Synthesis of Trifluoromethane -Sulfinamidines and –Sulfanylamides.

Aurélien FERRY, Thierry BILLARD, Bernard R. LANGLOIS,* Eric BACQUÉ*

ICBMS, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Laboratoire SERCOF, 43 boulevard du 11 novembre 1918, Villeurbanne, F-69622, France.

billard@univ-lyon1.fr

SUPPORTING INFORMATION

Typical procedure: Synthesis of **1aab to 1aai, 1abi** S3
N,N-diethyl-1,1,1-trifluoro-N'-(4-nitrophenyl)methane sulfinimidamide (**1aab**) S3
N,N-diethyl-1,1,1-trifluoro-N'-(3-nitrophenyl)methane sulfinimidamide (**1aac**) S4
N,N-diehyl-1,1,1-trifluoro-N'-(2-nitrophenyl)methanesulfinimidamide (**1aad**) S4
N,N-diethyl-1,1,1-trifluoro-N'-[2-(trifluoromethyl)phenyl]methanesulfinimidamide (**1aae**) S4
N-[(diethylamino)(trifluoromethyl)-λ^4-sulfanylidene]-4-methylbenzenesulfonamide (**1aaf**) S4
N-[(diethylamino)(trifluoromethyl)-λ^4-sulfanylidene]-1,1,1-trifluoromethanesulfonamide (**1aag**) S5
Benzyl[diethylamino(trifluoromethyl)-λ^4-sulfanylidene]carbamate (**1aah**) S5
N-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazol-5-yl}-N',N'-diethyl-1,1,1-trifluoromethanesulfinimidamide (**1aai**) S5
N-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazol-5-yl}-N',N'-diethyl-1,1,2,2,2-pentafluoroethane sulfinimidamide (**1abi**) S6
Typical procedure: Synthesis of **1baf, 1bai, 1baj5** .....
4-methyl-N-[morpholin-4-yl(trifluoromethyl)-λ^4-sulfanylidene] benzenesulfonamide (**1baf**) S6
1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-{[morpholin-4-yl(trifluoromethyl)-λ^4-sulfanylidene]amino}-1H-pyrazole-3-carbonitrile (**1bai**) S7
1-(4-{[morpholin-4-yl(trifluoromethyl)-λ^4-sulfanylidene]amino}phenyl)ethanone (**1baj**) S8
Typical procedure: Synthesis of **5aa, 5ak, 5al, 5am, 5an, 5ap, 5aq, 5ar, 5ba, 5bp, 5br** S8
N-[(trifluoromethyl)thio]aniline (**5aa**) S8
4-methyl-N-[(trifluoromethyl)thio]aniline (**5ak**) S8
4-methoxy-N-[(trifluoromethyl)thio]aniline (**5al)** S9
4-methoxy-N-[(trifluoromethyl)thio]aniline (**5al)** S9

4-fluoro-N-[(trifluoromethyl)thio]aniline (**5an**) S9
1-phenyl-N-[(trifluoromethyl)thio]methanamine (**5ap**) S9
1-phenyl-N-[(trifluoromethyl)thio]ethanamine (**5aq**) S9
N,N-diethyl-N'-[(trifluoromethyl)thio]pentane-1,4-diamine (**5ar**) S10
N-[(pentafluoroethyl)thio]aniline (**5ba**) S10
N-[(pentafluoroethyl)thio]-1-phenylmethanamine (**5bp**) S10
N,N-diethyl-N'-[(pentafluoroethyl)thio]pentane-1,4-diamine (**5br**) S10
Typical procedure: Synthesis of **5ca** S11
N-{[difluoro(phenylthio)methyl]thio}aniline (**5ca**) S11
Typical procedure: Synthesis of **5dp** S11
N-{[1,3-benzoxazol-2-yl(difluoro)methyl]thio}-1-phenylmethanamine (**5dp**) S12
Typical procedure: Synthesis of **5ab, 5aj, 5ao** S12
4-nitro-N-[(trifluoromethyl)thio]aniline (**5ab**) S12
1-(4-{[(trifluoromethyl)thio]amino}phenyl)ethanone (**5aj**) S13
4-(trifluoromethyl)-N-[(trifluoromethyl)thio]aniline (**5ao**) S13
Typical procedure: Synthesis of **5af, 5ah** S13
4-methyl-N-[(trifluoromethyl)thio]benzenesulfonamide (**5af**) S13
Benzyloxytrifluorométhanesulfacarbamide (**5ah**) S14

1H and 13C NMR spectra of compounds S15-S75

^{1}H, ^{13}C, ^{19}F NMR spectra were recorded in $CDCl_3$ (except in CD_2Cl_2 for compounds **1aac**, **1aad**, **1aae**) at 300, 75, and 282 MHz, respectively. Chemical shifts are given in ppm relative to TMS (^{1}H, ^{13}C) or $CFCl_3$ (^{19}F) as internal references. Coupling constants are given in Hertz.

Typical procedure: Synthesis of **1aab to 1aai, 1abi**

A flame-dried double-necked vessel was successively charged, under nitrogen, with diisopropylethylamine (14 mL, 80 mmol) and anhydrous dichloromethane (80 mL). The resulting mixture was cooled to -20°C before addition of diethylaminosulfurtrifluoride (5.5 mL, 44 mmol), followed by the addition of trimethylsilyltrifluoromethane (5.9 mL, 40 mmol) or trimethylsilylpentafluoroethane (7.7 mL, 40 mmol) in 20 min interval. After 1 hour under stirring at -20°C, the amine (1eq.) bearing an electron withdrawing group is added at 0°C (in its liquid form, solid form, or in 0,5 M solution from ethylacetate or dichloromethane). The reaction medium is then warmed to room temperature and kept under stirring for further 4 hours. The reaction medium was then washed with 6% aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude residue was simply washed with pentane or purified by chromatography over silica gel in presence of 0.5% of Et_3N to afford the corresponding sulfinamidines.

N,N-diethyl-1,1,1-trifluoro-N'-(4-nitrophenyl)methane sulfinimidamide (**1aab**): Orange solid. mp: 40-41°C. ^{1}H NMR: δ= 7.97 (m, 2H), 6.78 (m, 2H), 3.31 (q, ^{3}J(H,H)= 7.3, 4H), 1.11 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 123.8 (q, ^{4}J(C,F)= 1.1), 140.9, 125.7, 123.8 (q, ^{1}J(C,F)= 329), 119.7, 41.0, 13.8. ^{19}F NMR: δ= -70.85. Elemental analysis calcd (%) for $C_{11}H_{14}F_3N_3O_2S$: C 42.71, H 4.56, N 13.59, S 10.37. Found: C 42.82, H 4.63, N 13.87, S 10.14.

N,N-diethyl-1,1,1-trifluoro-N'-(3-nitrophenyl)methane sulfinimidamide (**1aac**): Brown oil. ^{1}H NMR: δ= 7.72-7.68 (massif, 2H), 7.36 (m, 1H), 7.24 (m, 1H), 3.43 (q, ^{3}J(H,H)= 7.2, 4H), 1.24 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 153.6 (q, ^{4}J(C,F)= 1.3), 149.5, 129.9, 127.1, 123.8 (q, ^{1}J(C,F)= 329), 114.9, 114.5, 40.6, 13.8. ^{19}F NMR: δ= -71.13. (not enough stable to obtain elemental analysis).

N,N-diehyl-1,1,1-trifluoro-N'-(2-nitrophenyl)methanesulfinimidamide (**1aad**): Brown oil. ^{1}H NMR: δ= 7.61 (m, 1H), 7.38 (m, 1H), 6.98-6.92 (massif, 2H), 3.41 (q, ^{3}J(H,H)= 7.1, 4H), 1.23 (t, ^{3}J(H,H)= 7.1, 6H). ^{13}C NMR: δ= 145.6 (q, ^{4}J(C,F)= 1.1), 136.6, 132.8, 124.7, 123.8 (q, ^{1}J(C,F)= 329), 121.4, 120.0, 41.1, 13.8. ^{19}F NMR: δ= -71.39. (not enough stable to obtain elemental analysis).

N,N-diethyl-1,1,1-trifluoro-N'-[2-(trifluoromethyl)phenyl]methanesulfinimidamide (**1aae**): Colorless oil. ^{1}H NMR: δ= 7.56 (m, 1H), 7.41 (m, 1H), 6.99–6.90 (massif, 2H), 3.42 (m, 4H), 1.24 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 151.0 (q, ^{4}J(C,F)= 1.1), 132.9 (q, ^{4}J(C,F)= 1.1), 127.2 (q, ^{3}J(C,F)= 5.5), 125.0 (q, ^{1}J(C,F)= 273), 123.9 (q, ^{1}J(C,F)= 329), 123.6 (q, ^{2}J(C,F)= 29), 119.7, 119.6, 40.8, 13.8. ^{19}F NMR: δ= -62.79, -68.68. (not enough stable to obtain elemental analysis).

N-[(diethylamino)(trifluoromethyl)-λ^{4}-sulfanylidene]-4-methylbenzenesulfonamide (**1aaf**): Yellow oil. ^{1}H NMR: δ= 7.77 (m, 2H), 7.25 (m, 2H), 3.36 (dq, ^{2}J(H,H)= 14.2, ^{3}J(H,H)= 7.2, 2H), 3.27 (dq, ^{2}J(H,H)= 14.2 ^{3}J(H,H)= 7.2, 2H), 2.39 (s, 3H), 1.17 (t, ^{3}J(H,H)= 7.2, 2H). ^{13}C NMR: δ= 142.9, 140.8, 129.7, 126.5, 123.5 (q, ^{1}J(C,F)= 328), 46.4, 21.7, 16.5. ^{19}F NMR: δ= -69.25. Elemental analysis calcd (%) for $C_{12}H_{17}F_3N_2O_2S_2$: C 42.09, H 5.00, N 8.18, S 18.73. Found: C 41.91, H 4.82, N 8.11, S 18.70.

N-[(diethylamino)(trifluoromethyl)-λ^4-sulfanylidene]-1,1,1-trifluoromethanesulfonamide (**1aag**): Colorless oil. ^{1}H NMR: δ= 3.49 (dq, ^2J(H,H)= 14.5, ^3J(H,H)= 7.2, 2H), 3.40 (dq, ^2J(H,H)= 14.5, ^3J(H,H)= 7.2, 2H), 1.25 (t, ^3J(H,H)= 7.2, 2H). ^{13}C NMR: δ= 123.3 (q, ^1J(C,F)= 328), 120.2 (q, ^1J(C,F)= 321), 43.8, 13.4. ^{19}F NMR: δ= -69.47 and -79.04. Elemental analysis calcd (%) for $C_6H_{10}F_2N_2O_2S_2$: C 22.50, H 3.15, N 8.75, S 20.02. Found: C 22.81, H 3.05, N 8.64, S 19.61.

Benzyl[diethylamino(trifluoromethyl)-λ^4-sulfanylidene]carbamate (**1aah**): Yellow oil. ^{1}H NMR: δ= 7.40–7.24 (massif, 5H), 5.18 (d, AB system, ^2J(H,H)= 12.3), 5.13 (d, AB system, ^2J(H,H)= 12.3), 3.35 (m, 4H), 1.20 (t, ^3J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 164.6 (q, ^4J(C,F)= 1.5), 137.0, 128.7, 128.6, 128.3, 123.8 (q, ^1J(C,F)= 325), 68.5, 13.8. ^{19}F NMR: δ= -69.19. Elemental analysis calcd (%) for $C_{13}H_{17}F_3N_2O_2S$: C 48.44, H 5.32, N 8.69, O 9.93, S 9.95. Found: C 48.56 H 5.45 N 8.42.

N-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazol-5-yl}-N',N'-diethyl-1,1,1-trifluoromethanesulfinimidamide (**1aai**): Brown solid. mp: 93-94°C. ^{1}H NMR: δ= 7.69 (s, 2H), 5.96 (s, 1H), 3.32 (q, ^3J(H,H)= 7.2, 4H), 1.18 (q, ^3J(H,H)= 7.2, 6H. ^{13}C NMR: δ= 153.2 (q, ^4J(C,F)= 1.6), 137.7 (q, ^5J(C,F)= 1.1), 136.8, 136,5, 133.6 (q, ^2J(C,F)= 34), 127.3, 125.82 (q, ^3J(C,F)= 3.4), 125.80 (q, ^3J(C,F)= 3.4), 123.3 (q, ^1J(C,F)= 329), 122.6 (q, ^1J(C,F)= 273), 114.5, 93.9, 41.1, 13.9. ^{19}F NMR: δ= -63,66 and -70,62. Elemental analysis calcd (%) for $C_{16}H_{13}Cl_2F_6N_5S$: C 39.04, H 2.66, Cl 14.40, N 14.23, S 6.51. Found: C 38.77, H 2.59, Cl 14.13, N 13.80 S 6.71.

N-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazol-5-yl}-N',N'-diethyl-1,1,2,2,2-pentafluoroethane sulfinimidamide (**1abi**): Brown solid. mp: 113-114°C. ^{1}H NMR: δ= 7.69 (m, 2H), 5.90 (s, 1H), 3.40 (m, 4H), 1.23 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 152.6 (q, ^{4}J(C,F)= 3.3), 137.6, 137.1, 136,6, 133.8 (q, ^{2}J(C,F)= 34), 127.3, 125.71 (q, ^{3}J(C,F)= 3.4), 125.70 (q, ^{3}J(C,F)= 3.4), 122.6 (q, ^{1}J(C,F)= 273), 115.9 (tq, ^{1}J(C,F)= 287, ^{2}J(C,F)= 34), 113.5 (qt, ^{1}J(C,F)= 284, ^{2}J(C,F)= 34), 114.4, 94.0, 40.8, 14.0. ^{19}F NMR: δ= -63.63, -79.35, -108.87 (d, ^{2}J(F,F)= 233), -120.66 (d, ^{2}J(F,F)= 233). Elemental analysis calcd (%) for $C_{17}H_{13}Cl_2F_8N_5S$: C 37.65, H 2.42, N 12.91. Found: C 37.51, H 2.63, N 13.19.

Typical procedure: Synthesis of **1baf, 1bai, 1baj**

A flame-dried double-necked vessel was successively charged, under nitrogen, with diisopropylethylamine (7 mL, 40 mmol) and anhydrous dichloromethane (80 mL). The resulting mixture was cooled to -20°C before addition of morpholinosulfurtrifluoride (5 mL, 40 mmol), followed by the addition of trimethylsilyltrifluoromethane (5.9 mL, 40 mmol) in 20 min interval. After 1 hour under stirring at -20°C, the amine (1eq.) is added at 0°C (in its liquid form, solid form, or in 0,5 M solution from ethylacetate or dichloromethane). The reaction medium is then cooled to room temperature and kept under stirring for further 4 hours. After this period, the reaction medium was washed with 6% aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude residue was simply washed with pentane or purified by chromatography over silica gel in presence of 0.5% of Et_3N to afford the corresponding sulfinamidines.

4-methyl-N-[morpholin-4-yl(trifluoromethyl)-λ^4-sulfanylidene] benzenesulfonamide (**1baf**): White solid. mp: 113-114°C. ^{1}H NMR: δ= 7.79 (m, 2H), 7.28 (m, 2H), 3.71 (ddd, ^{2}J(H,H)= 11.7, ^{3}J(H,H)= 3.3, ^{3}J(H,H)= 6.4, 2H), 3.61 (ddd, ^{2}J(H,H)= 11.7, ^{3}J(H,H)= 6.3,

^{3}J(H,H)= 3.1, 2H), 3.43 (ddd, ^{2}J(H,H)= 12.4, ^{3}J(H,H)= 3.3, ^{3}J(H,H)= 6.3, 2H), 3.24 (ddd, ^{2}J(H,H)= 12.4, ^{3}J(H,H)= 6.4, ^{3}J(H,H)= 3.1, 2H), 2.41 (s, 3H). ^{13}C NMR: δ= 143.3, 140.6, 129.9, 126.7, 123.9 (q, ^{1}J(C,F)= 330), 66.7, 46.7, 21.9. ^{19}F NMR: δ= -66.93. Elemental analysis calcd (%) for $C_{12}H_{15}F_3N_2O_3S_2$: C 40.44, H 4.24, N 7.86, S 17.99. Found C 40.48, H 4.13, N 7.83, S 17.99.

1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-{[morpholin-4-yl(trifluoromethyl)-λ^4-sulfanylidene]amino}-1H-pyrazole-3-carbonitrile (**1bai**): White solid. mp: 129-130°C. ^{1}H NMR: δ= 7.70 (s, 2H), 6.07 (s, 1H), 3.80-3.65 (massif, 4H), 3.41 (m, 2H), 3.19 (m, 2H). ^{13}C NMR: δ= 152.5 (q, ^{4}J(C,F)= 1.6), 137.4 (q, ^{5}J(C,F)= 1.1), 136.8, 136.4, 133.8 (q, ^{2}J(C,F)= 34), 127.4, 125.9 (q, ^{3}J(C,F)= 3.8), 125.9 (q, ^{3}J(C,F)= 3.8), 123.7 (q, ^{1}J(C,F)= 331), 122.6 (q, ^{1}J(C,F)= 274), 114.3, 94.0, 67.1, 45.4. ^{19}F NMR: δ= -63,58 and -67,88. Elemental analysis calcd (%) for $C_{16}H_{11}Cl_2F_6N_5OS$: C 37.96, H 2.19, Cl 14.01, N 13.83, O 3.16, S 6.33. Found: C 38.09, H 2.17, Cl 14.22, N 13.73, S 6.48.

1-(4-{[morpholin-4-yl(trifluoromethyl)-λ^4-sulfanylidene]amino}phenyl)ethanone (**1baj**): White solid. mp: 61-62°C. ^{1}H NMR: δ= 7.81-7.76 (massif, 2H), 6.94-6.90 (massif, 2H), 3.75 (ddd, ^{2}J(H,H)= 11.5, ^{3}J(H,H)= 3.3, ^{3}J(H,H)= 6.3, 2H), 3.67 (ddd, ^{2}J(H,H)= 11.5, ^{3}J(H,H)= 6.3, ^{3}J(H,H)= 3.3), 3.44 (ddd, ^{2}J(H,H)= 12.3, ^{3}J(H,H)= 3.3, ^{3}J(H,H)= 6.3, 2H), 3.25 (ddd, ^{2}J(H,H)= 12.3, ^{3}J(H,H)= 6.3, ^{3}J(H,H)= 3,3, 2H), 2.4 (s, 3H). ^{13}C NMR: δ= 197.1, 156.6 (q, ^{4}J(C,F)= 1.1), 130.5, 130.4, 124.1 (q, ^{1}J(C,F)= 331), 120.4, 67.2, 45.1, 26.6. ^{19}F NMR: δ= -68.06. Elemental analysis calcd (%) for $C_{13}H_{15}F_3N_2O_2S$: C 48.74, H 4.72, N 8.75. Found: C 48.99, H 4.96, N 8.49.

Typical procedure: Synthesis of **5aa, 5ak, 5al, 5am, 5an, 5ap, 5aq, 5ar, 5ba, 5bp, 5br**

A flame-dried double-necked vessel was successively charged, under nitrogen, with diisopropylethylamine (7 mL, 40 mmol) and anhydrous dichloromethane (80 mL). The resulting mixture was cooled to -20°C before addition of diethylaminosulfurtrifluoride (5.5 mL, 44 mmol), followed by the addition of trimethylsilyltrifluoromethane (5.9 mL, 40 mmol) or trimethylsilylpentafluoroethane (7.7 mL, 40 mmol) in 20 min interval.. After 1 hour under stirring at -20°C, the amine (1eq.) bearing an electron withdrawing group is added at 0°C (in its liquid form, solid form, or in 0,5 M solution from ethylacetate or dichloromethane). The reaction medium is then cooled to room temperature and kept under stirring overnight. After this period, the reaction medium was washed with distilled water. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude residue was purified by chromatography over silica gel to afford the corresponding sulfanylamides.

N-[(trifluoromethyl)thio]aniline (**5aa**): Yellow oil. ^{1}H NMR: δ= 7.35 (m, 2H), 7.15 (m, 2H), 7.06 (m, 1H), 5.09 (NH). ^{13}C NMR: δ= 145.5, 129.8 (q, ^1J(C,F)= 315), 129.7, 122.3, 115,6. ^{19}F NMR: δ= -53.33. Elemental analysis calcd (%) for $C_7H_6F_3NS$: C 43.52, H 3.13, N 7.25 S 16.60. Found: C 43.55, H 3.08, N 7.36, S 16.24.

4-methyl-N-[(trifluoromethyl)thio]aniline (**5ak**): Orange oil. ^{1}H NMR: δ= 7.10 (d, ^3J(H,H)= 8.3, 2H), 6.99 (d, ^3J(H,H)= 8.3, 2H), 4.99 (NH), 2.31 (s, 3H). ^{13}C NMR: δ= 143.1, 131.7, 130.2, 129.9 (q, ^1J(C,F)= 317), 115.5, 20.9. ^{19}F NMR: δ= -53.40. Elemental analysis calcd (%) for $C_8H_8F_3NS$: C 46.37, H 3.89, N 6.76. Found: C 46.56, H 4.01, N 6.65.

4-methoxy-N-[(trifluoromethyl)thio]aniline (**5al**): Orange oil. ^{1}H NMR: δ= 7.02 (m, 2H), 6.85 (m, 2H) ; 4.97 (NH), 3.78 (s, 3H). ^{13}C NMR: δ= 155.4, 139.1, 129.9 (q, ^{1}J(C,F)= 318), 117.0, 115.0 56.0. ^{19}F NMR: δ= -53.45. Elemental analysis calcd (%) for $C_8H_8F_3NOS$: C 43.05, H 3.61, N 6.27. Found: C 42.98, H 3.70, N 6.03.

4-chloro-*N*-[(trifluoromethyl)thio]aniline (**5am**): Yellow oil. ^{1}H NMR: δ= 7.26 (d, ^{3}J(H,H)= 9.0, 2H), 7.04 (d, ^{3}J(H,H)= 9.0, 2H), 5.14 (NH). ^{13}C NMR: δ= 144.1, 129.7 (q, ^{1}J(C,F)= 317), 129.6, 127.2, 116.8. ^{19}F NMR: δ= -53.25. Elemental analysis calcd (%) for $C_7H_5ClF_3NS$: C 36.93, H 2.21, N 6.15. Found: C 36.78, H 2.07, N 6.38.

4-fluoro-N-[(trifluoromethyl)thio]aniline (**5an**): Yellow oil. ^{1}H NMR: δ= 7.00–6.94 (massif, 4H), 5.03 (NH). ^{13}C NMR: δ= 158.7 (d, ^{1}J(C,F)= 240), 141.6 (d, ^{4}J(C,F)= 2.2), 129.8 (q, ^{1}J(C,F)= 318), 116.8 (d, ^{3}J(C,F)= 8.8) , 116.2 (d, ^{2}J(C,F)=23). ^{19}F NMR: δ= -53,38, -122,93 (tt, ^{3}J(H,F)= 8.5, ^{4}J(H,F)= 4.2). Elemental analysis calcd (%) for $C_7H_5F_4NS$: C 39.81, H 2.39, N 6.63. Found: C 39.55, H 2.51, N 6.52.

1-phenyl-N-[(trifluoromethyl)thio]methanamine (**5ap**): Colorless oil. ^{1}H NMR: δ= 7.36–7.40 (massif, 5H), 4,26 (d, ^{3}J(H,H)= 5.4, 2H), 3.17 (NH). ^{13}C NMR: δ= 138.7, 131.0 (q, ^{1}J(C,F)= 318), 129.1, 128.6, 128.3, 58.1. ^{19}F NMR: δ= -52.45. Elemental analysis calcd (%) for $C_8H_8F_3NS$: C 46.37, H 3.89, N 6.76. Found: C 46.25, H 3.94, N 6.62.

1-phenyl-N-[(trifluoromethyl)thio]ethanamine (**5aq**): Colorless oil. ^{1}H NMR: δ= 7.33–7.35 (massif, 5H), 4.28 (m, 1H), 3.31 (NH), 1.53 (d, ^{3}J(H,H)= 6.6, 3H). ^{13}C NMR: δ= 143.8, 130.8 (q, ^{1}J(C,F)= 317), 129.1, 128.3, 127.1, 61.0, 22.9. ^{19}F NMR: δ= -52.30. Elemental analysis calcd (%) for $C_9H_{10}F_3NS$: C 48.86, H 4.56, N 6.33. Found: C 49.02, H 4.77, N 6.41.

N,N-diethyl-N'-[(trifluoromethyl)thio]pentane-1,4-diamine (**5ar**): Colorless oil. ^{1}H NMR: δ= 3.48 (NH), 3.05 (m, 1H), 2.51 (q, ^{3}J(H,H)= 7.1, 4H), 2.40 (t, ^{3}J(H,H)= 7.0, 2H), 1.53–1.41 (massif, 4H), 1.14 (d, ^{3}J(H,H)= 6.4, 3H), 1.01 (t, ^{3}J(H,H)= 7.1, 6H). ^{13}C NMR: δ= 130.7 (q, ^{1}J(C,F)= 317), 57.1, 53.3, 47.0, 35.7, 23.9, 20.8, 11.8. ^{19}F NMR: δ= -53.35. Elemental analysis calcd (%) for $C_{10}H_{21}F_3N_2S$: C 46.49, H 8.19, N 10.84. Found: C 46.40, H 8.04, N 11.01.

N-[(pentafluoroethyl)thio]aniline (**5ba**): Colorless oil. ^{1}H NMR: δ= 7.28 (m, 2H), 7.08 (m, 2H), 6.97 (m, 1H), 4.97 (NH). ^{13}C NMR: δ= 145.6, 129.8, 122.4, 120.0 (tq, ^{1}J(C,F)= 292, ^{2}J(C,F)= 39), 119.2 (qt, ^{1}J(C,F)= 286, ^{2}J(C,F)= 37), 115.6. ^{19}F NMR: δ= -83.09 (t, ^{3}J(F,F)= 2.87), -103.45 (t, ^{3}J(F,F)= 2.87). Elemental analysis calcd (%) for $C_8H_6F_5NS$: C 39.51, H 2.49, N 5.76.Found: C 39.39, H 2.35, N 5.92.

N-[(pentafluoroethyl)thio]-1-phenylmethanamine (**5bp**): Colorless oil. ^{1}H NMR: δ= 7.28–7.36 (massif, 5H), 4.24 (d, ^{3}J(H,H)= 5.3, 2H), 3.06 (NH). ^{13}C NMR: δ= 138.6, 129.1, 128.5, 128.4, 121.0 (tq, ^{1}J(C,F)= 291, ^{2}J(C,F)= 38), 119.3 (qt, ^{1}J(C,F)= 286, ^{2}J(C,F)= 38), 58.5. ^{19}F NMR: δ= -83,19 (t, ^{3}J(F,F)= 2.77) and -102.93 (s, ^{3}J(F,F)= 2.77). Elemental analysis calcd (%) for $C_9H_8F_5NS$: C 42.02, H 3.13, N 5.45. Found: C 41.70, H 2.98, N 5.67.

N,N-diethyl-N'-[(pentafluoroethyl)thio]pentane-1,4-diamine (**5br**): Colorless oil. ^{1}H NMR: δ= 3.34 (NH), 3.05 (m, 1H), 2.60 (q, ^{3}J(H,H)= 7.2, 4H), 2.49 (t, ^{3}J(H,H)= 6.4, 2H), 1.55–1.44 (massif, 4H), 1.16 (d, ^{3}J(H,H)= 6.4, 3H), 1.07 (t, ^{3}J(H,H)= 7.2, 6H). ^{13}C NMR: δ= 121.1 (tq, ^{1}J(C,F)= 289, ^{2}J(C,F)= 38), 119.0 (qt, ^{1}J(C,F)= 286, ^{2}J(C,F)= 38), 57.5, 53.1, 47.0, 35.5, 23.3, 20.9, 11.4. ^{19}F NMR: δ= -83.05 (t, ^{3}J(F,F)= 3.4), -103.15 (m). Elemental analysis calcd (%) for $C_{11}H_{21}F_5N_2S$: C 42.85, H 6.86, N 9.08. Found: C 42.64, H 6.52, N 9.33.

Typical procedure: Synthesis of **5ca**

To a cooled solution of diisopropylethylamine (175 µL, 1 mmol) and anhydrous dichloromethane (2 mL) at -20°C, is added under nitrogen, diethylaminosulfurtrifluoride (135 µL, 1.1 mmol), followed by the addition of (Difluorophenylsulfanylmethyl)trimethylsilane (232 mg, 1 mmol) in 20 min interval. After 1 hour under stirring at -20°C, aniline (91 µL, 1mmol) is added in its liquid form. The reaction medium is then cooled to room temperature and kept under stirring overnight. After this period, the reaction medium was washed with distilled water. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The crude residue was purified by chromatography over silica gel to afford the corresponding sulfanylamide **5cb**.

N-{[difluoro(phenylthio)methyl]thio}aniline (**5ca**): Colorless oil. ^{1}H NMR: δ= 7.69 (m, 2H), 7.55–7.42 (massif, 3H), 7.24 (m, 2H), 7.00–6.92 (massif, 3H), 5.23 (NH). ^{13}C NMR: δ= 146.3, 136.9 (t, ^4J(C,F)= 1.1), 134.2 (t, ^1J(C,F)= 319), 130.8, 129.7, 129.6, 127.3 (t, ^3J(C,F)= 1.6), 121.7, 115.4. ^{19}F NMR: δ= -59,37. Elemental analysis calcd (%) for $C_{13}H_{11}F_2NS_2$: C 55.10, H 3.91, N 4.94. Found: C 55.18, H 4.03, N 4.81.

Typical procedure: Synthesis of **5dp**

To a cooled solution of diisopropylethylamine (175 µL, 1 mmol) and anhydrous dichloromethane (2 mL) at -20°C, is added under nitrogen, diethylaminosulfurtrifluoride (135 µL, 1,1 mmol), followed by the addition of 2-(Difluorotrimethylsilanylmethyl)benzooxazole (241 mg in 2 mL of CH_2Cl_2) in 20 min interval. After 1 hour under stirring at -20°C, benzylamine (110 µL, 1 mmol) is added in its liquid form. The reaction medium is then cooled to room temperature and kept under stirring for 4 hours. After this period, the reaction medium was washed with distilled water. The organic phase was dried over Na_2SO_4 and

evaporated in vacuo. The crude residue was washed with cooled pentane to afford the corresponding sulfanylamide **5dp**.

N-{[1,3-benzoxazol-2-yl(difluoro)methyl]thio}-1-phenylmethanamine (**5dp**): White solid. mp: 46-47°C. ^{1}H NMR: δ= 7.86 (m, 1H), 7.64 (m, 1H), 7.53-7.44 (massif, 2H), 7.40-7.26 (massif, 5H), 4.28 (d, ^{3}J(H,H)= 4.9, 2H), 3.27 (NH). ^{13}C NMR: δ= 156.9 (t, ^{2}J(C,F)= 33), 151.0, 140.5, 139.0, 128.9, 128.6, 128.2, 127.5, 125.9, 123,4 (t, ^{1}J(C,F)= 279), 121.9, 111.9, 58.35. ^{19}F NMR: δ= -84.41. Elemental analysis calcd (%) for $C_{15}H_{12}F_2N_2OS$: C 58.81, H 3.95, N 9.14, S 10.47. Found: C 59.11, H 4.21, N 8.95, S 10.06.

Typical procedure: Synthesis of **5ab, 5aj, 5ao**

In a solution of pure sulfinamidine (or a mixture of sulfanylamide/sulfinamidine) in dichloromethane (2 mL/mmol) is added 1.2 eq. of trifluoroacetic acid per mmol of sulfinamidine. The resulting mixture is then kept under stirring for 1 hour at room temperature. After this period, the reaction medium is washed with distilled water. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The corresponding sulfanylamide is directly obtained pure after work up.

4-nitro-N-[(trifluoromethyl)thio]aniline (**5ab**): Brown solid. mp: 88-89°C. ^{1}H NMR: δ= 8.22 (m, 2H), 7.20 (m, 2H), 5.64 (NH). ^{13}C NMR: δ= 151.9, 142.4, 129.4 (q, ^{1}J(C,F)= 317), 126.1, 115.3. ^{19}F NMR: δ= -52.71. Elemental analysis calcd (%) for $C_7H_5F_3N_2O_2S$: C 35.30, H 2.12, N 11.76. Found: C 35.41, H 2.21, N 11.63.

1-(4-{[(trifluoromethyl)thio]amino}phenyl)ethanone (**5aj**): Beige solid. mp: 90-91°C. ^{1}H NMR: δ= 7.91 (d, ^{3}J(H,H)= 8.7, 2H), 7.16 (d, ^{3}J(H,H)= 8.7, 2H), 6.11 (NH), 2.56 (s, 3H). ^{13}C NMR: δ= 197.6, 150.3, 131.4, 130.8, 129.6 (q, ^{1}J(C,F)= 317), 115.1, 26.7. ^{19}F NMR: δ= -52.93. Elemental analysis calcd (%) for $C_9H_8F_3NOS$: C 45.95, H 3.43, N 5.95. Found: C 46.19, H 3.61, N 5.78.

