Ni-Catalyzed Regioselective 1,2-Diarylation of Unactivated Olefins by Stabilizing Heck Intermediates as Pyridylsilyl-Coordinated Transient Metallacycles

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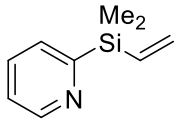
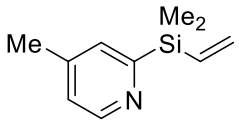
1. General Information

Reactions were set up in a nitrogen-filled glovebox unless stated otherwise. All glassware were properly dried in an oven before use. Bulk solvents were obtained from EMD and BDH. Anhydrous solvents (DMF, DMA, DMSO, NMP, THF, toluene, dioxane) were obtained from Sigma-Aldrich and were used directly without further purification. Deuterated solvents were purchased from Sigma-Aldrich. Aryl halides were purchased from Acros, Sigma-Aldrich, Oakwood, TCI-America, Matrix and Alfa-Aesar. $NiBr_2$ was procured from Alfa-Aesar and 2-bromopyridine was obtained from Oxychem. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker instrument (300, 75, and 282, respectively) and internally referenced to the residual solvent signals of $CDCl_3$ for ^1H and ^{13}C NMR at 7.26 and 77.16 ppm, respectively, and C_6F_6 for ^{19}F NMR at −164.9 ppm. NMR chemical shifts (δ) and the coupling constants (*J*) for ^1H, ^{13}C, and ^{19}F NMR are reported in parts per million (ppm) and in Hertz, respectively. The following conventions are used for multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; and dd, doublet of doublet. High resolution mass and NMR spectra of new compounds were recorded at the Mass Spectrometry and NMR Facilities, Department of Chemistry and Chemical Biology, University of New Mexico (UNM). Infrared (IR) spectra were recorded on Bruker Alpha-P ATR-IR, ν_{max} in cm^{-1}.

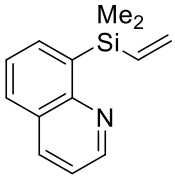
2. Substrate Preparation



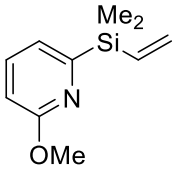
*2-(Dimethyl(vinyl)silyl)pyridine (**7**)*: This compound was prepared according to a literature procedure.[1]



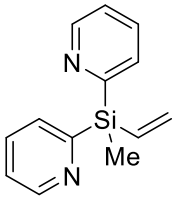
*2-(Dimethyl(vinyl)silyl)-4-methylpyridine (**8**)*: This compound was prepared according to a literature procedure.[1] ^1H NMR (300 MHz, $CDCl_3$) δ 0.39 (s, 6H), 2.30 (s, 3H), 5.80 (dd, *J* = 5.4, 20.9 Hz, 1H), 6.08 (dd, *J* = 5.6, 16.5 Hz, 1H), 6.33 (dd, *J* = 16.3, 21.8 Hz, 1H), 7.00 (d, *J* = 4.6 Hz, 1H), 7.29 (d, *J* = 16.5 Hz, 1H), 8.62 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -3.5, 21.1, 123.9, 130.6, 133.4, 137.2, 144.9, 150.1, 166.1.



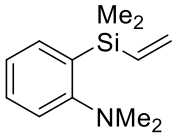
*8-(Dimethyl(vinyl)silyl)quinolone (**9**):* This compound was prepared according to a literature procedure.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (s, 6H), 5.86 (dd, *J* = 7.0, 20.4 Hz, 1H), 6.09 (dd, *J* = 6.7, 14.6 Hz, 1H), 6.68 (dd, *J* = 14.6, 20.4 Hz, 1H), 7.37 (dd, *J* = 4.1, 8.2 Hz, 1H), 7.52 (dd, *J* = 6.8, 8.0 Hz, 1H), 7.82 (d, *J* = 9.3 Hz, 1H), 7.91 (d, *J* = 6.7 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.93 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.8, 120.8, 126.1, 127.8, 129.3, 131.8, 136.1, 136.3, 139.8, 140.3, 149.2, 152.7.



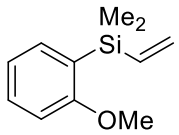
*8-(Dimethyl(vinyl)silyl)quinolone (**10**):* This compound was prepared according to a literature procedure.[2]



*2,2'-(Methyl(vinyl)silanediyl)dipyridine (**11**):* This compound was prepared according to a literature procedure.[3]



*2-(Dimethyl(vinyl)silyl)-N,N-dimethylaniline (**12**):* This compound was prepared according to a literature procedure.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.41 (s, 6H), 2.65 (s, 6H), 5.76 (dd, *J* = 18.0, 6.0 Hz, 1H), 6.03 (dd, *J* = 15.0, 6.0 Hz, 1H), 6.45 (dd, *J* = 18.0, 12.0 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 9.0 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.80, 47.0, 121.7, 125.0, 130.6, 131.1, 135.8, 136.9, 140.2, 161.4.



*2-(Dimethyl(vinyl)silyl)-4-methylpyridine (**13**)*: This compound was prepared according to a literature procedure.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.42 (s, 6H), 3.85 (s, 3H), 5.76-5.85 (m, 1H), 6.04-6.11 (m, 1H), 6.39-6.51 (m, 1H), 6.88 (d, *J* = 6.0 Hz, 1H), 6.97-7.03 (m, 1H), 7.37-7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -2.63, 55.2, 109.8, 120.6, 126.4, 131.1, 131.8, 135.6, 138.9, 164.5.

3. Experimental Section

3.1. General Procedure for the Preparation of Organozinc Reagents[4]

To a Schlenk flask under nitrogen, anhydrous LiCl (1.0 equiv) and Zinc powder (1.5 equiv) was added and dried under high vacuum at 150°C to 170°C for 2 h. Then the flask was taken to a glovebox, anhydrous THF was added and stirred at room temperature. Zinc was activated by adding 5 mol% of $BrCH_2CH_2Br$ and 3 mol% of TMSCl to the zinc/THF suspension and the mixture was stirred for 5 minutes. To this stirred solution was added corresponding aryl iodides (neat) dropwise and the reaction mixture was refluxed for electron-deficient and electron rich aryl iodides. The final concentration of the arylzinc reagent was determined by titration with molecular iodine in THF.[5]

3.2. General Procedure for Screening Reaction Conditions

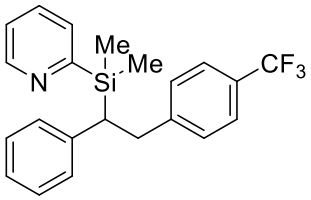
In a glovebox, arylzinc reagent (0.15 mmol) prepared in the lab according to the general procedure was transferred to a 1-dram borosilicate scintillation vial and the solvent was pumped off under high vacuum. To the ArZnI residue was added $NiBr_2$ (0.4-1.1 mg, 2-5 mol%), 2-(dimethyl(vinyl)silyl)pyridine (16.3 mg, 0.1 mmol), and aryl halide (0.10 mmol). The mixture was then dissolved in 0.5 ml of NMP. The vial was tightly capped and placed in a hotplate preheated to 50 °C or at room temperature with vigorous stirring. After 24 h, the reaction mixture was cooled to room temperature and 50 μL of pyrene (0.01 mmol, 0.2 M stock solution) as an internal standard was added, diluted with EtOAc (2 mL) and filtered through a short pad of silica gel in a pipette. The filtrate was then analyzed by GC, GC-MS and ^{1}H NMR.

3.3. General Procedure for Table 2 and 3

In a glovebox, arylzinc reagent (0.75 mmol) prepared in the lab according to the general procedure was transferred to 15 mL sealed tube and the solvent was removed under vacuum. To the residue of ArZnI was added $NiBr_2$ (2.1-5.5 mg, 2-5 mol%), 2-(dimethyl(vinyl)silyl)pyridine (81.5 mg, 0.5 mmol), and aryl halide (0.5 mmol). The mixture was then dissolved in NMP (2.5 mL). The sealed tube was tightly capped, and

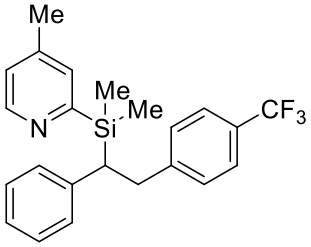
placed in an oil-bath preheated to 50 °C or at room temperature with vigorous stirring. After 24 h, the reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL) and washed with H_2O (5 mL × 3). The aqueous fraction was extracted back with ethyl acetate (5 mL × 3) and combined with the first ethyl acetate fraction. The combined ethyl acetate fraction was dried over Na_2SO_4 and the solvent was removed in a rotary evaporator. The product was purified by silica gel column chromatography using diethyl ether/hexanes as eluent.

3.4. Characterization Data for New Compounds



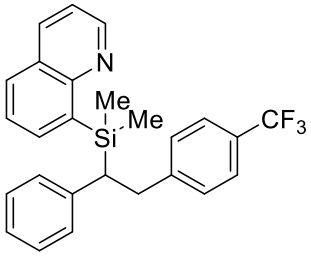
2-((1-(4-Fluorophenyl)-2-(3-(trifluoromethyl)phenyl)ethyl)dimethylsilyl)pyridine ***(15a)***: The title compound **15a** was obtained as a colorless oil (138.9 mg, 72% yield, using 2 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 2-10% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 3H), 0.39 (s, 3H), 2.84 (app. t, J = 7.9 Hz, 1H), 3.09-3.16 (m, 2H), 6.95-6.98 (m, 2H), 7.01-7.08 (m, 3H), 7.13-7.17 (m, 2H), 7.18-7.23 (m, 1H), 7.30-7.35 (m, 3H), 7.53 (ddd, J = 1.7, 1.7, 1.7 Hz, 1H), 8.80 (d, J = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.7, -4.1, 35.7, 37.1, 122.7, 123.1, 124.9 (q, J_{CF} = 3.75 Hz), 126.3, 128.1 (q, J_{CF} = 31.5 Hz), 128.2, 128.3, 128.8, 129.9, 134.0, 141.7, 146.3, 150.3, 166.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.0; IR (neat) cm^{-1} 2923, 1322, 1117, 1065; GC-MS for $C_{22}H_{22}F_3NSi$ was found to be 385.2.



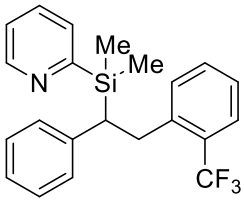
2-(Dimethyl(1-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)silyl)-4-methylpyridine ***(15b)***: The title compound **15b** was obtained as a colorless oil (101.9 mg, 51% yield, using 2 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5-20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 3H), 0.39 (s, 3H), 2.28 (s, 3H), 2.85 (t, J = 7.6 Hz, 1H), 3.08-3.15 (m, 2H), 6.98-7.09 (m, 7H), 7.13-7.18 (m, 3H), 7.31 (d, J = 7.7 Hz, 1H), 8.66 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.3, -3.6, 21.6, 36.2, 37.4, 124.5, 125.3 (q, J_{CF} = 4.2 Hz), 128.4, 128.5, 128.7, 129.3, 131.5, 142.3, 145.4, 145.7, 150.3, 150.4, 165.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.8; IR (neat) cm^{-1} 2922, 1324, 1121.



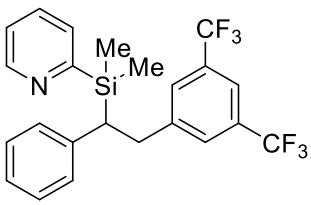
*8-(Dimethyl(1-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)silyl)quinoline (**15c**)*: The title compound **15c** was obtained as a colorless oil (122.0 mg, 56% yield, using 2 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 2-10% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 3H), 0.45 (s, 3H), 3.00-3.18 (m, 2H), 3.52 (dd, *J* = 5.3, 10.3 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 2H), 7.04 (dd, *J* = 7.5, 14.1 Hz, 3H), 7.15 (t, *J* = 6.1 Hz, 4H), 7.38-7.43 (m, 1H); 7.47 (d, *J* = 7.4 Hz, 1H), 7.78 (dd, *J* = 6.7, 10.5 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.96 (d, *J* = 4.1 Hz, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ -4.6, -2.5, 36.0, 37.2, 120.9, 124.5 (q, J_{CF} = 3.7 Hz), 126.1, 127.3, 127.7, 127.8, 128.0, 128.3, 128.7, 129.6, 136.3, 136.8, 139.4, 143.1, 146.7, 149.1, 152.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.8; IR (neat) cm^{-1} 2957, 1322, 1118.



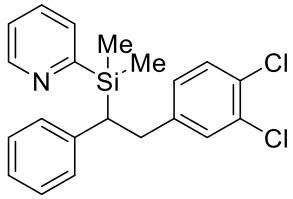
*2-(Dimethyl(1-phenyl-2-(2-(trifluoromethyl)phenyl)ethyl)silyl)pyridine (**16**)*: The title compound **16** was obtained as a colorless oil (144.6 mg, 75% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 2-10% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 3H), 0.40 (s, 3H), 2.87 (dd, *J* = 4.5, 10.9 Hz, 1H), 3.25-3.40 (m, 2H), 6.94-7.05 (m, 4H), 7.10-7.21 (m, 5H), 7.36 (app. dd, *J* = 1.0, 7.5 Hz, 1H), 7.53 (app. dd, *J* = 6.7, 14.1 Hz, 2H), 8.82 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.4, -4.4, 31.6, 36.0, 123.0, 124.9, 125.8 (q, J_{CF} = 7.2 Hz), 126.6, 128.2, 128.5, 128.6, 130.0, 130.7, 131.1, 133.9, 140.4, 141.7, 150.2, 166.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -58.0; IR (neat) cm^{-1} 2959, 1309, 1114; HRMS (ESI) Calcd for $C_{22}H_{22}F_3NSi$ $(M+H)^+$ 385.1474, found 385.1485.



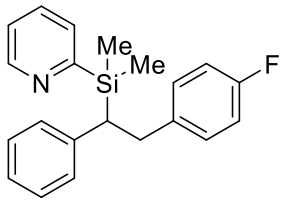
*2-((2-(3,5-Bis(trifluoromethyl)phenyl)-1-phenylethyl)dimethylsilyl)pyridine (**17**)*: The title compound **17** was obtained as a colorless oil (118.07 mg, 52% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 2-10% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.41 (s, 3H), 2.84 (dd, J = 6.2, 9.7 Hz, 1H), 3.15-3.27 (m, 2H), 6.95-6.95 (m, 2H), 7.05 (app. t, J = 7.3 Hz, 1H), 7.14-7.24 (m, 3H), 7.35-7.40 (m, 3H), 7.55 (ddd, J = 1.5, 1.7, 1.7 Hz, 2H), 8.82 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.6, -4.0, 35.9, 37.1, 119.7 (app. q, J_{CF} = 3.75 Hz), 121.7, 123.2, 125.4, 128.2, 128.5, 128.8, 129.9, 131.1 (q, J_{CF} = 32.2 Hz), 134.1, 141.1, 144.6, 150.4, 165.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.4; IR (neat) cm^{-1} 2959, 1375, 1275, 1125; HRMS (ESI) Calcd for $C_{23}H_{21}F_6NSi$ $(M+H)^+$ 453.1347, found 453.1410.



*2-((2-(3,4-Dichlorophenyl)-1-phenylethyl)dimethylsilyl)pyridine (**18**)*: The title compound **18** was obtained as a colorless oil (94.7 mg, 49% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

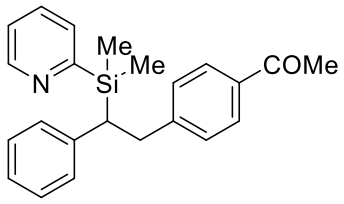
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 3H), 0.38 (s, 3H), 2.78 (dd, J = 6.7, 9.0 Hz, 1H), 2.98-3.09 (m, 2H), 6.79 (dd, J = 1.8, 8.2 Hz, 1H), 6.96 (d, J = 8.1 Hz, 2H), 7.02-7.18 (m, 5H), 7.21-7.23 (m, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.51-7.56 (ddd, J = 1.6, 1.5, 1.4 Hz, 1H), 8.81 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.6, -4.0, 35.2, 37.3, 123.1, 125.1, 128.1, 128.2, 128.3, 129.5, 129.8, 129.9, 130.6, 131.9, 134.0, 141.7, 142.5, 150.3, 166.1; IR (neat) cm^{-1} 2956, 1471, 1268; HRMS (ESI) Calcd for $C_{21}H_{21}Cl_2NSi$ $(M+H)^+$ 385.0820, found 385.0767.



*2-((2-(4-Fluorophenyl)-1-phenylethyl)dimethylsilyl)pyridine (**19**)*: The title compound **19** was obtained as a colorless oil (117.4 mg, 70% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 2-15% ether/hexanes.

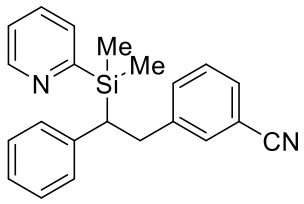
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.38 (s, 3H), 2.80 (dd, J = 7.9, 15.7 Hz, 1H), 3.06 (dd, J = 15.1, 23.0 Hz, 2H), 6.75 (t, J = 8.7 Hz, 2H), 6.90-6.97 (m, 4H), 7.00-7.05 (m, 1H), 7.12-7.23 (m, 3H), 7.33 (d, J = 7.5 Hz, 1H), 7.53 (ddd, J = 1.6, 1.6, 1.6 Hz, 1H), 8.81 (d, J = 4.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.6, -4.1, 35.0, 37.6, 114.7 (d, J_{CF} = 21.0 Hz), 123.9 (d, J_{CF} = 138.0 Hz), 128.2, 128.3 (d, J_{CF} = 42.0 Hz), 129.8, 129.9, 129.9, 133.9, 137.7 (d, J_{CF} = 3.0 Hz), 142.1, 150.3, 161.1 (d, J_{CF} = 241.5 Hz), 166.3; ^{19}F NMR

(282 MHz, $CDCl_3$) δ -116.6; IR (neat) cm^{-1} 2926, 1507, 1218; HRMS (ESI) Calcd for $C_{21}H_{22}FNSi$ $(M+H)^+$ 335.1506, found 335.1499.



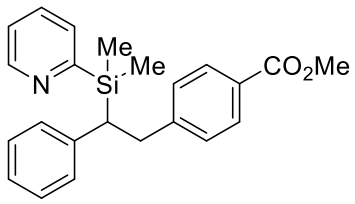
*1-(4-(2-(Dimethyl(pyridin-2-yl)silyl)-2-phenylethyl)phenyl)ethan-1-one (**20**)*: The title compound **20** was obtained as a colorless oil (75.5 mg, 42% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^1H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.39 (s, 3H), 2.48 (s, 3H), 2.85 (app. t, J = 7.9 Hz, 1H), 3.15 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 7.1 Hz, 2H), 6.99-7.15 (m, 5H), 7.19-7.23 (m, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.53 (ddd, J = 1.6, 1.6, 1.6 Hz, 1H), 7.67 (d, J = 8.2 Hz, 2H), 8.82 (d, J = 4.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.6, -4.2, 26.6, 35.8, 37.1, 123.1, 124.9, 128.2, 128.8, 129.9, 134.0, 134.9, 141.7, 148.1, 150.3, 166.1, 198.0; IR (neat) cm^{-1} 2920, 1678, 1604, 1267; HRMS (ESI) Calcd for $C_{23}H_{25}NOSi$ $(M+H)^+$ 359.1705, found 359.1718.



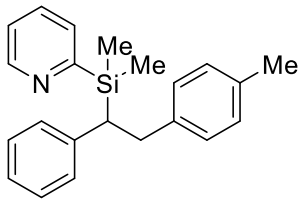
*3-(2-(Dimethyl(pyridin-2-yl)silyl)-2-phenylethyl)benzonitrile (**21**)*: The title compound **21** was obtained as a colorless oil (90.8 mg, 53% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^1H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 3H), 0.39 (s, 3H), 2.80 (dd, J = 6.1, 9.7 Hz, 1H), 3.04-3.16 (m, 2H), 6.94 (d, J = 7.1 Hz, 2H), 7.04 (app. t, J = 7.3 Hz, 1H), 7.15 (app. t, J = 7.4 Hz, 3H), 7.19-7.24 (m, 3H), 7.29 (app. d, J = 7.2 Hz, 1H), 7.36 (app. d, J = 7.5 Hz, 1H), 7.55 (ddd, J = 1.6, 1.6, 1.6 Hz, 1H), 8.82 (d, J = 4.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.7, -4.1, 35.5, 37.2, 112.0, 119.2, 123.2, 125.1, 128.2, 128.3, 128.7, 129.5, 129.9, 132.1, 133.1, 134.1, 141.3, 143.6, 150.3, 165.9; IR (neat) cm^{-1} 2956, 2227, 1417, 1246; HRMS (ESI) Calcd for $C_{22}H_{22}N_2Si$ $(M+H)^+$ 342.1552, found 342.1548.



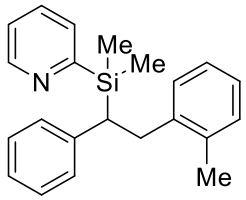
*Methyl 4-(2-(dimethyl(pyridin-2-yl)silyl)-2-phenylethyl)benzoate (**22**)*: The title compound **22** was obtained as a white solid (107.0 mg, 57% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.38 (s, 3H), 2.84 (dd, *J* = 7.0, 8.7 Hz, 1H), 3.07-3.18 (m, 2H), 3.82 (s, 3H), 6.93-6.96 (m, 2H), 6.98-7.05 (m, 3H), 7.10-7.14 (m, 2H), 7.18-7.23 (m, 1H), 7.33-7.36 (m, 1H), 7.53 (ddd, *J* = 1.7, 1.7, 1.7 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 8.82 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.6, -4.2, 35.9, 37.2, 51.9, 123.1, 124.9, 127.6, 128.2, 128.2, 128.6, 129.4, 129.9, 134.0, 141.7, 147.8, 150.3, 166.1, 167.2; IR (neat) cm^{-1} 2951, 1716, 1275; HRMS (ESI) Calcd for $C_{23}H_{25}NO_2Si$ $(M+H)^+$ 375.1655, found 375.1634.



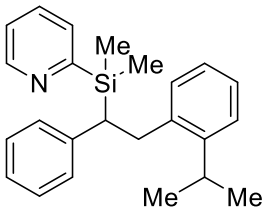
*2-(Dimethyl(1-phenyl-2-(p-tolyl)ethyl)silyl)pyridine (**23**)*: The title compound **23** was obtained as a white solid (107.7 mg, 65% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 3H), 0.40 (s, 3H), 2.22 (s, 3H), 2.86 (app. t, *J* = 8.2 Hz, 1H), 3.11 (dd, *J* = 7.5, 15.6 Hz, 2H), 6.91 (s, 4H), 7.03 (dd, *J* = 8.0, 13.0 Hz, 3H), 7.13-7.22 (m, 3H), 7.34 (dd, *J* = 0.9, 7.5 Hz, 1H), 7.52 (ddd, *J* = 1.7, 1.7, 1.7 Hz, 1H), 8.83 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.2, 21.0, 35.2, 37.3, 122.8, 124.6, 128.0, 128.3, 128.4, 128.7, 129.8, 133.8, 134.9, 138.9, 142.4, 150.2, 166.4; IR (neat) cm^{-1} 2924, 1183, 1134; HRMS (ESI) Calcd for $C_{22}H_{25}NSi$ $(M+H)^+$ 331.1756, found 331.1785.



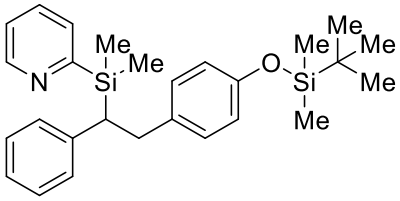
*2-(Dimethyl(1-phenyl-2-(o-tolyl)ethyl)silyl)pyridine (**24**)*: The title compound **24** was obtained as a colorless oil (91.2 mg, 55% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.41 (s, 3H), 2.10 (s, 3H), 2.75 (dd, *J* = 4.7, 10.1 Hz, 1H), 2.99-3.14 (m, 2H), 6.79-7.05 (m, 7H), 7.11-7.22 (m, 3H), 7.36 (app. d, *J* = 7.5 Hz, 1H), 7.53 (app. t, *J* = 7.6 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.1, 19.5, 33.1, 36.1, 123.0, 124.8, 125.4, 125.7, 128.1, 128.4, 129.1, 129.9, 130.0, 133.9, 135.9, 140.1, 142.5, 150.2, 166.4; IR (neat) cm^{-1} 3022, 2954, 1449, 1246.



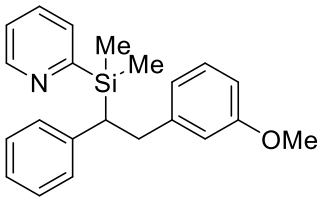
*2-((2-(2-Isopropylphenyl)-1-phenylethyl)dimethylsilyl)pyridine (**25**)*: The title compound **25** was obtained as a colorless oil (109.7 mg, 61% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 3H), 0.44 (s, 3H), 0.95 (d, J = 6.8 Hz, 3H), 1.12 (app. d, J = 6.8 Hz, 3H), 2.64 (dd, J = 3.4, 11.2 Hz, 1H), 2.75-2.89 (m, 1H), 3.03 (dd, J = 11.3, 14.5 Hz, 1H), 3.17 (dd, J = 3.3, 14.5 Hz, 1H), 6.75-6.85 (m, 2H), 6.98-7.06 (m, 4H), 7.14 (dd, J = 9.8, 17.4 Hz, 3H), 7.20-7.26 (m, 1H), 7.5 (d, J = 7.5 Hz, 1H), 7.57 (ddd, J = 1.7, 1.7, 1.7 Hz, 1H), 8.83 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.7, -4.1, 23.9, 24.2, 28.4, 32.8, 37.8, 122.9, 124.8, 125.0, 125.1, 126.1, 128.2, 128.5, 129.6, 129.9, 133.9, 138.8, 142.4, 146.6, 150.2, 166.6; IR (neat) cm^{-1} 2929, 1383, 1246; HRMS (ESI) Calcd for $C_{24}H_{29}NSi$ $(M+H)^+$ 359.2069, found 359.2072.



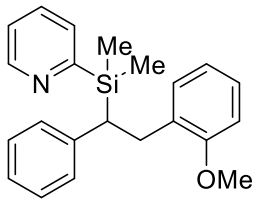
*2-((2-(4-((tert-Butyldimethylsilyl)oxy)phenyl)-1-phenylethyl)dimethylsilyl)pyridine (**26**)*: The title compound **26** was obtained as a colorless oil (98.5 mg, 44% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.21 (s, 3H), 0.35 (s, 3H), 0.92 (s, 9H), 2.77 (t, J = 7.8 Hz, 1H), 3.01 (dd, J = 7.8, 22.9 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 6.93-7.03 (m, 3H), 7.09-7.21 (m, 3H), 7.31 (d, J = 7.5 Hz, 1H), 7.51 (ddd, J = 1.6, 1.6, 1.7 Hz, 1H), 8.80 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.4, -4.3, -4.2, 18.3, 25.8, 35.1, 37.6, 119.6, 122.9, 124.6, 128.0, 128.4, 129.4, 129.9, 133.9, 134.8, 142.5, 150.2, 153.5, 166.5; IR (neat) cm^{-1} 2955, 2928, 1507, 1247; HRMS (ESI) Calcd for $C_{27}H_{37}NOSi_2$ $(M+H)^+$ 447.2414, found 447.2388.



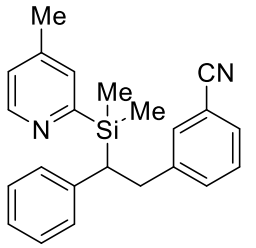
*2-((2-(3-Methoxyphenyl)-1-phenylethyl)dimethylsilyl)pyridine (**27**)*: The title compound **27** was obtained as a colorless oil (99.0 mg, 57% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.38 (s, 3H), 2.84 (app. t, *J* = 8.0 Hz, 1H), 3.09 (app. d, *J* = 7.9 Hz, 2H), 3.63 (s, 3H), 6.53 (s, 1H), 6.59 (app. t, *J* = 9.9 Hz, 2H), 6.98-7.05 (m, 4H), 7.12-7.22 (m, 3H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.52 (app. t, *J* = 7.6 Hz, 1H), 8.81 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.2, 35.8, 37.2, 55.1, 111.2, 114.2, 121.1, 122.9, 124.7, 128.1, 128.3, 128.9, 129.9, 133.9, 142.3, 143.7, 150.2, 159.3, 166.4; IR (neat) cm^{-1} 2954, 1598, 1488, 1246; HRMS (ESI) Calcd for $C_{22}H_{25}NOSi$ $(M+H)^+$ 347.1705, found 347.1684.



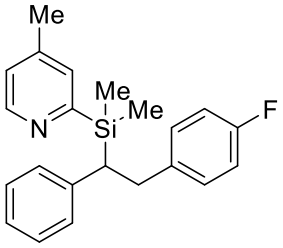
*2-((2-(2-Methoxyphenyl)-1-phenylethyl)dimethylsilyl)pyridine (**28**)*: The title compound **28** was obtained as a colorless oil (95.6 mg, 55% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 3H), 0.41 (s, 3H), 2.90 (dd, *J* = 4.5, 10.7 Hz, 1H), 3.07 (dd, *J* = 10.8, 14.3 Hz, 1H), 3.18 (dd, *J* = 4.5, 14.3 Hz, 1H), 3.71 (s, 3H), 6.67 (dd, *J* = 7.4, 14.7 Hz, 2H), 6.89 (dd, *J* = 1.4, 7.4 Hz, 1H), 6.99-7.05 (m, 4H), 7.11-7.20 (m, 3H), 7.35-7.38 (m, 1H), 7.51 (ddd, *J* = 1.7, 1.7, 1.7 Hz, 1H), 8.81 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.2, 29.9, 35.6, 55.2, 110.0, 120.0, 122.7, 124.5, 126.7, 127.9, 128.3, 129.8, 130.0, 130.3, 133.7, 142.9, 150.1, 157.4, 166.7; IR (neat) cm^{-1} 2955, 1490, 1239; HRMS (ESI) Calcd for $C_{22}H_{25}NOSi$ $(M+H)^+$ 347.1705, found 347.1664.



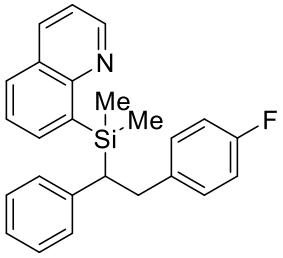
*3-(2-(Dimethyl(4-methylpyridin-2-yl)silyl)-2-phenylethyl)benzonitrile (**29**)*: The title compound **29** was obtained as a colorless oil (99.7 mg, 56% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 3H), 0.38 (s, 3H), 2.30 (s, 3H), 2.79 (dd, *J* = 6.3, 9.4 Hz, 1H), 3.03-3.14 (m, 2H), 6.95 (d, *J* = 7.0 Hz, 2H), 7.01-7.07 (m, 2H), 7.11-7.23 (m, 6H), 7.27-7.30 (m, 1H), 8.66 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.7, -4.0, 21.2, 35.5, 37.1, 111.9, 119.2, 124.1, 125.1, 128.1, 128.3, 128.7, 129.4, 131.0, 132.1, 133.1, 141.4, 143.6, 144.9, 150.1, 165.1.



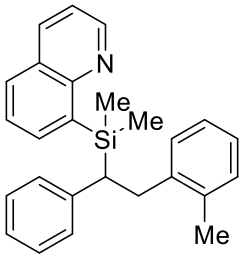
*2-((2-(4-Fluorophenyl)-1-phenylethyl)dimethylsilyl)-4-methylpyridine (**30**)*: The title compound **30** was obtained as a colorless oil (87.3 mg, 50% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 3H), 0.37 (s, 3H), 2.28 (s, 3H), 2.78 (t, J = 7.9 Hz, 1H), 3.05 (d, J = 7.9 Hz, 2H), 6.74 (t, J = 8.7 Hz, 2H), 6.89-7.06 (m, 6H), 7.11-7.17 (m, 3H), 8.66 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.6, -4.0, 21.1, 35.1, 37.5, 114.7 (d, J_{CF} = 21.0 Hz), 124.4 (d, J_{CF} = 64.5 Hz), 128.1, 128.3, 129.8, 129.9, 131.0, 137.7 (d, J_{CF} = 3.0 Hz), 142.2, 144.7, 150.0, 161.1 (d, J_{CF} = 241.5 Hz), 165.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.8.



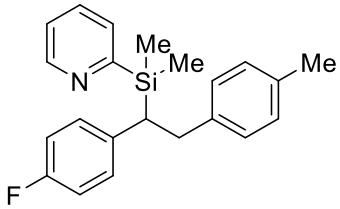
*8-((2-(4-Fluorophenyl)-1-phenylethyl)dimethylsilyl)quinoline (**31**)*: The title compound **31** was obtained as a colorless oil (100.3 mg, 52% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 3H), 0.45 (s, 3H), 2.94-3.10 (m, 2H), 3.46 (dd, J = 4.9, 10.6 Hz, 1H), 6.64 (t, J = 8.1 Hz, 2H), 6.81 (t, J = 5.9 Hz, 2H), 7.01 (dd, J = 7.6, 12.2 Hz, 3H), 7.13 (t, J = 6.9 Hz, 2H), 7.39-7.49 (m, 2H), 7.78 (dd, J = 6.8, 14.9 Hz, 2H), 8.13 (d, J = 8.6 Hz, 1H), 8.96-8.99 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -4.4, -2.6, 35.2, 37.7, 114.4 (d, J_{CF} = 21.0 Hz), 120.9, 124.4, 126.1, 127.8, 128.1 (d, J_{CF} = 34.5 Hz), 129.4, 129.7, 129.8, 136.2, 136.7, 138.2 (d, J_{CF} = 2.2 Hz), 139.6, 143.2, 149.1, 152.6, 160.9 (d, J_{CF} = 241.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.3.



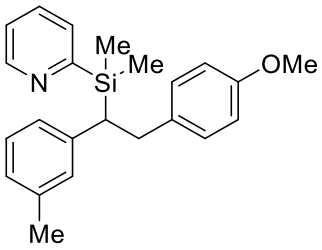
*8-(Dimethyl(1-phenyl-2-(o-tolyl)ethyl)silyl)quinoline (**32**)*: The title compound **32** was obtained as a colorless oil (103.1 mg, 54% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.33 (s, 3H), 0.50 (s, 3H), 1.93 (s, 3H), 2.99-3.11 (m, 2H), 3.41 (dd, *J* = 5.3, 9.9 Hz, 1H), 6.77 (s, 2H), 6.84 (dd, *J* = 7.3, 11.2 Hz, 2H), 6.96-7.13 (m, 5H), 7.38 (dd, *J* = 4.2, 8.2 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.79 (t, *J* = 5.25 Hz, 2H), 8.12 (d, *J* = 8.2 Hz, 1H), 8.94 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -4.1, -2.6, 19.3, 33.2, 35.9, 120.8, 124.3, 125.2, 125.4, 126.0, 127.8, 128.4, 129.0, 129.4, 129.8, 135.9, 136.2, 136.8, 139.7, 140.6, 143.6, 149.1, 152.7.



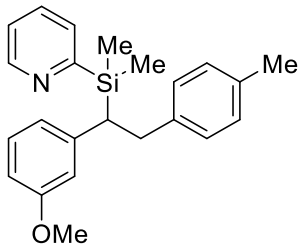
*2-((1-(4-Fluorophenyl)-2-(p-tolyl)ethyl)dimethylsilyl)pyridine (**33**)*: The title compound **33** was obtained as a colorless oil (96.1 mg, 55% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 2-15% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 3H), 0.36 (s, 3H), 2.21 (s, 3H), 2.81 (dd, *J* = 4.7, 10.9Hz, 1H), 2.95-3.11 (m, 2H), 6.78-6.92 (m, 8H), 7.18-7.33 (m, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.53 (ddd, *J* = 1.6, 1.6, 1.6 Hz, 1H), 8.81 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.4, -4.4, 21.0, 35.4, 36.6, 114.8 (d, J_{CF} = 21.0 Hz), 123.0, 128.4, 128.8, 129.4 (d, J_{CF} = 7.5 Hz), 129.9, 133.9, 135.1, 137.9, 138.7, 150.3, 160.6 (d, J_{CF} = 240.7 Hz), 166.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.1; IR (neat) cm^{-1} 2955, 2922, 1505, 1157; GC-MS for $C_{22}H_{24}FNSi$ was found to be 349.2.



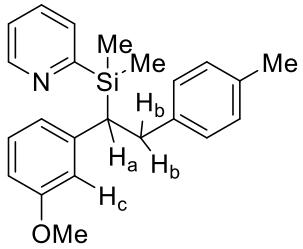
*2-((2-(4-Methoxyphenyl)-1-(m-tolyl)ethyl)dimethylsilyl)pyridine (**34**)*: The title compound **34** was obtained as a colorless oil (90.4 mg, 50% yield, using 3 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20 (s, 3H), 0.35 (s, 3H), 2.21 (s, 3H), 2.76 (dd, *J* = 6.1, 9.3 Hz, 1H), 2.99-3.10 (m, 2H), 3.69 (s, 3H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.75 (s, 1H), 6.81 (dd, *J* = 7.8, 11.8 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 7.16-7.21 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.51 (ddd, *J* = 1.6, 1.6, 1.7 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.2, 21.6, 34.8, 37.3, 55.2, 113.5, 122.9, 125.2, 125.4, 127.9, 129.2, 129.5, 129.9, 133.8, 134.3, 137.4, 142.3, 150.1, 157.5, 166.5; IR (neat) cm^{-1} 2954, 1509, 1242.

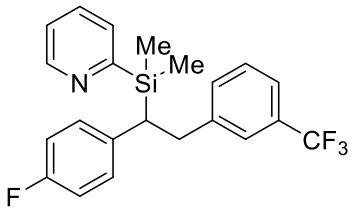


*2-((1-(3-Methoxyphenyl)-2-(p-tolyl)ethyl)dimethylsilyl)pyridine (**35**)*: The title compound **35** was obtained as a colorless oil (108.5 mg, 60% yield, using 3 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.37 (s, 3H), 2.20 (s, 3H), 2.81 (dd, *J* = 6.8, 8.6 Hz, 1H), 3.05 (app. d, *J* = 7.0 Hz, 2H), 3.67 (s, 3H), 6.50 (s, 1H), 6.57 (app. t, *J* = 8.9 Hz, 2H), 6.89 (s, 4H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.19 (app. t, *J* = 6.4 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.51 (app. t, *J* = 7.5 Hz, 1H), 8.80 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.7, -4.1, 35.7, 37.1, 55.1, 110.2, 114.0, 120.9, 122.9, 128.4, 128.8, 128.9, 129.9, 133.8, 134.9, 138.9, 144.2, 150.2, 159.4, 166.5; IR (neat) cm^{-1} 2919, 1596, 1575, 1246; GC-MS for $C_{23}H_{27}NOSi$ was found to be 361.2.

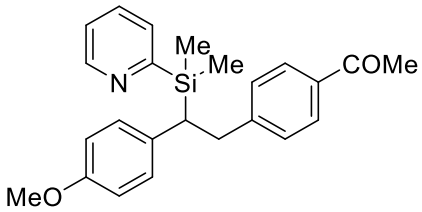


H_a NOE correlation		H_c NOE correlation	
H_b	4.5%	H_a	1.8%
H_c	2.2%	H_b	1.8%
		OMe	1.8%



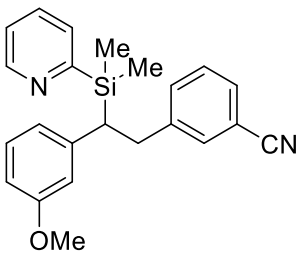
*2-((1-(4-Fluorophenyl)-2-(3-(trifluoromethyl)phenyl)ethyl)dimethylsilyl)pyridine (**36**)*: The title compound **36** was obtained as a colorless oil (105.0 mg, 52% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 2-10% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 3H), 0.38 (s, 3H), 2.82 (dd, J = 4.6, 11.2 Hz, 1H), 3.03-3.20 (m, 2H), 6.74-6.92 (m, 4H), 7.11-7.29 (m, 5H), 7.32-7.35 (m, 1H), 7.54 (ddd, J = 1.7, 1.7, 1.7 Hz, 1H), 8.81 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.3, 36.0, 36.4, 115.0 (d, J_{CF} = 20.2 Hz), 122.6 (q, J_{CF} = 3.75 Hz), 123.2, 125.3 (q, J_{CF} = 3.0 Hz), 126.1, 128.4, 129.3, 129.4, 129.9, 130.3 (q, J_{CF} = 31.5 Hz), 131.9, 134.1, 137.3 (d, J_{CF} = 3.0 Hz), 142.7, 150.3, 160.7 (d, J_{CF} = 241.5 Hz), 166.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.2, -117.3; IR (neat) cm^{-1} 2931, 1505, 1327, 1119; GC-MS for $C_{22}H_{21}F_4NSi$ was found to be 403.1.



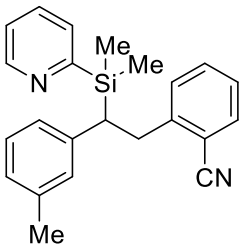
*1-(4-(2-(Dimethyl(pyridin-2-yl)silyl)-2-(4-methoxyphenyl)ethyl)phenyl)ethan-1-one (**37**)*: The title compound **37** was obtained as a white solid (85.7 mg, 44% yield, using 3 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.37 (s, 3H), 2.23 (s, 3H), 2.79 (dd, J = 6.8, 8.9 Hz, 1H), 3.04-3.15 (m, 2H), 3.82 (s, 3H), 6.83 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 7.9 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 7.18-7.22 (m, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.53 (ddd, J = 1.7, 1.7, 1.7 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 8.81 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.2, -3.7, 21.4, 36.4, 37.0, 52.4, 123.4, 127.9, 128.5, 129.1, 129.3, 129.8, 130.3, 134.4, 134.6, 138.8, 148.4, 150.7, 166.7, 167.7; IR (neat) cm^{-1} 2921, 1716, 1274; HRMS (ESI) Calcd for $C_{24}H_{27}NO_2Si$ $(M+H)^+$ 389.1811, found 389.1753.



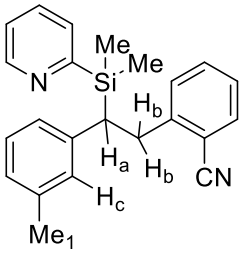
*3-(2-(Dimethyl(pyridin-2-yl)silyl)-2-(3-methoxyphenyl)ethyl)benzonitrile (**38**)*: The title compound **38** was obtained as a colorless oil (96.9 mg, 52% yield, using 2 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.39 (s, 3H), 2.77 (dd, *J* = 6.6, 9.1 Hz, 1H), 3.03-3.13 (m, 2H), 3.68 (s, 3H), 6.47 (d, *J* = 1.7 Hz, 1H), 6.57 (dd, *J* = 7.9, 16.1 Hz, 2H), 7.07 (t, *J* = 7.9 Hz, 1H), 7.13-731 (m, 5H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.56 (ddd, *J* = 1.7, 1.7, 1.7 Hz, 1H), 8.81 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.6, -4.1, 35.5, 37.2, 55.1, 110.4, 111.9, 114.0, 119.2, 120.6, 123.2, 128.7, 129.2, 129.5, 129.9, 132.1, 133.1, 134.1, 143.0, 143.6, 150.3, 159.6, 165.9; IR (neat) cm^{-1} 2955, 2227, 1576, 1557, 1247; HRMS (ESI) Calcd for $C_{23}H_{24}N_2OSi$ $(M+H)^+$ 372.1658, found 372.1651.

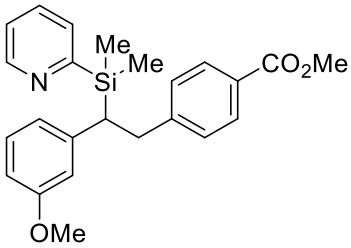


*2-(2-(Dimethyl(pyridin-2-yl)silyl)-2-(m-tolyl)ethyl)benzonitrile (**39**)*: The title compound **39** was obtained as a colorless oil (90.9 mg, 51% yield, using 3 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 3H), 0.41 (s, 3H), 2.20 (s, 3H), 2.89 (dd, *J* = 6.9, 9.2 Hz, 1H), 3.27-3.38 (m, 2H), 6.75-6.84 (m, 3H), 7.01 (t, *J* = 7.4 Hz, 1H), 7.07-7.11 (m, 2H), 7.18-7.28 (m, 2H), 7.38-7.45 (m, 2H), 7.55 (ddd, *J* = 1.6, 1.6, 1.7 Hz, 1H), 8.80 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.2, 21.5, 34.1, 36.6, 112.4, 118.5, 123.1, 125.3, 125.8, 126.2, 128.0, 129.1, 129.6, 130.1, 132.3, 132.6, 134.0, 137.6, 140.9, 146.1, 150.2, 165.8; IR (neat) cm^{-1} 2955, 2222, 1601, 1269.

