

**Supporting Information For**  
**Dynamic Kinetic Resolution of Allylic Azides via Asymmetric**  
**Dihydroxylation**

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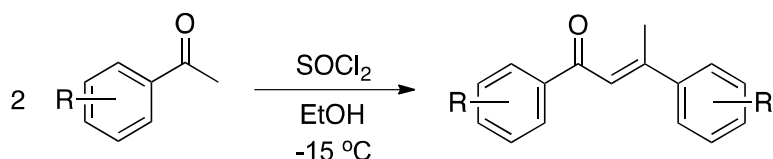
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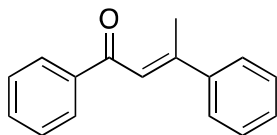
**Azide Safety:** Azides are known to be high energy materials and explosions have been reported when working with azides. In the course of this work, no issues were encountered. All of the azides synthesized in this report have C/N ratios equal to or above the recommended guideline of 3. Precautionary safety shields were used for all reactions using or producing more than 1 mmol of azide. Safety shields were used both in the fume hood and during rotary evaporation. All waste and aqueous solution which could be contaminated with azide were kept in individually labeled containers and were kept STRICTLY free of acid to avoid the accidental production of  $\text{HN}_3$  – DO NOT use aqueous HCl during work up of any of the reactions reported herein. Further reading on azide safety is available.<sup>1</sup>

**Methods and Reagents:** All reactions used magnetic stirring (500 - 800 rpm). All reactions conducted at elevated temperatures used aluminum block heating. Temperatures reported are based on an external thermocouple. All commercially available reagents were used without further purification. Dry tetrahydrofuran and methylene chloride were obtained from a commercial solvent system utilizing activated alumina columns under a positive pressure of argon. Thin-layer chromatography (TLC) was used to monitor reaction progress. TLC was performed using pre-coated glass or plastic plates with fluorescent indicator (254 nm) impregnated silica gel. Visualization was achieved using UV light, PMA, vanillin, or  $\text{KMnO}_4$  stains. Organic solutions were concentrated by rotary evaporation at or below 40 °C under reduced pressure. Flash chromatography was performed on a Teledyne Isco CombiFlash Rf system utilizing normal phase pre-column load cartridges and gold high performance columns.

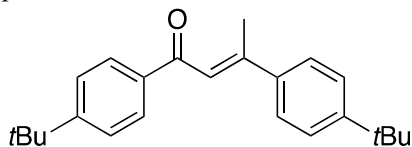
**Instrumentation.** All proton ( $^1\text{H}$ ) nuclear magnetic resonance spectra were recorded at 400 MHz or 500 MHz. All carbon ( $^{13}\text{C}$ ) nuclear magnetic resonance spectra were recorded at 100 MHz or 125 MHz. The fluorine ( $^{19}\text{F}$ ) nuclear magnetic resonance spectra was recorded at 376 MHz with proton decoupling. Chemical shifts are expressed in parts per million and are referenced to residual solvent ( $\text{CDCl}_3$ : 7.26 ppm), to the central carbon in the NMR solvent ( $\text{CDCl}_3$ : 77.2 ppm). Data is presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, ad = apparent doublet – para disubstituted pattern, t = triplet, q = quartet and m = multiplet), integration, and coupling constant in Hertz (Hz). Infrared (IR) spectra were taken in a Nicolet Nexus 670 FT-IR with salt plates. IR spectra were reported in  $\text{cm}^{-1}$ . A Bruker 400 MHz spectrometer was used to quantify yields based on NMR. All spectra were generated from one scan with a 7 s acquisition time and relaxation delay. Triphenyl methane was used as an internal standard. Enantiomeric excesses were determined using a Shimadzu HPLC with a PDA detector and a Phenomenex column (Lux  $3\mu$  cellulose-1 column; 250 mm x 4.6 mm).



**General Procedure 1 dimerization of acetophenones:** Example given for R = H. This procedure was adapted from a known method.<sup>2</sup> To a solution of acetophenone (5.0 g, 28 mmol) in ethanol (11 mL) cooled in a brine bath, thionyl chloride (3.2 mL, 43 mmol) was added dropwise over 20 min by addition funnel. After the addition was complete, the reaction temperature was maintained. After an additional 35 min, the reaction was quenched by addition of  $\text{K}_2\text{CO}_3$  (CAUTION EXOTHERMIC). The resulting solution was extracted with ethyl acetate (3 × 40 mL). The combined organic phase was washed with brine, dried ( $\text{MgSO}_4$ ), filtered, and concentrated under reduced pressure. Purification was conducted by short pass distillation under vacuum. Distillation commonly afforded product in ~85-90% purity, which was sufficient for use in the subsequent methyl addition. To obtain characterization data, the distillate was further purified via column chromatography (5%-25% EtOAc in hexanes) to yield final product **S1a** (2.7 g, 8.2 mmol, 58%). A similar procedure was used to prepare compounds **S1b** - **S1j**.



**Compound S1a:** General procedure 1 was used and the product was isolated in 58% yield. Characterization data for this compound has been reported.<sup>3</sup> The material obtained from this method provided an identical <sup>1</sup>H NMR. An image of the <sup>1</sup>H NMR is supplied in the accompanying file.



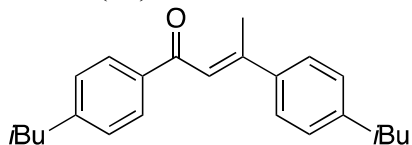
**Compound S1b:** General procedure 1 was used and the product was isolated in 58% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.11 – 8.03 (m, 2H), 7.65 (ad, *J* = 8.4, 2H), 7.61 – 7.51 (m, 4H), 7.33 (q, *J* = 1.2 Hz, 1H), 2.72 (d, *J* = 1.3 Hz, 3H), 1.45 (s, 9H), 1.44 (s, 9H).

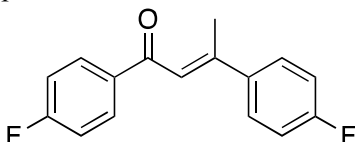
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 191.1, 155.9, 154.2, 152.2, 139.7, 136.9, 128.2, 126.2, 125.4, 125.3, 121.3, 34.9, 34.6, 31.2, 31.0, 18.6.

**IR (cm<sup>-1</sup>):** 2963, 2905, 1655, 1606, 1220, 824.

**HRMS (CI):** Calculated for C<sub>24</sub>H<sub>30</sub>Na<sup>+</sup>, (*M* + Na)<sup>+</sup> 357.2189, observed 357.2196.



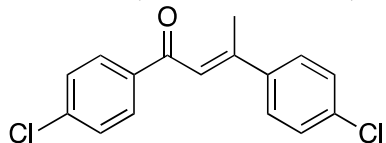
**Compound S1c:** General procedure 1 was used and the product was isolated in 60% yield. Characterization data for this compound has been reported.<sup>3</sup> The material obtained from this method provided an identical <sup>1</sup>H NMR. An image of the <sup>1</sup>H NMR is supplied in the accompanying file.



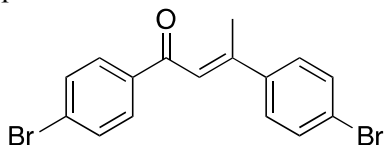
**Compound S1d:** General procedure 1 was used and the product was isolated in 61% yield. Characterization data for this compound has been reported.<sup>3</sup> The material obtained from this method provided an identical <sup>1</sup>H NMR. An image of the <sup>1</sup>H NMR is supplied in the accompanying file. A <sup>13</sup>C NMR and <sup>19</sup>F NMR was absent from that report and is provided here:

**<sup>13</sup>C NMR, (CDCl<sub>3</sub>, 125 MHz):** δ 190.0, 165.3 (d, *J*<sub>C-F</sub> = 266.1 Hz), 163.4 (d, *J*<sub>C-F</sub> = 261.5 Hz), 154.1, 138.6 (d, *J*<sub>C-F</sub> = 3.5 Hz), 135.6 (d, *J*<sub>C-F</sub> = 2.8 Hz), 130.8 (d, *J*<sub>C-F</sub> = 8.4 Hz), 128.3 (d, *J*<sub>C-F</sub> = 8.1 Hz), 121.6, 115.7 (d, *J*<sub>C-F</sub> = 2.8 Hz), 115.5 (d, *J*<sub>C-F</sub> = 2.8 Hz), 18.9.

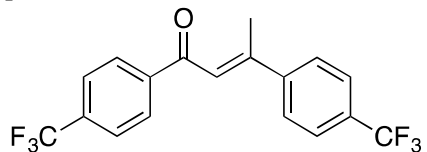
**<sup>19</sup>F NMR, (CDCl<sub>3</sub>, 471 MHz):** δ -105.9 (s), -111.9 (s).



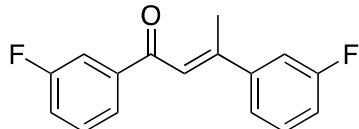
**Compound S1e:** General procedure 1 was used and the product was isolated in 51% yield. Characterization data for this compound has been reported.<sup>3</sup> The material obtained from this method provided an identical <sup>1</sup>H NMR. An image of the <sup>1</sup>H NMR is supplied in the accompanying file.



**Compound S1f:** General procedure 1 was used and the product was isolated in 21% yield. Characterization data for this compound has been reported.<sup>3</sup> The material obtained from this method provided an identical <sup>1</sup>H NMR. An image of the <sup>1</sup>H NMR is supplied in the accompanying file.



**Compound S1g:** General procedure 1 was used and the product was isolated in 61% yield. Characterization data for this compound has been reported.<sup>3</sup> The material obtained from this method provided an identical <sup>1</sup>H NMR. An image of the <sup>1</sup>H NMR is supplied in the accompanying file.



**Compound S1h:** General procedure 1 was used and the product was isolated in 65% yield.

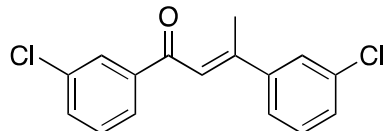
**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.78 (ad,  $J = 7.8$  Hz, 1H), 7.70-7.67 (m, 1H), 7.49-7.44(m, 1H), 7.42-7.36 (m, 2H), 7.29-7.24 (m, 2H), 7.14-7.09 (m, 2H), 2.59 (d,  $J = 1.3$  Hz, 3H).

**<sup>13</sup>C NMR, (CDCl<sub>3</sub>, 100 MHz):**  $\delta$  190.0 (d,  $J_{C-F} = 2.2$  Hz), 162.9 (d,  $J_{C-F} = 247.8$  Hz), 162.9 (d,  $J_{C-F} = 245.0$  Hz) 154.4 (d,  $J_{C-F} = 2.2$  Hz), 144.7 (d,  $J_{C-F} = 7.2$  Hz), 141.2 (d,  $J_{C-F} = 5.8$  Hz), 130.2 (d,  $J_{C-F} = 7.4$  Hz), 130.2 (d,  $J_{C-F} = 8.5$  Hz), 123.9 (d,  $J_{C-F} = 2.9$  Hz), 122.2 (d,  $J_{C-F} = 2.8$  Hz), 122.1, 119.7 (d,  $J_{C-F} = 21.2$  Hz), 116.1 (d,  $J_{C-F} = 21.1$  Hz), 115.0 (d,  $J_{C-F} = 22.4$  Hz), 113.4 (d,  $J_{C-F} = 22.4$  Hz), 18.9.

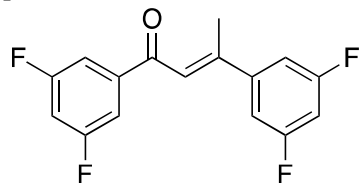
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -111.8, -1112.4.

**IR (cm<sup>-1</sup>):** 3072, 1660, 1585, 1444, 1248, 1189, 1043.

**HRMS (CI):** Calculated for C<sub>16</sub>H<sub>13</sub>F<sub>2</sub>O<sup>+</sup>, (M+H)<sup>+</sup> 259.0929, observed 259.0929; calculated for C<sub>16</sub>H<sub>16</sub>F<sub>2</sub>NO<sup>+</sup> (M + NH<sub>4</sub>)<sup>+</sup> 276.1194, observed 276.1191.



**Compound S1i:** General procedure 1 was used and the product was isolated in 68% yield. Characterization data for this compound has been reported.<sup>3</sup> The material obtained from this method provided an identical <sup>1</sup>H NMR. An image of the <sup>1</sup>H NMR is supplied in the accompanying file.



**Compound S1j:** General procedure 1 was followed, but the SOCl<sub>2</sub> addition was conducted in an ice bath. The product was isolated in 63% yield.

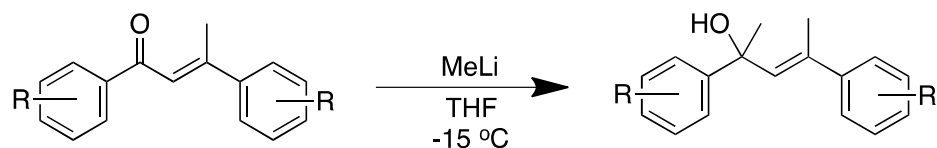
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.47 (m, 2H), 7.02 (m, 4H), 6.86 (m, 1H), 2.54 (d,  $J = 1.0$  Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  188.5 (t,  $J_{C-F} = 2.4$  Hz), 164.3 (m), 161.9 (m), 154.3 (t,  $J_{C-F} = 2.4$  Hz), 145.5 (t,  $J_{C-F} = 8.9$ Hz) 141.8 (t,  $J_{C-F} = 7.4$  Hz), 122.1, 111.2 (m), 109.6 (m), 108.1 (t,  $J_{C-F} = 25.4$  Hz), 104.7 (t,  $J_{C-F} = 25.4$  Hz), 18.8.

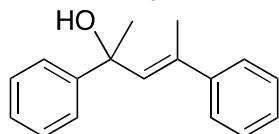
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -107.9 (s), -108.7 (s).

**IR (cm<sup>-1</sup>):** 3081, 1665, 1586, 1439, 1302, 1121, 985.

**HRMS (CI):** Calculated for C<sub>16</sub>H<sub>11</sub>F<sub>2</sub>O<sup>+</sup>, (M+H)<sup>+</sup> 295.0741, observed 295.0744; calculated for C<sub>16</sub>H<sub>20</sub>F<sub>2</sub>NO<sup>+</sup> (M + NH<sub>4</sub>)<sup>+</sup> 312.1006, observed 312.1006.



**General Procedure 2 Methyl addition:** Example given for R = H. An oven dried two-neck round bottom flask was equipped with a stir bar, fitted with a septum, sealed under argon, charged with THF (120 mL), cooled in a brine bath, and charged with methyl lithium (6.5 mL, 3.0 M in Et<sub>2</sub>O, 20 mmol). Acetophenone dimer **S1a** (2.0 g, 6.9 mmol) was dissolved in THF (15 mL) and added drop-wise via syringe to the solution of methyl lithium. After 15 minutes, the reaction mixture was quenched by addition of water. The resulting solution was extracted with EtOAc (3 × 30 mL). The combined organic phase was washed with brine, dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Purification by column chromatography on Et<sub>3</sub>N basified SiO<sub>2</sub> (5%-25% EtOAc in hexanes with 1% Et<sub>3</sub>N) afforded the product (1.8 g, 5.7 mmol, 83%). **Note:** Many of these alcohols are acid sensitive and prone to elimination on SiO<sub>2</sub> and in CDCl<sub>3</sub>. A similar procedure was used to prepare compounds **S2b** – **S2j**.



**Compound S2a:** General procedure 2 was used and the product was isolated in 92% yield.

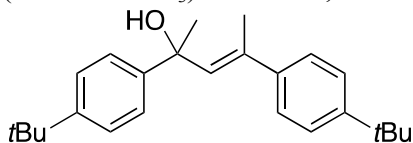
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.57 – 7.49 (m, 2H), 7.43 – 7.17 (m, 8H), 6.27 (q, *J* = 1.3 Hz, 1H), 2.05 (s, 1H), 1.89 (d, *J* = 1.3 Hz, 3H), 1.72 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 148.5, 143.9, 139.5, 135.3, 128.3, 128.2, 127.3, 126.7, 125.9, 125.2, 74.4, 33.8, 17.3.

**IR (cm<sup>-1</sup>):** 3440, 3026, 1492, 1444, 1065, 1027.

**TGA:** T<sub>d,5%</sub> N<sub>2</sub> = 149 °C, T<sub>d,5%</sub> air = 147 °C

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>17</sub><sup>+</sup>, (M - OH)<sup>+</sup> 221.1325, observed 221.1318; calculated for C<sub>17</sub>H<sub>20</sub>N<sup>+</sup> (M - OH + NH<sub>3</sub>)<sup>+</sup> 238.1590, observed 238.1580.



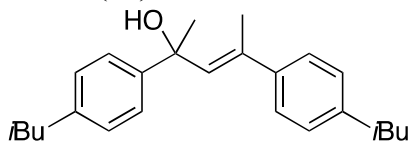
**Compound S2b:** General procedure 2 was used and the product was isolated in 66% yield.

**<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>):** δ 7.50 (ad, *J* = 8.5 Hz, 2H), 7.44 – 7.36 (m, 6H), 6.25 (q, *J* = 1.5 Hz, 1H), 3.32 (s, OH, 1H), 1.94 (d, *J* = 1.3 Hz, 3H), 1.68 (s, 3H), 1.35 (s, 9H), 1.34 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>):** δ 160.0, 149.9, 147.4, 142.4, 138.5, 136.2, 126.4, 126.1, 125.9, 125.8, 74.4, 35.1, 35.0, 34.2, 31.8, 31.7, 17.5.

**IR (cm<sup>-1</sup>):** 3438, 2962, 1509, 1362, 822.

**HRMS (CI):** Calculated for C<sub>25</sub>H<sub>33</sub><sup>+</sup> (M - OH)<sup>+</sup> 333.2577, observed 333.2588.



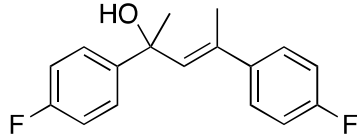
**Compound S2c:** General procedure 2 was used and the product was isolated in 80% yield.

**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ 7.56 – 7.41 (ad, *J* = 8.4, 2H), 7.43 – 7.40 (ad, *J* = 8.0, 2H), 7.20 – 7.17 (overlapping ad, *J* = 8.3, 4H), 6.36 (q, *J* = 1.2 Hz, 1H), 3.41 (s, OH, 1H), 2.55 (overlapping d, *J* = 7.2 Hz, 4H), 1.98 (d, *J* = 1.2 Hz, 3H), 1.94 (overlapping sept, *J* = 6.8, 2H), 1.76 (s, 3H), 0.98 (overlapping d, *J* = 6.8 Hz, 12H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):** δ 147.9, 142.8, 141.6, 140.6, 138.9, 136.4, 130.1, 129.8, 126.7, 126.3, 74.7, 45.9, 45.9, 34.5, 31.3, 31.3, 23.2, 23.1, 17.9.

**IR (cm<sup>-1</sup>):** 3442, 2922, 1509, 1465, 1066, 797.

**HRMS (CI):** Calculated for C<sub>25</sub>H<sub>33</sub><sup>+</sup> (M - OH)<sup>+</sup> 333.2577, observed 333.2590.



**Compound S2d:** General procedure 2 was used and the product was isolated in 90% yield.

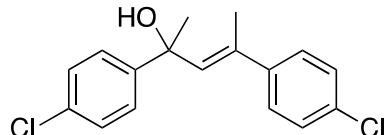
**<sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):** δ 7.64 – 7.60 (m, 2H), 7.47 – 7.43 (m, 2H), 7.09 – 7.04 (m, 4H), 6.28 (d, *J* = 1.6 Hz, 1H), 4.42 (s, OH, 1H), 1.92 (d, *J* = 1.6 Hz, 3H), 1.70 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>):** δ 162.0 (d, *J*<sub>C-F</sub> = 242.7 Hz), 161.3 (d, *J*<sub>C-F</sub> = 240.6 Hz), 146.5 (d, *J*<sub>C-F</sub> = 8.0 Hz), 141.4 (d, *J*<sub>C-F</sub> = 2.5 Hz), 138.1, 136.7 (d, *J*<sub>C-F</sub> = 1.6 Hz), 128.4 (d, *J*<sub>C-F</sub> = 8.1 Hz), 128.0 (d, *J*<sub>C-F</sub> = 2.6 Hz), 115.6 (d, *J*<sub>C-F</sub> = 21.2 Hz), 115.1 (d, *J*<sub>C-F</sub> = 19.1 Hz), 73.7, 34.4, 17.4.

**<sup>19</sup>F NMR (376 MHz, acetone-*d*<sub>6</sub>):** δ -117.3 (s), -118.7 (s).

**IR (cm<sup>-1</sup>):** 3434, 2976, 1508, 1225, 1159, 829.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub><sup>+</sup> (M - OH)<sup>+</sup> 257.1136, observed 257.1139; calculated for C<sub>17</sub>H<sub>18</sub>F<sub>2</sub>N<sup>+</sup> (M - OH + NH<sub>3</sub>) 274.1402, observed 274.1401.



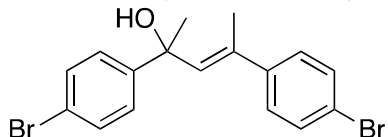
**Compound S2e:** General procedure 2 was used and the product was isolated in 83% yield.

**<sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):** δ 7.60 (ad, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.34-7.31 (m, 4H), 6.33 (q, *J* = 1.2 Hz, 1H), 4.50 (s, OH, 1H), 1.93 (d, *J* = 1.2 Hz, 3H), 1.71 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>):** δ 149.2, 143.6, 138.1, 136.8, 133.0, 132.1, 128.9, 128.5, 128.1, 127.8, 73.6, 34.3, 17.2.

**IR (cm<sup>-1</sup>):** 3440, 2975, 1488, 1093, 1012, 818.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>Cl<sub>2</sub><sup>+</sup> (M - OH)<sup>+</sup> 289.0545, observed 289.0541; calculated for C<sub>17</sub>H<sub>18</sub>Cl<sub>2</sub>N<sup>+</sup> (M - OH + NH<sub>3</sub>) 306.0811, observed 306.0802.



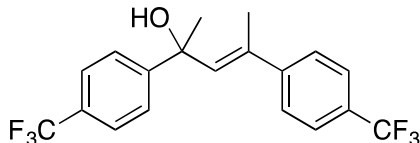
**Compound S2f:** General procedure 2 was used and the product was isolated in 93% yield.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.50 – 7.42 (m, 6H), 7.29 – 7.27 (m, 2H), 6.26 (q, *J* = 1.4 Hz, 1H), 2.26 (s, OH, 1H), 1.91 (d, *J* = 1.5 Hz, 3H), 1.73 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 147.4, 142.6, 139.0, 135.1, 131.4, 131.3, 127.6, 127.1, 121.4, 120.6, 73.9, 33.9, 17.3.

**IR (cm<sup>-1</sup>):** 3442, 2972, 1483, 1396, 1075, 1008, 816.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>Br<sub>2</sub><sup>+</sup> (M - OH)<sup>+</sup> 378.9515, observed 378.9515.



**Compound S2g:** General procedure 2 was used and the product was isolated in 87% yield.

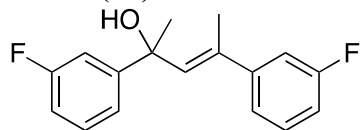
**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ 7.80 (ad, *J* = 8.4 Hz, 2H), 7.74 - 7.70 (m, 4H), 7.65 (ad, *J* = 8.0 Hz, 2H), 6.45 (q, *J* = 1.6 Hz, 1H), 3.83 (s, OH, 1H), 1.98 (d, *J* = 1.2 Hz, 3H), 1.79 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):** δ 154.7, 149.0, 139.1, 138.0, 129.6 (q, *J*<sub>C-F</sub> = 31.7 Hz), 129.0 (q, *J*<sub>C-F</sub> = 31.7 Hz), 127.5 (m), 126.9 (m), 126.2 (m), 125.9 (m), 125.7 (q, *J*<sub>C-F</sub> = 269.3 Hz), 125.6 (q, *J*<sub>C-F</sub> = 269.4 Hz), 74.4, 34.2, 12.5.

**<sup>19</sup>F NMR (376 MHz, CDCN):**  $\delta$  -62.76 (s), -62.91 (s).

**IR (cm<sup>-1</sup>):** 3441, 2977, 1616, 1325, 1166, 1123, 1071, 1015, 844.

**HRMS (CI):** Calculated for C<sub>19</sub>H<sub>15</sub>F<sub>2</sub><sup>+</sup> (M - OH)<sup>+</sup> 357.1078, observed 357.1072.



**Compound S2h:** General procedure 2 was used and the product was isolated in 50% yield.

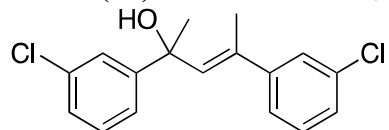
**<sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN):**  $\delta$  7.39-7.30 (m, 4H), 7.28-7.25 (m, 1H), 7.22-7.18 (m, 1H), 7.06-6.97 (m, 2H), 6.31 (q,  $J$  = 1.3 Hz, 1H), 3.56 (s, OH, 1H), 1.89 (d,  $J$  = 1.3 Hz, 3H), 1.68 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):**  $\delta$  162.8 (d,  $J_{C-F}$  = 241.5 Hz), 162.7 (d,  $J_{C-F}$  = 241.3 Hz), 152.8 (d,  $J_{C-F}$  = 6.5 Hz), 146.8 (d,  $J_{C-F}$  = 7.4 Hz), 137.5 (d,  $J_{C-F}$  = 2.1 Hz), 136.4, 129.9 (d,  $J_{C-F}$  = 8.7 Hz), 129.6 (d,  $J_{C-F}$  = 8.1 Hz), 121.7 (d,  $J_{C-F}$  = 2.3 Hz), 121.2 (d,  $J_{C-F}$  = 2.5 Hz), 113.6 (d,  $J_{C-F}$  = 21.2 Hz), 112.7 (d,  $J_{C-F}$  = 21.1 Hz), 112.5 (d,  $J_{C-F}$  = 21.9 Hz), 112.1 (d,  $J_{C-F}$  = 22.1 Hz), 72.9, 33.5, 16.4.

**<sup>19</sup>F NMR (471 MHz, CD<sub>3</sub>CN):**  $\delta$  -115.05 (s), -115.24 (s).

**IR (cm<sup>-1</sup>):** 3440, 2976, 1611, 1583, 1484, 1270.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub><sup>+</sup> (M - OH)<sup>+</sup> 257.1136, observed 257.1134.



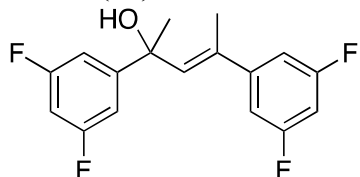
**Compound S2i:** General procedure 2 was used and the product was isolated in 83% yield.

**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):**  $\delta$  7.67 (t,  $J$  = 1.9 Hz, 1H), 7.49-7.47 (m, 2H), 7.36-7.24 (m, 5H), 6.32 (q,  $J$  = 1.3 Hz, 1H), 3.72 (s, 1H), 1.92 (d,  $J$  = 1.3 Hz, 3H), 1.72 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  152.6, 147.1, 138.8, 137.1, 134.8, 134.6, 130.82, 130.71, 128.1, 127.4, 126.9, 126.3, 125.3, 124.8, 74.3, 34.3, 17.7.

**IR (cm<sup>-1</sup>):** 3581, 3423, 2974, 1593, 782.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>Cl<sub>2</sub><sup>+</sup> (M - OH)<sup>+</sup> 289.0545, observed 289.0540.



**Compound S2j:** General procedure 2 was modified and addition of ketone to MeLi solution was conducted at -78 °C. The product was isolated in 77% yield.

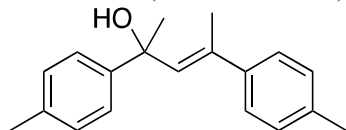
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.03 (m, 2H), 6.90 (m, 2H), 6.70 (m, 2H), 6.22 (q,  $J$  = 1.0 Hz, 1H), 1.95 (s, OH, 1H), 1.89 (d,  $J$  = 1.0 Hz, 3H), 1.70 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  163.0 (dd,  $J_{C-F}$  = 248, 5.6 Hz), 162.9 (dd,  $J_{C-F}$  = 248, 6.0 Hz), 152.3 (t,  $J_{C-F}$  = 8.0 Hz), 146.8 (t,  $J_{C-F}$  = 9.0 Hz), 139.0, 135.4, 108.9 (m), 108.2 (m), 102.8 (t,  $J_{C-F}$  = 25 Hz), 102.2 (t,  $J_{C-F}$  = 25 Hz), 73.7, 34.0, 17.1.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -109.47 (s), -110.05 (s).

**IR (cm<sup>-1</sup>):** 3448, 2976, 1621, 1432, 1118, 984, 848.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>13</sub>F<sub>4</sub><sup>+</sup> (M - OH)<sup>+</sup> 293.0948, observed 293.0949, calculated for C<sub>17</sub>H<sub>16</sub>F<sub>4</sub>N<sup>+</sup> (M - OH + NH<sub>3</sub>)<sup>+</sup> 310.1213, observed 310.1210.



**Compound S2k:** General procedure 2 was used and the product was isolated in 89% yield.

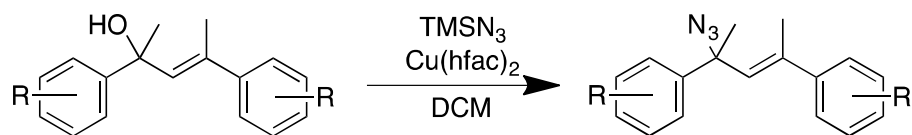
**<sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>):** δ 7.51 – 7.49 (ad, *J* = 8.4, 2H), 7.33 – 7.31 (ad, *J* = 8.4 2H), 7.15 (d, *J* = 8.4 Hz, 4H), 6.30 (q, *J* = 1.2 Hz, 1H), 4.19 (s, 1H, OH), 2.31 (s, 6H), 1.95 (d, *J* = 1.2 Hz, 3H), 1.71 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, Acetone-*d*<sub>6</sub>):** δ 146.9, 141.6, 137.6, 136.3, 135.4, 135.2, 128.8, 128.5, 125.7, 125.3, 73.2, 33.6, 20.3, 20.1, 16.6.

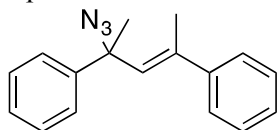
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 145.9, 141.4, 139.1, 137.0, 136.2, 134.9, 129.2, 129.1, 126.0, 125.5, 75.5, 33.8, 21.3, 17.6, 17.5.

**IR (cm<sup>-1</sup>):** 3445, 3023, 2973, 2920, 1511, 1445, 1067, 810.

**HRMS (CI):** Calculated for C<sub>19</sub>H<sub>21</sub><sup>+</sup> (M - OH)<sup>+</sup> 249.1638, observed 249.1630.



**General Procedure 3 Azide Formation:** Example given for R = H. To a solution of allylic alcohol **S2a** (808 mg, 3.03 mmol) in DCM (18 mL) was added TMS-N<sub>3</sub> (0.80 mL, 6.1 mmol) and Cu(hfac)<sub>2</sub>·H<sub>2</sub>O (251 mg, 0.525 mmol) at room temperature. The vessel was sealed. After 18-24 h, the solution was filtered through basic alumina and washed with excess DCM. The resulting solution was concentrated under reduced pressure. Purification by column chromatography (2% EtOAc/hexanes) afforded azide **1a** (562 mg, 1.9 mmol, 64%). Analysis by <sup>1</sup>H NMR showed that the azide contained ca 5% of the alkene isomer. The peaks are fully labeled for the 4-CF<sub>3</sub> azide in the spectral section. Due to the Winstein rearrangement, separation of the isomers was impractical. The data reported below are for the major isomer.



**Compound 1a:** General procedure 3 was used and the product was isolated in 66% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.62 – 7.49 (m, 4H), 7.49 – 7.30 (m, 6H), 6.25 (q, *J* = 1.2 Hz, 1H), 1.94 (d, *J* = 1.2 Hz, 3H), 1.89 (s, 3H).

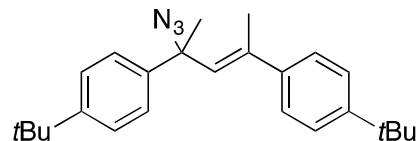
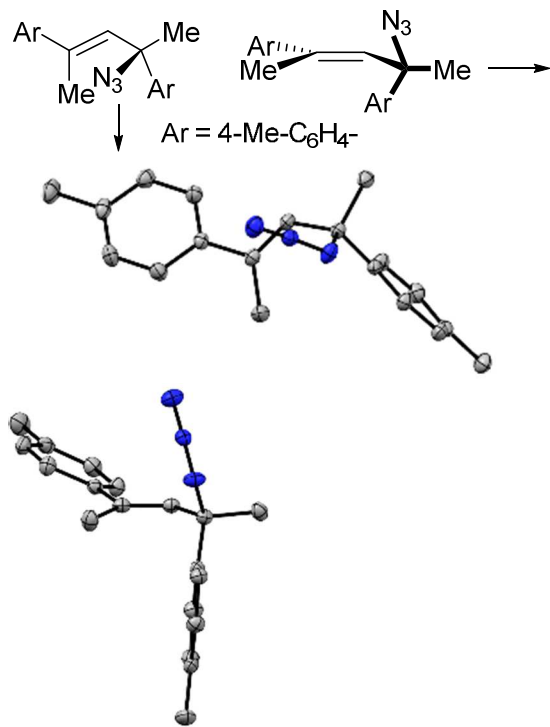
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 145.2, 143.7, 143.0, 130.9, 128.8, 128.7, 128.0, 127.5, 126.4, 126.1, 67.0, 31.6, 18.0.

**IR (cm<sup>-1</sup>):** 3026, 2968, 2103, 1492, 1445, 1253, 757.

**TGA:** T<sub>d,5%</sub> N<sub>2</sub> = 152 °C, T<sub>d,5%</sub> air = 125 °C

**DSC:** -80 °C to 115 °C, 10 °C/min, no decomposition for 2 cycles.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>17</sub><sup>+</sup> (M - N<sub>3</sub>)<sup>+</sup> 221.1330, observed 221.1333; calculated for C<sub>17</sub>H<sub>18</sub>N<sup>+</sup> (M - N<sub>2</sub> + H)<sup>+</sup> 236.1439, observed 236.1440.



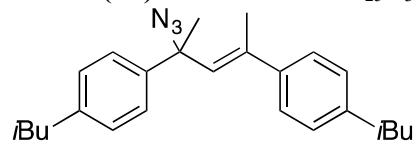
**Compound 1b:** General procedure 3 was used and the product was isolated in 43% yield.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.56 – 7.46 (m, 8H), 6.28, (s, 1H), 2.01 (s, 3H), 1.91 (s, 3H), 1.47 (s, 9H), 1.45 (s, 9H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 150.7, 149.9, 141.9, 141.8, 140.5, 130.1, 125.8, 125.5, 125.3, 125.3, 66.7, 34.6, 34.5, 31.5, 31.5, 31.1, 17.6.

**IR (cm<sup>-1</sup>):** 2963, 2904, 2103, 1508, 1269, 1252, 834.

**HRMS (CI):** Calculated for C<sub>25</sub>H<sub>33</sub><sup>+</sup> (M – N<sub>3</sub>)<sup>+</sup> 333.2577, observed 333.2589.



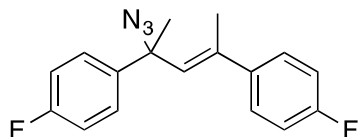
**Compound 1c:** General procedure 3 was used and the product was isolated in 82% yield.

**<sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>):** δ 7.41 (m, 4H), 7.16 (m, 4H), 6.18 (s, 1H), 2.52 (d *J* = 7.2 Hz, 4H), 1.92 (m, 2H), 1.88 (s, 3H), 1.83 (s, 3H), 0.97 (d, *J* = 5.2 Hz, 6H), 0.95 (d, *J* = 5.2 Hz, 6H).

**<sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>):** δ 142.2, 142.1, 141.4, 140.8, 140.6, 130.1, 129.2, 129.2, 125.9, 125.6, 66.9, 45.2, 45.1, 31.1, 30.4, 30.3, 22.5, 22.5, 17.7.

**IR (cm<sup>-1</sup>):** 2955, 2923, 2103, 1509, 1465, 1251, 795.

**HRMS (CI):** Calculated for C<sub>25</sub>H<sub>33</sub><sup>+</sup> (M – N<sub>3</sub>)<sup>+</sup> 333.2577, observed 333.2590.



**Compound 1d:** General procedure 3 was used and the product was isolated in 51% yield.

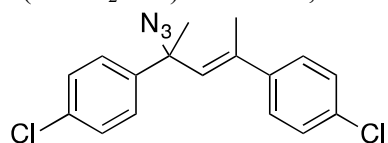
**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ 7.51-7.46 (m, 4H), 7.11 – 7.06 (m, 4H), 6.16 (q, *J* = 1.2 Hz, 1H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.76 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):** δ 164.3 (d, *J*<sub>C-F</sub> = 243.8 Hz), 161.8 (d, *J*<sub>C-F</sub> = 242.9 Hz), 142.2, 141.8 (d, *J*<sub>C-F</sub> = 3.4 Hz), 140.2 (d, *J*<sub>C-F</sub> = 3.1 Hz), 131.4, 128.8 (d, *J*<sub>C-F</sub> = 12.4 Hz), 128.7 (d, *J*<sub>C-F</sub> = 12.4 Hz), 116.1, 115.9, 67.2, 31.4, 18.0.

**<sup>19</sup>F NMR (371 MHz, CD<sub>3</sub>CN):** δ -116.3 (s), -117.1 (s).

**IR (cm<sup>-1</sup>):** 2970, 2103, 1601, 1506, 1233, 1159, 836.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub><sup>+</sup> (M – N<sub>3</sub>)<sup>+</sup> 257.1136, observed 257.1134, calculated for C<sub>17</sub>H<sub>16</sub>F<sub>2</sub>N<sup>+</sup> (M – N<sub>2</sub> + H)<sup>+</sup> 272.1245, observed 272.1245.



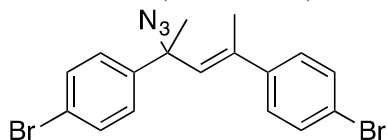
**Compound 1e:** General procedure 3 was used and the product was isolated in 73% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.53 – 7.48 (m, 4H), 7.43 – 7.38 (m, 4H), 6.27 (q, *J* = 1.2 Hz, 1H), 1.84 (d, *J* = 1.2 Hz, 3H), 1.83 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):** δ 144.6, 142.5, 142.4, 134.2, 133.6, 131.7, 129.5, 129.4, 128.6, 128.5, 67.2, 31.5, 18.0.

**IR (cm<sup>-1</sup>):** 2970, 2924, 2103, 1487, 1095, 1012, 829.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>Cl<sub>2</sub><sup>+</sup> (M – N<sub>3</sub>)<sup>+</sup> 289.0545, observed 289.0539, calculated for C<sub>17</sub>H<sub>16</sub>Cl<sub>2</sub>N<sup>+</sup> (M – N<sub>2</sub> + H)<sup>+</sup> 304.0654, observed 304.0647.



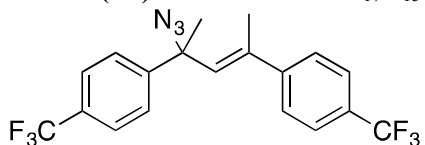
**Compound 1f:** General procedure 3 was used and the product was isolated in 70% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.49 – 7.46 (m, 4H), 7.35 (ad, *J* = 2H), 7.29 (ad, *J* = 2H), 6.13 (q, *J* = 1.3 Hz, 1H), 1.83 (d, *J* = 1.4 Hz, 3H), 1.78 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 143.7, 142.0, 141.8, 131.5, 131.4, 130.4, 127.6, 127.4, 121.7, 121.1, 66.0, 31.2, 17.6.

**IR (cm<sup>-1</sup>):** 2968, 2105, 1484, 1076, 1008, 825.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>Br<sub>2</sub><sup>+</sup> (M – N<sub>3</sub>)<sup>+</sup> 378.9515, observed 378.9532.



**Compound 1g:** General procedure 3 was modified. Zn(OTf)<sub>2</sub> was used as the Lewis acid. The product was isolated in 68% yield.

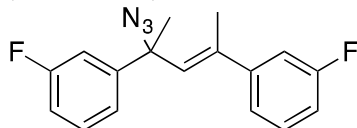
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.70 – 7.58 (m, 6H), 7.57 (d, *J* = 8.2 Hz, 2H), 6.25 (q, *J* = 1.4 Hz, 1H), 1.89 (d, *J* = 1.5 Hz, 3H), 1.86, (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 148.8, 146.6, 142.7, 131.7, 130.05 (q, *J*<sub>C-F</sub> = 32.5 Hz), 129.7 (q, *J*<sub>C-F</sub> = 32.5 Hz), 126.5, 126.2, 125.7 (q, *J*<sub>C-F</sub> = 3.8 Hz), 125.5 (q, *J*<sub>C-F</sub> = 3.8 Hz), 124.3 (q, *J*<sub>C-F</sub> = 270 Hz), 124.2 (q, *J*<sub>C-F</sub> = 270 Hz), 66.1, 31.4, 17.8.

**<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>):** δ -62.53, -62.57.

**IR (cm<sup>-1</sup>):** 2975, 2931, 2108, 1616, 1326, 1166, 1125, 1015, 843.

**HRMS (CI):** Calculated for C<sub>19</sub>H<sub>21</sub><sup>+</sup> (M - N<sub>3</sub>)<sup>+</sup> 357.10778, observed 357.1072, calculated for C<sub>19</sub>H<sub>22</sub>N<sup>+</sup> (M - N<sub>2</sub> + H)<sup>+</sup> 372.11867, observed 372.1181.



**Compound 1h:** General procedure 3 was modified. Zn(TFA)<sub>2</sub> (0.2 eq) was used as the Lewis acid. The product was isolated in 70% yield.

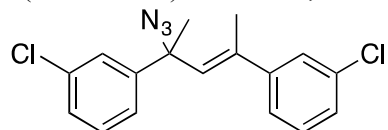
**<sup>1</sup>H-NMR (400 MHz; CD<sub>3</sub>CN):** δ 7.43-7.36 (m, 2H), 7.34-7.31 (m, 2H), 7.30-7.25 (m, 2H), 7.10-7.03 (m, 2H), 6.27 (q, *J* = 1.3 Hz, 1H), 1.82 (d, *J* = 1.3 Hz, 3H), 1.81 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN)** δ 162.8 (d, *J*<sub>C-F</sub> = 241.6 Hz), 162.7 (d, *J*<sub>C-F</sub> = 242.3 Hz), 147.7 (d *J*<sub>C-F</sub> = 8.5 Hz), 145.3 (d, *J*<sub>C-F</sub> = 7.3 Hz), 141.4 (d, *J*<sub>C-F</sub> = 2.1 Hz), 131.1, 130.3 (d, *J*<sub>C-F</sub> = 17.6 Hz), 130.2 (d, *J*<sub>C-F</sub> = 18.2 Hz), 121.9 (d, *J*<sub>C-F</sub> = 2.8 Hz), 121.6 (d, *J*<sub>C-F</sub> = 2.5 Hz), 114.4 (d, *J*<sub>C-F</sub> = 2.1 Hz), 113.9 (d, *J*<sub>C-F</sub> = 2.1 Hz), 112.9 (d, *J*<sub>C-F</sub> = 10.7 Hz), 112.6 (d, *J*<sub>C-F</sub> = 9.5 Hz), 66.1, 30.3, 16.8.

**<sup>19</sup>F NMR (376 MHz; CD<sub>3</sub>CN):** δ -114.0, -114.8.

**IR (cm<sup>-1</sup>):** 2971.84, 2104, 1612, 1583, 1435, 1253.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub><sup>+</sup> (M - N<sub>3</sub>)<sup>+</sup> 257.1136, observed 257.1128, calculated for C<sub>17</sub>H<sub>16</sub>F<sub>2</sub>N<sup>+</sup> (M - N<sub>2</sub> + H)<sup>+</sup> 272.1245, observed 272.1236.



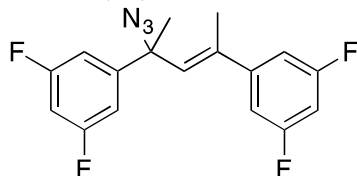
**Compound 1i:** General procedure 3 was modified. Sm(OTf)<sub>3</sub> (0.2 eq) was used as the Lewis acid. The product was isolated in 63% yield.

**<sup>1</sup>H-NMR (400 MHz; acetone-*d*<sub>6</sub>):** δ 7.59-7.57 (m, 2H), 7.52-7.47 (m, 2H), 7.44-7.38 (m, 2H), 7.37-7.33 (m, 2H), 6.36 (q, *J* = 1.3 Hz, 1H), 1.87 (d, *J* = 1.2, 3H), 1.86 (s, 3H).

**<sup>13</sup>C NMR (100 MHz; acetone-*d*<sub>6</sub>):** δ 148.3, 146.0, 142.4, 134.9, 134.9, 132.3, 131.2, 131.0, 128.6, 128.2, 127.0, 126.7, 125.6, 125.3, 67.0, 31.6, 17.8

**IR (cm<sup>-1</sup>):** 2970, 2103, 1594, 1256.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>15</sub>Cl<sub>2</sub><sup>+</sup> (M - N<sub>3</sub>)<sup>+</sup> 289.0545, observed 289.0539.



**Compound 1j:** General procedure 3 was modified. Zn(TFA)<sub>2</sub> was used as the Lewis acid. The product was isolated in 74% yield.

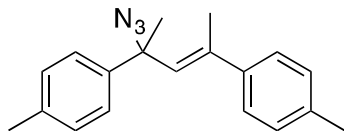
**<sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>):** δ 7.02-6.95 (m, 4H), 6.80-6.73 (m, 2H), 6.14 (d, *J* = 1.3 Hz, 1H), 1.86 (d, *J* = 1.3 Hz, 3H), 1.80 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 163.2 (dd, *J*<sub>C-F</sub> = 247.2, 8.2 Hz), 163.1 (dd, *J*<sub>C-F</sub> = 247.2, 8.2 Hz), 148.8 (t, *J*<sub>C-F</sub> = 8.5 Hz), 146.1 (t, *J*<sub>C-F</sub> = 8.8 Hz), 142.1 (t, *J*<sub>C-F</sub> = 2.3 Hz), 131.2, 103.3 (t, *J*<sub>C-F</sub> = 25.5 Hz), 102.9 (t, *J*<sub>C-F</sub> = 25.2 Hz), 109.3 – 108.8 (m, 2C), 65.6, 31.4, 17.7.

**<sup>19</sup>F NMR (376 MHz; CD<sub>3</sub>CN):** δ -108.7, -109.7.

**IR (cm<sup>-1</sup>):** 2974, 2928, 2107, 1621, 1591, 1433, 1119, 848.

**HRMS (CI):** Calculated for C<sub>17</sub>H<sub>13</sub>F<sub>4</sub><sup>+</sup> (M - N<sub>3</sub>)<sup>+</sup> 293.0948, observed 293.0949, calculated for C<sub>17</sub>H<sub>14</sub>F<sub>4</sub>N<sup>+</sup> (M - N<sub>2</sub> + H)<sup>+</sup> 308.1057, observed 308.1060.



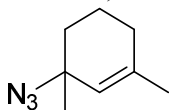
**Compound 1k:** General procedure 3 was used and the product was isolated in 64% yield.

**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ 7.42 – 7.37 (m, 4H), 7.19 – 7.17 (m, 4H), 6.20 (q, *J* = 1.3 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 1.84 (d, *J* = 1.4 Hz, 3H), 1.78 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):** δ 142.8, 142.6, 141.2, 138.4, 137.7, 130.8, 130.0, 129.9, 126.8, 126.6, 67.7, 31.3, 21.4, 21.3, 18.0.

**IR (cm<sup>-1</sup>):** 3032, 2970, 2921, 2098, 1511, 1256, 805.

**HRMS (CI):** Calculated for C<sub>19</sub>H<sub>21</sub><sup>+</sup> (M – N<sub>3</sub>)<sup>+</sup> 249.1638, observed 249.1635, calculated for C<sub>19</sub>H<sub>22</sub>N<sup>+</sup> (M – N<sub>2</sub> + H)<sup>+</sup> 264.1747, observed 264.1745.



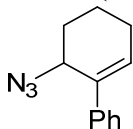
**Compound S3a:** A modified version of general procedure 3 was used with Zn(OTf)<sub>2</sub>. After 15 min at room temperature, the reaction was quenched by the addition of TEA (3 equivalents), the crude mixture was passed through a short path of silica gel, and the resulting solution was concentrated under slightly reduced pressure. The residue was reconstituted (10% DCM in hexanes), passed through a second short path of silica gel, and concentrated under slightly reduced pressure. This afforded the product in 71% yield. Due to the volatility of this compound it was used in the next step without further purification.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 5.37 (bs, 1H), 2.01 – 1.96 (m, 2H), 1.84 – 1.68 (m, 3H), 1.76 (s, 3H), 1.56 – 1.49 (m, 1H), 1.31 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 139.8, 123.8, 77.5, 77.2, 76.8, 61.0, 35.7, 29.9, 27.7, 23.7, 19.6.

**IR:** 2934, 2868, 2098, 1669, 1557, 1251, 1136.

**HRMS (EI):** Calculated for C<sub>8</sub>H<sub>13</sub><sup>+</sup> (M – N<sub>3</sub>)<sup>+</sup> 109.1012, observed 109.1016



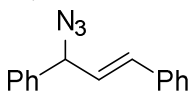
**Compound S3b:** General procedure 3 was modified. Zn(OTf)<sub>2</sub> was used as the Lewis acid. The product was isolated in 70% yield.

**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ 7.53 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.30 (m, 1H), 6.41 (dd, *J* = 4.8, 3.3 Hz, 1H), 4.51 (t, *J* = 3.9 Hz, 1H), 2.40 – 2.15 (m, 2H), 2.15 – 2.02 (m, 1H), 2.02 – 1.86 (m, 1H), 1.83 – 1.68 (m, 2H).

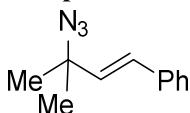
**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):** δ 141.2, 135.6, 131.7, 129.6, 128.4, 126.8, 57.7, 30.3, 26.4, 18.4.

**IR:** 3058, 2939, 2867, 2093, 1599, 1444, 1223, 905, 757, 696.

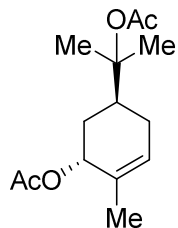
**HRMS (EI):** Calculated for C<sub>12</sub>H<sub>13</sub> (M – N<sub>3</sub>)<sup>+</sup> 157.1012, observed 157.0935; calculated for C<sub>12</sub>H<sub>13</sub> (M – N<sub>2</sub>)<sup>+</sup> 171.1042, observed 171.1043.



**Compound S3c:** This azide is a known compound and was prepared as previously reported.<sup>4</sup>



**Compound S3d:** This azide is a known compound and was prepared as previously reported.<sup>4</sup>



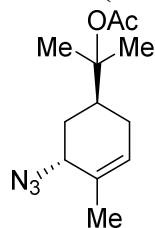
**Compound S3e:** To a solution of *trans*-sobrerol (965 mg, 5.67 mmol) in pyridine (7 mL) at room temperature was subsequently added DMAP (188 mg, 1.54 mmol) and acetic anhydride (3.5 mL, 31 mmol). After 8h, the reaction was quenched by the addition of water and extracted with DCM (3 x 20 mL). The combined organic phases were washed with 1M HCl, water, brine, dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Final purification by column chromatography (gradient EtOAc/Hex from 10% - 50%) afforded the bis-acetate (828 mg, 57%).

**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ 5.66 (d, *J* = 5.6 Hz, 1H), 5.16 (s, 1H), 2.19 (dddd, *J* = 13.5, 11.6, 4.8, 2.4 Hz, 1H), 2.12 – 2.03 (m, 1H), 2.01 (s, 3H), 1.92 – 1.88 (m, 1H), 1.90 (s, 3H), 1.86 – 1.74 (m, 1H), 1.63 (s, 3H), 1.50 – 1.41 (m, 1H), 1.38 (s, 3H), 1.36 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):** δ 170.9, 170.1, 131.0, 127.5, 83.6, 70.7, 37.5, 29.6, 26.5, 23.5, 23.2, 22.3, 21.2, 20.6.

**IR:** 2937, 1731, 1368, 1240, 1029, 667.

**HRMS (ESI):** Calculated for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>Na (M + Na)<sup>+</sup> 277.1410, observed 277.1417.



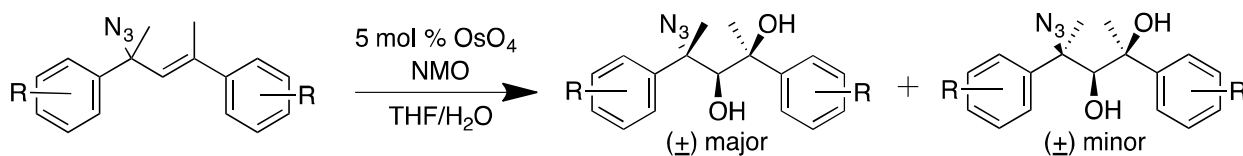
**Compound S3f:** According to the procedure of Murahashi,<sup>5</sup> acetate **S3e** (826 mg, 3.25 mmol), NaN<sub>3</sub> (440 mg, 6.77 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (103 mg, 0.09 mmol, 2.7 mol%) were dissolved in THF (10 mL) and water (2 mL). The vial was sealed and heated to 50 °C. After 22h, the vial was cooled to room temperature and diluted with water. The resulting solution was extracted with EtOAc. The combined organic phases were washed with brine, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. Final purification by column chromatography (gradient EtOAc/Hex from 10% - 50%) afforded azide **S3f** (586 mg, 82%) as a 25:1 mixture of diastereomers as a colorless oil.

**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ 5.70 (ddq, *J* = 5.1, 3.2, 1.4 Hz, 1H), 3.80 (dd, *J* = 4.4, 2.2 Hz, 1H), 2.21 – 2.03 (m, 3H), 1.99 (s, 3H), 1.94 – 1.80 (m, 1H), 1.79 (d, *J* = 1.5 Hz, 3H), 1.56 (ddd, *J* = 13.6, 12.5, 4.2 Hz, 1H), 1.47 (s, 3H), 1.45 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):** δ 170.2, 130.5, 126.8, 83.5, 60.5, 37.9, 29.7, 26.3, 23.4, 22.9, 22.4, 21.4.

**IR:** 2979, 2936, 2099, 2731, 1367, 1252, 1134, 1020.

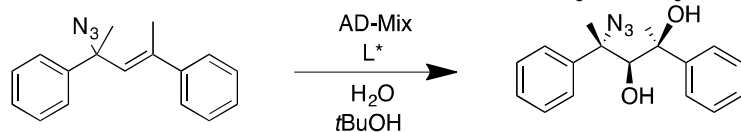
**HRMS (ESI):** Calculated for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>Na (M + Na)<sup>+</sup> 277.1410, observed 277.1417.



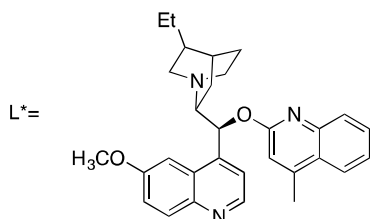
**General Procedure 4 Upjohn Dihydroxylation:** Example given for R = Br. To a solution of azide (76.1 mg, 0.18 mmol) in THF (2 mL), NMO (90 μL, 50% in H<sub>2</sub>O, 0.38 mmol), OsO<sub>4</sub> (40 μL, 0.22 M in H<sub>2</sub>O, 5 mol %) and H<sub>2</sub>O (0.1 mL) were sequentially added. The vial was sealed under air and heated to 35 °C. After 18h, the reaction was diluted with water and the resulting solution was extracted with EtOAc (10 mL x 3). The combined organic phase was washed with brine, dried (MgSO<sub>4</sub>), and concentrated under

vacuum. Final purification via column chromatography (5%-35% EtOAc in hexanes) yielded racemic diol (67 mg, 81%).

## General Procedures for DKR by Dihydroxylation:



AD-Mix = 3 eq.  $K_3FeCN$ , 3 eq.  $NH_2SO_2Me$ , 3 eq.  $K_2CO_3$ , 5%  $OsO_4$  in  $H_2O$



**Preparation of AD-mix solution:** A vial was sequentially charged with solid methane sulfonamide (285 mg, 3 mmol, 3 equiv.), potassium ferrocyanide (970 mg, 3 mmol, 3 equiv.), potassium carbonate (410 mg, 3 mmol, 3 equiv.), and a solution of  $OsO_4$  (0.26 mL, 0.196 M in water, 5 mol%), and diluted with water to a final volume of 5 mL. This solution was kept for no more than 48 h because over time it became less effective for dihydroxylation. This solution was used in dihydroxylation reactions below. Based on the stoichiometry of the solution, 1 mL of solution was used for every 0.2 mmol substrate. Using this volume of solution provides 3 equiv. of methane sulfonamide, potassium ferrocyanide, and potassium carbonate and 5 mol %  $OsO_4$ .

**Procedure for Ligand Screen:** A solution of substrate (658 mg, 2.50 mmol) and triphenylmethane (207 mg, 0.848 mmol) was prepared in *t*-BuOH (50 mL). Separate vials were charged with varying ligands (9.4 – 18.1 mg each, 0.020 mmol). To each vial containing ligand, an aliquot of substrate solution (2.0 mL, 0.20 mmol), water (0.87 mL), and AD-mix solution (1.1 mL, described above) were sequentially added. The vials were sealed under air and heated to 40 °C. After 48 h, each reaction was cooled to room temperature and diluted with water (1 mL) and ethyl acetate (1 mL). The phases were separated. The organic layer was filtered through a plug of silica gel, rinsed with additional ethyl acetate, and then concentrated under reduced pressure. A crude NMR spectrum was obtained to determine dr and yield relative to triphenylmethane. The crude sample was purified by preparative TLC (50% EtOAc/hexanes) and subjected to chiral HPLC to determine er.

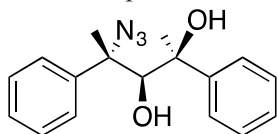
### Procedure for Temperature Screen:

A solution of substrate (224 mg, 0.851 mmol), DHQ-MEQ (40 mg, 0.084 mmol) and triphenylmethane (59 mg, 0.24 mmol, internal standard) was made in *t*-BuOH (8.5 mL). Aliquots (0.8 mL, 0.08 mmol substrate) of this solution were added to several vials followed subsequently by water (0.26 mL) and AD-mix solution (0.53 mL, described above). The vials were sealed under air and maintained at various temperatures. After 48 h, each reaction was diluted with water (1 mL) and ethyl acetate (1 mL). The phases were separated. The organic layer was filtered through a plug of silica gel, rinsed with additional ethyl acetate, and then concentrated under reduced pressure. A crude NMR spectrum was obtained to determine dr and yield. The crude sample was purified by preparative TLC (50% EtOAc/hexanes) and subjected to chiral HPLC to determine er.

**General Procedure 5: Asymmetric Dihydroxylation:** Example given for R = H. A vial was sequentially charged with azide (125 mg, 0.47 mmol, 1 equiv), hydroquinone 4-methyl-2-quinolyl ether (30 mg, 0.05 mmol, 10 mol%), *t*-BuOH (4.8 mL), water (2.6 mL), and AD-mix solution (2.2 mL, described above).

The vial was sealed under air and heated to 40 °C. After 48 h, the reaction was diluted with water and extracted with DCM (3 x 5 mL). Final purification by chromatography (gradient EtOAc/Hex from 0% - 30%) afforded the final product (115 mg, 81%, 11:1 dr). The er of the product was determined by chiral HPLC (99:1 er).

**Procedure for the Gram Scale Asymmetric Dihydroxylation:** A 250 mL round bottom flask was sequentially charged with azide **1** (1.38 g, 5.24 mmol, 1 equiv), hydroquinine 4-methyl-2-quinolyl ether (240 mg, 0.51 mmol, 10 mol%), *t*-BuOH (50 mL), water (50 mL), K<sub>2</sub>CO<sub>3</sub> (2.31 g, 16.6 mmol, 3 equiv), MeSO<sub>2</sub>NH<sub>2</sub> (1.68 g, 16.8 mmol), K<sub>3</sub>Fe(CN)<sub>6</sub> (5.56 g, 16.8 mmol), and OsO<sub>4</sub> (1.3 ml, 0.20 M in water, 5 mol%). The flask was sealed under air and heated to 40 °C. After 48 h, the reaction was diluted with water. The resulting solution was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with brine, dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Final purification by chromatography (gradient EtOAc in Hex from 0% - 30%) afforded diol **2** (1.29 g, 83%) as a colorless oil. In a duplicate experiment, 1.27 g of azide **1** afforded 1.11 g of diol **2** (77%). The average yield of 80% is reported in the paper. The dr of the reaction was determined by crude NMR to be 9.8:1 and 10.6 :1 in duplicate trials. The average dr of 10:1 is reported in the paper. The er of the product was determined by chiral HPLC after purification. The er was determined to be 99:1 in both experiments and 99:1 is reported in the paper. The diastereomers could be separated by silica gel chromatography using isocratic separation at 10% EtOAc in Hex.



**Compound 2a:** General procedure 4 was used and gave the product as the racemate in 60% yield. General procedure 5 was used to give the product in 77% and 81% isolated yield with a 10.6:1 and 10.9:1 dr. The average yield of 79% and 11:1 dr is reported.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.46 – 7.44 (m, 2H), 7.40 – 7.35 (m, 4H), 7.31-7.28 (m, 3H), 7.26 – 7.18 (m, 1H), 4.10 (d, *J* = 6.8 Hz, 1H), 3.46 (s, 1H), 2.75 (d, OH, *J* = 6.9 Hz, 1H), 1.73 (s, 3H), 1.15 (s, 3H).

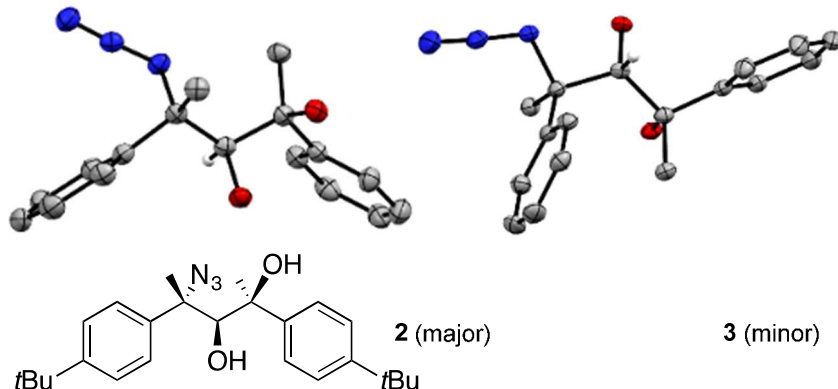
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 146.7, 143.5, 128.9, 128.4, 127.8, 127.1, 125.9, 124.9, 81.6, 77.5, 70.2, 28.6, 25.1.

**HRMS (ESI):** Calculated for C<sub>17</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>Na<sup>+</sup> (M + Na)<sup>+</sup> 320.1375, observed 320.1367.

**IR (cm<sup>-1</sup>):** 3426, 3027, 2111, 1446, 1253, 1026, 764.

**Chiral HPLC:** Phenomenex Lux 3μ cellulose-1 column, hexane/*i*PrOH = 98:2 at 1.0 mL/min, λ = 210 nm: For the major diastereomer: *t*<sub>major</sub> = 23.0 min, *t*<sub>minor</sub> = 16.6 min, er = 98.8:1.2, 98.6:1.4. The average er 99:1 is reported; For the minor diastereomer: *t*<sub>major</sub> = 24.0 min, *t*<sub>minor</sub> = 25.2 min, er = not determined.

#### X-Ray Structures of Diols **2** and **3**



**Compound 2b:** General procedure 4 was used and gave the product as the racemate in 73% yield. General procedure 5 was modified. The reaction was conducted at 35 °C. The product was isolated in 73% and 80% isolated yield with a 10:1 dr. The average yield of 77% is reported.

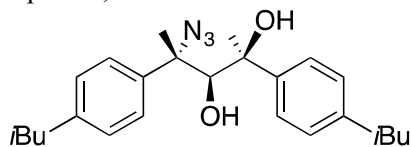
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.42 – 7.36 (ad, *J* = 4.4 Hz, 4H), 7.35 – 7.29 (ad *J* = 5.6, 4H), 4.05 (d, *J* = 6.6 Hz, 1H), 3.47 (s, 1H), 2.68 (d, *J* = 6.8 Hz, 1H), 1.74 (s, 3H), 1.34 (s, 9H), 1.31 (s, 9H) 1.17 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 150.5, 149.5, 143.7, 140.3, 125.6, 125.4, 125.0, 124.4, 81.1, 77.2, 69.9, 34.5, 34.4, 31.4, 31.3, 28.3, 24.5.

**IR (cm<sup>-1</sup>):** 3351, 2963, 2108, 1269, 1033, 835.

**HRMS (ESI):** Calculated for C<sub>25</sub>H<sub>35</sub>N<sub>3</sub>O<sub>2</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 432.2621, observed 432.2632.

**Chiral HPLC:** Phenomenex column, hexane/iPrOH = 96:4 at 0.5 mL/min, λ = 210 nm: For the major diastereomer: *t*<sub>major</sub> = 13.1 min, *t*<sub>minor</sub> = 11.0 min, er = 99.1:0.9 and 99.2:0.8. The average er 99:1 is reported; For the minor diastereomer: *t*<sub>major</sub> = 11.6 min, *t*<sub>minor</sub> = 12.7 min, er = not determined.



**Compound 2c:** General procedure 4 was used and gave the product as the racemate in 71% yield. General procedure 5 was modified. The reaction was conducted at 35 °C. The product was isolated in 80% and 81% yield with 11.4:1 and 9.0:1 dr. The average yield of 81% and 10:1 dr is reported.

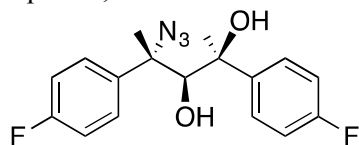
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.37 (ad, *J* = 8.2 Hz, 2H), 7.29 (ad, *J* = 8.0 Hz, 2H), 7.18 (ad, *J* = 8.0 Hz, 2H), 7.10 (ad, *J* = 8.0 Hz, 2H), 4.08 (d, *J* = 5.9 Hz, 1H), 3.51 (s, 1H), 2.74 (d, OH, *J* = 6.3 Hz, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.98 – 1.79 (m, 2H), 1.73 (s, 3H), 1.16 (s, 3H), 0.94 (d, *J* = 6.0 Hz, 6H) 0.92 (d, *J* = 6.0 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 143.9, 141.1, 140.5, 140.2, 129.4, 128.8, 125.4, 124.5, 81.4, 77.3, 69.91, 45.0, 44.9, 30.2, 30.1, 28.3, 24.7, 22.4, 22.4.

**IR (cm<sup>-1</sup>):** 3427, 2953, 2110, 1382, 1256, 1035.

**HRMS (ESI):** Calculated for C<sub>25</sub>H<sub>35</sub>N<sub>3</sub>O<sub>2</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 432.2621, observed 432.2629.

**Chiral HPLC:** Phenomenex column, hexane/iPrOH = 96:4 at 0.5 mL/min, λ = 210 nm: For the major diastereomer: *t*<sub>major</sub> = 12.5 min, *t*<sub>minor</sub> = 11.0 min, er = 95.0:5.0 and 94.7:5.3. The average er of 95:5 is reported; For the minor diastereomer: *t*<sub>major</sub> = 12.1 min, *t*<sub>minor</sub> = 11.7 min, er = 96:4.



**Compound 2d:** General procedure 4 was used and gave the product as the racemate in 75% yield. General procedure 5 was used to give the product in 72% and 78% isolated yield with a 11.0:1 and 8.1:1 dr in duplicate trials. The average yield of 75% and 9.5:1 dr is reported.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.08 – 6.96 (m, 4H), 4.03 (d, *J* = 6.5 Hz, 1H), 3.42 (s, 1H), 2.90 (d, OH, *J* = 6.5 Hz, 1H), 1.71 (s, 3H), 1.24 (s, 3H).

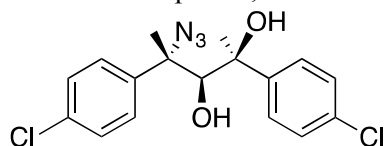
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 162.0 (d, *J*<sub>C-F</sub> = 246.2), 161.7 (d, *J*<sub>C-F</sub> = 243.8), 142.0, 138.7, 127.4 (d, *J*<sub>C-F</sub> = 7.9) 126.7 (d, *J*<sub>C-F</sub> = 8.0 Hz), 115.5 (d, *J*<sub>C-F</sub> = 21.2), 114.8 (d, *J*<sub>C-F</sub> = 21.0), 81.8, 76.8, 69.1 27.8, 24.8.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -114.7 (s), -116.2 (s).

**IR (cm<sup>-1</sup>):** 3421, 2984, 2115, 1508, 1232, 1162, 836.

**HRMS (ESI):** Calculated for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup> 356.1181, observed 356.1186.

**Chiral HPLC:** Phenomenex column, hexane/iPrOH = 99:1 at 1.75 mL/min, λ = 210 nm: For the major diastereomer: *t*<sub>major</sub> = 46.9 min, *t*<sub>minor</sub> = 42.3 min, er = 98.4:1.6 and 98.6:1.4 in duplicate trials. The average er of 98:2 is reported; For the minor diastereomer: *t*<sub>major</sub> = 49.4 min, *t*<sub>minor</sub> = 37.2 min, er = 96:4.



**Compound 2e:** General procedure 4 was used and gave the product as the racemate in 87% yield. General procedure 5 was used to give the product in 80% and 79% isolated yield with a 9.9:1 and 10.9:1 dr. The average yield of 80% and 10:1 dr is reported.

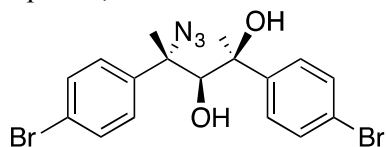
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.31 (m, 4H), 7.23 (m, 4H), 4.00 (s, 1H), 3.32 (s, 1H), 2.86 (s, 1H), 1.70 (s, 3H), 1.20 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 144.7, 141.5, 133.7, 133.0, 128.9, 128.3, 127.2, 126.6, 81.8, 77.0, 69.30, 27.8, 25.05.

**IR (cm<sup>-1</sup>):** 3417, 2984, 2116, 1491, 1096, 1012.

**HRMS (ESI):** Calculated for C<sub>17</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup> 388.0590, observed 388.0606.

**Chiral HPLC:** Phenomenex column, hexane/iPrOH = 78:22 at 0.3 mL/min, λ = 220 nm: For the major diastereomer: t<sub>major</sub> = 19.5 min, t<sub>minor</sub> = 17.2 min, er = 97.7:2.3 and 97.8:2.2. The average er of 98:2 is reported; For the minor diastereomer: t<sub>major</sub> = 16.7 min, t<sub>minor</sub> = 15.5 min, er = not determined.



**Compound 2f:** General procedure 4 was used and gave the product as the racemate in 81% yield. General procedure 5 was used to give the product in 81% and 63% isolated yield with a 8.1:1 and 10.0:1 dr. The average yield of 72% yield and 9:1 dr is reported.

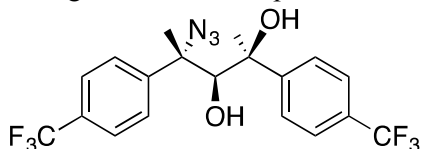
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.47 – 7.43 (ad, J = 8.4 Hz, 2H), 7.40 – 7.36 (ad, J = 8.6 Hz, 2H), 7.25 – 7.21 (ad, J = 8.8 Hz, 2H), 7.17 – 7.14 (ad, J = 8.8 Hz, 2H), 3.98 (d, J = 4.6 Hz, 1H), 3.32 (s, 1H), 2.93 (d, OH, J = 6.0 Hz, 1H), 1.69 (s, 3H), 1.22 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 145.0, 141.8, 131.7, 131.1, 127.4, 126.8, 121.6, 121.0, 81.6, 76.7, 69.1, 27.4, 24.8.

**HRMS (ESI):** Calculated for C<sub>17</sub>H<sub>17</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup> 477.9559, observed 477.9553.

**IR (cm<sup>-1</sup>):** 3415, 2981, 2115, 1488, 1008, 823.

**Chiral HPLC:** Phenomenex Lux 3μ cellulose-1 column, hexane/iPrOH = 90:10 at 0.5 mL/min, λ = 220 nm: For the major diastereomer: t<sub>major</sub> = 24.7 min, t<sub>minor</sub> = 20.2 min, er = 98.1:1.9 and 98.0:2.0. The average er of 98:2 is reported; For the minor diastereomer: t<sub>major</sub> = 19.2 min, t<sub>minor</sub> = 17.2 min, er = 94:6.



**Compound 2g:** General procedure 4 was used and gave the product as the racemate in 83% yield. General procedure 5 was used to give the product in 70% and 75% isolated yield with a 8.7:1 and 9.7:1 dr. The average yield of 73% and 9:1 dr is reported.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.54 (d, J = 8.4 Hz, 2H), 7.48 – 7.45 (m, 4H), 7.37 (d, J = 8.4 Hz, 2H), 4.13 (s, 1H), 3.28 (s, 1H), 3.08 (s, 1H), 1.76 (s, 3H), 1.29 (s, 3H).

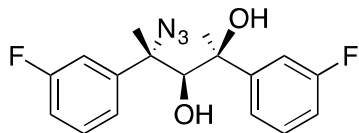
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.8, 146.7, 130.0 (q, J = 32.5 Hz), 129.4 (q, J = 32.3 Hz), 126.3, 125.7, 125.6 (m), 125.1 (q, J = 3.8 Hz), 124.2 (q, J = 270.2 Hz), 123.9 (q, J = 270.4 Hz), 82.0, 77.01, 69.2, 27.1, 25.4.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -62.7 (s), -62.7 (s).

**IR (cm<sup>-1</sup>):** 3428, 2988, 2940, 2120, 1329, 1121, 1015.

**HRMS (ESI):** Calculated for C<sub>19</sub>H<sub>17</sub>F<sub>6</sub>N<sub>3</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup> 456.1112, observed 456.1117.

**Chiral HPLC:** Phenomenex column, hexane/iPrOH = 98:2 at 1.25 mL/min, λ = 215 nm: For the major diastereomer: t<sub>major</sub> = 61.7 min, t<sub>minor</sub> = 49.6 min, er = 96.5:3.5 and 97.0:3.0. The average er 97:3 is reported; For the minor diastereomer: t<sub>major</sub> = 32.9 min, t<sub>minor</sub> = 33.9 min, er = not determined.



**Compound 2h:** General procedure 4 was used and gave the product as the racemate in 75% yield. General procedure 5 was modified. The reaction was conducted at 35 °C. The product was isolated in 78% and 73% isolated yield with a 9:1 dr. The average yield of 76% is reported.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.35-7.31 (m, 1H), 7.27-7.23 (m, 1H), 7.19-7.06 (m, 4H), 7.00-6.92 (m, 2H), 4.03 (d, *J* = 6.7 Hz, 1H), 3.48 (s, 1H), 3.04 (d, *J* = 6.9 Hz, 1H), 1.72 (s, 3H), 1.22 (s, 3H).

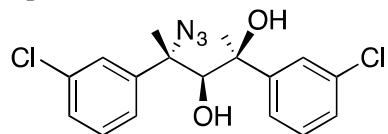
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 163.0 (d, *J*<sub>C-F</sub> = 245.1 Hz), 162.8 (d, *J*<sub>C-F</sub> = 243.6 Hz), 149.1 (d, *J*<sub>C-F</sub> = 6.6 Hz), 145.8 (d, *J*<sub>C-F</sub> = 6.5 Hz), 130.3 (d, *J*<sub>C-F</sub> = 8.4 Hz), 129.7 (d, *J*<sub>C-F</sub> = 8.1 Hz), 121.4 (d, *J*<sub>C-F</sub> = 2.9 Hz), 120.6 (d, *J*<sub>C-F</sub> = 2.7 Hz), 114.6 (d, *J*<sub>C-F</sub> = 21.1 Hz), 113.9 (d, *J*<sub>C-F</sub> = 21.0 Hz), 113.2 (d, *J*<sub>C-F</sub> = 23.3 Hz), 112.5 (d, *J*<sub>C-F</sub> = 22.7 Hz), 81.5, 77.0 (d, *J*<sub>C-F</sub> = 2.0 Hz), 69.2 (d, *J*<sub>C-F</sub> = 2.0 Hz), 27.7, 24.9.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -111.6 (s), -112.9 (s).

**IR (cm<sup>-1</sup>):** 3526, 3344, 3077, 2120, 784.

**HRMS (ESI):** Calculated for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup> 356.1181, observed 356.1178.

**Chiral HPLC:** Phenomenex column, hexane/iPrOH = 97:3 at 1.0 mL/min, λ = 270 nm: For the major diastereomer: *t*<sub>major</sub> = 40.6 min, *t*<sub>minor</sub> = 23.9 min, er = 97.6:2.4 and 97.8:2.2. The average er of 98:2 is reported; For the minor diastereomer: *t*<sub>major</sub> = 28.0 min, *t*<sub>minor</sub> = 32.8 min, er = not determined.



**Compound 2i:** General procedure 4 was used and gave the product as the racemate in 71% yield. General procedure 5 was used to give the product in 85% and 77% isolated yield with a 10:1 dr. The average yield of 81% is reported.

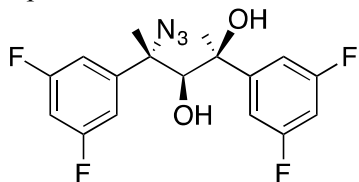
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.38-7.37 (m, 1H), 7.29-7.25 (m, 4H), 7.22-7.28 (m, 3H), 4.04 (s, 1H), 3.30 (s, 1H), 2.94 (s, 1H), 1.74 (s, 3H), 1.28 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 148.2, 144.9, 134.8, 134.2, 130.0, 129.4, 127.9, 127.3, 126.2, 125.6, 123.9, 123.4, 81.8, 77.0, 69.0, 27.4, 25.1

**IR (cm<sup>-1</sup>):** 3419, 2986, 2117, 1259, 785.

**HRMS (ESI):** Calculated for C<sub>17</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Na (M+Na)<sup>+</sup> 388.0590, observed 388.0600.

**Chiral HPLC:** Phenomenex column, hexane/iPrOH = 78:22 at 0.3 mL/min, λ = 210 nm: For the major diastereomer: *t*<sub>major</sub> = 21.8 min, *t*<sub>minor</sub> = 17.1 min, er = 96.2:3.8, 97.3:2.7. The average er of 97:3 is reported. For the minor diastereomer: *t*<sub>major</sub> = 17.7 min, *t*<sub>minor</sub> = 16.5 min, er = not determined.



**Compound 2j:** General procedure 4 was used and gave the product as the racemate in 23% yield. General procedure 5 was modified. The reaction was conducted at 35 °C. The product was isolated in 67% and 62% isolated yield with a 6.0:1 and 5.8:1 dr. The average yield of 65% and 6:1 dr is reported.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.95-6.90 (m, 2H), 6.89-6.84 (m, 2H), 6.73 (tt, *J* = 8.6, 2.3 Hz, 1H), 6.65 (tt, *J* = 8.7, 2.3 Hz, 1H), 3.96 (d, *J* = 5.6 Hz, 1H), 3.37 (s, 1H), 3.00 (d, *J* = 6.3 Hz, 1H), 1.71 (s, 3H), 1.27 (s, 3H).

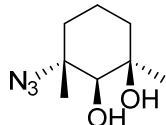
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 163.2 (q, *J*<sub>C-F</sub> = 247.9, 12.9 Hz), 162.9 (q, *J*<sub>C-F</sub> = 247.9, 12.5 Hz), 150.3 (t, *J*<sub>C-F</sub> = 8.0 Hz), 147.1 (t, *J*<sub>C-F</sub> = 8.2 Hz), 109.3 – 108.3 (m, 2C), 103.3 (t, *J*<sub>C-F</sub> = 25.1 Hz), 102.6 (t, *J*<sub>C-F</sub> = 25.2 Hz), 81.5, 76.9 (t, *J*<sub>C-F</sub> = 2.0 Hz), 68.9 (t, *J*<sub>C-F</sub> = 2.0 Hz), 27.4, 24.8.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -107.9 (s), -109.5 (s).

**IR (cm<sup>-1</sup>):** 3523, 3323, 3081, 2123, 1625, 1120, 989.

**HRMS (EI):** Calculated for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub> (M)<sup>+</sup> 369.1100, observed 369.1118

**Chiral HPLC:** Phenomenex column, hexane/iPrOH = 95:5 at 1.0 mL/min, λ = 210 nm: For the major diastereomer: t<sub>major</sub> = 19.9 min, t<sub>minor</sub> = 14.4 min, er = 96.2:3.8 and 95.6:4.4. The average er of 96:4 is reported; For the minor diastereomer: t<sub>major</sub> = 12.9 min, t<sub>minor</sub> = 13.4 min, er = not determined.



**Compound 5a:** General procedure 4 was used and gave the product as the racemate in 67% yield (3.5:1 dr). General procedure 5 was modified to use DHQ-PHEN instead of DHQ-MEQ to give the product in 79% and 84% isolated yield with a 4.0:1 and 3.0:1 dr. The average yield of 82% and 3.5:1 dr is reported.

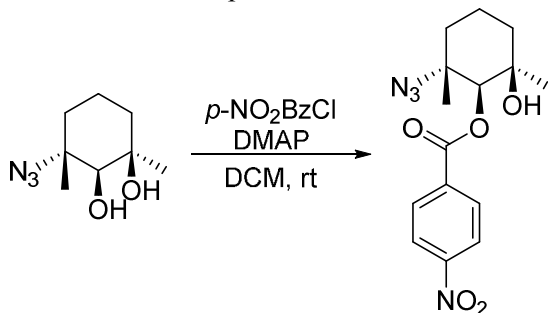
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** major diastereomer δ 3.30 (s, 1H), 2.89 (bs, 1H), 2.22 (bs, 1H), 1.82 – 1.73 (m, 1H), 1.67 (m, 1H), 1.50 (m, 3H), 1.47 (s, 3H), 1.46 – 1.35 (m, 1H), 1.31 (s, 3H), minor diastereomer δ 3.30 (bs, 1H), 3.09 (d, *J* = 8.9 Hz, 1H), 2.69 (d, *J* = 9.2 Hz, 1H), 1.98 – 1.83 (m, 2H), 1.82 – 1.73 (m, 2H), 1.50 (m, 1H), 1.47 (s, 3H), 1.46 – 1.35 (m, 1H), 1.24 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** major diastereomer δ 79.0, 72.6, 65.8, 36.8, 35.6, 28.2, 18.4, 18.3. minor diastereomer δ 77.9, 72.9, 65.3, 38.3, 36.3, 26.6, 23.1, 16.7.

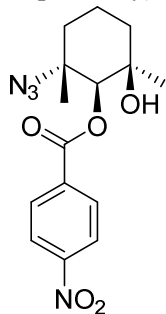
**IR:** 3443, 2934, 2104, 1256, 1075.

**MS (ESI):** C<sub>8</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>Na (M + Na)<sup>+</sup> calculated 208.1056, observed 208.1053.

The er for this compound was determined after derivatization with *p*-NO<sub>2</sub>BzCl.



**Ester Derivatization S4a:** To a solution of diol **5a** (55 mg, 0.30 mmol) in DCM (0.5 mL) at room temperature, DMAP (51 mg, 0.42 mmol), and *p*-NO<sub>2</sub>BzCl (63 mg, 0.34 mmol) were subsequently added. After 4h, the reaction was quenched by the addition of water. The resulting solution was extracted with DCM (3 x 5 mL). The combined organic phases were washed with brine, dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Final purification by column chromatography (gradient EtOAc/Hex from 0% - 50%) afforded ester **S4a** as a separable pair of diastereomers (54 mg, 55% and 15 mg, 15% respectively).



**Compound S4a: Major Diastereomer**

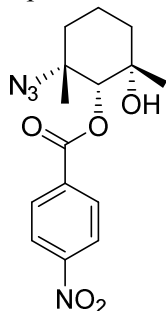
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.39 – 8.24 (m, 4H), 5.09 (s, 1H), 2.02 – 1.77 (m, 3H), 1.75 – 1.66 (m, 1H), 1.70 – 1.49 (m, 3H), 1.65 (s, 3H), 1.26 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.1, 150.8, 134.9, 130.9, 123.7, 80.9, 72.7, 64.5, 37.5, 36.6, 28.4, 19.0, 18.2.

IR: 3566, 2942, 2101, 1731, 1527, 1267, 1100, 718.

HRMS (ESI): Calculated for  $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_3\text{Na}$  ( $\text{M} + \text{Na}$ ) $^+$  357.1169, observed 357.1157.

Chiral HPLC: Phenomenex Lux  $3\mu$  cellulose-1 column, hexane/*i*PrOH = 90:10 at 0.5 mL/min,  $\lambda$  = 254 nm: For compound S4a:  $t_{\text{major}}$  = 17.9 min,  $t_{\text{minor}}$  = 21.2 min, er = 94.7:5.3, 94.8:5.2. The average er 95:5 is reported.



**Compound S4a': Minor Diastereomer**

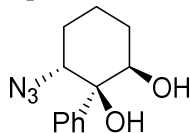
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.41 – 8.26 (m, 4H), 5.03 (s, 1H), 3.81 (s, 1H), 1.98 – 1.77 (m, 3H), 1.62 – 1.51 (m, 3H), 1.38 (s, 3H), 1.15 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.5, 150.9, 134.4, 131.3, 123.7, 80.3, 72.3, 64.0, 38.7, 37.1, 26.6, 23.2, 16.6.

IR: 3566, 2942, 2101, 1731, 1527, 1267, 1100, 718.

HRMS (ESI): Calculated for  $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_3\text{Na}$  ( $\text{M} + \text{Na}$ ) $^+$  357.1169, observed 357.1160.

Chiral HPLC: Phenomenex Lux  $3\mu$  cellulose-1 column, hexane/*i*PrOH = 90:10 at 0.5 mL/min,  $\lambda$  = 254 nm: For compound S4a':  $t_{\text{major}}$  = 14.3 min,  $t_{\text{minor}}$  = 13.4 min, er = 95.0:5.0, 94.7:5.3. The average er 95:5 is reported.



**Compound 5b:** General procedure 4 was used and gave the product as the racemate in 87% yield. General procedure 5 was used to give the product in 83%, 84%, and 74% isolated yield all with >20:1 dr. The average yield of 81% and >20:1 dr is reported.

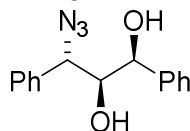
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 – 7.56 (m, 2H), 7.47 – 7.39 (m, 2H), 7.39 – 7.34 (m, 1H), 4.42 (dd,  $J$  = 9.8, 5.3 Hz, 1H), 3.73 (ap t,  $J$  = 3.1 Hz, 1H), 2.90 (s, 1H), 2.21 – 2.05 (m, 1H), 1.90 – 1.57 (m, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.7, 128.7, 128.0, 126.8, 76.4, 69.1, 67.6, 28.6, 26.0, 18.8.

IR: 3438, 2941, 2867, 2102, 1446, 1275, 1057, 868, 762.

HRMS (ESI): Calculated for  $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2\text{Na}$  ( $\text{M} + \text{Na}$ ) $^+$  256.1056, observed 256.1066.

Chiral HPLC: Phenomenex Lux  $3\mu$  cellulose-1 column, hexane/*i*PrOH = 95:5 at 0.5 mL/min,  $\lambda$  = 210 nm: For the compound 5b:  $t_{\text{major}}$  = 34.7 min,  $t_{\text{minor}}$  = 33.5 min, er = 84.4:15.6, 88.3:11.7, 78.4:21.6. The average er of 84:16 is reported.



**Compound 5c:** General procedure 4 was used and gave the product as the racemate in 73% yield (2:1 dr). General procedure 5 was modified to use DHQ-PHEN instead of DHQ-MEQ to give the product in 83% and 83% isolated yield with a 3.8:1 and 3.6:1 dr. The average yield of 83% and 3.7:1 dr is reported. The mixture of diastereomers was separated by column chromatography using a gradient of acetone in dichloromethane (0% to 15%).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** major diastereomer δ 7.48 – 7.29 (m, 10H), 4.86 (d, *J* = 3.3 Hz, 1H), 4.65 (d, *J* = 6.9 Hz, 1H), 3.94 (dd, *J* = 7.0, 3.4 Hz), 2.76 (br s, 1H), 2.32 (br s, 1H).

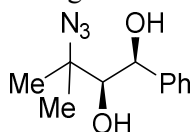
minor diastereomer δ 7.45 – 7.31 (m, 10H), 4.59 (d, *J* = 6.1 Hz, 1H), 4.56 (d, *J* = 4.2 Hz, 1H), 3.90 (dd, *J* = 6.1, 4.2 Hz, 1H), 2.70 (br s, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ major diastereomer δ 140.8, 136.0, 128.9, 128.8, 128.0, 128.6, 128.5, 126.4, 77.1, 72.4, 66.9, minor diastereomer δ 140.8, 136.5, 129.0, 128.8, 128.6, 128.1, 127.7, 126.3, 78.5, 73.3, 67.4.

**IR:** 3402, 2921, 2103, 1453, 699.

**HRMS (ESI):** Calculated for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>Na (M + Na)<sup>+</sup> 292.1056, observed 292.1058.

