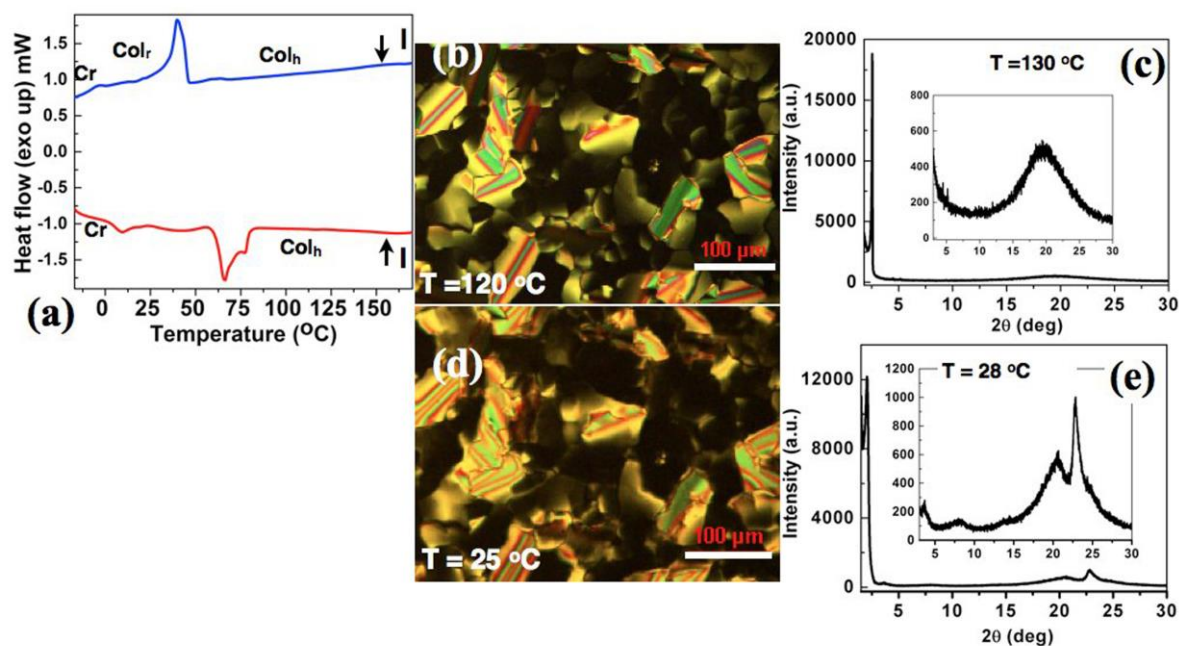
**Figure S2.** DSC scans of compound **8/3/MI** in the first cooling and second heating scans (a); POM image obtained for compound **8/3/MI** at 150 °C in  $Col_{ob1}$  phase (b); at 100 °C in  $Col_{ob2}$  phase (c); at 28 °C in  $Col_{ob2}$  phase (d); XRD profile of compound **8/3/MI** depicting the intensity vs  $2\theta$  obtained in  $Col_{ob1}$  phase at 150 °C (e);  $Col_{ob2}$  phase at 100 °C (f) and  $Col_{ob2}$  phase at 28 °C (g). Scale bar corresponds to 100  $\mu m$ .



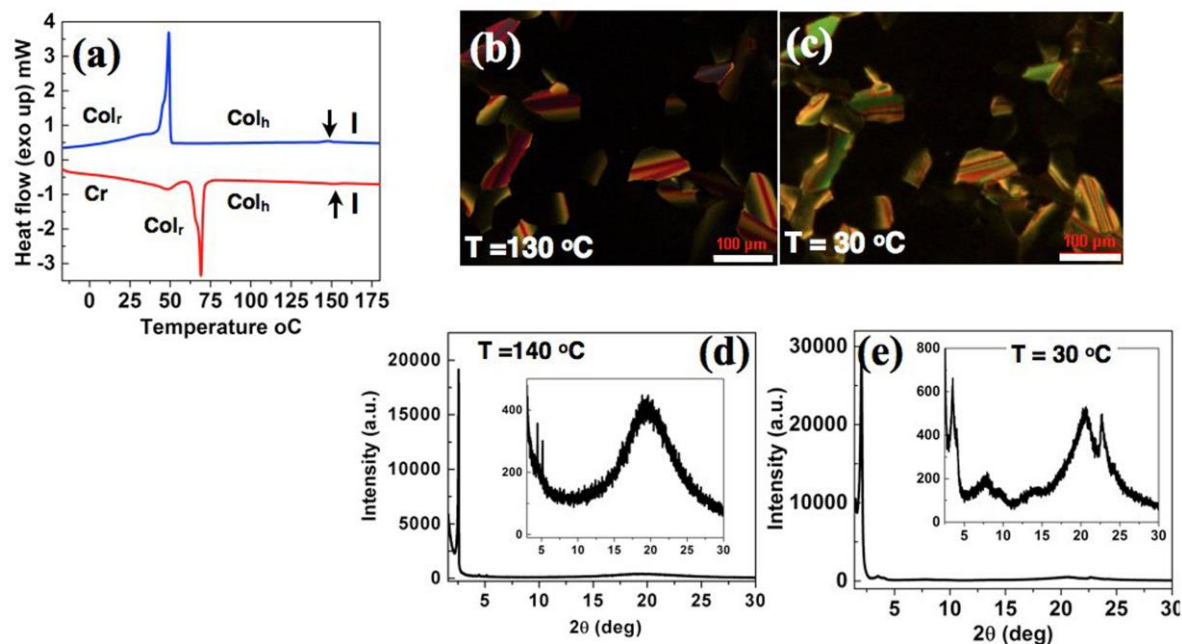
**Figure S3.** DSC scans of compound **12/3/EI** in the first cooling and second heating scans (a); POM images obtained for compound **12/3/EI** at 135 °C in Col<sub>h1</sub> phase (b); at 50 °C in Col<sub>h2</sub> phase (c); at 25 °C in Col<sub>h2</sub> phase (d); XRD profiles of compound **12/3/EI** depicting the intensity vs 2 $\theta$  obtained for Col<sub>h1</sub> phase (e); for the Col<sub>h2</sub> phase at 60 °C (e) and for the Col<sub>h2</sub> phase at 25 °C (f). Scale bar corresponds to 100  $\mu$ m.



**Figure S4.** DSC scans of compound **12/3/C12I** in the first cooling and second heating scans (a); POM image obtained for compound **12/3/C12I** at 80 °C in Col<sub>r</sub> phase (b); XRD profiles of compound **12/3/C12I** depicting the intensity vs 2 $\theta$  obtained for Col<sub>r</sub> phase at 80 °C (c). Scale bar corresponds to 100  $\mu$ m.

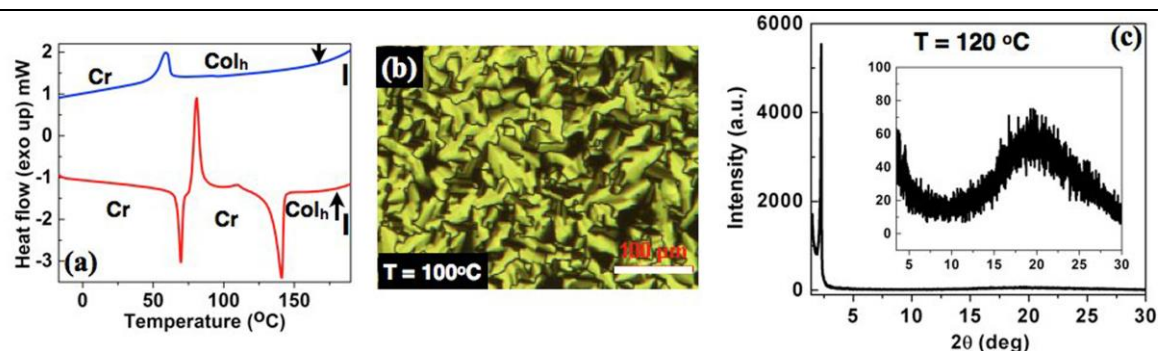


**Figure S5.** DSC scans of compound **12/3/MBF** in the first cooling and second heating scans (a); POM images obtained for compound **12/3/MBF** at 120 °C in Col<sub>h</sub> phase (b); and at 20 °C in Col<sub>r</sub> phase (c); XRD profiles of compound **12/3/MBF** depicting the intensity vs 2θ obtained for Col<sub>h</sub> phase (d) and for the Col<sub>r</sub> phase (e). Scale bar corresponds to 100 μm.

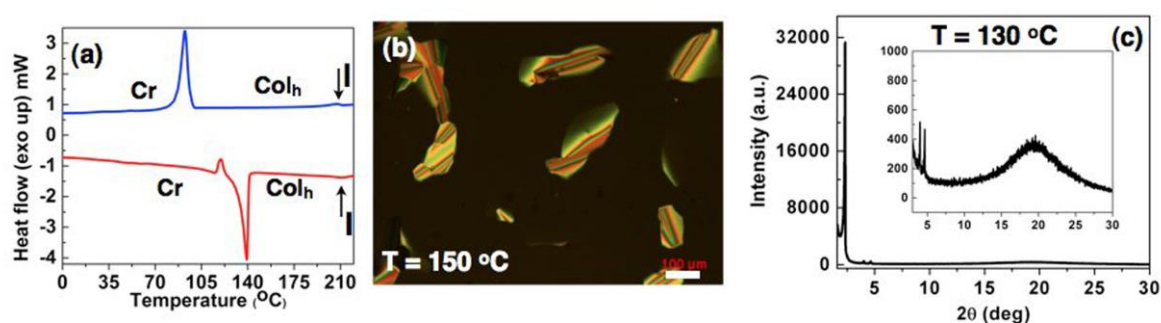


**Figure S6.** DSC scans of compound **12/3/EBF** in the first cooling and second heating scans (a); POM images obtained for compound **12/3/EBF** at 130 °C in Col<sub>h</sub> phase (b); and at 30 °C in Col<sub>r</sub> phase (c); XRD profiles of compound **12/3/EBF** depicting the intensity vs 2θ obtained for Col<sub>h</sub> phase (d) and for the Col<sub>r</sub> phase (e). Scale bar corresponds to 100 μm.

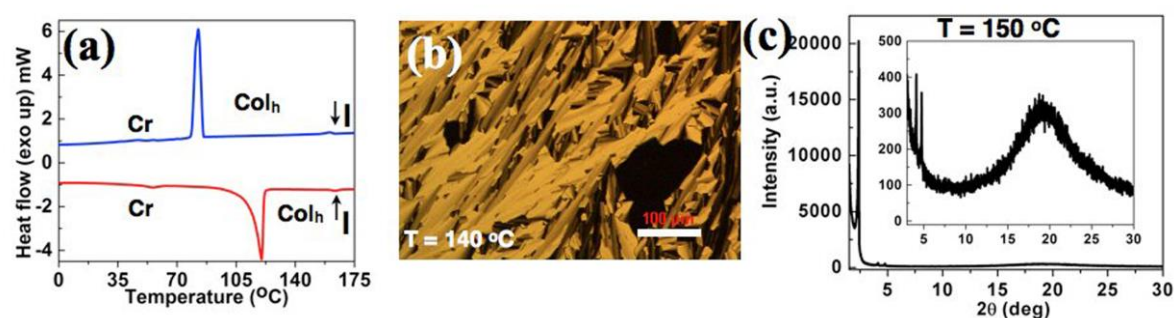




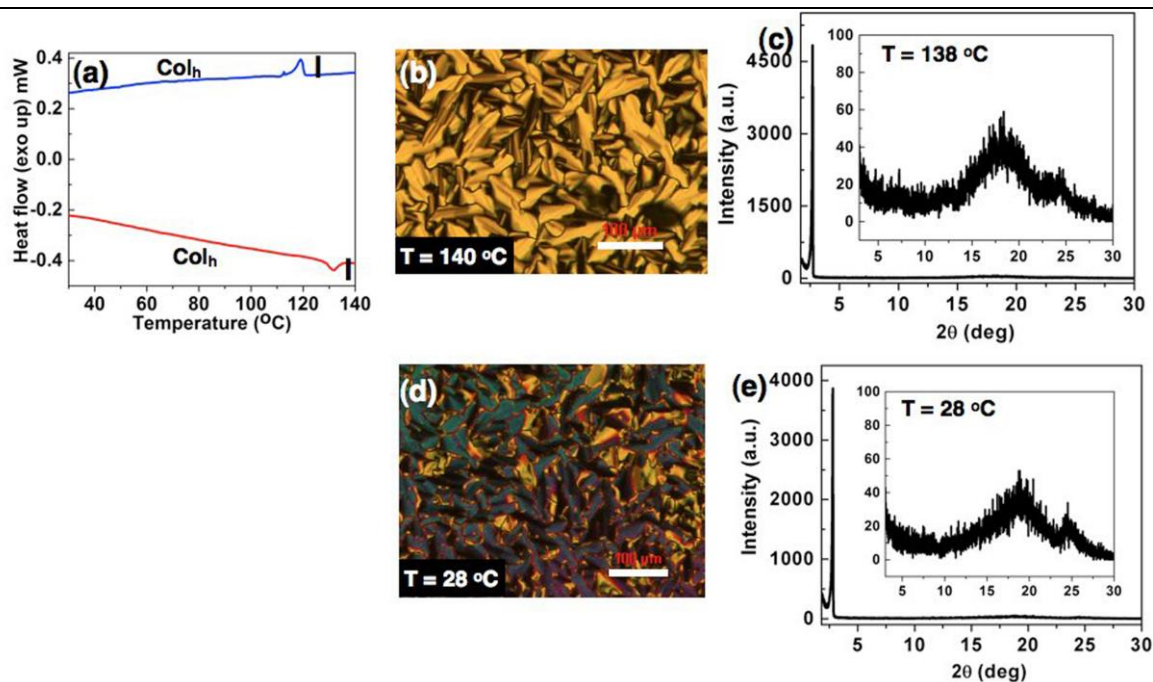
**Figure S7.** DSC scans of compound **12(3,4)/MI** in the first cooling and second heating scans (a); POM image obtained for the Sm phase of compound **12(3,4)/MI** (b); the XRD profiles of compound **12(3,4)/MI** depicting the intensity vs  $2\theta$  obtained for Col<sub>h</sub> phase (c). Scale bar corresponds to 100 μm.



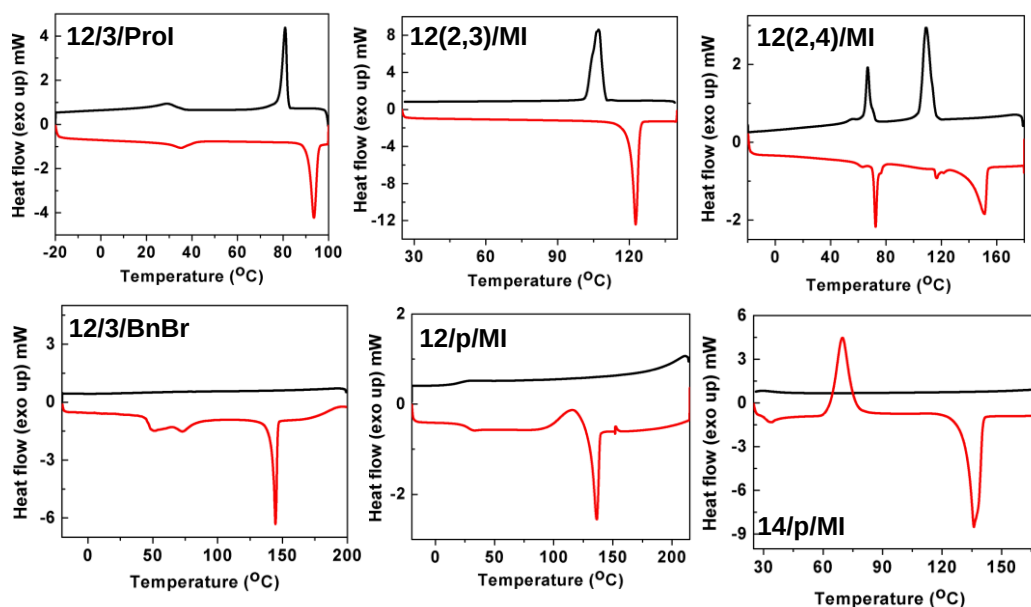
**Figure S8.** DSC scans of compound **12(3,4)/MBF** in the first cooling and second heating scans (a); POM image obtained for the Col<sub>h</sub> phase of compound **12(3,4)/MBF** at 150 °C (b); the XRD profiles of compound **12(3,4)/MBF** depicting the intensity vs  $2\theta$  obtained for Col<sub>h</sub> phase (c). Scale bar corresponds to 100 μm.



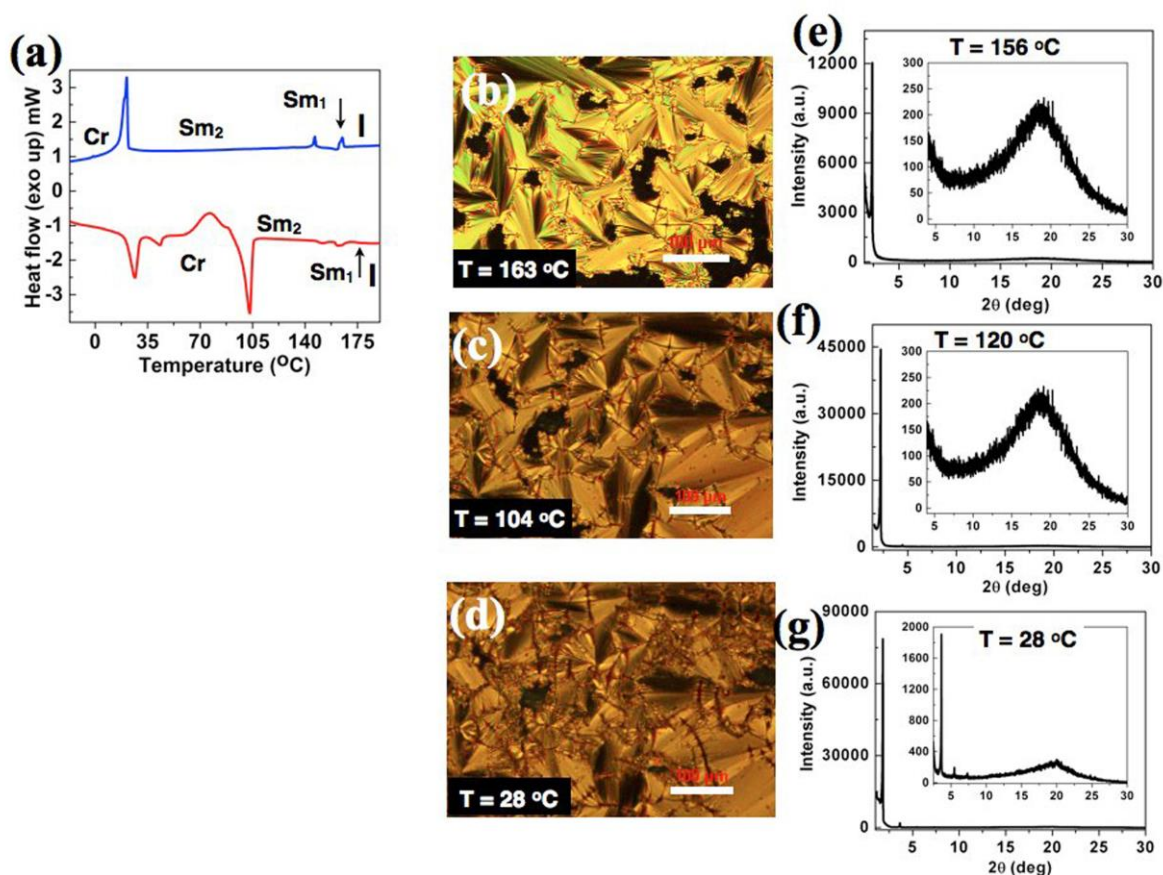
**Figure S9.** DSC scans of compound **12(3,4)/EBF** in the first cooling and second heating scans (a); POM image obtained for compound **12(3,4)/EBF** at 140 °C in Col<sub>h</sub> phase (b); XRD profile of compound **12(3,4)/EBF** depicting the intensity vs  $2\theta$  obtained for Col<sub>h</sub> phase at 150 °C (c). Scale bar corresponds to 100 μm.



**Figure S10.** DSC scans of compound **12(3,5)/MI** in the first cooling and second heating scans (a); POM image obtained for compound **12(3,5)/MI** at 140 °C (b); at 28 °C in Col<sub>h</sub> phase (c); XRD profile of compound **12(3,5)/MI** depicting the intensity vs 2θ obtained for Col<sub>h</sub> phase at 138 °C (d) and at 28 °C (e). Scale bar corresponds to 100 μm.



**Figure S11.** DSC scans of obtained for the crystalline compounds **12(3,5)/Prol**, **12(3,5)/BnBr**, **12(2,3)/MI**, **12(p)/MI**, **12(2,4)/MI** and **14(p)/MI** in the first cooling (black trace) and second heating (red trace) scans.



**Figure S12.** DSC scans of compound **12/p/EBF** in the first cooling and second heating scans (a); POM image obtained for compound **12/p/EBF** at 156 °C in Sm<sub>1</sub> phase (b); at 120 °C (c); at 28 °C in Sm<sub>2</sub> phase (d); XRD profile of compound **12/p/EBF** depicting the intensity vs 2θ obtained in Sm<sub>1</sub> phase at 156 °C (e); in Sm<sub>1</sub> phase at 120 °C (f) and in Sm<sub>2</sub> phase at 28 °C (g). Scale bar corresponds to 100 μm.

**Table S1.** Results of (*hkl*) indexation of the XRD profiles of ionic LCs at a given temperature (*T*) of the mesophases<sup>a</sup>

| Entry/<br>Molecular length<br>(Å) | Phase<br>(T/°C)           | <i>d</i> <sub>obs</sub> (Å)                                                     | <i>d</i> <sub>cal</sub> (Å) | Miller<br>indices<br>( <i>hk</i> ) | Lattice parameters (Å)                                                                                   |
|-----------------------------------|---------------------------|---------------------------------------------------------------------------------|-----------------------------|------------------------------------|----------------------------------------------------------------------------------------------------------|
| <b>12/3/MI</b><br>24.99           | 130<br>Col <sub>h</sub>   | 35.08<br>4.37 ( <i>h<sub>a</sub></i> )                                          | 35.08                       | 10                                 | <i>a</i> = 40.50; <i>c</i> = 4.37; <i>S</i> = 1230.5; <i>V</i> = 5376.6; <i>Z</i> = 3.8. <sup>b</sup>    |
|                                   | 28<br>Col <sub>r</sub>    | 40.98<br>20.37<br>4.44<br>3.73                                                  | 40.98<br>20.37              | 01<br>10                           | <i>a</i> = 40.98; <i>b</i> = 20.37; <i>S</i> = 834.8; <i>c</i> = 3.73; <i>V</i> = 3117.6; <i>Z</i> = 2.2 |
| <b>10/3/MI</b><br>22.6            | 80<br>Col <sub>h</sub>    | 34.54<br>4.07<br>3.78 ( <i>h<sub>a</sub></i> )<br>3.27 ( <i>h<sub>c</sub></i> ) | 34.54                       | 10                                 | <i>a</i> = 39.88; <i>S</i> = 1193.1; <i>c</i> = 3.27; <i>V</i> = 3905.8; <i>Z</i> = 3.1.                 |
| <b>8/3/MI</b><br>20               | 150<br>Col <sub>ob1</sub> | 33.35                                                                           | 33.35                       | 01                                 | <i>a</i> = 38.68; <i>b</i> = 40.55; <i>γ</i> = 55.3°                                                     |
|                                   |                           | 31.82                                                                           | 31.82                       | 10                                 |                                                                                                          |
|                                   |                           | 18.38                                                                           | 18.39                       | 11                                 |                                                                                                          |

|                          |                           |                                                                                              |                                                                  |                                              |                                                                                                    |
|--------------------------|---------------------------|----------------------------------------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------------|----------------------------------------------------------------------------------------------------|
|                          |                           | 15.87<br>4.17 ( $h_a$ )                                                                      | 15.91                                                            | 20                                           | $S = 1290.3$ , $V = 5383.8$ ,<br>$Z = 4.7^b$                                                       |
|                          | 100<br>Col <sub>ob2</sub> | 31.86<br>30.92<br>18.35<br>15.85<br>4.72 ( $h_a$ )<br>3.71 ( $h_c$ )                         | 31.86<br>30.92<br>18.35<br>15.93                                 | 10<br>01<br>11<br>20                         | $a = 35.94$ , $b = 34.88$ ,<br>$\gamma = 62.4^\circ$<br>$S = 1111.2$ , $V = 5242.5$ ,<br>$Z = 4.6$ |
|                          | 28<br>Col <sub>ob2</sub>  | 31.31<br>18.08<br>15.70<br>14.49<br>7.25<br>4.81<br>4.47                                     | 31.31<br>18.08<br>15.65<br>14.49<br>7.25                         | 11<br>01<br>22<br>10<br>20                   | $a = 31.91$ , $b = 39.81$ ,<br>$\gamma = 27^\circ$<br>$S = 576.92$ , $V = 4185.5$ ,<br>$Z = 3.7$   |
| <b>12/3/EI</b><br>26.2   | 130<br>Col <sub>h1</sub>  | 35.48<br>4.43 ( $h_a$ )                                                                      | 35.48                                                            | 10                                           | $a = 40.97$ ; $S = 1259$ ; $c = 4.43$ ;<br>$V = 5575.9$ ; $Z = 3.9$ . <sup>b</sup>                 |
|                          | 60<br>Col <sub>h2</sub>   | 45.60<br>4.14 ( $h_a$ )<br>3.94 ( $h_c$ )                                                    | 45.60                                                            | 10                                           | $a = 52.7$ , $S = 2401$ , $c = 3.94$ ;<br>$V = 9460$ , $Z = 6.6$                                   |
|                          | 25<br>Col <sub>h2</sub>   | 46.02<br>4.10 ( $h_a$ )<br>3.87 ( $h_c$ )                                                    | 46.02                                                            | 10                                           | $a = 53.1$ ; $S = 2117.4$ ; $c = 3.87$ ;<br>$V = 8192.4$ ; $Z = 5.7$                               |
| <b>12/3/C12I</b><br>38.4 | 80<br>Col <sub>r</sub>    | 38.82<br>30.90<br>19.34<br>12.88<br>9.94<br>5.26<br>4.32<br>4.21 ( $h_a$ )<br>4.15 ( $h_c$ ) | 38.82<br>30.90<br>19.41<br>12.94<br>9.92<br>5.22<br>4.30<br>4.18 | 01<br>10<br>02<br>03<br>23<br>27<br>72<br>73 | $a = 30.9$ ; $b = 38.82$ ; $S = 1199.5$ ;<br>$c = 4.32$ ; $V = 4977.8$ ; $Z = 3.0$                 |
| <b>12/3/MBF</b><br>25.1  | 130<br>Col <sub>h1</sub>  | 34.38<br>19.78<br>17.10<br>4.51 ( $h_a$ )                                                    | 34.38<br>19.85<br>17.19                                          | 10<br>11<br>20                               | $a = 39.70$ ; $S = 1182.2$ ; $c = 4.51$ ;<br>$V = 5327.3$ ; $Z = 4.0$ . <sup>b</sup>               |
|                          | 28<br>Col <sub>r</sub>    | 43.0<br>23.99<br>11.06<br>4.32<br>3.89                                                       | 43.01<br>23.99<br>11.55<br>3.64                                  | 01<br>10<br>21                               | $a = 23.99$ ; $b = 43.01$ $c = 3.89$ ;<br>$S = 1031.8$ ; $V = 4017.2$ ;<br>$Z = 3.0$               |
| <b>12/3/EBF</b><br>25.1  | 140<br>Col <sub>h</sub>   | 34.52<br>19.86<br>17.17<br>4.51 ( $h_a$ )                                                    | 34.52<br>19.93<br>17.26                                          | 10<br>11<br>20                               | $a = 39.86$ ; $S = 1191.8$ ; $c = 4.51$ ;<br>$V = 5375.7$ ; $Z = 3.9$ . <sup>b</sup>               |
|                          | 30<br>Col <sub>r</sub>    | 43.46<br>25.03<br>11.28                                                                      | 43.46<br>25.03<br>10.87                                          | 01<br>11<br>04                               | $a = 30.62$ ; $b = 43.46$ ; $S = 1330.7$ ;                                                         |



|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                                         |      |    |                                          |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|-----------------------------------------|------|----|------------------------------------------|
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  | 9.34<br>4.3 ( $h_a$ )<br>3.91 ( $h_c$ ) | 9.24 | 32 | $c = 3.91$ ; $V = 5203.2$ ; $Z = 3.79$ . |
| <sup>a</sup> The length ( $L$ ) of the molecule (estimated from the Chem 3D 17 molecular model software from Cambridge Soft). $d_{\text{obs}}$ : spacing observed; $d_{\text{cal}}$ : spacing calculated (deduced from the lattice parameters; $a$ for Col <sub>h</sub> phase, $a$ and $b$ for Col <sub>r</sub> phase). The spacings marked $h_a$ and $h_c$ correspond to the diffused reflections in the wide-angle region arising from correlations between the alkyl chains and core regions, respectively. $Z$ indicates the number of molecules per columnar slice of thickness $h_c$ , estimated from the lattice area $S$ and the volume $V$ . <sup>b</sup> In the absence of the core–core peak, the spacing of the alkyl chain stacking ( $h_a$ ) is used in these calculations. |  |                                         |      |    |                                          |

**Table S2.** Results of ( $hkl$ ) indexation of the XRD profiles of ionic LCs at a given temperature ( $T$ ) of the mesophases<sup>a</sup>

| Entry/<br>Molecular length (Å) | Phase<br>(T/°C)                           | $d_{\text{obs}}$<br>(Å)                         | $d_{\text{cal}}$ (Å)    | Miller<br>indices<br>( $hk$ ) | Lattice parameters (Å)                                                |
|--------------------------------|-------------------------------------------|-------------------------------------------------|-------------------------|-------------------------------|-----------------------------------------------------------------------|
| <b>12(3,4)/MI</b><br>25.9      | 120<br>Col <sub>h</sub>                   | 39.13<br>19.46<br>4.41<br>( $h_a$ )             | 39.13<br>19.57          | 10<br>20                      | $a = 45.19$ , $c = 4.41$ , $S = 1531.4$ ,<br>$V = 6749.4$ , $Z = 7.5$ |
| <b>12(3,4)/MBF</b><br>25.7     | 130<br>Col <sub>h</sub>                   | 38.30<br>22.03<br>19.06<br>4.56<br>( $h_a$ )    | 38.30<br>22.11<br>19.15 | 10<br>11<br>20                | $a = 44.22$ ; $S = 1466.7$ ; $c = 4.56$<br>$V = 6689.3$ ; $Z = 6.4$   |
| <b>12(3,4)/EBF</b><br>25.8     | 150<br>Col <sub>h</sub>                   | 37.42<br>21.54<br>18.63<br>4.59                 | 37.43<br>21.61<br>18.71 | 10<br>11<br>20                | $a = 43.21$ ; $S = 1400.6$ ; $c = 4.59$<br>$V = 6437.1$ ; $Z = 6$     |
| <b>12(3,5)/MI</b><br>24.7      | 138<br>Col <sub>h</sub>                   | 32.50<br>4.88<br>( $h_a$ )<br>3.66<br>( $h_c$ ) | 32.50                   | 10                            | $a = 37.57$ ; $S = 1056$ ; $c = 3.66$<br>$V = 3868.2$ ; $Z = 3.5$     |
|                                | 28<br>Col <sub>h</sub>                    | 31.64<br>4.74<br>( $h_a$ )<br>3.58<br>( $h_c$ ) | 31.64                   | 10                            | $a = 36.58$ ; $S = 1001.1$ ; $c = 3.58$<br>$V = 3584.2$ ; $Z = 3.2$   |
| <b>12/p/EBF</b><br>27          | 156<br>Sm <sub>1</sub>                    | 37.18<br>4.72<br>( $h_a$ )                      |                         |                               | $d/L = 1.4$                                                           |
|                                | 120<br>Sm <sub>2</sub><br>Ratio:<br>1:0.5 | 39.62<br>19.71<br>4.70<br>( $h_a$ )             |                         |                               | $d/L = 1.5$                                                           |
|                                | 28<br>Sm <sub>2</sub>                     | 48.83<br>24.23<br>16.12                         |                         |                               | $d/L = 1.8$                                                           |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                   |                                                 |  |  |  |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|-------------------------------------------------|--|--|--|
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | Ratio:<br>1:0.5:<br>0.33:0.2<br>5 | 12.07<br>4.64<br>( $h_a$ )<br>4.44<br>( $h_c$ ) |  |  |  |
| <sup>a</sup> The length (L) of the molecule (estimated from the Chem 3D 17 molecular model software from Cambridge Soft). $d_{\text{obs}}$ : spacing observed; $d_{\text{cal}}$ : spacing calculated (deduced from the lattice parameters; $a$ for Col <sub>h</sub> phase, $a$ and $b$ for Col <sub>r</sub> phase). The spacings marked $h_a$ and $h_c$ correspond to the diffused reflections in the wide-angle region arising from correlations between the alkyl chains and core regions, respectively. $Z$ indicates the number of molecules per columnar slice of thickness $h_c$ , estimated from the lattice area $S$ and the volume $V$ . <sup>b</sup> In the absence of the core–core peak, the spacing of the alkyl chain stacking ( $h_a$ ) is used in these calculations. |                                   |                                                 |  |  |  |

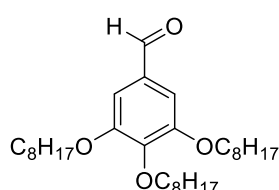
### Experimental Section:

**General:** All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was freshly distilled from phosphorus (V) oxide (P<sub>2</sub>O<sub>5</sub>). Secondary amines were distilled from KOH and stored under argon. Commercial grade xylene, DMF, THF were distilled before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. <sup>1</sup>H, <sup>13</sup>CNMR spectroscopy: *Varian Mercury plus 400 MHz*, *Bruker 600 MHz* (at 298 K). Chemical shifts,  $\delta$  (in ppm), are reported relative to TMS  $\delta$  (1H) 0.0 ppm,  $\delta$  (13C) 0.0 ppm which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance (CHCl<sub>3</sub>,  $\delta$  (1H) 7.26 ppm,  $\delta$  (13C) 77.2 ppm; CD<sub>3</sub>OD, (1H) 3.31 ppm,  $\delta$  (13C) 49.0 ppm) were used for calibration. Column chromatography: Merck, Spectrochem or FischerScientific silica gel 60-120 and neutral Al<sub>2</sub>O<sub>3</sub> under gravity. IR spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-MassQ-TOF LC/MS 6520 and peaks are given in  $m/z$  (% of basis peak). The mesogenic compounds were investigated for their liquid crystalline behavior (birefringence and fluidity) by employing a polarizing optical microscope (Nikon Eclipse LV100POL) equipped with a programmable hot stage (Mettler Toledo FP90). Clean glass slides and coverslips were employed for the polarizing optical microscopic observations. The transition temperatures and associated enthalpy changes were determined by differential scanning calorimeter (Mettler Toledo DSC1) under nitrogen atmosphere. Peak temperatures obtained in DSC corresponding to transitions were in agreement with the polarizing optical microscopic observations. The transition temperatures obtained from calorimetric measurements of the first heating and cooling cycles at a rate of 5 °C/min are tabulated. In the cases where the DSC signatures are not observed for the phase transitions, the transition temperatures have been taken from microscopic observations. Temperature dependent X-ray diffraction studies were carried on unaligned powder samples in

Lindemanncapillaries (1mm diameter) held in programmable hot stage and irradiated with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The samples were filled in the capillary tube in their isotropic state and their both ends were flame sealed. The apparatus essentially consisted of a high resolution powder X-ray diffractometer (Xenocs) equipped with a focusing elliptical mirror and a high resolution fast detector. UV-Vis spectra were obtained by using Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer. Fluorescence emission spectra in solution state were recorded with Horiba Fluoromax-4 fluorescence spectrophotometer or *Perkin Elmer* LS 50B spectrometer.

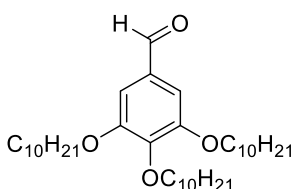
### Experimental procedure:

#### 3,4,5-Tris(octyloxy)benzaldehyde (**1a**):<sup>1</sup>



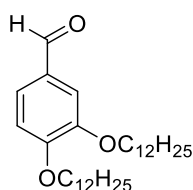
The compound was synthesized through a reported procedure. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.82 (s, 1H), 7.08 (s, 2H), 4.06 – 4.02 (m, 6H), 1.85 – 1.80 (m, 4H), 1.77 – 1.72 (m, 2H), 1.63 – 1.62 (m, 2H), 1.50 – 1.45 (m, 6H), 1.38 – 1.25 (m, 22H), 0.89 – 0.87 (m, 9H) ppm.

#### 3,4,5-Tris(decyloxy)benzaldehyde (**1b**):<sup>1</sup>



The compound was synthesized in a known procedure used for **1a** preparation. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.83 (s, 1H), 7.08 (s, 2H), 4.07 – 4.02 (m, 6H), 1.85 – 1.81 (m, 4H), 1.78 – 1.73 (m, 2H), 1.51 – 1.46 (m, 6H), 1.37 – 1.27 (m, 36H), 0.89 – 0.87 (m, 9H) ppm.

#### 3,4-Bis(dodecyloxy)benzaldehyde (**1e**):<sup>2</sup>



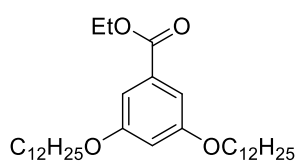
The compound was synthesized in a known procedure used for **1a** preparation. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.82 (s, 1H), 7.41 – 7.39 (m, 2H), 6.94 (d,  $J$  = 7.8 Hz, 1H), 4.08 – 4.03 (m, 4H), 1.88 – 1.83 (m, 4H), 1.49 – 1.45 (m, 4H), 1.38 – 1.26 (m, 32H), 0.88 (t,  $J$  = 7.2 Hz, 6H) ppm.

#### Ethyl 3,5-dihydroxybenzoate:<sup>3</sup>

Conc. H<sub>2</sub>SO<sub>4</sub> was added drop wise to a solution of 3,5-dihydroxybenzoic acid (10.0 g, 64.93 mmol) soluble in EtOH (50 mL) and was refluxed for 24 hours. After completion of reaction (checked by TLC), the reaction was stopped, EtOH was evaporated under reduced pressure, the reaction mixture was quenched with saturated NaHCO<sub>3</sub> solution, diluted with ethyl acetate, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo* to get crude product which was recrystallized from EtOH to give desired product (1.06 g, 90%). <sup>1</sup>H NMR (600 MHz, MeOD)  $\delta$  = 6.934 (s, 1H), 6.930 (s, 1H), 6.48 – 6.47 (m, 1H), 4.29 (q,  $J$  = 7.2 Hz, 2H), 1.34 (t,  $J$  = 7.2 Hz, 3H) ppm. <sup>13</sup>C NMR (151 MHz, MeOD)  $\delta$  = 168.2, 159.6, 133.3, 108.7, 108.1, 62.0, 14.5 ppm.

#### Ethyl 3,5-bis(dodecyloxy)benzoate:<sup>4</sup>

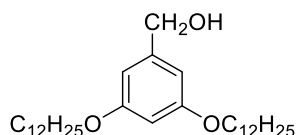
A mixture of ethyl 3,5-dihydroxybenzoate (6.50 g, 12.50 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (7.59 g, 55.01



mmol), *n*-bromododecane (6.60 mL, 27.61 mmol) and KI (41 mg, 0.25 mmol) were taken in dry DMF (10 mL) and heated at 80 °C for 24 hours under nitrogen atmosphere. Then the reaction mixture was poured into ice-water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extract was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by (ethyl acetate:hexane, 1:15) yielded the desired product (5.50 g, 85%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.164 (s, 1H), 7.160 (s, 1H), 6.63 – 6.62 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.97 – 3.95 (m, 4H), 1.79 – 1.75 (m, 4H), 1.47 – 1.42 (m, 4H), 1.39 – 1.26 (m, 35H), 0.89 – 0.87 (m, 6H) ppm.

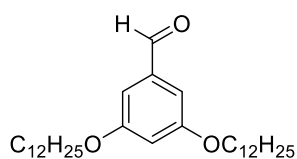
### 3,5-Bis(dodecyloxy)phenyl)methanol:<sup>5</sup>

To a stirred suspension of lithium aluminium hydride (LAH) (0.38 g, 9.97 mmol) in dry THF (15 mL)



under nitrogen atmosphere, ethyl 3,5-bis(dodecyloxy)benzoate (3.44 g, 6.65 mmol) soluble in THF (5 mL) was added drop wise at 0 °C. Then the reaction mixture was allowed to reach room temperature and stirred for 2 hours. Excess LAH present was quenched by the addition of moist sodium sulphate. Reaction mixture was extracted with EtOAc (5 X 50 mL). The combined extracts were washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in *vacuo*. Purification was done by column chromatography over silica gel (60-120) with (ethyl acetate:hexane, 1:10) as eluent to give the desired product (2.50 g, 79%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 6.471 (s, 1H), 6.468 (s, 1H), 6.36 – 6.35 (m, 1H), 4.56 (s, 2H), 3.91 (t, *J* = 6.6 Hz, 4H), 2.15 (br. s, 1H), 1.77 – 1.72 (m, 4H), 1.45 – 1.40 (m, 4H), 1.33 – 1.26 (m, 32H), 0.89 – 0.87 (m, 6H) ppm.

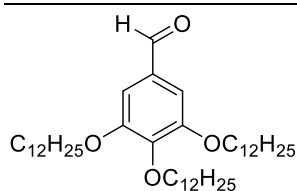
### 3,5-Bis(dodecyloxy)benzaldehyde (1g):<sup>6</sup>



An appropriate (3,5-bis(dodecyloxy)phenyl)methanol (2.17 g, 4.56 mmol) was taken in DCM (15 mL). To this pyridiniumchlorochromate (1.08 g, 5.02 mmol) adsorbed over equal amount of silica gel is added and stirred at room temperature for 1 hour. The reaction mixture was filtered over celite bed and concentrated to get the crude product, which was further purified by column chromatography on silica gel (60-120) with (ethyl acetate:hexane, 1:10) as eluent to give **1g** (1.72 g, 80%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 9.87 (s, 1H), 6.974 – 6.971 (m, 2H), 6.69 (s, 1H), 3.97 (t, *J* = 6.6 Hz, 4H), 1.80 – 1.76 (m, 4H), 1.47 – 1.42 (m, 4H), 1.35 – 1.27 (m, 32H), 0.89 – 0.87 (m, 6H) ppm.

### 3,4,5-Tris(dodecyloxy)benzaldehyde (1i):<sup>1</sup>

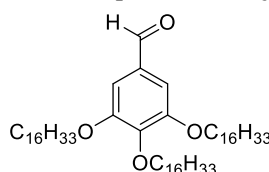




The compound was synthesized in same procedure used for **1a** preparation.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.82 (s, 1H), 7.08 (s, 2H), 4.06 – 4.02 (m, 6H), 1.85 – 1.80 (m, 4H), 1.77 – 1.72 (m, 2H), 1.50 – 1.45 (m, 6H), 1.35 – 1.26 (m, 48H), 0.89 – 0.86 (m, 9H) ppm.

### 3,4,5-Tris(hexadecyloxy)benzaldehyde (**1l**):<sup>7</sup>

The compound was synthesized in a known procedure used for **1a** preparation.  $^1\text{H}$  NMR (600 MHz,



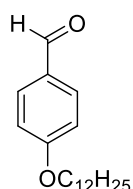
$\text{CDCl}_3$ )  $\delta$  = 9.83 (s, 1H), 7.08 (s, 2H), 4.06 – 4.02 (m, 6H), 1.85 – 1.80 (m, 4H), 1.76 – 1.72 (m, 2H), 1.50 – 1.45 (m, 6H), 1.35 – 1.26 (m, 72H), 0.89 – 0.87 (m, 9H).

### General procedure for the alkylation of aldehydes (GP I):

In a clean round bottom flask, a mixture of hydroxy benzaldehyde (3.38 – 10.86 mmol, 1.0 equiv.), anhydrous  $\text{K}_2\text{CO}_3$  (7.22 – 47.83 mmol, 2.2 equiv.), alkyl bromide (3.94 – 26.06 mmol, 1.2 equiv.) and KI (0.07 – 0.22 mmol, 0.02 equiv.) was taken in dry DMF (4 – 10 mL) and heated at 85-90 °C for 24 hours under nitrogen atmosphere. Then the reaction mixture was poured into ice water and extracted with ethyl acetate (3 X 30 mL). The organic layer was washed with brine (40 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in *vacuo*. The crude product was purified by column chromatography on silica.

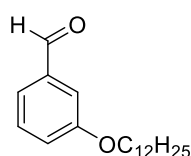
### 4-(Dodecyloxy)benzaldehyde (**1c**):<sup>8</sup>

According to GP I, 4-hydroxybenzaldehyde (1.0 g, 8.20 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (2.49 g, 18.04 mmol), *n*-bromododecane (2.30 mL, 9.60 mmol) and KI (27 mg, 0.16 mmol) were taken in 10 mL dry DMF and heated at 80 °C for 24 hours under nitrogen atmosphere and then  $\text{SiO}_2$ -column chromatography (ethyl acetate:hexane, 1:30) gave product **1c** as white solid (2.2 g, 93%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.86 (s, 1H), 7.81 (d,  $J$  = 8.4 Hz, 2H), 6.98 (d,  $J$  = 8.4 Hz, 2H), 4.02 (t,  $J$  = 6.6 Hz, 2H), 1.83 – 1.78 (m, 2H), 1.48 – 1.26 (m, 18H), 0.89 – 0.87 (m, 3H) ppm.



### 3-(Dodecyloxy)benzaldehyde (**1d**):

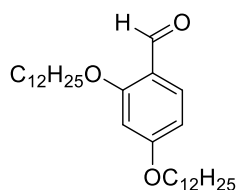
According to GP I, 3-hydroxybenzaldehyde (1.0 g, 8.20 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (2.49 g, 18.04 mmol), *n*-bromododecane (2.30 mL, 9.61 mmol) and KI (27 mg, 0.16 mmol) was taken in 10 mL dry DMF and heated at 80 °C for 24 hours under nitrogen atmosphere and then  $\text{SiO}_2$ -column chromatography (ethyl acetate:hexane, 1:30) gave product **1d** as colourless liquid (2.19 g, 92%). FTIR (KBr):  $\tilde{\nu}$  = 3383, 2925, 2854, 2723, 1702, 1599, 1585, 1486, 1467, 1454, 1386, 1321, 1287, 1263, 1168, 1148, 1078, 1033, 869, 787, 757, 683, 648, 605, 442  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.96 (s, 1H), 7.43 – 7.40 (m,



2H), 7.38 – 7.37 (m, 1H), 7.17 – 7.15 (m, 1H), 4.00 (t,  $J = 6.6$  Hz, 2H), 1.82 – 1.77 (m, 2H), 1.48 – 1.43 (m, 2H), 1.37 – 1.26 (m, 16H), 0.88 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta = 192.3$ , 159.9, 137.9, 130.1, 123.4, 122.1, 112.9, 68.4, 32.1, 29.84, 29.81, 29.77, 29.7, 29.54, 29.53, 29.3, 26.2, 22.9, 14.3 ppm. HRMS (ESI): Exact mass calculated for  $\text{C}_{19}\text{H}_{31}\text{O}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 291.2319; Found: 291.2312.

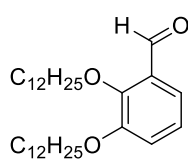
### 2,4-Bis(dodecyloxy)benzaldehyde (1f):

According to GP I, 2,4-dihydroxybenzaldehyde (1.5 g, 10.86 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (6.6 g, 47.83 mmol), *n*-bromododecane (6.2 mL, 26.06 mmol) and KI (36 mg, 0.22 mmol) was taken in 10 mL dry DMF and heated at 80 °C for 24 hours under nitrogen atmosphere and then  $\text{SiO}_2$ -column chromatography (ethyl acetate:hexane, 1:30) gave product **1f** as white solid (4.0 g, 77%). Mp 40–45 °C. FTIR (KBr):  $\tilde{\nu} = 3434$ , 2957, 2919, 2850, 1693, 1584, 1483, 1464, 1397, 1383, 131305, 1269, 1251, 1208, 1171, 1079, 1059, 1046, 1024, 994, 893, 791, 729, 719, 674, 546  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.45$  (s, 1H), 7.39 (d,  $J = 7.8$  Hz, 1H), 7.12 – 7.06 (m, 2H), 4.13 (t,  $J = 6.6$  Hz, 2H), 4.00 (t,  $J = 6.0$  Hz, 2H), 1.86 – 1.83 (m, 2H), 1.81 – 1.77 (m, 2H), 1.52 – 1.44 (m, 4H), 1.37 – 1.27 (m, 32H), 0.89 – 0.87 (m, 6H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta = 190.6$ , 152.8, 152.5, 130.3, 123.9, 119.3, 119.1, 75.2, 69.3, 32.1, 30.3, 29.9, 29.85, 29.82, 29.7, 29.6, 29.5, 26.4, 26.2, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{31}\text{H}_{55}\text{O}_3^+$  ( $[\text{M}+\text{H}]^+$ ): 475.4146; Found: 475.4167.



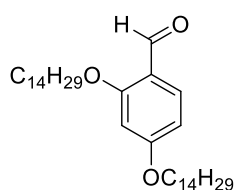
### 2,3-Bis(dodecyloxy)benzaldehyde (1h):

According to GP I, 2,3-dihydroxybenzaldehyde (1.0 g, 7.25 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (4.4 g, 31.88 mmol), *n*-bromododecane (4.1 mL, 17.40 mmol) and (24 mg, 0.14 mmol) was taken in 7 mL dry DMF and heated at 80 °C for 24 hours under nitrogen atmosphere and then  $\text{SiO}_2$ -column chromatography (ethyl acetate:hexane, 1:30) gave product **1h** as white solid (2.5 g, 72%). Mp 40–45 °C. FTIR (KBr):  $\tilde{\nu} = 3434$ , 2954, 2917, 2851, 1668, 1644, 1601, 1503, 1466, 1435, 1330, 1261, 1190, 1100, 1066, 1017, 997, 958, 835, 823, 806, 719, 676, 601, 552, 500, 461  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta = 10.32$  (s, 1H), 7.79 (d,  $J = 9.0$  Hz, 1H), 6.50 (d,  $J = 8.4$  Hz, 1H), 6.42 – 6.41 (m, 1H), 4.03 – 3.99 (m, 4H), 1.85 – 1.82 (m, 2H), 1.80 – 1.76 (m, 2H), 1.50 – 1.43 (m, 4H), 1.35 – 1.26 (m, 32H), 0.89 – 0.87 (m, 6H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta = 188.4$ , 165.9, 163.5, 130.3, 119.1, 106.4, 99.1, 68.6, 32.1, 29.84, 29.82, 29.77, 29.7, 29.5, 29.3, 29.2, 26.24, 26.16, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{31}\text{H}_{55}\text{O}_3^+$  ( $[\text{M}+\text{H}]^+$ ): 475.4146; Found: 475.4145.



### 2,4-Bis(tetradecyloxy)benzaldehyde (1j):

According to GP I, 2,4-dihydroxybenzaldehyde (0.5 g, 3.62 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (2.2 g, 15.90



mmol), *n*-bromotetradecane (2.36 mL, 7.96 mmol) and KI (12 mg, 0.07 mmol)

was taken in 5 mL dry DMF and heated at 80 °C for 24 hours under nitrogen atmosphere and then SiO<sub>2</sub>-column chromatography (ethyl acetate:hexane, 1:30)

gave product **1j** as white solid (1.35 g, 70%). Mp 38–43 °C. FTIR (KBr):

$\tilde{\nu}$  = 3430, 2953, 2918, 2849, 1678, 1607, 1572, 1494, 1467, 1439, 1402, 1386,

1311, 1297, 1265, 1192, 1114, 1021, 861, 822, 792, 718, 644, 609, 575, 464 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>)  $\delta$  = 10.33 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 6.52 – 6.50 (m, 1H), 6.42 (d, *J* = 2.0 Hz, 1H), 4.04

– 3.99 (m, 4H), 1.87 – 1.75 (m, 4H), 1.51 – 1.43 (m, 4H), 1.36 – 1.26 (m, 40H), 0.90 – 0.86 (m, 6H)

ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 188.6, 166.0, 163.5, 130.3, 119.1, 106.4, 99.1, 68.7, 68.6, 32.1,

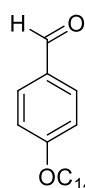
29.90, 29.88, 29.86, 29.80, 29.76 (2C), 29.6, 29.55, 29.54, 29.3, 29.2, 26.25, 26.17, 22.9, 14.3 ppm.

Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS

(ESI): Exact mass calculated for C<sub>35</sub>H<sub>63</sub>O<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>): 531.4772; Found: 531.4757.

#### 4-(Tetradecyloxy)benzaldehyde (**1k**):

According to GP I, 4-hydroxybenzaldehyde (0.4 g, 3.28 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.0 g, 7.22 mmol),



*n*-bromotetradecane (1.18 mL, 3.94 mmol) and KI (11 mg, 0.66 mmol) was taken in 4

mL dry DMF and heated at 80 °C for 24 hours under nitrogen atmosphere and then SiO<sub>2</sub>-column chromatography (ethyl acetate:hexane, 1:30) gave product **1k** as white solid

(1.03 gm, 90%). Mp 45–50 °C. FTIR (KBr):  $\tilde{\nu}$  = 3366, 2918, 2849, 2733, 1693, 1603,

1578, 1509, 1469, 1428, 1396, 1386, 1311, 1255, 1216, 1161, 1109, 1039, 1024, 1013, 858, 832, 720,

651, 640, 616, 514 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.88 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 6.99

(d, *J* = 8.4 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.75 – 3.70 (m, 2H), 1.85 – 1.78 (m, 2H), 1.49 – 1.44 (m,

2H), 1.37 – 1.23 (m, 18H), 0.90 – 0.86 (m, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 191.0, 164.4,

132.1, 129.9, 114.9, 68.6, 32.1, 29.88, 29.86, 29.84, 29.77, 29.7, 29.55, 29.53, 29.2, 26.1, 22.9, 14.3

ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region.

HRMS (ESI): Exact mass calculated for C<sub>21</sub>H<sub>35</sub>O<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>): 319.2632; Found: 319.2645.

#### General procedure for the synthesis of $\beta$ -substituted secondary cyclic imines (GP II):

3,5-Dinitrobenzoic acid (0.28 – 4.37 mmol, 0.6 equiv.) was added to a solution of aldehydes (0.44 –

6.72 mmol, 1 equiv.) and pyrrolidine (1.74 – 28.89 mmol, 4 equiv.) in *m*-xylene (5 – 10 mL) and the

mixture was refluxed for 18 hours. After disappearance of starting materials (indicated by TLC), the

reaction was quenched by addition of saturated sodium bicarbonate solution (50 mL). The mixture

was extracted with dichloromethane (3 X 40 mL). The combined organic layers were washed (brine),

dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude product was subjected to column

chromatography (neutral alumina) to afford the analytically pure product.

---

**(E)-4-(3,4,5-Tris(octyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2a):**

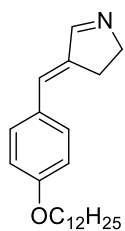
According to GP II, a mixture of 3,4,5-tris(octyloxy)benzaldehyde (0.4 g, 0.82 mmol), pyrrolidine (0.27 mL, 3.26 mmol), 3,5-dinitrobenzoic acid (0.11 g, 0.53 mmol) was refluxed for 18 hours in 5 mL *m*-xylene and column chromatography (neutral-Al<sub>2</sub>O<sub>3</sub>; ethyl acetate:hexane, 1:5) gave **2a** as brownish gum (0.42 g, 48%). FTIR (KBr):  $\tilde{\nu}$  = 3433, 2954, 2925, 2855, 1685, 1638, 1577, 1504, 1467, 1432, 1334, 1236, 1161, 1115, 1037, 976, 925, 873, 817, 723, 633, 516, 425, 411 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.84 (s, 1H), 6.73 (s, 1H), 6.67 (s, 2H), 4.22 – 4.18 (m, 2H), 3.98 (t, *J* = 6.6 Hz, 6H), 2.83 – 2.81 (m, 2H), 1.84 – 1.79 (m, 4H), 1.77 – 1.72 (m, 2H), 1.49 – 1.45 (m, 6H), 1.37 – 1.28 (m, 24H), 0.89 (t, *J* = 6.6 Hz, 9H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.6, 153.4, 142.6, 139.0, 132.1, 127.6, 108.2, 73.8, 69.6, 62.4, 32.1, 32.0, 30.6, 29.74, 29.67, 29.58, 29.56, 29.5, 28.4, 26.3, 22.89, 22.86, 14.3 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): HRMS (ESI): Exact mass calculated for C<sub>35</sub>H<sub>60</sub>NO<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>): 542.4568; Found: 542.4568.

**(E)-4-(3,4,5-Tris(decyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2b):**

According to GP II, a mixture of 3,4,5-tris(decyloxy)benzaldehyde (0.46 g, 0.81 mmol), pyrrolidine (0.27 mL, 3.24 mmol), 3,5-dinitrobenzoic acid (0.11 g, 0.53 mmol) was refluxed for 18 hours in 5 mL *m*-xylene and column chromatography (neutral-Al<sub>2</sub>O<sub>3</sub>; ethyl acetate:hexane, 1:5) gave **2b** as brownish gum (0.20 g, 40%). FTIR (KBr):  $\tilde{\nu}$  = 3416, 2955, 2925, 2854, 1637, 1577, 1504, 1466, 1434, 1378, 1335, 1238, 1116, 803, 721, 518, 470, 444, 413, 403 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.83 (s, 1H), 6.72 (s, 1H), 6.67 (s, 2H), 4.21 – 4.18 (m, 2H), 4.00 – 3.97 (m, 6H), 2.82 – 2.80 (m, 2H), 1.83 – 1.79 (m, 4H), 1.77 – 1.72 (m, 2H), 1.50 – 1.45 (m, 6H), 1.35 – 1.27 (m, 36H), 0.89 – 0.87 (m, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.6, 153.3, 142.6, 138.8, 132.1, 127.6, 108.0, 73.7, 69.4, 62.4, 32.14, 32.12, 30.5, 29.94, 29.87, 29.85, 29.79, 29.6, 29.5, 28.4, 26.3, 22.9, 14.3 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for C<sub>41</sub>H<sub>72</sub>NO<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>): 626.5507; Found: 626.5535.

