

Efficient Synthesis of Biscarbazoles by Palladium-Catalyzed Twofold C-N Coupling and C-H Activation Reactions

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Supporting Information

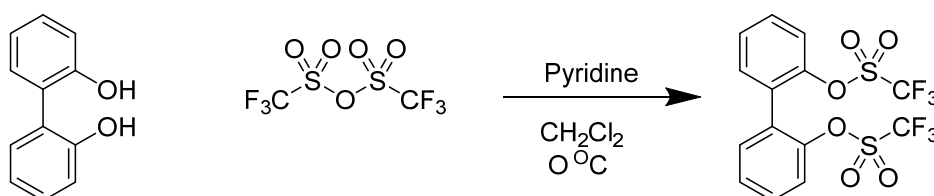
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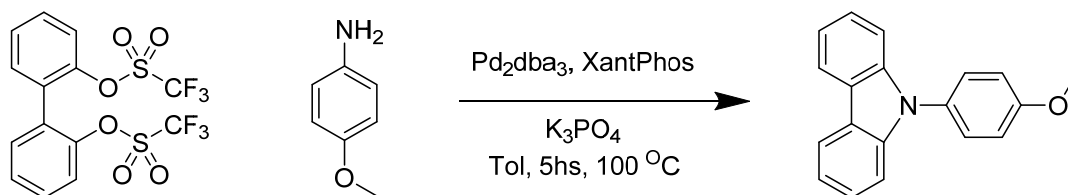
Experimental Section

Synthesis of 2,2'-biphenylene ditriflate **1**.

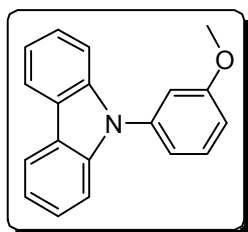


To a solution of 2,2'-dihydroxyl biphenyl (4.3 g, 23 mmol) in DCM was added pyridine (7.0 mL) under Argon atmosphere. Then, Tf₂O (13.0 g, 46 mmol) was slowly added at 0 °C. The reaction was stirred at the same temperature for 3 h until the reaction was completed (tlc control). The reaction mixture was diluted by DCM and subsequently washed with 1M HCl, 1M NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered and the solvent was evaporated *in vacuo*. The colorless residue was purified by column chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **1** (9.3 g, 90.3 %, white solid); m.p. 35-36 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.48 – 7.26 (m, 8H); ¹⁹F NMR (282 MHz, CDCl₃) δ -74.38 (s); ¹³C NMR (75 MHz, CDCl₃) δ 147.01, 132.75, 130.90, 129.55, 128.68, 118.50 (q, *J* = 320.1 Hz), 121.81; IR (ATR, cm⁻¹): ν = 1504 (w), 1473 (m), 1452 (w), 1439 (w), 1414 (vs), 1400 (s), 1277 (w), 1244 (s), 1201 (vs), 1165 (m), 1149 (s), 1132 (vs), 1111 (s), 1084 (s), 1045 (m), 1012 (w), 991 (w), 955 (w), 935 (w), 893 (s), 872 (vs), 779 (s), 769 (vs), 760 (s), 735 (m), 725 (s), 667 (w), 646 (w), 619 (s), 588 (s), 571 (vs); GC-MS (EI, 70 eV): *m/z* (%) = 450 (64), 317 (6), 184 (100), 168 (90), 156 (25), 139 (20), 128 (37), 102 (19), 69 (30); HRMS (EI): calcd. for C₁₄H₈O₆F₆S₂ ([M]⁺): 449.96610; found: 449.96583.

Synthesis of *N*-(4-methoxyphenyl)carbazole **4a**.

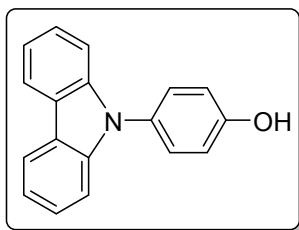


In a 50 mL dried pressure tube were added **1** (460 mg, 1.021 mmol), *p*-anisidine (151 mg, 1.226 mmol), Pd₂dba₃ (23 mg, 0.026 mmol), XantPhos (59 mg, 0.102 mmol), and K₃PO₄ (650 mg, 3.062 mmol) and the flask was backfilled with Argon 3 times. Then, the mixture was dissolved in 20 mL of toluene and, subsequently, backfilled with Argon 3 times. The reaction mixture was stirred at 100 °C under Argon atmosphere for 5 hours (tlc control). The reaction was cooled down to ambient temperature, then the solvent was removed by evaporation *in vacuo*. The crude product was extracted with EtOAc and water several times. The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethylacetate/heptane = 1:10) to give **4a** (265 mg, 95 %) as a white solid. M.p. 156-157 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.19 – 8.10 (m, 2H, ArH), 7.48 – 7.24 (m, 9H, ArH), 7.12 (d, *J* = 9.0 Hz, 2H, ArH), 3.92 (s, 3H, OCH₃); ¹³C NMR (75 MHz, CDCl₃) δ 159.02, 141.53, 130.47, 128.73, 125.98, 123.25, 120.39, 119.78, 115.21, 109.83, 55.75; IR (ATR, cm⁻¹): ν = 1591 (w), 1510 (s), 1479 (m), 1450 (s), 1336 (m), 1317 (m), 1246 (s), 1240 (s), 1228 (s), 1178 (s), 1147 (m), 1120 (m), 1107 (m), 1028 (s), 997 (m), 908 (m), 852 (w), 829 (s), 810 (m), 798 (m), 748 (vs), 725 (s), 698 (m), 642 (m), 621 (s), 611 (m), 584 (s), 569 (s), 532 (s); GC-MS (EI, 70 eV): *m/z* (%) = 273 (100), 258 (47), 230 (12), 228 (30); HRMS (EI): calcd. for C₁₉H₁₅ON ([M]⁺): 273.11482; found: 273.11474.

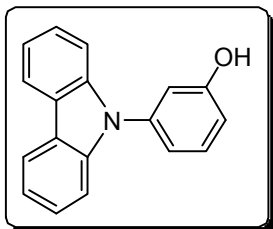


***N*-(4-Methoxyphenyl)carbazole (4b).** Prepared following the procedure given for the synthesis of **4a** using **1** (460 mg, 1.021 mmol) and *m*-anisidine (138 μL, 1.226 mmol). The crude product was separated via flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **4b** (265 mg, 95 %) as a colorless syrup; ¹H NMR (300 MHz, CDCl₃) δ 8.05 (dd, *J* = 7.7, 0.6 Hz, 2H), 7.46 – 7.27 (m, 5H), 7.25 – 7.12 (m, 2H), 7.12 – 6.97 (m, 2H), 6.91 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.76 (s, 3H); ¹³C NMR (63 MHz, CDCl₃) δ 160.94, 140.95, 138.96, 130.66, 126.07, 123.49, 120.41, 120.04, 119.44, 113.38, 112.80, 110.04, 55.63; IR (ATR, cm⁻¹):

$\nu = 3051$ (w), 2955 (w), 2933 (w), 2833 (w), 1927 (w), 1890 (w), 1861 (vw), 1593 (s), 1576 (m), 1495 (s), 1477 (s), 1450 (s), 1362 (m), 1335 (m), 1311 (s), 1281 (s), 1250 (s), 1227 (s), 1184 (m), 1153 (s), 1119 (m), 1099 (m), 1088 (m), 1078 (m), 1039 (s), 1003 (m), 995 (m), 984 (m), 970 (m), 918 (m), 872 (m), 845 (m), 833 (m), 825 (m), 779 (m), 744 (vs), 721 (vs), 692 (vs), 652 (m), 636 (m), 615 (m), 588 (m), 559 (m); GC-MS (EI, 70 eV): m/z (%) = 273 (100), 258 (7), 241 (5), 228 (19); HRMS (EI): calcd. for $C_{19}H_{15}ON$ ($[M]^+$): 273.11484; found: 273.11482.



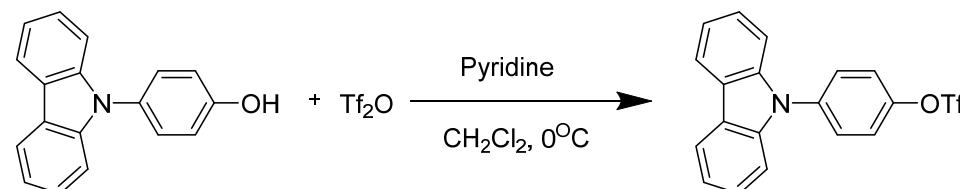
***N*-(4-Hydroxyphenyl)carbazole (5a).** To solution of **4a** (265 mg, 0.970 mmol) in DCM at $-78\text{ }^{\circ}\text{C}$ was slowly added BBr_3 (367 μl , 3.880 mmol). The temperature was allowed to rise to ambient temperature. The reaction was controlled by TLC until the starting material completely disappeared. The reaction mixture was poured to an icecold aqueous solution of NaHCO_3 . The aqueous layer was extracted with DCM three times. The organic residue was dried over MgSO_4 , filtered and then the solvent was evaporated *in vacuo*. The crude product was purified over flash silica gel column chromatography (silica gel, ethylacetate/heptane = 1:10) to give **5a** (239 mg, 95 %). M.p. $106\text{--}107\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 8.18 – 8.11 (m, 2H, ArH), 7.44 – 7.36 (m, 4H, ArH), 7.35 – 7.23 (m, 4H, ArH), 7.05 (d, $J = 8.8$ Hz, 2H, ArH). ^{13}C NMR (63 MHz, CDCl_3) δ 155.00, 141.50, 130.72, 128.99, 126.00, 123.28, 120.40, 119.82, 116.72, 109.81; IR (ATR, cm^{-1}): $\nu = 3196$ (m), 3043 (w), 1622 (w), 1593 (m), 1512 (s), 1479 (m), 1450 (s), 1363 (m), 1335 (m), 1315 (m), 1248 (m), 1228 (s), 1219 (s), 1178 (s), 1165 (m), 1147 (m), 1099 (m), 1028 (w), 1014 (m), 1003 (w), 910 (m), 833 (s), 820 (m), 746 (vs), 723 (vs), 665 (m), 623 (s), 611 (m), 584 (s), 567 (m), 532 (m); GC-MS (EI, 70 eV): m/z (%) = 259 (100), 241 (6), 228 (10); HRMS (ESI): calcd. for $C_{18}H_{14}ON$ ($[M + H]^+$): 260.10699; found: 260.10686; calcd. for $C_{18}H_{13}ONNa$ ($[M + Na]^+$): 282.08894; found: 282.08872.



***N*-(4-Hydroxyphenyl)carbazole (5b).** Prepared, following the procedure given for the synthesis of **5a**, starting with carbazole **4b** (265 mg, 0.970 mmol) to give **5b** (231 mg, 92 %) as a colorless syrup; ^1H NMR (250 MHz, CDCl_3) δ 8.09 – 8.03 (m, 2H), 7.41 – 7.31 (m, 5H), 7.25 – 7.16 (m, 2H), 7.07 (ddd, $J = 7.9, 1.9, 0.9$ Hz, 1H), 6.96 (t, $J = 2.2$ Hz, 1H), 6.84 (ddd, $J = 8.2, 2.5, 0.9$ Hz, 1H), 4.86 (s, 1H); ^{13}C NMR (63 MHz, CDCl_3) δ 156.67,

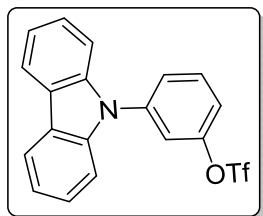
140.71, 138.99, 130.79, 125.93, 123.37, 120.26, 119.96, 119.48, 114.48, 114.06, 109.88; IR (ATR, cm^{-1}): ν = 3537 (w), 3271 (m), 3047 (w), 1599 (s), 1576 (m), 1498 (s), 1485 (m), 1471 (m), 1450 (s), 1367 (m), 1346 (m), 1335 (m), 1321 (m), 1304 (m), 1261 (m), 1252 (m), 1230 (s), 1209 (m), 1178 (m), 1165 (m), 1151 (s), 1124 (m), 991 (m), 920 (m), 872 (m), 849 (m), 781 (m), 748 (vs), 742 (vs), 719 (vs), 696 (vs), 667 (m), 636 (m), 615 (m), 584 (m), 573 (m), 557 (m); GC-MS (EI, 70 eV): m/z (%) = 259(100), 241 (4), 228 (8), 204 (4); HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{13}\text{ON}$ ($[\text{M}]^+$): 259.09917; found: 259.09925.

Synthesis of *N*-(4- trifluoromethanesulfonate)carbazole (**6a**).



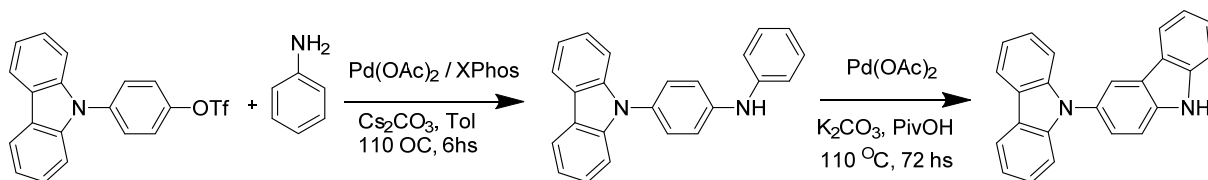
To solution of **5a** (239 mg, 0.921 mmol) in DCM was added pyridine (298 μL , 3.690 mmol) under Argon atmosphere. Then, $\text{O}_2\text{S}(\text{CF}_3)_2$ (234 μL , 1.383 mmol) was dropwise added at 0 °C. The reaction mixture was stirred at the same temperature for 3 h until all starting material disappeared (controlled by tlc). The reaction mixture was diluted by DCM and subsequently washed with 1M HCl, 1M NaHCO_3 and brine. The organic layer was dried over MgSO_4 , filtered and the solvent was evaporated *in vacuo*. The colorless residue was purified by column chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **6a** (310 mg, 86 %) as a white solid. M.p. 112 - 114 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.18 – 8.12 (m, 1H), 7.72 – 7.65 (m, 1H), 7.57 – 7.50 (m, 1H), 7.48 – 7.36 (m, 2H), 7.36 – 7.29 (m, 1H); ^{19}F NMR (282 MHz, CDCl_3) δ -72.65 (s); ^{13}C NMR (63 MHz, CDCl_3) δ 147.99, 140.64, 138.12, 128.89, 126.40, 123.82, 123.19, 120.72, 120.65, 109.59; IR (ATR, cm^{-1}): ν = 3063 (w), 2924 (w), 1593 (w), 1504 (s), 1477 (m), 1452 (s), 1421 (s), 1412 (s), 1365 (w), 1335 (m), 1315 (m), 1248 (m), 1228 (s), 1215 (vs), 1167 (m), 1134 (vs), 1101 (m), 1026 (w), 1016 (m), 1001 (w), 916 (m), 887 (vs), 841 (s), 820 (m), 787 (m), 764 (w), 752 (vs), 725 (s), 696 (s), 644 (m), 619 (s), 611 (vs), 602 (vs), 573 (s), 565 (m), 530 (s); GC-MS (EI, 70 eV): m/z (%) = 391 (51), 259 (20), 258

(100), 230 (15), 228 (28), 69 (9); HRMS (EI): calcd. for $C_{19}H_{12}O_3NF_3S$ ($[M]^+$): 391.04845; found: 391.04852.



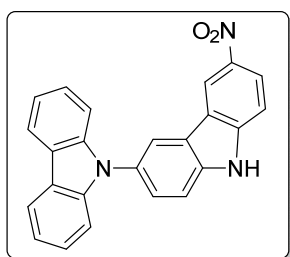
N-(3-Trifluoromethanesulfonate)carbazole (6b). Prepared, following the procedure given for the synthesis of **6a**, from carbazole **5b** (231 mg, 0.891 mmol) to give **6b** (328 mg, 94 %) as a white solid. Mp. 76-78 °C, 1H NMR (300 MHz, $CDCl_3$) δ 7.97 (dt, J = 7.7, 1.0 Hz, 2H), 7.50 (dd, J = 6.4, 4.6 Hz, 2H), 7.38 (t, J = 2.0 Hz, 1H), 7.29 – 7.24 (m, 4H), 7.16 (ddd, J = 9.6, 8.1, 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -72.63 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.33, 140.40, 139.83, 131.53, 126.90, 126.51, 123.92, 120.90, 120.67, 120.32, 120.14, 109.56; IR (ATR, cm^{-1}): ν = 3072 (w), 3047 (w), 3024 (w), 1605 (m), 1585 (w), 1574 (w), 1495 (s), 1483 (s), 1454 (s), 1417 (vs), 1404 (m), 1365 (m), 1335 (m), 1315 (m), 1250 (m), 1230 (m), 1209 (vs), 1184 (s), 1163 (m), 1136 (s), 1119 (s), 1095 (s), 1084 (m), 1028 (m), 1003 (w), 984 (s), 964 (w), 924 (m), 904 (m), 877 (s), 847 (m), 798 (s), 771 (m), 764 (m), 750 (vs), 741 (s), 725 (s), 692 (s), 660 (m), 636 (m), 623 (m), 606 (s), 567 (s), 536 (m); GC-MS (EI, 70 eV): m/z (%) = 391 (100), 258 (57), 230 (58), 228 (42), 202 (12), 69 (13); HRMS (EI): calcd. for $C_{19}H_{12}O_3NF_3S$ ($[M]^+$): 391.04845; found: 391.04816.

Typical procedure for the synthesis of biscarbazoles **3a-j** and **7a-j**.

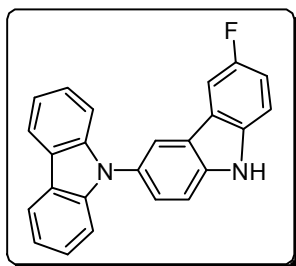


9H-3,9'-Biscarbazole 3a. Cesium carbonate (125 mg, 0.383 mmol) was added to a pressure tube charged with $Pd(OAc)_2$ (3 mg, 0.013 mmol) and XPhos (12 mg, 0.026 mmol) under argon atmosphere. Compound **6a** (100 mg, 0.256 mmol) and aniline (26 μ L, 0.281 mmol) was added to the mixture and the tube was backfilled with argon several times. The mixture was stirred at 110 °C in anhydrous toluene (5 mL) for 6 hours. After cooling, the reaction mixture was diluted with dichloromethane (10 mL), filtered through a celite pad, and washed with dichloromethane (20 mL). The filtrate was concentrated *in vacuo*. Pivalic acid was added to the filtrate charged with $Pd(OAc)_2$ (3 mg, 0.013 mmol) and potassium carbonate (35 mg, 0.256 mmol). The mixture was stirred at 110 °C under air atmosphere for 72 hours (controlled by tlc). The solution was then

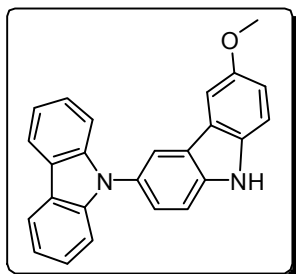
cooled to room temperature, diluted with DCM and washed with a saturated aqueous solution of sodium carbonate, dried over Magnesium sulfate, filtered and evaporated in *vacuo*. The product was purified by flash chromatography (silica gel, ethylacetate/heptanes = 1:10) to yield **3a** (73 mg, 86%) as a white solid; mp 211-212 °C; ^1H NMR (250 MHz, CDCl_3) δ 8.05 (dd, J = 10.4, 3.9 Hz, 4H), 7.90 (d, J = 7.8 Hz, 1H), 7.46 – 7.07 (m, 12H); ^{13}C NMR (63 MHz, CDCl_3) δ 142.06, 140.30, 138.71, 129.56, 126.71, 125.99, 125.58, 124.50, 123.21, 123.14, 120.72, 120.40, 120.05, 119.71, 111.73, 111.05, 109.99; IR (ATR, cm^{-1}): ν = 3394 (m), 3076 (w), 3051 (m), 3020 (w), 2926 (w), 1595 (m), 1574 (m), 1495 (m), 1485 (m), 1475 (s), 1462 (s), 1448 (s), 1346 (m), 1333 (m), 1311 (s), 1273 (m), 1230 (s), 1203 (m), 1163 (m), 1149 (m), 1126 (m), 1117 (m), 1097 (m), 1024 (m), 1011 (m), 1003 (m), 957 (m), 926 (m), 918 (m), 845 (m), 820 (s), 742 (vs), 733 (s), 719 (vs), 660 (m), 650 (s), 631 (m), 615 (m), 580 (m), 571 (s); GC-MS (EI, 70 eV): m/z (%) = 332 (100), 166 (14), 139 (4); HRMS (EI): calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_2$ ($[\text{M}]^+$): 332.13080; found: 332.13072.



6-Nitro-9H-3,9'-biscarbazole 3b. The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and 4-nitroaniline (39 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:3) to yield **3b** (96 mg, 95 %) as a red solid; mp 306-308 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 12.35 (s, 2H), 9.32 (d, J = 2.2 Hz, 3H), 8.72 (d, J = 1.8 Hz, 3H), 8.39 – 8.22 (m, 9H), 7.87 (d, J = 8.5 Hz, 3H), 7.79 – 7.65 (m, 6H), 7.37 (dq, J = 9.0, 6.8, 1.3 Hz, 18H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 144.00, 140.97, 140.13, 140.10, 129.42, 126.29, 126.14, 123.68, 122.49, 122.09, 121.71, 120.43, 120.34, 119.76, 118.33, 113.27, 111.50, 109.70; IR (ATR, cm^{-1}): ν = 3307 (m), 2955 (w), 2922 (w), 2850 (w), 1608 (m), 1585 (m), 1495 (s), 1475 (s), 1448 (s), 1315 (s), 1308 (s), 1288 (s), 1228 (s), 1200 (s), 1163 (s), 1147 (m), 1128 (s), 1103 (m), 1078 (s), 1030 (m), 1016 (m), 889 (m), 852 (m), 823 (s), 816 (s), 748 (vs), 741 (s), 731 (s), 721 (vs), 683 (s), 654 (s), 640 (s), 625 (s), 613 (s), 590 (s), 567 (s), 557 (s), 528 (s); GC-MS (EI, 70 eV): m/z (%) = 329 (51), 314 (16), 114 (14), 73 (33), 60 (45), 44 (100); HRMS (ESI): calcd. for $\text{C}_{24}\text{H}_{16}\text{O}_2\text{N}_3$ ($[\text{M} + \text{H}]^+$): 378.1237; found: 378.12327; calcd. for $\text{C}_{24}\text{H}_{15}\text{O}_2\text{N}_3\text{Na}$ ($[\text{M} + \text{Na}]^+$): 400.10565; found: 400.10522.

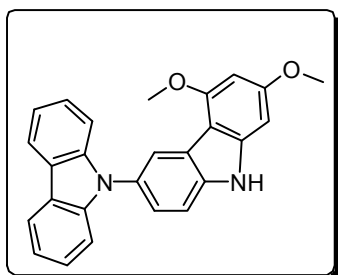


6-Fluoro-9H-3,9'-bicarbazole 3c. The product was prepared following general procedure using compound **6a** (100 mg, 0.256 mmol) and 4-fluoroaniline (27 μ L, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **3c** (90 mg, 63 %) as a red solid; mp 238-240 $^{\circ}$ C; ^1H NMR (300 MHz, DMSO- d_6) δ 11.62 (s, 1H), 8.41 (d, J = 2.0 Hz, 1H), 8.26 (d, J = 7.6 Hz, 2H), 8.06 (dd, J = 9.4, 2.6 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.57 (dt, J = 8.6, 3.5 Hz, 2H), 7.42 (ddd, J = 8.2, 7.0, 1.2 Hz, 2H), 7.37 – 7.22 (m, 5H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 156.47 (d, J = 232.6 Hz), 141.23, 139.92, 136.95, 127.70, 126.08, 125.30, 123.19 (d, J = 4.2 Hz), 122.69 (d, J = 10.1 Hz), 122.35, 120.40, 119.71, 119.59, 113.95 (d, J = 25.6 Hz), 112.51, 112.18 (d, J = 9.1 Hz), 109.64, 106.35 (d, J = 23.9 Hz); IR (ATR, cm^{-1}): ν = 3394 (m), 3053 (w), 2953 (w), 2920 (w), 2850 (w), 1587 (m), 1574 (m), 1495 (s), 1466 (s), 1448 (s), 1315 (m), 1284 (m), 1244 (m), 1228 (s), 1171 (m), 1151 (s), 1140 (m), 1124 (m), 1115 (m), 850 (m), 812 (s), 752 (vs), 744 (s), 721 (s), 656 (s), 646 (s), 615 (m), 596 (m), 575 (s), 565 (s), 544 (s), 532 (m); GC-MS (EI, 70 eV): m/z (%) = 350 (100), 174 (15); HRMS (ESI): calcd. for $\text{C}_{24}\text{H}_{16}\text{FN}_2$ ($[\text{M} + \text{H}]^+$): 351.1292; found: 351.12844; calcd. for $\text{C}_{24}\text{H}_{15}\text{OFN}_2\text{Na}$ ($[\text{M} + \text{Na}]^+$): 373.11115; found: 373.11065.



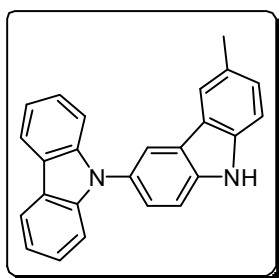
6-Methoxy-9H-3,9'-biscarbazole 3d. The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and *p*-anisidine (35 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:5) to yield **3d** (93 mg, 53 %) as a white solid; mp 256-257 $^{\circ}$ C; ^1H NMR (300 MHz, DMSO- d_6) δ 11.46 (s, 1H), 8.31 (dd, J = 28.0, 4.8 Hz, 3H), 7.75 (dd, J = 27.7, 5.5 Hz, 2H), 7.40 (dddd, J = 44.2, 15.9, 8.1, 1.5 Hz, 8H), 7.08 (dd, J = 8.8, 2.5 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 153.17, 141.32, 139.54, 135.31, 127.23, 126.06, 124.45, 123.48, 122.64, 122.33, 120.40, 119.52, 119.29, 115.66, 112.20, 111.95, 109.68, 103.39, 55.56; IR (ATR, cm^{-1}): ν = 3417 (m), 3045 (w), 2928 (w), 2829 (m), 1622 (m), 1589 (s), 1581 (s), 1574 (s), 1497 (s), 1470 (m), 1464 (m), 1450 (s), 1435 (m), 1360 (s), 1335 (m), 1313 (m), 1294 (s), 1232 (s), 1201 (s), 1173 (m), 1151 (m), 1140 (m), 1032 (m), 808 (m), 773 (s), 752 (vs), 727 (s), 656 (m), 648 (m), 617 (m), 607 (m), 569 (s),

528 (m); GC-MS (EI, 70 eV): m/z (%) = 362 (100), 347 (26), 319 (16), 290 (5), 174 (14); HRMS (ESI): calcd. for $C_{25}H_{17}N_2O$ ($[M - H]^-$): 361.13464; found: 361.13557.



5,7-Dimethoxy-9H-3,9'-biscarbazole 3e. The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and 3,5-dimethoxyaniline (43 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:4) to yield **3e** (100 mg, 50 %) as a white solid; mp 125-127 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.32

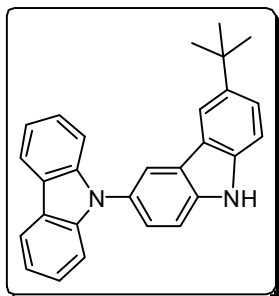
(d, J = 2.0 Hz, 1H), 8.26 – 8.15 (m, 2H), 8.09 (s, 1H), 7.50 (dd, J = 8.4, 0.4 Hz, 1H), 7.46 – 7.34 (m, 5H), 7.34 – 7.25 (m, 3H), 6.56 (d, J = 1.9 Hz, 1H), 6.34 (d, J = 1.9 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.97, 156.90, 142.35, 142.24, 137.96, 129.65, 125.89, 124.09, 123.44, 123.09, 121.42, 120.30, 119.49, 110.65, 110.20, 106.90, 91.59, 87.00, 55.85, 55.52; IR (ATR, cm^{-1}): ν = 3400 (w), 2918 (w), 2839 (w), 1633 (m), 1622 (m), 1614 (m), 1591 (m), 1495 (s), 1464 (s), 1450 (s), 1435 (m), 1335 (m), 1329 (m), 1315 (m), 1290 (s), 1230 (s), 1209 (s), 1196 (s), 1149 (s), 1120 (s), 1099 (m), 1049 (m), 918 (m), 806 (s), 750 (vs), 723 (s), 656 (s), 642 (m), 557 (m); GC-MS (EI, 70 eV): m/z (%) = 392 (100), 334 (22), 196 (12), 167 (7), 140 (22); HRMS (ESI): calcd. for $C_{26}H_{21}N_2O_2$ ($[M + H]^+$): 393.15975; found: 393.1595; calcd. for $C_{26}H_{20}N_2O_2Na$ ($[M + Na]^+$): 415.1417; found: 415.14155.



6-Methyl-9H-3,9'-biscarbazole 3g. The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and *p*-toluidine (30 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **3g** (89 mg, 34 %) as a white solid; mp 231-232 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 3H), 7.76 (d, J = 0.7 Hz, 1H), 7.46

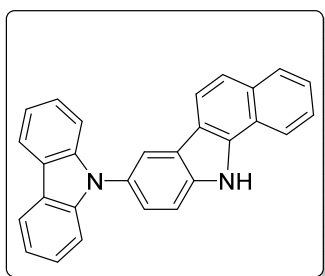
(ddd, J = 10.4, 8.5, 1.2 Hz, 2H), 7.39 – 7.14 (m, 9H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.08, 139.05, 138.57, 129.45, 129.38, 128.09, 125.96, 125.39, 124.38, 123.36, 123.21, 120.59, 120.38, 119.67, 119.60, 111.69, 110.73, 110.01, 21.56; IR (ATR, cm^{-1}): ν = 3410 (m), 3057 (w), 2916 (w), 2852 (w), 2831 (w), 1593 (m), 1583 (m), 1574 (m), 1497 (s), 1479 (m), 1464 (s), 1452 (s), 1358 (m), 1338 (m), 1317 (m), 1296 (m), 1277 (m), 1242 (m), 1230 (s), 1153 (m), 820 (s), 806 (m), 748 (vs), 723 (vs), 658 (m), 646 (m), 575 (s), 540 (m), 528 (m); GC-

MS (EI, 70 eV): m/z (%) = 346 (100), 173 (9); HRMS (ESI): calcd. for $C_{25}H_{19}N_2$ ($[M + H]^+$): 347.15428; found: 347.15337; calcd. for $C_{25}H_{18}N_2Na$ ($[M + Na]^+$): 369.13622; found: 369.13578.



6-(*tert*-Butyl)-9H-3,9'-bicarbazole 3h. The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and 4-(*tert*-butyl)aniline (45 μ L, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **3h** (99 mg, 70 %) as a white solid; mp 183-185 $^{\circ}$ C; 1H NMR (250 MHz, $CDCl_3$) δ 8.28 – 7.87 (m, 4H), 7.60 – 7.05 (m, 10H),

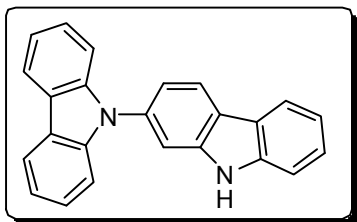
1.34 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 143.20, 142.16, 139.18, 138.43, 129.36, 125.94, 125.36, 124.80, 123.20, 122.90, 120.39, 119.65, 116.72, 111.67, 110.57, 110.02, 34.86, 32.06; IR (ATR, cm^{-1}): ν = 3408 (m), 3045 (w), 2953 (m), 2862 (w), 1622 (m), 1614 (m), 1595 (m), 1574 (m), 1495 (s), 1470 (s), 1450 (s), 1362 (m), 1335 (m), 1315 (m), 1294 (m), 1281 (m), 1242 (m), 1230 (s), 1201 (m), 1163 (m), 1138 (m), 1117 (m), 808 (s), 746 (vs), 723 (vs), 661 (m), 648 (m), 627 (vs), 577 (m), 546 (m), 536 (m); GC-MS (EI, 70 eV): m/z (%) = 388 (100), 373 (63), 332 (10), 207 (9), 187 (13), 173 (24); HRMS (ESI): calcd. for $C_{28}H_{25}N_2$ ($[M + H]^+$): 389.20123; found: 389.20074;



8-(9H-Carbazol-9-yl)-11H-benzo[a]carbazole 3j. The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and 2-aminonaphthalene (40 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **3j** (98 mg, 42 %) as a white solid; mp 220-222 $^{\circ}$ C; 1H NMR (300 MHz, $CDCl_3$) δ 8.90 (s,

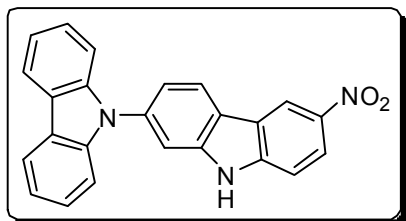
1H), 8.18 (d, J = 1.9 Hz, 1H), 8.11 (dd, J = 4.3, 3.4 Hz, 3H), 8.00 (d, J = 8.6 Hz, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.7 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.34 (dd, J = 4.4, 0.8 Hz, 4H), 7.25 – 7.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.95, 137.57, 135.86, 132.74, 130.05, 129.21, 125.86, 125.68, 125.21, 124.52, 123.13, 121.15, 120.80, 120.55, 120.28, 119.60, 119.24, 119.12, 118.30, 112.11, 109.90; IR (ATR, cm^{-1}): ν = 3417 (w), 3045 (w), 2918 (w), 2848 (w), 1593 (m), 1514 (m), 1495 (s), 1477 (m), 1464 (m), 1450 (s), 1417 (m), 1385 (m), 1358 (m), 1335 (m), 1313 (m), 1304 (m), 1281 (m), 1230 (s), 1205 (m), 1169 (m),

1157 (m), 1146 (m), 1117 (m), 1105 (m), 806 (s), 748 (vs), 723 (s), 687 (m), 650 (m), 604 (m), 565 (m), 550 (m); GC-MS (EI, 70 eV): m/z (%) = 382 (100), 216 (6), 190 (25); HRMS (ESI): calcd. for $C_{28}H_{19}N_2$ ($[M + H]^+$): 383.15428; found: 383.15362; calcd. for $C_{28}H_{18}N_2Na$ ($[M + Na]^+$): 405.13622; found: 405.13638.



9H-2,9'-Biscarbazole 7a. The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and aniline (26 μ L, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **7a** (65 mg, 77 %) as a

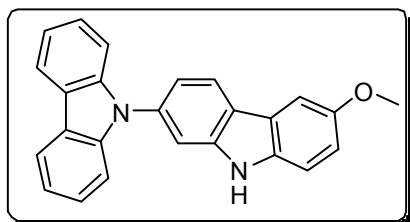
white solid; mp 298-300 $^{\circ}C$; 1H NMR (300 MHz, acetone- d_6) δ 10.61 (s, 1H), 8.40 (d, J = 8.2 Hz, 1H), 8.29 – 8.20 (m, 3H), 7.78 – 7.72 (m, 1H), 7.61 (dt, J = 8.2, 0.8 Hz, 1H), 7.50 – 7.38 (m, 6H), 7.33 – 7.23 (m, 3H); ^{13}C NMR (63 MHz, acetone- d_6) δ 142.28, 141.82, 141.72, 135.91, 126.95, 126.89, 124.14, 123.66, 123.52, 122.23, 121.18, 121.11, 120.72, 120.28, 118.82, 112.02, 110.76, 110.47; IR (ATR, cm^{-1}): ν = 3414 (m), 3053 (w), 2926 (w), 1603 (m), 1489 (m), 1460 (m), 1450 (s), 1441 (s), 1362 (m), 1336 (m), 1321 (m), 1230 (s), 1201 (m), 1157 (m), 1095 (m), 999 (m), 978 (m), 937 (m), 918 (m), 849 (m), 818 (m), 752 (s), 742 (s), 723 (vs), 663 (s), 631 (m), 615 (m), 565 (s); GC-MS (EI, 70 eV): m/z (%) = 332 (100), 166 (16); HRMS (EI): calcd. for $C_{24}H_{16}N_2$ ($[M]^+$): 332.13080; found: 332.13106.



6-Nitro-9H-2,9'-biscarbazole 7b. The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 4-nitroaniline (39 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:3) to yield **7b** (61 mg, 63 %) as a red

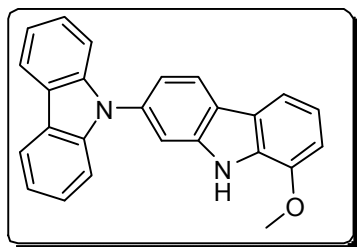
solid; mp 310-312 $^{\circ}C$; 1H NMR (300 MHz, DMSO- d_6) δ 12.25 (s, 1H), 9.29 (d, J = 2.3 Hz, 1H), 8.66 (d, J = 8.3 Hz, 1H), 8.36 (dd, J = 9.0, 2.3 Hz, 1H), 8.28 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 1.5 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.57 – 7.39 (m, 5H), 7.39 – 7.25 (m, 2H); ^{13}C NMR (63 MHz, DMSO- d_6) δ 144.02, 141.82, 140.47, 140.28, 135.81, 126.29, 122.92, 122.76, 121.97, 121.82, 121.56, 120.54, 120.10, 119.04, 117.68, 111.45, 110.14, 109.76; IR (ATR, cm^{-1}): ν = 3348 (m), 3059 (w), 2916 (w), 1610 (s), 1593 (m), 1583 (m), 1506 (s), 1477 (s), 1464 (m), 1450 (s), 1365 (m), 1331 (s), 1319 (s), 1309 (s), 1279 (s), 1248 (s), 1228 (s), 1196 (m), 1159 (s),

1124 (s), 1099 (s), 1084 (s), 1028 (m), 1014 (m), 1003 (m), 982 (m), 916 (m), 893 (m), 866 (m), 849 (m), 841 (m), 823 (s), 748 (vs), 725 (vs), 692 (s), 663 (s), 636 (m), 627 (m), 615 (m), 584 (s), 573 (s), 565 (s), 528 (m); GC-MS (EI, 70 eV): m/z (%) = 377 (100), 331 (34), 281 (4), 189 (8), 173 (26); HRMS (ESI): calcd. for $C_{24}H_{15}O_2N_3Na$ ($[M + Na]^+$): 400.10565; found: 400.10564.



6-Methoxy-9H-2,9'-biscarbazole 7c. The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and *p*-anisidine (35 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:5) to yield **7c** (47 mg, 51

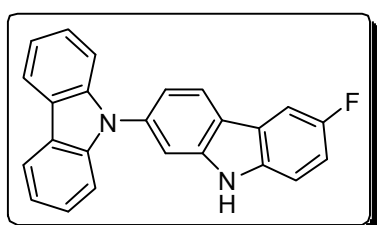
% as a white solid; mp 225-227 °C; 1H NMR (300 MHz, acetone- d_6) δ 10.42 (s, 1H), 8.36 (d, J = 8.3 Hz, 1H), 8.27 – 8.20 (m, 2H), 7.80 (d, J = 2.5 Hz, 1H), 7.71 (d, J = 1.5 Hz, 1H), 7.56 – 7.25 (m, 9H), 7.12 (dd, J = 8.8, 2.5 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (63 MHz, acetone- d_6) δ 155.14, 142.32, 142.25, 136.59, 135.74, 126.86, 124.11, 123.56, 122.28, 121.10, 120.69, 118.31, 116.35, 112.71, 110.76, 110.48, 103.79, 56.15; IR (ATR, cm^{-1}): ν = 3415 (m), 3053 (w), 2993 (w), 1608 (m), 1589 (m), 1489 (s), 1471 (m), 1462 (m), 1448 (s), 1427 (s), 1335 (m), 1319 (m), 1308 (m), 1288 (s), 1252 (m), 1225 (s), 1217 (s), 1201 (s), 1169 (s), 1159 (s), 1126 (m), 1115 (m), 1095 (m), 1030 (s), 1012 (m), 1003 (m), 980 (m), 914 (m), 906 (m), 895 (m), 860 (m), 850 (m), 837 (s), 822 (m), 804 (vs), 775 (m), 754 (vs), 744 (vs), 725 (vs), 708 (s), 663 (s), 652 (m), 615 (m), 606 (s), 588 (m), 565 (m), 553 (m), 528 (s); GC-MS (EI, 70 eV): m/z (%) = 362 (100), 347 (21), 330 (14), 290 (6), 207 (6), 159 (68), 145 (29), 133 (15); HRMS (EI): calcd. for $C_{25}H_{18}N_2O$ ($[M]^+$): 362.14136; found: 362.14150.



8-Methoxy-9H-2,9'-biscarbazole 7d. The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and *o*-anisidine (32 μ L, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:5) to yield **7d** (75 mg, 81 %) as a white

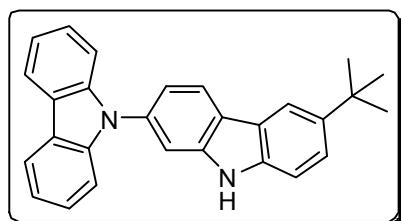
solid; mp 269-270 °C; 1H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 2H), 8.19 (ddd, J = 9.5, 7.7, 4.7 Hz, 6H), 7.75 (d, J = 7.9 Hz, 2H), 7.62 (d, J = 1.4 Hz, 2H), 7.51 – 7.37 (m, 10H), 7.34 – 7.20 (m, 9H), 7.01 – 6.94 (m, 2H), 4.05 (s, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 145.75, 141.38, 139.72,

135.26, 130.49, 125.88, 123.92, 123.26, 123.04, 121.61, 120.37, 120.25, 119.76, 118.83, 112.86, 109.93, 109.70, 106.29, 55.58; IR (ATR, cm^{-1}): ν = 3412 (m), 3055 (w), 2931 (w), 2839 (w), 1614 (w), 1579 (m), 1504 (m), 1450 (s), 1433 (s), 1381 (m), 1365 (m), 1335 (m), 1323 (m), 1313 (m), 1306 (m), 1269 (m), 1259 (m), 1240 (m), 1230 (s), 1188 (w), 1155 (m), 1093 (m), 1063 (w), 1016 (s), 980 (w), 931 (w), 918 (m), 893 (w), 868 (w), 847 (m), 823 (m), 781 (m), 746 (vs), 723 (s), 685 (m), 665 (m), 617 (m), 577 (m), 563 (m), 555 (m), 536 (m); GC-MS (EI, 70 eV): m/z (%) = 362 (100), 347 (7), 319 (27), 181 (7), 159 (10); HRMS (ESI): calcd. for $\text{C}_{25}\text{H}_{19}\text{N}_2\text{O}$ ($[\text{M} + \text{H}]^+$): 363.14919; found: 363.14883; calcd. for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O Na}$ ($[\text{M} + \text{Na}]^+$): 385.13113; found: 385.13157.



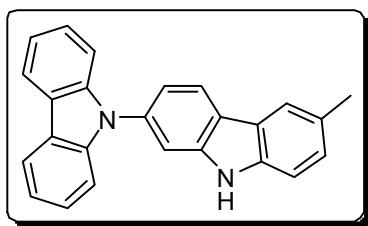
6-Fluoro-9H-2,9'-biscarbazole 7e. The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 4-fluoroaniline (27 μL , 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **7e** (56 mg, 63 %) as a

white solid; mp 274-276 $^{\circ}\text{C}$; ^1H NMR (300 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.40 (d, J = 8.3 Hz, 1H), 8.27 (d, J = 7.7 Hz, 2H), 8.08 (dd, J = 9.4, 2.6 Hz, 1H), 7.70 (d, J = 1.5 Hz, 1H), 7.57 (dd, J = 8.9, 4.4 Hz, 1H), 7.49 – 7.24 (m, 8H); ^{19}F NMR (282 MHz, DMSO-d_6) δ -124.46 (s); ^{13}C NMR (63 MHz, DMSO) δ 156.61 (d, J = 232.4 Hz), 141.35, 140.55, 136.91, 134.71, 126.17, 122.61, 122.53 (d, J = 10.4 Hz), 122.09, 121.55 (d, J = 4.2 Hz), 120.47, 119.89, 117.28, 113.61 (d, J = 25.1 Hz), 112.08 (d, J = 9.3 Hz), 109.72, 109.40, 105.98 (d, J = 23.8 Hz); IR (ATR, cm^{-1}): ν = 3412 (m), 3051 (w), 2918 (w), 1610 (m), 1593 (m), 1585 (m), 1487 (m), 1464 (m), 1450 (s), 1362 (m), 1336 (m), 1317 (m), 1282 (m), 1271 (m), 1248 (m), 1230 (s), 1169 (s), 1157 (s), 1122 (m), 1111 (m), 1095 (m), 1053 (m), 1024 (m), 1014 (m), 999 (m), 978 (m), 935 (m), 912 (m), 860 (m), 849 (m), 816 (s), 800 (m), 779 (m), 750 (vs), 723 (vs), 710 (s), 663 (s), 654 (m), 638 (m), 615 (m), 594 (s), 575 (m), 563 (s), 540 (m), 528 (m); GC-MS (EI, 70 eV): m/z (%) = 350 (100), 175 (11), 157 (6); HRMS (EI): calcd. for $\text{C}_{24}\text{H}_{15}\text{FN}_2$ ($[\text{M}]^+$): 350.12138; found: 350.12096.