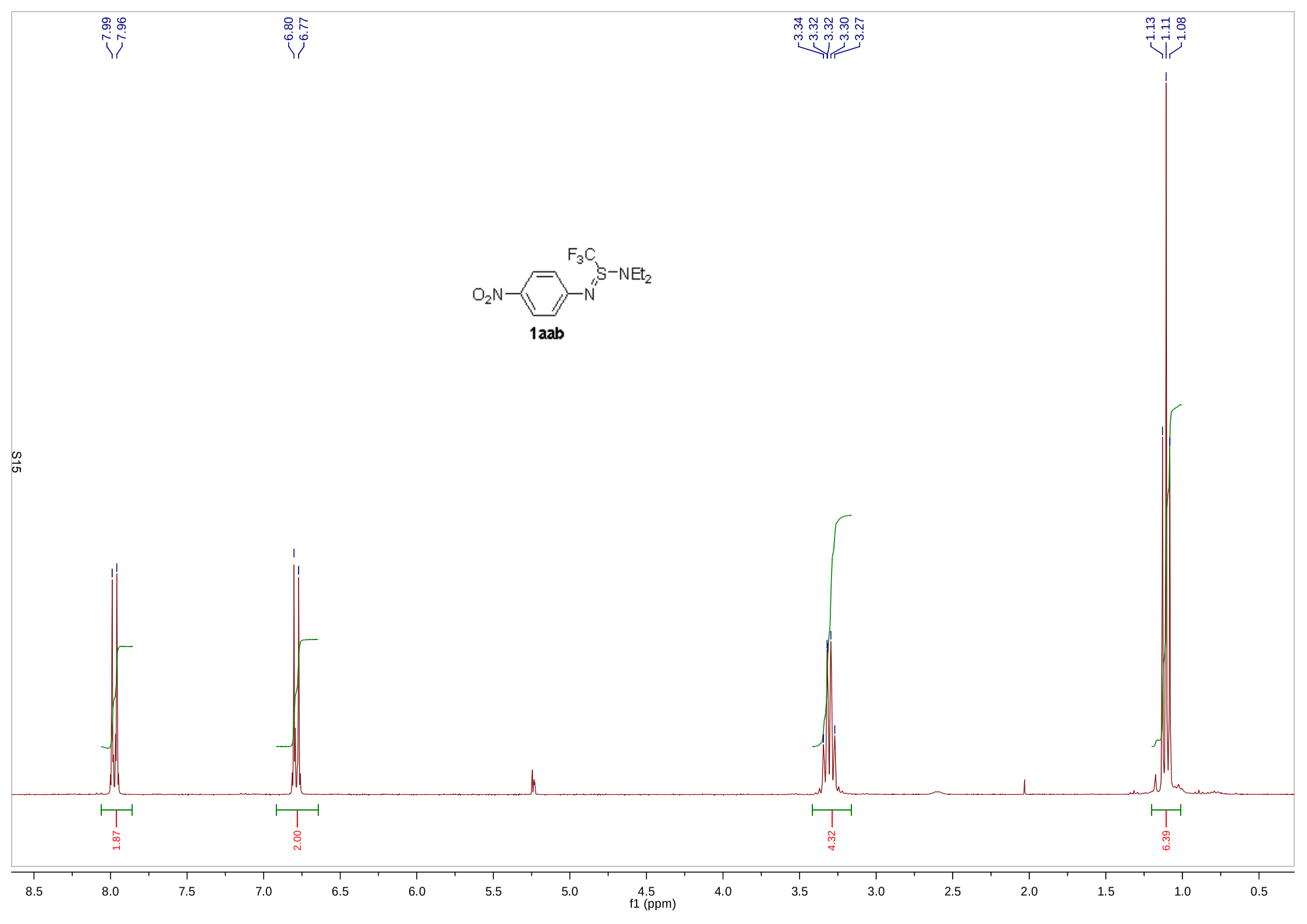
4-(trifluoromethyl)-N-[(trifluoromethyl)thio]aniline (**5ao**): Yellow oil. ^{1}H NMR: δ= 7.54 (d, ^{3}J(H,H)= 8.5, 2H), 7.16 (d, ^{3}J(H,H)= 8.5, 2H), 5.35 (NH). ^{13}C NMR: δ= 148.4 (q, ^{5}J(C,F)= 1.1), 129.6 (q, ^{1}J(C,F)= 317), 127.1 (q, ^{3}J(C,F)= 3.7), 124.7 (q, ^{1}J(C,F)= 271), 124.5 (q, ^{2}J(C,F)= 32.7), 115.3. ^{19}F NMR: δ= -53.14 and -63.24. Elemental analysis calcd (%) for $C_8H_5F_6NS$: C 36.79, H 1.93, N 5.36,. Found: C 37.01, H 2.07, N 5.74.

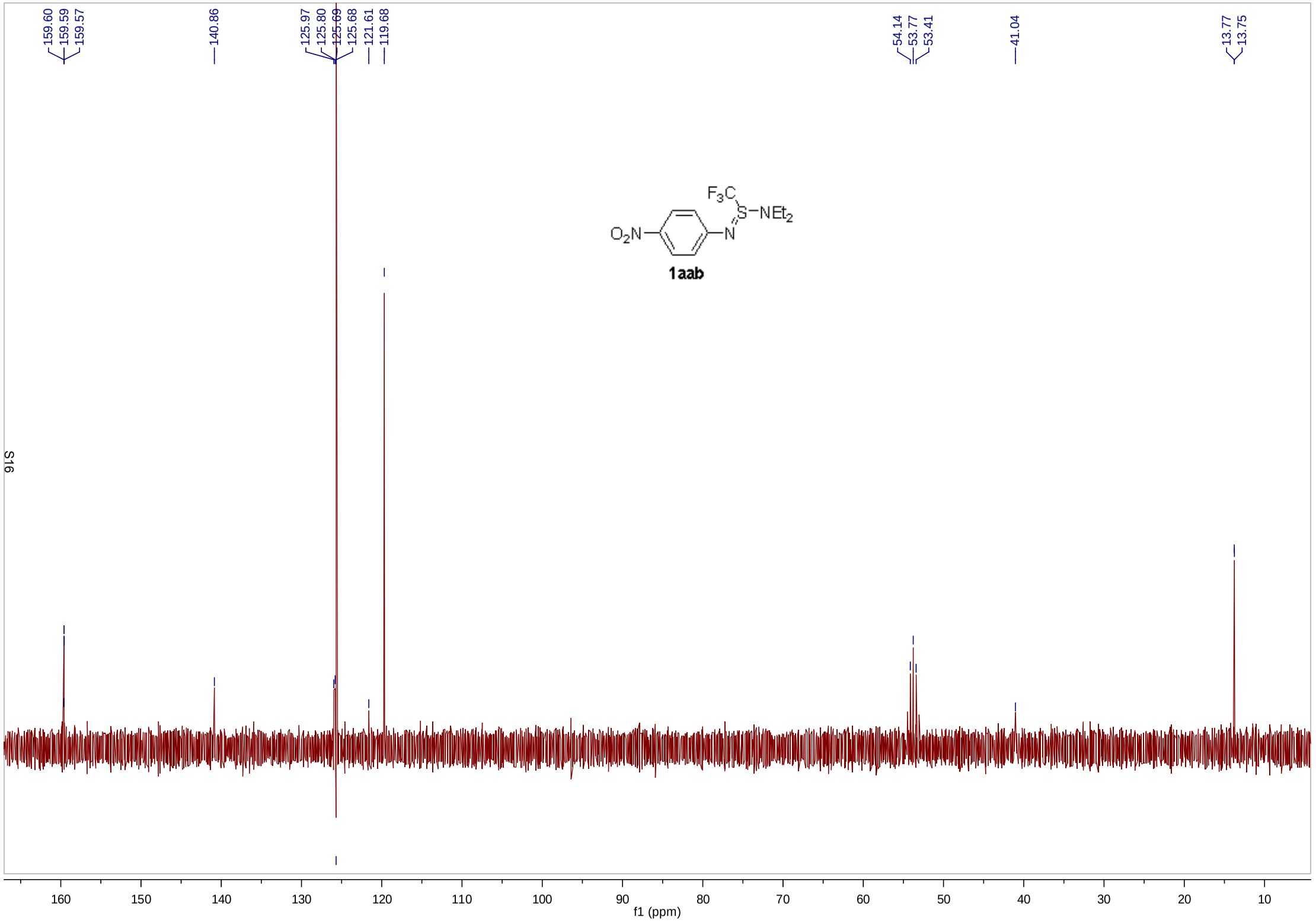
Typical procedure: Synthesis of **5af, 5ah**

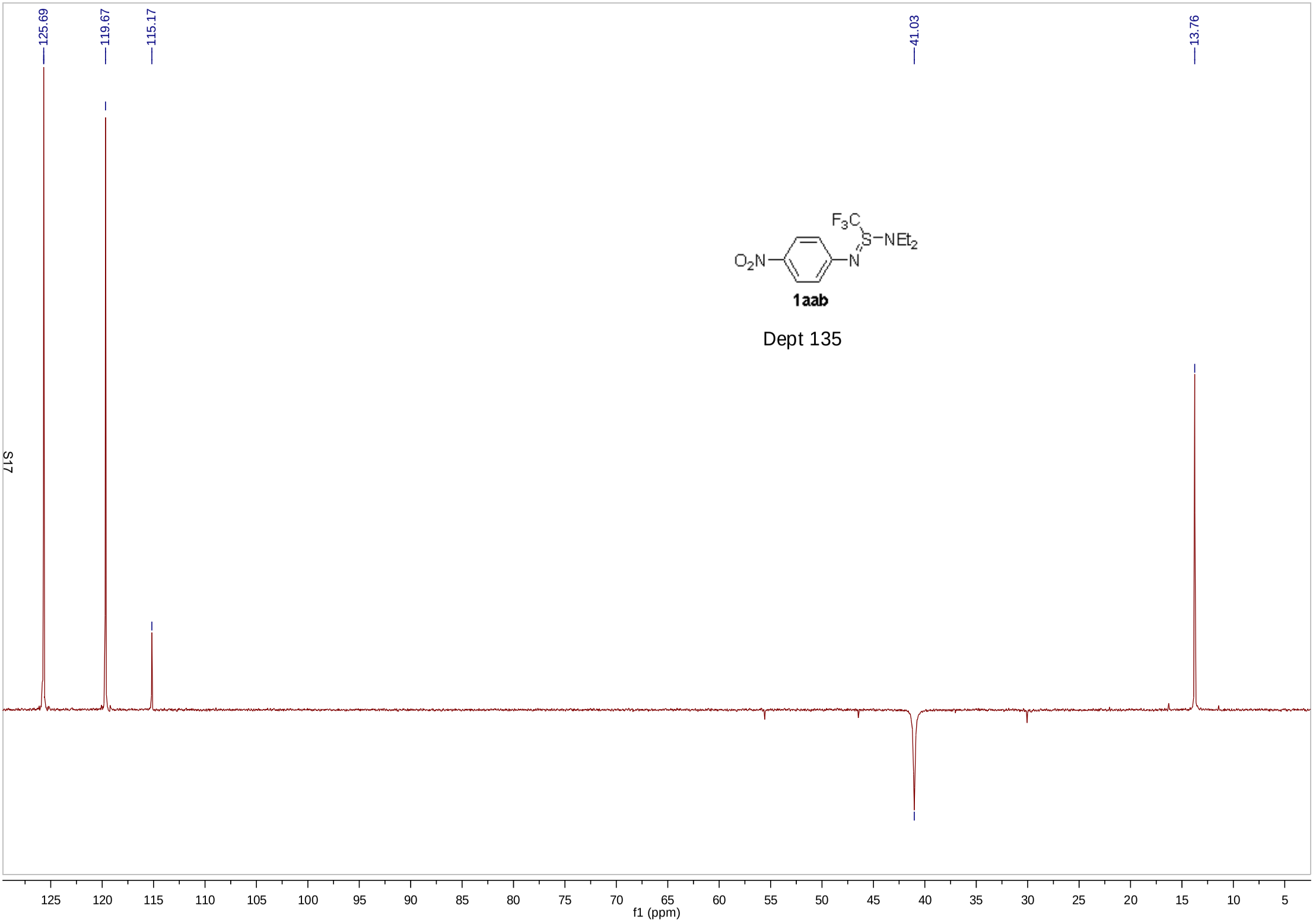
In a solution of sulfinamidine (1 mmol of **1aaf** or **1aah**) in dichloromethane (2 mL) is added (26 μL, 3.5 mmol) of trifluoroacetic acid. The resulting mixture is then stirred at 50°C for 24h. After this period, the reaction medium is washed with distilled water. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The corresponding sulfanylamide is directly obtained pure after work up.

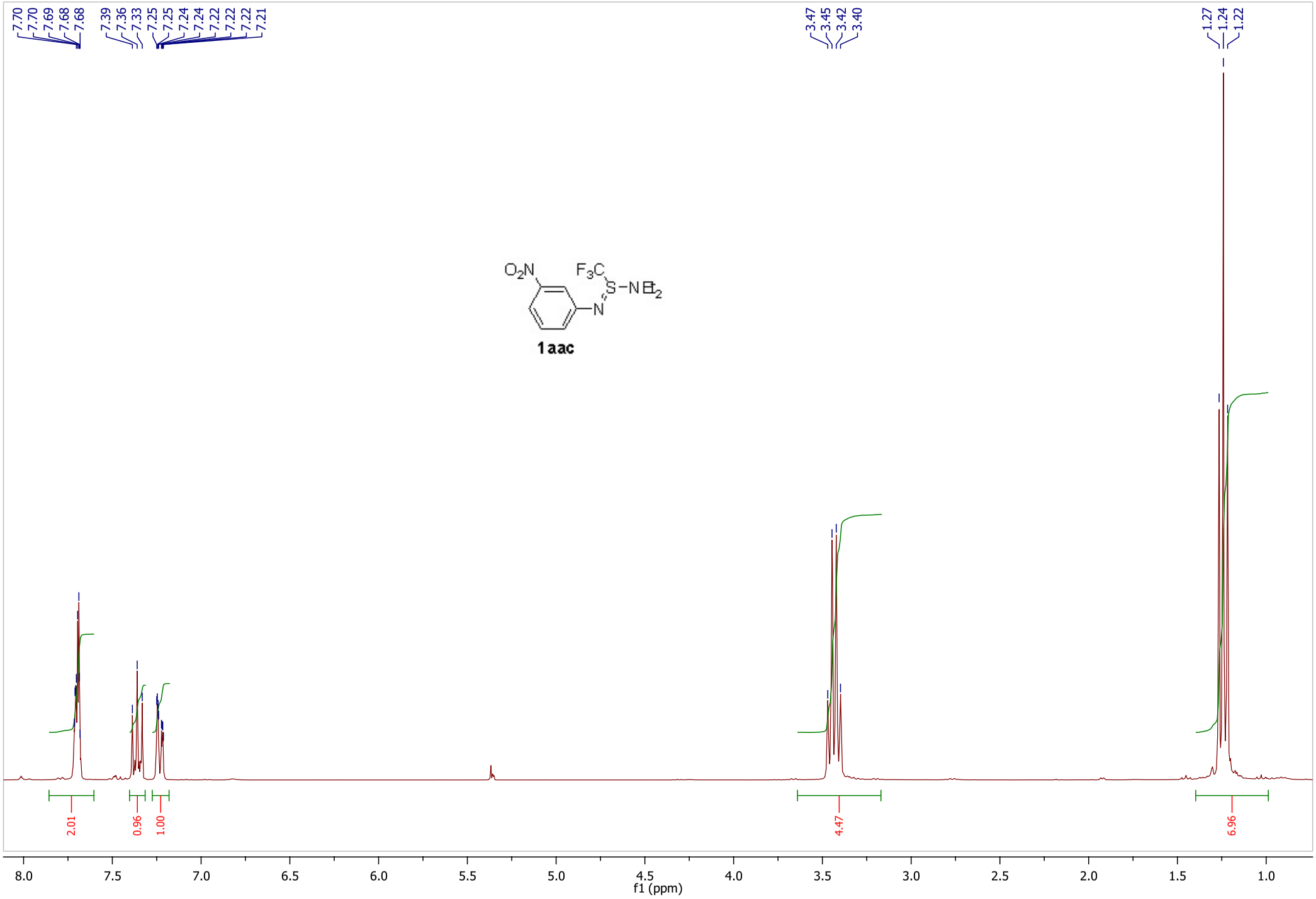
4-methyl-N-[(trifluoromethyl)thio]benzenesulfonamide (**5af**): White solid. mp: 85-86°C. ^{1}H NMR: δ= 7.81 (d, ^{3}J(H,H)= 8.1, 2H), 7.35 (d, ^{3}J(H,H)= 8.1, 2H), 6.75 (NH), 2.45. ^{13}C NMR: δ= 145.6, 135.4, 130.3, 128.4 (q, ^{1}J(C,F)= 314), 128.2, 22.0. ^{19}F NMR: δ= -51.86. Elemental analysis calcd (%) for $C_8H_8F_3NO_2S_2$: C 35.42, H 2.97, N 5.16, S 23.64. Found: C 35.61, H 3.36, N 5.16, S 23.23.

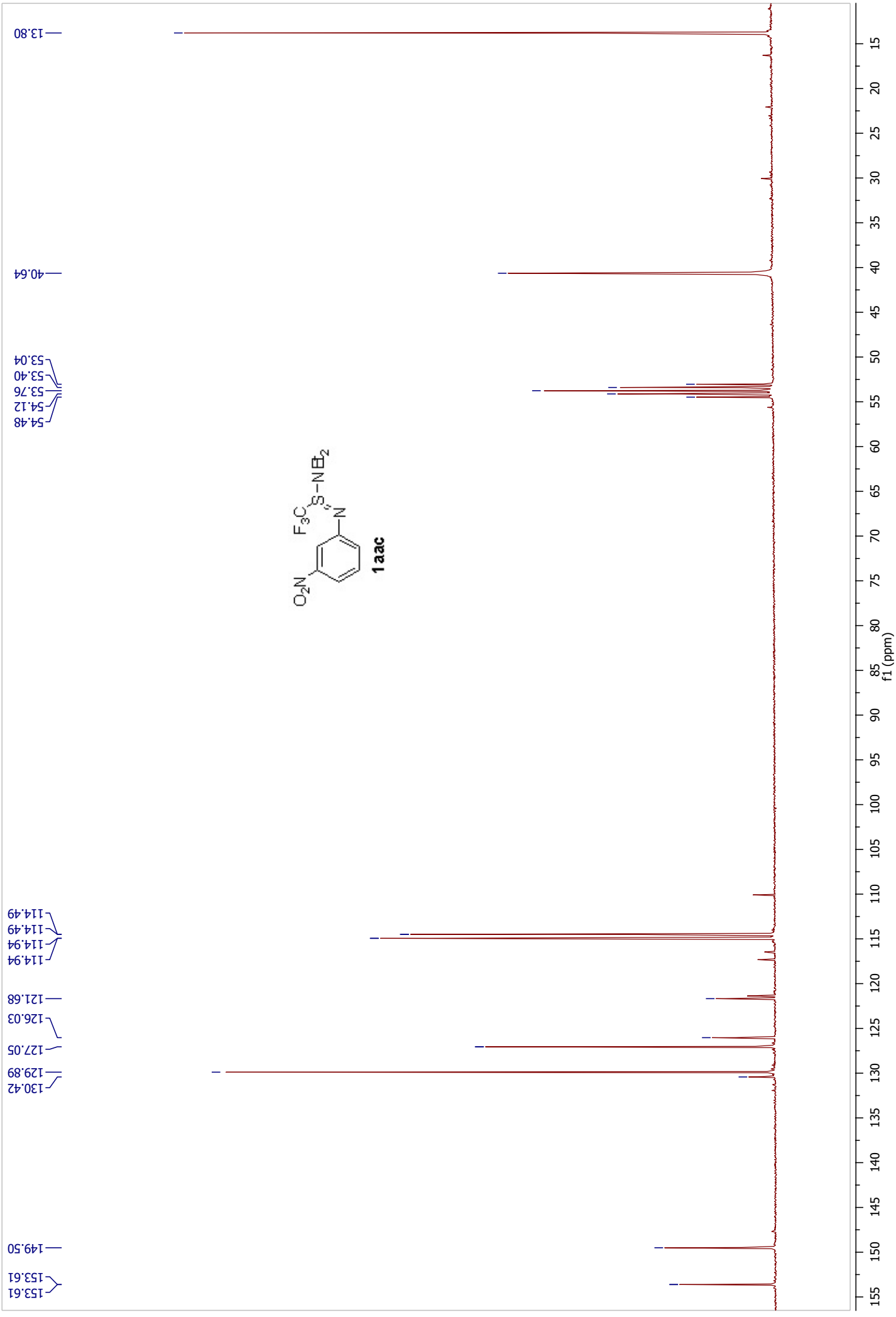
Benzyloxytrifluorométhanesulfacarbamide (**5ah**): Orange solid. mp: 73-74°C. ^{1}H NMR: δ= 7.43-7.39 (massif, 5H), 6.15 (NH), 5.42 (s, 2H). ^{13}C NMR: δ= 156.4, 135.3, 129.1, 129.09 (q, ^{1}J(C,F)= 314), 129.08, 128.8, 69.7. ^{19}F NMR: δ= -53.31. Elemental analysis calcd (%) for $C_9H_8F_3NO_2S$: C 43.03, H 3.21, N 5.58, S 12.76. Found: C 43.25, H 3.10, N 5.74, S 12.62.

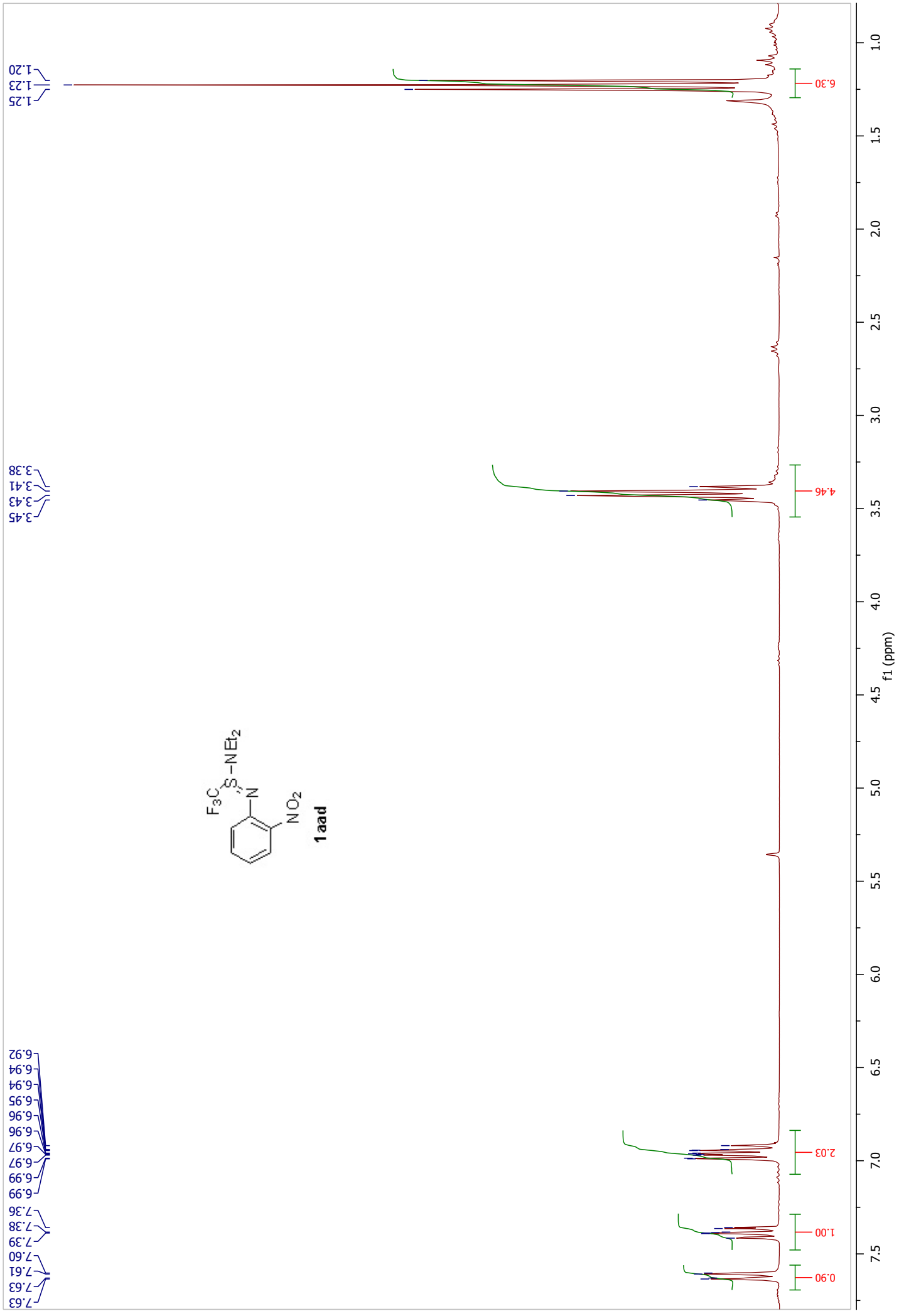

7.99
7.96
6.80
6.77
3.34
3.32
3.32
3.30
3.27
1.13
1.11
1.08
F3C
S
NEt2
O2N
N
1aab
1.87
2.00
4.32
6.39
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

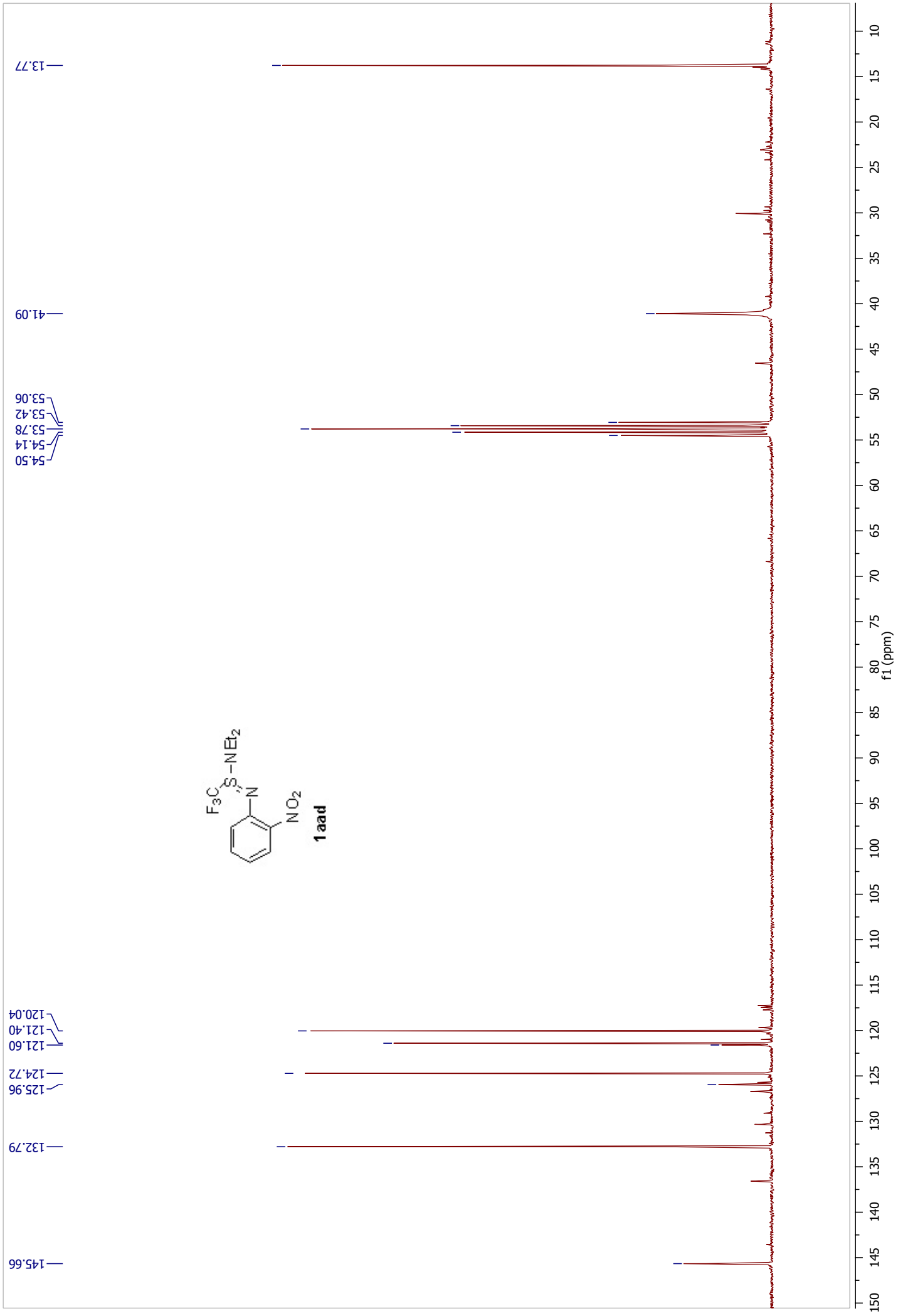

159.60
159.59
159.57
140.86
125.97
125.80
125.69
125.68
121.61
119.68
54.14
53.77
53.41
41.04
13.77
13.75
F3C
S–NEt2
O2N
N
1aab
S16
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

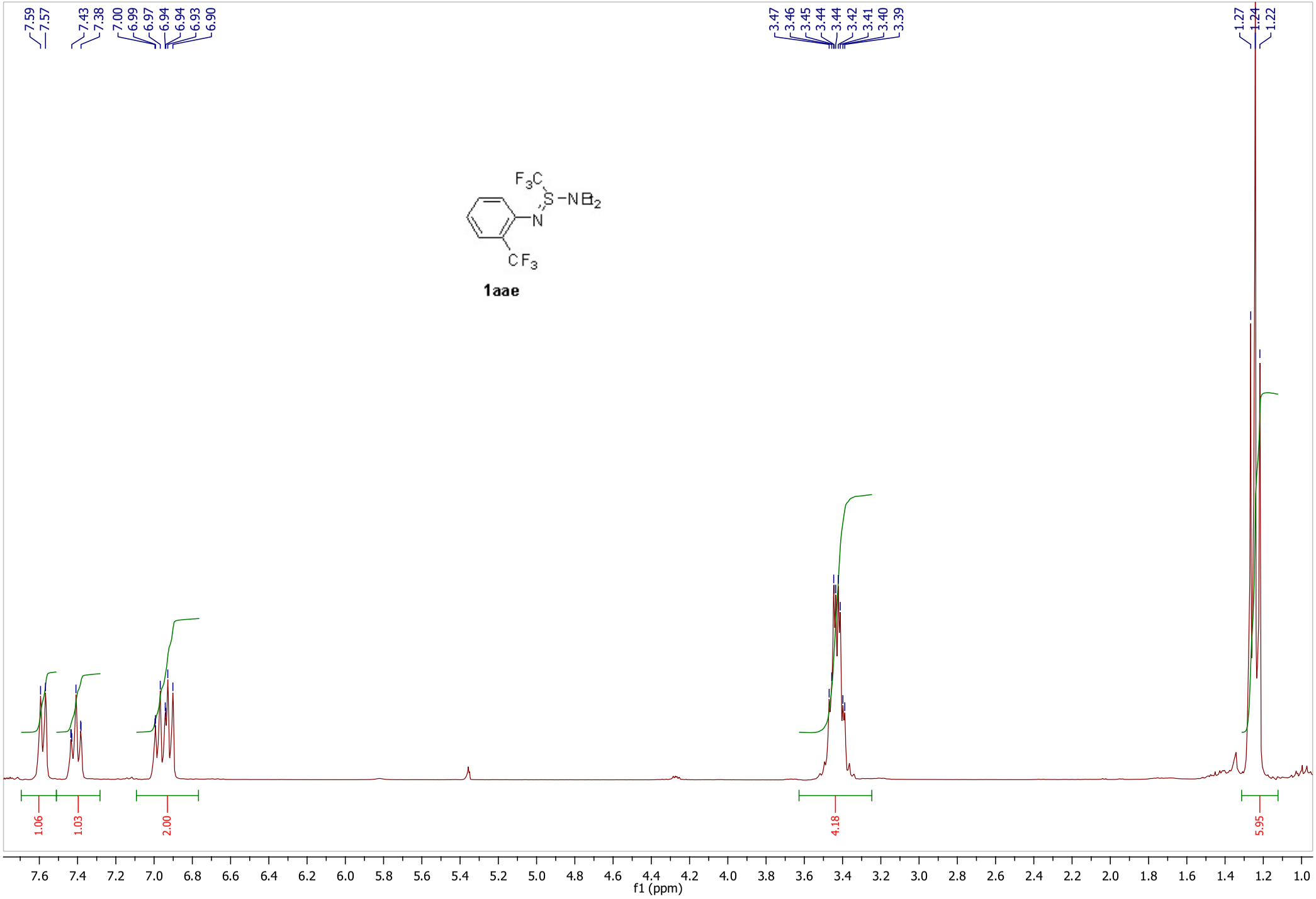

125.69
119.67
115.17
41.03
13.76
F3C
S
NEt2
O2N
N
1aab
Dept 135
S17
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

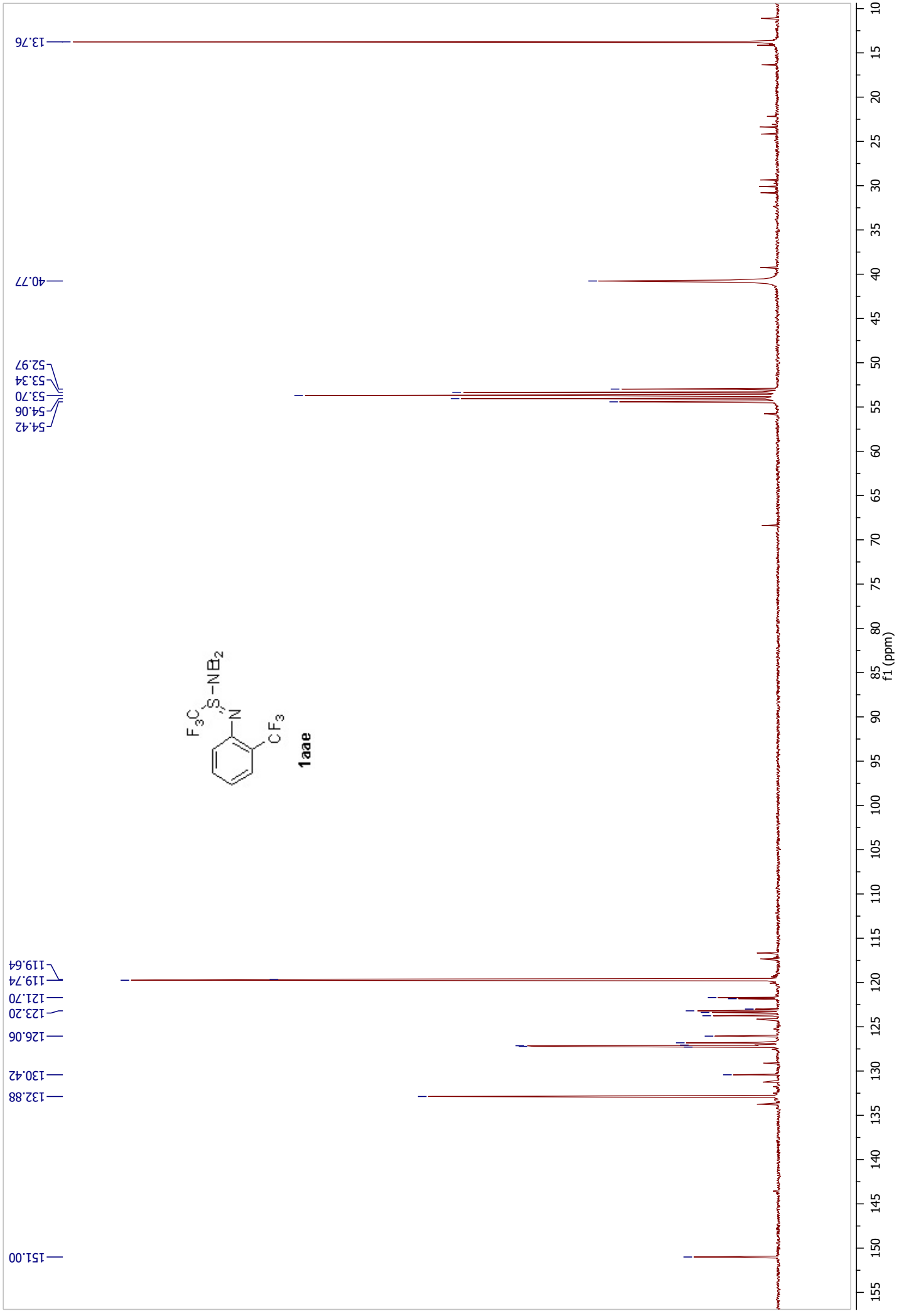

7.70
7.70
7.69
7.68
7.68
7.39
7.36
7.33
7.25
7.25
7.24
7.24
7.22
7.22
7.22
7.21
3.47
3.45
3.42
3.40
1.27
1.24
1.22
O2N
F3C
S
N
NEt2
1aac
2.01
0.96
1.00
4.47
6.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

