Supporting Information

Palladium and Nickel-Catalyzed Decarbonylative C–S Coupling to Convert Thioesters to Thioethers

Naoko Ichiishi, Christian A. Malapit, Łukasz Woźniak, Melanie S. Sanford*
Department of Chemistry, University of Michigan
930 North University Avenue, Ann Arbor, Michigan 48109 United States

*Email: mssanfor@umich.edu

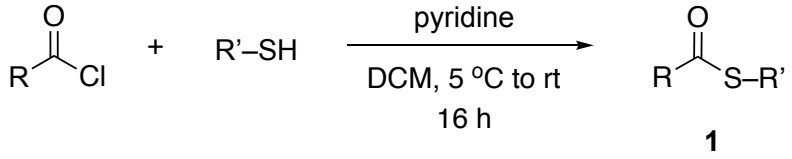
Table of Contents

I. Instrumental Information. NMR spectra were obtained on a Varian MR400 (400.52 MHz for ^{1}H; 100.71 MHz for ^{13}C; 376.87 MHz for ^{19}F), a Varian vnmrs 500 (500.10 MHz for ^{1}H), or a Varian vnmrs 700 (699.76 MHz for ^{1}H; 175.95 MHz for ^{13}C) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) with the residual solvent peak ($CHCl_3$, 7.26 ppm for ^{1}H NMR and 77.23 for ^{13}C NMR) as an internal reference. Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). High resolution mass spectra were recorded on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer. Gas chromatography was carried out on a Shimadzu 17A GC using a Restek Rtx®-5 (Crossbond 5% diphenyl – 95% dimethyl polysiloxane; 15 m, 0.25 mm ID, 0.25 μm df) column.

II. Materials and Methods. Catalysts $Pd[P(o\text{-}tol_3)]_2$ and $Ni(cod)_2$ were obtained from Alfa Aesar and Strem, respectively. Phosphine ligands, $P(Ad)_2Bn$ and PCy_3 were obtained from Aldrich. All commercially available acid chlorides were purchased from commercial sources and were used as received. Non-commercial acid chlorides were synthesized according to the literature procedure.[1-2] *p*-Xylene was refluxed with P_2O_5 overnight, fractionally distilled, and stored over 4Å MS. All reactions were conducted under a nitrogen/argon atmosphere or using standard Schlenk techniques unless otherwise stated. All reactions conducted at elevated temperatures were heated on a hot plate using an aluminum block.

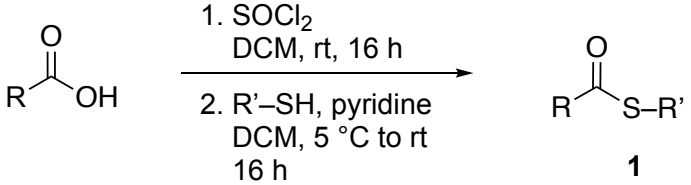
III. General Procedure for Synthesis of Thioesters

From commercially available acid chlorides:



1

From carboxylic acids:

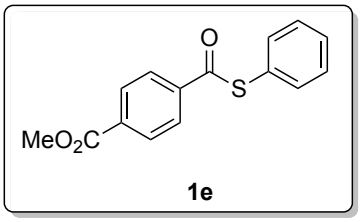


1

A reaction flask was equipped with a magnetic stir bar and a rubber septum, and then was evacuated and back-filled with N_2 three times. Thiol (1.0 equiv) and pyridine (1.0 equiv) were added and then dissolved in methylene chloride (0.1 M), and this solution cooled to 5 ºC. The acyl chloride (1.0 equiv) was added by syringe over 5 min. The resulting suspension was stirred at 5 ºC for an additional 5 min, and then stirred at room temperature overnight. The progress of the reaction was monitored by TLC. The reaction was quenched by pouring over ice water (twice the volume of the solvent). The aqueous phase was separated and extracted with methylene chloride (twice the volume of the reaction solvent x 2), and the combined organic extracts were dried over Na_2SO_4 and concentrated. The crude mixture was purified by flash column chromatography on silica gel to afford the desired thioesters. Non-commercial acid chlorides were prepared from the reaction of the corresponding carboxylic acid with thionyl chloride (1.5 to 2.0 equiv) in the presence of catalytic DMF (5 mol %) in methylene chloride (0.2 M) at room temperature.[1-2] Evaporation of solvent and unreacted thionyl chloride afforded the crude acid chlorides, which were used for thioester synthesis without further purification.

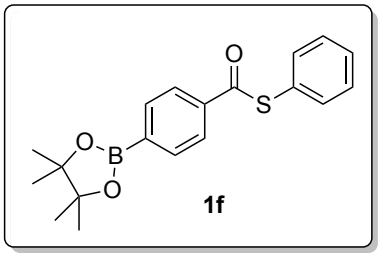
Previously known and reported thioester substrates; *S*-phenyl benzothioate (**1a),**[3] *S*-phenyl 4-methylbenzothioate (**1b**),[3] *S*-phenyl 4-methoxybenzothioate (**1c**),[3] *S*-phenyl 4-(trifluoromethyl)benzothioate (**1d**),[3] *S*-phenyl 2-methylbenzothioate (**1g**),[3] *S*-phenyl naphthalene-1-carbothioate (**1h**),[3] *S*-(4-methoxyphenyl) benzothioate (**1i**),[4] *S*-(4-fluorophenyl) benzothioate (**1j**),[4] *S*-(4-(trifluoromethyl)phenyl) benzothioate (**1k**),[5] *S*-(pyridin-4-yl) benzothioate (**1l**),[6] *S*-phenyl thiophene-2-carbothioate (**1m**),[3] *S*-phenyl

pyridine-3-carbothioate (**1n**),[7] *S*-phenyl (*E*)-3-phenylprop-2-enethioate (**1p**),[8] *S*-phenyl 2-phenylethanethioate (**1q**),[9] *S*-benzyl benzothioate (**1s**),[10] and *S*-ethyl 2-phenylethanethioate (**1t**)[11] were prepared according to the general procedure using commercially available acid chlorides and thiols. ^{1}H and ^{13}C NMR specta are attached in SI Section VI and data matched those reported in the literature.[3-11]



1e

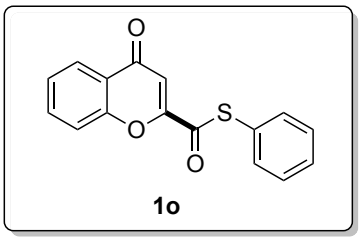
Methyl 4-((phenylthio)carbonyl)benzoate (1e). General procedure was followed using 4-(methoxycarbonyl)benzoic acid (2.0 mmol). Compound **1e** was obtained as a white solid in 75% yield: **mp** 146–148 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H), 7.53 (m, 2H), 7.50–7.44 (multiple peaks, 3H), 3.97 (s, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 189.9, 166.3, 140.2, 135.2, 134.6, 130.2, 130.0, 129.6, 127.6, 127.0, 52.8; **HRMS** ESI calcd for $C_{15}H_{13}O_3S$ $[M+H]^+$ *m*/*z* 273.0585, found 273.0590.



1f

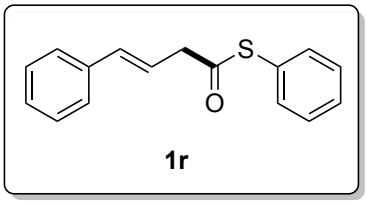
***S*-Phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzothioate (1f).** General procedure was followed using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (2.0 mmol). Compound **1f** was obtained as a white solid in 72% yield: **mp** 93–94 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.54–7.50 (m, 2H), 7.48–7.45 (multiple peaks, 3H), 1.37 (s, 12H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 190.6, 138.8, 135.3, 135.3, 129.8, 129.5, 127.5, 126.7, 84.5, 25.1 (the carbon directly

attached to the boron atom was not detected, likely due to quadropolar relaxation); **HRMS** ESI calcd for $C_{19}H_{22}BO_3S$ $[M+H]^+$ *m*/*z* 341.1383, found 341.1389.



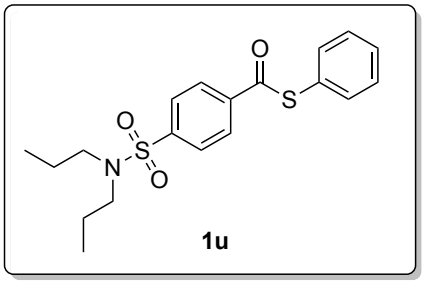
1o

***S*-Phenyl 4-oxo-4*H*-chromene-2-carbothioate (1o).** General procedure was followed using 4-oxo-4*H*-chromene-2-carboxylic acid (2.0 mmol). Compound **1o** was obtained in 45% yield as a white solid: **mp** 152–154 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.79 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.64 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.55-7.46 (multiple peaks, 6H), 7.02 (s, 1H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 185.7, 178.2, 156, 155.7, 135.1, 135.0, 130.5, 129.8, 126.4, 126.2, 125.3, 124.9, 118.8, 110.7; **HRMS** ESI calcd for $C_{16}H_{11}O_3S$ $[M+H]^+$ *m*/*z* 283.0429, found 283.0426.



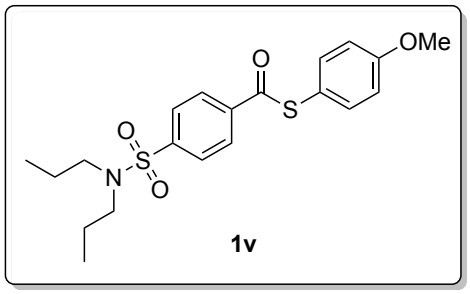
1r

***S*-phenyl (*E*)-4-phenylbut-3-enethioate (1r).** General procedure was followed using *(E)*-4-phenyl-3-butenoyl chloride (900 mg, 5.0 mmol). Purification by flash chromatography afforded the compound as a yellow oil (260 mg, 25% yield):[12] **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.44-7.40 (multiple peaks, 7H), 7.33 (t, *J* = 7 Hz, 2H), 7.26 (s, 1H), 6.60 (d, *J* = 7 Hz, 1H), 6.33 (dt, *J* = 18, 7 Hz, 1H), 3.55 (d, *J* = 7 Hz, 2H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 195.5, 136.6, 135.1, 134.5, 129.4, 129.2, 128.6, 127.8, 127.7, 126.4, 120.7, 47.5; **HRMS** ESI calcd for $C_{16}H_{15}OS$ $[M+H]^+$ *m/z* 255.0844, found 255.0847.



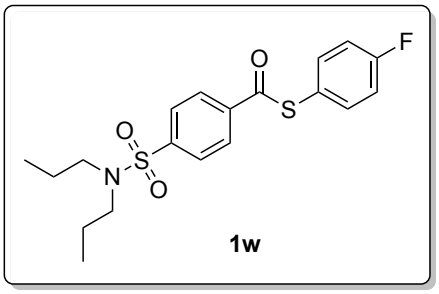
1u

***S*-Phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzothioate (1u).** General procedure was followed using probenecid (2.0 mmol). Compound **1u** was obtained in 85% yield as a white solid: **mp** 93–94 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.53–7.50 (m, 2H), 7.49-7.45 (multiple peaks, 3H), 3.12–3.10 (m, 4H), 1.56 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 189.4, 144.9, 139.6, 135.2, 130.1, 129.6, 128.2, 127.6, 126.7, 50.2, 22.2, 11.4; **HRMS** ESI calcd for $C_{19}H_{24}NO_3S_2$ $[M+H]^+$ *m/z* 378.1198, found 378.1199.



1v

***S*-(4-Methoxyphenyl) 4-(*N*,*N*-dipropylsulfamoyl)benzothioate (1v).** General procedure was followed using probenecid (2.0 mmol). Compound **1v** was obtained in 92% yield as a white solid: **mp** 88–89 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 3.18–2.95 (m, 4H), 1.56 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 190.38, 161.24, 144.82, 139.61, 136.71, 128.21, 127.55, 117.13, 115.33, 55.62, 50.17, 22.17, 11.4; **HRMS** ESI calcd for $C_{20}H_{26}NO_4S_2$ $[M+H]^+$ *m/z* 408.1303, found 408.1306.

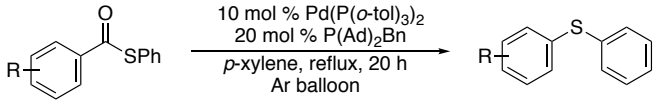


1w

***S*-(4-Fluorophenyl) 4-(*N*,*N*-dipropylsulfamoyl)benzothioate (1w).** General procedure was followed using probenecid (2.0 mmol). Compound **1w** was obtained in 67% yield as a white solid: **mp** 86-87 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.56–7.39 (m, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 3.29–2.92 (m, 4H), 1.56 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 189.4, 164.0 (d, *J* = 251.0 Hz), 145.1, 139.3, 137.3 (d, *J* = 8.7 Hz), 128.2, 127.6, 121.9 (d, *J* = 3.7 Hz), 117.0 (d, *J* = 22.2 Hz), 50.2, 22.2, 11.4; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –110.4; **HRMS** ESI calcd for $C_{19}H_{23}FNO_3S_2$ $[M+H]^+$ *m/z* 396.1103, found 396.1108.

IV. General Procedure for the Decarbonylative Thioetherification

General Procedure A: Pd (or Ni-)-Catalyzed Reaction on Small Scale



In a glovebox, the thioester substrate (0.05 mmol, 1 equiv), $Pd(P(o\text{-tol})_3)_2$ (2.9 mg, 0.005 mmol, 0.1 equiv), $P(Ad)_2Bn$ (3.6 mg, 0.2 equiv), and 5Å molecular sieves were combined in *p*-xylene (0.3 mL) in a 4 mL vial. The vial was connected to a reflux condenser that was capped with a rubber septum, and the reaction mixture was removed from the glovebox. An argon balloon was placed on the top of the condenser (Figure S1, **Set-up A**), and the reaction was heated for 20 h at the indicated temperature. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (2 mL) and passed through a pad of silica gel before being analyzed by GC and GCMS. Neopentylbenzene (0.05 mmol) was used for internal standard to determine GC yields of products. Under Ni catalysis, an analogous procedure was performed using $Ni(cod)_2$ (0.005 mmol, 0.1 equiv), PCy_3 (0.2 equiv), and toluene as the solvent with heating at 130 °C, and using reaction **Set-up B**.

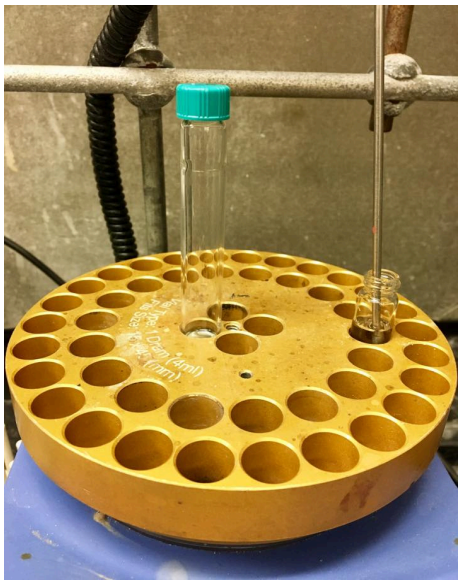
General Procedure B: Pd(or Ni-)-Catalyzed Reaction on Larger Scale for Isolation

Reactions were conducted analogously to **General Procedure A**, but on a 0.3 mmol scale using **Set-up A**. The reaction mixture was diluted with Et_2O, passed through a plug of silica and concentrated by rotavap. The resulting crude residue was purified by flash column chromatography on a Biotage Isolera Flash Purification System. In a few cases, the phosphine ligands co-eluted with the product. In these cases, the isolated product/phosphine mixture was re-dissolved in methylene chloride, and CuCl (0.4 equiv) was added. This mixture was stirred for 20 min at room temperature. The Cl–Cu–P(*o*-$tol_3)_2$ precipitated from solution and was removed by passing through a plug of silica gel using 4:1 hexanes/EtOAc as the eluent. The filtrate was concentrated to afford the thioether product. Under Ni catalysis, an analogous procedure was performed on a 0.1

to 0.3 mmol scale with toluene as the solvent, heating at 130 °C using reaction **Set-up A**.

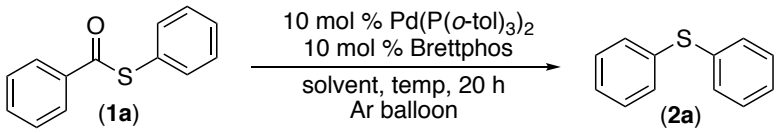
Figure S1. Reaction Set-up. **Set-up A**: 4-mL vial fitted with a condenser and Ar balloon; **Set-up B**: a 10-mL tall vial.

Set-up A
(4-mL vial fitted with a condenser and Ar balloon)



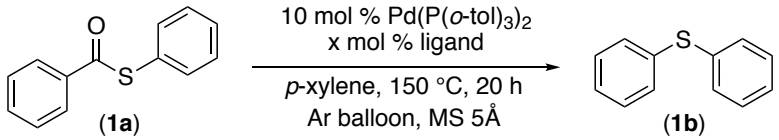
Set-up B
(a 10-mL tall vial)

Table S1. Preliminary Investigation of Decarbonylative C–S Coupling Using General Procedure A and BrettPhos as Ligand: Effect of Temperature



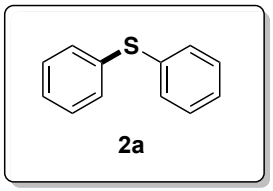
Entry	Solvent	Temperature (°C)	GC Yield (%)
1	toluene	130	32
2	*p*-xylene	130	46
3	*p*-xylene	150	58

Table S2. Ligand Screen for Pd-Catalyzed Decarbonylative C–S Coupling Using General Procedure A



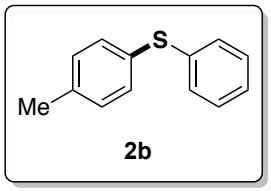
Entry	Ligand (L)	L mol%	GC Yield (%)
1	JohnPhos	10	22
2	Xantphos	10	52
3	Xantphos	20	61
4	*t*Bu-Xantphos	20	15
5	*rac*-BINAP	20	59
6	dppf	20	61
7	dppb	20	64
8	dppe	20	19
9	PAd_2n-Bu	20	67
10	PAd_2Bn	20	78
11	none	0	28

Isolated Thioether Products from Pd and Ni-Catalyzed Decarbonylation



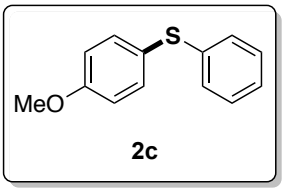
2a

Diphenylsulfide (2a). General procedure B was followed using substrate **1a** (64.2 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the title compound as colorless oil:[13] with [Pd] catalyst, 48 mg, 85% yield; with [Ni] catalyst, 52 mg, 92% yield. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.35–7.30 (multiple peaks, 5H), 7.28–7.19 (multiple peaks, 5H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 135.8, 131.0, 129.2, 127.0. **HRMS** EI calcd for $C_{12}H_{10}S$ $[M]^+$ *m*/*z* 186.0503, found 186.0502.



2b

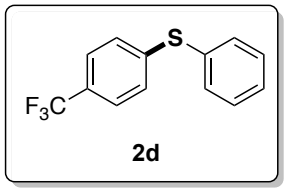
Phenyl(*p*-tolyl)sulfide (2b). General procedure B was followed using substrate **1b** (68.5 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–15% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 45 mg, 68% yield; with [Ni] catalyst, 52 mg, 78% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2b**.[13] **HRMS** EI calcd for $C_{13}H_{12}S$ $[M]^+$ *m*/*z* 200.0660, found 200.0662



2c

(4-Methoxyphenyl)(phenyl)sulfide (2c). General procedure B was followed using substrate **1c** (73 mg, 0.3 mmol) and the crude mixture was purified via flash column

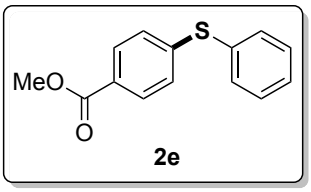
chromatography with elution using a gradient of 0–20% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 18 mg, 27% yield; with [Ni] catalyst, 50 mg, 75% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2c**.[13] **HRMS** EI calcd for $C_{13}H_{12}OS$ $[M]^+$ *m*/*z* 216.0609, found 216.0612.



2d

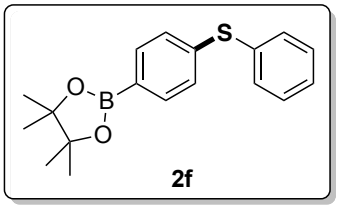
Phenyl(4-(trifluoromethyl)phenyl)sulfide (2d). General procedure B was followed using substrate **1d** (85 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 60 mg, 79% yield; with [Ni] catalyst, 62 mg, 82% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2d**.[13] **HRMS** EI calcd for $C_{13}H_9F_3S$ $[M]^+$ *m*/*z* 254.0377, found 254.0369.

For a 1.0 mmol scale reaction: General procedure B and reaction **Set-up A** were followed using substrate **1d** (283 mg, 1.0 mmol), $Ni(cod)_2$ (0.1 equiv), PCy_3 (0.2 equiv), and toluene (3 mL) as the solvent with heating at 130 °C. After 20 h, the reaction mixture was cooled to room temperature, diluted with Et_2O (5 mL), passed through a plug of silica and concentrated by rotavap. The resulting crude residue was purified by flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford compound **2d** as a colorless oil: 219 mg, 87% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2d**.[13]



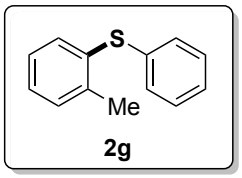
2e

Methyl 4-(phenylthio)benzoate (2e). General procedure B was followed using substrate **1e** (82 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a white solid: with [Pd] catalyst, 59 mg, 80% yield; with [Ni] catalyst, 63 mg, 85% yield. **Mp** 73–74 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.53–7.46 (multiple peaks, 2H), 7.41–7.35 (multiple peaks, 3H), 7.21 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 166.9, 144.6, 133.9, 132.6, 130.3, 129.8, 128.9, 127.8, 127.7, 52.3; **HRMS** ESI calcd for $C_{14}H_{13}O_2S$ $[M+H]^+$ *m*/*z* 245.0636, found 245.0641.



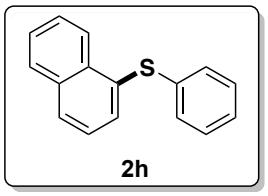
2f

4,4,5,5-Tetramethyl-2-(4-(phenylthio)phenyl)-1,3,2-dioxaborolane (2f). General procedure B was followed using substrate **1d** (102 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 67 mg, 72% yield; with [Ni] catalyst, 74 mg, 80% yield. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.39 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.34–7.31 (m, 2H), 7.30–7.26 (m, 3H), 1.33 (s, 12H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 140.6, 135.6, 134.8, 132.3, 129.5, 129.2, 127.8, 84.1, 25.1 (the carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation); **HRMS** ESI calcd for $C_{18}H_{22}BO_2S$ $[M+H]^+$ *m*/*z* 313.1434, found 313.1439.



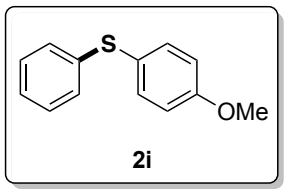
2g

Phenyl(*o*-tolyl)sulfide (2g). General procedure B was followed using substrate **1g** (68 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 60 mg, 79% yield; with [Ni] catalyst, 75 mg, 98% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2g**.[13] **HRMS** EI calcd for $C_{13}H_{12}S$ $[M]^{+}$ *m*/*z* 200.0660, found 200.0664.



2h

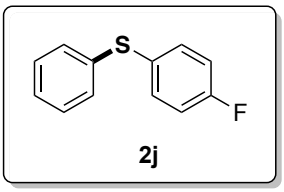
Naphthalen-1-yl(phenyl)sulfide (2h). General procedure B was followed using substrate **1h** (79 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 48 mg, 68% yield; with [Ni] catalyst, 70 mg, 99% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2h**.[13] **HRMS** EI calcd for $C_{16}H_{12}S$ $[M]^{+}$ *m*/*z* 236.0660, found 236.0653.



2i

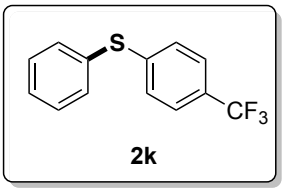
(4-Methoxyphenyl)(phenyl)sulfide (2i). General procedure B was followed using substrate **1i** (73 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–20% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 52 mg, 80% yield; with [Ni] catalyst, 53

mg, 82% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2i** (identical to compound **2c**).[13]



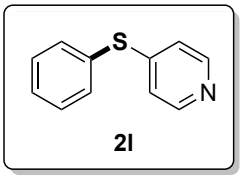
2j

(4-Fluorophenyl)(phenyl)sulfide (2j). General procedure B is followed using substrate **1j** (70 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–20% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 52 mg, 85% yield; with [Ni] catalyst, 54 mg, 88% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2j**.[14] **HRMS** EI calcd for $C_{12}H_9FS$ $[M]^+$ *m*/*z* 204.0409, found 204.0410.



2k

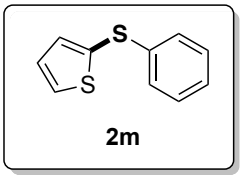
Phenyl(4-(trifluoromethyl)phenyl)sulfide (2k). General procedure B was followed using substrate **1k** (85 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–20% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 42 mg, 55% yield; with [Ni] catalyst, 55 mg, 72% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2k** (identical to compound **2d**).[13]



2l

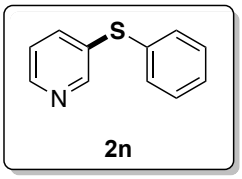
4-(Phenylthio)pyridine (2l). General procedure B was followed using substrate **1k** (65 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography

with elution using a gradient of 5–40% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 29 mg, 52% yield; with [Ni] catalyst, 36 mg, 65% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2l**.[15] **HRMS** EI calcd for $C_{11}H_9NS$ $[M]^+$ *m*/*z* 187.0456, found 187.0458.



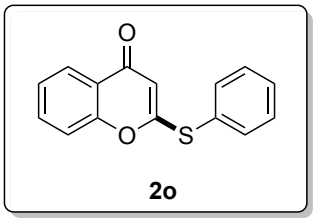
2m

2-(Phenylthio)thiophene (2m). General procedure B was followed using substrate **1m** (66 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 5–40% EtOAc/hexane to afford the compound as a colorless oil: with [Ni] catalyst, 41 mg, 72% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2m**.[15] **HRMS** EI calcd for $C_{10}H_8S_2$ $[M]^+$ *m*/*z* 192.0067, found 192.0069.



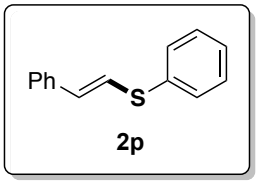
2n

3-(Phenylthio)pyridine (2n). General procedure B was followed using substrate **1n** (65 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 5–50% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 30 mg, 54% yield; with [Ni] catalyst, 37 mg, 66% yield. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2n**.[15] **HRMS** EI calcd for $C_{11}H_9NS$ $[M]^+$ *m*/*z* 187.0456, found 187.0456.



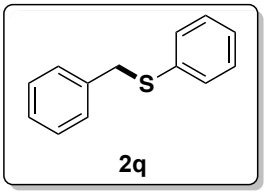
2o

2-(Phenylthio)-4*H*-chromen-4-one (2o). General procedure B was followed using substrate **1o** (85 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 5–30% EtOAc/hexane to afford the compound as a white solid: with [Pd] catalyst, 30 mg, 40% yield; with [Ni] catalyts, 57 mg, 76% yield. **Mp** 107–108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.67-7.57 (multiple peaks, 3H), 7.52–7.44 (multiple peaks, 3H), 7.36 (dd, *J* = 7.9, 6.7 Hz, 2H), 5.90 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 170.5, 156.9, 135.9, 133.7, 130.9, 130.3, 126.6, 126.0, 125.5, 123.7, 117.6, 109.0; **HRMS** ESI calcd for $C_{15}H_{11}O_2S$ $[M+H]^+$ *m*/*z* 255.0480, found 255.0487.



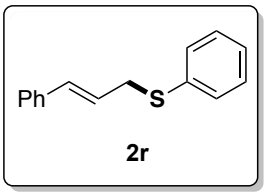
2p

(*E*)-Phenyl(styryl)sulfide (2p). General procedure B was followed using substrate **1p** (72 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 32 mg, 50% yield (*E*/*Z* ratio = 9:1); with [Ni] catalyst, 52 mg, 82% yield (*E*/*Z* ratio = >20:1). The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2p**.[16] **HRMS** EI calcd for $C_{14}H_{12}S$ $[M]^+$ *m*/*z* 212.0660, found 212.0659.



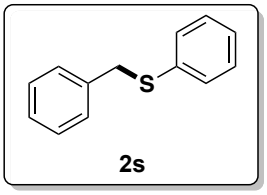
2q

Benzyl(phenyl)sulfide (2q). General procedure B was followed using substrate **1q** (76 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a white solid: with [Pd] catalyst, 32.9 mg, 49% yield. **Mp** 40–41 °C. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2q**.[17] **HRMS** EI calcd for $C_{13}H_{12}S$ $[M]^+$ *m*/*z* 200.0660, found 200.0665.



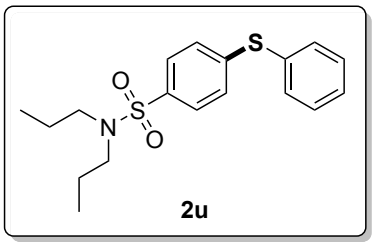
2r

Cinnamyl(phenyl)sulfide (2r). General procedure B was followed using substrate **1r** (68 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a yellowish oil: with [Pd] catalyst, 48.6 mg, 81% yield. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.18–7.22 (multiple peaks, 10H), 6.64 (m, 1H), 6.45 (m, 1H), 3.92 (s, 2H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 136.9, 136.0, 132.9, 130.4, 129.0, 128.7, 127.7, 126.6, 126.5, 125.2, 37.3; **HRMS** EI calcd for $C_{15}H_{14}S$ $[M]^+$ *m*/*z* 226.0816, found 226.0818.



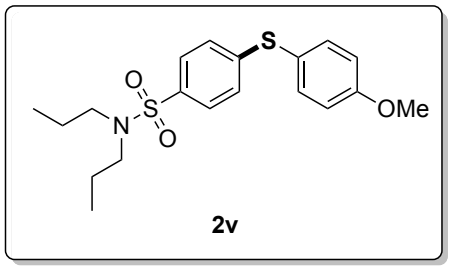
2s

Benzyl(phenyl)sulfide (2s). General procedure B was followed using substrate **1s** (76 mg, 0.3 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 0–10% EtOAc/hexane to afford the compound as a white solid: with [Pd] catalyst, 55 mg, 82% yield. **Mp** 40–41 °C. The ^{1}H and ^{13}C NMR spectroscopic data were identical to those reported previously in the literature for **2s** (identical to compound **2q**).[17] **HRMS** EI calcd for $C_{13}H_{12}S$ $[M]^+$ *m*/*z* 200.0660, found 200.0660.



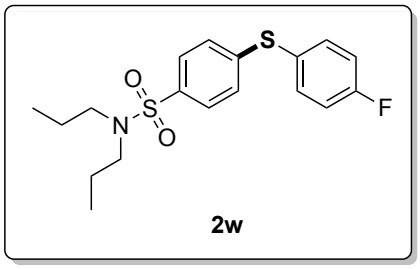
2u

4-(Phenylthio)-*N*,*N*-dipropylbenzenesulfonamide (2u). General procedure B was followed using substrate **1u** (76 mg, 0.2 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 5–30% EtOAc/hexane to afford the compound as a white solid: with [Pd] catalyst, 39 mg, 55% yield; with [Ni] catalyst, 64 mg, 92% yield. **Mp** 63–64 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.53–7.46 (multiple peaks, 2H), 7.43–7.40 (multiple peaks, 3H), 7.22 (d, *J* = 8.5 Hz, 2H), 3.04 (dd, *J* = 8.7, 6.7 Hz, 4H), 1.54 (multiple peaks, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 144.3, 137.4, 134.2, 131.9, 130.0, 129.2, 127.8, 127.8, 50.3, 22.3, 11.4; **HRMS** ESI calcd for $C_{18}H_{24}NO_2S_2$ $[M+H]^+$ *m*/*z* 350.1248, found 350.1253.



2v

4-((4-Methoxyphenyl)thio)-*N*,*N*-dipropylbenzenesulfonamide (2v). General procedure B was followed using substrate **1v** (82 mg, 0.2 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 5–30% EtOAc/hexane to afford the compound as a colorless oil: with [Ni] catalyst, 42 mg, 55% yield. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 3.06–2.96 (multiple peaks, 4H), 1.57–1.48 (multiple peaks, 4H), 0.85 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 161.0, 146.2, 137.1, 136.5, 127.6, 126.2, 121.1, 115.6, 55.6, 50.3, 22.3, 11.4; **HRMS** ESI calcd for $C_{19}H_{26}NO_3S_2$ $[M+H]^+$ *m*/*z* 380.1354, found 380.1357.



2w

4-((4-Fluorophenyl)thio)-*N*,*N*-dipropylbenzenesulfonamide (2w). General procedure B was followed using substrate **1w** (79 mg, 0.2 mmol), and the crude mixture was purified via flash column chromatography with elution using a gradient of 5–30% EtOAc/hexane to afford the compound as a colorless oil: with [Pd] catalyst, 50 mg, 67% yield; with [Ni] catalyst, 62 mg, 84% yield. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.50 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.17–7.14 (multiple peaks, 2H), 7.13–7.10 (multiple peaks, 2H), 3.09–2.79 (multiple peaks, 4H), 1.54 (multiple peaks, 4H), 0.85 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 163.5 (d, *J* = 250.5 Hz), 144.5, 137.3, 136.9 (d, *J* = 8.5 Hz), 127.8, 127.2, 126.7 (d, *J* = 3.3 Hz), 117.3 (d, *J* = 22.1 Hz), 50.3, 22.3, 11.4; **HRMS** ESI calcd for $C_{18}H_{23}FNO_2S_2$ $[M+H]^+$ *m*/*z* 368.1154, found 368.1156.

V. Competition Experiments

A. Effect of electronics on thioester substrates

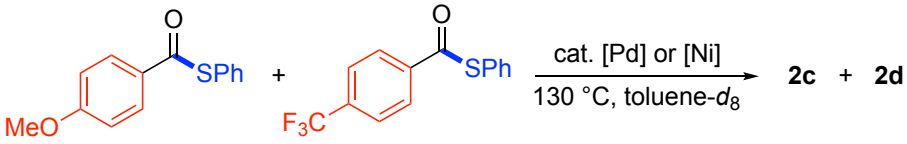
Using the general procedure for Pd and Ni catalysis (2 mol % catalyst and 4 mol % ligand, Figure S1, **Set-up A**), the thioester substrates **1c** (0.05 mmol, 0.5 equiv), and **1d** (0.05 mmol, 0.5 equiv) were allowed to react in deuterated toluene at 130 °C. Reactions mixtures were assayed after 0.5 and 2 h by ^{1}H and ^{19}F NMR spectroscopy using trimethoxybenzene and trifluoromethoxybenzene as internal standards. Results are summarized in **Table S3(a)**.

B. Reactivity of thioester **1g** under Pd and Ni catalysis

Using the general procedure for Pd and Ni catalysis (2 mol % catalyst and 4 mol % ligand, Figure S1, **Set-up A**), the thioester substrate **1g** (0.1 mmol, 1 equiv) was allowed to react in deuterated toluene at 130 °C. Reactions mixtures were assayed after 0.5 and 2 h by ^{1}H NMR spectroscopy using trimethoxybenzene as internal standard. Results are summarized in **Table S3(b)**.

Table S3. Competition experiments of various thioesters under Pd and Ni methods[a]

(a) Effect of electronics on thioester substrates

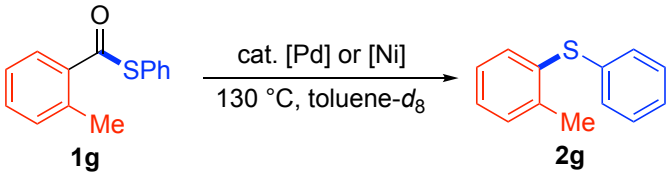


1c (0.5 equiv) **1d** (0.5 equiv)

[Pd]: 2 mol % $Pd[P(o\text{-}tol)_3]_2$, 4 mol % PAd_2Bn
[Ni]: 2 mol % $Ni(cod)_2$, 4 mol % PCy_3

entry	[M]; *t* (h)	**2c**+**2d** (% yield) (ratio **2c**:**2d**)[b]	unreacted **1c** (%)[b]	unreacted **1d** (%)[b]
1	[Pd]; 0.5	18 (1:99)	>49	32
2[c]	[Pd]; 2	35 (4:96)	48	12
3	[Ni]; 0.5	31 (6:94)	48	21
4	[Ni]; 2	49 (9:91)	46	5

(b) Reactivity of thioester **1g** under Pd and Ni catalysis



1g **2g**

[Pd]: 2 mol % $Pd[P(o\text{-}tol)_3]_2$, 4 mol % PAd_2Bn
[Ni]: 2 mol % $Ni(cod)_2$, 4 mol % PCy_3

entry	[M]; *t* (h)	**2g** (% yield)[b]	unreacted **1g** (%)[b]
1	[Pd]; 0.5	>99	<1
2[c]	[Pd]; 2	>99	<1
3	[Ni]; 0.5	40	60
4	[Ni]; 2	70	30

[a]Conditions: (a) **1c** (0.05 mmol), **1d** (0.05 mmol), [M] (0.002 mmol), ligand (0.004 mmol), toluene-d_8, 130 °C, 0.5 and 2 h. (b) **1g** (0.1 mmol), [M] (0.002 mmol), ligand (0.004 mmol), toluene-d_8, 130 °C, 0.5 and 2 h. [b]Ratio and yield analyses were obtained by ^1H and ^{19}F NMR. [c]Unwanted biarylsulfide byproducts (~5%) were observed.

VI. References

(1) Crabb, T.; Soilleux, S. L. *J. Chem. Soc., Perkin Trans.* 1 **1985**, 1381.

(2) Cera, G.; Haven, T.; Ackermann, L. *Angew. Chem. Int. Ed.* **2016**, *55*, 1484.

(3) Burhardt, M. N.; Taaning, R. H.; Skrydstrup, T. *Org. Lett.* **2013**, *15*, 948.

(4) Cao, H.; McNamee, L.; Alper, H. *J. Org. Chem.* **2008**, *73*, 3530.

(5) Qiao, Z.; Jiang, X. *Org. Lett.* **2016**, *18*, 1550.

(6) Ho, D. K. H.; Chan, L.; Hooper, A.; Brennan, P. E. *Tetrahedron Lett.* **2011**, *52*, 820.

(7) Bandgar, S. B.; Bandgar, B. P.; Korbad, B. L.; Sawant, S. S. *Tetrahedron Lett.* **2007**, *48*, 1287.

(8) Yan, Y.; Chen, J.; Zhang, L.; Zheng, Q.; Han, Y.; Zhang, H.; Zhang, D.; Awakawa, T.; Abe, I.; Liu, W. *Angew. Chem. Int. Ed.* **2013**, *52*, 12308.

(9) Bordwell, F.G.; Fried, H. E. *J. Org. Chem.* **1991**, *56*, 4218.

(10) Ranu, B. C.; Jana, R. *Adv. Synth. Catal.* **2005**, *347*, 1811.

(11) Wang, F.; Liu, H.; Fu, H.; Jiang, Y.; Zhao, Y. *Adv. Synth. Catal.* **2009**, *351*, 246.

(12) Xiao, W.-J.; Alper, H. *J. Org. Chem.* **1997**, *62*, 3422.

(13) Fernández-Rodríguez, M. A.; Shen, Q.; Hartwig, J. F. *Chem. Eur. J.* **2006**, *12*, 7782.