**Chiral HPLC:** Major diastereomer: Phenomenex column, hexane/iPrOH = 90:10 at 0.5 mL/min, λ = 210 nm: For the major diastereomer: *t*<sub>major</sub> = 23.7 min, *t*<sub>minor</sub> = 21.4 min, er = 98.5:1.5, 98.4:1.6. The average er of 98:2 is reported. Minor diastereomer: Phenomenex column, hexane/iPrOH = 90:10 at 0.5 mL/min, λ = 210 nm: For the minor diastereomer: *t*<sub>major</sub> = 21.6 min, *t*<sub>minor</sub> = 22.4 min, er = 93.0:7.0, 93.6:6.4. The average er of 93:7 is reported.



**Compound 5d:** General procedure 4 was used and gave the product as the racemate in 62% yield. General procedure 5 was used to give the product in 82% and 82% isolated yield. The average yield of 82% is reported.

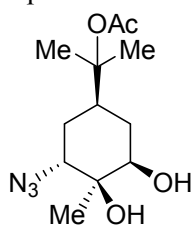
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.40 – 7.38 (m, 4H), 7.36 – 7.29 (m, 1H), 4.97 (dd, *J* = 3.5, 1.9 Hz, 1H), 3.48 (dd, *J* = 6.9, 1.9 Hz, 1H), 3.02 (d, *J* = 3.6 Hz, 1H), 2.79 (d, *J* = 6.9 Hz, 1H), 1.43 (s, 3H), 1.41 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 141.9, 128.6, 127.9, 126.0, 79.6, 71.7, 64.6, 23.5, 22.8.

**IR:** 3994, 2341, 2107, 1261.

**HRMS (ESI):** Calculated for C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>Na (M + Na)<sup>+</sup> 244.1056, observed 244.1054.

**Chiral HPLC:** Phenomenex Lux 3μ cellulose-1 column, hexane/iPrOH = 92:8 at 1.0 mL/min, λ = 210 nm: For compound 5d: *t*<sub>major</sub> = 14.2 min, *t*<sub>minor</sub> = 11.8 min, er = 98.4:1.6, 98.1:1.8. The average er of 98:2 is reported.



**Compound 5e:** General procedure 4 was used and gave the product as the racemate in 80% yield. General procedure 5 was modified to use commercial AD Mix (2.1 g/mmol) instead of DHQ-MEQ to give the product in 90% and 92% isolated yield with a 11:1 and 10:1 dr. The average yield of 91% and 11:1 dr is reported.

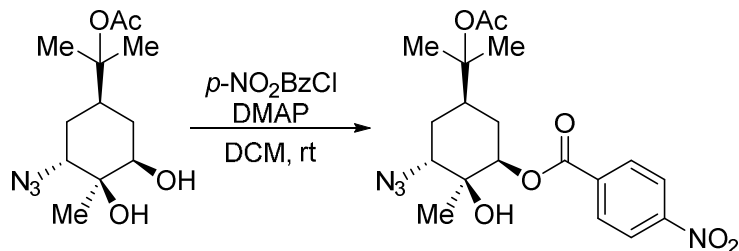
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 3.71 (t, *J* = 3.0 Hz, 1H), 3.61 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.33 (bs, 2H), 2.26 (tt, *J* = 12.6, 3.4 Hz, 1H), 2.00 (s, 3H), 1.85 (ddd, *J* = 15.2, 12.5, 3.0 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.47 (s, 3H), 1.45 (m, 1H), 1.44 (s, 3H), 1.35 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.6, 83.8, 72.4, 71.5, 66.4, 39.1, 30.6, 25.8, 23.9, 23.5, 23.2, 22.4.

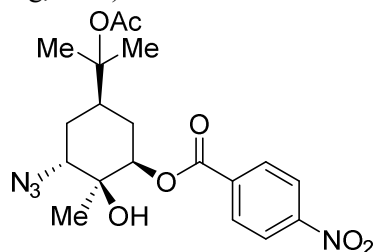
**IR:** 3427, 2982, 2938, 2099, 1731, 1707, 1369, 1261, 1139, 1048.

**HRMS (ESI):** Calculated for C<sub>12</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>Na (M + Na)<sup>+</sup> 294.1424, observed 294.1423.

The er for this compound was determined after derivatization with *p*-NO<sub>2</sub>BzCl (below).



**Ester Derivatization S4e:** To a solution of diol **5e** (27 mg, 0.10 mmol) in DCM (0.5 mL) at room temperature, DMAP (13 mg, 0.11 mmol), and *p*-NO<sub>2</sub>BzCl (21 mg, 0.11 mmol) were subsequently added. After 4h, the reaction was concentrated under a stream of air. Final purification by column chromatography (gradient EtOAc/Hex from 0% - 50%) afforded ester **S4e** (33 mg, 80%).



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.36 – 8.28 (m, 2H), 8.28 – 8.20 (m, 2H), 5.20 (dd, *J* = 11.7, 4.7 Hz, 1H), 3.80 (t, *J* = 3.1 Hz, 1H), 2.35 (tt, *J* = 12.7, 3.4 Hz, 1H), 2.01 (s, 3H), 2.09 – 1.93 (m, 1H), 1.98 – 1.83 (m, 2H), 1.76 (dt, *J* = 12.8, 11.7 Hz, 1H), 1.52 (s, 3H), 1.49 (s, 3H), 1.36 (s, 3H).

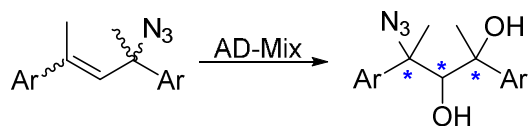
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.3, 163.7, 150.6, 135.3, 130.7, 123.6, 83.2, 76.2, 72.1, 66.4, 39.4, 27.2, 25.5, 24.1, 23.5, 23.2, 22.4.

**IR:** 3436, 2980, 2103, 1726, 1529, 1273

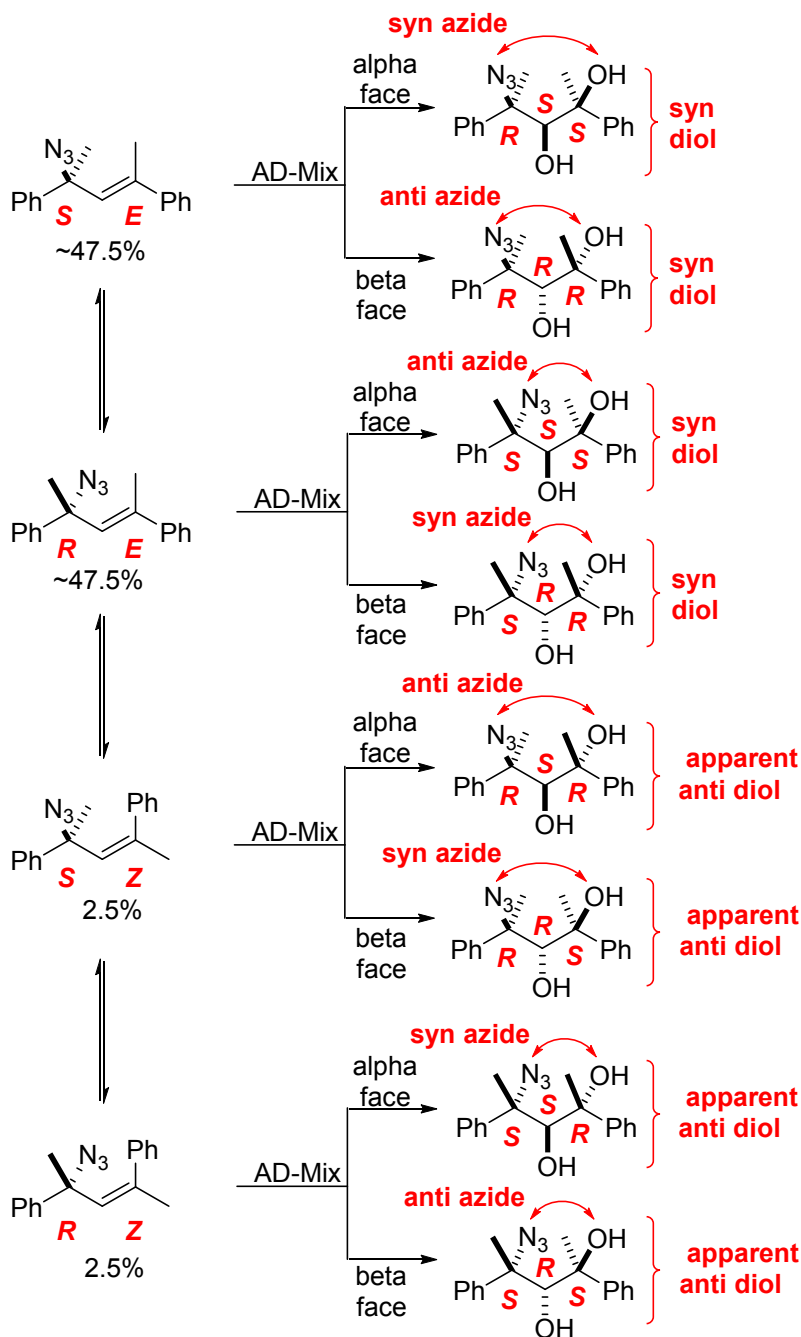
**HRMS (ESI):** Calculated for C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>Na (M + Na)<sup>+</sup> 357.1169, observed 357.1157.

**Chiral HPLC:** Phenomenex Lux 3μ cellulose-1 column, hexane/iPrOH = 95:5 at 1.0 mL/min, λ = 254 nm: For compound S4e: *t*<sub>major</sub> = 20.0 min, *t*<sub>minor</sub> = 24.2 min, er = 72.0:28.0, 71.3:28.7. The average er of 72:28 is reported.

## Discussion of Stereochemical Outcome and Diastereoselectivity:



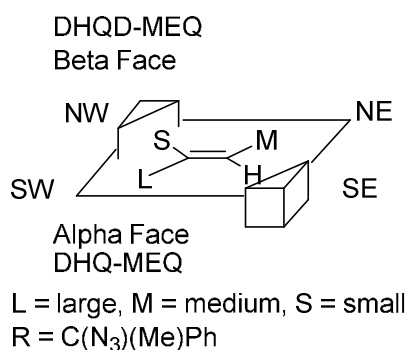
The dynamic kinetic resolution of allylic azides via asymmetric dihydroxylation produces an azido diol with three contiguous stereocenters (denoted \* above). All 8 stereoisomers are possible products from this reaction. The figure below depicts all 8 possible stereoisomers and the starting azide from which they could be derived.



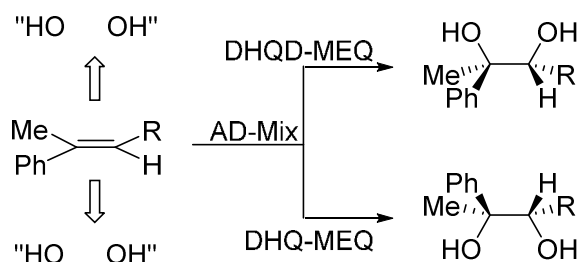
Three control elements are present that lead to selectivity in this reaction. They are 1) alkene geometry, 2) enantiocontrol from the ligand, and 3) conformational diastereocontrol.

- 1) Osmium tetroxide catalyzed dihydroxylation is stereospecific and results in syn dihydroxylation of the alkene. The stereochemical outcome is dependent on the alkene geometry. In the azide equilibrium mixture, about 95% of the azide is the *E* isomer and about 5% of the azide is the *Z* isomer. The *E* isomer would undergo syn dihydroxylation to provide the syn diol (top four possibilities). The *Z* isomer would undergo syn dihydroxylation followed by sigma bond rotation to provide apparent anti-dihydroxylation (bottom four possibilities). We have only observed product diols that arise from the *E* isomer. This is likely due to two reasons 1) the *E* isomer is present in a much higher concentration and 2) Sharpless Dihydroxylation of a *Z* alkene is known to be slow relative to the *E* isomer. The remainder of this discussion will be restricted to the *E* isomers.
- 2) The Sharpless Dihydroxylation has a well-established enantiocontrol model<sup>6</sup> that has been reproduced below. We have applied this model to our system and have labeled the appropriate faces for dihydroxylation on our system. The use of either DHQD-MEQ or DHQ-MEQ as a ligand provides enantiocontrol via this model. We chose arbitrarily to conduct these studies with the DHQ-MEQ isomer. The remainder of the discussion will be restricted to approach from the alpha face.

#### Sharpless Model

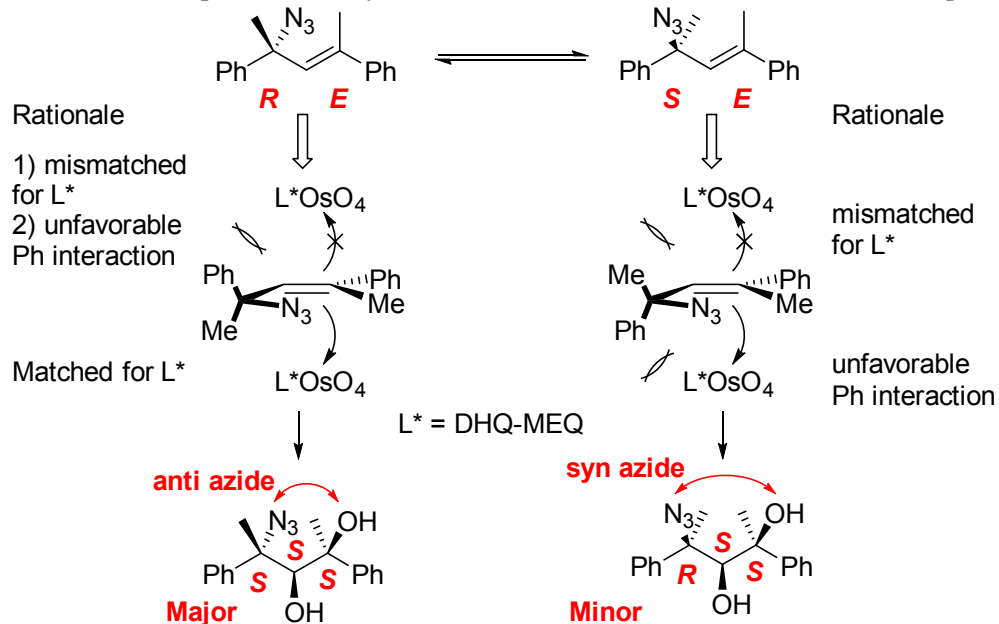


#### Application of Model to this system

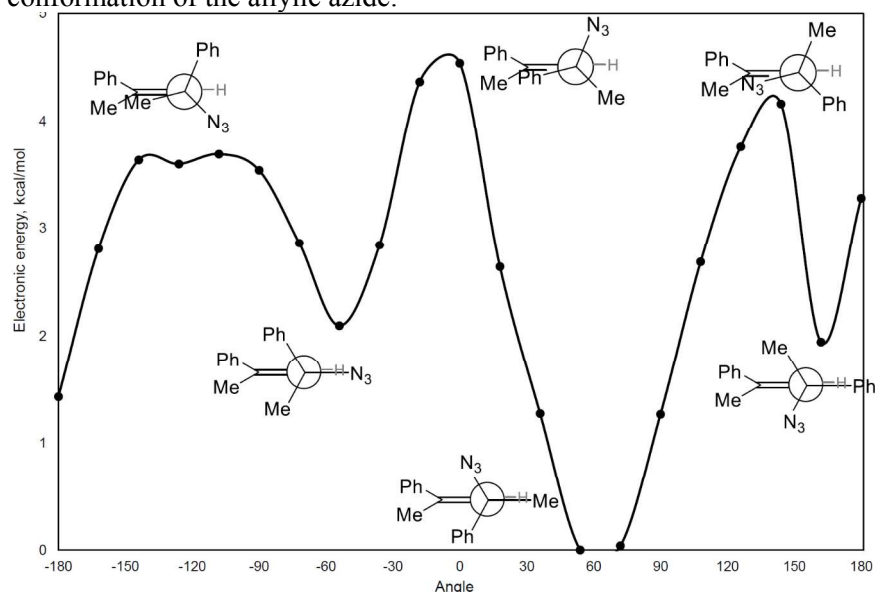


- 3) Conformational diastereocontrol is needed to establish the relative configuration of the azide with respect to the diol (denoted as "syn azide" or "anti azide" above and below). Our qualitative understanding of this system indicates that control from the ligand is more powerful in directing the system than conformational diastereocontrol. This leads to potential "matching" and "mismatching", which is known for double diastereoselective processes. Two possible diastereocontrol models are capable of explaining the observed anti azide product (a) Allylic A<sub>1,3</sub> strain and (b) stereoelectronic effects of the azide. These models are based on ground state conformations and the assumption that the transition state resembles the ground state conformation in a kinetically controlled system. Both models assume that reaction from minor conformations are not relevant and would not be significantly faster than reaction from the major conformation (i.e. we assume Curtin-Hammett kinetics are not relevant). We make this assumption because any conformation requires Os to approach from at least one substituent (N<sub>3</sub>, Me, or Ph).
  - a. Allylic A<sub>1,3</sub> strain is a well-accepted model of acyclic stereocontrol.<sup>7</sup> This model is steric in nature and the application of this model to our system is depicted below. This model assumes that in the most stable allylic conformation the smallest group (N<sub>3</sub>) resides in the

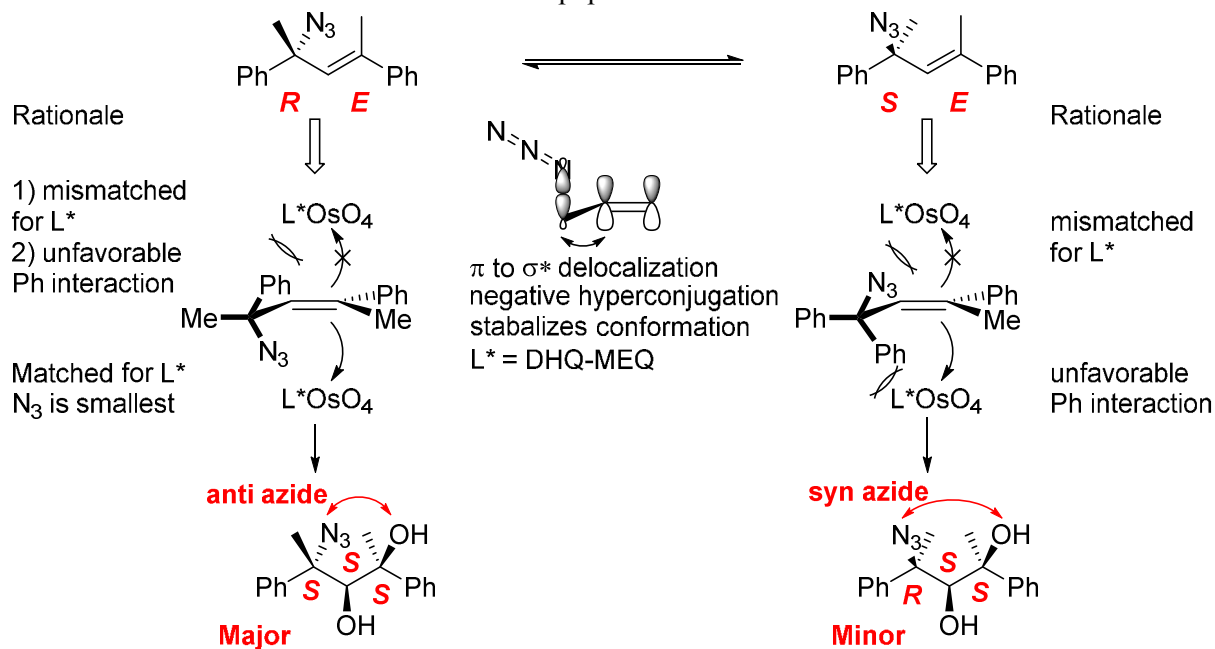
plane of the alkene. The relative size of the other two groups then leads to stereocontrol. In this instance  $\text{Me} < \text{Ph}$  and, in the absence of a chiral ligand, approach should be from the Me face. The “anti azide” is observed as the major product and this is consistent with the  $A_{1,3}$  model. It is possible in a minor more reactive conformation where Me is in the plane, that approach from the smaller  $\text{N}_3$  would be significantly faster than approach from Me. This would provide the “syn azide” and is not consistent with the observed product.



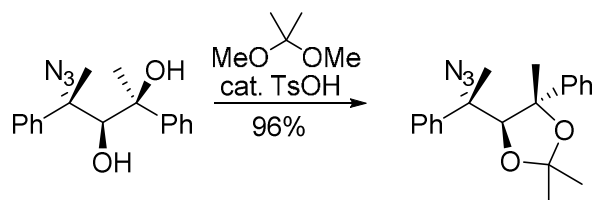
- b. The allylic  $A_{1,3}$  strain model above ignores stereoelectronic effects that could arise from negative hyperconjugation of the alkene  $\pi$  electrons into the  $\sigma^*$  antibonding orbital of the C-azide bond.<sup>8</sup> To probe the likely impact of negative hyperconjugation, a conformational DFT analysis (Gaussian '09 software, rb3lyp/6-31G(d)) was conducted on the azide. The results are depicted below for bond rotation about the allylic carbon and suggest that negative hyperconjugation is a relevant factor in controlling the ground state conformation of the allylic azide.



A model based on this conformation is provided below and is consistent with the observed anti-azide being the major product. This model makes the same assumptions as the A<sub>1,3</sub> model. In this model, the Os reagent approaches from the same direction as the smallest of the allylic groups (N<sub>3</sub> < Me < Ph). Therefore, it is likely that this conformation is both the most populated and most reactive.



## Elaboration of Azido-Diol Product:



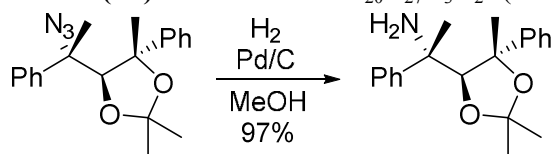
**Acetonide S5.** To a solution of diol **2a** (192 mg, 0.646 mmol) in 2,2-dimethoxypropane (1.5 mL) was added *p*-toluenesulfonic acid monohydrate (8 mg, 0.042 mmol). The solution was sealed and heated to 70 °C. After 2h, the mixture was cooled to room temperature, quenched by the addition of Et<sub>3</sub>N (20 μL), filtered through Celite, and concentrated under reduced pressure. This afforded the product acetonide **S5** (210 mg, 96%) as a colorless oil in sufficient purity to warrant no further purification.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ 7.10 - 7.07 (m, 3H), 7.02-6.98 (m, 3H), 6.96 – 6.93 (m, 2H), 6.78-6.75 (m, 2H), 4.34 (s, 1H), 1.81 (s, 3H), 1.67 (s, 3H), 1.62 (s, 6H).

<sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>): δ 143.8, 139.6, 128.0, 127.7, 127.3, 126.5, 125.84, 125.72, 107.3, 91.4, 84.4, 64.5, 28.6, 27.5, 27.2, 22.1

IR (cm<sup>-1</sup>): 2991, 2114, 1370, 759, 698.

HRMS (CI): Calculated for C<sub>20</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> (M + NH<sub>4</sub>)<sup>+</sup> 355.2129, observed 355.2143.



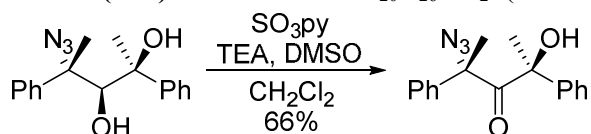
**Amine 6:** To a solution of acetonide **S4** (432 mg, 0.78 mmol) in methanol (5 mL) at room temperature was added palladium on carbon (105 mg, 10% Pd on C). The vial was sealed under air and was subsequently purged with a continuous flow of hydrogen gas. After 5 min, the flow of hydrogen was ceased and the vessel was sealed under a positive pressure of hydrogen gas (balloon). After 18h, the reaction was diluted with EtOAc, filtered through Celite, and concentrated under vacuum. This afforded amine **6** (371 mg, 93%) in sufficient purity to warrant no further purification.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 7.22-7.20 (m, 2H), 7.09-7.00 (m, 6H), 6.86-6.84 (m, 2H), 4.25 (s, 1H), 1.77 (bs, 2H), 1.67 (s, 3H), 1.65 (s, 3H), 1.57 (s, 3H), 1.54 (s, 3H).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>): δ 144.0, 143.8, 127.67, 127.60, 126.36, 126.32, 125.83, 125.81, 106.2, 90.3, 84.3, 55.6, 33.9, 28.8, 27.0, 22.1

IR (cm<sup>-1</sup>): 3371, 2984, 2936, 1374, 1231, 1066, 697.

HRMS (ESI): Calculated for C<sub>20</sub>H<sub>26</sub>NO<sub>2</sub><sup>+</sup> (M + H)<sup>+</sup> 312.1958, observed 312.1960.



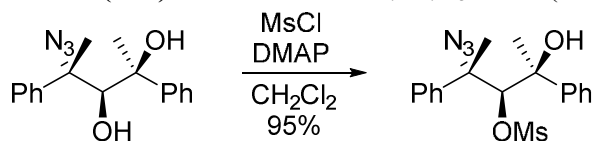
**Ketone 7:** To a solution of diol **2a** (53 mg, 0.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.4 mL) and DMSO (0.2 mL) at room temperature SO<sub>3</sub>·py (51 mg, 0.32 mmol) and Et<sub>3</sub>N (0.1 mL) were subsequently added. The vial was sealed under air. After 18h, the reaction was diluted with water and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with brine, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. Purification by column chromatography (20% - 80% IPA:hexanes) afforded the product ketone **7** (35 mg, 66%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ 7.45-7.30 (m, 10H), 3.92 (q, *J* = 0.9 Hz, 1H), 1.78 (s, 3H), 1.61 (d, *J* = 0.9 Hz, 3H).

<sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>): δ 207.1, 142.6, 139.3, 129.0, 128.9, 128.3, 127.8, 125.1, 124.1, 82.9, 73.0, 28.8, 25.5.

IR (cm<sup>-1</sup>): 3525, 2976, 2108, 1708, 1445, 1262, 1004, 761, 696.

**HRMS (ESI):** Calculated for  $C_{17}H_{17}N_3O_2Na^+$  ( $M + Na$ )<sup>+</sup> 318.1213, observed 318.1214.



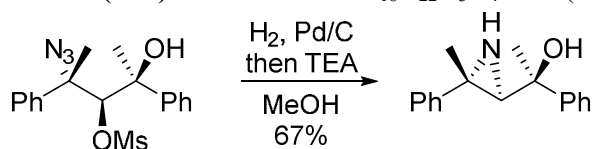
**Mesylate S6.** To a solution of diol **2a** (50 mg, 0.17 mmol) in  $CH_2Cl_2$  (2.5 mL) at room temperature was sequentially added DMAP (42 mg, 0.34 mmol) and methanesulfonyl chloride (20  $\mu$ L, 0.25 mmol). The vial was sealed under air. After 1h, the reaction was filtered through silica gel, rinsed (50% EtOAc in Hex) and the organic solution was concentrated under reduced pressure to afford mesylate **S6** (60 mg, 95%). Mesylate obtained by this means was sufficiently pure to warrant no further purification.

**$^1H$  NMR (500 MHz;  $CD_3CN$ ):**  $\delta$  7.40-7.39 (m, 2H), 7.36-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.18 (m, 4H), 5.40 (s, 1H), 2.42 (s, 3H), 1.73 (s, 3H), 1.24 (s, 3H).

**$^{13}C$  NMR (126 MHz;  $CD_3CN$ ):**  $\delta$  146.7, 142.4, 129.4, 129.0, 128.5, 128.2, 127.0, 126.9, 93.6, 77.5, 68.8, 39.1, 28.1, 27.0.

**IR ( $cm^{-1}$ ):** 3525, 3029, 2937, 2120, 1350, 1170, 950, 702.

**HRMS (ESI):** Calculated for  $C_{18}H_{22}N_3O_4SNa^+$  ( $M + Na$ )<sup>+</sup> 398.1145, observed 398.1157.



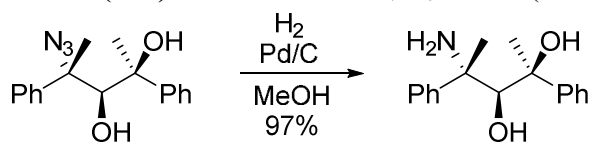
**Aziridine 8:** To a solution of mesylate **S6** (27 mg, 0.072 mmol) in methanol (2.5 mL) at room temperature was added palladium on carbon (16 mg, 10% Pd on C). The vial was sealed under air and was subsequently purged with a continuous flow of hydrogen gas. After 5 min, the flow of hydrogen was ceased and the vessel was sealed under a positive pressure of hydrogen gas (balloon). After 18h, the reaction was diluted with EtOAc, filtered through Celite, and concentrated under vacuum. The residue was reconstituted in acetonitrile (2 mL) and  $Et_3N$  (0.5 mL) was added. After 72h at room temperature, the reaction was concentrated under vacuum. Final purification by column chromatography (0% - 40% IPA in hexanes) afforded aziridine **8** (12 mg, 67%) as a colorless oil.

**$^1H$  NMR (500 MHz,  $CDCl_3$ ):**  $\delta$  7.60 (d,  $J = 8.0$  Hz, 2H), 7.41 (t,  $J = 7.6$  Hz, 2H), 7.32 (m, 3H), 7.27 (m, 1H), 7.22 (dd,  $J = 7.1, 1.7$  Hz, 2H), 2.82 (s, 1H), 1.69 (s, 3H), 1.30 (s, 3H).

**$^{13}C$  NMR (125 MHz,  $CDCl_3$ ):**  $\delta$  146.8, 144.9, 128.6, 128.1, 127.2, 126.6, 125.7, 124.6, 70.3, 50.6, 44.2, 33.9, 19.5.

**IR ( $cm^{-1}$ ):** 3278, 2969, 1445, 700.

**HRMS (ESI):** Calculated for  $C_{17}H_{19}NONa^+$  ( $M + Na$ )<sup>+</sup> 276.1359, observed 276.1358.



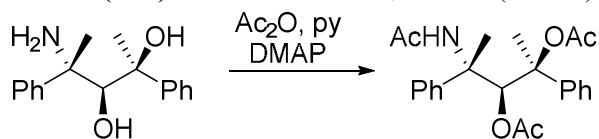
**Amino-Diol S7:** To a solution of azide **2a** (221 mg, 0.743 mmol) in methanol (4 mL) at room temperature was added palladium on carbon (236 mg, 10% Pd on C). The vial was sealed under air and was subsequently purged with a continuous flow of hydrogen gas. After 5 min, the flow of hydrogen was ceased and the vessel was sealed under a positive pressure of hydrogen gas (balloon). After 18h, the reaction was diluted with EtOAc, filtered through Celite, and the organic solution was concentrated under reduced pressure to afford amine **S7** (198 mg, 97%). Amine obtained by this means was sufficiently pure to warrant no further purification.

**$^1H$  NMR (400 MHz;  $CDCl_3$ ):**  $\delta$  7.55-7.25 (m, 10H), 4.39 (bs, NH and OH, 4H), 4.14 (s, 1H), 1.56 (s, 3H), 0.92 (s, 3H).

**$^{13}C$  NMR (100 MHz;  $CDCl_3$ ):**  $\delta$  147.2, 144.5, 128.6, 128.3, 127.3, 126.7, 125.5, 125.1, 80.7, 78.4, 60.8, 31.1, 29.4.

**IR ( $cm^{-1}$ ):** 3365, 3059, 2976, 1446, 1026, 768.

**HRMS (ESI):** Calculated for  $C_{17}H_{22}NO_2$  ( $M + H$ )<sup>+</sup> 272.1645, observed 272.1658.



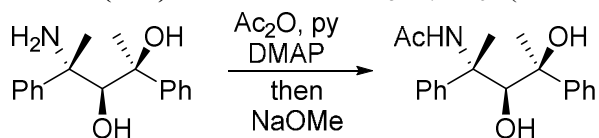
**Acetate S8:** To a solution of amine **S7** (55 mg, 0.20 mmol) in pyridine (0.25 mL) was added DMAP (48 mg, 0.39 mmol) and  $Ac_2O$  (0.15 mL, 1.6 mmol). The solution was sealed under air. After 18h, the solution was diluted with ethyl acetate and water. The resulting solution was extracted with ethyl acetate ( $3 \times 5$  mL) and washed with water ( $3 \times 15$  mL) to remove pyridine and acetic acid. The combined organic phases were washed with brine, dried ( $MgSO_4$ ) and concentrated under reduced pressure. Purification by column chromatography (20% - 80% IPA:hexanes) afforded triacetate **S8** (53.8 mg, 67%) as a yellow oil.

**$^1H$  NMR (400 MHz;  $CDCl_3$ ):**  $\delta$  7.39-7.32 (m, 7H), 7.28-7.25 (m, 3H), 6.57 (bs, NH, 1H), 5.51 (s, 1H), 1.97 (s, 3H), 1.97 (s, 3H), 1.88 (s, 3H), 1.80 (s, 3H), 1.54 (s, 3H).

**$^{13}C$  NMR (100 MHz;  $CDCl_3$ ):**  $\delta$  169.3, 168.7, 167.9, 141.5, 141.1, 128.36, 128.29, 128.09, 127.3, 126.6, 125.9, 86.6, 81.7, 63.3, 26.2, 24.5, 23.8, 22.1, 20.5.

**IR ( $cm^{-1}$ ):** 3430, 3059, 1750, 1686, 1369, 1221, 1029, 701.

**HRMS (ESI):** Calculated for  $C_{23}H_{27}NO_5^+$  ( $M + Na$ )<sup>+</sup> 420.1781, observed 420.1790.



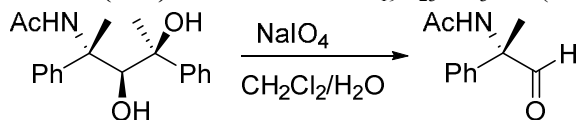
**Acetamide S9:** To a solution of amine **S7** (96 mg, 0.35 mmol) in pyridine (0.25 mL) was added DMAP (126 mg, 1.1 mmol) and  $Ac_2O$  (0.33 mL, 3.5 mmol). The solution was sealed under air. After 2h, KOMe (3.1 mL, 25% in MeOH, 10.5 mmol) was added dropwise. After an additional 2h, the solution was diluted with ethyl acetate and water. The resulting mixture was extracted with ethyl acetate ( $3 \times 5$  mL) and washed with water ( $3 \times 15$  mL). The combined organic phases were washed with brine, dried ( $MgSO_4$ ), and concentrated under reduced pressure. Purification by column chromatography (50% - 100% EtOAc:hexanes) afforded amide **S9** (59 mg, 54%) as a white solid.

**$^1H$  NMR (500 MHz, MeOD):**  $\delta$  7.59 (d,  $J = 8.0$  Hz, 2H), 7.39 - 7.27 (m, 6H), 7.25 (t,  $J = 8.0$  Hz, 1H), 7.19 (t,  $J = 8.1$  Hz, 1H), 3.84 (s, 1H), 2.02 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H).

**$^{13}C$  NMR (125 MHz, MeOD):**  $\delta$  170.1, 146.3, 146.2, 127.4, 127.3, 126.2, 126.0, 125.8, 125.4, 81.8, 78.0, 63.7, 29.4, 22.8, 20.2.

**IR ( $cm^{-1}$ ):** 3295, 1653, 1445, 1029, 701.

**HRMS (ESI):** Calculated for  $C_{19}H_{23}NO_3Na^+$  ( $M + Na$ )<sup>+</sup> 336.1570, observed 336.1575.

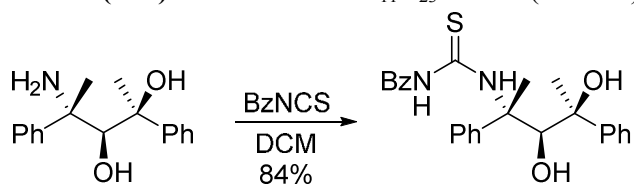


**Aldehyde 9:** To a solution of amide **S9** (59 mg, 0.35 mmol) in  $CH_2Cl_2$  (2.0 mL) and water (0.2 mL) was added  $NaIO_4$  (201 mg, 0.93 mmol). The heterogeneous mixture was sealed under air and stirred vigorously. After 18h, the reaction was diluted with water and extracted with  $CH_2Cl_2$  ( $3 \times 10$  mL). The combined organic phases were washed with water, dried ( $MgSO_4$ ), and concentrated under reduced pressure. Removal of acetophenone under high vacuum at 40 °C afforded aldehyde **9** (11 mg, 72%) as an oil.

**$^1H$  NMR (500 MHz,  $CDCl_3$ ):**  $\delta$  9.31 (s, 1H), 7.72 - 7.28 (m, 5H), 6.68 (bs, 1H), 2.08 (s, 3H), 1.91 (s, 3H).

**$^{13}C$  NMR (125 MHz,  $CDCl_3$ ):**  $\delta$  195.6, 169.4, 136.8, 129.3, 128.5, 126.5, 65.3, 23.6, 19.3.

**HRMS (ESI):** Calculated for  $C_{11}H_{23}NONa^+$  ( $M + Na$ )<sup>+</sup> 214.0838, observed 214.0842.



**Thiourea 10:** To a solution of amine **S7** (96 mg, 0.35 mmol) in DCM (1 mL) at room temperature was added benzoyl isothiocyanate (52  $\mu$ L, 0.38 mmol) by micropipette. After 18h, the reaction was concentrated under reduced pressure and purified by column chromatography (30% EtOAc in hexanes) to afford thiourea **10** (128 mg, 84%) as a colorless oil.

**<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):**  $\delta$  12.09 (s, NH, 1H), 8.91 (s, NH, 1H), 7.88 – 7.85 (m, 2H), 7.65 – 7.60 (m, 1H), 7.52-7.49 (m, 4H), 7.46 - 7.44 (m, 2H), 7.38 - 7.27 (m, 6H), 4.31 (d,  $J$  = 4.6 Hz, 1H), 2.87 (s, OH, 1H), 2.77 (d, OH,  $J$  = 4.6 Hz, 1H), 1.94 (s, 3H), 1.51 (s, 3H).

**<sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>):**  $\delta$  177.8, 166.2, 145.9, 141.4, 133.4, 132.0, 129.1, 128.3, 128.2, 127.6, 127.4, 127.2, 127.2, 125.6, 82.9, 77.4, 66.1, 28.3, 20.6.

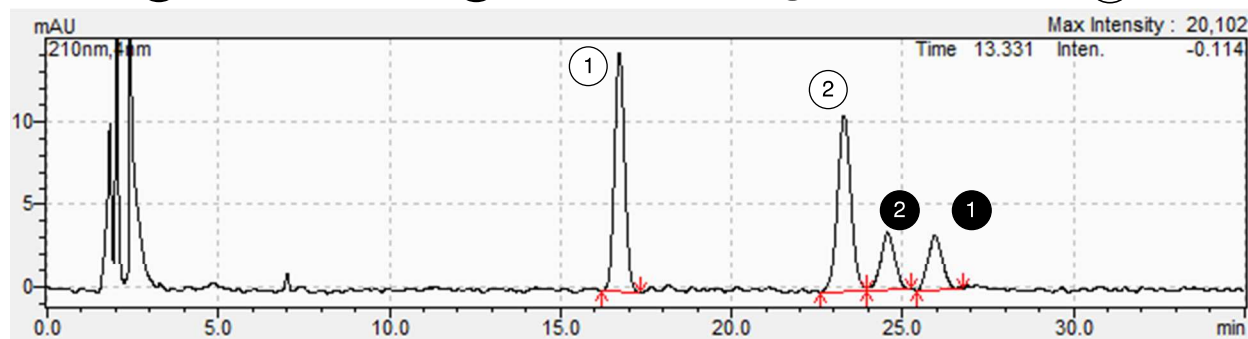
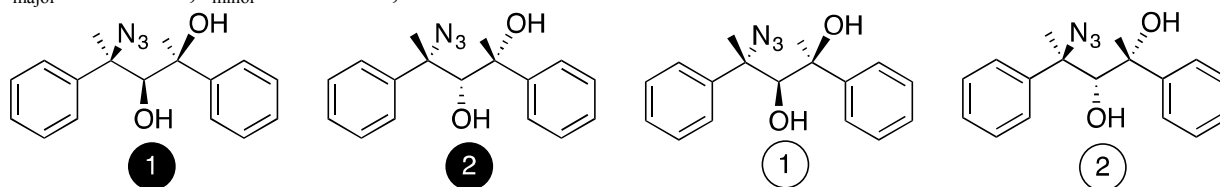
**IR (cm<sup>-1</sup>):** 3400, 2960, 2854, 1649, 1535, 1254, 1119, 872, 702.

**HRMS (ESI):** Calculated for  $C_{25}H_{26}N_2O_3SNa^+$  ( $M + Na$ )<sup>+</sup> 457.1556, observed 457.1547.

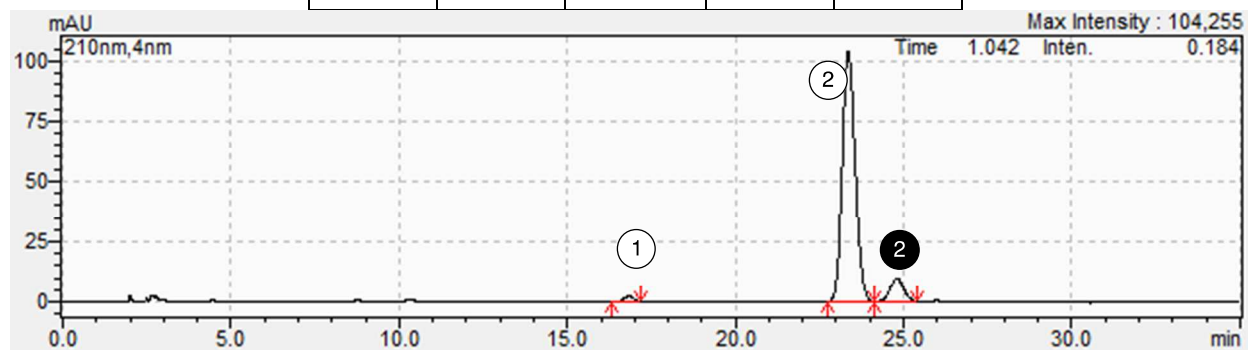
## HPLC data

**General:** Enantiomeric ratios were determined using a Shimadzu HPLC with a PDA detector and a phenomenex column (Lux 3 $\mu$  cellulose-1, 250 mm x 4.6 mm). During purification the minor diastereomer was purposefully collected with the major diastereomer. This was to ensure that the HPLC analysis was able to fully separate the minor diastereomer from the enantiomers of the major diastereomer and to ensure that partial resolution did not occur during purification. For this reason, each HPLC trace contains four peaks. Each peak corresponds to a specific stereoisomer and each peak is labeled. Assignments of the minor stereoisomer are tentative. For each DKR sample, the sample was injected in duplicate. For each sample, the racemic retention time standard was run before and after the sample (4 total injections per sample). The reported er was determined by averaging the measured er at three to five different wavelengths. The er at all wavelengths were within 1% of the average. The reported er is thus the average of duplicate injections of duplicate DKR trials (2 samples, 4 injections, 12 – 30 measurement).

**Compound 2a:** Phenomenex Lux 3 $\mu$  cellulose-1 column, hexane/iPrOH = 98:2 at 1.0 mL/min,  $\lambda$  = 210 nm: For the major diastereomer:  $t_{\text{major}} = 23.0$  min,  $t_{\text{minor}} = 16.6$  min, er = 99:1; For the minor diastereomer:  $t_{\text{major}} = 24.0$  min,  $t_{\text{minor}} = 25.2$  min, er = not determined.

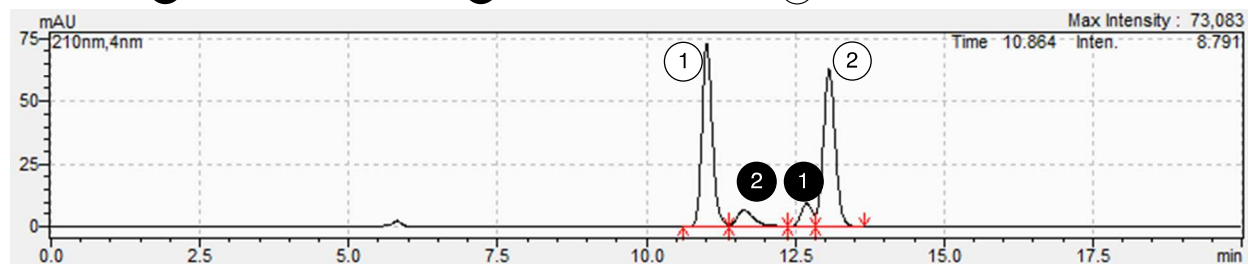
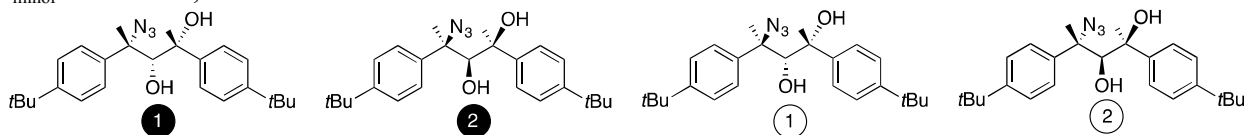


Peak#	Ret. Time	Area	Height	Area%
1	16.6	156144	8157	10.7
2	23.0	164482	6442	11.3
3	24.0	569970	20296	39.2
4	25.2	562833	19045	38.7
Total		1453428	53940	100

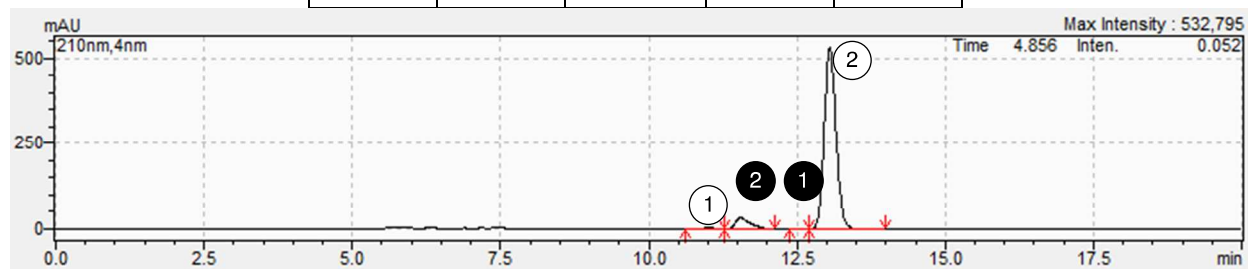


Peak#	Ret. Time	Area	Height	Area%
1	16.8	43126	2147	1.4
2	23.4	2790786	104284	89.6
3	24.8	280182	9768	9.0
Total		3114093	116198	100

**Compound 2b:** Phenomenex column, hexane/iPrOH = 96:4 at 0.5 mL/min,  $\lambda = 210$  nm: For the major diastereomer:  $t_{\text{major}} = 13.1$  min,  $t_{\text{minor}} = 11.0$  min, er = 99:1; For the minor diastereomer:  $t_{\text{major}} = 11.6$  min,  $t_{\text{minor}} = 12.7$  min, er = not determined.

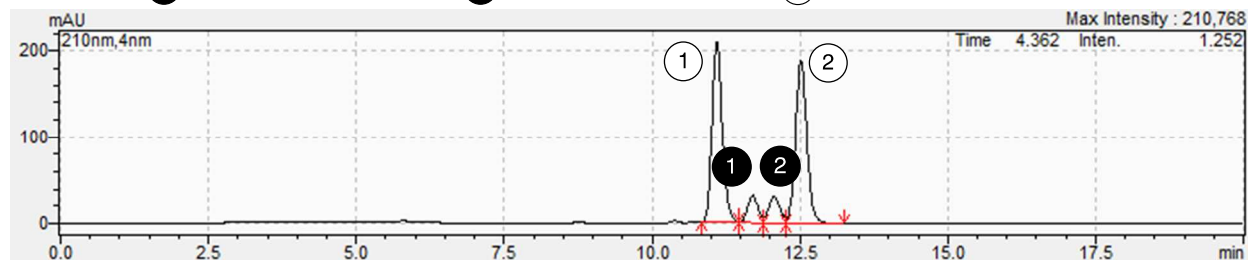
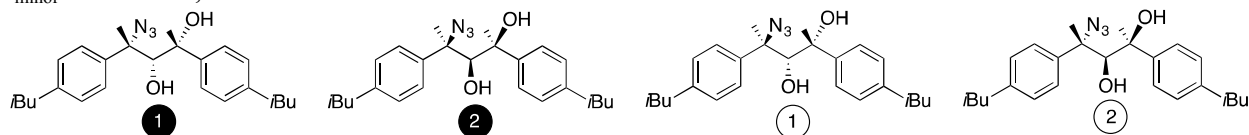


Peak#	Ret. Time	Area	Height	Area%
1	11.0	883125	73080	43.8
2	11.6	131997	6583	6.5
3	12.7	125924	9650	6.2
4	13.1	876361	62947	43.4
Total		2017408	152259	100

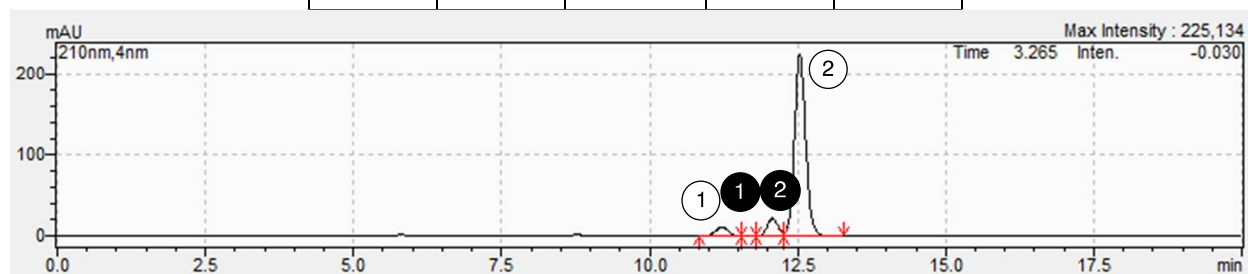


Peak#	Ret. Time	Area	Height	Area%
1	11.0	61990	5303	0.8
2	11.6	586994	32571	7.2
3	12.6	21763	1565	0.3
4	13.1	7427112	536015	91.7
Total		8097860	575455	100

**Compound 2c:** Phenomenex column, hexane/iPrOH = 96:4 at 0.5 mL/min,  $\lambda = 210$  nm: For the major diastereomer:  $t_{\text{major}} = 12.5$  min,  $t_{\text{minor}} = 11.0$  min, er = 95:5; For the minor diastereomer:  $t_{\text{major}} = 12.1$  min,  $t_{\text{minor}} = 11.7$  min, er = not determined.

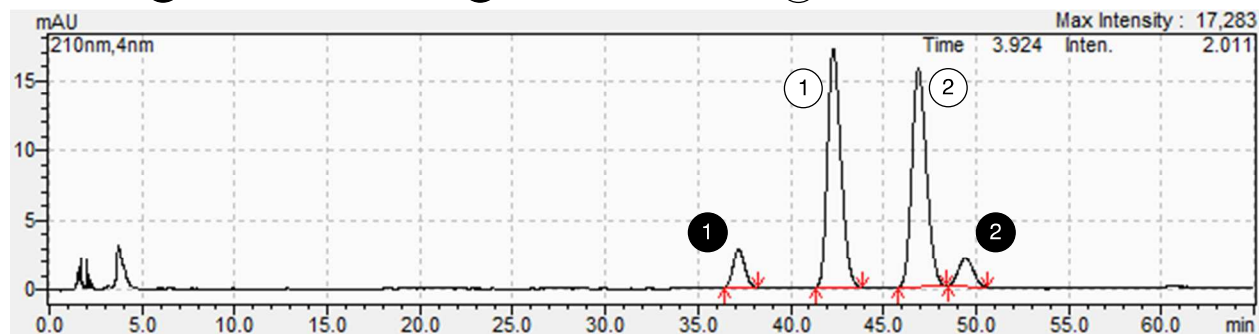
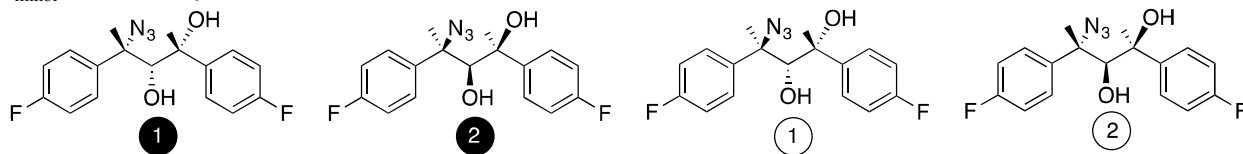


Peak#	Ret. Time	Area	Height	Area%
1	11.0	2523781	209619	43.1
2	11.7	389038	32122	6.7
3	12.1	406375	31069	6.9
4	12.5	2529815	189805	43.3
Total		5849009	462616	100

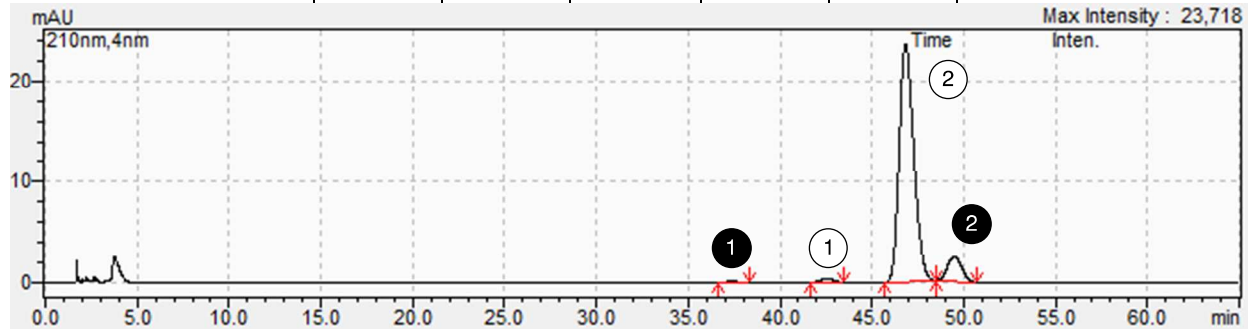


Peak#	Ret. Time	Area	Height	Area%
1	11.2	175298	11353	5.1
2	11.7	8359	708	0.2
3	12.1	277631	21554	8.1
4	12.5	2983142	225087	86.6
Total		3444431	258701	100

**Compound 2d:** (Phenomenex column, hexane/iPrOH = 99:1 at 1.75 mL/min,  $\lambda = 210$  nm For the major diastereomer:  $t_{\text{major}} = 46.9$  min,  $t_{\text{minor}} = 42.3$  min, er = 98:2; For the minor diastereomer:  $t_{\text{major}} = 49.4$  min,  $t_{\text{minor}} = 37.2$  min, er = 94:6.

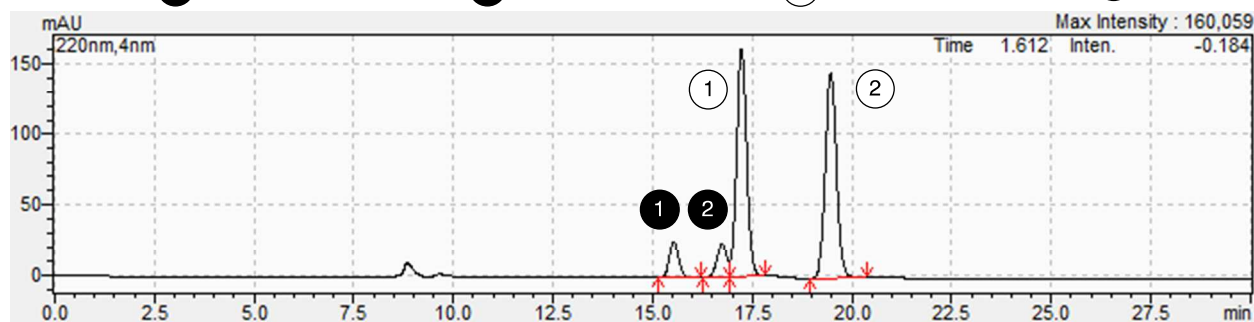
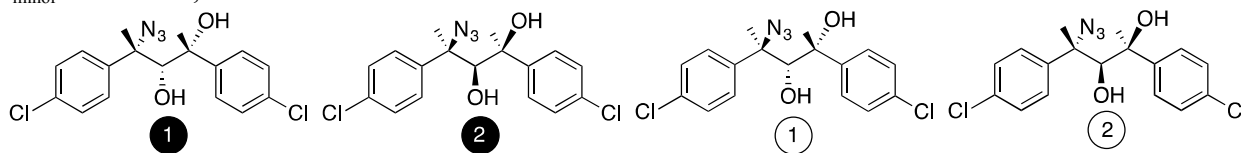


Peak#	Ret. Time	Area	Height	Area%
1	37.2	120944	2800	6.2
2	42.3	861250	17095	44.2
3	46.9	853109	15597	43.8
4	49.4	112252	2035	5.8
Total		1947555	37527	100

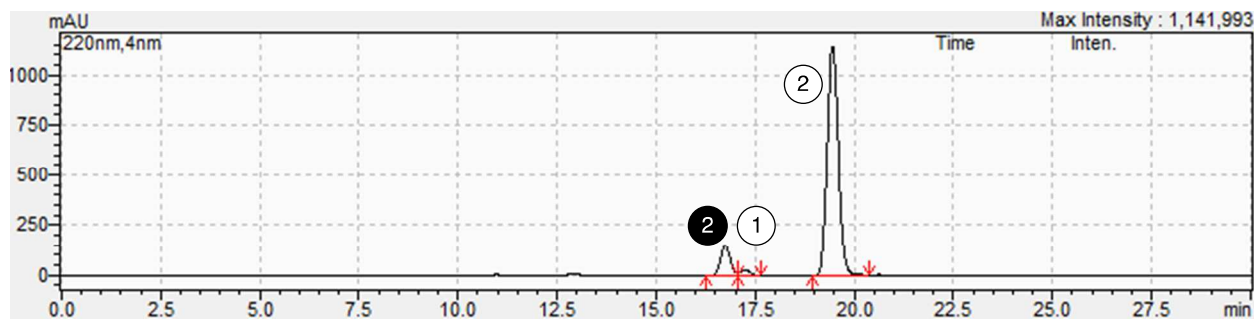


Peak#	Ret. Time	Area	Height	Area%
1	37.4	8665	193	0.6
2	42.6	21897	438	1.5
3	46.8	1307645	23664	88.6
4	49.5	137392	2467	9.3
Total		1475599	26762	100

**Compound 2e:** (Phenomenex column, hexane/iPrOH = 78:22 at 0.3 mL/min,  $\lambda = 220$  nm): For the major diastereomer:  $t_{\text{major}} = 19.5$  min,  $t_{\text{minor}} = 17.2$  min, er = 98:2; For the minor diastereomer:  $t_{\text{major}} = 16.7$  min,  $t_{\text{minor}} = 15.5$  min, er = not determined.

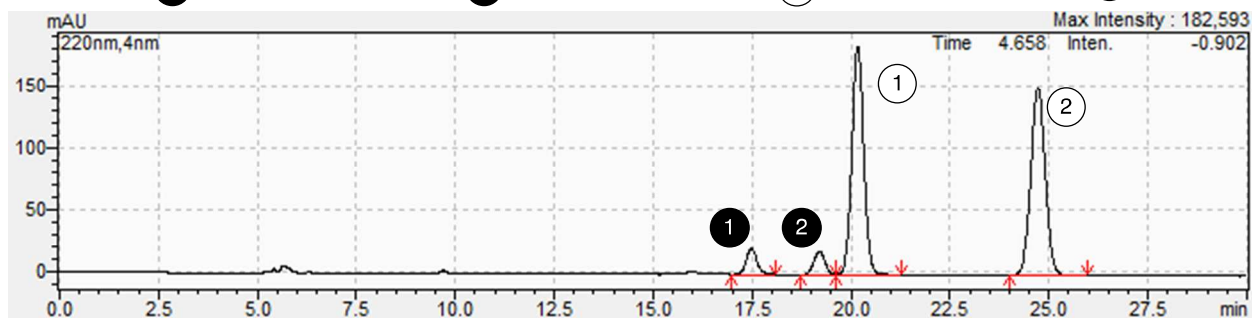
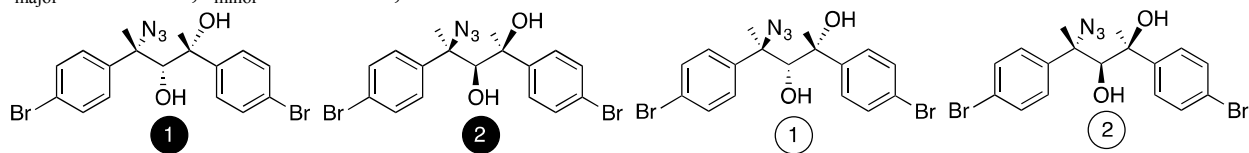


Peak#	Ret. Time	Area	Height	Area%
1	15.5	421149	25747	6.5
2	16.7	412995	24313	6.3
3	17.2	2827579	160514	43.4
4	19.5	2846526	144708	43.7
Total		6508249	355283	100

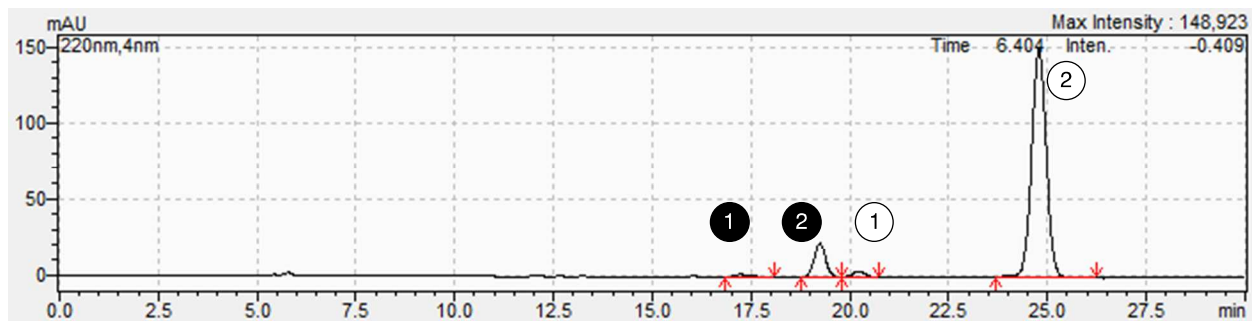


Peak#	Ret. Time	Area	Height	Area%
1	16.7	2567548	152191	10.0
2	17.2	529253	29911	2.1
3	19.5	22487346	1145416	87.9
Total		25584147	1327518	100

**Compound 2f:** Phenomenex Lux 3 $\mu$  cellulose-1 column, hexane/iPrOH = 90:10 at 0.5 mL/min,  $\lambda$  = 220 nm: For the major diastereomer:  $t_{\text{major}}$  = 24.7 min,  $t_{\text{minor}}$  = 20.2 min, er = 98:2; For the minor diastereomer:  $t_{\text{major}}$  = 19.2 min,  $t_{\text{minor}}$  = 17.5 min, er = 94:6.

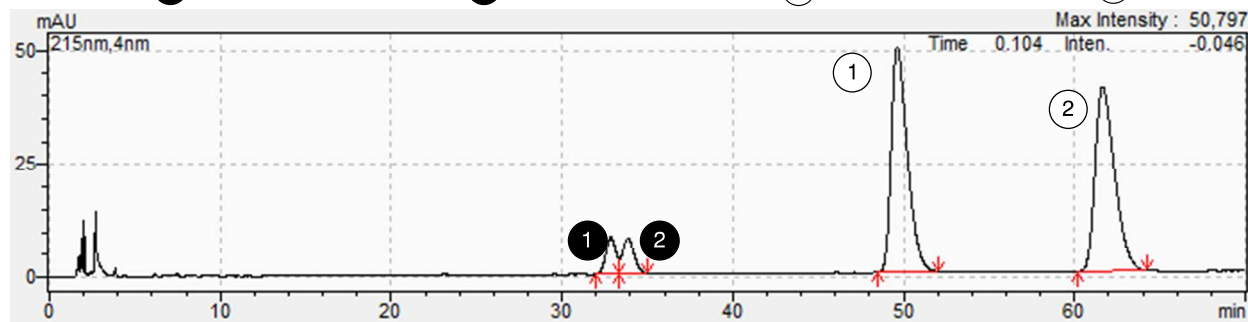
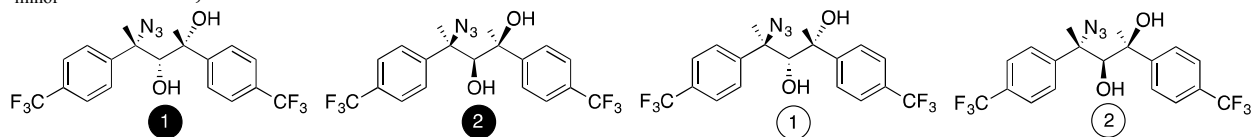


Peak#	Ret. Time	Area	Height	Area%
1	17.5	392369	20744	4.6
2	19.2	368696	18633	4.4
3	20.2	3848958	184434	45.4
4	24.7	3858290	151227	45.6
Total		8468313	375038	100

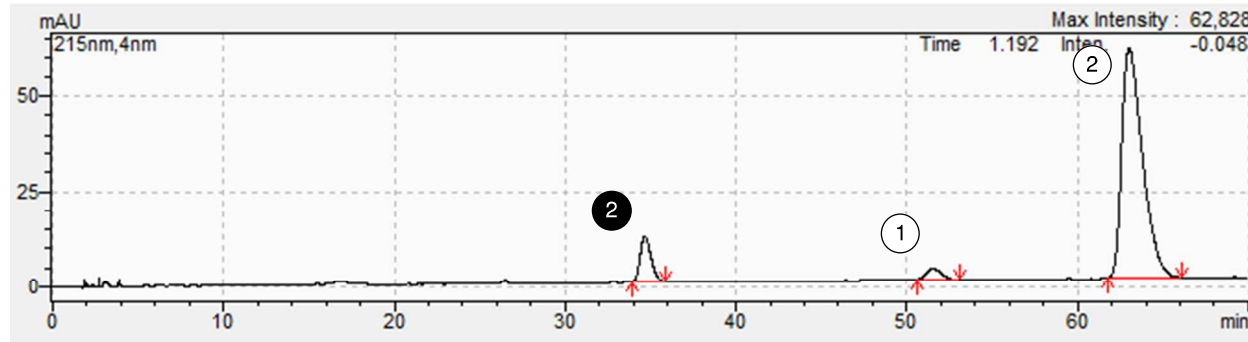


Peak#	Ret. Time	Area	Height	Area%
1	17.2	30538	1316	0.7
2	19.2	450110	22819	10.1
3	20.2	79153	3810	1.8
4	24.8	3905699	151945	87.5
Total		4465500	179890	100

**Compound 2g** (Phenomenex column, hexane/iPrOH = 98:2 at 1.25 mL/min,  $\lambda = 215$  nm): For the major diastereomer:  $t_{\text{major}} = 61.7$  min,  $t_{\text{minor}} = 49.6$  min, er = 97:3; For the minor diastereomer:  $t_{\text{major}} = 32.9$  min,  $t_{\text{minor}} = 33.9$  min, er = not determined.

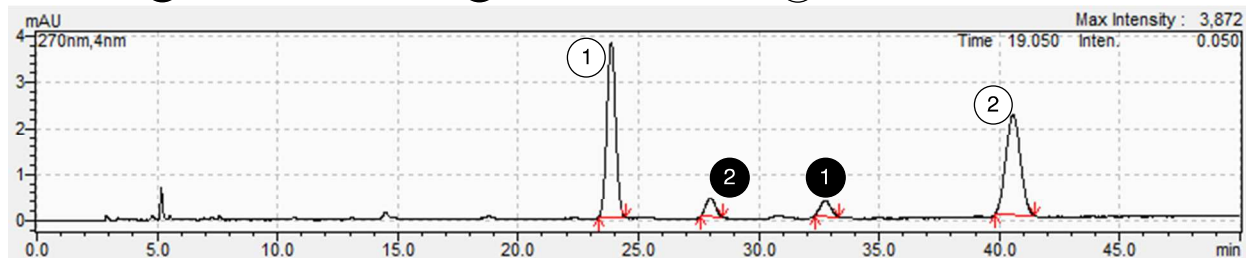
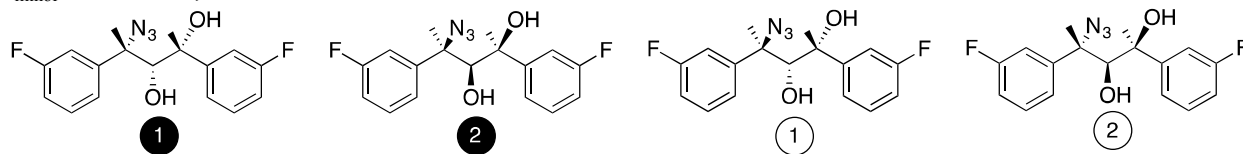


Peak#	Ret. Time	Area	Height	Area%
1	32.9	343055	8182	4.8
2	33.9	366528	7847	5.1
3	49.6	3246895	49650	45.0
4	61.7	3254345	40894	45.1
Total		7210823	106573	100

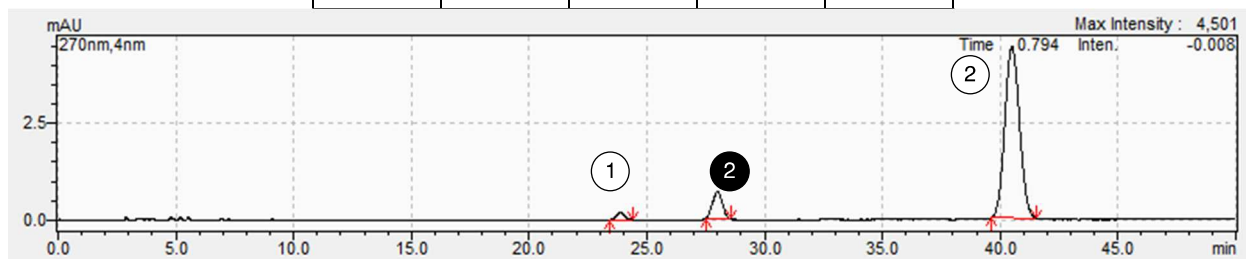


Peak#	Ret. Time	Area	Height	Area%
1	34.7	521469	11848	9.0
2	51.5	191053	3026	3.3
3	63.0	5063544	60435	87.7
Total		5776066	75309	100

**Compound 2h:** Phenomenex column, hexane/iPrOH = 97:3 at 1.0 mL/min,  $\lambda = 270$  nm: For the major diastereomer:  $t_{\text{major}} = 40.6$  min,  $t_{\text{minor}} = 23.9$  min, er = 98:2; For the minor diastereomer:  $t_{\text{major}} = 28.0$  min,  $t_{\text{minor}} = 32.8$  min, er = not determined.

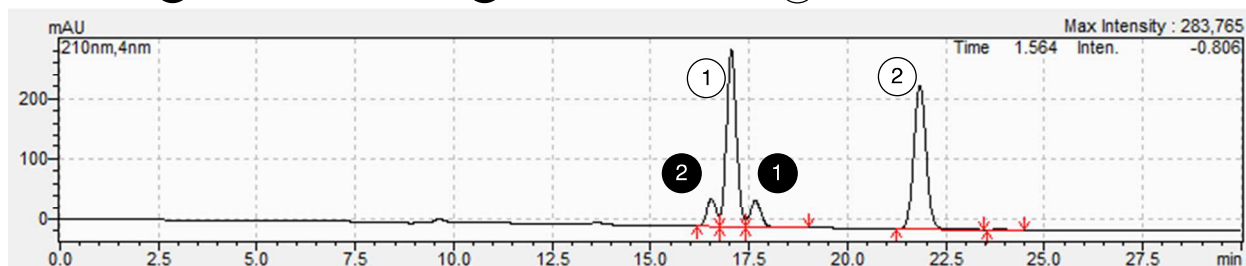
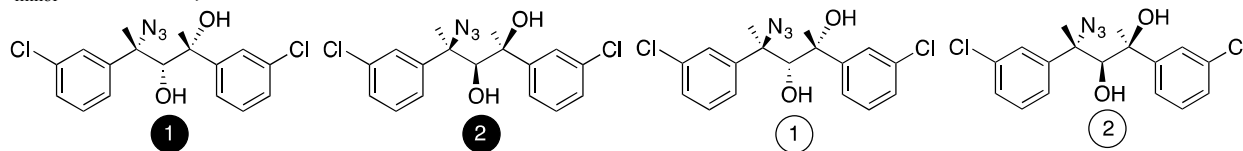


Peak#	Ret. Time	Area	Height	Area%
1	23.9	97112	3814	46.0
2	28.0	11053	409	5.2
3	32.8	9590	320	4.5
4	40.6	93342	2200	44.2
Total		211097	6743	100

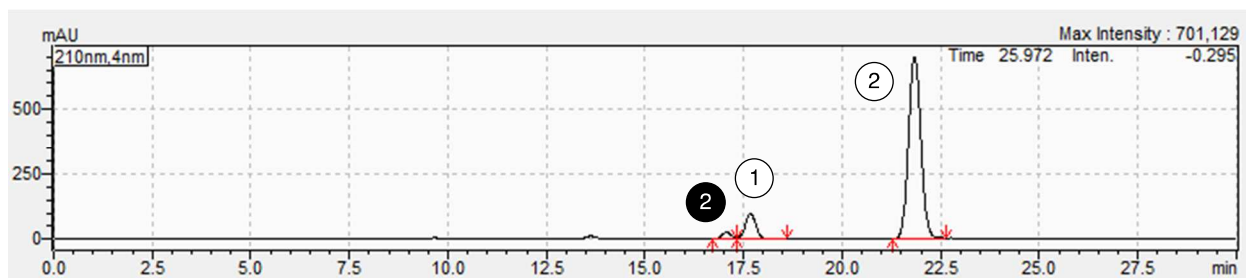


Peak#	Ret. Time	Area	Height	Area%
1	23.9	4742	185	2.2
2	28.0	20857	728	9.5
3	40.5	193927	4465	88.3
Total		219527	5379	100

**Compound 2i:** Phenomenex column, hexane/iPrOH = 78:22 at 0.3 mL/min,  $\lambda = 210$  nm: For the major diastereomer:  $t_{\text{major}} = 21.8$  min,  $t_{\text{minor}} = 17.1$  min, er = 97:3; For the minor diastereomer:  $t_{\text{major}} = 17.7$  min,  $t_{\text{minor}} = 16.5$  min, er = not determined.

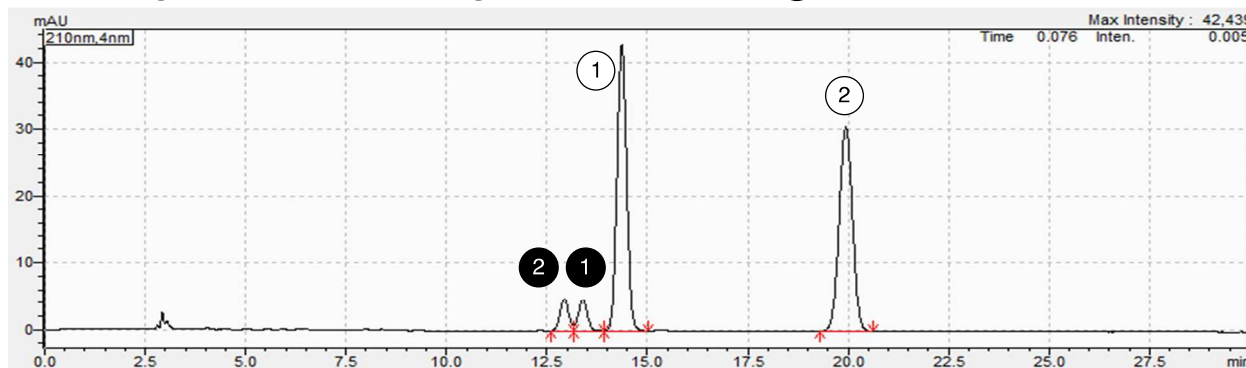
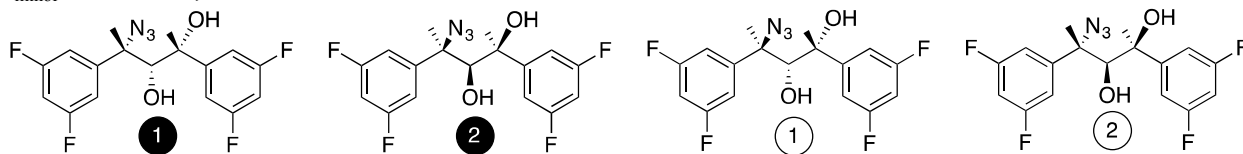


Peak#	Ret. Time	Area	Height	Area%
1	16.5	776430	47726	6.5
2	17.1	5163721	296208	43.0
3	17.7	856546	45881	7.1
4	21.8	5200313	238032	43.3
Total		11997010	627847	100

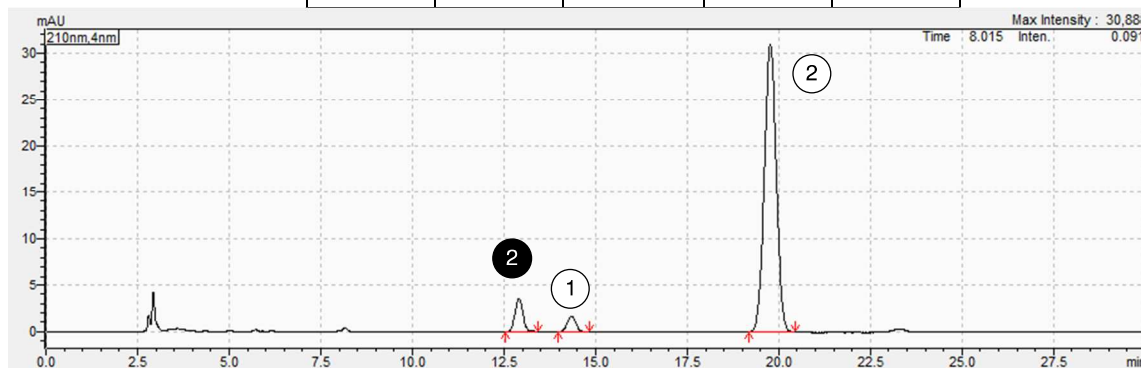


Peak#	Ret. Time	Area	Height	Area%
1	17.1	423175	24992	2.4
2	17.7	1825158	102260	10.4
3	21.8	15304853	699319	87.2
Total		17553185	826571	100

**Compound 2j:** Phenomenex column, hexane/iPrOH = 95:5 at 1.0 mL/min,  $\lambda = 210$  nm: For the major diastereomer:  $t_{\text{major}} = 19.9$  min,  $t_{\text{minor}} = 14.4$  min, er = 96:4; For the minor diastereomer:  $t_{\text{major}} = 12.9$  min,  $t_{\text{minor}} = 13.4$  min, er = not determined.

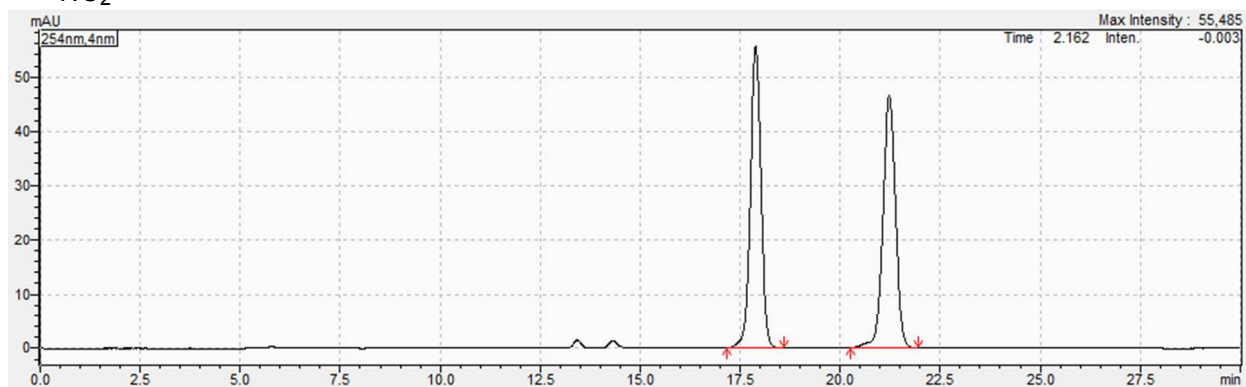
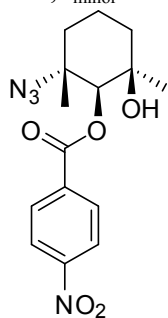


Peak#	Ret. Time	Area	Height	Area%
1	12.9	71805	4784	4.6
2	13.4	72712	4626	4.7
3	14.4	707212	42622	45.5
4	19.9	702070	30538	45.2
Total		1553799	82570	100

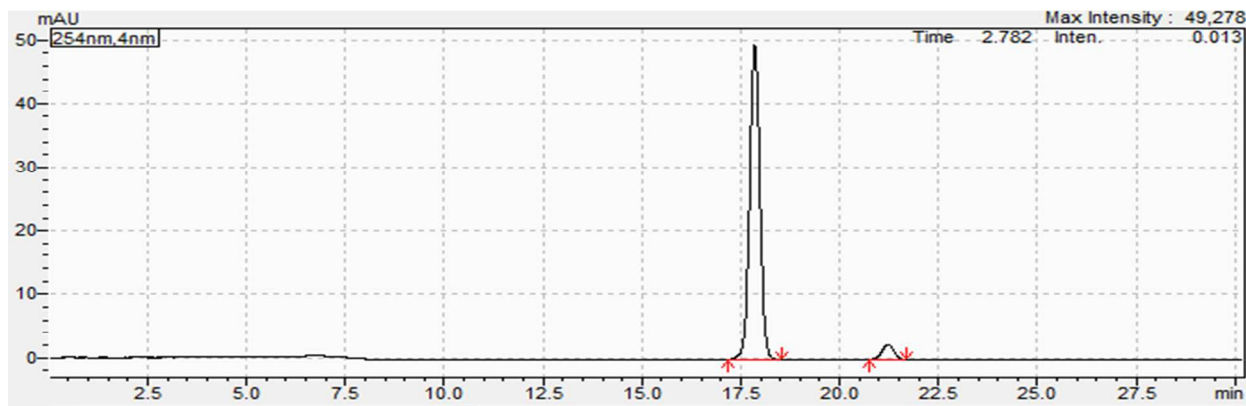


Peak#	Ret. Time	Area	Height	Area%
1	12.9	53991	3568	6.9
2	14.3	27880	1684	3.5
3	19.8	703622	30943	89.6
Total		785494	36195	100

**Compound 5a:** Compound 5a was derivatized for er determination by chiral HPLC. Phenomenex Lux 3 $\mu$  cellulose-1 column, hexane/iPrOH = 90:10 at 0.5 mL/min,  $\lambda$  = 254 nm: For compound S4a:  $t_{\text{major}}$  = 17.9 min,  $t_{\text{minor}}$  = 21.2 min, er = 95:5.

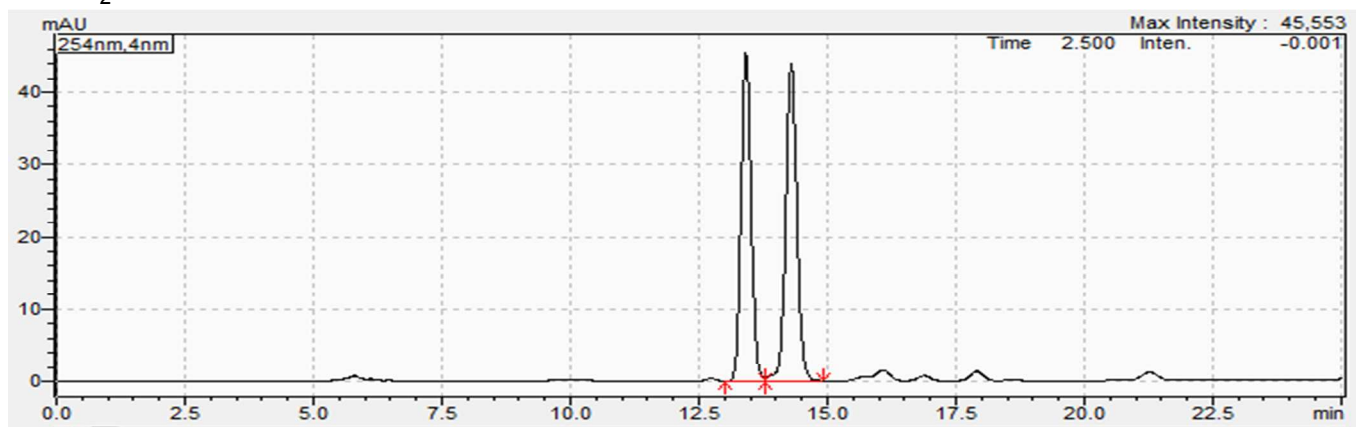
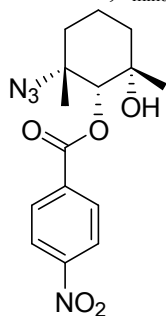


Peak#	Ret. Time	Area	Height	Area%
1	17.9	1020645	55420	50.1
2	21.2	1018330	46395	50.0
Total		2038975	101816	100

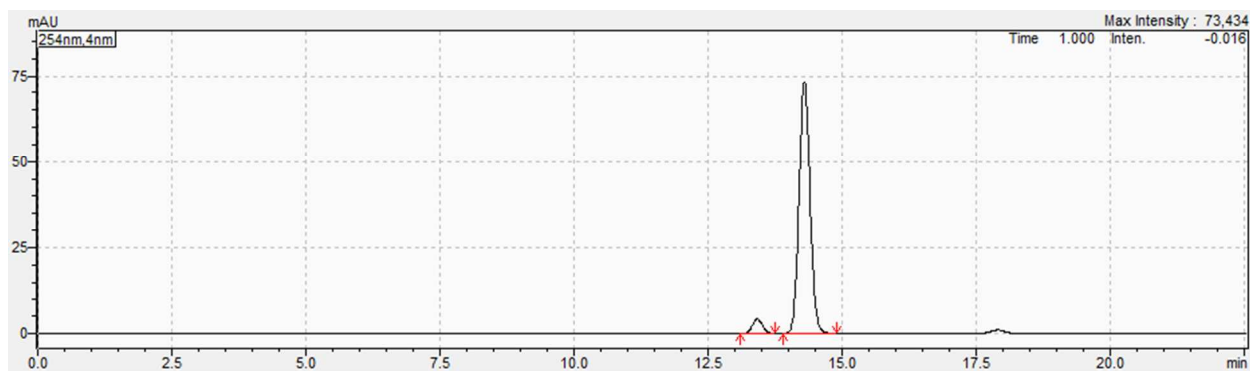


Peak#	Ret. Time	Area	Height	Area%
1	17.9	450952	24950	94.6
2	21.2	25687	1231	5.3
Total		476639	26180	100

**Compound 5a'**: Compound 5a' was derivatized for er determination by chiral HPLC. Phenomenex Lux 3 $\mu$  cellulose-1 column, hexane/iPrOH = 90:10 at 0.5 mL/min,  $\lambda$  = 254 nm: For compound S4a':  $t_{\text{major}}$  = 14.3 min,  $t_{\text{minor}}$  = 13.4 min, er = 95:5.