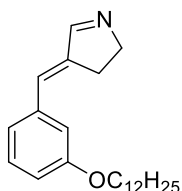
**(E)-4-(4-(Dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2c):**

According to GP II, a mixture of 4-(dodecyloxy)benzaldehyde (1.95 g, 6.72 mmol), pyrrolidine (2.21 mL, 28.89 mmol), 3,5-dinitrobenzoic acid (0.93 g, 4.37 mmol) was refluxed for 18 hours in 10 mL *m*-xylene and column chromatography (neutral- $\text{Al}_2\text{O}_3$ ; ethyl acetate:hexane, 1:5) gave **2c** as brownish gum (1.13 g, 50%). FTIR (KBr):  $\tilde{\nu}$  = 3428, 2917, 2850, 1605, 1578, 1511, 1473, 1423, 1395, 1385, 1314, 1289, 1254, 1240, 1181, 1166, 1118, 1033, 1023, 1002, 969, 924, 885, 851, 829, 810, 775, 719, 597, 538, 516, 413  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.81 (s, 1H), 7.37 (d,  $J$  = 8.4 Hz, 2H), 6.90 (d,  $J$  = 7.8 Hz, 2H), 6.74 (s, 1H), 4.18 – 4.15 (m, 2H), 3.96 (t,  $J$  = 6.0 Hz, 2H), 2.78 – 2.75 (m, 2H), 1.79 – 1.76 (m, 2H), 1.45 – 1.44 (m, 2H), 1.34 – 1.26 (m, 16H), 0.89 – 0.87 (m, 3H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.6, 159.1, 141.4, 130.3, 129.4, 126.7, 114.8, 68.2, 62.3, 32.0, 29.79, 29.77, 29.73, 29.71, 29.52, 29.48, 29.3, 28.2, 26.1, 22.8, 14.2 ppm. HRMS (ESI): Exact mass calculated for  $\text{C}_{23}\text{H}_{36}\text{NO}^+$  ( $[\text{M}+\text{H}]^+$ ): 342.2791; Found: 342.2796.



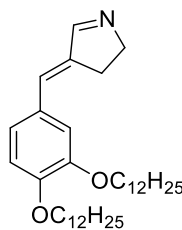
**(E)-4-(3-(Dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2d):**

According to GP II, a mixture of 3-(dodecyloxy)benzaldehyde (0.40 g, 1.38 mmol), pyrrolidine (0.45 mL, 5.52 mmol), 3,5-dinitrobenzoic acid (0.19 g, 0.90 mmol) was refluxed for 18 hours in 7 mL *m*-xylene and column chromatography (neutral- $\text{Al}_2\text{O}_3$ ; ethyl acetate:hexane, 1:5) gave **2d** as brownish gum (0.21 g, 44%). FTIR (KBr):  $\tilde{\nu}$  = 3435, 2954, 2918, 2852, 1640, 1593, 1582, 1488, 1474, 1384, 1318, 1299, 1268, 1239, 1175, 1165, 1035, 973, 954, 925, 898, 868, 838, 805, 778, 719, 684, 596, 521, 454  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.87 (s, 1H), 7.31 – 7.28 (m, 1H), 7.04 (d,  $J$  = 7.8 Hz, 1H), 6.99 (s, 1H), 6.85 – 6.84 (m, 1H), 6.79 (s, 1H), 4.21 – 4.19 (m, 2H), 3.97 (t,  $J$  = 6.6 Hz, 2H), 2.85 – 2.82 (m, 2H), 1.81 – 1.77 (m, 2H), 1.67 – 1.65 (m, 2H), 1.48 – 1.43 (m, 2H), 1.37 – 1.26 (m, 14H), 0.89 – 0.87 (m, 3H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.6, 159.5, 143.9, 138.2, 129.7, 127.3, 121.4, 115.1, 114.3, 68.2, 62.4, 32.1, 29.9, 29.84, 29.81, 29.78, 29.6, 29.55, 29.48, 28.5, 26.3, 22.9, 14.3 ppm. HRMS (ESI): Exact mass calculated for  $\text{C}_{23}\text{H}_{36}\text{NO}^+$  ( $[\text{M}+\text{H}]^+$ ): 342.2791; Found: 342.2804.



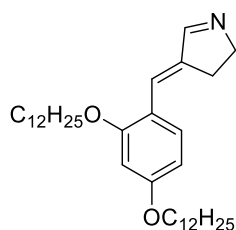
**(E)-4-(3,4-Bis(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2e):**

According to GP II, a mixture of 3,4-bis(dodecyloxy)benzaldehyde (0.4 g, 0.84 mmol), pyrrolidine (1.6 mL, 3.37 mmol), 3,5-dinitrobenzoic acid (0.12 g, 0.55 mmol) was refluxed for 18 hours in 5 mL *m*-xylene and column chromatography (neutral- $\text{Al}_2\text{O}_3$ ; ethyl acetate:hexane, 1:5) gave **2e** as brownish gum (0.23 g, 51%). FTIR (KBr):  $\tilde{\nu}$  = 3430, 2955, 2921, 2851, 1632, 1599, 1572, 1518, 1470, 1380, 1328, 1263, 1239, 1179, 1156, 1136, 1064, 1025, 917, 882, 796, 719, 625, 605, 519, 468  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.83 (s, 1H), 7.02 – 7.00 (m, 2H), 6.89 (d,  $J$  = 7.8 Hz, 1H), 6.74 (s, 1H), 4.21 – 4.18 (m, 2H), 4.02 (t,  $J$  = 6.0 Hz, 4H), 2.85 – 2.75 (m, 2H), 1.84 – 1.81 (m, 4H), 1.50 – 1.44 (m, 4H), 1.38–



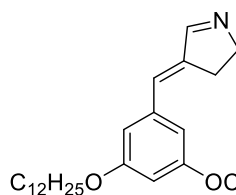
1.26 (m, 32H), 0.89 – 0.87 (m, 6H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.7, 149.5, 149.1, 141.7, 130.0, 127.2, 122.5, 114.6, 113.6, 69.6, 69.3, 62.4, 32.1, 29.91, 29.87, 29.8, 29.65, 29.62, 29.58, 29.5, 29.4, 28.3, 26.3, 26.2, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{35}\text{H}_{60}\text{NO}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 526.4619; Found: 526.4637.

**(E)-4-(2,4-Bis(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2f):**



According to GP II, a mixture of 2,4-bis(dodecyloxy)benzaldehyde (2.23 g, 4.71 mmol), pyrrolidine (1.6 mL, 18.8 mmol), 3,5-dinitrobenzoic acid (0.65 g, 3.06 mmol) was refluxed for 18 hours in 7 mL *m*-xylene and column chromatography (neutral- $\text{Al}_2\text{O}_3$ ; ethyl acetate:hexane, 1:5) gave **2f** as brownish gum (1.0 g, 40%). FTIR (KBr):  $\tilde{\nu}$  = 3421, 2954, 2921, 2852, 1604, 1575, 1502, 1469, 1428, 1385, 1312, 1288, 1273, 1226, 1184, 1159, 1106, 1069, 1032, 925, 972, 926, 882, 871, 820, 798, 786, 719, 632, 610, 598, 515, 487, 472, 441, 422  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.86 (s, 1H), 7.43 (d,  $J$  = 8.4 Hz, 1H), 7.17 – 7.16 (m, 1H), 6.50 – 6.48 (m, 1H), 6.46 – 6.45 (m, 1H), 4.16 – 4.13 (m, 2H), 3.98 – 3.95 (m, 4H), 2.77 – 2.74 (m, 2H), 1.85 – 1.81 (m, 2H), 1.80 – 1.75 (m, 2H), 1.50 – 1.43 (m, 4H), 1.39 – 1.26 (m, 32H), 0.89 – 0.87 (m, 6H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 169.2, 160.5, 158.5, 141.0, 128.8, 120.9, 118.8, 105.2, 99.9, 68.7, 68.3, 62.1, 32.1, 29.9, 29.83, 29.80, 29.77, 29.6, 29.5, 29.4, 29.3, 28.4, 26.3, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{35}\text{H}_{60}\text{NO}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 526.4619; Found: 526.4634.

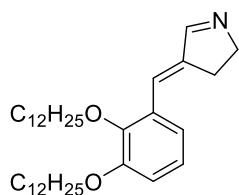
**(E)-4-(3,5-Bis(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2g):**



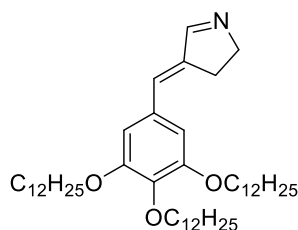
According to GP II, a mixture of 3,5-bis(dodecyloxy)benzaldehyde (0.42 g, 0.89 mmol), pyrrolidine (0.29 mL, 3.56 mmol), 3,5-dinitrobenzoic acid (0.12 g, 0.38 mmol) was refluxed for 18 hours in 5 mL *m*-xylene and column chromatography (neutral- $\text{Al}_2\text{O}_3$ ; ethyl acetate:hexane, 1:5) gave **2g** as brownish gum (0.38 g, 43%). FTIR (KBr):  $\tilde{\nu}$  = 3430, 3065, 3003, 2956, 2924, 2851, 1639, 1590, 1466, 1392, 1373, 1352, 1293, 1178, 1152, 1129, 1070, 1050, 971, 945, 928, 919, 871, 833, 813, 767, 734, 724, 685, 593, 514  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.83 (s, 1H), 6.71 (s, 1H), 6.571 – 6.569 (m, 2H), 6.41 (s, 1H), 4.18 – 4.16 (m, 2H), 3.93 (t,  $J$  = 6.6 Hz, 4H), 2.81 – 2.80 (m, 2H), 1.79 – 1.74 (m, 4H), 1.46 – 1.42 (m, 4H), 1.34 – 1.26 (m, 32H), 0.88 (t,  $J$  = 7.2 Hz, 6H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.5, 160.5, 143.9, 138.5, 127.4, 107.5, 101.3, 68.2, 62.4, 32.1, 29.83, 29.80, 29.77, 29.7, 29.6, 29.5, 29.4, 28.5, 26.2, 22.8, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{35}\text{H}_{60}\text{NO}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 526.4619; Found: 526.4621.



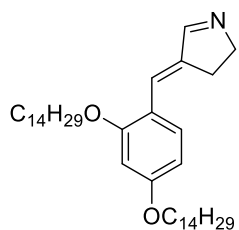
---

**(E)-4-(2,3-Bis(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2h):**

According to GP II, a mixture of 2,3-bis(dodecyloxy)benzaldehyde (1.82 g, 3.85 mmol), pyrrolidine (1.3 mL, 15.4 mmol), 3,5-dinitrobenzoic acid (0.53 g, 2.50 mmol) was refluxed for 18 hours in 7 mL *m*-xylene and column chromatography (neutral- $\text{Al}_2\text{O}_3$ ; ethyl acetate:hexane, 1:5) gave **2h** as brownish gum (1.03 g, 51%). FTIR (KBr):  $\tilde{\nu}$  = 3431, 2956, 2924, 2854, 1639, 1595, 1577, 1466, 1383, 1273, 1259, 1214, 1154, 1075, 1031, 924, 749, 721, 515  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.89 (s, 1H), 7.22 – 7.21 (m, 1H), 7.12 (d,  $J$  = 7.8 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.88 – 6.85 (m, 1H), 4.19 – 4.16 (m, 2H), 3.99 – 3.93 (m, 4H), 2.80 – 2.77 (m, 2H), 1.85 – 1.76 (m, 6H), 1.51 – 1.46 (m, 4H), 1.38 – 1.26 (m, 30H), 0.89 – 0.87 (m, 6H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 169.1, 152.7, 147.4, 144.1, 131.3, 123.7, 121.6, 119.8, 113.4, 74.1, 68.9, 62.3, 56.0, 32.1, 30.5, 29.92, 29.88, 29.86, 29.8, 29.63, 29.59, 28.3, 26.4, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{35}\text{H}_{60}\text{NO}_2^+$  ( $[\text{M}+\text{H}]^+$ ): 526.4619; Found: 526.4629.

**(E)-4-(3,4,5-Tris(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2i):**

According to GP II, a mixture of 3,4,5-tris(dodecyloxy)benzaldehyde (0.29 g, 0.44 mmol), pyrrolidine (0.14 mL, 1.74 mmol), 3,5-dinitrobenzoic acid (0.06 g, 0.28 mmol) was refluxed for 18 hours in 5 mL *m*-xylene and column chromatography (neutral- $\text{Al}_2\text{O}_3$ ; ethyl acetate:hexane, 1:5) gave **2i** as brownish gum (0.11 g, 35%). FTIR (KBr):  $\tilde{\nu}$  = 3443, 2921, 2851, 1630, 1575, 1507, 1468, 1432, 1384, 1337, 1293, 1244, 1232, 1160, 1123, 970, 921, 874, 814, 721, 636, 513  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.84 (s, 1H), 6.72 (s, 1H), 6.67 (s, 2H), 4.22 – 4.18 (m, 2H), 4.00 – 3.97 (m, 6H), 2.83 – 2.79 (m, 2H), 1.83 – 1.79 (m, 4H), 1.76 – 1.72 (m, 4H), 1.48 – 1.45 (m, 8H), 1.37 – 1.26 (m, 44H), 0.89 – 0.87 (m, 9H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 168.7, 153.3, 142.6, 138.7, 132.1, 127.6, 107.9, 73.8, 69.4, 62.4, 32.15, 32.14, 30.5, 30.0, 29.95, 29.92, 29.87, 29.86, 29.8, 29.63, 29.61, 29.58, 28.4, 26.3, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{47}\text{H}_{84}\text{NO}_3^+$  ( $[\text{M}+\text{H}]^+$ ): 710.6446; Found: 710.6452.

**(E)-4-(2,4-Bis(tetradecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2j):**

According to GP II, a mixture of 2,4-bis(tetradecyloxy)benzaldehyde (0.57 g, 1.07 mmol), pyrrolidine (0.35 mL, 4.28 mmol), 3,5-dinitrobenzoic acid (0.15 g, 0.69 mmol) was refluxed for 18 hours in 6 mL *m*-xylene and column chromatography (neutral- $\text{Al}_2\text{O}_3$ ; ethyl acetate:hexane, 1:5) gave **2j** as brownish gum (0.27 g, 43%). FTIR (KBr):  $\tilde{\nu}$  = 3426, 2954, 2918, 2852, 1604, 1574, 1502,

1472, 1438, 1386, 1313, 1288, 1276, 1201, 1184, 1159, 1073, 1040, 1030, 1050, 1018, 1007, 926, 882, 871, 814, 799, 717, 631, 640, 598, 535, 515, 487, 426 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.89 – 7.84 (m, 1H), 7.47 – 7.42 (m, 1H), 7.20 – 7.17 (m, 1H), 6.53 – 6.46 (m, 2H), 4.21 – 4.11 (m, 2H), 4.00 – 3.95 (m, 4H), 2.80 – 2.73 (m, 2H), 1.87 – 1.75 (m, 4H), 1.52 – 1.26 (m, 44H), 0.91 – 0.86 (m, 6H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ = 169.3, 160.5, 158.5, 141.1, 128.8, 120.9, 118.9, 105.3, 99.9, 68.7, 68.3, 62.1, 32.1, 29.90, 29.89, 29.87, 29.82, 29.81, 29.78, 29.60, 29.57, 29.5, 29.4, 28.4, 26.3, 26.2, 22.9, 14.3 ppm. HRMS (ESI): Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. Exact mass calculated for C<sub>39</sub>H<sub>68</sub>NO<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>): 582.5245; Found: 582.5263.

**(E)-4-(4-(Tetradecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2k):**

According to GP II, a mixture of 4-(tetradecyloxy)benzaldehyde (0.87 g, 2.86 mmol), pyrrolidine (0.94 mL, 11.43 mmol), 3,5-dinitrobenzoic acid (0.4 g, 1.89 mmol) was refluxed for 18 hours in 16 mL *m*-xylene and column chromatography (neutral-Al<sub>2</sub>O<sub>3</sub>; ethyl acetate:hexane, 1:5) gave **2k** as brownish gum (0.50 g, 47%). FTIR (KBr):  $\tilde{\nu}$  = 3433, 2939, 2917, 2850, 1605, 1578, 1510, 1474, 1395, 1385, 1307, 1290, 1254, 1240, 1181, 1166, 1118, 1040, 1021, 969, 957, 924, 885, 851, 829, 799, 775, 751, 718, 667, 597, 538, 517 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.83 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.76 (s, 1H), 4.24 – 4.15 (m, 2H), 3.99 – 3.96 (m, 2H), 2.82 – 2.76 (m, 2H), 1.80 – 1.77 (m, 2H), 1.45 – 1.26 (m, 22H), 0.89 – 0.86 (m, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ = 168.7, 159.1, 141.5, 130.3, 129.4, 126.8, 114.8, 68.2, 62.4, 32.1, 29.9, 29.84, 29.78, 29.76, 29.6, 29.5, 29.4, 28.3, 26.2, 22.9, 14.3 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for C<sub>25</sub>H<sub>40</sub>NO<sup>+</sup> ([M+H]<sup>+</sup>): 370.3104; Found: 370.3119.

**(E)-4-(3,4,5-Tris(hexadecyloxy)benzylidene)-3,4-dihydro-2H-pyrrole (2l):**

According to GP II, a mixture of 3,4,5-tris(hexadecyloxy)benzaldehyde (1.04 g, 1.26 mmol), pyrrolidine (0.41 mL, 5.03 mmol), 3,5-dinitrobenzoic acid (0.17 g, 0.82 mmol) was refluxed for 18 hours in 10 mL *m*-xylene and column chromatography (neutral-Al<sub>2</sub>O<sub>3</sub>; ethyl acetate:hexane, 1:5) gave **2l** as brownish gum (0.61 g, 55%). FTIR (KBr):  $\tilde{\nu}$  = 3431, 2955, 2918, 2849, 1630, 1572, 1508, 1469, 1432, 1384, 1371, 1337, 1293, 1251, 1232, 1160, 1023, 986, 969, 934, 921, 875, 814, 790, 635, 586 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.84 (s, 1H), 6.73 (s, 1H), 6.66 (s, 2H), 4.21 – 4.19 (m, 2H), 4.00 – 3.97 (m, 6H), 2.83 – 2.80 (m, 2H), 1.83 – 1.72 (m, 8H), 1.50 – 1.45 (m, 6H), 1.37 – 1.34 (m, 6H), 1.31 – 1.26 (m, 64H), 0.89 – 0.87 (m, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ = 168.6, 153.3, 142.5, 138.7, 132.0, 127.7, 107.8, 73.7, 69.4, 62.3, 32.1, 30.5, 29.95, 29.93, 29.88, 29.86, 29.8, 29.63, 29.59, 28.3, 26.3, 22.9, 14.3 ppm. Total count of <sup>13</sup>C is less than expected

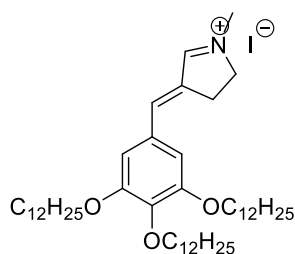
due to the merging of signals in the aromatic region. HRMS (ESI): Exact mass calculated for  $C_{59}H_{108}NO_3^+$  ( $[M+H]^+$ ): 878.8324; Found: 878.8342.

**General procedure for the synthesis of  $\alpha,\beta$ -unsaturated secondary cyclic iminium ions (GP III):**

Alkylating reagent (MeI,  $Me_3O^+BF_4^-$ ,  $Et_3O^+BF_4^-$ ) (0.14 – 1.59 mmol, 1.5 equiv.) was added to solution of  $\beta$ -unsaturated cyclic imines (0.09 – 0.72 mmol, 1.0 equiv.) in mixture of DCM and  $CH_3CN$  (1:3, 1 – 4 mL) solvents and the mixture was stirred at room temperature for next 24-72 hours under inert atmosphere. After completion of reaction (checked by TLC), the reaction mixture was concentrated *in vacuo*, the solid was filtered through a filter paper, washed with ETOAc (4 X 20 mL) and dried to give the iminium ions.

**(E)-1-methyl-4-(3,4,5-tris(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium iodide (12/3/MI):**

According to GP III, methyl iodide (32  $\mu$ L, 0.50 mmol) was reacted with **2i** (0.18 g, 0.25 mmol) in 4

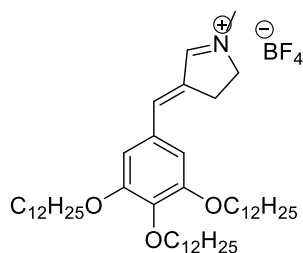


mL DCM: $CH_3CN$  (1:3) for 24 hours. Filtration of the solid precipitate gave **12/3/MI** as yellow solid (0.17 g, 79%). FTIR (KBr):  $\tilde{\nu}$  = 3427, 2953, 2918, 2849, 1609, 1578, 1568, 1506, 1464, 1443, 1378, 1340, 1316, 1253, 1177, 1154, 1123, 1092, 1029, 989, 969, 871, 803, 720, 627, 504  $cm^{-1}$ .  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  = 9.80 (s, 1H), 7.74 (s, 1H), 6.72 (s, 2H), 4.42 – 4.39 (m, 2H), 4.05 – 4.03 (m, 2H), 3.97 – 3.95 (m, 4H), 3.85 (s, 3H),

3.37 – 3.35 (m, 2H), 1.82 – 1.79 (m, 4H), 1.76 – 1.71 (m, 2H), 1.49 – 1.44 (m, 6H), 1.35 – 1.33 (m, 6H), 1.31 – 1.26 (m, 42H), 0.88 (t,  $J$  = 7.2 Hz, 9H) ppm.  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  = 173.1, 153.5, 146.5, 142.3, 133.8, 129.0, 110.1, 73.9, 69.6, 60.3, 41.3, 32.1, 30.5, 29.92, 29.90, 29.87, 29.8, 29.7, 29.6, 29.5, 27.6, 26.2, 22.9, 14.3 ppm. Total count of  $^{13}C$  is less than expected due to the merging of signals in the aliphatic region. Exact mass calculated for  $C_{48}H_{86}NO_3^+$  ( $[M]^+$ ): 724.6602; Found: 724.6613.

**(E)-1-methyl-4-(3,4,5-tris(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium tetrafluoroborate (12/3/MBF):**

According to GP III, trimethyloxonium tetrafluoroborate (0.06 g, 0.42 mmol) was reacted with **2i**



(0.15 g, 0.21 mmol) in 3 mL DCM: $CH_3CN$  (1:1) for 24 hours. Filtration of the solid precipitate gave **12/3/MBF** as yellow solid (0.12 g, 70%). FTIR (KBr):  $\tilde{\nu}$  = 3429, 2954, 2919, 2850, 1615, 1572, 1504, 1469, 1443, 1381, 1342, 1306, 1253, 1178, 1124, 1084, 1064, 1035, 919, 873, 808, 721, 522, 499  $cm^{-1}$ .  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  = 8.66 (s, 1H), 7.53 (s, 1H), 6.70 (s, 2H), 4.33 – 4.31 (m, 2H), 4.01 (t,  $J$  = 6.6 Hz, 2H), 3.94 – 3.92 (m, 4H), 3.68 (s, 3H), 3.32 – 3.30 (m, 2H), 1.81 – 1.77 (m, 4H), 1.76 – 1.70 (m, 2H), 1.48 – 1.43

(m, 6H), 1.34 – 1.26 (m, 48H), 0.89 – 0.87 (m, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 173.5, 153.5, 146.1, 142.1, 134.3, 129.1, 110.0, 73.9, 69.5, 59.6, 40.2, 32.1, 30.6, 30.0, 29.95, 29.91, 29.89, 29.8, 29.7, 29.6, 27.4, 26.35, 26.27, 22.9, 14.3. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{48}\text{H}_{86}\text{NO}_3^+$  ( $[\text{M}]^+$ ): 724.6602; Found: 724.6608.

**(E)-1-ethyl-4-(3,4,5-tris(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium tetrafluoroborate (12/3/EBF):**

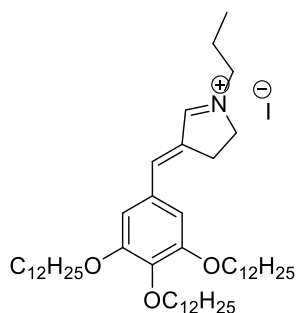
According to GP III, triethyloxonium tetrafluoroborate (0.06 g, 0.31 mmol) was reacted with **2i** (0.15 g, 0.21 mmol) in 3 mL  $\text{DCM}:\text{CH}_3\text{CN}$  (1:1) for 24 hours. Filtration of the solid precipitate gave **12/3/EBF** as yellow solid (0.13 g, 76%). FTIR (KBr):  $\tilde{\nu}$  = 3401, 3058, 2954, 2918, 2849, 2872, 1608, 1577, 1507, 1446, 1388, 1316, 1471, 1342, 1252, 1180, 1151, 1132, 1062, 1124, 1038, 990, 970, 809, 720, 928, 899, 871, 841, 629, 694, 522  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.74 (s, 1H), 7.64 (s, 1H), 6.76 (s, 2H), 4.40 – 4.37 (m, 2H), 4.03 (t,  $J$  = 6.4 Hz, 2H), 3.96 (t,  $J$  = 6.0 Hz, 4H), 3.26 – 3.21 (m, 2H), 1.83 – 1.78 (m, 4H), 1.76 – 1.70 (m, 2H), 1.50 – 1.43 (m, 6H), 1.36 – 1.26 (m, 53H), 0.90 – 0.86 (m, 9H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 174.1, 153.5, 147.7, 142.3, 134.3, 129.0, 110.1, 74.0, 69.5, 53.9, 32.2, 32.1, 30.6, 30.0, 29.95, 29.93, 29.90, 29.89, 29.8, 29.7, 29.62, 29.60, 29.5, 26.35, 26.26, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{49}\text{H}_{88}\text{NO}_3^+$  ( $[\text{M}]^+$ ): 738.6759; Found: 738.6770.

**(E)-1-ethyl-4-(3,4,5-tris(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium iodide (12/3/EI):**

According to GP III, ethyl iodide (28  $\mu\text{L}$ , 0.35 mmol) was reacted with **2i** (0.12 g, 0.18 mmol) in 2 mL  $\text{DCM}:\text{CH}_3\text{CN}$  (1:3) for 24 hours. Filtration of the solid precipitate gave **12/3/EI** as yellow solid (0.08 g, 50%). FTIR (KBr):  $\tilde{\nu}$  = 3435, 2954, 2918, 2849, 1604, 1575, 1506, 1464, 1443, 1386, 1315, 1342, 1250, 1153, 1177, 1132, 1124, 990, 806, 720, 630, 511  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.80 (s, 1H), 7.83 (s, 1H), 6.74 (s, 2H), 4.37 – 4.35 (m, 2H), 4.16 – 4.03 (m, 2H), 4.06 – 4.04 (m, 2H), 3.98 – 3.96 (m, 4H), 3.38 – 3.35 (m, 2H), 1.83 – 1.79 (m, 4H), 1.76 – 1.72 (m, 2H), 1.57 (t,  $J$  = 7.2 Hz, 3H), 1.50 – 1.45 (m, 6H), 1.38 – 1.26 (m, 48H), 0.89 – 0.87 (m, 9H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 171.5, 153.5, 146.7, 142.4, 133.9, 129.1, 110.2, 73.9, 69.6, 58.1, 49.1, 32.0, 30.5, 29.85, 29.78, 29.7, 29.6, 29.5, 27.3, 26.3, 26.2, 22.8, 14.2, 13.2 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{49}\text{H}_{88}\text{NO}_3^+$  ( $[\text{M}]^+$ ): 738.6759; Found: 738.6769.

**(E)-1-propyl-4-(3,4,5-tris(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium iodide (12/3/ProI):**

According to GP III, propyl iodide (53  $\mu$ L, 0.50 mmol) was reacted with **2i** (0.19 g, 0.27 mmol) in 4

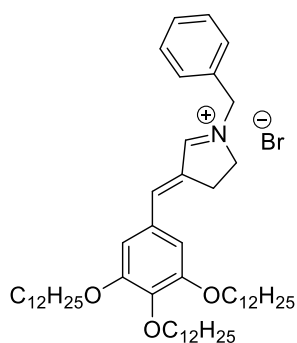


mL DCM:CH<sub>3</sub>CN (1:3) for 72 hours. Filtration of the solid precipitate gave **12/3/ProI** as yellow solid (0.11 g, 68%). FTIR (KBr):  $\tilde{\nu}$  = 3456, 2955, 2850, 1919, 1612, 1574, 1504, 1467, 1439, 1383, 1340, 1249, 1192, 1174, 1123, 1028, 990, 921, 811, 721, 630, 497 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.84 (s, 1H), 7.84 (s, 1H), 6.74 (s, 2H), 4.39 – 4.37 (m, 2H), 4.08 – 4.03 (m, 4H), 3.97 – 3.95 (m, 4H), 3.38 – 3.36 (m, 2H), 1.96 – 1.90 (m, 2H), 1.83 – 1.78 (m, 4H), 1.76 – 1.71 (m, 2H), 1.49 – 1.45 (m, 6H),

1.38 – 1.26 (m, 48H), 1.04 – 1.01 (m, 3H), 0.88 (t,  $J$  = 7.2 Hz, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.4, 153.5, 147.2, 142.4, 133.4, 129.0, 110.1, 74.0, 69.6, 57.8, 55.3, 32.14, 32.13, 30.6, 30.0, 29.95, 29.94, 29.92, 29.90, 29.87, 29.86, 29.8, 29.64, 29.60, 29.58, 29.5, 27.3, 26.3, 26.2, 22.9, 21.2, 14.3, 11.1 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for C<sub>50</sub>H<sub>90</sub>NO<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>): 752.6915; Found: 752.6932.

**(E)-1-benzyl-4-(3,4,5-tris(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium bromide (12/3/BnBr):**

According to GP III, benzyl bromide (46  $\mu$ L, 0.39 mmol) was reacted with **2i** (0.14 g, 0.19 mmol) in

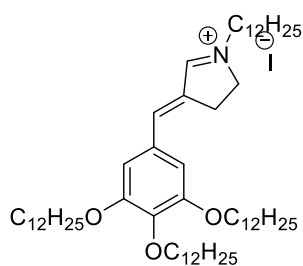


2 mL DCM:CH<sub>3</sub>CN (1:3) for 72 hours. Filtration of the solid precipitate gave **12/3/BnBr** as yellow solid (0.04 g, 23%). FTIR (KBr):  $\tilde{\nu}$  = 3435, 3043, 2953, 2919, 2849, 2870, 1622, 1574, 1504, 1444, 1393, 1264, 1210, 1173, 1155, 1028, 1465, 1339, 1324, 1251, 11888, 1119, 929, 856, 973, 964, 1044, 994, 807, 766, 722, 699, 640, 625, 498 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.32 (s, 1H), 7.77 (s, 1H), 7.55 – 7.54 (m, 2H), 7.40 – 7.38 (m, 3H), 6.67 (s, 2H), 5.49 (s, 2H), 4.34 – 4.32 (m, 2H), 4.02 (t,  $J$  =

6.6 Hz, 2H), 3.93 – 3.91 (m, 4H), 3.27 – 3.25 (m, 2H), 1.81 – 1.76 (m, 4H), 1.74 – 1.70 (m, 2H), 1.47 – 1.43 (m, 6H), 1.34 – 1.26 (m, 48H), 0.89 – 0.87 (m, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 173.0, 153.4, 147.5, 142.4, 133.7, 131.3, 129.9, 129.8, 129.6, 129.0, 110.1, 73.9, 69.5, 57.2, 56.9, 32.1, 30.5, 29.92, 29.90, 29.8, 29.7, 29.62, 29.58, 29.56, 29.5, 27.1, 26.3, 26.2, 22.9, 14.3 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for C<sub>54</sub>H<sub>90</sub>NO<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>): 800.6915; Found: 800.6937.

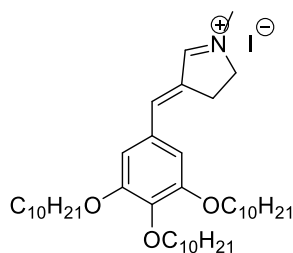
**(E)-1-dodecyl-4-(3,4,5-tris(dodecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium iodide (12/3/C12I):**

According to GP III, n-iodohexadecane (0.12 mL, 0.50 mmol) was reacted with **2i** (0.18 g, 0.25 mmol)



in 4 mL DCM:CH<sub>3</sub>CN (1:3) for 72 hours. Filtration of the solid precipitate gave **12/3/C12I** as yellow solid (0.04 g, 16%). FTIR (KBr):  $\tilde{\nu}$  = 3434, 2955, 2920, 2851, 1614, 1575, 1504, 1468, 1439, 1382, 1340, 1250, 1172, 1123, 1027, 990, 813, 721, 634, 493, 427 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.77 (s, 1H), 7.84 (s, 1H), 6.74 (s, 2H), 4.42 – 4.38 (m, 2H), 4.09 (t, *J* = 7.2 Hz, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.0 Hz, 4H), 3.37 – 3.34 (m, 2H), 1.85 – 1.71 (m, 12H), 1.49 – 1.24 (m, 71H), 0.88 (t, *J* = 6.6 Hz, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.1, 153.5, 146.9, 142.5, 133.6, 129.0, 110.3, 73.9, 69.7, 58.0, 54.0, 32.1, 30.6, 29.91, 29.89, 29.83, 29.78, 29.75, 29.69, 29.64, 29.56, 29.5, 29.3, 27.7, 27.4, 26.6, 26.3, 26.2, 22.8, 14.2 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for C<sub>59</sub>H<sub>108</sub>NO<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>): 878.8324; Found: 878.8335.

**(E)-1-methyl-4-(3,4,5-tris(decyloxy)benzylidene)-3,4-dihydro-2H-pyrrolidium iodide (10/3/MI):**

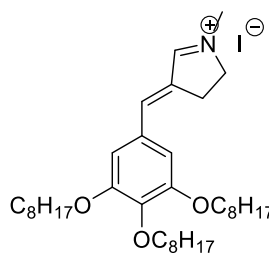


According to GP III, methyl iodide (21  $\mu$ L, 0.34 mmol) was reacted with **2b** (0.11 g, 0.17 mmol) in 4 mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours.

Filtration of the solid precipitate gave **10/3/MI** as yellow solid (0.08 g, 75%). FTIR (KBr):  $\tilde{\nu}$  = 3429, 2955, 2922, 2851, 1609, 1578, 1506, 1466, 1443, 1378, 1316, 1253, 1177, 1156, 1128, 1122, 1089, 972, 845, 804, 720, 626, 503 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.74 (s, 1H), 7.76 (s, 1H), 6.74 (s, 2H), 4.42 – 4.39 (m, 2H), 4.04 – 4.02 (m, 2H), 3.97 – 3.95 (m, 4H), 3.85 (s, 3H), 3.36 – 3.34 (m, 2H), 1.82 – 1.77 (m, 4H), 1.76 – 1.71 (m, 2H), 1.678 – 1.676 (m, 2H), 1.49 – 1.44 (m, 6H), 1.35 – 1.27 (m, 34H), 0.88 (t, *J* = 7.2 Hz, 9H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 173.2, 153.5, 146.6, 142.4, 133.7, 129.0, 110.2, 74.0, 69.6, 60.3, 41.3, 32.1, 30.6, 29.93, 29.87, 29.85, 29.80, 29.76, 29.65, 29.59, 29.56, 27.6, 26.3, 26.2, 22.9, 14.3 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. Exact mass calculated for C<sub>42</sub>H<sub>74</sub>NO<sub>3</sub><sup>+</sup> ([M]<sup>+</sup>): 640.5663; Found: 640.5681.

**(E)-1-methyl-4-(3,4,5-tris(octyloxy)benzylidene)-3,4-dihydro-2H-pyrrolidium iodide (8/3/MI):**

According to GP III, methyl iodide (35  $\mu$ L, 0.34 mmol) was reacted with **2a** (0.15 g, 0.28 mmol) in 6



mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours. Filtration of the solid precipitate gave **8/3/MI** as yellow solid (0.12 g, 63%). FTIR (KBr):  $\tilde{\nu}$  = 3426, 2955, 2921, 2851, 1609, 1577, 1504, 1468, 14443, 1378, 1339, 1315, 1253, 1208, 1176, 1154, 1131, 1121, 1091, 1031, 978, 925, 869, 845, 804, 722, 626, 503 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.73 (s, 1H), 7.73 (s, 1H), 6.73 (s, 2H), 4.48 – 4.43 (m, 2H), 4.05 – 3.94 (m, 6H), 3.86 (s, 3H), 3.38 – 3.33 (m, 2H), 1.87 – 1.70 (m, 6H), 1.50

– 1.29 (m, 30H), 0.91 – 0.87 (m, 9H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 173.2, 153.5, 146.5, 142.4, 133.8, 128.9, 110.2, 74.0, 69.6, 60.3, 41.3, 32.1, 32.0, 30.5, 29.7, 29.6, 29.54, 29.52, 29.46, 27.6, 26.3, 26.2, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{36}\text{H}_{62}\text{NO}_3^+$  ( $[\text{M}]^+$ ): 556.4724; Found: 556.4726.

**(E)-4-(3,4-bis(dodecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolium iodide**

**(12/(3,4)/MI):**

According to GP III, methyl iodide (13  $\mu\text{L}$ , 0.20 mmol) was reacted with **2e** (0.05 g, 0.10 mmol) in 2 mL DCM: $\text{CH}_3\text{CN}$  (1:3) for 24 hours. Filtration of the solid precipitate gave **12/(3,4)/MI** as yellow solid (0.06 g, 88%). FTIR (KBr):  $\tilde{\nu}$  = 3436, 2956, 2917, 2873, 2848, 1616, 1586, 1518, 1439, 1394, 1337, 1283, 1248, 1149, 1181, 1072, 1031, 994, 954, 915, 871, 805, 721, 614, 599, 494  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.65 (s, 1H), 7.77 (s, 1H), 7.14 (d,  $J$  = 8.4 Hz, 1H), 7.01 – 7.00 (m, 1H), 6.89 (d,  $J$  = 8.4 Hz, 1H), 4.42 – 4.40 (m, 2H), 4.05 – 4.03 (m, 2H), 4.00 – 3.97 (m, 2H), 3.83 (s, 3H), 3.35 – 3.33 (m, 2H), 1.86 – 1.79 (m, 4H), 1.49 – 1.45 (m, 4H), 1.36 – 1.26 (m, 32H), 0.89 – 0.87 (m, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 172.6, 152.9, 149.2, 145.9, 132.6, 126.8, 126.3, 115.7, 112.9, 69.6, 69.2, 60.2, 41.1, 32.0, 29.80, 29.78, 29.74, 29.71, 29.6, 29.5, 29.4, 29.3, 29.1, 27.6, 26.1, 26.1, 22.8, 14.2 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{36}\text{H}_{62}\text{NO}_2^+$  ( $[\text{M}]^+$ ): 540.4775; Found: 540.4776.

**(E)-4-(3,4-bis(dodecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolium tetrafluoroborate (12/(3,4)/MBF):**

According to GP III, trimethyloxonium tetrafluoroborate (32 mg, 0.22 mmol) was reacted with **2e** (0.06 g, 0.11 mmol) in 2 mL DCM: $\text{CH}_3\text{CN}$  (1:3) for 24 hours. Filtration of the solid precipitate gave **12/(3,4)/MBF** as yellow solid (0.04 g, 59%). FTIR (KBr):  $\tilde{\nu}$  = 3428, 2955, 2918, 2849, 1646, 1619, 1590, 1519, 1468, 1419, 1390, 1325, 1283, 1251, 1184, 1150, 1071, 1040, 995, 955, 915, 871, 832, 916, 721, 631, 616, 600, 521, 499  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.67 (s, 1H), 7.56 (s, 1H), 7.10 (d,  $J$  = 7.8 Hz, 1H), 6.98 (s, 1H), 6.87 (d,  $J$  = 8.4 Hz, 1H), 4.33 – 4.30 (m, 2H), 4.02 (t,  $J$  = 6.6 Hz, 2H), 3.96 (t,  $J$  = 6.6 Hz, 2H), 3.67 (s, 3H), 3.31 – 3.29 (m, 2H), 1.85 – 1.78 (m, 4H), 1.49 – 1.44 (m, 4H), 1.36 – 1.26 (m, 32H), 0.89 – 0.87 (m, 6H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 173.4, 153.1, 149.4, 146.1, 132.9, 127.0, 126.3, 115.9, 113.0, 69.7, 69.3, 59.5, 40.1, 32.1, 29.95, 29.93, 29.88, 29.8, 29.7, 29.63, 29.59, 29.5, 29.3, 27.5, 26.3, 26.2, 22.9, 14.3 ppm. Total



count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{36}\text{H}_{62}\text{NO}_2^+$  ( $[\text{M}]^+$ ): 540.4775; Found: 540.4778.

**(E)-4-(3,4-bis(dodecyloxy)benzylidene)-1-ethyl-3,4-dihydro-2H-pyrrolium tetrafluoroborate (12/(3,4)/EBF):**

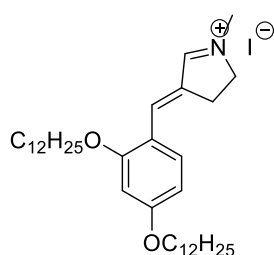
According to GP III, triethyloxonium tetrafluoroborate (27 mg, 0.14 mmol) was reacted with **2e** (49 mg, 0.09 mmol) in 1 mL DCM:CH<sub>3</sub>CN (1:1) for 24 hours. Filtration of the solid precipitate gave **12/(3,4)/EBF** as yellow solid (41 mg, 68%). FTIR (KBr):  $\tilde{\nu}$  = 3266, 2955, 2918, 2849, 1618, 1587, 1517, 1467, 1440, 1396, 1282, 1249, 1183, 1149, 1073, 957, 914, 874, 835, 798, 721, 600, 522, 500 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.65 (s, 1H), 7.58 (s, 1H), 7.09 (d,  $J$  = 8.4 Hz, 1H), 6.97 (s, 1H), 6.85 (d,  $J$  = 8.4 Hz, 1H), 4.33 – 4.29 (m, 2H), 4.02 – 3.98 (m, 2H), 3.95 – 3.90 (m, 4H), 3.29 – 3.26 (m, 2H), 1.85 – 1.76 (m, 4H), 1.47 – 1.43 (m, 8H), 1.32 – 1.26 (m, 31H), 0.90 – 0.86 (m, 6H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 171.5, 152.9, 149.2, 146.0, 133.0, 127.1, 126.3, 115.8, 112.9, 69.6, 69.2, 57.3, 48.4, 32.1, 29.93, 29.91, 29.87, 29.8, 29.7, 29.63, 29.58, 29.57, 29.4, 29.3, 27.0, 26.25, 26.18, 22.9, 14.3, 12.7 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{37}\text{H}_{64}\text{NO}_2^+$  ( $[\text{M}]^+$ ): 554.4932; Found: 554.4922.

**(E)-4-(2,3-bis(dodecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolium iodide (12/(2,3)MI):**

According to GP III, methyl iodide (31  $\mu\text{L}$ , 0.49 mmol) was reacted with **2h** (0.12 g, 0.24 mmol) in 4 mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours. Filtration of the solid precipitate gave **12/(2,3)MI** as yellow solid (93 mg, 57%). FTIR (KBr):  $\tilde{\nu}$  = 3435, 3041, 2953, 2920, 2849, 2870, 1613, 1642, 1589, 1573, 1479, 1467, 1455, 1425, 1379, 1304, 1278, 1263, 1219, 1159, 1193, 1088, 1057, 986, 964, 948, 908, 863, 832, 786, 764, 746, 721, 616, 497 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.36 (s, 1H), 8.06 (s, 1H), 7.08 – 7.06 (m, 2H), 7.01 – 7.00 (m, 1H), 4.49 – 4.47 (m, 2H), 4.03 – 4.01 (m, 2H), 3.97 (t,  $J$  = 6.6 Hz, 2H), 3.91 (s, 3H), 3.35 – 3.34 (m, 2H), 1.85 – 1.77 (m, 6H), 1.50 – 1.45 (m, 2H), 1.44 – 1.41 (m, 2H), 1.36 – 1.26 (m, 30H), 0.89 – 0.87 (m, 6H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 173.2, 152.7, 149.4, 140.6, 135.8, 128.3, 124.2, 120.7, 117.0, 75.0, 69.0, 60.7, 41.8, 32.09, 32.08, 30.4, 29.91, 29.88, 29.86, 29.8, 29.7, 29.6, 29.55, 29.52, 29.48, 27.7, 26.4, 26.1, 22.8, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aromatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{36}\text{H}_{62}\text{NO}_2^+$  ( $[\text{M}]^+$ ): 540.4775; Found: 540.4771.

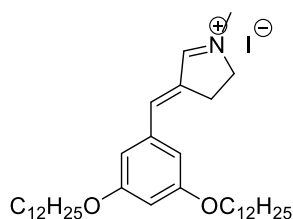
**(E)-4-(2,4-bis(dodecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolium iodide (12/(2,4)MI):**

According to GP III, methyl iodide (40  $\mu$ L, 0.63 mmol) was reacted with **2f** (0.15 g, 0.32 mmol) in 4



mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours. Filtration of the solid precipitate gave **12/(2,4)/MI** as yellow solid (0.14 g, 66%). FTIR (KBr):  $\tilde{\nu}$  = 3432, 2872, 2922, 2851, 1640, 1584, 1499, 1469, 1447, 1435, 1389, 1318, 1266, 1230, 1193, 1164, 1110, 1079, 1029, 1008, 989, 912, 826, 721, 616, 594, 535, 498, 490 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.07 (s, 1H), 8.03 (s, 1H), 7.45 (d,  $J$  = 9.0 Hz, 1H), 6.55 – 6.53 (m, 1H), 6.41 (s, 1H), 4.46 – 4.44 (m, 2H), 4.02 – 3.97 (m, 4H), 3.86 (s, 3H), 3.34 – 3.22 (m, 2H), 1.87 – 1.84 (m, 2H), 1.81 – 1.78 (m, 2H), 1.48 – 1.41 (m, 4H), 1.36 – 1.26 (m, 31H), 0.89 – 0.87 (m, 6H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.5, 164.7, 161.1, 140.2, 131.6, 131.2, 116.4, 106.8, 99.6, 69.2, 68.7, 60.1, 41.3, 32.1, 29.84, 29.81, 29.77, 29.7, 29.54, 29.50, 29.2, 29.1, 28.0, 26.1, 22.9, 14.3 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aromatic region. HRMS (ESI): Exact mass calculated for C<sub>36</sub>H<sub>62</sub>NO<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 540.4775; Found: 540.4787.

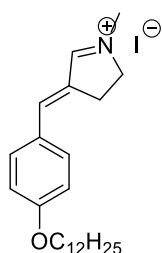
**(E)-4-(3,5-bis(dodecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolidium iodide (12/(3,5)/MI):**



According to GP III, methyl iodide (31  $\mu$ L, 0.50 mmol) was reacted with **2g** (0.13 g, 0.25 mmol) in 4 mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours. Filtration of the solid precipitate gave **12/(3,5)/MI** as yellow solid (59 mg, 35%).

FTIR (KBr):  $\tilde{\nu}$  = 3435, 2955, 2920, 2851, 1618, 1585, 1466, 1418, 1384, 1341, 1302, 1260, 1165, 1196, 1090, 1059, 890, 835, 721, 680, 494 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.77 (s, 1H), 7.75 (s, 1H), 6.59 (s, 2H), 6.51 (s, 1H), 4.46 – 4.43 (m, 2H), 3.91 – 3.89 (m, 6H), 3.37 – 3.34 (m, 2H), 1.92 – 1.89 (m, 2H), 1.78 – 1.73 (m, 4H), 1.45 – 1.41 (m, 4H), 1.35 – 1.27 (m, 31H), 0.89 – 0.87 (m, 6H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 173.4, 160.7, 146.1, 135.8, 135.4, 109.4, 105.1, 68.6, 60.6, 41.6, 32.1, 29.84, 29.80, 29.76, 29.6, 29.5, 29.3, 27.7, 26.2, 22.8, 14.3 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for C<sub>36</sub>H<sub>62</sub>NO<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 540.4775; Found: 540.4769.

**(E)-4-(4-(dodecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolidium iodide (12/p/MI):**

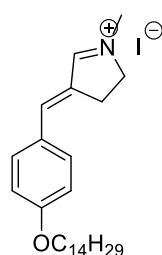


According to GP III, methyl iodide (15  $\mu$ L, 0.25 mmol) was reacted with **2c** (42 mg, 0.12 mmol) in 2 mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours. Filtration of the solid precipitate gave **12/p/MI** as yellow solid (49 mg, 83%). FTIR (KBr):  $\tilde{\nu}$  = 3436, 2948, 2867, 2948, 2921, 1643, 1617, 1594, 1575, 1560, 1511, 1471, 1448, 1423, 1381, 1312, 1274, 1257, 1189, 1178, 1160, 1120, 1090, 1058, 1043, 913, 1003, 1025, 991, 896, 848, 811, 835,

788, 765, 720, 609, 587, 540, 494  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.55 (s, 1H), 7.79 (s, 1H), 7.48 (d,  $J$  = 8.8 Hz, 2H), 6.92 (d,  $J$  = 8.4 Hz, 2H), 4.48 – 4.45 (m, 2H), 3.98 (t,  $J$  = 6.4 Hz, 2H), 3.83 (s, 3H), 3.33 – 3.30 (m, 2H), 1.82 – 1.75 (m, 2H), 1.45 – 1.41 (m, 2H), 1.32 – 1.27 (m, 16H), 0.90 – 0.86 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{cdcl}_3$ )  $\delta$  = 172.6, 162.4, 145.6, 133.6, 132.5, 126.6, 115.4, 68.5, 60.3, 32.0, 29.74, 29.71, 29.68, 29.6, 29.5, 29.4, 29.1, 27.69, 27.68, 26.0, 22.8, 14.2 ppm. HRMS (ESI): Exact mass calculated for  $\text{C}_{24}\text{H}_{38}\text{NO}^+$  ( $[\text{M}]^+$ ): 356.2948; Found: 356.2955.

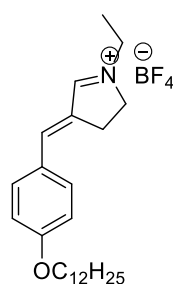
**(E)-1-methyl-4-(4-(tetradecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium iodide (14/p/MI):**

According to GP III, methyl iodide (31  $\mu\text{L}$ , 0.49 mmol) was reacted with **2k** (0.09 g, 0.24 mmol) in 2 mL DCM: $\text{CH}_3\text{CN}$  (1:3) for 24 hours. Filtration of the solid precipitate gave **14/p/MI** as yellow solid (0.08 g, 67%). FTIR (KBr):  $\tilde{\nu}$  = 3436, 2948, 2920, 2851, 1617, 1594, 1561, 1512, 1471, 1448, 1423, 1382, 1312, 1275, 1259, 1179, 1161, 1120, 1037, 1024, 1013, 976, 914, 896, 811, 719, 610, 588, 540, 494  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.62 (s, 1H), 7.81 (s, 1H), 7.49 (d,  $J$  = 9.0 Hz, 2H), 6.94 (d,  $J$  = 8.4 Hz, 2H), 4.41 – 4.38 (m, 2H), 4.01 – 3.99 (m, 2H), 3.83 (s, 3H), 3.35 – 3.33 (m, 2H), 1.82 – 1.78 (m, 2H), 1.67 – 1.64 (m, 4H), 1.48 – 1.43 (m, 2H), 1.36 – 1.26 (m, 16H), 0.88 (t,  $J$  = 7.2 Hz, 3H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 173.0, 162.6, 146.1, 133.7, 132.4, 126.7, 115.6, 68.7, 60.2, 41.1, 32.1, 29.88, 29.86, 29.85, 29.84, 29.79, 29.7, 29.6, 29.5, 29.2, 27.7, 26.1, 22.9, 14.3 ppm. HRMS (ESI): Exact mass calculated for  $\text{C}_{26}\text{H}_{42}\text{NO}^+$  ( $[\text{M}]^+$ ): 384.3261; Found: 384.3256.



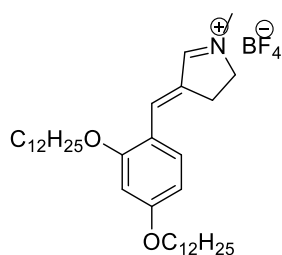
**(E)-4-(4-(dodecyloxy)benzylidene)-1-ethyl-3,4-dihydro-2H-pyrrolium tetrafluoroborate (12/p/EBF):**

According to GP III, triethyloxonium tetrafluoroborate (0.19 g, 1.0 mmol) was reacted with **2c** (0.17 g, 0.50 mmol) in 4 mL DCM: $\text{CH}_3\text{CN}$  (1:1) for 24 hours. Filtration of the solid precipitate gave **12/p/EBF** as yellow solid (0.12 g, 53%). FTIR (KBr):  $\tilde{\nu}$  = 3443, 3495, 3084, 3291, 2919, 2849, 1593, 1562, 1513, 1617, 1469, 1430, 1395, 1386, 1324, 1311, 1256, 1175, 1159, 1072, 1055, 1024, 904, 834, 813, 765, 722, 622, 589, 541, 521, 503  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.67 (s, 1H), 7.63 – 7.62 (m, 1H), 7.45 – 7.43 (m, 2H), 6.90 – 6.88 (m, 2H), 4.32 – 4.30 (m, 2H), 3.98 – 3.92 (m, 4H), 3.28 – 3.27 (m, 2H), 1.80 – 1.75 (m, 3H), 1.47 – 1.43 (m, 4H), 1.35 – 1.27 (m, 16H), 0.88 (t,  $J$  = 7.2 Hz, 3H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 171.3, 162.1, 145.1, 133.4, 133.1, 126.9, 115.3, 68.5, 57.4, 48.3, 32.0, 29.8, 29.75, 29.70, 29.55, 29.46, 29.2, 26.9, 26.1, 22.8, 14.2, 12.5 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{25}\text{H}_{40}\text{NO}^+$  ( $[\text{M}]^+$ ): 370.3104; Found: 370.3126.



**(E)-4-(2,4-bis(dodecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolium tetrafluoroborate (12/(2,4)/MBF):**

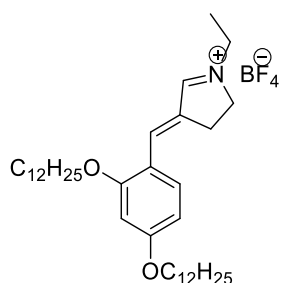
According to GP III, trimethyloxonium tetrafluoroborate (0.1 g, 0.67 mmol) was reacted with **2f** (0.16



g, 0.33 mmol) in 4 mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours. Filtration of the solid precipitate gave **12/(2,4)/MBF** as yellow solid (0.10 g, 48%). FTIR (KBr):  $\tilde{\nu}$  = 3428, 3089, 2921, 2851, 1587, 1502, 1470, 1436, 1405, 1390, 1319, 1269, 1232, 1194, 1164, 1113, 1067, 1033, 913, 826, 721, 643, 614, 594, 535, 522, 497 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.47 (s, 1H), 7.95 (s, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.40 (s, 1H), 4.32 (t, *J* = 6.6 Hz, 2H), 4.00 – 3.95 (m, 4H), 3.67 (s, 3H), 3.31 – 3.26 (m, 2H), 1.86 – 1.83 (m, 2H), 1.81 – 1.78 (m, 2H), 1.47 – 1.41 (m, 4H), 1.35 – 1.27 (m, 32H), 0.89 – 0.86 (m, 6H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.6, 164.4, 160.8, 139.3, 132.0, 131.4, 116.5, 106.6, 99.5, 69.1, 68.6, 59.3, 39.8, 32.0, 29.80, 29.77, 29.74, 29.71, 29.53, 29.48, 29.4, 29.2, 29.0, 27.7, 26.1, 26.0, 22.8, 14.2 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aromatic region. HRMS (ESI): Exact mass calculated for C<sub>36</sub>H<sub>62</sub>NO<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 540.4775; Found: 540.4750.

**(*E*)-4-(2,4-bis(dodecyloxy)benzylidene)-1-ethyl-3,4-dihydro-2H-pyrrolium tetrafluoroborate (12/(2,4)/EBF):**

According to GP III, triethyloxonium tetrafluoroborate (0.13 g, 0.70 mmol) was reacted with **2f** (0.16

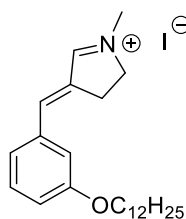


g, 0.35 mmol) in 4 mL DCM:CH<sub>3</sub>CN (1:1) for 24 hours. Filtration of the solid precipitate gave **12/(2,4)/EBF** as yellow solid (0.12 g, 52%). FTIR (KBr):  $\tilde{\nu}$  = 3443, 2921, 2851, 1584, 1501, 1470, 1435, 1391, 1320, 1271, 1216, 1194, 1159, 1111, 1083, 1060, 1033, 908, 826, 721, 643, 613, 595, 521, 501 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.49 (s, 1H), 7.99 (s, 1H), 7.43 (d, *J* = 9.0 Hz, 1H), 6.53 (d, *J* = 9.0 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H),

4.33 – 4.31 (m, 2H), 4.01 – 3.96 (m, 6H), 3.31 – 3.28 (m, 2H), 1.87 – 1.82 (m, 2H), 1.81 – 1.76 (m, 2H), 1.49 – 1.41 (m, 8H), 1.38 – 1.27 (m, 31H), 0.89 – 0.86 (m, 6H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 171.1, 164.6, 161.1, 140.1, 131.61, 131.56, 116.6, 106.7, 99.6, 69.2, 68.7, 57.2, 48.3, 32.1, 29.9, 29.85, 29.80, 29.78, 29.6, 29.5, 29.3, 29.0, 27.4, 26.1, 22.9, 14.3, 12.9 ppm. Total count of <sup>13</sup>C is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for C<sub>37</sub>H<sub>64</sub>NO<sub>2</sub><sup>+</sup> ([M]<sup>+</sup>): 554.4932; Found: 554.4933.

