

Copper-Catalyzed Cross-Coupling of Arylboronate Esters with Aryl and Heteroaryl Iodides and Bromides

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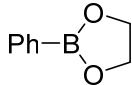
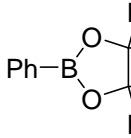
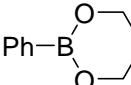
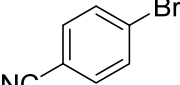
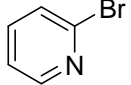
1. General Information

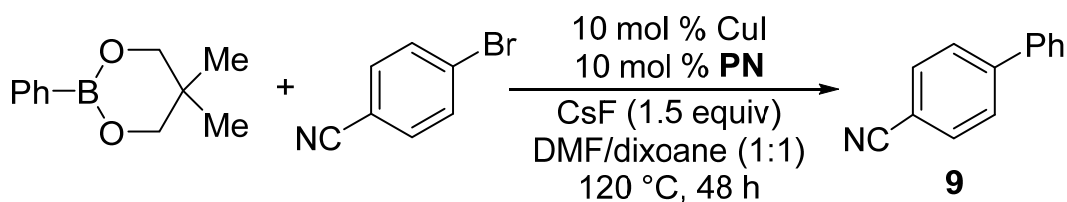
All the reactions and handling of chemicals were done inside a nitrogen-filled glovebox unless stated otherwise. All the glassware including 1-dram borosilicate (Kimble-Chase) vials for screening reactions and pressure vessels for large scale reactions for isolation were properly dried in an oven before use. Bulk solvents were obtained from EMD and anhydrous solvents (DMF, dioxane) were obtained from Sigma-Aldrich (Sure/SealTM) and were used directly without further purification. Deuterated solvents were purchased from the Cambridge Isotope. Aryl halides were purchased from Acros, Sigma-Aldrich, Oakwood, TCI-America, Matrix and Alfa-Aesar. CuI (99.999%) and CsF (99.9%) were procured from Sigma-Aldrich and Alfa-Aesar, respectively. Arylboronate esters were prepared by following the literature procedure from arylboronic acids.¹ P,N ligand (**PN**) was purchased from Sigma-Aldrich and was purified by three successive runs through silica gel columns using first 3% diethyl ether in hexanes, and then the second and third times 6% triethylamine in hexanes. 2-(Phenyl)pyridine (**16**) (Table 2, entry 8) arising from the cross-coupling of phenylboronic acid neopentylglycol ester with 2-Bromopyridine was identified by comparing ¹H and ¹³C NMR spectra of the isolated compounds with the commercially available standard sample. ¹H, ¹³C ¹⁹F and ¹¹B NMR spectra were recorded on a Bruker instrument (300, 75, 282 and 96 MHz, respectively) and internally referenced to the residual solvent signals of CDCl₃ at 7.26 ppm for ¹H NMR, CDCl₃ at 77.16 ppm for ¹³C, C₆D₆ at 7.15 ppm for ¹H NMR, C₆F₆ at -164.9 ppm for ¹⁹F NMR, and boric acid at 36.0 ppm for ¹¹B NMR. NMR chemical shifts and the coupling constants (*J*) for ¹H, ¹³C and ¹⁹F NMR are reported in δ parts per millions (ppm) and in Hertz respectively. The following conventions are used for multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; ddd, doublet of double doublet. High resolution mass and NMR spectra for new compounds were recorded at the Mass Spectrometry and NMR Facilities, Department of Chemistry and Chemical Biology, University of New Mexico.

2. Experimental Section

2.1. Screening of Various Organoboron Reagents with Aryl Bromides and Reaction Optimization

In a glovebox, arylboron reagents (0.10 mmol), aryl halide (0.10 mmol), CsF (22.8 mg, 0.15 mmol), CuI (0.9 mg, 0.0050 mmol, or 1.90 mg, 0.010 mmol) and PN ligand (1.4 mg, 0.0050 mmol, or 2.7 mg, 0.010 mmol) were weighed in a 1 dram vial and dissolved in DMF/dioxane (0.5 mL, 1:1). For reactions with 2-bromopyridine, PN ligand was not used. The vial was then tightly capped, taken out of the glovebox and placed in an oil bath pre-heated to 120 °C with vigorous stirring. After 36-48 h, the reaction mixture was cooled down to room temperature, diluted with ethyl acetate (2 mL), filtered through a pad of Silica gel in a pipette and analyzed by GC using 2-nitrobiphenyl as a standard. The percentage yields of the products are tabulated below:

	Ph-B(OH) ₂	Ph-BF ₃ K			
	11%	0%	26%	10%	74%
	trace	0%	65%	0%	47%



entry	modified conditions	yield (%) ^b
1	none	74 (69)
2	2-(diphenylphosphino)- <i>N,N</i> -dimethylaniline instead of PN	43
3	1,10-phenanthroline instead of PN	52
4	without PN	36
5	without CsF	0
6	without CuI	0
7	NaOMe, KF or K ₂ CO ₃ instead of CsF	0

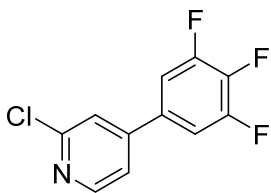
2.2. General Procedure A (in the Presence of Ligand PN)

In a glovebox, arylboronate ester (1.0 mmol), aryl halide (1.0 mmol), CsF (228 mg, 1.5 mmol), CuI (9.5 mg, 0.050 mmol, or 19.0 mg, 0.10 mmol) and **PN** ligand (13.5 mg, 0.050 mmol, or 27 mg, 0.10 mmol) were weighed in a 15-mL pressure vessel and dissolved in DMF/dioxane (5 mL, 1:1). The pressure vessel was then tightly capped, taken out of the glovebox and placed in an oil bath pre-heated to 120 °C with vigorous stirring. After 48 h, the reaction mixture was cooled down to room temperature, diluted with H₂O (10 mL) and extracted with ethyl acetate (5 mL × 3). The combined organic fraction was dried over Na₂SO₄, cotton-filtered and the solvent was removed in a rotary evaporator. The product was purified by silica gel column chromatography using hexanes and a combination of hexanes with diethyl ether or ethyl acetate as an eluting solvent.

2.3. General Procedure B (in the Absence of Ligand)

In a glovebox, arylboronate ester (1.0 mmol), aryl halide (1.0 mmol), CsF (228 mg, 1.5 mmol) and CuI (9.5 mg, 0.050 mmol, or 19.0 mg, 0.1 mmol) were weighed were weighed in a 15-mL pressure vessel and dissolved in DMF (5 mL). The pressure vessel was then tightly capped, taken out of the glovebox and placed in an oil bath pre-heated to 120 °C with vigorous stirring. After 24 h, the reaction mixture was cooled down to room temperature, diluted with H₂O (10 mL) and extracted with ethyl acetate (5 mL × 3). The combined organic fraction was dried over Na₂SO₄, cotton-filtered and the solvent was removed in a rotary evaporator. The product was purified by silica gel column chromatography using hexanes and a combination of hexanes and ethyl acetate as an eluting solvent.

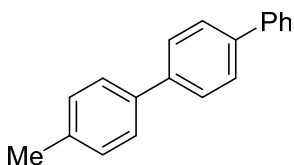
2.4. Characterization Data for New Compounds



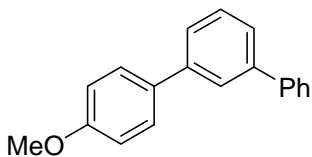
2-Chloro-4-(3,4,5-trifluorophenyl)pyridine (1): The title compound **1** was obtained as a white solid (171 mg, 70% yield) after purification by silica gel column chromatography.

¹H NMR (300 MHz, CDCl₃) δ 7.15-7.20 (m, 2H), 7.26 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.38 (d,

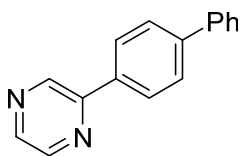
$J = 1.5$ Hz, 1H), 8.39 (d, $J = 5.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 111.6 (dd, $J_{\text{CF}} = 7.7$ Hz), 120.2, 121.9, 133.1 (q, $J_{\text{CF}} = 8.4$ Hz), 140.8 (dt, $J_{\text{CF}} = 254.5, 14.9$ Hz), 148.5, 150.5, 151.8 (ddd, $J_{\text{CF}} = 250.7, 10.4, 4.2$ Hz), 152.7; ^{19}F NMR (282 Hz, CDCl_3) δ -158.0 (t, $J_{\text{FF}} = 22.6$ Hz), -132.2 (d, $J_{\text{FF}} = 0.8$ Hz); HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_6\text{ClF}_3\text{N}$ (MH^+) 244.0141, found 244.0135.



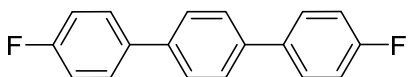
4-(4-Methylphenyl)-biphenyl (2): The title compound **2** was obtained as a white solid (172 mg, 64% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 2.44 (s, 3H), 7.30(d, $J = 8.1$ Hz, 2H), 7.38(t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 2H), 7.57 (d, $J = 8.1$ Hz, 2H), 7.67 (d, $J = 7.2$ Hz, 2H), 7.69 (s, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.3, 127.0, 127.2, 127.4, 127.6, 128.9, 129.7, 137.3, 137.9, 140.0, 140.2, 140.9; HRMS (APPI) Calcd for $\text{C}_{19}\text{H}_{16}$ (M^+) 244.1252, found 244.1259.



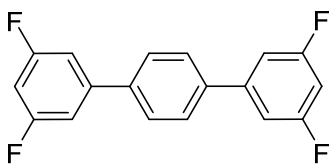
3-(4-Methoxyphenyl)-biphenyl (3): The title compound **3** was obtained as a white solid (172 mg, 66% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 3.87 (s, 3H), 7.01(d, $J = 8.7$ Hz, 2H), 7.35-7.67 (m, 10H), 7.77 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.4, 114.3, 125.6, 125.8, 127.3, 127.4, 128.3, 128.9, 129.2, 133.8, 141.4, 141.4, 141.8, 159.3; HRMS (APPI) Calcd for $\text{C}_{19}\text{H}_{16}\text{O}$ (M^+) 260.1201, found 260.1202.



2-(4-Biphenyl)-pyrazine (4): The title compound **4** was obtained as a white solid (160 mg, 69% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.42 (m, 1H), 7.46-7.51 (m, 2H), 7.66-7.68 (m, 2H), 7.74-7.77 (m, 2H), 8.10-8.13 (m, 2H), 8.52 (d, $J = 2.4\text{Hz}$, 1H), 8.65 (dd, $J = 2.1, 1.5\text{ Hz}$, 1H), 9.09 (d, $J = 1.5\text{ Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 127.2, 127.5, 127.8, 127.9, 129.0, 135.3, 140.3, 142.3, 142.8, 143.0, 144.3, 152.6; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{13}\text{N}_2$ (MH) $^+$ 233.1079, found 233.1082.

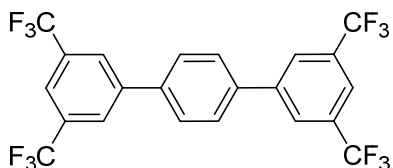


4,4''-Difluoro-p-terphenyl (5): The title compound **5** was obtained as a white solid (184 mg, 69% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.11-7.19 (m, 4H), 7.56-7.62 (m, 8H); ^{19}F NMR (282 Hz, CDCl_3) δ -113.9; HRMS (APPI) Calcd for $\text{C}_{18}\text{H}_{12}\text{F}_2$ (M) $^+$ 266.0907, found 266.090.

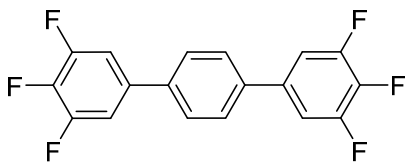


3,3'',5,5''-Tetrafluoro-p-terphenyl (6): The title compound **6** was obtained as a white solid (215 mg, 71% yield) after purification by silica gel column chromatography. ^1H

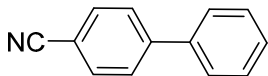
NMR (300 MHz, CDCl₃) δ 6.82 (t, $J = 8.7$ Hz, 2H), 7.15 (d, $J = 6.9$ Hz, 4H), 7.64 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 103.0 (t, $J_{CF} = 25.2$ Hz), 110.0 (q, $J_{CF} = 8.1$ Hz), 127.7, 139.1, 143.7 (t, $J_{CF} = 9.4$ Hz), 163.6 (dd, $J_{CF} = 246.8, 13.0$ Hz); ¹⁹F NMR (282 Hz, CDCl₃) δ -107.8; HRMS (APPI) Calcd for C₁₈H₁₀F₄ (M)⁺ 302.0719, found 302.0718.



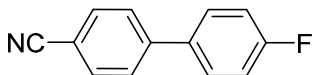
3,3',5,5'-Tetrakis(trifluoromethyl)-p-terphenyl (7): The title compound **7** was obtained as a white solid (236 mg, 47% yield) after purification by silica gel column chromatography. ¹H NMR (300 MHz, CDCl₃) δ 7.76 (s, 4H), 7.91 (s, 2H), 8.06 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 121.6 (t, $J_{CF} = 4.4$ Hz), 125.3, 127.3, 128.3, 132.6 (q, $J_{CF} = 33.1$ Hz), 138.9, 142.4; ¹⁹F NMR (282 Hz, CDCl₃) δ -62.8; HRMS (APPI) Calcd for C₂₂H₁₀F₁₂ (M)⁺ 502.0591, found 502.0589.



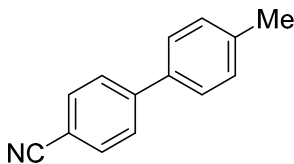
3,4,5,3',4',5'-Hexafluoro-p-terphenyl (8): The title compound **8** was obtained as a white solid (247 mg, 73% yield) after purification by silica gel column chromatography. ¹H NMR (300 MHz, C₆D₆) δ 6.70-6.76 (m, 4H), 6.98 (s, 4H); ¹⁹F NMR (282 Hz, C₆D₆) δ -160.3 (t, $J_{FF} = 17.5$ Hz), -132.1 (d, $J_{FF} = 18.1$ Hz); HRMS (APPI) Calcd for C₁₈H₈F₆ (M)⁺ 338.053, found 338.0526.



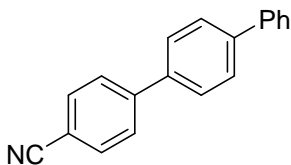
4-phenylbenzonitrile (9): The title compound **9** was obtained as a white solid (124 mg, 69% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.52 (m, 3H), 7.58-7.61 (m, 2H), 7.67-7.74 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 111.0, 119.0, 127.3, 127.8, 128.8, 129.2, 132.7, 139.3, 145.8; HRMS (APPI) Calcd for $\text{C}_{13}\text{H}_9\text{N}$ (M) $^+$ 179.0735, found 179.0742.



4-(4-Fluorophenyl)benzonitrile (10): The title compound **10** was obtained as a white solid (97 mg, 49% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.18 (t, $J = 8.7$ Hz, 2H), 7.56 (dd, $J = 8.7, 5.4$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 111.1, 1116.3 (d, $J_{\text{CF}} = 21.5$ Hz), 119.0, 127.7, 129.1 (d, $J_{\text{CF}} = 8.2$ Hz), 132.8, 135.4, 144.8, 163.3 (d, $J_{\text{CF}} = 247.0$ Hz); ^{19}F NMR (282 Hz, CDCl_3) δ -111.6; GCMS (M) 197.

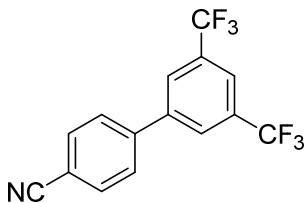


4-(4-Tolyl)benzonitrile (11): The title compound **11** was obtained as a white solid (87 mg, 45% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 2.42 (s, 3H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.65-7.72 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.3, 110.7, 119.1, 127.1, 127.5, 129.9, 132.7, 136.4, 138.9, 145.7; HRMS (APPI) Calcd for $\text{C}_{14}\text{H}_{11}\text{N}$ (M) $^+$ 193.0891 found 193.0896.

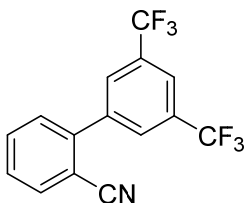


4-Cyano-p-terphenyl (12): The title compound **12** was obtained as a white solid (123 mg, 48% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz,

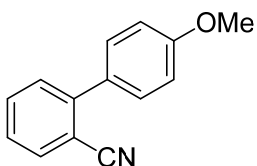
CDCl₃) δ 7.37-7.42 (m, 1H), 7.46-7.51 (m, 2H), 7.63-7.73 (m, 6H), 7.74 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 111.1, 119.1, 127.2, 127.7, 127.8, 127.9, 128.0, 129.1, 132.8, 138.1, 140.3, 141.7, 145.3; HRMS (APPI) Calcd for C₁₉H₁₃N (M)⁺ 255.1048, found 255.1050.



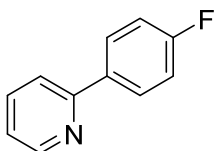
4-(3,5-Bis(trifluoromethyl)phenyl)benzonitrile (13): The title compound **13** was obtained as a white solid (107 mg, 34% yield) after purification by silica gel column chromatography. ¹H NMR (300 MHz, CDCl₃) δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.94 (s, 1H), 8.02 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 113.0, 118.4, 121.5, 122.4 (t, *J*_{CF} = 3.4 Hz), 123.3 (d, *J*_{CF} = 271.3 Hz), 127.5, 128.2, 132.8 (t, *J*_{CF} = 28.7 Hz), 133.2, 141.5, 142.6; ¹⁹F NMR (282 Hz, CDCl₃) δ -63.0; GCMS (M/z) 315.



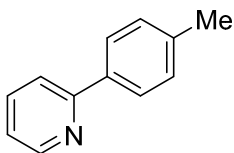
2-(3,5-Bis(trifluoromethyl)phenyl)benzonitrile (14): The title compound **14** was obtained as a white solid (167 mg, 53% yield) after purification by silica gel column chromatography. ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.61 (m, 2H), 7.75 (td, *J* = 7.8, 1.2 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.98-8.02 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 111.7, 117.8, 122.7 (t, *J*_{CF} = 3.8 Hz), 123.2 (d, *J*_{CF} = 271.2 Hz), 129.3, 130.2, (127.6, 129.2, 129.5, 129.7, 132.4 (q, *J*_{CF} = 33.8 Hz), 133.5, 134.1, 140.2, 142.4; ¹⁹F NMR (282 Hz, CDCl₃) δ -61.3; GCMS (M/z) 315.



2-(4-anisoyl)benzonitrile (15): The title compound **15** was obtained as a white solid (84 mg, 42% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 3.87 (s, 3H), 7.02 (d, $J = 9.0$ Hz, 2H), 7.40 (dt, $J = 7.5, 1.2$ Hz, 1H), 7.48-7.54 (m, 3H), 7.62 (dt, $J = 7.8, 1.2$ Hz, 1H), 7.74 (dd, $J = 7.5, 1.8$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 55.5, 111.2, 114.3, 119.1, 127.2, 130.0, 130.1, 130.6, 132.9, 133.9, 145.3, 160.2; HRMS (APPI) Calcd for $\text{C}_{14}\text{H}_{11}\text{NO}$ (M) $^+$ 209.0841, found 209.0843.

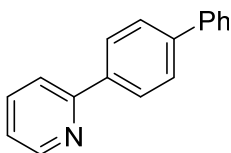


2-(4-Fluorophenyl)pyridine (17): The title compound **17** was obtained as a colorless oil (128 mg, 74% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.12-7.26 (m, 3H), 7.65 (m, 2H), 7.95-8.01 (m, 2H), 8.66-8.68 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 115.8 (d, $J_{\text{CF}} = 21.5$ Hz), 120.3, 122.2, 128.8 (d, $J_{\text{CF}} = 8.3$ Hz), 135.7, 136.9, 149.8, 156.6, 163.7 (d, $J_{\text{CF}} = 247.0$ Hz); ^{19}F NMR (282 Hz, CDCl_3) δ -111.6; HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_9\text{FN}$ (MH) $^+$ 174.0719, found 174.0715.

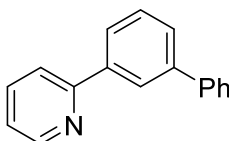


2-(4-Tolyl)pyridine (18): The title compound **18** was obtained as a colorless oil (80 mg, 47% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.19-7.21 (m, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.68-7.75 (m, 2H), 7.90 (d, $J = 8.1$

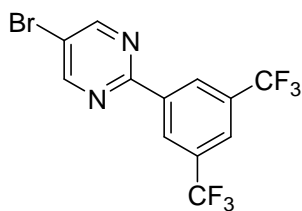
Hz, 2H), 8.68 (dt, $J = 3.9, 1.8$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.4, 120.3, 121.9, 126.9, 129.6, 136.8, 139.0, 149.7, 157.6; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{12}\text{N}$ (MH) $^+$ 170.0970, found 170.0964.



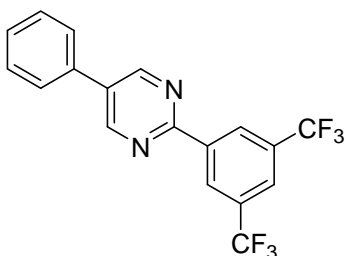
2-(4-Biphenyl)pyridine (19): The title compound **19** was obtained as a white solid (141 mg, 61% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.05-7.09 (m, 1H), 7.18-7.23 (m, 1H), 7.27-7.33 (m, 2H), 7.48-7.90(m, 6H), 7.92 (d, $J = 8.4$ Hz, 2H), 8.55 (dt, $J = 4.8, 1.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 120.5, 122.2, 127.2, 127.4, 127.5, 127.6, 129.0, 136.8, 138.4, 140.7, 141.8, 149.8, 157.1; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{14}\text{N}$ (MH) $^+$ 232.1126, found 232.1120.



2-(3-Biphenyl)pyridine (20): The title compound **20** was obtained as a greasy solid (194 mg, 84% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.39 (m, 1H), 7.46-7.52(m, 1H), 7.56-7.61 (m, 2H), 7.67 (t, $J = 7.8$ Hz, 1H), 7.76-7.83 (m, 5H), 8.09 (dt, $J = 7.5, 1.2$ Hz, 1H), 8.37 (t, $J = 1.8$ Hz, 1H), 8.85 (ddd, $J = 4.8, 2.4, 1.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 120.8, 122.4, 125.9, 126.0, 127.4, 127.5, 127.9, 128.9, 129.3, 136.9, 140.1, 141.2, 141.9, 149.8, 157.5; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{14}\text{N}$ (MH) $^+$ 232.1126, found 232.1125.



5-Bromo-2-[3,5-bis(trifluoromethyl)phenyl]Pyrimidine (21): The title compound **21** was obtained as a white solid (204 mg, 55% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 8.00 (s, 1H), 8.90-8.92 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 118.0, 120.1, 121.6, 124.5, 125.2, 128.4, 132.4 (q, $J_{\text{CF}} = 33.2$ Hz), 138.7, 158.4, 160.1; ^{19}F NMR (282 Hz, CDCl_3) δ -61.3; GCMS (M/z) 371.



5-Phenyl-2-[3,5-bis(trifluoromethyl)phenyl]Pyrimidine (22): The title compound **22** was obtained as a white solid (224.7 mg, 61% yield) after purification by silica gel column chromatography. ^1H NMR (300 MHz, CDCl_3) δ 7.49-7.59 (m, 3H), 7.63-7.67 (m, 2H), 8.00 (s, 1H), 9.01 (s, 2H), 9.08 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 121.8, 124.2, 125.4, 127.1, 128.4, 129.4, 129.7, 132.3 (q, $J_{\text{CF}} = 33.2$ Hz), 133.3, 134.1, 139.6, 155.6, 158.4, 160.7; ^{19}F NMR (282 Hz, CDCl_3) δ -61.3; GCMS (M/z) 368.