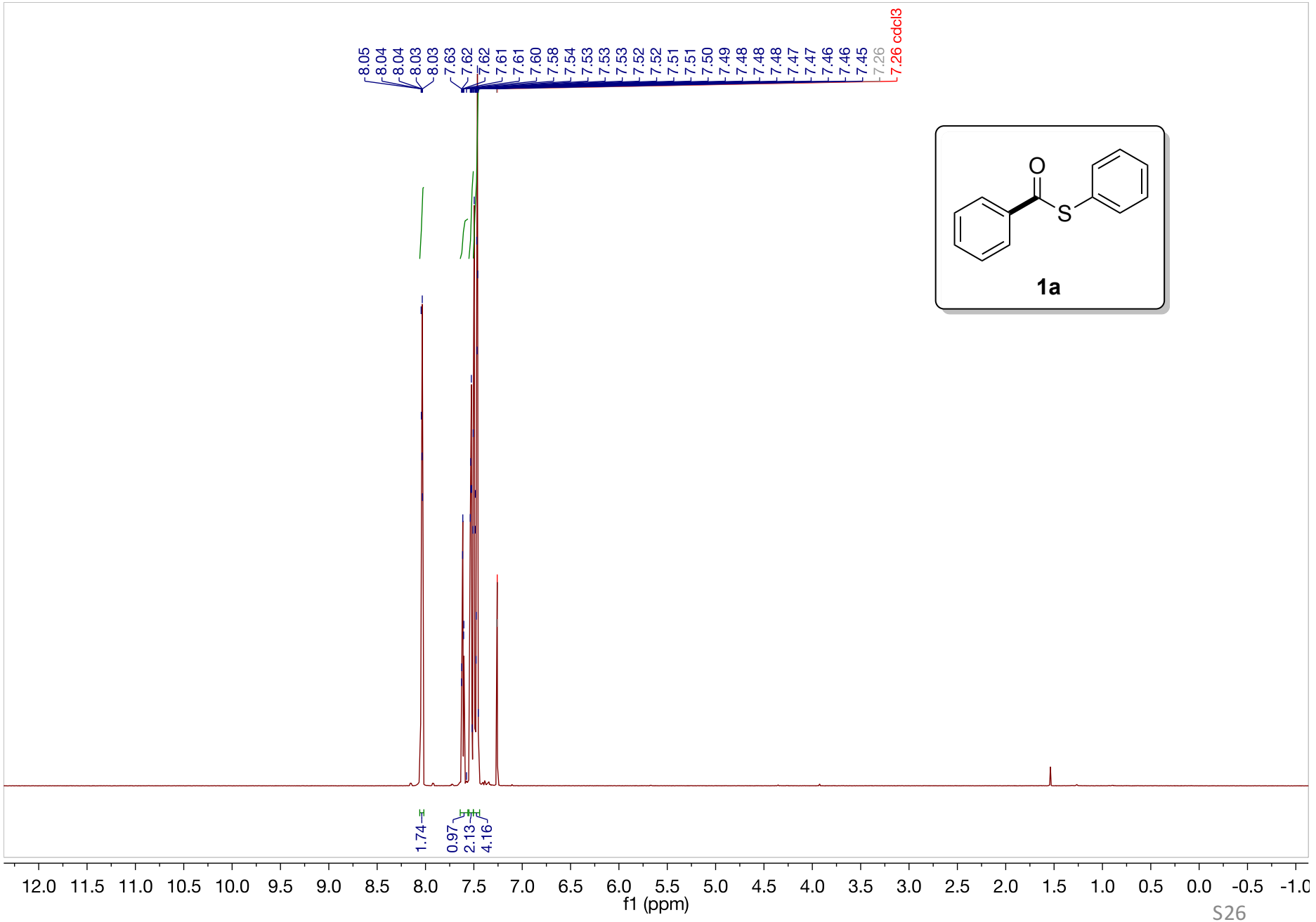
(14) Zhang, Y.; Ngeow, K, C.; Ying, J. Y. *Org. Lett.* **2007**, *9*, 3495.

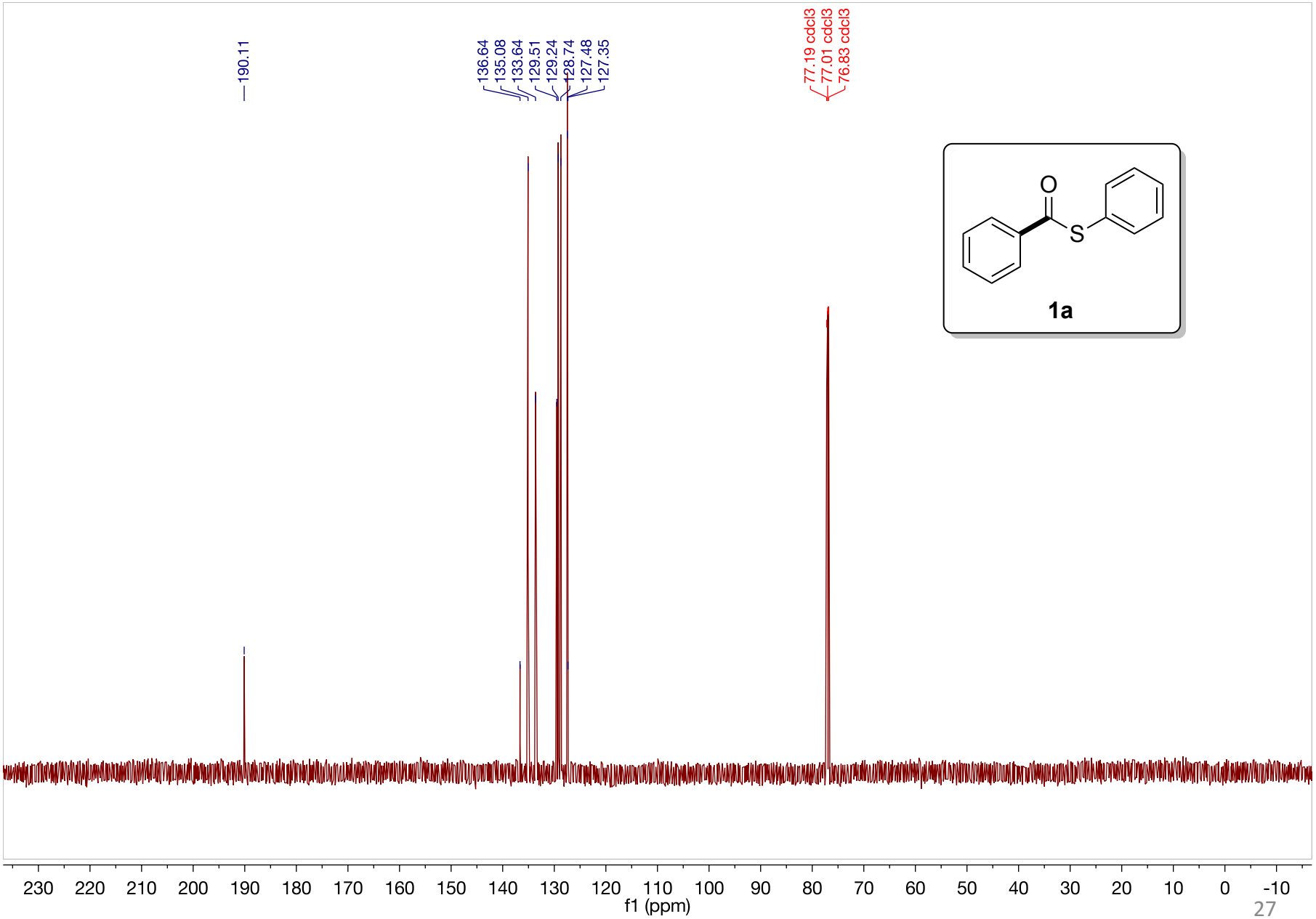
(15) Uyeda, C.; Tan, Y.; Fu, G. C.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 9548.

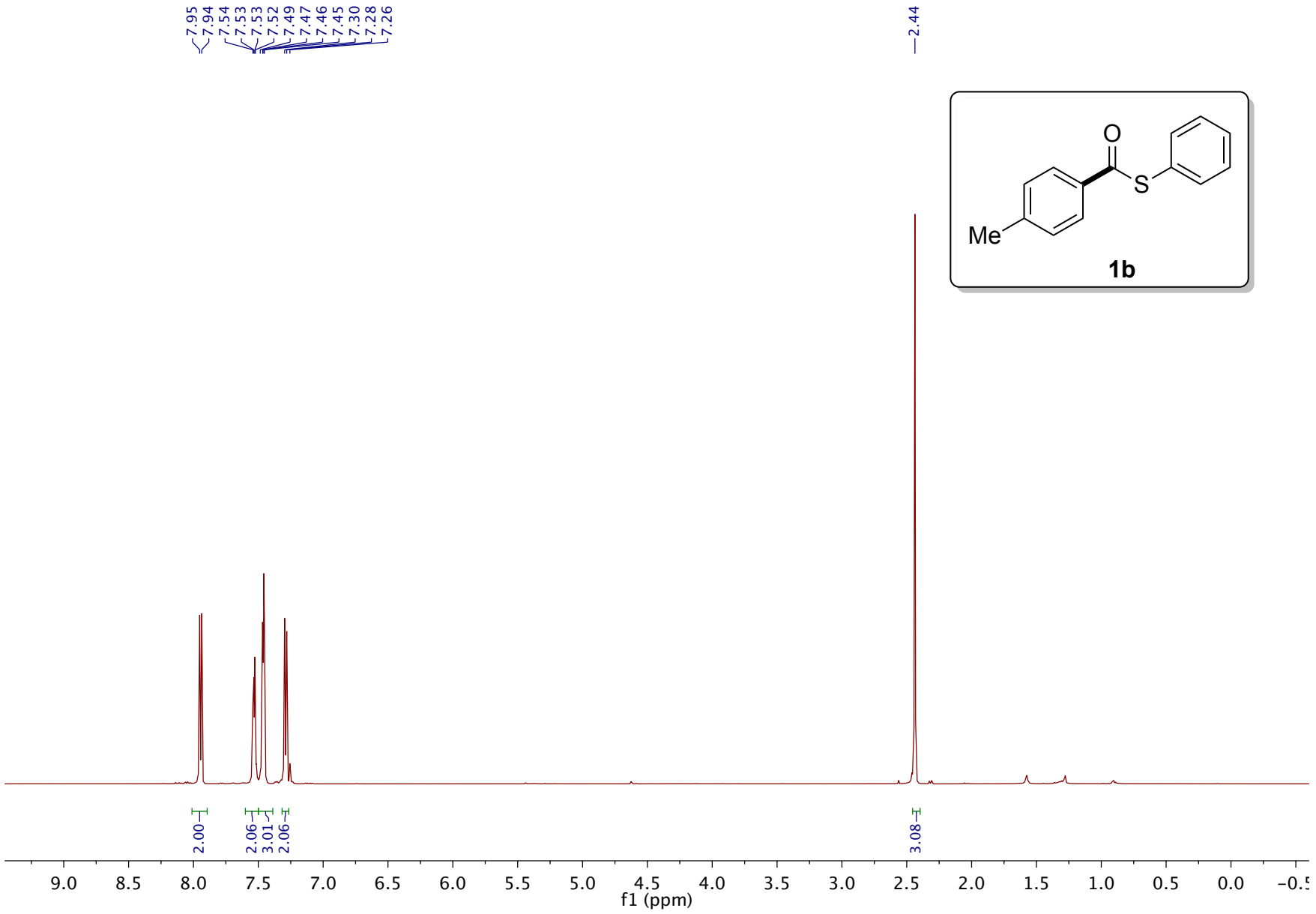
(16) Tidei, C.; Sancineto, L.; Bagnoli, L.; Battistelli, B.; Marini, F.; Santi, C. *Eur. J. Org. Chem.* **2014**, 5968.

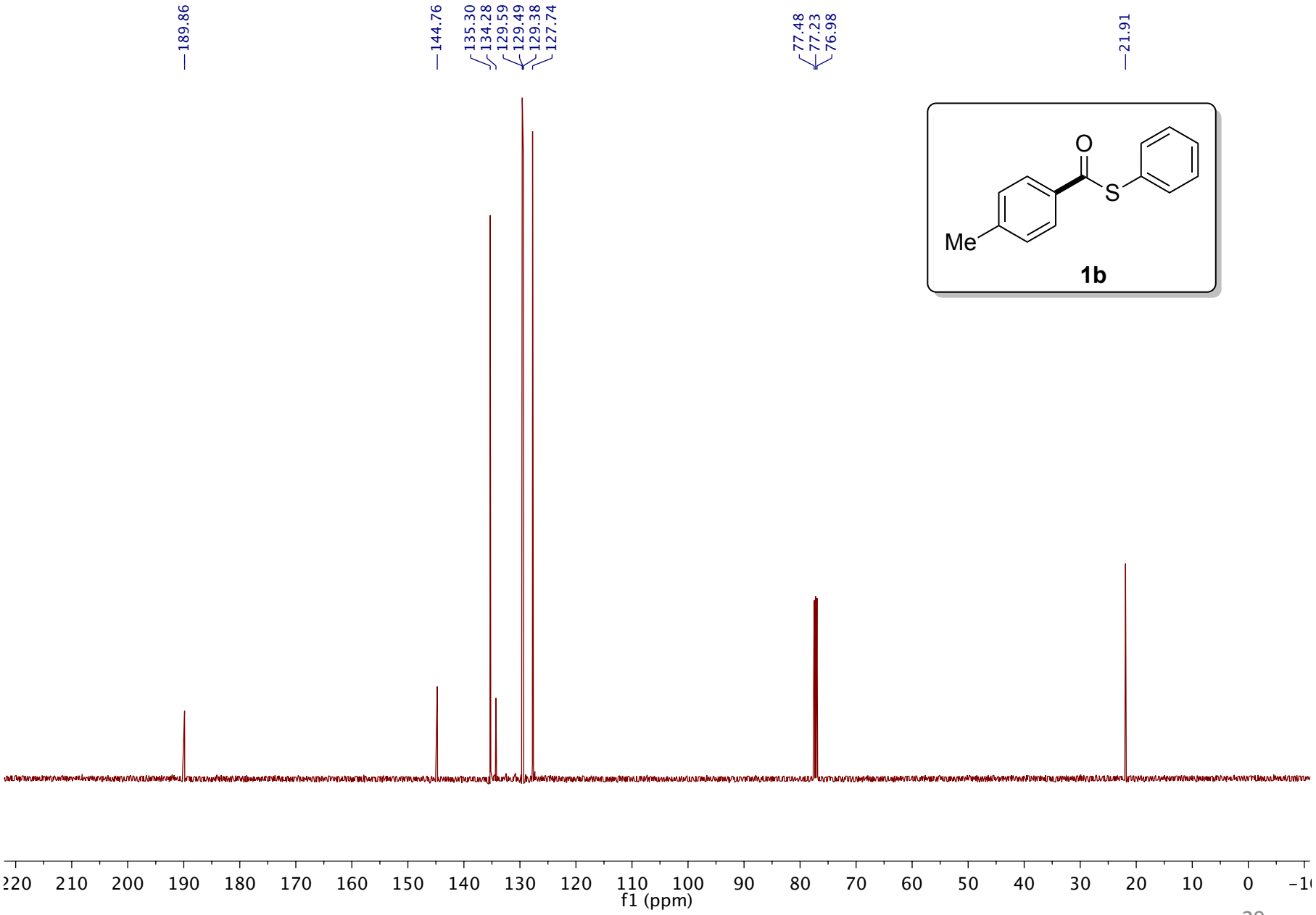
(17) Itoh, T.; Mase, T. *Org. Lett.* **2004**, *6,* 4587.

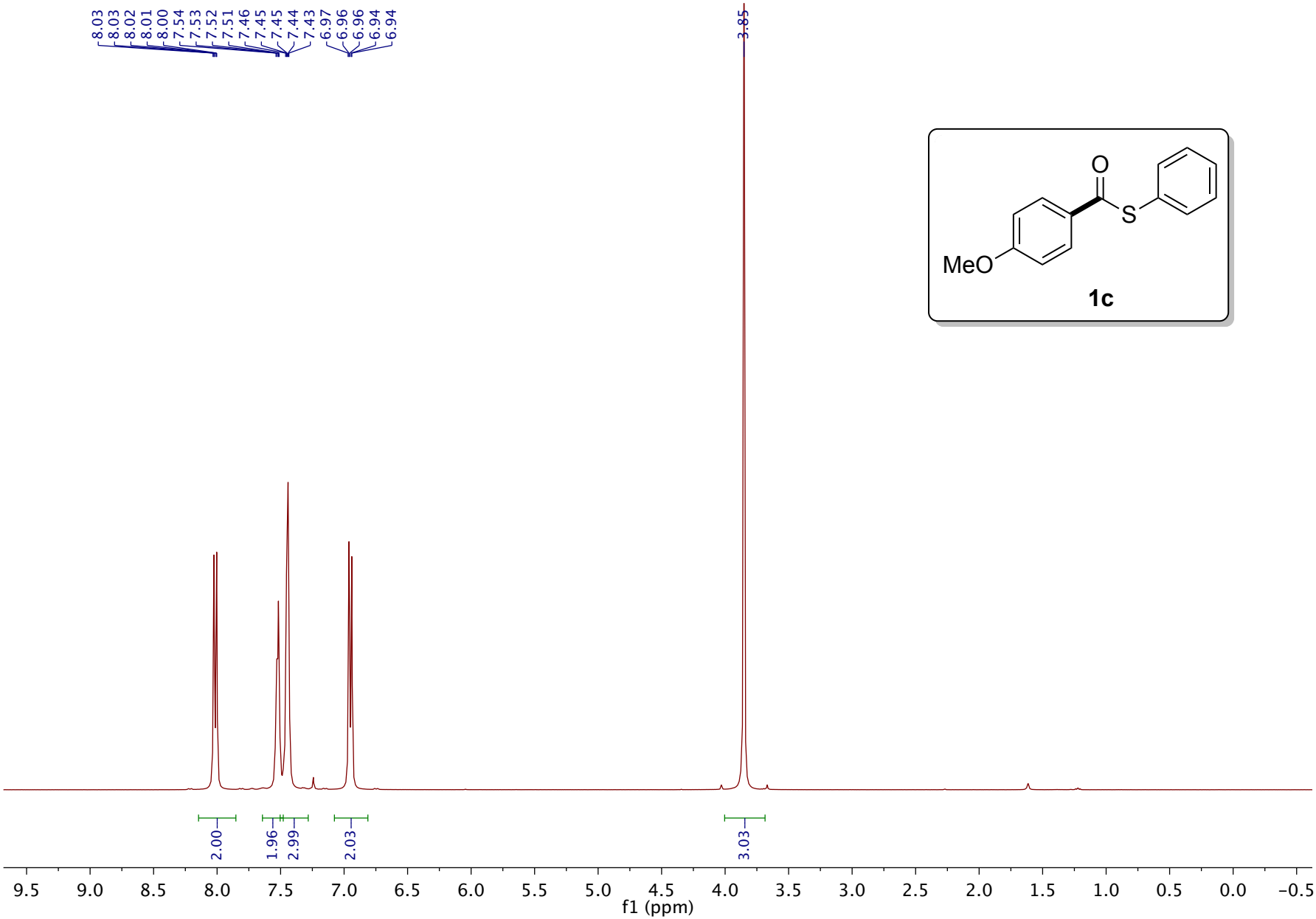
VII. ^{1}H and ^{13}C NMR Data of Compounds

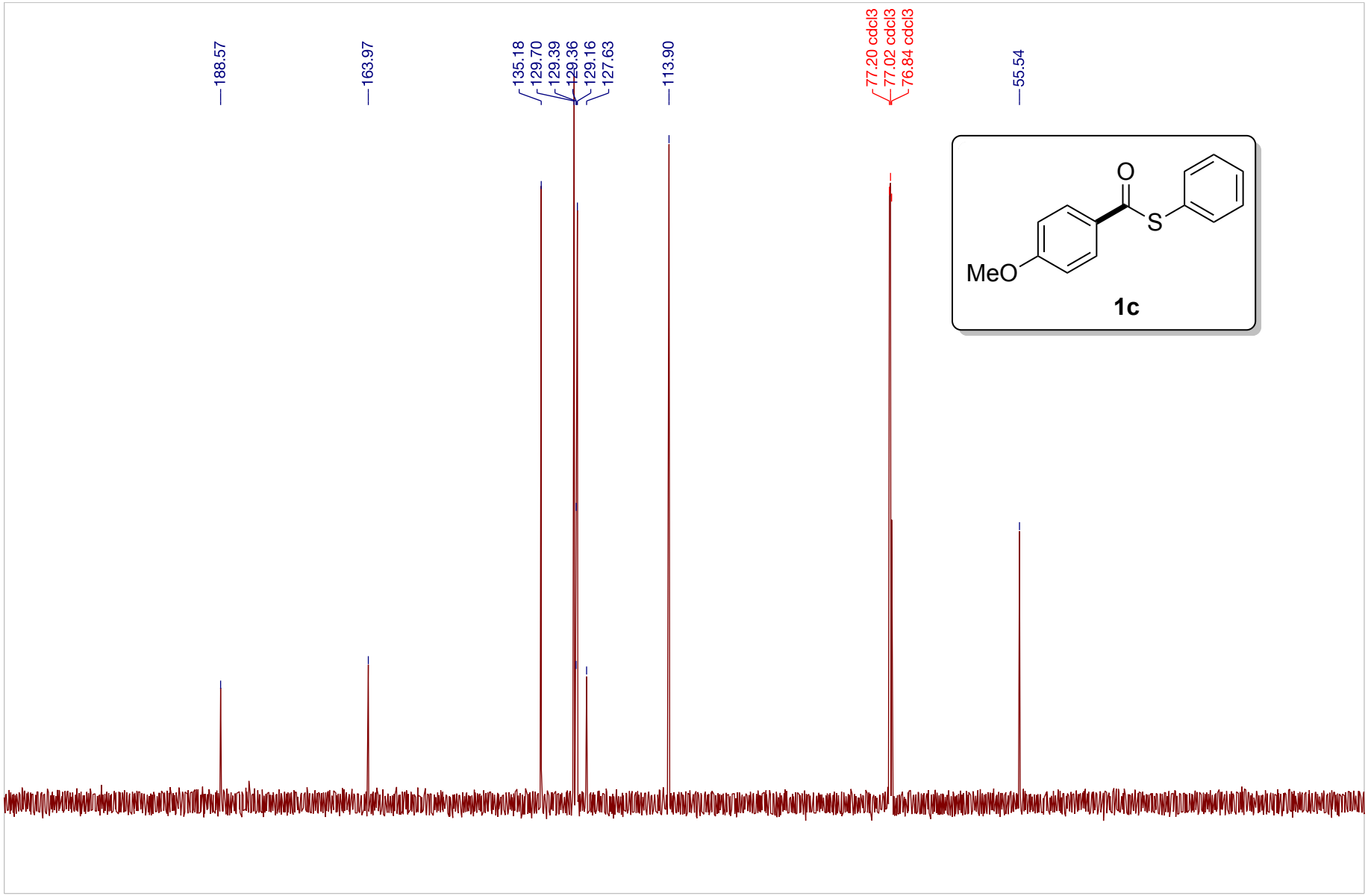

8.05
8.04
8.04
8.03
8.03
7.63
7.62
7.62
7.61
7.61
7.60
7.58
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.26
7.26 cdcl3
O
S
1a
1.74
0.97
2.13
4.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

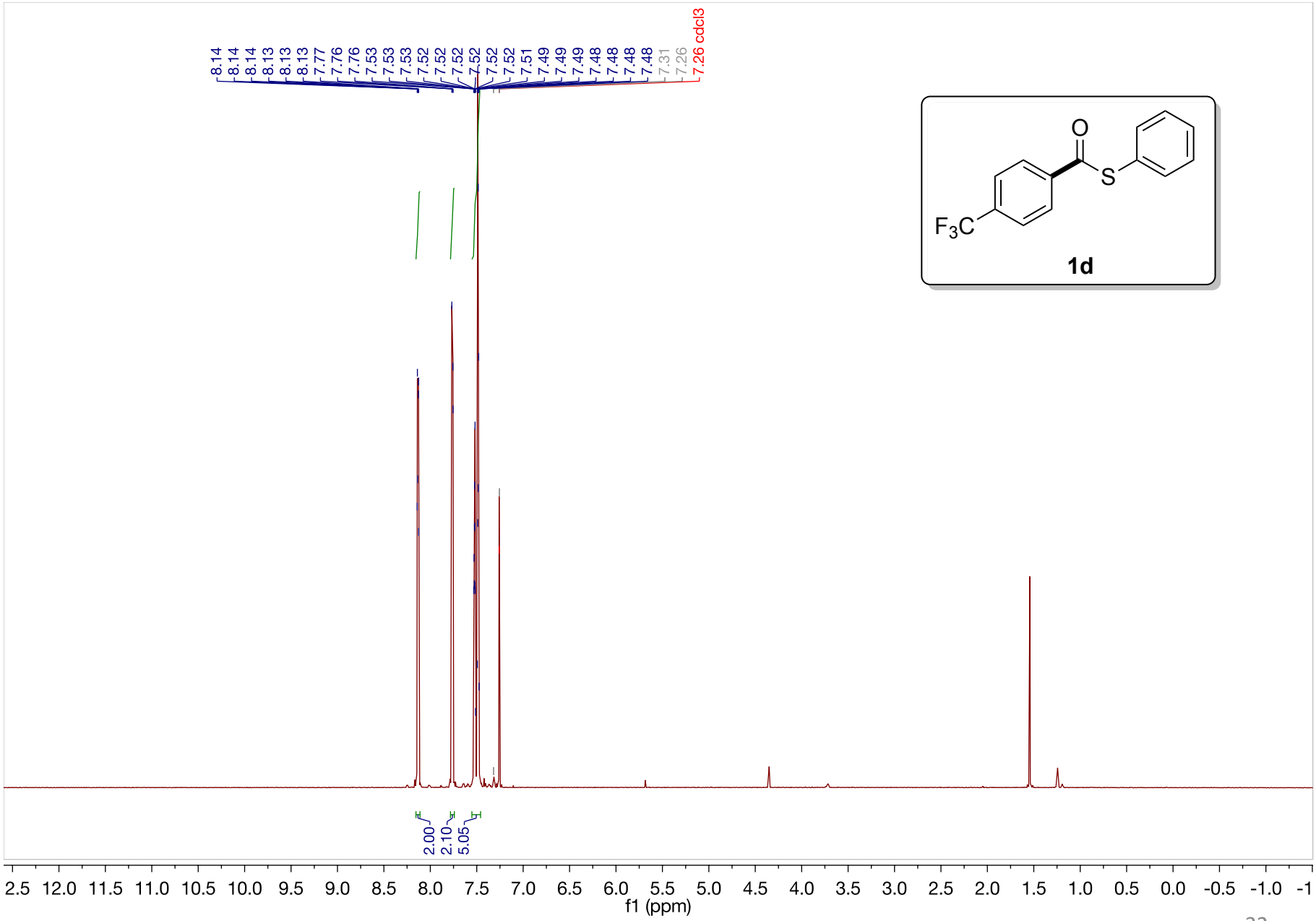

190.11
136.64
135.08
133.64
129.51
129.24
128.74
127.48
127.35
77.19 cdcl3
77.01 cdcl3
76.83 cdcl3
O
S
1a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

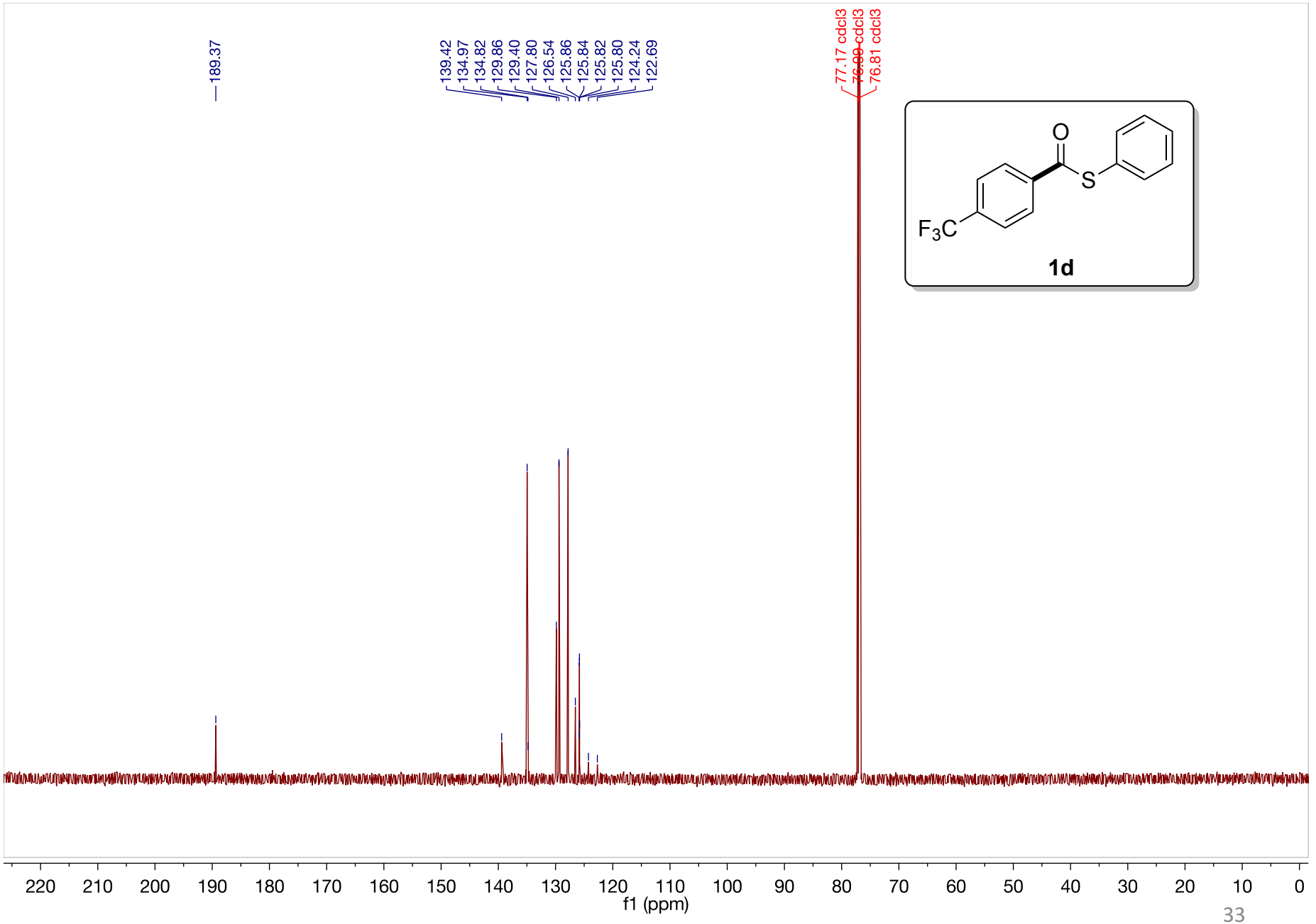

7.95
7.94
7.54
7.53
7.53
7.52
7.49
7.47
7.46
7.45
7.30
7.28
7.26
2.44
O
S
Me
1b
2.00
2.06
3.01
2.06
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

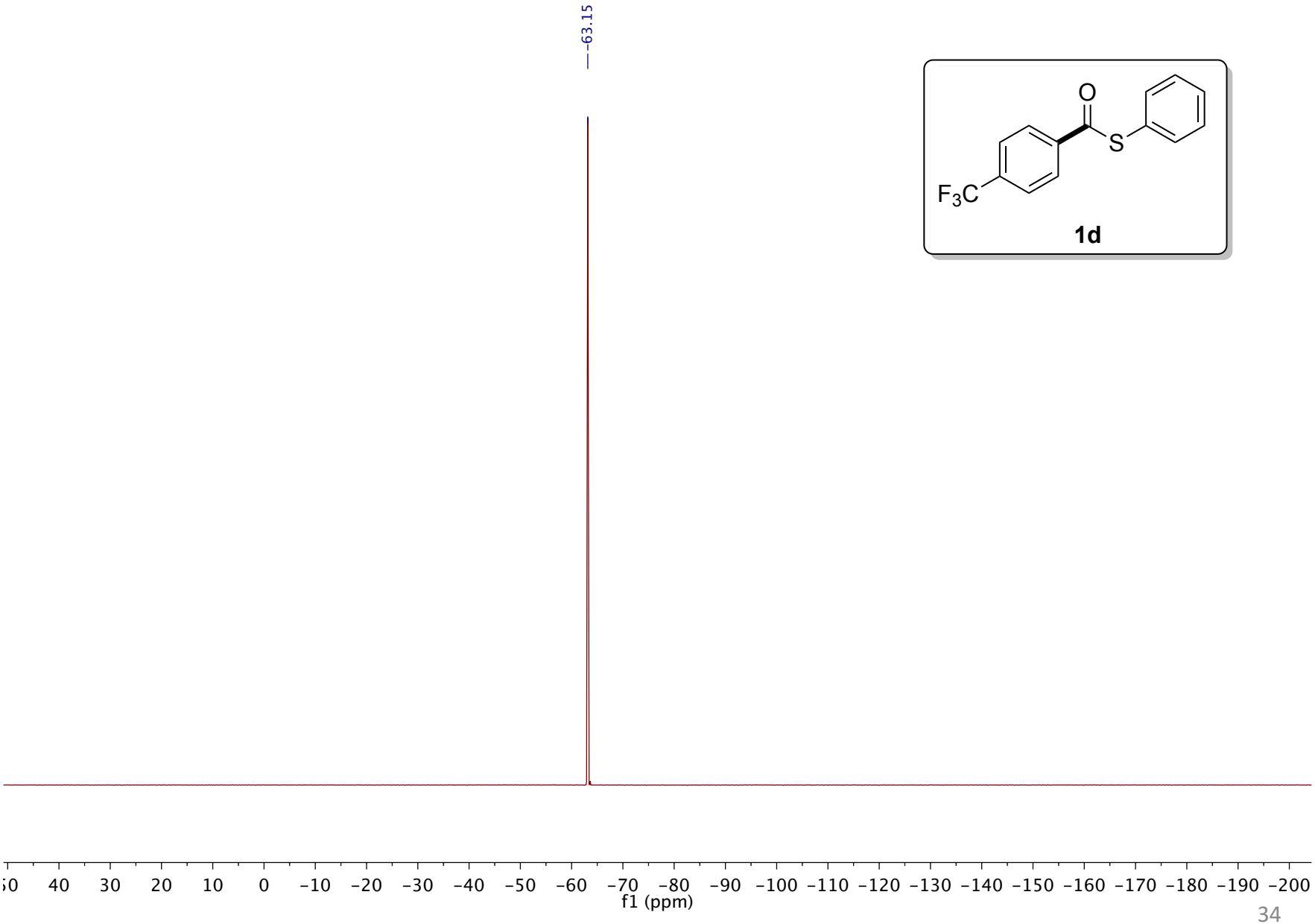

189.86
144.76
135.30
134.28
129.59
129.49
129.38
127.74
77.48
77.23
76.98
21.91
O
S
Me
1b
f1 (ppm)

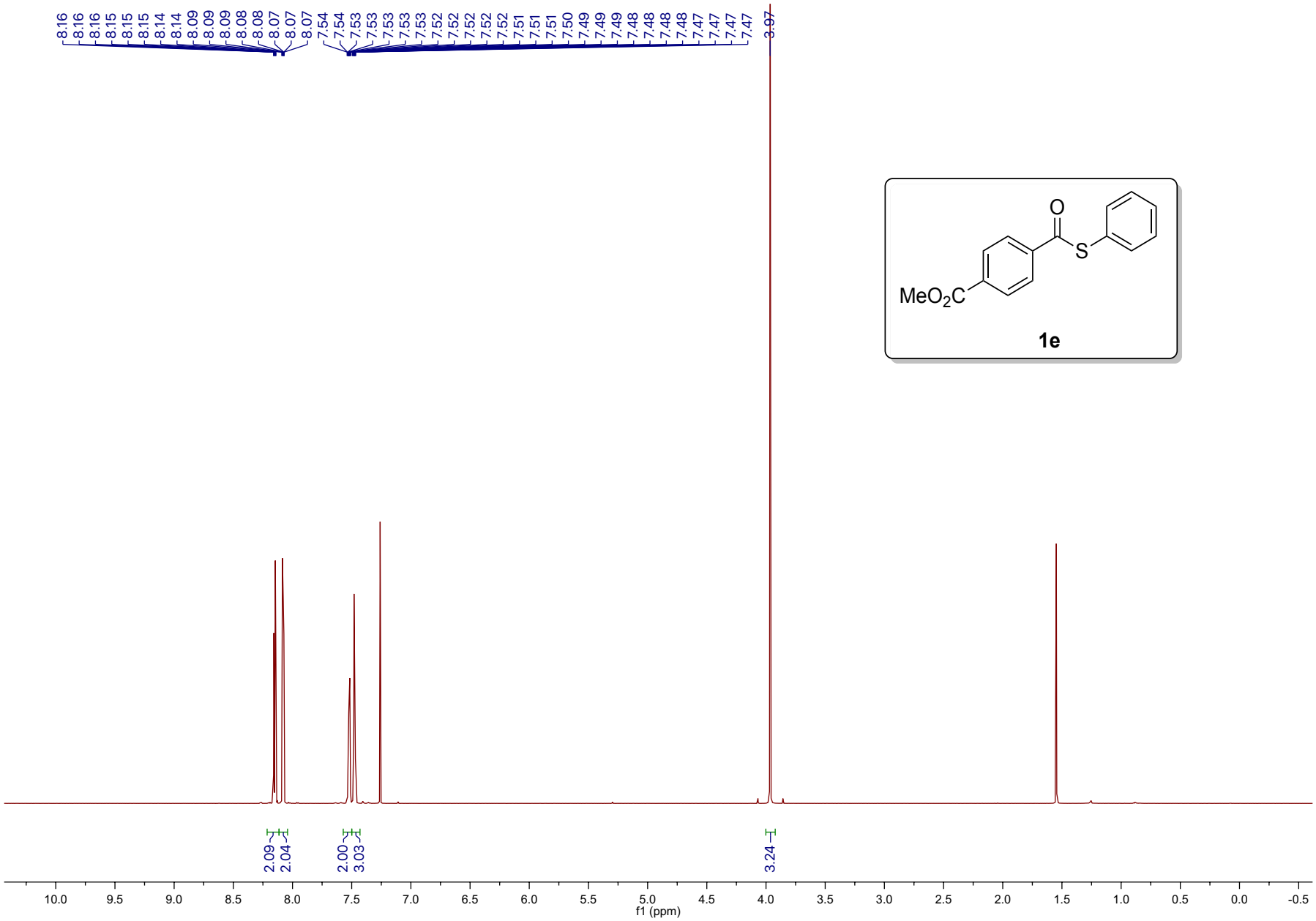

8.03
8.03
8.02
8.01
8.00
7.54
7.53
7.52
7.51
7.46
7.45
7.45
7.44
7.43
6.97
6.96
6.96
6.94
6.94
3.85
O
S
MeO
1c
2.00
1.96
2.99
2.03
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

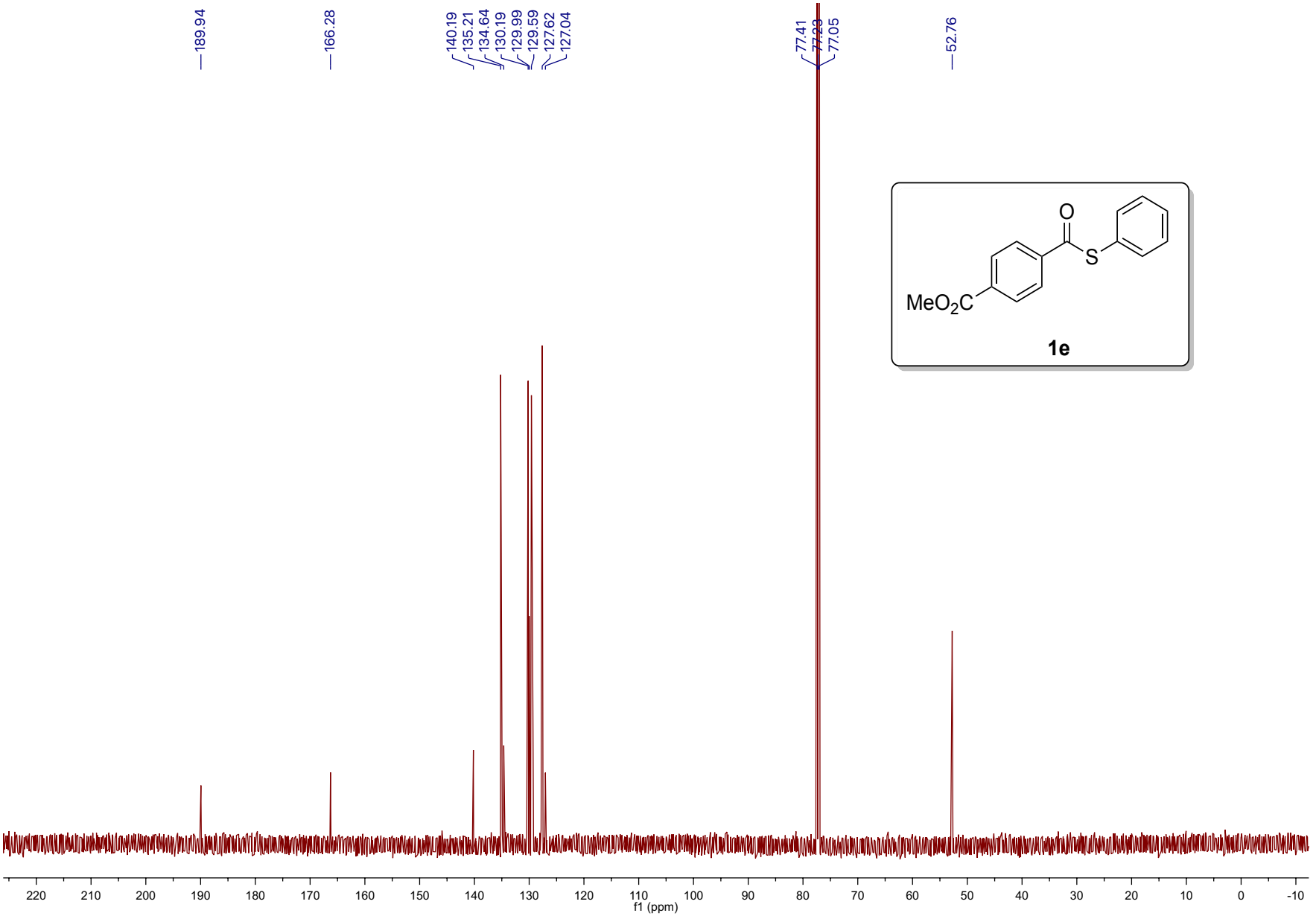

188.57
163.97
135.18
129.70
129.39
129.36
129.16
127.63
113.90
77.20 cdcl3
77.02 cdcl3
76.84 cdcl3
55.54
O
S
MeO
1c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