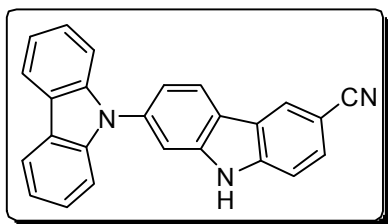


6-(tert-Butyl)-9H-2,9'-biscarbazole 7g. The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 4-(tert-butyl)aniline (45 μL , 0.281

mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **7g** (60 mg, 60 %) as a white solid; mp 238-239 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 11.36 (s, 1H), 8.42 (d, *J* = 8.2 Hz, 1H), 8.26 (dd, *J* = 13.1, 4.6 Hz, 3H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.62 – 7.40 (m, 6H), 7.38 – 7.26 (m, *J* = 11.4, 6.7, 2.9 Hz, 3H), 1.45 (s, 10H); ¹³C NMR (75 MHz, DMSO-d₆) δ 141.59, 140.71, 140.67, 138.62, 133.89, 126.18, 123.85, 122.62, 122.17, 121.84, 121.42, 120.50, 119.86, 117.00, 116.33, 110.65, 109.74, 109.07, 34.45, 31.87; IR (ATR, cm⁻¹): ν = 3400 (m), 3080 (w), 3051 (w), 3020 (w), 2956 (m), 2899 (w), 2866 (w), 1608 (m), 1500 (m), 1477 (m), 1462 (m), 1450 (s), 1429 (m), 1381 (w), 1363 (m), 1331 (m), 1313 (m), 1294 (m), 1279 (w), 1255 (m), 1246 (m), 1232 (s), 1207 (w), 1155 (m), 1140 (m), 1117 (w), 980 (w), 928 (w), 918 (w), 889 (w), 839 (m), 812 (s), 746 (vs), 723 (s), 702 (w), 665 (s), 634 (s), 615 (m), 565 (m); GC-MS (EI, 70 eV): *m/z* (%) = 388 (100), 373 (79), 332 (13), 207 (12), 187 (16), 172 (32), 41 (10); HRMS (EI): calcd. for C₂₈H₂₄N₂ ([M]⁺): 388.19340; found: 388.19264.

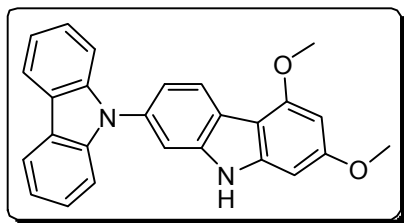


6-Methyl-9H-2,9'-biscarbazole 7h. The product was prepared following general procedure using compound **6b** (100 mg, 0.256 mmol) and *p*-toluidine (31 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **7h** (45 mg, 51 %) as a white solid; mp 287-289 °C; ¹H NMR (250 MHz, DMSO-d₆) δ 11.36 (s, 2H), 8.29 (dd, *J* = 14.4, 8.0 Hz, 7H), 8.01 (s, 2H), 7.64 (d, *J* = 1.6 Hz, 2H), 7.45 (dd, *J* = 8.4, 3.6 Hz, 11H), 7.40 – 7.20 (m, 10H), 2.49 (s, 1H); ¹³C NMR (63 MHz, DMSO-d₆) δ 140.70, 140.64, 138.77, 134.06, 127.79, 127.38, 126.23, 122.65, 122.27, 121.75, 121.44, 120.53, 120.17, 119.91, 117.11, 110.95, 109.81, 109.15, 21.18; IR (ATR, cm⁻¹): ν = 3417 (m), 3047 (w), 2916 (w), 2850 (w), 1608 (m), 1595 (m), 1504 (m), 1489 (m), 1477 (m), 1450 (s), 1377 (m), 1362 (m), 1335 (m), 1315 (m), 1304 (m), 1294 (m), 1277 (m), 1244 (m), 1230 (s), 1174 (m), 1155 (m), 1146 (m), 1134 (m), 1120 (m), 1095 (m), 1039 (m), 1024 (m), 980 (m), 935 (m), 916 (m), 876 (m), 860 (m), 847 (m), 818 (m), 804 (s), 750 (vs), 723 (vs), 663 (s), 654 (m), 638 (m), 615 (m), 584 (s), 563 (s), 532 (m); GC-MS (EI, 70 eV): *m/z* (%) = 346 (100), 330 (9), 173 (9); HRMS (EI): calcd. for C₂₅H₁₈N₂ ([M]⁺): 346.14645; found: 346.14639.



9H-[2,9'-Biscarbazole]-6-carbonitrile 7i. The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 4-aminobenzonitrile (33 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:5) to yield **7i** (19 mg, 21

%) as a white solid; mp 297-299 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 12.06 (s, 1H), 8.83 (d, J = 1.1 Hz, 1H), 8.52 (d, J = 8.3 Hz, 1H), 8.27 (d, J = 7.7 Hz, 2H), 7.85 – 7.77 (m, 2H), 7.77 – 7.69 (m, 1H), 7.55 – 7.38 (m, 5H), 7.38 – 7.25 (m, 2H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 142.47, 141.05, 140.52, 135.54, 128.98, 126.29, 125.91, 122.74, 122.49, 122.37, 121.00, 120.56, 120.48, 120.08, 118.74, 112.35, 109.86, 109.77, 100.84; IR (ATR, cm^{-1}): ν = 3284 (w), 3059 (w), 2918 (w), 2848 (w), 2229 (m), 1603 (s), 1477 (s), 1450 (s), 1435 (m), 1396 (m), 1365 (m), 1335 (s), 1319 (m), 1308 (m), 1288 (m), 1254 (s), 1228 (s), 1200 (m), 1155 (m), 1146 (m), 1132 (m), 1120 (m), 1097 (m), 1016 (m), 1003 (m), 914 (m), 899 (m), 885 (m), 847 (m), 816 (s), 810 (s), 748 (vs), 723 (s), 663 (m), 629 (s), 615 (s), 592 (m), 575 (m), 563 (m), 544 (m), 528 (m); GC-MS (EI, 70 eV): m/z (%) = 357 (100), 281 (9), 253 (8), 207 (29), 191 (15), 178 (48), 164 (15), 97 (10); HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{15}\text{N}_3$ ($[\text{M}]^+$): 357.12605; found: 357.12555.

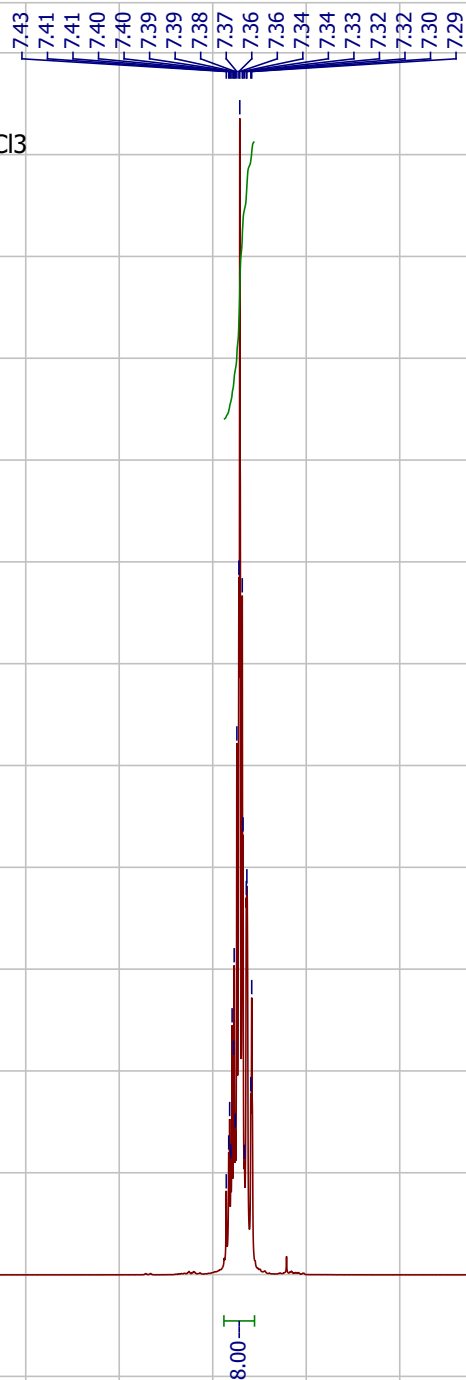


5,7-Dimethoxy-9H-2,9'-bicarbazole 7j. The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 3,5-dimethoxyaniline (43 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:4) to yield **7j** (47 mg, 47 %)

as a white solid; mp 282-284 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 10.51 (s, 1H), 7.39 (dd, J = 11.6, 8.0 Hz, 3H), 6.73 (d, J = 1.6 Hz, 1H), 6.66 – 6.51 (m, 4H), 6.48 – 6.37 (m, 3H), 5.82 (d, J = 1.8 Hz, 1H), 5.55 (d, J = 1.8 Hz, 1H), 3.18 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (63 MHz, DMSO- d_6) δ 160.12, 156.02, 142.54, 140.72, 139.47, 132.01, 126.09, 122.48, 121.97, 121.46, 120.42, 119.72, 117.48, 109.68, 108.47, 105.32, 90.99, 87.21, 55.48, 55.42; IR (ATR, cm^{-1}): ν = 3398 (s), 3003 (w), 2968 (w), 2933 (m), 2918 (m), 2839 (m), 1628 (m), 1606 (s), 1585 (s), 1574 (m), 1514 (m), 1502 (m), 1477 (m), 1446 (s), 1427 (s), 1360 (m), 1333 (m), 1315 (s), 1306 (s), 1279 (s), 1234 (s), 1223 (m), 1205 (s), 1198 (s), 1147 (s), 1124 (s), 1117 (s), 1095 (m), 1049 (s), 1020 (m), 1011 (m), 997 (m), 991 (m), 980 (m), 947 (m), 933 (m),

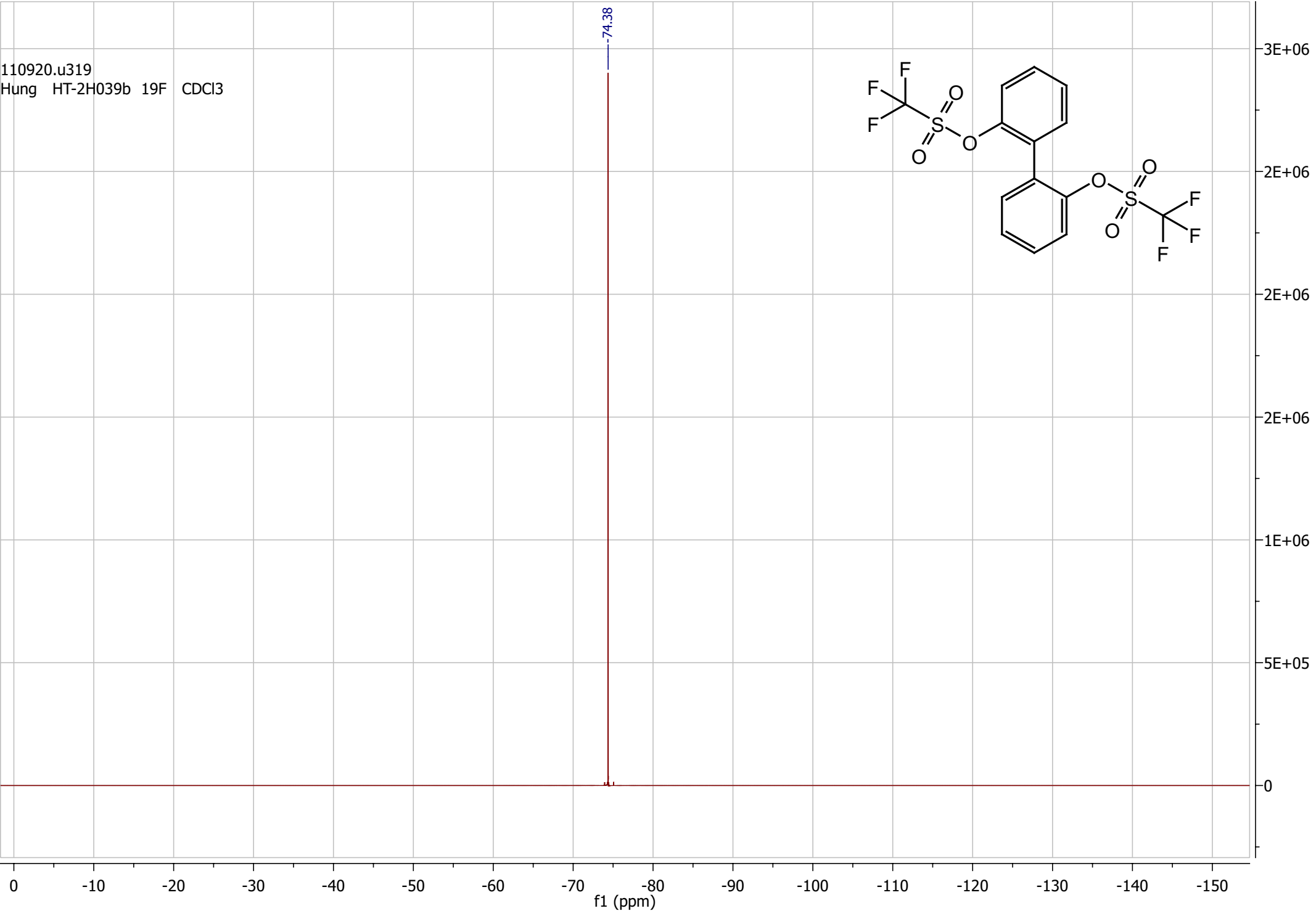
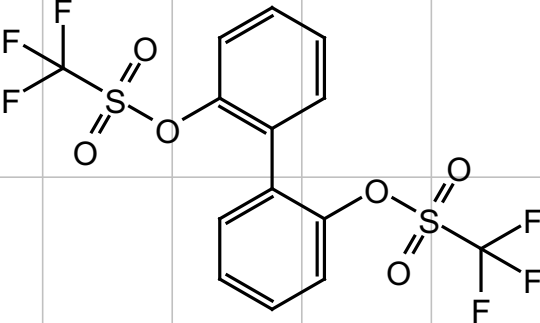
920 (m), 874 (m), 850 (m), 820 (m), 804 (vs), 789 (m), 756 (vs), 744 (s), 727 (vs), 690 (m), 665 (s), 644 (m), 633 (m), 615 (m), 598 (m), 582 (m), 569 (m), 550 (m); GC-MS (EI, 70 eV): m/z (%) = 392 (100), 377 (17), 349 (6), 334 (22), 196 (10); HRMS (ESI): calcd. for $C_{26}H_{21}N_2O_2$ ($[M + H]^+$): 393.15975; found: 393.15893; calcd. for $C_{26}H_{21}N_2O_2Na$ ($[M + Na]^+$): 415.1417; found: 415.14089.

110920.u319
Hung HT-2H039b 1H CDCl3

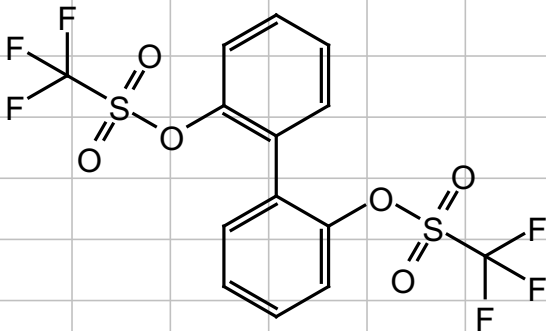
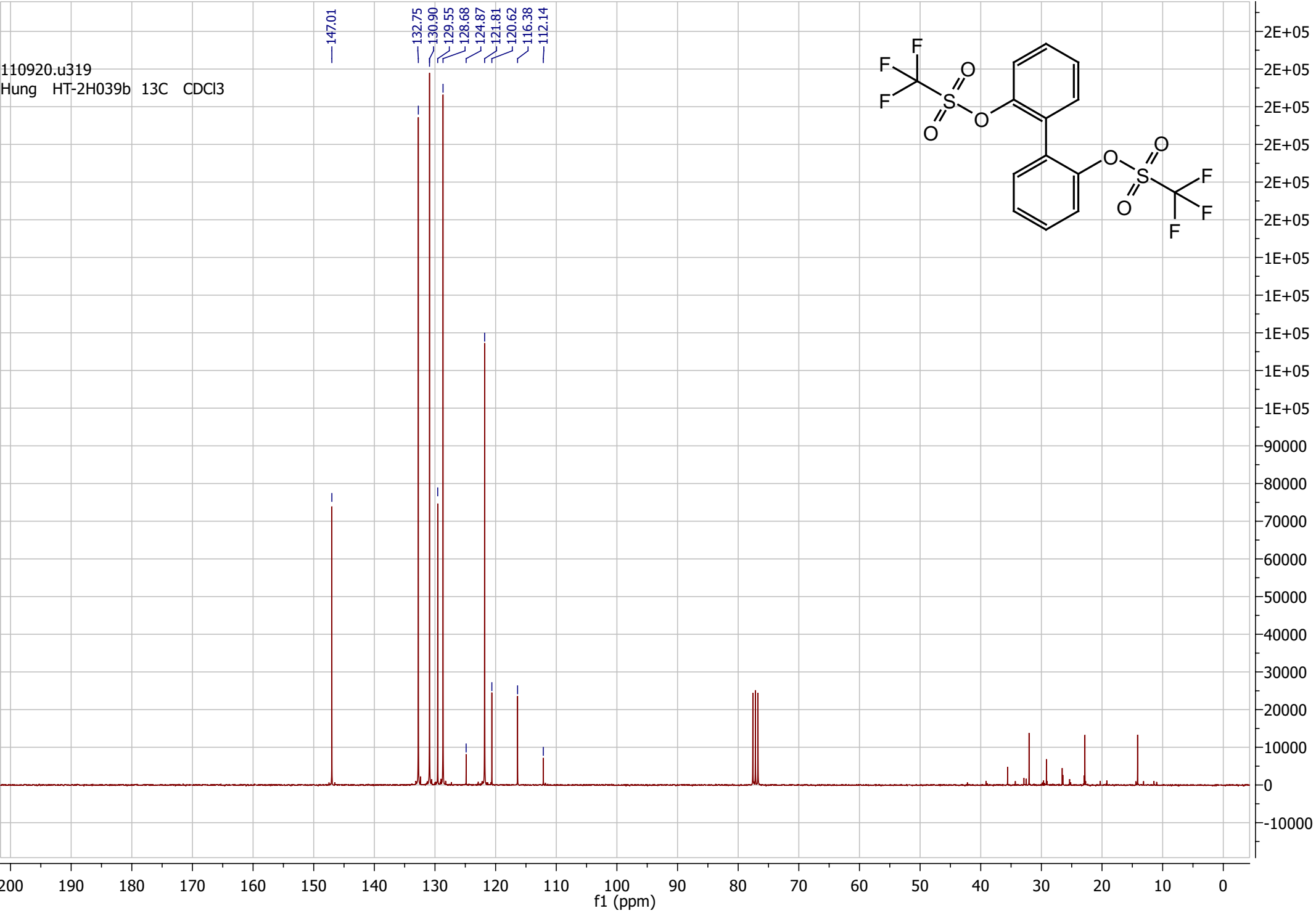


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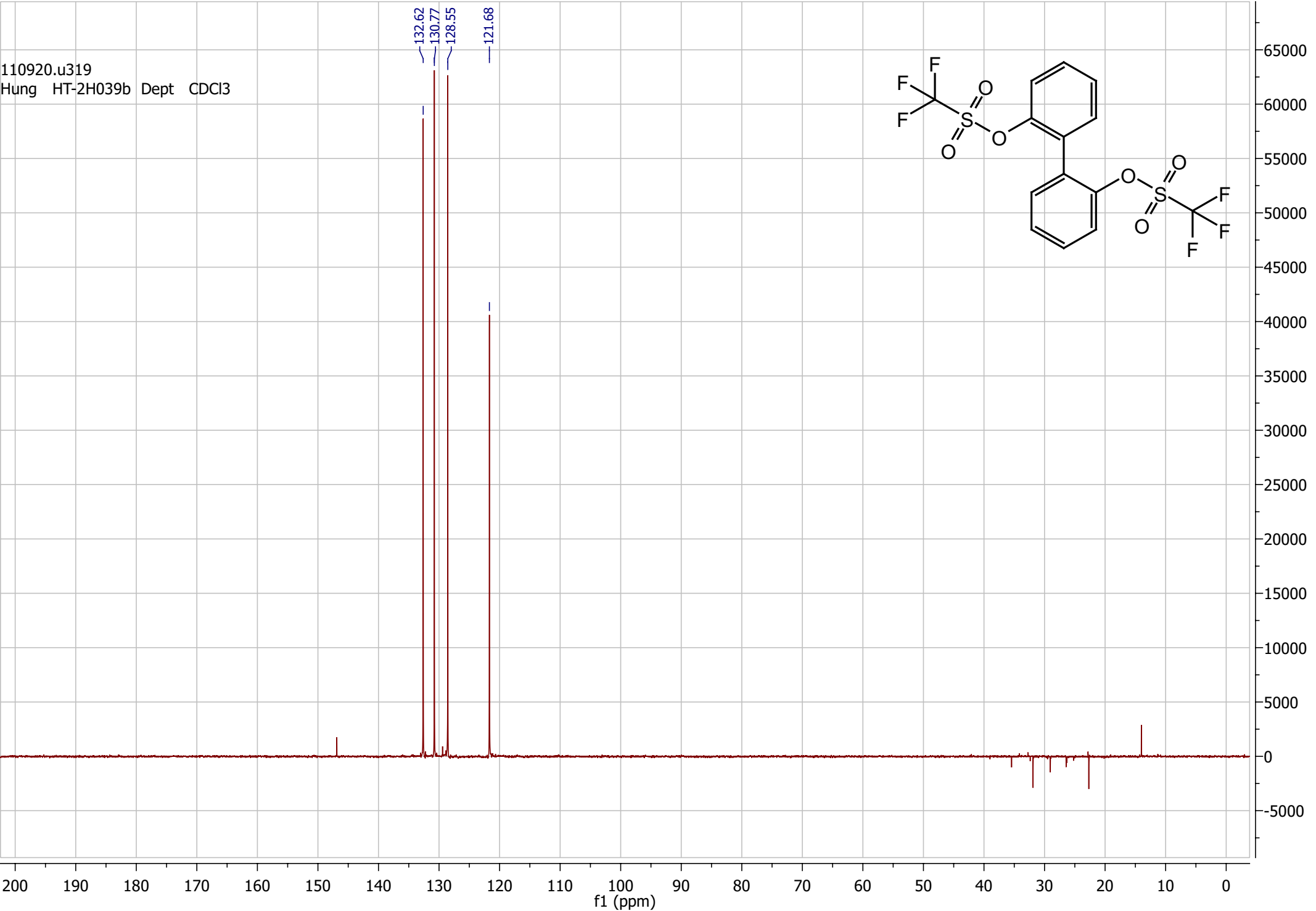
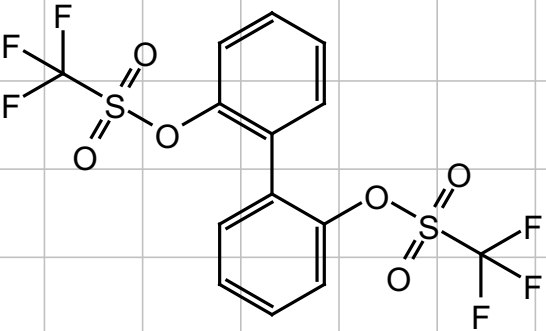
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Hung HT-2H039b 19F CDCl3



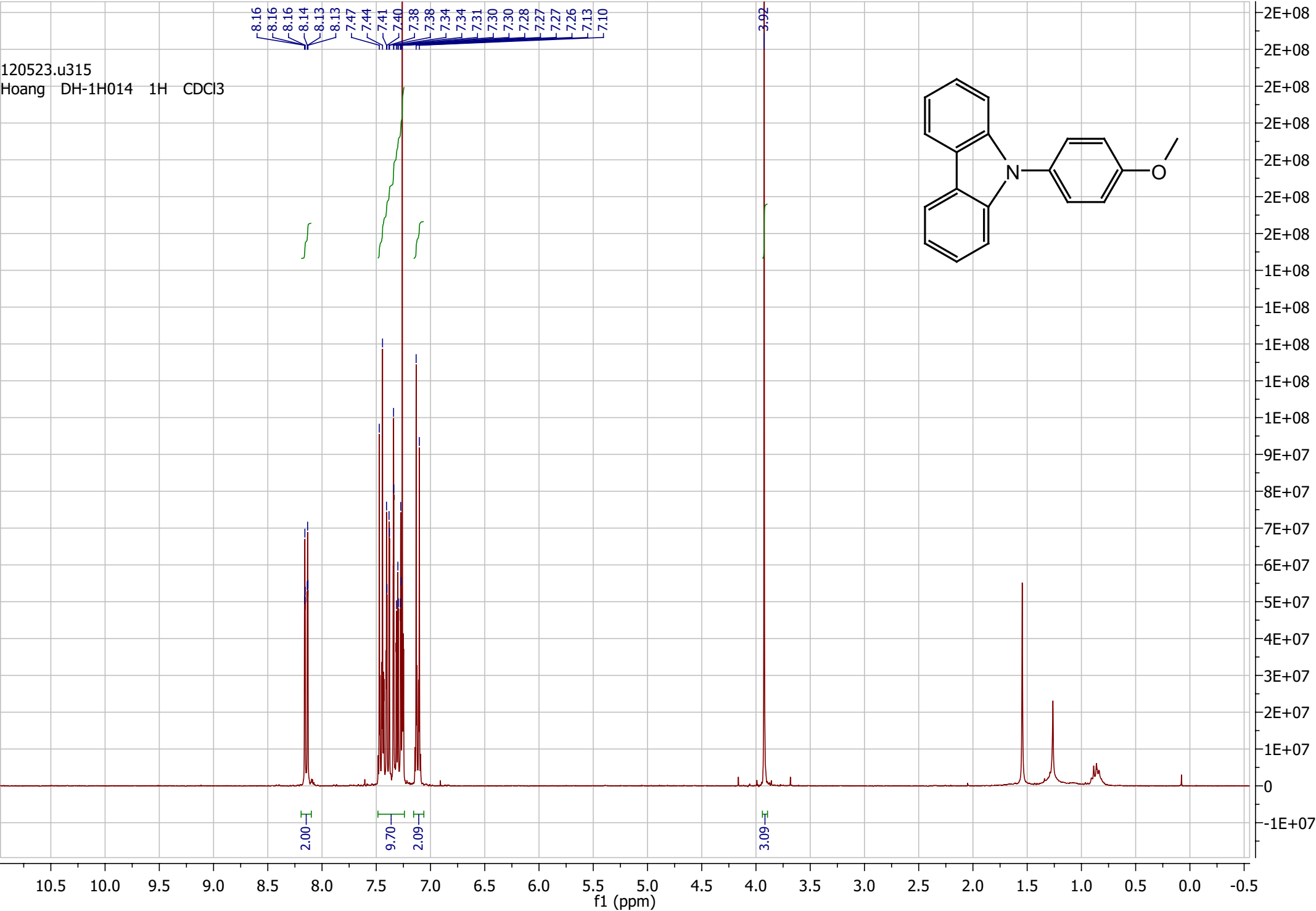
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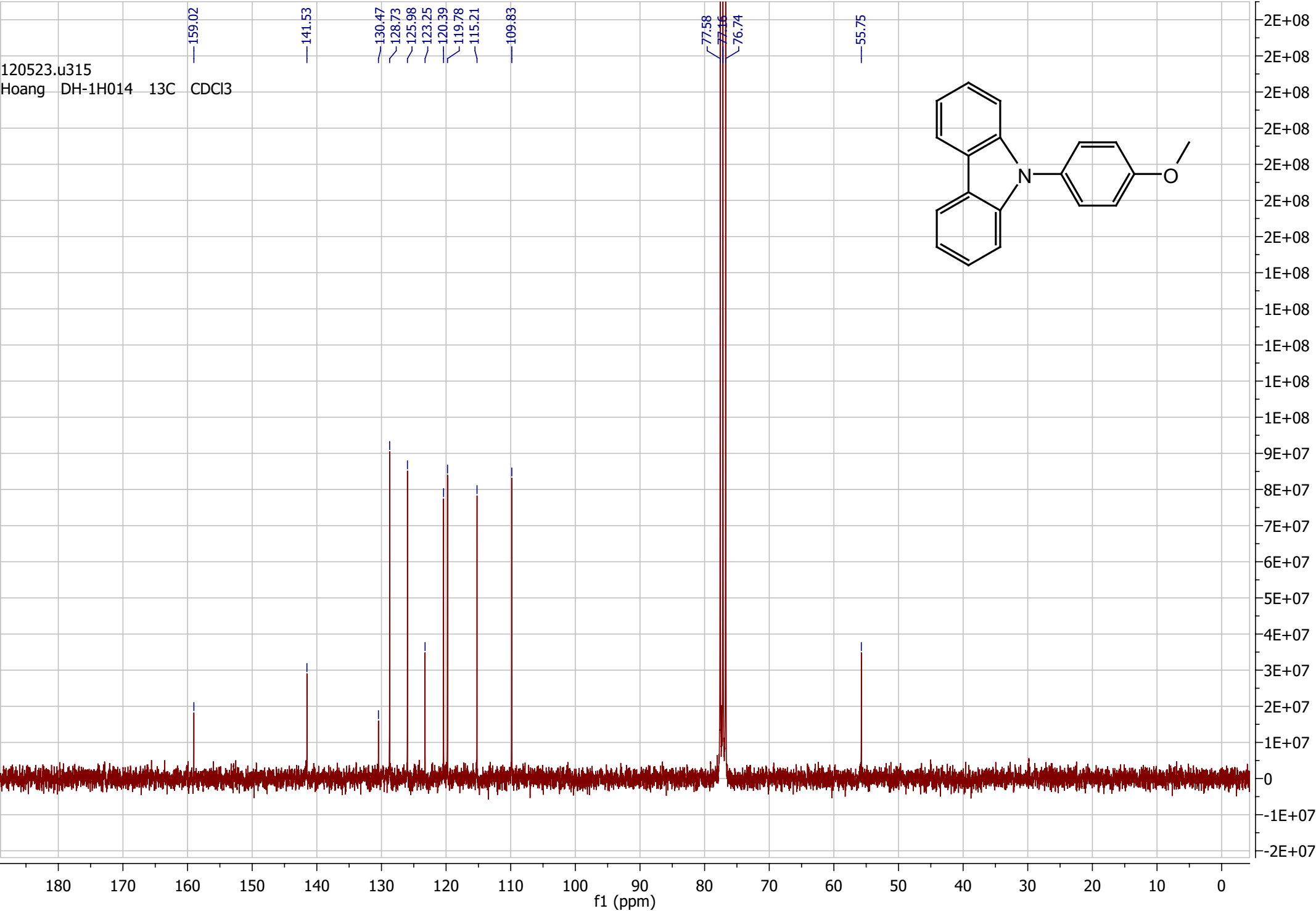
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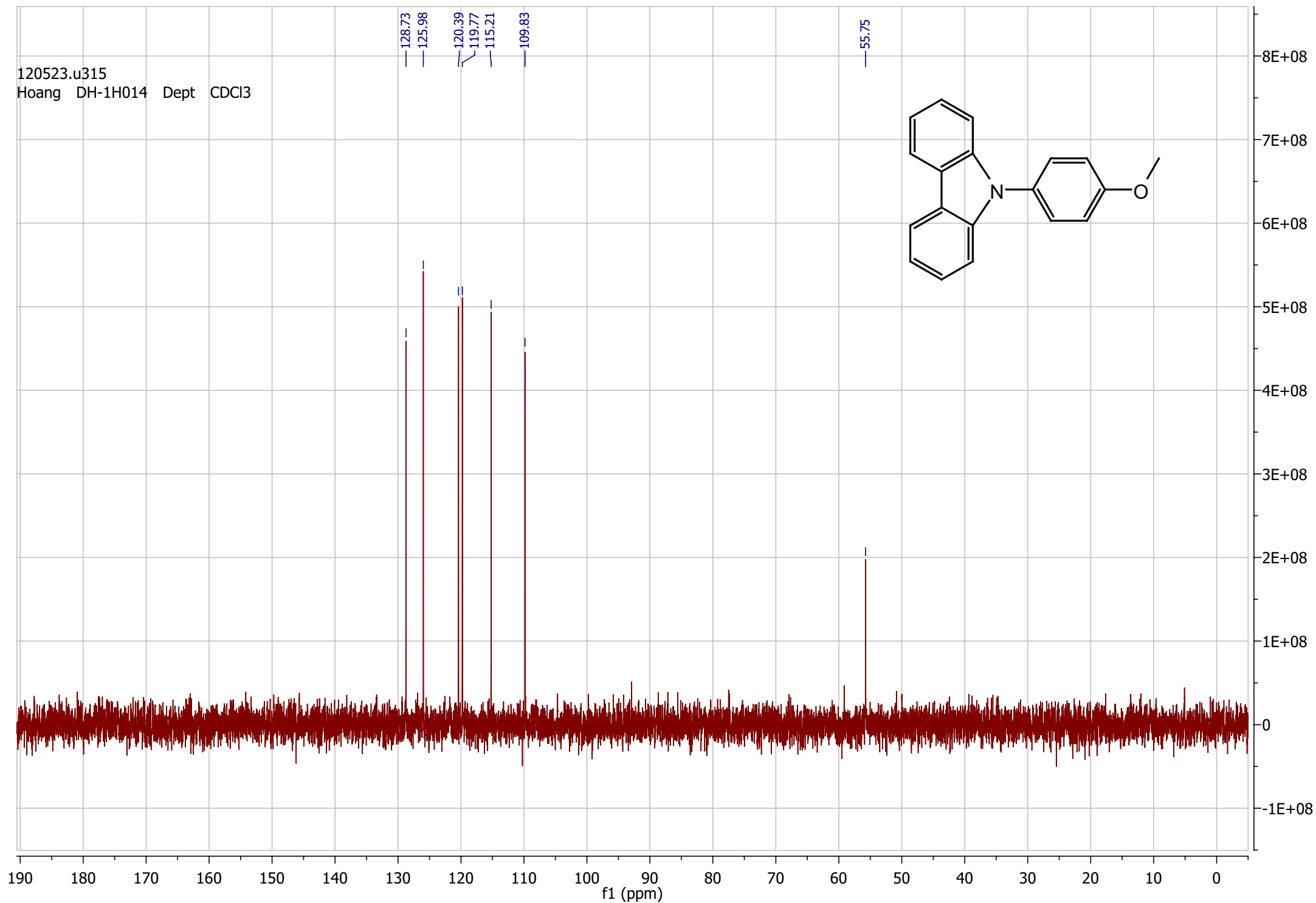
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Hoang DH-1H014 1H CDCl3



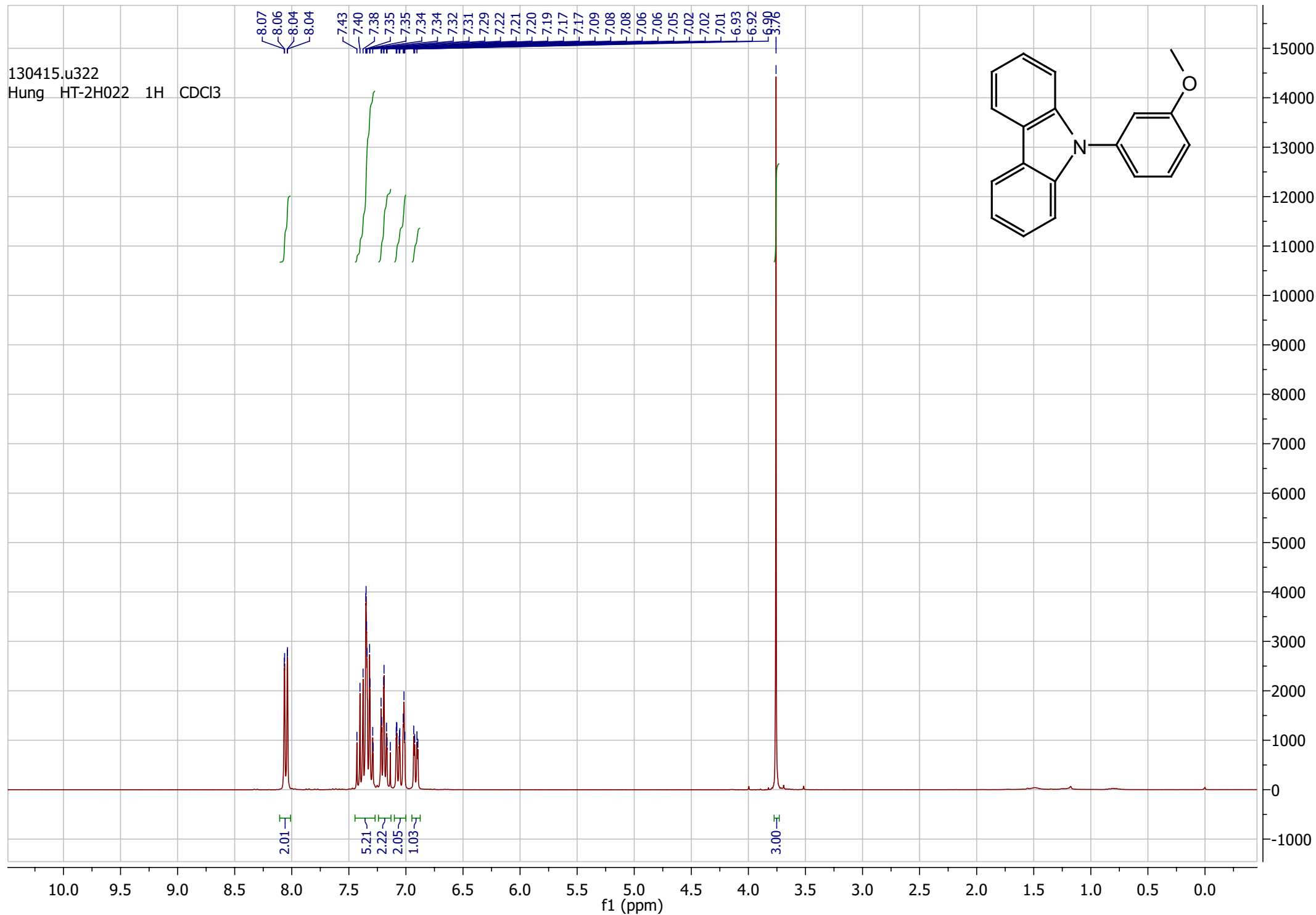
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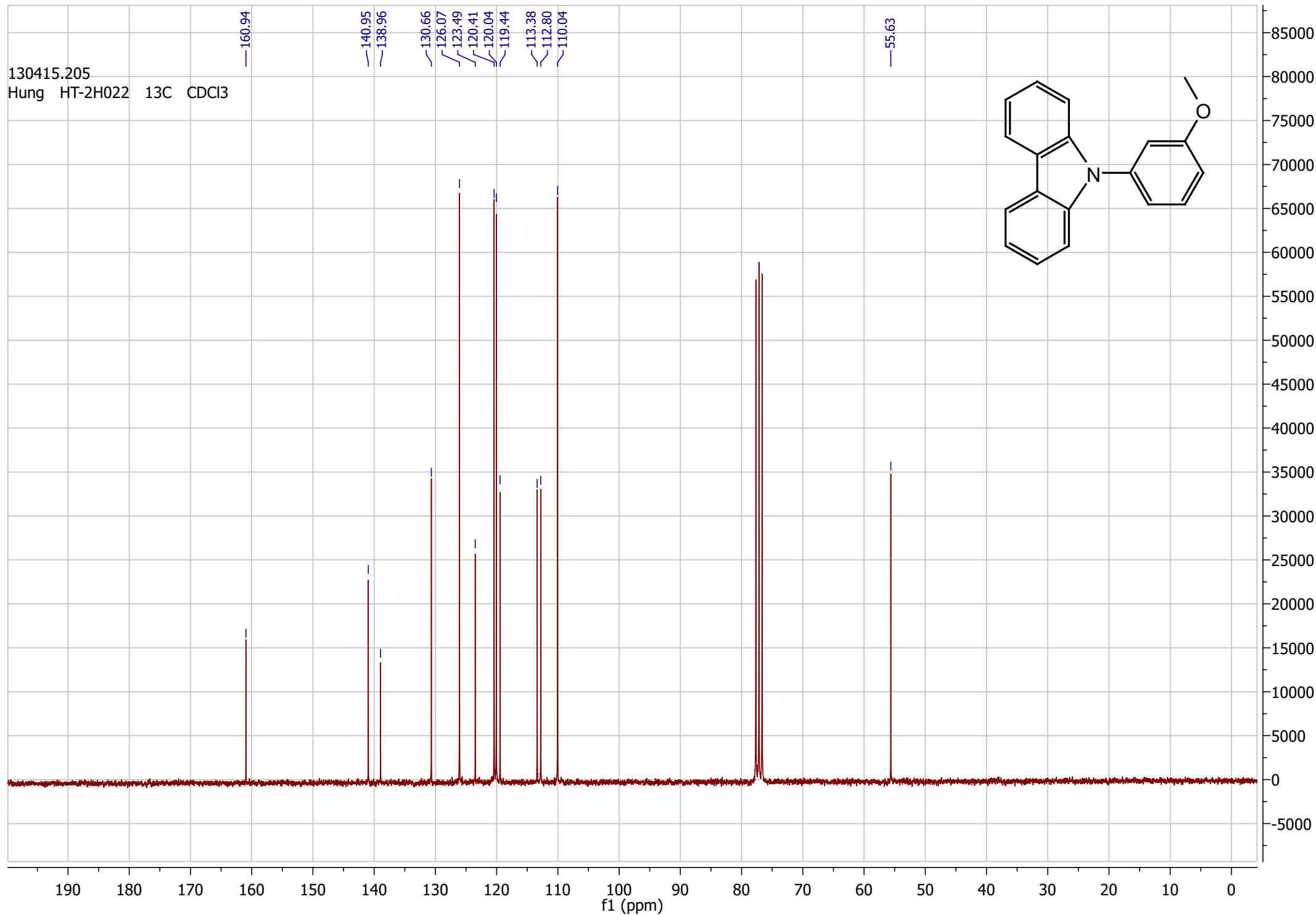