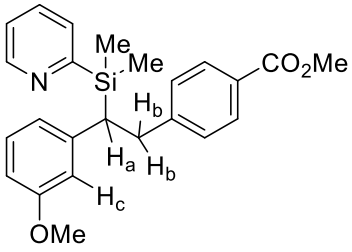


H_a NOE correlation		H_c NOE correlation			
H_b	5.4%	H_a	3.0%		
H_c	3.6%	H_b	2.9%	Me_1	2.9%

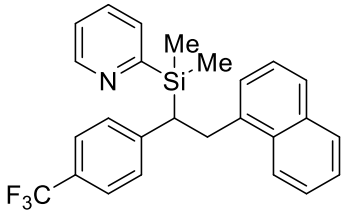


*Methyl 4-(2-(dimethyl(pyridin-2-yl)silyl)-2-(3-methoxyphenyl)ethyl)benzoate (**40**)*: The title compound **40** was obtained as a colorless oil (127.8 mg, 63% yield, using 3 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 3H), 0.39 (s, 3H), 2.82 (app. t, *J* = 7.9 Hz, 1H), 3.11 (app. dd, *J* = 15.1, 22.9 Hz, 2H), 3.66 (s, 3H), 3.83 (s, 3H), 6.47 (s, 1H), 6.55 (d, *J* = 8.2 Hz, 2H), 7.04 (app. t, *J* = 7.7 Hz, 3H), 7.19-7.23 (m, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.54 (ddd, *J* = 1.6, 1.6, 1.6 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 8.82 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.2, 35.9, 37.3, 51.9, 55.1, 110.3, 114.0, 120.8, 123.1, 127.6, 128.6, 129.0, 129.4, 129.9, 134.0, 143.5, 147.8, 150.3, 159.5, 166.1, 167.3; IR (neat) cm^{-1} 2951, 1716, 1605, 1275; HRMS (ESI) Calcd for $C_{24}H_{27}NO_3Si$ $(M+H)^+$ 405.1760, found 405.1726.



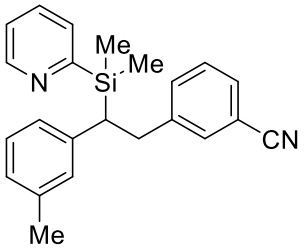
H_a NOE correlation		H_c NOE correlation	
H_b	4.4%	H_a	2.0%
H_c	2.4%	H_b	1.9%
		OMe	1.9%



*2-(Dimethyl(2-(naphthalen-1-yl)-1-(4-(trifluoromethyl)phenyl)ethyl)silyl)pyridine (**41**)*: The title compound **41** was obtained as a yellow solid (108.9 mg, 50% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 2-10% ether/hexanes.

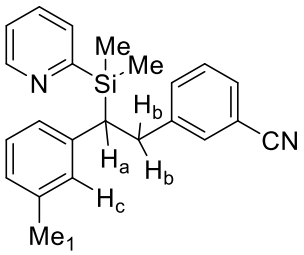
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.38 (s, 3H), 0.58 (s, 3H), 3.21 (dd, *J* = 3.6, 11.3 Hz, 1H), 3.55 (dd, *J* = 11.3, 26.8 Hz, 1H), 3.82 (dd, *J* = 3.6, 14.8 Hz, 1H), 7.07 (d, *J* = 6.9 Hz, 1H), 7.21 (app. t, *J* = 7.5 Hz, 3H), 7.35-7.39 (m, 1H), 7.48-7.54 (m, 5H), 7.66-7.72 (m, 2H), 7.86-7.94 (m, 2H), 8.97 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ -5.6, -4.1, 33.0, 36.9, 123.3, 123.8, 125.2 (q, J_{CF} = 7.5 Hz), 125.8, 126.5, 126.7, 126.8, 127.3, 128.4, 128.9, 130.0, 131.8, 134.0, 134.1, 137.1, 147.3, 150.4, 165.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.5; IR (neat) cm^{-1} 2956, 1324, 1119; HRMS (ESI) Calcd for $C_{26}H_{24}F_3NSi$ $(M+H)^+$ 435.1630, found 435.1610.

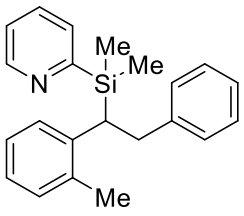


*3-(2-(Dimethyl(pyridin-2-yl)silyl)-2-(m-tolyl)ethyl)benzonitrile (**42**)*: The title compound **42** was obtained as a colorless oil (94.5 mg, 53% yield, using 2 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^1H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 3H), 0.38 (s, 3H), 2.22 (s, 3H), 2.75 (dd, *J* = 7.0, 8.6 Hz, 1H), 3.03-3.14 (m, 2H), 6.71 (s, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.13-7.25 (m, 4H), 7.28-7.36 (m, 2H), 7.55 (ddd, *J* = 1.7, 1.7, 1.7 Hz, 1H), 8.81 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.7, -4.1, 21.6, 35.5, 37.0, 111.9, 119.3, 123.1, 125.1, 125.9, 128.2, 128.7, 129.1, 129.5, 129.9, 132.2, 133.2, 134.0, 137.7, 141.2, 143.7, 150.3, 166.1; IR (neat) cm^{-1} 2920, 2227, 1246; HRMS (ESI) Calcd for $C_{23}H_{24}N_2Si$ $(M+H)^+$ 356.1709, found 356.1732.

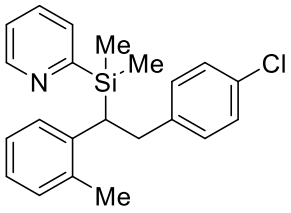


H_a NOE correlation		H_c NOE correlation	
H_b	4.5%	H_a	2.5%
H_c	3.4%	H_b	2.1%
		Me_1	2.2%



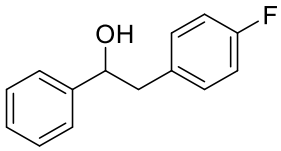
*2-(Dimethyl(2-phenyl-1-(o-tolyl)ethyl)silyl)pyridine (**43**)*: The title compound **43** was obtained as a colorless oil (84.5 mg, 51% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.42 (s, 3H), 195 (s, 3H), 2.98-3.08 (m, 2H), 3.12-3.22 (m, 1H), 6.92-6.95 (m, 4H), 7.02-7.22 (m, 6H), 7.29 (d, J = 7.5 Hz, 1H), 7.51 (app. t, J = 8.3 Hz, 1H), 8.81 (d, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.1, -4.0, 20.5, 32.3, 37.0, 122.9, 124.5, 125.6, 125.8, 127.1, 128.0, 128.4, 129.8, 130.1, 133.8, 136.0, 141.1, 142.5, 150.2, 166.6; IR (neat) cm^{-1} 3024, 2954, 1246.



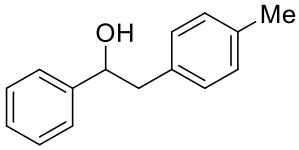
*2-(Dimethyl(2-phenyl-1-(o-tolyl)ethyl)silyl)pyridine (**44**)*: The title compound **44** was obtained as a colorless oil (102.5 mg, 56% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.42 (s, 3H), 196 (s, 3H), 2.96-3.04 (m, 2H), 3.08-3.18 (m, 1H), 6.84 (d, J = 6.0 Hz, 2H), 6.94-6.97 (m, 2H), 7.02 (d, J = 6.0 Hz, 2H), 7.09-7.10 (m, 2H), 7.21 (t, J = 6.0 Hz, 1H), 7.30 (d, J = 6.0 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 8.81 (d, J = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.1, -4.0, 20.5, 32.3, 36.4, 123.0, 124.6, 125.9, 127.1, 128.1, 129.7, 129.8, 130.1, 131.3, 133.9, 136.0, 140.6, 141.0, 150.2, 166.4.



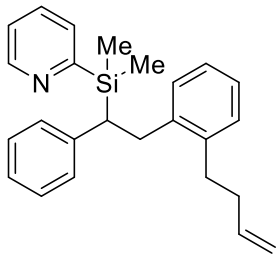
*2-(4-Fluorophenyl)-1-phenylethan-1-ol (**45**)*[6]: The title compound **45** was obtained as a colorless oil (86.5 mg, 80% yield) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 1H), 2.99 (d, J = 6.7 Hz, 2H), 4.83 (t, J = 6.6 Hz, 1H), 6.98 (app. t, J = 8.7 Hz, 2H), 7.09-7.14 (m, 2H), 7.29-7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.0, 75.4, 115.2 (d, J_{CF} = 21.0 Hz), 126.0, 127.7, 128.5, 131.0 (d, J_{CF} = 8.2 Hz), 133.8 (d, J_{CF} = 3.0 Hz), 143.7, 161.8 (d, J_{CF} = 243.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -115.1; IR (neat) cm^{-1} 3378, 2921, 1508, 1219.



*1-Phenyl-2-(p-tolyl)ethan-1-ol (**46**)*[6]: The title compound **46** was obtained as a white solid (87.0 mg, 82% yield) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93 (s, 1H), 2.33 (s, 3H), 2.90-3.05 (m, 2H), 4.89 (dd, *J* = 4.8, 8.6 Hz, 1H), 7.08-7.14 (m, 4H), 7.27-7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 45.7, 75.4, 126.0, 127.6, 128.4, 129.2, 129.5, 135.0, 136.1, 144.0; IR (neat) cm^{-1} 3282, 2916, 1454, 1203.



*2-((2-(2-(But-3-en-1-yl)phenyl)-1-phenylethyl)dimethylsilyl)pyridine (**51**)*: The title compound **51** was obtained as a colorless oil (139.4 mg, 75% yield, using 5 mol % catalyst) after purification by silica gel column chromatography by gradient elution using 5–20% ether/hexanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.43 (s, 3H), 2.15-2.23 (m, 2H), 2.53 (t, *J* = 7.8 Hz, 2H), 2.74 (dd, *J* = 3.8, 11.0 Hz, 1H), 3.02-3.19 (m, 2H), 4.97 (dd, *J* = 4.8, 9.5 Hz, 2H), 5.70-5.83 (m, 1H), 6.84 (app. dd, *J* = 7.5, 15.5 Hz, 2H), 6.95-7.06 (m, 5H), 7.12-7.23 (m, 3H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 8.82 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.5, -4.1, 32.0, 32.5, 35.2, 36.8, 114.8, 123.0, 124.8, 125.5, 125.8, 128.1, 128.4, 129.0, 129.4, 129.9, 133.9, 138.4, 139.6, 139.7, 142.4, 150.3, 166.4; IR (neat) cm^{-1} 3061, 2956, 1449, 1246.

4. References

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(2) Struk, Ł.; Sośnicki, J. G.; Idzik, T. J.; Maciejewska, G. *Eur. J. Org. Chem.* **2016**, *2016*, 1292.

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(5) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, *2006*, 0890.

