An Aromatic Glaser-Hay Reaction

SUPPORTING INFORMATION

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Experimental Section

General considerations. Reactions were performed in 1-dram vials using polypropylene screw caps with 13 mm hole and white silicone septa with white teflon face (SUPELCO). Column chromatography was performed on 60Å silica gel (Sorbent Technologies). Purification by preparative HPLC was performed on a Shimadzu Prominence LC (LC-20AB) equipped with a SPD-20A UV-Vis detector and a Varian Dynamax (250 mm x 21.4 mm) column. GC-MS analyses were performed on a Shimadzu GCMS-QP5000 chromatograph equipped with a Restek column (Rtx-XLB, 30 m x 0.25 mm I.D.). The ^{1}H, ^{19}F and ^{13}C NMR were recorded on a JEOL ECX-400 spectrometer using residual solvent peak as a reference. Trifluorotoluene (neat, δ = -62.3 ppm) was employed as an external standard in ^{19}F NMR. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. IR spectra were obtained using ThermoNicolet Avatar 370 FT-IR instrument. Analytical thin layer chromatography was performed on silica gel IB-F (Baker-flex) by J. T. Baker.

Materials. The following starting materials were obtained from commercial sources and were used without further purification: thiazole, 2-chlorothiophene, 1,3-difluorobenzene, 2,3,5,6-tetrafluoroanisole, 2,4-difluoronitrobenzene, 2,2,6,6-tetramethylpiperidine, ethyl 3,4-difluorobenzoate, 2,3,5,6-tetrafluoroaniline and 3,5-difluorobenzonitrile were bought from Matrix Scientific. 1-Butylimidazole, 3,5-dichloropyridine, copper(II) chloride (99.999%) and isopropylmagnesium chloride-lithium chloride complex solution (1.3 M in THF) were purchased from Aldrich. Benzofuran was obtained from TCI. Copper(II) chloride (anhydrous), 2-methoxypyrazine, iodomethane, zinc chloride (anhydrous), and 1,2,4-triazole were from Alfa Aesar. 1-Butyl-1,2,4-triazole was made from 1,2,4-triazole.[1]

Base 1 (TMPMgCl*LiCl, 1.0 M):[2] A dry 50-mL Schlenk flask equipped with a magnetic stir bar was charged with *i*PrMgCl.LiCl (23 mL, 1.3 M in THF, 30 mmol) and dry THF (7 mL). TMPH (tetramethylpiperidine; 4650 mg, 33 mmol) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 24 hours followed by concentration under vacuum to 30 mL. All base preparations were performed under Ar.

Base 2 (TMPMgCl*LiCl (1.0 M) + 0.25 eq $ZnCl_2$): Inside the glove box, a dry 25-mL Schlenk flask equipped with a magnetic stir bar was charged with anhydrous $ZnCl_2$ (340 mg, 2.5 mmol). The flask was fitted with a septum and taken out of the glove box. Base 1 (10

mL, 10 mmol) was added dropwise at room temperature. The resulting mixture was stirred at room temperature for 5 hours.

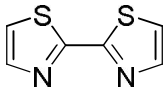
Base 3 (Cy_2NMgCl*LiCl (1.0 M) + 0.25 eq $ZnCl_2$): Inside the glove box, a dry 25-mL Schlenk flask equipped with a magnetic stir bar was charged with anhydrous $ZnCl_2$ (340 mg, 2.5 mmol). The flask was fitted with a septum and taken out of the glove box. The solution of Cy_2NMgCl.LiCl (1.0 M, 10 mL, 10 mmol, prepared by reacting Cy_2NH with *i*PrMgCl.LiCl following example with base 1) was added dropwise at room temperature. The resulting mixture was stirred at room temperature for 5 hours.

Base 4 [$(TMP)_2Zn$*2$MgCl_2$*2LiCl, 0.5 M]:[3] Inside the glove box, a dry 25-mL Schlenk flask equipped with a magnetic stir bar was charged with anhydrous $ZnCl_2$ (680 mg, 5.0 mmol). The flask was fitted with a septum and taken out of the glovebox. Base 1 (10 mL, 10 mmol) was added dropwise at room temperature. The resulting mixture was stirred at room temperature for 5 hours. Note that 1 equiv of this base is used to deprotonate 2 equiv of C-H.

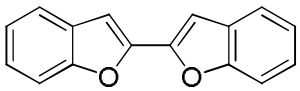
Combination of Base 1 and Base 4 allows for a relatively rapid deprotonation (provided by Base 1) and higher substrate stability (provided by base 4; enhanced functional group tolerance and phenol byproduct formation prevented). Mixing Base 1 and Base 4 in equimolar amounts affords base 2. If Base 1 is used for sensitive substrates, lower yields are obtained.

Preparation of 2,3,5,6-tetrafluoro-*N*,*N*-dimethylaniline: A dried 50 mL-Schlenk flask was charged with 2,3,5,6-tetrafluoroaniline (3.30 g, 20 mmol) and dry THF (20 mL). To this mixture was added dropwise BuLi (2.5 M in hexanes, 8 mL, 20 mmol) at -78 ^oC. The reaction was stirred for 10 minutes at the same temperature following by the addition of iodomethane (5.68 g, 40 mmol). The temperature was slowly raised to 0 ^oC with stirring in 1 hour. Solvents was then partially removed under reduced pressure to the volume of 10 mL. The reaction mixture was subjected to flash chromatography with hexanes as eluent to afford monomethylated product as a light tan oil. This compound was subjected to another methylation by following the same procedure to produce a light tan oil (3.50 g, 91% overall yield). This compound is known.[4] ^1H NMR (400 MHz, $CDCl_3$) δ 2.96 (t, J_{H-F} = 2.0 Hz, 6H), 2.63-2.67 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -151.6- -151.3 (m, 2F), -141.1- -140.8 (m, 2F).

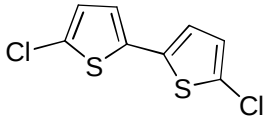
General dimerization procedure: A 1-dram vial equipped with a magnetic stir bar was charged with anhydrous copper(II) chloride (1-3 mol %) and substrate (1 mmol). The vial was flushed with argon and capped by a septum fitted cap. To this mixture was added through the septum via syringe the appropriate base solution (1.2-1.5 equiv). Dry oxygen was introduced to the reaction via needle. The vial was flushed by dry oxygen in 15 seconds then stirred under 1 atmosphere of oxygen for indicated time. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with brine (1 x 7 mL). The resulting aqueous phase was extracted by ethyl acetate (2 x 20 mL). Combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was dissolved in minimal amount of DCM and subjected to column chromatography on silica gel (hexanes followed by appropriate solvent to elute the products). After concentrating the fractions containing the product, the residue was dried under reduced pressure.



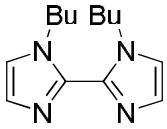
2,2'-Bithiazole (Entry 1, Table 1): Copper(II) chloride (1.4 mg, 0.01 mmol), thiazole (85 mg, 1.0 mmol), base 4 (1.2 mL, 0.6 mmol), rt, 30 minutes. After column chromatography (hexanes, then 1/9 followed by 1/3 ethyl acetate/hexanes) 60 mg (71%) of a yellow solid was obtained. R_f = 0.28 (SiO_2, 2/8 ethyl acetate/hexanes). This compound is known.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 3.2 Hz, 2H), 7.90 (d, *J* = 3.2 Hz, 2H).



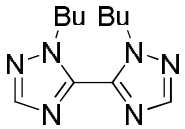
2,2'-Bibenzofuran (Entry 2, Table 1): Copper(II) chloride (1.4 mg, 0.01 mmol), benzofuran (118 mg, 1.0 mmol), base 1 (1.4 mL, 1.4 mmol), 50 ^oC, 1 hour. After column chromatography (hexanes, then 1/19 ethyl acetate/hexanes) and preparative HPLC (2% AcOEt in hexanes) 65 mg (56%) of a colorless solid was obtained. R_f = 0.26 (SiO_2, hexanes). This compound is known.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 0.9 Hz, 2H), 7.27 (dt, *J* = 7.6 Hz, 0.9 Hz, 2H), 7.34 (dt, *J* = 7.6 Hz, 1.8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.62-7.65 (m, 2H).



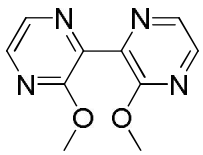
5,5'-Dichloro-2,2'-bithiophene (Entry 3, Table 1): Copper(II) chloride (1.4 mg, 0.01 mmol), 2-chlorothiophene (118.5 mg, 1.0 mmol), base 3 (1.3 mL, 1.3 mmol), rt, 2 hours. After column chromatography (hexanes) 87 mg (74%) of a yellow solid was obtained. R_f = 0.54 (SiO_2, hexanes). This compound is known.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 4.0 Hz, 2H), 6.86 (d, *J* = 4.0 Hz, 2H).