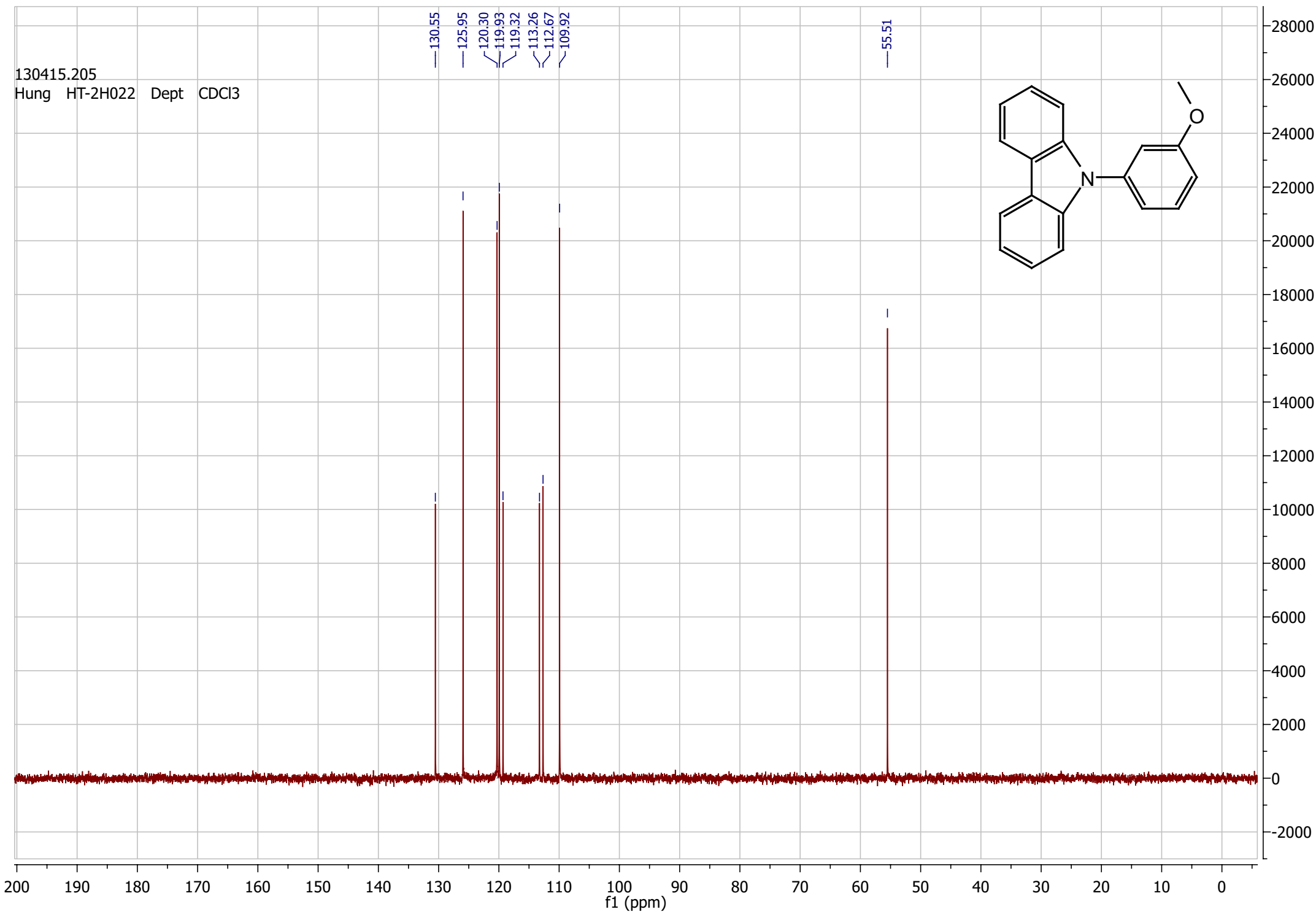
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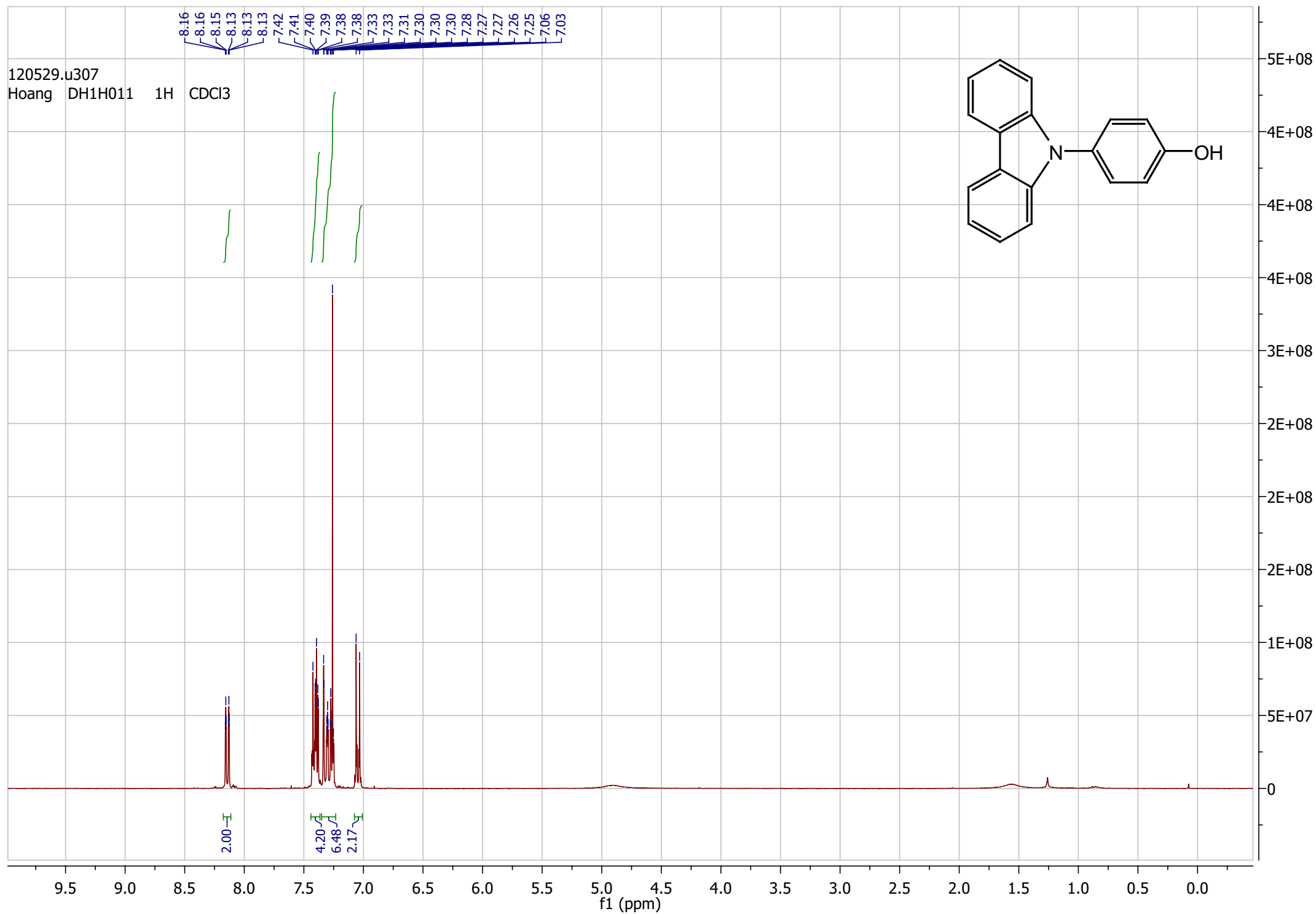


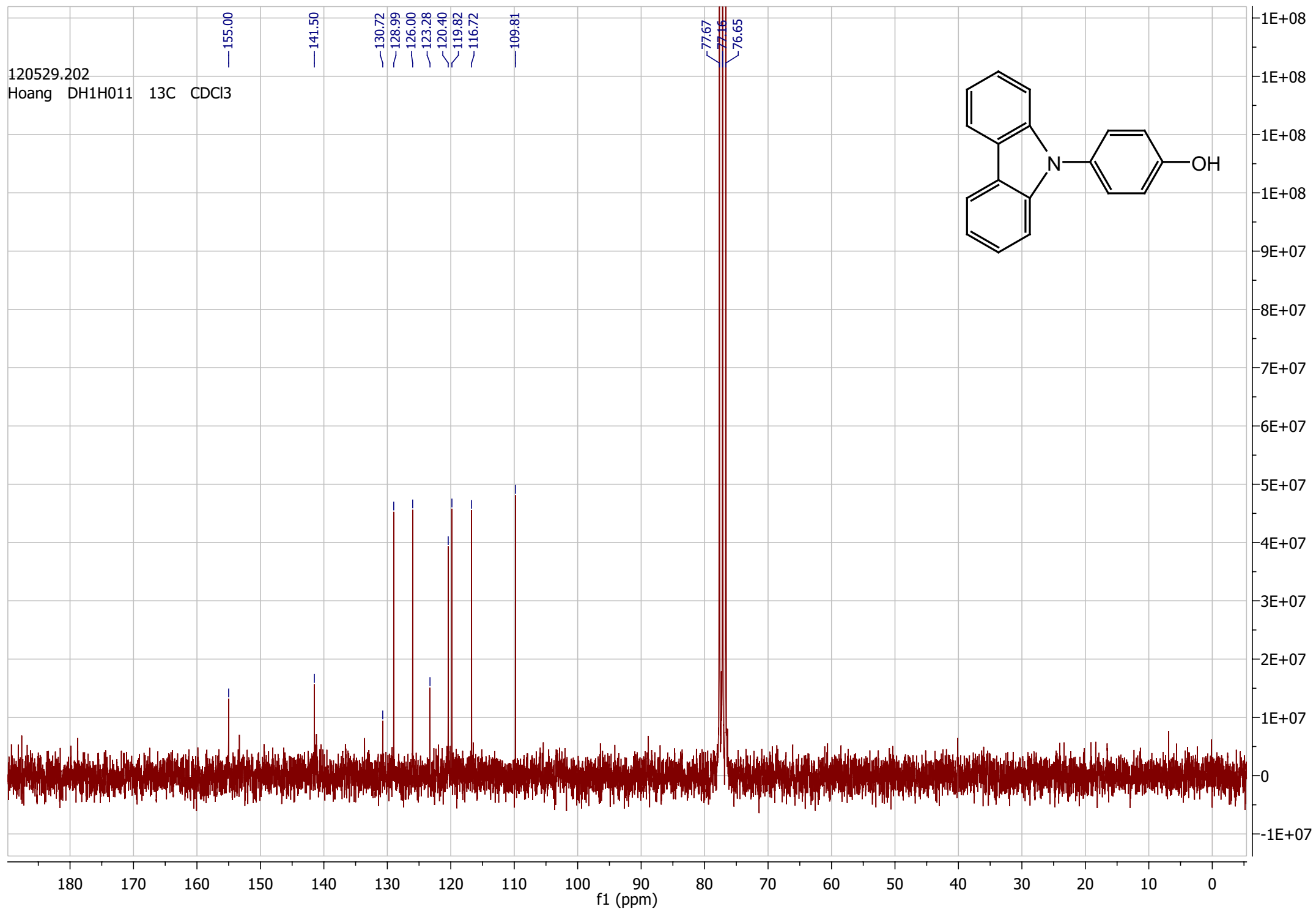
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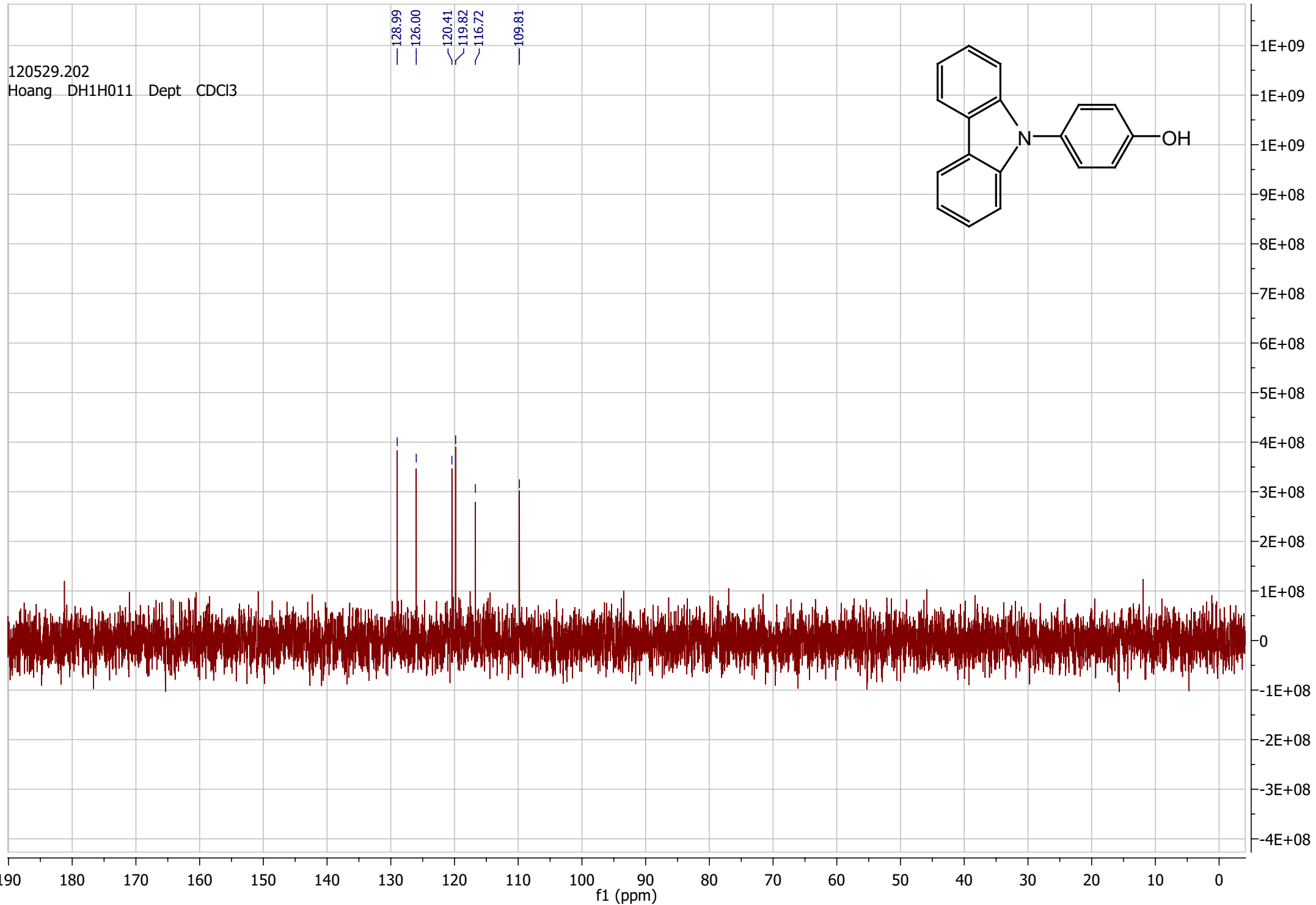


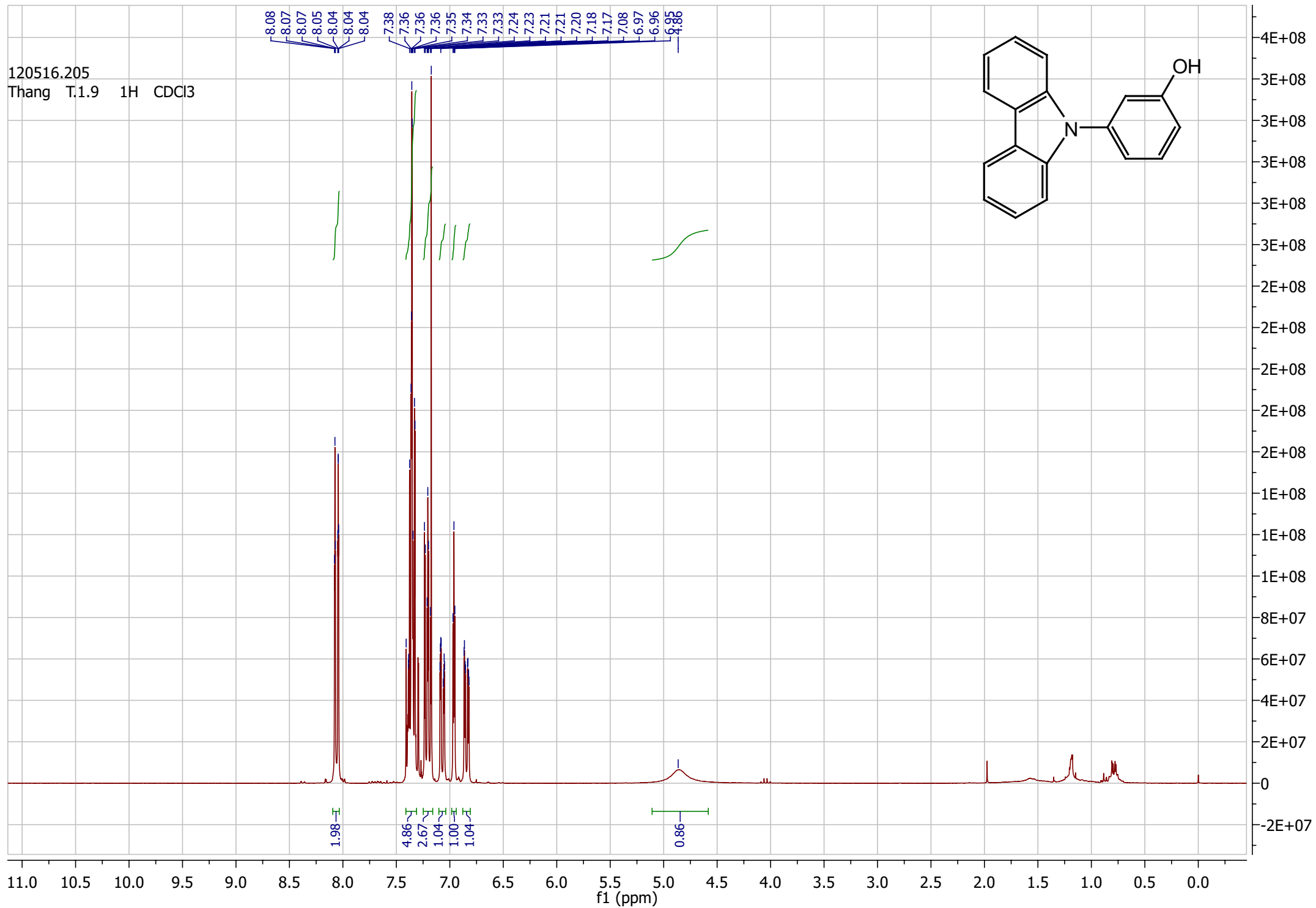


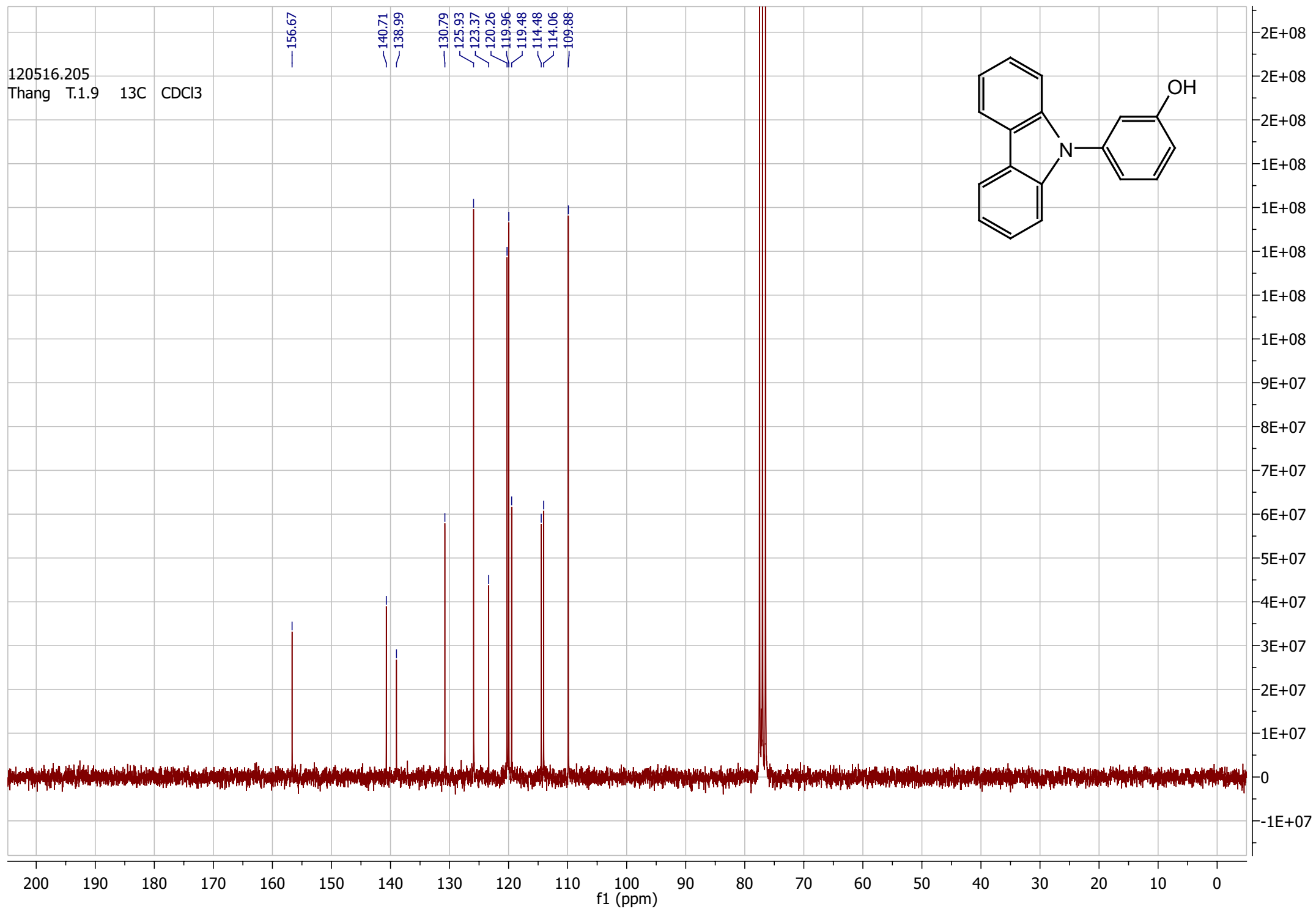






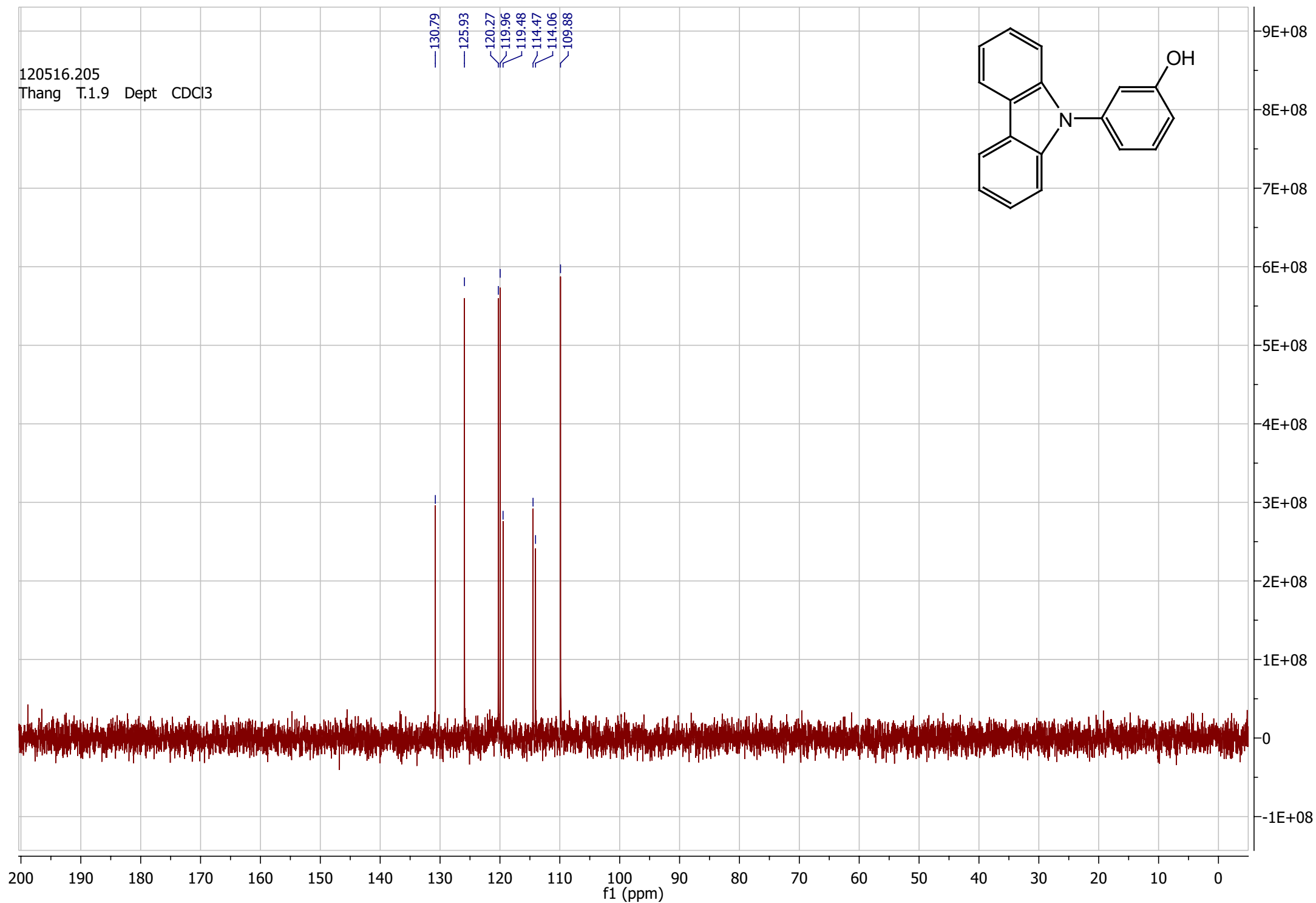
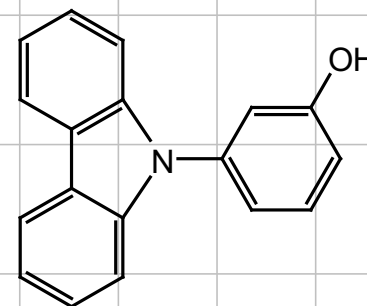




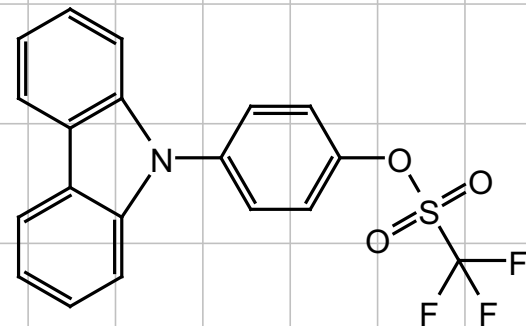
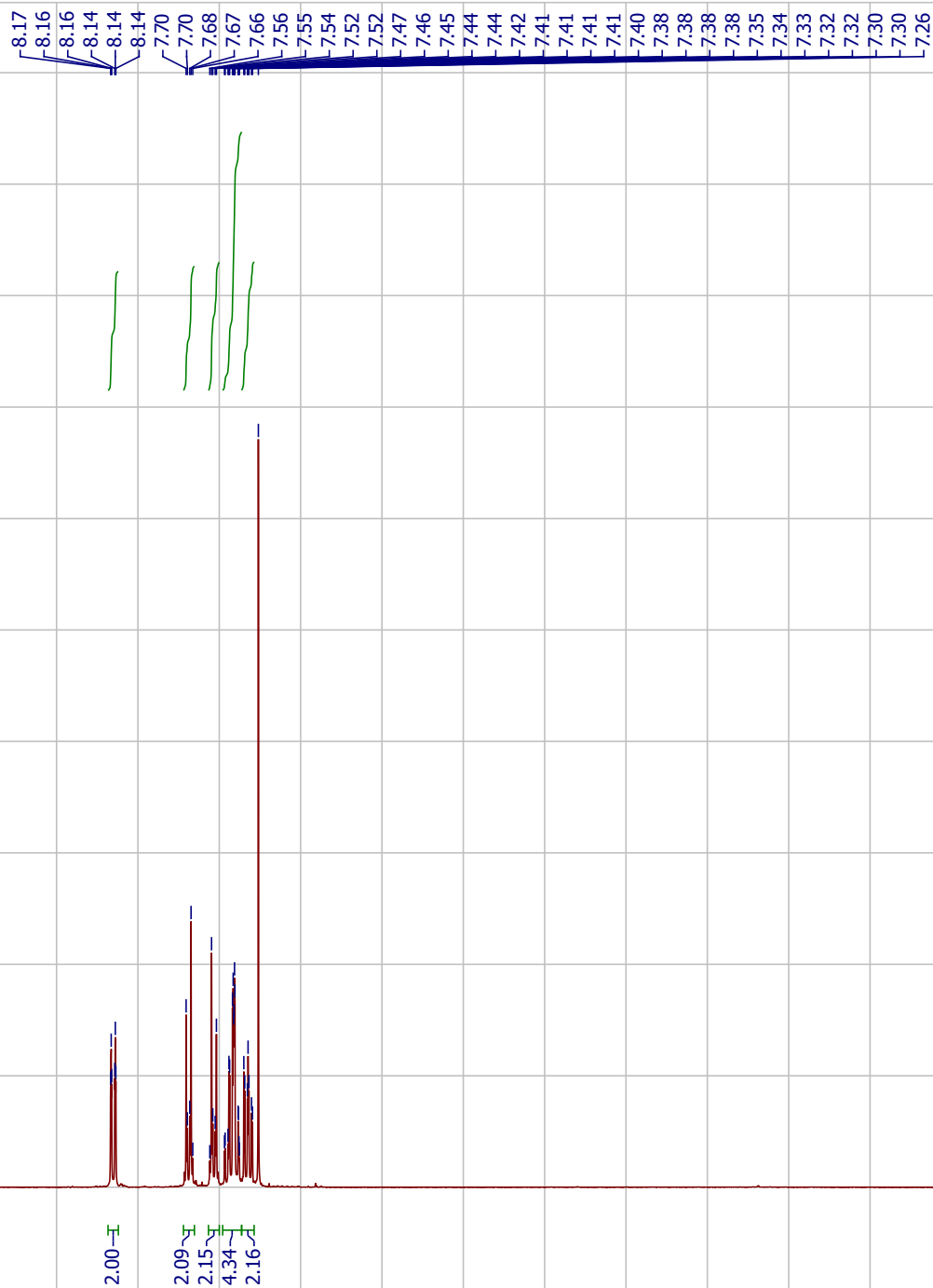


120516.205
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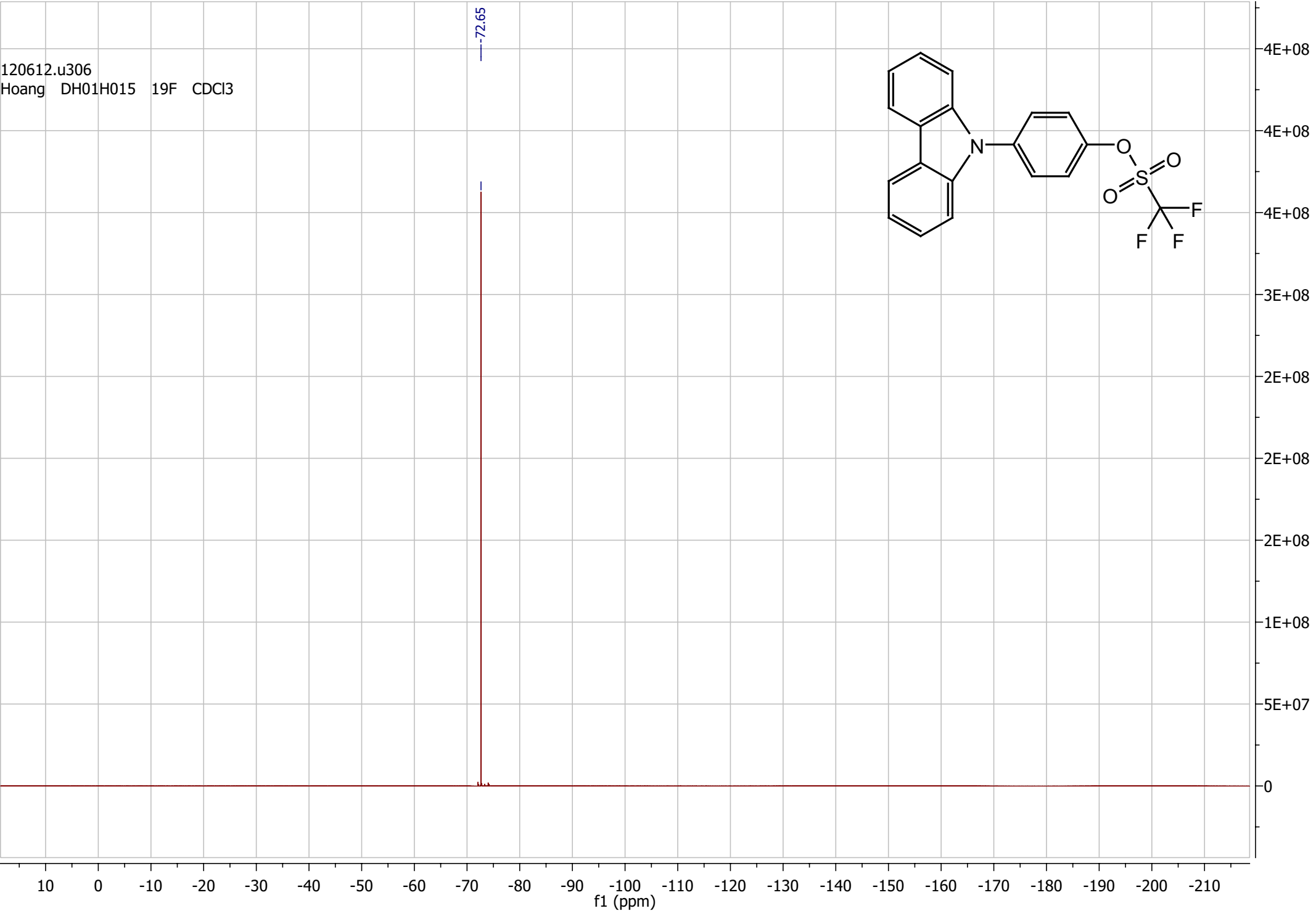
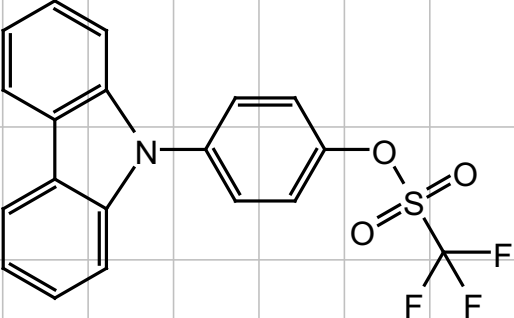
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119.48
114.47
114.06
109.88

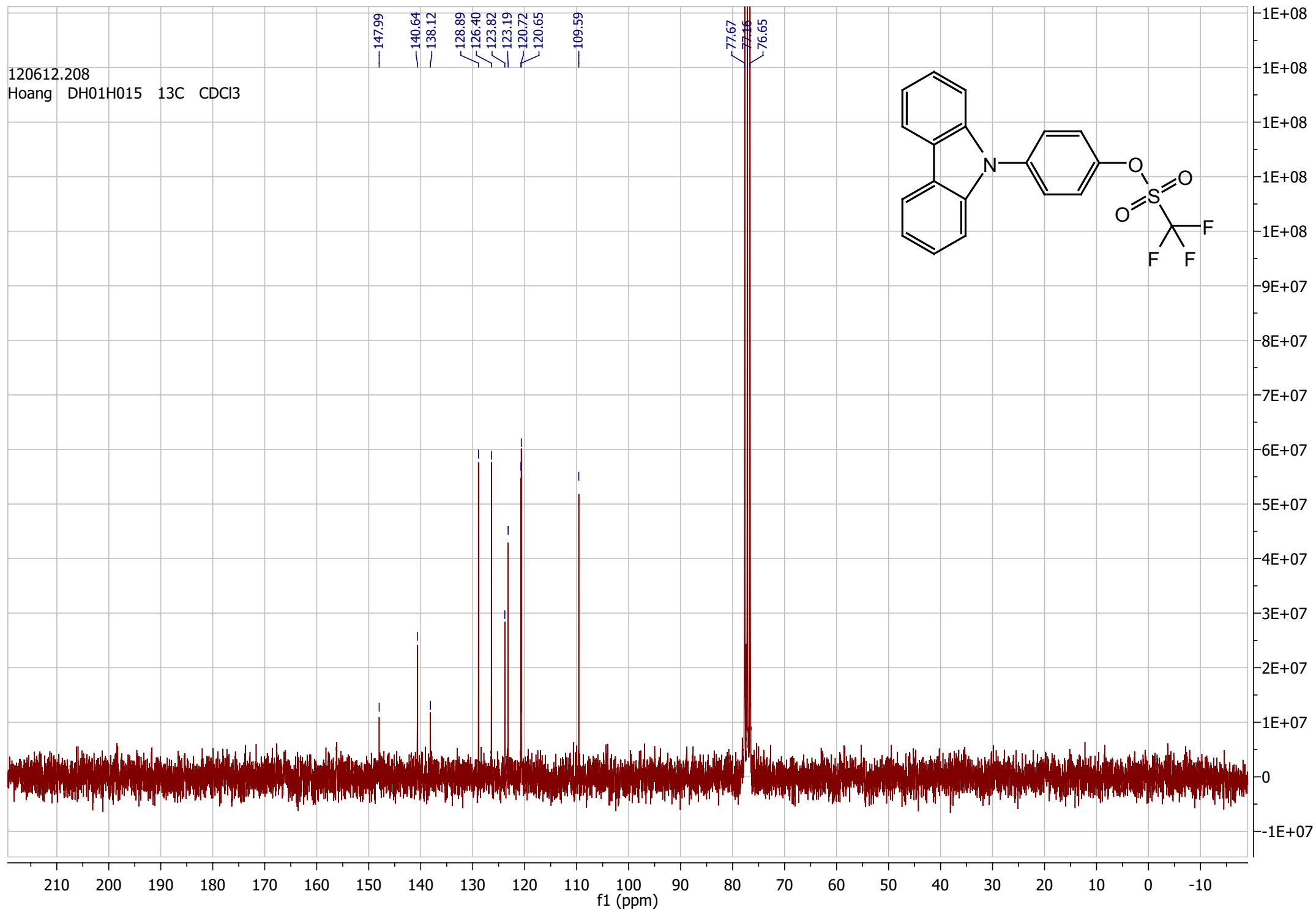


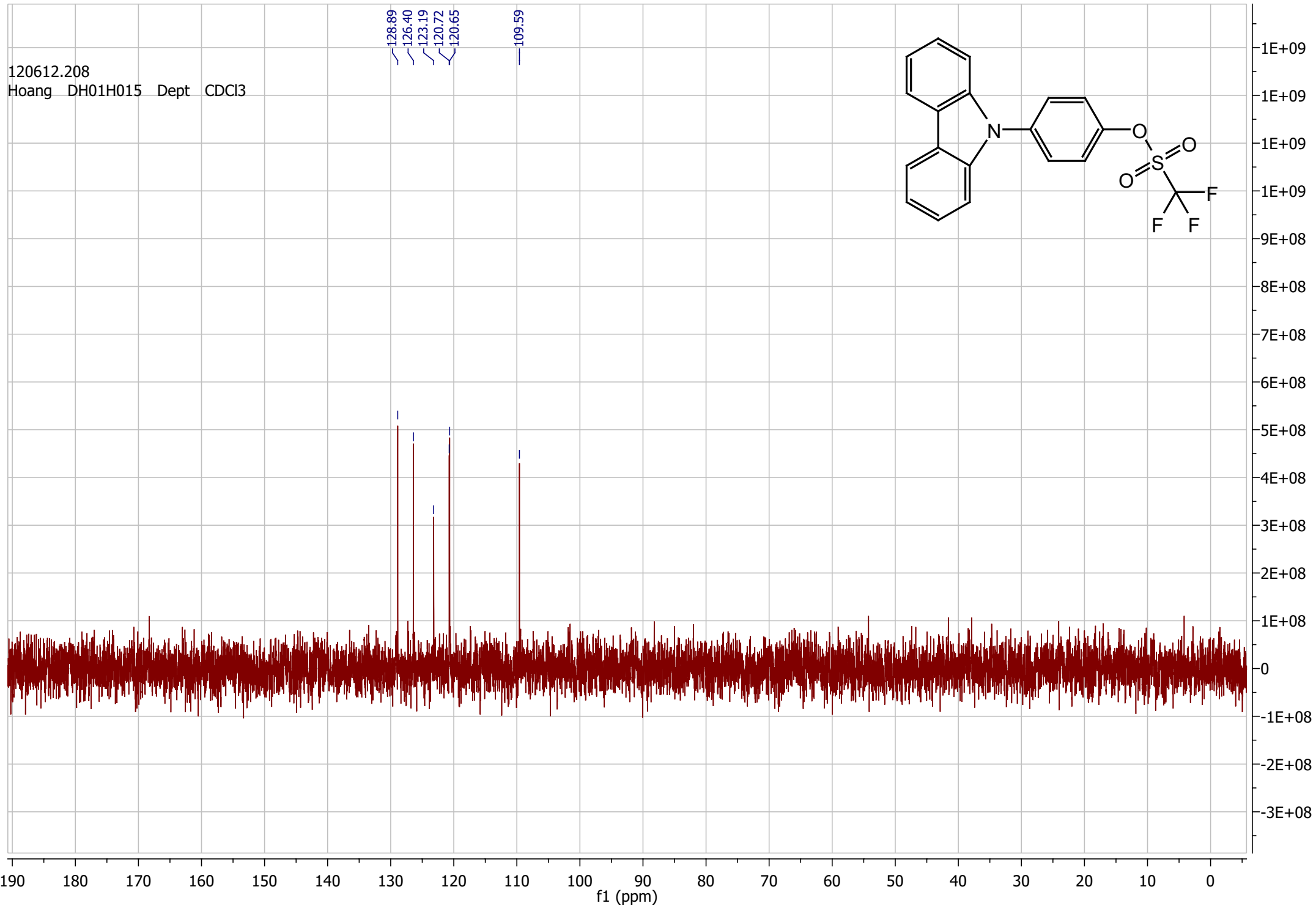
120612.u306
Hoang DH01H015 1H CDCl3



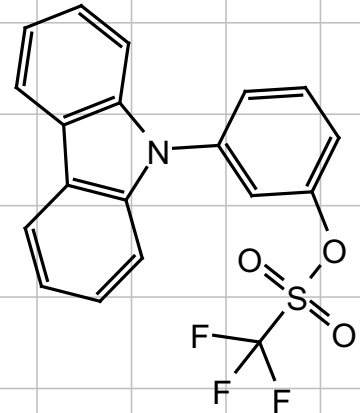
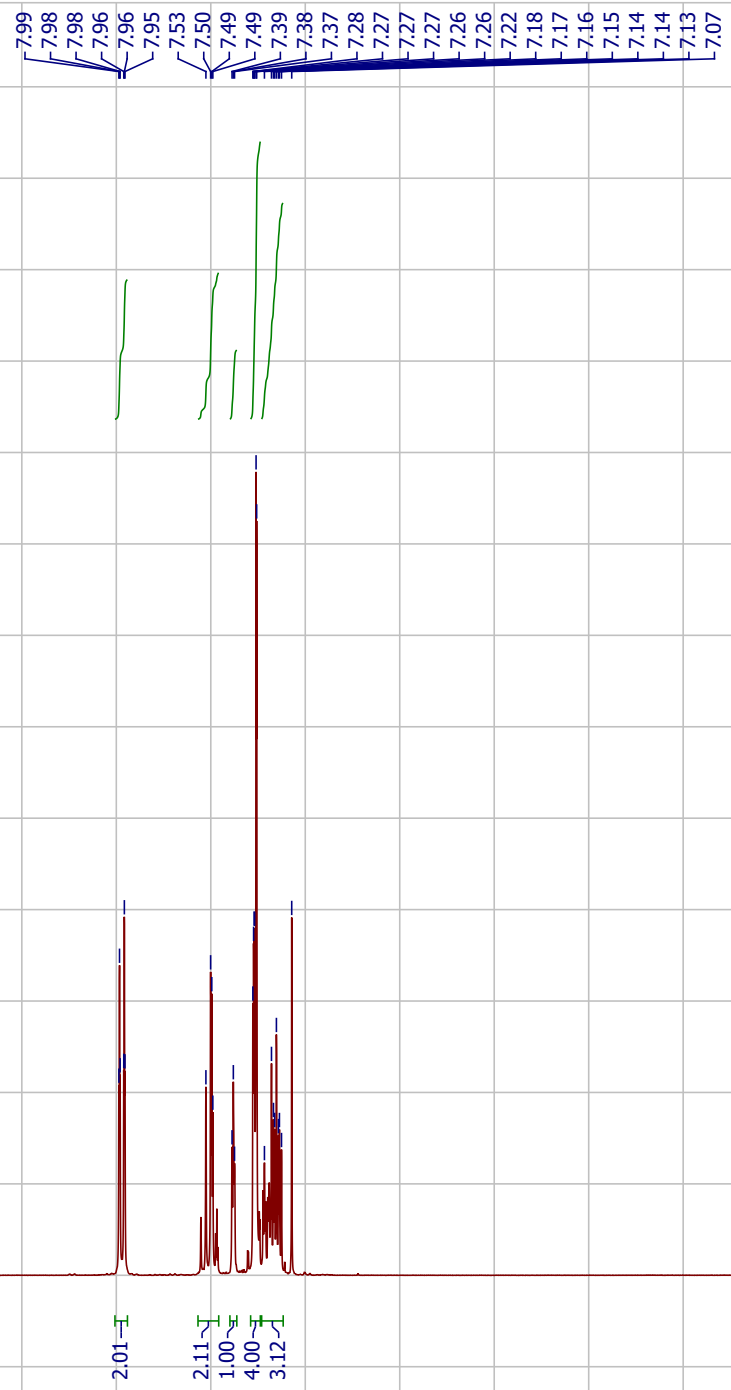
120612.u306
Hoang DH01H015 19F CDCl3







