

## Efficient Approaches to $\alpha,\delta$ -Carbolines *via* Sequential Pd-Catalyzed Site-selective C-C and Two-fold C-N Coupling Reactions

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### Supporting Information

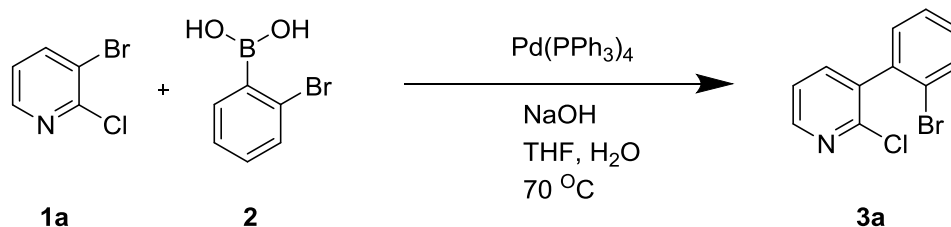
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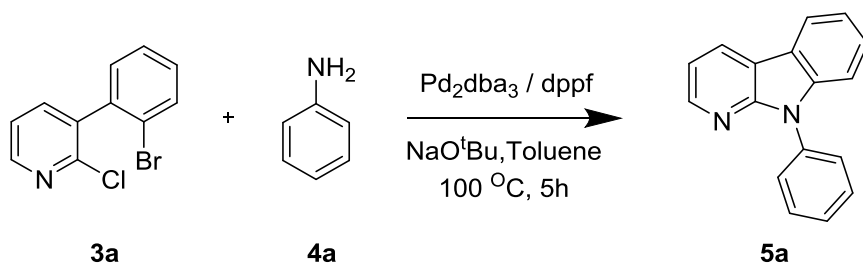
## Experimental Section

### General procedure for prepared of 3-(2-bromophenyl)-2-chloropyridine **3a**.

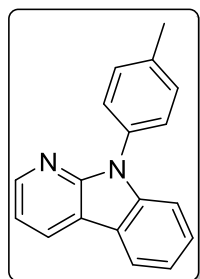


3-bromo-2-chloropyridine **1a** (1 g, 5.2 mmol), 2-bromophenyl boronic acid **2** (1.25 g, 6.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (300 mg, 260 μmol) and sodium hydroxide (624 mg, 15.6 mmol) were added to 500 mL Schlenk flask. The mixture was back-filled several times with Argon. To the mixture 70 mL THF and 10 mL distilled water were added, then, back-filled several times. The reaction was heated at 70 °C for 4h. The solvent was evaporated *in vacuo*. The residue was extracted with dichloromethane and water. The organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated *in vacuo*. The yellow residue was purified by column chromatography (silica gel, Heptane/ethylacetate 4:1) to yield 3-(2-bromophenyl)-2-chloropyridine **3a** (1.19 g, 85 %) as colorless syrup; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.38 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.54 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 – 7.13 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 150.36, 149.18, 139.84, 138.41, 136.39, 132.88, 130.95, 130.07, 127.42, 123.40, 122.16; IR (ATR, cm<sup>-1</sup>): ν = 3051 (w), 1576 (m), 1558 (m), 1479 (w), 1441 (m), 1427 (m), 1390 (vs), 1300 (w), 1255 (w), 1242 (w), 1207 (m), 1122 (m), 1103 (s), 1063 (s), 1053 (m), 1026 (m), 997 (s), 945 (w), 802 (m), 781 (m), 748 (vs), 723 (s), 694 (s), 654 (s), 615 (m), 569 (m), 553 (m); GC-MS (EI, 70 eV): *m/z* (%) = 269 (59), 188 (100), 153 (58), 126(29); HRMS (EI): calcd. for C<sub>11</sub>H<sub>7</sub>N<sub>1</sub>Br<sub>1</sub>Cl<sub>1</sub> ([M]<sup>+</sup>): 266.94449; found: 266.94495; calcd. for C<sub>11</sub>H<sub>7</sub>N<sub>1</sub><sup>81</sup>Br<sub>1</sub>Cl<sub>1</sub> ([M]<sup>+</sup>): 268.94244; found: 268.94288; calcd. for C<sub>11</sub>H<sub>7</sub>N<sub>1</sub>Br<sub>1</sub><sup>37</sup>Cl<sub>1</sub> ([M]<sup>+</sup>): 270.93949; found: 270.94012.

**General procedure A for double C-N coupling with aniline derivatives, exemplified by: 9-phenyl-9H-pyrido[2,3-*b*]indole **8a****

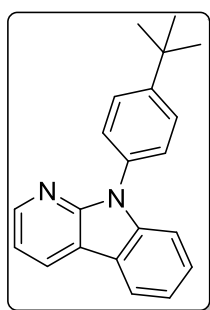


Aniline (52  $\mu\text{L}$ , 0.56 mmol) was added to pressure tube charged with **3a** (100 mg, 0.37 mmol),  $\text{Pd}_2(\text{dba})_3$  (17 mg, 19  $\mu\text{mol}$ ), ligand dppf (21 mg, 37  $\mu\text{mol}$ ) and sodium tert-butoxide (107 mg, 1.12 mmol) under Argon. The mixture was back-filled with Argon several times. The mixture was dissolved in anhydrous Toluene (10 mL) and heated at 110  $^\circ\text{C}$  for 7 h. After cooling, the reaction mixture was diluted with dichloromethane (20 mL) and filtered through a celite pad, washing with dichloromethane (40 mL). The filtrate was reduced *in vacuo*. The product was separated via flash chromatography (silica gel, heptanes/ethylacetate 3:1) to yield 9-phenyl-9H-pyrido[2,3-*b*]indole **5a** (84 mg, 92%) as a white solid; m.p. 110-111  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (dd,  $J = 4.9, 1.6$  Hz, 1H), 8.31 (dd,  $J = 7.7, 1.6$  Hz, 1H), 8.05 (dt,  $J = 7.7, 0.9$  Hz, 1H), 7.63 – 7.48 (m, 4H), 7.47 – 7.33 (m, 3H), 7.33 – 7.22 (m, 1H), 7.20 – 7.10 (m, 1H);  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ )  $\delta$  151.93, 146.47, 140.11, 136.26, 129.65, 128.28, 127.64, 127.38, 126.93, 120.91, 120.81, 120.71, 116.36, 116.04, 110.41; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 3037$  (m), 1591 (s), 1568 (m), 1504 (s), 1473 (s), 1452 (s), 1414 (vs), 1377 (m), 1354 (m), 1335 (s), 1309 (m), 1290 (s), 1228 (s), 1176 (m), 1167 (m), 1115 (s), 1074 (m), 1051 (m), 1026 (m), 997 (m), 970 (m), 958 (m), 951 (m), 937 (m), 766 (s), 756 (s), 748 (s), 735 (vs), 715 (m), 692 (vs), 636 (s), 617 (s), 579 (s), 569 (m); GC-MS (EI, 70 eV):  $m/z$  (%) = 243 (100), 122 (17); HRMS (ESI): calcd. for  $\text{C}_{17}\text{H}_{12}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 245.10732; found: 245.10756.

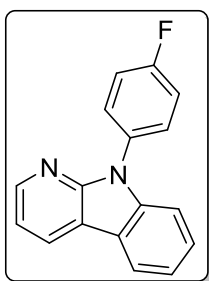


**9-(p-tolyl)-9H-pyrido[2,3-*b*]indole 5b** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and 4-toluidine (60 mg, 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 3:1) to yield **5b** (91 mg, 95 %) as a white solid; m.p. 102-103  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (dd,  $J = 4.9, 1.6$  Hz, 1H), 8.29 (dd,  $J = 7.7, 1.6$  Hz, 1H), 8.04 (d,  $J = 7.7$  Hz, 1H), 7.48 – 7.29 (m, 6H), 7.28 – 7.19 (m, 1H), 7.18 – 7.09 (m, 1H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ )  $\delta$  152.10, 146.50, 140.28, 137.60, 133.56, 130.30, 128.21, 127.25, 126.85, 120.87, 120.71, 120.54, 116.24, 115.87,

110.39, 21.26; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 3039$  (w), 2920 (w), 1589 (m), 1568 (m), 1514 (s), 1475 (m), 1456 (s), 1412 (vs), 1377 (m), 1354 (m), 1336 (s), 1311 (m), 1290 (s), 1228 (s), 1219 (s), 1200 (m), 1182 (m), 1169 (m), 1155 (w), 1120 (m), 1109 (m), 1051 (w), 1038 (w), 1018 (m), 997 (m), 966 (w), 951 (w), 941 (w), 924 (m), 841 (w), 812 (s), 798 (m), 771 (vs), 744 (s), 735 (vs), 714 (s), 702 (s), 646 (m), 633 (s), 617 (m), 577 (s), 571 (s); GC-MS (EI, 70 eV):  $m/z$  (%) = 258 (100), 242 (17), 128 (9); HRMS (ESI): calcd. for  $\text{C}_{18}\text{H}_{14}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 259.12297; found: 259.12331.

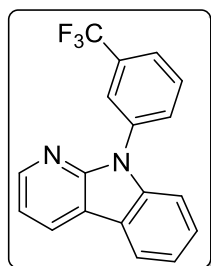


**9-(4-(tert-butyl)phenyl)-9H-pyrido[2,3-b]indole 5c** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and 4-*tert*-butylaniline (83 mg, 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 3:1) to yield **5c** (105 mg, 94 %) as a white solid; m.p. 147-148 °C;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (dd,  $J = 4.9, 1.6$  Hz, 1H), 8.29 (dd,  $J = 7.7, 1.6$  Hz, 1H), 8.06 – 7.99 (m, 1H), 7.58 – 7.32 (m, 6H), 7.23 (ddd,  $J = 8.1, 6.7, 1.6$  Hz, 1H), 7.19 – 7.08 (m, 1H), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ )  $\delta$  152.01, 150.43, 146.50, 140.26, 133.51, 128.22, 126.84, 126.77, 126.63, 120.84, 120.72, 120.56, 116.31, 115.87, 110.55, 34.76, 31.42; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 2960$  (m), 2902 (w), 2868 (w), 1587 (m), 1568 (m), 1520 (s), 1475 (m), 1454 (s), 1414 (vs), 1360 (m), 1335 (s), 1288 (s), 1269 (m), 1228 (s), 1186 (m), 1169 (m), 1153 (w), 1119 (m), 1097 (w), 1018 (m), 997 (m), 930 (m), 833 (m), 825 (m), 800 (w), 769 (vs), 748 (s), 739 (vs), 687 (m), 638 (s), 617 (m), 580 (m), 569 (m), 552 (s); GC-MS (EI, 70 eV):  $m/z$  (%) = 300 (45), 285 (100), 128 (13); HRMS (EI): calcd. for  $\text{C}_{21}\text{H}_{20}\text{N}_2$  ( $[\text{M}]^+$ ): 300.16210; found: 300.16183.



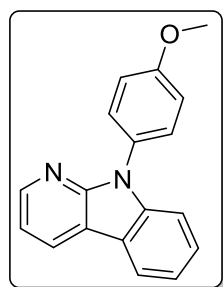
**9-(4-fluorophenyl)-9H-pyrido[2,3-b]indole 5d** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and 4-fluoroaniline (53  $\mu\text{L}$ , 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 3:1) to yield **5d** (87 mg, 89 %) as a white solid; m.p. 156-157 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (dd,  $J = 4.9, 1.6$  Hz, 1H), 8.27 (dt,  $J = 5.0, 2.5$  Hz, 1H), 8.02 (d,  $J = 7.8$  Hz, 1H), 7.55 – 7.46 (m, 2H), 7.42 – 7.29 (m, 2H), 7.28 – 7.10 (m, 4H);  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.83 (s);  $^{13}\text{C}$  NMR

(75 MHz, CDCl<sub>3</sub>)  $\delta$  161.79 (d,  $J$  = 247.2 Hz), 152.02, 146.54, 140.17, 132.23 (d,  $J$  = 3.1 Hz), 129.23 (d,  $J$  = 8.6 Hz), 128.39, 127.08, 121.04, 120.89, 120.83, 116.66 (d,  $J$  = 22.8 Hz), 116.35, 116.22, 110.19; IR (ATR, cm<sup>-1</sup>):  $\nu$  = 3061 (w), 1589 (m), 1570 (m), 1510 (s), 1475 (s), 1456 (s), 1416 (s), 1356 (m), 1336 (s), 1294 (s), 1228 (s), 1213 (s), 1173 (s), 1151 (s), 1119 (s), 1092 (s), 1053 (m), 1020 (m), 1012 (m), 997 (m), 964 (m), 953 (m), 941 (m), 931 (m), 924 (m), 899 (w), 870 (w), 856 (w), 833 (s), 816 (s), 798 (m), 769 (vs), 762 (s), 746 (s), 737 (vs), 715 (s), 704 (s), 665 (m), 644 (m), 629 (m), 617 (m), 579 (s), 569 (s); GC-MS (EI, 70 eV):  $m/z$  (%) = 261 (100), 131 (9); HRMS (ESI): calcd. for C<sub>17</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub> ([M + H]<sup>+</sup>): 263.0979; found: 263.09813.



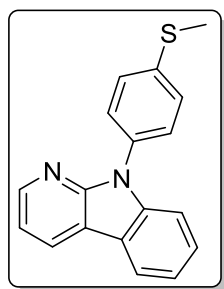
**9-(3-(trifluoromethyl)phenyl)-9H-pyrido[2,3-b]indole 5e** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and 4-fluoroaniline (53  $\mu$ L, 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 3:1) to yield **5e** (87 mg, 89 %) as a white solid; m.p. 71-72 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (dd,  $J$  = 4.9, 1.6 Hz, 1H), 8.28 (dd,  $J$  = 7.7, 1.6 Hz, 1H), 8.02 (dt,  $J$  = 7.8, 0.9 Hz, 1H), 7.87 (s, 1H),

7.84 – 7.76 (m, 1H), 7.68 – 7.59 (m, 2H), 7.41 – 7.35 (m, 2H), 7.26 (ddd,  $J$  = 8.2, 5.4, 2.9 Hz, 1H), 7.20 – 7.13 (m, 1H) ; <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  -62.70 (s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  151.71, 146.56, 139.59, 136.99, 132.14 (q,  $J$  = 32.8 Hz), 130.73 (d,  $J$  = 1.0 Hz), 130.25, 128.49, 127.28, 124.47 – 123.68 (m, 2xC), 123.83 (q,  $J$  = 272.6 Hz), 121.31, 121.17, 121.14, 116.66, 116.57, 110.10; IR (ATR, cm<sup>-1</sup>):  $\nu$  = 3051 (w), 1612 (w), 1591 (m), 1574 (m), 1497 (m), 1477 (m), 1458 (s), 1410 (s), 1358 (m), 1338 (m), 1321 (s), 1306 (s), 1290 (s), 1275 (s), 1228 (s), 1178 (m), 1167 (s), 1155 (s), 1119 (vs), 1103 (s), 1093 (s), 1068 (s), 1020 (m), 999 (m), 972 (s), 937 (m), 931 (m), 914 (m), 889 (m), 852 (m), 810 (s), 796 (s), 771 (s), 760 (m), 744 (s), 737 (vs), 715 (m), 694 (vs), 661 (s), 642 (s), 619 (s), 582 (m), 565 (m), 528 (s); GC-MS (EI, 70 eV):  $m/z$  (%) = 311 (100), 243 (11); HRMS (ESI): calcd. for C<sub>18</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub> ([M + H]<sup>+</sup>): 313.09471; found: 313.09460.

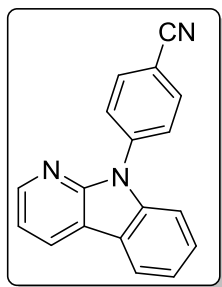


**9-(4-methoxyphenyl)-9H-pyrido[2,3-b]indole 5f** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and *p*-anisidine (69 mg, 0.56 mmol). The product was purified by flash chromatography (silica gel,

heptanes/ethylacetate 2:1) to yield **5f** (100 mg, 98 %) as a white solid; m.p. 137-138 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.40 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.30 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.40 – 7.30 (m, 2H), 7.29 – 7.19 (m, 1H), 7.18 – 7.09 (m, 1H), 7.09 – 7.01 (m, 2H), 3.82 (s, 3H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 159.00, 152.24, 146.51, 140.55, 128.90, 128.73, 128.22, 126.86, 120.86, 120.60, 120.49, 116.17, 115.81, 115.00, 110.30, 55.58; IR (ATR, cm<sup>-1</sup>): ν = 3057 (w), 2960 (w), 2935 (w), 2908 (w), 2835 (w), 1589 (m), 1570 (m), 1512 (s), 1477 (m), 1456 (s), 1441 (m), 1416 (s), 1358 (m), 1336 (m), 1298 (m), 1288 (s), 1230 (vs), 1190 (m), 1174 (s), 1149 (m), 1117 (s), 1103 (s), 1053 (w), 1028 (s), 999 (m), 962 (m), 951 (m), 939 (m), 930 (m), 918 (m), 847 (w), 827 (s), 814 (m), 798 (m), 769 (vs), 744 (s), 735 (vs), 721 (s), 702 (m), 646 (s), 631 (s), 617 (m), 586 (s), 579 (s), 571 (m), 530 (vs); GC-MS (EI, 70 eV): m/z (%) = 274 (100), 259 (55), 231 (25), 168 (10), 115 (9); HRMS (ED): calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>1</sub>N<sub>2</sub> ([M]<sup>+</sup>): 274.11006; found: 274.10996.

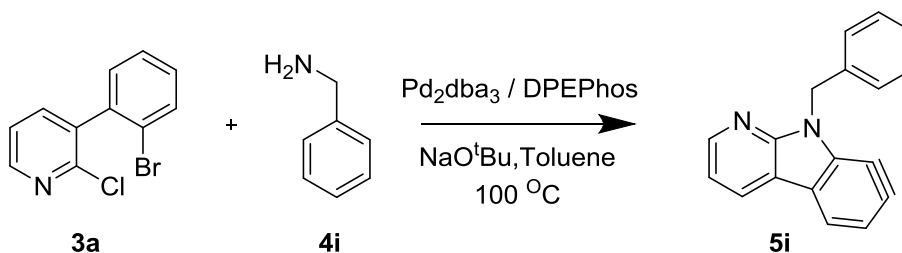


**9-(4-(methylthio)phenyl)-9H-pyrido[2,3-b]indole 5g** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and 4-(methylthio)aniline (69 μL, 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 2:1) to yield **5g** (99 mg, 92 %) as a white solid; m.p. 136-137 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.40 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.30 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.04 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.52 – 7.36 (m, 6H), 7.31 – 7.21 (m, 1H), 7.15 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.48 (s, 3H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 150.92, 145.46, 139.03, 137.06, 132.25, 127.27, 126.70, 125.94, 119.92, 119.78, 119.73, 115.32, 115.05, 109.30, 15.00; IR (ATR, cm<sup>-1</sup>): ν = 3039 (w), 2960 (m), 2920 (m), 1626 (w), 1589 (m), 1568 (m), 1500 (s), 1475 (m), 1452 (m), 1437 (m), 1414 (s), 1356 (m), 1335 (m), 1309 (m), 1300 (m), 1290 (s), 1259 (m), 1228 (s), 1182 (m), 1169 (m), 1151 (m), 1117 (m), 1103 (m), 1090 (s), 1049 (m), 1014 (s), 997 (s), 980 (m), 970 (m), 953 (m), 933 (m), 924 (m), 858 (m), 814 (s), 798 (s), 769 (vs), 735 (vs), 714 (s), 679 (m), 642 (s), 629 (s), 617 (m), 580 (m), 569 (m); GC-MS (EI, 70 eV): m/z (%) = 290 (100), 275 (50), 243 (24); HRMS (ED): calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>S<sub>1</sub> ([M]<sup>+</sup>): 290.08722; found: 290.08702.



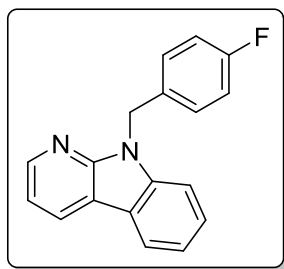
**9-(4-cyanophenyl)-9H-pyrido[2,3-b]indole 5h** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and 4-aminobenzonitrile (66 mg, 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 1.5:1) to yield **5h** (83 mg, 83 %) as a white solid; m.p. 179-180 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.38 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.29 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.36 (m, 2H), 7.33 – 7.24 (m, 1H), 7.19 (dd, *J* = 7.8, 4.9 Hz, 1H) ; <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 151.32, 146.45, 140.52, 138.85, 133.45, 128.58, 127.37, 127.28, 121.74, 121.45, 121.28, 118.52, 117.11, 116.85, 110.41, 110.23; IR (ATR, cm<sup>-1</sup>): ν = 3057 (w), 2227 (m), 1603 (m), 1591 (m), 1574 (m), 1512 (m), 1487 (w), 1475 (w), 1450 (m), 1410 (s), 1356 (m), 1336 (m), 1311 (w), 1286 (m), 1228 (m), 1217 (m), 1184 (w), 1169 (m), 1155 (w), 1119 (m), 1103 (w), 1057 (w), 1020 (w), 1001 (w), 960 (w), 953 (w), 945 (w), 928 (w), 856 (m), 833 (m), 823 (m), 800 (w), 789 (w), 773 (m), 766 (s), 744 (m), 735 (vs), 694 (m), 656 (w), 631 (m), 619 (w), 577 (m), 569 (m), 550 (s), 532 (m); GC-MS (EI, 70 eV): *m/z* (%) = 268 (100), 134 (7); HRMS (EI): calcd. for C<sub>18</sub>H<sub>10</sub>N<sub>3</sub> ([M]<sup>+</sup>): 268.08692; found: 268.08700.

**General procedure B for double C-N coupling with chain amine derivatives, exemplified by: 5-benzyl-5H-pyrido[3,2-b]indole 5i**



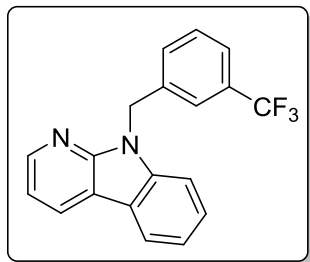
To pressure tube charged with **3a** (100 mg, 0.37 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (17 mg, 19 μmol), ligand DPEPhos (21 mg, 37 μmol) and sodium tert-butoxide (107 mg, 0.12 mmol) under Argon. The mixture was back-filled with Argon several times. The mixture was dissolved in anhydrous Toluene (10 mL). benzylamine (61 μL, 0.56 mmol) was added to the mixture and heated at 100 °C for 7 h. After cooling, the reaction mixture was diluted with dichloromethane (20 mL) and filtered through a celite pad, washing with dichloromethane (40 mL). The filtrate was reduced *in vacuo*. The product was separated via flash chromatography (silica gel, heptanes/ethylacetate

3:1) to yield **5i** (85 mg, 88 %) as a white solid; m.p. 98-99 °C;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (dd,  $J = 4.9, 1.6$  Hz, 1H), 8.20 (dd,  $J = 7.7, 1.6$  Hz, 1H), 7.99 – 7.92 (m, 1H), 7.36 – 7.20 (m, 2H), 7.19 – 7.01 (m, 7H), 5.58 (s, 2H) ;  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ )  $\delta$  150.65, 145.10, 138.49, 136.25, 127.55, 127.08, 126.26, 125.88, 125.68, 119.92, 119.56, 118.93, 114.79, 114.24, 108.80, 43.87; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 3028$  (w), 2960 (w), 2918 (w), 1626 (w), 1589 (m), 1568 (m), 1483 (s), 1466 (s), 1452 (m), 1431 (s), 1412 (s), 1356 (m), 1348 (m), 1333 (m), 1315 (w), 1292 (m), 1259 (s), 1211 (s), 1194 (m), 1155 (m), 1128 (m), 1119 (m), 1092 (m), 1078 (m), 1065 (m), 1053 (m), 1030 (s), 1020 (s), 995 (s), 970 (m), 947 (m), 928 (w), 906 (w), 870 (w), 850 (m), 839 (m), 800 (s), 791 (s), 773 (vs), 748 (s), 729 (vs), 694 (s), 652 (s), 619 (m), 606 (m), 582 (m), 569 (m), 555 (s), 528 (s); GC-MS (EI, 70 eV):  $m/z$  (%) = 257 (100), 181 (34), 91 (45); HRMS (ESI): calcd. for  $\text{C}_{18}\text{H}_{14}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 259.12297; found: 259.12298.

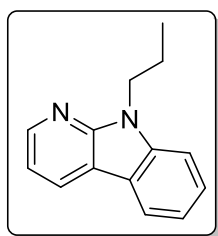


**5-(4-fluorobenzyl)-5H-pyrido[3,2-b]indole 5j** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and 4-fluorobenzylamine (61  $\mu\text{L}$ , 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 3:1) to yield **5j** (90 mg, 87 %) as a white solid; m.p. 103-104 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (dd,  $J = 4.9, 1.6$  Hz, 1H), 8.25 (dd,  $J = 7.7, 1.6$  Hz, 1H), 8.02 – 7.96 (m, 1H), 7.36 (ddd,  $J = 8.3, 7.2, 1.2$  Hz, 1H), 7.28 – 7.07 (m, 5H), 6.89 – 6.79 (m, 2H), 5.57 (s, 2H) ;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.23 (s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  161.07 (d,  $J = 245.4$  Hz), 150.56, 145.15, 138.33, 132.02 (d,  $J = 3.2$  Hz), 127.62 (d,  $J = 8.1$  Hz), 127.20, 125.77, 120.05, 119.63, 119.09, 114.85, 114.47 (d,  $J = 21.6$  Hz), 114.39, 108.65, 43.24; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 3053$  (w), 3034 (w), 2935 (w), 1624 (w), 1587 (m), 1572 (m), 1508 (s), 1481 (m), 1464 (s), 1439 (m), 1416 (s), 1383 (w), 1354 (m), 1335 (m), 1294 (m), 1252 (m), 1217 (s), 1207 (s), 1163 (m), 1128 (m), 1119 (m), 1101 (m), 1061 (m), 1049 (m), 1030 (w), 1020 (m), 1001 (w), 987 (m), 966 (w), 928 (w), 862 (m), 849 (m), 823 (m), 800 (m), 791 (m), 777 (vs), 762 (s), 746 (s), 735 (vs), 704 (m), 665 (w), 638 (m), 629 (s), 619 (m), 609 (m), 580 (m), 565 (m); GC-MS (EI, 70 eV):  $m/z$  (%) = 276 (100), 181 (30), 109 (73); HRMS (ESI): calcd. for  $\text{C}_{18}\text{H}_{13}\text{F}_1\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 277.11355; found: 277.11394.





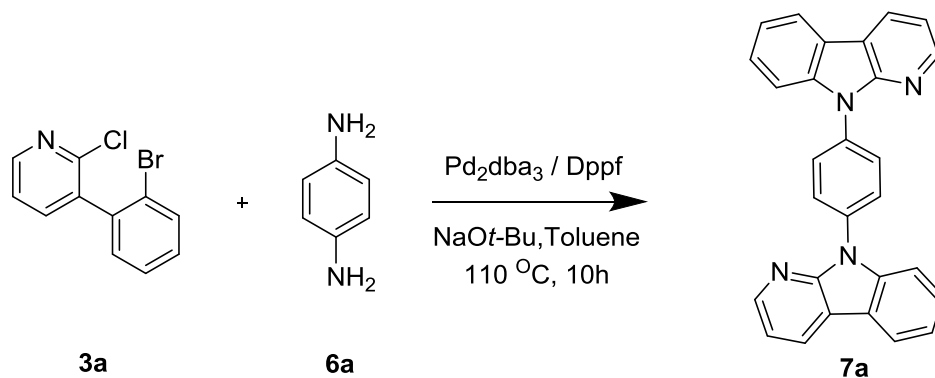
**5-(3-(trifluoromethyl)benzyl)-5H-pyrido[3,2-b]indole 5k** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and 3-(trifluoromethyl)benzylamine (80  $\mu$ L, 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 3:1) to yield **5k** (109 mg, 90 %) as a white solid; m.p. 81-82  $^{\circ}$ C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (dd,  $J = 4.9, 1.6$  Hz, 1H), 8.21 (dd,  $J = 7.7, 1.6$  Hz, 1H), 7.96 (d,  $J = 7.8$  Hz, 1H), 7.49 (s, 1H), 7.39 – 7.30 (m, 2H), 7.17 (ddd,  $J = 11.9, 6.6, 0.9$  Hz, 4H), 7.12 – 7.03 (m, 1H), 5.60 (s, 2H);  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.51 (s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  151.65, 146.29, 139.36, 138.47, 131.04 (q,  $J = 32.3$  Hz), 130.30, 129.26, 128.36, 126.99, 124.38 (q,  $J = 3.8$  Hz), 124.06 (q,  $J = 272.4$  Hz), 123.89 (q,  $J = 3.8$  Hz), 121.23, 120.81, 120.37, 115.99, 115.68, 109.55, 44.61; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 3053$  (w), 1628 (w), 1591 (m), 1572 (m), 1483 (m), 1466 (m), 1450 (w), 1433 (m), 1416 (s), 1325 (vs), 1296 (m), 1281 (m), 1261 (m), 1217 (m), 1205 (m), 1186 (m), 1157 (s), 1117 (vs), 1097 (s), 1072 (vs), 1022 (m), 1011 (m), 993 (m), 966 (m), 937 (m), 922 (m), 903 (m), 868 (m), 852 (m), 800 (s), 791 (s), 771 (s), 744 (s), 735 (s), 702 (vs), 671 (m), 646 (s), 619 (m), 600 (m), 575 (m), 559 (m); GC-MS (EI, 70 eV):  $m/z$  (%) = 326 (100), 181 (62), 159 (20), 140 (13), 109 (13); HRMS (ESI): calcd. for  $\text{C}_{19}\text{H}_{13}\text{F}_3\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 327.11036; found: 327.11066.



**5-propyl-5H-pyrido[3,2-b]indole 5l** prepared following general procedure A using **3a** (100 mg, 0.37 mmol) and n-propylamine (46  $\mu$ L, 0.56 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 3:1) to yield **5l** (71 mg, 91 %) as a white liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (dd,  $J = 4.9, 1.6$  Hz, 1H), 8.16 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.97 – 7.89 (m, 1H), 7.43 – 7.29 (m, 2H), 7.14 (ddd,  $J = 8.0, 6.9, 1.4$  Hz, 1H), 7.01 (dd,  $J = 7.6, 4.9$  Hz, 1H), 4.37 – 4.26 (m, 2H), 1.90 – 1.73 (m, 2H), 0.86 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  151.61, 145.94, 139.71, 128.03, 126.61, 121.03, 120.44, 119.62, 115.83, 114.86, 109.38, 43.16, 22.32, 11.65; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 3049$  (w), 2962 (m), 2929 (m), 2874 (w), 1626 (w), 1589 (m), 1570 (m), 1481 (s), 1466 (s), 1443 (m), 1414 (vs), 1381 (m), 1371 (m), 1360 (m), 1342 (s), 1333 (s), 1313 (w), 1290 (s), 1255 (m), 1219 (s), 1157 (m), 1138 (m), 1128 (m), 1119 (s), 1090 (w), 1068 (m), 1049 (w), 1018 (w), 997 (m), 960 (w), 926 (w), 893 (w), 845 (w), 800 (w), 771 (vs), 748 (s), 733 (vs), 712 (m), 633 (m), 619 (m), 580 (m), 561 (m); GC-

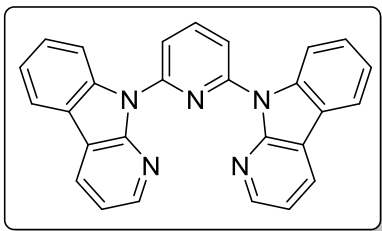
MS (EI, 70 eV):  $m/z$  (%) = 210 (32), 181 (100), 168 (82), 140 (12), 127 (14); HRMS (EI): calcd. for  $C_{14}H_{14}N_2$  ( $[M]^+$ ): 210.11515; found: 210.11500.

**General procedure C for double C-N coupling with diamine derivatives, exemplified by: 1,4-bis(9H-pyrido[2,3-b]indol-9-yl)benzene 7a**



To pressure tube was charged with **3a** (200 mg, 0.75 mmol), 1,4-diaminobenzene (37 mg, 0.34 mmol),  $Pd_2(dba)_3$  (15 mg, 17  $\mu$ mol), ligand dppf (19 mg, 34  $\mu$ mol) and sodium tert-butoxide (195 mg, 2.0 mmol) under Argon. The mixture was back-filled with Argon several times. The mixture was dissolved in anhydrous Toluene (10 mL) and heated at 110 °C for 10 h. After cooling, the reaction mixture was diluted with dichloromethane (20 mL) and filtered through a celite pad, washing with dichloromethane (40 mL). The filtrate was reduced *in vacuo*. The product was separated via flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 1:1:1) to yield 1,4-bis(9H-pyrido[2,3-b]indol-9-yl)benzene **7a** (64 mg, 46 %) as a white solid; m.p. 307-308 °C;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.46 (dd,  $J = 4.8, 1.4$  Hz, 2H), 8.34 (dt,  $J = 9.4, 4.7$  Hz, 2H), 8.09 (d,  $J = 7.7$  Hz, 2H), 7.87 (s, 4H), 7.62 (d,  $J = 8.2$  Hz, 2H), 7.50 – 7.37 (m, 3H), 7.30 (t,  $J = 7.5$  Hz, 2H), 7.25 – 7.16 (m, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  151.90, 146.48, 139.94, 135.34, 128.42, 128.32, 127.14, 121.02, 116.61, 116.37, 110.73; IR (ATR,  $cm^{-1}$ ):  $\nu = 3045$  (m), 2922 (m), 1591 (m), 1572 (m), 1518 (s), 1481 (m), 1450 (s), 1406 (s), 1356 (m), 1338 (s), 1317 (m), 1290 (s), 1228 (s), 1173 (m), 1128 (m), 1120 (m), 1111 (m), 1051 (m), 1018 (m), 999 (m), 928 (m), 918 (m), 827 (m), 762 (s), 742 (s), 727 (vs), 700 (s), 642 (s), 619 (m), 579 (m), 567 (m), 534 (s); GC-MS (EI, 70 eV):  $m/z$  (%) =

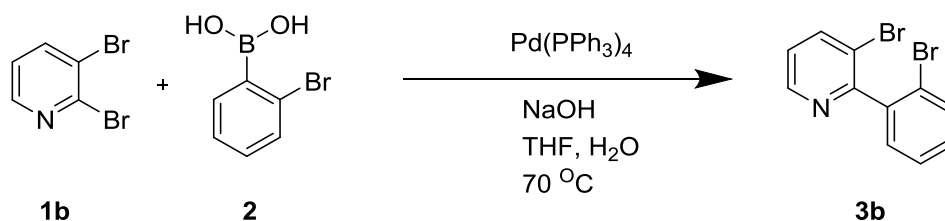
410 (100), 242 (24), 205 (23), 191 (12); HRMS (EI): calcd. for C<sub>28</sub>H<sub>18</sub>N<sub>4</sub> ([M]<sup>+</sup>): 410.15260; found: 410.15147.



**9-(6-(9H-indeno[2,1-b]pyridin-9-yl)pyridin-2-yl)-9H-pyrido[2,3-b]indole 7b** prepared following general procedure C using **3a** (200 mg, 0.75 mmol) and 2,6-diaminopyridine (37 mg, 0.34 mmol). The product was purified by flash chromatography (silica gel,

heptanes/dichloromethane/ethylacetate 1:1:1) to yield **7b** (70 mg, 50 %) as a white solid; m.p. 236-237 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.51 (dd, *J* = 4.8, 1.5 Hz, 2H), 8.43 – 8.29 (m, 4H), 8.29 – 8.21 (m, 2H), 8.13 (dd, *J* = 8.8, 7.1 Hz, 1H), 8.00 (t, *J* = 9.9 Hz, 2H), 7.38 – 7.14 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 151.36, 149.76, 146.01, 140.02, 139.02, 128.26, 127.54, 121.79, 121.57, 120.37, 117.76, 117.15, 116.61, 114.34; IR (ATR, cm<sup>-1</sup>): ν = 3047 (w), 2922 (w), 1599 (m), 1591 (s), 1570 (m), 1485 (w), 1450 (vs), 1414 (m), 1400 (vs), 1362 (m), 1340 (m), 1331 (s), 1286 (s), 1242 (m), 1223 (m), 1209 (m), 1180 (s), 1165 (m), 1155 (m), 1120 (m), 1105 (m), 1095 (m), 1057 (m), 1039 (m), 1026 (m), 999 (m), 985 (w), 974 (w), 968 (w), 957 (w), 943 (m), 933 (m), 922 (m), 849 (w), 796 (m), 764 (vs), 744 (s), 727 (vs), 700 (m), 683 (m), 658 (m), 634 (m), 619 (m), 611 (m), 579 (m), 567 (w), 559 (m); GC-MS (EI, 70 eV): *m/z* (%) = 410 (100), 244 (28), 206 (89); HRMS (EI): calcd. for C<sub>27</sub>H<sub>16</sub>N<sub>5</sub> ([M]<sup>+</sup>): 410.14002; found: 410.13958.

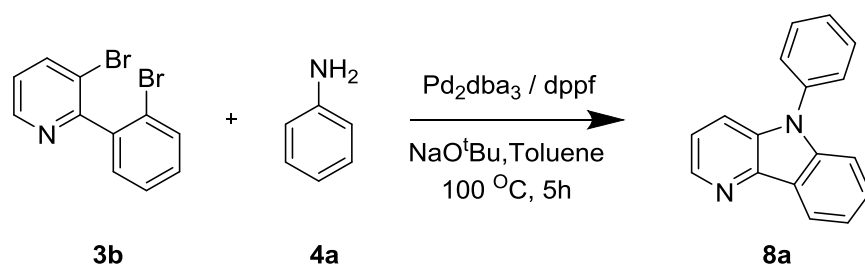
### General procedure for prepared of 3-bromo-2-(2-bromophenyl)pyridine **3b**.



2,3-dibromopyridine **1b** (1 g, 4.2 mmol), 2-bromophenyl boronic acid **2** (1.0 g, 5.1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (244 mg, 211 μmol) and sodium hydroxide (507 mg, 12.7 mmol) were added to 500 mL Schlenk flask. The mixture was back-filled several times with Argon. To the mixture 70 mL

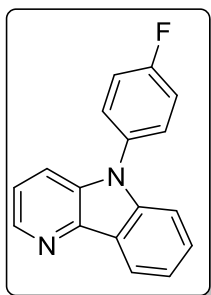
THF and 10 mL distilled water were added, then, back-filled several times. The reaction was heated at 70 °C for 4h. The solvent was evaporated *in vacuo*. The residue was extracted with dichloromethane and water. The organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated *in vacuo*. The yellow residue was purified by column chromatography (silica gel, Heptane/dichloromethane/ethylacetate 4:1:1) to yield 3-bromo-2-(2-bromophenyl)pyridine **3b** (1.27 g, 96 %) as colorless syrup; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.57 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.93 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.39 – 7.32 (m, 1H), 7.29 – 7.13 (m, 7H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 147.84, 140.99, 140.46, 132.69, 130.23, 130.08, 127.34, 124.13, 122.46, 121.35; IR (ATR, cm<sup>-1</sup>): ν = 3053 (w), 2920 (w), 2850 (w), 1593 (m), 1568 (m), 1549 (m), 1479 (m), 1437 (m), 1412 (s), 1298 (w), 1269 (w), 1252 (m), 1230 (w), 1211 (w), 1201 (w), 1159 (w), 1124 (m), 1093 (m), 1055 (m), 1024 (s), 1011 (vs), 943 (m), 793 (s), 777 (m), 748 (vs), 723 (s), 694 (m), 681 (s), 650 (m), 615 (s), 561 (m); GC-MS (EI, 70 eV): *m/z* (%) = 313 (37), 234 (99), 233 (100), 153 (82), 126 (28), 99 (10), 75 (14), 63 (10), 50 (12); HRMS (EI): calcd. for C<sub>11</sub>H<sub>7</sub>N<sub>1</sub>Br<sub>2</sub> ([M]<sup>+</sup>): 310.89398; found: 310.89479; calcd. for C<sub>11</sub>H<sub>7</sub>N<sub>1</sub>Br<sub>1</sub><sup>81</sup>Br<sub>1</sub> ([M]<sup>+</sup>): 312.89193; found: 312.89233; calcd. for C<sub>11</sub>H<sub>7</sub>N<sub>1</sub><sup>81</sup>Br<sub>2</sub> ([M]<sup>+</sup>): 314.88988; found: 314.89073.

**General procedure D for double C-N coupling with aniline derivatives, exemplified by: 5-phenyl-5H-pyrido[3,2-*b*]indole **8a****

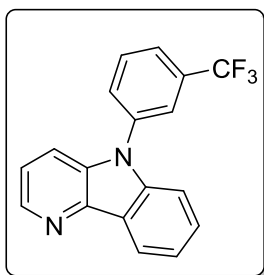


Aniline (44 μL, 479 μmol) was added to pressure tube charged with **3b** (100 mg, 0.32 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (15 mg, 16 μmol), ligand dppf (18 mg, 32 μmol) and sodium tert-butoxide (92 mg, 0.96 mmol) under Argon. The mixture was back-filled with Argon several times. The mixture was dissolved in anhydrous Toluene (10 mL) and heated at 100 °C for 4 h. After cooling, the

reaction mixture was diluted with dichloromethane (20 mL) and filtered through a celite pad, washing with dichloromethane (40 mL). The filtrate was reduced *in vacuo*. The product was separated via flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 10:1:1) to yield 5-phenyl-5*H*-pyrido[3,2-*b*]indole **8a** (65 mg, 83%) as a white solid; m.p. 99-101 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.50 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.40 – 8.30 (m, 1H), 7.60 – 7.12 (m, 11H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 142.54, 142.26, 141.54, 136.84, 134.31, 130.04, 127.95, 127.80, 126.79, 122.45, 120.87, 120.83, 120.18, 116.72, 110.04; IR (ATR, cm<sup>-1</sup>): ν = 3053 (m), 1622 (m), 1593 (s), 1574 (m), 1502 (s), 1481 (s), 1452 (s), 1412 (vs), 1371 (m), 1340 (m), 1315 (m), 1304 (s), 1282 (m), 1234 (m), 1209 (s), 1178 (m), 1167 (m), 1147 (m), 1119 (m), 1107 (m), 1072 (m), 1026 (m), 1011 (m), 931 (m), 906 (m), 787 (m), 777 (s), 762 (s), 744 (vs), 727 (vs), 698 (vs), 665 (m), 642 (m), 633 (s), 615 (s), 582 (m), 567 (m), 534 (m); GC-MS (EI, 70 eV): *m/z* (%) = 244 (100), 216 (4), 189 (3), 167 (3), 152 (3), 140 (4), 122 (9), 88 (3), 77 (4), 63 (3), 51 (5), 39 (4); HRMS (EI): calcd. for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub> ([M]<sup>+</sup>): 244.09950; found: 244.09922;

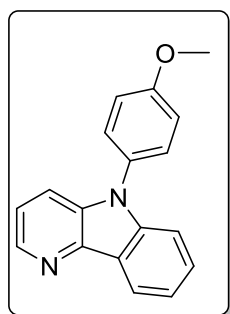


**5-(4-fluorophenyl)-5*H*-pyrido[3,2-*b*]indole **8b**** prepared following general procedure D using **3b** (100 mg, 0.32 mmol) and 4-fluoroaniline (45 μL, 0.48 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 8:1:1) to yield **8b** (61 mg, 73 %) as a white solid; m.p. 115-117 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.49 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.39 – 8.29 (m, 1H), 7.53 – 7.32 (m, 4H), 7.31 – 7.11 (m, 3H), 6.78 – 6.65 (m, 1H), 6.48 (ddd, *J* = 6.7, 5.2, 2.9 Hz, 1H); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -112.83 (s); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 161.79 (d, *J* = 248.2 Hz), 142.62, 141.69, 134.45, 132.77, 128.73 (d, *J* = 8.6 Hz), 128.06, 122.38, 120.94, 120.27, 117.24, 116.88, 116.50, 115.61 (d, *J* = 22.4 Hz), 109.80; IR (ATR, cm<sup>-1</sup>): ν = 3055 (m), 3037 (m), 1620 (m), 1587 (m), 1506 (vs), 1477 (s), 1452 (s), 1412 (s), 1354 (m), 1342 (m), 1311 (s), 1294 (m), 1281 (m), 1215 (s), 1207 (s), 1169 (s), 1151 (s), 1119 (m), 1105 (m), 1093 (s), 1049 (m), 1034 (m), 1028 (m), 1011 (m), 937 (m), 912 (s), 845 (s), 833 (s), 816 (s), 781 (s), 764 (m), 742 (vs), 727 (vs), 715 (s), 700 (s), 646 (m), 627 (m), 617 (s), 575 (s), 534 (s); GC-MS (EI, 70 eV): *m/z* (%) = 262 (100), 261 (29), 131 (10); HRMS (EI): calcd. for C<sub>17</sub>H<sub>11</sub>F<sub>1</sub>N<sub>2</sub> ([M]<sup>+</sup>): 262.09008; found: 262.08948.



**5-(3-(trifluoromethyl)phenyl)-5H-pyrido[3,2-b]indole 8c** prepared following general procedure D using **3b** (100 mg, 0.32 mmol) and 3-(trifluoromethyl)aniline (60  $\mu$ L, 0.48 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 8:1:1) to yield **8c** (64 mg, 64 %) as a white solid; m.p. 144-146  $^{\circ}$ C;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (dd,  $J = 4.7, 1.3$  Hz, 1H), 8.47 – 8.29 (m, 1H), 7.84 – 7.53 (m, 4H), 7.52

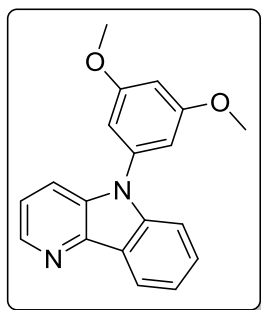
– 7.14 (m, 4H);  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.70 (s);  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ )  $\delta$  143.08, 142.52, 141.17, 137.65, 133.96, 132.76 (q,  $J = 33.2$  Hz), 130.80, 130.03, 128.26, 124.44 (q,  $J = 3.6$  Hz), 123.61 (q,  $J = 3.6$  Hz), 122.75, 121.41, 121.09, 120.39, 116.43, 109.66; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 3055$  (w), 3041 (w), 1622 (m), 1606 (w), 1595 (m), 1579 (w), 1498 (m), 1481 (m), 1456 (s), 1412 (s), 1362 (m), 1356 (m), 1333 (m), 1309 (s), 1292 (m), 1275 (m), 1232 (m), 1217 (m), 1207 (m), 1182 (s), 1163 (s), 1155 (s), 1117 (vs), 1095 (s), 1074 (s), 1028 (m), 1014 (m), 1001 (m), 966 (m), 945 (m), 935 (m), 928 (m), 918 (m), 906 (m), 854 (w), 810 (m), 802 (s), 791 (m), 781 (s), 760 (w), 744 (vs), 727 (s), 715 (s), 706 (vs), 673 (m), 663 (s), 638 (m), 621 (m), 607 (m), 582 (w), 563 (w), 536 (m); GC-MS (EI, 70 eV):  $m/z$  (%) = 312 (100), 242 (8); HRMS (EI): calcd. for  $\text{C}_{18}\text{H}_{11}\text{F}_3\text{N}_2$  ( $[\text{M}]^+$ ): 312.08688; found: 312.08662.



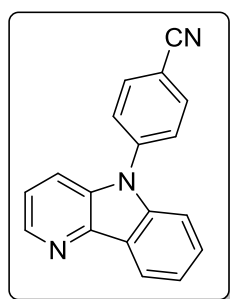
**5-(4-methoxyphenyl)-5H-pyrido[3,2-b]indole 8d** prepared following general procedure D using **3b** (100 mg, 0.32 mmol) and *p*-anisidine (59 mg, 0.48 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 5:1:1) to yield **8d** (88 mg, 94 %) as a white solid; m.p. 128-130  $^{\circ}$ C;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (dd,  $J = 4.7, 1.3$  Hz, 1H), 8.43 – 8.30 (m, 1H), 7.55 (dd,  $J = 8.3, 1.4$  Hz, 1H), 7.50 –

7.21 (m, 6H), 7.11 – 6.99 (m, 2H), 3.85 (s, 3H);  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ )  $\delta$  159.13, 142.22, 142.06, 134.81, 129.36, 128.30, 127.90, 122.13, 120.85, 120.59, 120.12, 116.68, 115.22, 109.97, 55.62; IR (ATR,  $\text{cm}^{-1}$ ):  $\nu = 2955$  (w), 2929 (w), 2837 (w), 1620 (m), 1510 (vs), 1479 (m), 1454 (s), 1441 (m), 1414 (s), 1385 (w), 1342 (m), 1313 (s), 1300 (m), 1286 (m), 1242 (s), 1209 (s), 1176 (s), 1149 (m), 1120 (m), 1107 (s), 1066 (m), 1028 (s), 1012 (m), 937 (m), 912 (m), 860 (w), 829 (s), 812 (m), 791 (s), 748 (vs), 729 (vs), 700 (s), 667 (m), 646 (m), 629 (m), 617 (s), 584 (s),

536 (s); GC-MS (EI, 70 eV):  $m/z$  (%) = 274 (100), 259 (55), 231 (13), 230 (15), 229 (14), 115 (9); HRMS (EI): calcd. for  $C_{18}H_{14}O_1N_2$  ( $[M]^+$ ): 274.11006; found: 274.11009.