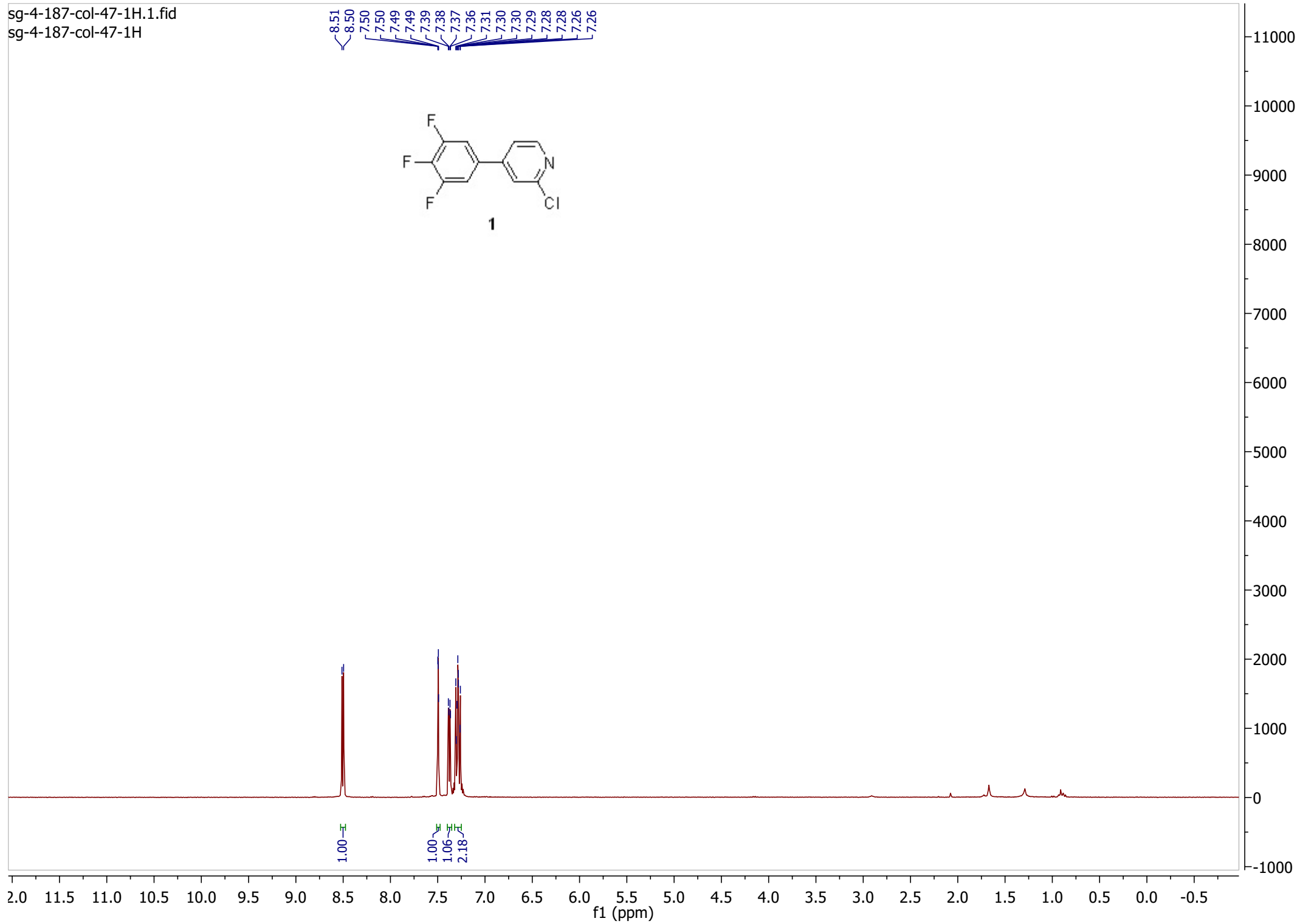
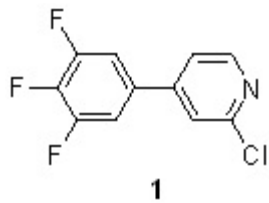
3. Reference

1. Berini, C.; Navarro, O.; *Chem. Commun.* **2012**, 48, 1538.

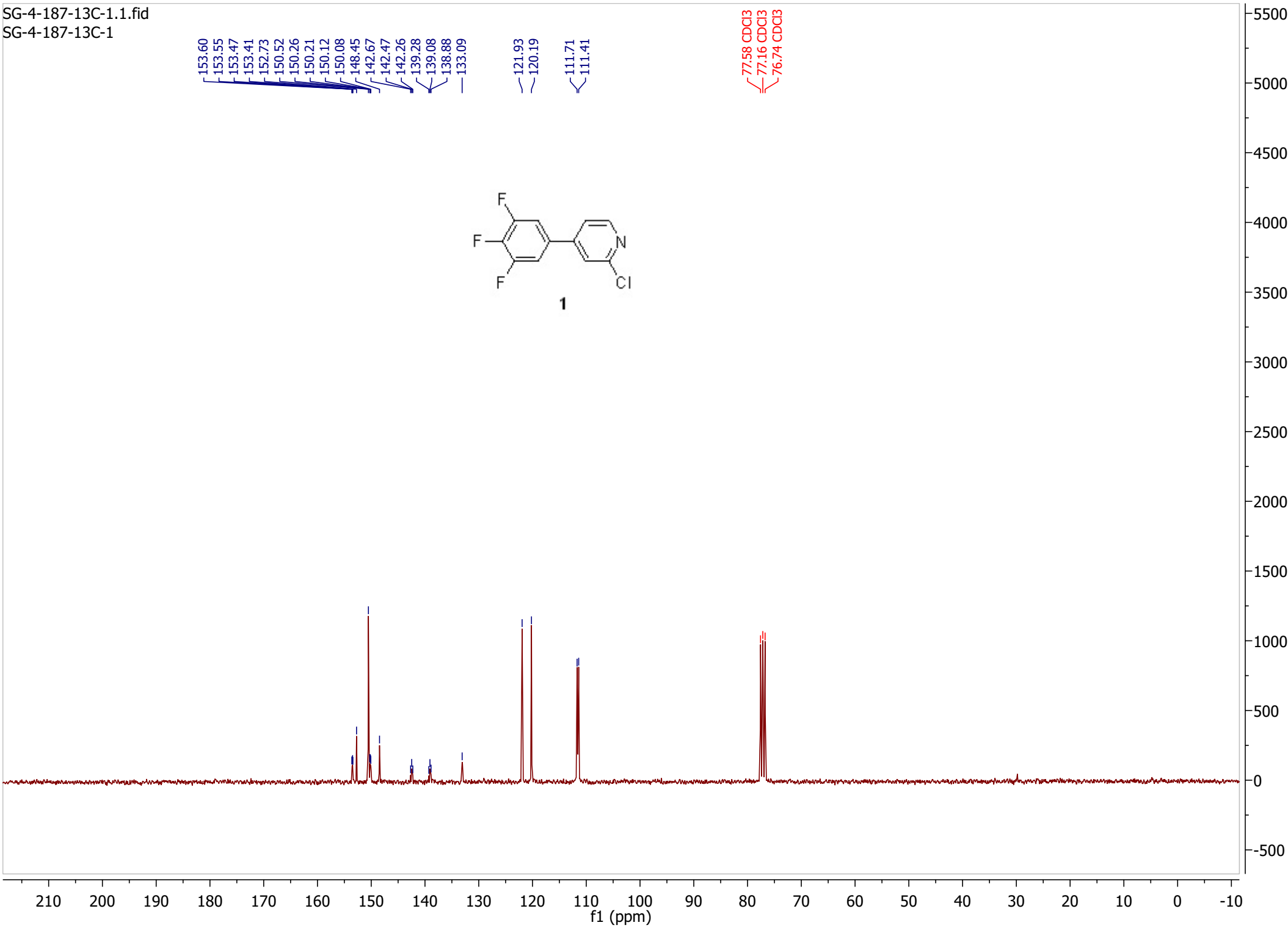
4. NMR Spectra

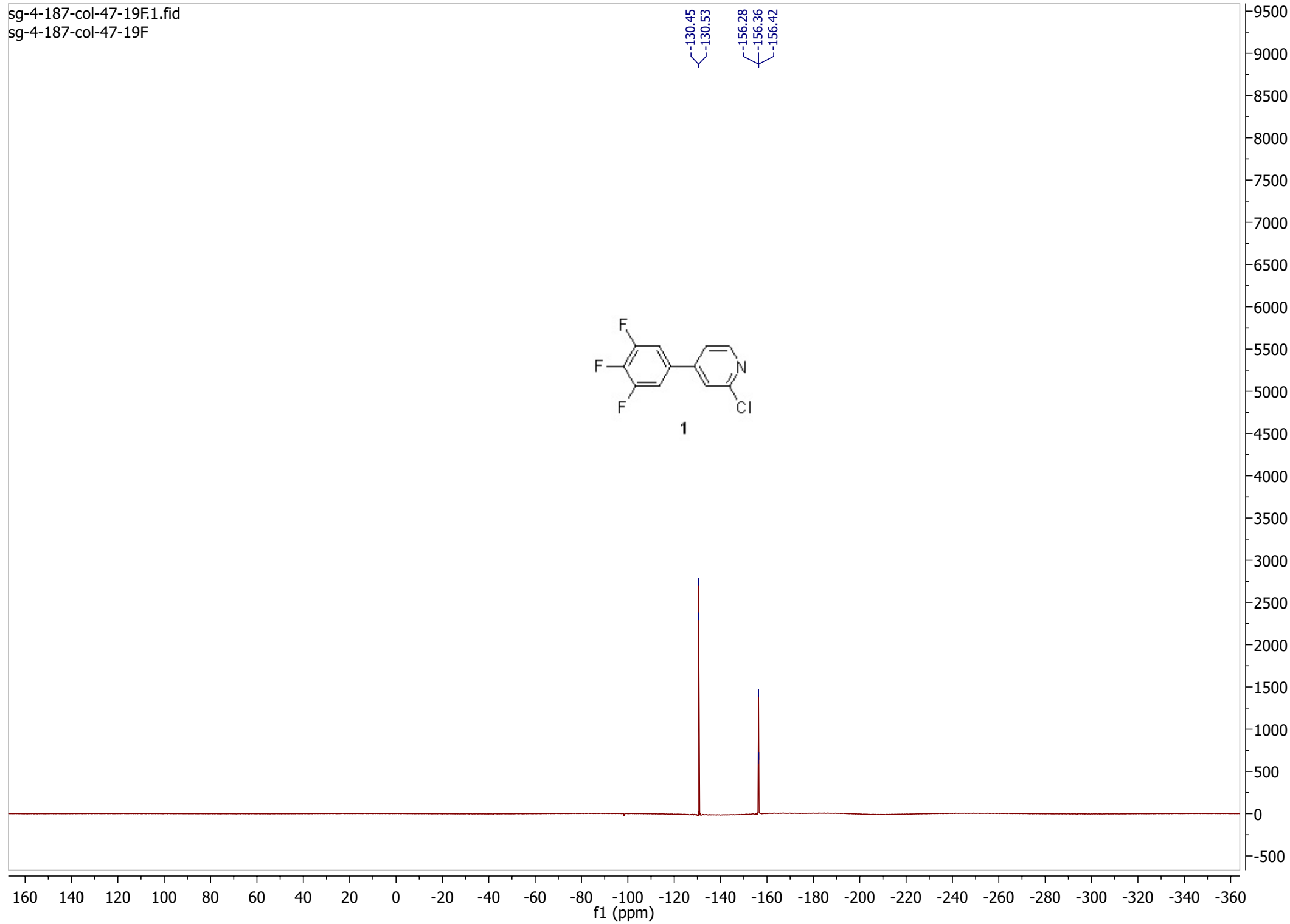
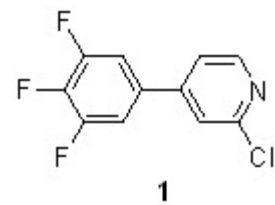
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sg-4-187-col-47-1H

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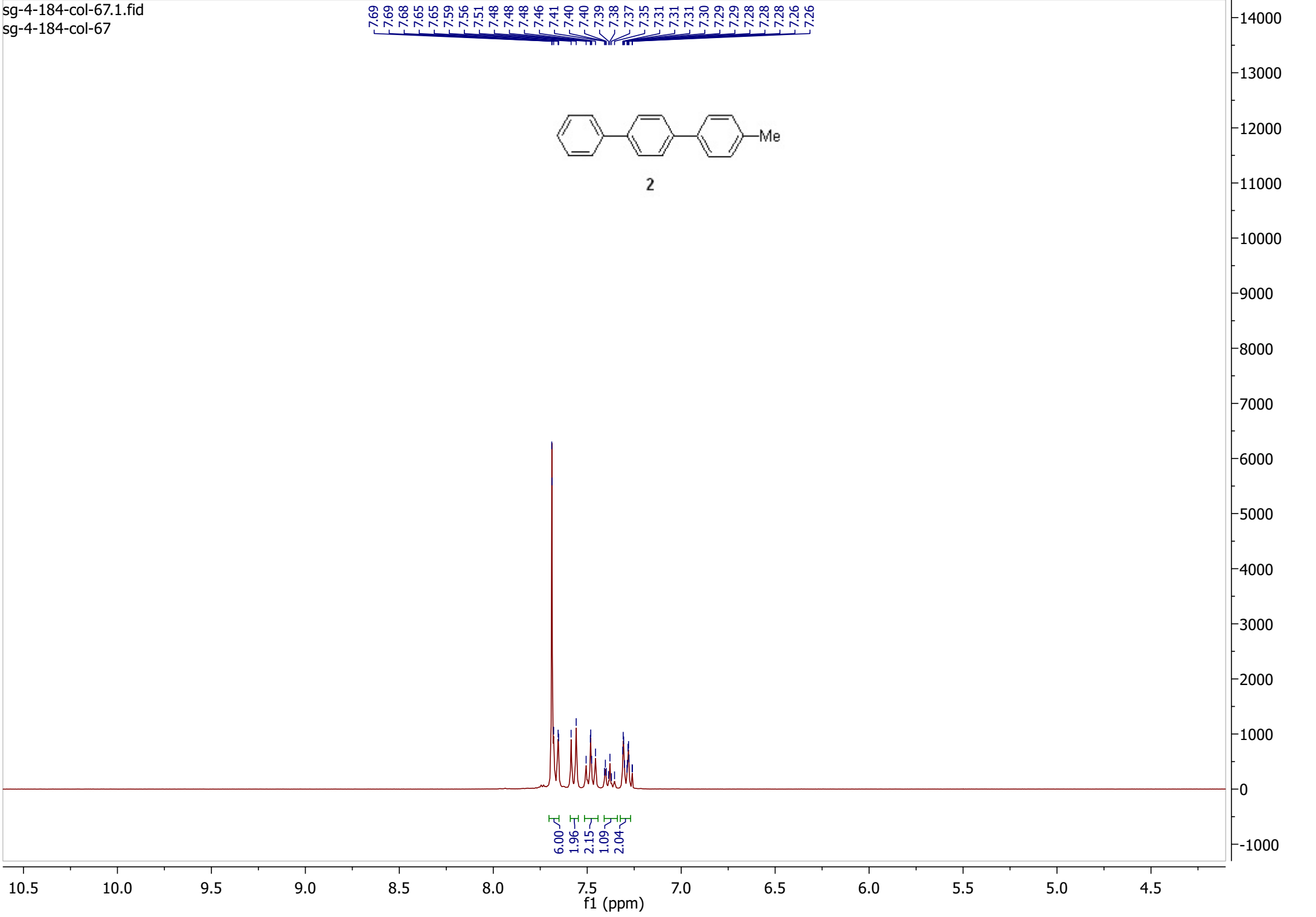
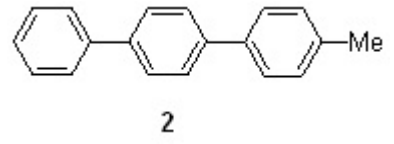
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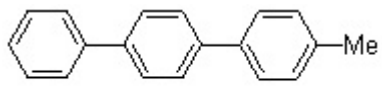


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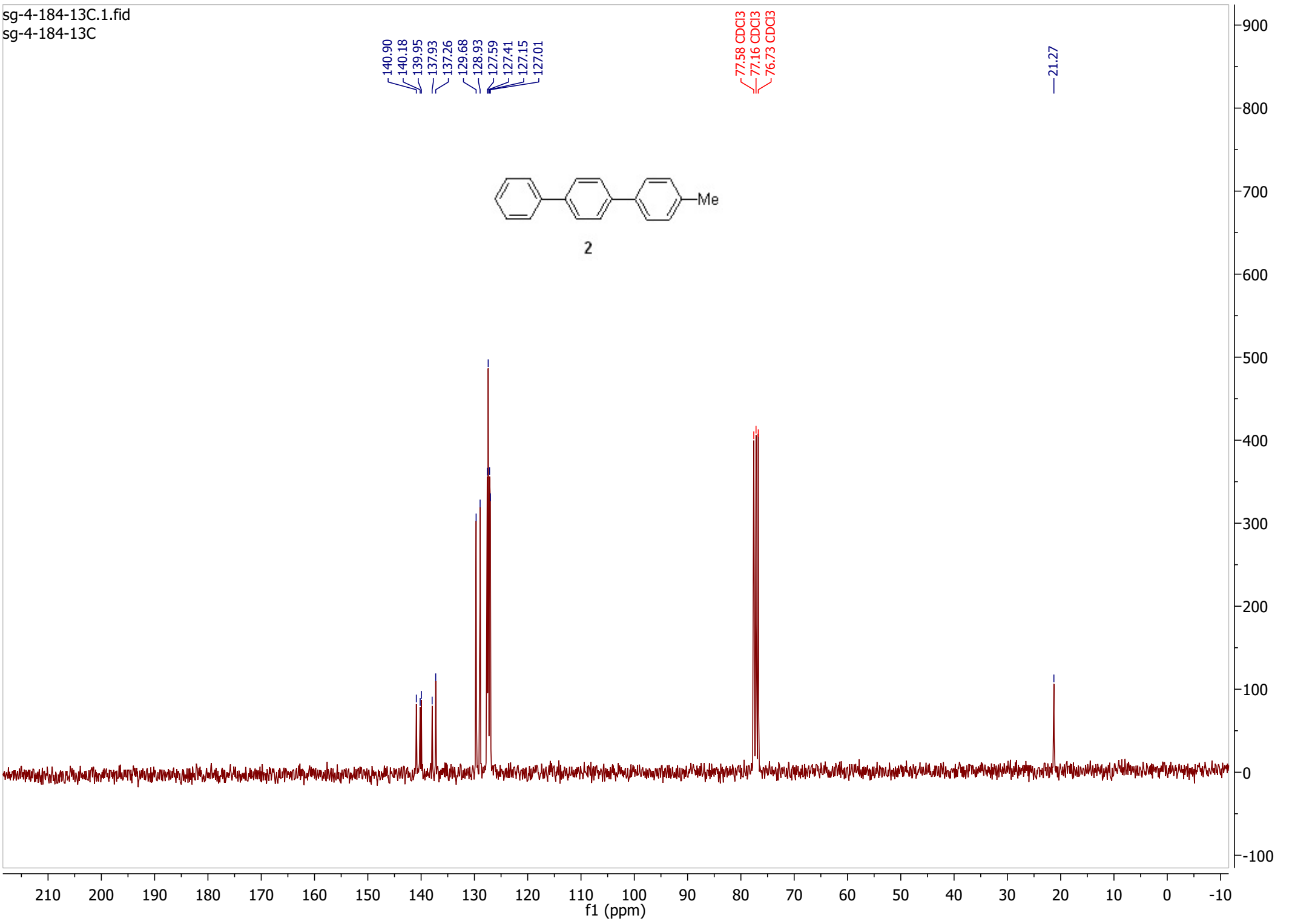
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77.58 CDCl3
77.16 CDCl3
76.73 CDCl3

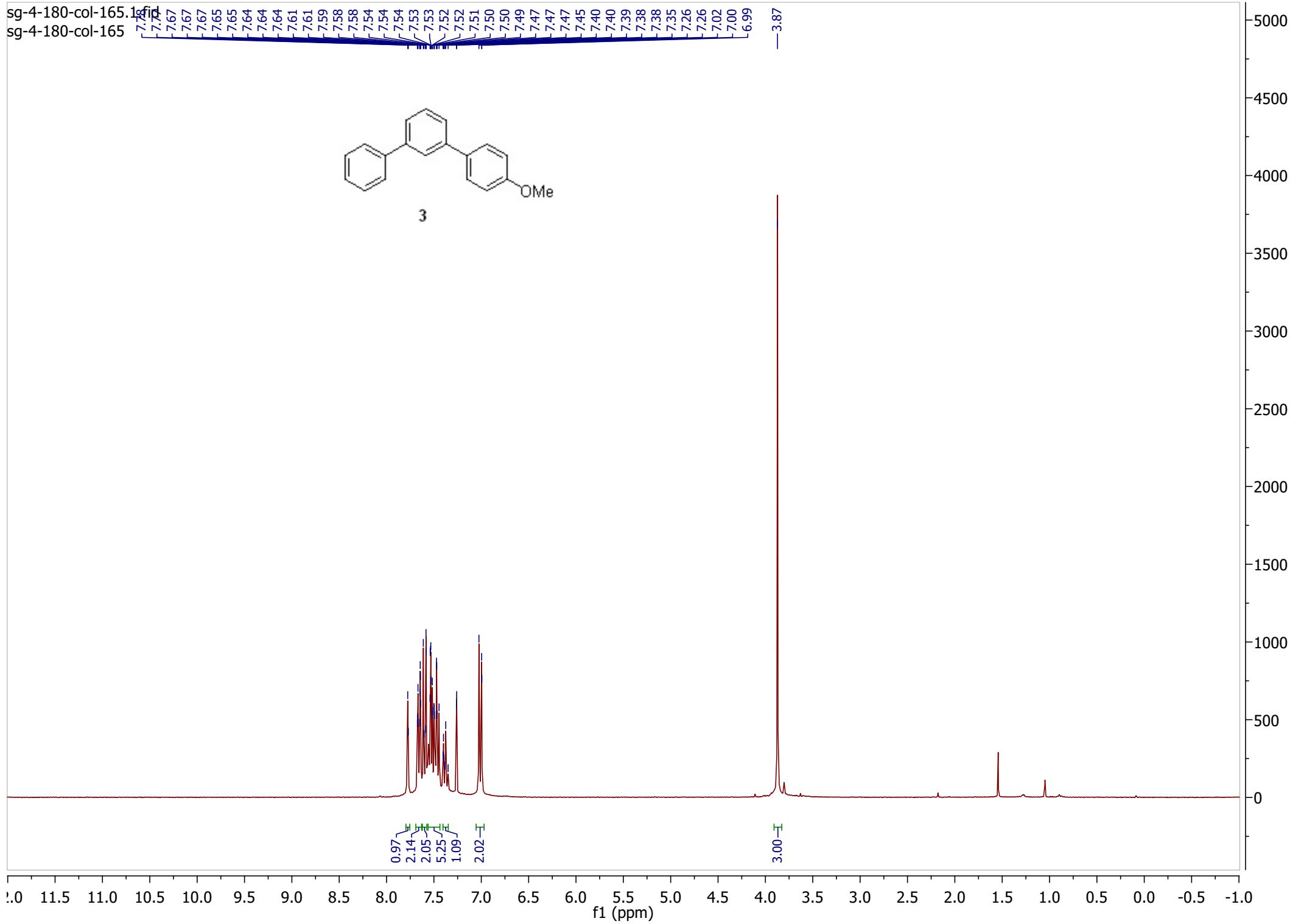
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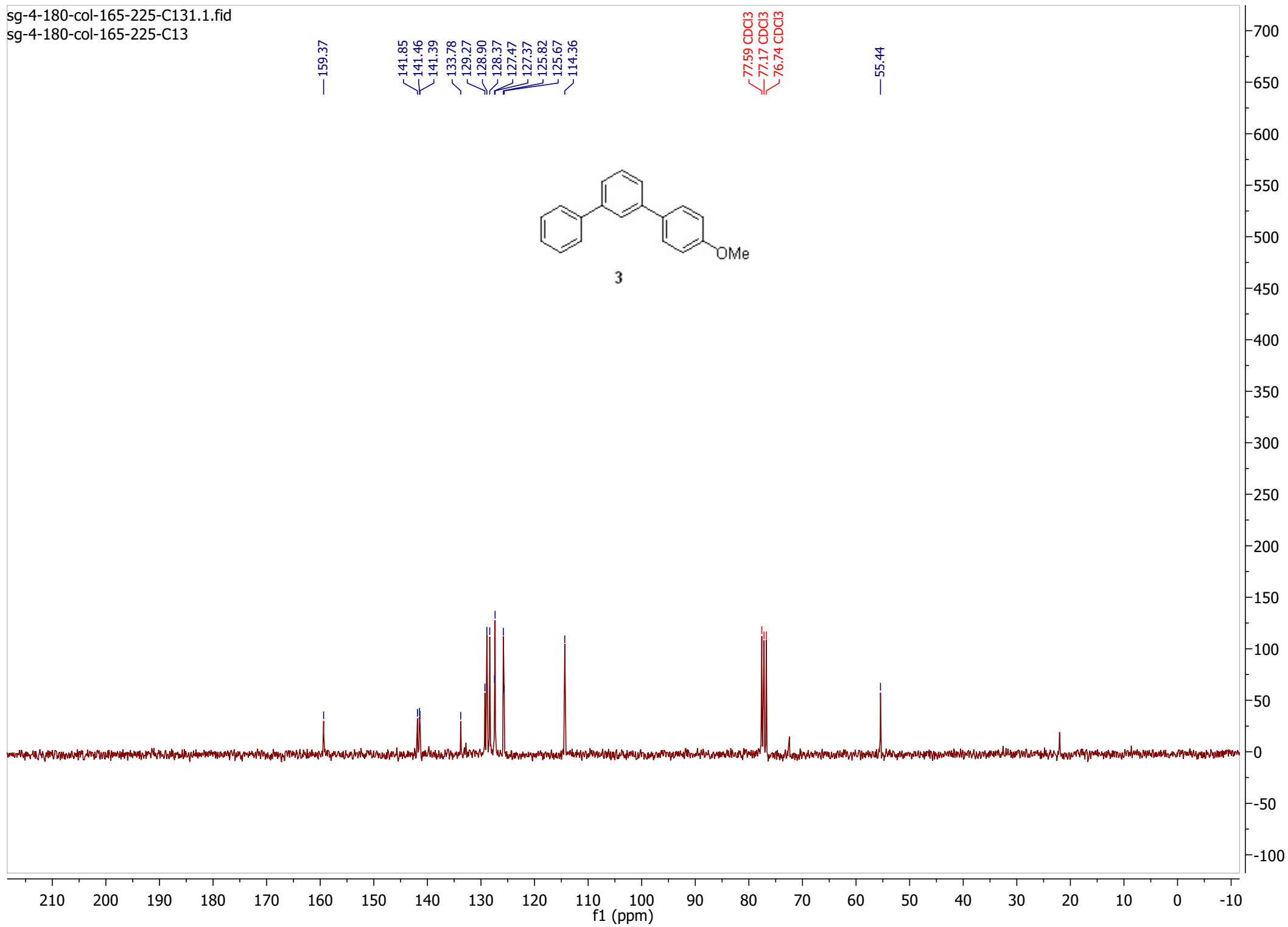