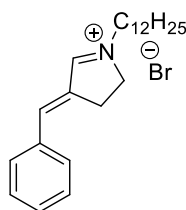
**(*E*)-4-(3-(dodecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolium iodide (12/m/MI):**

According to GP III, methyl iodide (13  $\mu$ L, 0.21 mmol) was reacted with **2d** (36 mg, 0.11 mmol) in 1 mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours. Filtration of the solid precipitate gave **12/m/MI** as yellow solid (21 mg, 40%). FTIR (KBr):  $\tilde{\nu}$  = 3489, 3422, 2954, 2922, 2851, 1616, 1594, 1576, 1494, 1457, 1385, 1331, 1309, 1264, 1206, 1181, 1158, 1093, 1030, 954, 909, 888, 787, 721, 684, 501, 463 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.78 (s, 1H), 7.81 (s, 1H), 7.34 – 7.32 (m, 1H), 7.09 (d,  $J$  = 7.8 Hz, 1H), 6.98 (s, 2H), 4.47 – 4.45 (m, 2H), 3.94 – 3.92 (m, 2H), 3.88 (s, 3H), 3.40 – 3.34 (m, 2H), 1.78 – 1.76 (m, 4H), 1.47 – 1.42 (m, 2H), 1.35 – 1.27 (m, 14H), 0.89 – 0.87 (m, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 173.4, 159.7, 146.0, 135.7, 135.1, 130.4, 123.5, 118.5, 116.7, 68.5, 60.7, 41.6, 32.1, 29.85, 29.81, 29.80, 29.8, 29.6, 29.5, 29.4, 27.7, 26.2, 22.9, 14.3 ppm. HRMS (ESI): Exact mass calculated for C<sub>24</sub>H<sub>38</sub>NO<sup>+</sup> ([M]<sup>+</sup>): 356.2948; Found: 356.2968.



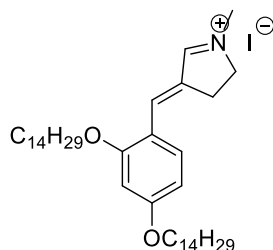
**(E)-4-benzylidene-1-dodecyl-3,4-dihydro-2H-pyrrolium bromide (PhC12Br):**

According to GP III, *n*-bromododecane (0.38 mL, 1.59 mmol) was reacted with previously synthesized (*E*)-4-benzylidene-3,4-dihydro-2H-pyrrole<sup>9</sup> (0.11 g, 0.72 mmol) in 4 mL DCM:CH<sub>3</sub>CN (1:3) in an inert atmosphere and allowed to heat at 60 °C for 72 hours. Filtration of the solid precipitate gave **PhC12Br** as brown soft solid (0.14 g, 47%). FTIR (KBr):  $\tilde{\nu}$  = 3476, 2955, 2922, 2852, 1622, 1595, 1574, 1493, 1470, 1457, 1388, 1357, 1327, 1192, 1182, 1104, 1029, 1003, 935, 895, 801, 773, 723, 693, 504, 435 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.00 (s, 1H), 7.96 (s, 1H), 7.53 – 7.52 (m, 2H), 7.46 – 7.41 (m, 3H), 4.50 – 4.48 (m, 2H), 4.18 – 4.16 (m, 2H), 3.39 – 3.38 (m, 2H), 1.88 – 1.83 (m, 2H), 1.35 – 1.23 (m, 18H), 0.89 – 0.86 (m, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.8, 146.2, 135.5, 134.0, 131.9, 131.2, 129.4, 58.0, 53.9, 45.3, 32.0, 29.7, 29.6, 29.5, 29.4, 29.1, 27.5, 27.1, 26.5, 24.4, 22.8, 14.2 ppm. HRMS (ESI): Exact mass calculated for C<sub>23</sub>H<sub>36</sub>N<sup>+</sup> ([M]<sup>+</sup>): 326.2842; Found: 326.2863.



**(E)-4-(2,4-bis(tetradecyloxy)benzylidene)-1-methyl-3,4-dihydro-2H-pyrrolium iodide (14/(2,4)/MI):**

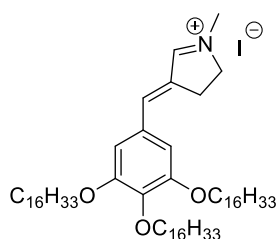
According to GP III, methyl iodide (31  $\mu$ L, 0.50 mmol) was reacted with **2j** (0.14 g, 0.25 mmol) in 2 mL DCM:CH<sub>3</sub>CN (1:3) for 24 hours. Filtration of the solid precipitate gave **14/(2,4)/MI** as yellow solid (0.11 g, 64%). FTIR (KBr):  $\tilde{\nu}$  = 3436, 2947, 2920, 2850, 1617, 1594, 1560, 1511, 1471, 1423, 1382, 1312, 1275, 1259, 1178, 1161, 1120, 1036, 1024, 1013, 896, 835, 811, 797, 719, 610, 588, 540, 494 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.07 (s, 1H), 8.03 (s, 1H), 7.45 (d,  $J$  = 8.8 Hz, 1H), 6.54 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 6.41 (d,  $J$  = 2.0 Hz, 1H), 4.47 – 4.44 (m, 2H), 4.02 – 3.96 (m, 4H), 3.86 (s, 3H), 3.35 – 3.32 (m, 2H), 1.87 – 1.77 (m, 4H), 1.47



– 1.42 (m, 4H), 1.31 – 1.26 (m, 40H), 0.89 – 0.86 (m, 6H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 172.5, 164.6, 161.0, 140.0, 131.6, 131.2, 116.4, 106.7, 99.5, 69.1, 68.7, 60.1, 41.3, 32.1, 29.88, 29.86, 29.83, 29.77, 29.7, 29.54, 29.53, 29.49, 29.2, 29.0, 28.0, 26.1, 22.9, 14.3 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aromatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{40}\text{H}_{70}\text{NO}_2^+$  ( $[\text{M}]^+$ ): 596.5401; Found: 596.5372.

**(E)-1-methyl-4-(3,4,5-tris(hexadecyloxy)benzylidene)-3,4-dihydro-2H-pyrrolium iodide (16/3/MI):**

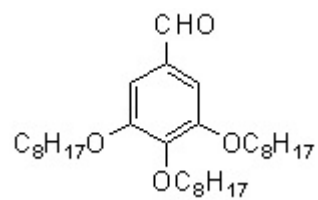
According to GP III, methyl iodide (28  $\mu\text{L}$ , 0.45 mmol) was reacted with **2I** (0.20 g, 0.22 mmol) in 2



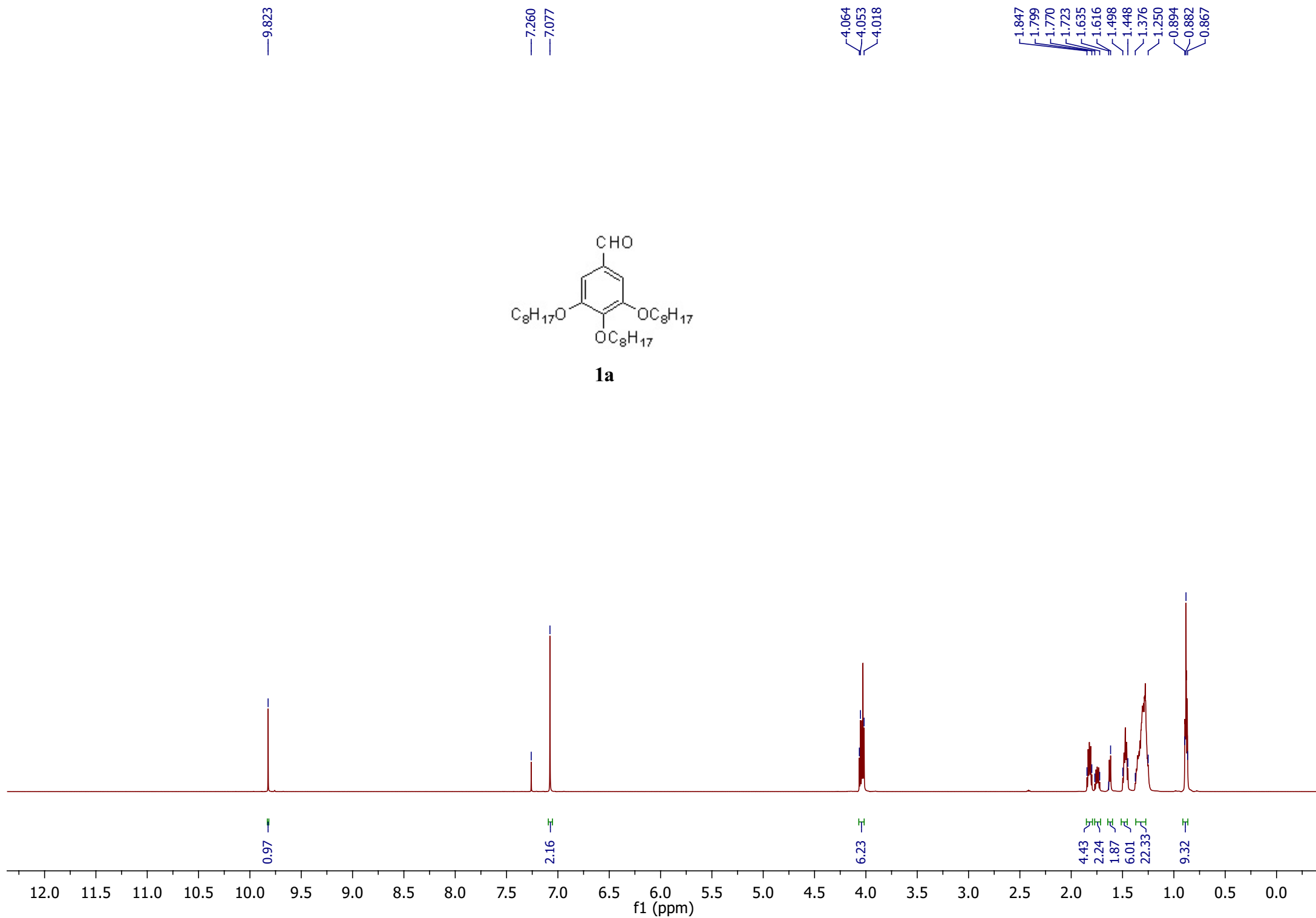
mL  $\text{DCM}:\text{CH}_3\text{CN}$  (1:3) for 24 hours. Filtration of the solid precipitate gave **16/3/MI** as yellow solid (0.88 g, 78%). FTIR (KBr):  $\tilde{\nu}$  = 3400, 2955, 2917, 2849, 1612, 1571, 1502, 1467, 1437, 1379, 1339, 1252, 1176, 1124, 987, 920, 815, 720, 633, 498  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.81 (s, 1H), 7.75 (s, 1H), 6.73 (s, 2H), 4.37 – 4.35 (m, 2H), 4.05 (t,  $J$  = 6.6 Hz, 2H), 3.96 (t,  $J$  = 6.6 Hz, 4H), 3.84 (s, 3H), 3.37 – 3.36 (m, 2H), 1.83 – 1.79 (m, 4H), 1.76 – 1.71 (m, 3H), 1.50 – 1.45 (m, 6H), 1.38 – 1.26 (m, 71H), 0.88 (t,  $J$  = 7.2 Hz, 9H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 173.5, 153.6, 147.2, 142.7, 133.2, 128.8, 110.3, 74.0, 69.7, 60.0, 41.1, 32.1, 30.6, 30.0, 29.90, 29.89, 29.8, 29.7, 29.6, 29.5 (2C), 26.3, 26.2, 22.9, 14.4 ppm. Total count of  $^{13}\text{C}$  is less than expected due to the merging of signals in the aliphatic region. HRMS (ESI): Exact mass calculated for  $\text{C}_{60}\text{H}_{110}\text{NO}_3^+$  ( $[\text{M}]^+$ ): 892.8480; Found: 892.8478.

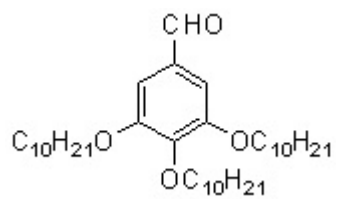
**References:**

- <sup>1</sup> Pathak, S. K.; Gupta, M.; Pal, S. K.; Achalkumar, A. S. *ChemistrySelect* **2016**, *1*, 5107.
- <sup>2</sup> Reddy, K. R.; Lobo, N. P.; Narasimhaswamy, T. *Journal of Physical Chemistry B* **2016**, *120*, 6897.
- <sup>3</sup> He, Q.; Han, Y.; Wang, Y.; Huang, Z. T.; Wang, D. X. *Chem. Eur. J.* **2014**, *20*, 1.
- <sup>4</sup> Pradhan, B.; Pathak, S. K.; Gupta, R. K.; Gupta, M.; Pal, S. K.; Achalkumar, A. S. *J. Mater. Chem. C* **2016**, *4*, 6117.
- <sup>5</sup> Nummelin, S.; Liljeström, V.; Saarikoski, E.; Ropponen, J.; Nykänen, A.; Linko, V.; Seppälä, J.; Hirvonen, J.; Ikkala, O.; Bimbo, L. M.; Kostiainen, M. A. *Chem. Eur. J.* **2015**, *21*, 14433.
- <sup>6</sup> Vela, S.; Berrocal, J. A.; Atienza, C.; Meijer, E. W.; Martin, N. *Chem Commun.* **2017**, 53, 4084.
- <sup>7</sup> Veerabhadraswamy, B. N.; Dambal, H. K.; Rao, D. S. S.; Yelamaggad, C. V. *ChemPhysChem* **2016**, *17*, 2225.
- <sup>8</sup> Charisiadis, A.; Nikolaou, V.; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G. D.; Coutsolelos, A. G. *New J. Chem.* **2016**, *40*, 5930.
- <sup>9</sup> Mandal, S.; Mahato, S.; Jana, C. K. *Org. Lett.* **2015**, *17*, 3762.