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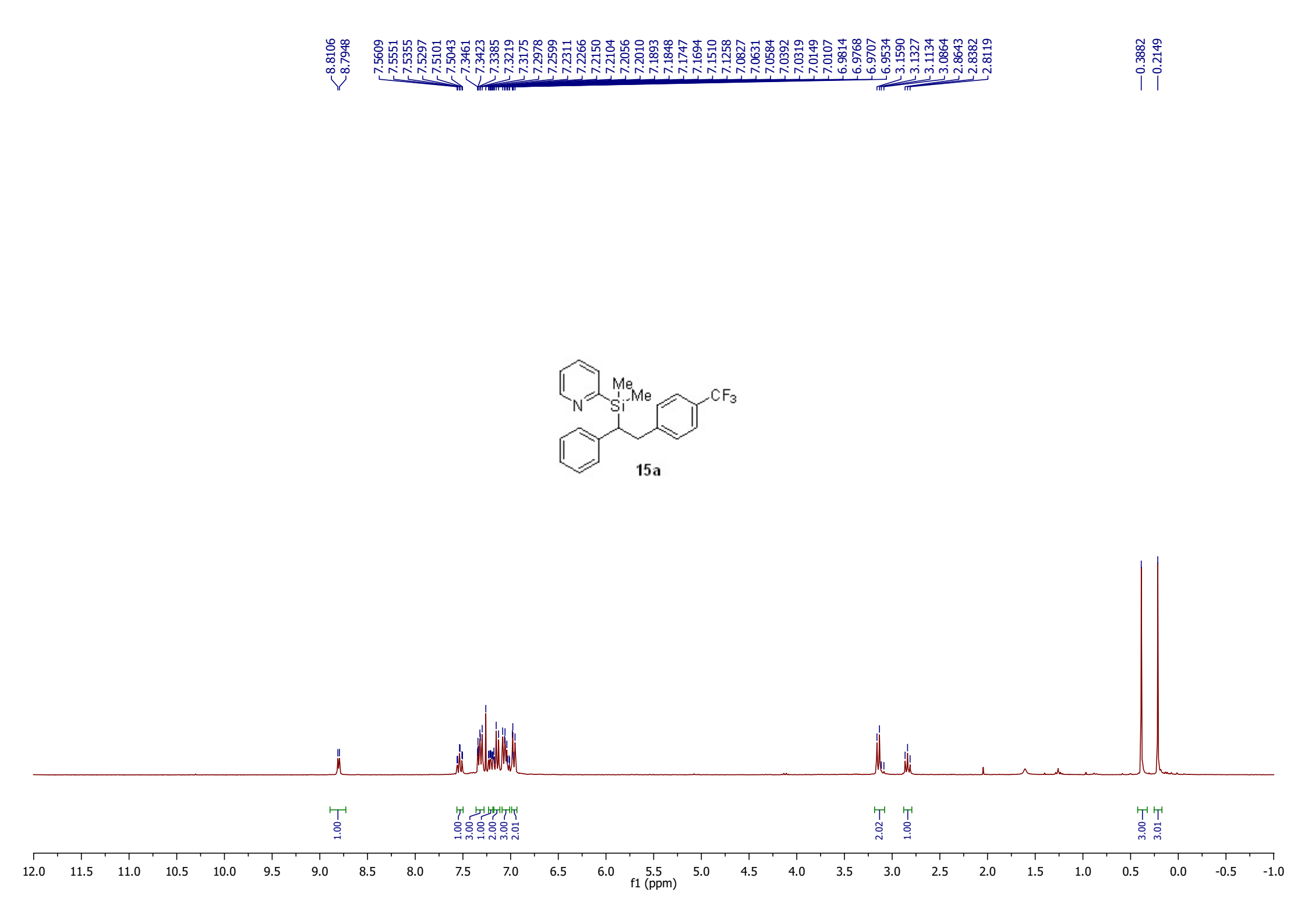
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7.1694
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3.0864
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0.2149
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Me
Si
N
CF3
15a
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1.00
3.00
1.00
2.00
3.00
2.01
2.02
1.00
3.00
3.01
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11.5
11.0
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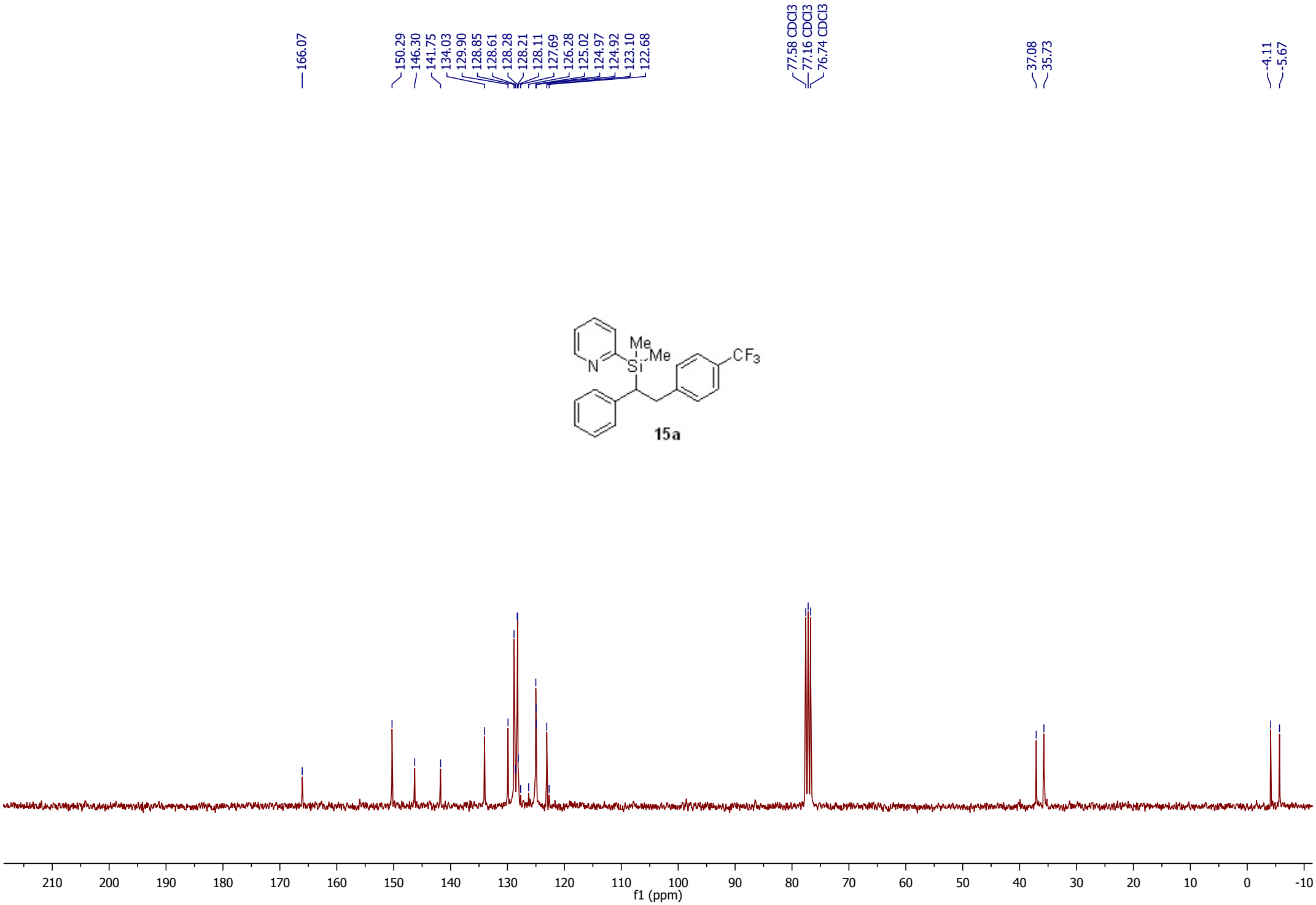
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122.68
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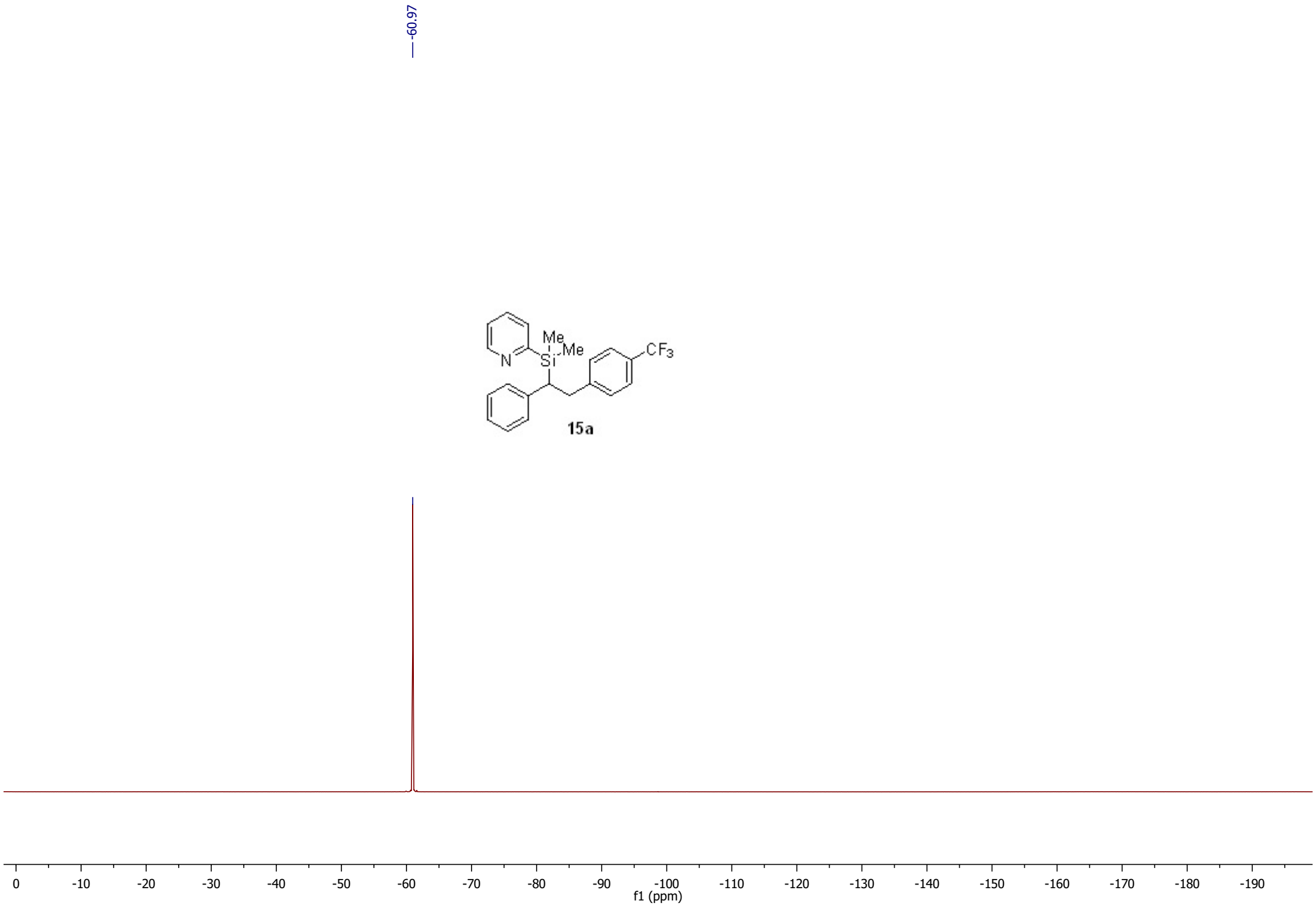
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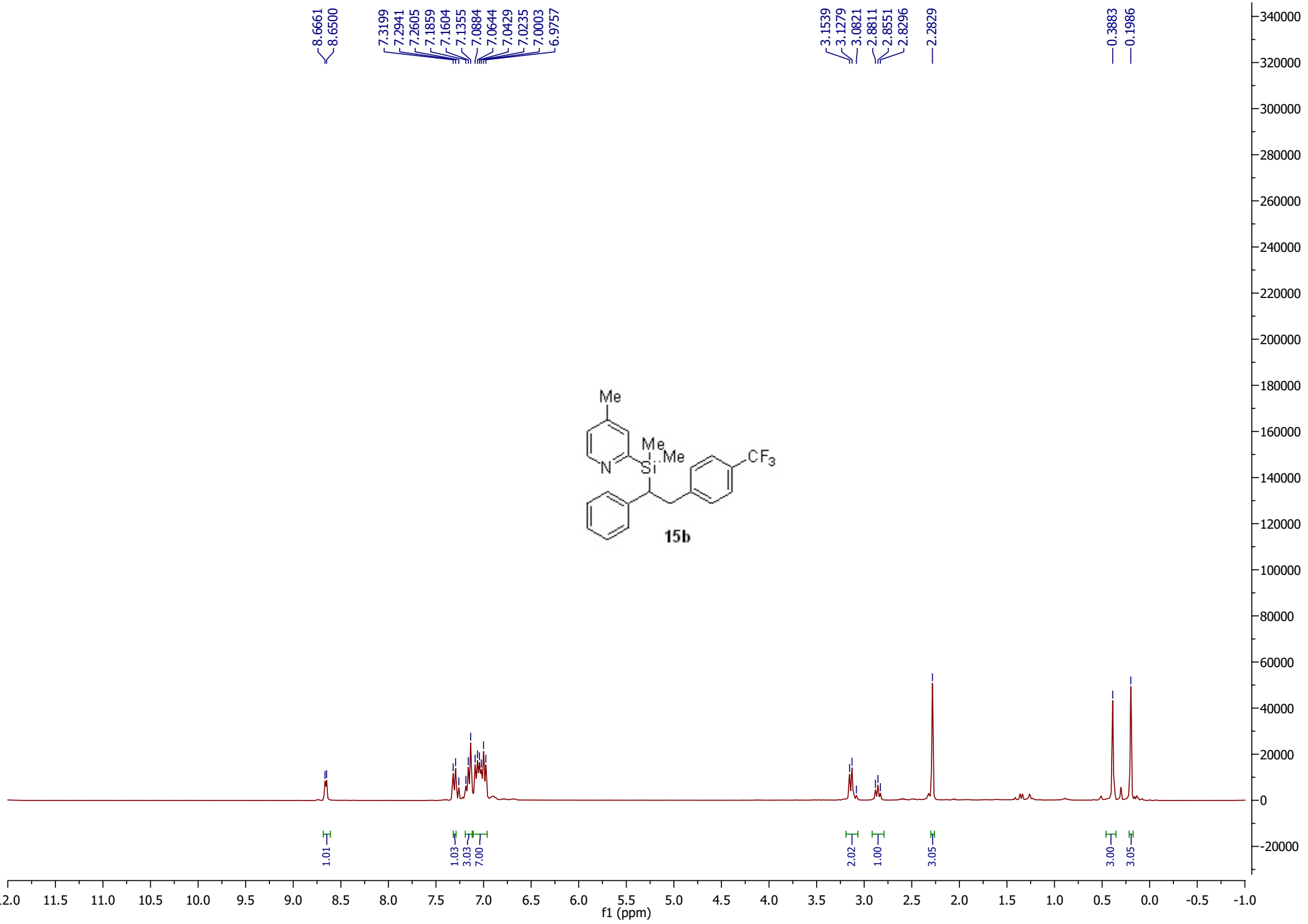
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7.0003
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3.0821
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2.8551
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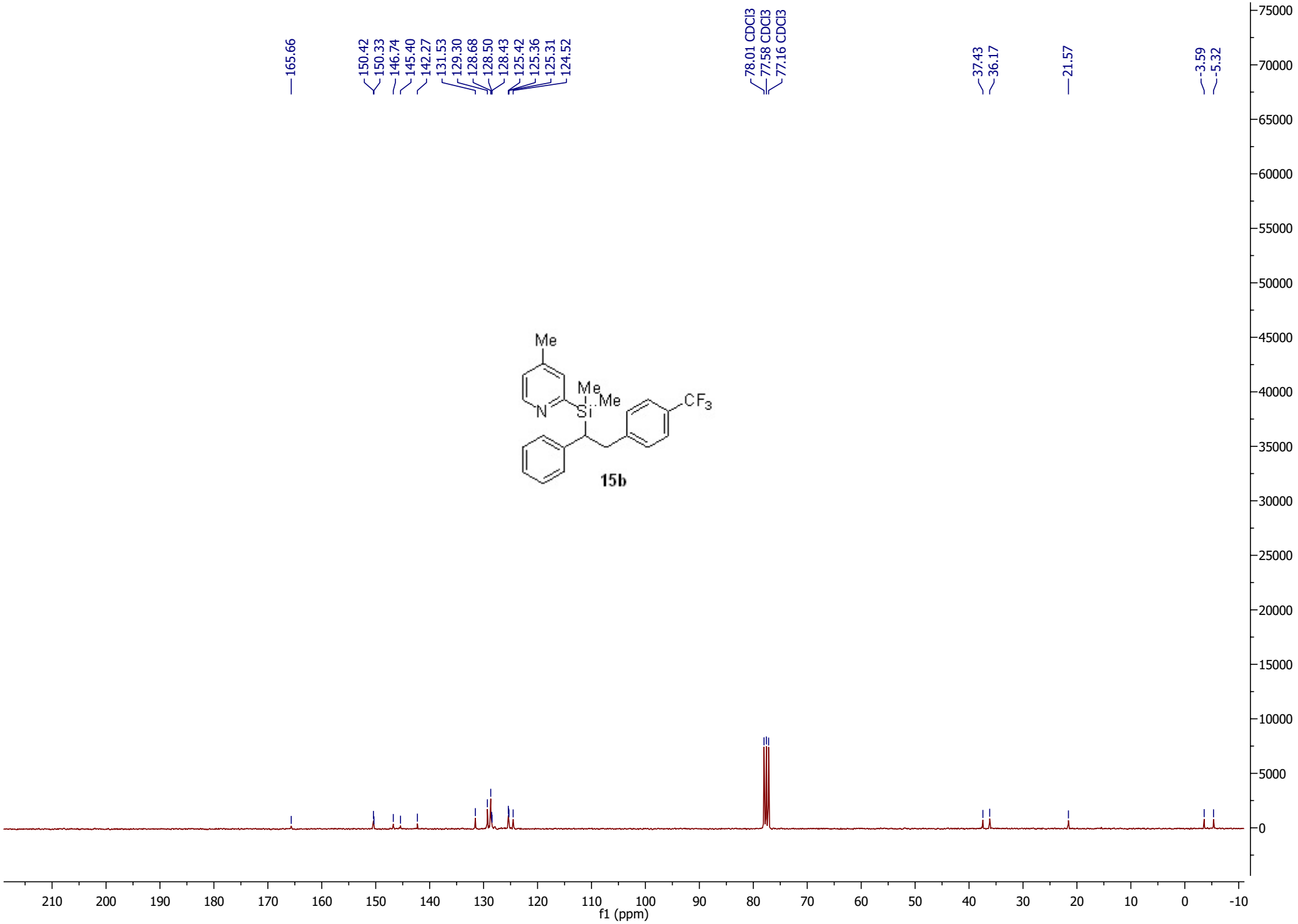
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125.36
125.31
124.52
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77.58 CDCl3
77.16 CDCl3
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Me
Si
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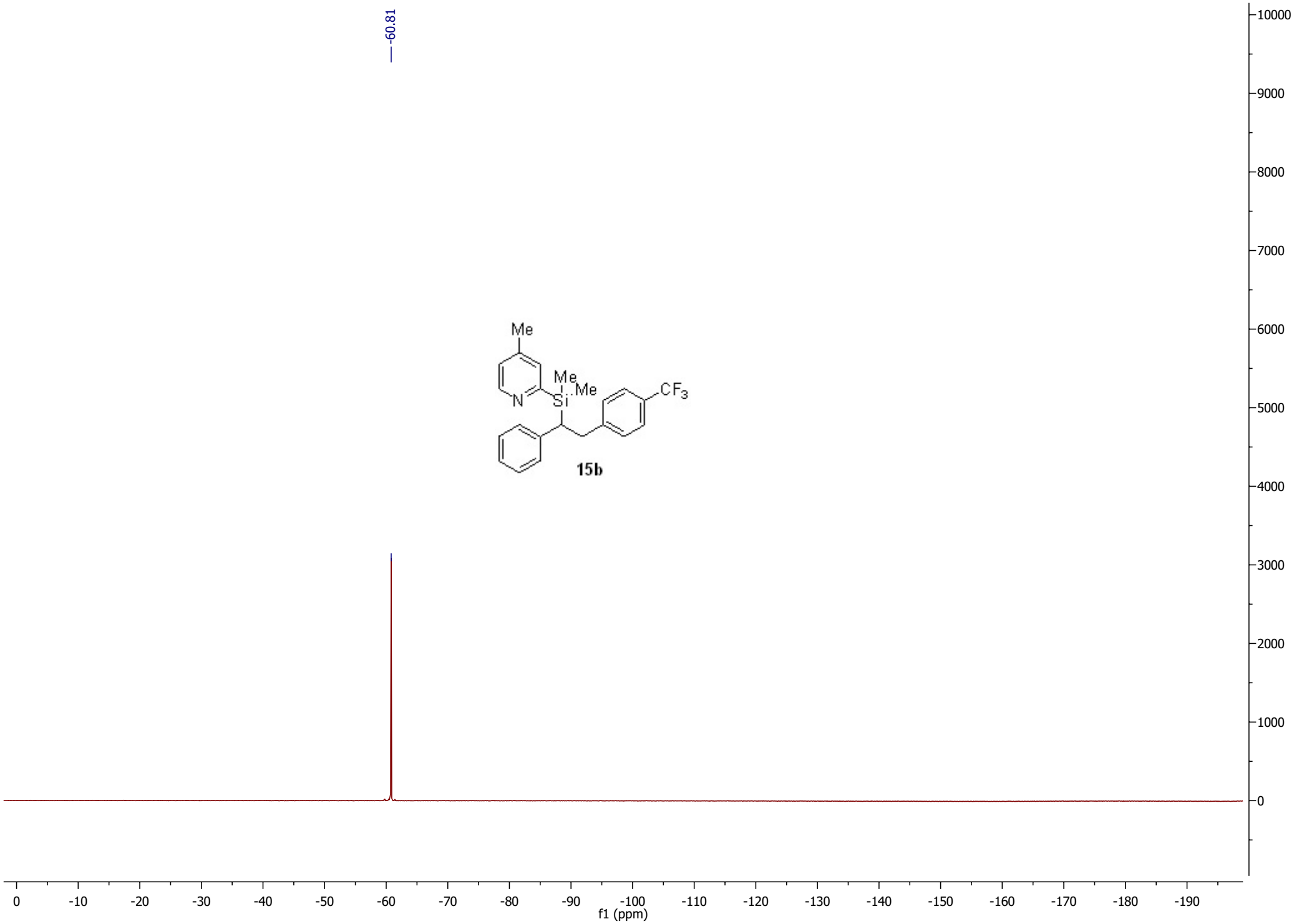
f1 (ppm)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1000
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-20
-30
-40
-50
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-150
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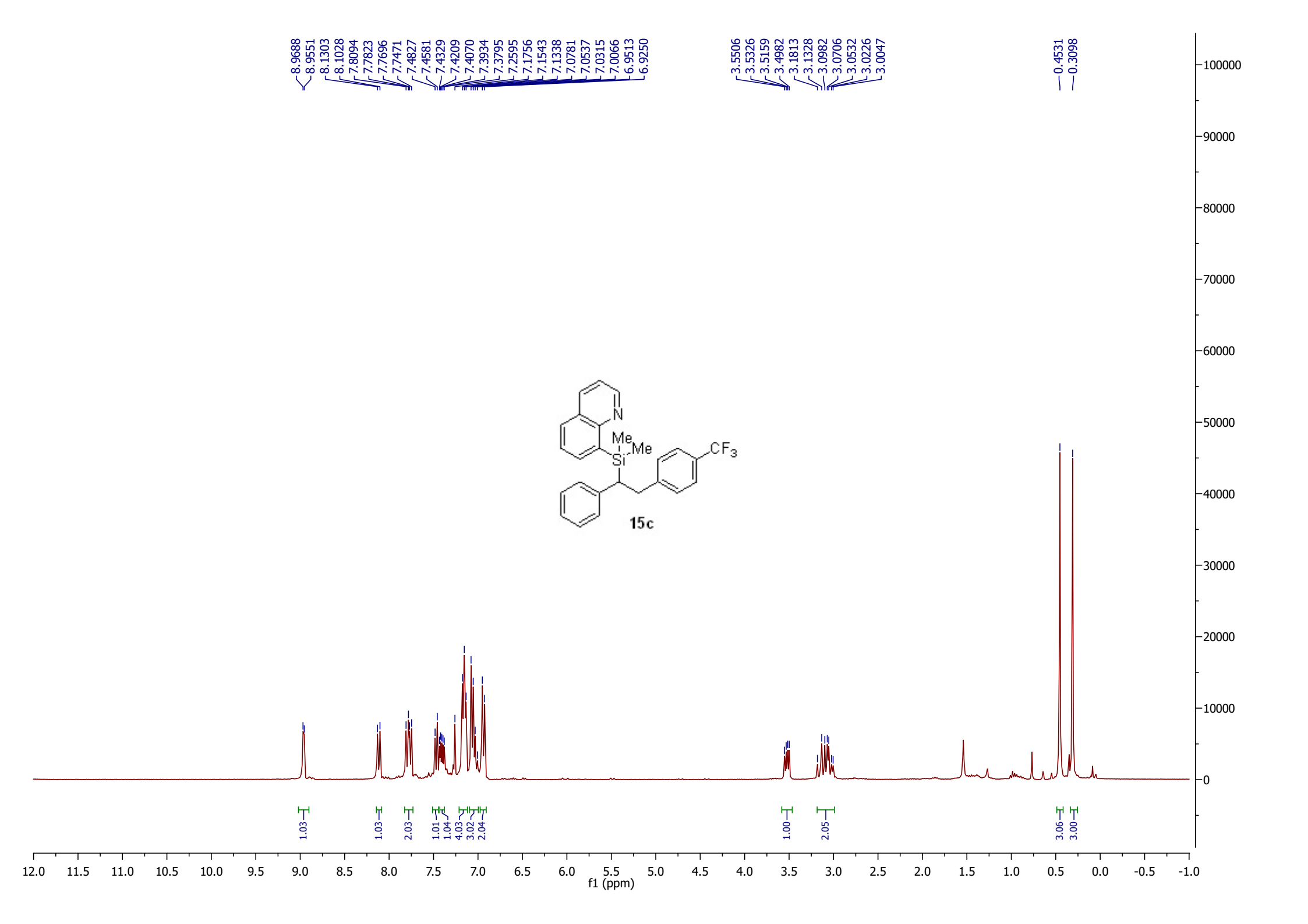
f1 (ppm)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7.4209
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7.2595
7.1756
7.1543
7.1338
7.0781
7.0537
7.0315
7.0066
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6.9250
3.5506
3.5326
3.5159
3.4982
3.1813
3.1328
3.0982
3.0706
3.0532
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3.0047
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0.3098
N
Me
Me
Si
CF3
15c
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1.04
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3.02
2.04
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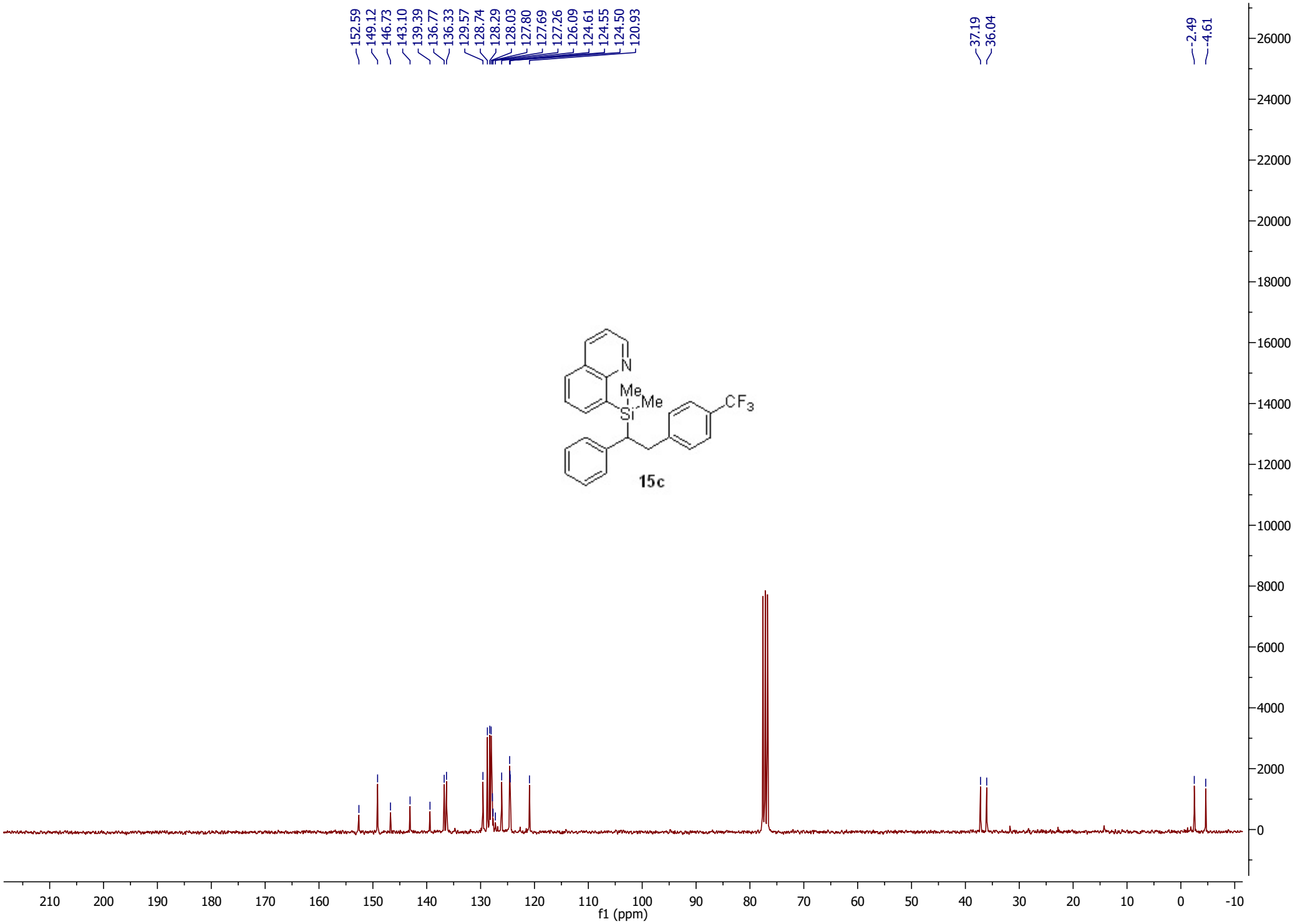
3.00
f1 (ppm)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128.29
128.03
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127.69
127.26
126.09
124.61
124.55
124.50
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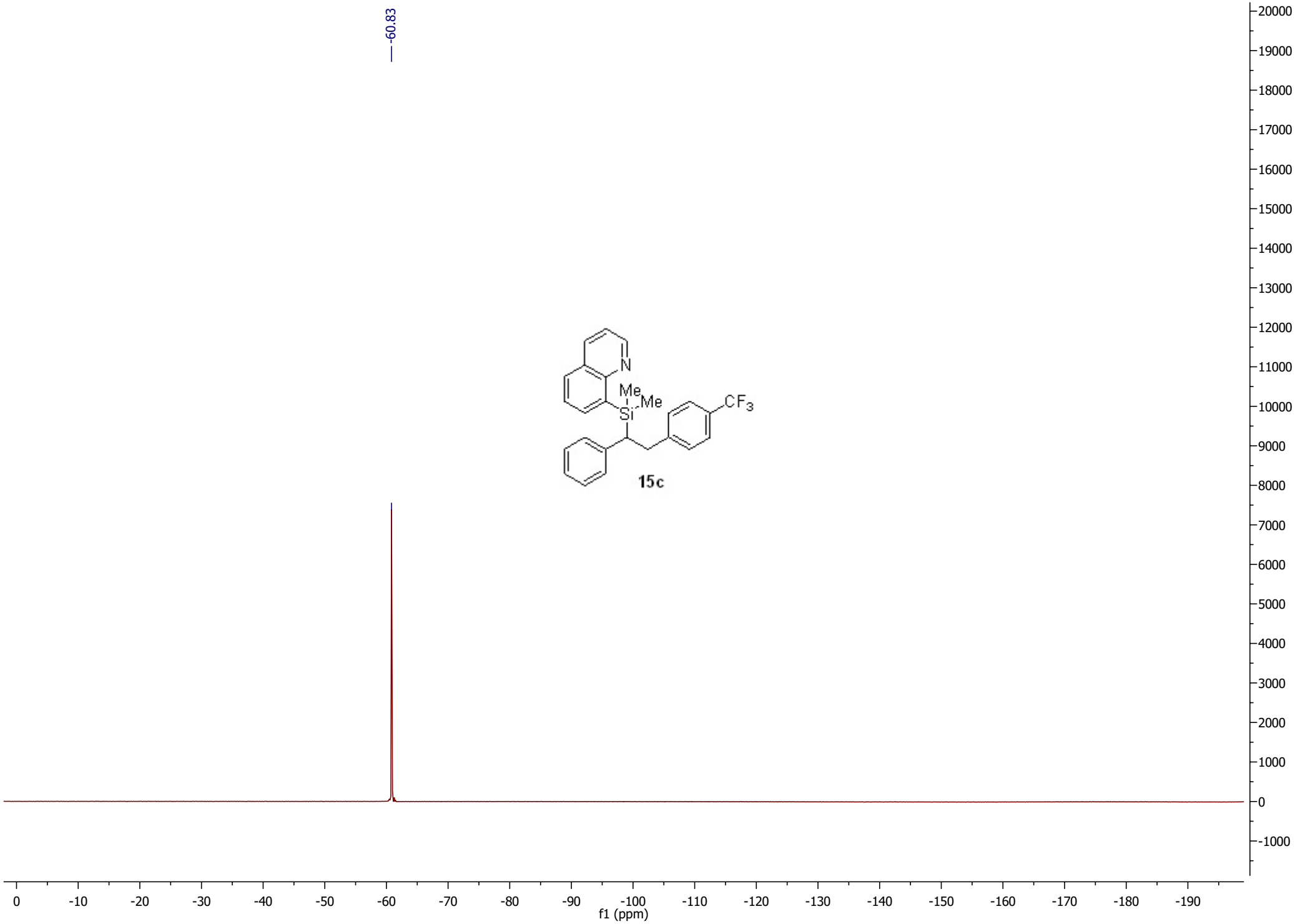
37.19
36.04
-2.49
-4.61
N
Me
Me
Si
CF3
15c
f1 (ppm)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6000
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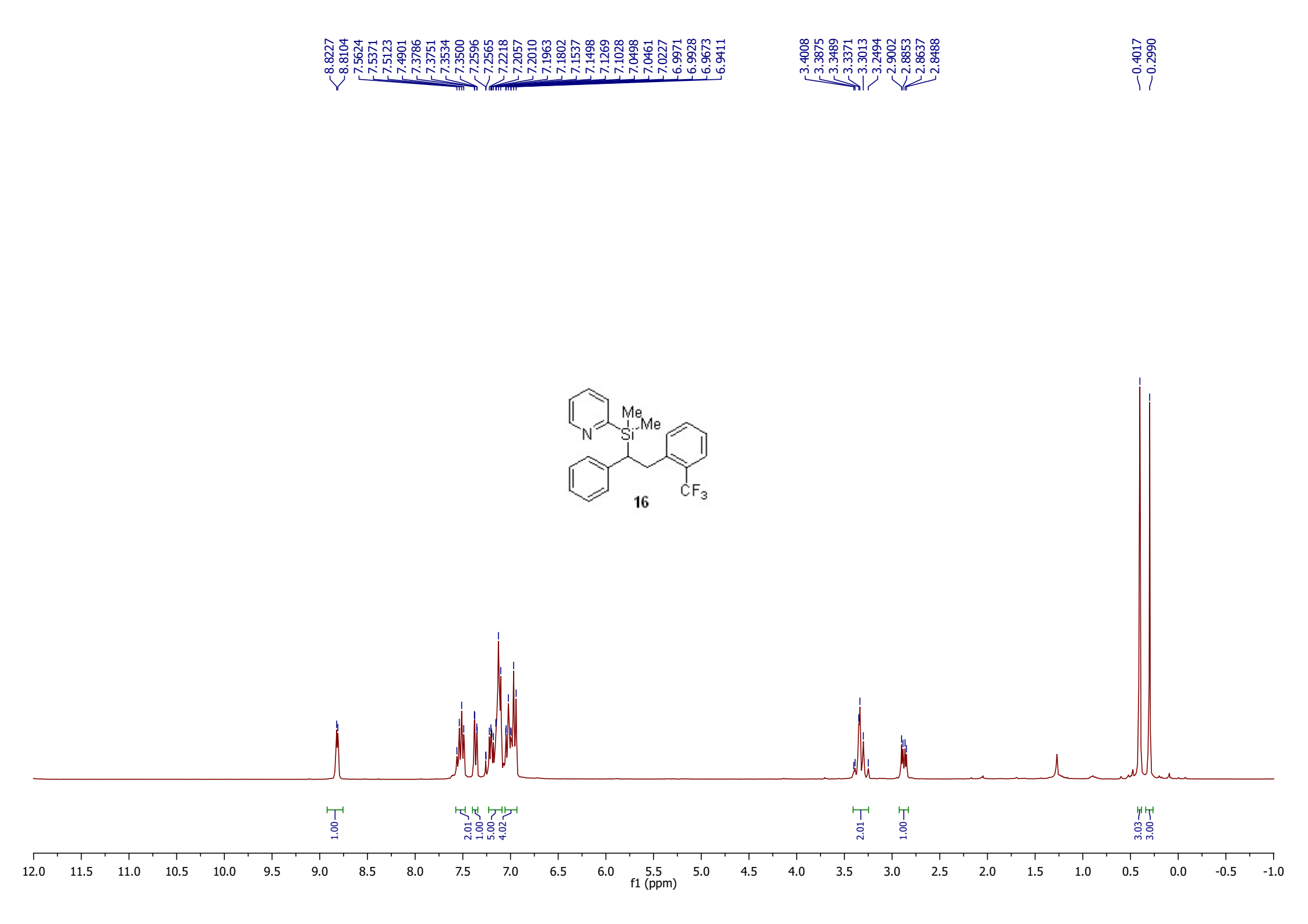
f1 (ppm)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Me
Si
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1.00
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1.00
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3.00
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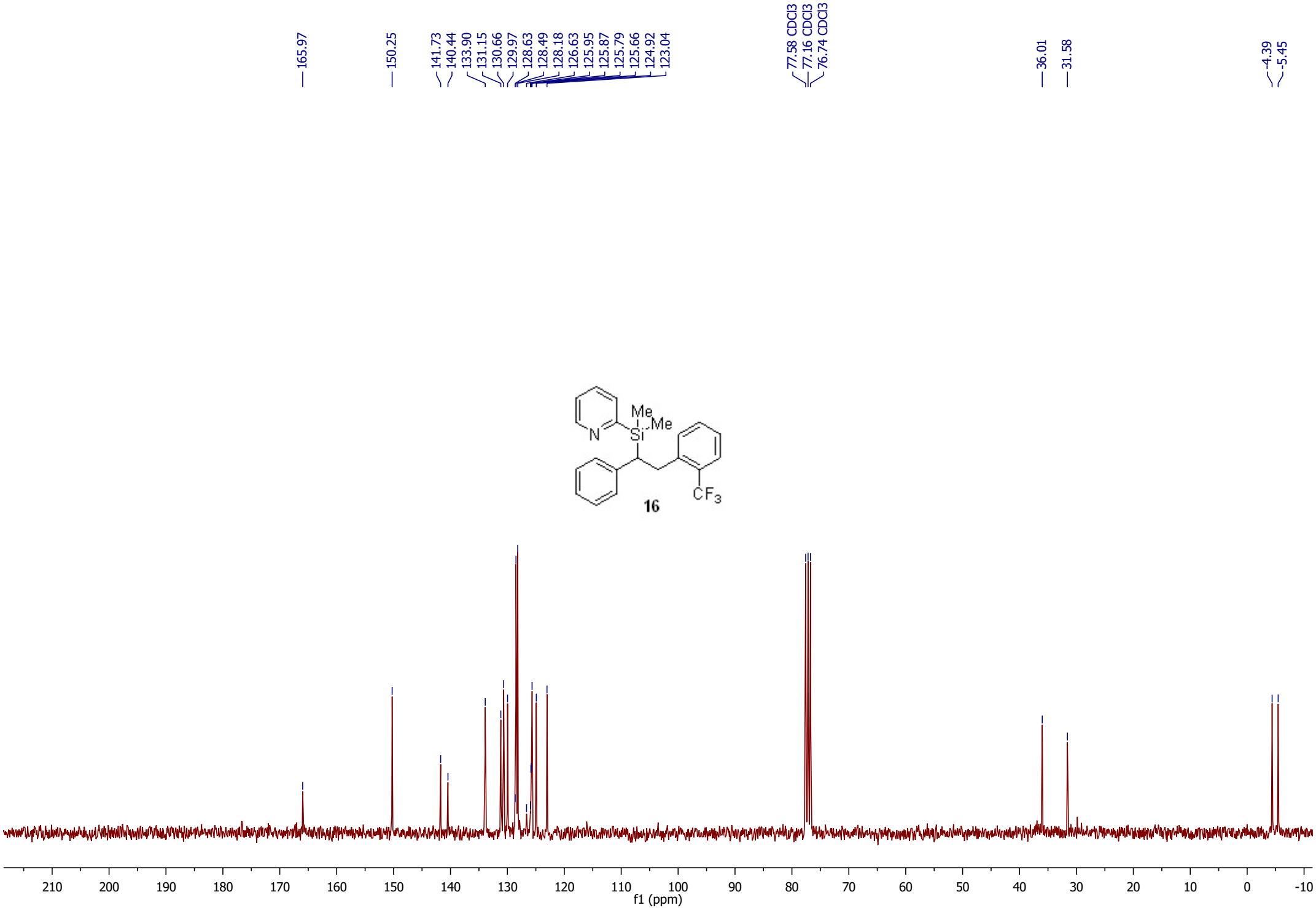
f1 (ppm)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125.66
124.92
123.04
77.58 CDCl3
77.16 CDCl3
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CF3
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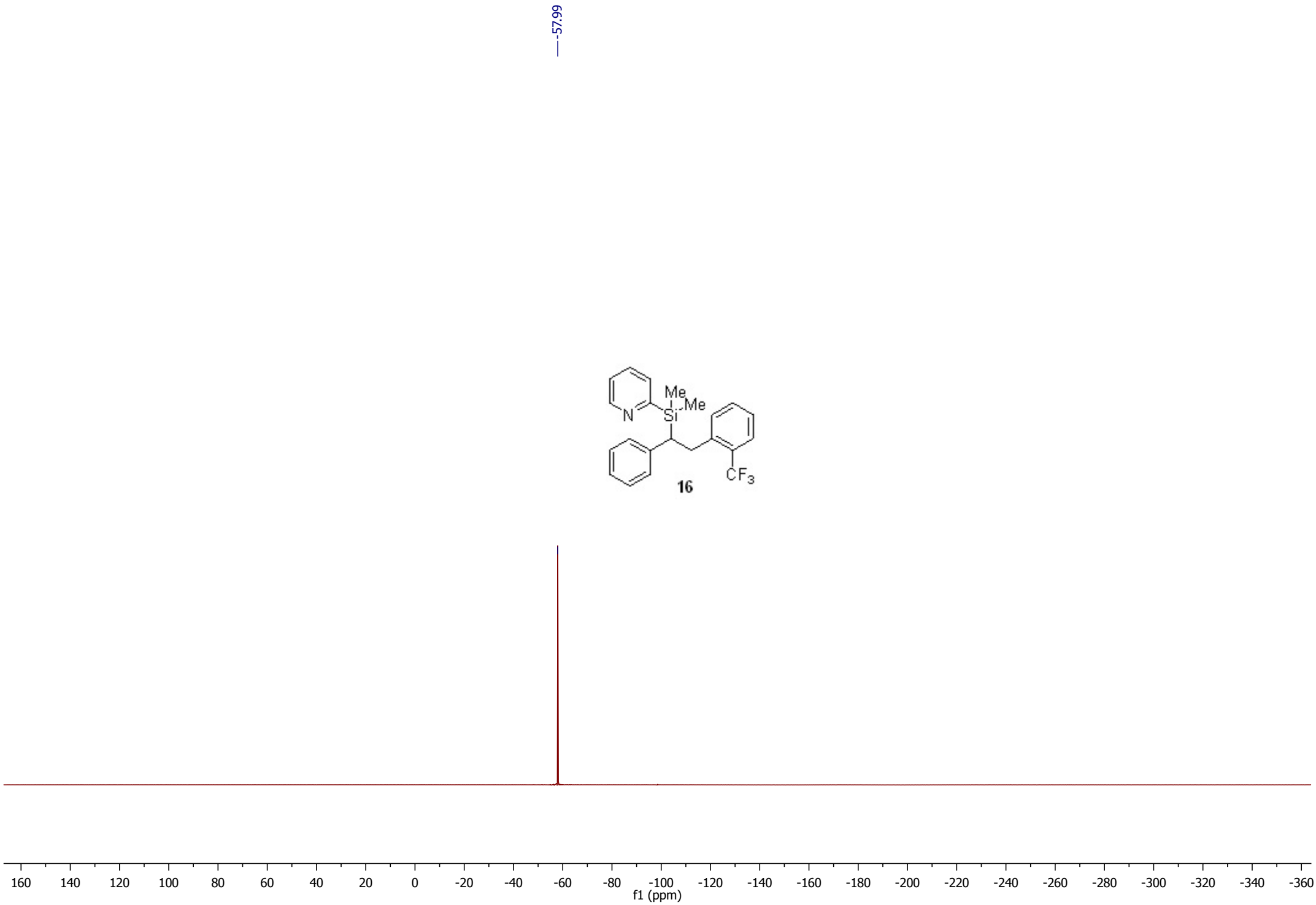
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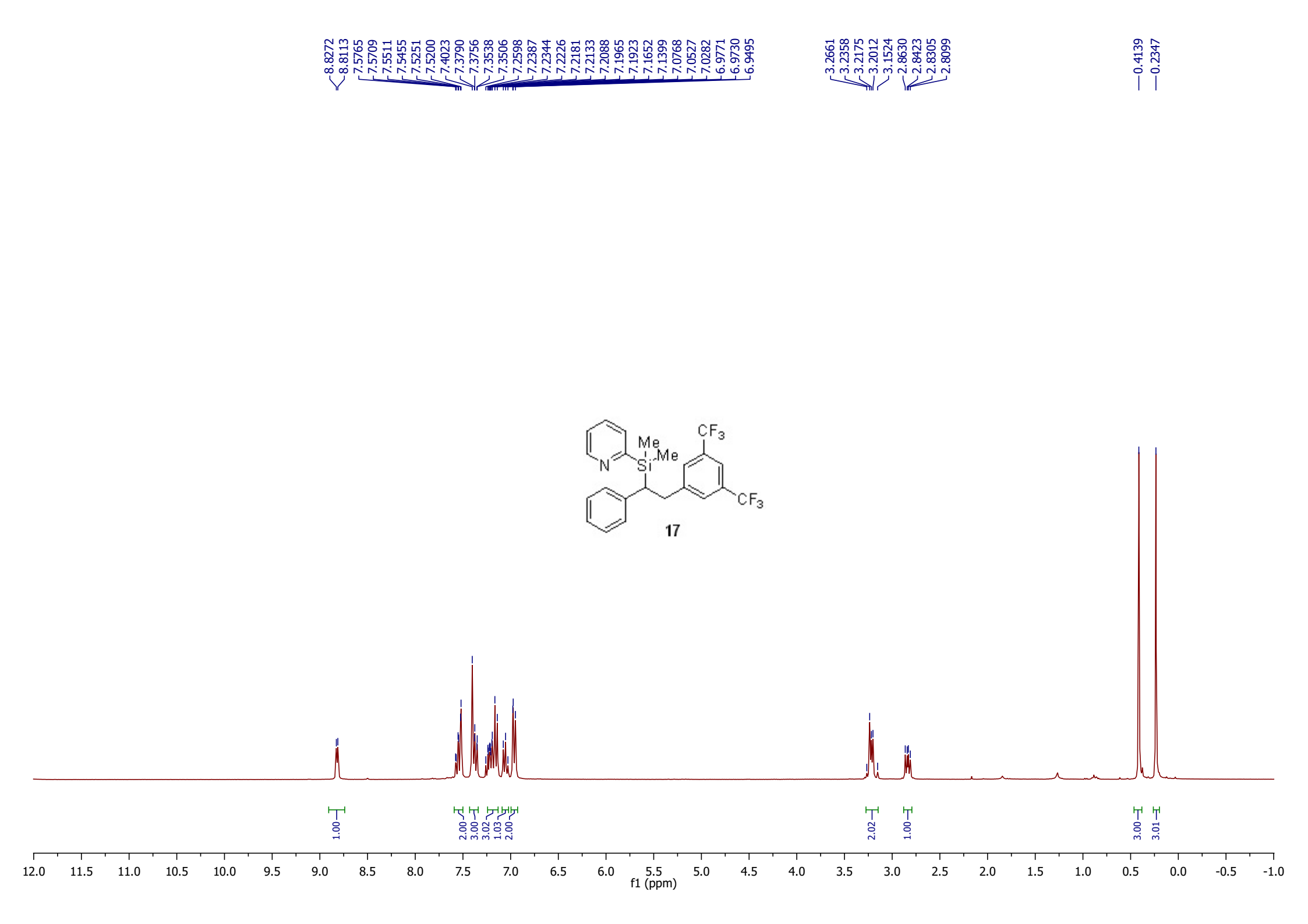
f1 (ppm)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CF3
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3.00
3.02
1.03
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2.02
1.00
3.00
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11.0
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4.0
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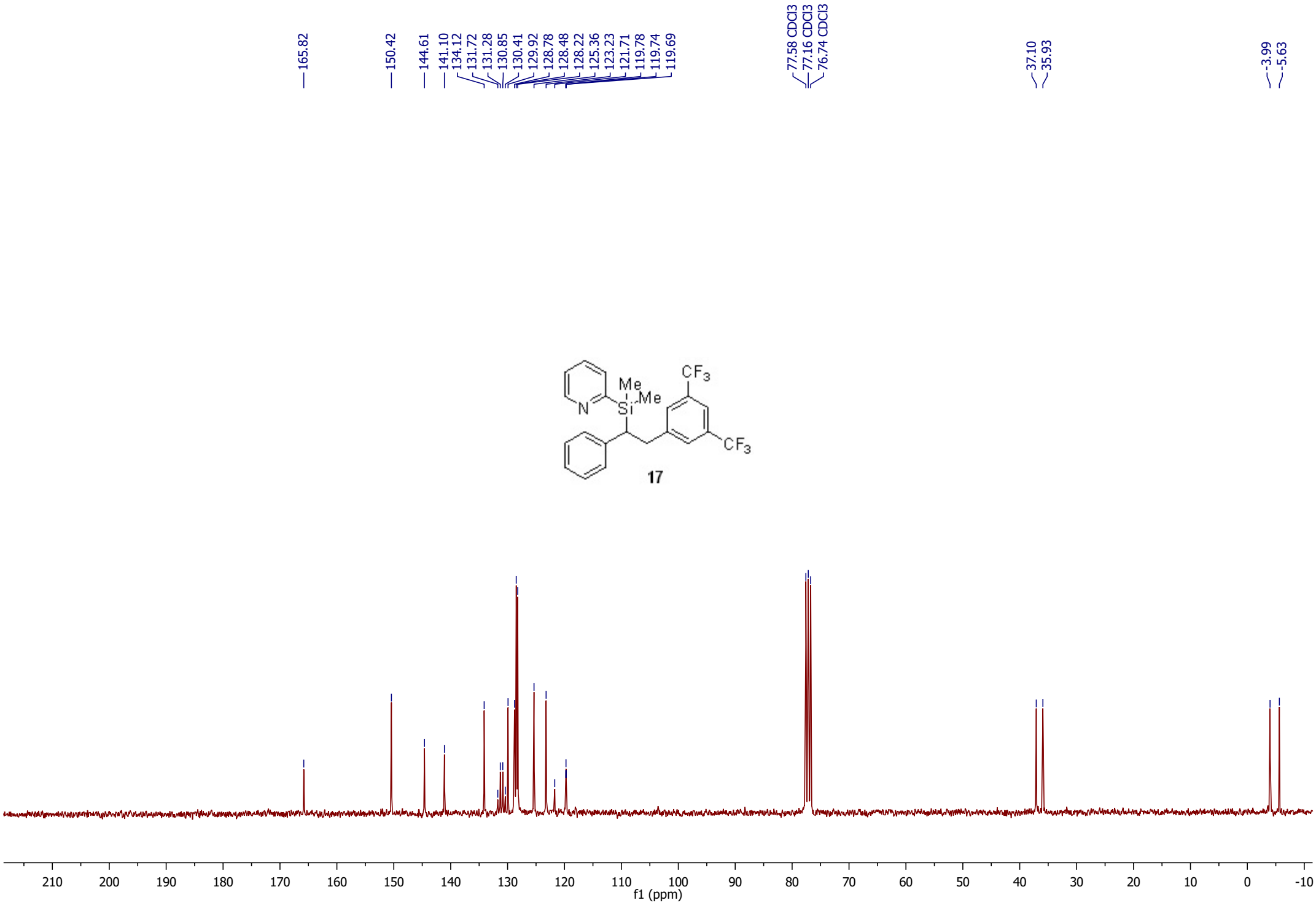
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128.22
125.36
123.23
121.71
119.78
119.74
119.69
77.58 CDCl3
77.16 CDCl3
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Me
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CF3
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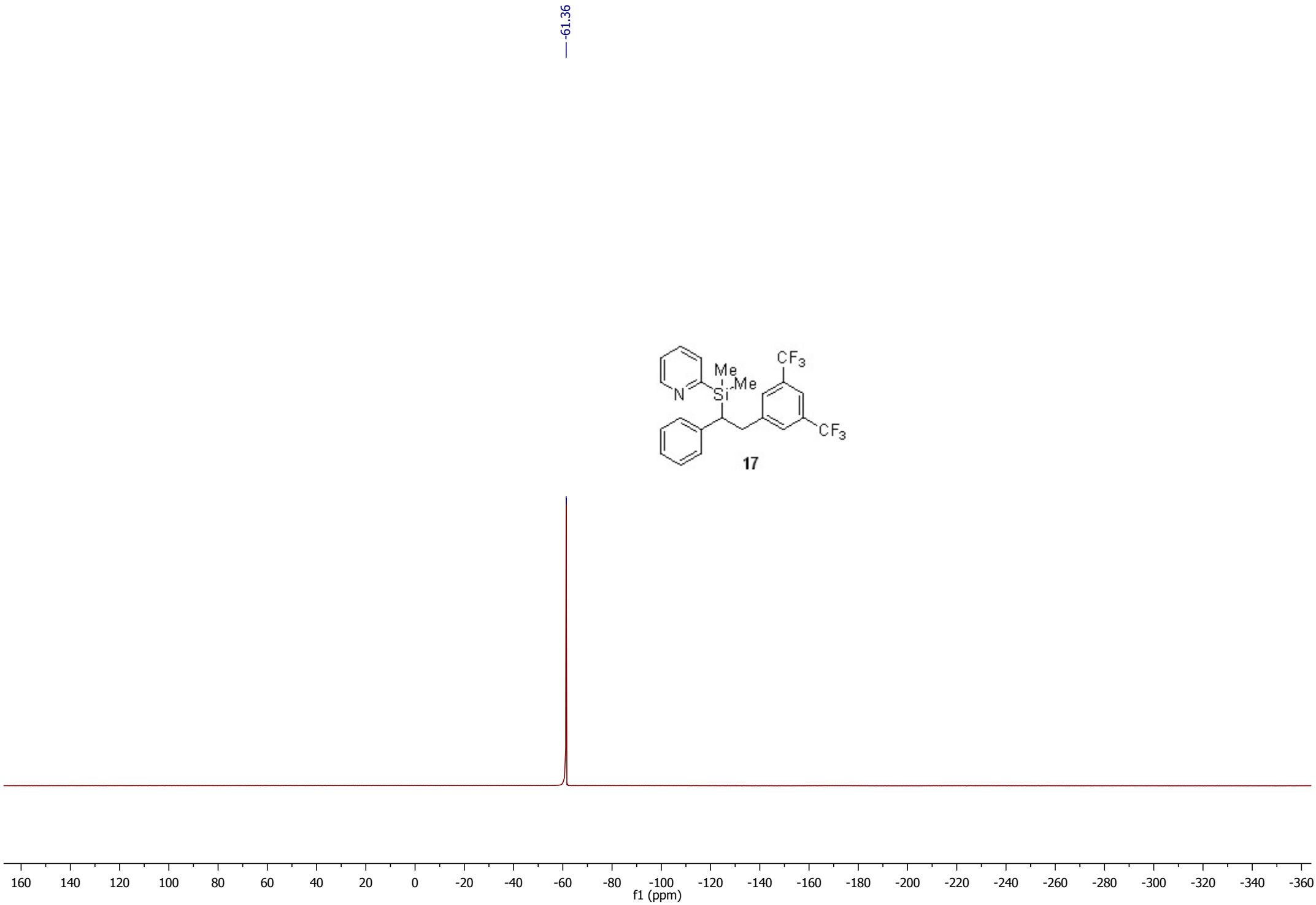
f1 (ppm)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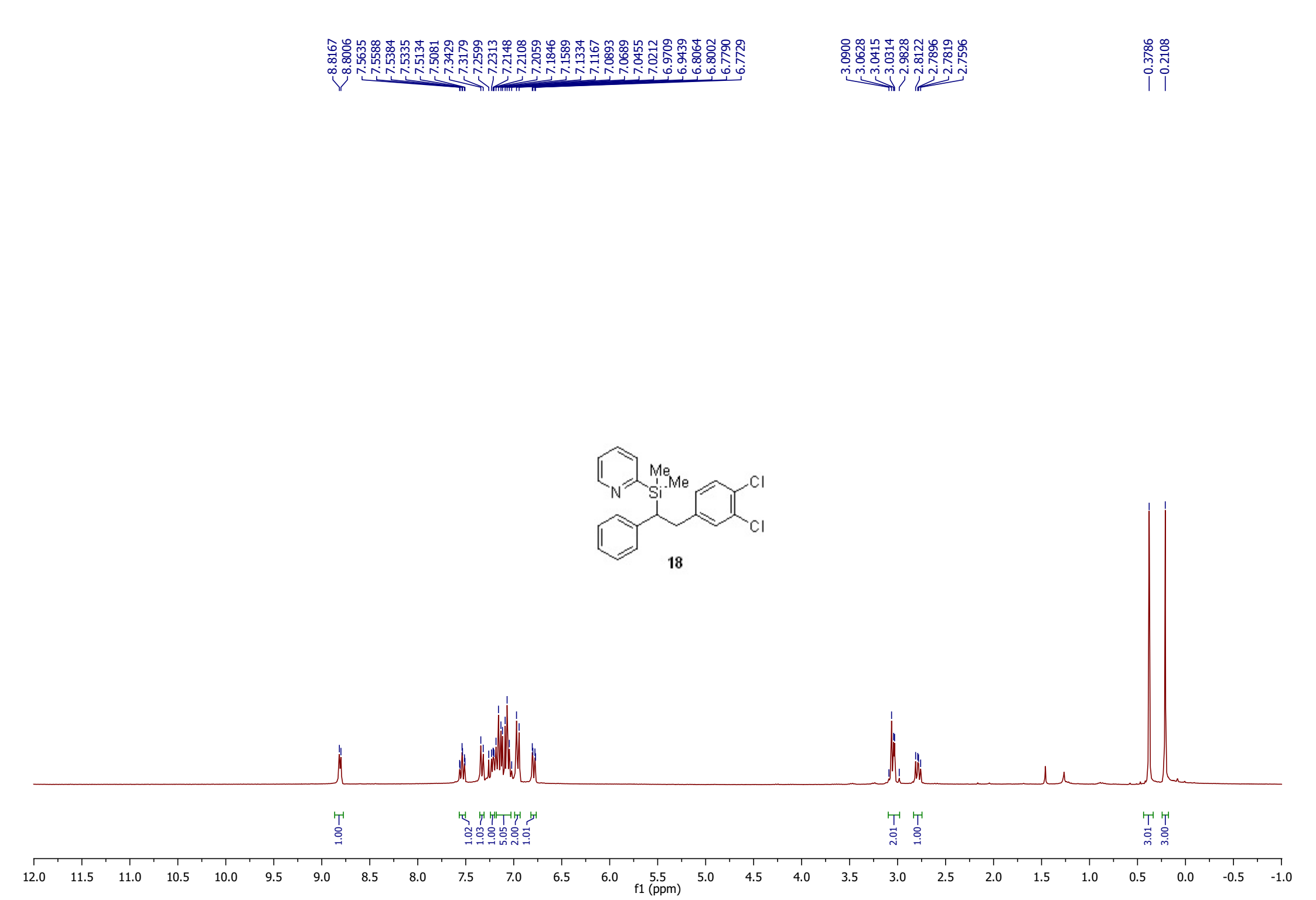
f1 (ppm)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7.0689
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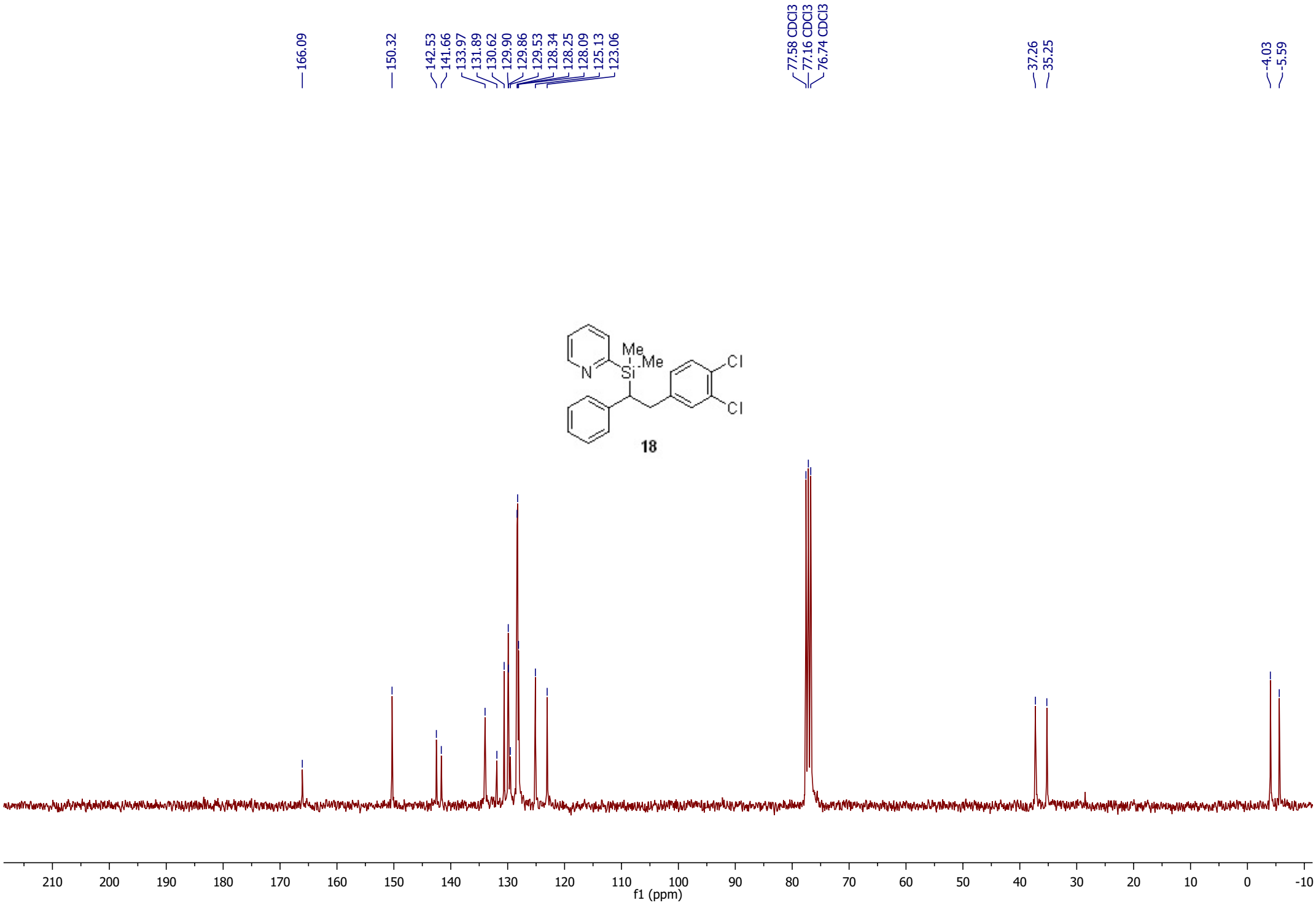