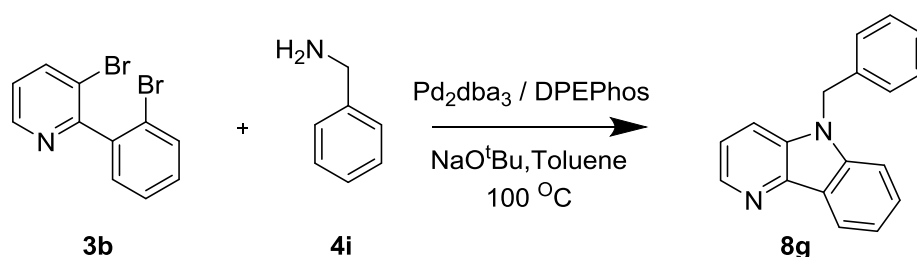
**55-(3,5-dimethoxyphenyl)-5H-pyrido[3,2-b]indole 8e** prepared following general procedure D using **3b** (100 mg, 0.32 mmol) and 3,5-dimethoxyaniline (73 mg, 0.48 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 3:1:1) to yield **8d** (88 mg, 94 %) as a white solid; m.p. 150-152 °C;  $^1H$  NMR (250 MHz,  $CDCl_3$ )  $\delta$  8.58 – 8.41 (m, 1H), 8.33 (dd,  $J = 7.7, 0.7$  Hz, 1H), 7.64 (dd,  $J = 8.3, 1.3$  Hz, 1H), 7.53 – 7.12 (m, 4H), 6.57 (d,  $J = 2.2$  Hz, 2H), 6.45 (t,  $J = 2.2$  Hz, 1H), 3.71 (s,  $J = 9.9$  Hz, 6H);  $^{13}C$  NMR (63 MHz,  $CDCl_3$ )  $\delta$  161.82, 142.55, 142.26, 141.37, 138.46, 134.17, 127.95, 122.48, 120.82, 120.20, 116.99, 110.33, 104.96, 99.76, 93.72, 55.59; IR (ATR,  $cm^{-1}$ ):  $\nu = 3051$  (m), 3007 (m), 2970 (m), 2945 (m), 2916 (m), 2841 (m), 1620 (m), 1605 (s), 1583 (s), 1495 (m), 1475 (m), 1452 (s), 1425 (s), 1416 (s), 1367 (m), 1342 (m), 1331 (m), 1313 (s), 1296 (s), 1282 (s), 1252 (m), 1223 (m), 1194 (s), 1147 (vs), 1057 (s), 1009 (s), 991 (m), 928 (m), 906 (m), 868 (m), 852 (m), 833 (s), 823 (s), 783 (s), 773 (s), 741 (s), 723 (vs), 696 (s), 690 (s), 675 (s), 660 (s), 621 (s), 607 (s), 573 (s), 557 (m), 532 (m); GC-MS (EI, 70 eV):  $m/z$  (%) = 304 (100), 261 (8), 245 (10), 218 (7); HRMS (EI): calcd. for  $C_{19}H_{16}O_2N_2$  ( $[M]^+$ ): 304.12063; found: 304.12015.



**5-(4-cyanophenyl)-5H-pyrido[3,2-b]indole 8f** prepared following general procedure D using **3b** (100 mg, 0.32 mmol) and 4-aminobenzonitrile (56 mg, 0.48 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 4:1:1) to yield **8f** (36 mg, 42 %) as a white solid; m.p. 162-164 °C;  $^1H$  NMR (250 MHz,  $CDCl_3$ )  $\delta$  8.57 (dd,  $J = 4.7, 1.3$  Hz, 1H), 8.41 – 8.33 (m, 1H), 7.90 – 7.81 (m, 2H), 7.71 – 7.60 (m, 3H), 7.52 – 7.23 (m, 4H),  $^{13}C$  NMR (63 MHz,  $CDCl_3$ )  $\delta$  143.51, 141.21, 134.10, 133.45, 128.42, 126.86, 123.12, 121.88, 121.23, 120.49, 116.59, 111.02, 109.77; IR (ATR,  $cm^{-1}$ ):  $\nu = 3051$  (w), 3007 (w), 2226 (m), 1616 (w), 1601 (s), 1587 (m), 1558 (w), 1506 (s), 1489 (w), 1479 (m), 1454 (m), 1412 (s), 1373 (w), 1354 (m), 1340 (m), 1315 (s), 1290 (m), 1246 (w), 1234 (m), 1221 (m), 1207 (s), 1182 (m), 1169 (m), 1153 (m), 1136 (m), 1128 (m), 1117 (m), 1107 (m),

1053 (w), 1028 (w), 1014 (m), 978 (w), 968 (w), 953 (w), 935 (w), 916 (m), 885 (w), 841 (s), 783 (s), 748 (vs), 731 (vs), 723 (s), 667 (m), 656 (m), 631 (m), 619 (s), 582 (w), 567 (m), 552 (s), 528 (m); GC-MS (EI, 70 eV): m/z (%) = 269 (100), 270 (25), 75 (7), 39 (7); HRMS (EI): calcd. for C<sub>18</sub>H<sub>11</sub>N<sub>3</sub> ([M]<sup>+</sup>): 269.09475; found: 269.09432.

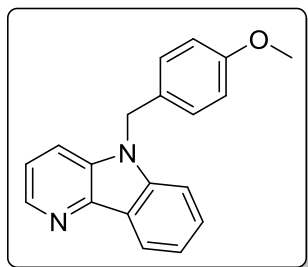
**General procedure E for double C-N coupling with chain amine derivatives, exemplified by: 5-benzyl-5H-pyrido[3,2-b]indole **8g****



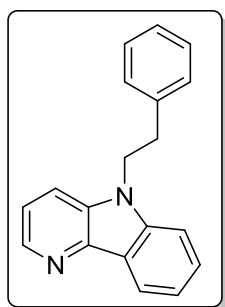
To pressure tube charged with **3b** (100 mg, 0.32 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (15 mg, 16 μmol), ligand DPEPhos (17 mg, 32 μmol) and sodium tert-butoxide (92 mg, 0.96 mmol) under Argon. The mixture was back-filled with Argon several times. The mixture was dissolved in anhydrous Toluene (10 mL). benzylamine **4i** (52 μL, 0.48 mmol) was added to the mixture and heated at 100 °C for 7 h. After cooling, the reaction mixture was diluted with dichloromethane (20 mL) and filtered through a celite pad, washing with dichloromethane (40 mL). The filtrate was reduced *in vacuo*. The product was separated via flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 5:1:1) to yield **8g** (76 mg, 92 %) as a white solid; m.p. 137-139 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.43 (dd, *J* = 4.7, 1.2 Hz, 1H), 8.32 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.30 (m, 2H), 7.28 – 7.01 (m, 6H), 6.93 (dd, *J* = 6.7, 2.6 Hz, 2H), 5.26 (s, 2H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 140.82, 140.75, 140.27, 135.40, 132.91, 127.78, 126.80, 126.62, 125.25, 121.08, 119.82, 119.07, 118.93, 114.75, 108.14, 45.35; IR (ATR, cm<sup>-1</sup>): ν = 3051 (w), 3028 (w), 2926 (w), 1622 (m), 1603 (w), 1589 (m), 1576 (w), 1558 (w), 1495 (m), 1483 (m), 1458 (s), 1450 (s), 1414 (s), 1373 (m), 1356 (w), 1335 (s), 1319 (s), 1281 (w), 1263 (w), 1242 (m), 1211 (m), 1194 (s), 1178 (m), 1149 (m), 1132 (m), 1117 (m), 1080 (m), 1057 (w), 1047 (w), 1028 (m), 1012 (m), 999 (w), 972 (w), 962 (w), 937 (w), 912 (w), 845 (m), 802 (w), 789 (m), 781 (s), 742 (vs), 731 (vs), 721 (vs), 694 (s), 644 (m), 621 (m), 600 (m), 584 (m), 567 (m), 557



(m), 536 (m); GC-MS (EI, 70 eV):  $m/z$  (%) = 258 (88), 181 (5), 167 (8), 91 (100), 39 (9); HRMS (EI): calcd. for  $C_{18}H_{14}N_2$  ( $[M]^+$ ): 258.11515; found: 258.11534.



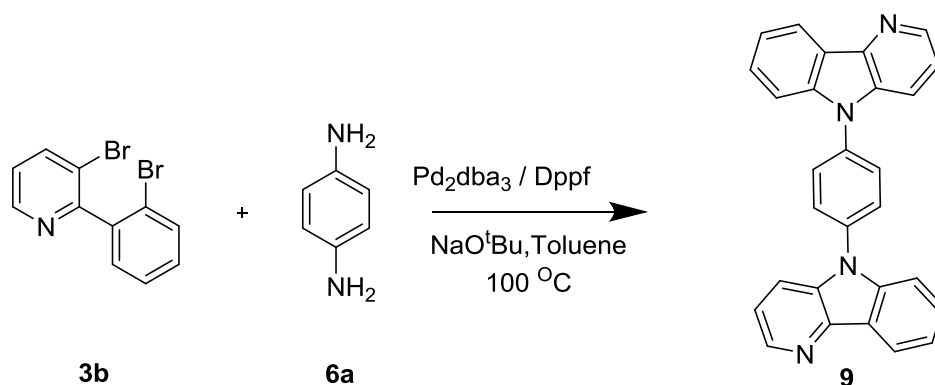
**5-(4-methoxybenzyl)-5H-pyrido[3,2-b]indole 8h** prepared following general procedure E using compound **3b** (100 mg, 0.32 mmol) and 4-methoxybenzylamine (63  $\mu$ L, 0.48 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 3:1:1) to yield **8h** (60 mg, 65 %) as a white solid; m.p. 124-126  $^{\circ}$ C;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.42 (dt,  $J$  = 5.7, 2.9 Hz, 1H), 8.36 – 8.28 (m, 1H), 7.48 – 7.31 (m, 2H), 7.30 – 7.07 (m, 3H), 6.88 (t,  $J$  = 5.8 Hz, 2H), 6.68 – 6.58 (m, 2H), 5.22 (s, 2H), 3.57 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  159.15, 141.92, 141.77, 141.37, 134.01, 128.51, 127.90, 127.71, 122.17, 120.94, 120.12, 120.02, 115.94, 114.27, 109.30, 55.24, 46.00; IR (ATR,  $cm^{-1}$ ):  $\nu$  = 2931 (w), 2835 (w), 1624 (m), 1610 (m), 1583 (m), 1512 (s), 1485 (s), 1460 (s), 1443 (m), 1412 (s), 1377 (m), 1354 (w), 1323 (s), 1308 (s), 1246 (vs), 1211 (m), 1203 (m), 1194 (s), 1178 (s), 1155 (m), 1134 (m), 1113 (s), 1059 (w), 1034 (s), 1009 (m), 984 (m), 962 (m), 939 (w), 864 (w), 845 (s), 837 (m), 820 (m), 791 (s), 775 (s), 746 (vs), 727 (vs), 708 (s), 665 (m), 640 (m), 625 (s), 600 (s), 582 (m), 565 (m), 540 (s); GC-MS (EI, 70 eV):  $m/z$  (%) = 288 (29), 242 (3), 167 (8), 140 (5), 121 (100), 91 (7), 78 (10), 77 (9); HRMS (EI): calcd. for  $C_{19}H_{16}N_2O_1$  ( $[M]^+$ ): 288.12571; found: 288.12541.



**5-phenethyl-5H-pyrido[3,2-b]indole 8i** prepared following general procedure E using compound **3b** (100 mg, 0.32 mmol) and 2-phenylethylamine (60  $\mu$ L, 0.48 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 5:1:1) to yield **8j** (67 mg, 77 %) as a white solid; m.p. 61-63  $^{\circ}$ C;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.38 (dd,  $J$  = 4.7, 1.3 Hz, 1H), 8.29 (d,  $J$  = 7.7 Hz, 1H), 7.38 (ddd,  $J$  = 8.2, 7.1, 1.2 Hz, 1H), 7.28 – 7.13 (m, 3H), 7.13 – 6.96 (m, 4H), 6.96 – 6.82 (m, 2H), 4.30 (t,  $J$  = 7.2 Hz, 2H), 2.93 (t,  $J$  = 7.2 Hz, 2H);  $^{13}C$  NMR (63 MHz,  $CDCl_3$ )  $\delta$  141.61, 141.46, 140.80, 138.37, 133.73, 128.73, 128.66, 127.66, 126.76, 122.05, 120.91, 119.88, 119.75, 115.45, 108.91, 44.82, 35.27; IR (ATR,  $cm^{-1}$ ):  $\nu$  = 3051 (w), 3041 (w), 3026 (w), 3001 (w), 2964 (w), 2939 (w), 2922 (w), 1622 (m), 1603 (w), 1587 (m), 1562 (w), 1483 (s), 1462 (s), 1452 (s), 1414 (vs), 1377

(m), 1360 (m), 1342 (s), 1319 (s), 1248 (w), 1223 (s), 1200 (m), 1186 (s), 1151 (m), 1132 (m), 1122 (m), 1080 (m), 1065 (w), 1049 (w), 1028 (m), 1009 (m), 974 (w), 962 (w), 939 (w), 926 (w), 881 (w), 856 (w), 839 (w), 791 (m), 777 (m), 764 (w), 742 (vs), 727 (vs), 696 (vs), 642 (w), 623 (m), 613 (m), 606 (m), 590 (m), 582 (w), 565 (w), 548 (m), 540 (m); GC-MS (EI, 70 eV):  $m/z$  (%) = 272 (23), 181 (100), 154 (5), 127 (12), 91 (5), 78 (5); HRMS (ED): calcd. for  $C_{19}H_{16}N_2$  ( $[M]^+$ ): 272.13080; found: 272.13063.

### Synthesis of 1,4-bis(5H-pyrido[3,2-b]indol-5-yl)benzene **9**



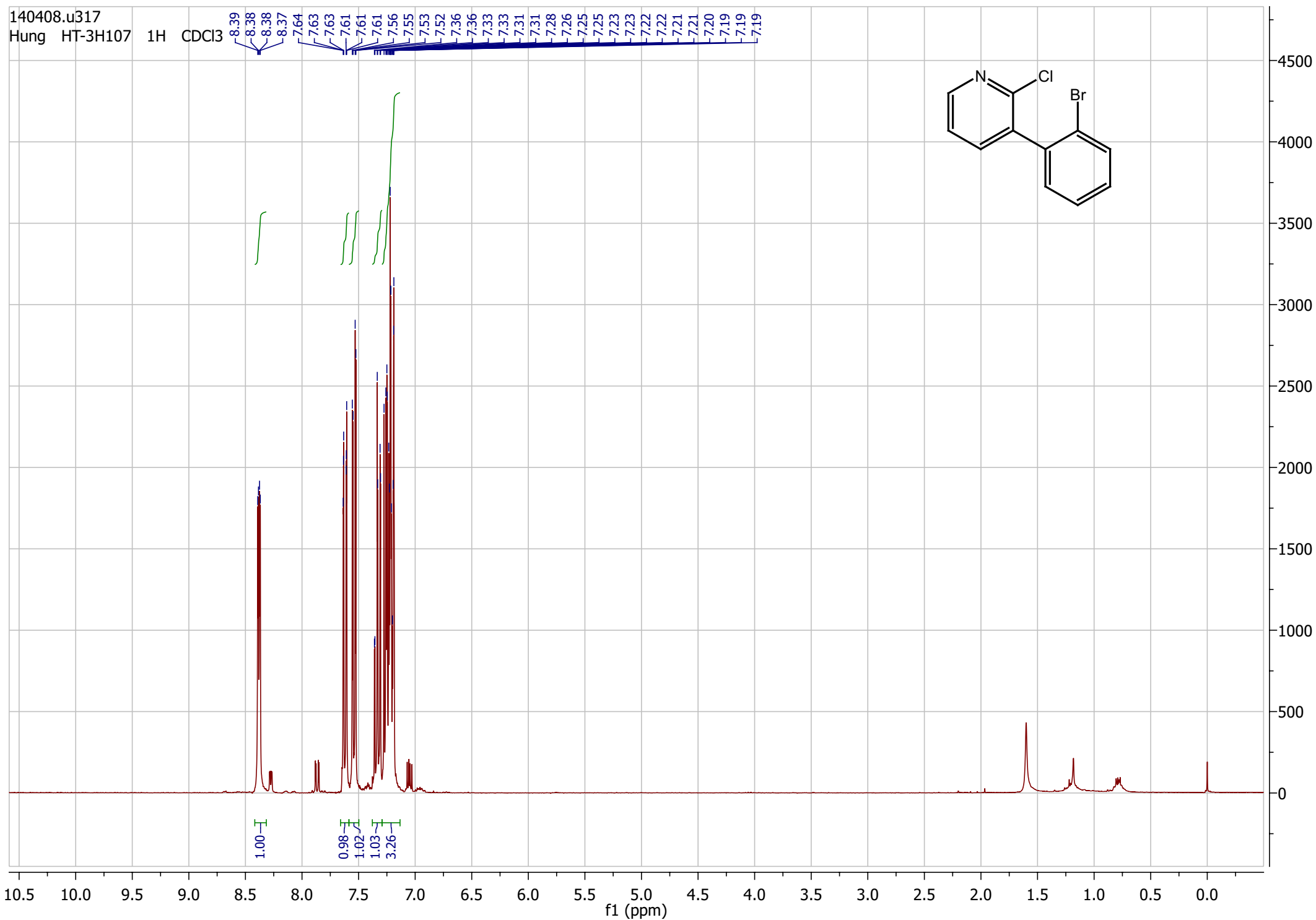
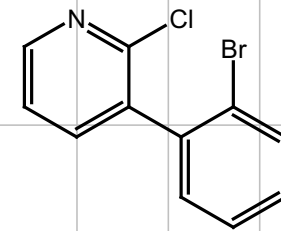
To pressure tube was charged with **3b** (200 mg, 0.64 mmol), 1,4-diaminobenzene (34 mg, 0.32 mmol),  $Pd_2(dba)_3$  (12 mg, 13  $\mu$ mol), ligand dppf (14 mg, 26  $\mu$ mol) and sodium tert-butoxide (147 mg, 1.53 mmol) under Argon. The mixture was back-filled with Argon several times. The mixture was dissolved in anhydrous Toluene (10 mL) and heated at  $100\text{ }^\circ C$  for 10 h. After cooling, the reaction mixture was diluted with dichloromethane (20 mL) and filtered through a celite pad, washing with dichloromethane (40 mL). The filtrate was reduced *in vacuo*. The product was separated via flash chromatography (silica gel, heptanes/dichloromethane/ethylacetate 1:1:1) to yield 1,4-bis(5H-pyrido[3,2-b]indol-5-yl)benzene **9** (52 mg, 40 %) as a white solid; m.p.  $277\text{--}279\text{ }^\circ C$ ;  $^1H$  NMR (250 MHz,  $CDCl_3$ )  $\delta$  8.76 – 8.33 (m, 4H), 7.96 – 7.06 (m, 14H);  $^{13}C$  NMR (63 MHz,  $CDCl_3$ )  $\delta$  142.02, 141.51, 140.20, 137.74, 132.99, 130.64, 127.24, 124.84, 123.60, 121.75, 120.36, 120.12, 119.37, 115.61, 108.83; IR (ATR,  $cm^{-1}$ ):  $\nu$  = 3053 (w), 1620 (w), 1595 (m), 1585 (m), 1576 (m), 1497 (s), 1475 (m), 1450 (s), 1408 (s), 1373 (w), 1362 (w), 1340 (m), 1315 (s), 1306 (s), 1288 (m), 1263 (m), 1238 (w), 1215 (m), 1203 (s), 1178 (m), 1155 (m), 1120 (m), 1111 (m), 1101 (m), 1090 (m),

1049 (m), 1026 (m), 1012 (m), 968 (w), 922 (m), 903 (w), 877 (w), 850 (w), 810 (m), 800 (m), 779 (s), 742 (vs), 727 (vs), 700 (s), 671 (m), 648 (m), 631 (m), 619 (s), 584 (m), 567 (m), 536 (m); GC-MS (EI, 70 eV): m/z (%) = 410 (100), 242 (28), 205 (11); HRMS (ESI): calcd. for  $C_{28}H_{18}N_4$  ( $[M + H]^+$ ): 411.16042; found: 411.15977.

140408.u317  
Hung HT-3H107

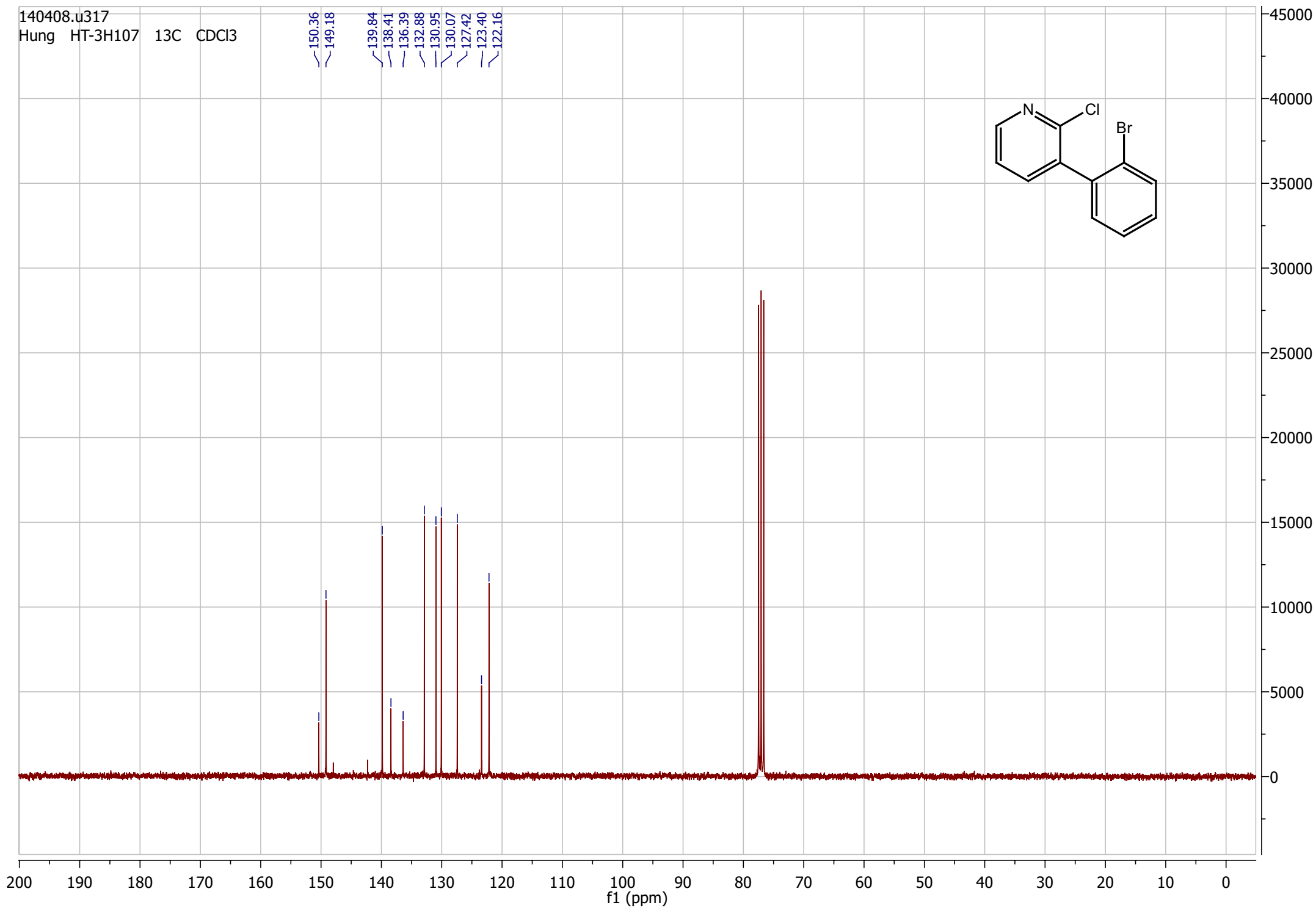
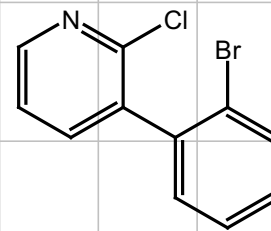
1H CDCl3

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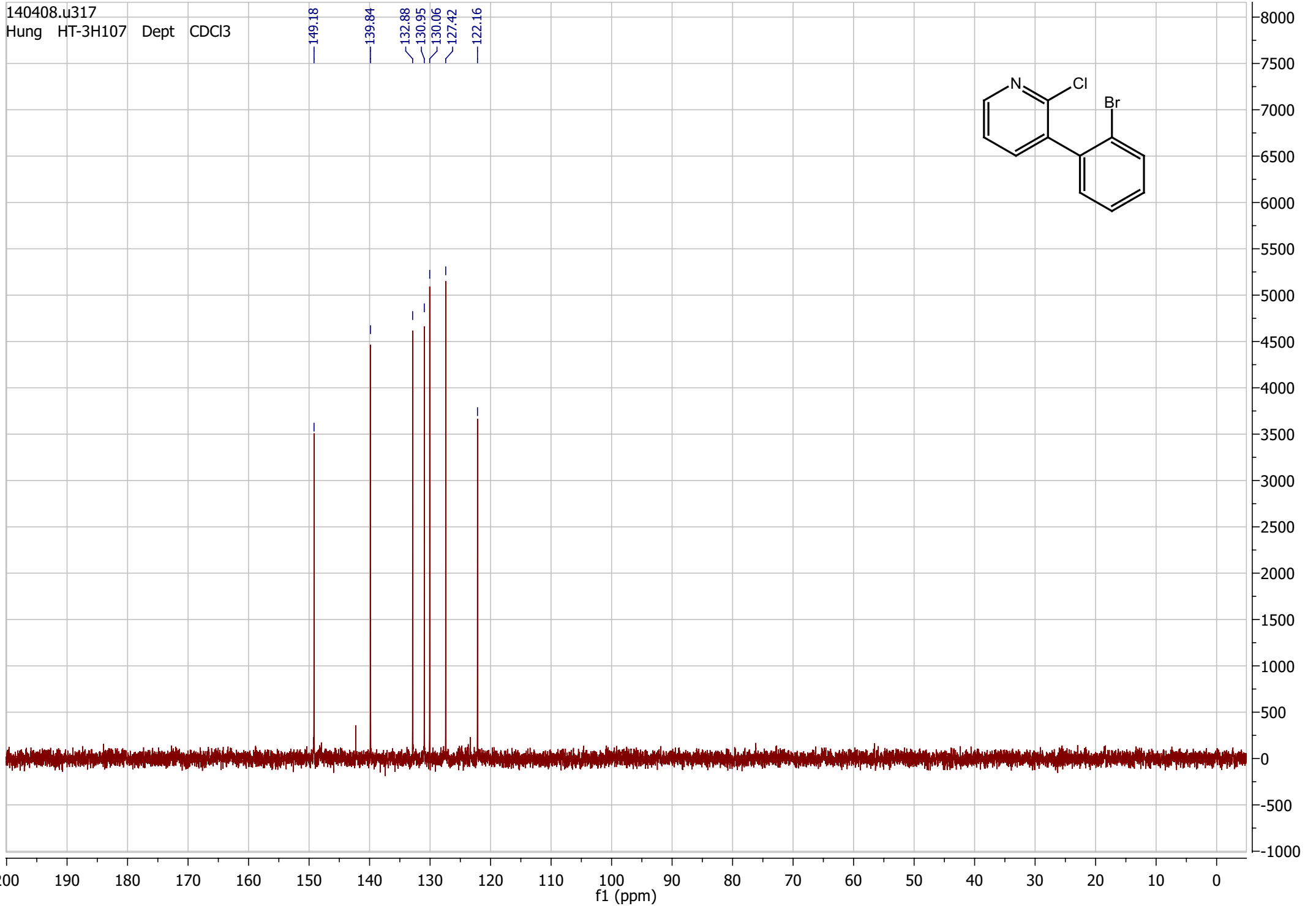


140408.u317  
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140408.u317  
Hung HT-3H107 Dept CDCl3



140411.202

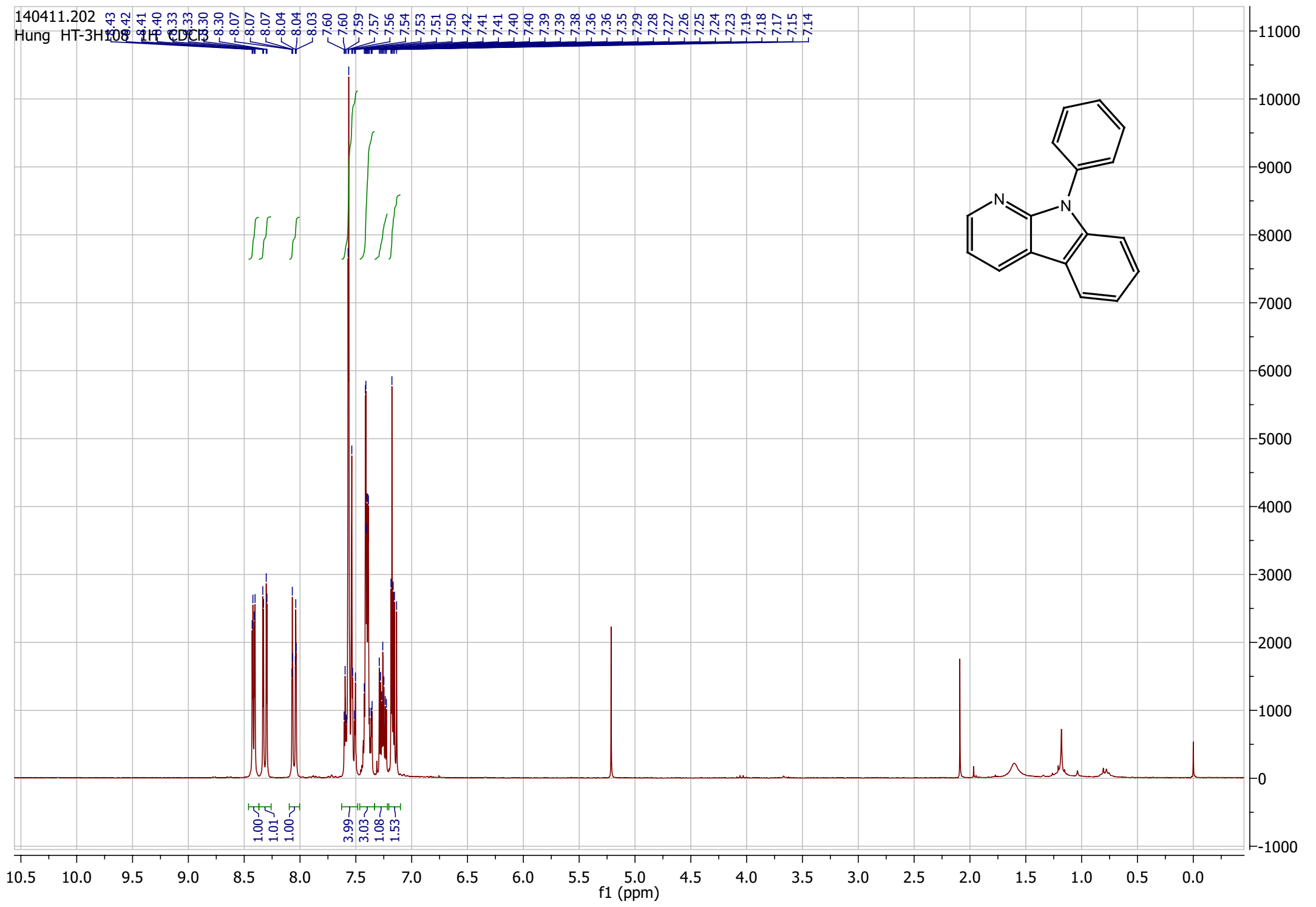
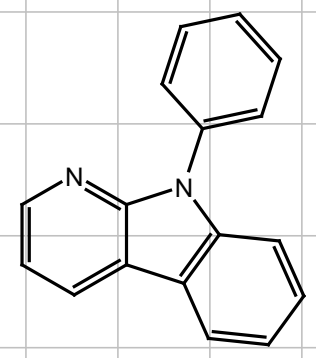
Hung HT-3H

108

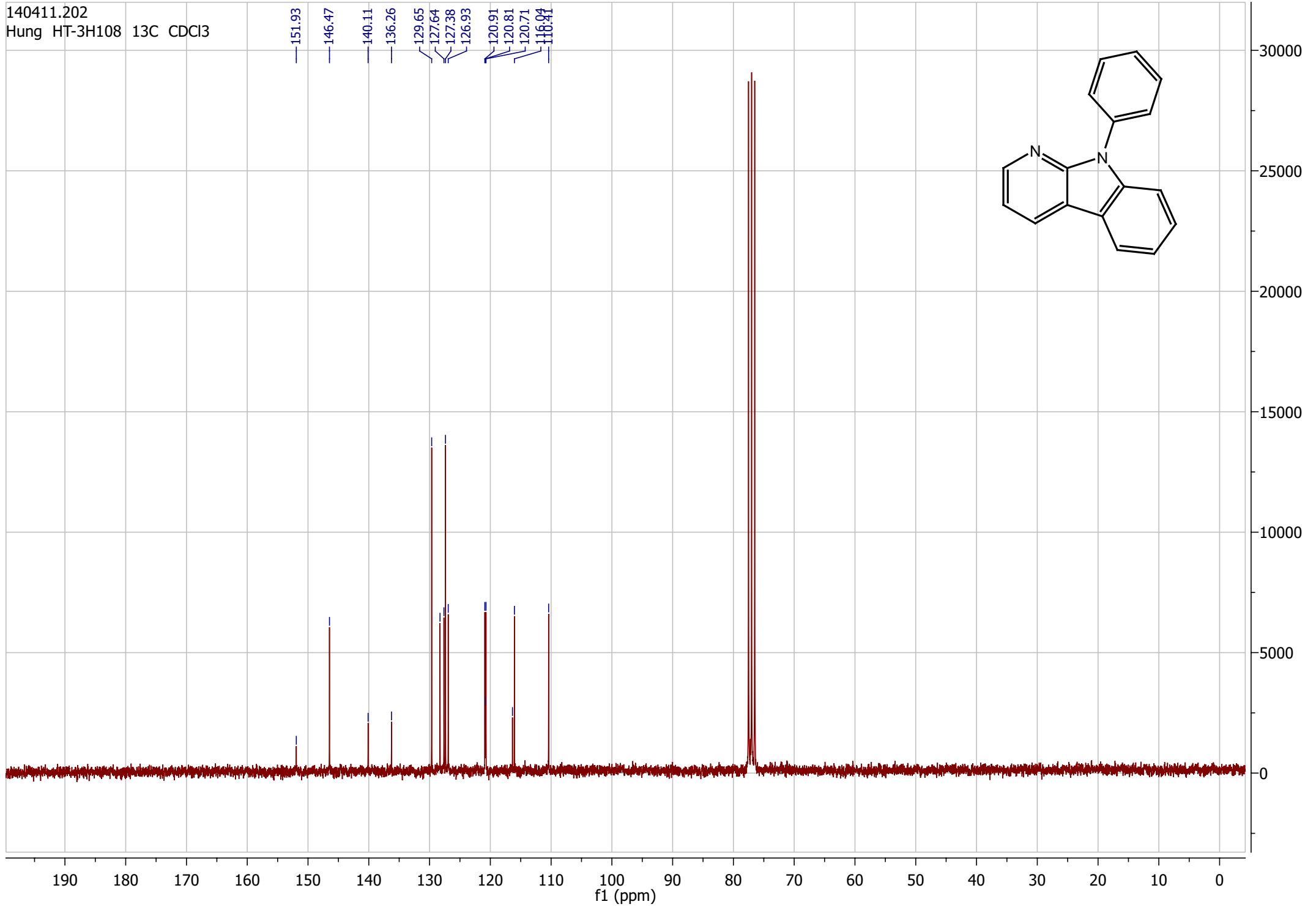
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1.53



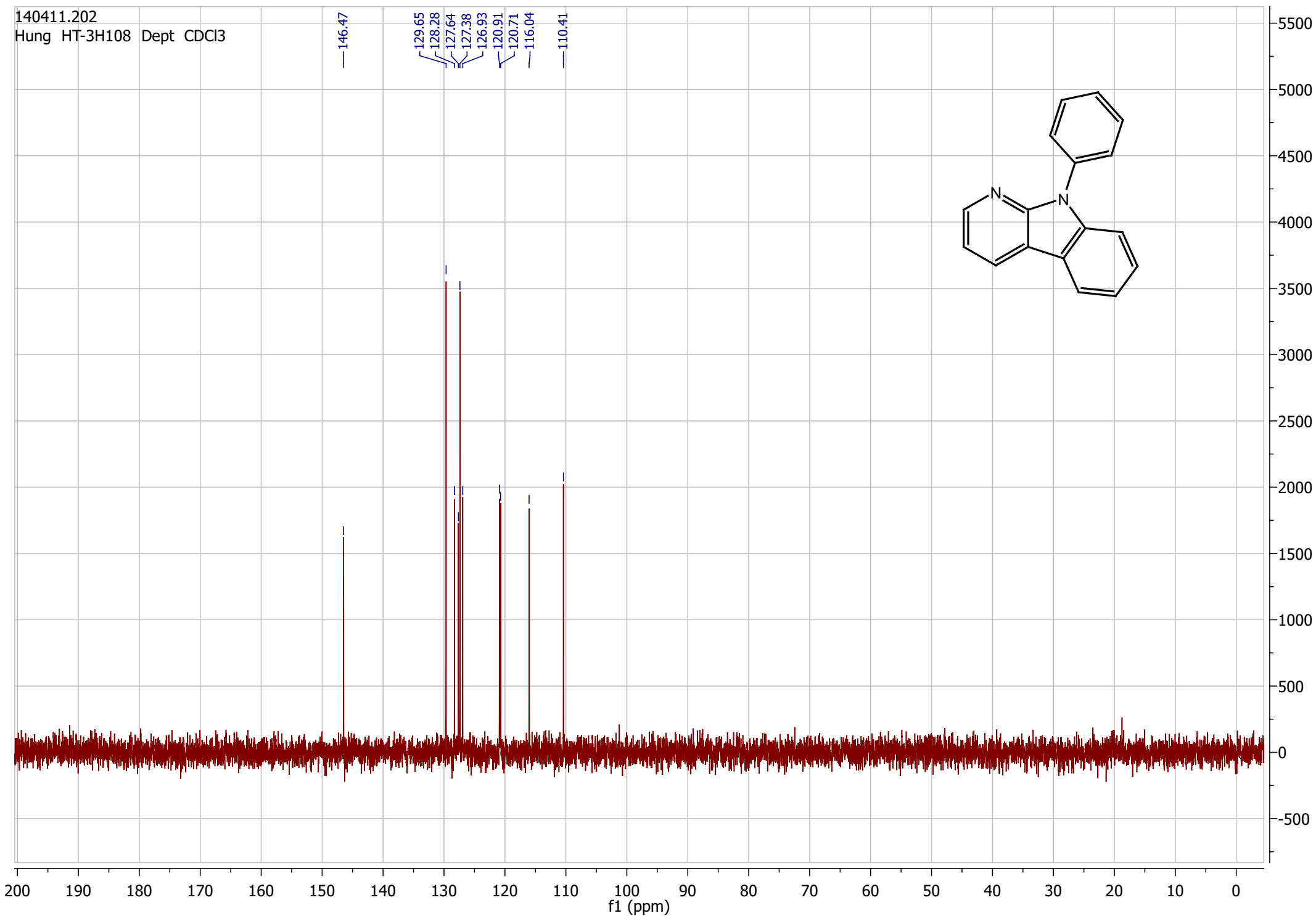
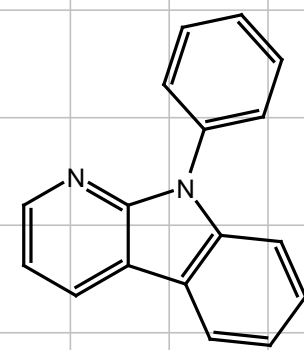
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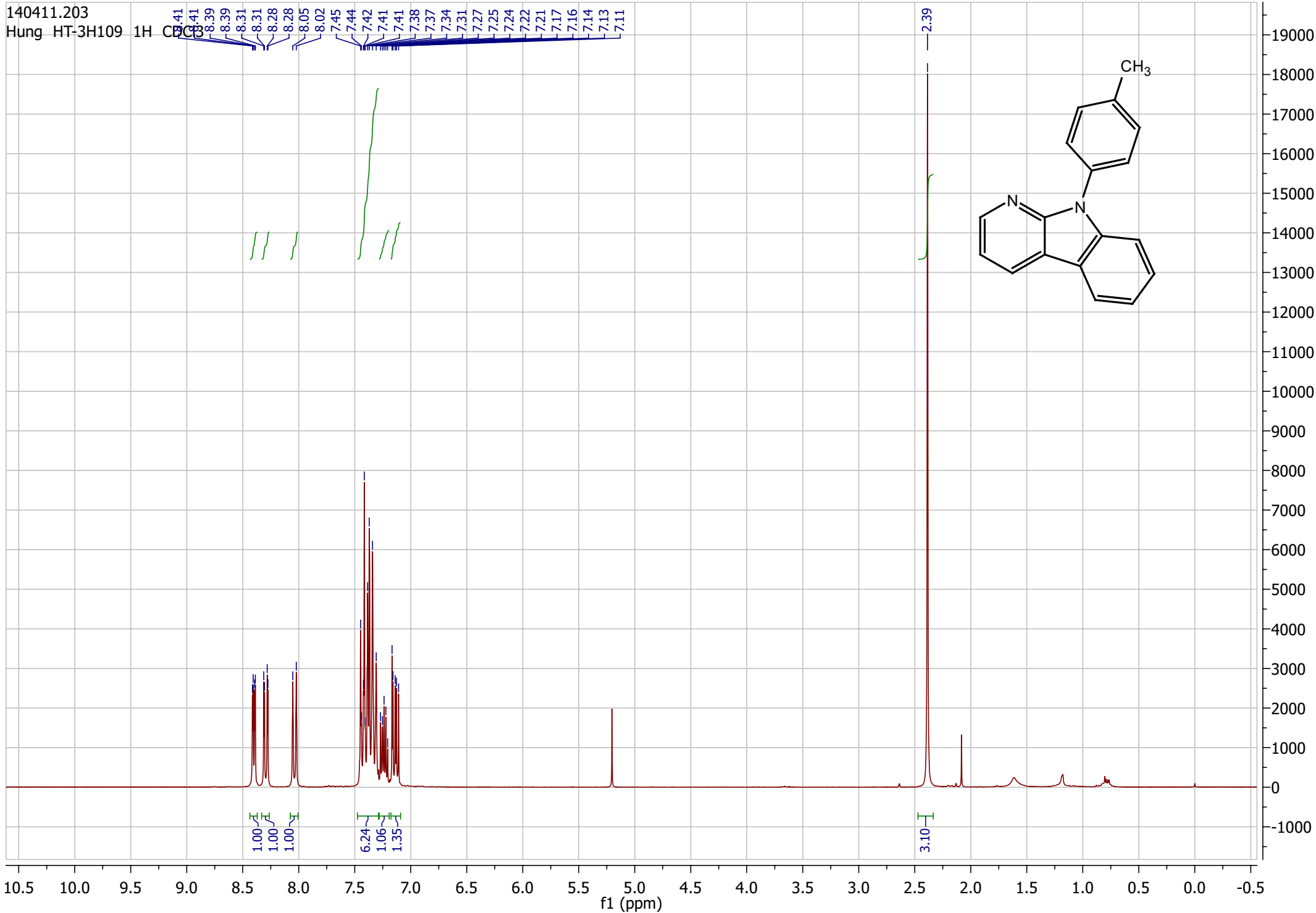
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140411.203  
Hung HT-3H109

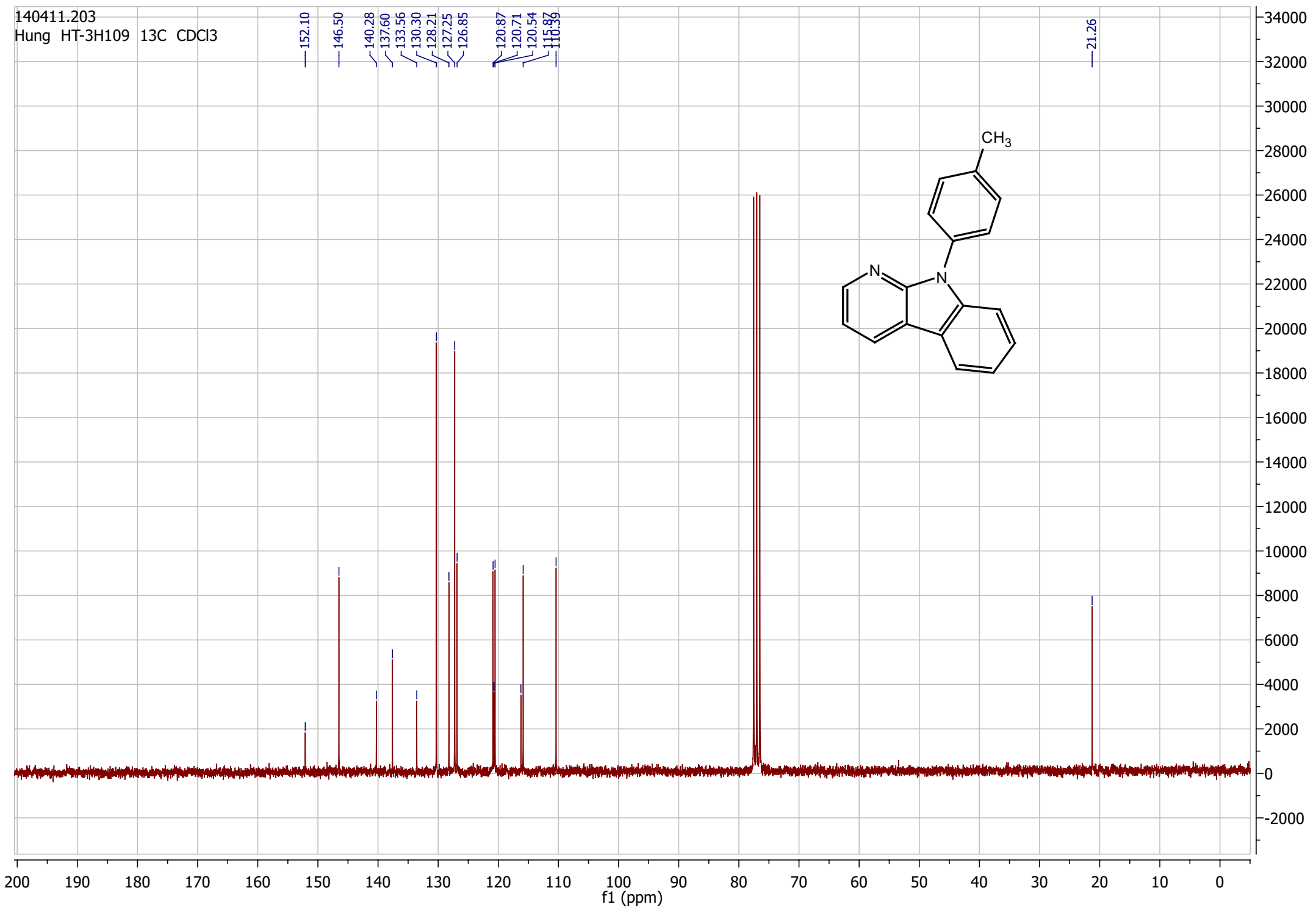
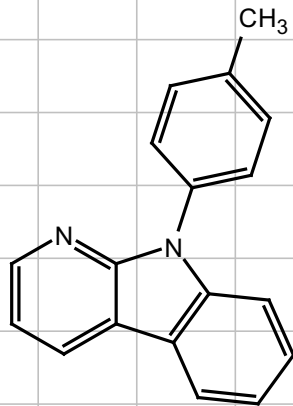
1H NMR