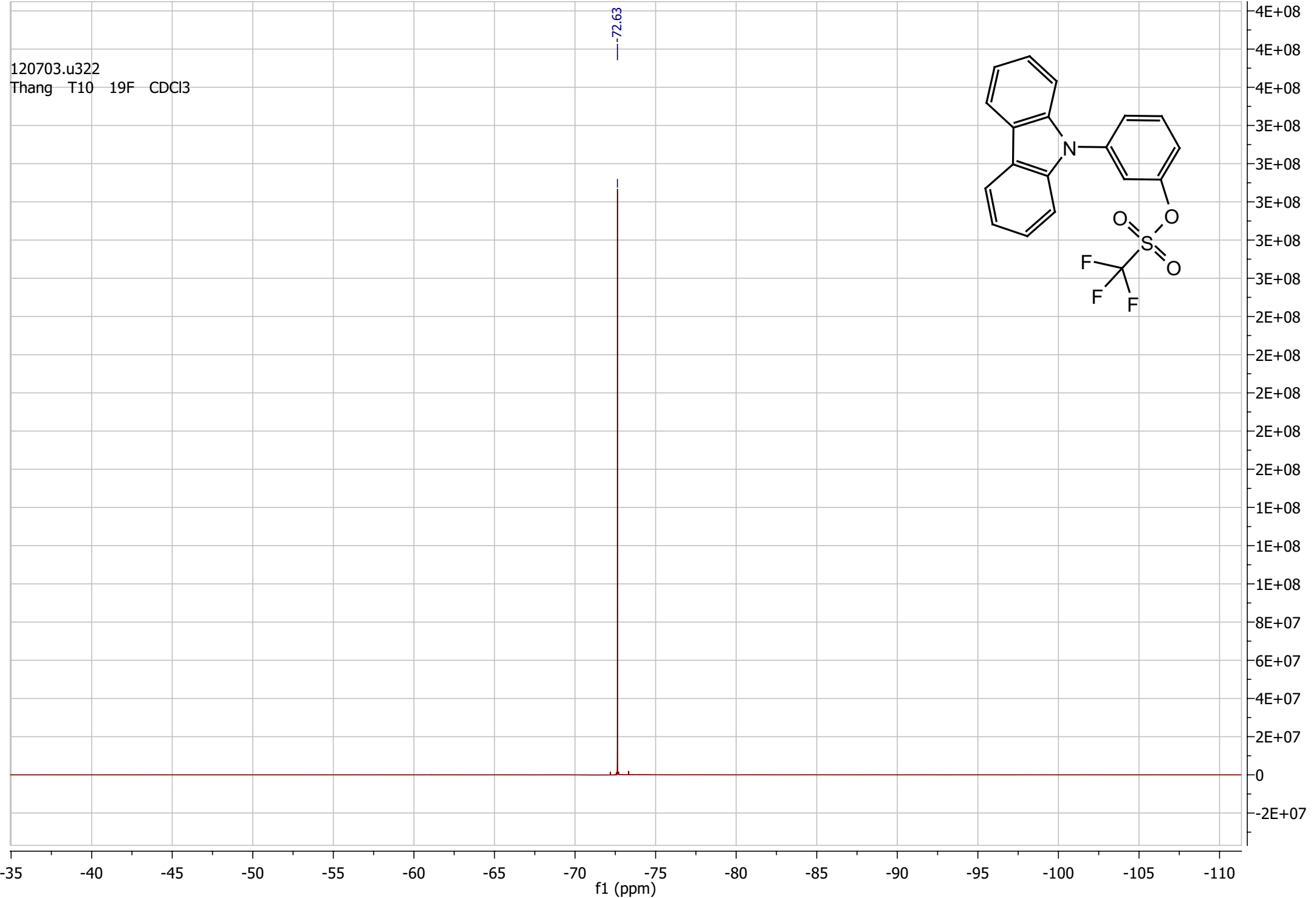
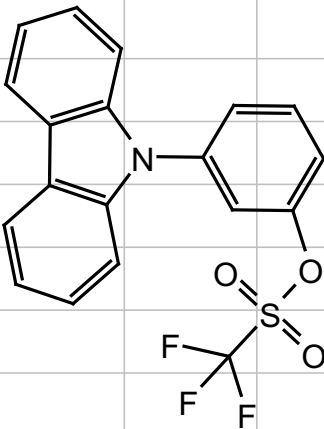
120703.u322
Thang T10 1H CDCl3



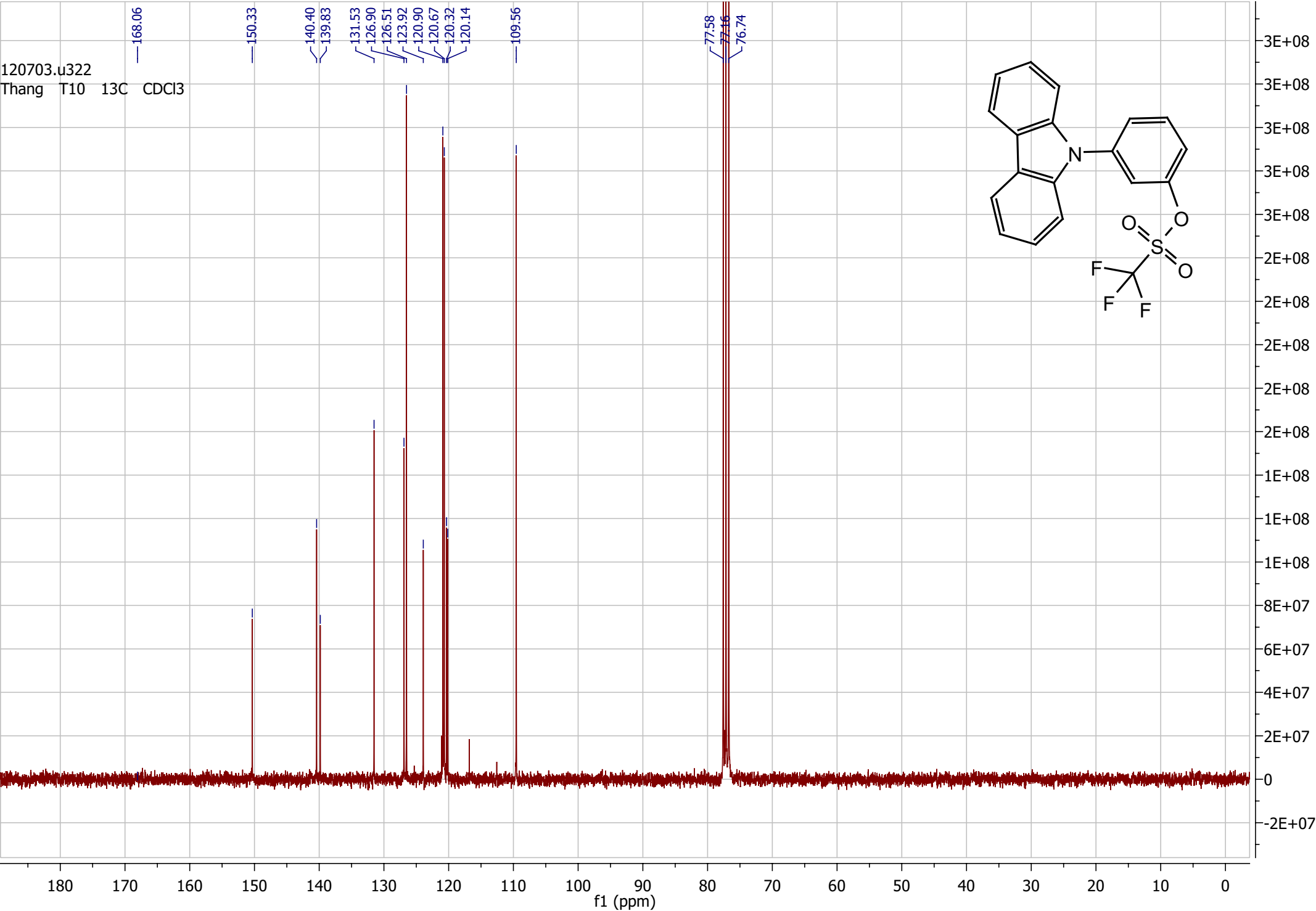
f1 (ppm)

120703.u322
Thang T10 19F CDCl3

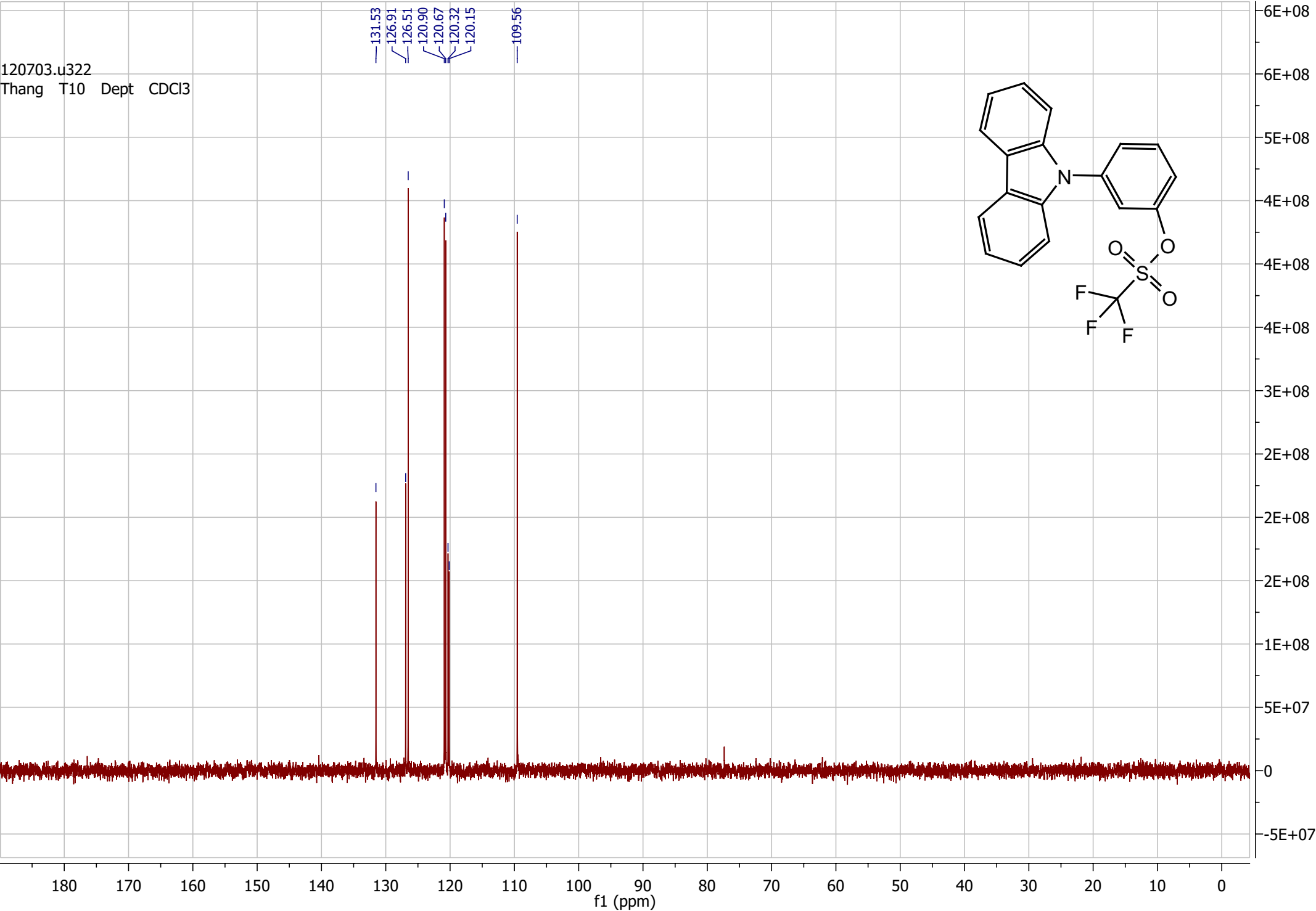
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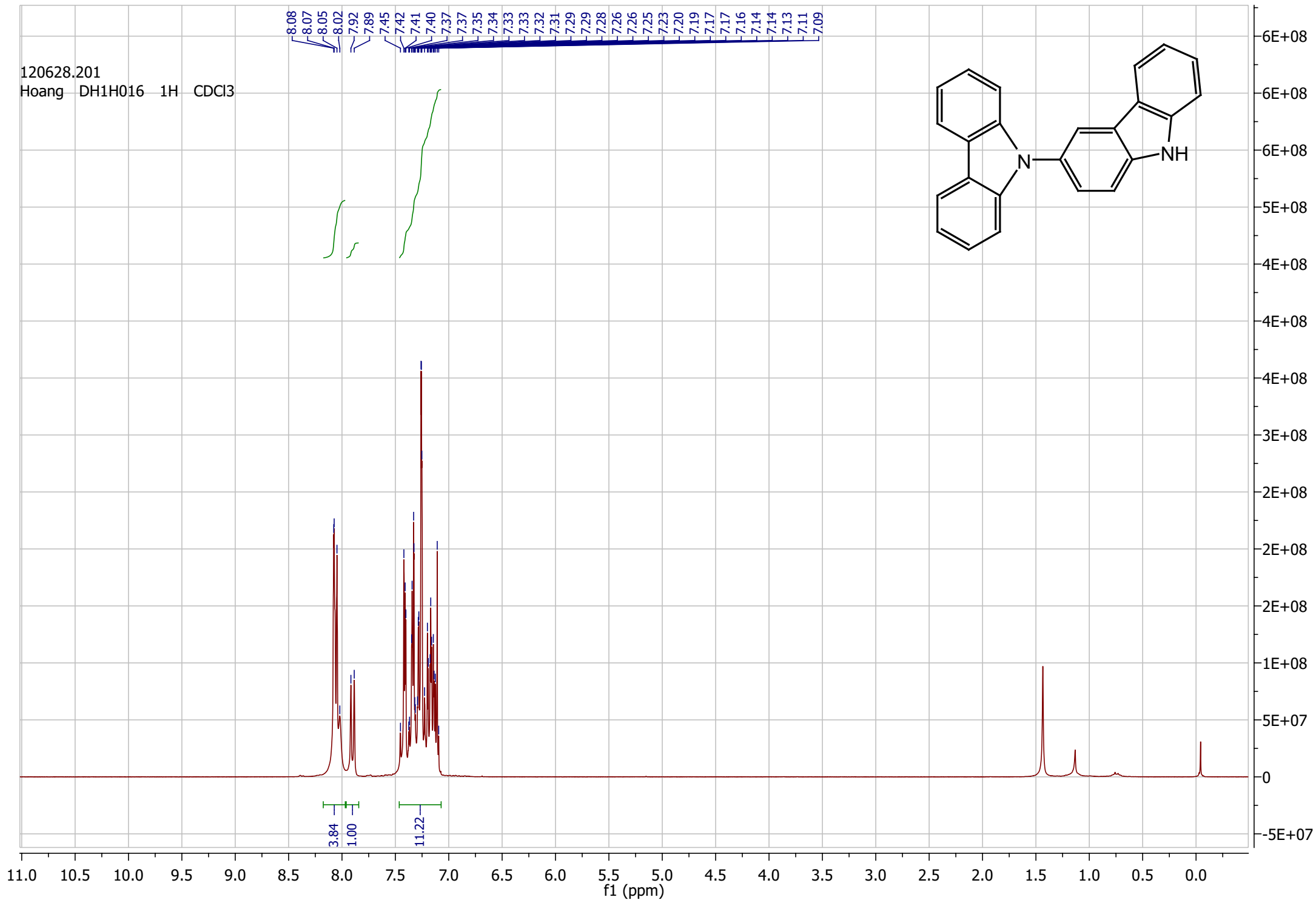
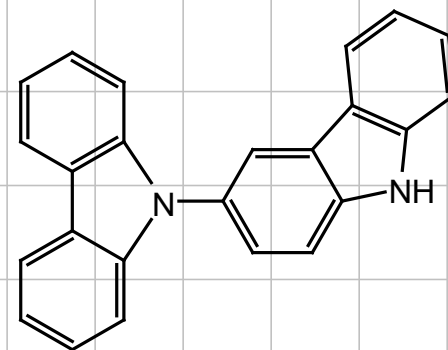
120703.u322
Thang T10 13C CDCl3



120703.u322
Thang T10 Dept CDCl3



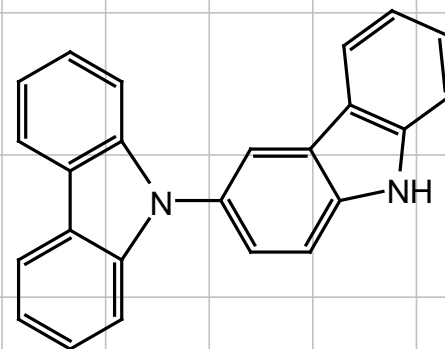
120628.201
Hoang DH1H016 1H CDCl3



120628.201
Hoang DH1H016 13C CDCl3

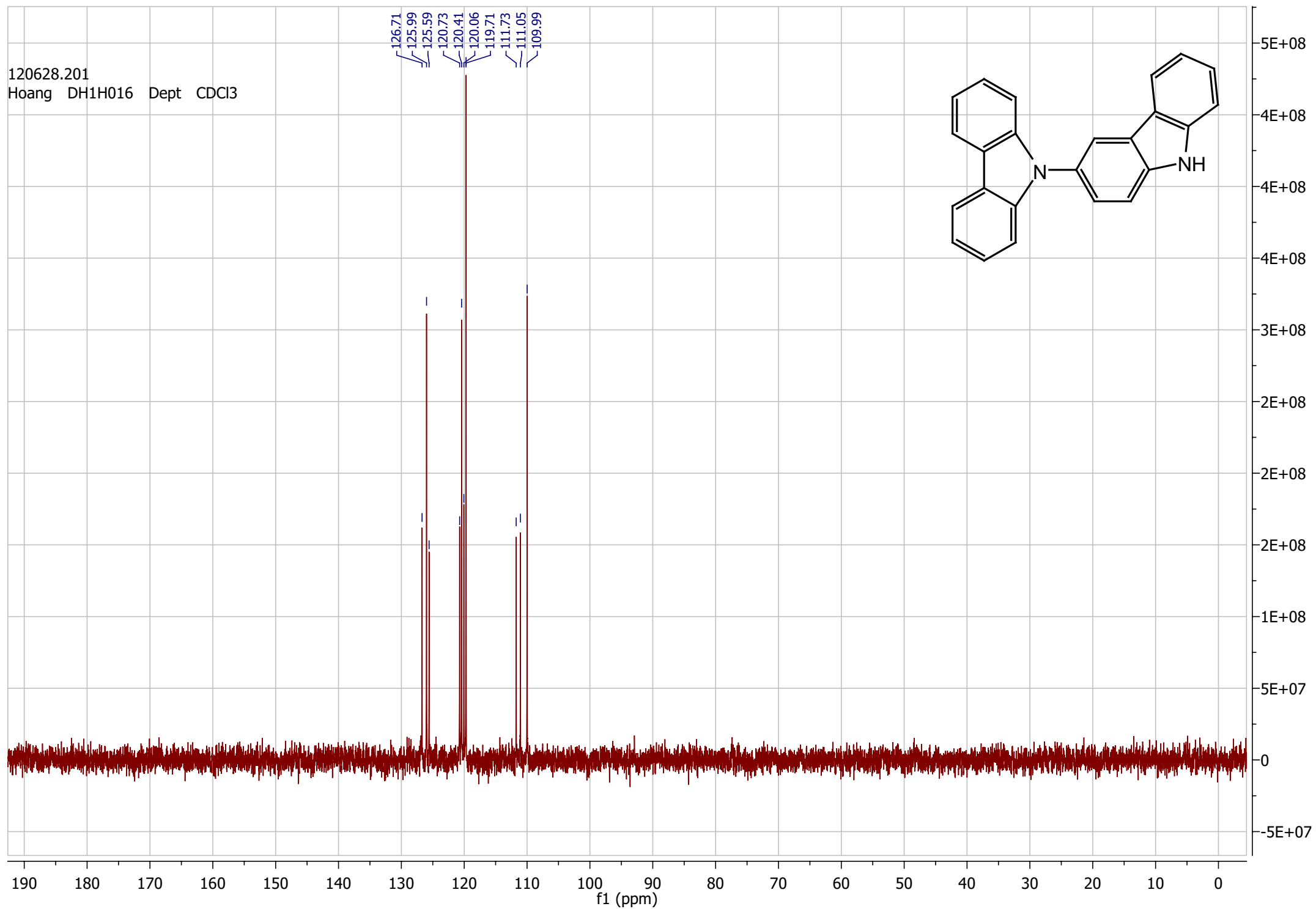
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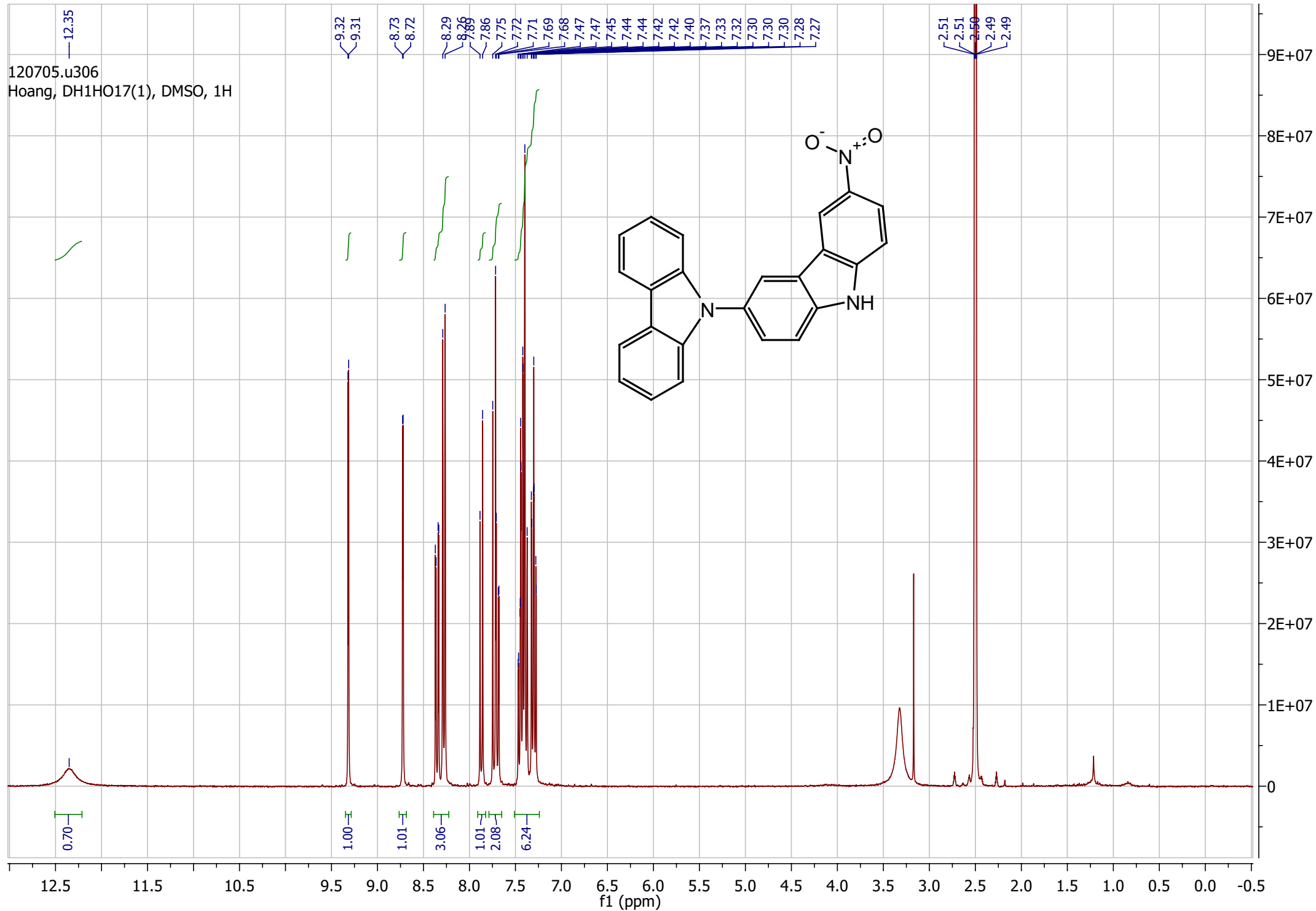
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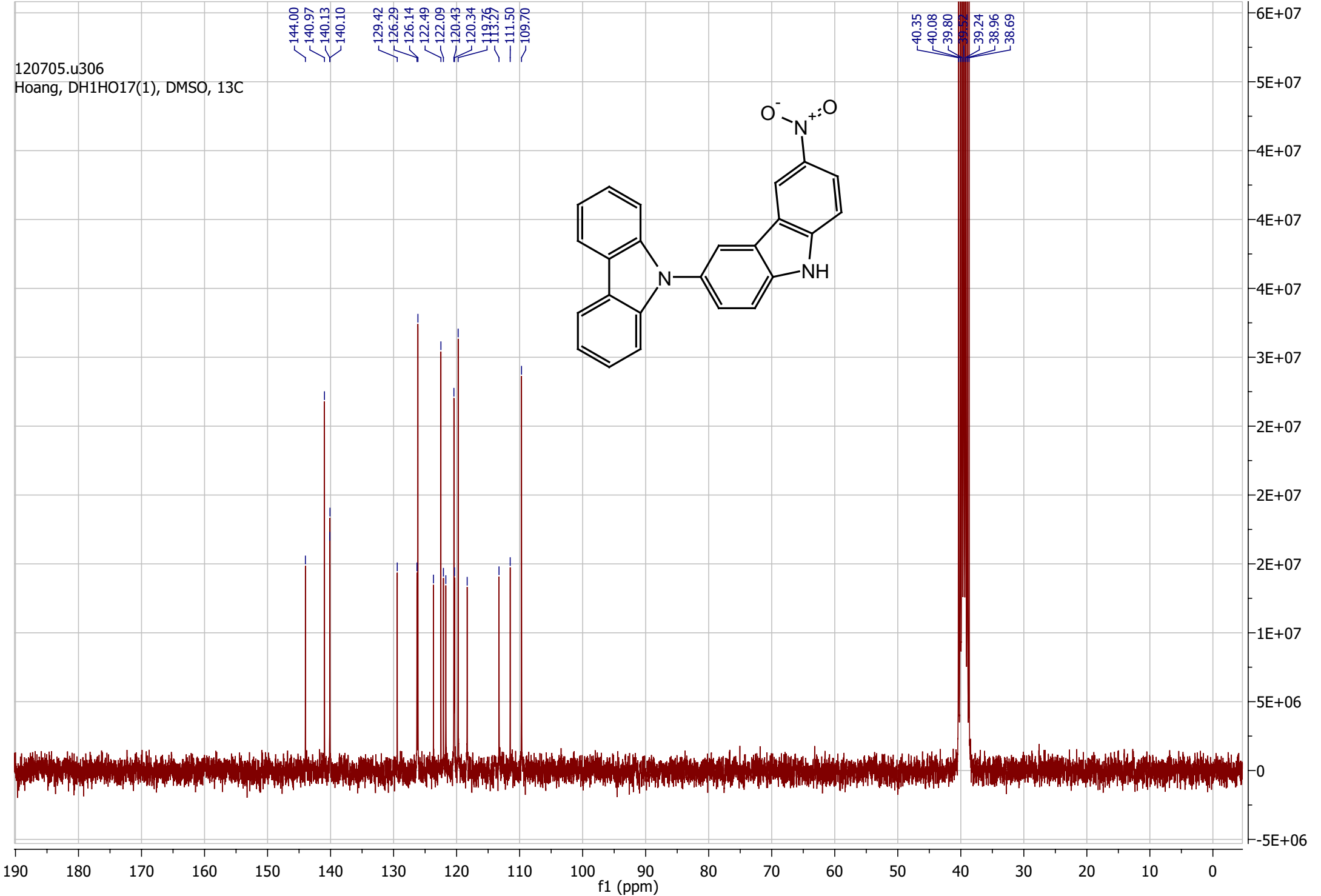
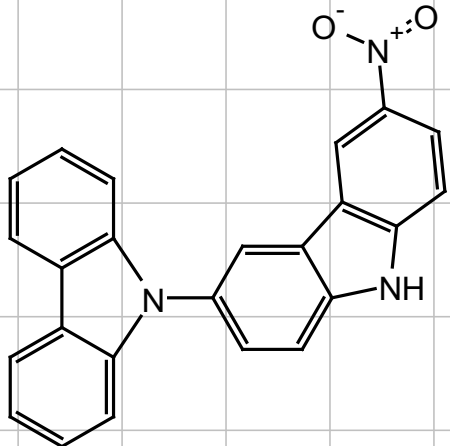
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f1 (ppm)

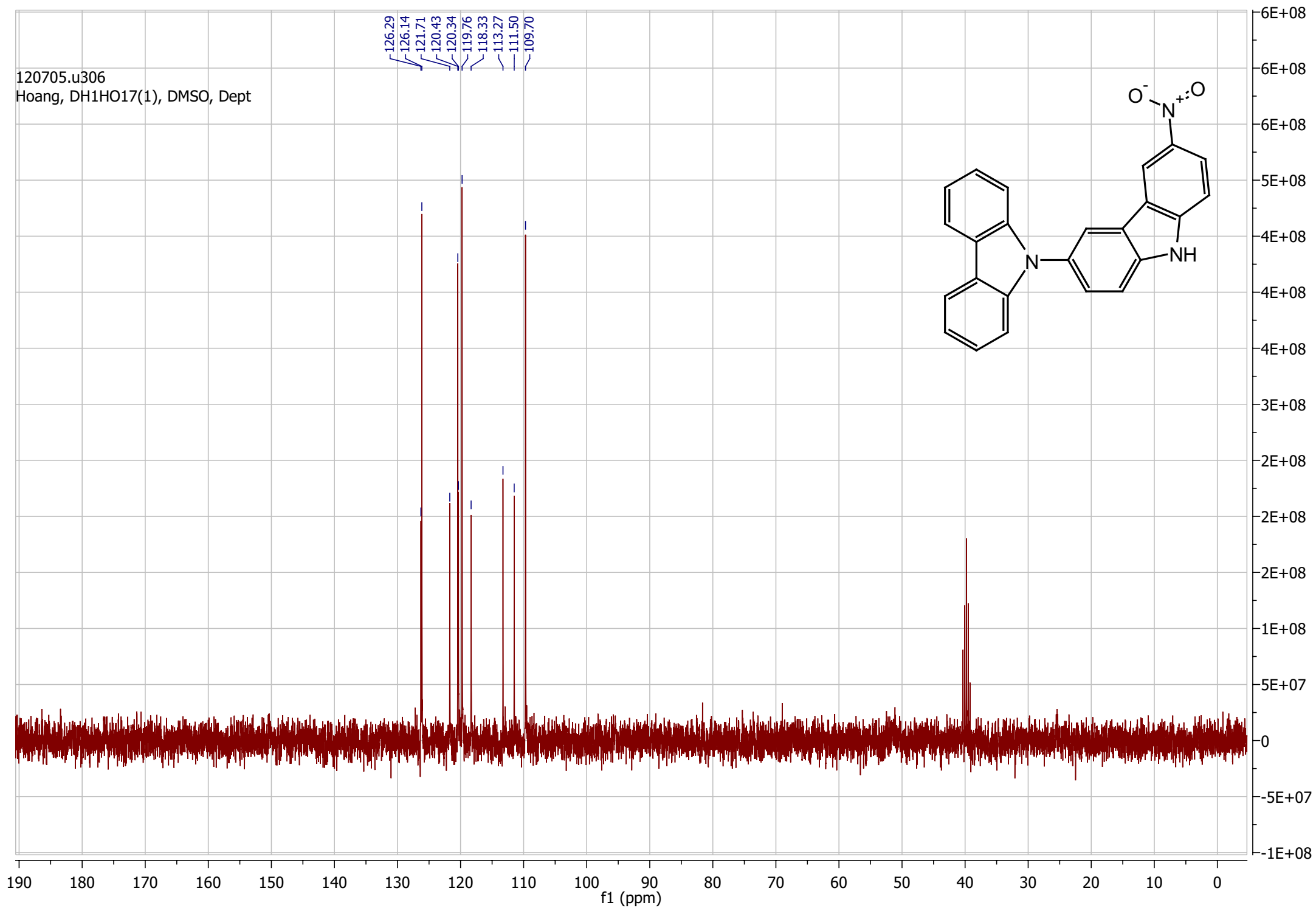


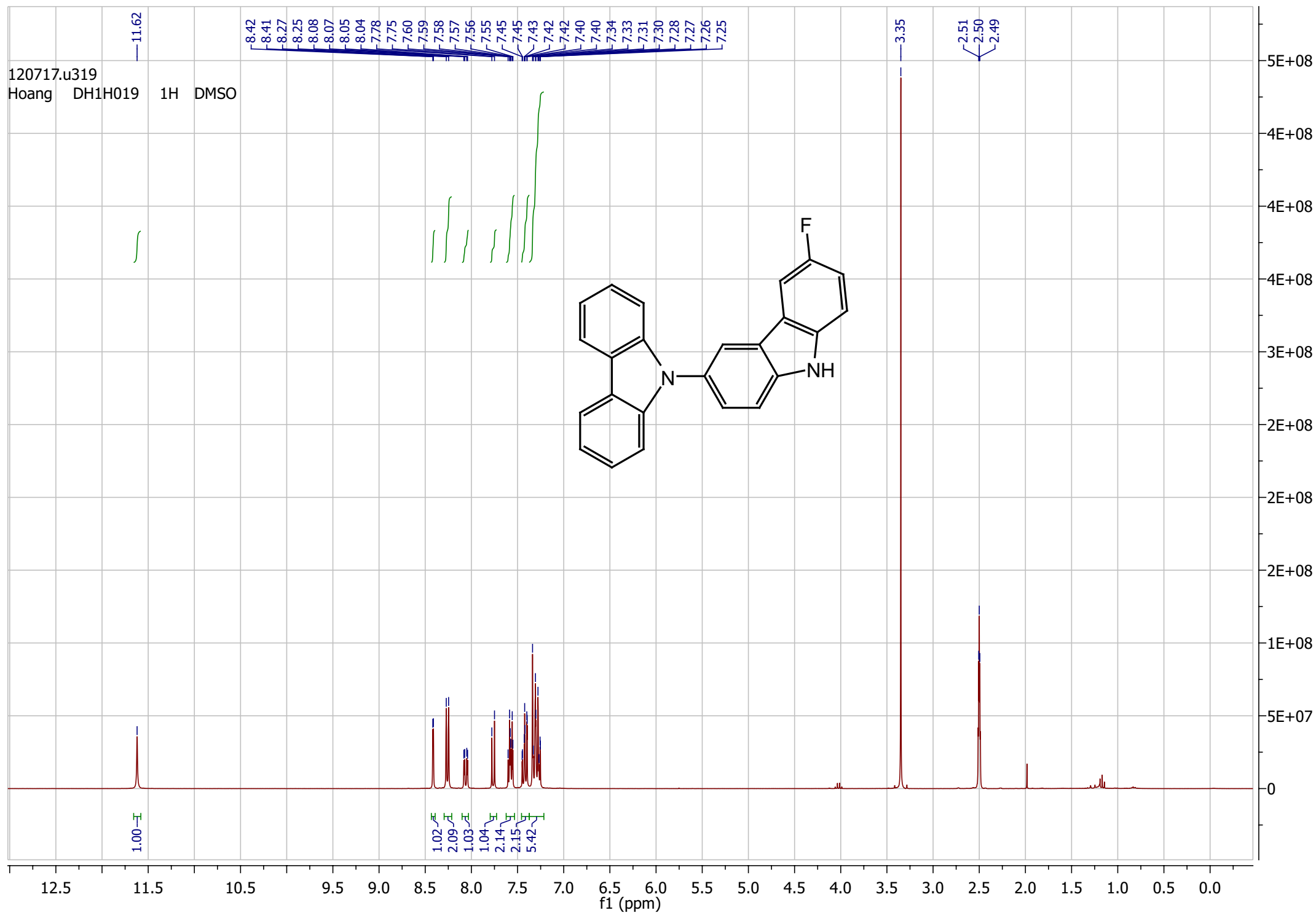


120705.u306
Hoang, DH1HO17(1), DMSO, 13C

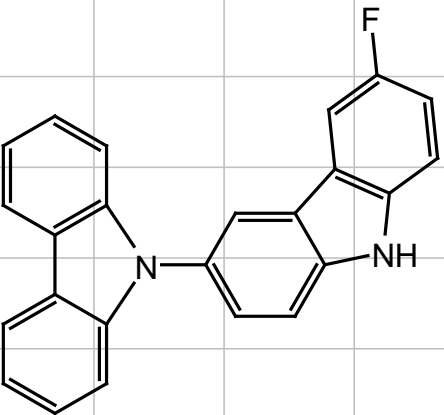


120705.u306
Hoang, DH1HO17(1), DMSO, Dept



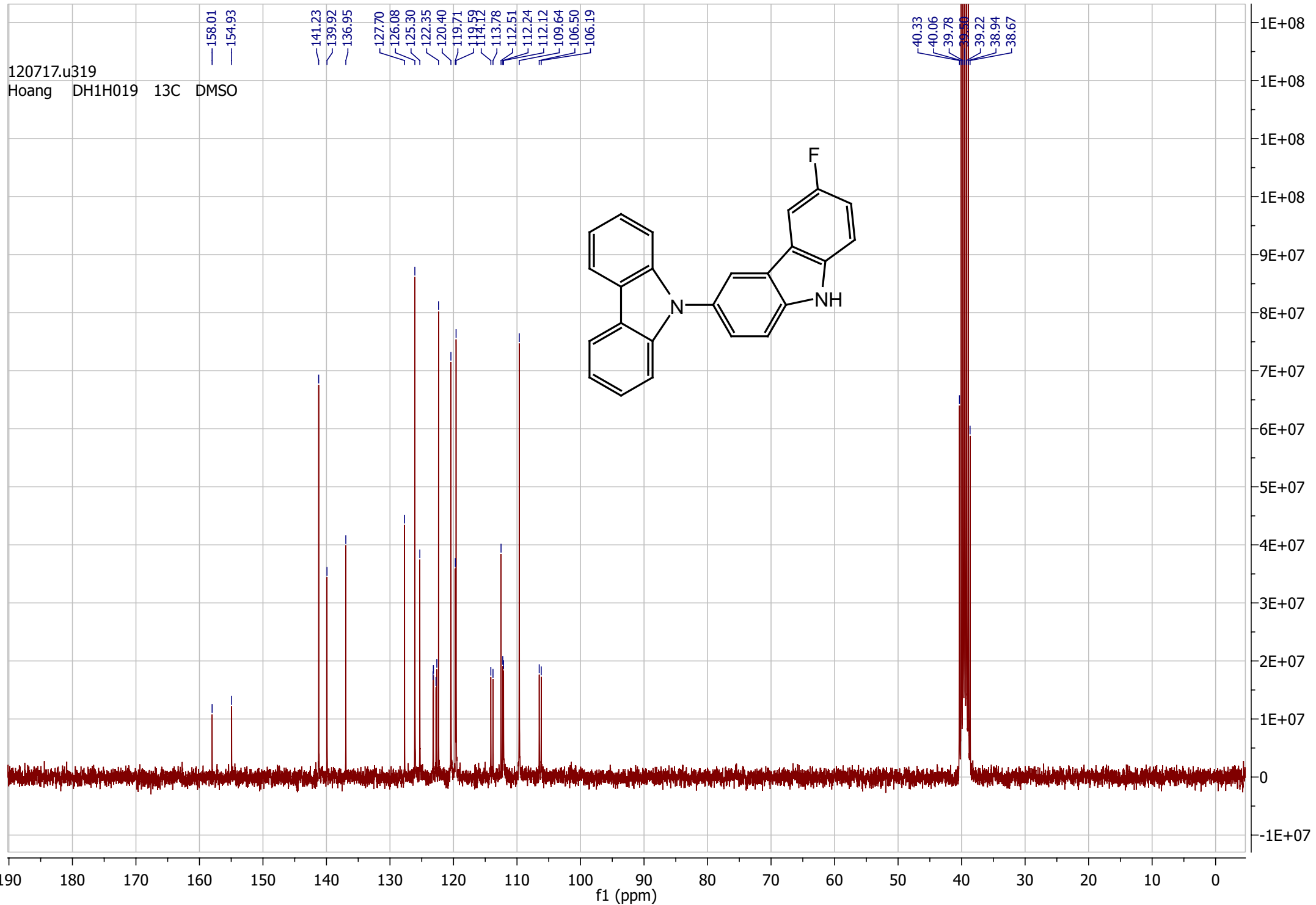


120717.u319
Hoang DH1H019 19F DMSO



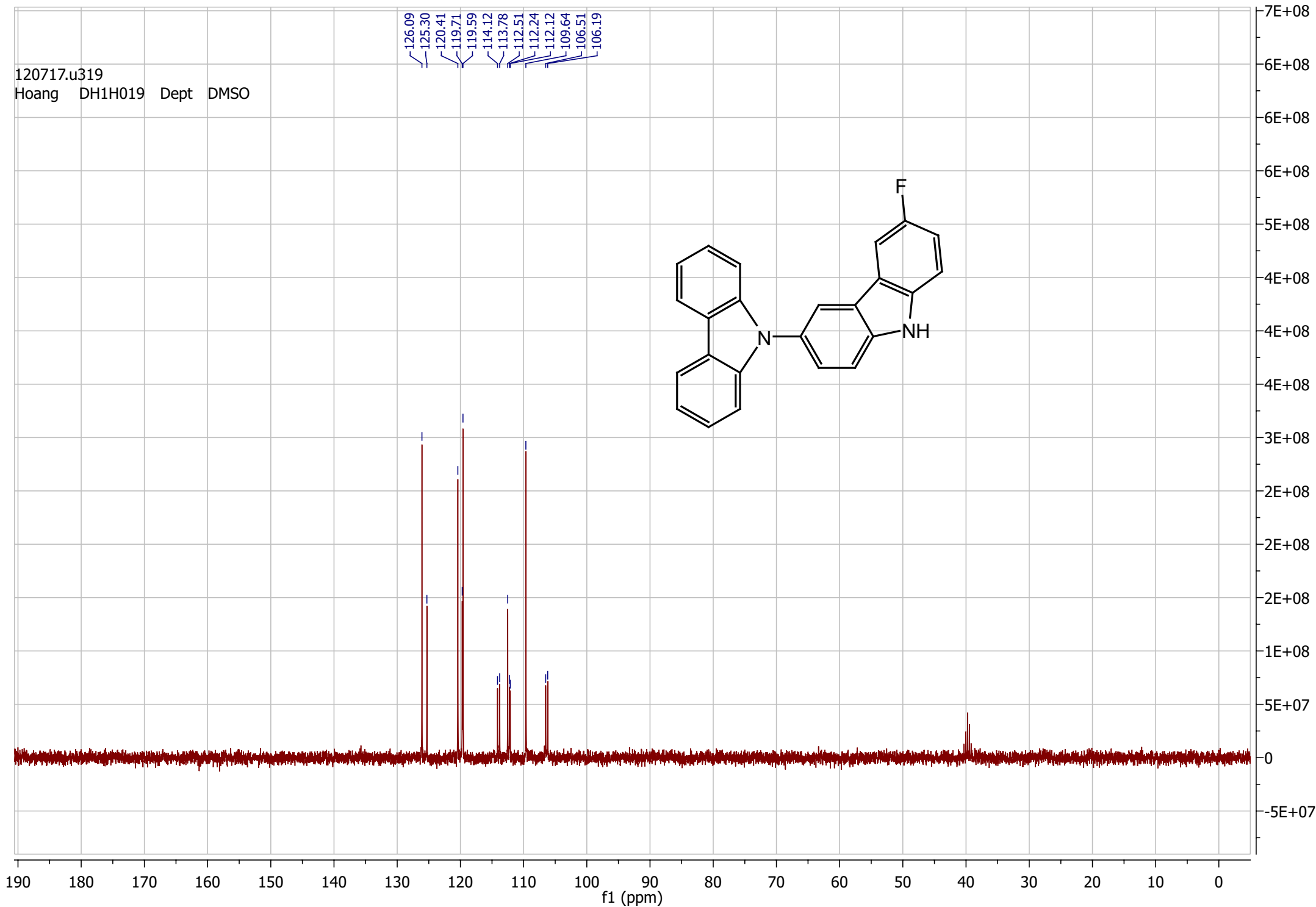
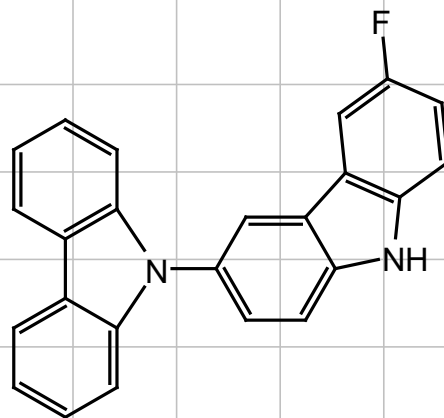
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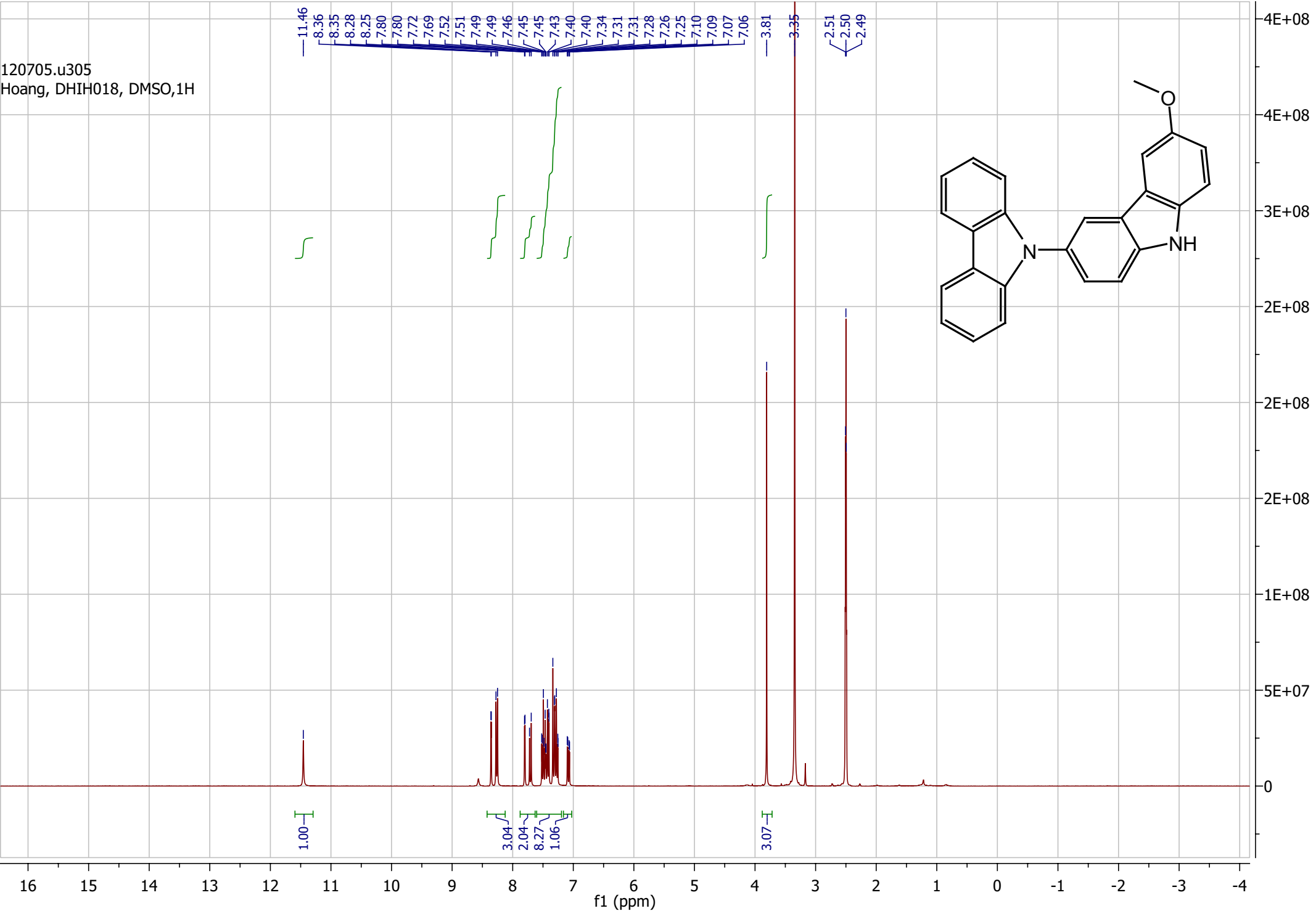