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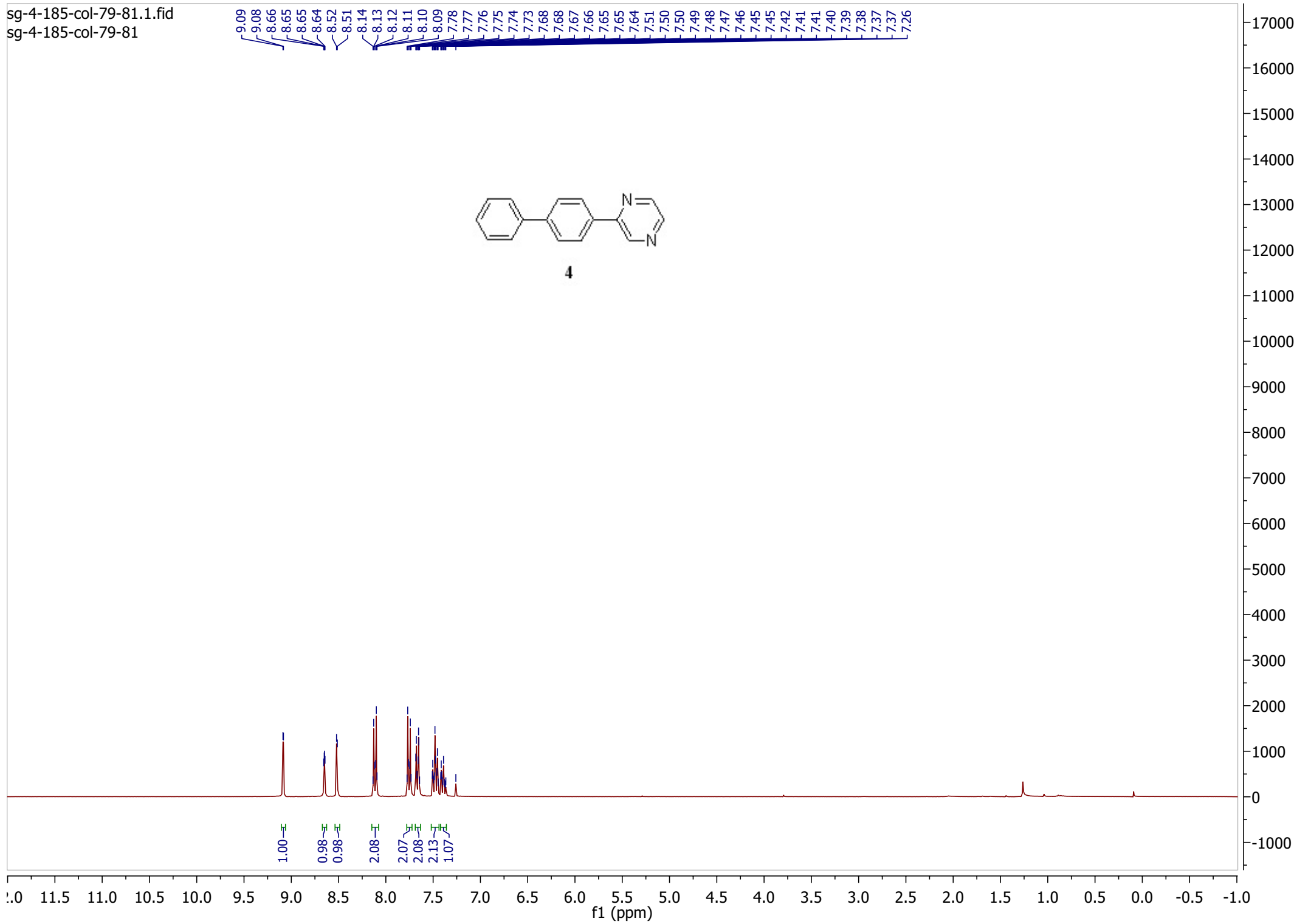


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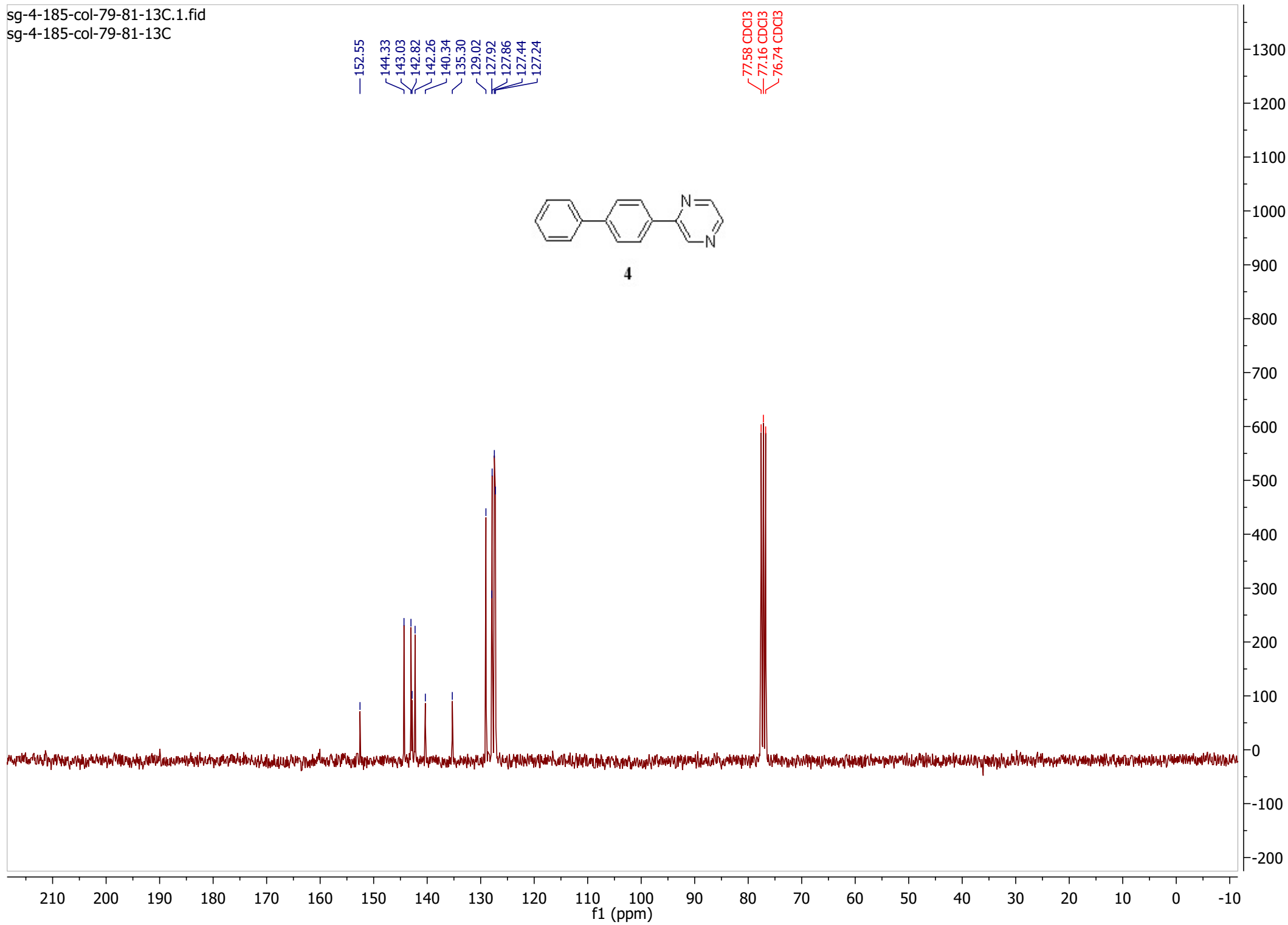




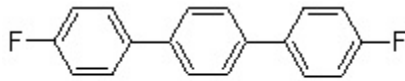
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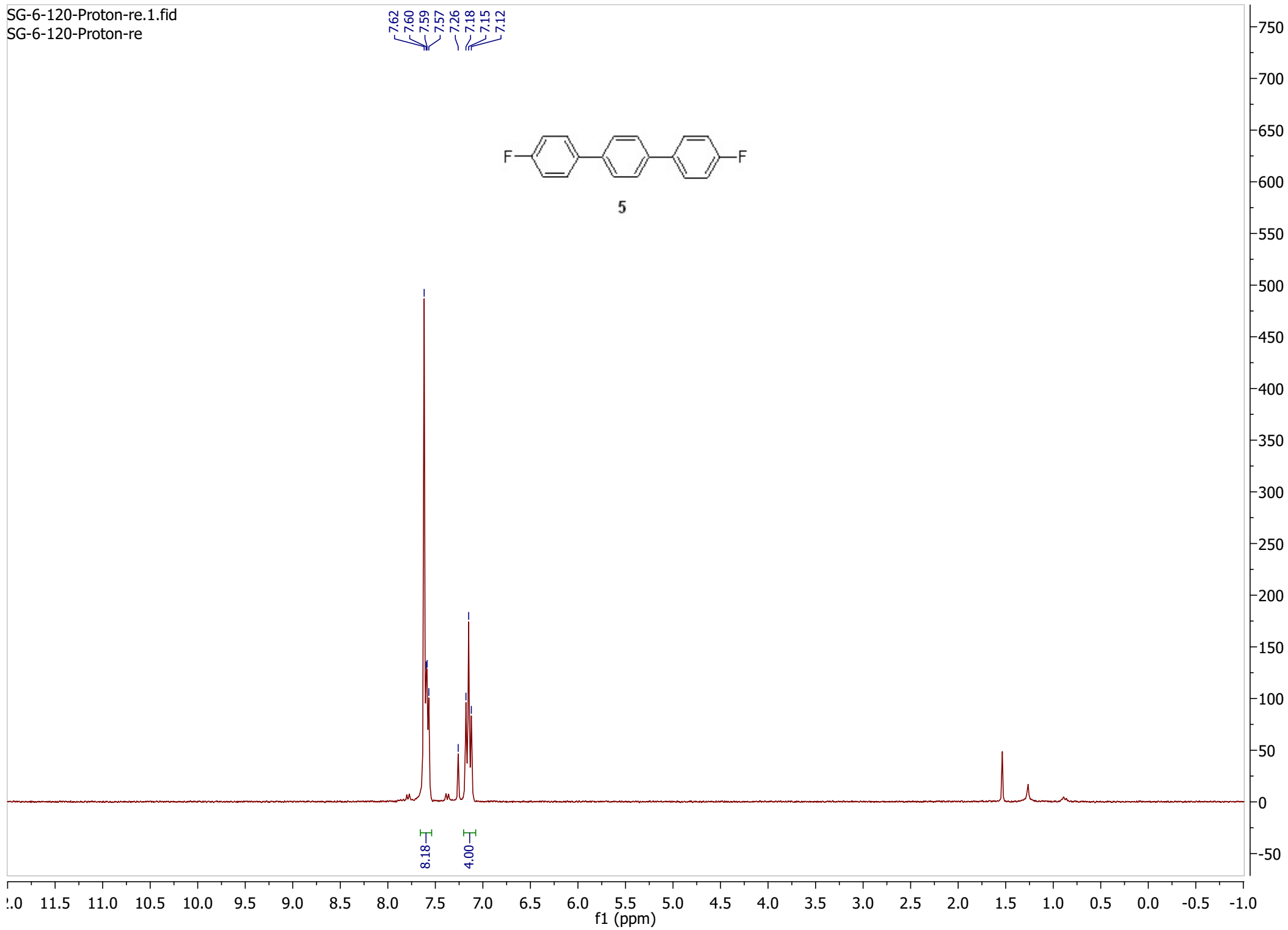
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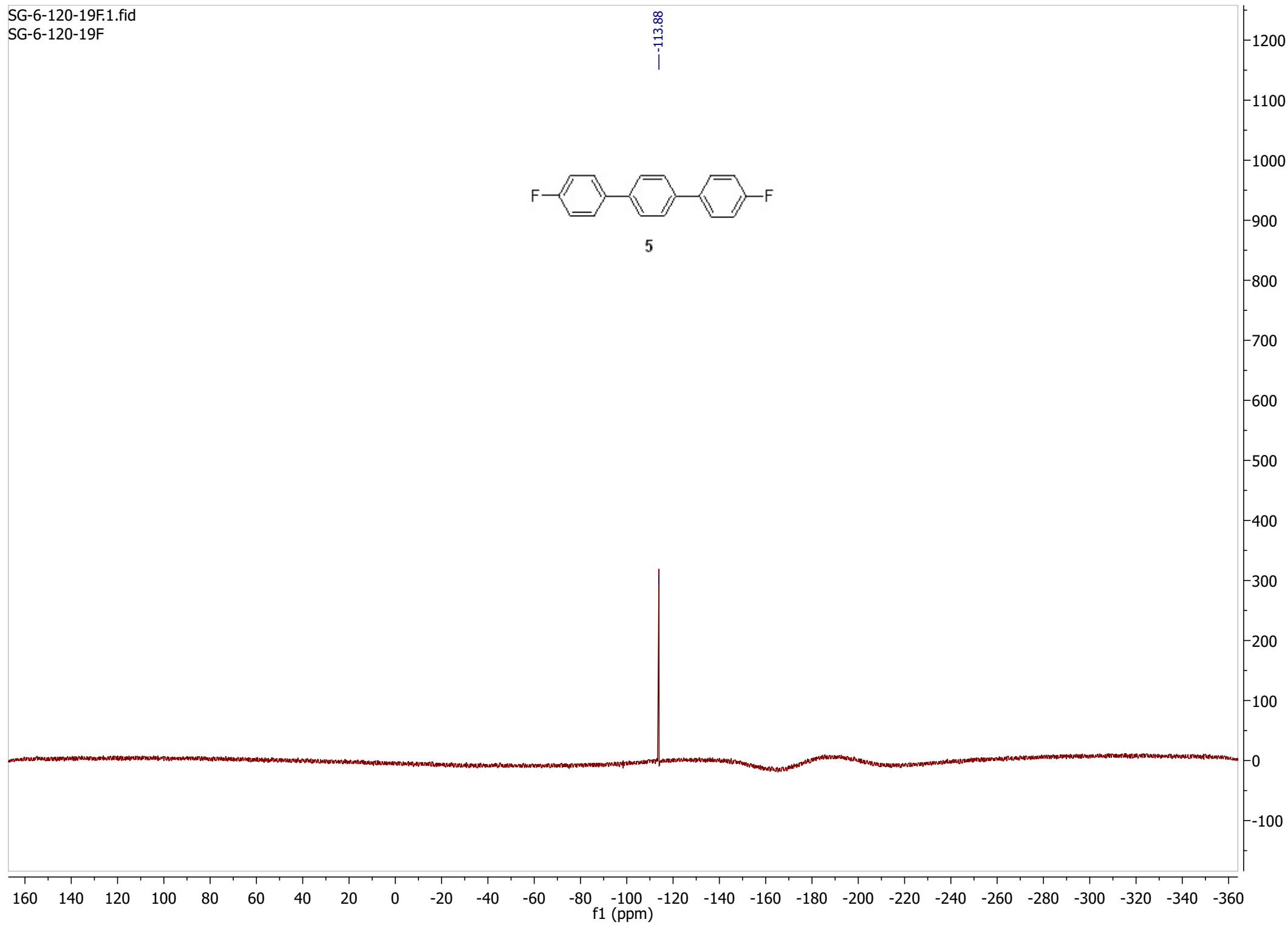
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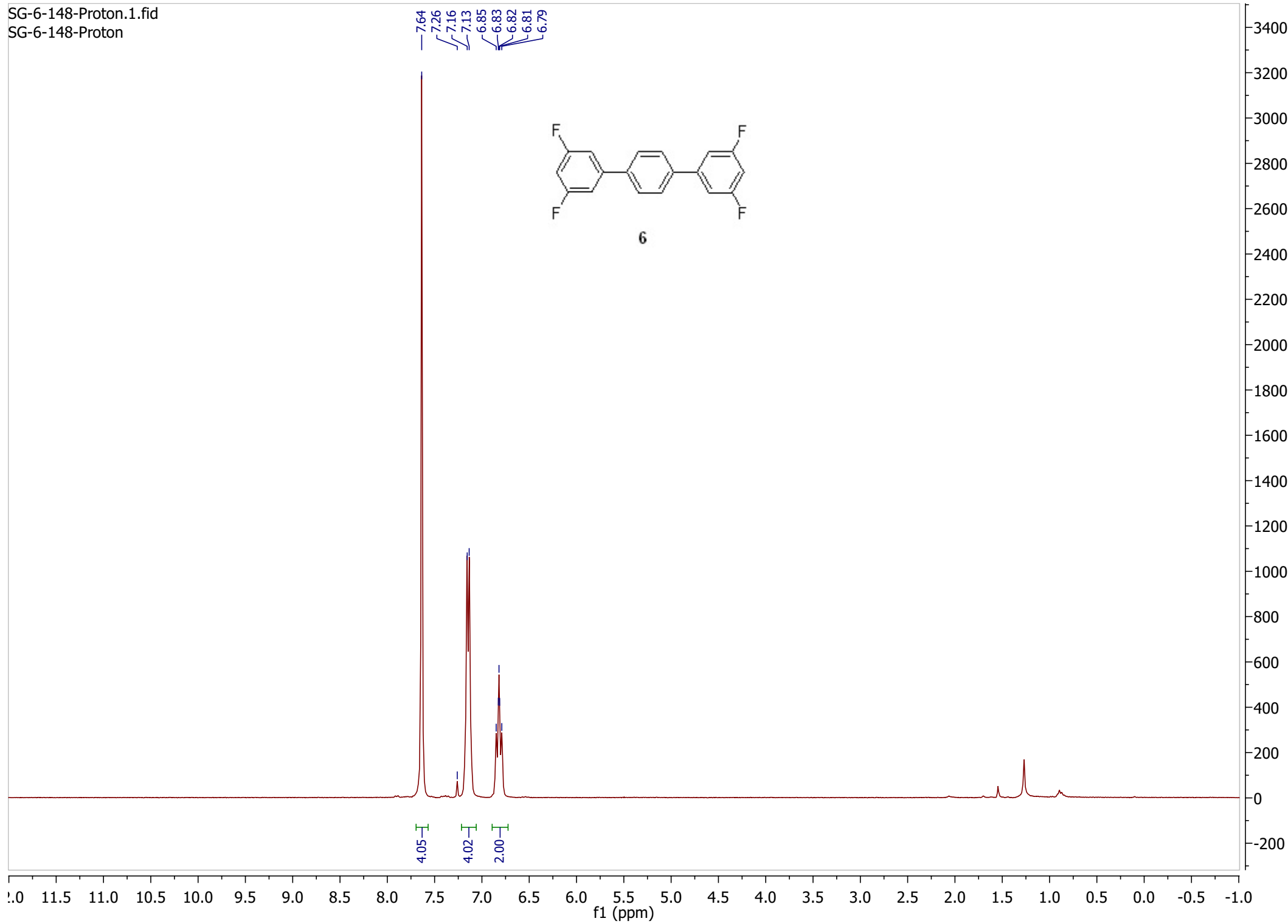


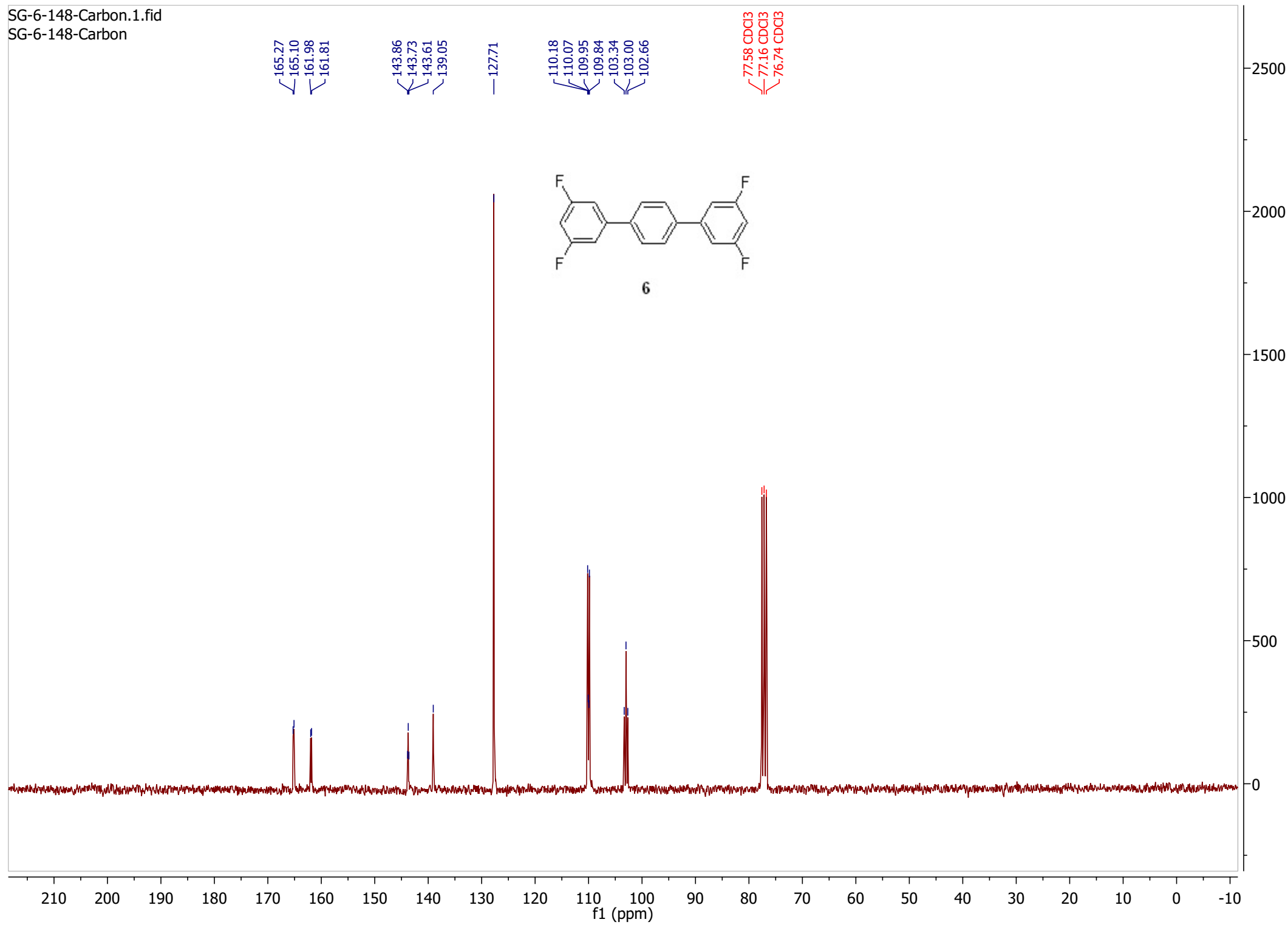
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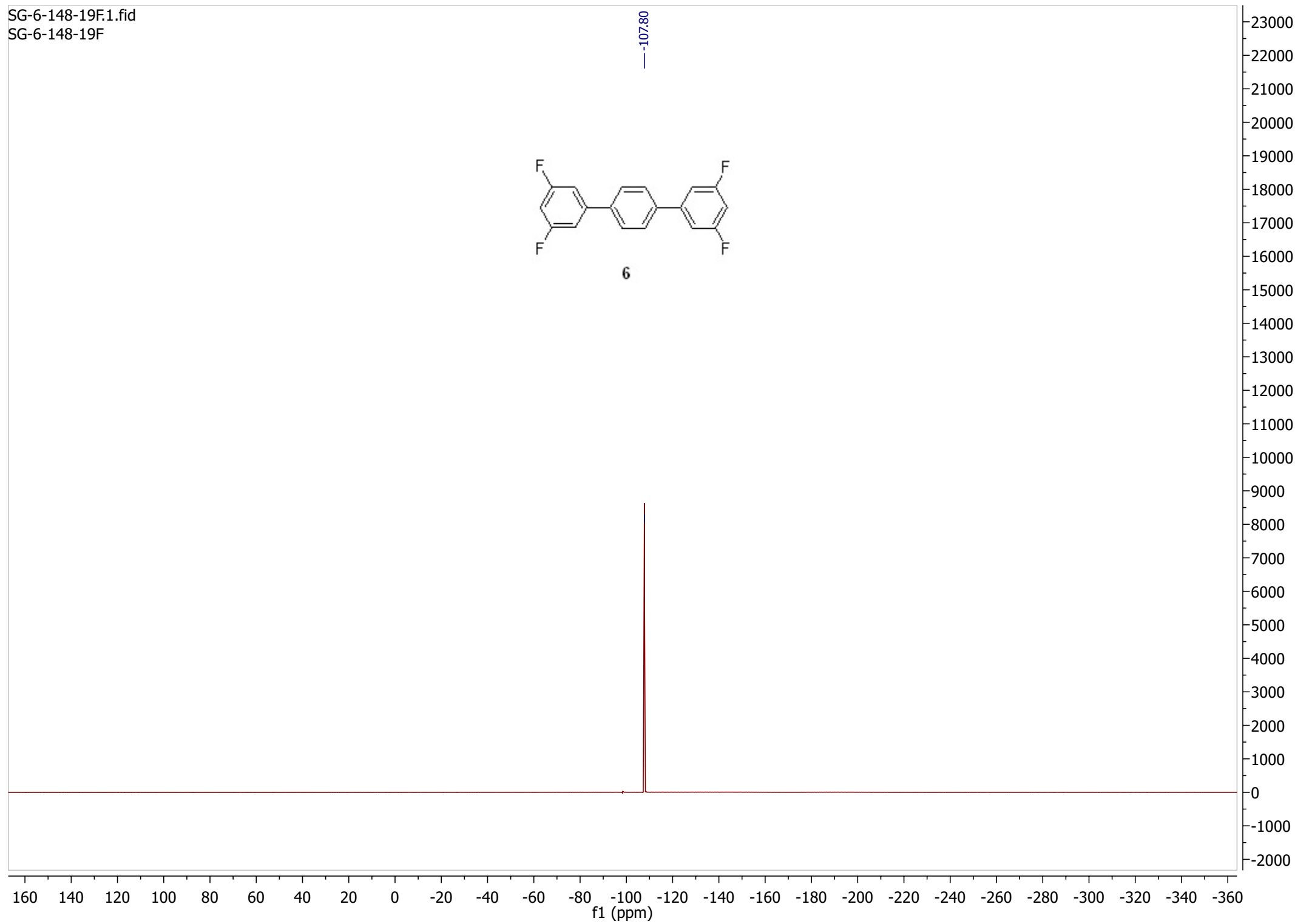
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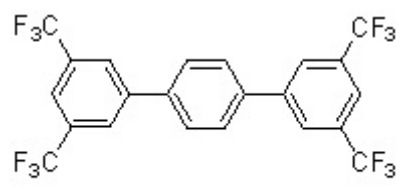