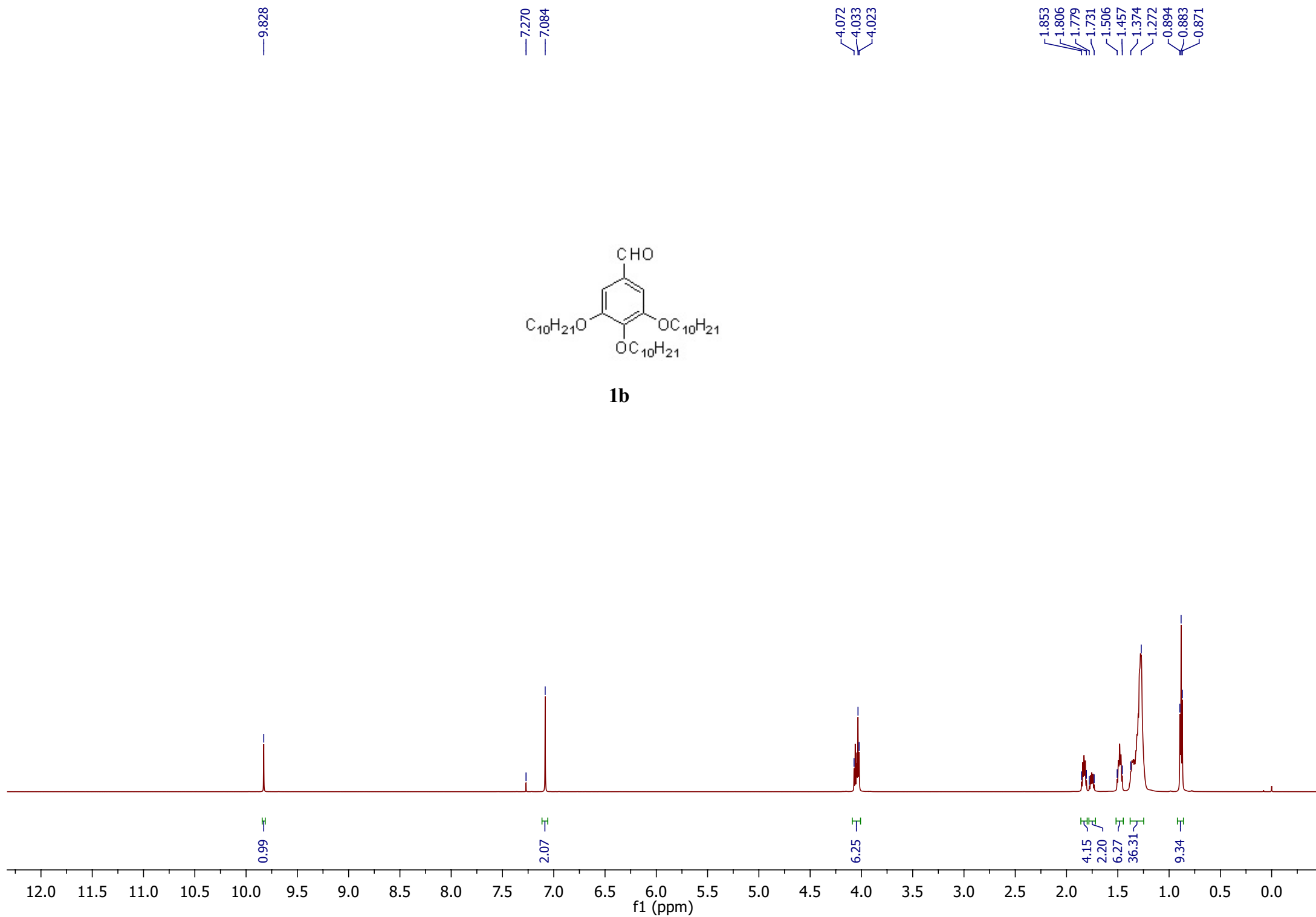


**1a**

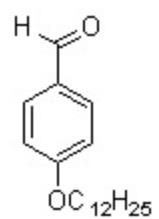




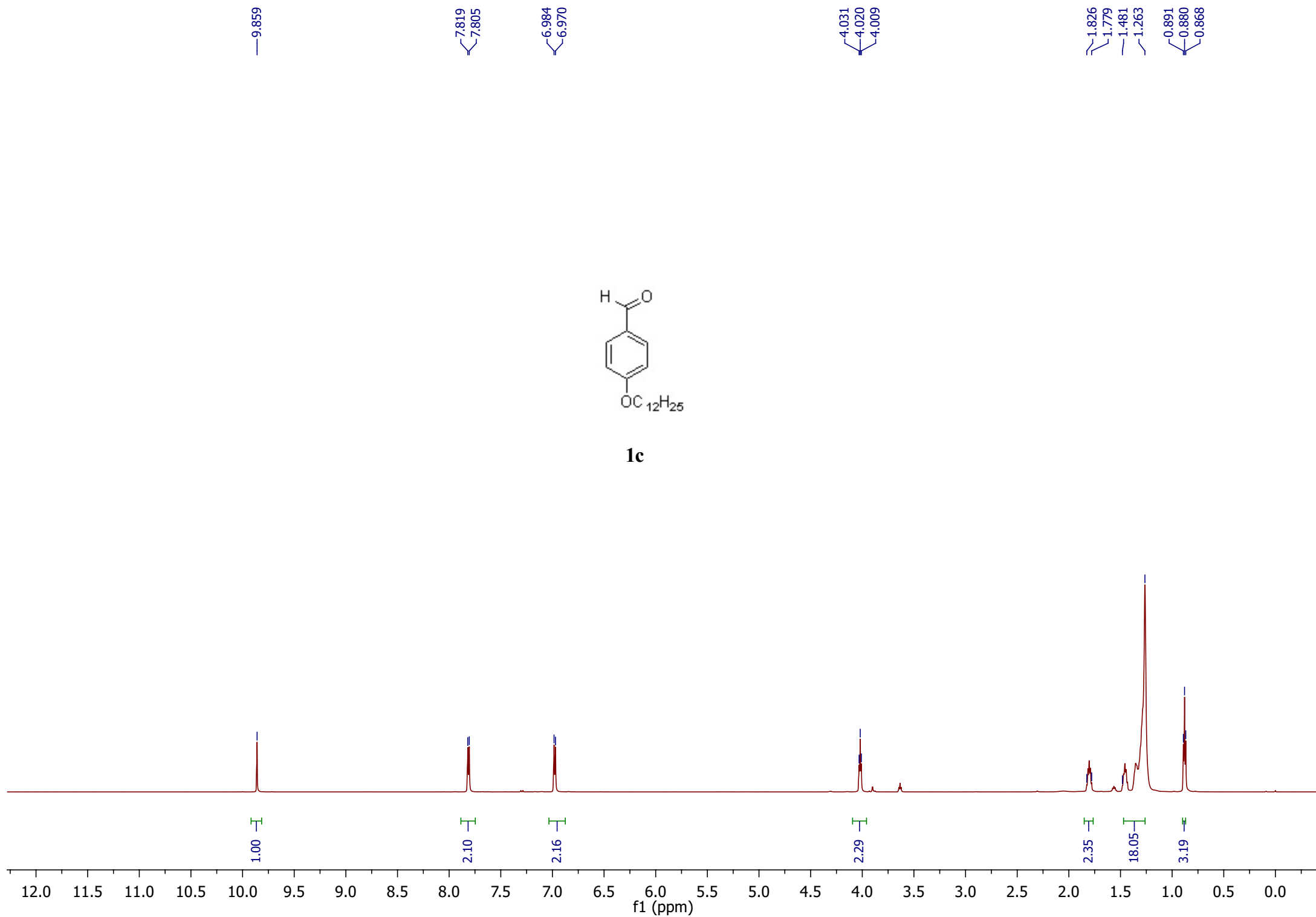
**1b**

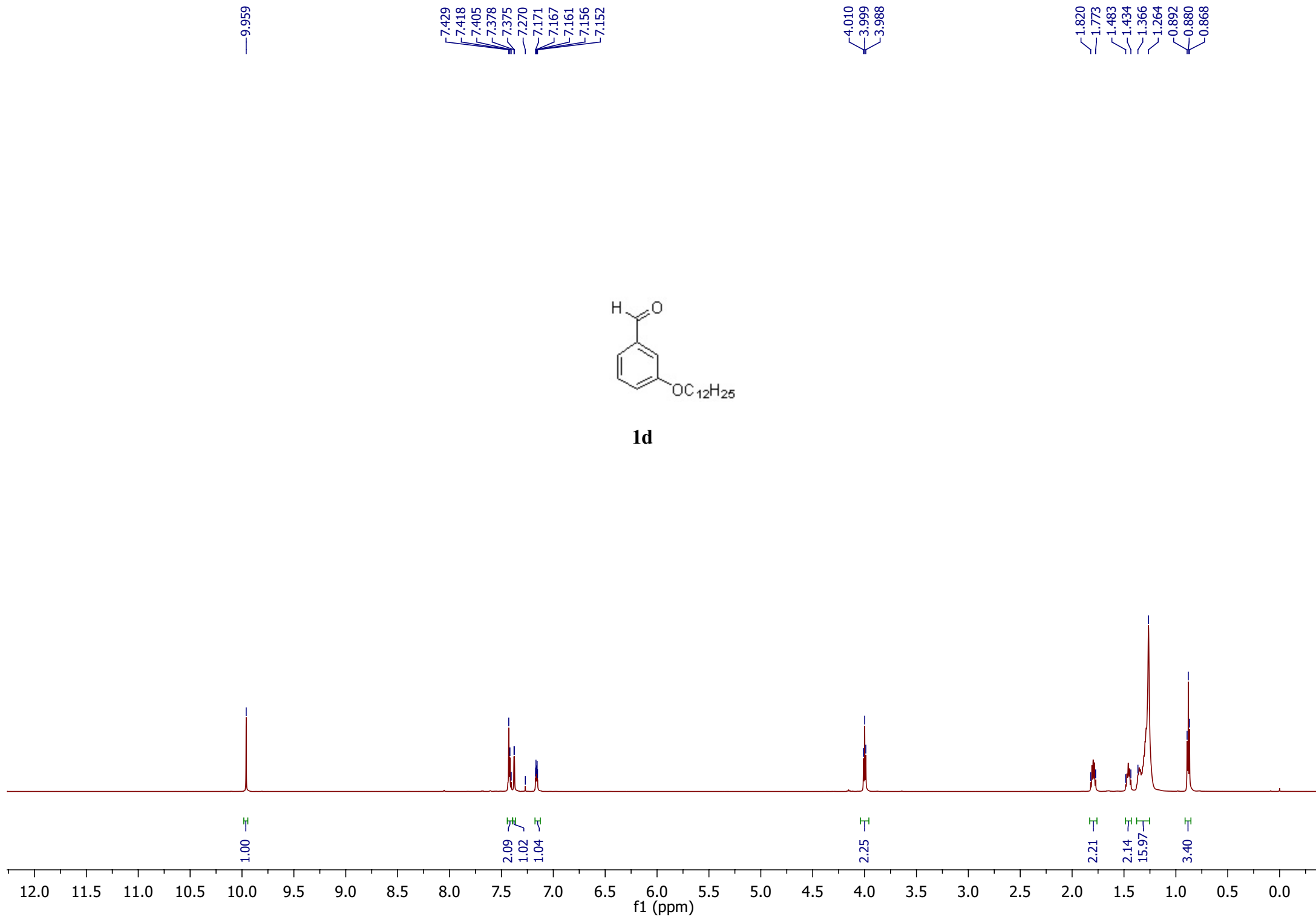


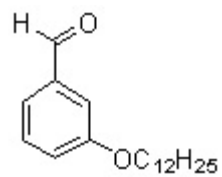




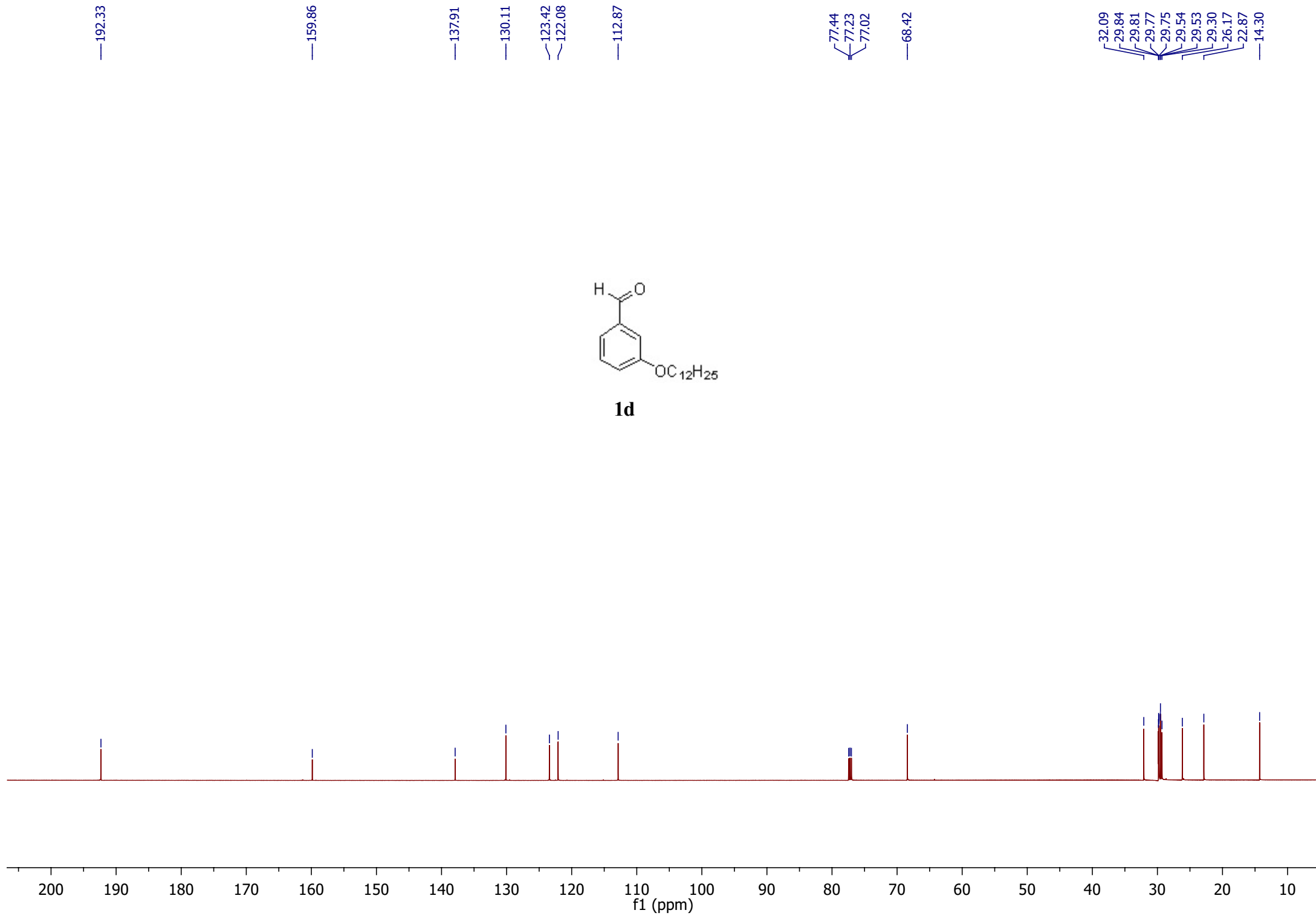
**1c**

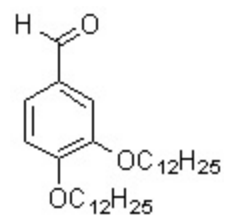




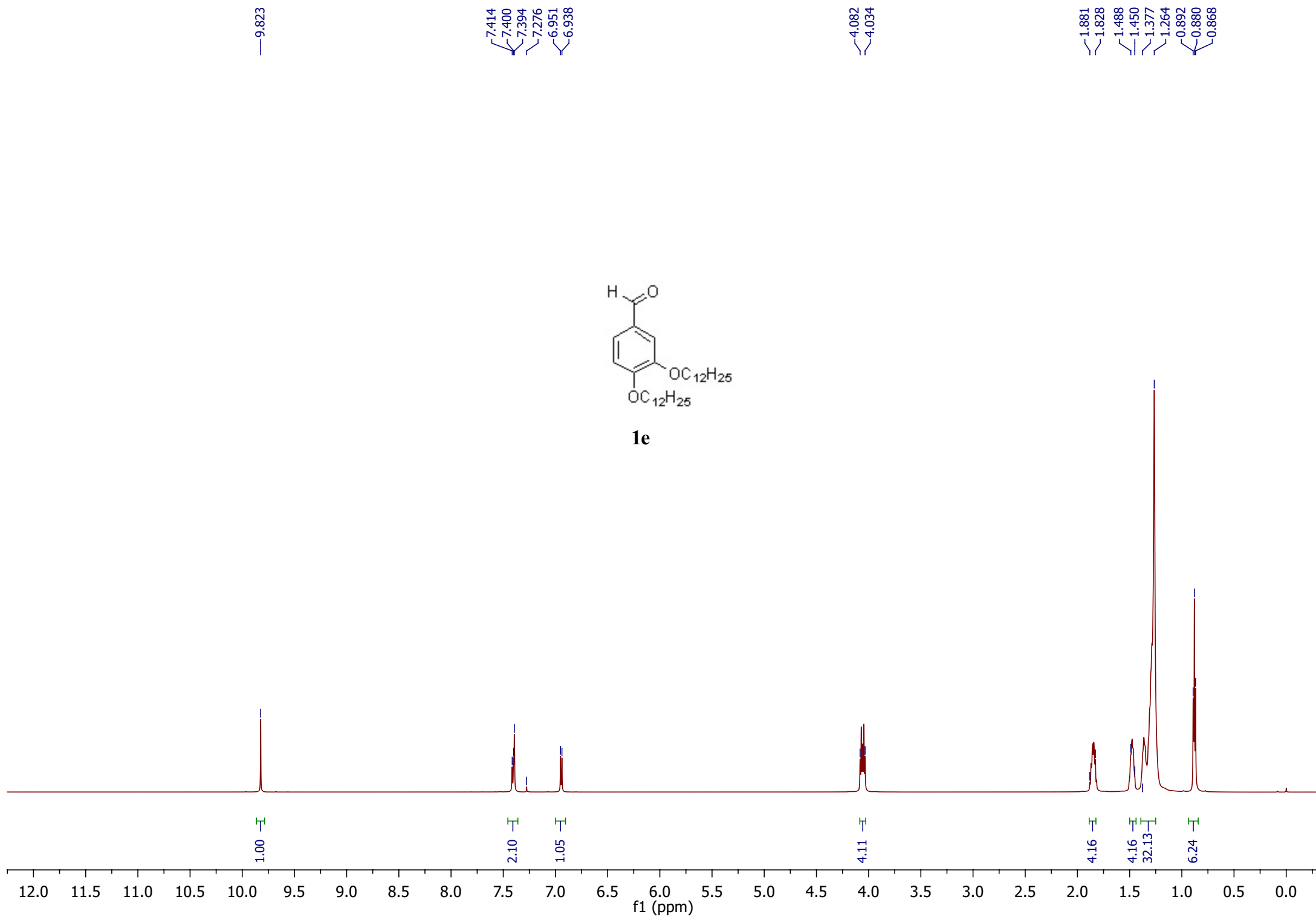


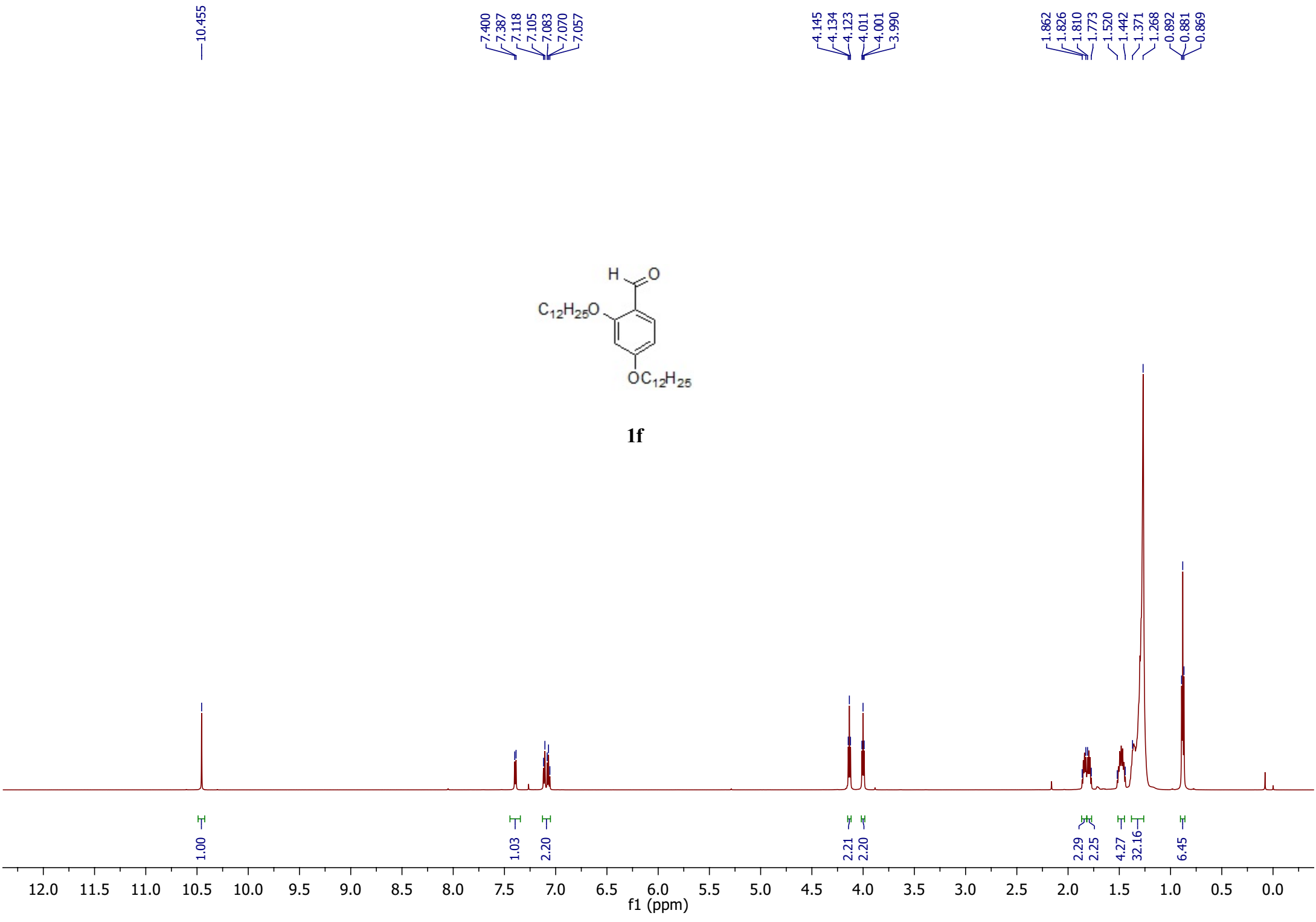
**1d**

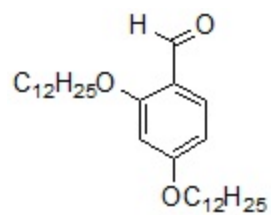




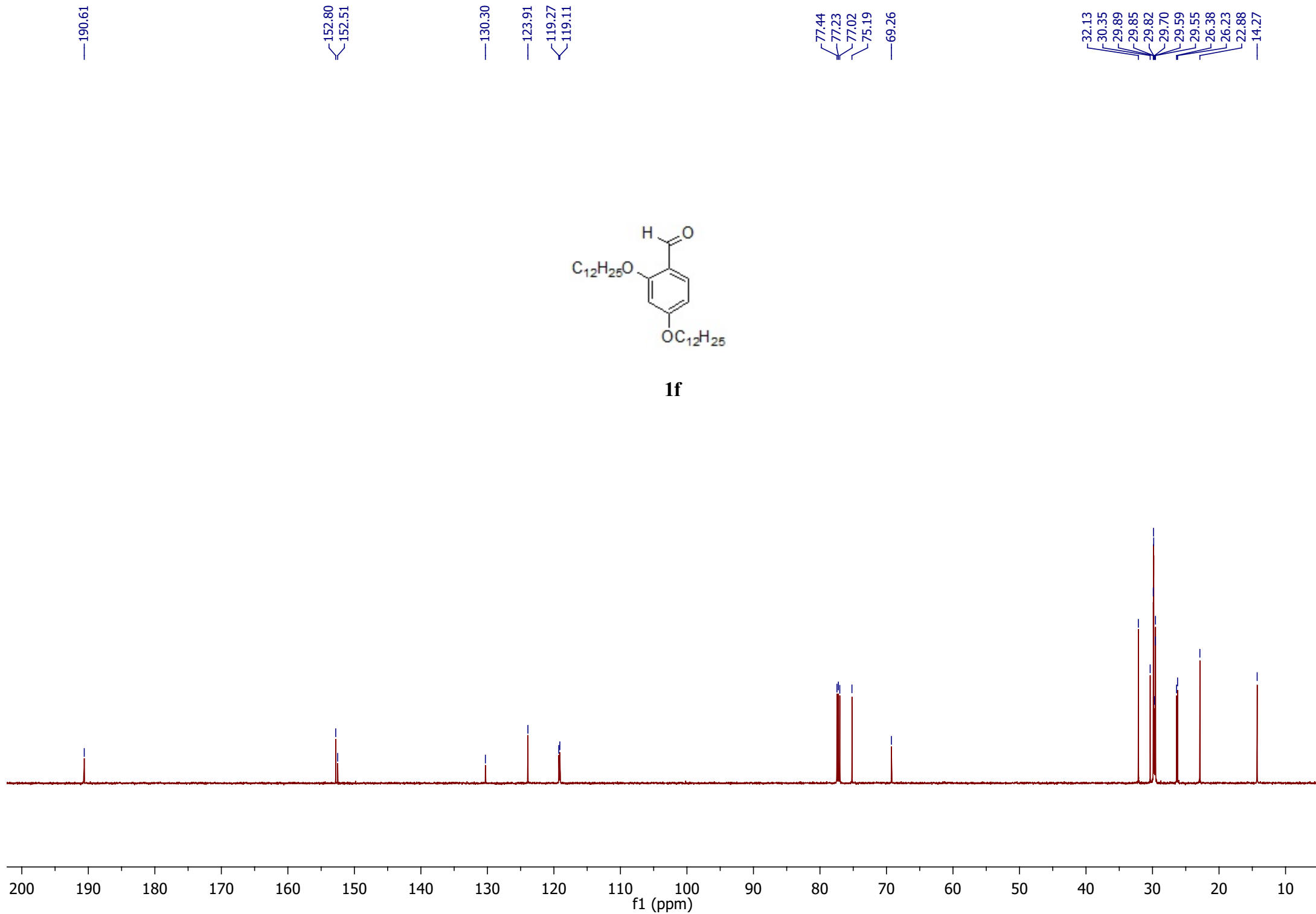
**1e**

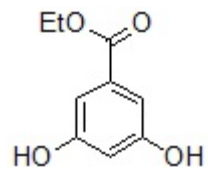




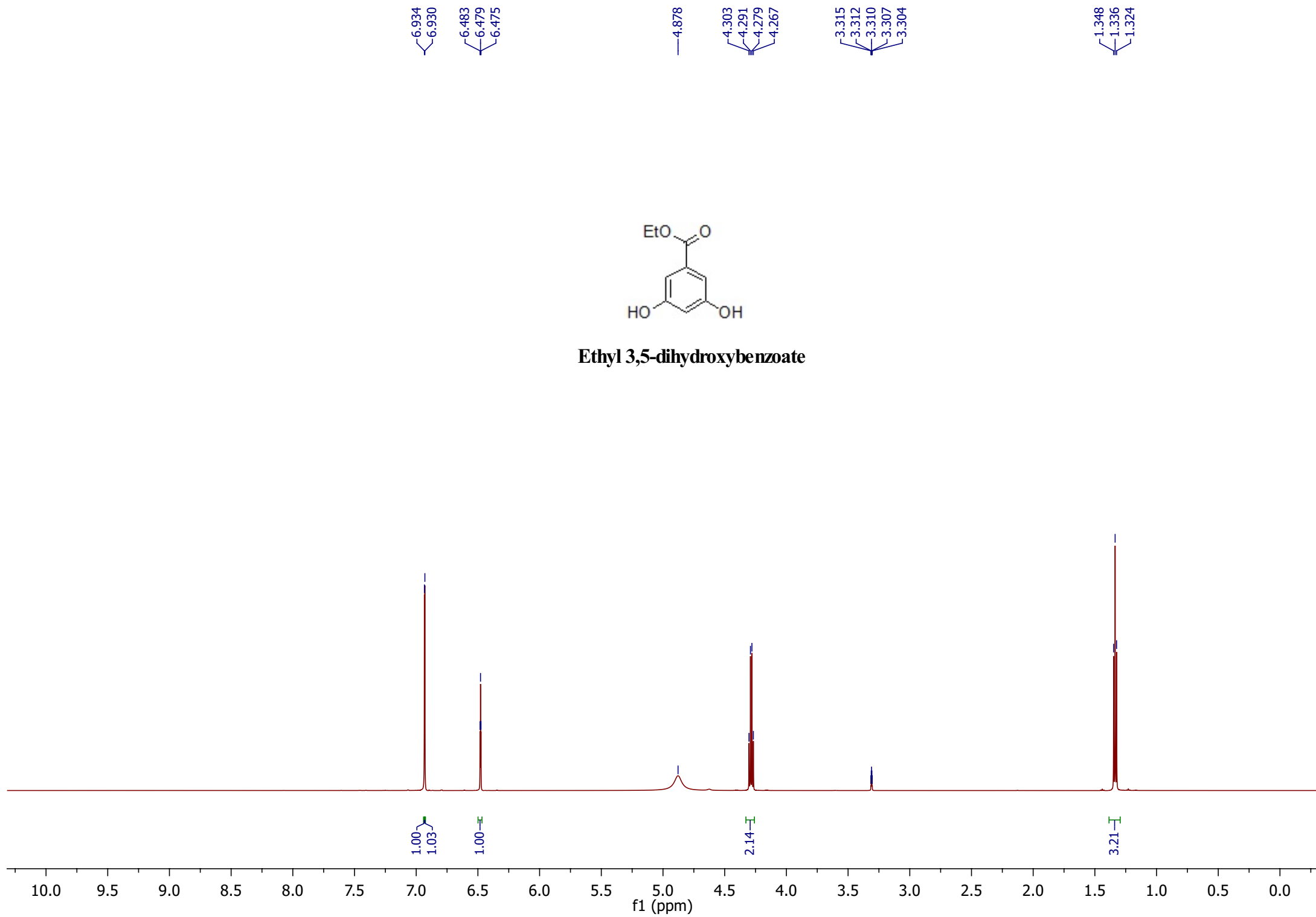


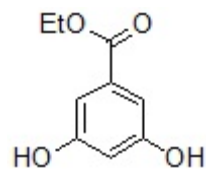
**1f**



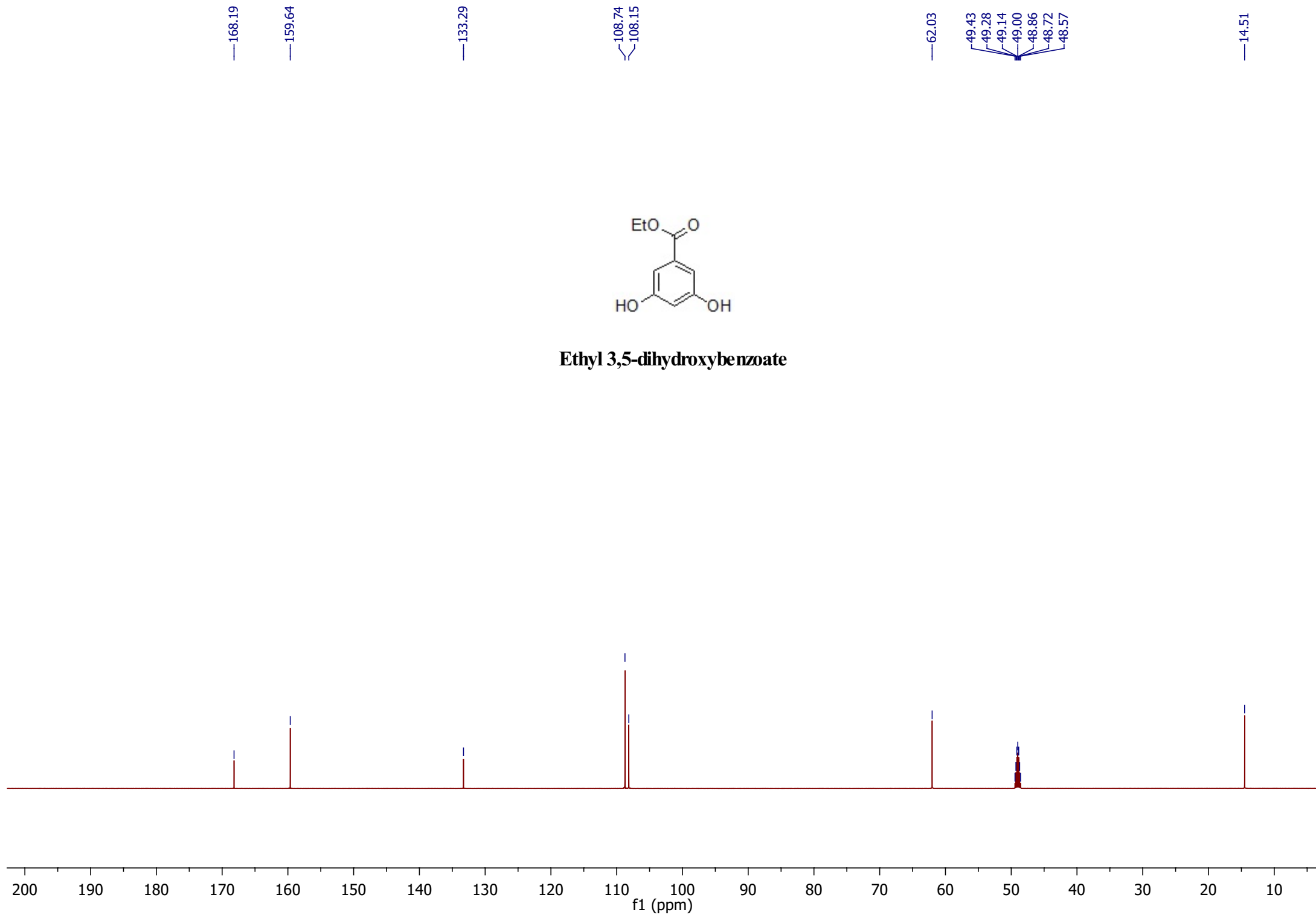


Ethyl 3,5-dihydroxybenzoate

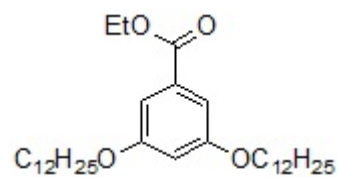




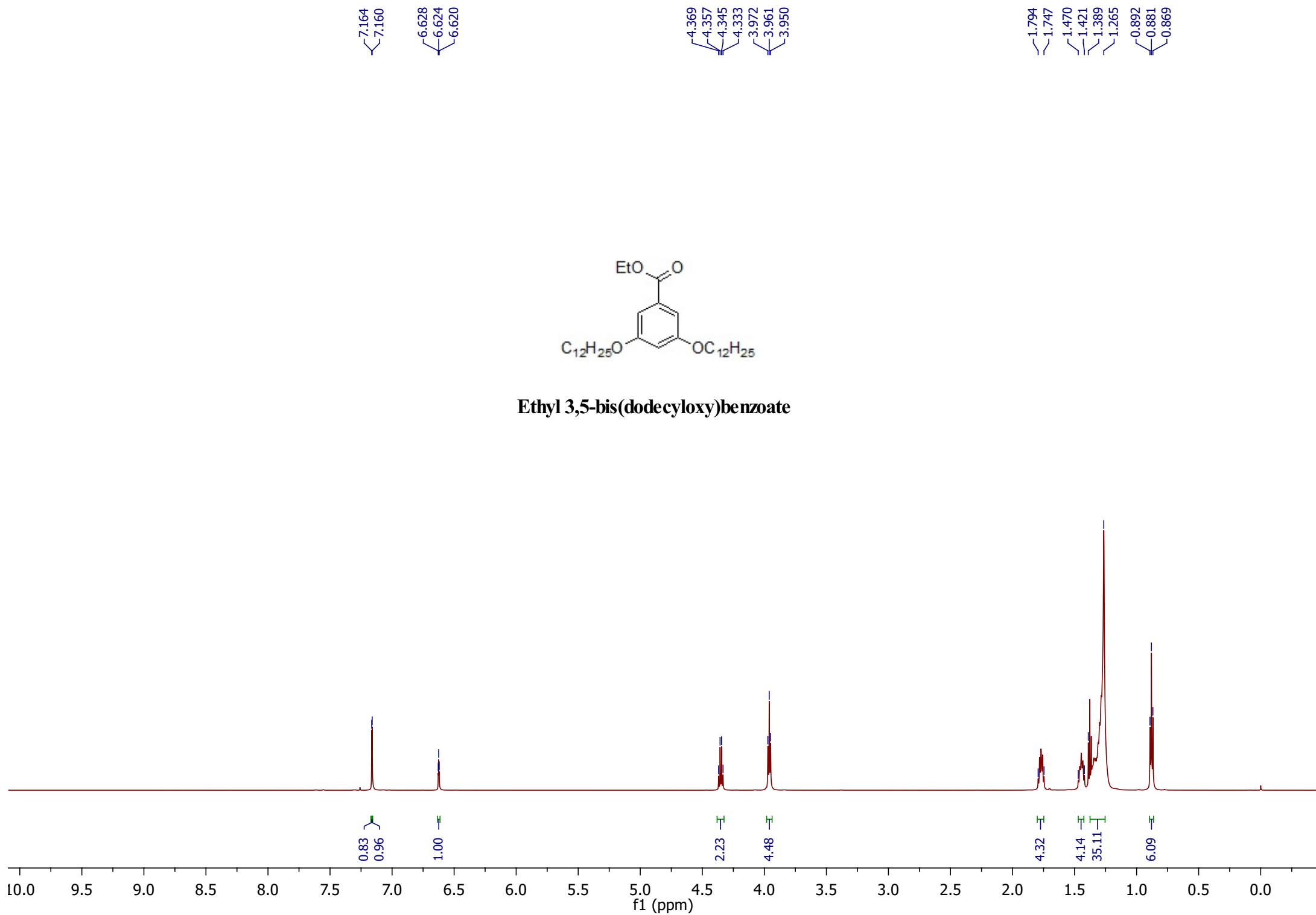
**Ethyl 3,5-dihydroxybenzoate**

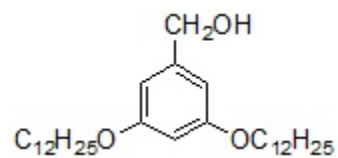




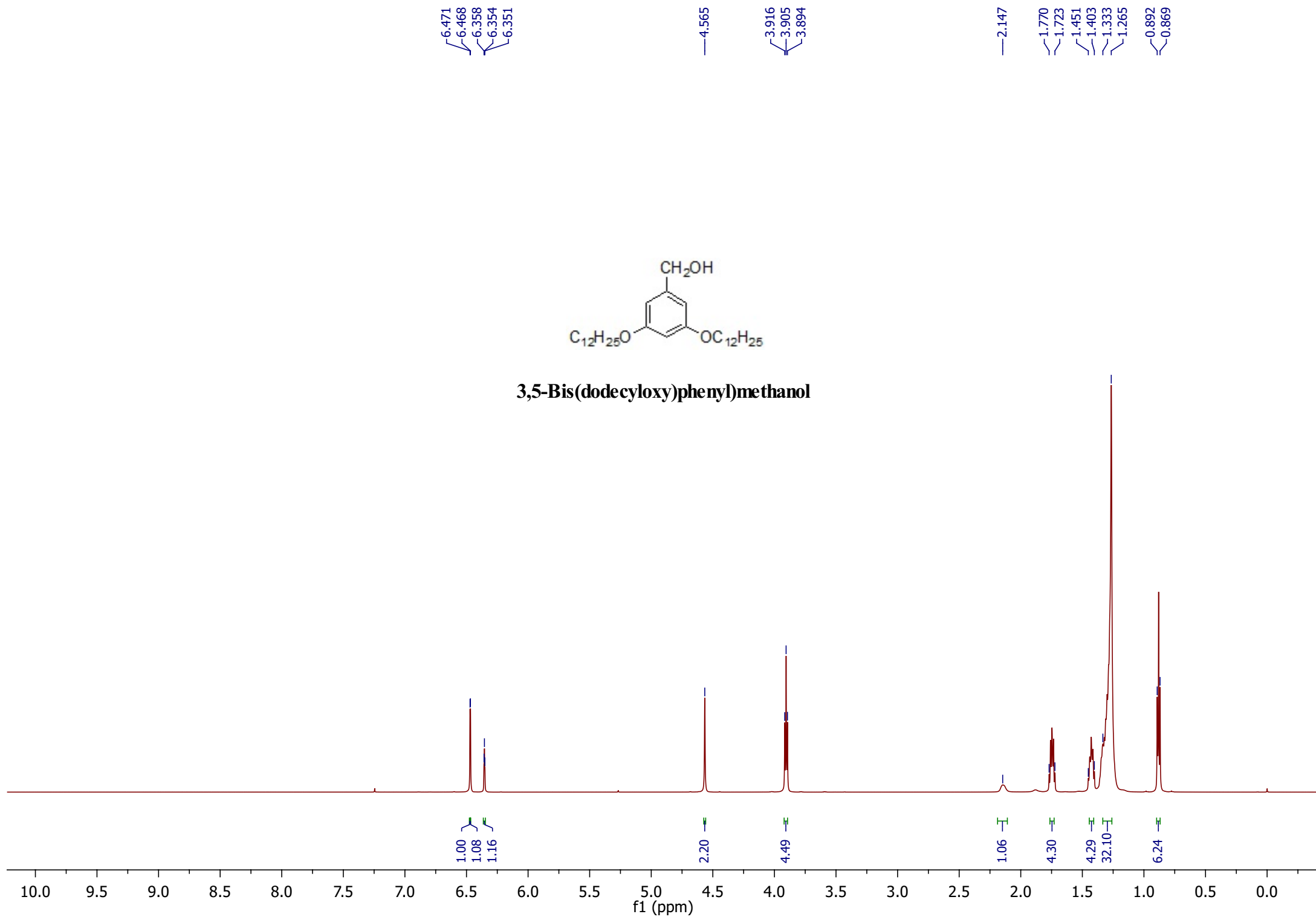


**Ethyl 3,5-bis(dodecyloxy)benzoate**





**3,5-Bis(dodecyloxy)phenylmethanol**

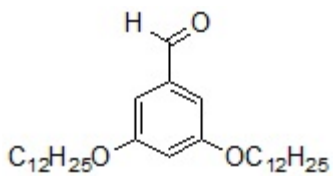


—9.875

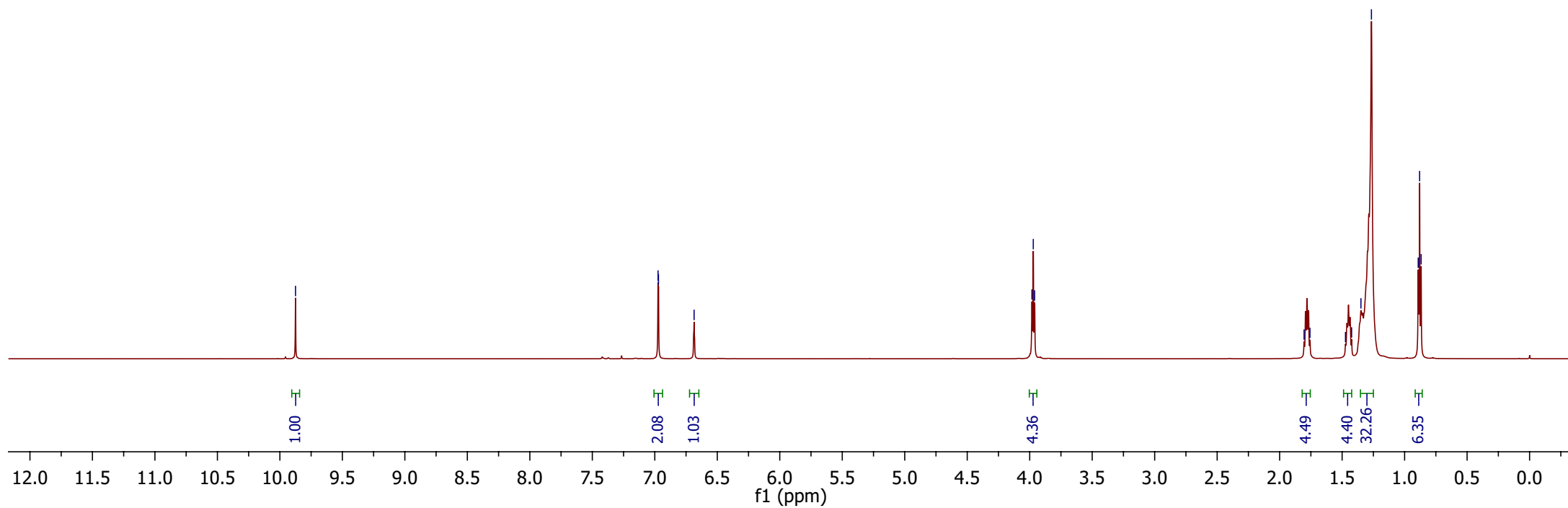
6.974  
6.971  
6.686

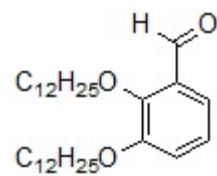
3.982  
3.971  
3.960

1.804  
1.757  
1.473  
1.424  
1.350  
1.266  
0.891  
0.880  
0.868

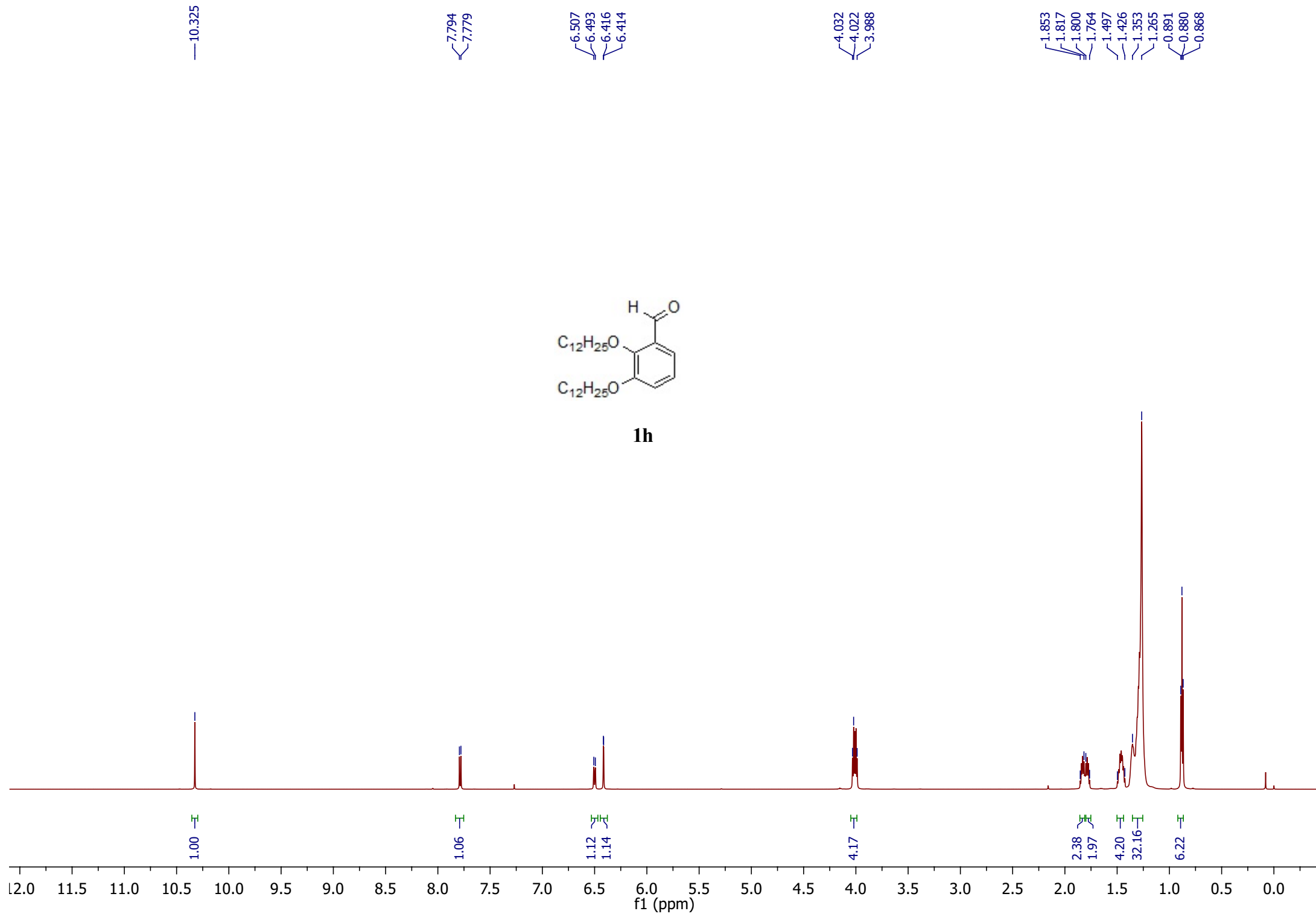


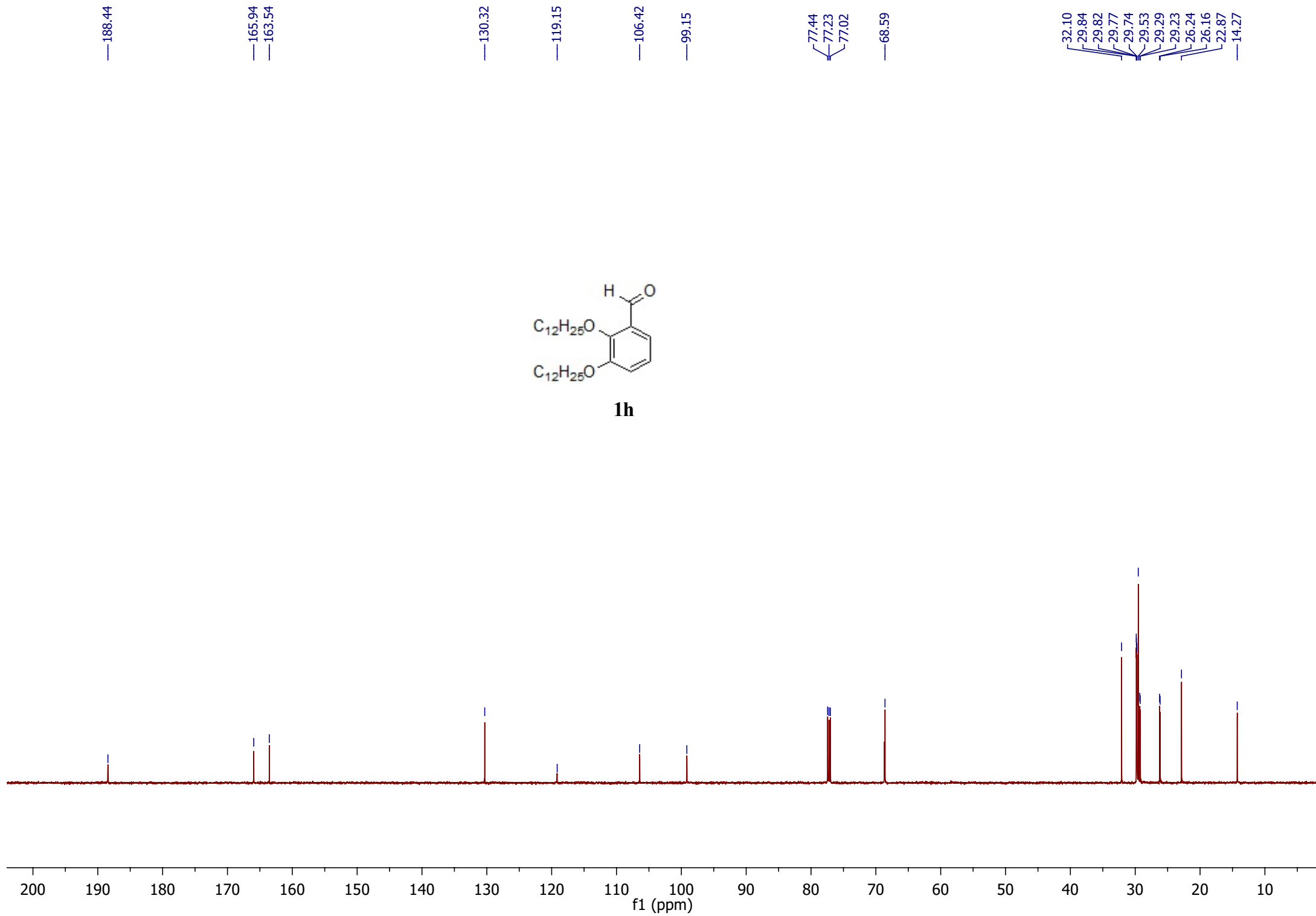
**1g**

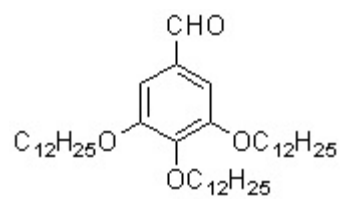




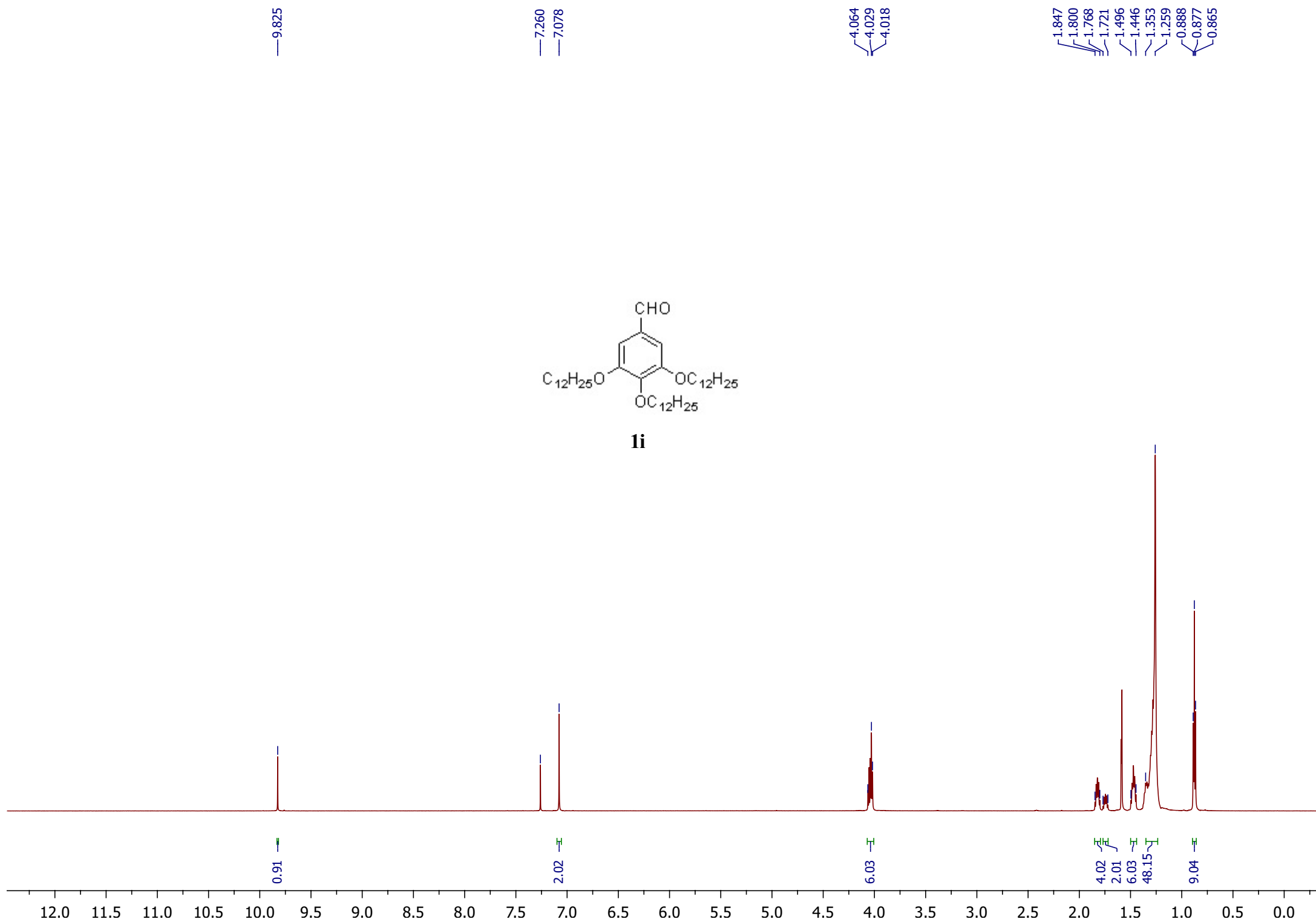
**1h**

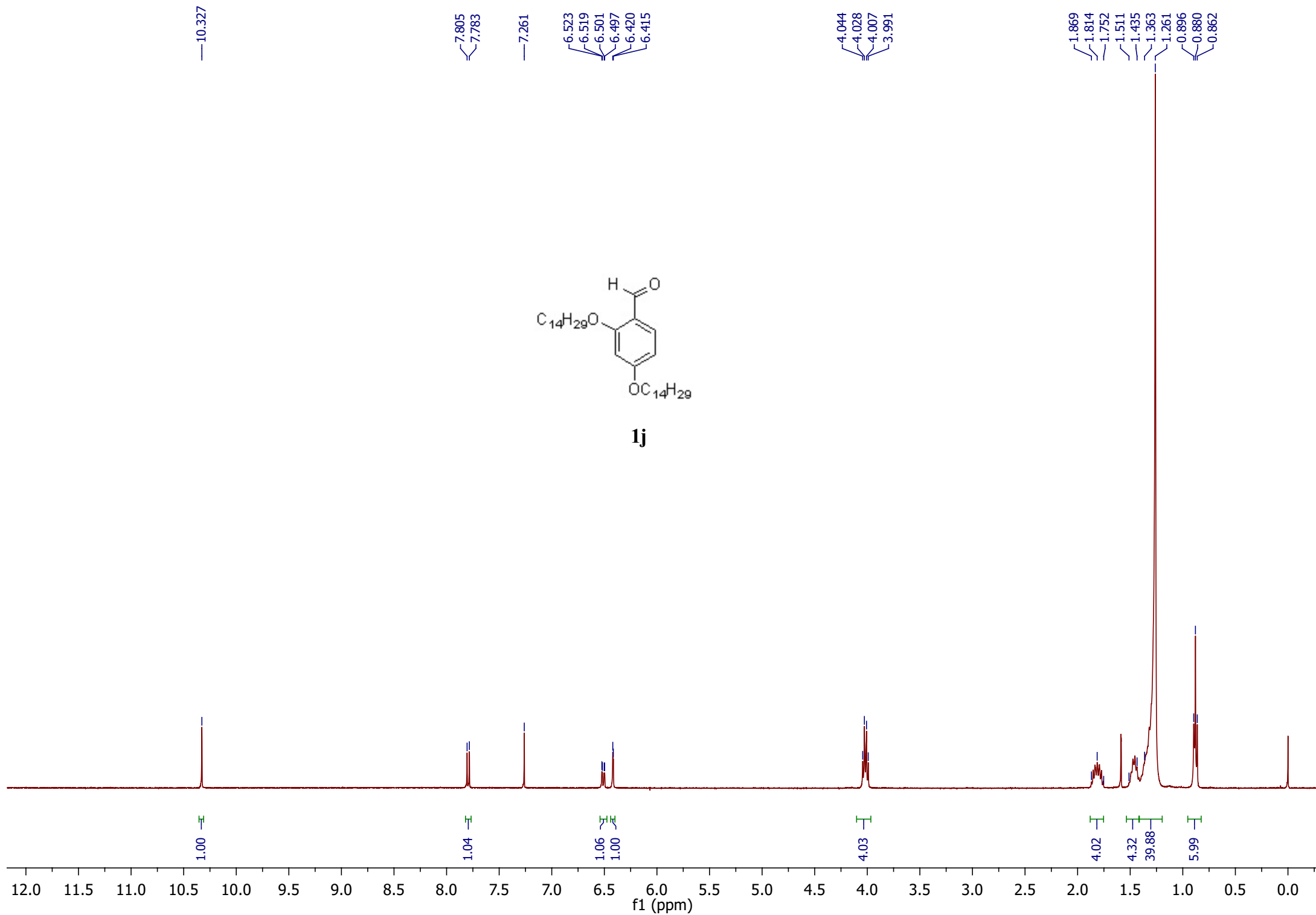


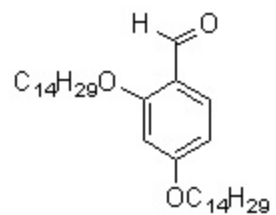




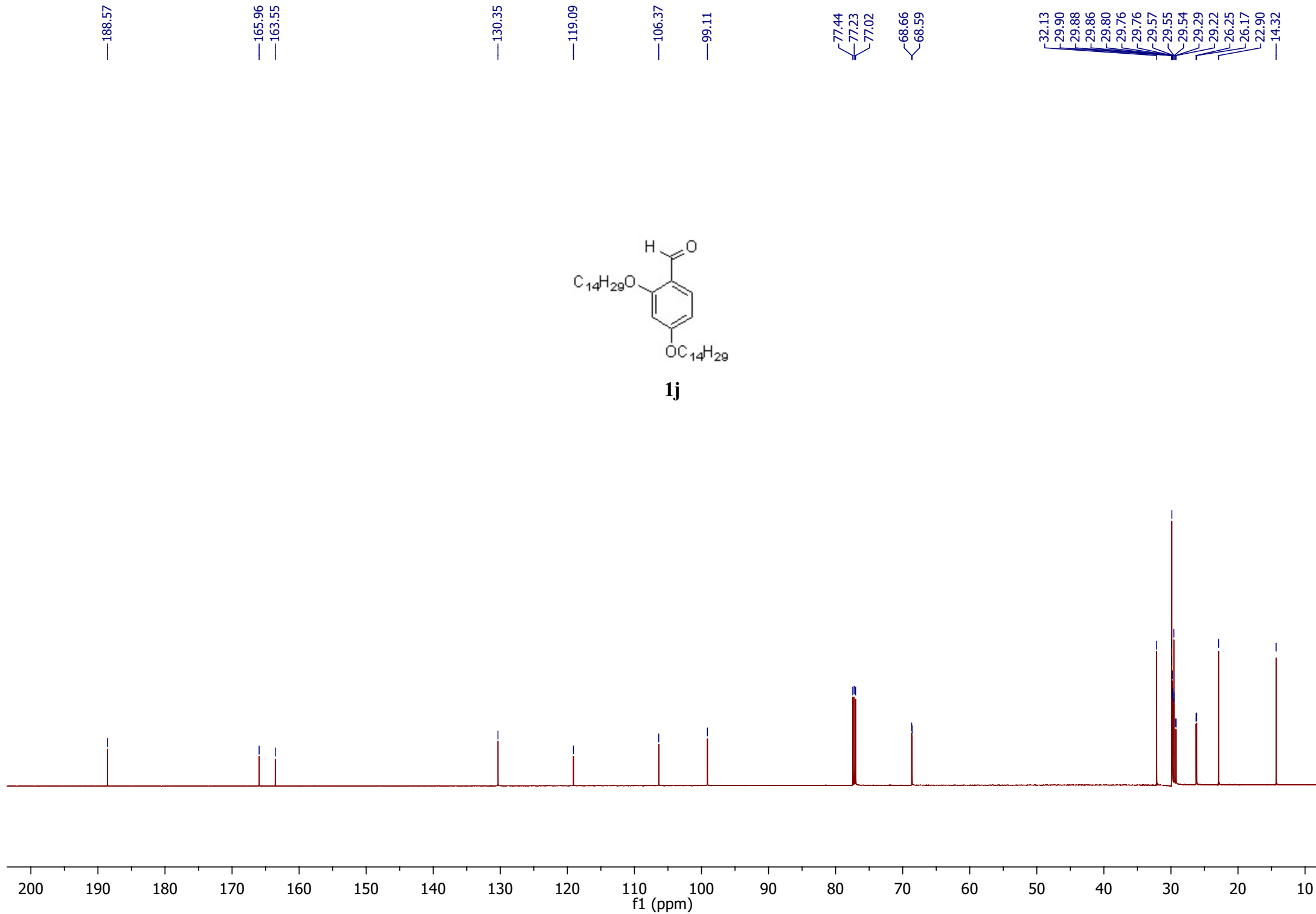
**1i**



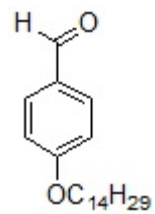




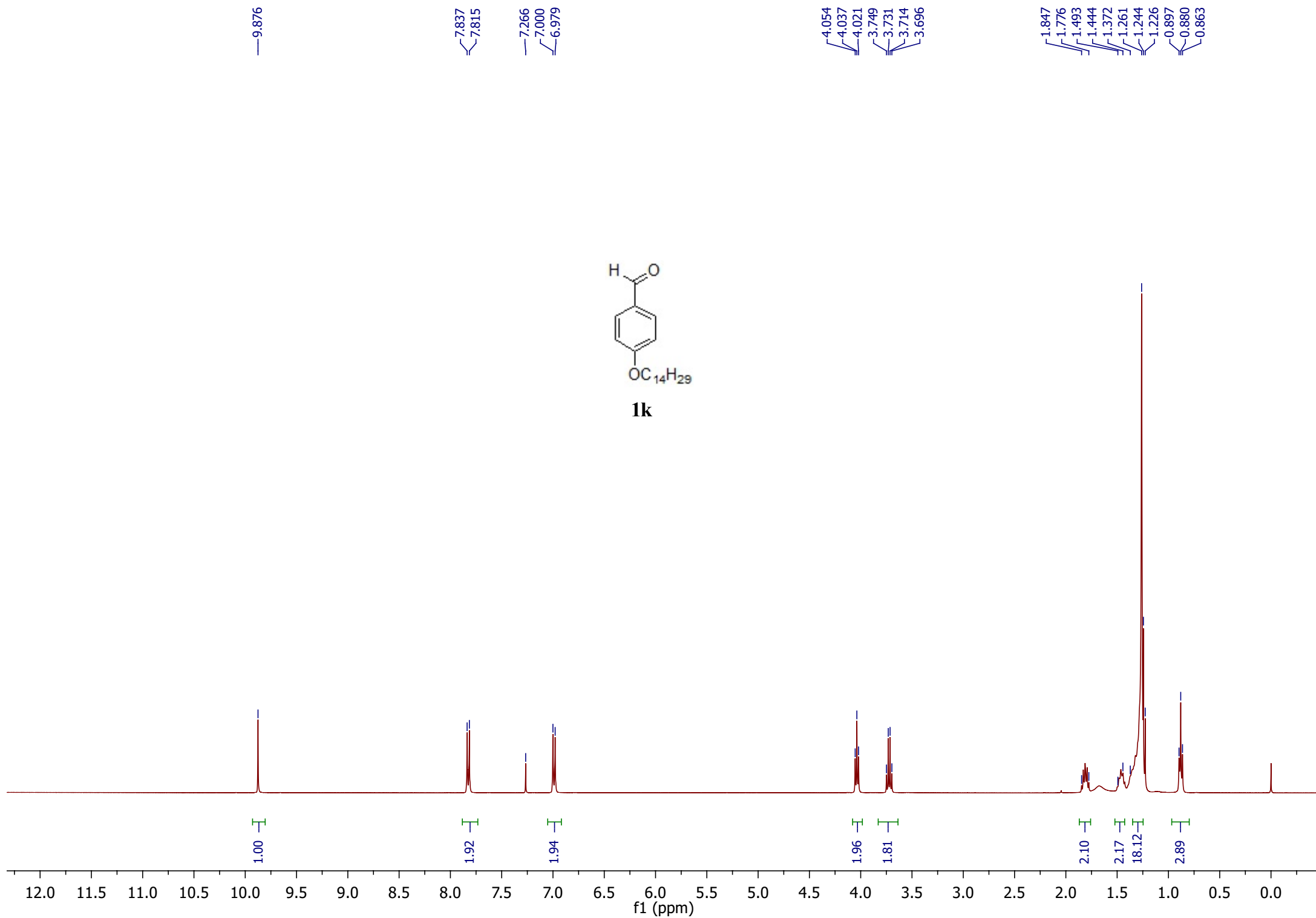
**1j**

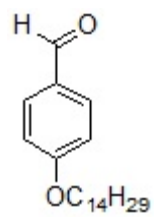




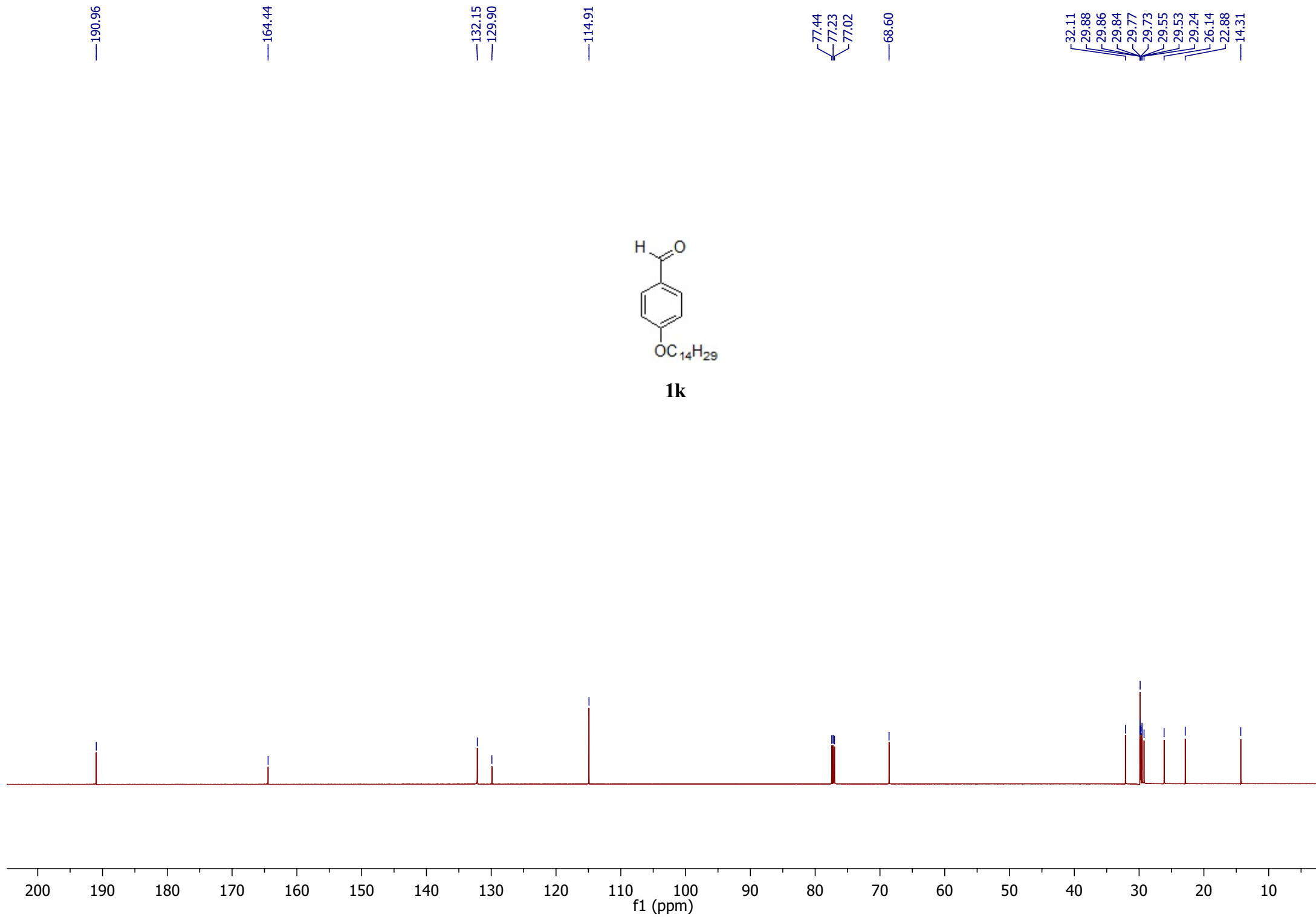


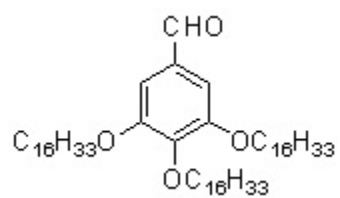
**1k**



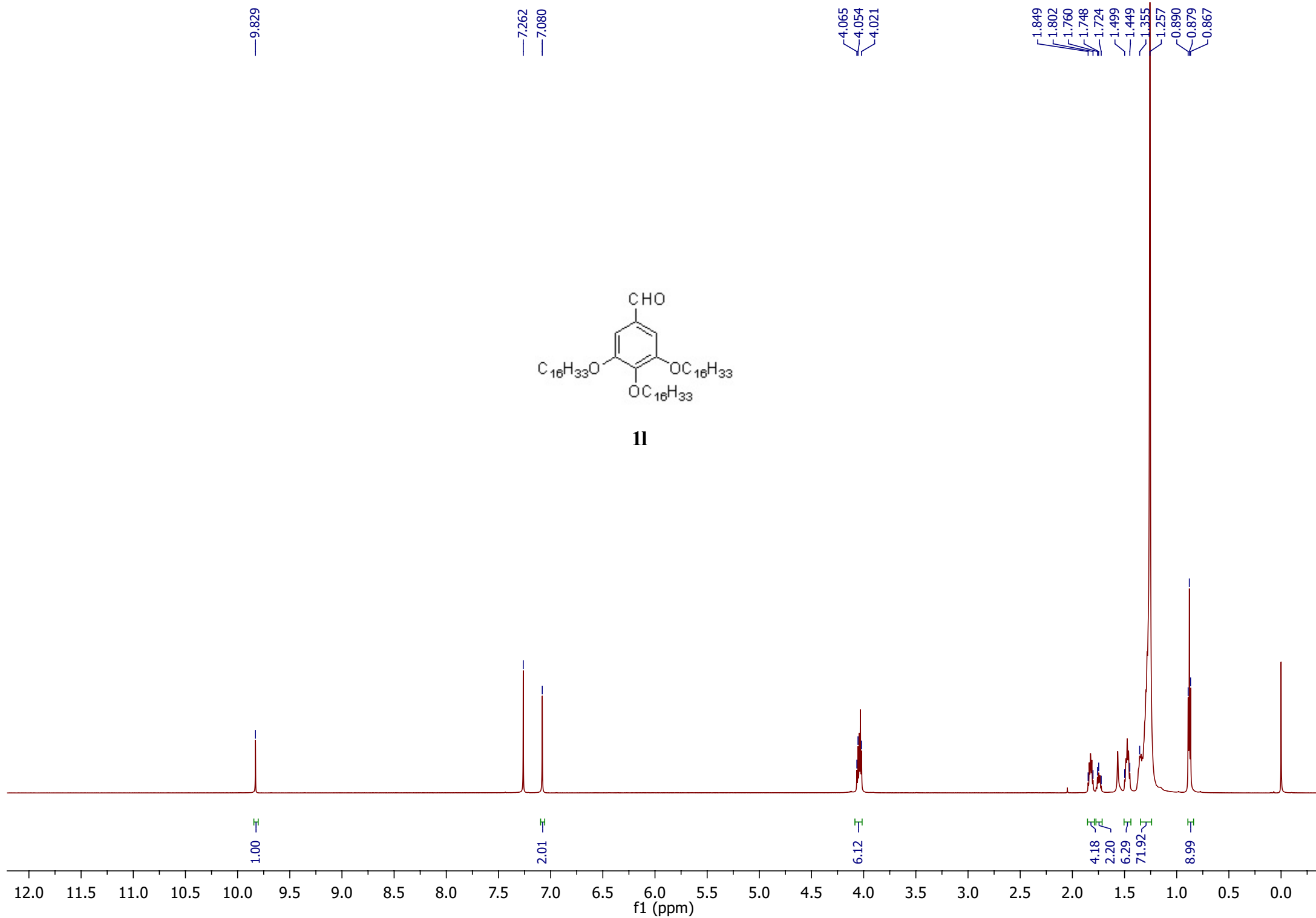


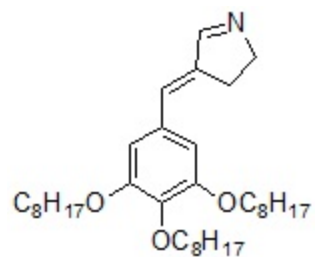
**1k**



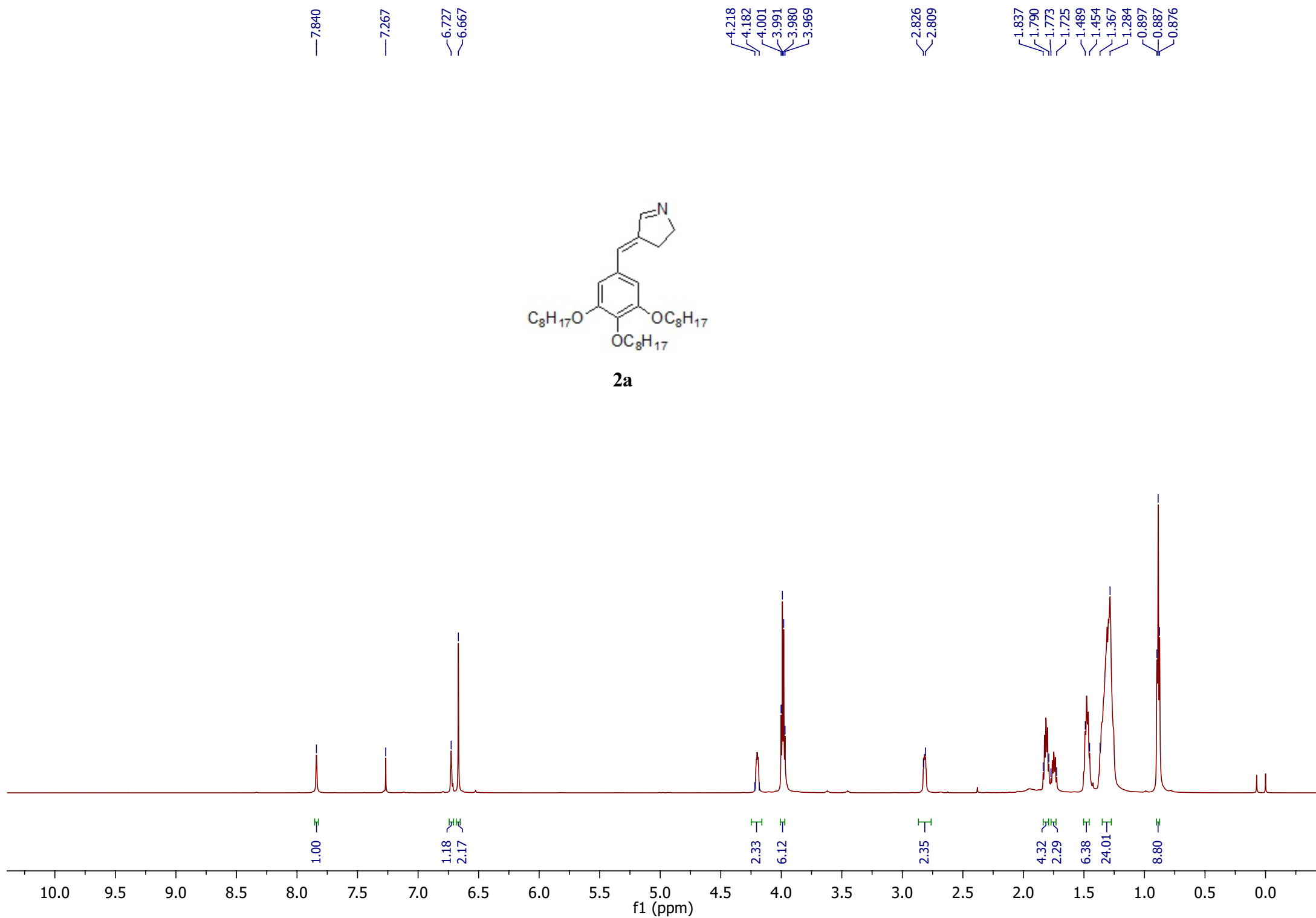


**11**





**2a**



—168.58

—153.38

—142.64

—139.04

—132.10

—127.58

—108.19

77.55

77.23

76.91

73.78

69.57

—62.40

32.11

32.04

30.56

29.74

29.67

29.58

29.56

29.49

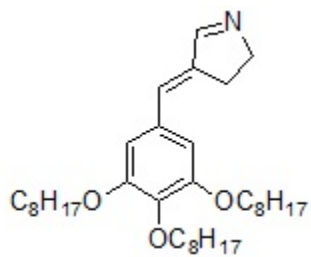
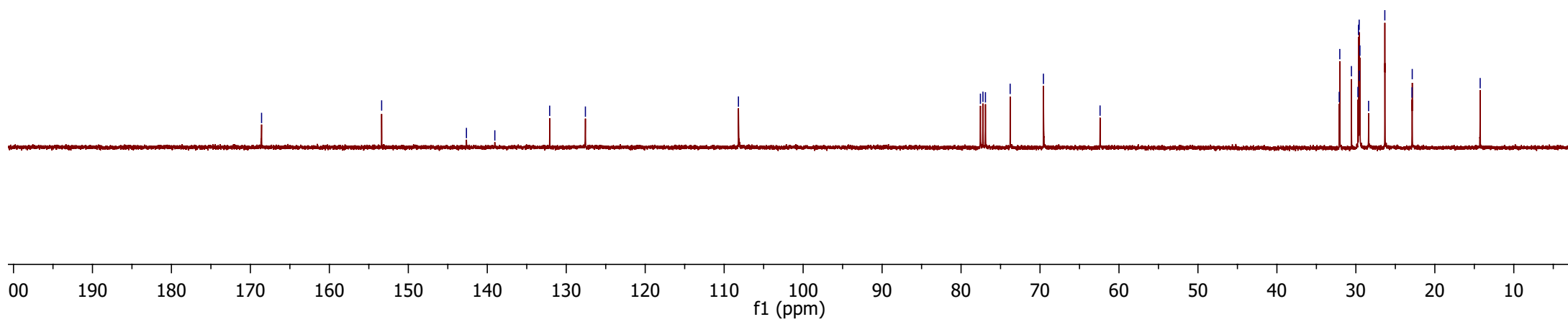
28.39