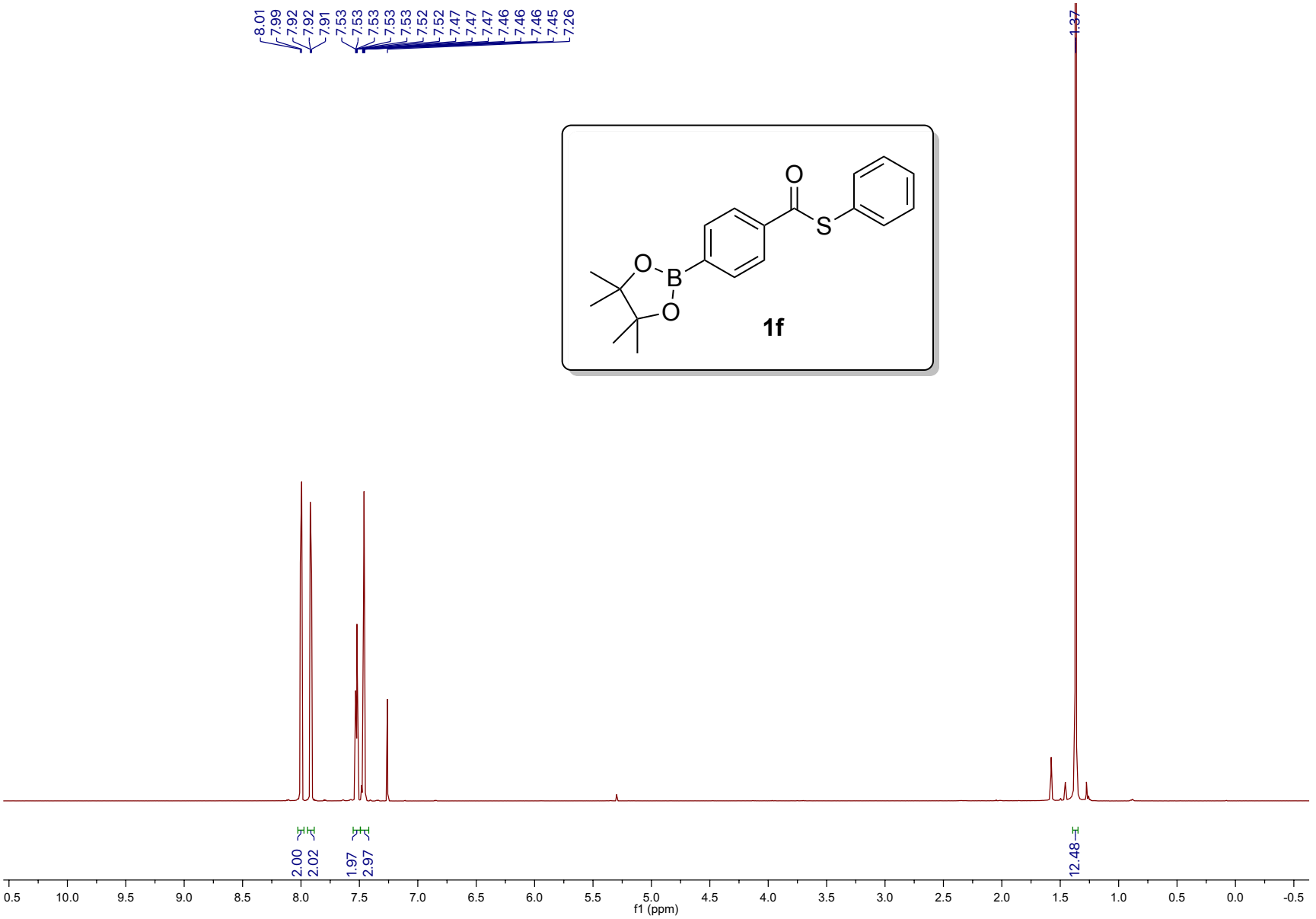

8.14
8.14
8.14
8.13
8.13
8.13
7.77
7.76
7.76
7.53
7.53
7.53
7.52
7.52
7.52
7.52
7.52
7.51
7.49
7.49
7.49
7.48
7.48
7.48
7.31
7.26
7.26 cdcl3
O
S
F3C
1d
2.00
2.10
5.05
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

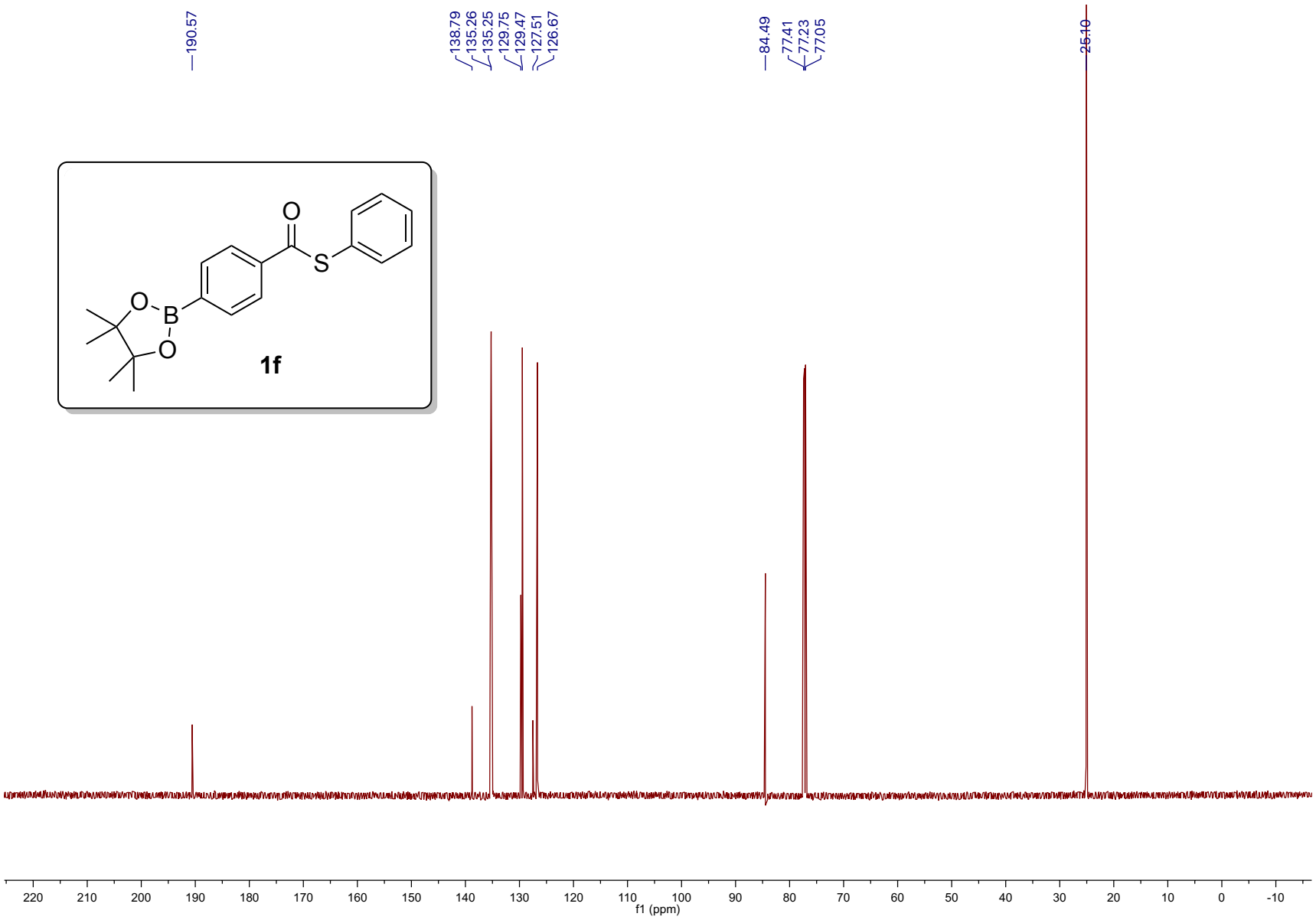

189.37
139.42
134.97
134.82
129.86
129.40
127.80
126.54
125.86
125.84
125.82
125.80
124.24
122.69
77.17 cdcl3
76.99 cdcl3
76.81 cdcl3
O
S
F3C
1d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

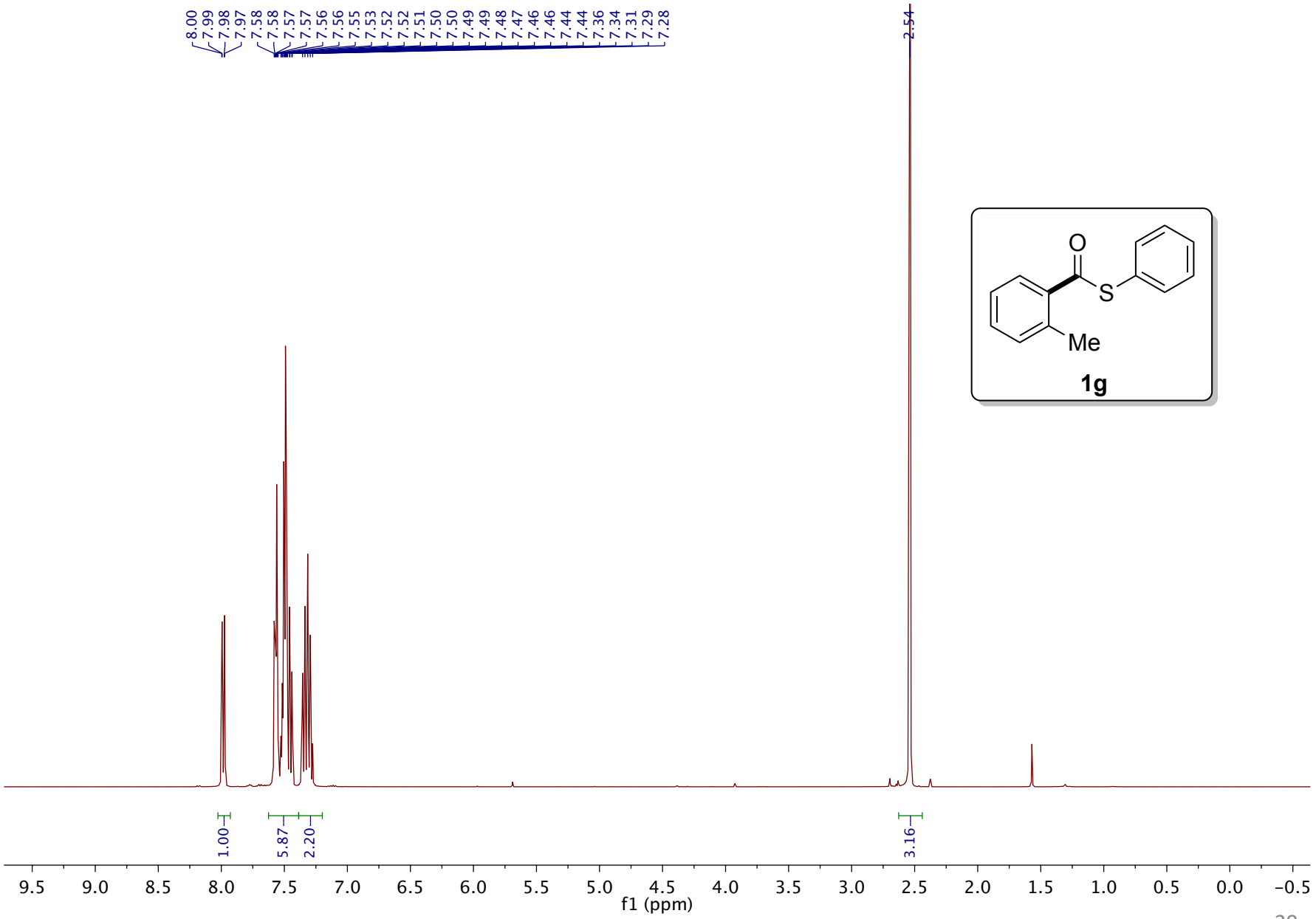

−63.15
O
S
F3C
1d
50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

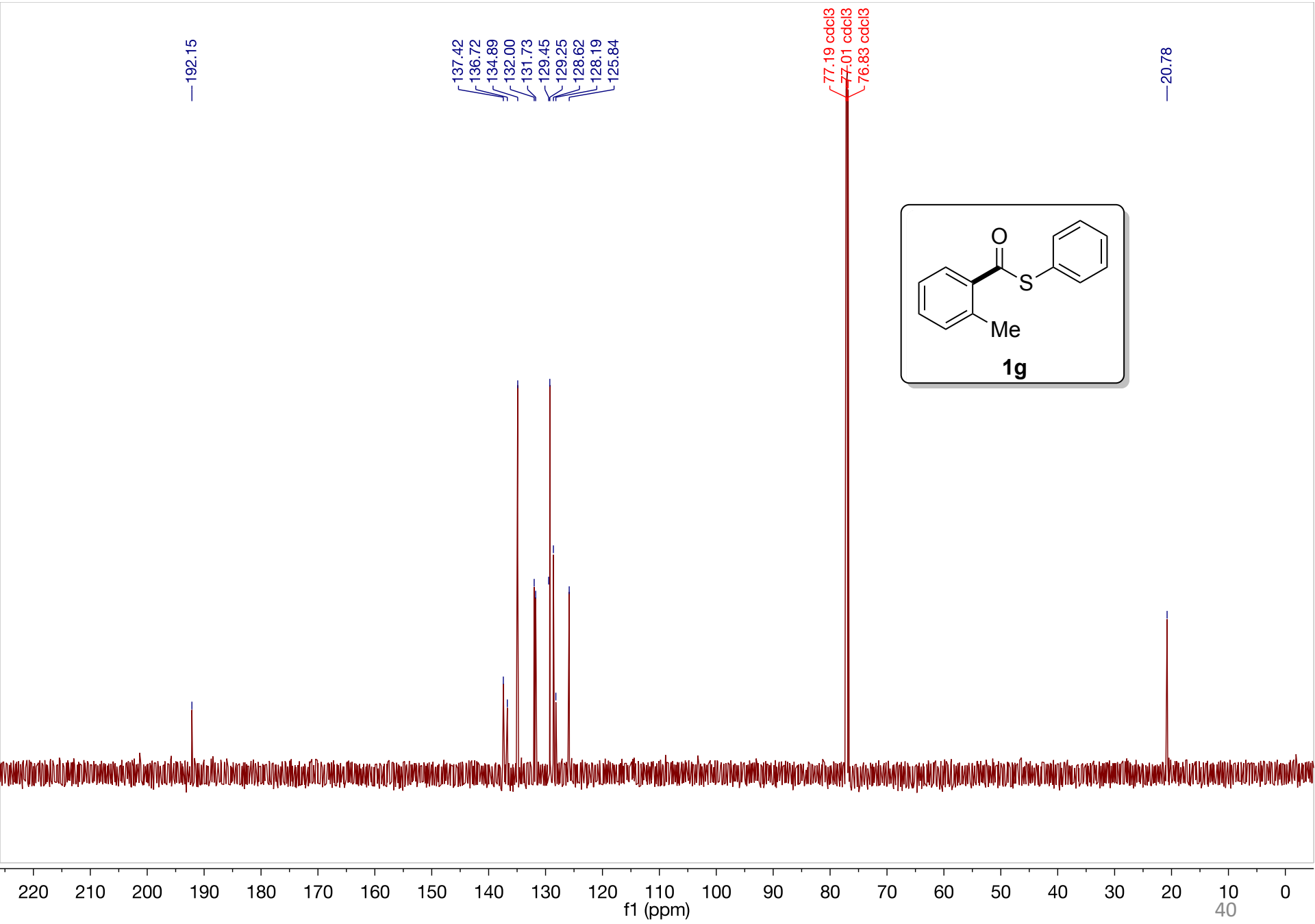

8.16
8.16
8.16
8.15
8.15
8.15
8.14
8.14
8.09
8.09
8.09
8.08
8.08
8.07
8.07
8.07
7.54
7.54
7.53
7.53
7.53
7.53
7.52
7.52
7.52
7.52
7.51
7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.47
3.97
2.09
2.04
2.00
3.03
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
O
S
MeO2C
1e

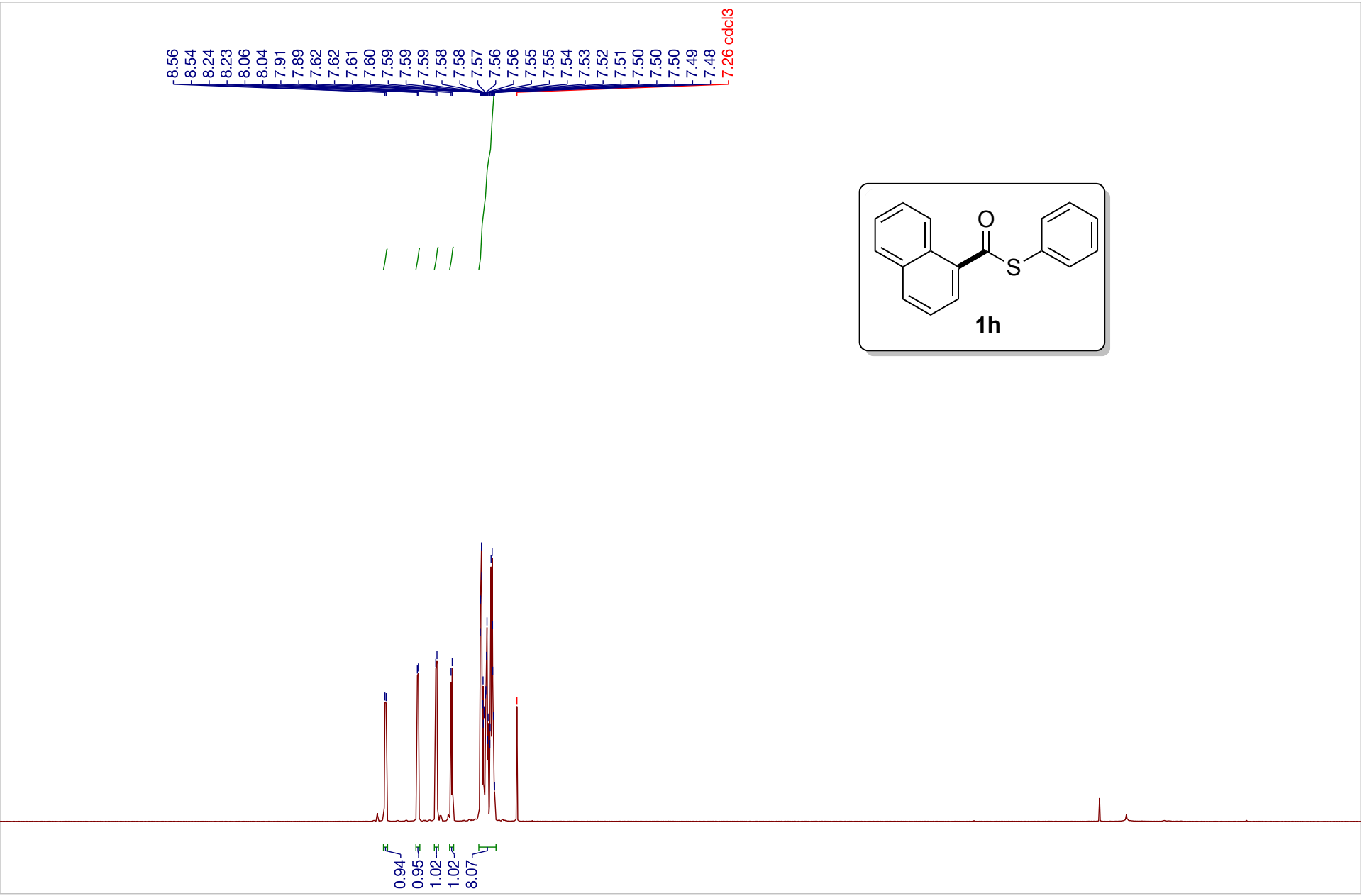

189.94
166.28
140.19
135.21
134.64
130.19
129.99
129.59
127.62
127.04
77.41
77.23
77.05
52.76
O
S
MeO2C
1e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

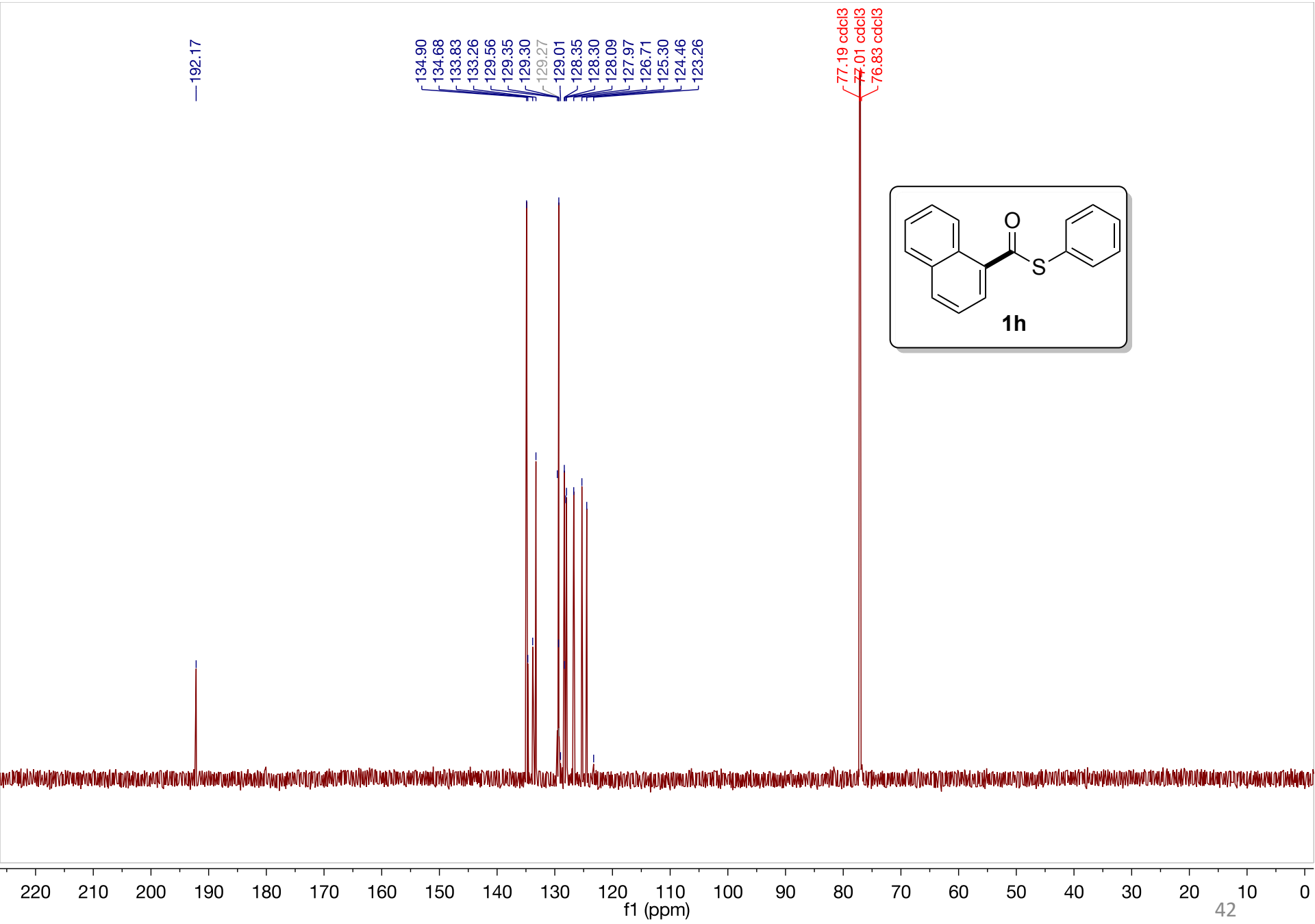

8.01
7.99
7.92
7.92
7.91
7.53
7.53
7.53
7.53
7.52
7.52
7.47
7.47
7.47
7.46
7.46
7.46
7.45
7.26
1.37
O
S
O
B
O
1f
2.00
2.02
1.97
2.97
12.48
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

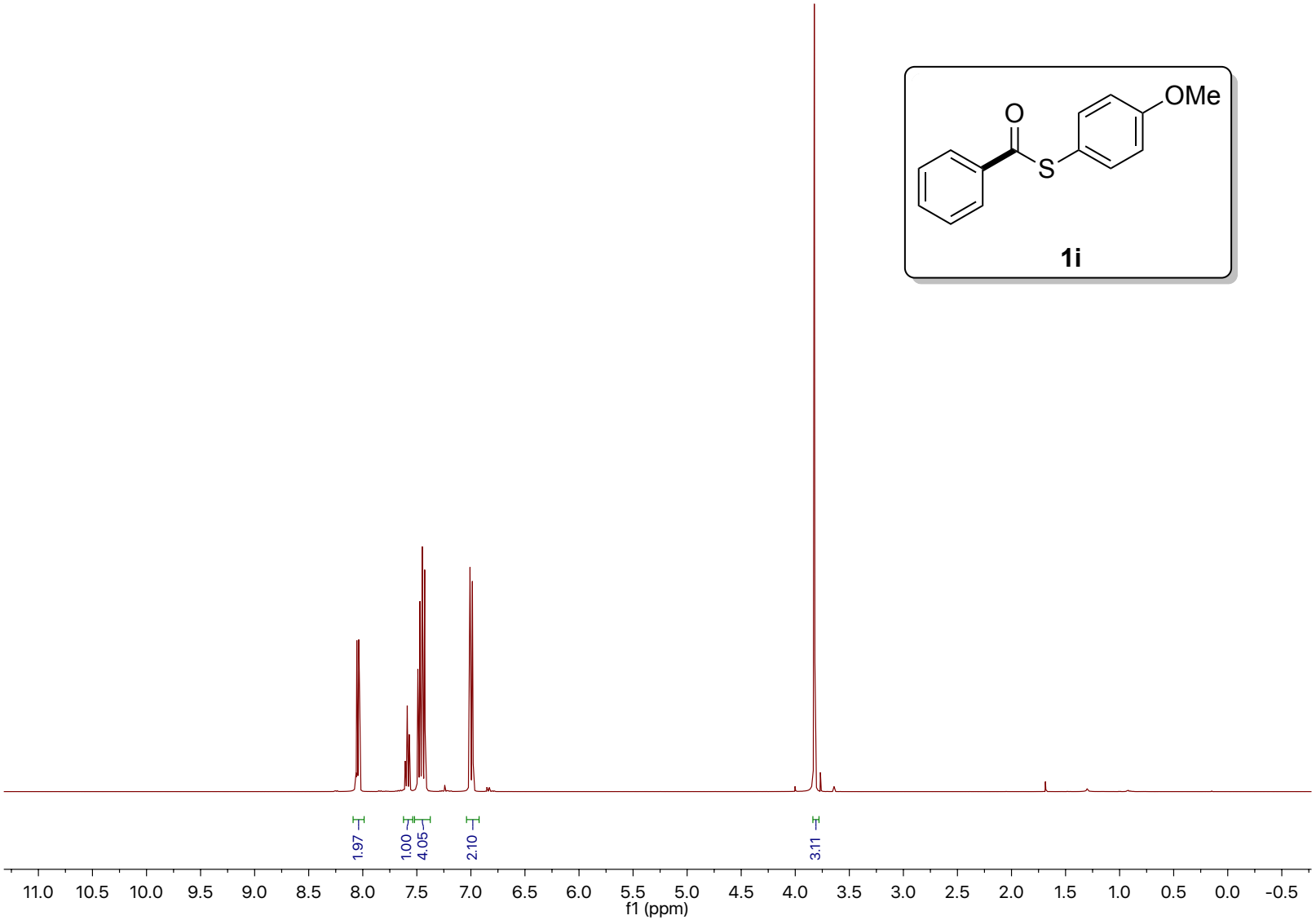

190.57
138.79
135.26
135.25
129.75
129.47
127.51
126.67
84.49
77.41
77.23
77.05
25.10
O
S
O
B
O
1f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

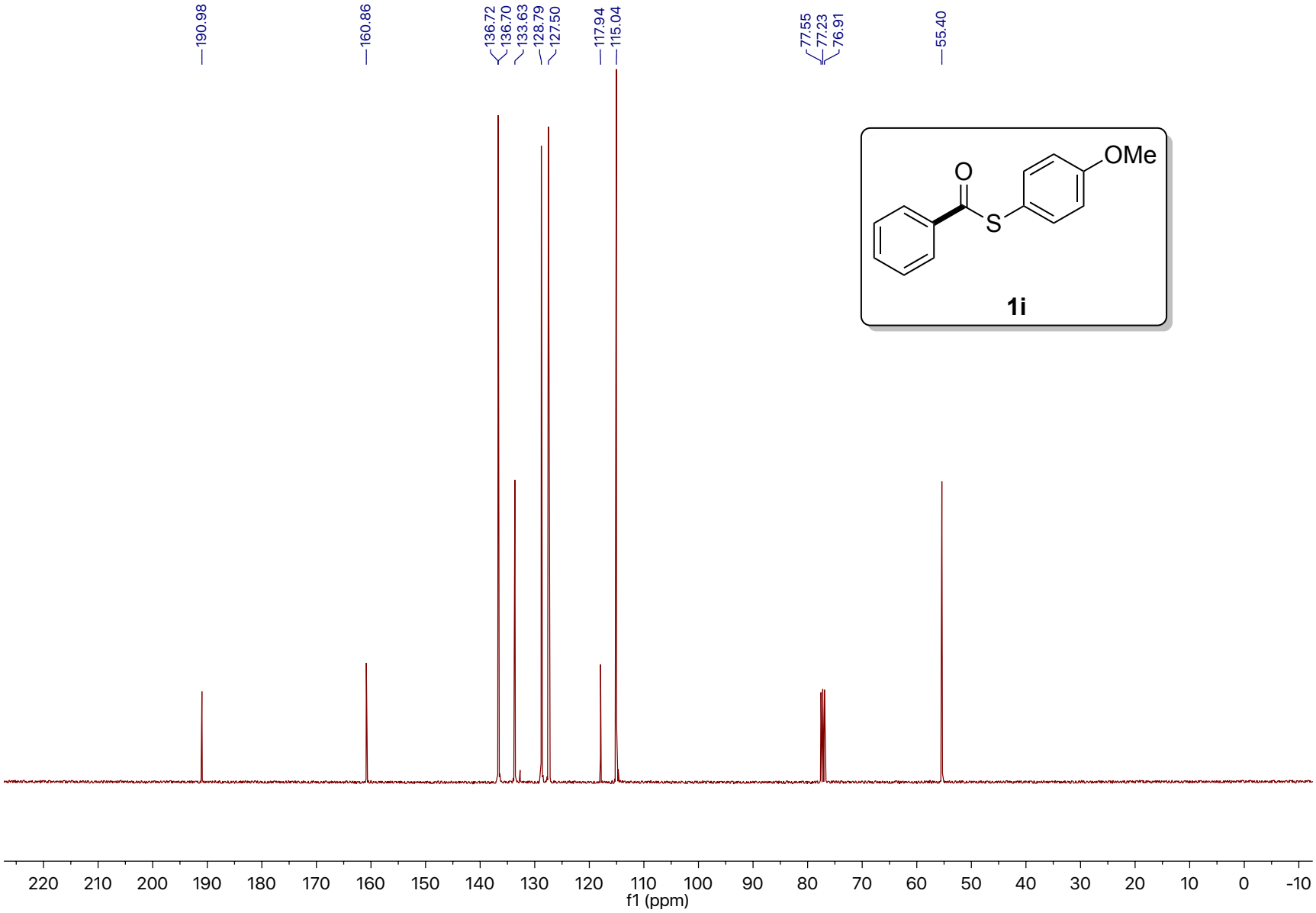

8.00
7.99
7.98
7.97
7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.46
7.46
7.44
7.44
7.36
7.34
7.31
7.29
7.28
2.54
O
S
Me
1g
1.00
5.87
2.20
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

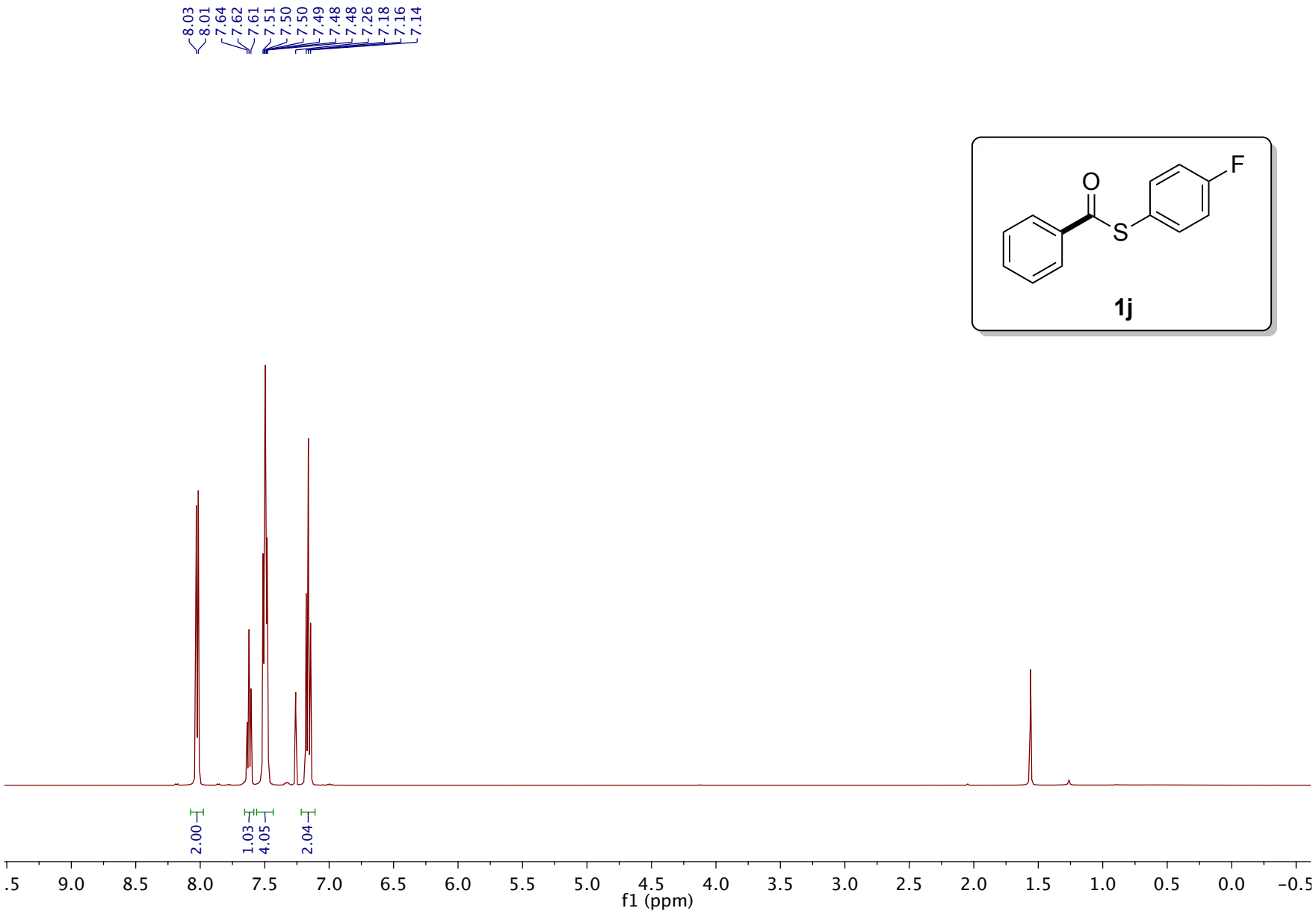

192.15
137.42
136.72
134.89
132.00
131.73
129.45
129.25
128.62
128.19
125.84
77.19 cdcl3
77.01 cdcl3
76.83 cdcl3
20.78
O
S
Me
1g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

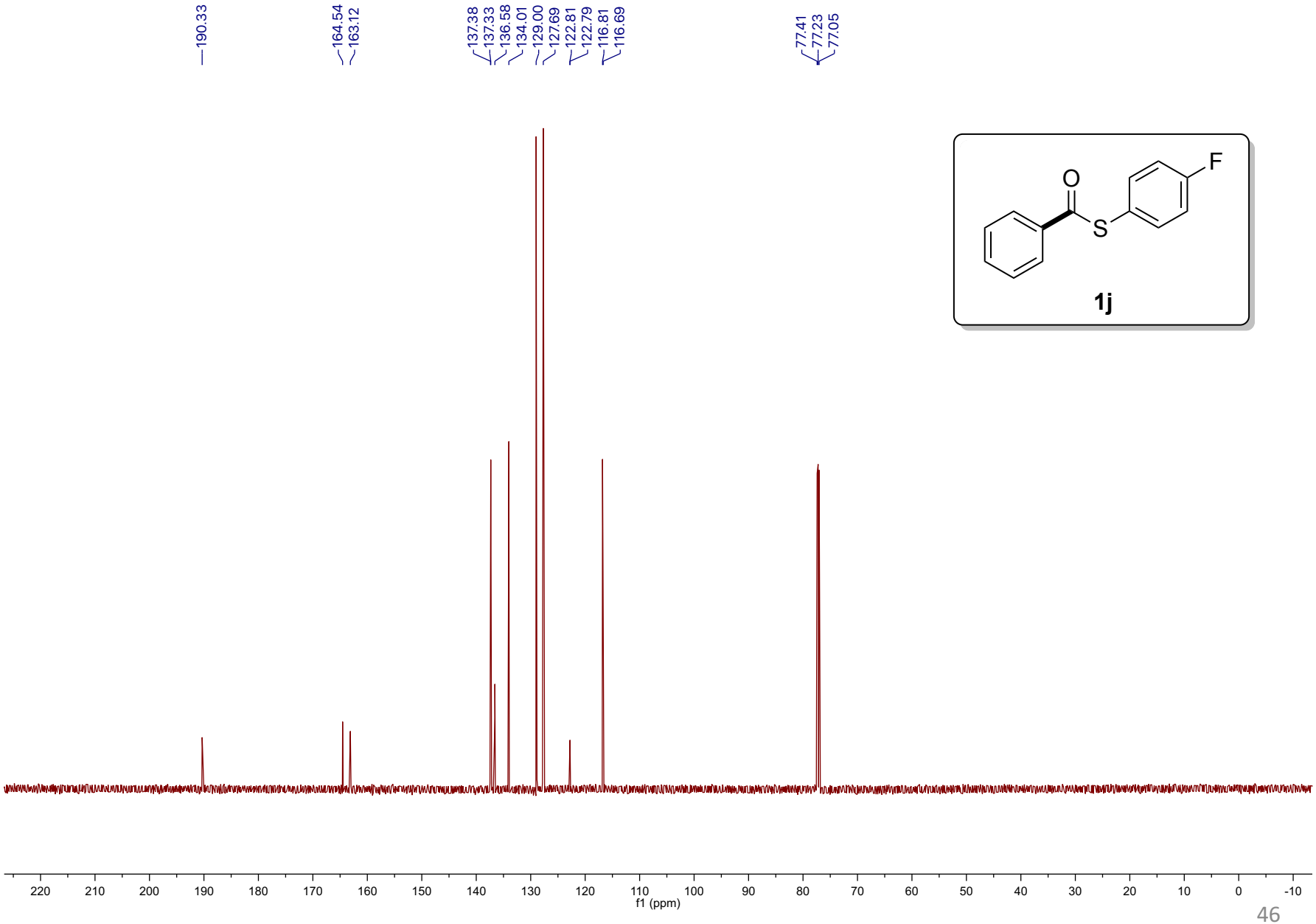

8.56
8.54
8.24
8.23
8.06
8.04
7.91
7.89
7.62
7.62
7.61
7.60
7.59
7.59
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.52
7.51
7.50
7.50
7.50
7.49
7.48
7.26 cdcl3
O
S
1h
0.94
0.95
1.02
1.02
8.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