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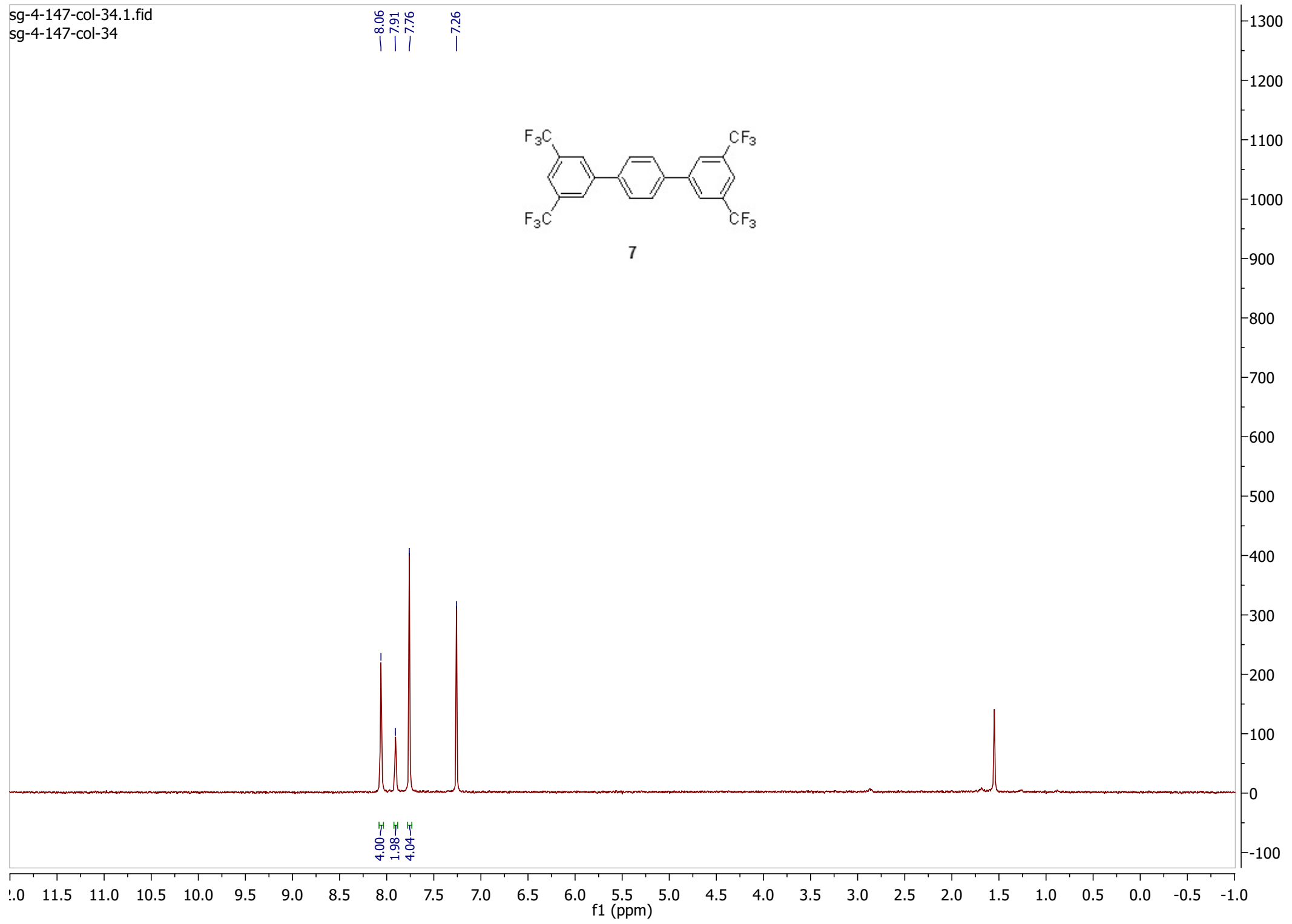


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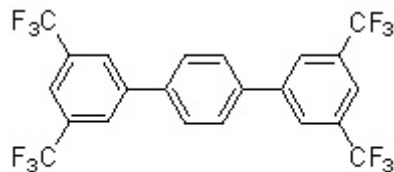


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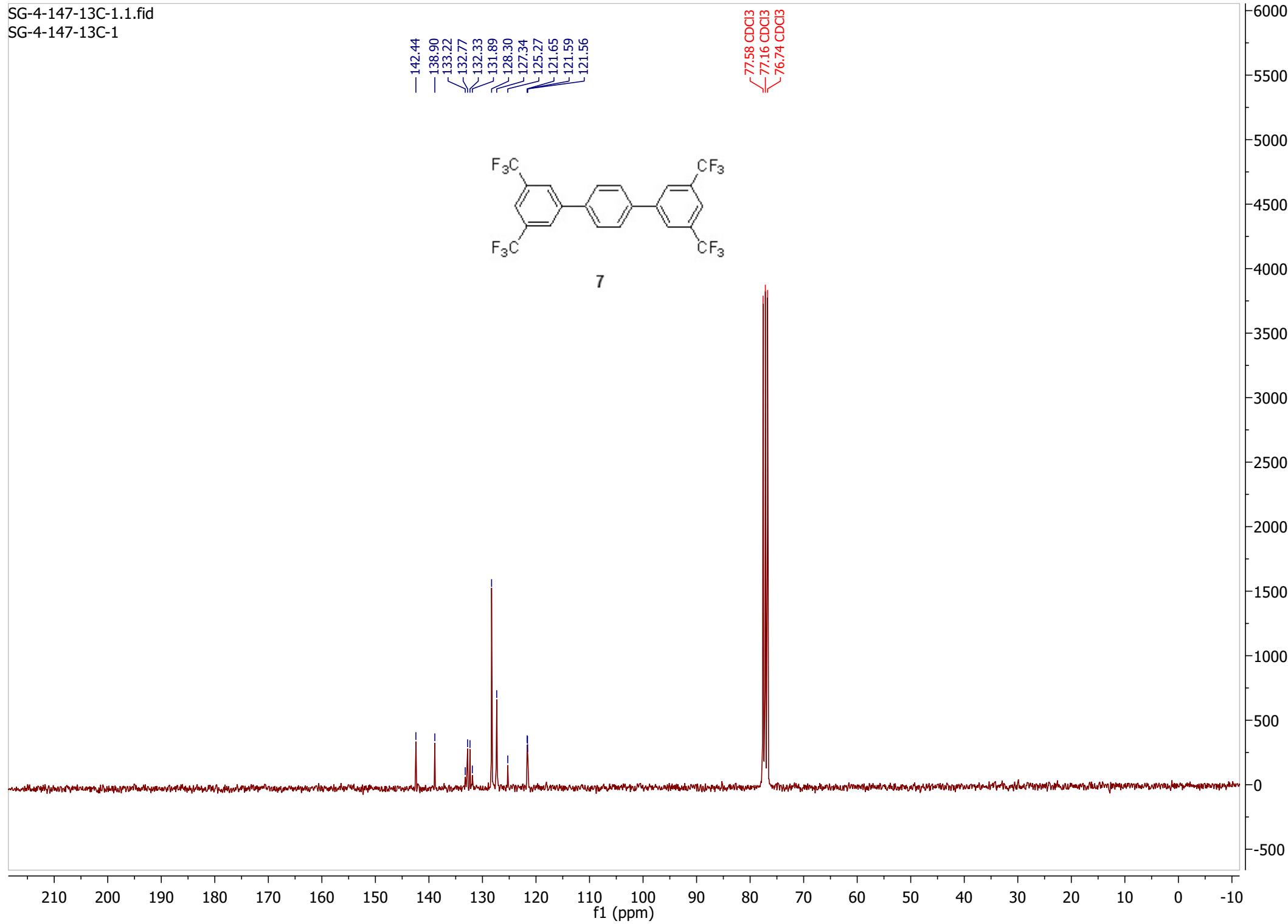


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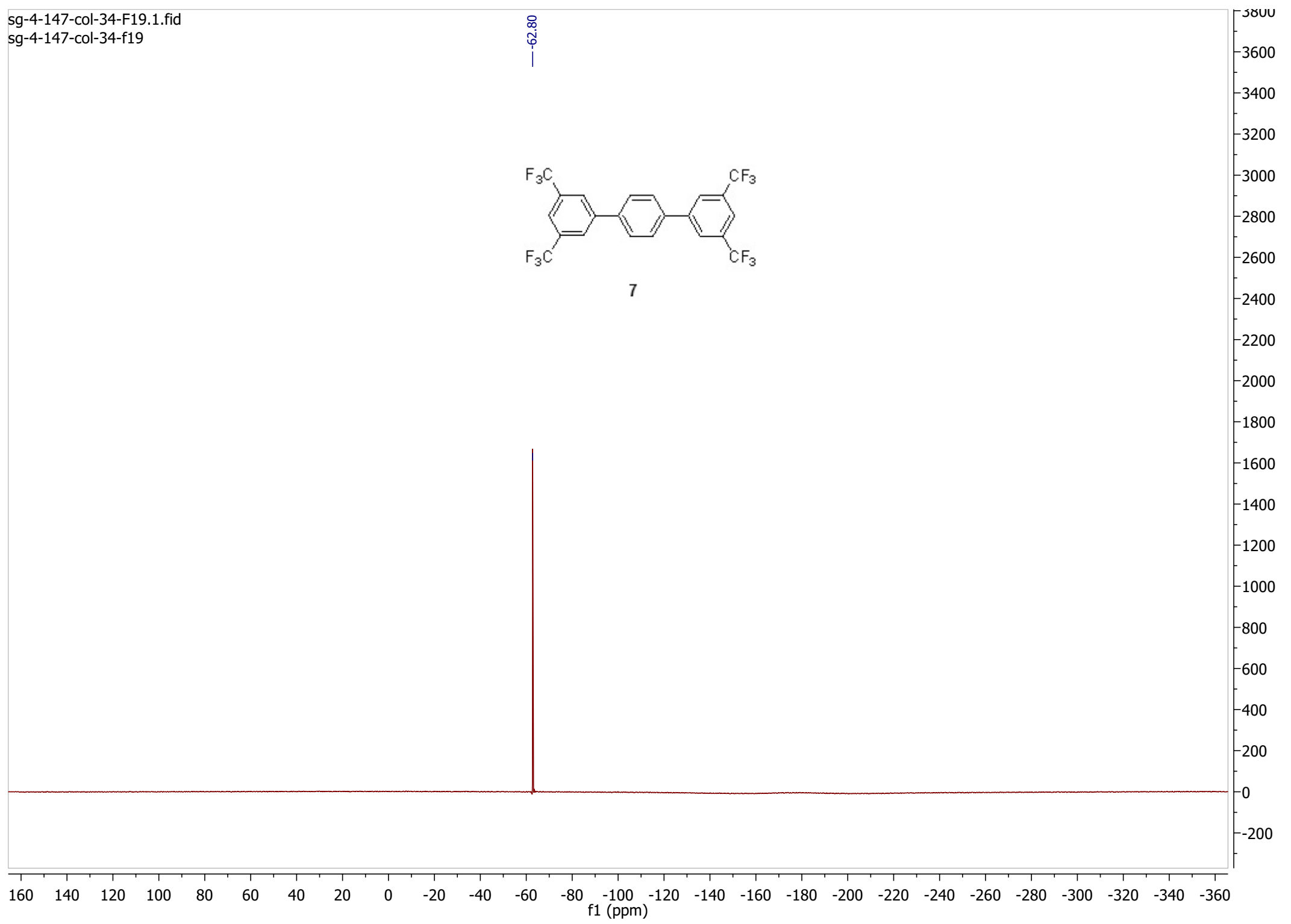
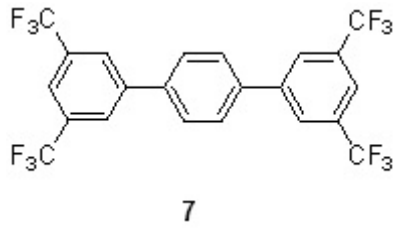
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77.16 CDCl3
76.74 CDCl3



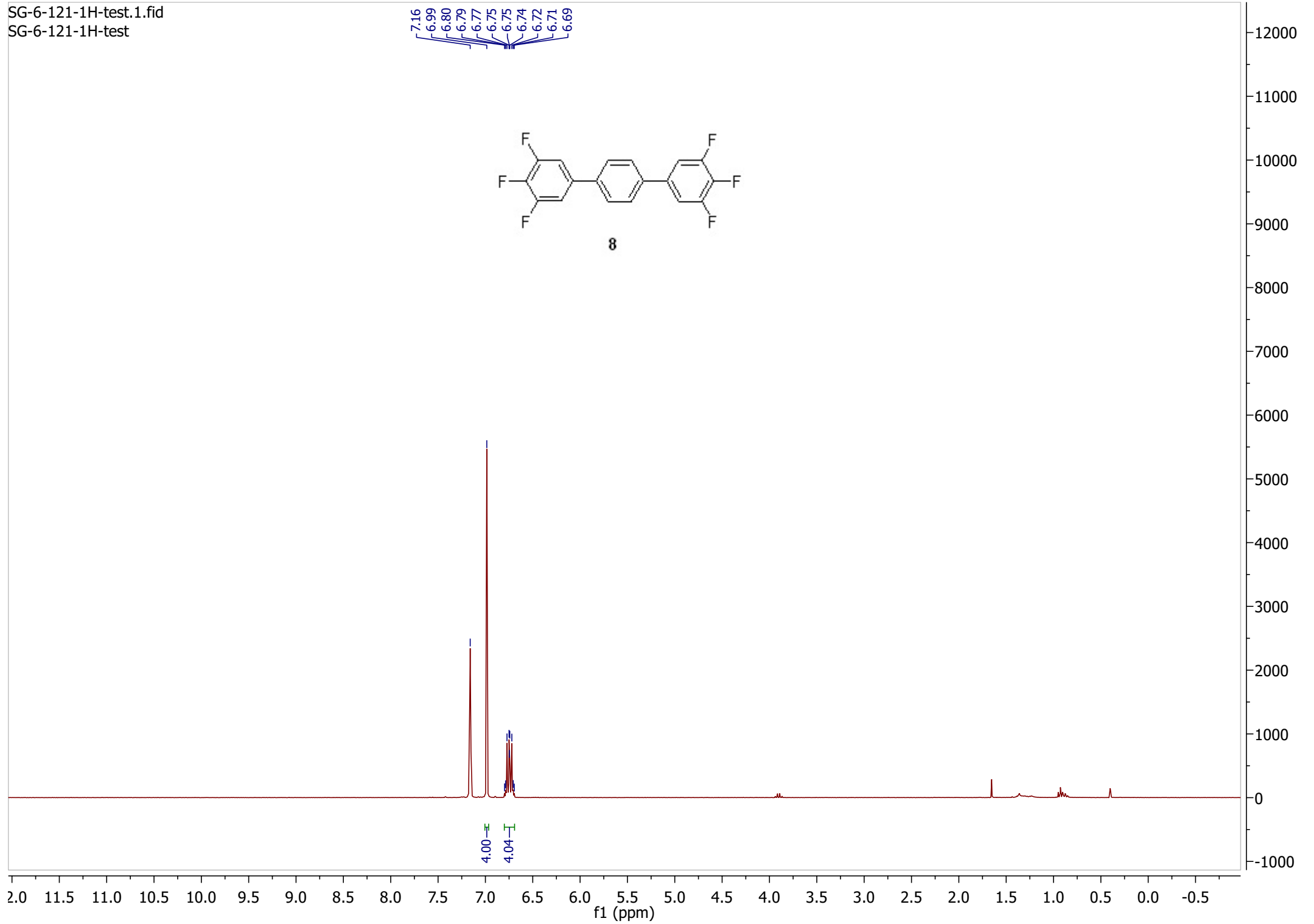
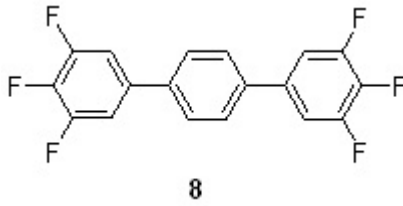
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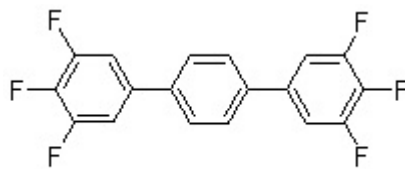
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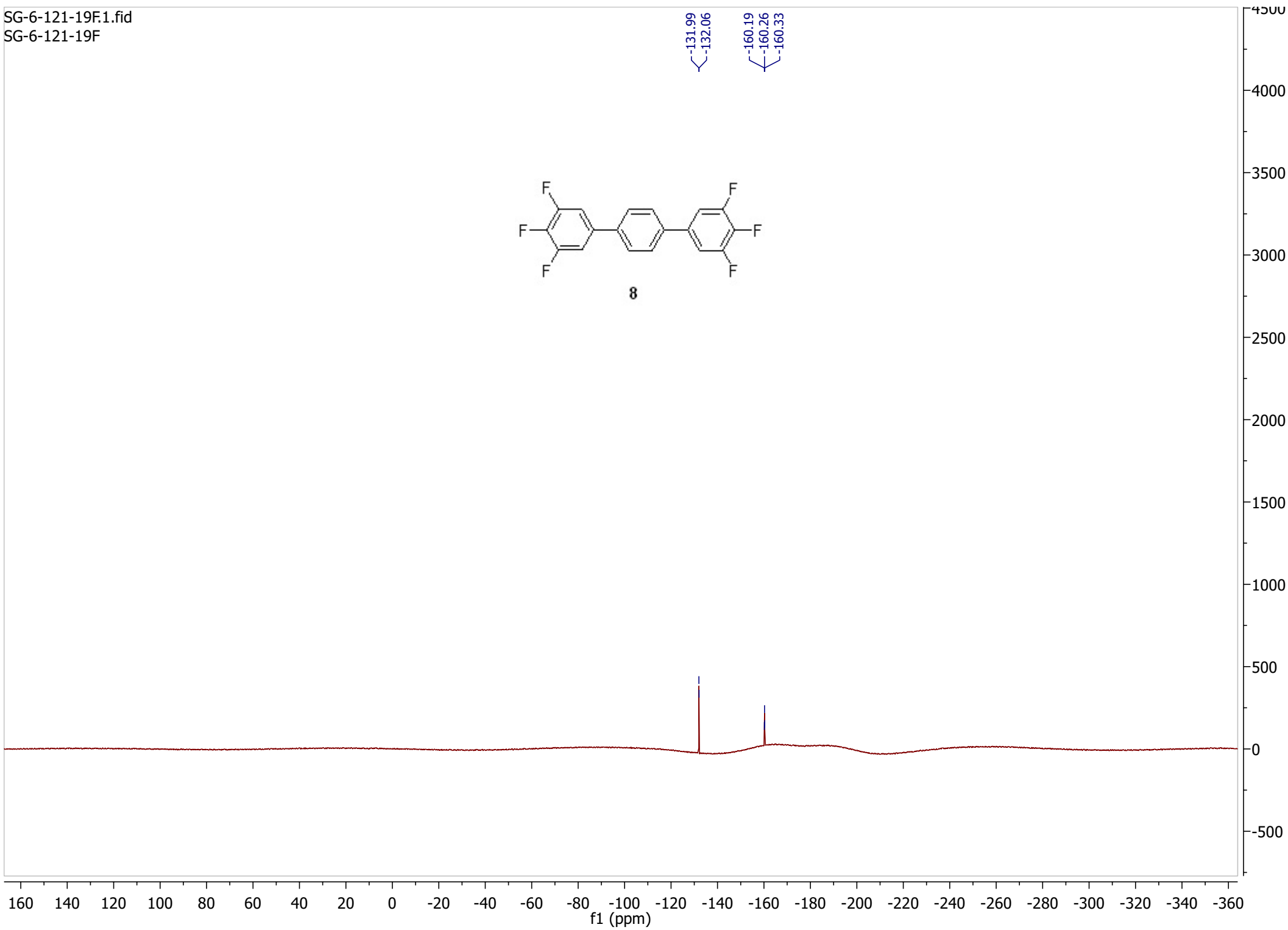
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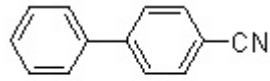
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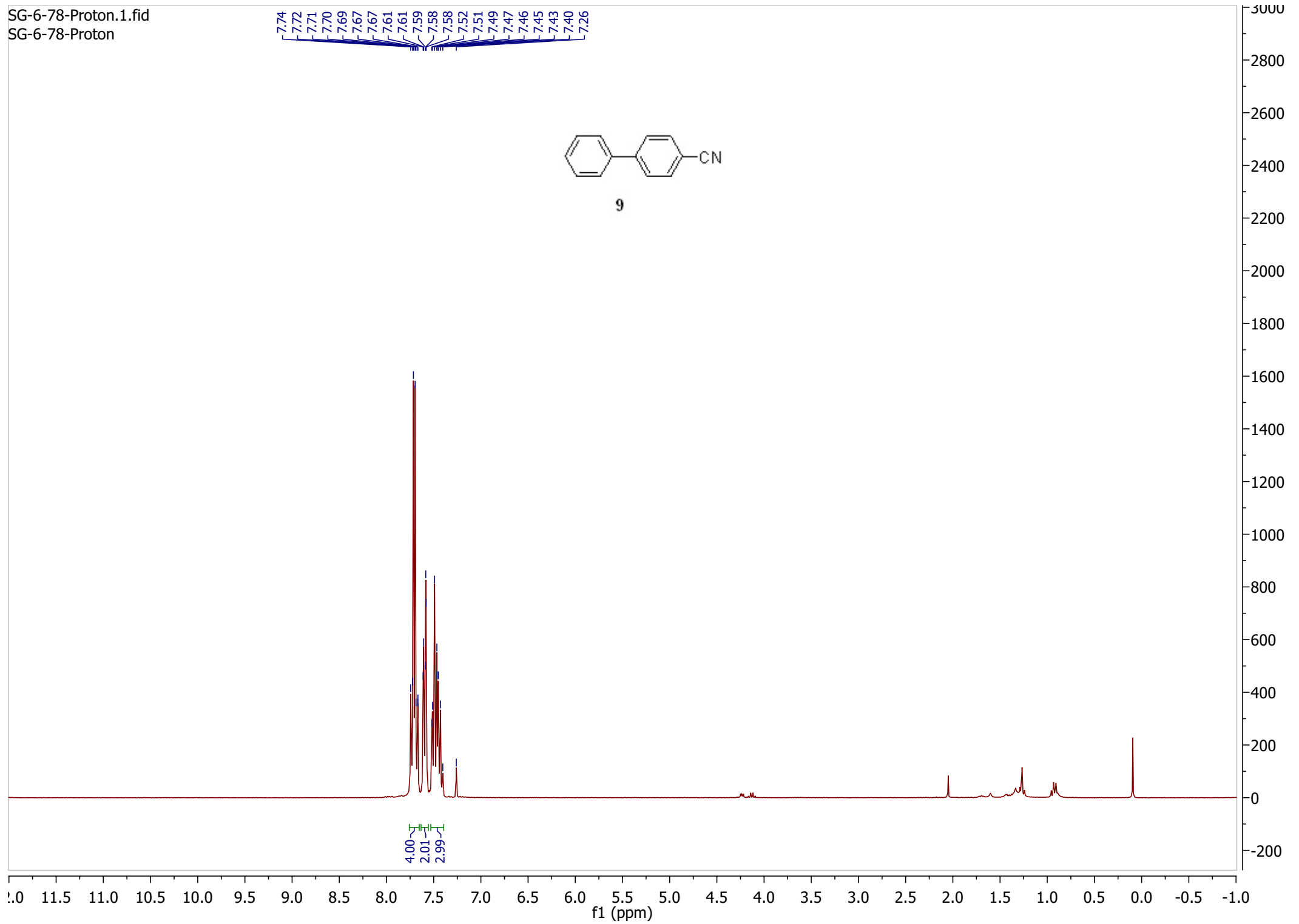