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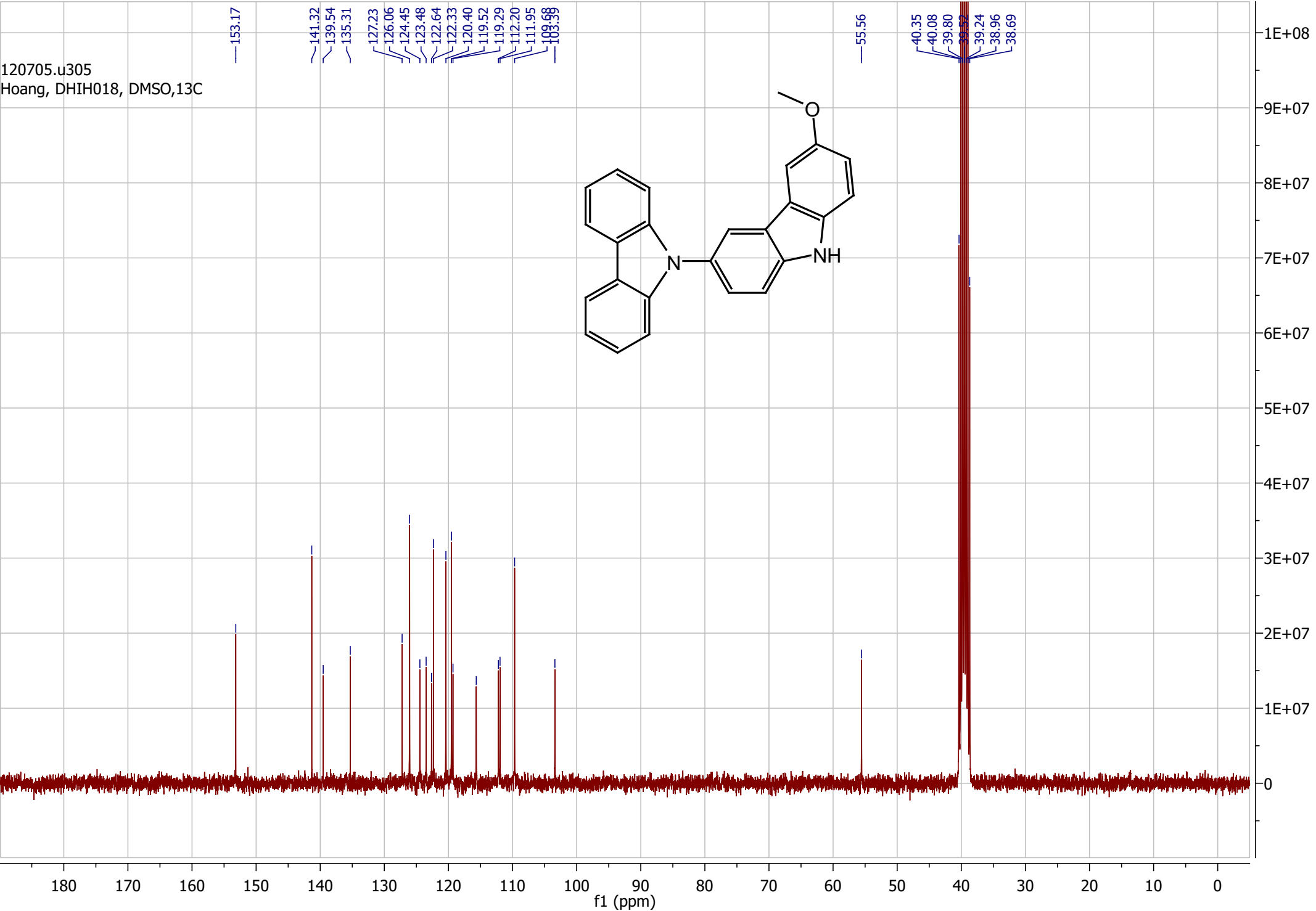
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106.19



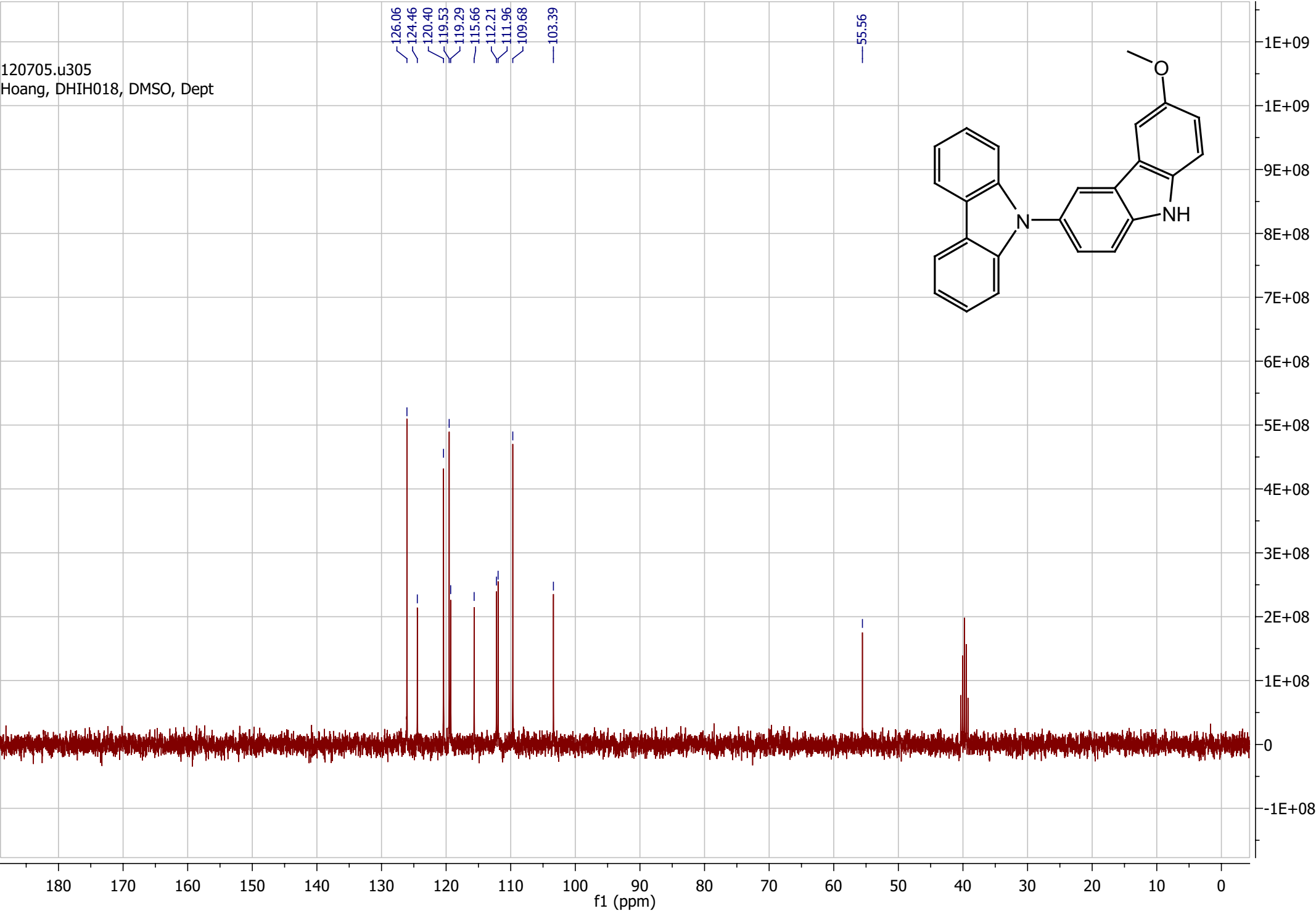
120705.u305
Hoang, DHIH018, DMSO,1H



120705.u305
Hoang, DHIH018, DMSO,13C



120705.u305
Hoang, DHIH018, DMSO, Dept



120717.u313
Hoang DH1H029(2) 1H CDCl3

8.32 8.32 8.21 8.21 8.20 8.19 8.18 8.18 8.09
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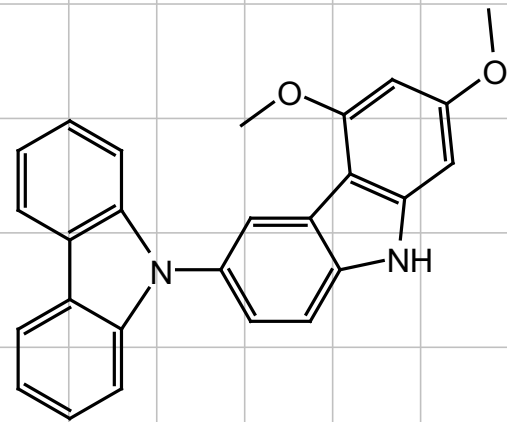
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1.09 5.62 3.21

1.02

1.01

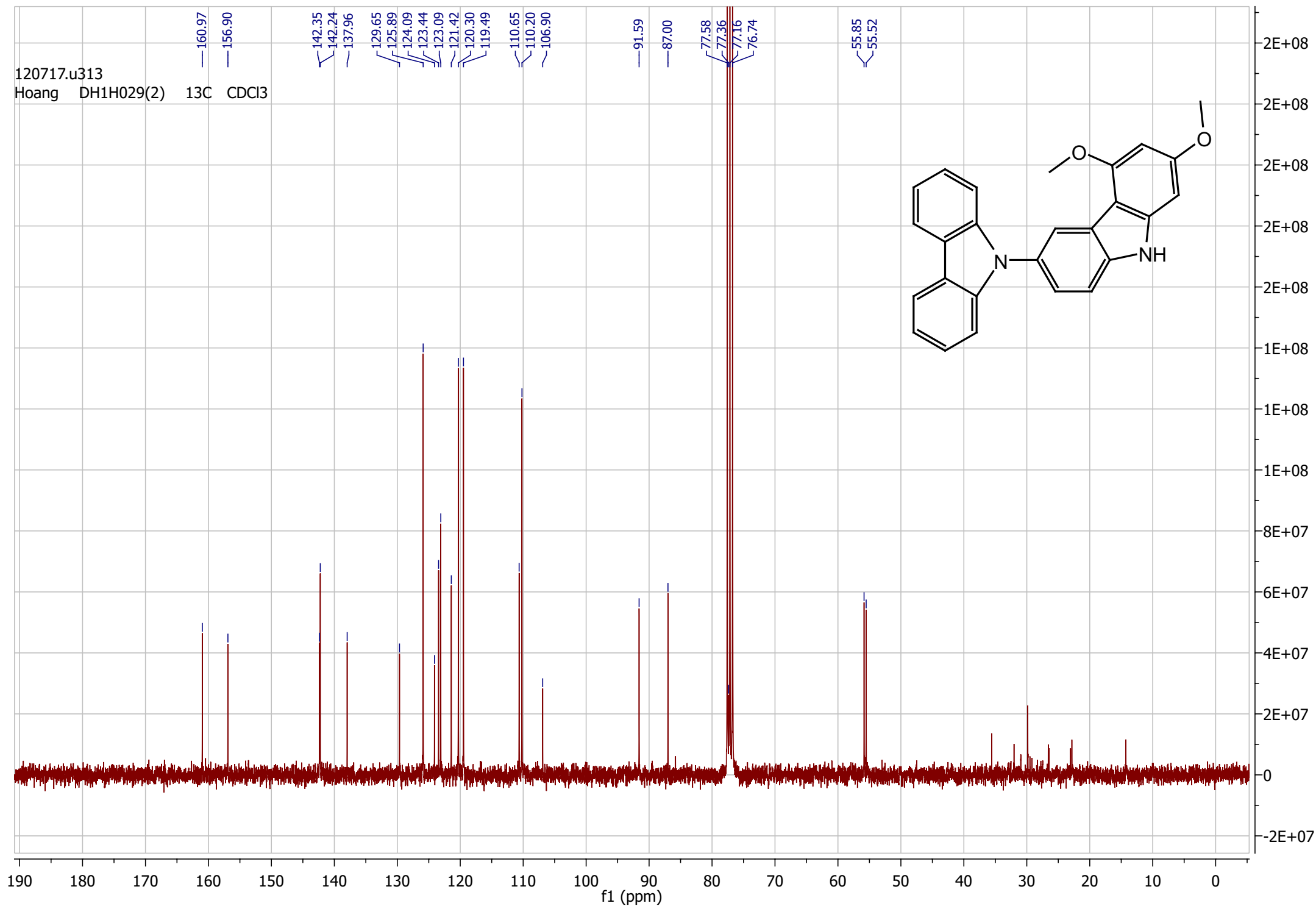
3.09 3.10



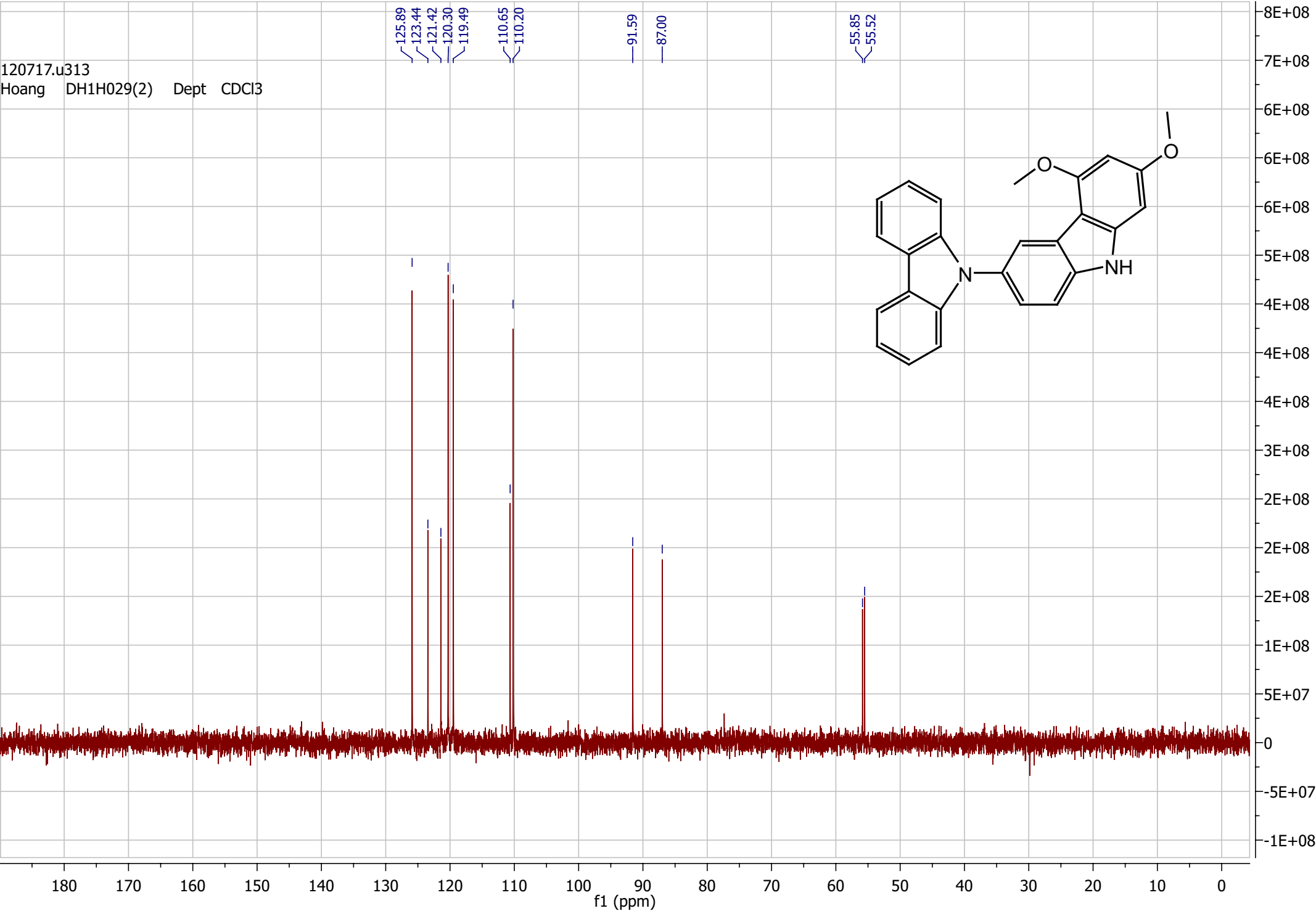
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f1 (ppm)

6E+08
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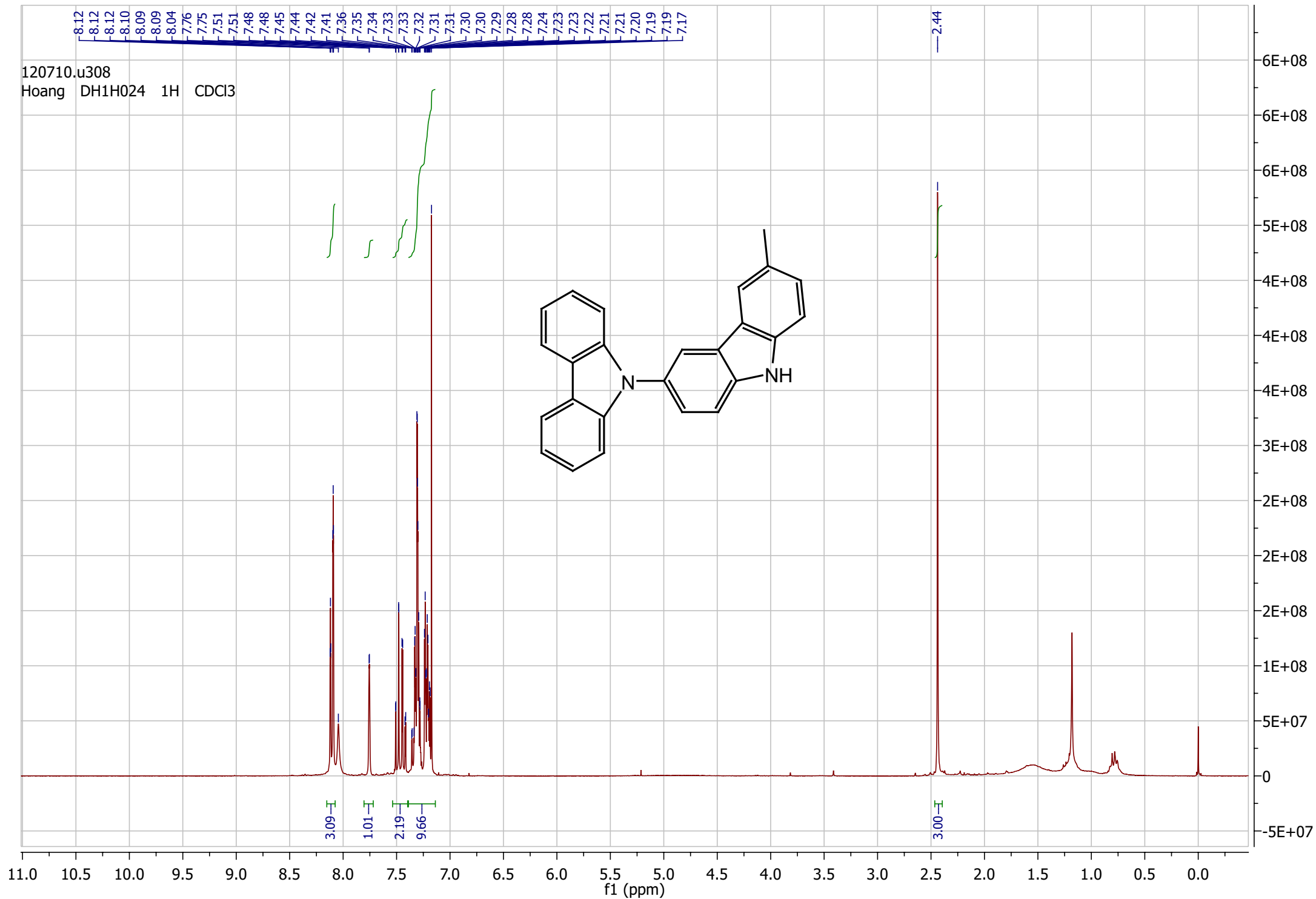
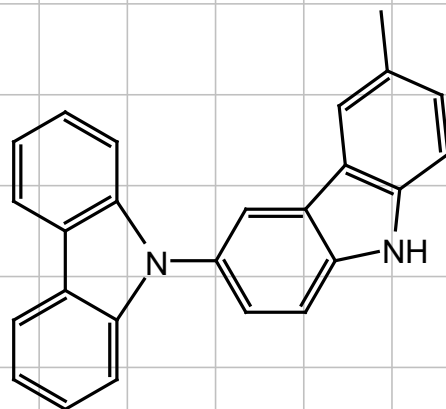
120717.u313
Hoang DH1H029(2) 13C CDCl3



120717.u313
Hoang DH1H029(2) Dept CDCl3



120710.u308
Hoang DH1H024 1H CDCl3

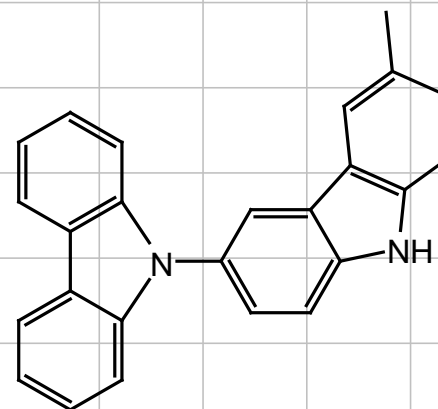


120710.u308
Hoang DH1H024 13C CDCl3

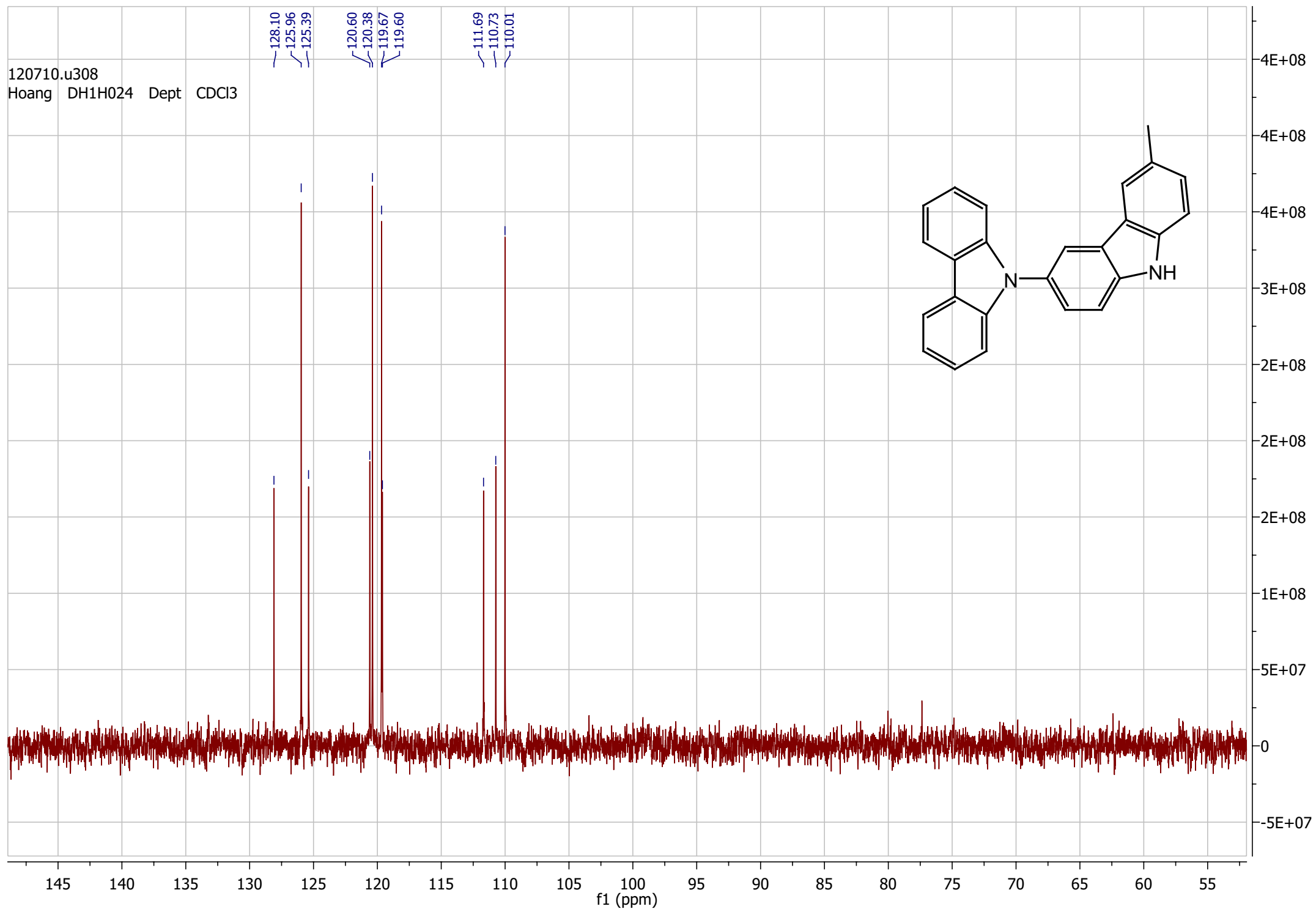
142.08
139.05
138.57
128.09
125.96
125.39
123.21
120.59
120.38
119.67
119.89
110.73
110.01

77.58
77.16
76.74

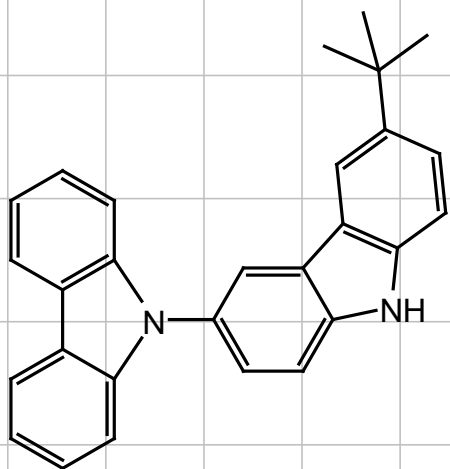
21.56



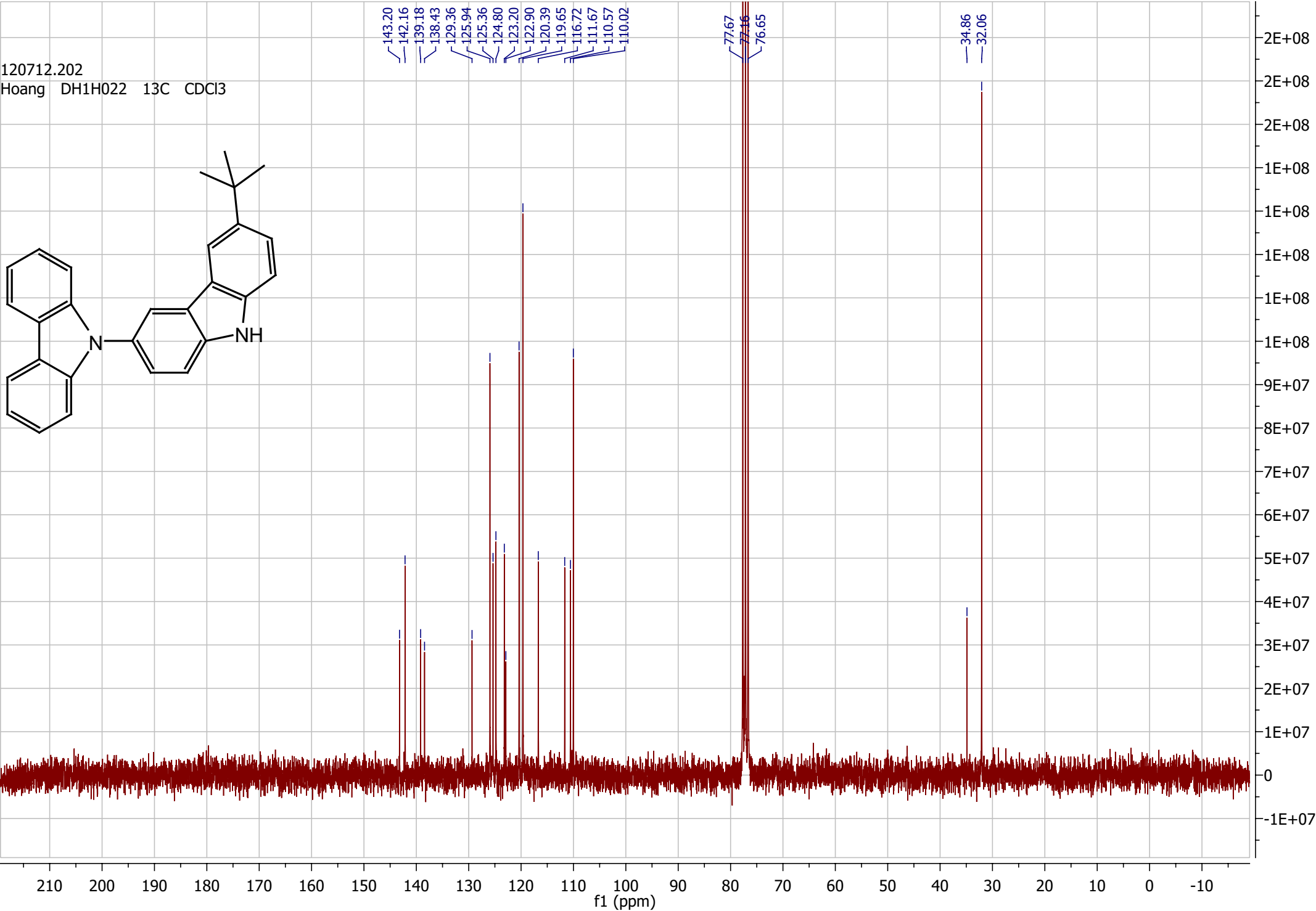
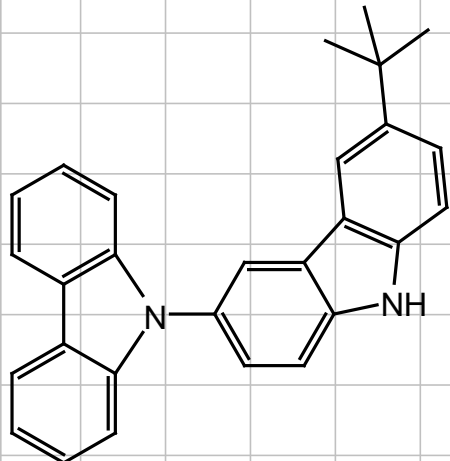
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f1 (ppm)



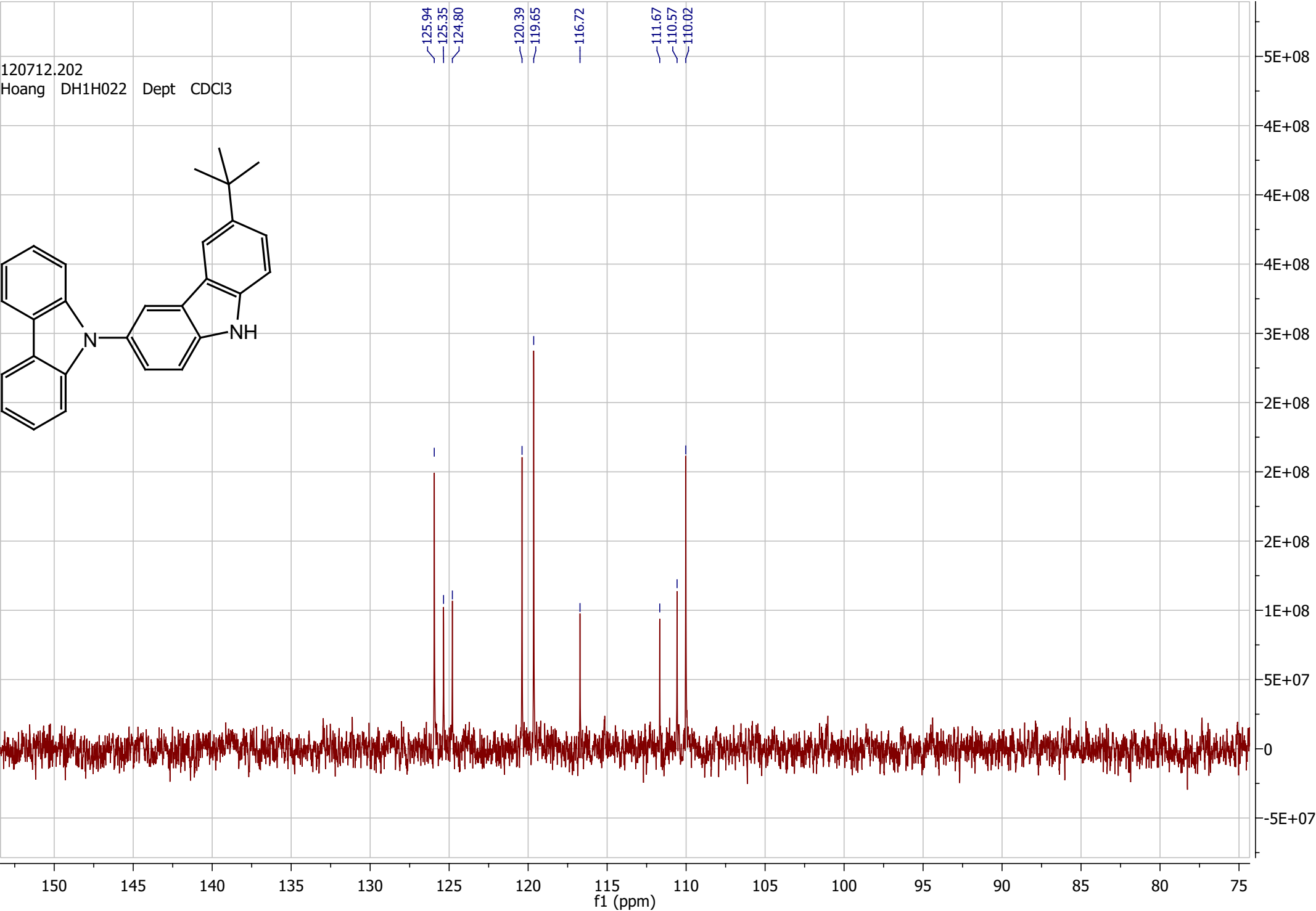
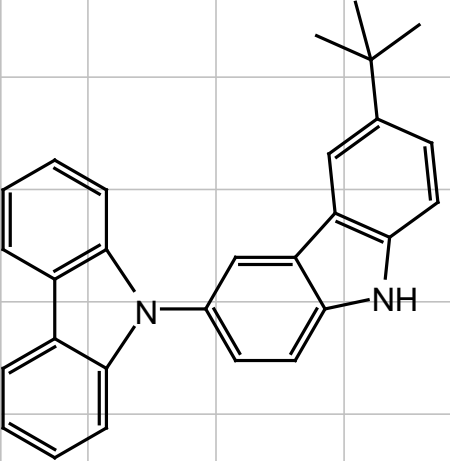
120712.202
Hoang DH1H022 1H CDCl3



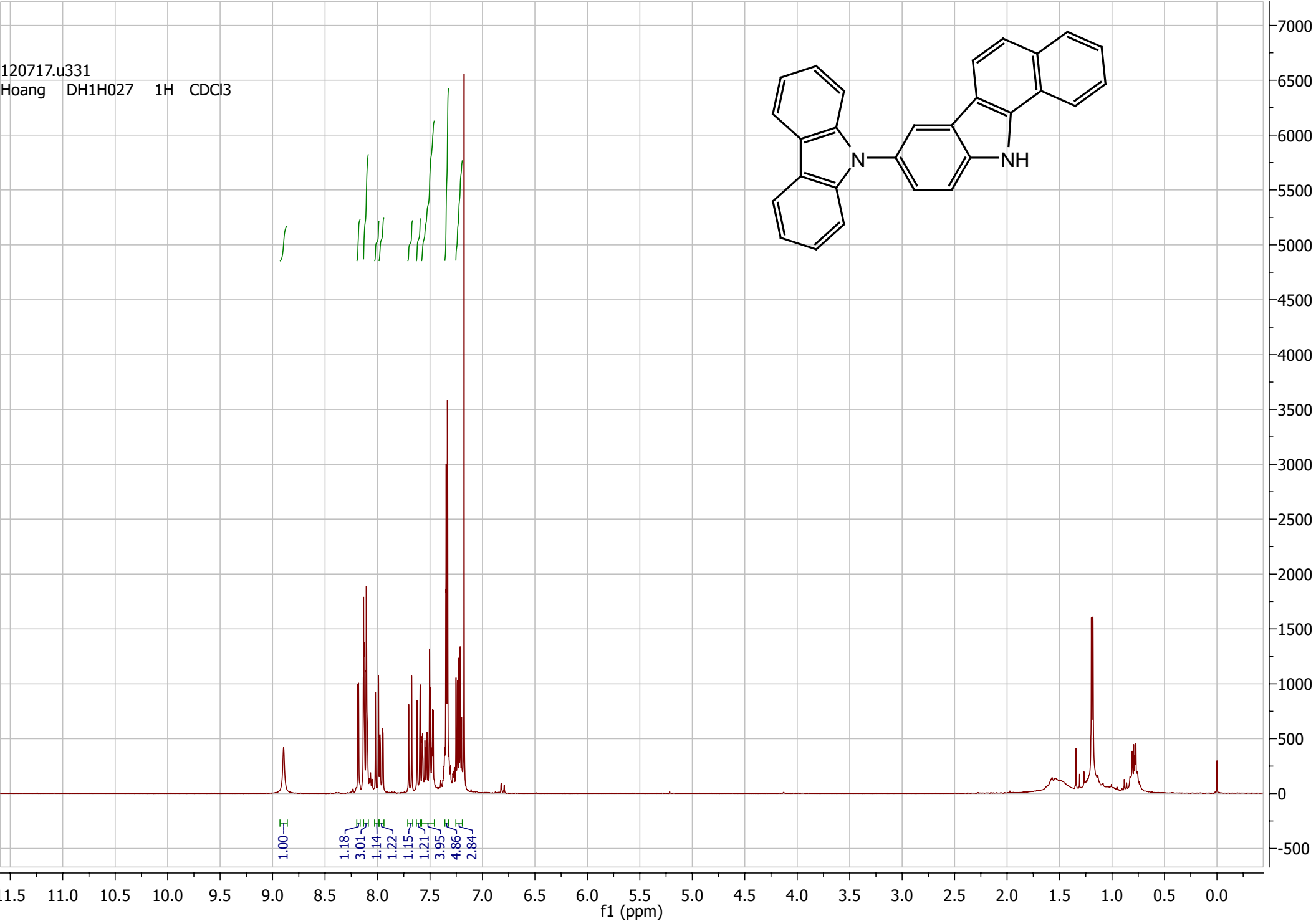
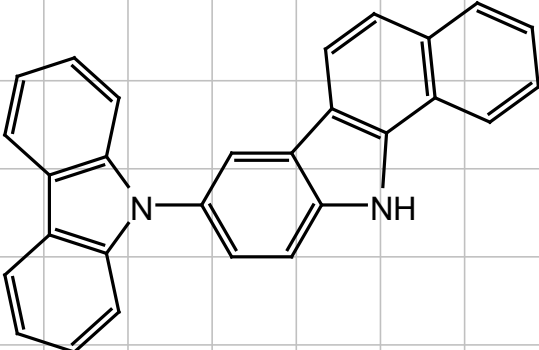
120712.202
Hoang DH1H022 13C CDCl3