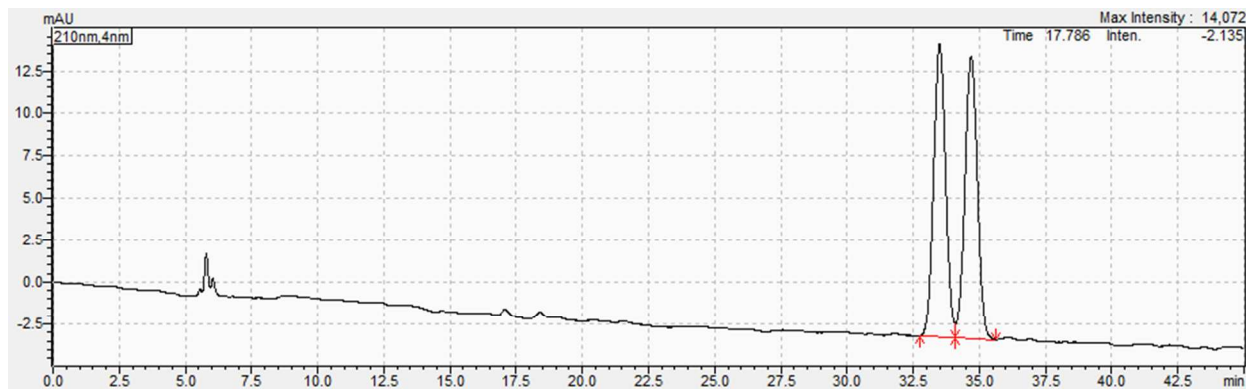
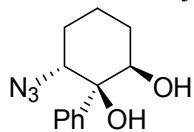


Peak#	Ret. Time	Area	Height	Area%
1	13.4	619612	45487	48.2
2	14.3	667141	44004	51.8
Total		1286753	89491	100

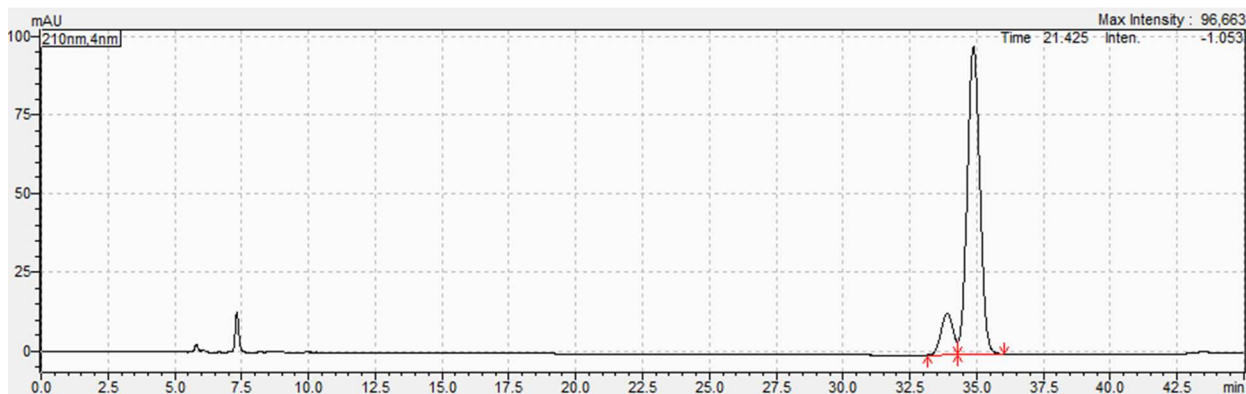


Peak#	Ret. Time	Area	Height	Area%
1	13.4	54502	4115	5.0
2	14.3	1040001	73300	95.0
Total		1094503	77415	100

**Compound 5b:** Phenomenex Lux 3 $\mu$  cellulose-1 column, hexane/iPrOH = 95:5 at 0.5 mL/min,  $\lambda$  = 210 nm: For the major enantiomer:  $t_{\text{major}}$  = 34.7 min,  $t_{\text{minor}}$  = 33.5 min, er = 89:11.

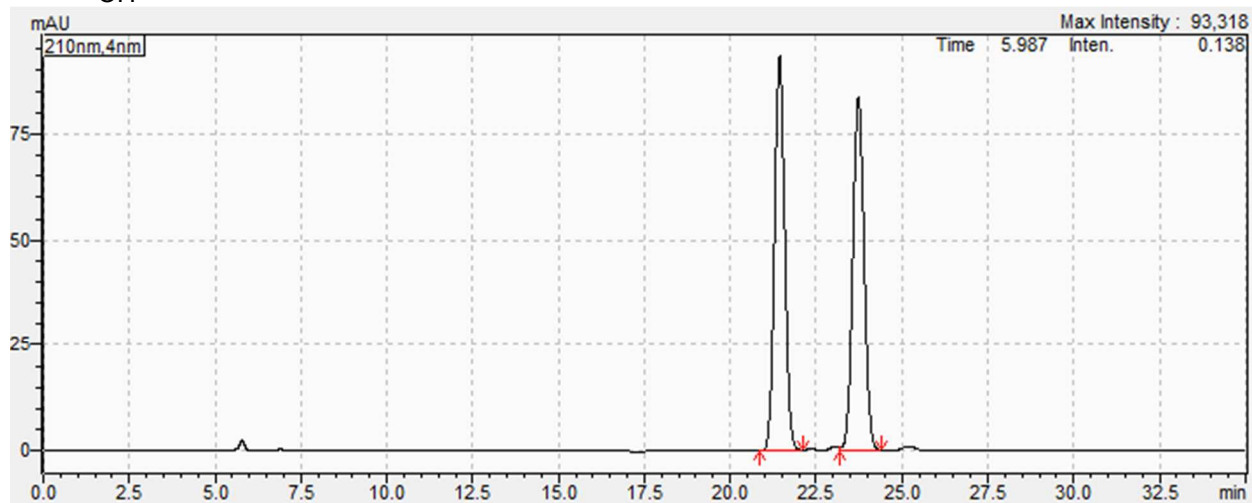
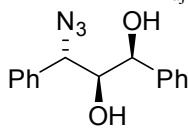


Peak#	Ret. Time	Area	Height	Area%
1	33.5	545102	17308	50.0
2	34.7	544300	16728	50.0
Total		1089402	34035	100

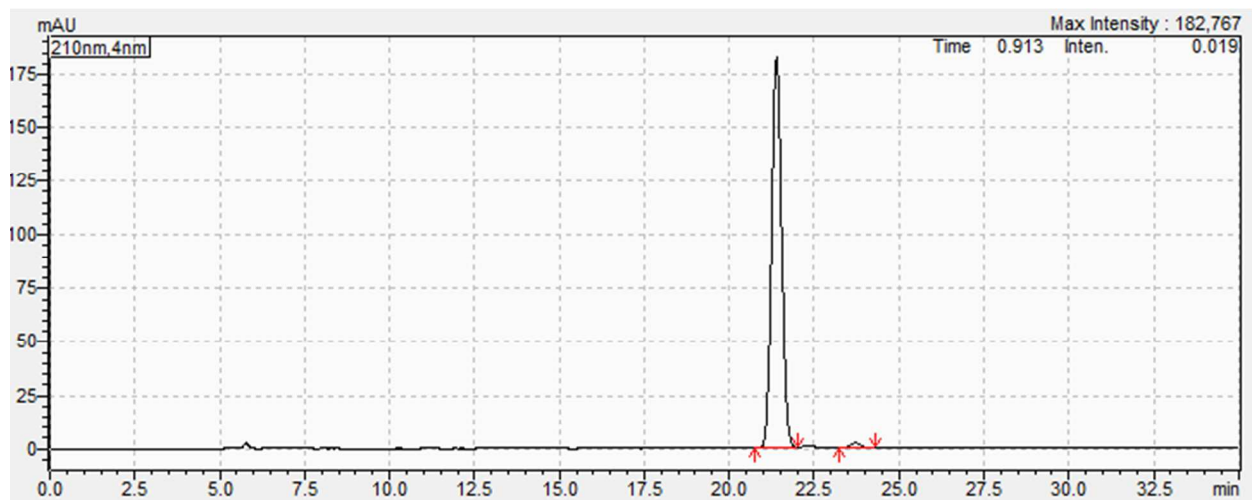


Peak#	Ret. Time	Area	Height	Area%
1	33.9	412743	13364	11.4
2	34.9	3200220	97672	88.6
Total		3612963	111036	100

**Compound 5c:** Phenomenex column, hexane/iPrOH = 90:10 at 0.5 mL/min,  $\lambda = 210$  nm: For the major enantiomer:  $t_{\text{major}} = 21.4$  min,  $t_{\text{minor}} = 23.7$  min, er = 96:4.

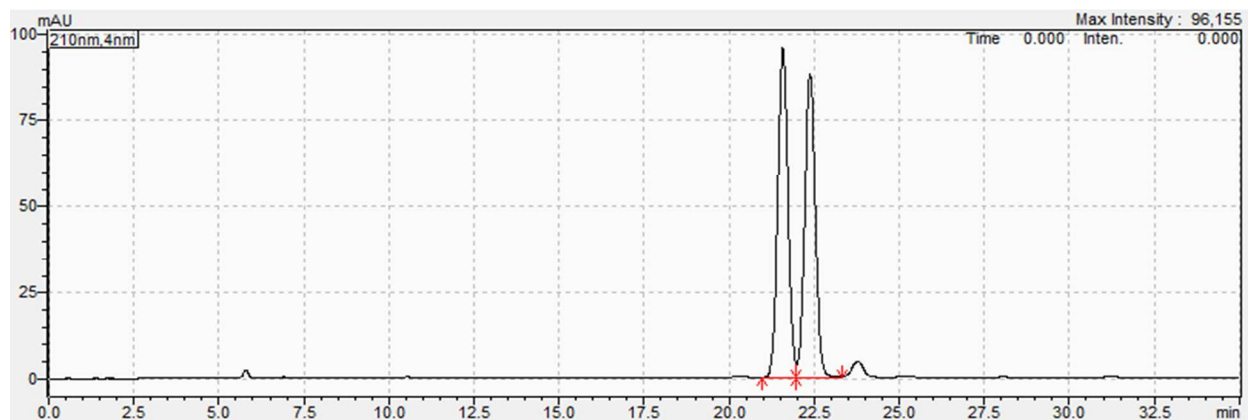
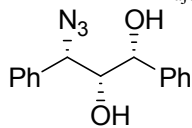


Peak#	Ret. Time	Area	Height	Area%
1	21.4	1919124	93206	50.1
2	23.7	1914496	83684	49.9
Total		3833620	176890	100

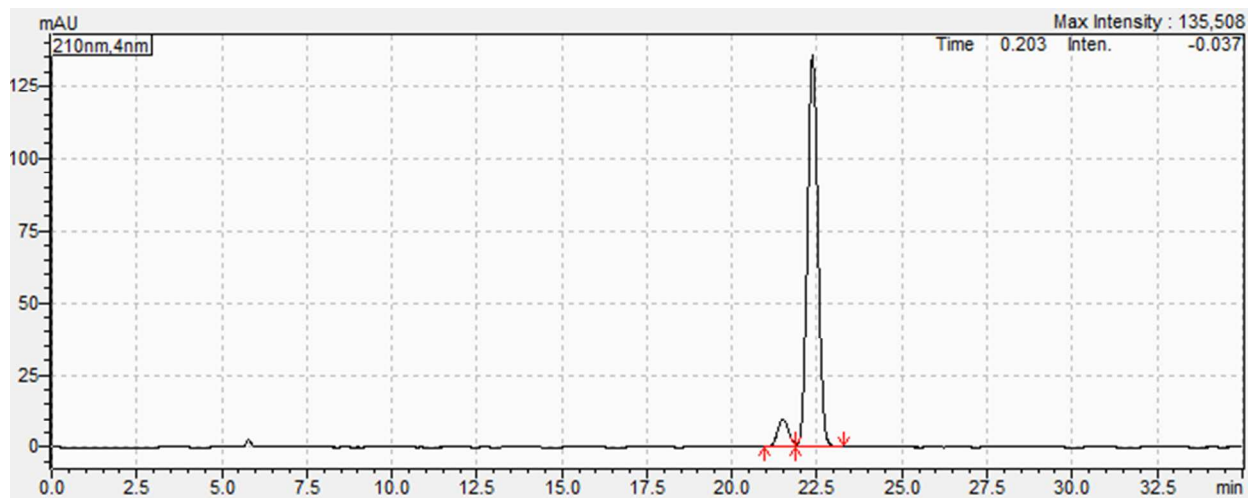


Peak#	Ret. Time	Area	Height	Area%
1	21.4	3746627	182375	98.5
2	23.7	56781	2483	1.5
Total		3803408	184858	100

**Compound 5c'**: Phenomenex column, hexane/iPrOH = 90:10 at 0.5 mL/min,  $\lambda = 210$  nm: For the major enantiomer:  $t_{\text{major}} = 22.4$  min,  $t_{\text{minor}} = 21.6$  min, er = 93:7.

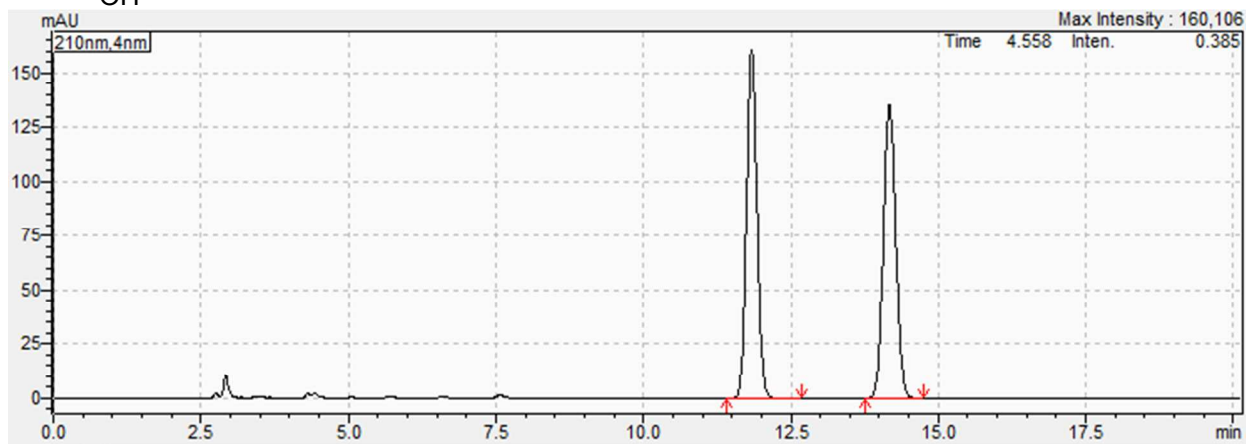
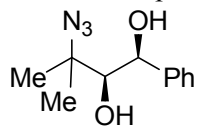


Peak#	Ret. Time	Area	Height	Area%
1	21.6	2009434	95825	51.1
2	22.4	1921731	88497	48.9
Total		3931164	184322	100

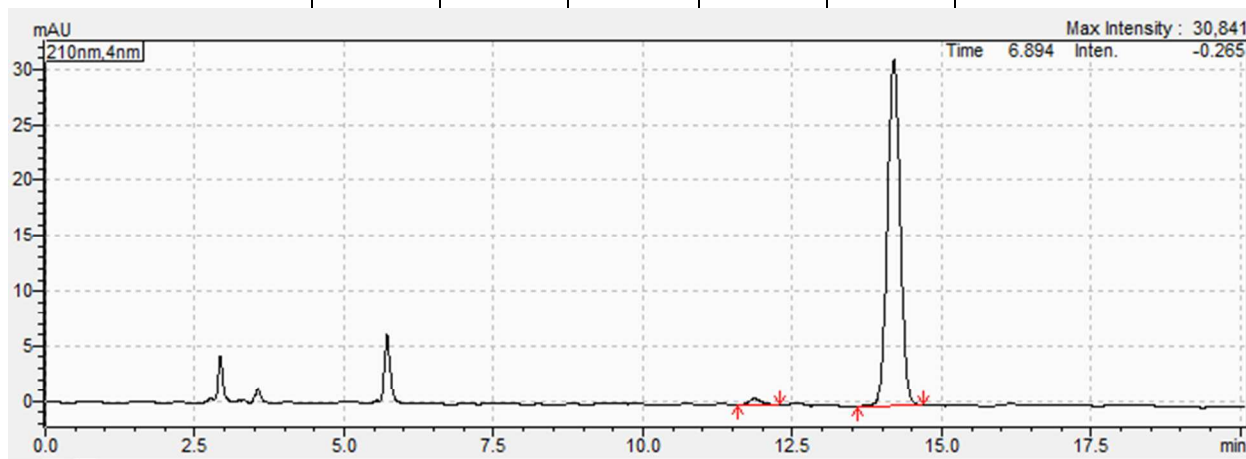


Peak#	Ret. Time	Area	Height	Area%
1	21.5	218153	9752	6.9
2	22.4	2922573	135383	93.1
Total		3140726	145135	100

**Compound 5d:** Phenomenex Lux 3 $\mu$  cellulose-1 column, hexane/iPrOH = 92:8 at 1.0 mL/min,  $\lambda$  = 210 nm: For compound 5d:  $t_{\text{major}}$  = 14.2 min,  $t_{\text{minor}}$  = 11.8 min, er = 98:2

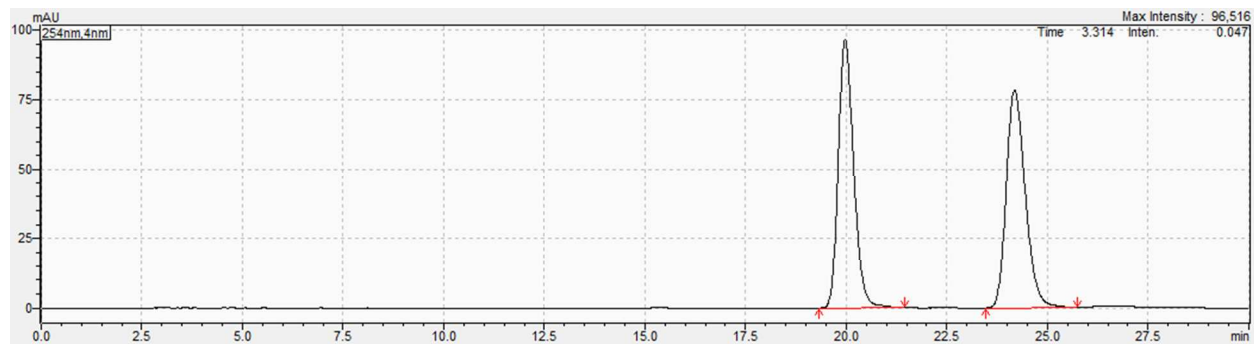
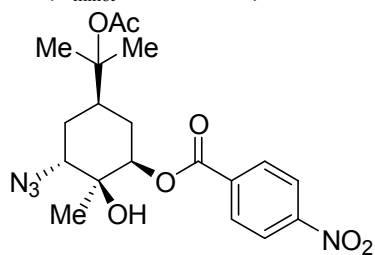


Peak#	Ret. Time	Area	Height	Area%
1	11.8	1997697	160189	50.0
2	14.2	1994768	135279	50.0
Total		3992465	295468	100

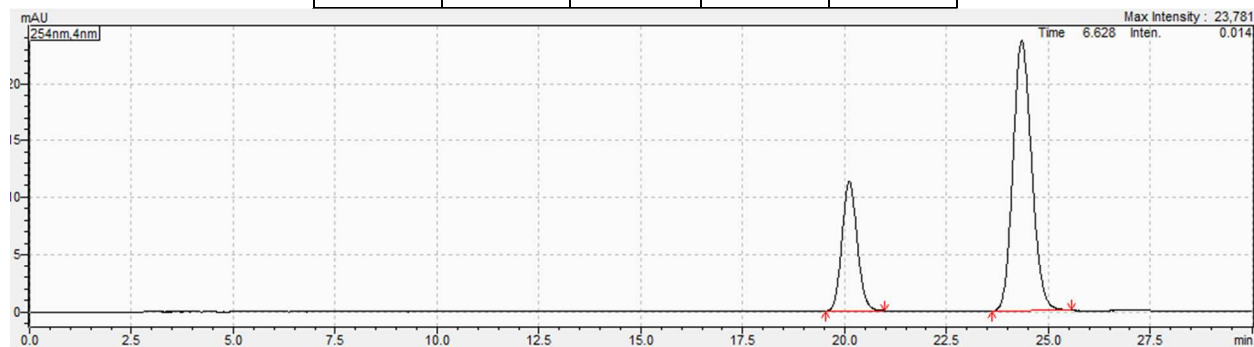


Peak#	Ret. Time	Area	Height	Area%
1	11.9	9779	599	2.1
2	14.2	461499	31248	98.0
Total		471279	31847	100.1

**Compound 5e:** Compound 5e was derivatized for er determination by chiral HPLC. Phenomenex Lux 3 $\mu$  cellulose-1 column, hexane/iPrOH = 95:5 at 1.0 mL/min,  $\lambda$  = 254 nm: For compound S4e:  $t_{\text{major}}$  = 20.0 min,  $t_{\text{minor}}$  = 24.2 min, er = 72:28.

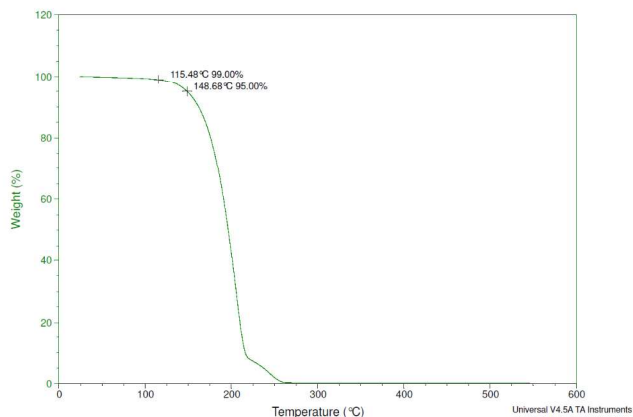


Peak#	Ret. Time	Area	Height	Area%
1	20.0	2564054	96435	50.0
2	24.2	2562144	78398	50.0
Total		5126199	174833	100

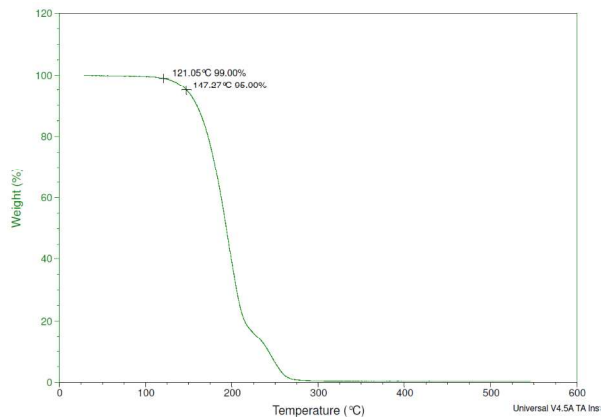


Peak#	Ret. Time	Area	Height	Area%
1	20.1	293541	11267	28.0
2	24.3	754781	23679	72.0
Total		1048322	34945	100

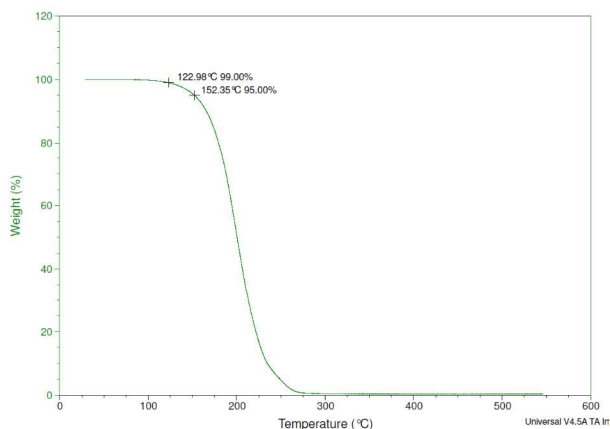
**TGA of Alcohol S2a**  
Under N<sub>2</sub>



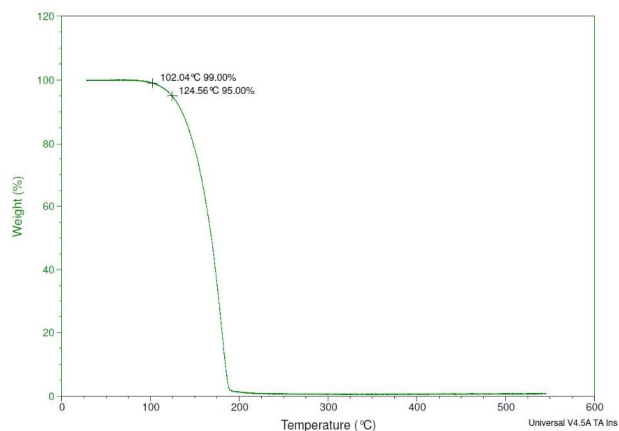
Under air



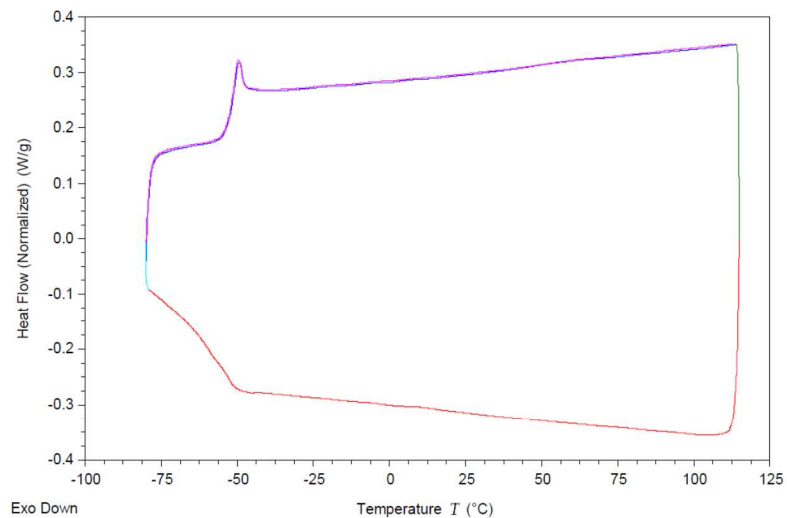
**TGA of Azide 1**  
Under N<sub>2</sub>

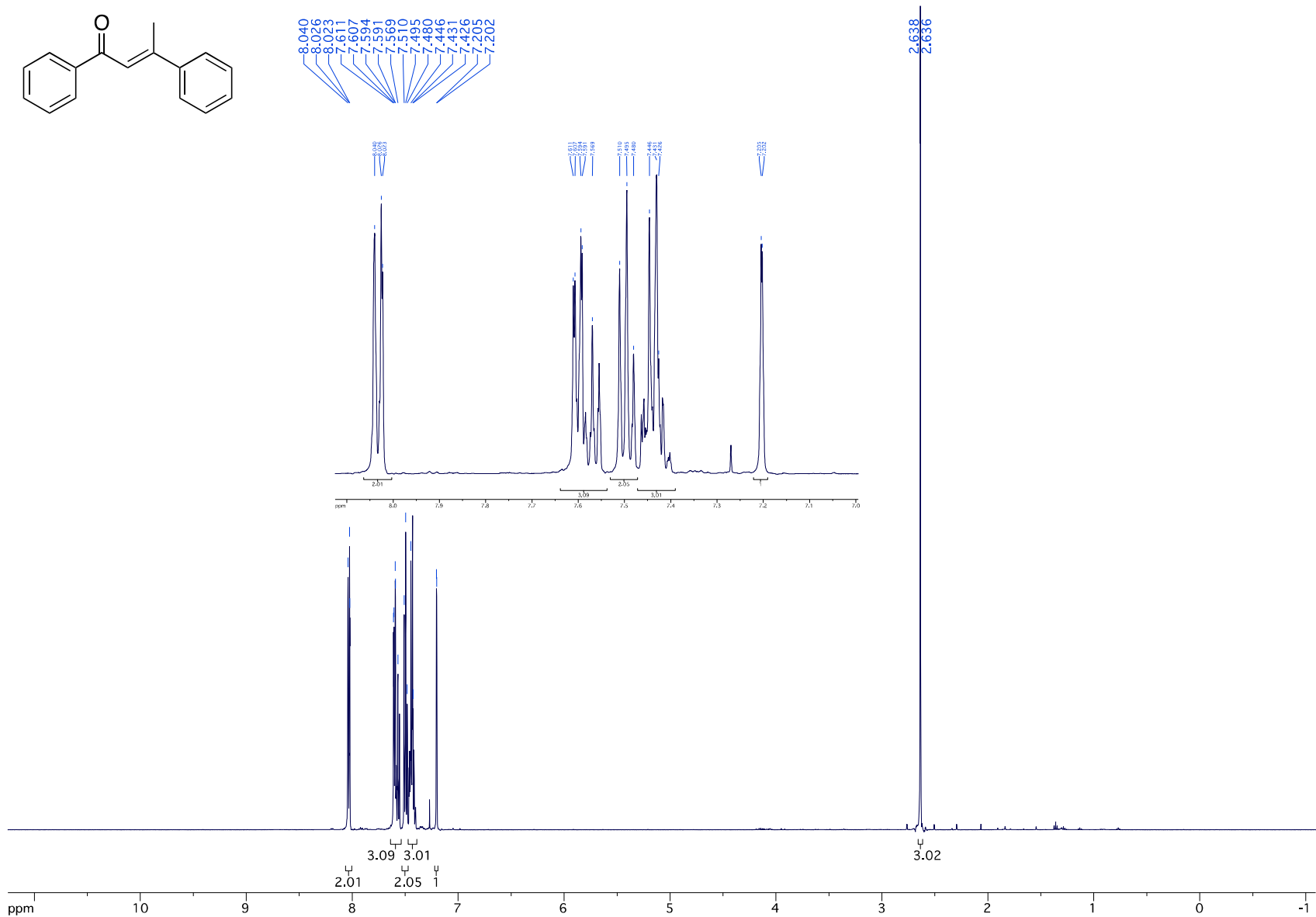
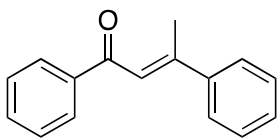


Under air

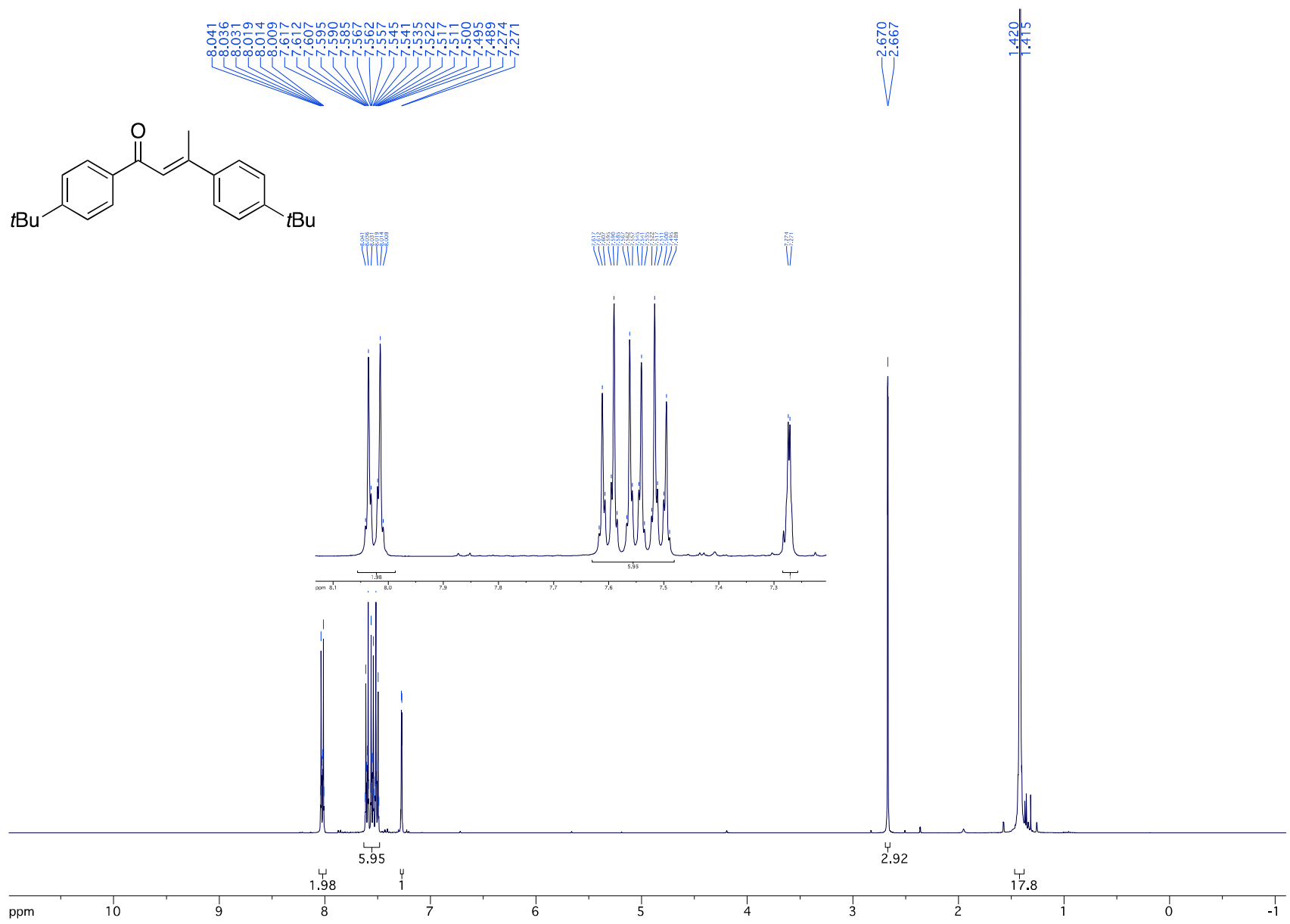


**DSC of Azide 1:**

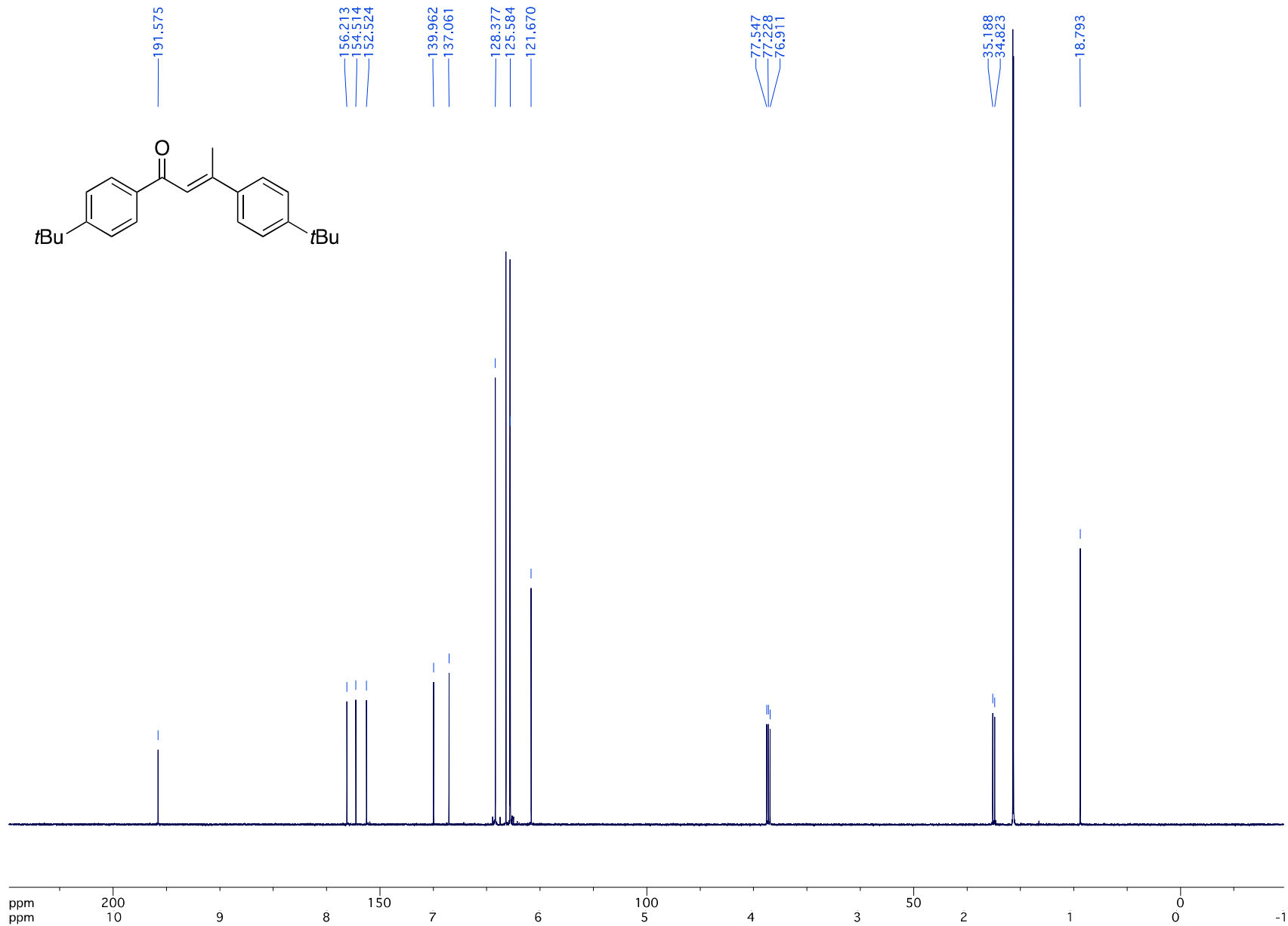




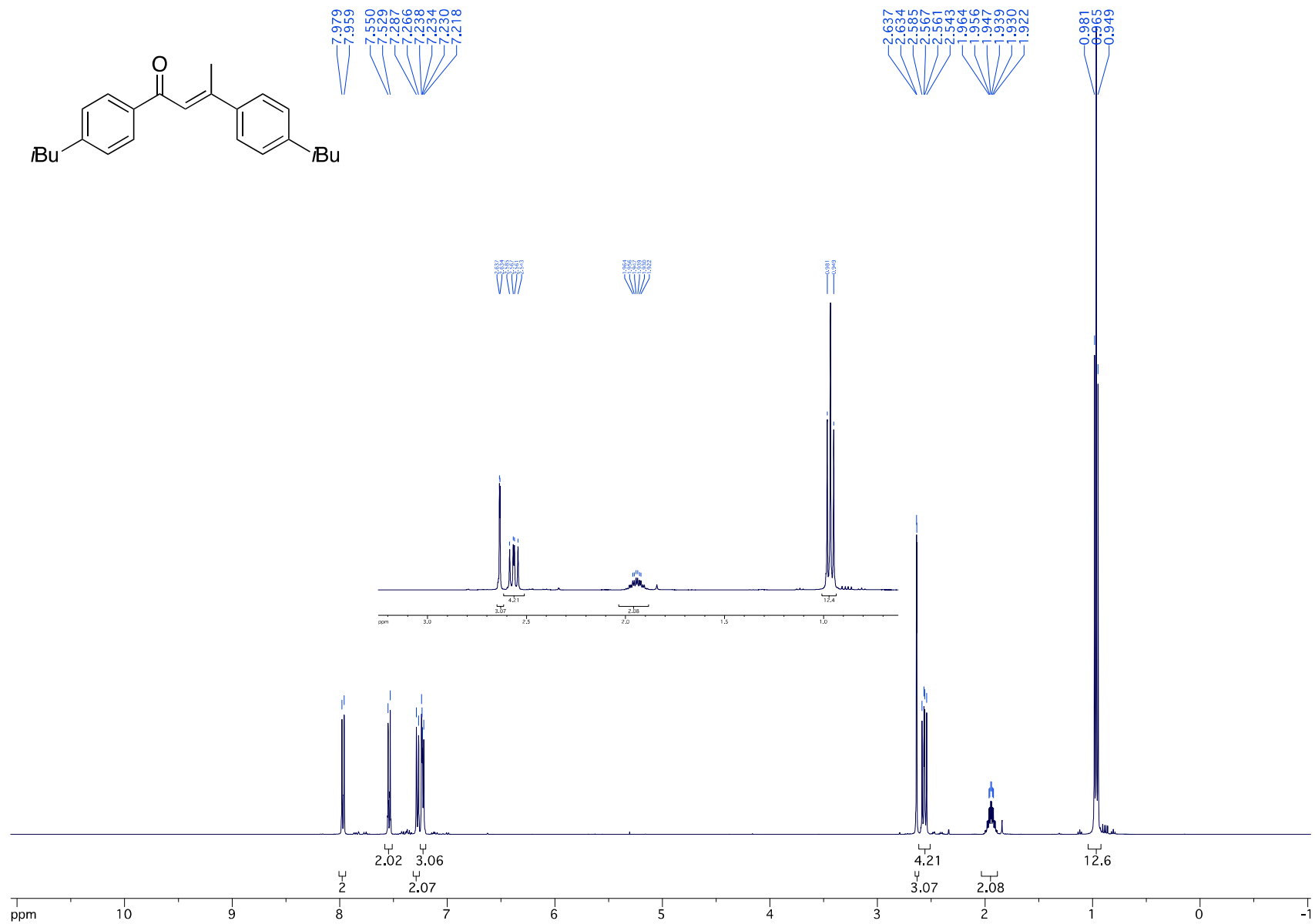
Compound S1a: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



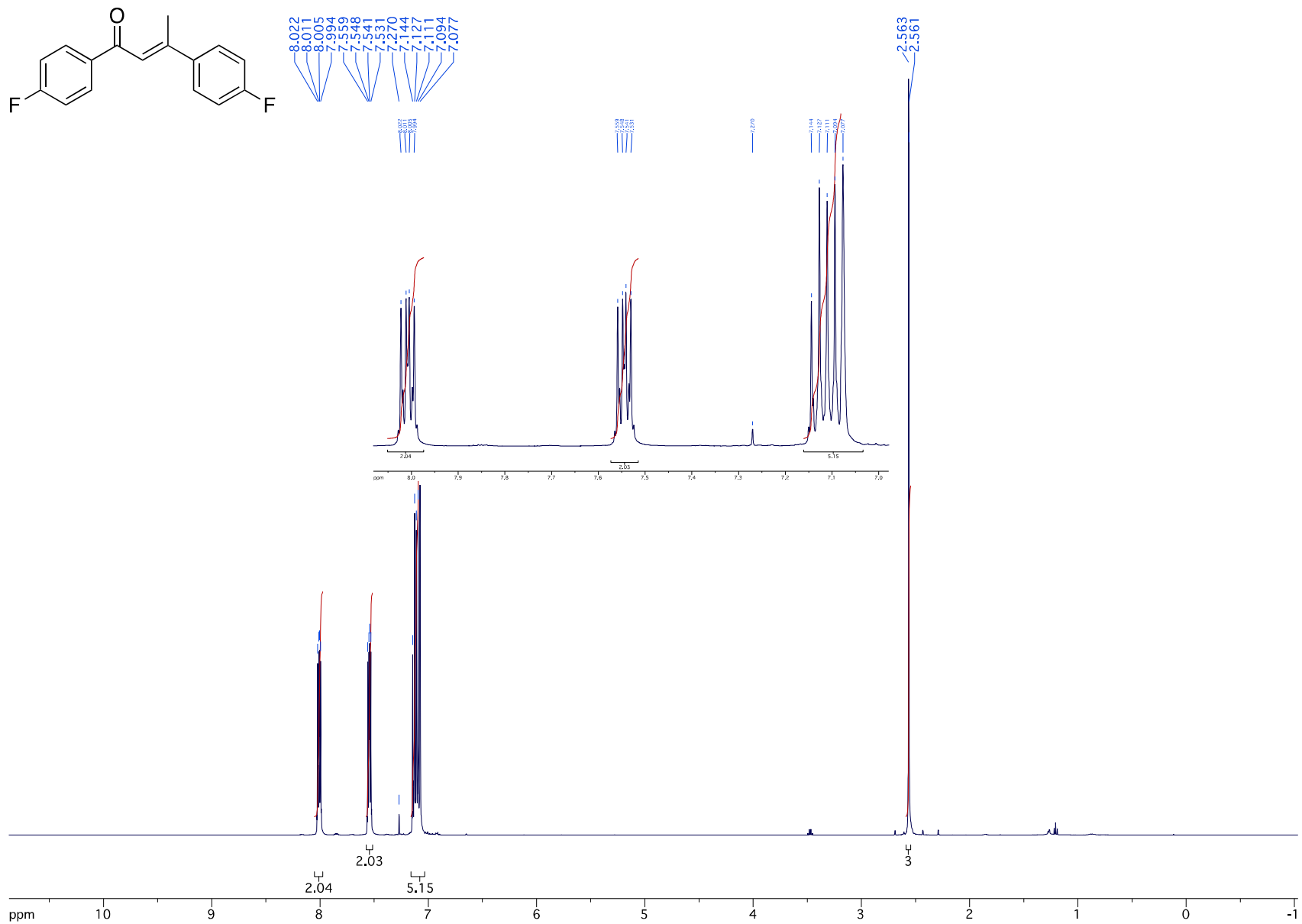
Compound S1b: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



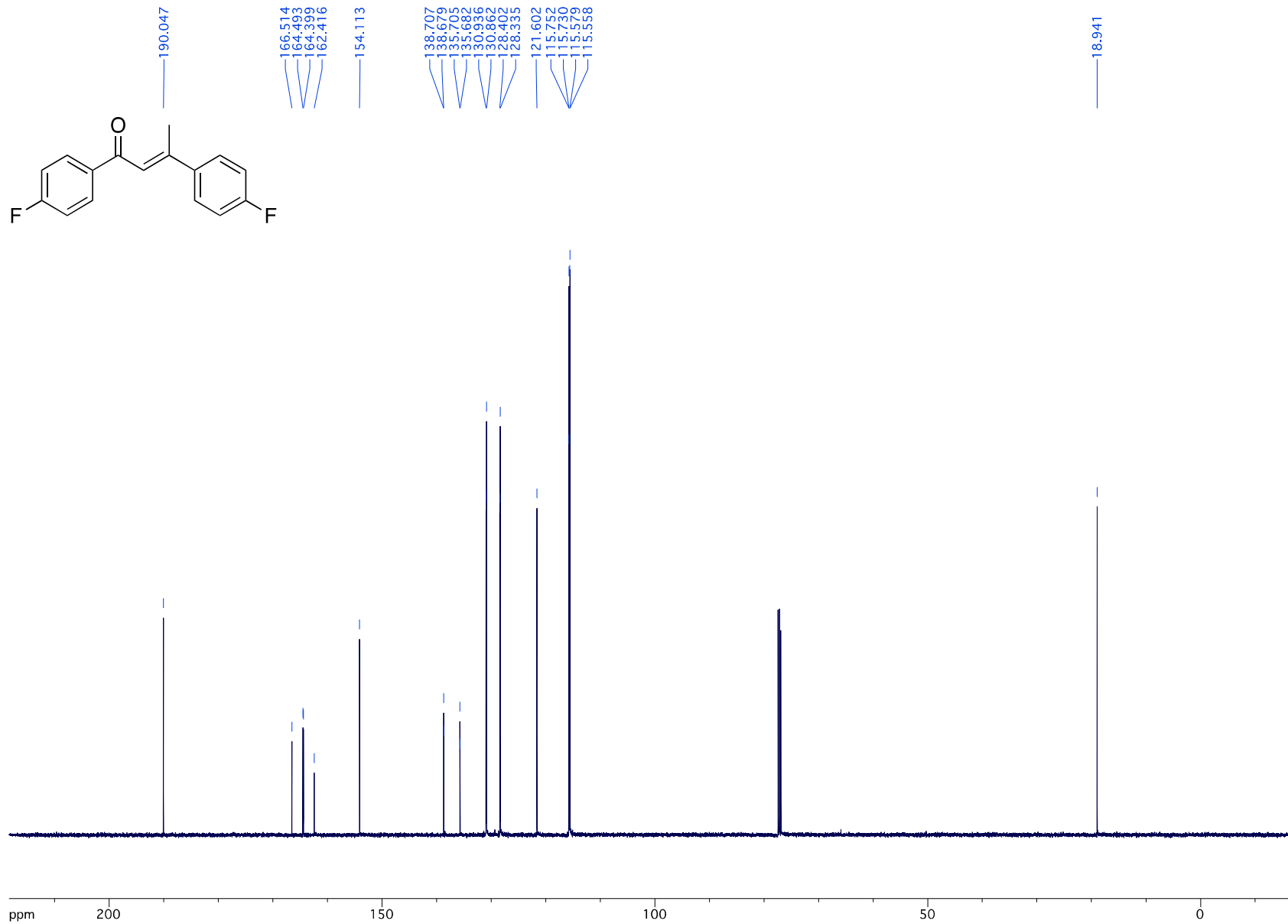
Compound S1b: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



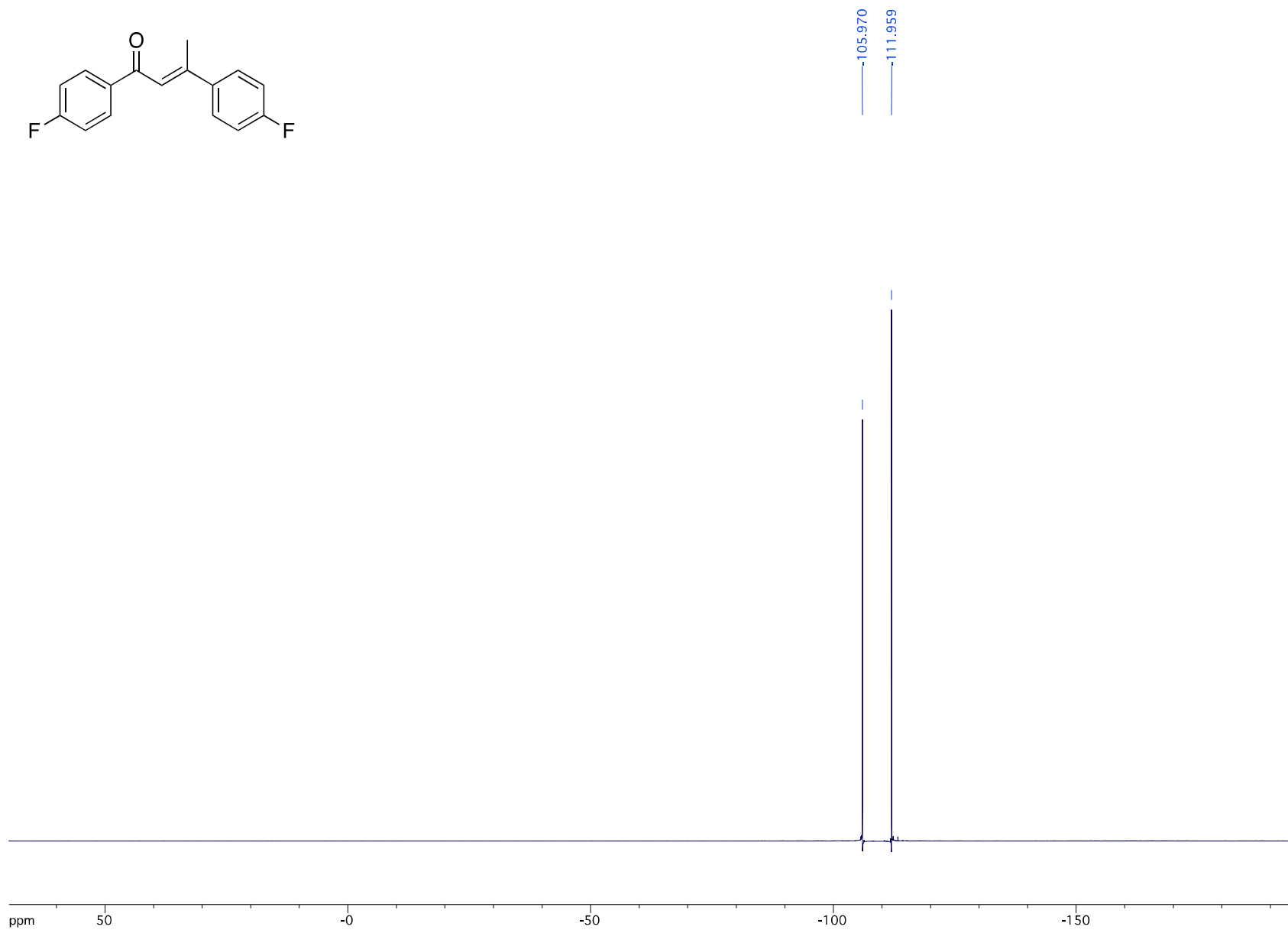
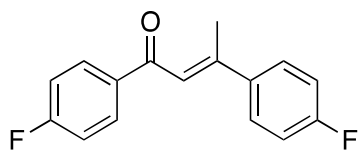
Compound S1c: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



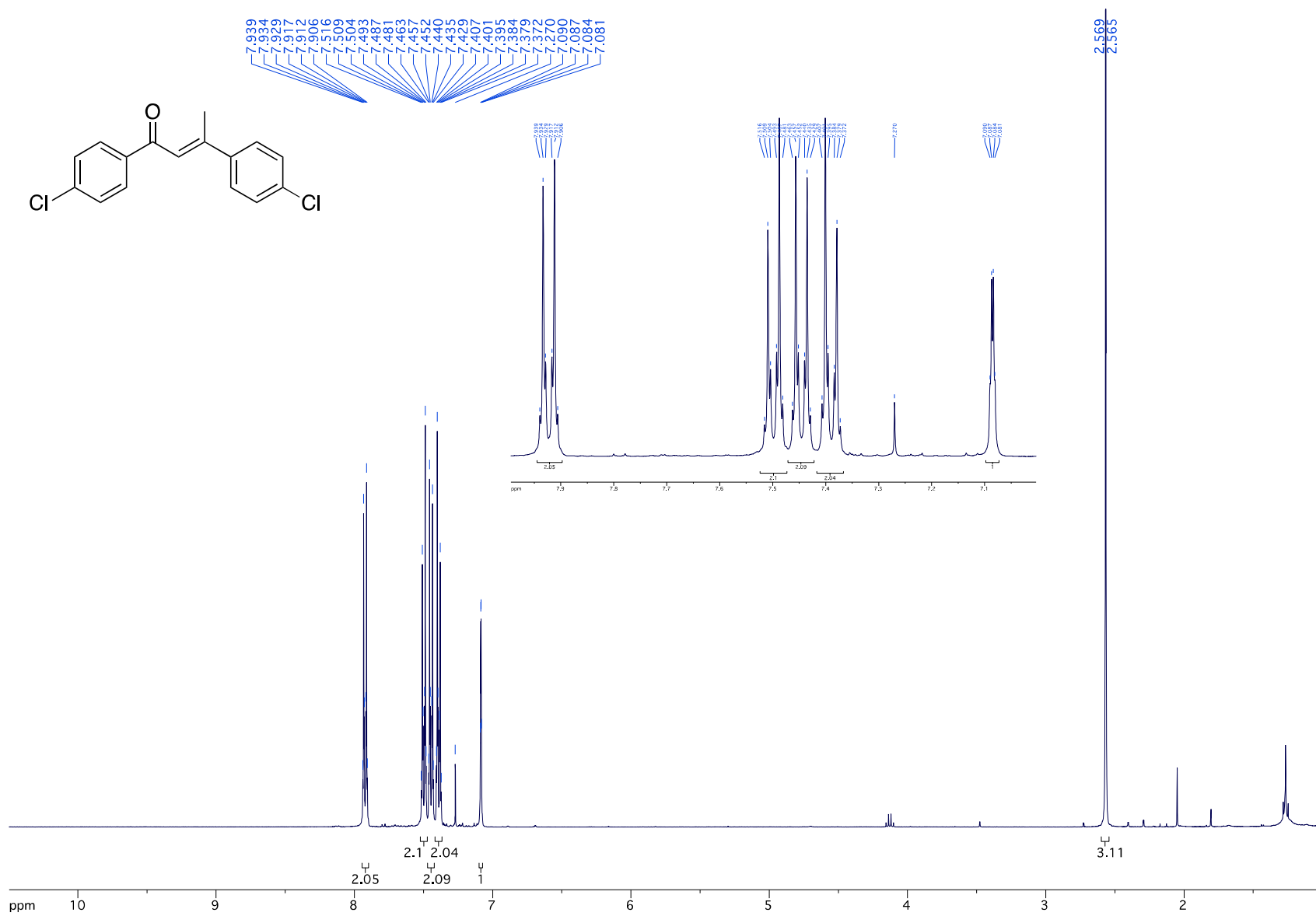
Compound S1d: 500 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



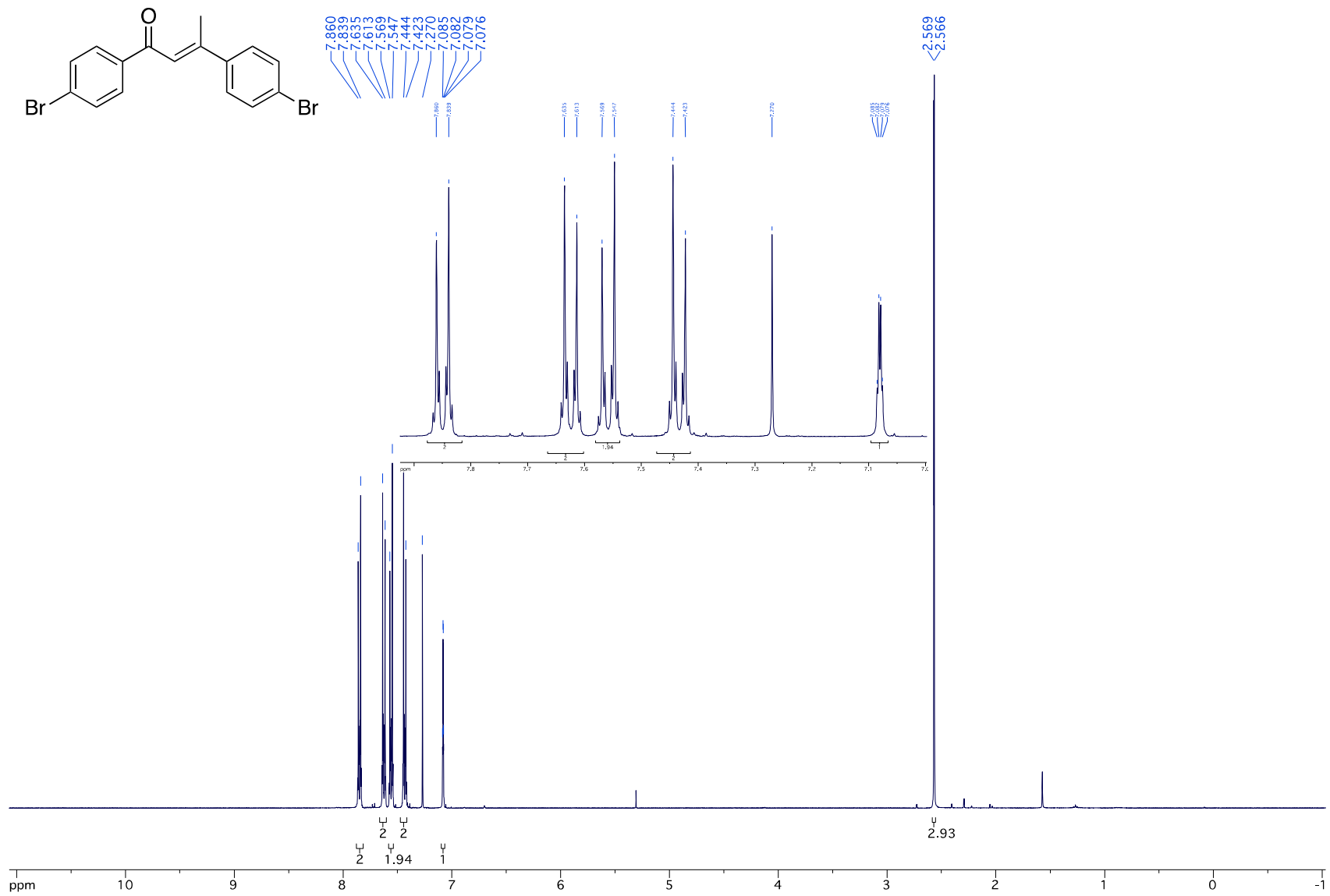
Compound S1d: 125 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



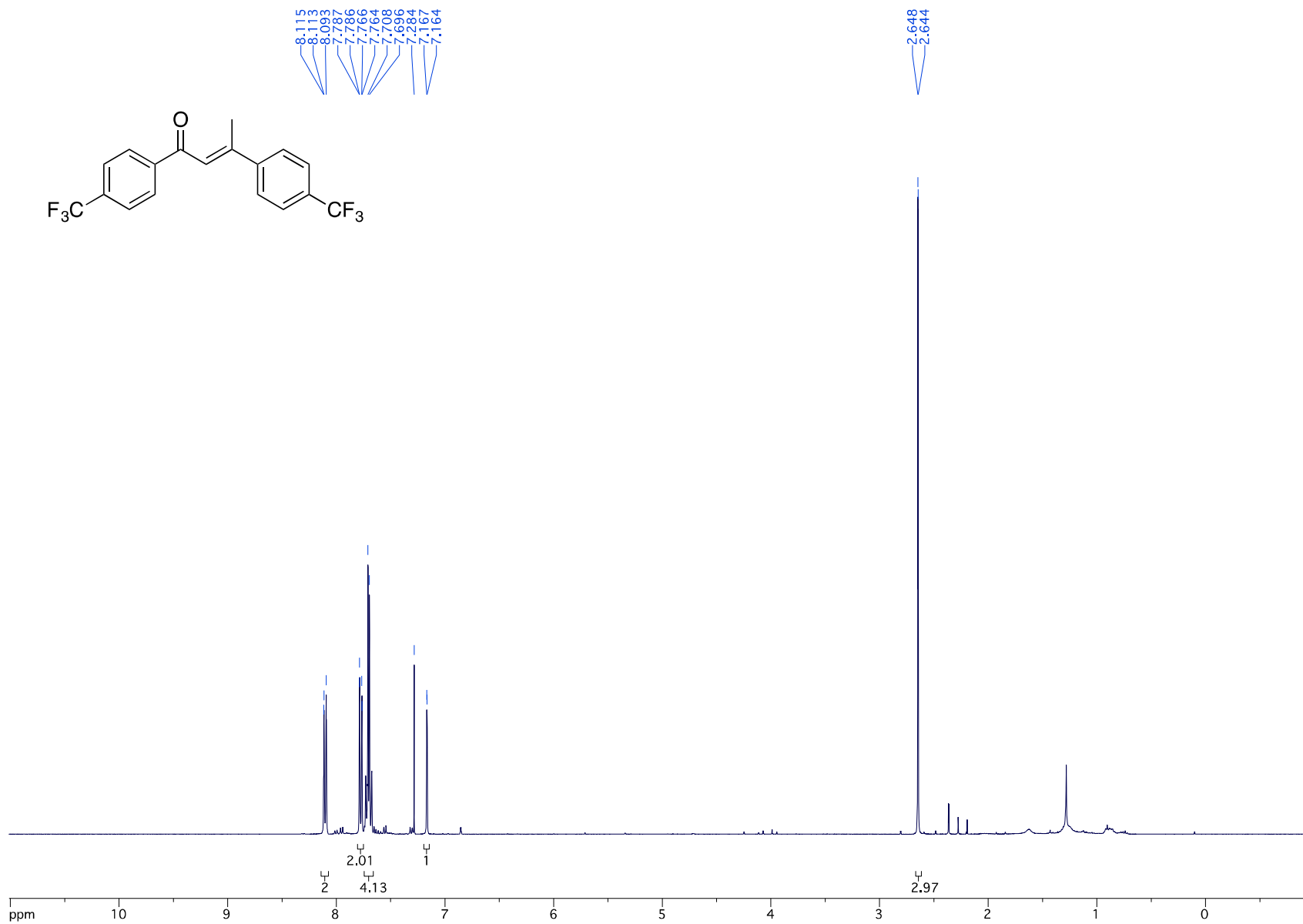
Compound S1d: 471 MHz  $^{19}\text{F}$  NMR spectrum in  $\text{CDCl}_3$



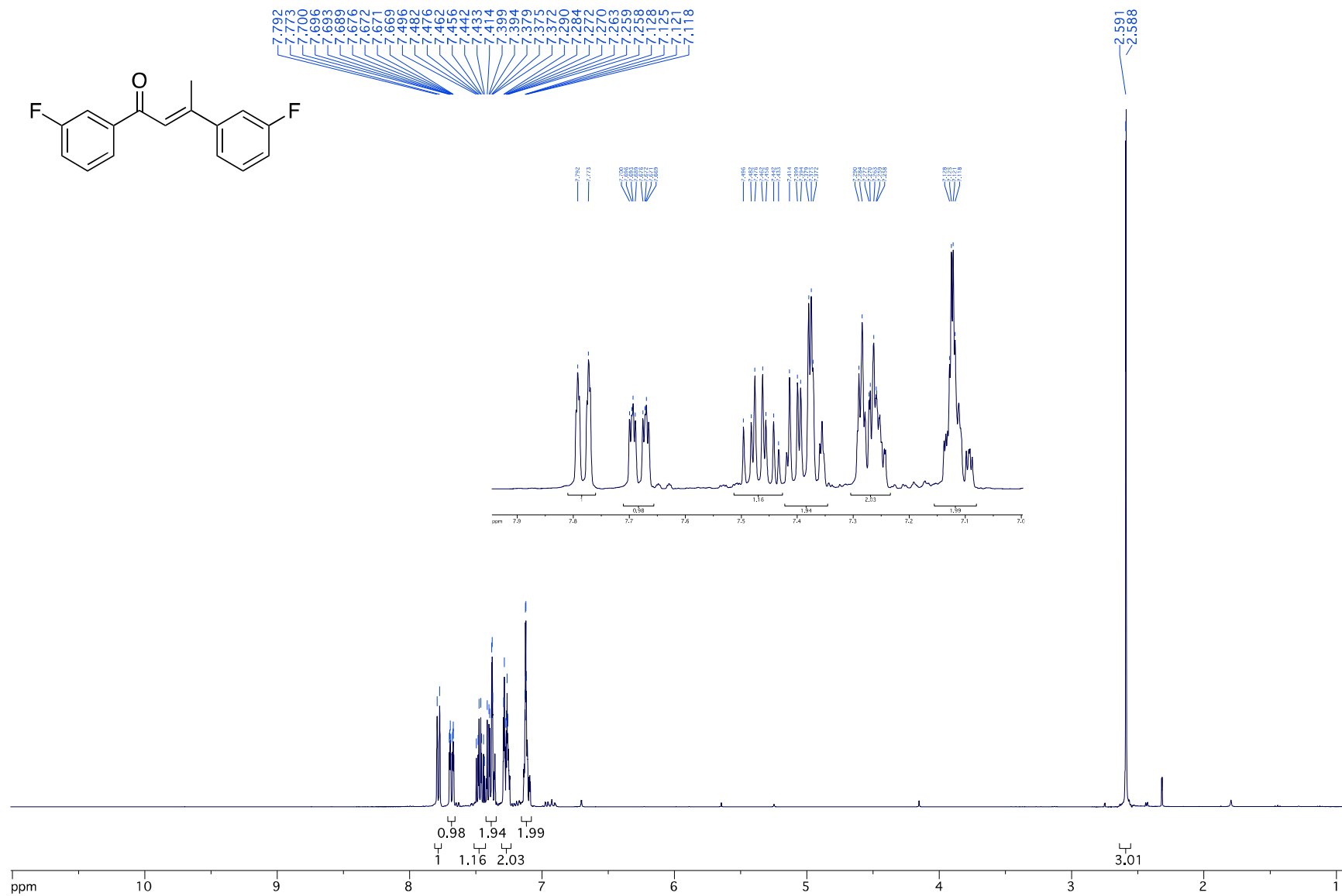
Compound S1e: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



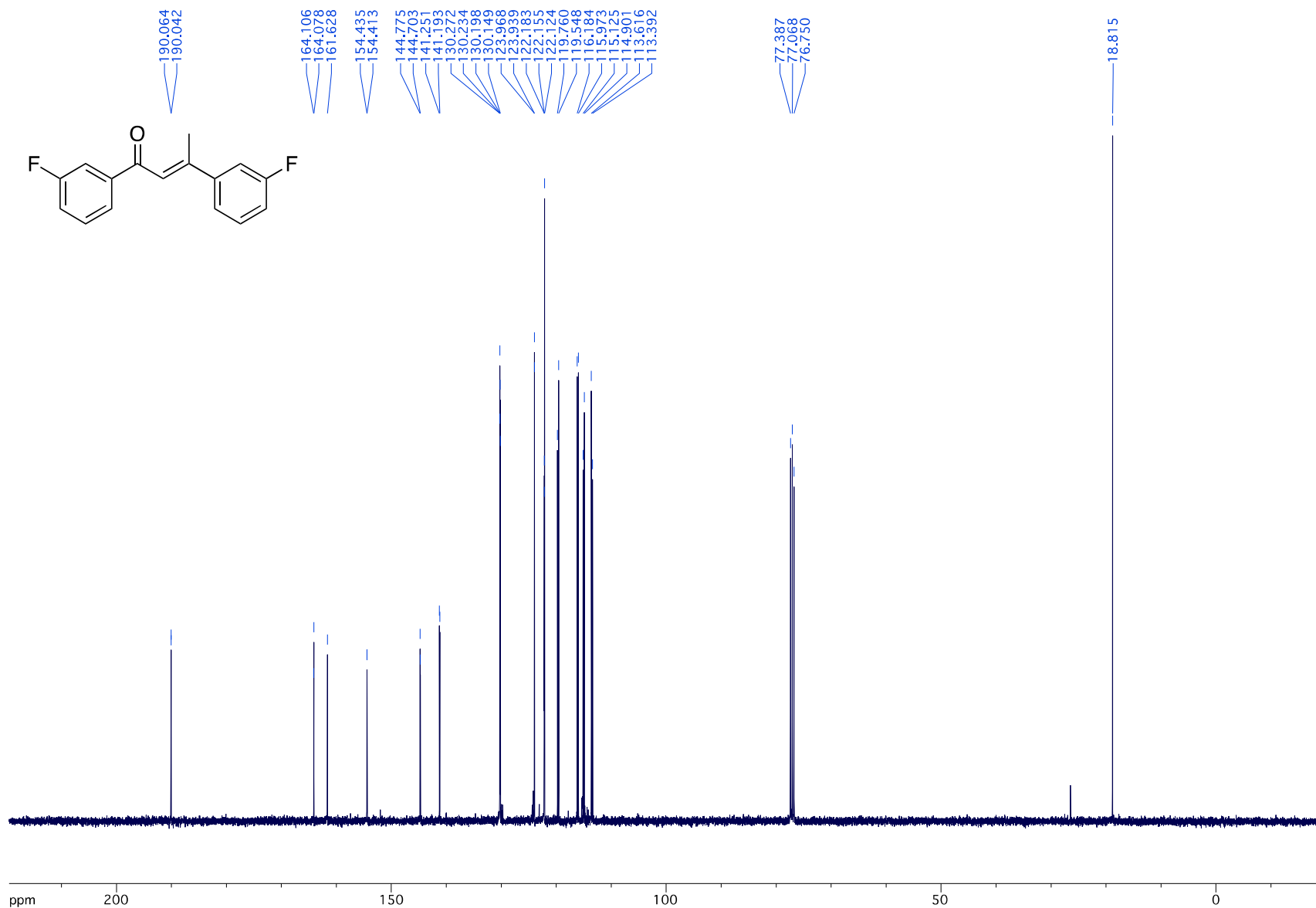
Compound S1f: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



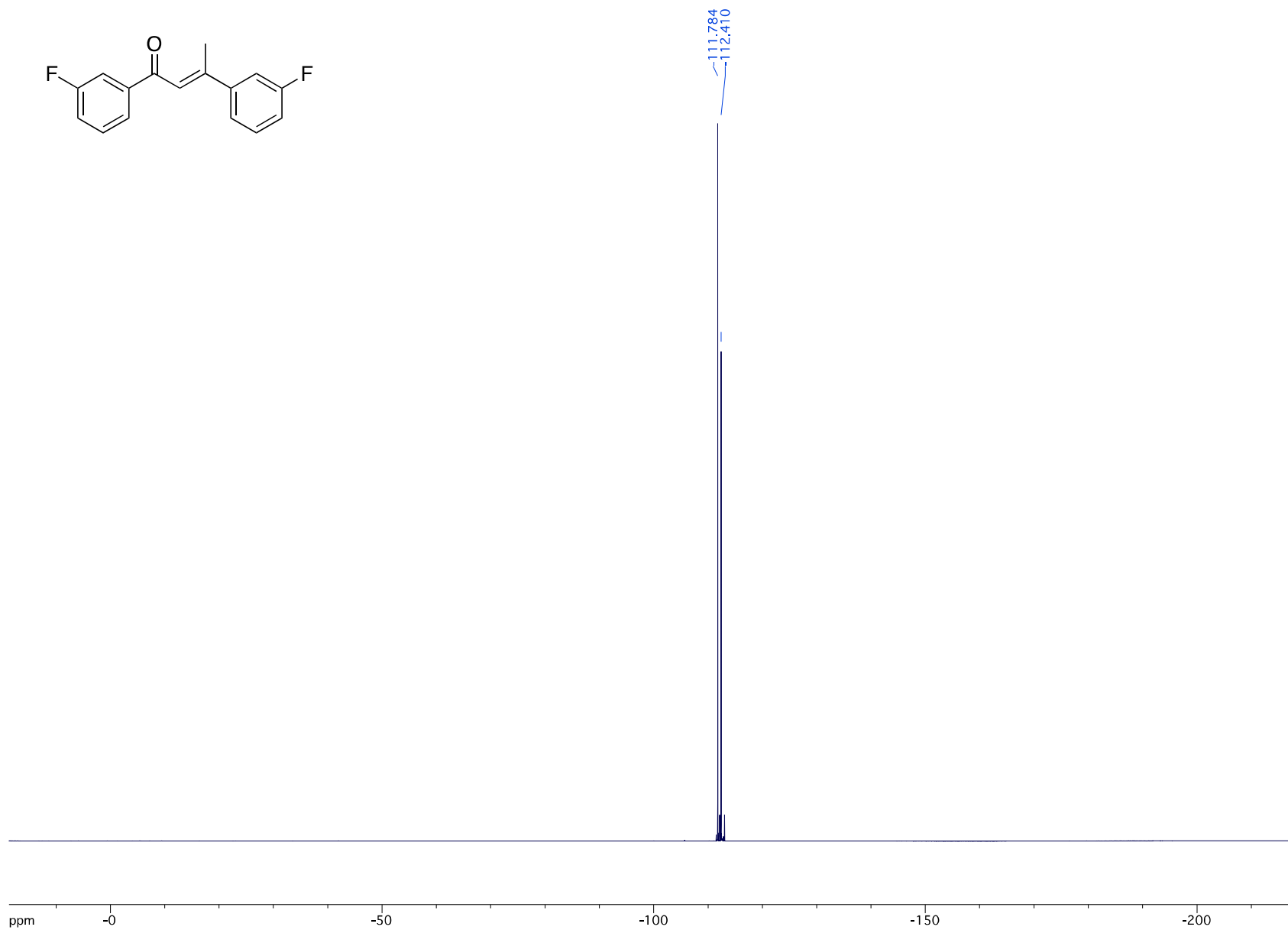
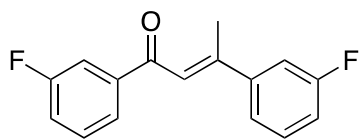
Compound S1g: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



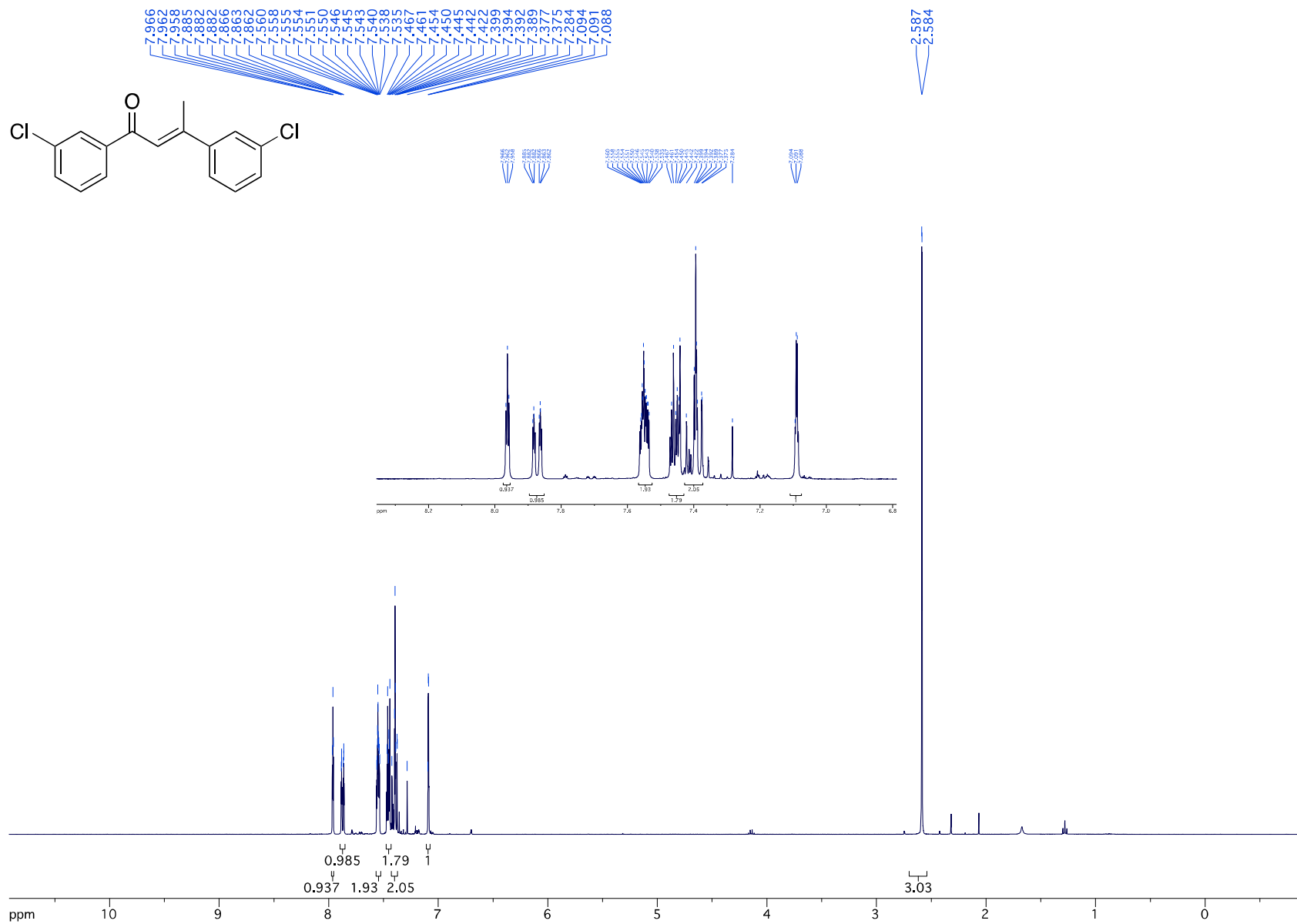
Compound S1h: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



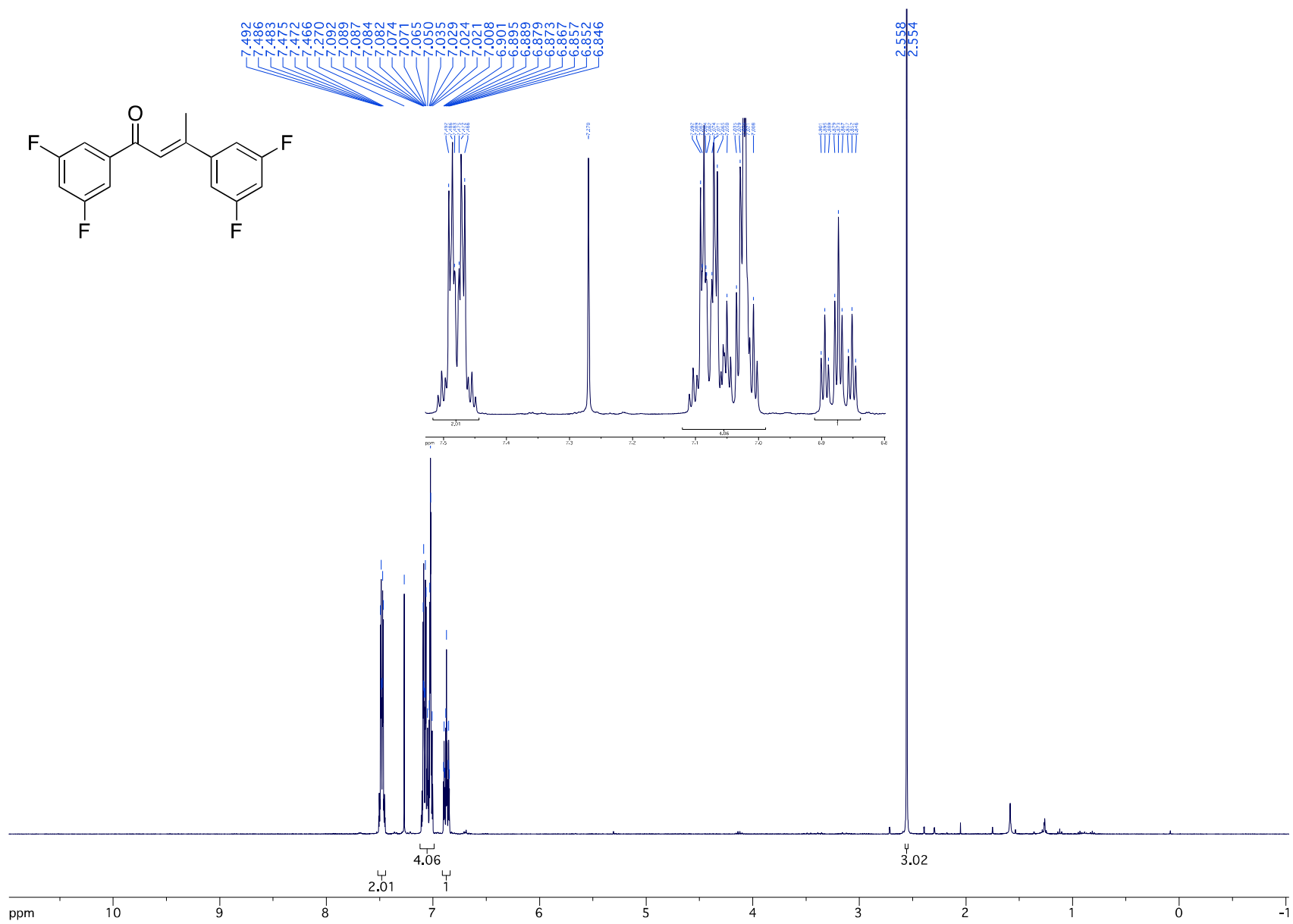
Compound S1h: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



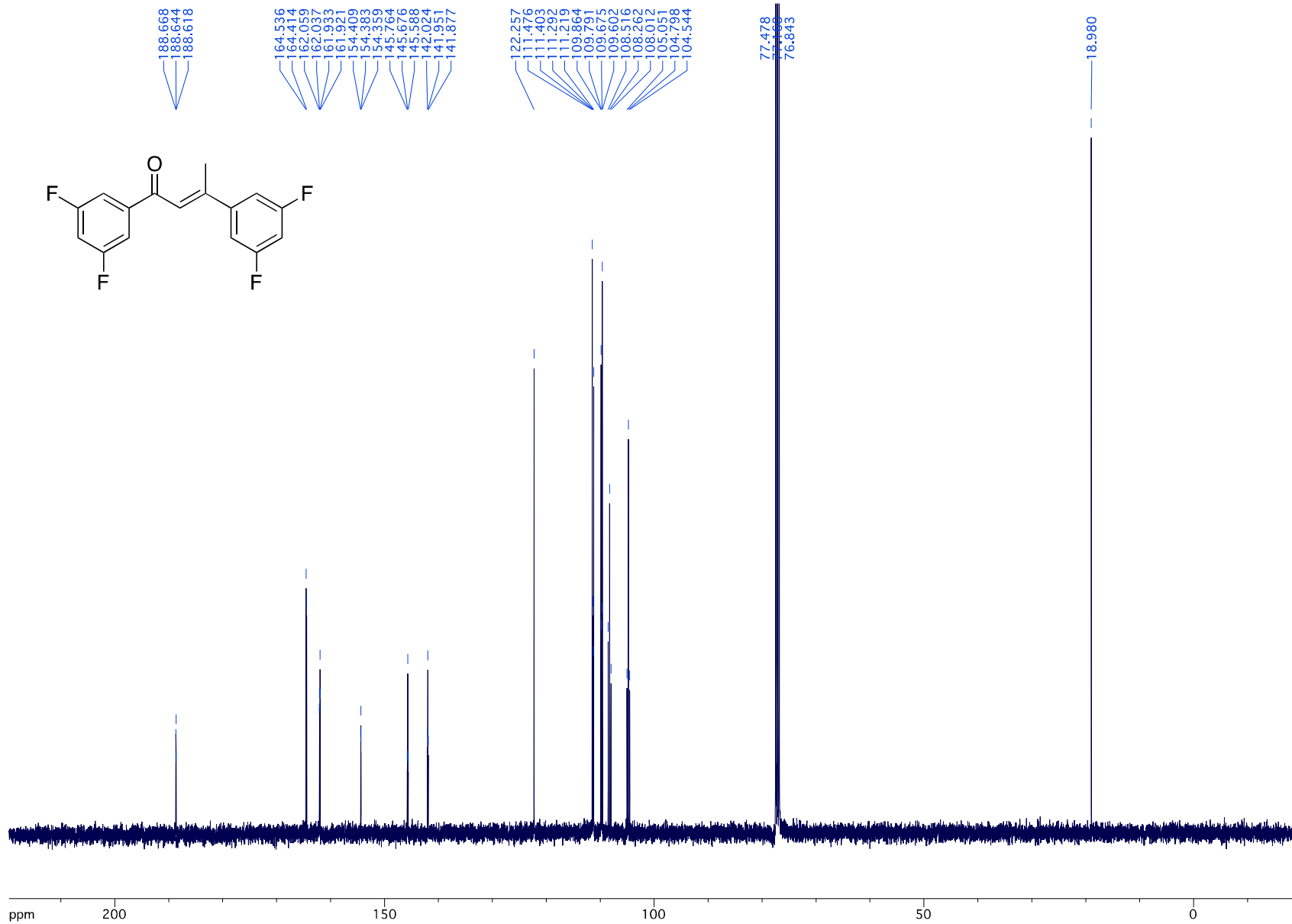
Compound S1h: 376 MHz  $^{19}\text{F}$  NMR spectrum in  $\text{CDCl}_3$



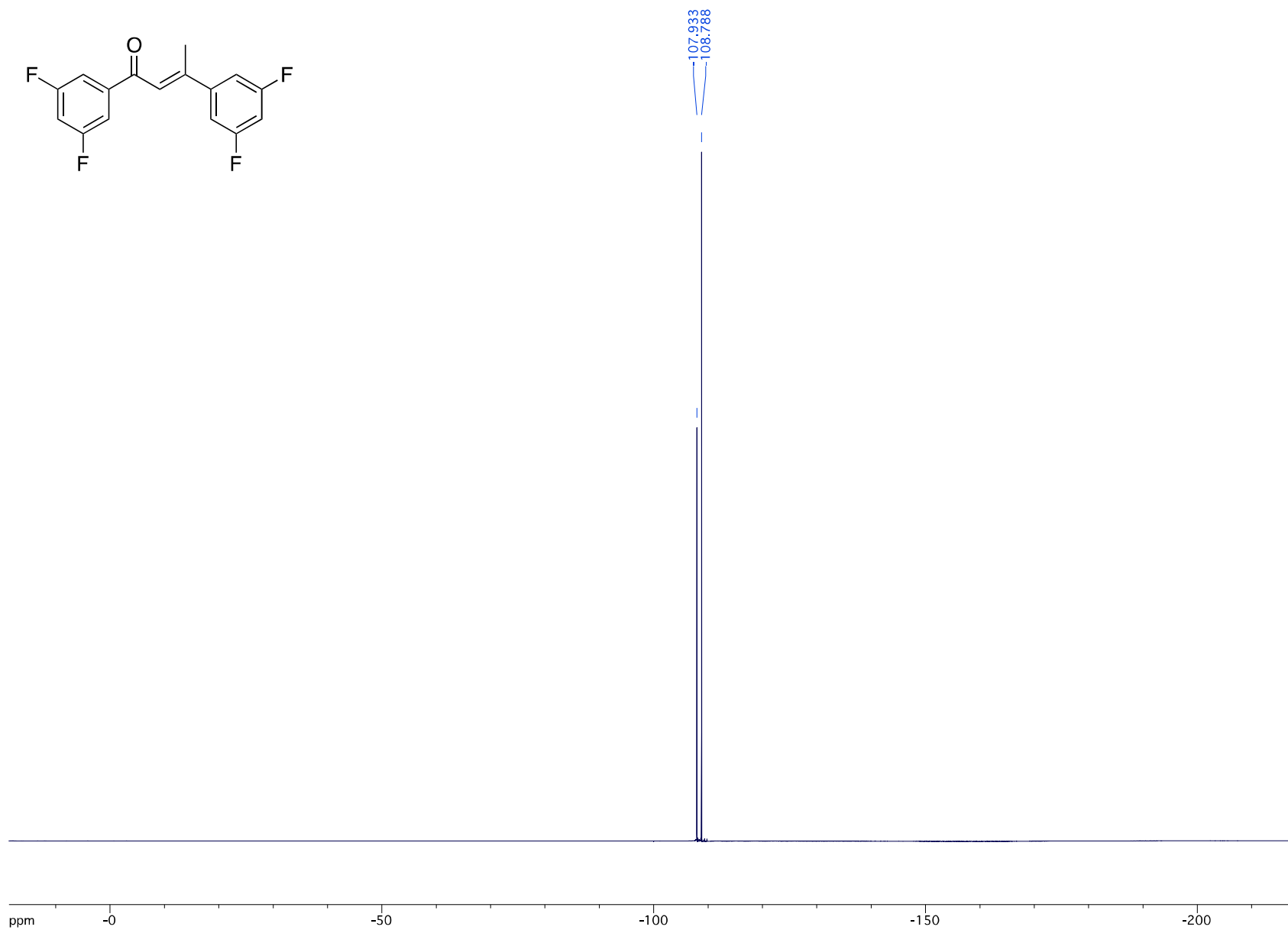
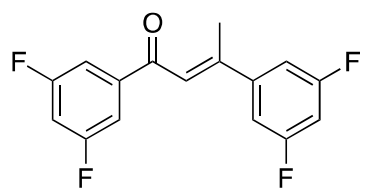
Compound S1i: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