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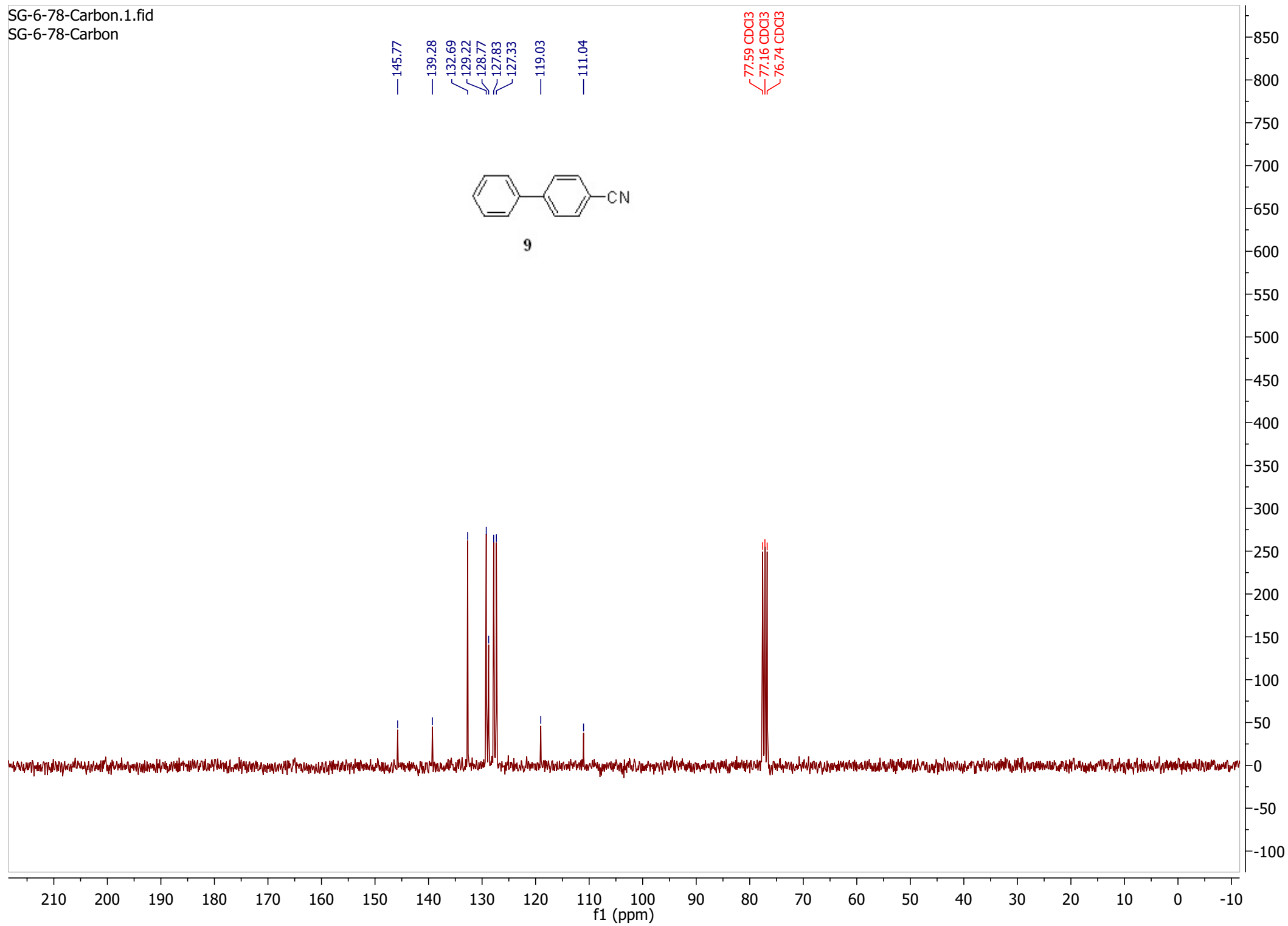
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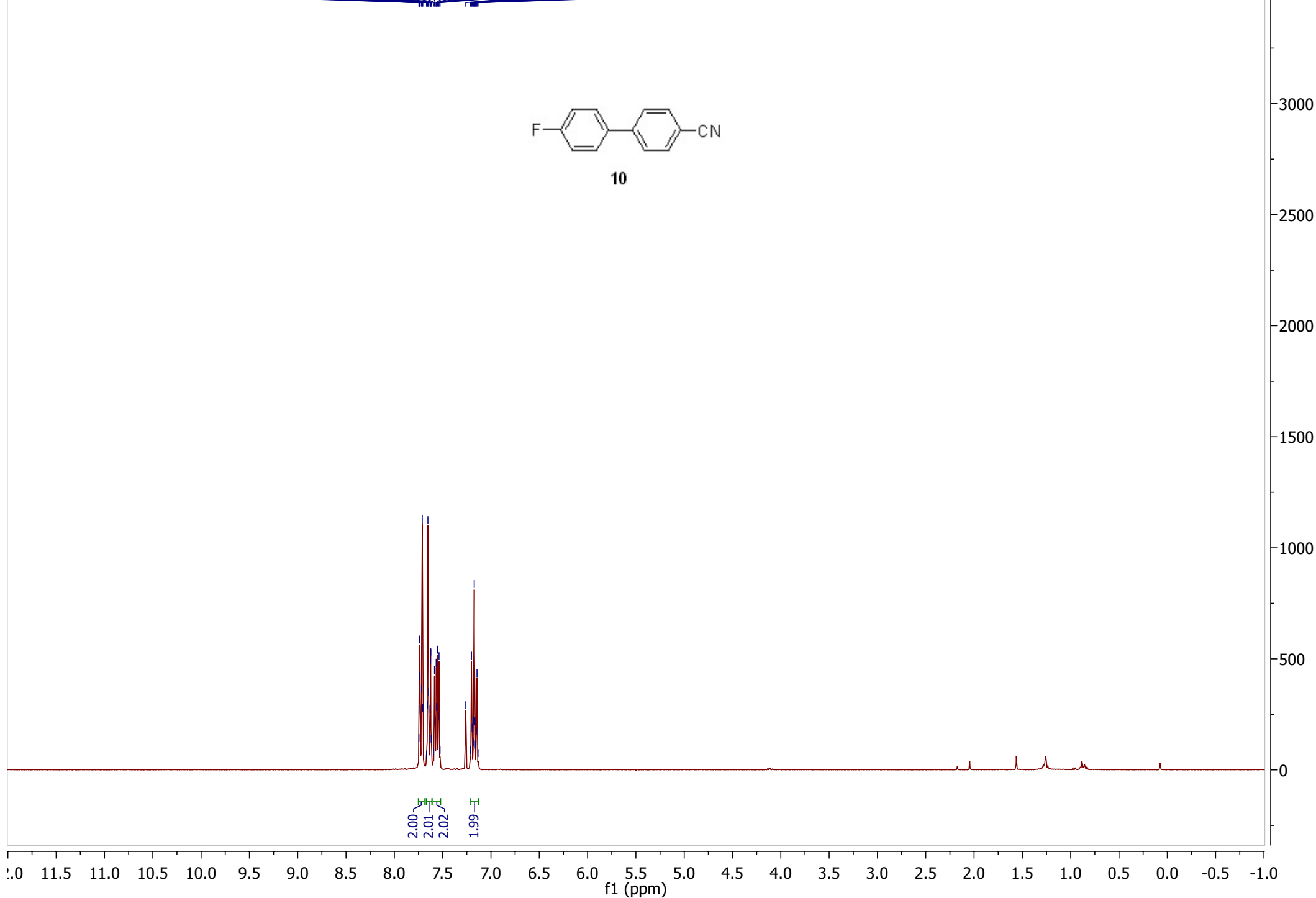
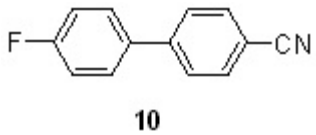
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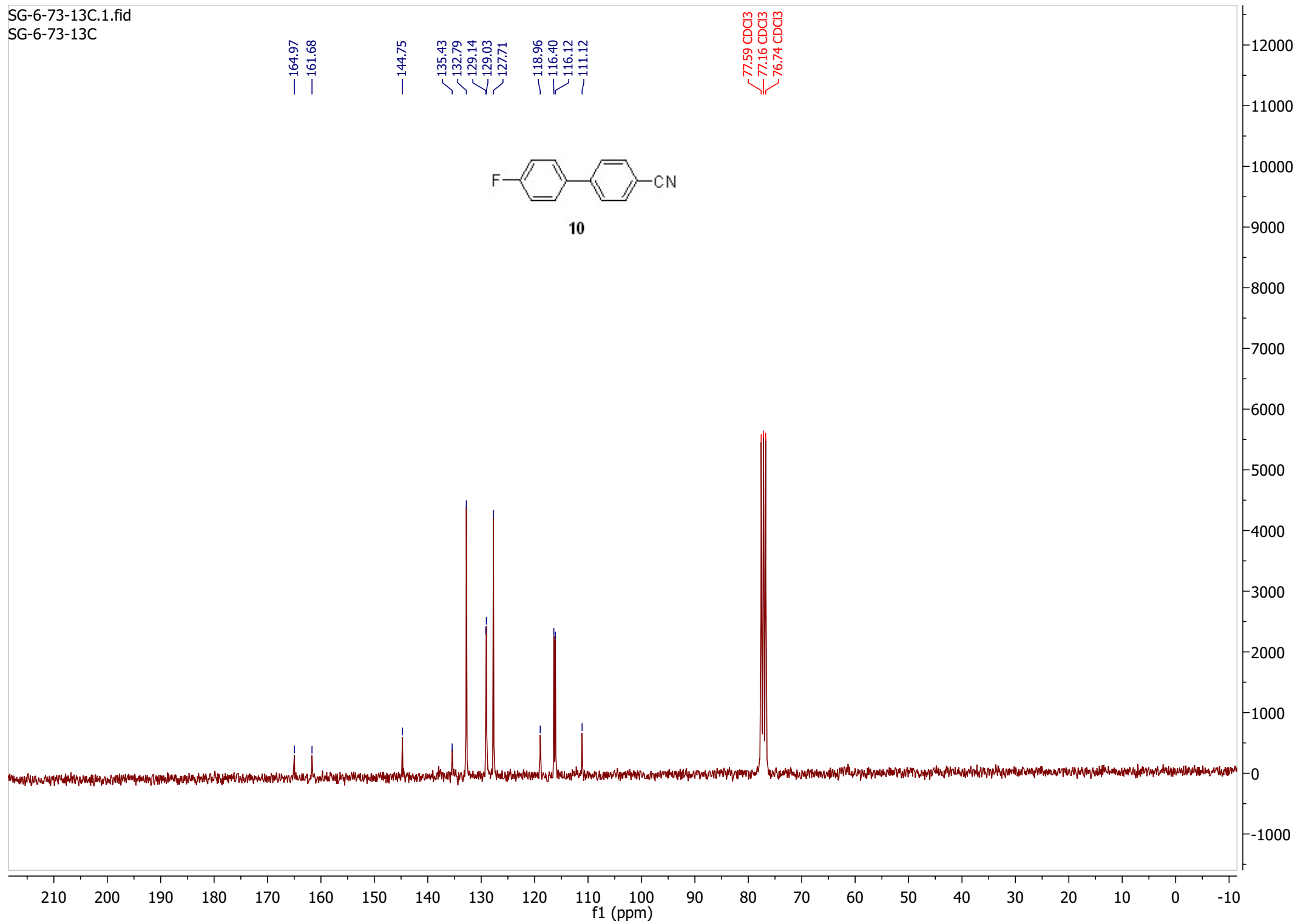
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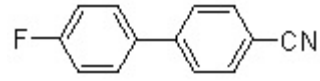
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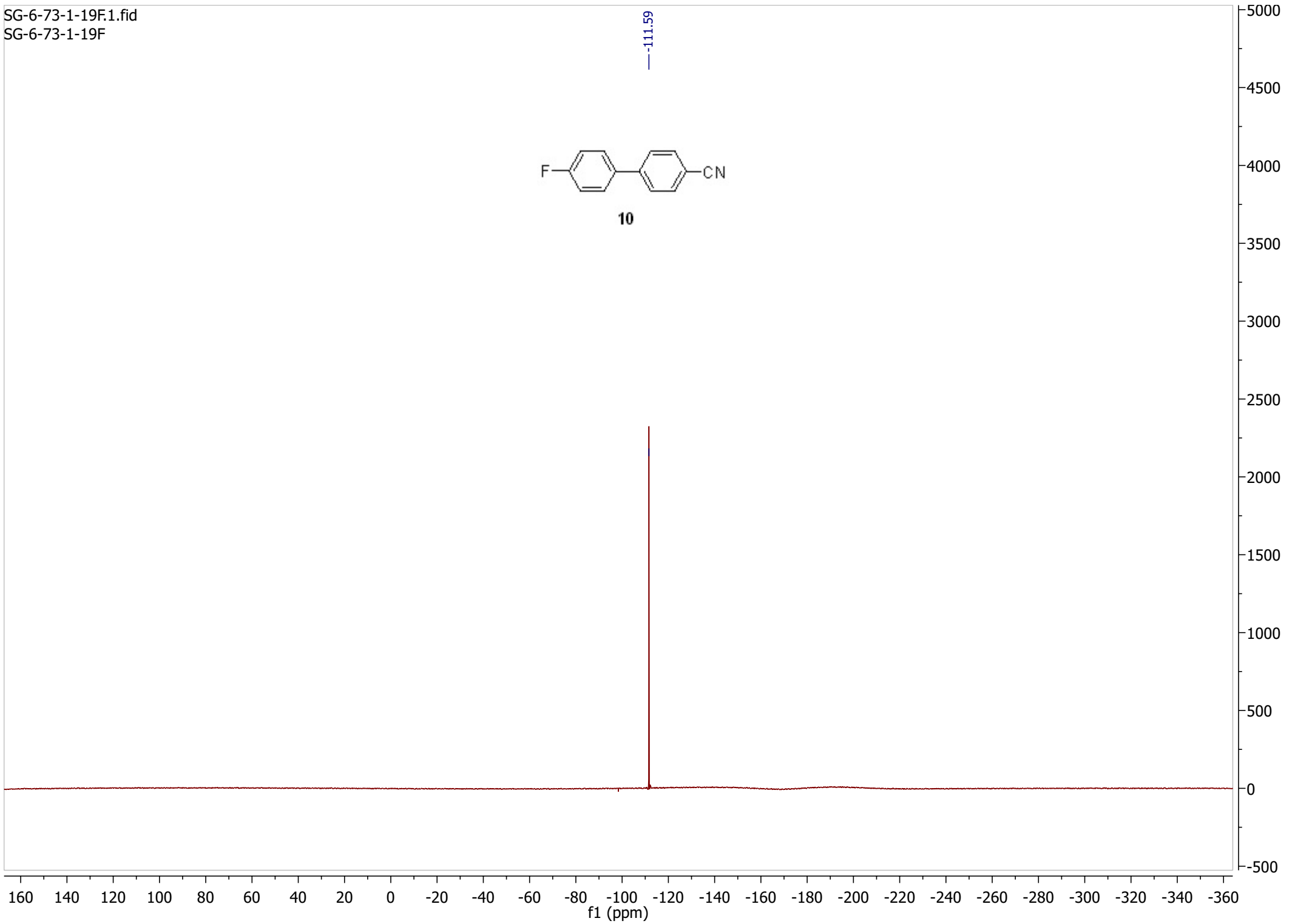


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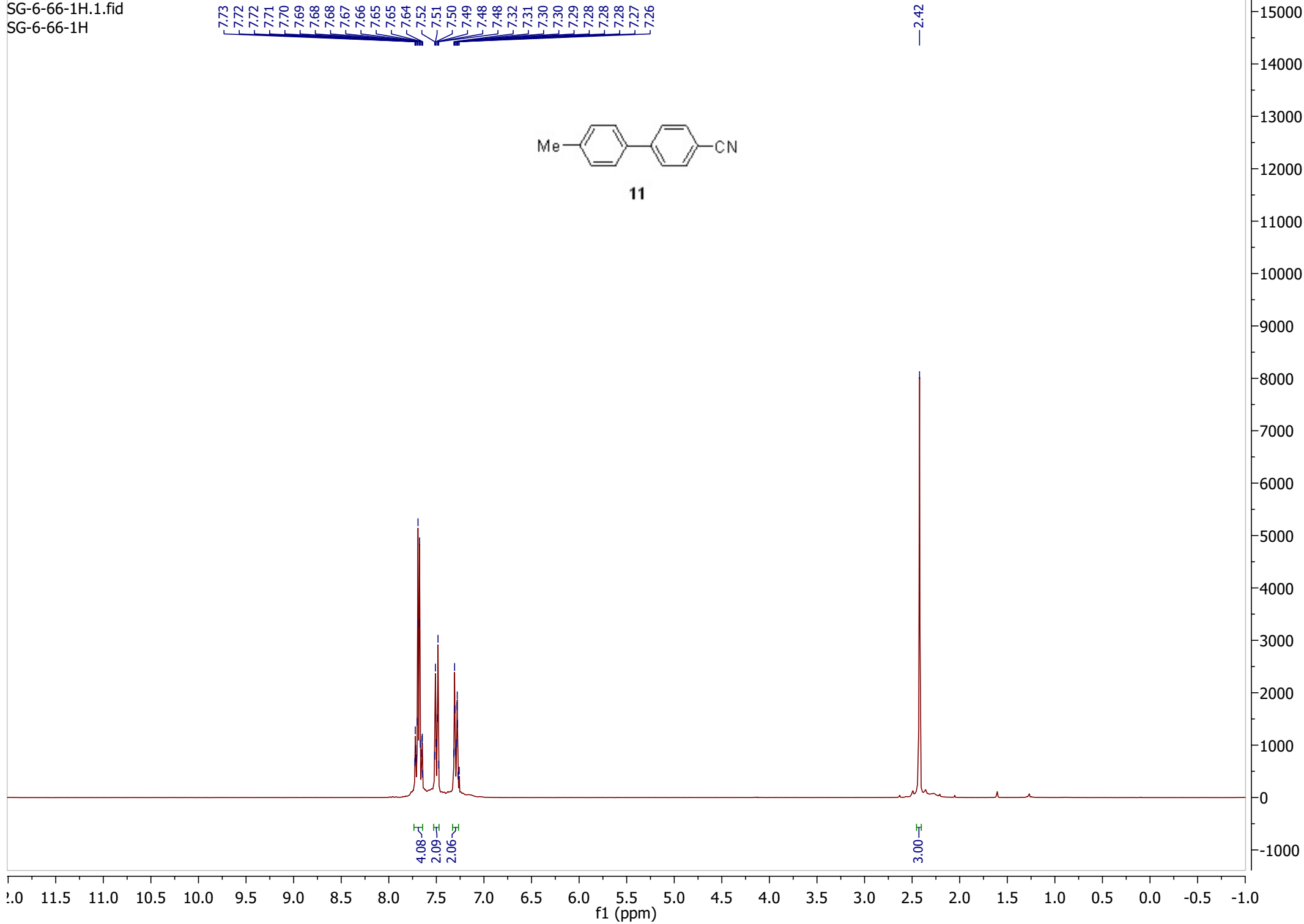
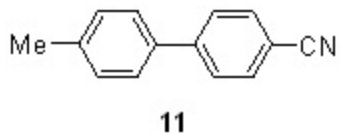
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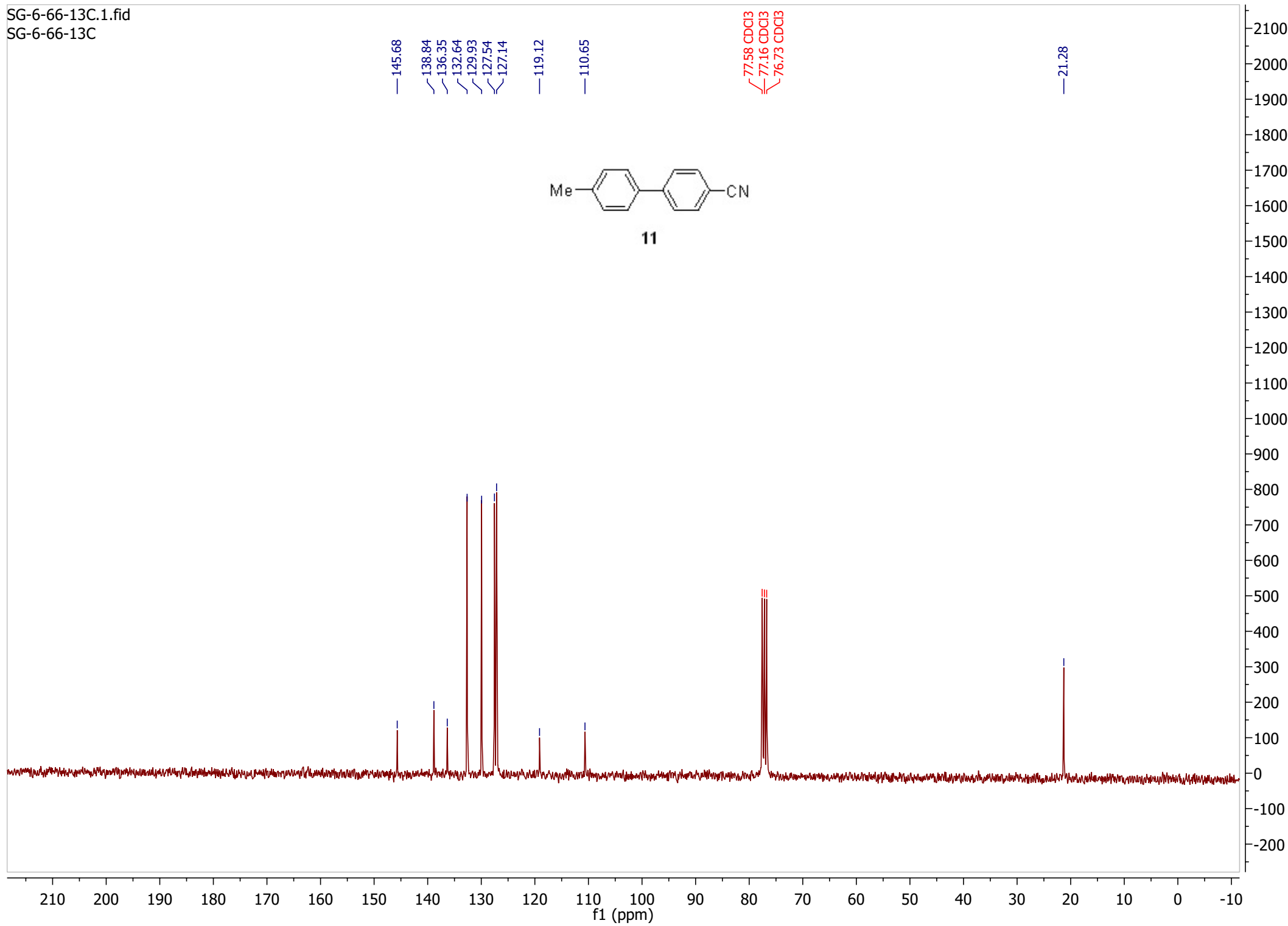
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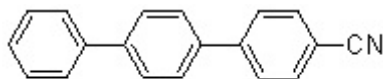
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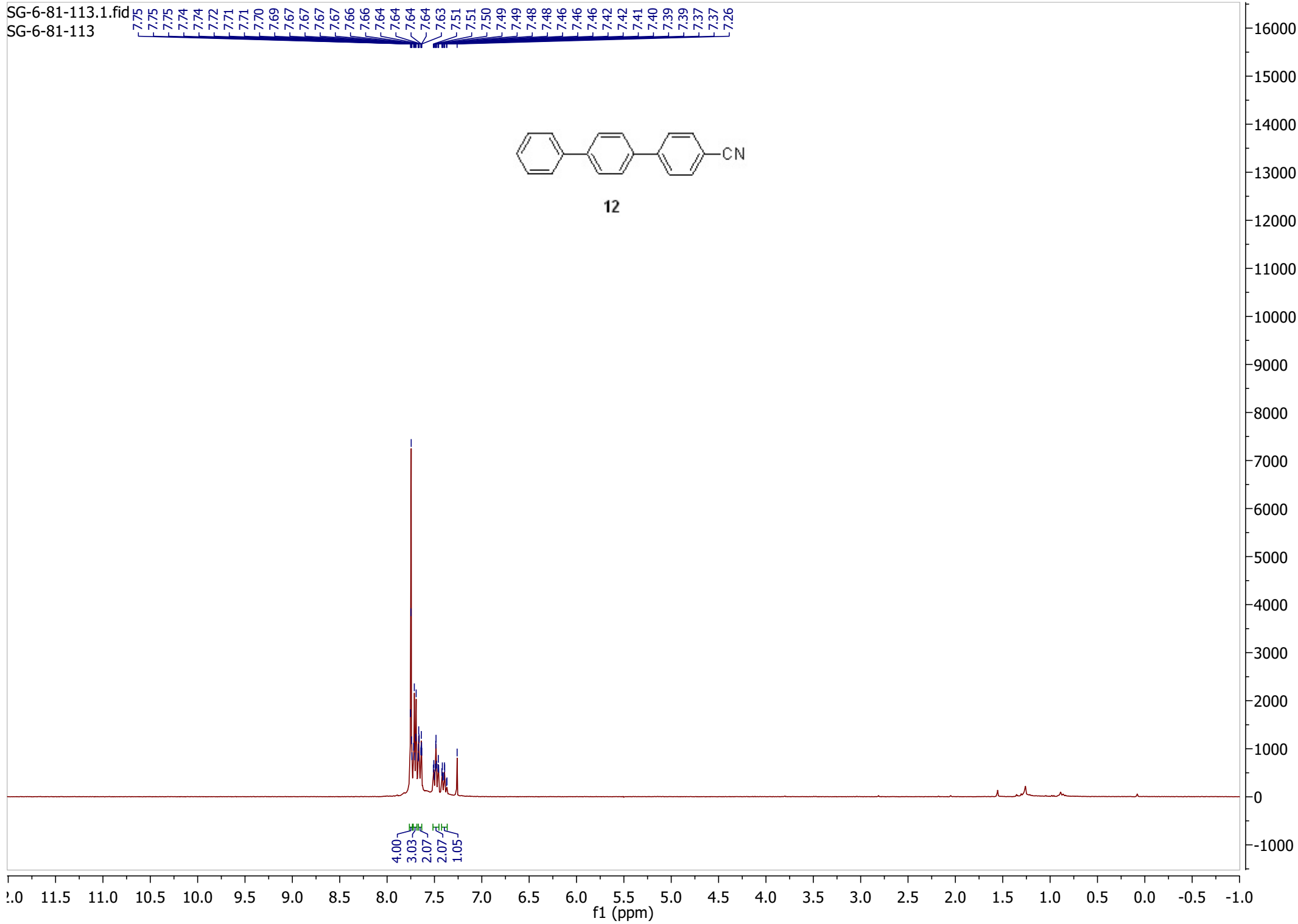