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125.13
123.06
77.58 CDCl3
77.16 CDCl3
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Me
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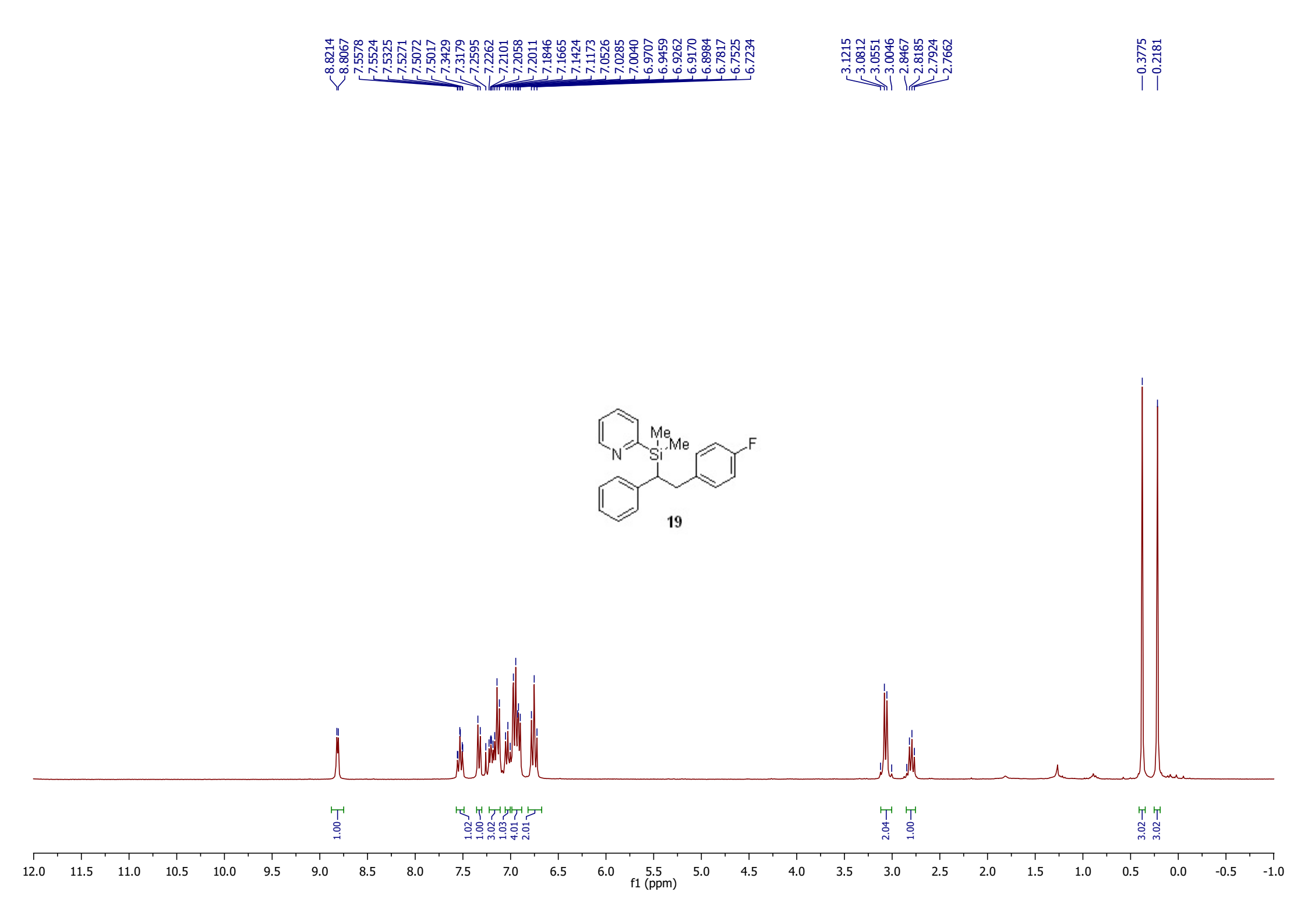
Cl
Cl
18
f1 (ppm)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3.02
1.03
4.01
2.01
2.04
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3.02
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4.0
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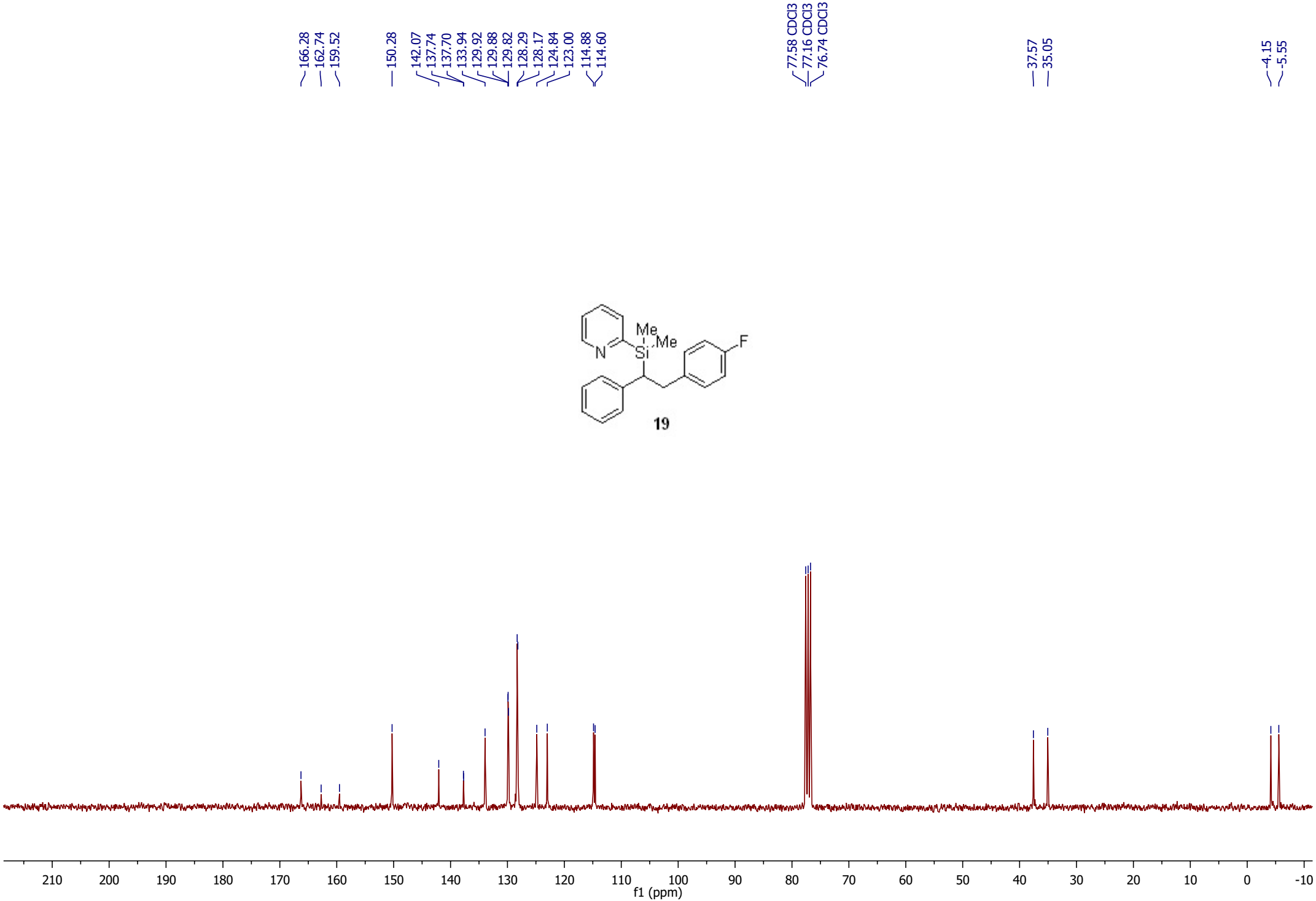
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124.84
123.00
114.88
114.60
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
37.57
35.05
-4.15
-5.55
Me
Me
Si
N
F
19
210
200
190
180
170
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100
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80
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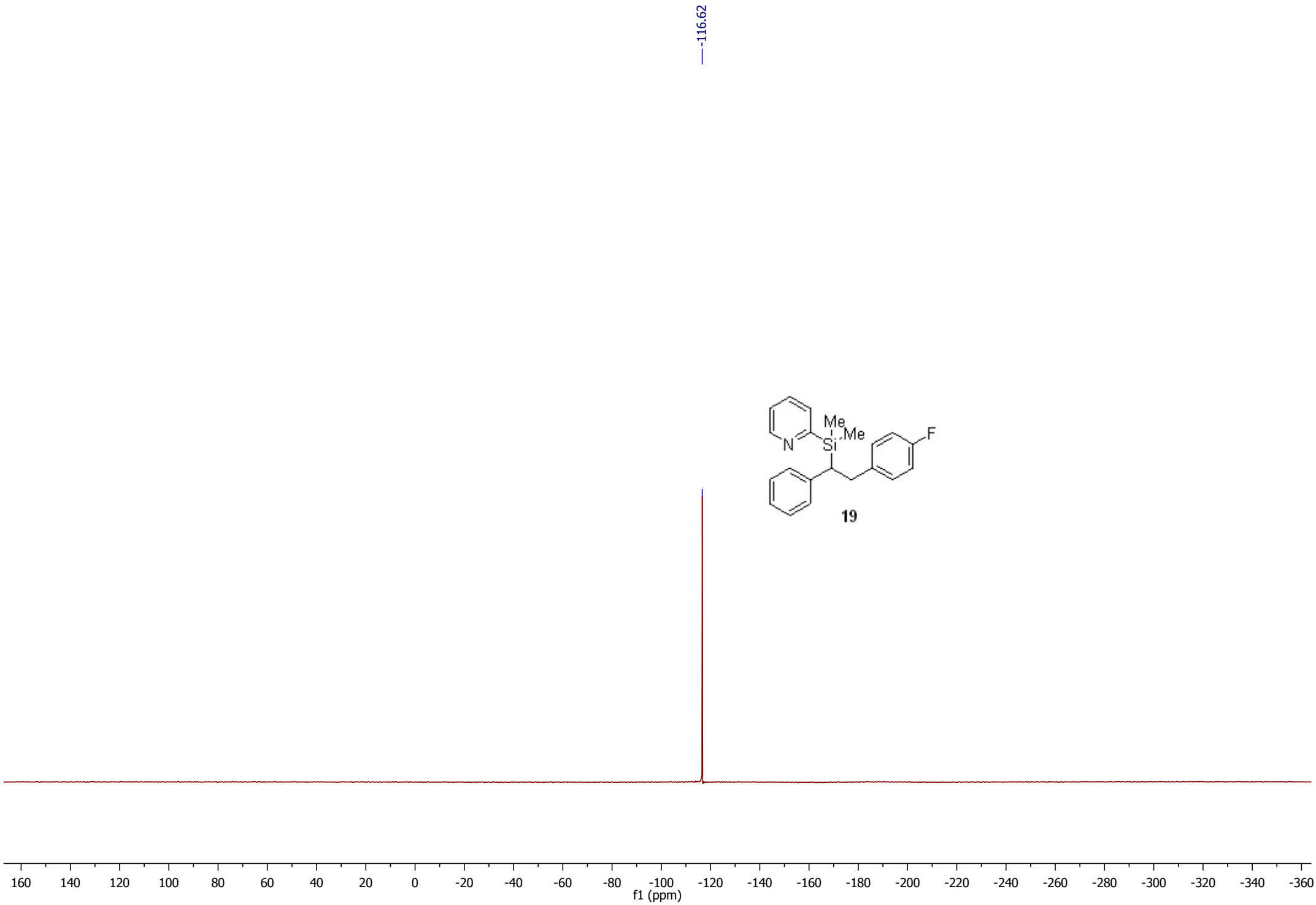
f1 (ppm)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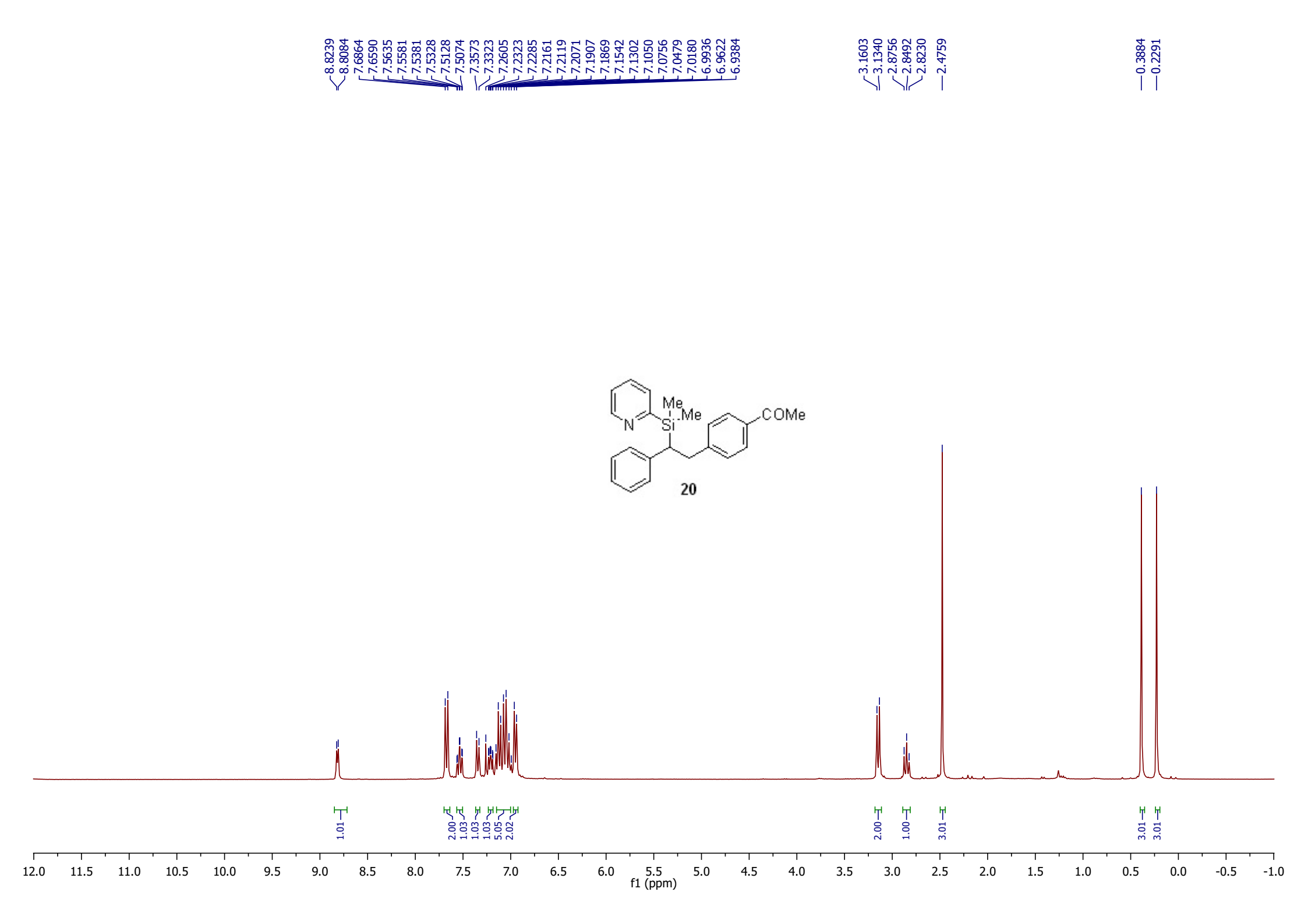
f1 (ppm)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7.2285
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7.2119
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7.1907
7.1869
7.1542
7.1302
7.1050
7.0756
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7.0180
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6.9622
6.9384
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2.8492
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0.2291
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Me
Si
N
COMe
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2.00
1.03
1.03
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2.02
2.00
1.00
3.01
3.01
3.01
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10.0
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4.0
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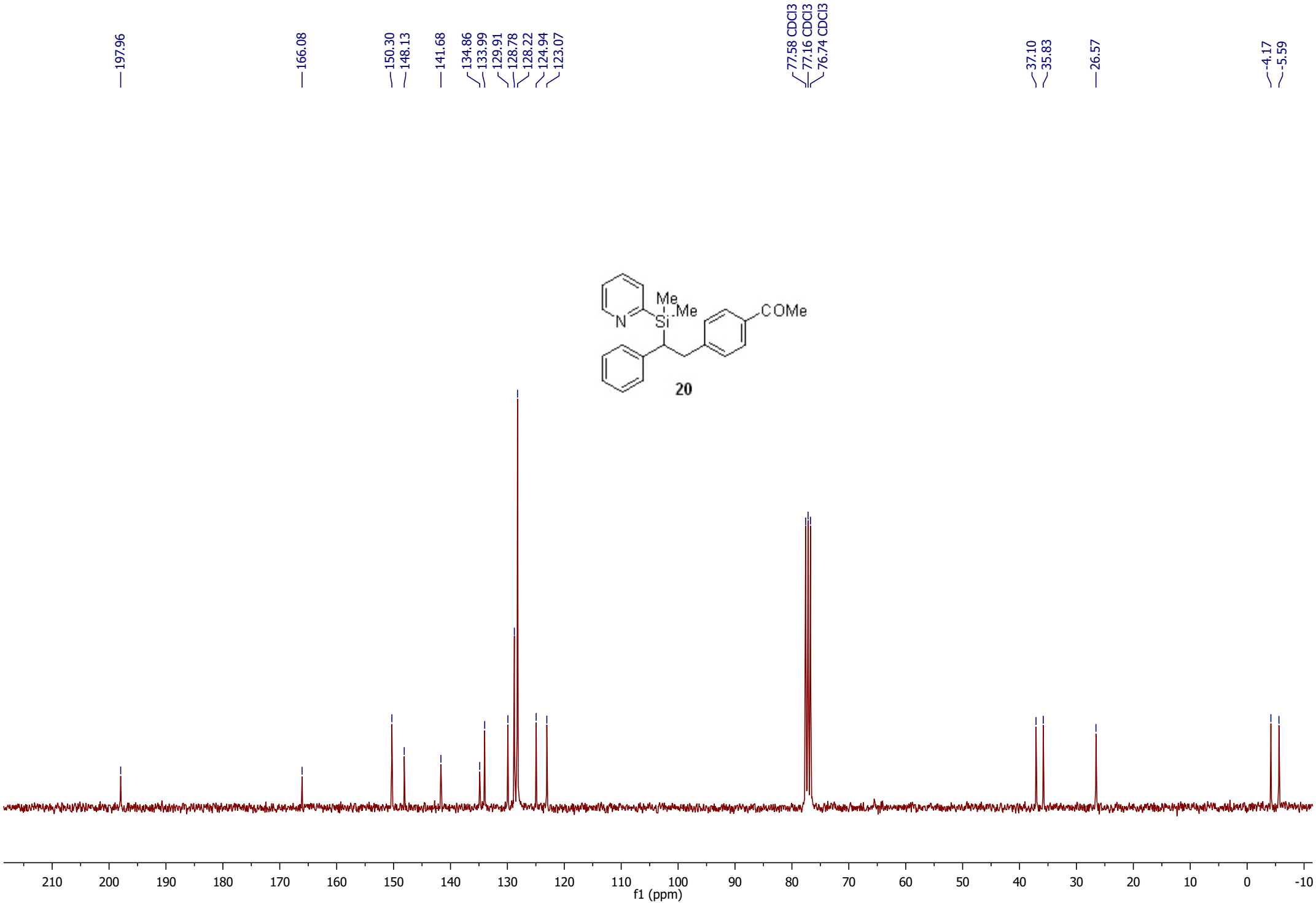
-1.0
f1 (ppm)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77.16 CDCl3
76.74 CDCl3
37.10
35.83
26.57
-4.17
-5.59
Me
Me
Si
N
COMe
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200
190
180
170
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100
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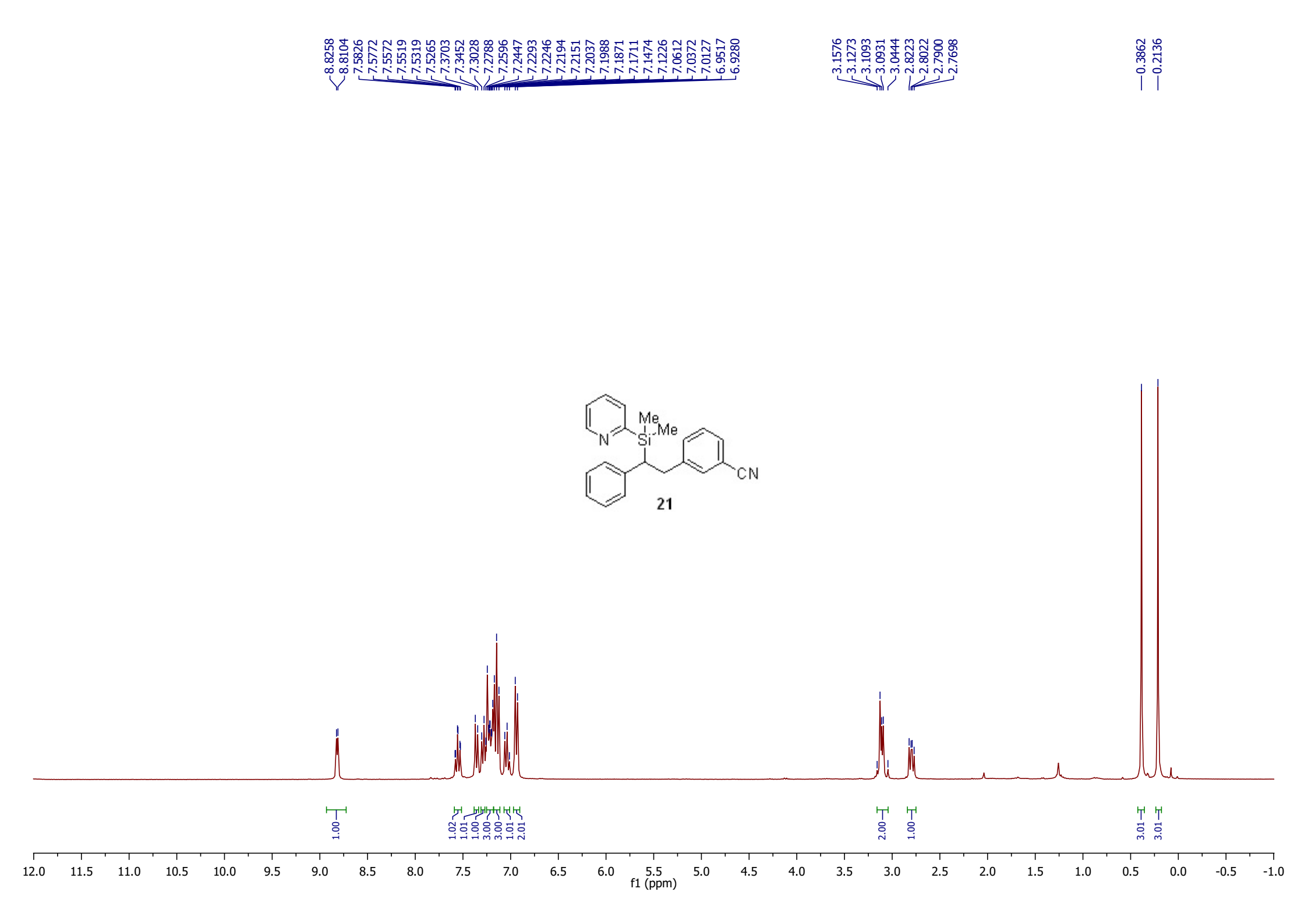
f1 (ppm)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7.2788
7.2596
7.2447
7.2293
7.2246
7.2194
7.2151
7.2037
7.1988
7.1871
7.1711
7.1474
7.1226
7.0612
7.0372
7.0127
6.9517
6.9280
3.1576
3.1273
3.1093
3.0931
3.0444
2.8223
2.8022
2.7900
2.7698
0.3862
0.2136
Me
Me
Si
N
CN
21
1.00
1.02
1.01
1.00
3.00
3.00
1.01
2.01
2.00
1.00
3.01
3.01
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
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2.0
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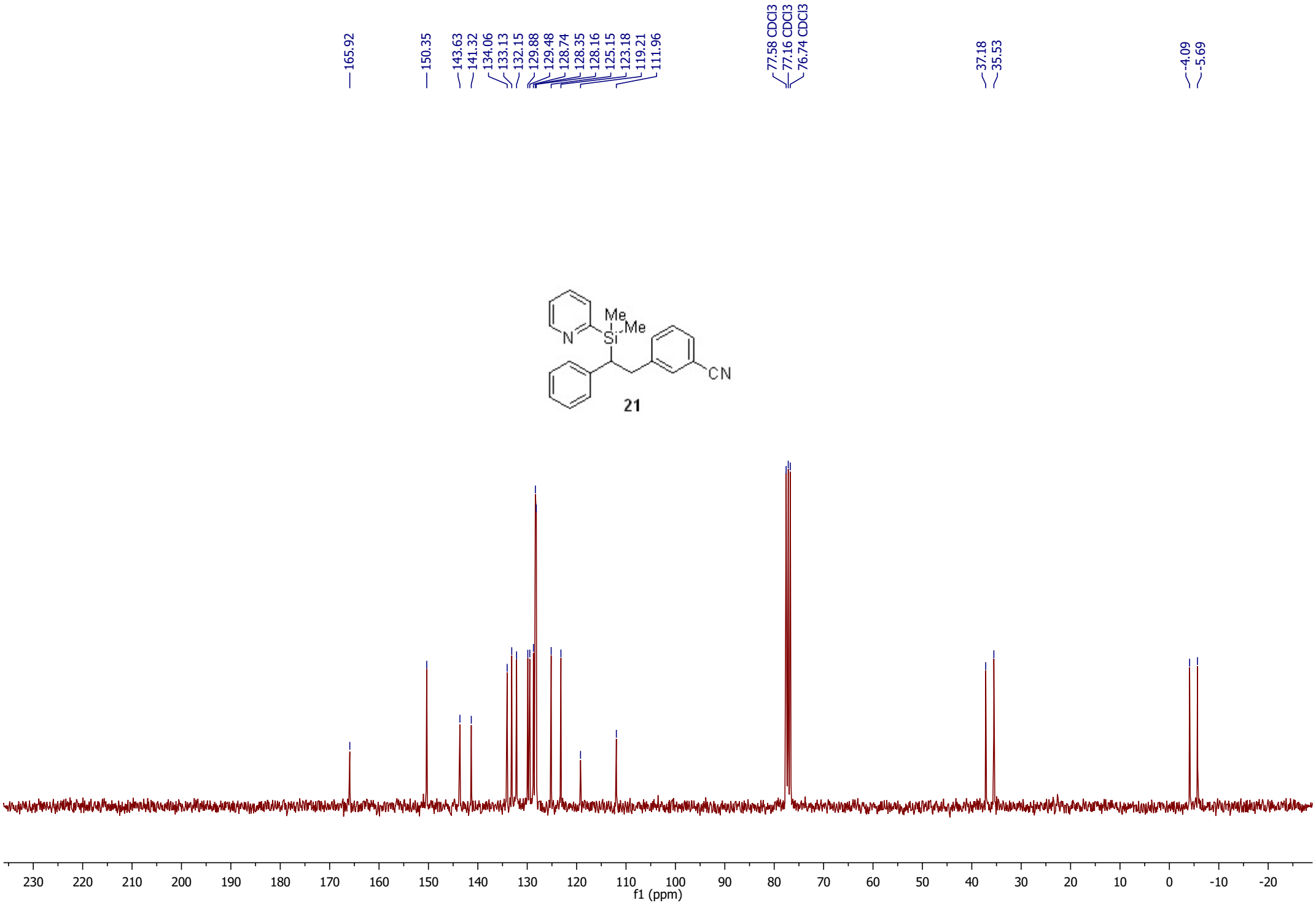
f1 (ppm)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128.16
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123.18
119.21
111.96
77.58 CDCl3
77.16 CDCl3
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35.53
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-5.69
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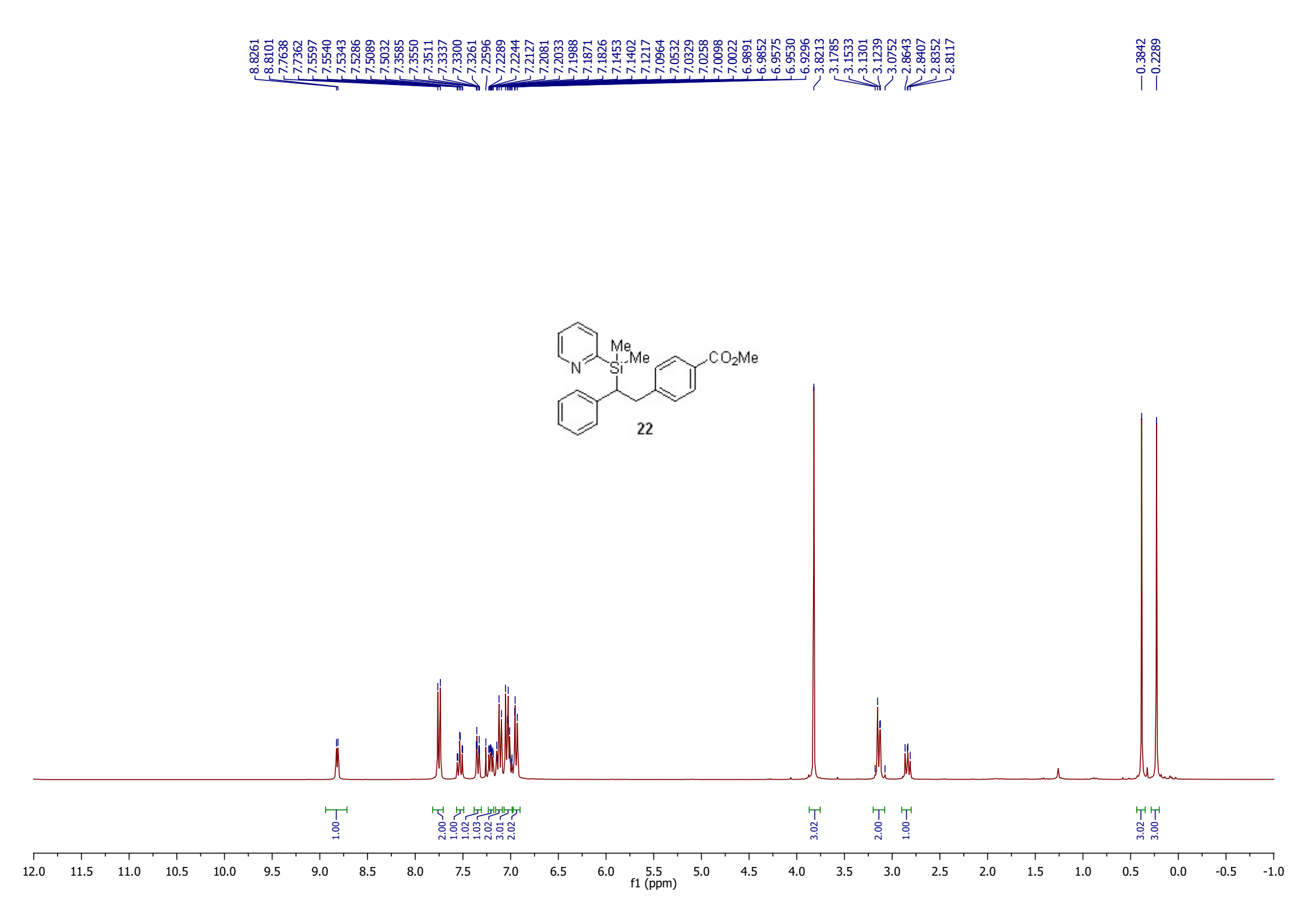
Me
Si
N
CN
21
f1 (ppm)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7.3550
7.3511
7.3337
7.3300
7.3261
7.2596
7.2289
7.2244
7.2127
7.2081
7.2033
7.1988
7.1871
7.1826
7.1453
7.1402
7.1217
7.0964
7.0532
7.0329
7.0258
7.0098
7.0022
6.9891
6.9852
6.9575
6.9530
6.9296
3.8213
3.1785
3.1533
3.1301
3.1239
3.0752
2.8643
2.8407
2.8352
2.8117
0.3842
0.2289
Me
Me
N
Si
CO2Me
22
1.00
2.00
1.00
1.02
1.03
2.02
3.01
2.02
3.02
2.00
1.00
3.02
3.00
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
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0.0
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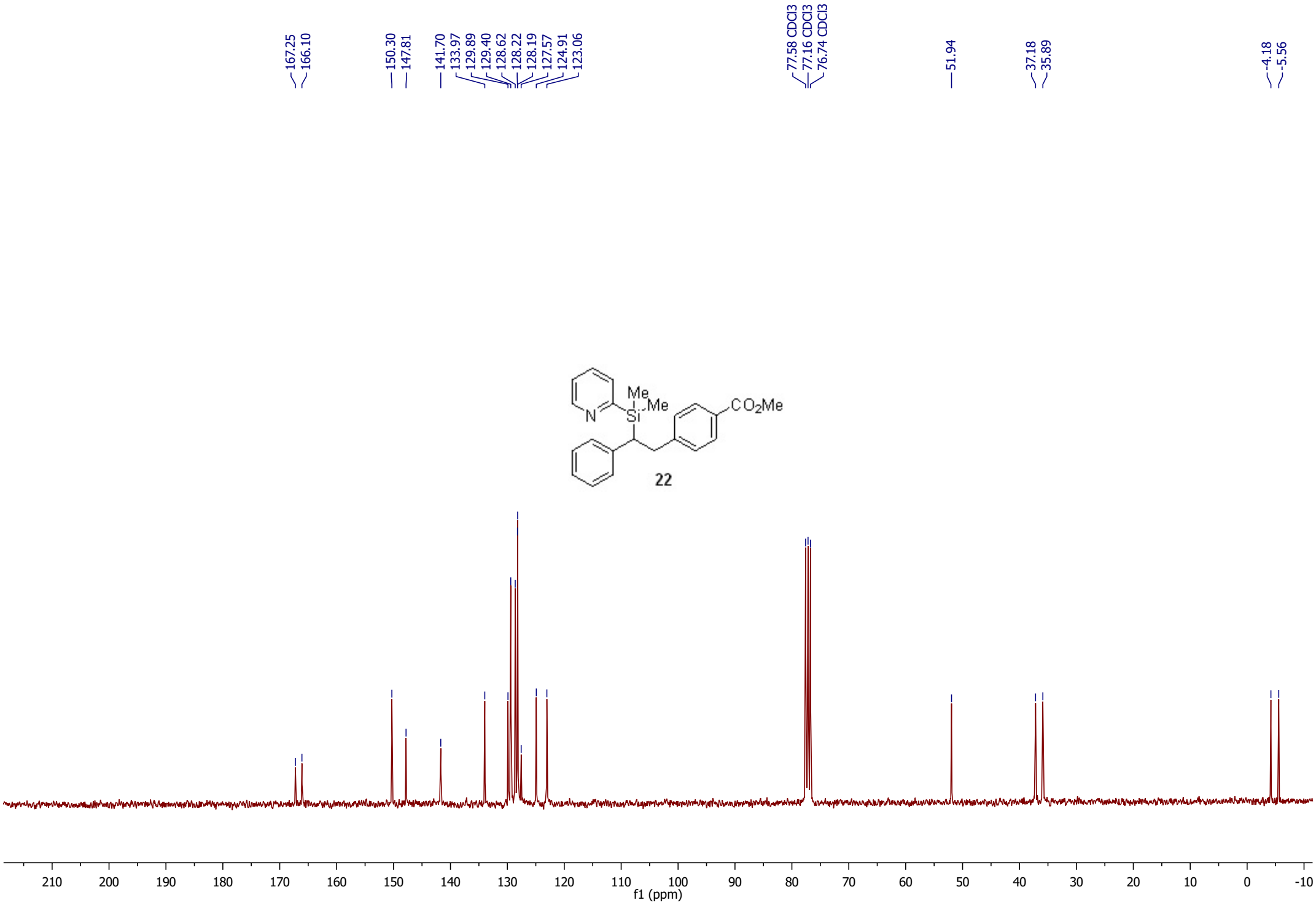
-1.0
f1 (ppm)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128.19
127.57
124.91
123.06
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
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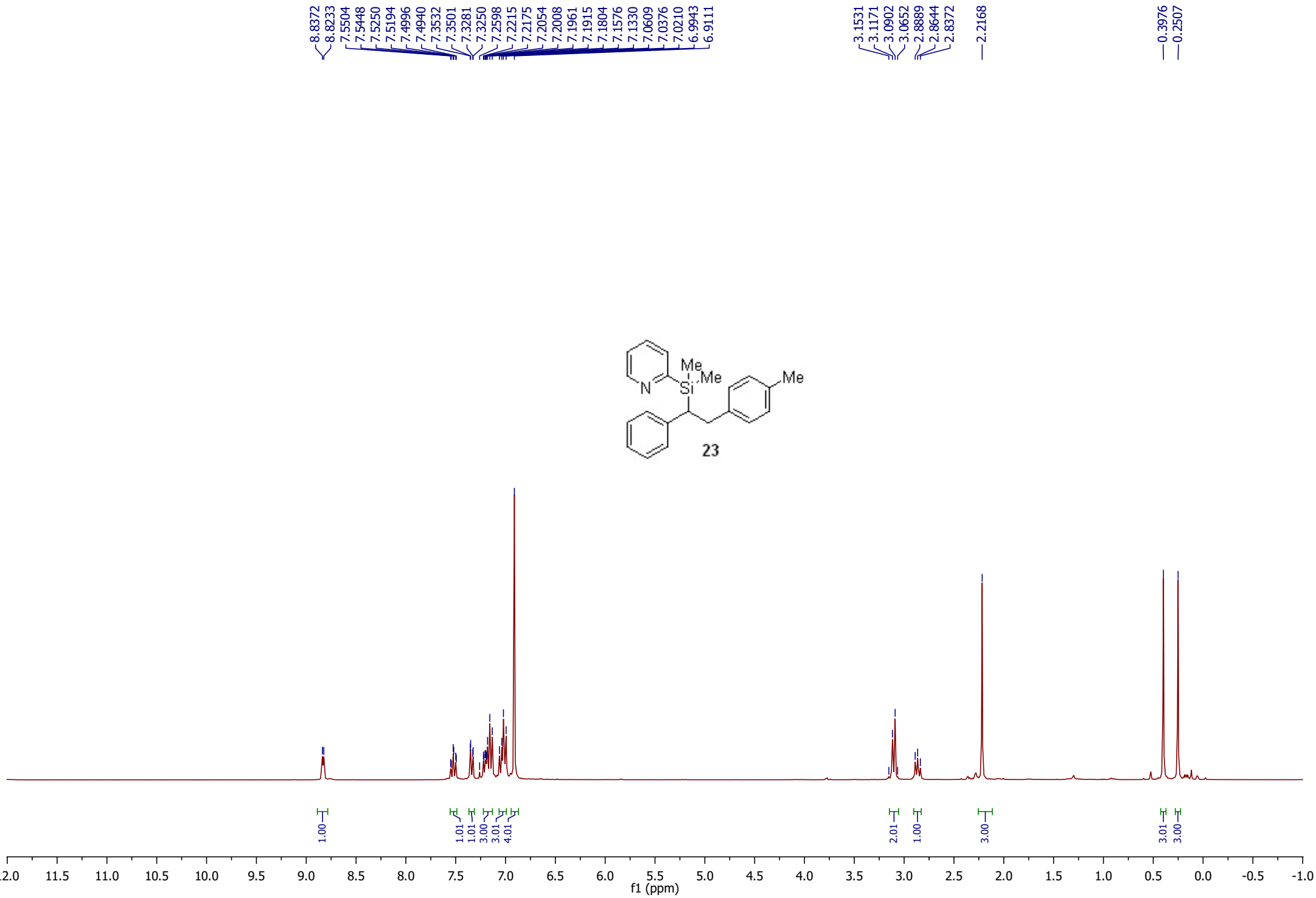
37.18
35.89
-4.18
-5.56
Me
Me
Si
N
CO2Me
22
f1 (ppm)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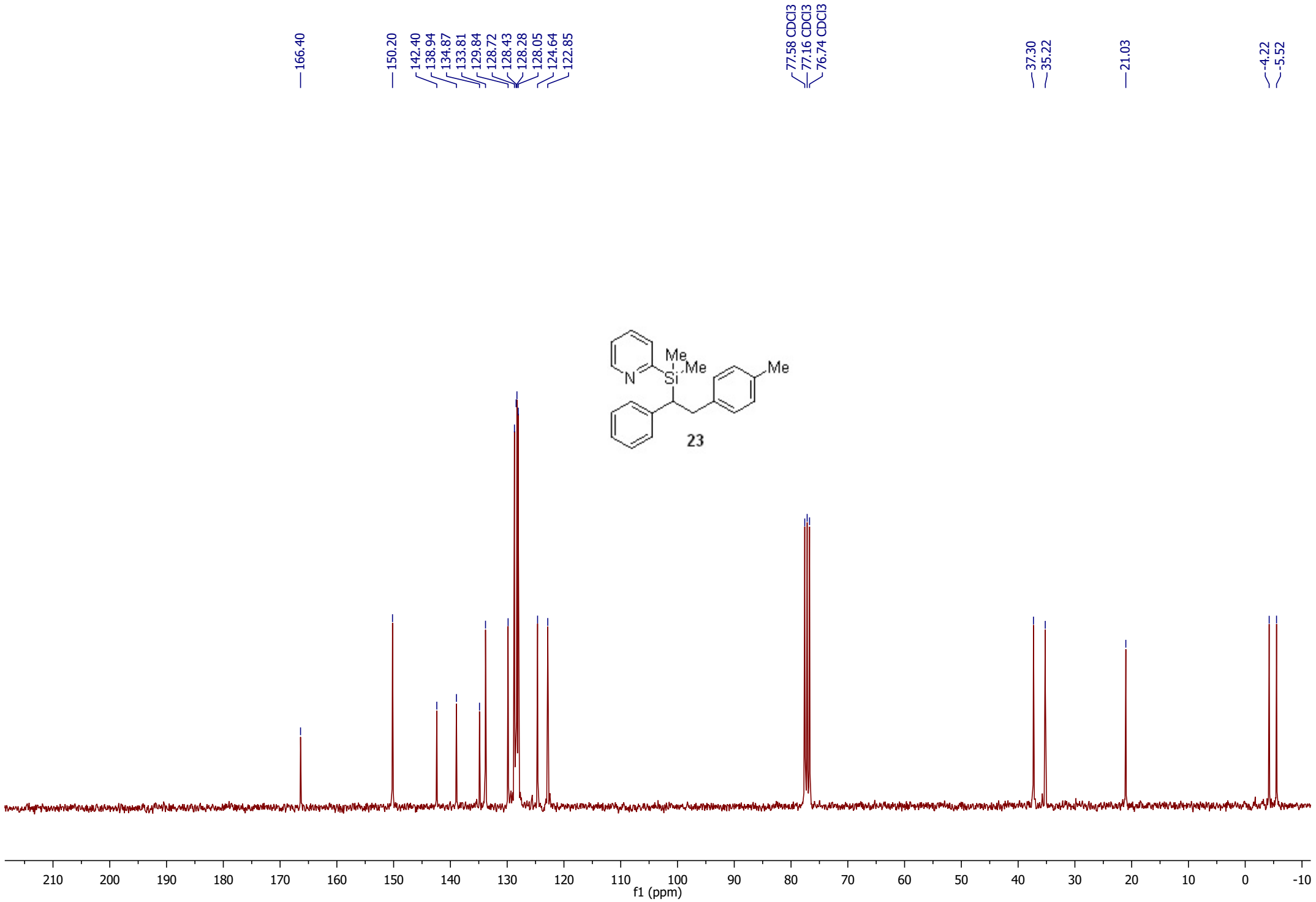
7.3281
7.3250
7.2598
7.2215
7.2175
7.2054
7.2008
7.1961
7.1915
7.1804
7.1576
7.1330
7.0609
7.0376
7.0210
6.9943
6.9111
3.1531
3.1171
3.0902
3.0652
2.8889
2.8644
2.8372
2.2168
0.3976
0.2507
Me
Me
Si
N
Me
23
1.00