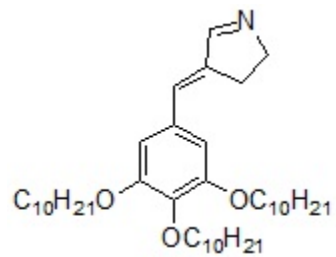
26.33

22.89

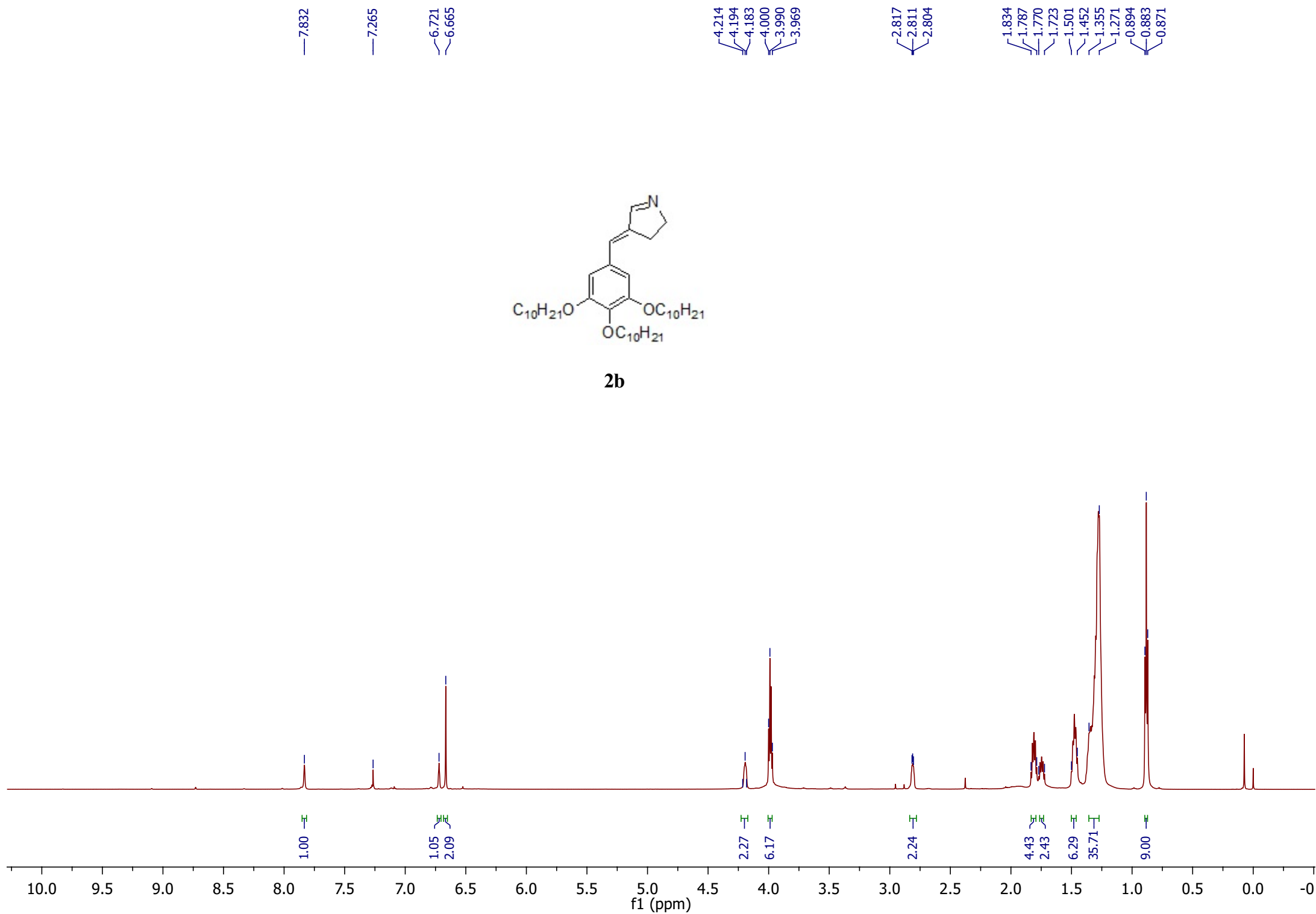
22.86

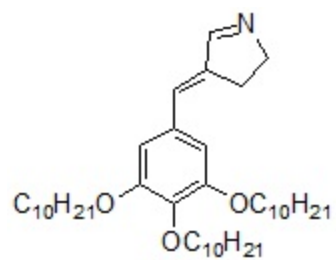
—14.26

**2a**

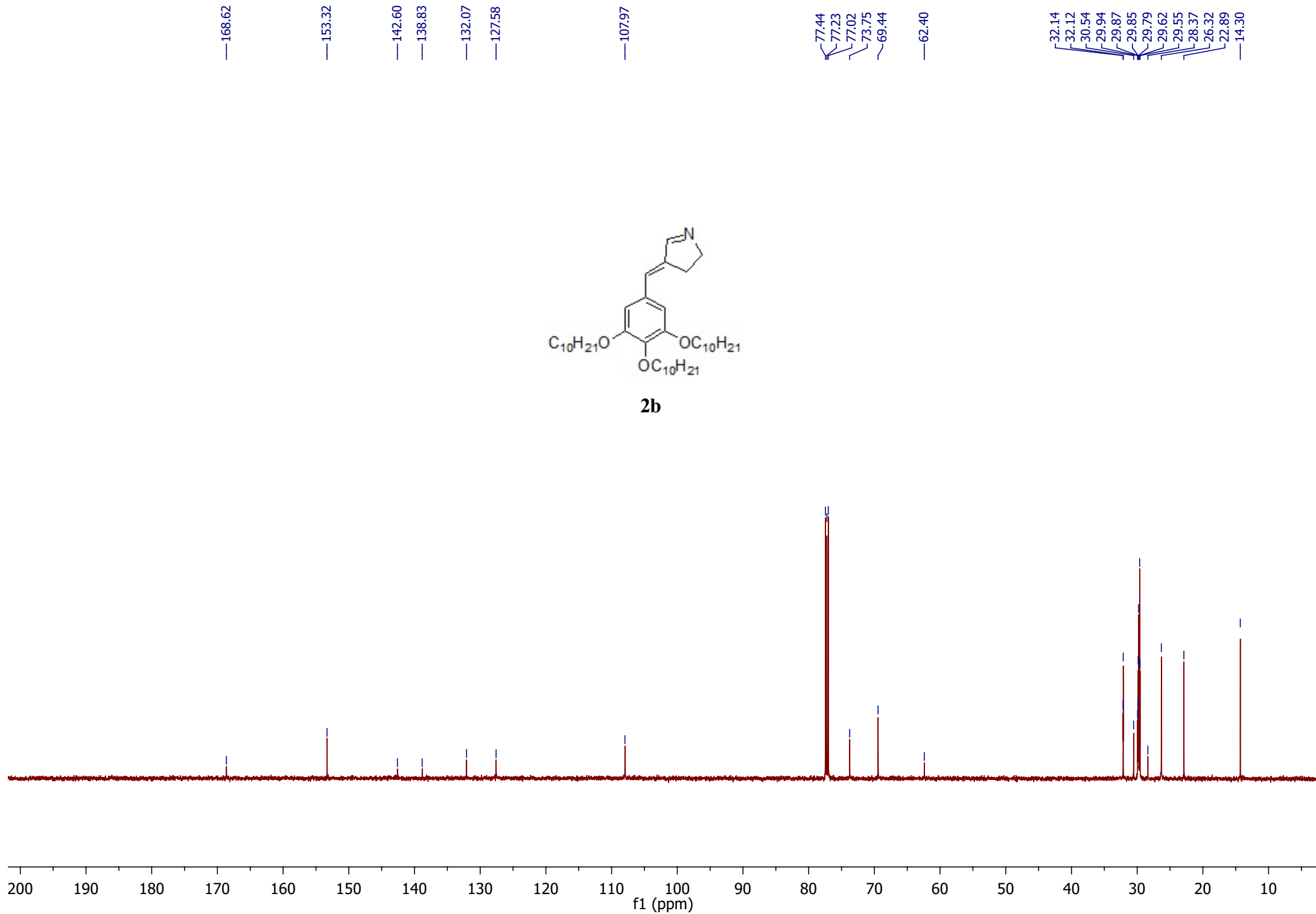


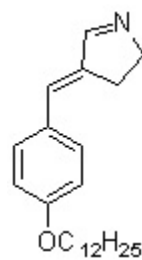
**2b**



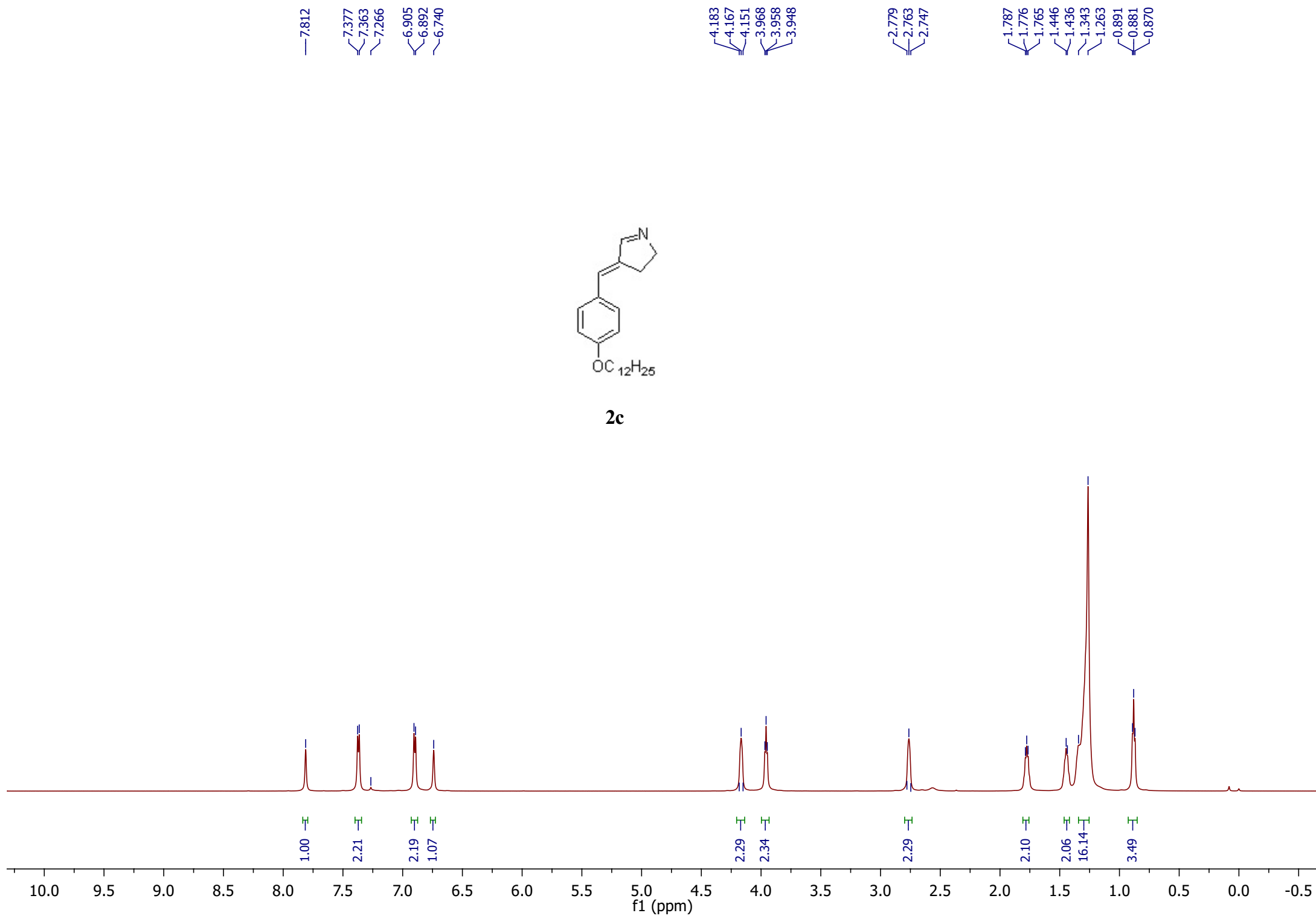


**2b**

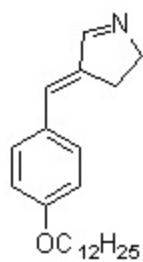




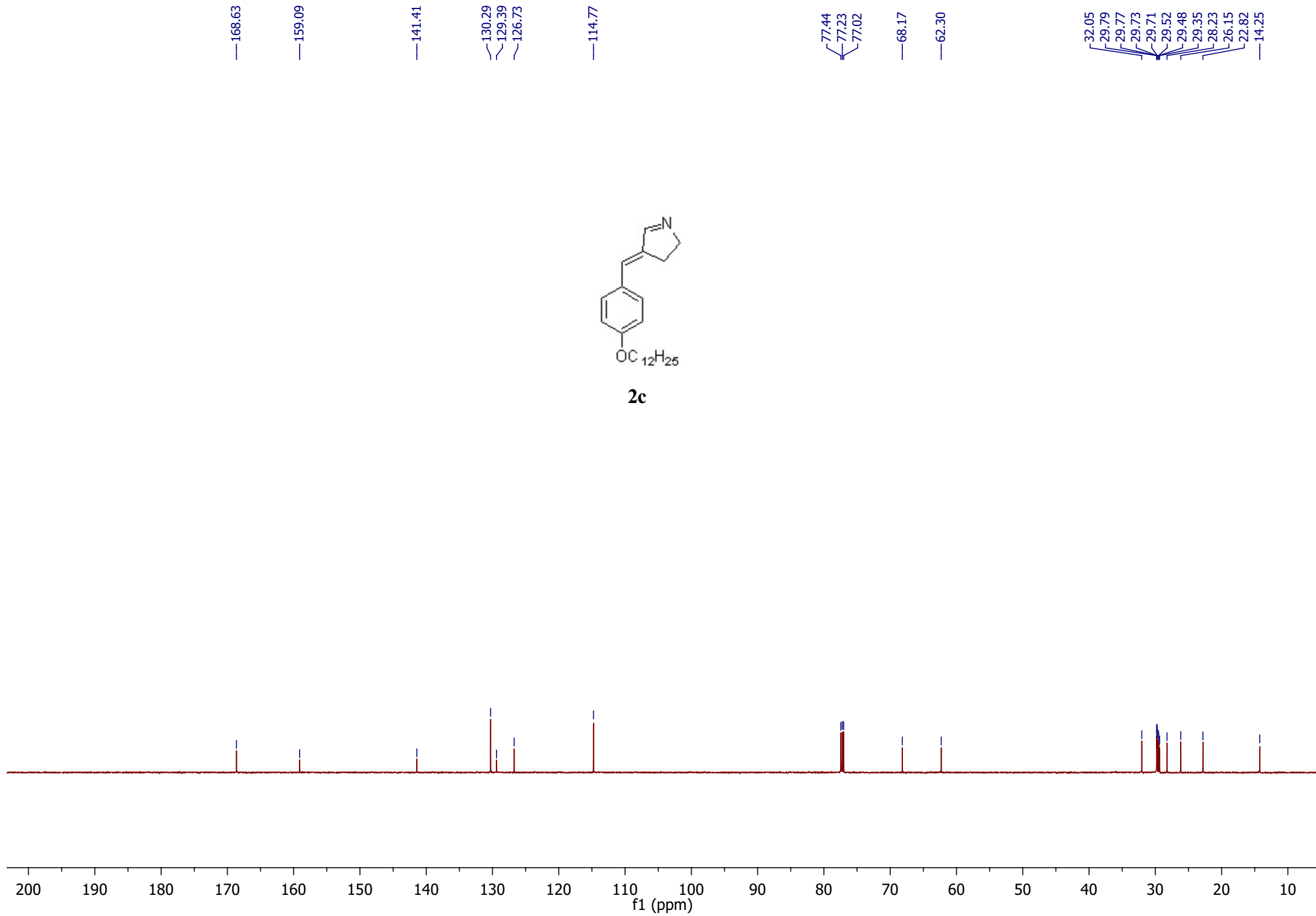
**2c**

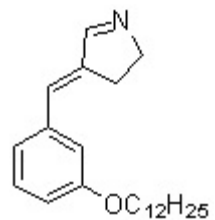




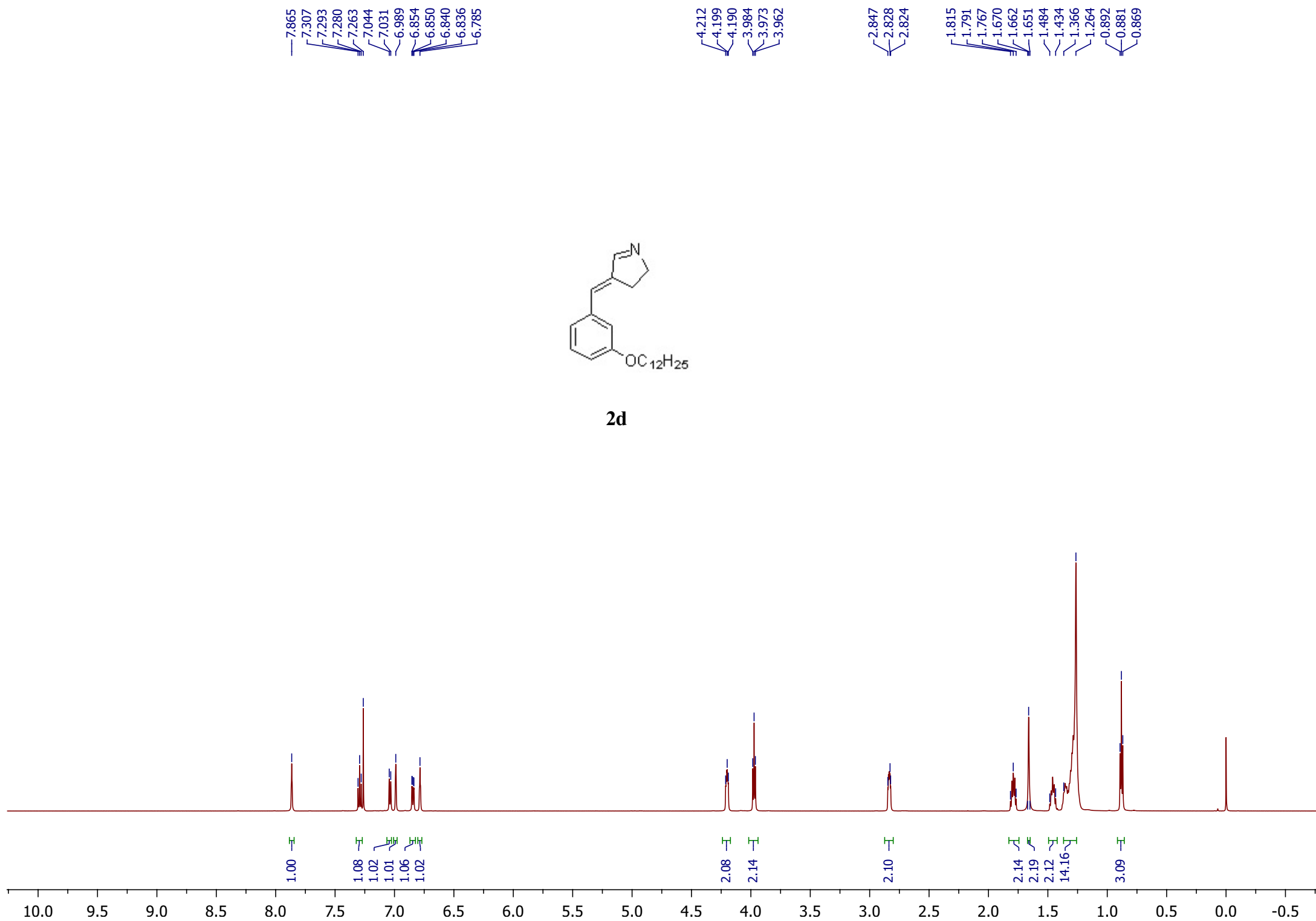


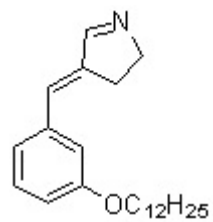
**2c**



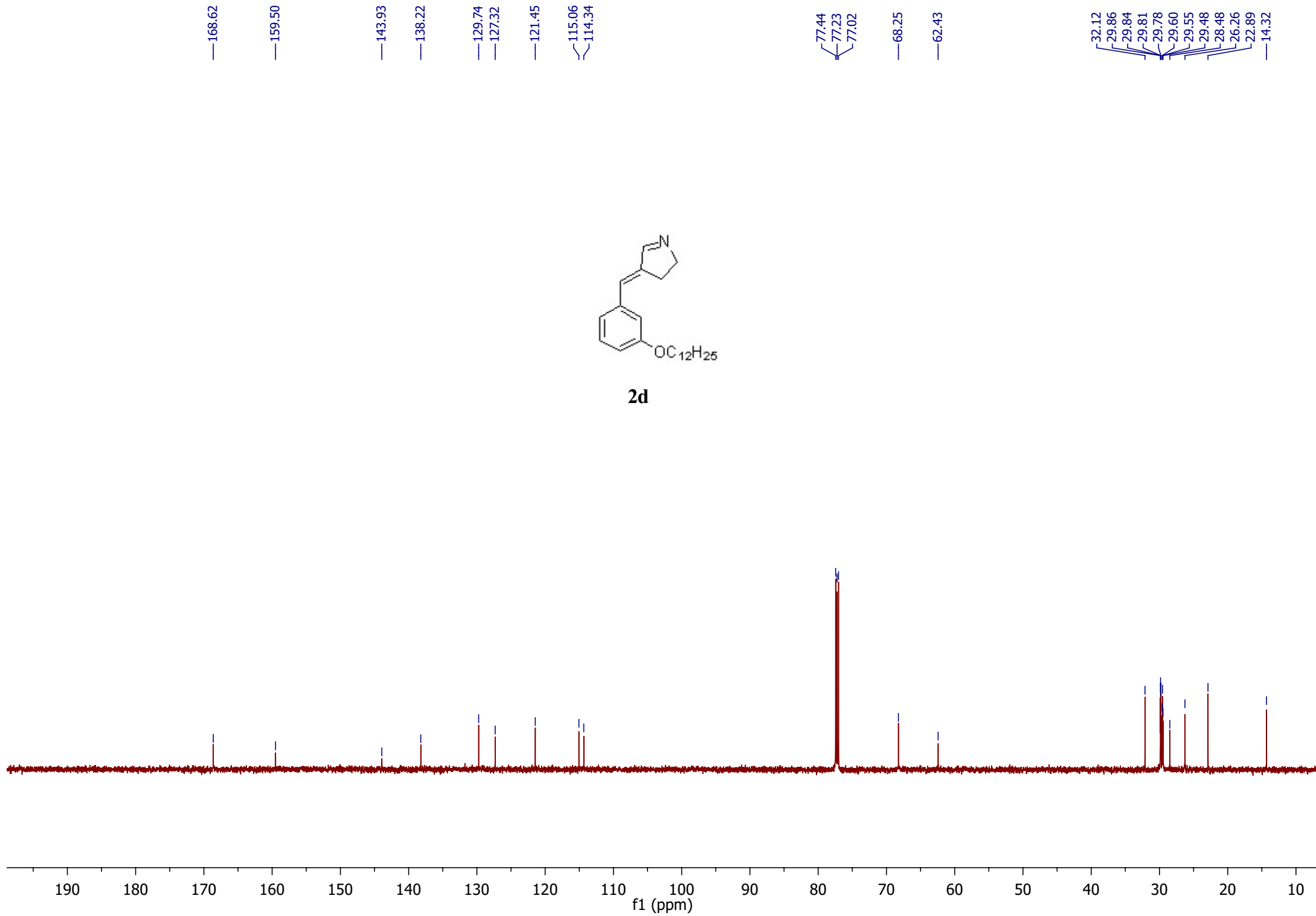


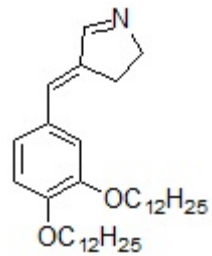
**2d**



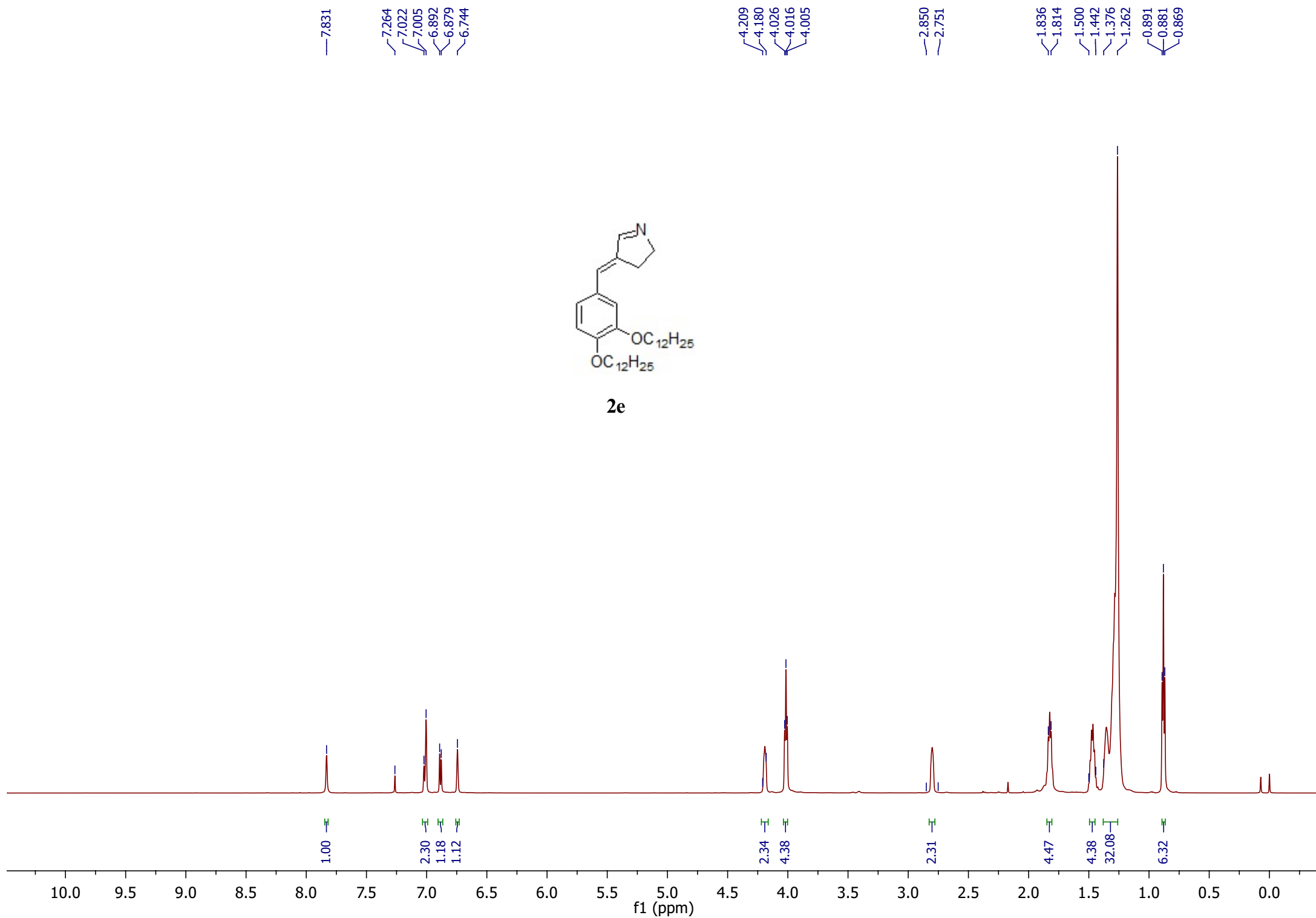


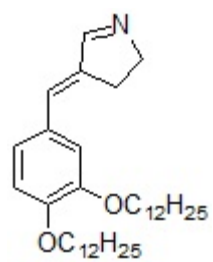
**2d**



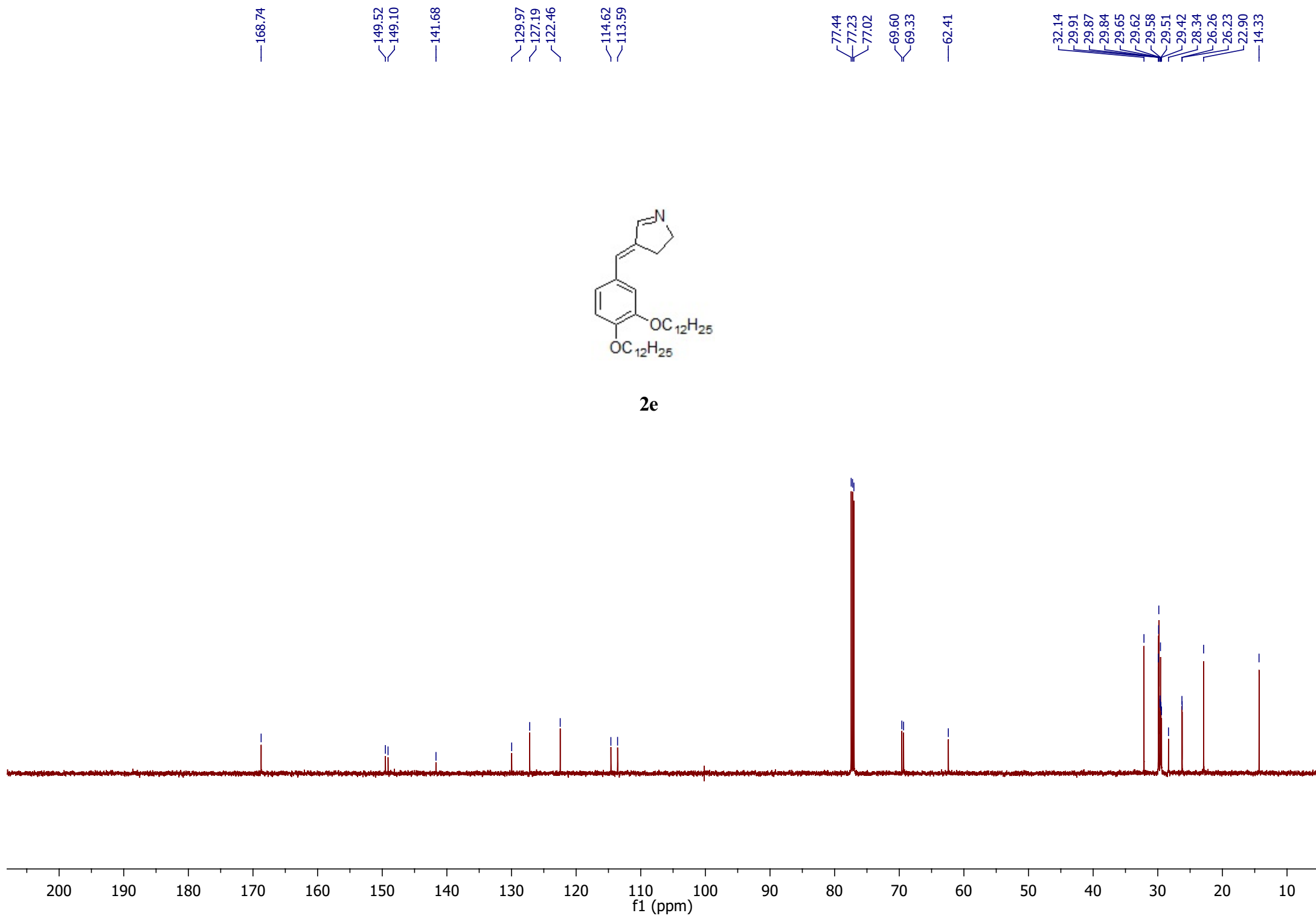


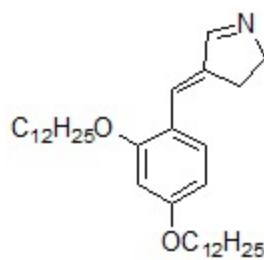
**2e**



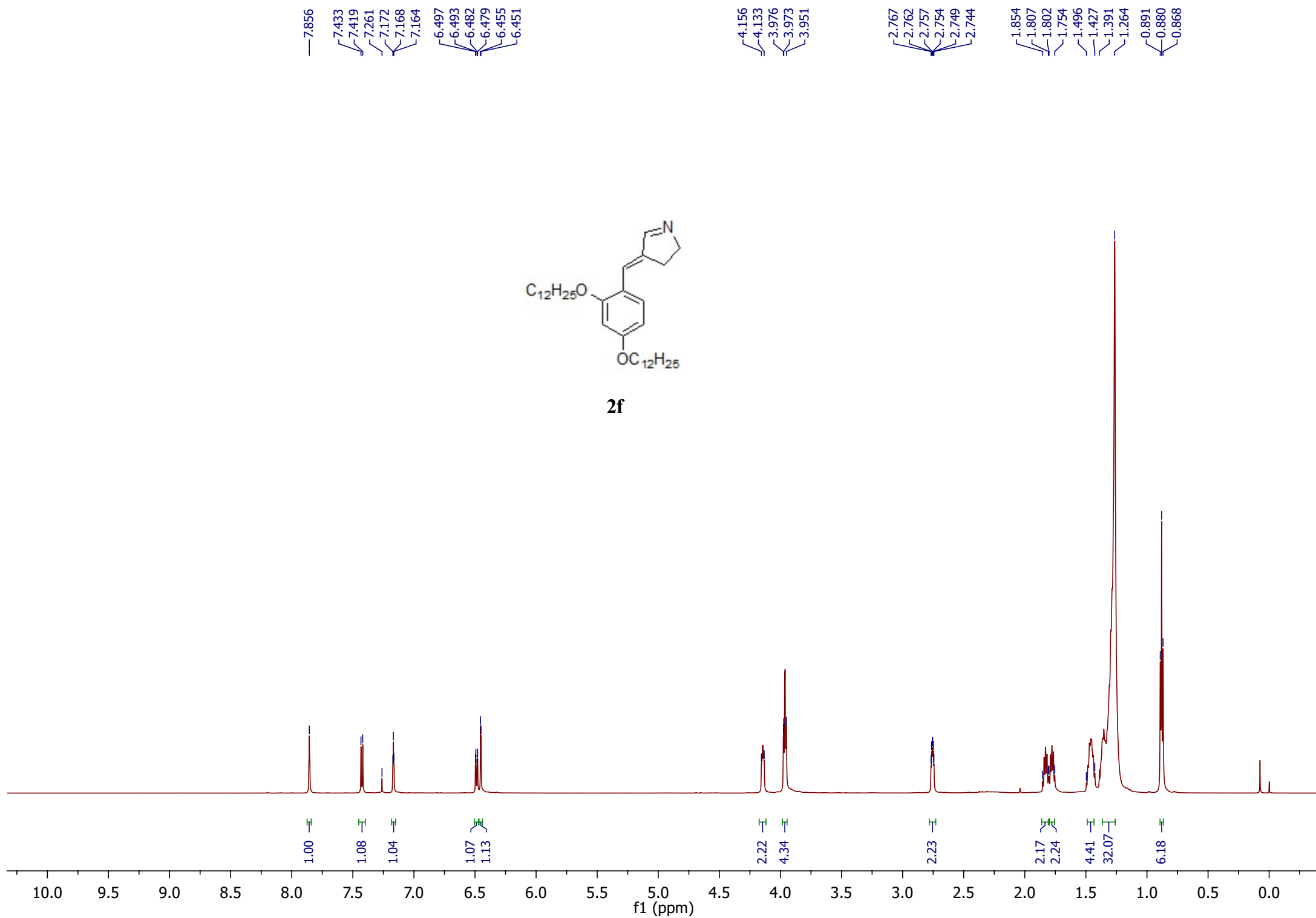


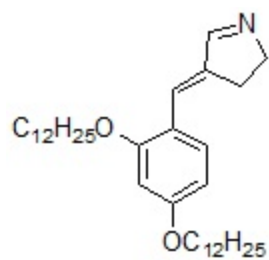
**2e**



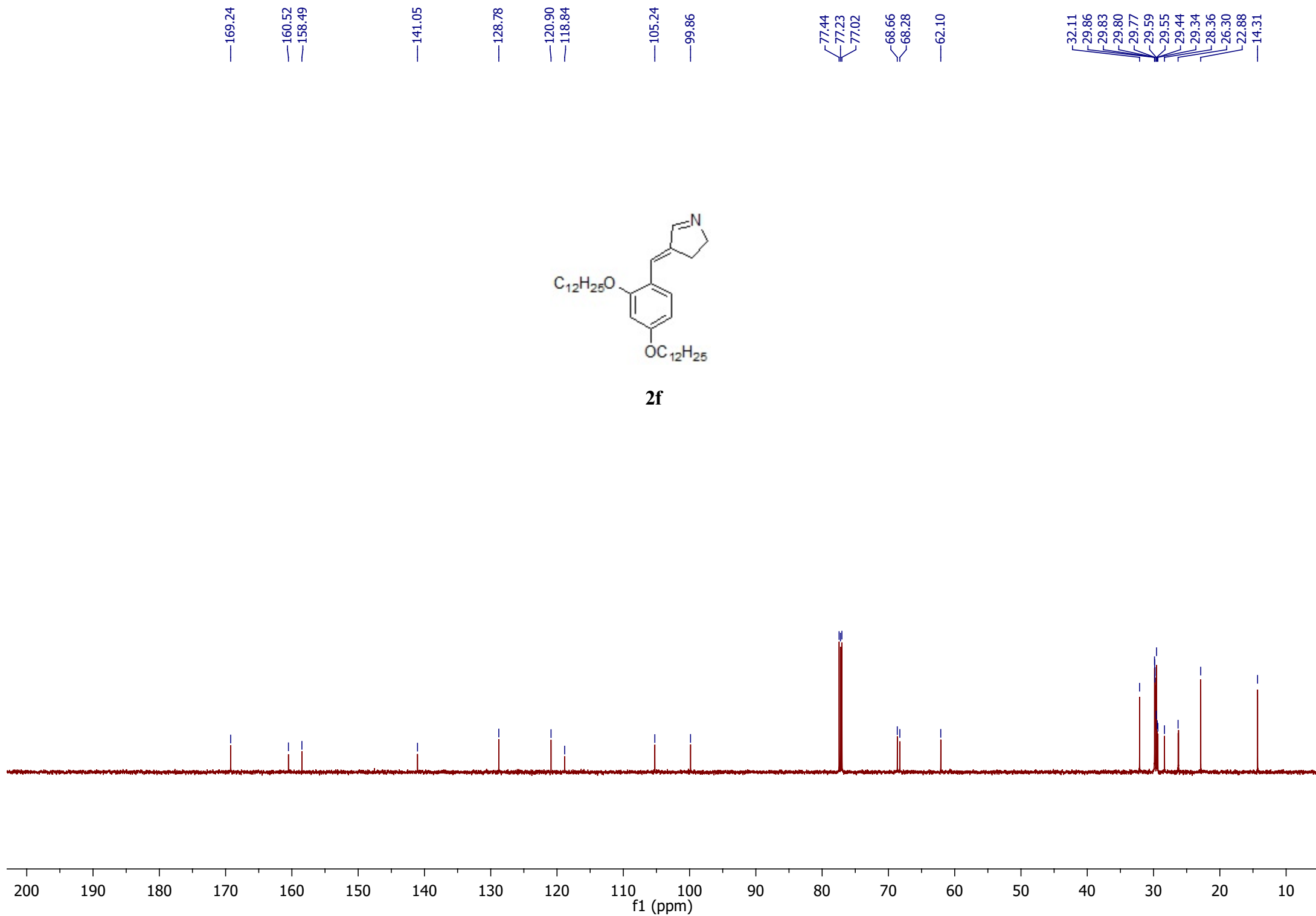


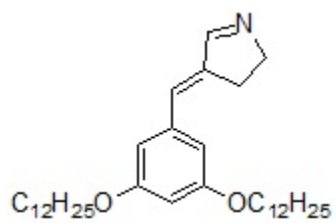
