

## Supporting Information

for

### Synthesis of fluoranthenes by hydroarylation of alkynes catalyzed by gold(I) or gallium trichloride

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## Experimental details

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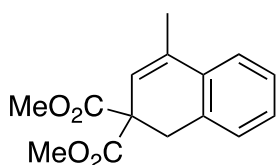
## General methods

All reactions were carried out under Ar in solvents dried in a Solvent Purification System (SPS). Thin layer chromatography was carried out by using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF<sub>234</sub>). Chromatography purifications were carried out using flash-grade silica gel (SDS Chromatogel 60 ACC, 40–60  $\mu$ m) or automated flash chromatographer CombyFlash Companion. NMR spectra were recorded at 23°C on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Mass spectra were recorded on a Waters LCT Premier (ESI) and Waters GCT (EI, CI) spectrometers. Elemental analyses were performed on a LECO CHNS 932 micro-analyzer at the Universidad Complutense de Madrid. Melting points were determined by using a Büchi melting-point apparatus.

Complexes **5** [1] and **6** [2] were prepared according to the reported procedures. Complex **5** is also available from Aldrich. Malonate **3** was prepared according to the described procedure [3].

## Experimental results

### Dimethyl 4-methylnaphthalene-2,2(1*H*)-dicarboxylate (**4'**) [3].



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.22 (m, 4H), 5.97 (s, 1H), 3.71 (s, 6H), 3.37 (s, 2H), 2.13 (d,  $J$  = 1.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  170.90, 134.95, 133.29, 132.59, 127.90, 127.69, 126.91, 123.41, 121.05, 54.73, 52.87, 34.57, 19.38; HRMS - ESI Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>4</sub>Na ( $M$  + Na): 283.0946 Found 283.0945.

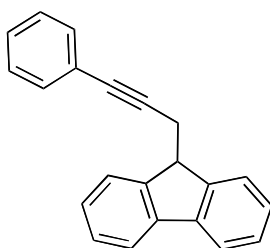
### Synthesis of fluorenes **7a–i**

**Procedure A (Propargylation of fluorene):** *n*-BuLi 2.5M in hexanes (1.1 equiv) was added dropwise over a solution of fluorene (1.0 equiv) in anhydrous THF at –80 °C and the mixture was stirred at –80 °C for 3 hours. Then, a solution of the corresponding propargylbromide (1.0 equiv) in anhydrous THF was added dropwise and the mixture

was allowed to warm to r.t. overnight. Saturated NaCl solution was added and the organic layer was extracted with ethyl acetate (3×). The combined organic fractions were dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO<sub>2</sub>) to give the corresponding alkynyl-fluorene.

**Procedure B (Sonogashira Coupling):** CuI (0.1 equiv) and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.5 equiv) were suspended in Et<sub>3</sub>N and the resulting mixture was stirred for 5 min. The corresponding aryl bromide (1.3 equiv) and 9-(prop-2-ynyl)-9*H*-fluorene (1.0 equiv) in benzene were added sequentially. The reaction was stirred at 80 °C under microwave irradiation until TLC showed total conversion. The crude mixture was diluted with Et<sub>2</sub>O, filtered through Celite and purified by flash chromatography (SiO<sub>2</sub>) to give the corresponding alkynyl-fluorene.

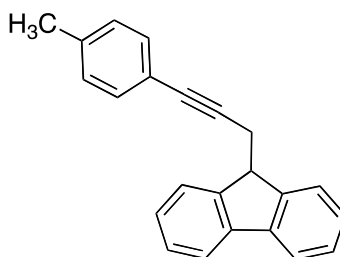
**9-(3-Phenylprop-2-ynyl)-9*H*-fluorene (7a).**



Prepared as a pale yellow solid by procedure A (yield = 87%).

$R_f$  (2:1 hexane-CH<sub>2</sub>Cl<sub>2</sub>) = 0.60; mp = 70–71 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) <sup>TM</sup> 7.76 (d,  $J$  = 7.8 Hz, 4H), 7.30–7.43 (m, 9H), 4.15 (t,  $J$  = 7.3 Hz, 1H), 2.88 (d,  $J$  = 7.3 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT) <sup>TM</sup> 146.3 (C), 140.8 (C), 131.6 (CH), 128.3 (CH), 127.8 (CH), 127.5 (CH), 127.0 (CH), 124.7 (CH), 123.7 (C), 119.8 (CH), 88.6 (C), 81.9 (C), 46.3 (CH), 24.5 (CH<sub>2</sub>). Anal. calcd (%) for C<sub>22</sub>H<sub>16</sub>: C 94.25, H 5.75. Found: C 93.85, H 5.93.

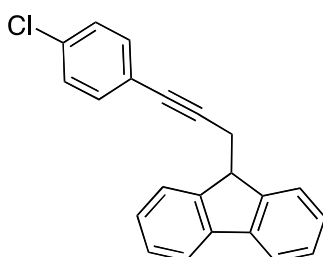
**9-(3-*p*-Tolylprop-2-ynyl)-9*H*-fluorene (7b).**



Prepared as a pale yellow solid by procedure B (yield = 52%).

$R_f$  (3:1 Hexane- $\text{CH}_2\text{Cl}_2$ ) = 0.22; mp = 119–120 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.76 (d,  $J$  = 8.0 Hz, 4H), 7.38 (t,  $J$  = 7.3 Hz, 2H), 7.32 (d,  $J$  = 8.0 Hz, 4H), 7.12 (d,  $J$  = 7.9 Hz, 2H), 4.14 (t,  $J$  = 7.4 Hz, 1H), 2.86 (d,  $J$  = 7.4 Hz, 2H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT)  $\delta$  146.3 (C), 140.8 (C), 137.8 (C), 131.4 (CH), 129.0 (CH), 127.5 (CH), 127.0 (CH), 124.7 (CH), 120.6 (C), 119.8 (CH), 87.9 (C), 81.9 (C), 46.3 (CH), 24.5 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_3$ ). HRMS: Calcd for  $\text{C}_{23}\text{H}_{19}$  ( $\text{M}^+\text{+H}$ ) 295.1487, Found 295.1485.

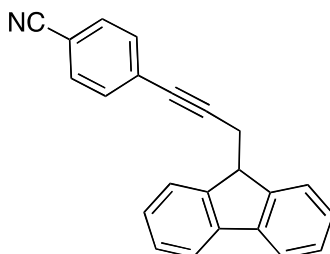
#### 9-(3-(4-Chlorophenyl)prop-2-ynyl)-9H-fluorene (7c).



Prepared as a pale yellow solid by procedure B (yield = 61%).

$R_f$  (3:1 hexane: $\text{CH}_2\text{Cl}_2$ ) = 0.43; mp = 142–143 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.76 (d,  $J$  = 7.5 Hz, 2H), 7.72 (d,  $J$  = 7.5 Hz, 2H), 7.40 (t,  $J$  = 7.4 Hz, 2H), 7.25–7.34 (m, 6H), 4.14 (t,  $J$  = 7.2 Hz, 1H), 2.89 (d,  $J$  = 7.2 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT)  $\delta$  146.1 (C), 140.9 (C), 133.8 (C), 132.8 (CH), 128.6 (CH), 127.6 (CH), 127.1 (CH), 124.6 (CH), 122.1 (C), 119.9 (CH), 89.6 (C), 80.8 (C), 46.1 (CH), 24.5 ( $\text{CH}_2$ ). HRMS: Calcd for  $\text{C}_{22}\text{H}_{16}^{35}\text{Cl}$  ( $\text{M}^+\text{+H}$ ) 315.0941, Found 315.0944.

#### 4-(3-(9H-Fluoren-9-yl)prop-1-ynyl)benzotrile (7d)

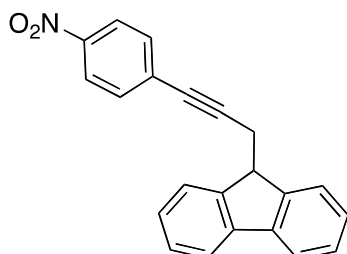


Prepared as a white solid by procedure B (yield = 60%).

$R_f$  (2:1 hexane- $\text{CH}_2\text{Cl}_2$ ) = 0.15; mp = 152–153 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.77 (d,  $J$  = 7.3 Hz, 2H), 7.69 (d,  $J$  = 7.5 Hz, 2H), 7.56 (d,  $J$  = 8.3 Hz, 2H), 7.58 (dt,  $J$  = 8.3, 1.6 Hz, 2H), 7.39–7.42 (m, 4H), 7.33 (dt,  $J$  = 7.4, 1.2 Hz, 2H), 4.16 (t,  $J$  = 7.2 Hz, 1H),

2.96 (d,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT)  $\delta$  145.9 (C), 140.9 (C), 132.1 (CH), 132.0 (CH), 128.6 (C), 127.7 (CH), 127.1 (CH), 124.5 (CH), 119.9 (CH), 118.5 (C), 111.1 (C), 93.5 (C), 80.6 (C), 45.9 (CH), 24.5 ( $\text{CH}_2$ ). HRMS: Calcd for  $\text{C}_{24}\text{H}_{20}\text{NO}$  ( $\text{M}^+ + \text{H} + \text{MeOH}$ ) 338.1545, Found 338.1555.

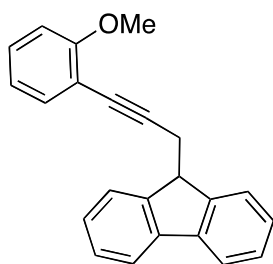
### 9-(3-(4-Nitrophenyl)prop-2-ynyl)-9H-fluorene (7e)



Prepared as a pale yellow solid following procedure B (yield = 79%).

$R_f$  (2:1 hexane- $\text{CH}_2\text{Cl}_2$ ): 0.30; mp = 135–136 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.16 (d,  $J = 8.9$  Hz, 2H), 7.78 (d,  $J = 8.9$  Hz, 2H), 7.70 (d,  $J = 7.2$  Hz, 2H), 7.47 (d,  $J = 8.9$ , 1.9 Hz, 2H), 7.42 (t,  $J = 7.3$  Hz, 2H), 7.34 (dd,  $J = 7.3$ , 6.3 Hz, 2H), 4.18 (t,  $J = 7.0$  Hz, 1H), 2.98 (d,  $J = 7.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  145.8, 141.0, 132.3, 130.6, 127.7, 127.1, 124.5, 123.5, 120.0, 94.5, 80.5, 45.9, 24.6. HRMS: Calcd for  $\text{C}_{22}\text{H}_{16}\text{NO}_2$  ( $\text{M}^+ + \text{H}$ ) 326.1181, Found 326.1169.

### 9-(3-(2-Methoxyphenyl)prop-2-ynyl)-9H-fluorene (7f)

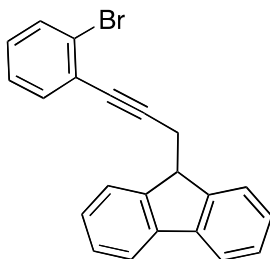


Prepared as a white solid following procedure B (yield = 45%).

$R_f$  (4:1 hexane- $\text{CH}_2\text{Cl}_2$ ): 0.21; mp = 109–110 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.87 (d,  $J = 7.2$  Hz, 2H), 7.76 (d,  $J = 7.5$  Hz, 2H), 7.37–7.42 (m, 3H), 7.39 (dt,  $J = 7.9$ , 1.8 Hz, 1H), 7.32 (dt,  $J = 7.5$ , 1.1 Hz, 2H), 6.92 (dt,  $J = 7.5$ , 1.1 Hz, 1H), 6.90 (d,  $J = 8.0$  Hz, 1H), 4.19 (t,  $J = 7.6$  Hz, 1H), 3.92 (s, 3H), 2.92 (d,  $J = 7.6$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT)  $\delta$  160.1 (C), 146.4 (C), 140.8 (C), 133.5 (CH), 129.2 (CH), 127.4 (CH), 127.0 (CH), 124.9 (CH), 120.4 (CH), 119.8 (CH), 112.9 (C), 110.6 (CH),

92.9 (C), 78.1 (C), 55.7 (CH<sub>3</sub>), 46.4 (CH), 24.8 (CH<sub>2</sub>). HRMS: Calcd for C<sub>23</sub>H<sub>19</sub>O (M<sup>+</sup>+H) 311.1436, Found 311.1427.

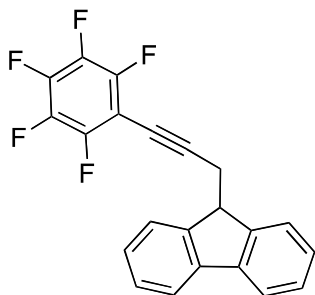
**9-(3-(2-Bromophenyl)prop-2-ynyl)-9H-fluorene (7g).**



Prepared as a colorless oil by procedure A (yield = 74%) or procedure B (yield = 41%).

*R*<sub>f</sub> (3:1 hexane–CH<sub>2</sub>Cl<sub>2</sub>) = 0.60. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) <sup>TM</sup> 7.80 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.37–7.43 (m, 3H), 7.31–7.34 (m, 2H), 7.22–7.25 (m, 1H), 7.11–7.15 (m, 1H), 4.19 (t, *J* = 7.1 Hz, 1H), 2.97 (d, *J* = 7.1 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT) <sup>TM</sup> 146.1 (C), 140.9 (C), 133.5 (CH), 132.3 (CH), 128.9 (CH), 127.5 (CH), 127.1 (CH), 126.9 (CH), 125.7 (C), 125.4 (C), 124.8 (CH), 119.9 (CH), 93.5 (C), 80.5 (C), 46.1 (CH), 24.6 (CH<sub>2</sub>). HRMS: Calcd for C<sub>22</sub>H<sub>16</sub><sup>79</sup>Br (M<sup>+</sup>+H) 359.0435, Found 359.0441.

**9-(3-(Pentafluorophenyl)prop-2-ynyl)-9H-fluorene (7h)**

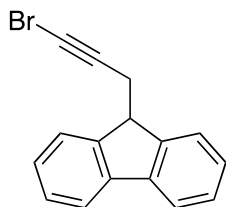


Prepared as a white solid following procedure B (yield = 57%).

*R*<sub>f</sub> (4:1 hexane–CH<sub>2</sub>Cl<sub>2</sub>): 0.50; mp = 128–129 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.33 (dt, *J* = 7.4, 1.2 Hz, 2H), 4.17 (t, *J* = 7.1 Hz, 1H), 2.99 (d, *J* = 7.1 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT) δ 145.6 (C), 140.9 (C), 127.7 (CH), 127.1 (CH), 124.5 (CH), 120.0 (CH), 101.9 (C), 66.0 (C), 45.6 (CH), 24.8 (CH<sub>2</sub>). HRMS: Calcd for C<sub>22</sub>H<sub>12</sub>F<sub>5</sub> (M<sup>+</sup>+H) 371.0859, Found 371.0867.

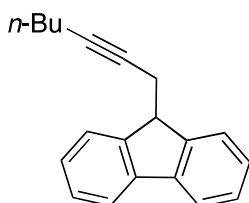
### 9-(3-Bromoprop-2-ynyl)-9H-fluorene (7i)

Prepared by reaction of 9-(prop-2-ynyl)-9H-fluorene with NBS and AgNO<sub>3</sub> in acetone at room temperature in the dark in 87% yield.



R<sub>f</sub> (Hexane): 0.21; mp = pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) <sup>TM</sup> 7.74 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.39 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 2H), 7.32 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.1 Hz, 2H), 4.05 (t, *J* = 7.4 Hz, 1H), 2.67 (d, *J* = 7.4 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT) <sup>TM</sup> 145.9 (C), 140.8 (C), 127.6 (CH), 127.1 (CH), 124.6 (CH), 119.9 (CH), 78.9 (C), 45.8 (CH), 39.6 (C-Br), 24.7 (CH<sub>2</sub>)

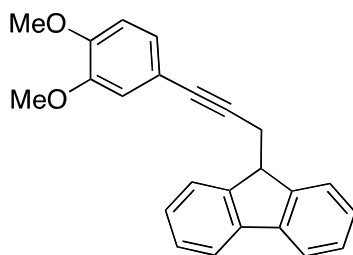
### 9-(Hept-2-ynyl)-9H-fluorene (7j)



Prepared as a pale yellow oil following procedure A (yield = 89%).

R<sub>f</sub> (5.1 hexane:CH<sub>2</sub>Cl<sub>2</sub>): 0.46. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.74 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.37 (dd, *J* = 7.4 Hz, *J* = 7.4 Hz, 2H), 7.31 (dd, *J* = 7.4 Hz, *J* = 7.4 Hz, 2H), 4.02 (t, *J* = 7.1 Hz, 1H), 2.63–2.66 (m, 2H), 2.17–2.21 (m, 2H), 1.32–1.51 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT)  $\delta$  146.5 (C), 140.8 (C), 127.3 (CH), 126.9 (CH), 124.6 (CH), 119.7 (CH), 81.7 (C), 78.4 (C), 46.5 (CH), 30.0 (CH<sub>2</sub>), 23.8 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 18.5 (CH<sub>2</sub>), 13.7 (CH<sub>3</sub>). HRMS: Calcd for C<sub>20</sub>H<sub>19</sub> (M<sup>+</sup>-H) 259.1487, Found 259.1483.

### 9-(3-(3,4-Dimethoxyphenyl)prop-2-ynyl)-9H-fluorene (7k)



Prepared as a pale orange solid following procedure B (yield = 85%).

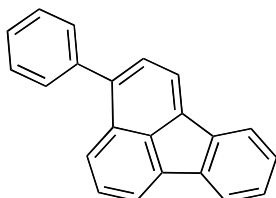
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.75–7.77 (m, 4H), 7.40 (dd,  $J = 7.7, 7.2$  Hz, 2H), 7.33 (dt,  $J = 7.4, 1.0$  Hz, 2H), 7.02 (dd,  $J = 8.3, 1.9$  Hz, 1H), 6.90 (d,  $J = 1.9$  Hz, 1H), 6.81 (d,  $J = 8.3$  Hz, 1H), 4.16 (t,  $J = 7.3$  Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.88 (d,  $J = 7.3$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT)  $\delta$  149.1 (C), 148.6 (C), 146.3 (2C), 140.9 (C), 127.5 (2CH), 127.0 (2CH), 124.7 (2CH), 124.6 (CH), 119.8 (2CH), 115.9 (C), 114.4 (CH), 111.0 (CH), 87.0 (C), 81.8 (C), 55.9 (2CH<sub>3</sub>), 46.3 (CH), 24.5 (CH<sub>2</sub>). HRMS: Calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_2\text{Na}$  ( $\text{M}^+\text{+Na}$ ) 363.1361, Found 363.1364.

#### General procedure for the hydroarylation reaction

A mixture of alkynylfluorene and the cationic gold catalyst or  $\text{GaCl}_3$  in anhydrous  $\text{CH}_2\text{Cl}_2$  (ca. 0.2 M) was stirred at the stated temperature (Tables 2 and 3). The solvent was evaporated under reduced pressure and the crude product was dissolved in toluene (ca. 0.1 M). This solution was added over a solution of DDQ (3 equiv) in toluene (final concentration ca. 0.03 M) and the mixture was heated under reflux overnight. The solvent was evaporated and the crude product was purified by flash chromatography ( $\text{SiO}_2$ , eluent: hexane).

Microwave irradiations were carried out in sealed tubes in a Biotage Initiator apparatus.

#### 3-Phenylfluoranthene (8a) [4]



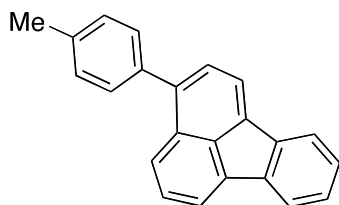
Prepared as a pale yellow solid with **6** as catalyst (yield = 70%).

$R_f$  (hexane: $\text{CH}_2\text{Cl}_2$ /3:1): 0.63; mp = 146–147 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.92–7.99 (m, 5H), 7.60–7.63 (m, 4H), 7.51–7.54 (m, 2H), 7.37–7.47 (m, 3H).  $^{13}\text{C}$  NMR



(CDCl<sub>3</sub>, 100 MHz, DEPT)  $\delta$  140.3 (C), 139.8 (C), 139.5 (C), 139.1 (C), 137.1 (C), 136.3 (C), 132.7 (C), 130.3 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 125.6 (CH), 121.5 (CH), 121.4 (CH), 120.0 (CH). Elemental analysis calcd (%) for C<sub>22</sub>H<sub>14</sub>: C 94.93, H 5.07; found: C 94.50, H 5.29

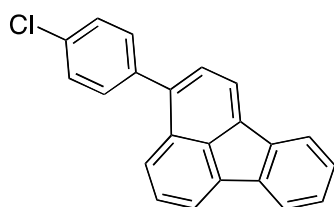
### 3-*p*-Tolylfluoranthene (8b)



Prepared as a yellow solid with GaCl<sub>3</sub> (yield = 45%) or **6** (yield = 28%) as catalyst.

R<sub>f</sub> (4:1 hexane-CH<sub>2</sub>Cl<sub>2</sub>): 0.61; mp = 147–148 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.90–7.97 (m, 5H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.37–7.39 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 2.46 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT)  $\delta$  140.3 (C), 139.5 (C), 139.1 (C), 137.1 (C), 137.0 (C), 136.8 (C), 136.1 (C), 130.1 (CH), 129.1 (CH), 128.5 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 125.7 (CH), 121.4 (CH), 121.3 (CH), 120.0 (CH), 119.9 (CH), 21.2 (CH<sub>3</sub>). HRMS: Calcd for C<sub>23</sub>H<sub>17</sub> (M<sup>+</sup>+H) 293.1330, Found 293.1324

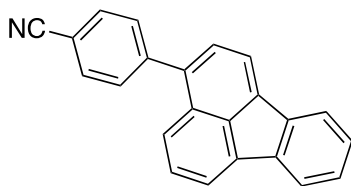
### 3-(4-Chlorophenyl)fluoranthene (8c)



Prepared as a yellow solid with GaCl<sub>3</sub> as catalyst (yield = 71%).

R<sub>f</sub> (4.1 hexane:CH<sub>2</sub>Cl<sub>2</sub>): 0.54; mp = 188–189 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.92–7.98 (m, 4H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.62 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.57 (d, *J* = 7.1 Hz, 1H), 7.48–7.52 (m, 4H), 7.39–7.41 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT)  $\delta$  139.5 (C), 139.0 (C), 138.9 (C), 138.2 (C), 137.2 (C), 136.7 (C), 133.6 (C), 132.7 (C), 131.5 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.2 (C), 127.7 (CH), 127.6 (CH), 125.2 (CH), 121.5 (CH), 121.4 (CH), 120.1 (CH), 119.9 (CH). HRMS: Calcd for C<sub>22</sub>H<sub>13</sub><sup>35</sup>Cl (M<sup>+</sup>) 312.0700, Found 312.0715.

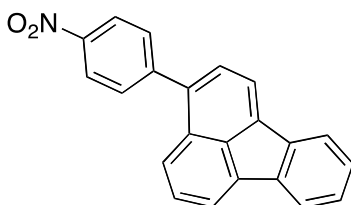
#### 4-(Fluoranthene-3-yl)benzotrile (8d)



Prepared as a solid with GaCl<sub>3</sub> as catalyst (yield = 88%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) *d* 8.00 (d, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 6.9 Hz, 1H), 7.92–7.95 (m, 2H), 7.80–7.83 (m, 3H), 7.71–7.74 (m, 2H), 7.65 (dd, *J* = 8.4, 6.9 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.41–7.43 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) *d* 144.8, 139.8, 139.0, 138.1, 137.8, 137.6, 132.9, 132.4, 131.1, 129.1, 128.9, 128.1, 128.0, 124.9, 121.9, 121.8, 120.6, 120.0, 119.1, 111.4 (CH).

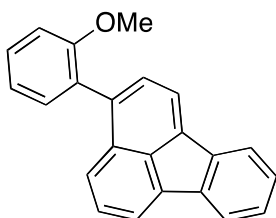
#### 3-(4-Nitrophenyl)fluoranthene (8e)



Prepared as a solid with GaCl<sub>3</sub> as catalyst (yield = 92%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  8.40 (dd, *J* = 8.6, 1.8 Hz, 2H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 6.9 Hz, 1H), 7.91–7.96 (m, 2H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.66 (dd, *J* = 8.6, 7.9 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.40–7.45 (m, 2H).

#### 3-(2-Methoxyphenyl)fluoranthene (8f)

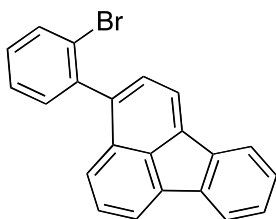


Prepared as a pale yellow solid with GaCl<sub>3</sub> (yield = 57%) or **6** (yield = 17%) as catalyst.

R<sub>f</sub> (2:1 hexane–CH<sub>2</sub>Cl<sub>2</sub>): 0.30; mp = 162–163 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.95 (d, *J* = 7.1 Hz, 1H), 7.88–7.91 (m, 3H), 7.51–7.62 (m, 3H), 7.42 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.35–7.37 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 3.71 (s, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT)  $\delta$  139.7 (C), 139.4 (C), 137.1 (C), 137.0 (C), 136.4 (C), 132.5 (C), 132.4 (CH), 129.4 (CH), 129.3 (C), 129.2 (CH), 128.6 (C), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.1 (CH), 121.5 (CH), 121.4 (CH), 120.6 (CH), 119.9 (CH), 119.8 (CH), 111.2 (CH). HRMS: Calcd for  $\text{C}_{23}\text{H}_{17}\text{O}$  ( $\text{M}^+\text{H}$ ) 309.1279, Found 309.1269.

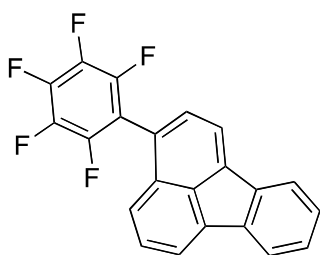
### 3-(2-Bromophenyl)fluoranthene (8g) [5]



Prepared as a pale yellow oil with  $\text{GaCl}_3$  as catalyst (yield = 44%).

$R_f$  (4:1 hexane- $\text{CH}_2\text{Cl}_2$ ): 0.32.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.97 (d,  $J = 7.1$  Hz, 1H), 7.89–7.93 (m, 3H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.48–7.58 (m, 3H), 7.37–7.43 (m, 4H), 7.29–7.33 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT)  $\delta$  140.3 (C), 139.7 (C), 139.2 (C), 139.0 (C), 137.1 (C), 136.9 (C), 132.8 (CH), 132.4 (C), 132.3 (CH), 129.2 (CH), 129.0 (CH), 128.7 (C), 128.1 (CH), 127.6 (CH), 127.0 (CH), 125.5 (CH), 124.1 (C), 121.5 (CH), 120.1 (CH), 119.6 (CH). HRMS: Calcd for  $\text{C}_{22}\text{H}_{14}^{79}\text{Br}$  ( $\text{M}^+\text{H}$ ) 357.0279, Found 357.0271

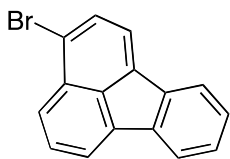
### 3-(Pentafluorophenyl)fluoranthene (8h)



Prepared as a pale yellow solid with  $\text{GaCl}_3$  as catalyst (yield = 74%).

$R_f$  (4:1 hexane- $\text{CH}_2\text{Cl}_2$ ): 0.57;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.00 (d,  $J = 7.2$  Hz, 1H), 7.95 (d,  $J = 6.8$  Hz, 1H), 7.90–7.93 (m, 2H), 7.58–7.65 (m, 2H), 7.48 (dt,  $J = 8.4, 1.6$  Hz, 1H), 7.38–7.43 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT)  $\delta$  139.8 (C), 139.1 (C), 139.0 (C), 137.7 (C), 132.8 (C), 131.1 (CH), 129.2 (CH), 128.8 (C), 128.5 (CH), 128.1 (CH), 124.4 (CH), 123.4 (C), 122.1 (CH), 121.9 (CH), 120.8 (CH), 119.7 (CH). HRMS: Calcd for  $\text{C}_{22}\text{H}_9\text{F}_5$  ( $\text{M}^+$ ) 368.0619, Found 368.0645.

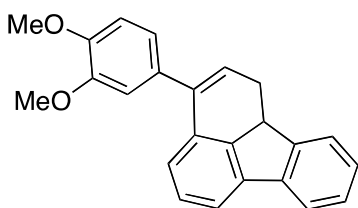
### 3-Bromofluoranthene (8i)



Prepared as a pale yellow solid with GaCl<sub>3</sub> (yield = 21%) or **6** (yield = 44%) as catalyst.

R<sub>f</sub> (3:1 hexane–CH<sub>2</sub>Cl<sub>2</sub>): 0.67; mp = 111–112 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 6.9 Hz, 1H), 7.78–7.83 (m, 2H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.61–7.66 (m, 2H), 7.31–7.38 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT) δ 139.0 (C), 138.7 (C), 137.2 (C), 136.7 (C), 133.5 (C), 131.1 (CH), 129.8 (C), 129.1 (CH), 127.9 (CH), 125.9 (CH), 121.8 (C), 121.6 (CH), 121.5 (CH), 120.7 (CH), 120.6 (CH). HRMS: Calcd for C<sub>16</sub>H<sub>9</sub><sup>79</sup>Br (M<sup>+</sup>) 279.9882, Found 279.9894.

### 3-(3,4-Dimethoxyphenyl)-1,10b-dihydrofluoranthene (9)

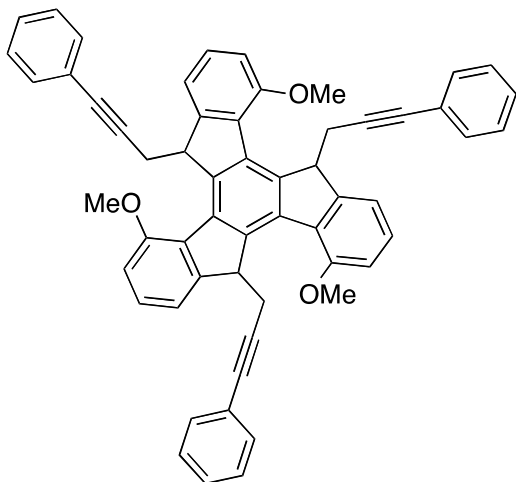


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.81 (d, *J* = 7.5, 1H), 7.65 (d, *J* = 7.2, 1H), 7.58 (d, *J* = 7.7, 1H), 7.41 (t app, *J* = 7.2 Hz, 1H), 7.07–7.09 (m, 3H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.22 (dd, *J* = 6.5, 2.4 Hz, 1H), 4.05 (q, *J* = 7.6 Hz, xH), 3.94 (s, 3H), 3.90 (s, 3H), 3.07 (td, *J* = 15.9, 7.0 Hz, 1H), 2.12 (td, *J* = 15.9, 2.5 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 148.8, 148.6, 147.0, 144.6, 142.4, 139.8, 138.7, 132.8, 132.0, 127.8, 127.2, 126.6, 124.4, 122.2, 120.7, 120.5, 119.1, 119.0, 111.4, 111.1, 56.0, 42.4, 26.8. HRMS: Calcd for C<sub>24</sub>H<sub>21</sub>O<sub>2</sub> (M<sup>+</sup>+H) 341.1542, Found 341.1556.

**General procedure for the synthesis of trialkylated truxenes:** *n*BuLi 2.5M in hexanes (3.5 equiv) was added dropwise over a solution of the truxene (1 equiv) in anhydrous THF at –80 °C and the mixture was allowed to warm up to –10 °C for 4 hours. Then, a solution of the alkynylbromide (4.0 equiv) in anhydrous THF was added dropwise and the mixture was allowed to warm to room temperature overnight. Saturated NaCl solution (x mL) was added and the organic layer was extracted with ethyl acetate. The combined organic fractions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and

filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO<sub>2</sub>, eluent = hexane:CH<sub>2</sub>Cl<sub>2</sub>).

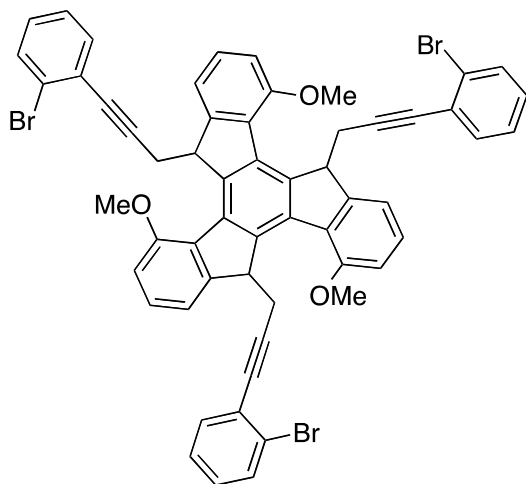
**4,9,14-Trimethoxy-5,10,15-tris(3-phenylprop-2-ynyl)-10,15-dihydro-5H-diindeno[1,2-*a*:1',2'-*c*]fluorene (1a).**



White solid (yield = 57%).

R<sub>f</sub> (1:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>): 0.35; mp =130–131 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.82–7.85 (m, 3H), 7.55–7.59 (m, 3H), 7.35–7.43 (m, 6H), 7.21–7.23 (m, 2H), 7.10–7.15 (m, 3H), 7.00 (d, *J* = 8.2 Hz, 3H), 5.29–5.35 (m, 2H), 5.22–5.25 (m, 1H), 4.20 (s, 6H), 4.17 (s, 3H), 3.39–3.51 (m, 3H), 2.23–2.30 (m, 1H), 2.08–2.17 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT) δ 154.2 (C), 154.2 (C), 154.1 (C), 151.2 (C), 151.0 (C), 150.4 (C), 141.2 (C), 139.8 (C), 139.8 (C), 136.5 (C), 136.1 (C), 136.0 (C), 133.5 (CH), 133.4 (CH), 132.4 (CH), 132.3 (CH), 128.7 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.0 (C), 127.6 (C), 127.5 (C), 126.9 (CH), 126.9 (CH), 126.8 (CH), 126.2 (C), 126.1 (C), 125.2 (C), 125.1 (C), 117.8 (CH), 117.7 (CH), 117.5 (CH), 109.6 (CH), 95.2 (C), 95.2 (C), 95.1 (C), 80.4 (C), 80.3 (C), 80.2 (C), 55.5 (CH<sub>3</sub>), 55.4 (CH<sub>3</sub>), 49.3 (CH), 48.8 (CH), 48.7 (CH), 27.6, (CH<sub>2</sub>), 27.4 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>). Elemental analysis calcd (%) for C<sub>57</sub>H<sub>42</sub>O<sub>3</sub>·H<sub>2</sub>O: C 86.34, H 5.59; found: C 86.60, H 5.72.