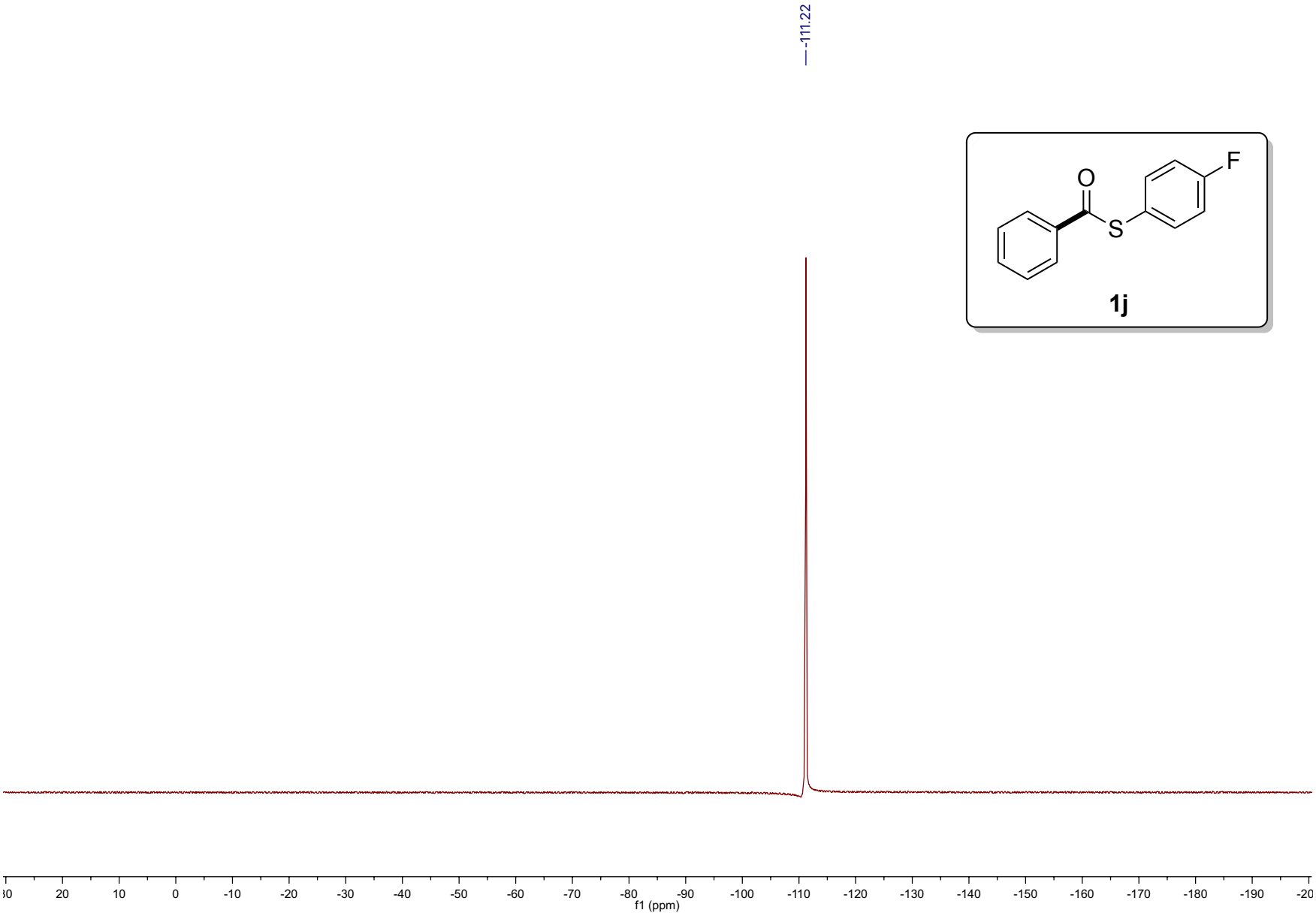

192.17
134.90
134.68
133.83
133.26
129.56
129.35
129.30
129.27
129.01
128.35
128.30
128.09
127.97
126.71
125.30
124.46
123.26
77.19 cdcl3
77.01 cdcl3
76.83 cdcl3
O
S
1h
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

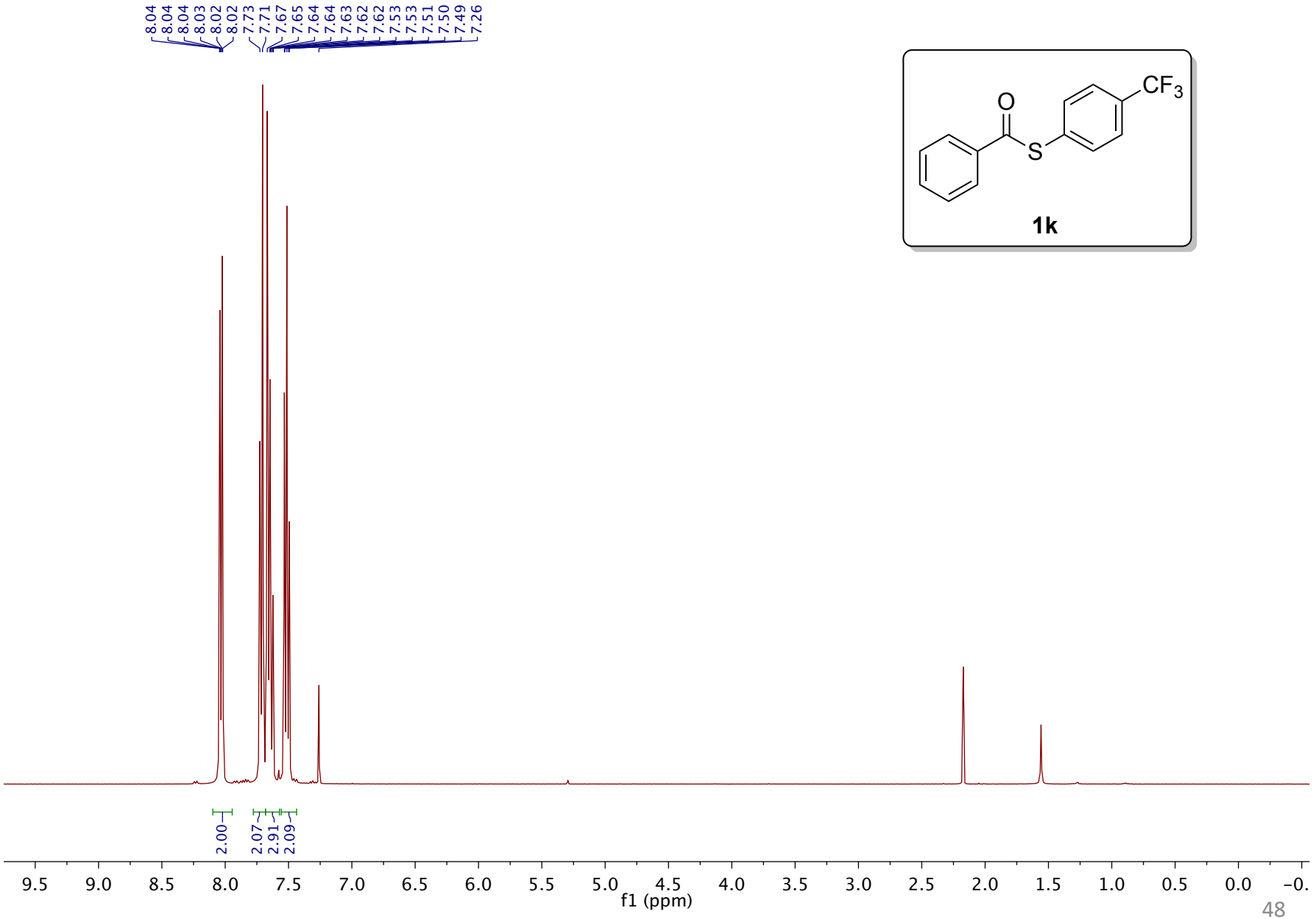

OMe
O
S
1i
1.97
1.00
4.05
2.10
3.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

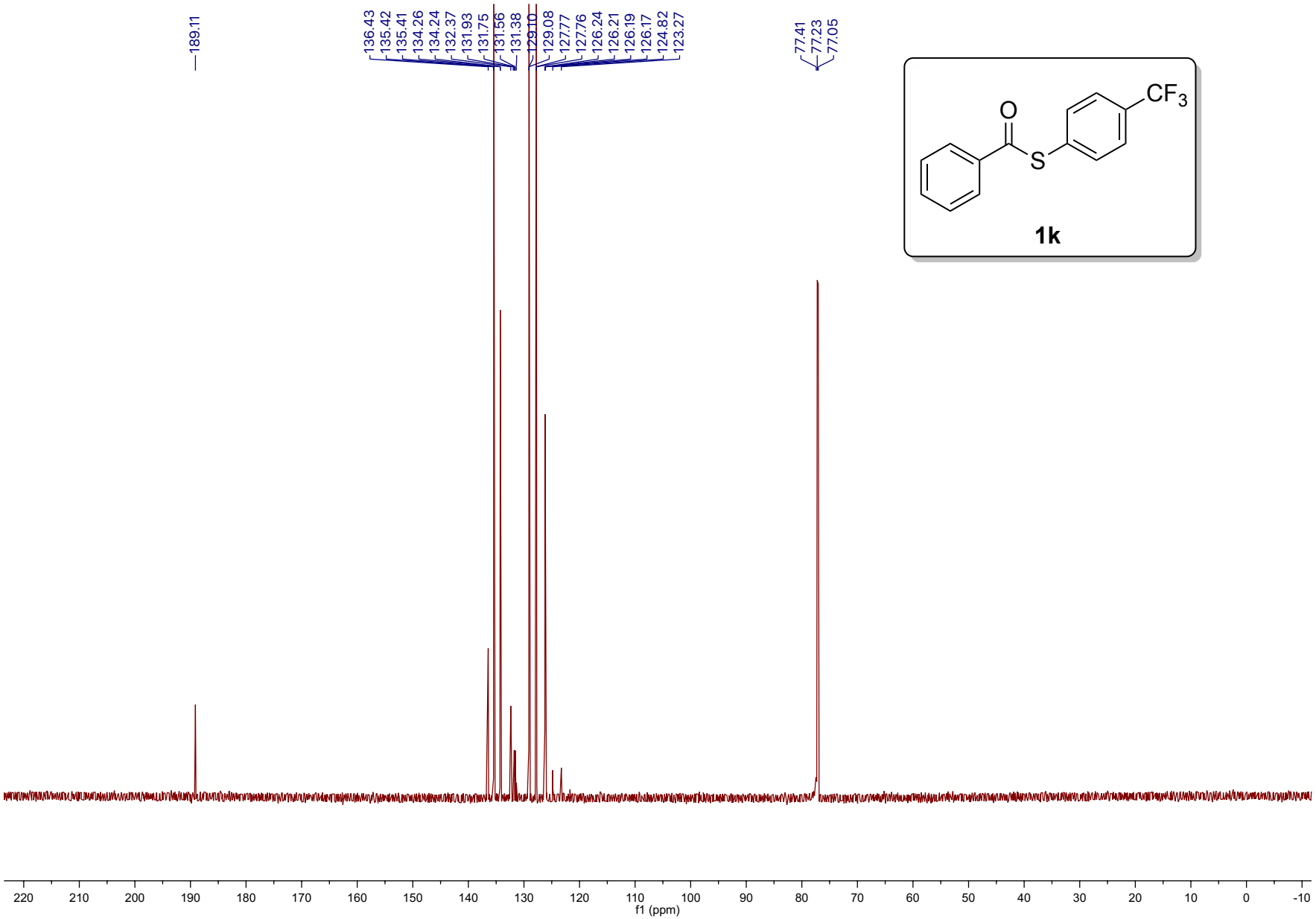

190.98
160.86
136.72
136.70
133.63
128.79
127.50
117.94
115.04
77.55
77.23
76.91
55.40
O
S
OMe
1i
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

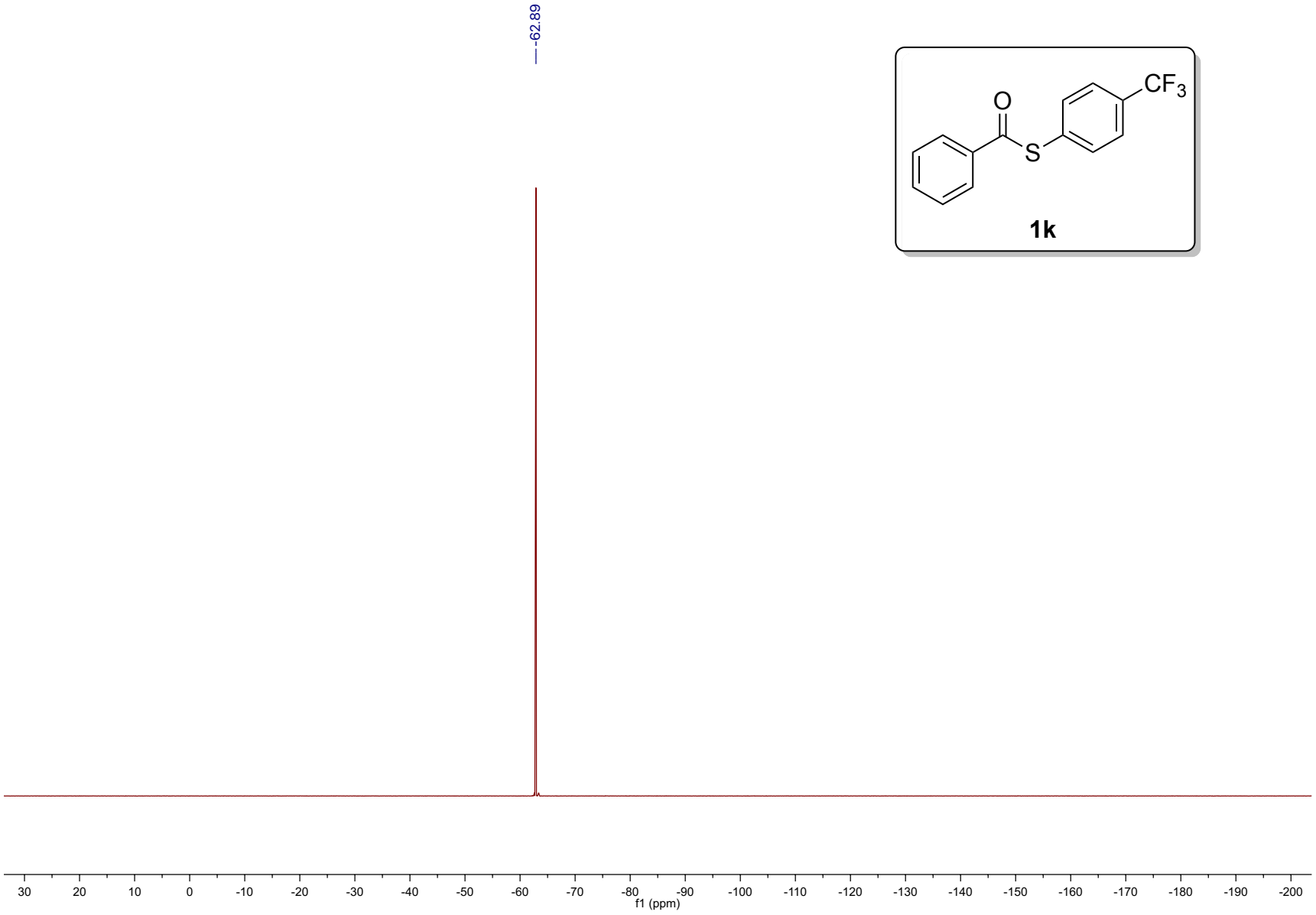

8.03
8.01
7.64
7.62
7.61
7.51
7.50
7.50
7.49
7.48
7.48
7.26
7.18
7.16
7.14
O
S
F
1j
2.00
1.03
4.05
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

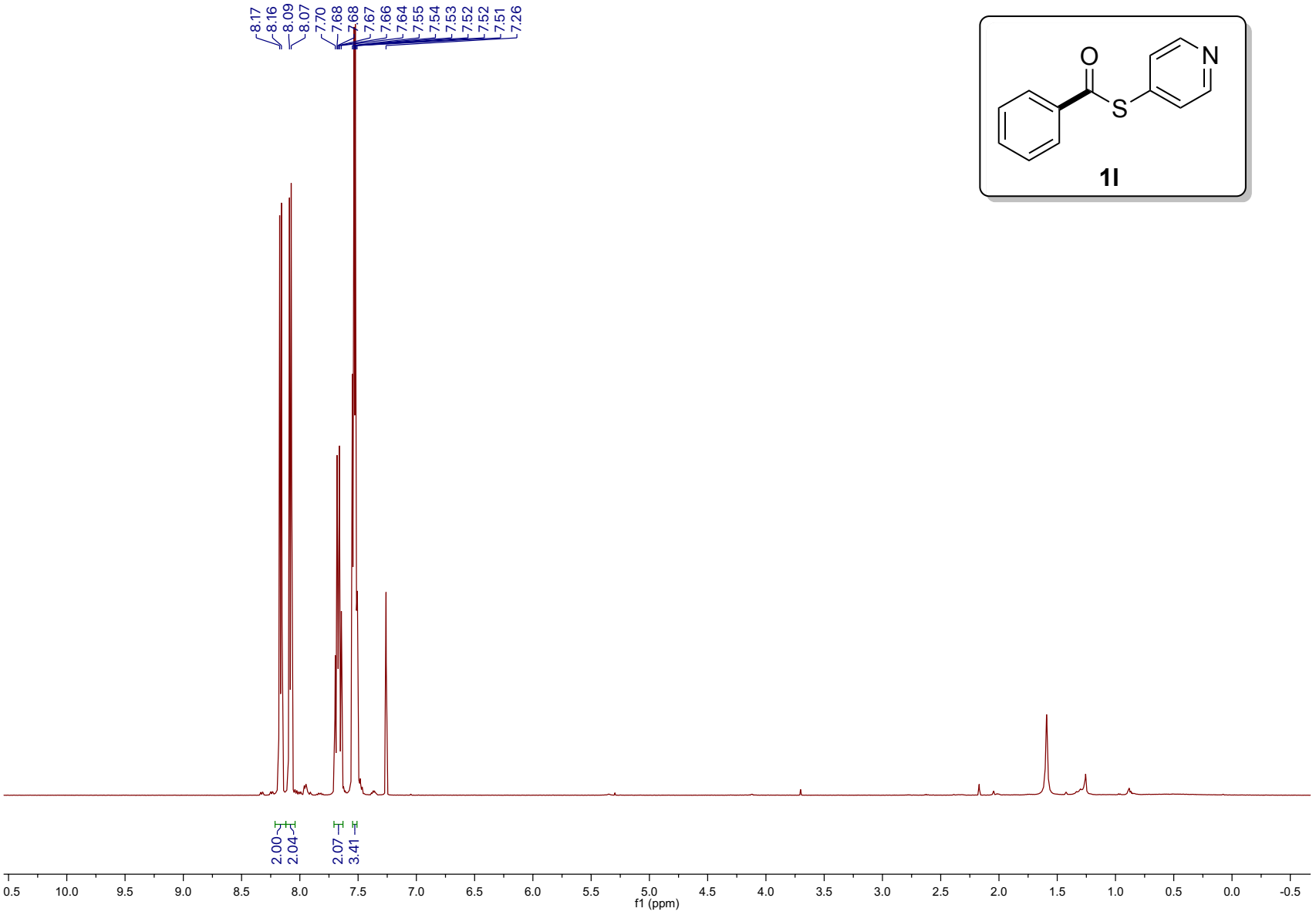

190.33
164.54
163.12
137.38
137.33
136.58
134.01
129.00
127.69
122.81
122.79
116.81
116.69
77.41
77.23
77.05
O
S
F
1j
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-111.22
O
S
F
1j
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)


8.04
8.04
8.04
8.03
8.02
8.02
7.73
7.71
7.67
7.65
7.64
7.64
7.63
7.62
7.62
7.53
7.53
7.51
7.50
7.49
7.26
2.00
2.07
2.91
2.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
S
CF3
1k

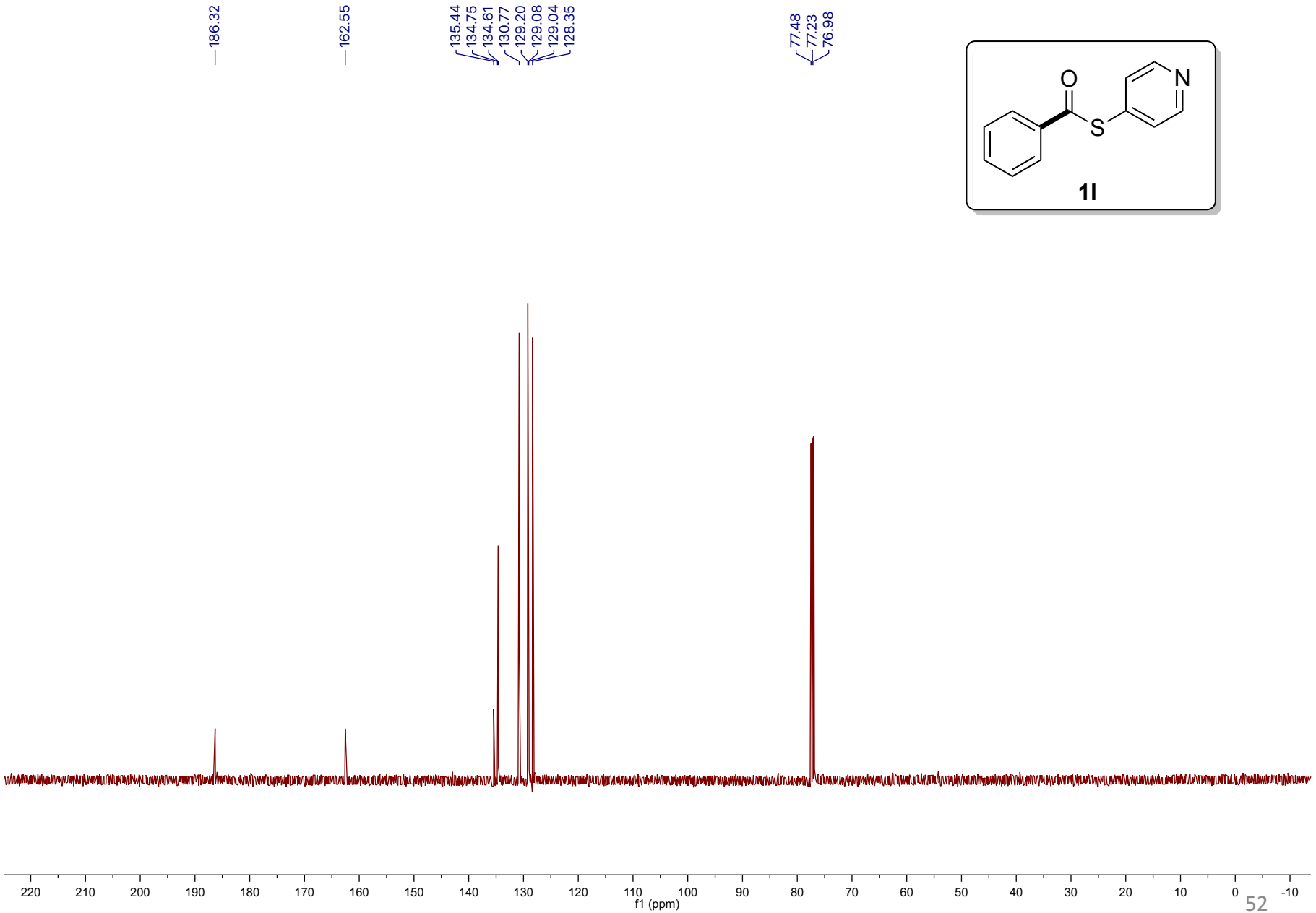

189.11
136.43
135.42
135.41
134.26
134.24
132.37
131.93
131.75
131.56
131.38
129.10
129.08
127.77
127.76
126.24
126.21
126.19
126.17
124.82
123.27
77.41
77.23
77.05
O
S
CF3
1k
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

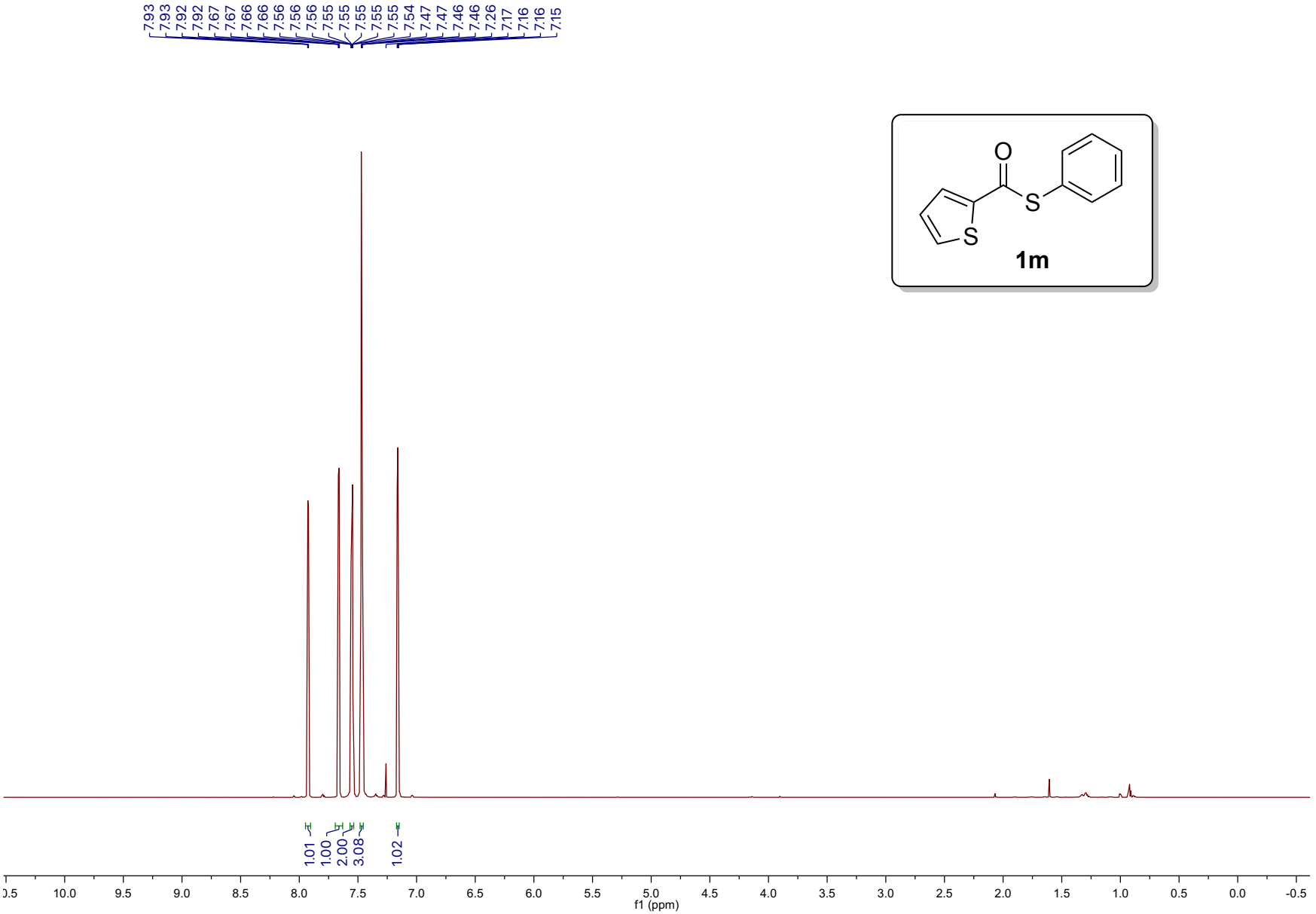

-62.89
O
S
CF3
1k
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

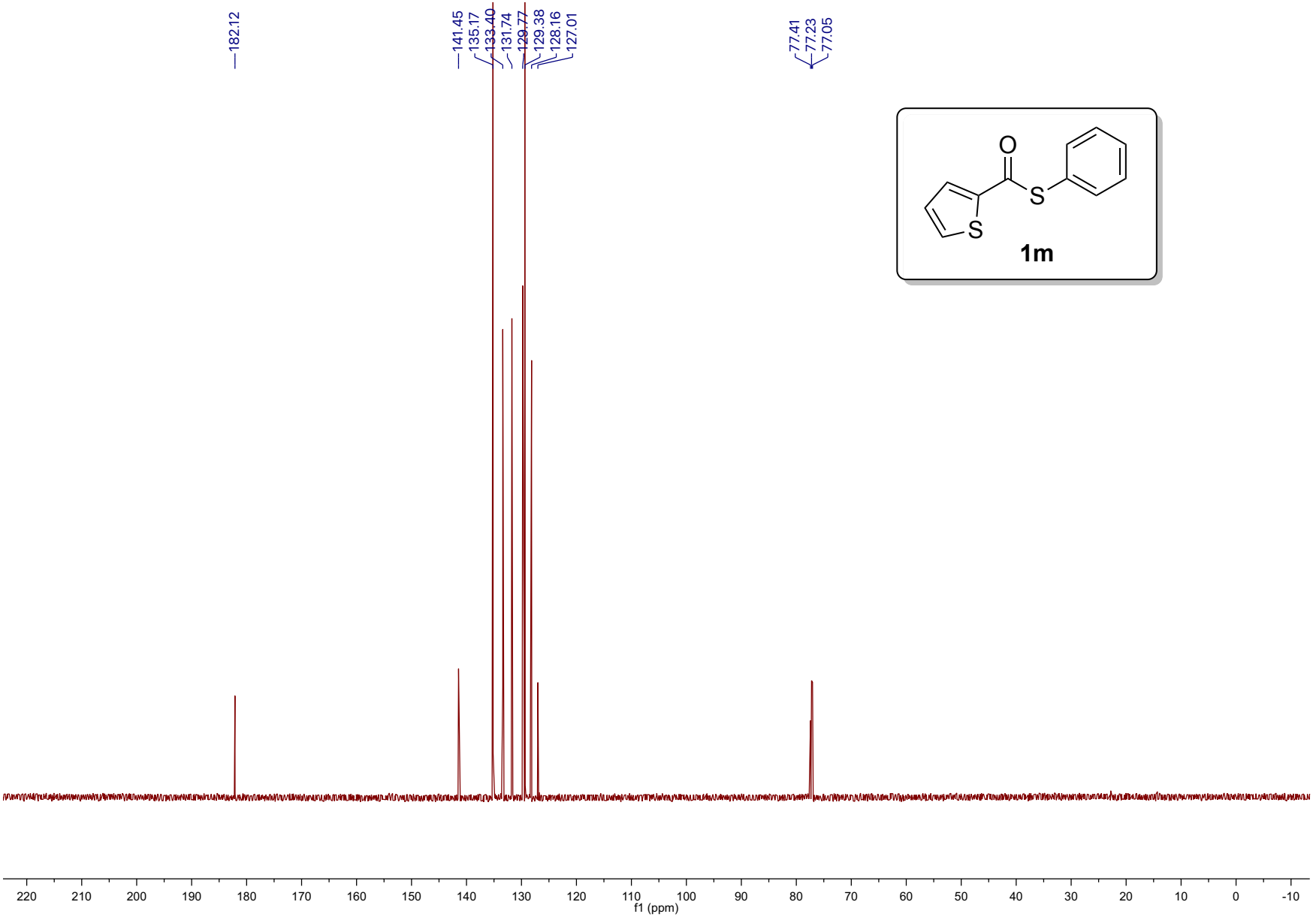

8.17
8.16
8.09
8.07
7.70
7.68
7.68
7.67
7.66
7.64
7.55
7.54
7.53
7.52
7.52
7.51
7.26
2.00
2.04
2.07
3.41
f1 (ppm)

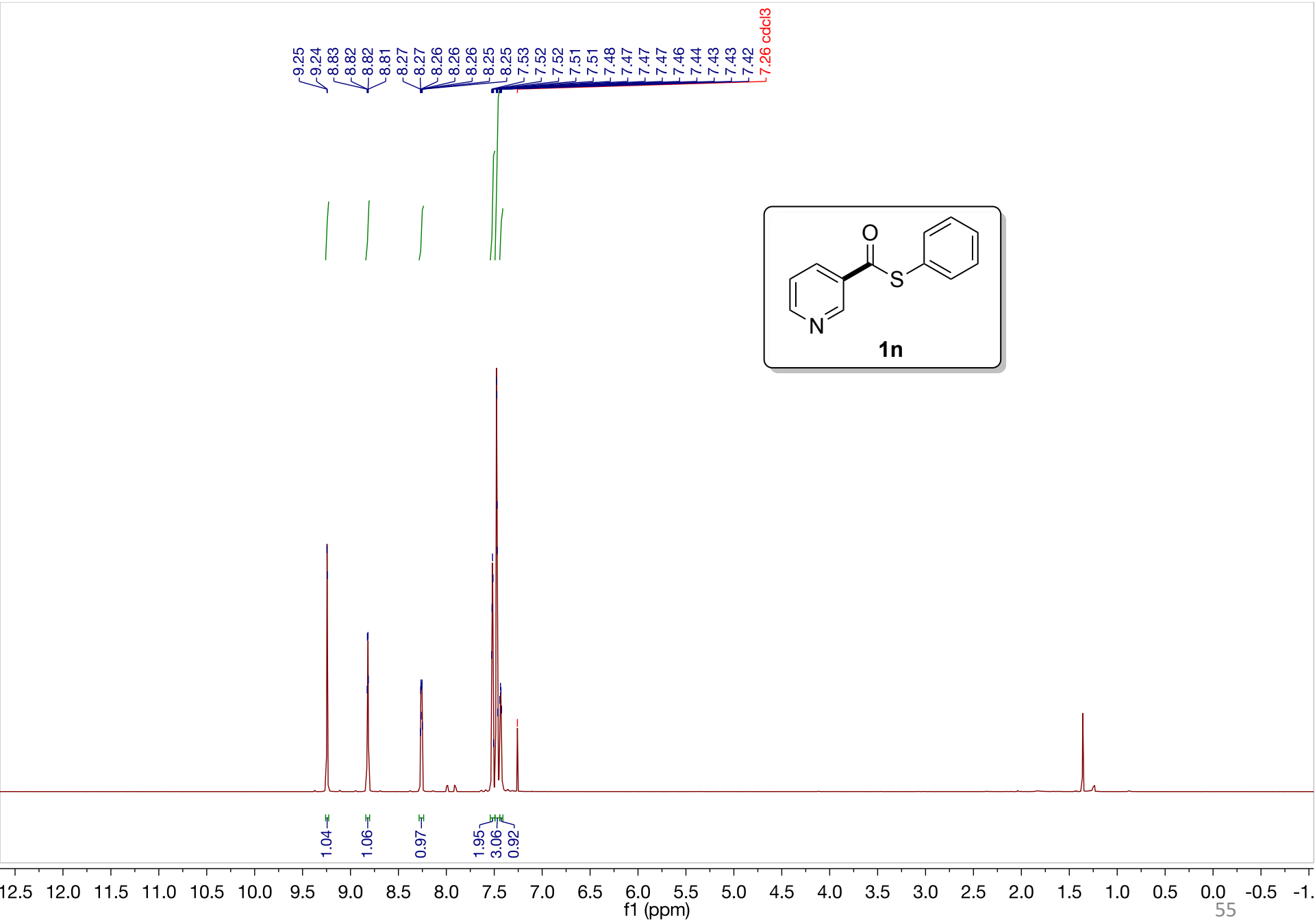
O
N
S

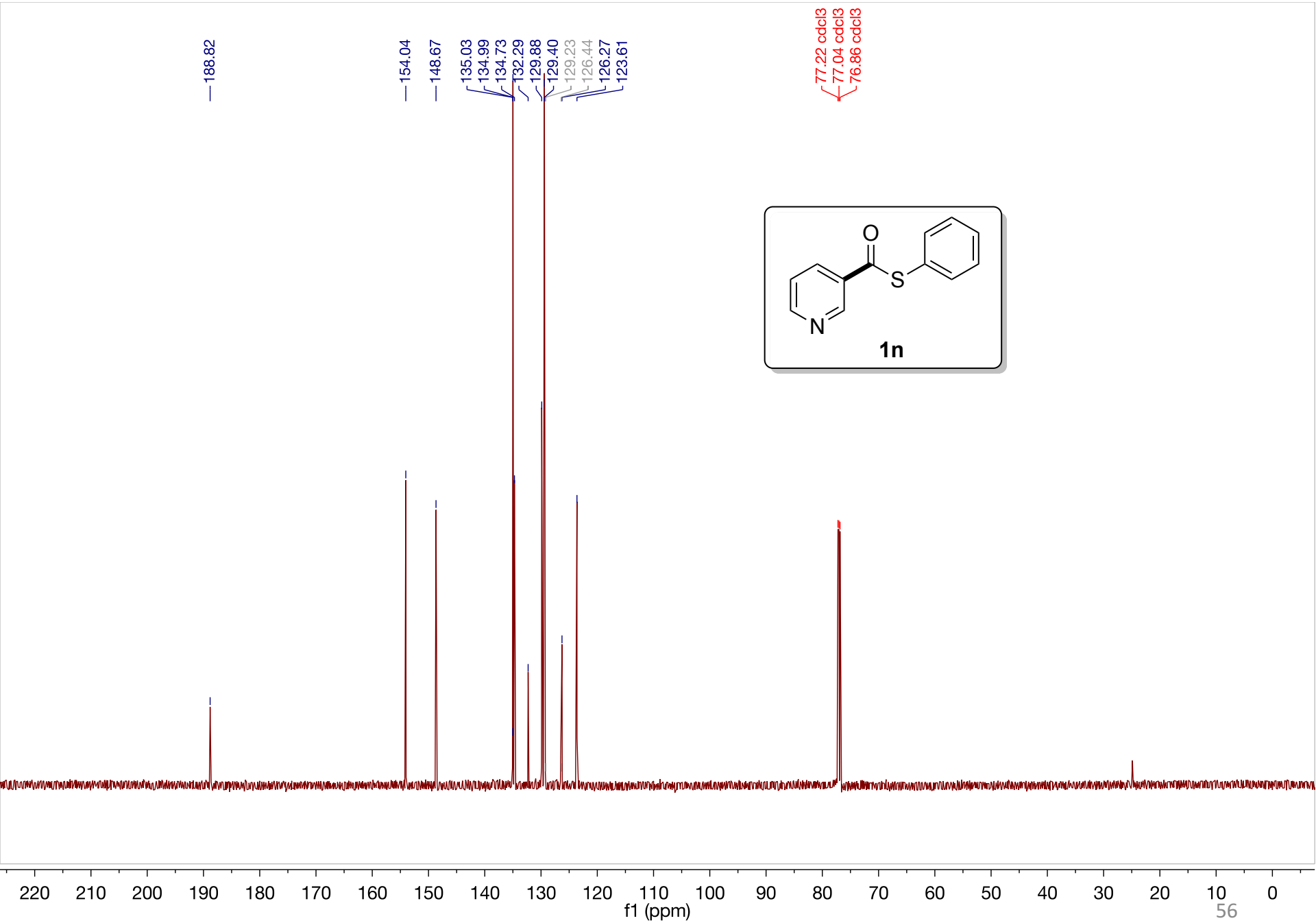
1l

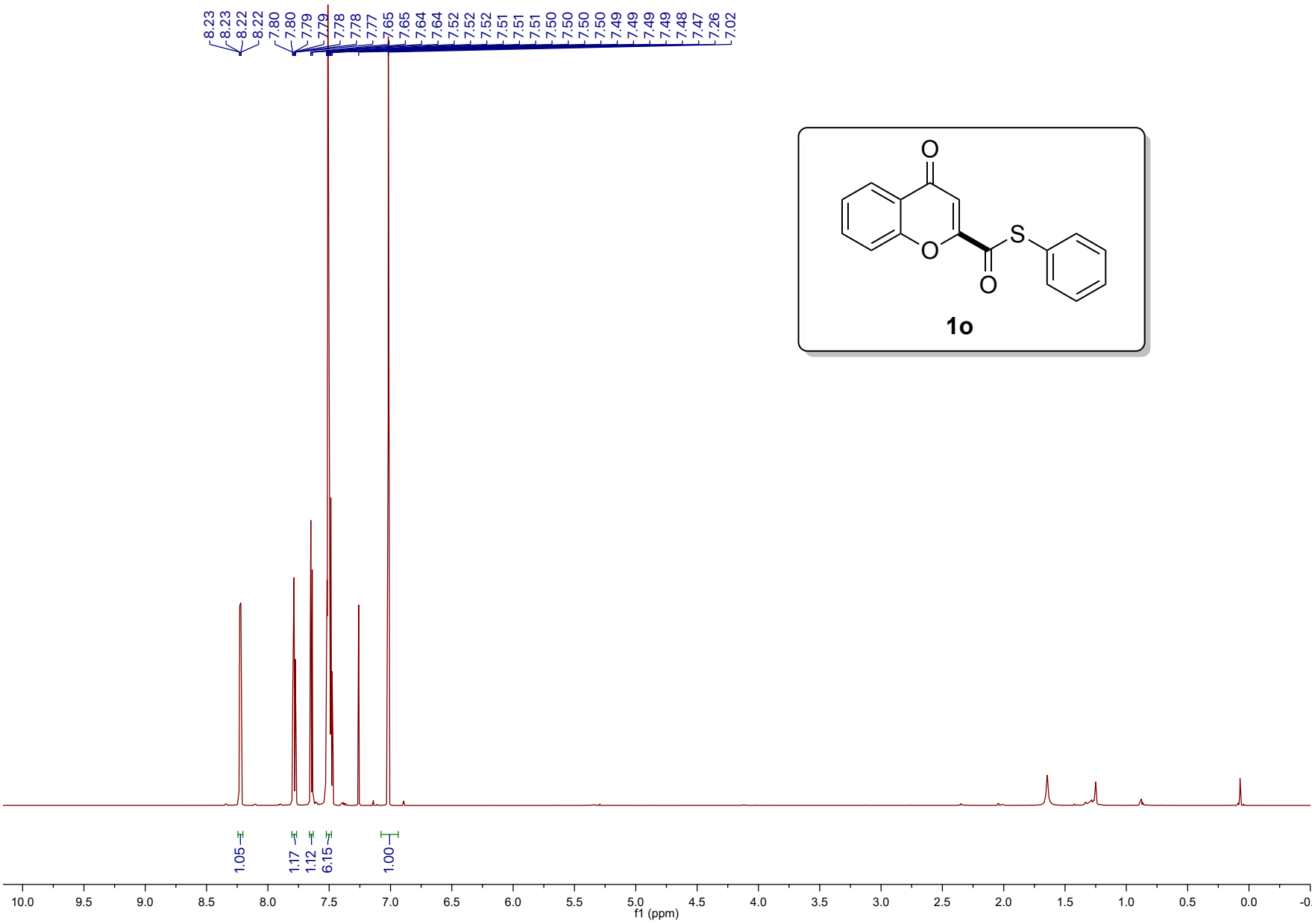

186.32
162.55
135.44
134.75
134.61
130.77
129.20
129.08
129.04
128.35
77.48
77.23
76.98
O
N
S
1l
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