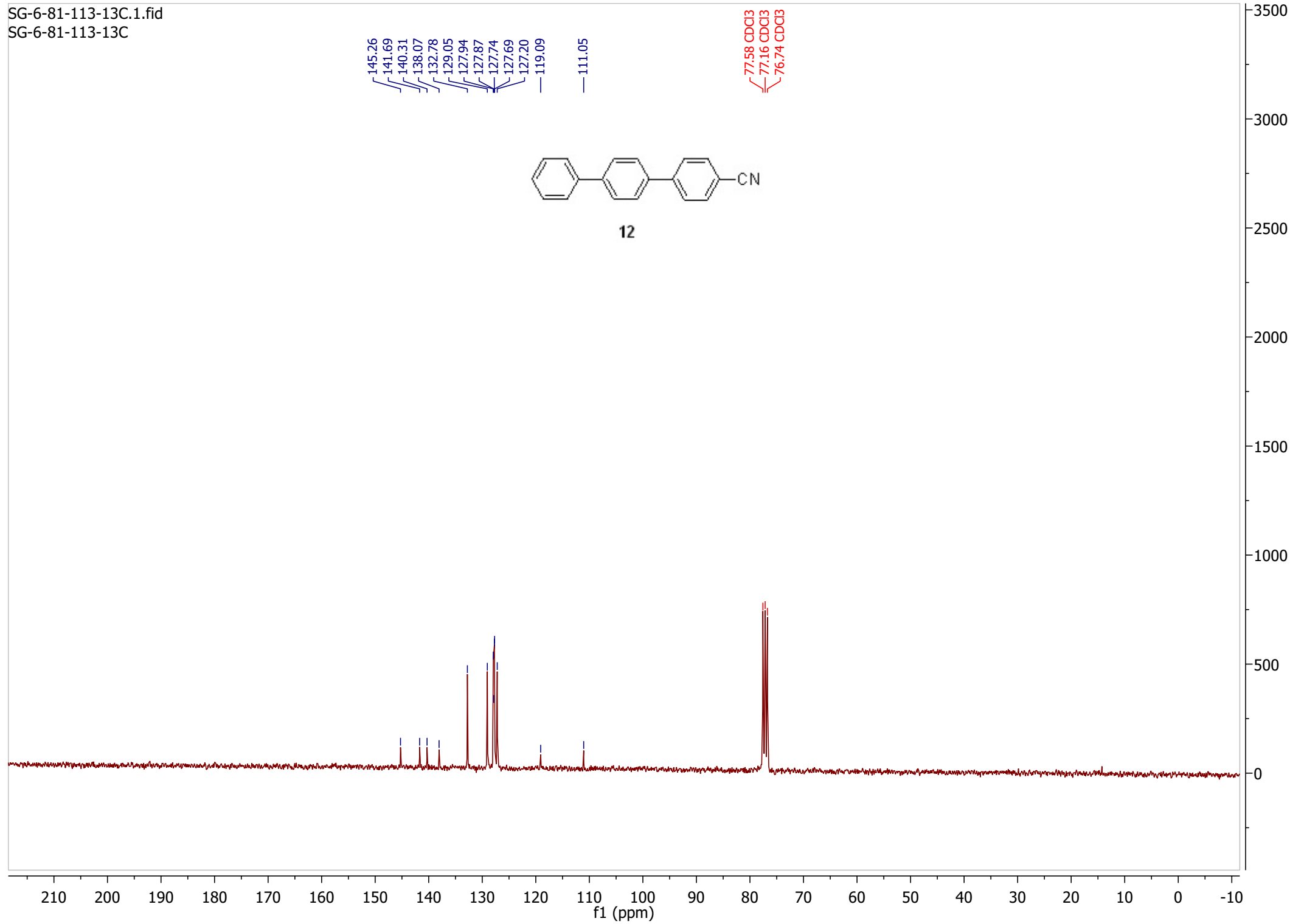
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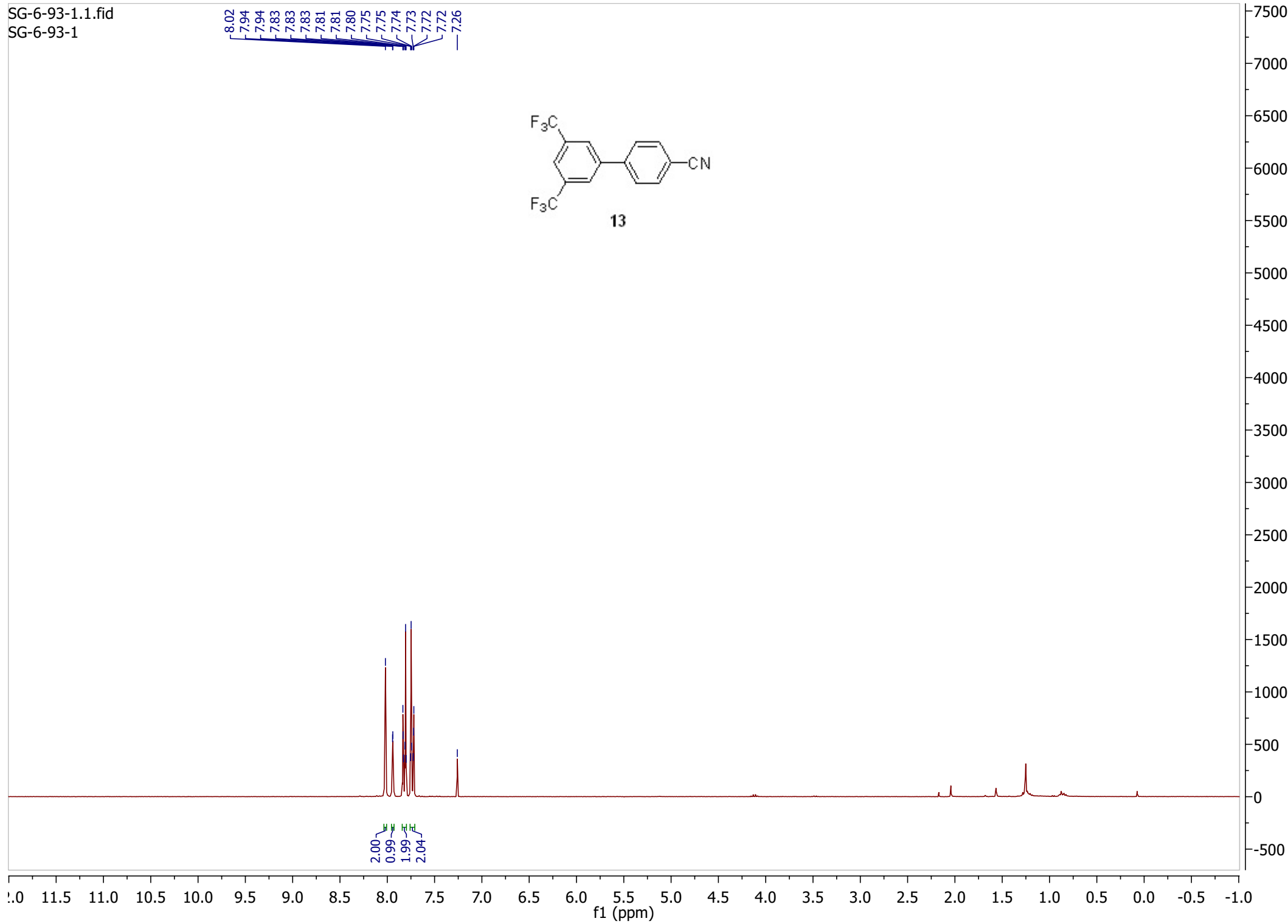
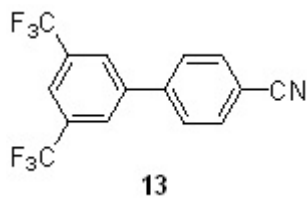
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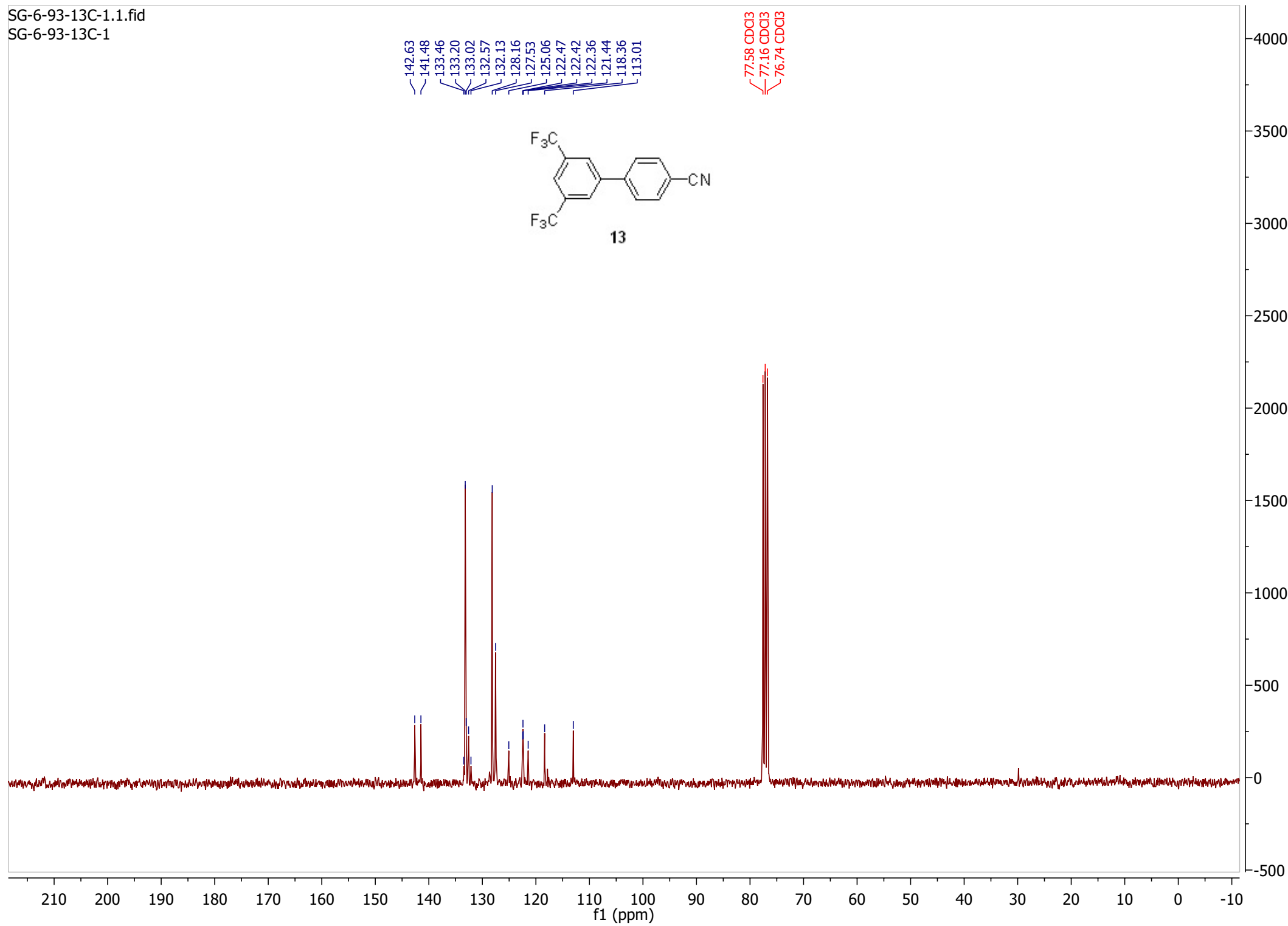
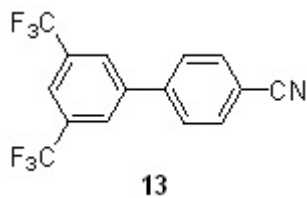
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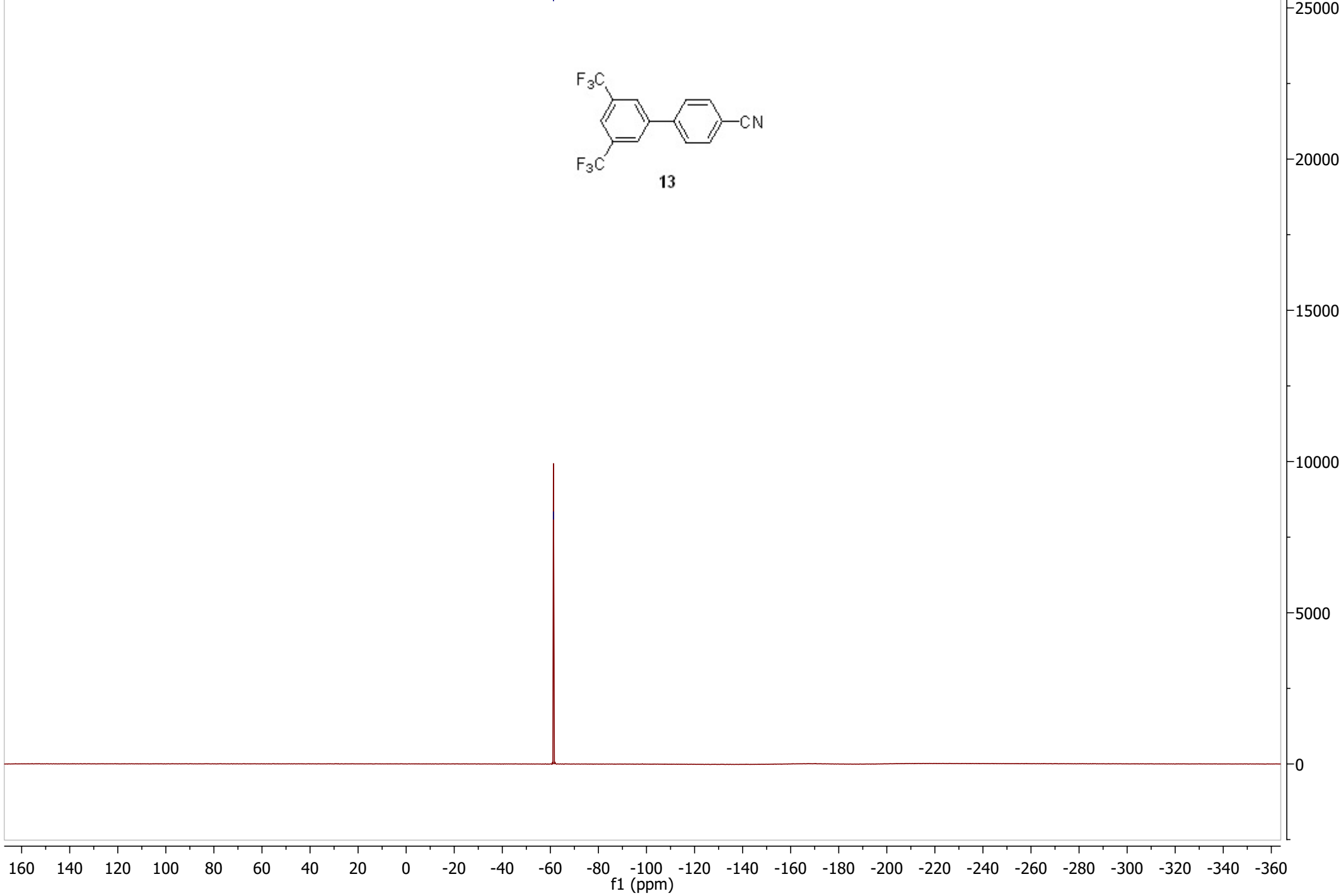
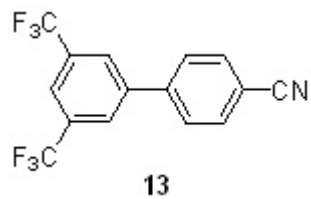


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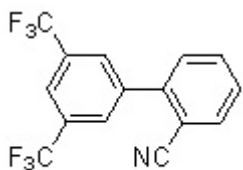
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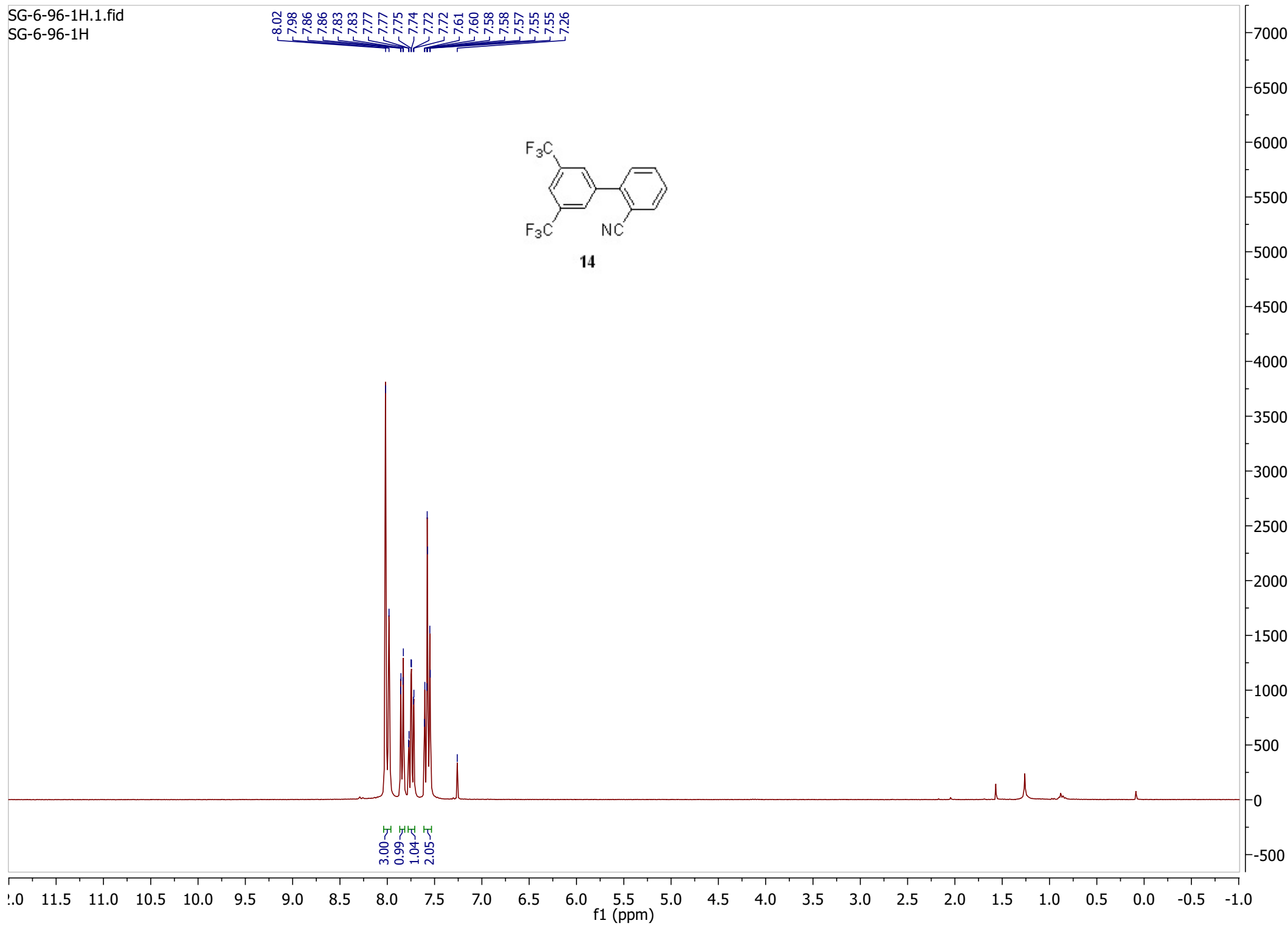
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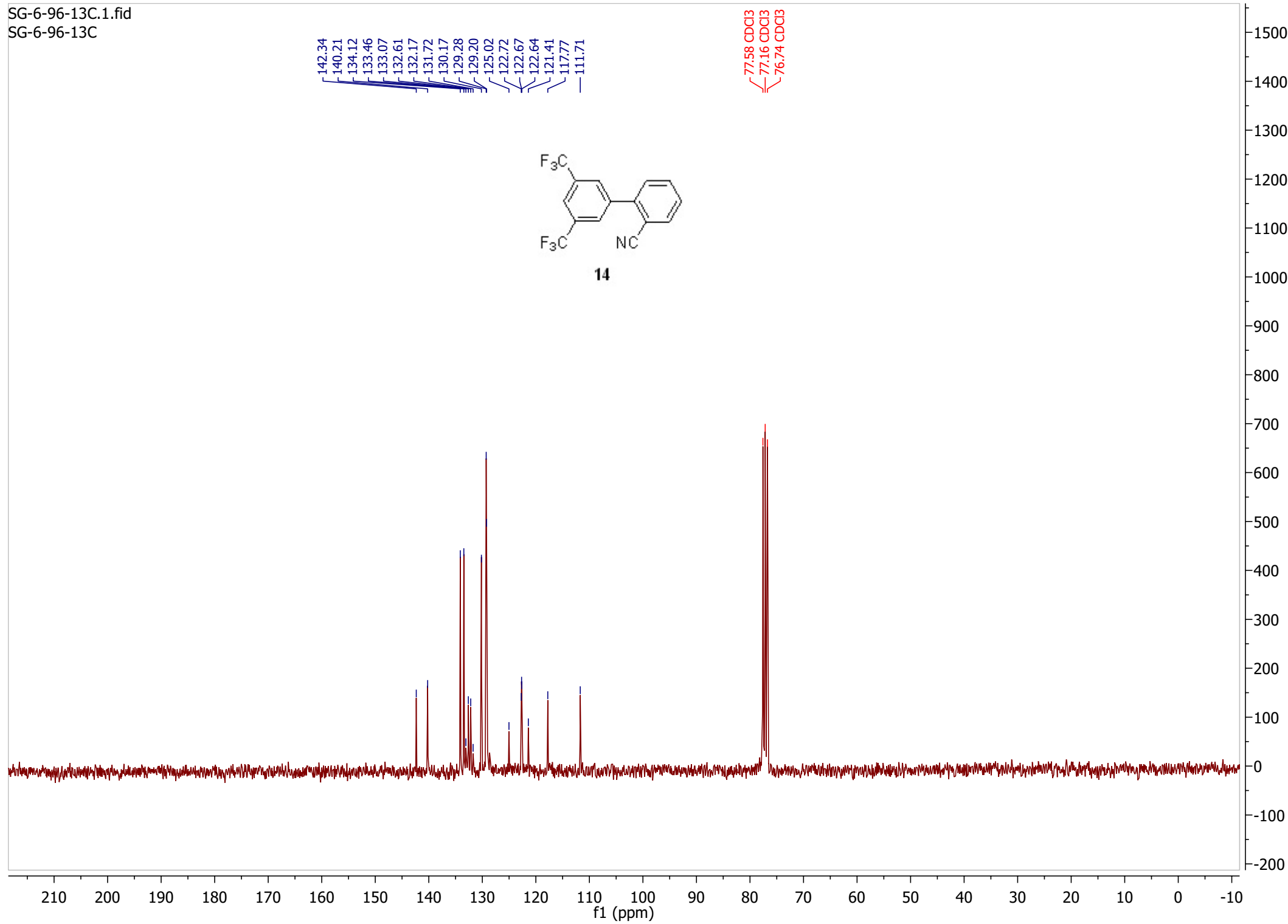


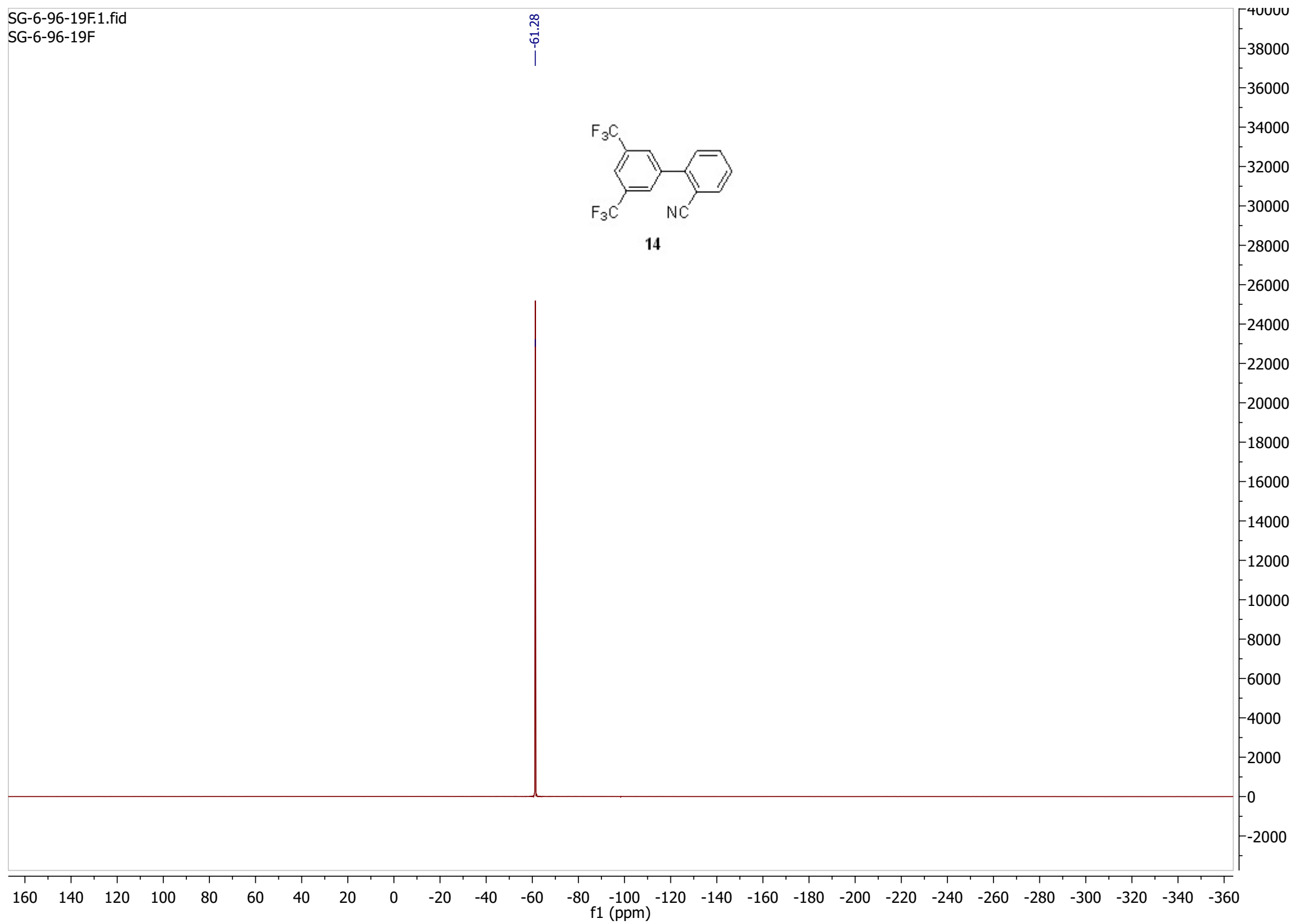
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14

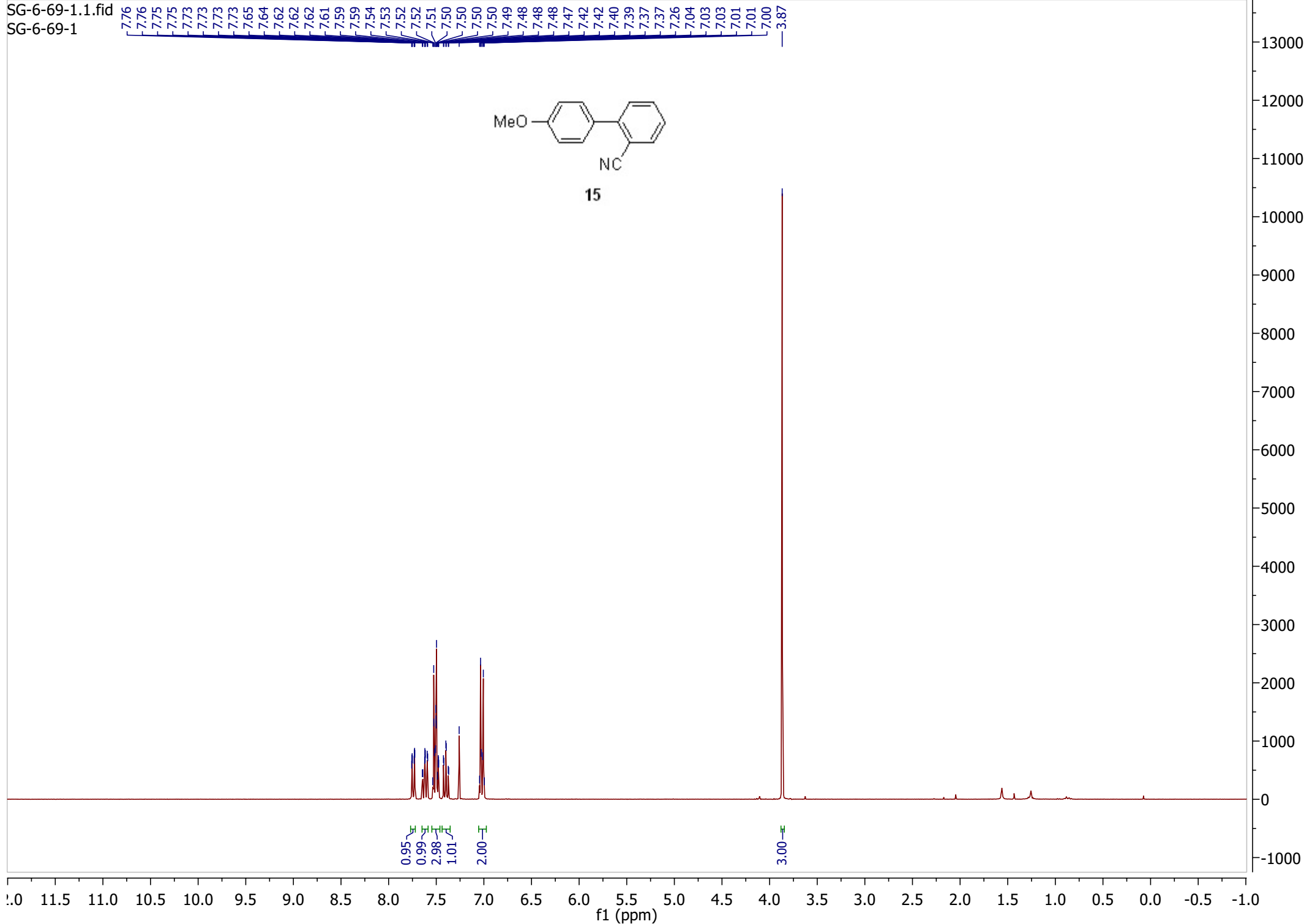
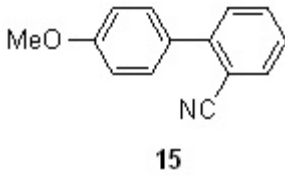