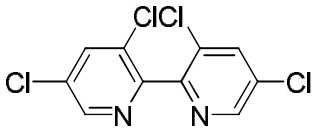
1,1'-Dibutyl-1H,1'H-2,2'-biimidazole (Entry 4, Table 1): Copper(II) chloride (2.7 mg, 0.02 mmol), 1-butylimidazole (124 mg, 1.0 mmol), base 1 (1.4 mL, 1.4 mmol), rt, 2 hours. After column chromatography (hexanes, then 1/4, 1/1 and 4/1 ethyl acetate/hexanes) 90 mg (73%) of a colorless oil was obtained. R_f = 0.19 (SiO_2, 5/5 ethyl acetate/hexanes). This compound is known.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.3 Hz, 6H; C**H$_3$** of butyl), 1.27 (sextet, *J* = 7.3 Hz, 4H; $NCH_2CH_2C\mathbf{H_2}CH_3$), 1.70 (quintet, *J* = 7.3 Hz, 4H; $NCH_2C\mathbf{H_2}CH_2CH_3$), 4.44 (t, *J* = 7.3 Hz, 4H; N-C**H$_2$**), 6.99 (d, *J* = 1.3 Hz, 2H), 7.10 (d, *J* = 1.3 Hz, 2H).



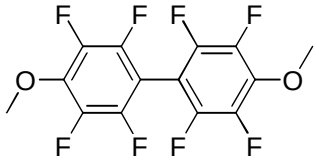
2,2'-Dibutyl-2H,2'H-3,3'-bi(1,2,4-triazole) (Entry 5, Table 1): Copper(II) chloride (1.4 mg, 0.01 mmol), 1-butyl-1,2,4-triazole (125 mg, 1.0 mmol), base 1 (1.2 mL, 1.2 mmol), rt, 1 hour. After column chromatography (CH_2Cl_2, then 1/9 followed by 1/4 ethyl acetate/CH_2Cl_2) 90 mg (73%) of a colorless oil was obtained. R_f = 0.63 (SiO_2, ethyl acetate). This compound is known.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 6H; C**H$_3$** of butyl), 1.34 (sextet, *J* = 7.3 Hz, 4H; $NCH_2CH_2C\mathbf{H_2}CH_3$), 1.88 (quintet, *J* = 7.3 Hz, 4H; $NCH_2C\mathbf{H_2}CH_2CH_3$), 4.74 (t, *J* = 7.3 Hz, 4H; N-C**H$_2$**), 8.00 (s, 2H; triazole C**H**).



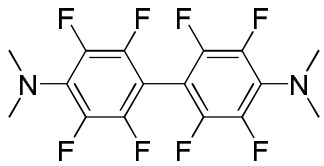
3,3'-Dimethoxy-2,2'-bipyrazine (Entry 6, Table 1): Copper(II) chloride (1.4 mg, 0.01 mmol), 2-methoxypyrazine (110 mg, 1.0 mmol), base 4 (0.5 mL, 0.25 mmol) + base 1 (0.8 mL, 0.8 mmol), rt, 1 hour. After column chromatography (hexanes, then 1/4, 1/1 and 3/1 ethyl acetate/hexanes) 55 mg (50%) of a light tan solid was obtained. R_f = 0.22 (SiO_2, 1/1 ethyl acetate/hexanes), mp 88.5-90.5 ^oC (from hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 6H; C**H**$_3$O), 8.21 (d, *J* = 2.8 Hz, 2H), 8.29 (d, *J* = 2.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.0 (**C**H_3), 136.4, 140.5, 141.3, 158.8. FT-IR (neat, cm^{-1}) υ 1532, 1462, 1396, 1369, 1312, 1299, 1162, 1094, 1024, 1005. Anal calcd for $C_{10}H_{10}N_4O_2$ (218.21 g/mol): C, 55.04; H, 4.62; N, 25.68; Found. C, 55.24; H, 4.71; N, 25.41.



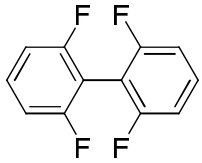
3,3',5,5'-Tetrachloro-2,2'-bipyridine (Entry 7, Table 1): Copper(II) chloride (4 mg, 0.03 mmol), 3,5-dichloropyridine (148 mg, 1.0 mmol), base 2 (1.5 mL, 1.5 mmol), rt, 2 hours. After column chromatography (hexanes, then 1/9 followed by 1/4 ethyl acetate/hexanes) 75 mg (51%) of a light tan solid was obtained. R_f = 0.47 (SiO_2, 2/8 ethyl acetate/hexanes). This compound is known.[10] ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.0 Hz, 2H), 8.60 (d, *J* = 2.0 Hz, 2H).



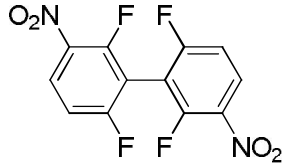
2,2',3,3',5,5',6,6'-Octafluoro-4,4'-dimethoxybiphenyl (Entry 8, Table 1) : Copper(II) chloride (1.4 mg, 0.01 mmol), 2,3,5,6-tetrafluoroanisole (180 mg, 1.0 mmol), base 3 (1.3 mL, 1.3 mmol), rt, 2.5 hours. After column chromatography (hexanes, then 1/9 ethyl acetate/hexanes) 163 mg (91%) of a colorless solid was obtained. R_f = 0.19 (SiO_2, hexanes). This compound is known.[11] ^1H NMR (400 MHz, $CDCl_3$) δ 4.17 (t, $J_{H\text{-}F}$ = 1.4 Hz, 6H; C**H**$_3$). ^{19}F NMR (376 MHz, $CDCl_3$) δ -157.3- -157.1 (m, 4F), -139.7- -139.5 (m, 4F).



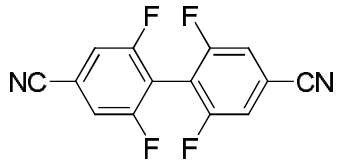
2,2',3,3',5,5',6,6'-Octafluoro-N4,N4,N4',N4'-tetramethylbiphenyl-4,4'-diamine (Entry 9, Table 1): Copper(II) chloride (1.4 mg, 0.01 mmol), 2,3,5,6-tetrafluoro-N,N-dimethylaniline (193 mg, 1.0 mmol), base 4 (1.4 mL, 1.4 mmol), rt, 1 hour. After column chromatography (hexanes, then 1/9 ethyl acetate/hexanes) 163 mg (85%) of a colorless solid was obtained. R_f = 0.11 (SiO_2, hexanes). This compound is known.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 (t, J_{H-F} = 2.3 Hz, 12H; C**H**$_3$). ^{19}F NMR (376 MHz, $CDCl_3$) δ -151.8- -151.5 (m, 4F), -141.2- -140.9 (m, 4F).



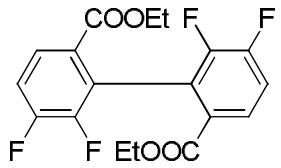
2,2',6,6'-Tetrafluorobiphenyl (Entry 10, Table 1): Copper(II) chloride (1.4 mg, 0.01 mmol), 1,3-difluorobenzene (114 mg, 1.0 mmol), base 2 (1.3 mL, 1.3 mmol), rt, 1 hour. After column chromatography (pentane) 80 mg (71%) of a light tan solid was obtained. R_f = 0.36 (SiO_2, hexanes). This compound is known.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96-7.08 (m, 4H), 7.35-7.45 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.5 (s, 4F).



2,2',6,6'-Tetrafluoro-3,3'-dinitrobiphenyl (Entry 11, Table 1): Copper(II) chloride (2.7 mg, 0.02 mmol), 2,4-difluoronitrobenzene (159 mg, 1.0 mmol), base 4 (1.3 mL, 0.65 mmol), 0 ^{o}C, 1 hour. Note: bases should be cooled to 0 °C before addition to substrate. After column chromatography (hexanes, then 1/9 followed by 1/3 ethyl acetate/hexanes) 110 mg (70%) of a light brown solid was obtained. R_f = 0.28 (SiO_2, 2/8 ethyl acetate/hexanes). This compound is known.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.32 (m, 2H), 8.29-8.40 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.8- -110.6 (m, 2F), -97.2- -96.9 (m, 2F).