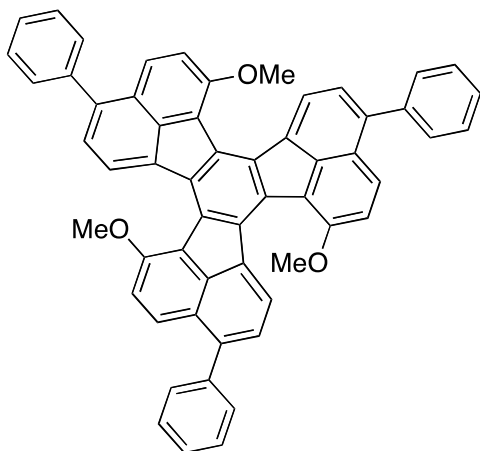
**5,10,15-Tris(3-(2-bromophenyl)prop-2-ynyl)-4,9,14-trimethoxy-10,15-dihydro-5H-diindeno[1,2-*a*:1',2'-*c*]fluorene (1b).**



White solid (yield = 54%).

$R_f$  (1:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>): 0.35; mp = 144–145 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.82–7.85 (m, 3H), 7.55–7.59 (m, 3H), 7.35–7.43 (m, 6H), 7.21–7.23 (m, 2H), 7.10–7.15 (m, 3H), 7.00 (d,  $J$  = 8.2 Hz, 3H), 5.29–5.35 (m, 2H), 5.22–5.25 (m, 1H), 4.20 (s, 6H), 4.17 (s, 3H), 3.39–3.51 (m, 3H), 2.23–2.30 (m, 1H), 2.08–2.17 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, DEPT) δ 154.3 (C), 153.2 (C), 153.1 (C), 151.2 (C), 151.0 (C), 150.4 (C), 141.2 (C), 139.8 (C), 139.7 (C), 136.5 (C), 136.1 (C), 136.0 (C), 133.5 (CH), 133.4 (CH), 132.3 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.0 (C), 127.6 (C), 127.5 (C), 126.9 (CH), 126.2 (C), 126.1 (C), 125.2 (C), 125.1 (C), 117.8 (CH), 117.7 (CH), 117.5 (CH), 109.5 (CH), 95.2 (C), 95.1 (C), 95.0 (C), 80.4 (C), 80.3 (C), 80.2 (C), 55.5 (CH<sub>3</sub>), 55.4 (CH<sub>3</sub>), 49.3 (CH), 48.8 (CH), 48.7 (CH), 27.6 (CH<sub>2</sub>), 27.4 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>). Elemental analysis calcd (%) for C<sub>57</sub>H<sub>39</sub>Br<sub>3</sub>O<sub>3</sub>: C 67.67, H 3.89; found: C 67.30, H 4.00.

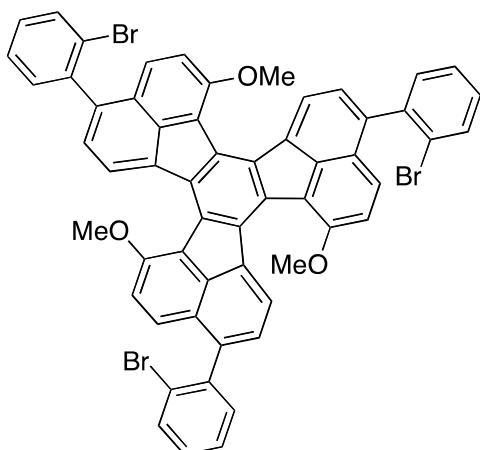
**1,7,13-Trimethoxy-4,10,16-triphenyldiacenaphtho[1,2-*j*:1',2'-*l*]fluoranthene (2a).**



Yellow solid (yield = 72%).

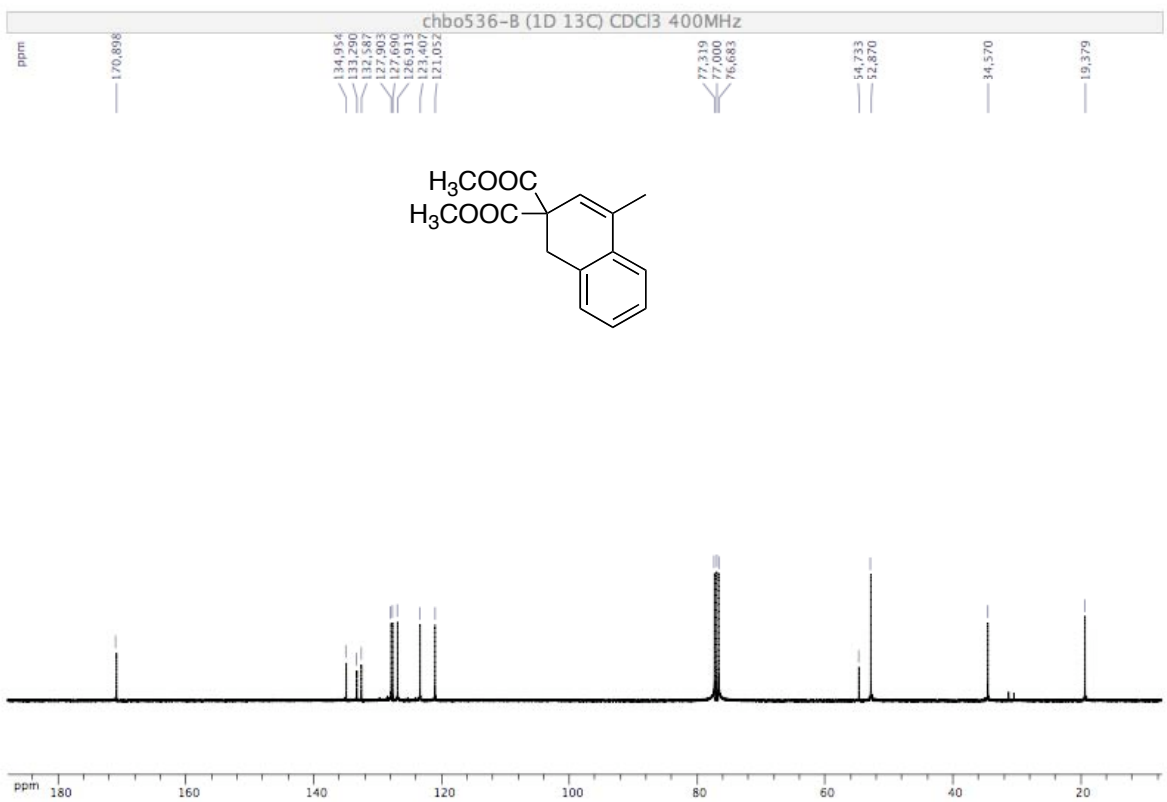
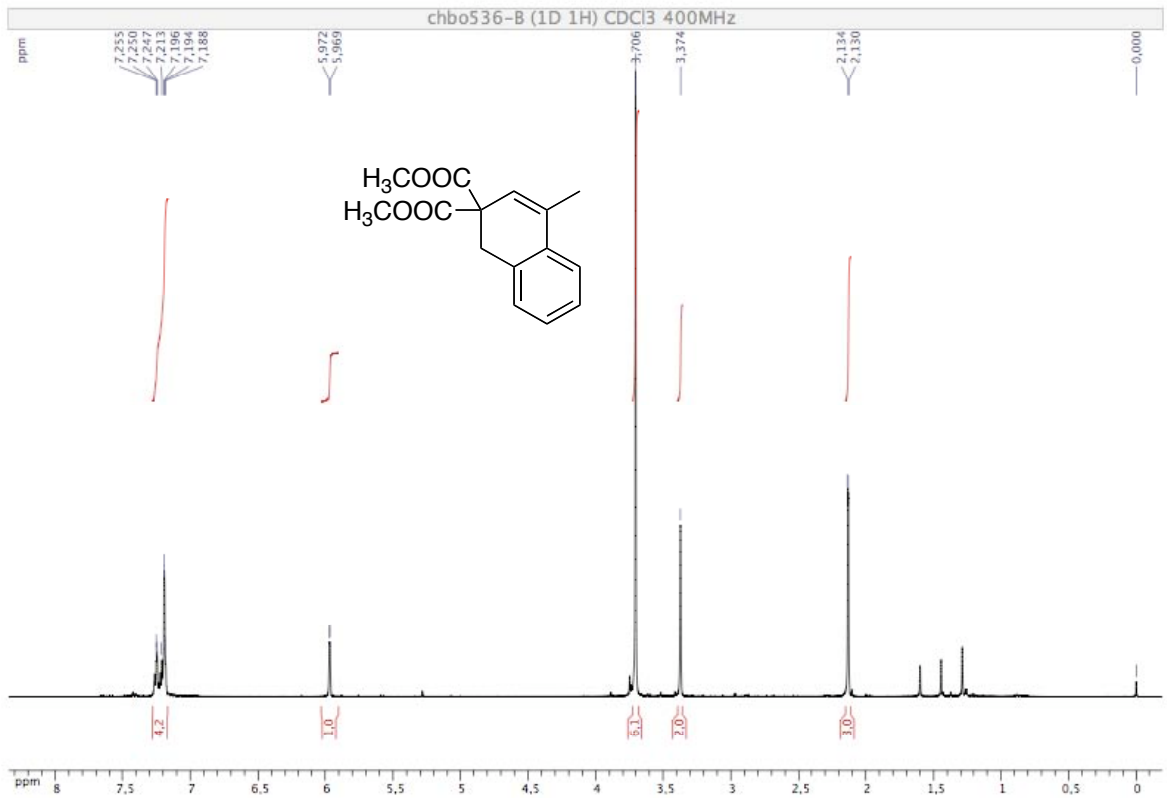
mp = > 300 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_2\text{CDCl}_2$ , 500 MHz, 403 K)  $\delta$  8.24 (d,  $J = 7.4$  Hz, 3H), 8.01 (d,  $J = 9.0$  Hz, 3H), 7.66 (d,  $J = 7.0$  Hz, 6H), 7.60 (d,  $J = 7.4$  Hz, 3H), 7.51 (t,  $J = 7.4$  Hz, 6H), 7.43 (d,  $J = 9.0$  Hz, 6H), 4.04 (s, 9H). MS (MALDI): 768.5 ( $\text{M}^+$ ).

**4,10,16-Tris(2-bromophenyl)-1,7,13-trimethoxydiacenaphtho[1,2-*j*:1',2'-*l*]fluoranthene (2b).**

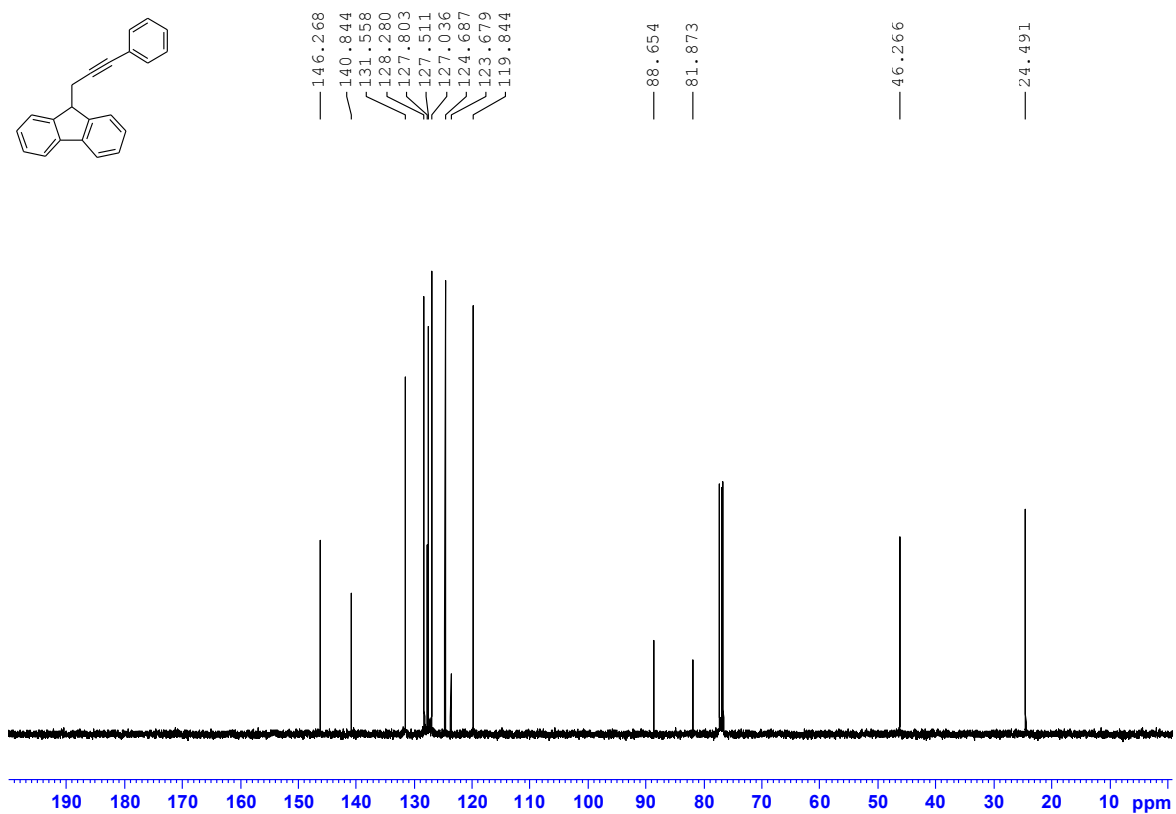
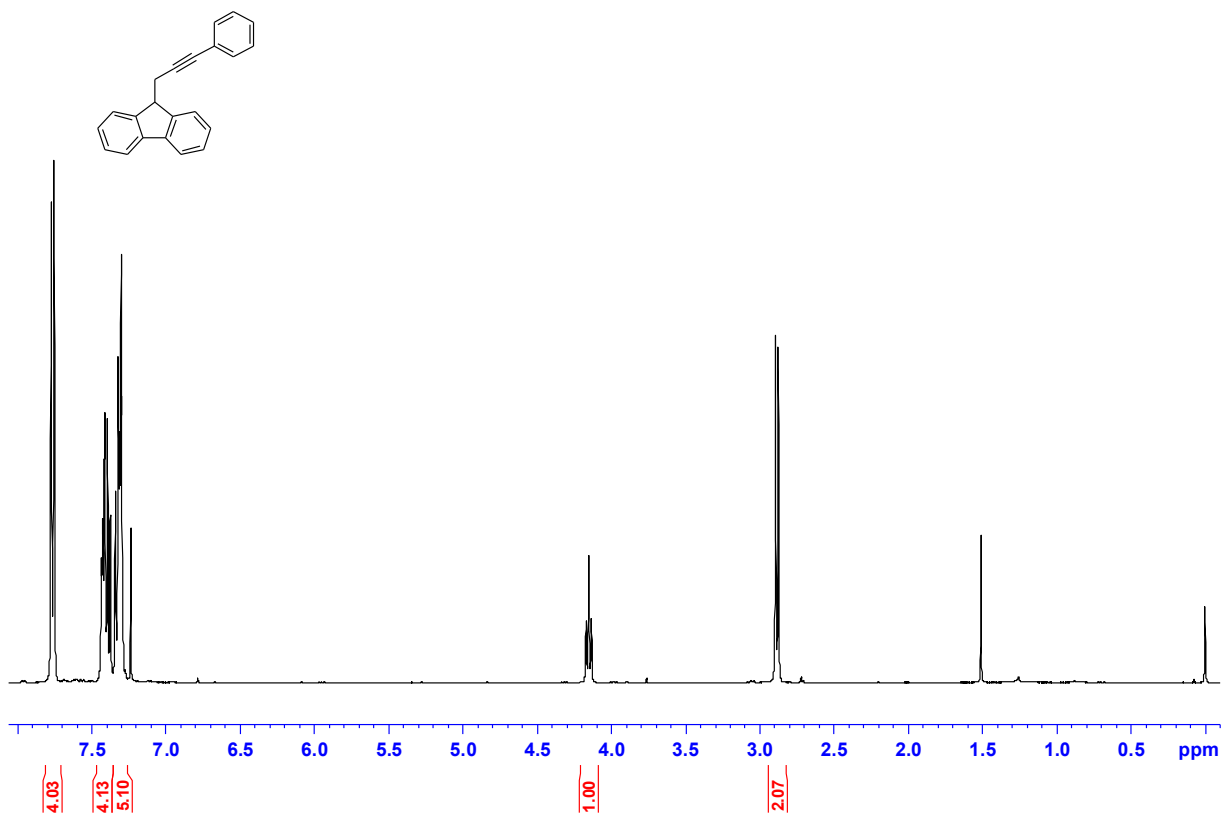


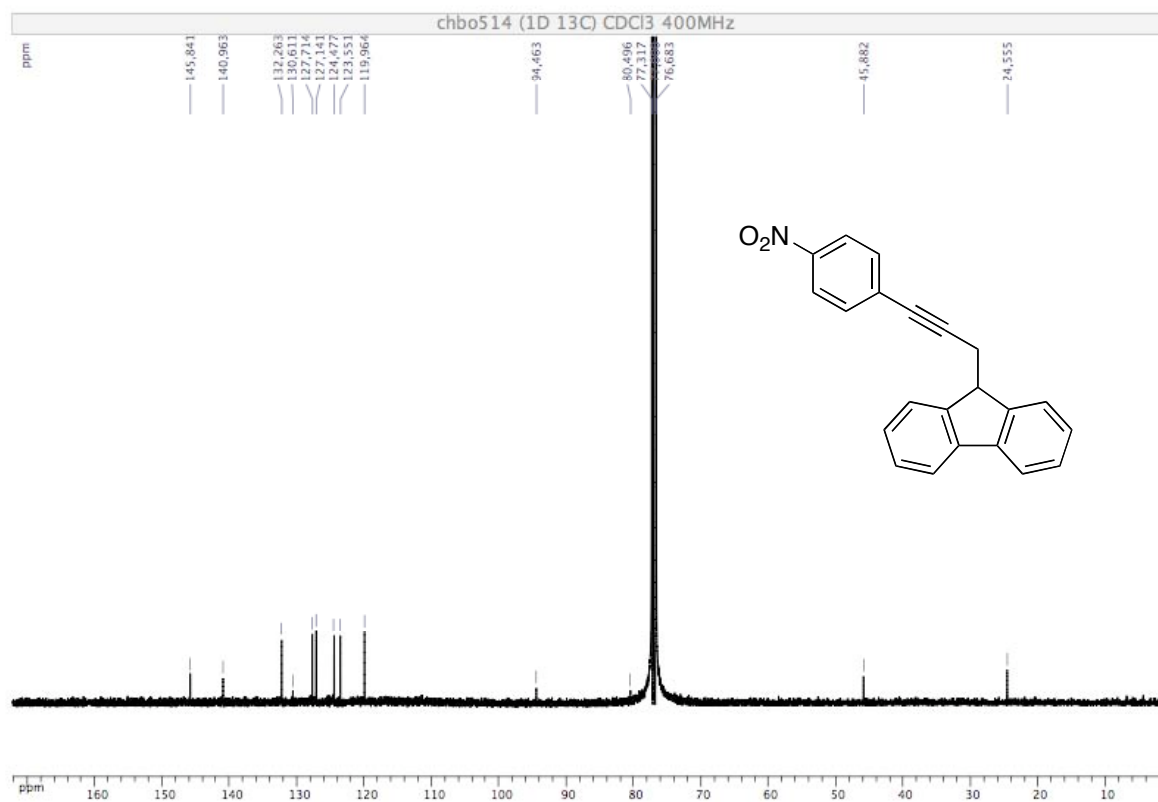
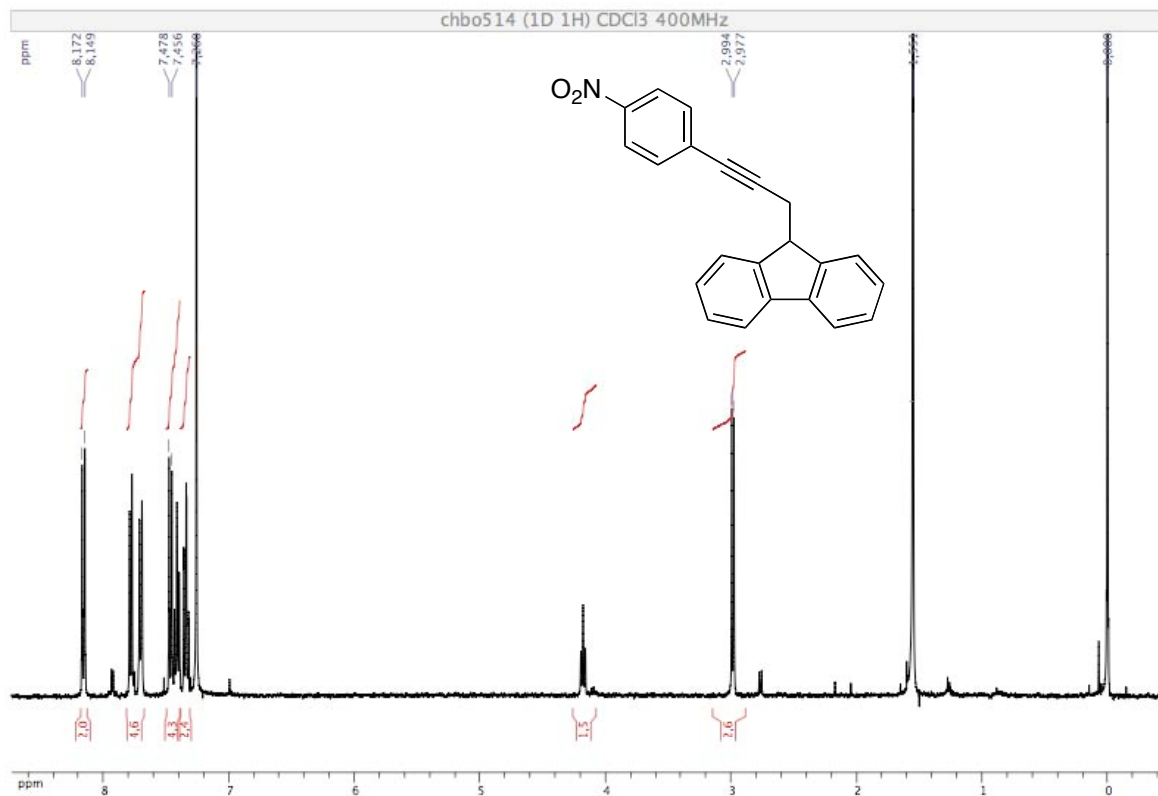
Yellow solid (yield = 77%).

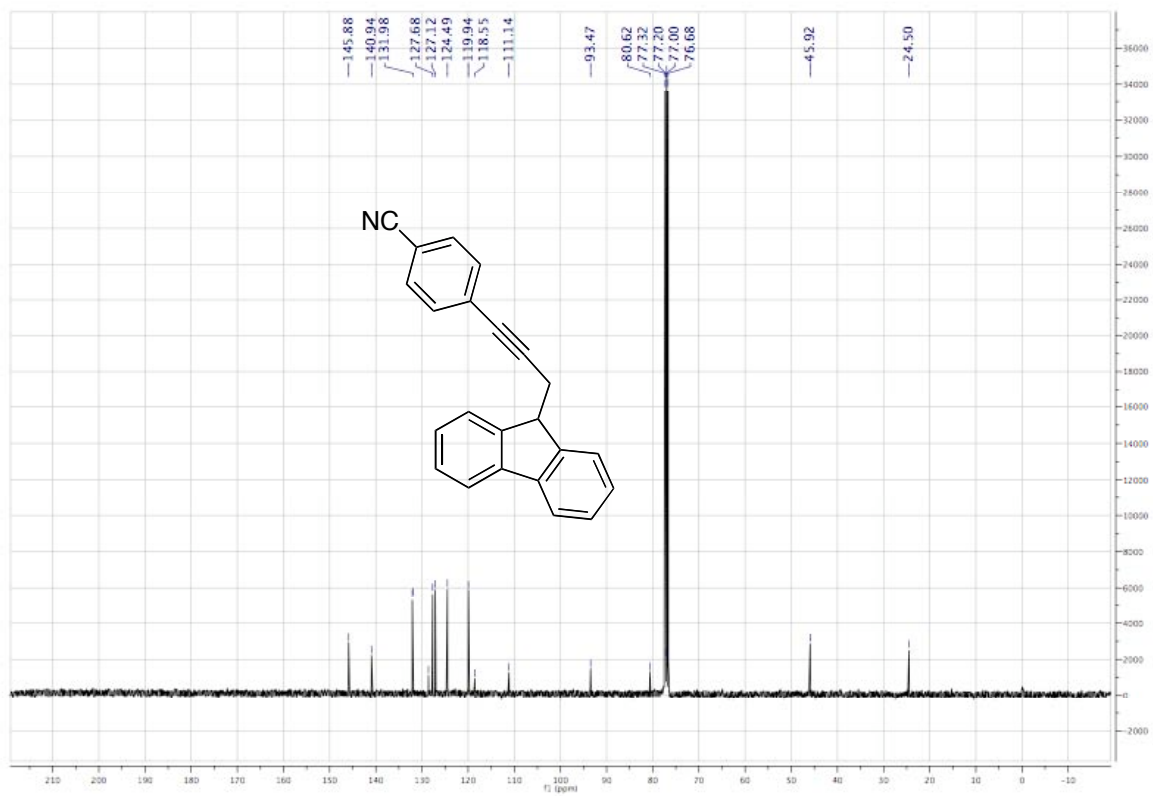
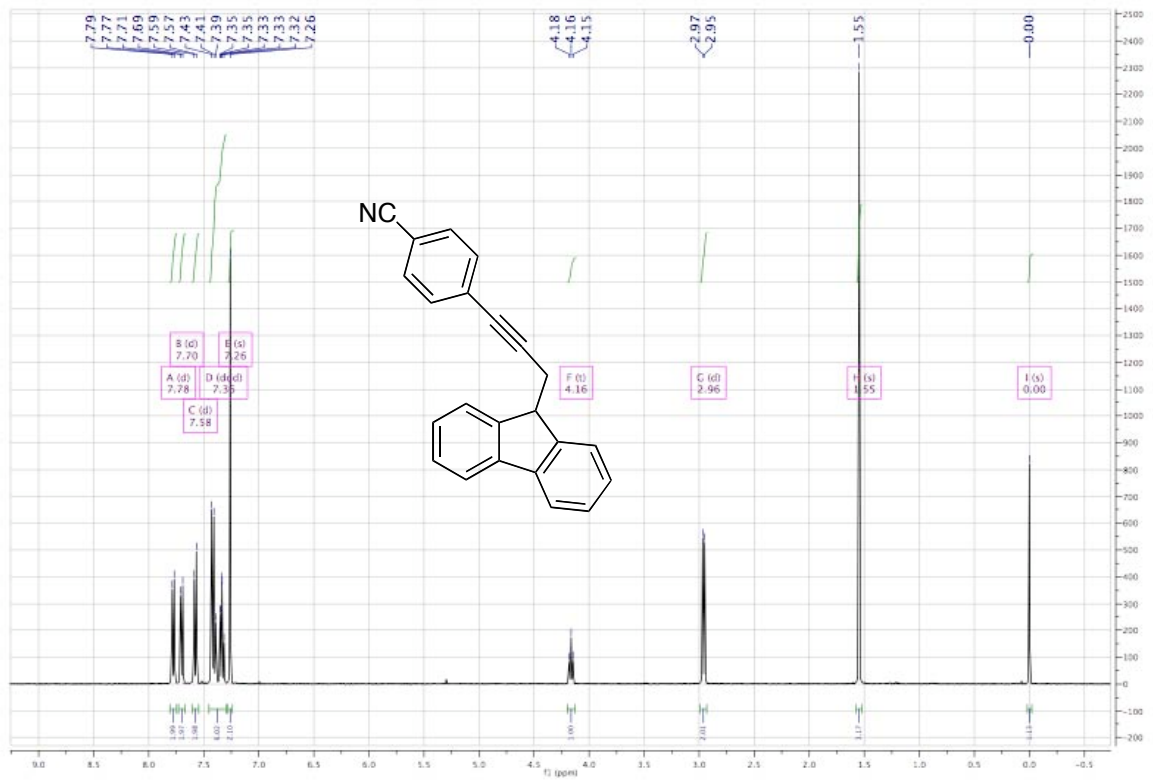
mp = > 300 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_2\text{CDCl}_2$ , 500 MHz, 403 K)  $\delta$  8.27 (d,  $J = 7.4$  Hz, 3H), 7.78 (d,  $J = 8.0$  Hz, 3H), 7.62 (d,  $J = 8.9$  Hz, 3H), 7.53 (t,  $J = 7.2$  Hz, 6H), 7.44 (t,  $J = 7.3$  Hz, 3H), 7.39 (d,  $J = 8.9$  Hz, 3H), 7.31 (t,  $J = 7.4$  Hz, 3H), 4.04 (s, 9H). MS (MALDI): 1004.1, 1006.1 ( $\text{M}^+$ ).

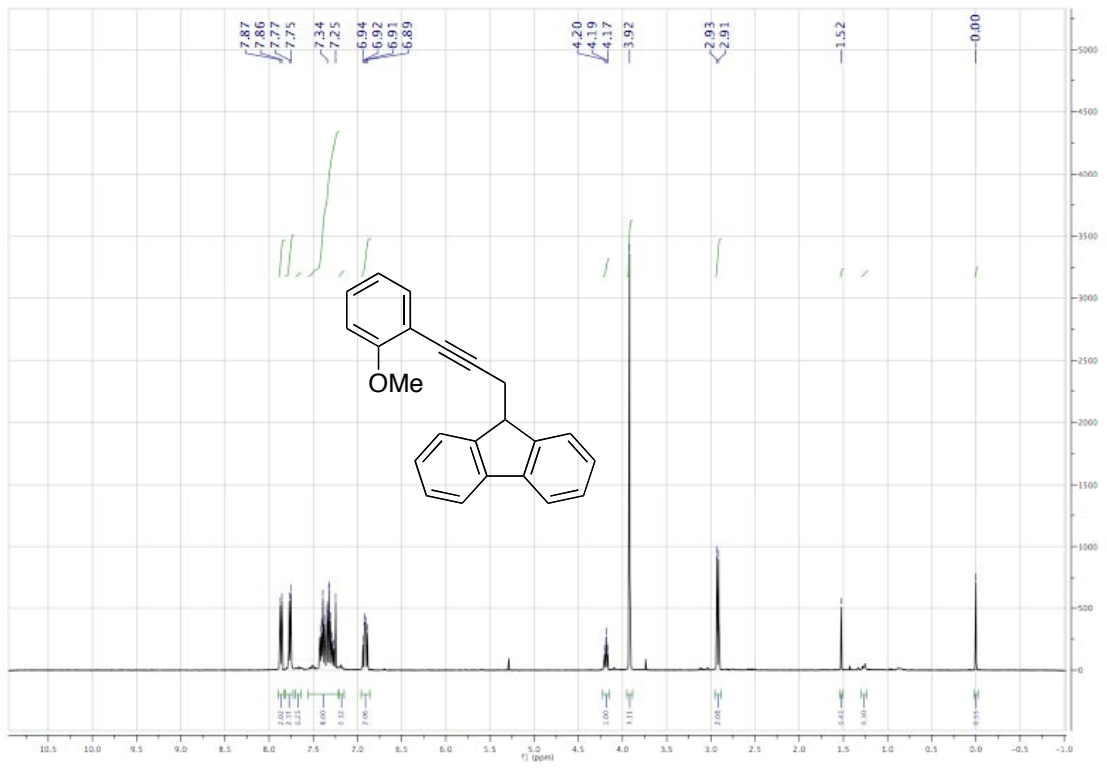


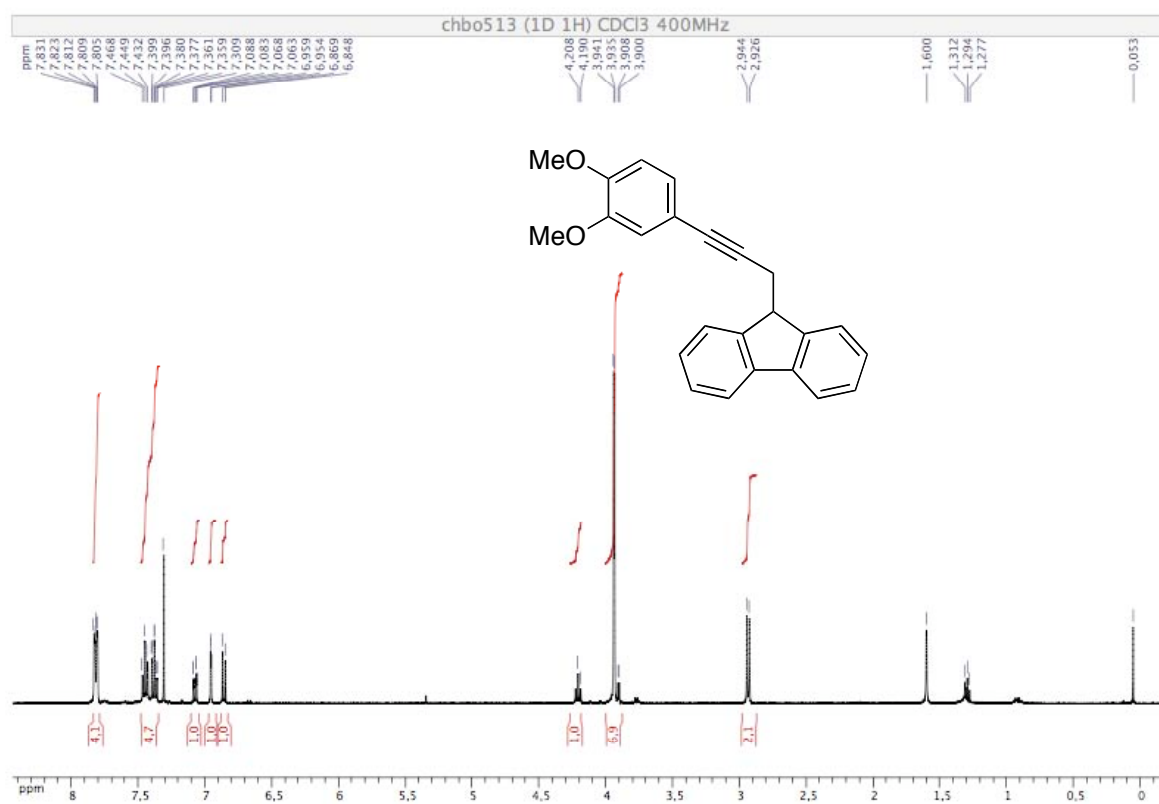
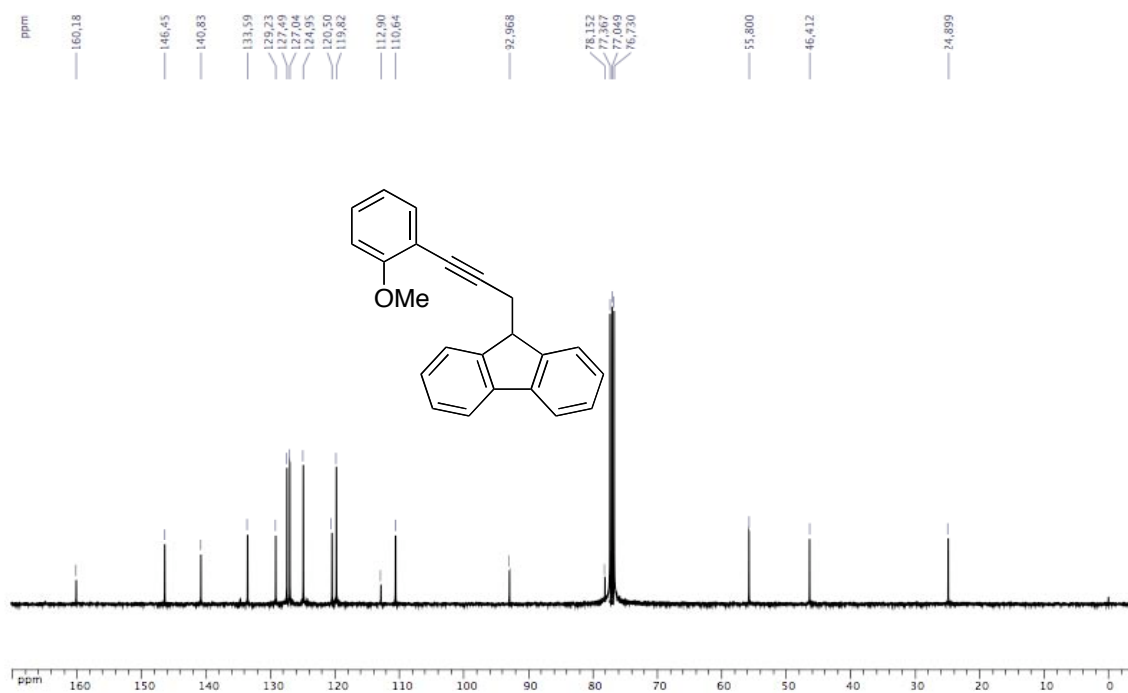