140411.203  
Hung HT-3H109 13C CDCl3

152.10  
146.50  
140.28  
137.60  
133.56  
130.30  
128.21  
127.25  
126.85  
120.87  
120.71  
120.54  
118.96

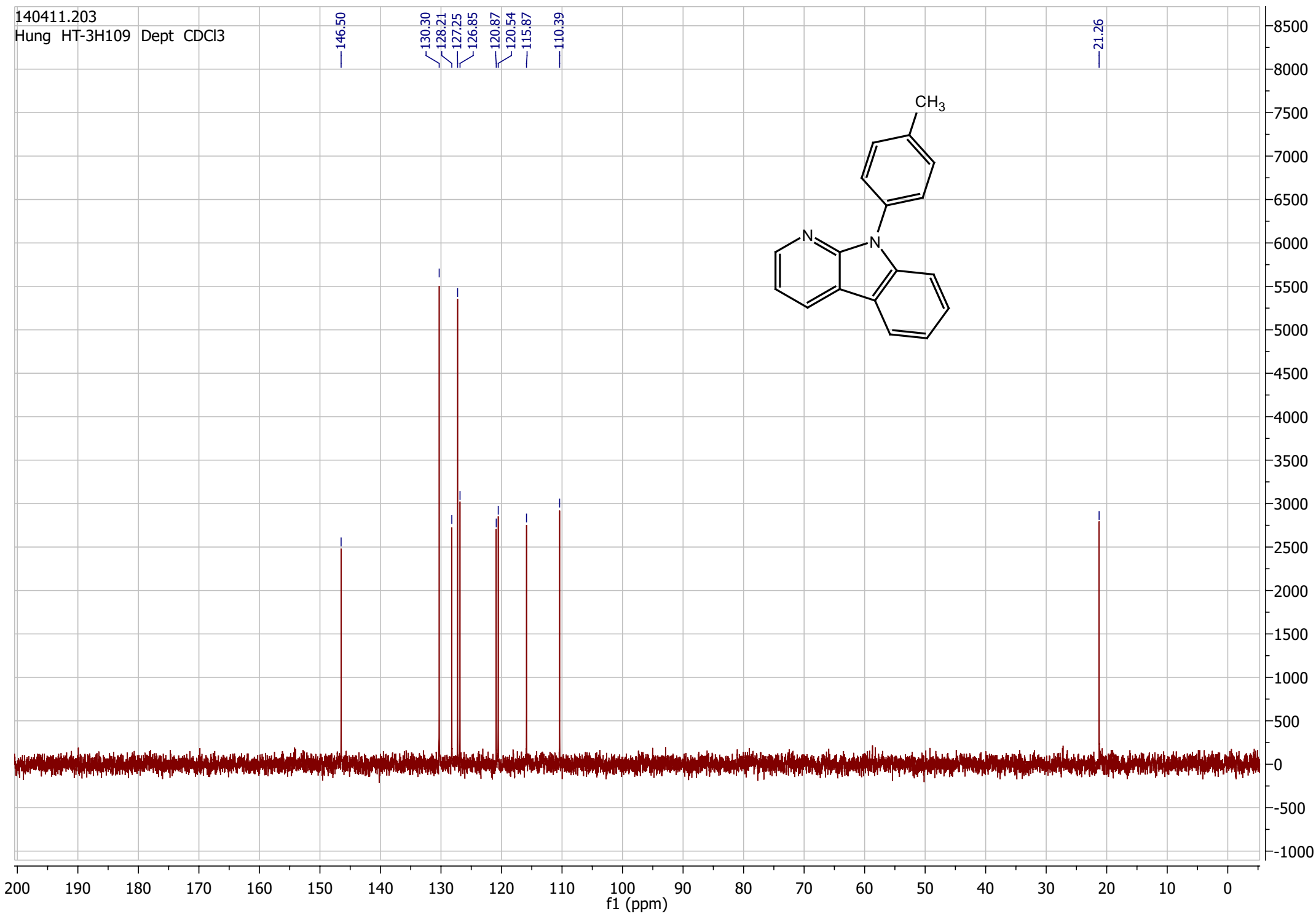
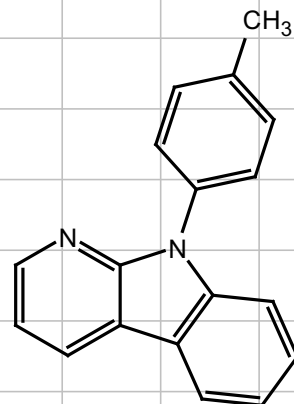
21.26



140411.203  
Hung HT-3H109 Dept CDCl3

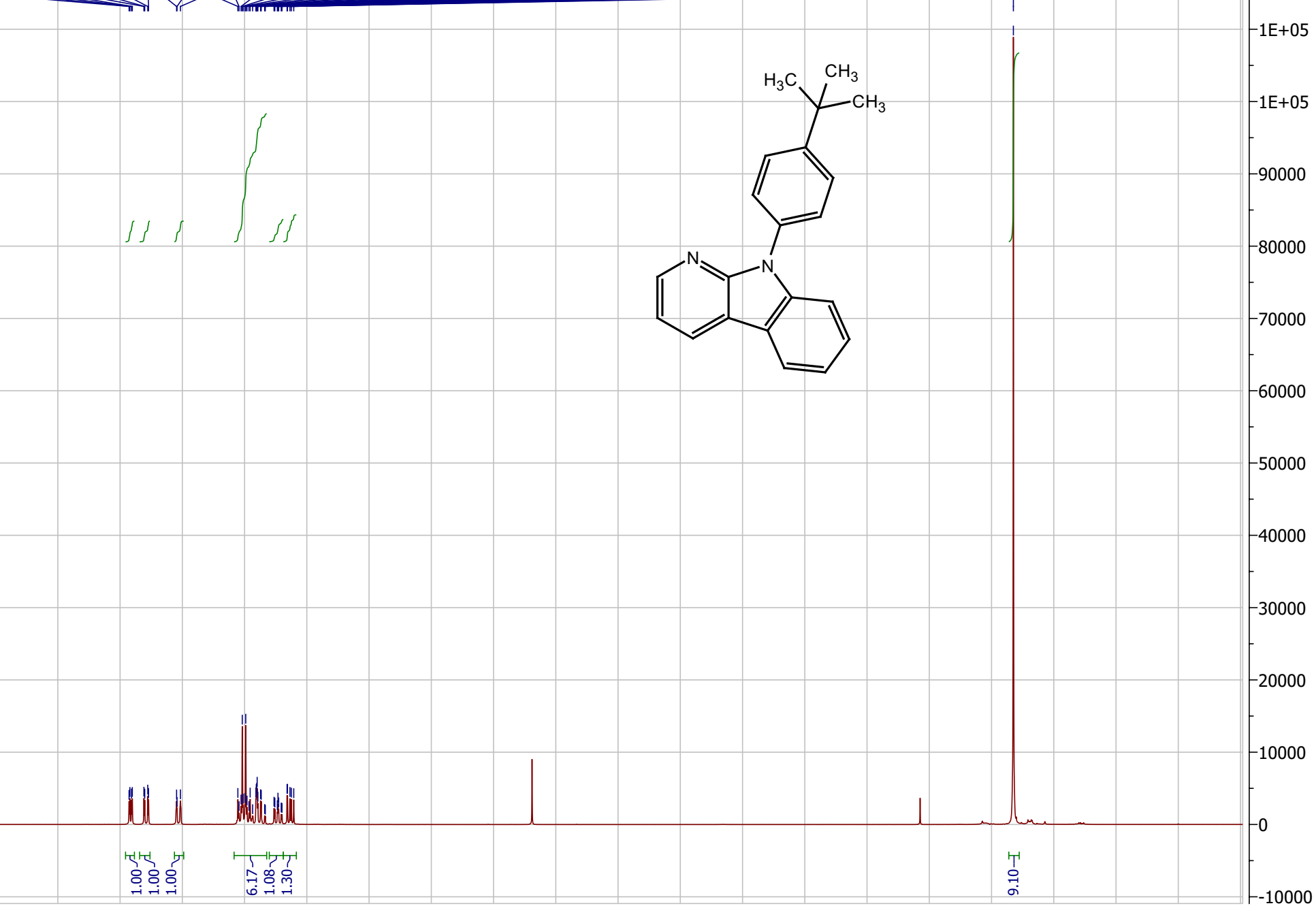
146.50  
130.30  
128.21  
127.25  
126.85  
120.87  
120.54  
115.87  
110.39

21.26



140411.204  
Hung HT-3H110

8.43 8.42 8.41 8.40 8.31 8.30 8.28 8.27 8.05 8.04 8.02 7.55 7.54 7.53 7.52 7.51 7.50 7.49 7.48 7.46 7.46 7.44 7.41 7.41 7.40 7.40 7.39 7.37 7.37 7.34 7.33 7.33 7.26 7.26 7.24 7.24 7.23 7.23 7.21 7.20 7.16 7.16 7.14 7.14 7.12 7.12 7.10 7.10

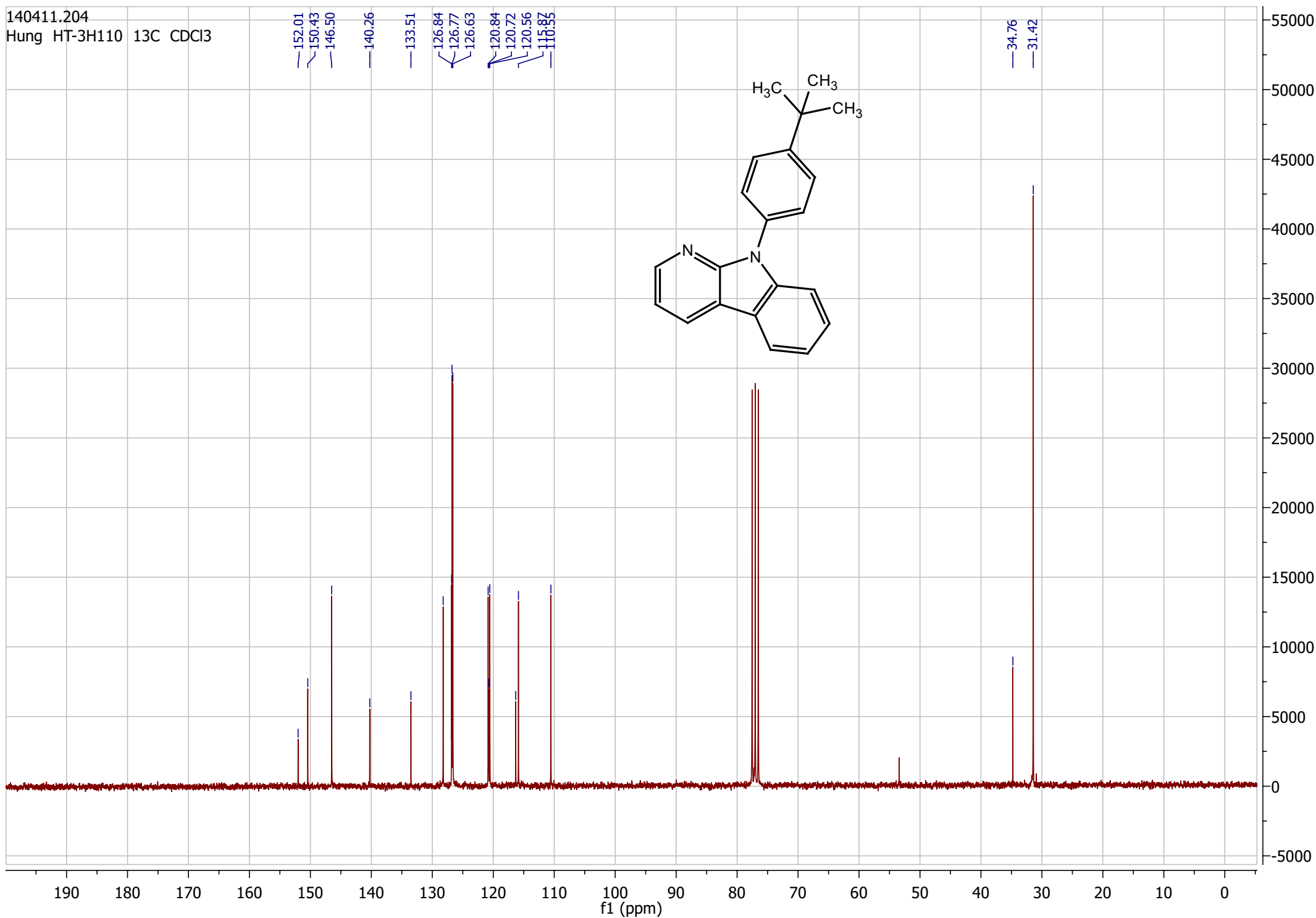
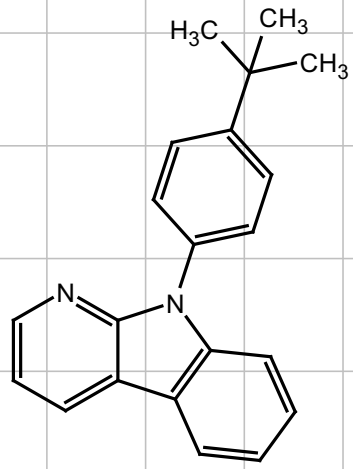


f1 (ppm)

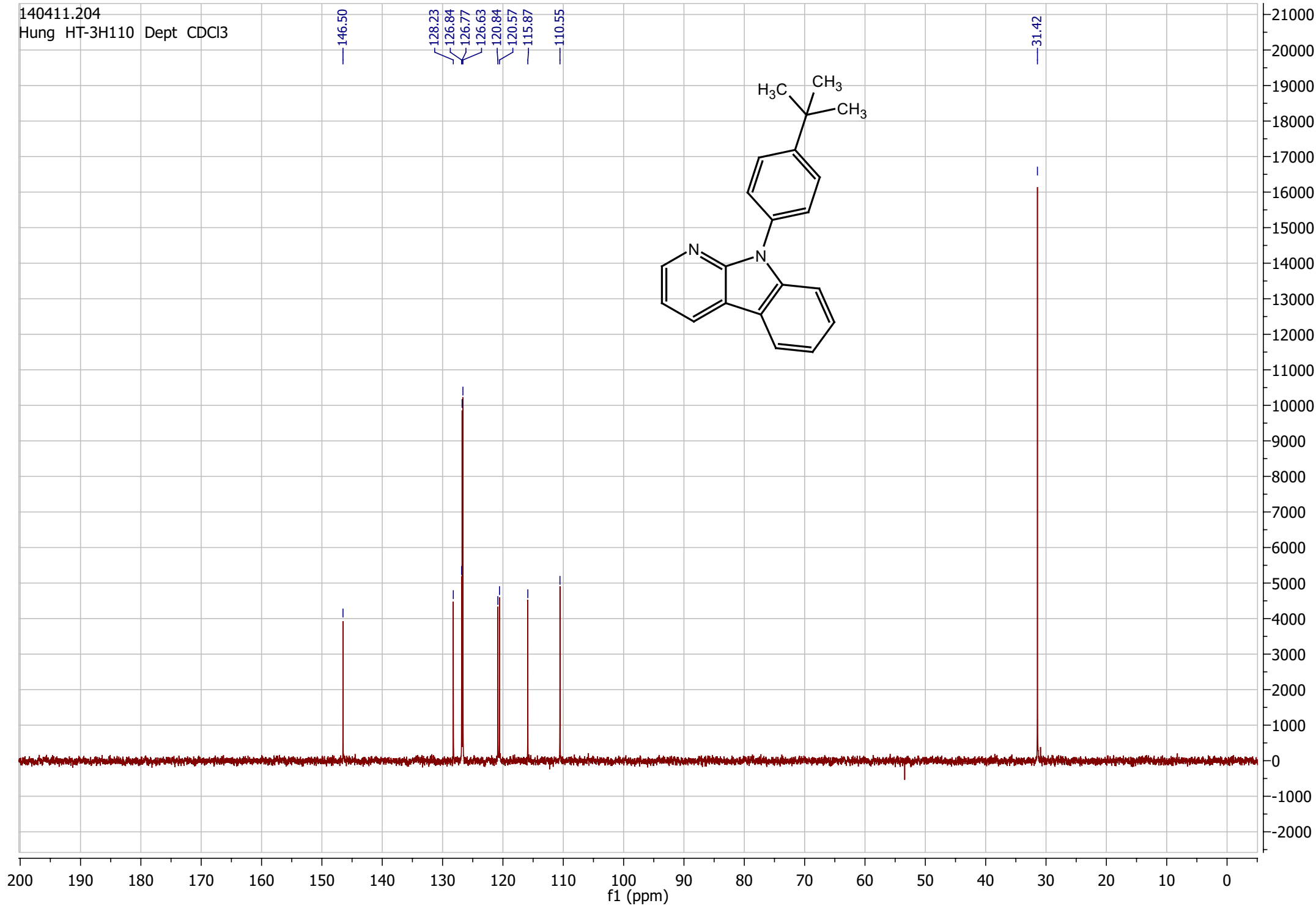
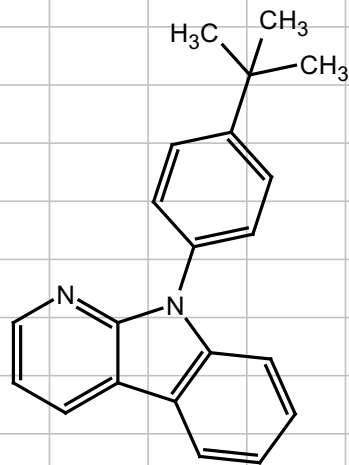
140411.204  
Hung HT-3H110 13C CDCl3

152.01  
150.43  
146.50  
140.26  
133.51  
126.84  
126.77  
126.63  
120.84  
120.72  
120.56  
115.85

34.76  
31.42

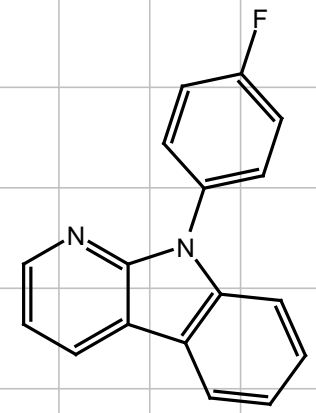
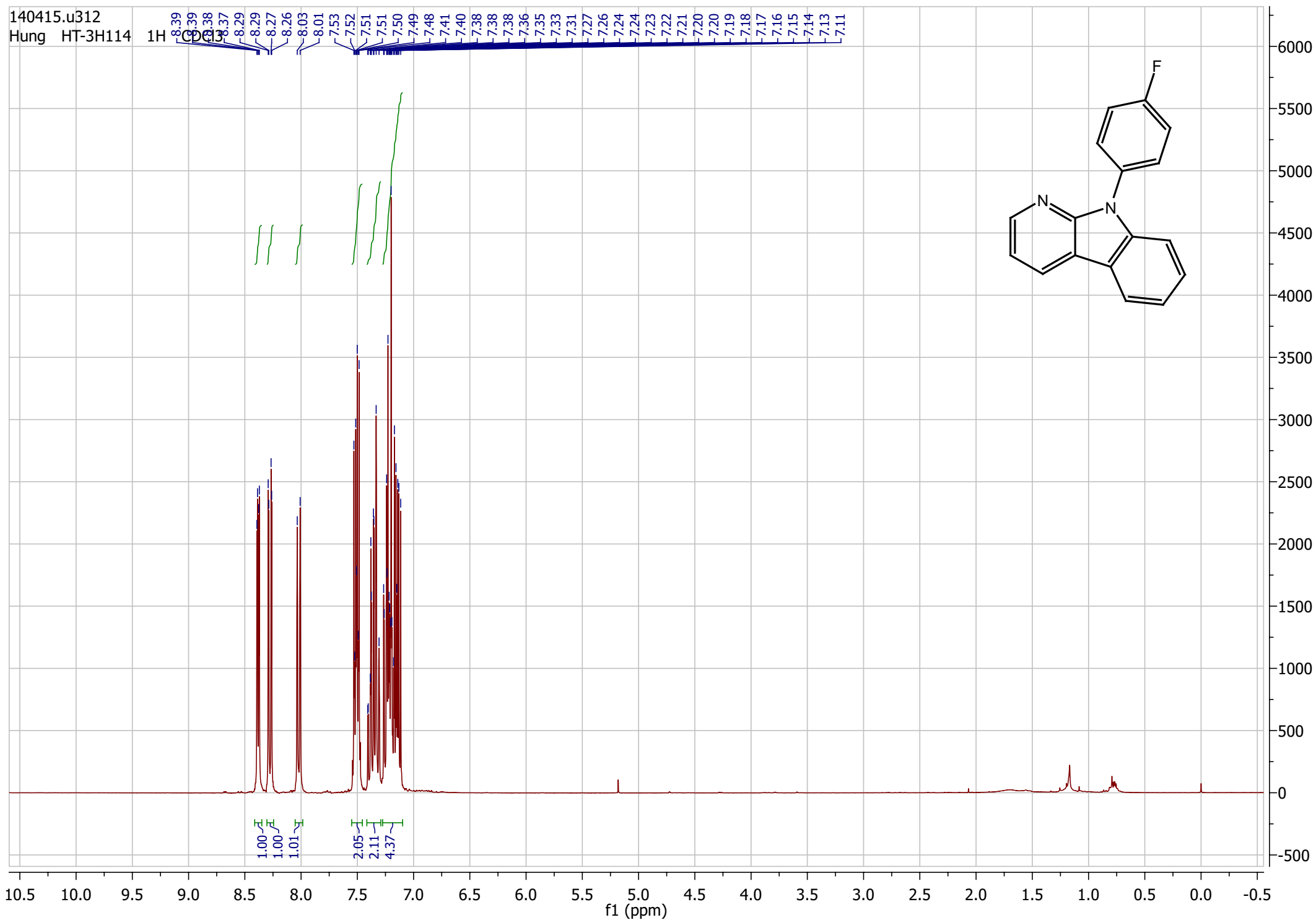


140411.204  
Hung HT-3H110 Dept CDCl3



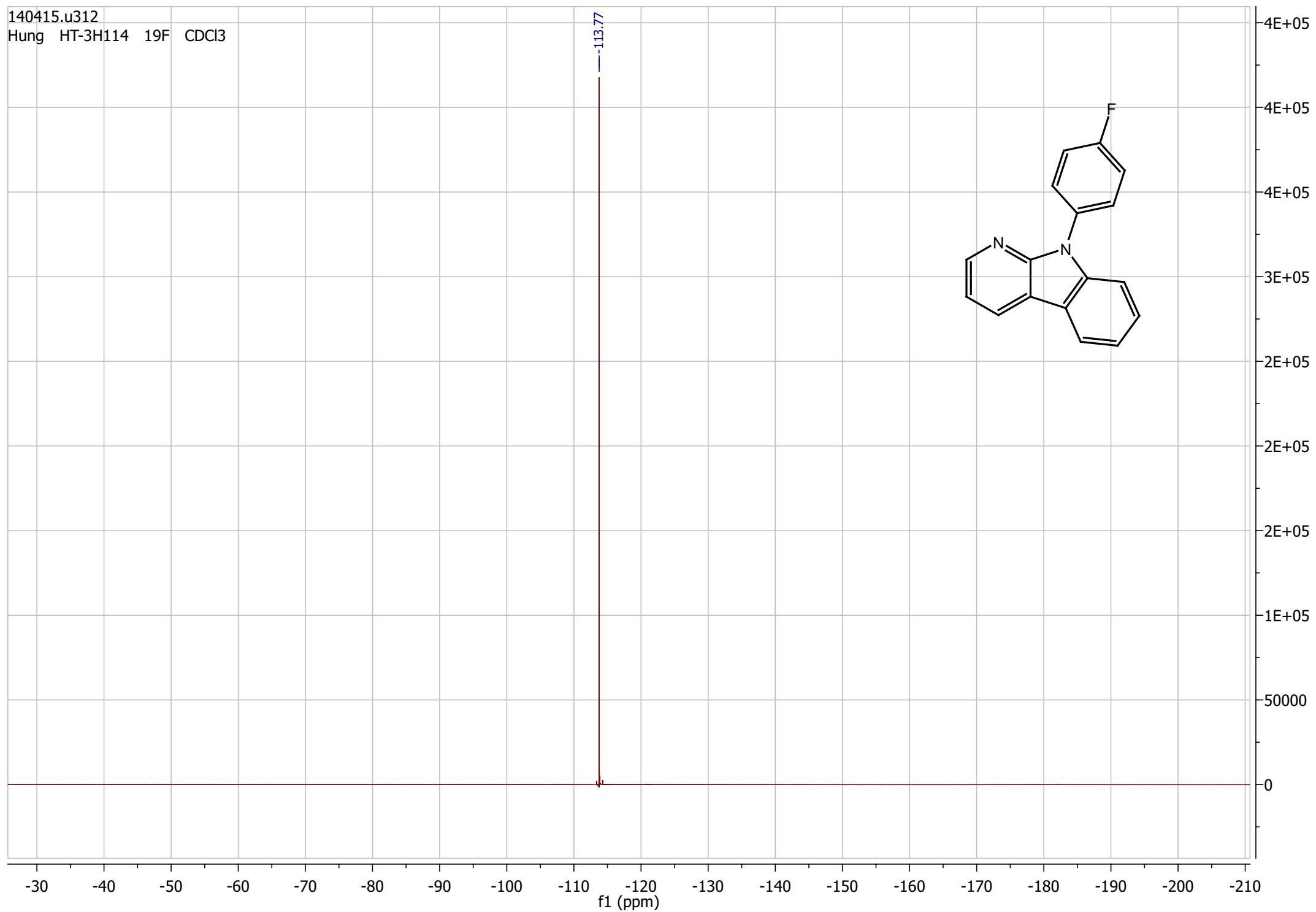
140415.u312  
Hung HT-3H114

1H  
8.39  
8.39  
8.38  
8.37  
8.29  
8.27  
8.26  
8.03  
8.01  
7.53  
7.52  
7.51  
7.51  
7.50  
7.49  
7.48  
7.41  
7.40  
7.38  
7.38  
7.38  
7.36  
7.35  
7.33  
7.31  
7.27  
7.26  
7.24  
7.24  
7.23  
7.22  
7.21  
7.20  
7.20  
7.19  
7.18  
7.17  
7.16  
7.15  
7.14  
7.13  
7.11





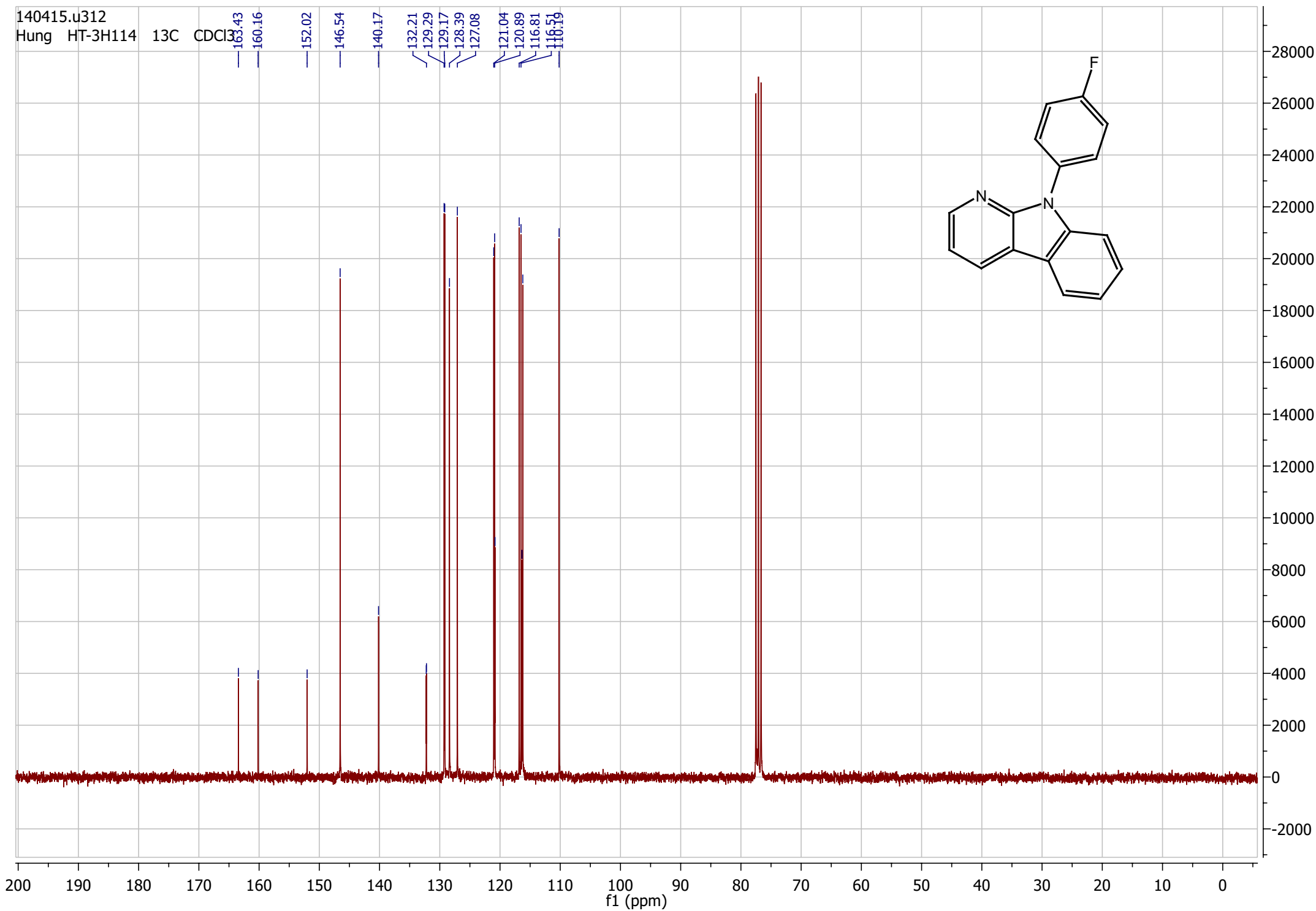
140415.u312  
Hung HT-3H114 19F CDCl3



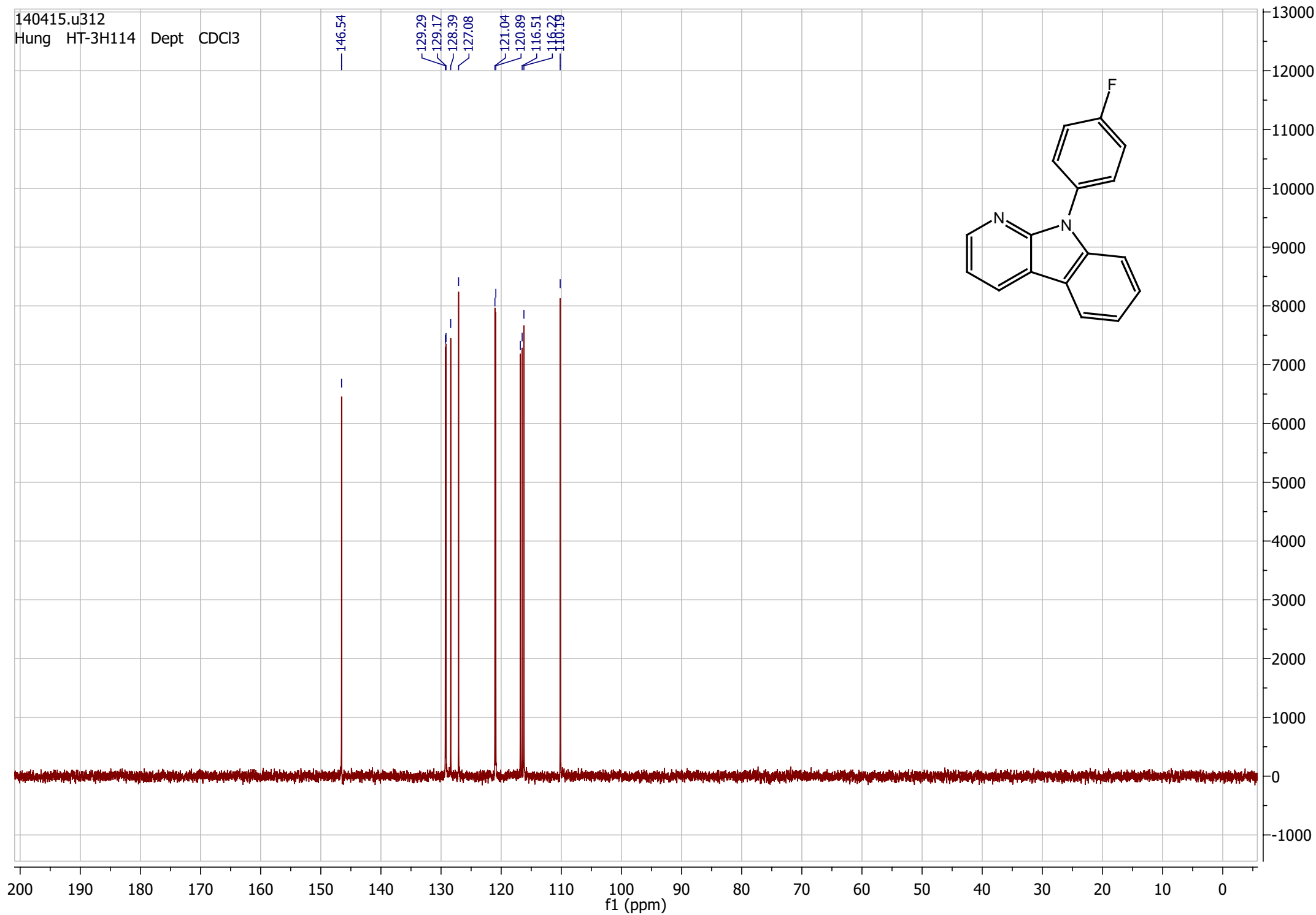
140415.u312  
Hung HT-3H114

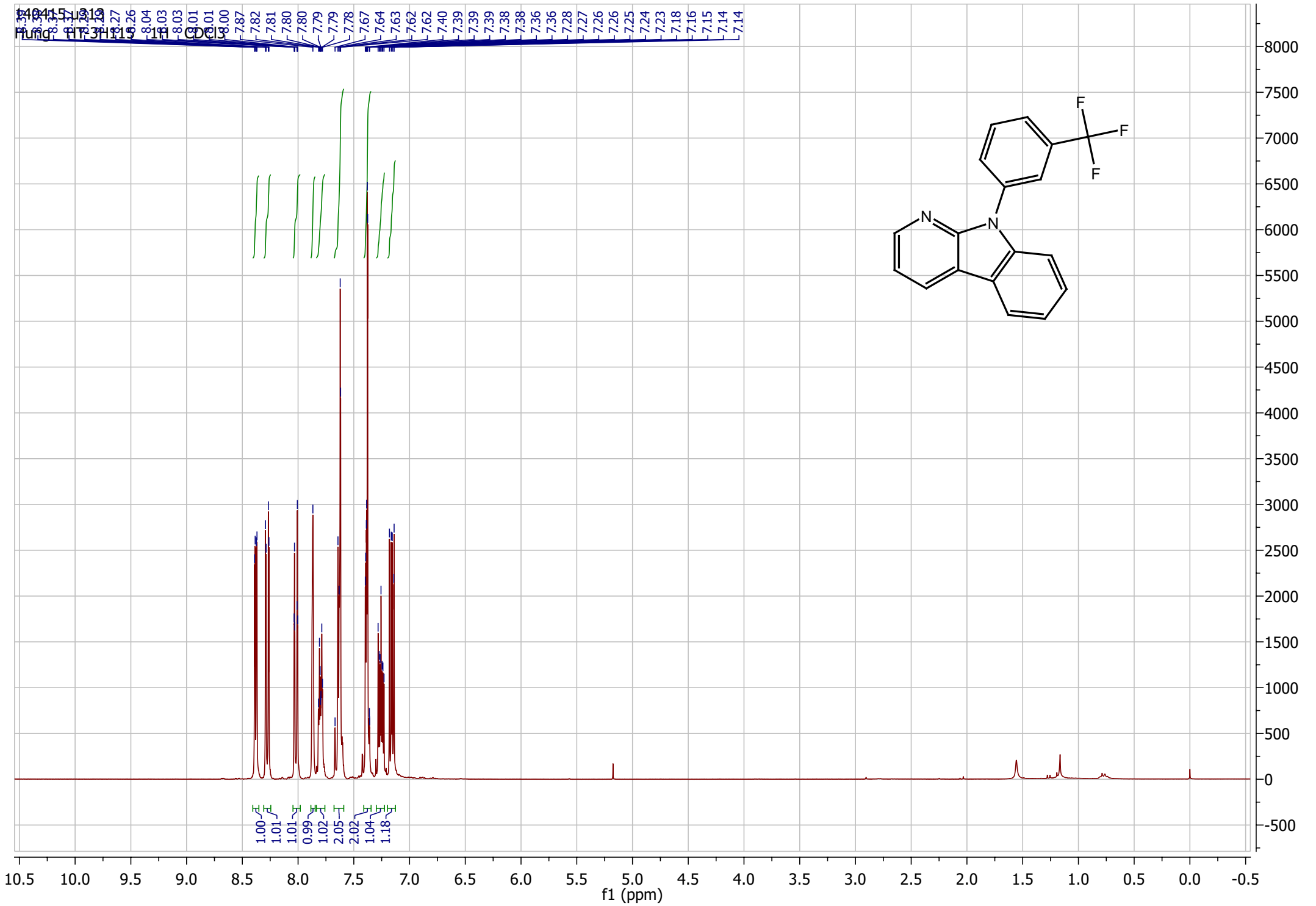
13C

CDCl<sub>3</sub>  
163.43  
160.16  
152.02  
146.54  
140.17  
132.21  
129.29  
129.17  
128.39  
127.08  
121.04  
120.89  
116.81  
116.59

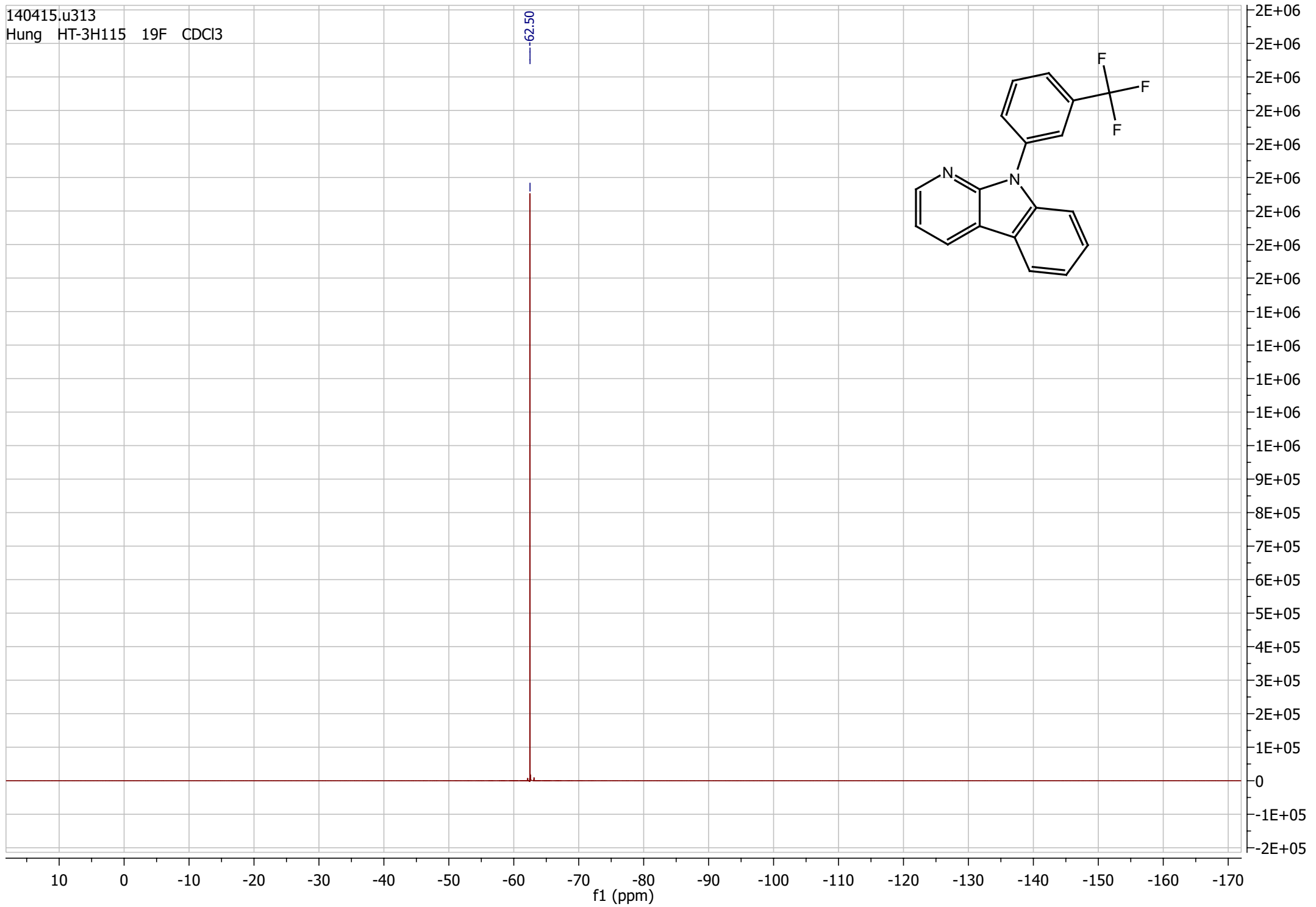


140415.u312  
Hung HT-3H114 Dept CDCl3



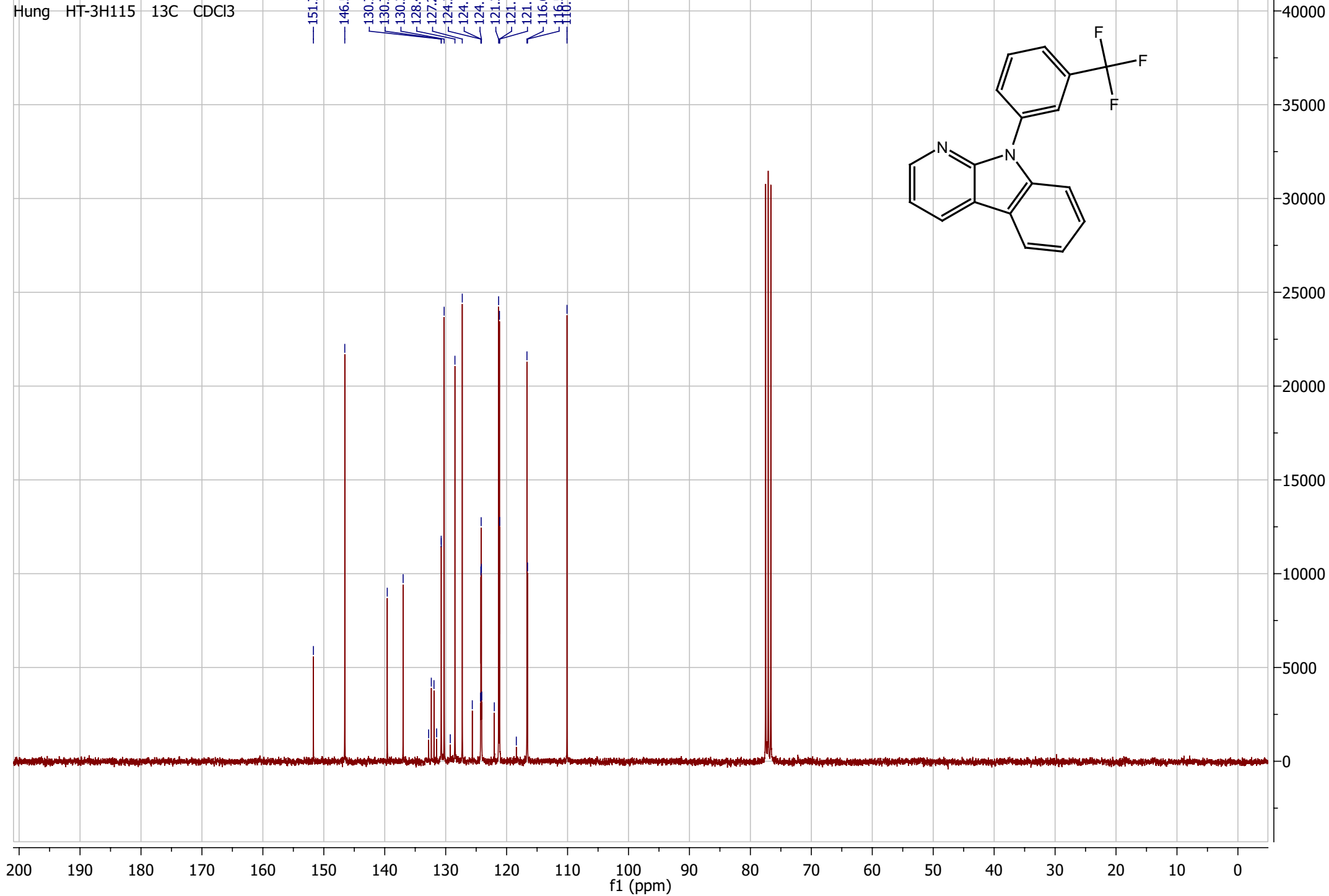
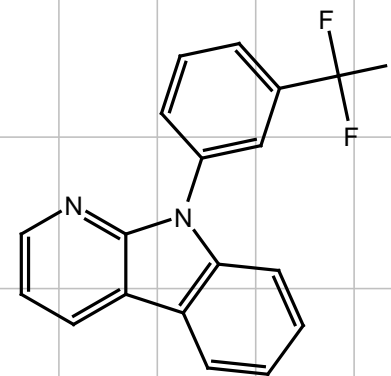


140415.u313  
Hung HT-3H115 19F CDCI3

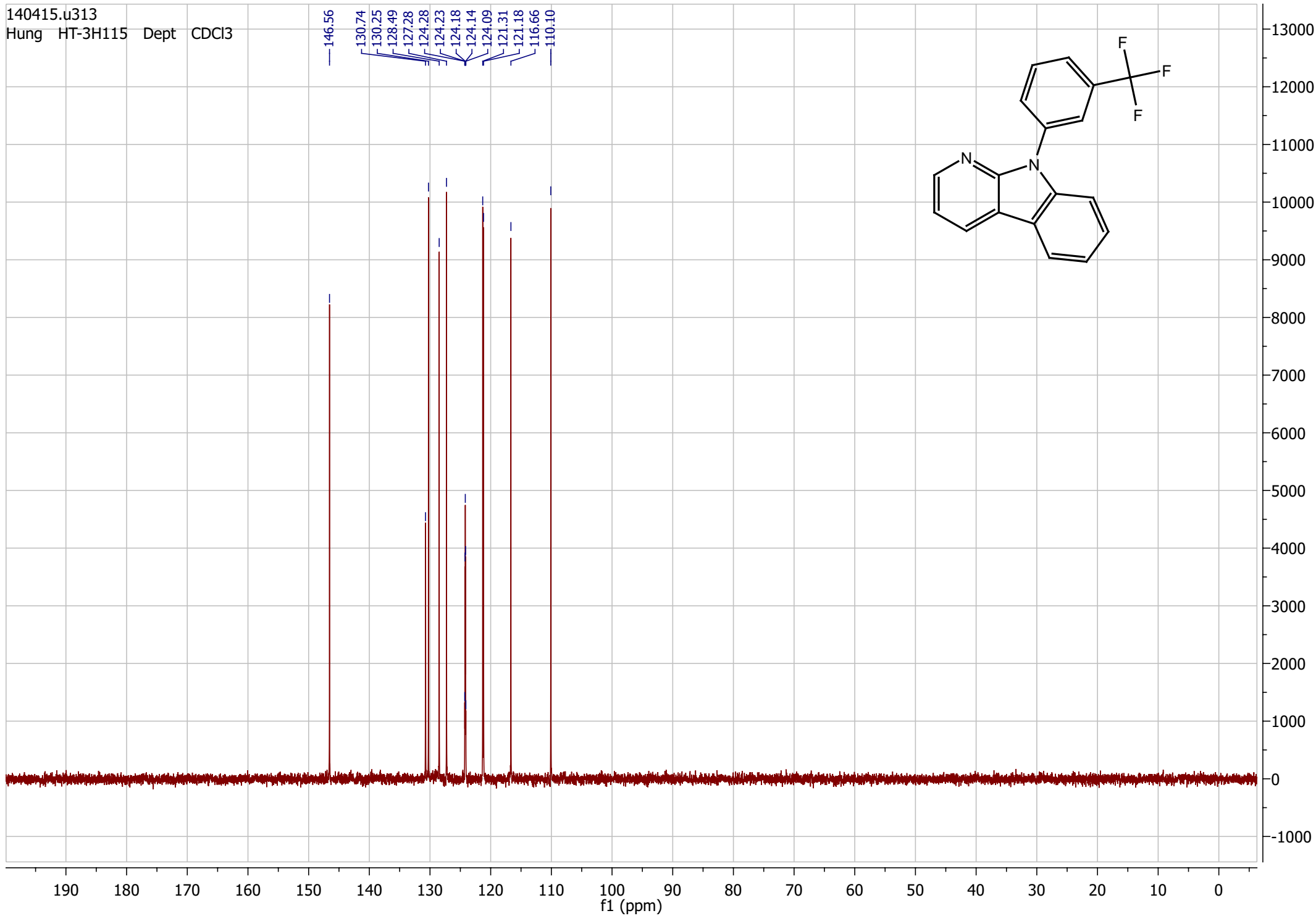


140415.u313  
Hung HT-3H115 13C CDCl3

151.71  
146.56  
130.74  
130.73  
130.25  
128.49  
127.28  
124.23  
124.18  
124.14  
121.31  
121.17  
121.14  
116.66  
116.57  
116.10