2,2',6,6'-Tetrafluorobiphenyl-4,4'-dicarbonitrile (Entry 12, Table 1): Copper(II) chloride (1.4 mg, 0.01 mmol), 3,5-difluorobenzonitrile (139 mg, 1.0 mmol), base 4 (1.3 mL, 0.65 mmol), rt, 1 hour. After column chromatography (hexanes, then 1/9 followed by 1/4 ethyl acetate/hexanes) 105 mg (76%) of a colorless solid was obtained. R_f = 0.4 (SiO_2, 2/8 ethyl acetate/hexanes), mp 215-217 ^oC (from 1/1 ethyl acetate/hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.42 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.2 (s, 4F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.7 (t, J_{C-F} = 3.6 Hz; 2 C that link aryl groups), 115.6-116.3 (m, 8C), 160.2 (dt, J_{C-F} = 256 Hz, 3.3 Hz; 4 C directly attached to F). FT-IR (neat, cm^{-1}) υ 2240, 1624, 1557, 1421, 1326, 1206, 1049, 1031. Anal calcd for $C_{14}H_4F_4N_2$ (276.19 g/mol): C, 60.88; H, 1.46; N, 10.14; Found. C, 60.83; H, 1.32; N, 9.94.



Diethyl 5,5',6,6'-tetrafluorobiphenyl-2,2'-dicarboxylate (Entry 13, Table 1) : Copper(II) chloride (1.4 mg, 0.01 mmol), ethyl 3,4-difluorobenzoate (186 mg, 1.0 mmol), base 4 (1.0 mL, 0.5 mmol) + base 1 (0.4 mL, 0.4 mmol), 0 ^oC, 2 hours. Note: bases should be cooled to 0 °C before addition to substrate. After column chromatography (hexanes, then 1/9 followed by 1/4 ethyl acetate/hexanes) 130 mg (70%) of a colorless solid was obtained. R_f = 0.35 (SiO_2, 2/8 ethyl acetate/hexanes), mp 53.5-55.0 ^oC (from 1/1 ethyl acetate/hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, J = 7.3 Hz, 6H; C**H$_3$**), 4.11 (q, J = 7.3 Hz, 4H; C**H$_2$**), 7.31 (dt, J = 7.6 Hz, 9.0 Hz, 2H; H-4,4'), 7.95 (ddd, J = 9.0 Hz, 5.0 Hz, 1.5 Hz, 2H; H-3,3'). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.2 - -136.1 (m, 2F), -130.4- -130.3 (m, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 61.3, 116.9 (d, J_{C-F} = 17.0 Hz), 125.6 (d, J_{C-F} = 14.0 Hz), 126.7 (d, J_{C-F} = 2.8 Hz), 127.1 (dd, J_{C-F} = 7.6 Hz, 3.8 Hz), 147.8 (dd, J_{C-F} = 246.0 Hz, 13.3 Hz), 152.9 (dd, J_{C-F} = 255.0 Hz, 13.3 Hz), 164.6. FT-IR (neat, cm^{-1}) υ 1714, 1476, 1428, 1369, 1282, 1203, 1153, 1135, 1036. Anal calcd for $C_{18}H_{14}F_4O_4$ (370.29 g/mol): C, 58.38; H, 3.81; Found. C, 58.63; H, 3.78.

Control reactions

- Using normal $CuCl_2$ (reagent grade, from Alfa Aesar, anhydrous, 98%) : Copper(II) chloride (1.4 mg, 0.01 mmol), 1-butyl-1,2,4-triazole (125 mg, 1.0 mmol), base 1 (1.2 mL, 1.2 mmol), rt, 1 hour. After column chromatography (CH_2Cl_2, then 1/9 followed by 1/4 ethyl acetate/CH_2Cl_2) 90 mg (73%) of homocoupling product was obtained.

- Using ultra pure $CuCl_2$ (from Aldrich, anhydrous, 99.999%) : Copper(II) chloride (1.4 mg, 0.01 mmol), 1-butyl-1,2,4-triazole (125 mg, 1.0 mmol), base 1 (1.2 mL, 1.2 mmol), rt, 1 hour. After column chromatography (CH_2Cl_2, then 1/9 followed by 1/4 ethyl acetate/CH_2Cl_2) 95 mg (77%) of homocoupling product was obtained.

- Without $CuCl_2$ catalyst : 1-Butyl-1,2,4-triazole (125mg, 1.0 mmol), base 1 (1.2 mL, 1.2 mmol), rt, 1 hour. No product was detected (by GCMS).

Using *t*BuOLi base : Outside the glovebox a 1-dram vial equipped with a magnetic stir bar was charged with anhydrous copper(II) chloride (6.7 mg, 0.05 mmol), 2,3,5,6-tetrafluoroanisole (180 mg, 1.0 mmol) and DMF (0.7 mL). The vial was flushed with argon and capped by a septum fitted cap and placed inside a glovebox. To this mixture was added *t*BuOLi (160 mg, 2.0 mmol). The capped vial was taken out of the glovebox, flushed by dry oxygen for 15 seconds and then stirred at room temperature under oxygen for 2 hours. To the reaction mixture was added trifluoroacetic acid (228 mg, 2.0 mmol) and ethyl acetate (1.0 mL). The mixture was subjected to flash chromatography on silica gel. After column chromatography (hexanes, then 15% ethyl acetate in hexanes) 100 mg (56%) of 2,2',3,3',5,5',6,6'-octafluoro-4,4'-dimethoxybiphenyl and 75 mg (38%) of 2,3,5,6-tetrafluoro-4-methoxyphenol were obtained.