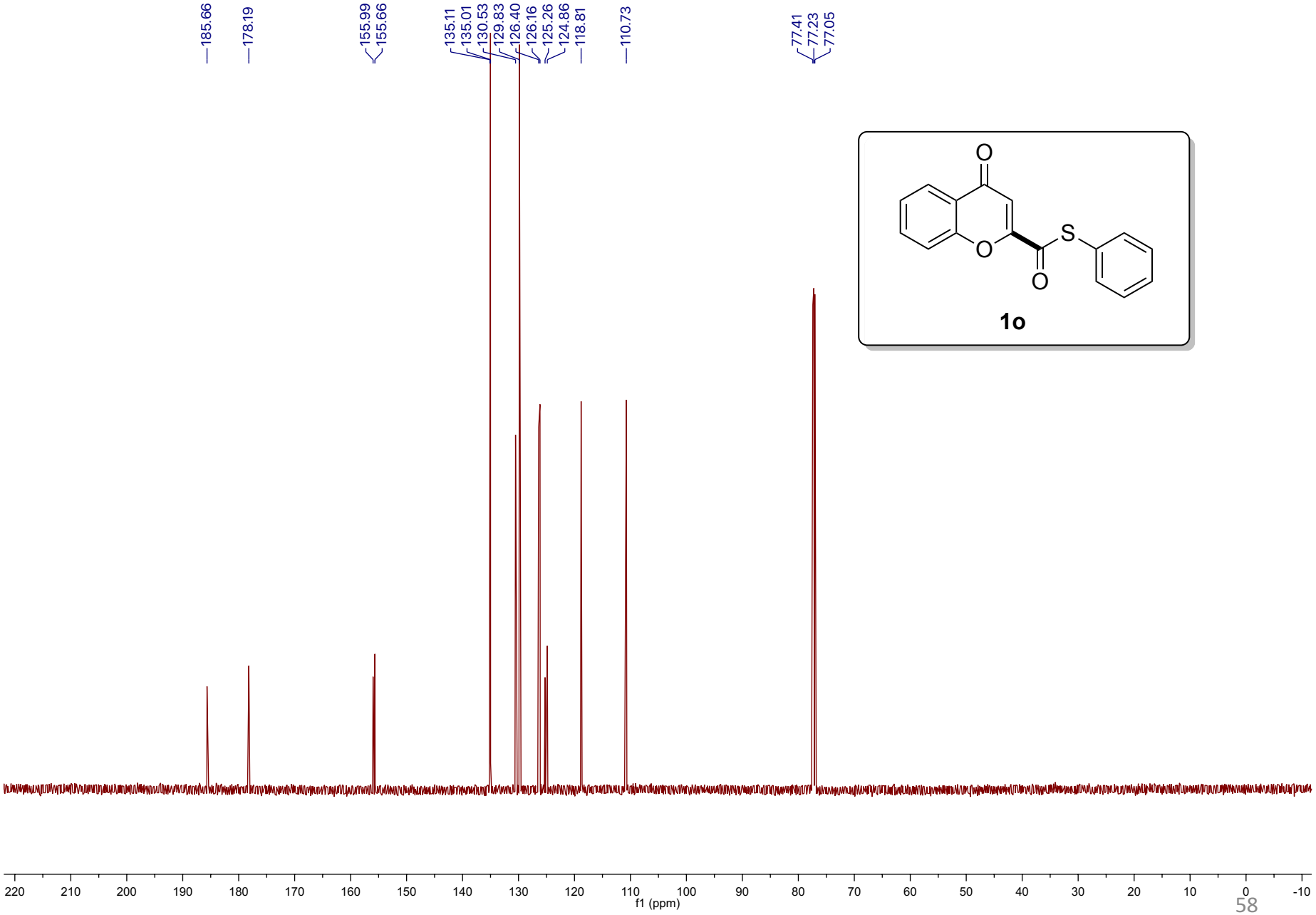

7.93
7.93
7.92
7.92
7.67
7.67
7.66
7.66
7.56
7.56
7.56
7.55
7.55
7.55
7.55
7.55
7.54
7.47
7.47
7.46
7.46
7.26
7.17
7.16
7.16
7.15
O
S
S
1m
1.01
1.00
2.00
3.08
1.02
f1 (ppm)

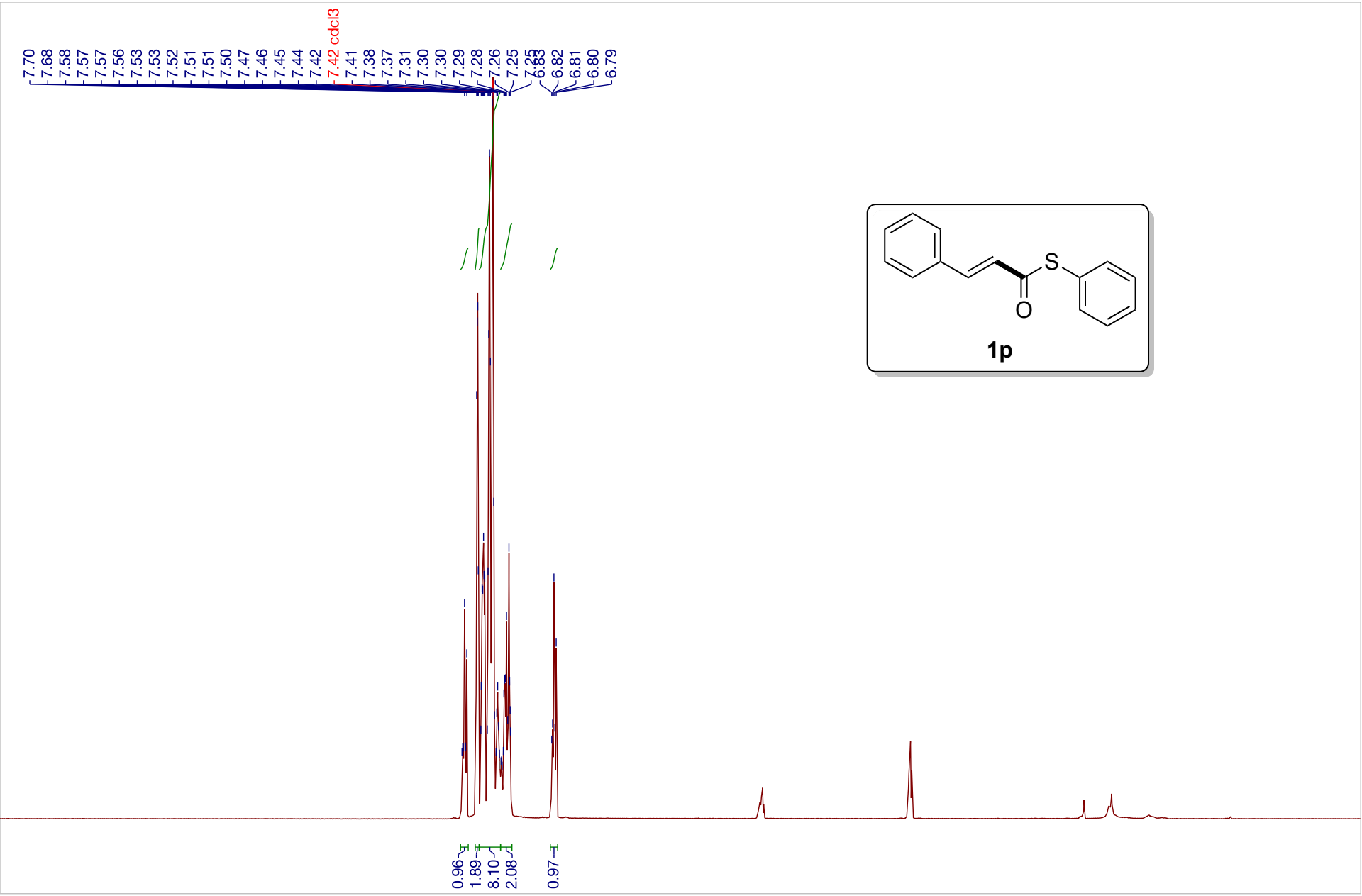

182.12
141.45
135.17
133.40
131.74
129.77
129.38
128.16
127.01
77.41
77.23
77.05
O
S
S
1m
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

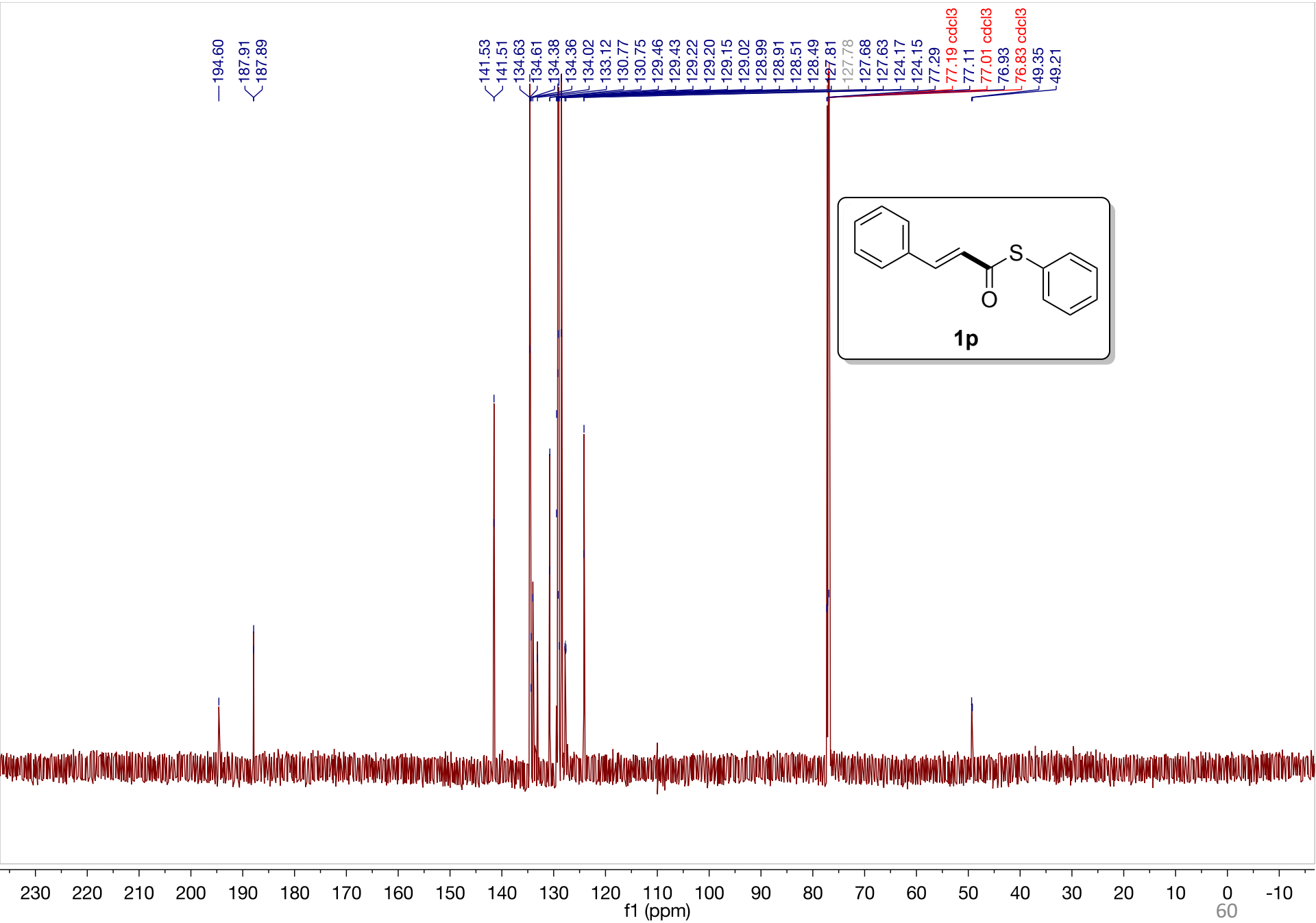

9.25
9.24
8.83
8.82
8.82
8.81
8.27
8.27
8.26
8.26
8.26
8.25
8.25
7.53
7.52
7.52
7.51
7.51
7.48
7.47
7.47
7.47
7.46
7.44
7.43
7.43
7.42
7.26 cdcl3
O
S
N
1n
1.04
1.06
0.97
1.95
3.06
0.92
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

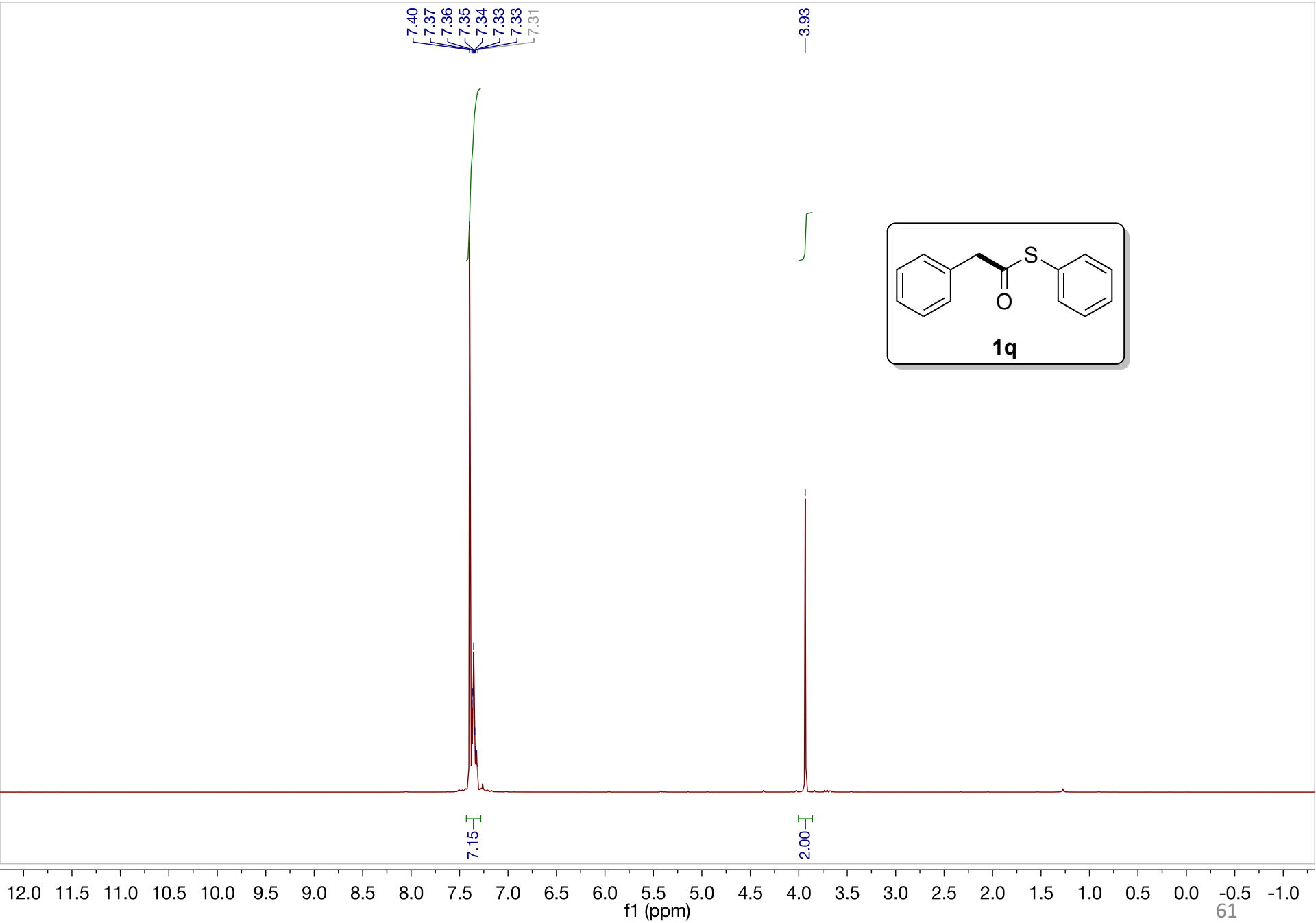

188.82
154.04
148.67
135.03
134.99
134.73
132.29
129.88
129.40
129.23
126.44
126.27
123.61
77.22 cdcl3
77.04 cdcl3
76.86 cdcl3
O
S
N
1n
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

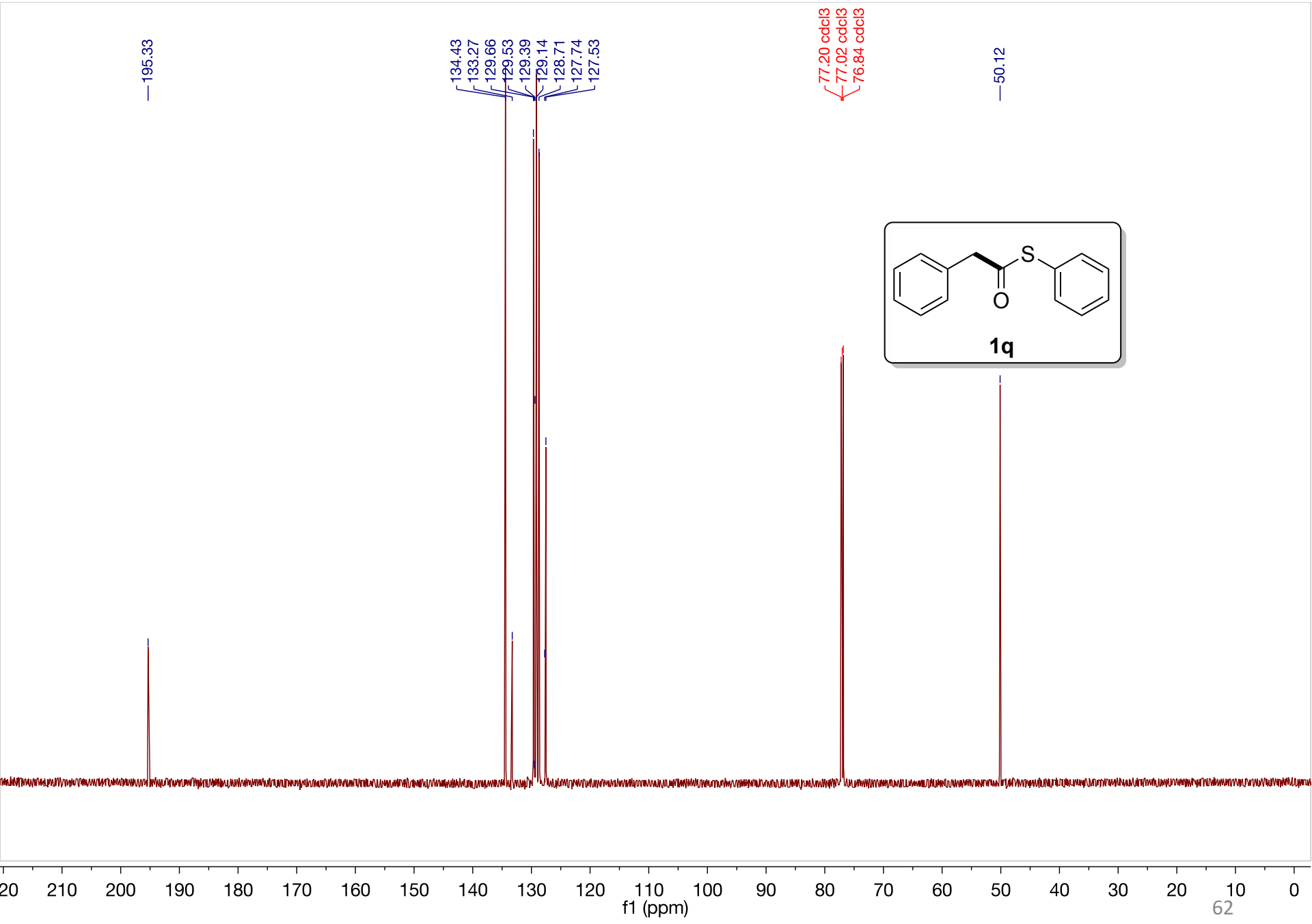

8.23
8.23
8.22
8.22
7.80
7.80
7.79
7.79
7.79
7.78
7.78
7.77
7.65
7.65
7.64
7.64
7.52
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.50
7.49
7.49
7.49
7.49
7.48
7.47
7.26
7.02
O
O
S
O
1o
1.05
1.17
1.12
6.15
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

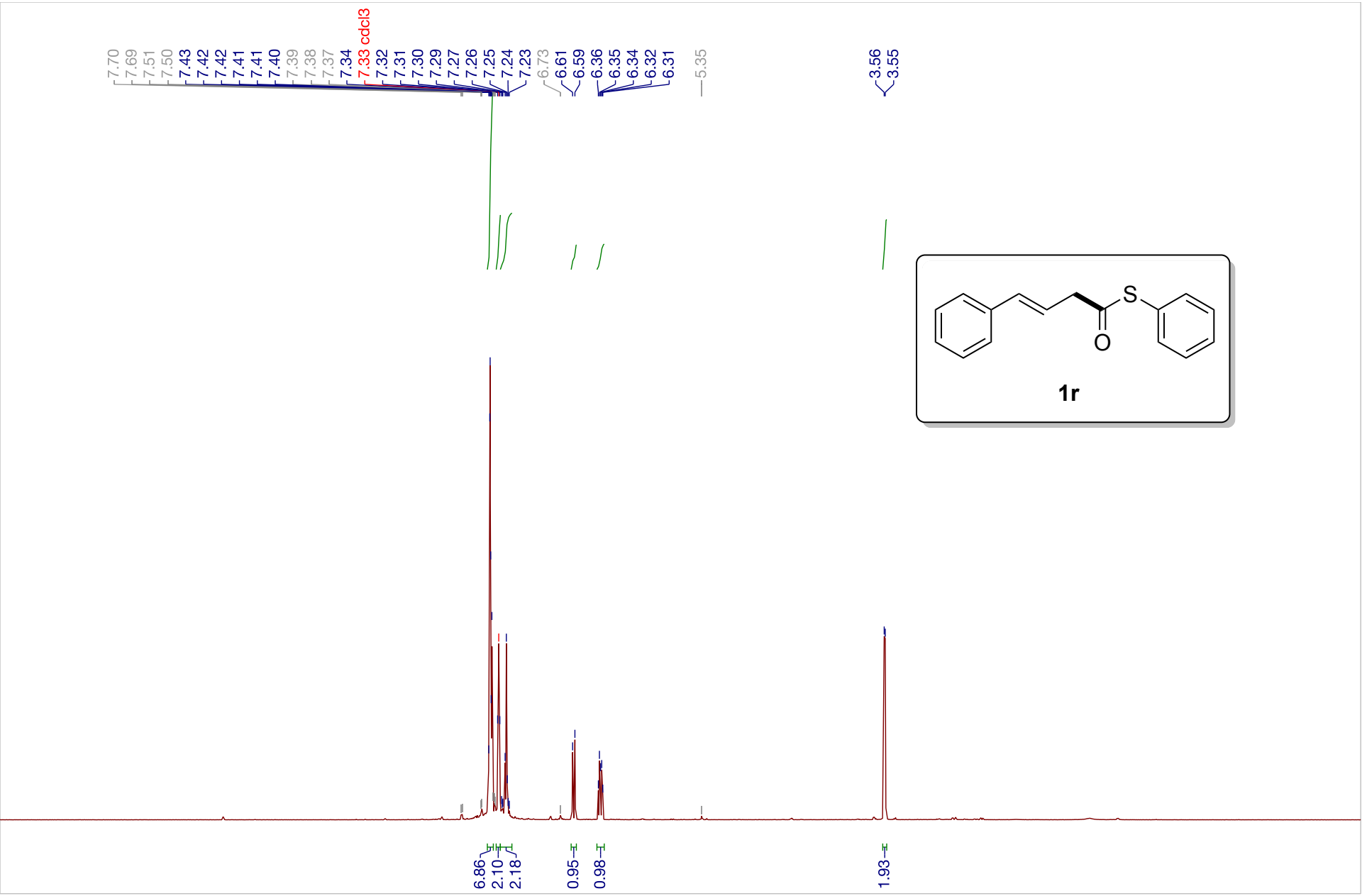

185.66
178.19
155.99
155.66
135.11
135.01
130.53
129.83
126.40
126.16
125.26
124.86
118.81
110.73
77.41
77.23
77.05
O
O
S
O
1o
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

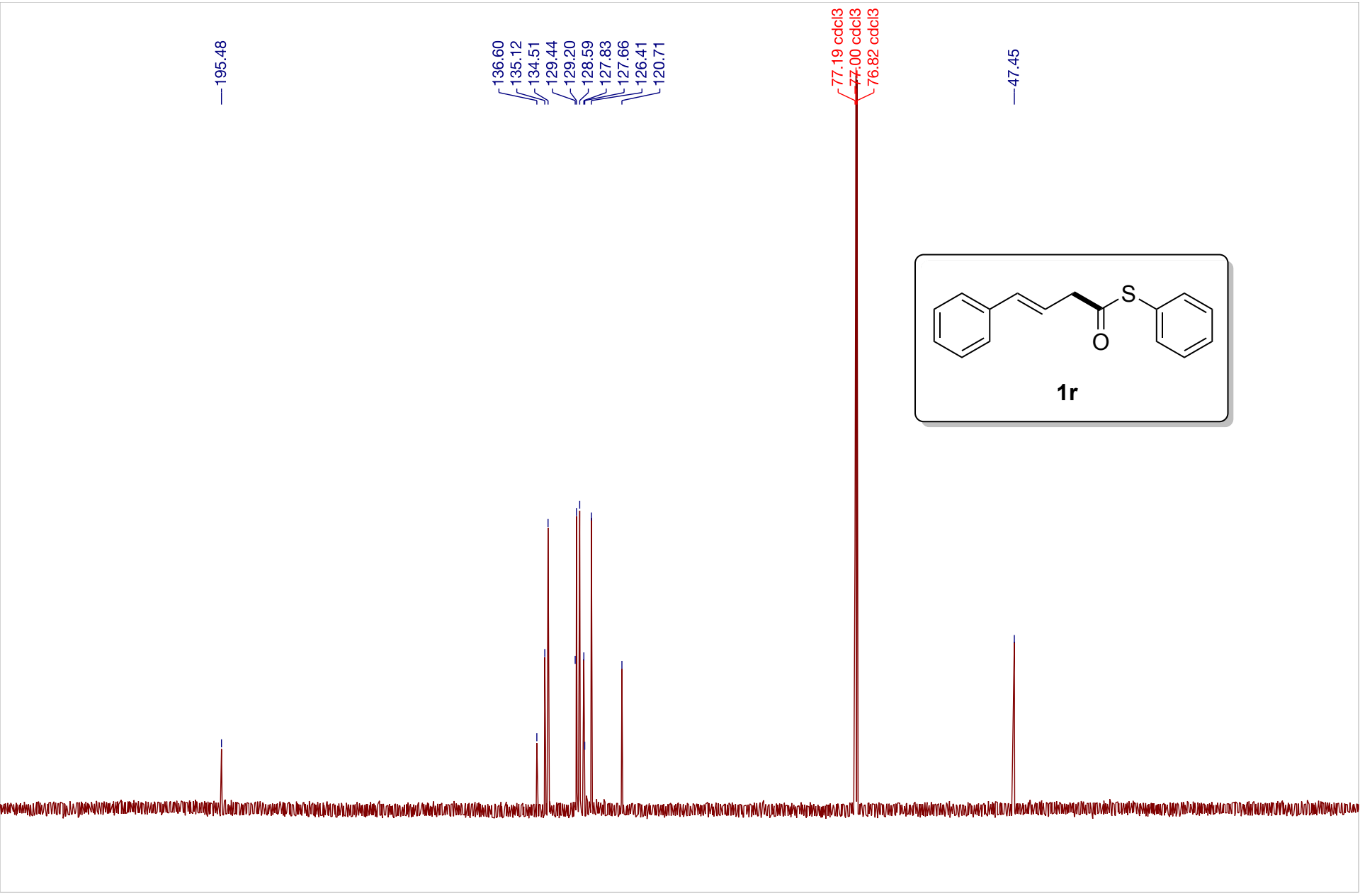

7.70
7.68
7.58
7.57
7.57
7.56
7.53
7.53
7.52
7.51
7.51
7.50
7.47
7.46
7.45
7.44
7.42
7.42 cdcl3
7.41
7.38
7.37
7.31
7.30
7.30
7.29
7.28
7.26
7.25
6.83
6.82
6.81
6.80
6.79
S
O
1p
0.96
1.89
8.10
2.08
0.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

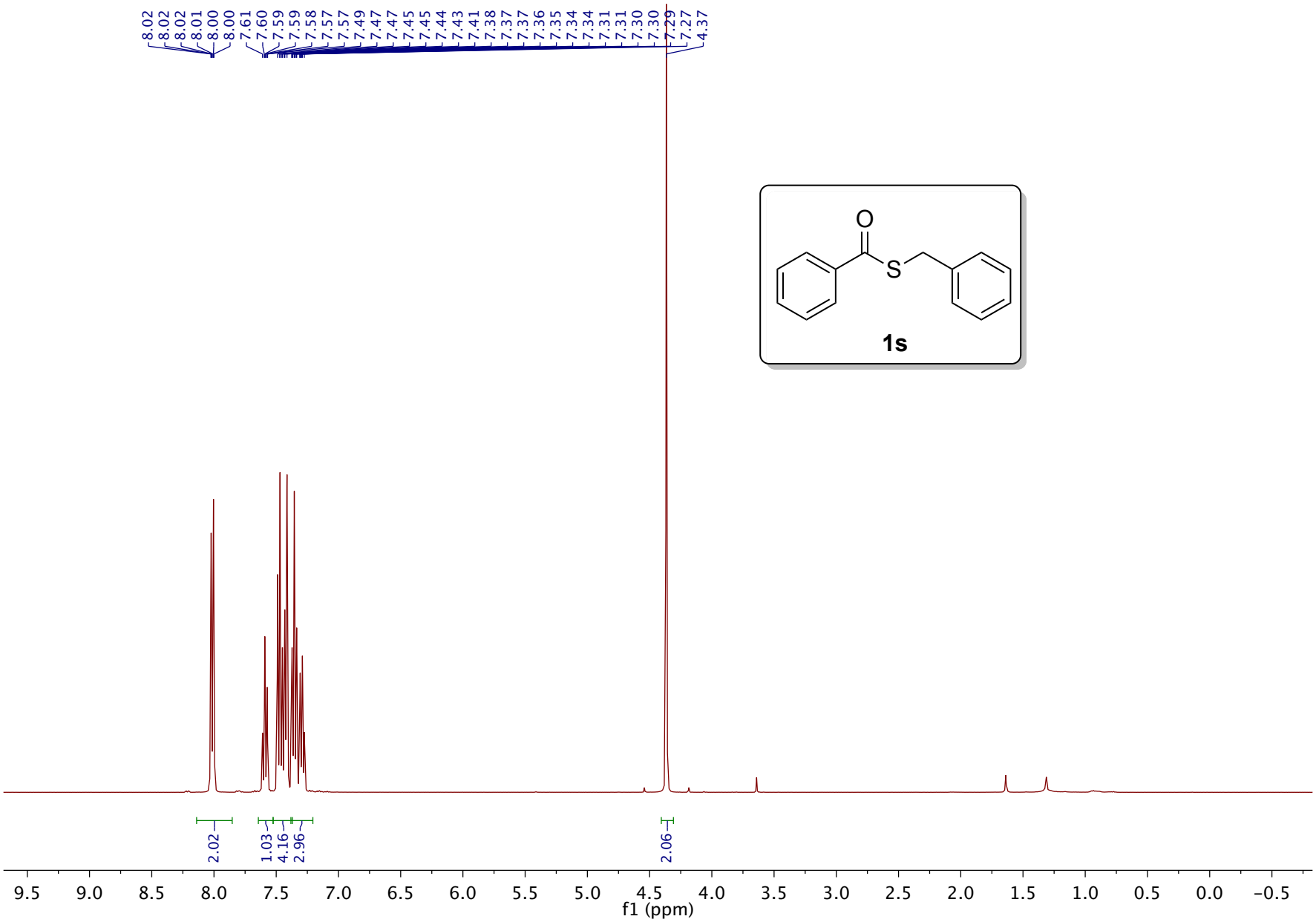

194.60
187.91
187.89
141.53
141.51
134.63
134.61
134.38
134.36
134.02
133.12
130.77
130.75
129.46
129.43
129.22
129.20
129.15
129.02
128.99
128.91
128.51
128.49
127.81
127.78
127.68
127.63
124.17
124.15
77.29
77.19 cdcl3
77.11
77.01 cdcl3
76.93
76.83 cdcl3
49.35
49.21
S
O
1p
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

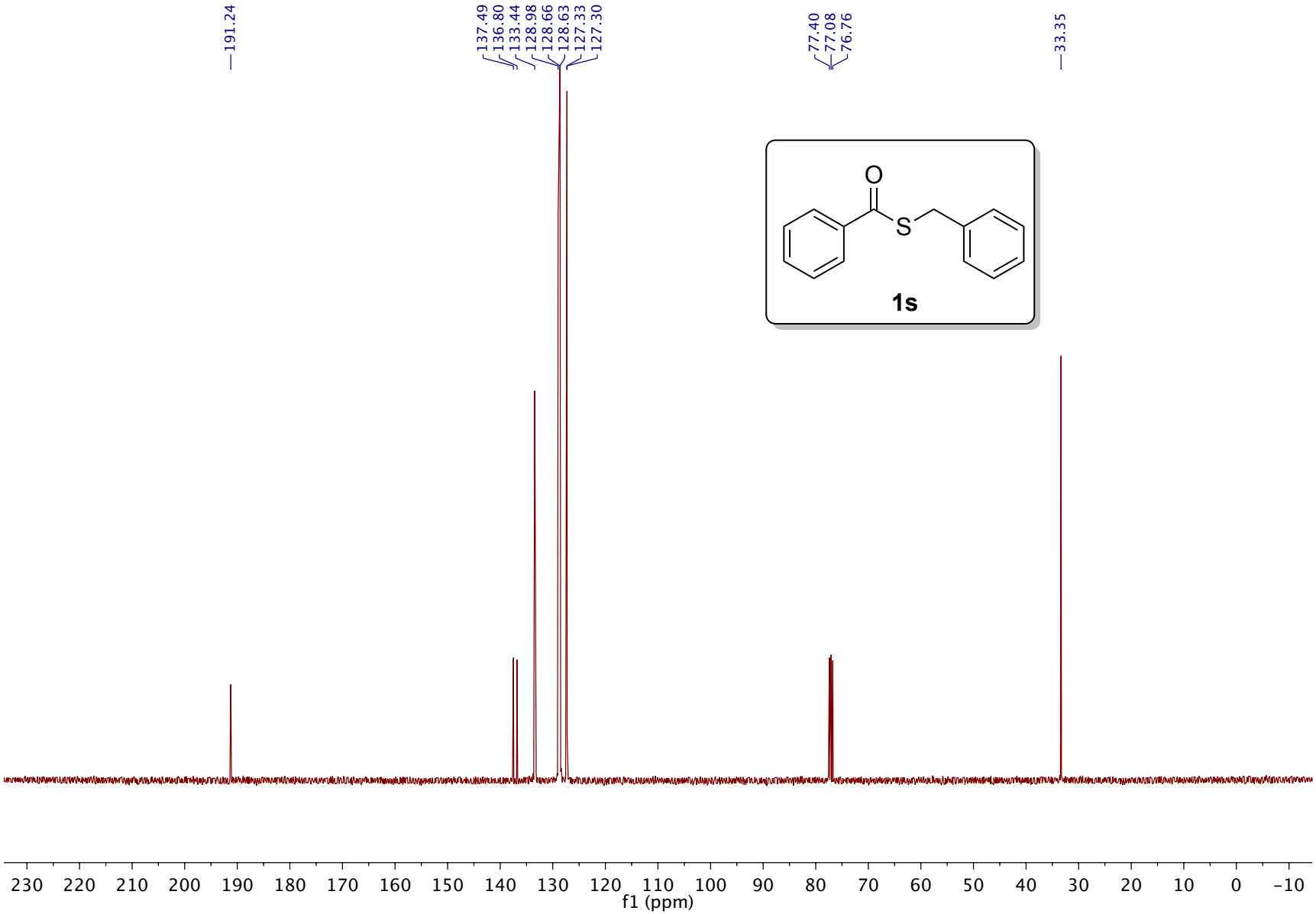

7.40
7.37
7.36
7.35
7.34
7.33
7.33
7.31
3.93
S
O
1q
7.15
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

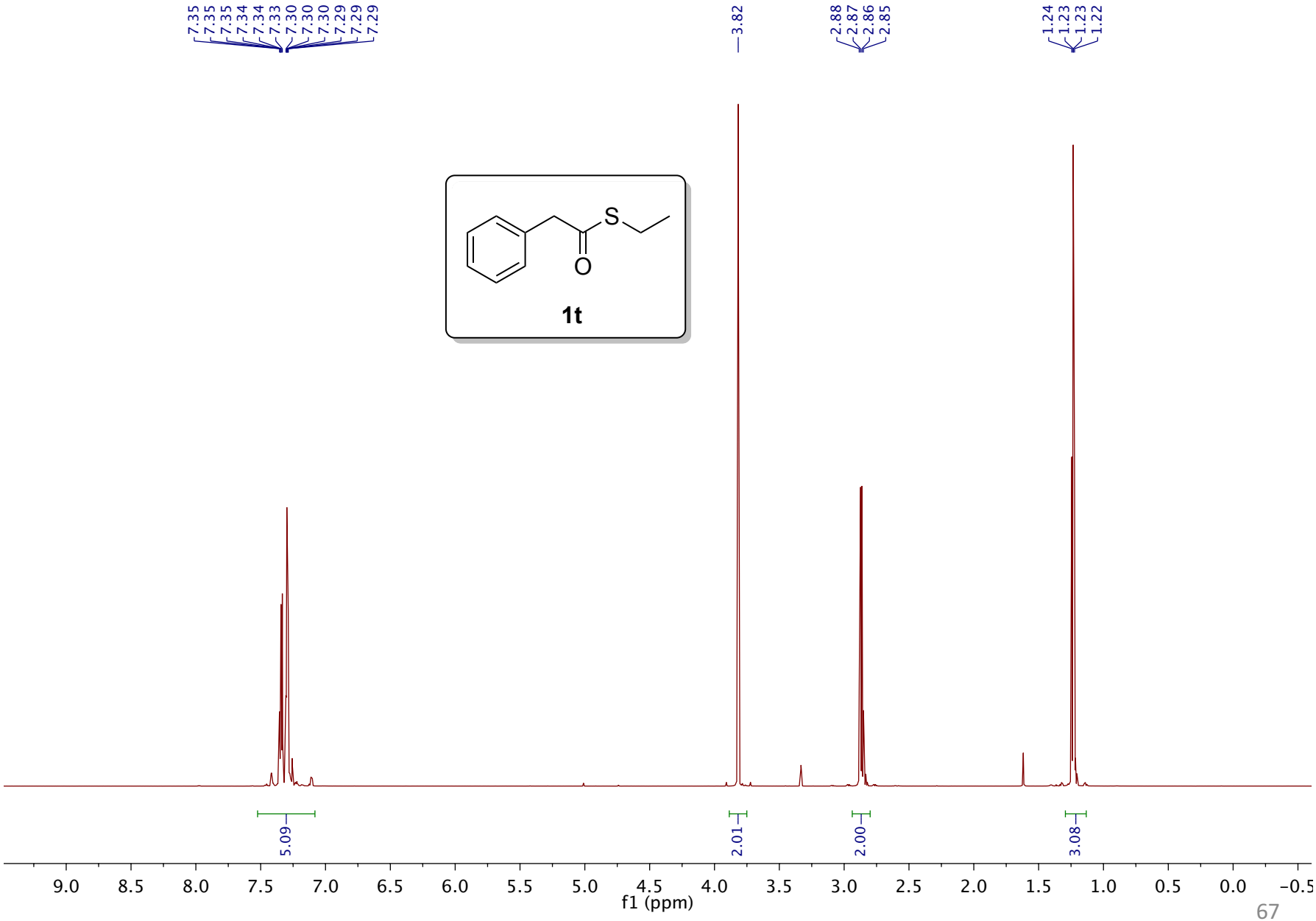

195.33
134.43
133.27
129.66
129.53
129.39
129.14
128.71
127.74
127.53
77.20 cdcl3
77.02 cdcl3
76.84 cdcl3
50.12
S
O
1q
f1 (ppm)