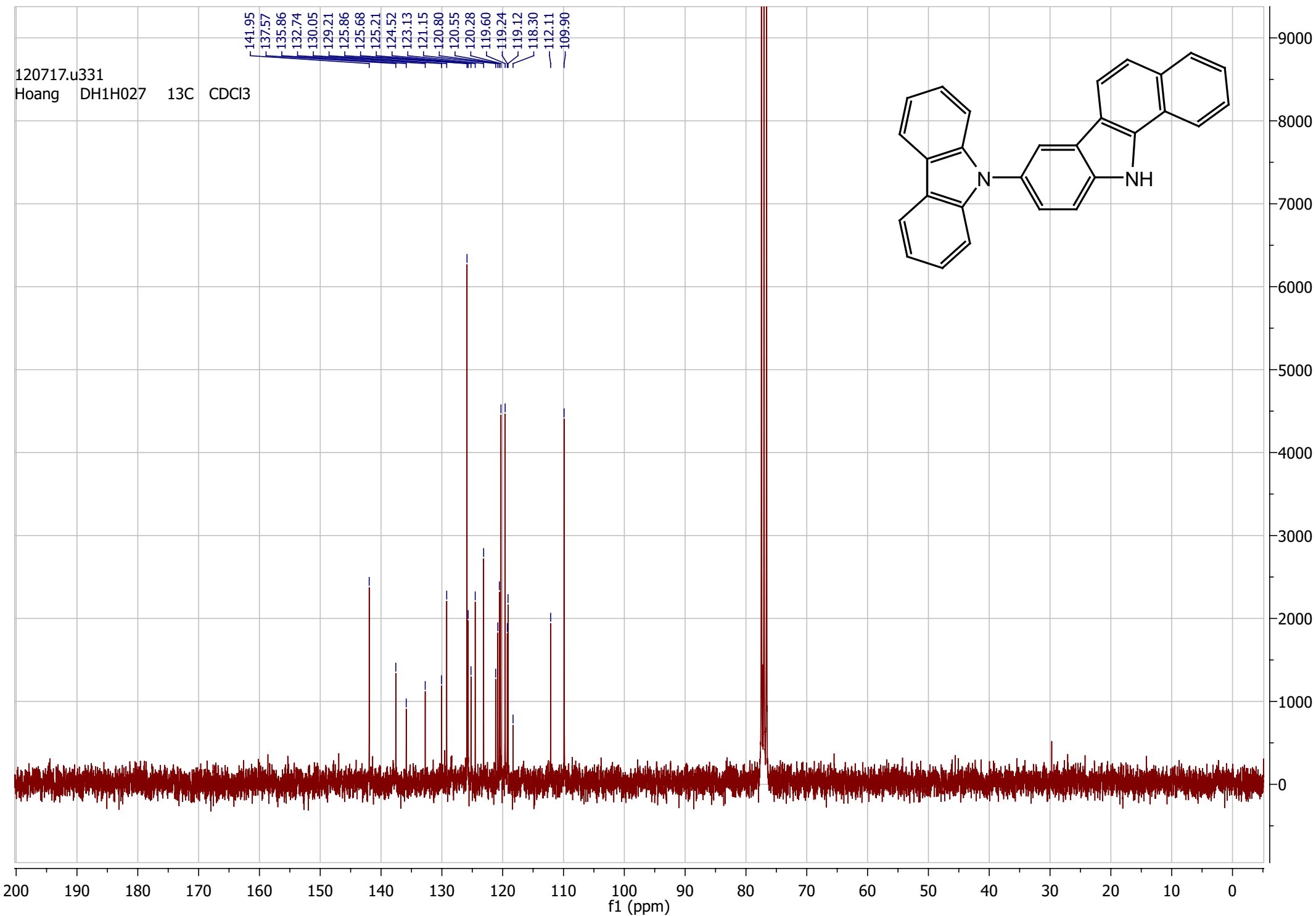


120712.202
Hoang DH1H022 Dept CDCl3



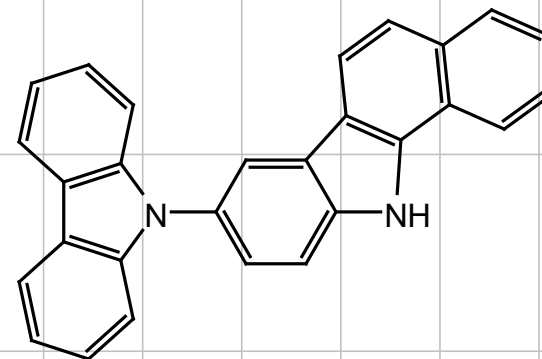
120717.u331
Hoang DH1H027 1H CDCl3



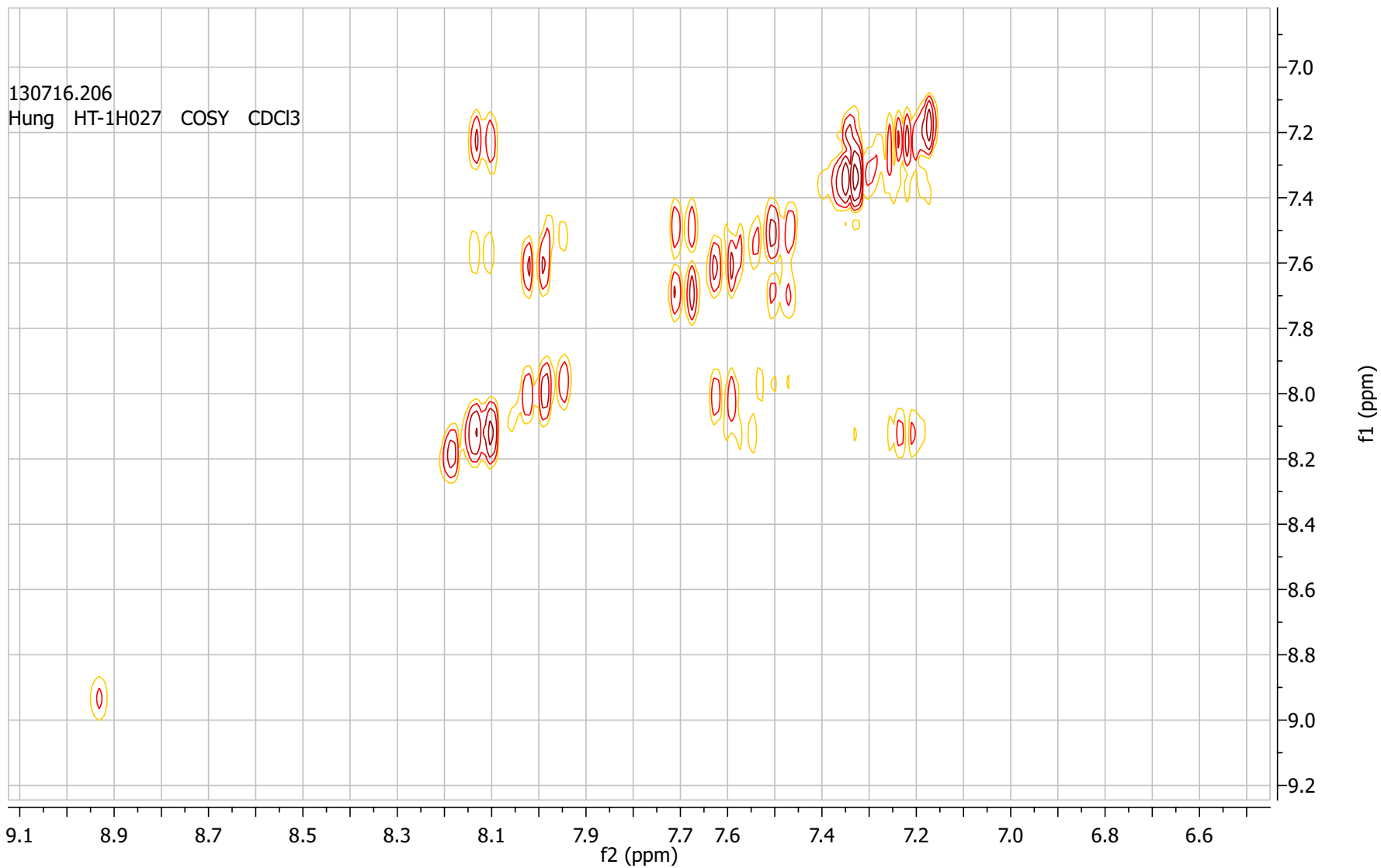
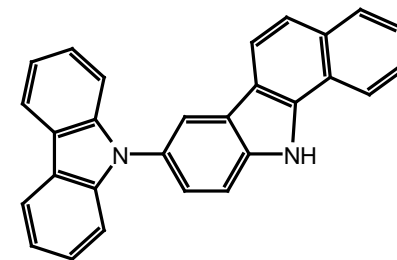


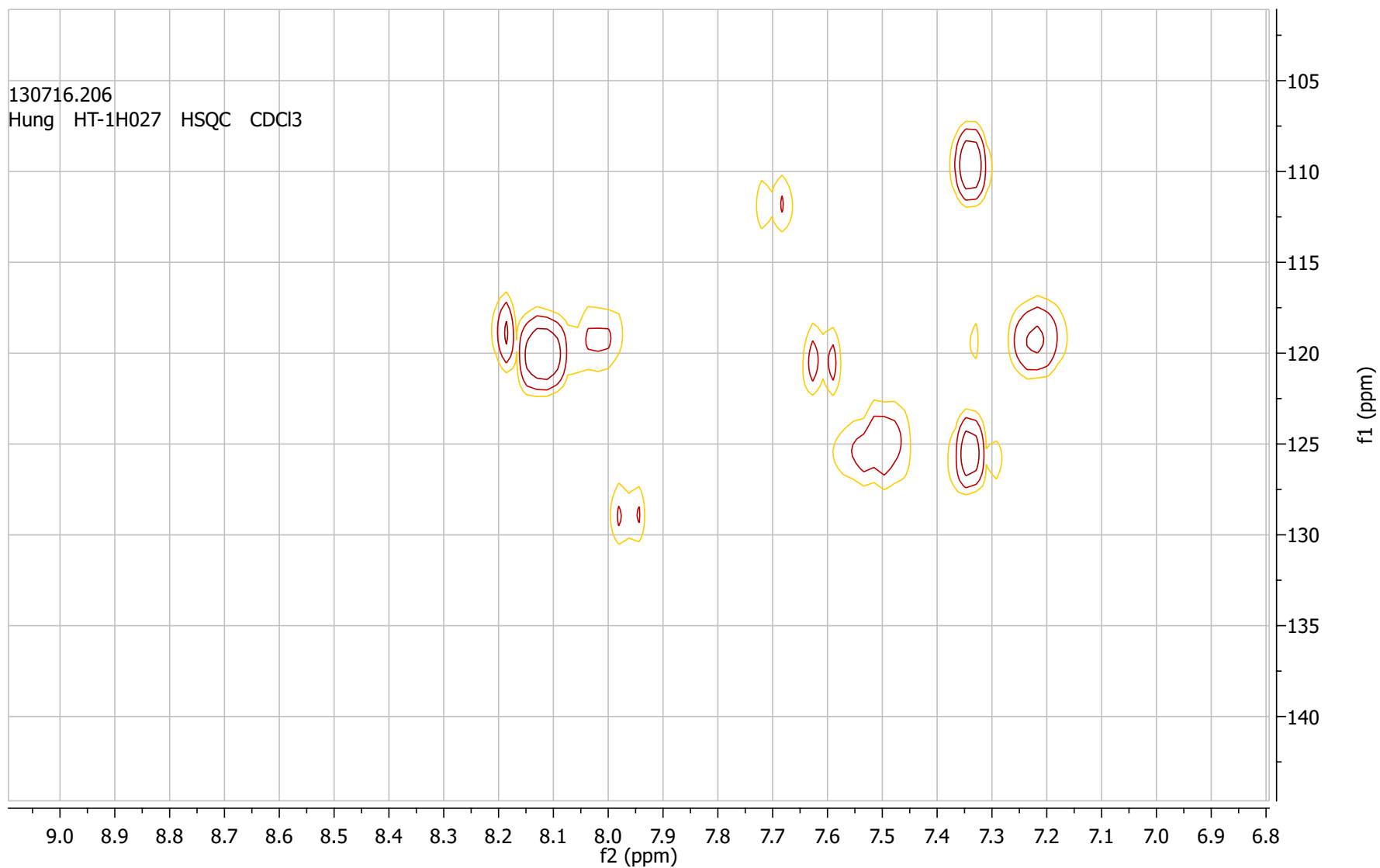
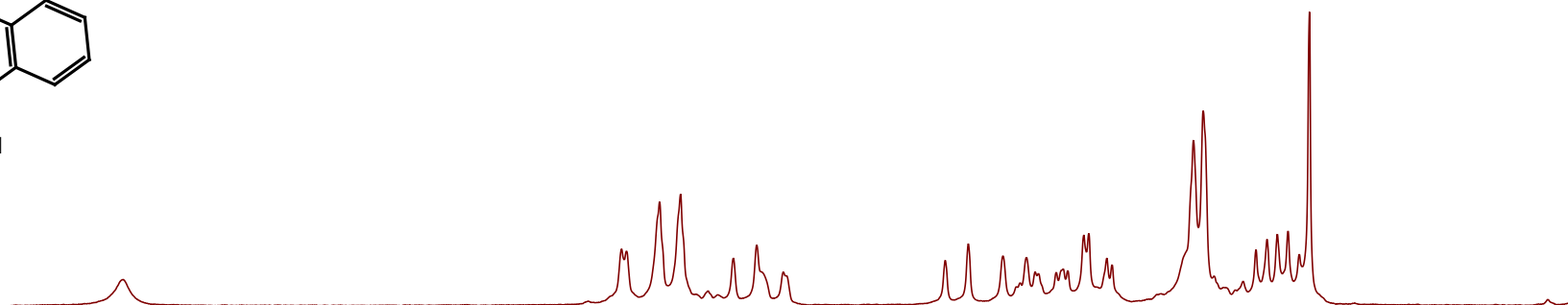
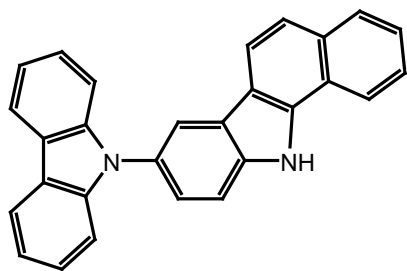
120717.u331
Hoang DH1H027 Dept CDCl3

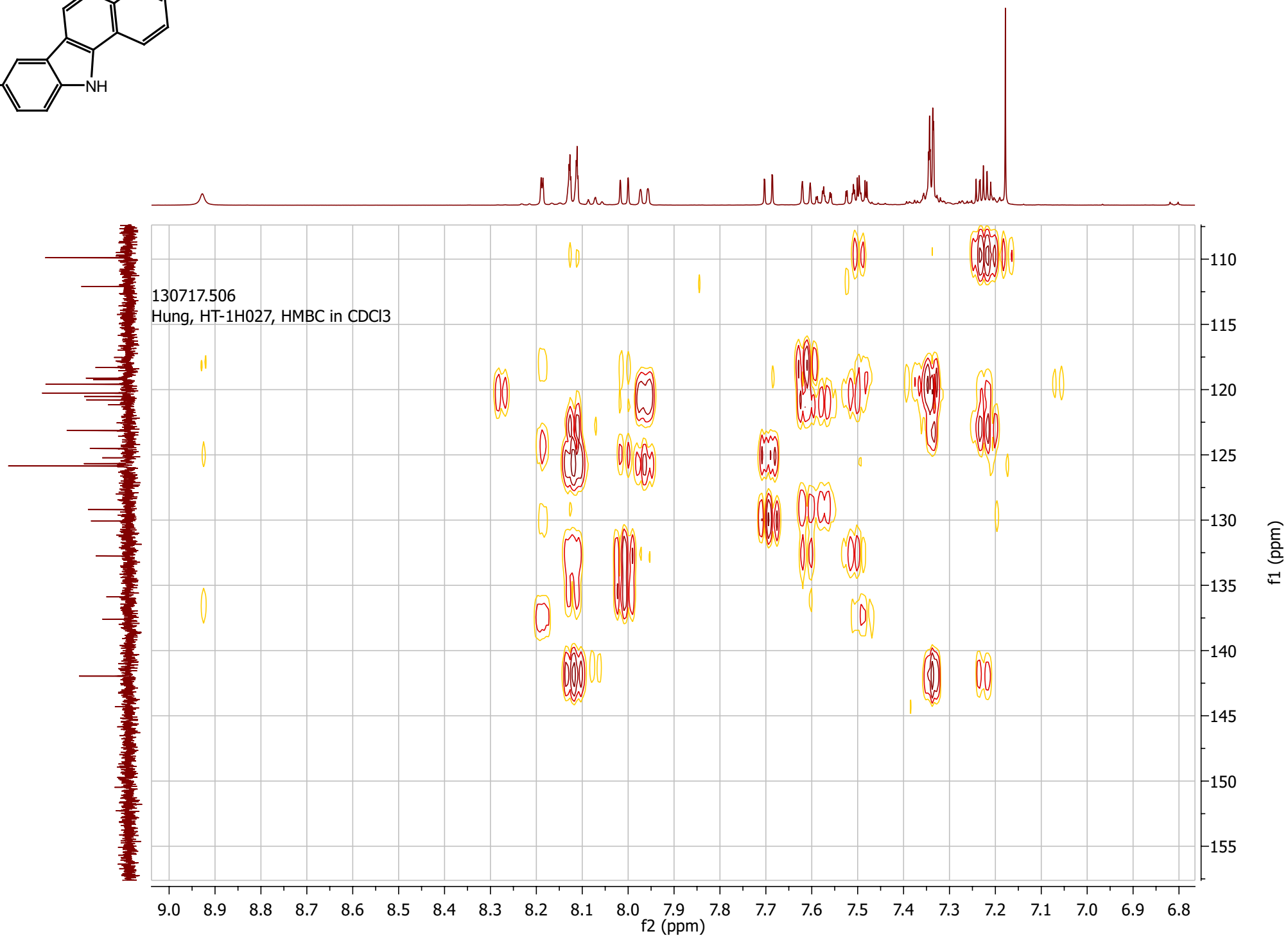
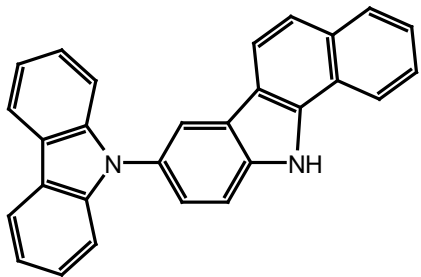
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120.55
120.28
119.59
119.24
119.12
112.11
109.90

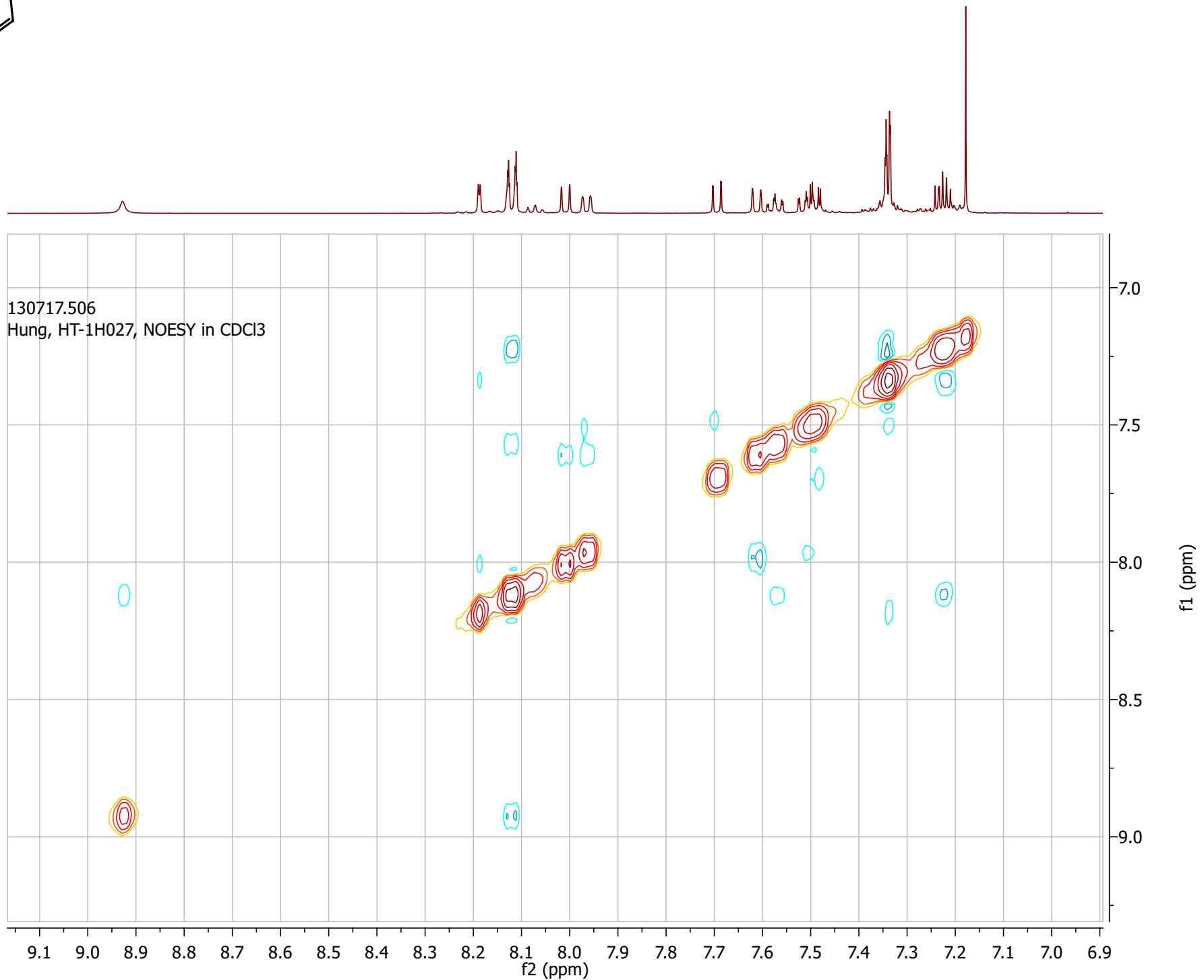
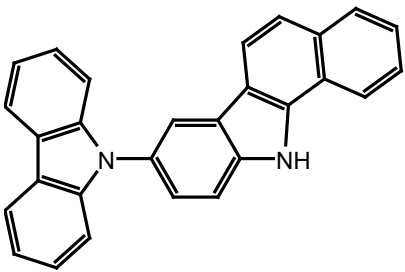


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f1 (ppm)

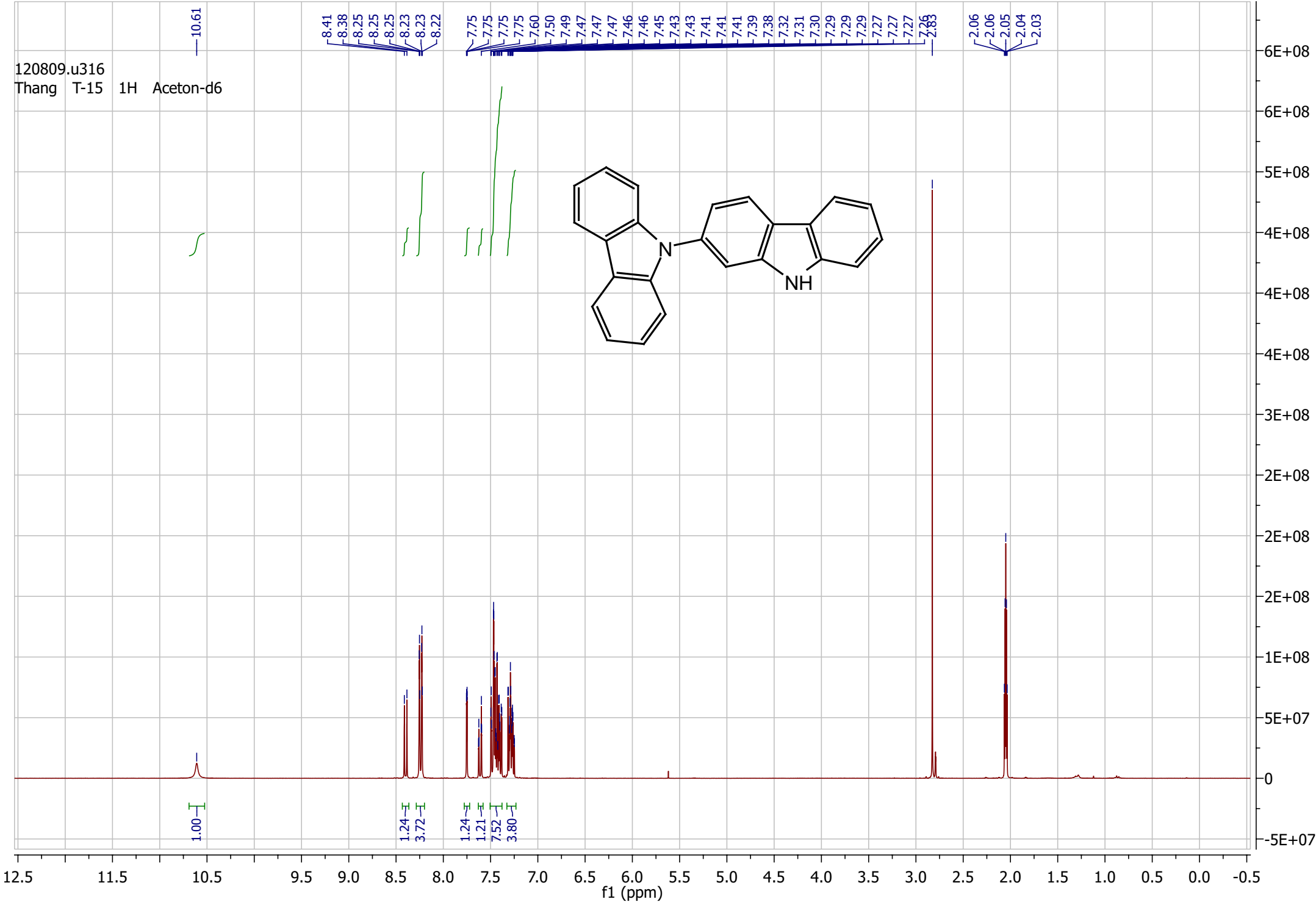
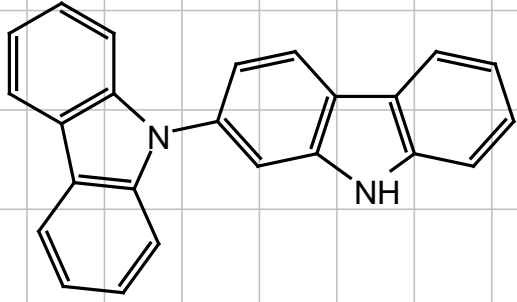


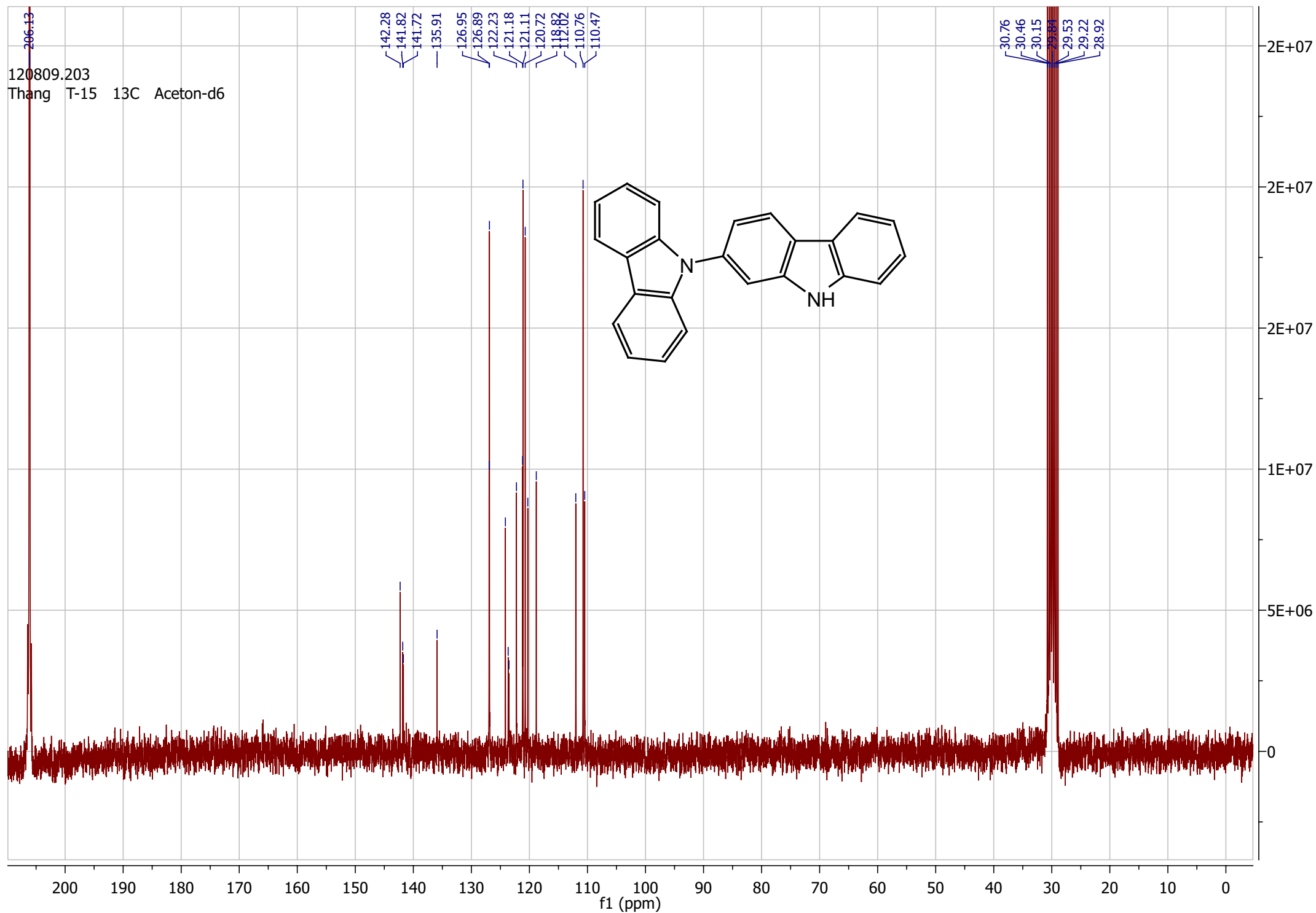


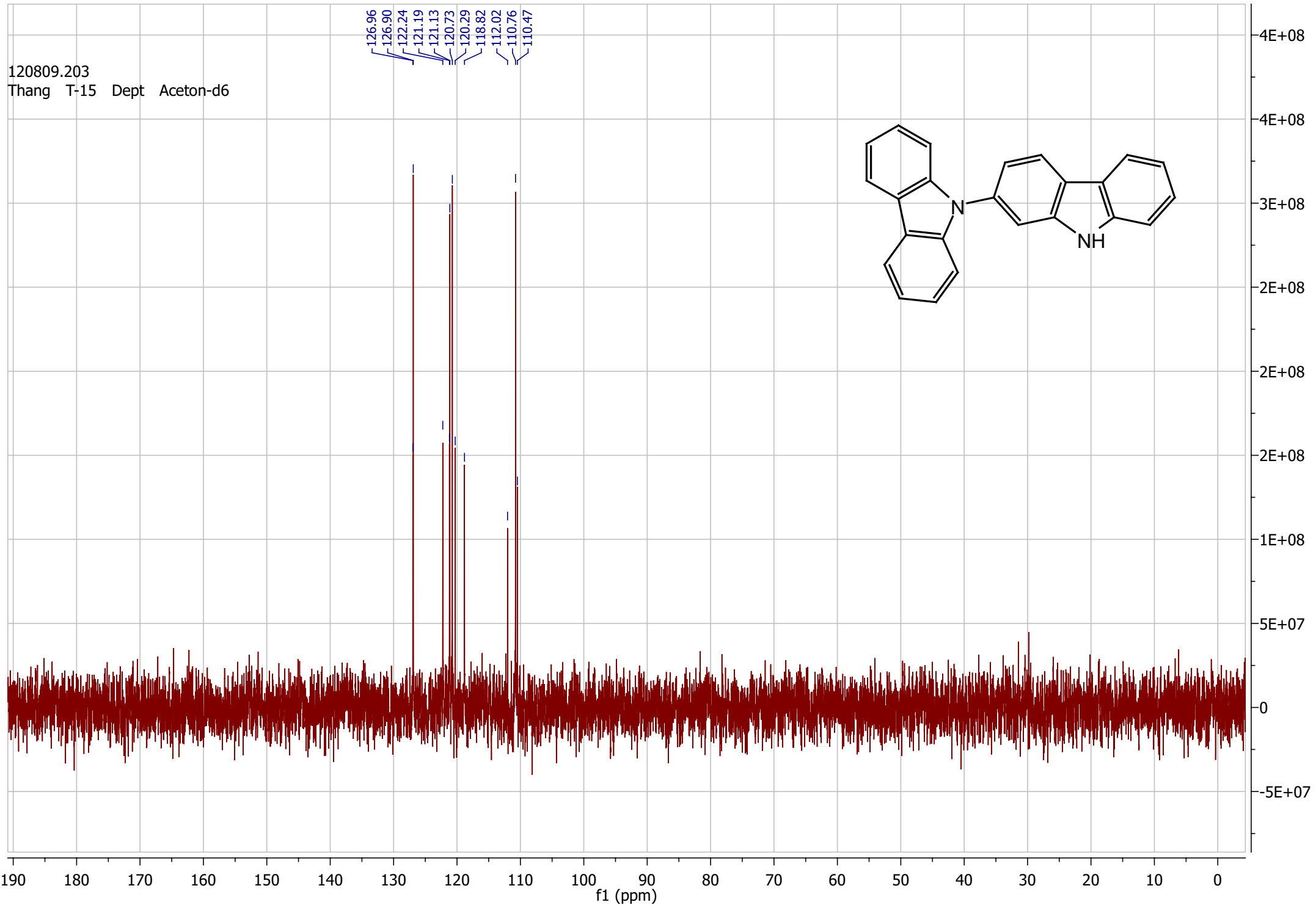




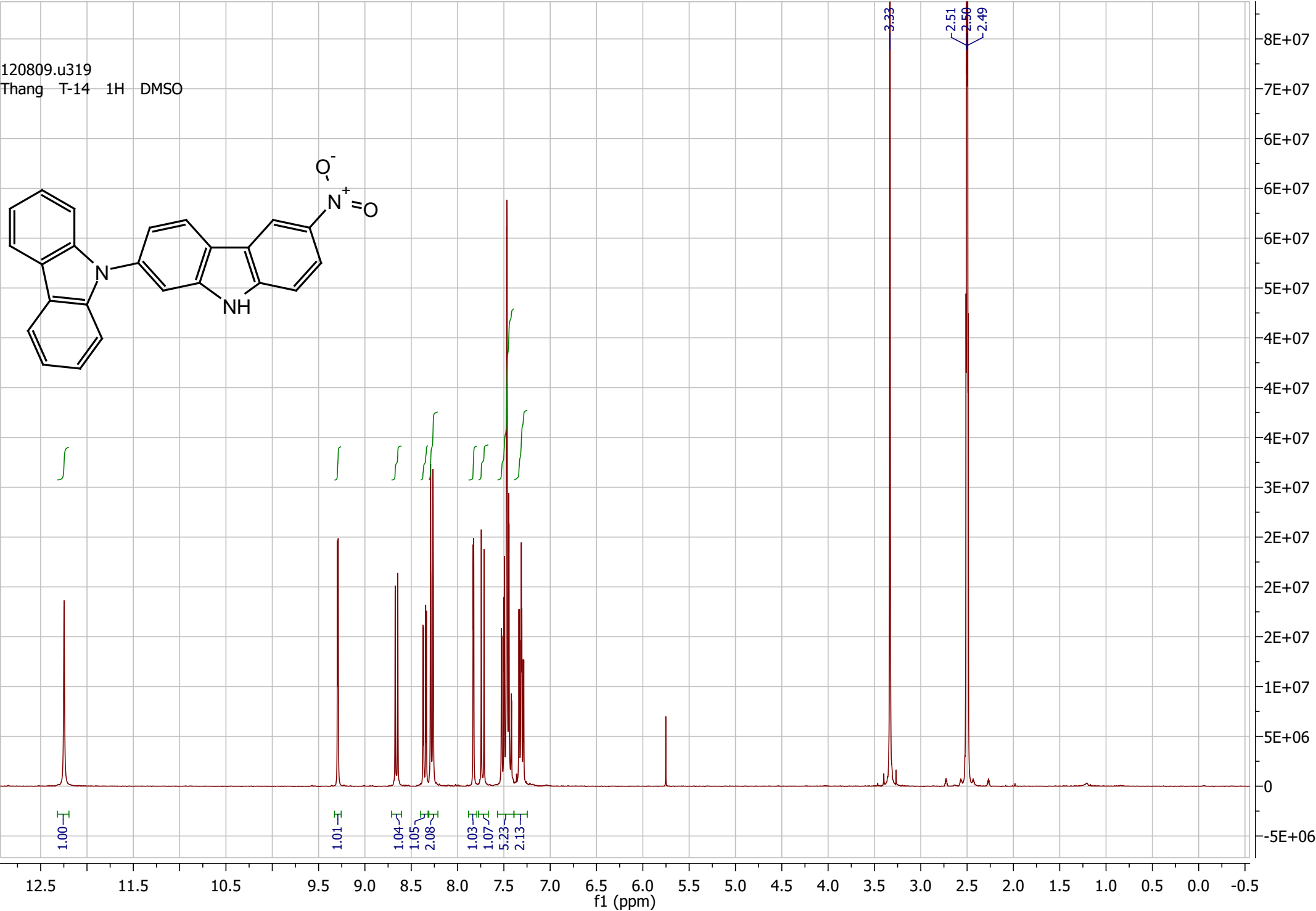
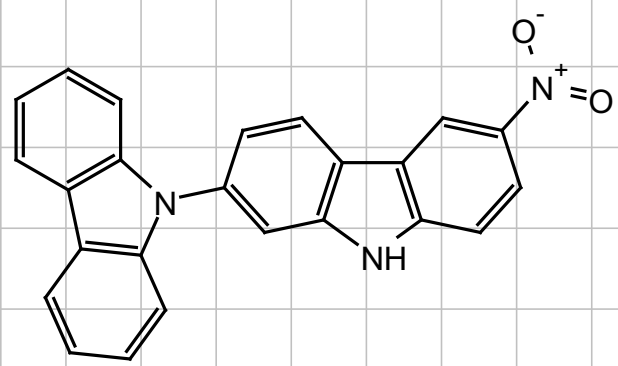
120809.u316
Thang T-15 1H Aceton-d6



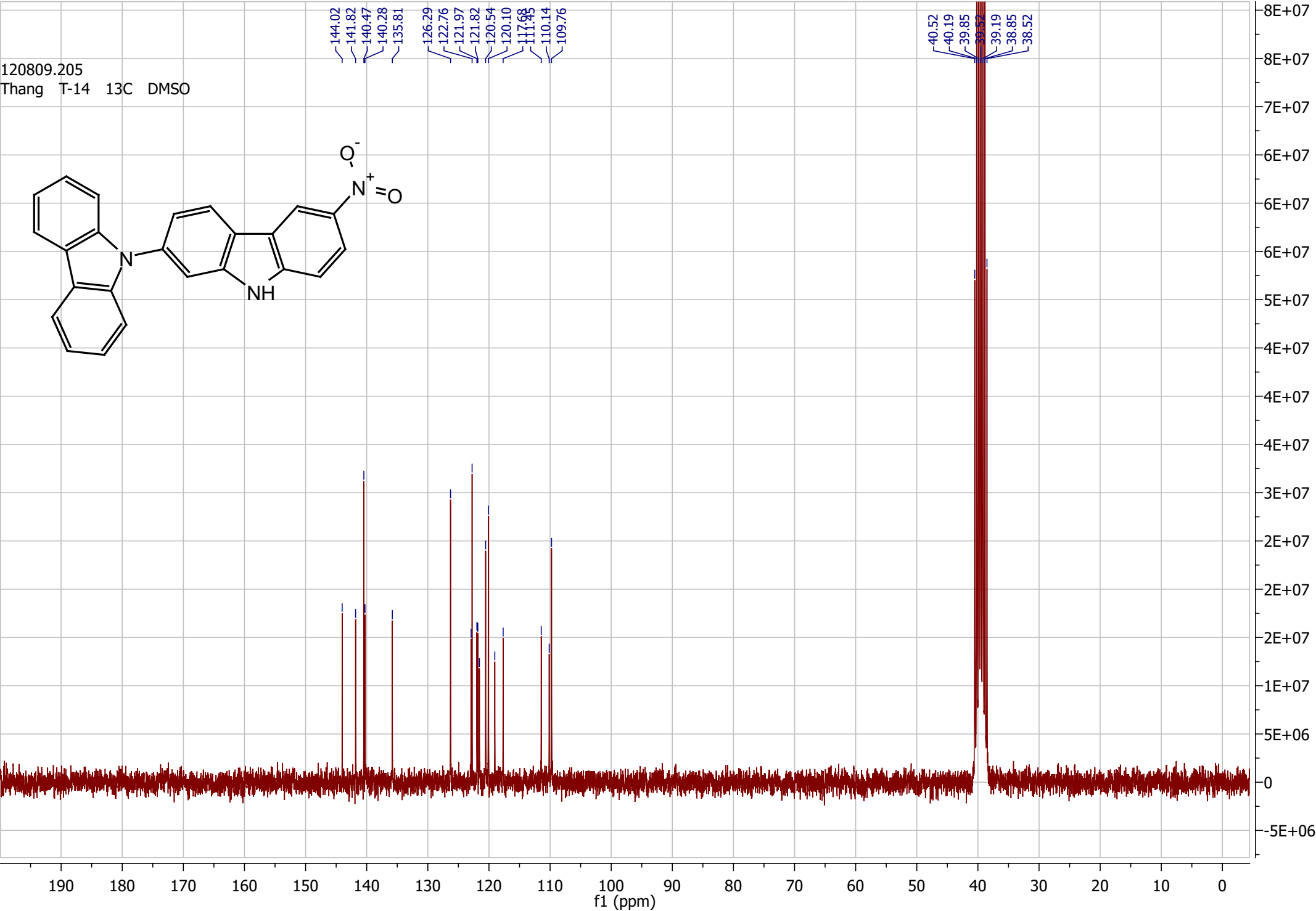
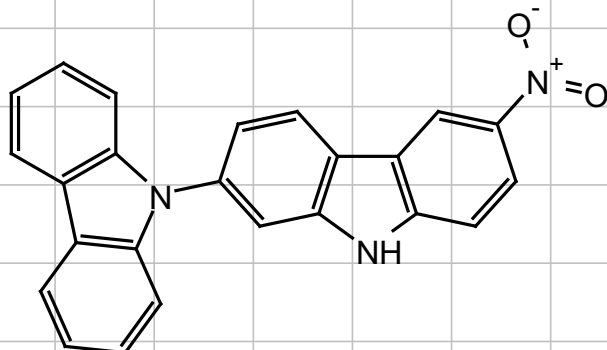