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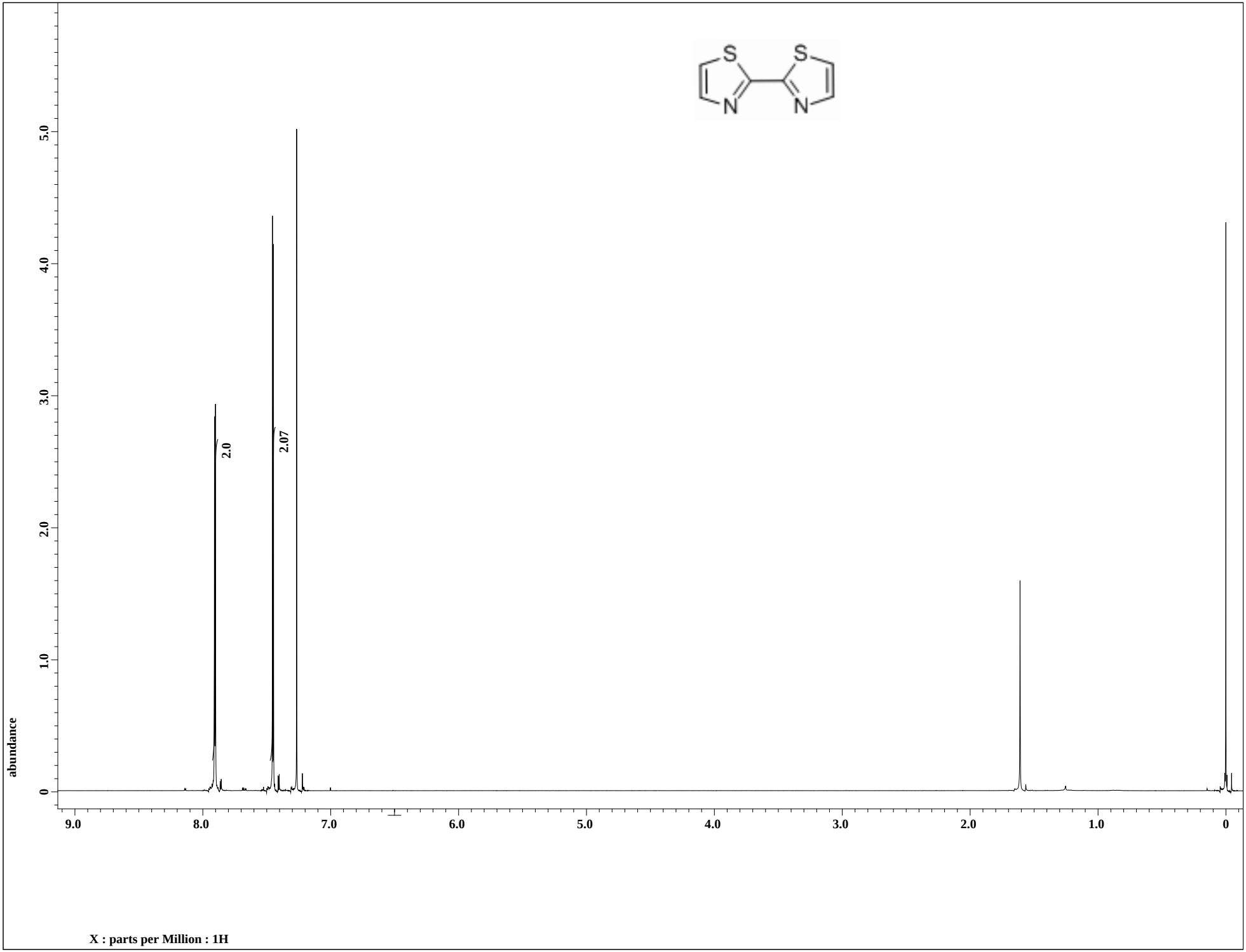
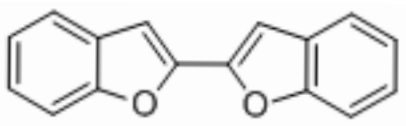
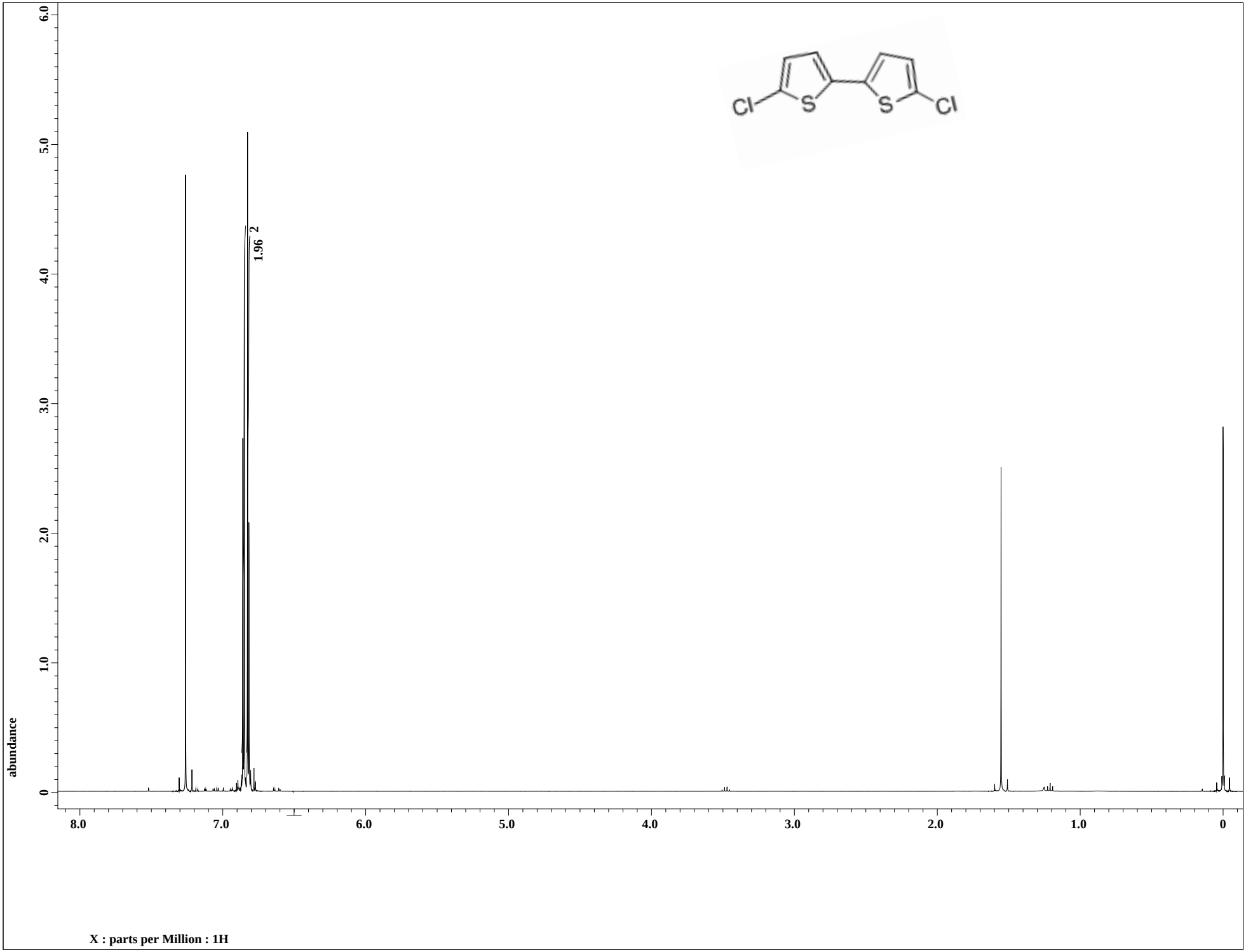
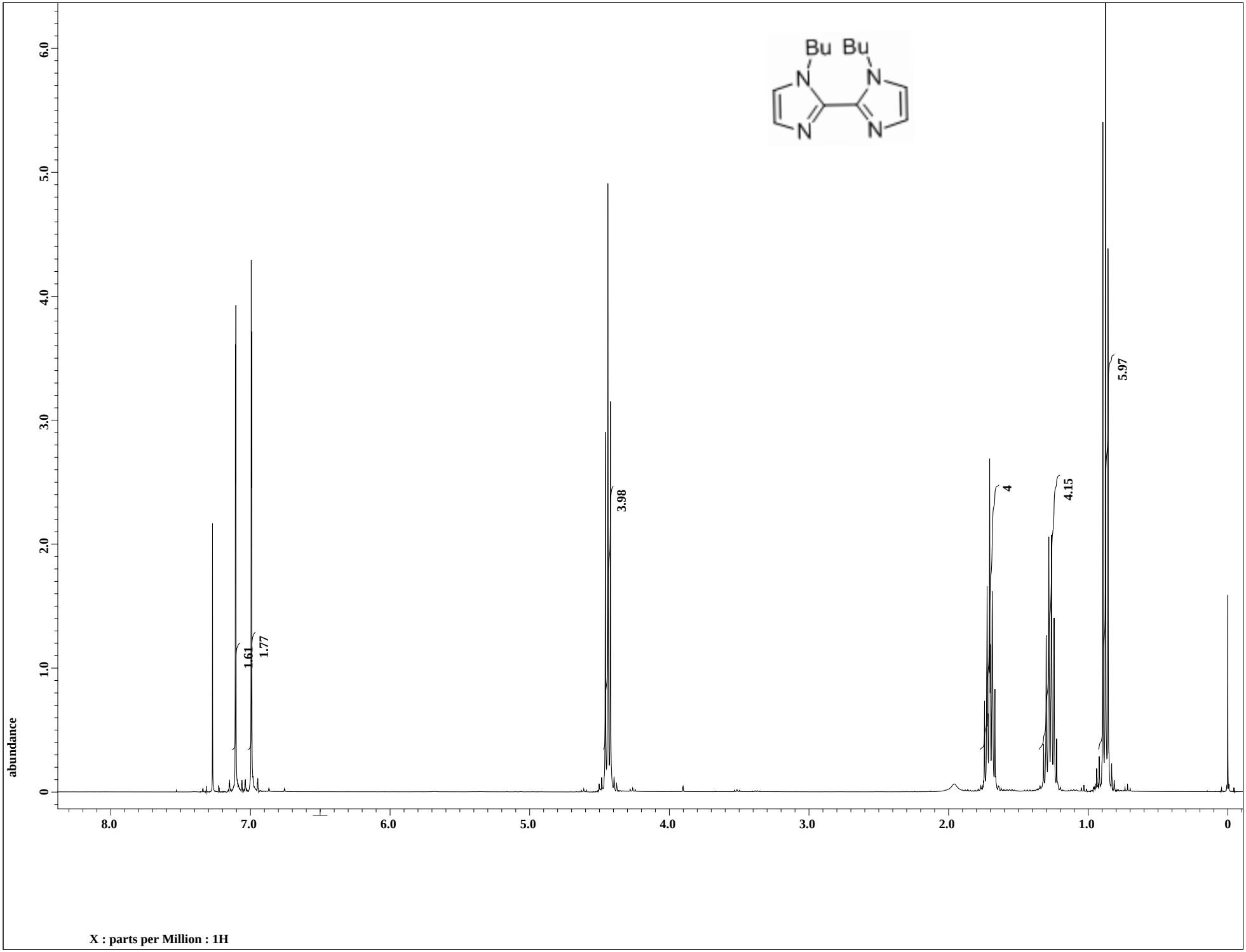
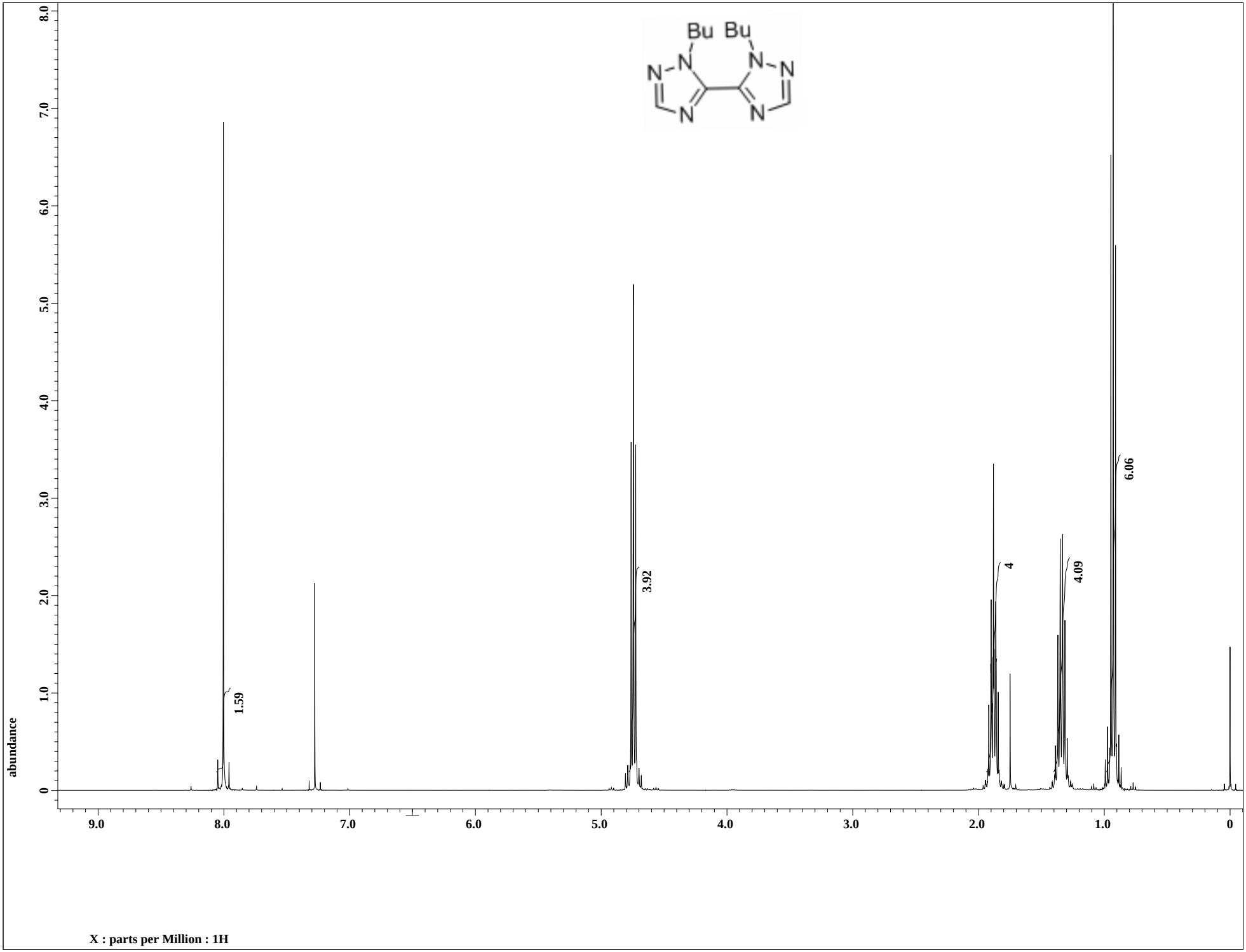