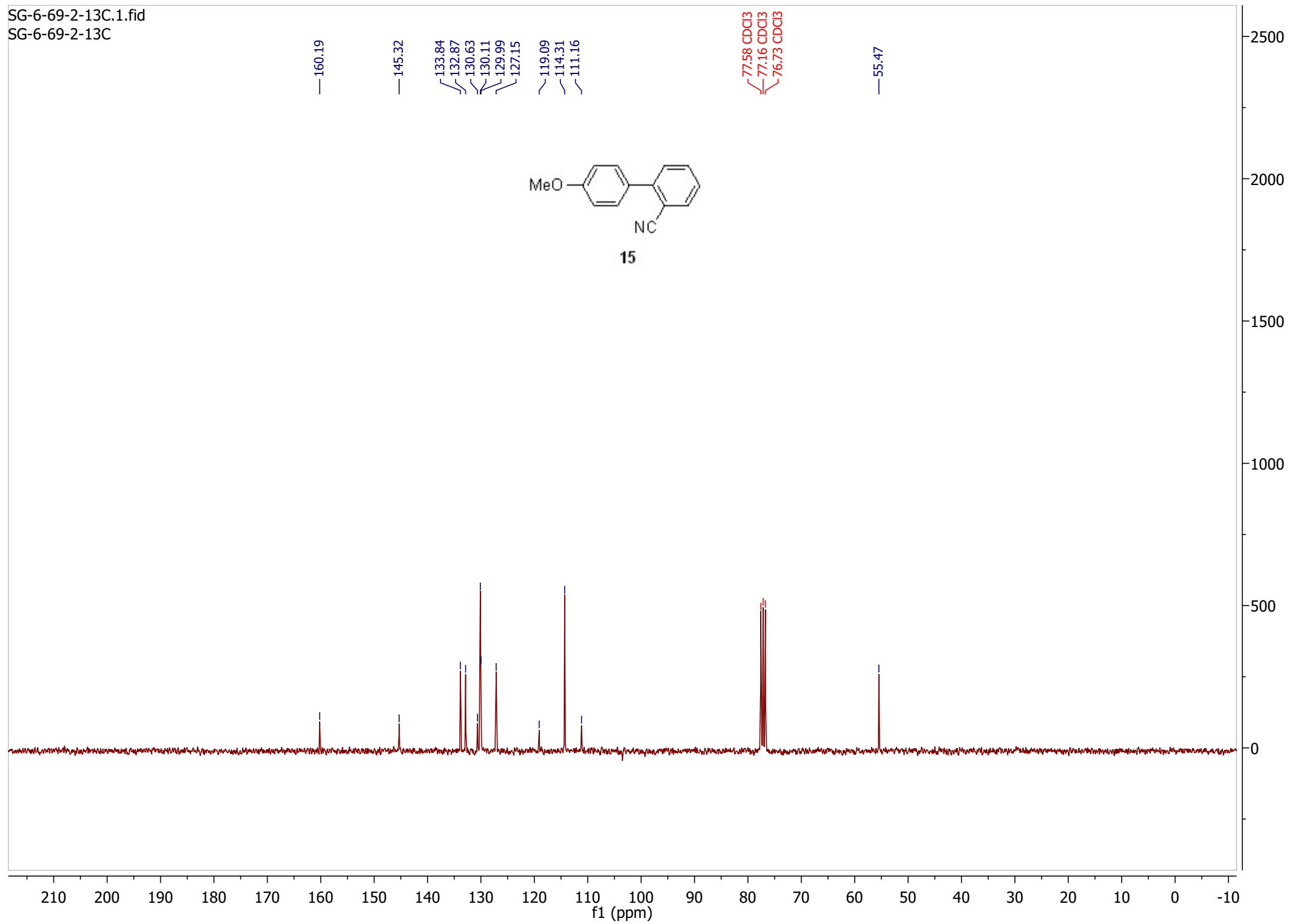




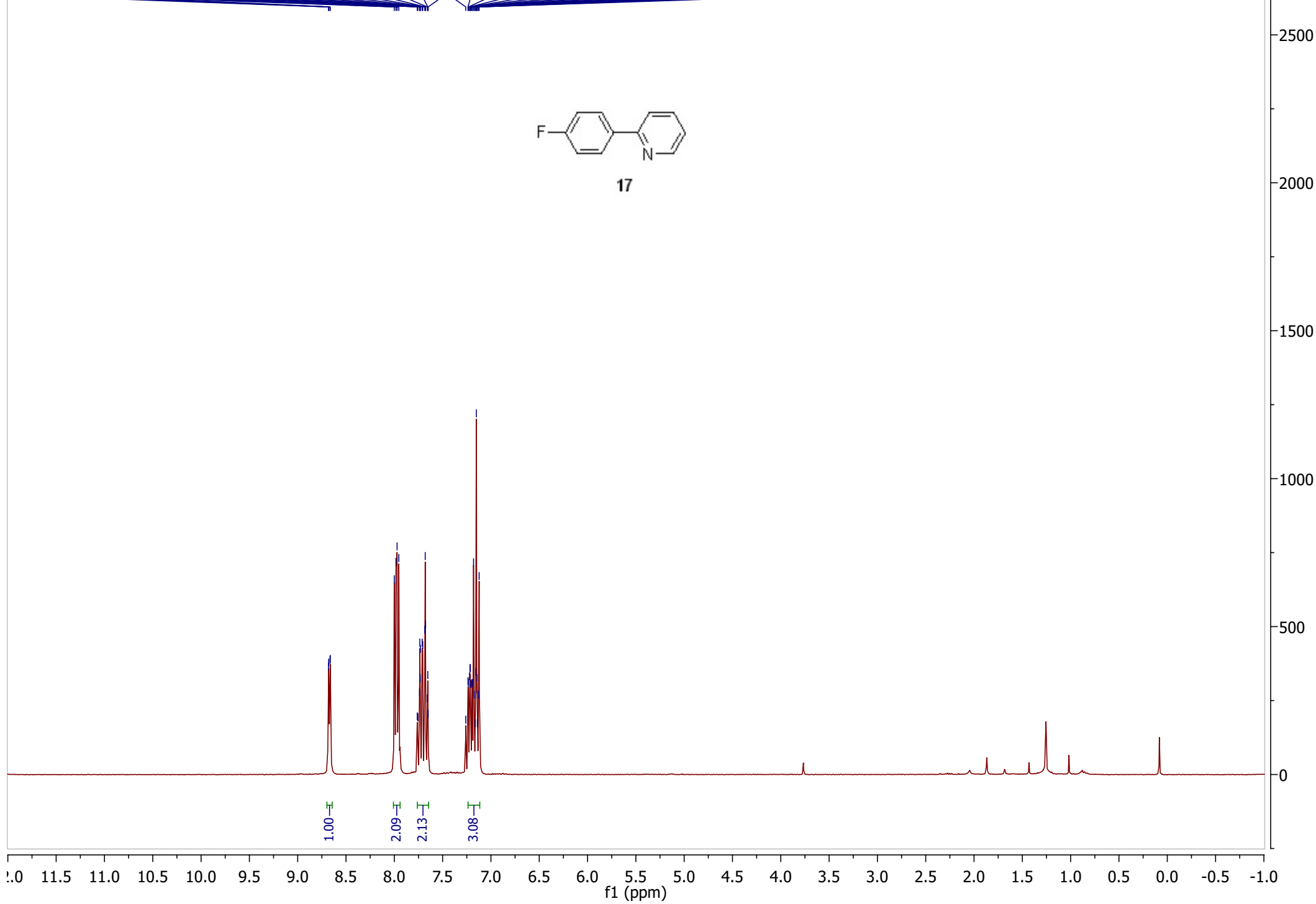
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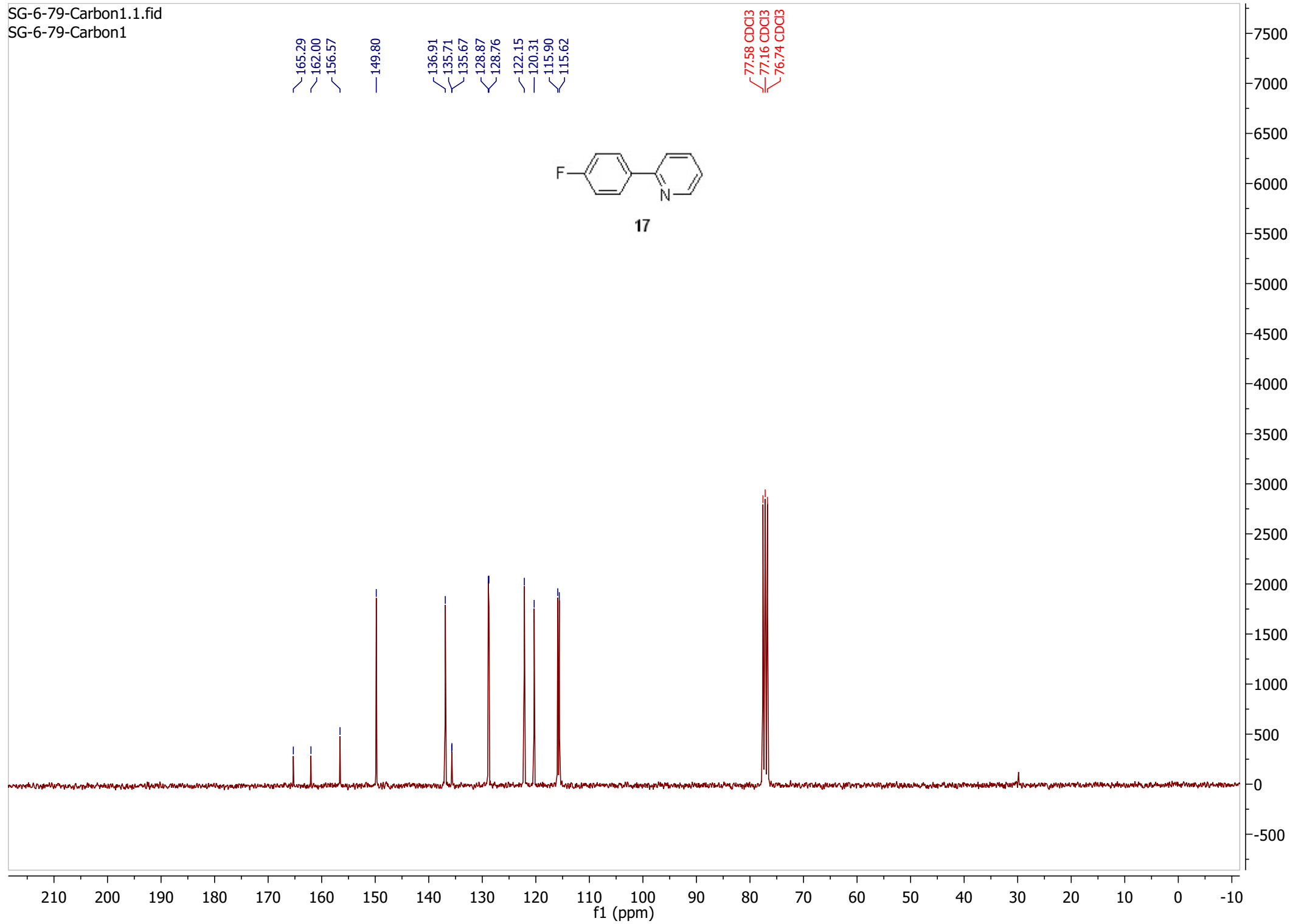
7.776 7.776 7.775 7.773 7.773 7.773 7.765 7.764 7.762 7.762 7.761 7.759 7.759 7.759 7.754 7.753 7.752 7.752 7.751 7.750 7.750 7.750 7.750 7.749 7.748 7.748 7.748 7.747 7.742 7.742 7.740 7.739 7.737 7.737 7.726 7.704 7.703 7.703 7.701 7.701 7.00 3.87

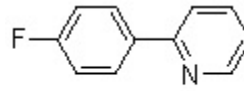




SG-6-79-Protom
SG-6-79-Protom

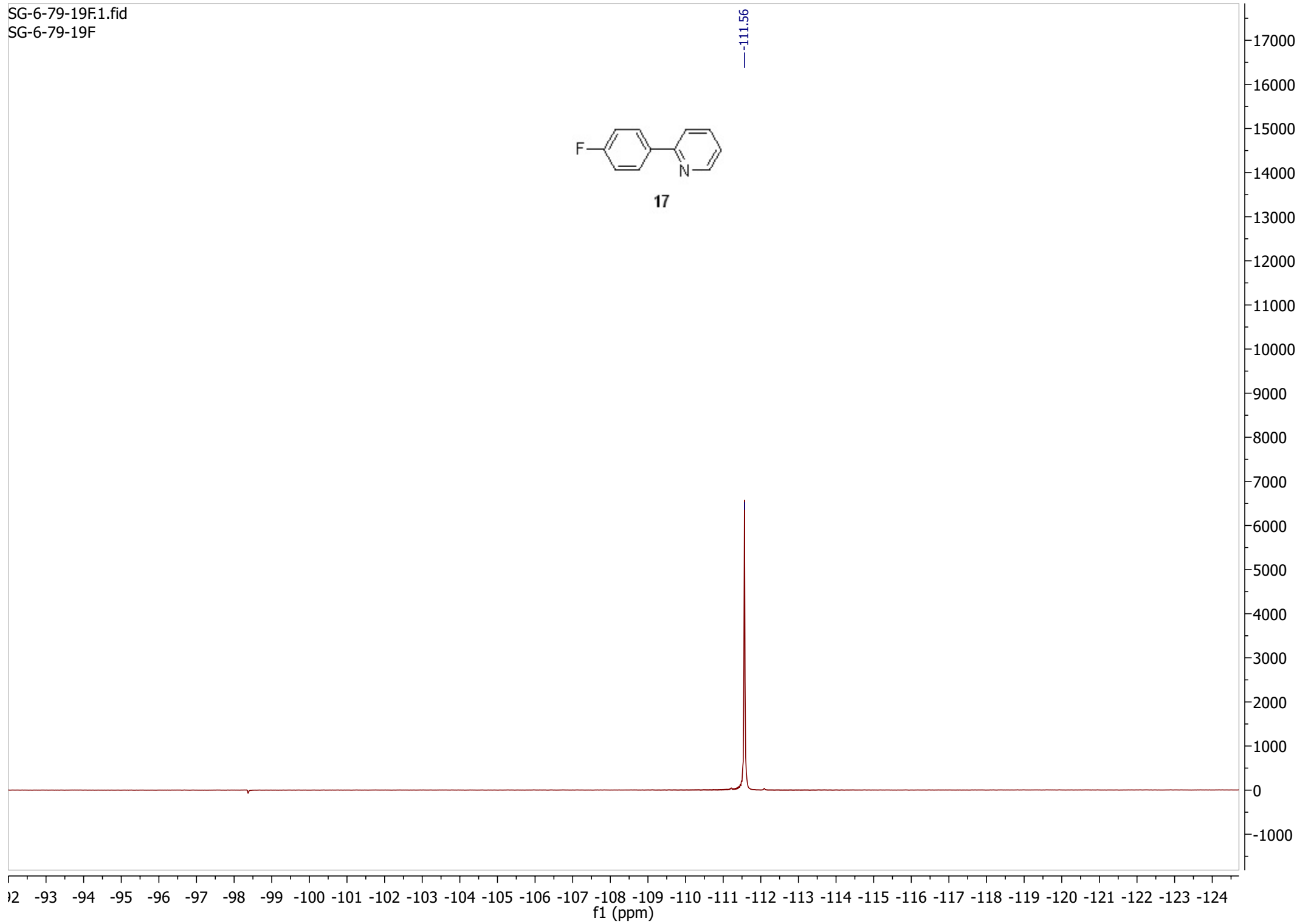






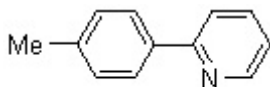
17

-111.56

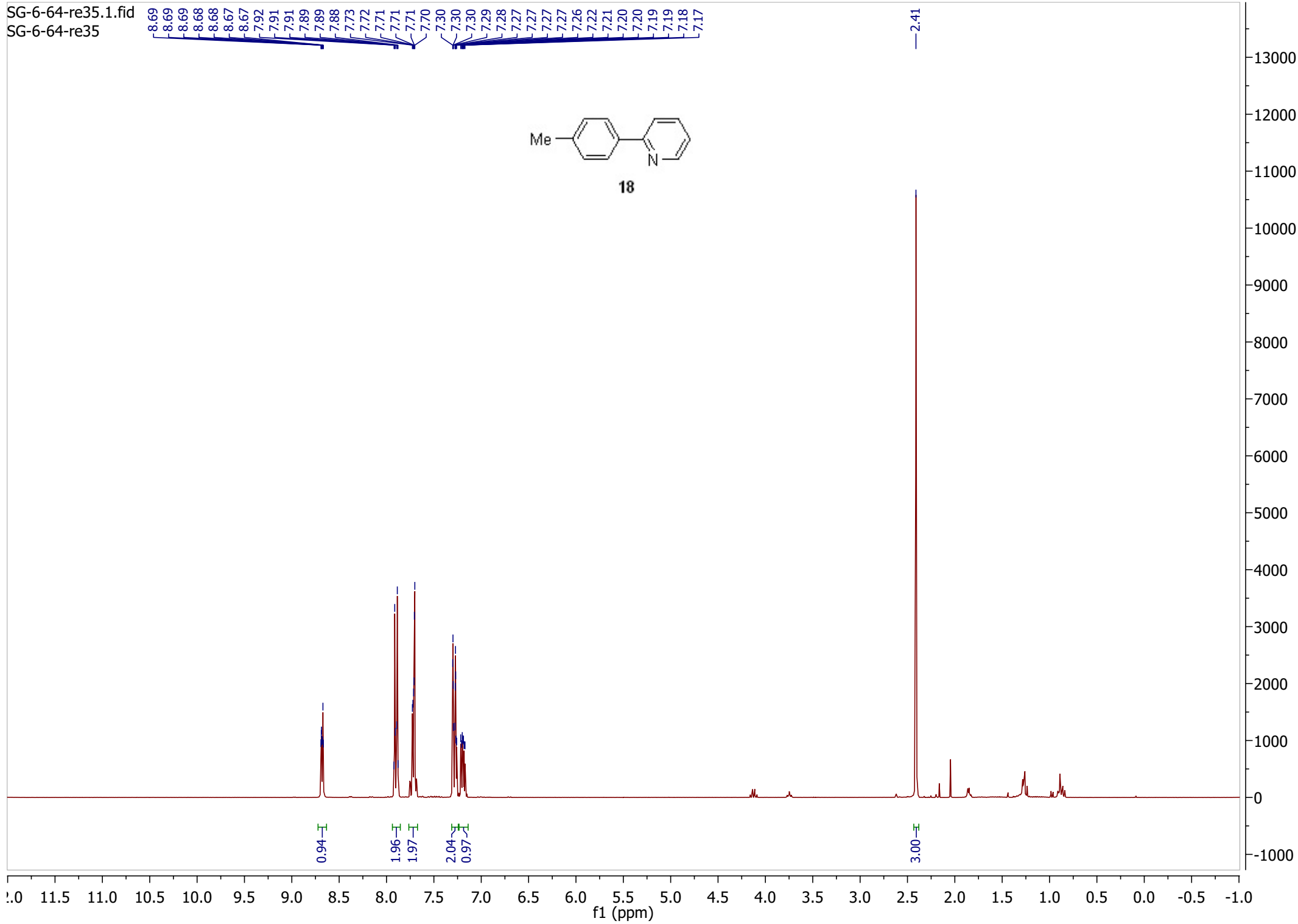


SG-6-64-re35.1.fid
SG-6-64-re35

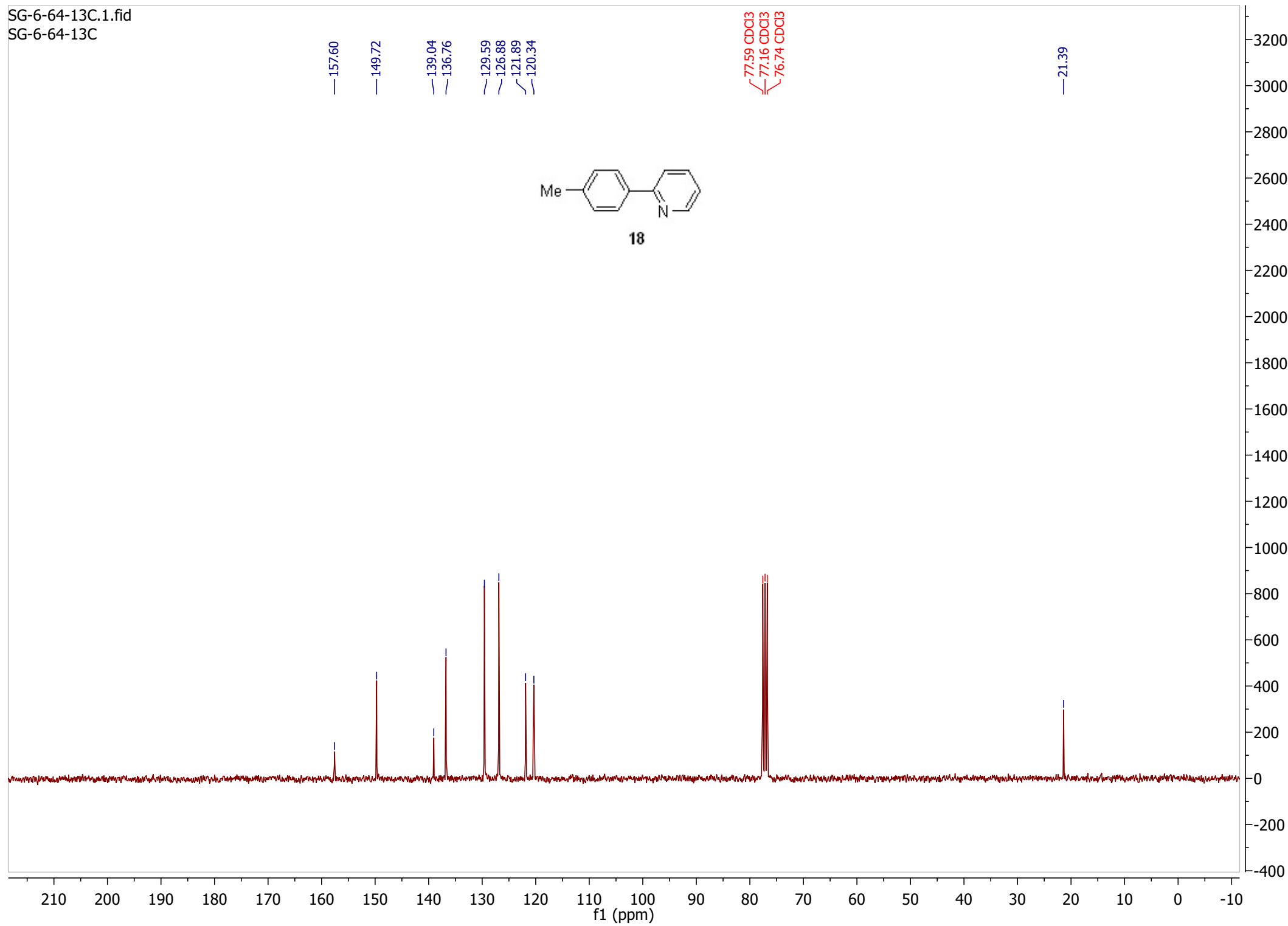
8.69
8.69
8.69
8.68
8.67
8.67
7.92
7.91
7.91
7.89
7.89
7.88
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18