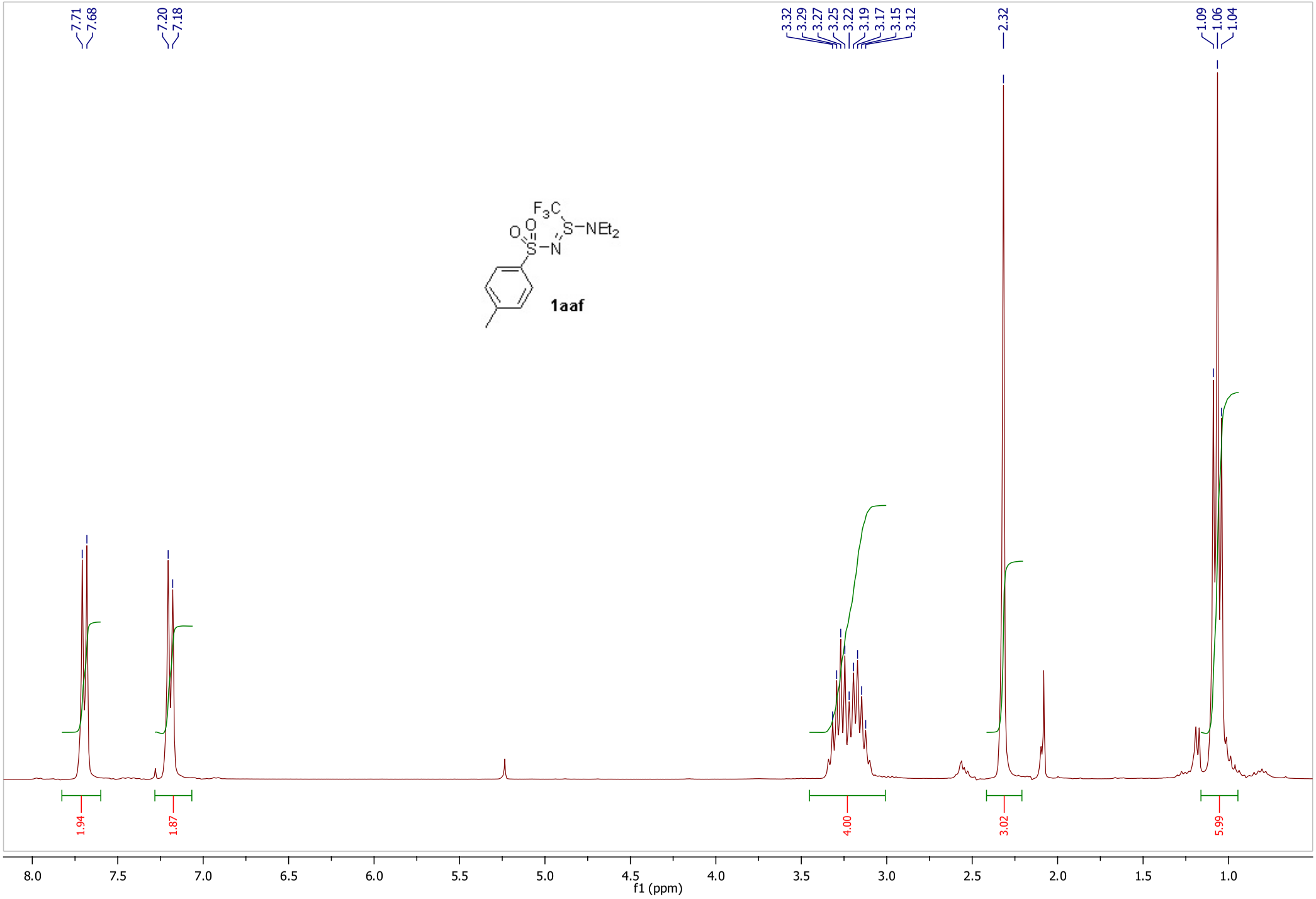

13.80
40.64
53.04
53.40
53.76
54.12
54.48
114.49
114.49
114.94
114.94
121.68
126.03
127.05
129.89
130.42
149.50
153.61
153.61
F3C
S
N
NH2
O2N
1aac
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
f1 (ppm)

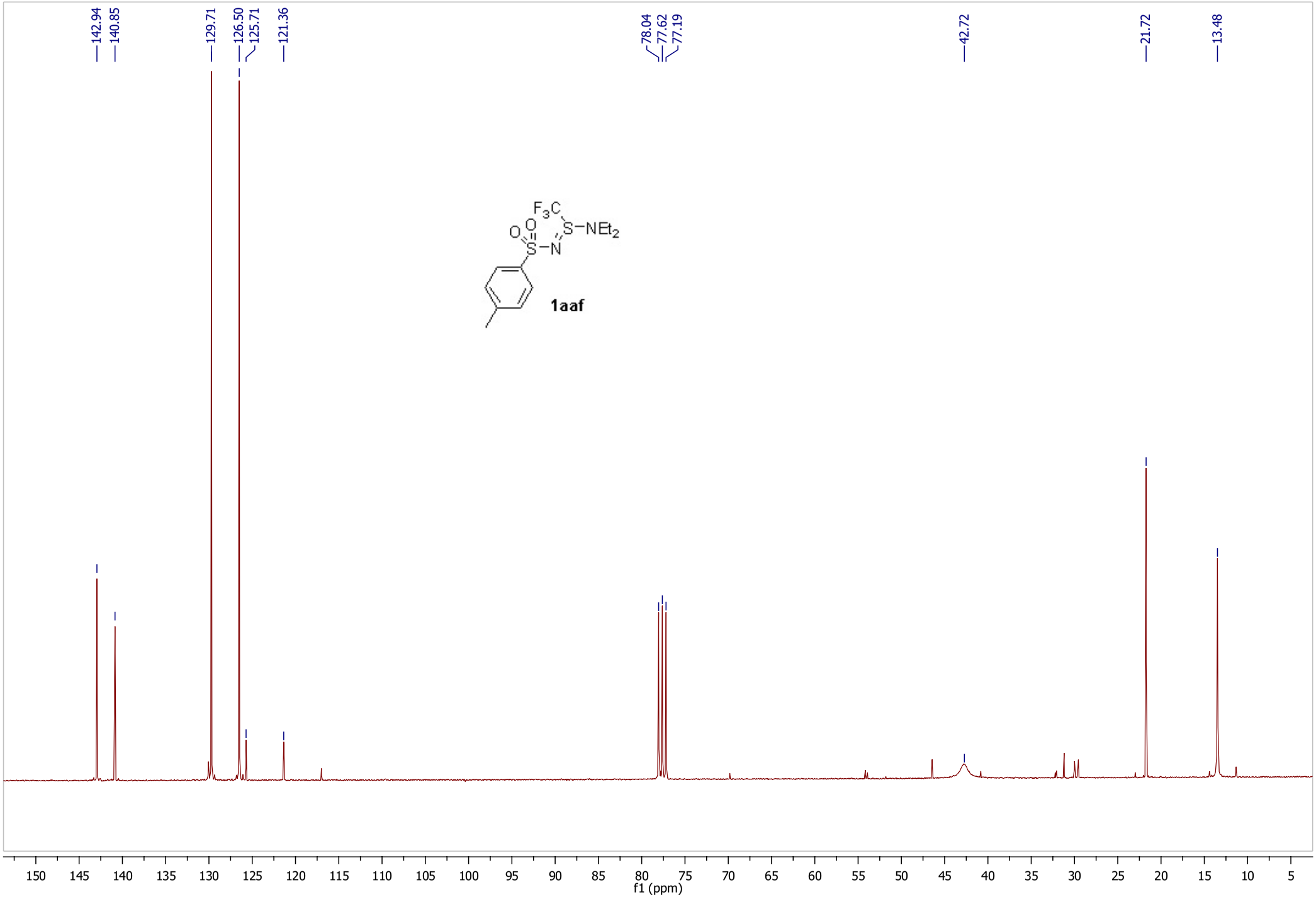

7.63
7.63
7.61
7.60
7.39
7.38
7.36
6.99
6.99
6.97
6.97
6.96
6.96
6.95
6.94
6.94
6.92
3.45
3.43
3.41
3.38
1.25
1.23
1.20
0.90
1.00
2.03
4.46
6.30
F3C
S
NEt2
N
NO2
1aad
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

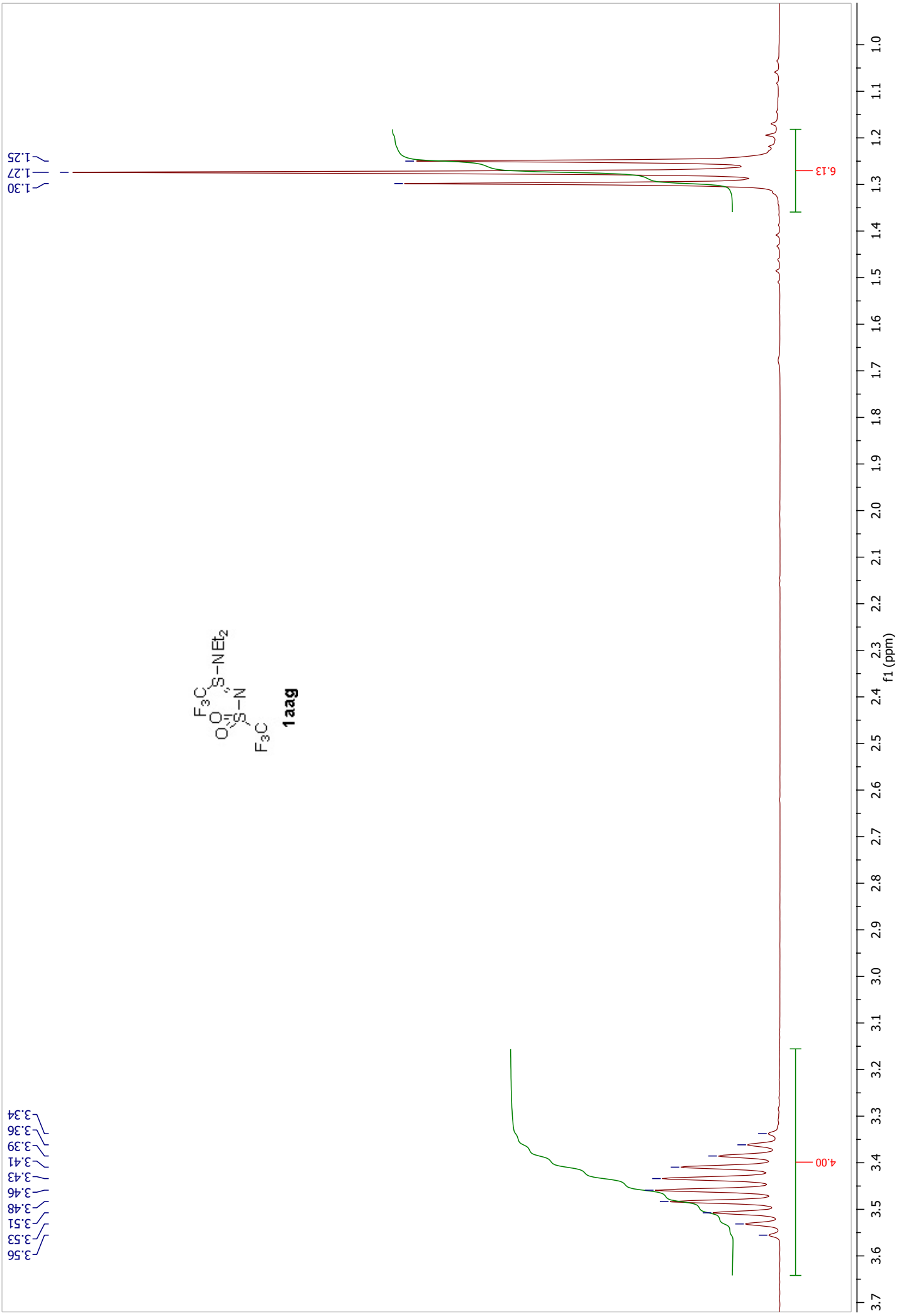

13.77
41.09
53.06
53.42
53.78
54.14
54.50
120.04
121.40
121.60
124.72
125.96
132.79
145.66
F3C
S
NEt2
N
NO2
1aad
f1 (ppm)

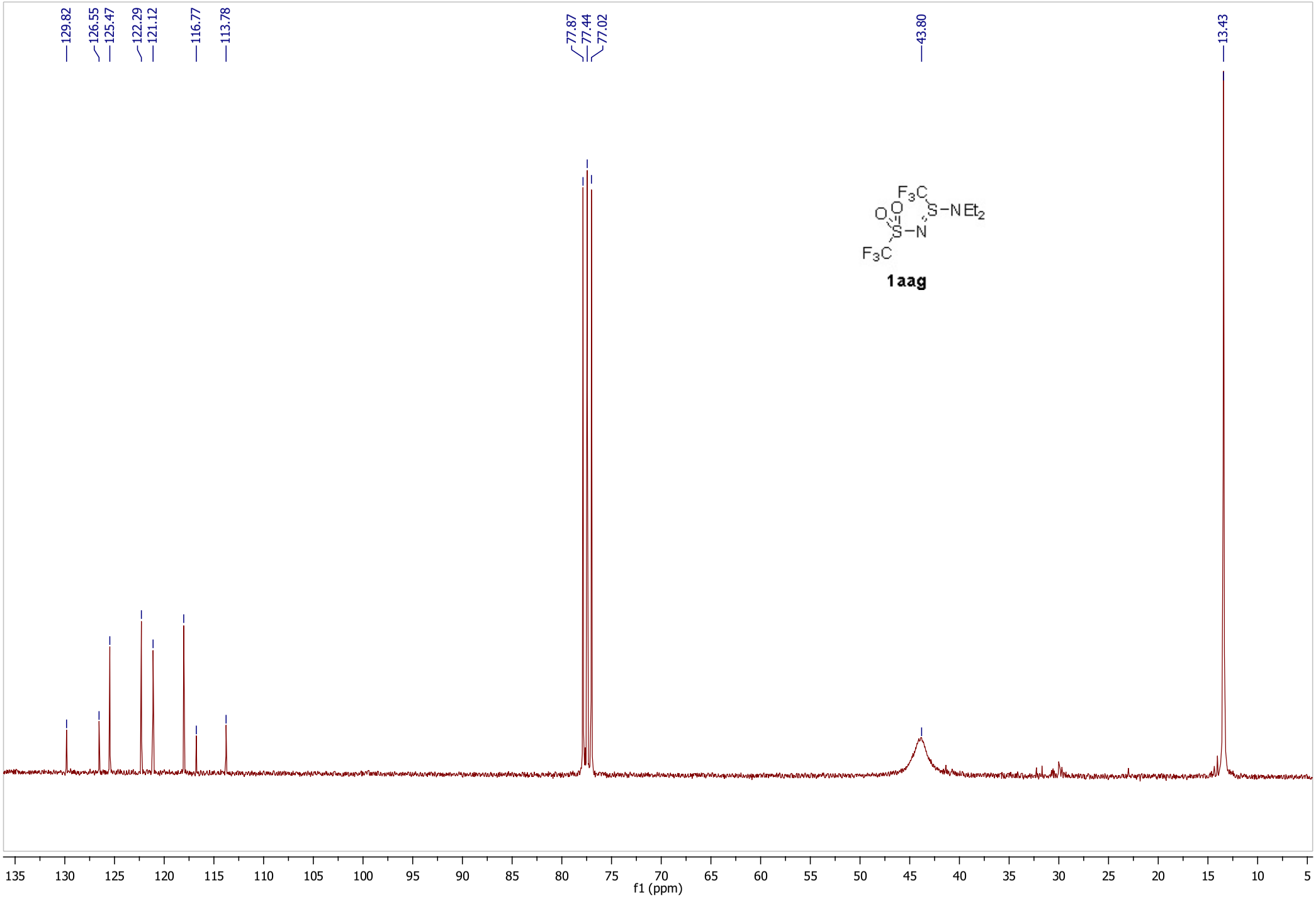

7.59
7.57
7.43
7.38
7.00
6.99
6.97
6.94
6.94
6.93
6.90
3.47
3.46
3.45
3.44
3.44
3.42
3.41
3.40
3.39
1.27
1.24
1.22
F3C
S
NEt2
N
CF3
1aae
1.06
1.03
2.00
4.18
5.95
f1 (ppm)

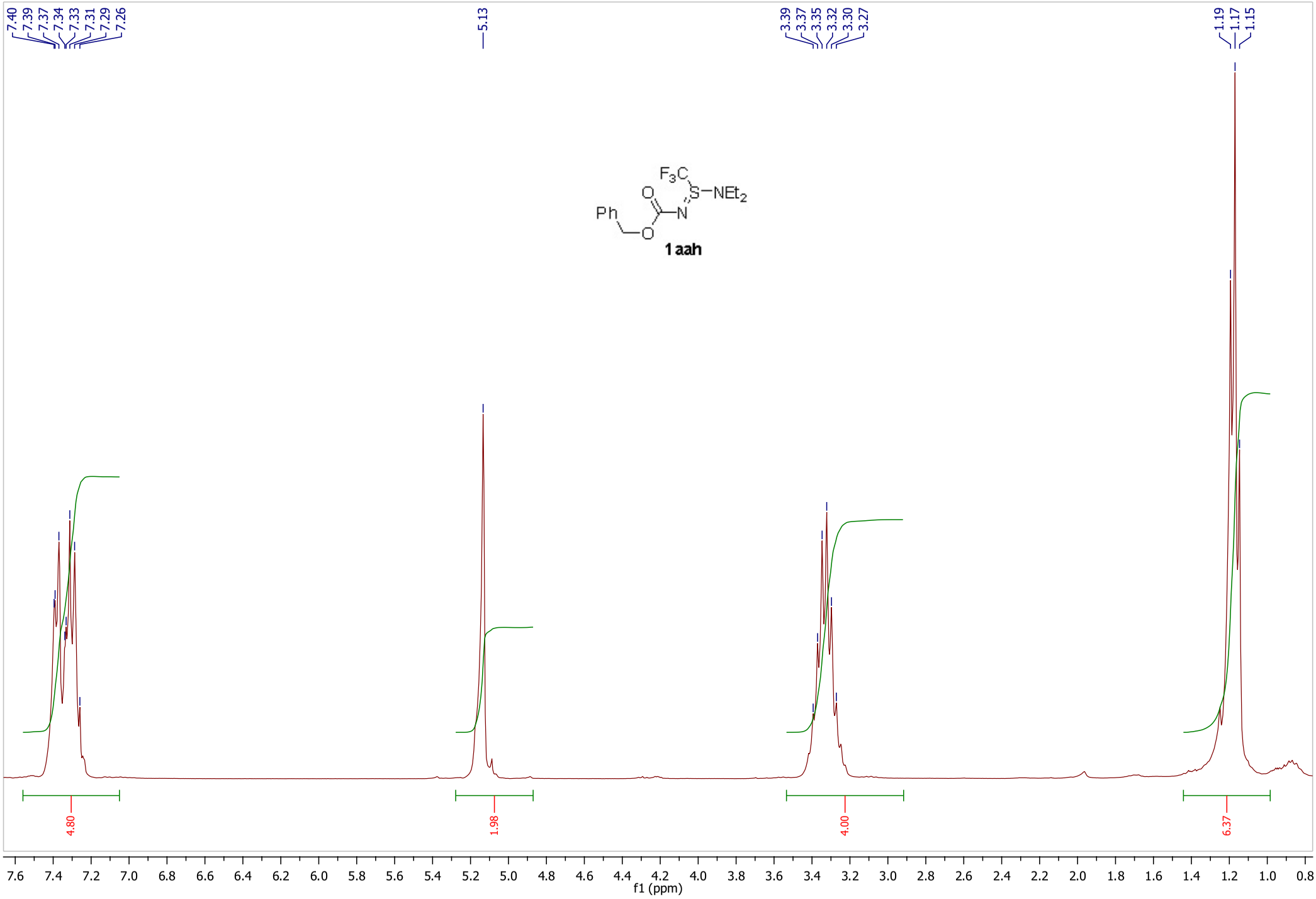

13.76
40.77
52.97
53.34
53.70
54.06
54.42
119.64
119.74
121.70
123.20
126.06
130.42
132.88
151.00
F3C
S
NB2
N
CF3
1aae
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
f1 (ppm)

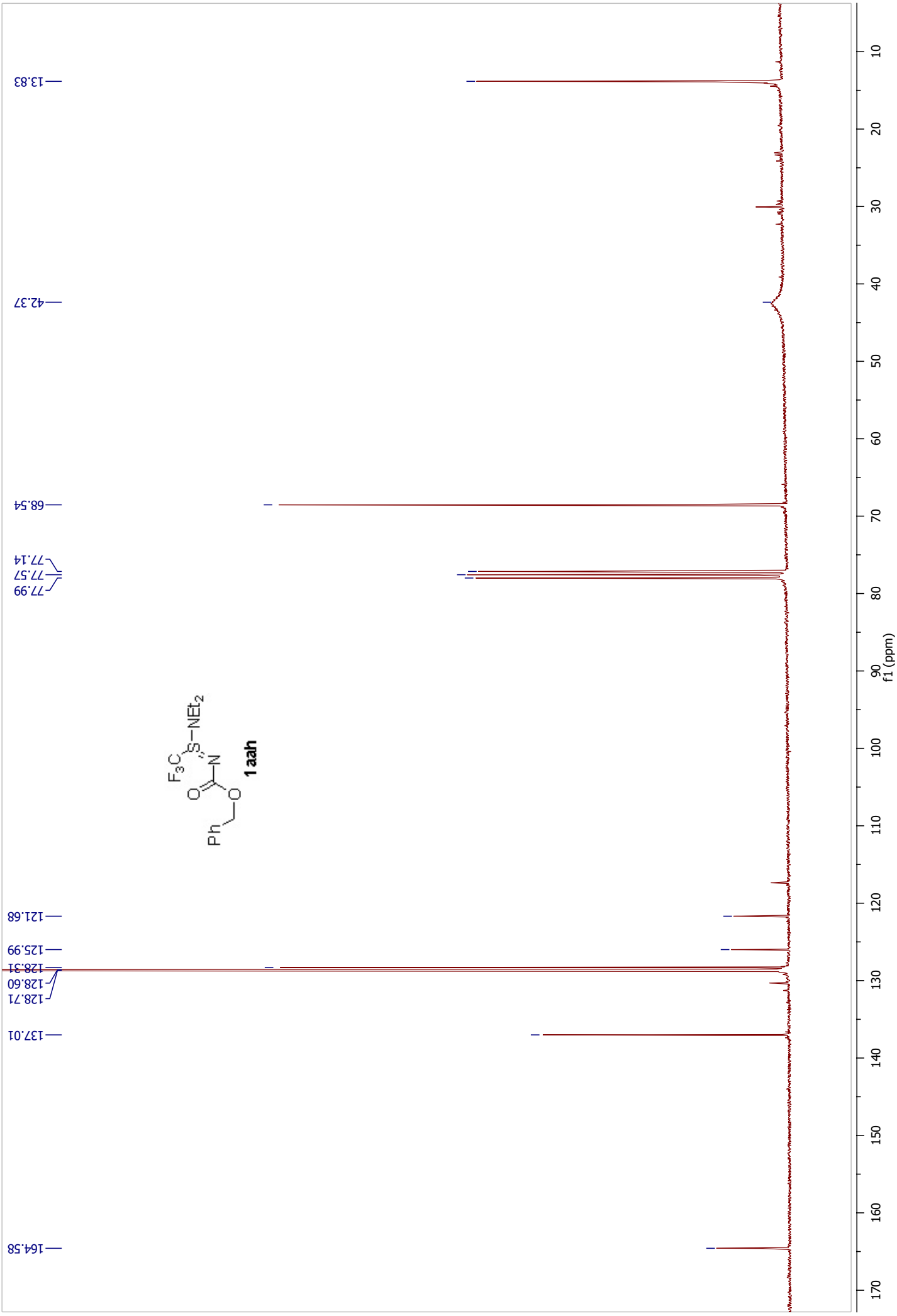

7.71
7.68
7.20
7.18
3.32
3.29
3.27
3.25
3.22
3.19
3.17
3.15
3.12
2.32
1.09
1.06
1.04
F3C
O
O
S–NEt2
S–N
1aaf
1.94
1.87
4.00
3.02
5.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

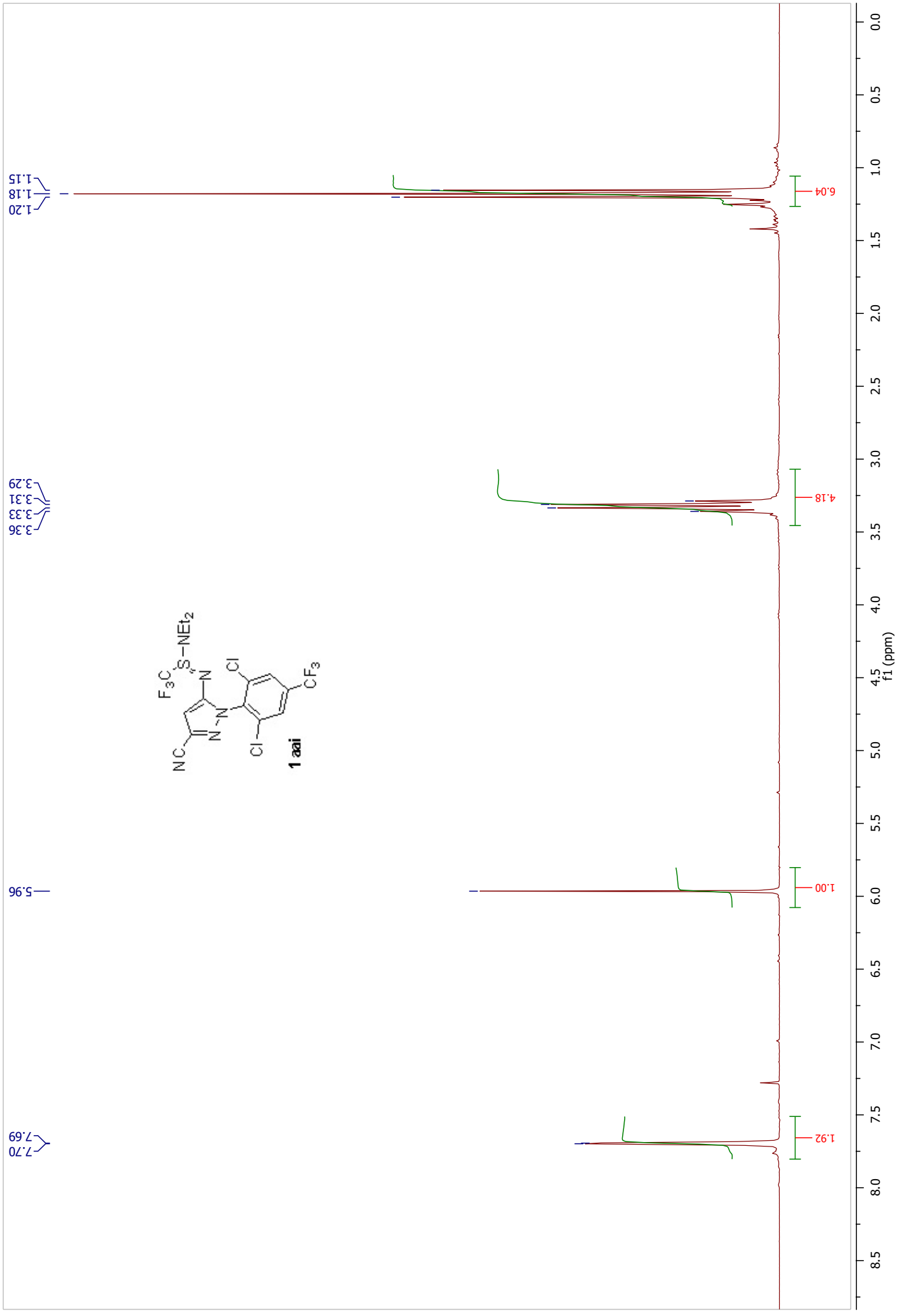

142.94
140.85
129.71
126.50
125.71
121.36
78.04
77.62
77.19
42.72
21.72
13.48
F3C
S–NEt2
O
O
S–N
1aaf
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

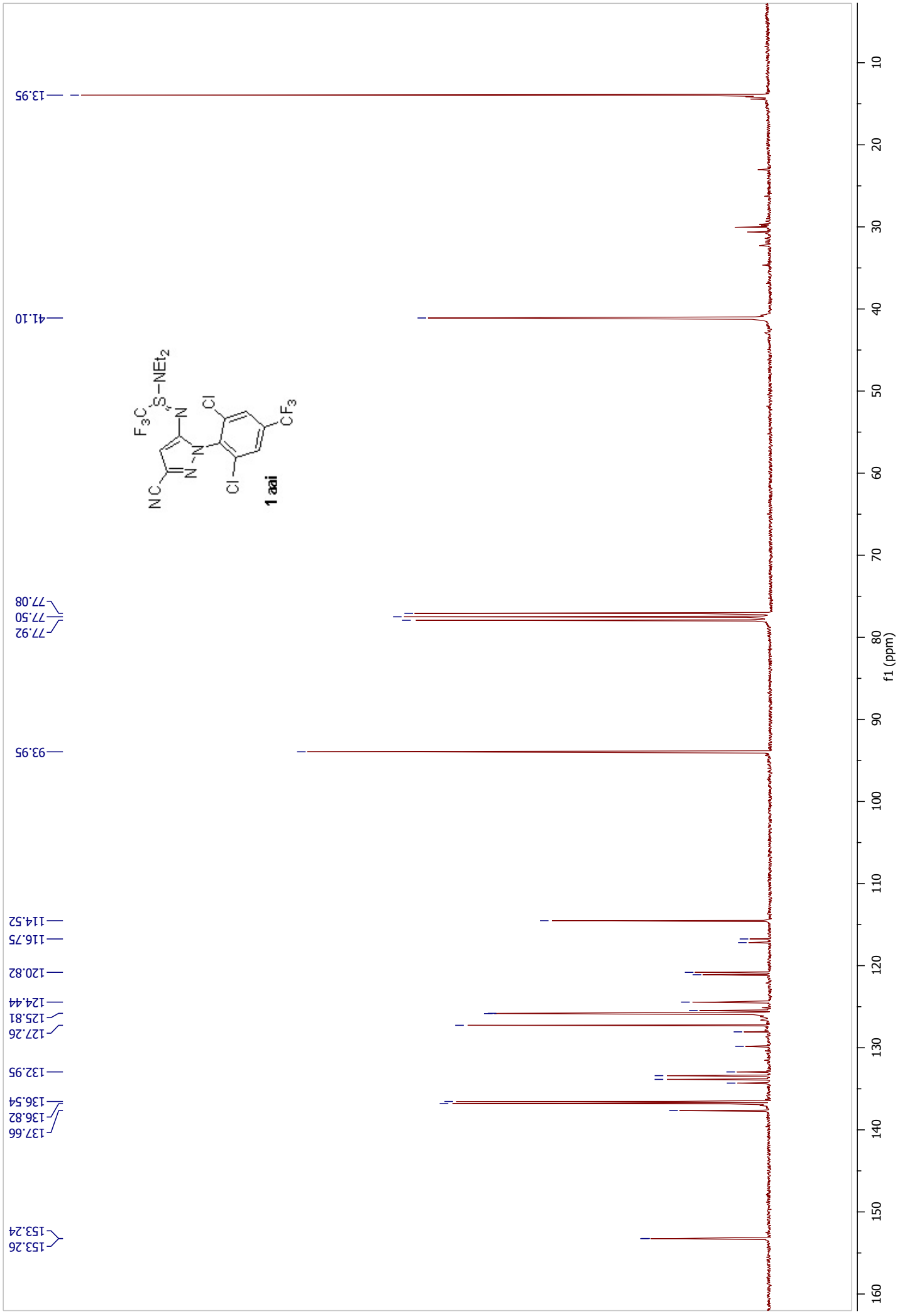

3.56
3.53
3.51
3.48
3.46
3.43
3.41
3.39
3.36
3.34
1.30
1.27
1.25
4.00
6.13
1aag
f1 (ppm)

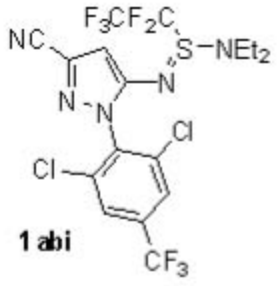

129.82
126.55
125.47
122.29
121.12
116.77
113.78
77.87
77.44
77.02
43.80
13.43
F3C
O
O
S–N
S–NEt2
F3C
1aag
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)