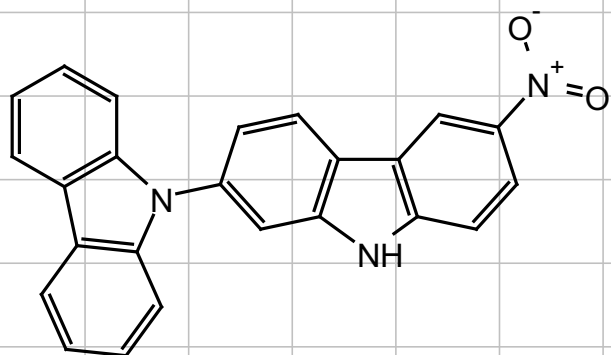
120809.u319
Thang T-14 1H DMSO



120809.205
Thang T-14 13C DMSO



120809.205
Thang T-14 Dept DMSO

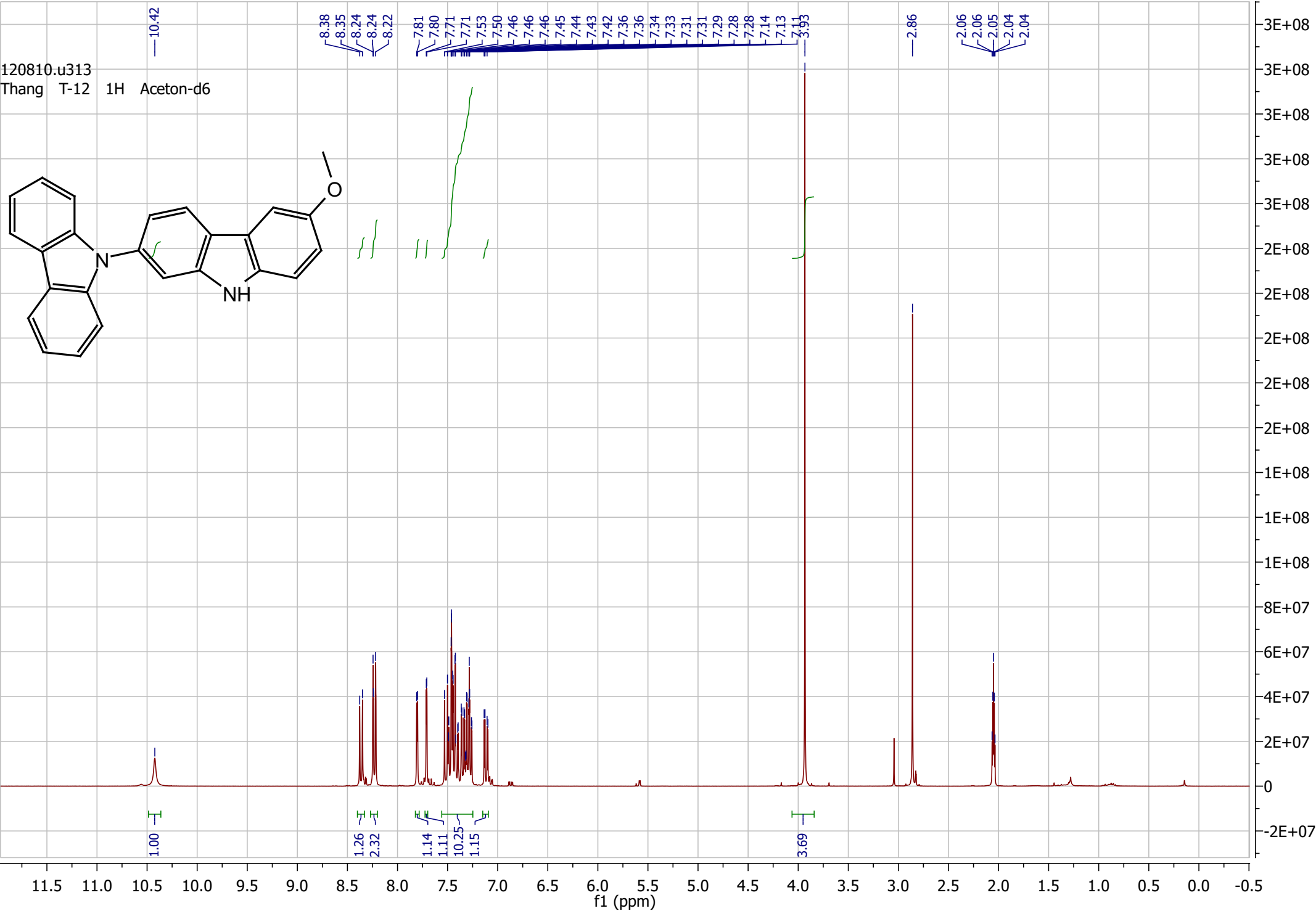
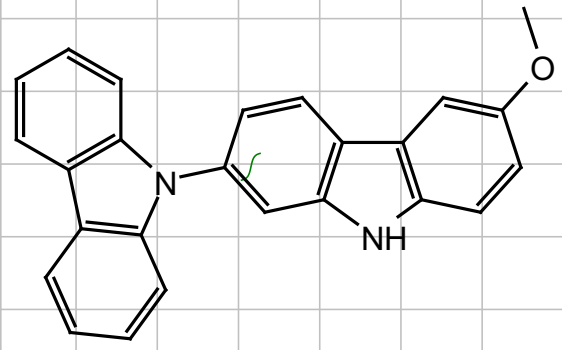


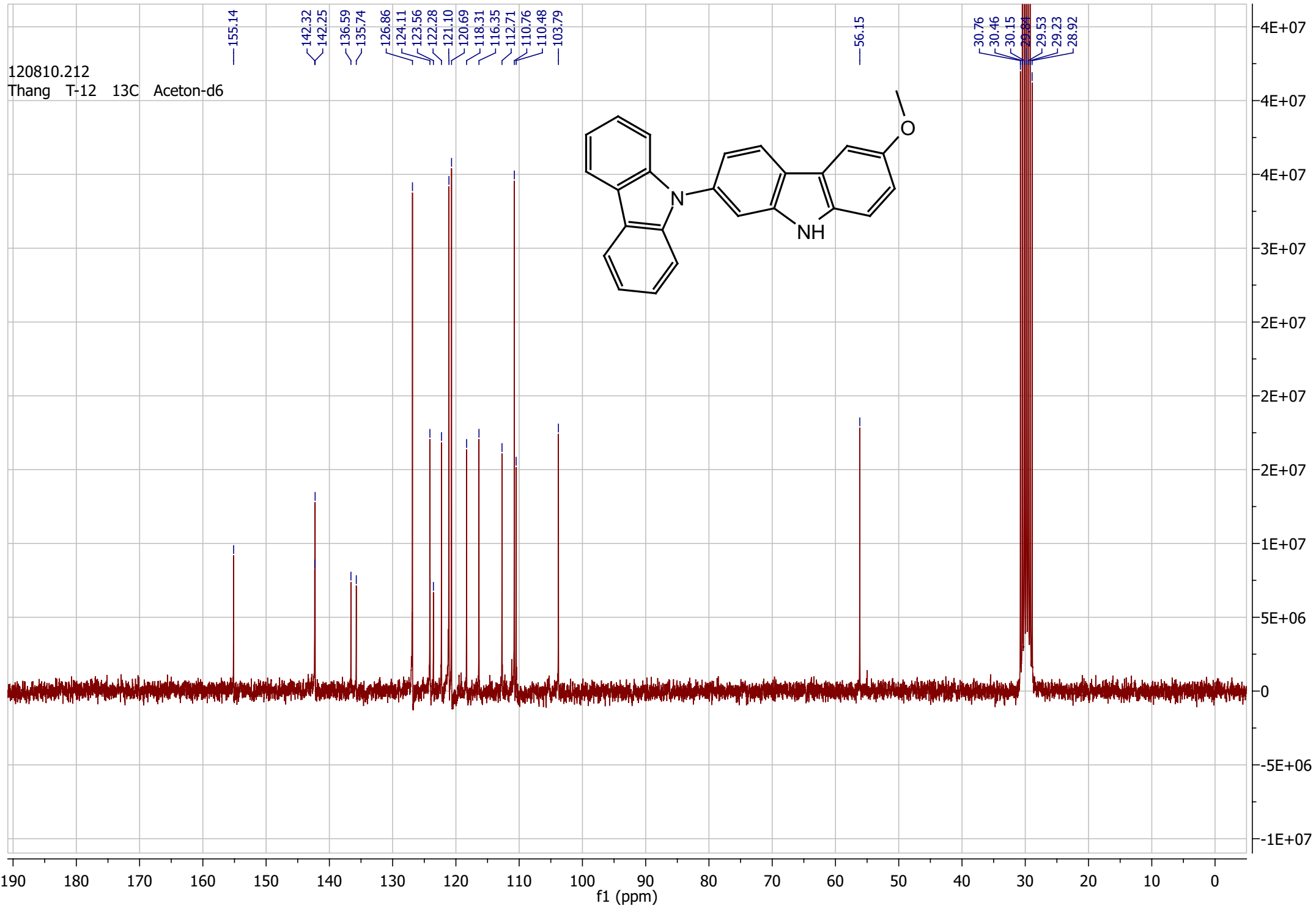
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121.57
120.55
120.10
119.05
117.69
111.45
110.15
109.76

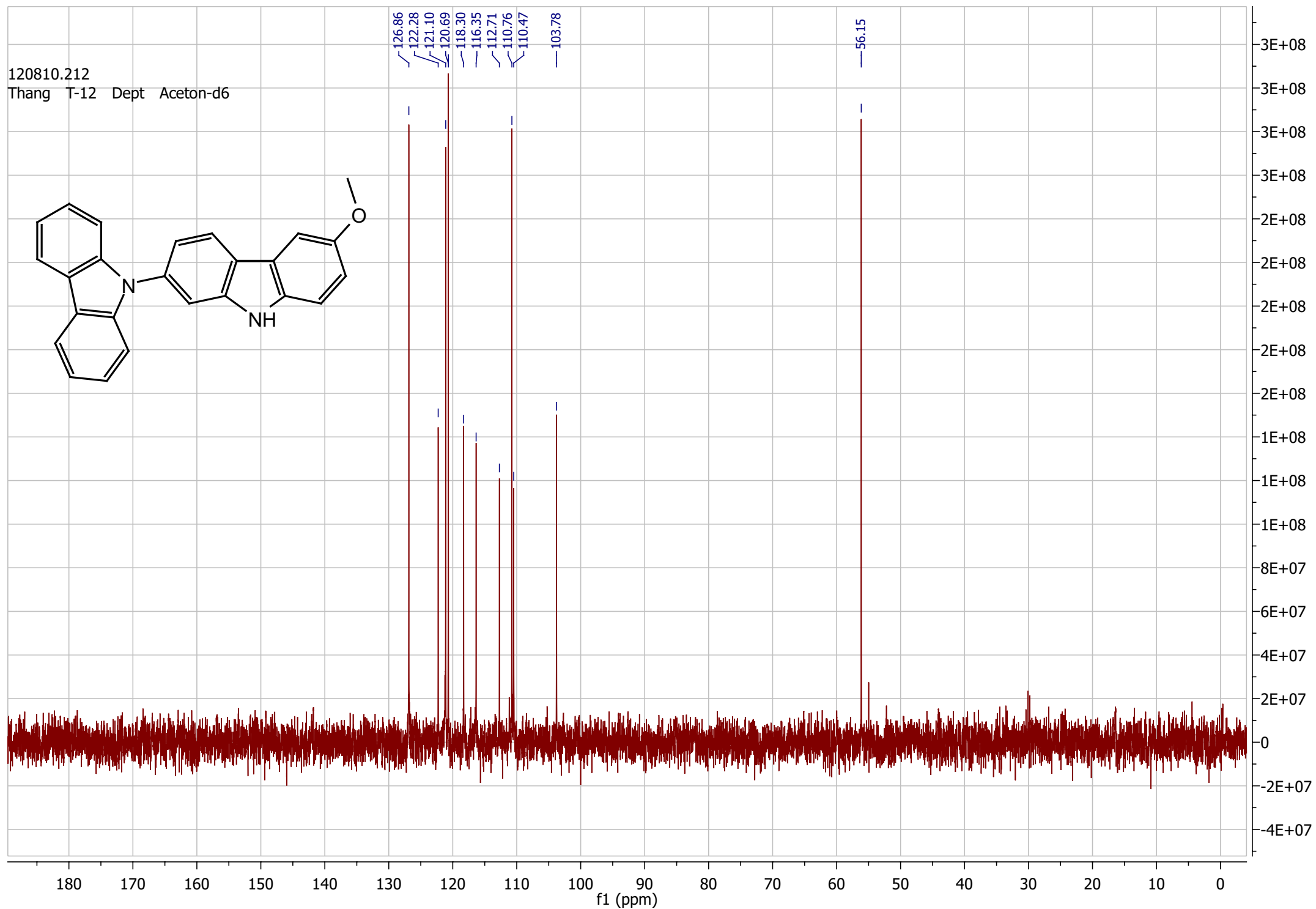
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f1 (ppm)

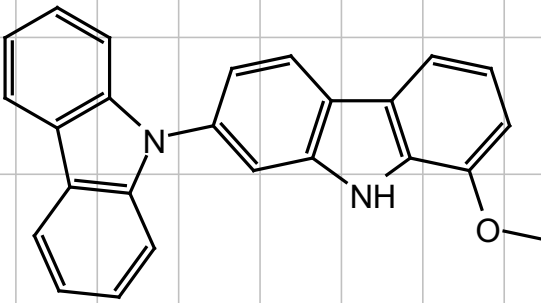
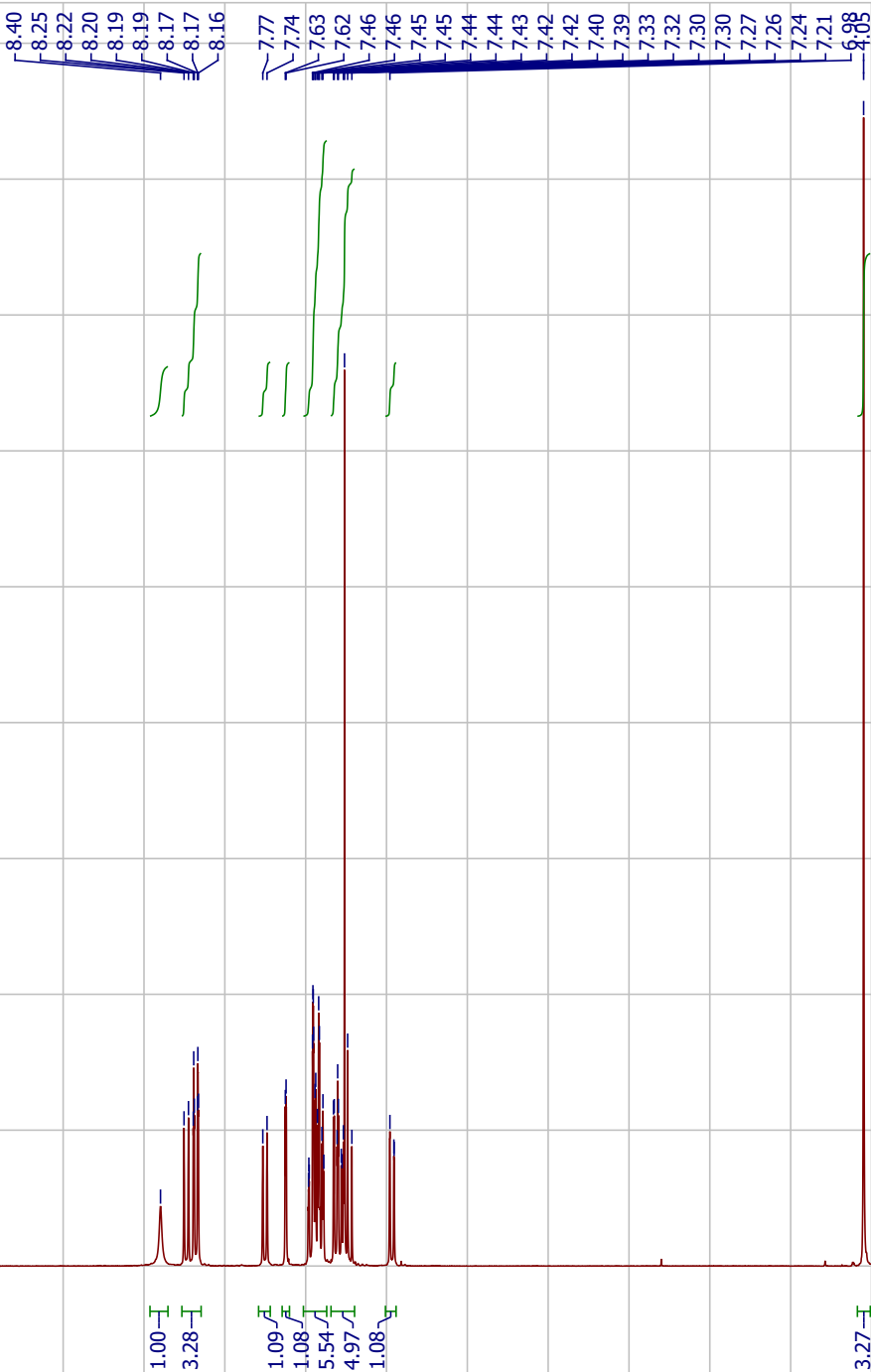
120810.u313
Thang T-12 1H Aceton-d6





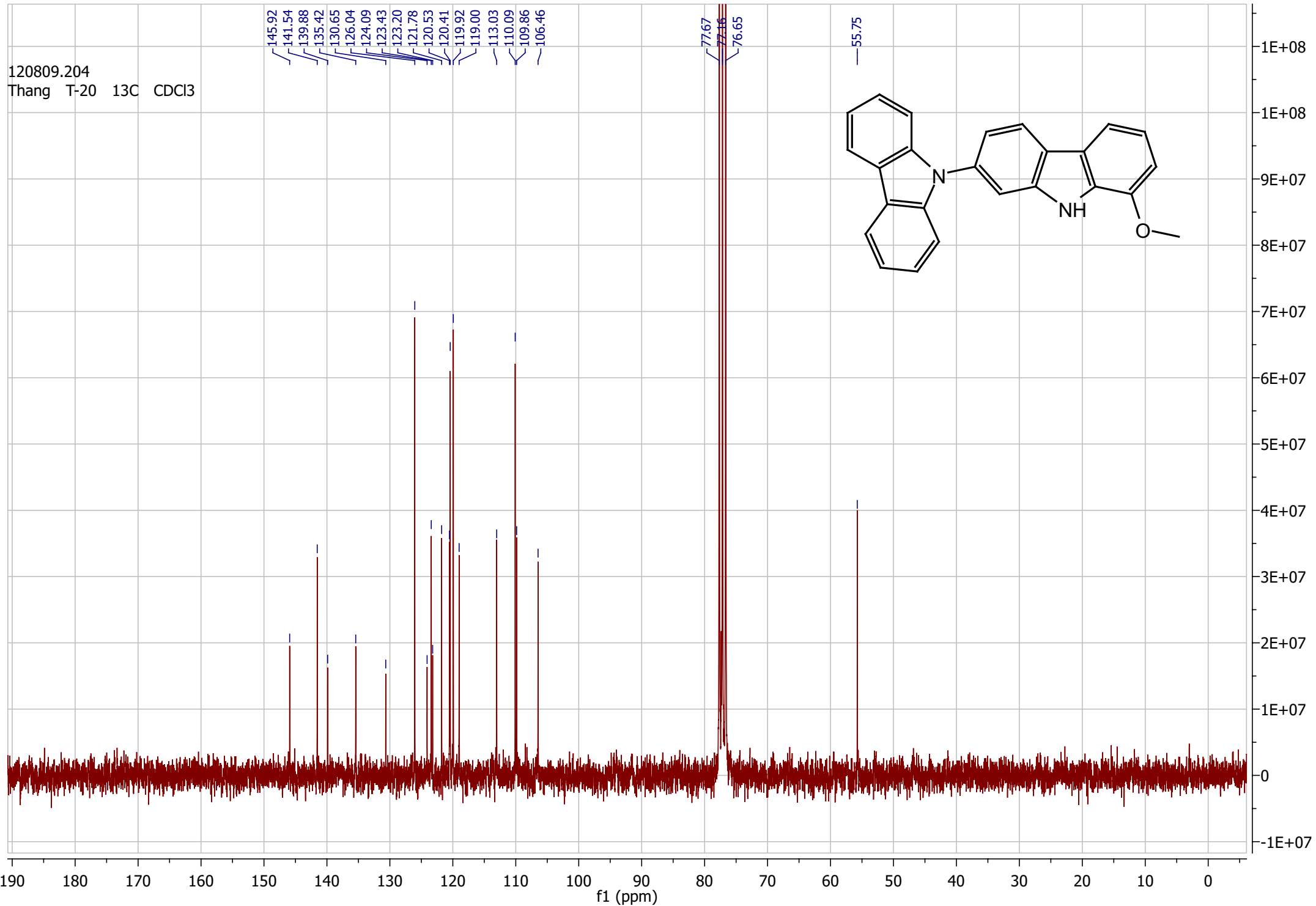


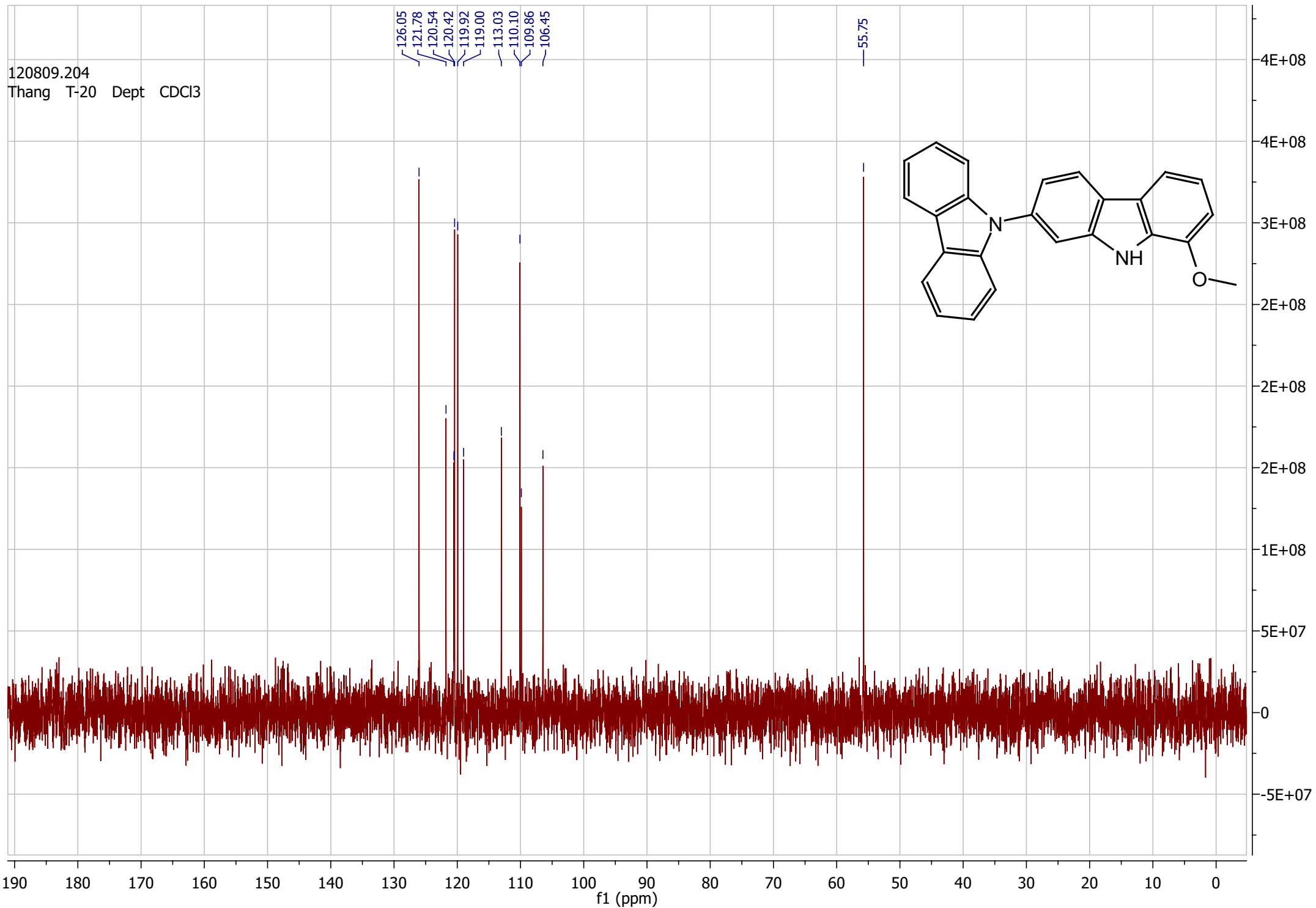
120809.u317
Thang T-20 1H CDCl3

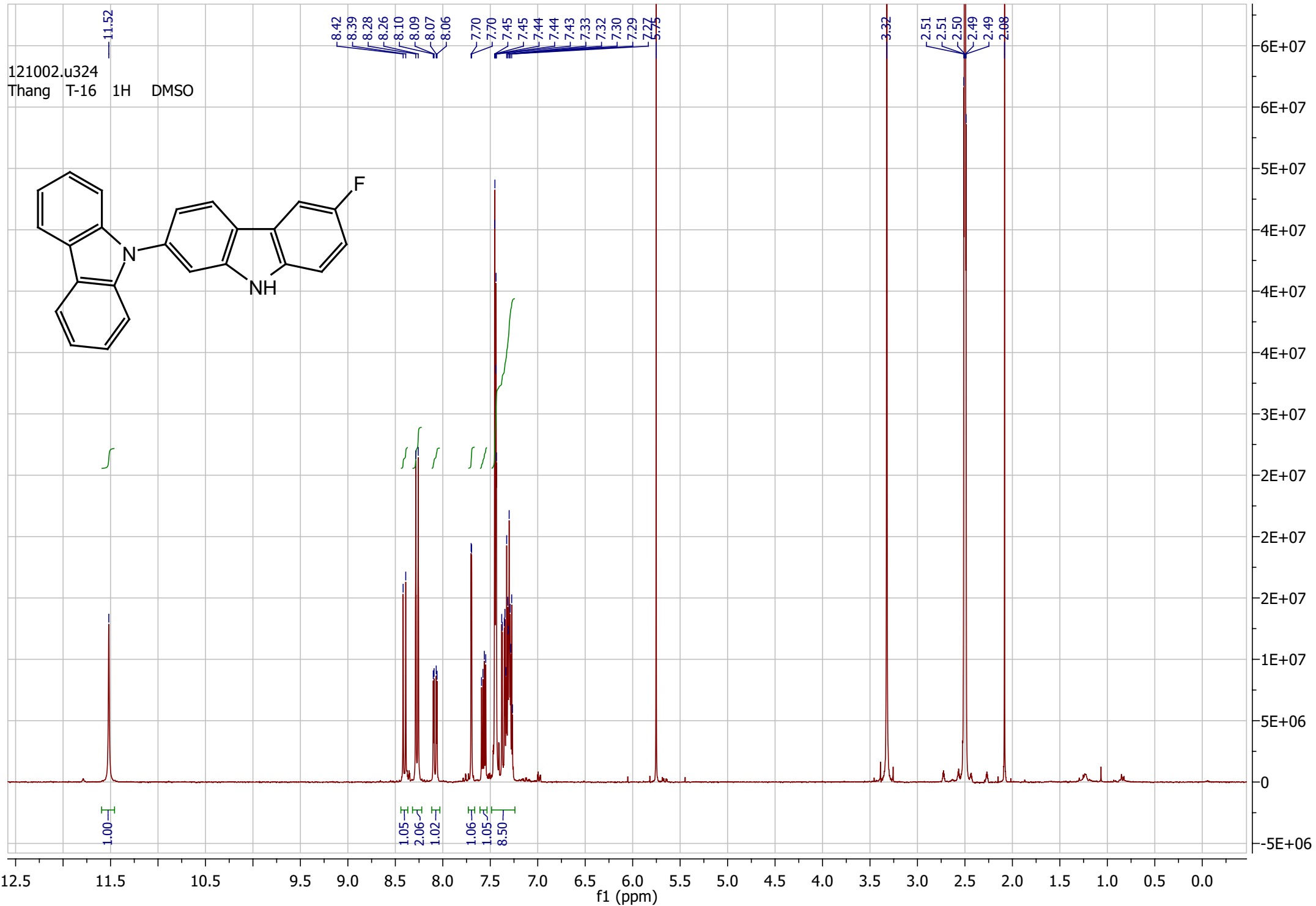


12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

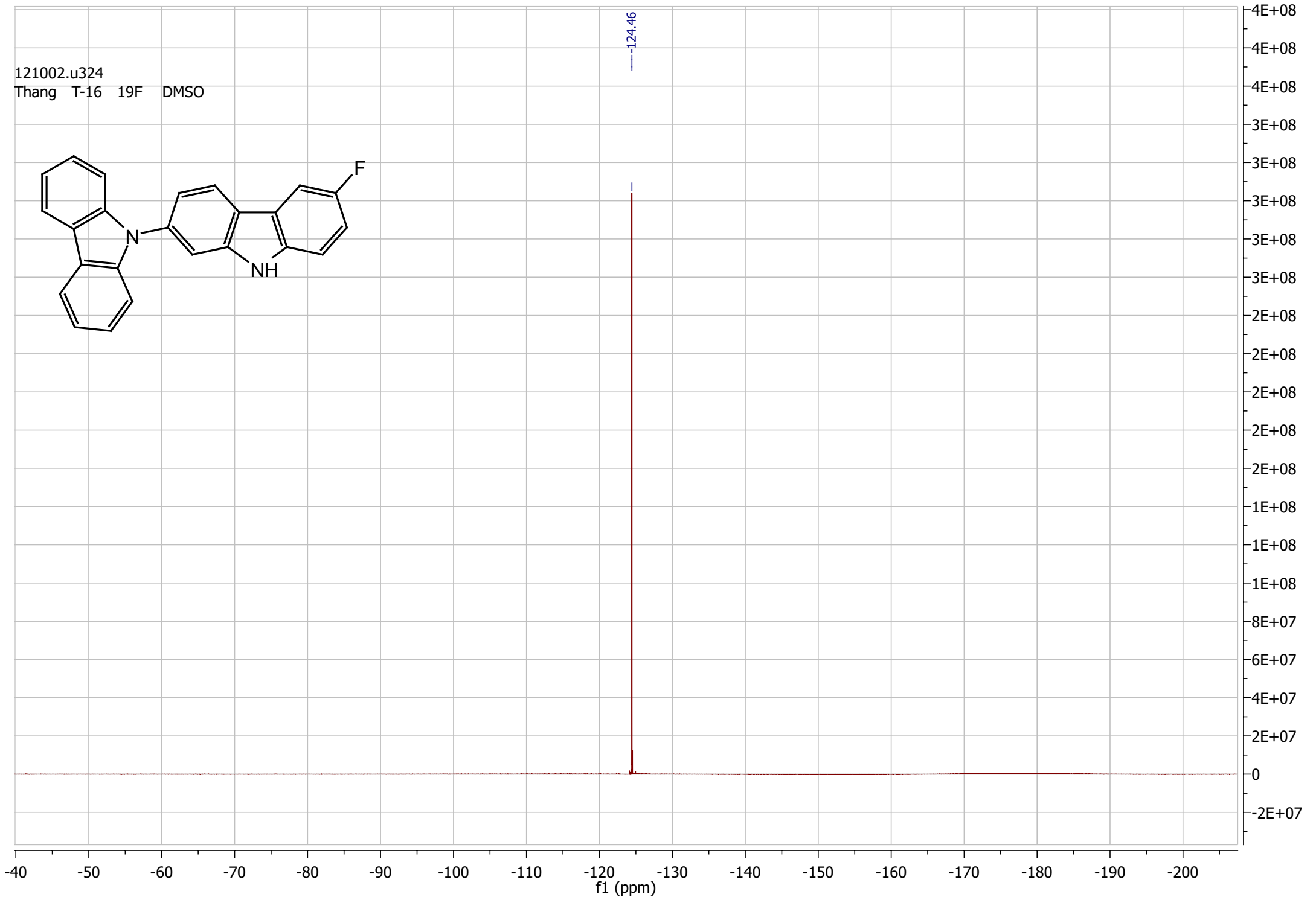
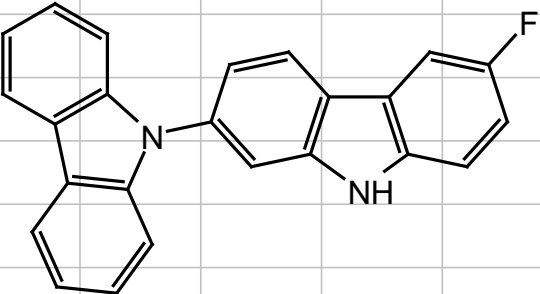
f1 (ppm)

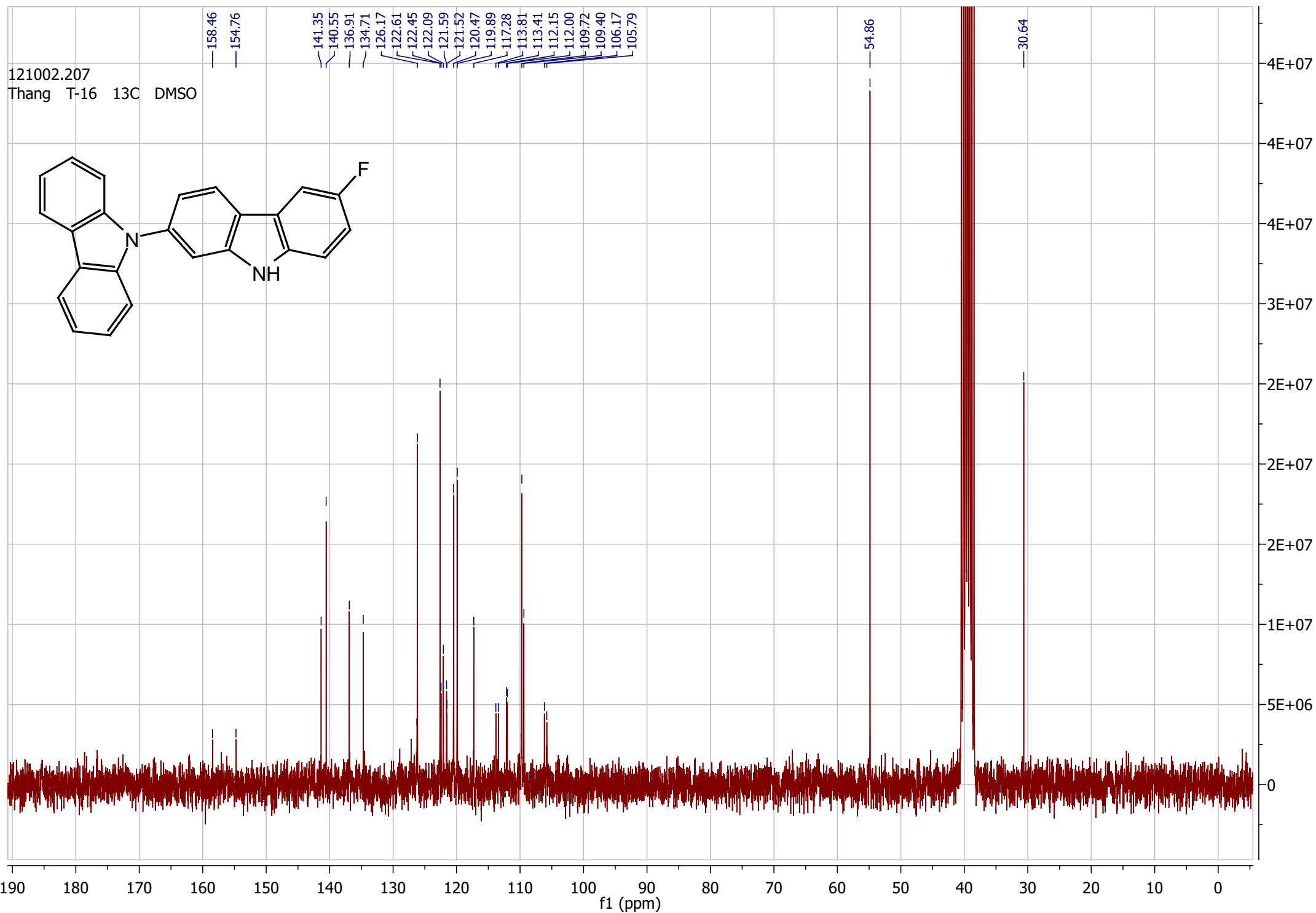


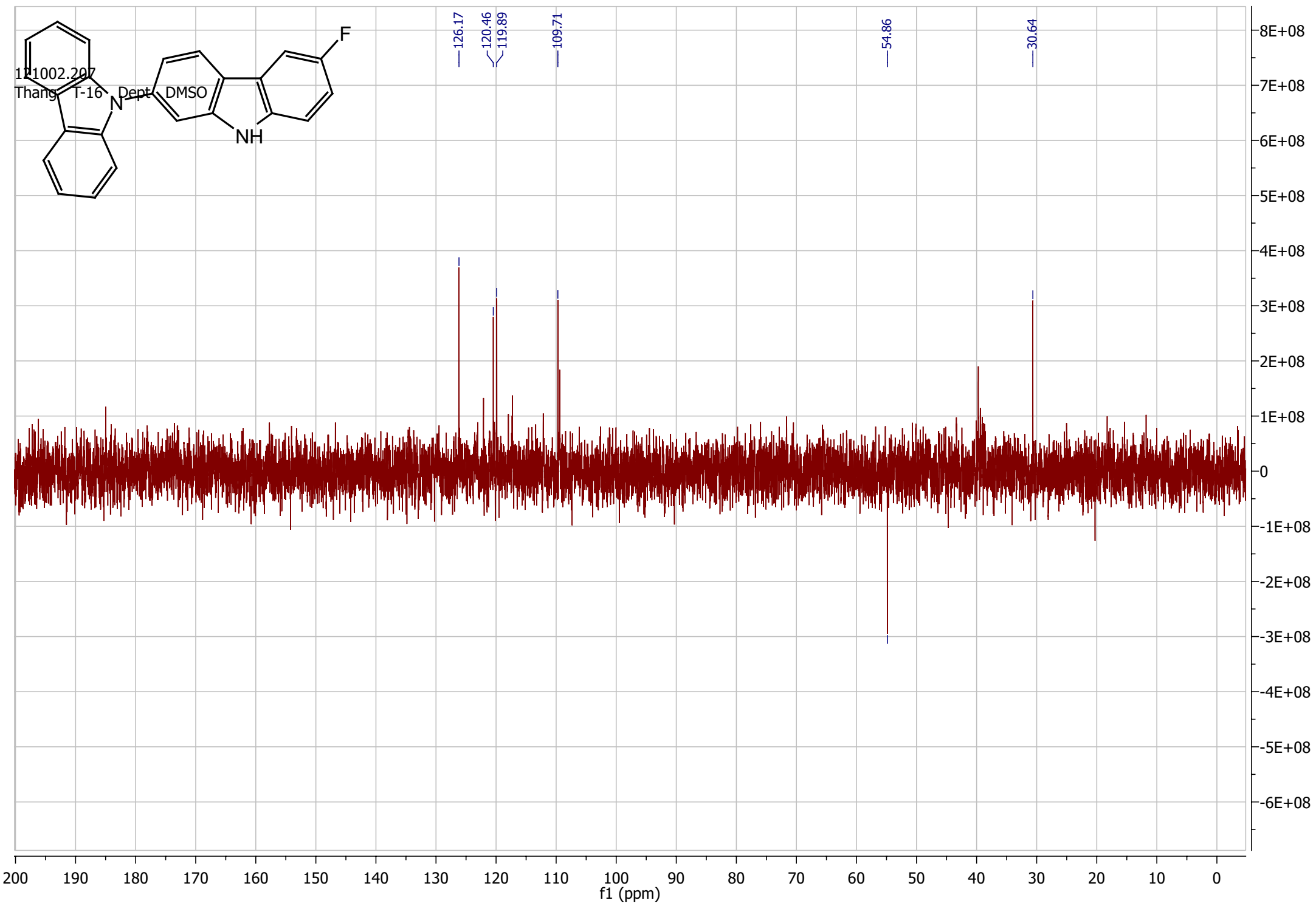




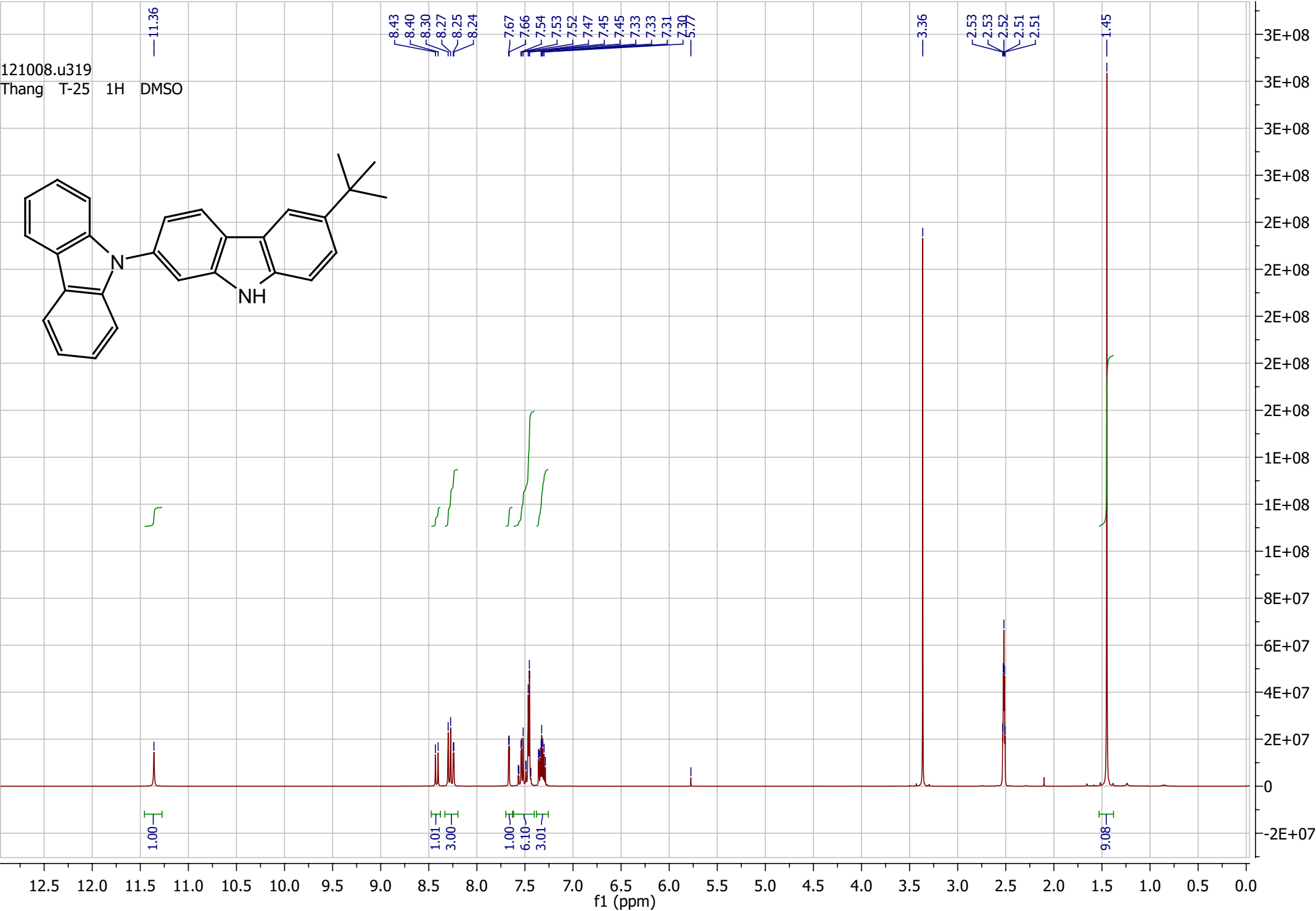
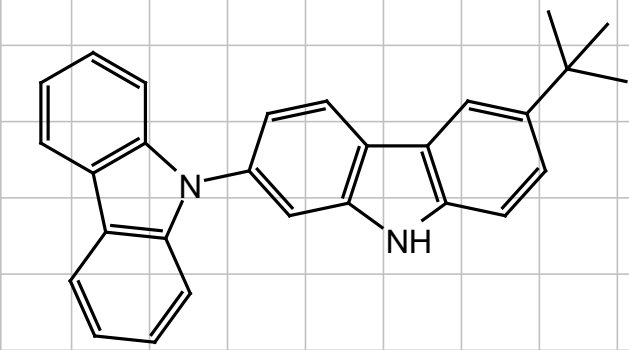
121002.u324
Thang T-16 19F DMSO