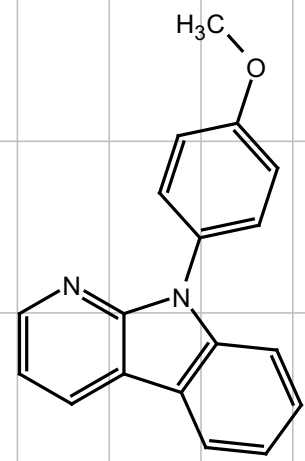
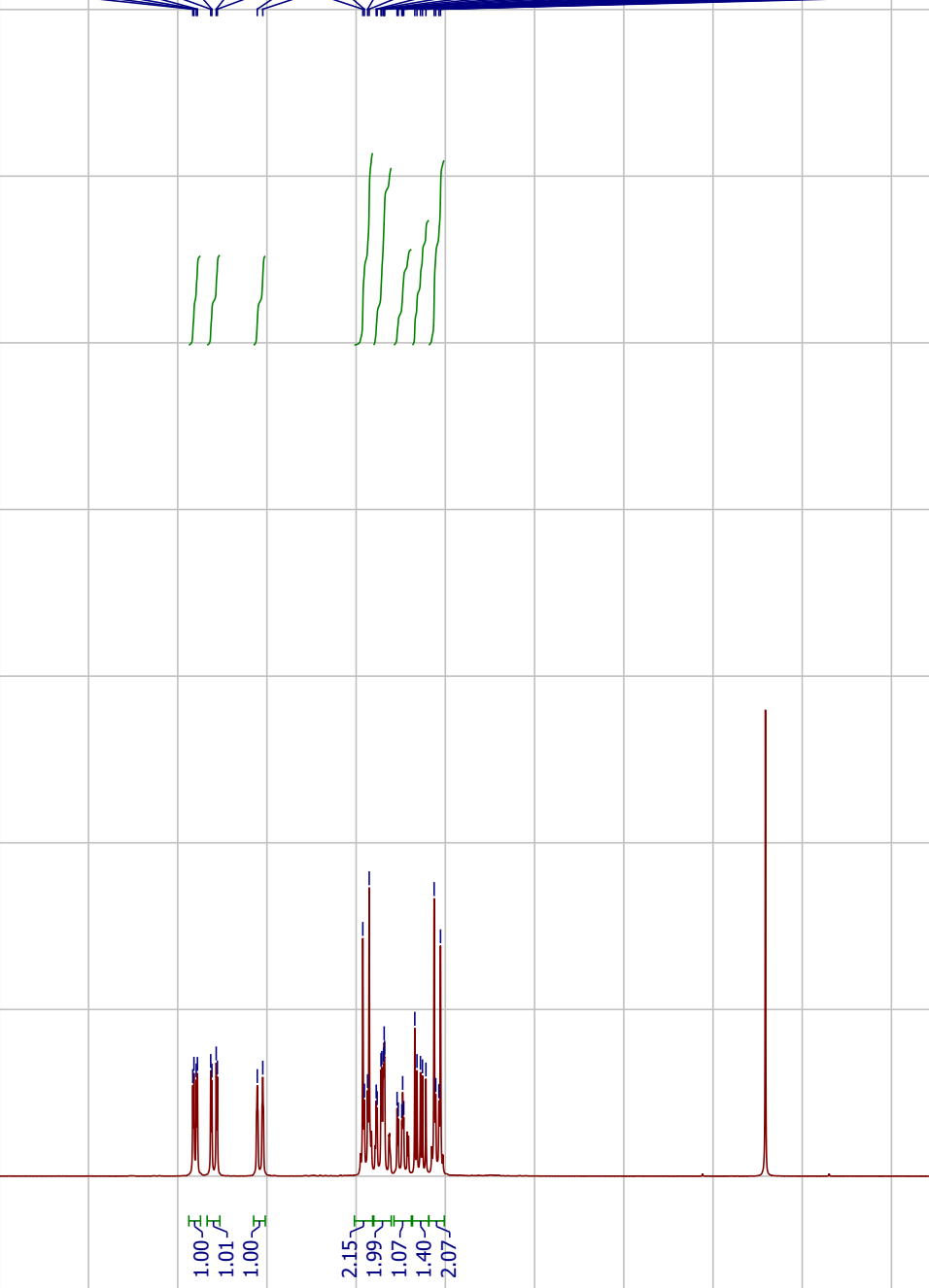


140415.u313  
Hung HT-3H115 Dept CDCl3



140411.205  
Hung HT-3H111

1H NMR (CDCl<sub>3</sub>)  
8.42, 8.41, 8.40, 8.39, 8.31, 8.31, 8.28, 8.28, 8.05, 8.02, 7.46, 7.45, 7.44, 7.43, 7.39, 7.38, 7.36, 7.36, 7.35, 7.34, 7.34, 7.27, 7.26, 7.24, 7.24, 7.23, 7.17, 7.16, 7.14, 7.13, 7.11, 7.06, 7.05, 7.04, 7.03



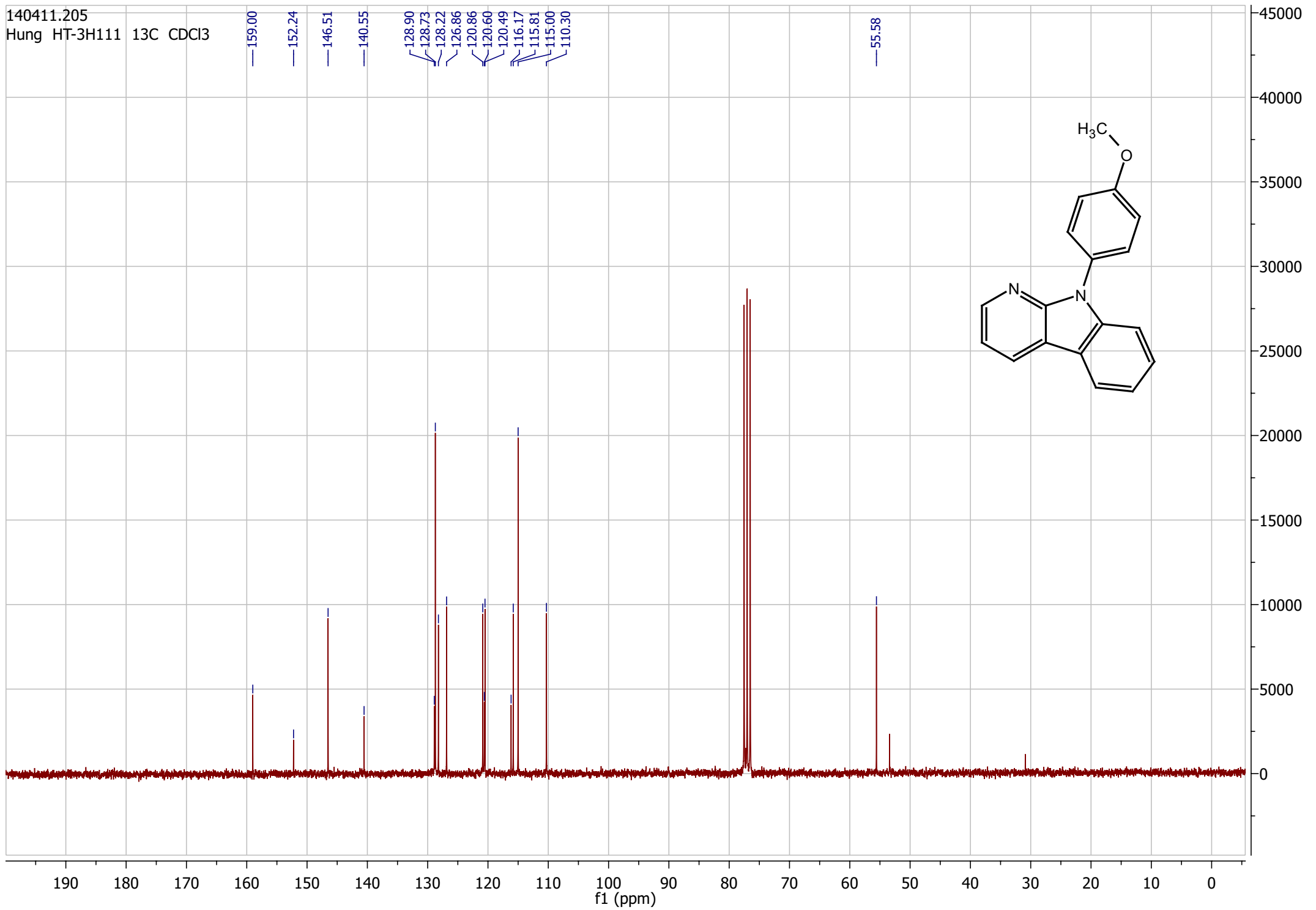
f1 (ppm)



140411.205  
Hung HT-3H111 13C CDCl3

159.00  
152.24  
146.51  
140.55  
128.90  
128.73  
128.22  
126.86  
120.86  
120.60  
120.49  
116.17  
115.81  
115.00  
110.30

55.58



140411.205  
Hung HT-3H111 Dept CDCl3

146.51

128.73

128.22

126.86

120.87

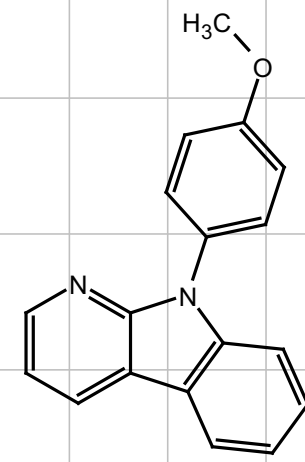
120.49

115.81

115.00

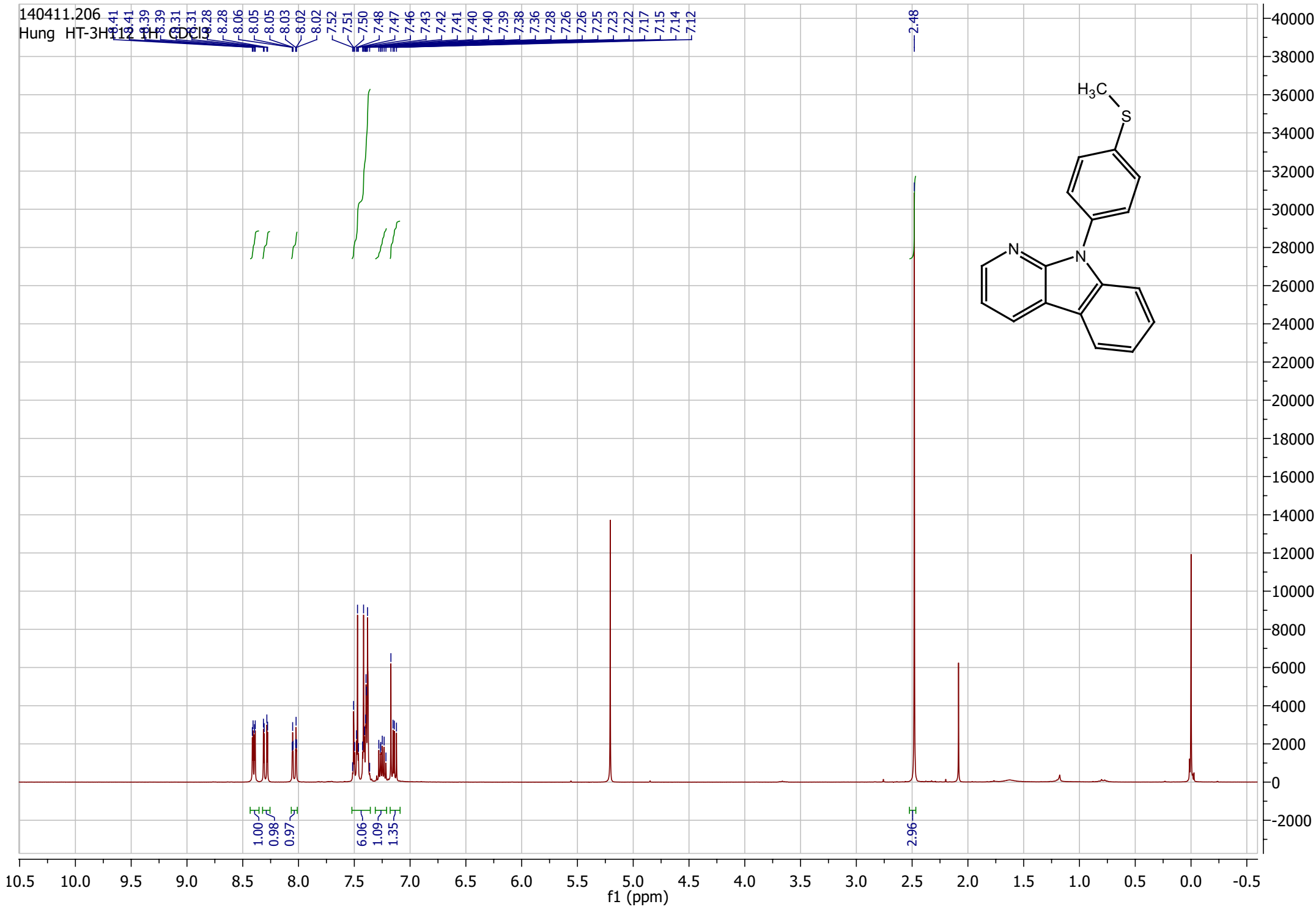
110.30

55.58

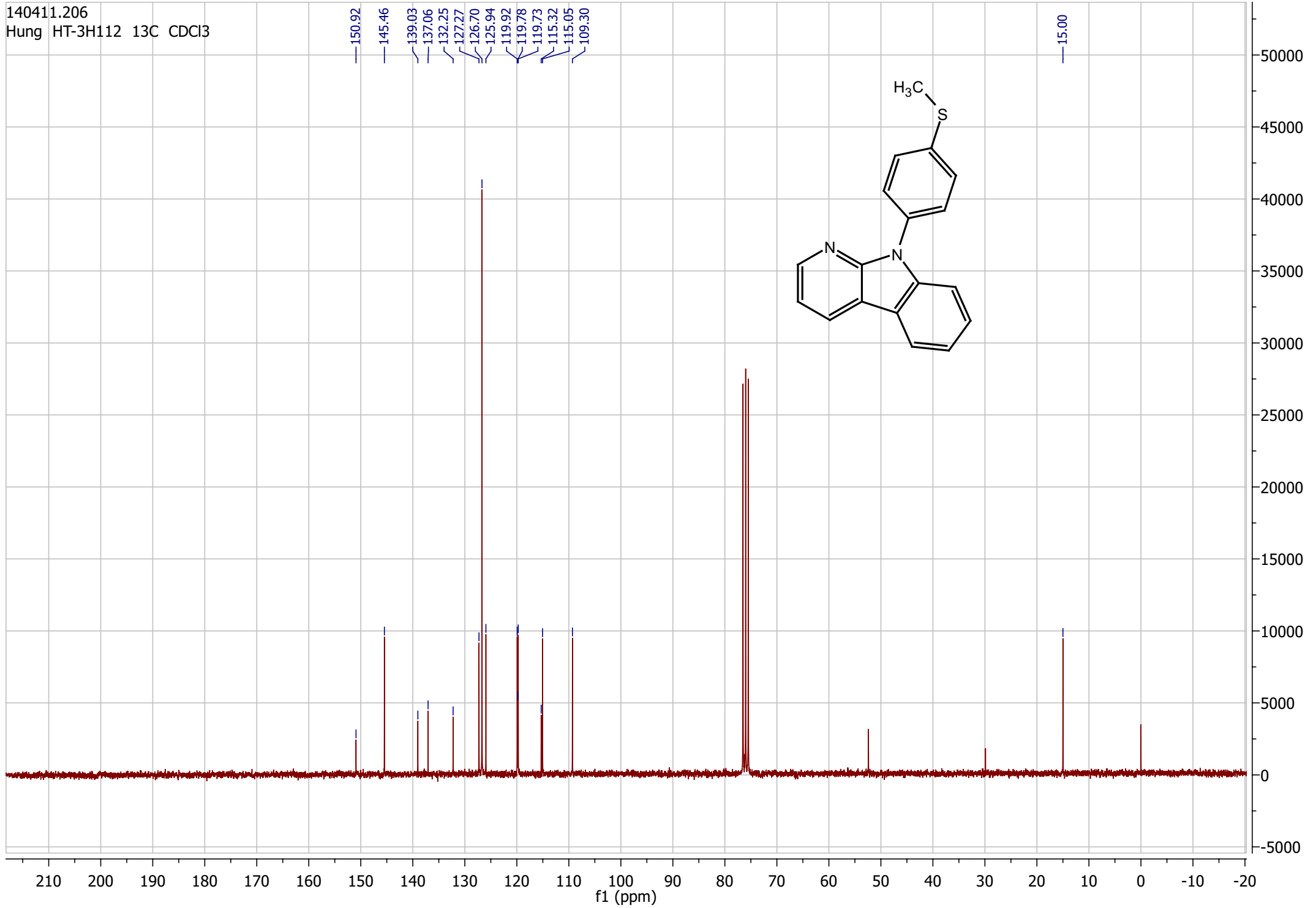


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0  
f1 (ppm)

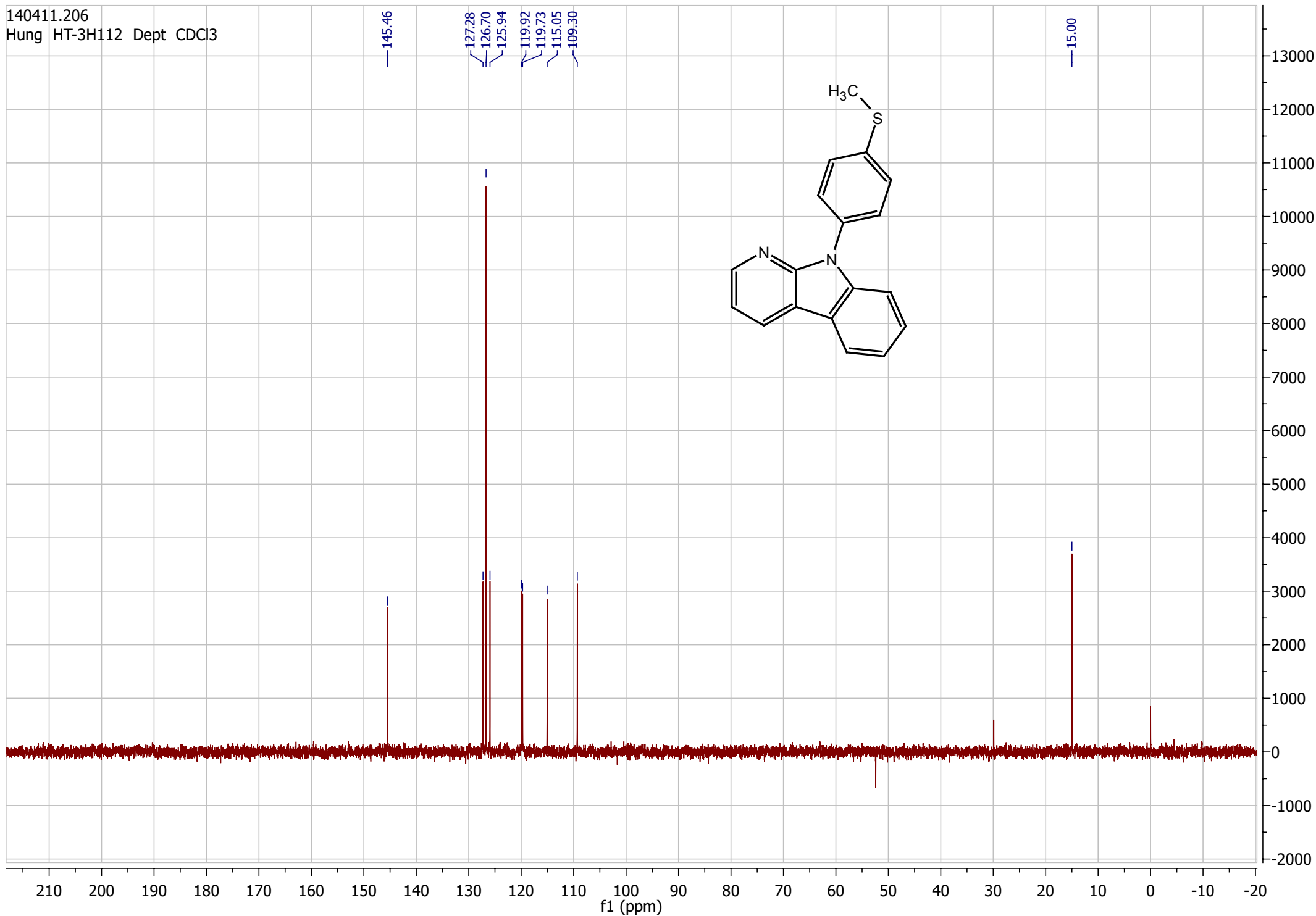
140411.206  
Hung HT-3H



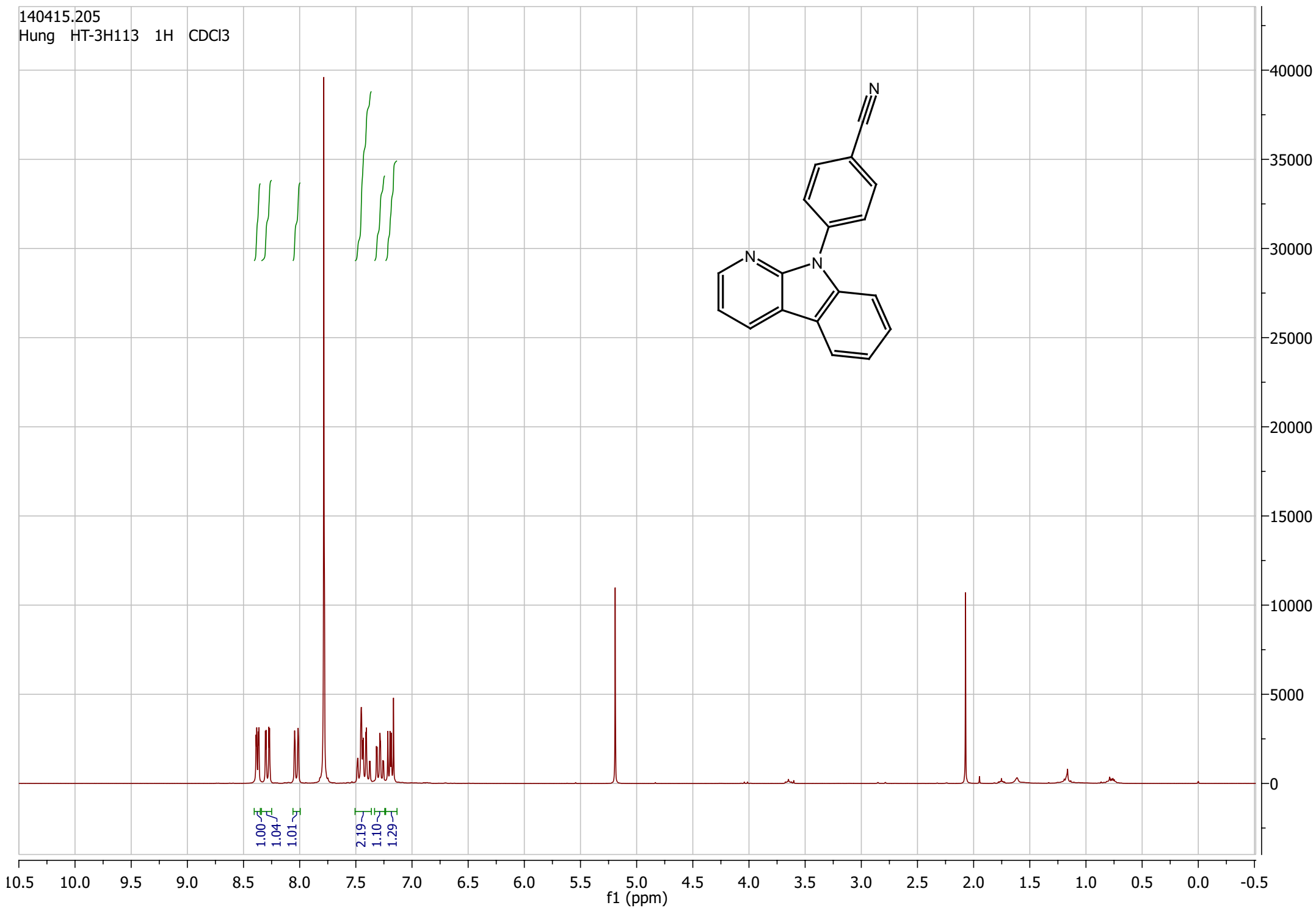
140411.206  
Hung HT-3H112 13C CDCl3



140411.206  
Hung HT-3H112 Dept CDCI3

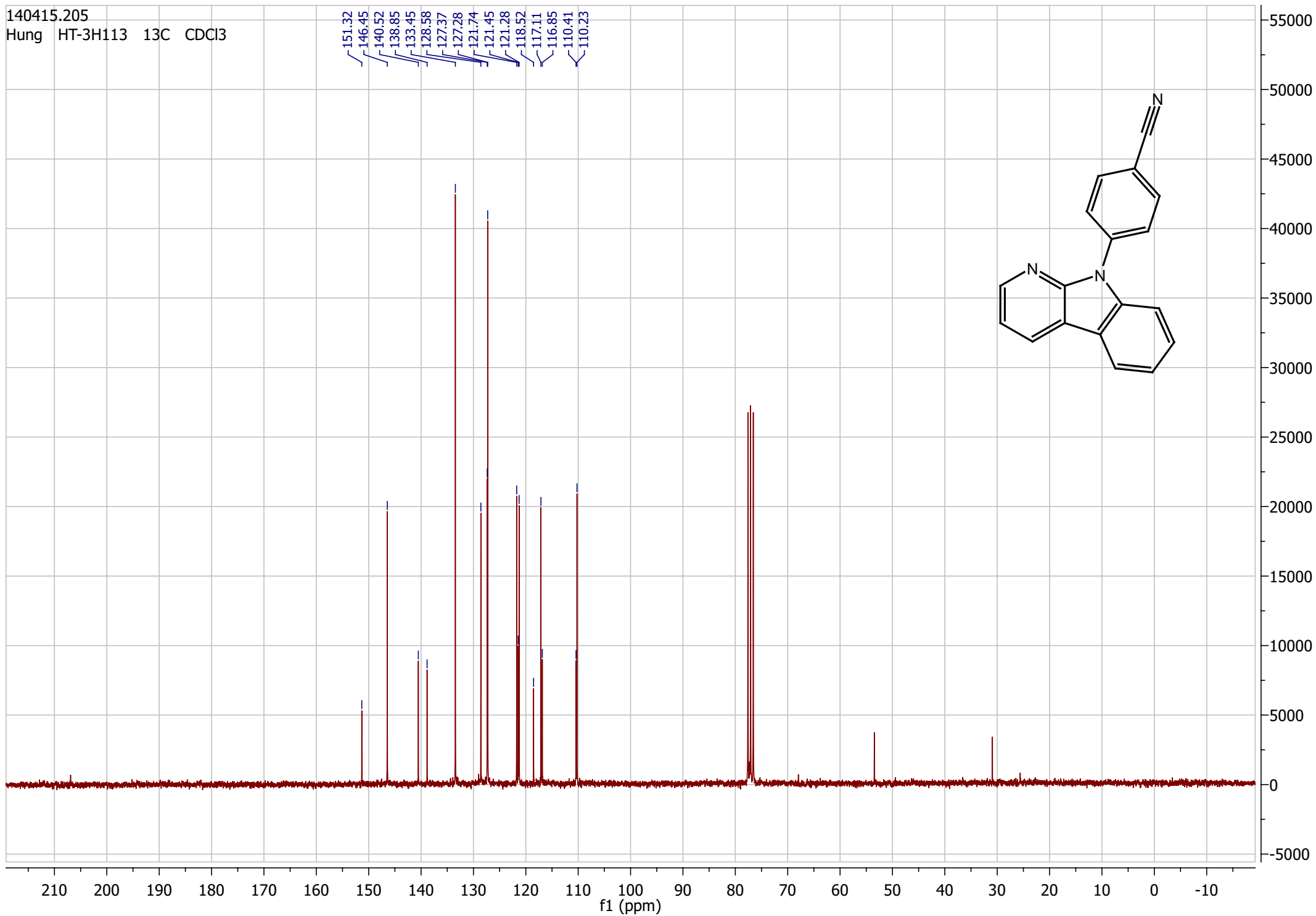


140415.205  
Hung HT-3H113 1H CDCl3



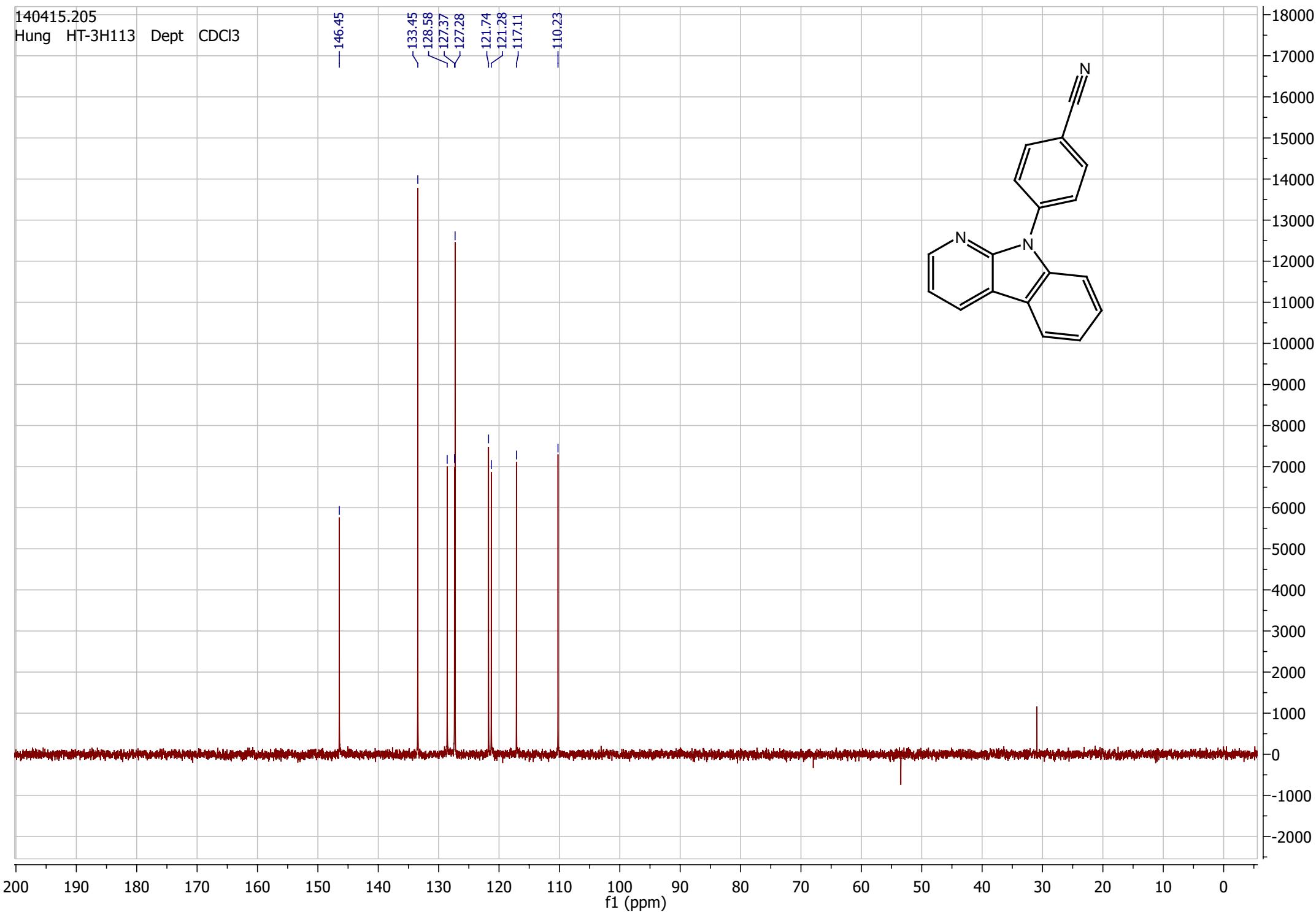
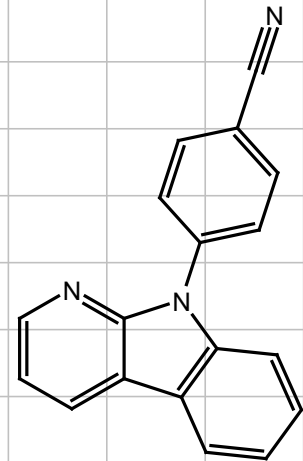
140415.205  
Hung HT-3H113 13C CDCl3

151.32  
146.45  
140.52  
138.85  
133.45  
128.58  
127.37  
127.28  
121.74  
121.45  
121.28  
118.52  
117.11  
116.85  
110.41  
110.23



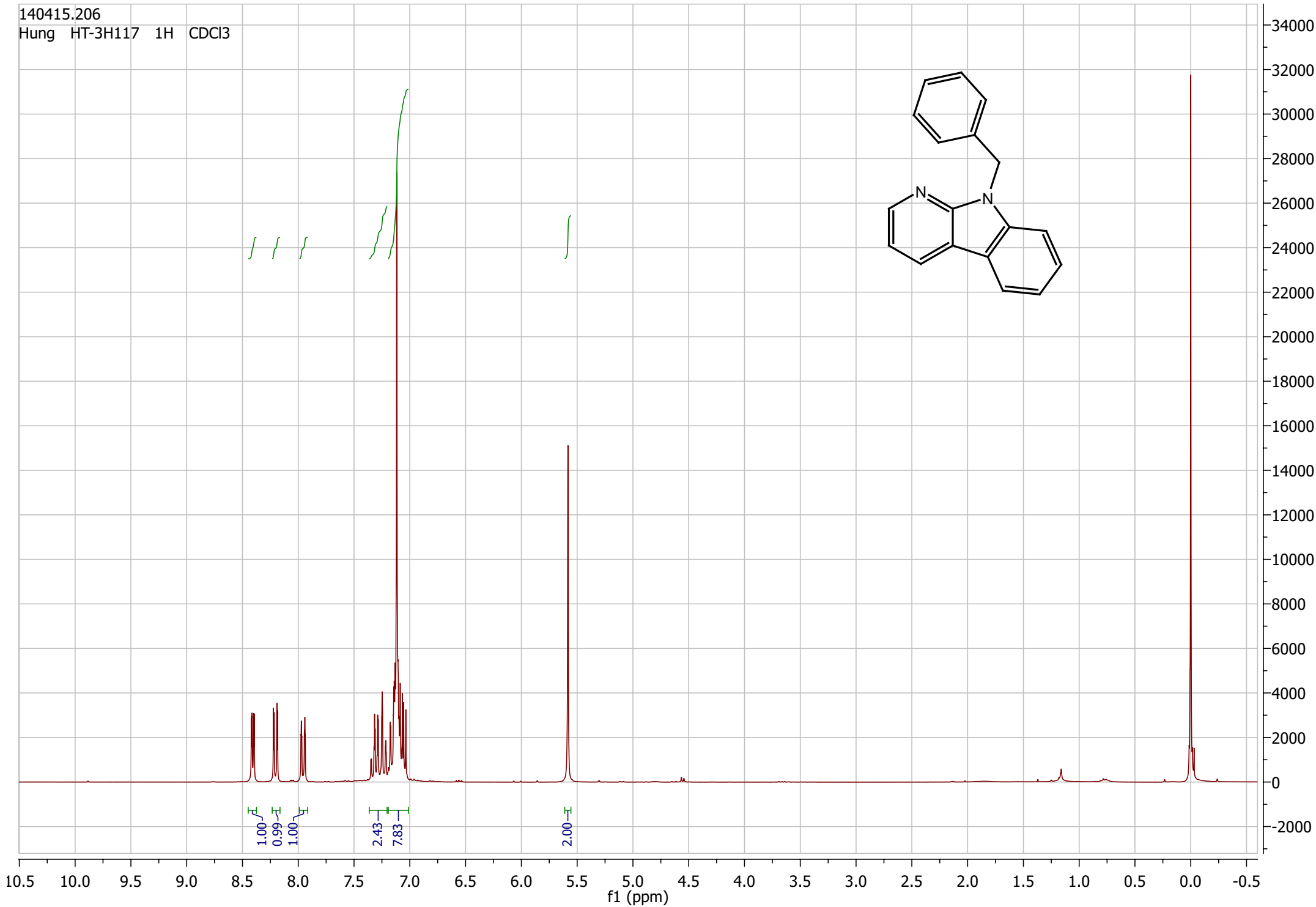
140415.205  
Hung HT-3H113 Dept CDCl3

146.45  
133.45  
128.58  
127.37  
127.28  
121.74  
121.28  
117.11  
110.23

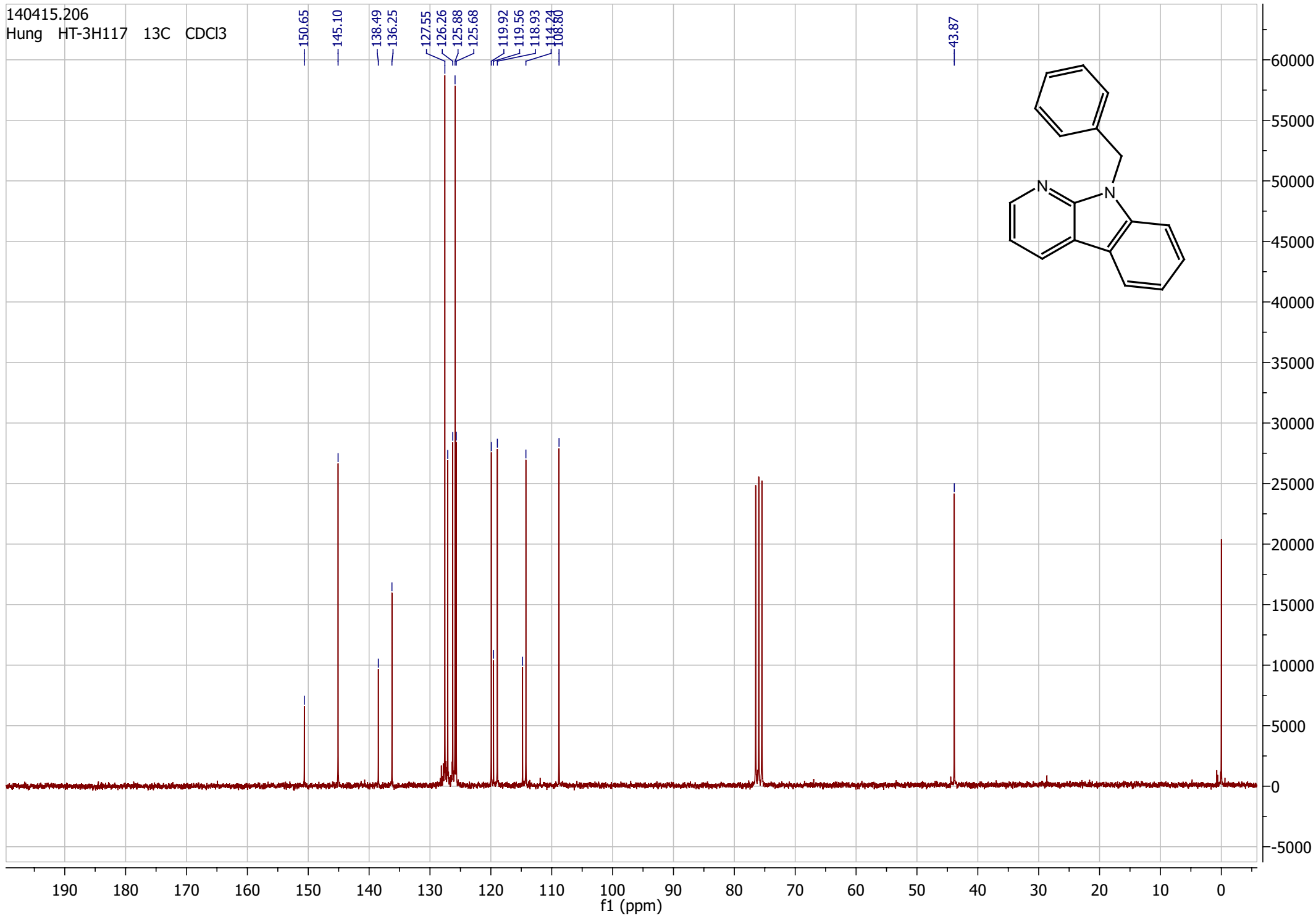




140415.206  
Hung HT-3H117 1H CDCl3



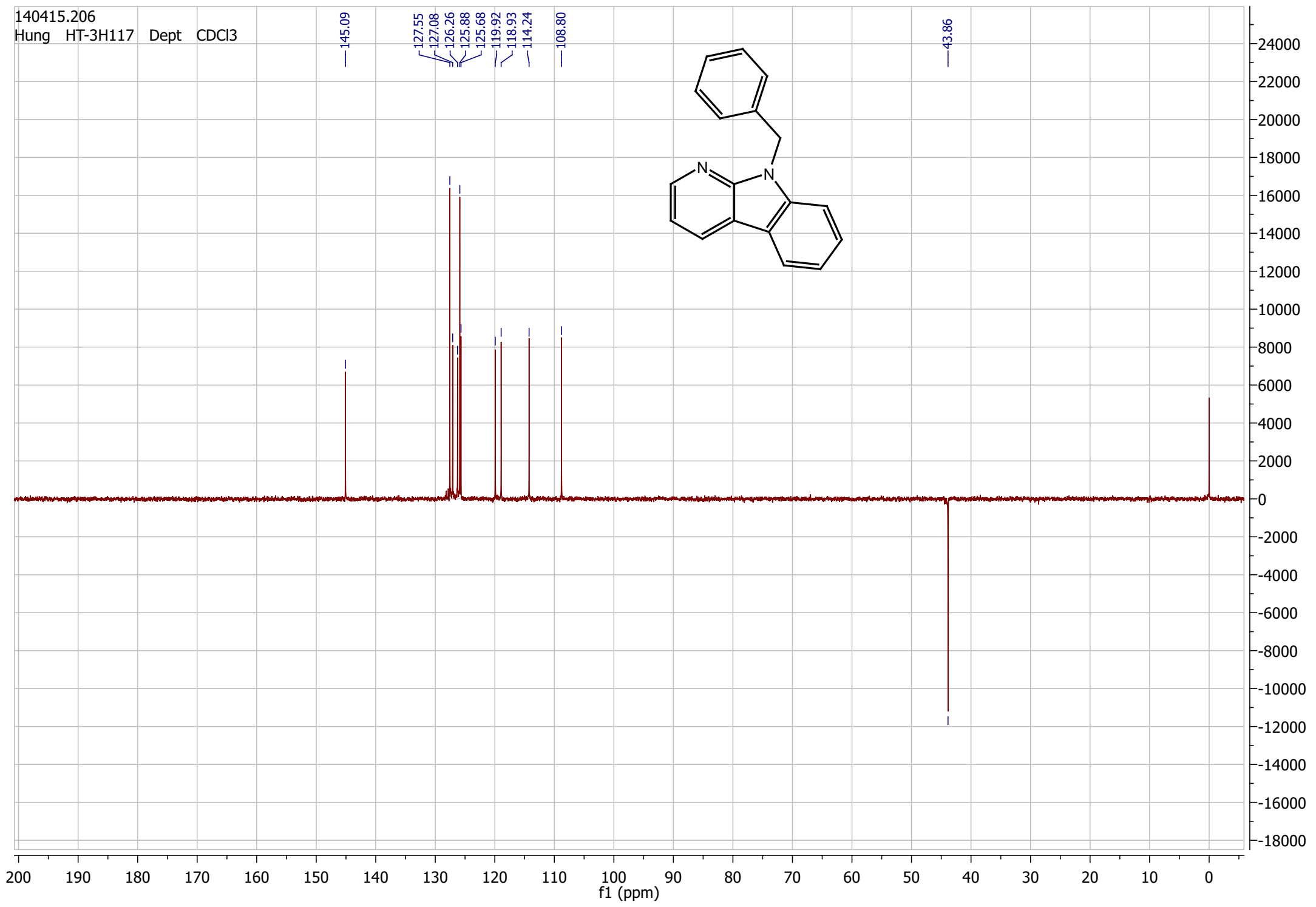
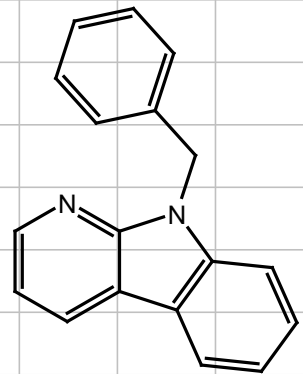
140415.206  
Hung HT-3H117 13C CDCl3



140415.206  
Hung HT-3H117 Dept CDCl3

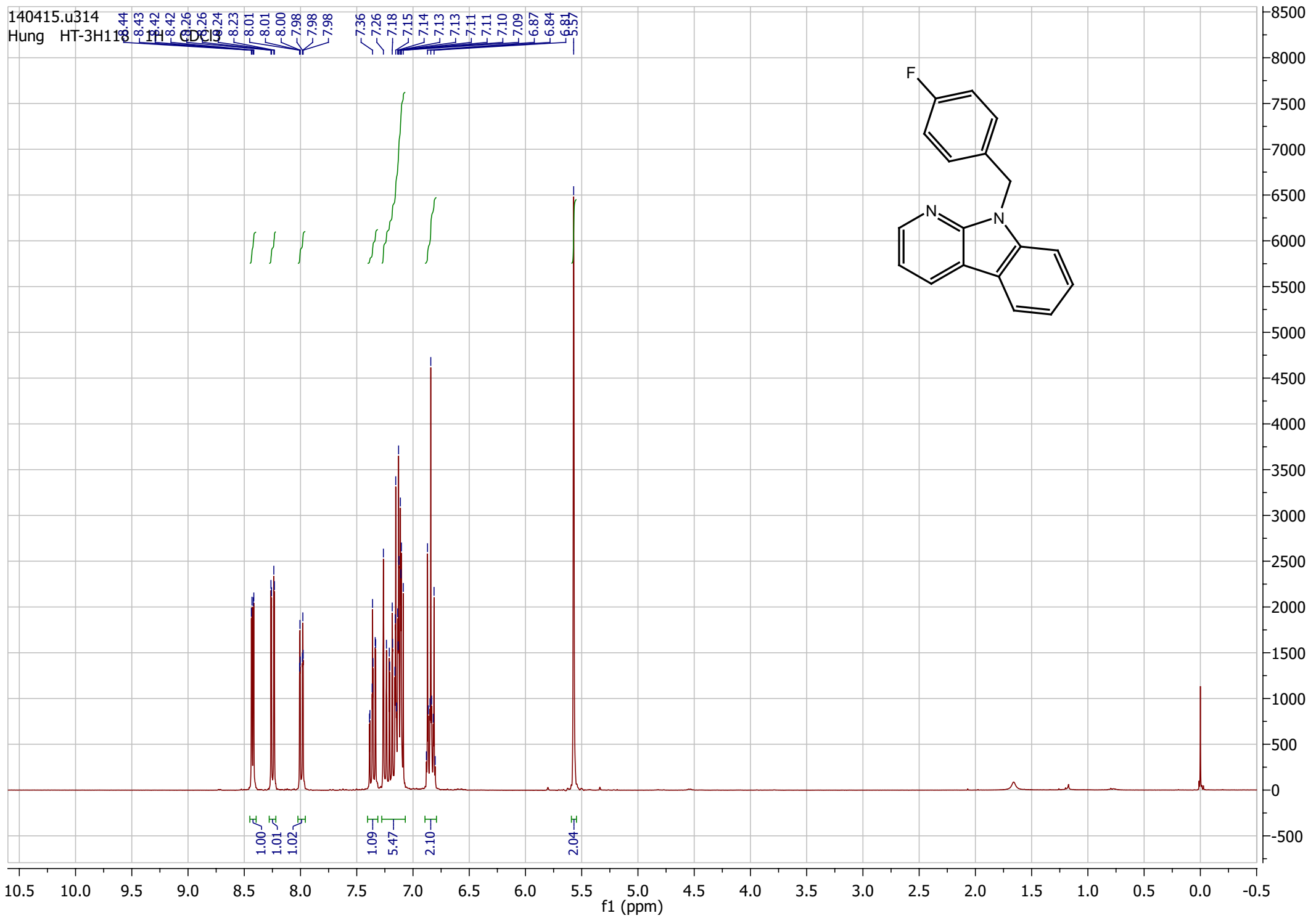
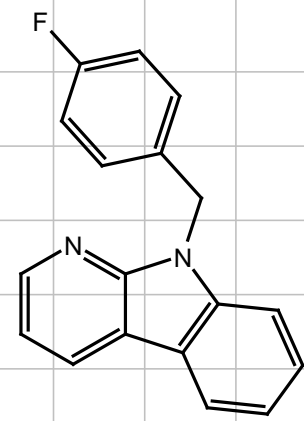
145.09  
127.55  
127.08  
126.26  
125.88  
125.68  
119.92  
118.93  
114.24  
108.80