7.40
7.39
7.37
7.34
7.33
7.31
7.29
7.26
5.13
3.39
3.37
3.35
3.32
3.30
3.27
1.19
1.17
1.15
F3C
S
NEt2
O
N
Ph
O
1aah
4.80
1.98
4.00
6.37
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)


13.83
42.37
68.54
77.14
77.57
77.99
121.68
125.99
128.31
128.60
128.71
137.01
164.58
F3C
S
NEt2
N
O
O
Ph
1aah
f1 (ppm)

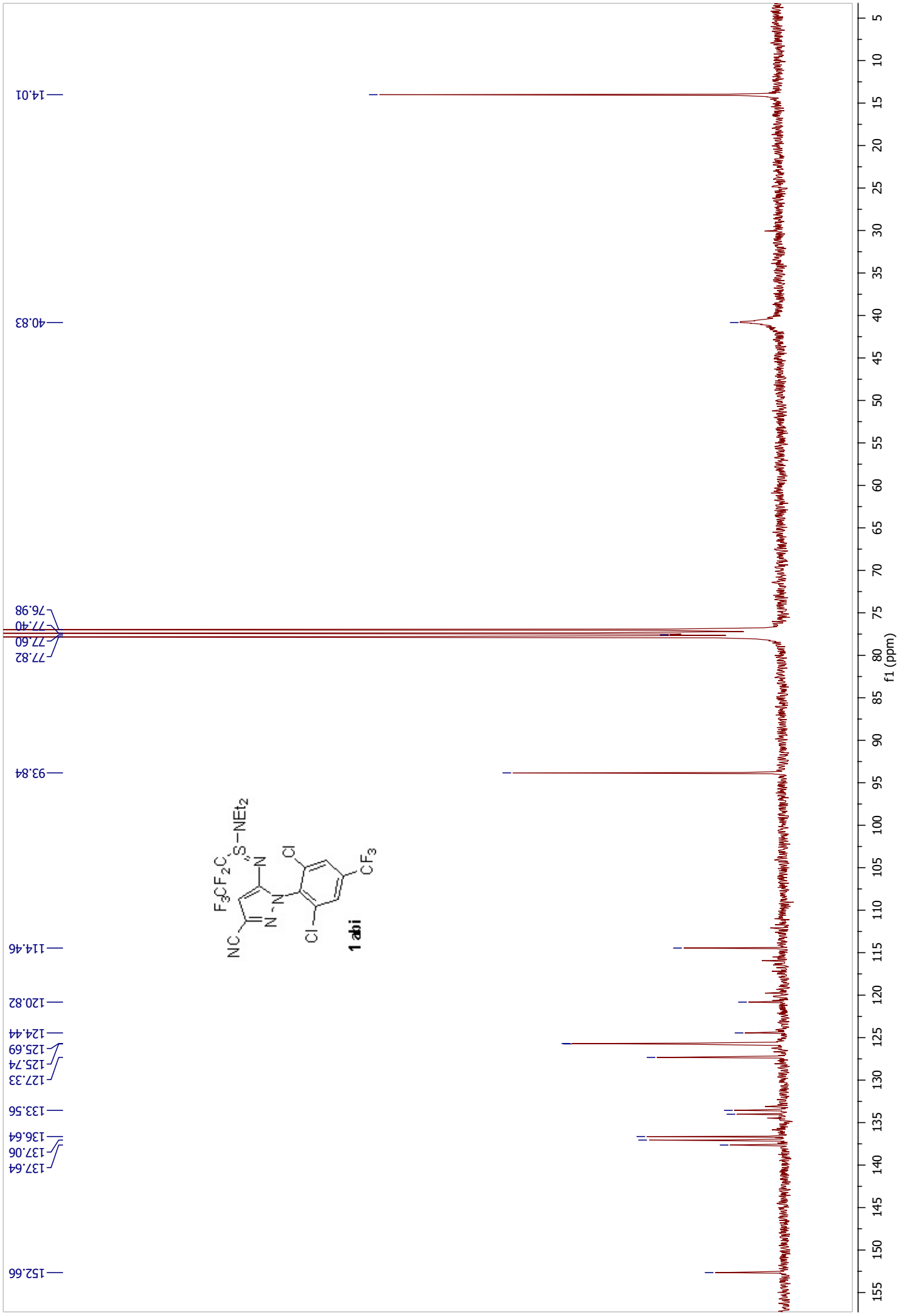

1.20
1.18
1.15
3.36
3.33
3.31
3.29
5.96
7.70
7.69
6.04
4.18
1.00
1.92
1 aai
f1 (ppm)

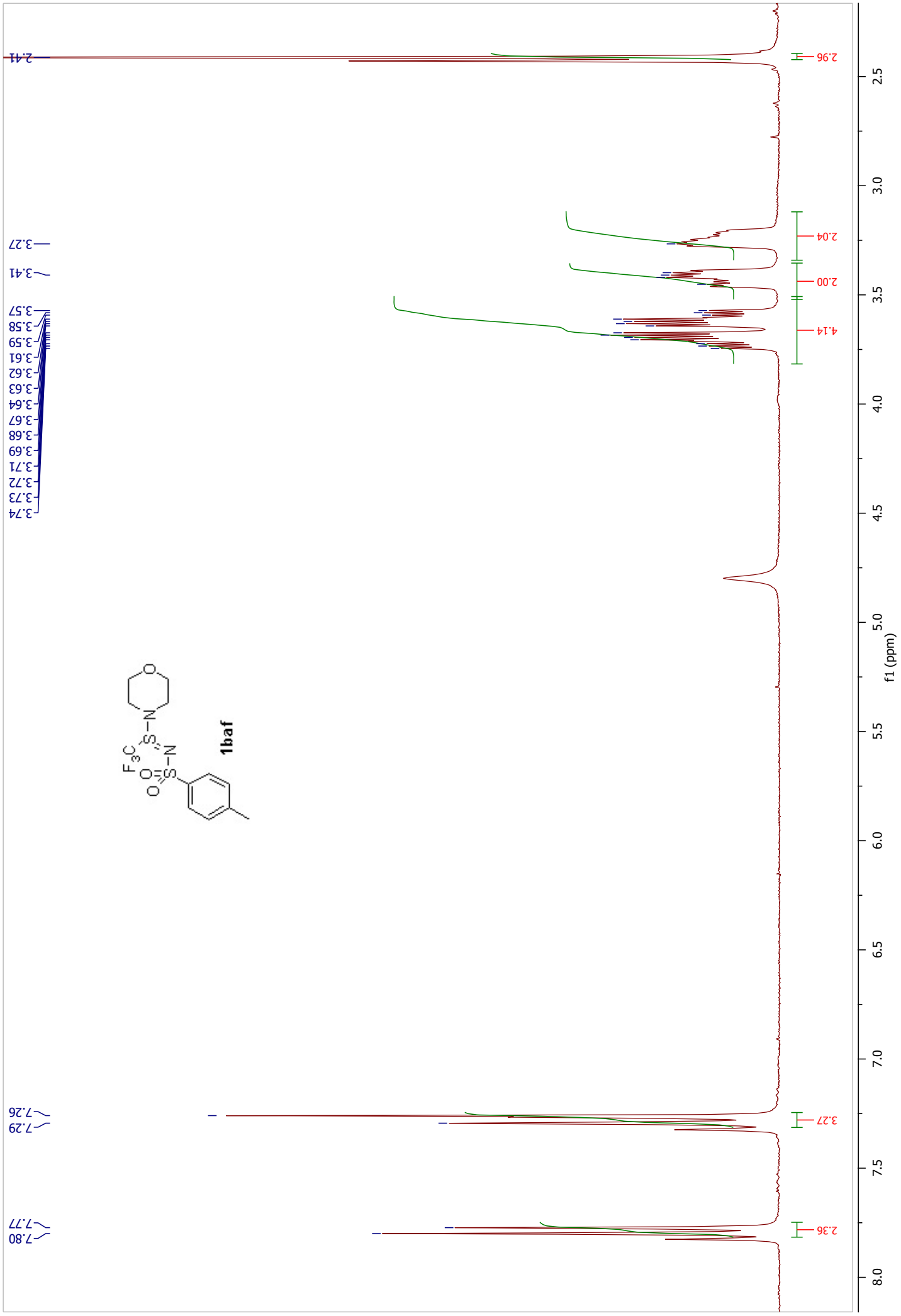

13.95
41.10
77.08
77.50
77.92
93.95
114.52
116.75
120.82
124.44
125.81
127.26
132.95
136.54
136.82
137.66
153.24
153.26
f1 (ppm)
1 aai

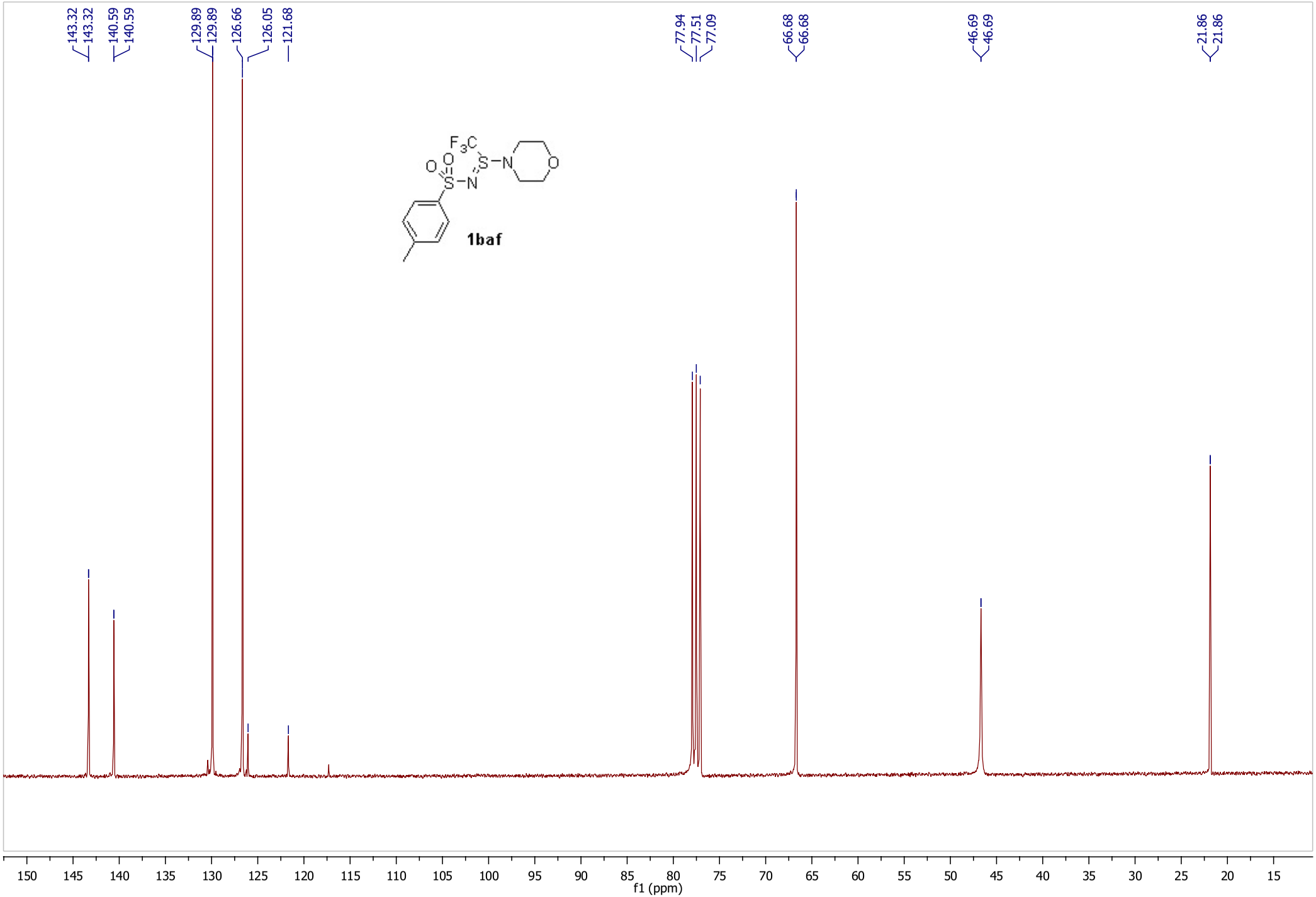


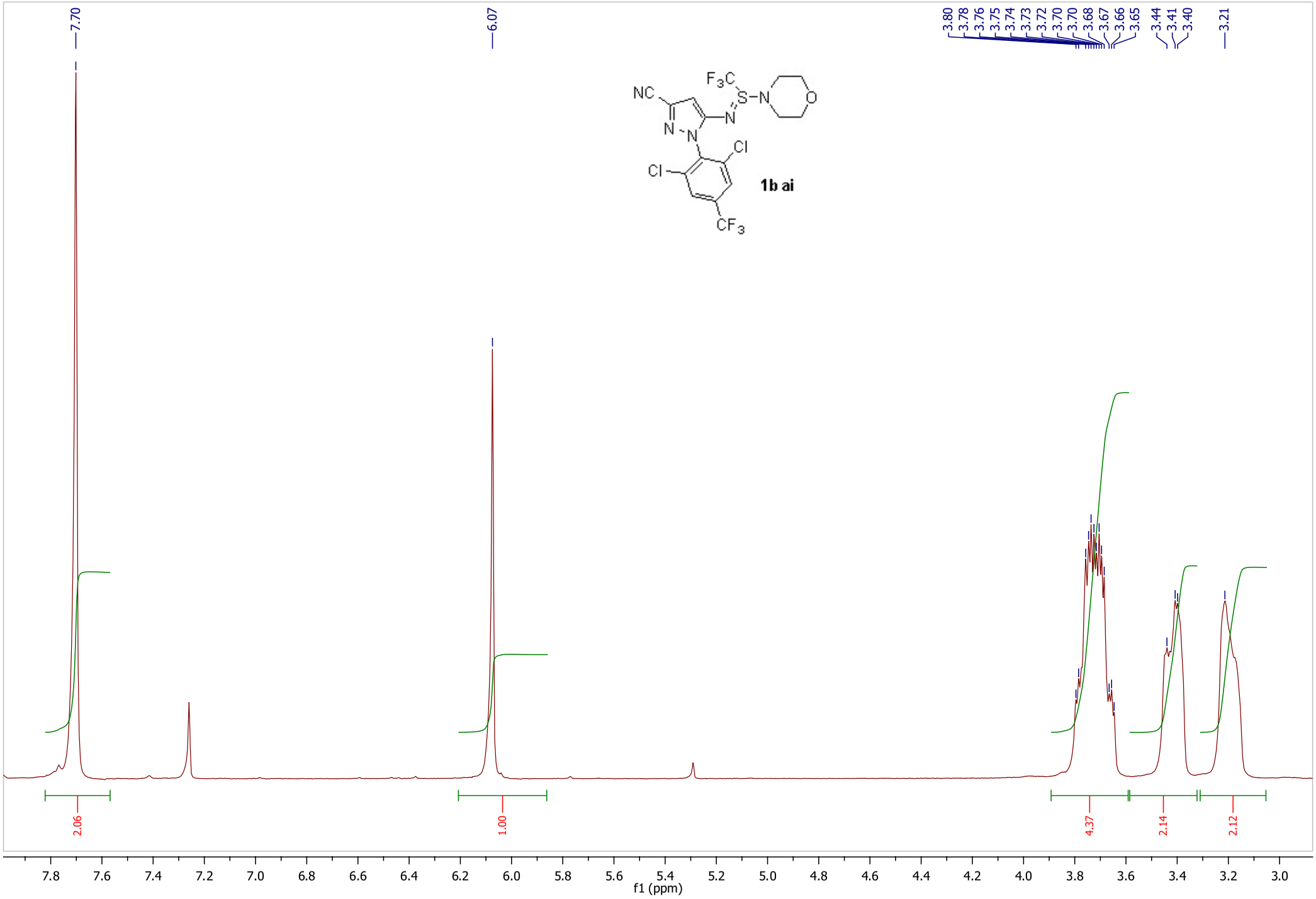
1abi

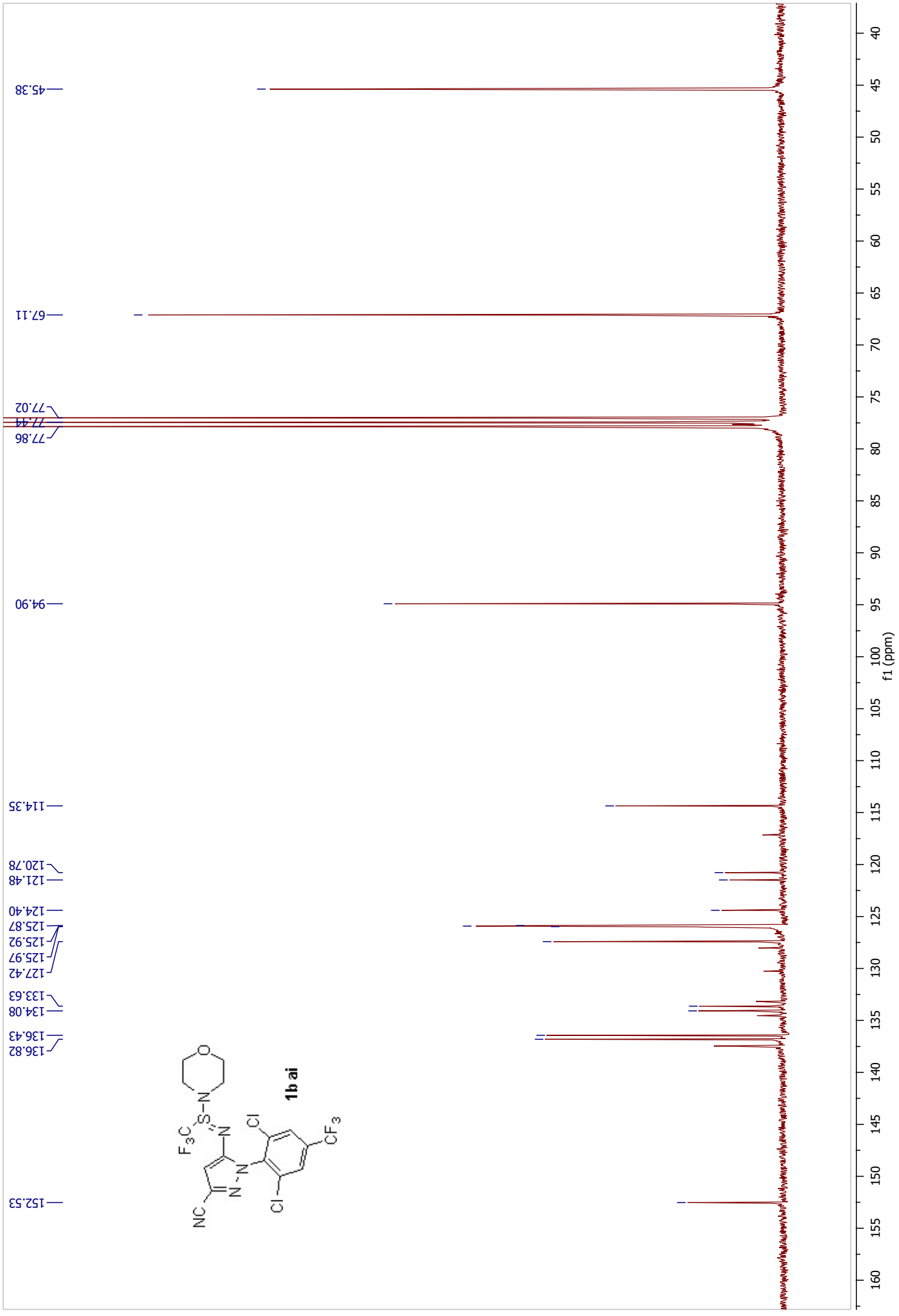
7.72
7.71
5.92
3.45
3.42
3.40
3.38
3.36
1.27
1.26
1.23
1.21
1.86
0.87
4.00
6.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

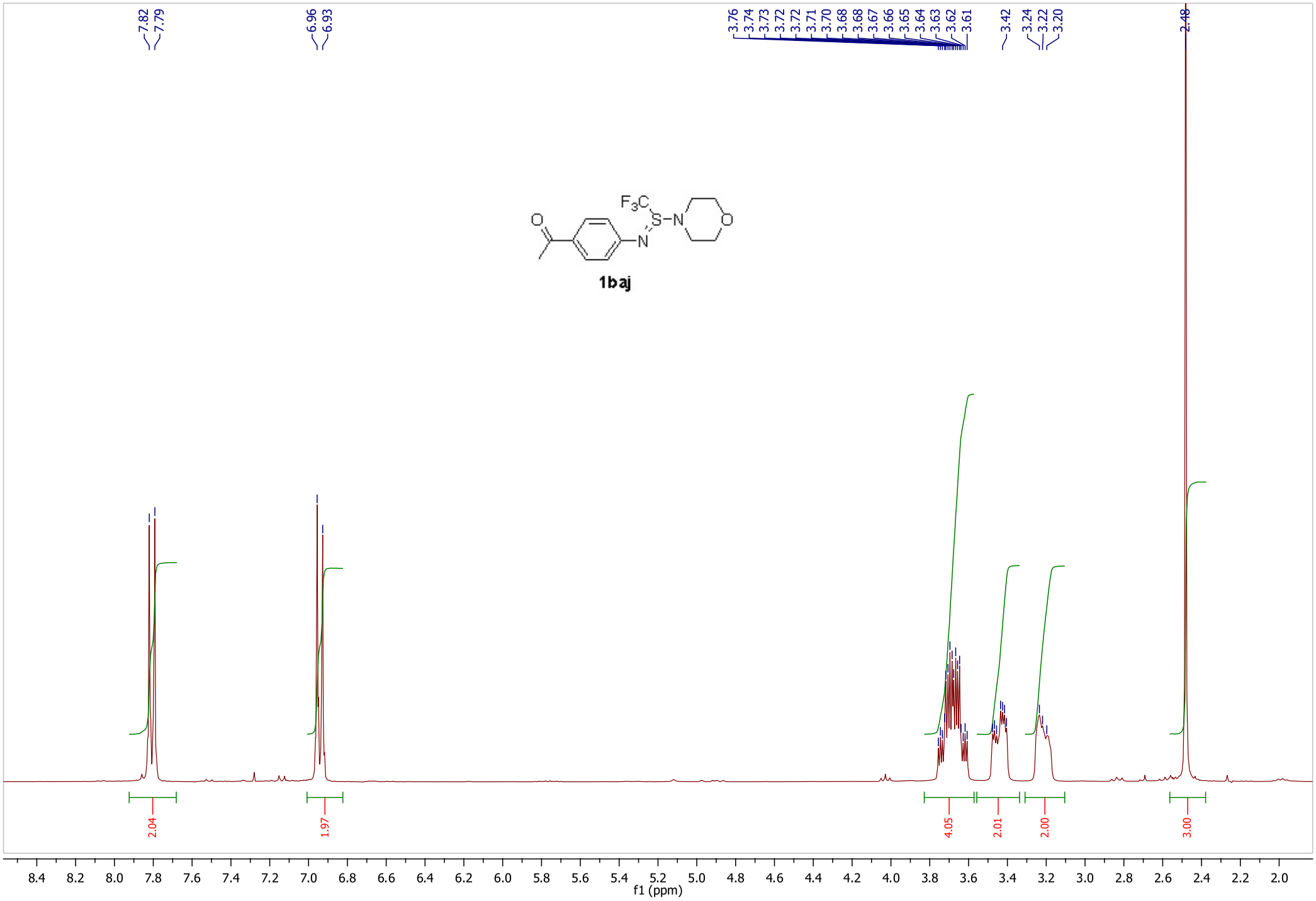

14.01
40.83
76.98
77.40
77.60
77.82
93.84
114.46
120.82
124.44
125.69
125.74
127.33
133.56
136.64
137.06
137.64
152.66
f1 (ppm)
1abi

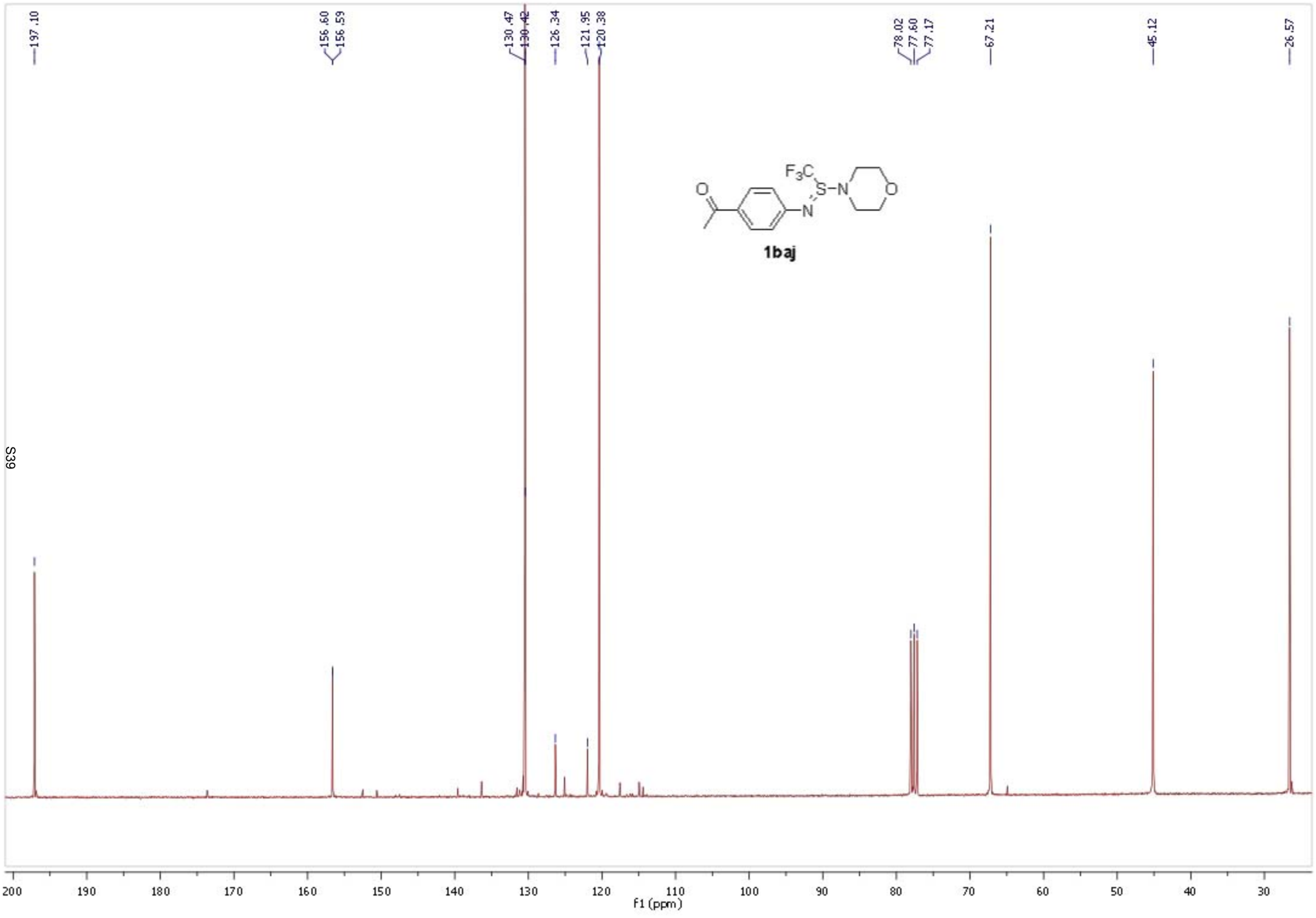

2.41
3.27
3.41
3.57
3.58
3.59
3.61
3.62
3.63
3.64
3.67
3.68
3.69
3.71
3.72
3.73
3.74
7.26
7.29
7.77
7.80
2.96
2.04
2.00
4.14
3.27
2.36
1baf
f1 (ppm)

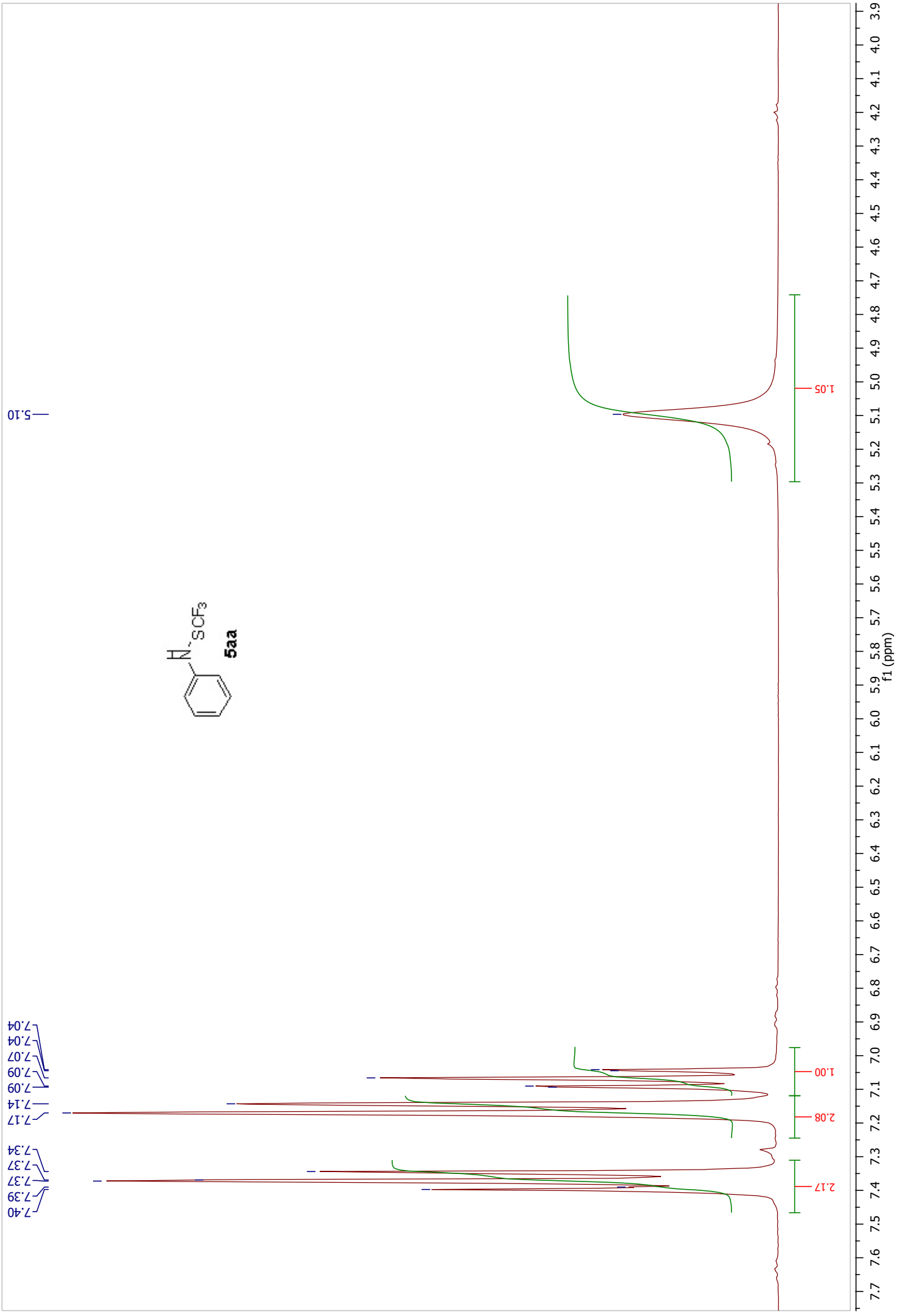

143.32
143.32
140.59
140.59
129.89
129.89
126.66
126.05
121.68
77.94
77.51
77.09
66.68
66.68
46.69
46.69
21.86
21.86
F3C
O
O
S
N
S
N
O
1baf
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

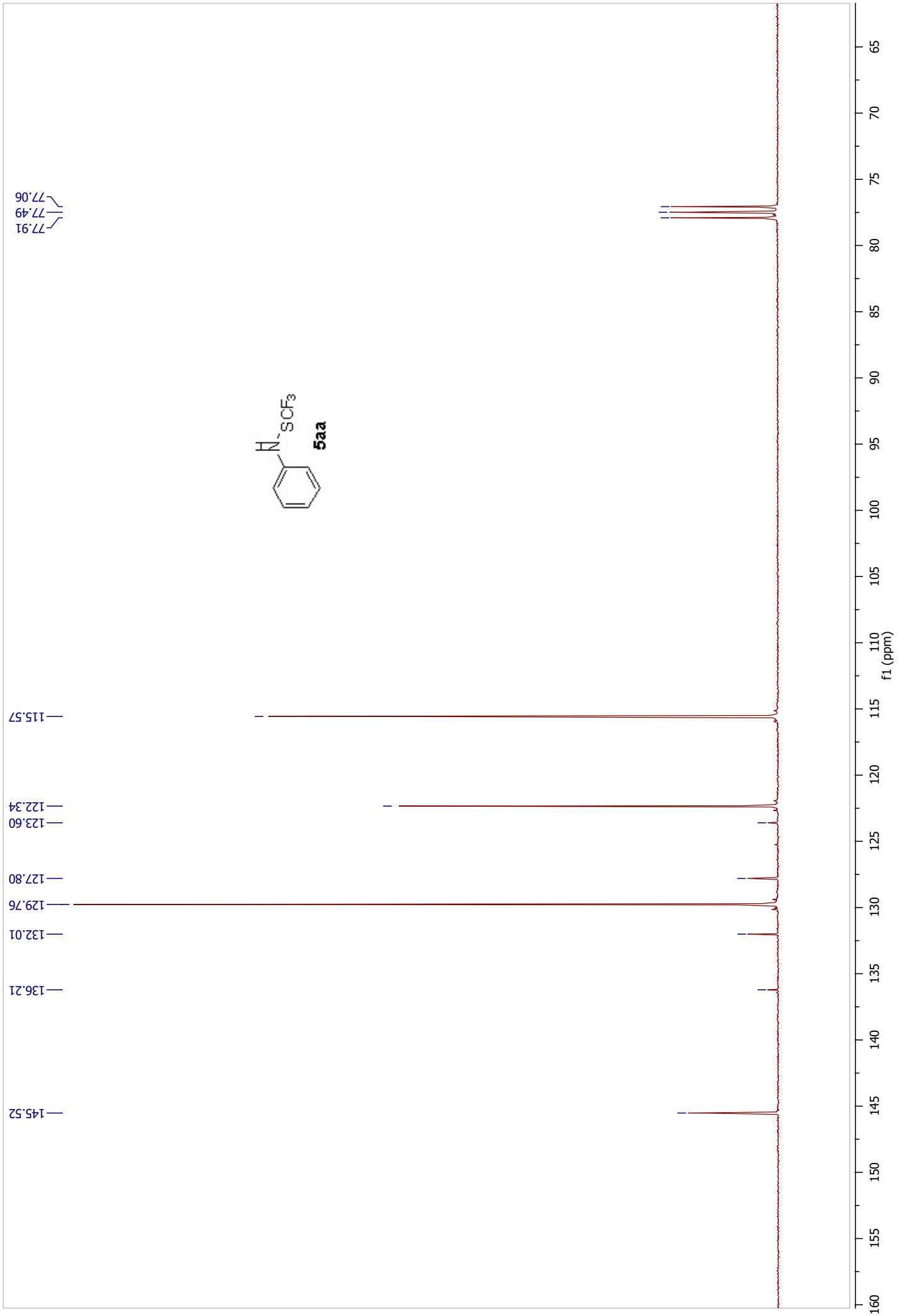

7.70
6.07
3.80
3.78
3.76
3.75
3.74
3.73
3.72
3.70
3.70
3.68
3.67
3.66
3.65
3.44
3.41
3.40
3.21
NC
F3C
S
N
O
N
N
Cl
Cl
CF3
1b ai
2.06
1.00
4.37
2.14
2.12
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
f1 (ppm)