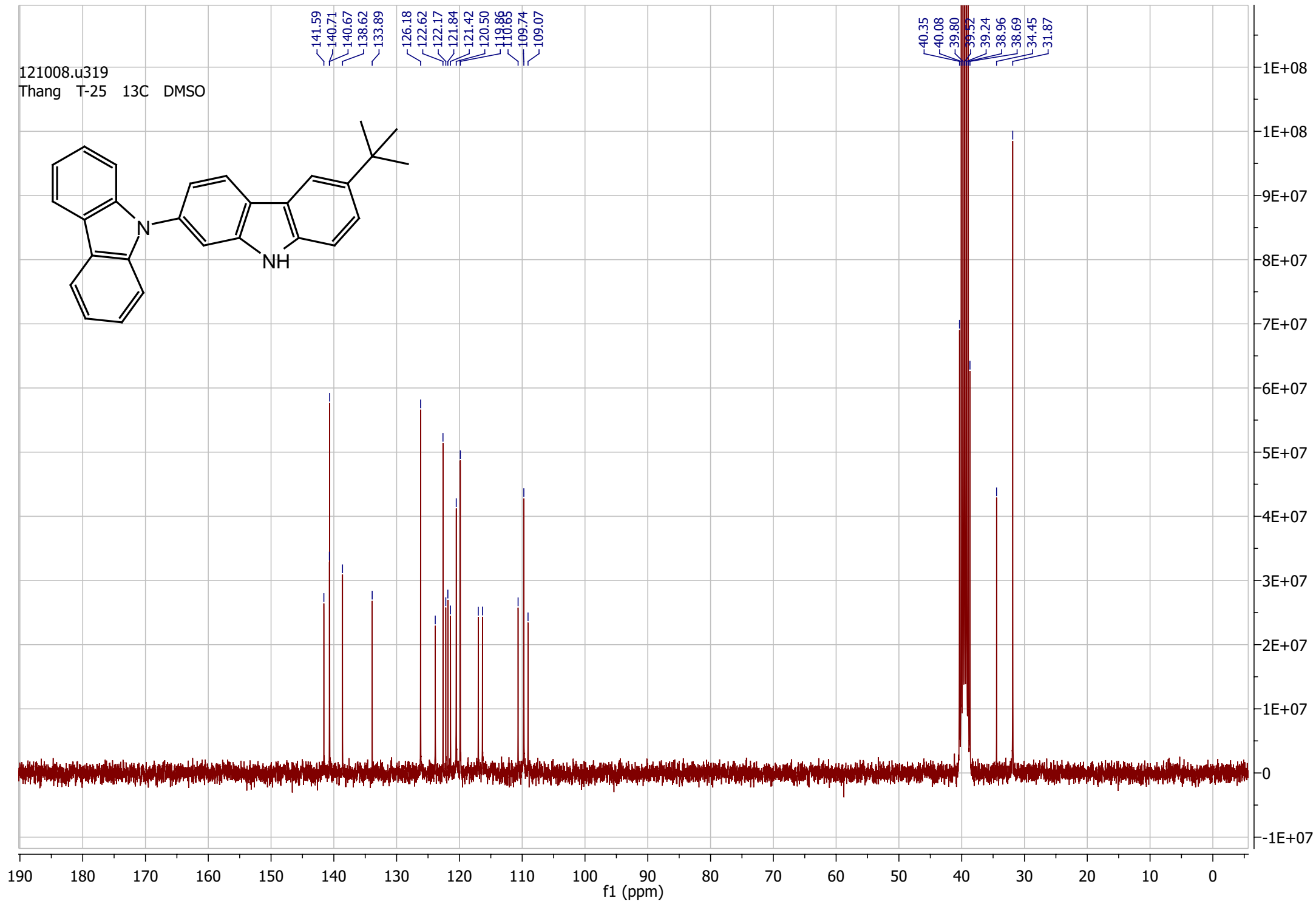
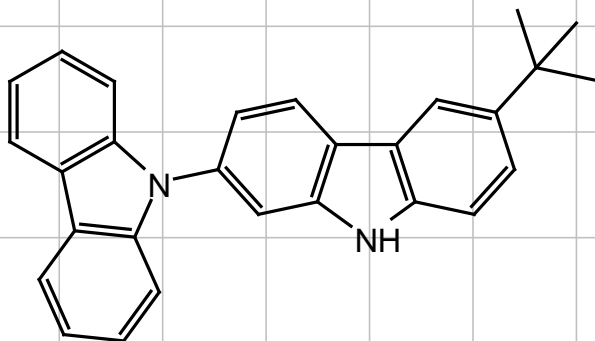




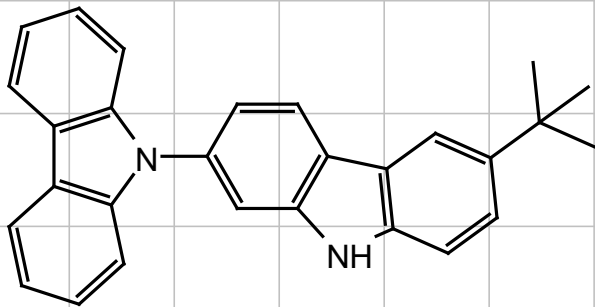
121008.u319
Thang T-25 1H DMSO



121008.u319
Thang T-25 13C DMSO

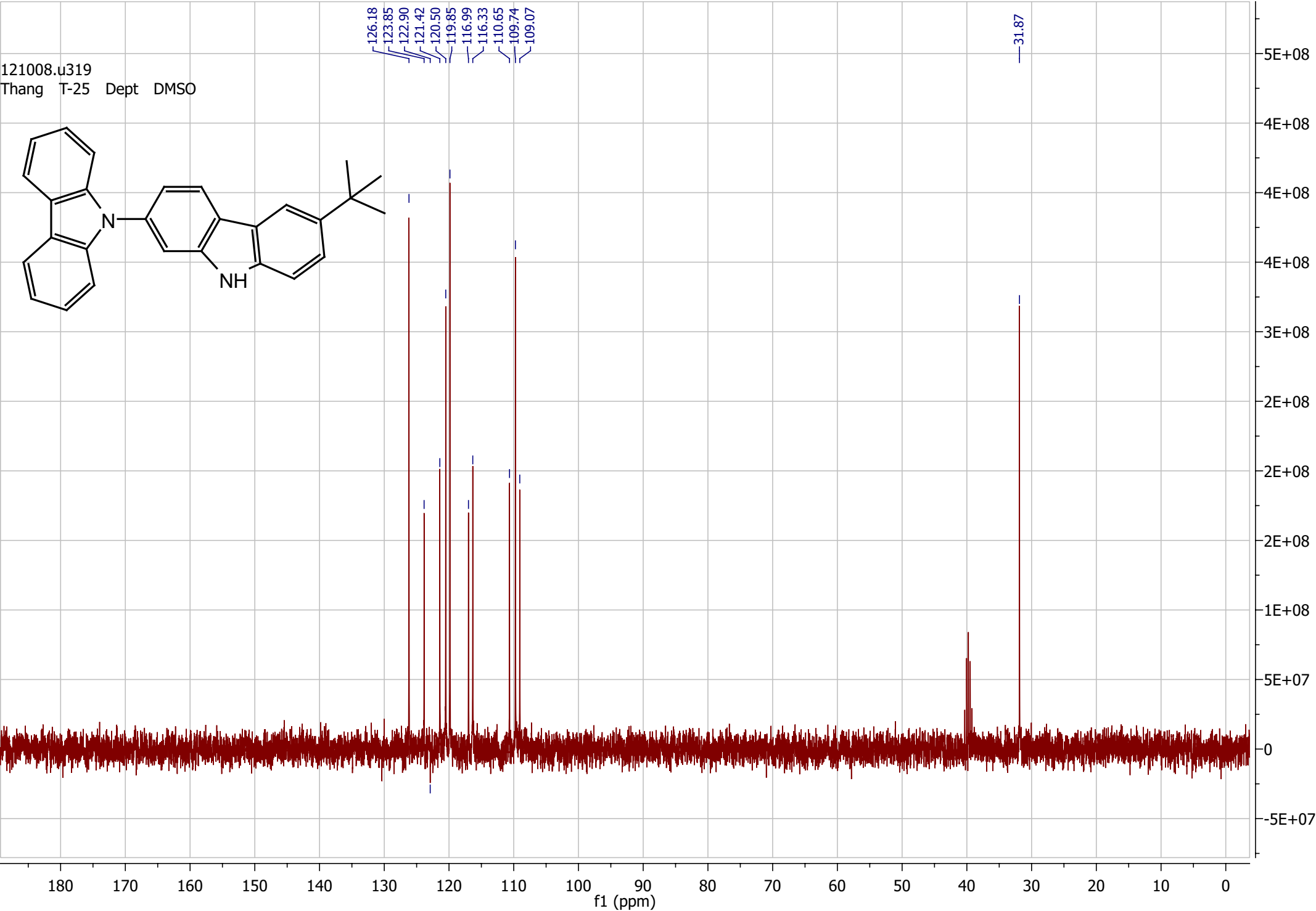


121008.u319
Thang T-25 Dept DMSO

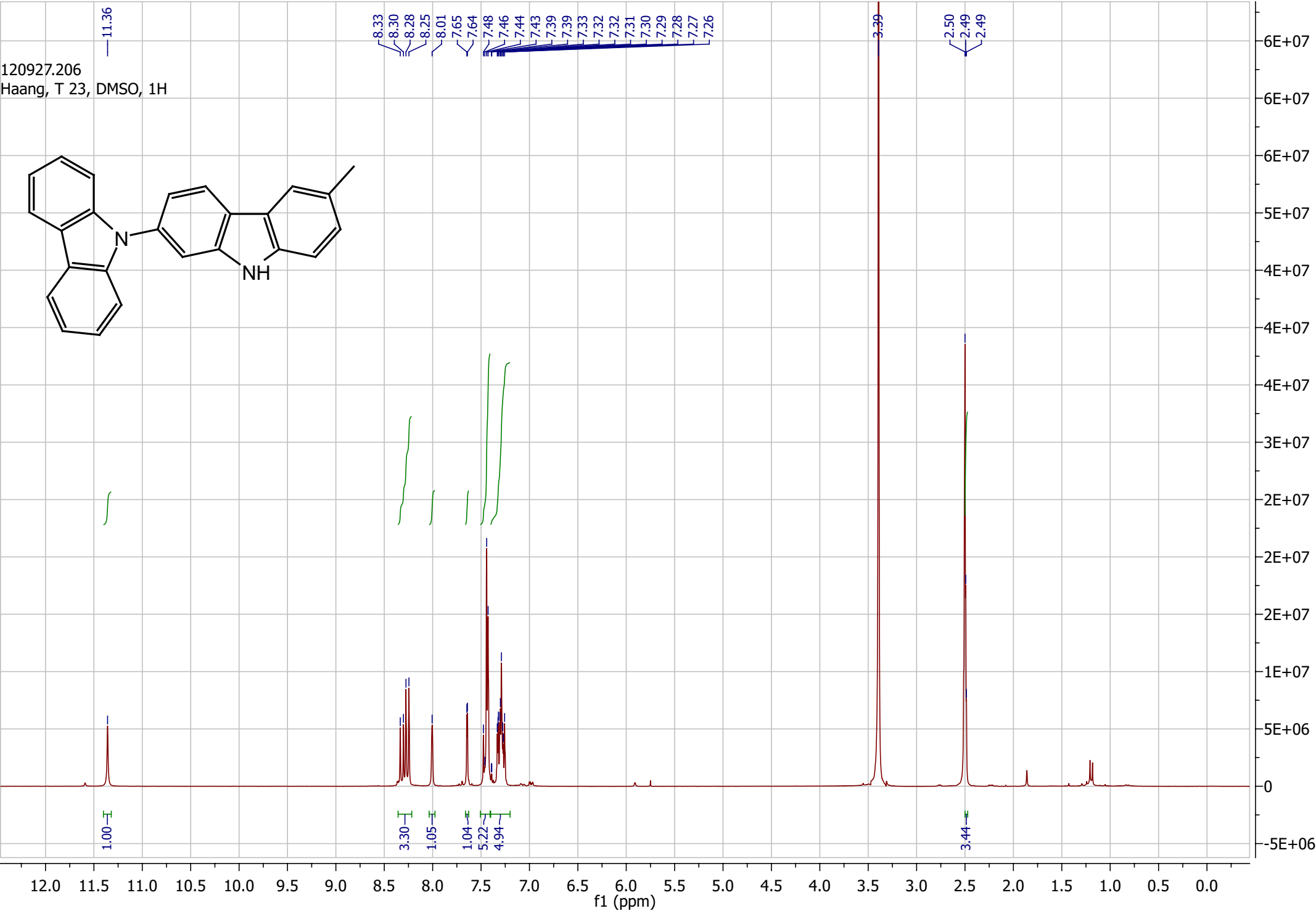
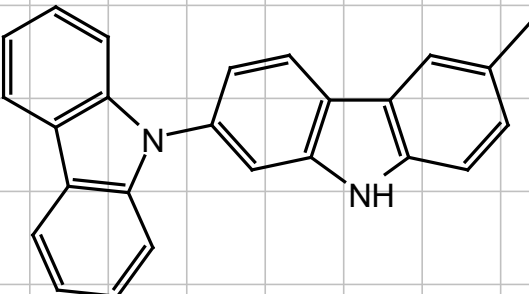


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123.85
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120.50
119.85
116.99
116.33
110.65
109.74
109.07

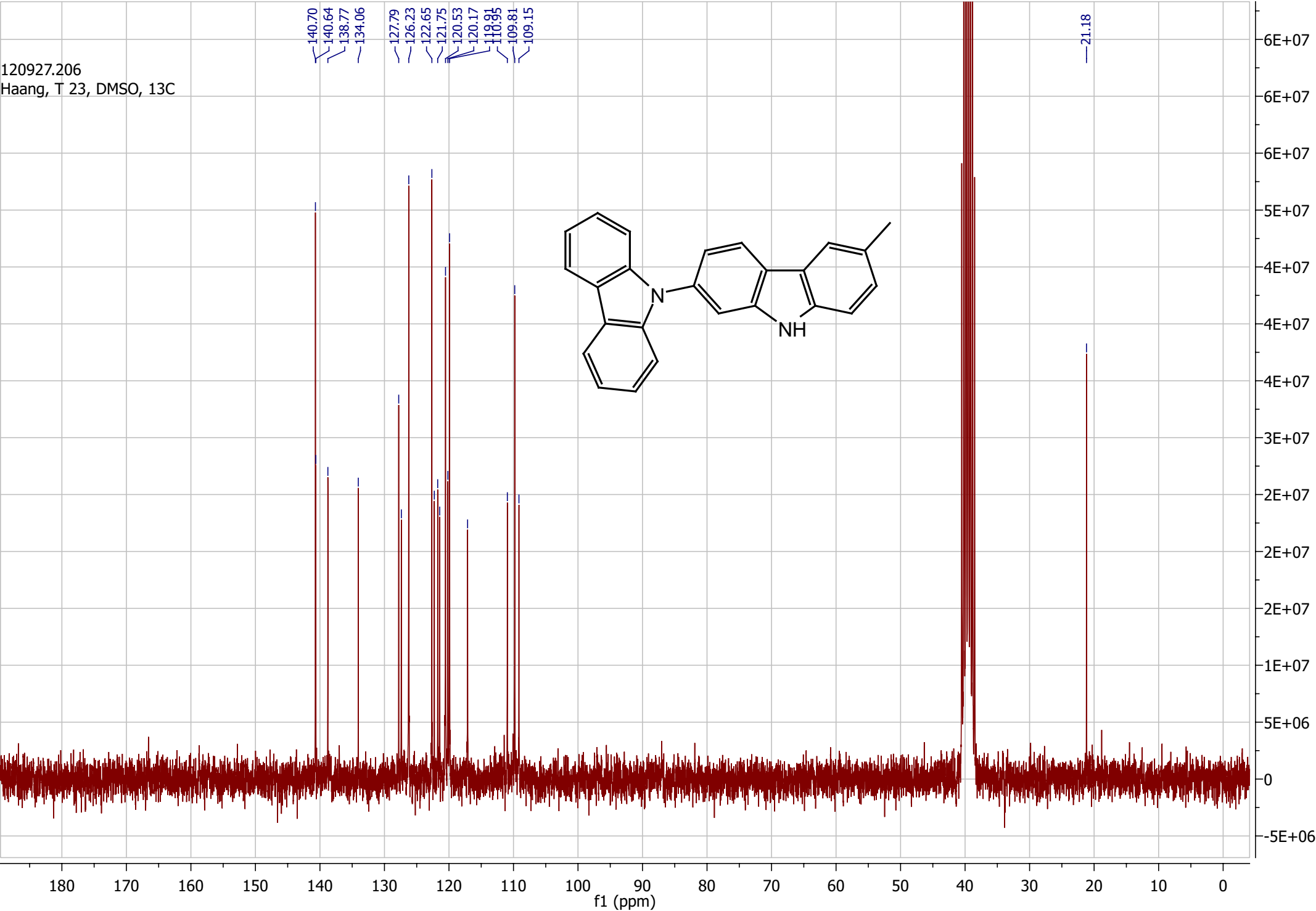
31.87



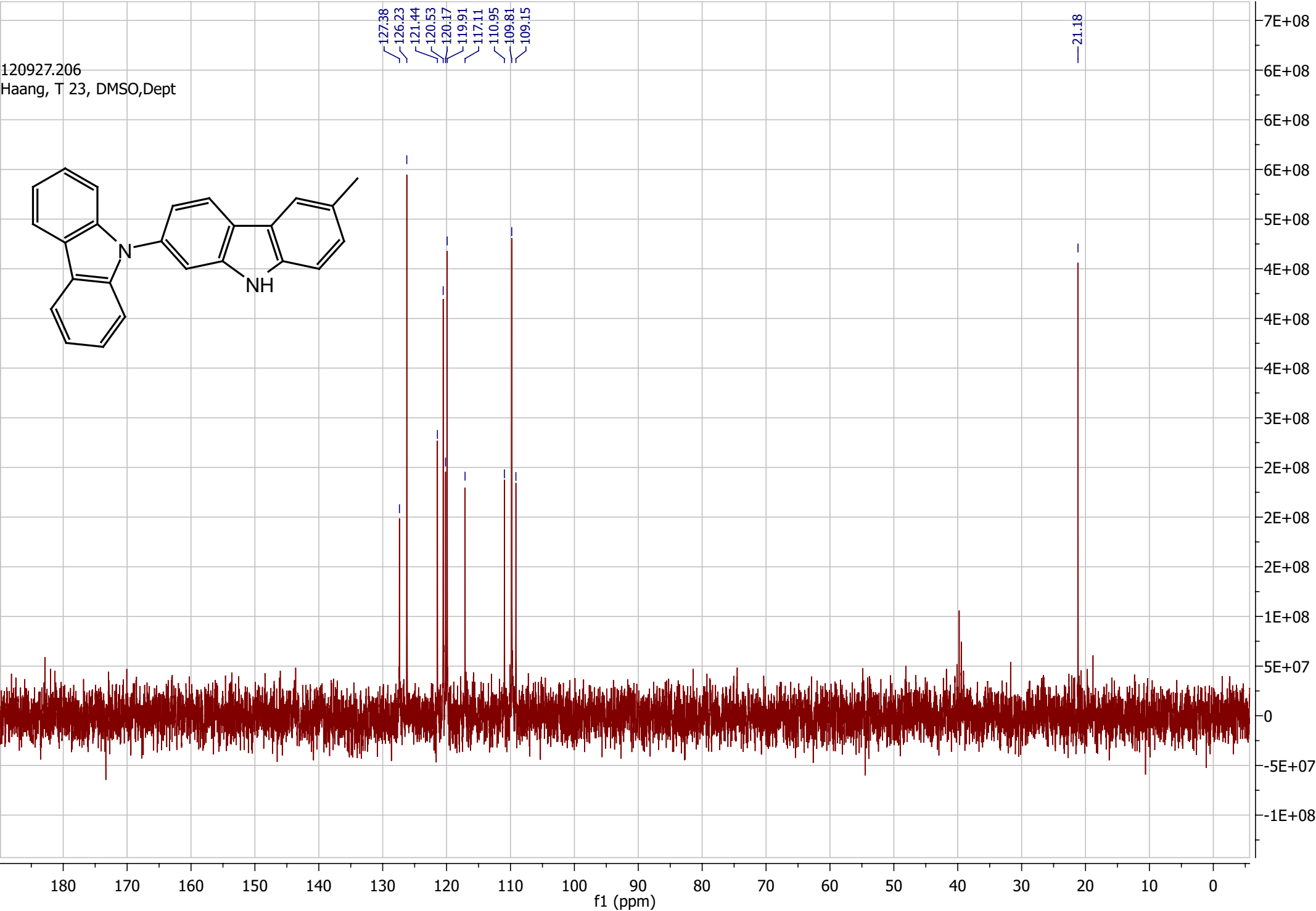
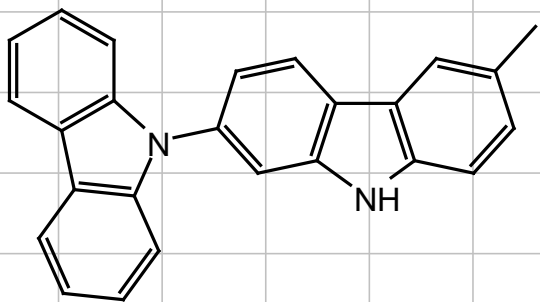
120927.206
Haang, T 23, DMSO, 1H



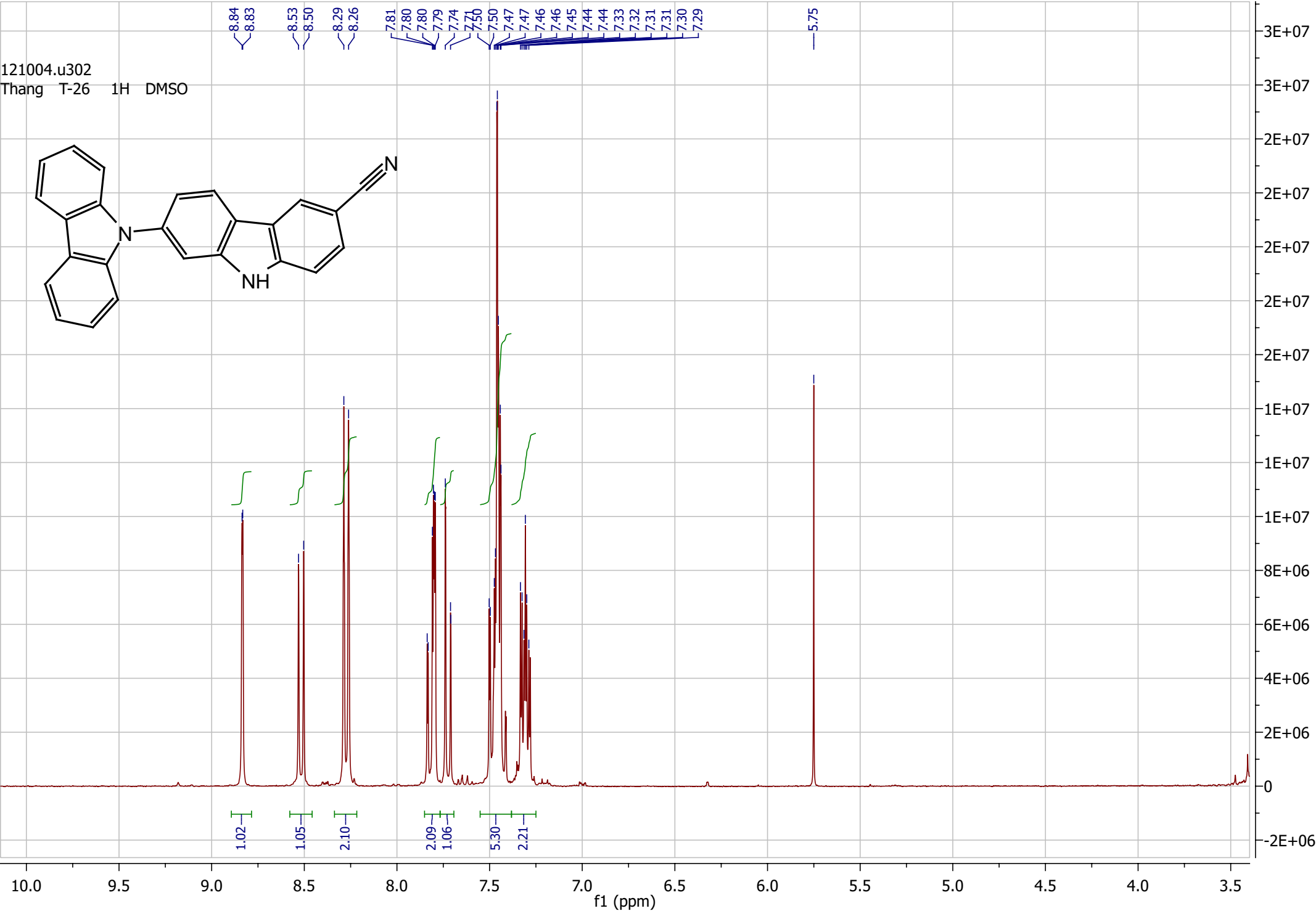
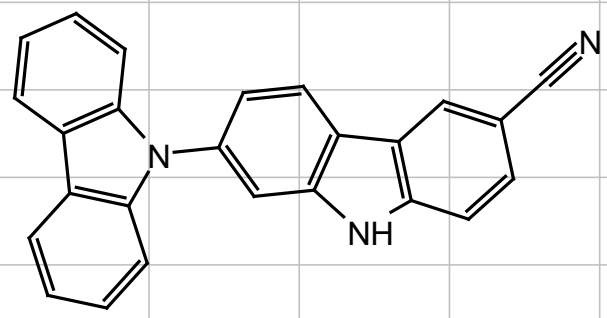
120927.206
Haang, T 23, DMSO, 13C



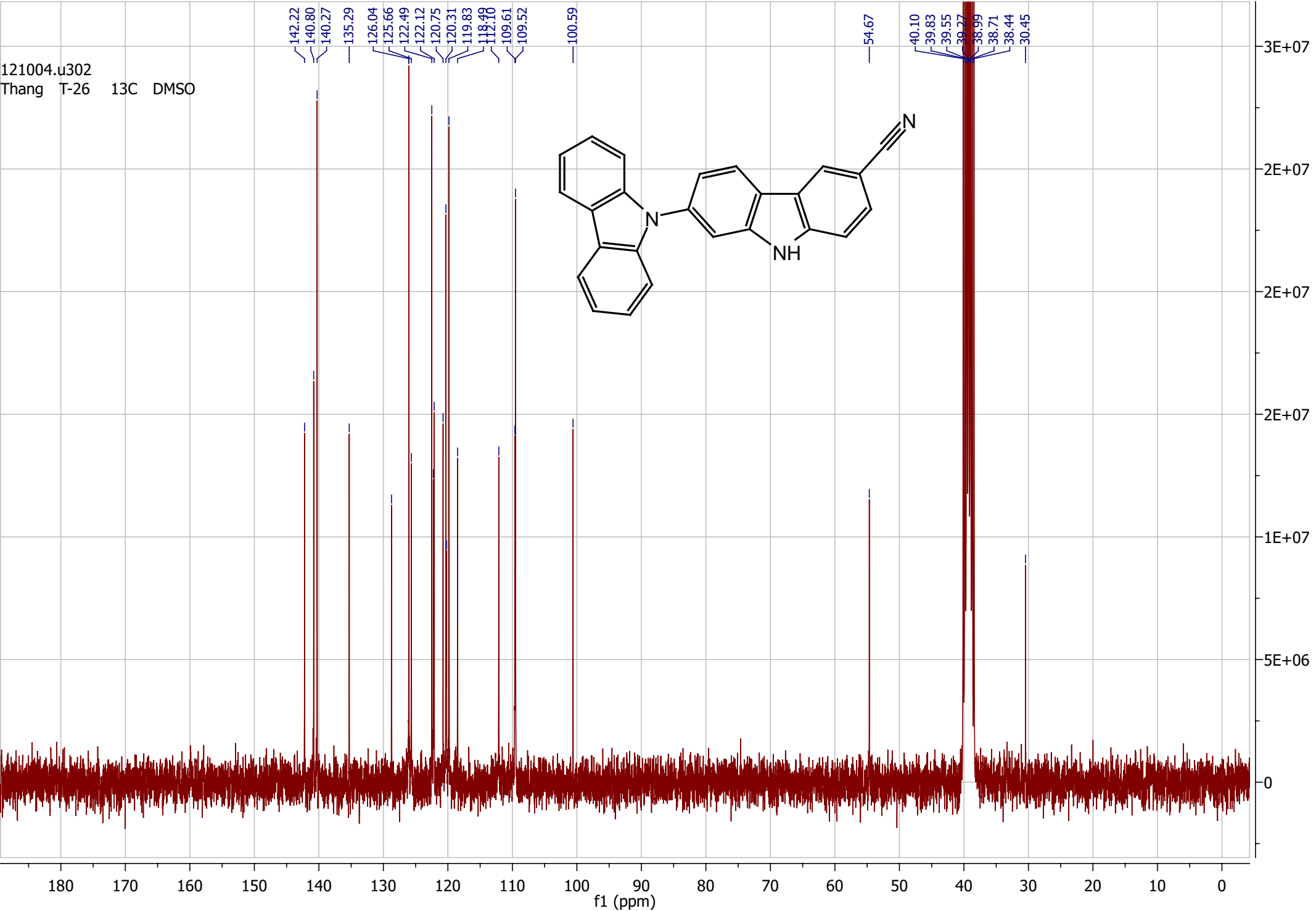
120927.206
Haang, T 23, DMSO,Dept



121004.u302
Thang T-26 1H DMSO

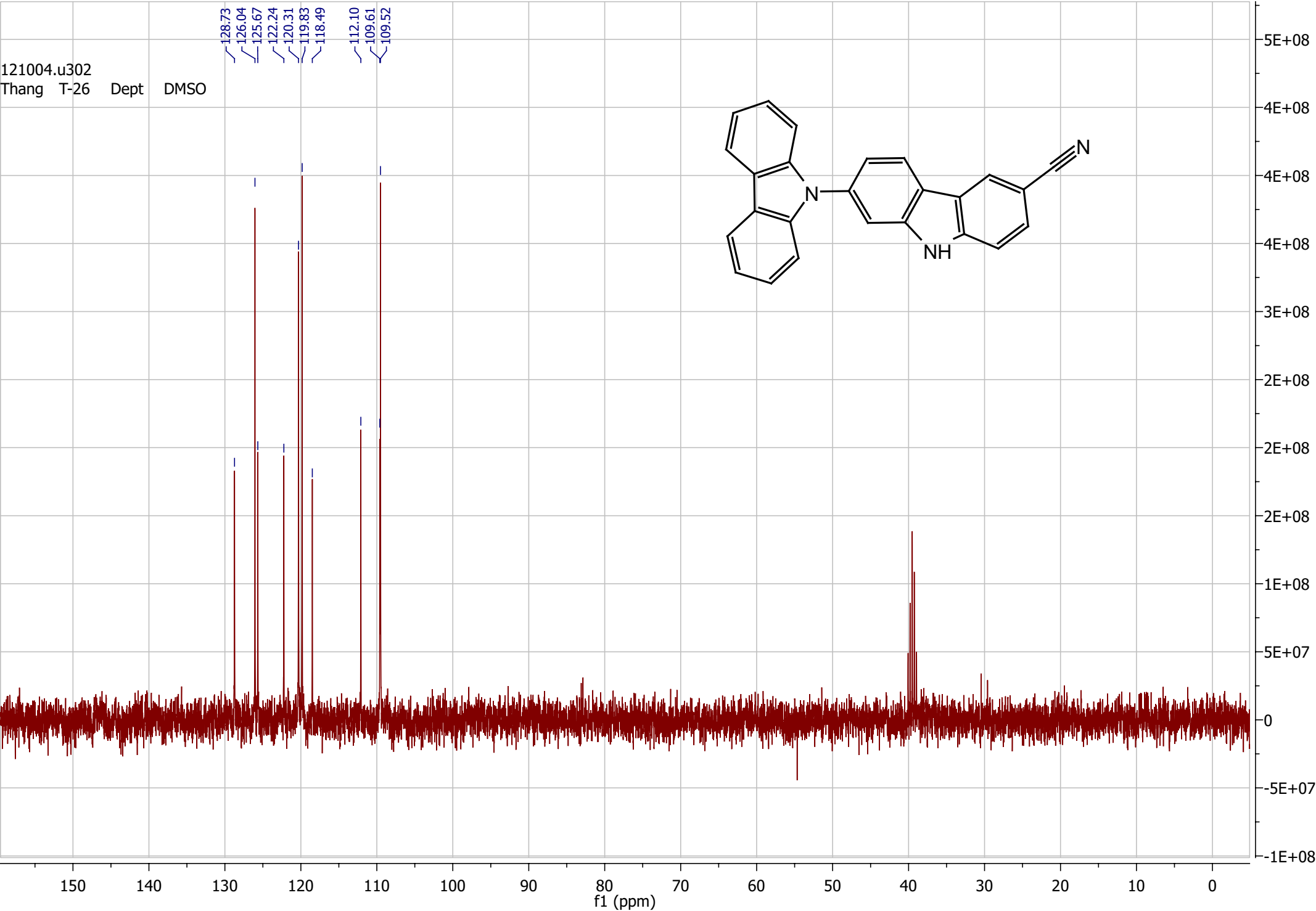
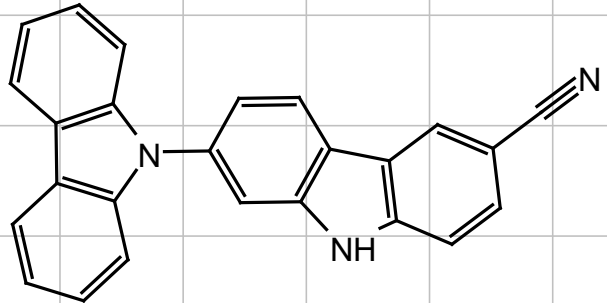


121004.u302
Thang T-26 13C DMSO

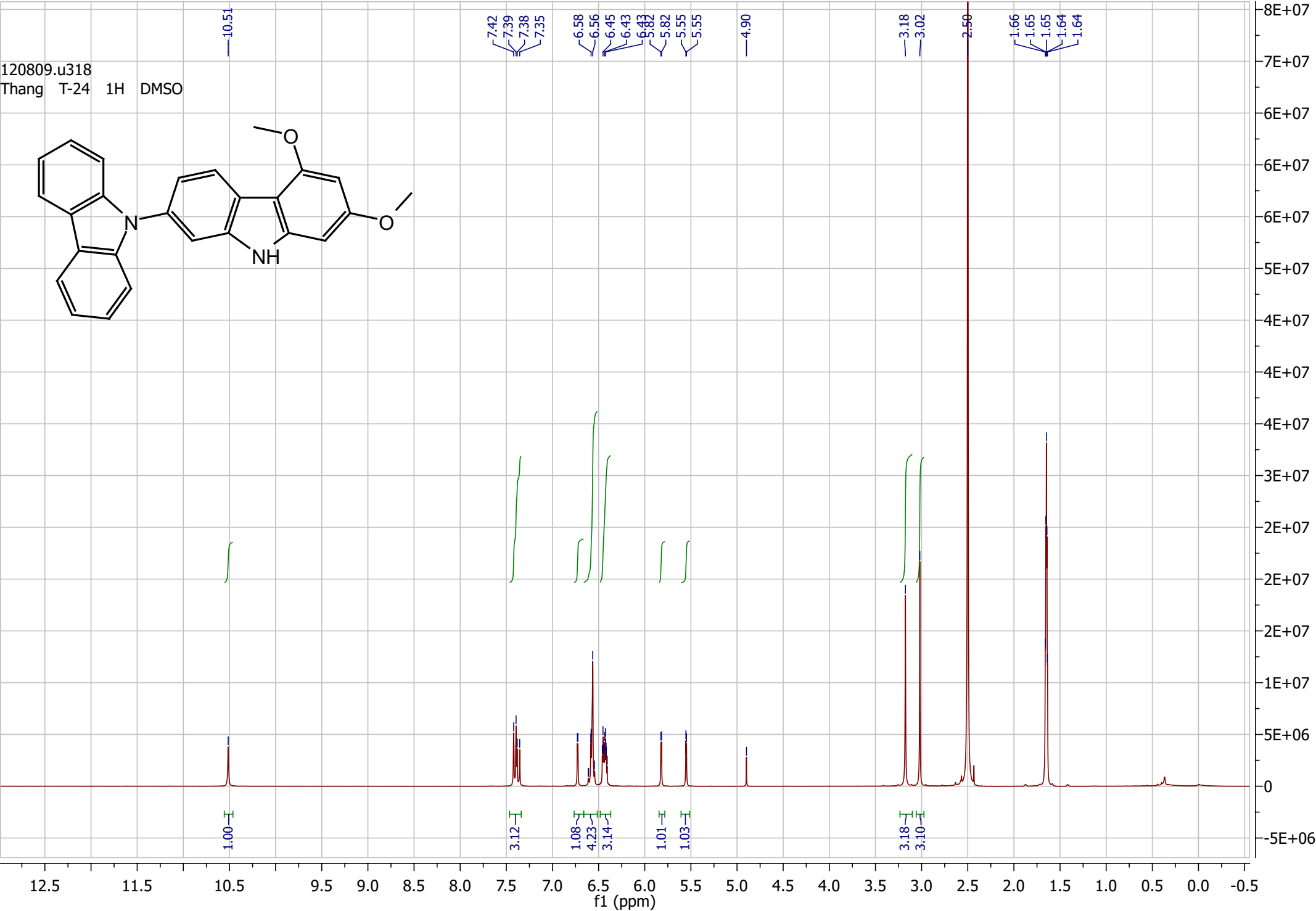
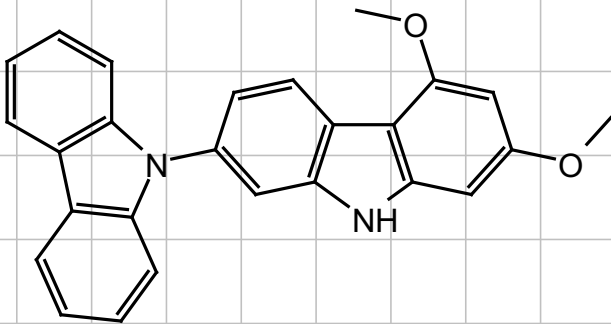


121004.u302
Thang T-26 Dept DMSO

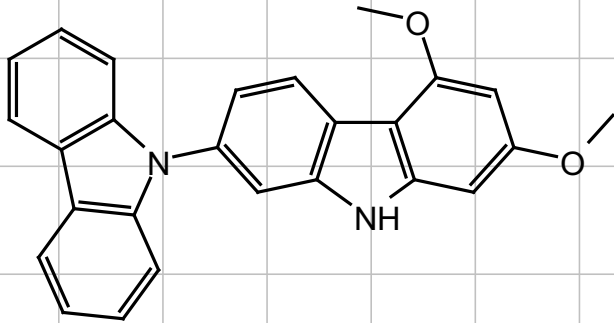
128.73
126.04
125.67
122.24
120.31
119.83
118.49
112.10
109.61
109.52



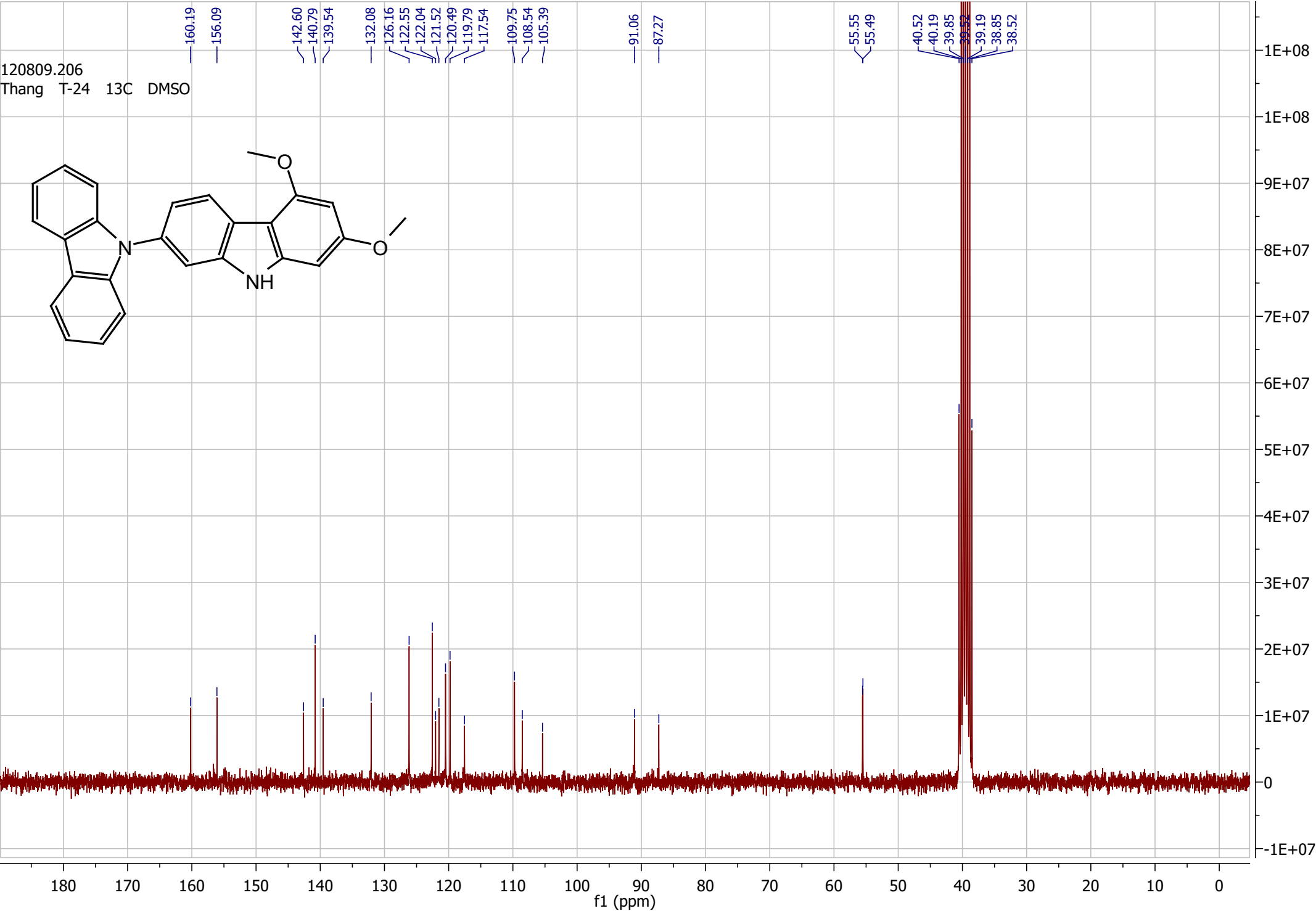
120809.u318
Thang T-24 1H DMSO



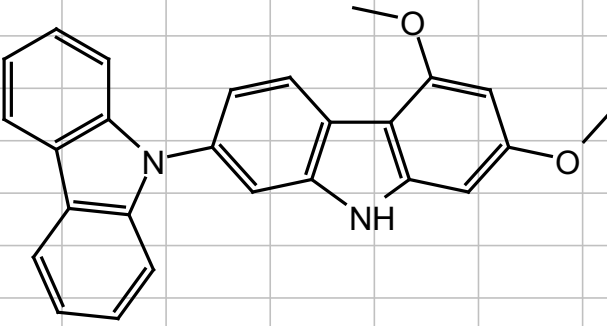
120809.206
Thang T-24 13C DMSO



160.19 156.09 142.60 140.79 139.54 132.08 126.16 122.55 122.04 121.52 120.49 119.79 117.54 109.75 108.54 105.39 91.06 87.27 55.55 55.49 40.52 40.19 39.85 39.52 39.19 38.85 38.52



120809.206
Thang T-24 Dept DMSO



126.17
122.04
120.49
119.79
117.55
109.75
108.53
91.06
87.27

55.56
55.49