**2f**



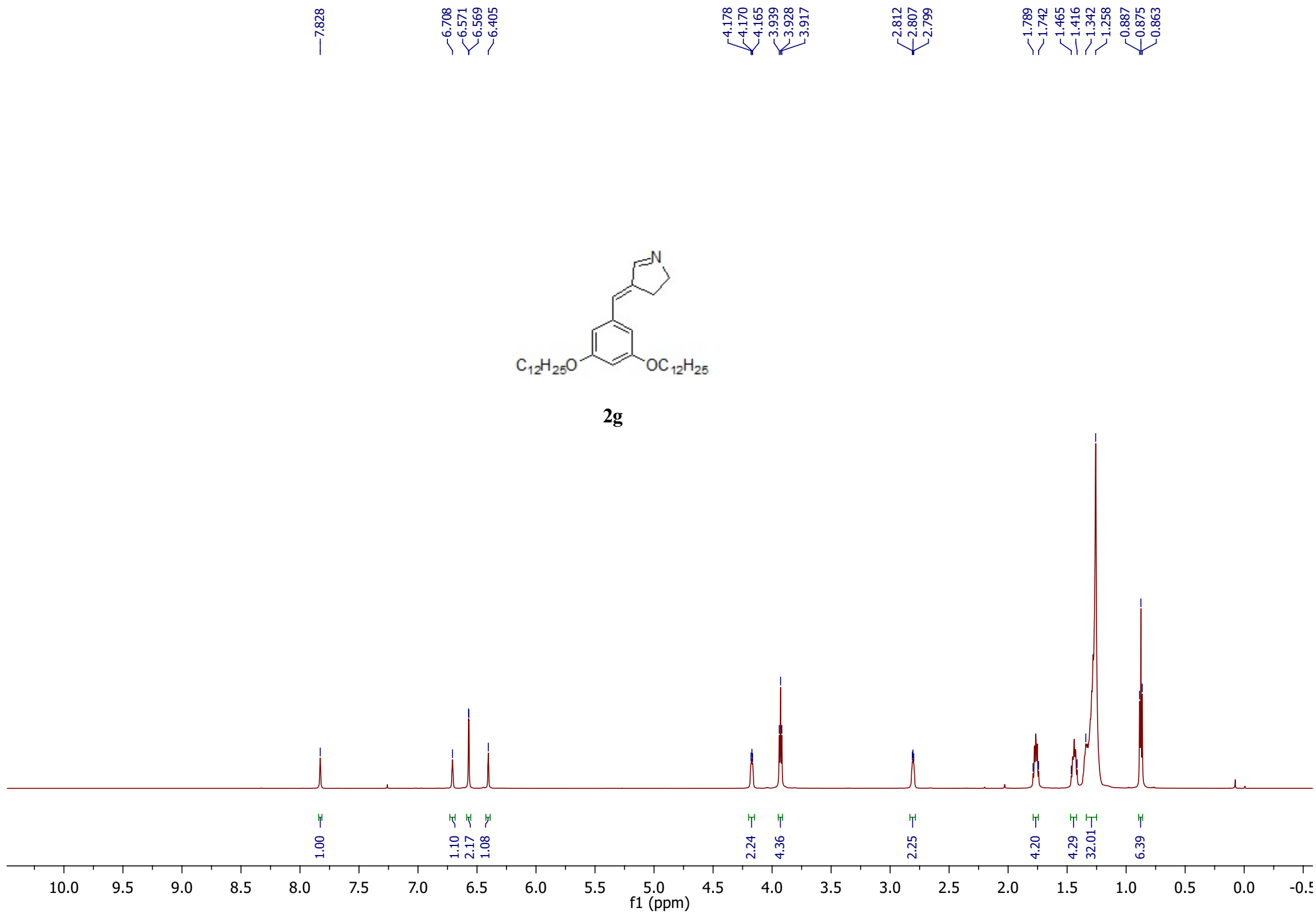


**2f**

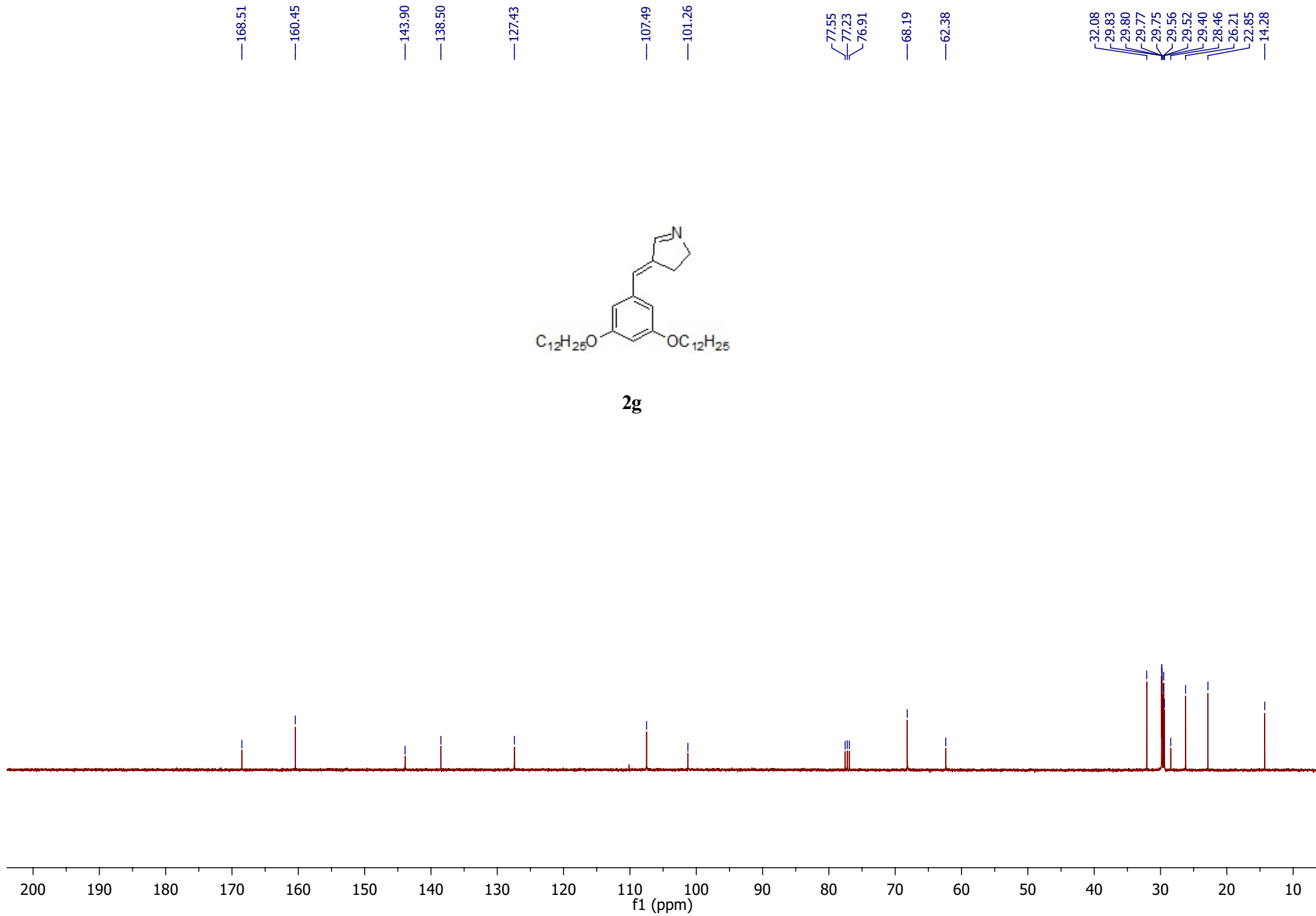


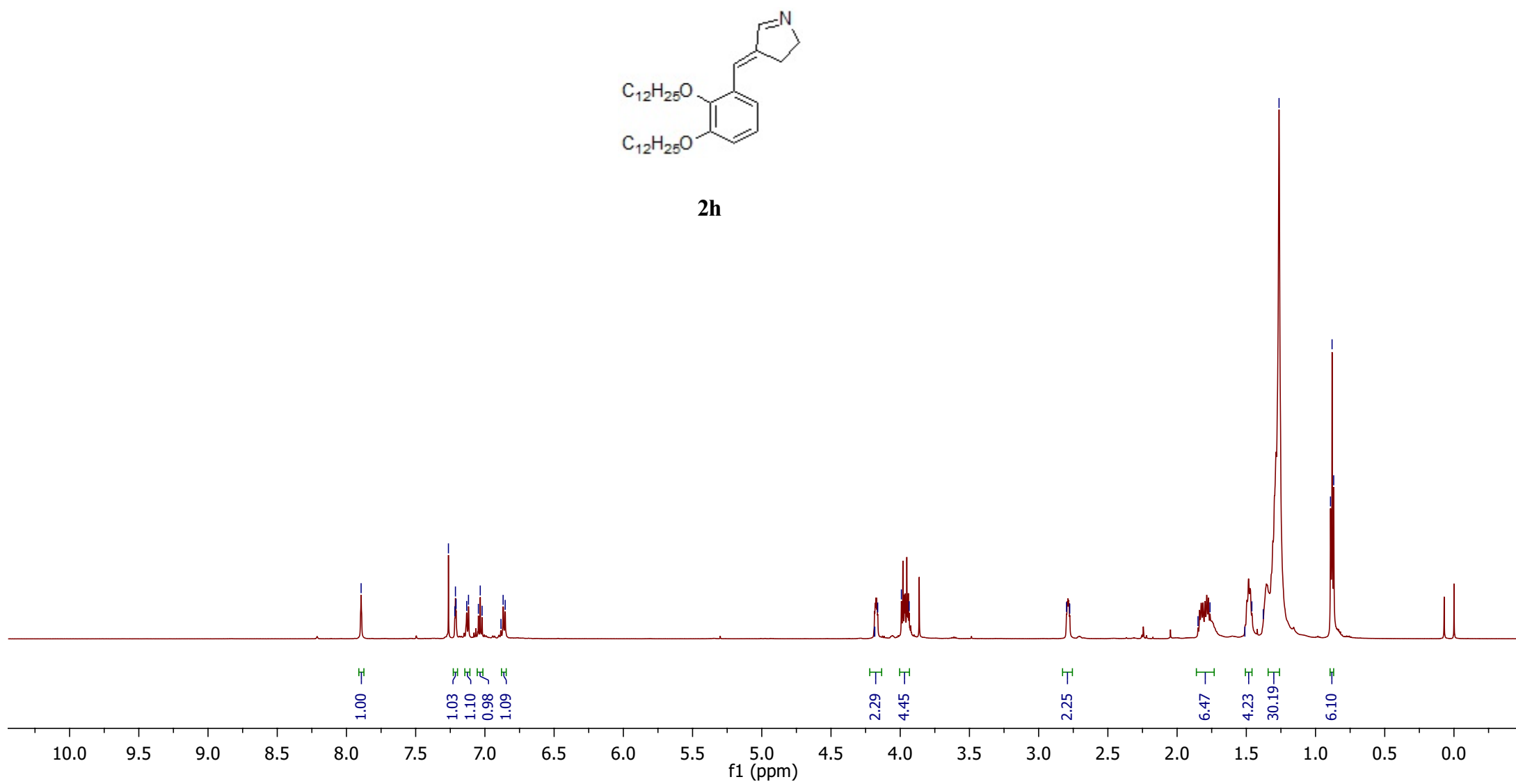


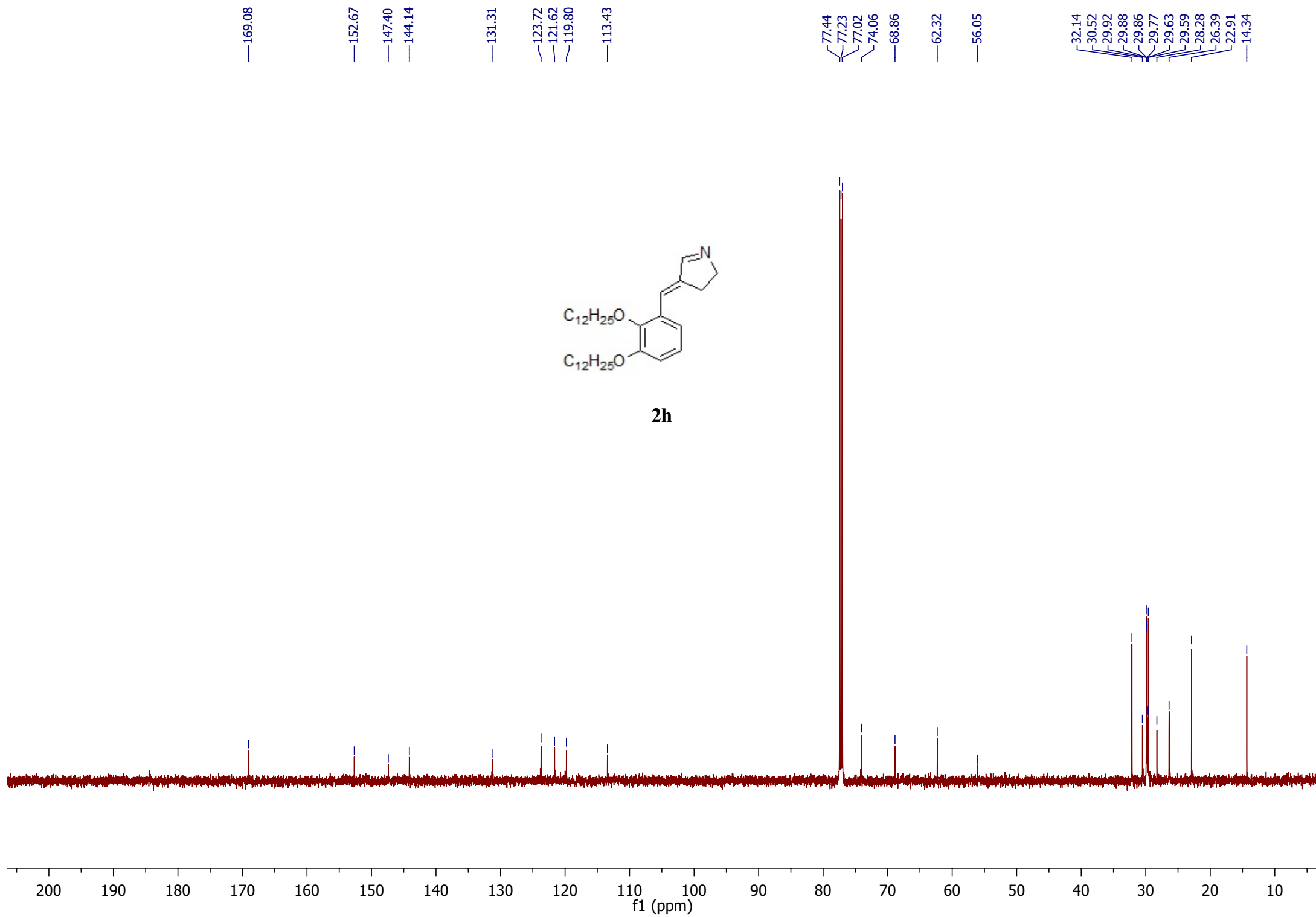
**2g**

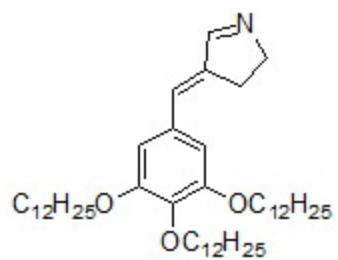




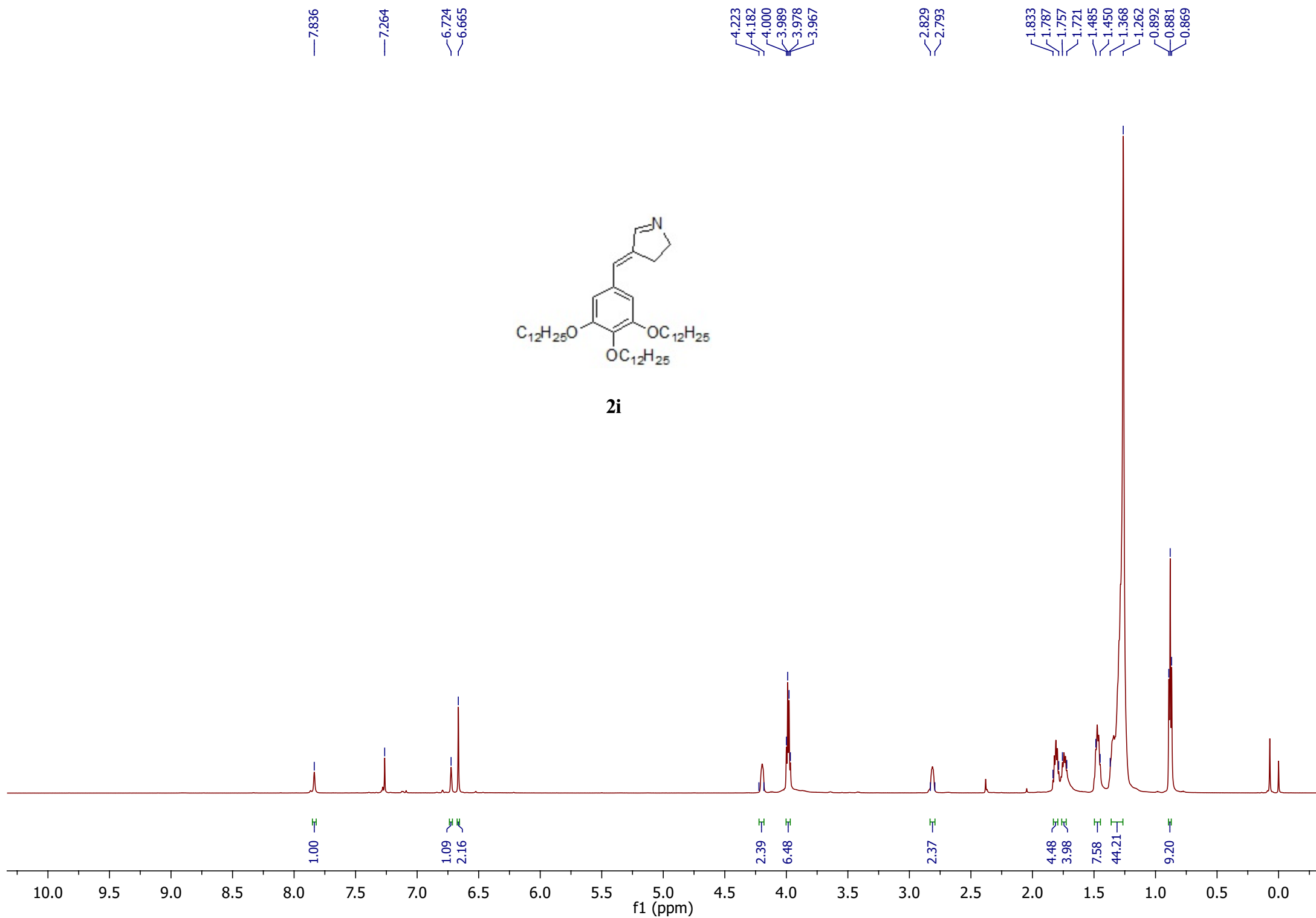


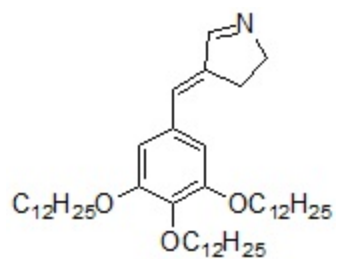




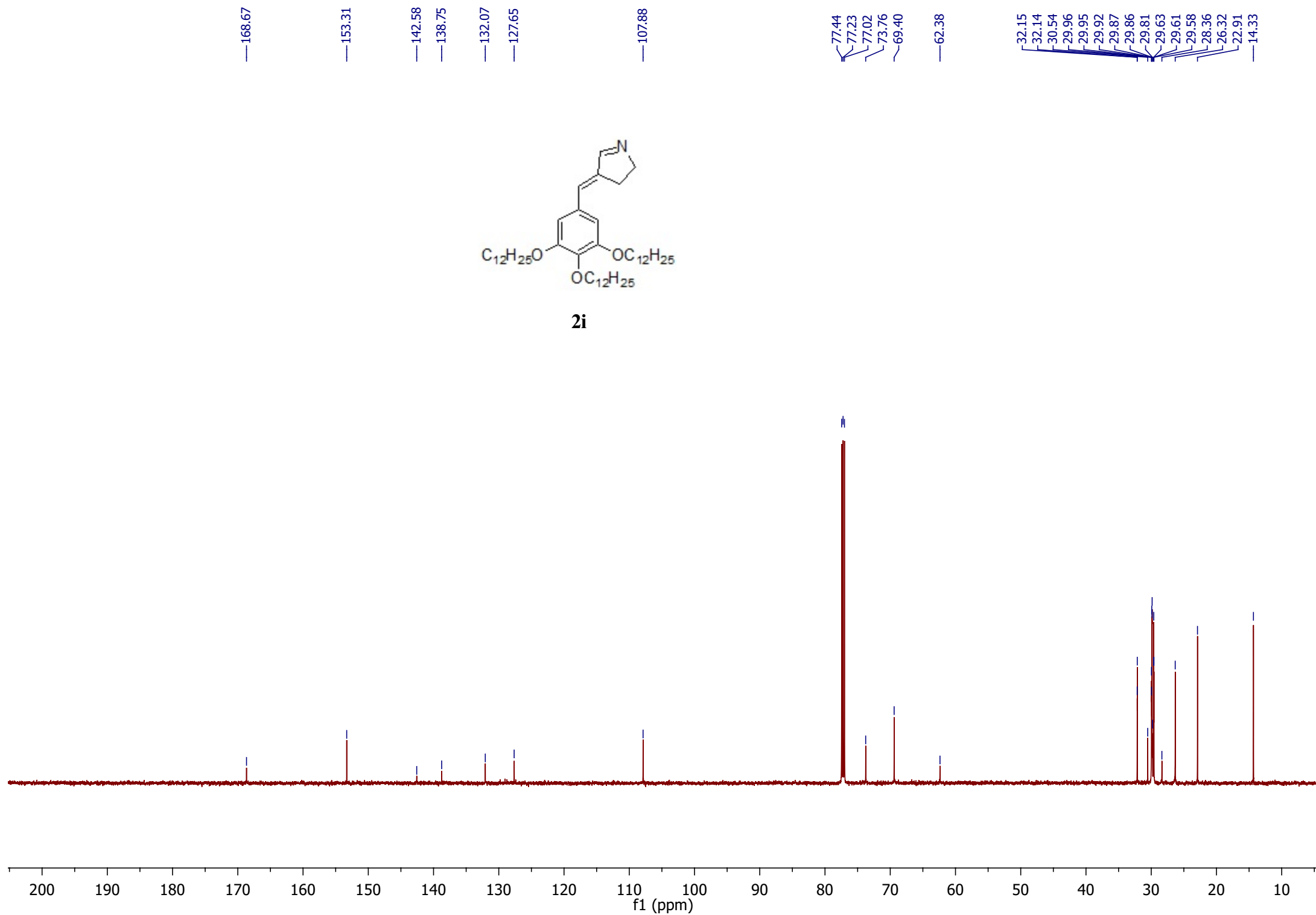


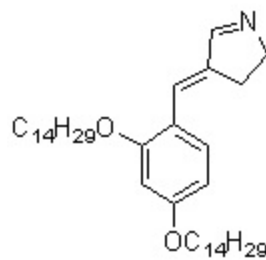
**2i**



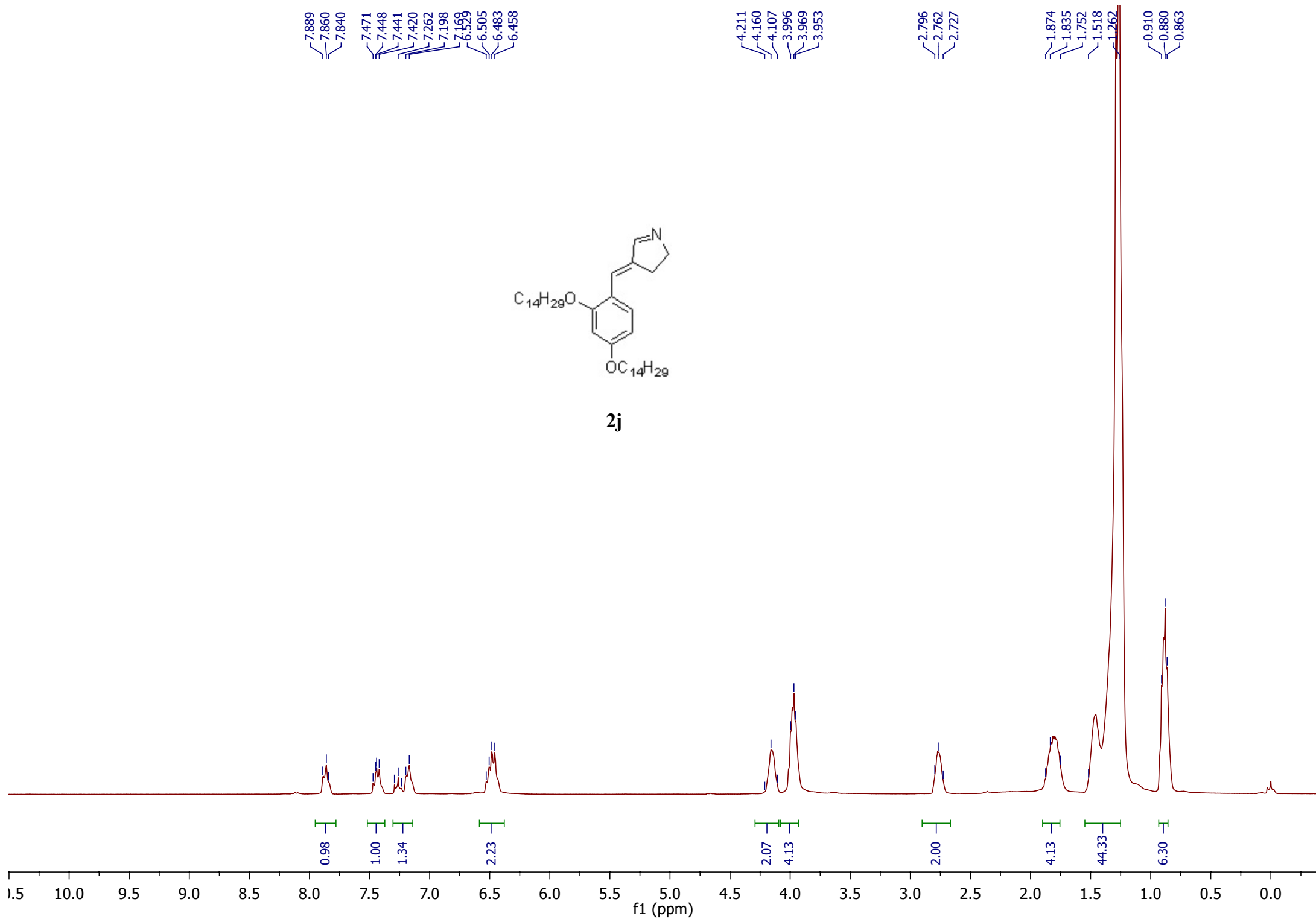


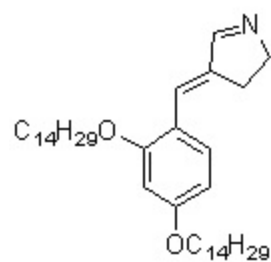
**2i**



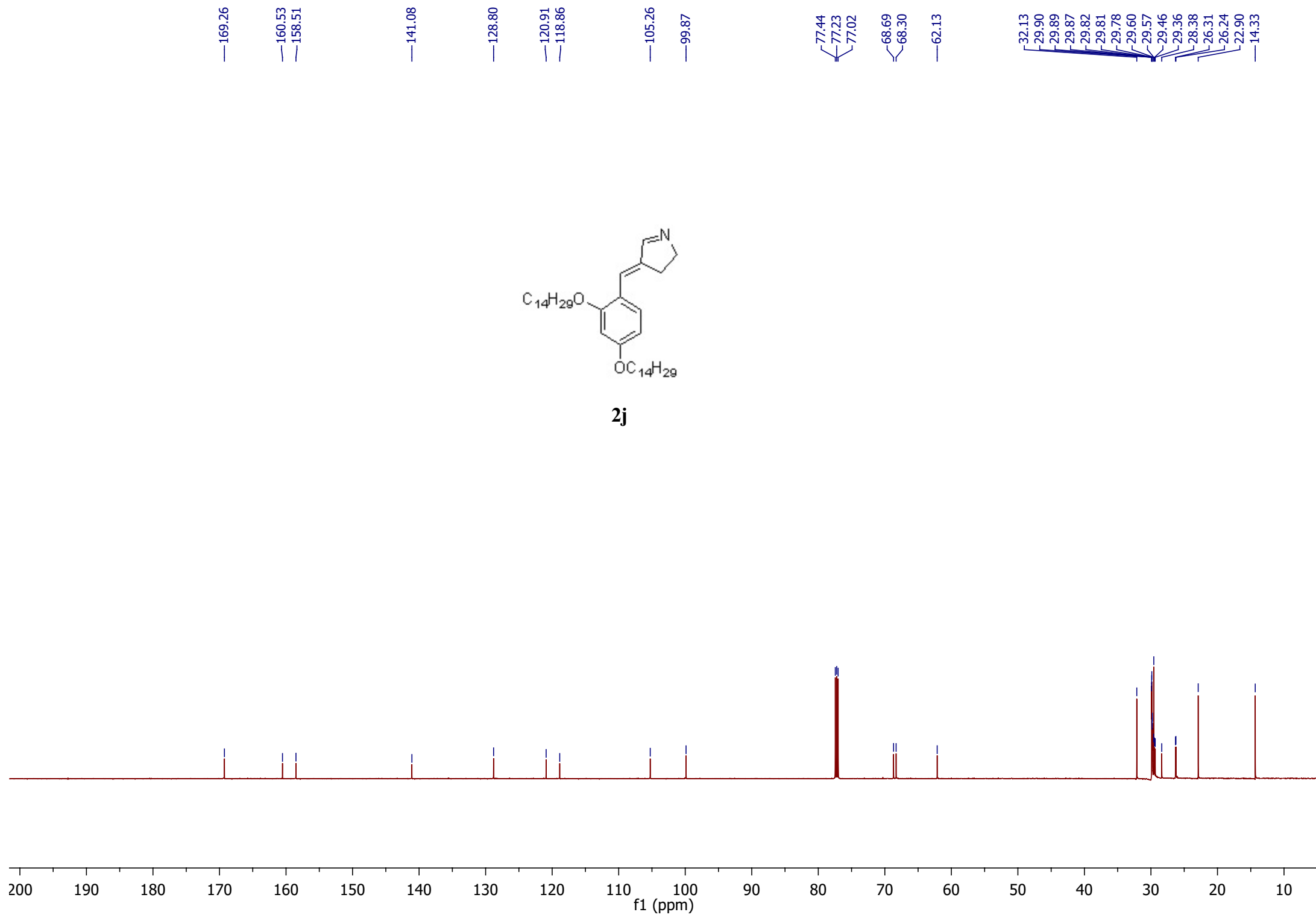


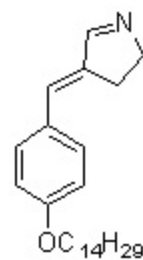
**2j**



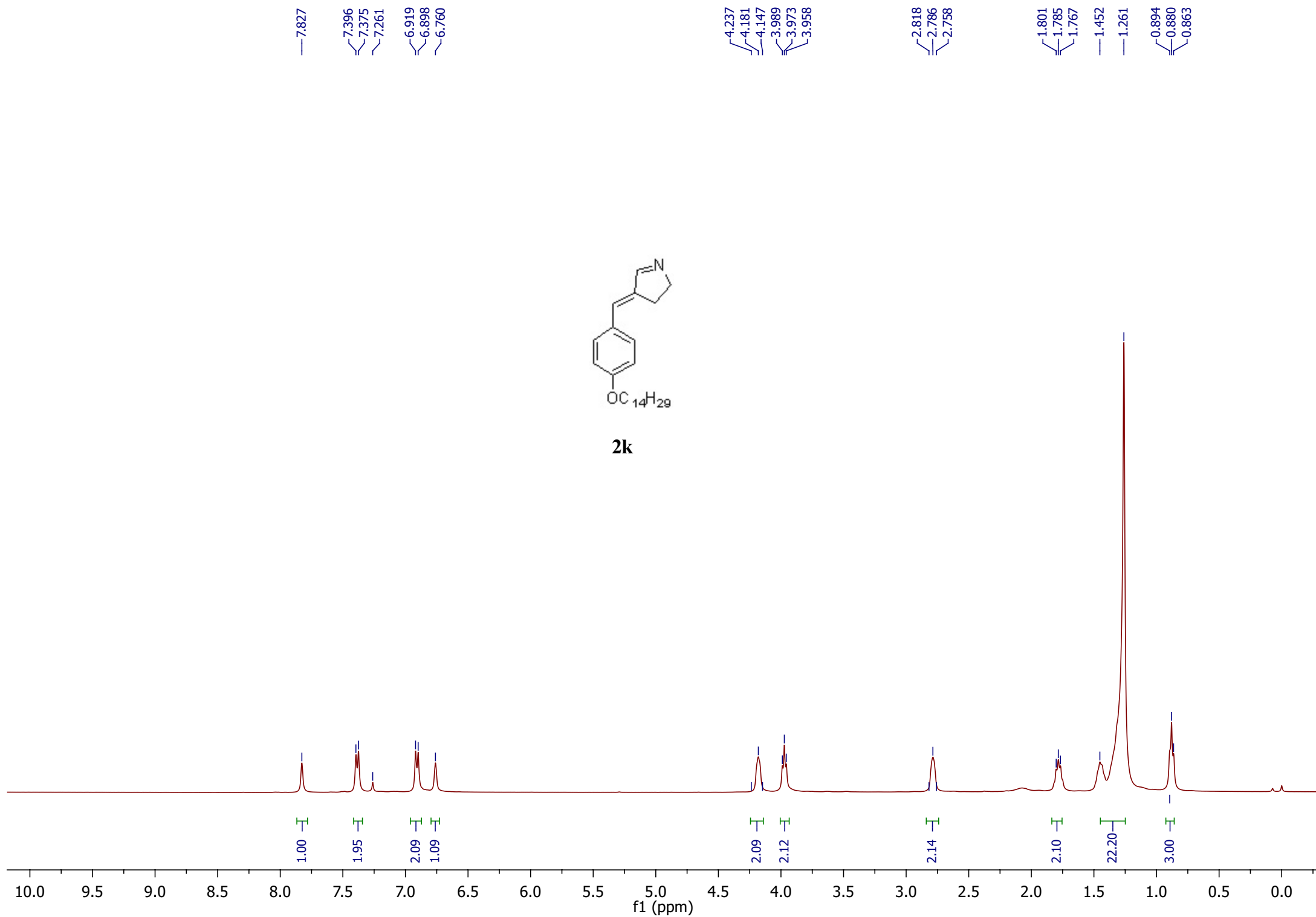


**2j**

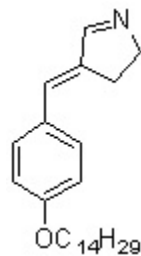




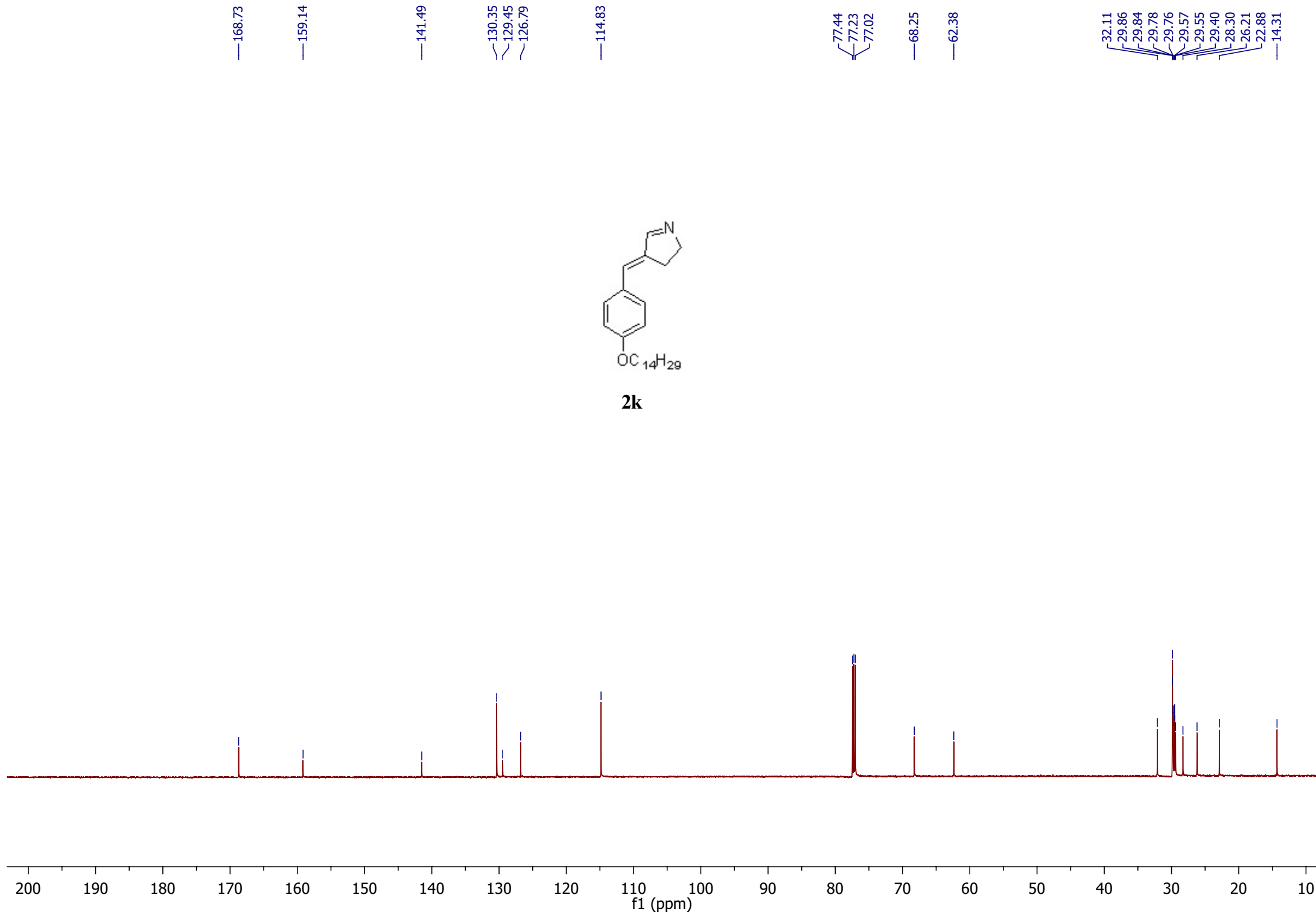
**2k**

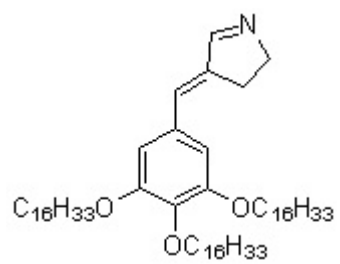




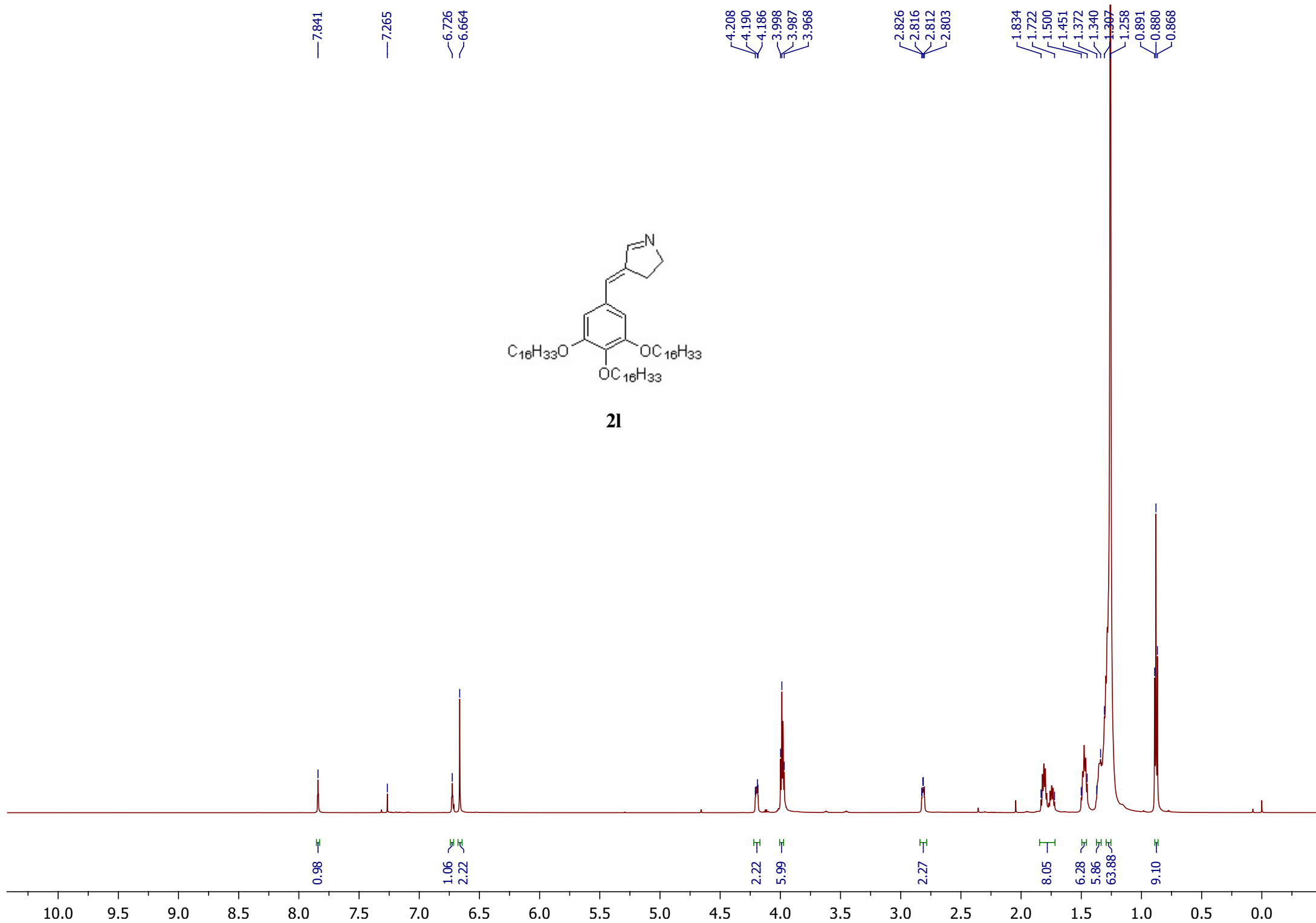


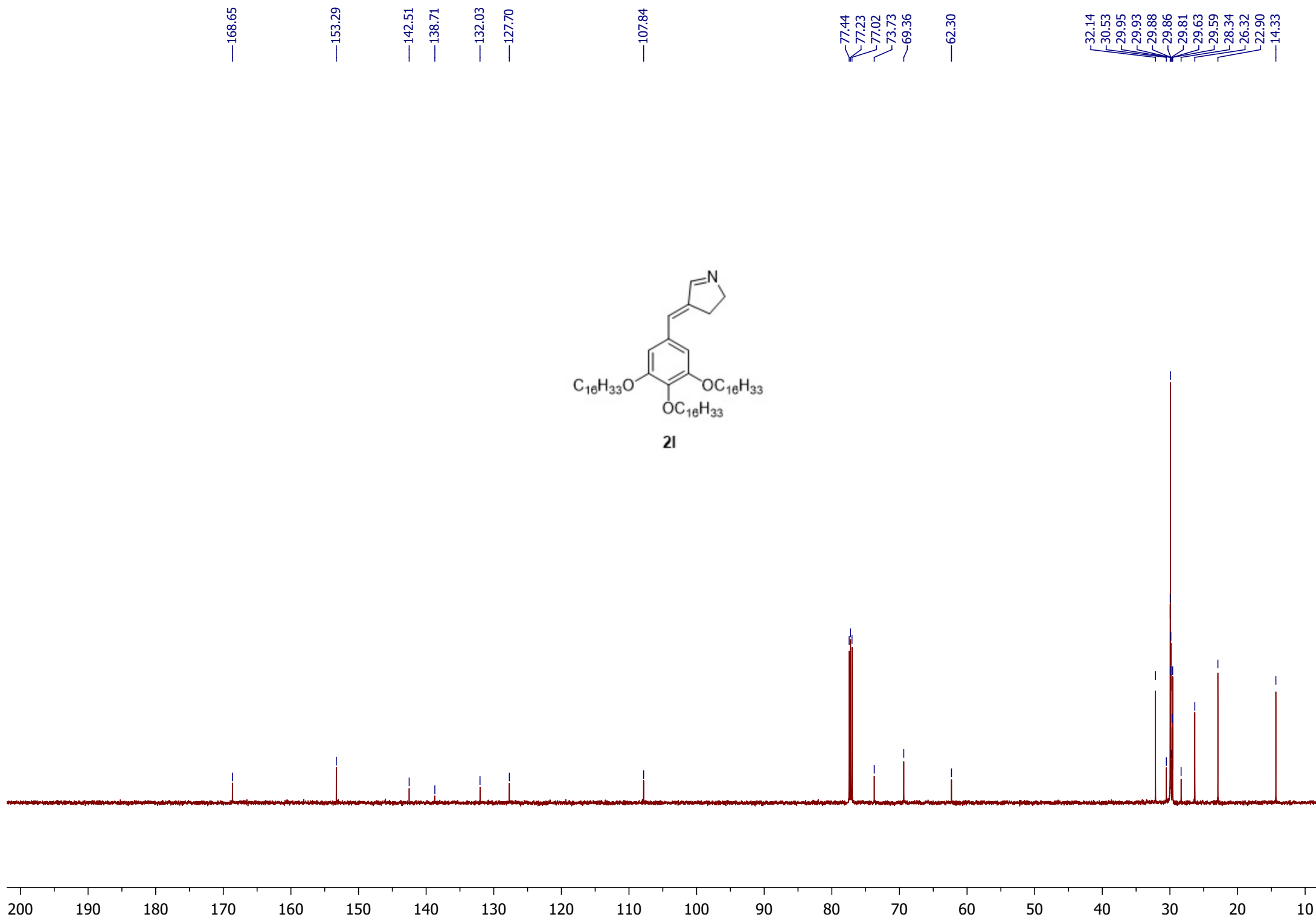
**2k**

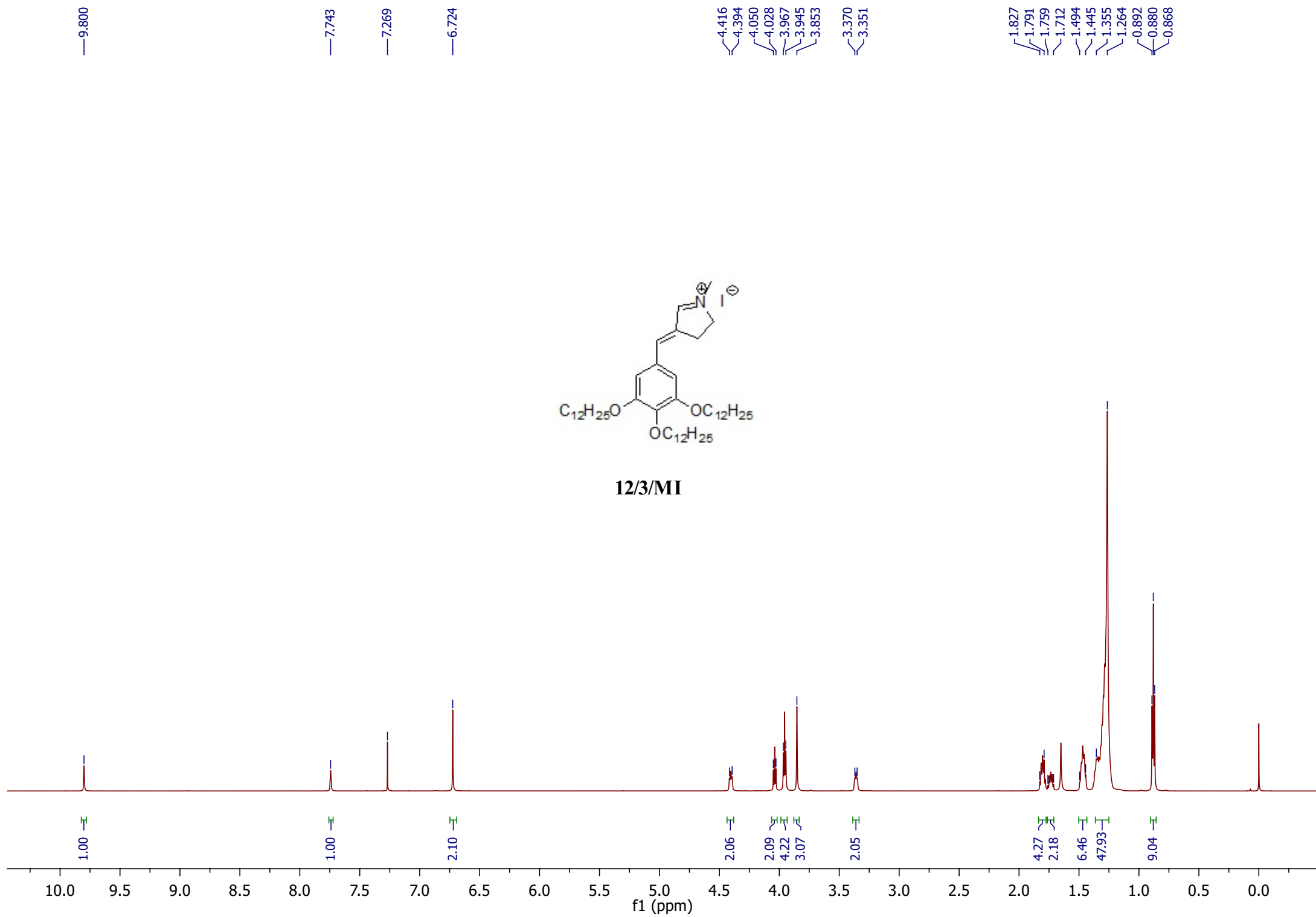


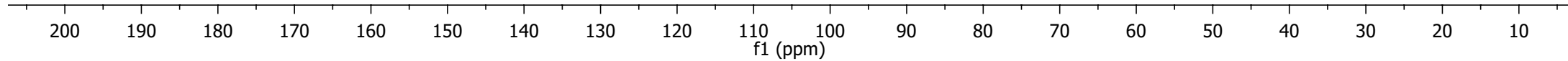
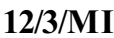