S
S
N
N
5.0
4.0
3.0
2.0
1.0
0
abundance
2.0
2.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

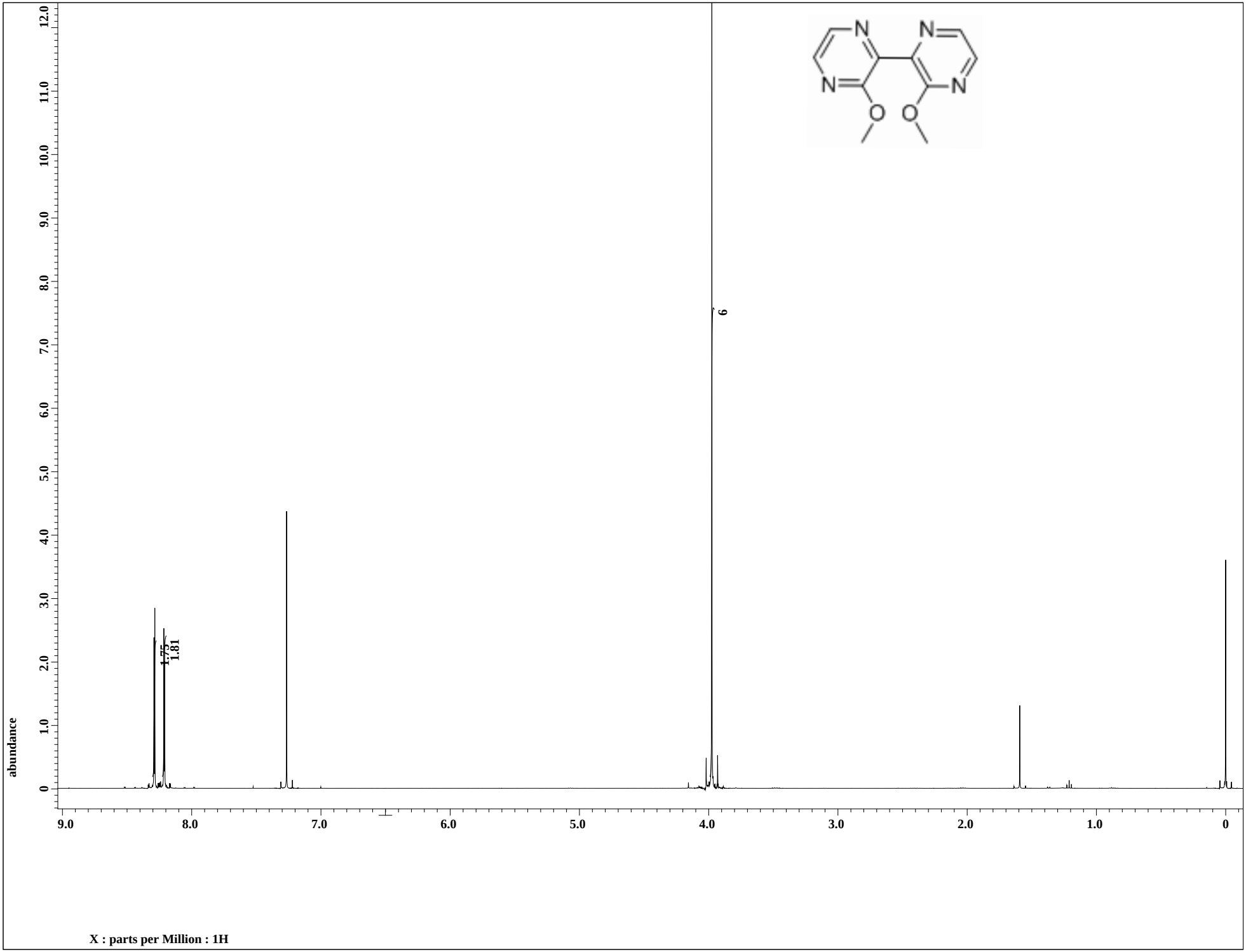


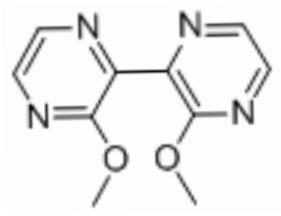
abundance
3.0
2.0
1.0
0
2
1.99
2.16
3.71
1.82
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


Cl
S
S
Cl
1.96
2
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


Bu Bu
N N
N N
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
1.61
1.77
3.98
4
4.15
5.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


Bu Bu
N
N
N
N
N
N
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
1.59
3.92
4
4.09
6.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.75
1.81
9
N
N
N
N
O
O
X : parts per Million : 1H