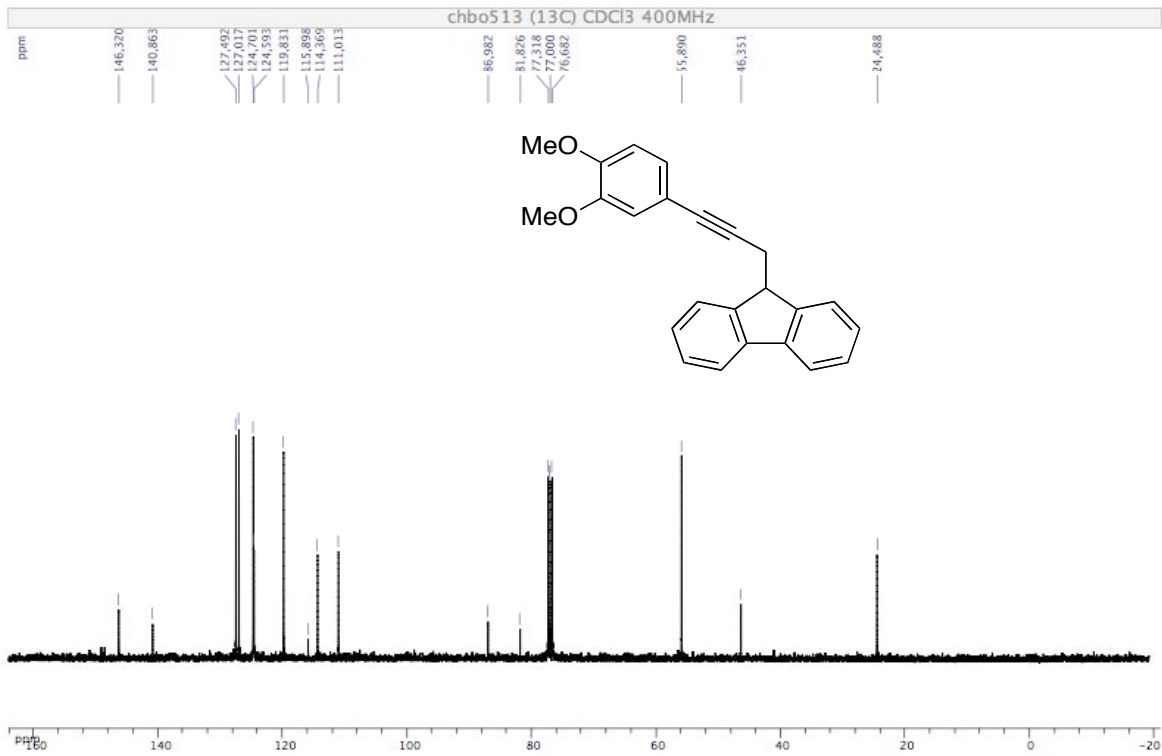


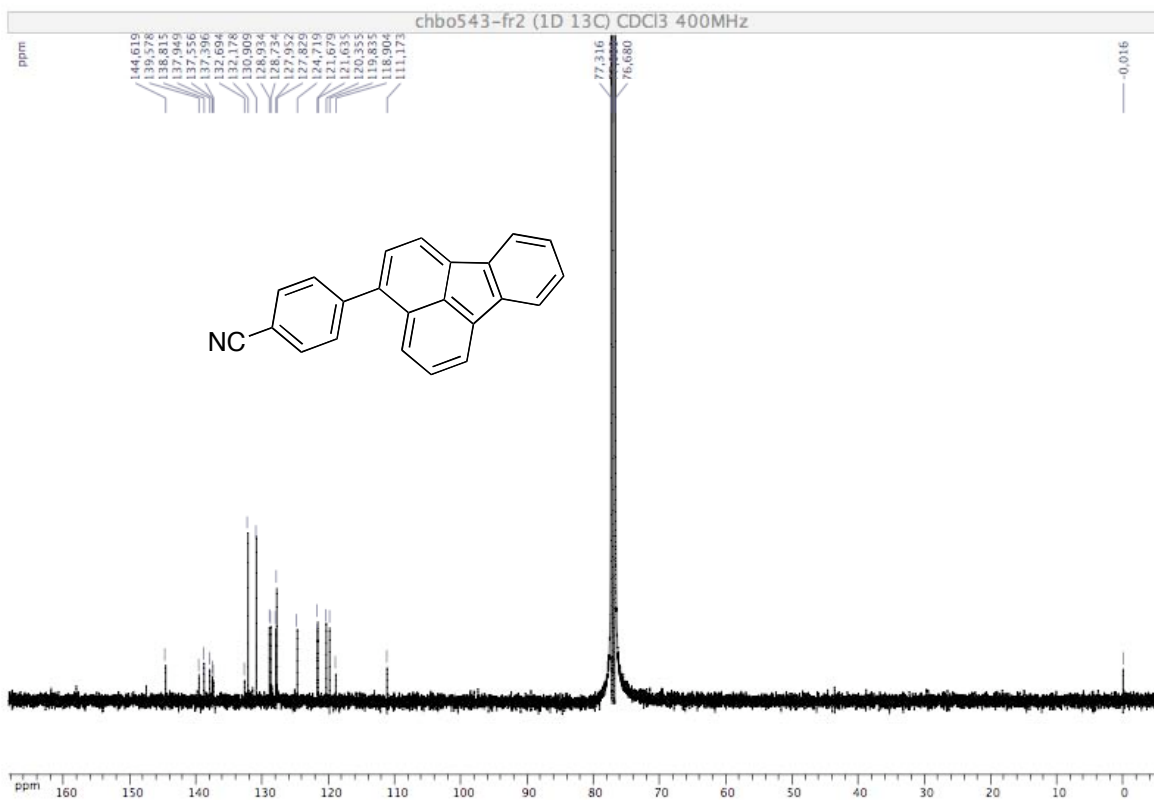
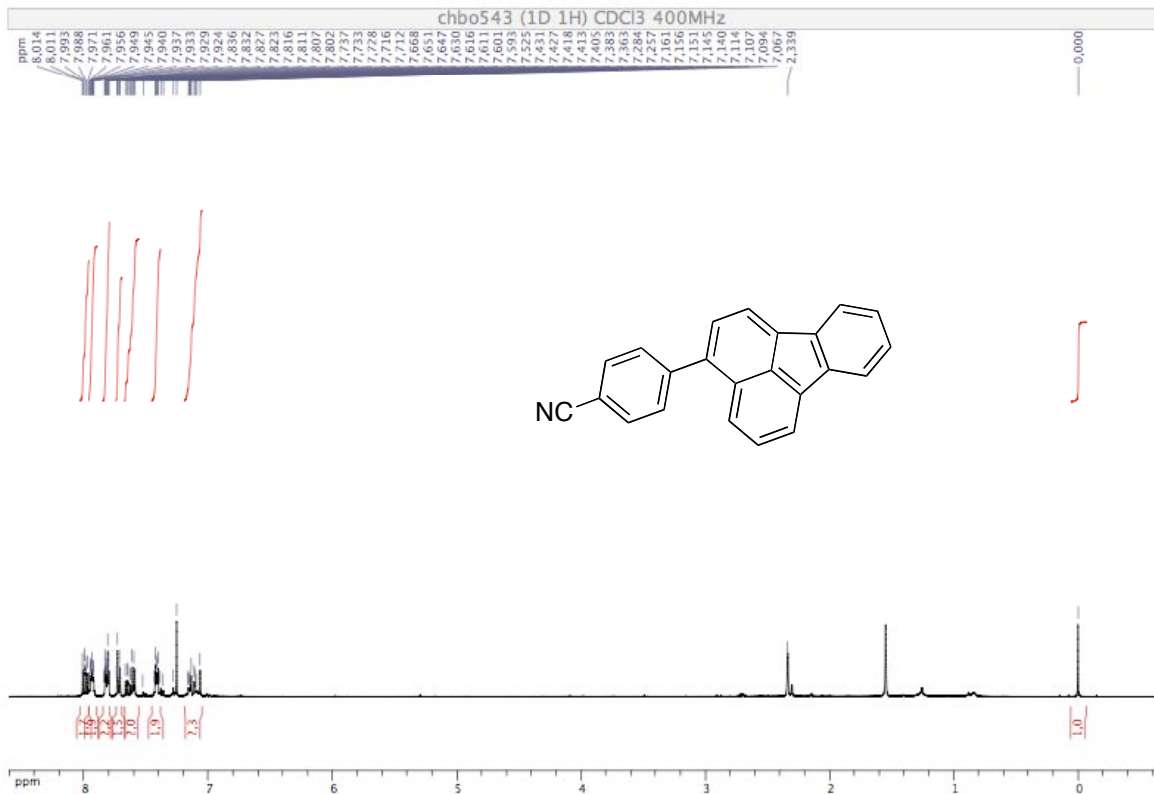


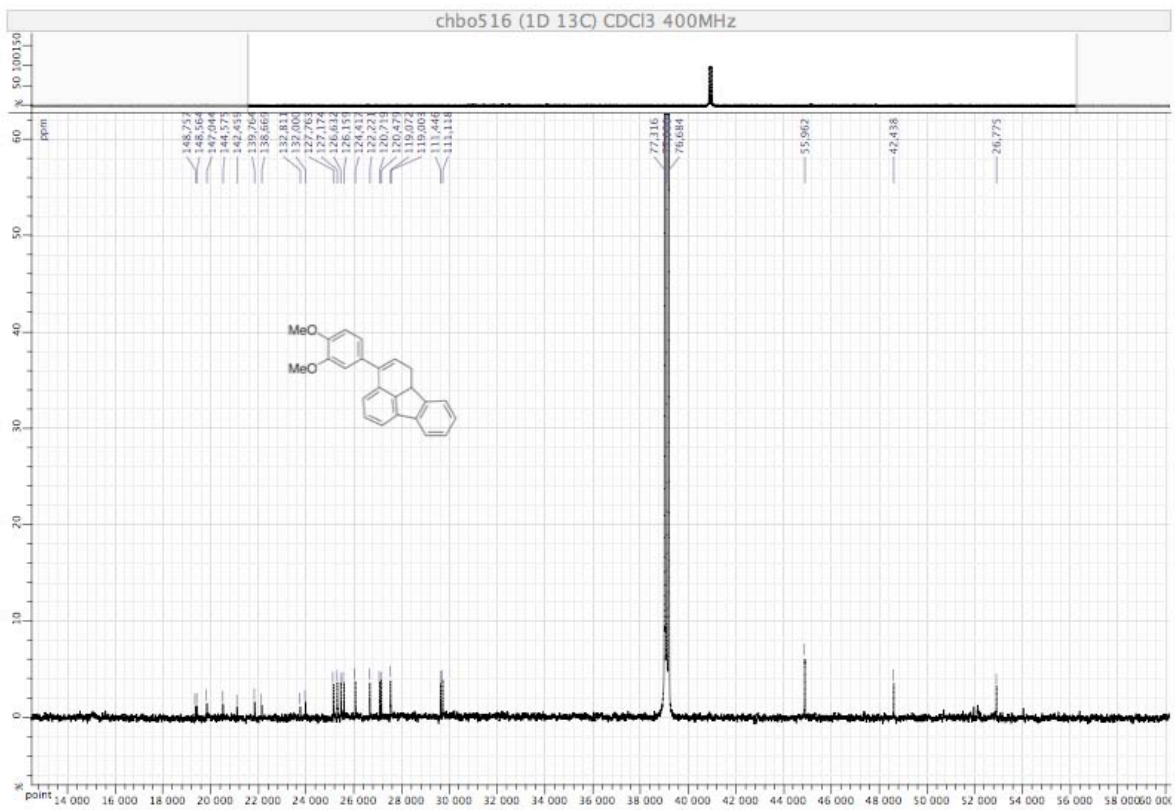
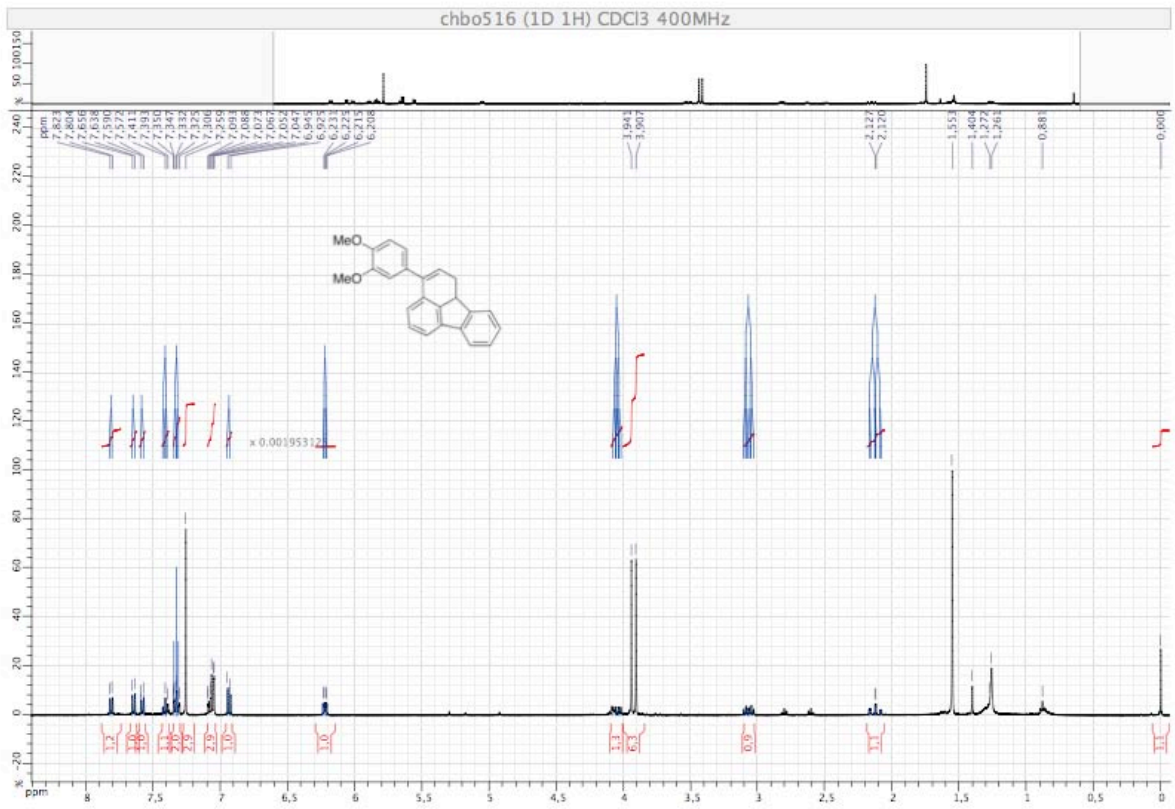






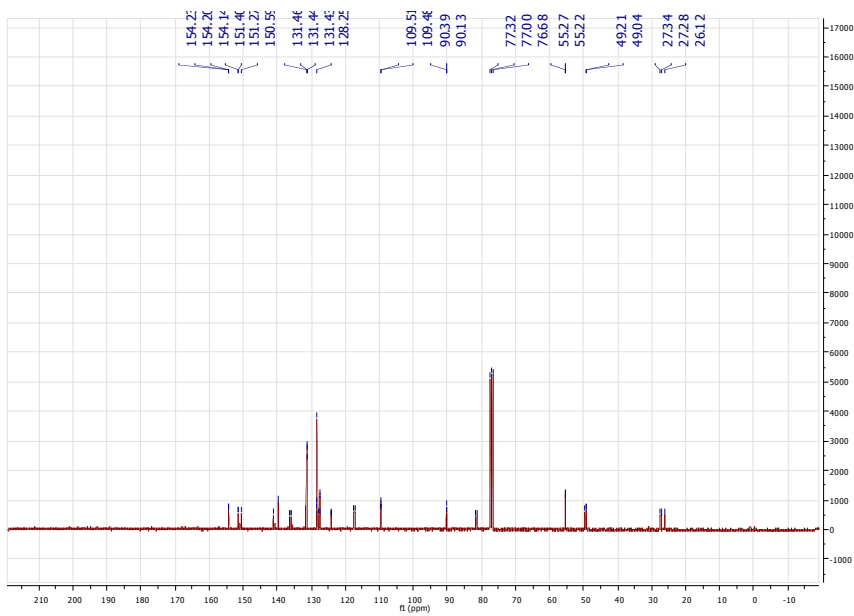
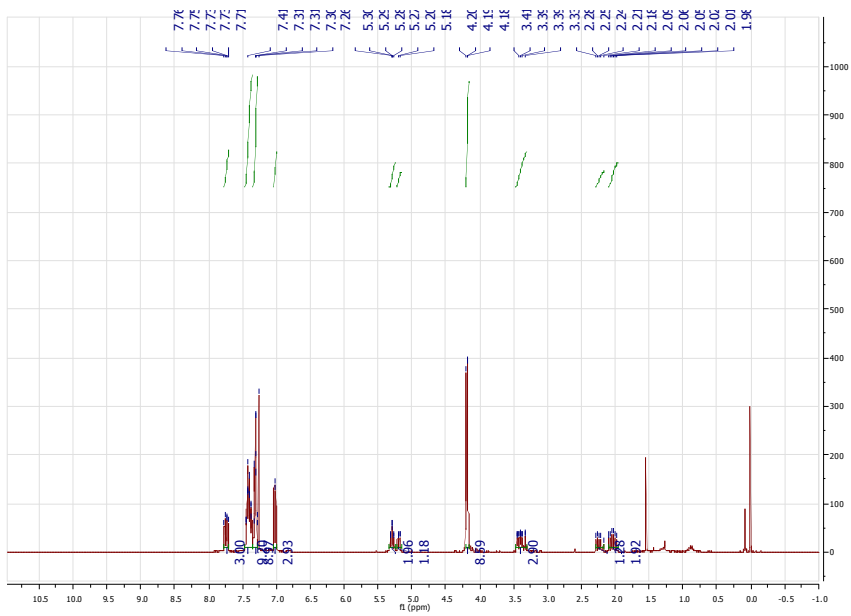




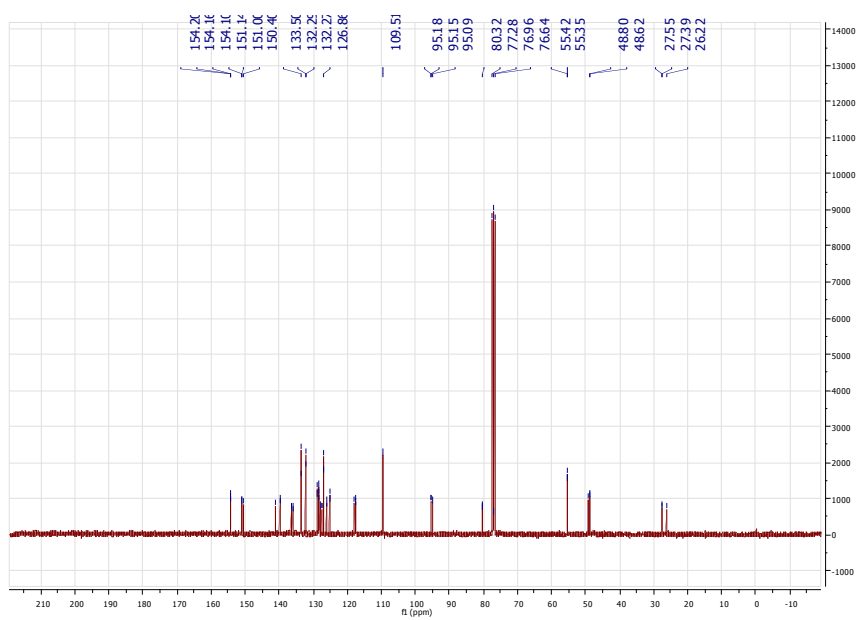
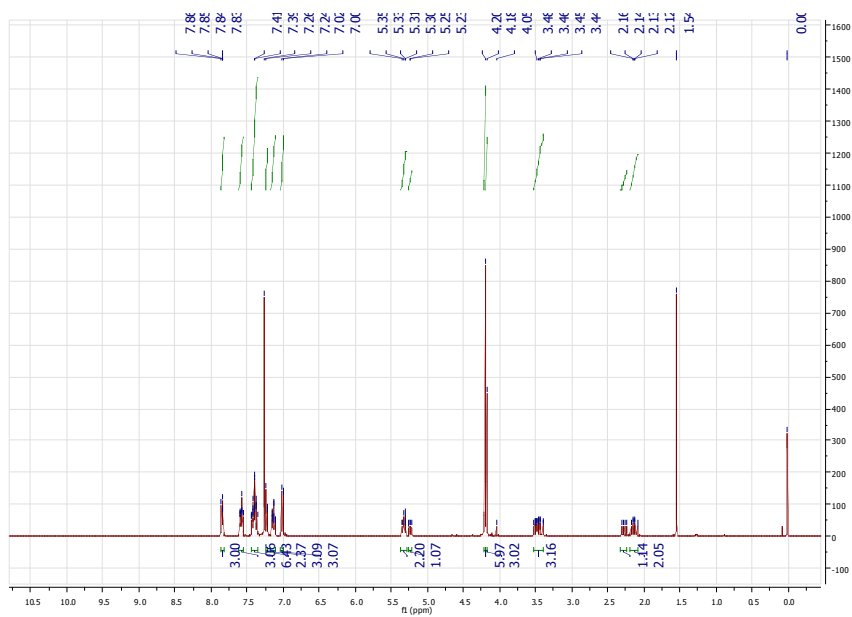


1a

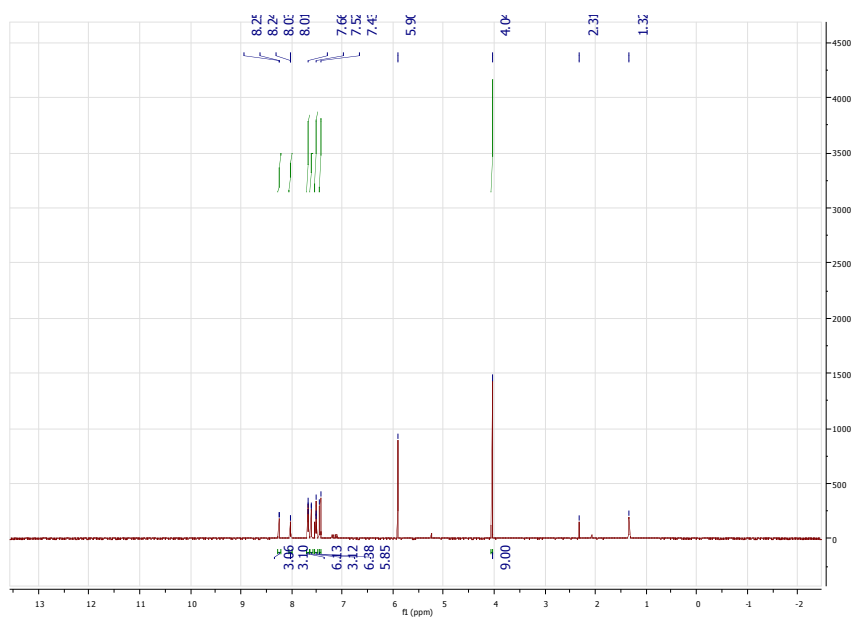




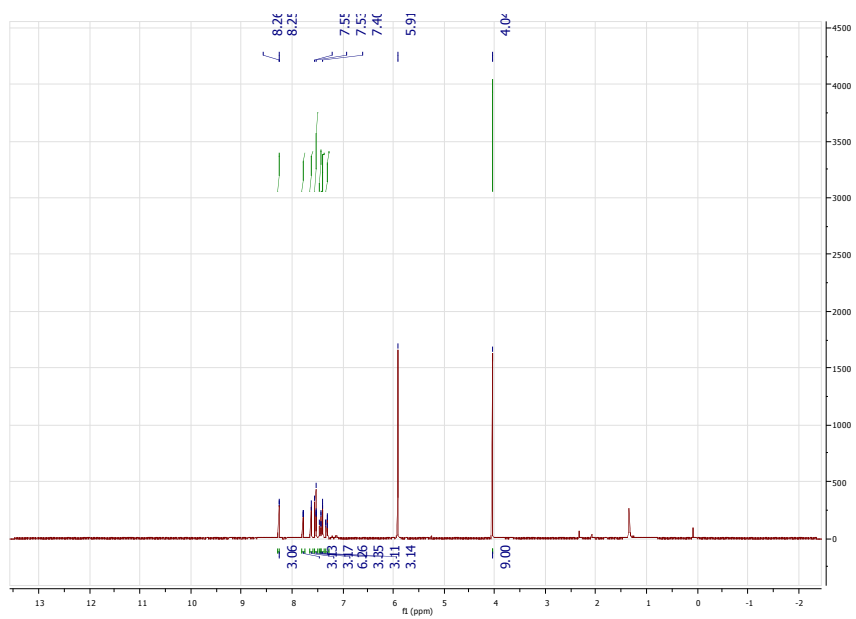
1b

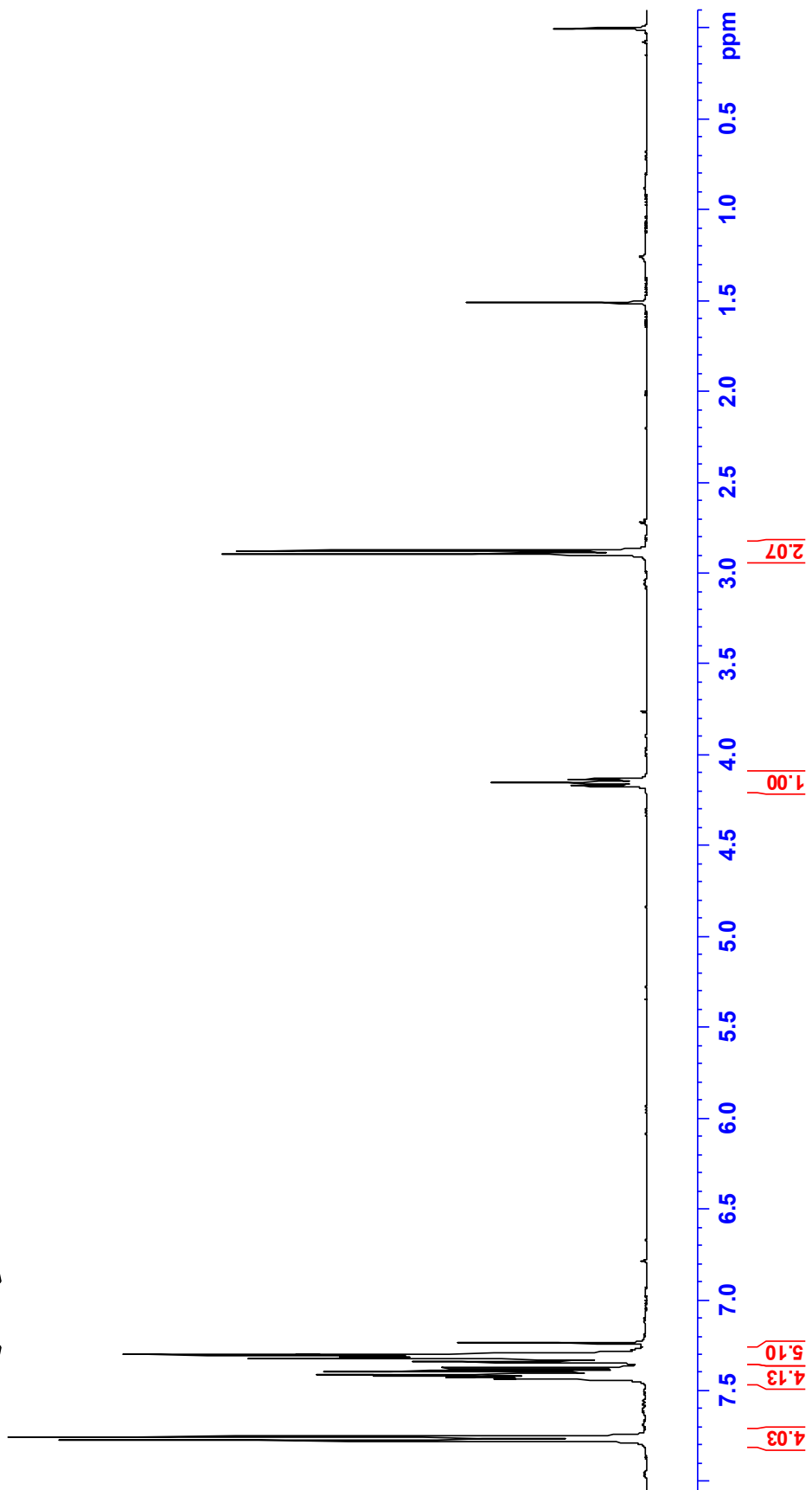
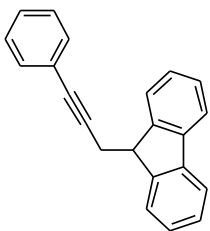


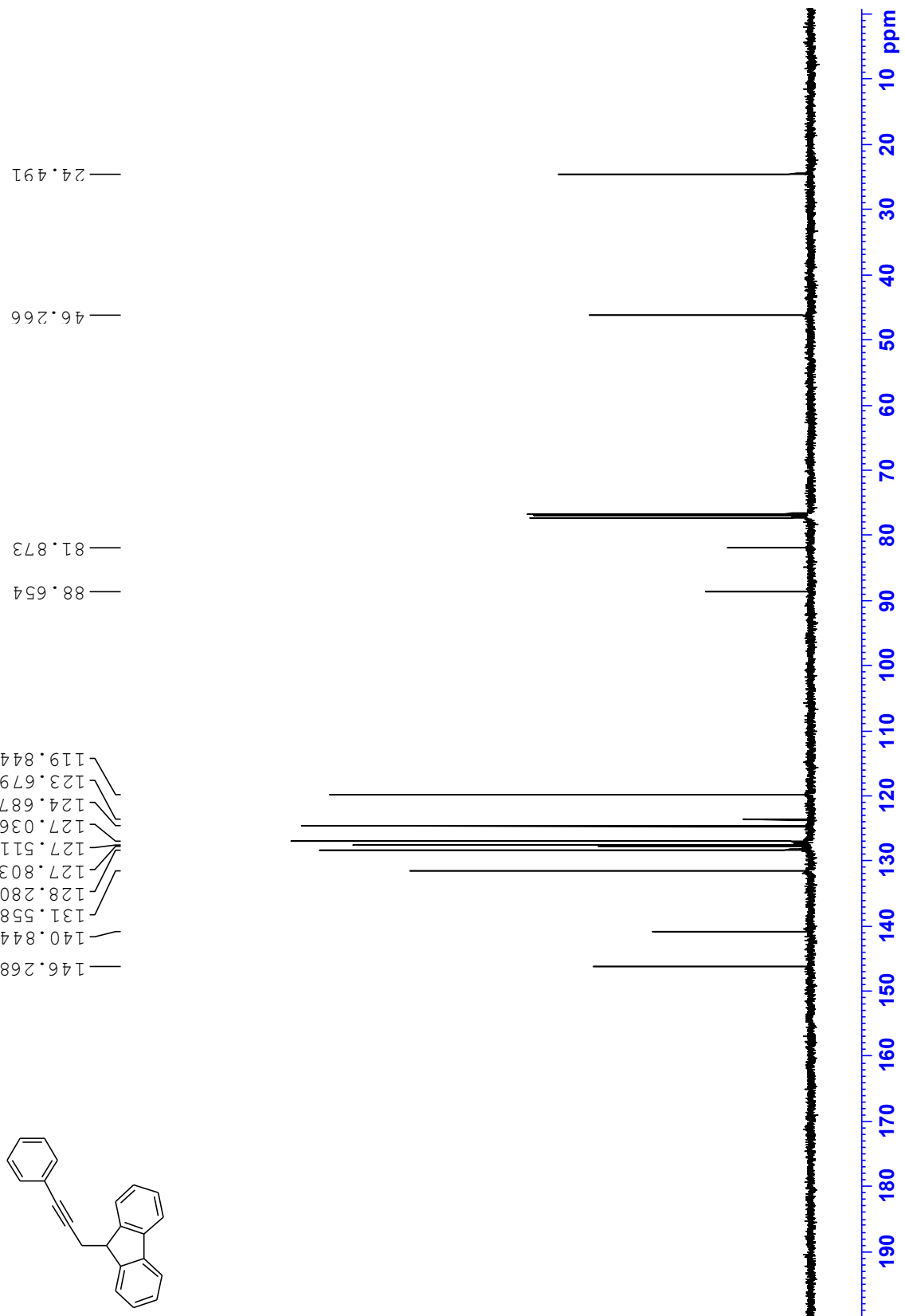
2a

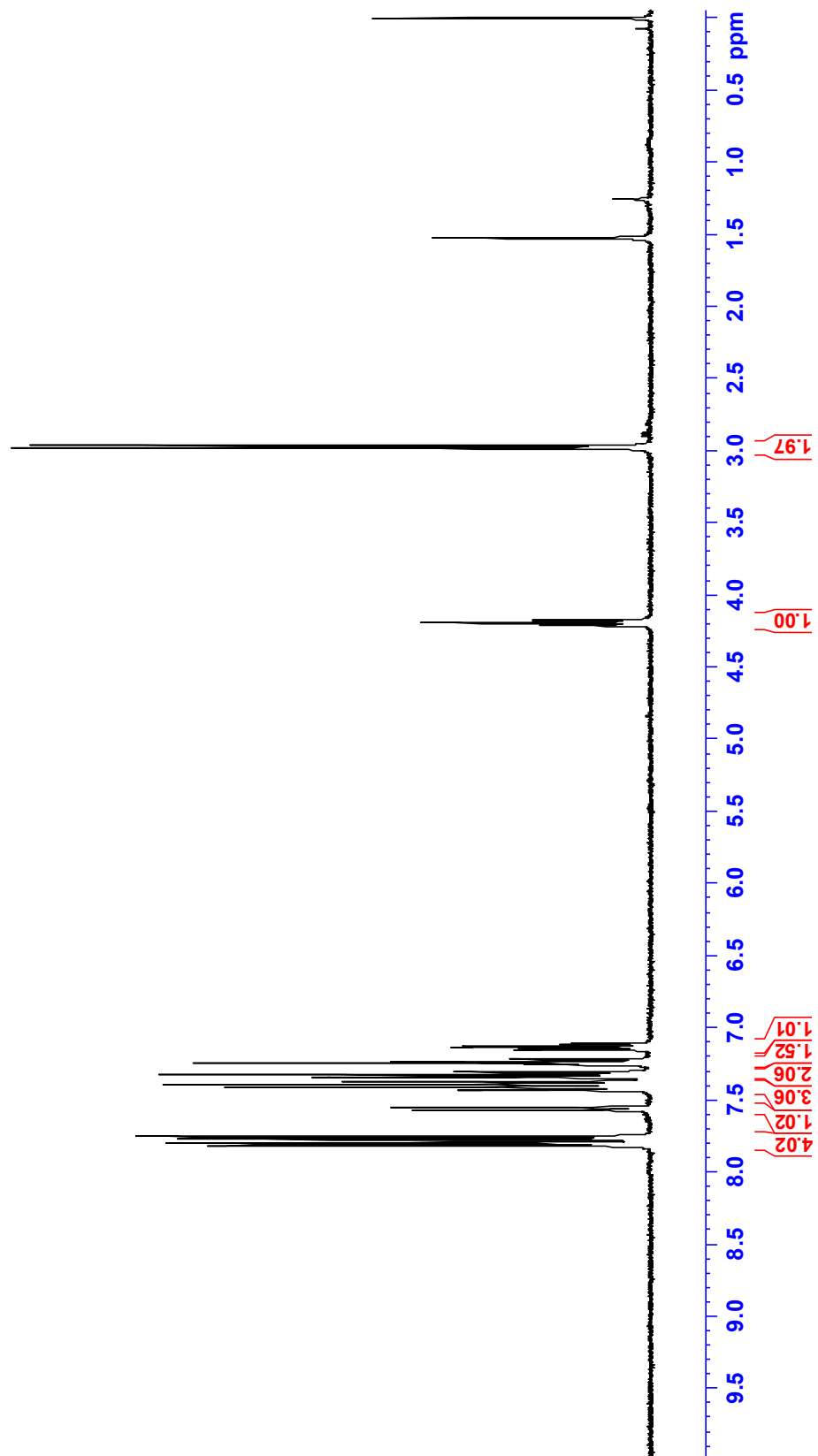
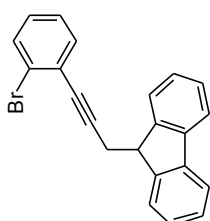