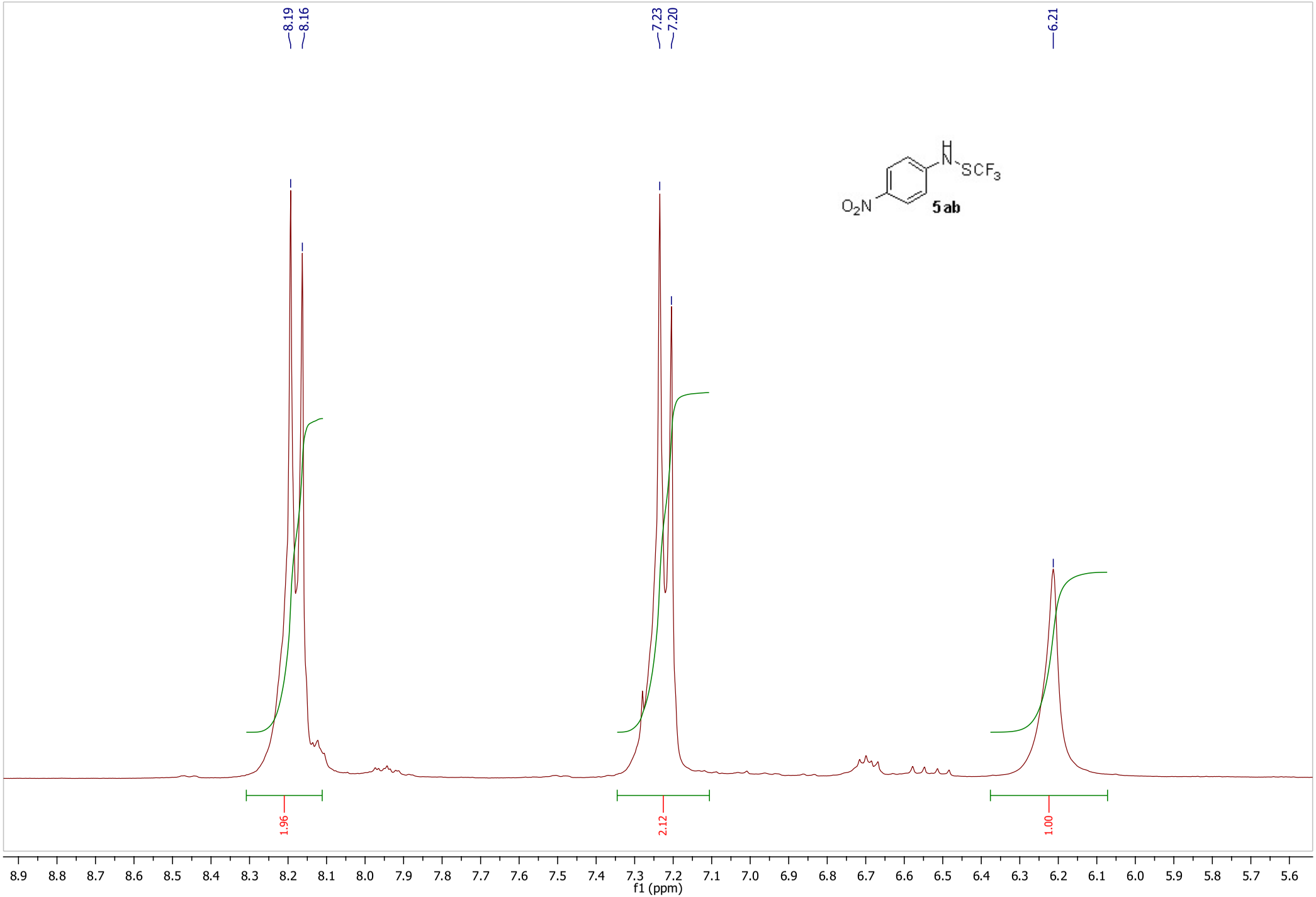

45.38
67.11
77.02
77.44
77.86
94.90
114.35
120.78
121.48
124.40
125.87
125.92
125.97
127.42
133.63
134.08
136.43
136.82
152.53
1b ai
f1 (ppm)

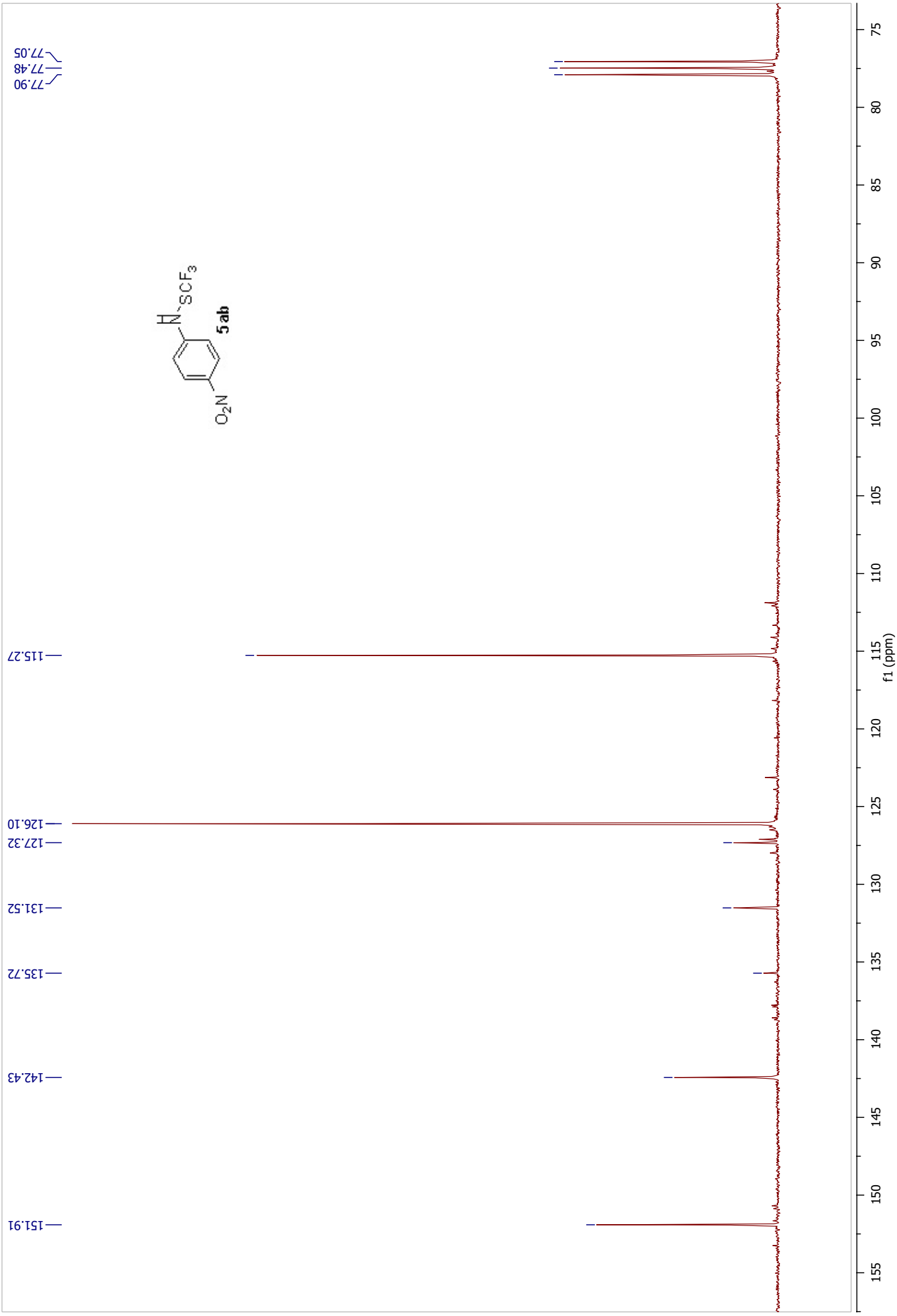

7.82
7.79
6.96
6.93
3.76
3.74
3.73
3.72
3.72
3.71
3.70
3.68
3.68
3.67
3.66
3.65
3.64
3.63
3.62
3.61
3.42
3.24
3.22
3.20
2.48
F3C
S
N
O
N
O
1baj
2.04
1.97
4.05
2.01
2.00
3.00
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
f1 (ppm)

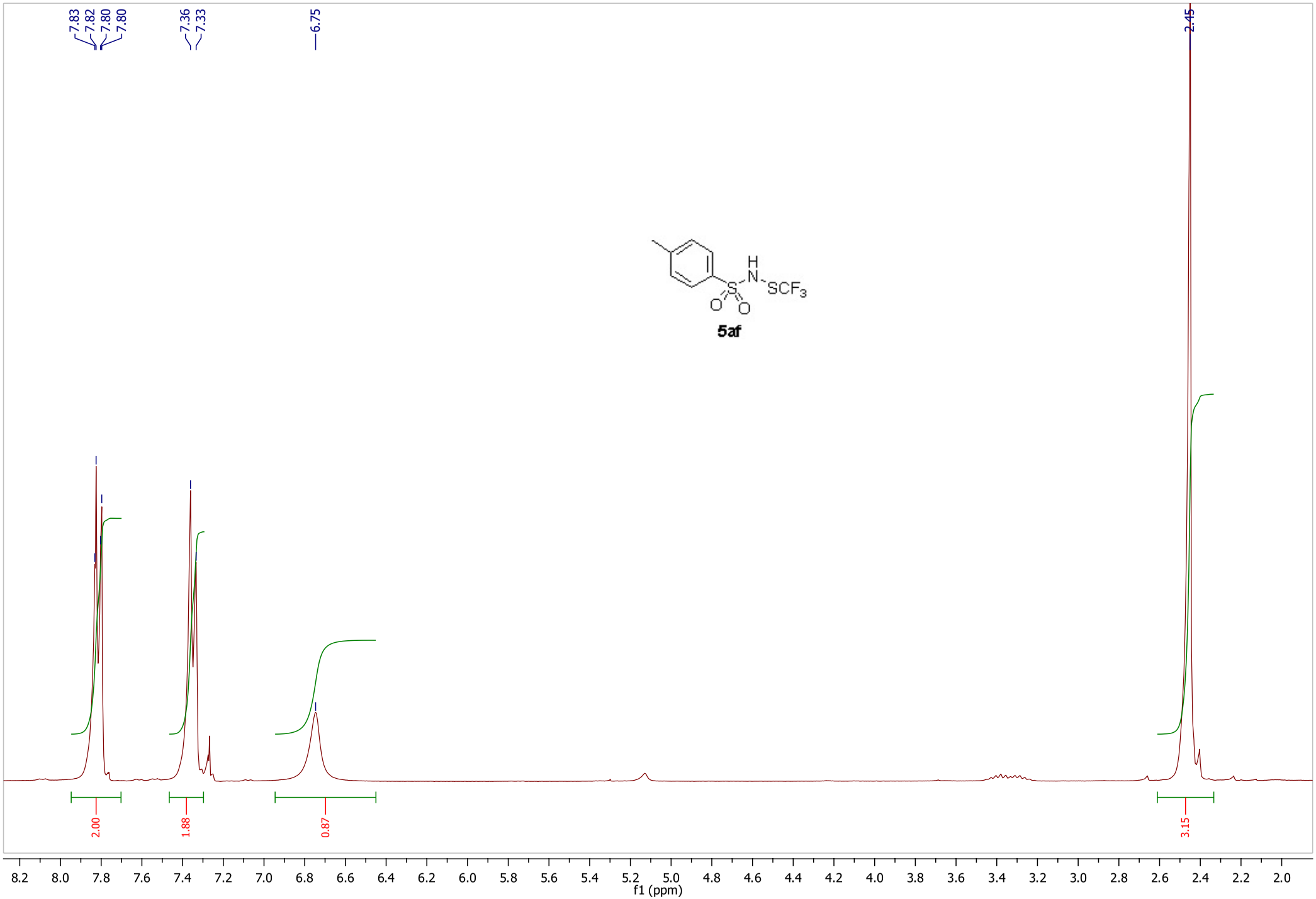

197.10
156.60
156.59
130.47
130.42
126.34
121.95
120.38
78.02
77.60
77.17
67.21
45.12
26.57
F3C
S
N
O
O
N
1baj
f1 (ppm)

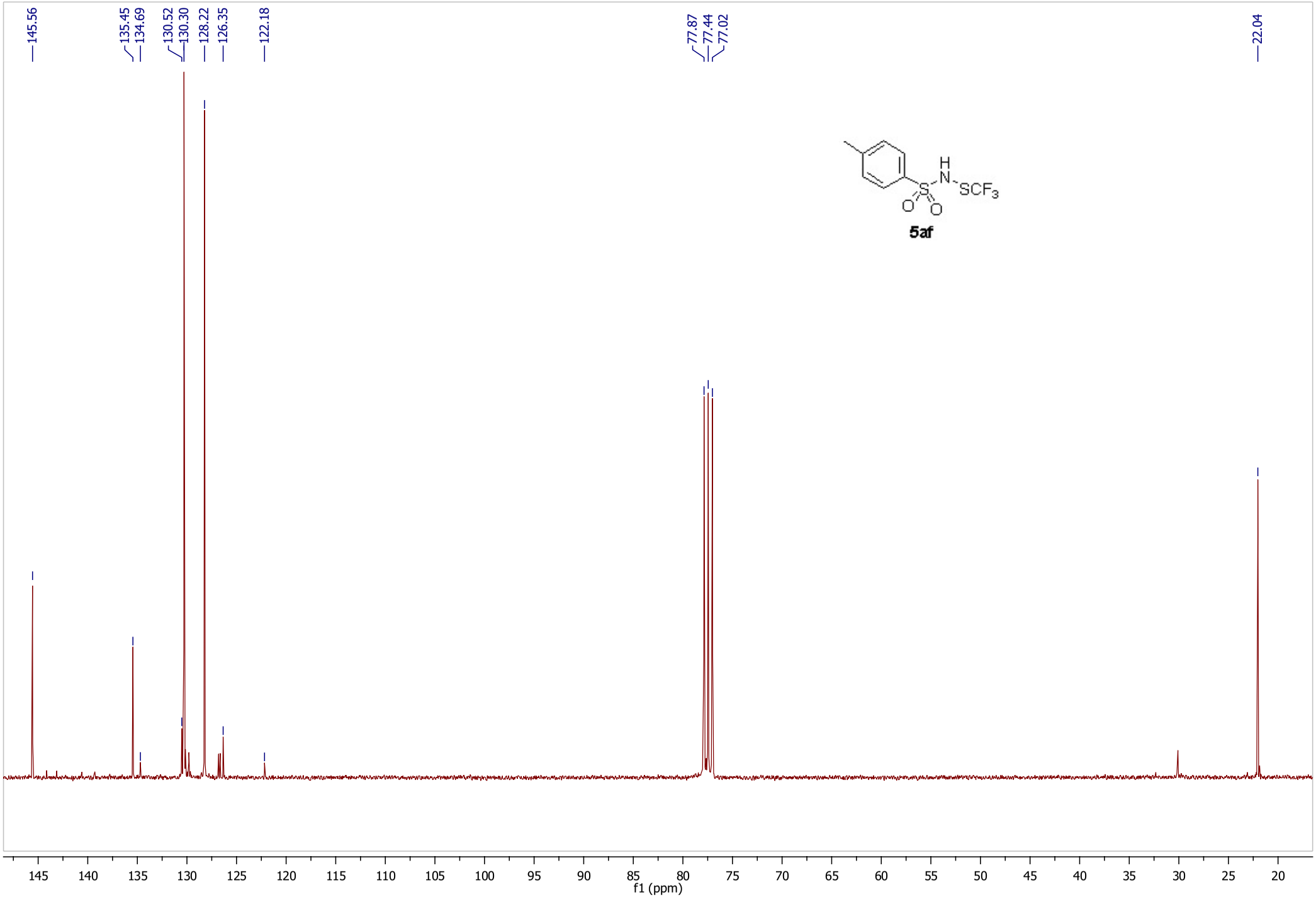

5.10
7.40
7.39
7.37
7.37
7.34
7.17
7.14
7.09
7.09
7.07
7.04
7.04
2.17
2.08
1.00
1.05
5aa
f1 (ppm)

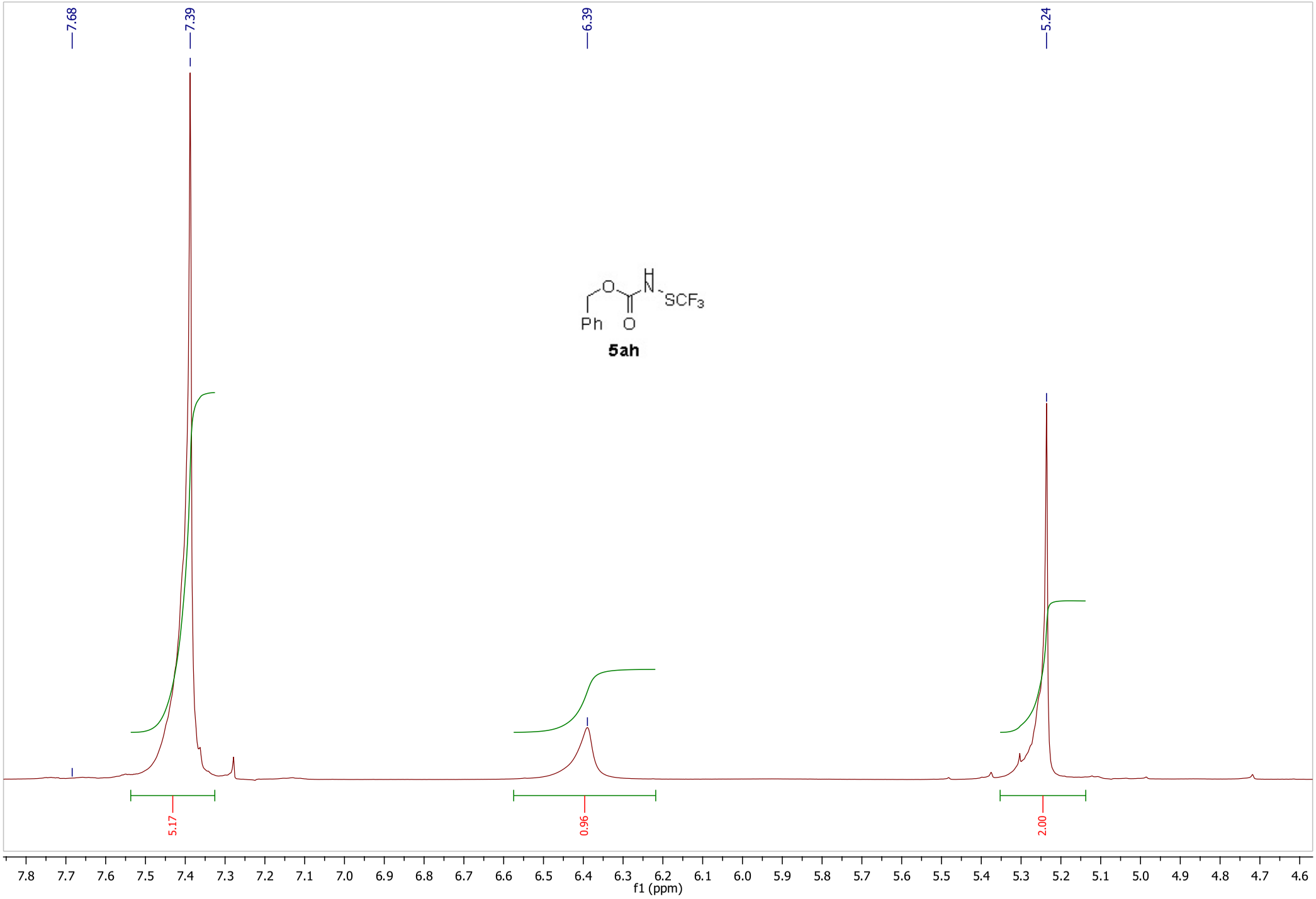

77.91
77.49
77.06
115.57
122.34
123.60
127.80
129.76
132.01
136.21
145.52
5aa
SCF3
H
N
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
f1 (ppm)

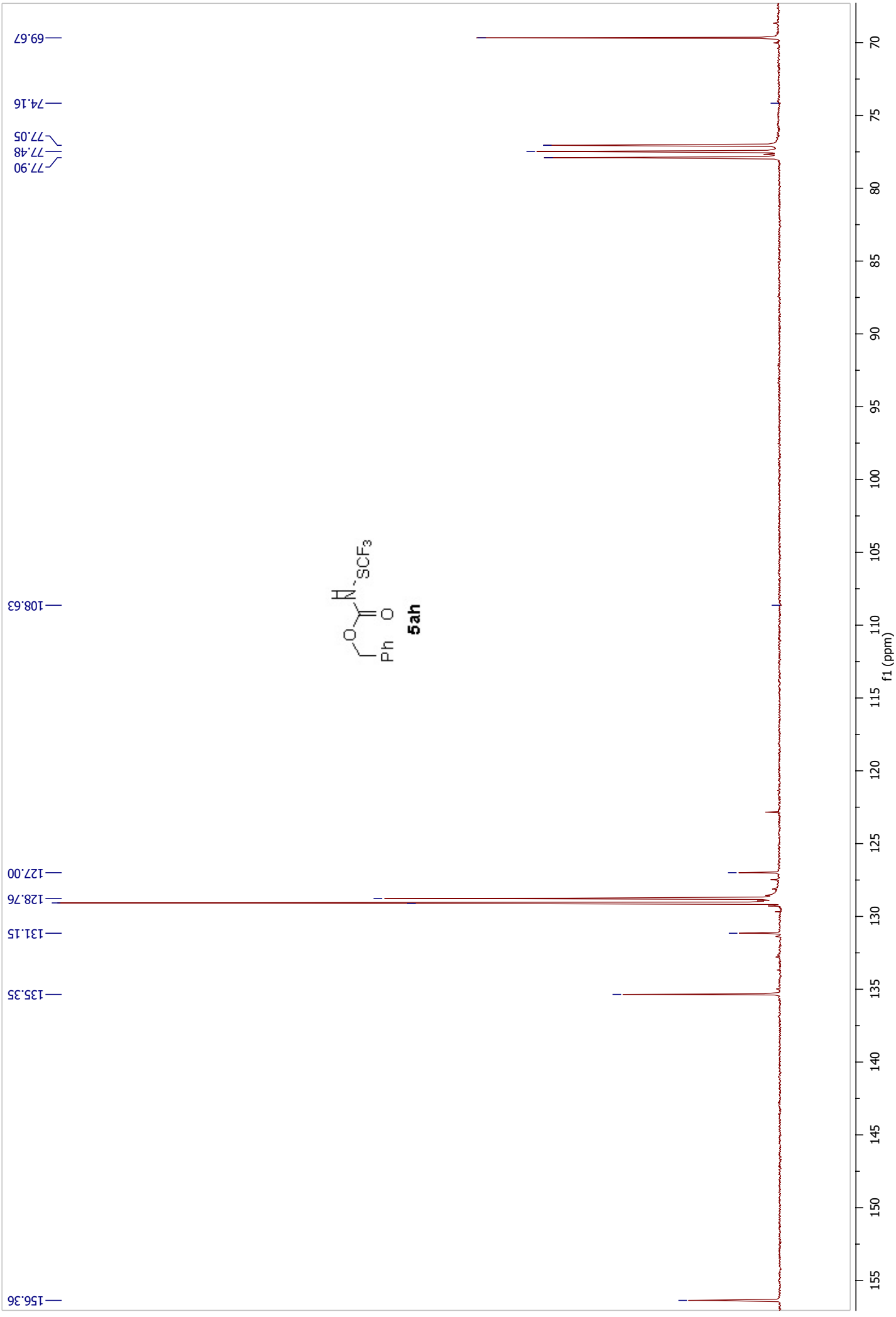

8.19
8.16
7.23
7.20
6.21
O_2N
SCF_3
5ab
1.96
2.12
1.00
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6
f1 (ppm)

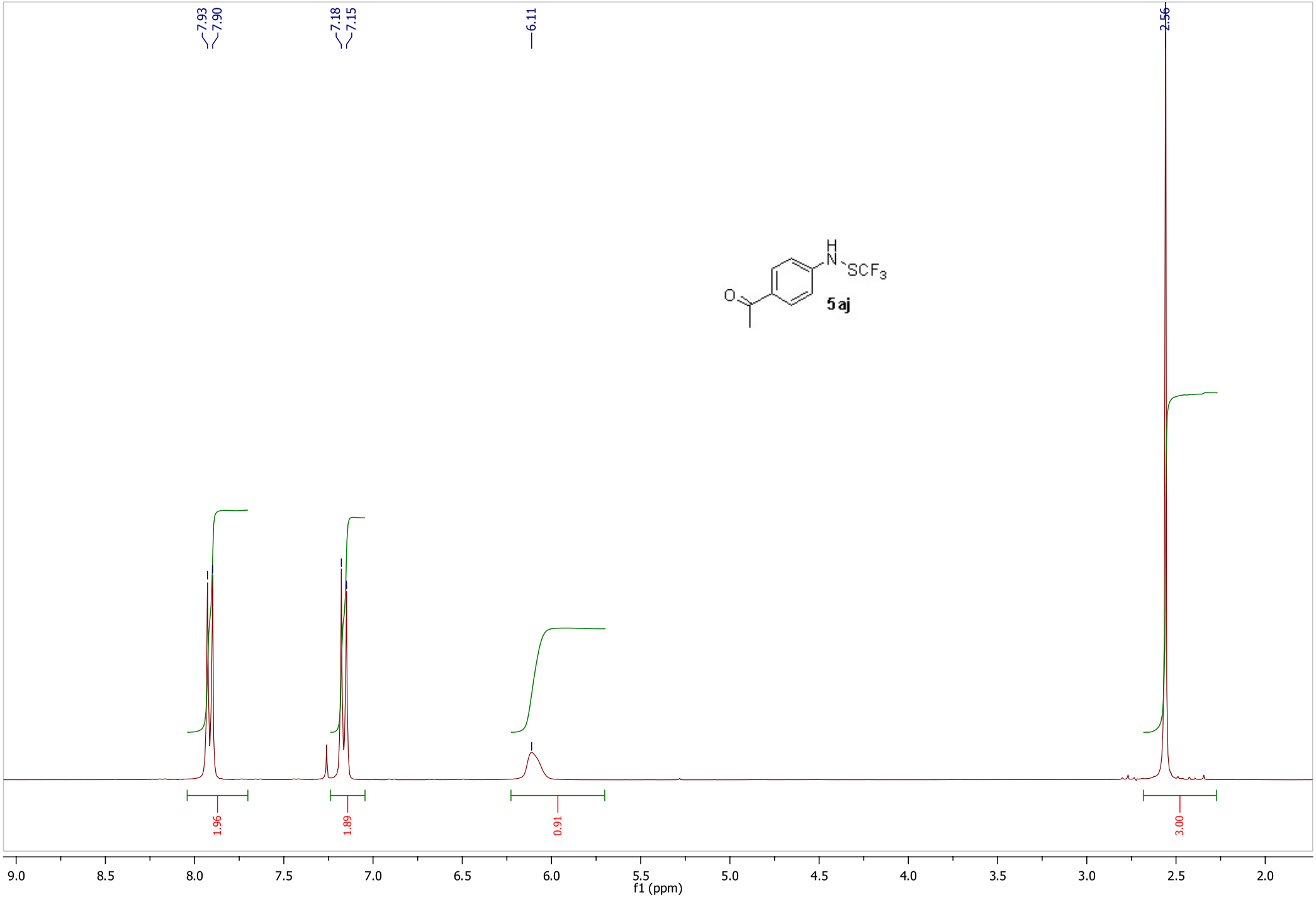

77.90
77.48
77.05
115.27
126.10
127.32
131.52
135.72
142.43
151.91
5ab
f1 (ppm)

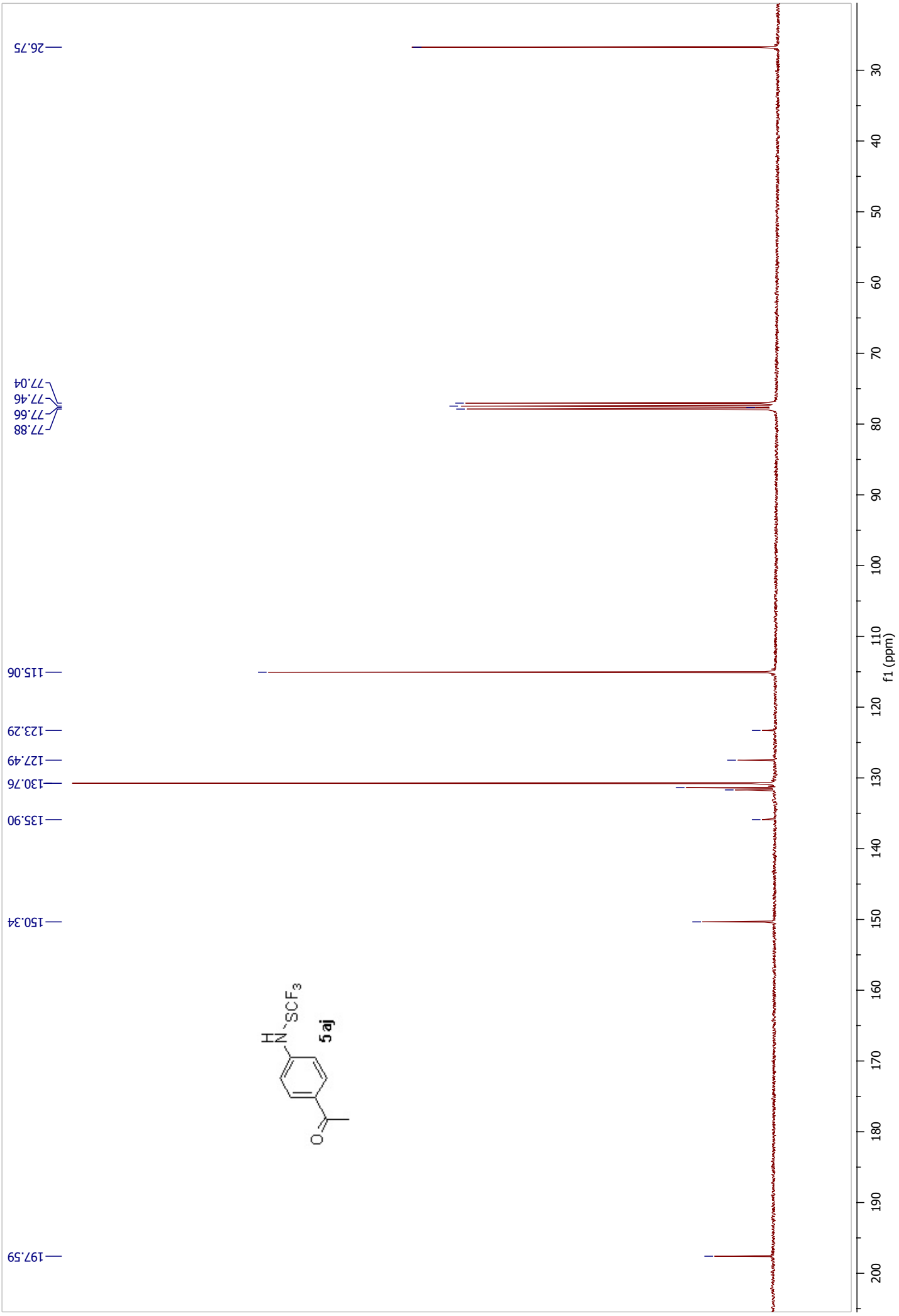

7.83
7.82
7.80
7.80
7.36
7.33
6.75
2.45
H
N
SCF3
S
O
O
5af
2.00
1.88
0.87
3.15
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