1.01
1.01
3.00
3.01
4.01
2.01
1.00
3.00
3.01
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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)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128.28
128.05
124.64
122.85
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
37.30
35.22
21.03
-4.22
-5.52
Me
Me
Me
N
Si
23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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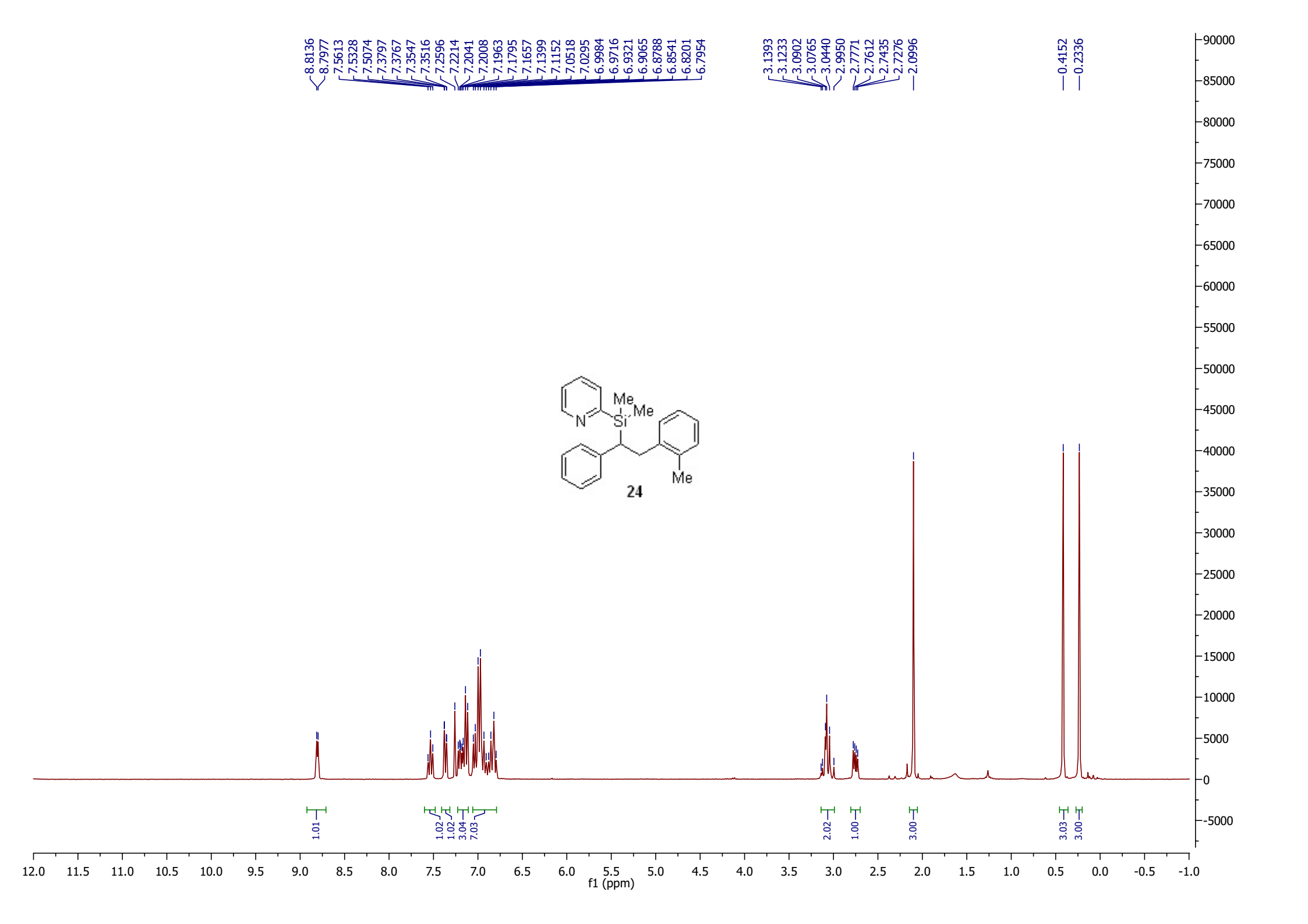
40
30
20
10
0
-10
f1 (ppm)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7.2214
7.2041
7.2008
7.1963
7.1795
7.1657
7.1399
7.1152
7.0518
7.0295
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6.9716
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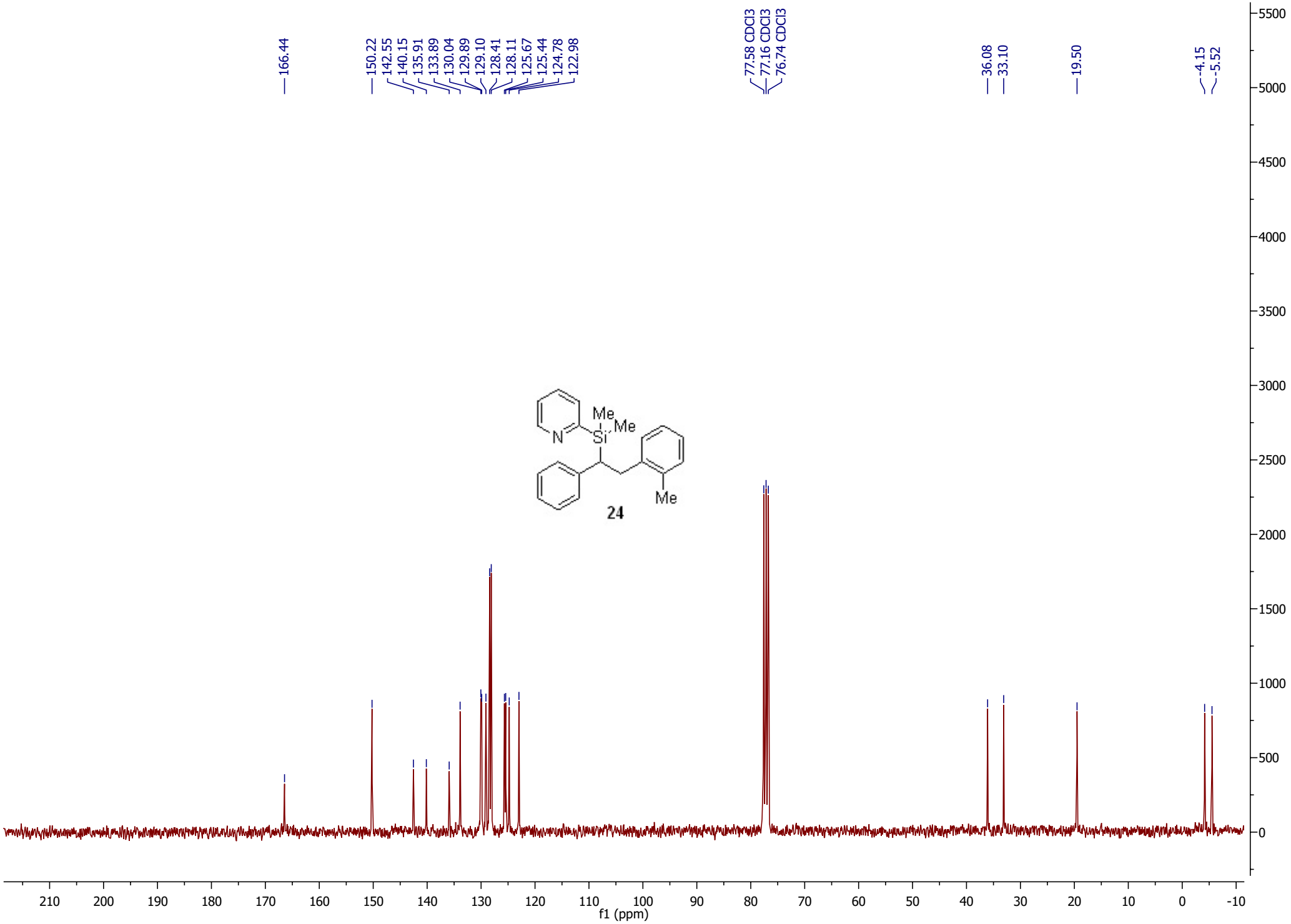
6.7954
3.1393
3.1233
3.0902
3.0765
3.0440
2.9950
2.7771
2.7612
2.7435
2.7276
2.0996
0.4152
0.2336
Me
Me
N
Si
Me
24
1.01
1.02
1.02
3.04
7.03
2.02
1.00
3.00
3.03
3.00
f1 (ppm)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129.89
129.10
128.41
128.11
125.67
125.44
124.78
122.98
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
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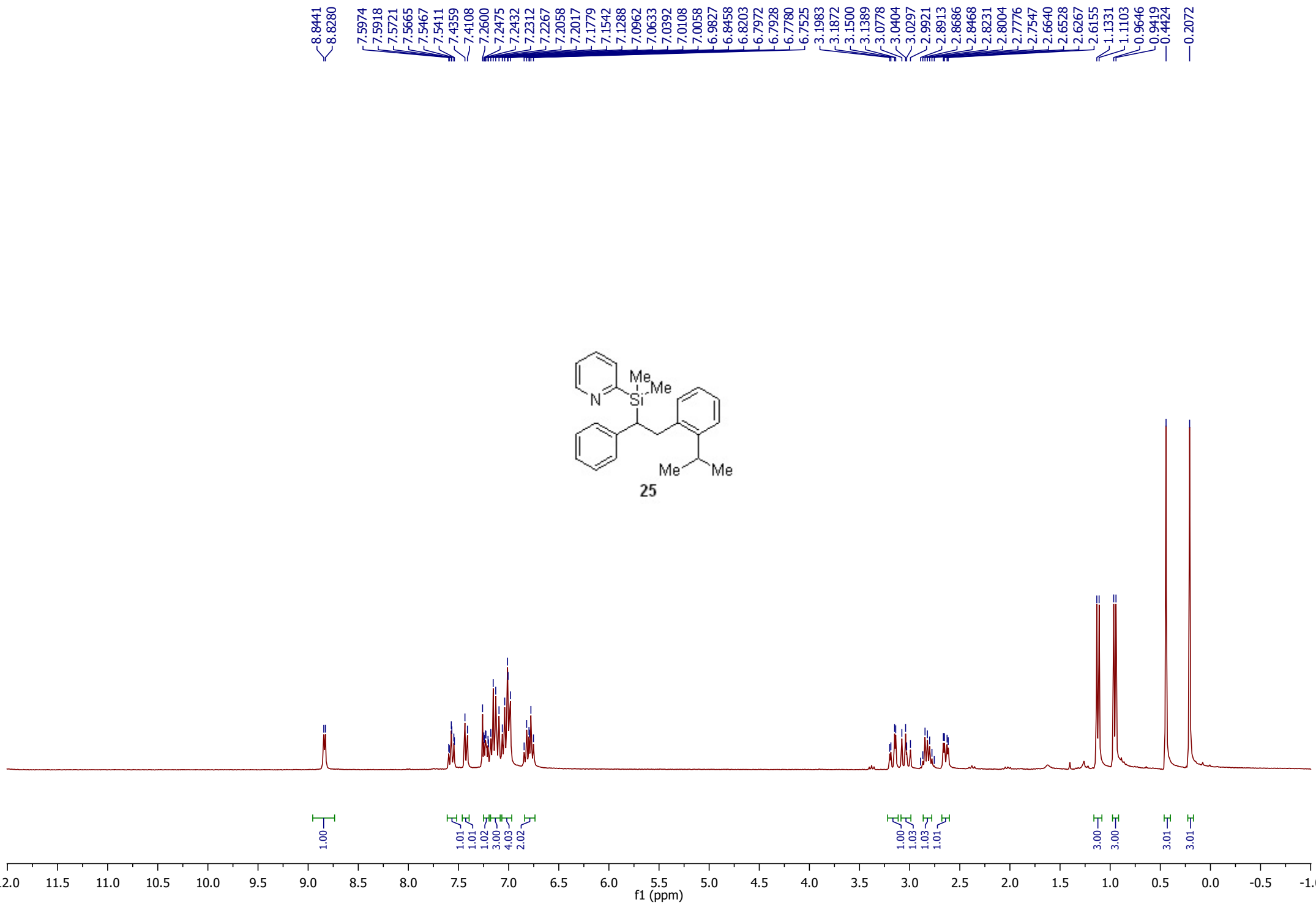
33.10
19.50
-4.15
-5.52
Me
Me
N
Si
Me
24
f1 (ppm)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7.2600
7.2475
7.2432
7.2312
7.2267
7.2058
7.2017
7.1779
7.1542
7.1288
7.0962
7.0633
7.0392
7.0108
7.0058
6.9827
6.8458
6.8203
6.7972
6.7928
6.7780
6.7525
3.1983
3.1872
3.1500
3.1389
3.0778
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3.0297
2.9921
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2.8468
2.8231
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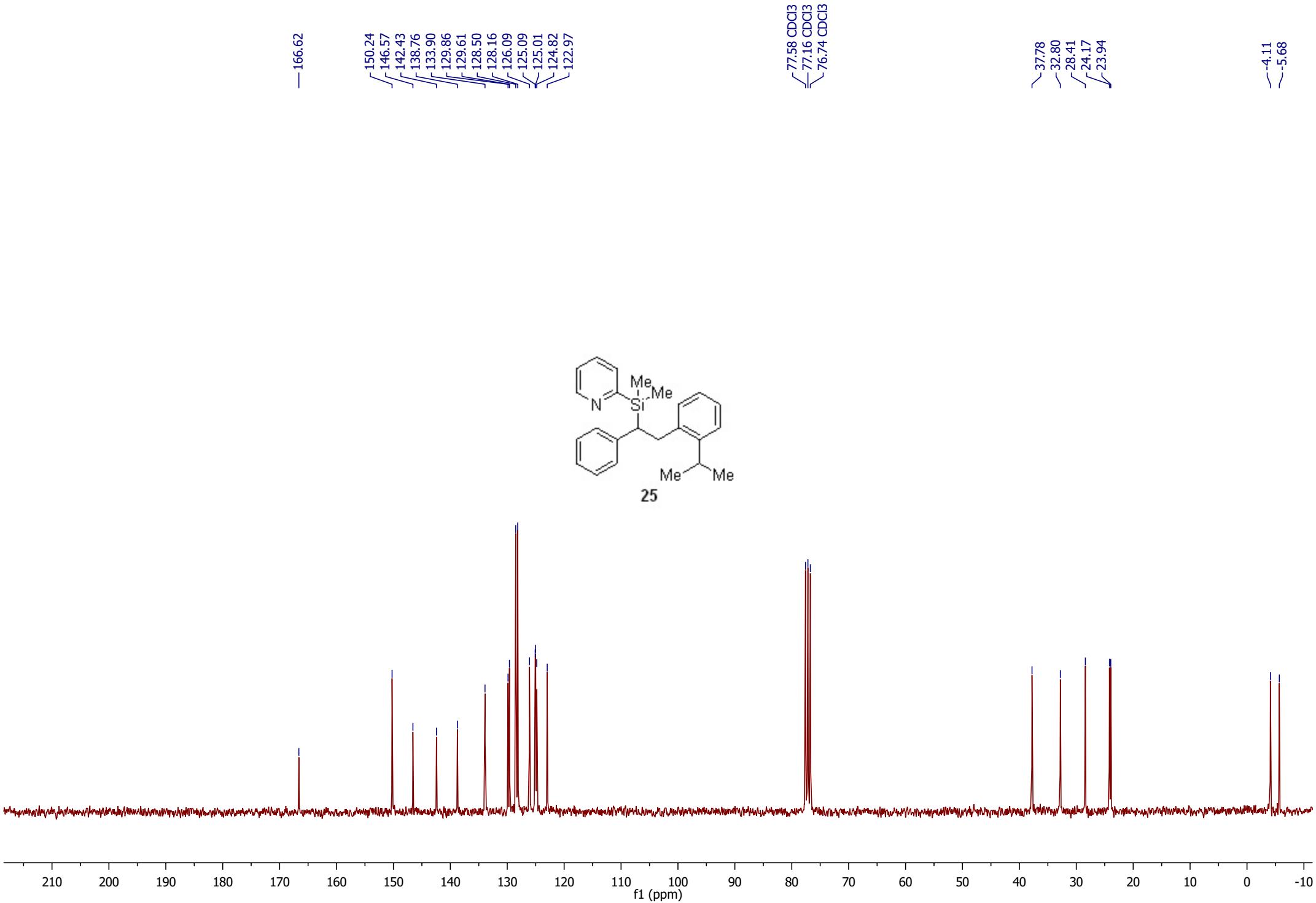
2.7776
2.7547
2.6640
2.6528
2.6267
2.6155
1.1331
1.1103
0.9646
0.9419
0.4424
0.2072
Me
Me
N
Si
Me
Me
25
1.00
1.01
1.01
1.02
3.00
4.03
2.02
1.00
1.03
1.03
1.01
3.00
3.00
3.01
3.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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129.61
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128.16
126.09
125.09
125.01
124.82
122.97
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
37.78
32.80
28.41
24.17
23.94
-4.11
-5.68
Me
Me
N
Si
Me
Me
25
210
200
190
180
170
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120
110
100
90
80
70
60
50
40
30
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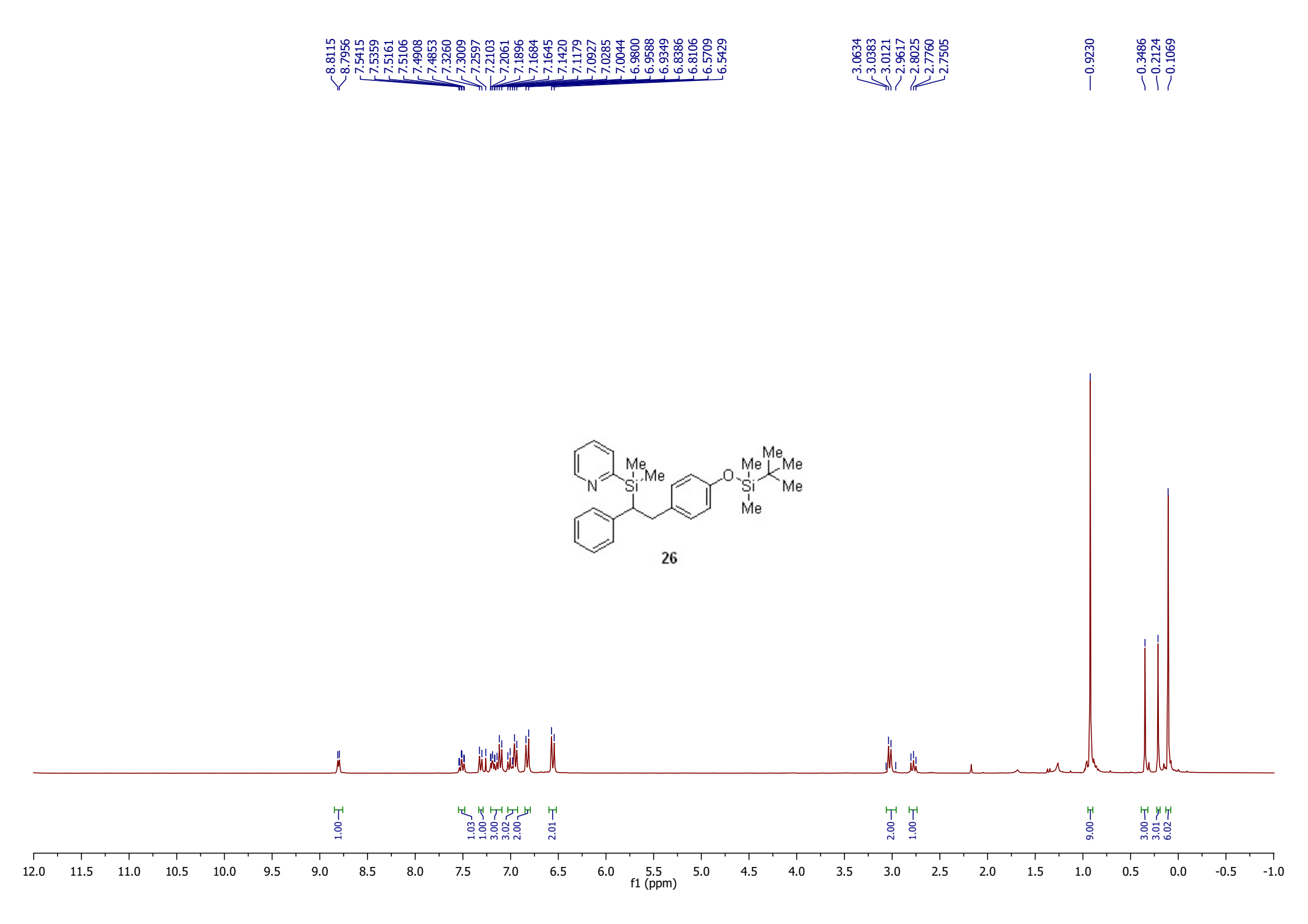
-10
f1 (ppm)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7.2597
7.2103
7.2061
7.1896
7.1684
7.1645
7.1420
7.1179
7.0927
7.0285
7.0044
6.9800
6.9588
6.9349
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6.8106
6.5709
6.5429
3.0634
3.0383
3.0121
2.9617
2.8025
2.7760
2.7505
0.9230
0.3486
0.2124
0.1069
Me
Me
N
Si
O
Si
Me
Me
Me
Me
Me
26
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1.03
1.00
3.00
3.02
2.00
2.01
2.00
1.00
9.00
3.00
3.01
6.02
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
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2.5
2.0
1.5
1.0
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0.0
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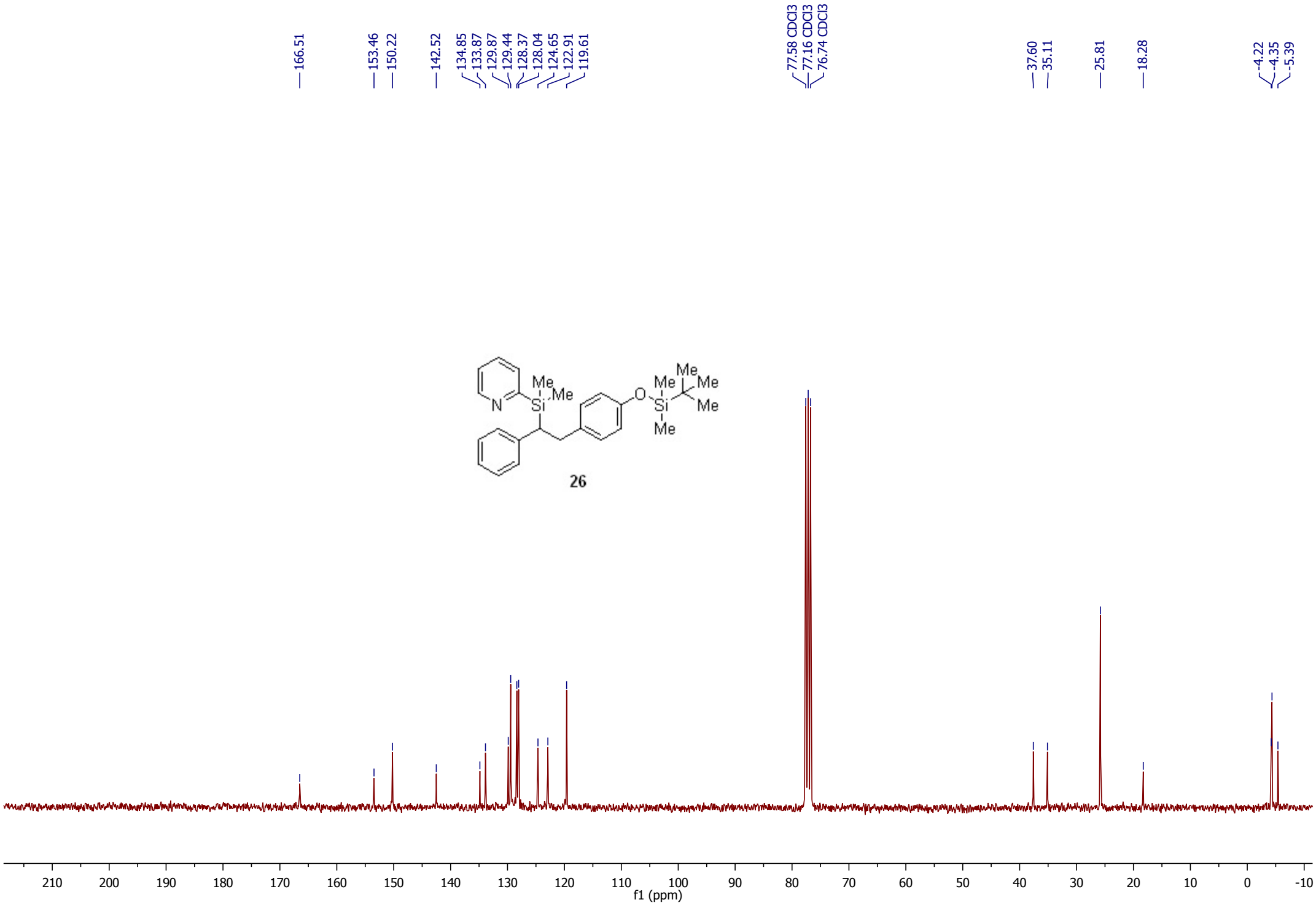
-1.0
f1 (ppm)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128.04
124.65
122.91
119.61
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
37.60
35.11
25.81
18.28
-4.22
-4.35
-5.39
N
Si
Me
Me
O
Si
Me
Me
Me
Me
Me
26
210
200
190
180
170
160
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140
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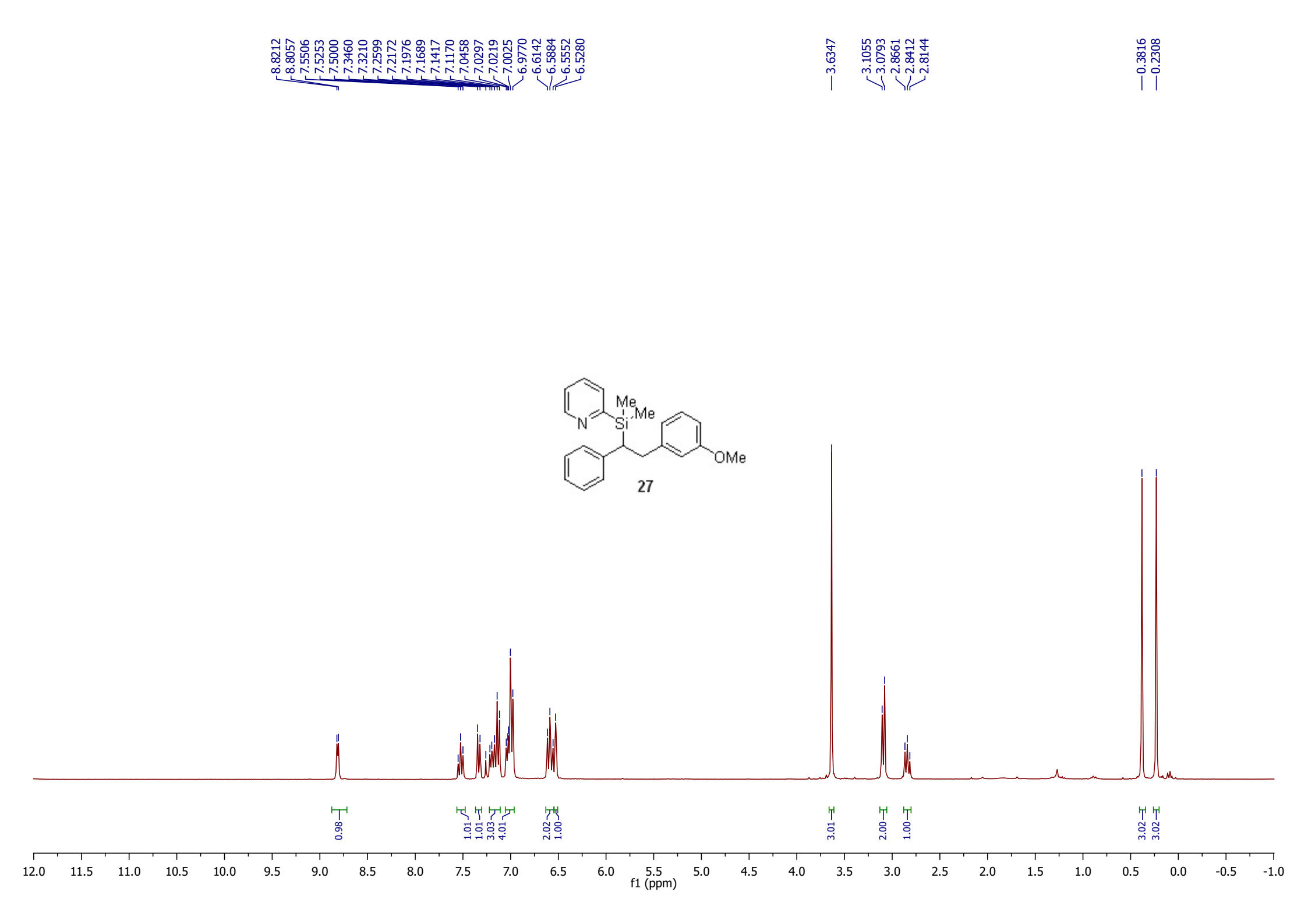
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2599
7.2172
7.1976
7.1689
7.1417
7.1170
7.0458
7.0297
7.0219
7.0025
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6.6142
6.5884
6.5552
6.5280
3.6347
3.1055
3.0793
2.8661
2.8412
2.8144
0.3816
0.2308
Me
Me
Si
N
OMe
27
0.98
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1.01
3.03
4.01
2.02
1.00
3.01
2.00
1.00
3.02
3.02
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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
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2.5
2.0
1.5
1.0
0.5
0.0
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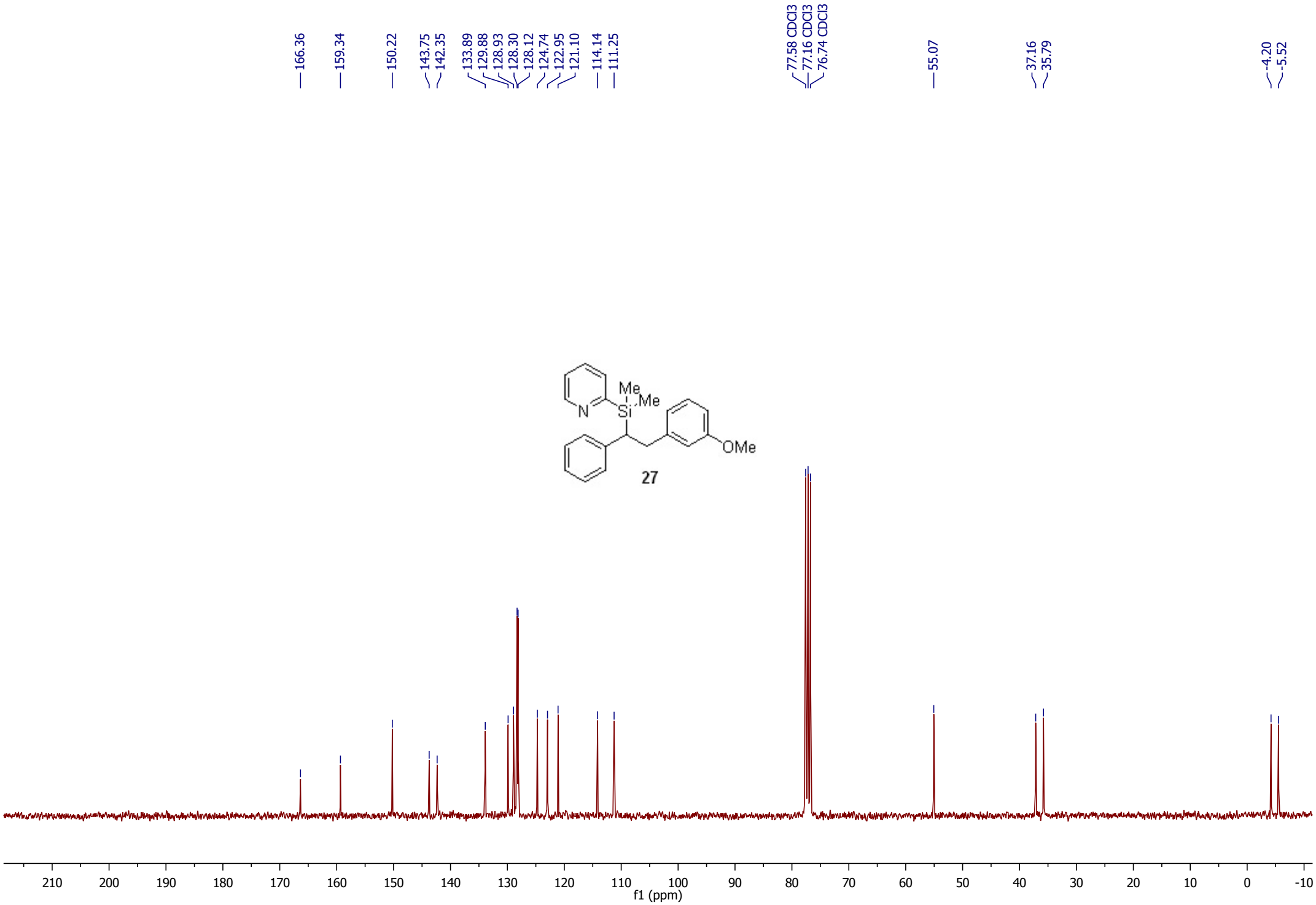
-1.0
f1 (ppm)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128.30
128.12
124.74
122.95
121.10
114.14
111.25
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
55.07
37.16
35.79
-4.20
-5.52
Me
Me
Si
N
OMe
27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