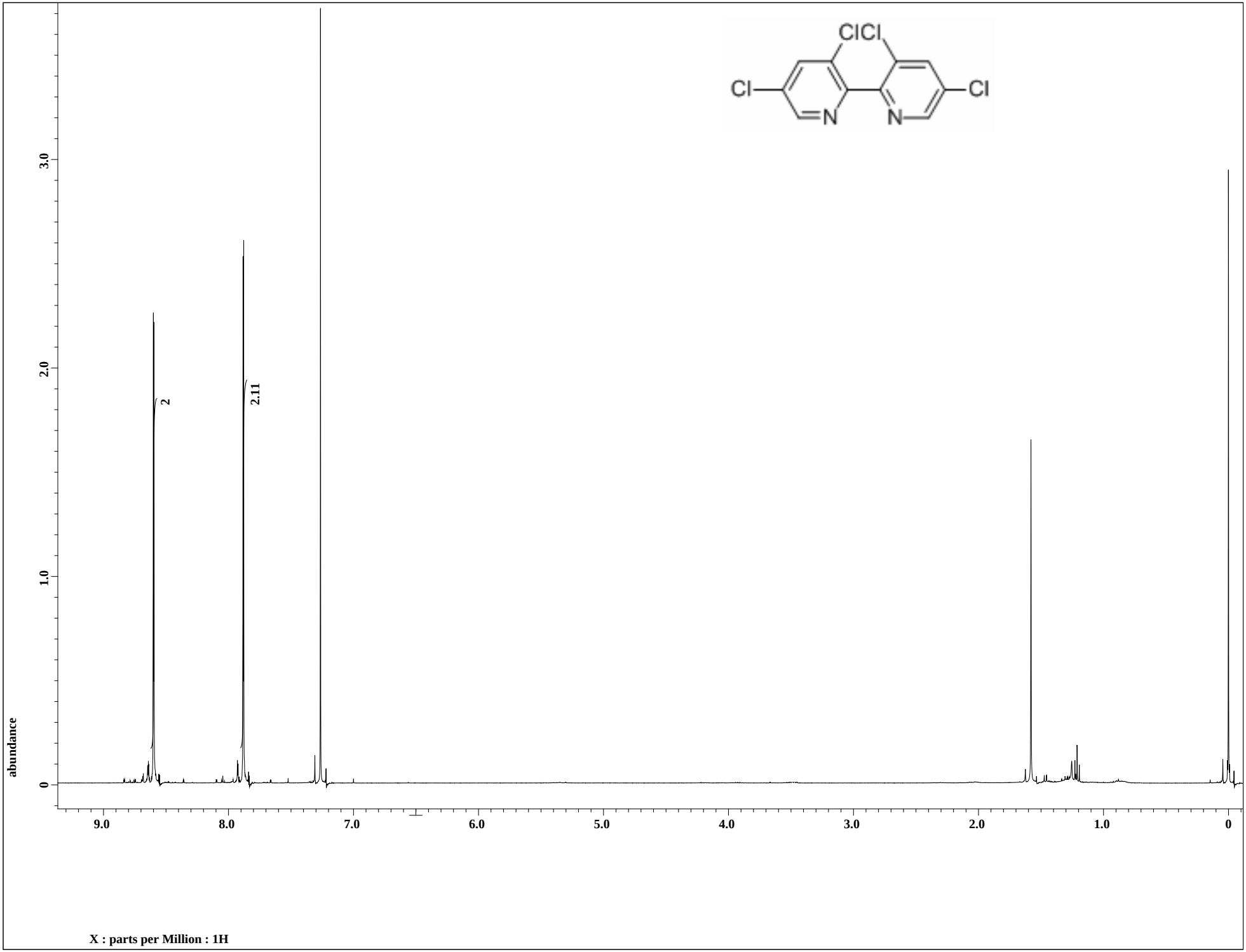


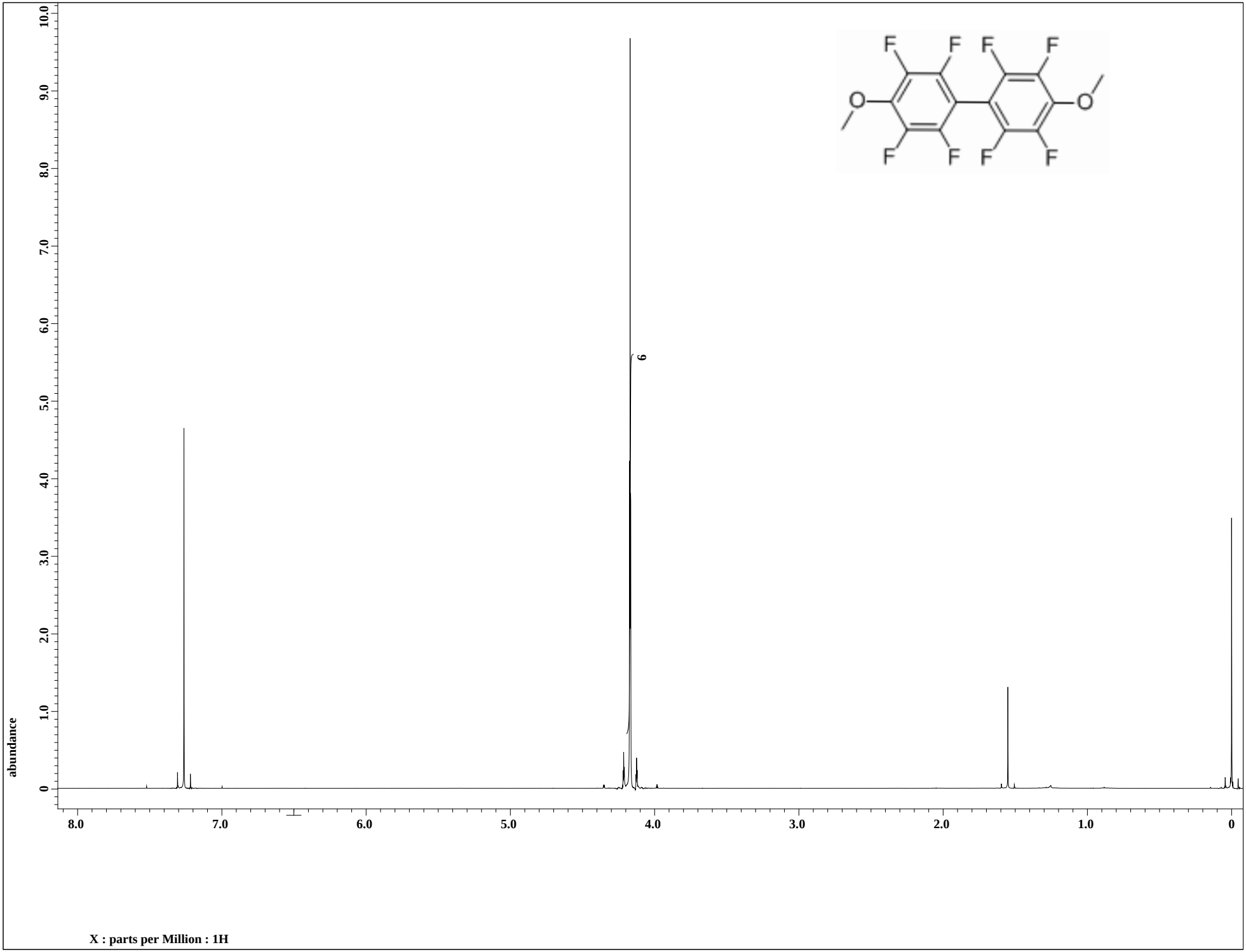
abundance

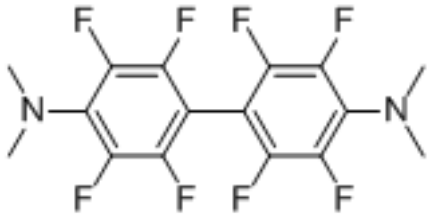
0 0.1 0.2 0.3 0.4 0.5

170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

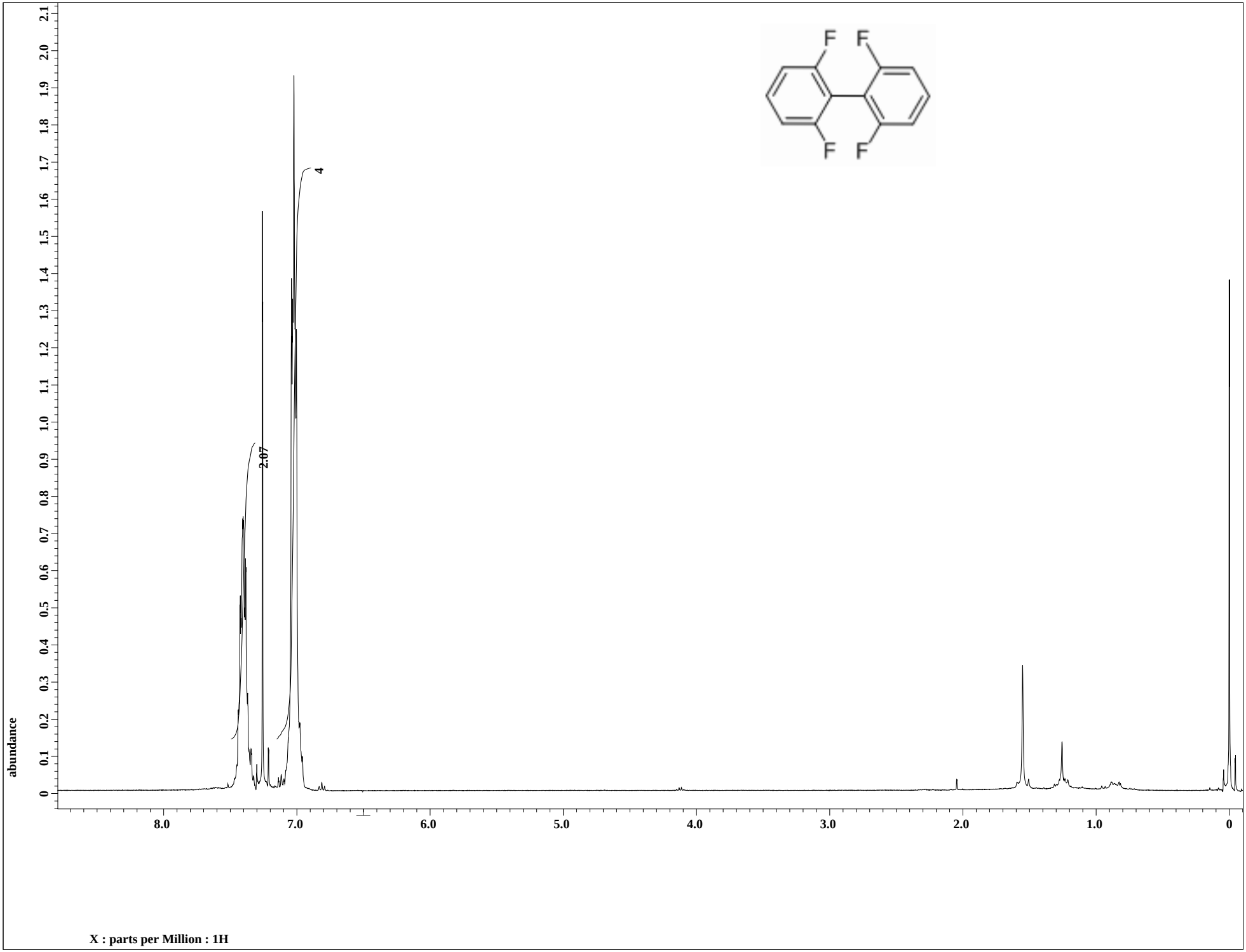
X : parts per Million : 13C

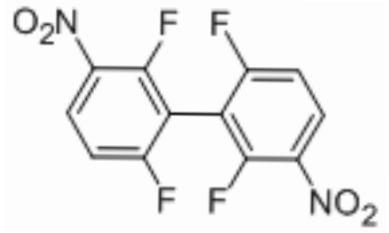

ClCl
Cl
Cl
N
N
2
2.11
abundance