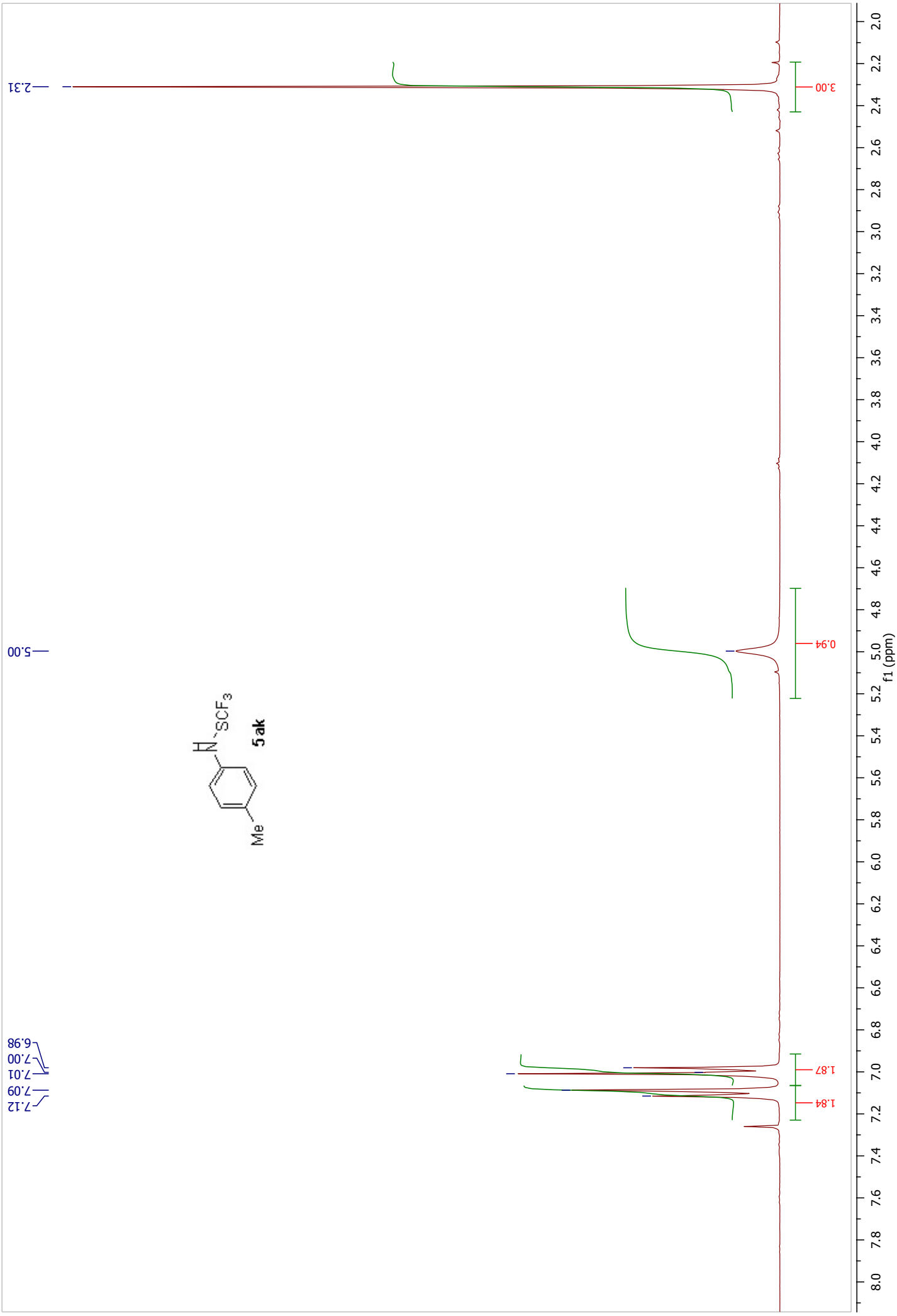

145.56
135.45
134.69
130.52
130.30
128.22
126.35
122.18
77.87
77.44
77.02
22.04
H
N
SCF3
S
O
O
5af
f1 (ppm)

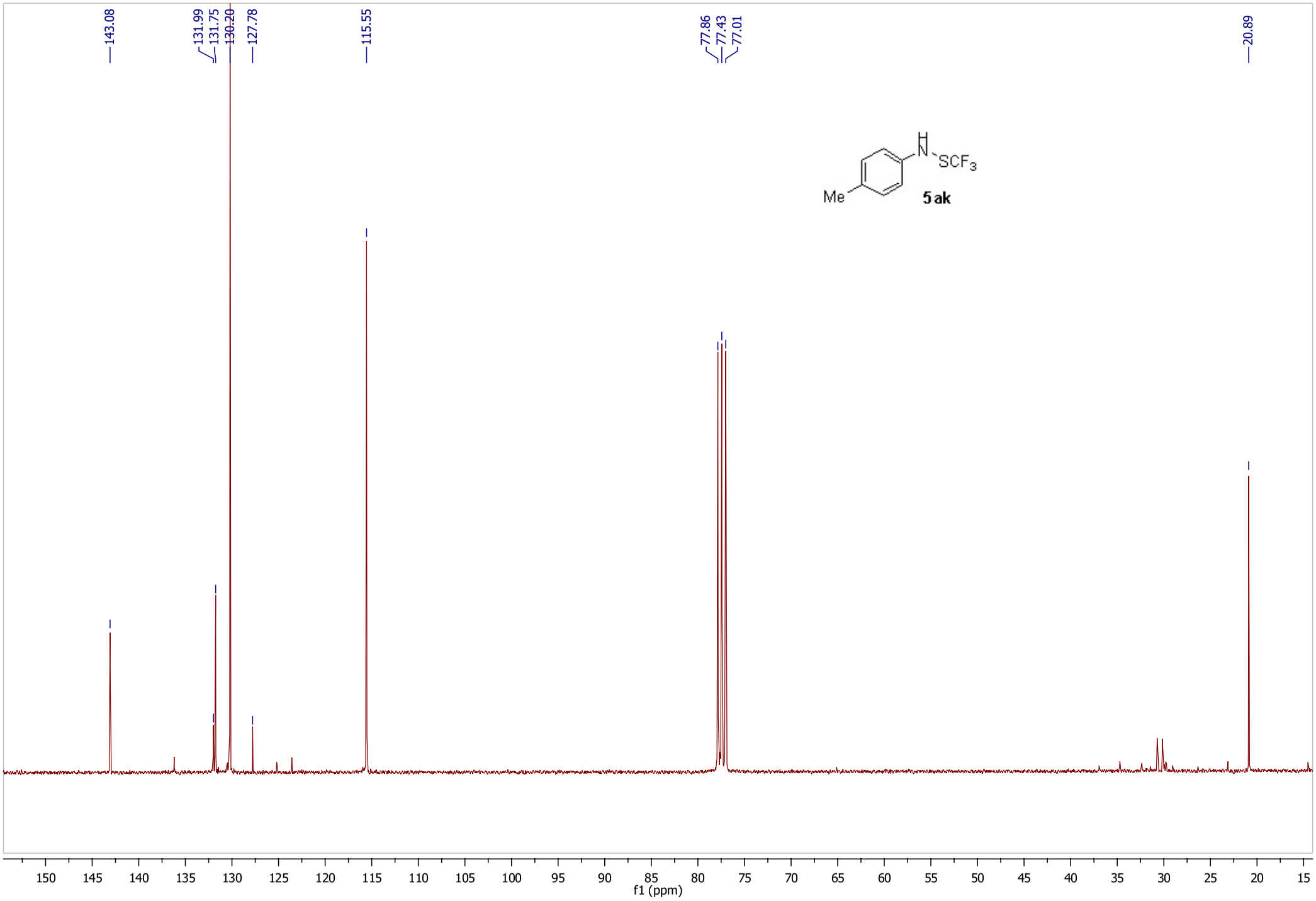

7.68
7.39
6.39
5.24
O
N
H
SCF3
Ph
O
5ah
5.17
0.96
2.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6
f1 (ppm)

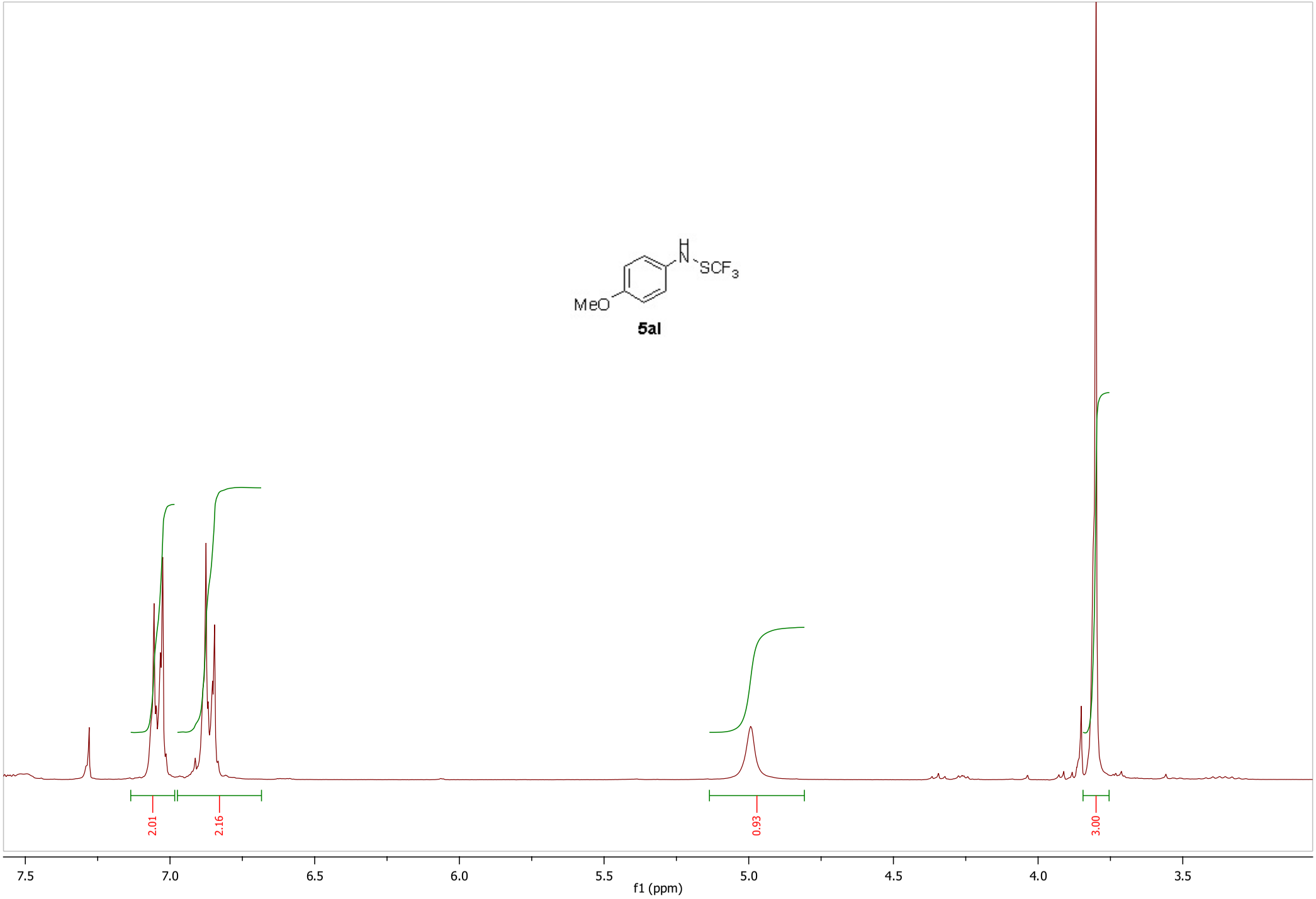

69.67
74.16
77.05
77.48
77.90
108.63
127.00
128.76
131.15
135.35
156.36
SCF3
N
H
O
O
Ph
5ah
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
f1 (ppm)

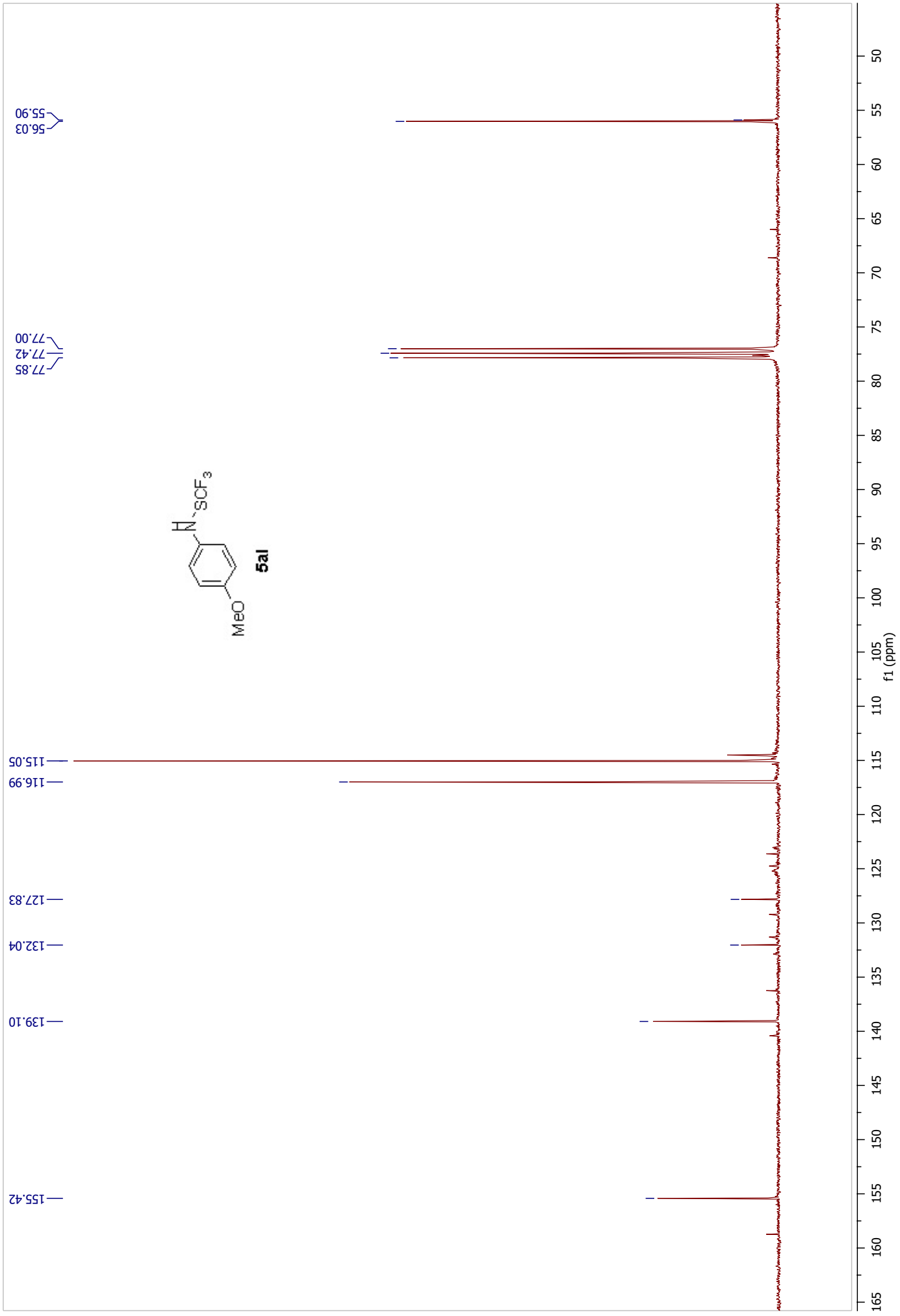

7.93
7.90
7.18
7.15
6.11
2.56
H
N
SCF3
O
5aj
1.96
1.89
0.91
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

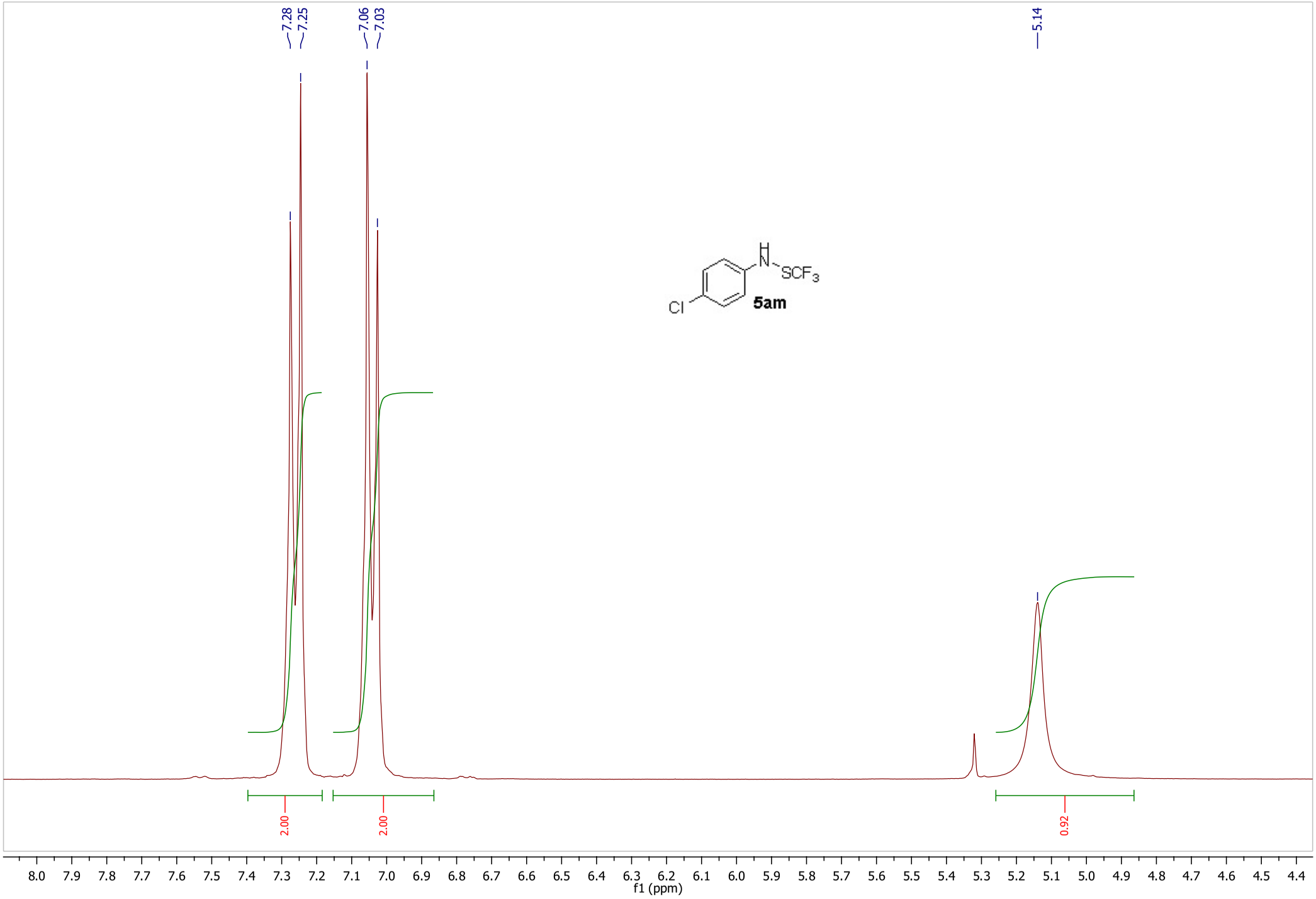

26.75
77.04
77.46
77.66
77.88
115.06
123.29
127.49
130.76
135.90
150.34
197.59
5aj
f1 (ppm)

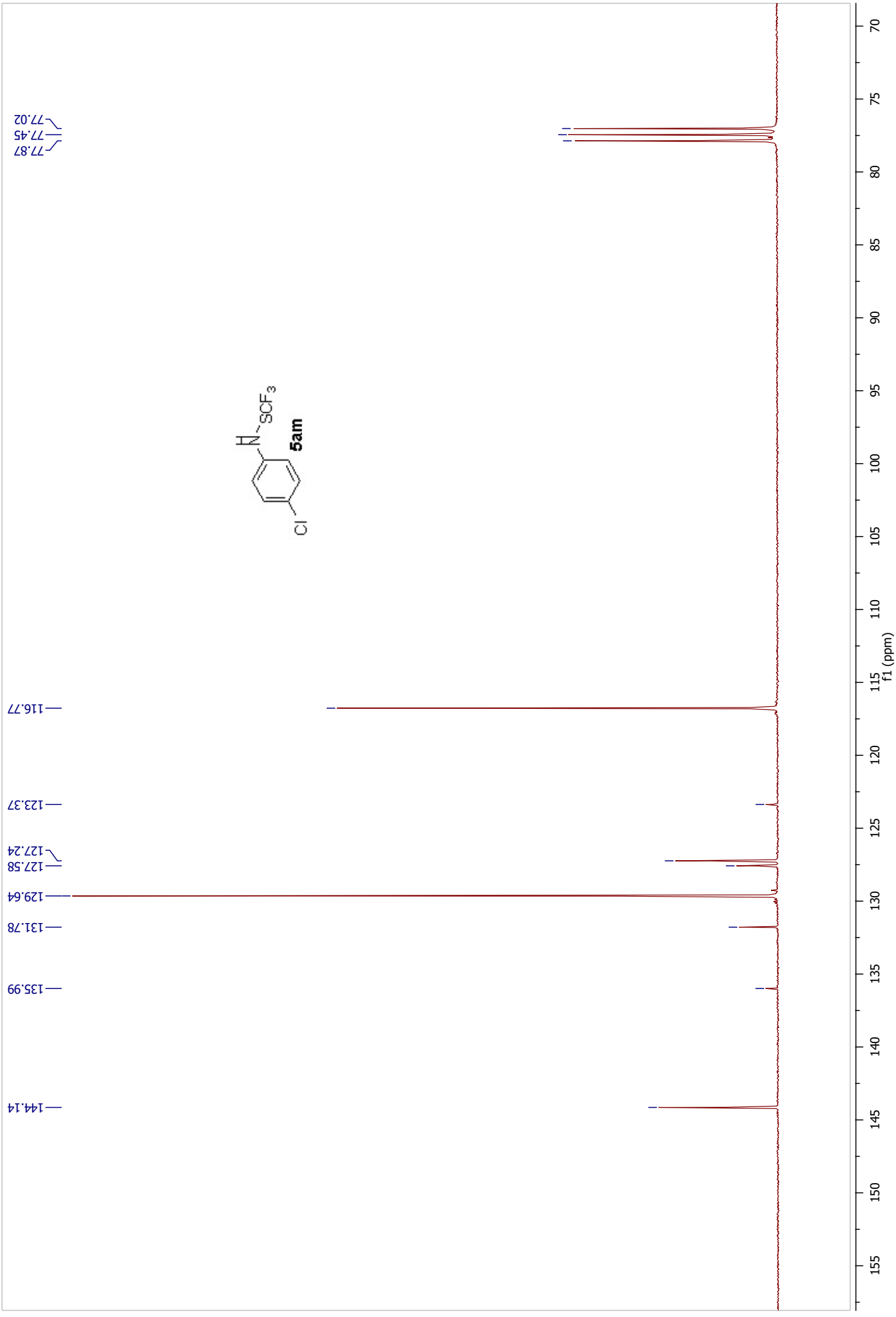

2.31
5.00
7.12
7.09
7.01
7.00
6.98
3.00
0.94
1.87
1.84
SCF3
Me
5ak
f1 (ppm)

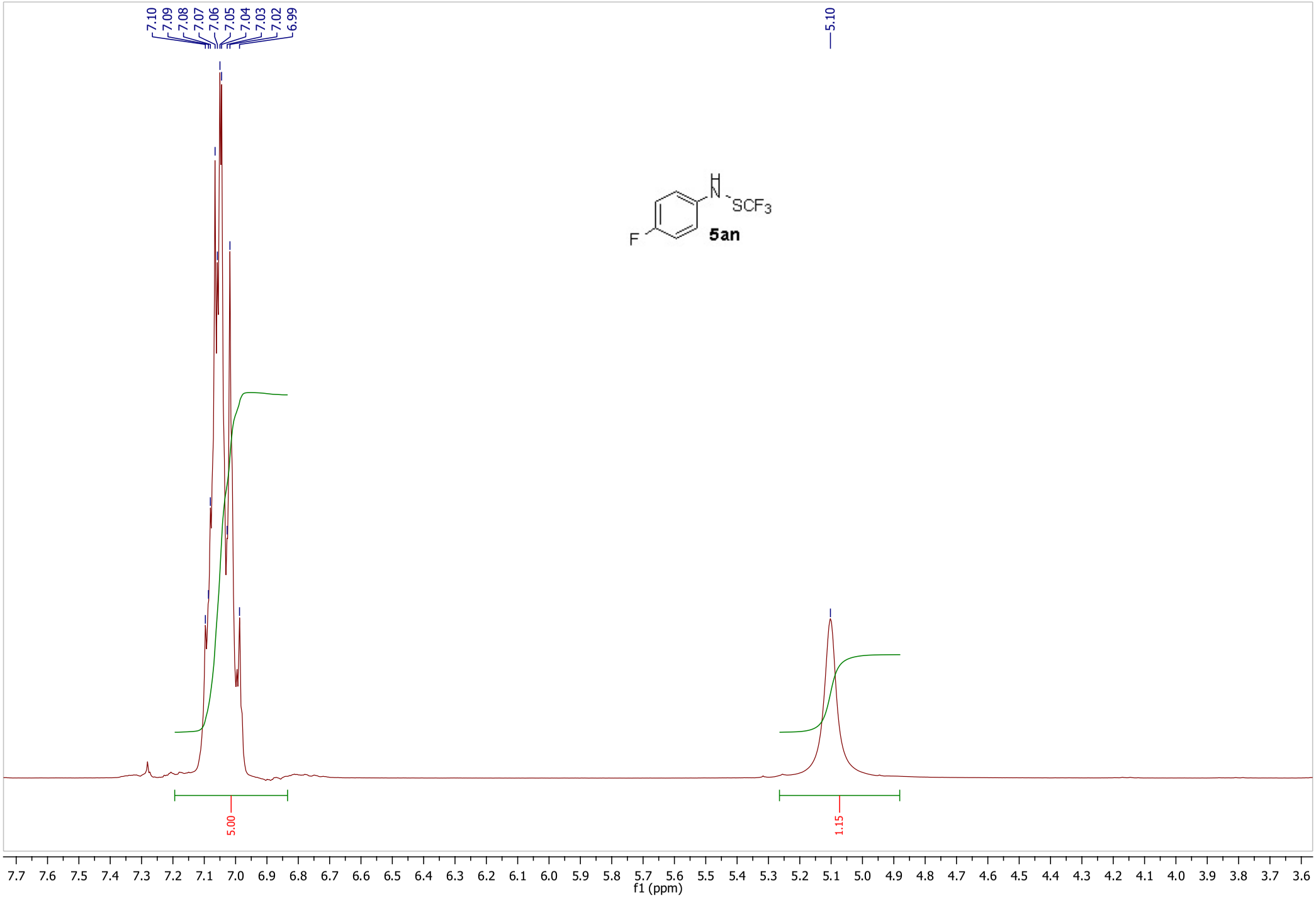

143.08
131.99
131.75
130.20
127.78
115.55
77.86
77.43
77.01
20.89
H
N
SCF3
Me
5ak
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

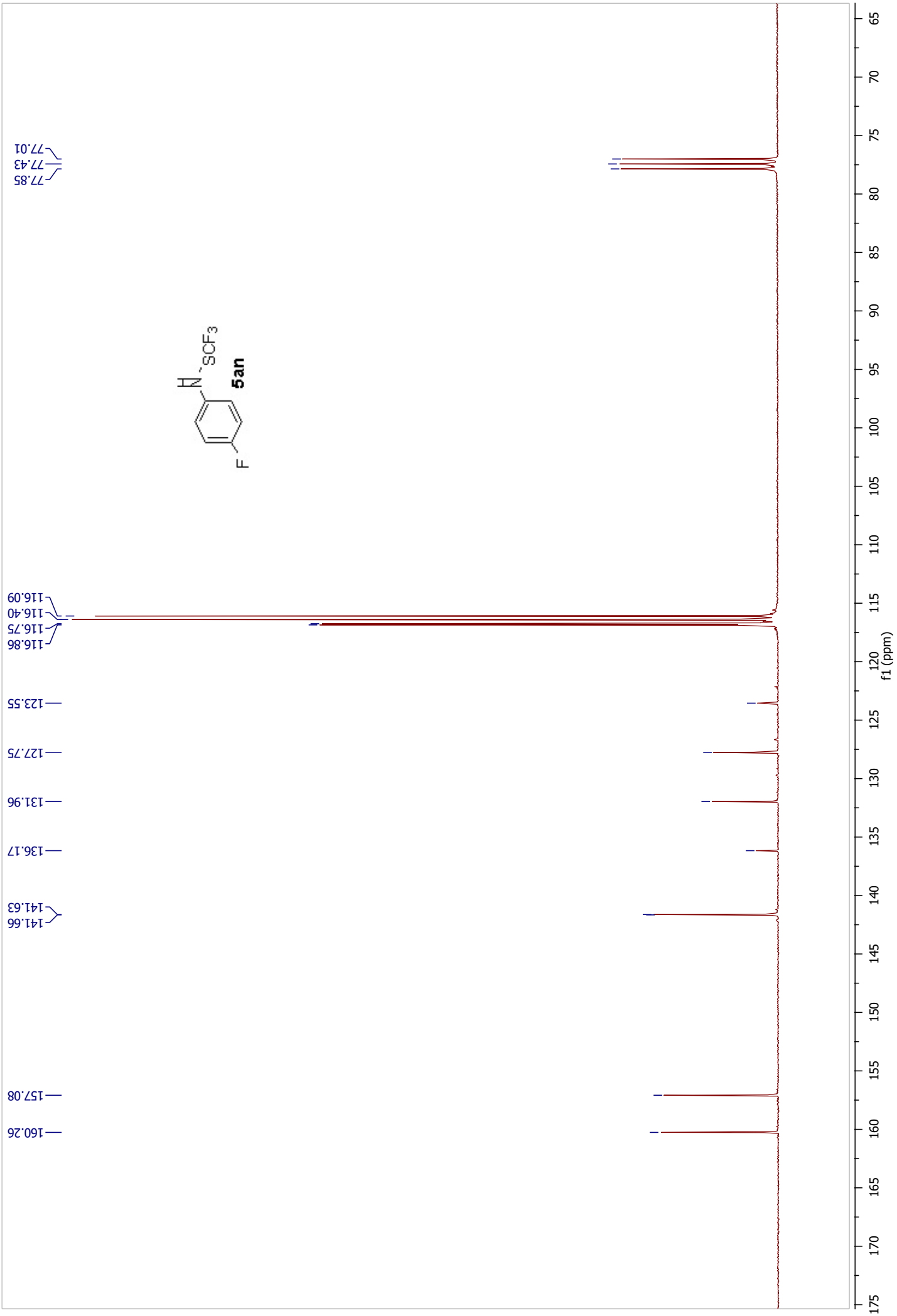

MeO
N
H
SCF3
5al
2.01
2.16
0.93
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)

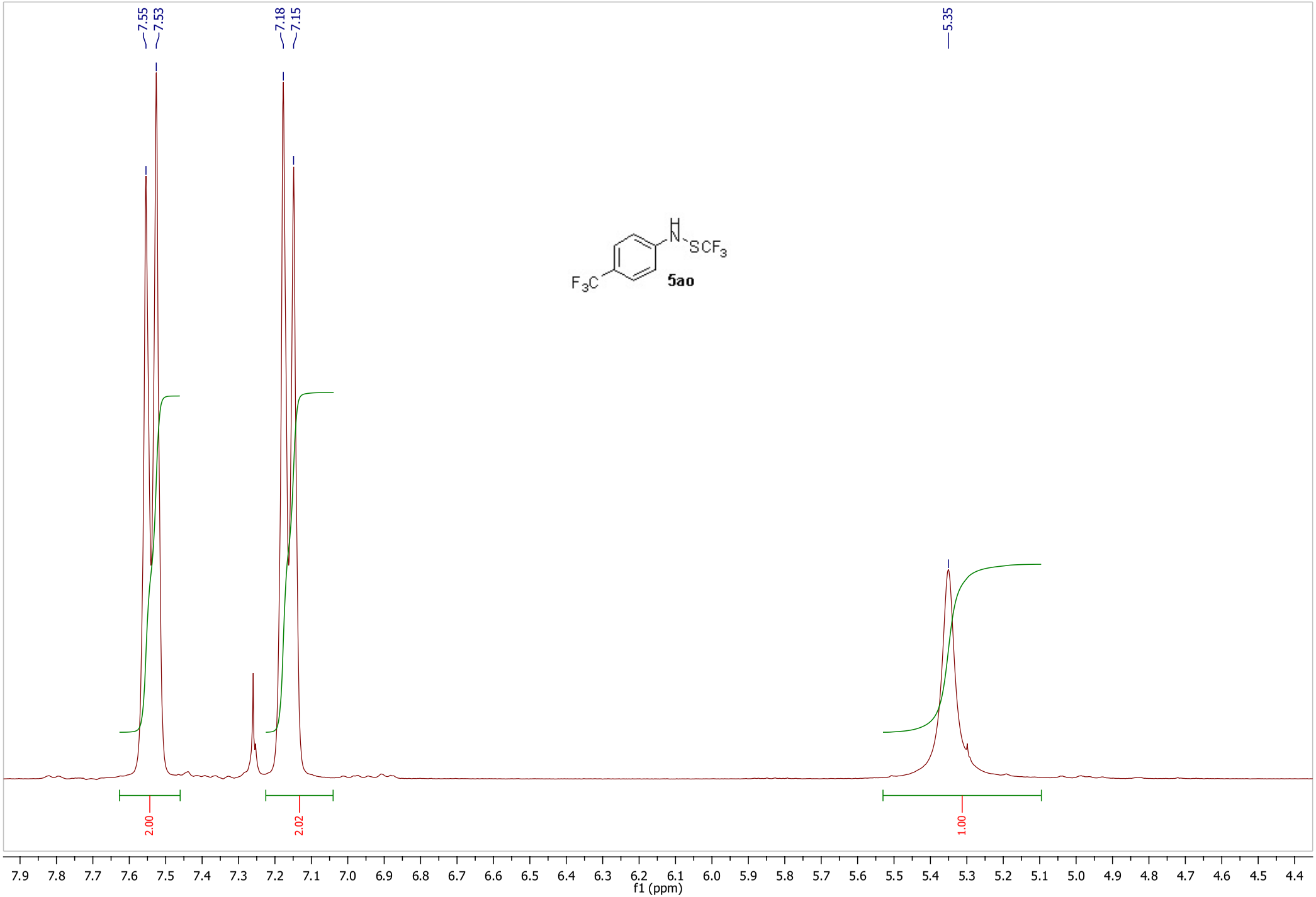

155.42
139.10
132.04
127.83
116.99
115.05
77.85
77.42
77.00
56.03
55.90
MeO
SCF3
5al
f1 (ppm)