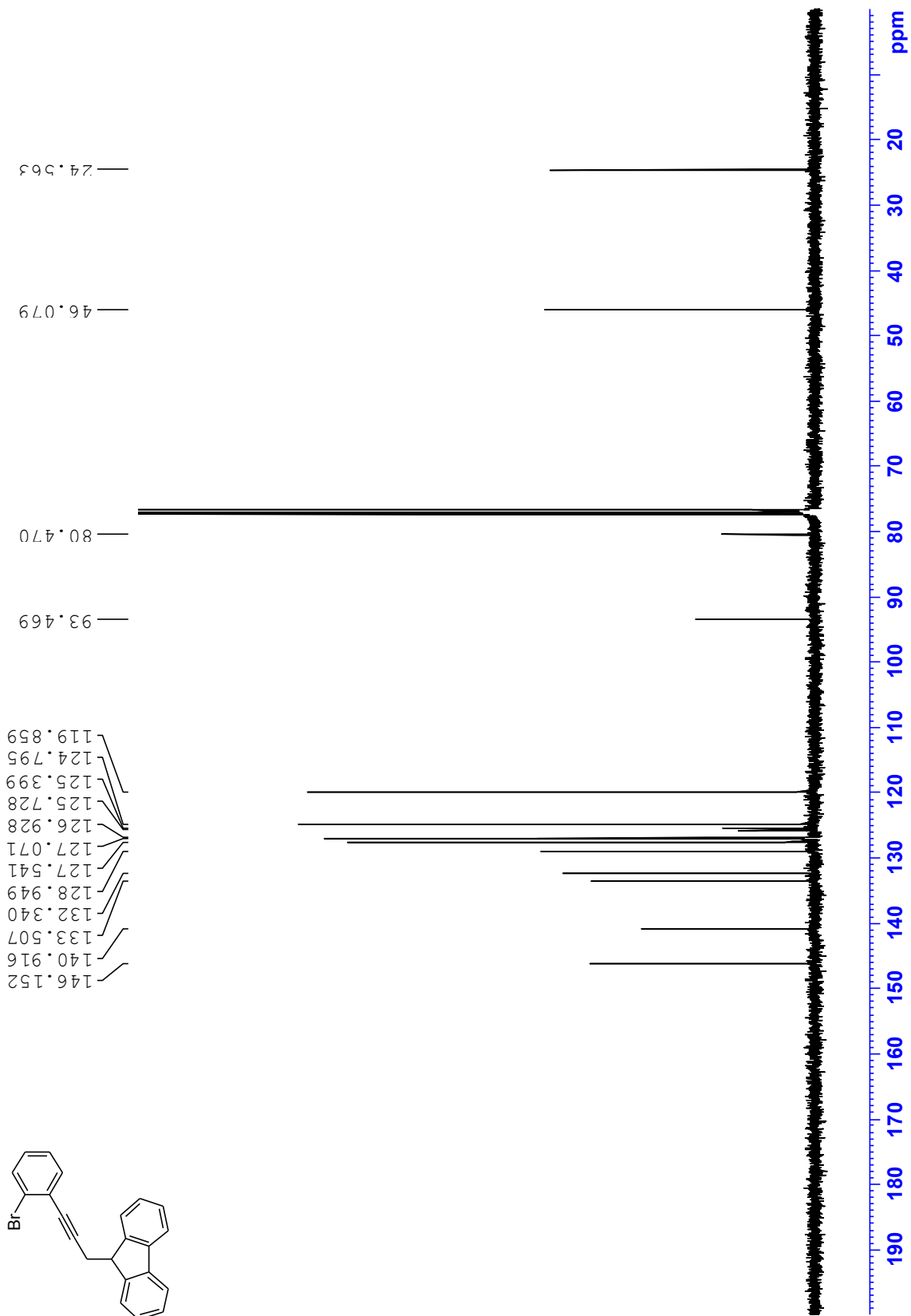
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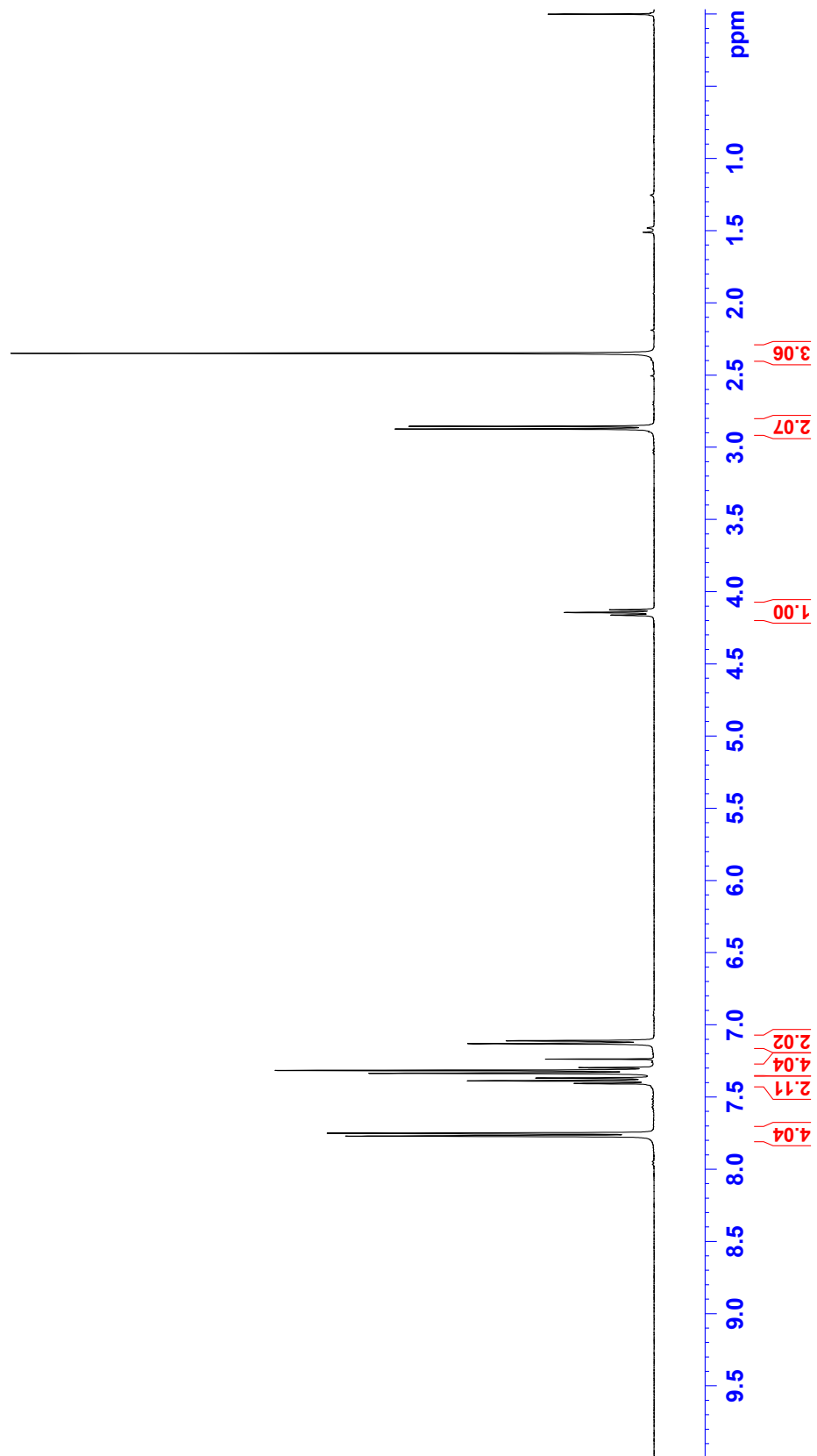
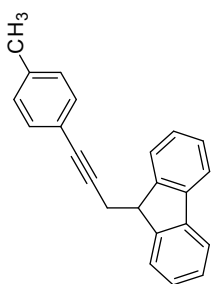




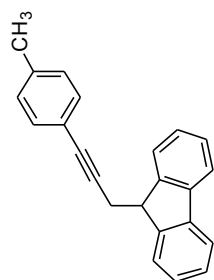










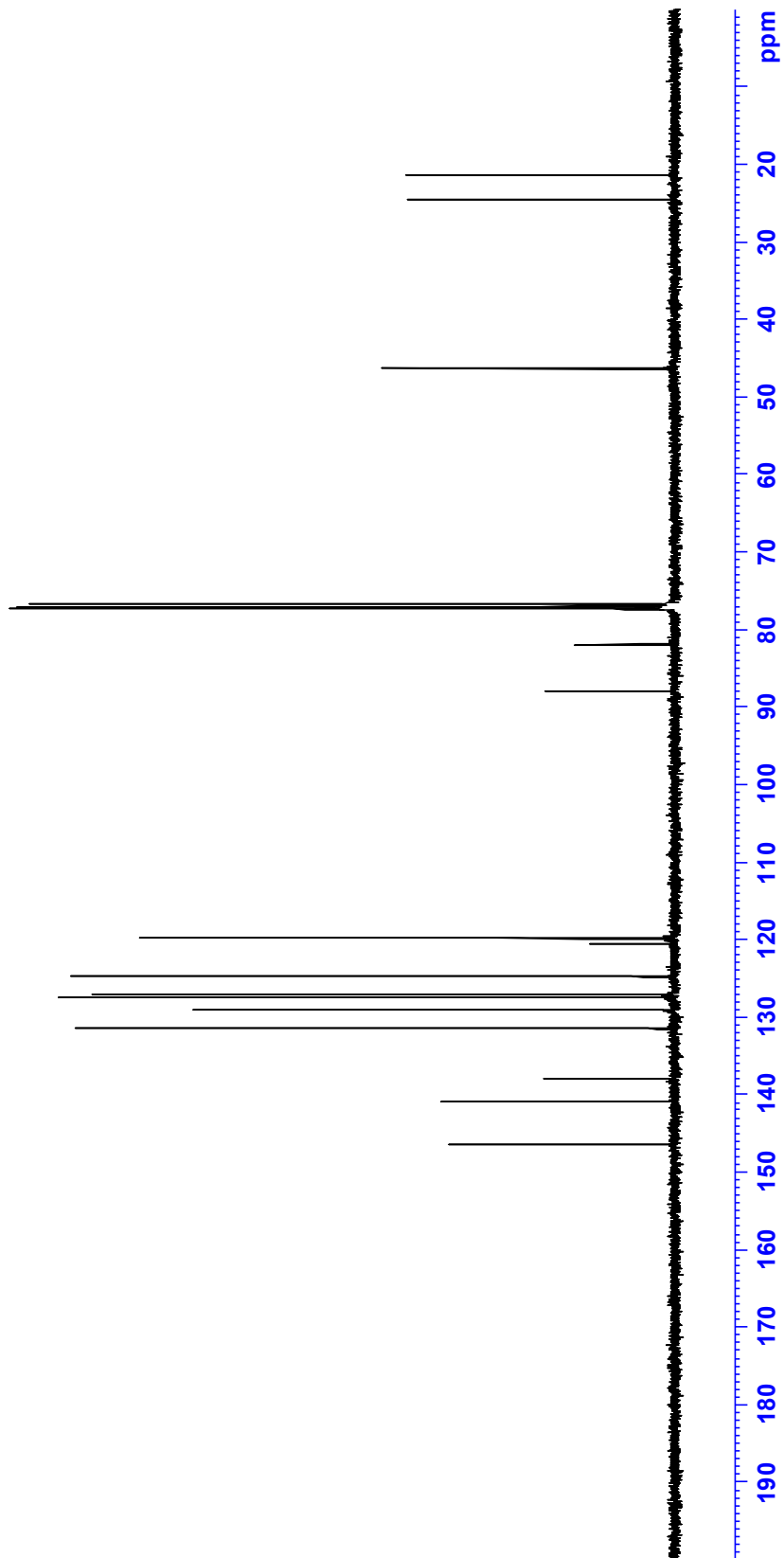


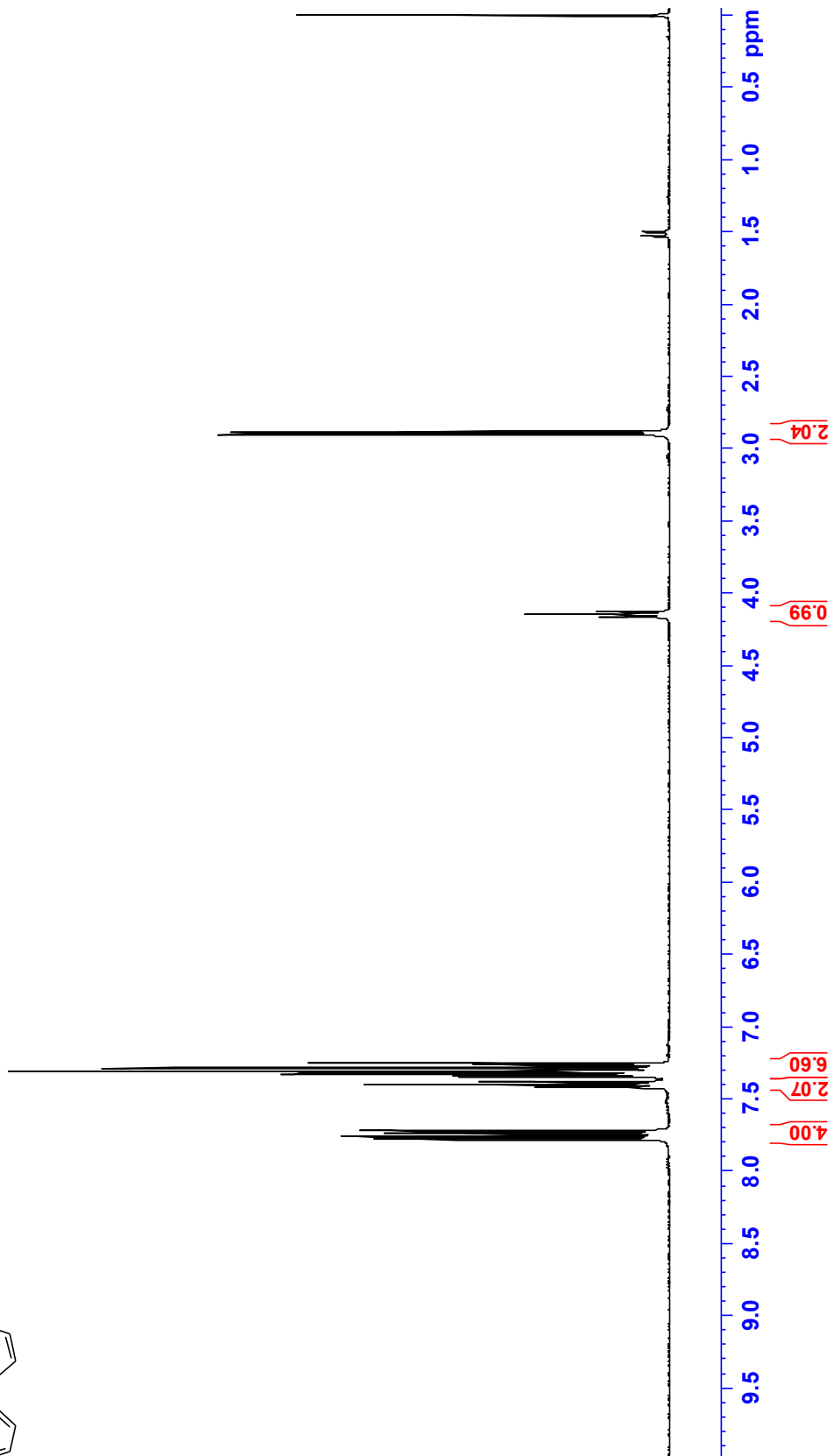
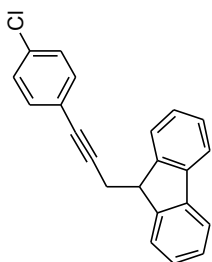
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131.437  
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119.830

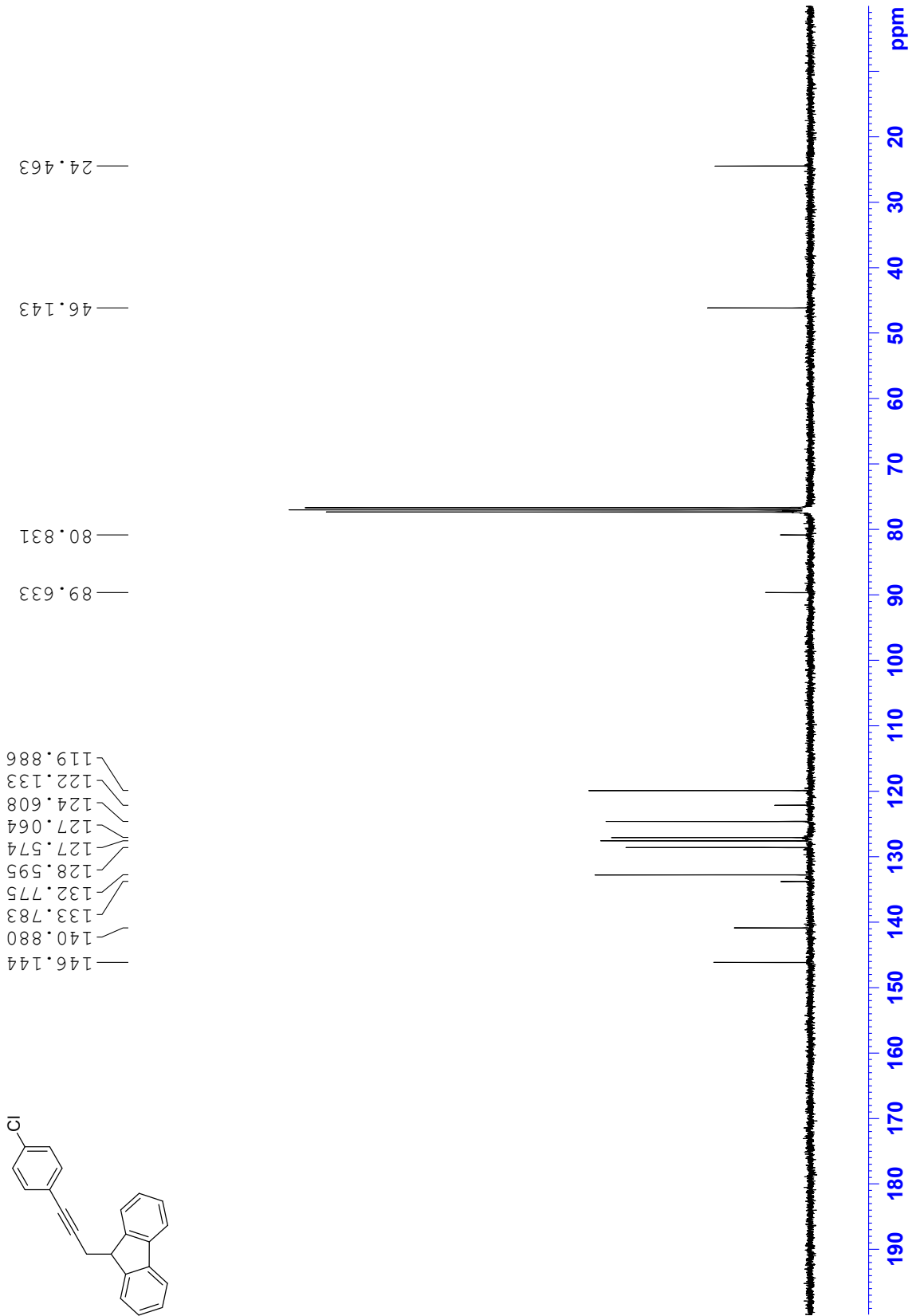
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81.919

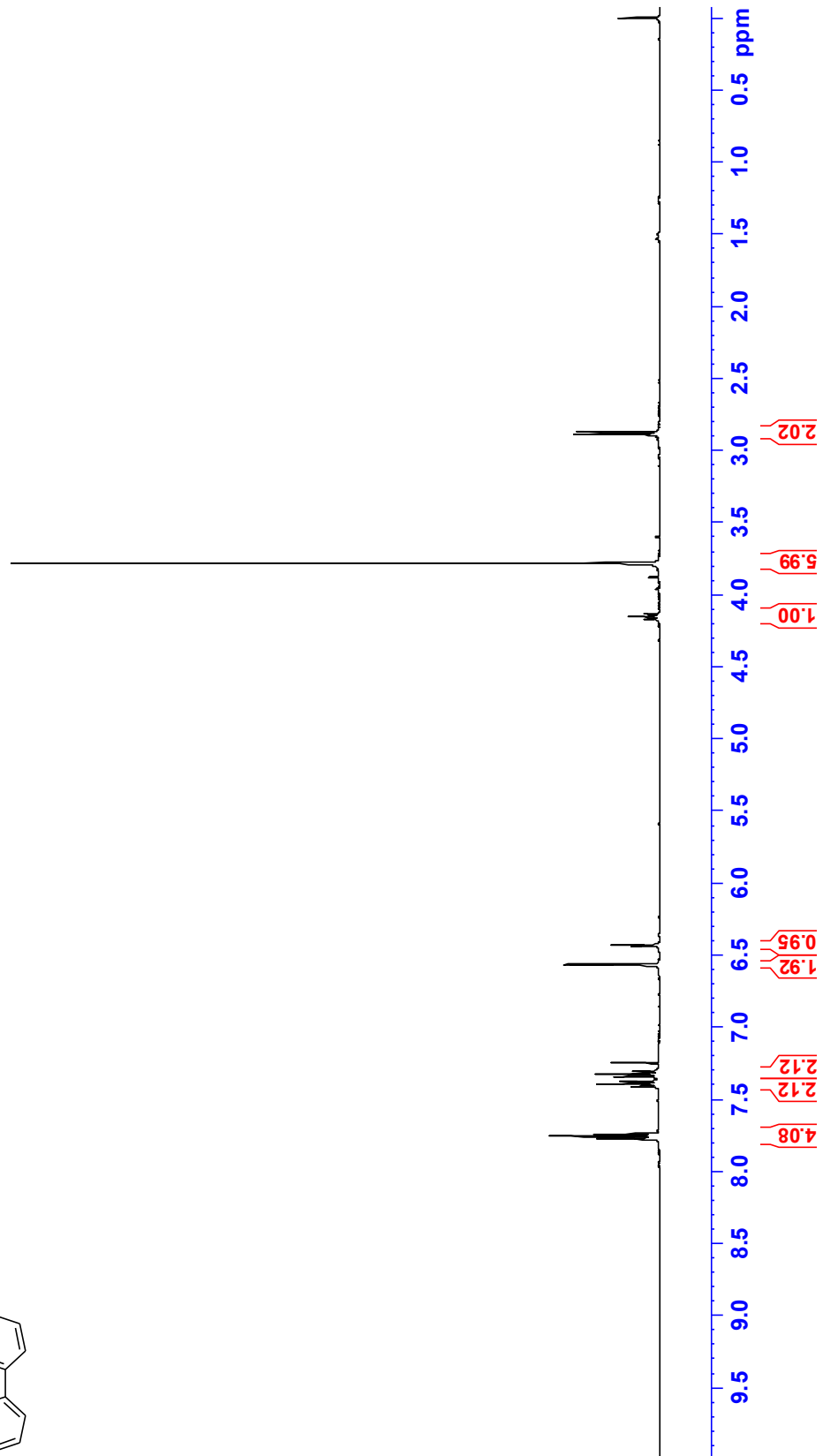
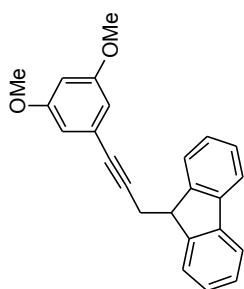
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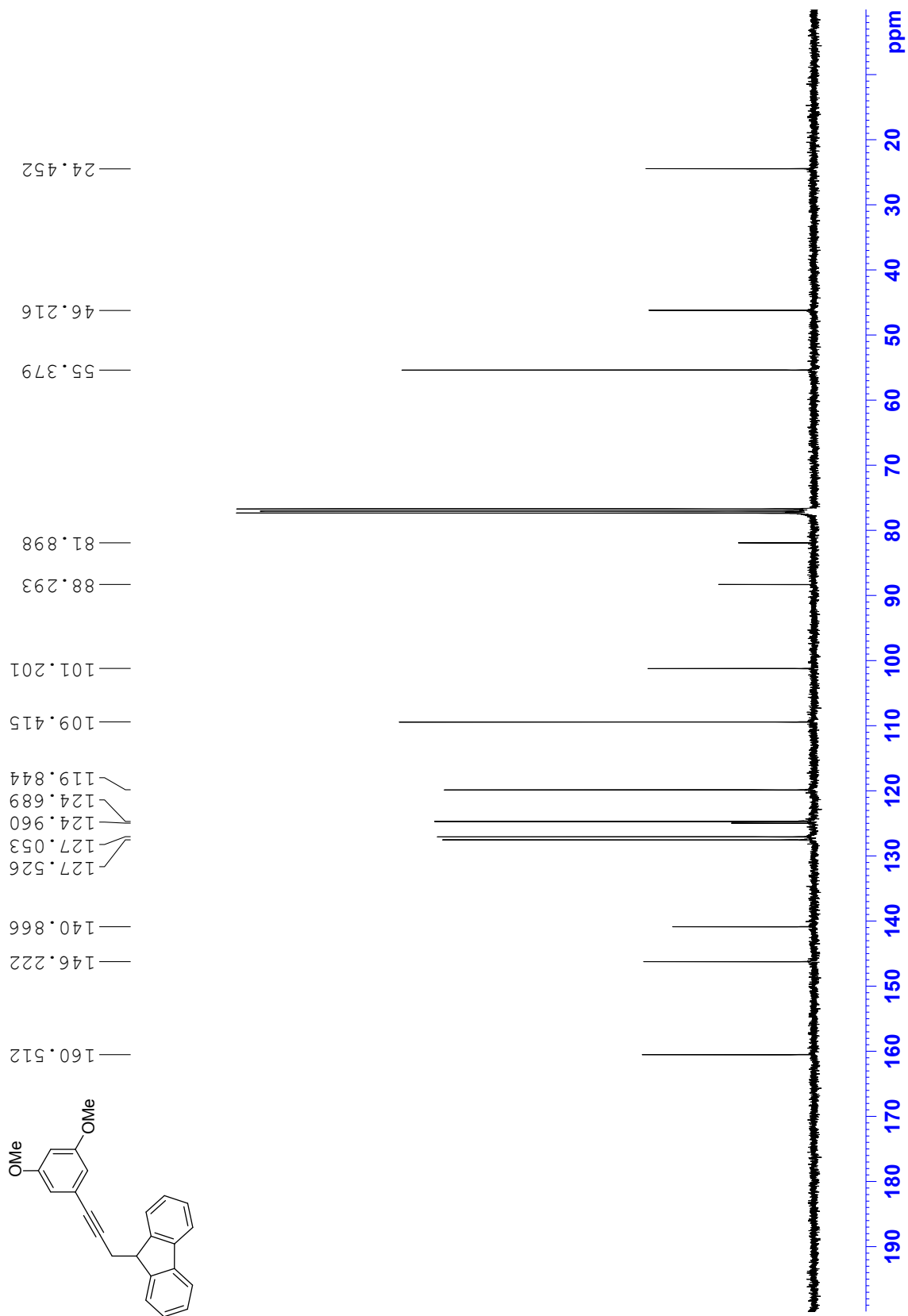
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21.428

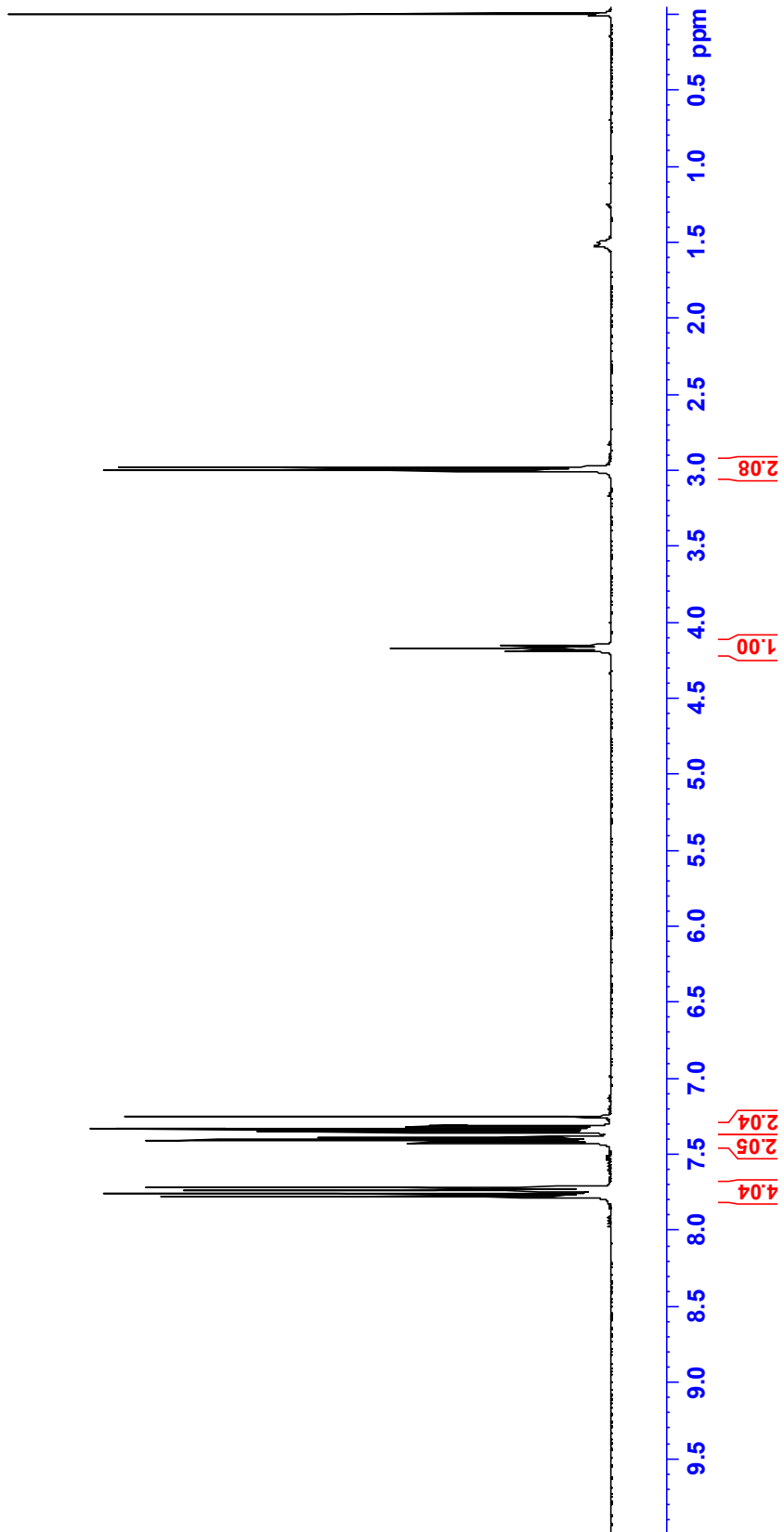
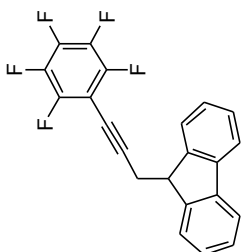