43.86

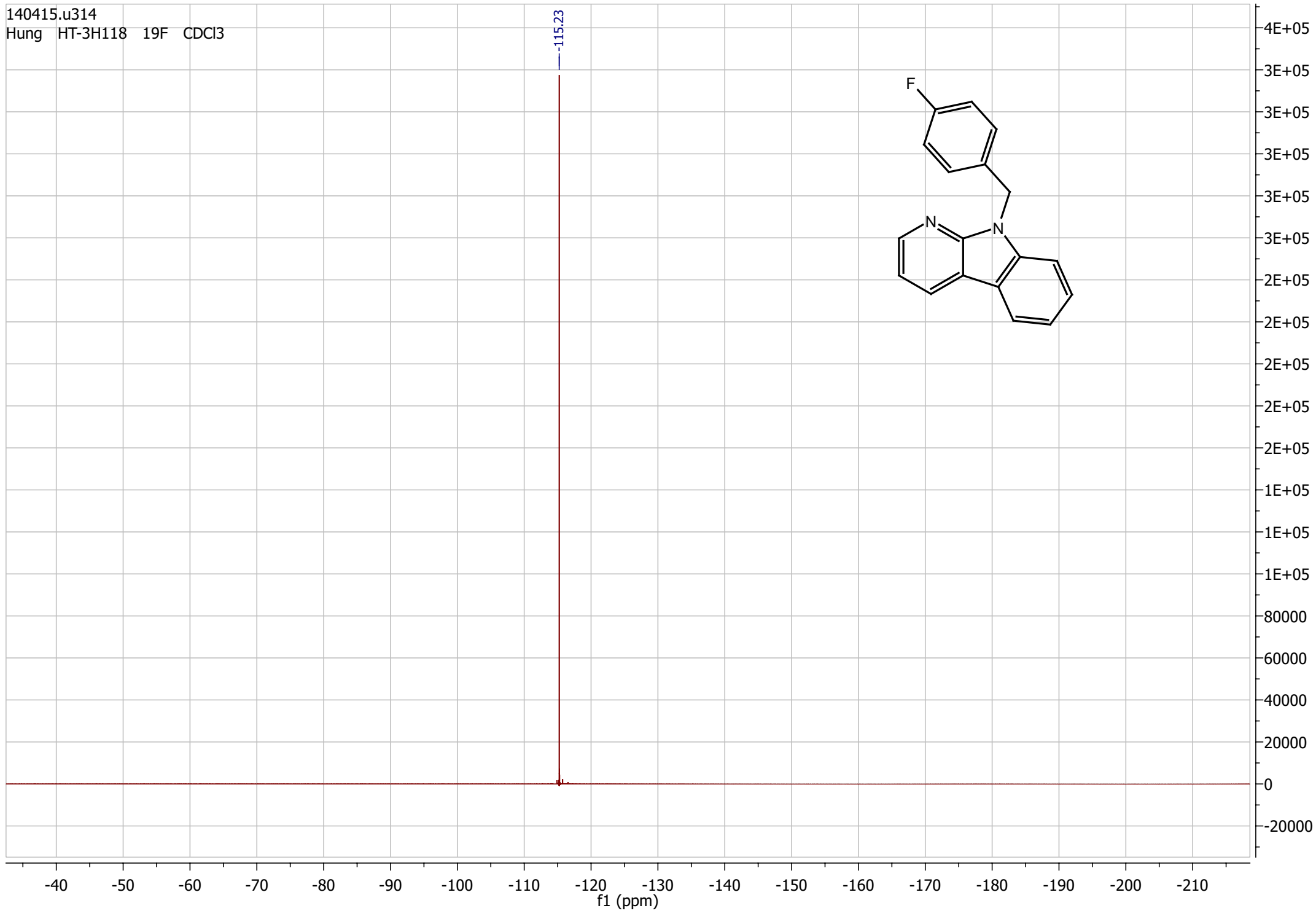


140415.u314  
Hung HT-3H118

8.44  
8.43  
8.42  
8.42  
8.26  
8.26  
8.24  
8.23  
8.01  
8.01  
8.00  
7.98  
7.98  
7.98  
7.36  
7.26  
7.18  
7.15  
7.14  
7.13  
7.13  
7.11  
7.11  
7.10  
7.09  
6.87  
6.84  
5.97



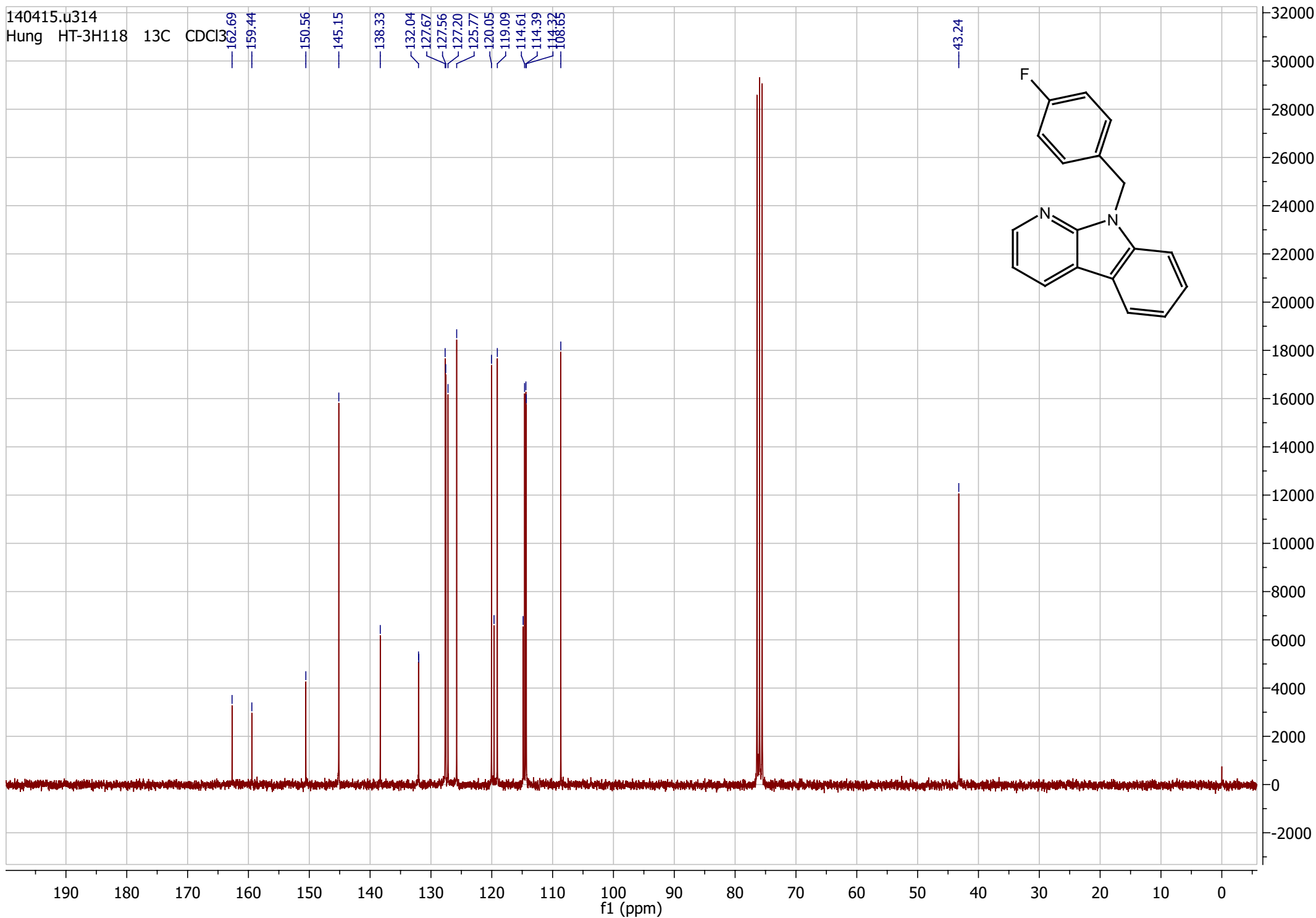
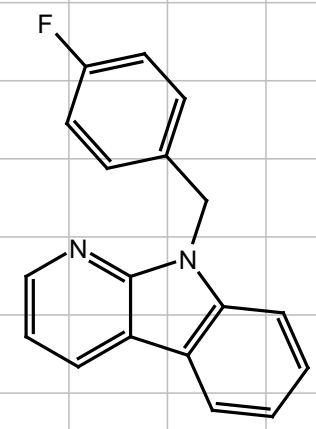
140415.u314  
Hung HT-3H118 19F CDCI3



140415.u314  
Hung HT-3H118 13C

CDCl<sub>3</sub>  
162.69  
159.44  
150.56  
145.15  
138.33  
132.04  
127.67  
127.56  
127.20  
125.77  
120.05  
119.09  
114.61  
114.39  
108.65

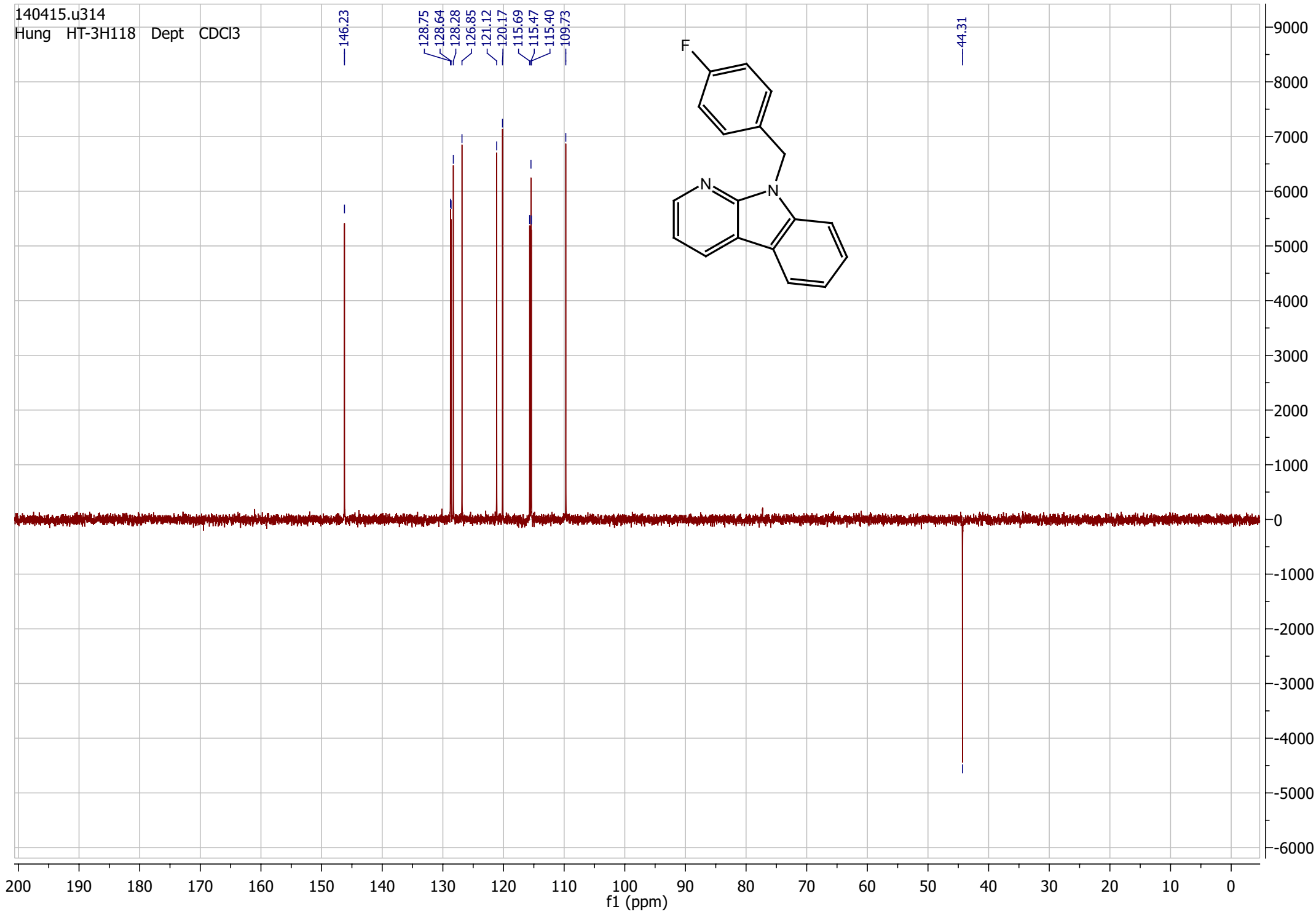
43.24



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

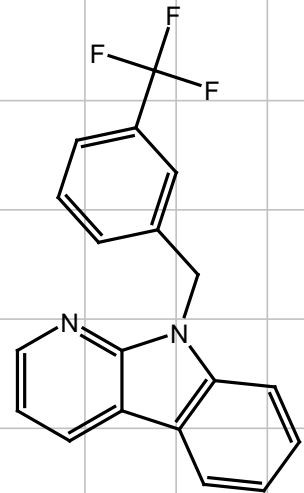
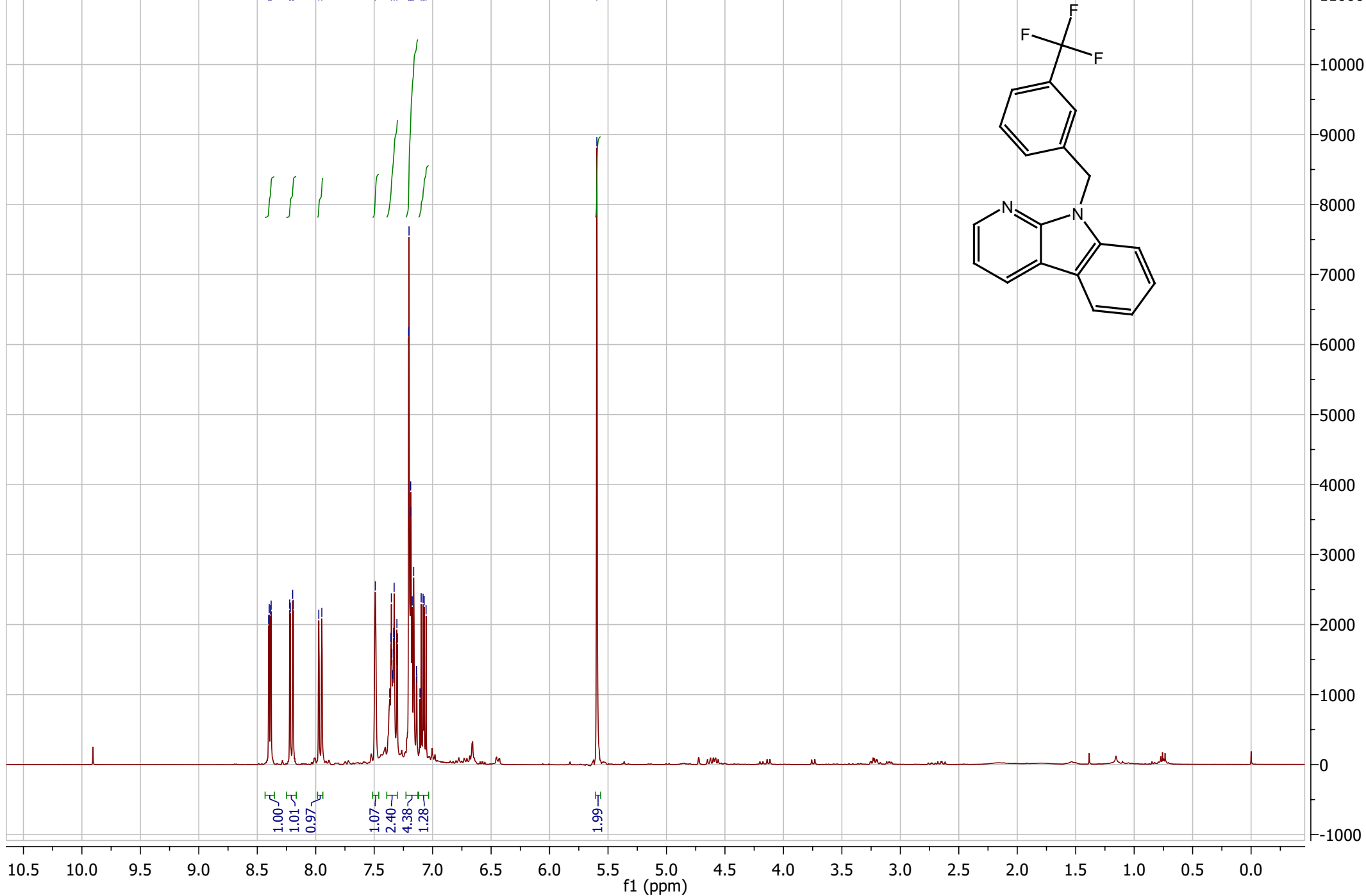
f1 (ppm)

140415.u314  
Hung HT-3H118 Dept CDCl3



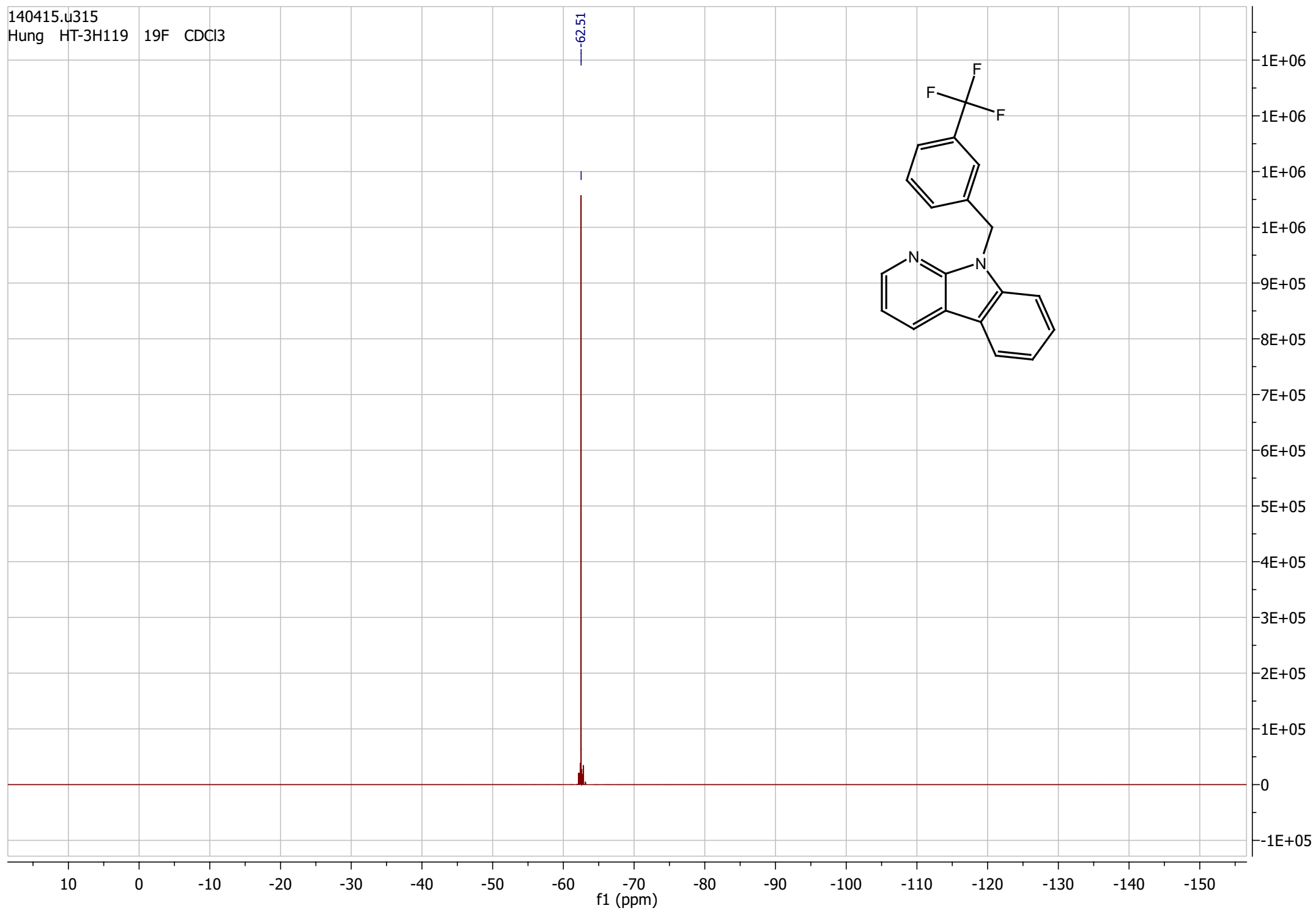
140415.u315  
Hung HT-3H119

1H  
8.40  
8.40  
8.39  
8.38  
8.22  
8.20  
8.19  
7.97  
7.95  
7.49  
7.35  
7.33  
7.31  
7.21  
7.20  
7.19  
7.17  
7.16  
7.10  
7.08  
7.07  
5.06





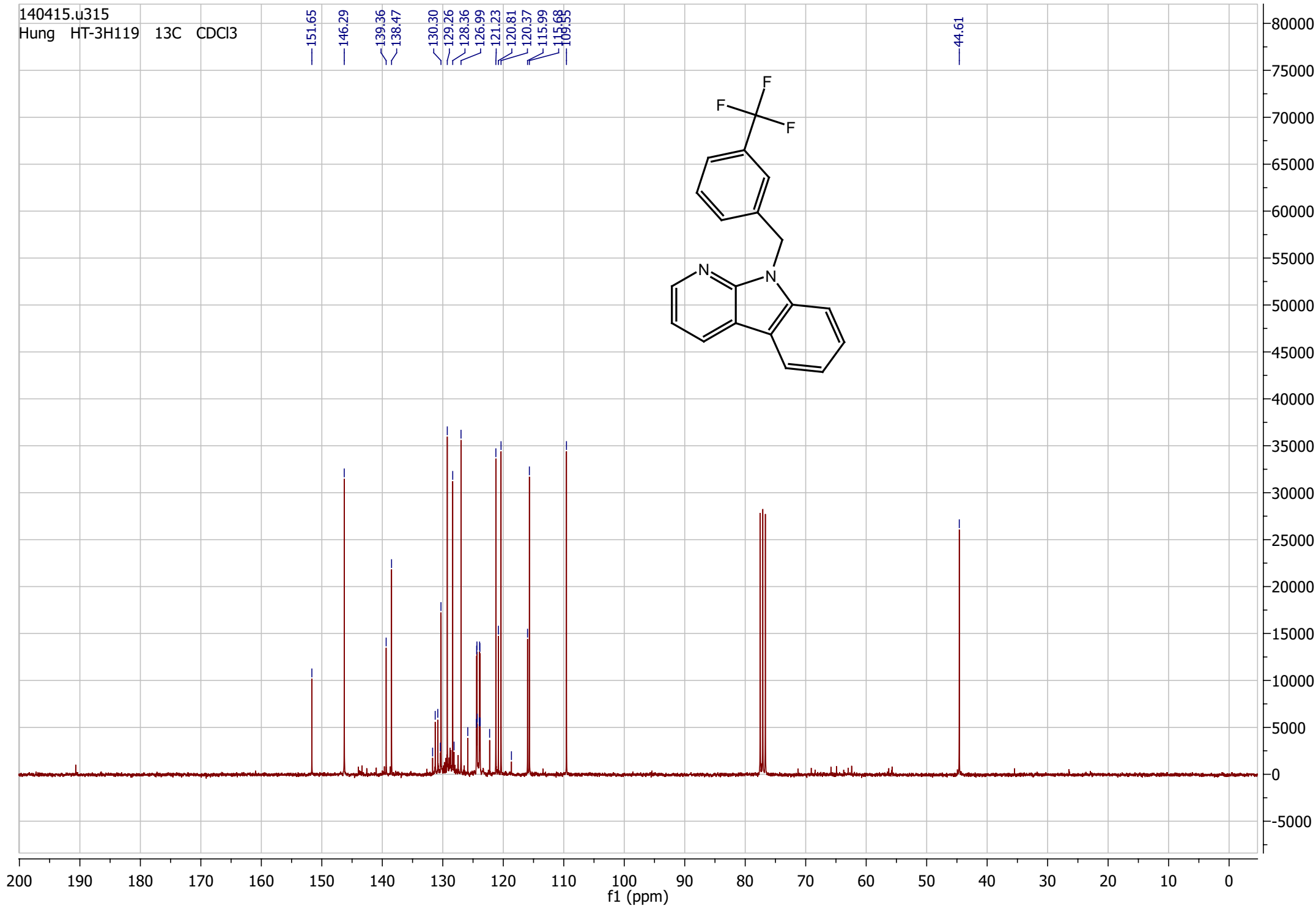
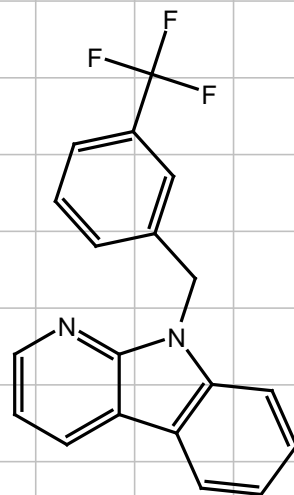
140415.u315  
Hung HT-3H119 19F CDCI3



140415.u315  
Hung HT-3H119 13C CDCl3

—151.65  
—146.29  
—139.36  
—138.47  
—130.30  
—129.26  
—128.36  
—126.99  
—121.23  
—120.81  
—120.37  
—115.99  
—109.58

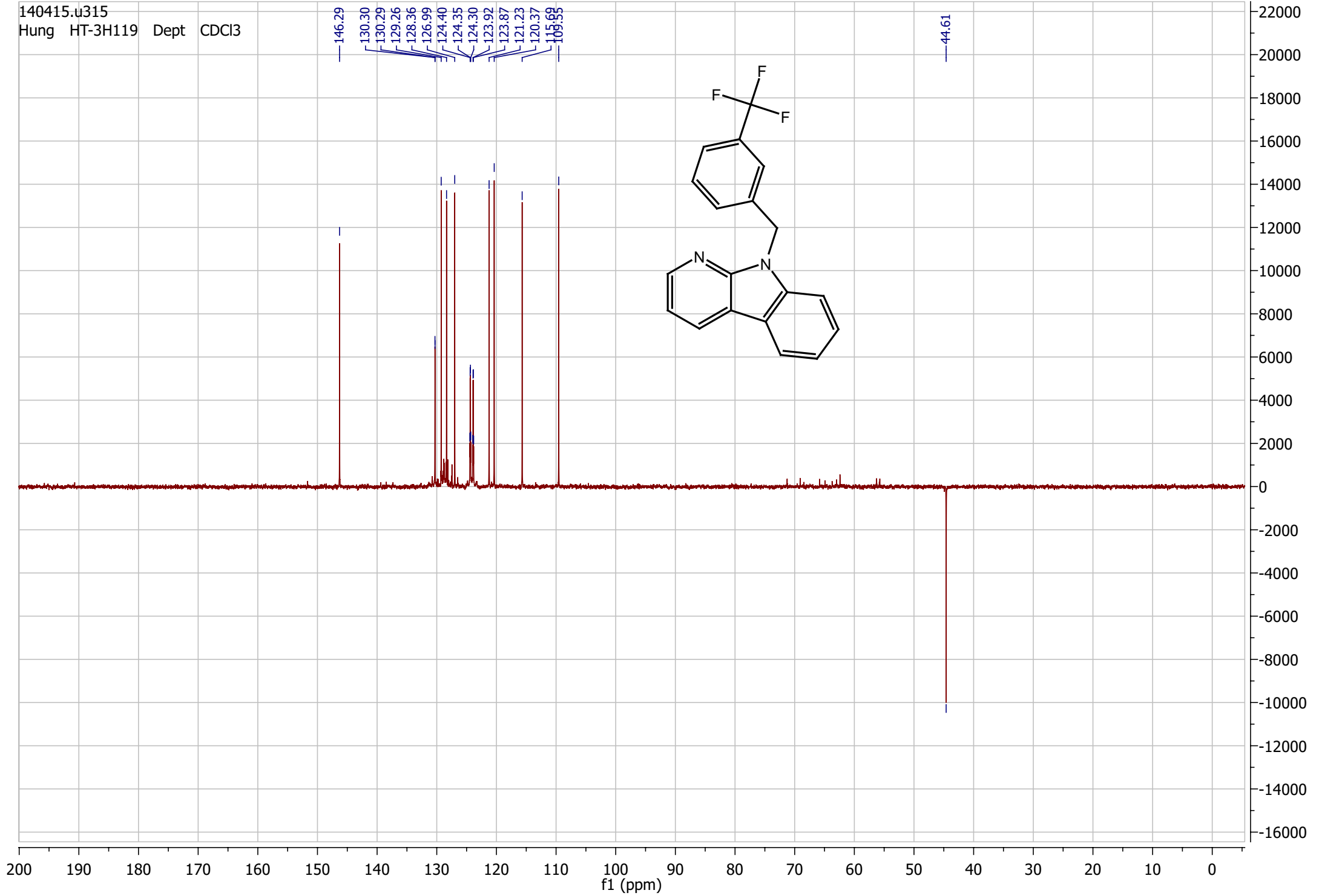
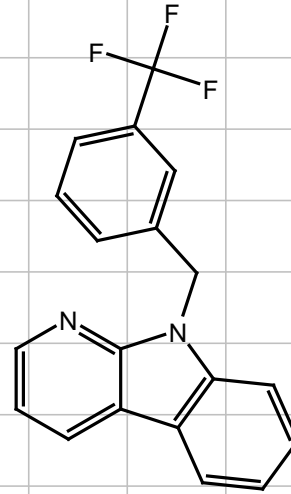
—44.61



140415.u315  
Hung HT-3H119 Dept CDCl3

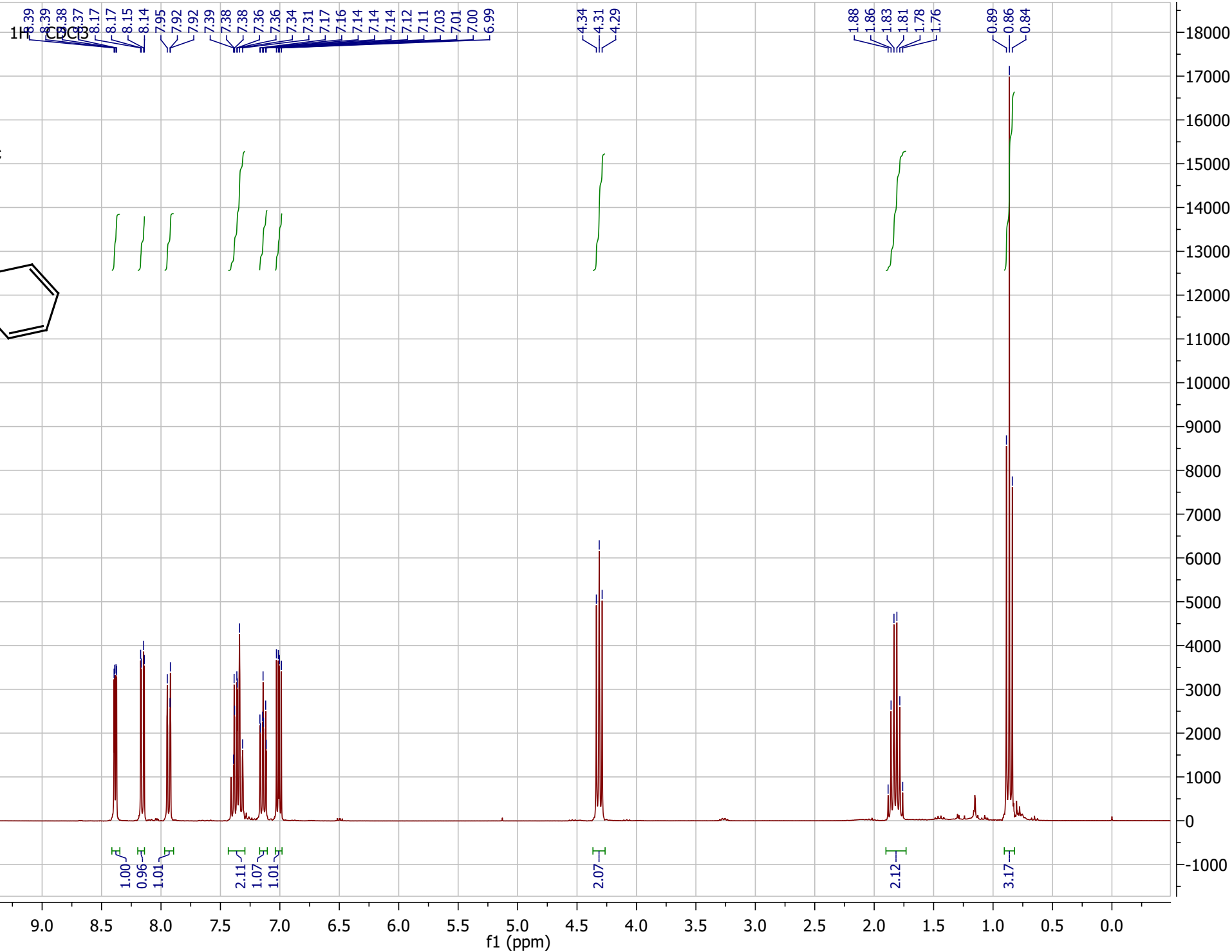
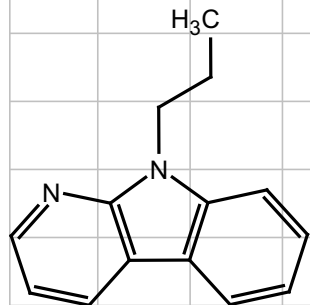
146.29  
130.30  
130.29  
129.26  
128.36  
126.99  
124.40  
124.35  
124.30  
123.92  
123.87  
121.23  
120.37  
109.68

44.61



140416.u316

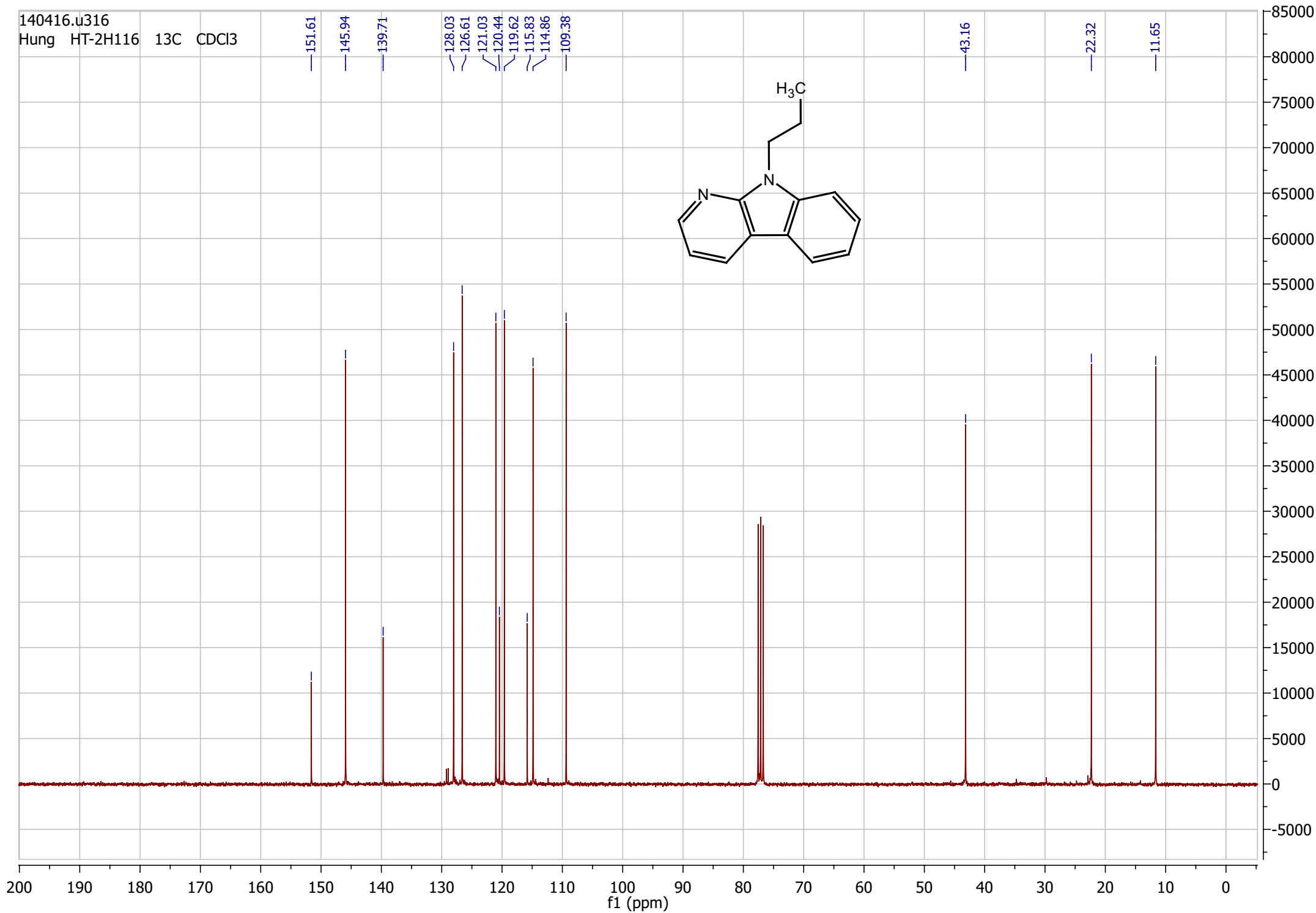
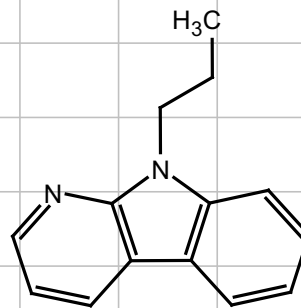
Hung HT-2H116



140416.u316  
Hung HT-2H116 13C CDCl3

—151.61 —145.94 —139.71  
—128.03 —126.61 —121.03 —120.44 —119.62 —115.83 —114.86 —109.38

—43.16 —22.32 —11.65



140416.u316  
Hung HT-2H116 Dept CDCl3

145.94

128.04

126.61

121.03

119.62

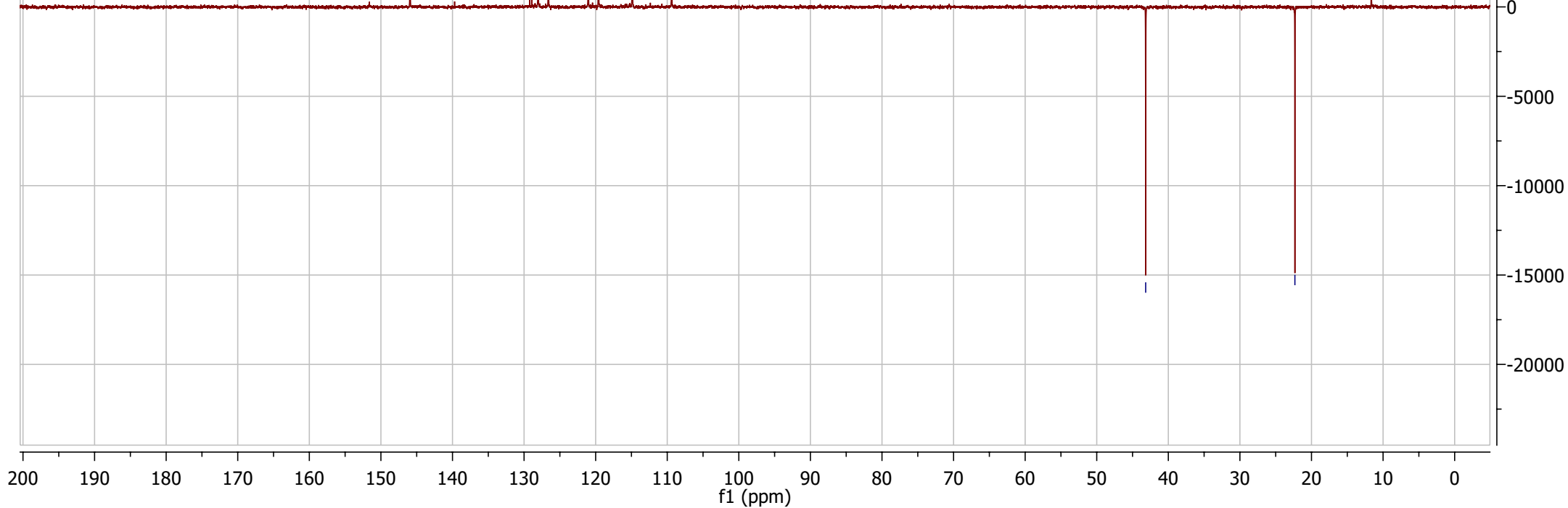
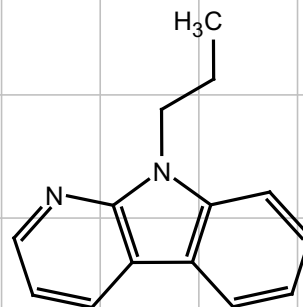
114.86

109.38

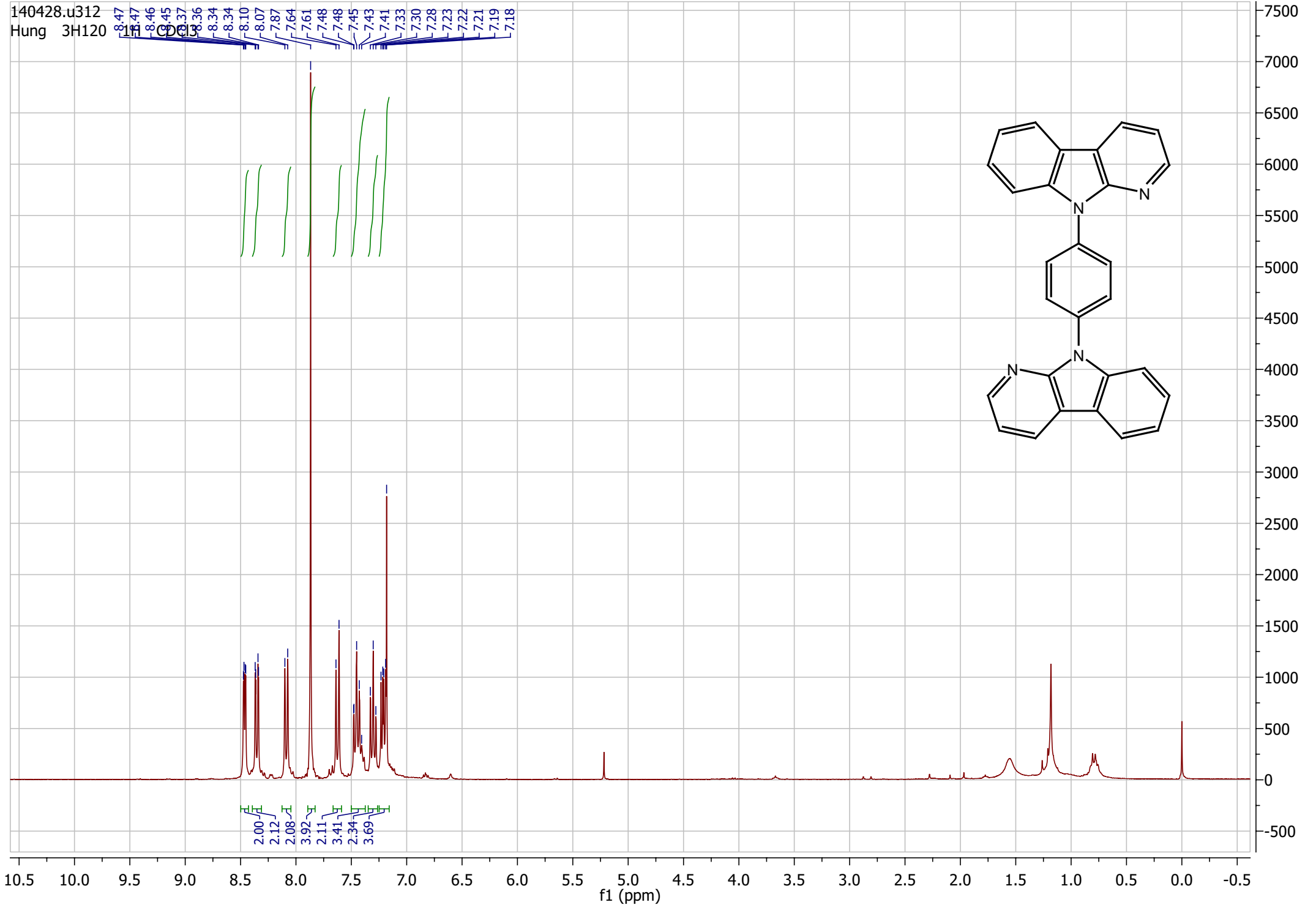
43.16

22.32

11.65

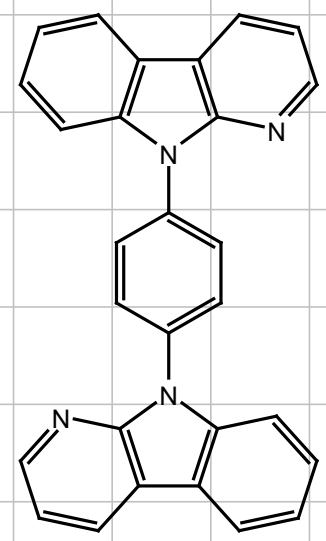
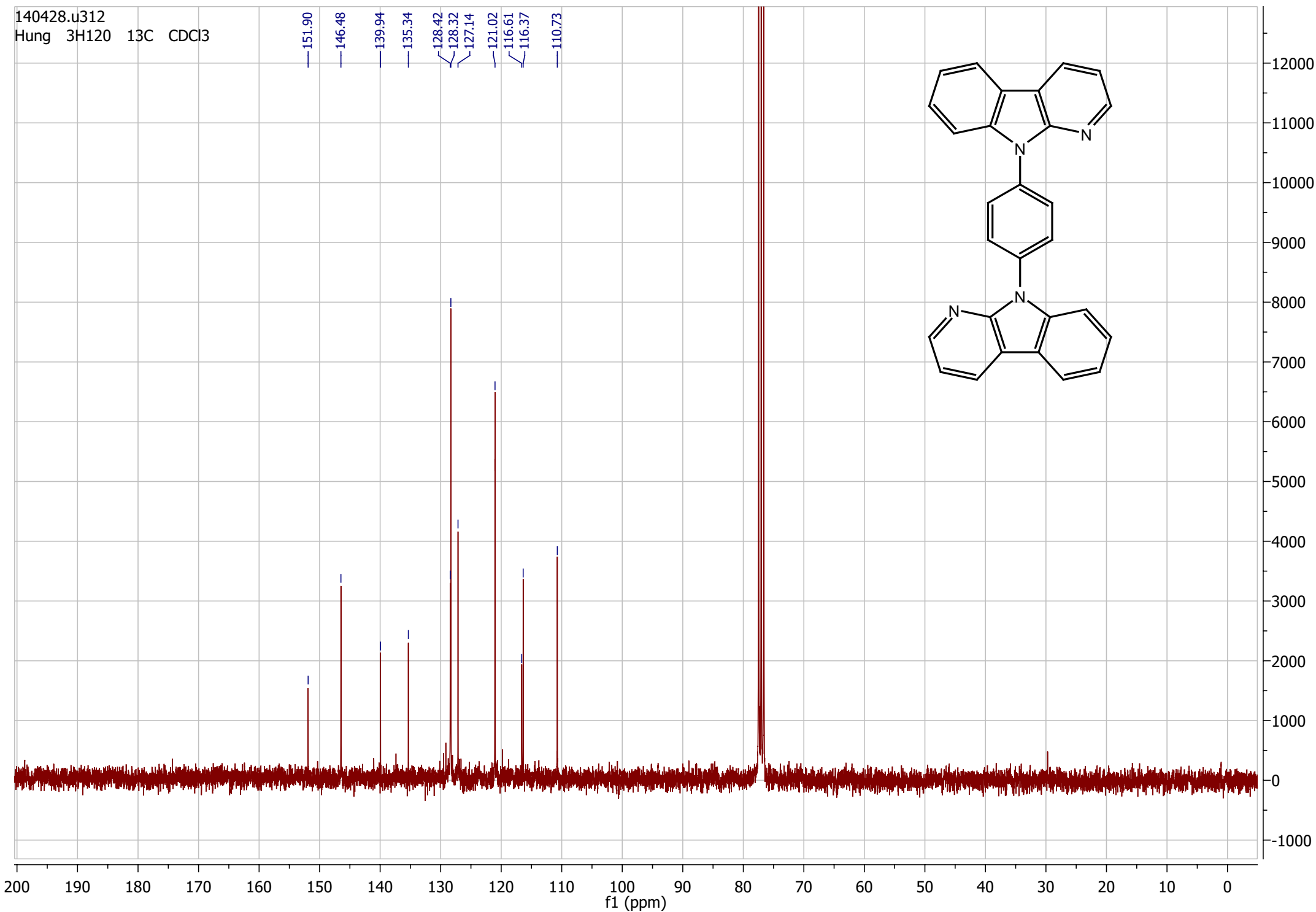