8.8137
8.7978
7.5362
7.5305
7.5109
7.5052
7.4856
7.4798
7.3758
7.3723
7.3506
7.3472
7.2605
7.1997
7.1952
7.1836
7.1790
7.1744
7.1697
7.1575
7.1549
7.1296
7.1155
7.1055
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7.0417
7.0323
7.0165
6.9910
6.9099
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6.8852
6.8805
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6.6333
3.7092
3.2140
3.1990
3.1662
3.1513
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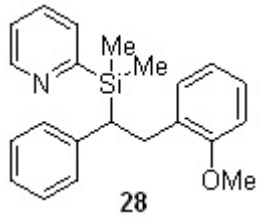
0.2458



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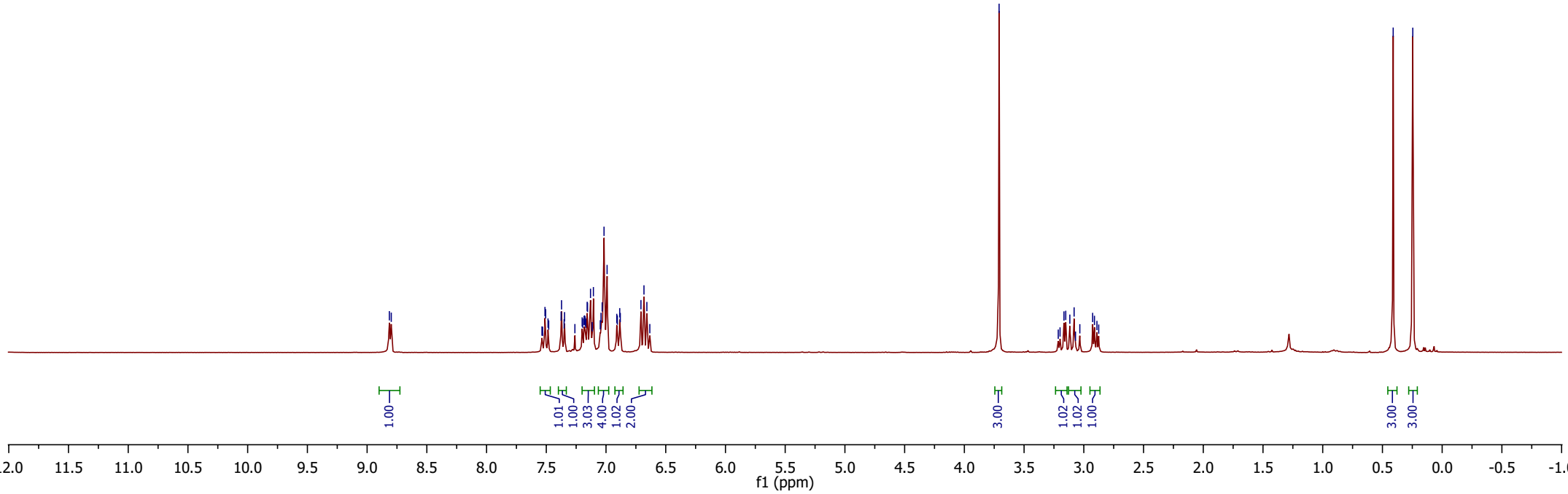

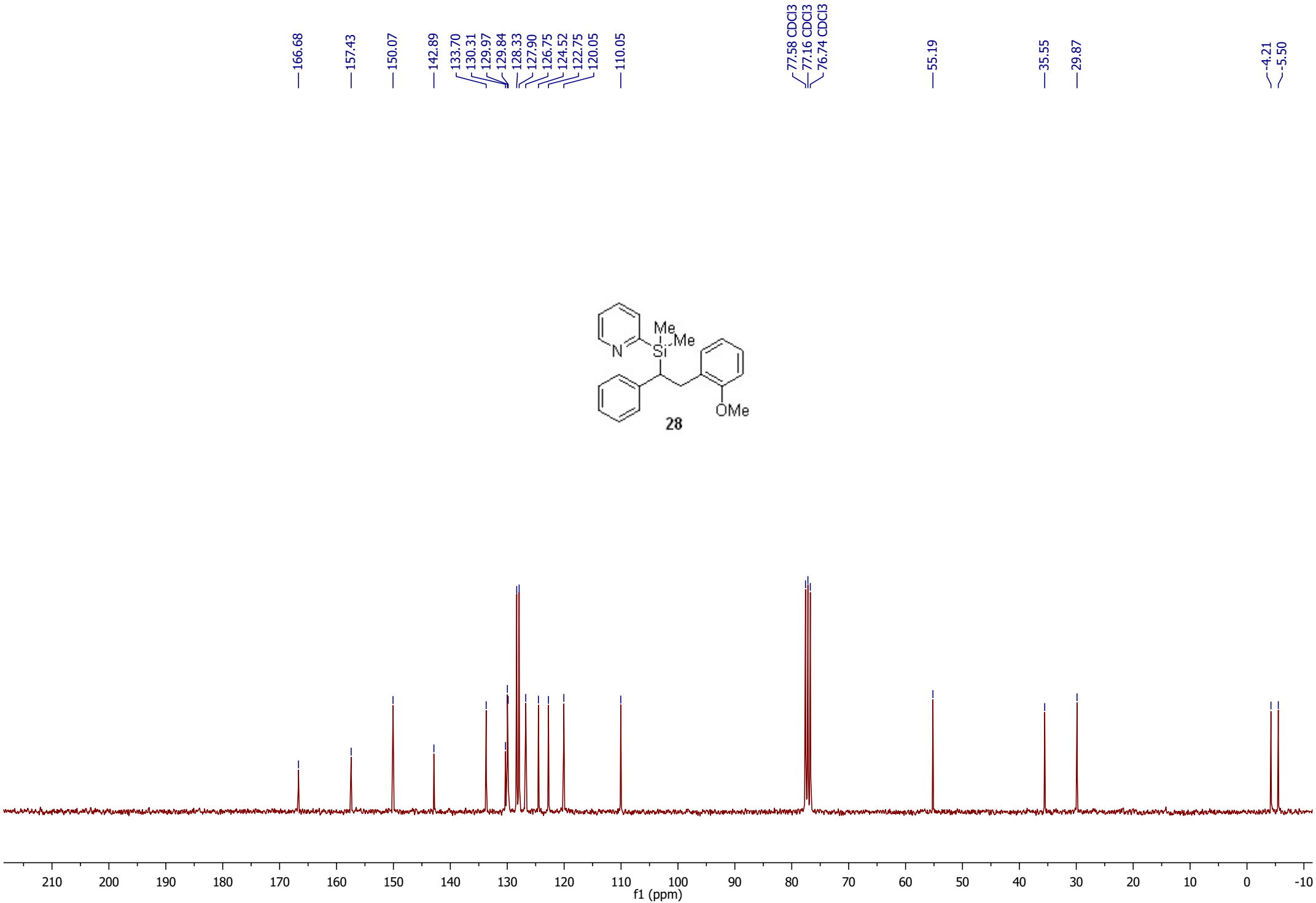
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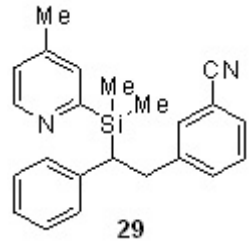
127.90
126.75
124.52
122.75
120.05
110.05
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
55.19
35.55
29.87
-4.21
-5.50
Me
Me
Si
N
OMe
28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

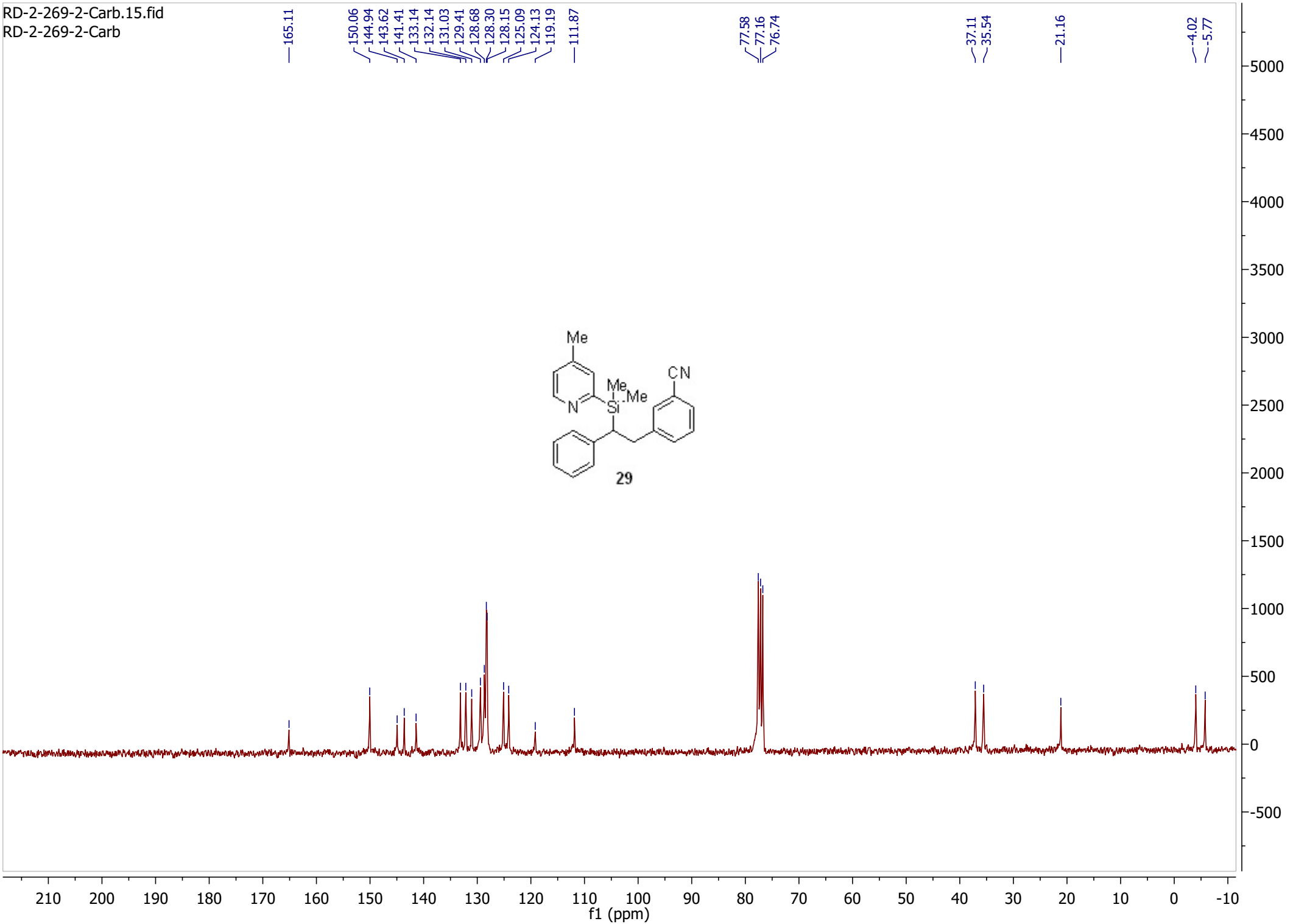
RD-2-269-2-Proton.3.fid
RD-2-269-2-Proton



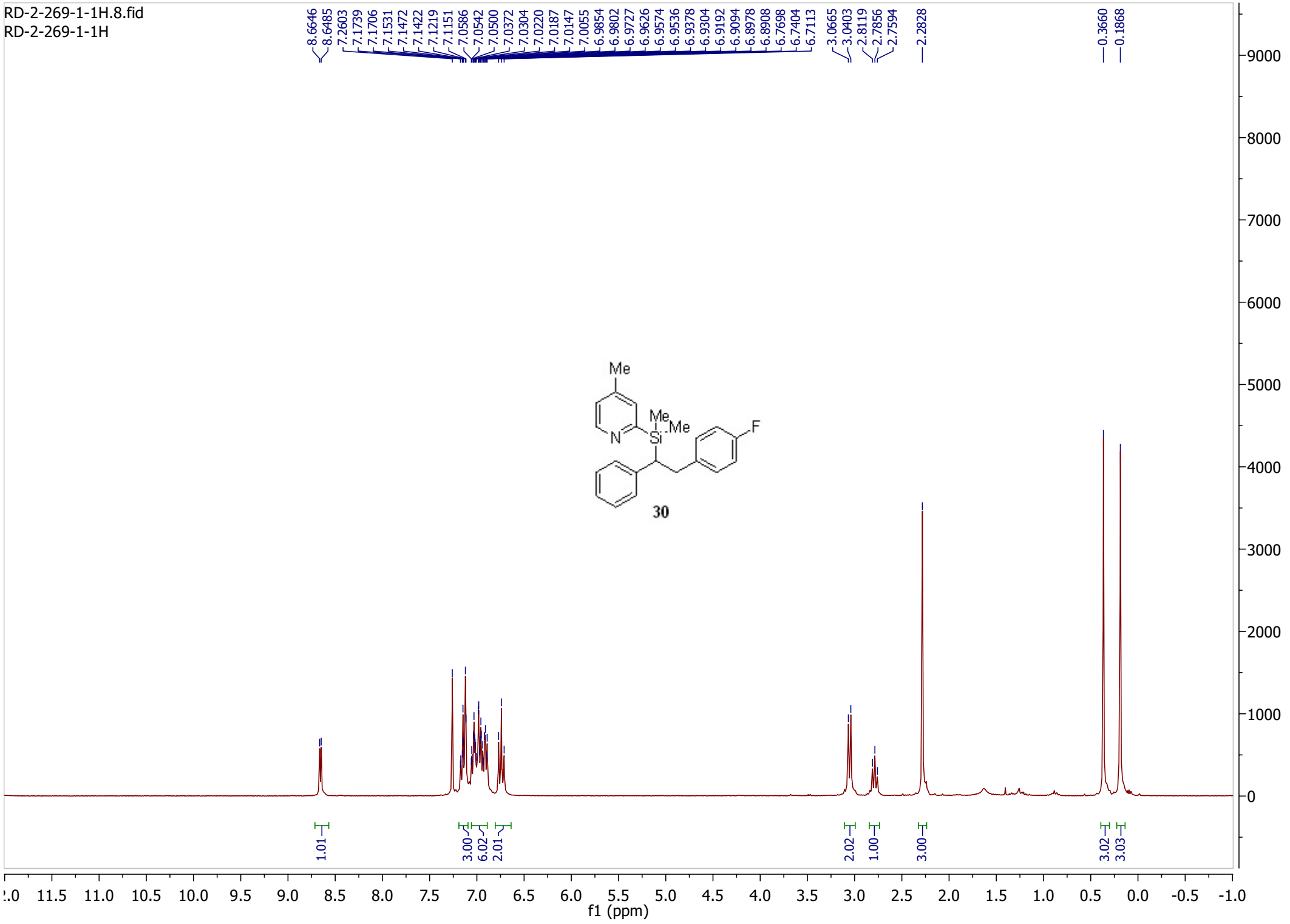
29

f1 (ppm)

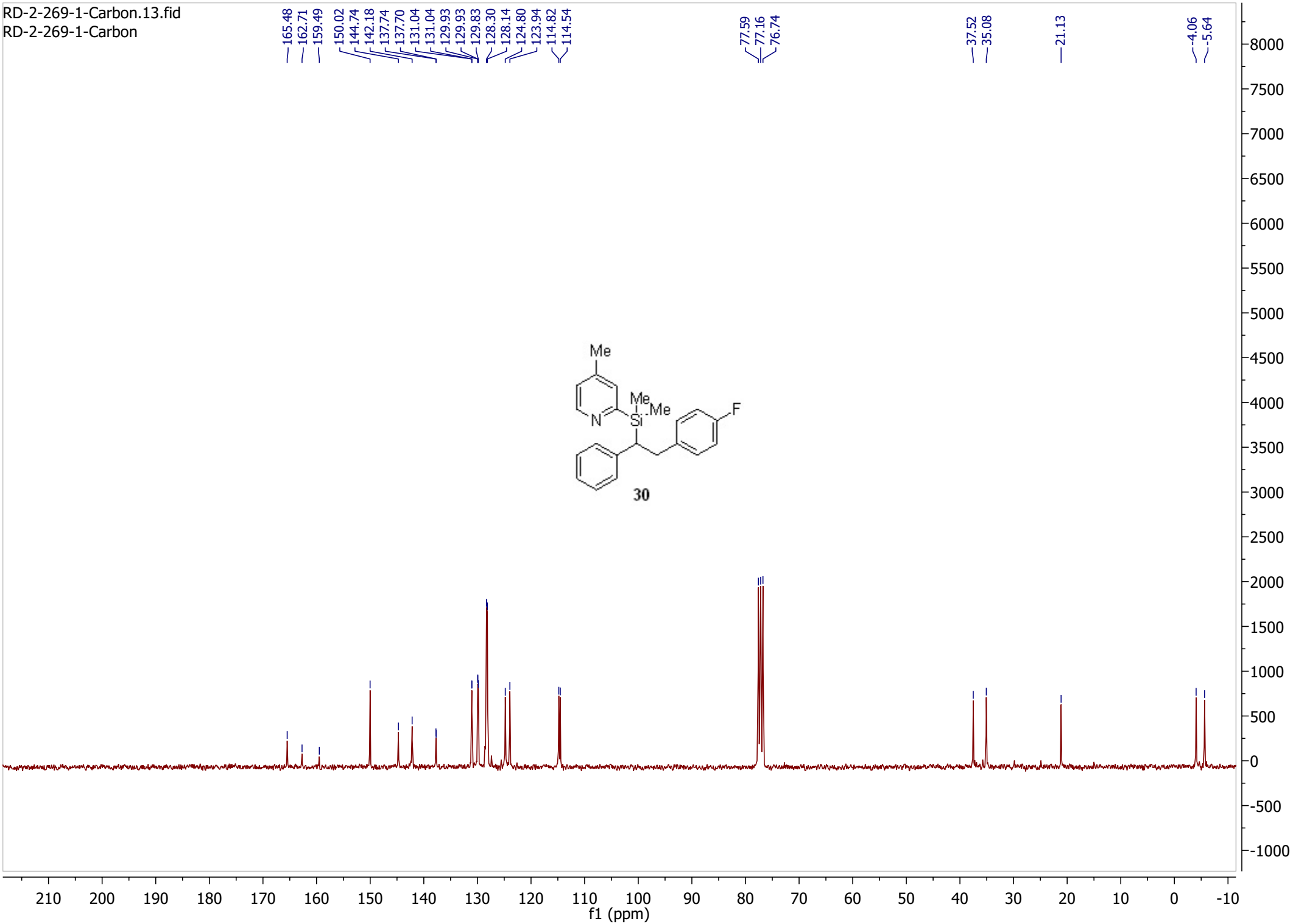
RD-2-269-2-Carb.15.fid
RD-2-269-2-Carb



RD-2-269-1-1H.8.fid
RD-2-269-1-1H

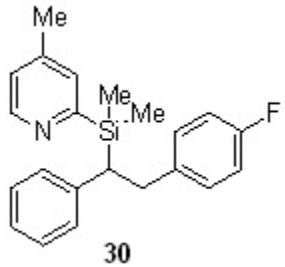


RD-2-269-1-Carbon.13.fid
RD-2-269-1-Carbon



RD-2-269-1-F.5.fid
RD-2-269-1-F

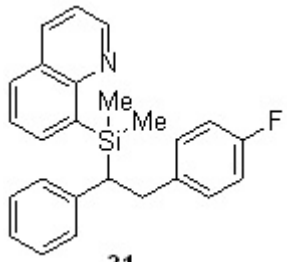
-116.77



30

f1 (ppm)

ST-8-72-1H.5.fid
ST-8-72-1H

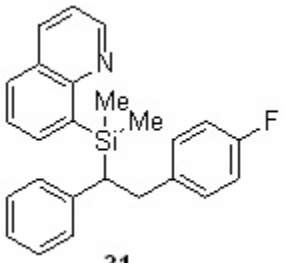


31

f1 (ppm)

ST-8-72-13C.1.fid
ST-8-72-13C

162.48
159.26
152.62
149.11
143.24
139.58
138.21
138.18
136.74
136.24
129.80
129.70
129.40
128.36
127.90
127.79
126.07
124.41
120.89
114.53
114.25
77.58
77.15
76.73
37.66
35.20
-2.56
-4.38

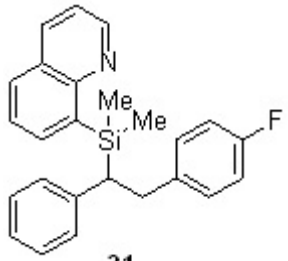


31

f1 (ppm)

ST-8-72-19F.4.fid
ST-8-72-19F

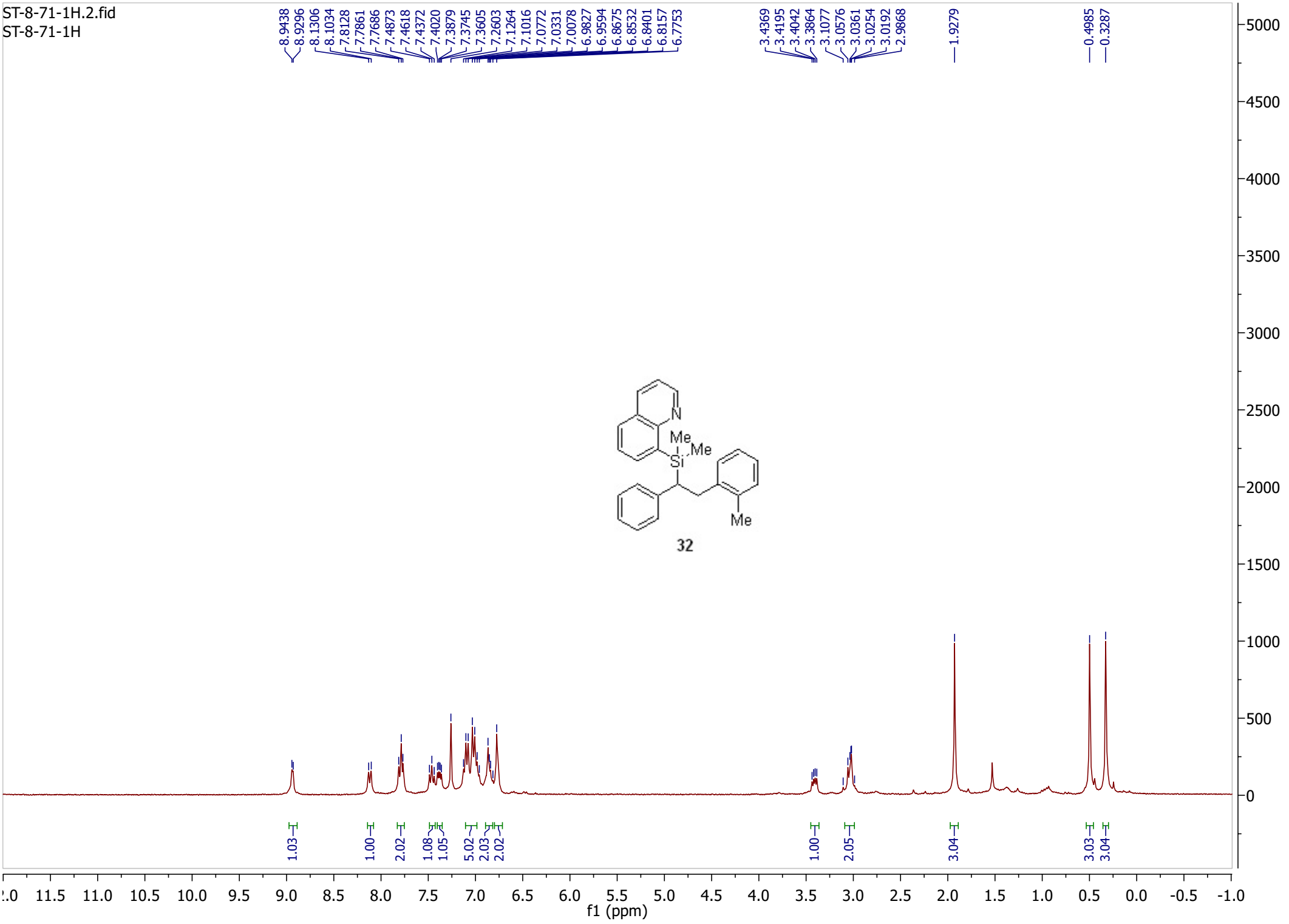
-117.35



31

f1 (ppm)

ST-8-71-1H.2.fid
ST-8-71-1H



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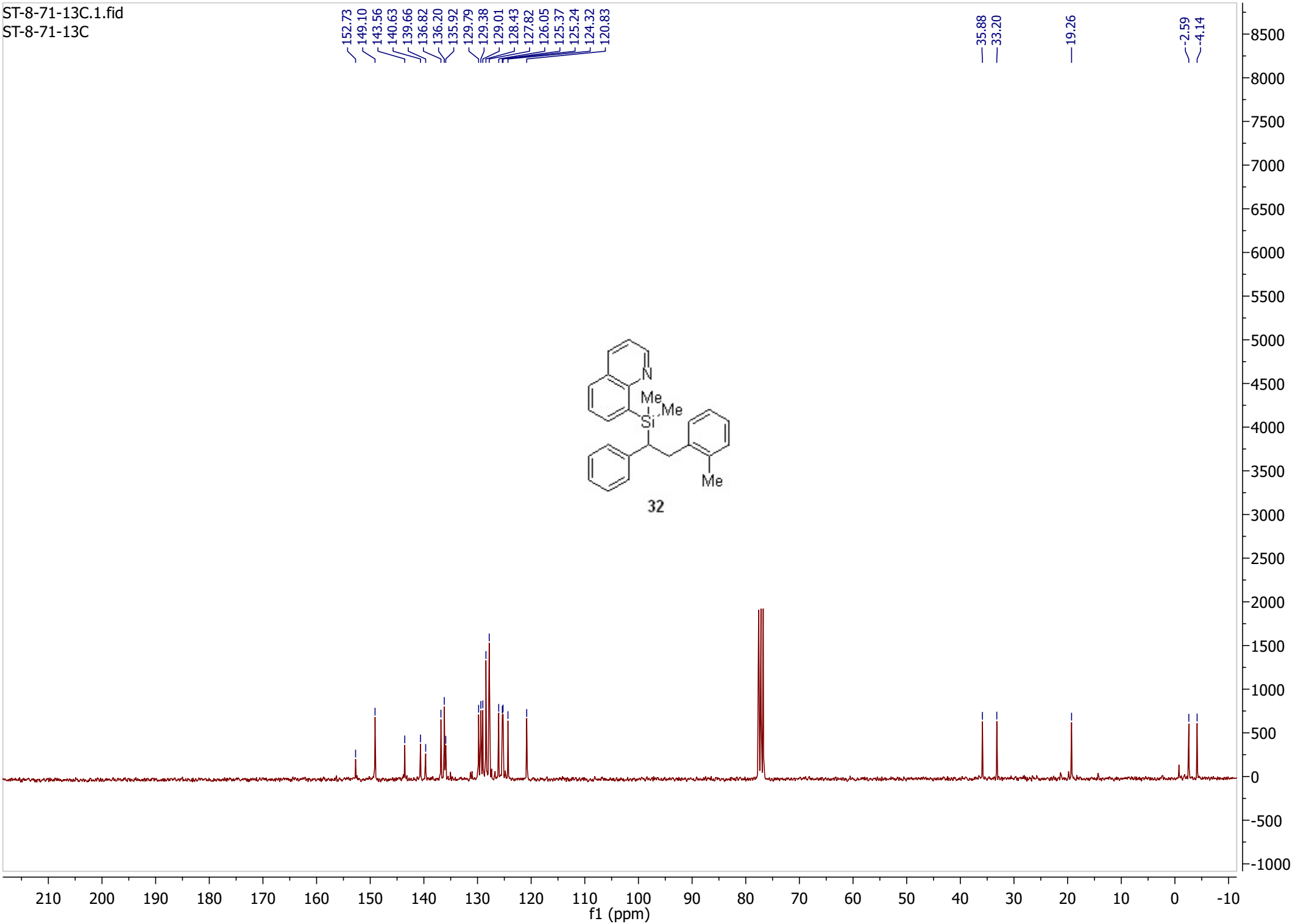