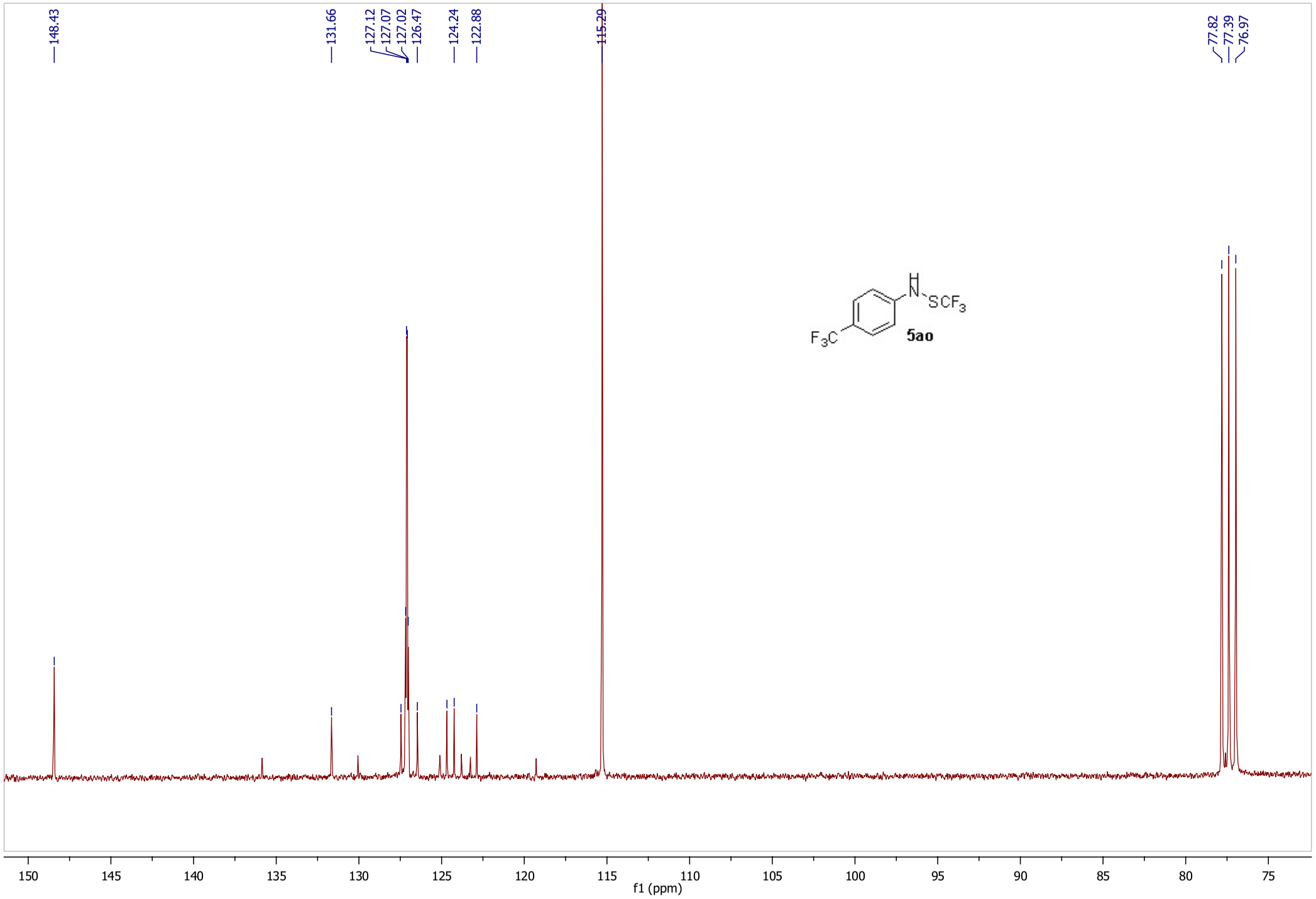

7.28
7.25
7.06
7.03
5.14
SCF3
Cl
5am
2.00
2.00
0.92
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
f1 (ppm)

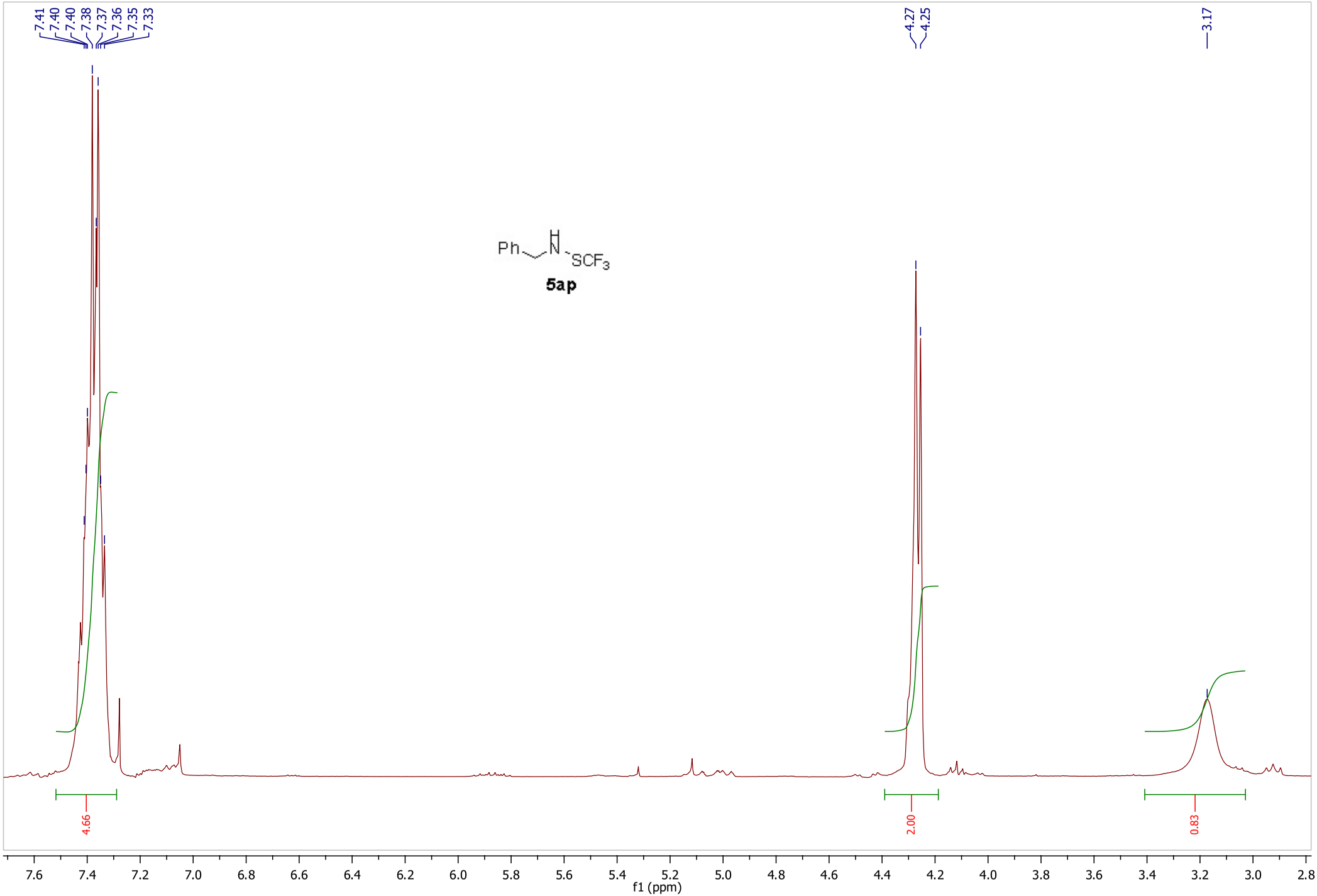

77.87
77.45
77.02
116.77
123.37
127.24
127.58
129.64
131.78
135.99
144.14
5am
SCF3
Cl
f1 (ppm)

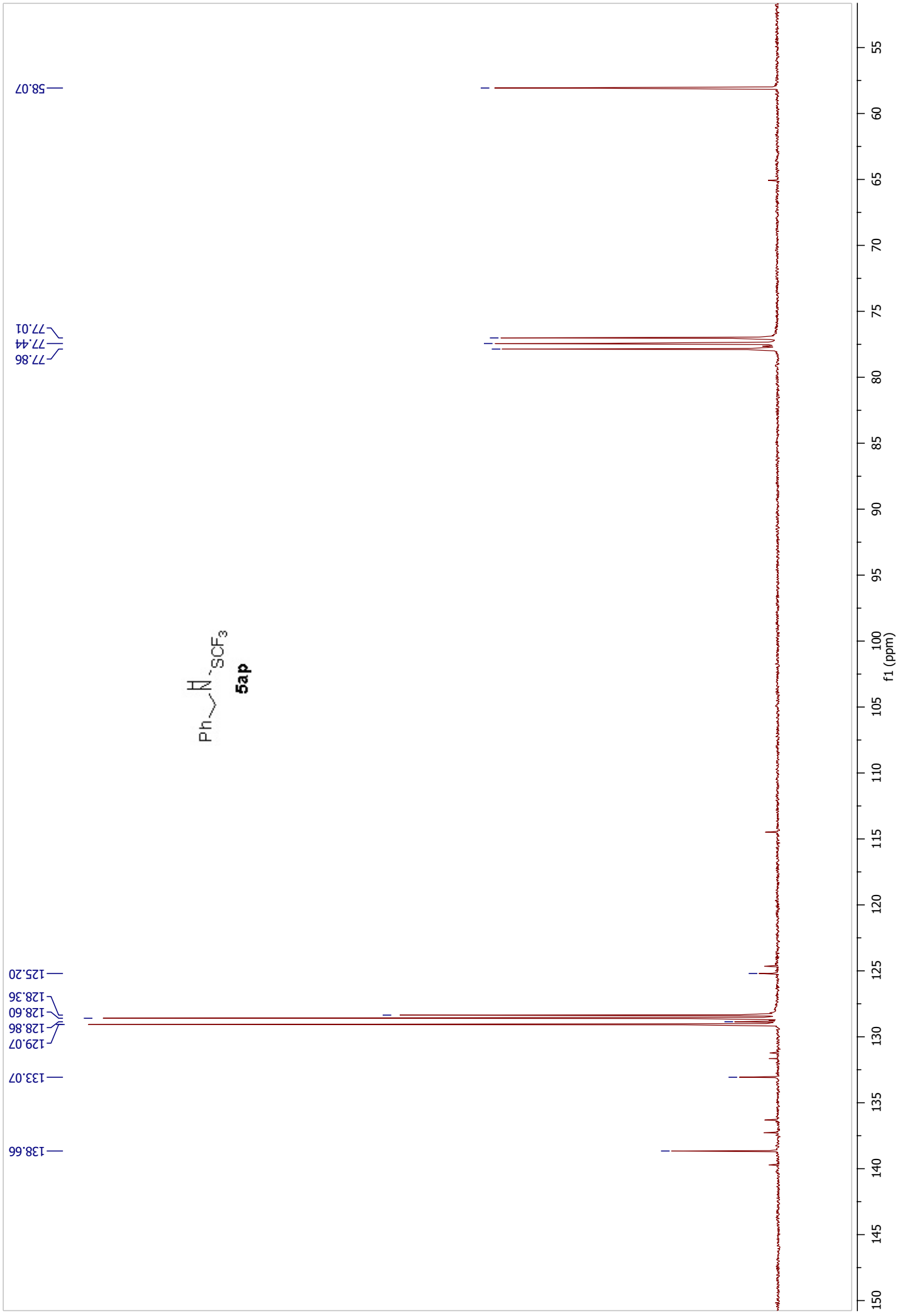

7.10
7.09
7.08
7.07
7.06
7.05
7.04
7.03
7.02
6.99
5.10
H
N
SCF3
F
5an
5.00
1.15
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6
f1 (ppm)

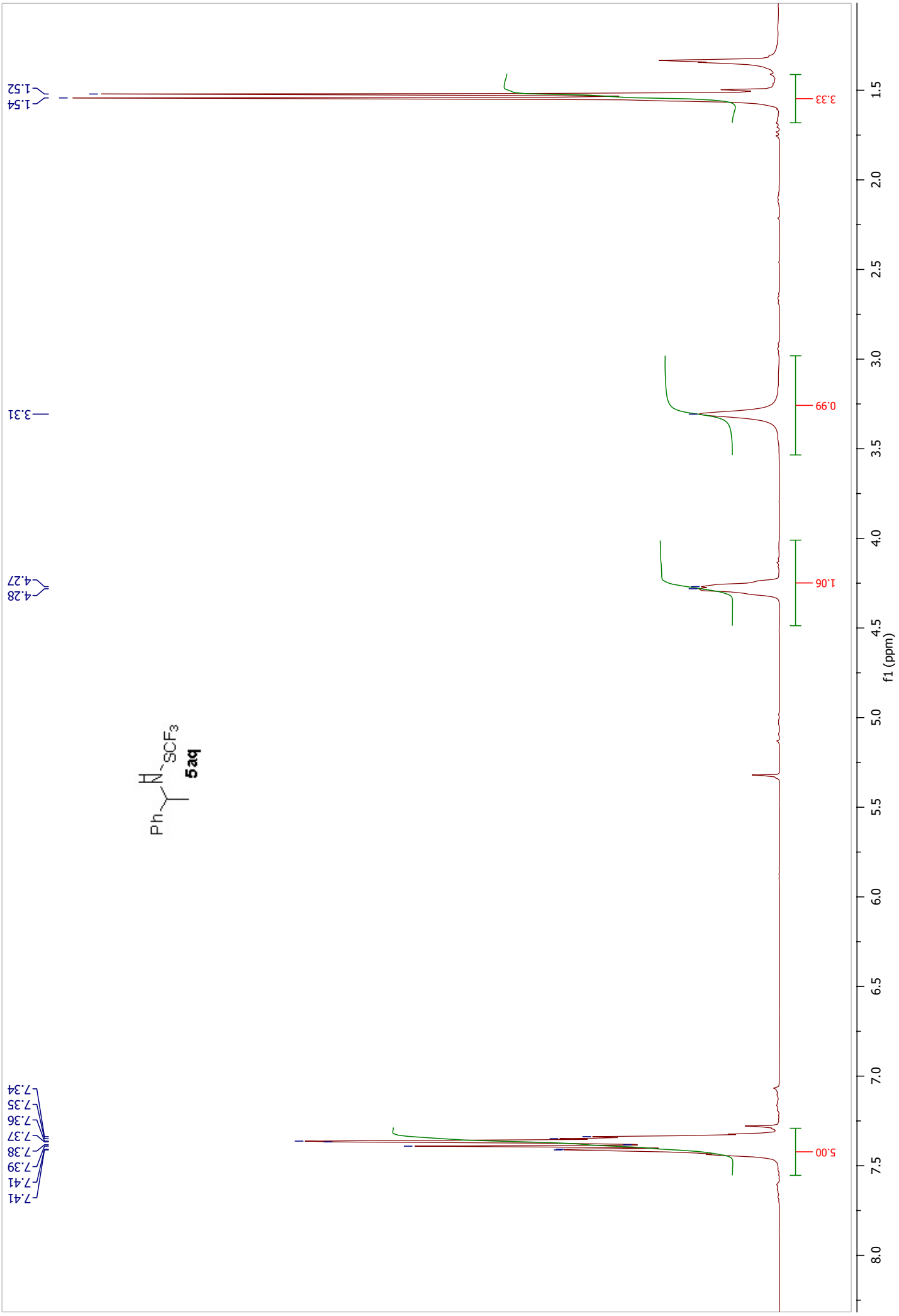

77.85
77.43
77.01
116.86
116.75
116.40
116.09
123.55
127.75
131.96
136.17
141.66
141.63
157.08
160.26
SCF3
5an
F
f1 (ppm)

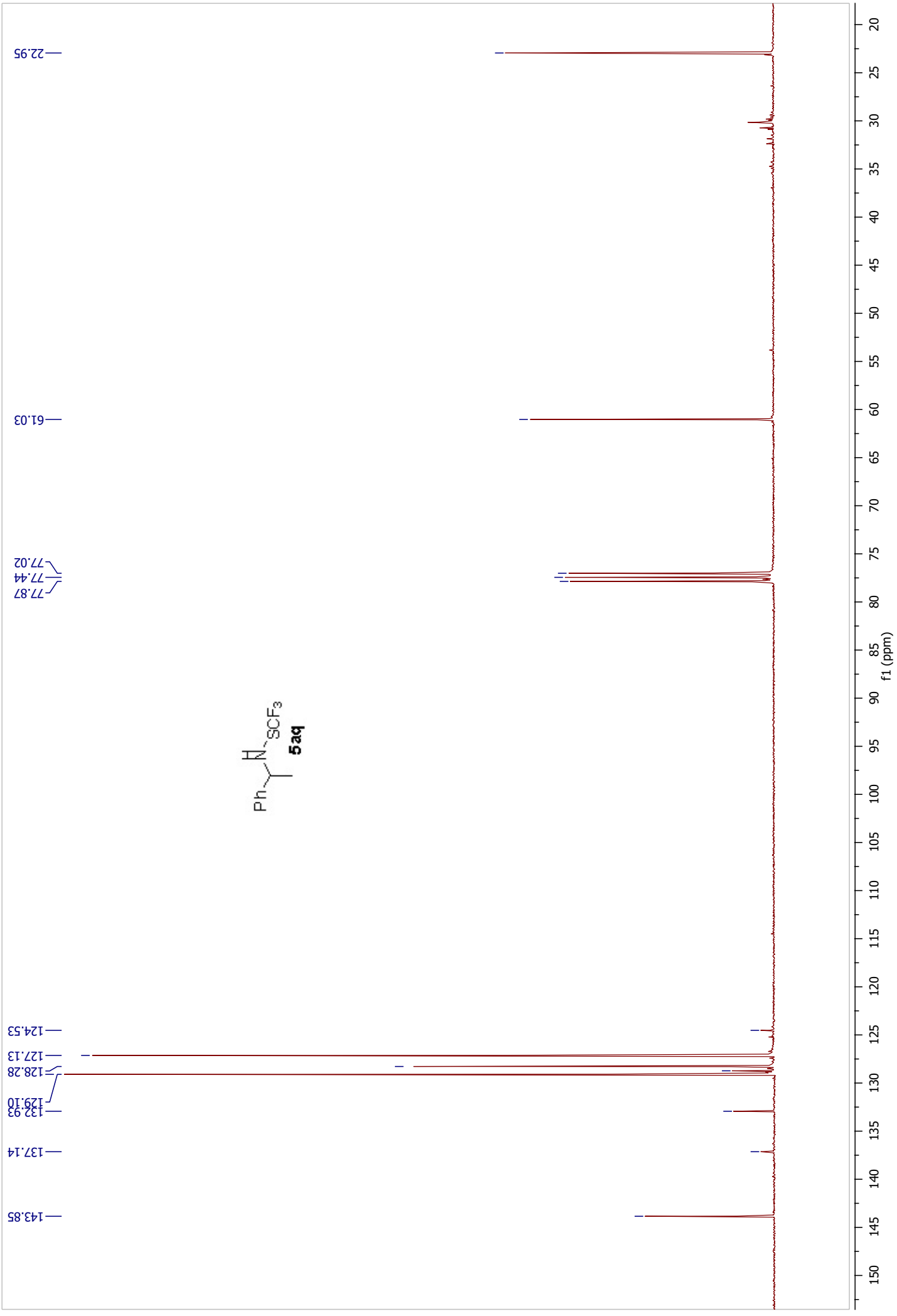

7.55
7.53
7.18
7.15
5.35
SCF3
F3C
5ao
2.00
2.02
1.00
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
f1 (ppm)

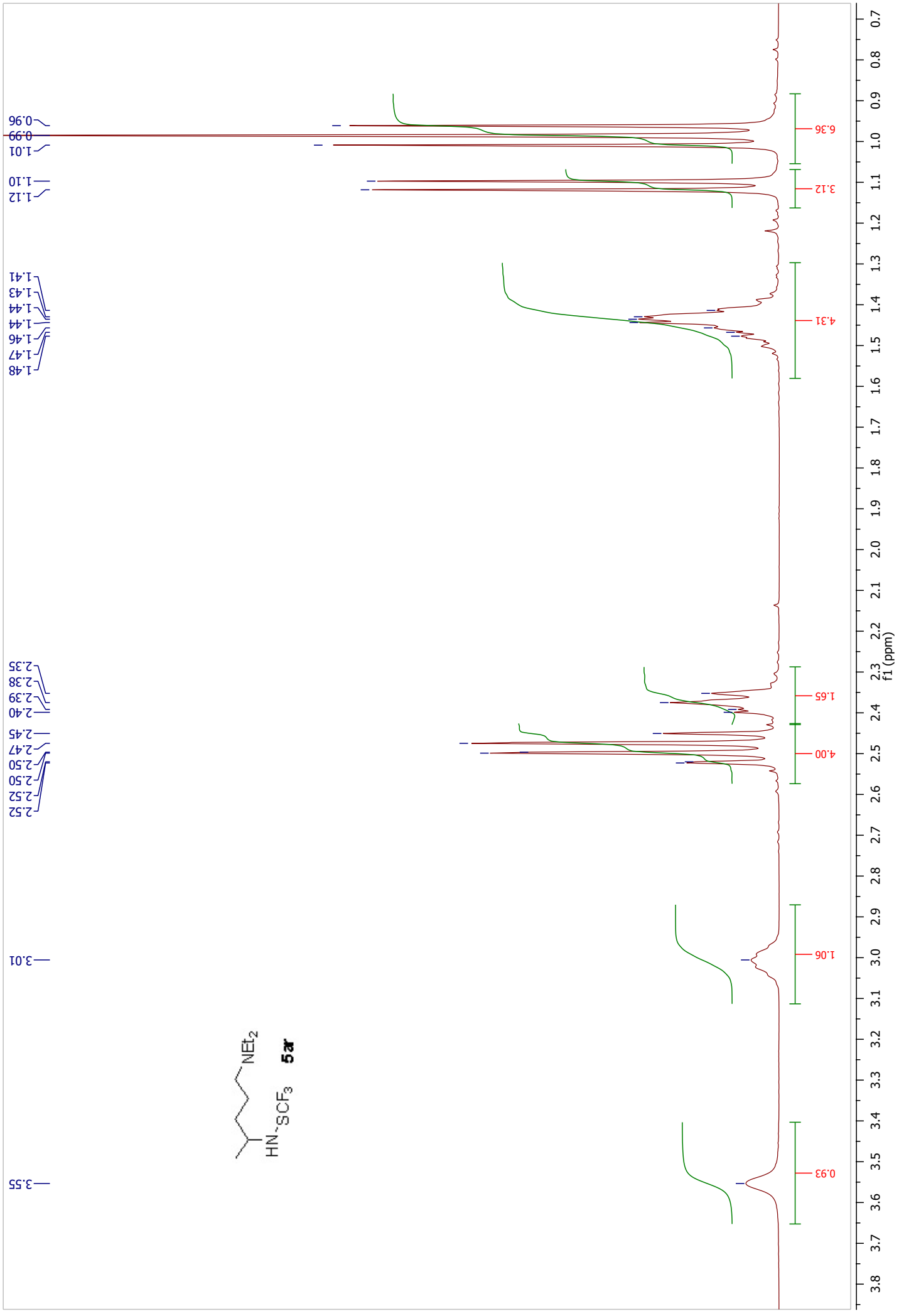

148.43
131.66
127.12
127.07
127.02
126.47
124.24
122.88
115.29
77.82
77.39
76.97
N
H
SCF3
F3C
5ao
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

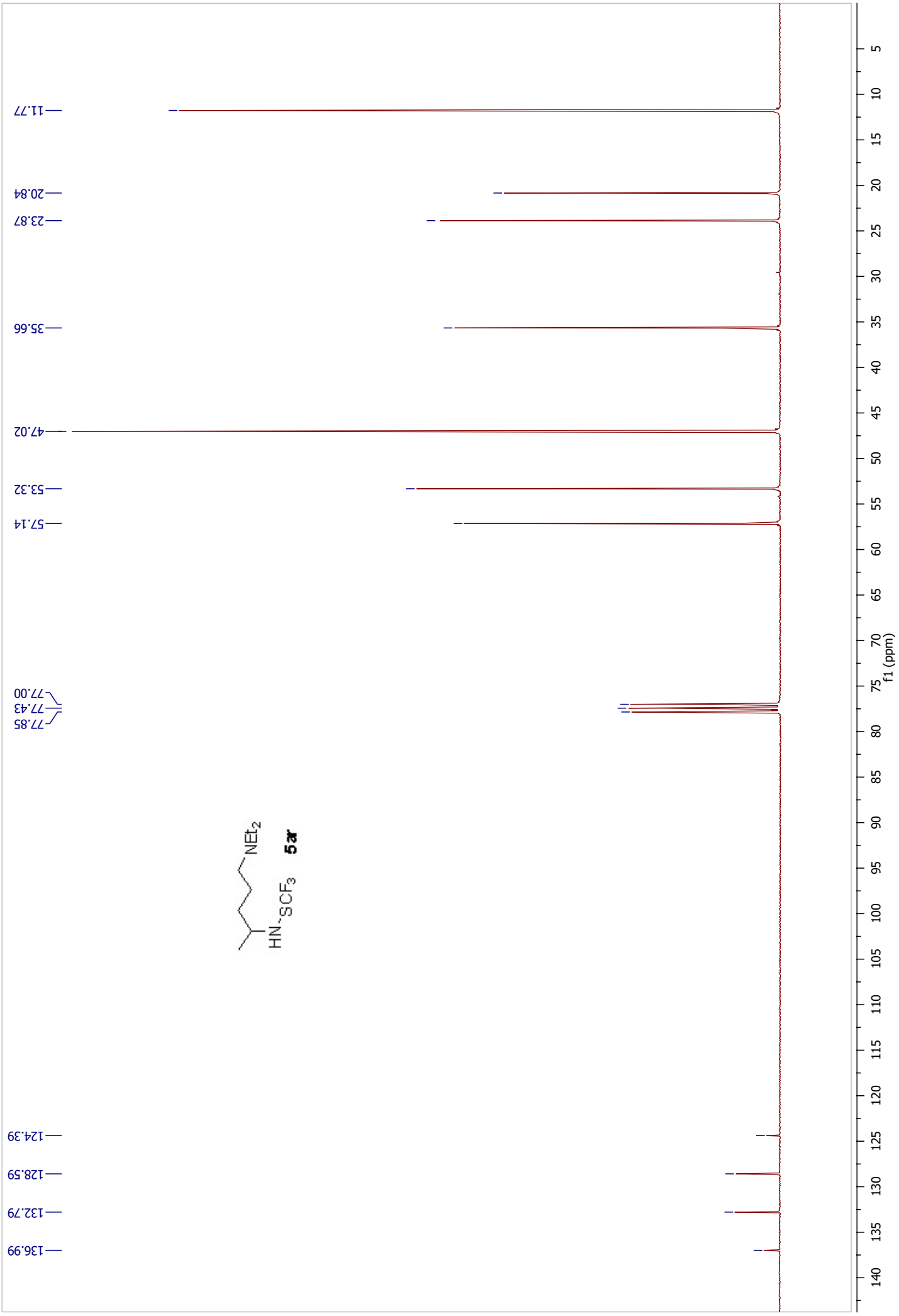

7.41
7.40
7.40
7.38
7.37
7.36
7.35
7.33
4.27
4.25
3.17
Ph
N
H
SCF3
5ap
4.66
2.00
0.83
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f1 (ppm)

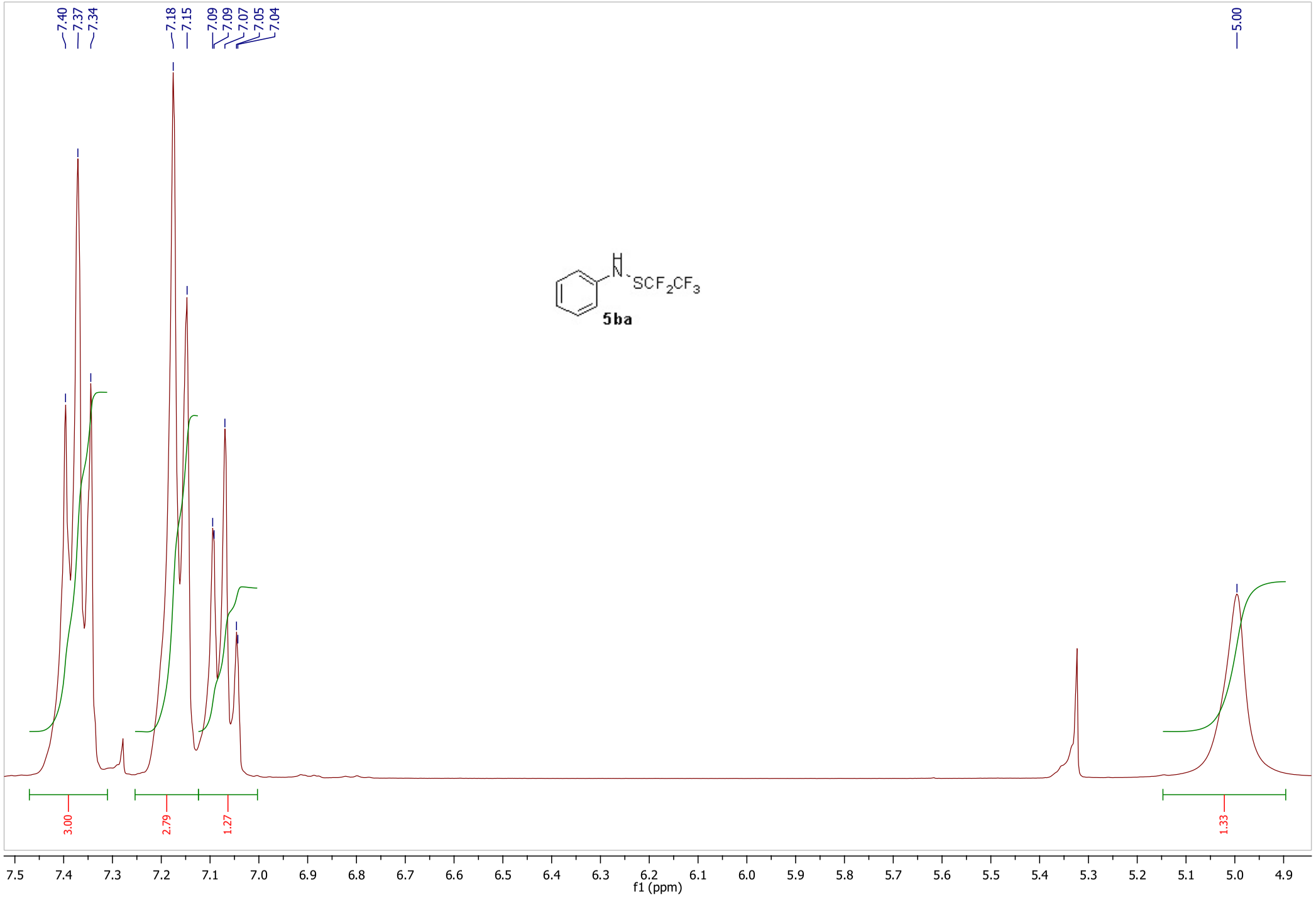

Ph
N
H
SCF3
5ap
58.07
77.86
77.44
77.01
125.20
128.36
128.60
128.86
129.07
133.07
138.66
f1 (ppm)

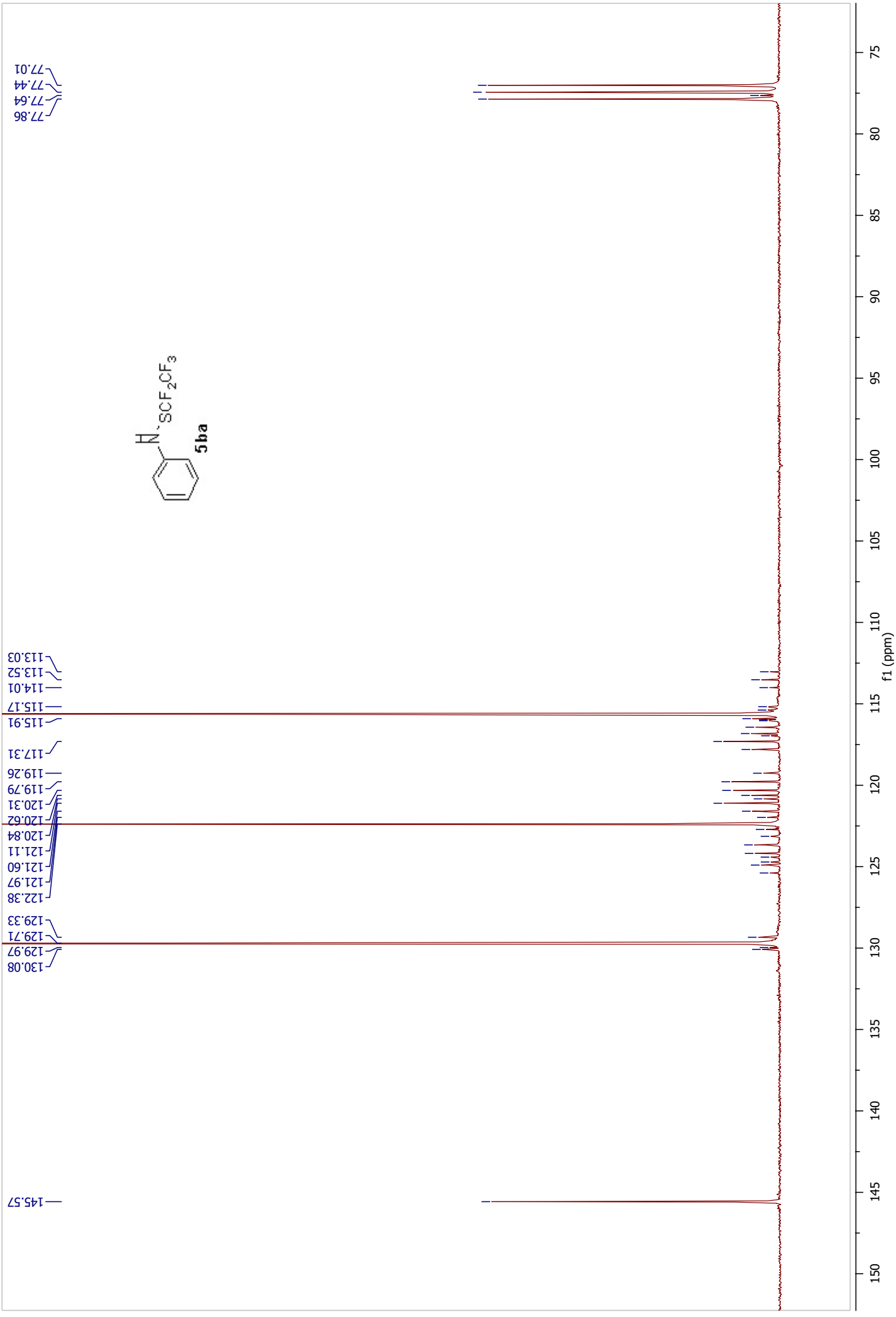

7.41
7.41
7.39
7.38
7.37
7.36
7.35
7.34
4.28
4.27
3.31
1.54
1.52
5.00
1.06
0.99
3.33
Ph
N
H
SCF3
5aq
f1 (ppm)