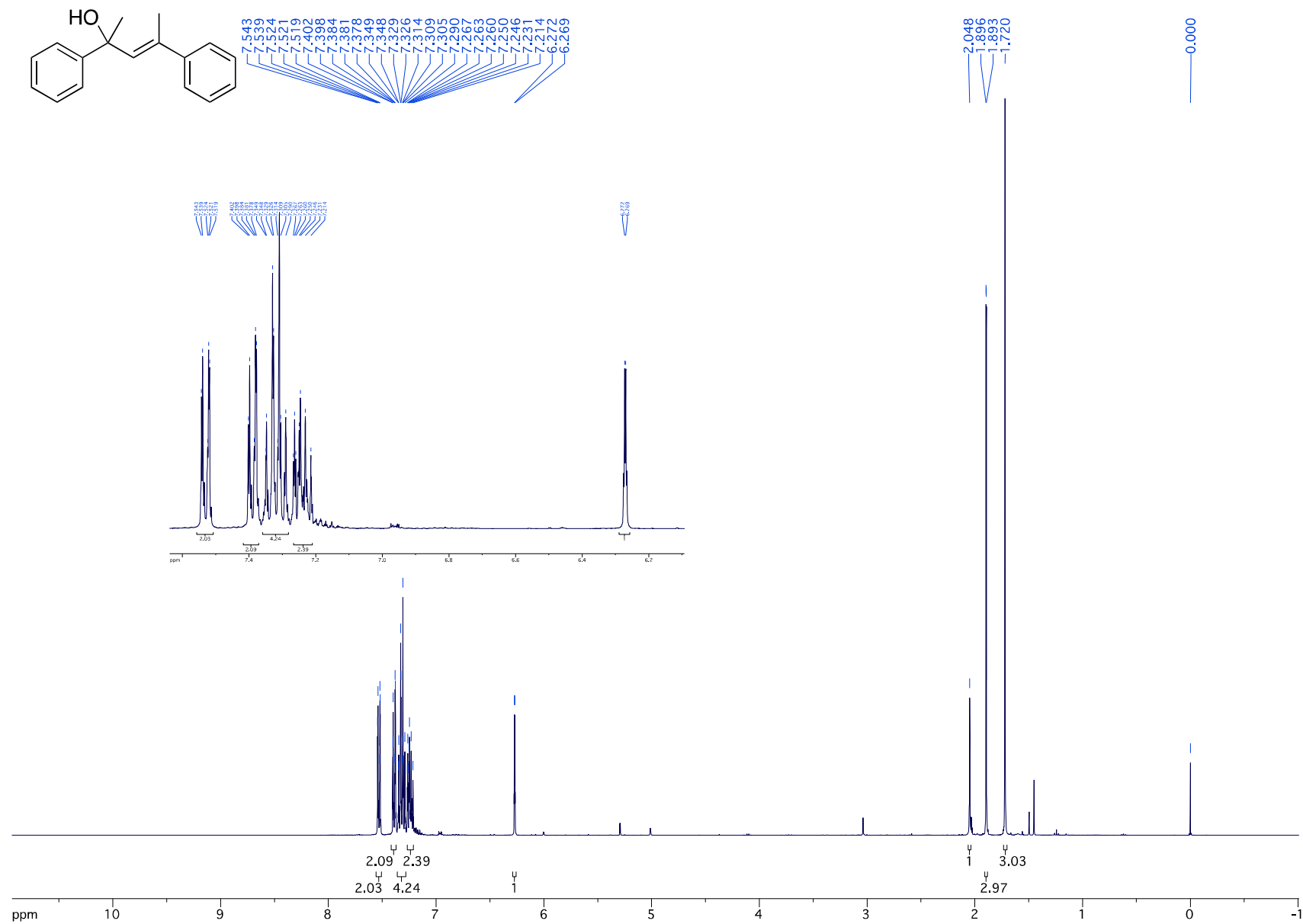
Compound S1j: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



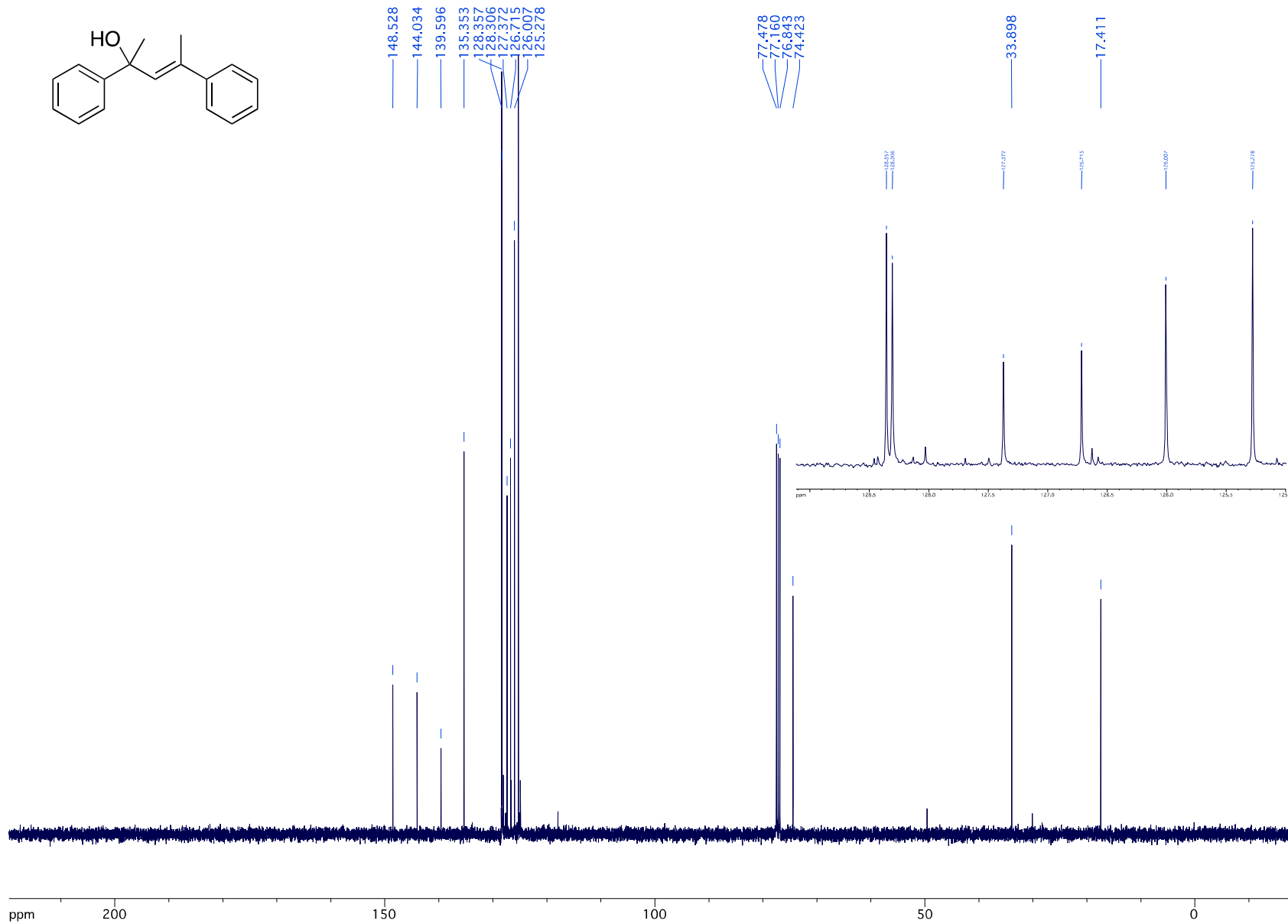
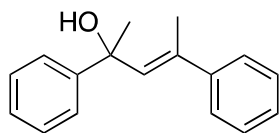
Compound S1j: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



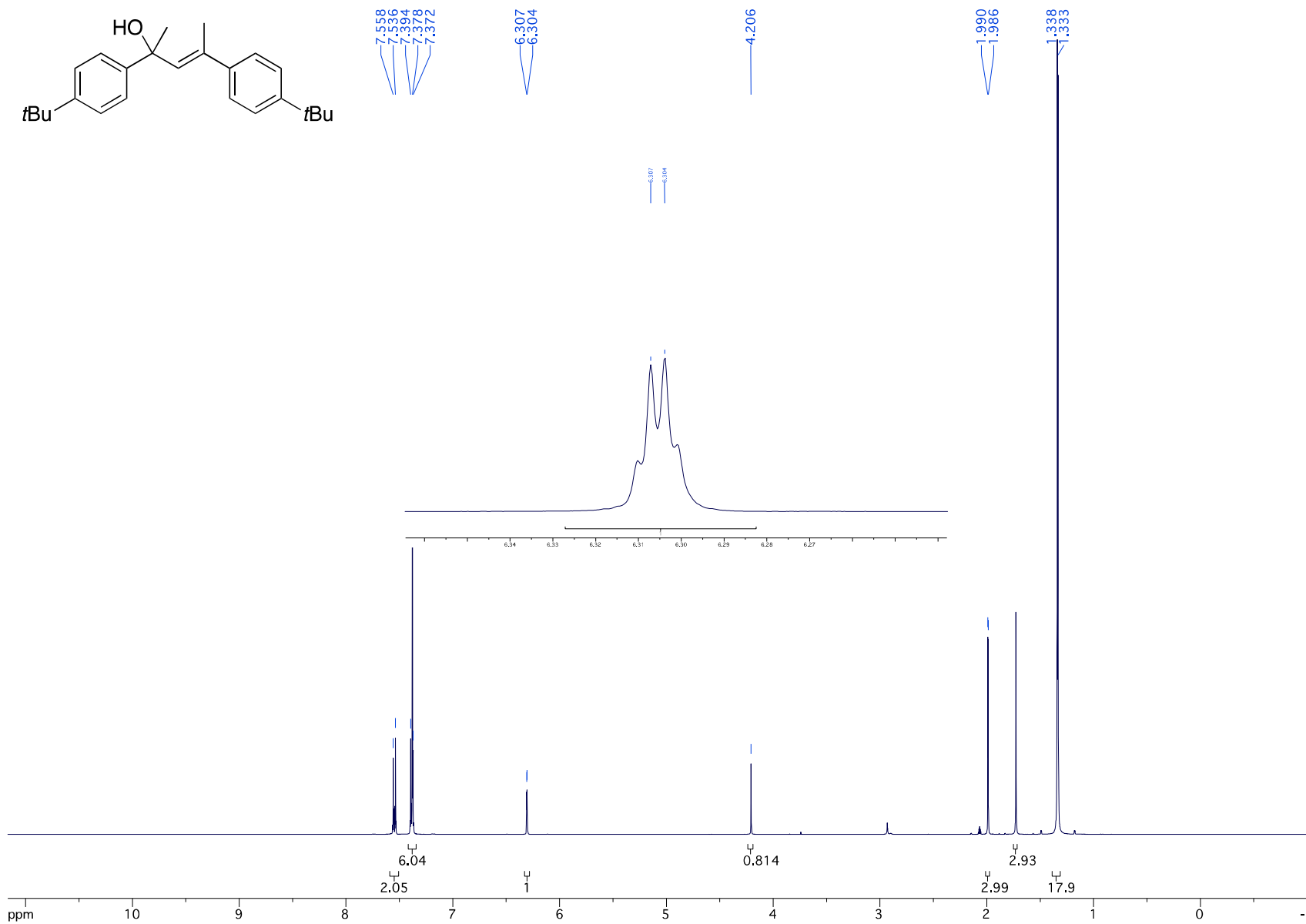
Compound S1j: 376 MHz  $^{19}\text{F}$  NMR spectrum in  $\text{CDCl}_3$



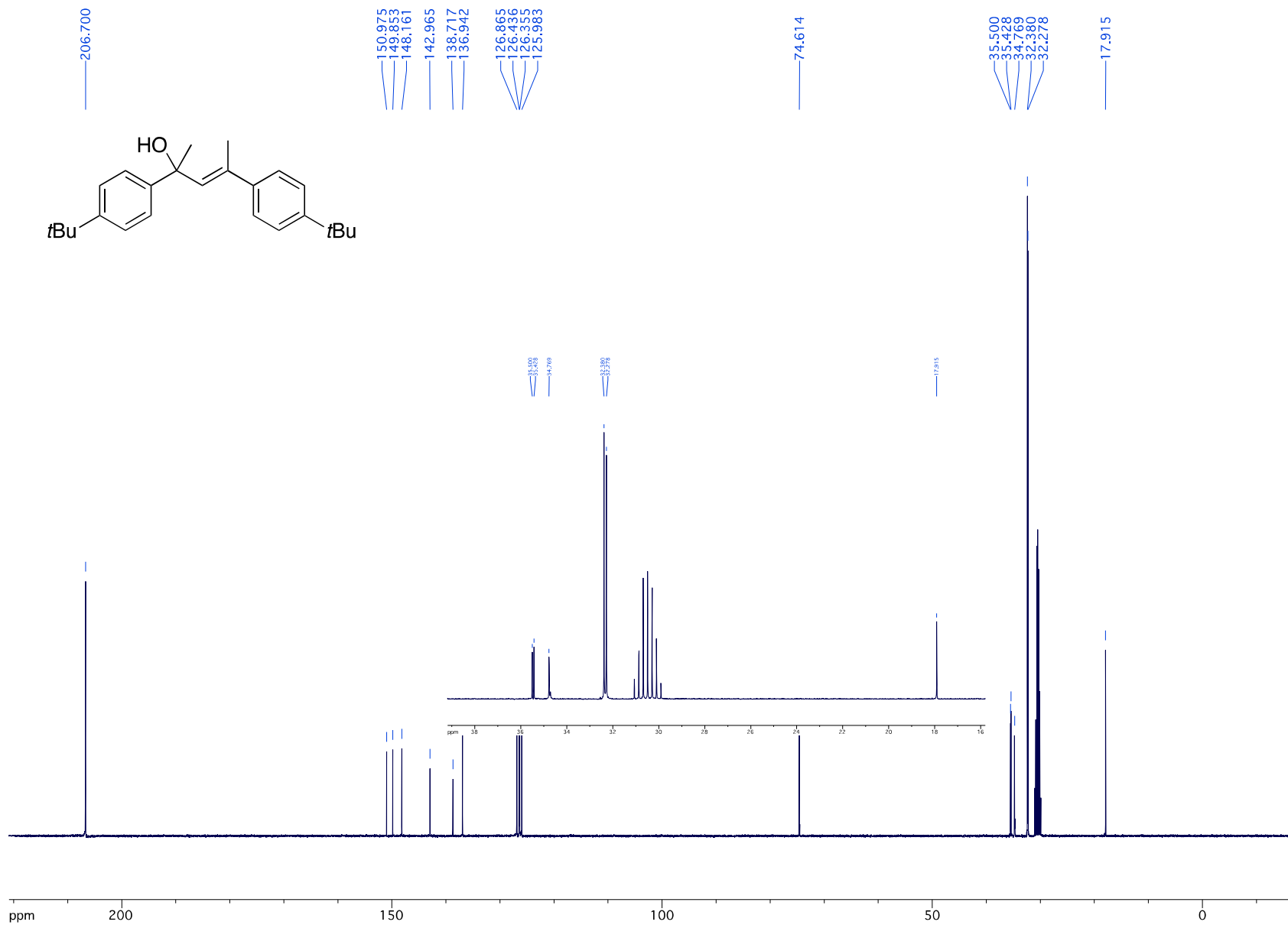
Compound S2a: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



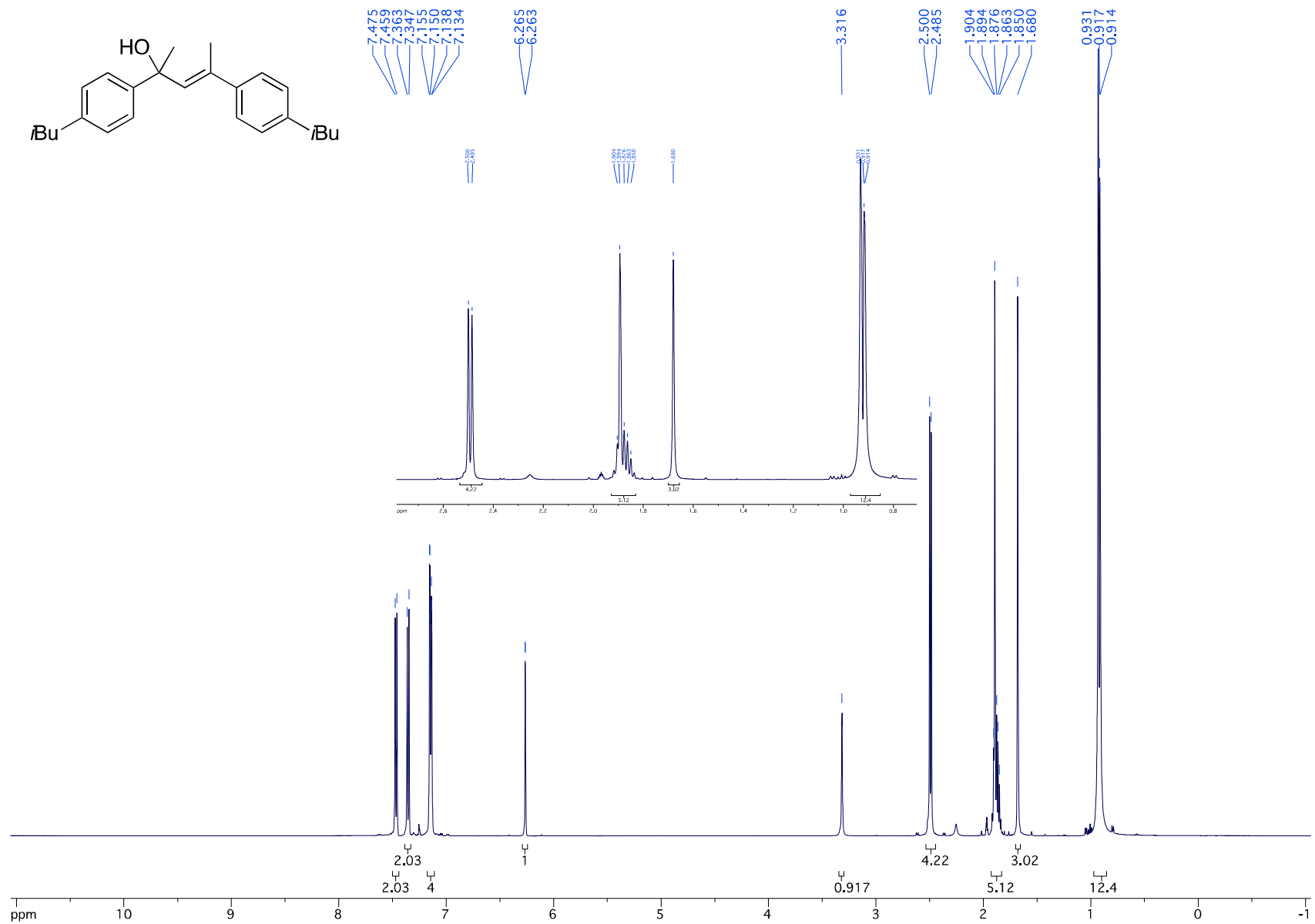
Compound S2a: 100 MHz  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$



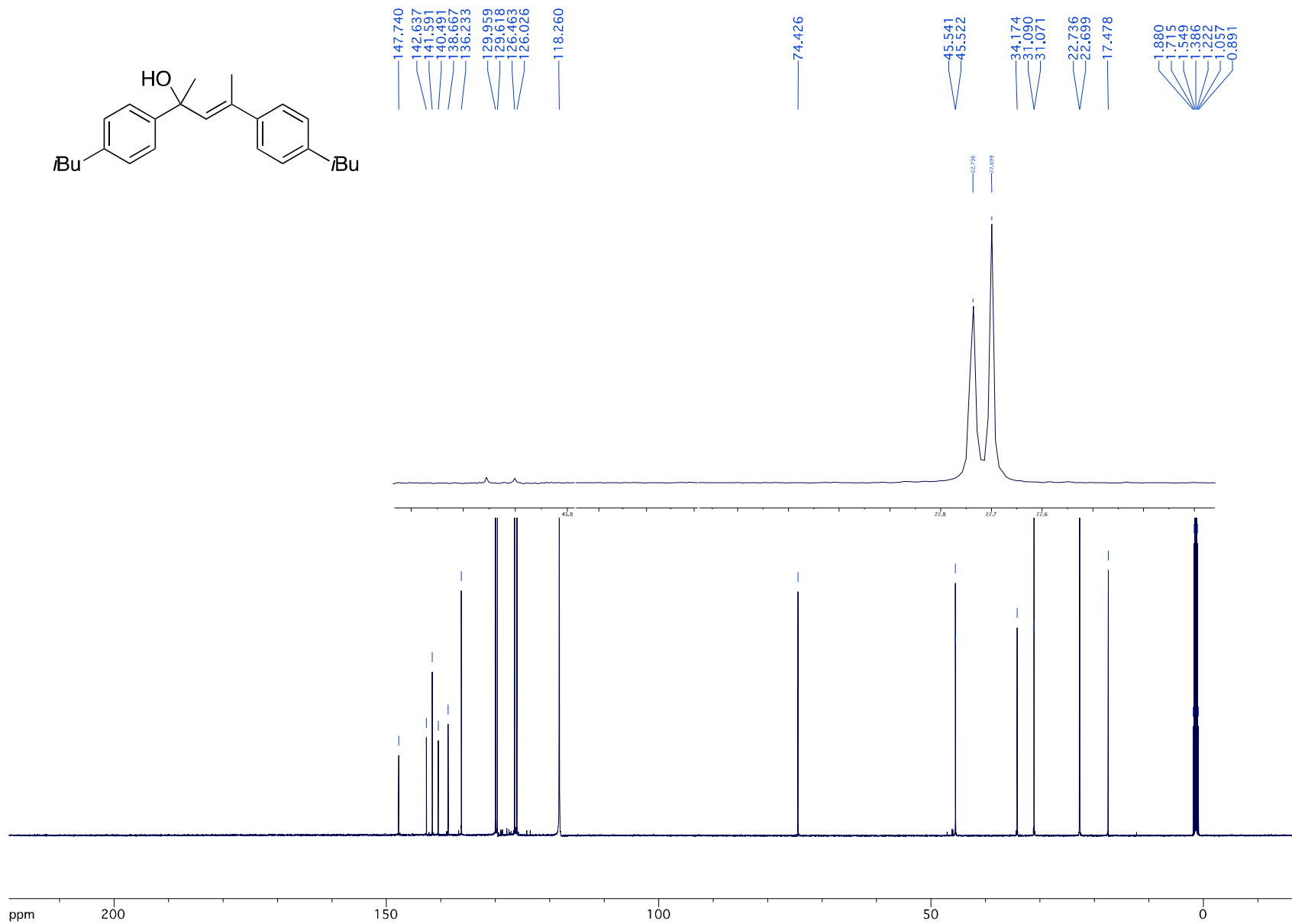
Compound S2b: 400 MHz <sup>1</sup>H NMR spectrum in acetone-d<sub>6</sub>



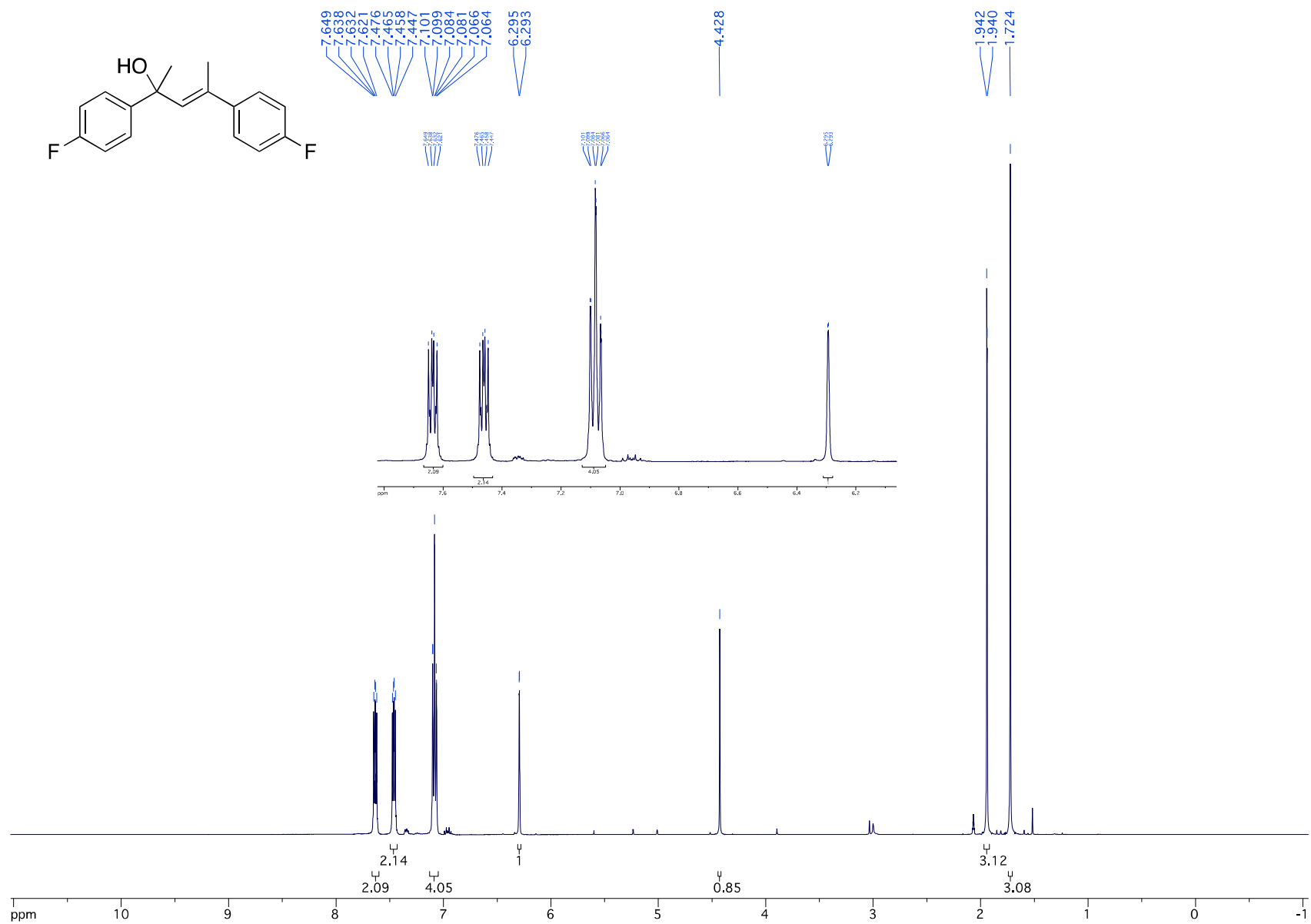
Compound S2b: 100 MHz <sup>13</sup>C NMR spectrum in *acetone-d*<sub>6</sub>



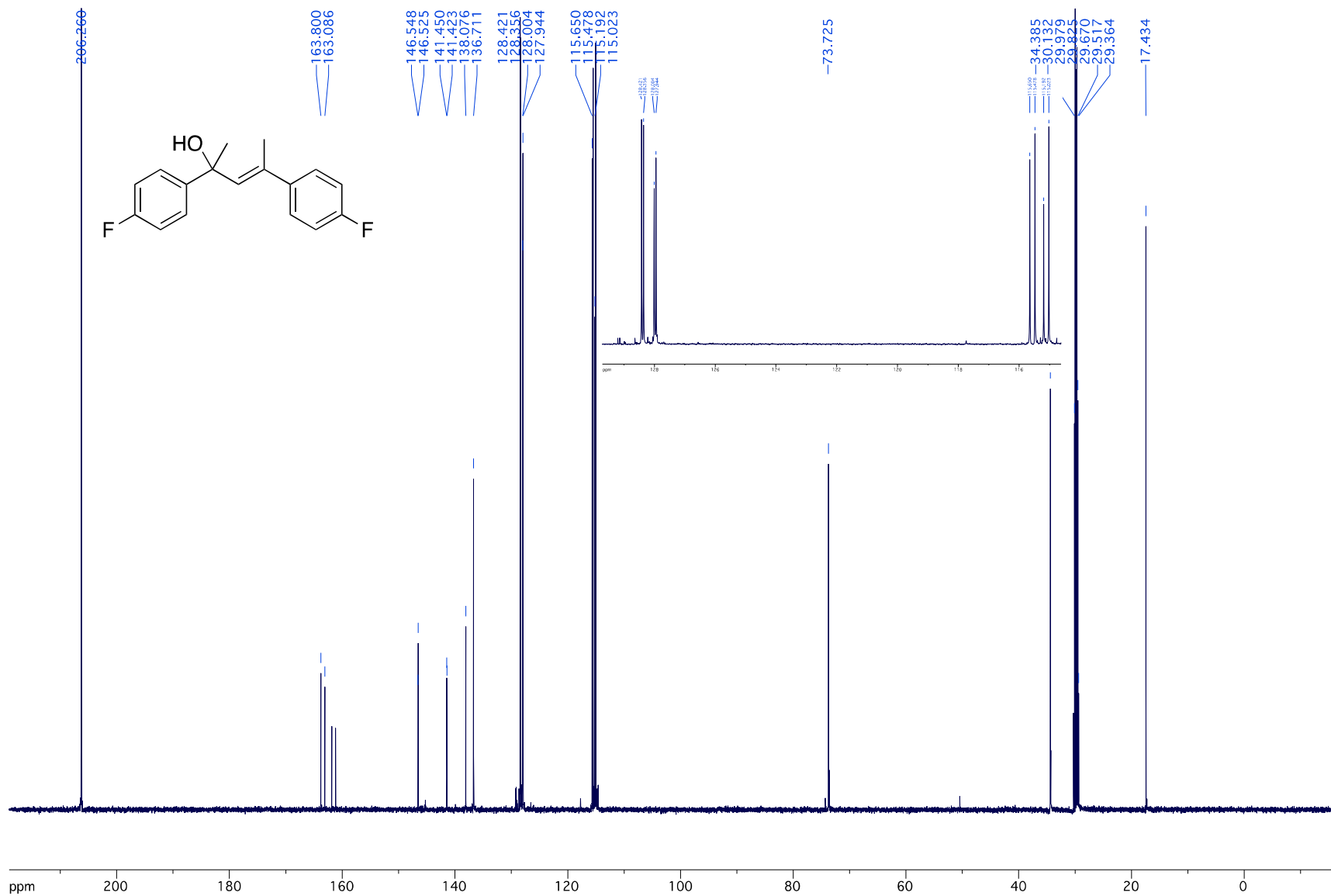
Compound S2c: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CD}_3\text{CN}$



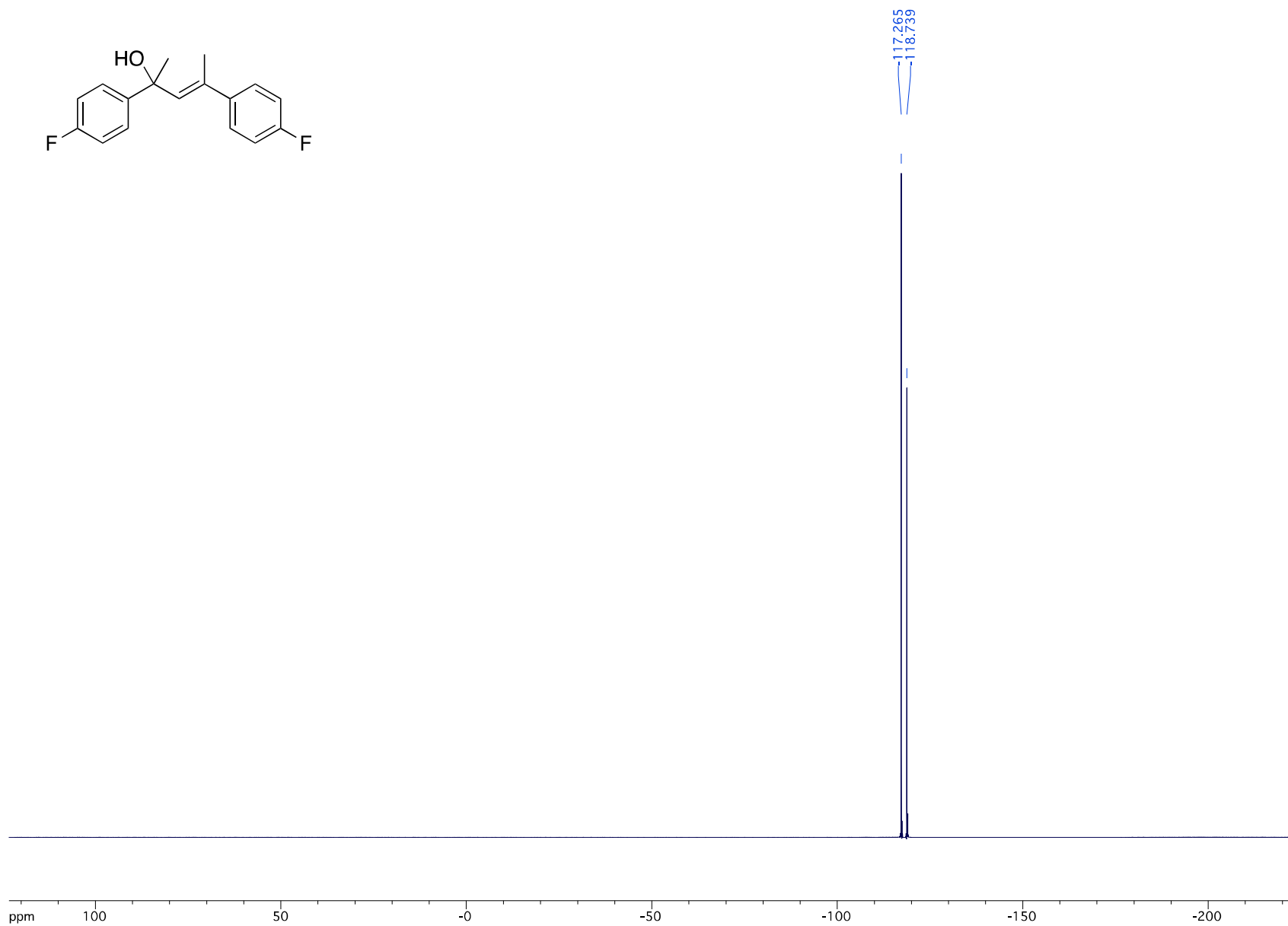
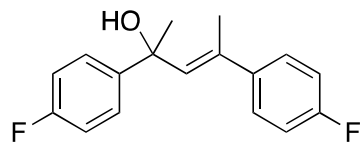
Compound S2c: 100 MHz <sup>13</sup>C NMR spectrum in CD<sub>3</sub>CN



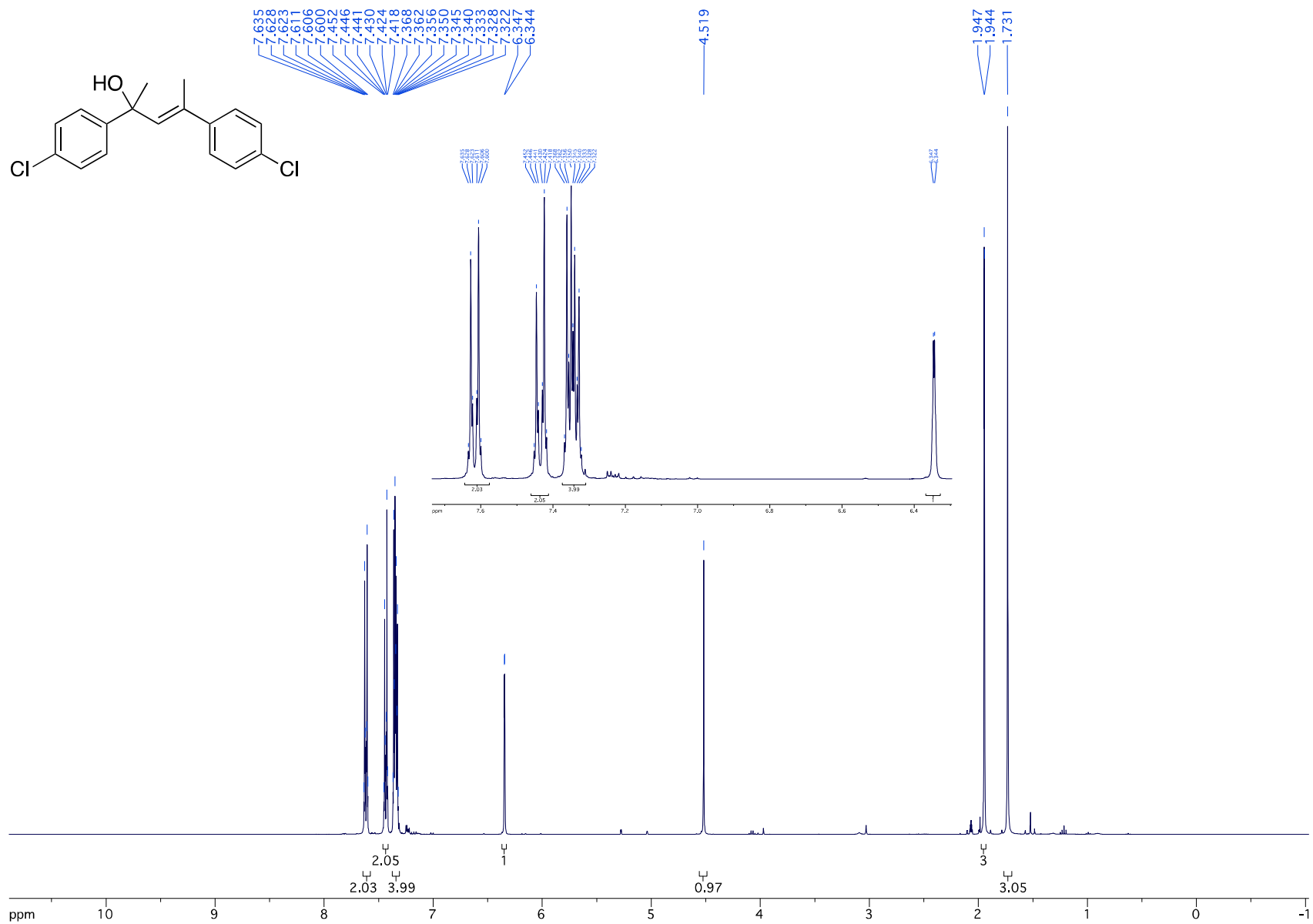
Compound S2d: 400 MHz <sup>1</sup>H NMR spectrum in acetone-*d*<sub>6</sub>



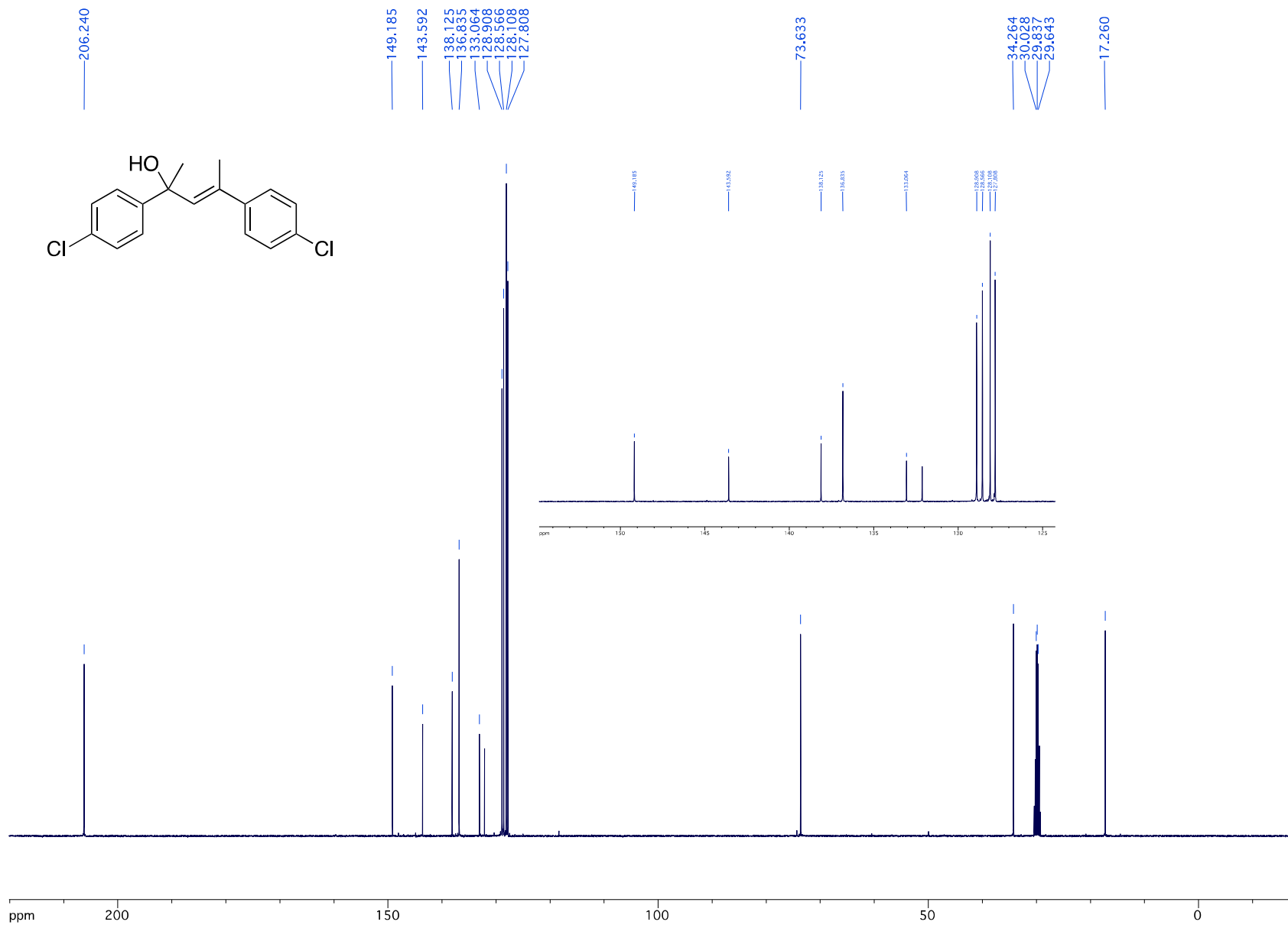
Compound S2d: 100 MHz <sup>13</sup>C NMR spectrum in acetone-*d*<sub>6</sub>



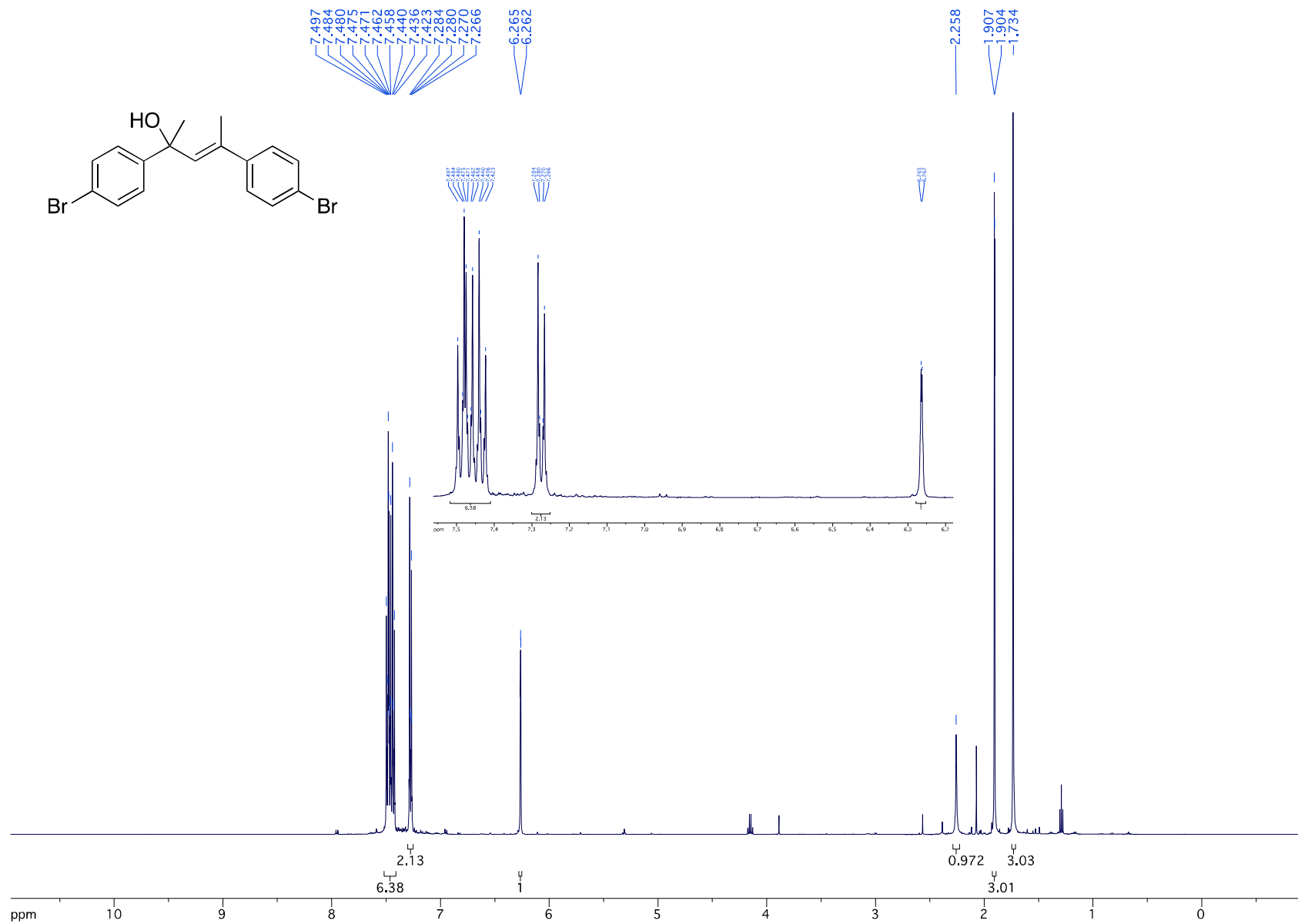
Compound S2d: 376 MHz <sup>19</sup>F NMR spectrum in acetone-*d*<sub>6</sub>



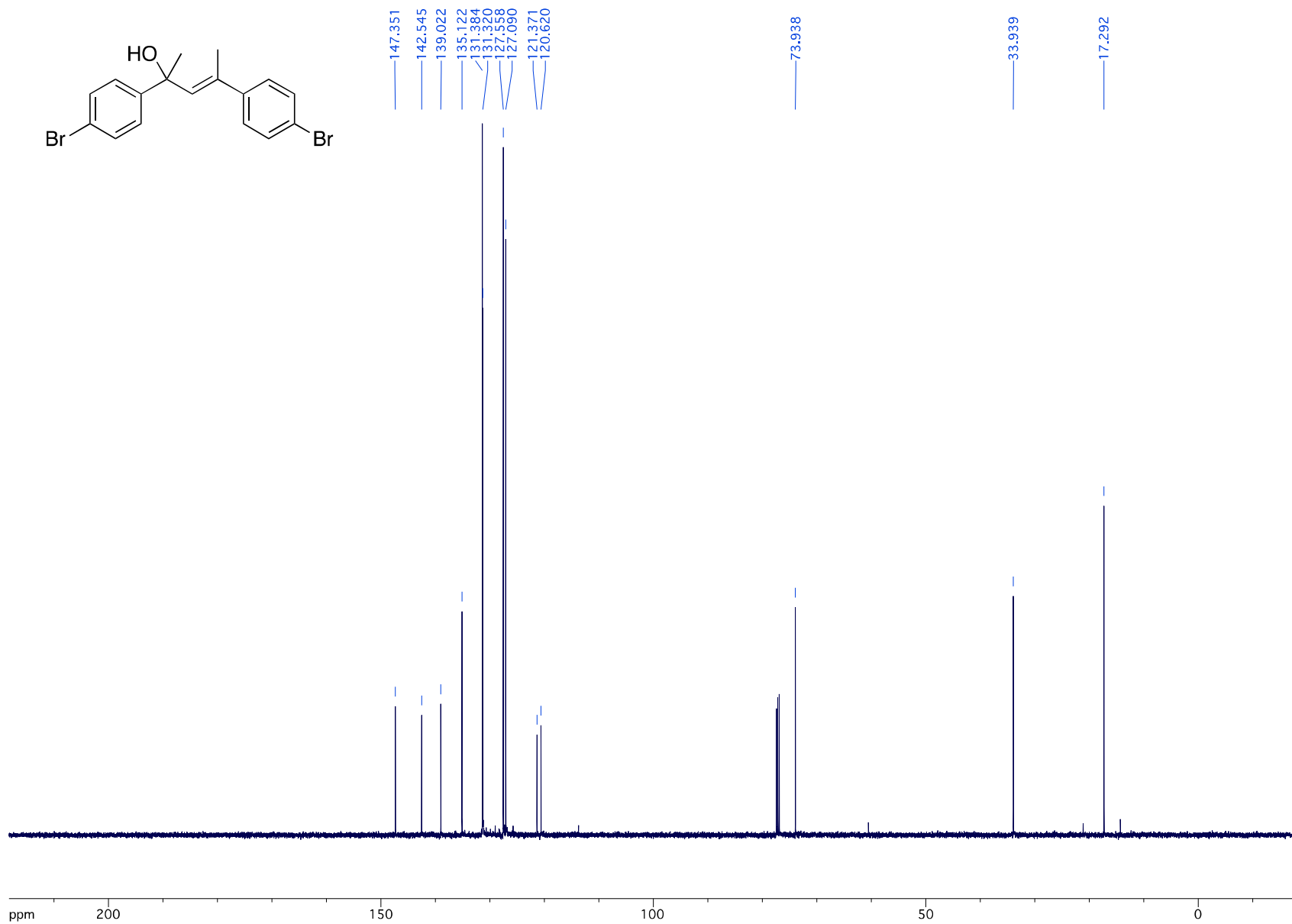
Compound S2e: 400 MHz <sup>1</sup>H NMR spectrum in acetone-*d*<sub>6</sub>



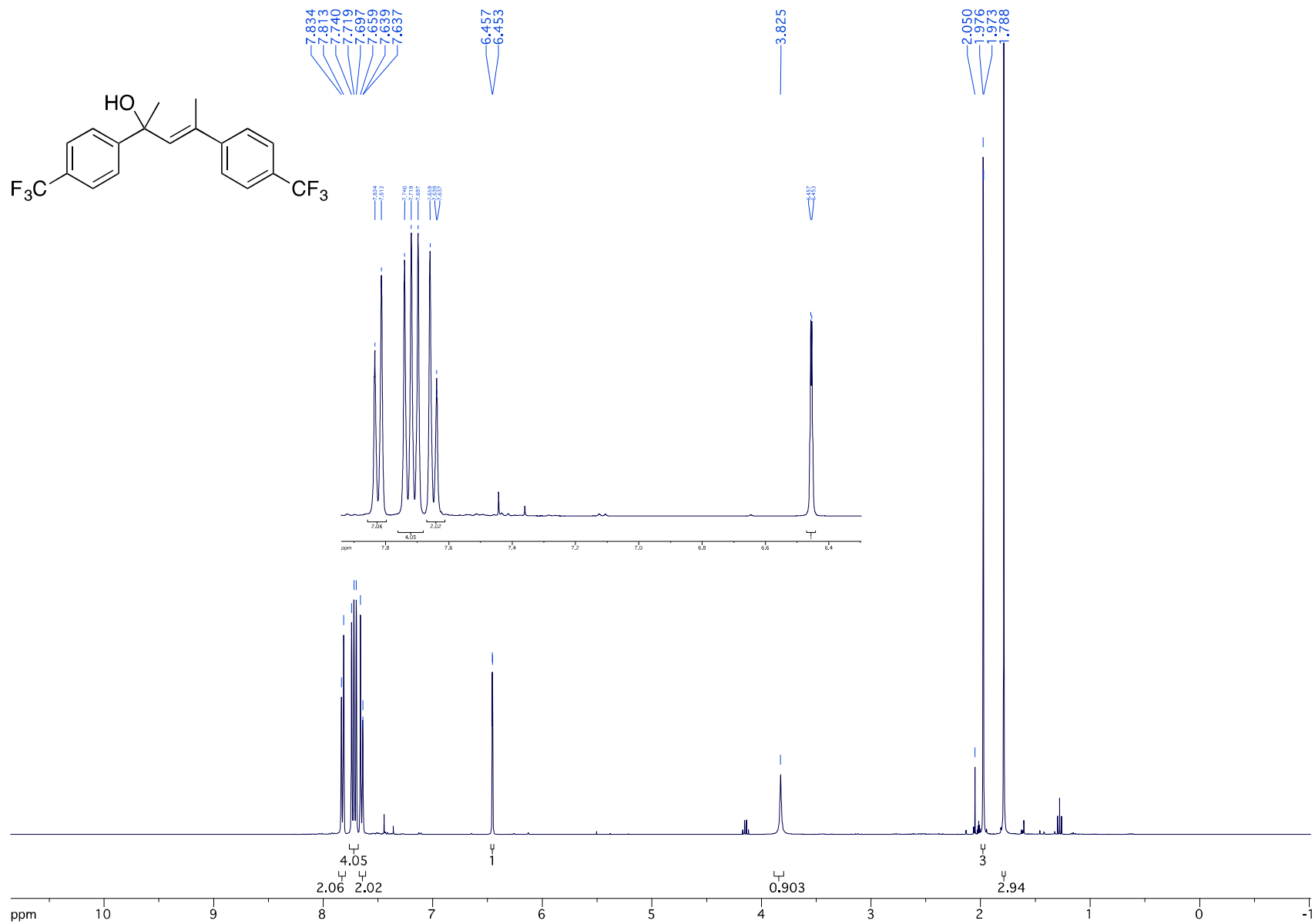
Compound S2e: 100 MHz <sup>13</sup>C NMR spectrum in acetone-*d*<sub>6</sub>



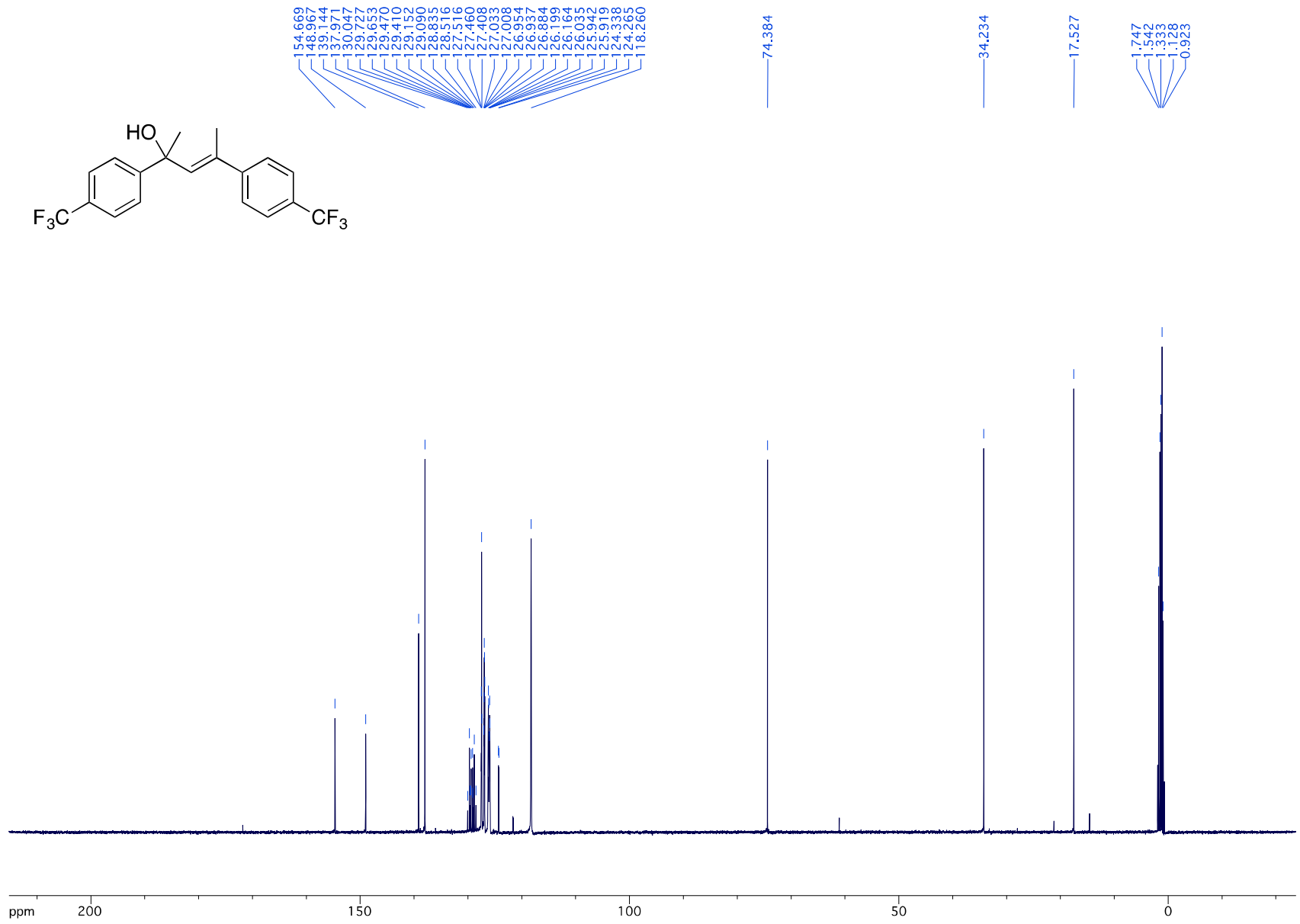
Compound S2f: 500 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



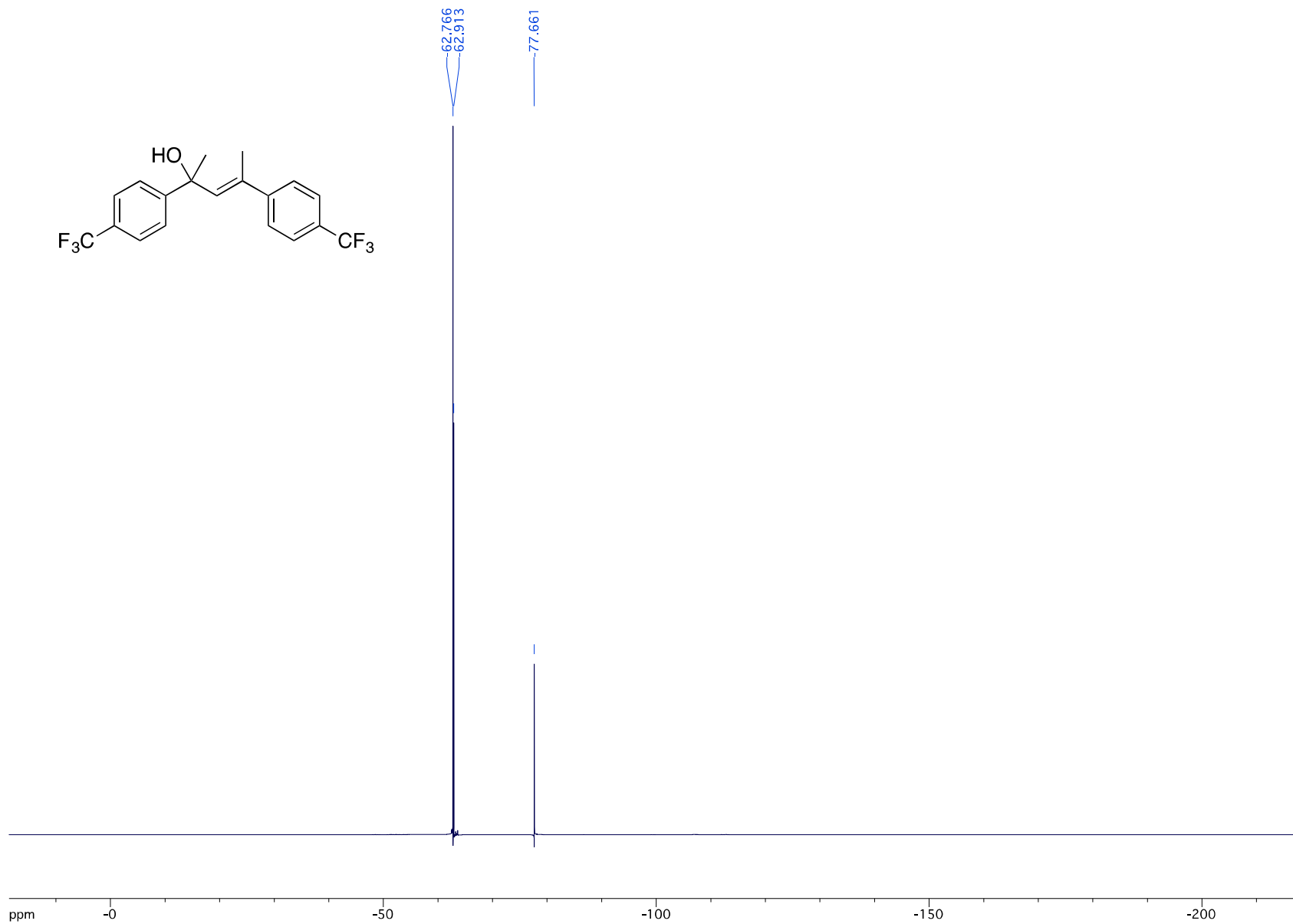
Compound S2f: 125 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



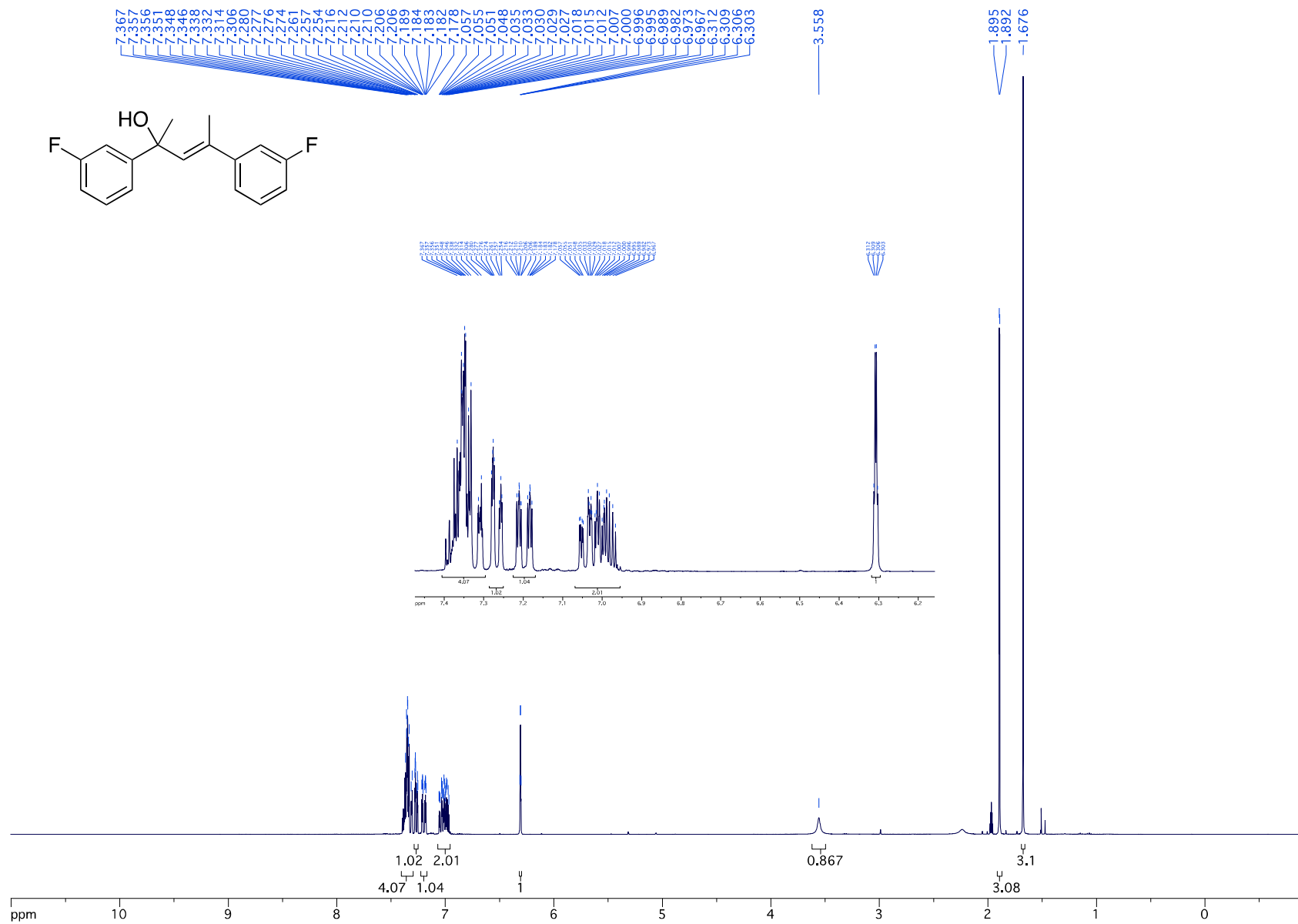
Compound S2g: 400 MHz <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN



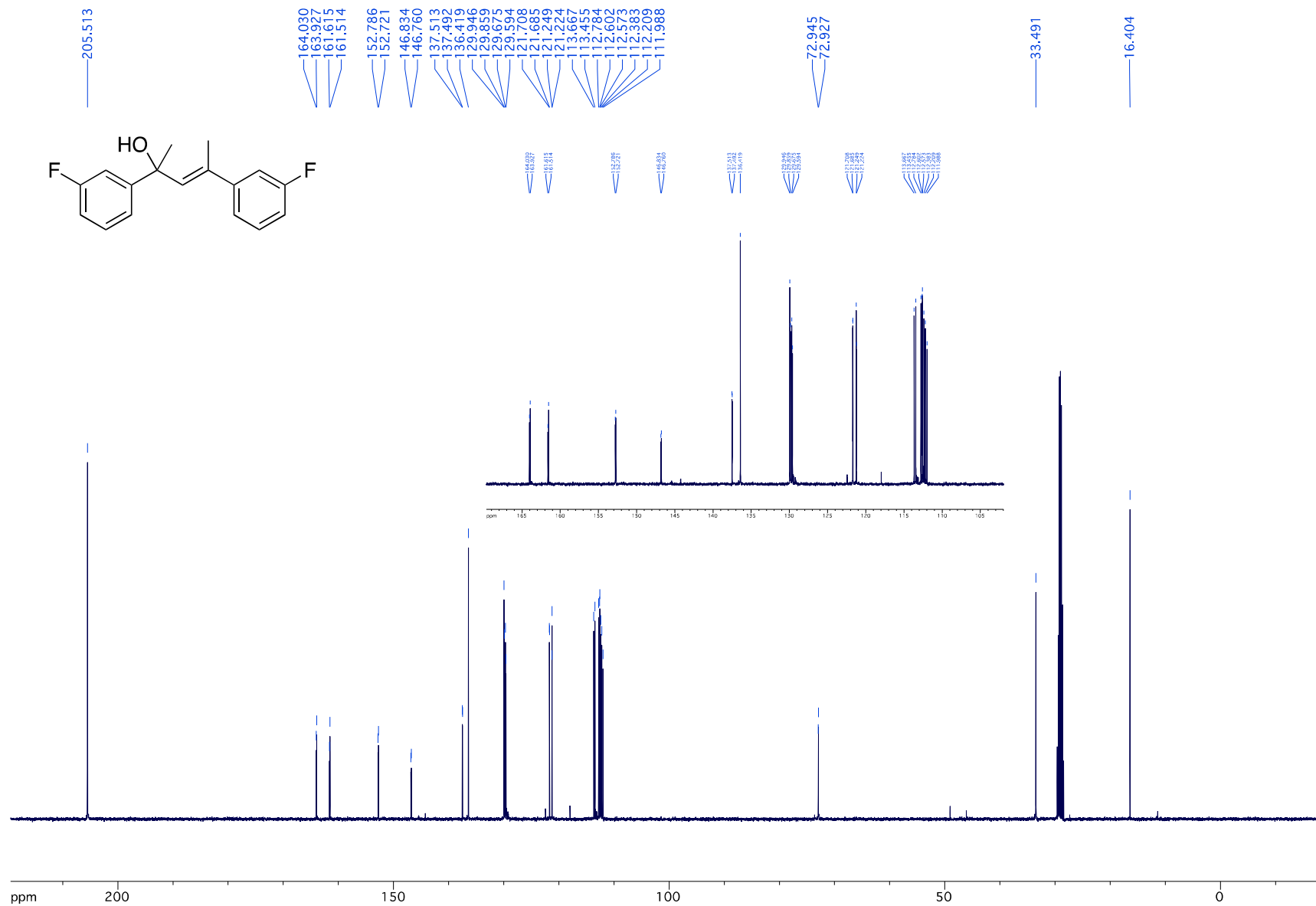
Compound S2g: 100 MHz <sup>13</sup>C NMR spectrum in CD<sub>3</sub>CN



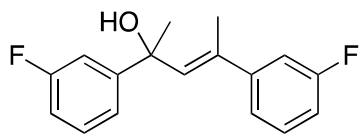
Compound S2g: 376 MHz  $^{19}\text{F}$  NMR spectrum in  $\text{CD}_3\text{CN}$  with  $\text{CF}_3\text{CH}_2\text{OH}$  standard



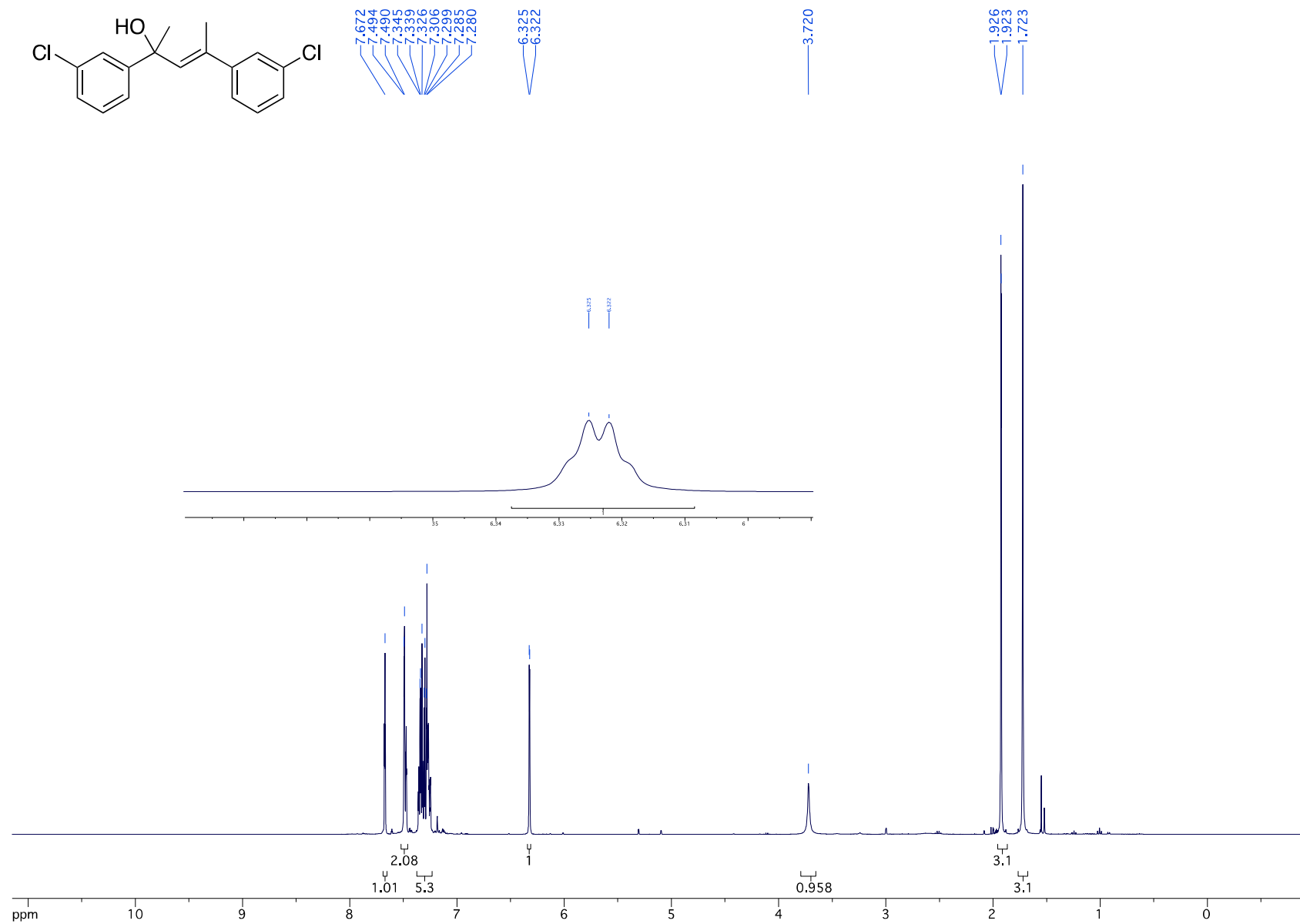
Compound S2h: 400 MHz <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN



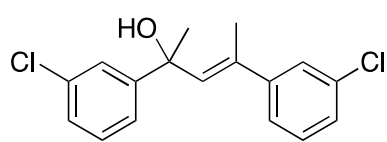
Compound S2h: 100 MHz <sup>13</sup>C NMR spectrum in CD<sub>3</sub>CN



Compound S2h: 376 MHz  $^{19}\text{F}$  NMR spectrum in  $\text{CD}_3\text{CN}$



Compound S2i: 400 MHz <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN

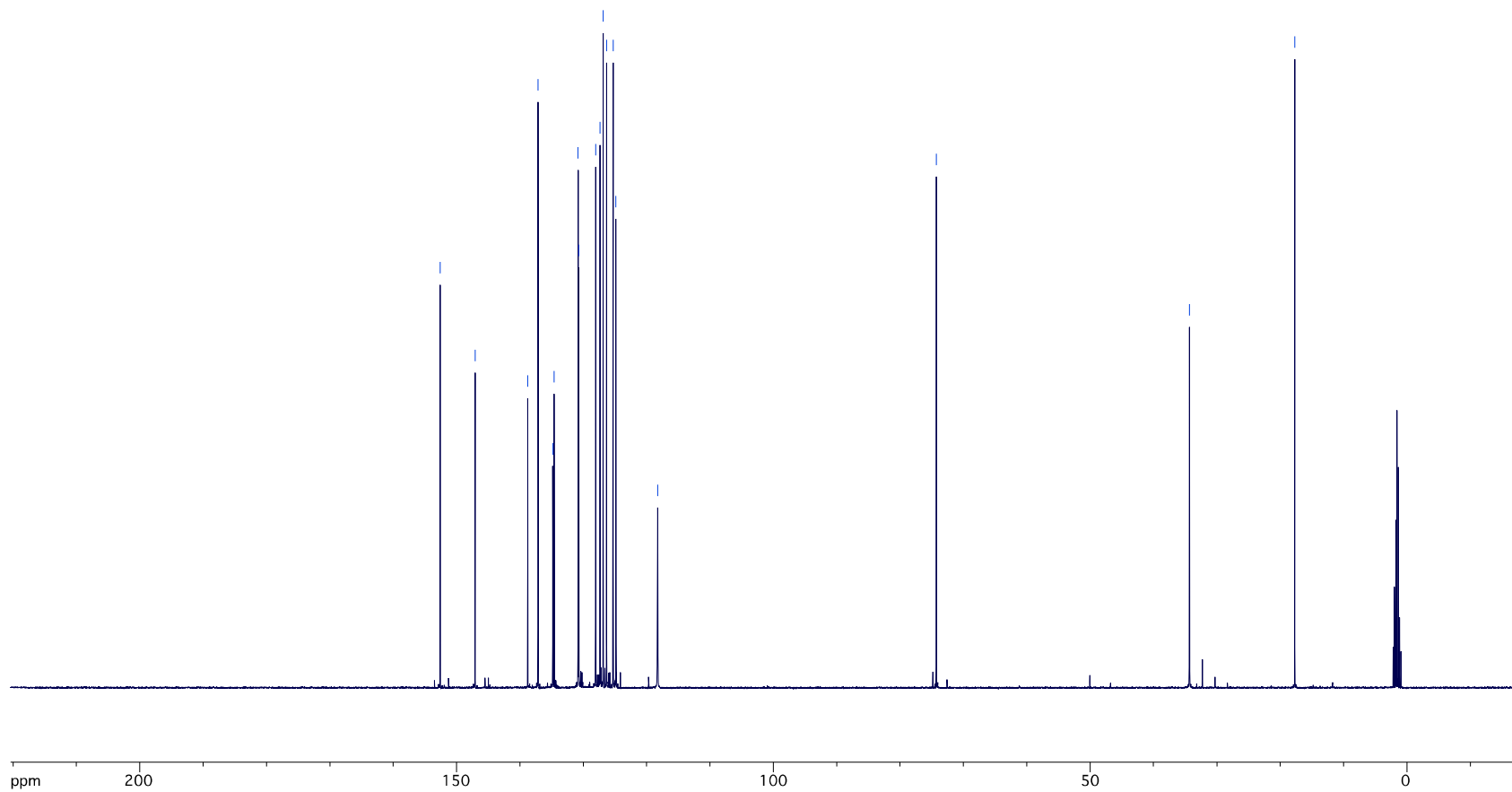


152.570  
147.066  
138.770  
137.121  
134.800  
134.583  
130.824  
130.709  
128.052  
127.352  
126.878  
125.297  
124.846  
118.260

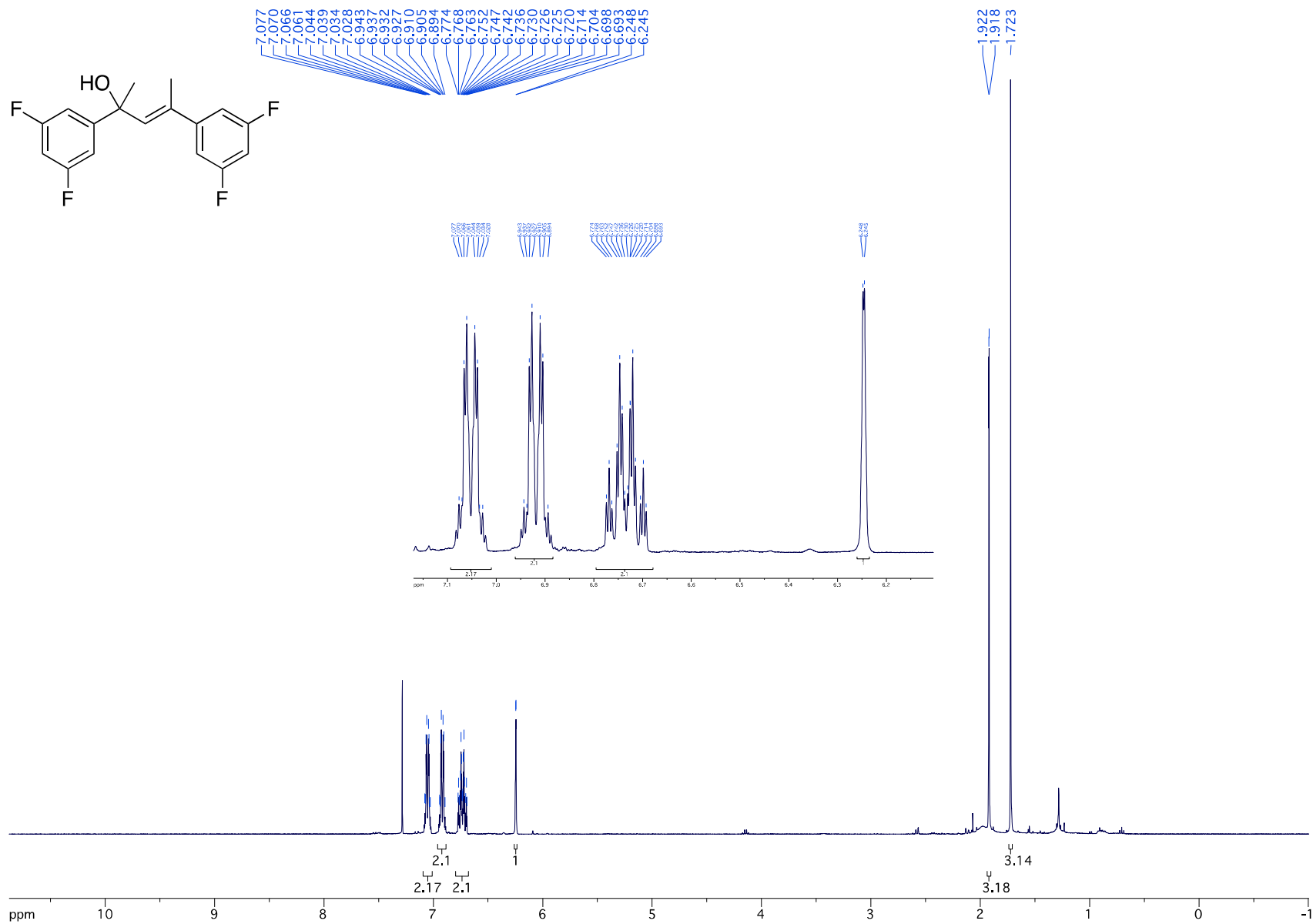
74.278

34.314

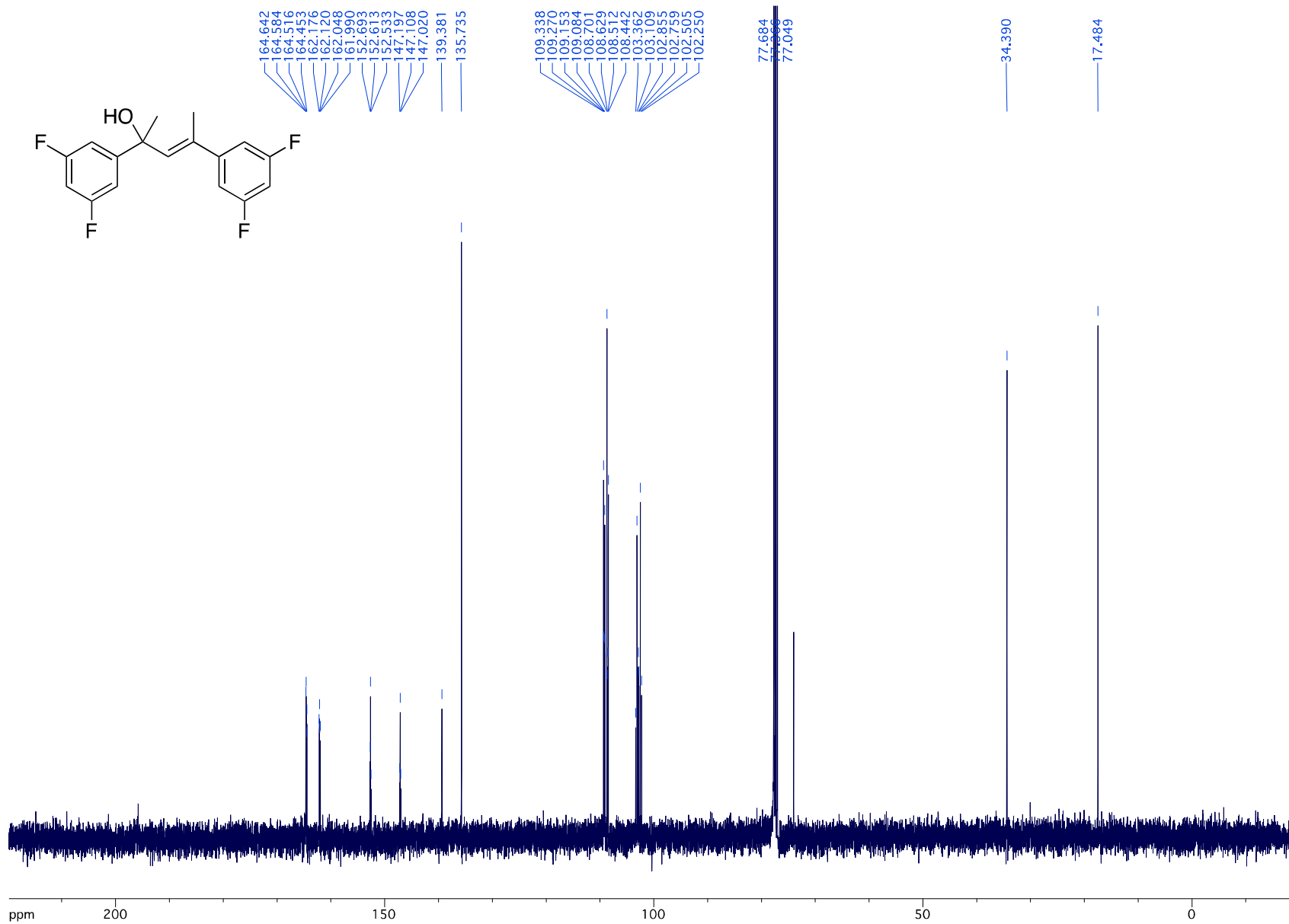
17.696



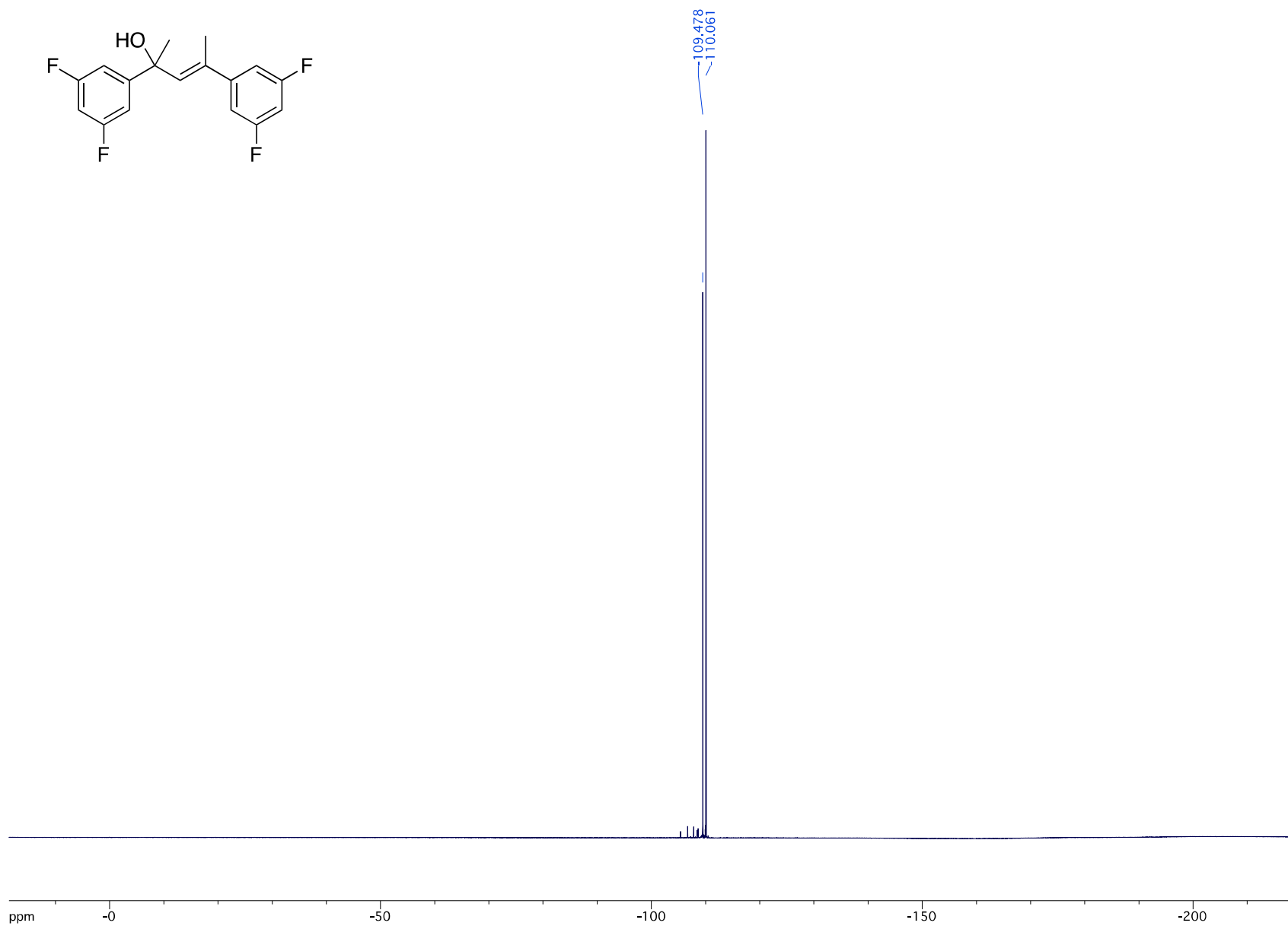
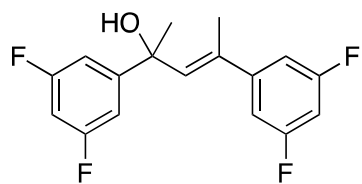
Compound S2i: 100 MHz  $^{13}\text{C}$  NMR spectrum in  $\text{CD}_3\text{CN}$