140428.u312  
Hung 3H120



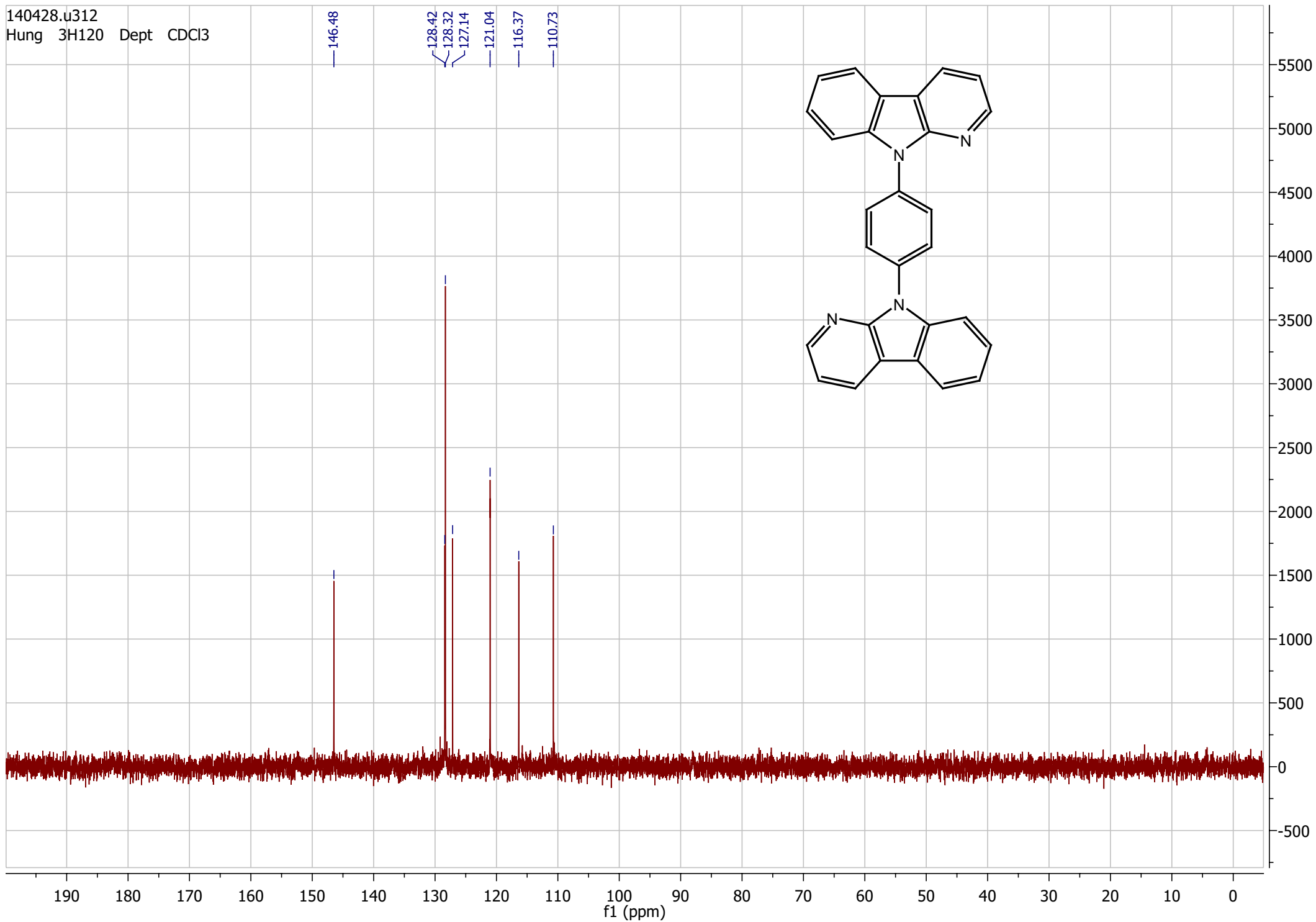
140428.u312  
Hung 3H120 13C CDCI3

151.90  
146.48  
139.94  
135.34  
128.42  
128.32  
127.14  
121.02  
116.61  
116.37  
110.73

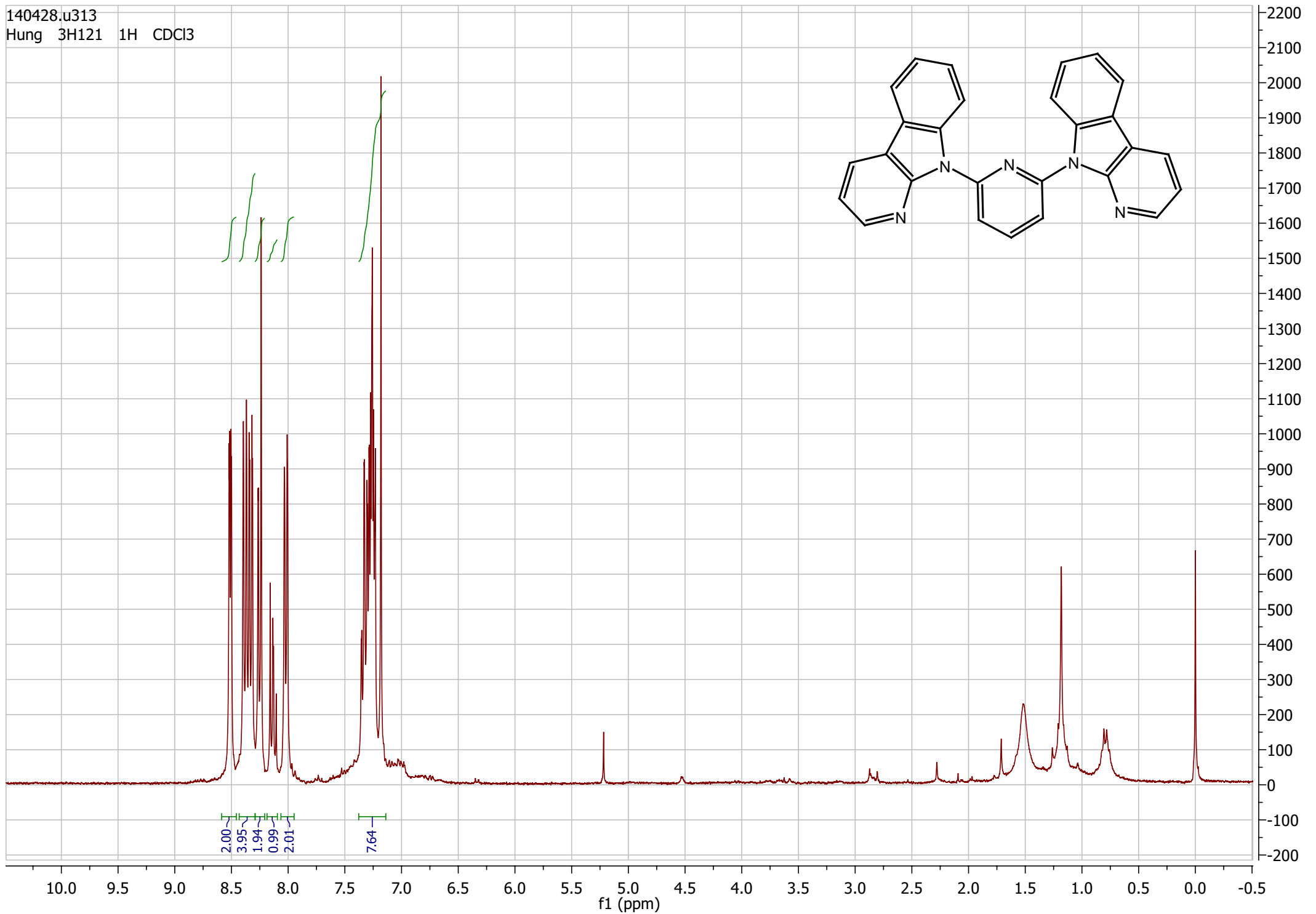




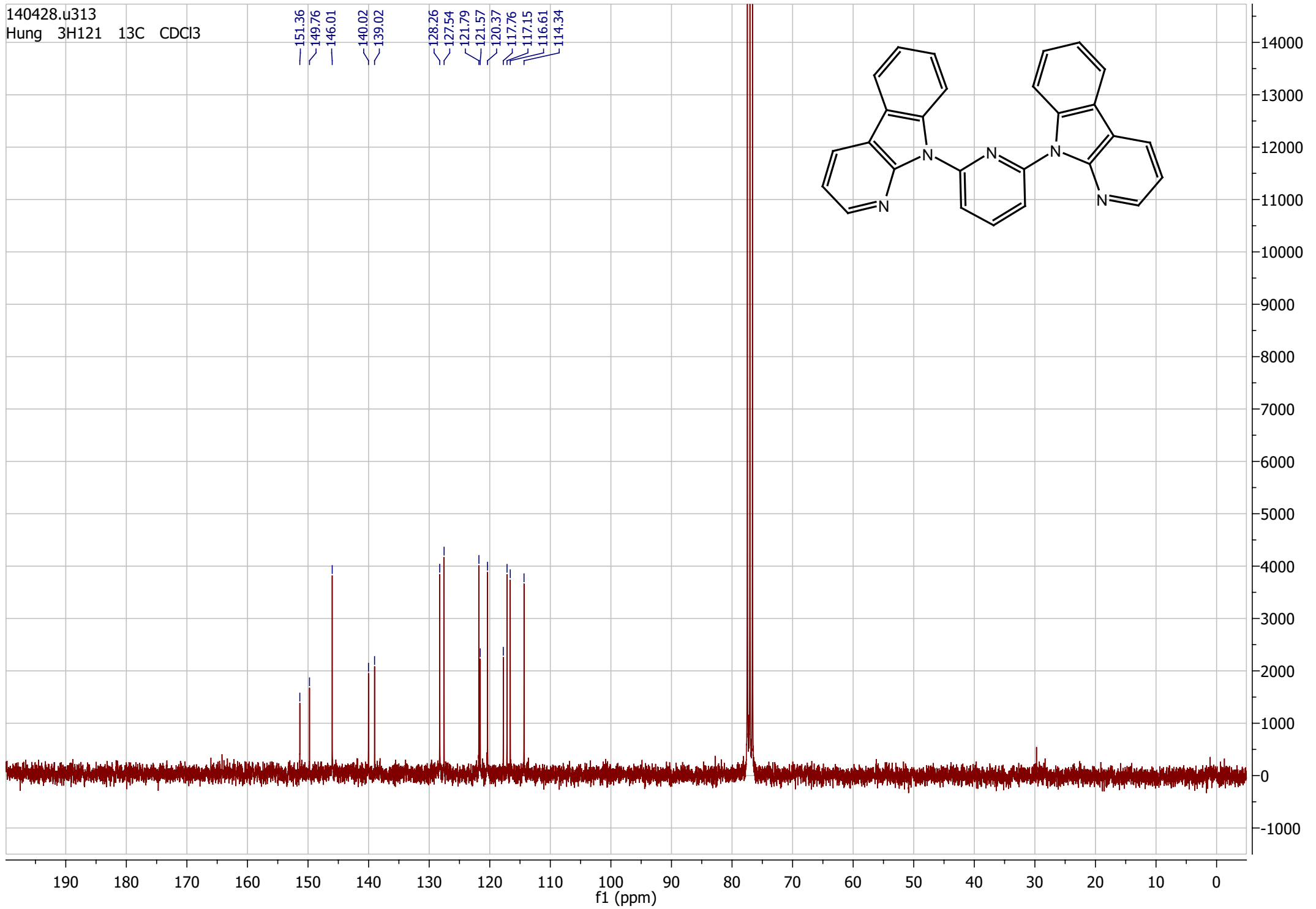
140428.u312  
Hung 3H120 Dept CDCl3



140428.u313  
Hung 3H121 1H CDCl3

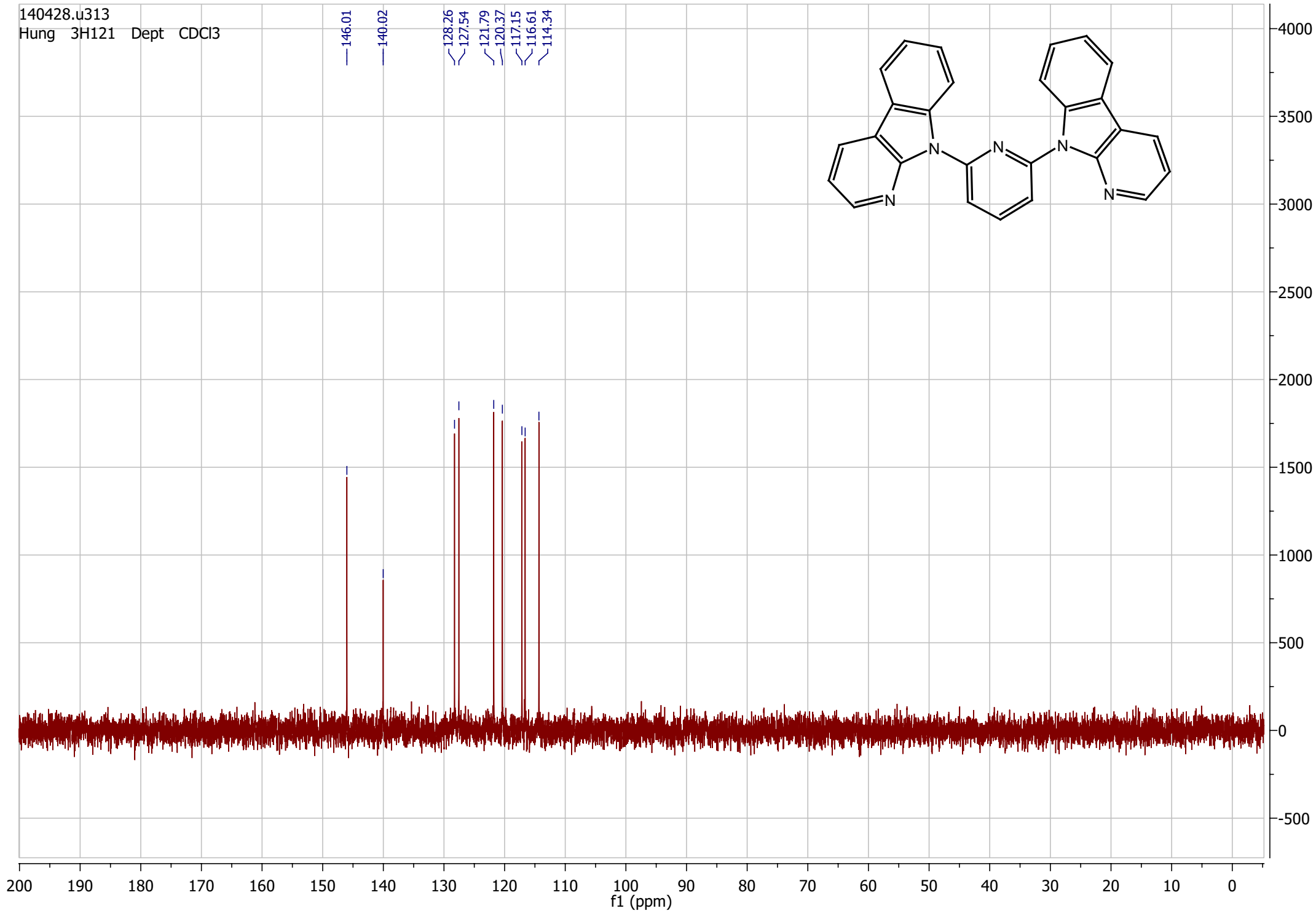
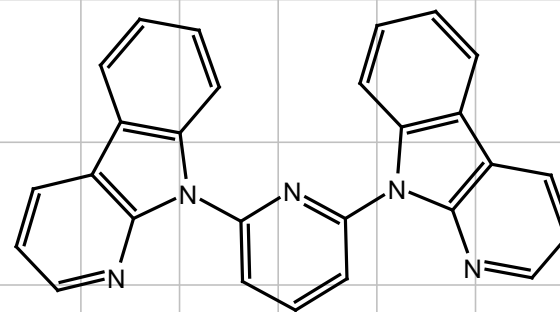


140428.u313  
Hung 3H121 13C CDCl3

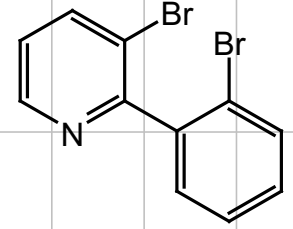


140428.u313  
Hung 3H121 Dept CDCl3

— 146.01  
— 140.02  
{ 128.26  
{ 127.54  
{ 121.79  
{ 120.37  
{ 117.15  
{ 116.61  
{ 114.34



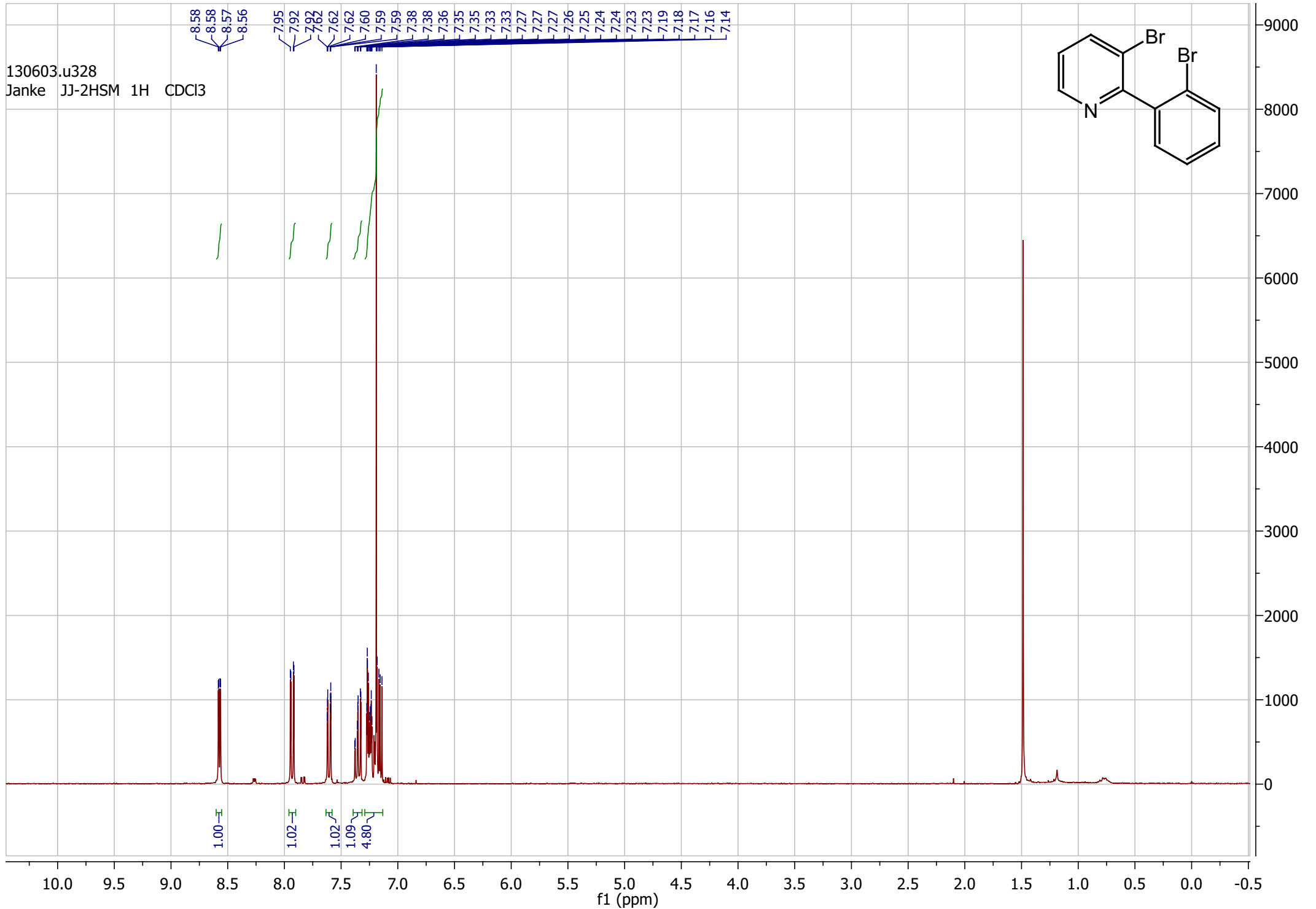
130603.u328  
Janke JJ-2HSM 1H CDCl3



8.58  
8.58  
8.57  
8.56  
7.95  
7.92  
7.92  
7.82  
7.62  
7.62  
7.60  
7.59  
7.59  
7.38  
7.38  
7.36  
7.35  
7.35  
7.33  
7.33  
7.33  
7.27  
7.27  
7.27  
7.26  
7.25  
7.24  
7.24  
7.23  
7.23  
7.19  
7.18  
7.17  
7.16  
7.14

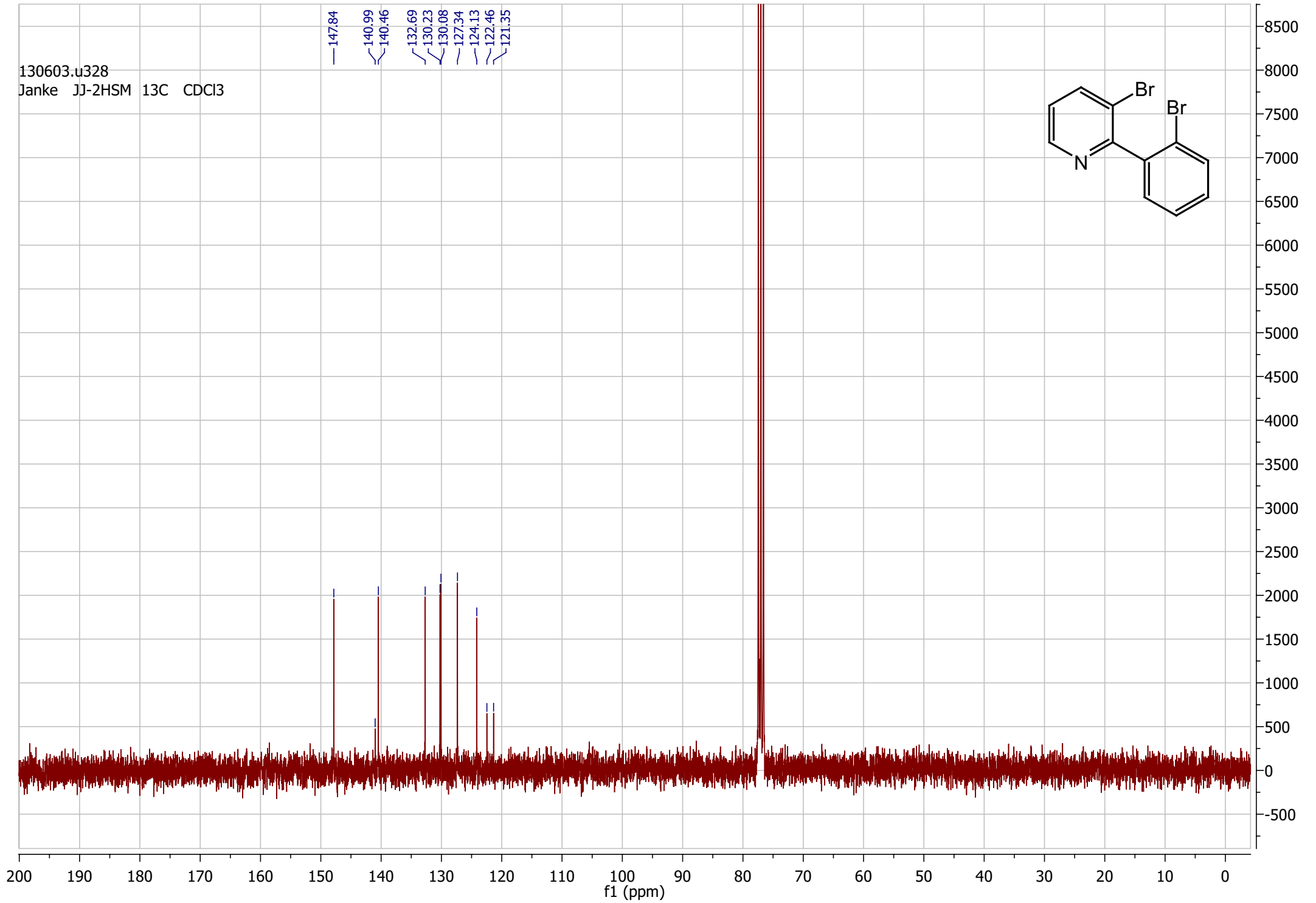
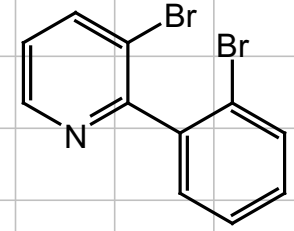
1.00  
1.02  
1.02  
1.09  
4.80

f1 (ppm)



130603.u328  
Janke JJ-2HSM 13C CDCl3

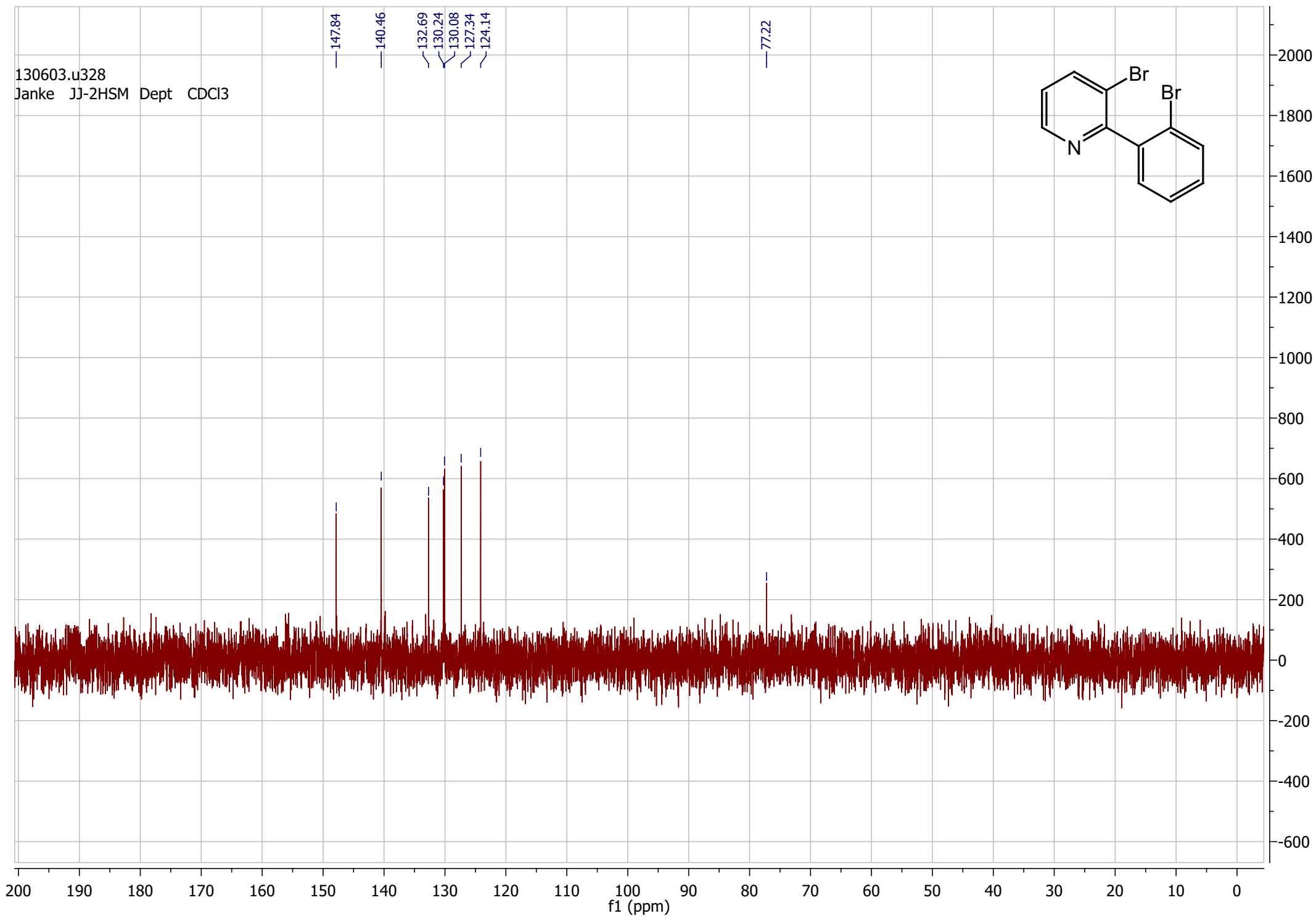
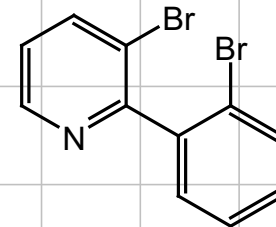
- 147.84
- 140.99
- 140.46
- 132.69
- 130.23
- 130.08
- 127.34
- 124.13
- 122.46
- 121.35



130603.u328  
Janke JJ-2HSM Dept CDCl3

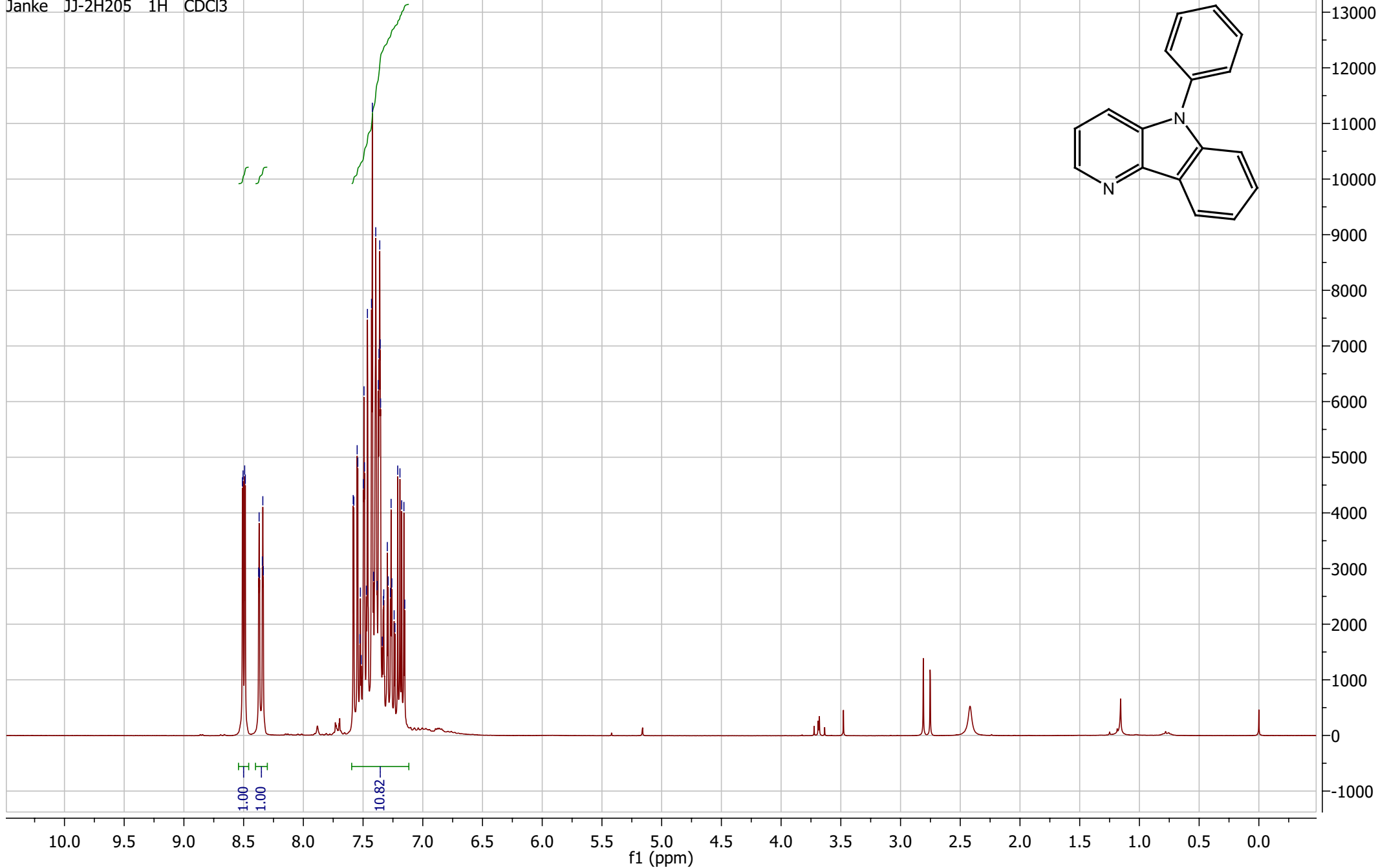
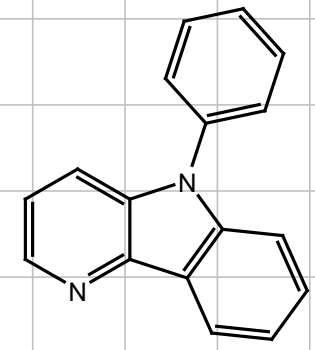
147.84  
140.46  
132.69  
130.24  
130.08  
127.34  
124.14

77.22

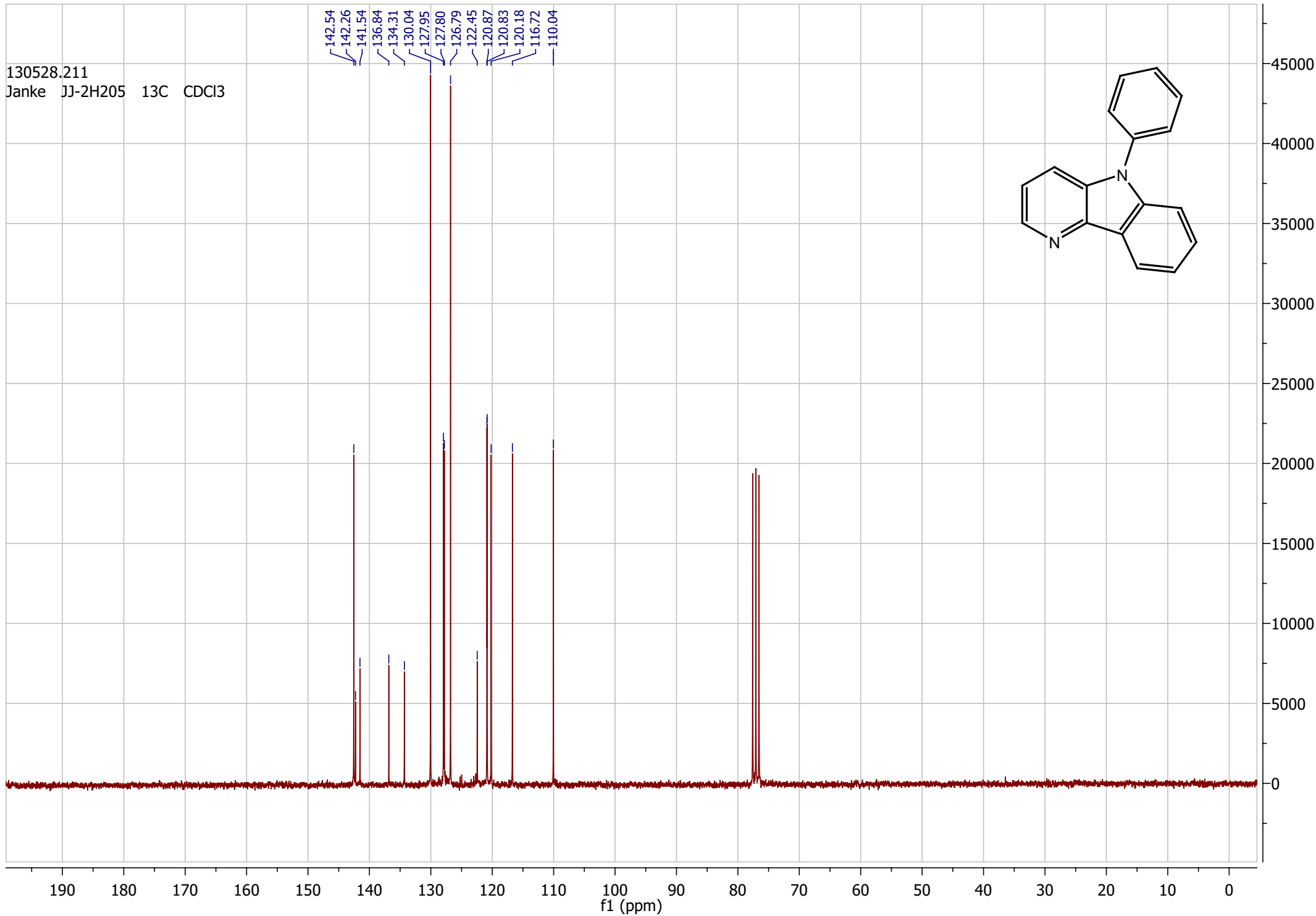


130528.211  
Janke JJ-2H205 1H CDCl3

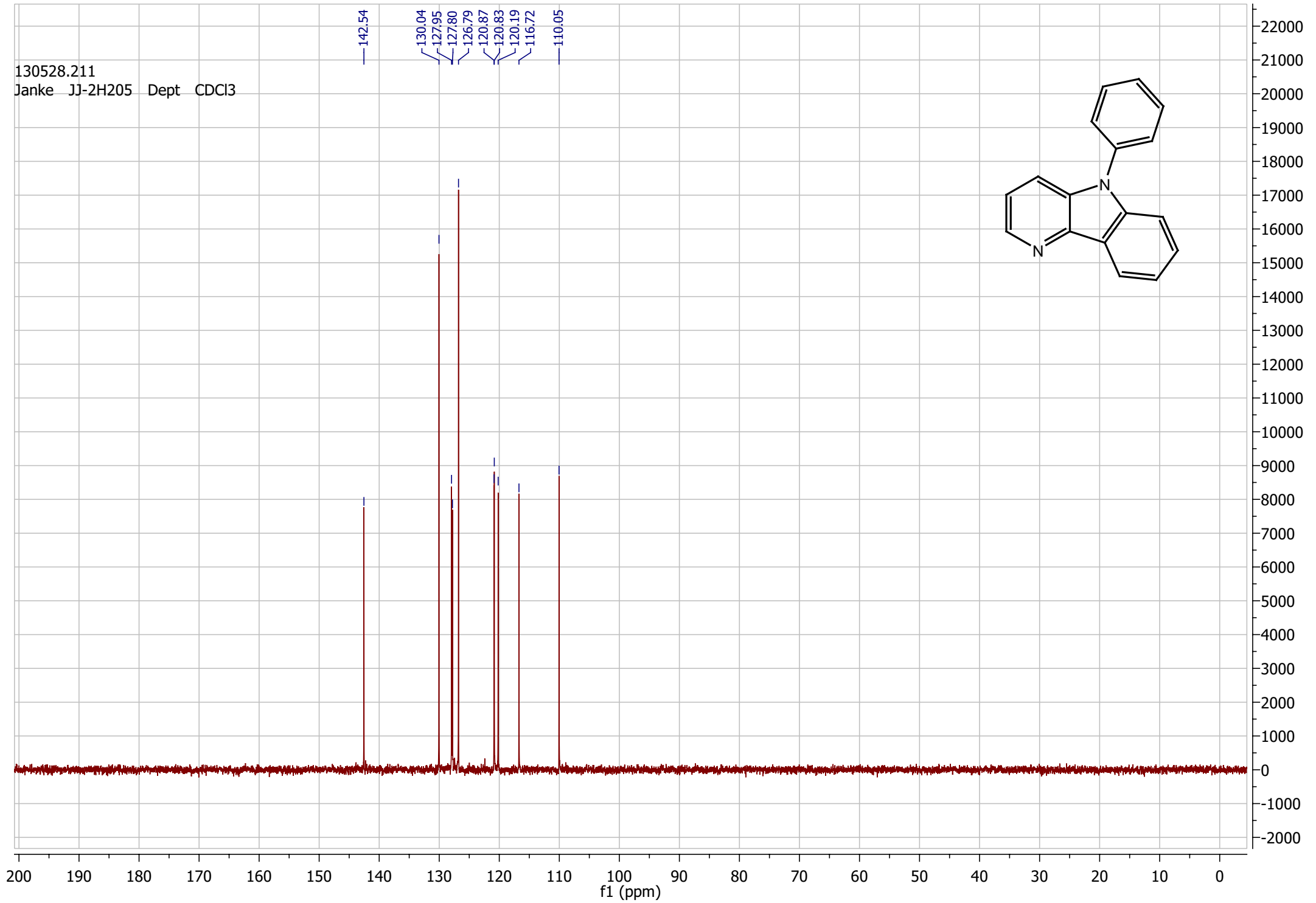
8.51 8.50 8.49 8.49 8.37 8.37 8.34 8.34 8.34 7.58 7.58 7.55 7.54 7.53 7.52 7.50 7.49 7.49 7.47 7.47 7.46 7.43 7.42 7.41 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.30 7.29 7.27 7.27 7.26 7.24 7.23 7.21 7.19 7.18 7.16 7.15





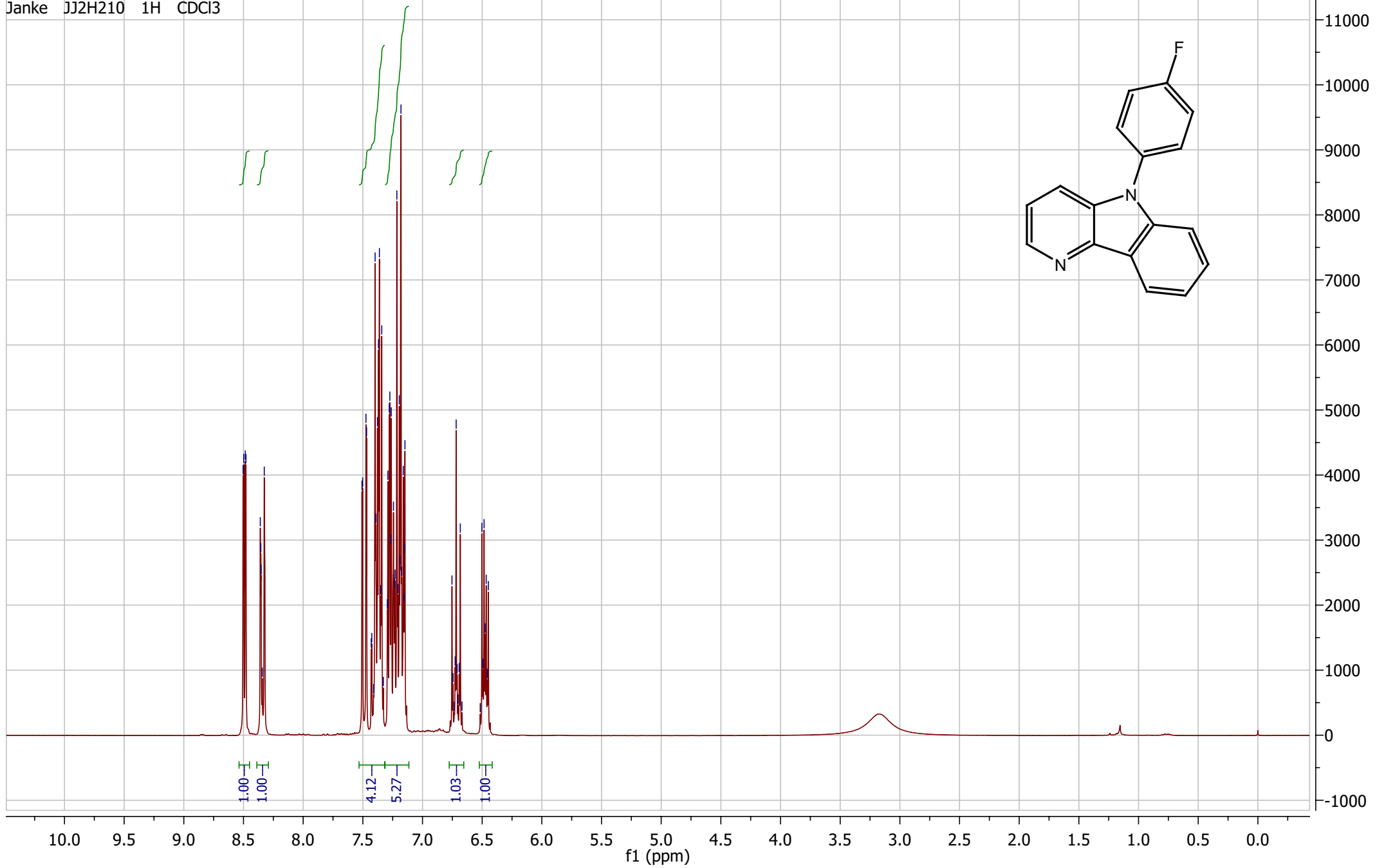


130528.211  
Janke JJ-2H205 Dept CDCl3

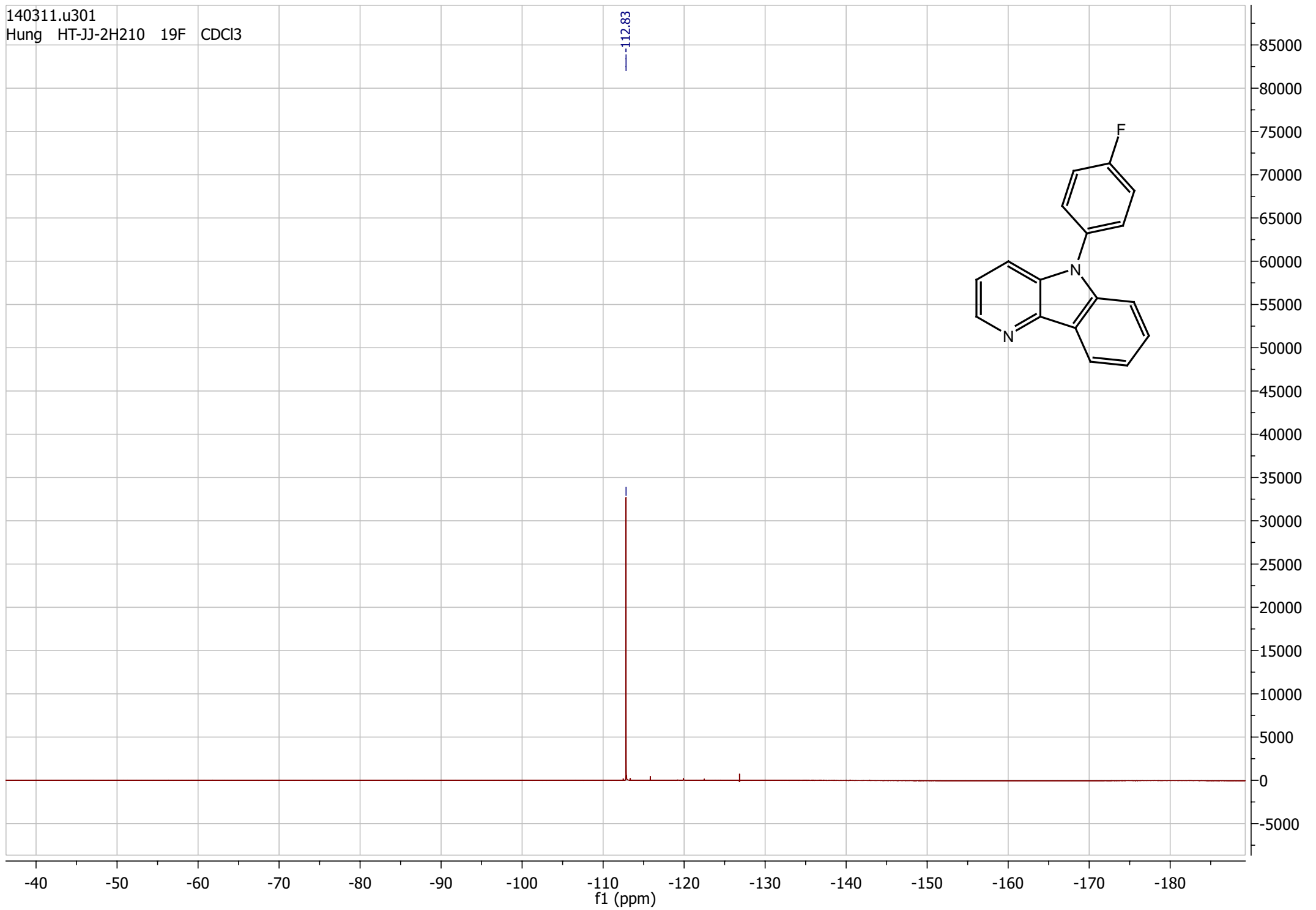


130613.203  
Janke JJ2H210 1H CDCl3

8.50  
8.50  
8.48  
8.48  
8.36  
8.35  
8.35  
8.34  
8.33  
7.40  
7.37  
7.36  
7.34  
7.27  
7.21  
7.18  
7.15  
6.74  
6.73  
6.73  
6.72  
6.71  
6.70  
6.69  
6.68  
6.67  
6.52  
6.50  
6.49  
6.48  
6.47  
6.47  
6.46  
6.45