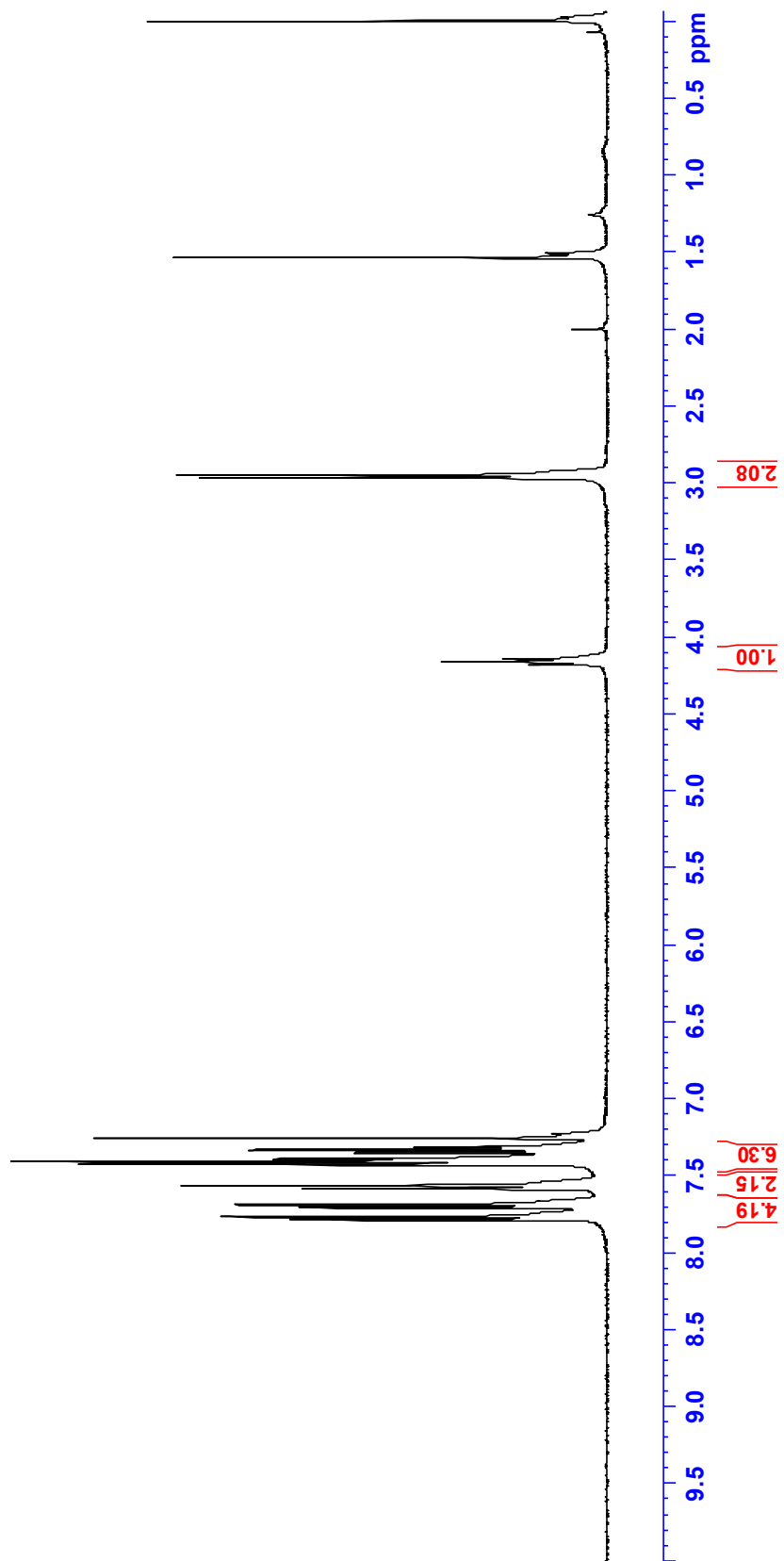
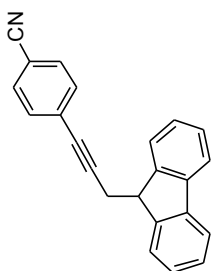




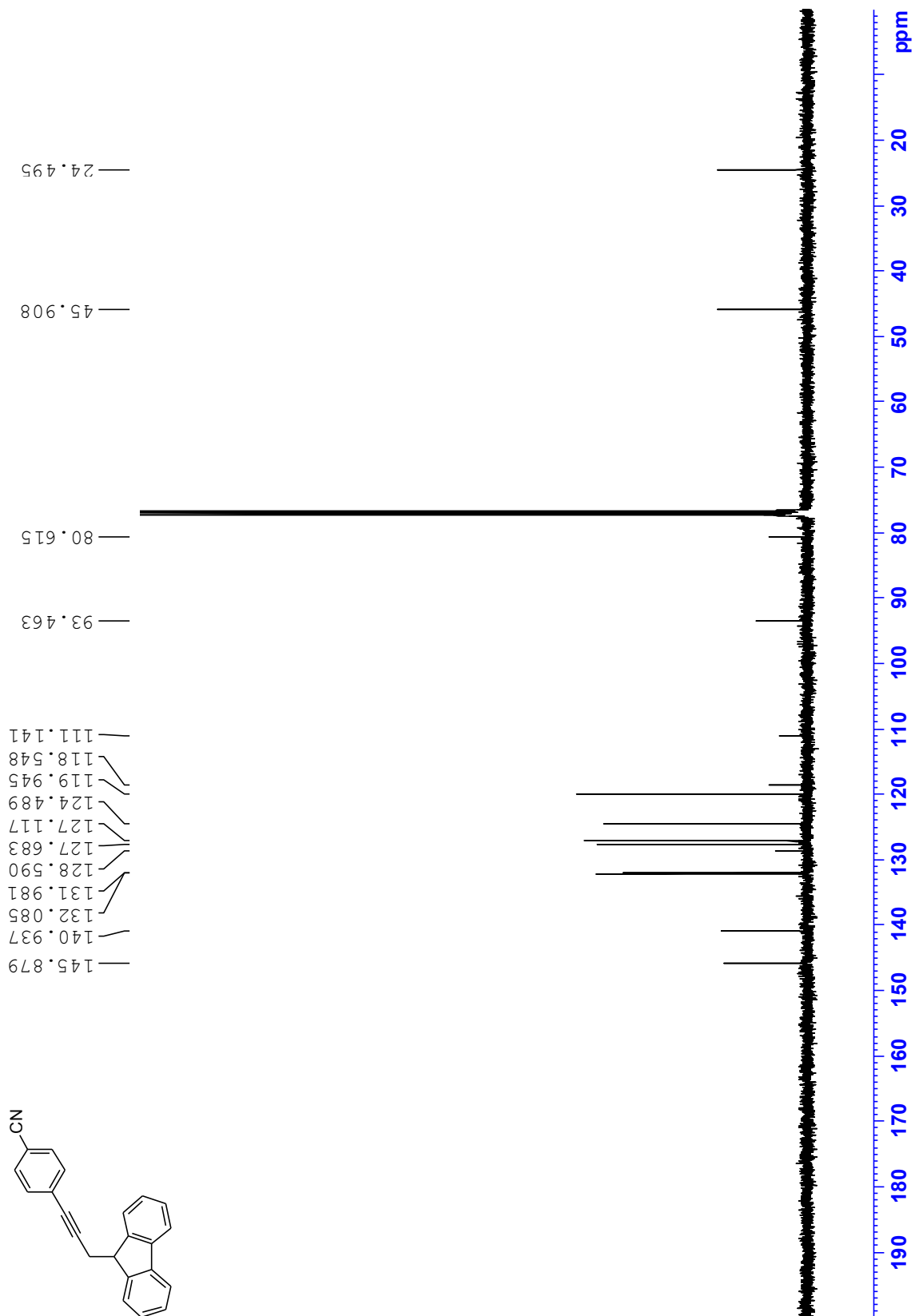


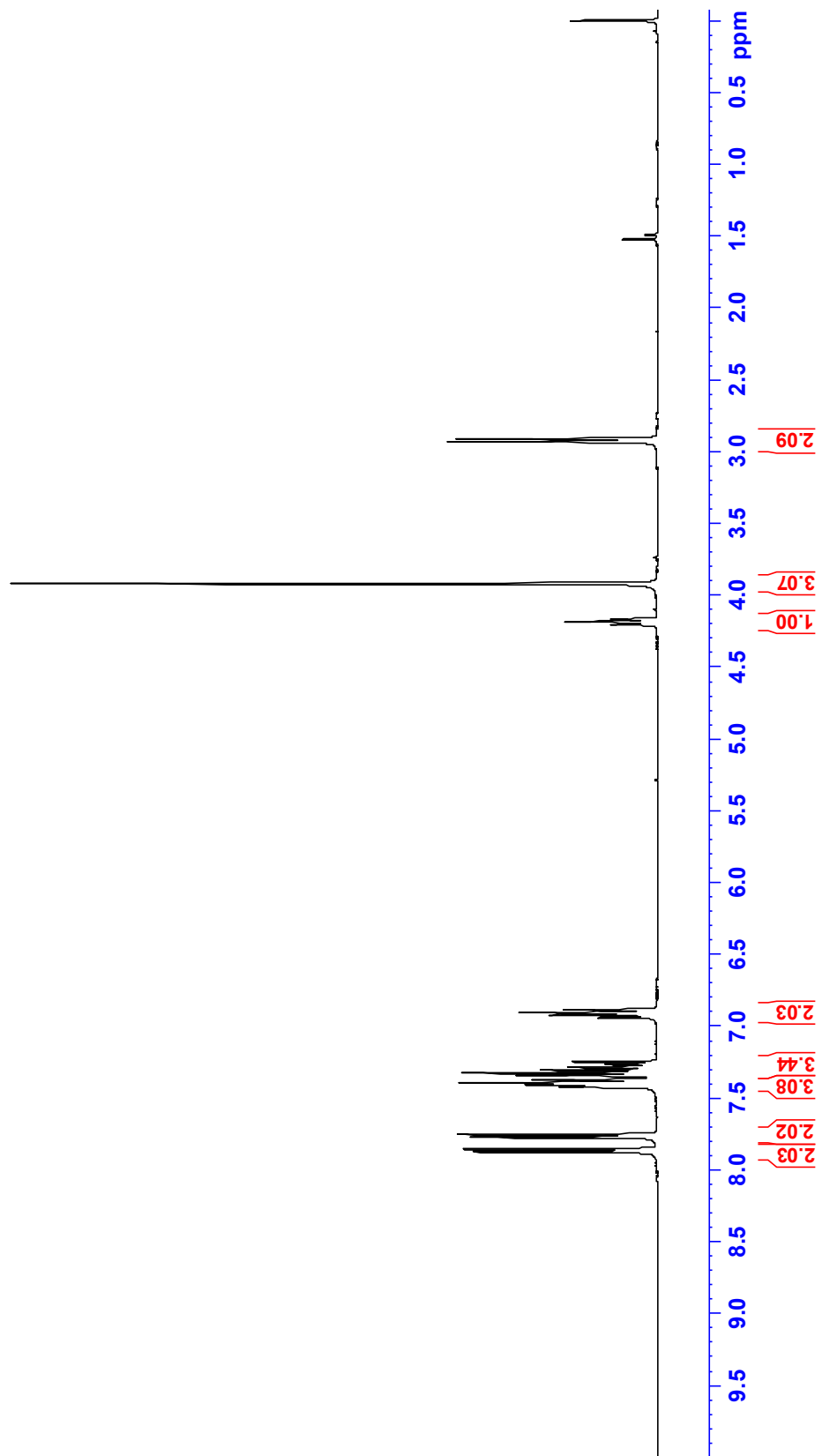
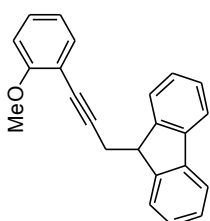


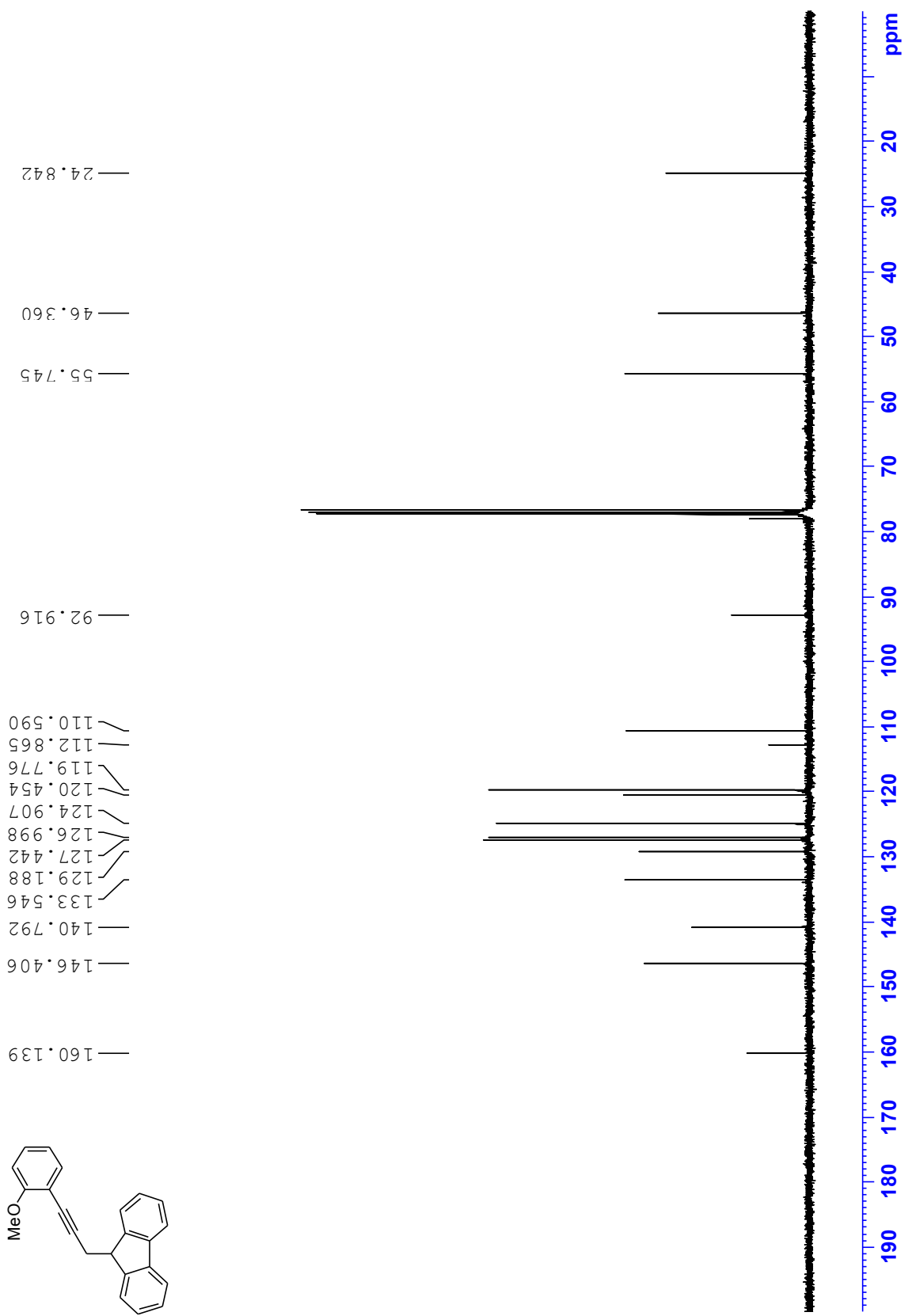
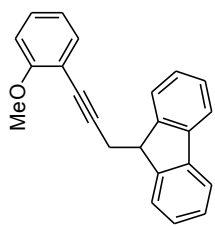


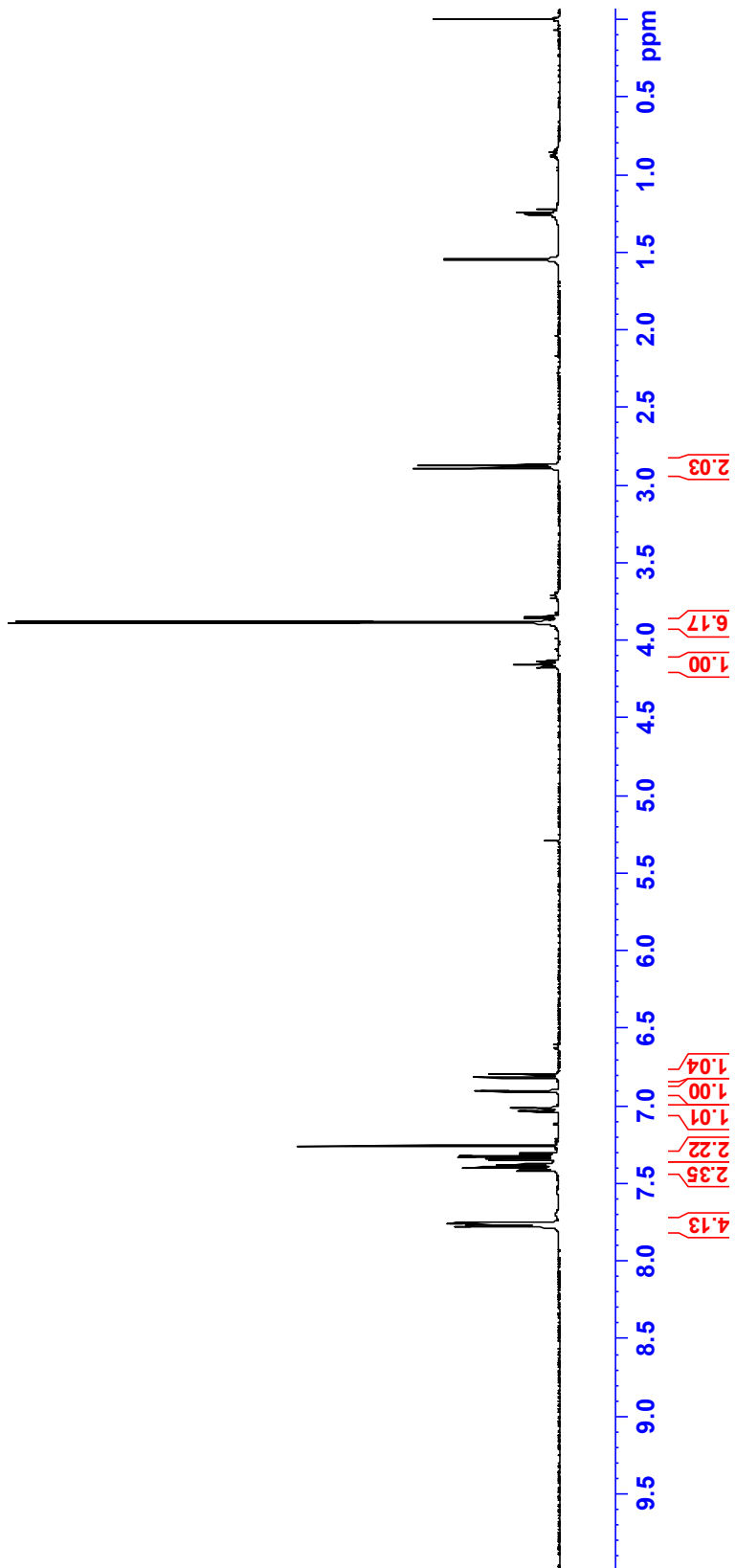
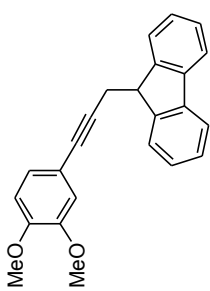


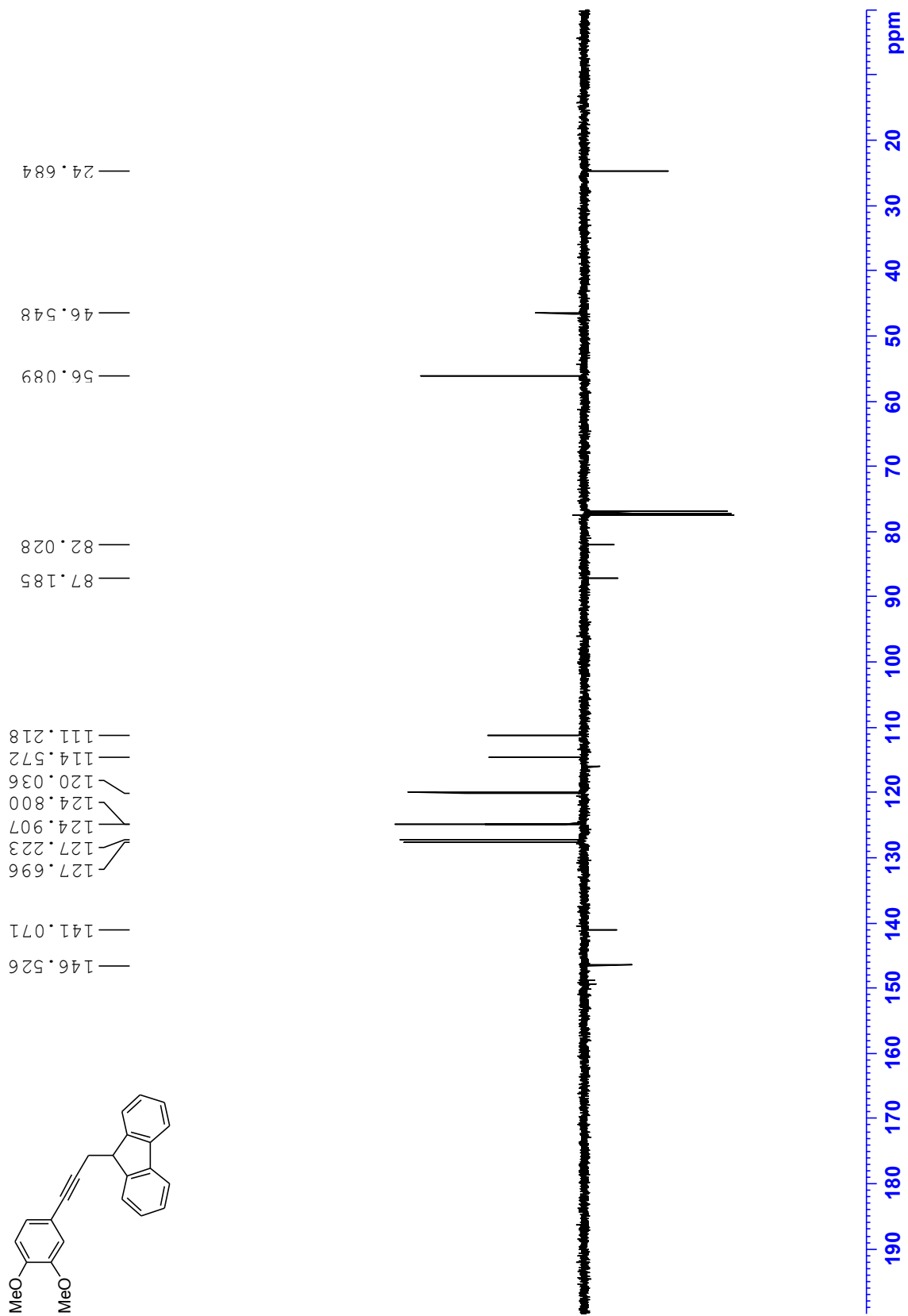
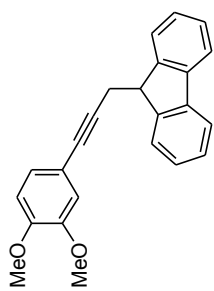


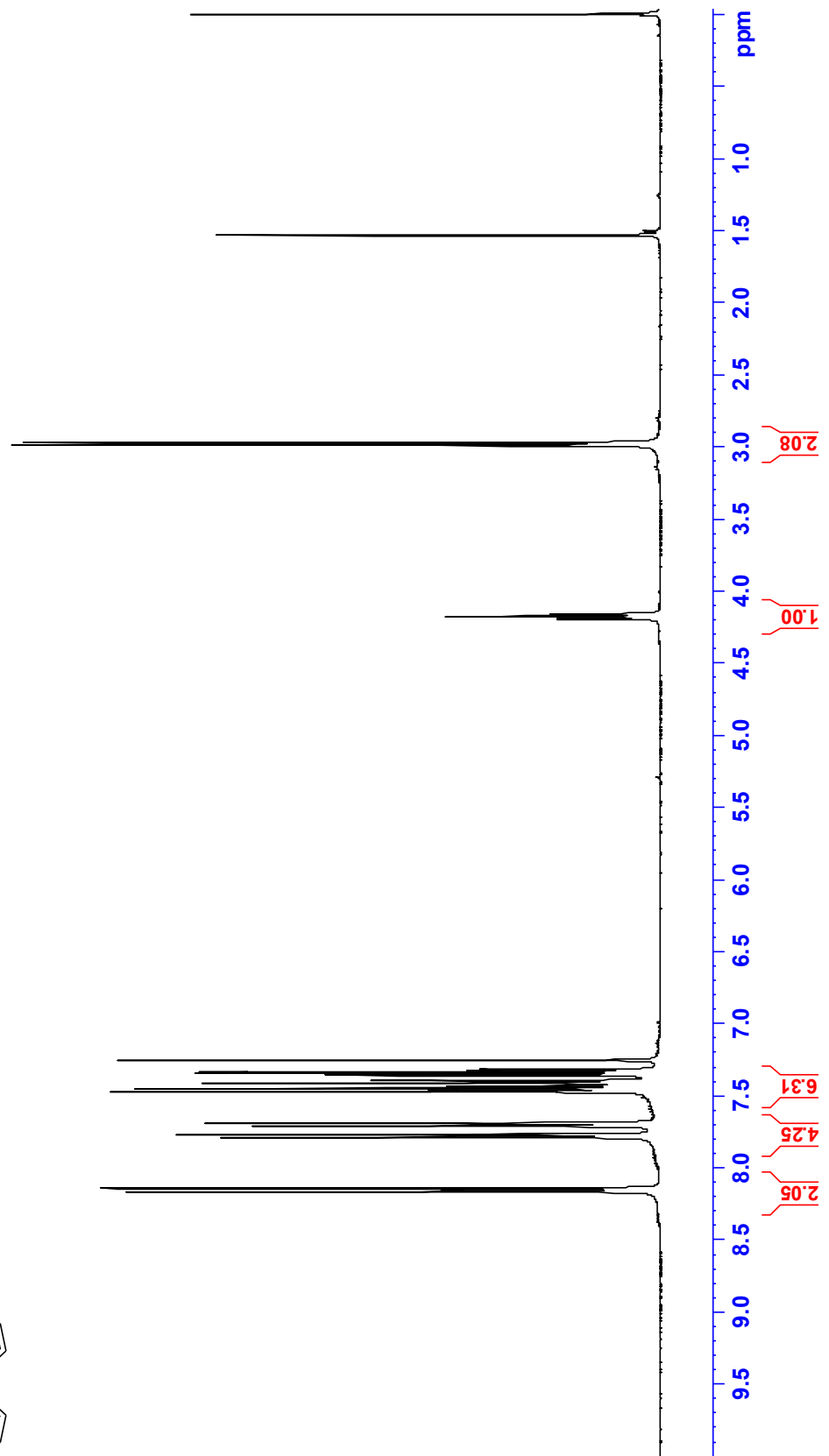
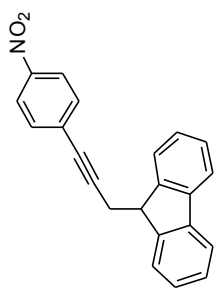


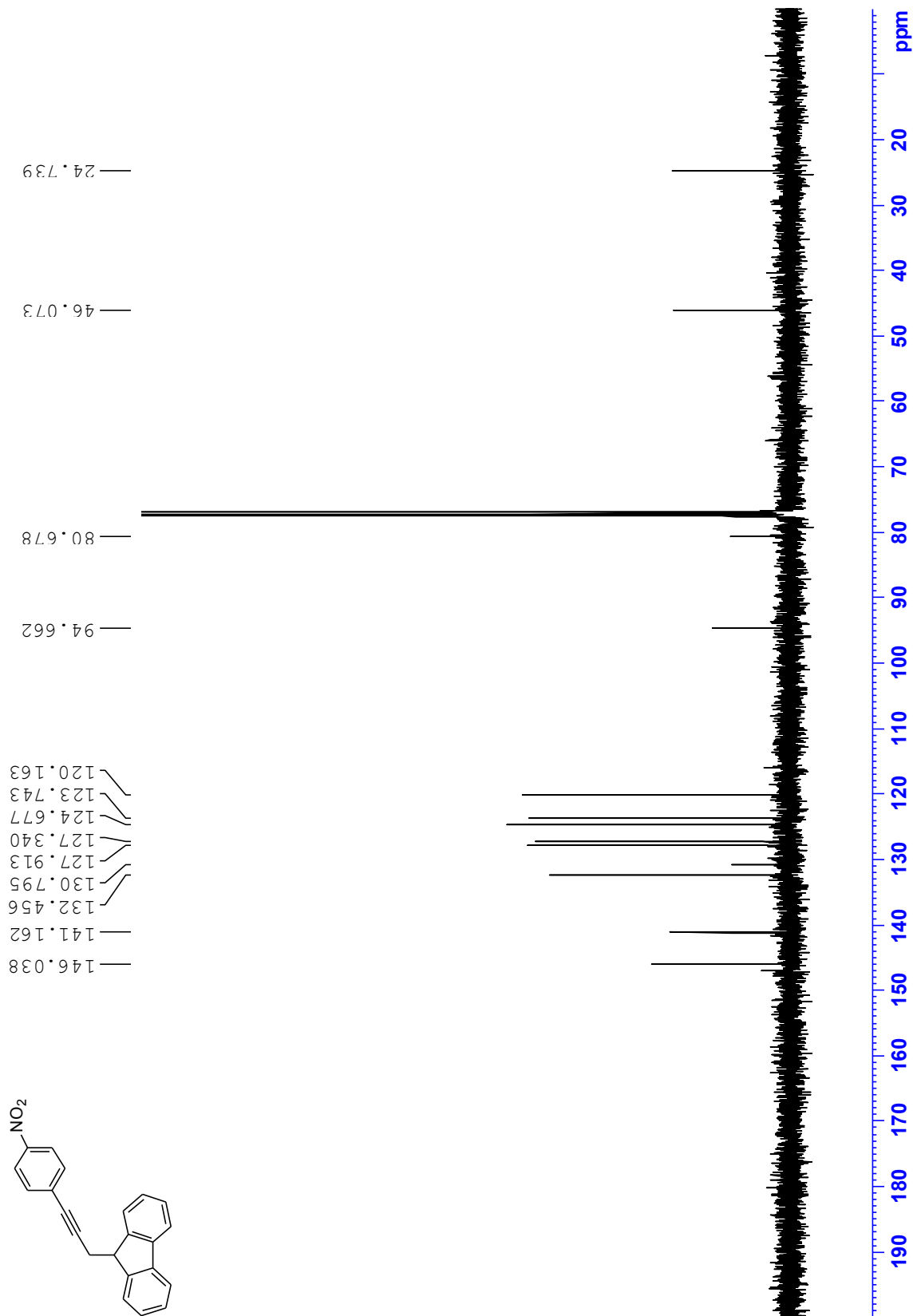


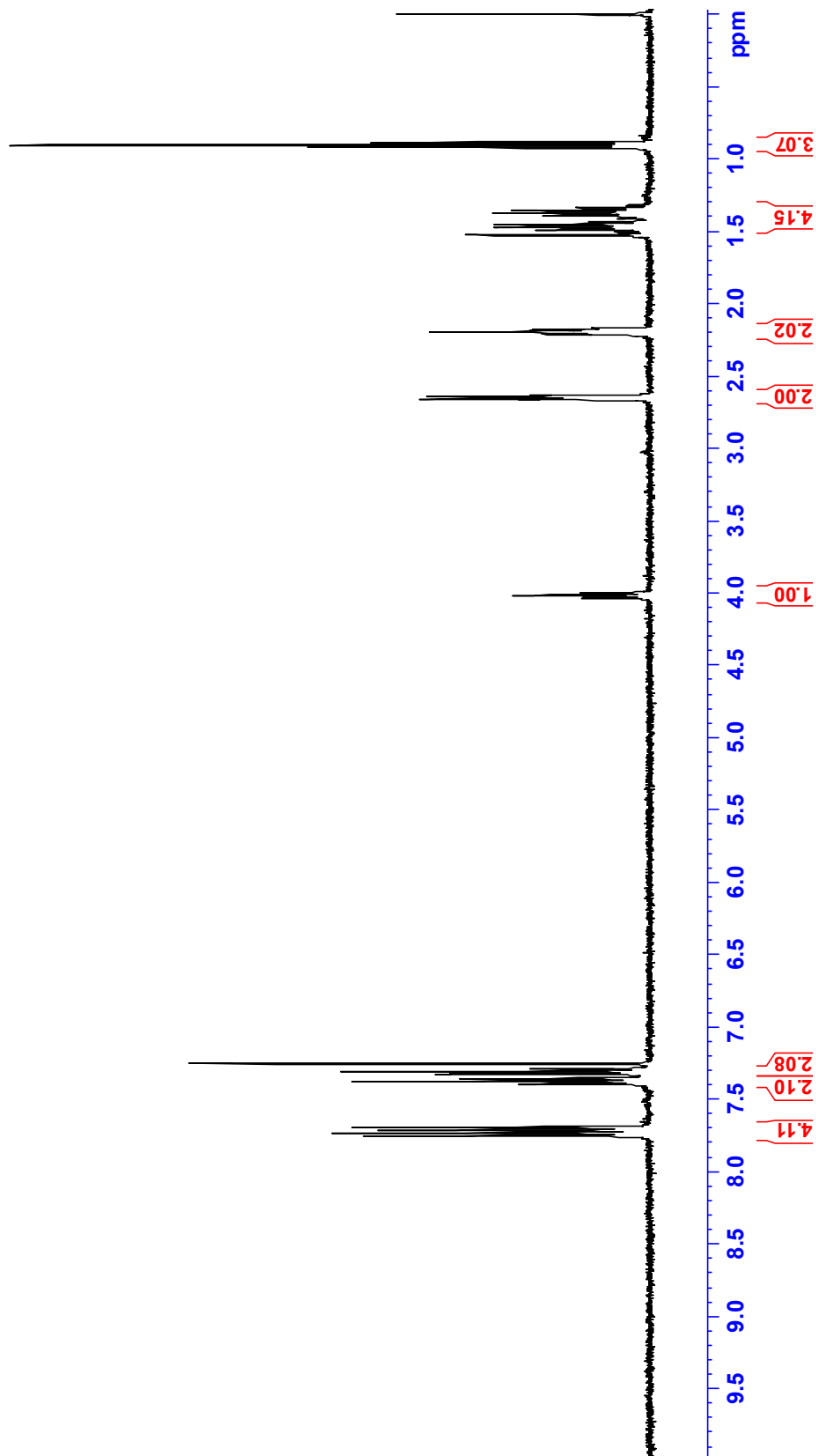
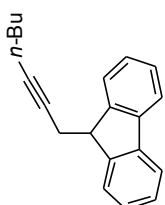