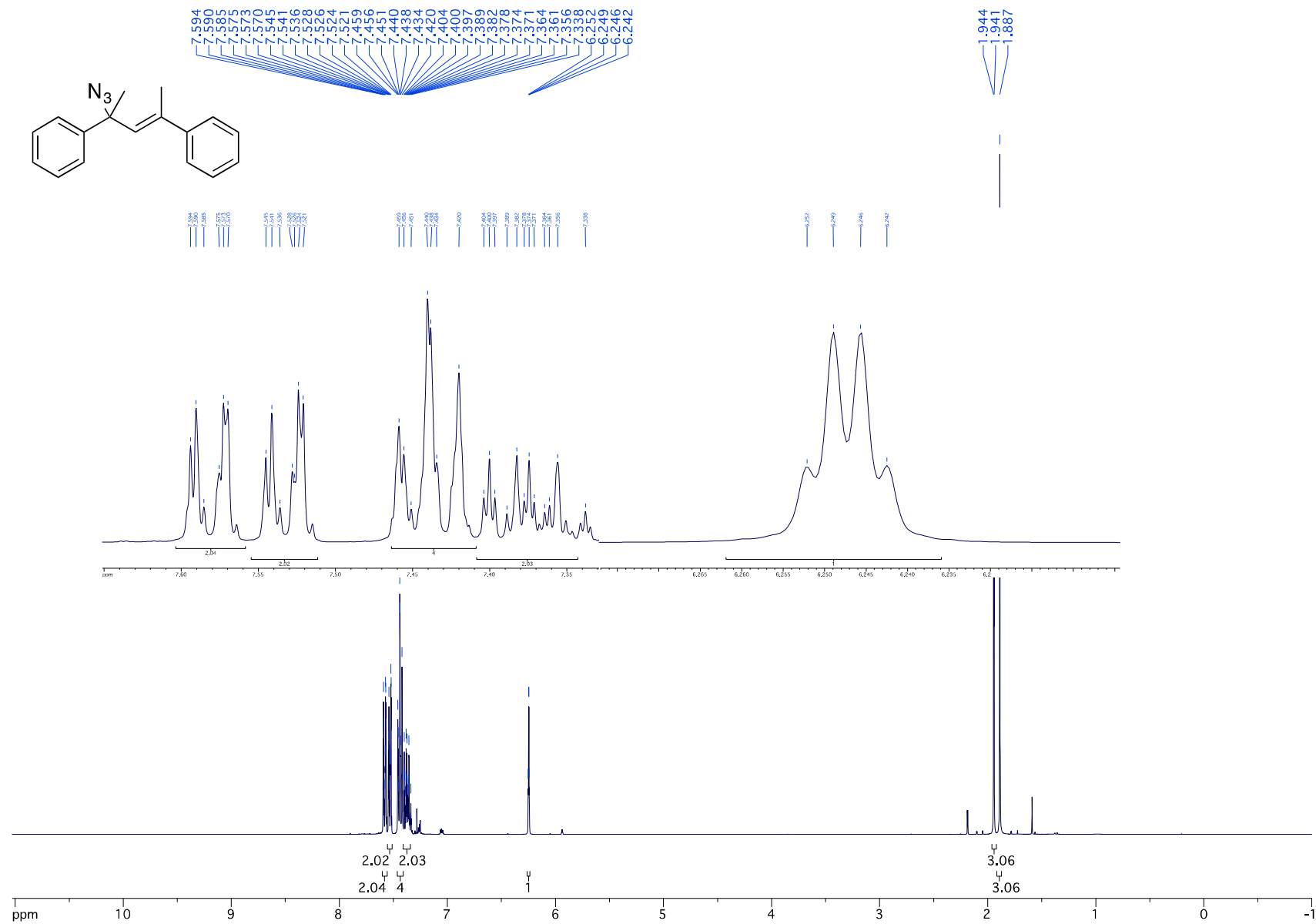
Compound S2j: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



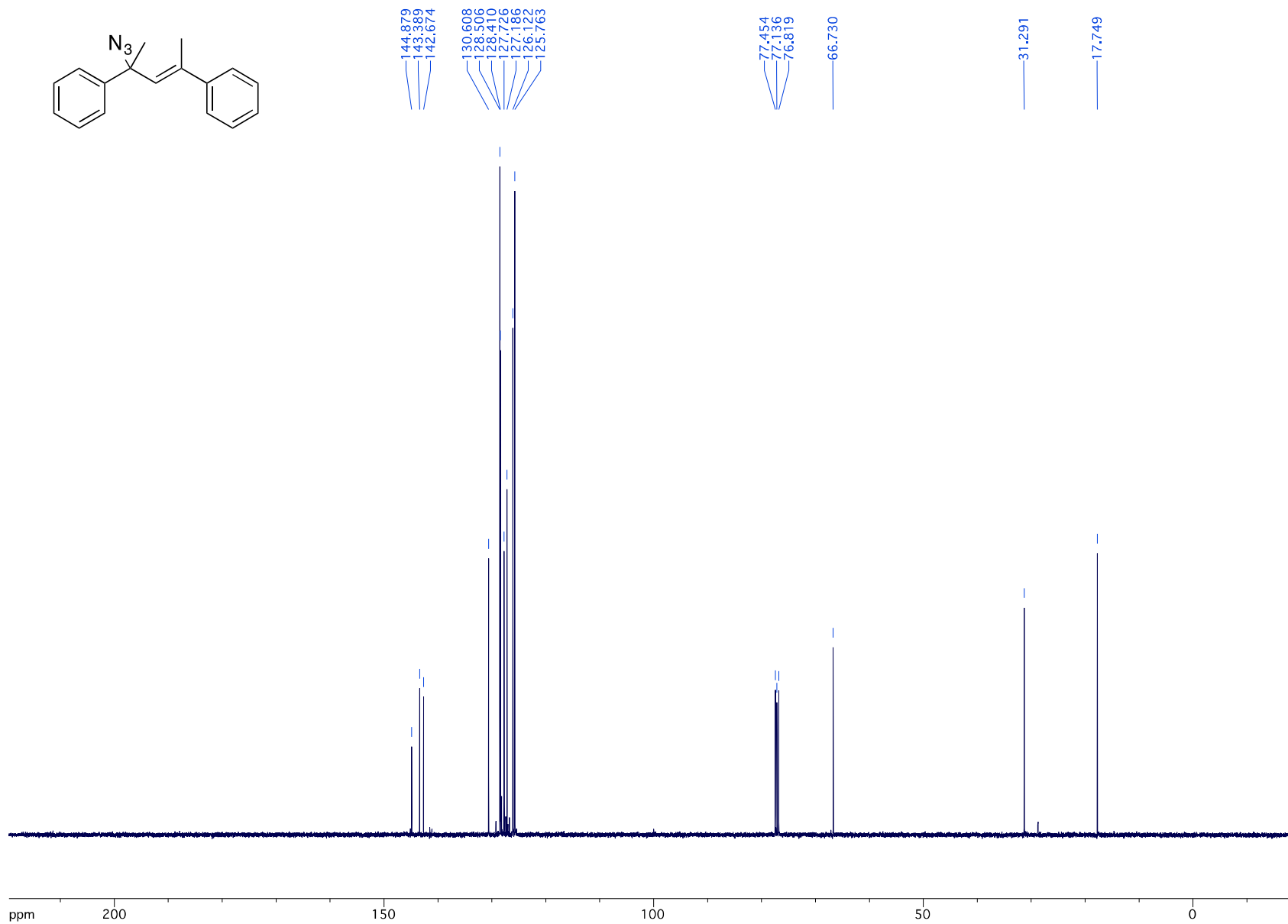
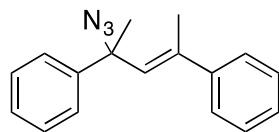
Compound S2j: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



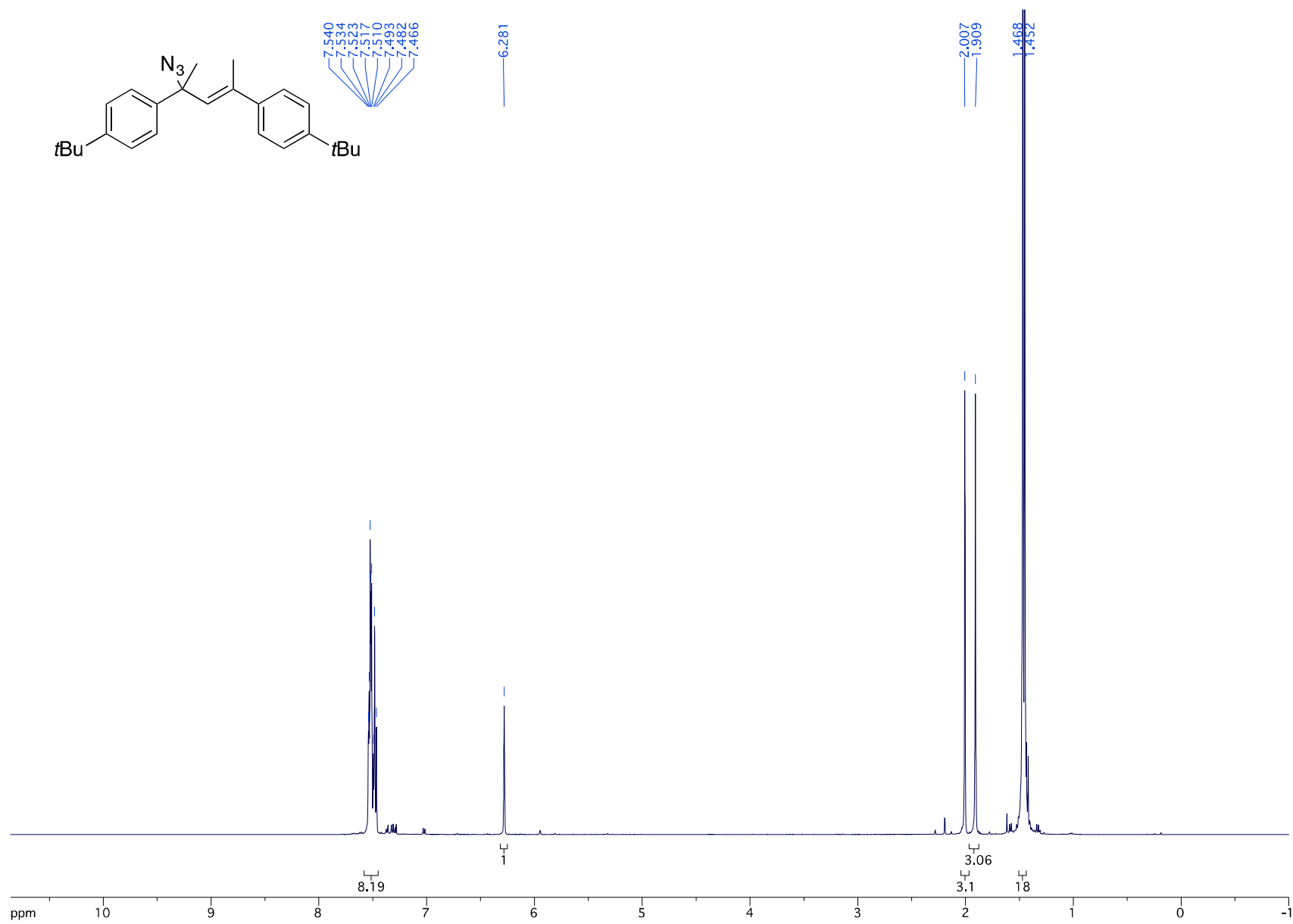
Compound S2j: 376 MHz  $^{19}\text{F}$  NMR spectrum in  $\text{CDCl}_3$



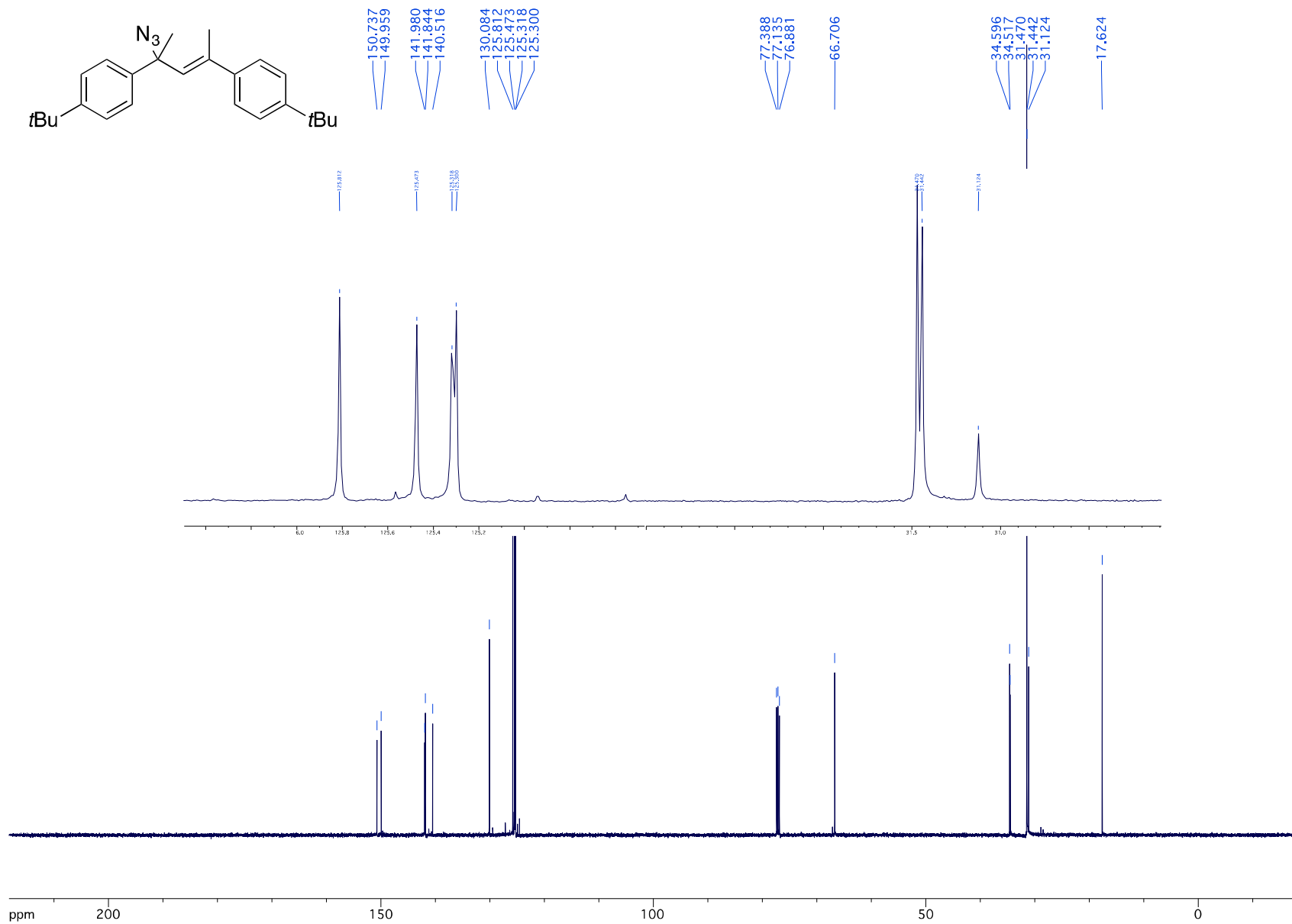
Compound 1a: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



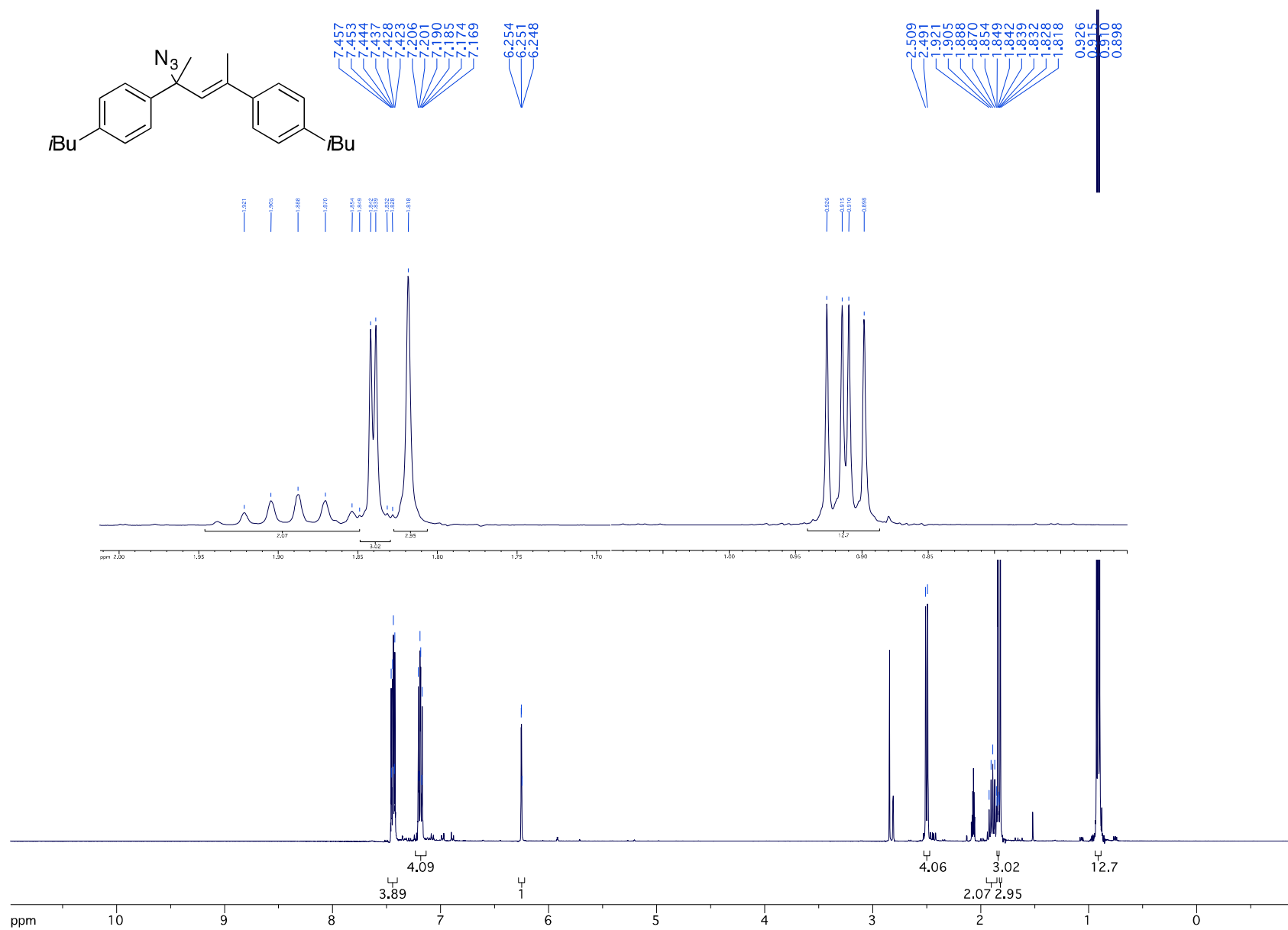
Compound 1a: 100 MHz  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$



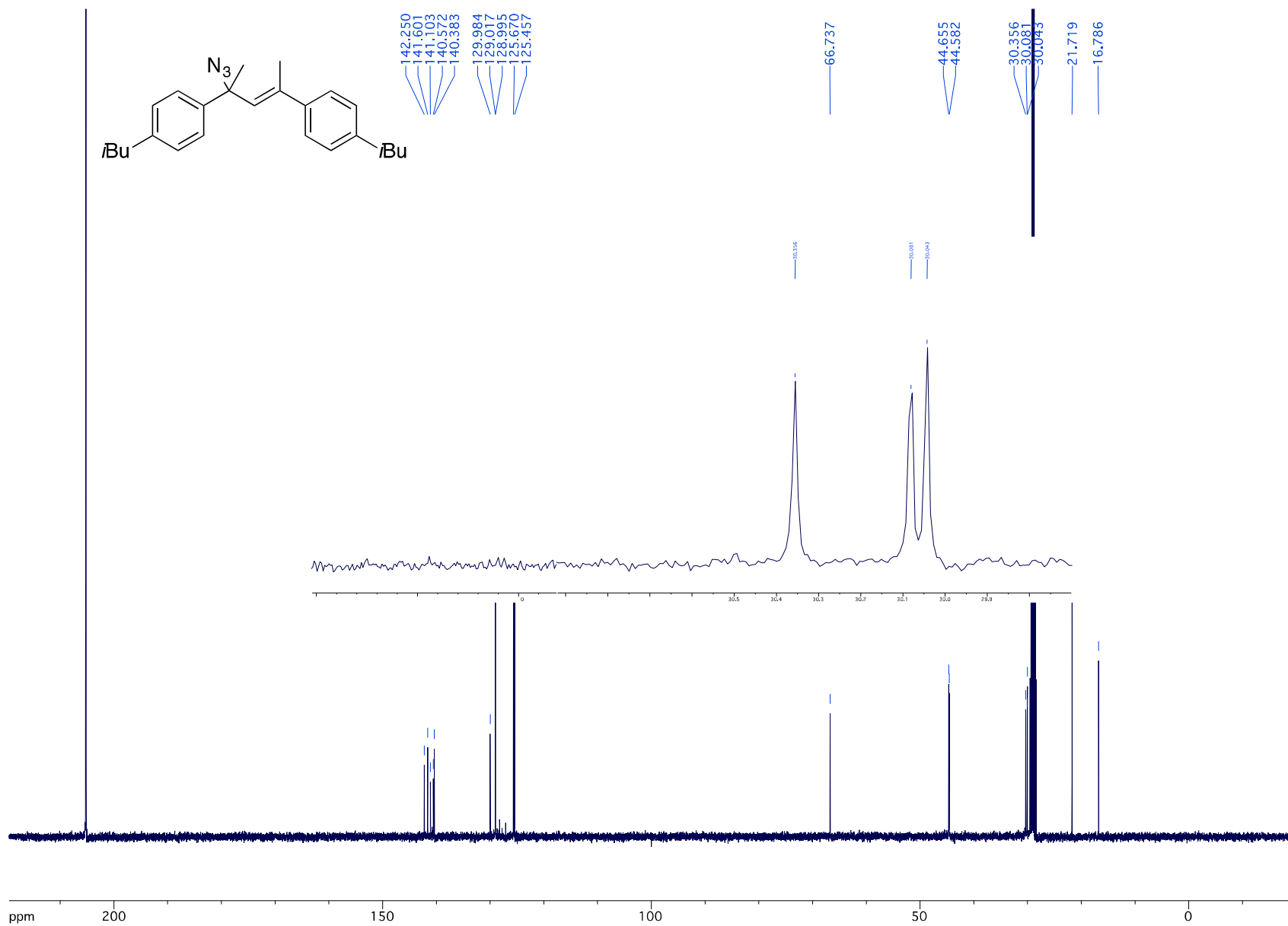
Compound 1b: 500 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



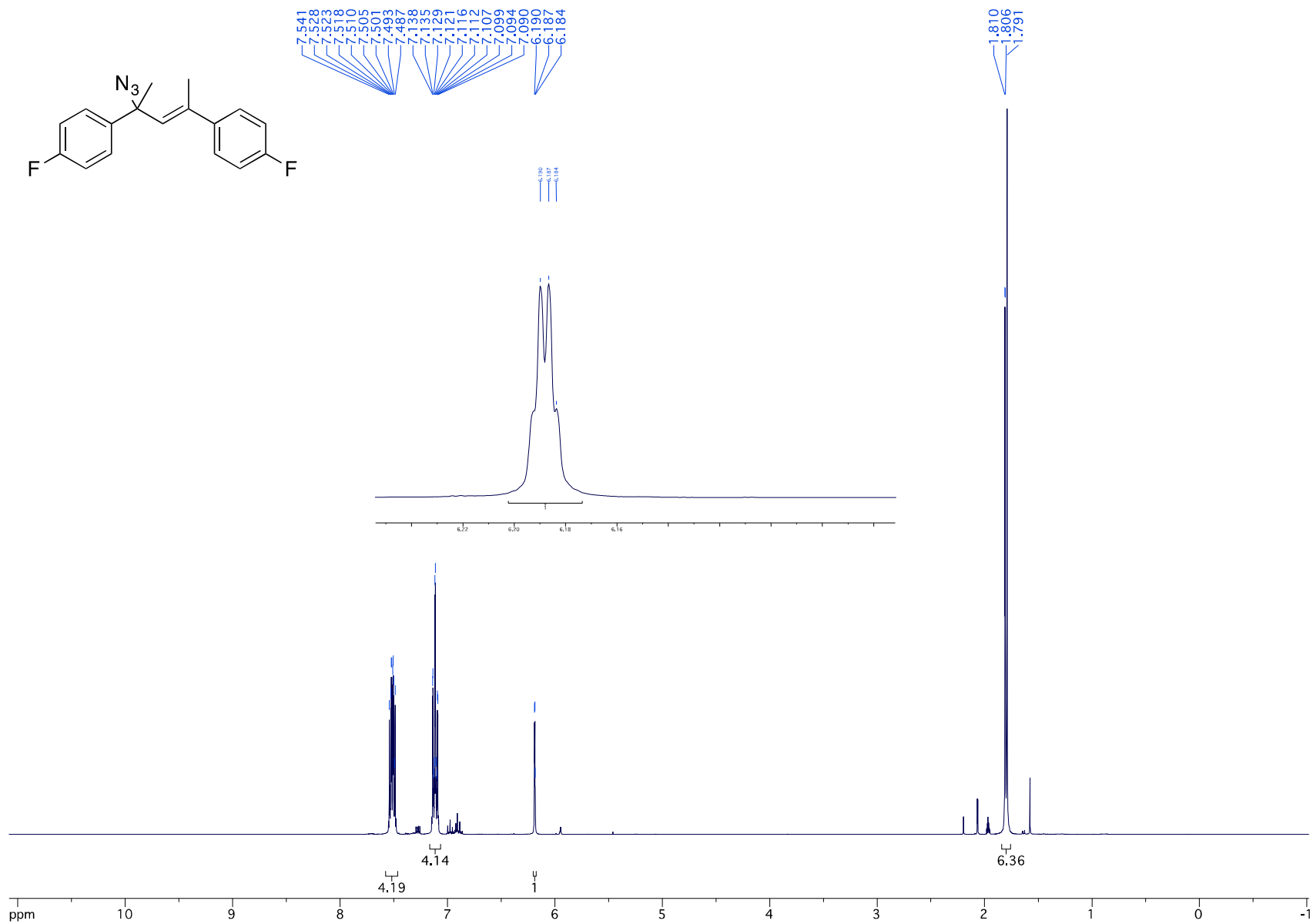
Compound 1b: 125 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



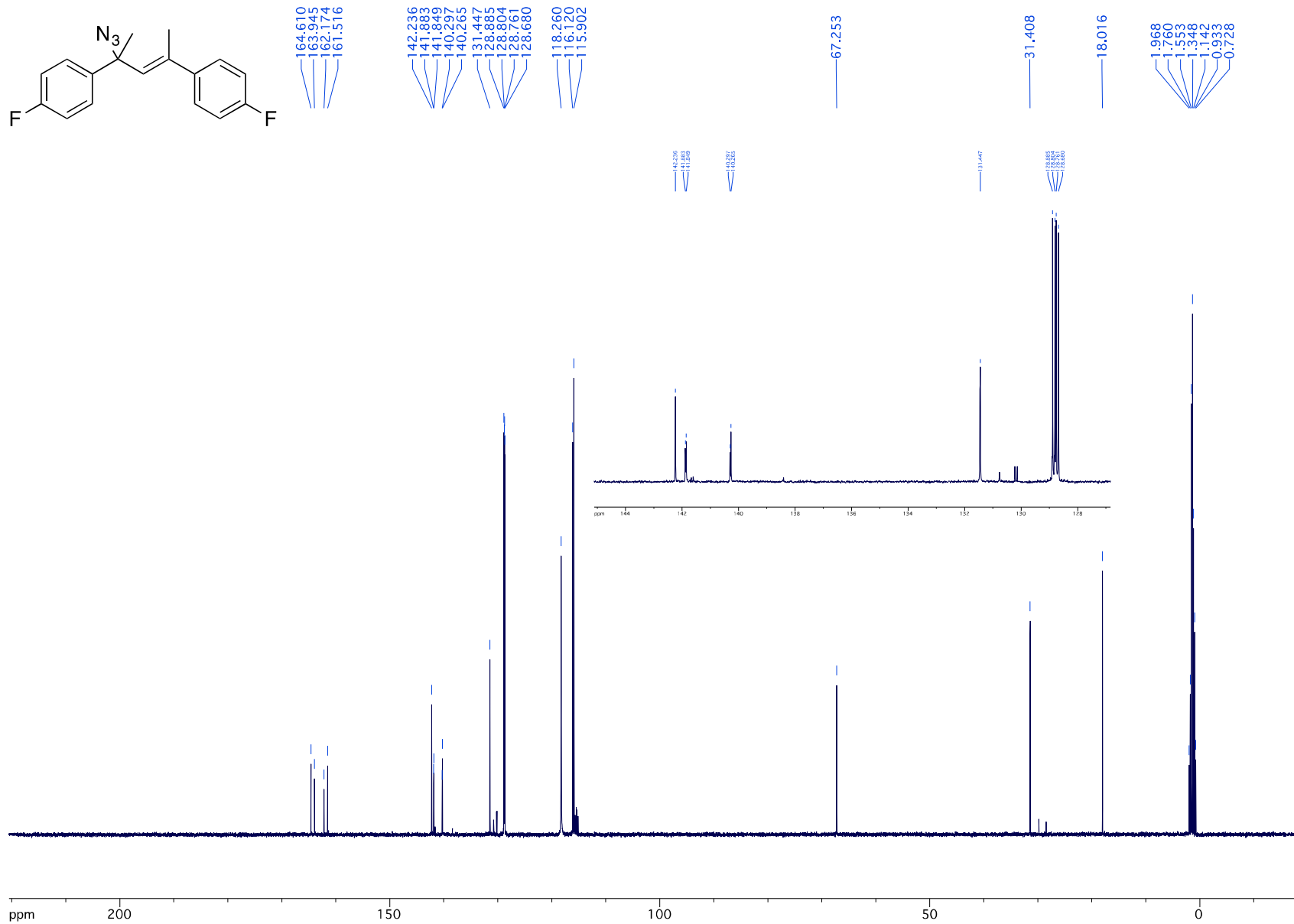
Compound 1c: 400 MHz  $^1\text{H}$  NMR spectrum in acetone- $d_6$



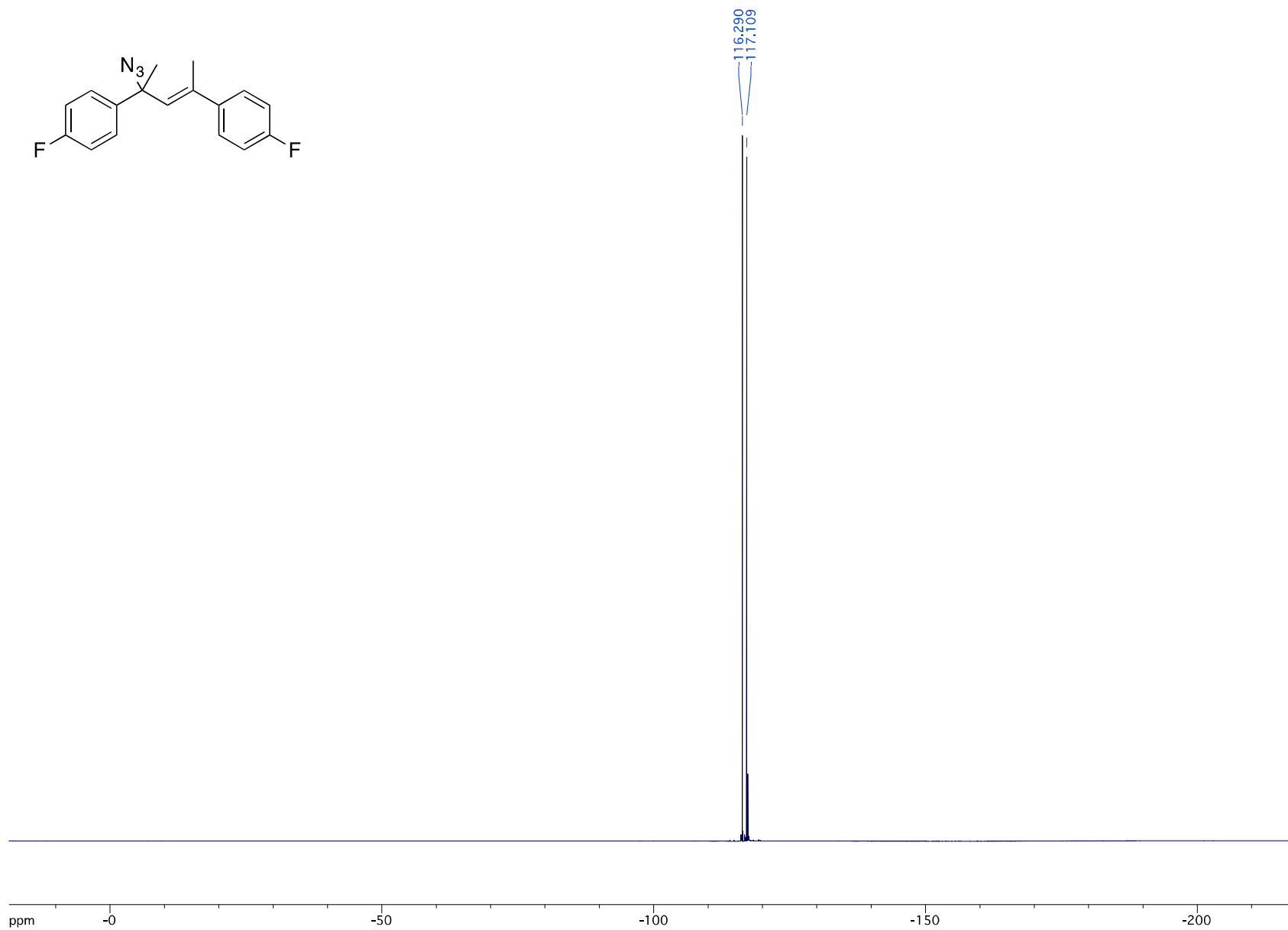
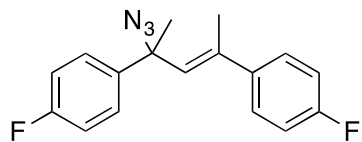
Compound 1c: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{acetone-}d_6$



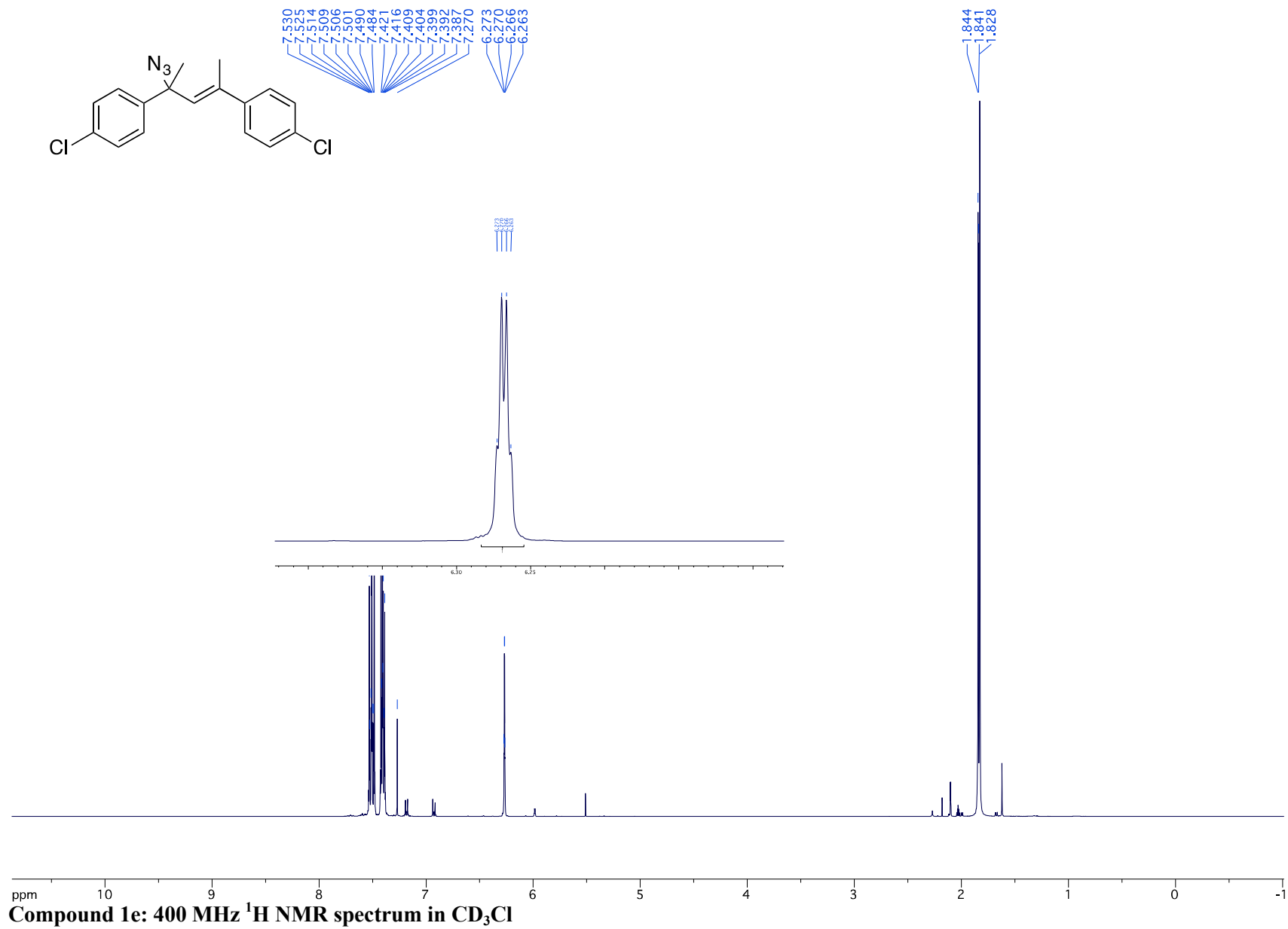
Compound 1d: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CD}_3\text{CN}$

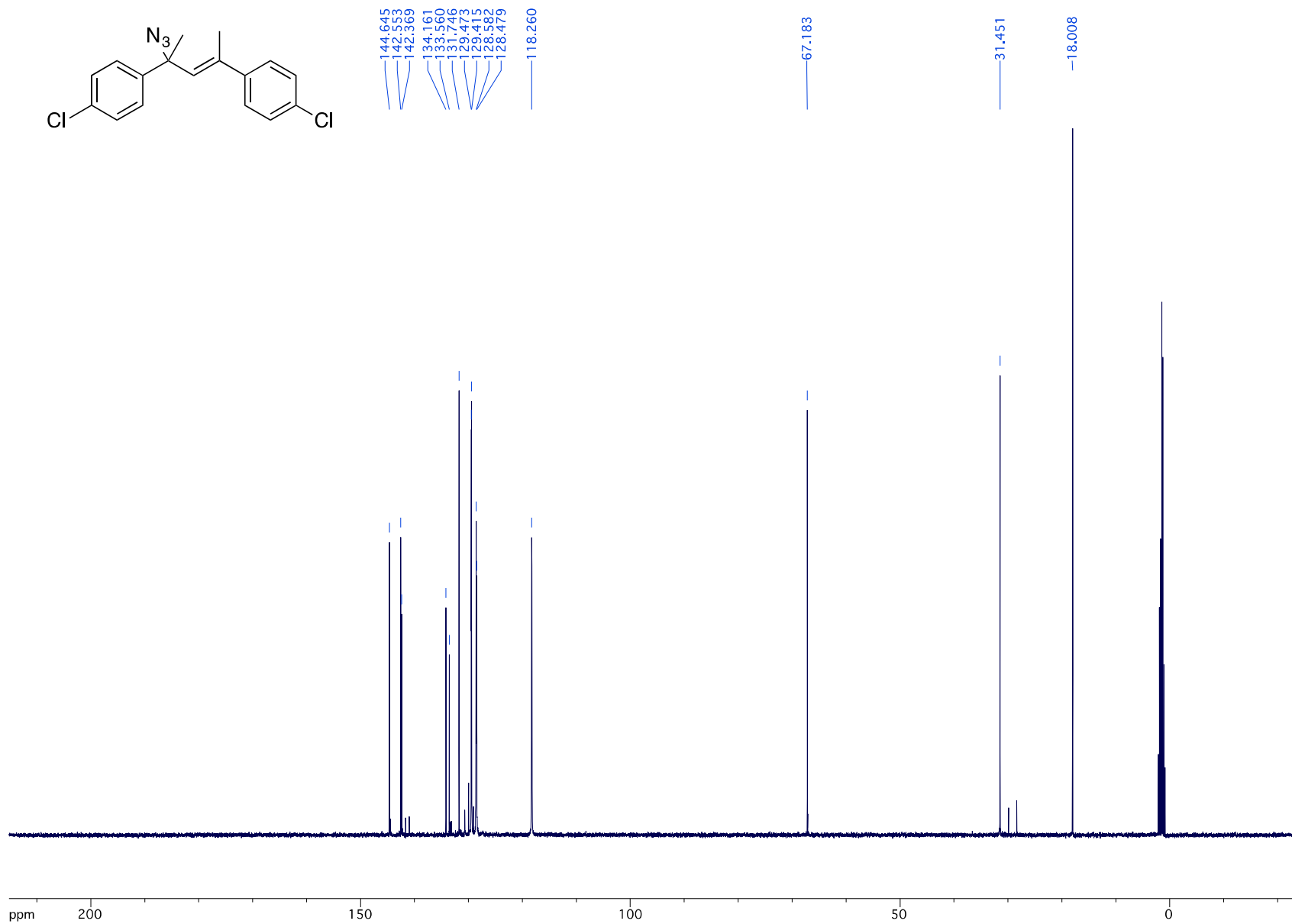
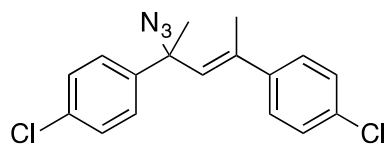


Compound 1d: 100 MHz <sup>13</sup>C NMR spectrum in CD<sub>3</sub>CN

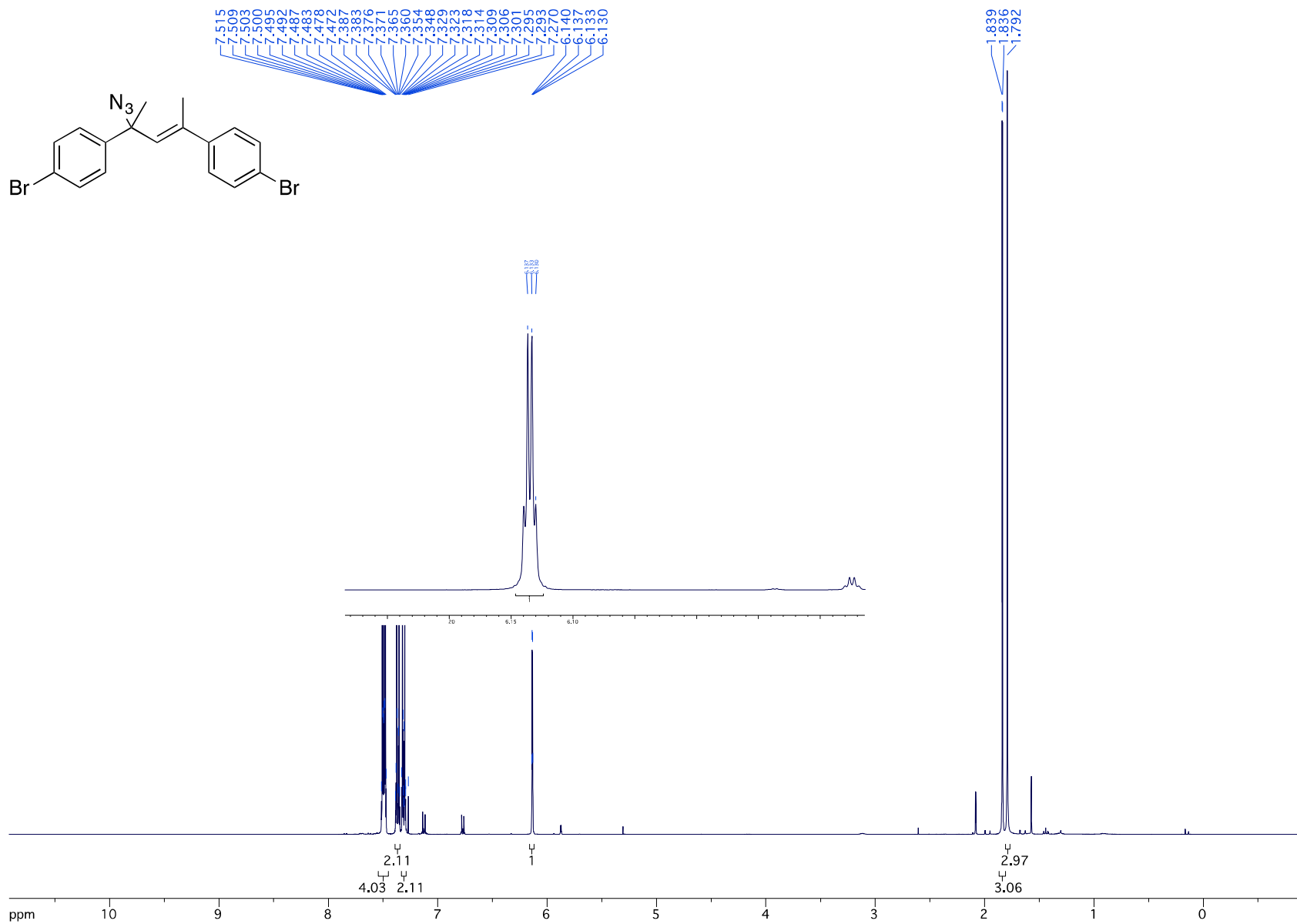


Compound 1d: 376 MHz <sup>19</sup>F NMR spectrum in CD<sub>3</sub>CN

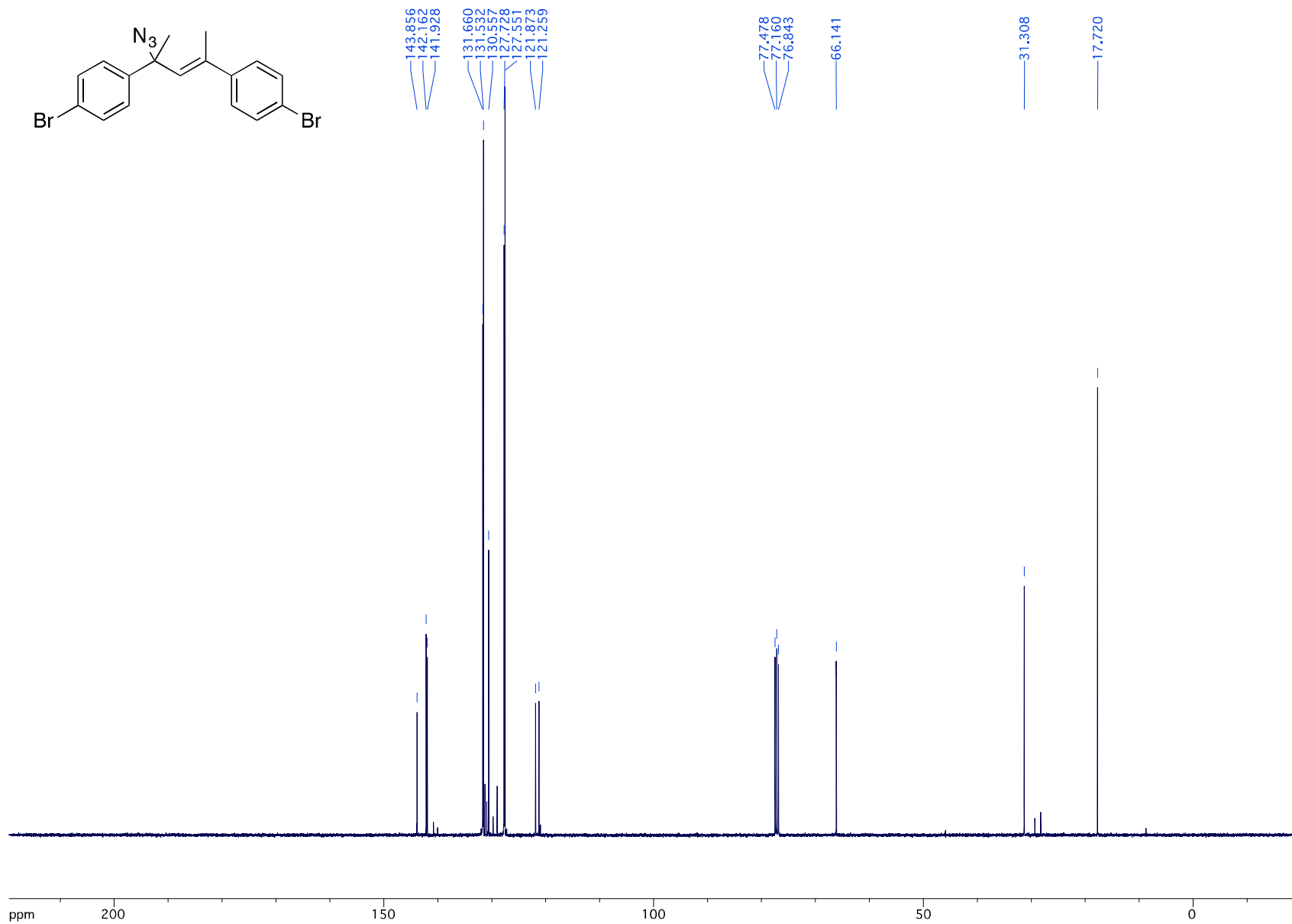




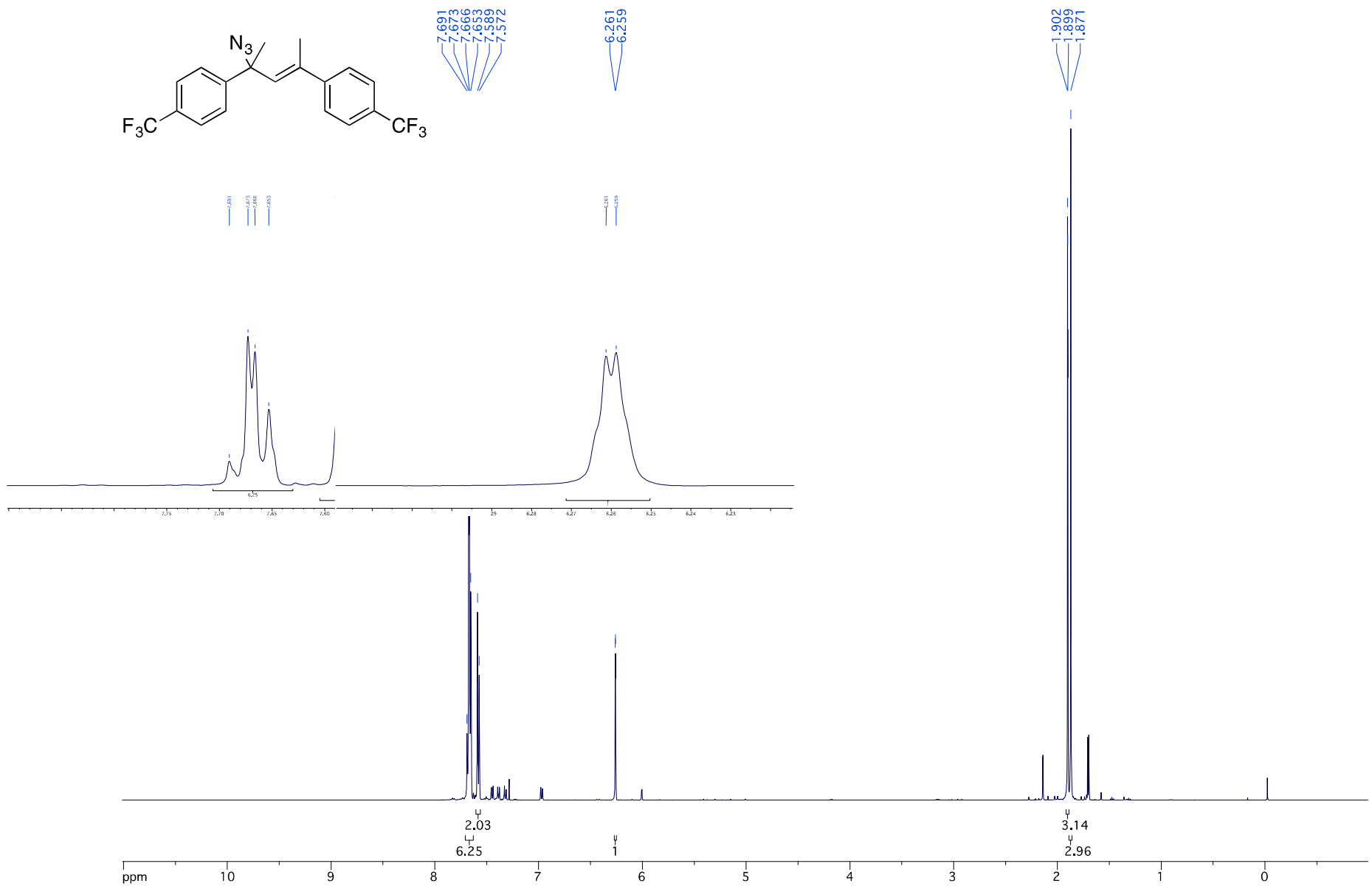
Compound 1e: 100 MHz <sup>13</sup>C NMR spectrum in CD<sub>3</sub>CN



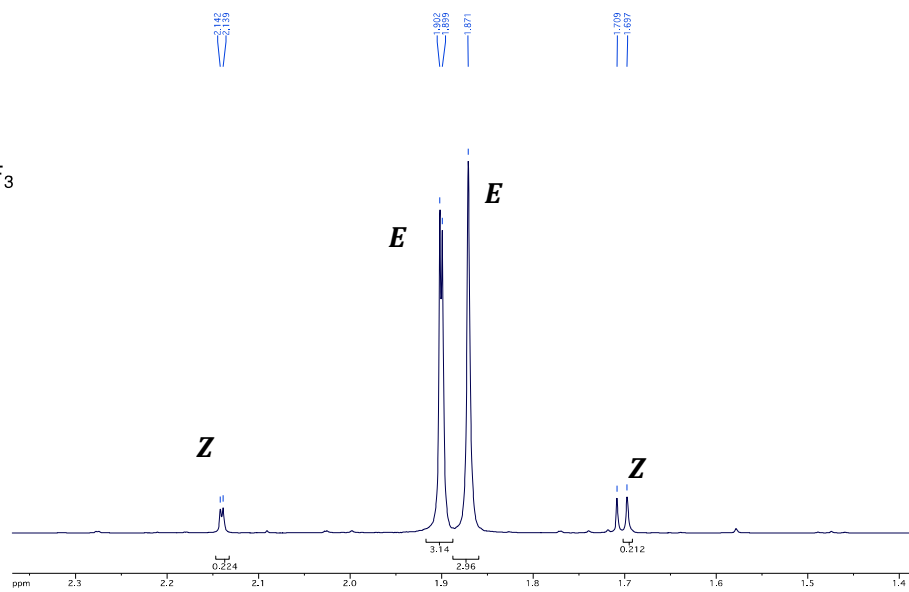
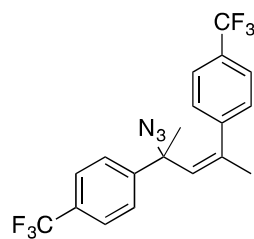
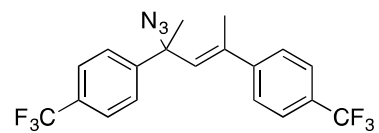
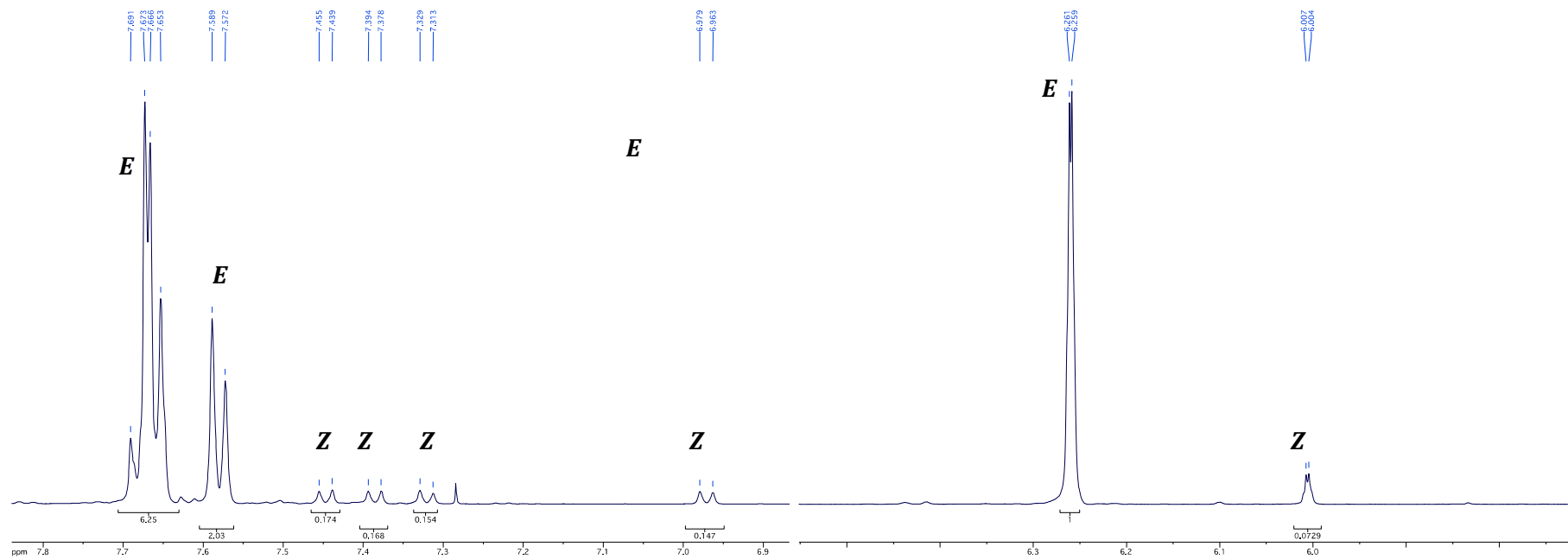
Compound 1f: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>

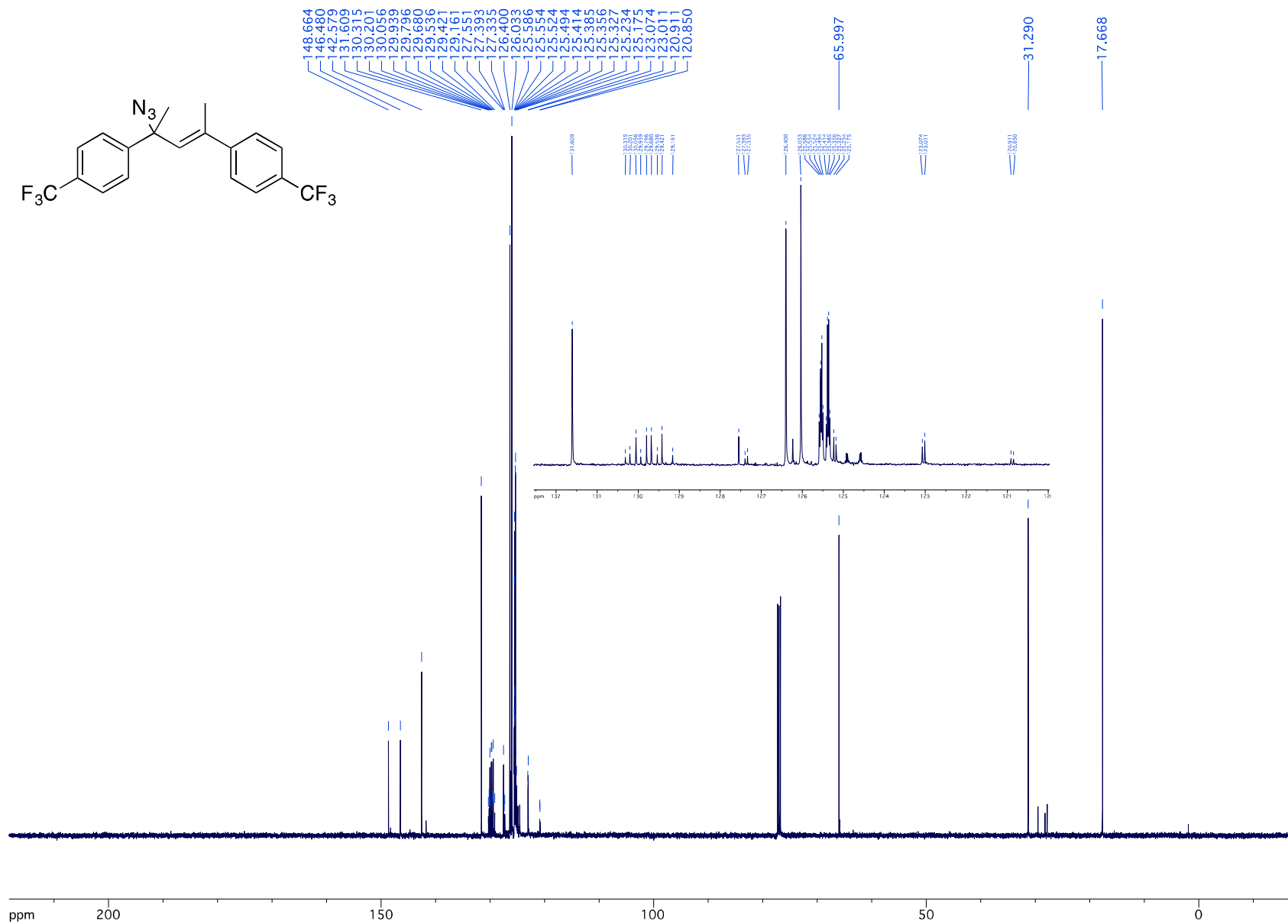
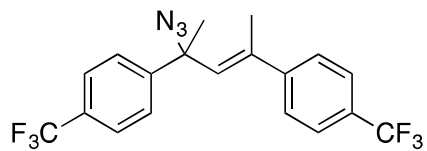


Compound 1f: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>

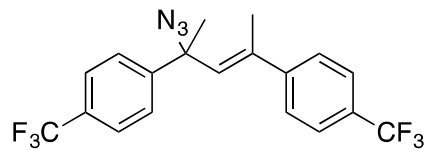


Compound 1g: 500 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>

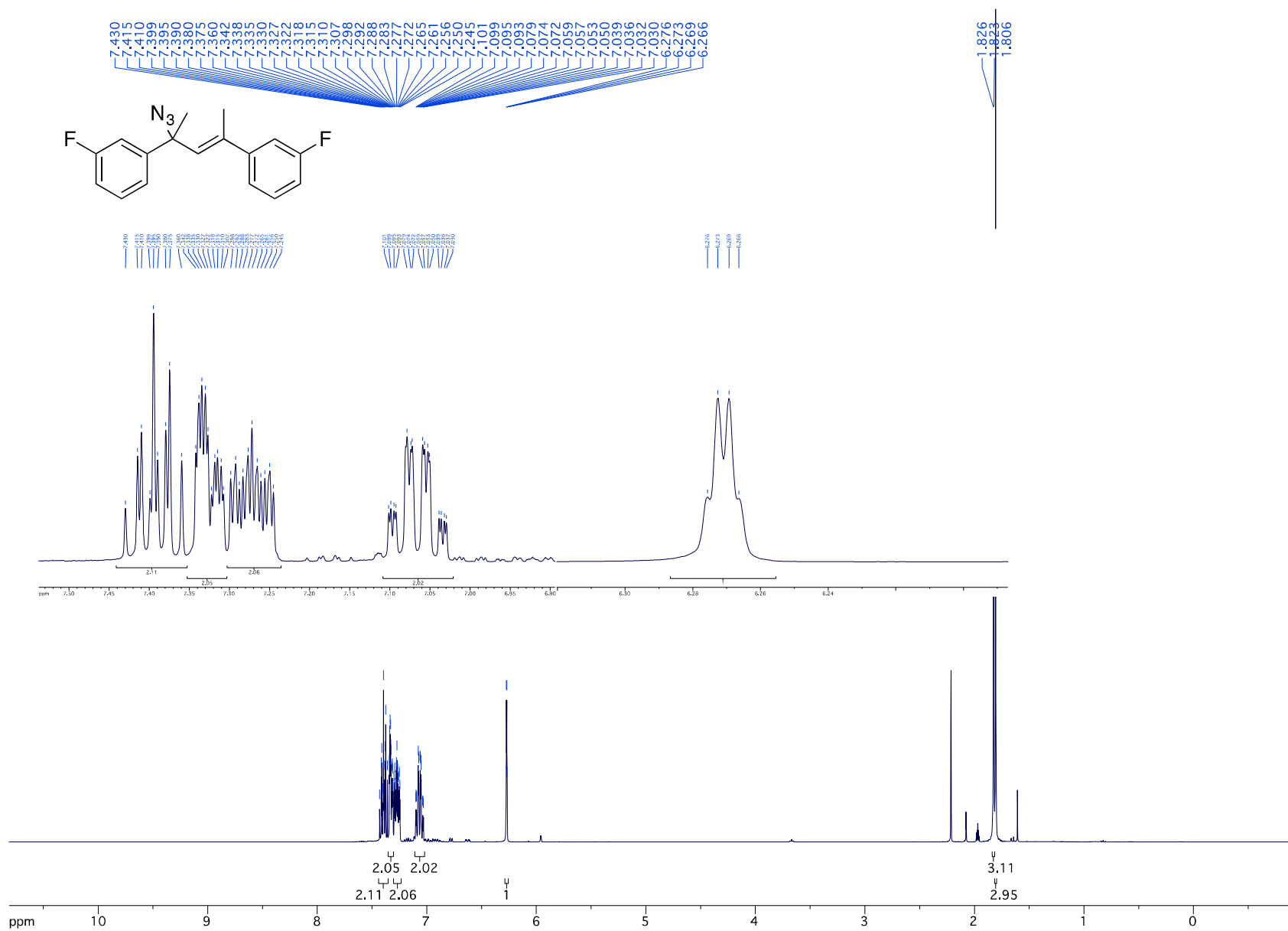




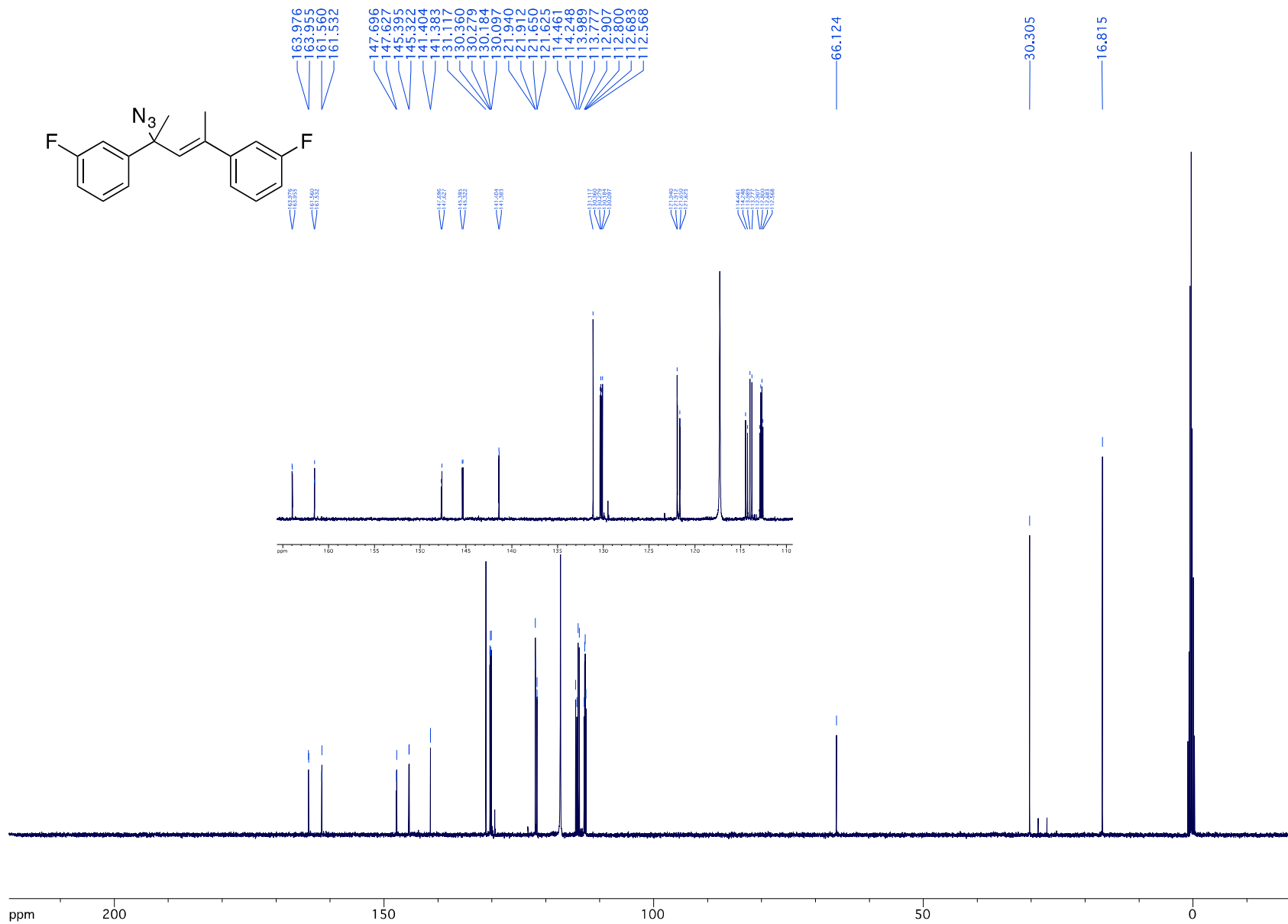
Compound 1g: 125 MHz  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$



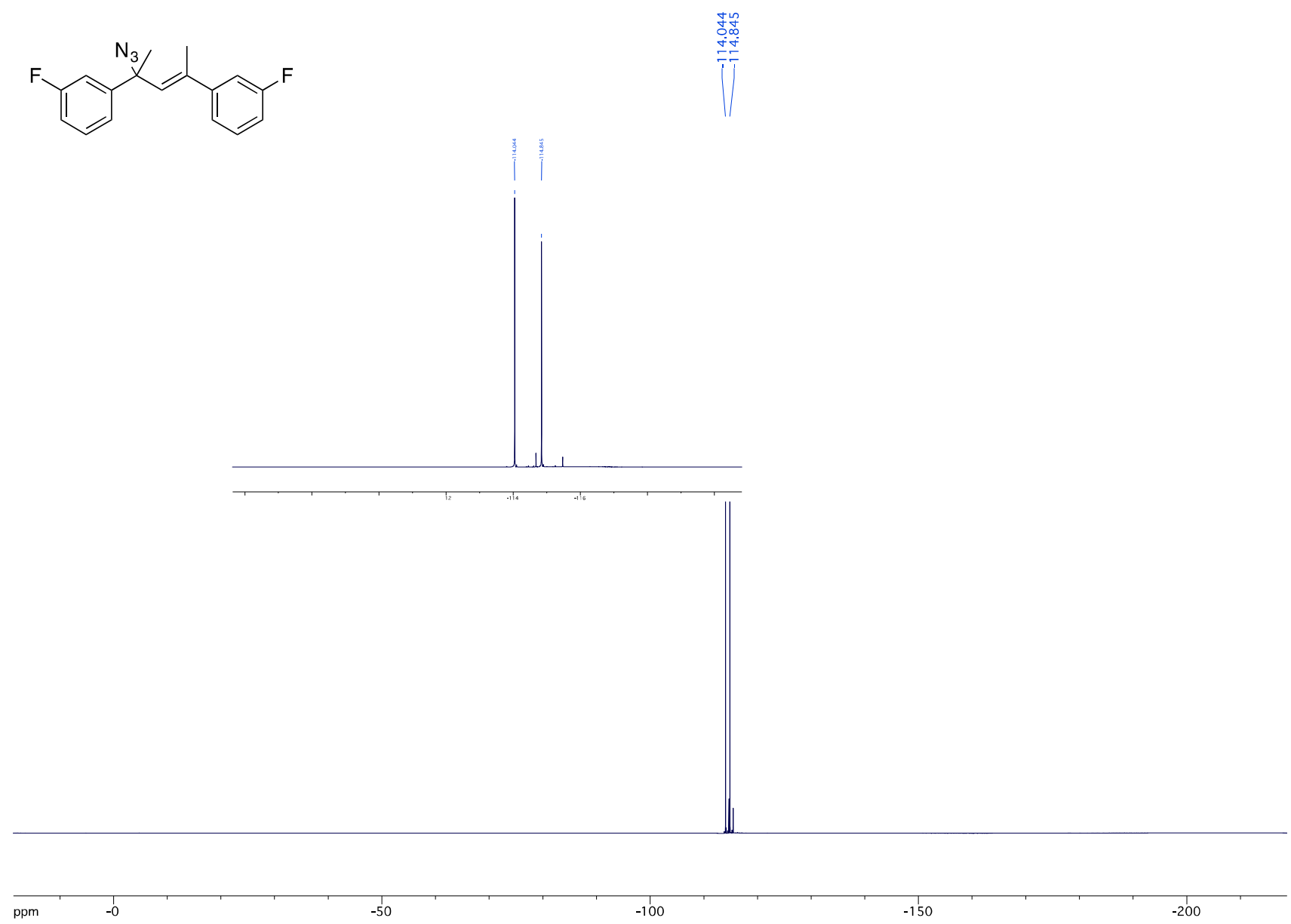
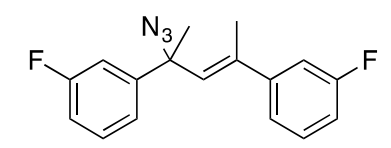
Compound 1g: 471 MHz  $^{19}\text{F}$  NMR spectrum in  $\text{CDCl}_3$



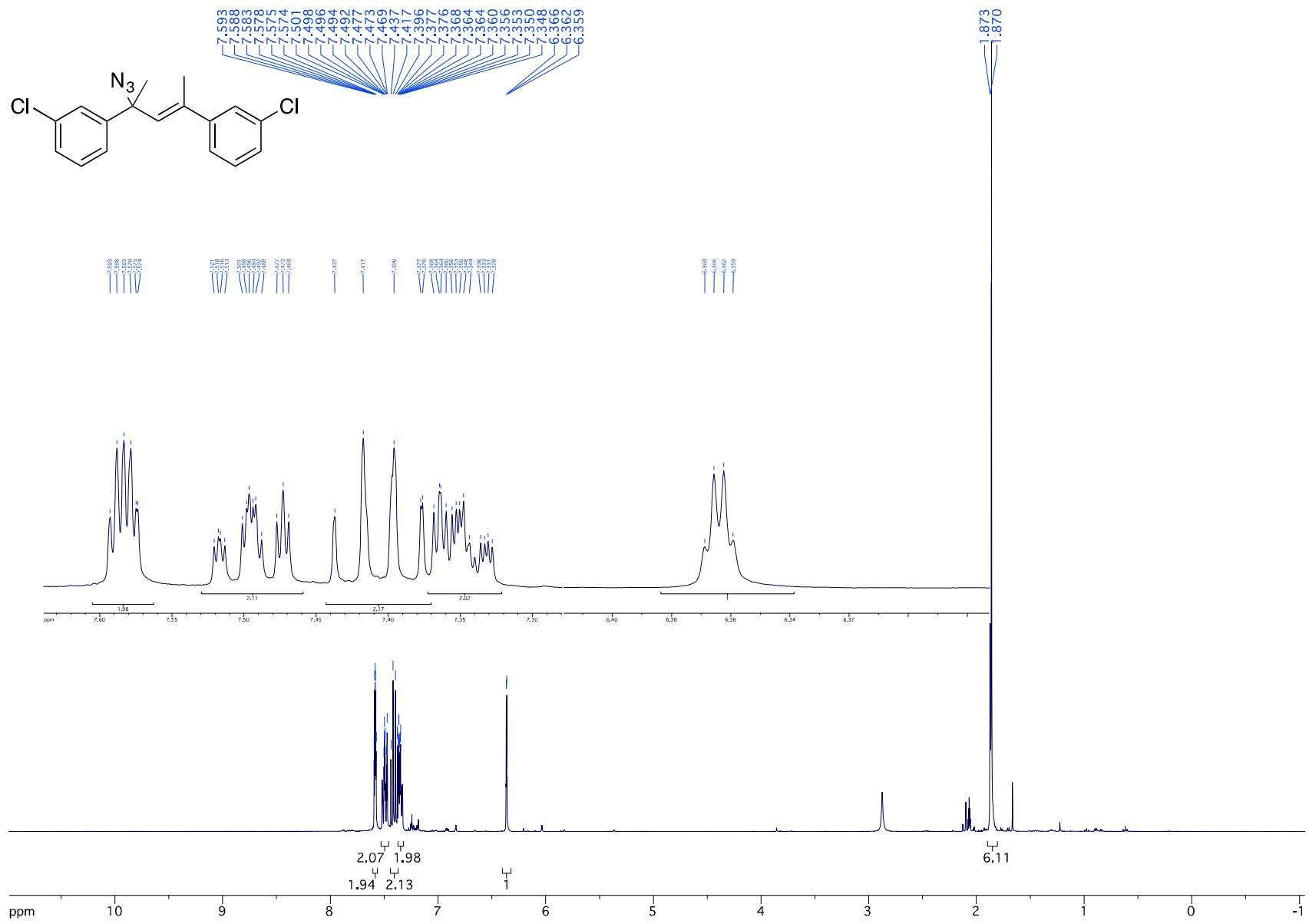
**Compound 1h: 400 MHz <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN**



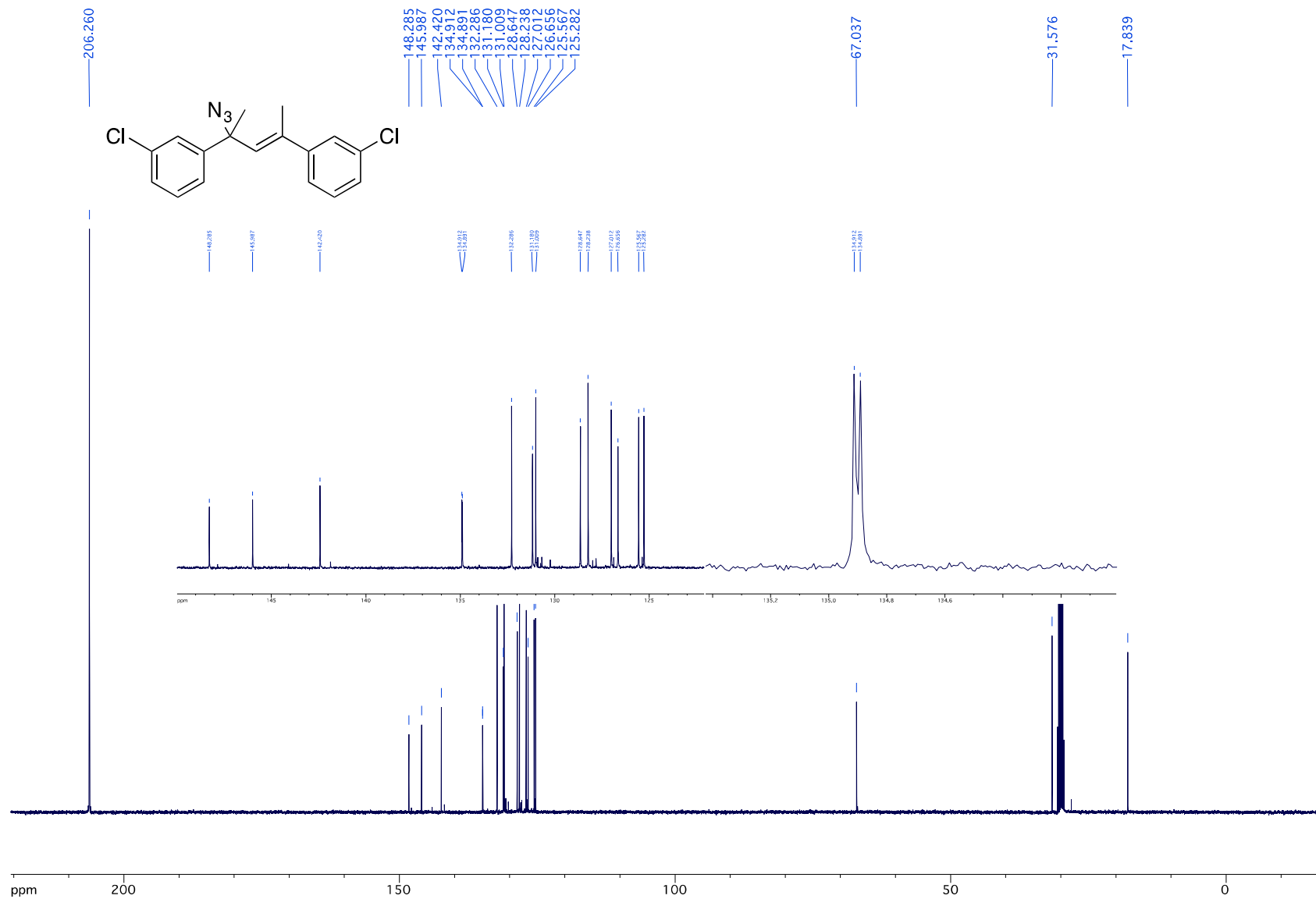
Compound 1h: 100 MHz <sup>13</sup>C NMR spectrum in CD<sub>3</sub>CN



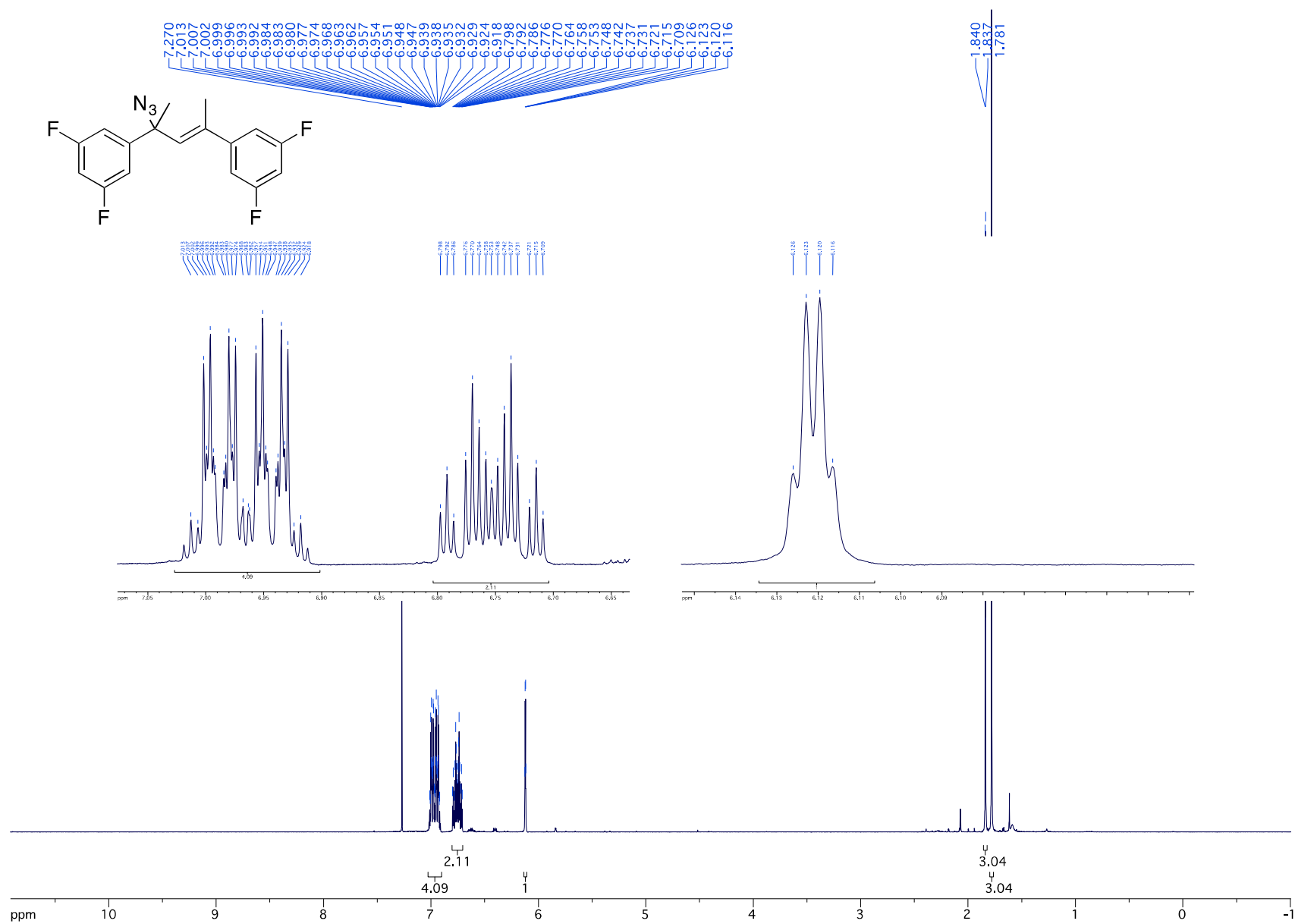
Compound 1h: 376 MHz <sup>19</sup>F NMR spectrum in CD<sub>3</sub>CN



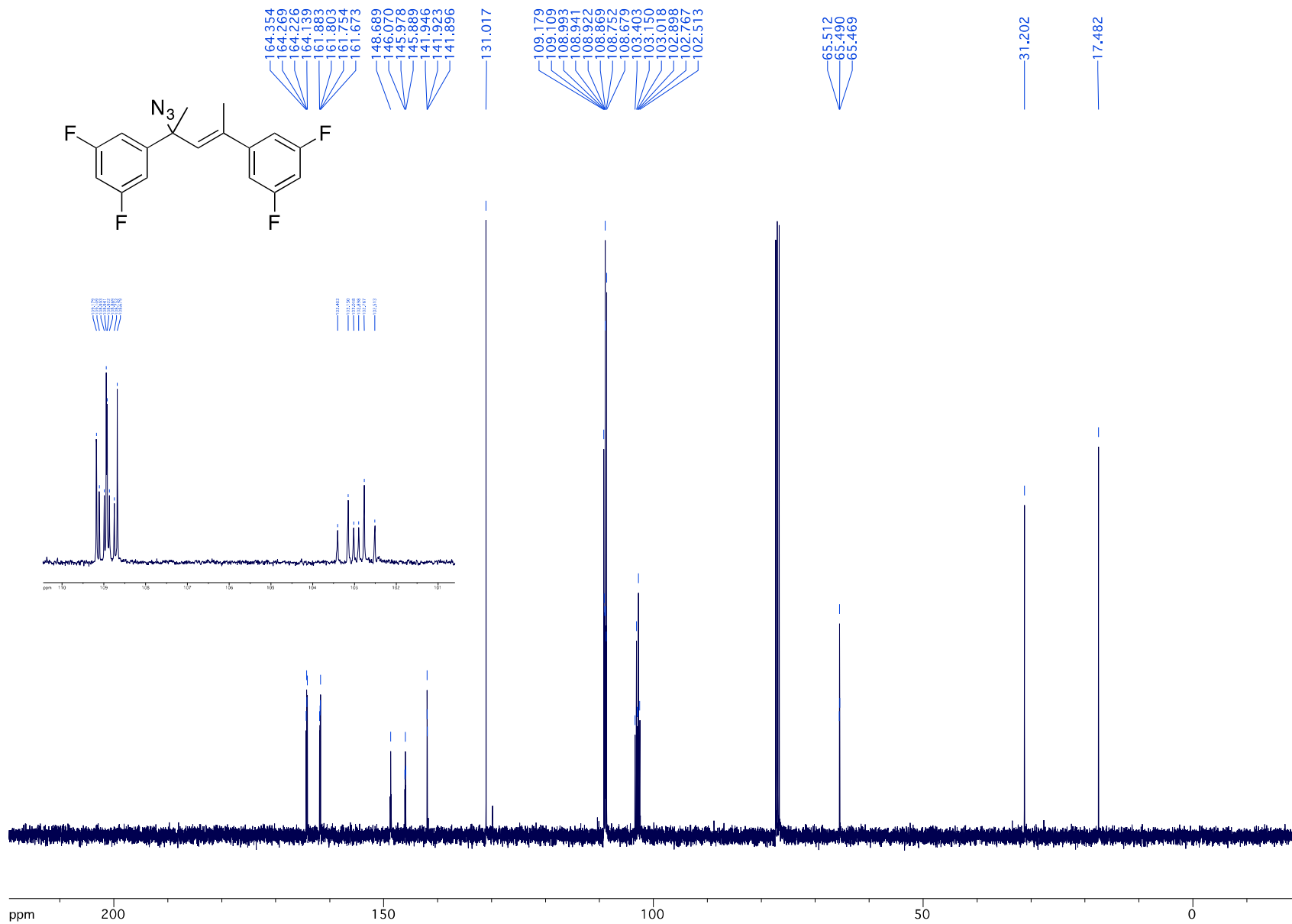
Compound 1i: 400 MHz <sup>1</sup>H NMR spectrum in acetone-*d*<sub>6</sub>