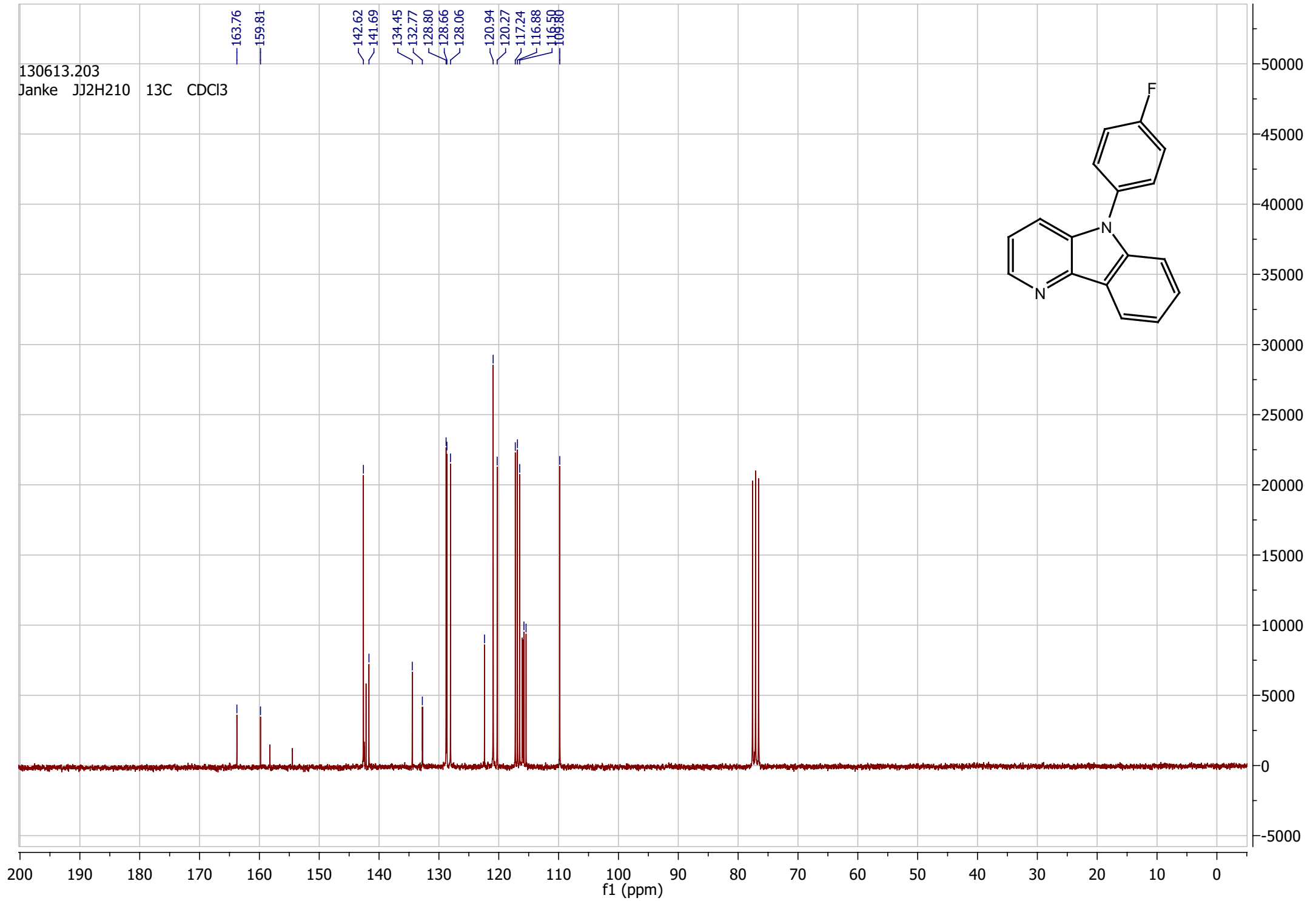
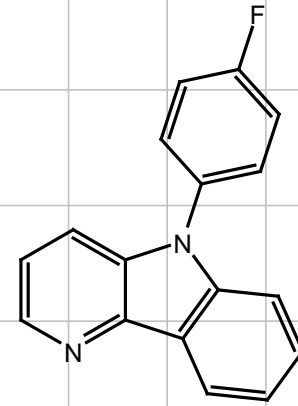


140311.u301  
Hung HT-JJ-2H210 19F CDCI3

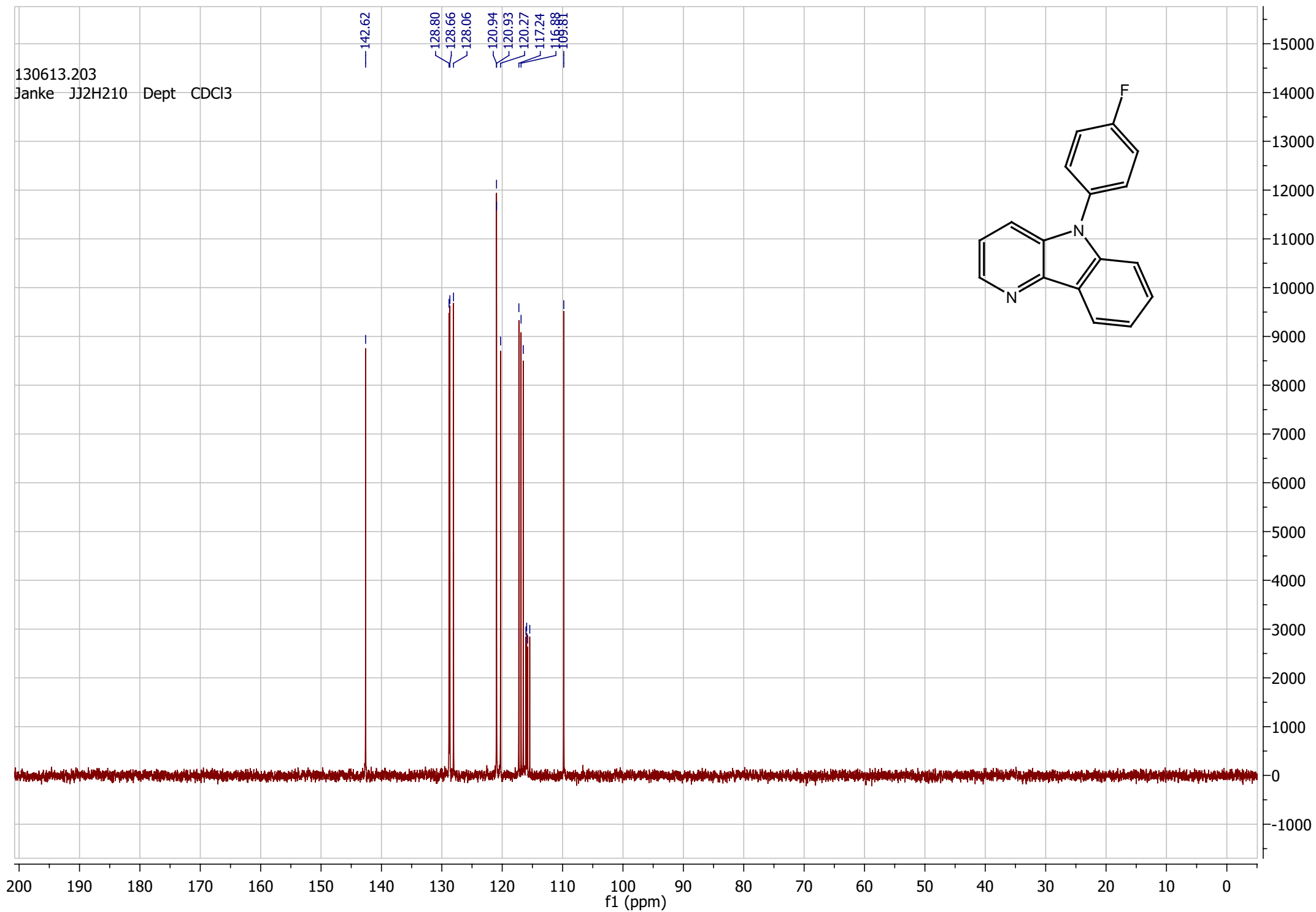


130613.203  
Janke JJ2H210 13C CDCI3

163.76  
159.81  
142.62  
141.69  
134.45  
132.77  
128.80  
128.66  
128.06  
120.94  
120.27  
117.24  
116.88  
109.80

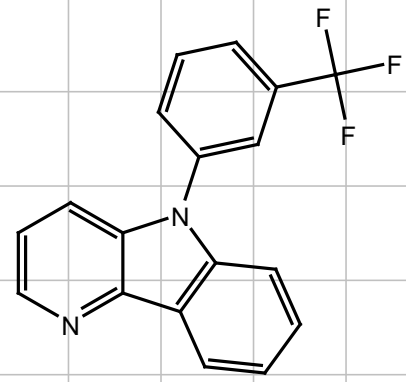


130613.203  
Janke JJ2H210 Dept CDCl3

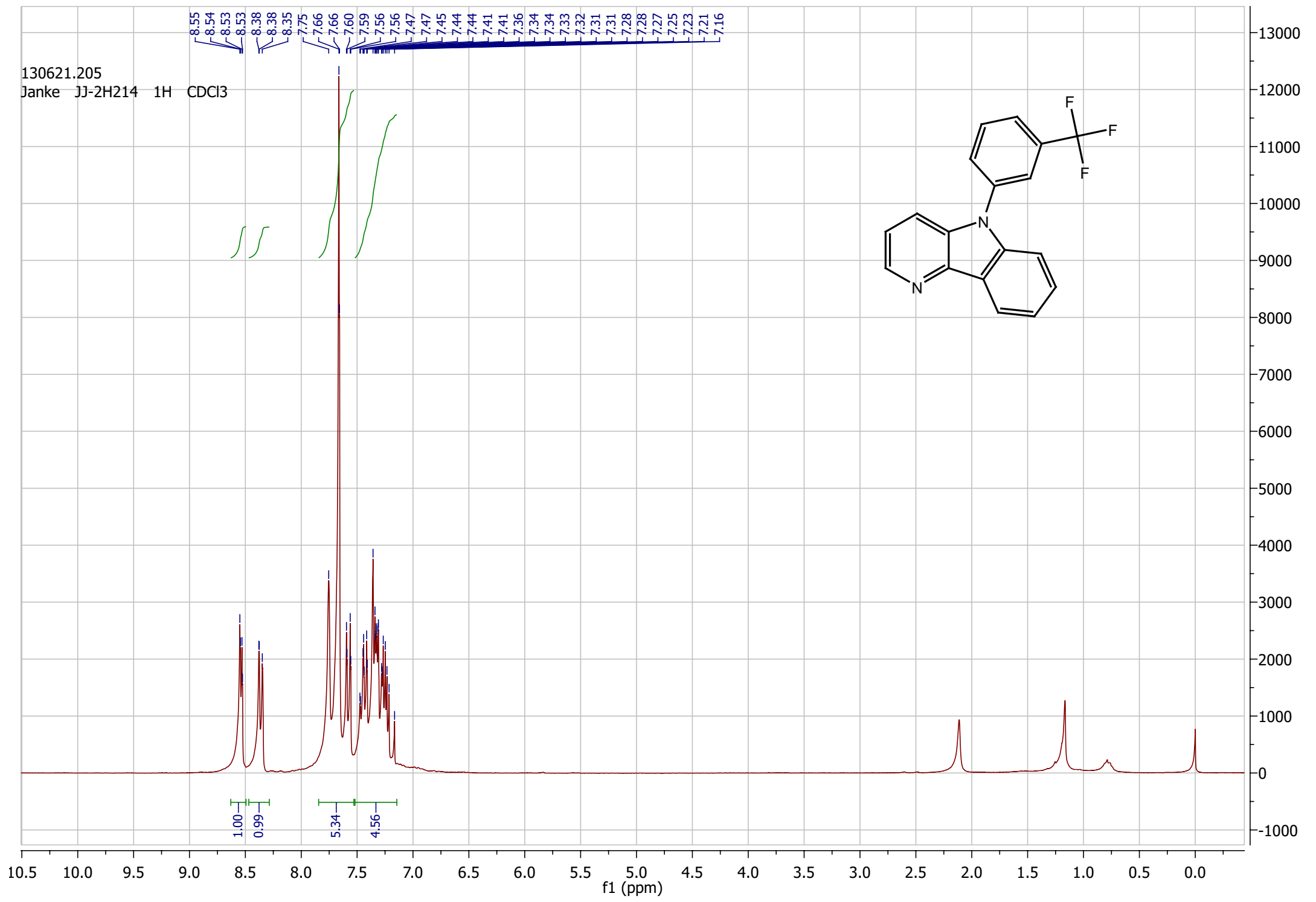


130621.205  
Janke JJ-2H214 1H CDCl3

8.55  
8.54  
8.53  
8.38  
8.38  
8.35  
7.75  
7.66  
7.60  
7.59  
7.56  
7.56  
7.47  
7.47  
7.45  
7.44  
7.44  
7.41  
7.41  
7.36  
7.34  
7.34  
7.33  
7.32  
7.31  
7.31  
7.28  
7.28  
7.27  
7.25  
7.23  
7.21  
7.16



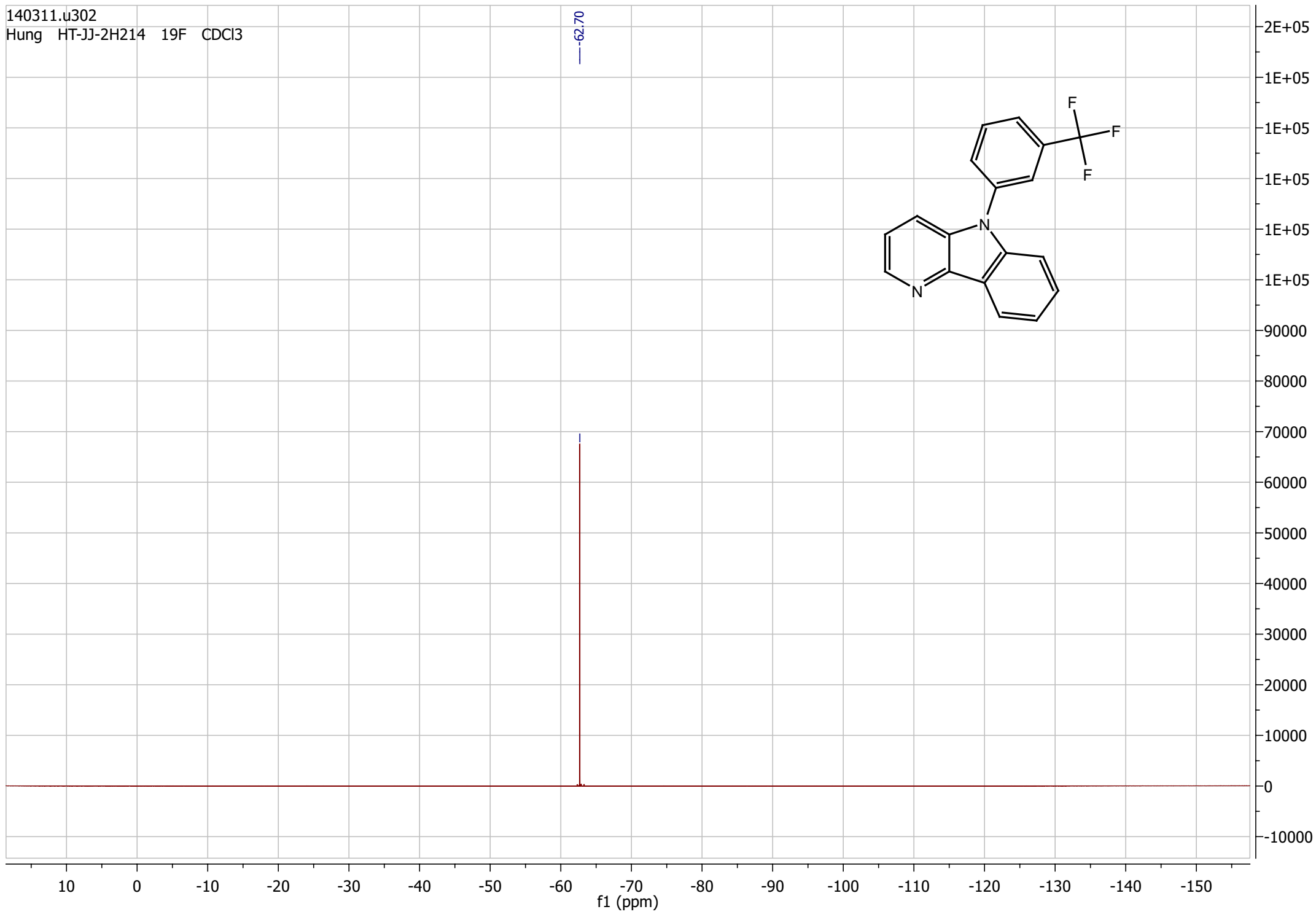
1.00  
0.99  
5.34  
4.56



140311.u302

Hung HT-JJ-2H214 19F CDCI3

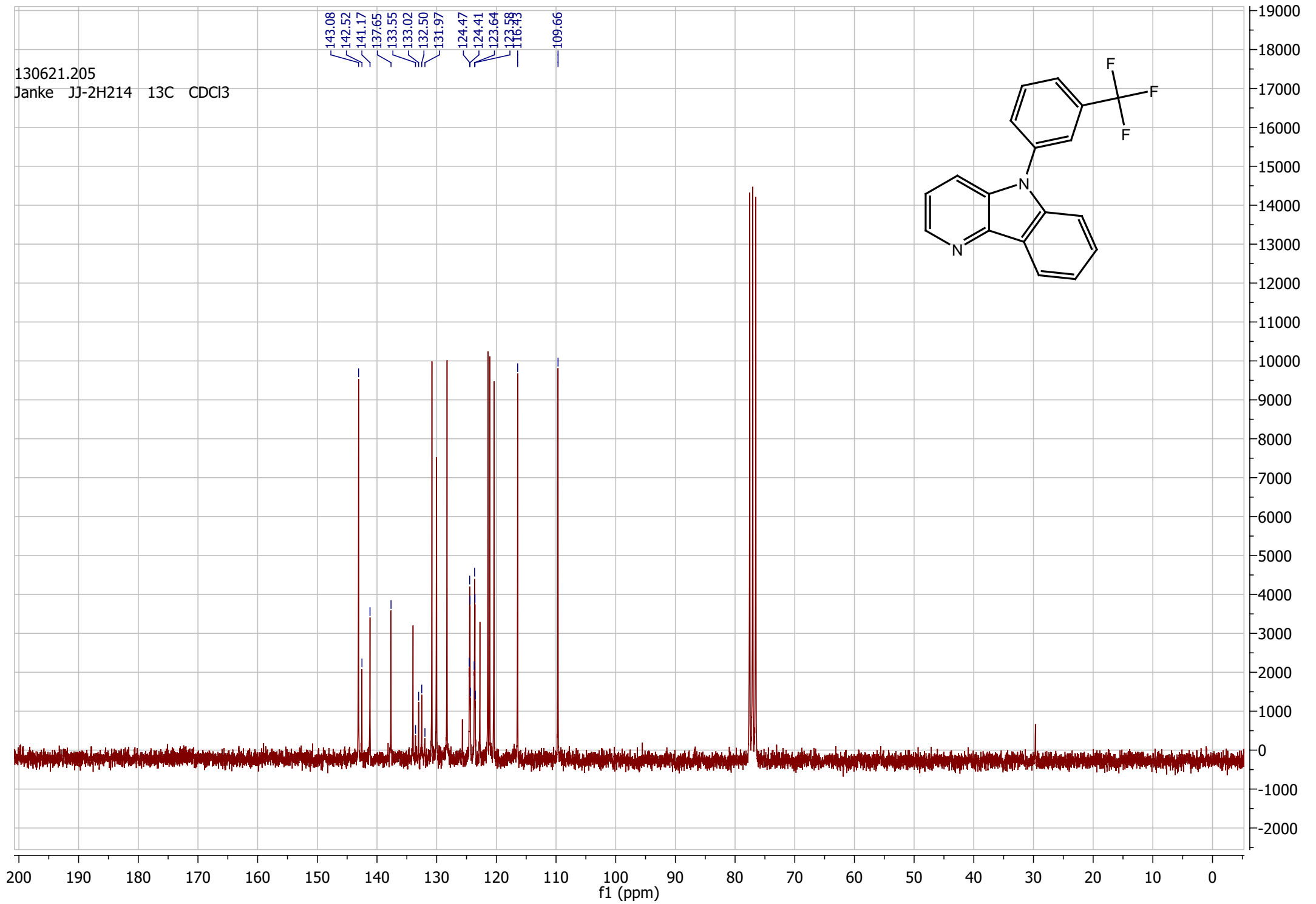
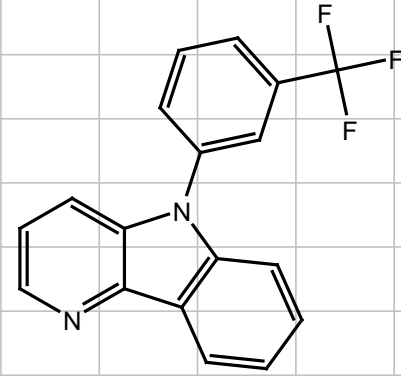
62.70



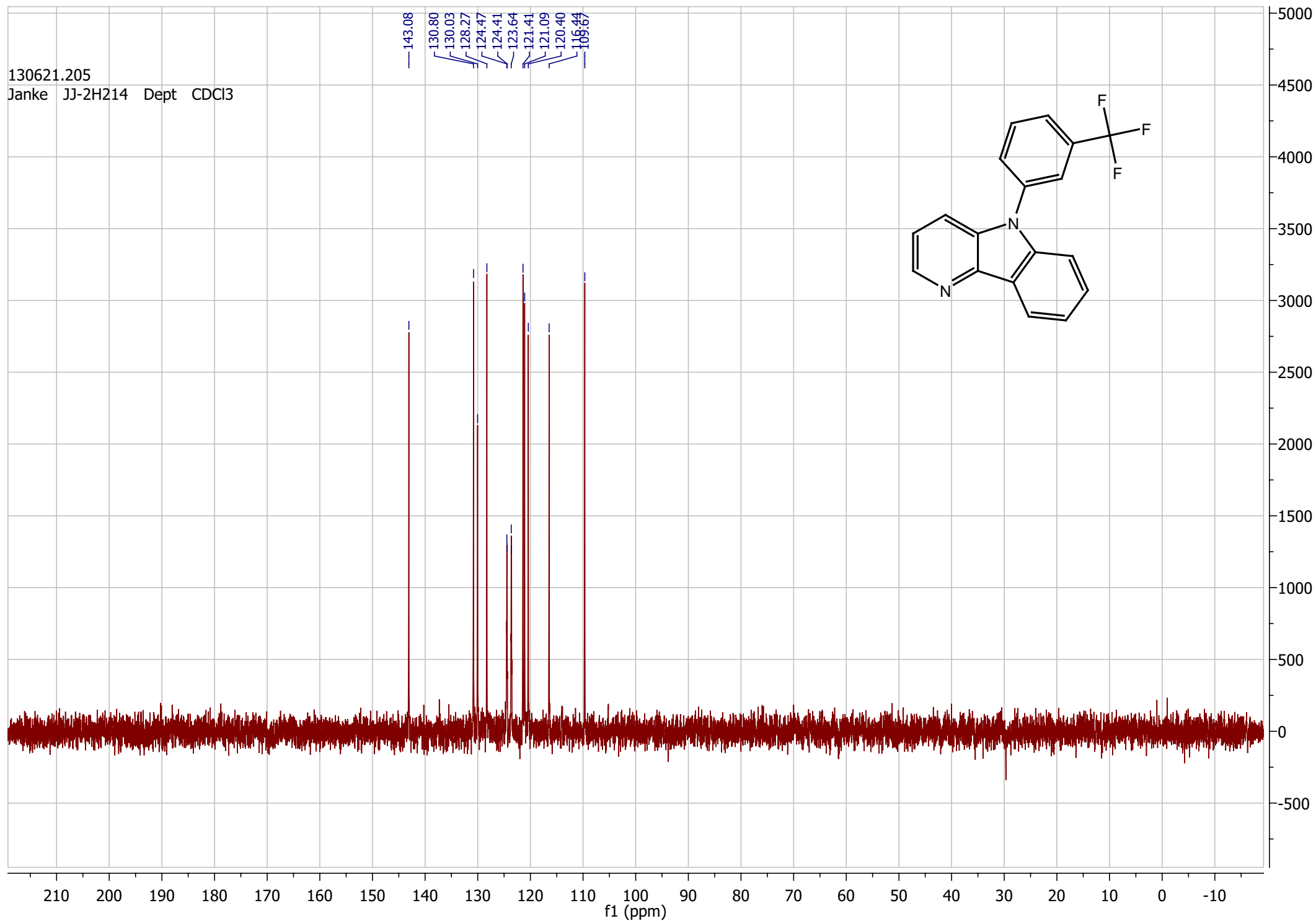


130621.205  
Janke JJ-2H214 13C CDCl3

143.08  
142.52  
141.17  
137.65  
133.55  
133.02  
132.50  
131.97  
124.47  
124.41  
123.64  
123.58  
116.43  
109.66

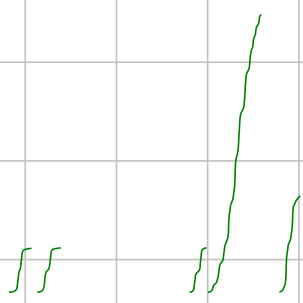


130621.205  
Janke JJ-2H214 Dept CDCl3



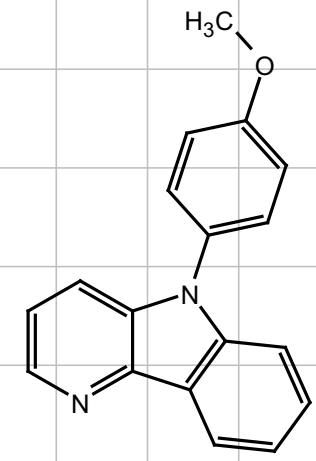
130503.207  
Janke JJ-2H201 1H CDCl3

8.54 8.54 8.52 8.52 8.40 8.39 8.37 8.36  
7.57 7.57 7.54 7.54 7.47 7.47 7.45 7.44 7.44 7.41 7.41 7.38 7.38 7.36 7.36 7.35 7.35 7.33 7.33 7.29 7.29 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.22 7.22 7.19 7.19 7.07 7.07 7.06 7.06 7.04 7.04 3.85



1.02 1.03  
1.04 6.46 2.24

3.00



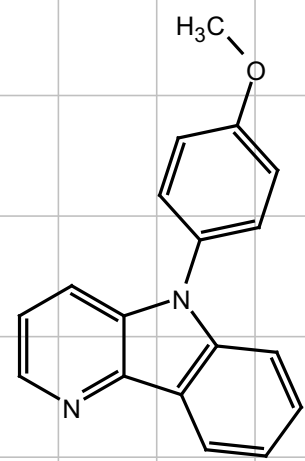
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5  
f1 (ppm)

24000  
22000  
20000  
18000  
16000  
14000  
12000  
10000  
8000  
6000  
4000  
2000  
0  
-2000

130503.207  
Janke JJ-2H201 13C CDCl3

159.13  
142.22  
142.06  
134.81  
129.36  
128.30  
127.90  
120.85  
120.59  
120.12  
116.68  
115.22  
108.97

55.62



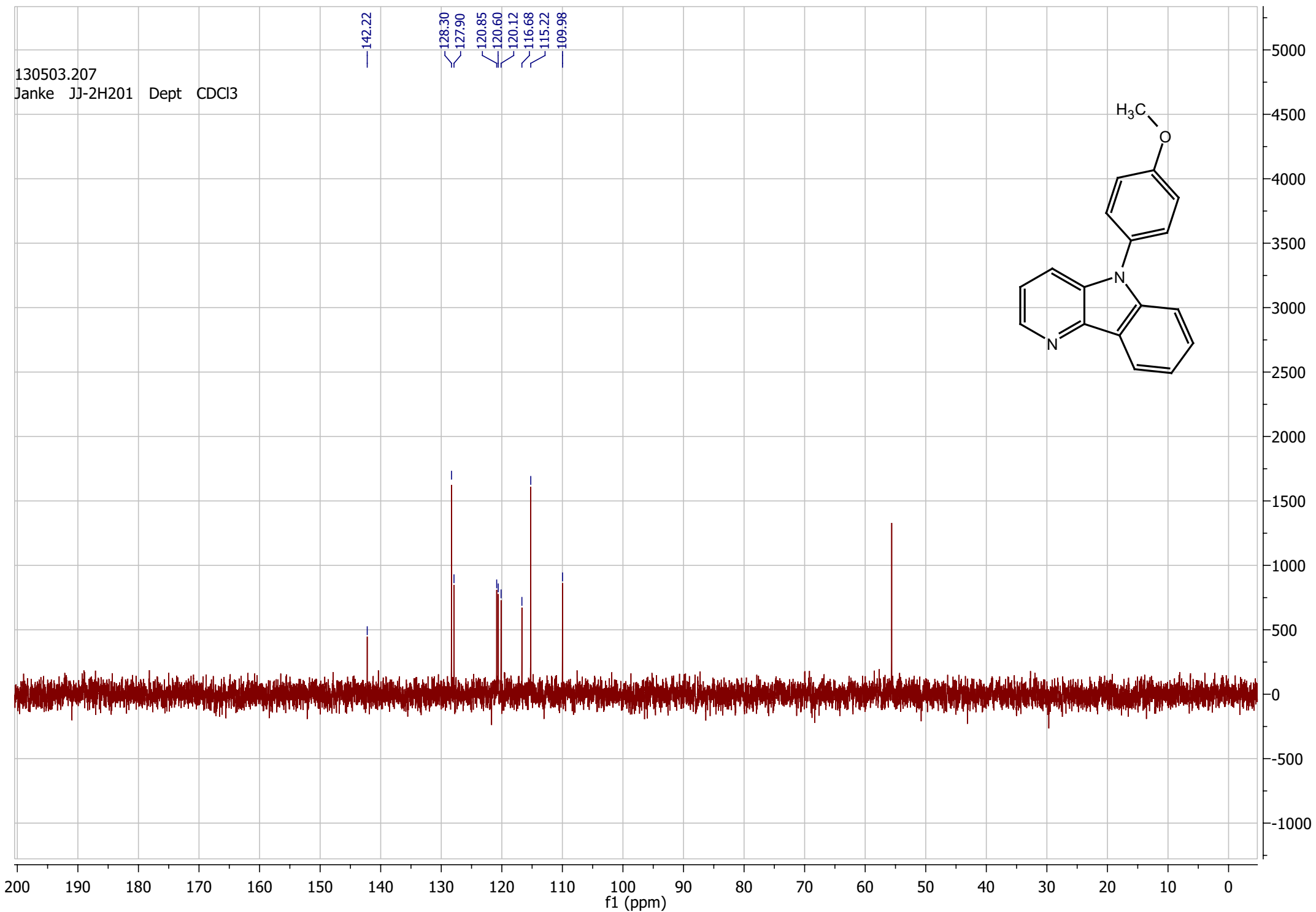
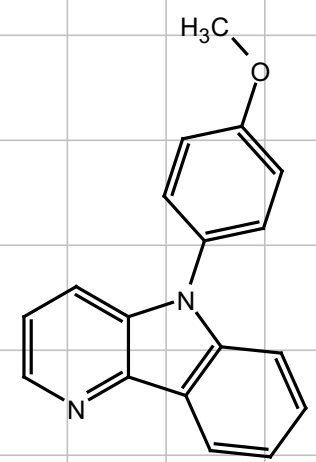
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

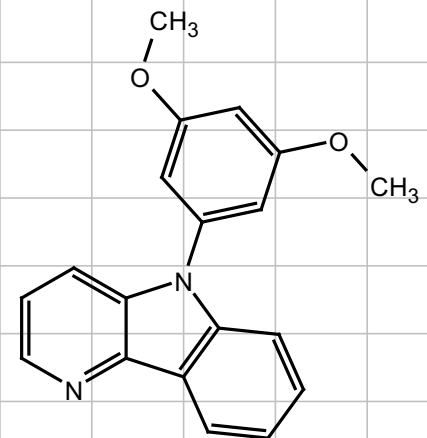
10000  
9000  
8000  
7000  
6000  
5000  
4000  
3000  
2000  
1000  
0  
-1000

130503.207  
Janke JJ-2H201 Dept CDCl3

142.22  
128.30 127.90  
120.85 120.60  
120.12 116.68 115.22  
109.98



130524.204  
Janke JJ-2H204 1H CDCl3



1.00  
0.89

0.93  
4.04

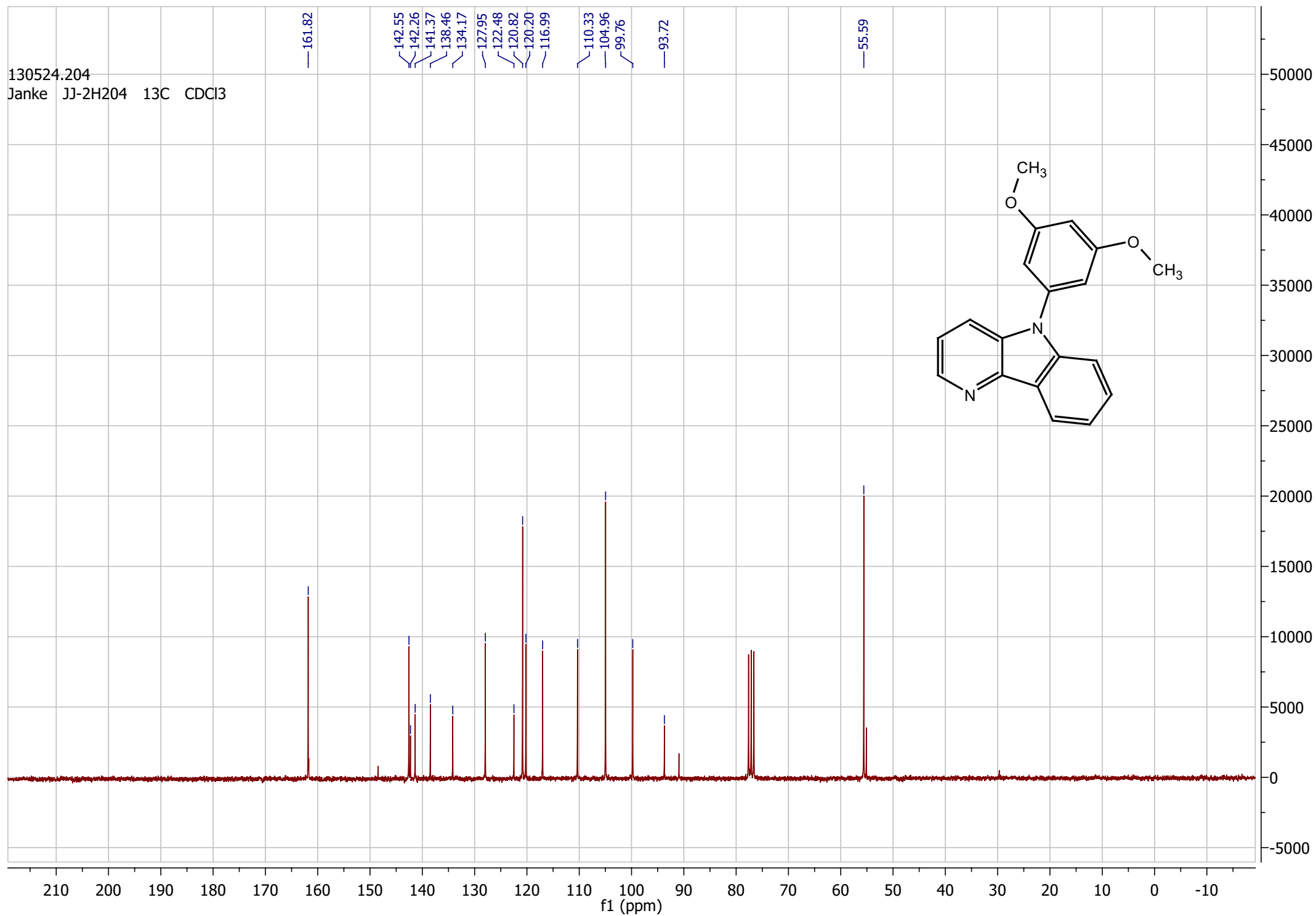
1.82  
0.81

5.86

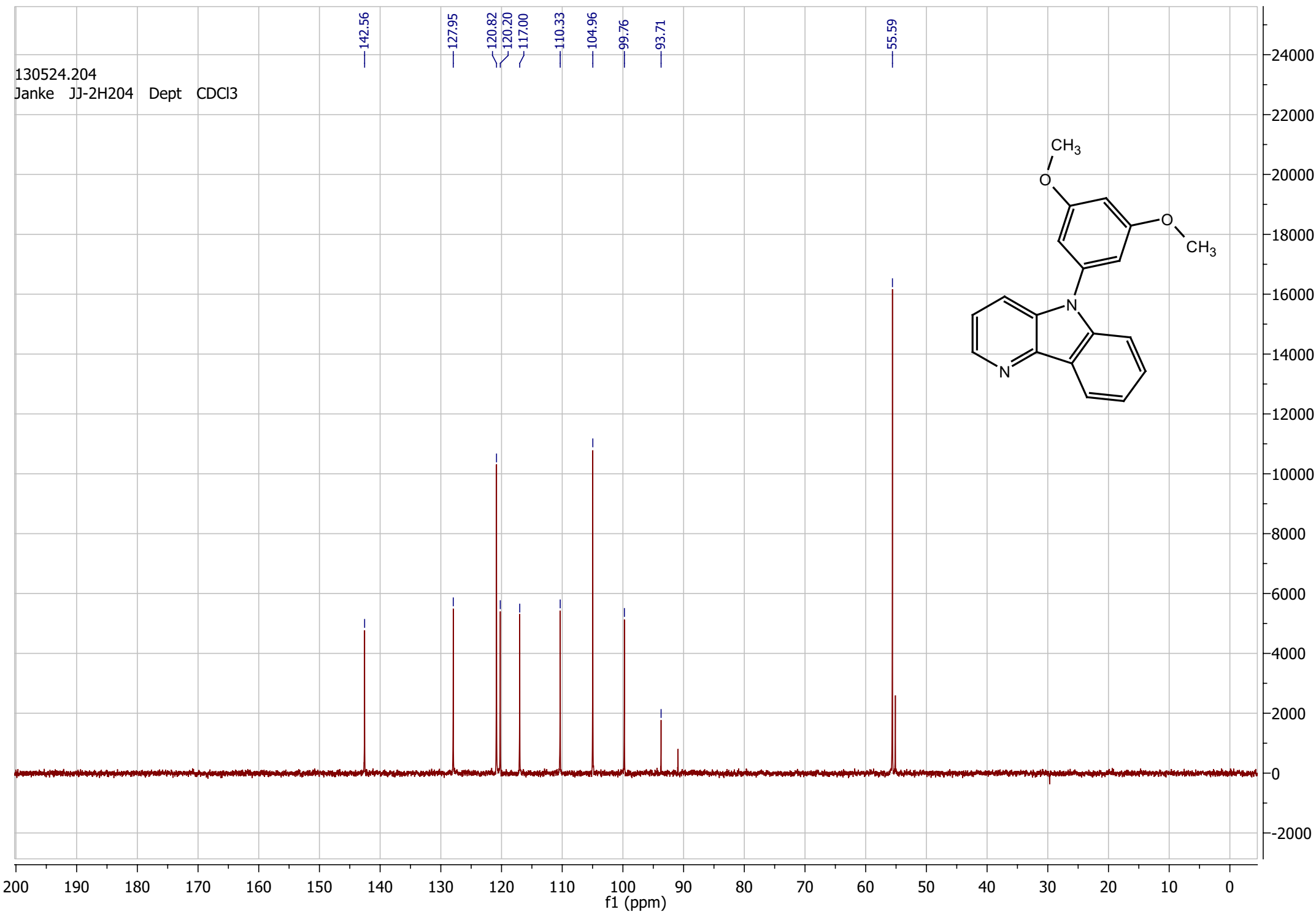
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5  
f1 (ppm)

36000  
34000  
32000  
30000  
28000  
26000  
24000  
22000  
20000  
18000  
16000  
14000  
12000  
10000  
8000  
6000  
4000  
2000  
0  
-2000