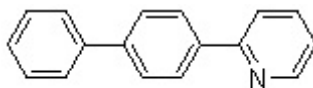


SG-6-64-13C.1.fid
SG-6-64-13C

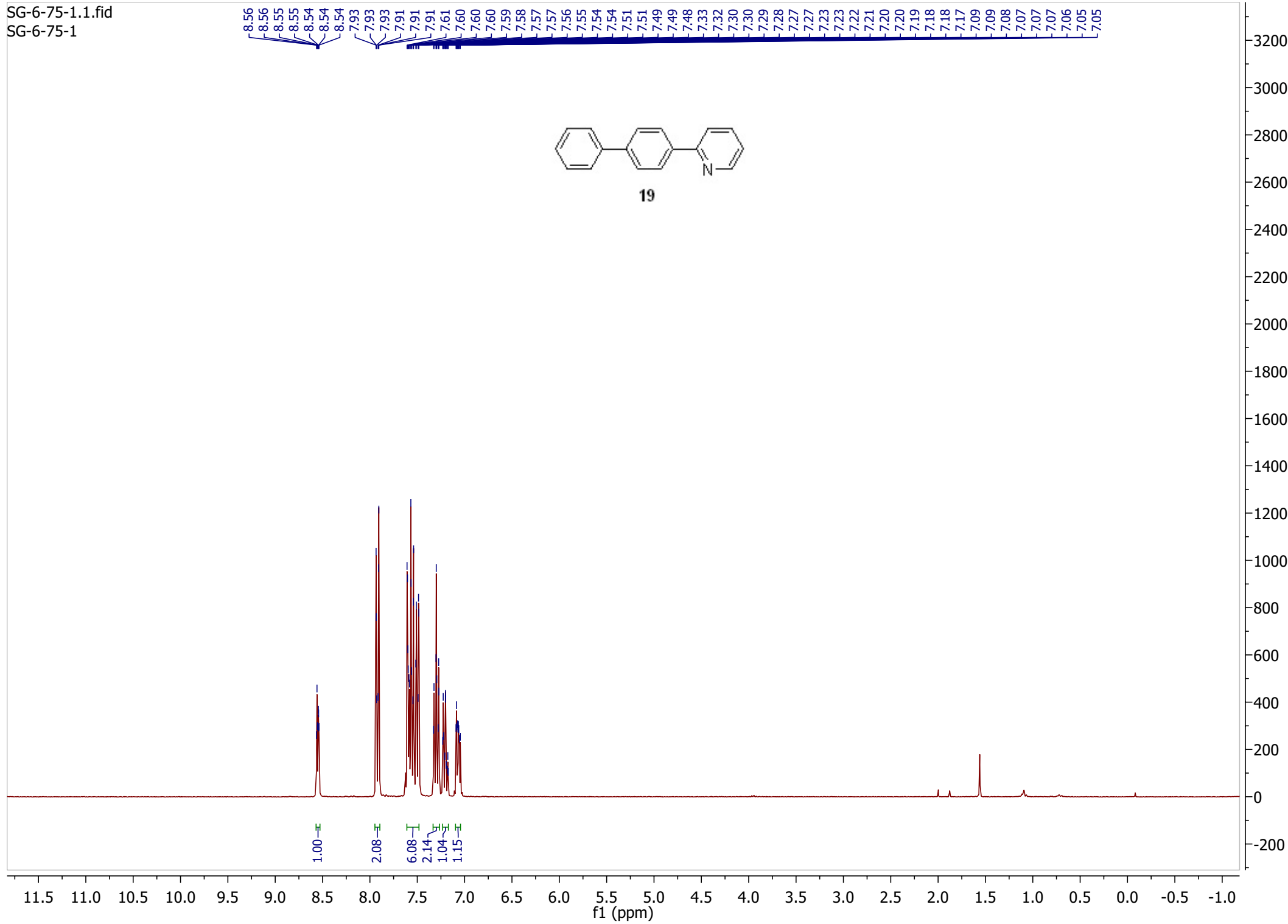


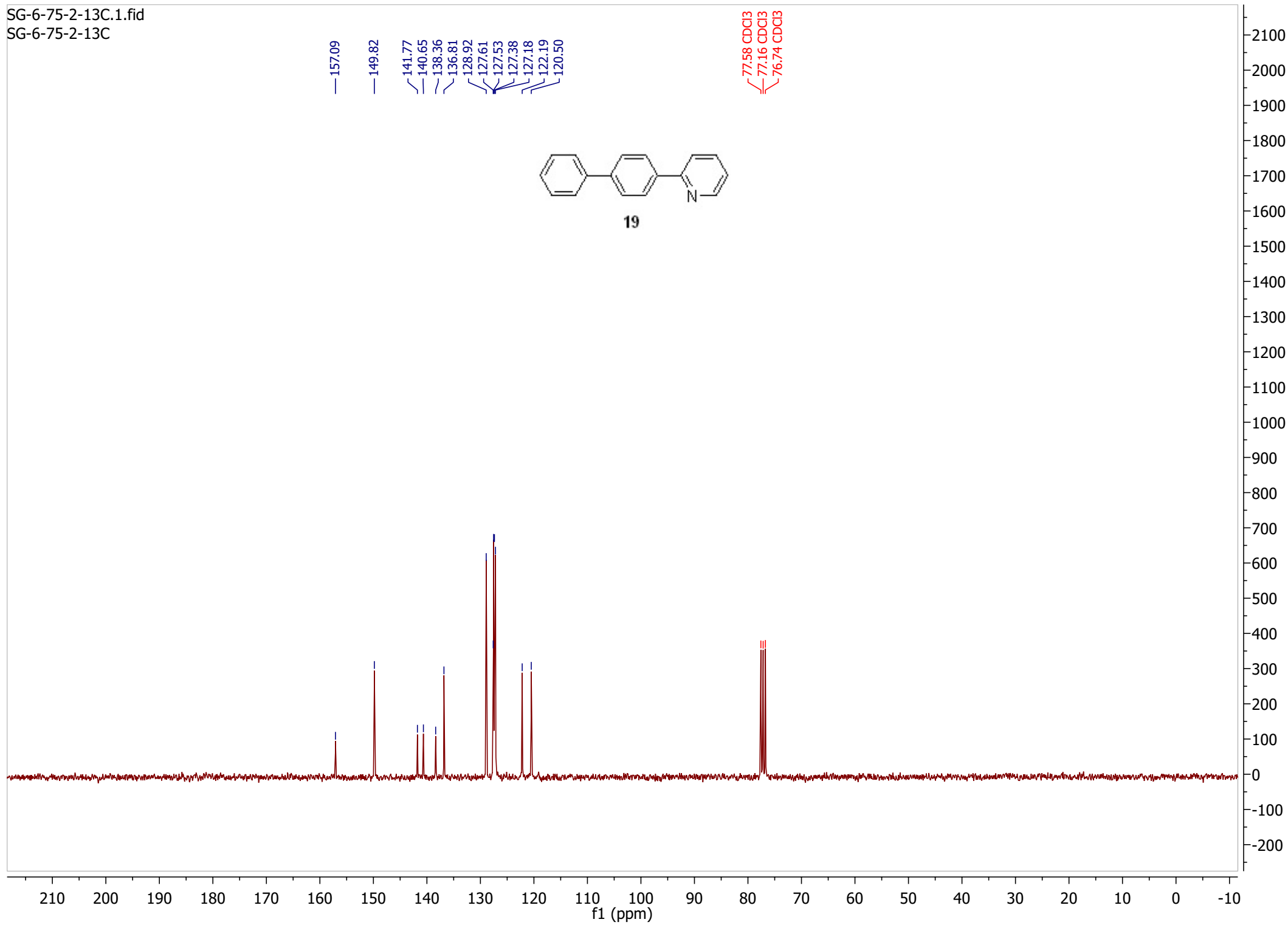
SG-6-75-1.1.fid
SG-6-75-1

8.56
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7.93
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7.08
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7.06
7.05
7.05

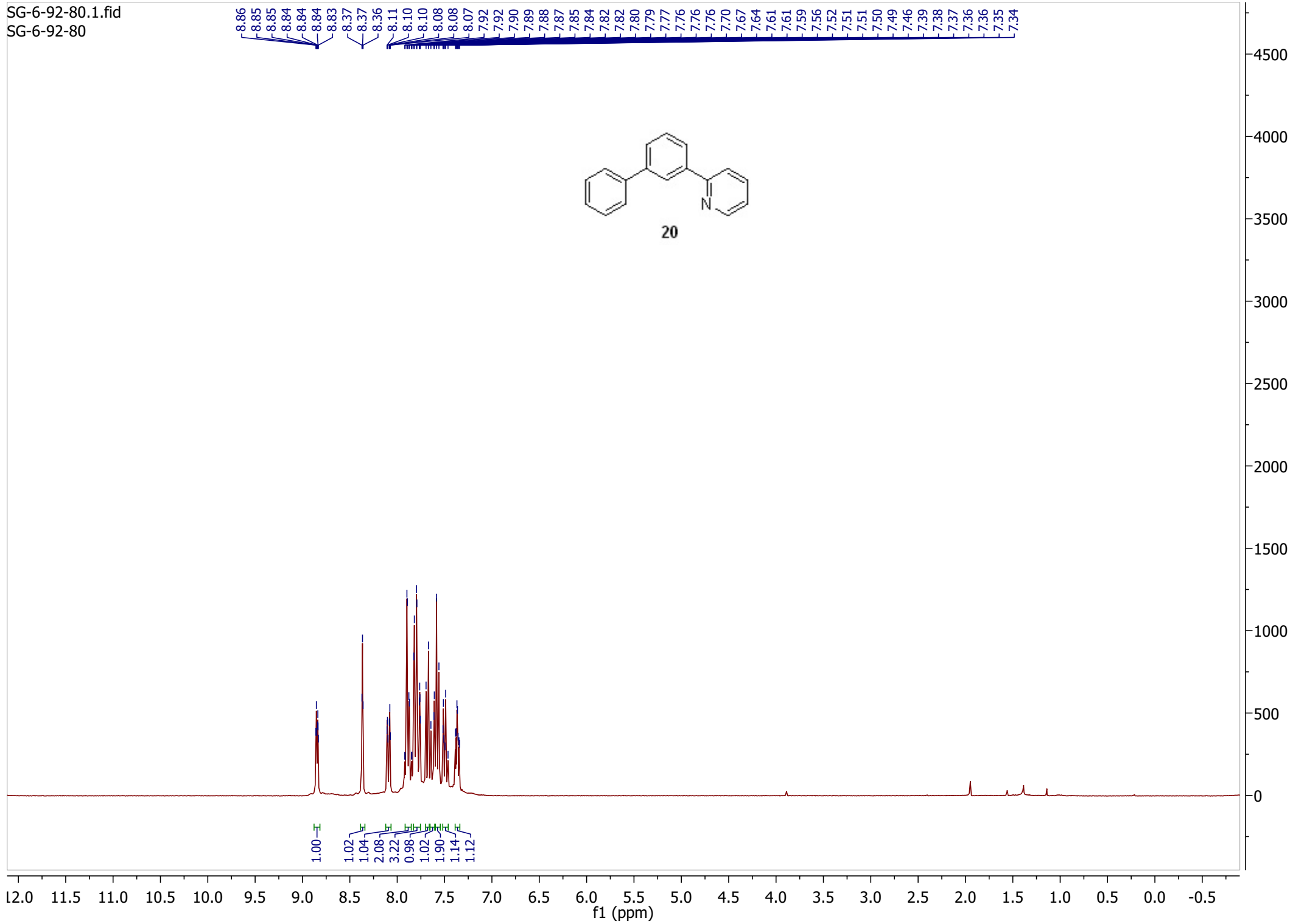


19

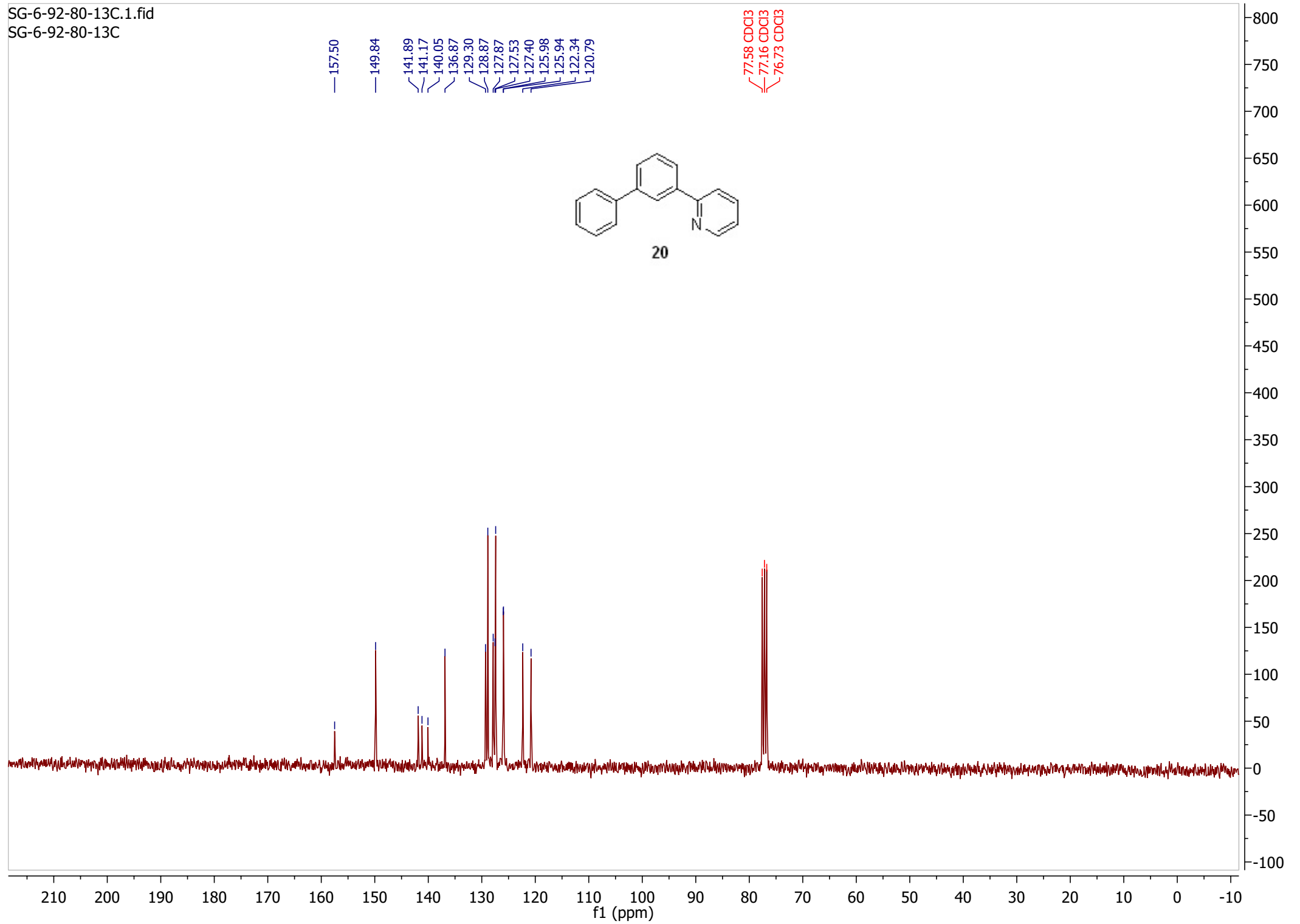




SG-6-92-80.1.fid
SG-6-92-80

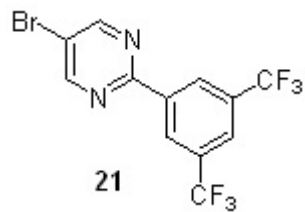


SG-6-92-80-13C.1.fid
SG-6-92-80-13C



ST-4-228-1H.1.fid
ST-4-228-1H

8.92
8.91
8.00
7.26

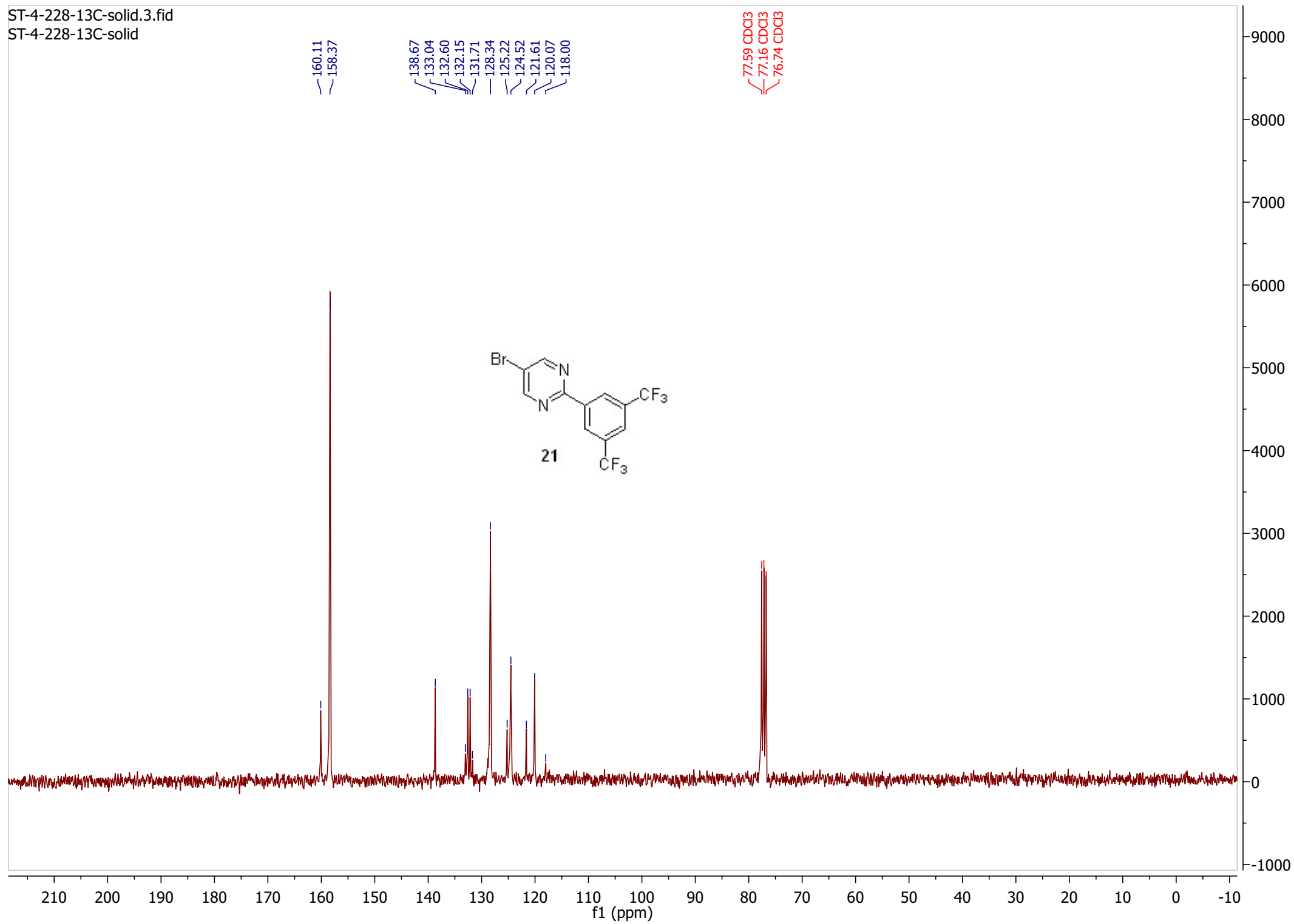


4.16
1.00

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 -0.5 -1.0
f1 (ppm)

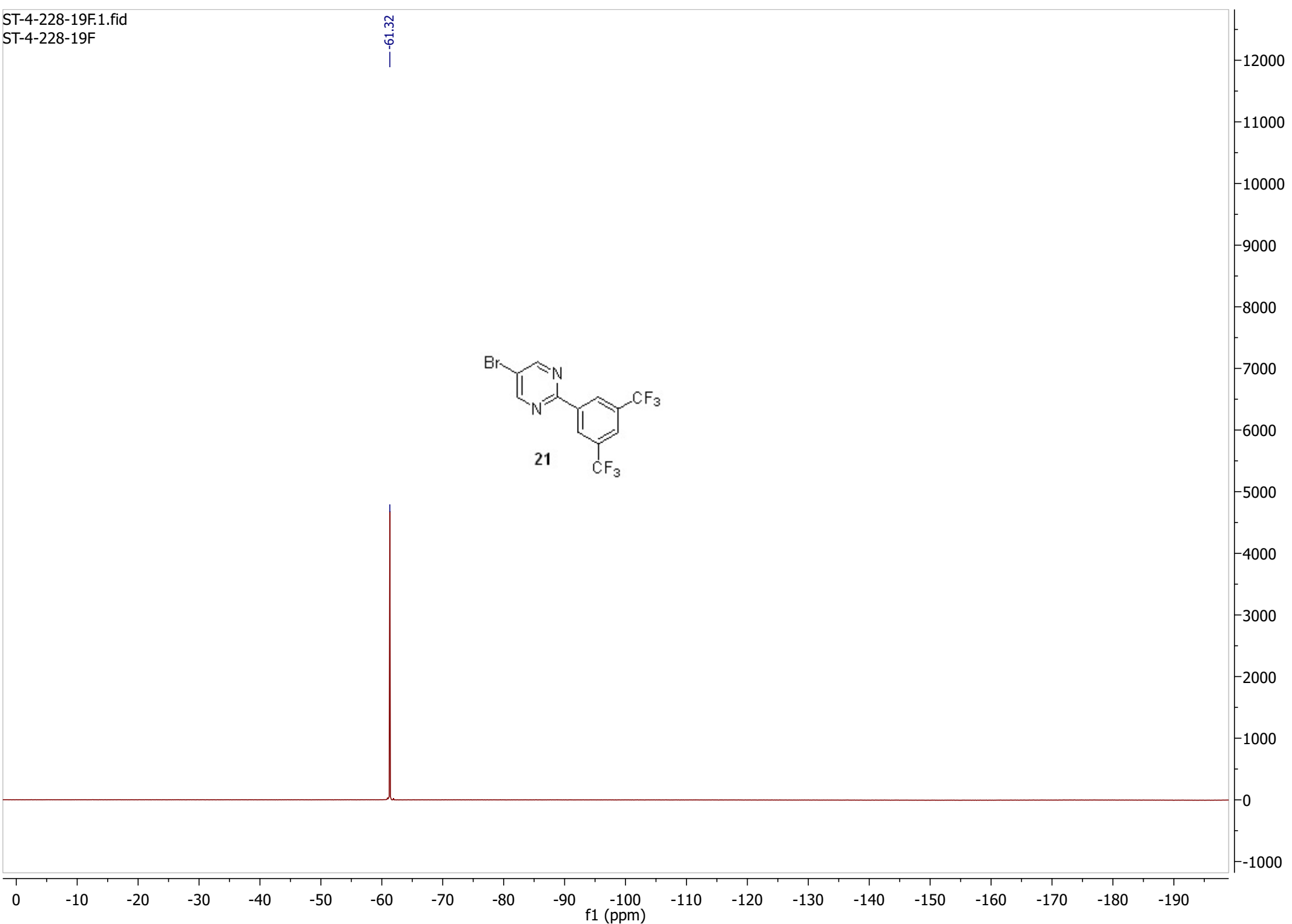
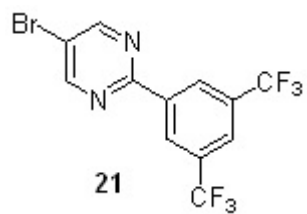
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

ST-4-228-13C-solid.3.fid
ST-4-228-13C-solid



ST-4-228-19F1.fid
ST-4-228-19F

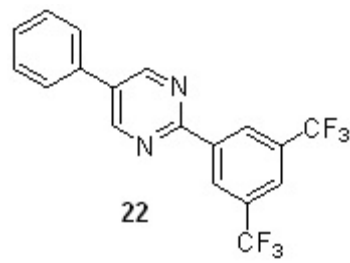
—61.32



BJ-2-242-1H.1.fid
BJ-2-242-1H

9.08
9.01
8.00
7.67
7.66
7.65
7.65
7.64
7.63
7.59
7.59
7.58
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7.53
7.53
7.52
7.51
7.50

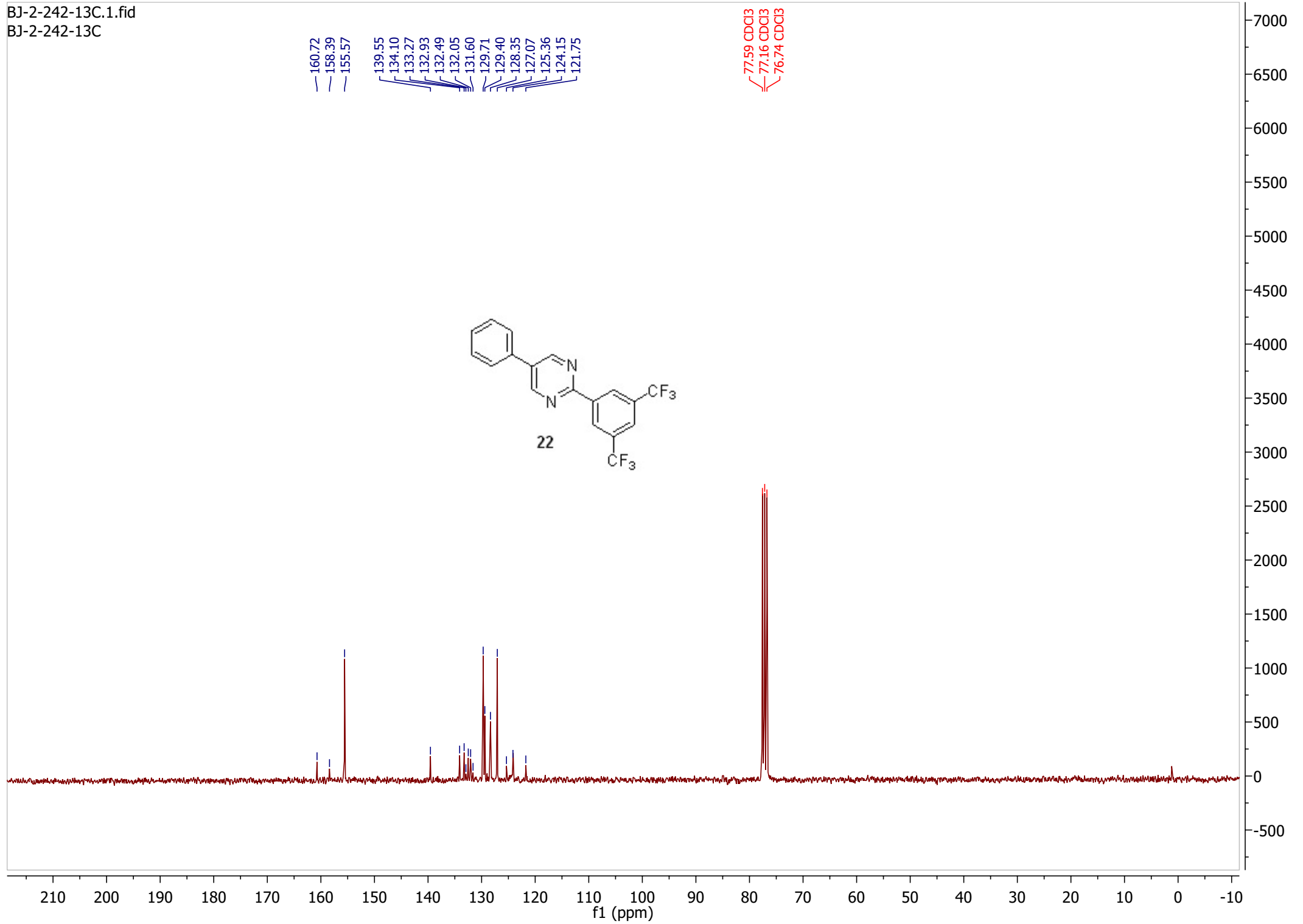
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000



2.02
2.03
1.00
1.96
3.07
f1 (ppm)

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 -0.5 -1.0

BJ-2-242-13C.1.fid
BJ-2-242-13C



BJ-2-242-19F.1.fid
BJ-2-242-19F