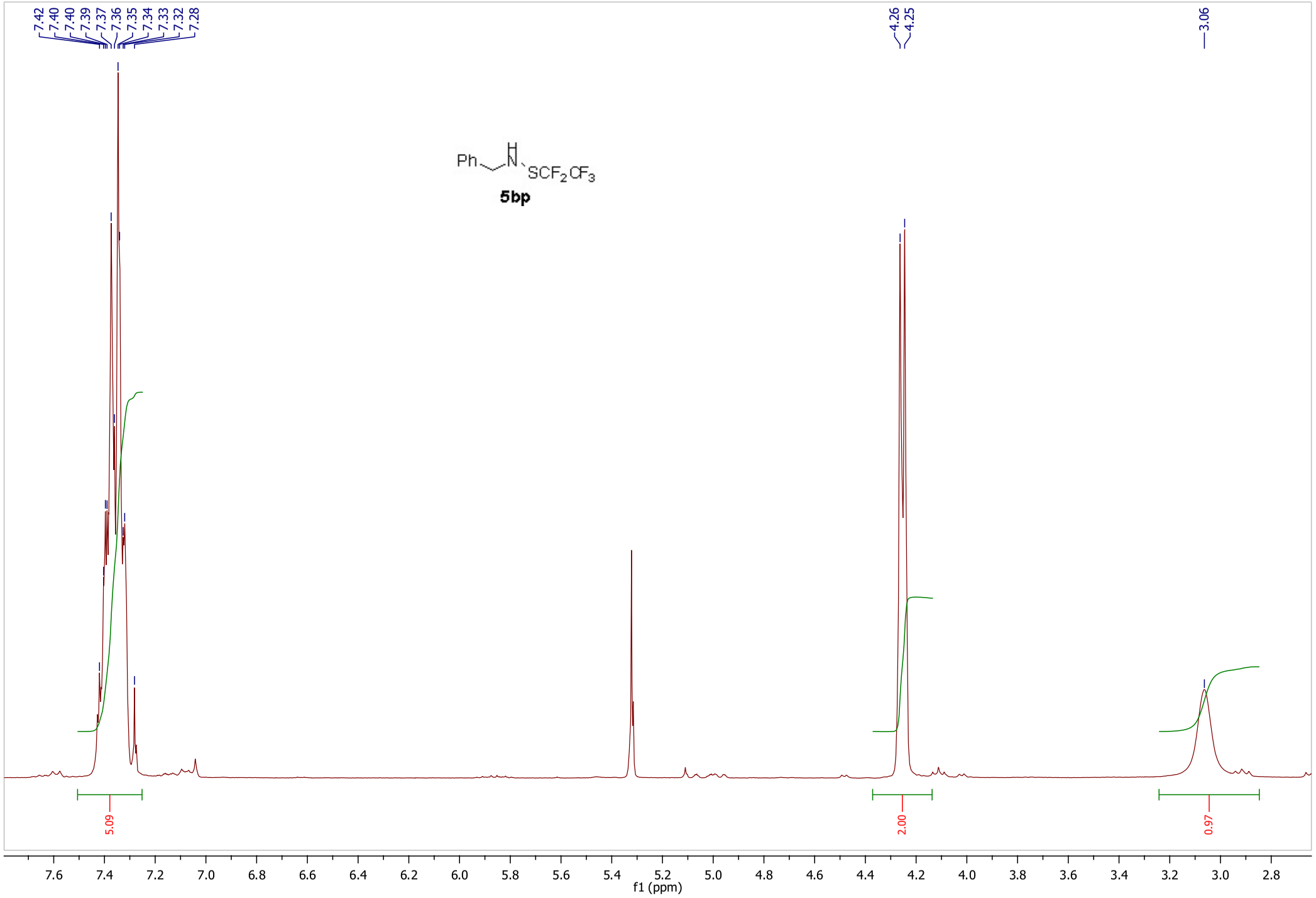

22.95
61.03
77.87
77.44
77.02
124.53
127.13
128.28
129.10
132.93
137.14
143.85
Ph
N
H
SCF3
5aq
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
f1 (ppm)

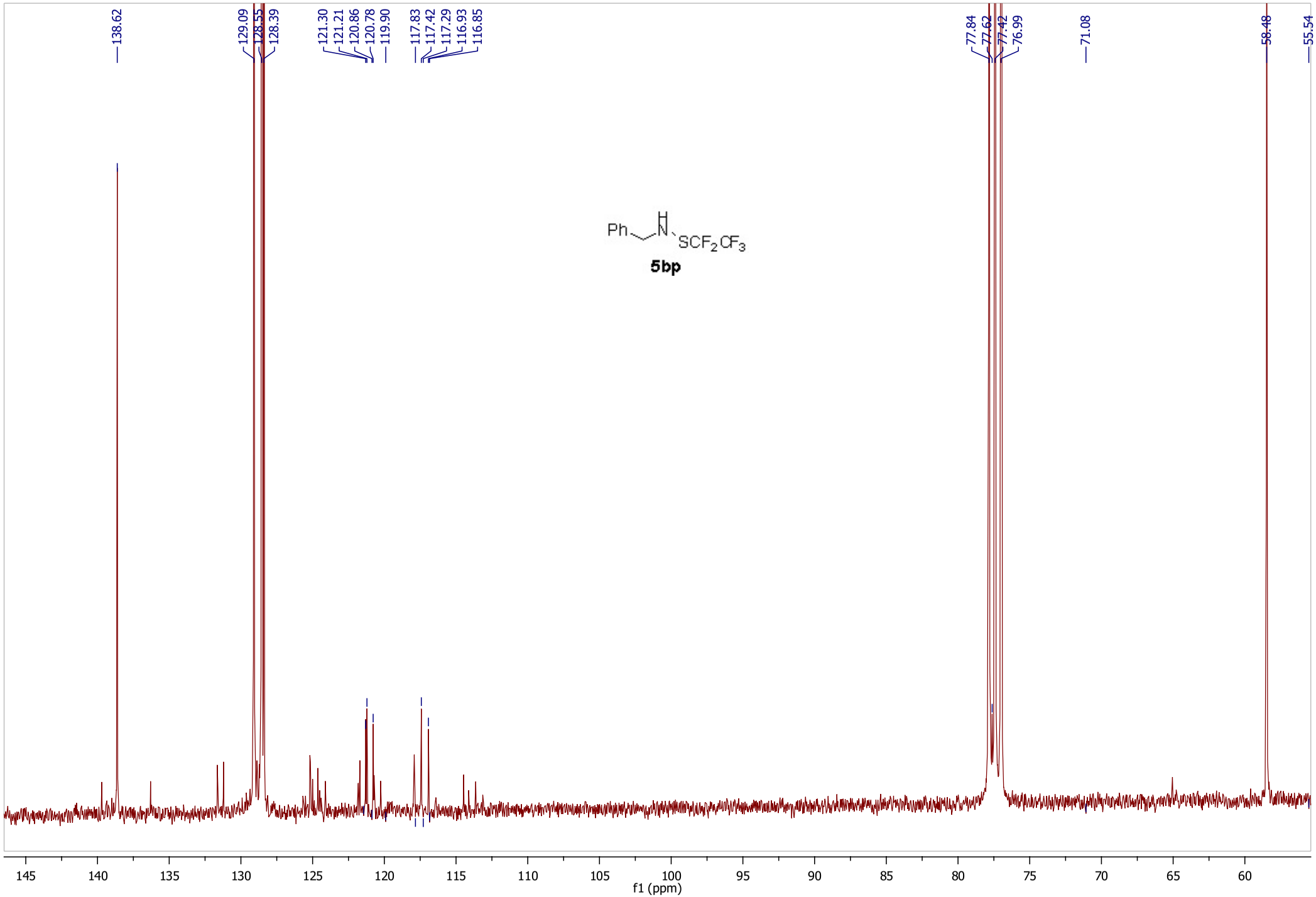

NEt2
HN-SCF3
5ar
0.96
0.99
1.01
1.10
1.12
1.41
1.43
1.44
1.44
1.46
1.47
1.48
2.35
2.38
2.39
2.40
2.45
2.47
2.50
2.50
2.52
2.52
3.01
3.55
6.36
3.12
4.31
1.65
4.00
1.06
0.93
f1 (ppm)

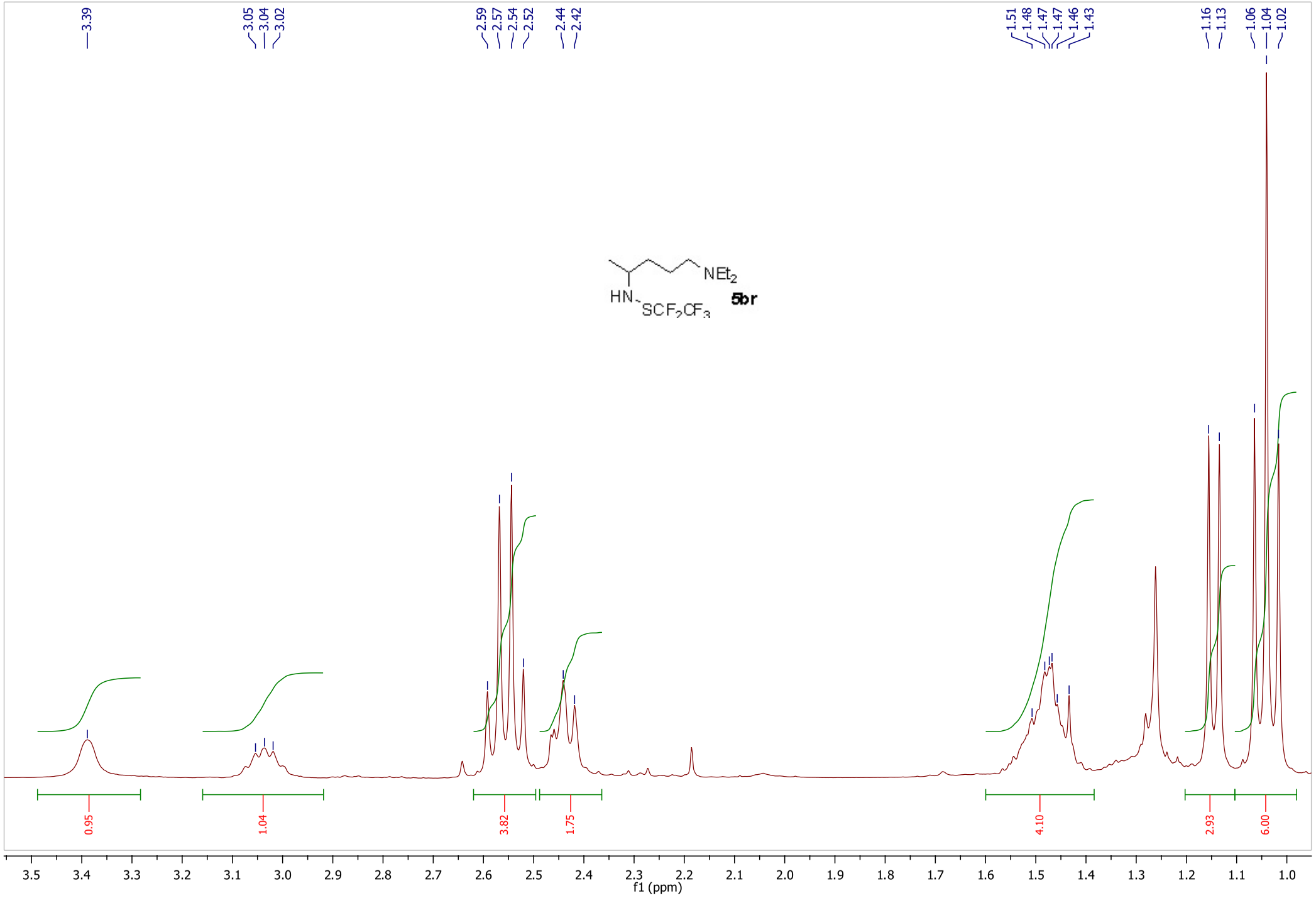

11.77
20.84
23.87
35.66
47.02
53.32
57.14
77.00
77.43
77.85
124.39
128.59
132.79
136.99
NEt2
HN
SCF3
5ar
f1 (ppm)

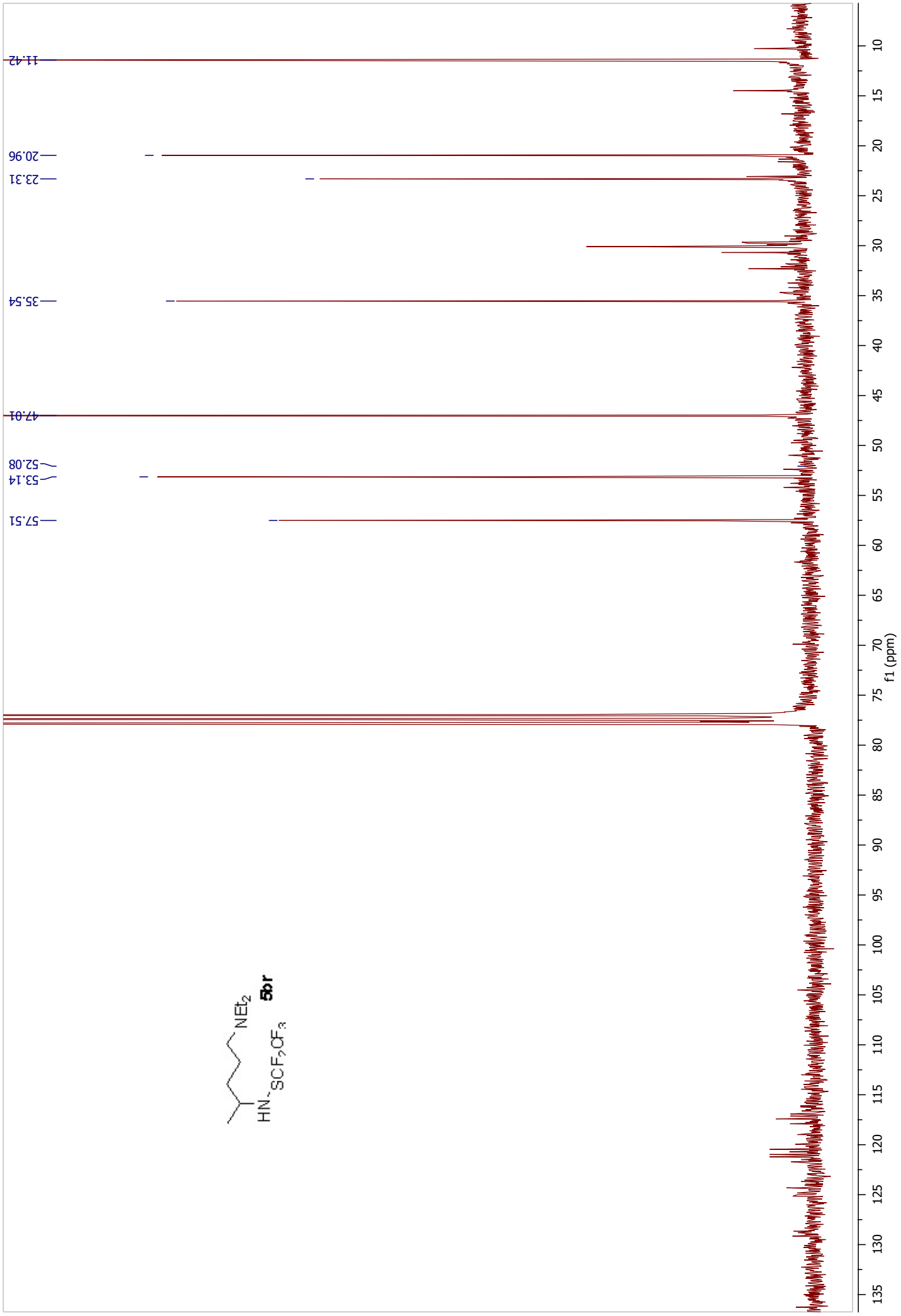

7.40
7.37
7.34
7.18
7.15
7.09
7.09
7.07
7.05
7.04
5.00
SCF2CF3
5ba
3.00
2.79
1.27
1.33
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9
f1 (ppm)

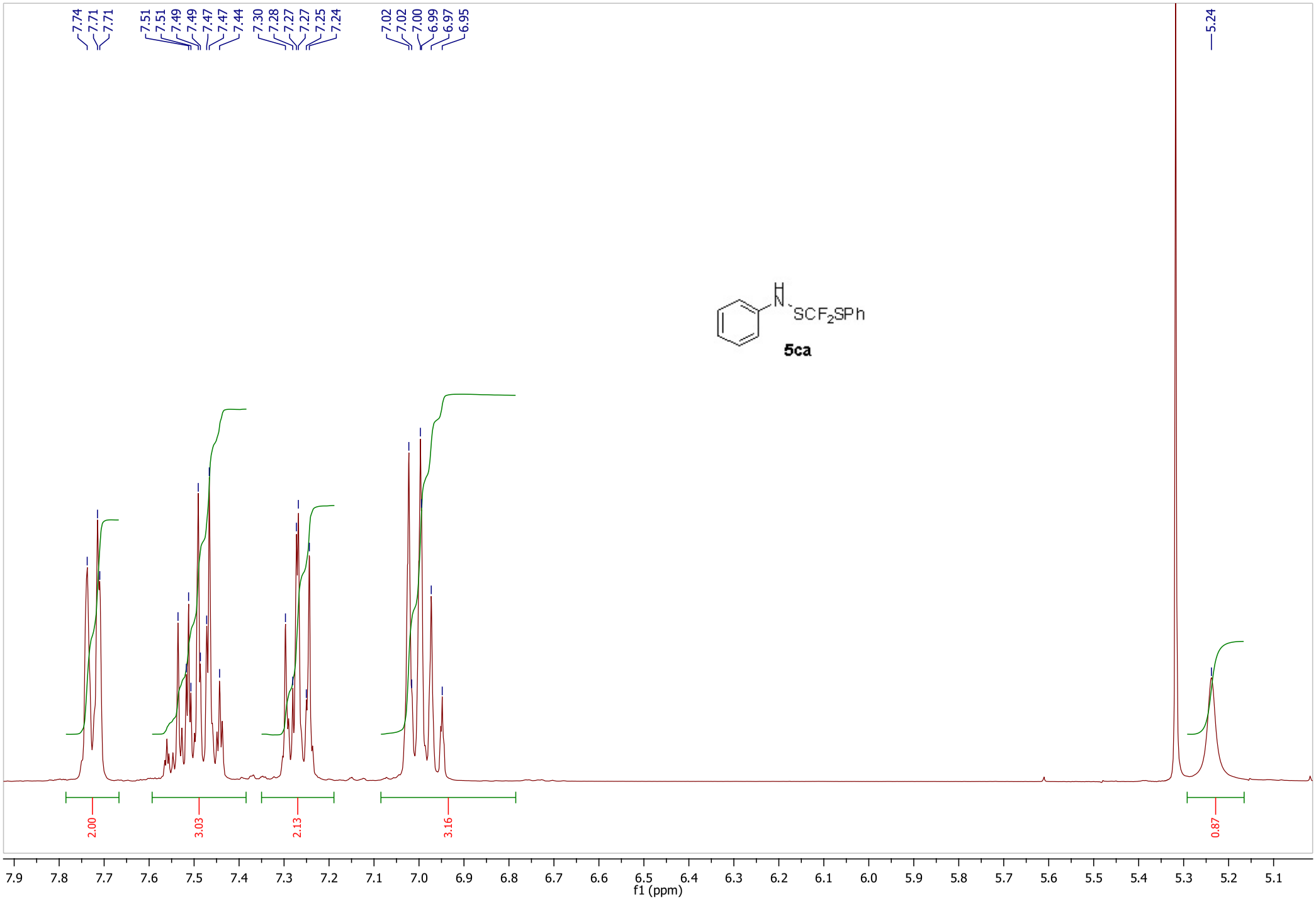

77.86
77.64
77.44
77.01
SCF2CF3
5ba
113.03
113.52
114.01
115.17
115.91
117.31
119.26
119.79
120.31
120.62
120.84
121.11
121.60
121.97
122.38
129.33
129.71
129.97
130.08
145.57
f1 (ppm)

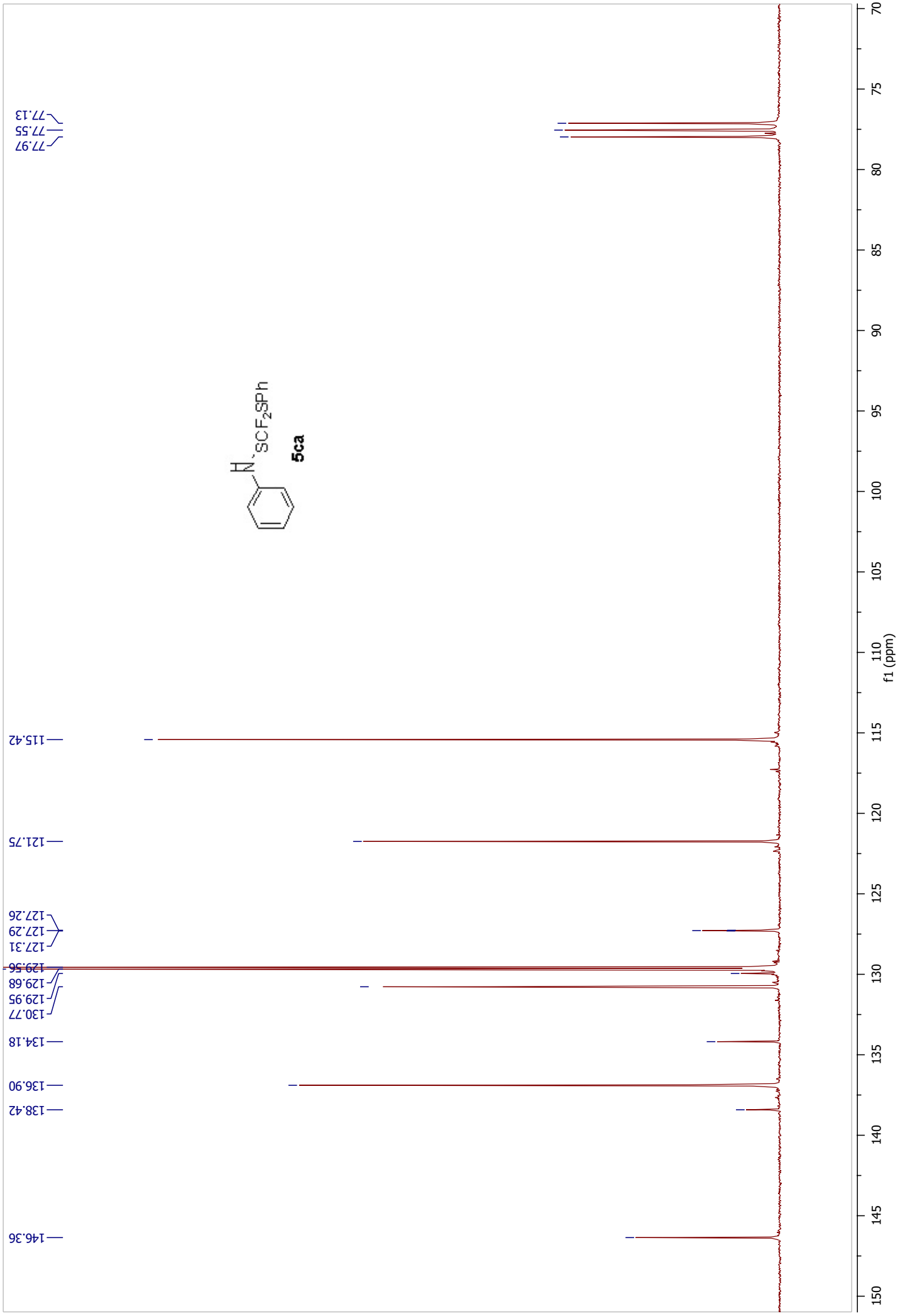

7.42
7.40
7.40
7.39
7.37
7.36
7.35
7.34
7.33
7.32
7.28
4.26
4.25
3.06
Ph
N
H
SCF2CF3
5bp
5.09
2.00
0.97
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f1 (ppm)

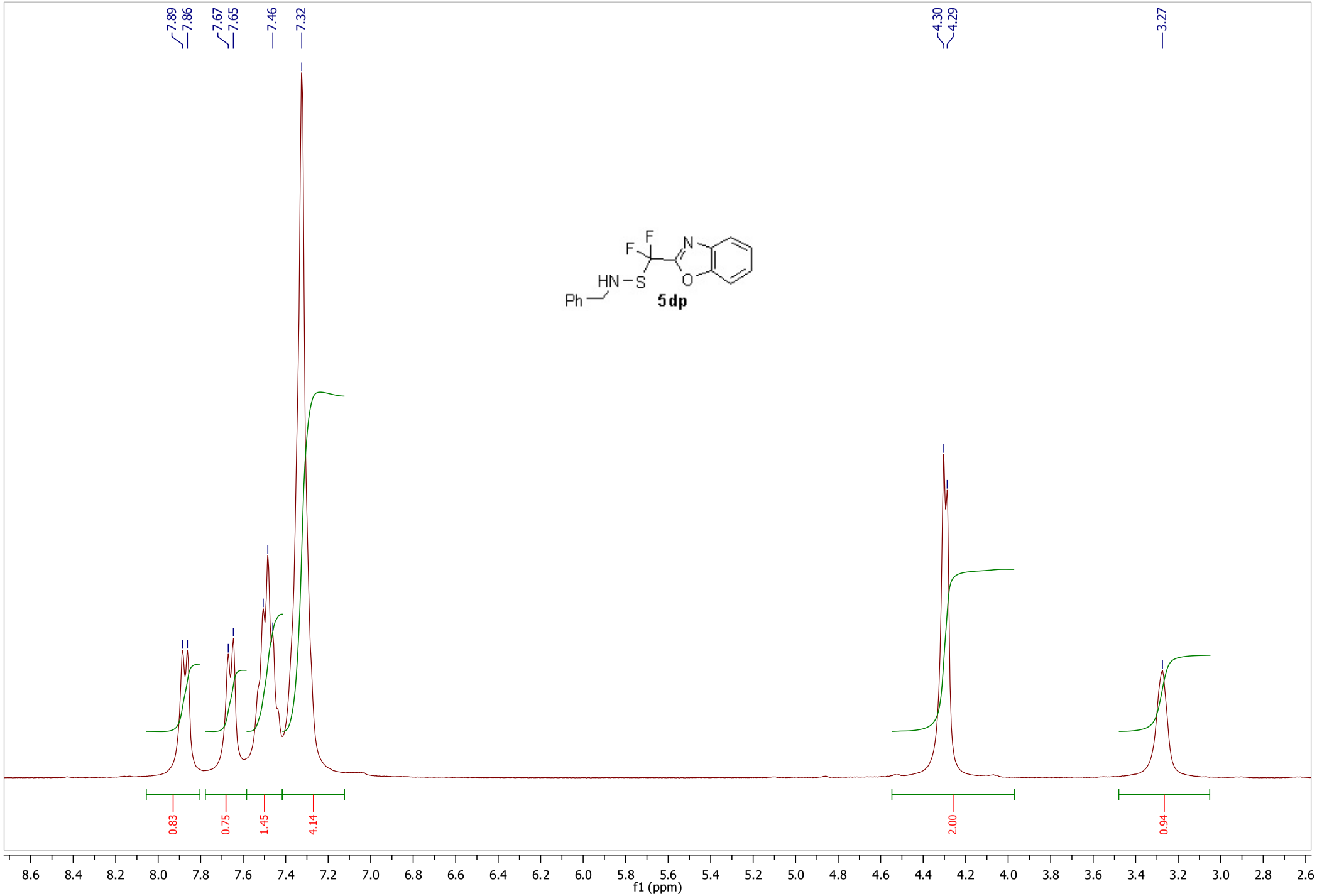

138.62
129.09
128.55
128.39
121.30
121.21
120.86
120.78
119.90
117.83
117.42
117.29
116.93
116.85
77.84
77.62
77.42
76.99
71.08
58.48
55.54
Ph
N
SCF2CF3
5bp
f1 (ppm)

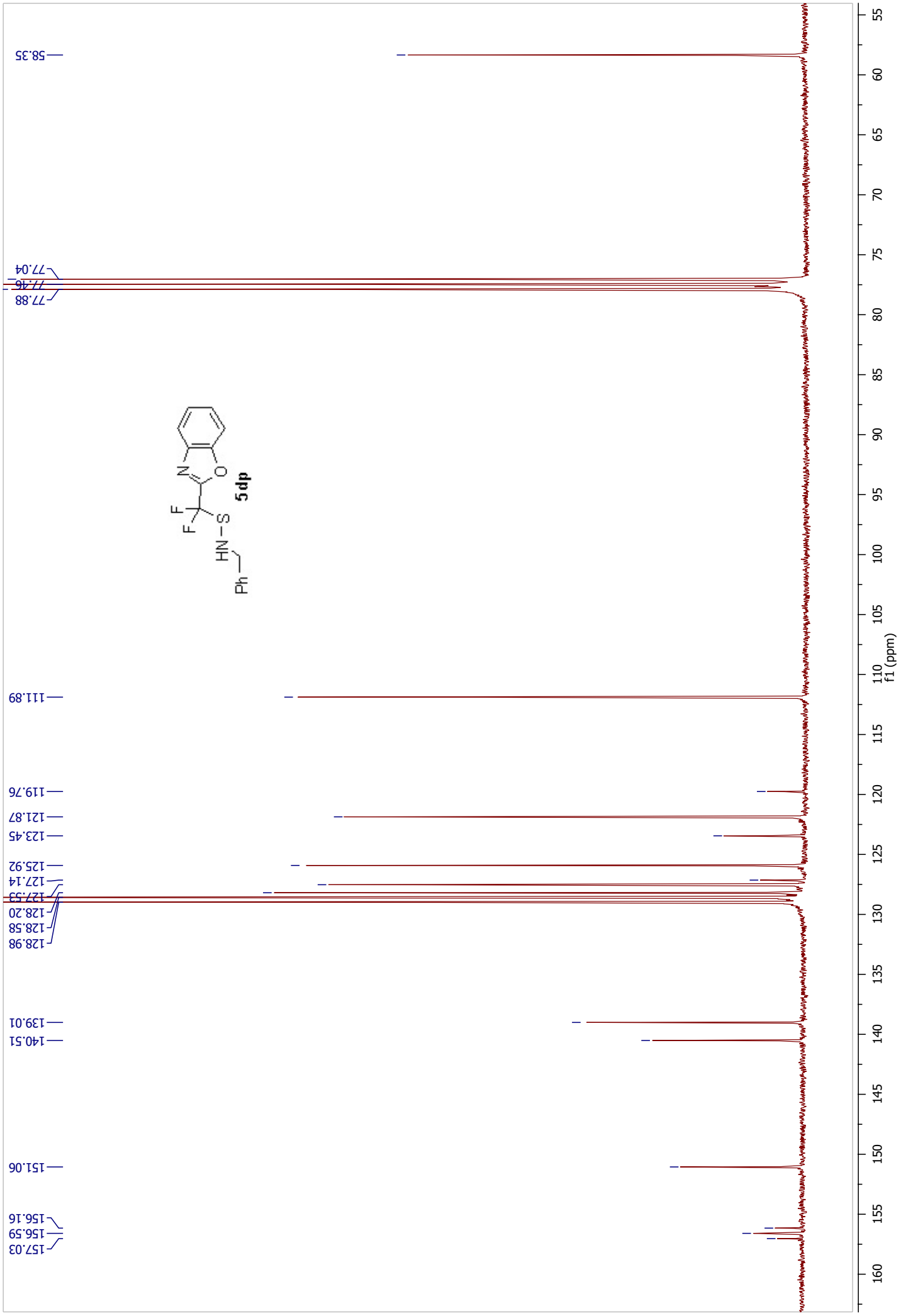

3.39
3.05
3.04
3.02
2.59
2.57
2.54
2.52
2.44
2.42
1.51
1.48
1.47
1.47
1.46
1.43
1.16
1.13
1.06
1.04
1.02
NEt2
HN
SCF2CF3
5br
0.95
1.04
3.82
1.75
4.10
2.93
6.00
f1 (ppm)


11.42
20.96
23.31
35.54
47.01
52.08
53.14
57.51
NEt2
HN
SCF2CF3
5br
f1 (ppm)


7.74
7.71
7.71
7.51
7.51
7.49
7.49
7.47
7.47
7.44
7.30
7.28
7.27
7.27
7.25
7.24
7.02
7.02
7.00
6.99
6.97
6.95
5.24
SCF2SPh
5ca
2.00
3.03
2.13
3.16
0.87
f1 (ppm)


77.97
77.55
77.13
115.42
121.75
127.26
127.29
127.31
129.56
129.68
129.95
130.77
134.18
136.90
138.42
146.36
5ca
f1 (ppm)


7.89
7.86
7.67
7.65
7.46
7.32
4.30
4.29
3.27
F
F
N
HN
S
O
Ph
5dp
0.83
0.75
1.45
4.14
2.00
0.94
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f1 (ppm)


58.35
77.04
77.46
77.88
111.89
119.76
121.87
123.45
125.92
127.14
127.53
128.20
128.58
128.98
139.01
140.51
151.06
156.16
156.59
157.03
5dp
F
F
S
HN
Ph
N
O
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
f1 (ppm)