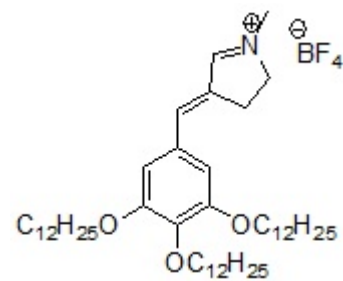
**2l**



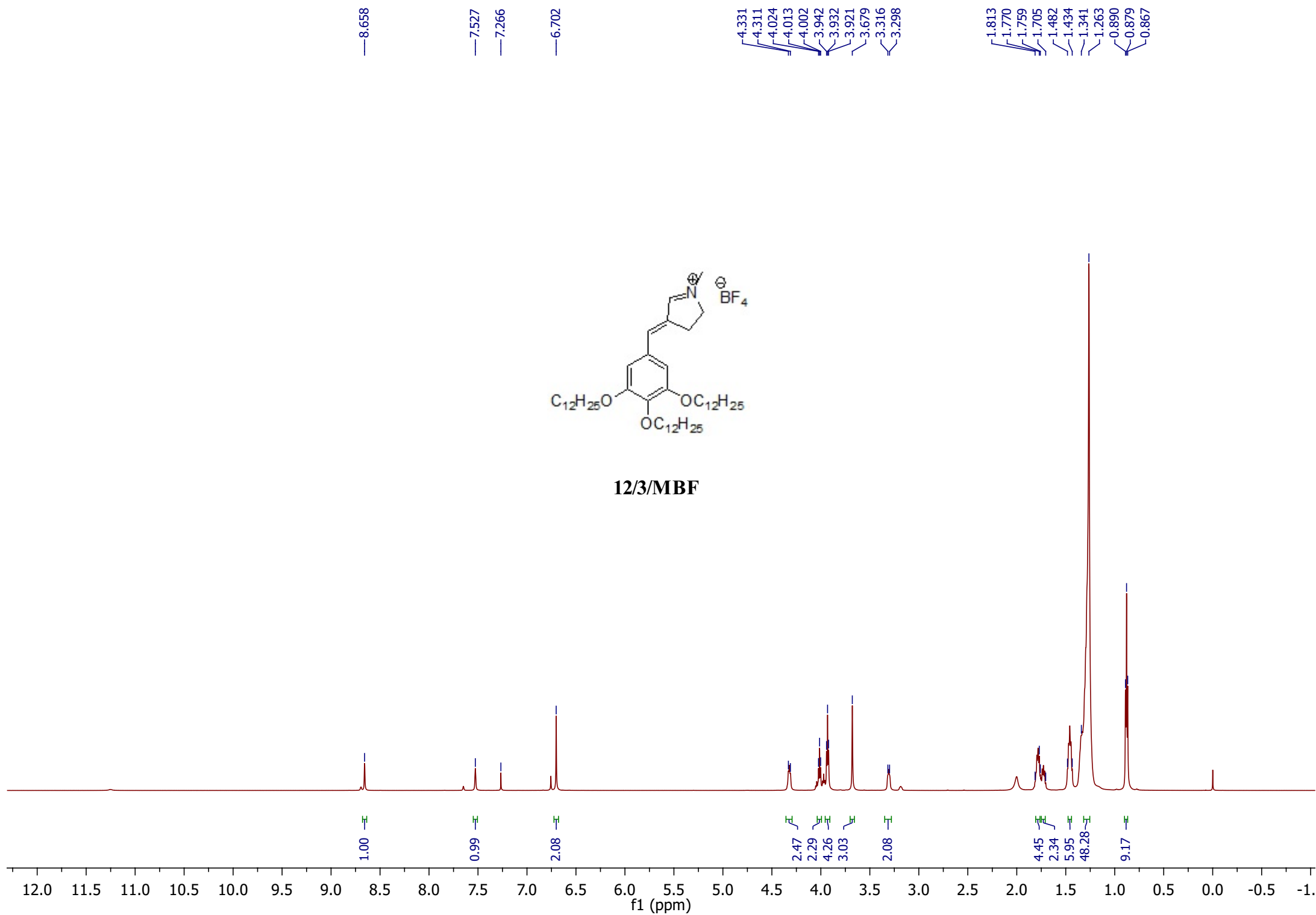


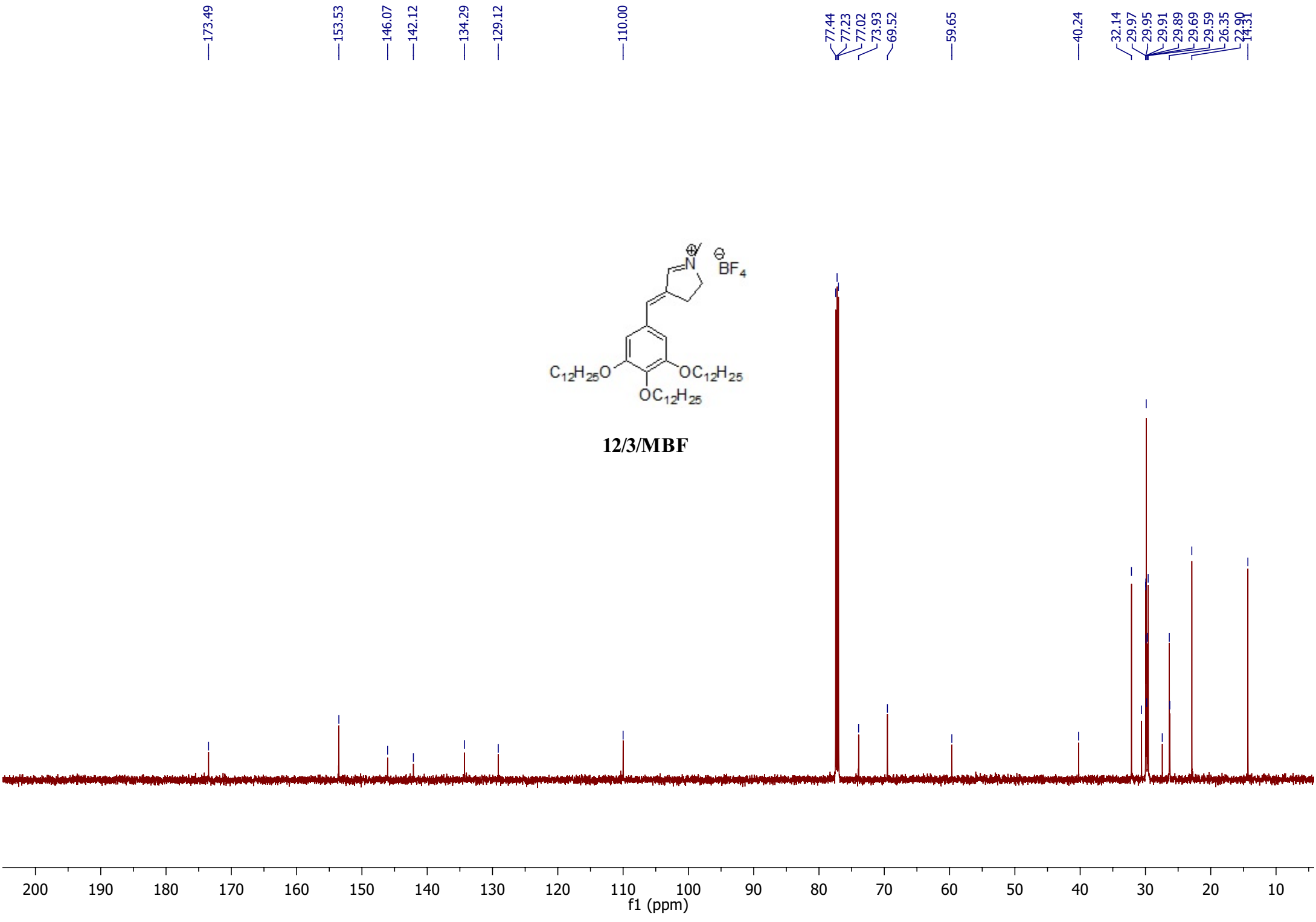




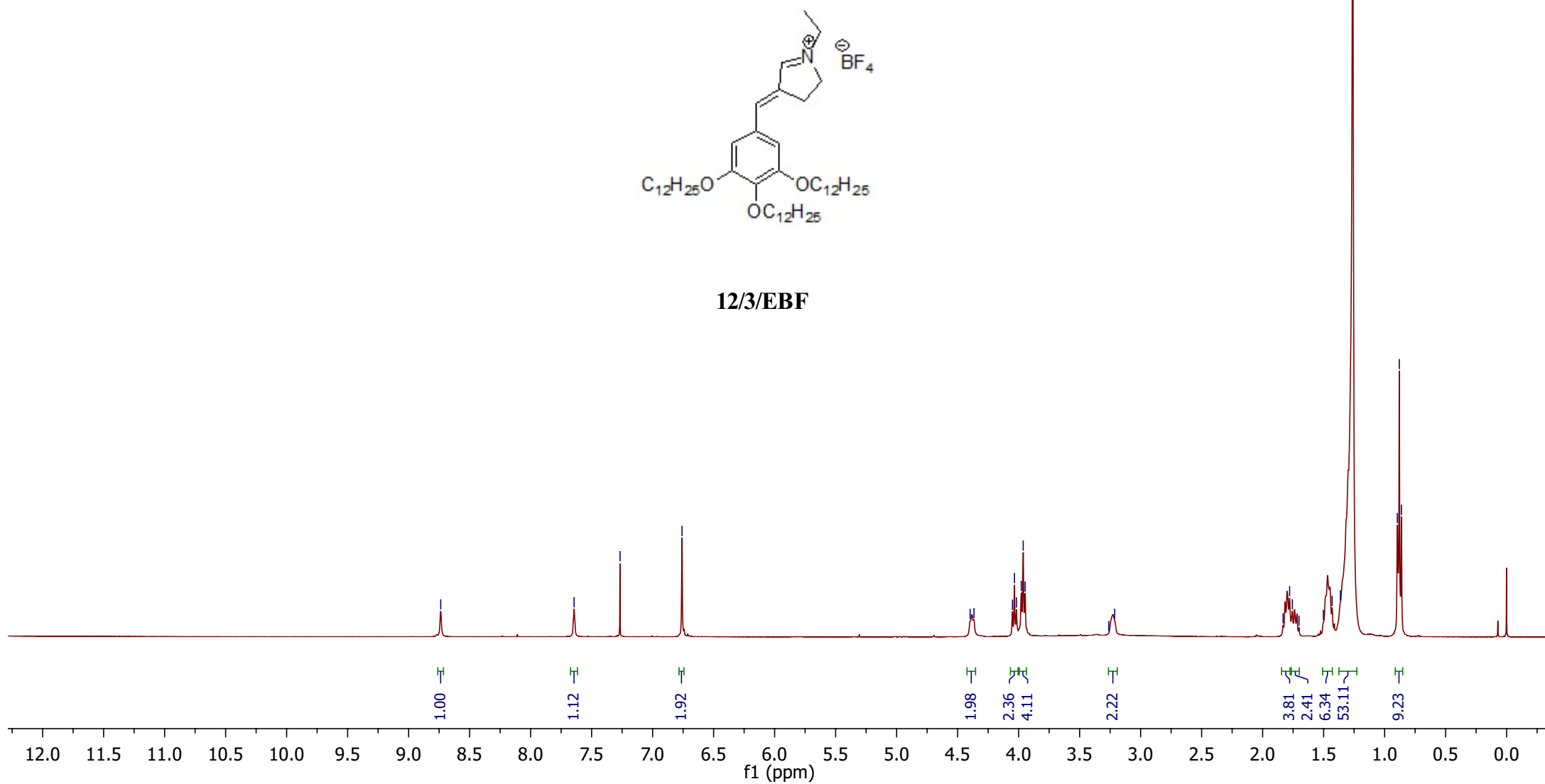


**12/3/MBF**

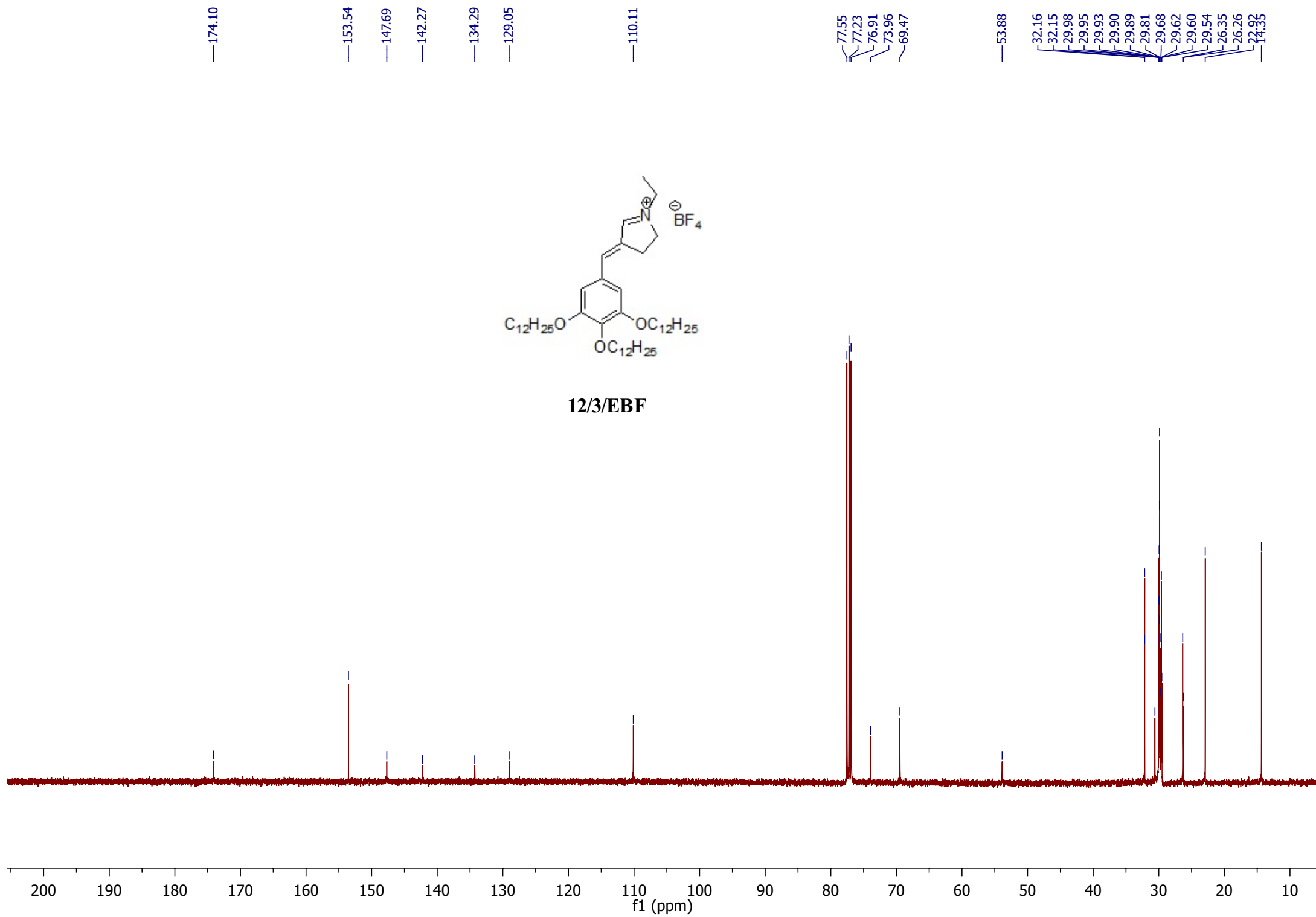


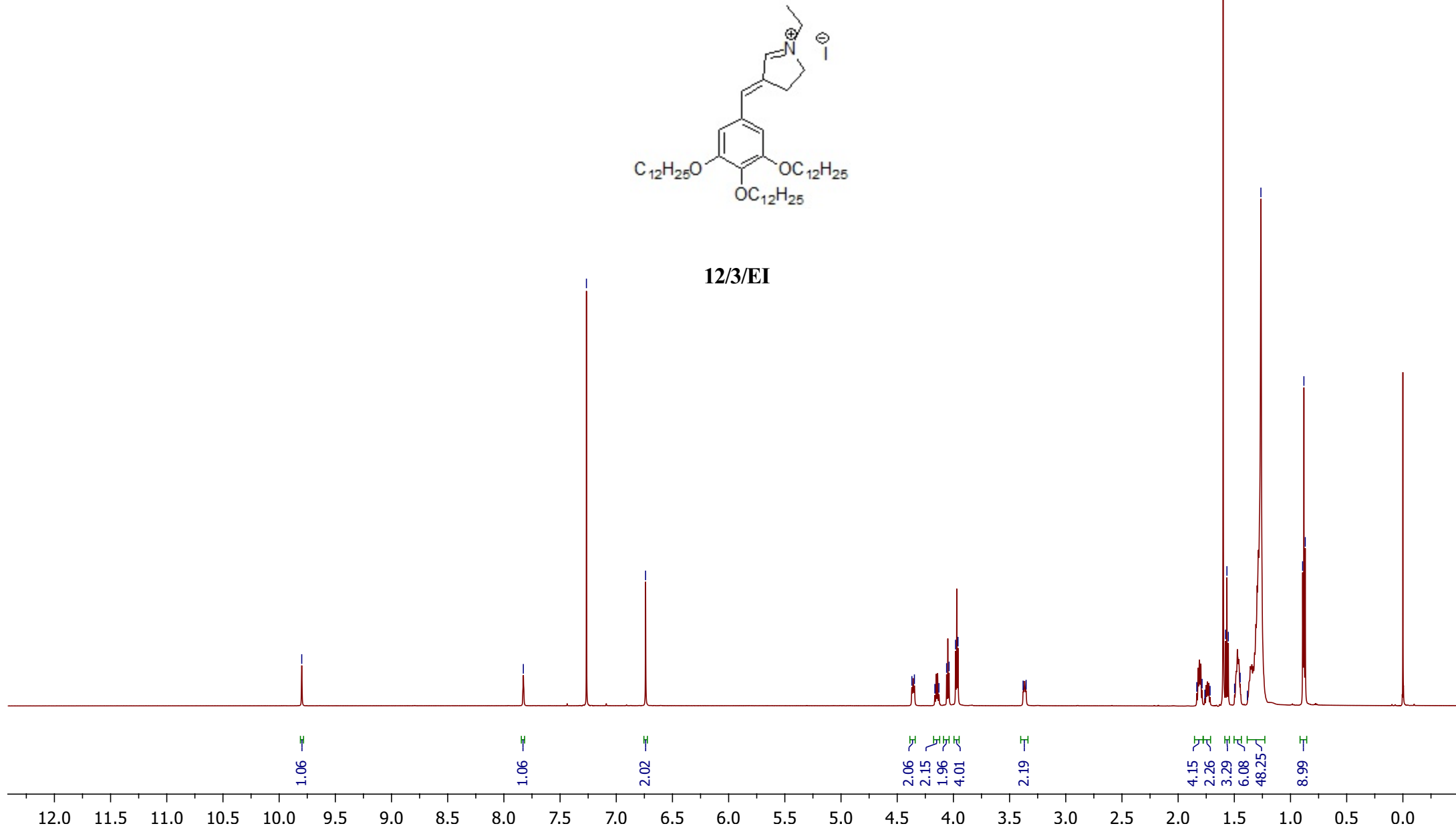


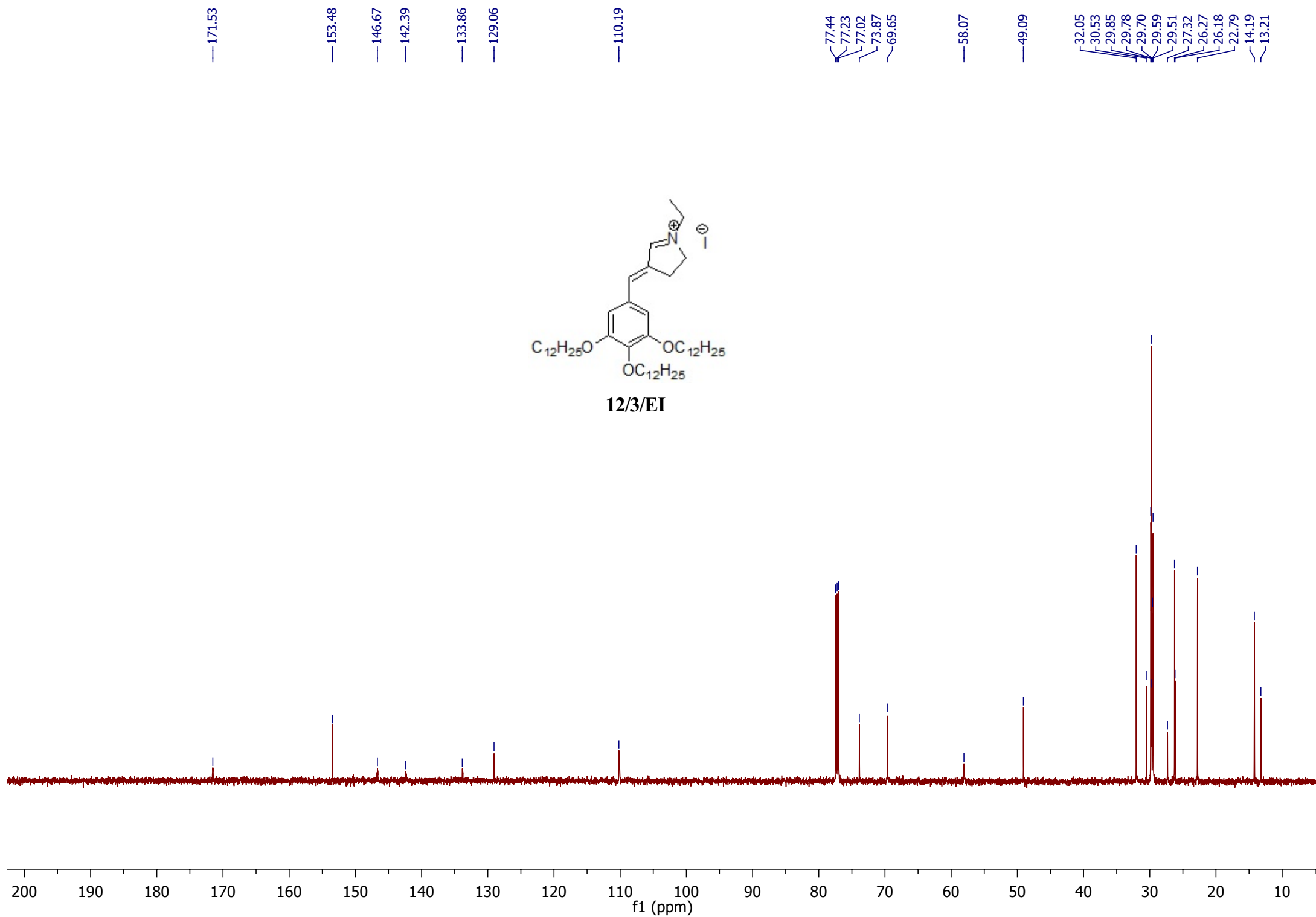
12/3/MBF

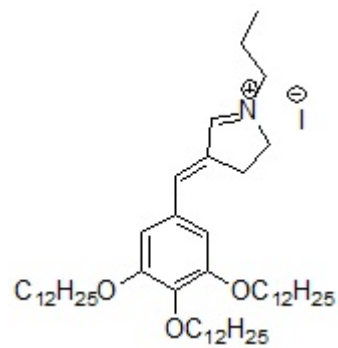




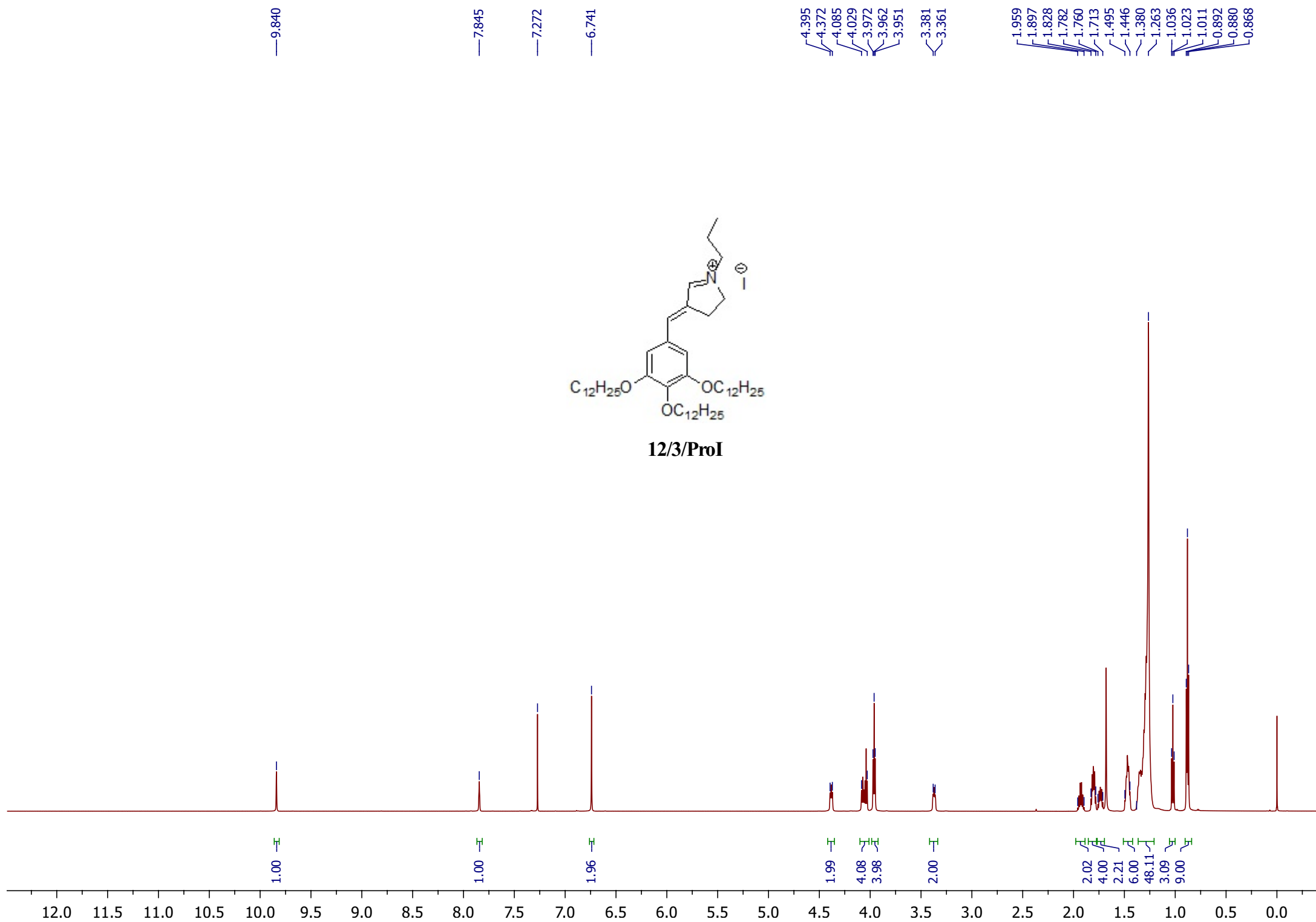


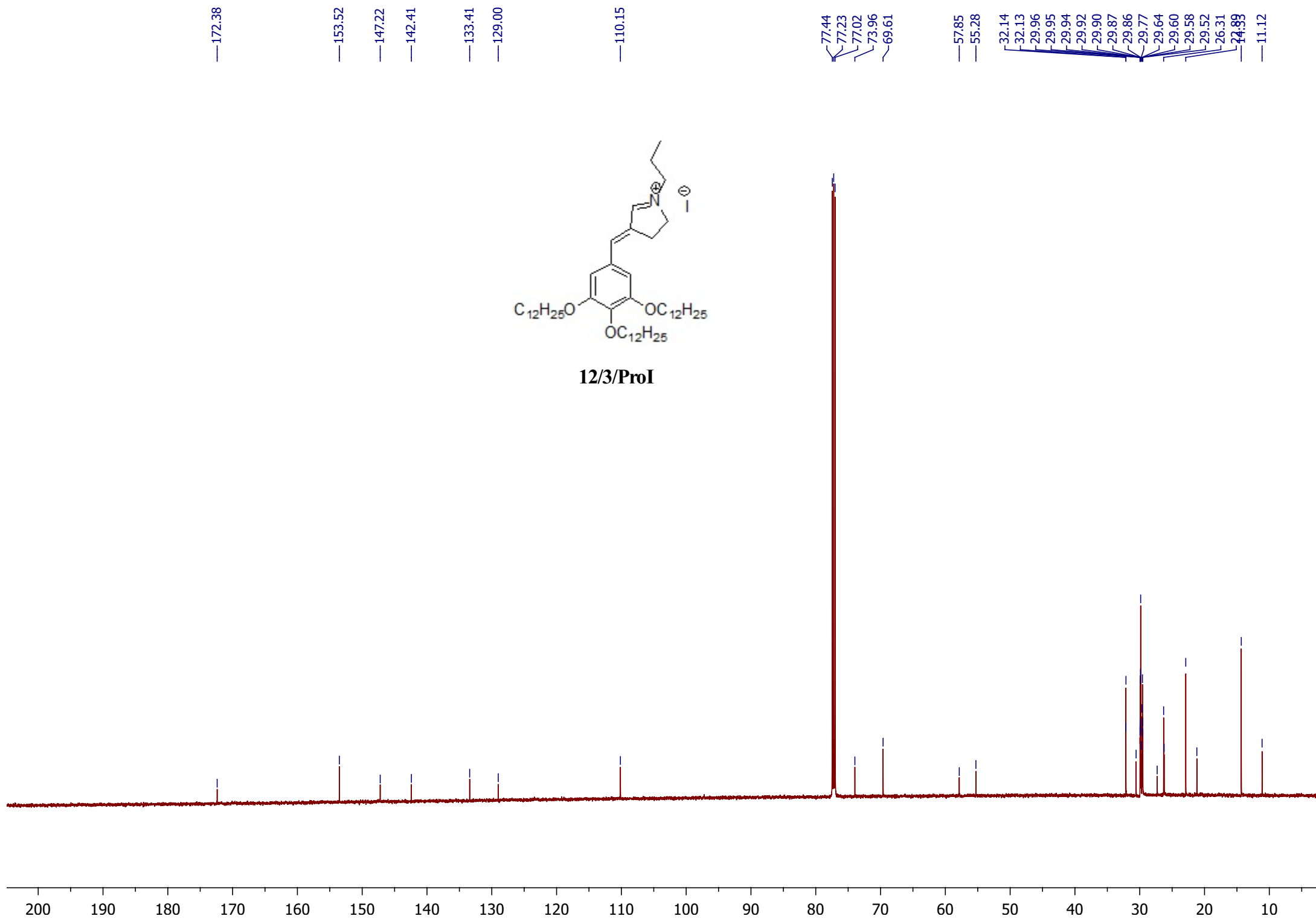




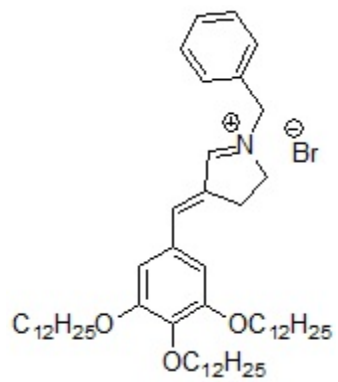


**12/3/ProI**

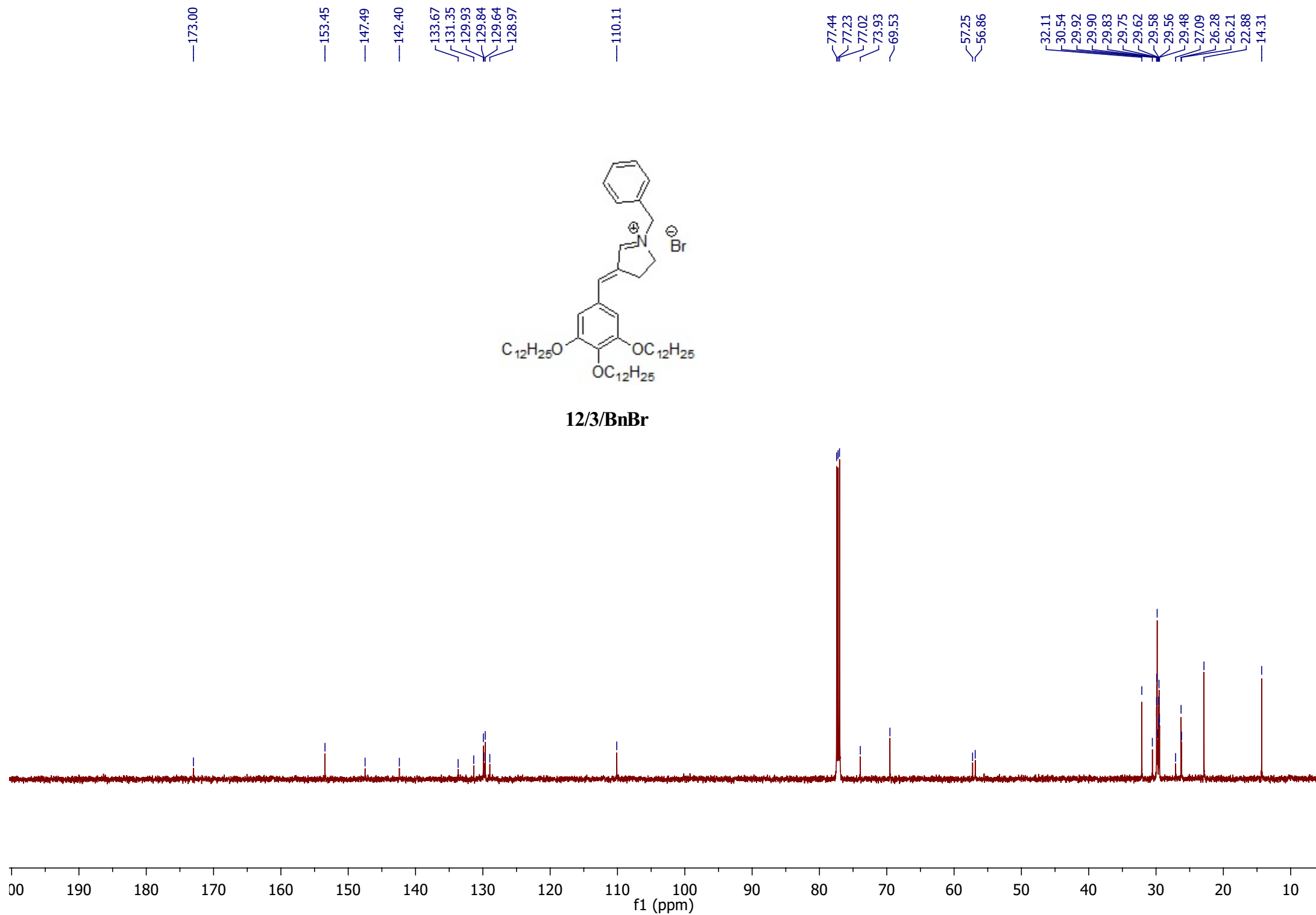


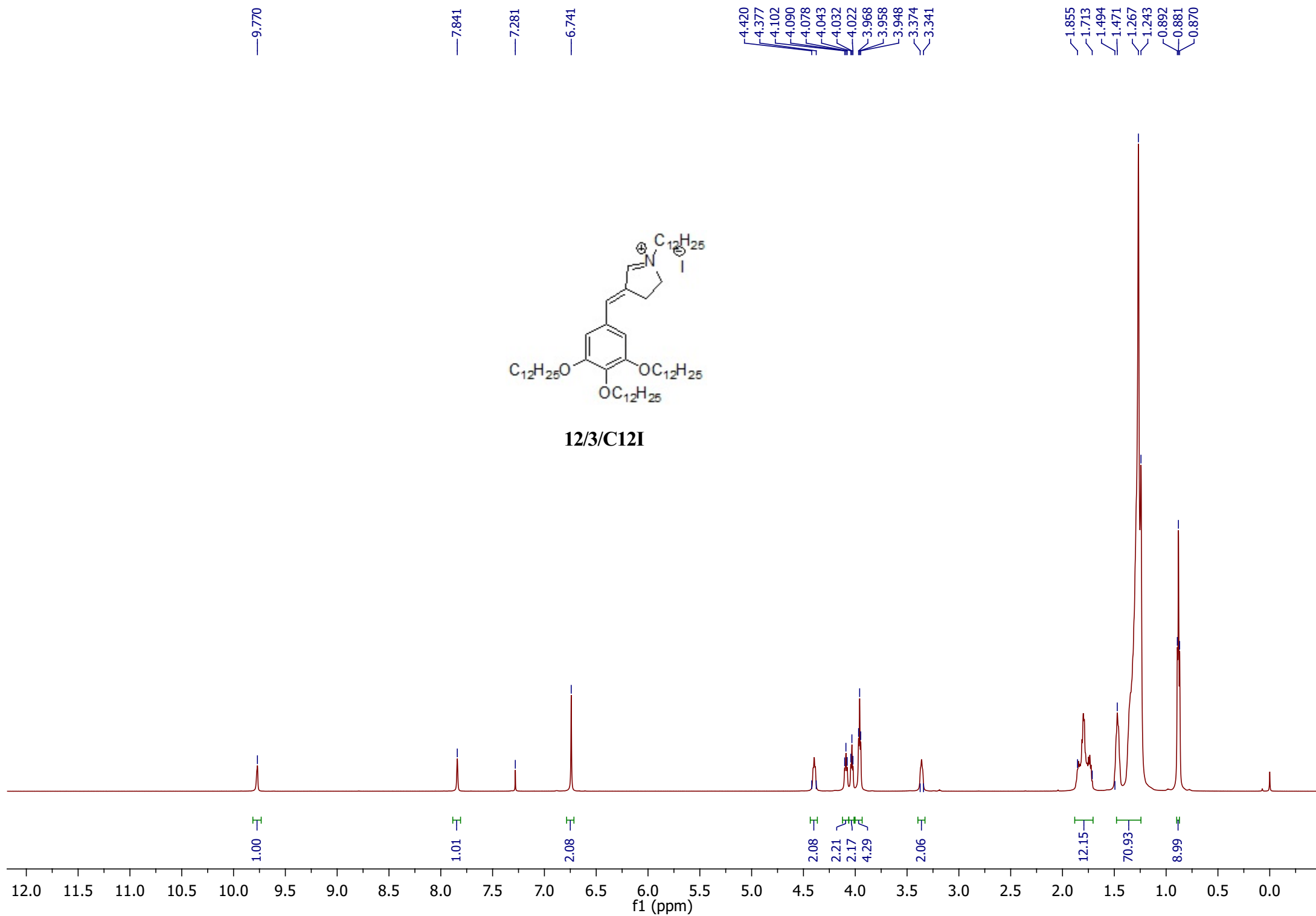




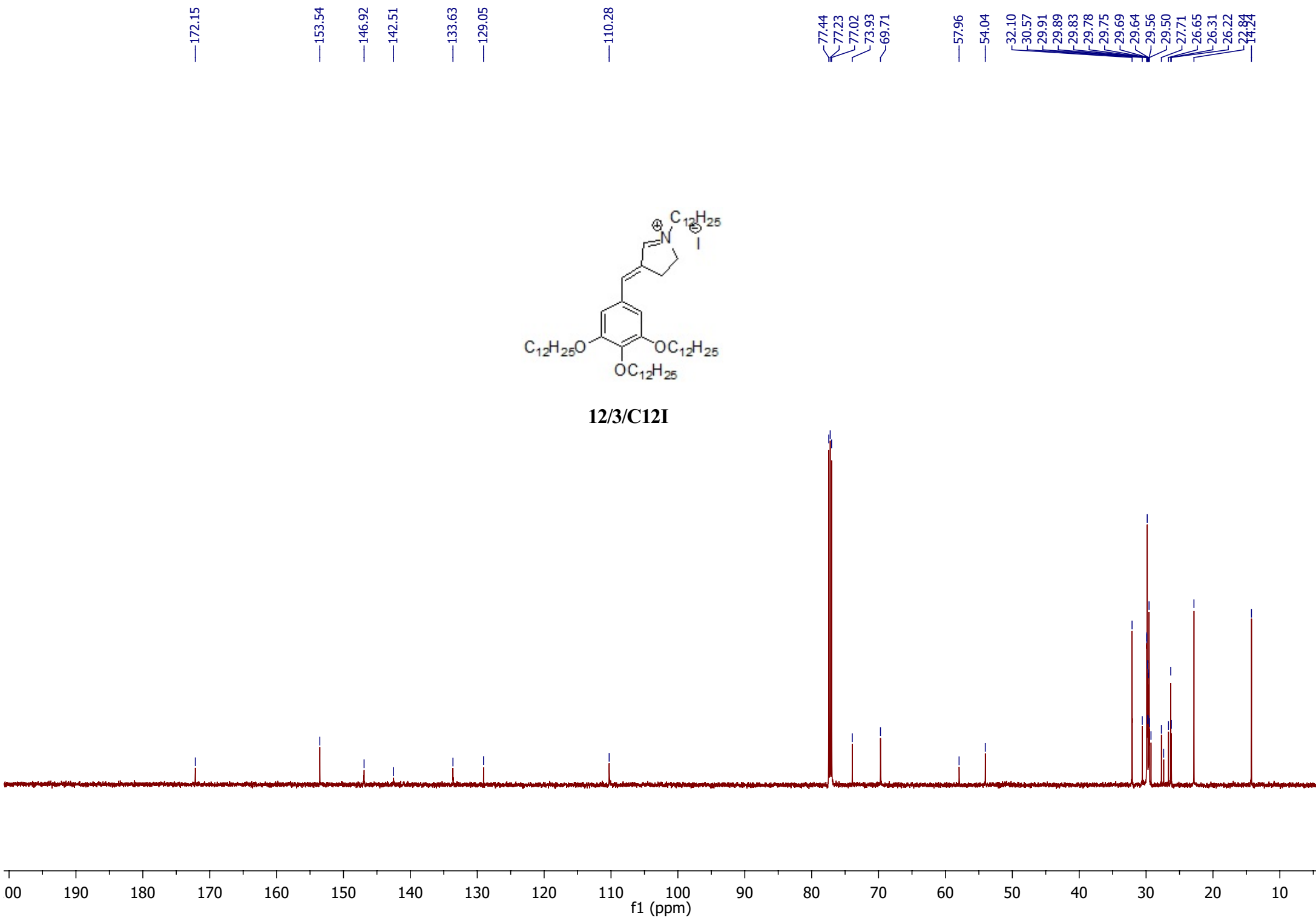


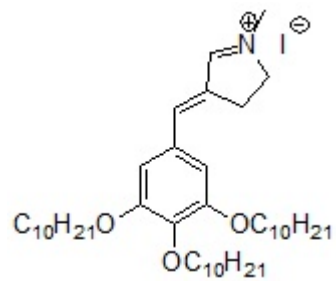
12/3/BnBr



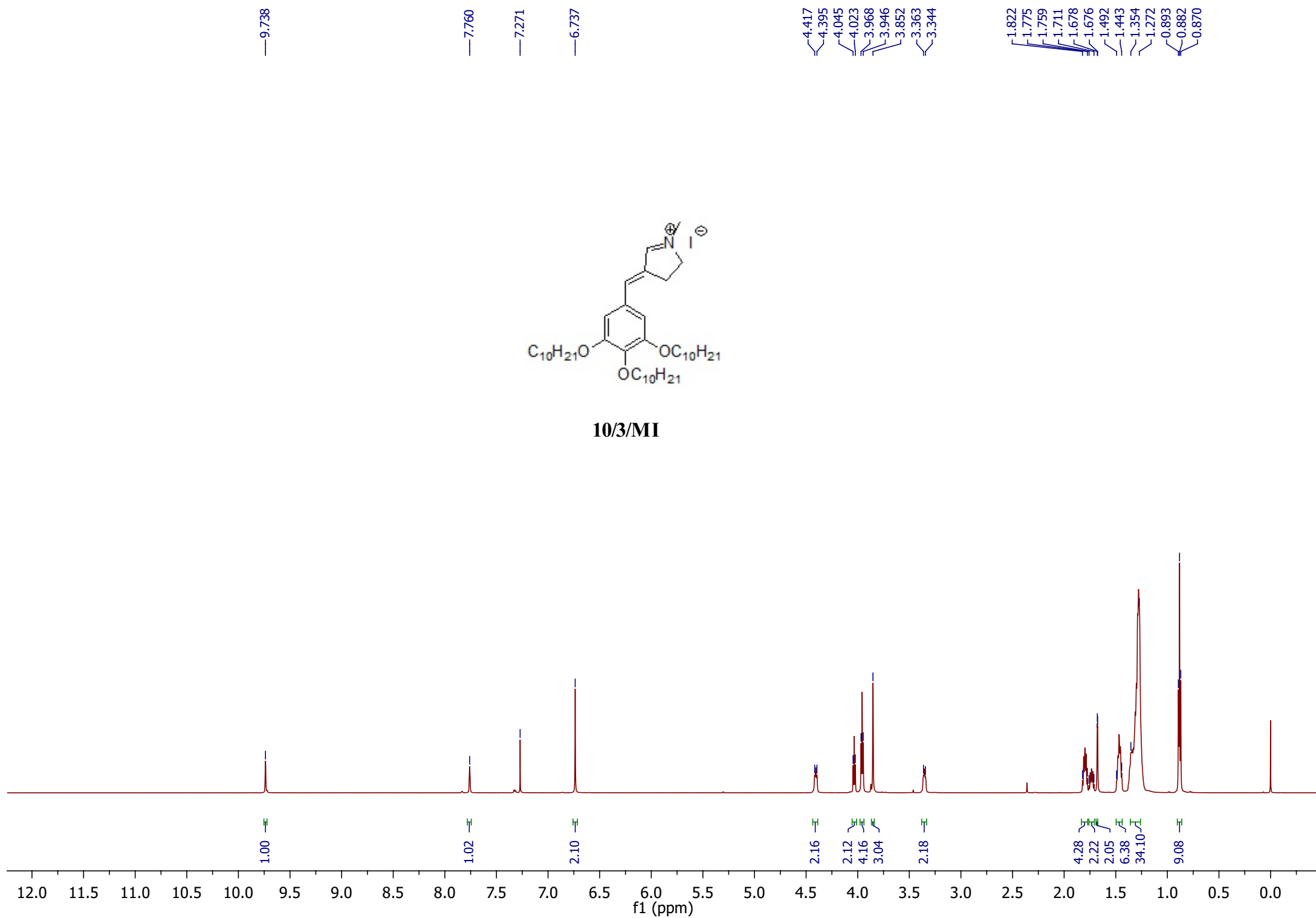


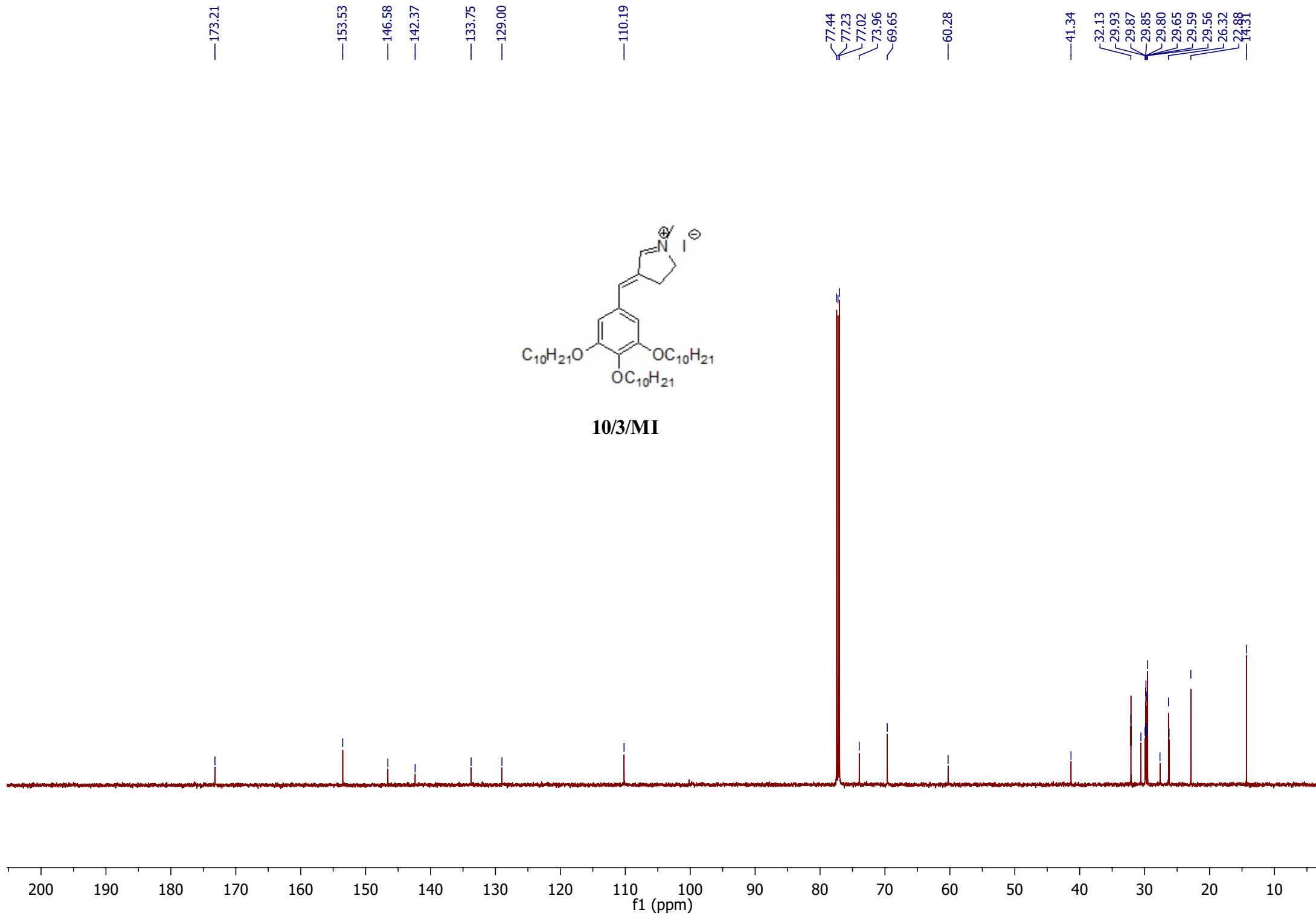






10/3/MI





—9.729

—7.734

—7.286

—6.727

4.477

4.450

4.427

4.050

3.938

3.861

3.379

3.355

3.332

1.866

1.703

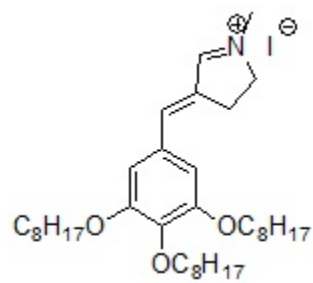
1.501

1.290

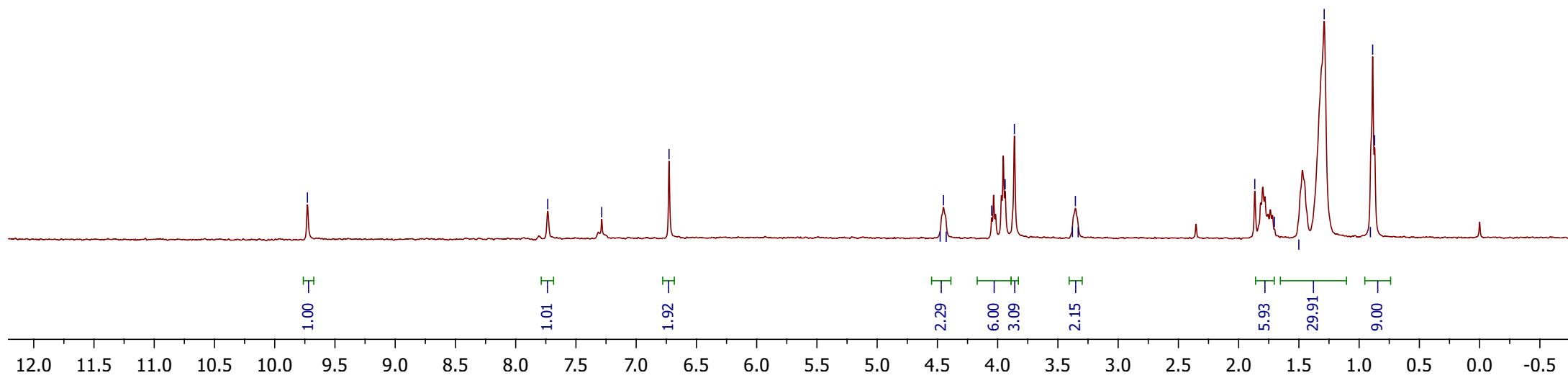
0.907

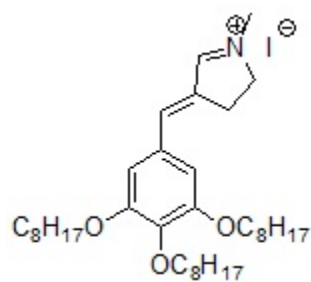
0.888

0.871

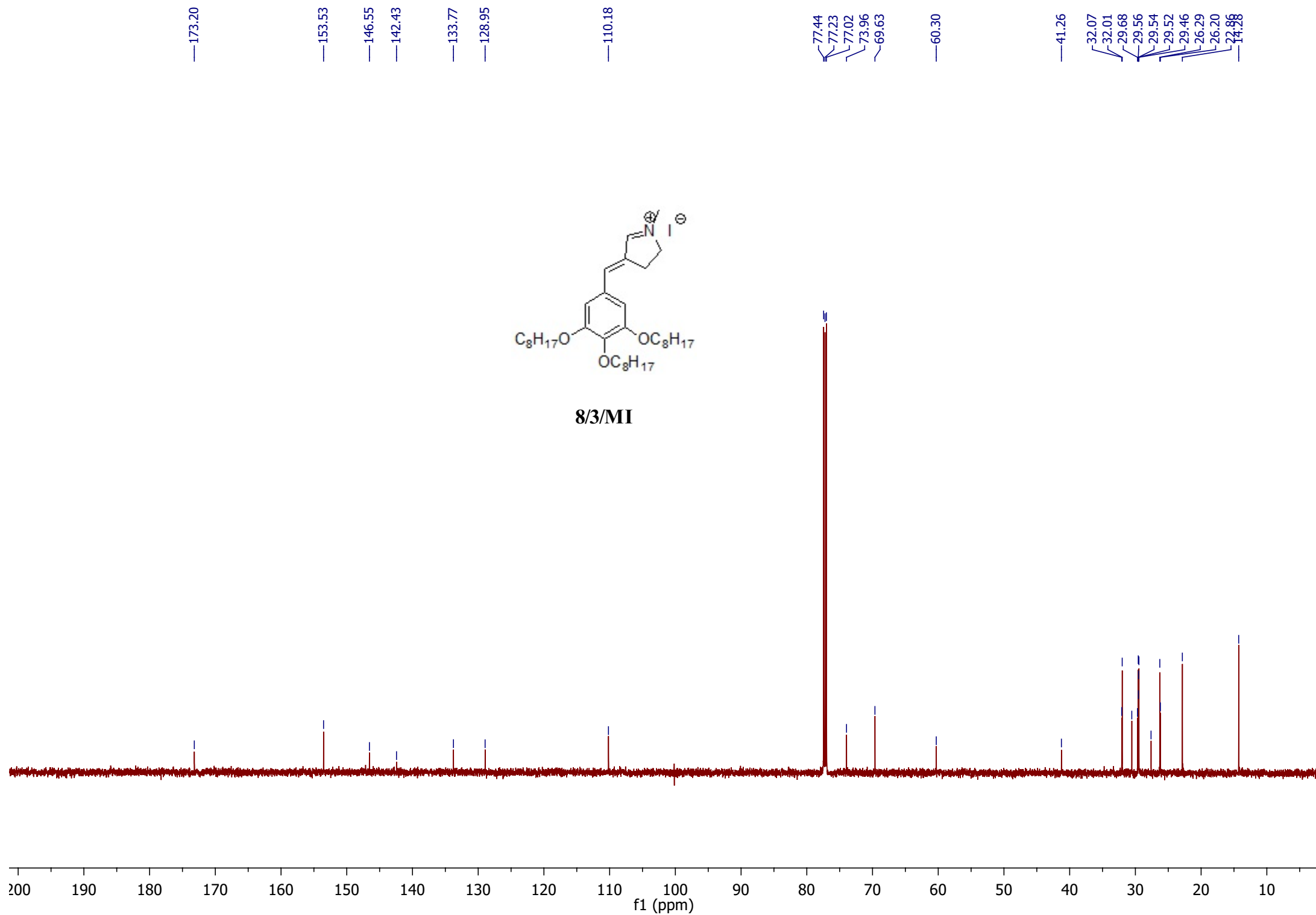


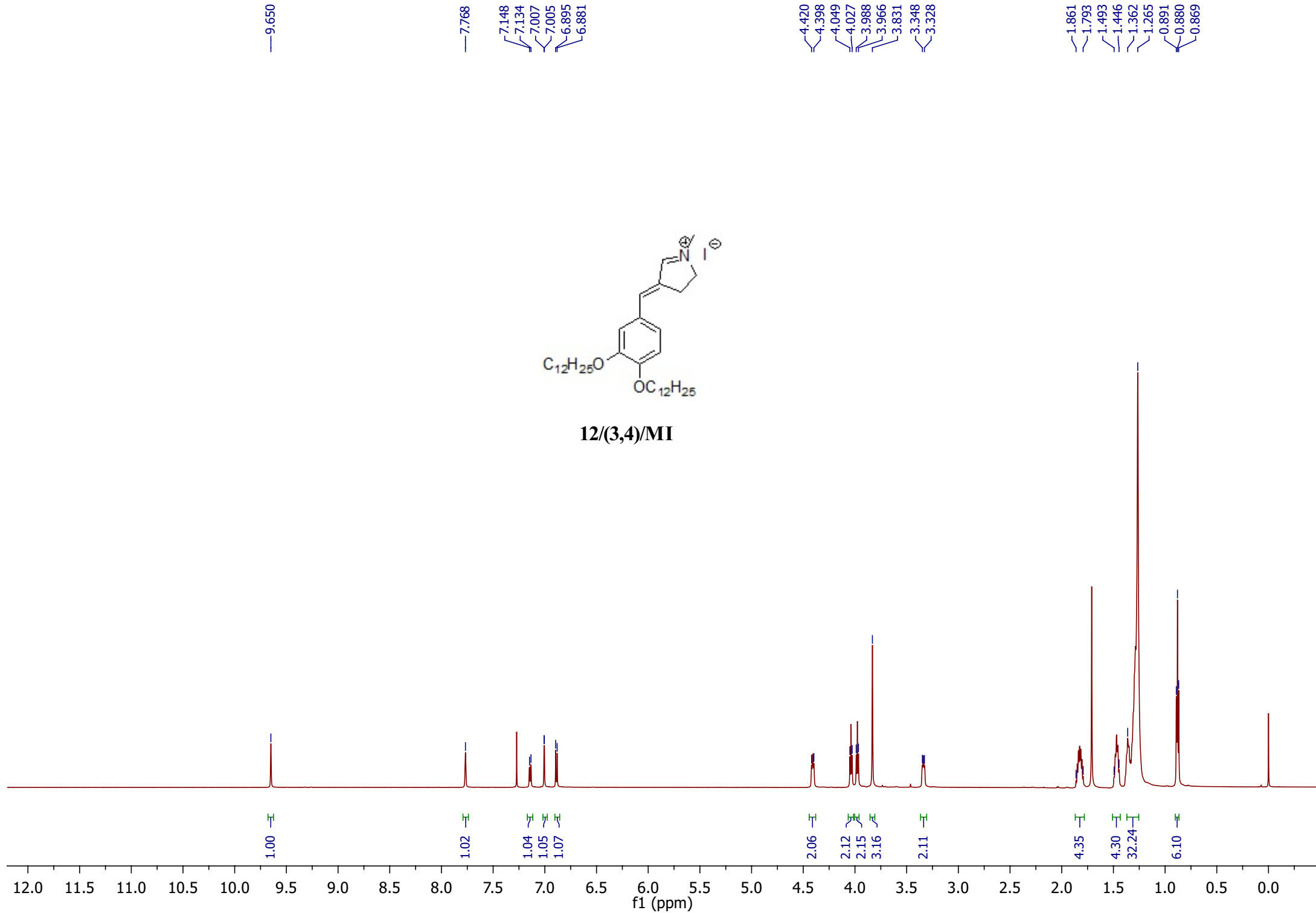
8/3/MI

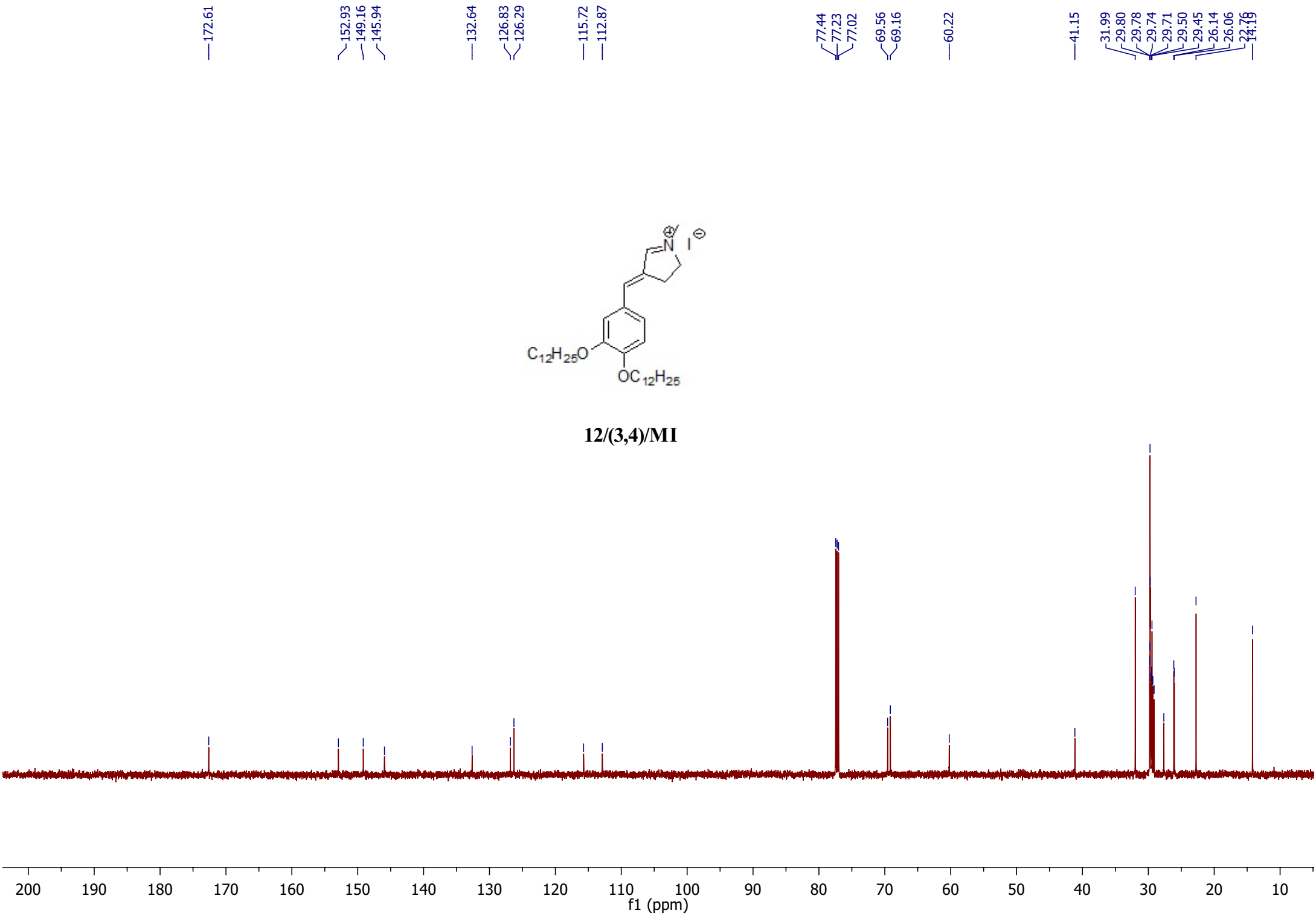


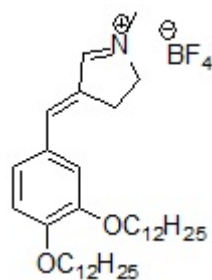


8/3/MI

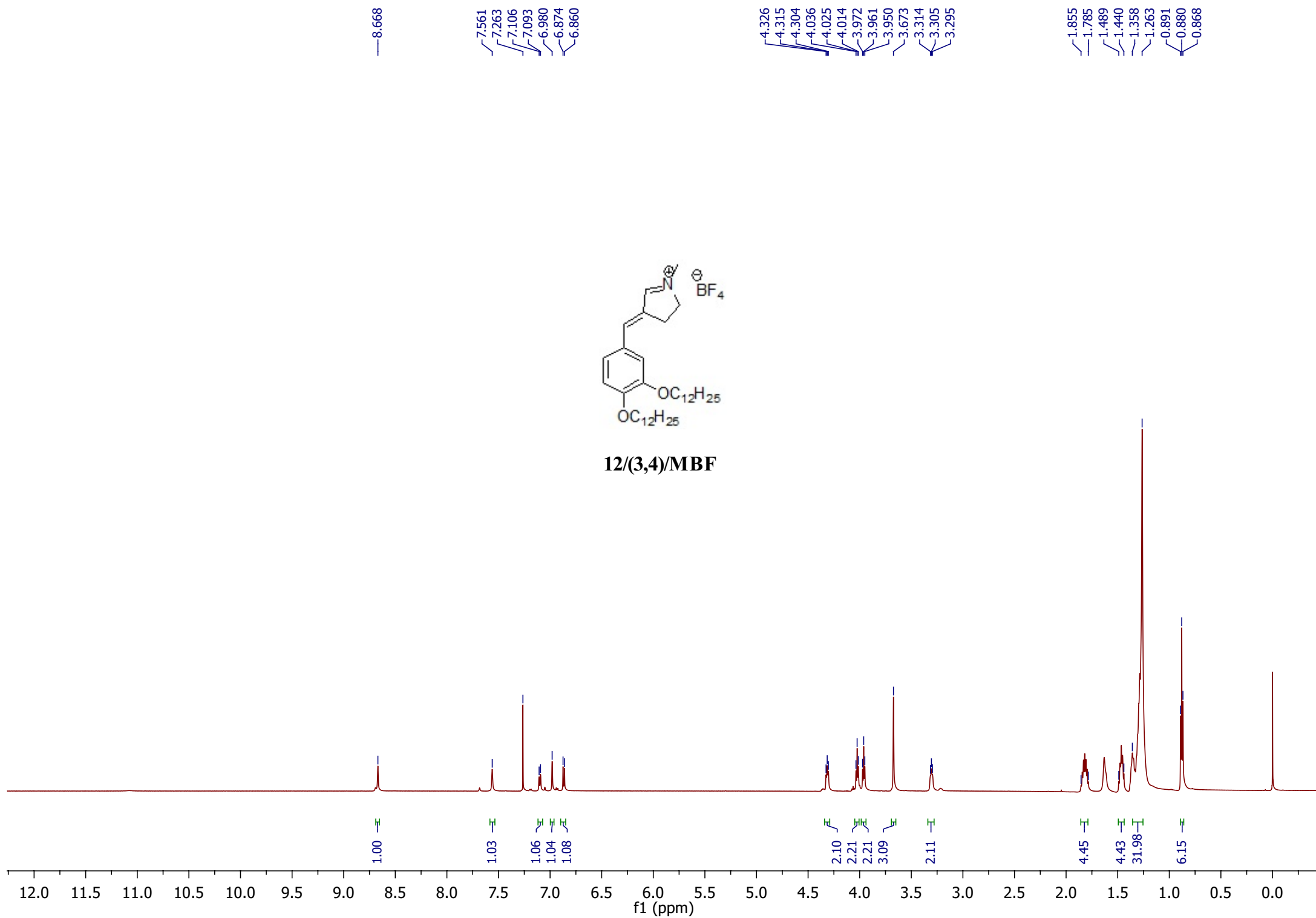




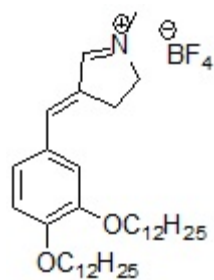




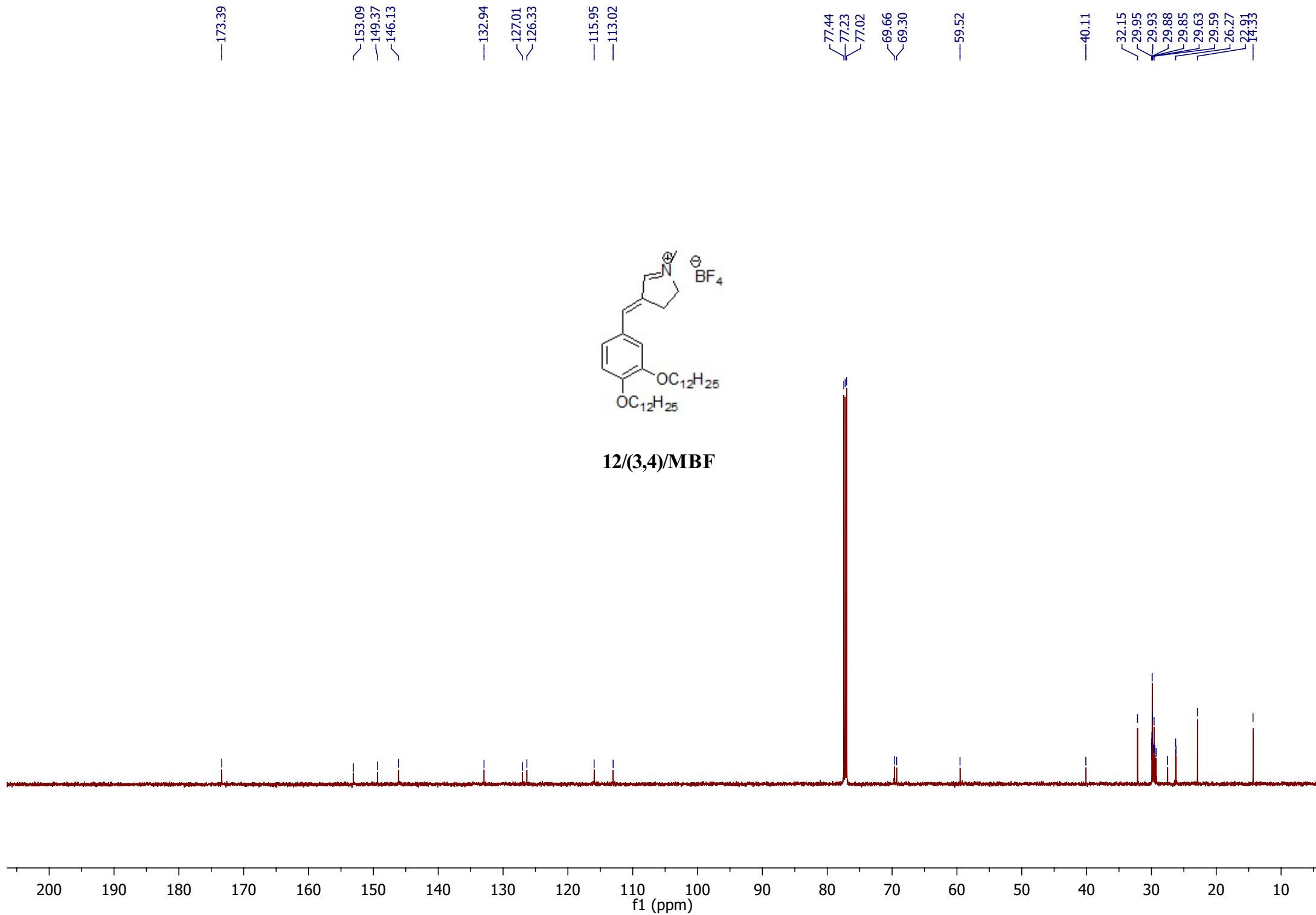
**12/(3,4)/MBF**

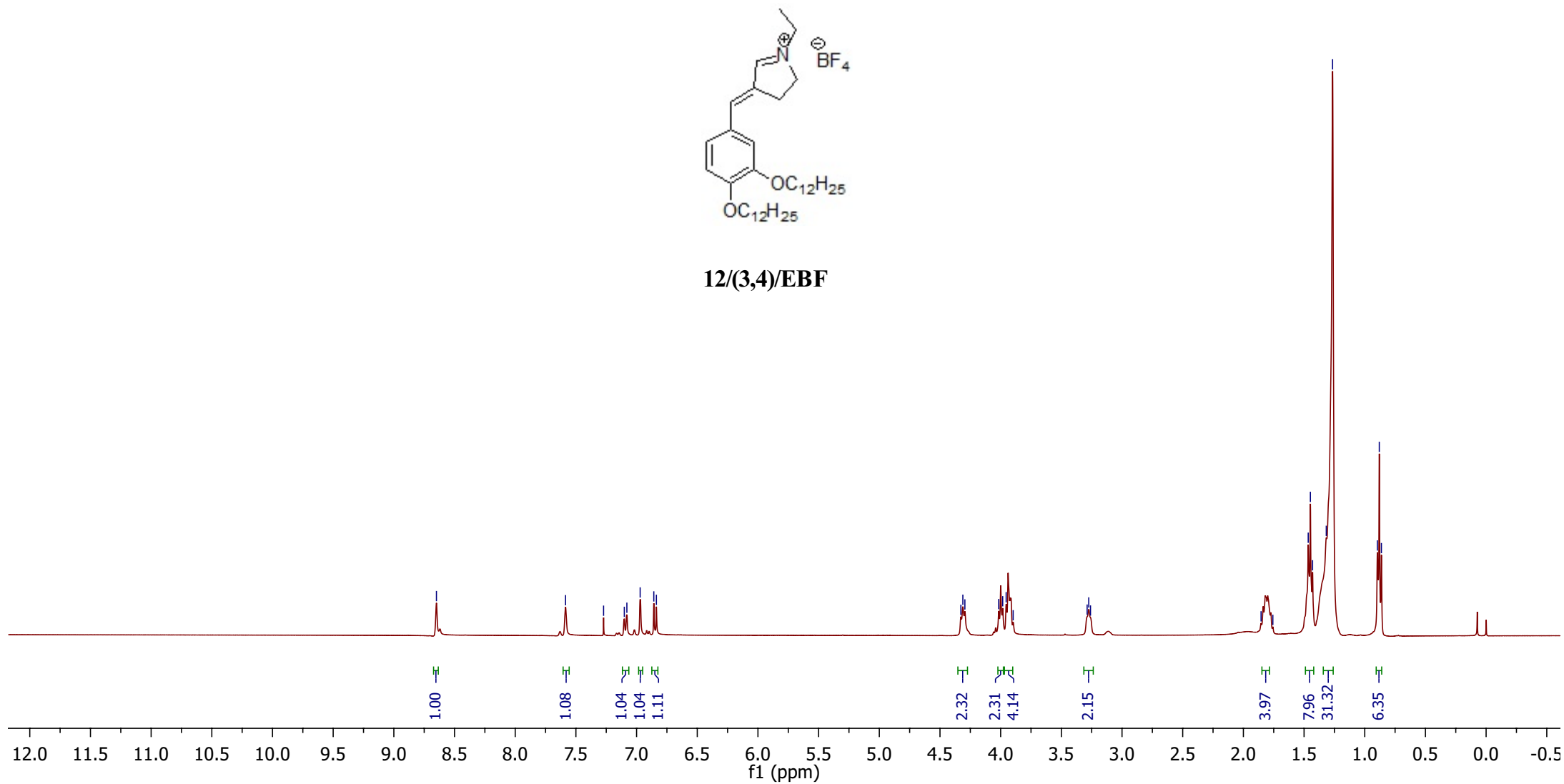


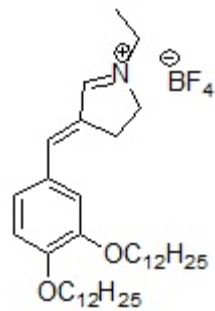




**12/(3,4)/MBF**

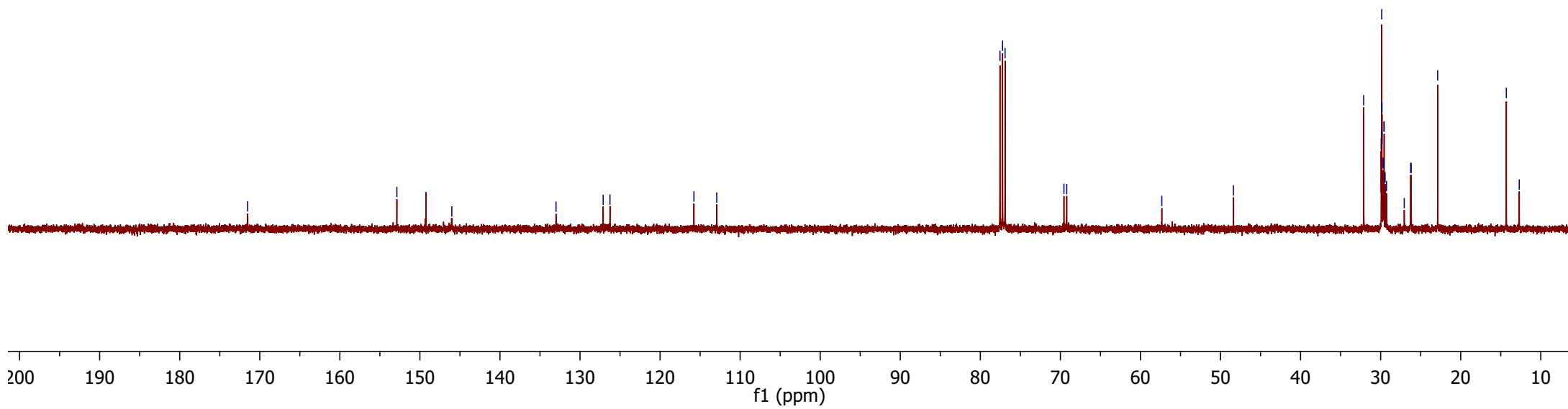


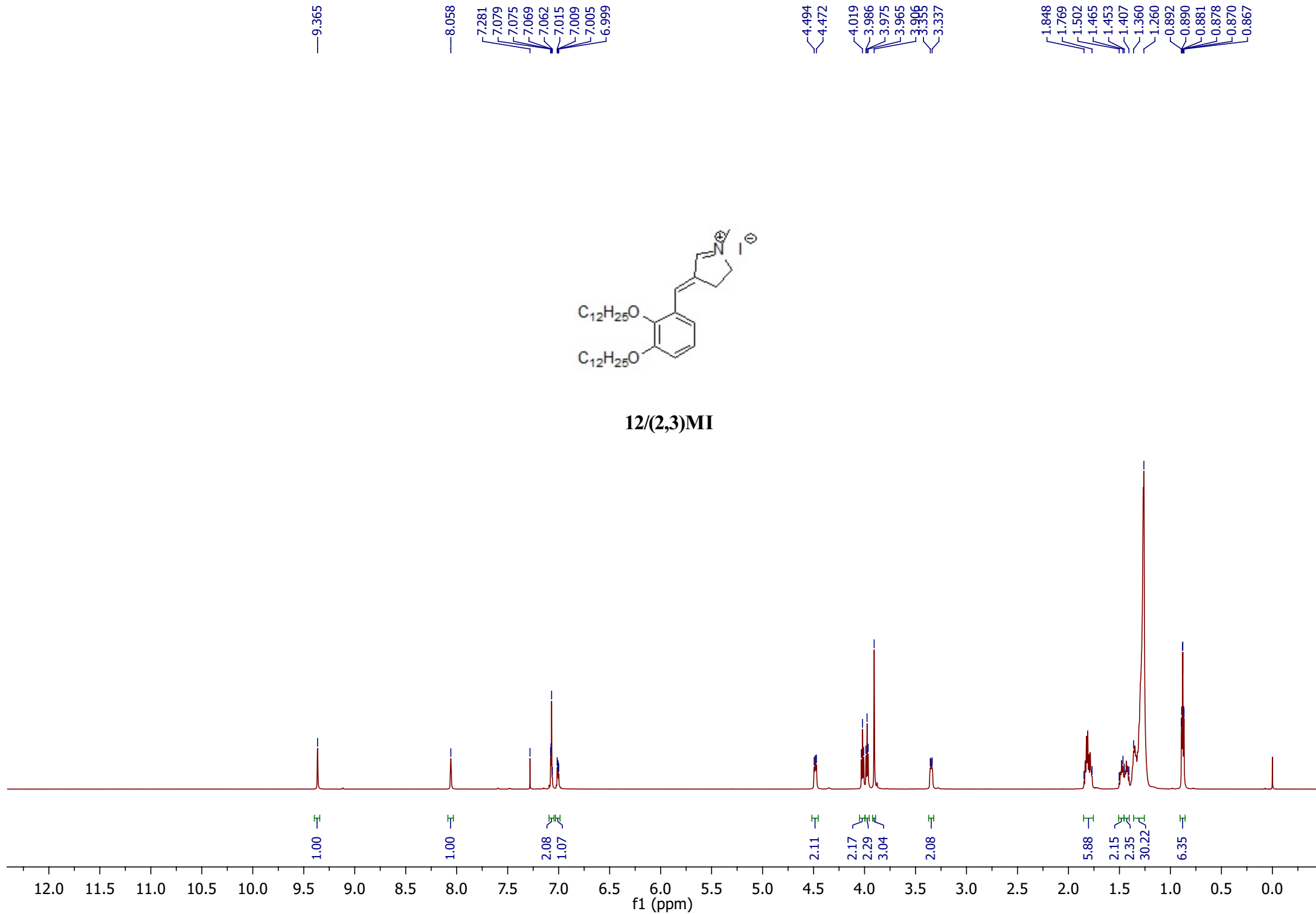


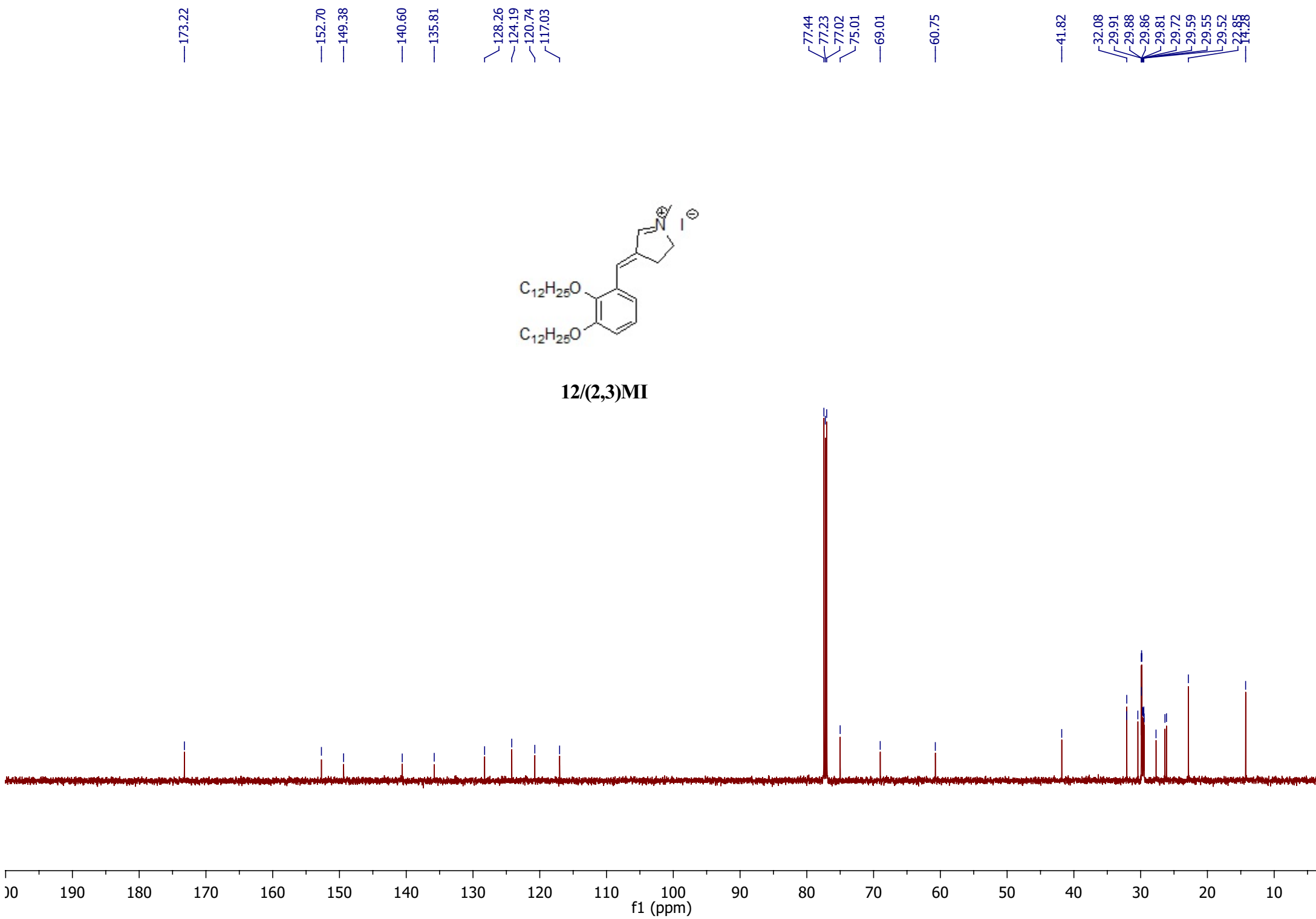


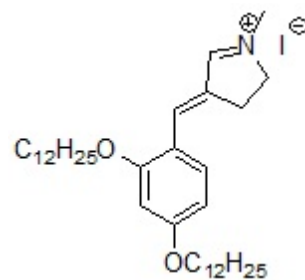
**12/(3,4)/EBF**

—171.51  
 —152.88  
 —146.01  
 —133.00  
 127.11  
 126.26  
 —115.77  
 —112.92  
 77.55  
 77.23  
 76.91  
 69.56  
 69.21  
 —57.33  
 —48.39  
 32.12  
 29.93  
 29.91  
 29.87  
 29.84  
 29.70  
 29.63  
 29.58  
 29.57  
 29.44  
 26.25  
 26.18  
 22.88  
 14.38  
 12.69