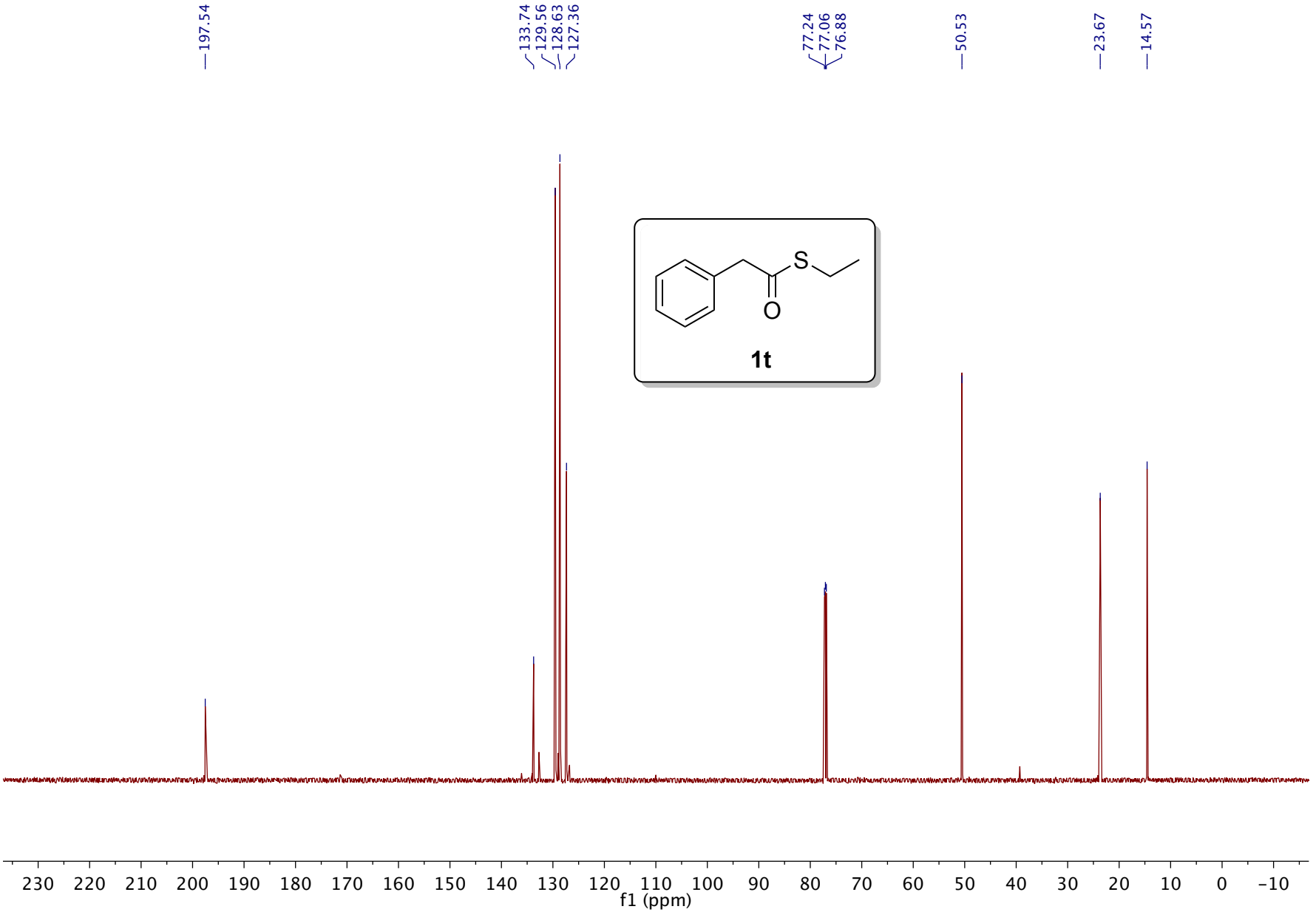

7.70
7.69
7.51
7.50
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.37
7.34
7.33 cdcl3
7.32
7.31
7.30
7.29
7.27
7.26
7.25
7.24
7.23
6.73
6.61
6.59
6.36
6.35
6.34
6.32
6.31
5.35
3.56
3.55
S
O
1r
6.86
2.10
2.18
0.95
0.98
1.93
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

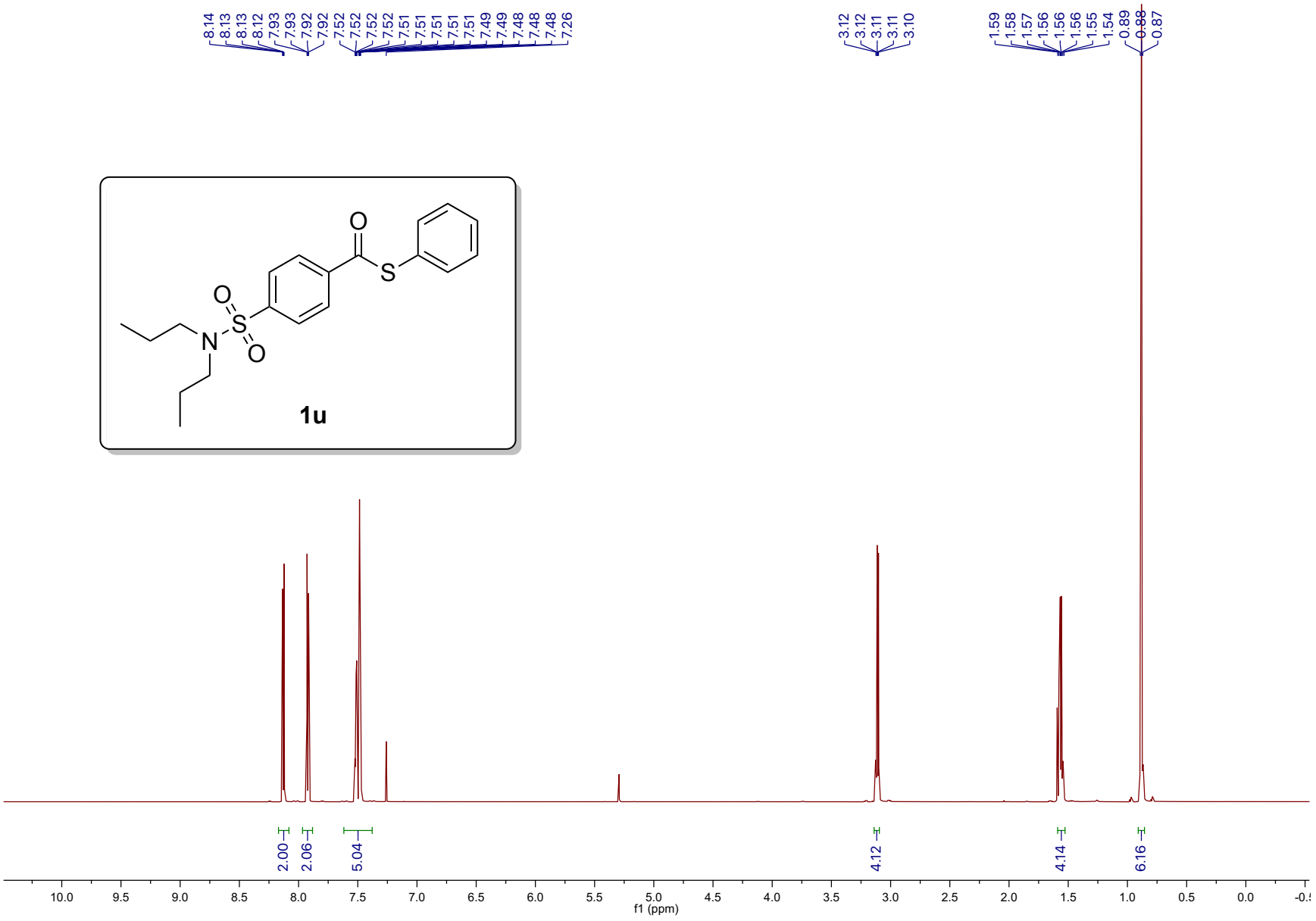

195.48
136.60
135.12
134.51
129.44
129.20
128.59
127.83
127.66
126.41
120.71
77.19 cdcl3
77.00 cdcl3
76.82 cdcl3
47.45
S
O
1r
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

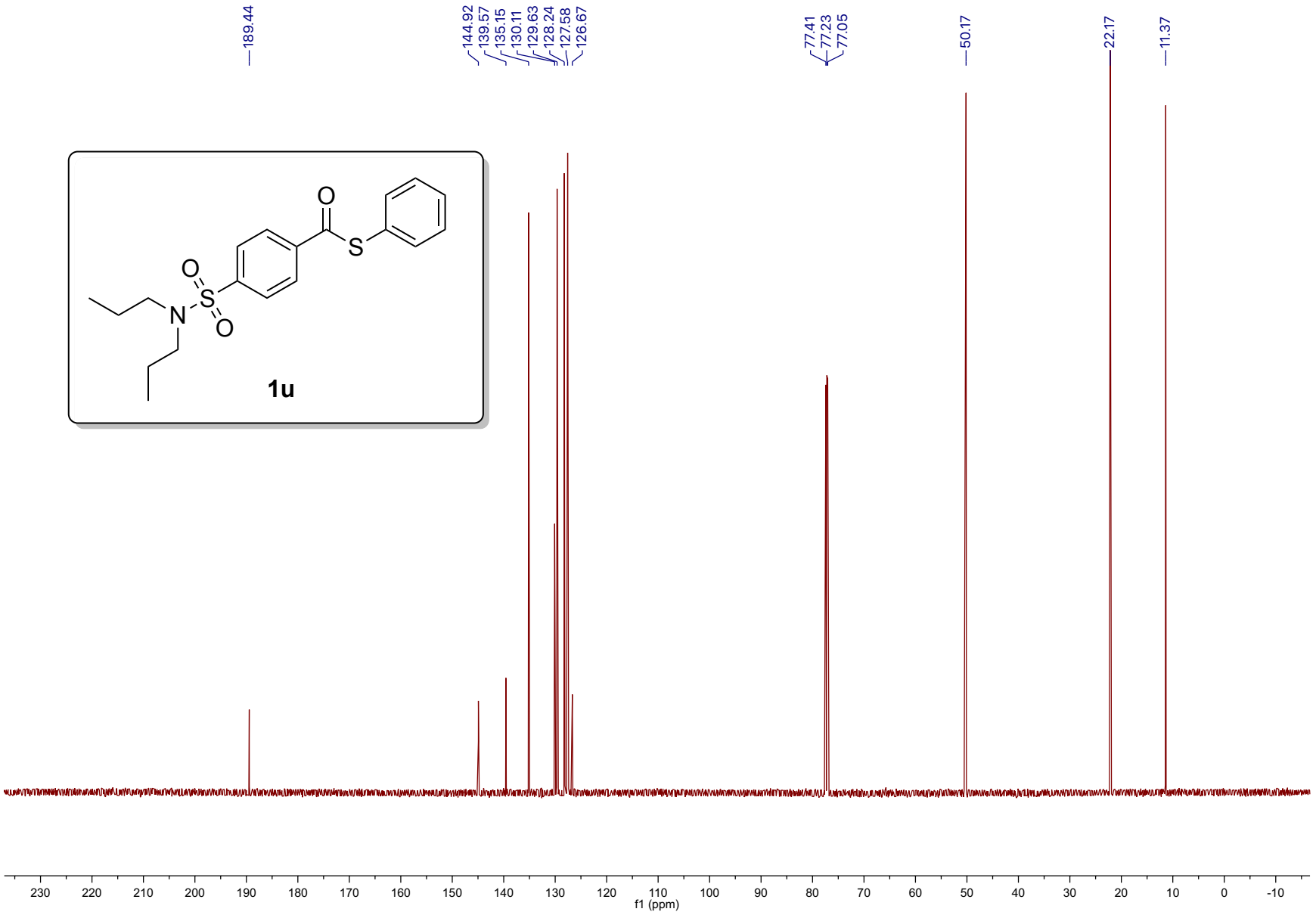

8.02
8.02
8.02
8.01
8.00
8.00
7.61
7.60
7.59
7.59
7.58
7.57
7.57
7.49
7.47
7.47
7.45
7.45
7.44
7.43
7.41
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.31
7.31
7.30
7.30
7.29
7.27
4.37
O
S
1s
2.02
1.03
4.16
2.96
2.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

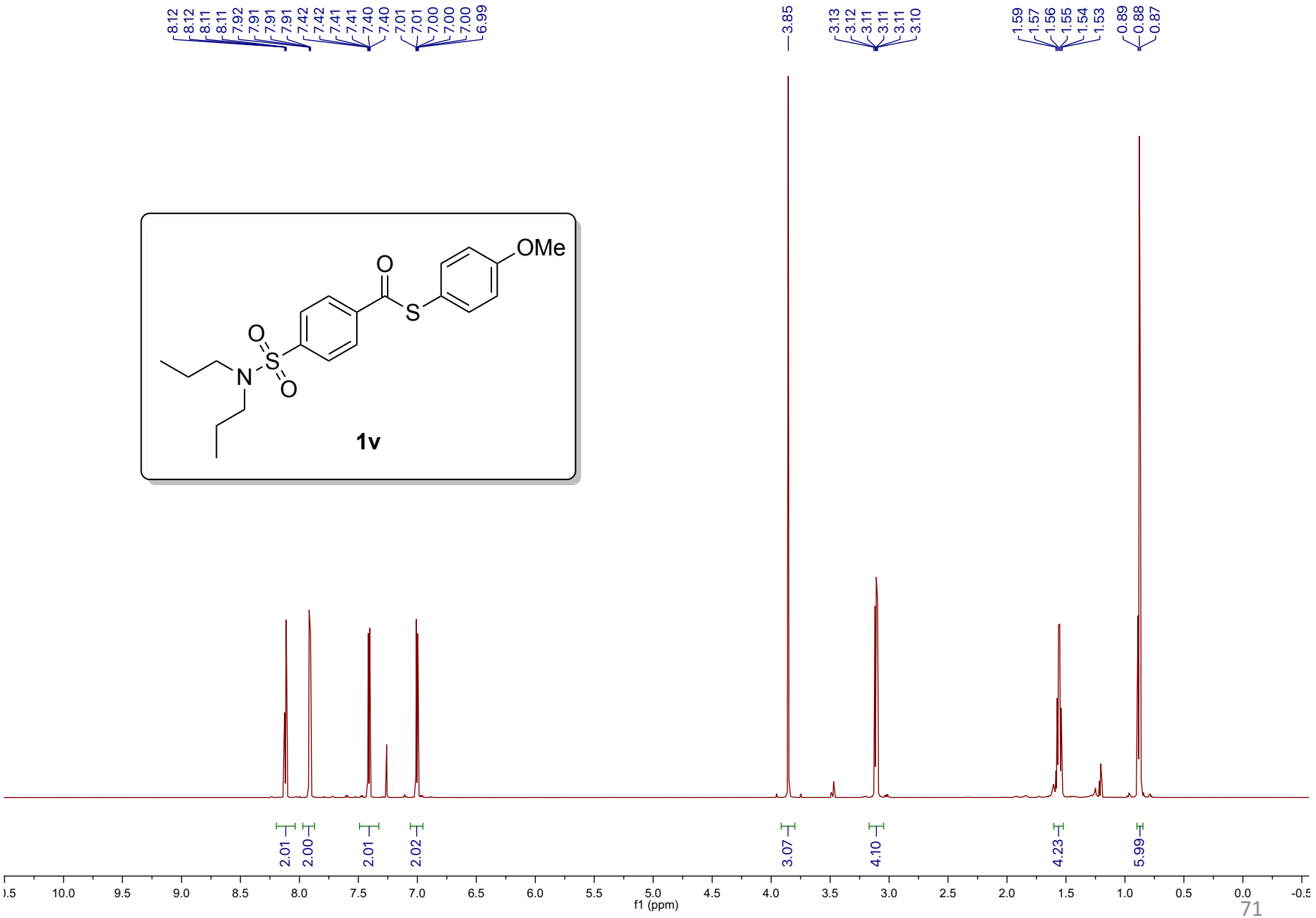

191.24
137.49
136.80
133.44
128.98
128.66
128.63
127.33
127.30
77.40
77.08
76.76
33.35
O
S
1s
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

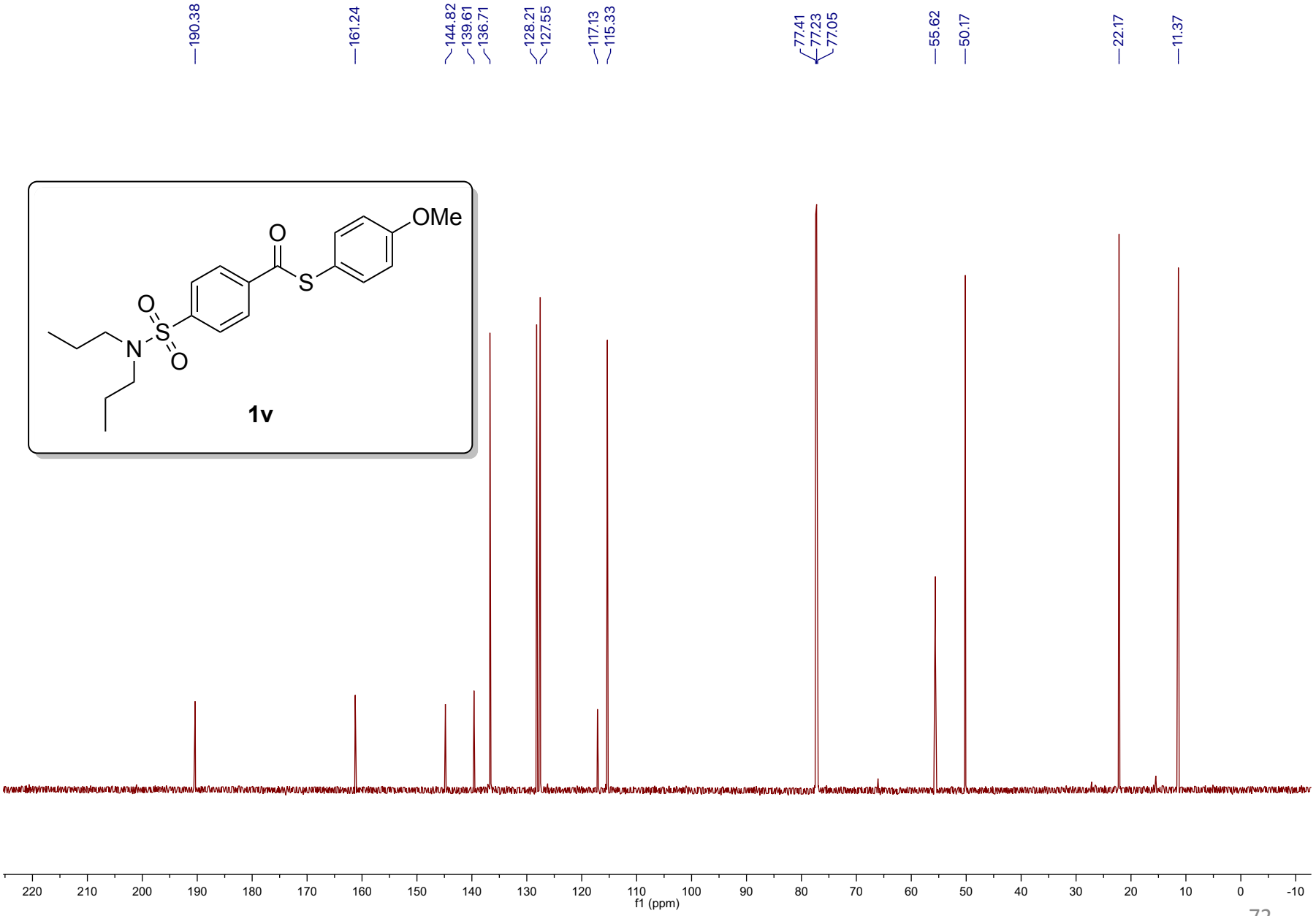

7.35
7.35
7.35
7.34
7.34
7.33
7.30
7.30
7.30
7.29
7.29
7.29
3.82
2.88
2.87
2.86
2.85
1.24
1.23
1.23
1.22
S
O
1t
5.09
2.01
2.00
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

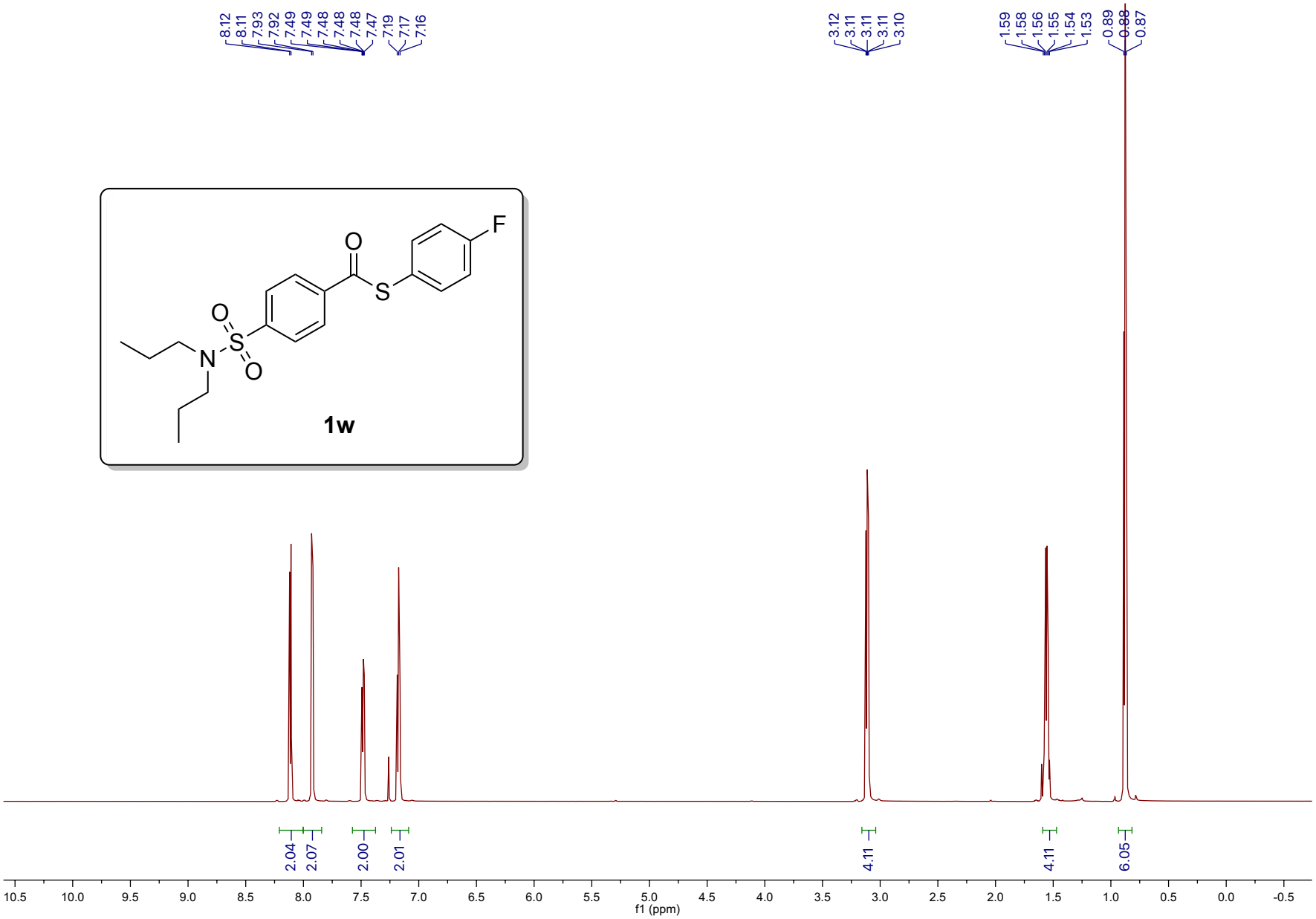

197.54
133.74
129.56
128.63
127.36
77.24
77.06
76.88
50.53
23.67
14.57
S
O
1t
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

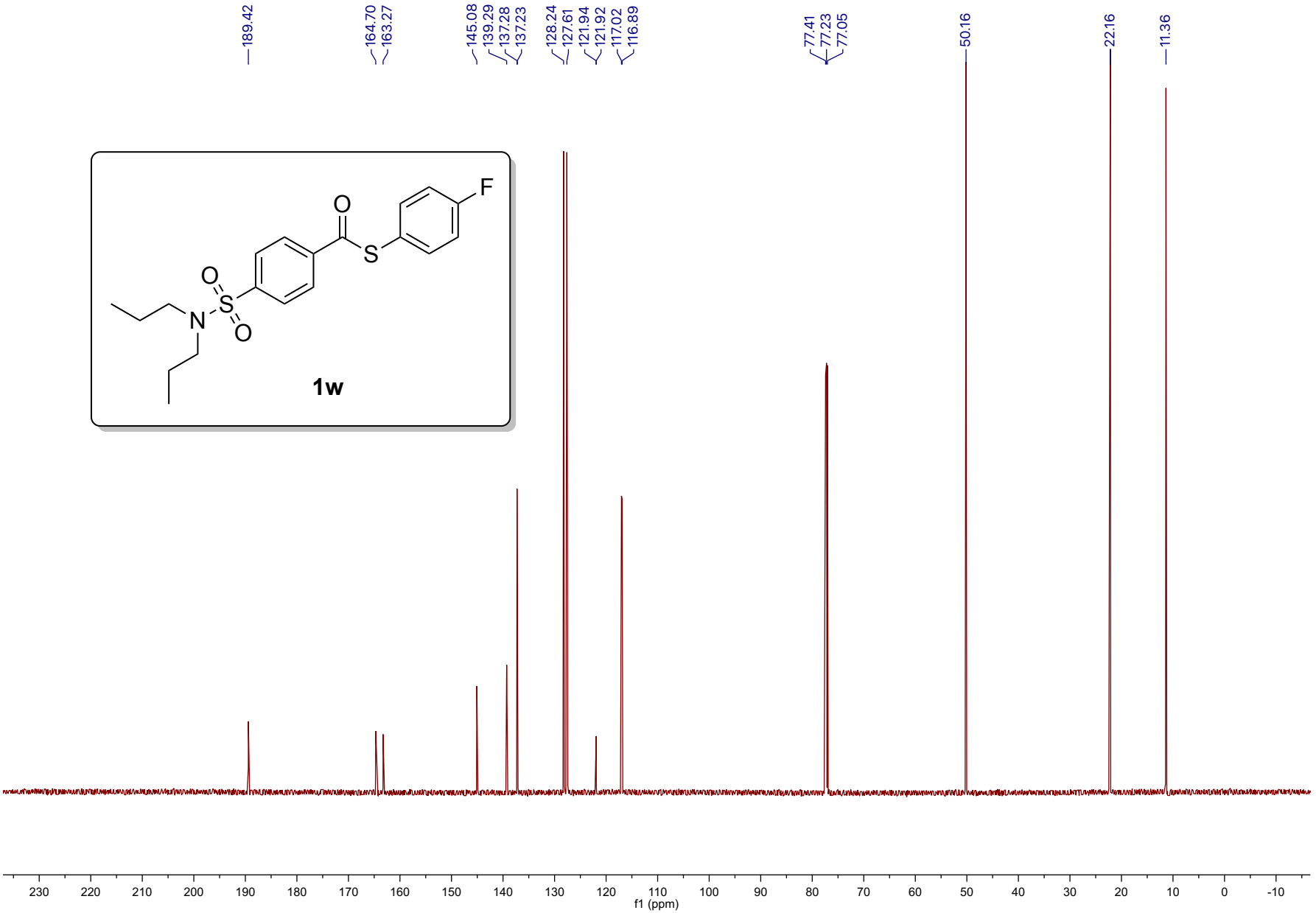

8.14
8.13
8.13
8.12
7.93
7.93
7.92
7.92
7.52
7.52
7.52
7.52
7.51
7.51
7.51
7.51
7.51
7.49
7.49
7.48
7.48
7.48
7.26
3.12
3.12
3.11
3.11
3.10
1.59
1.58
1.57
1.56
1.56
1.56
1.55
1.54
0.89
0.88
0.87
O
S
O
S
O
N
1u
2.00
2.06
5.04
4.12
4.14
6.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

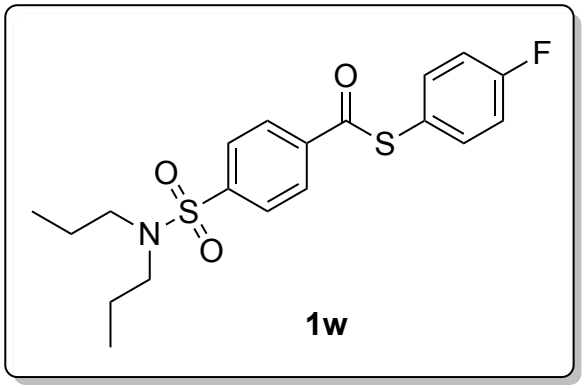

189.44
144.92
139.57
135.15
130.11
129.63
128.24
127.58
126.67
77.41
77.23
77.05
50.17
22.17
11.37
O
S
O
S
O
N
1u
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.12
8.12
8.11
8.11
7.92
7.91
7.91
7.91
7.42
7.42
7.41
7.41
7.40
7.40
7.01
7.01
7.00
7.00
7.00
6.99
3.85
3.13
3.12
3.11
3.11
3.11
3.10
1.59
1.57
1.56
1.55
1.54
1.53
0.89
0.88
0.87
OMe
O
S
O
S
O
N
1v
2.01
2.00
2.01
2.02
3.07
4.10
4.23
5.99
f1 (ppm)

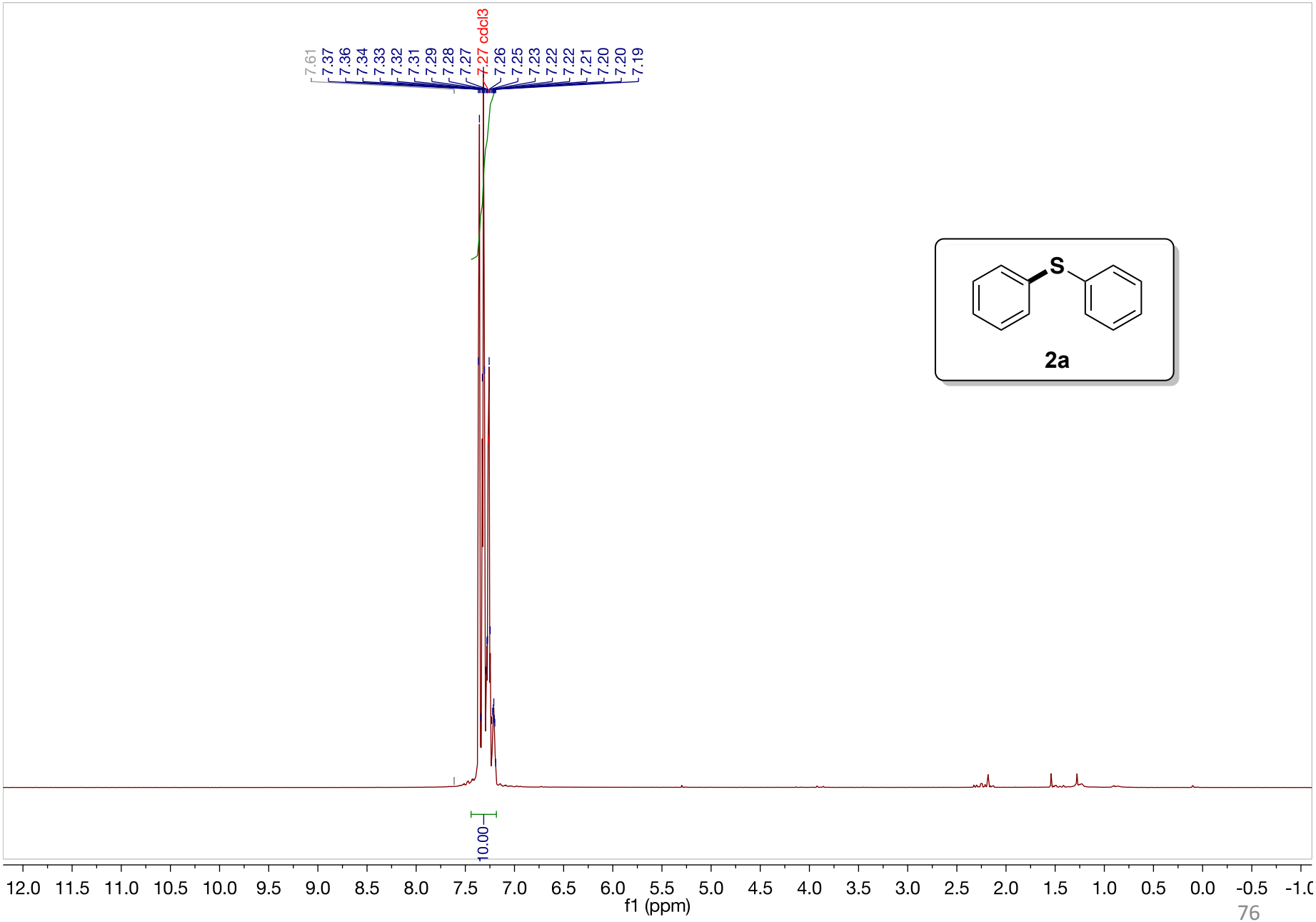

190.38
161.24
144.82
139.61
136.71
128.21
127.55
117.13
115.33
77.41
77.23
77.05
55.62
50.17
22.17
11.37
OMe
O
S
O
S
O
N
1v
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

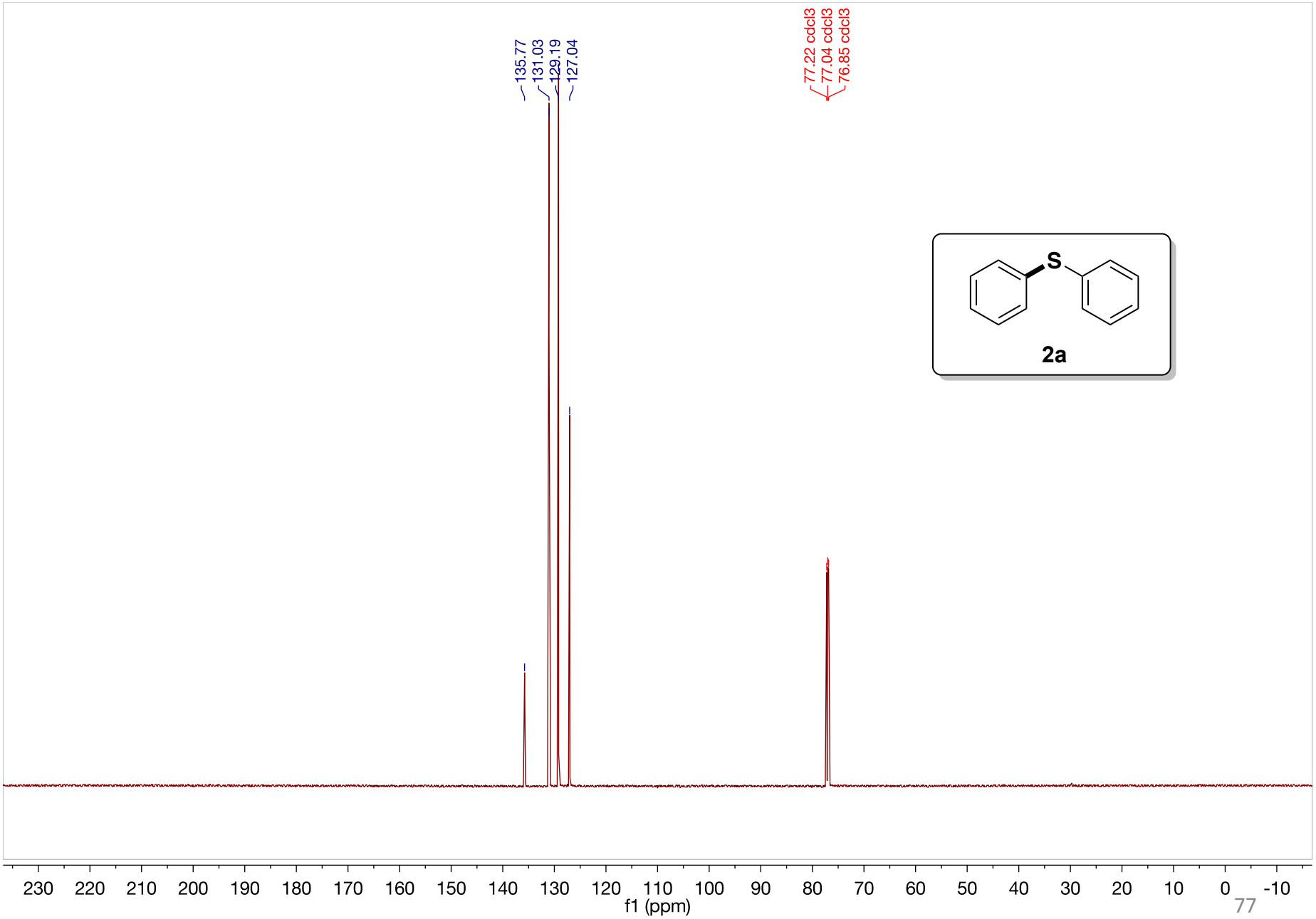

8.12
8.11
7.93
7.92
7.49
7.49
7.48
7.48
7.48
7.47
7.19
7.17
7.16
3.12
3.11
3.11
3.11
3.10
1.59
1.58
1.56
1.55
1.54
1.53
0.89
0.88
0.87
O
S
F
O
S
N
O
1w
2.04
2.07
2.00
2.01
4.11
4.11
6.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