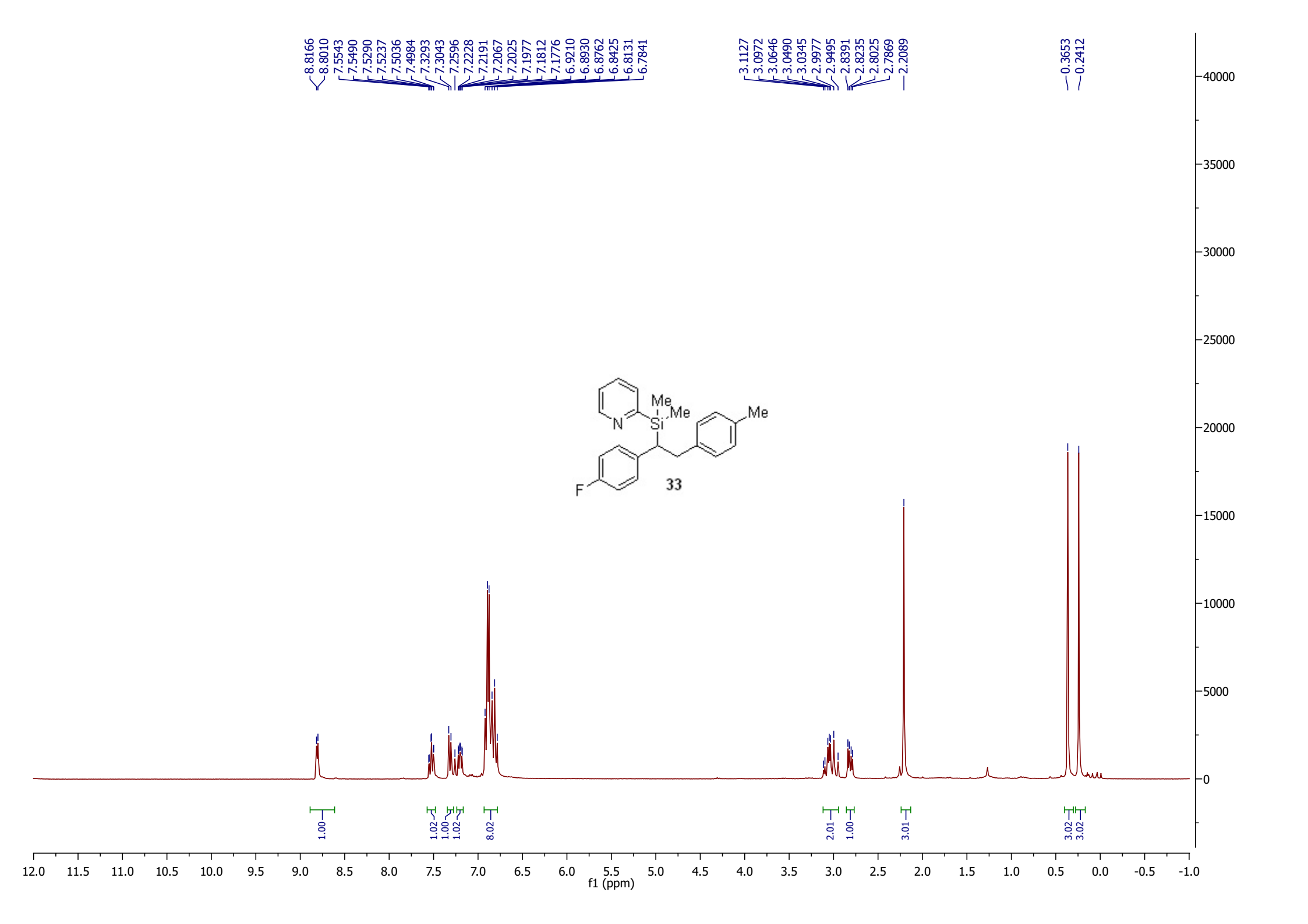
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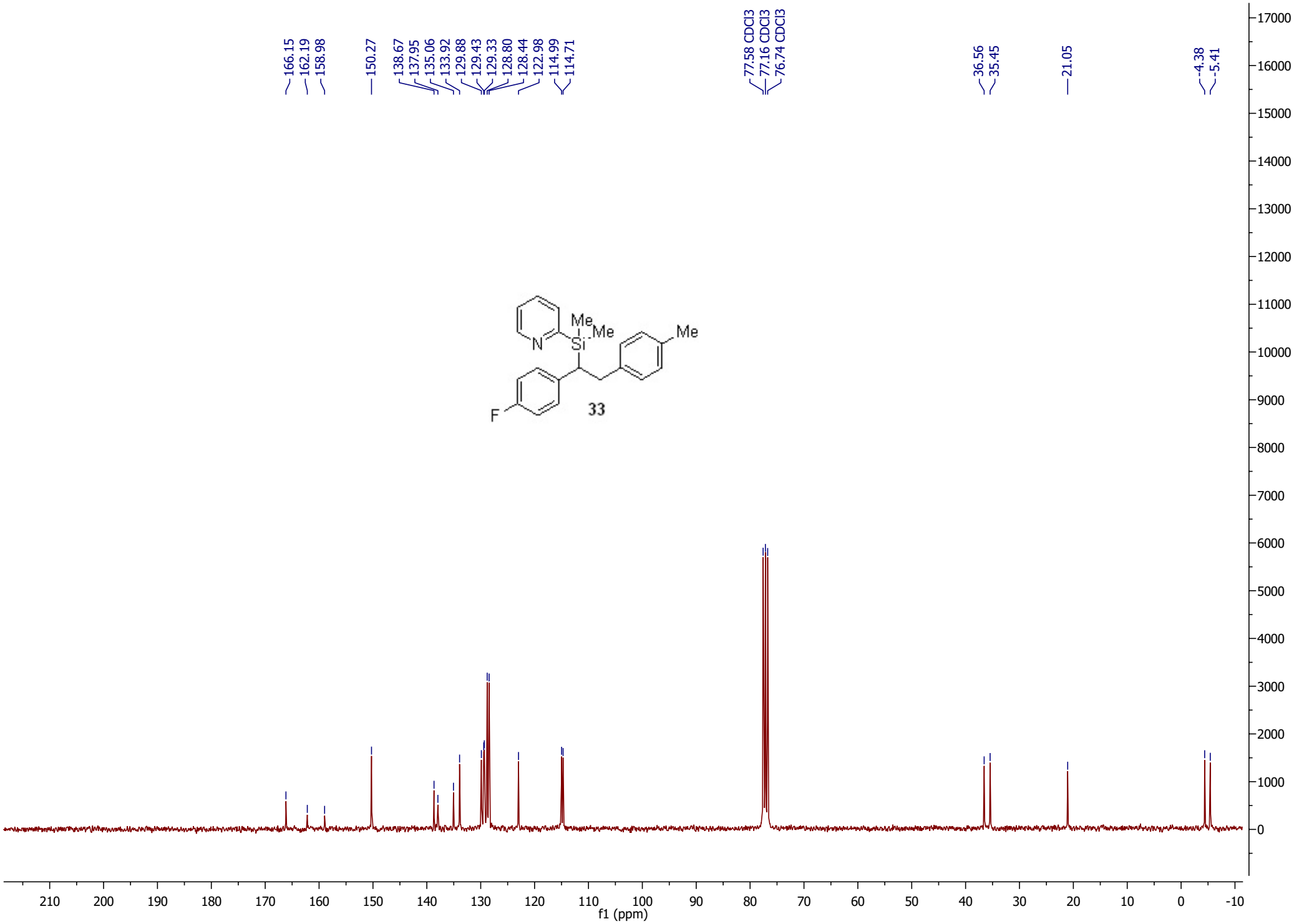
7.5543
7.5490
7.5290
7.5237
7.5036
7.4984
7.3293
7.3043
7.2596
7.2228
7.2191
7.2067
7.2025
7.1977
7.1812
7.1776
6.9210
6.8930
6.8762
6.8425
6.8131
6.7841
3.1127
3.0972
3.0646
3.0490
3.0345
2.9977
2.9495
2.8391
2.8235
2.8025
2.7869
2.2089
0.3653
0.2412
Me
Me
Si
N
Me
F
33
1.00
1.02
1.00
1.02
8.02
2.01
1.00
3.01
3.02
3.02
f1 (ppm)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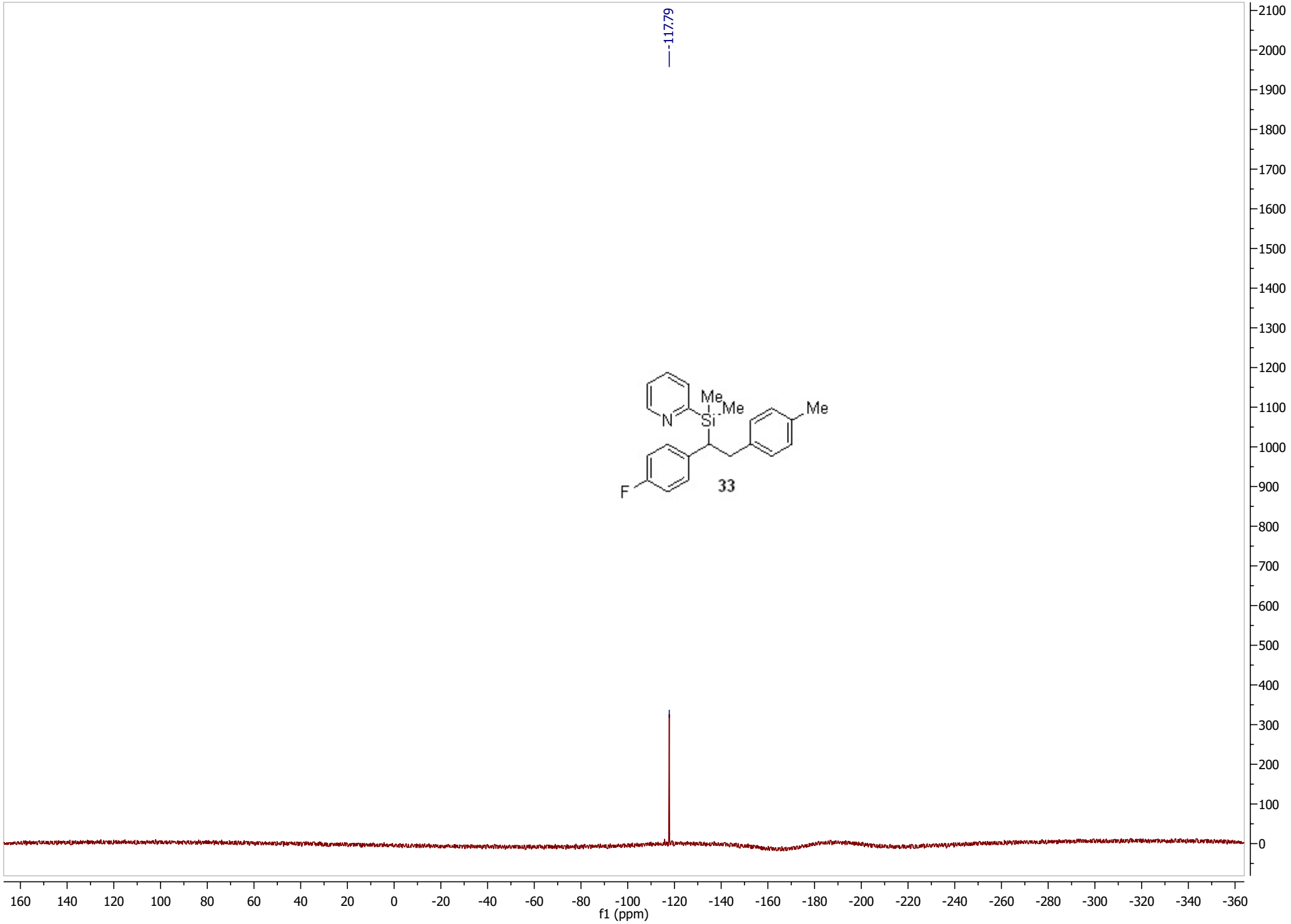
162.19
158.98
150.27
138.67
137.95
135.06
133.92
129.88
129.43
129.33
128.80
128.44
122.98
114.99
114.71
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
36.56
35.45
21.05
-4.38
-5.41
Me
Me
Si
N
Me
F
33
f1 (ppm)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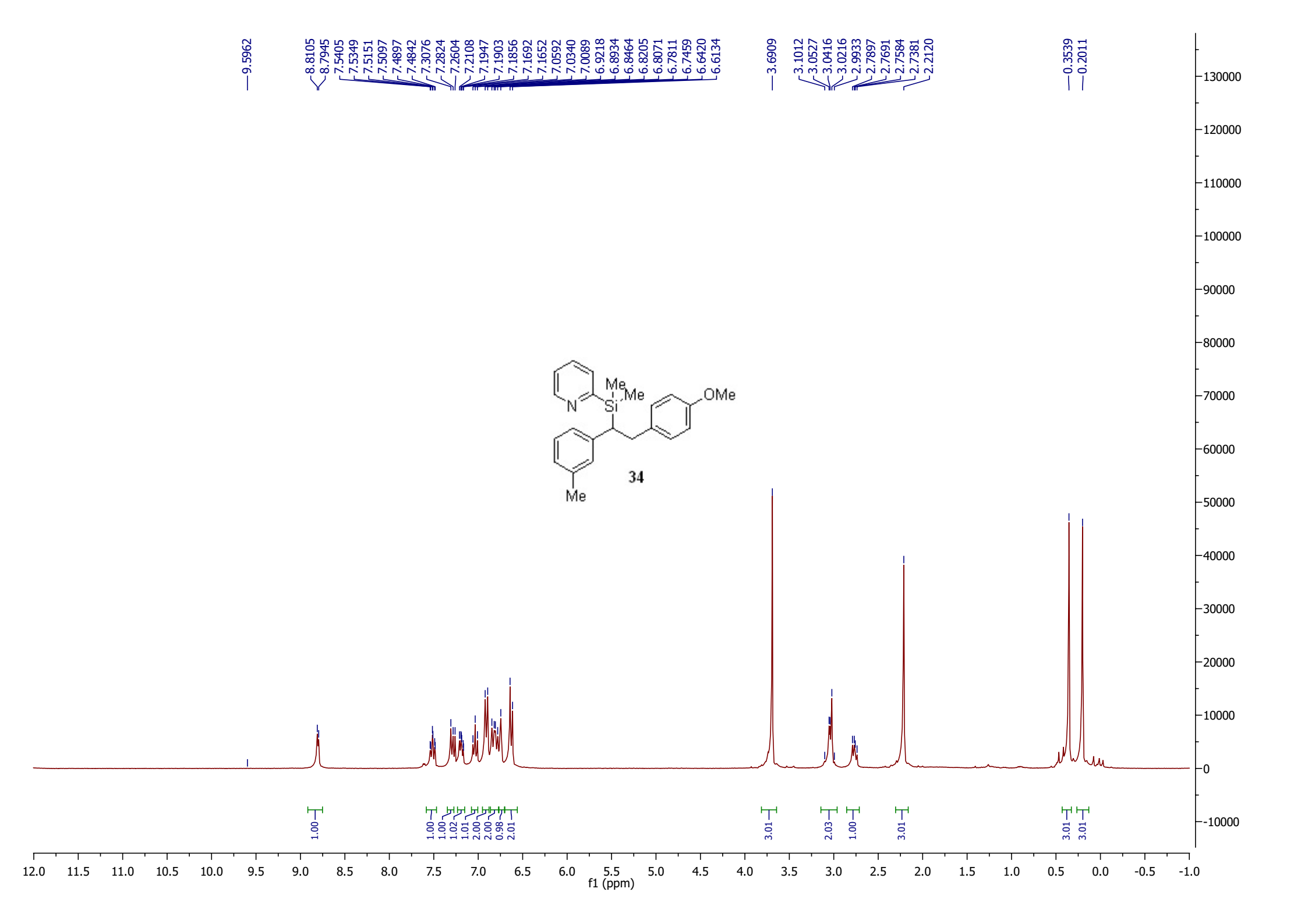
Me
Me
Si
N
Me
F
33
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
-320
-340
-360
f1 (ppm)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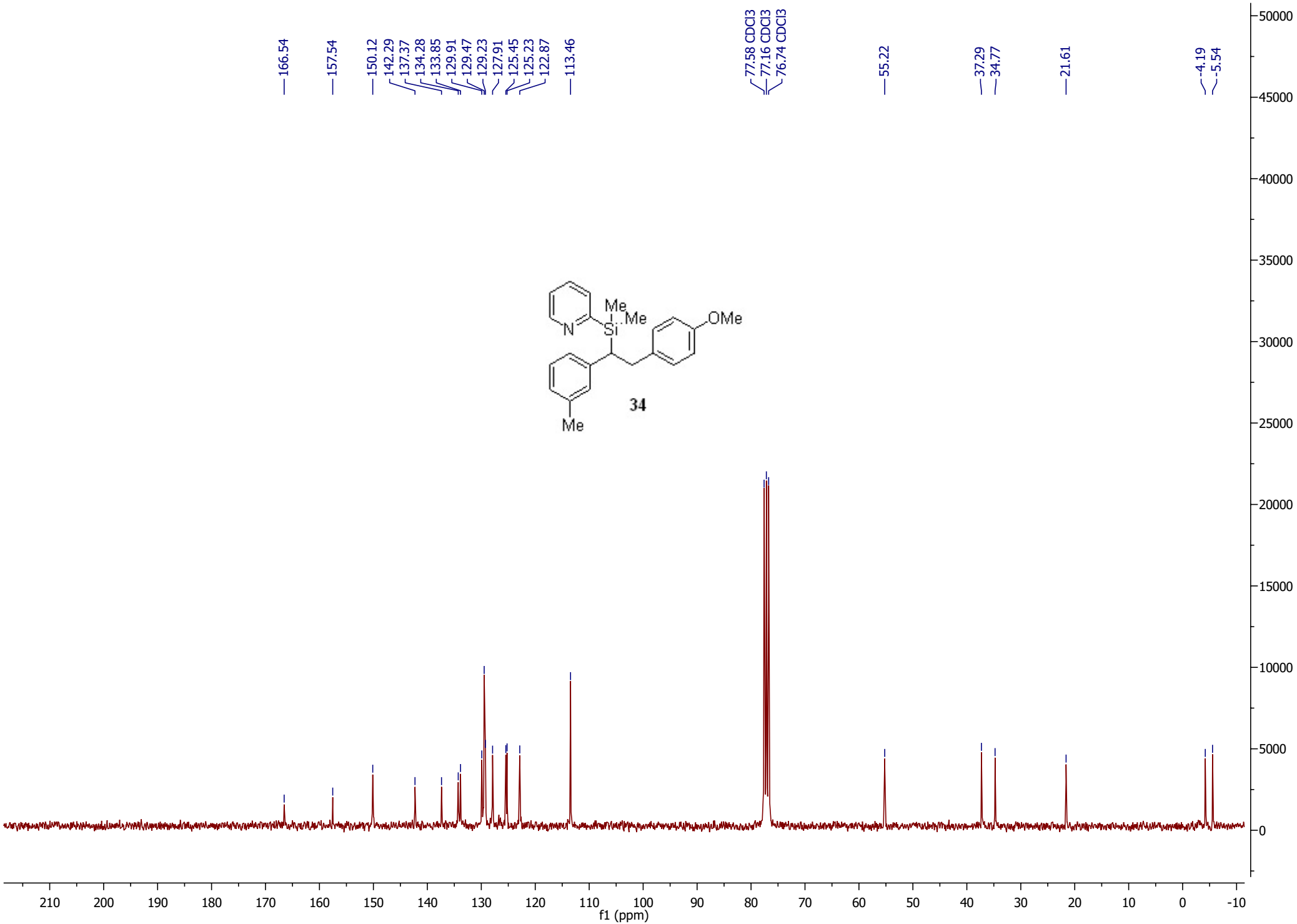
8.8105
8.7945
7.5405
7.5349
7.5151
7.5097
7.4897
7.4842
7.3076
7.2824
7.2604
7.2108
7.1947
7.1903
7.1856
7.1692
7.1652
7.0592
7.0340
7.0089
6.9218
6.8934
6.8464
6.8205
6.8071
6.7811
6.7459
6.6420
6.6134
3.6909
3.1012
3.0527
3.0416
3.0216
2.9933
2.7897
2.7691
2.7584
2.7381
2.2120
0.3539
0.2011
Me
Me
Si
N
OMe
Me
34
1.00
1.00
1.00
1.02
1.01
2.00
2.00
0.98
2.01
3.01
2.03
1.00
3.01
3.01
3.01
f1 (ppm)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157.54
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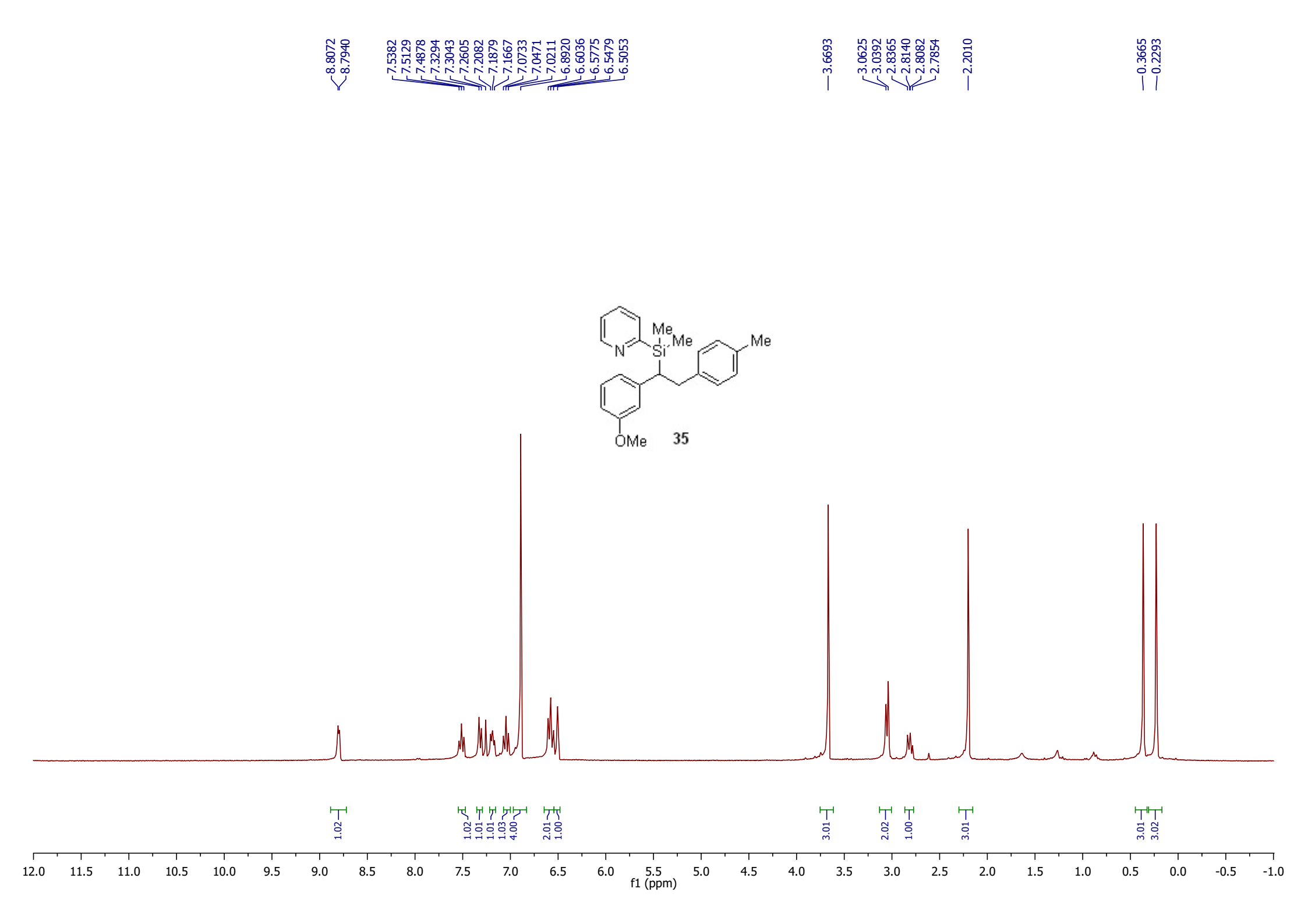
142.29
137.37
134.28
133.85
129.91
129.47
129.23
127.91
125.45
125.23
122.87
113.46
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
55.22
37.29
34.77
21.61
-4.19
-5.54
Me
Me
Si
N
OMe
Me
34
f1 (ppm)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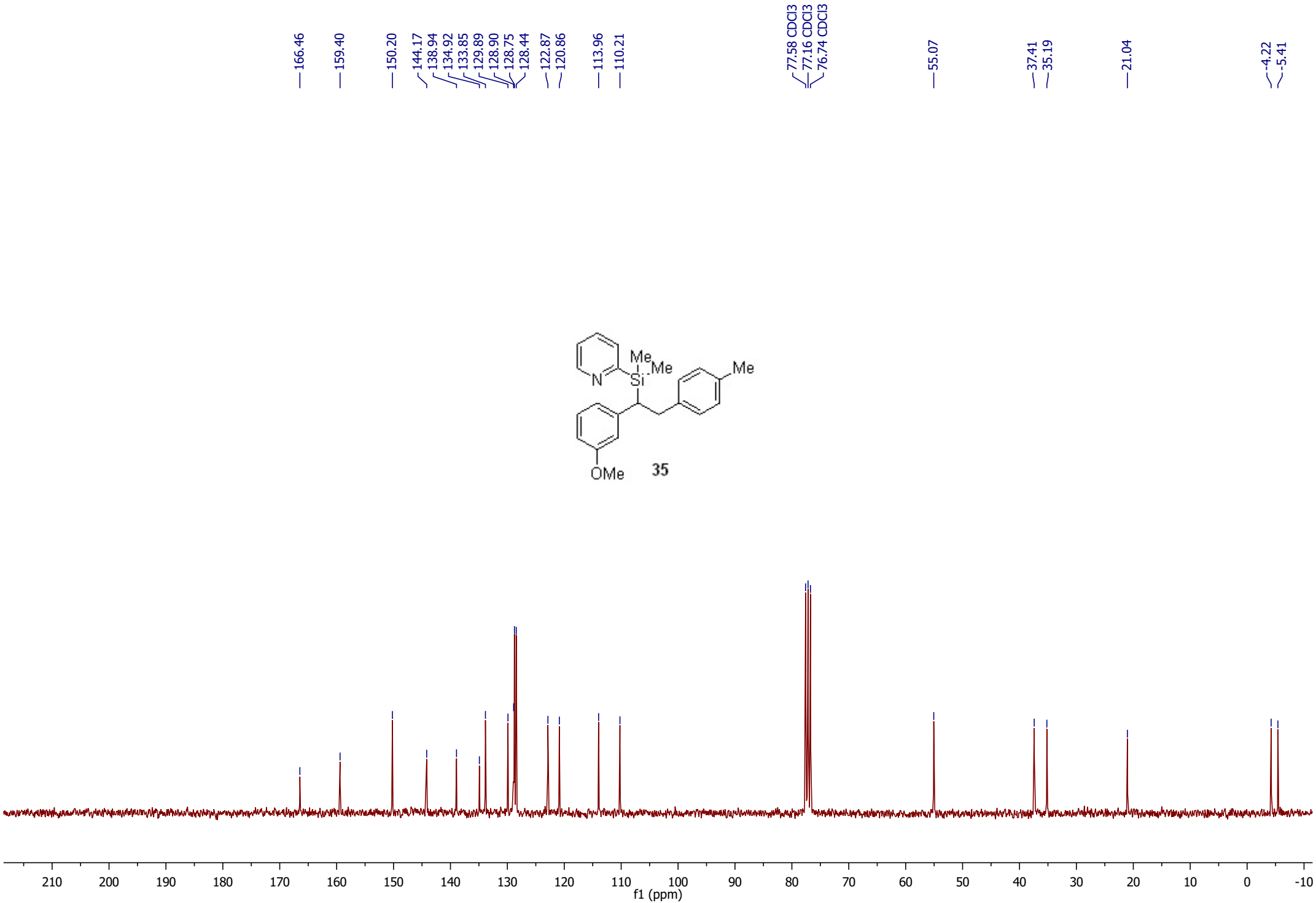
8.7940
7.5382
7.5129
7.4878
7.3294
7.3043
7.2605
7.2082
7.1879
7.1667
7.0733
7.0471
7.0211
6.8920
6.6036
6.5775
6.5479
6.5053
3.6693
3.0625
3.0392
2.8365
2.8140
2.8082
2.7854
2.2010
0.3665
0.2293
Me
Me
Si
N
Me
OMe
35
1.02
1.02
1.01
1.01
1.03
4.00
2.01
1.00
3.01
2.02
1.00
3.01
3.01
3.02
12.0
11.5
11.0
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)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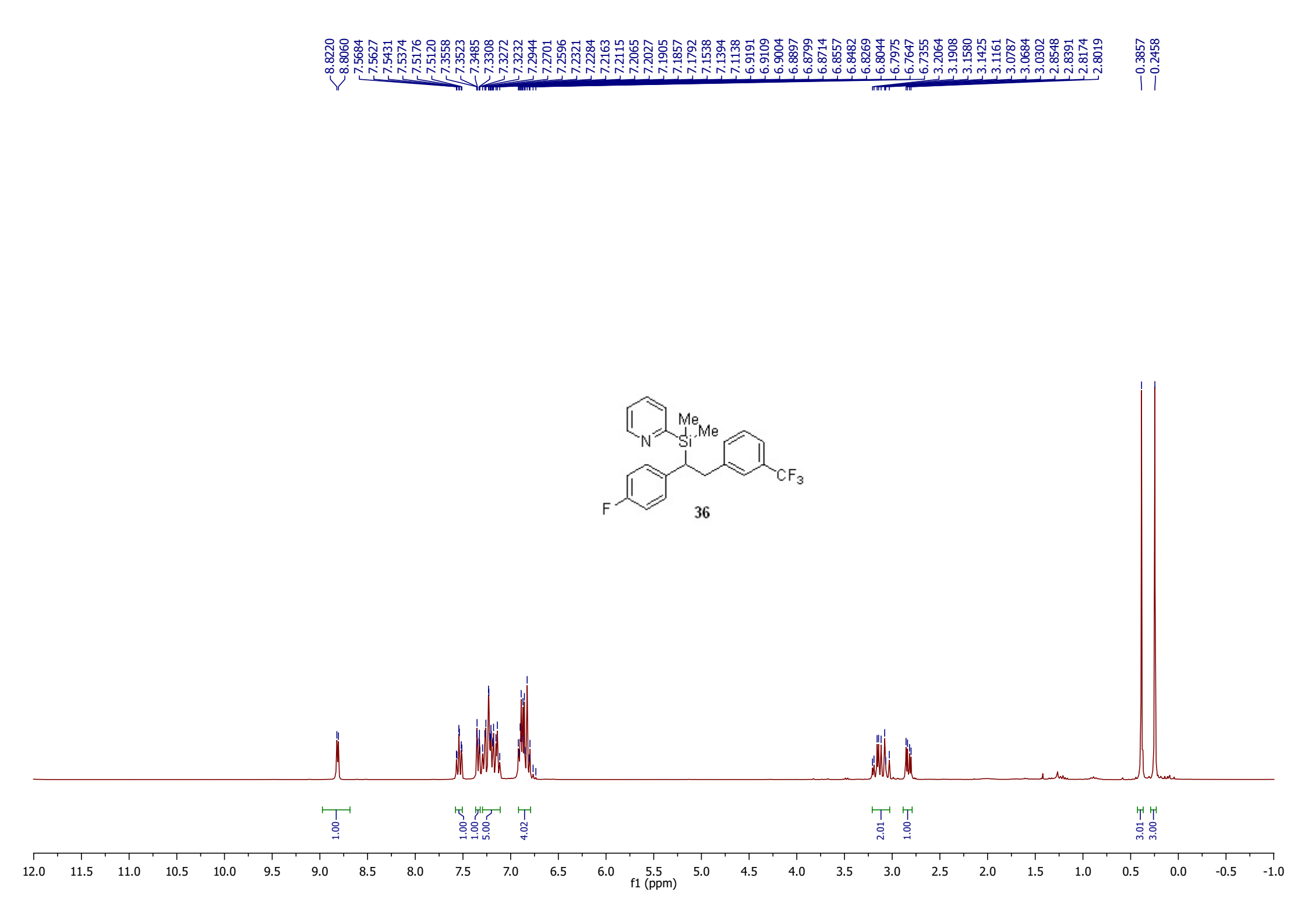
144.17
138.94
134.92
133.85
129.89
128.90
128.75
128.44
122.87
120.86
113.96
110.21
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
55.07
37.41
35.19
21.04
-4.22
-5.41
Me
Me
Me
N
Si
OMe
35
f1 (ppm)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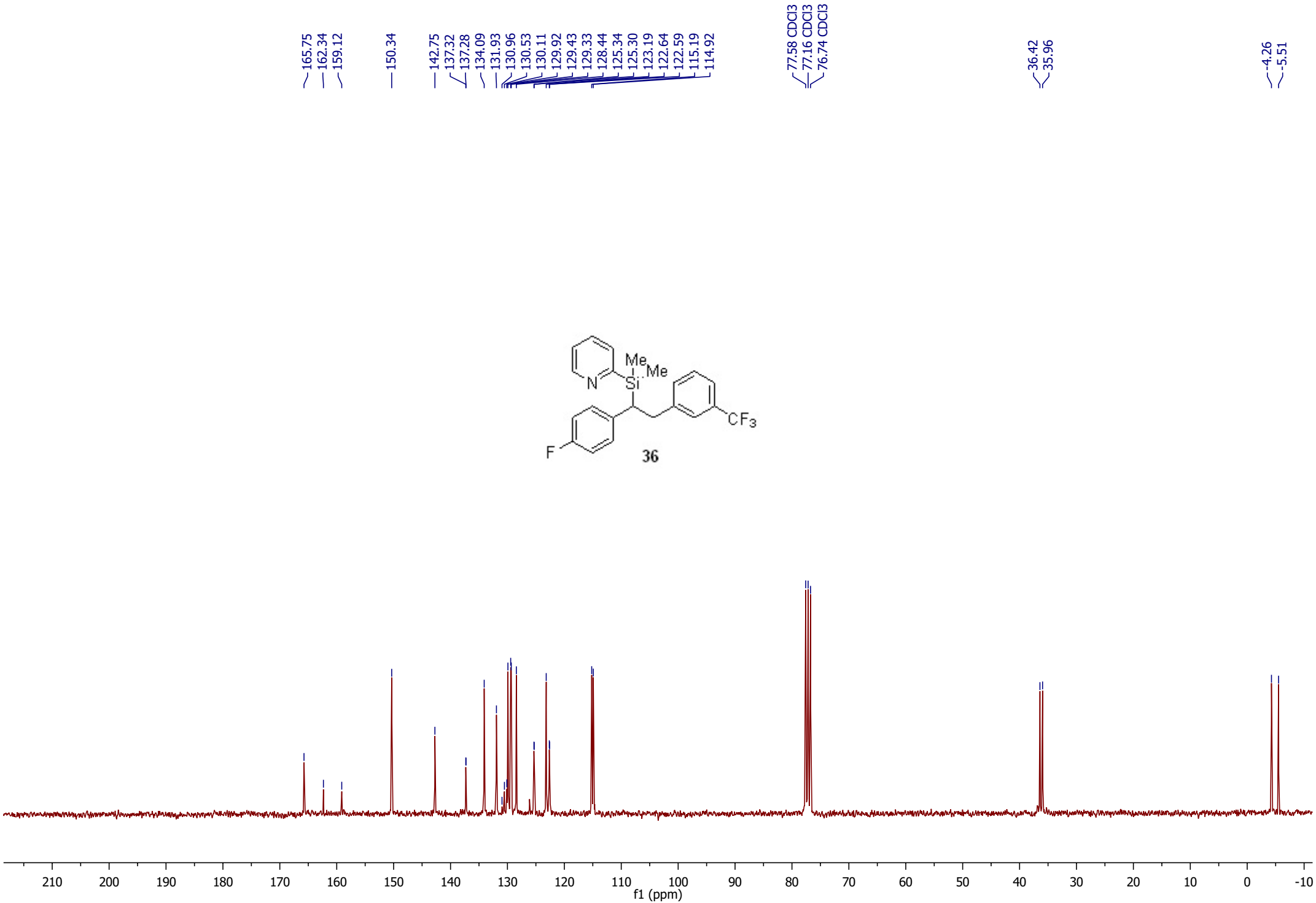
8.8060
7.5684
7.5627
7.5431
7.5374
7.5176
7.5120
7.3558
7.3523
7.3485
7.3308
7.3272
7.3232
7.2944
7.2701
7.2596
7.2321
7.2284
7.2163
7.2115
7.2065
7.2027
7.1905
7.1857
7.1792
7.1538
7.1394
7.1138
6.9191
6.9109
6.9004
6.8897
6.8799
6.8714
6.8557
6.8482
6.8269
6.8044
6.7975
6.7647
6.7355
3.2064
3.1908
3.1580
3.1425
3.1161
3.0787
3.0684
3.0302
2.8548
2.8391
2.8174
2.8019
0.3857
0.2458
Me
Me
Si
N
CF3
F
36
1.00
1.00
1.00
5.00
4.02
2.01
1.00
3.01
3.00
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)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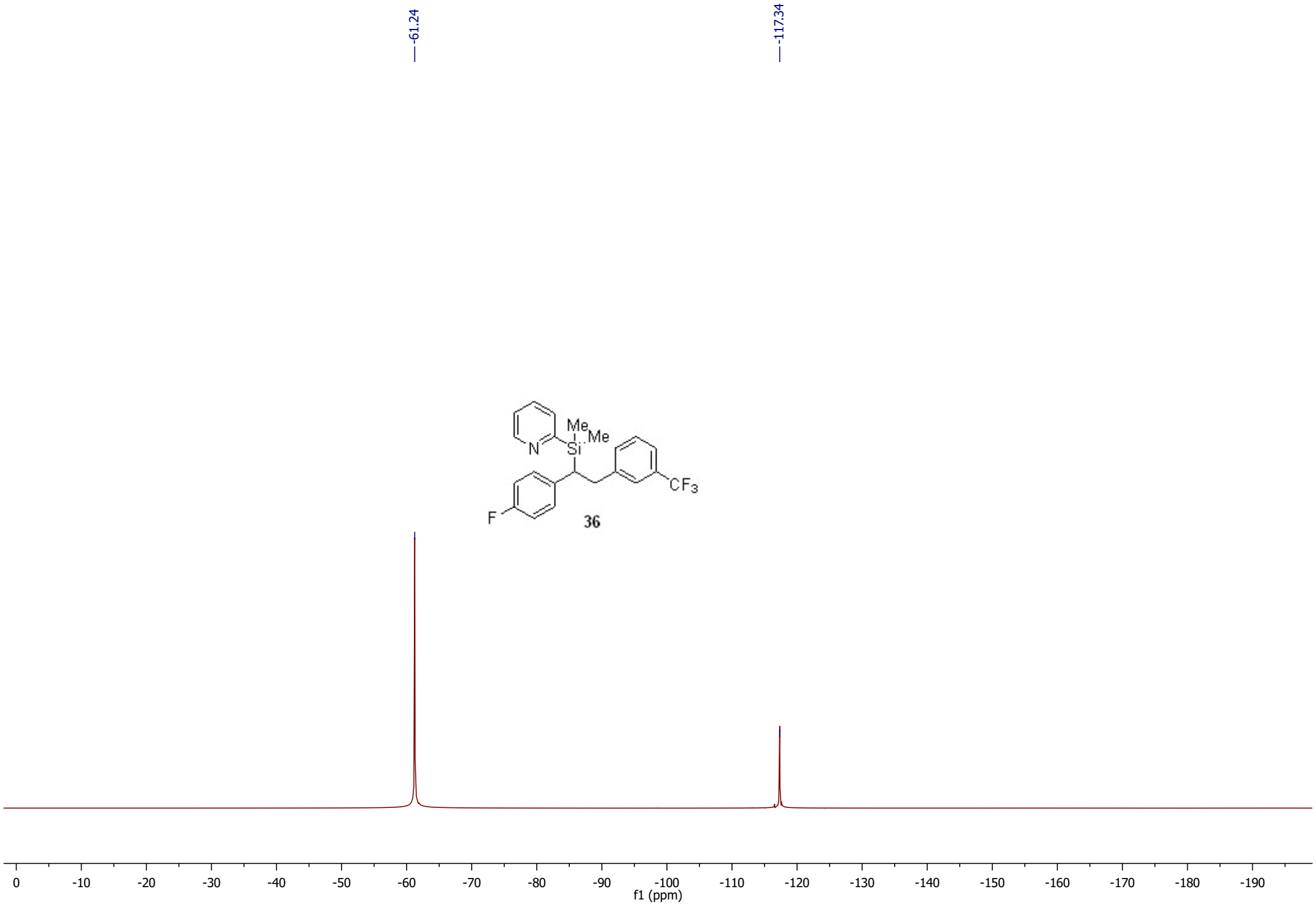
137.28
134.09
131.93
130.96
130.53
130.11
129.92
129.43
129.33
128.44
125.34
125.30
123.19
122.64
122.59
115.19
114.92
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
36.42
35.96
-4.26
-5.51
Me
Me
N
Si
CF3
F
36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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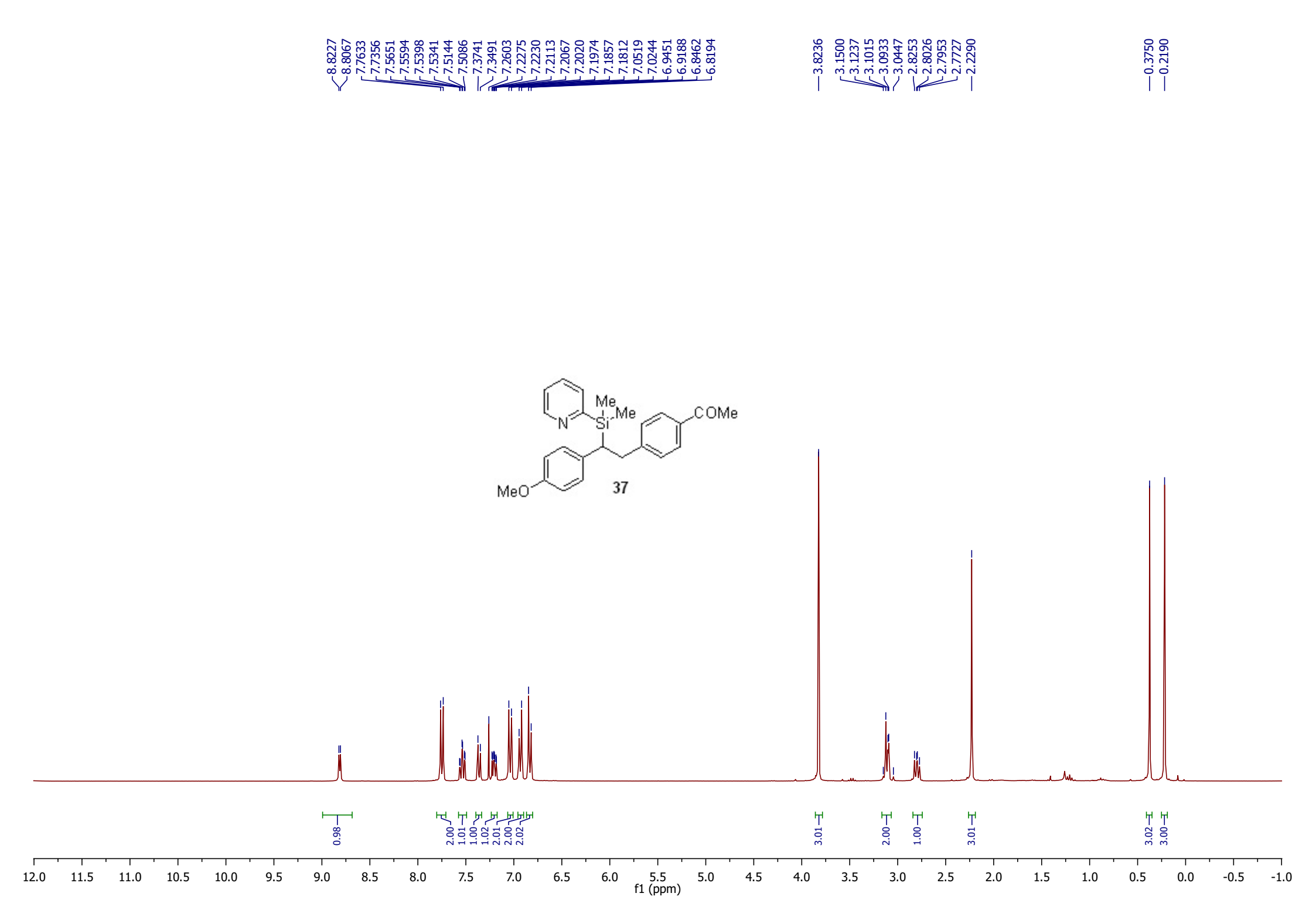
-117.34
Me
Me
Si
N
CF3
F
36
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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7.5594
7.5398
7.5341
7.5144
7.5086
7.3741
7.3491
7.2603
7.2275
7.2230
7.2113
7.2067
7.2020
7.1974
7.1857
7.1812
7.0519
7.0244
6.9451
6.9188
6.8462
6.8194
3.8236
3.1500
3.1237
3.1015
3.0933
3.0447
2.8253
2.8026
2.7953
2.7727
2.2290
0.3750
0.2190
Me
Me
Si
N
COMe
MeO
37
0.98
2.00
1.01
1.00
1.02
2.01
2.00
2.02
3.01
2.00
1.00
3.01
3.02
3.00
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
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2.5
2.0
1.5
1.0
0.5
0.0
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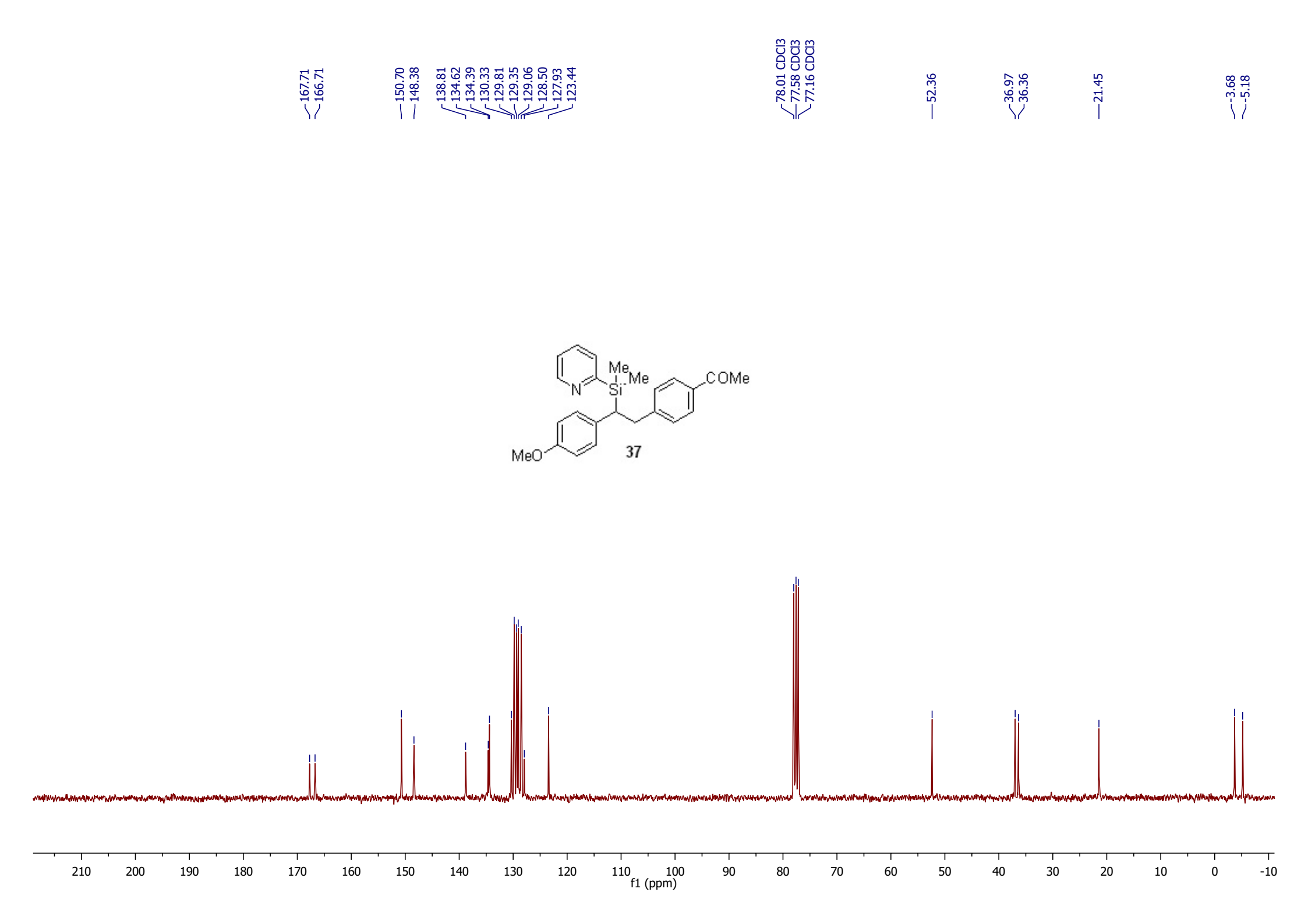
-1.0
f1 (ppm)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130.33
129.81
129.35
129.06
128.50
127.93
123.44
78.01 CDCl3
77.58 CDCl3
77.16 CDCl3
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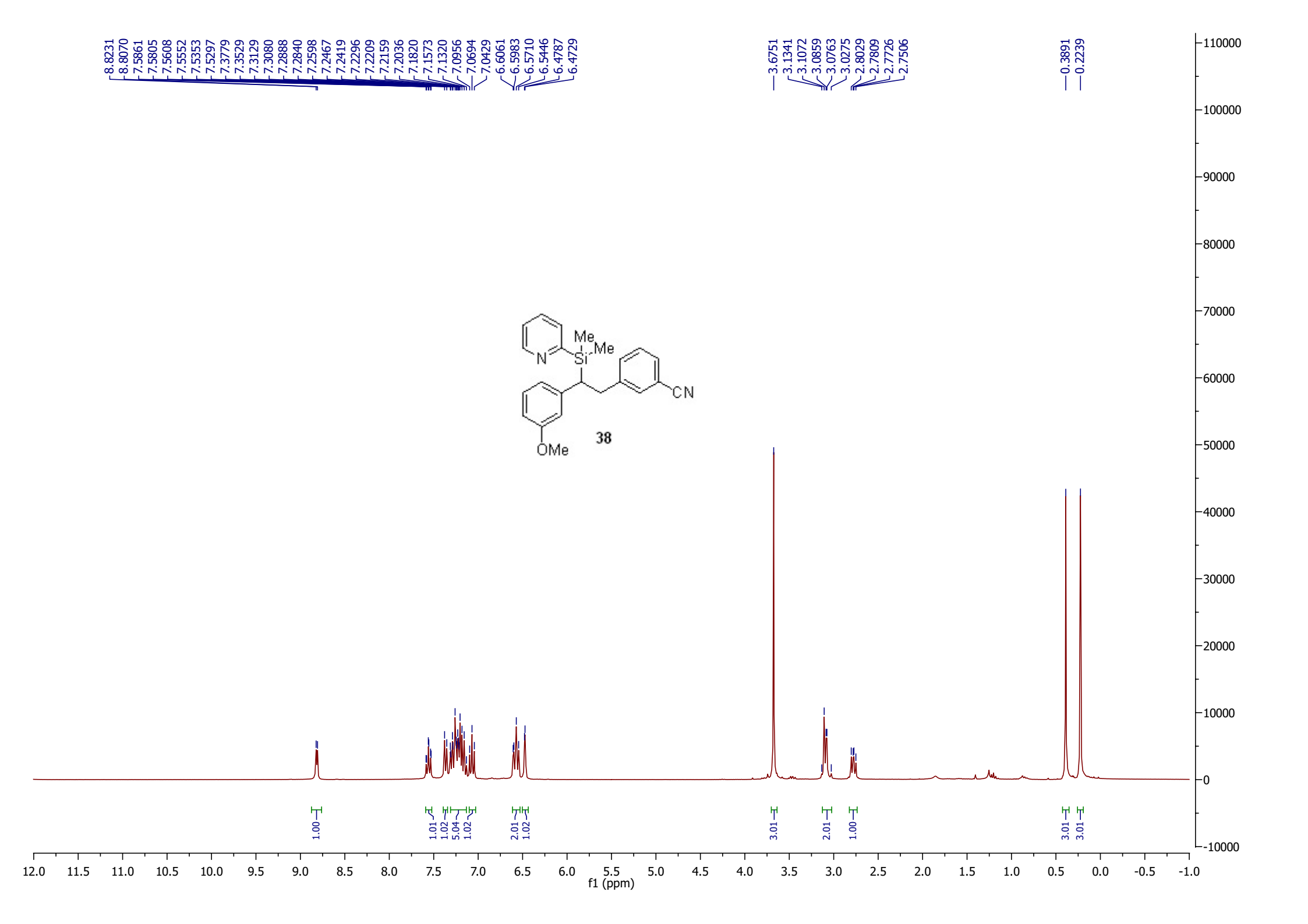
36.97
36.36
21.45
-3.68
-5.18
Me
Me
Si
N
COMe
MeO
37
f1 (ppm)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7.3779
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7.3129
7.3080
7.2888
7.2840
7.2598
7.2467
7.2419
7.2296
7.2209
7.2159
7.2036
7.1820
7.1573
7.1320
7.0956
7.0694
7.0429
6.6061
6.5983
6.5710
6.5446
6.4787
6.4729
3.6751
3.1341
3.1072
3.0859
3.0763
3.0275
2.8029
2.7809
2.7726
2.7506
0.3891
0.2239
Me
Me
Si
N
CN
OMe
38
1.00
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1.02
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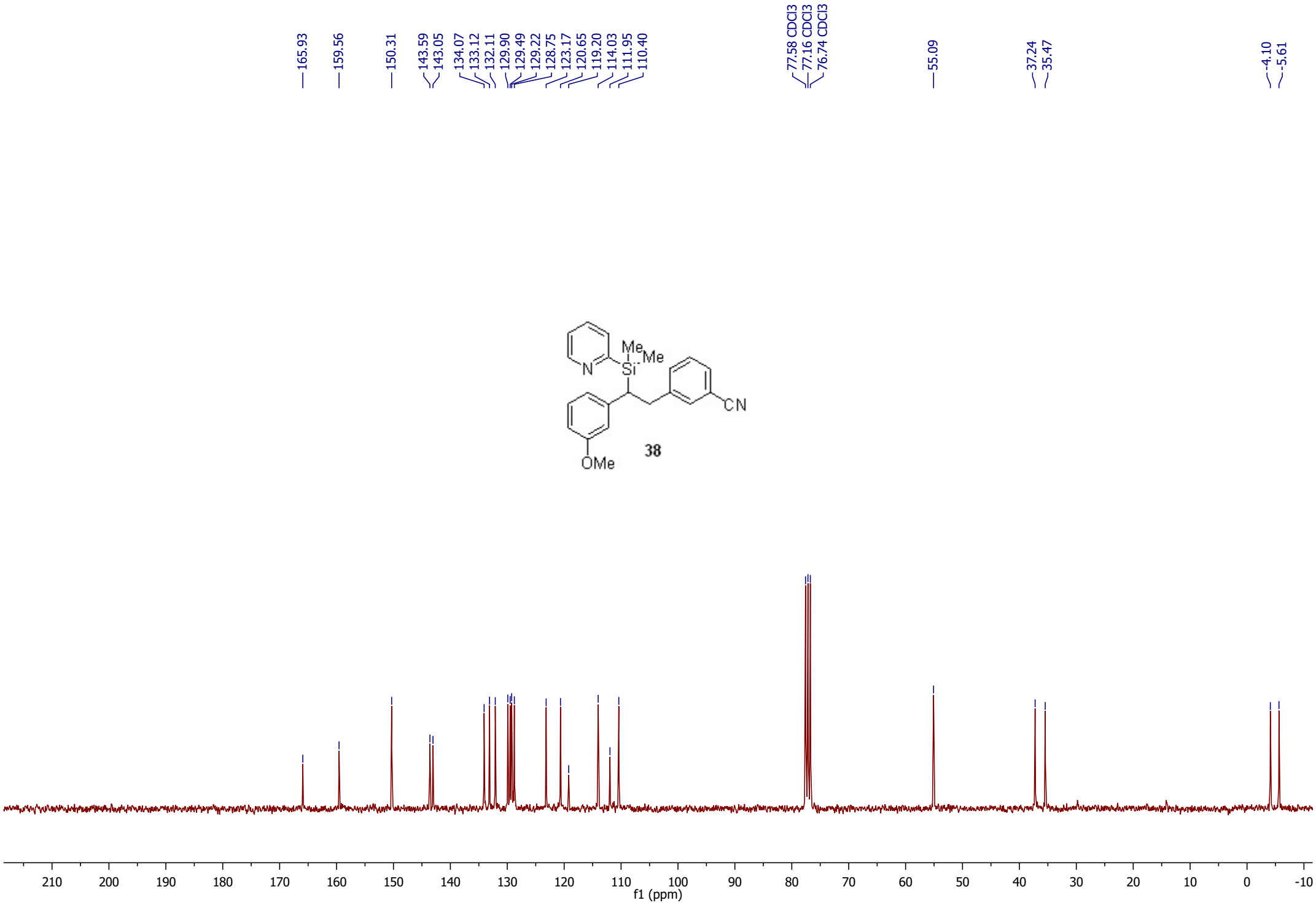
1.02
2.01
1.02
3.01
2.01
1.00
3.01
3.01
f1 (ppm)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143.05
134.07
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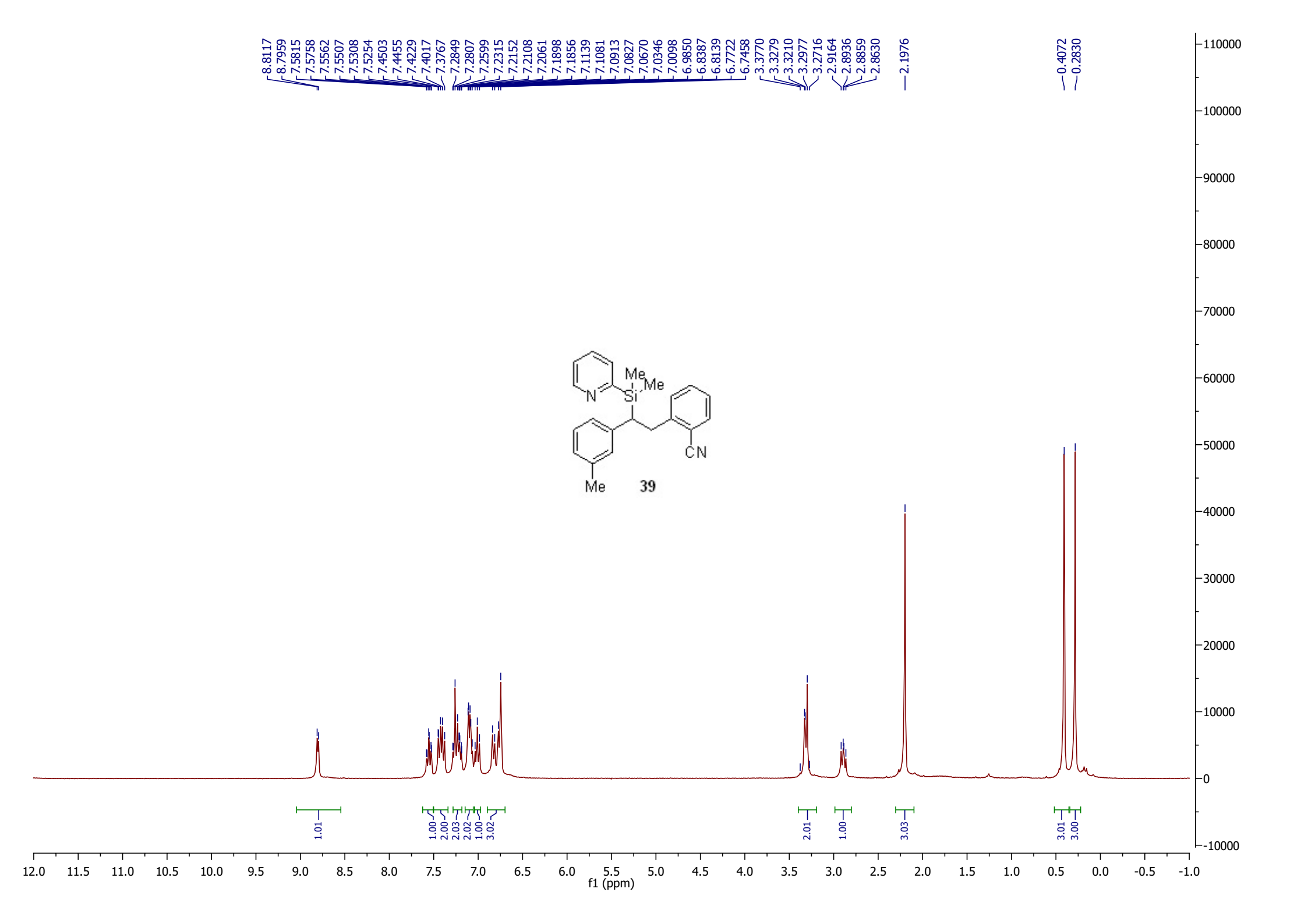
132.11
129.90
129.49
129.22
128.75
123.17
120.65
119.20
114.03
111.95
110.40
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
55.09
37.24
35.47
-4.10
-5.61
Me
Me
Si
N
CN
OMe
38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.5562
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7.5308
7.5254
7.4503
7.4455
7.4229
7.4017
7.3767
7.2849
7.2807
7.2599
7.2315
7.2152
7.2108
7.2061
7.1898
7.1856
7.1139
7.1081
7.0913
7.0827
7.0670
7.0346
7.0098
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6.8387
6.8139
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6.7458
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3.3279
3.3210
3.2977
3.2716
2.9164
2.8936
2.8859
2.8630
2.1976
0.4072
0.2830
Me
Me
N
Si
CN
Me
39
1.01
1.00
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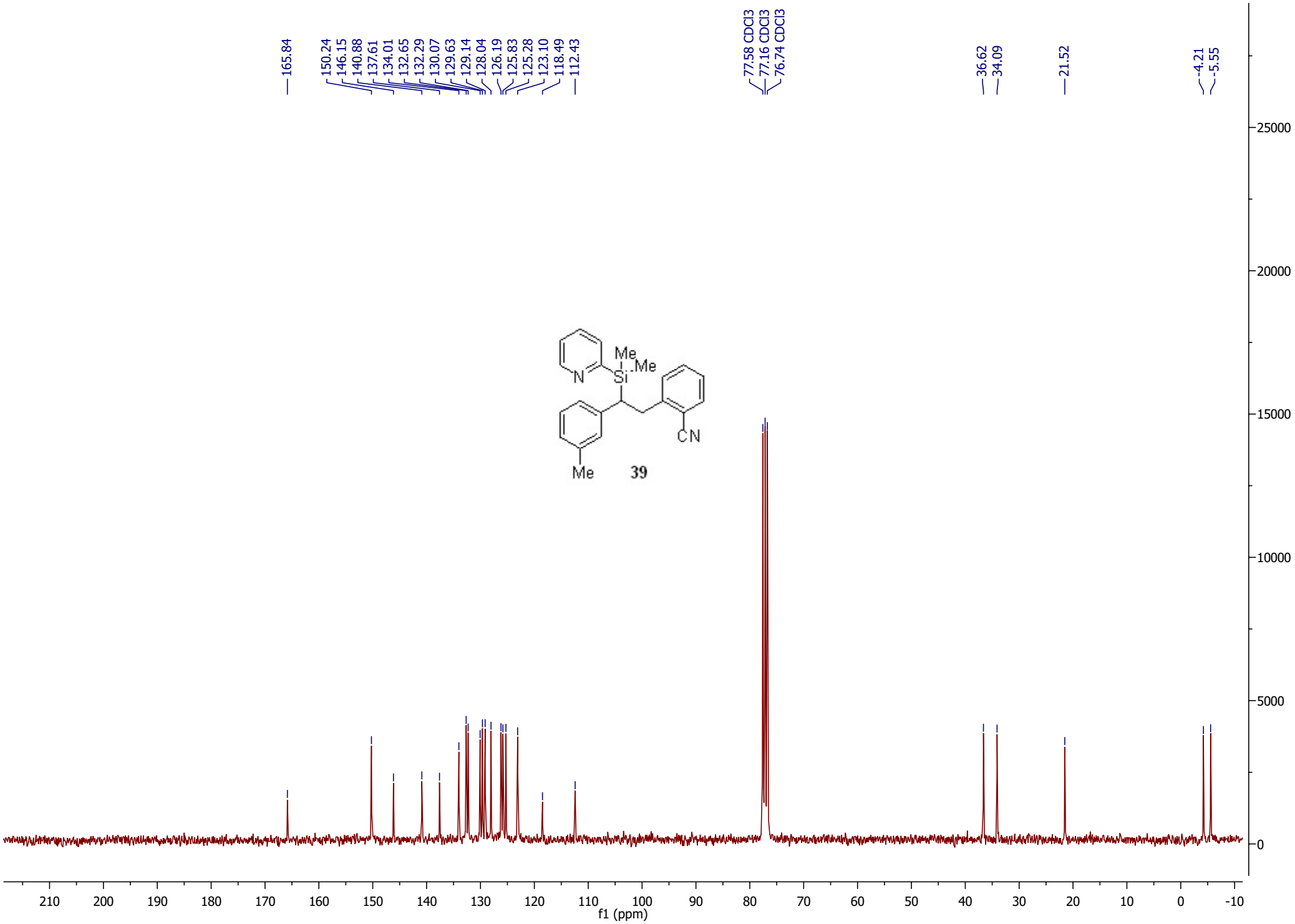
2.02
1.00
3.02
2.01
1.00
3.03
3.01
3.00
f1 (ppm)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137.61
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132.65
132.29
130.07
129.63
129.14
128.04
126.19
125.83
125.28
123.10
118.49
112.43
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
36.62
34.09
21.52
-4.21
-5.55
Me
Me
Si
N
CN
Me
39
25000
20000
15000
10000
5000
0
210
200
190
180
170
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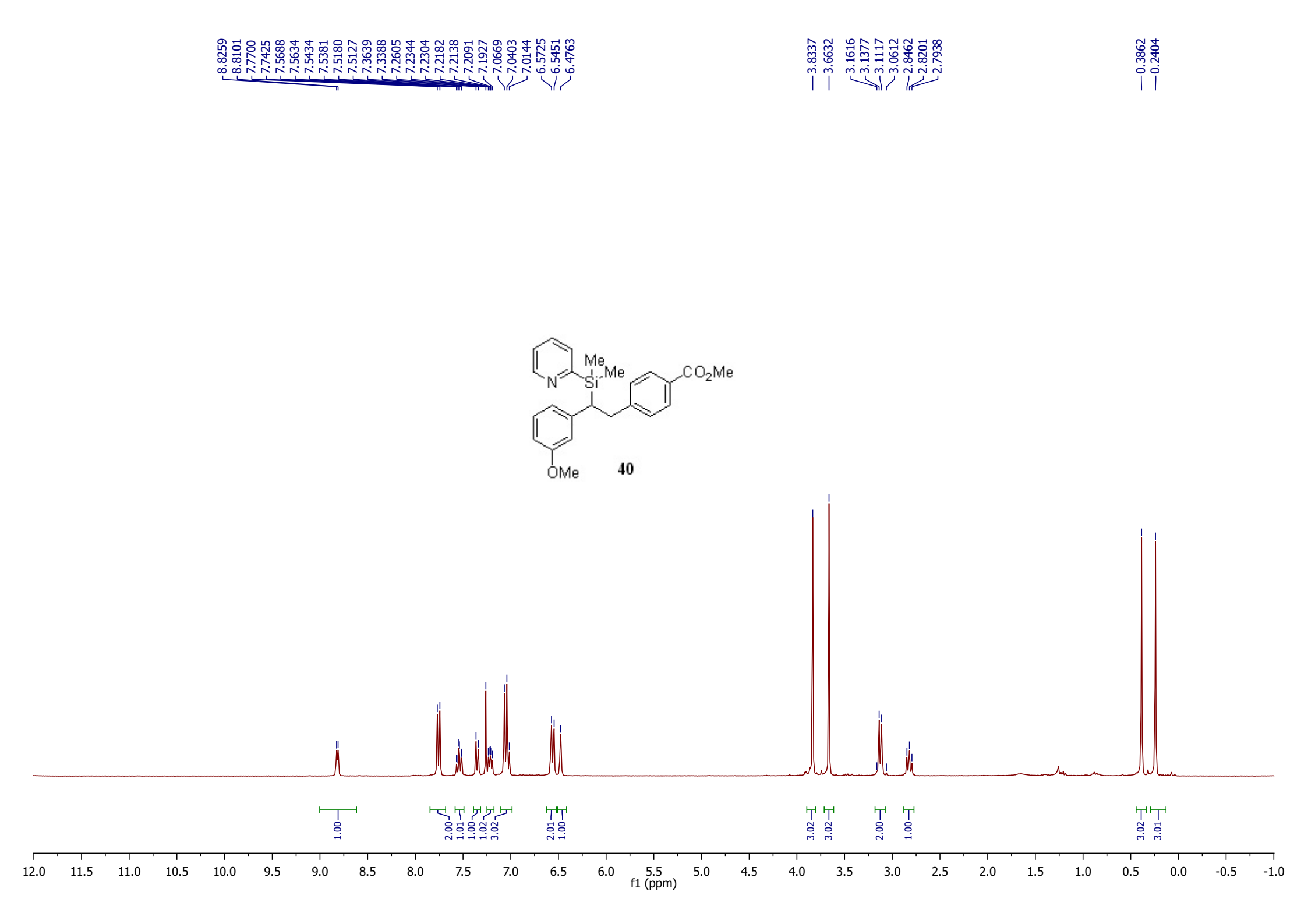
f1 (ppm)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7.3388
7.2605
7.2344
7.2304
7.2182
7.2138
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7.1927
7.0669
7.0403
7.0144
6.5725
6.5451
6.4763
3.8337
3.6632
3.1616
3.1377
3.1117
3.0612
2.8462
2.8201
2.7938
0.3862
0.2404
Me
Me
Si
N
CO2Me
OMe
40
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2.00
1.01
1.00
1.02
3.02
2.01
1.00
3.02
3.02
2.00
1.00
3.02
3.01
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11.0
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5.5
5.0
4.5
4.0