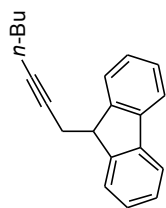




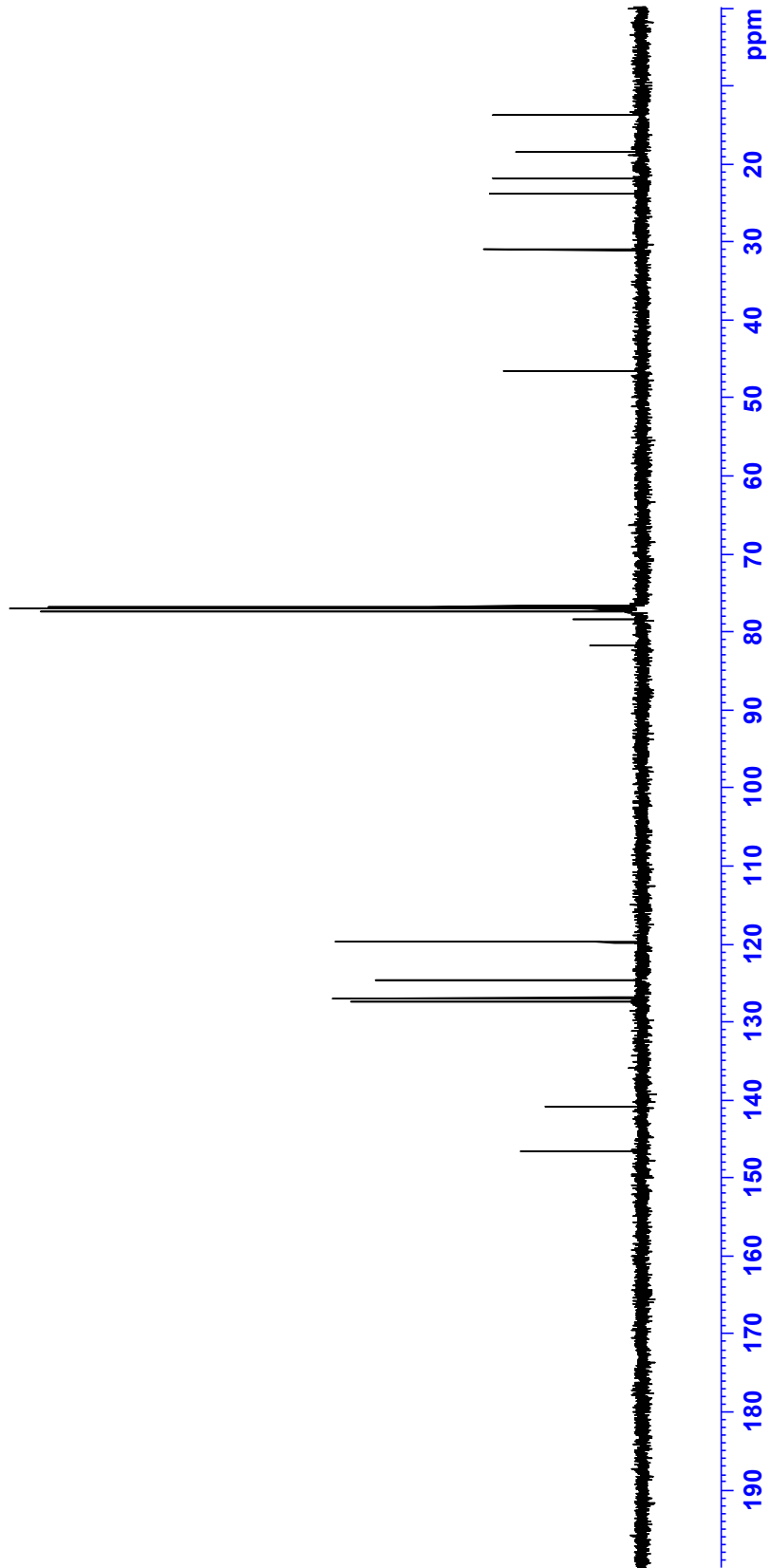


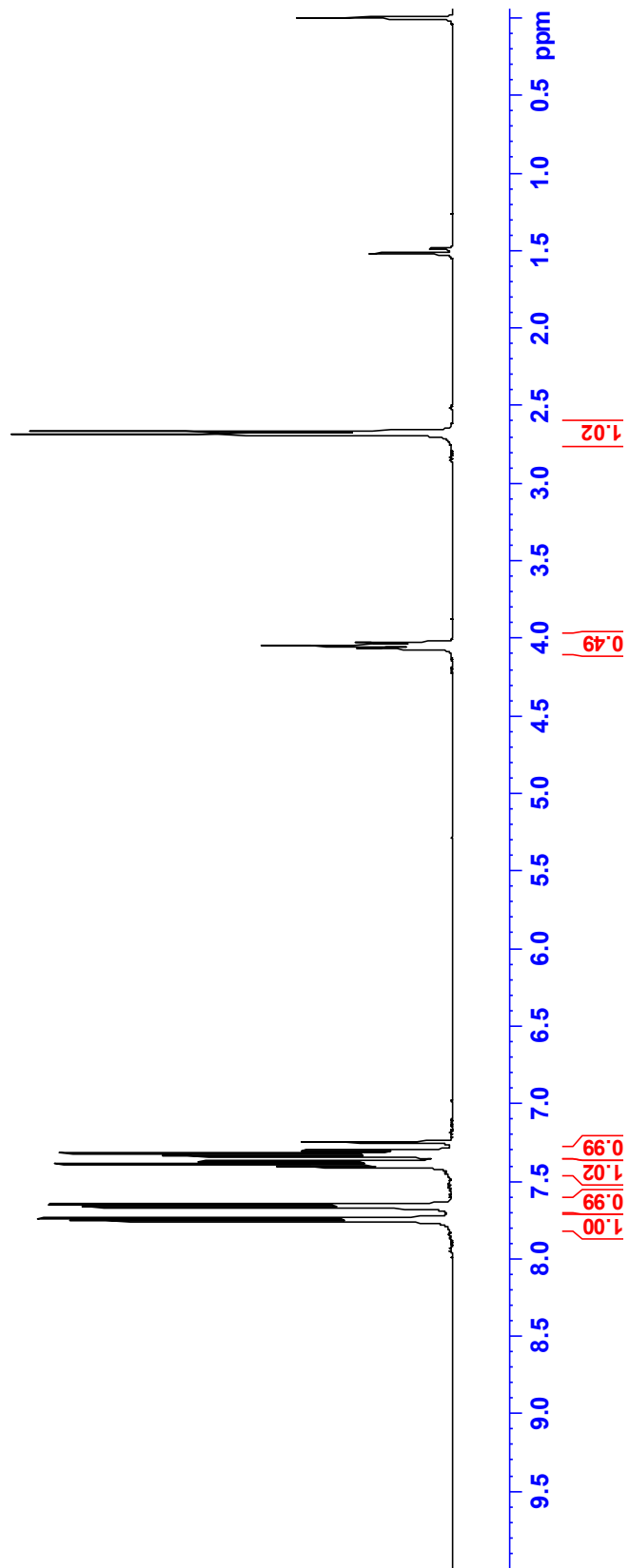
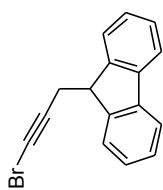


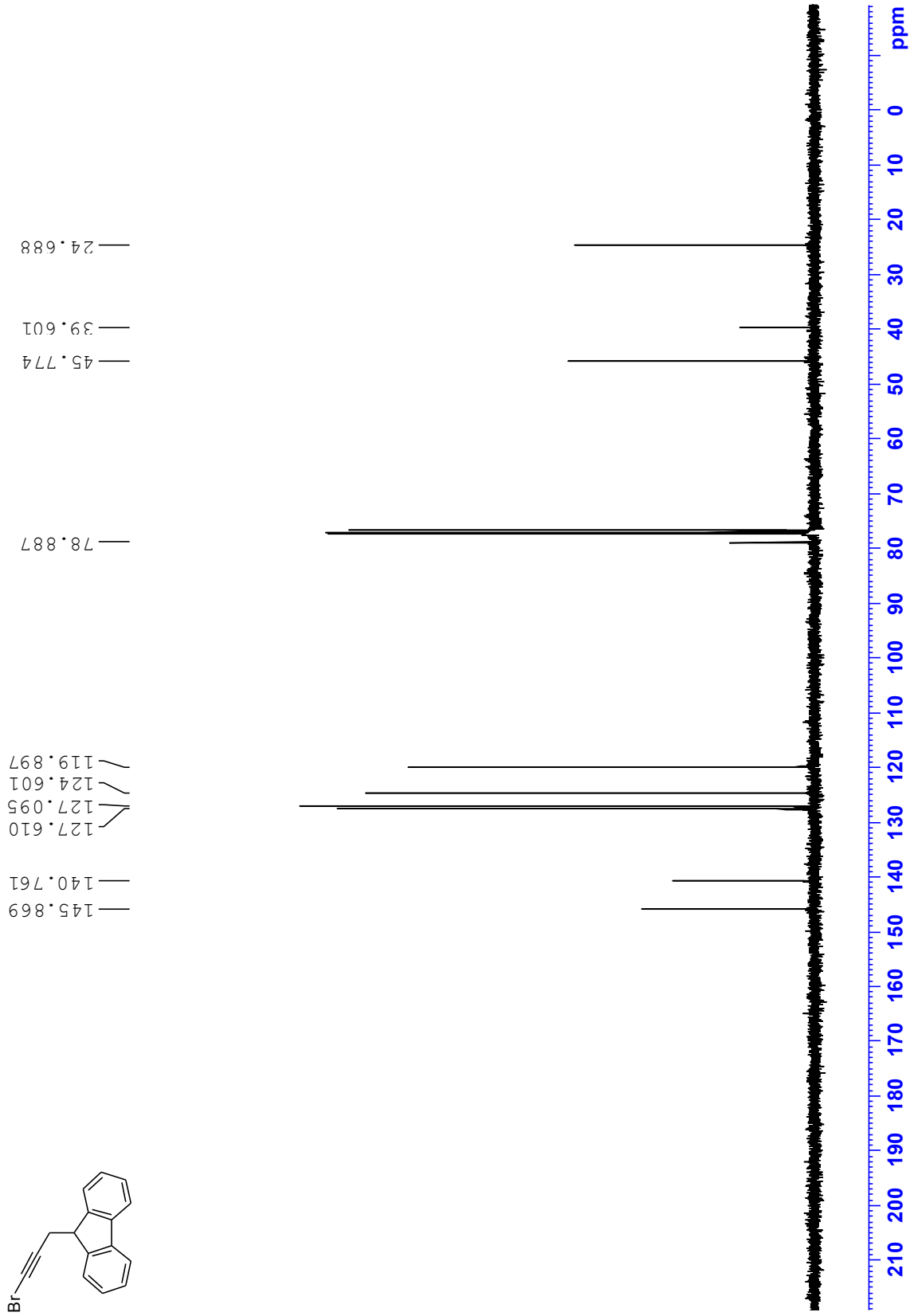
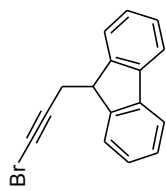


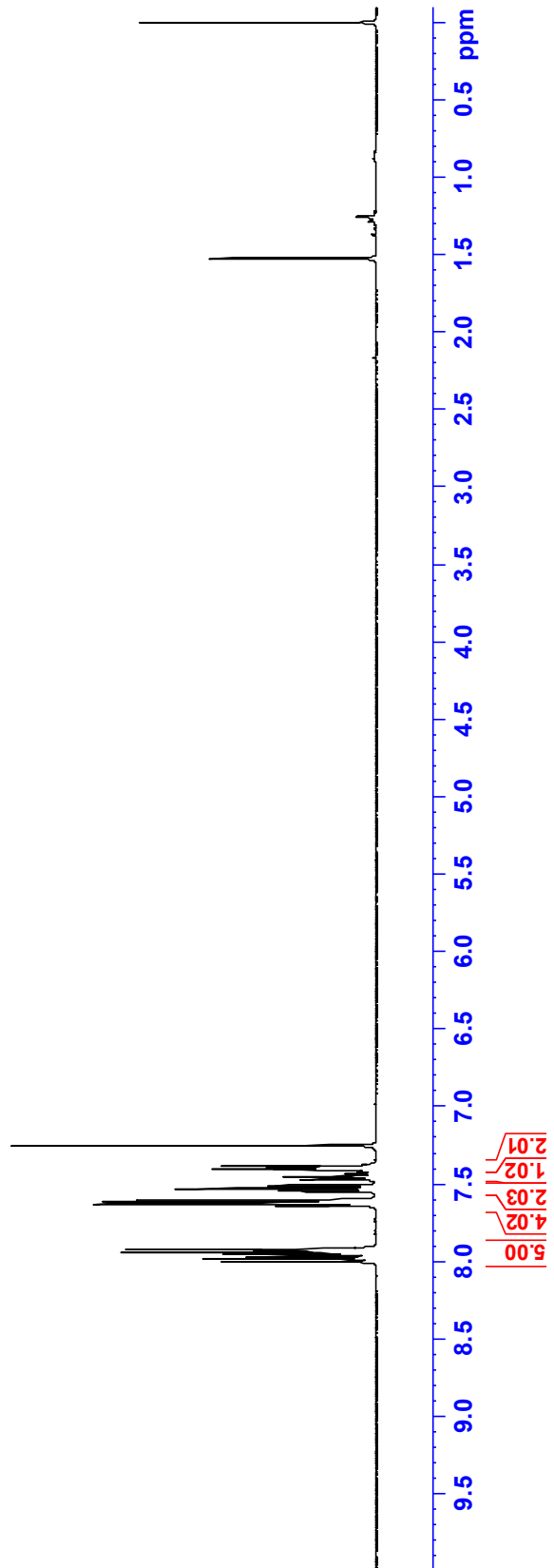
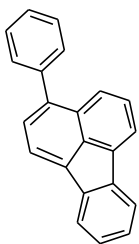


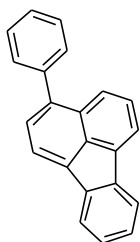
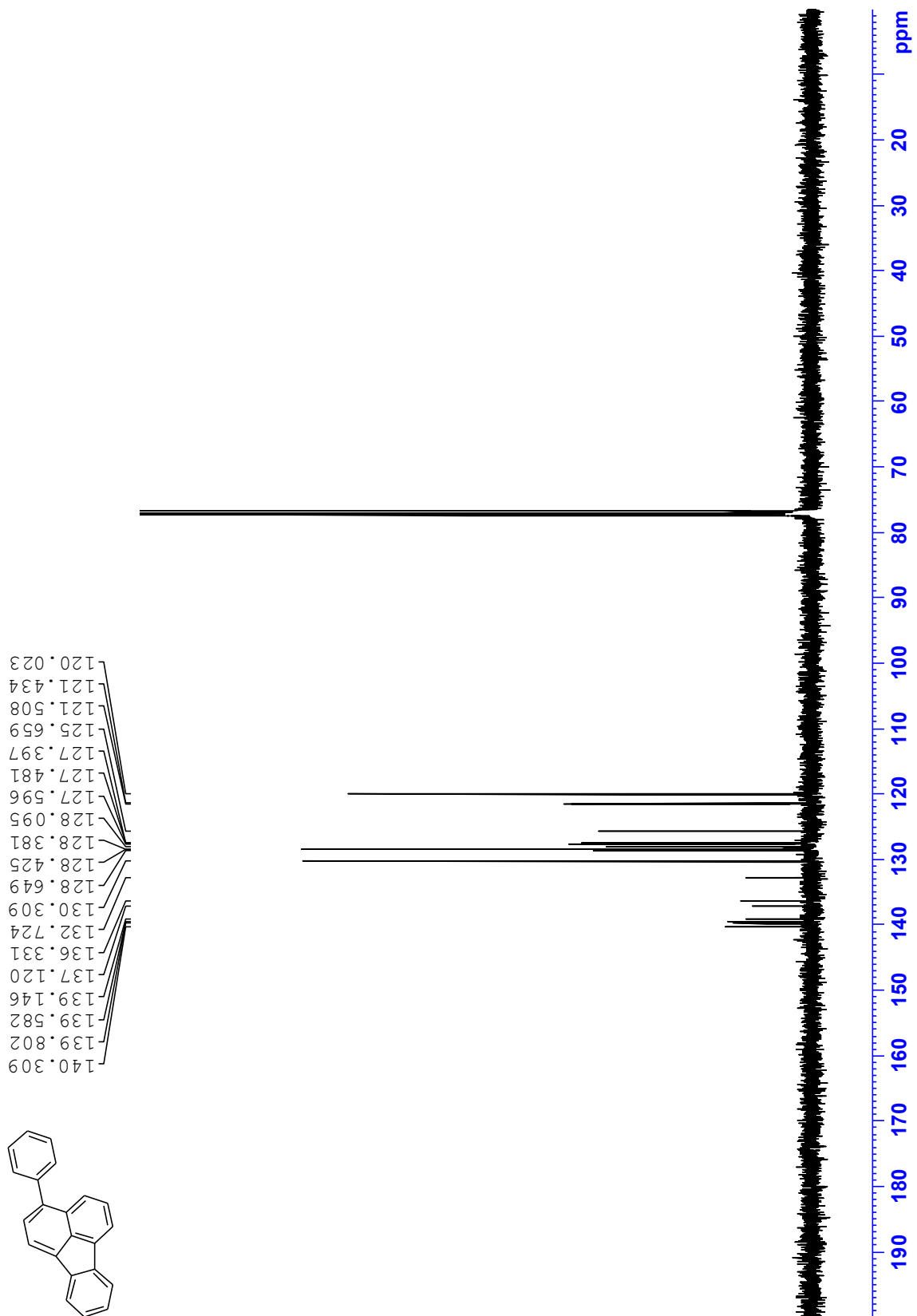
- 146.553
- 140.850
- 127.334
- 126.891
- 124.638
- 119.741
- 81.695
- 78.411
- 46.531
- 30.986
- 23.756
- 21.858
- 18.442
- 13.638

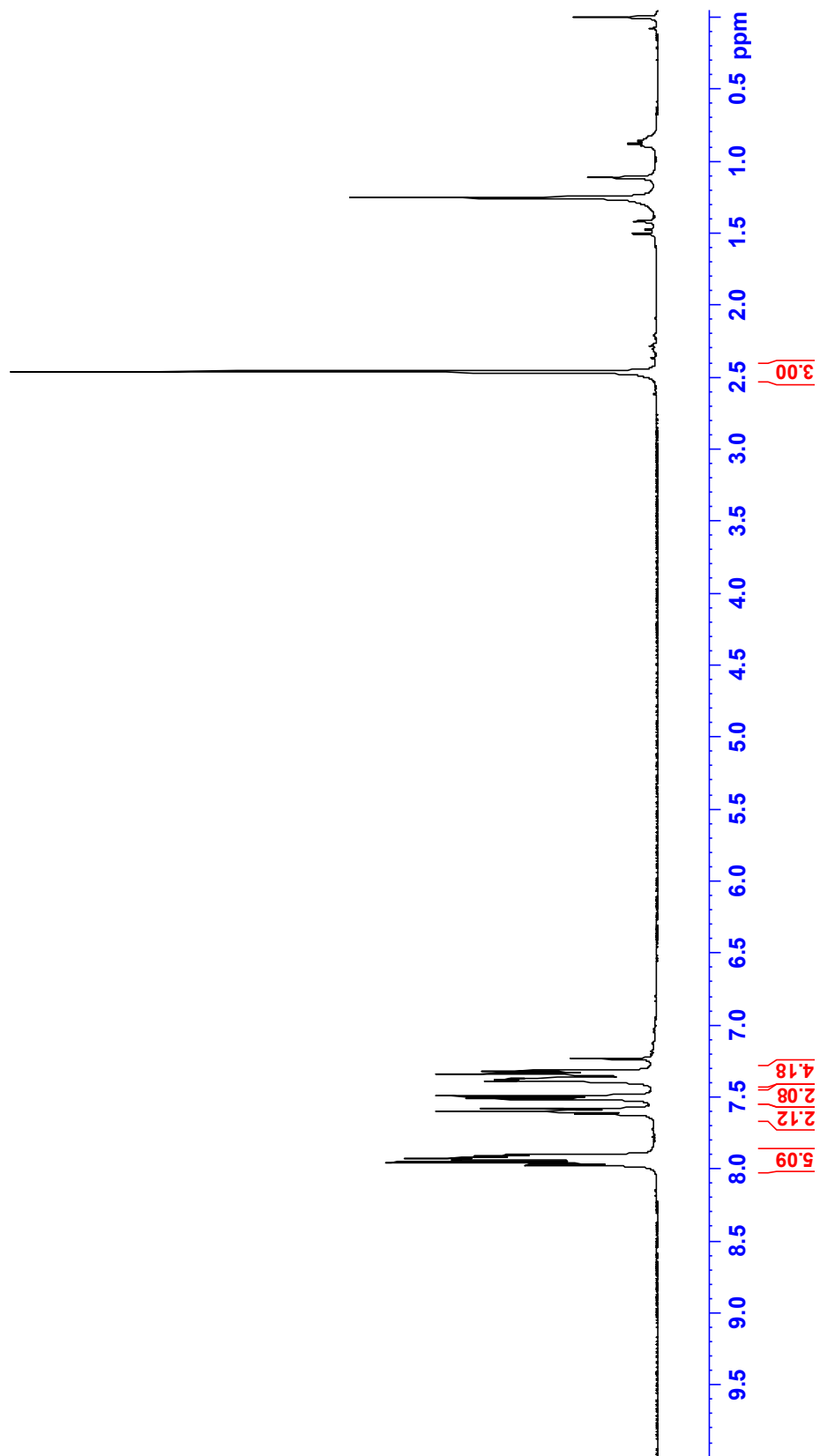
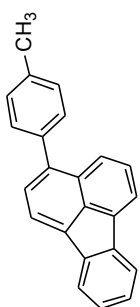


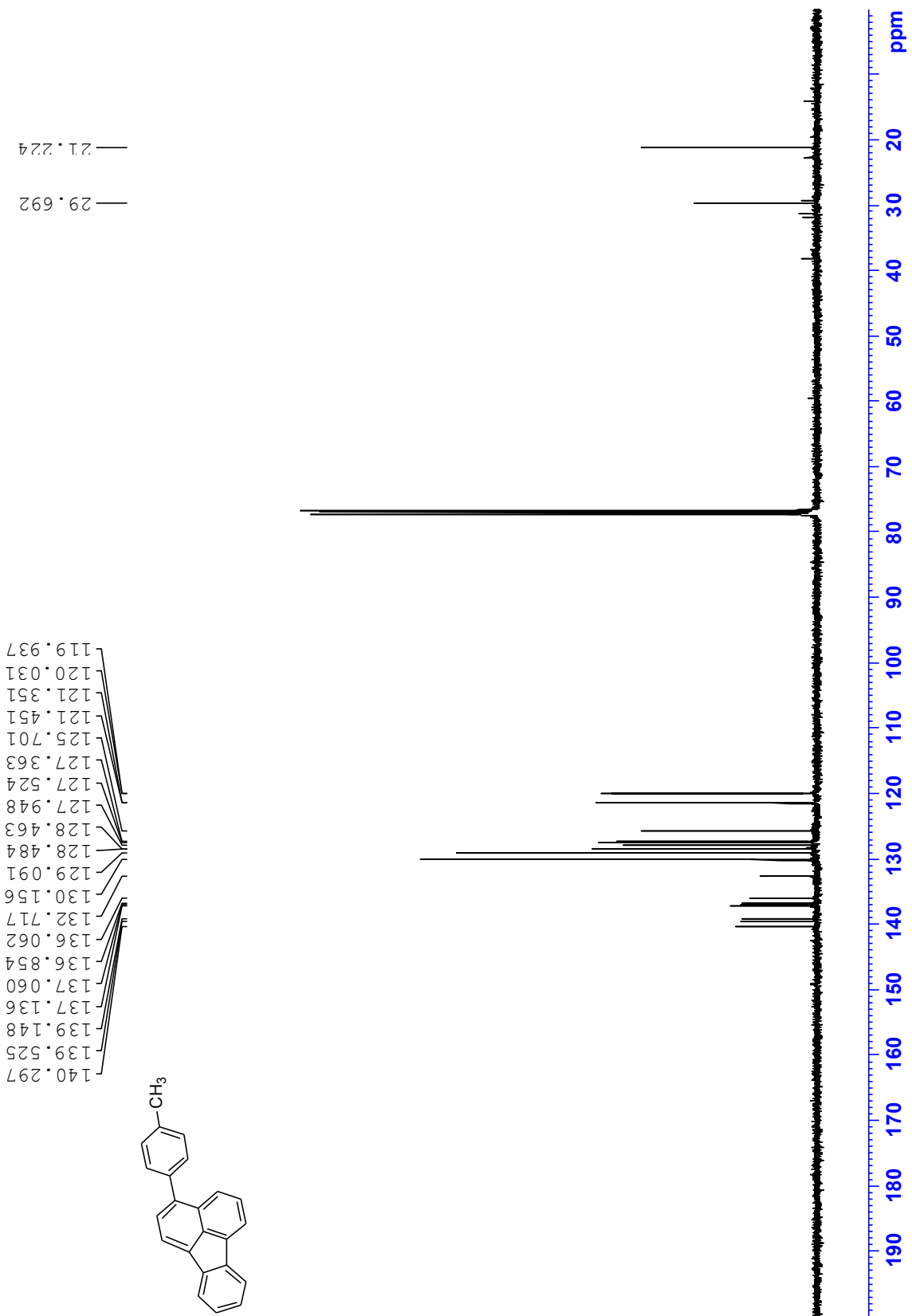


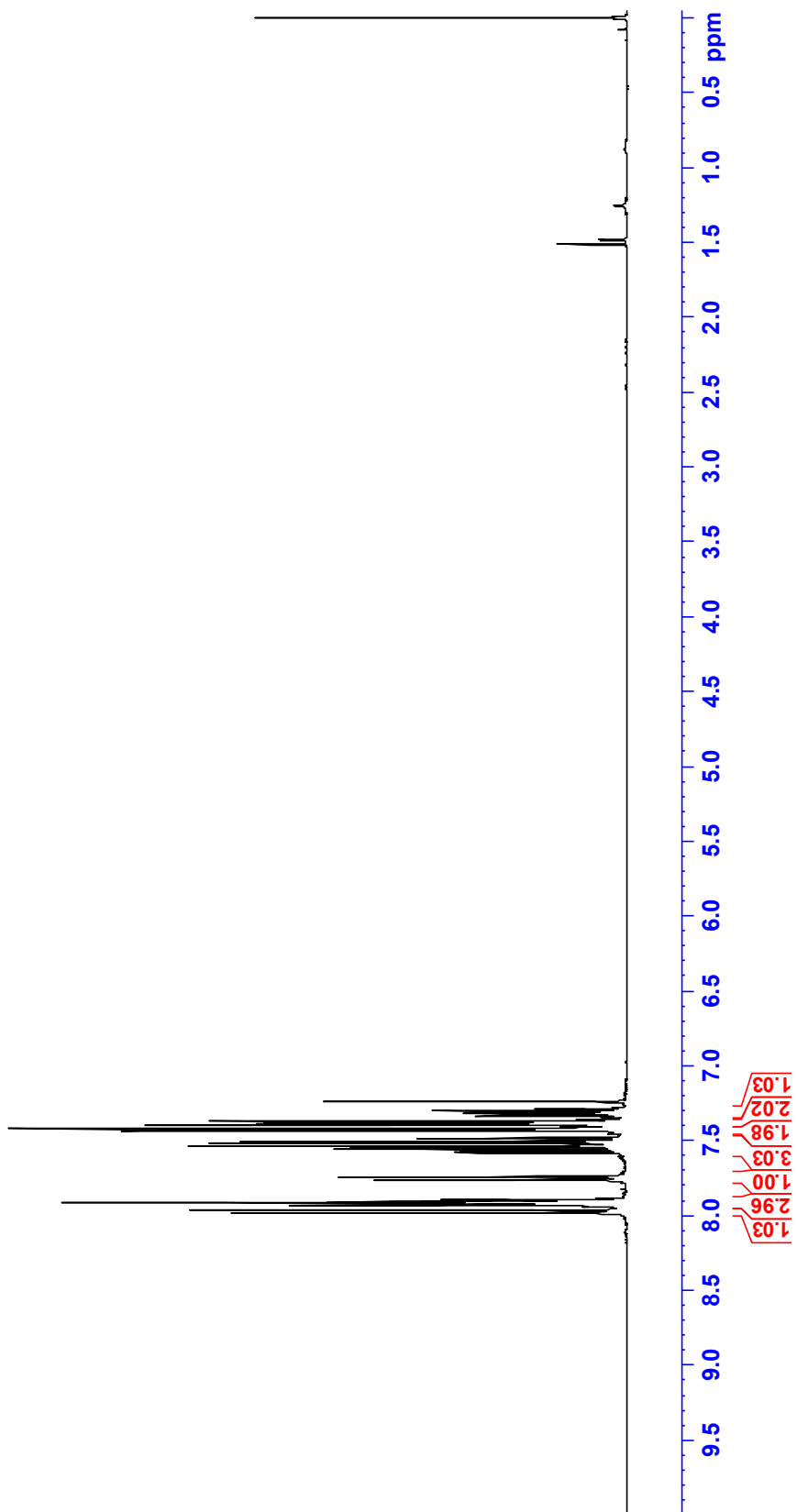
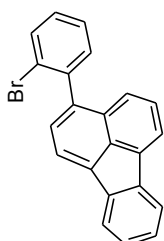




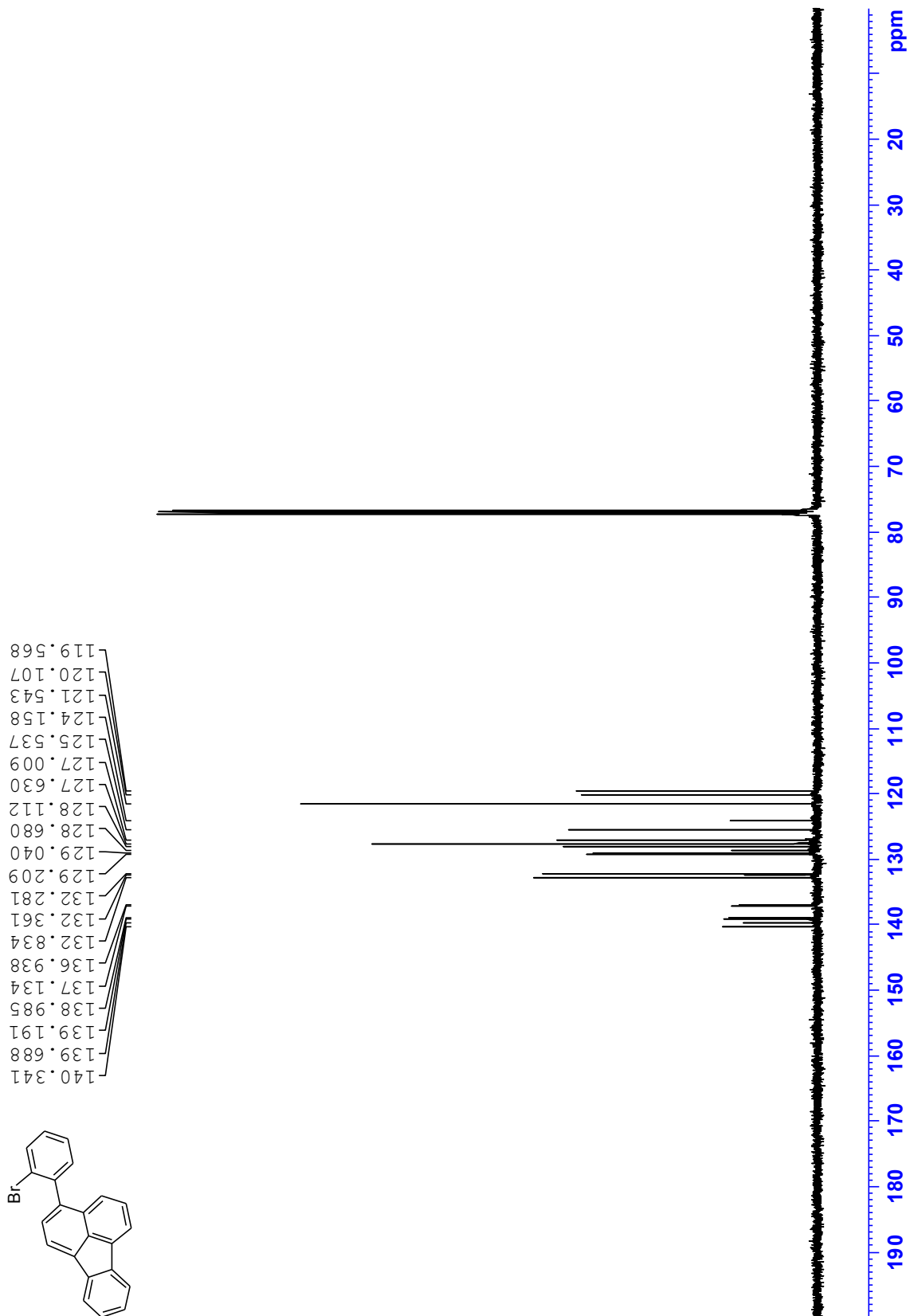


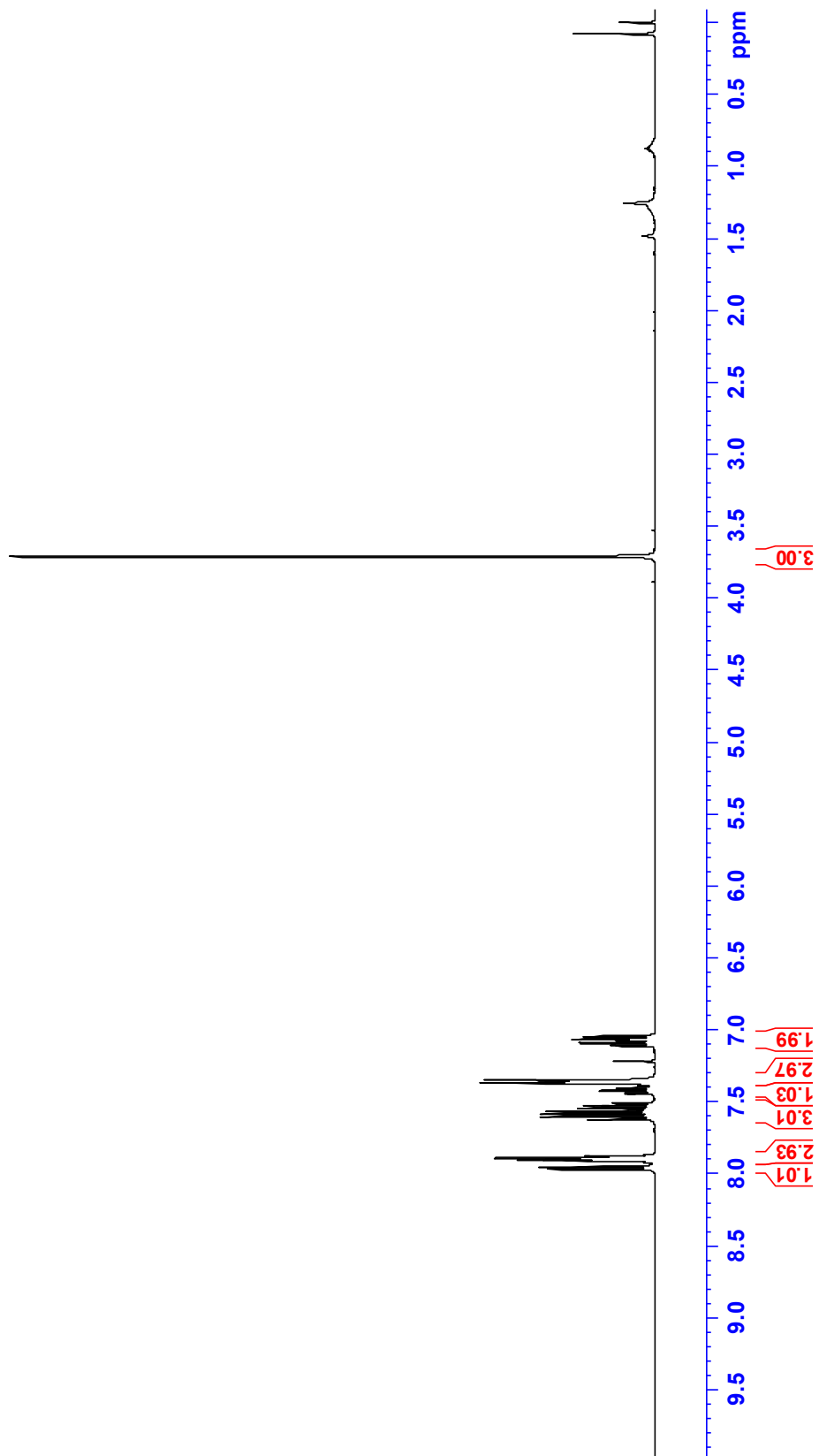
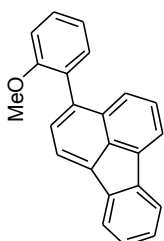