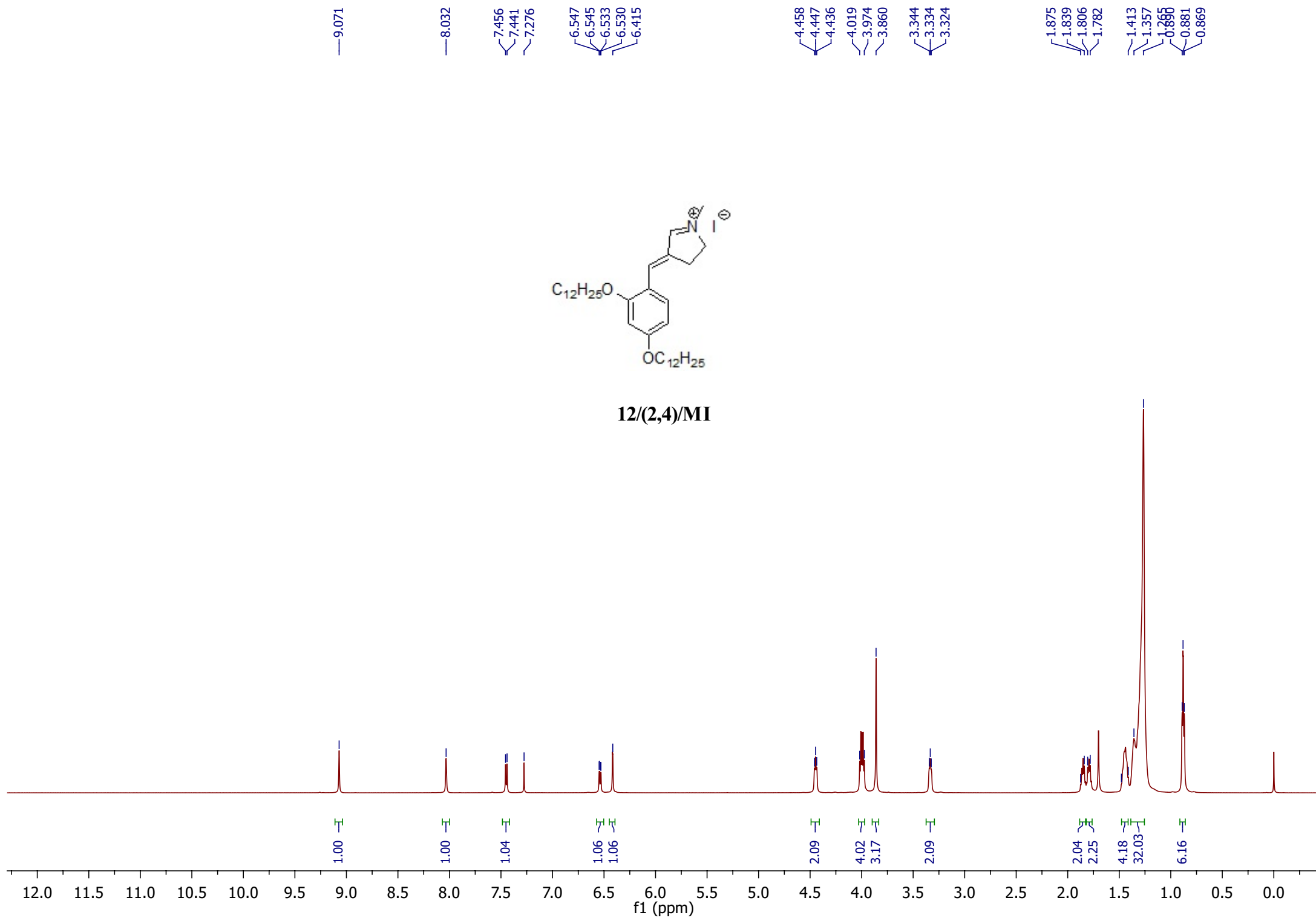


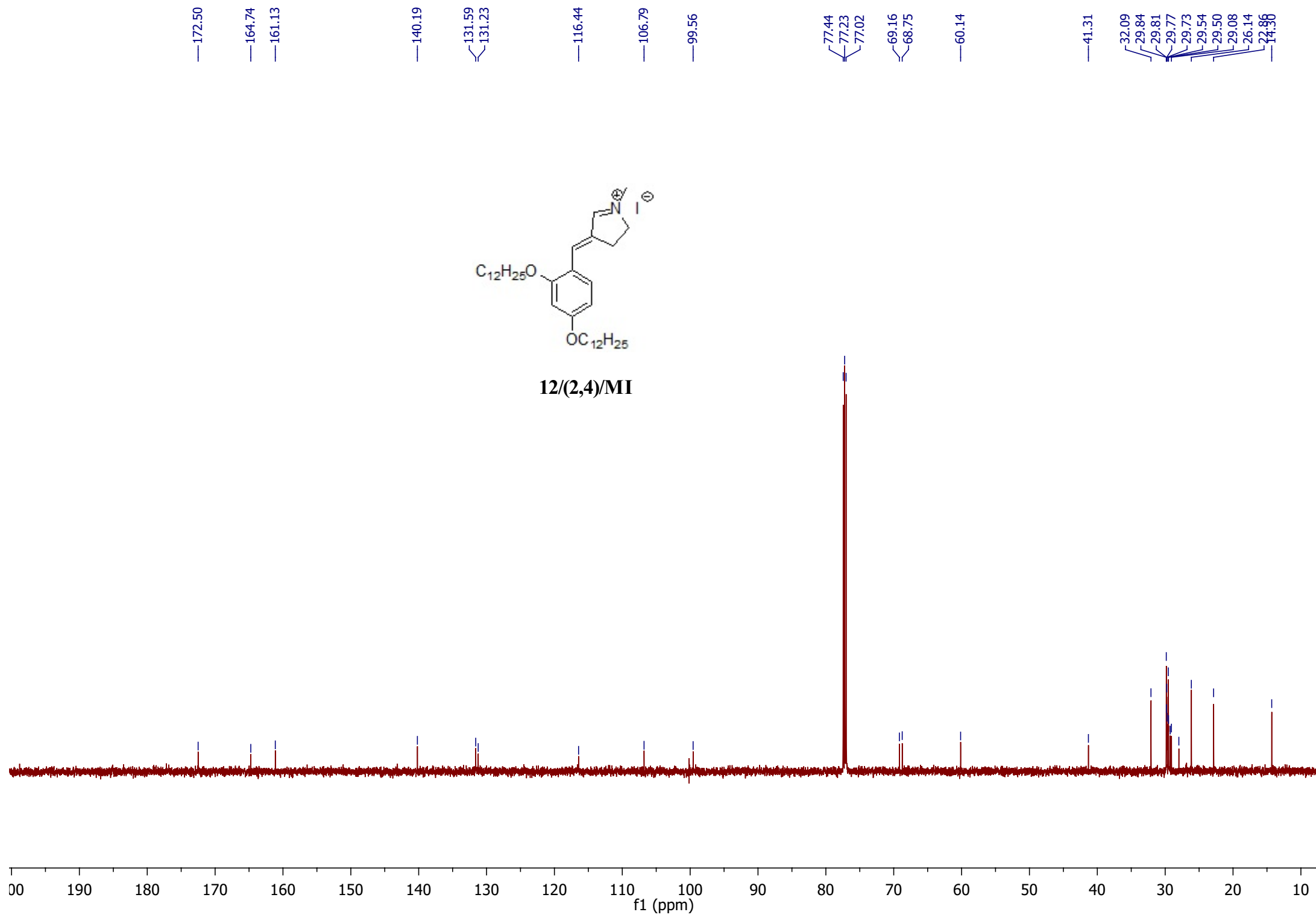


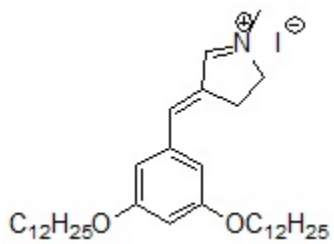




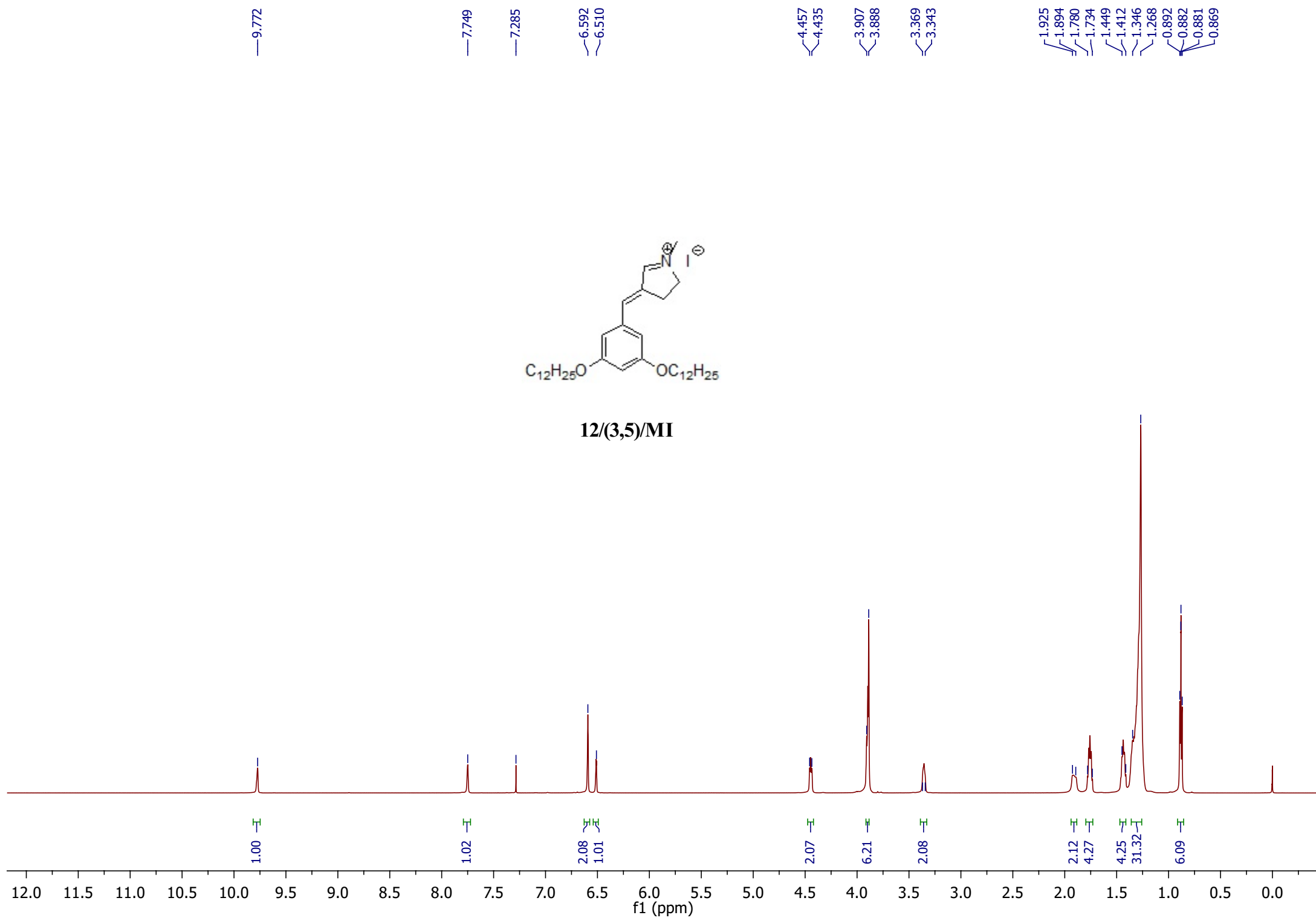
12/(2,4)/MI



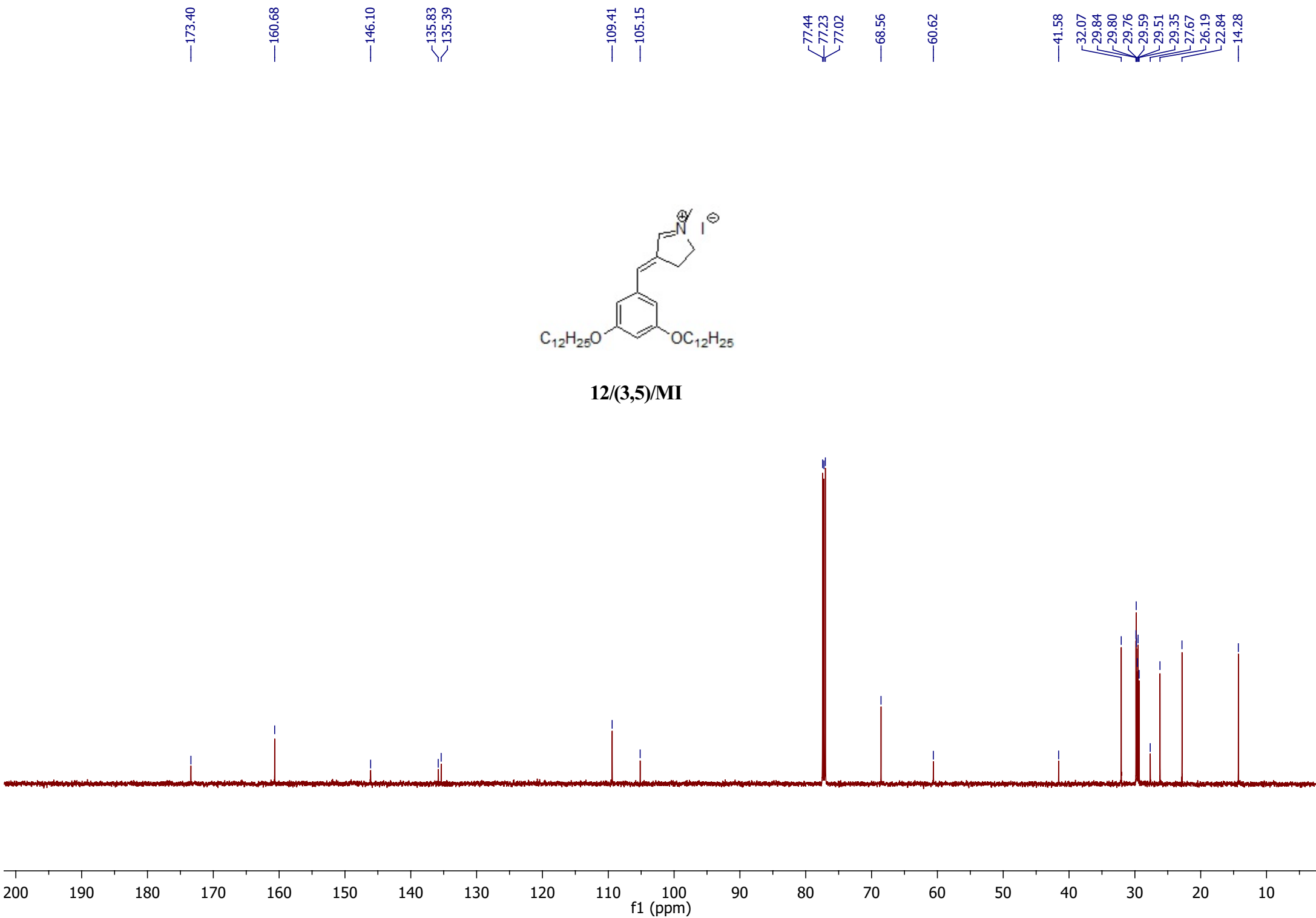


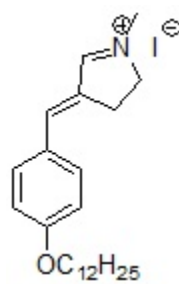


12/(3,5)MI

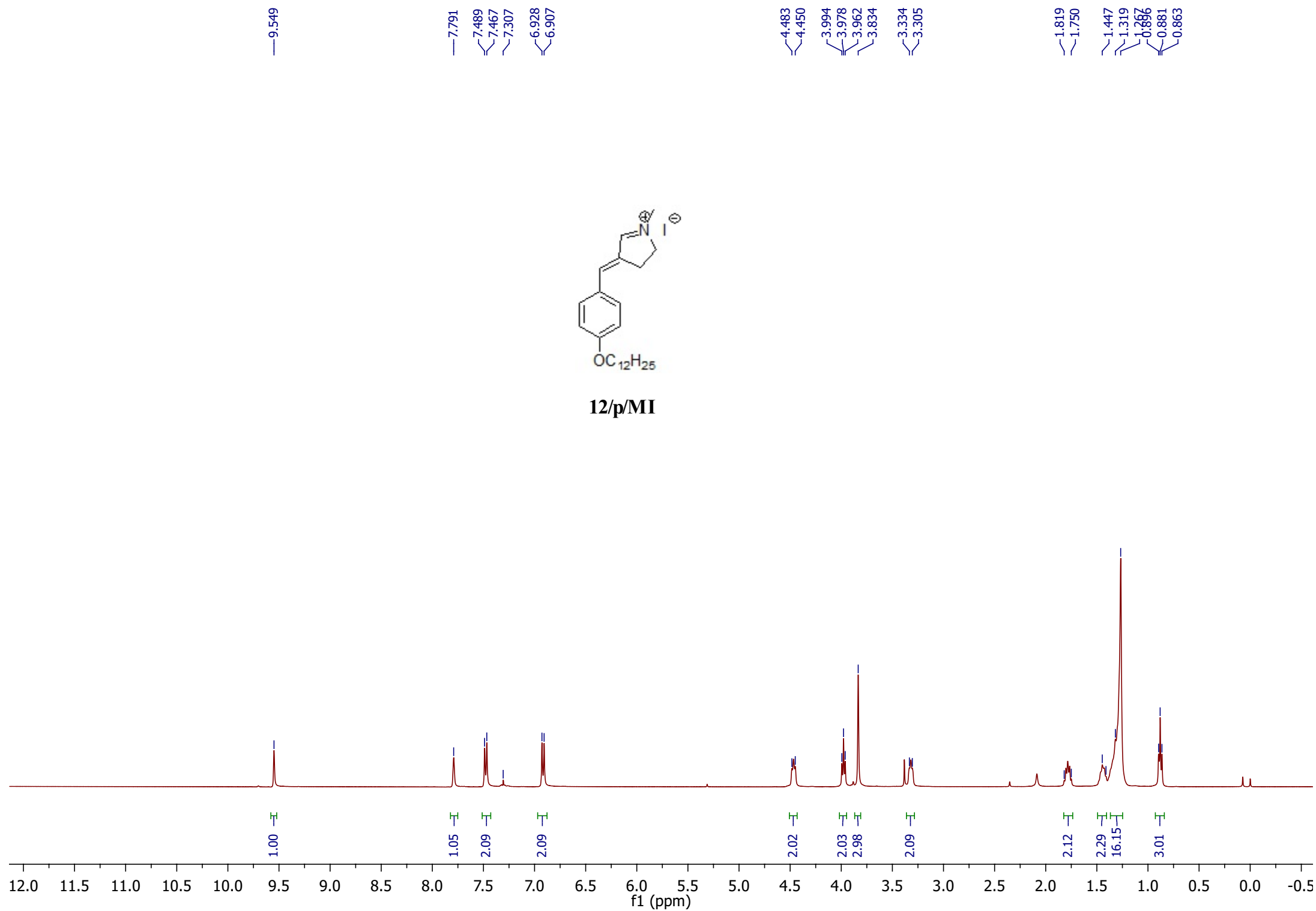


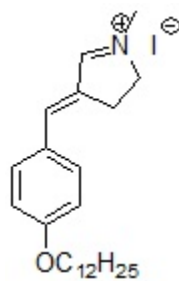




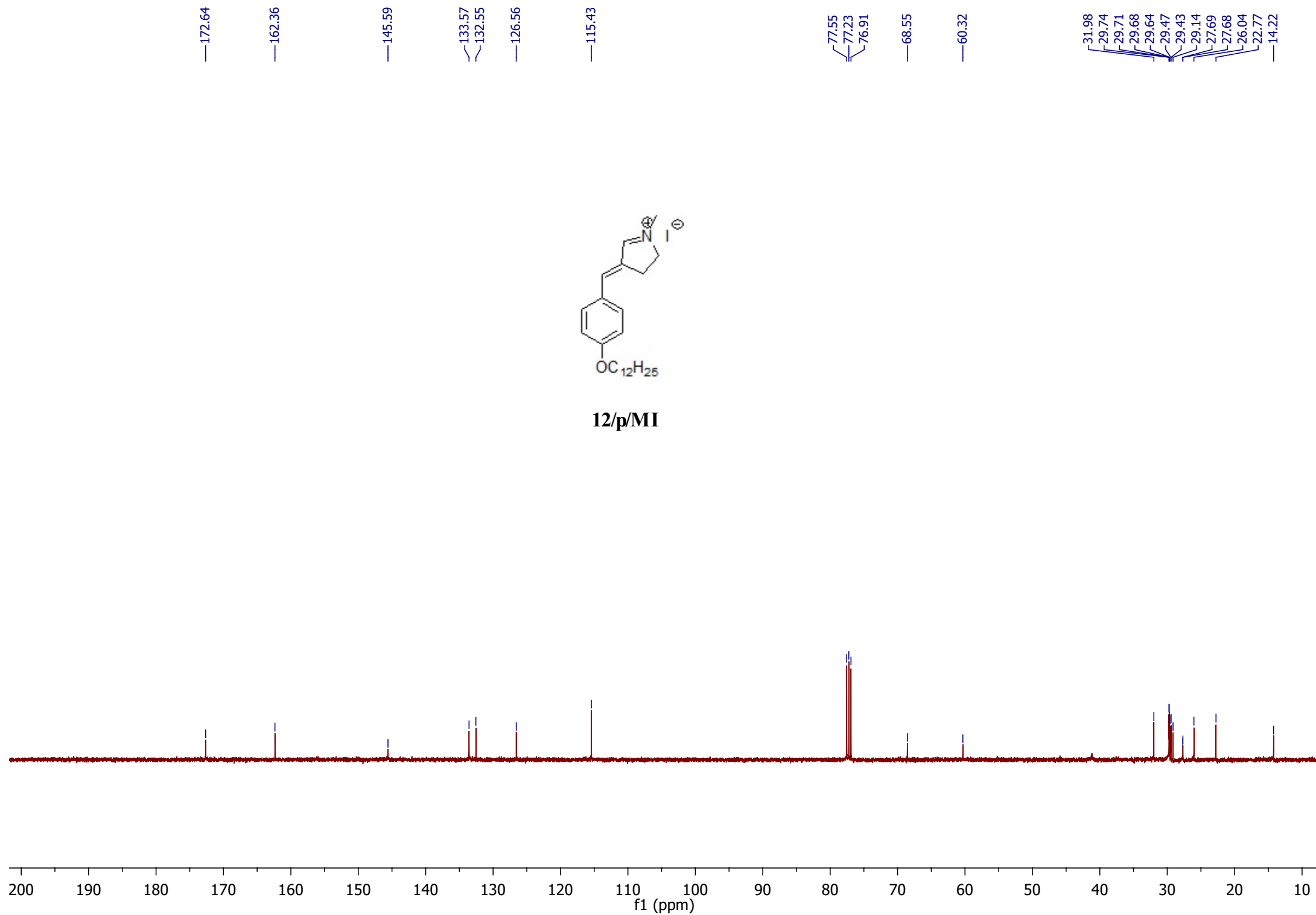


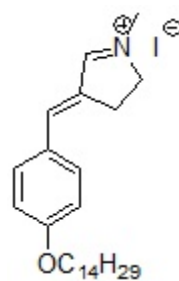
12/p/MI



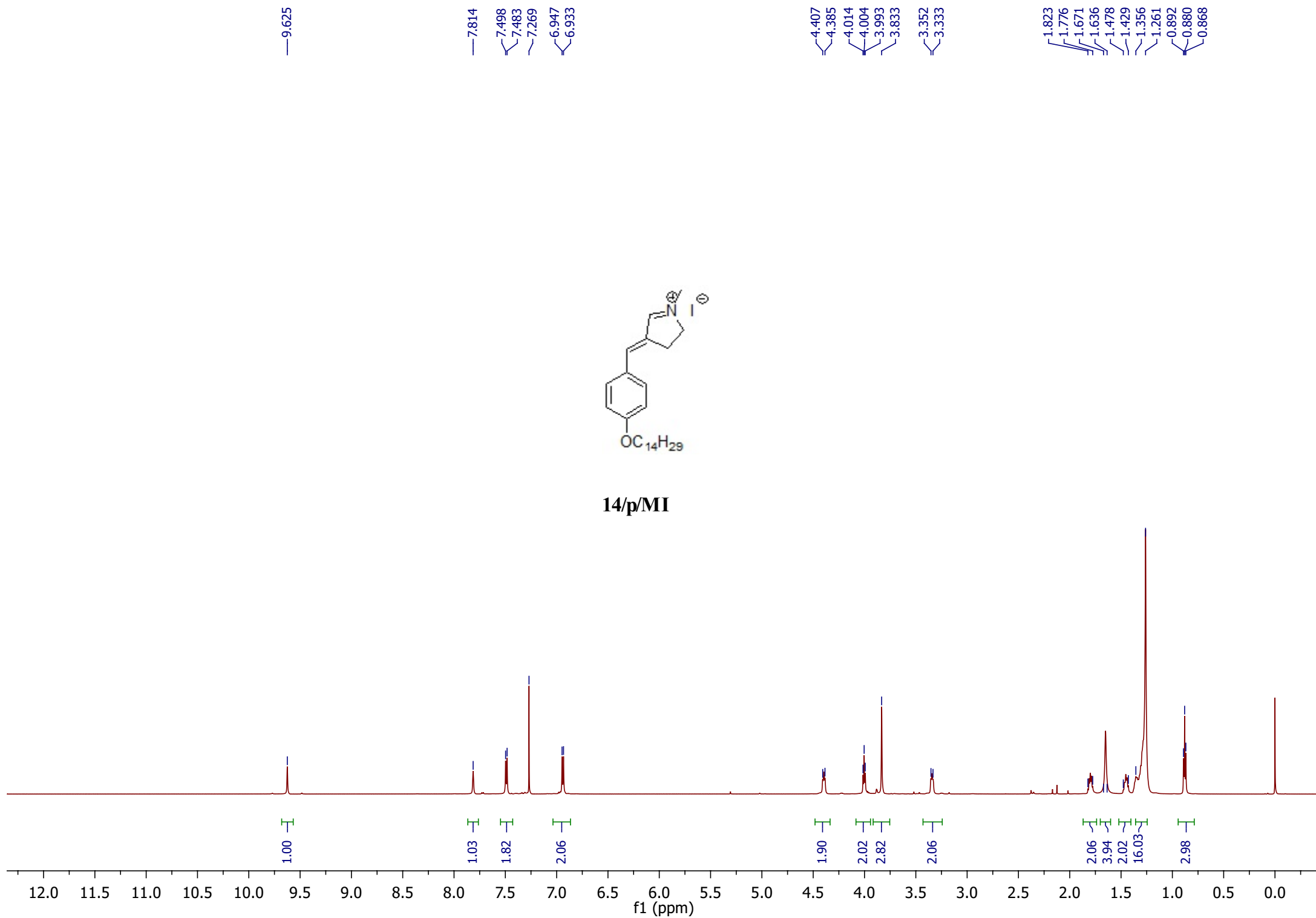


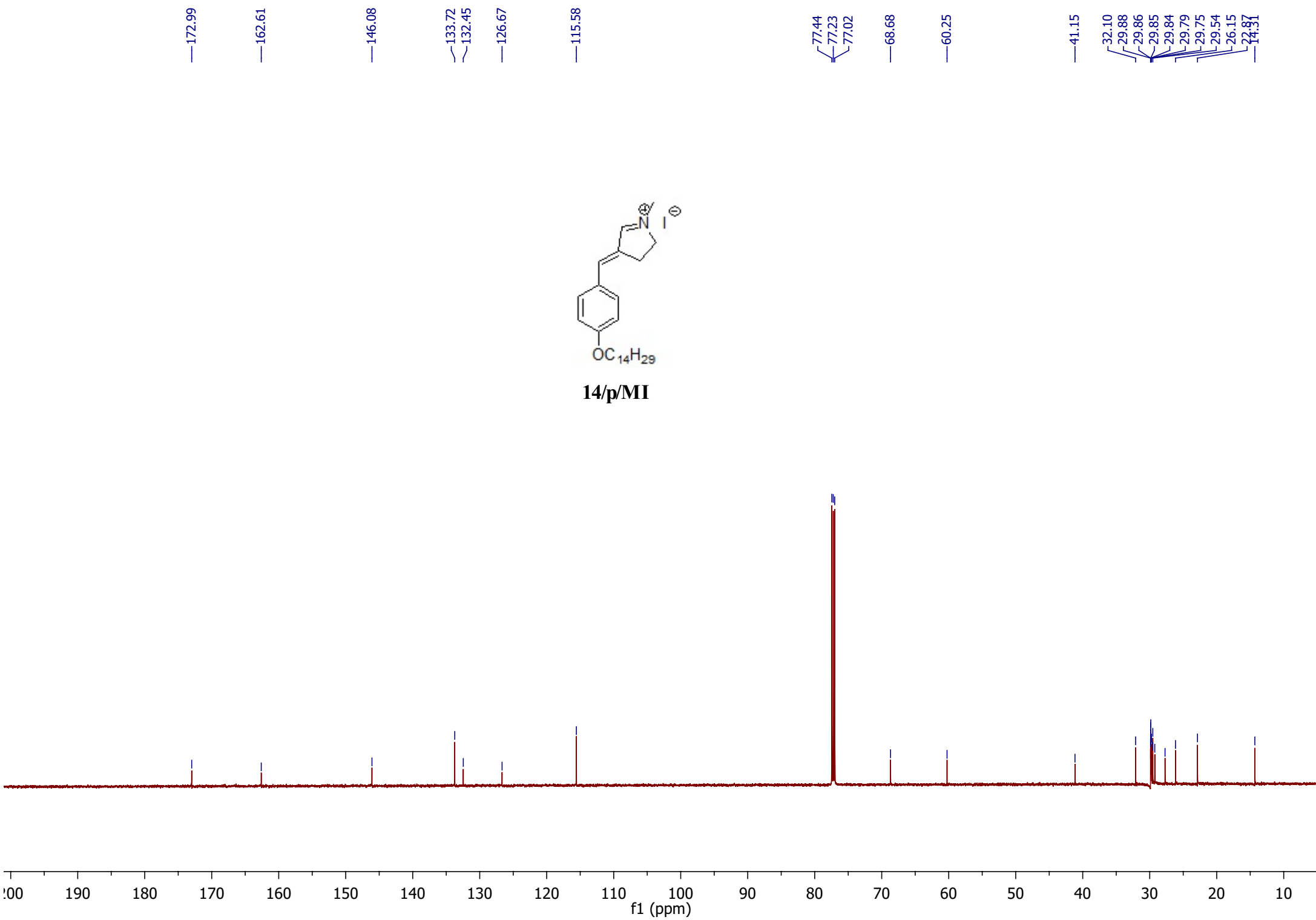
12/p/MI

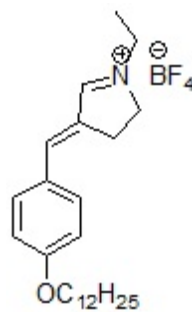




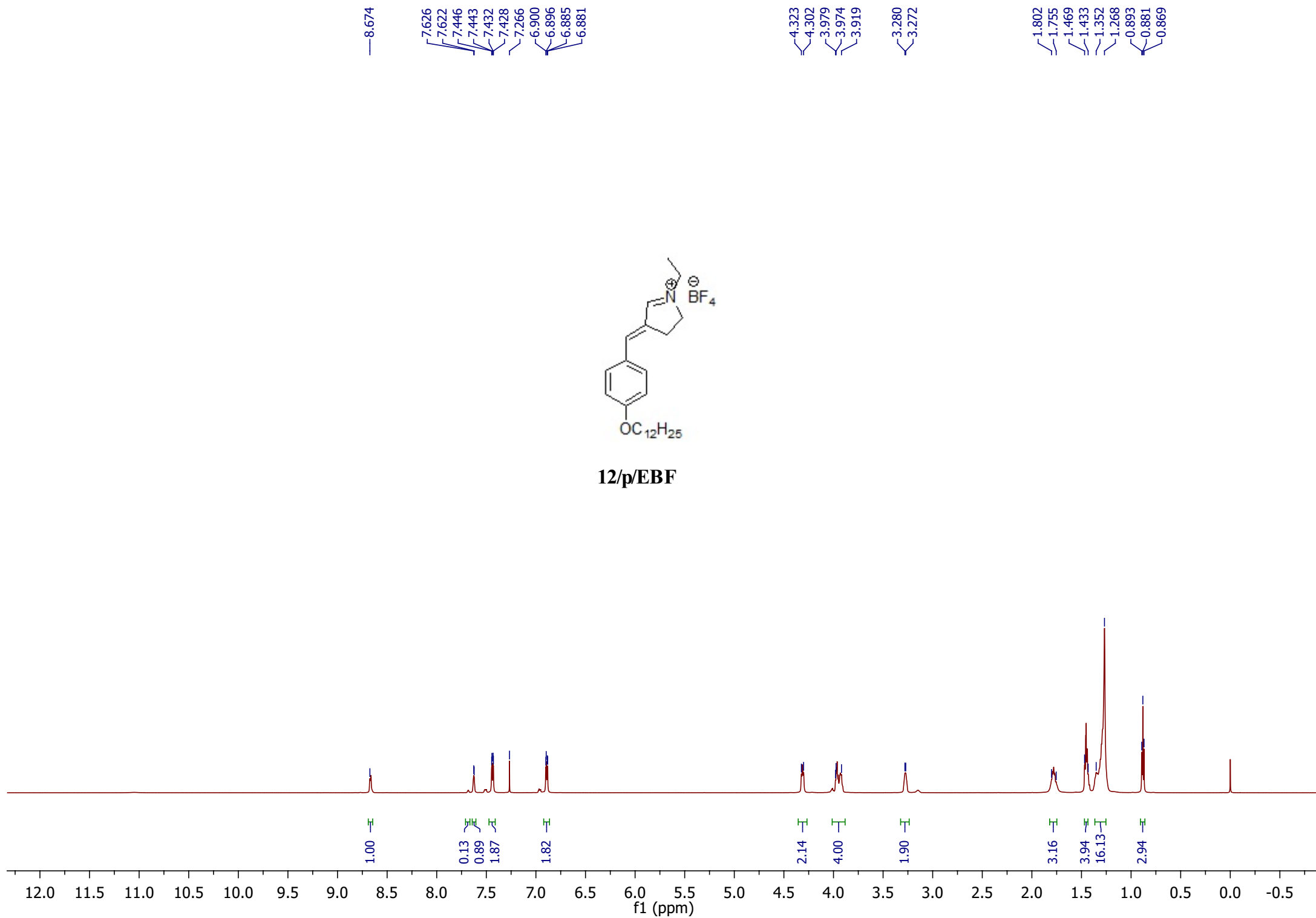
**14/p/MI**

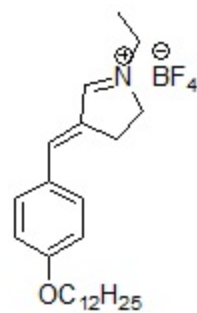




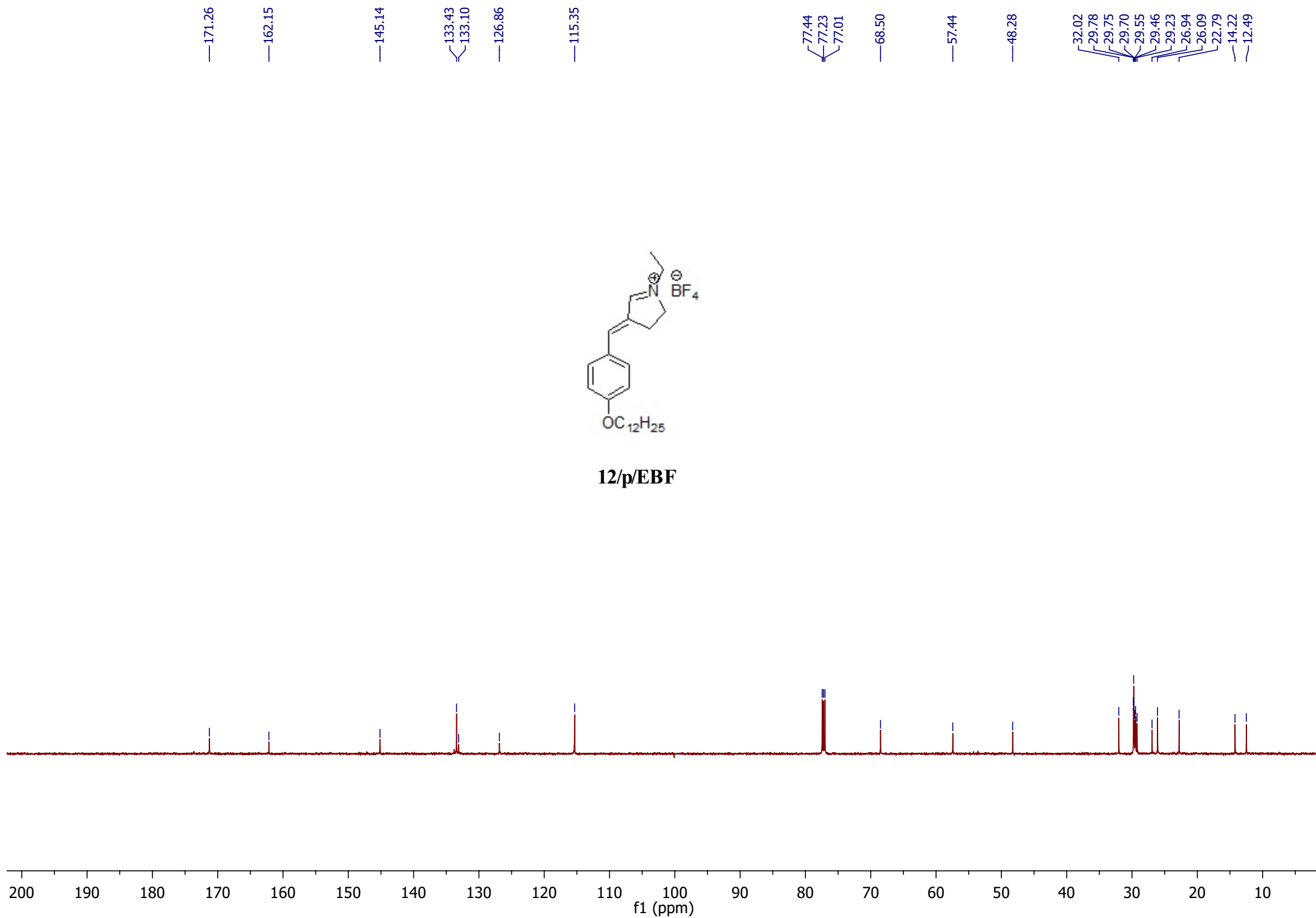


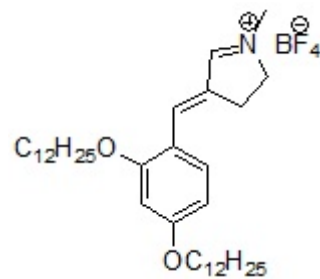
**12/p/EBF**



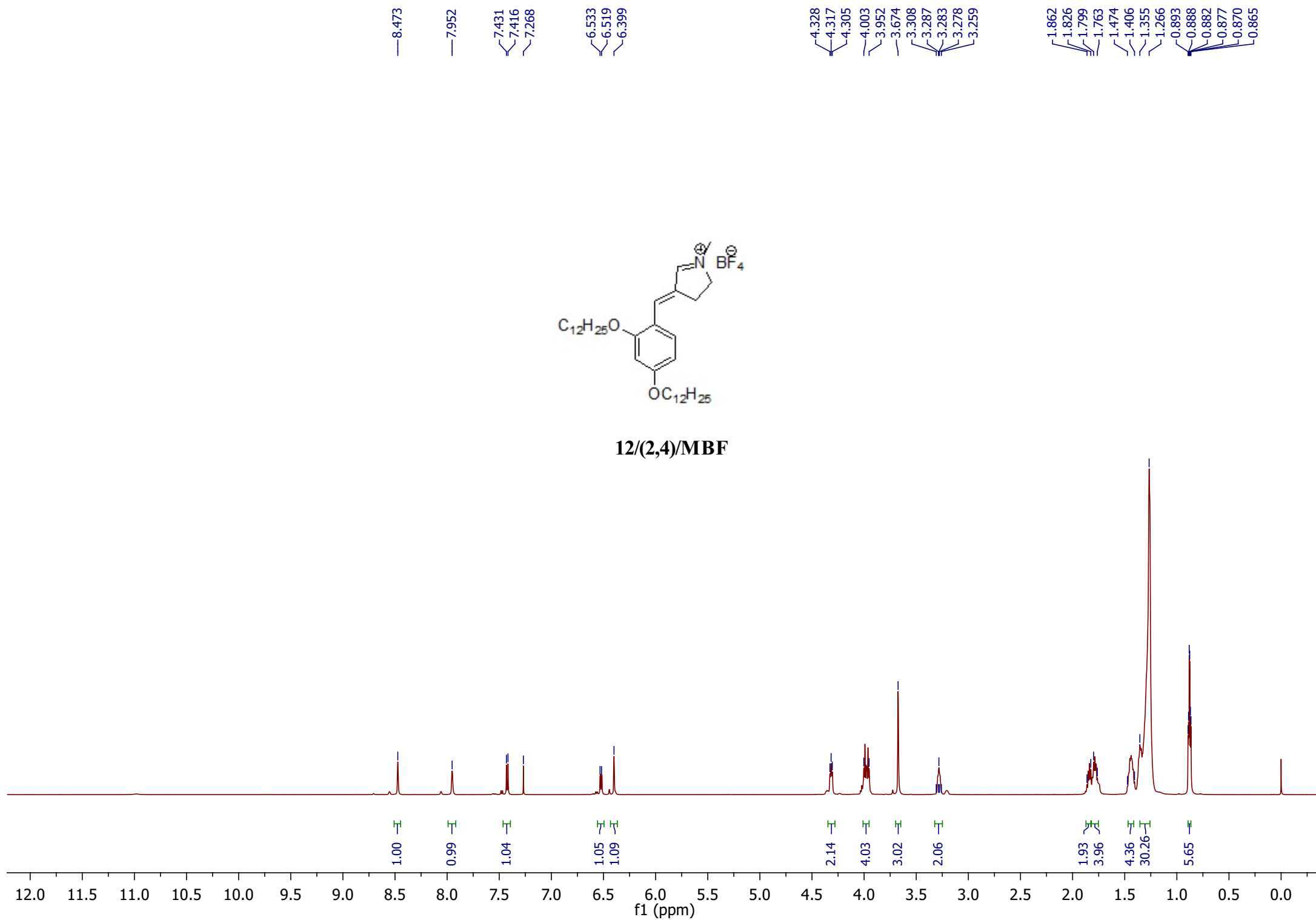


**12/p/EBF**

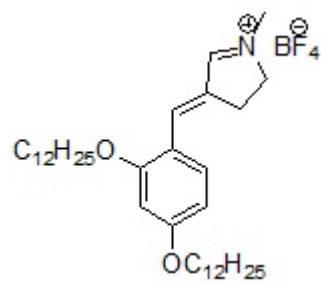




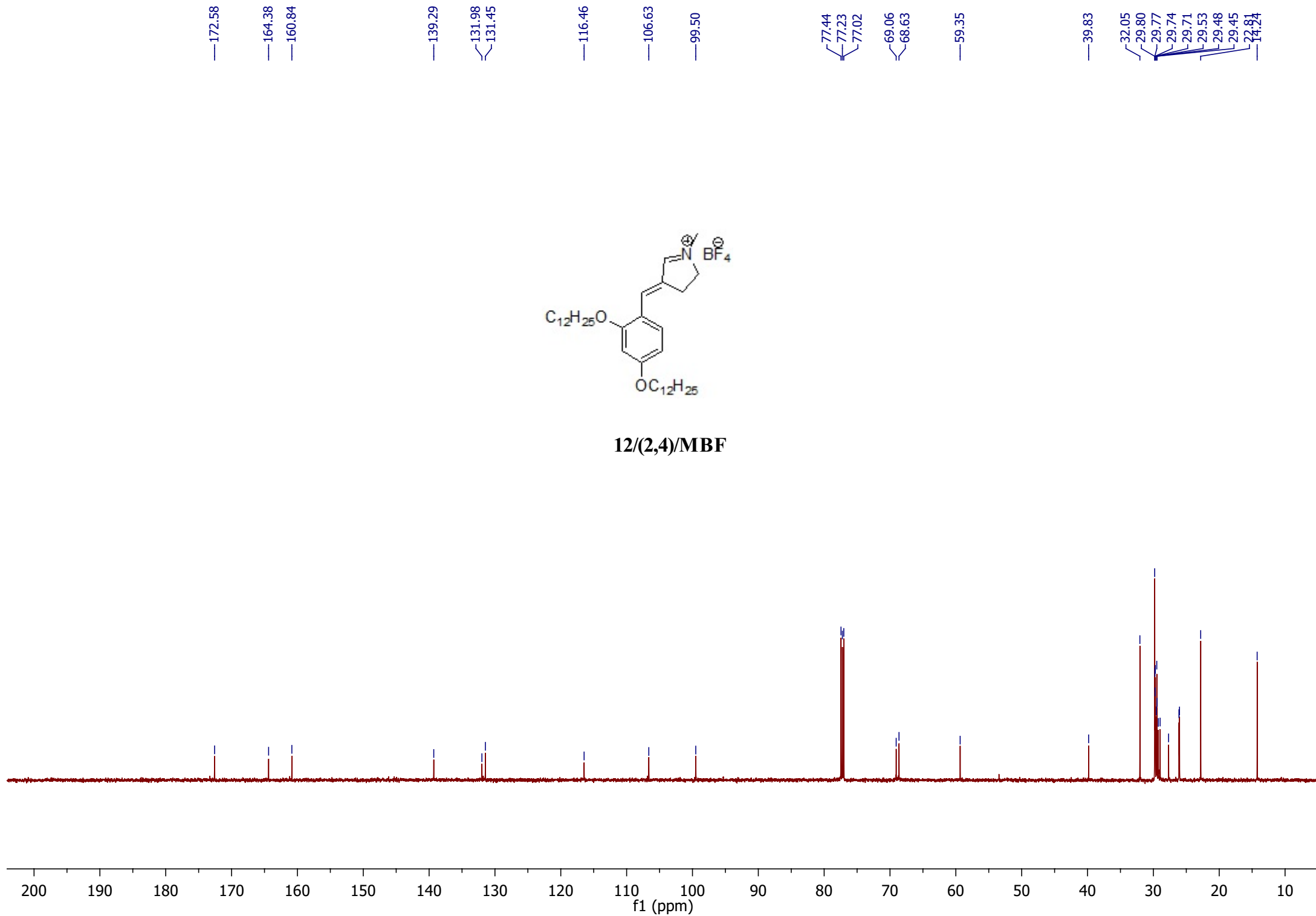
12/(2,4)/MBF

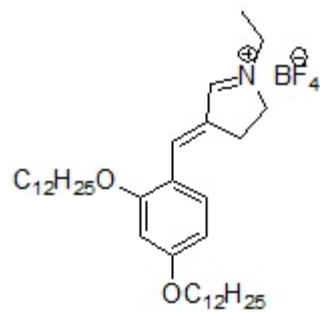




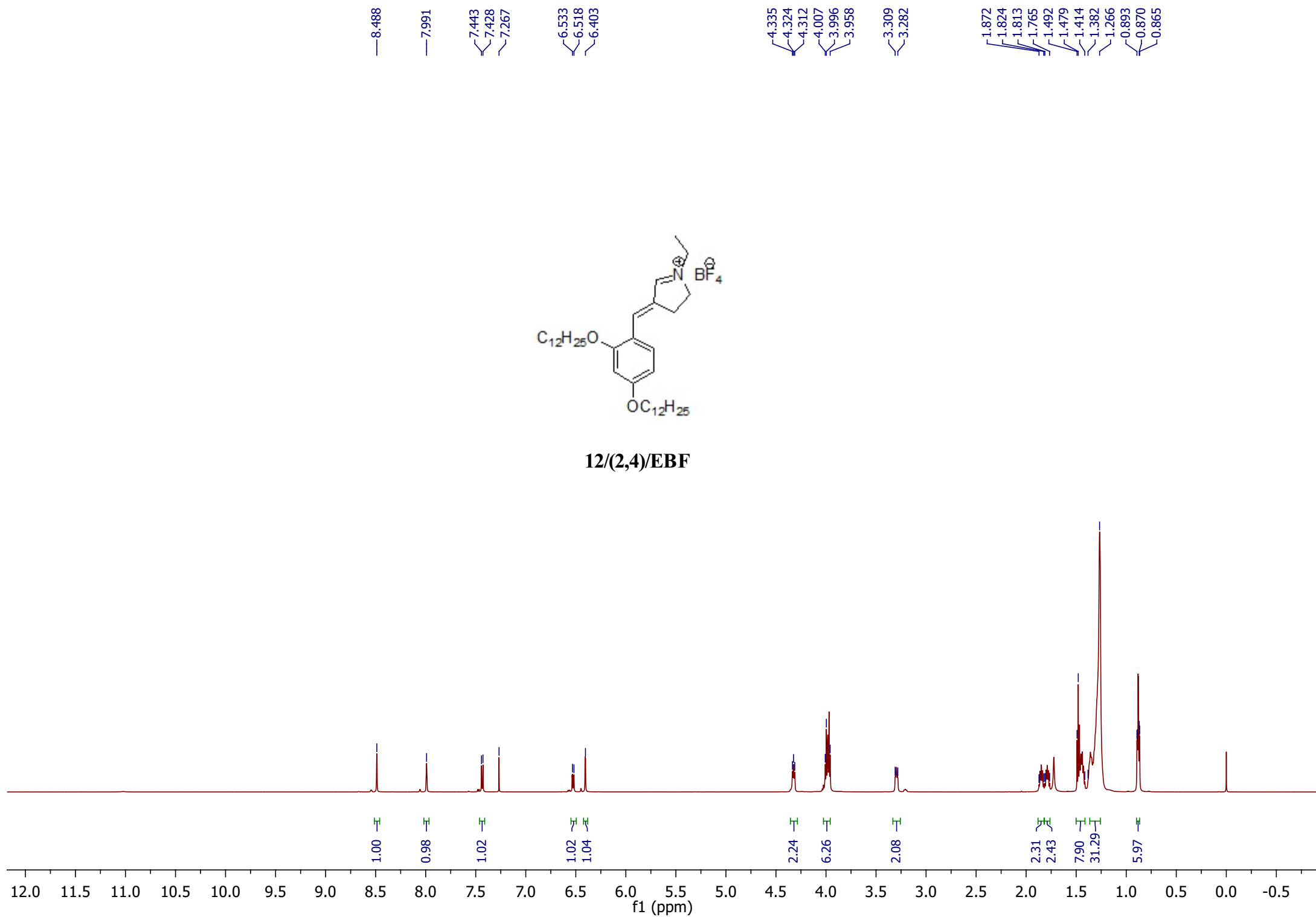


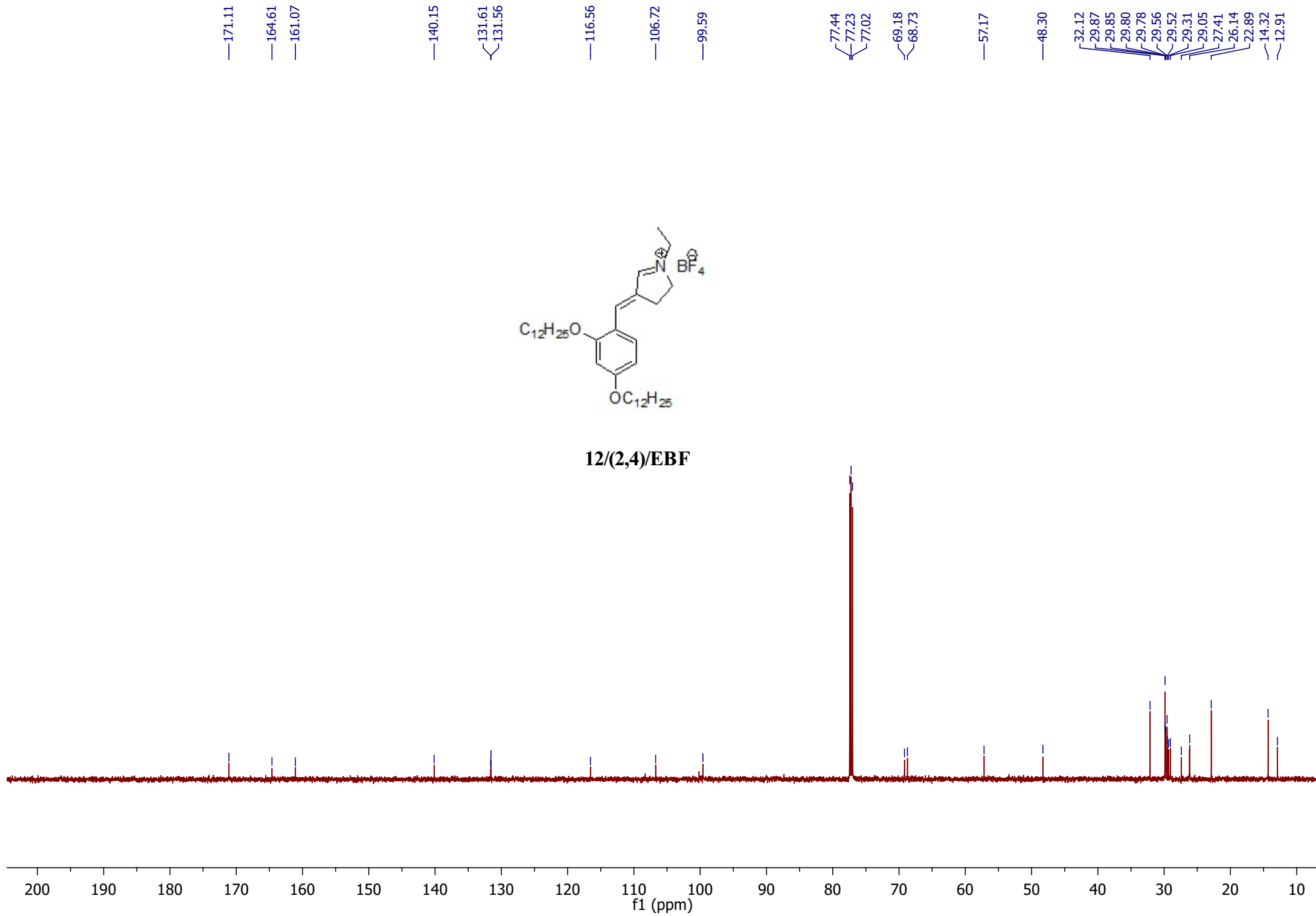
12/(2,4)/MBF

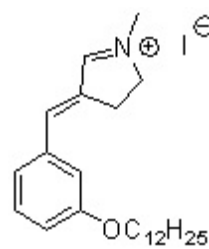




**12/(2,4)/EBF**







**12/m/MI**

9.784

7.812  
7.343  
7.329  
7.316  
7.277  
7.095  
7.082  
6.985

4.471  
4.456  
4.446  
3.941  
3.930  
3.920  
3.884  
3.401  
3.343

1.785  
1.762  
1.467  
1.425  
1.352  
1.268  
0.891  
0.881  
0.869

1.00

1.03

1.02

1.02

2.03

2.10

2.11

3.19

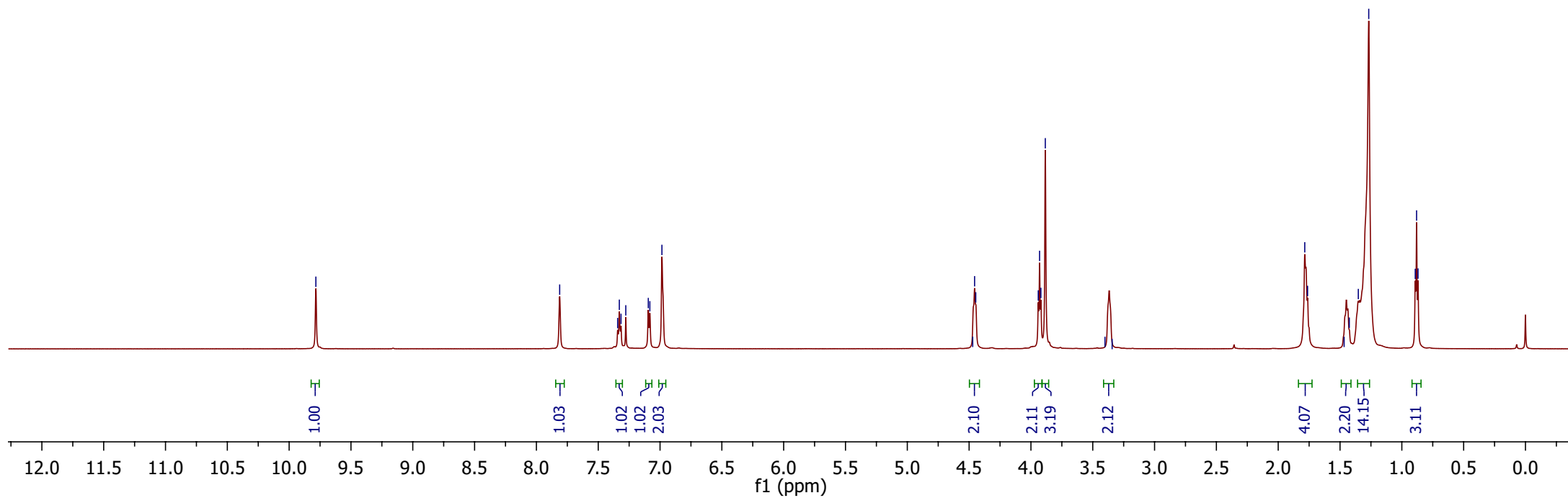
2.12

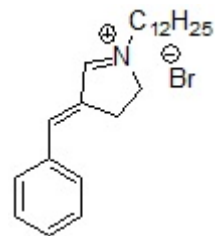
4.07

2.20

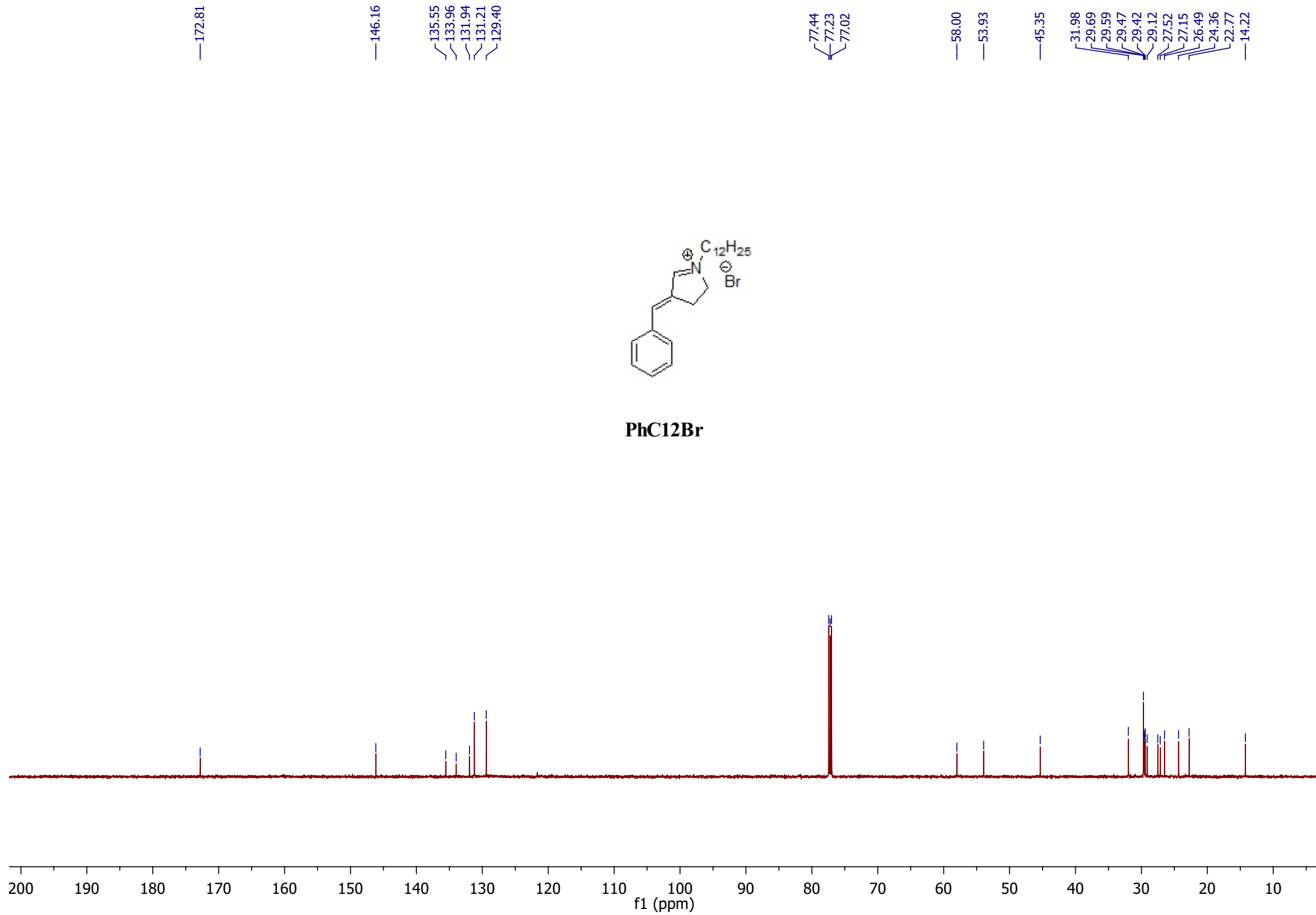
14.15

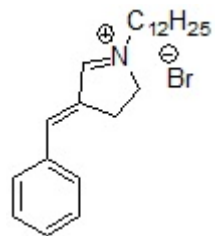
3.11



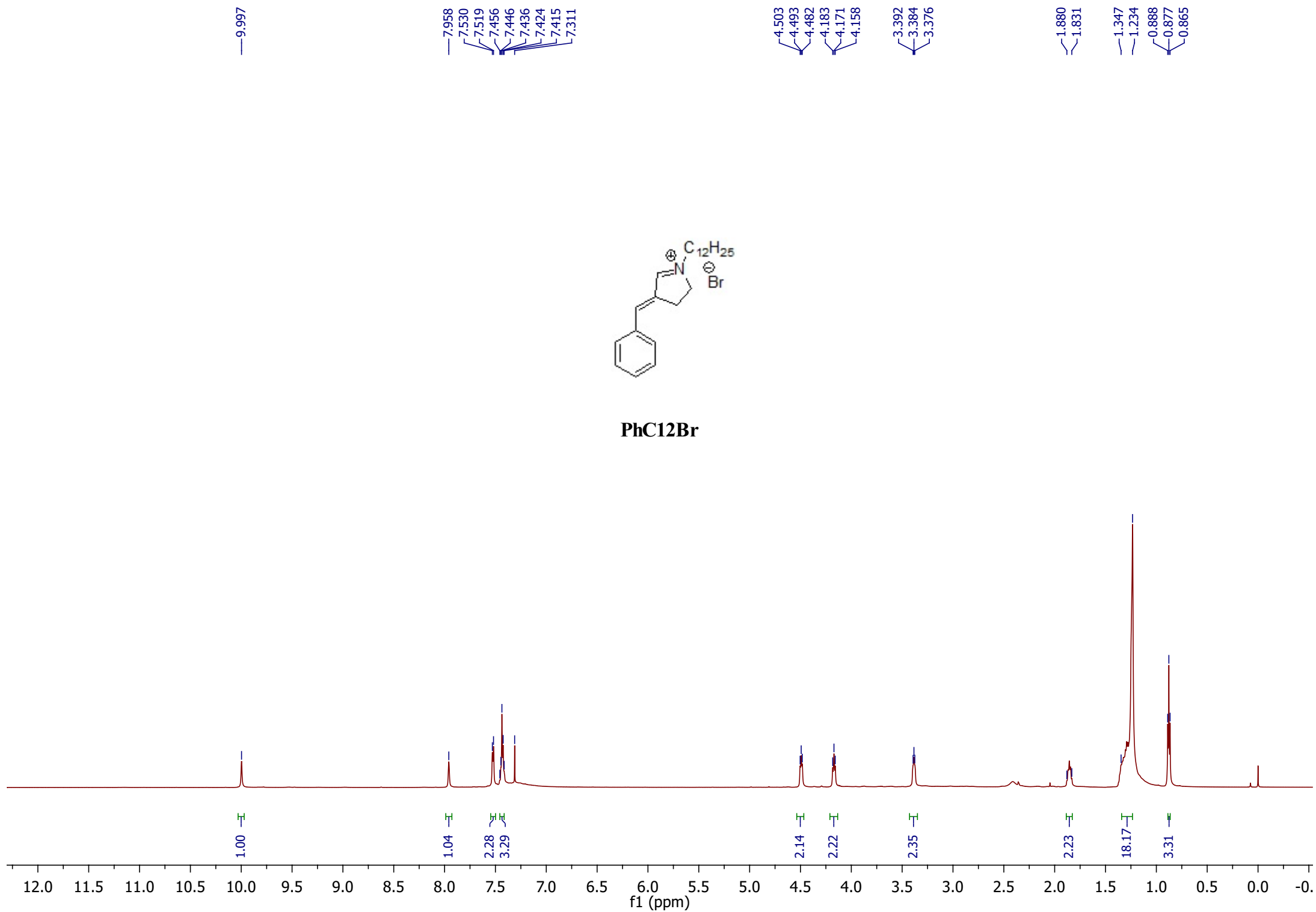


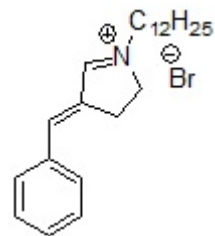
**PhC<sub>12</sub>Br**



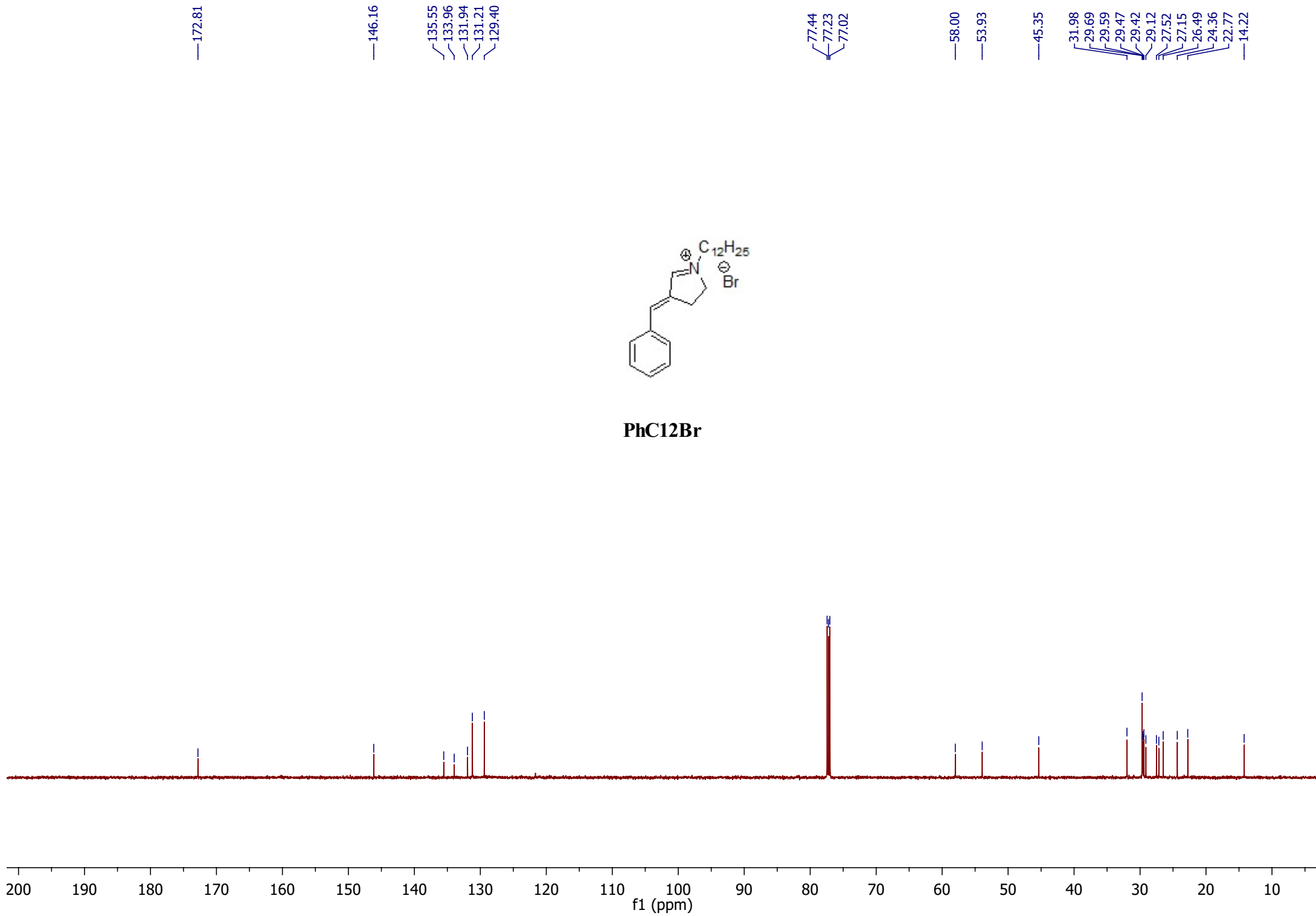


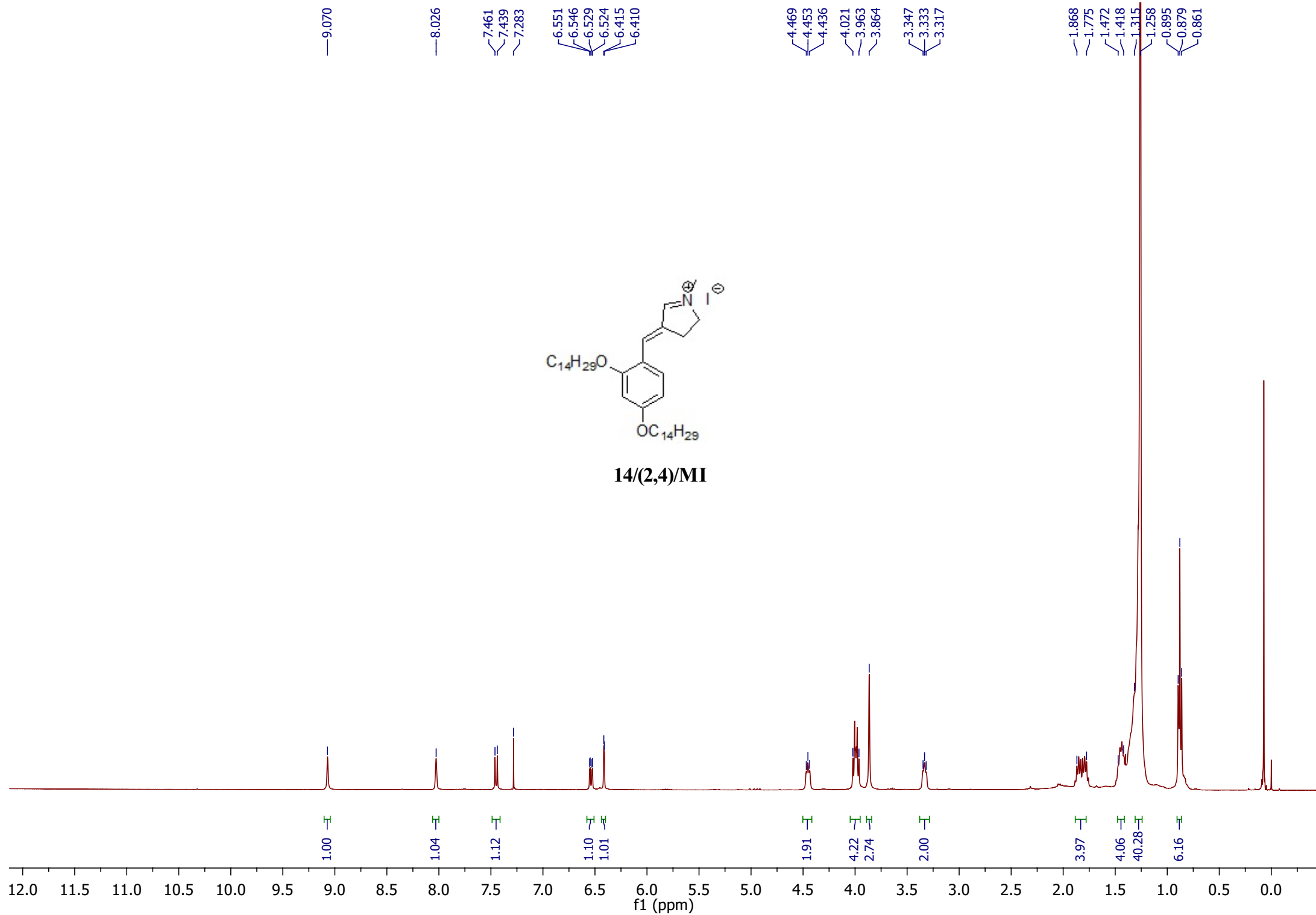
**PhC12Br**



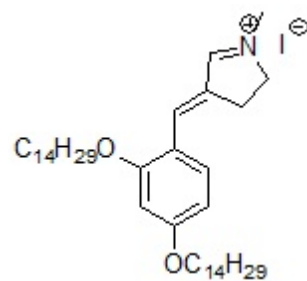


PhC12Br









14/(2,4)/MI