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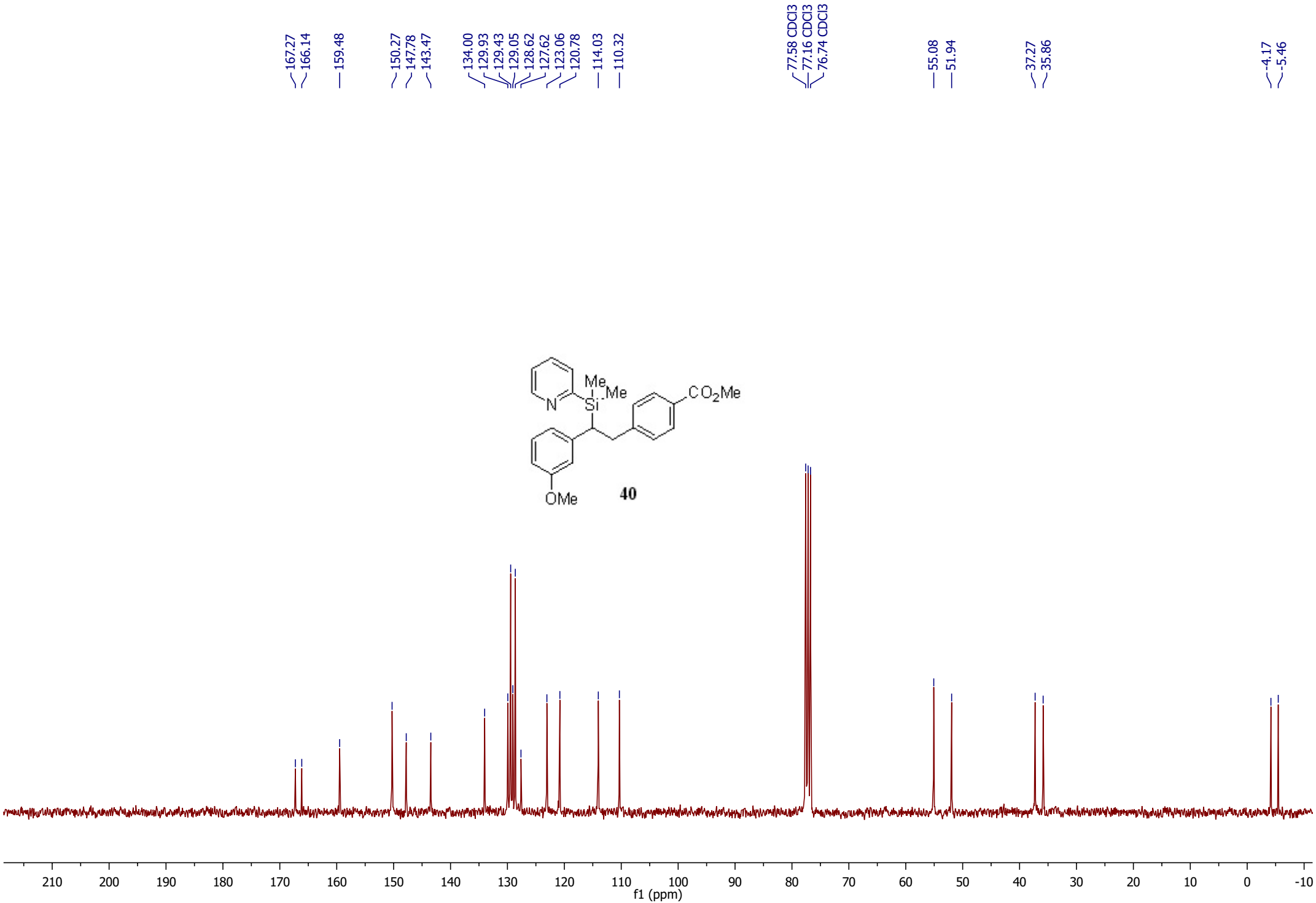
f1 (ppm)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128.62
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123.06
120.78
114.03
110.32
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
55.08
51.94
37.27
35.86
-4.17
-5.46
Me
Me
Si
N
CO2Me
OMe
40
210
200
190
180
170
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100
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80
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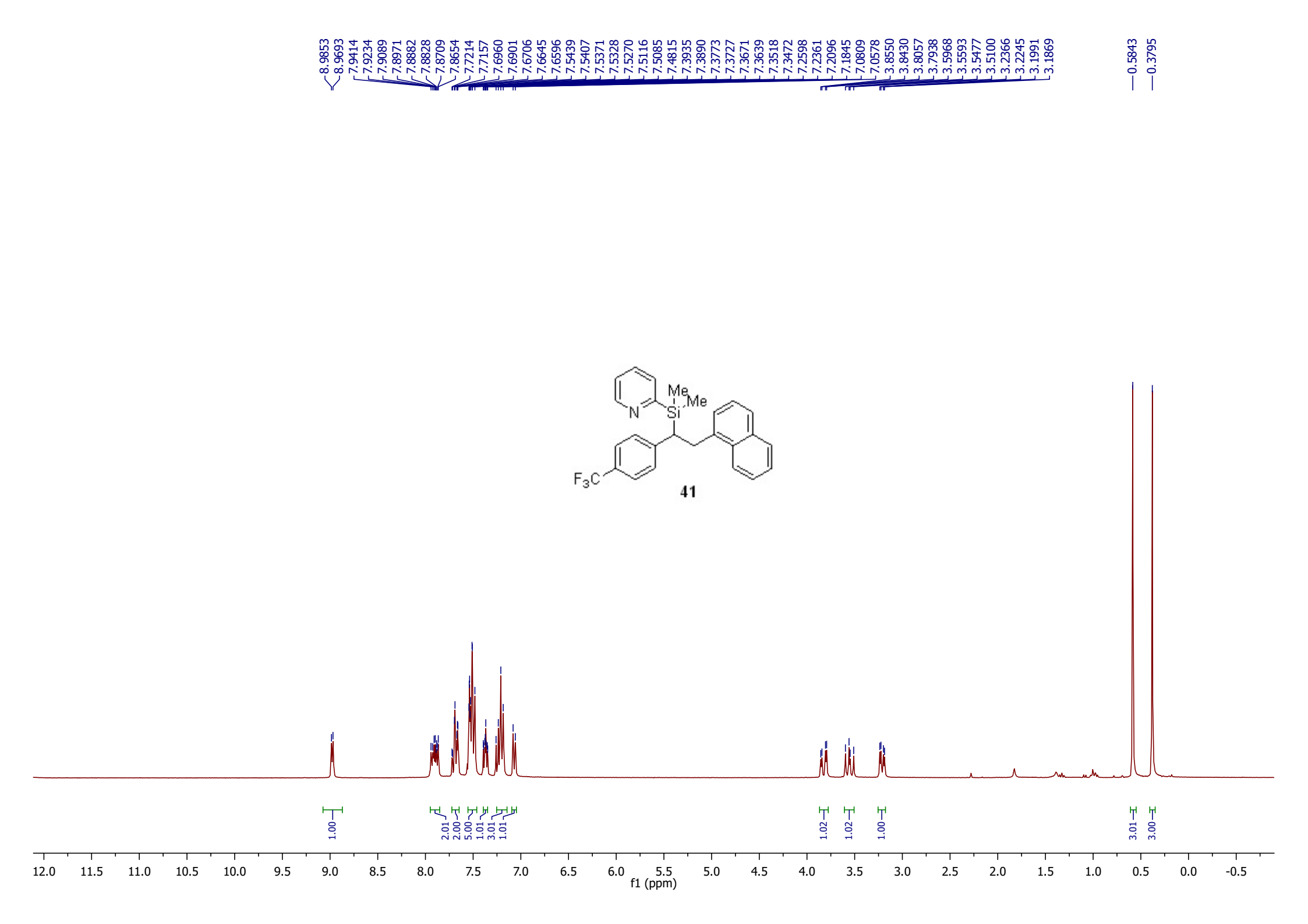
f1 (ppm)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7.6960
7.6901
7.6706
7.6645
7.6596
7.5439
7.5407
7.5371
7.5328
7.5270
7.5116
7.5085
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7.3890
7.3773
7.3727
7.3671
7.3639
7.3518
7.3472
7.2598
7.2361
7.2096
7.1845
7.0809
7.0578
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3.8430
3.8057
3.7938
3.5968
3.5593
3.5477
3.5100
3.2366
3.2245
3.1991
3.1869
0.5843
0.3795
Me
Me
Si
N
F3C
41
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2.00
5.00
1.01
3.01
1.01
1.02
1.02
1.00
3.01
3.00
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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
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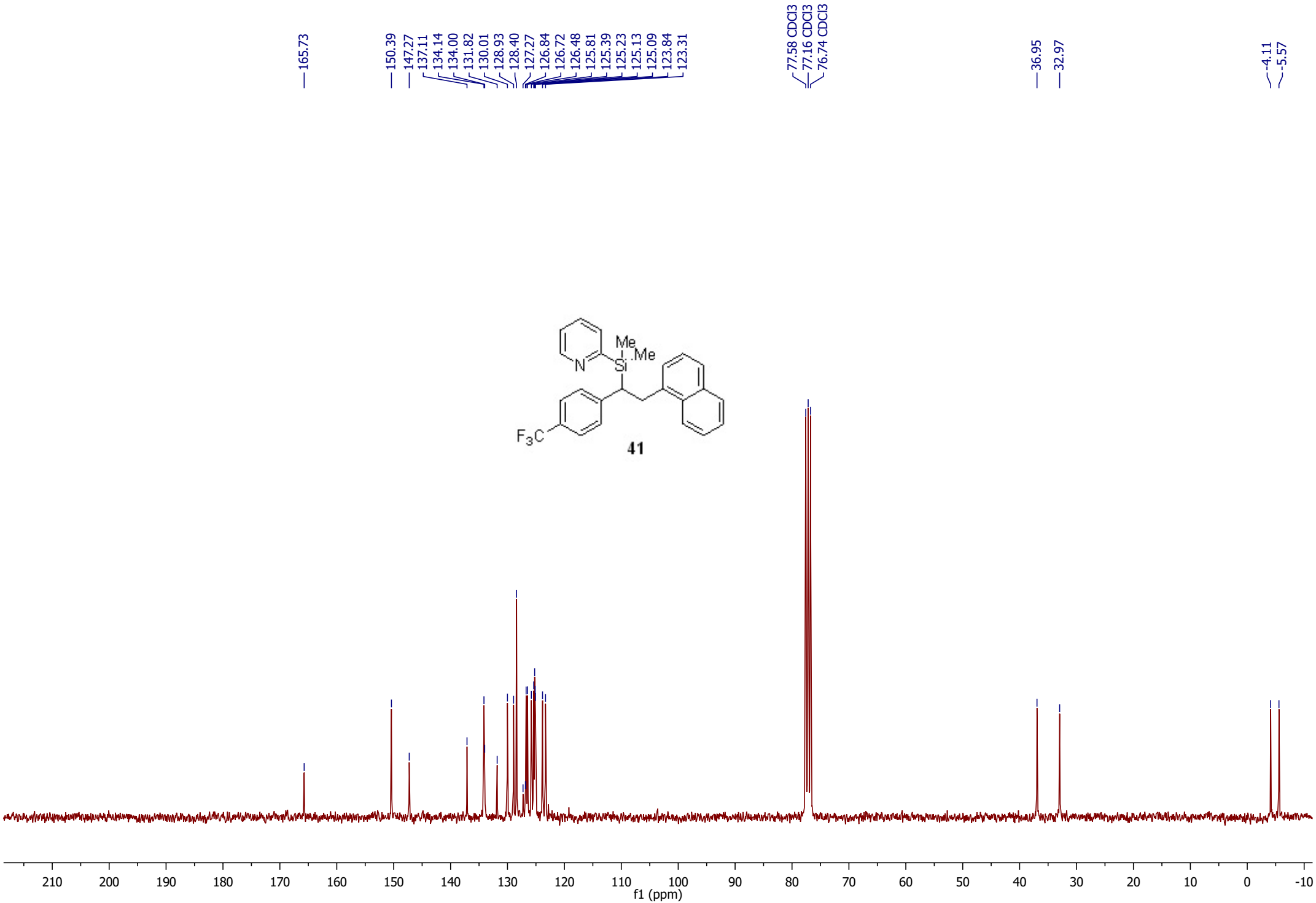
f1 (ppm)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130.01
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128.40
127.27
126.84
126.72
126.48
125.81
125.39
125.23
125.13
125.09
123.84
123.31
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
36.95
32.97
-4.11
-5.57
Me
Me
Si
N
F3C
41
210
200
190
180
170
160
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140
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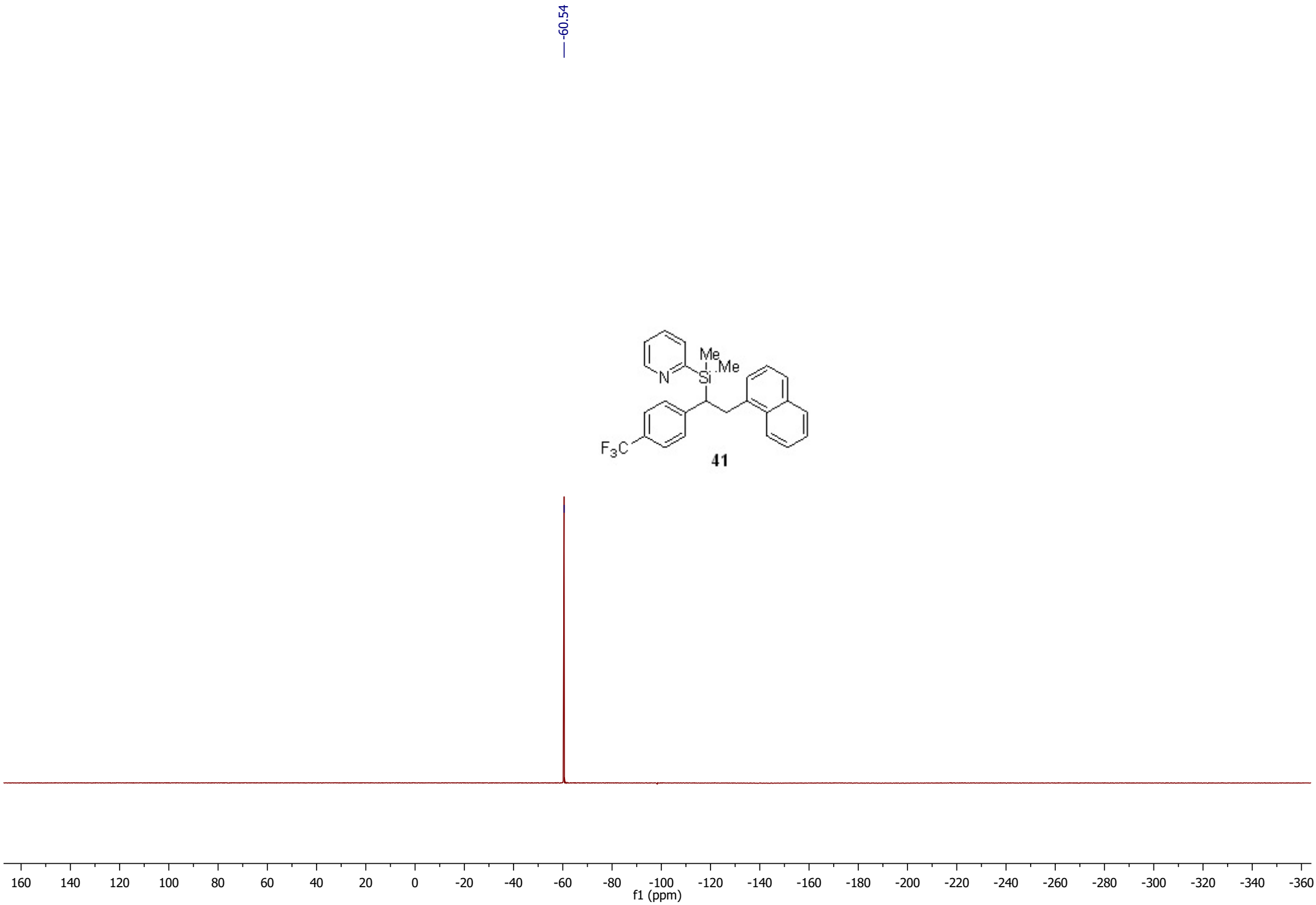
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Me
Si
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120
100
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60
40
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-40
-60
-80
-100
-120
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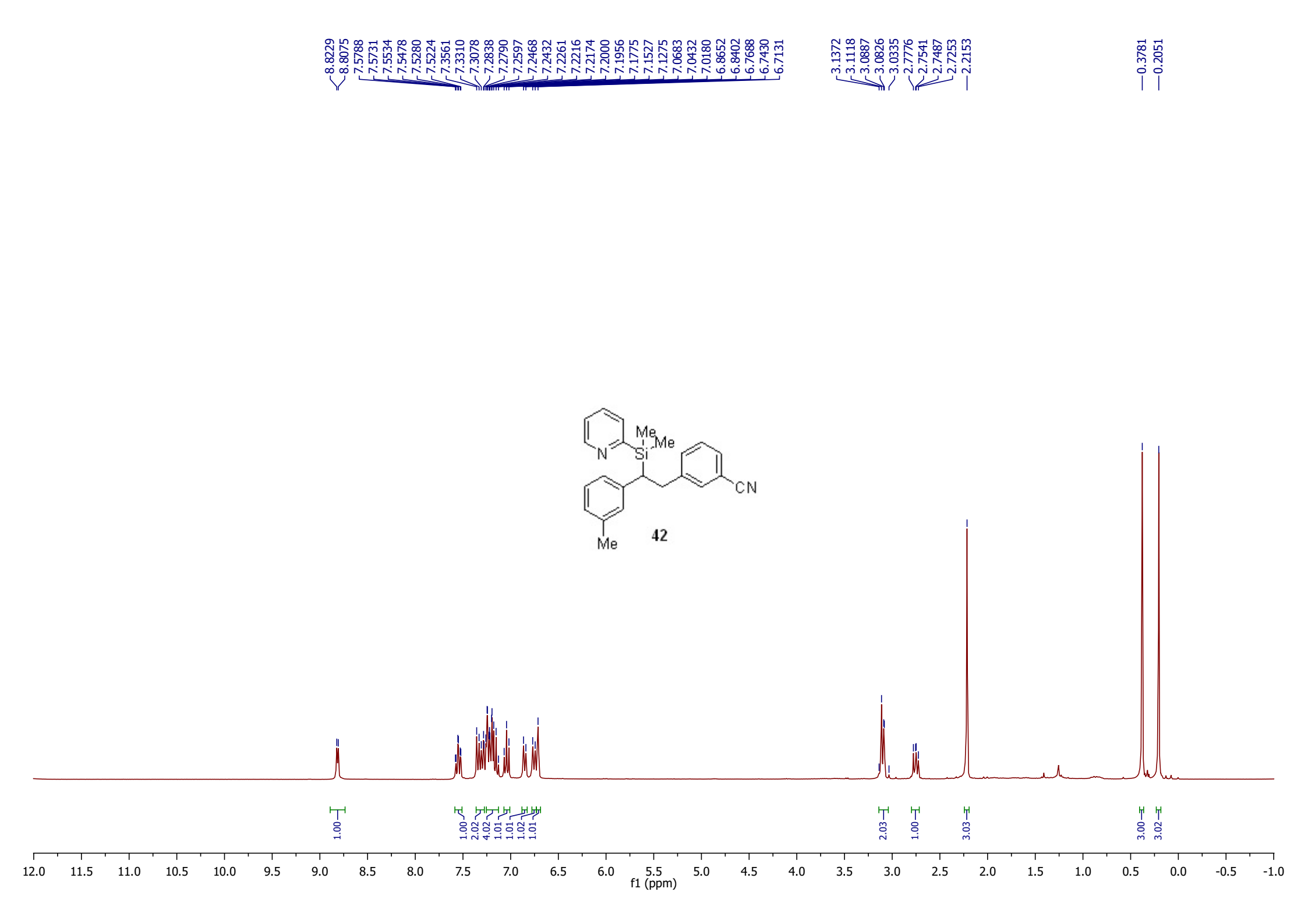
-180
-200
-220
-240
-260
-280
-300
-320
-340
-360
f1 (ppm)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7.3310
7.3078
7.2838
7.2790
7.2597
7.2468
7.2432
7.2261
7.2216
7.2174
7.2000
7.1956
7.1775
7.1527
7.1275
7.0683
7.0432
7.0180
6.8652
6.8402
6.7688
6.7430
6.7131
3.1372
3.1118
3.0887
3.0826
3.0335
2.7776
2.7541
2.7487
2.7253
2.2153
0.3781
0.2051
Me
Me
N
Si
CN
Me
42
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1.00
2.02
4.02
1.01
1.01
1.02
1.01
2.03
1.00
3.03
3.00
3.02
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
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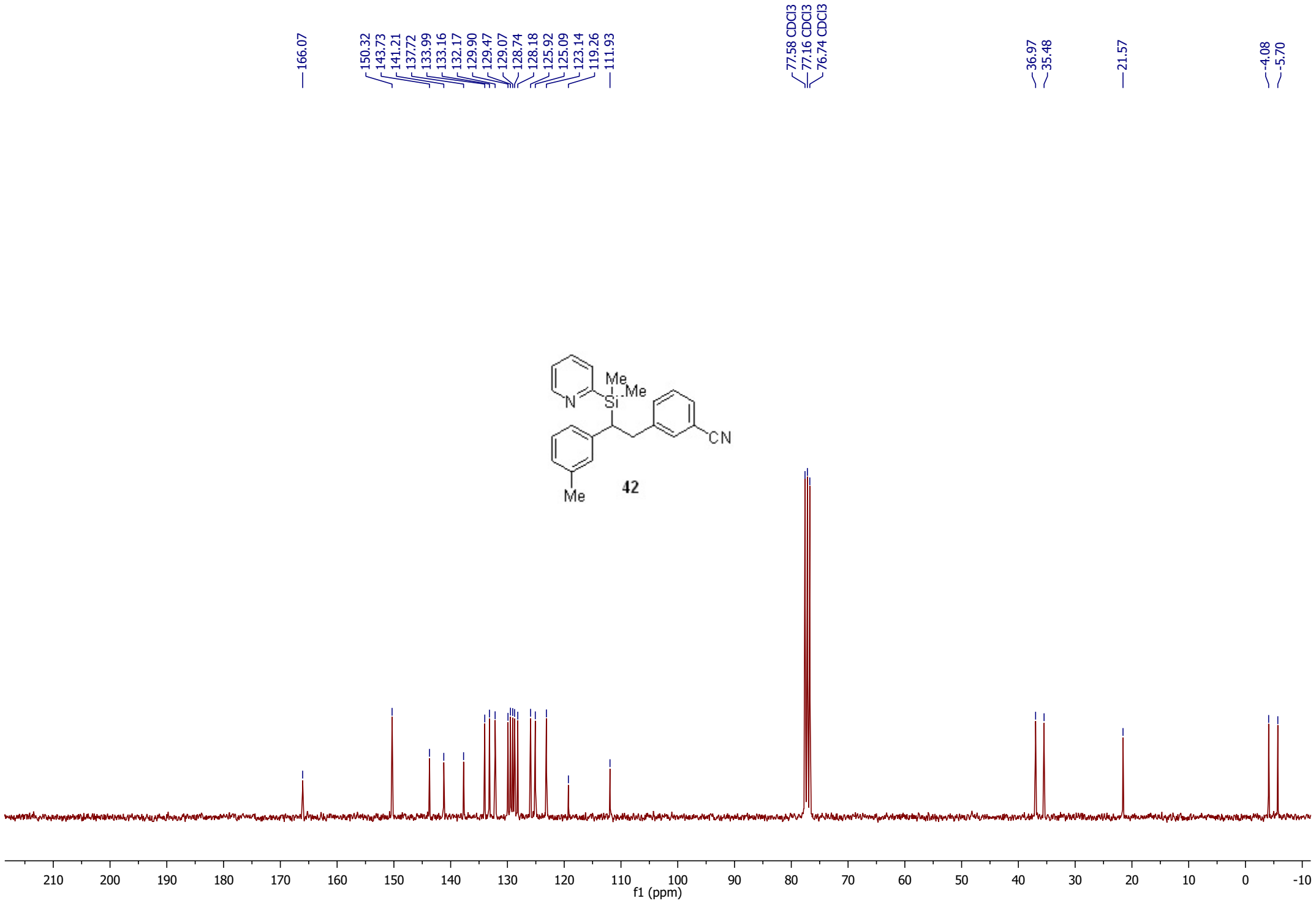
f1 (ppm)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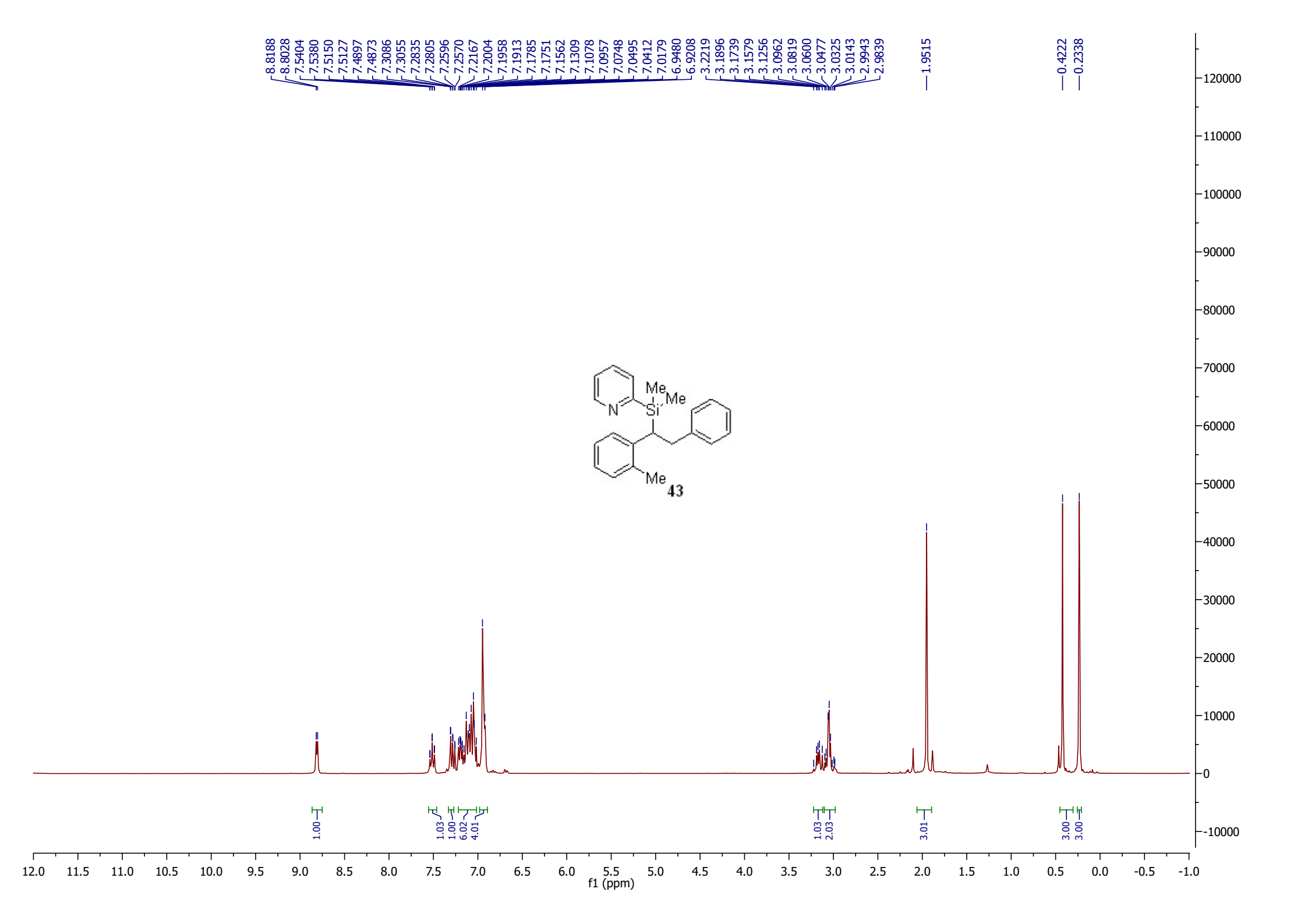
137.72
133.99
133.16
132.17
129.90
129.47
129.07
128.74
128.18
125.92
125.09
123.14
119.26
111.93
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
36.97
35.48
21.57
-4.08
-5.70
Me
Me
Si
N
CN
Me
42
f1 (ppm)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7.2835
7.2805
7.2596
7.2570
7.2167
7.2004
7.1958
7.1913
7.1785
7.1751
7.1562
7.1309
7.1078
7.0957
7.0748
7.0495
7.0412
7.0179
6.9480
6.9208
3.2219
3.1896
3.1739
3.1579
3.1256
3.0962
3.0819
3.0600
3.0477
3.0325
3.0143
2.9943
2.9839
1.9515
0.4222
0.2338
Me
Me
Si
N
Me
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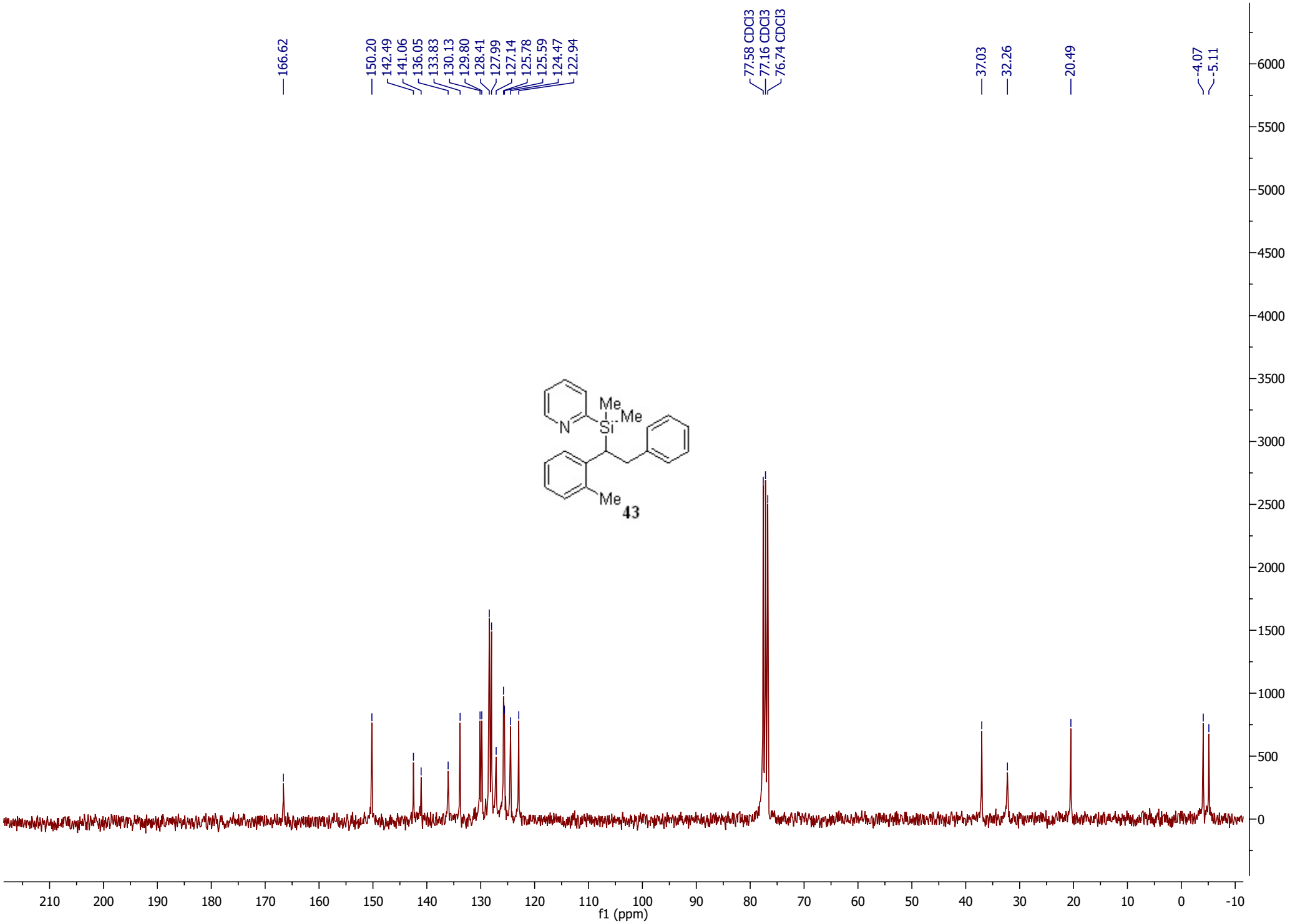
1.00
6.02
4.01
1.03
2.03
3.01
3.00
3.00
f1 (ppm)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129.80
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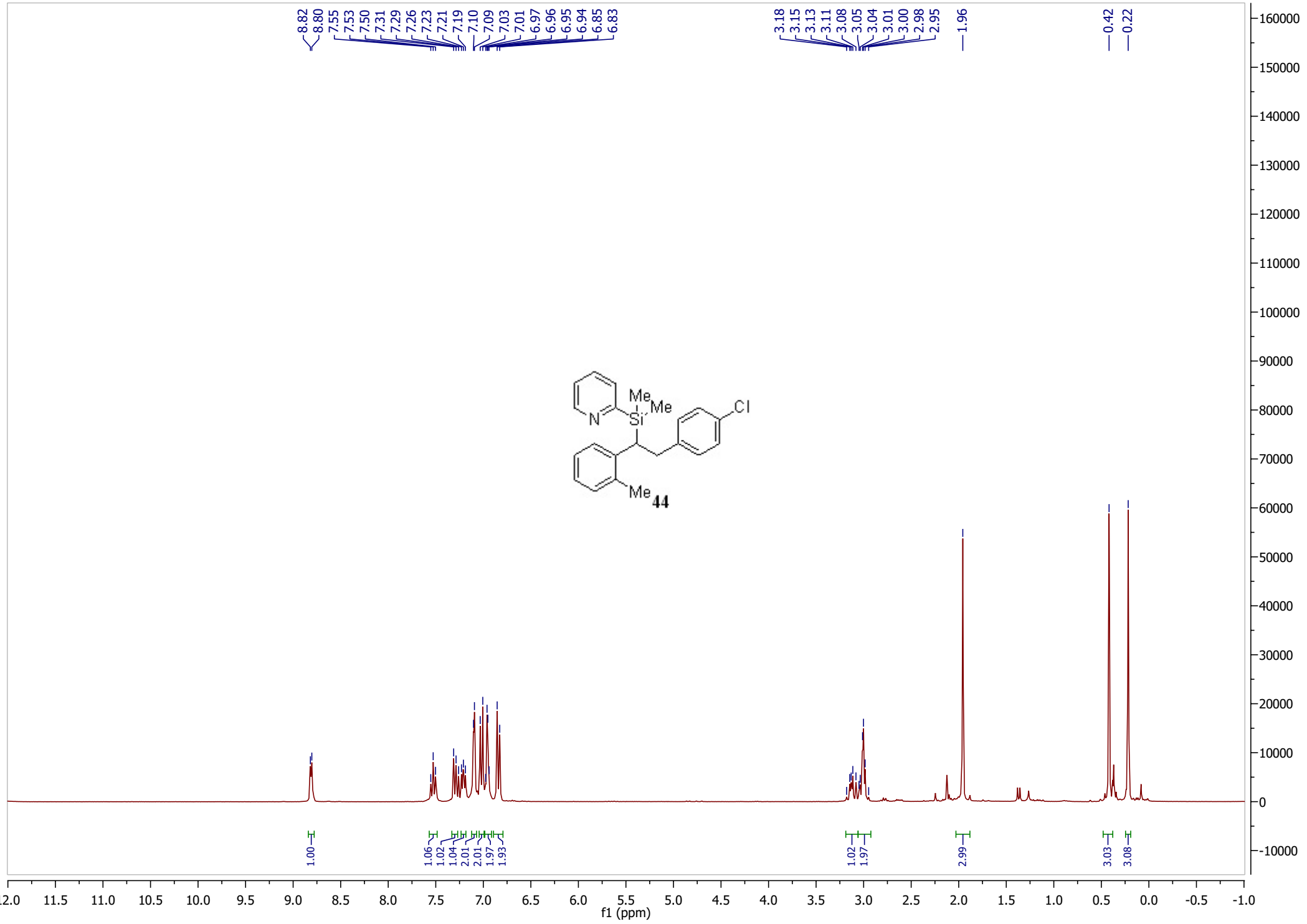
127.99
127.14
125.78
125.59
124.47
122.94
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
37.03
32.26
20.49
-4.07
-5.11
Me
Me
Si
N
Me
43
f1 (ppm)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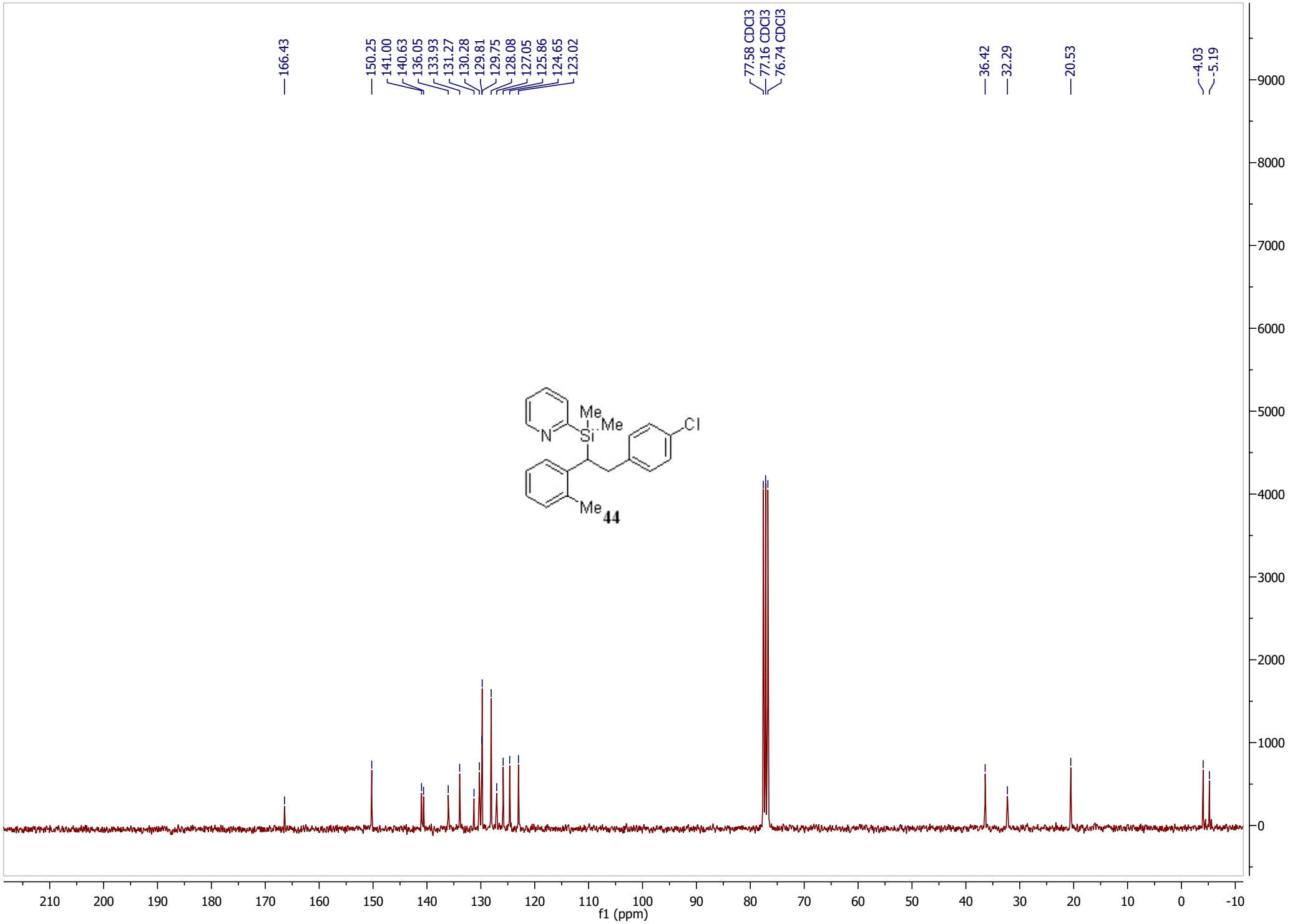
7.31
7.29
7.26
7.23
7.21
7.19
7.10
7.09
7.03
7.01
6.97
6.96
6.95
6.94
6.85
6.83
3.18
3.15
3.13
3.11
3.08
3.05
3.04
3.01
3.00
2.98
2.95
1.96
0.42
0.22
Me
Me
Si
N
Cl
Me
44
1.00
1.06
1.02
1.04
2.01
2.01
1.97
1.93
1.02
1.97
2.99
3.03
3.08
f1 (ppm)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130.28
129.81
129.75
128.08
127.05
125.86
124.65
123.02
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
36.42
32.29
20.53
-4.03
-5.19
Me
Me
Si
N
Cl
Me
44
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210
200
190
180
170
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120
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100
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80
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40
30
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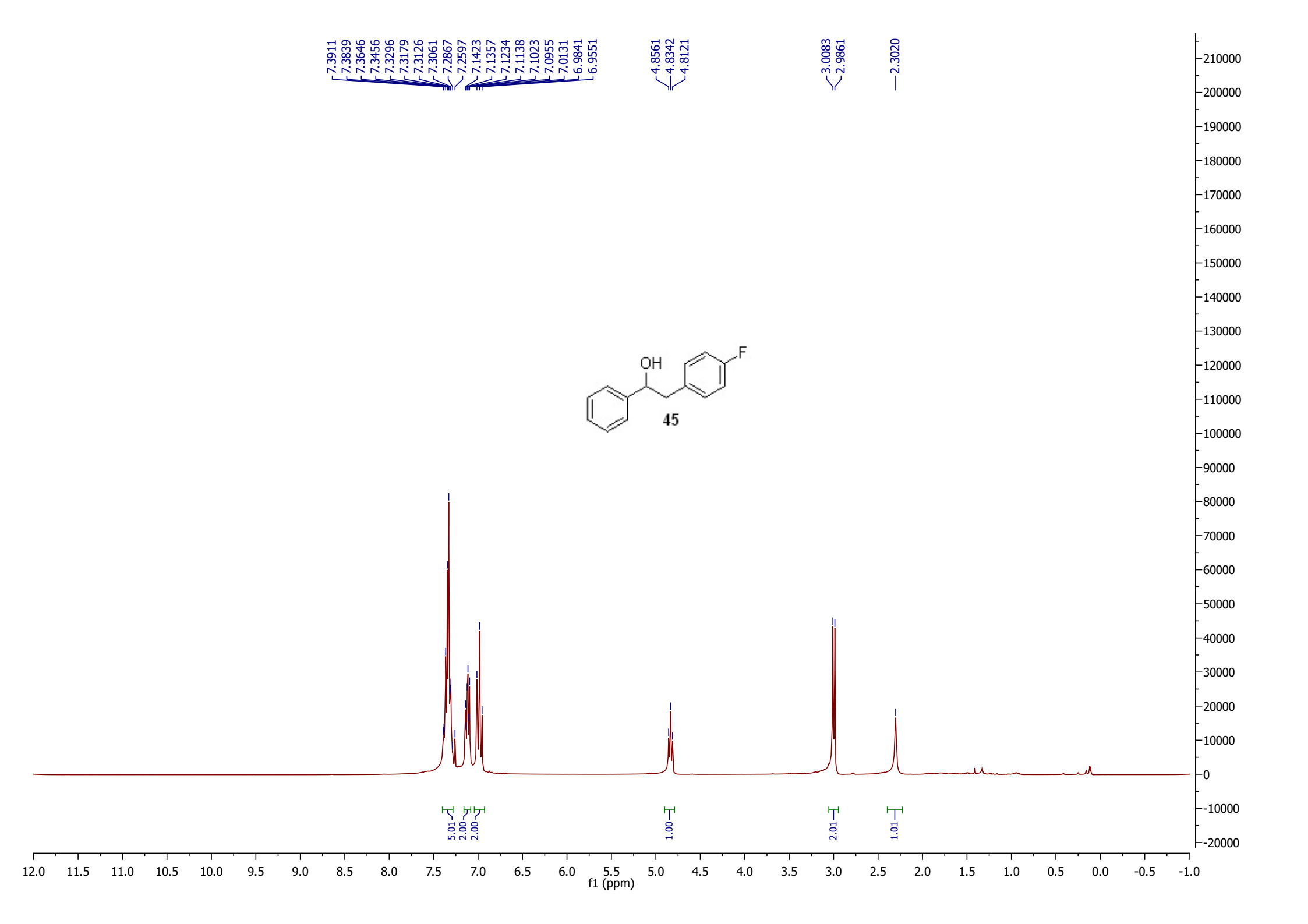
0
-10
f1 (ppm)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7.1234
7.1138
7.1023
7.0955
7.0131
6.9841
6.9551
4.8561
4.8342
4.8121
3.0083
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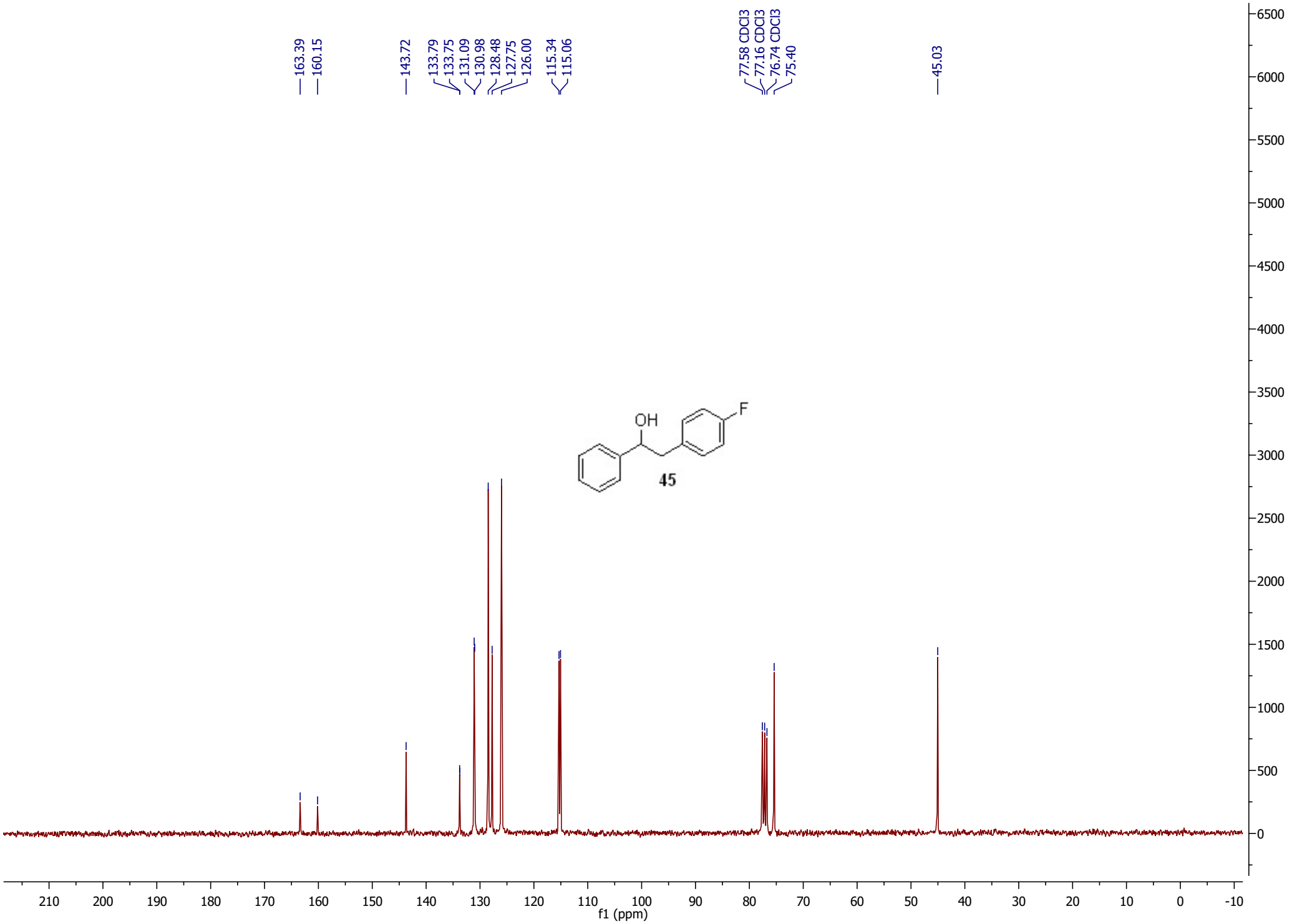
2.00
2.00
1.00
2.01
1.01
f1 (ppm)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126.00
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77.16 CDCl3
76.74 CDCl3
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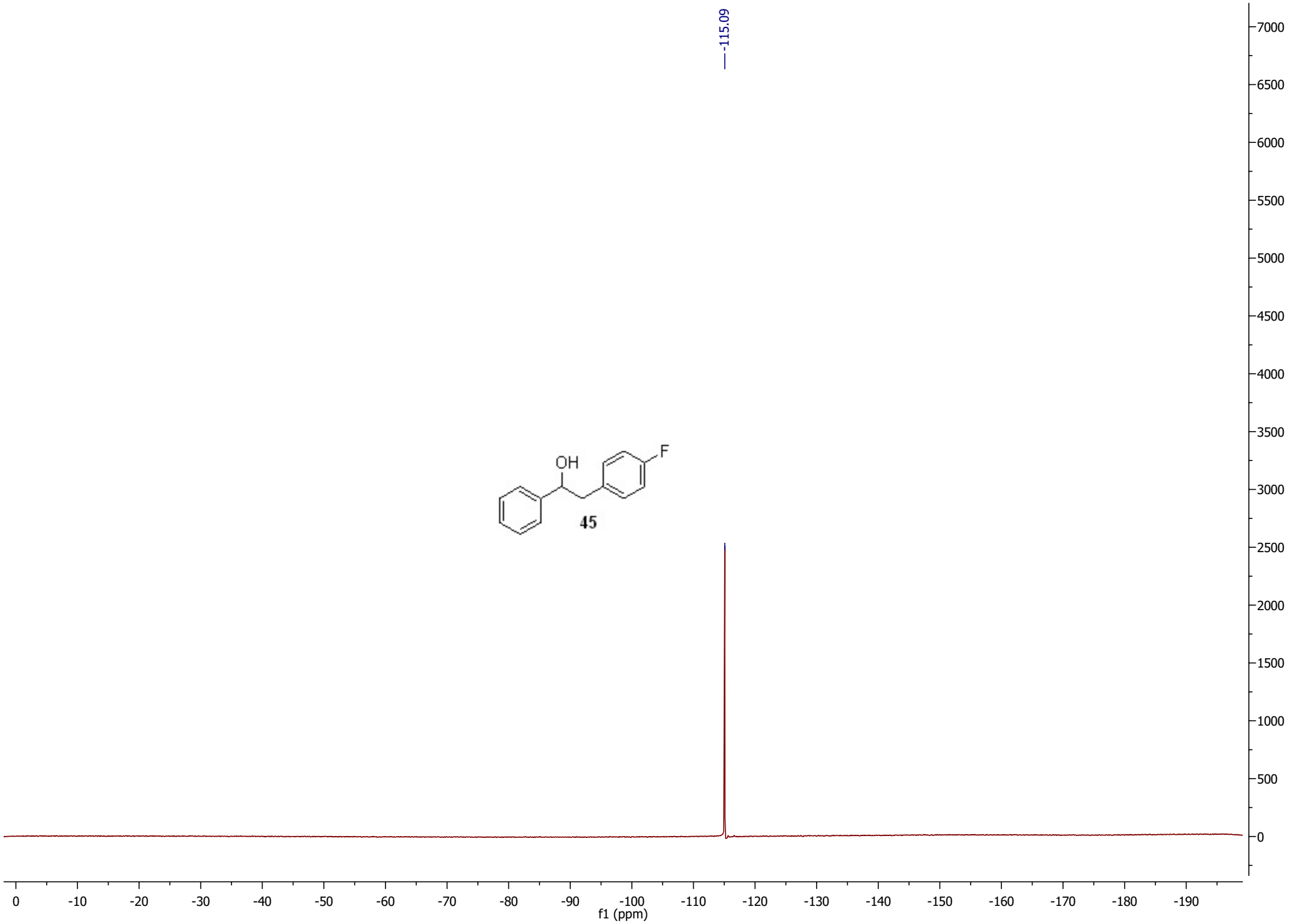
OH
F
45
f1 (ppm)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OH
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6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
-10
-20
-30
-40
-50
-60
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-80
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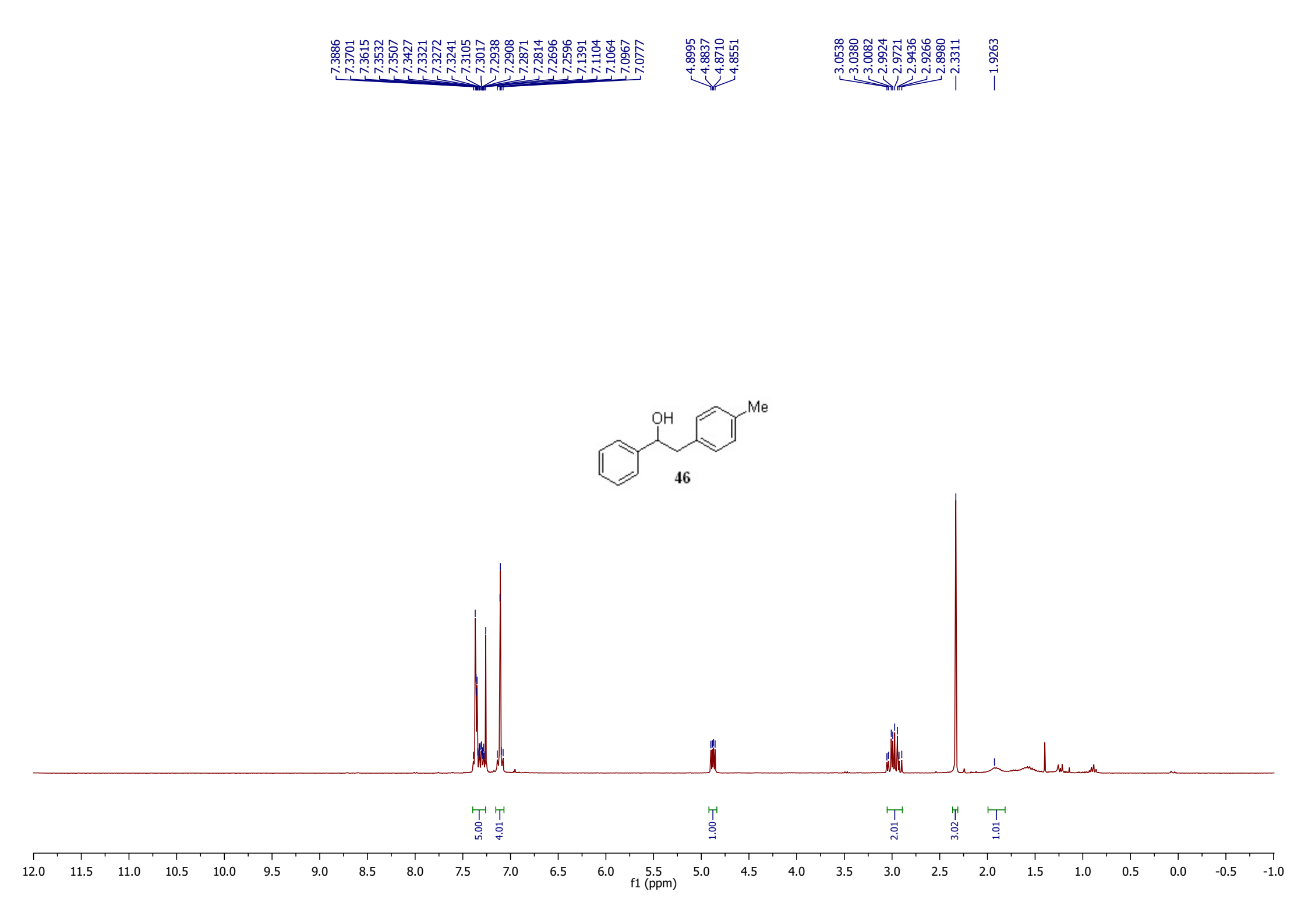
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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7.2871
7.2814
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7.2596
7.1391
7.1104
7.1064
7.0967
7.0777
4.8995
4.8837
4.8710
4.8551
3.0538
3.0380
3.0082
2.9924
2.9721
2.9436
2.9266
2.8980
2.3311
1.9263
OH
Me
46
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1.00
2.01
3.02
1.01
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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
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2.0
1.5
1.0
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0.0
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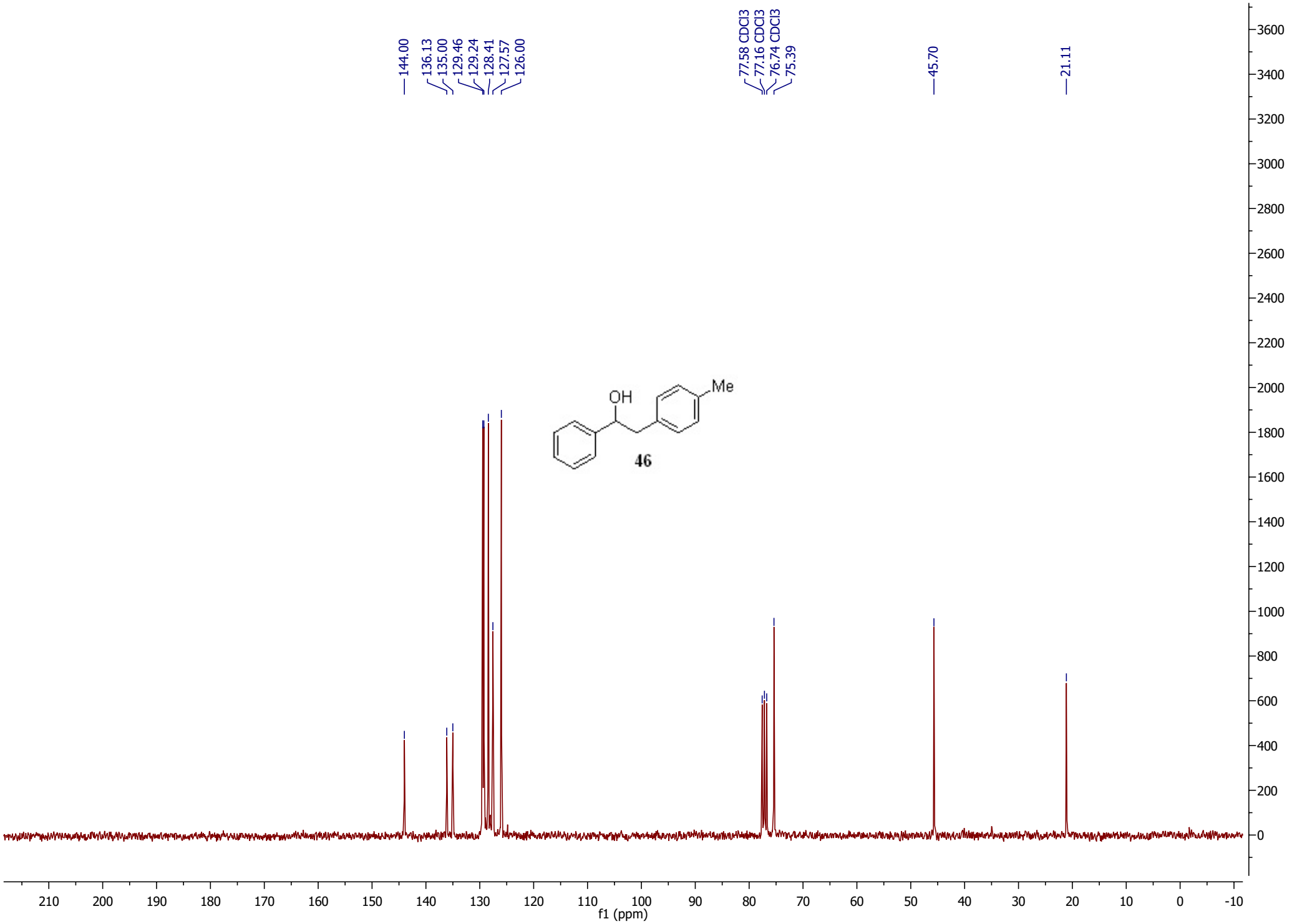
-1.0
f1 (ppm)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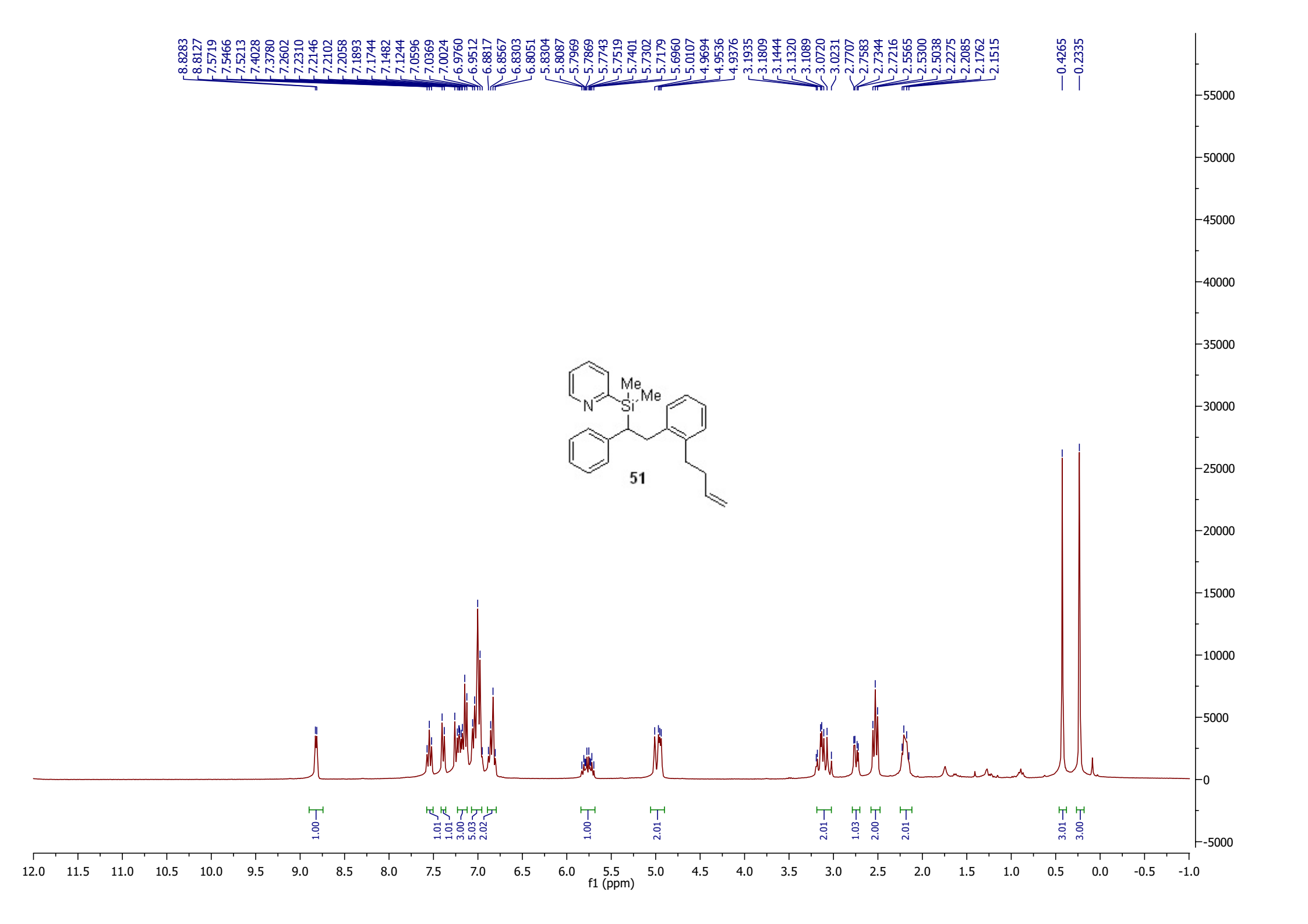
77.16 CDCl3
76.74 CDCl3
75.39
45.70
21.11
OH
Me
46
f1 (ppm)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7.0024
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3.1809
3.1444
3.1320
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2.7216
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2.1762
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0.2335
Me
Me
Si
N
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1.01
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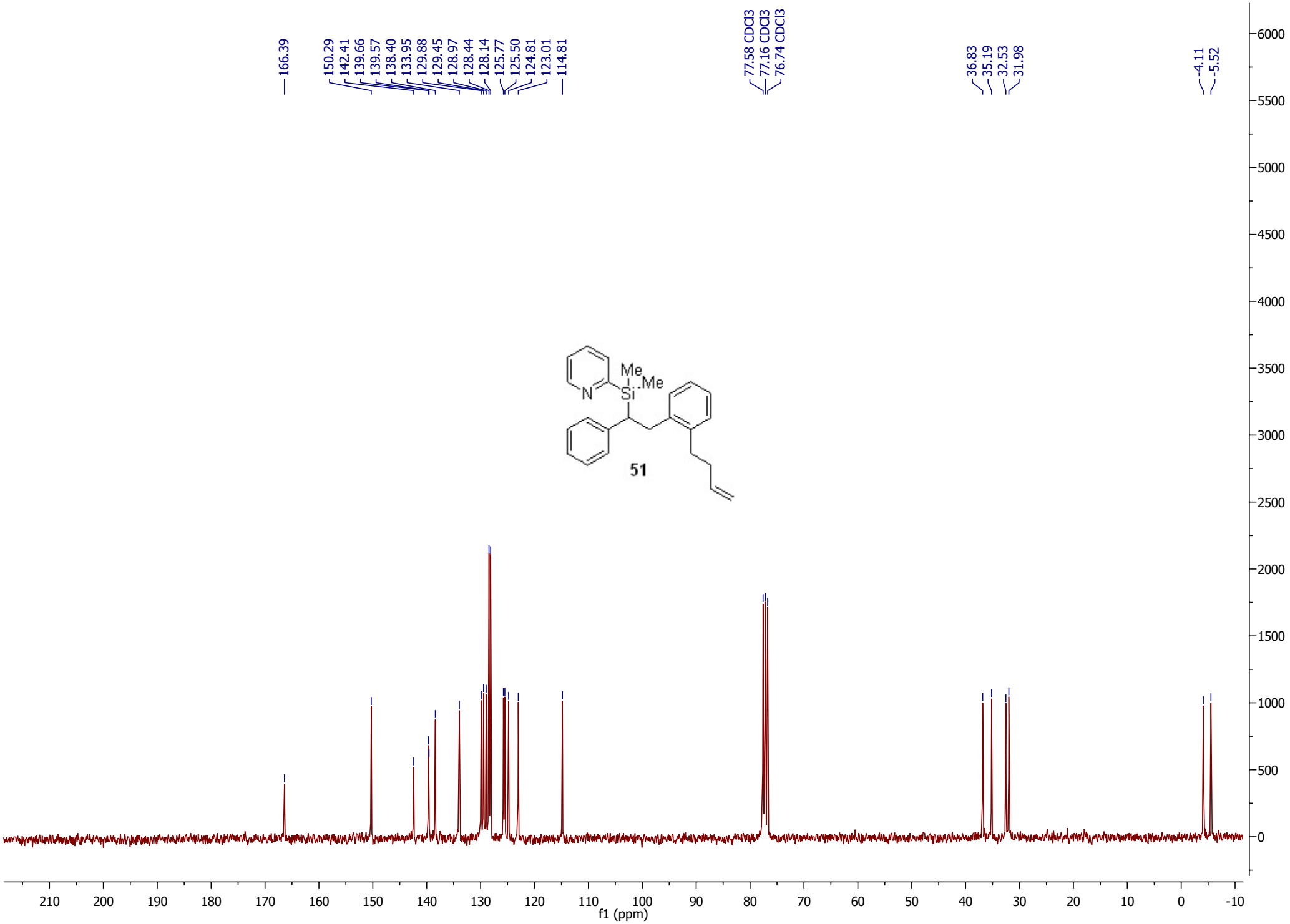
1.00
2.01
2.01
1.03
2.00
2.01
3.01
3.00
f1 (ppm)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128.44
128.14
125.77
125.50
124.81
123.01
114.81
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
36.83
35.19
32.53
31.98
-4.11
-5.52
Me
Me
N
Si
51
f1 (ppm)