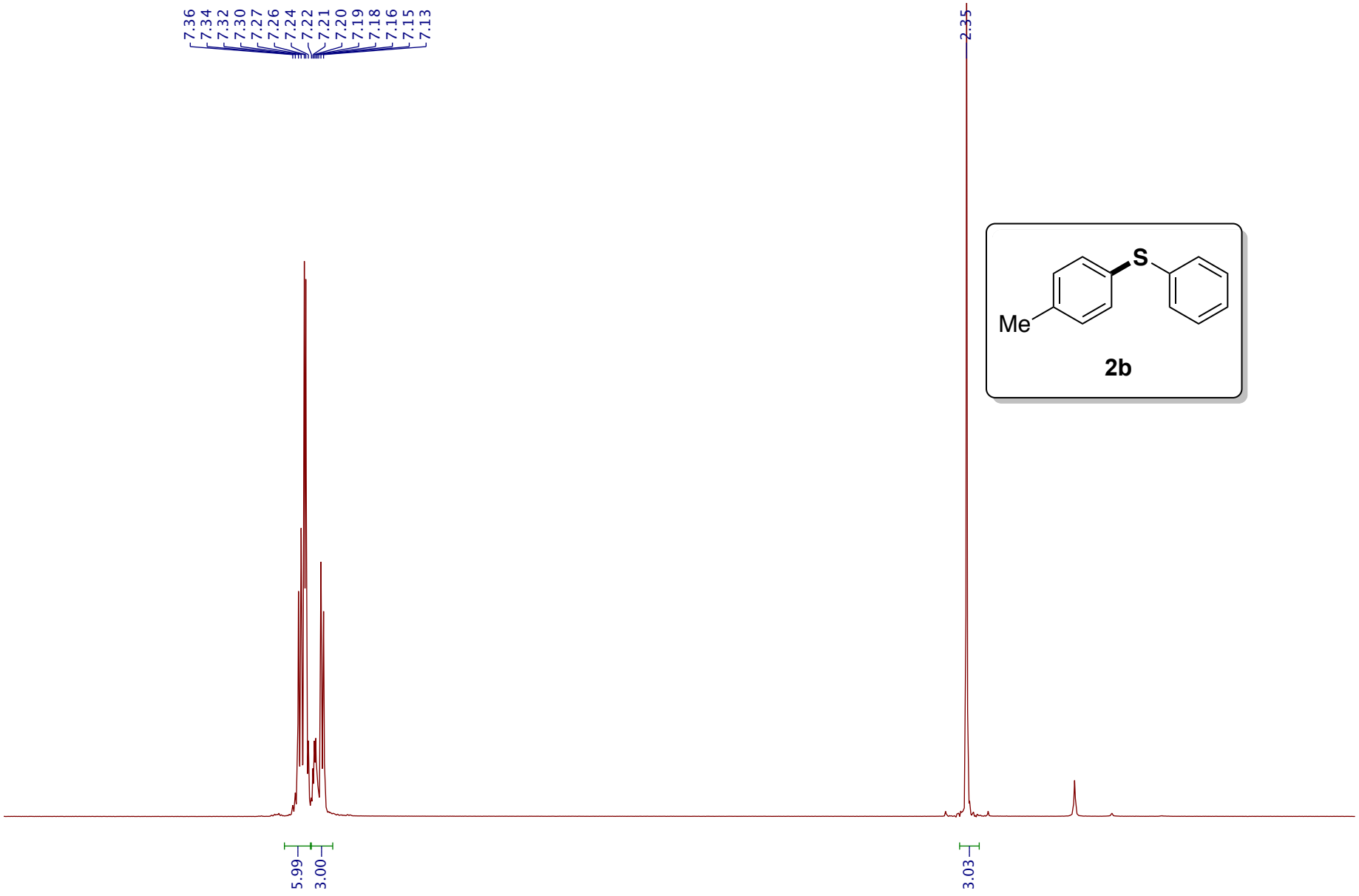

189.42
164.70
163.27
145.08
139.29
137.28
137.23
128.24
127.61
121.94
121.92
117.02
116.89
77.41
77.23
77.05
50.16
22.16
11.36
O
F
S
O
S
O
N
1w
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

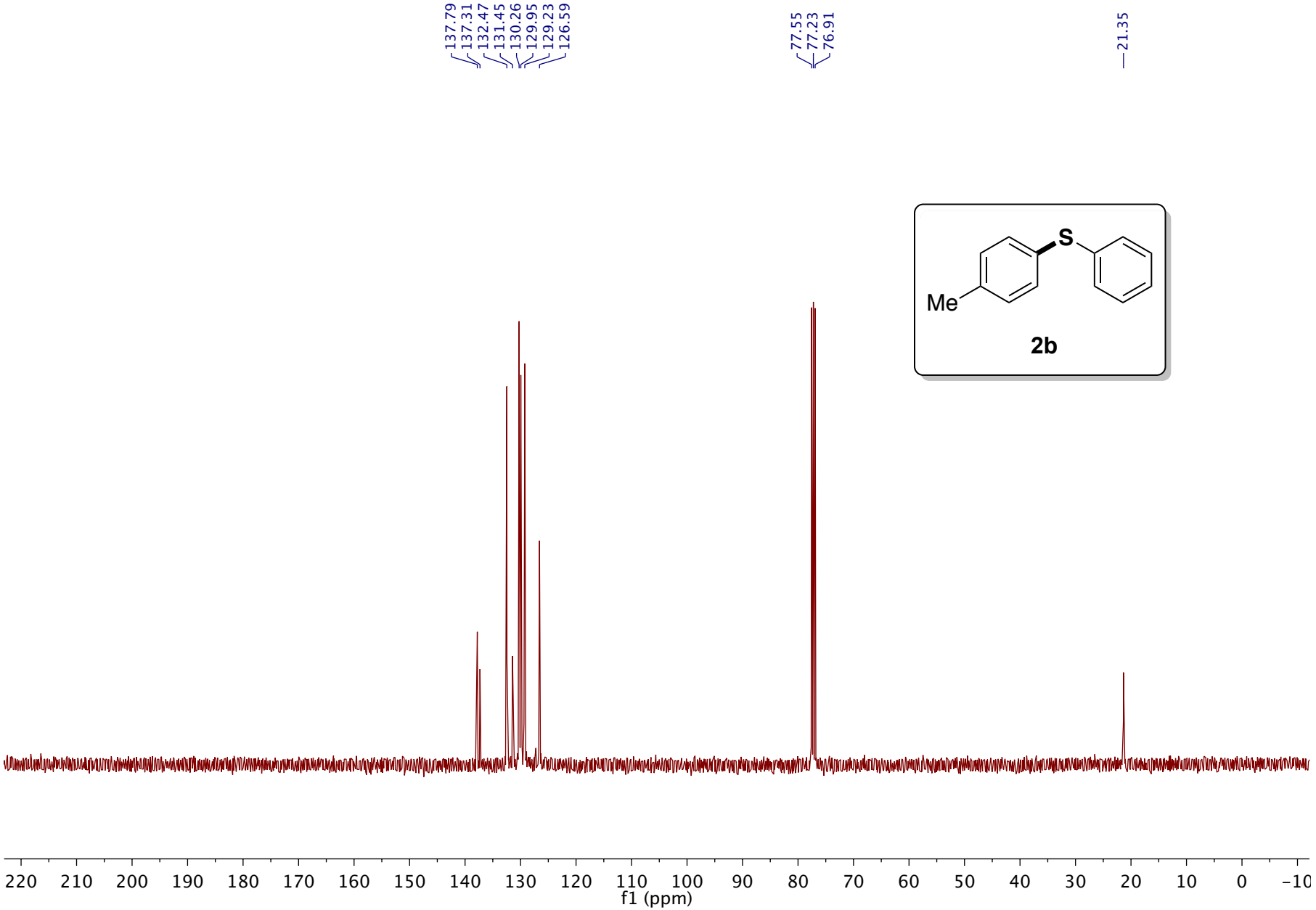

O
F
S
O
S
N
O
1w

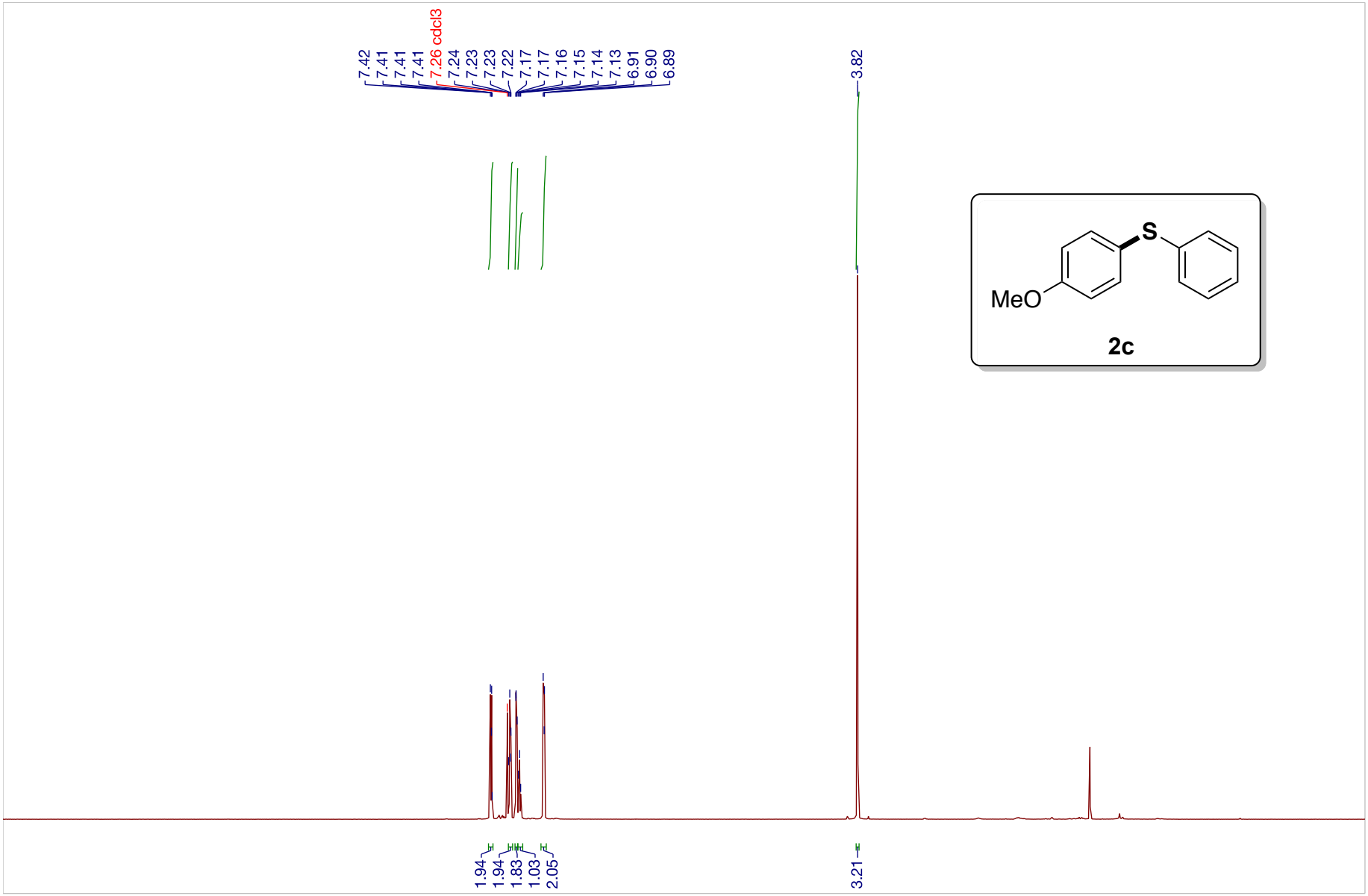
-110.37
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

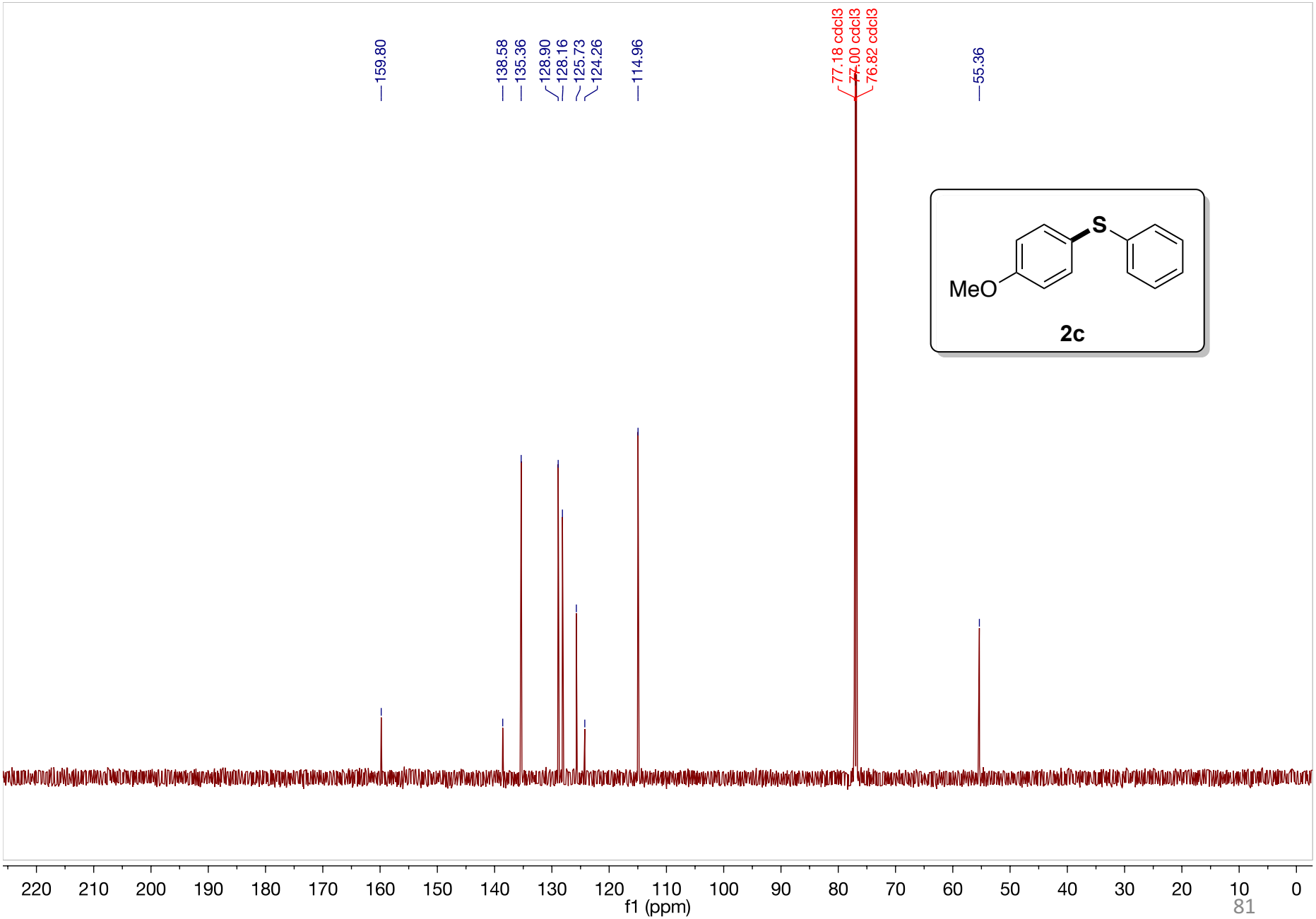

7.61
7.37
7.36
7.34
7.33
7.32
7.31
7.29
7.28
7.27
7.27 cdcl3
7.26
7.25
7.23
7.22
7.22
7.21
7.20
7.20
7.19
S
2a
10.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

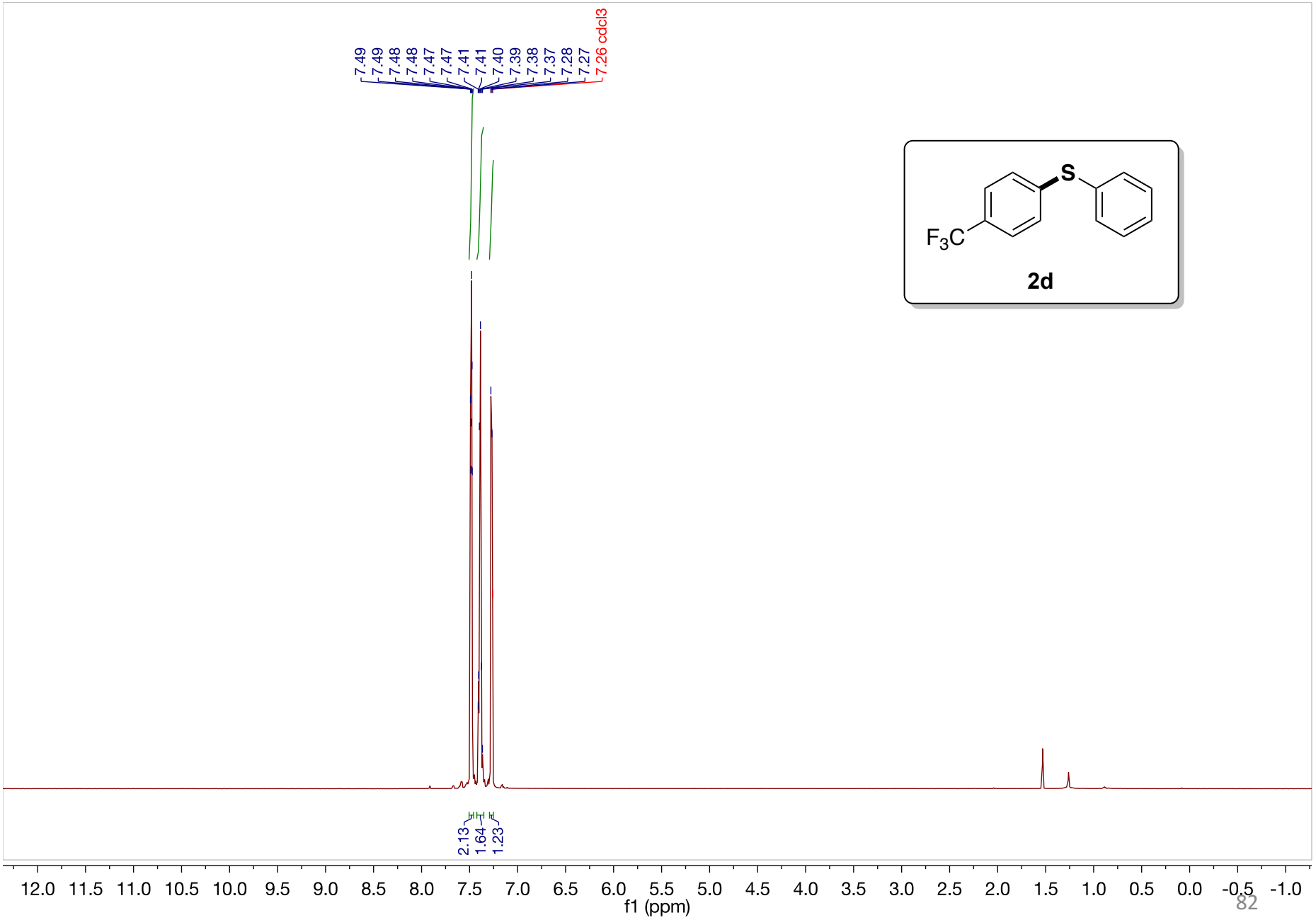

135.77
131.03
129.19
127.04
77.22 cdcl3
77.04 cdcl3
76.85 cdcl3
S
2a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

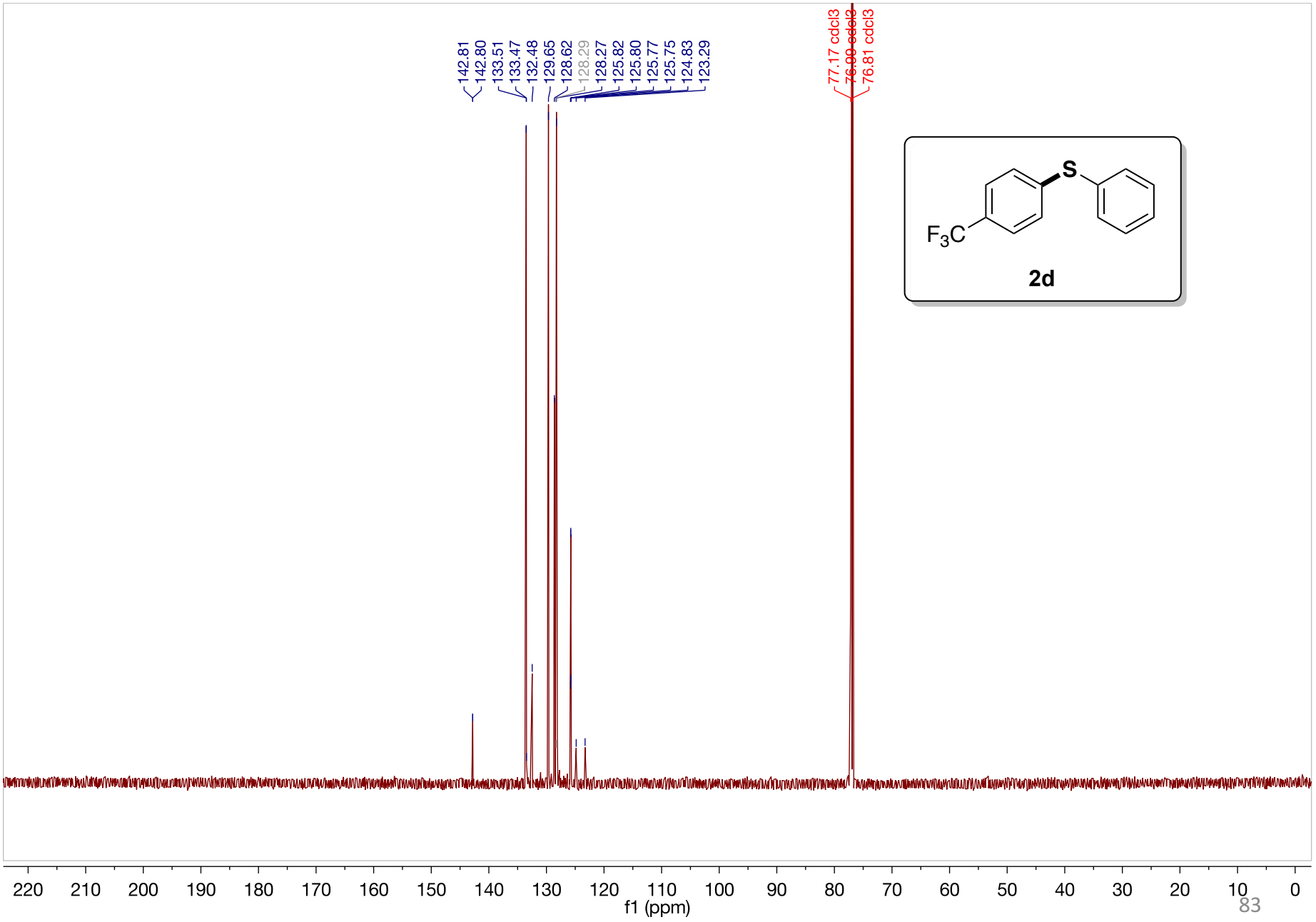

7.36
7.34
7.32
7.30
7.27
7.26
7.24
7.22
7.21
7.20
7.19
7.18
7.16
7.15
7.13
2.35
S
Me
2b
5.99
3.00
3.03
f1 (ppm)

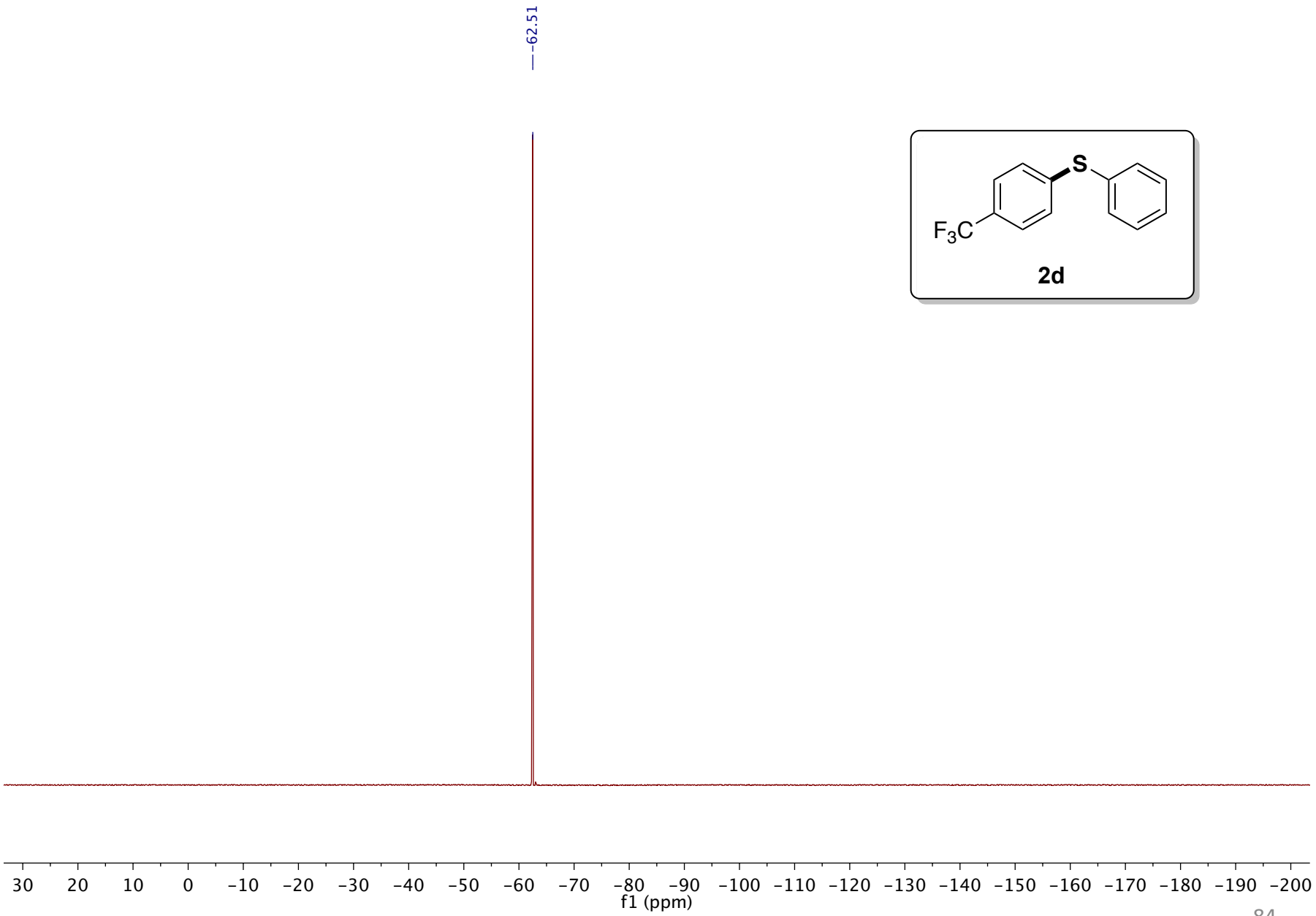

137.79
137.31
132.47
131.45
130.26
129.95
129.23
126.59
77.55
77.23
76.91
21.35
S
Me
2b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

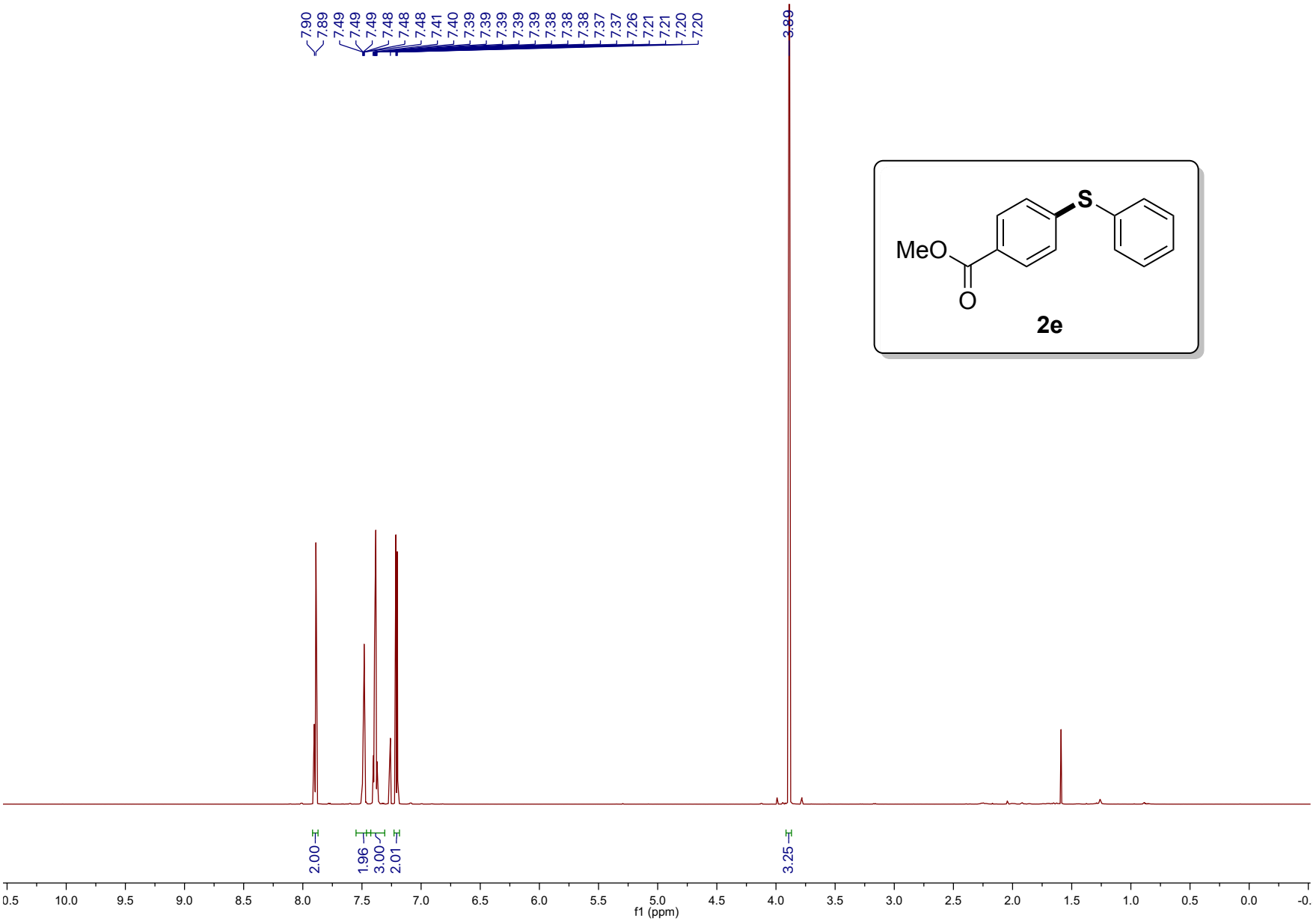

7.42
7.41
7.41
7.41
7.26 cdcl3
7.24
7.23
7.23
7.22
7.17
7.17
7.16
7.15
7.14
7.13
6.91
6.90
6.89
3.82
MeO
S
2c
1.94
1.94
1.83
1.03
2.05
3.21
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

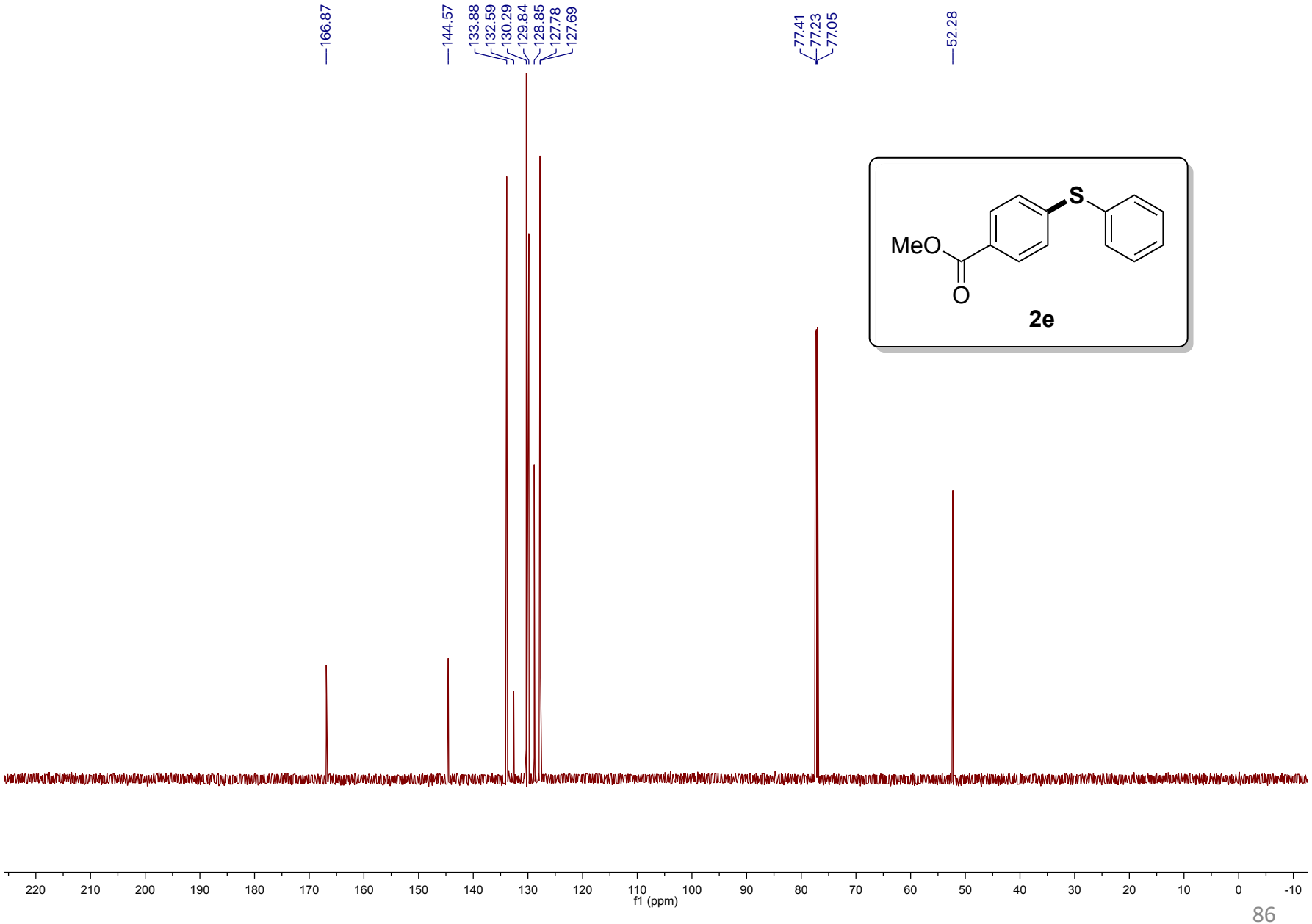

159.80
138.58
135.36
128.90
128.16
125.73
124.26
114.96
77.18 cdcl3
77.00 cdcl3
76.82 cdcl3
55.36
S
MeO
2c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

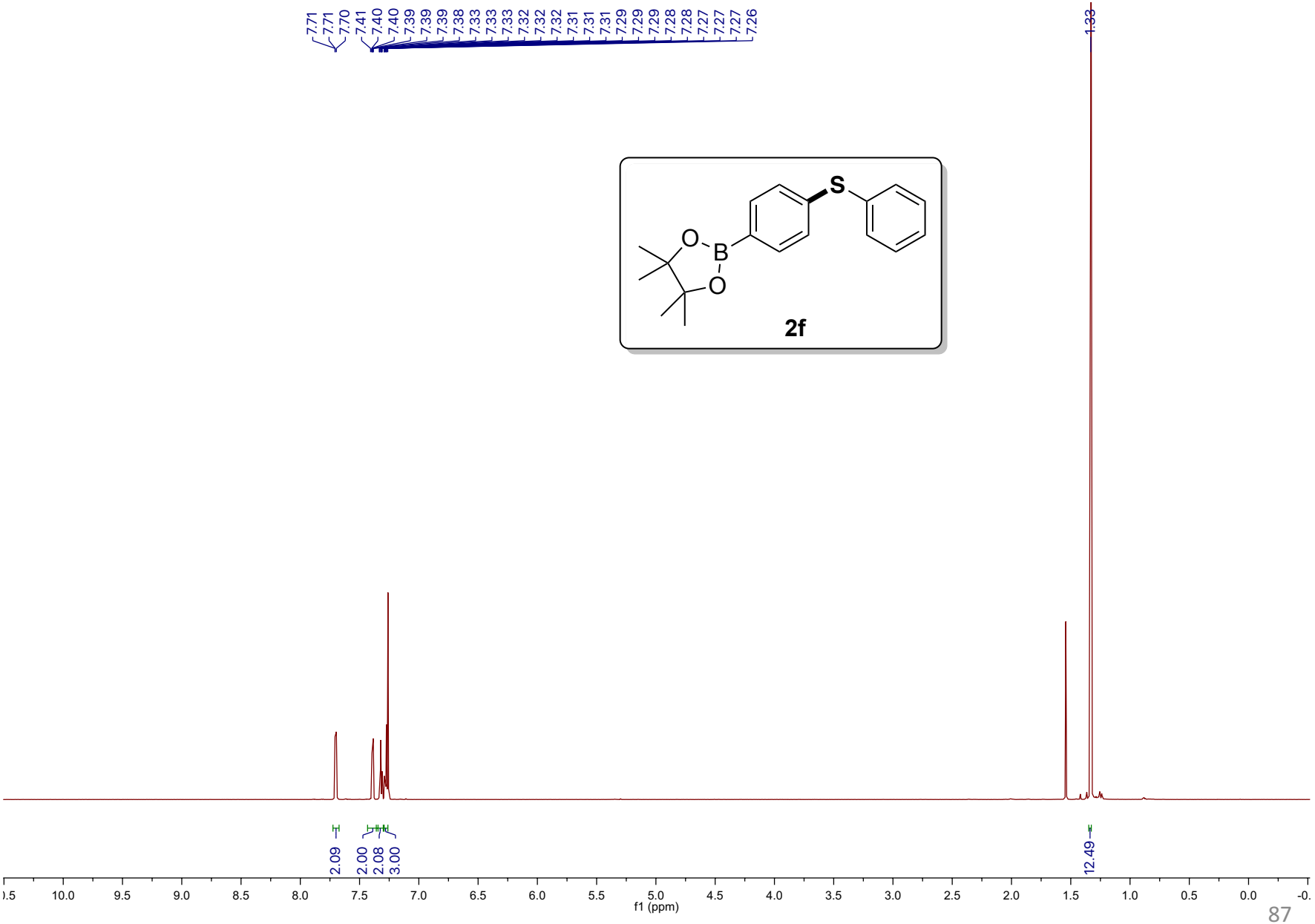

7.49
7.49
7.48
7.48
7.47
7.47
7.41
7.41
7.40
7.39
7.38
7.37
7.28
7.27
7.26 cdcl3
S
F3C
2d
2.13
1.64
1.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

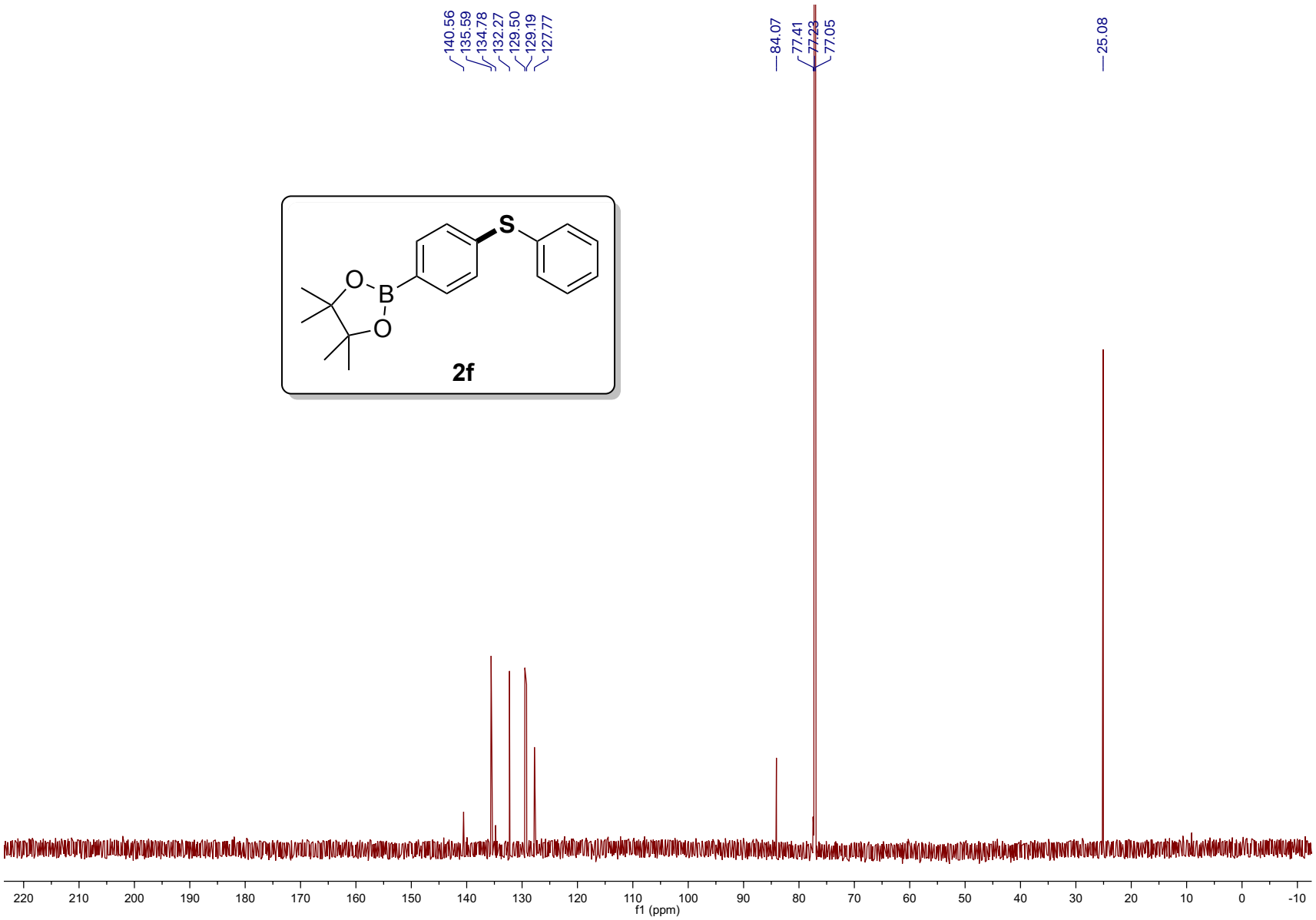

142.81
142.80
133.51
133.47
132.48
129.65
128.62
128.29
128.27
125.82
125.80
125.77
125.75
124.83
123.29
77.17 cdcl3
76.81 cdcl3
S
F3C
2d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