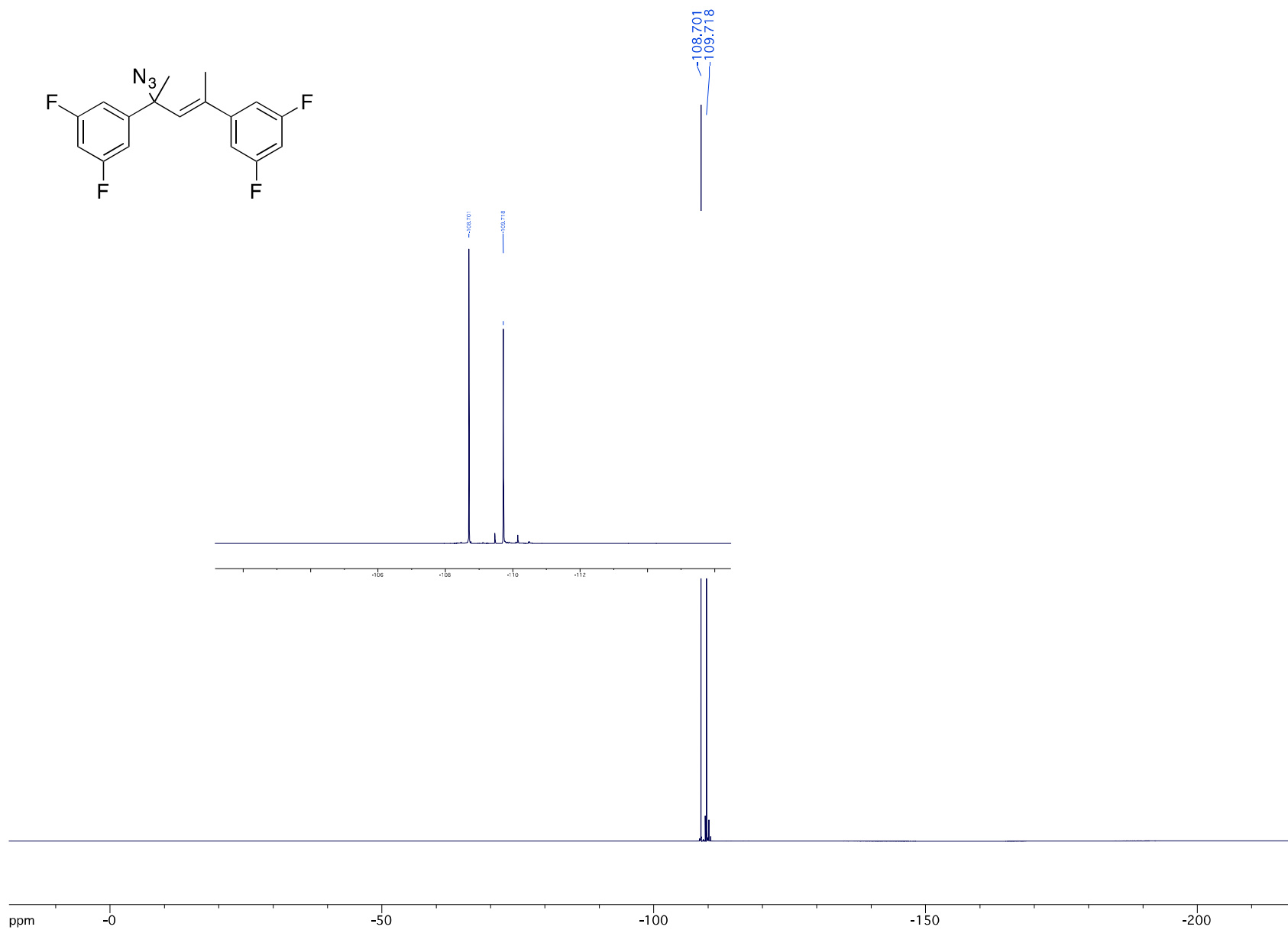
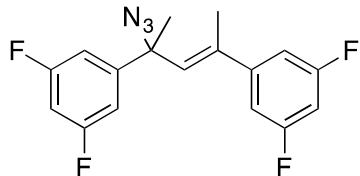


Compound 1i: 100 MHz  $^{13}\text{C}$  NMR spectrum in acetone- $d_6$

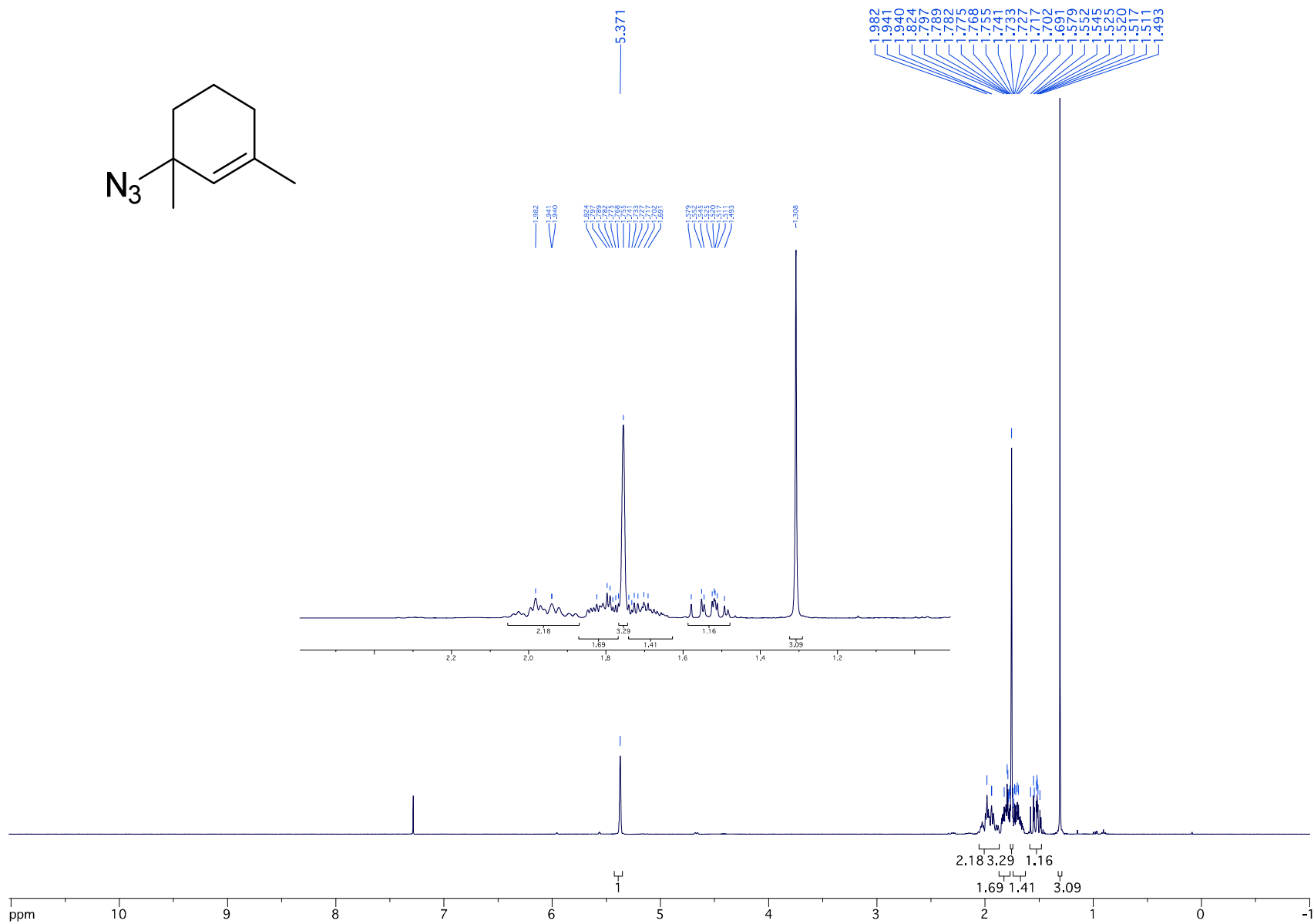
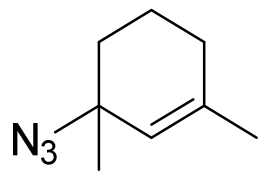


Compound 1j: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>

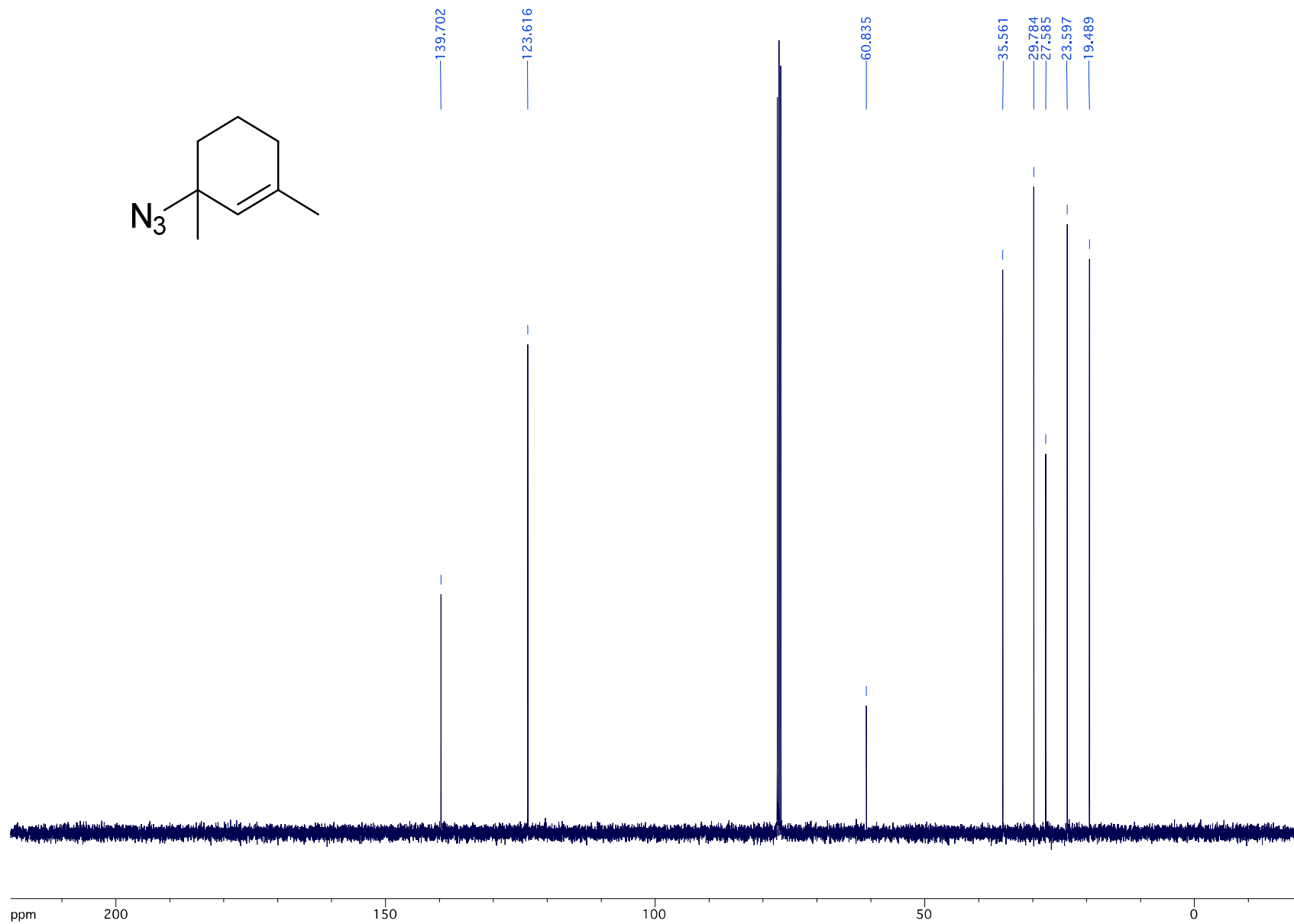
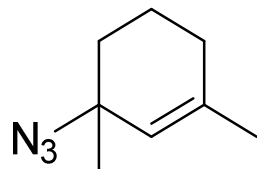




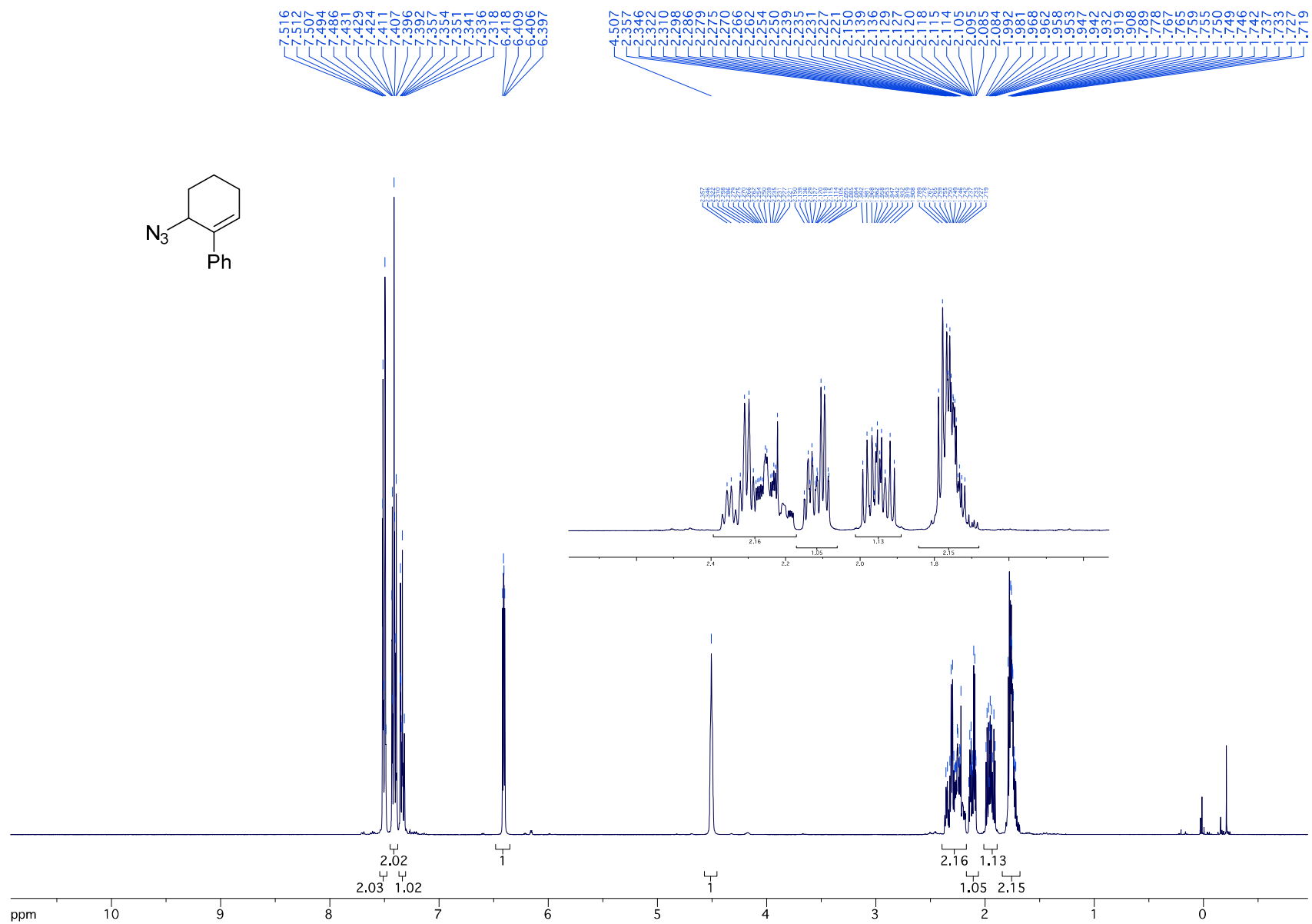
Compound 1j: 376 MHz <sup>19</sup>F NMR spectrum in CDCl<sub>3</sub>



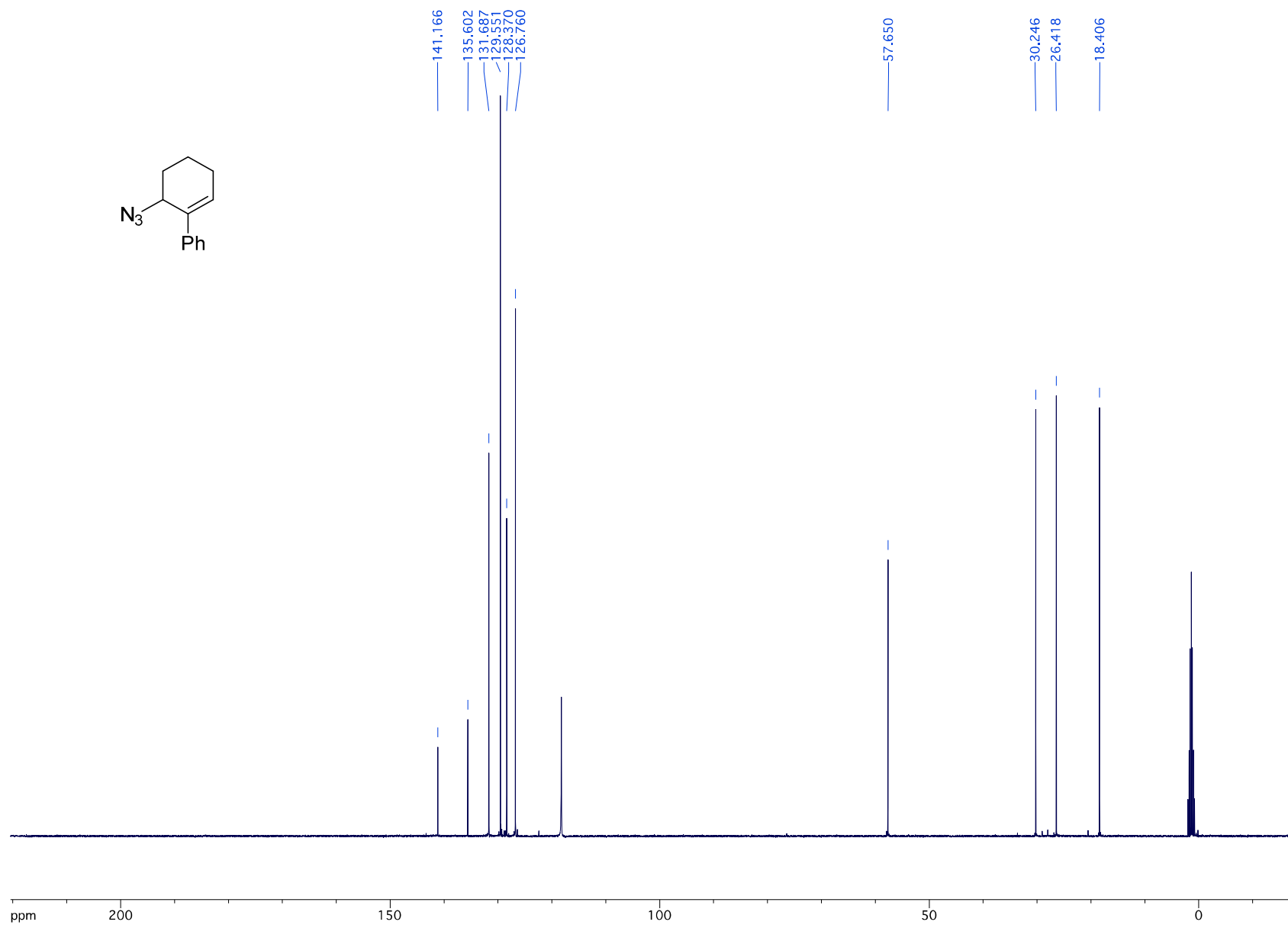
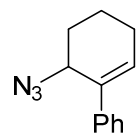
Compound S3a: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



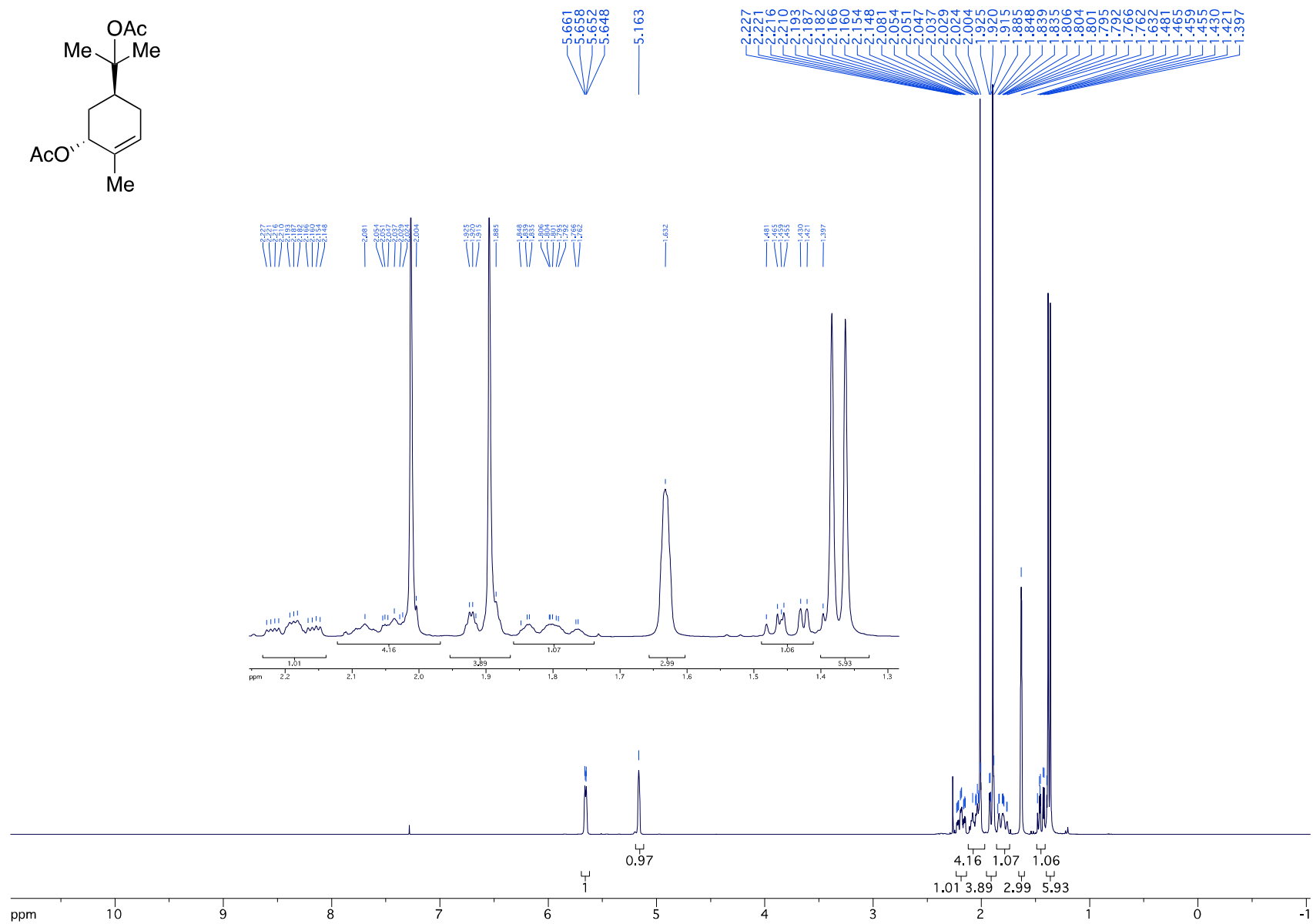
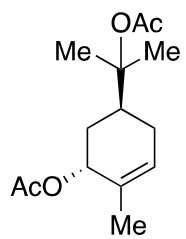
Compound S3a: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



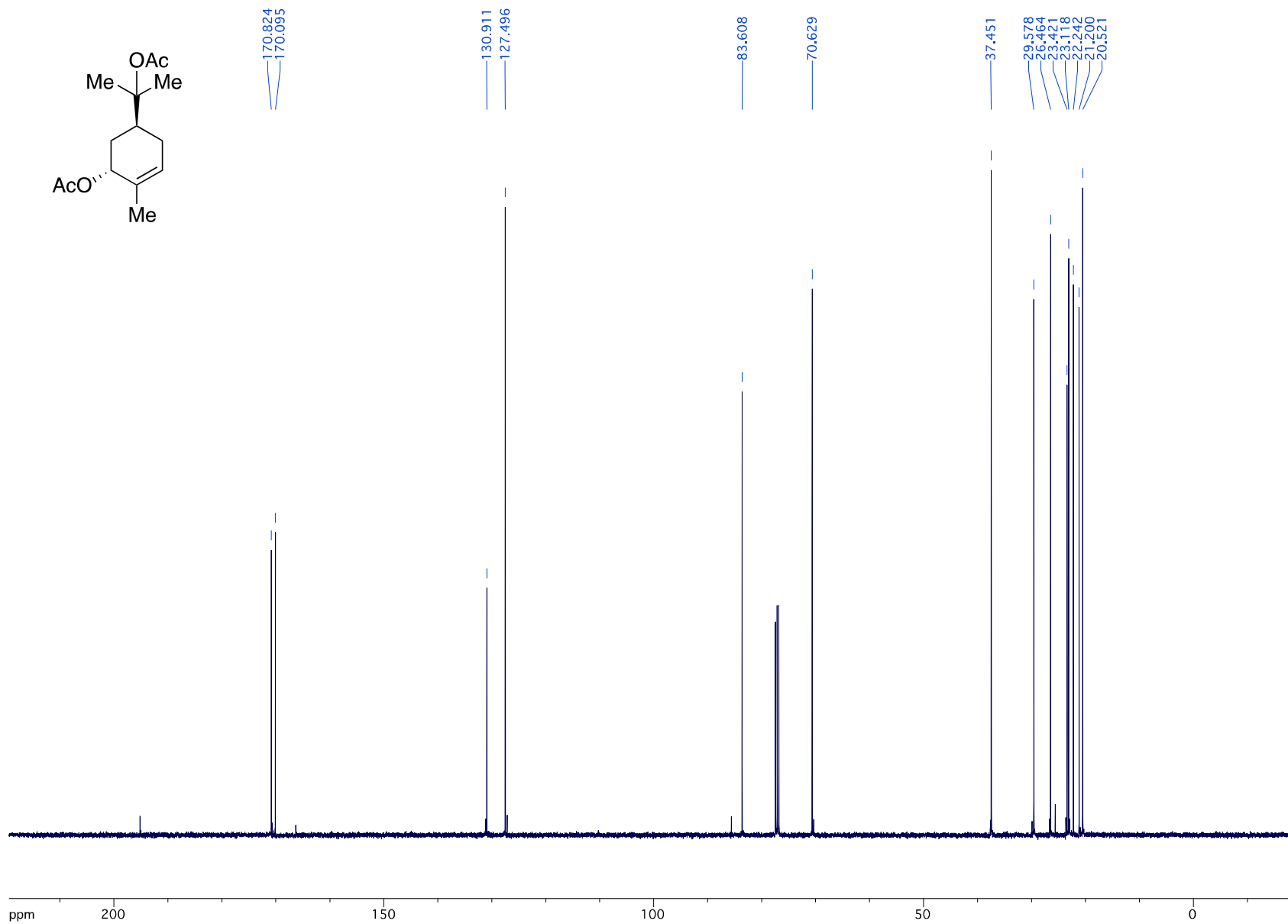
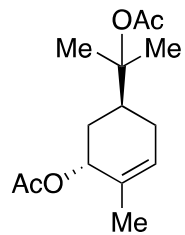
Compound S3b: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



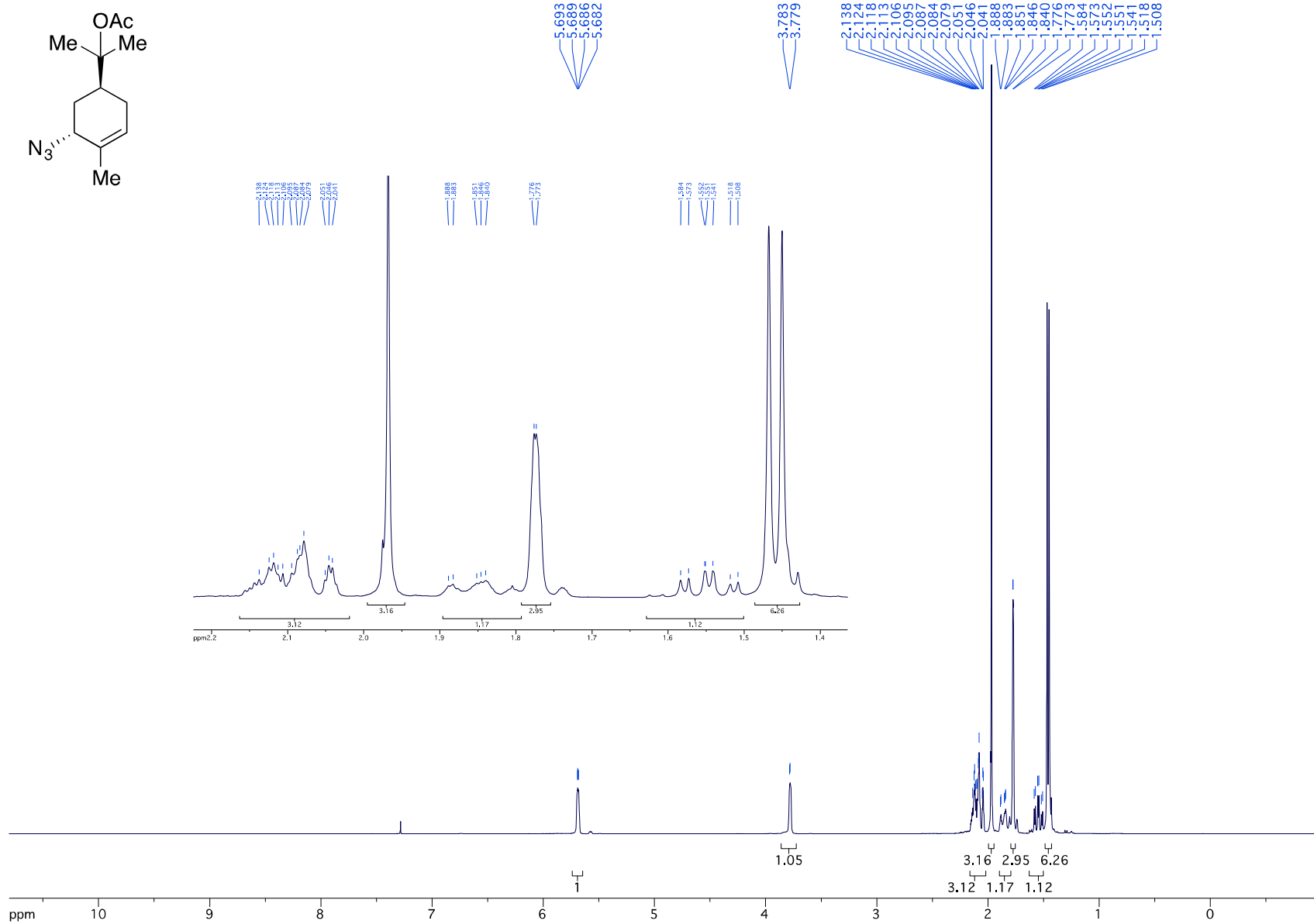
Compound S3b: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



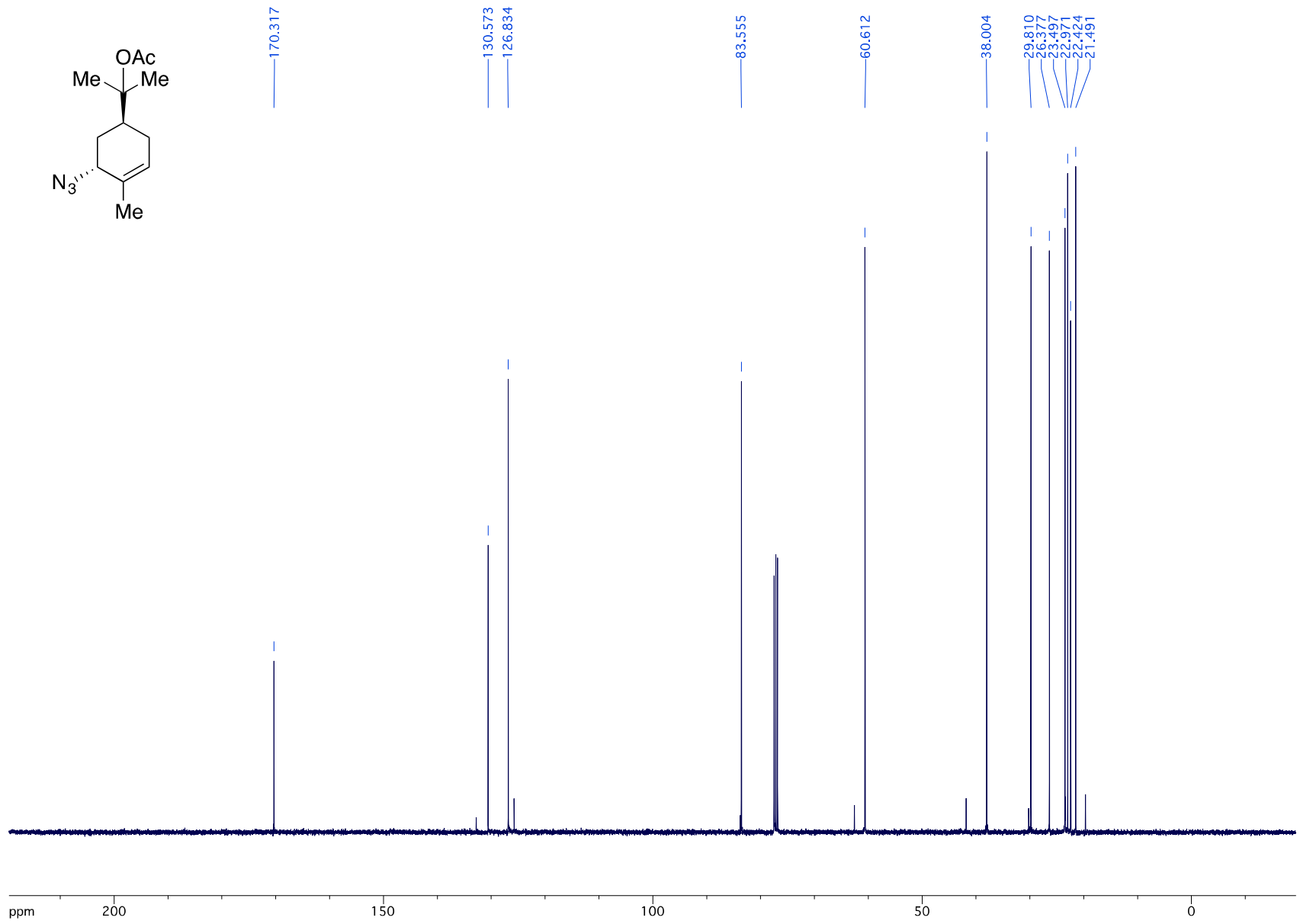
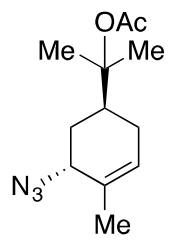
Compound S3e: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



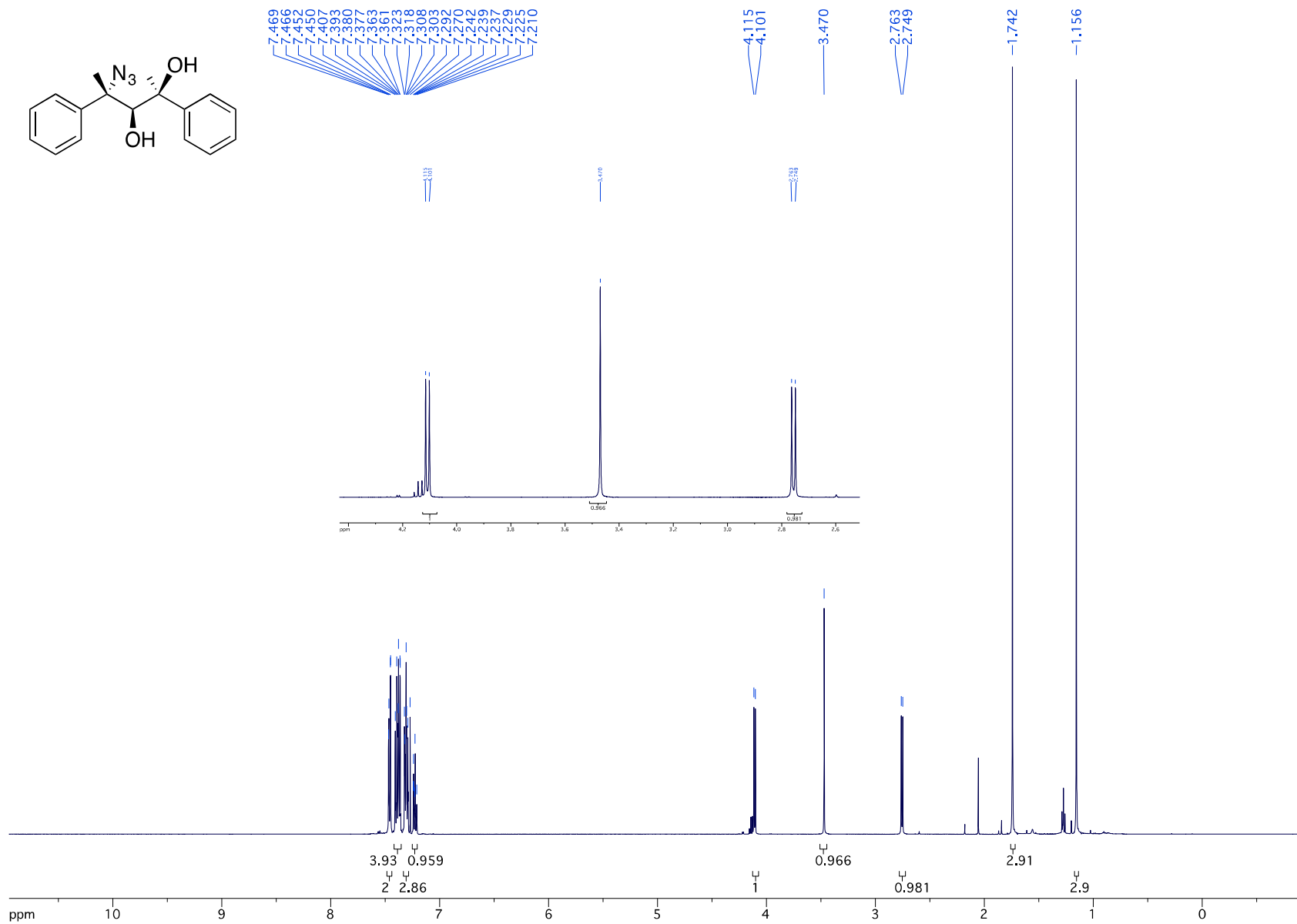
Compound S3e: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



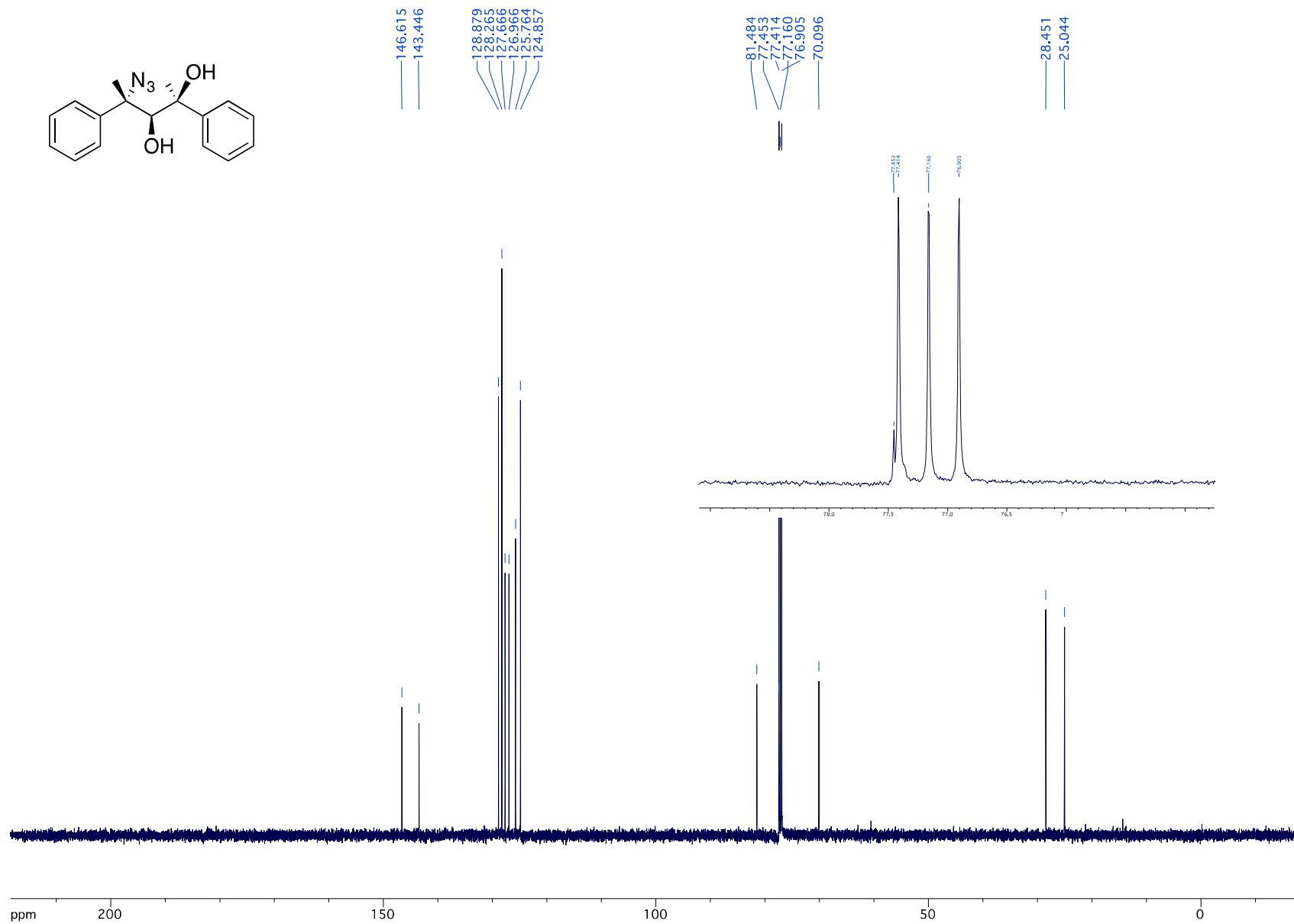
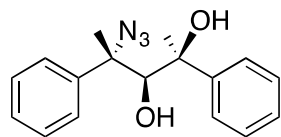
Compound S3f: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



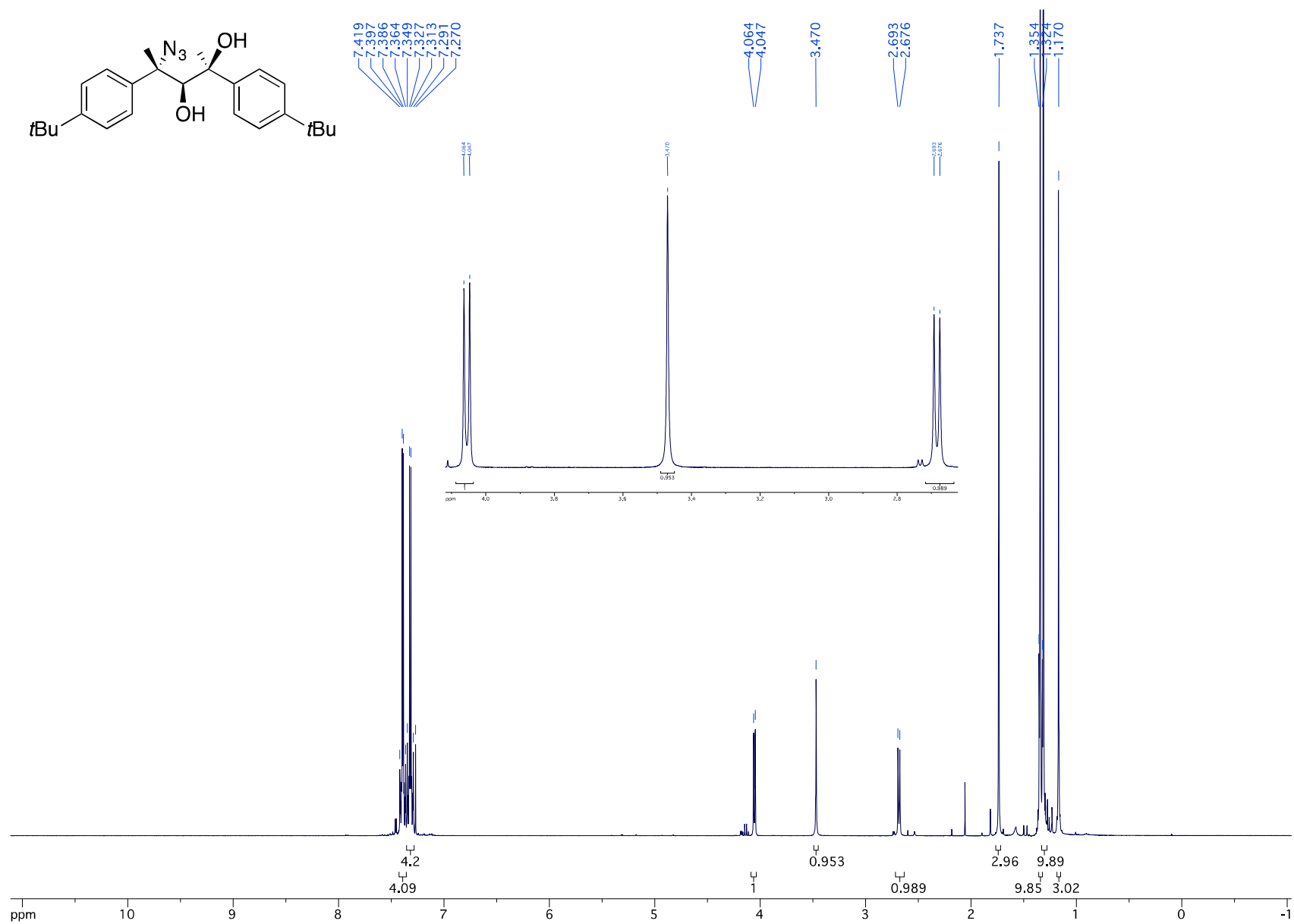
Compound S3f: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



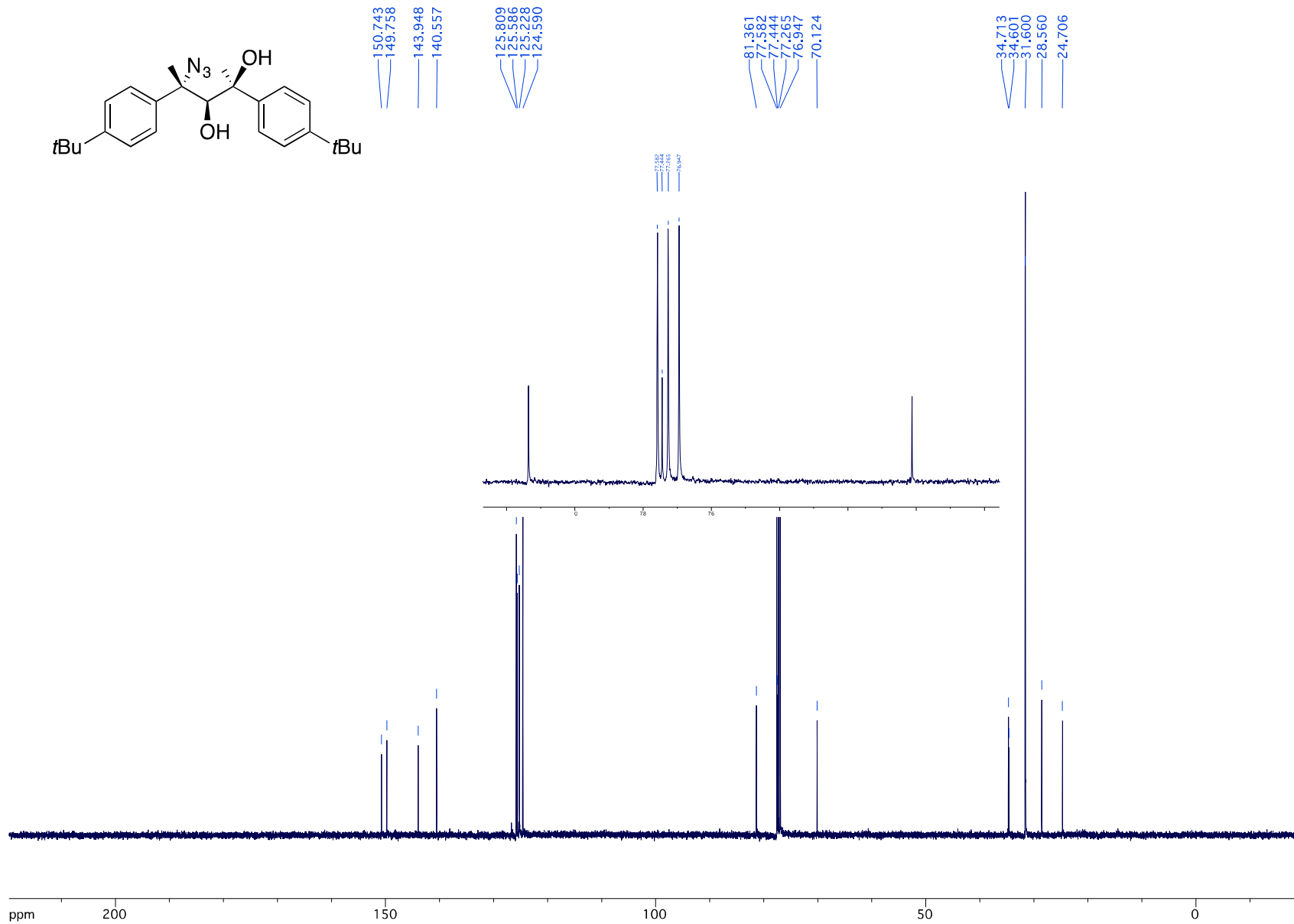
Compound 2a: 500 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



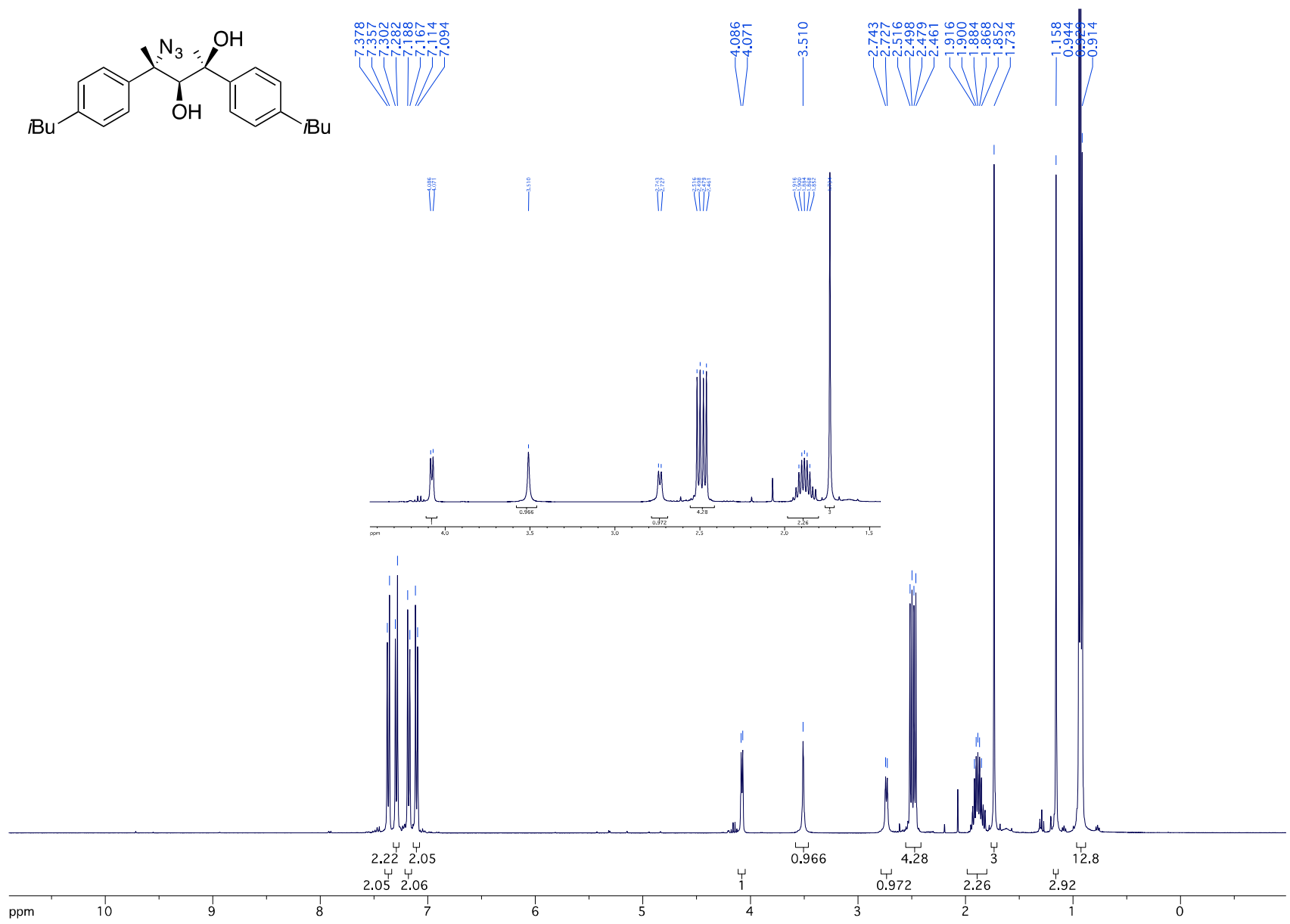
Compound 2a: 125 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



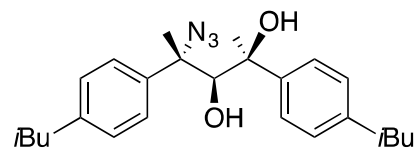
Compound 2b: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



Compound 2b: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



Compound 2c: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



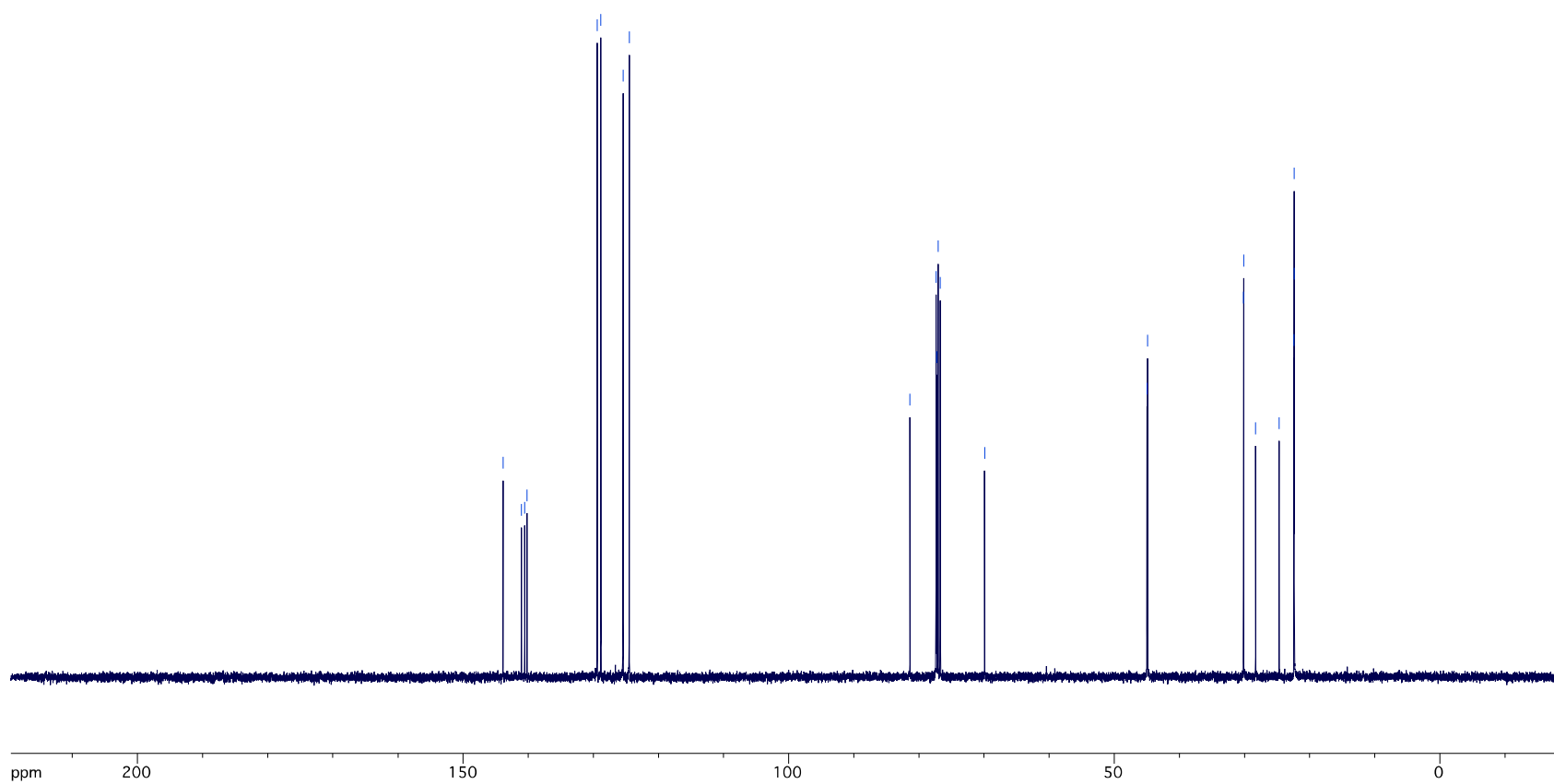
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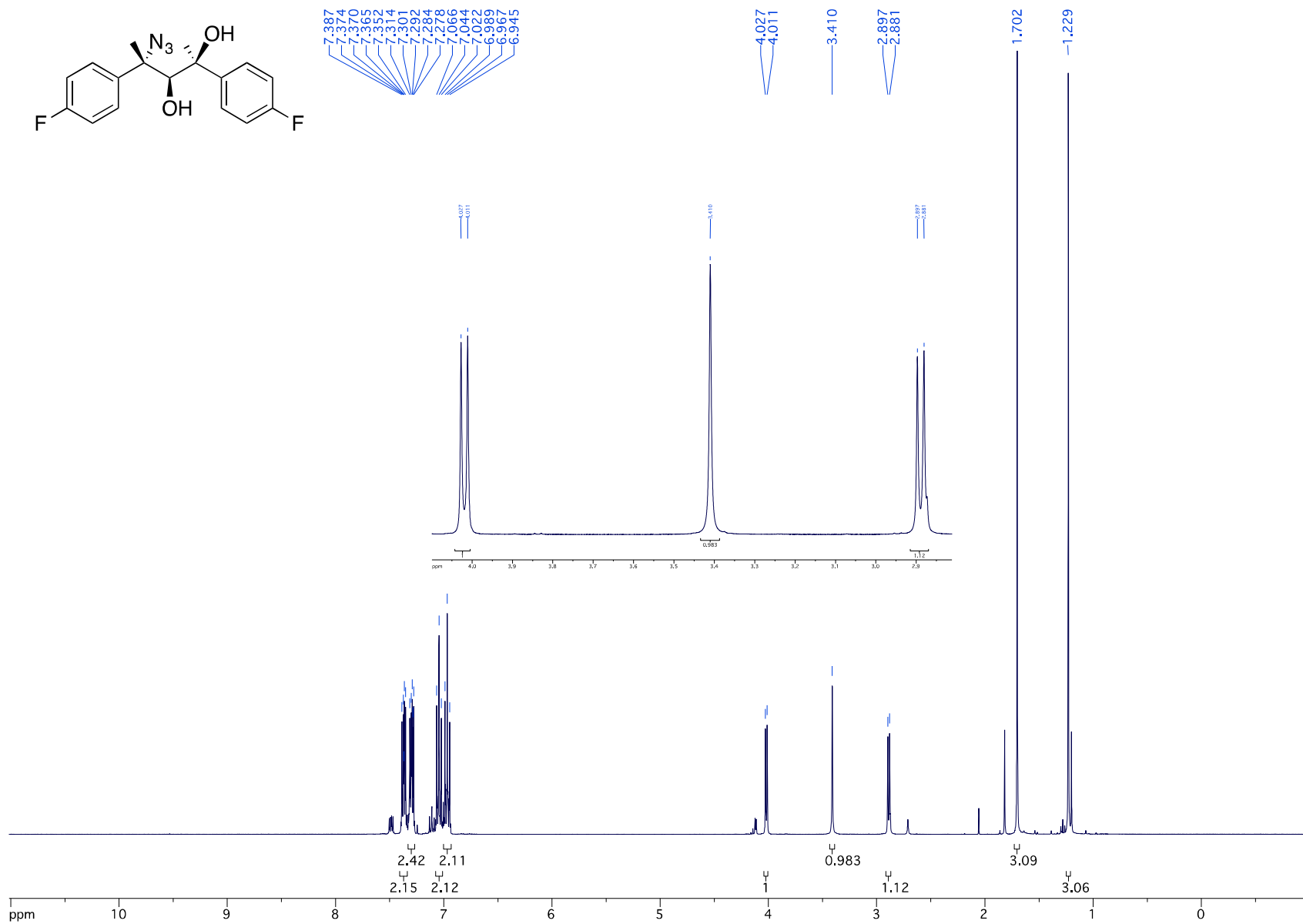
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77.280  
77.038  
76.721  
69.905

44.977  
44.887

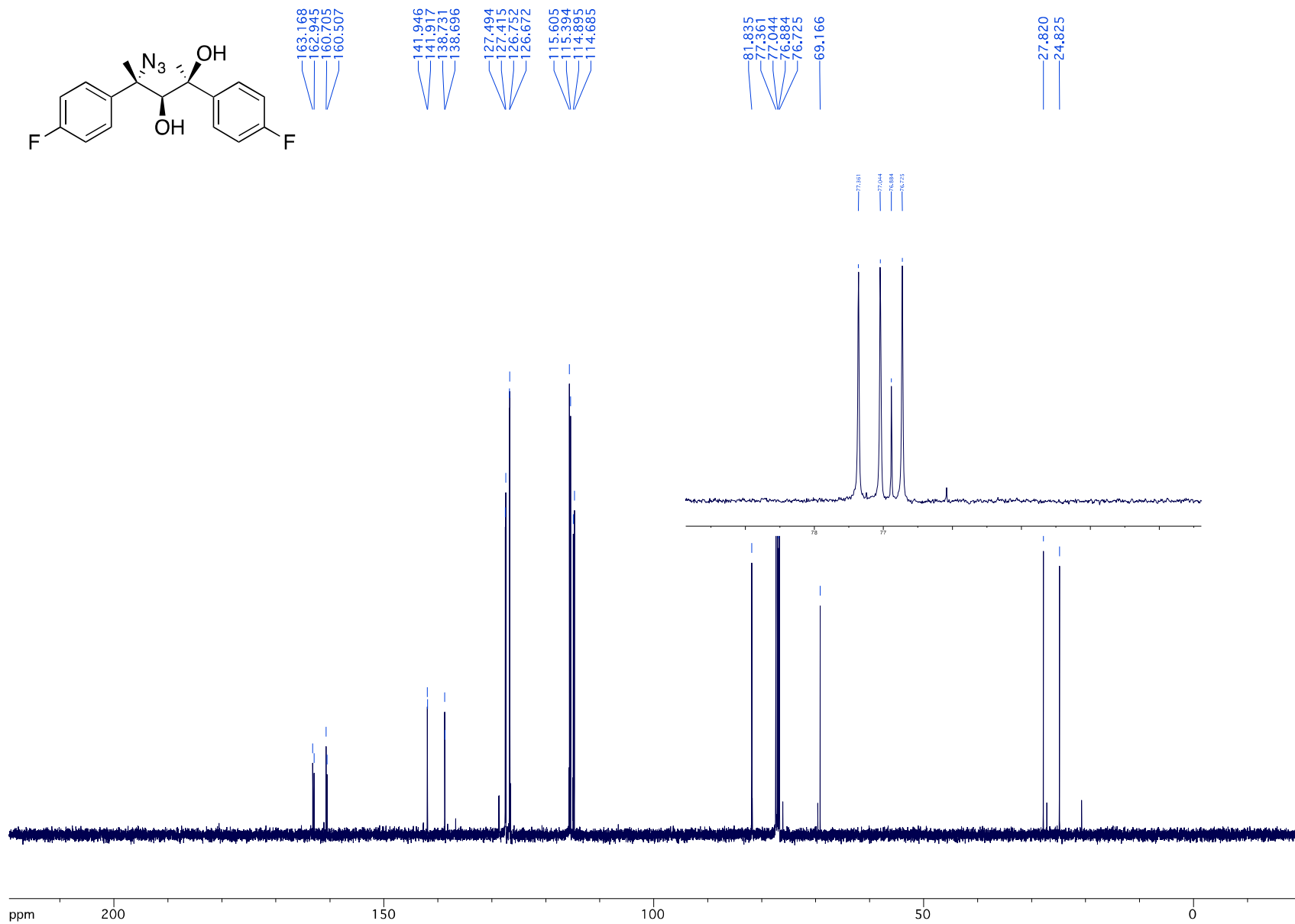
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22.395  
22.362



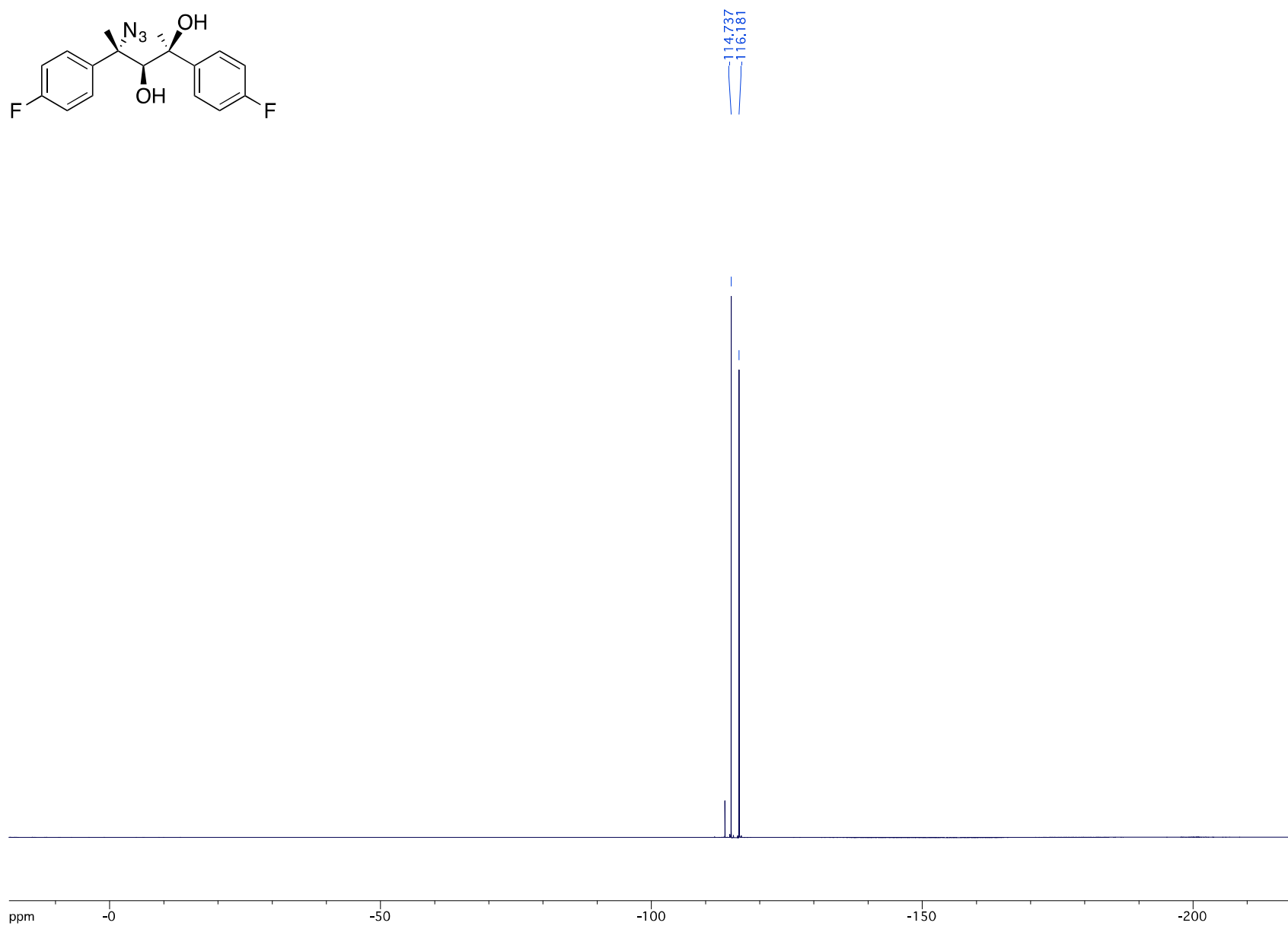
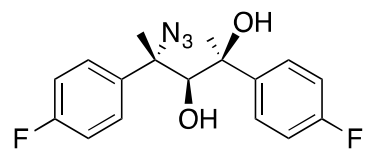
Compound 2c: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



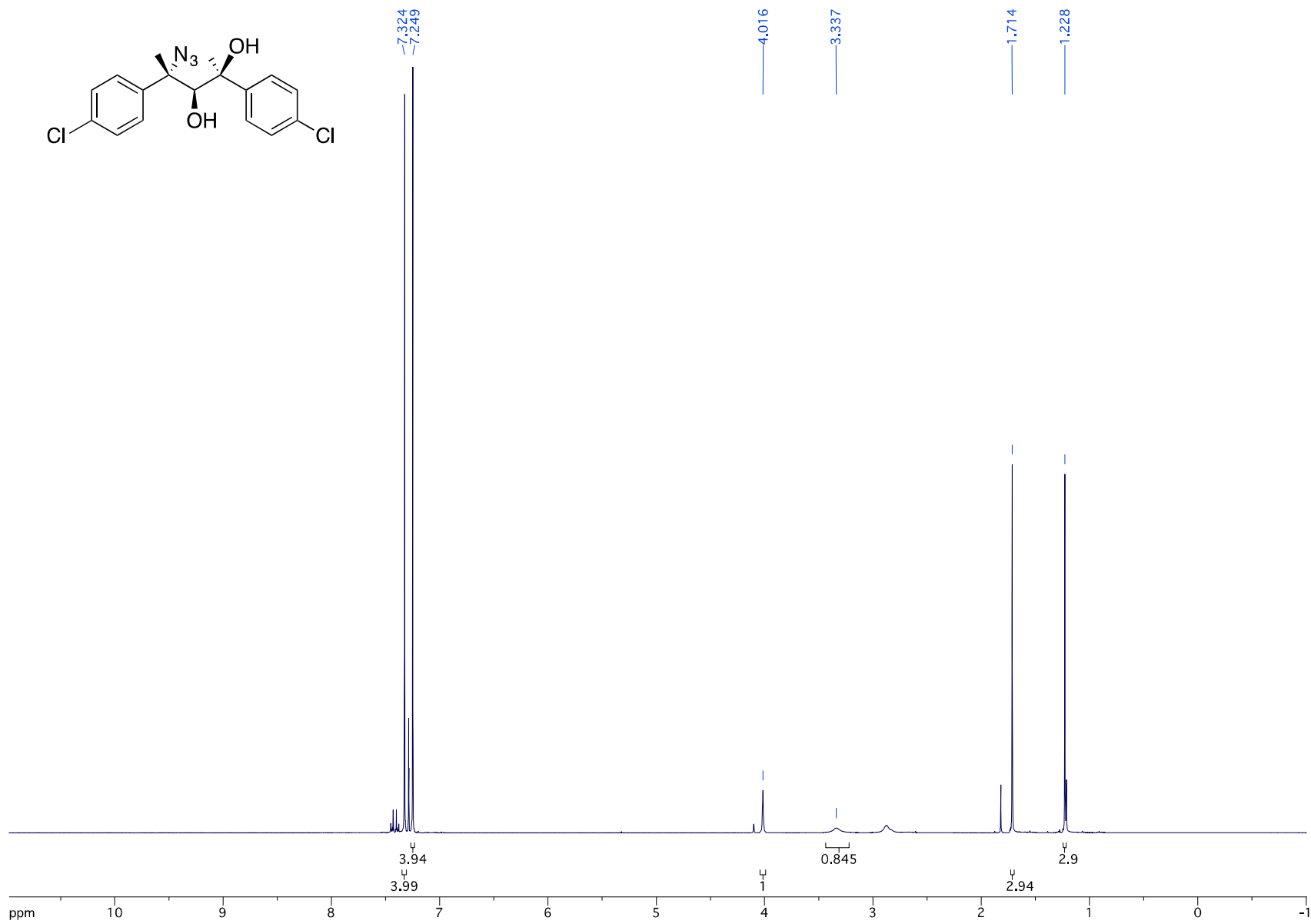
Compound 2d: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



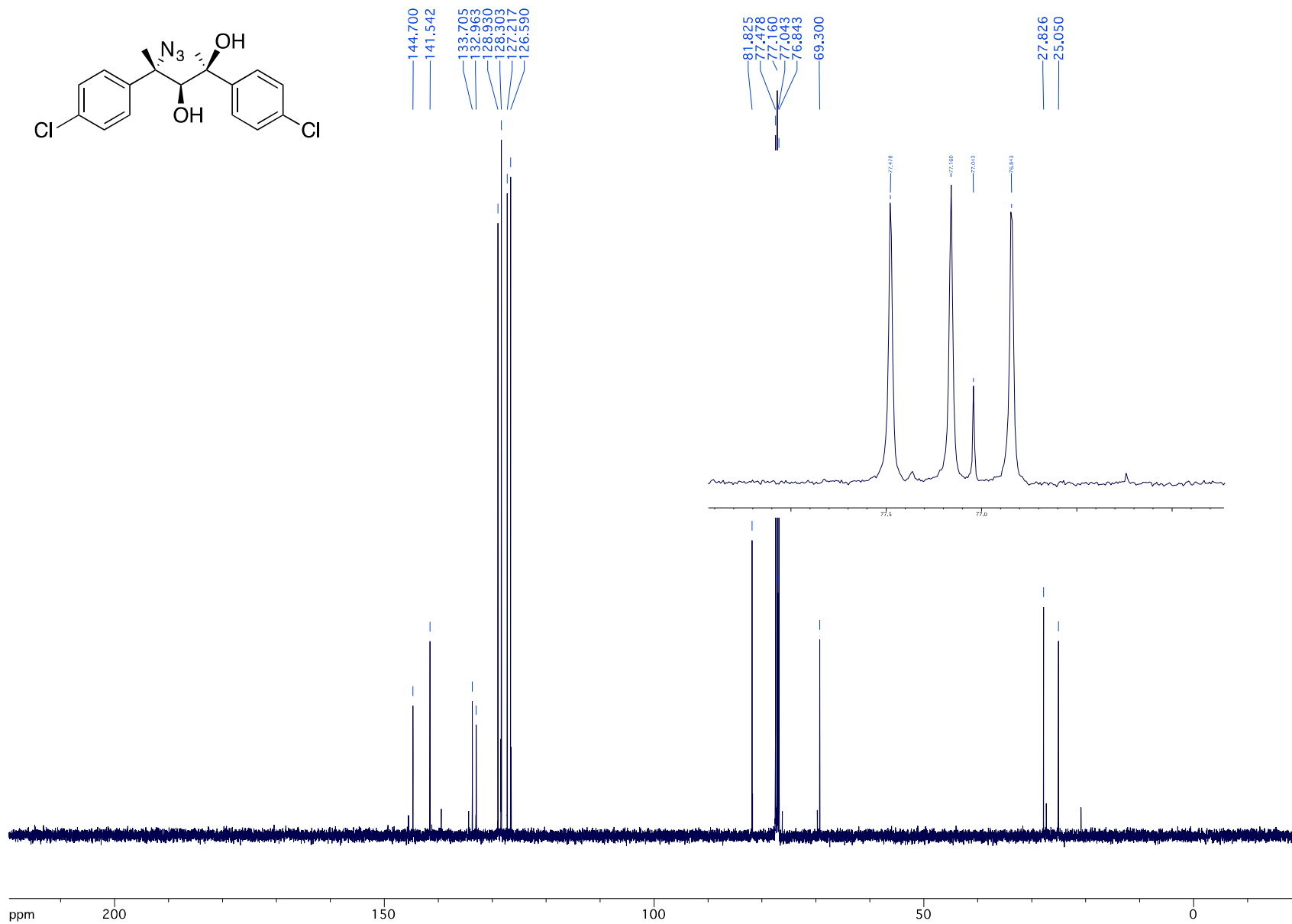
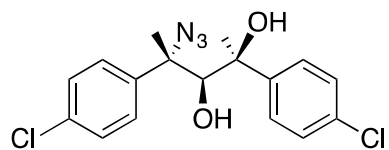
Compound 2d: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



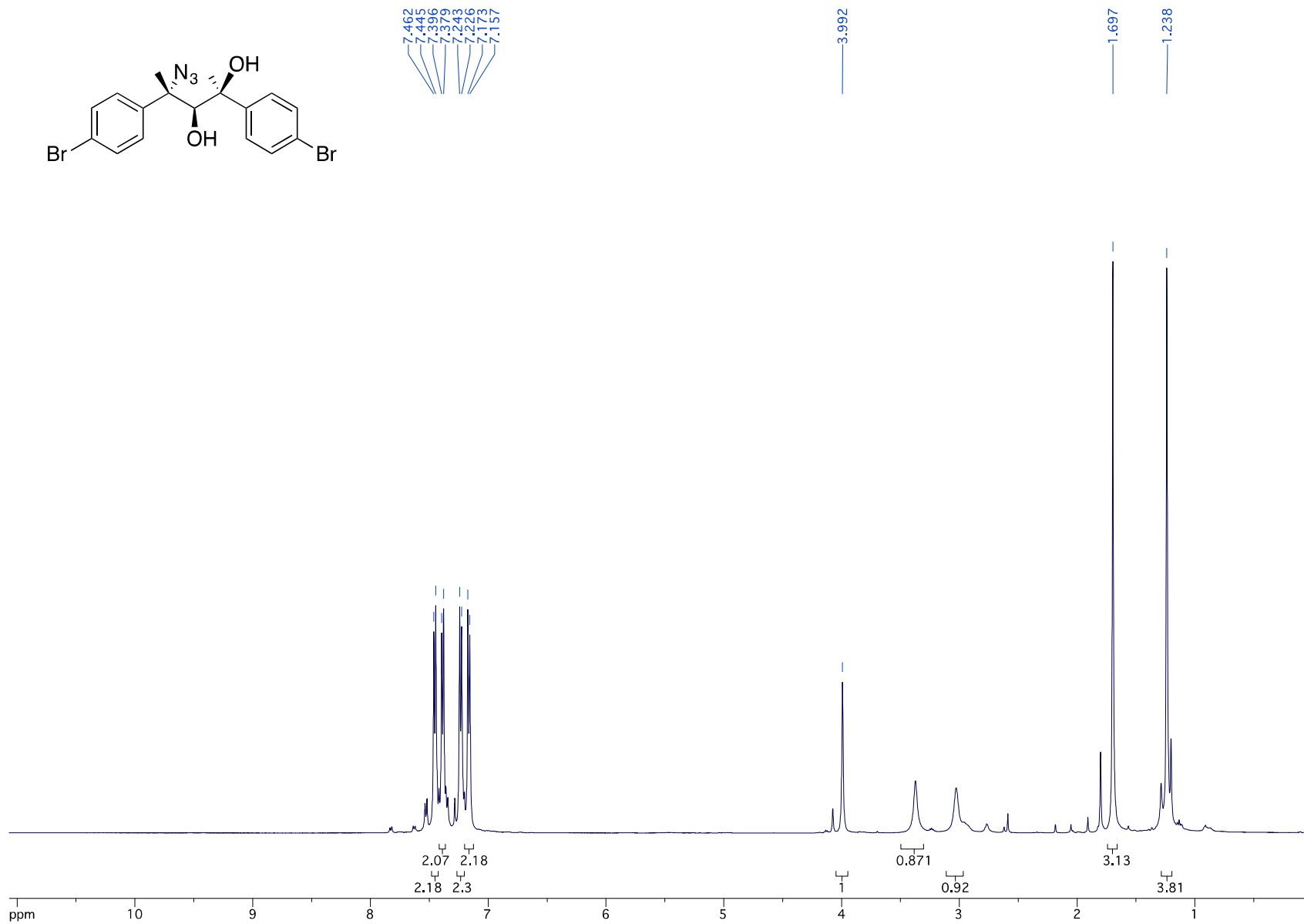
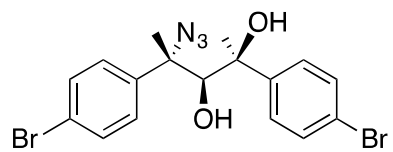
Compound 2d: 376 MHz <sup>19</sup>F NMR spectrum in CDCl<sub>3</sub>



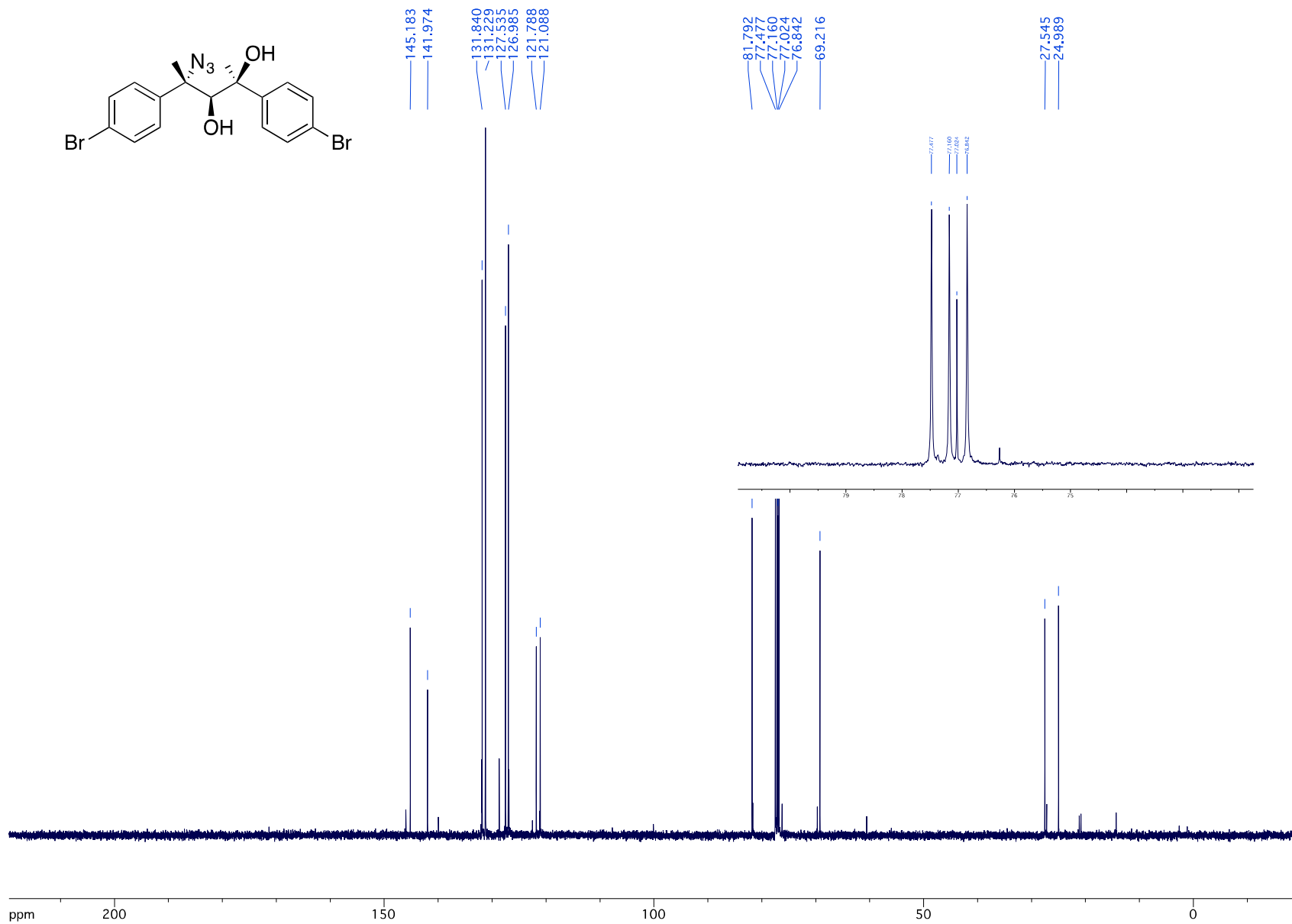
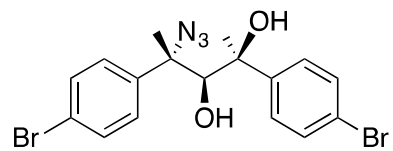
Compound 2e: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



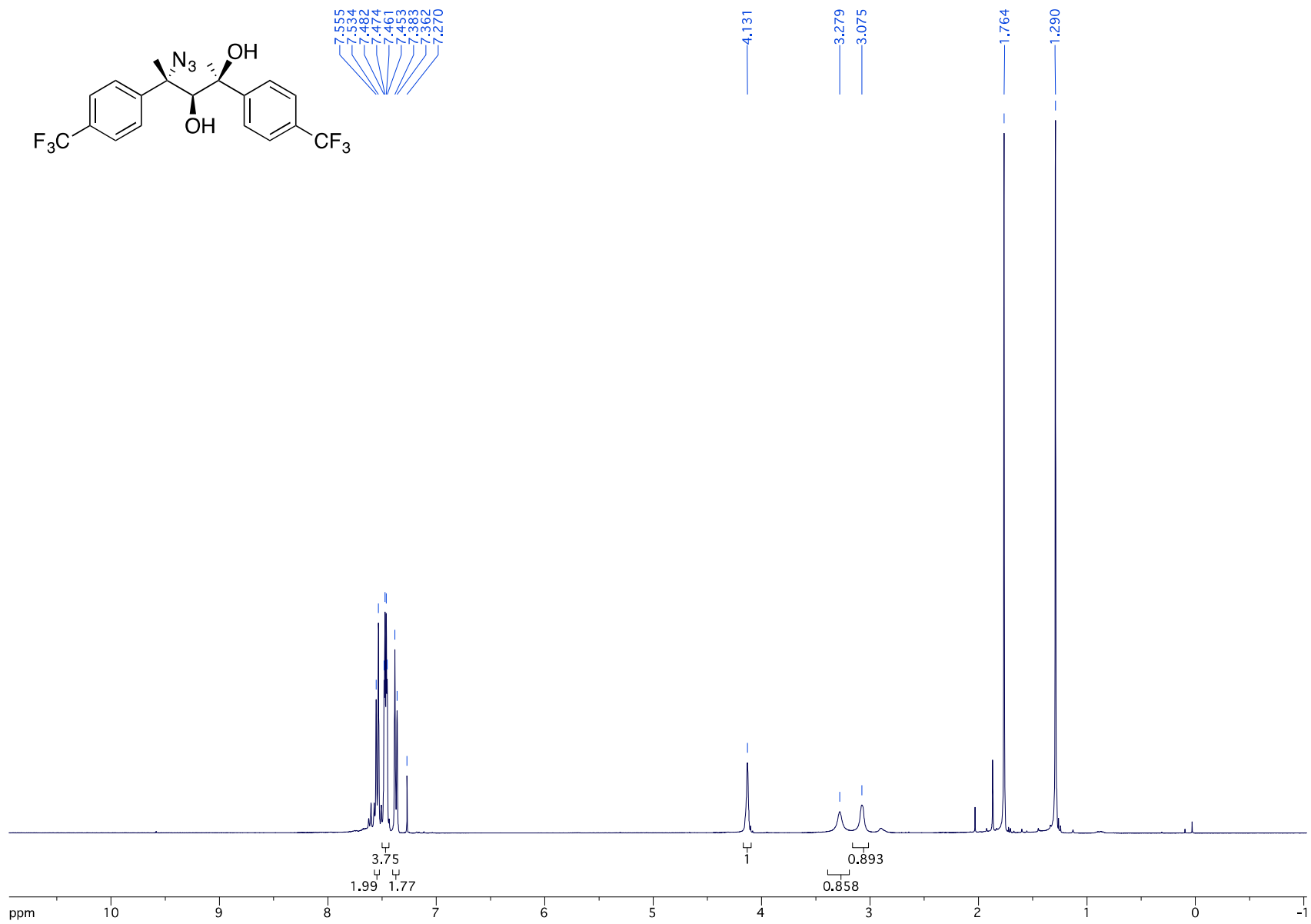
Compound 2e: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