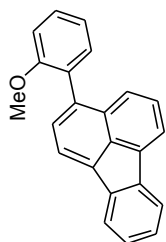






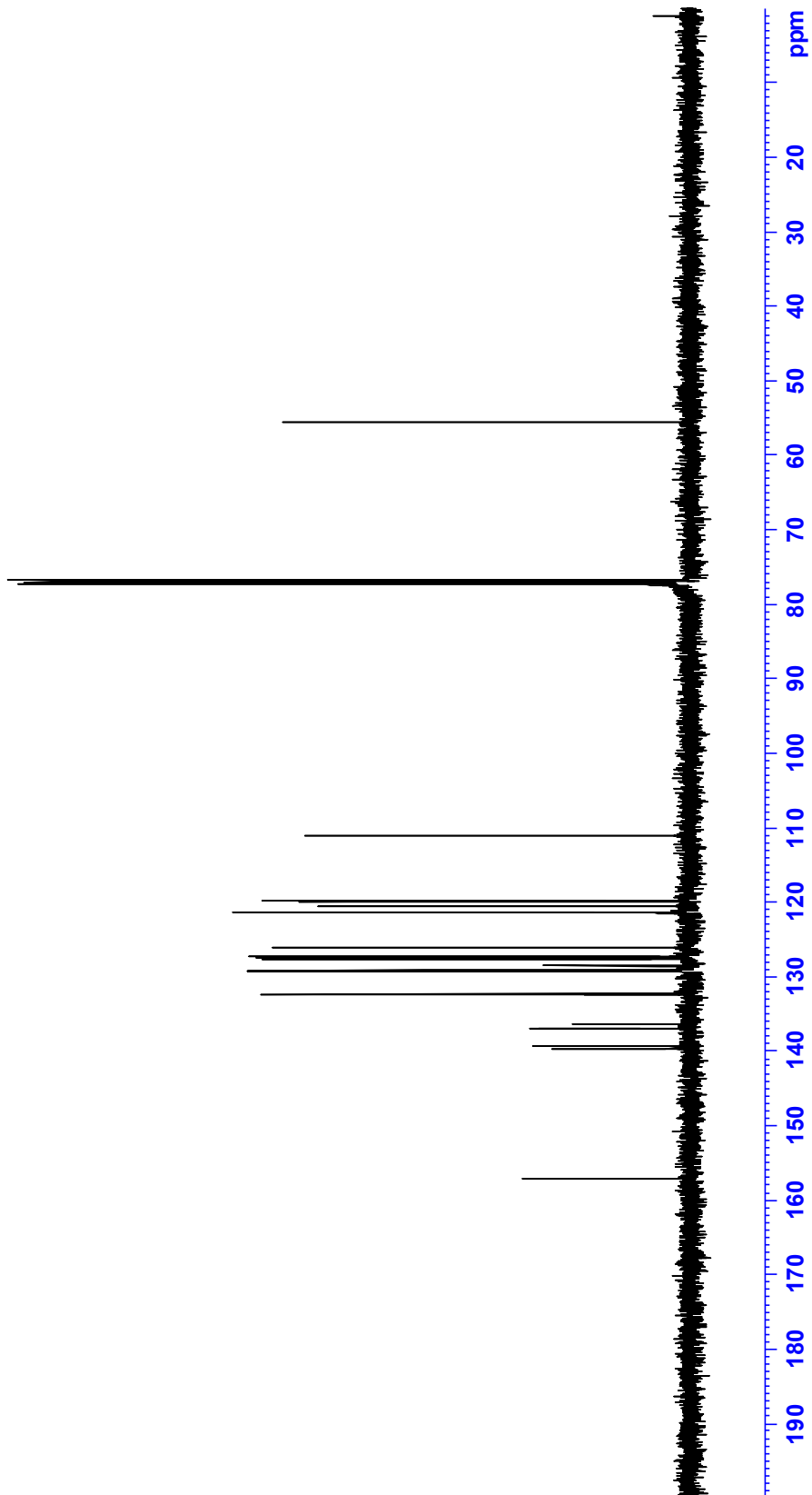


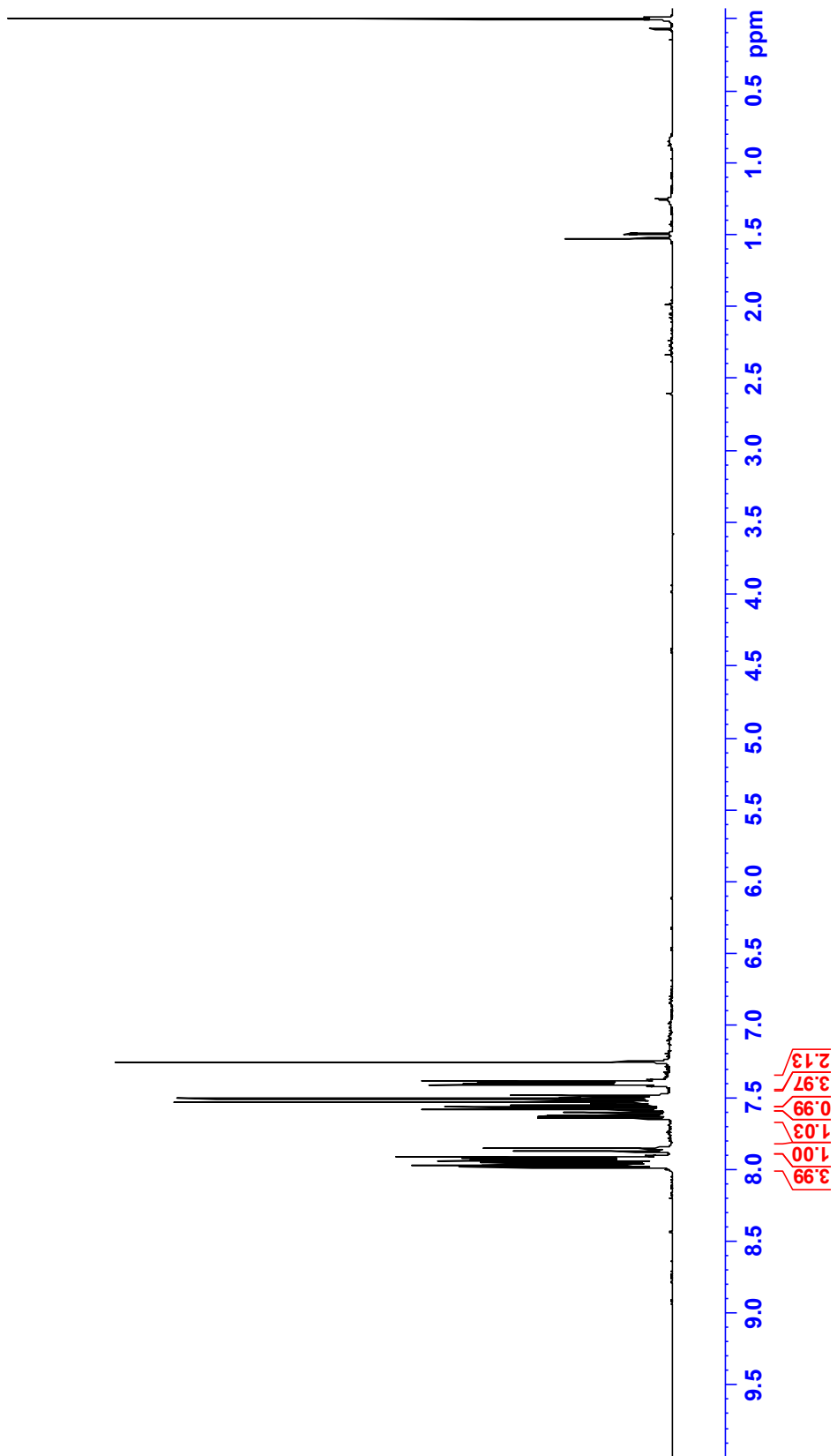
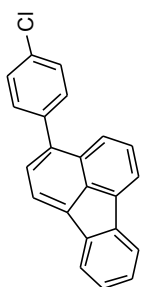


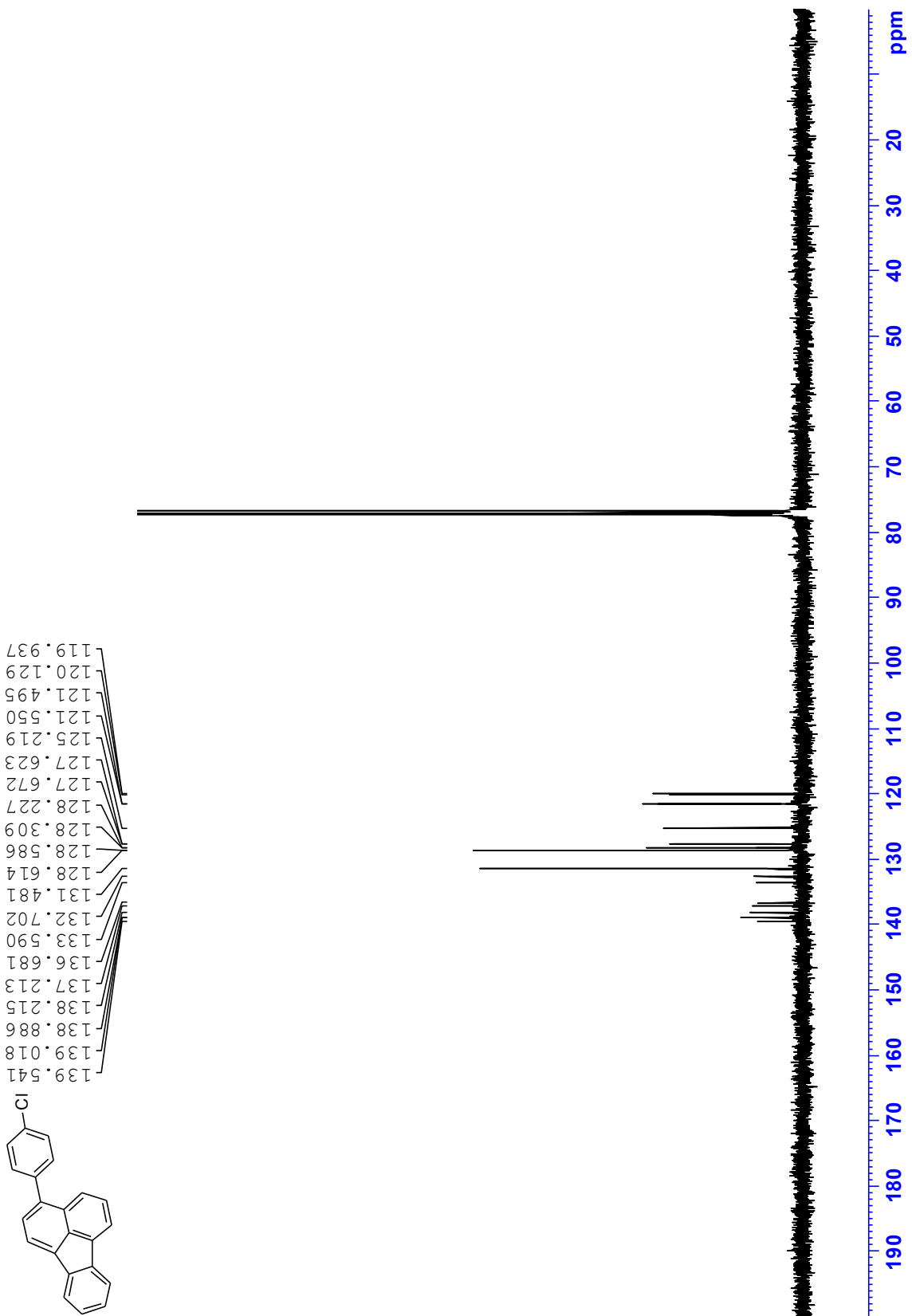


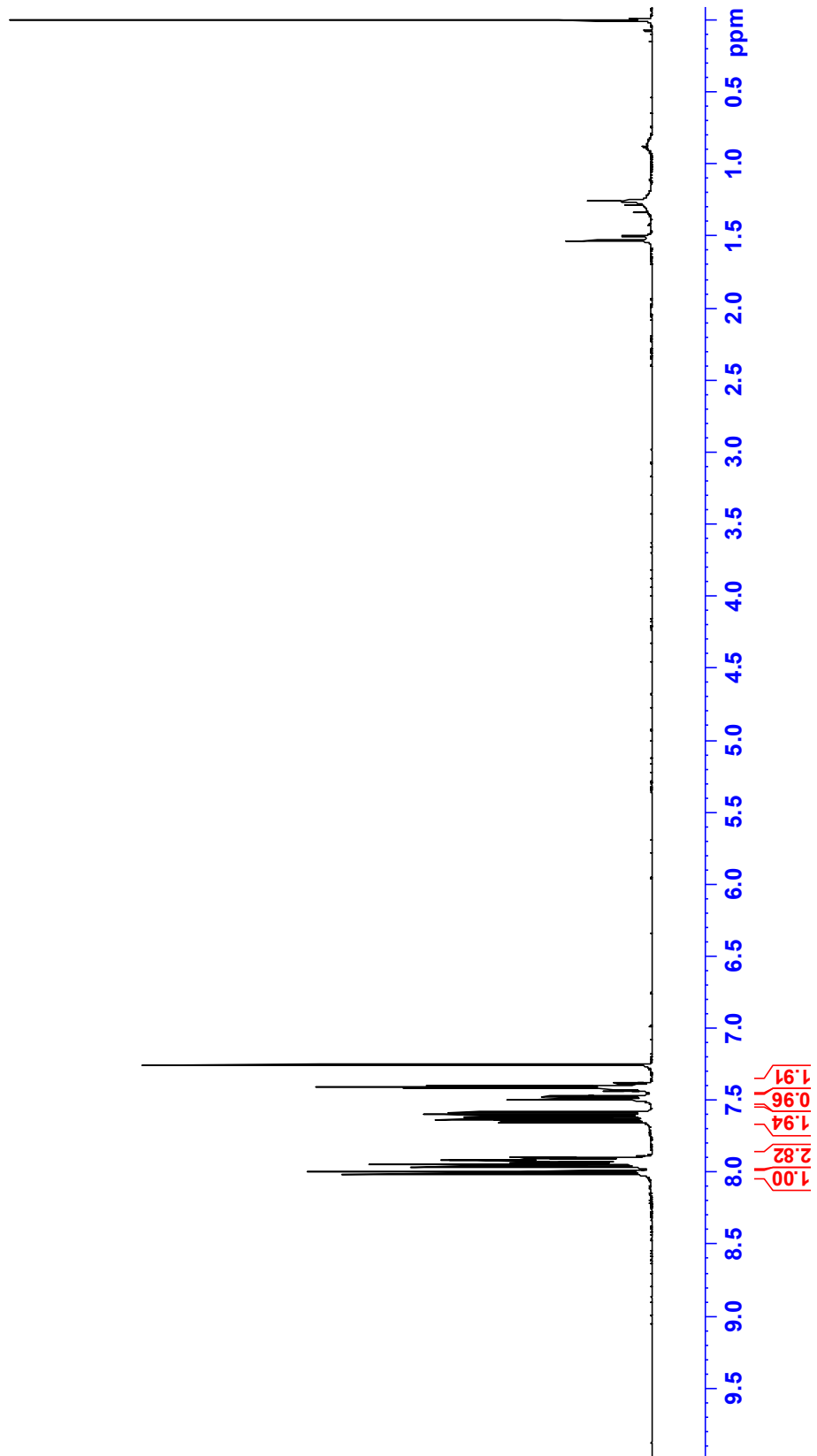
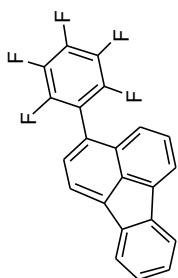
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139.633  
139.322  
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136.945  
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129.123  
128.521  
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121.347  
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119.790  
111.111

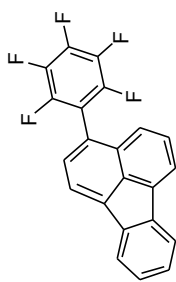
— 55.511



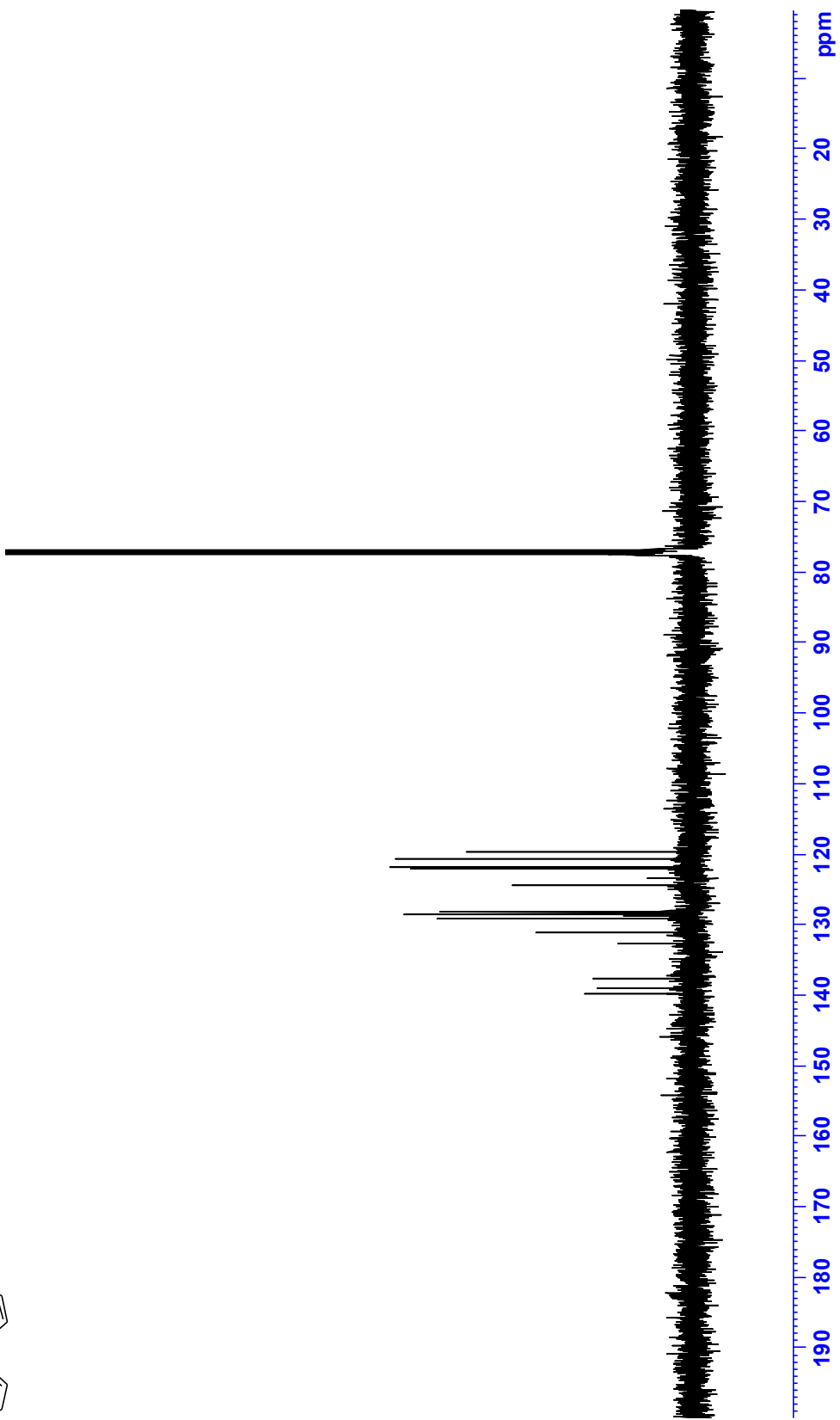


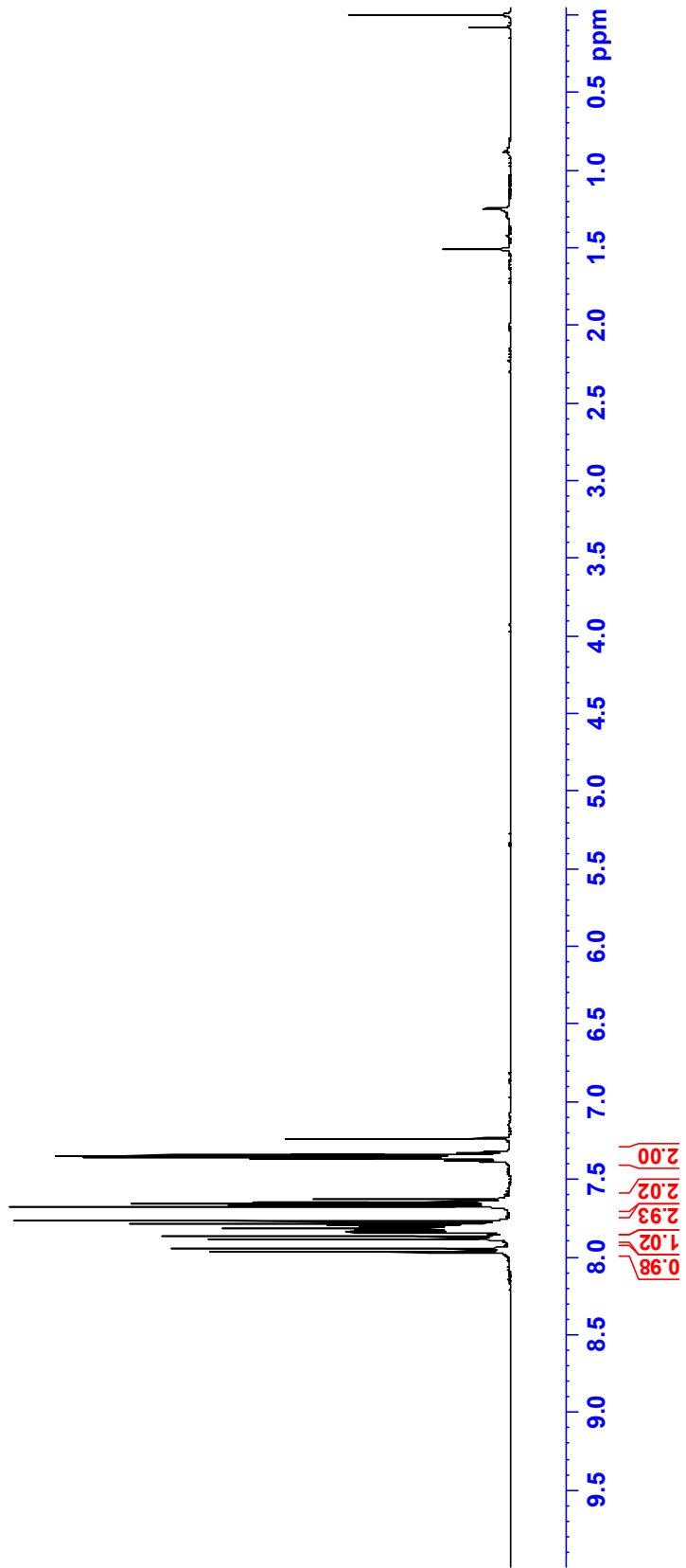
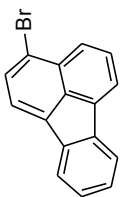




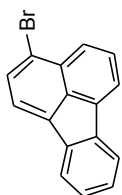


- 139.841
- 139.085
- 138.963
- 137.733
- 132.808
- 131.130
- 129.205
- 128.821
- 128.494
- 128.122
- 124.443
- 123.396
- 122.087
- 121.905
- 120.762
- 119.712

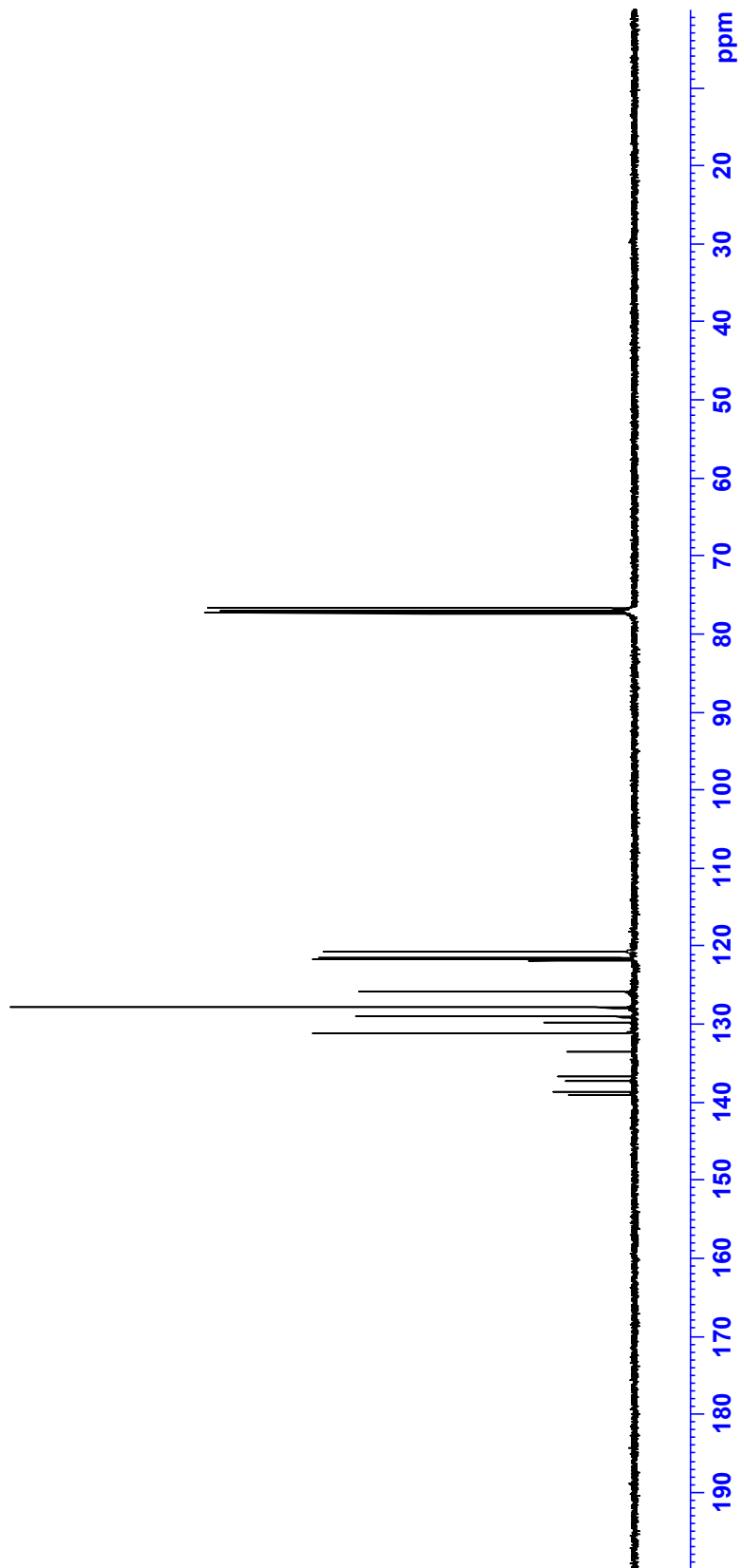


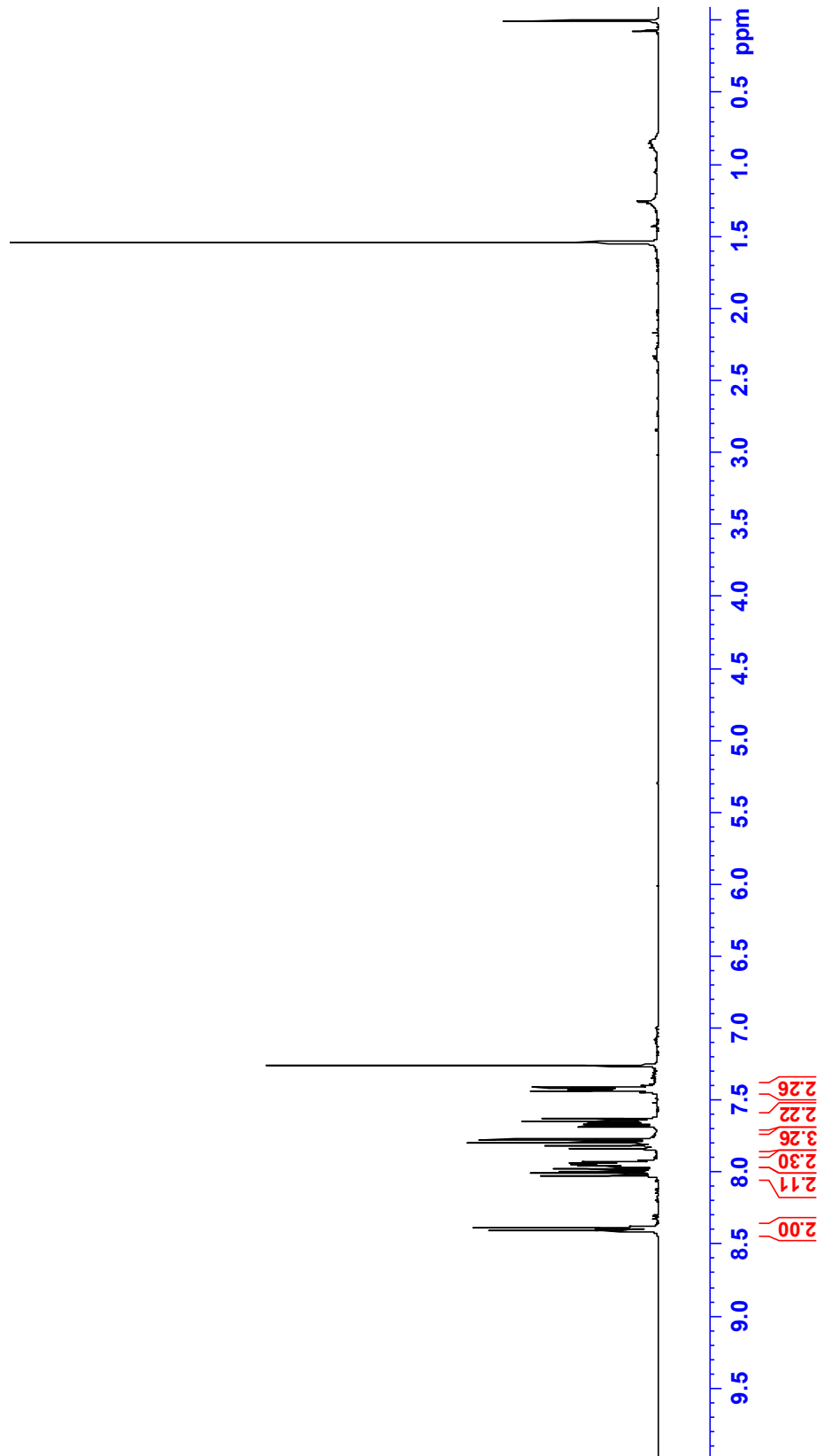
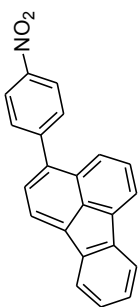


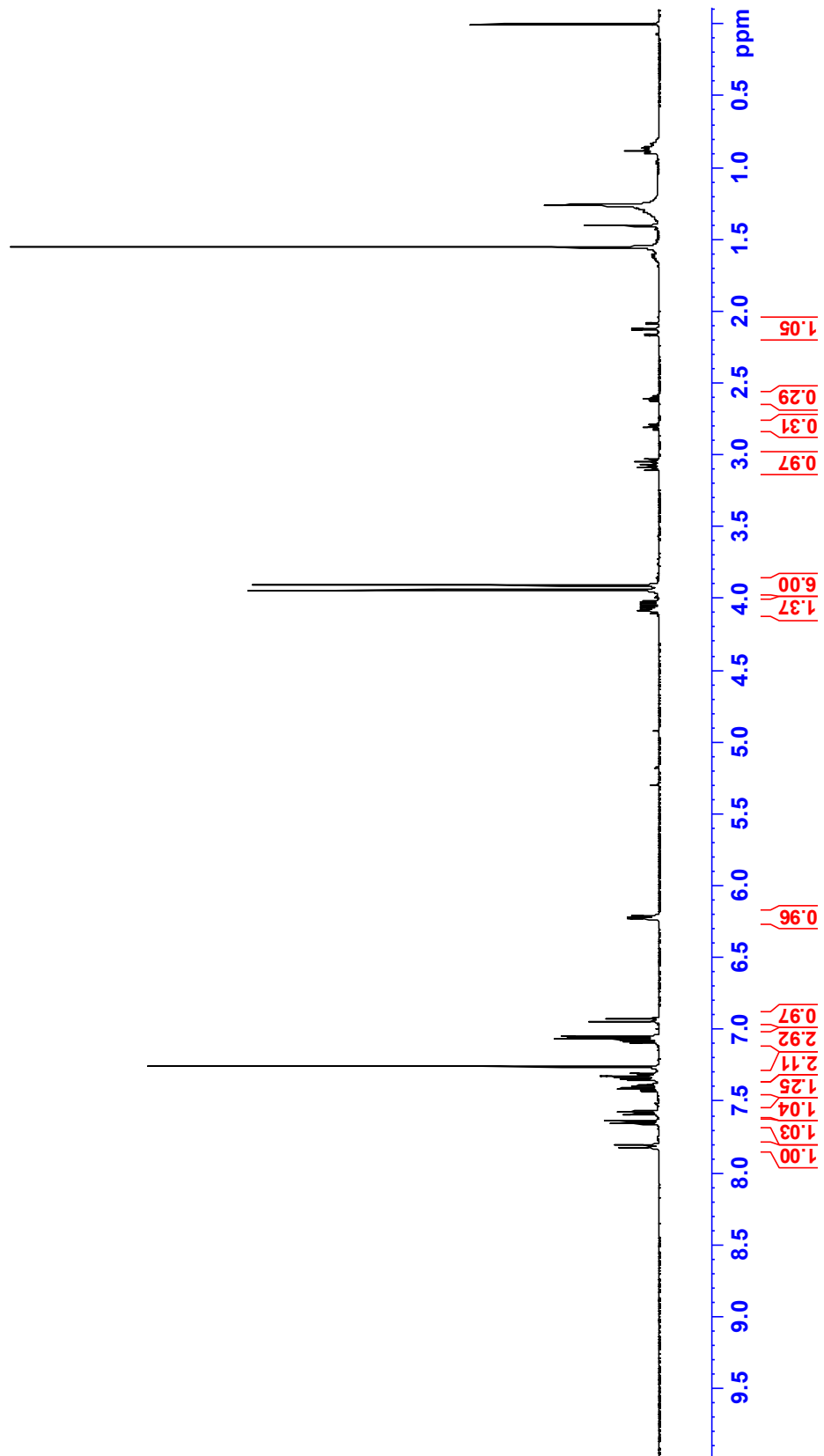
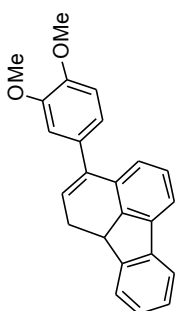