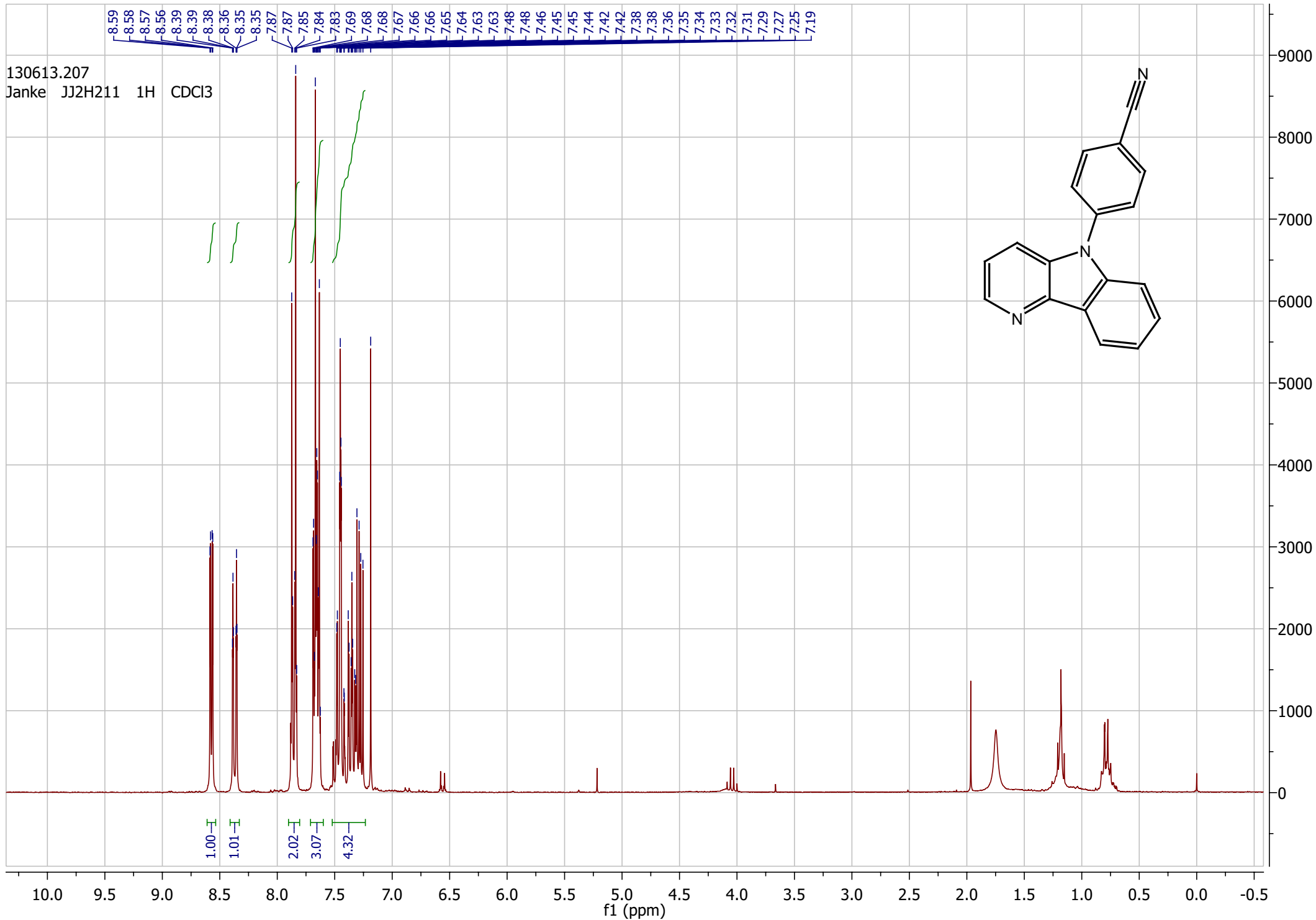
130524.204  
Janke JJ-2H204 13C CDCl3



130524.204  
Janke JJ-2H204 Dept CDCl3

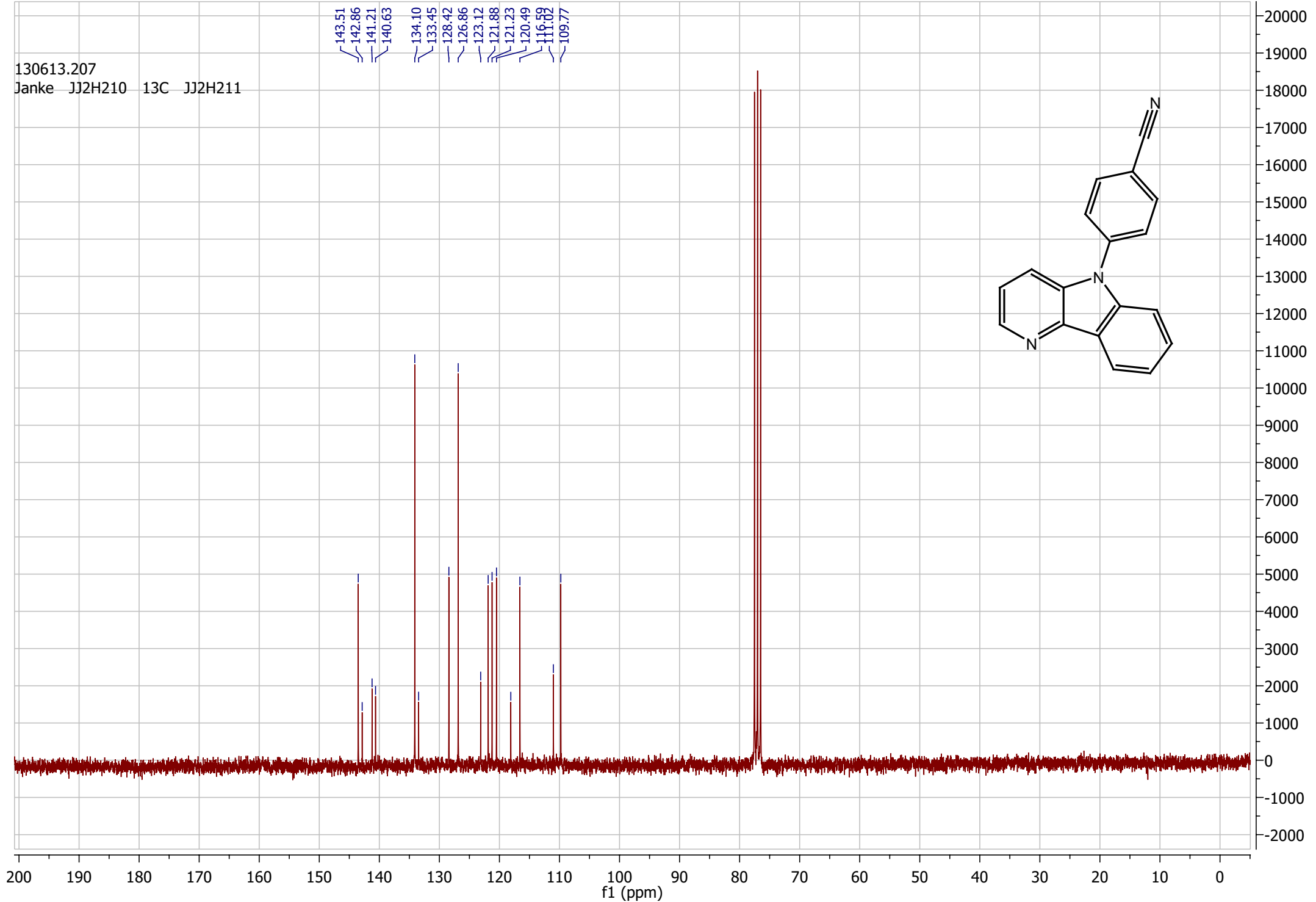




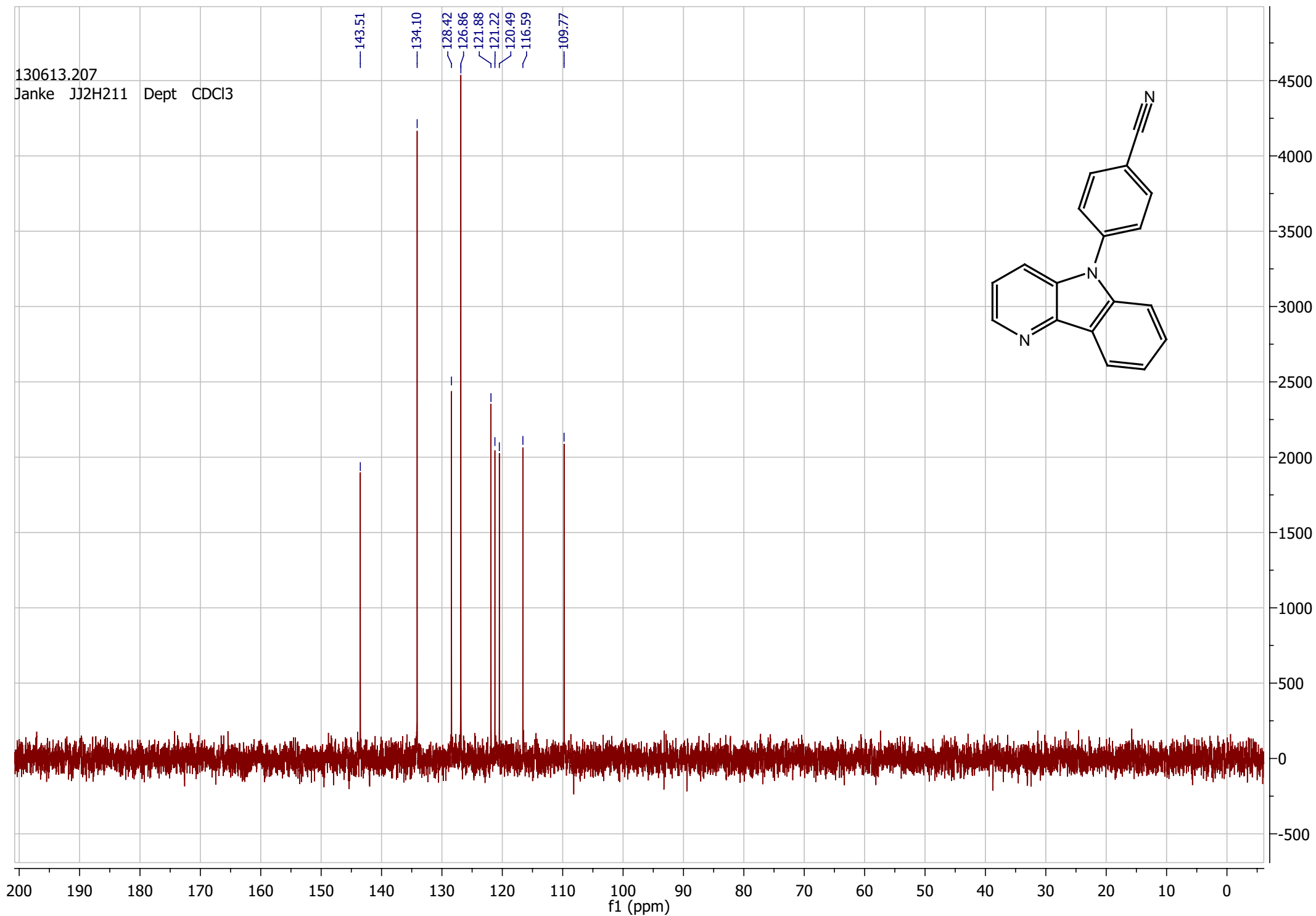


130613.207  
Janke JJ2H210 13C JJ2H211

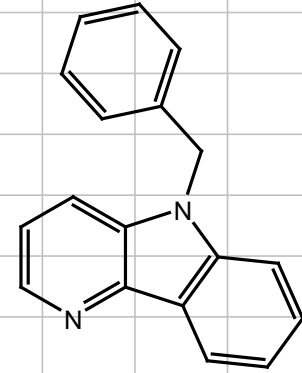
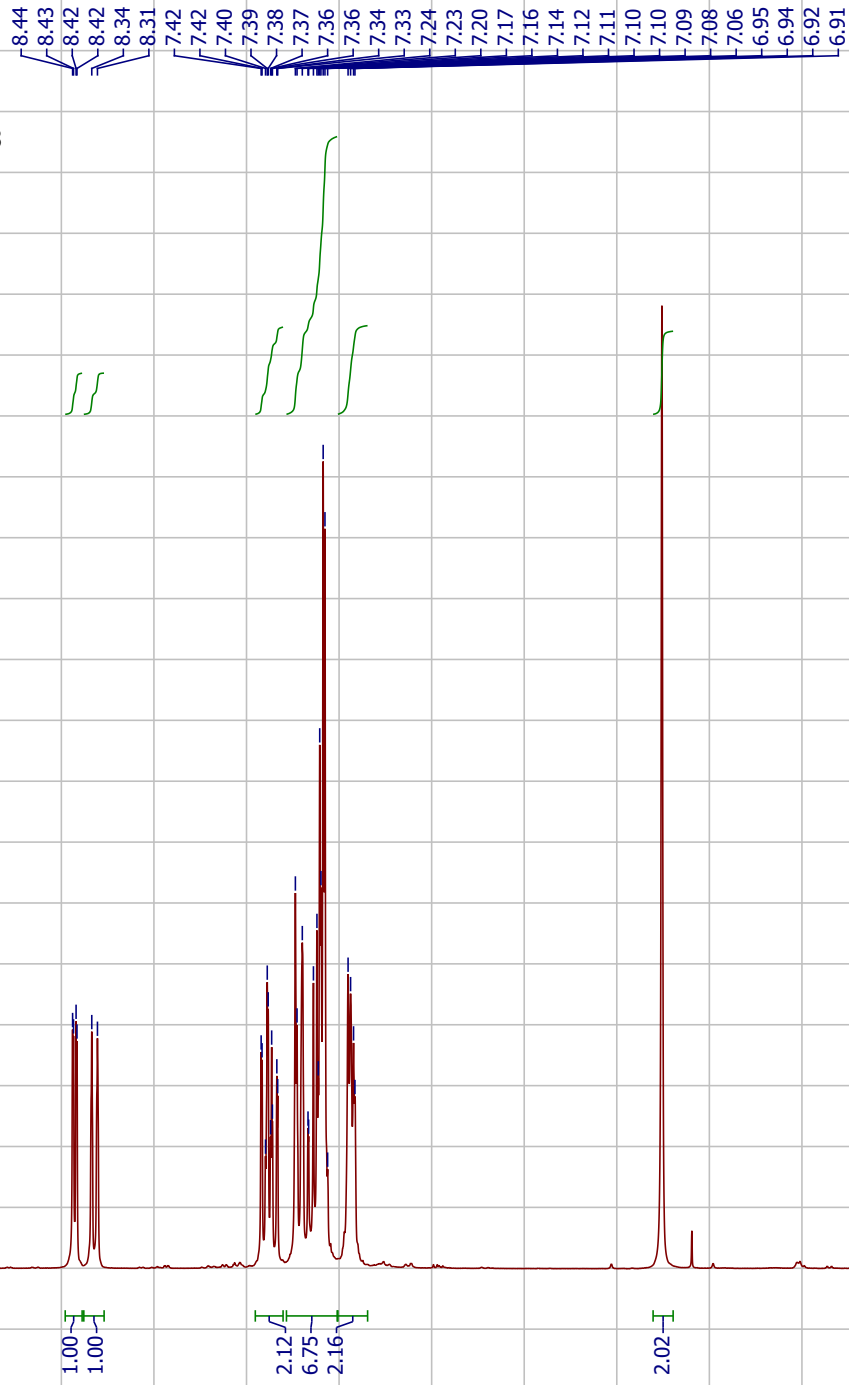
- 143.51
- 142.86
- 141.21
- 140.63
- 134.10
- 133.45
- 128.42
- 126.86
- 123.12
- 121.88
- 121.23
- 120.49
- 116.59
- 111.02
- 109.77



130613.207  
Janke JJ2H211 Dept CDCl3

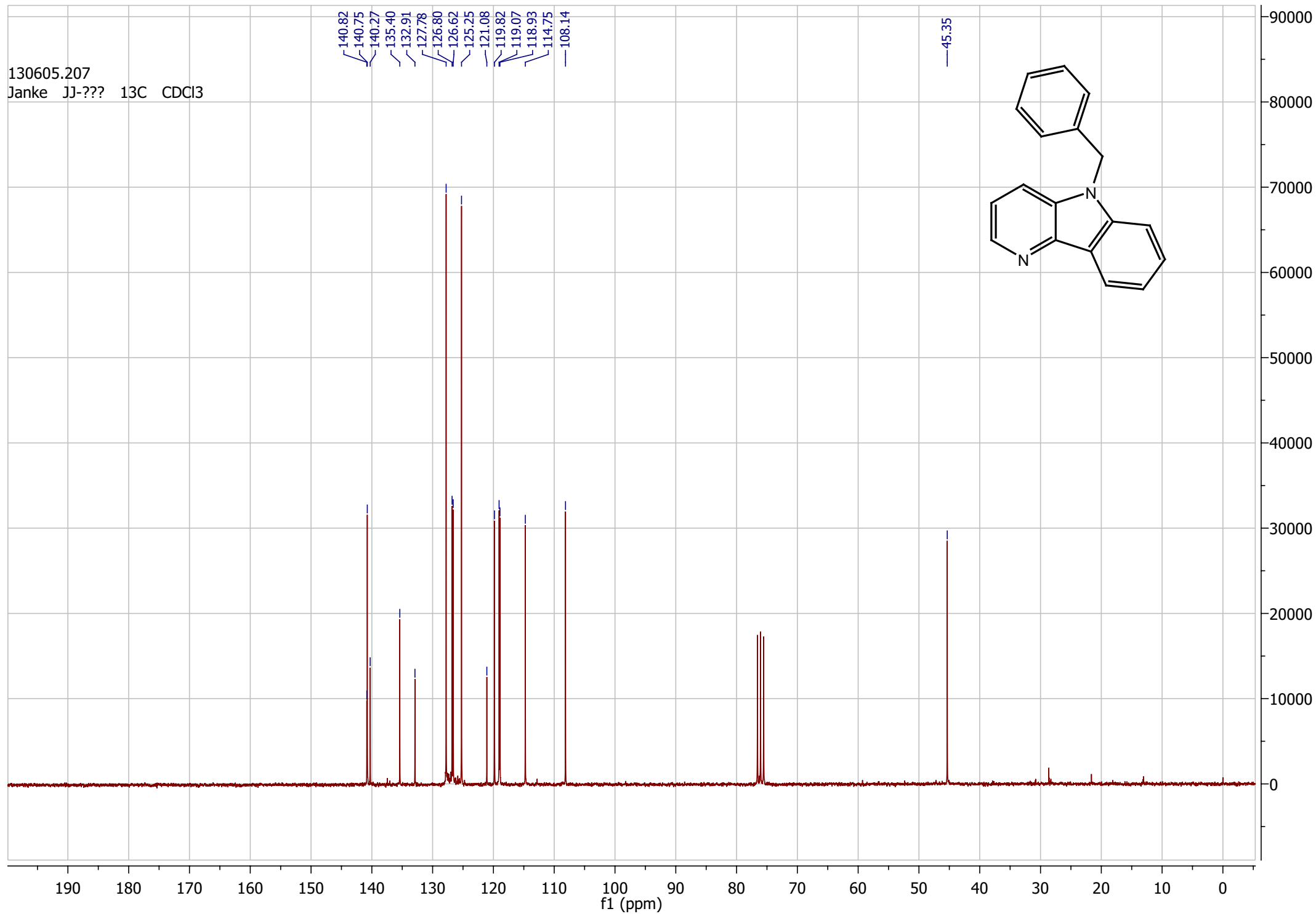


130605.207  
Janke JJ-??? 1H CDCl3

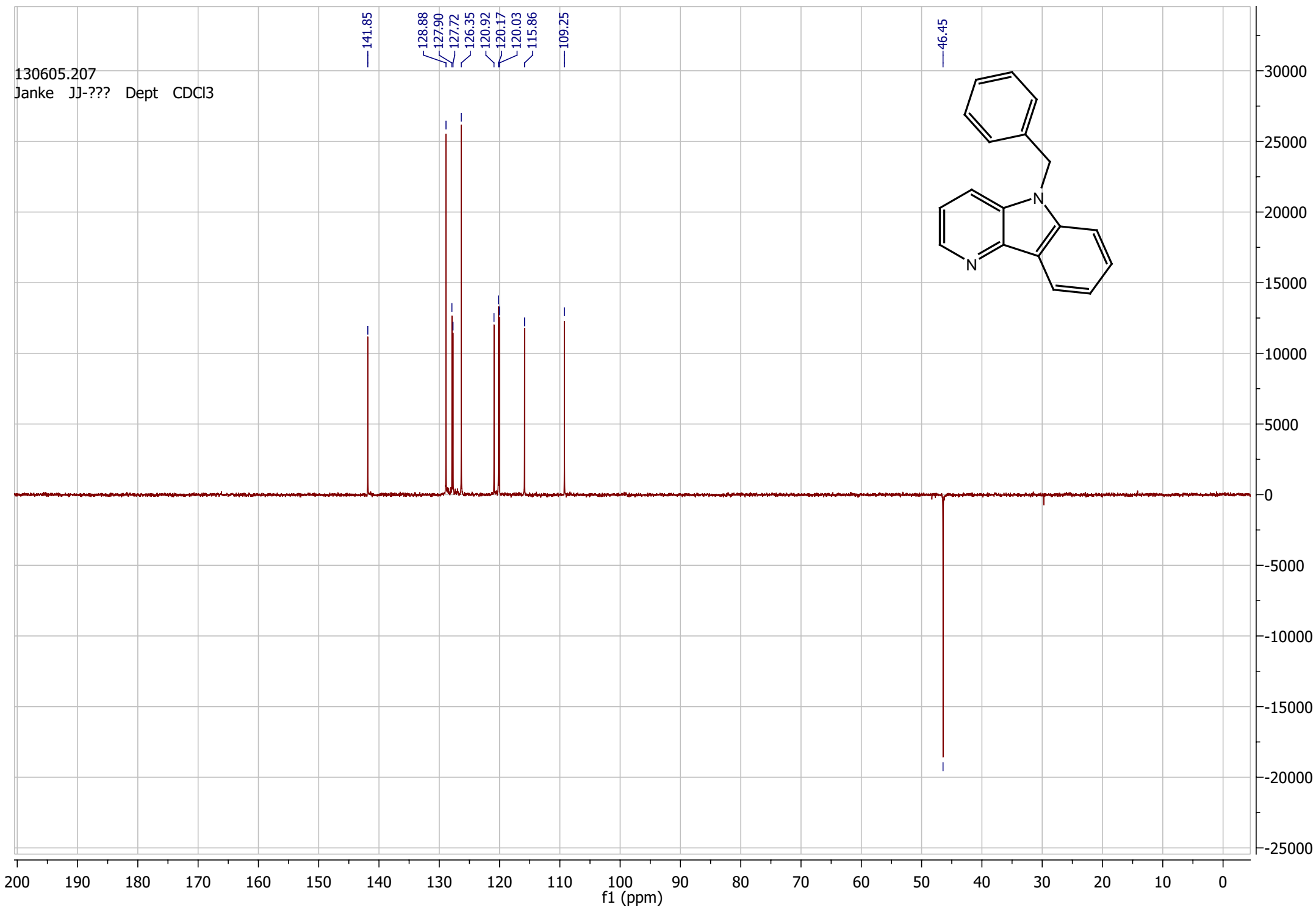


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0  
f1 (ppm)

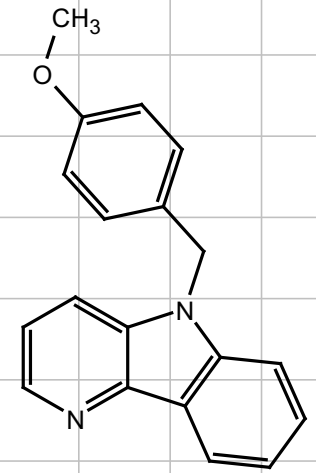
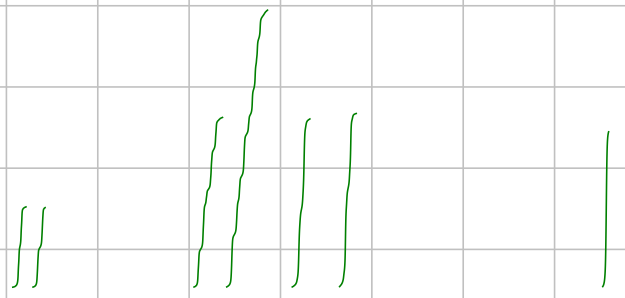
130605.207  
Janke JJ-??? 13C CDCl3



130605.207  
Janke JJ-??? Dept CDCl3



130612.u311  
Janke JJ-2H208 1H CDCl3



1.00  
0.99

2.11  
3.44

2.09

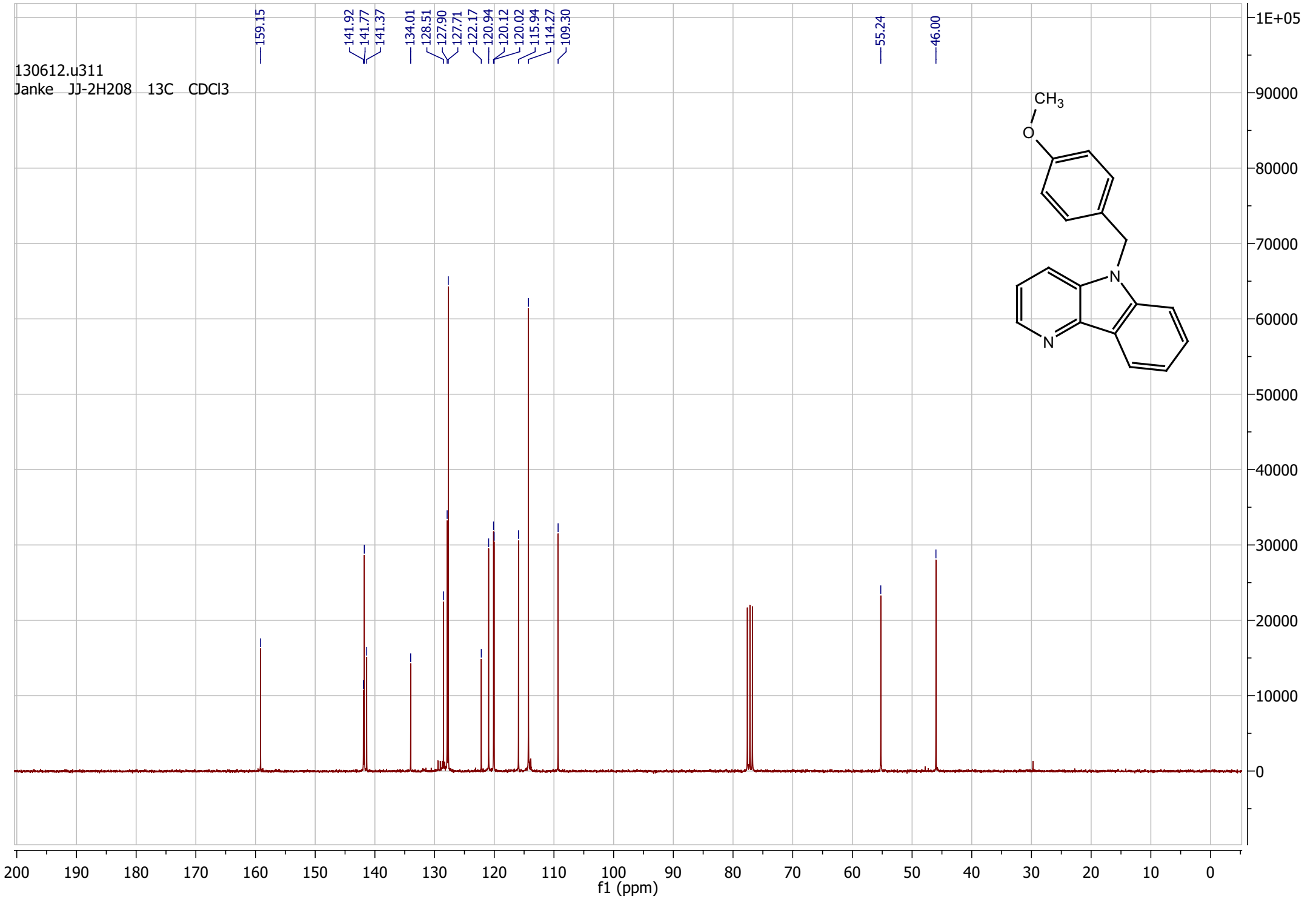
2.16

1.94

2.92

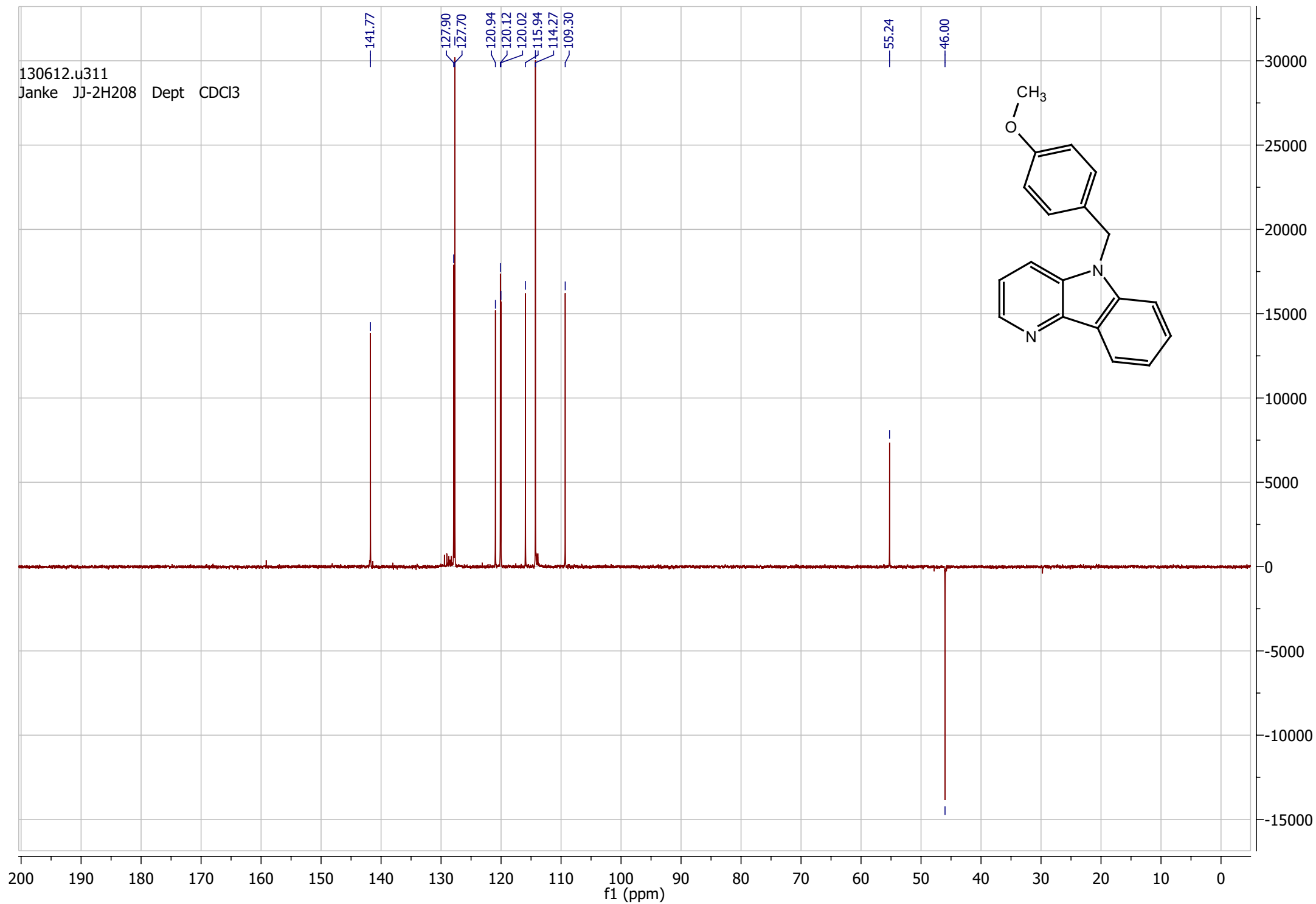
f1 (ppm)

130612.u311  
Janke JJ-2H208 13C CDCl3

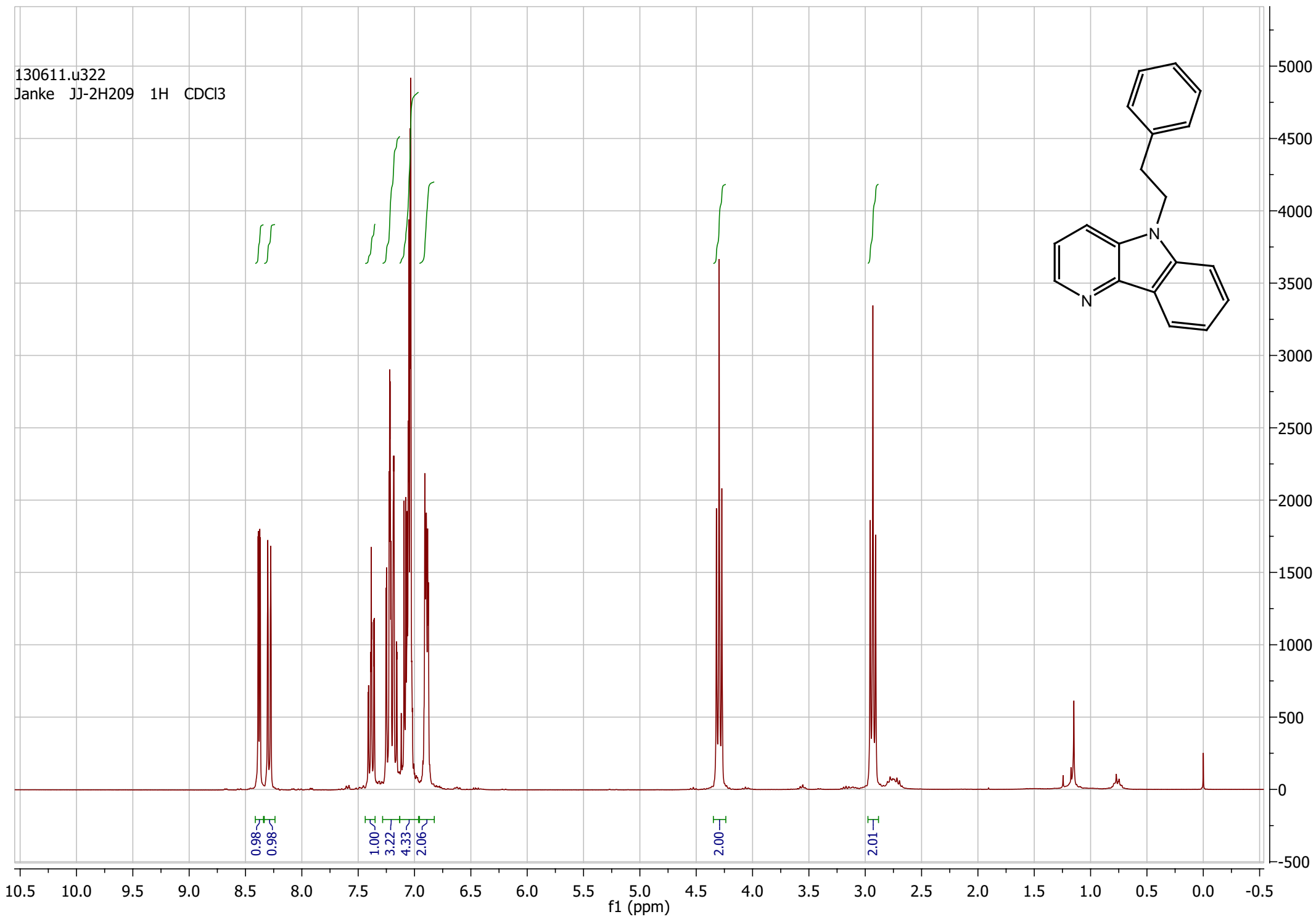




130612.u311  
Janke JJ-2H208 Dept CDCl3



130611.u322  
Janke JJ-2H209 1H CDCl3

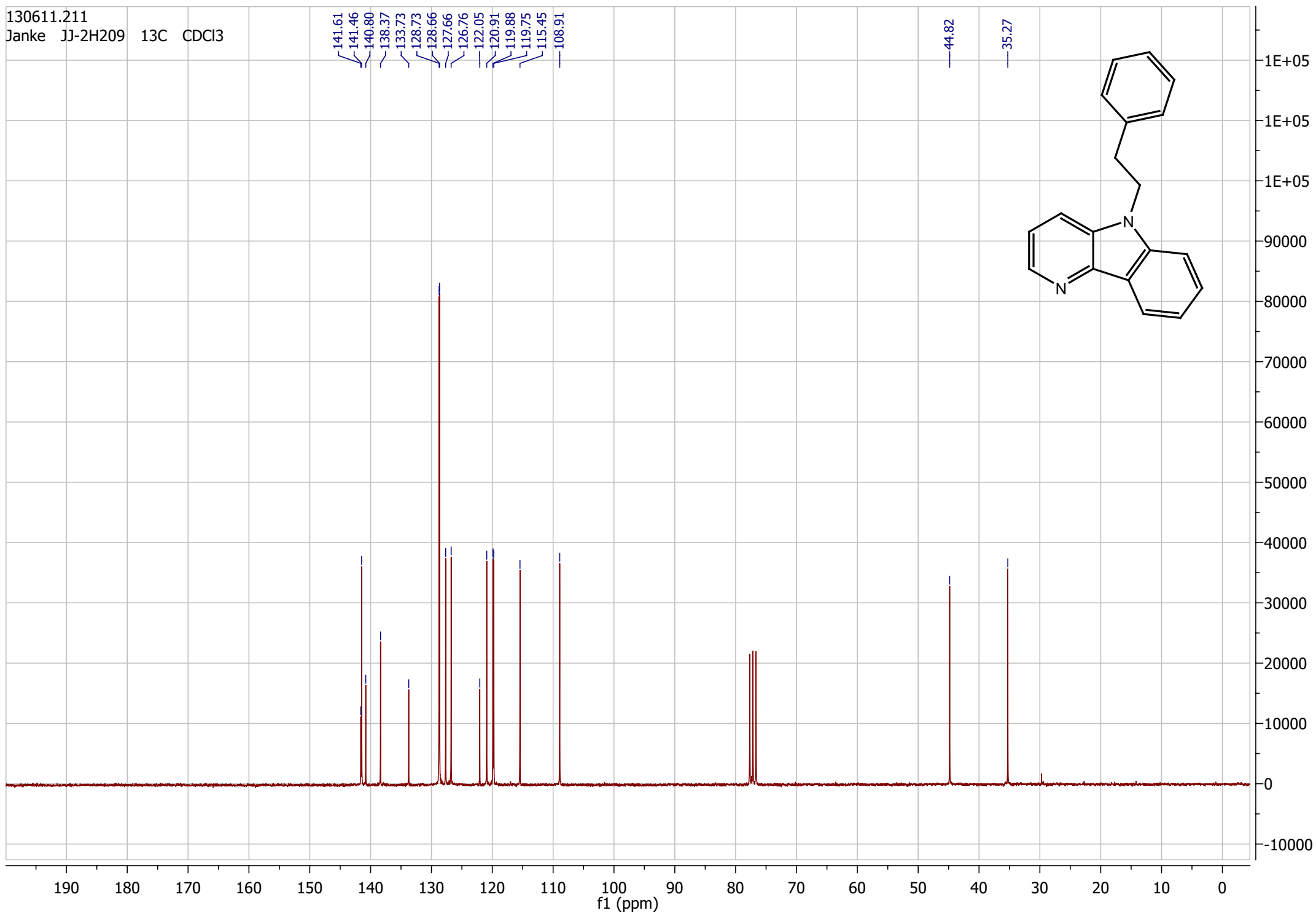
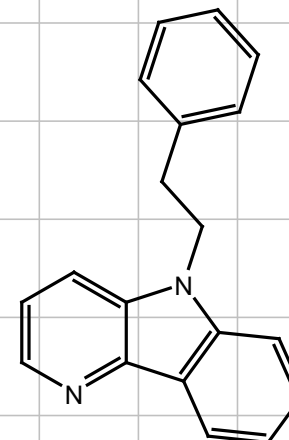


130611.211  
Janke JJ-2H209 13C CDCl3

141.61  
141.46  
140.80  
138.37  
133.73  
128.73  
128.66  
127.66  
122.05  
120.91  
119.88  
119.75  
115.45  
108.91

44.82

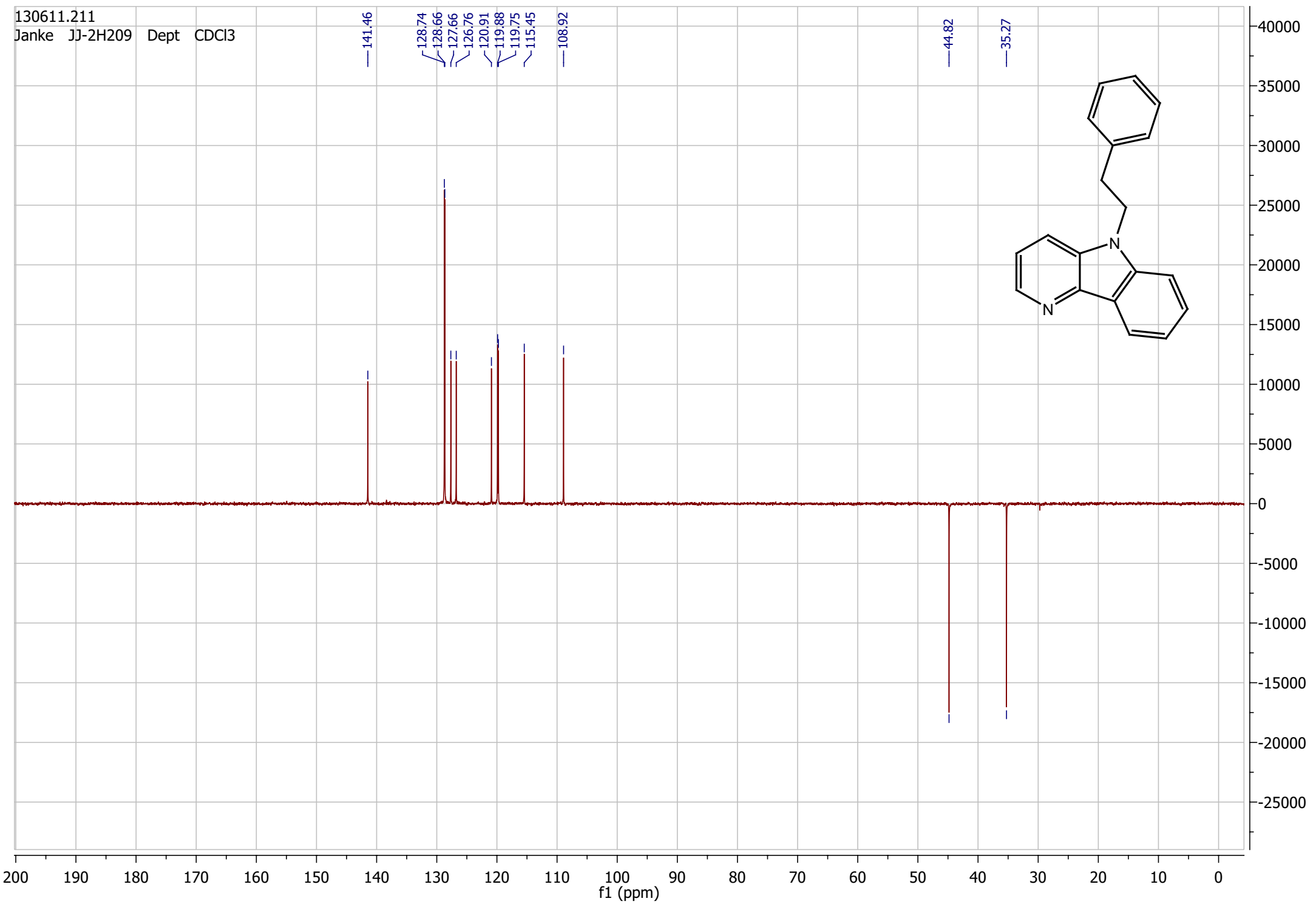
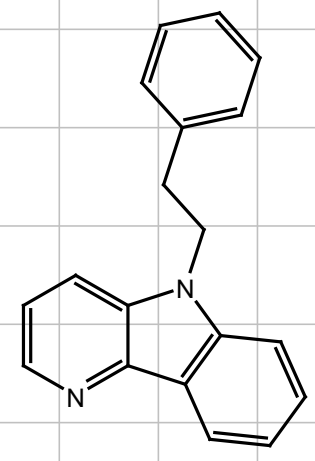
35.27



130611.211  
Janke JJ-2H209 Dept CDCl3

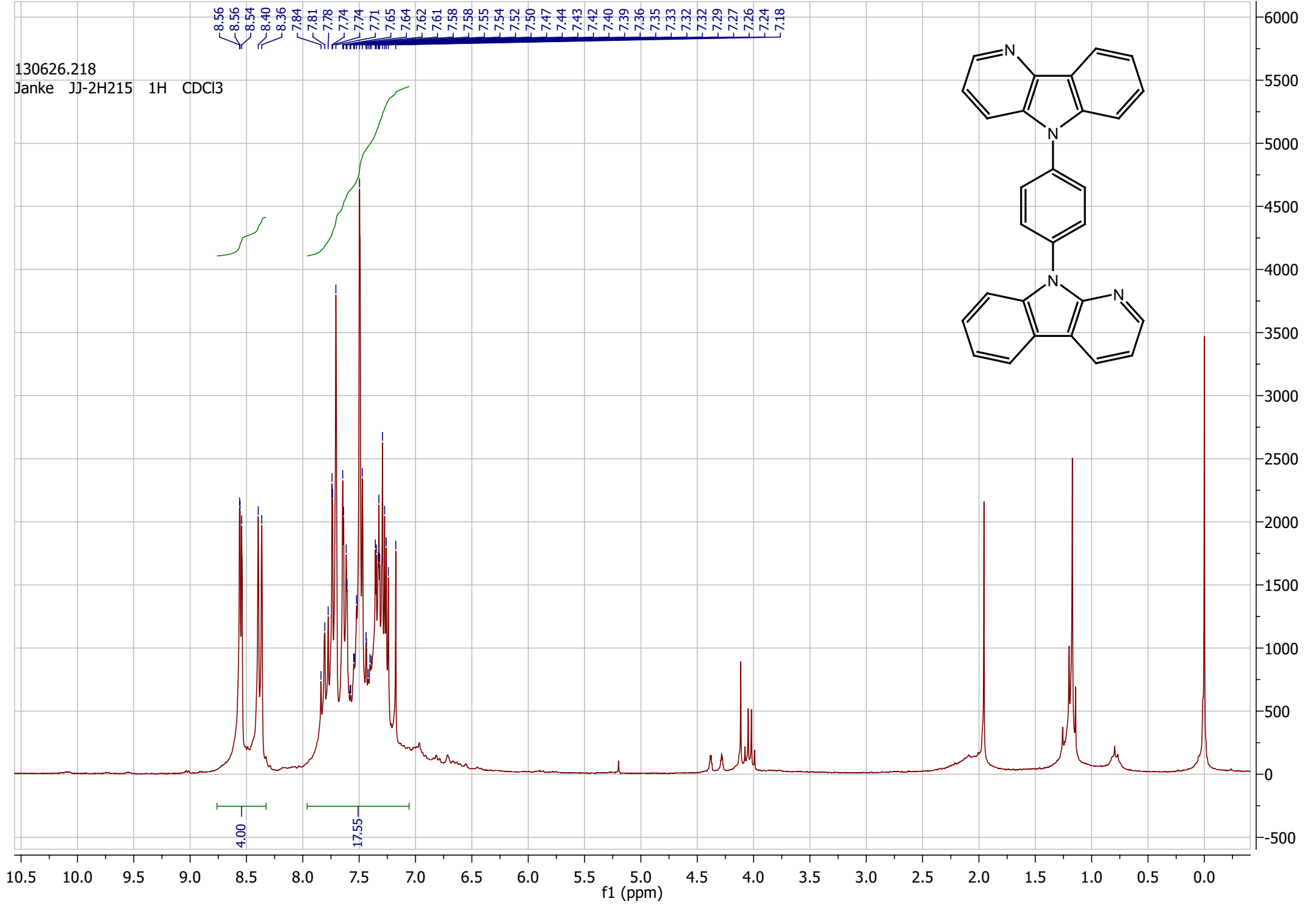
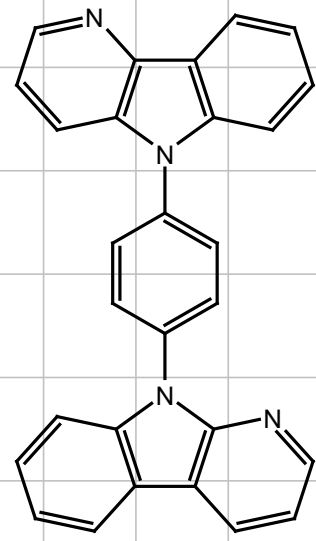
141.46  
128.74  
128.66  
127.66  
126.76  
120.91  
119.88  
119.75  
115.45  
108.92

44.82  
35.27



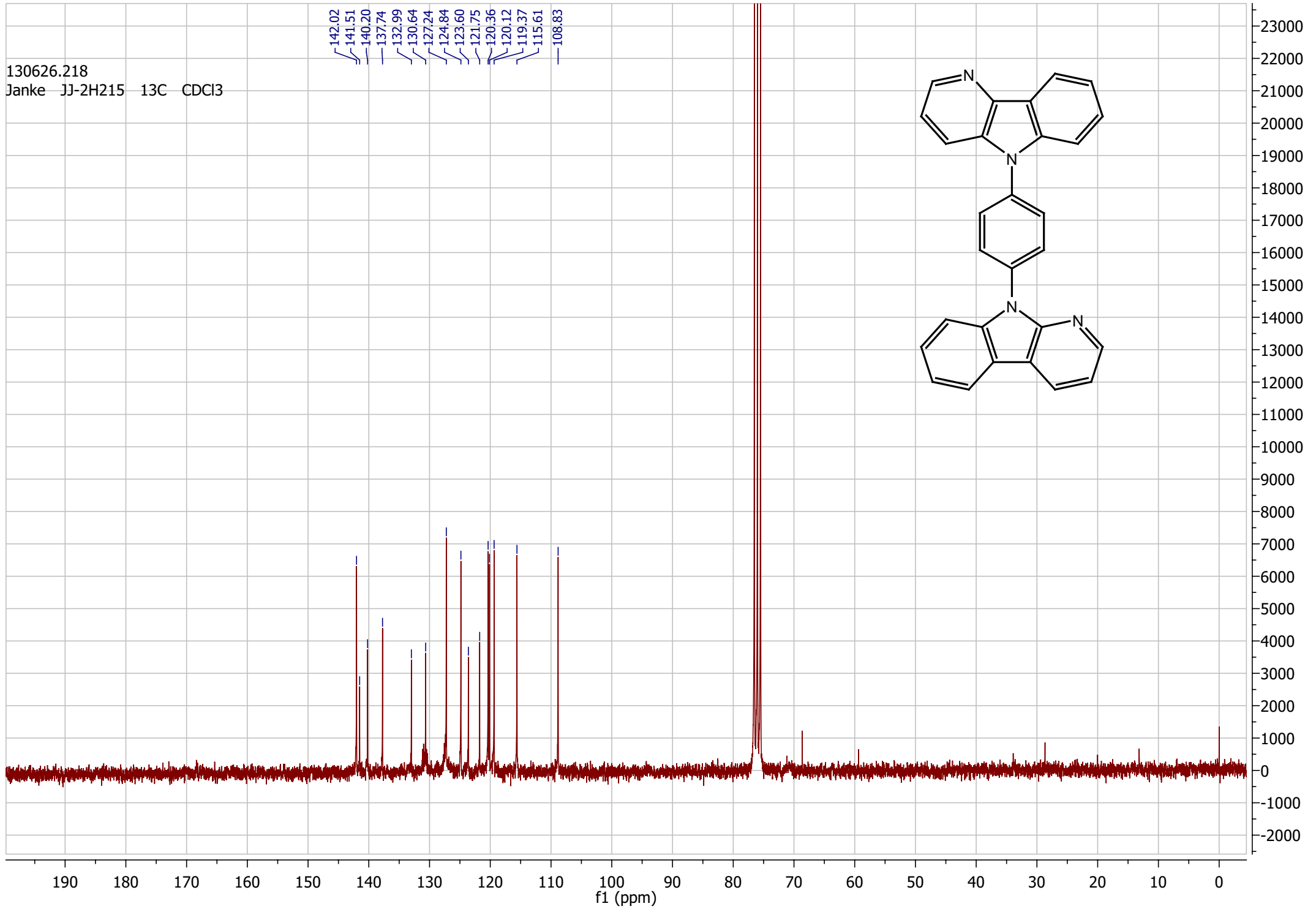
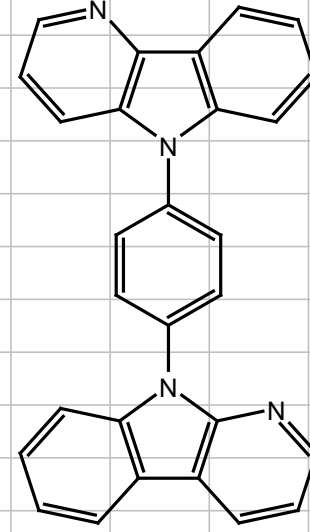
130626.218  
Janke JJ-2H215 1H CDCl3

8.56  
8.56  
8.54  
8.40  
8.36  
7.84  
7.81  
7.78  
7.74  
7.74  
7.71  
7.65  
7.64  
7.62  
7.61  
7.58  
7.58  
7.55  
7.54  
7.52  
7.50  
7.47  
7.44  
7.43  
7.42  
7.40  
7.39  
7.36  
7.35  
7.33  
7.32  
7.32  
7.29  
7.27  
7.26  
7.24  
7.18



130626.218  
Janke JJ-2H215 13C CDCl3

- 142.02
- 141.51
- 140.20
- 137.74
- 132.99
- 130.64
- 127.24
- 124.84
- 123.60
- 121.75
- 120.36
- 120.12
- 119.37
- 115.61
- 108.83



130626.218  
Janke JJ-2H215 Dept CDCl3

- 142.01
- 130.64
- 127.23
- 124.83
- 123.60
- 120.35
- 120.12
- 119.37
- 115.61
- 108.83