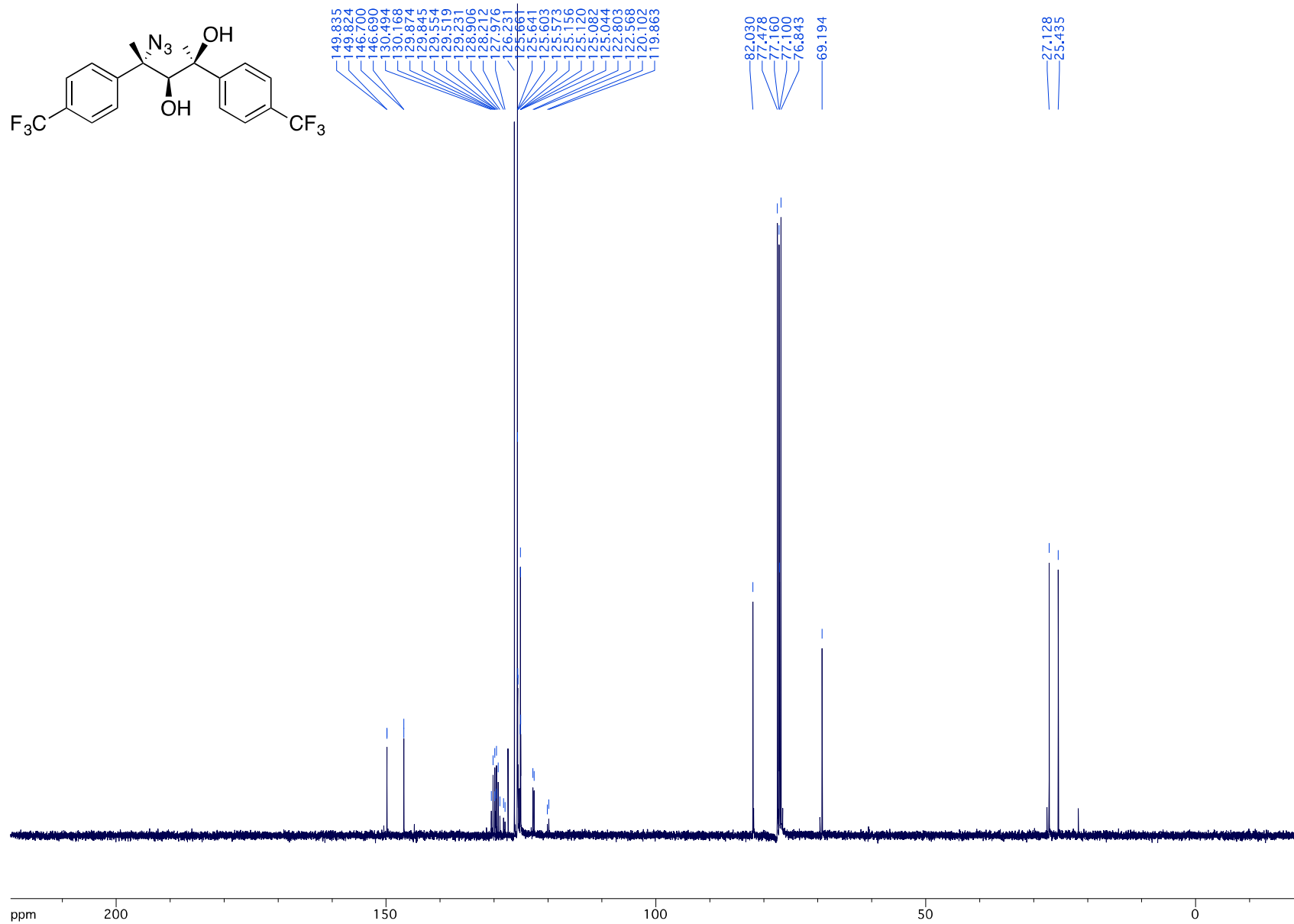
Compound 2f: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



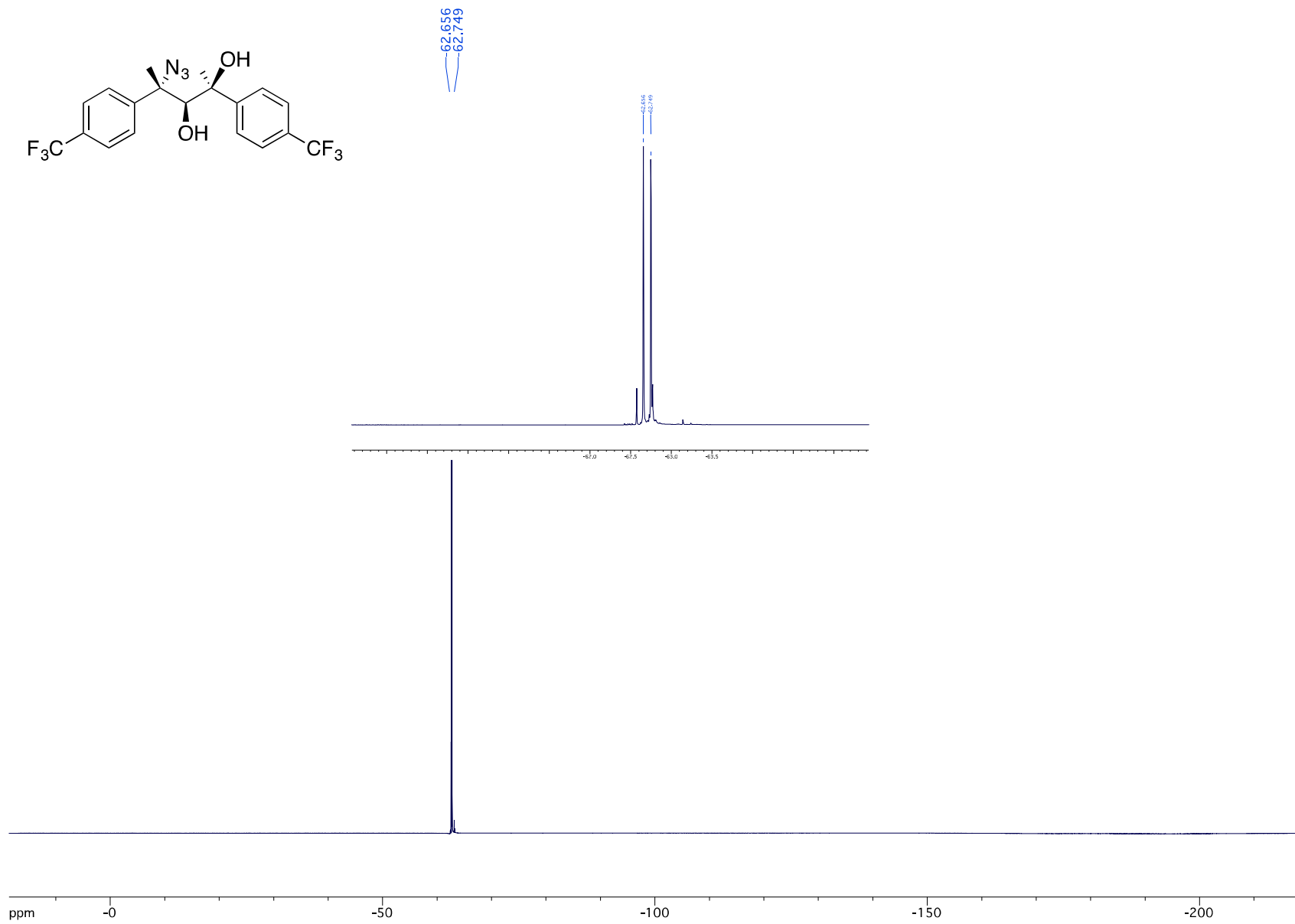
Compound 2f: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



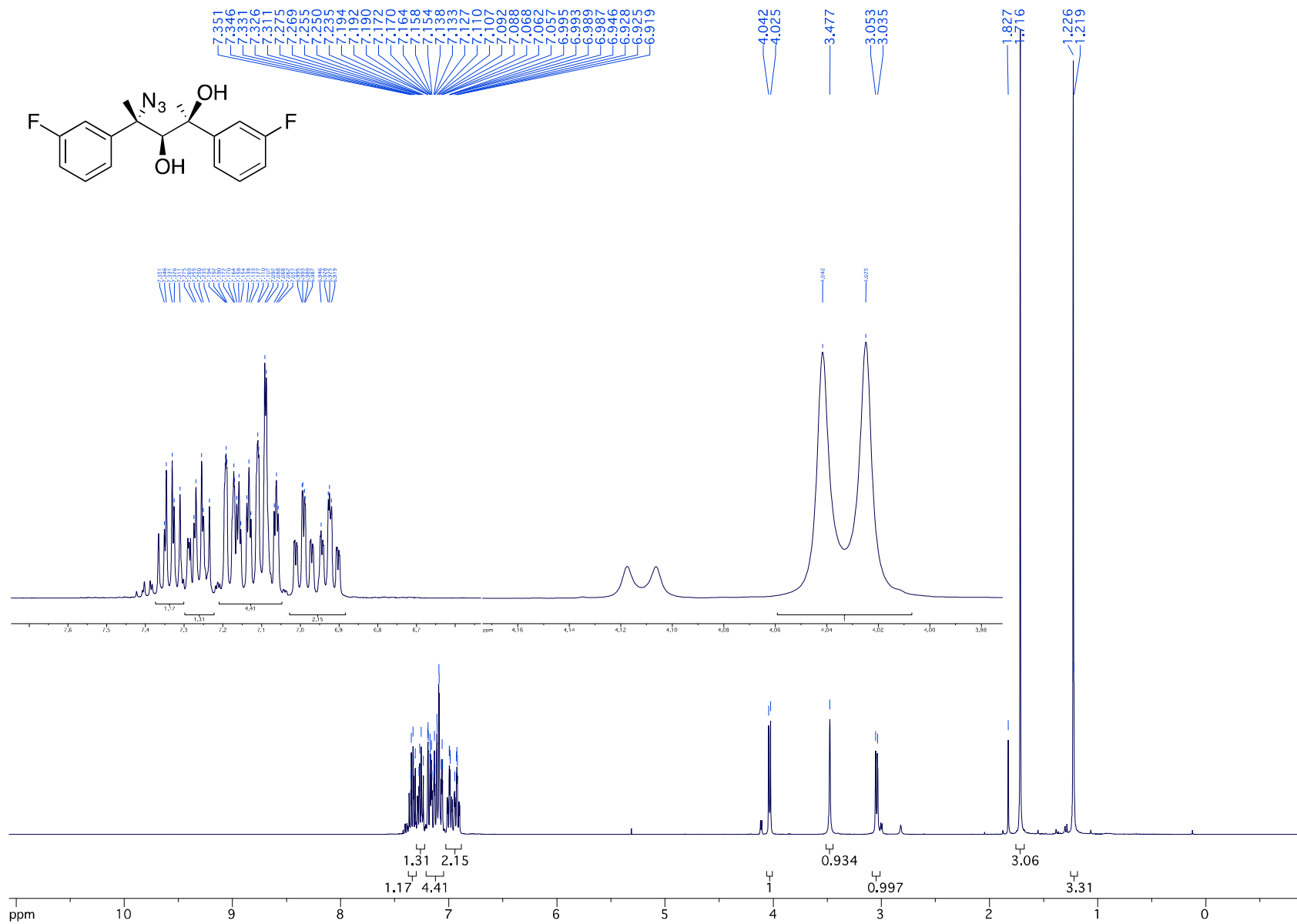
Compound 2g: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



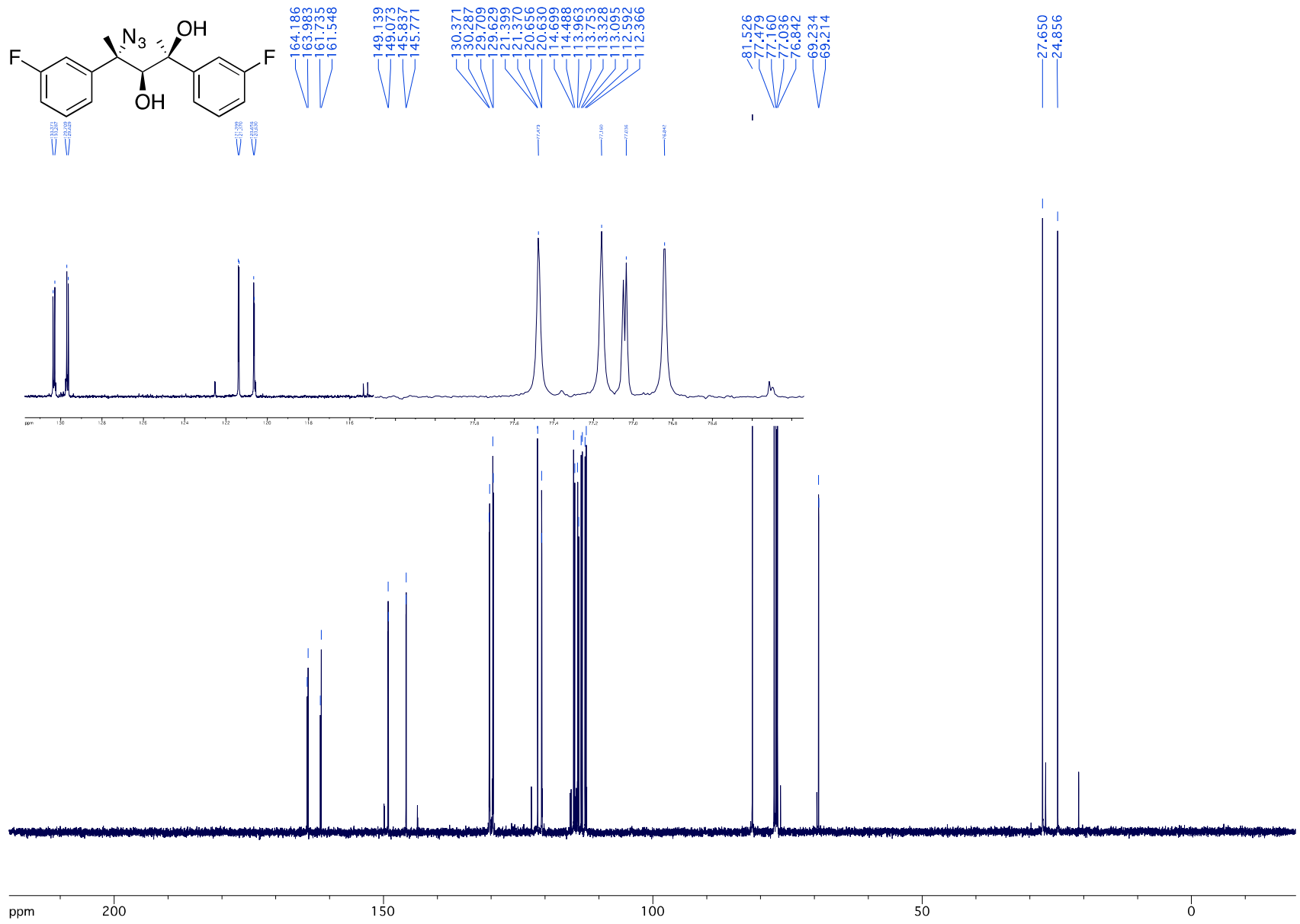
Compound 2g: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



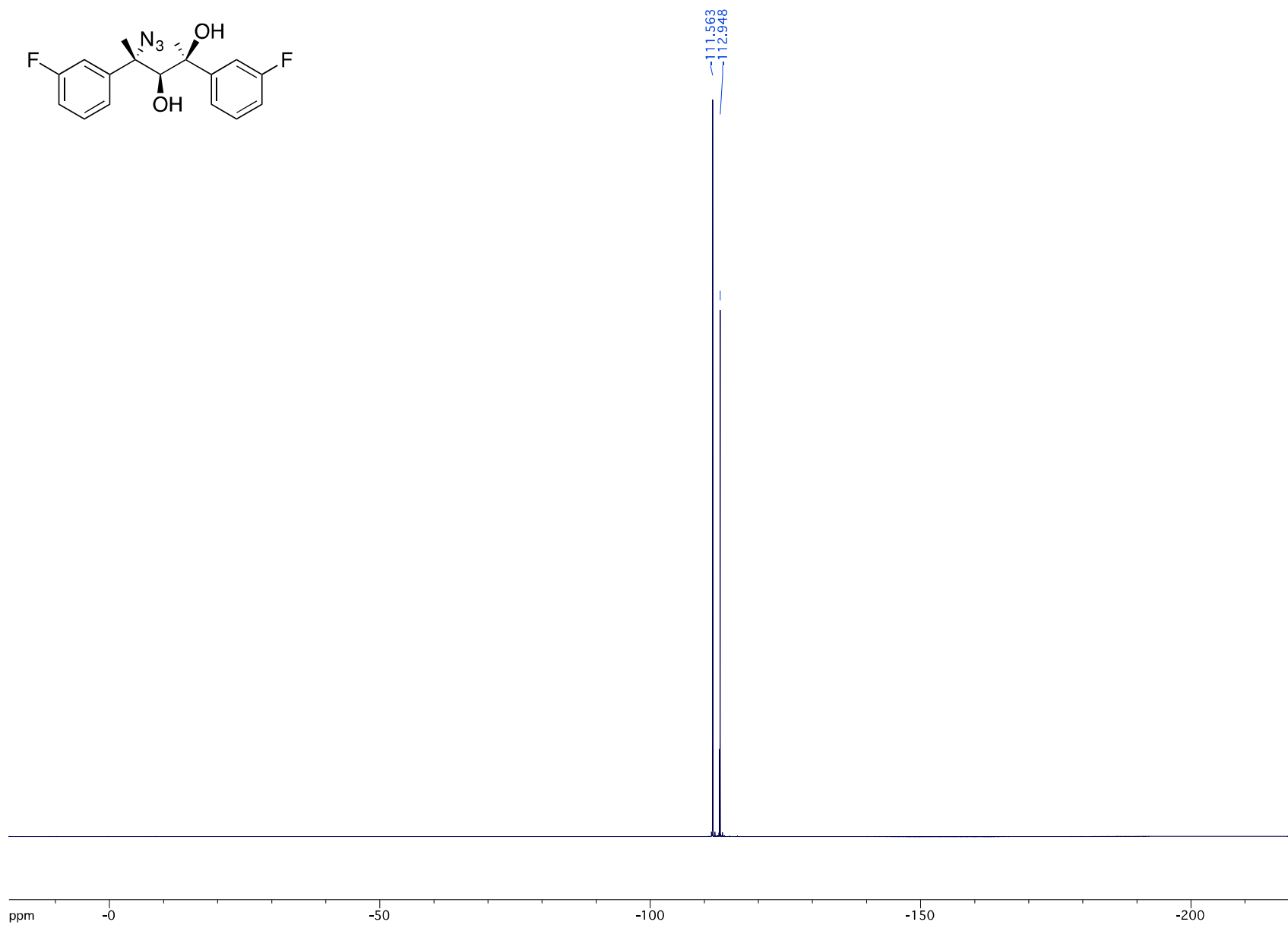
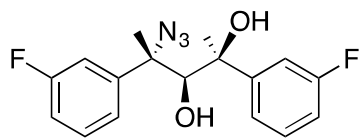
Compound 2g: 376 MHz  $^{13}\text{F}$  NMR spectrum in  $\text{CDCl}_3$



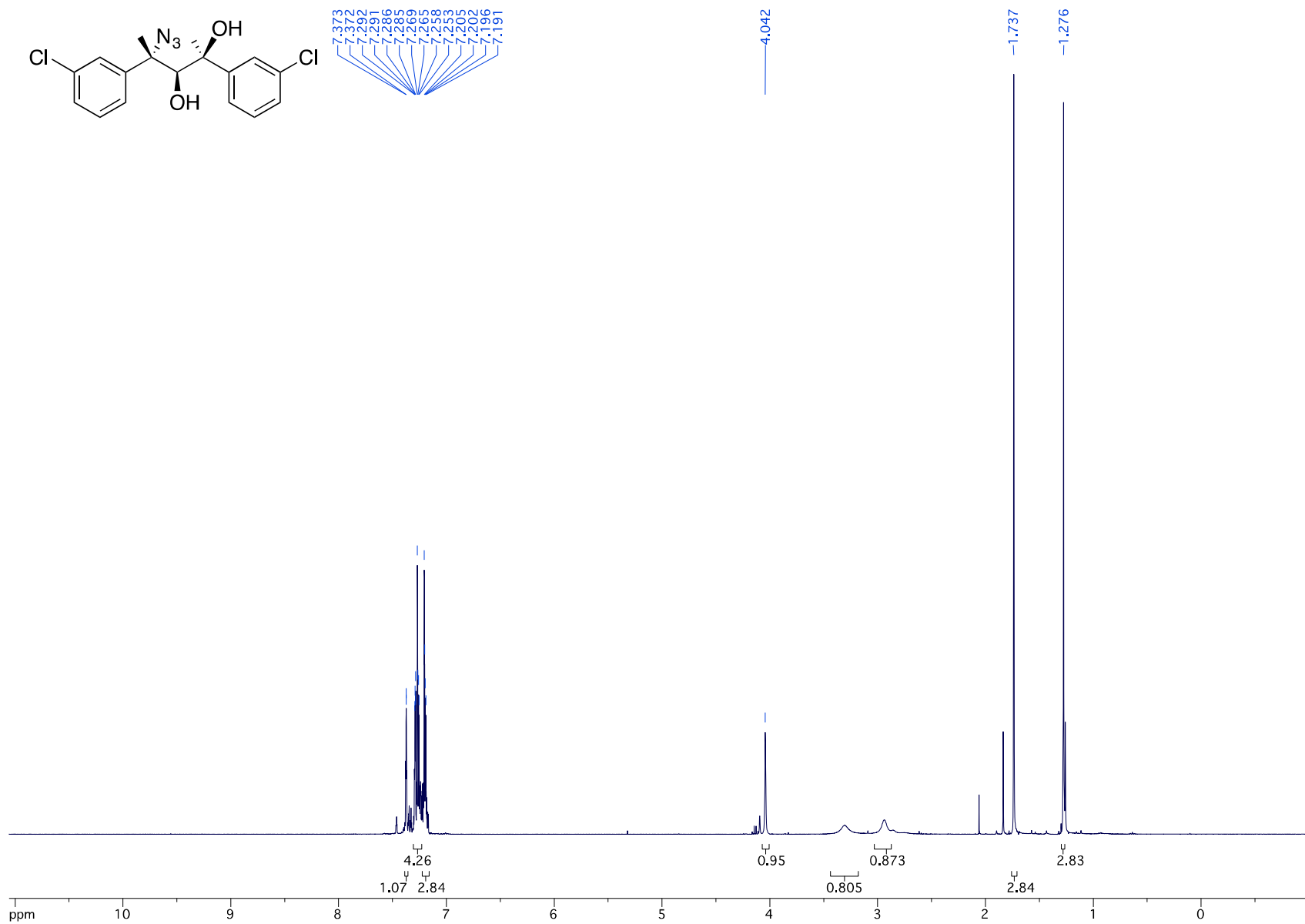
Compound 2h: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



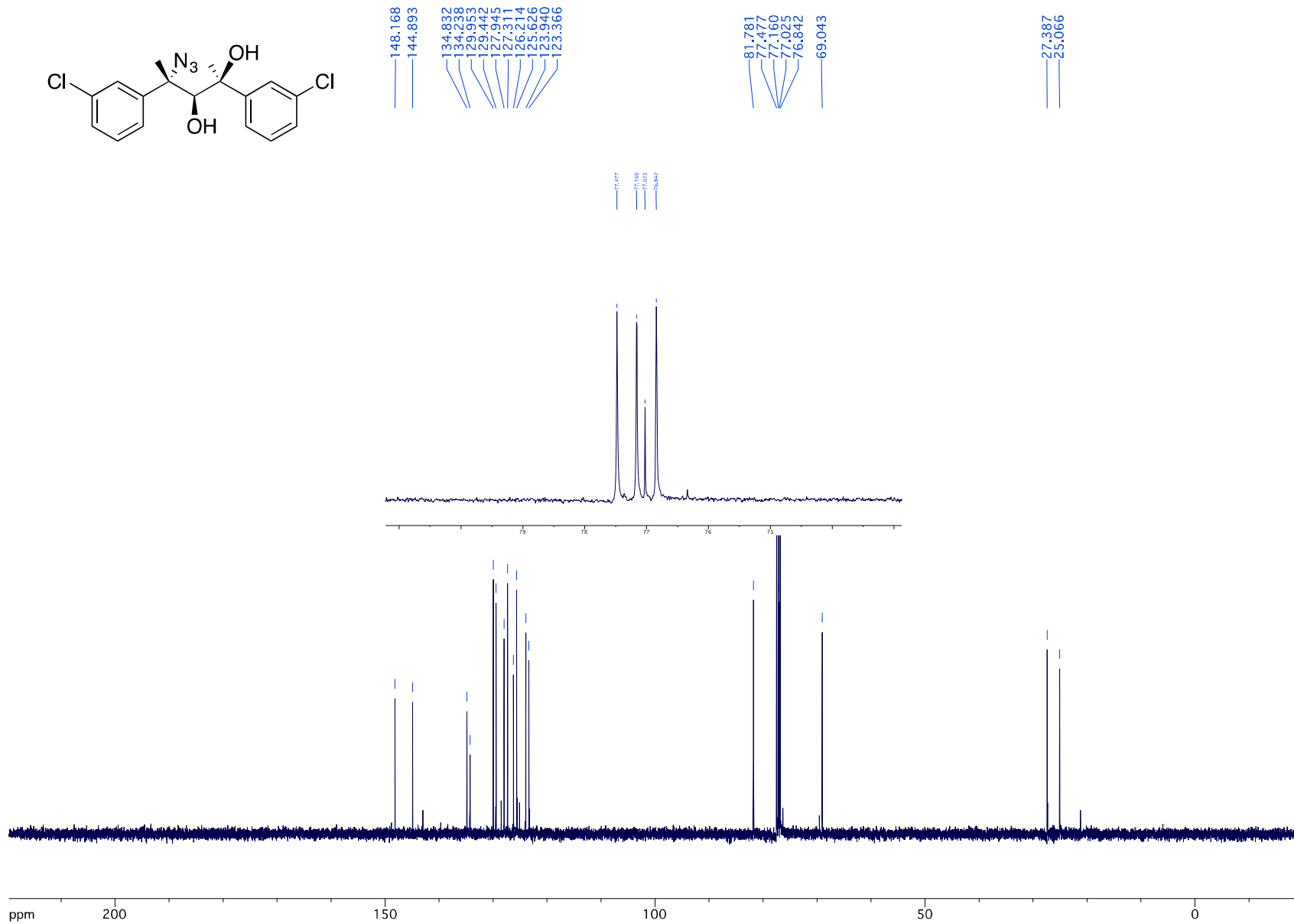
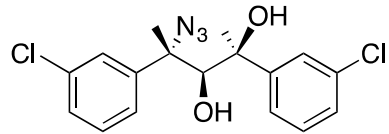
Compound 2h: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



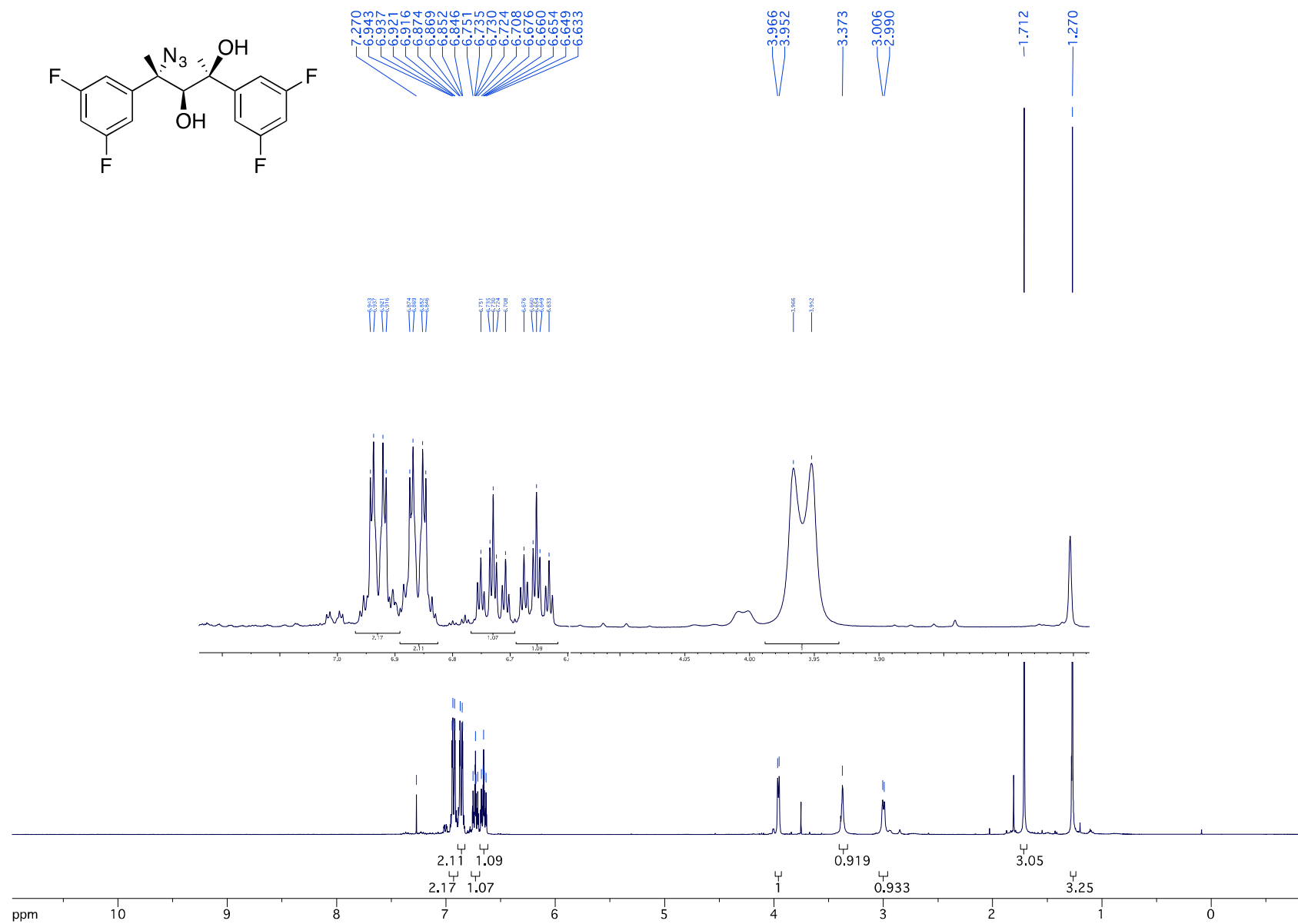
Compound 2h: 376 MHz <sup>19</sup>F NMR spectrum in CDCl<sub>3</sub>



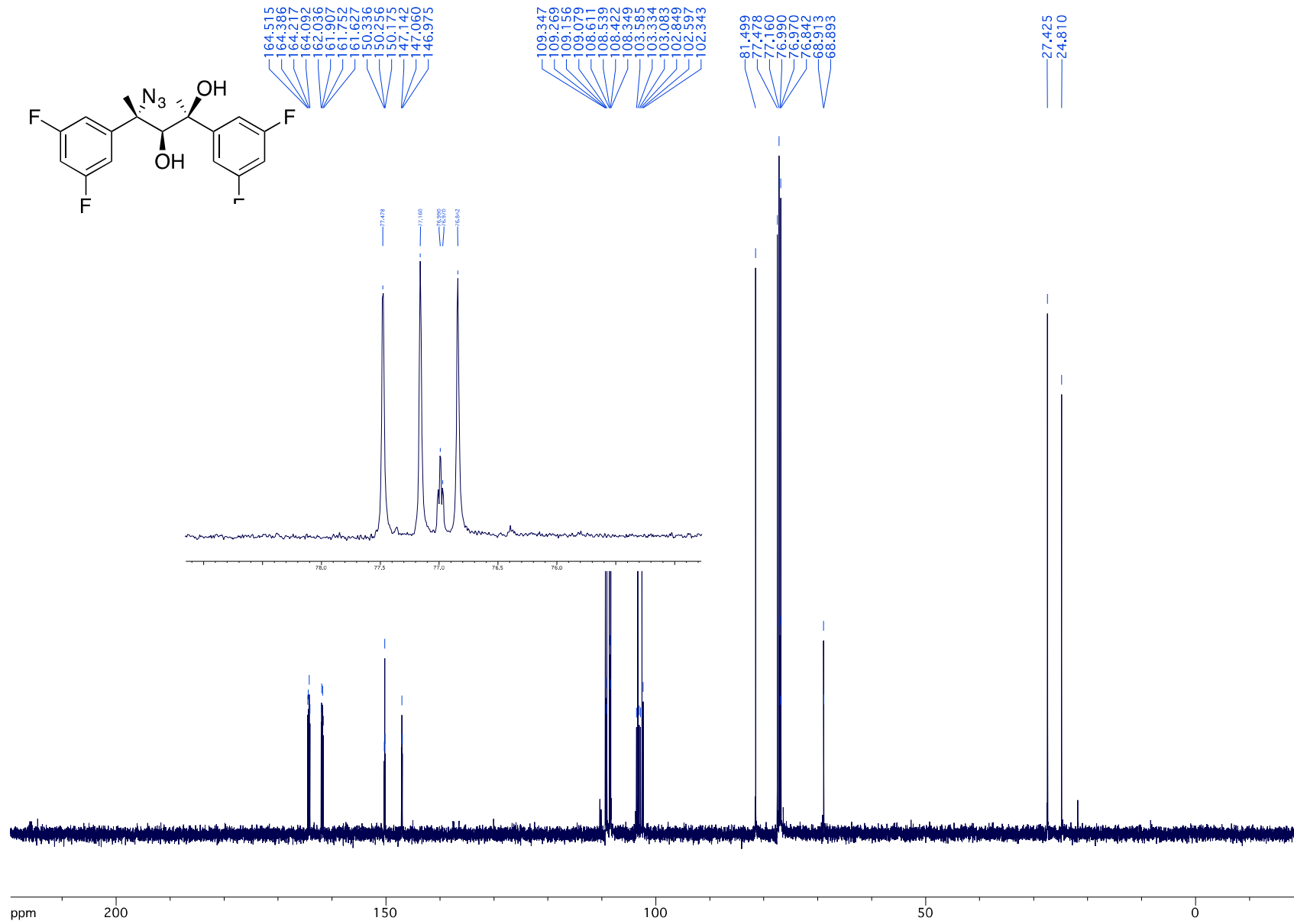
Compound 2i: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



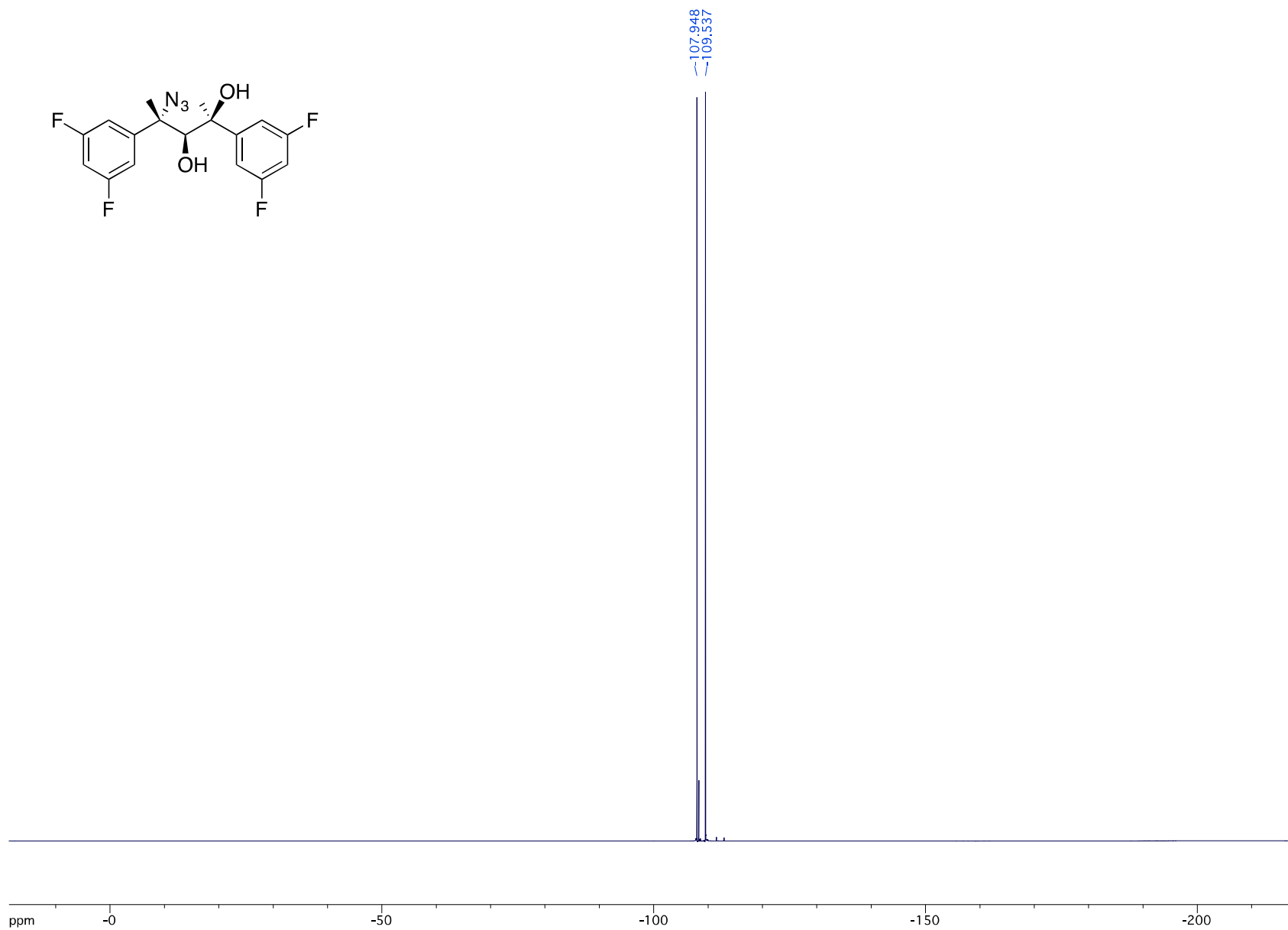
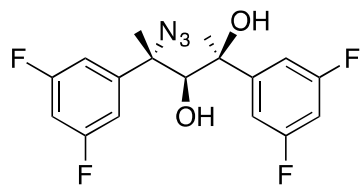
Compound 2i: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



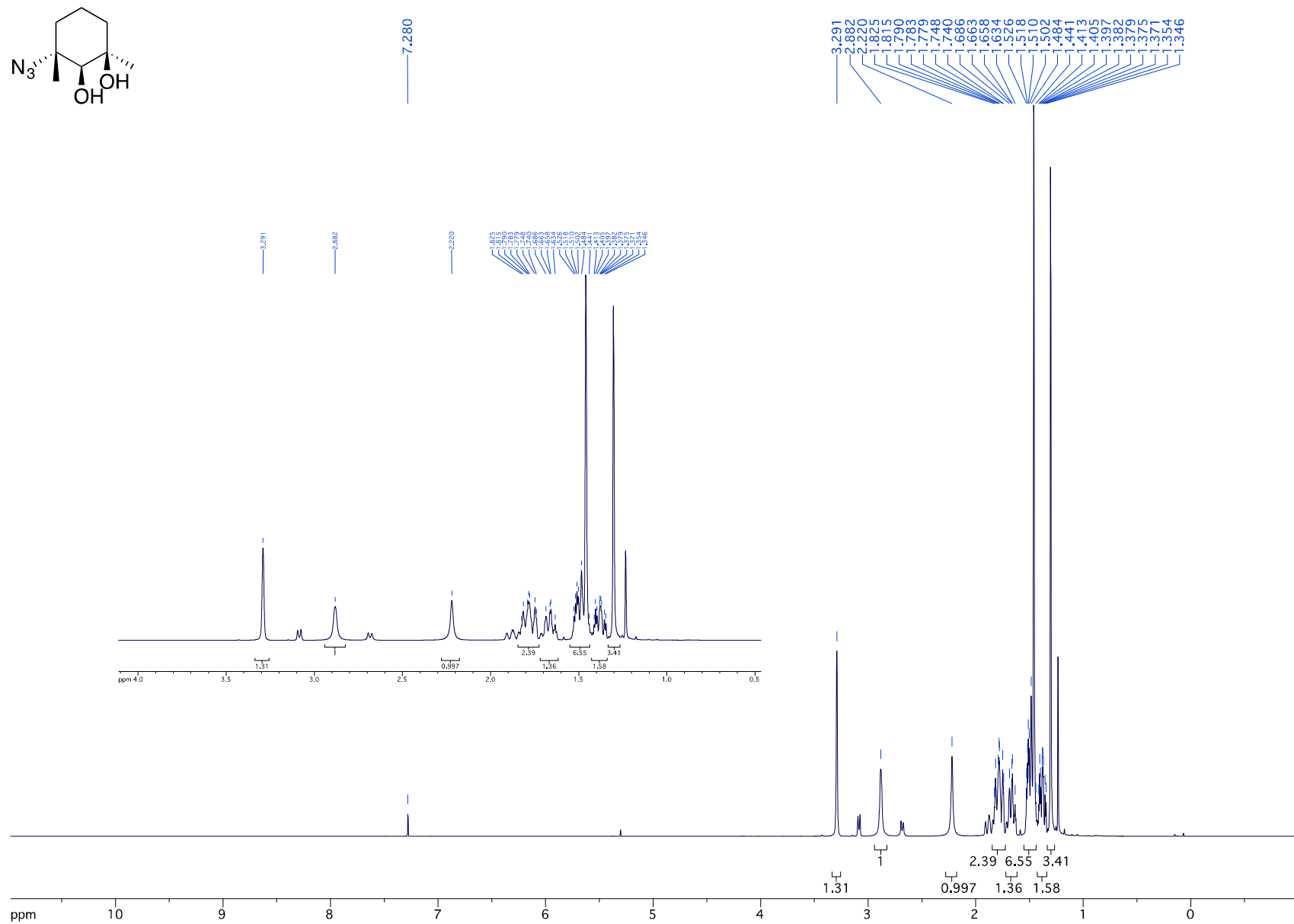
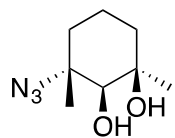
Compound 2j: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



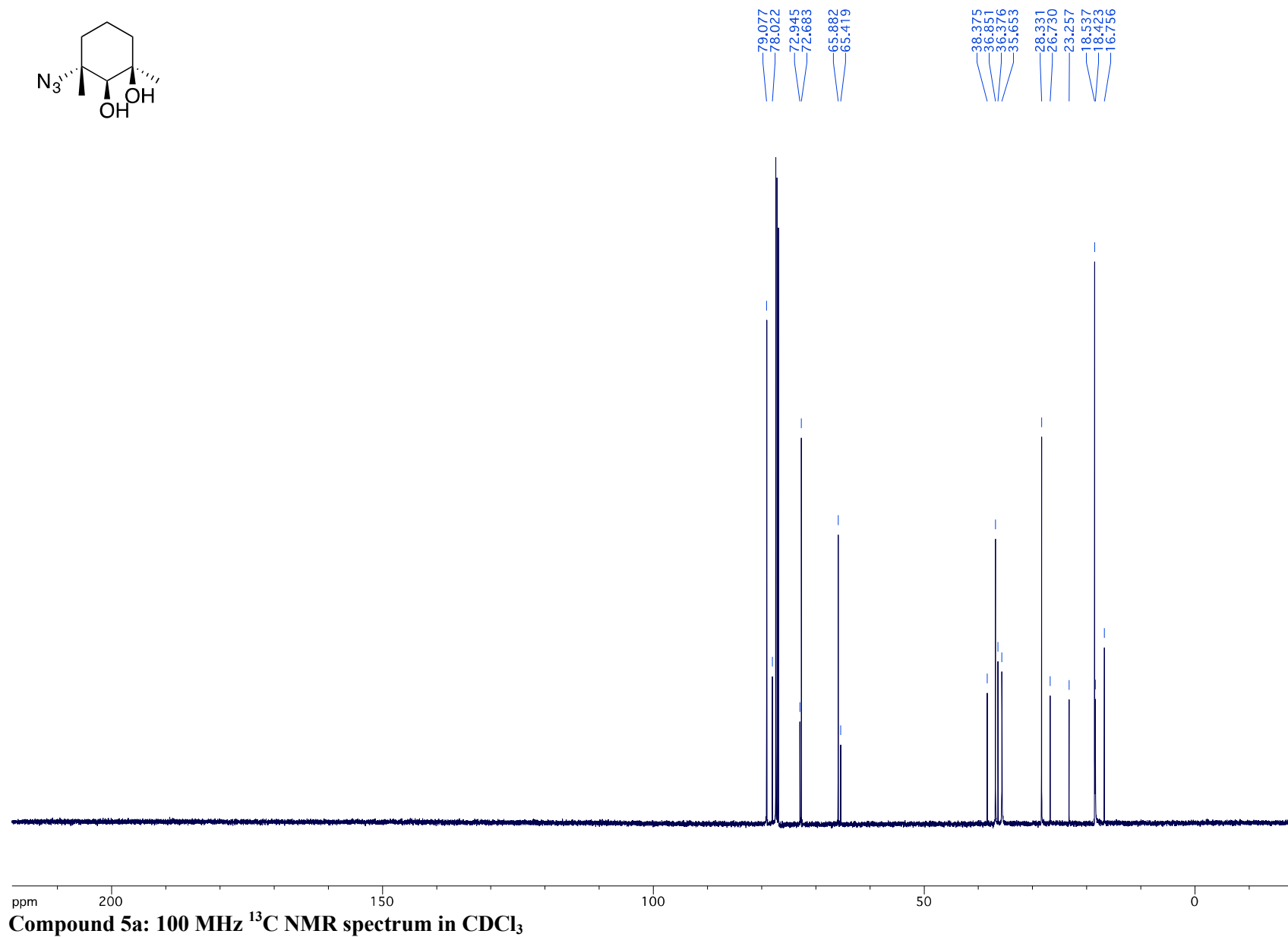
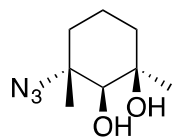
Compound 2j: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>

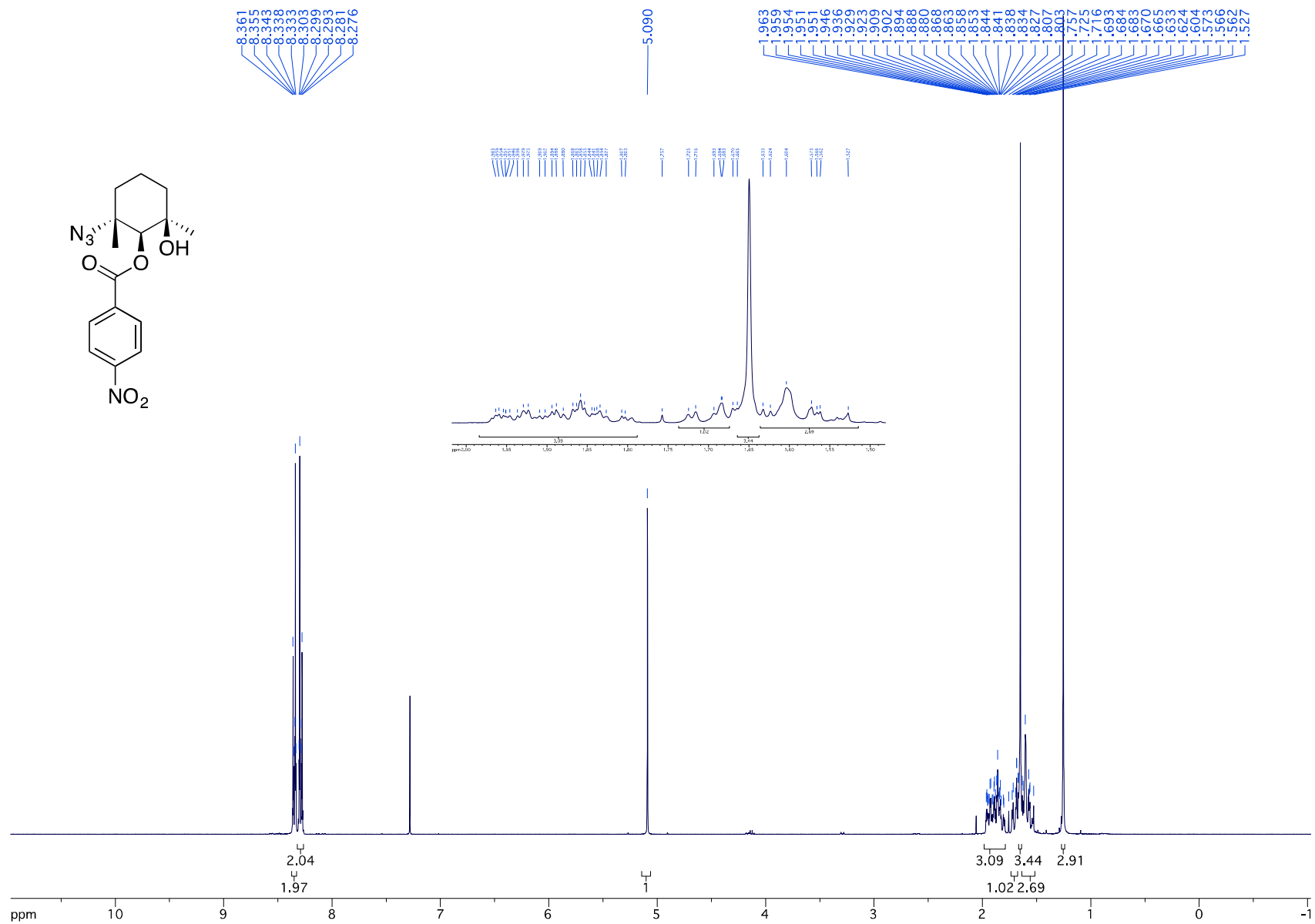


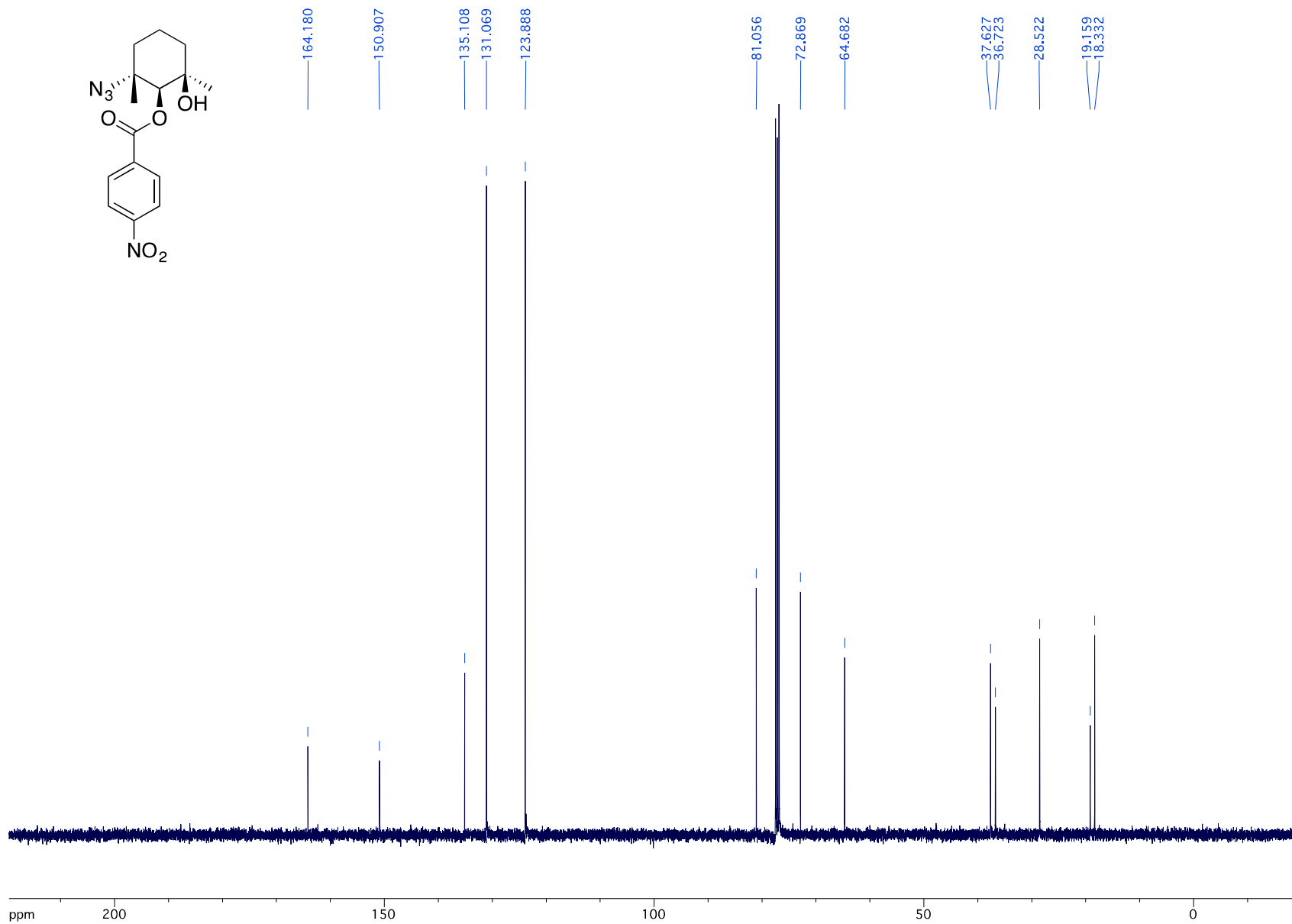
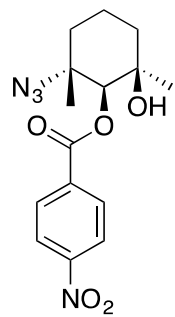
Compound 2j: 376 MHz <sup>19</sup>F NMR spectrum in CDCl<sub>3</sub>



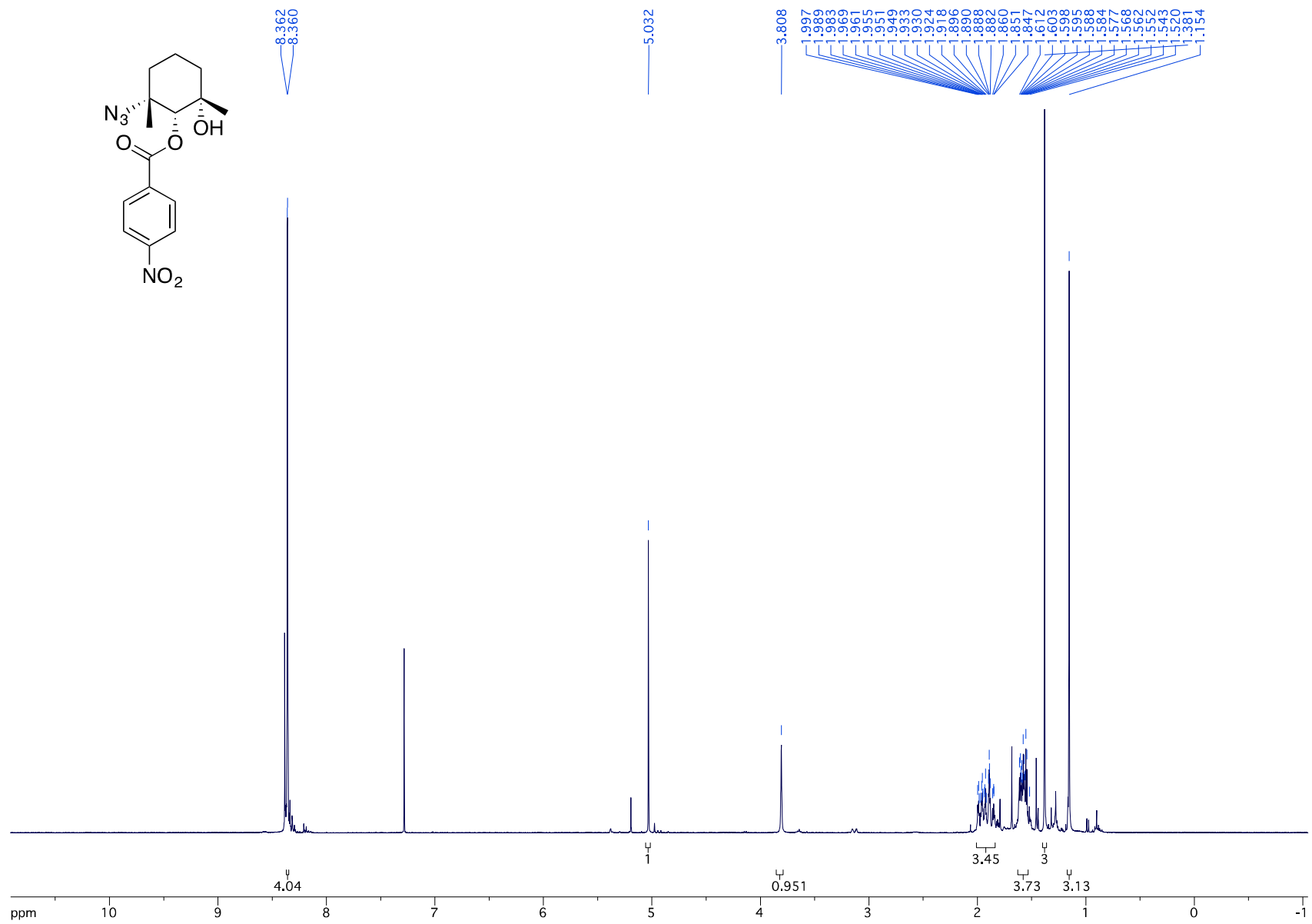
Compound 5a: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



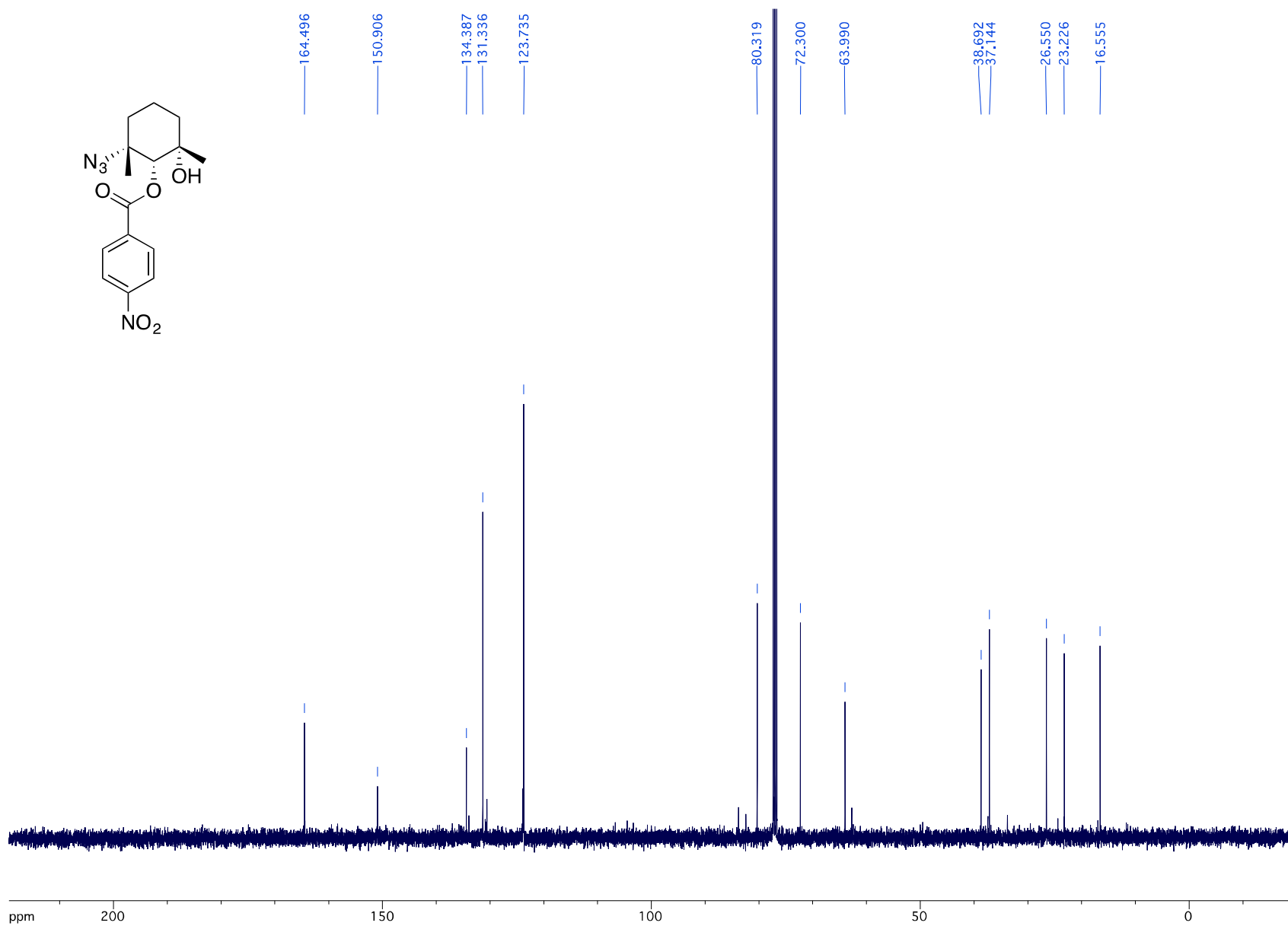
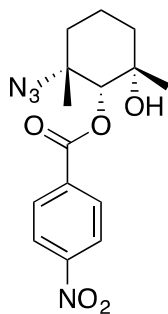




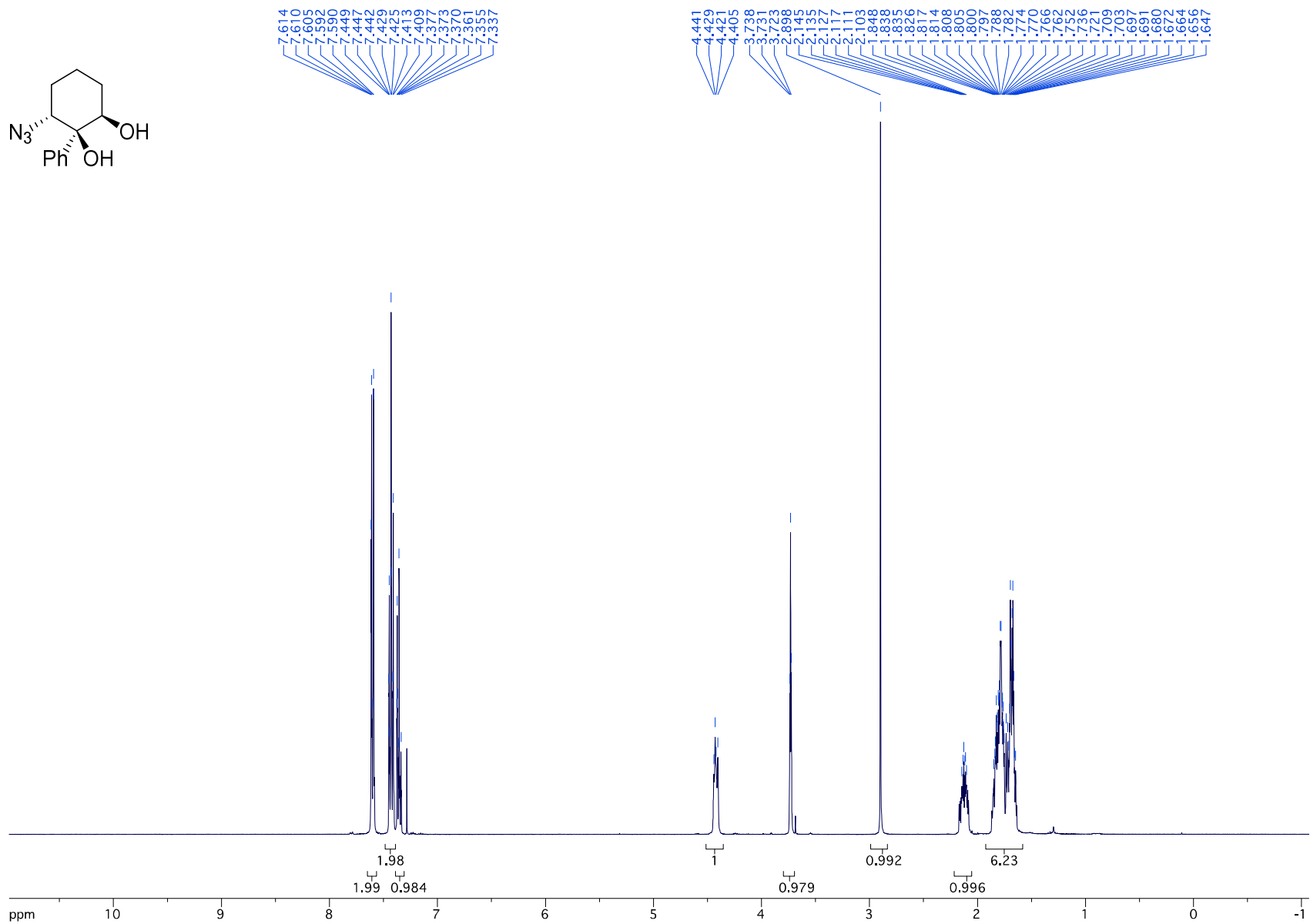
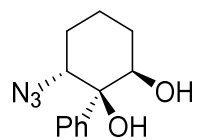
Compound S4a: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



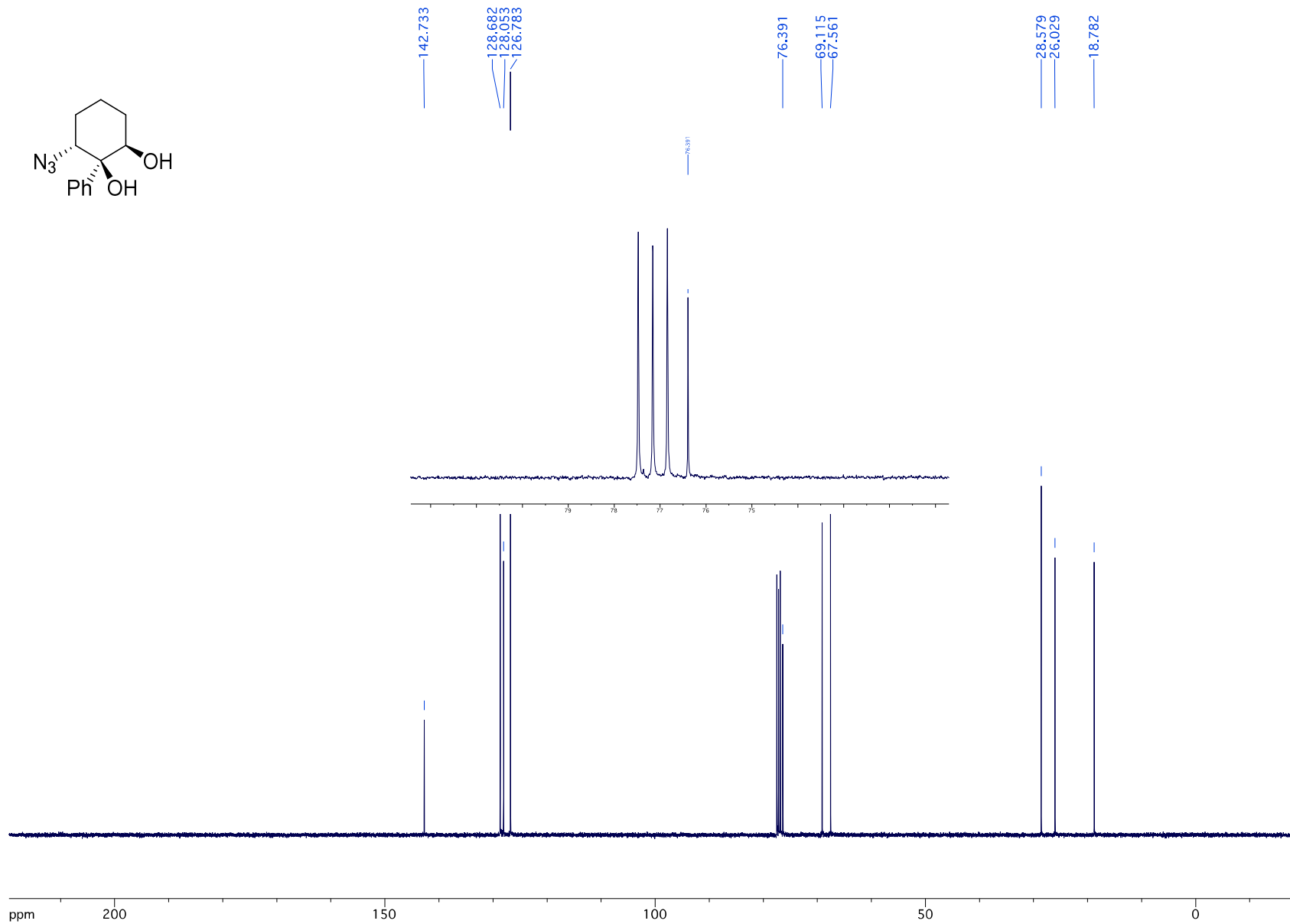
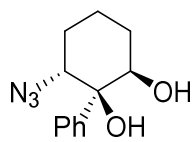
Compound S4a': 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



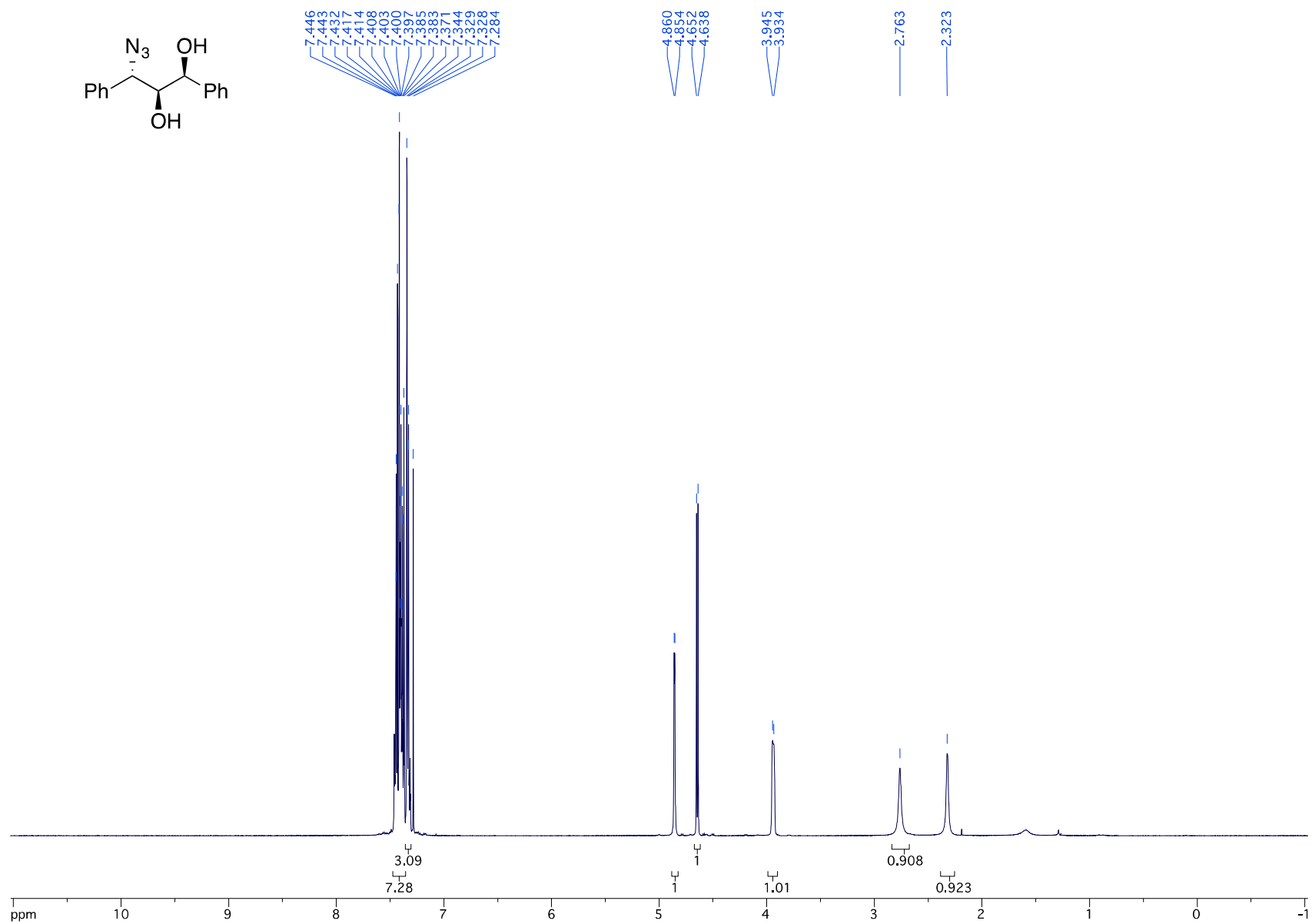
Compound S4a': 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



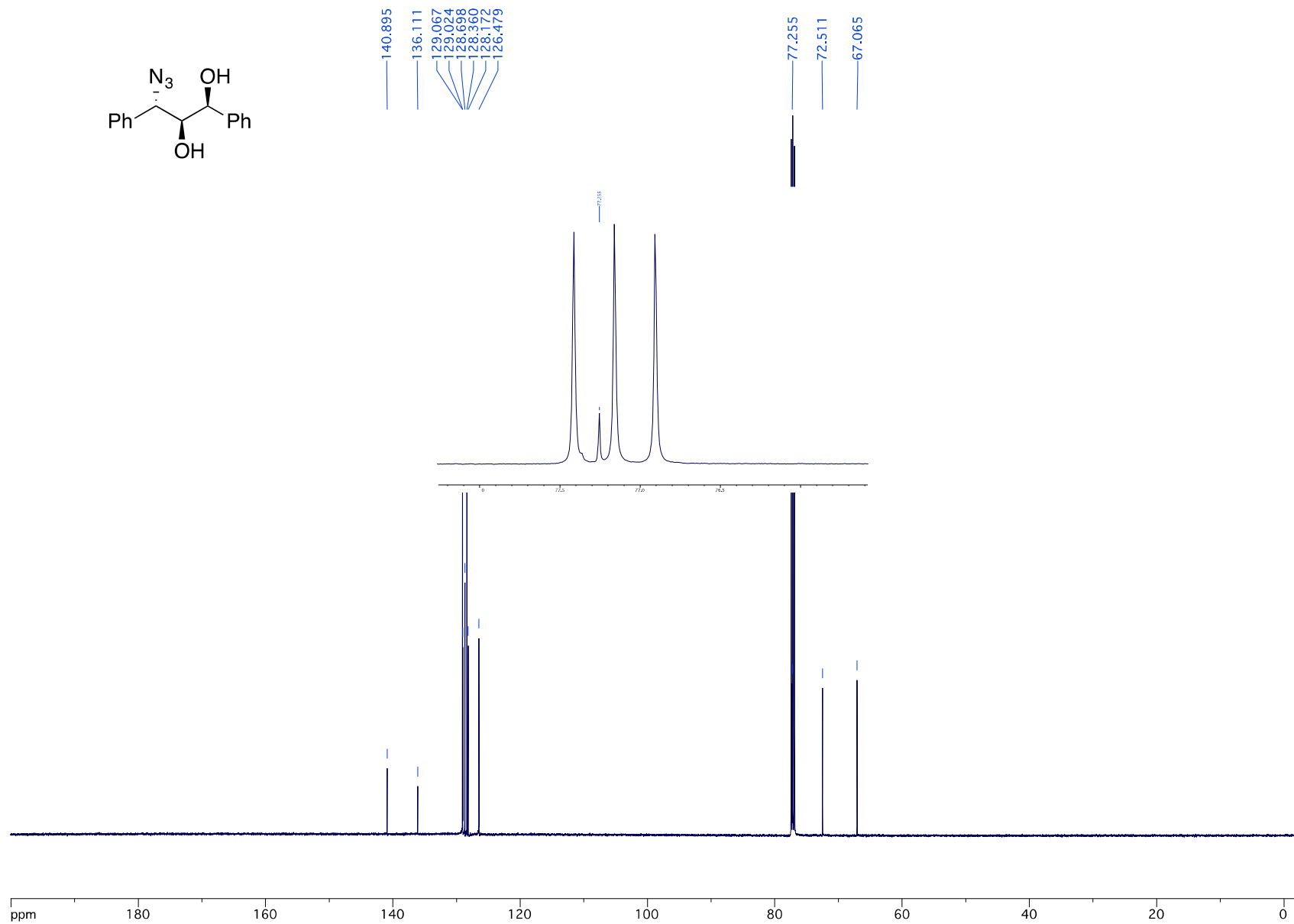
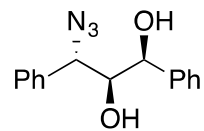
Compound 5b: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



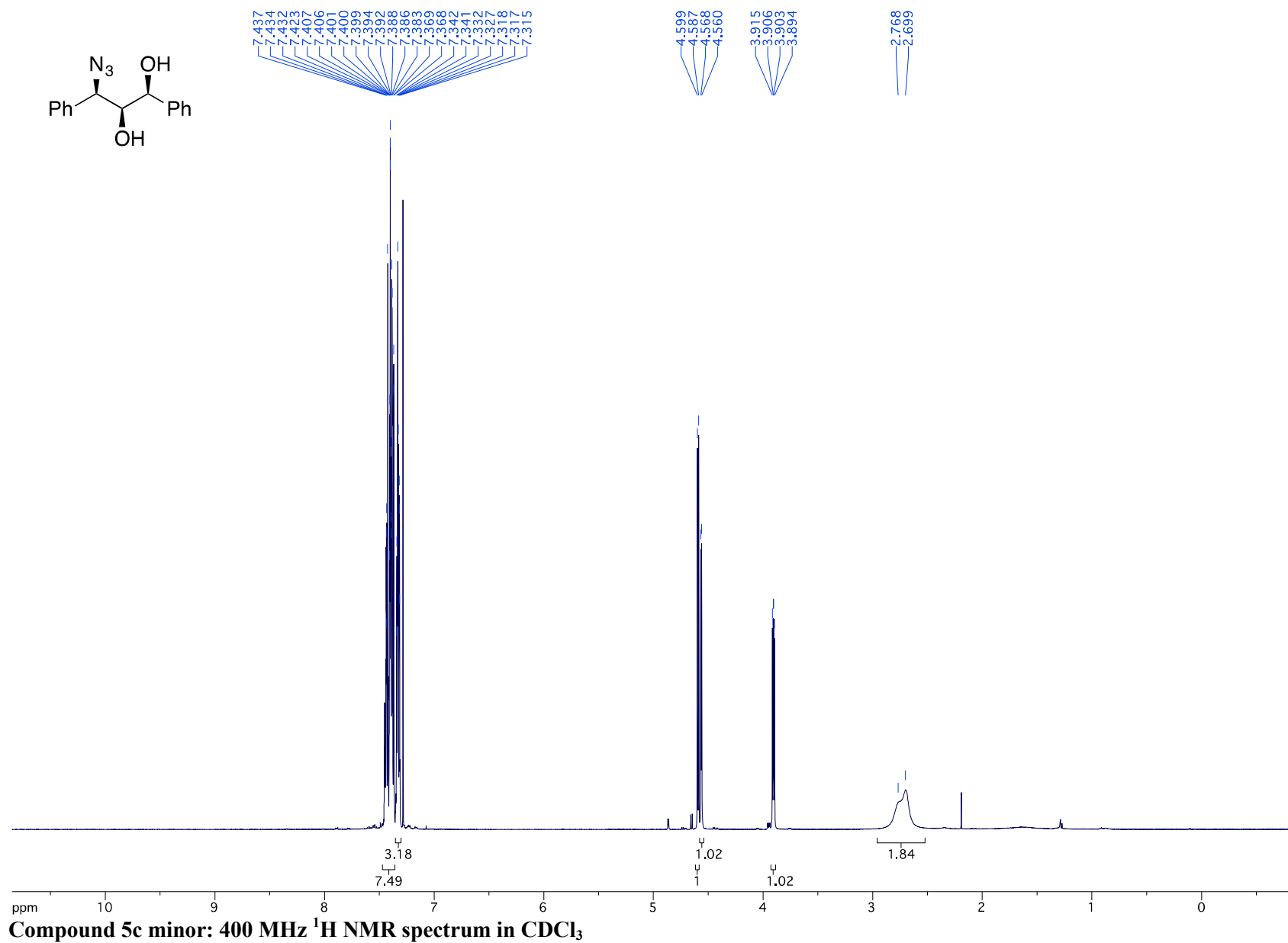
Compound 5b: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>

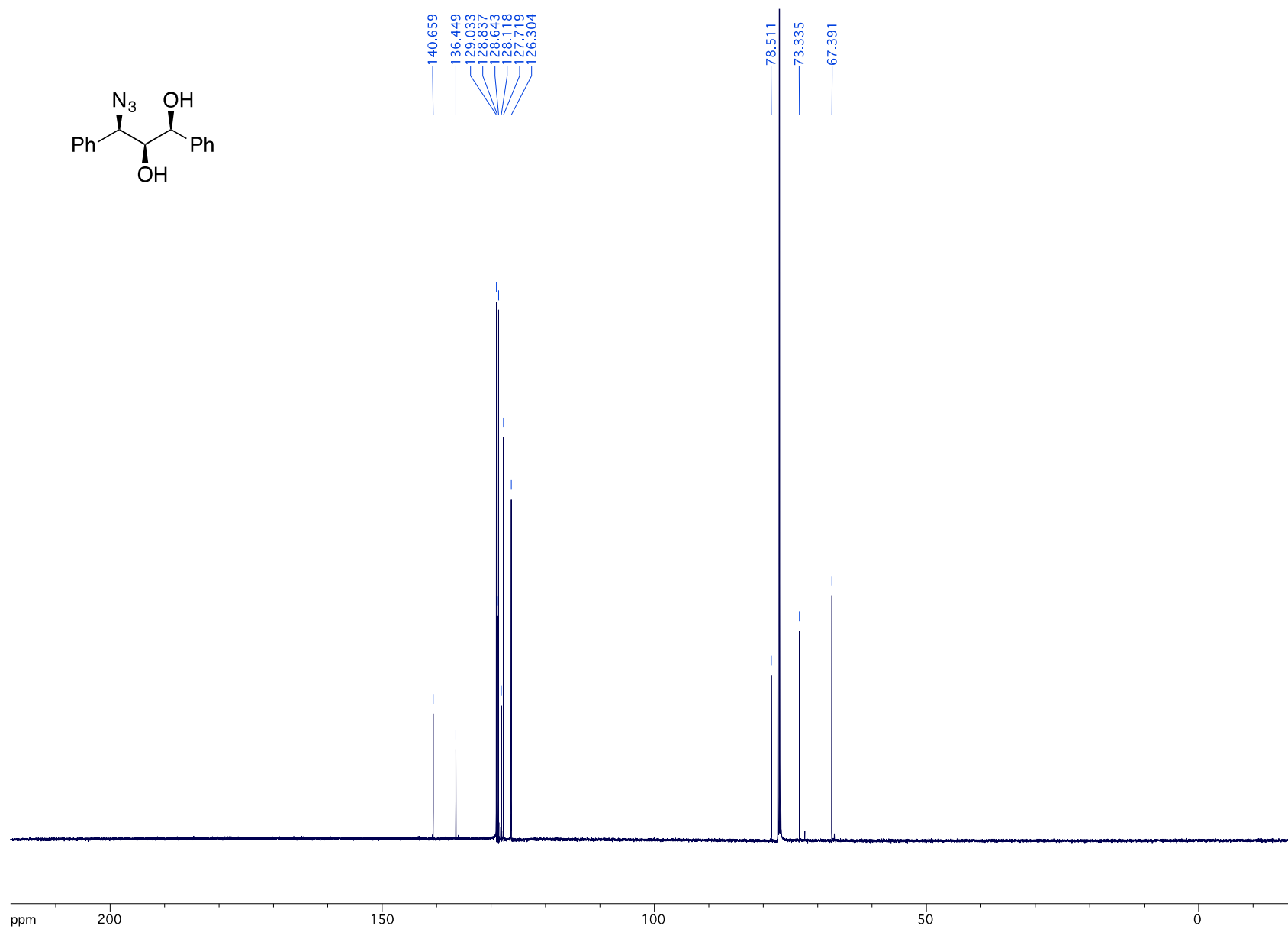
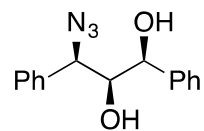


Compound 5c major: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$

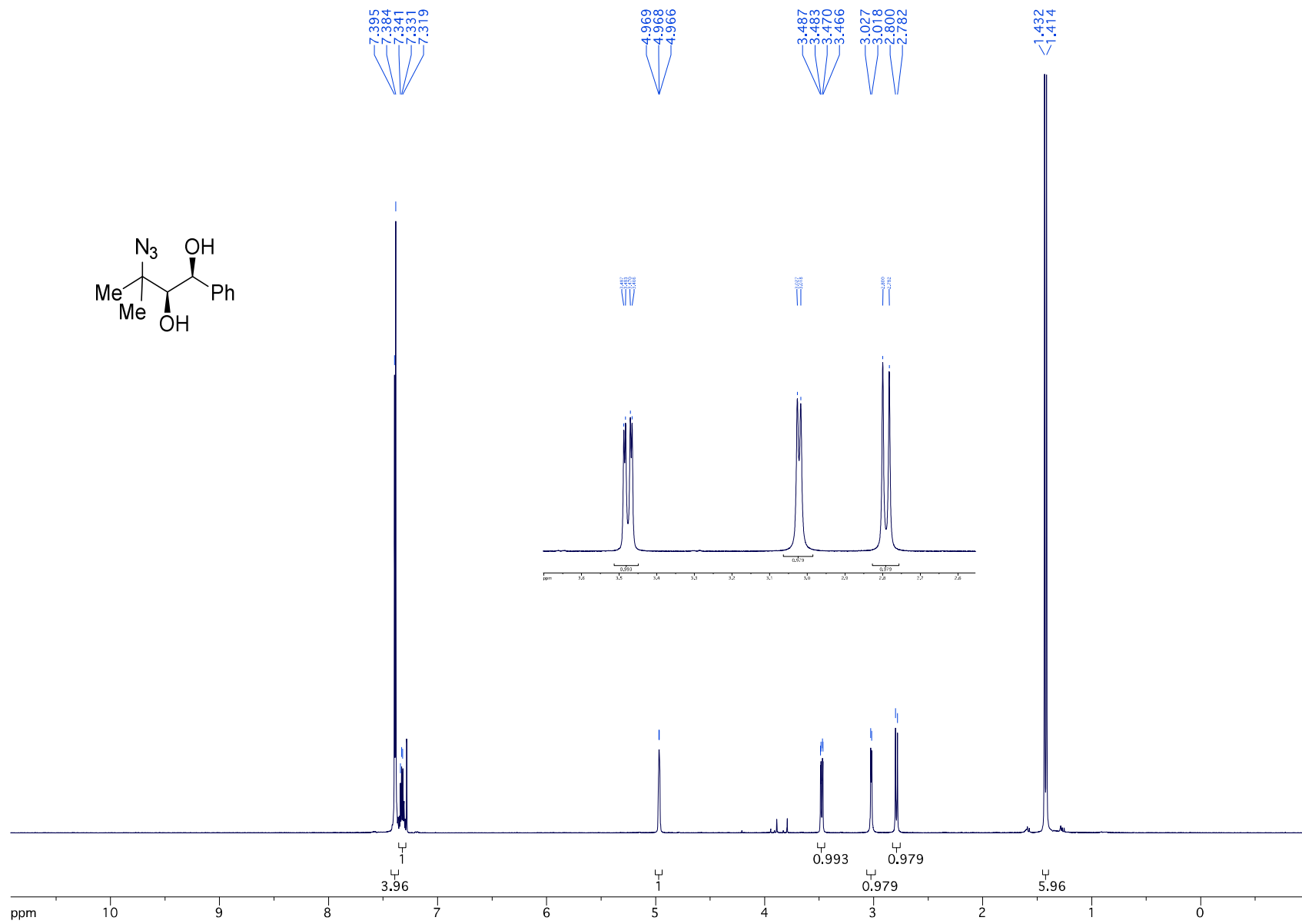


Compound 5c major: 100 MHz  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$