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


F
F
F
F
O
O
F
F
F
F
6
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


F
F
F
F
N
N
F
F
F
F

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


F
F
F
F
4
2.07
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H



abundance

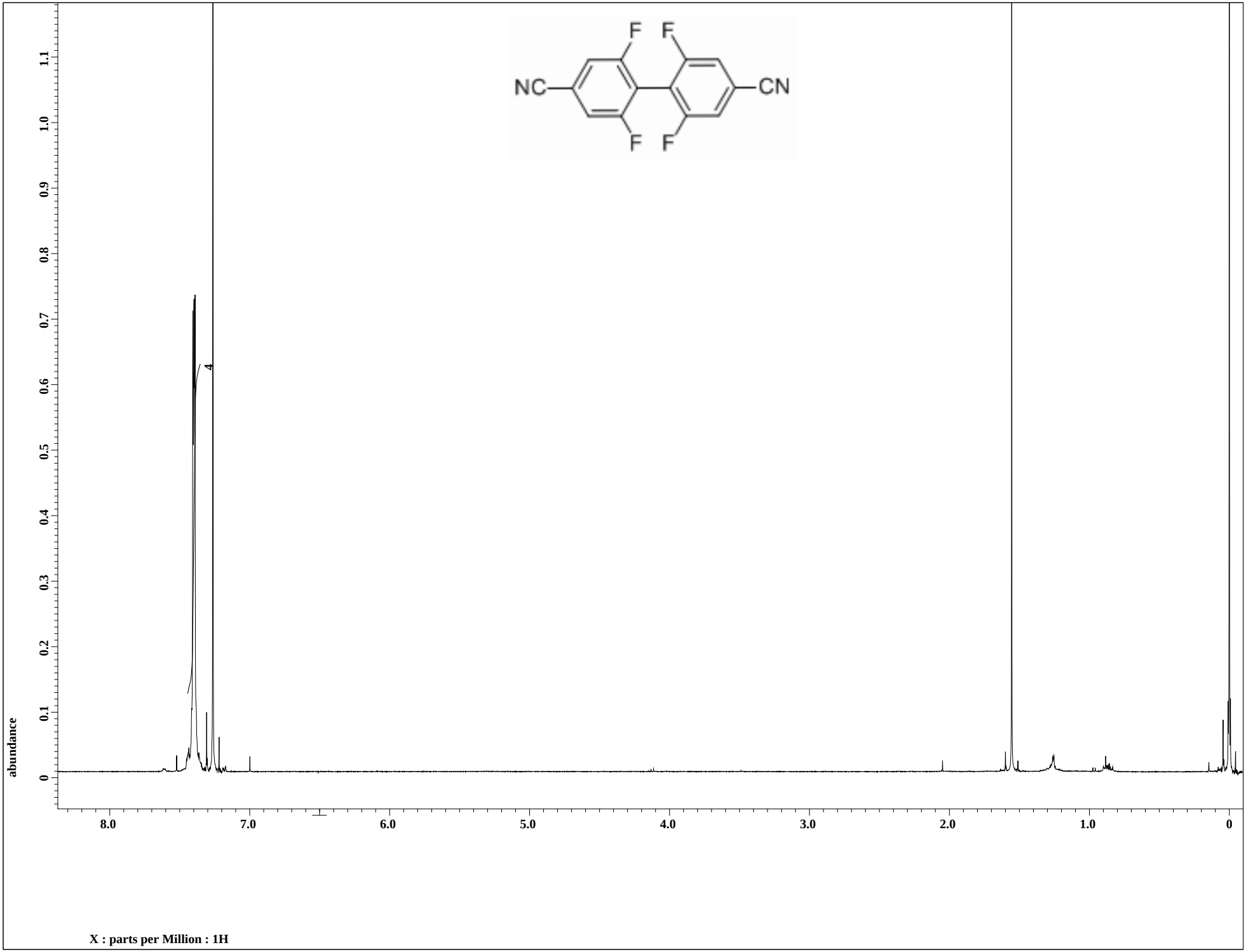
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8