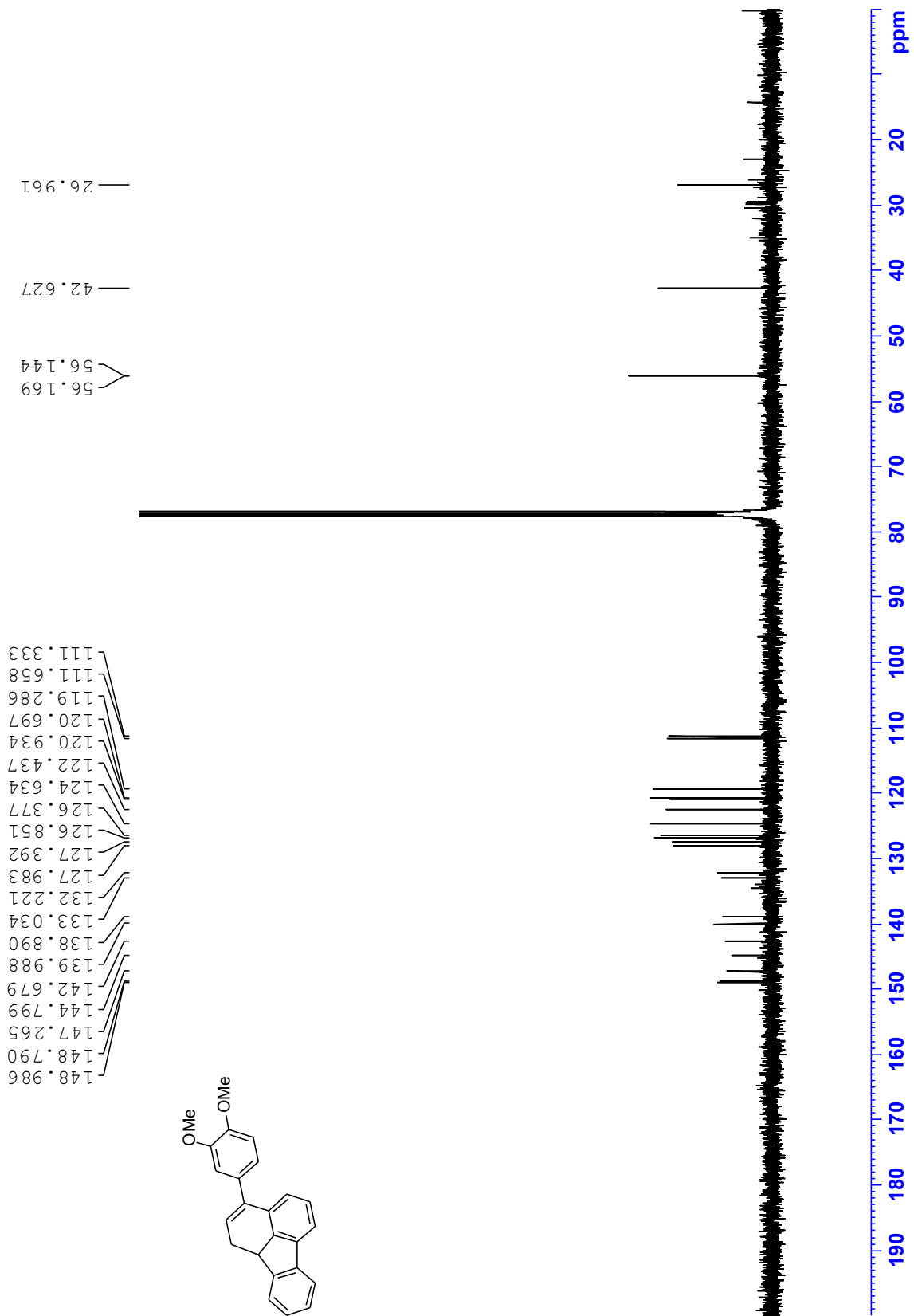


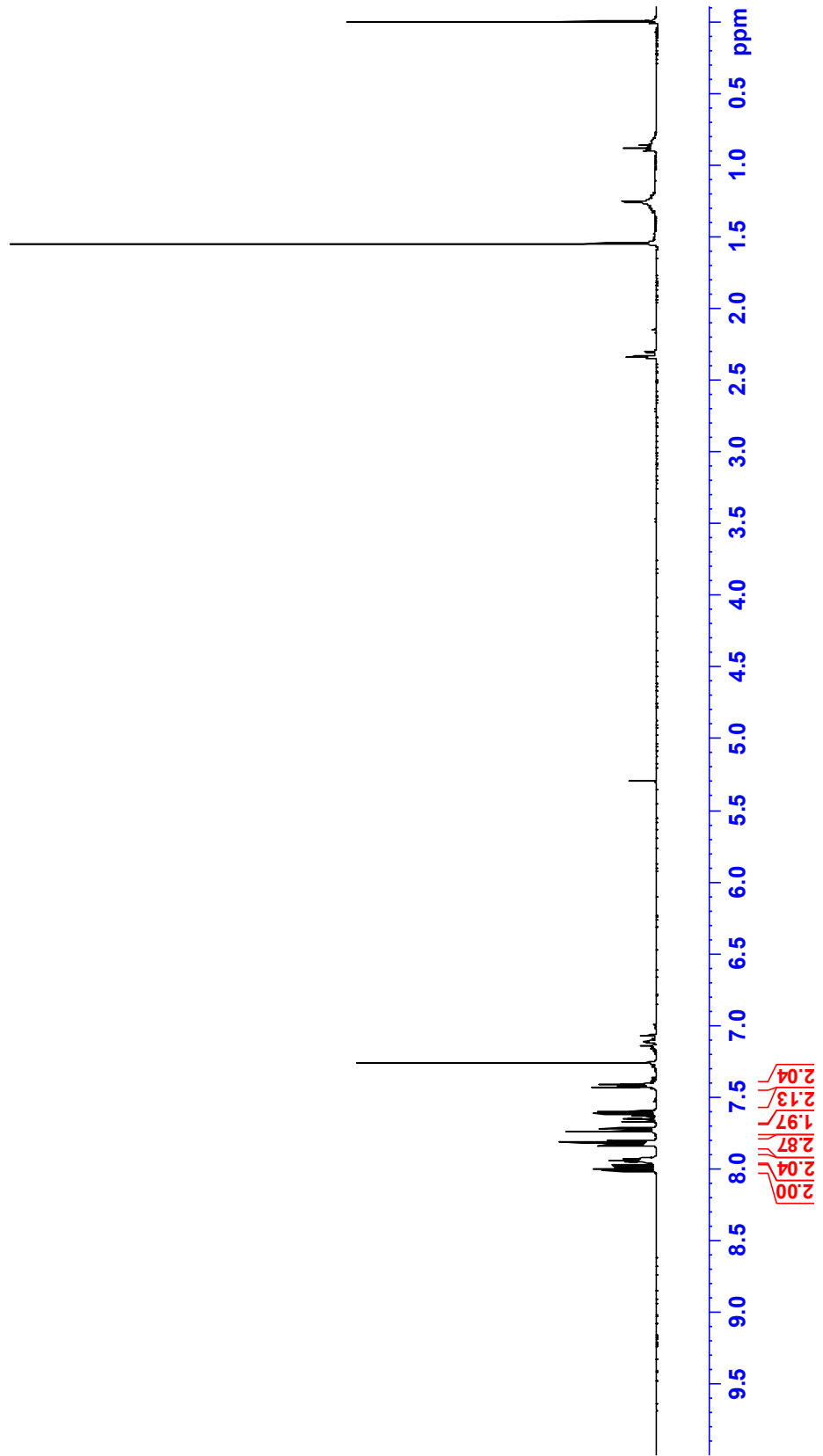
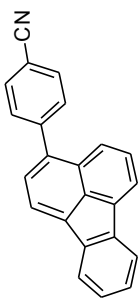
139.062  
138.710  
137.247  
136.739  
133.502  
131.124  
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129.060  
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120.737  
120.634

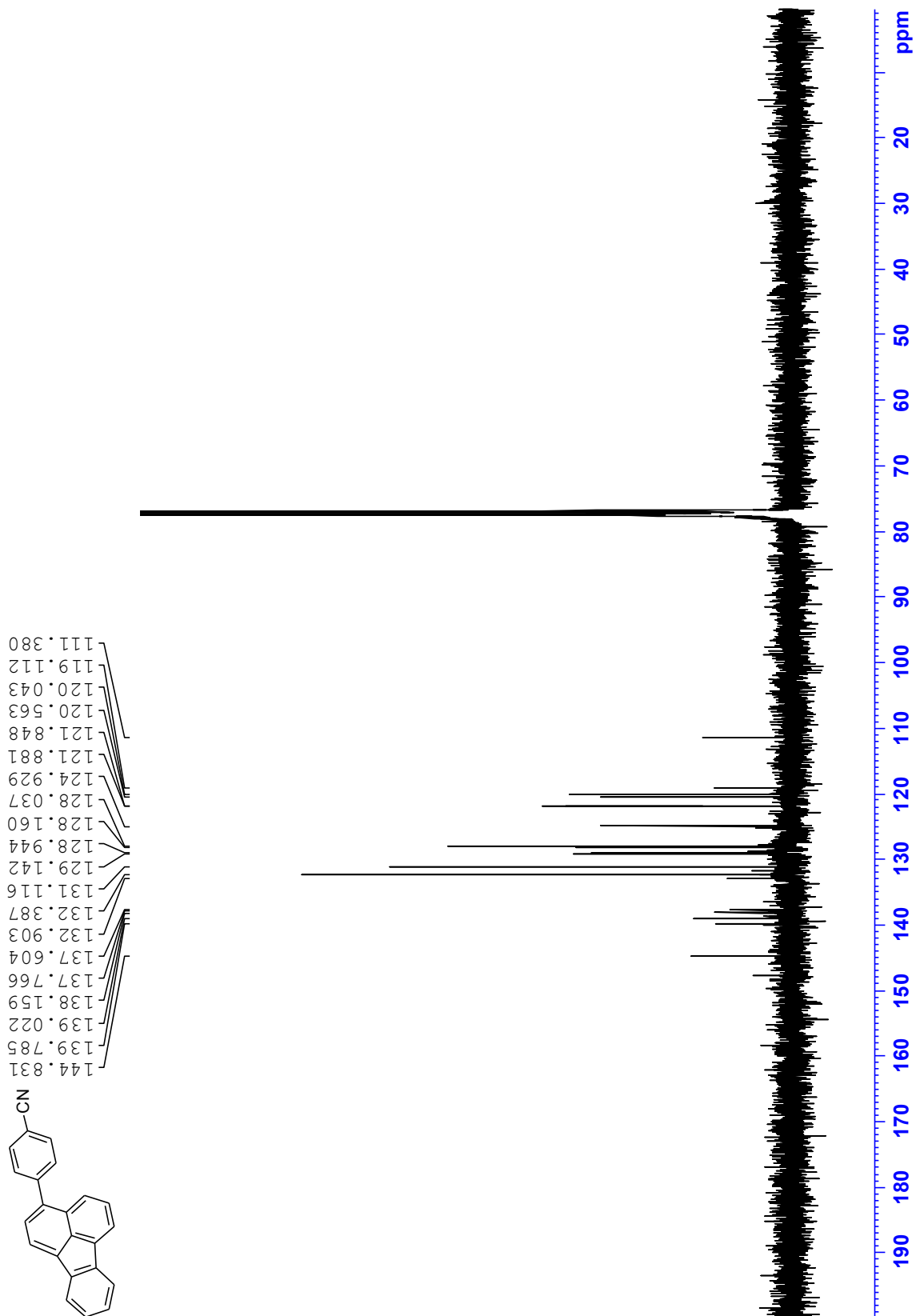


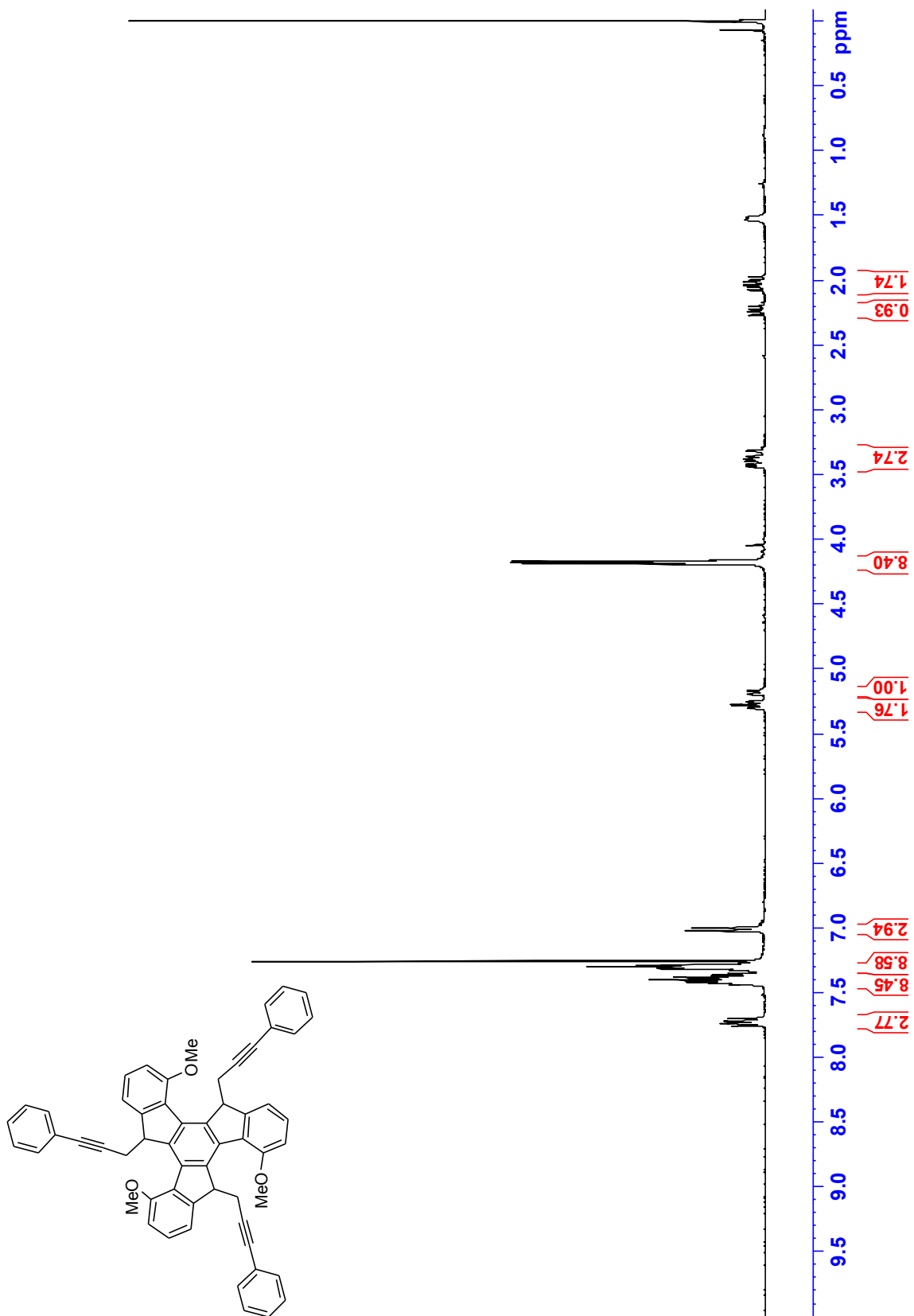


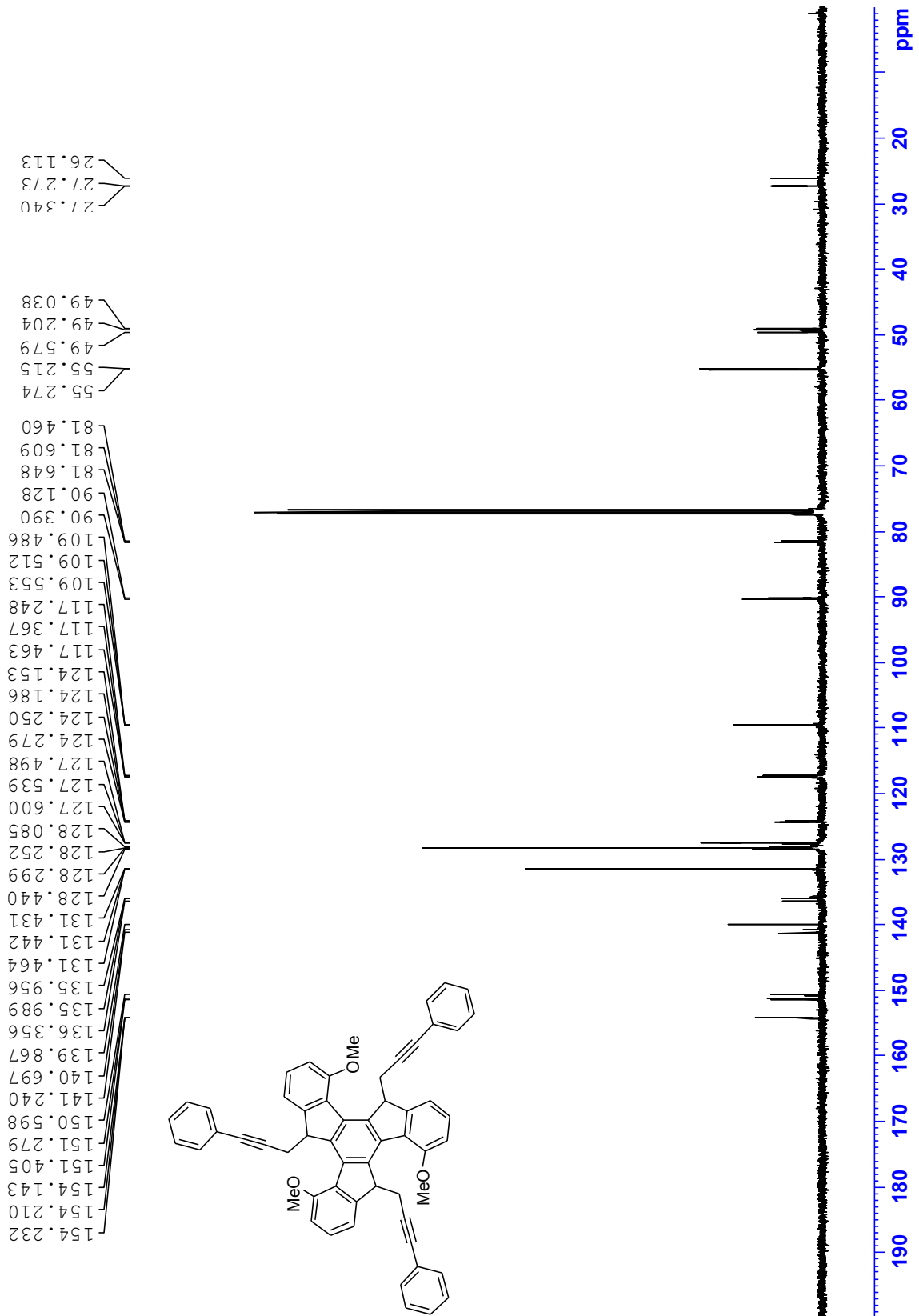




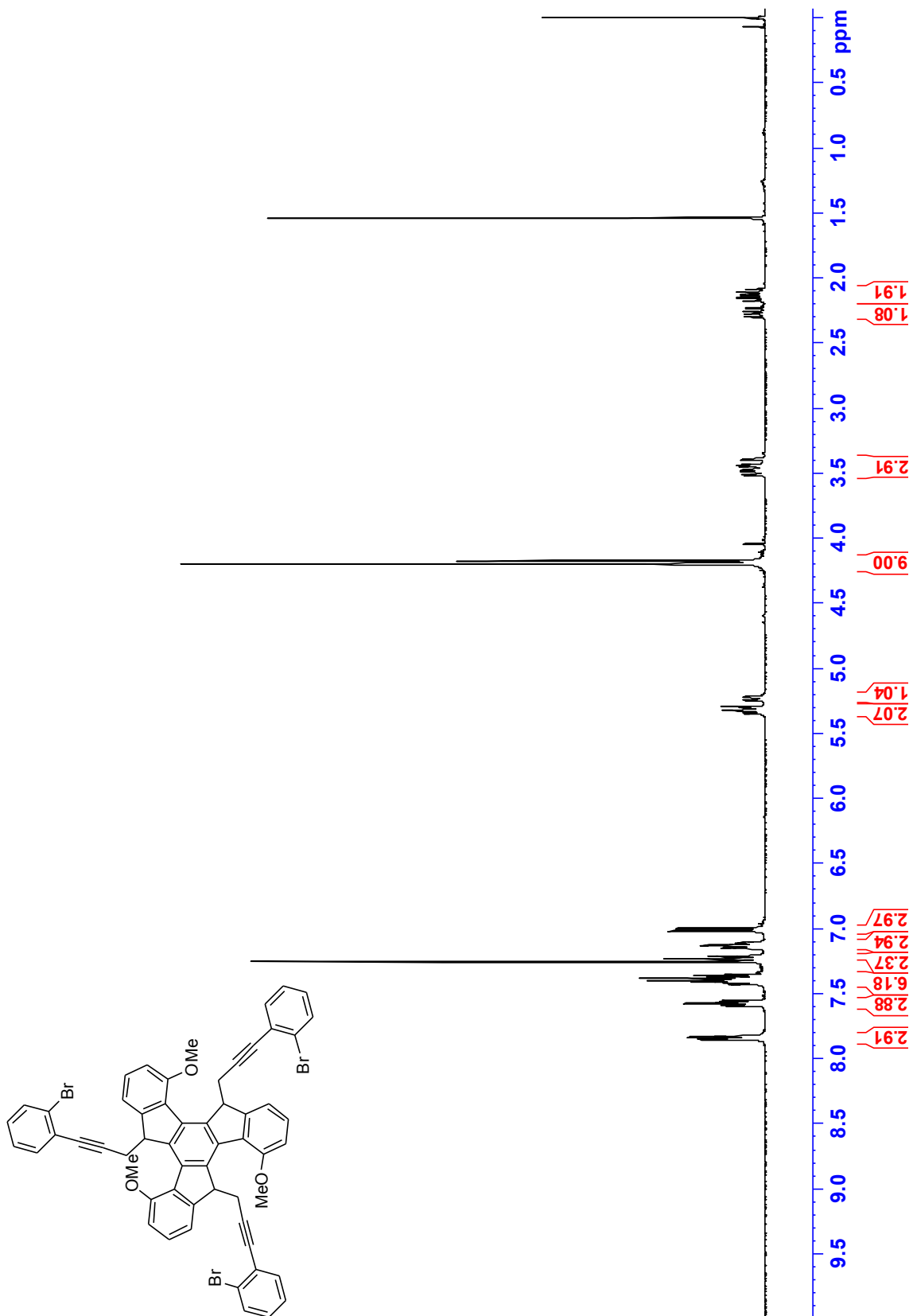


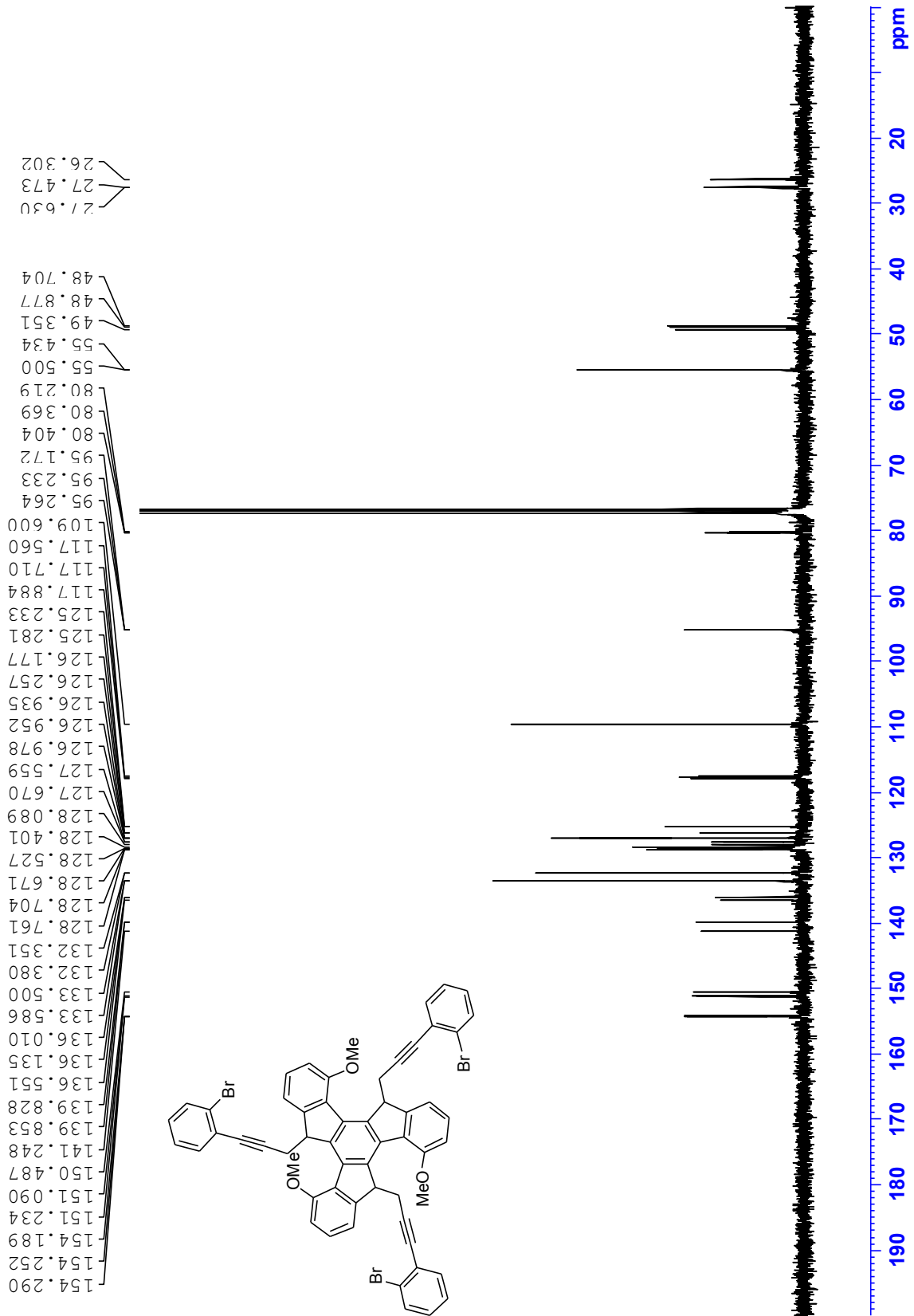


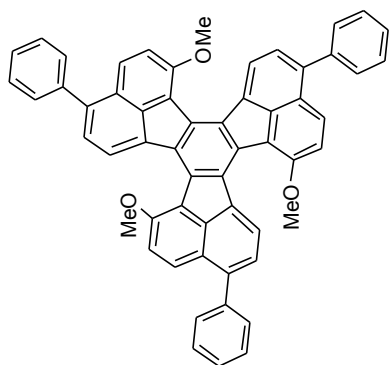




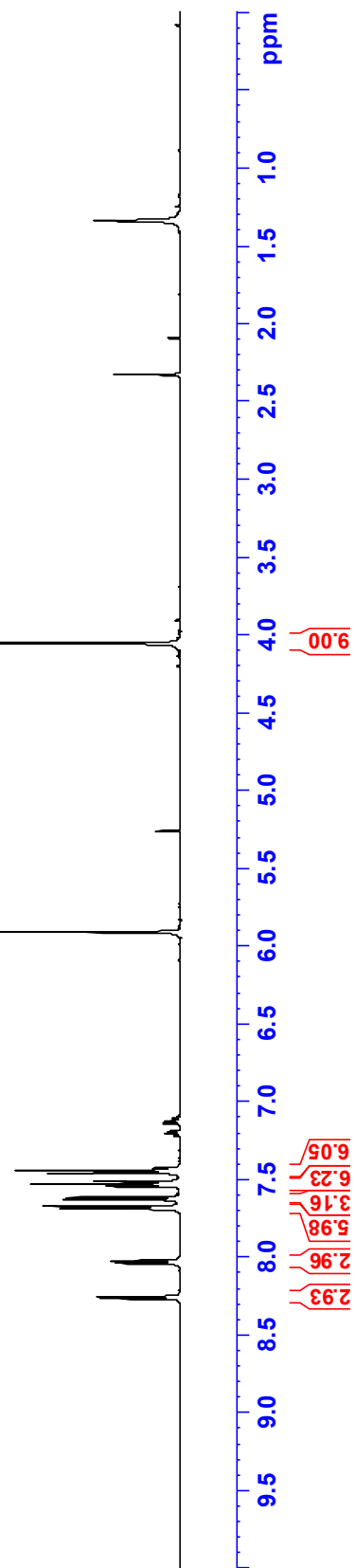


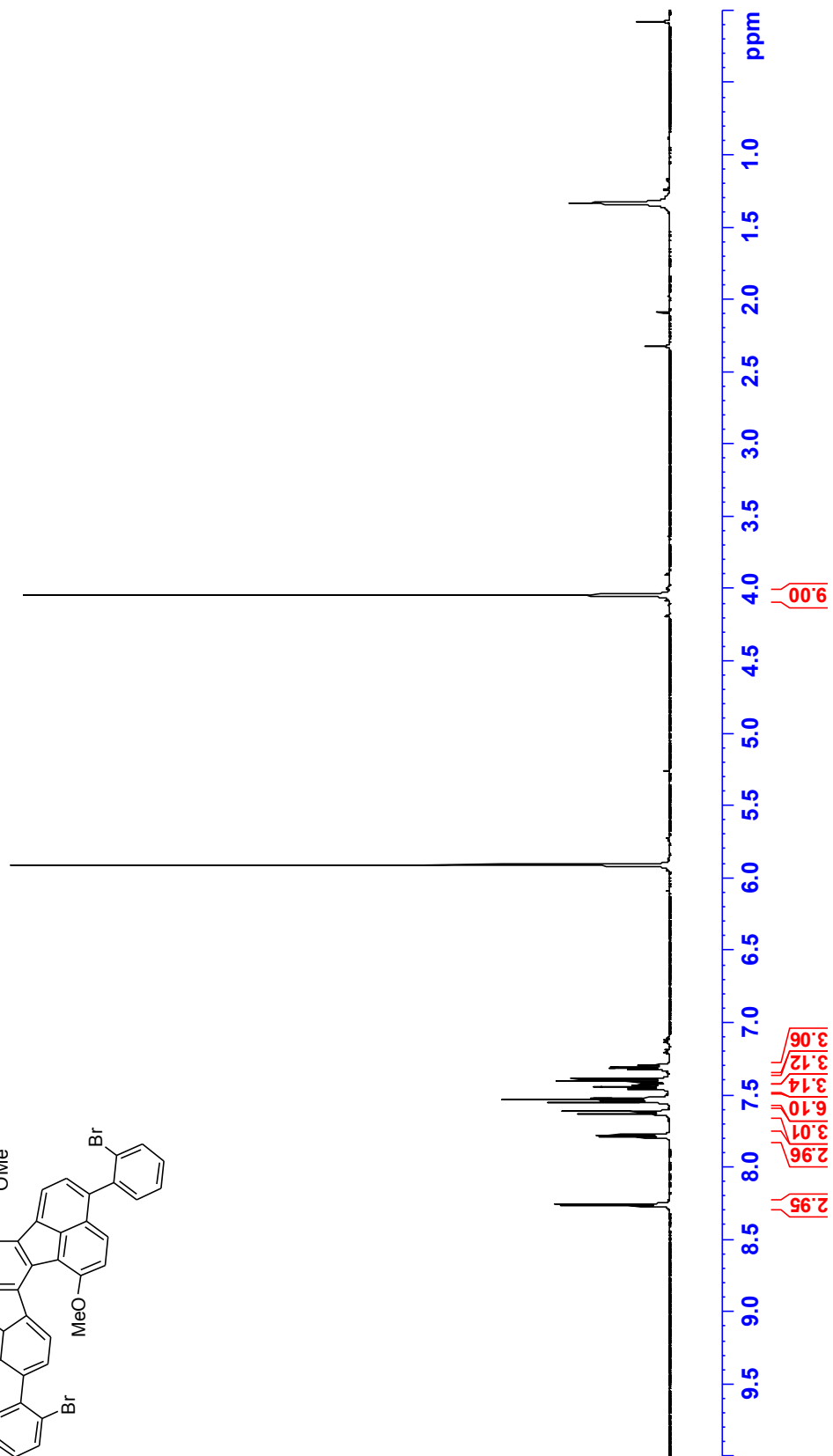
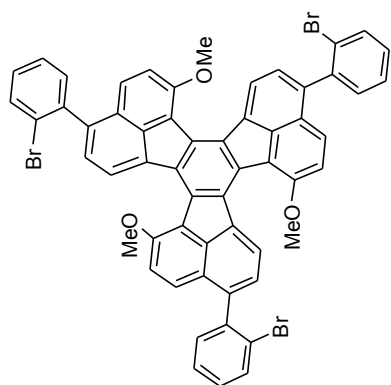






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