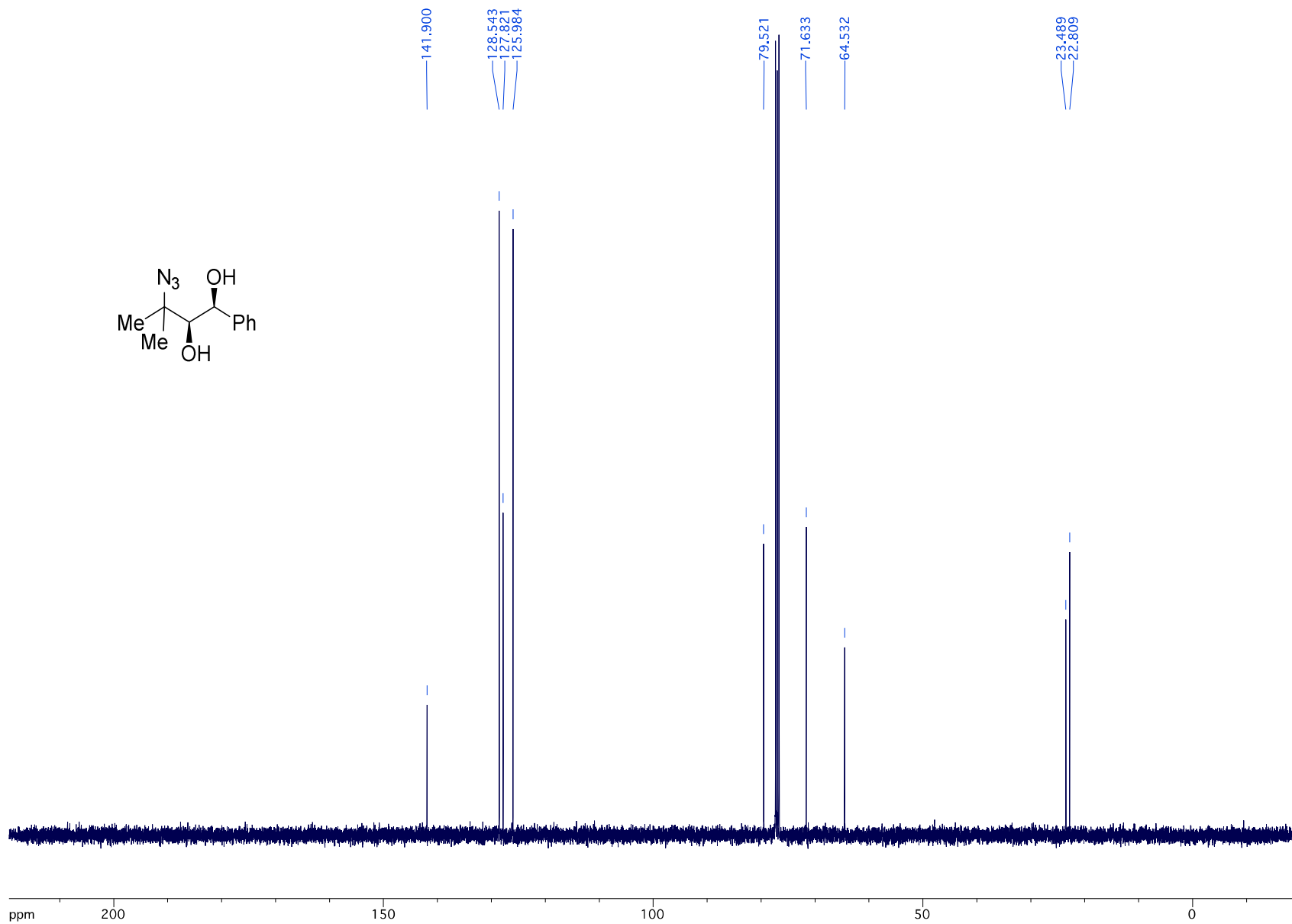




Compound 5c minor: 100 MHz  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$

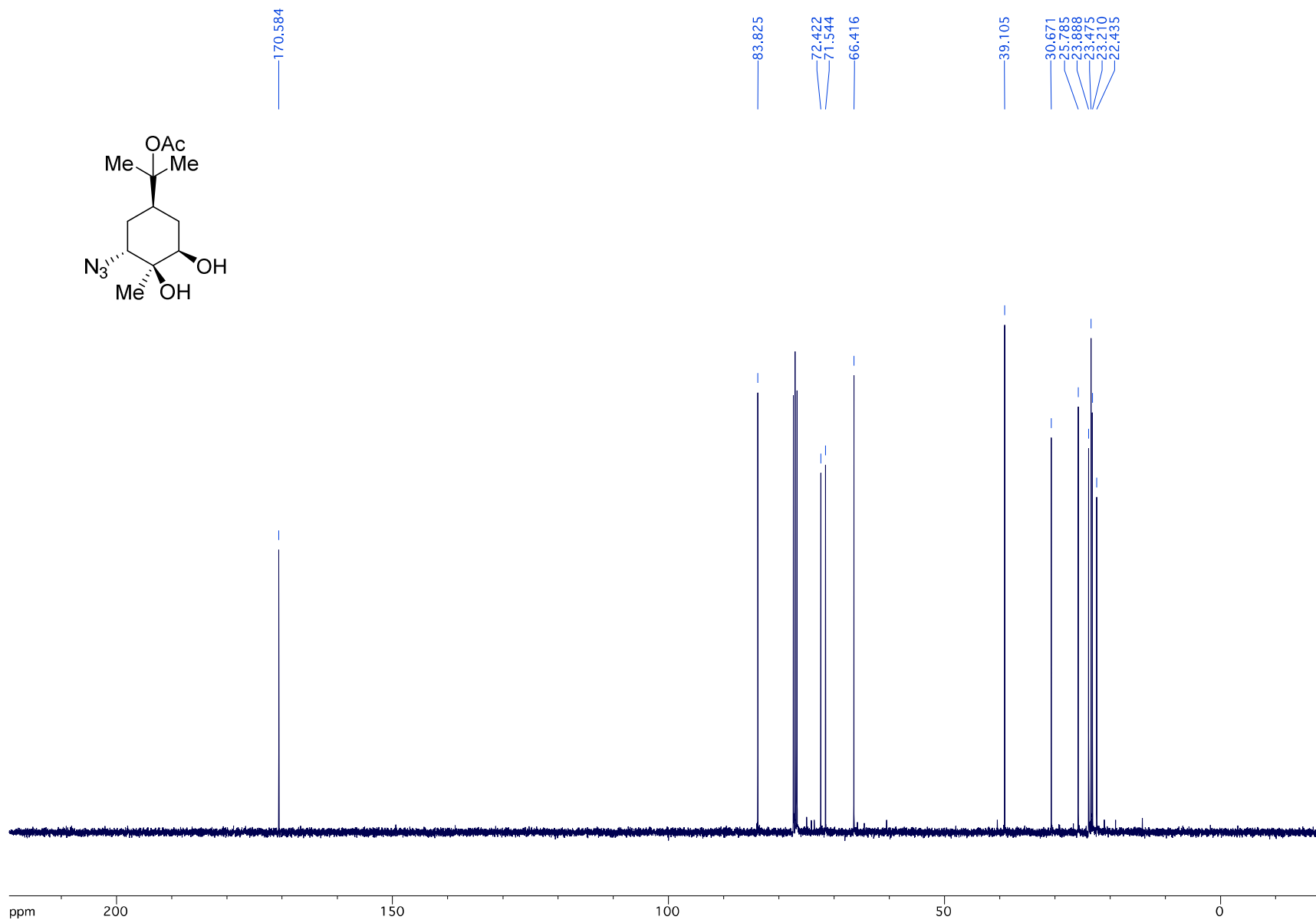
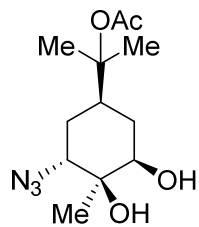


Compound 5d: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$

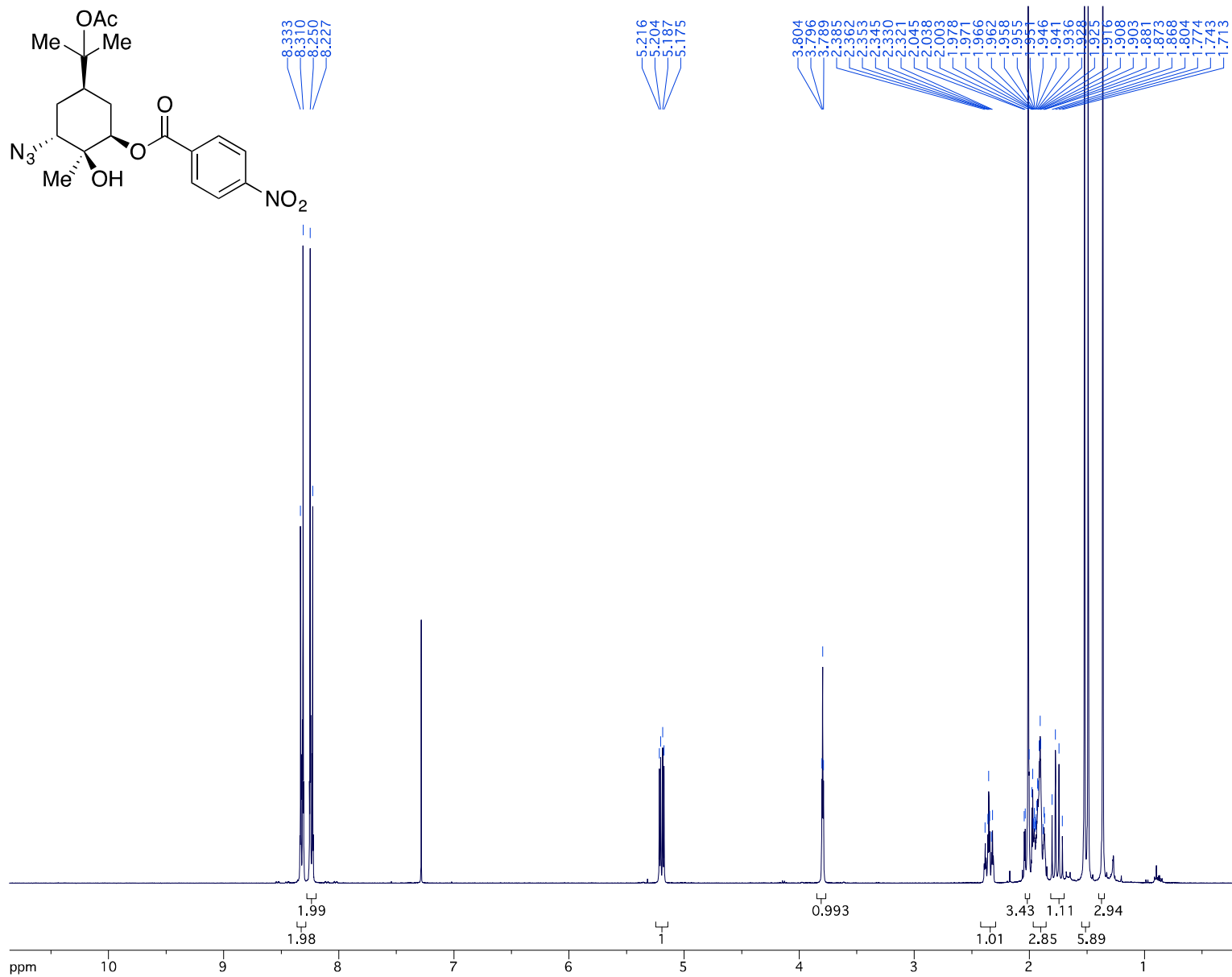


Compound 5d: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>

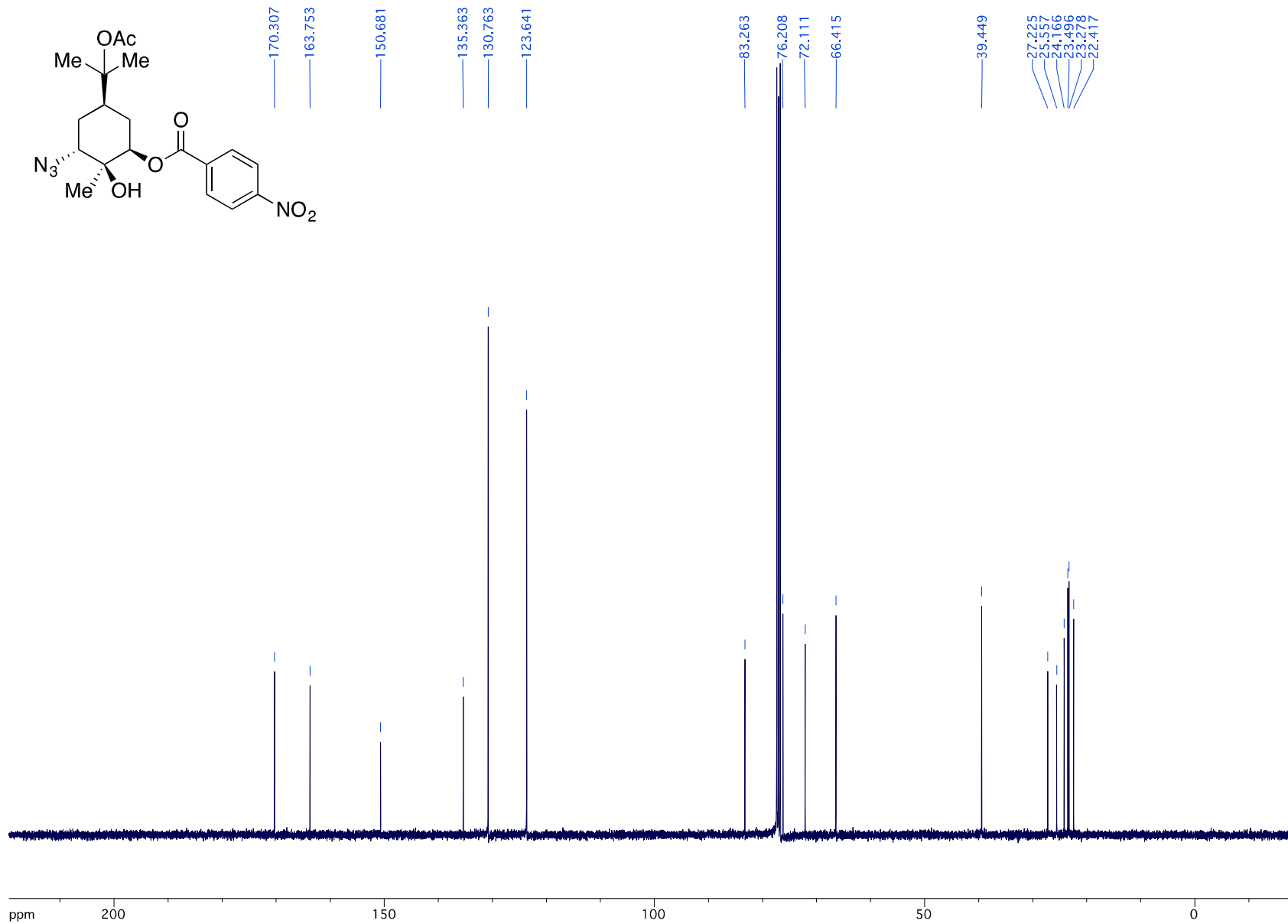




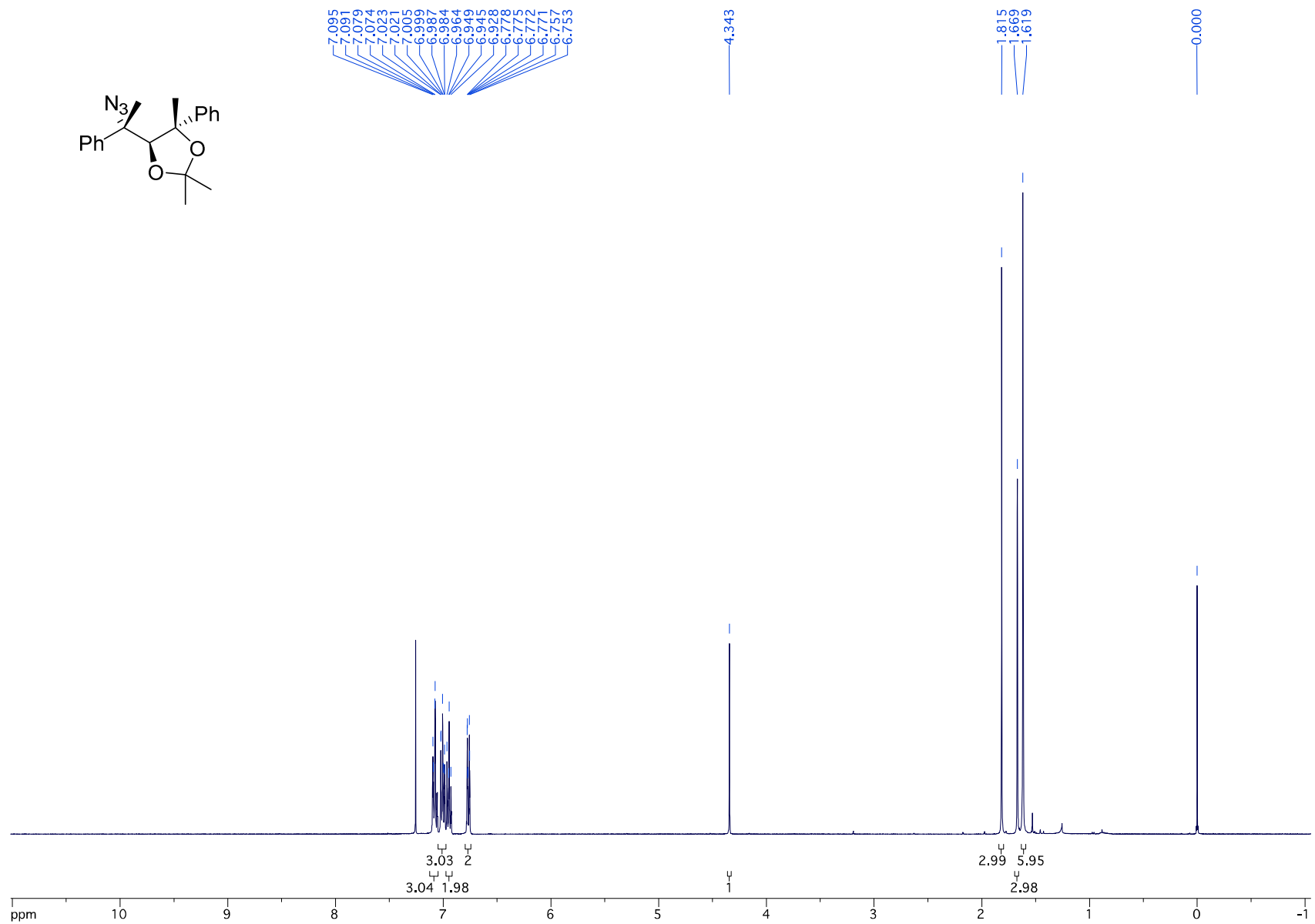
Compound 5e: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



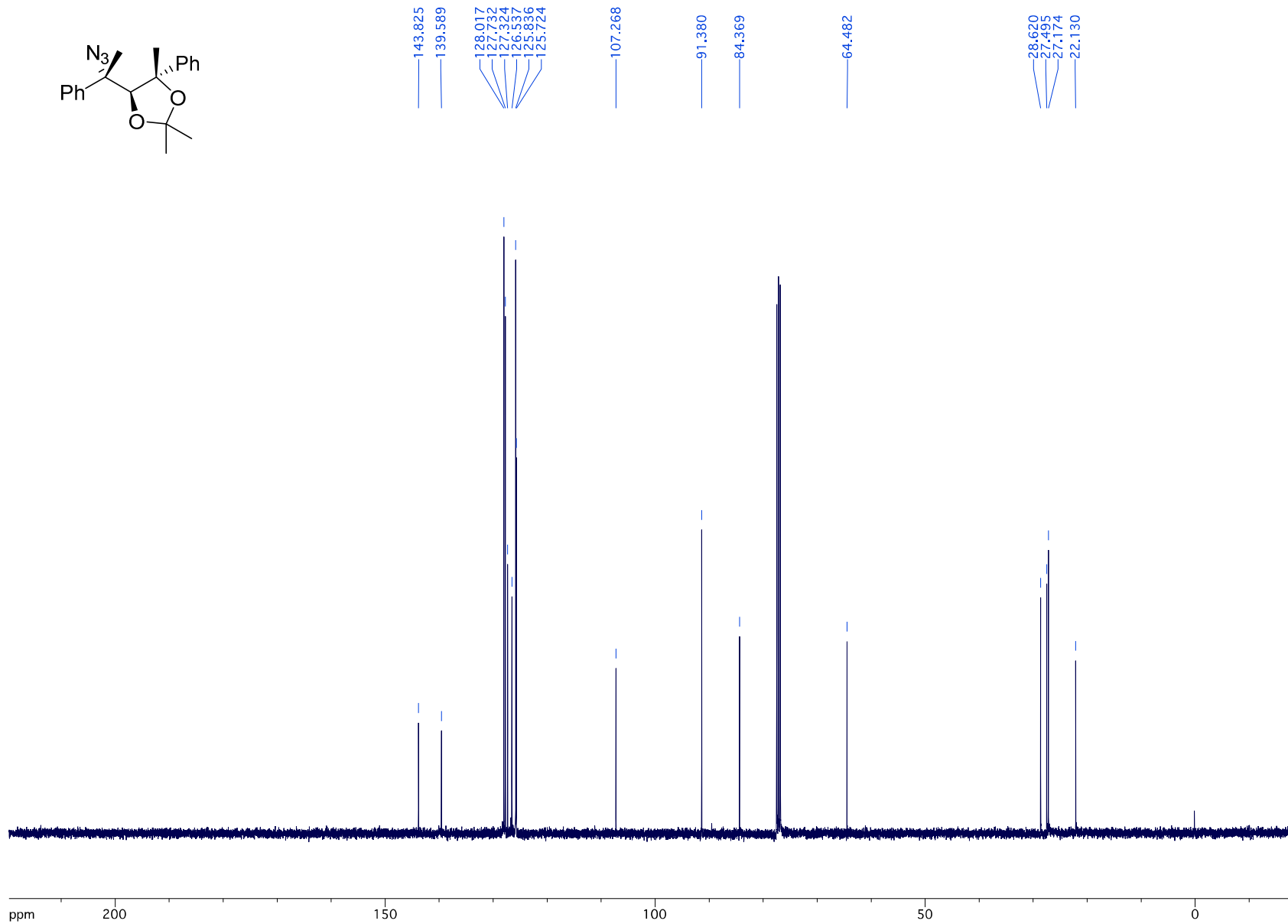
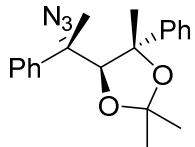
Compound S4e: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



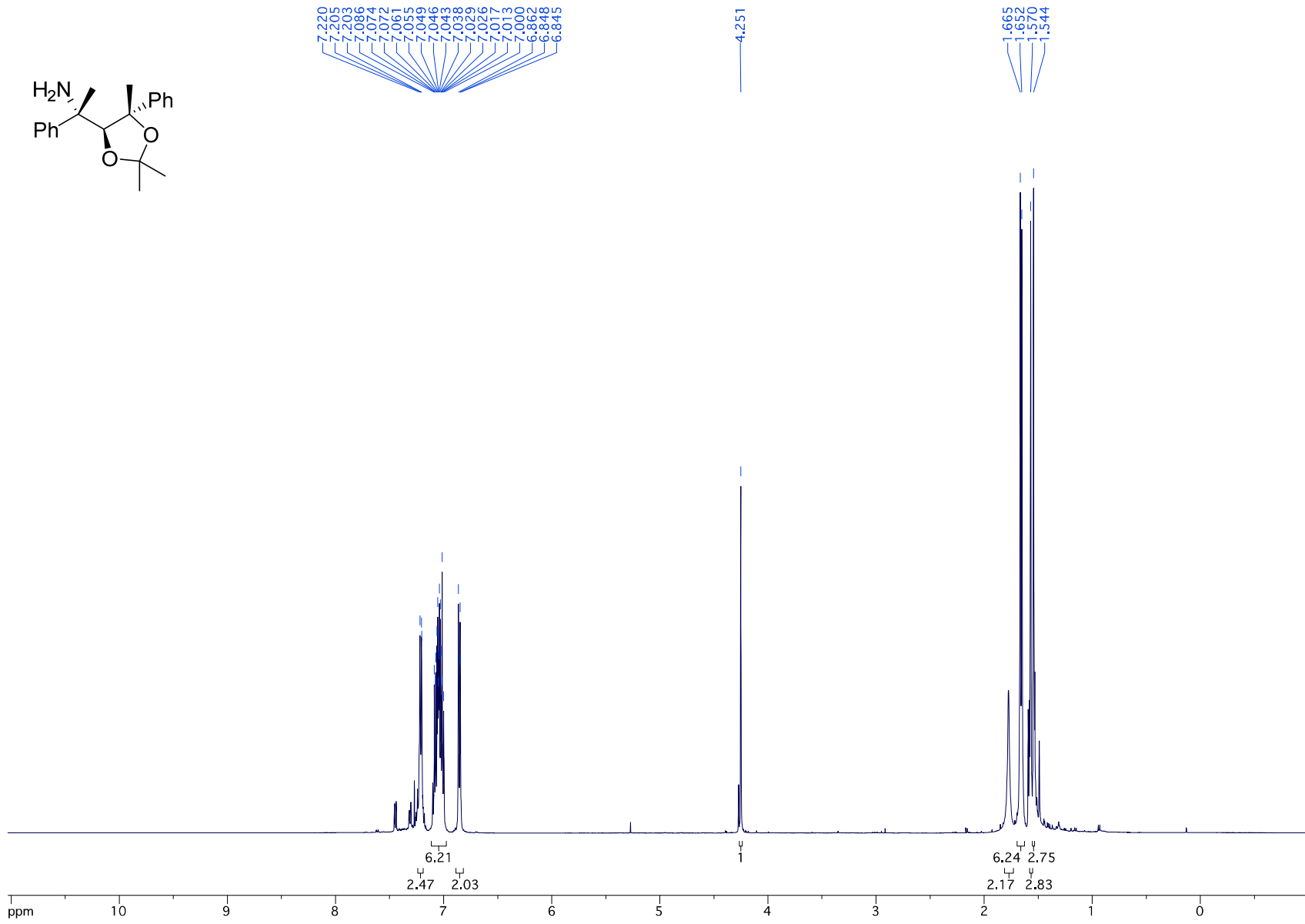
Compound S4e: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



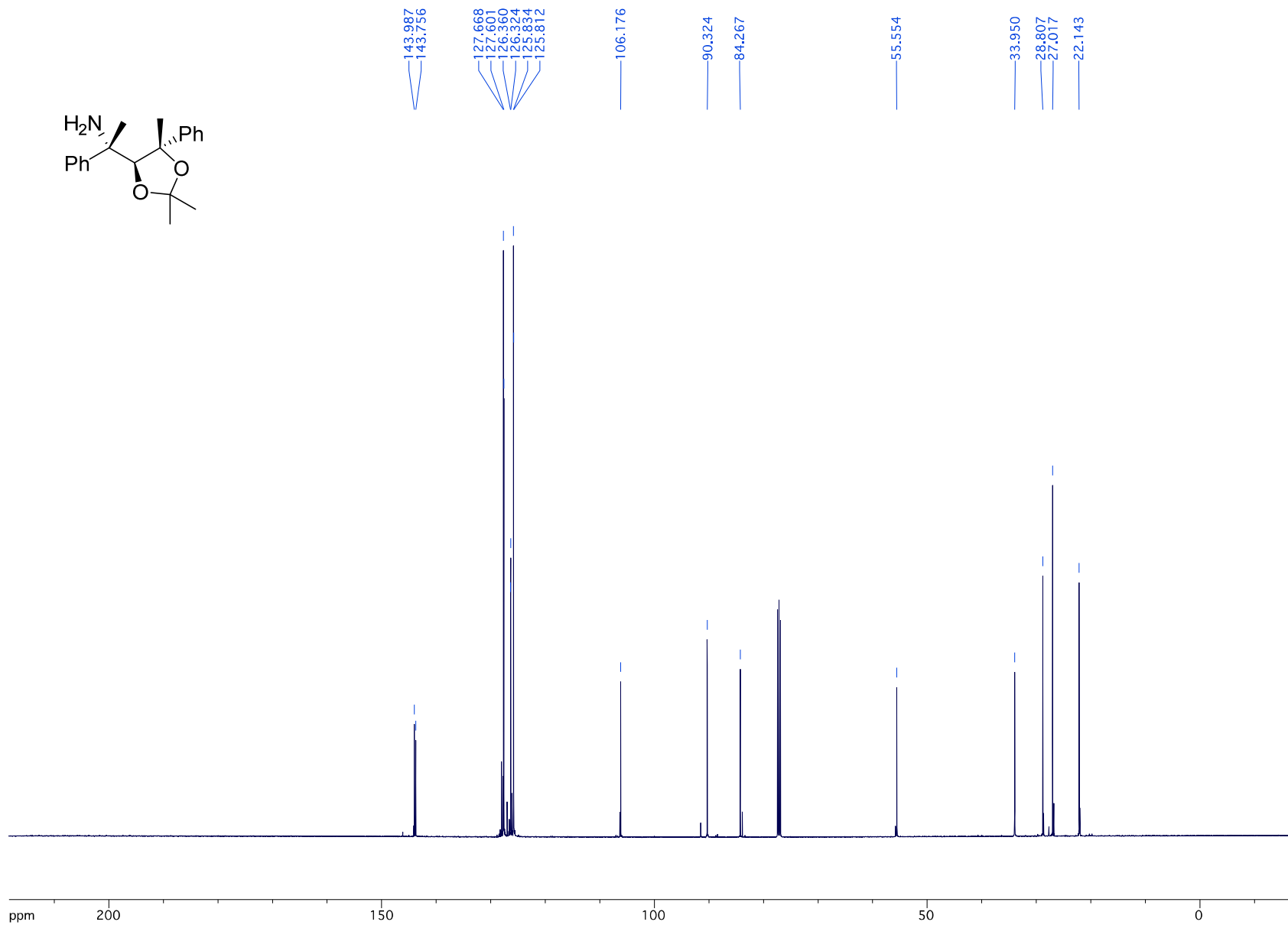
Compound S3: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



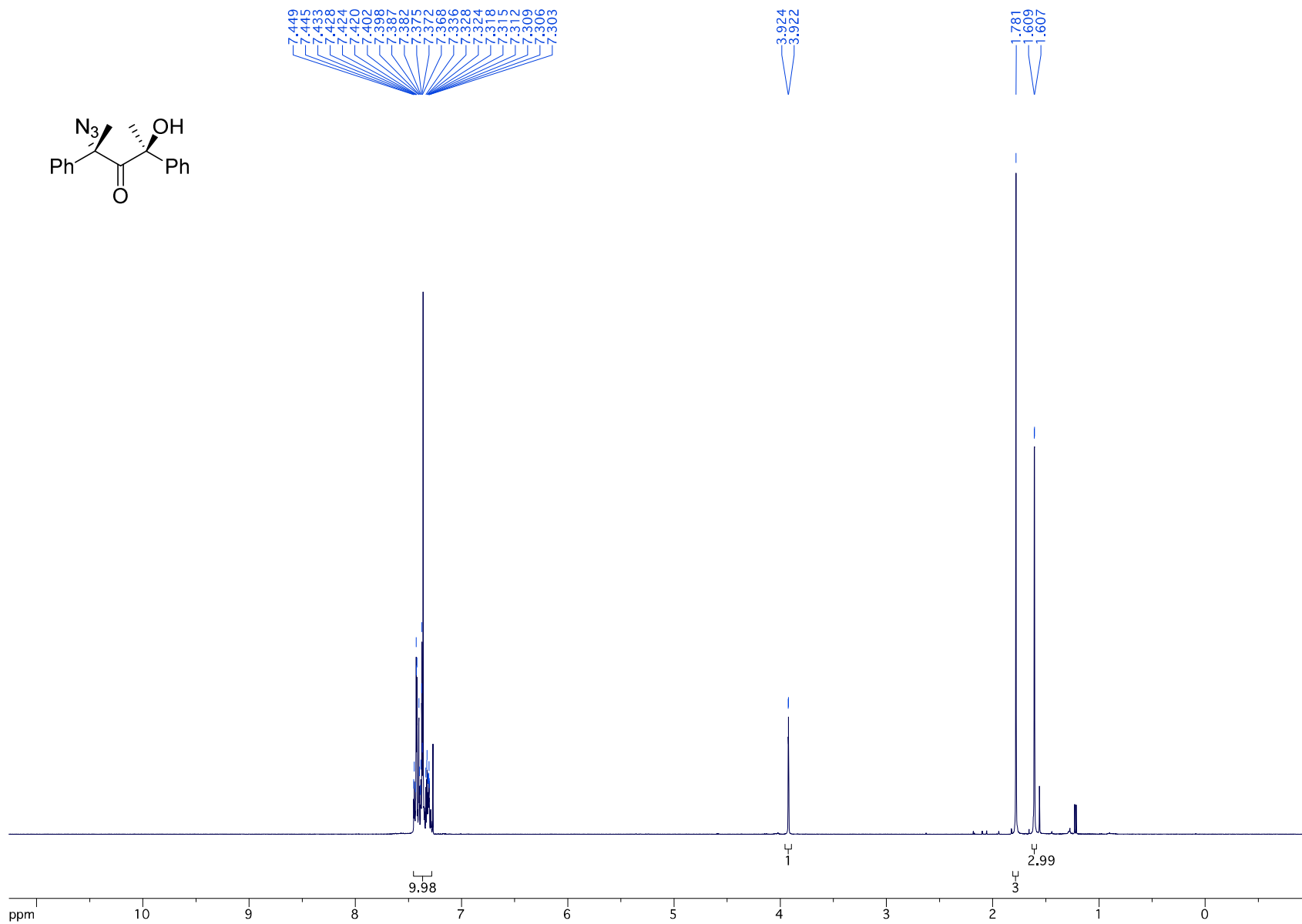
Compound S3: 100 MHz  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$



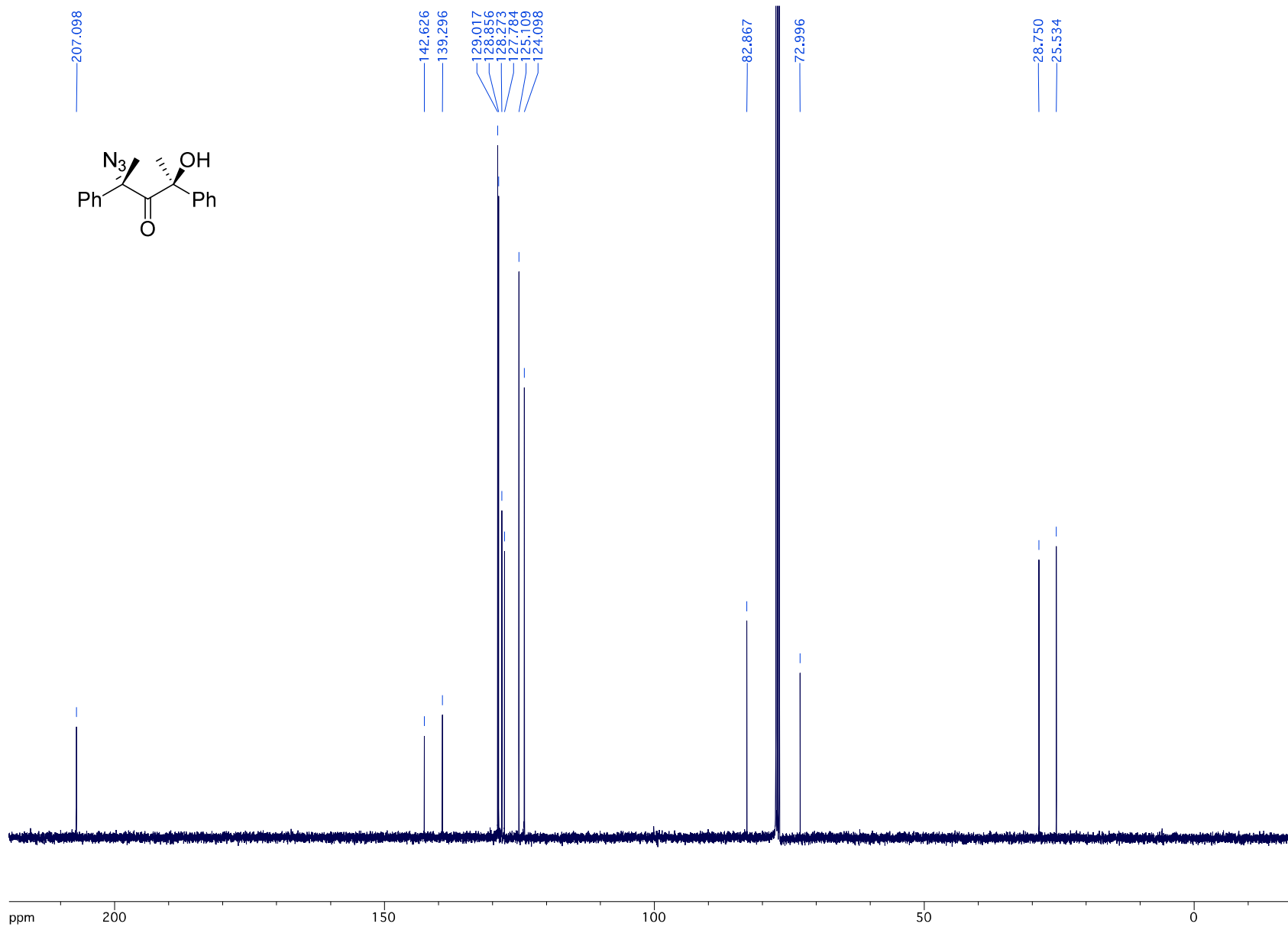
Compound 6: 500 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



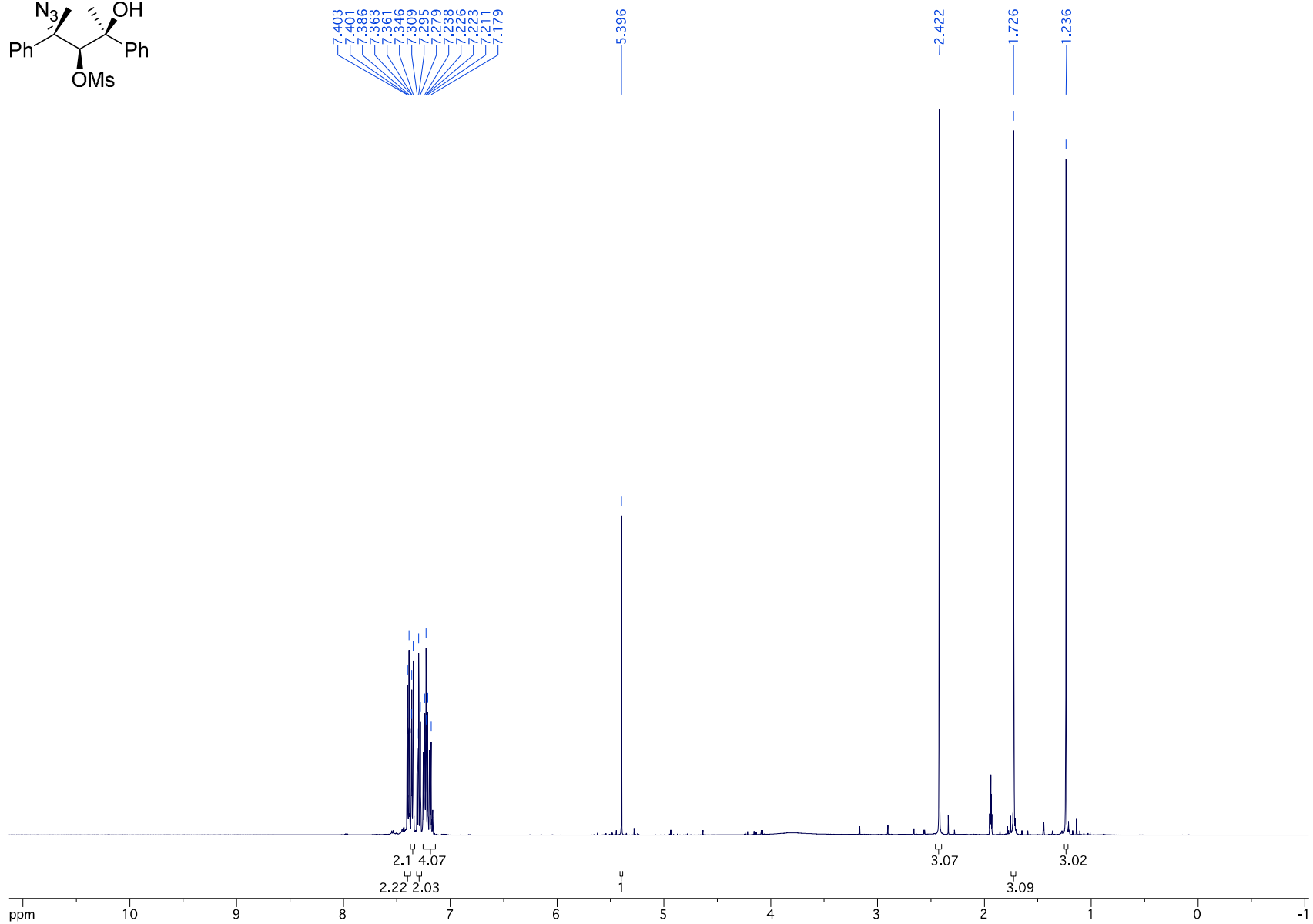
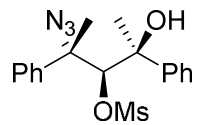
Compound 6: 125 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



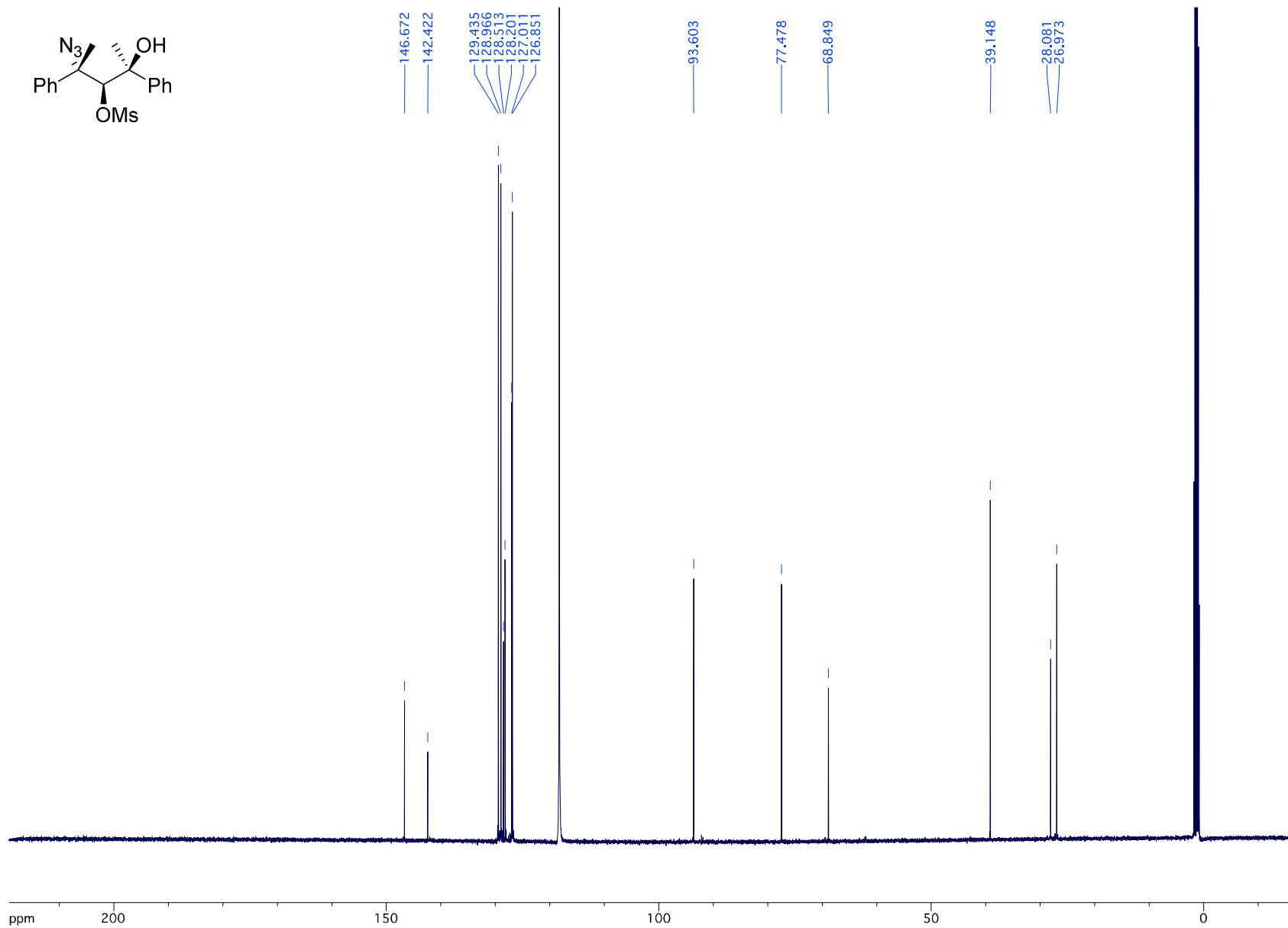
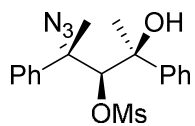
Compound 7: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



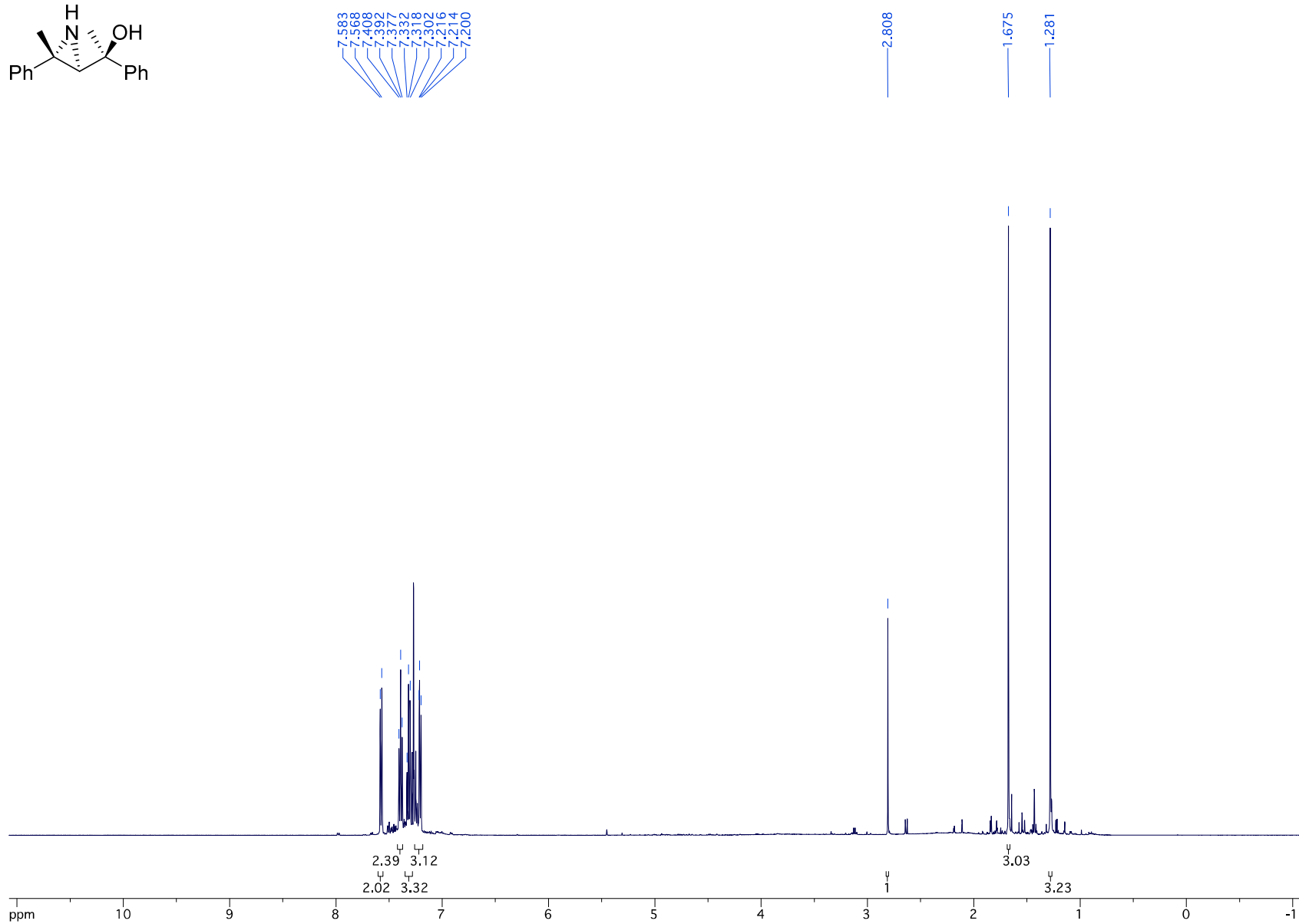
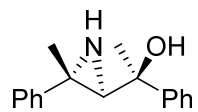
Compound 7: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



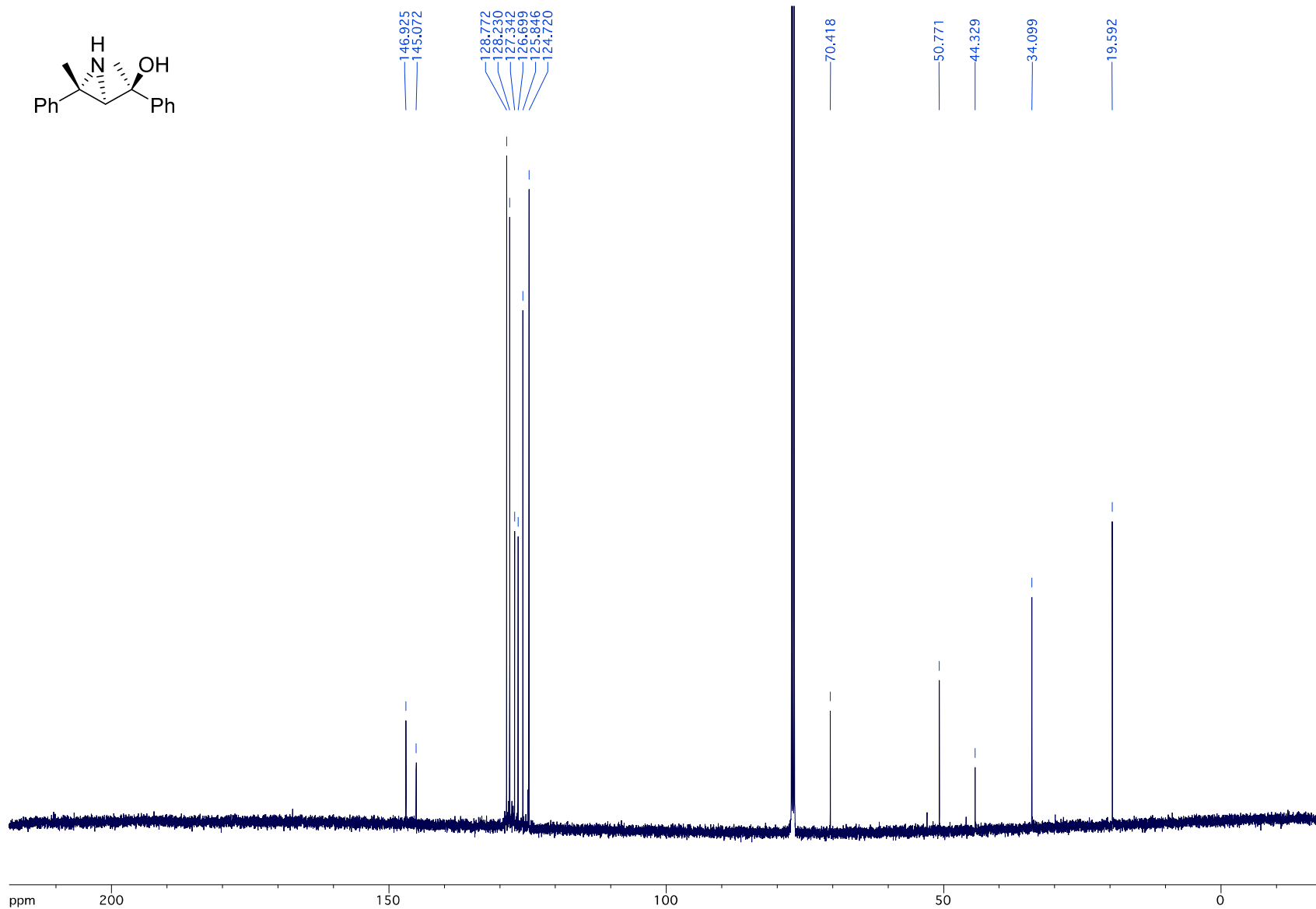
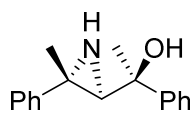
Compound S4: 500 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



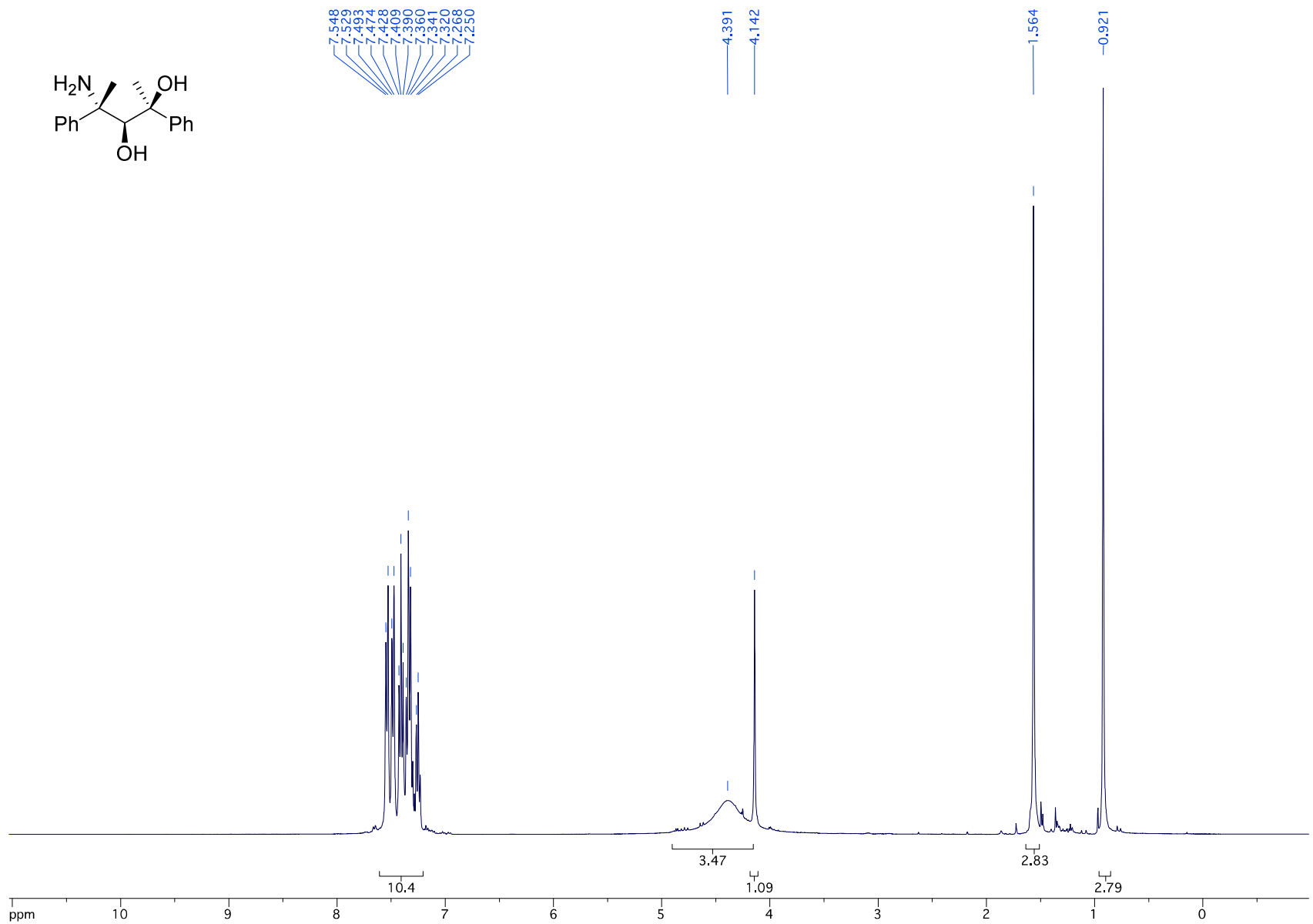
Compound S4: 125 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



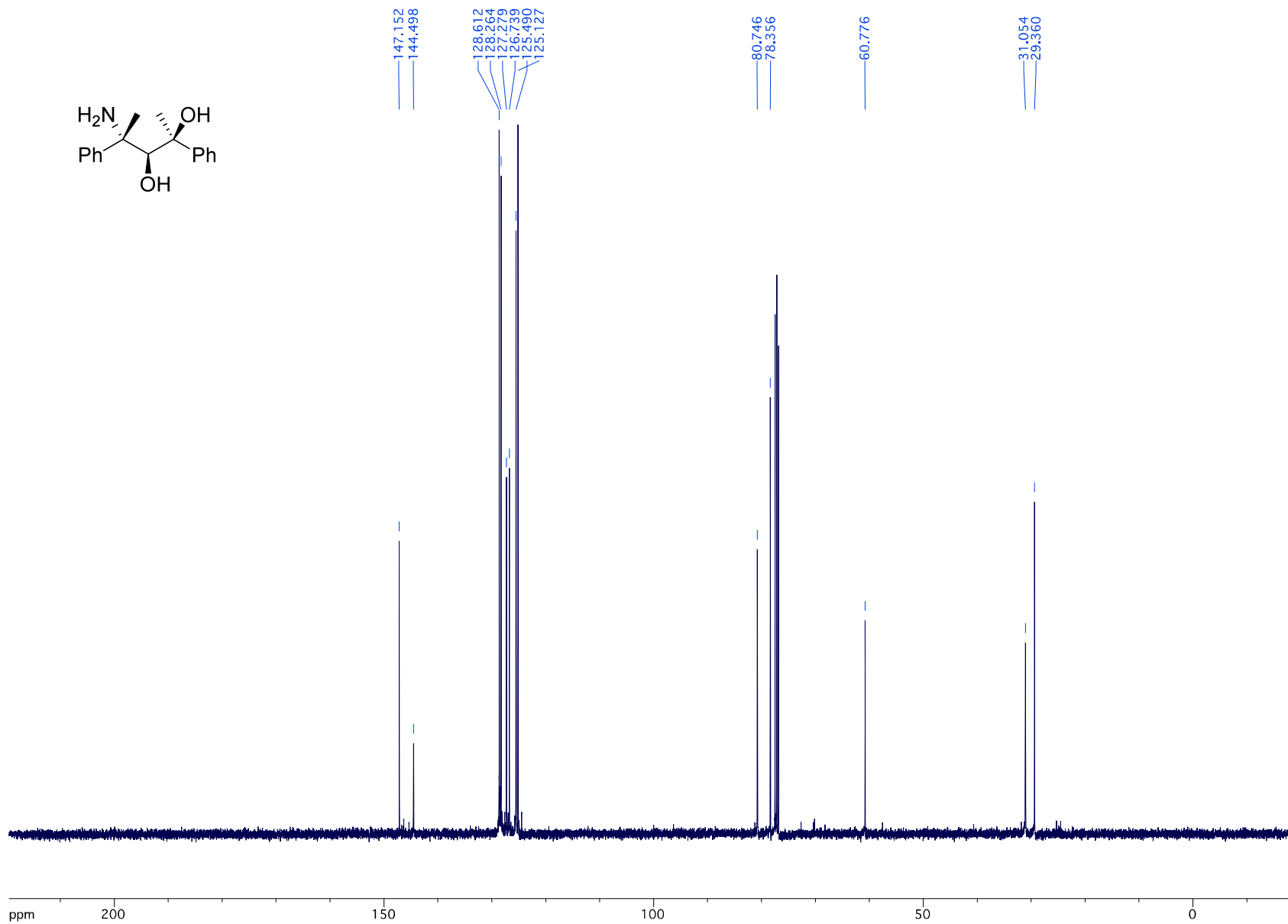
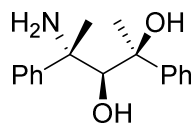
Compound 8: 500 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



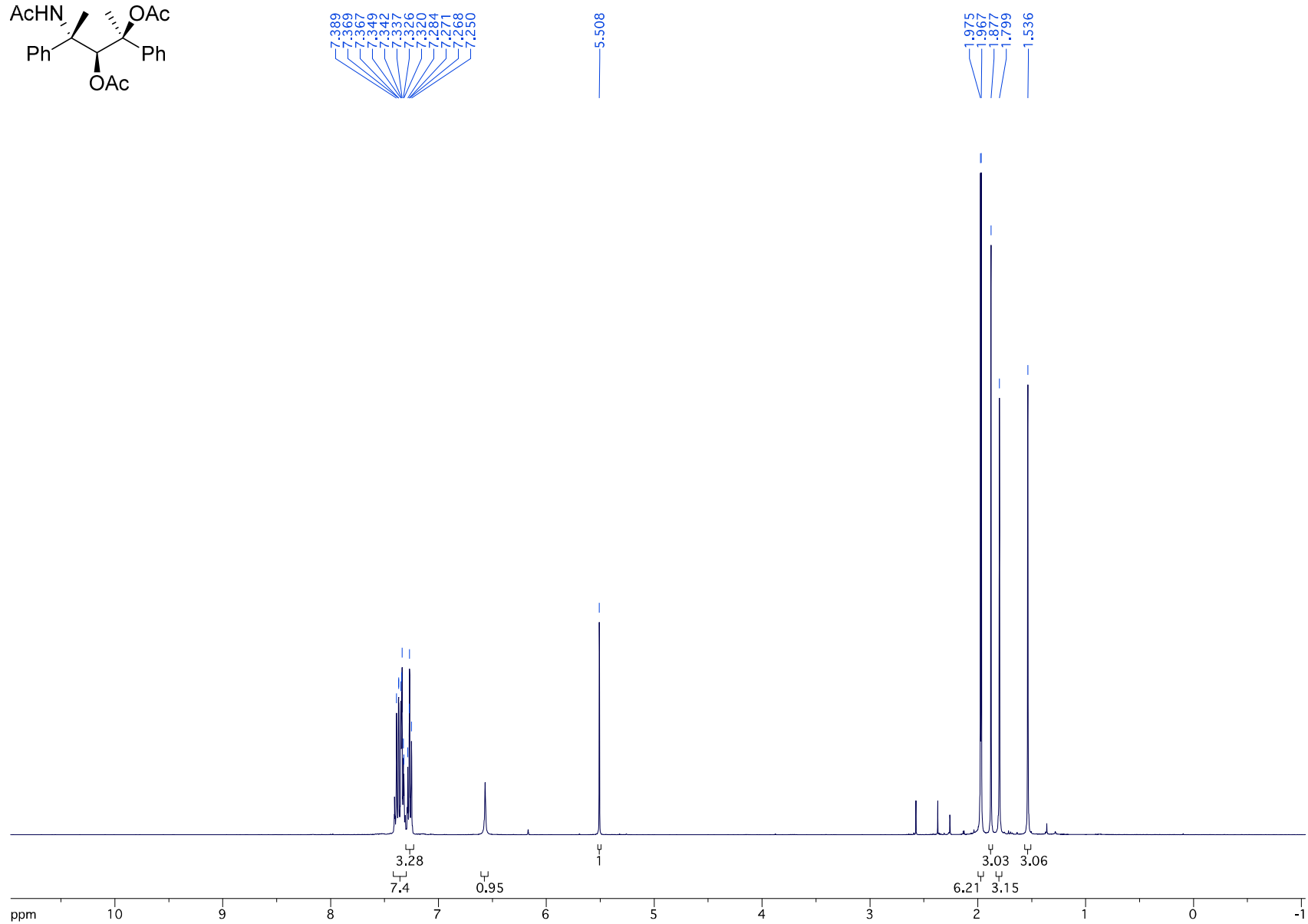
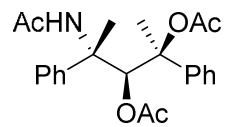
Compound 8: 125 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



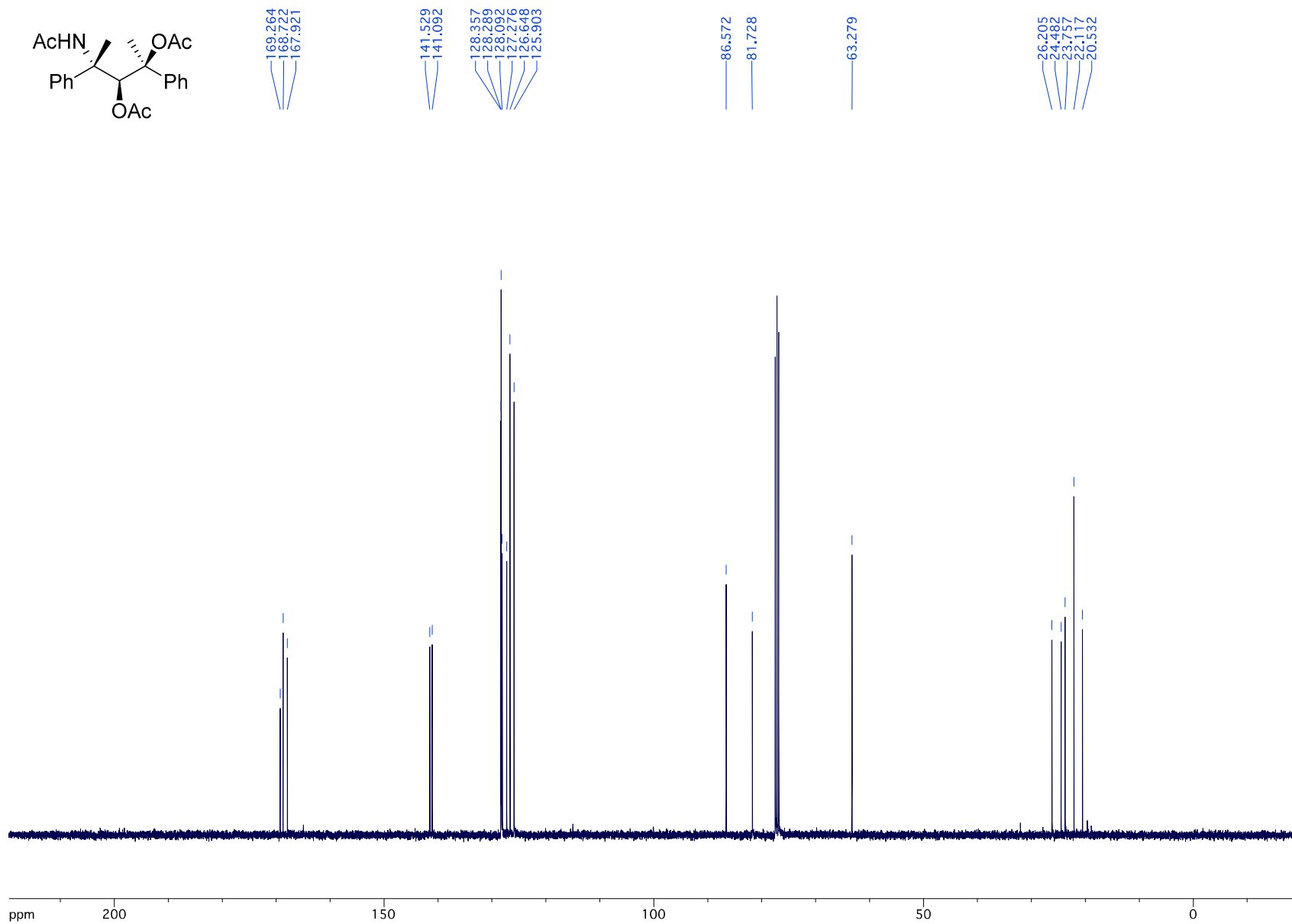
Compound S5: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



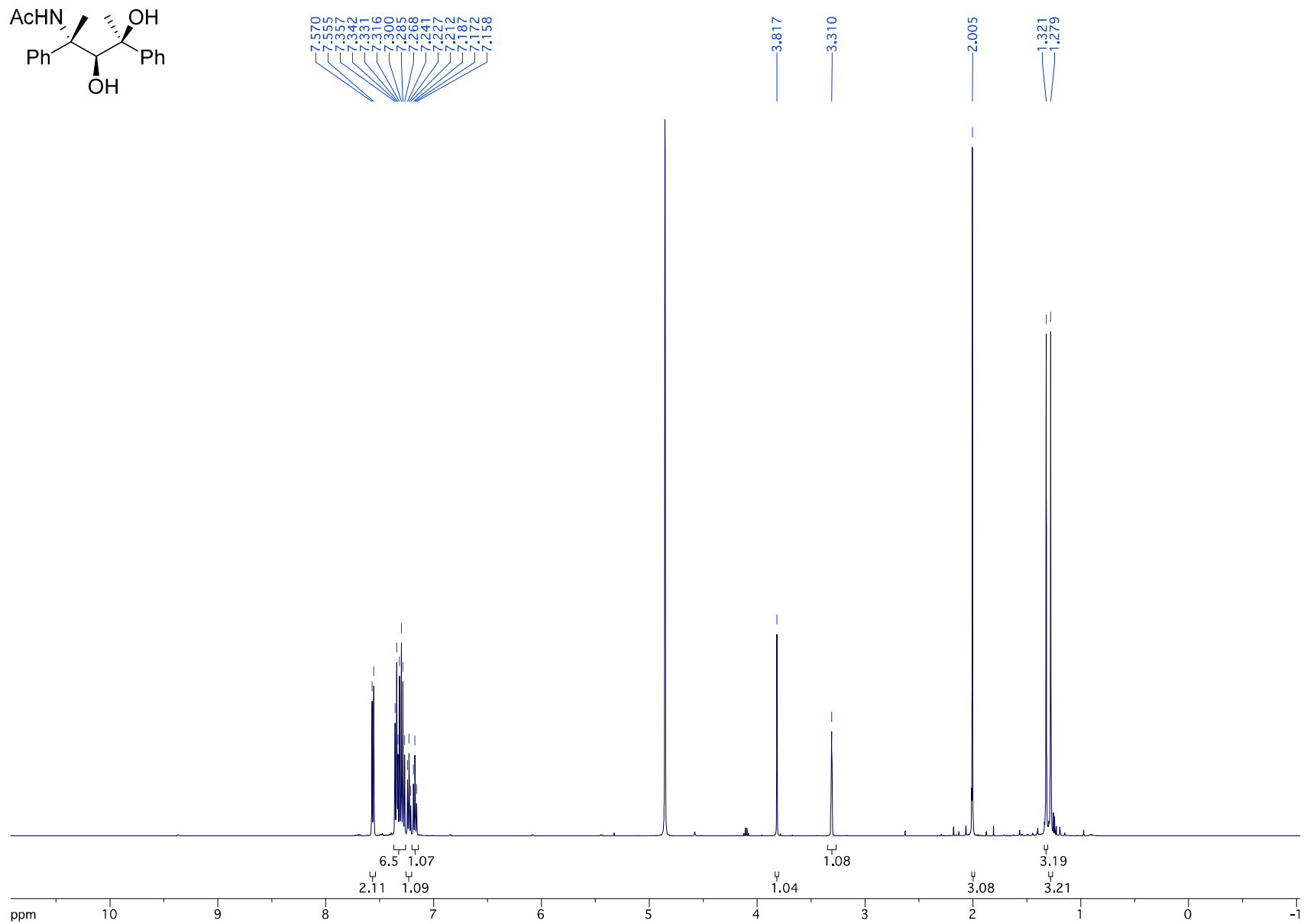
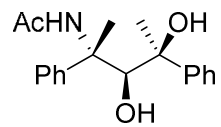
Compound S5: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



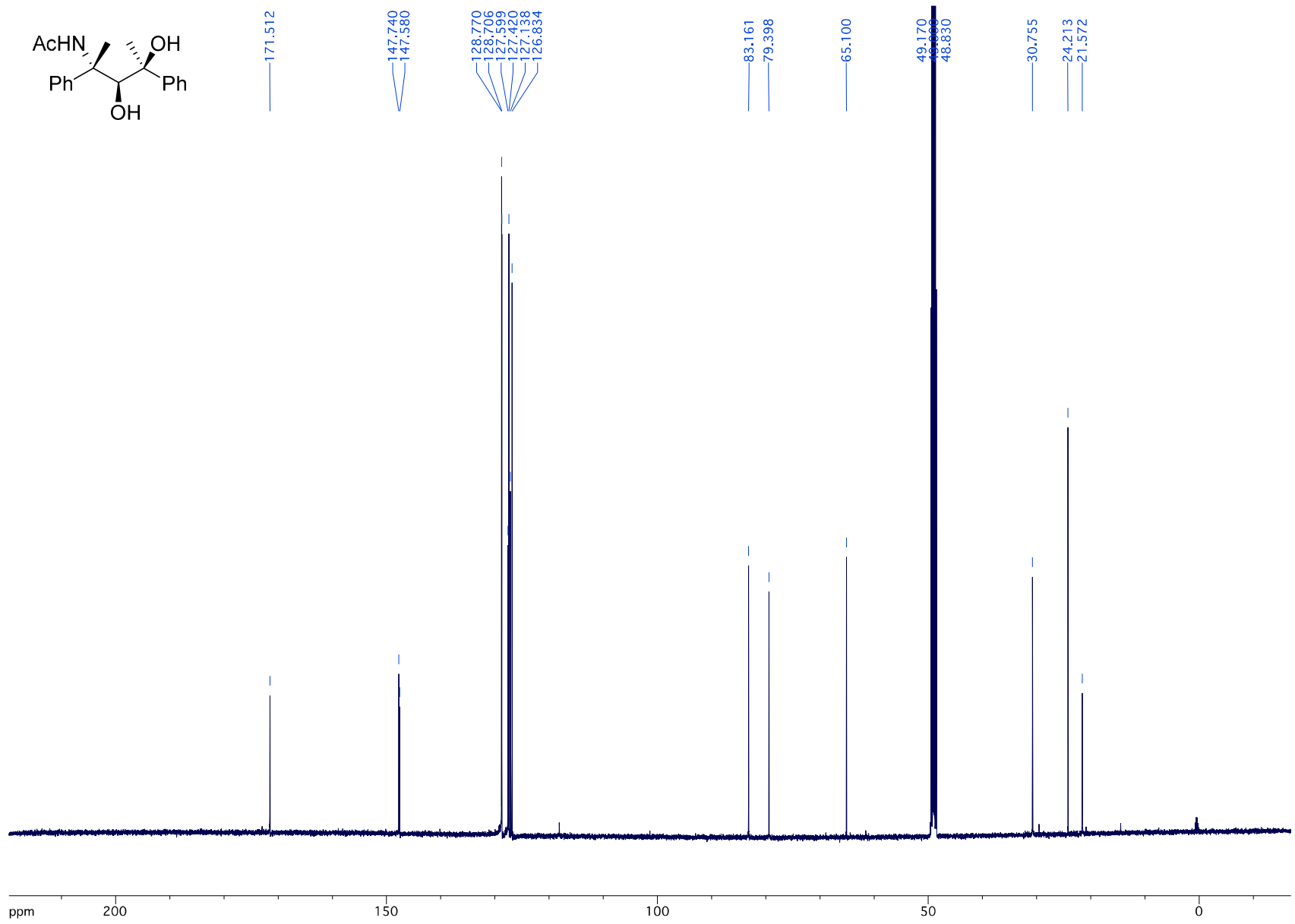
Compound S6: 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$



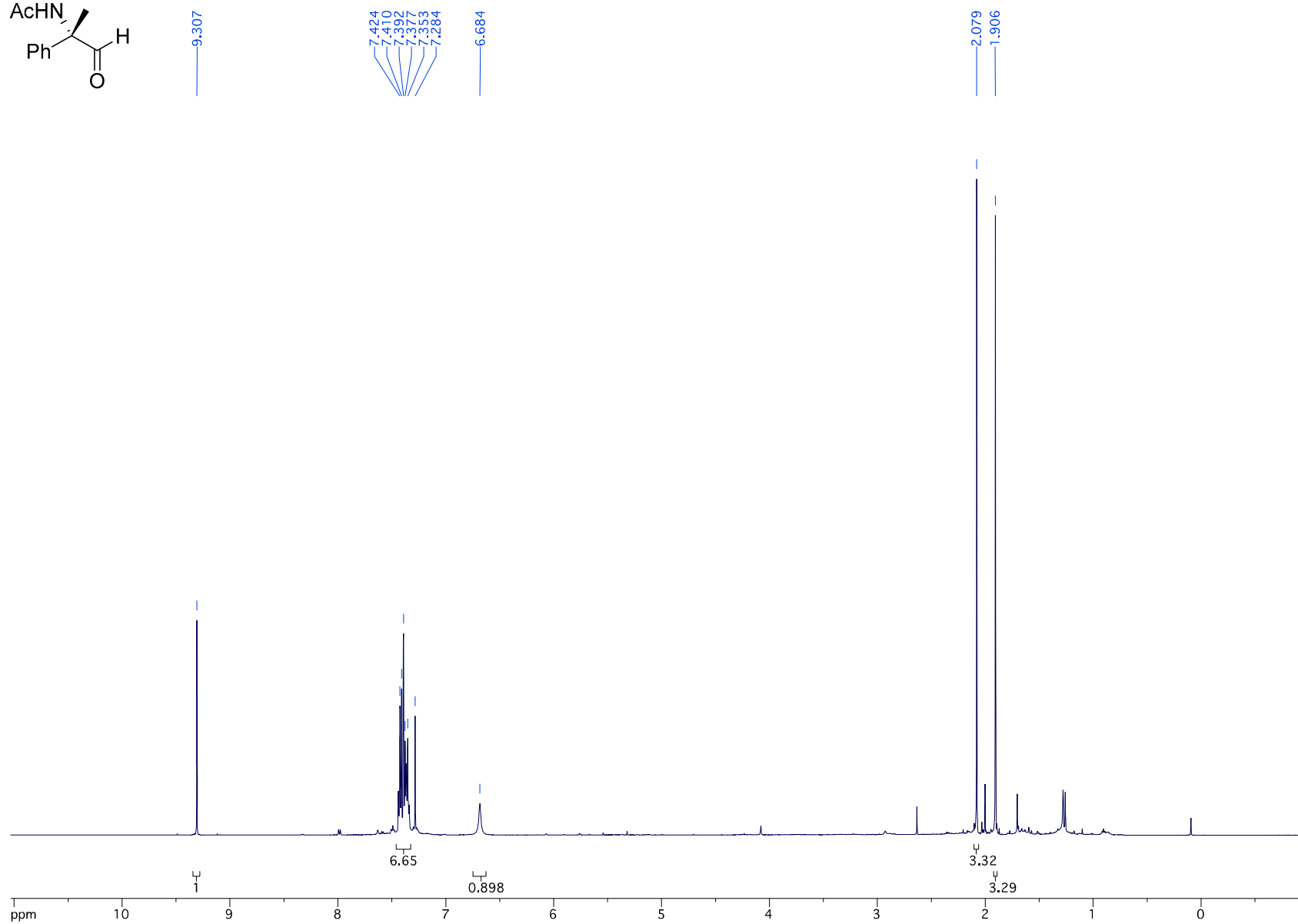
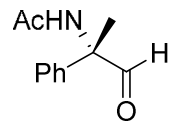
Compound S6: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>



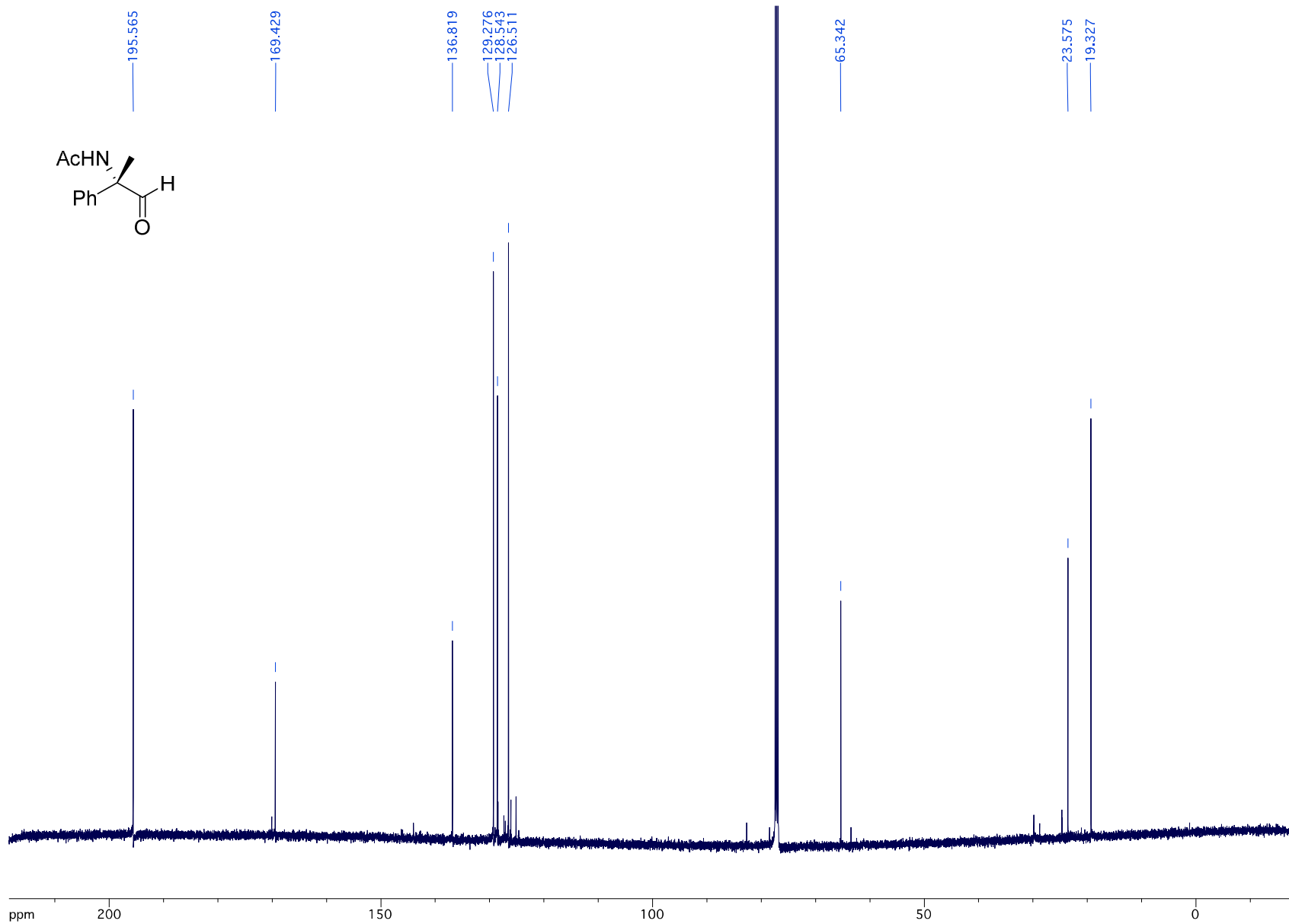
Compound S7: 400 MHz  $^1\text{H}$  NMR spectrum in MeOD



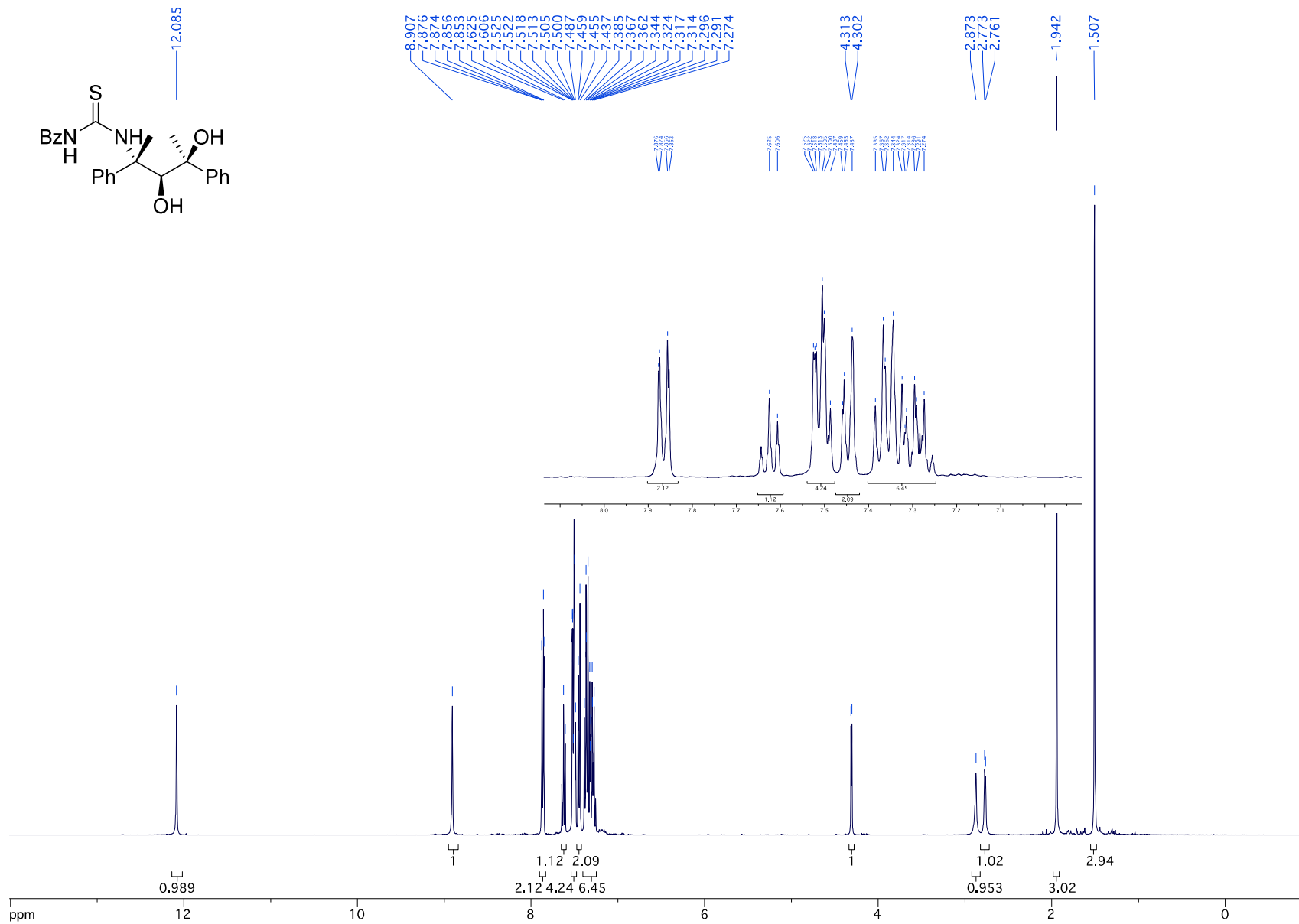
Compound S7: 100 MHz <sup>13</sup>C NMR spectrum in MeOD



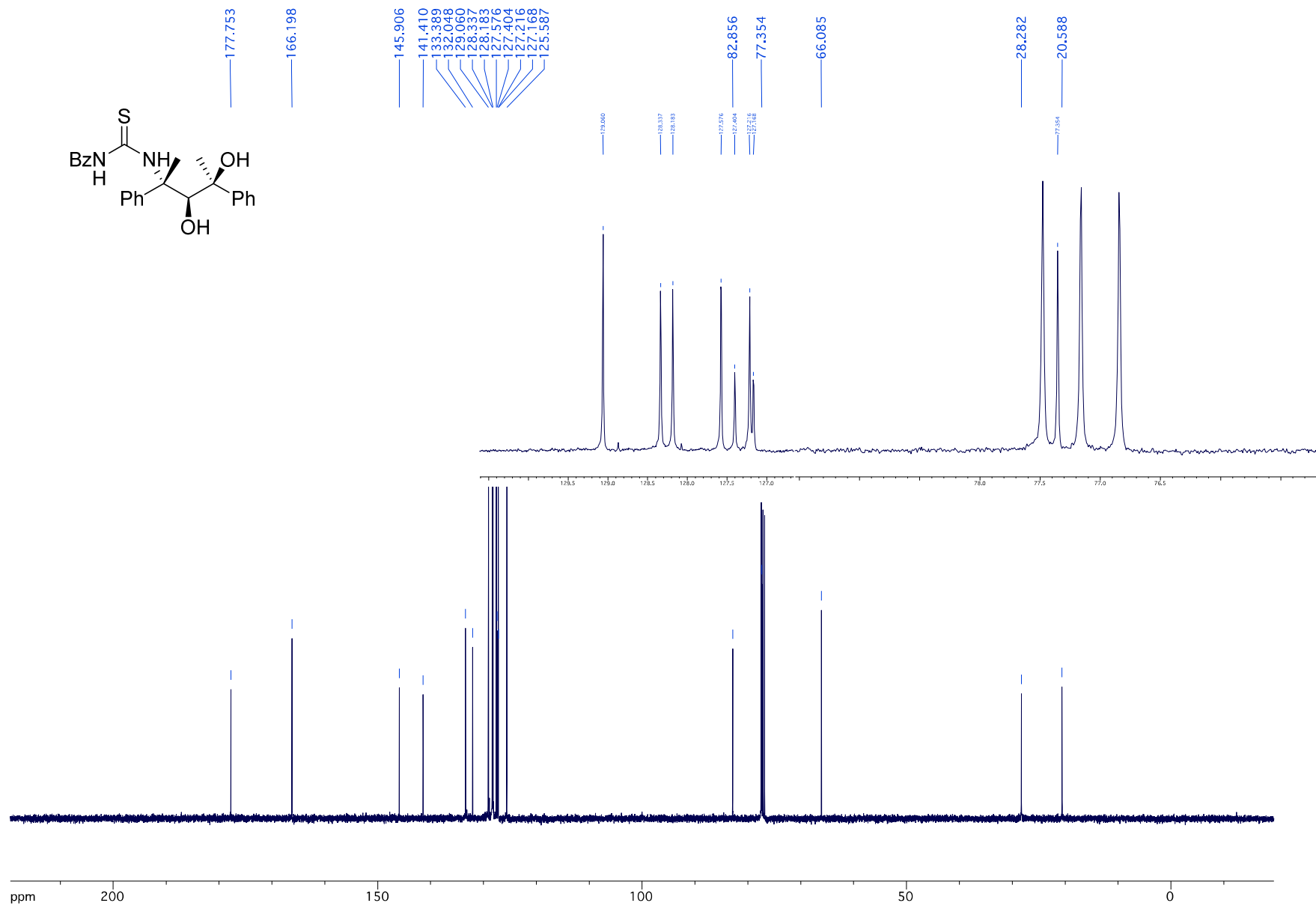
Compound 9: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



Compound 9: 100 MHz  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$



Compound 10: 400 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>



Compound 10: 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub>

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