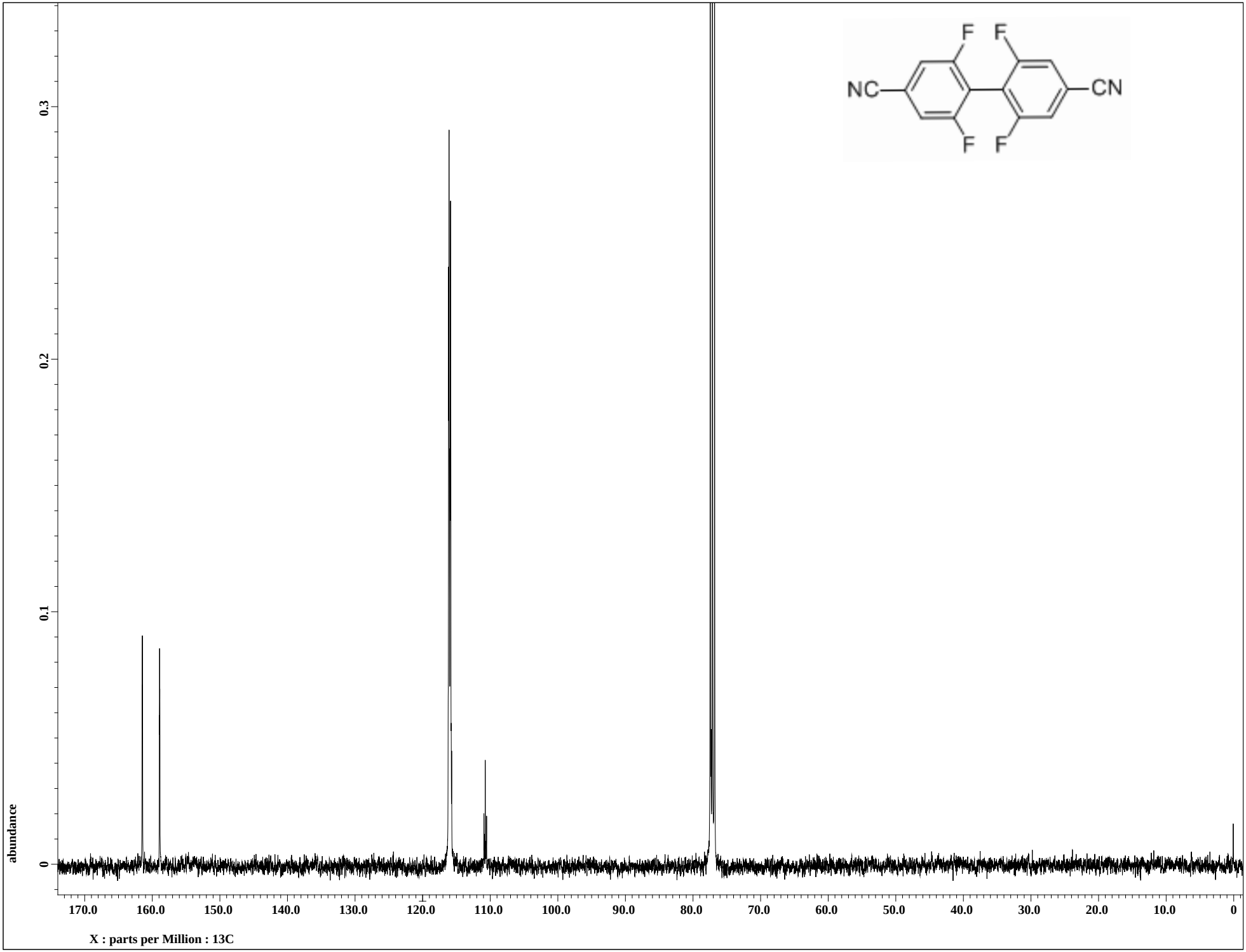
2

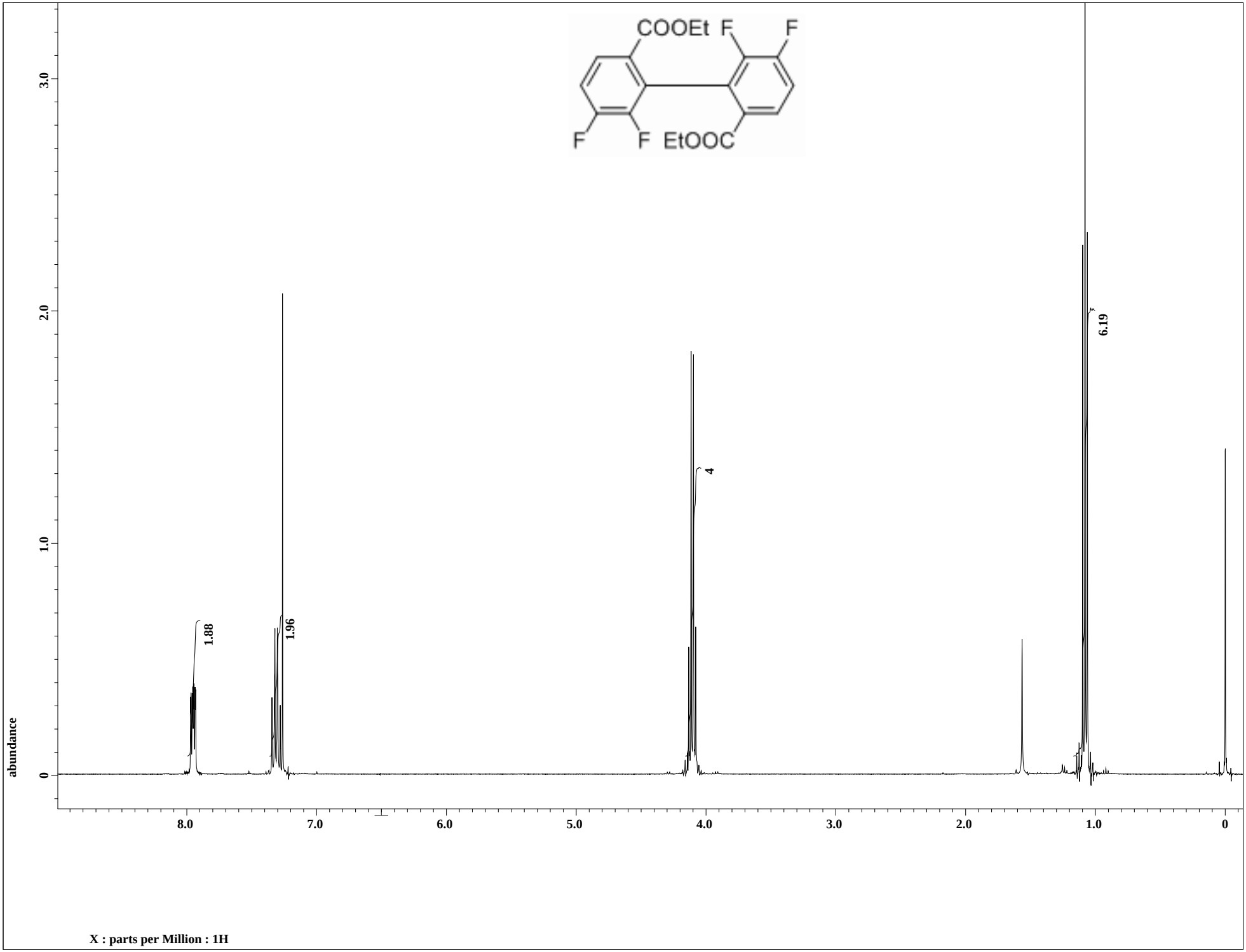
4.27

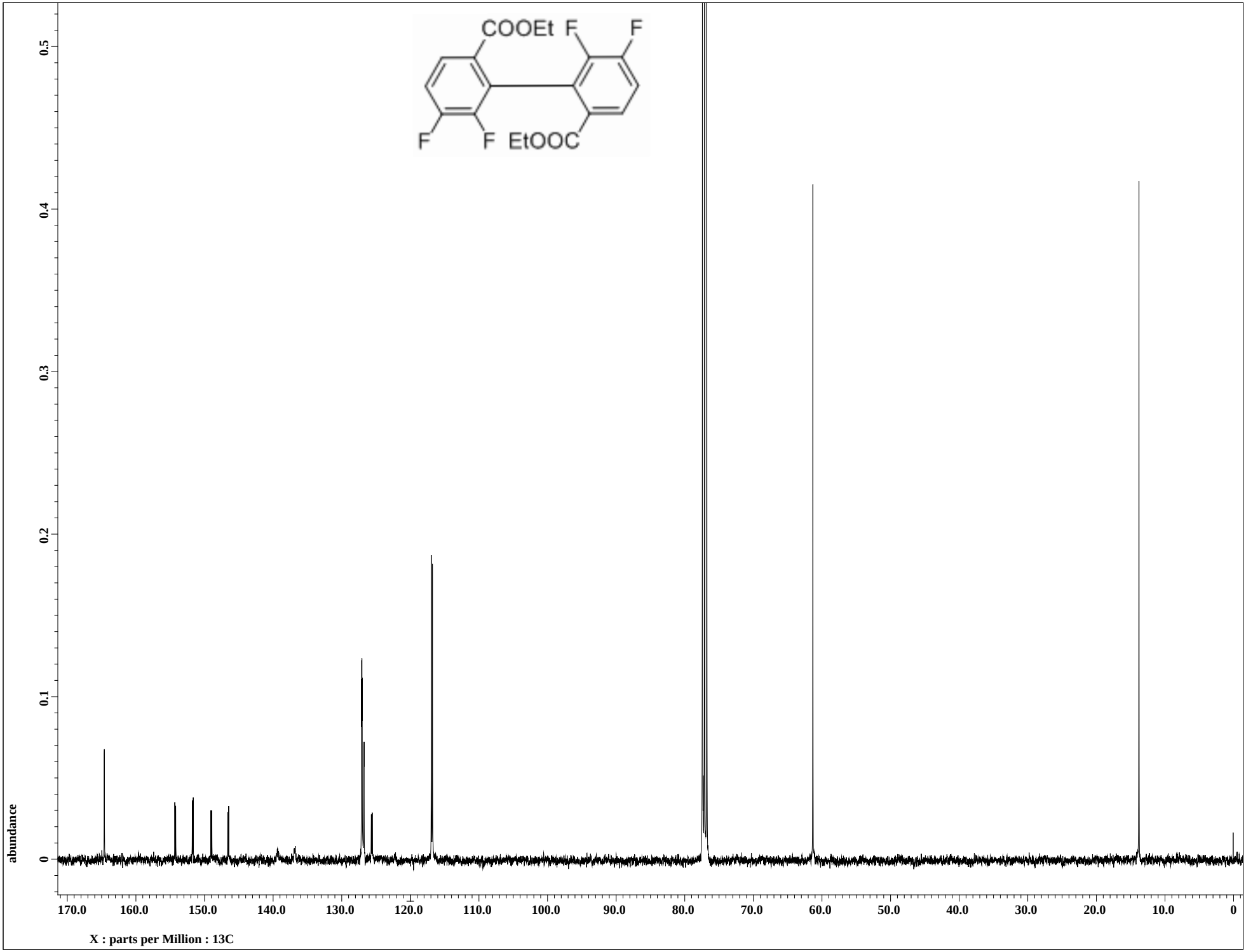
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

X : parts per Million : 1H


F
F
NC
CN
F
F
4
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


F
F
NC
CN
F
F
0.3
0.2
0.1
0
abundance
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C


COOEt F F
F F EtOOC
3.0
2.0
1.0
0
abundance
1.88
1.96
4
6.19
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


COOEt F F
F F EtOOC
abundance
0
0.1
0.2
0.3
0.4
0.5
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C