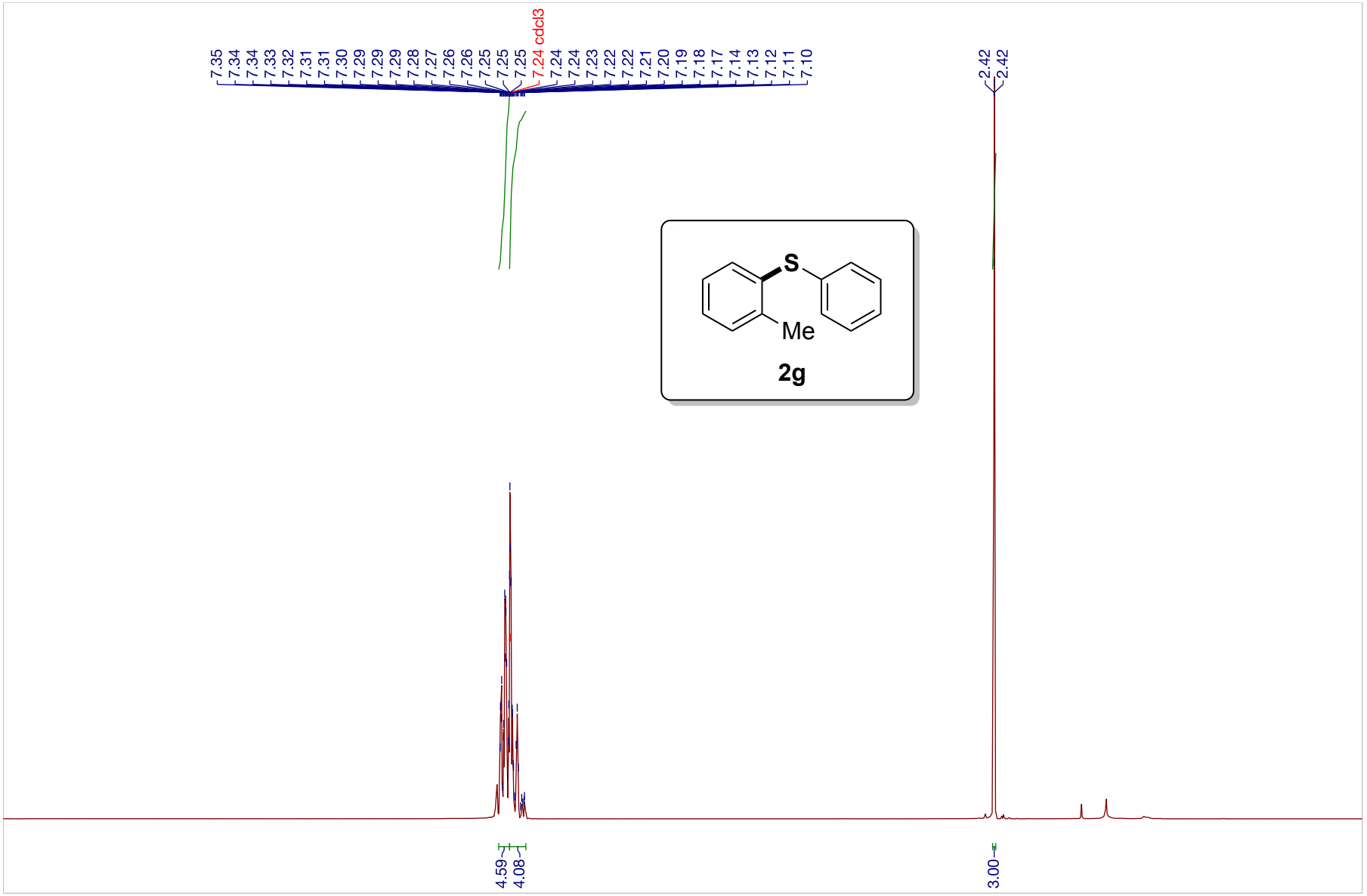

-62.51
S
F3C
2d
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

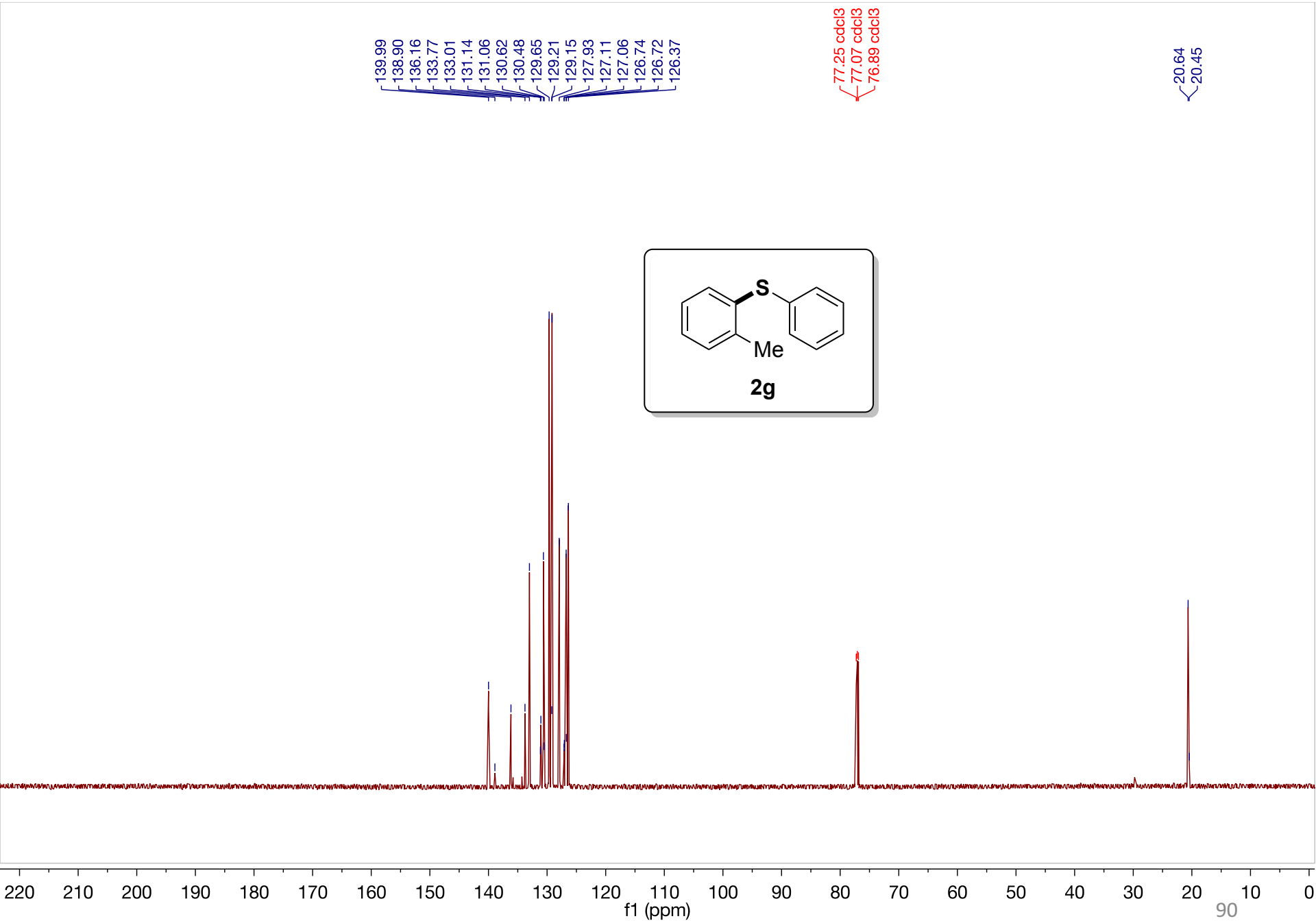

7.90
7.89
7.49
7.49
7.49
7.48
7.48
7.48
7.41
7.40
7.39
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.26
7.21
7.21
7.20
7.20
3.89
MeO
O
S
2e
2.00
1.96
3.00
2.01
3.25
f1 (ppm)

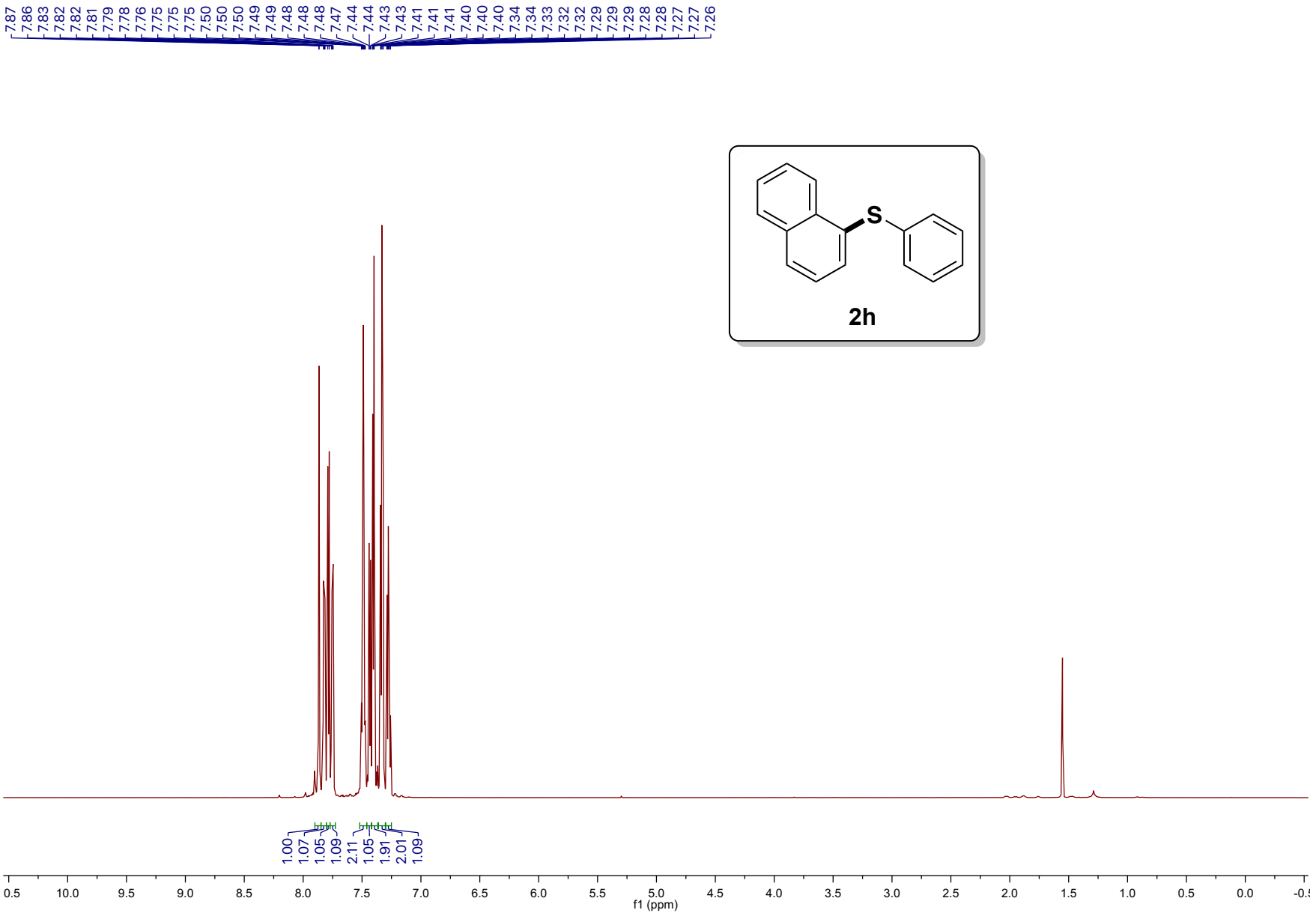

166.87
144.57
133.88
132.59
130.29
129.84
128.85
127.78
127.69
77.41
77.23
77.05
52.28
MeO
O
S
2e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

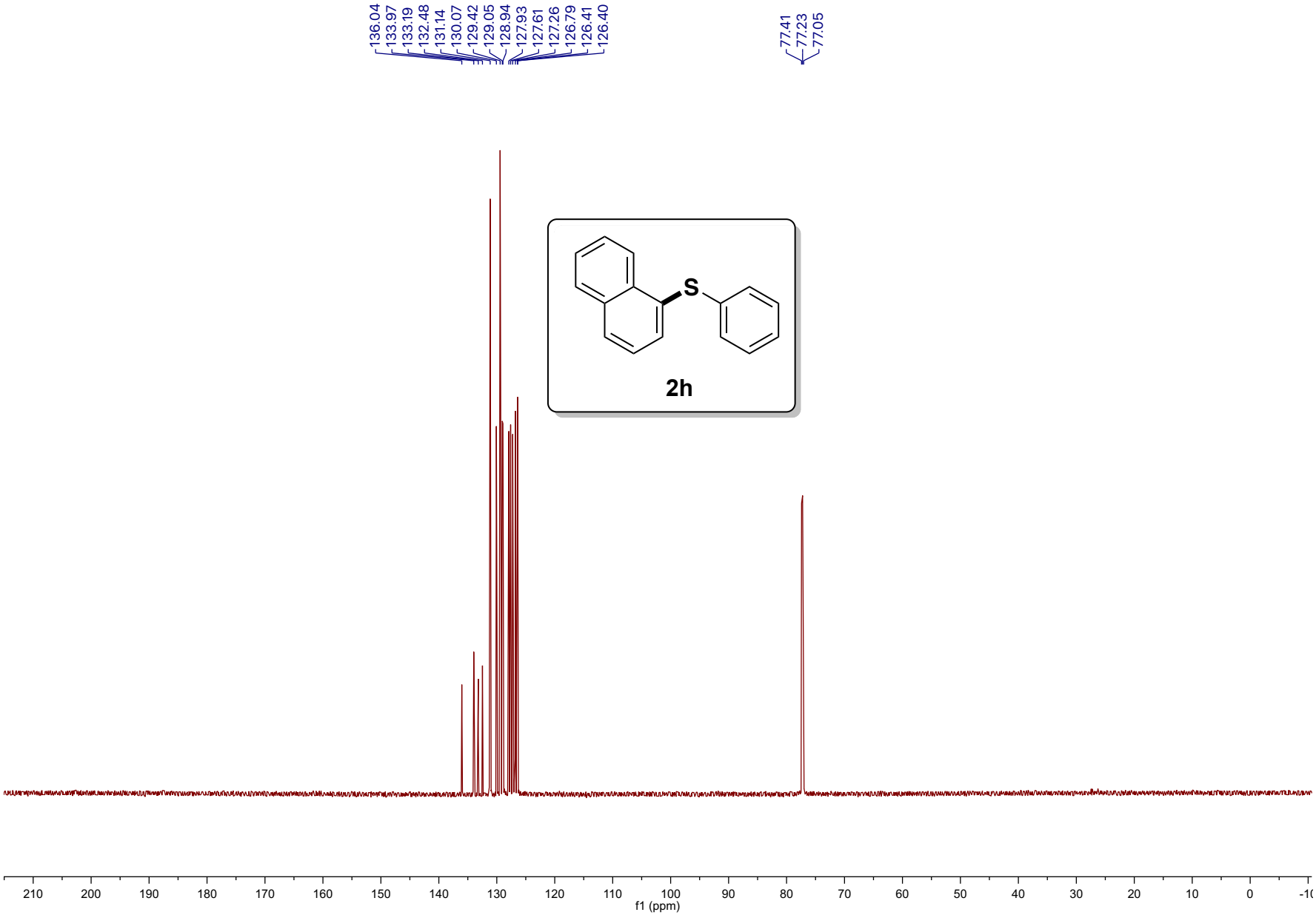

7.71
7.71
7.70
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.29
7.29
7.28
7.28
7.27
7.27
7.26
1.33
S
O
B
O
2f
2.09
2.00
2.08
3.00
12.49
f1 (ppm)

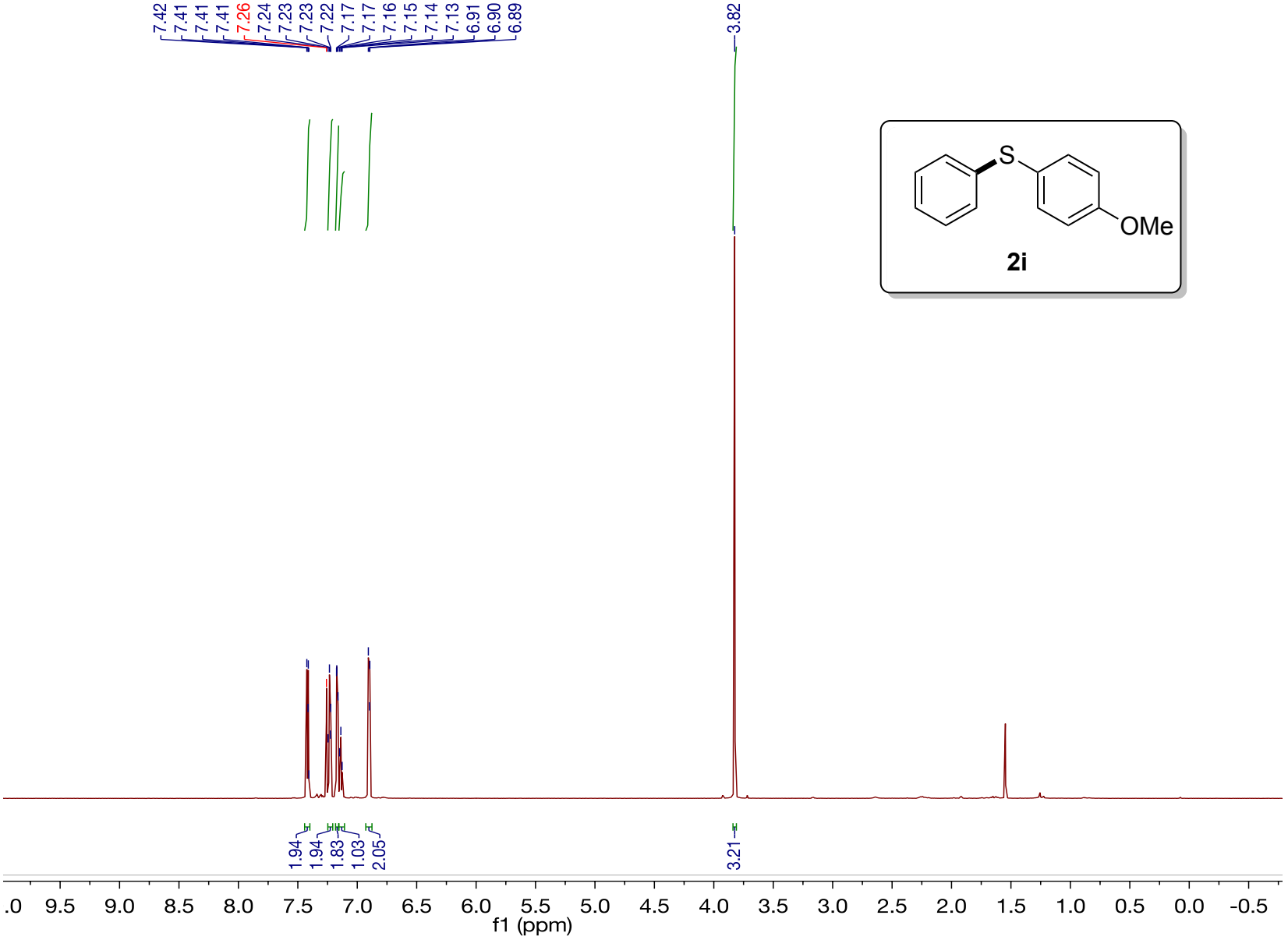

140.56
135.59
134.78
132.27
129.50
129.19
127.77
84.07
77.41
77.23
77.05
25.08
S
O
B
O
2f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

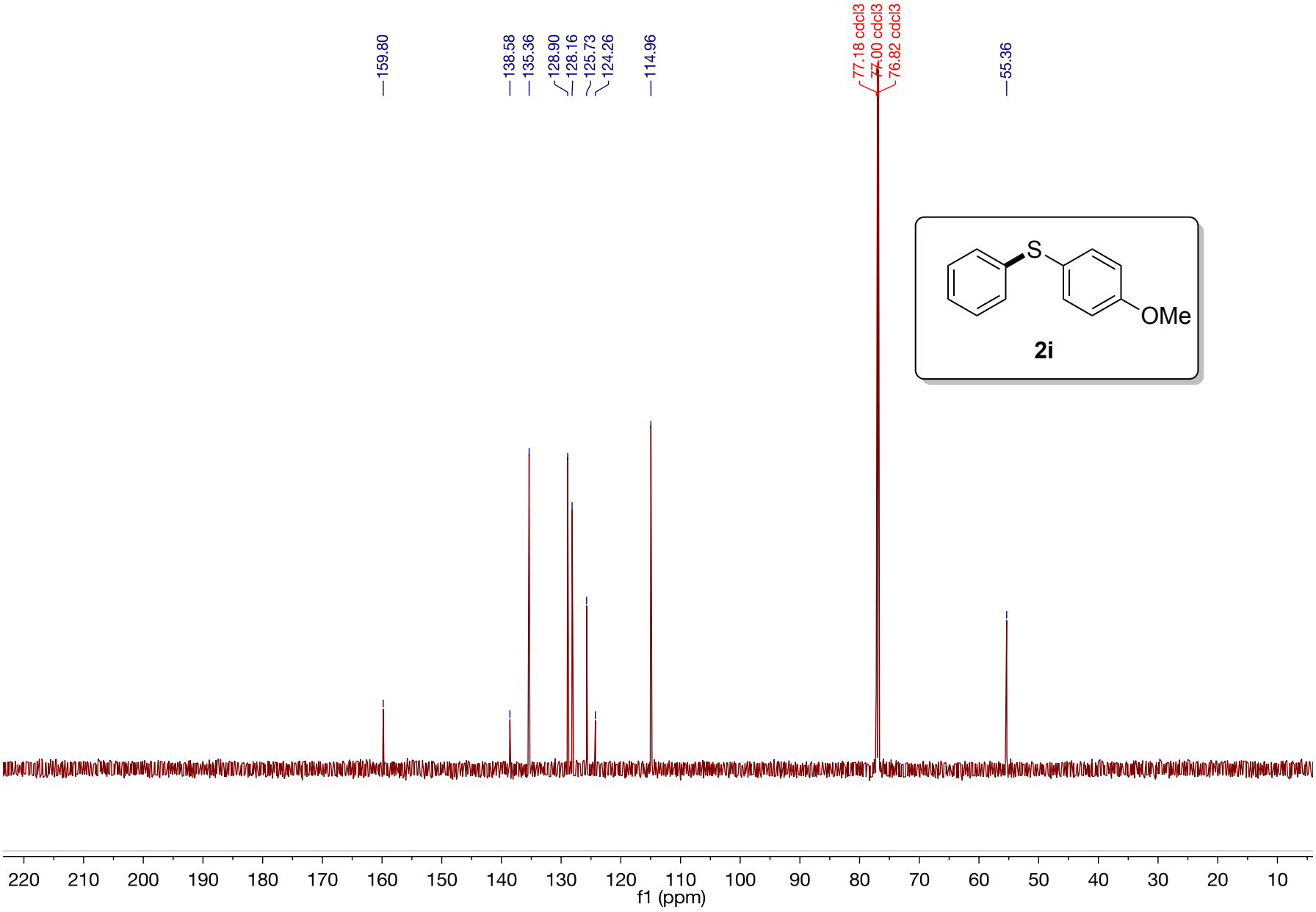

7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.29
7.28
7.27
7.26
7.26
7.25
7.25
7.25
7.24 cdcl3
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.18
7.17
7.14
7.13
7.12
7.11
7.10
2.42
2.42
S
Me
2g
4.59
4.08
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

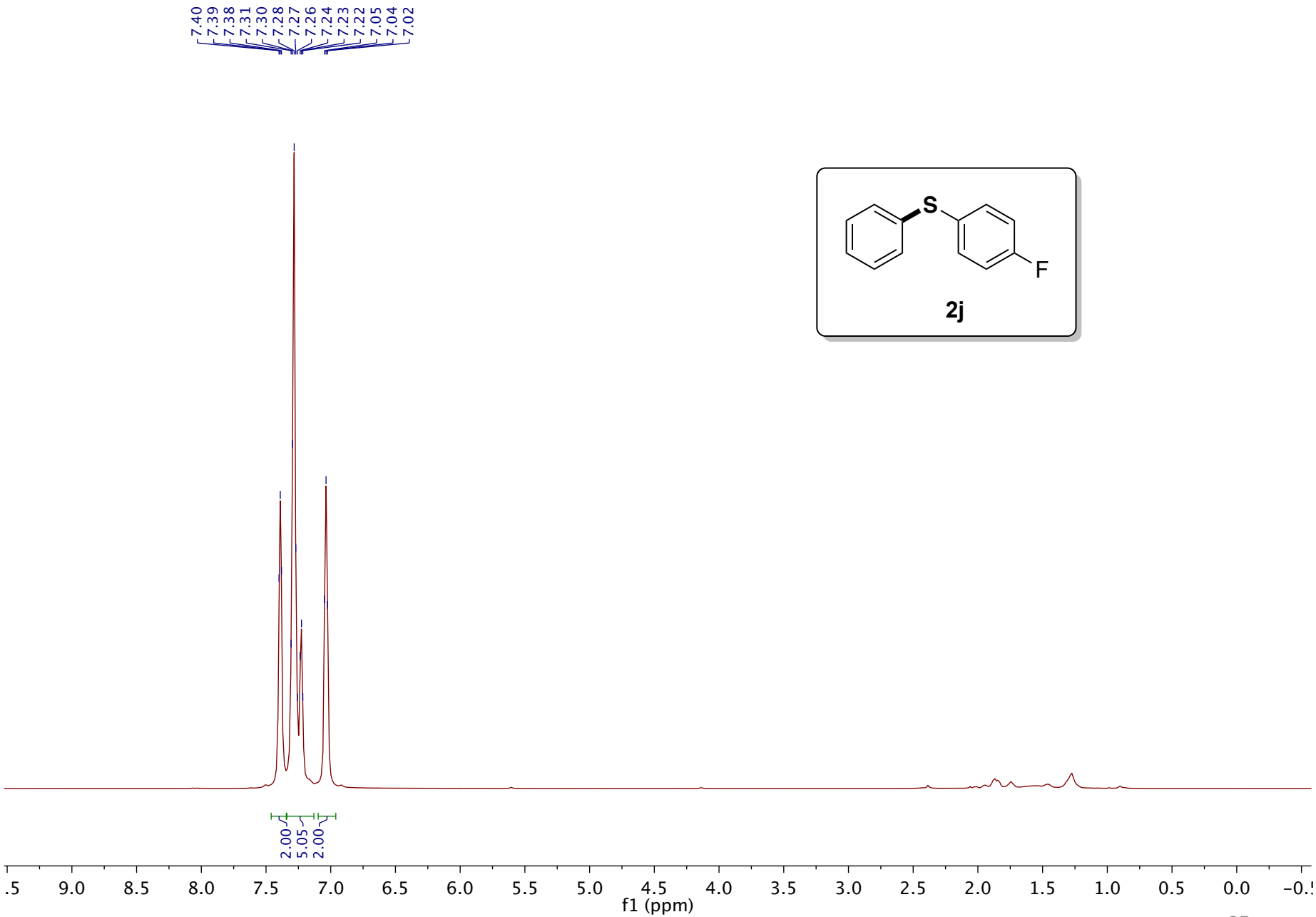

139.99
138.90
136.16
133.77
133.01
131.14
131.06
130.62
130.48
129.65
129.21
129.15
127.93
127.11
127.06
126.74
126.72
126.37
77.25 cdcl3
77.07 cdcl3
76.89 cdcl3
20.64
20.45
S
Me
2g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

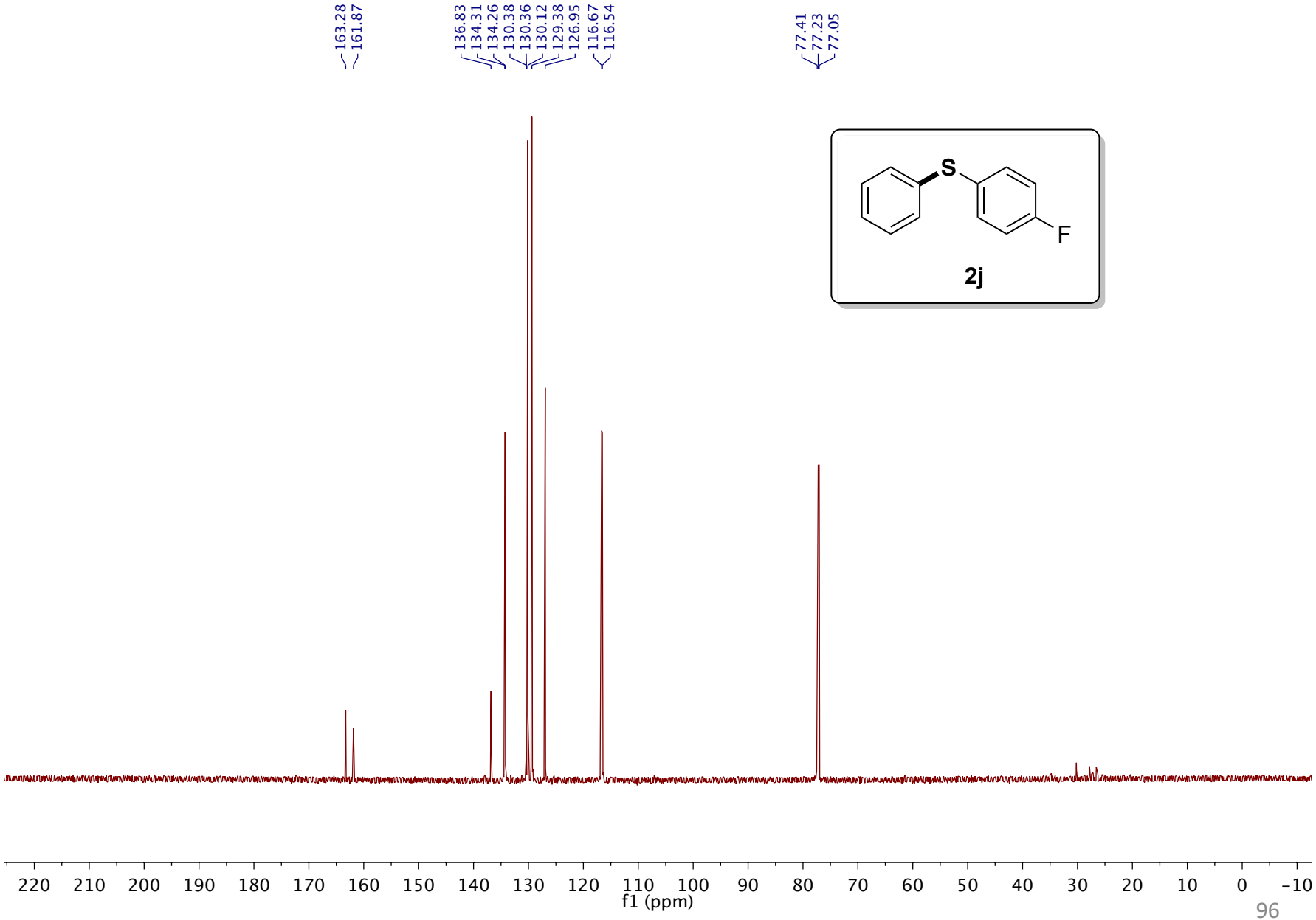

7.87
7.86
7.83
7.82
7.82
7.81
7.79
7.78
7.76
7.75
7.75
7.75
7.50
7.50
7.50
7.49
7.49
7.48
7.48
7.48
7.47
7.44
7.44
7.43
7.43
7.41
7.41
7.41
7.40
7.40
7.40
7.34
7.33
7.32
7.32
7.29
7.29
7.29
7.28
7.28
7.27
7.26
S
2h
1.00
1.07
1.05
1.09
2.11
1.05
1.91
2.01
1.09
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

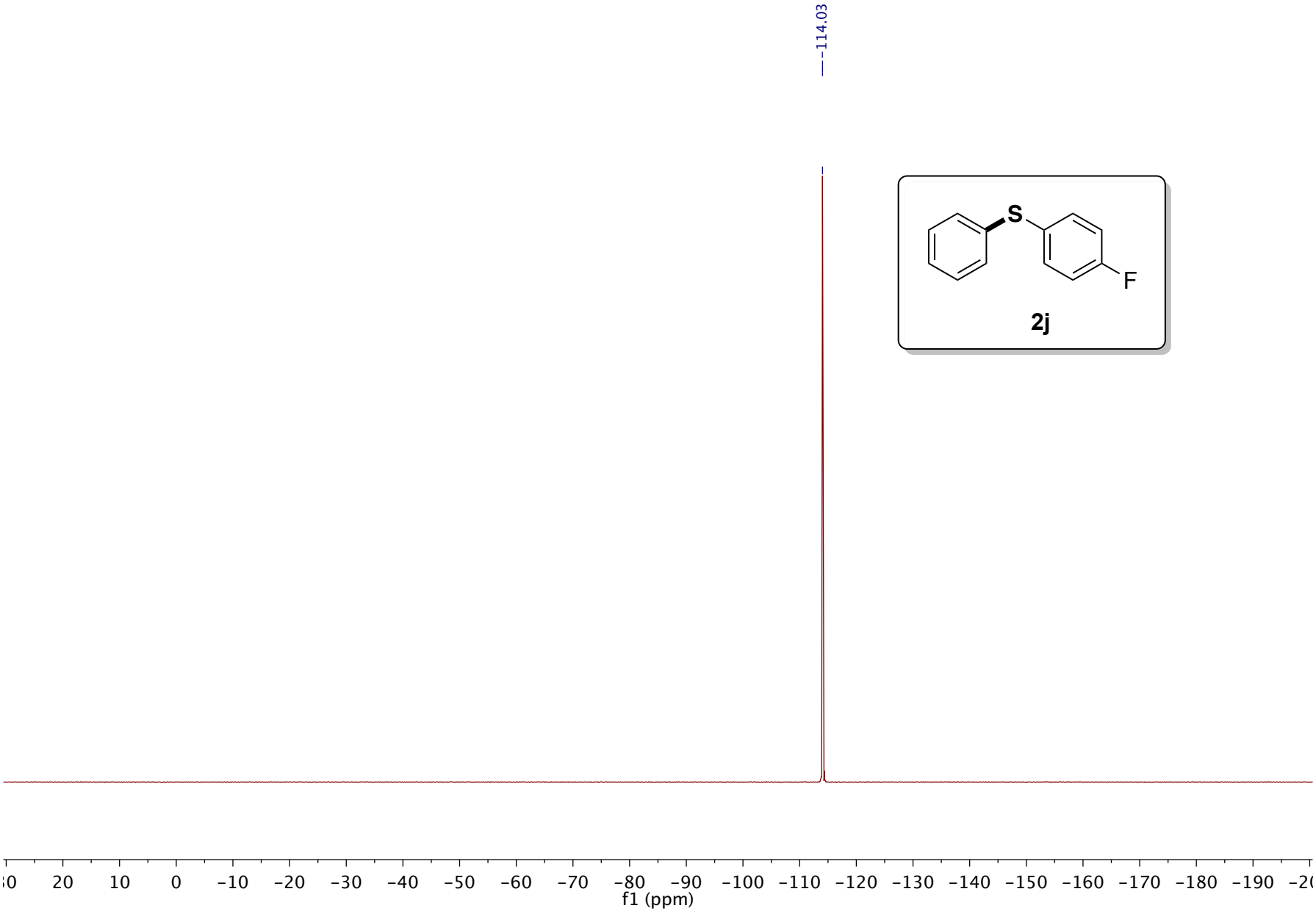

136.04
133.97
133.19
132.48
131.14
130.07
129.42
129.05
128.94
127.93
127.61
127.26
126.79
126.41
126.40
77.41
77.23
77.05
S
2h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

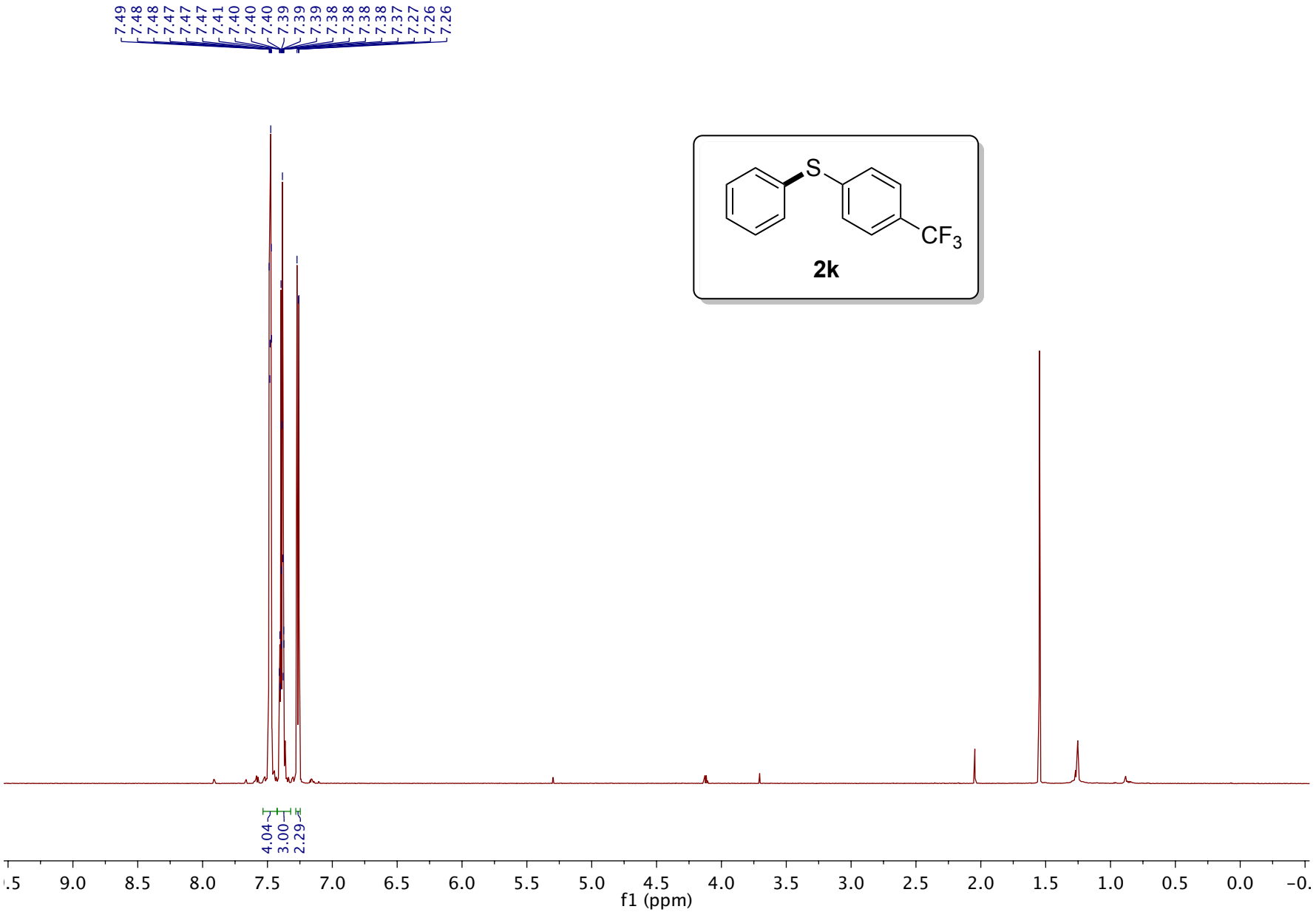

7.42
7.41
7.41
7.41
7.26 c
7.24
7.23
7.23
7.22
7.17
7.17
7.16
7.15
7.14
7.13
6.91
6.90
6.89
3.82
S
OMe
2i
1.94
1.94
1.83
1.03
2.05
3.21
f1 (ppm)

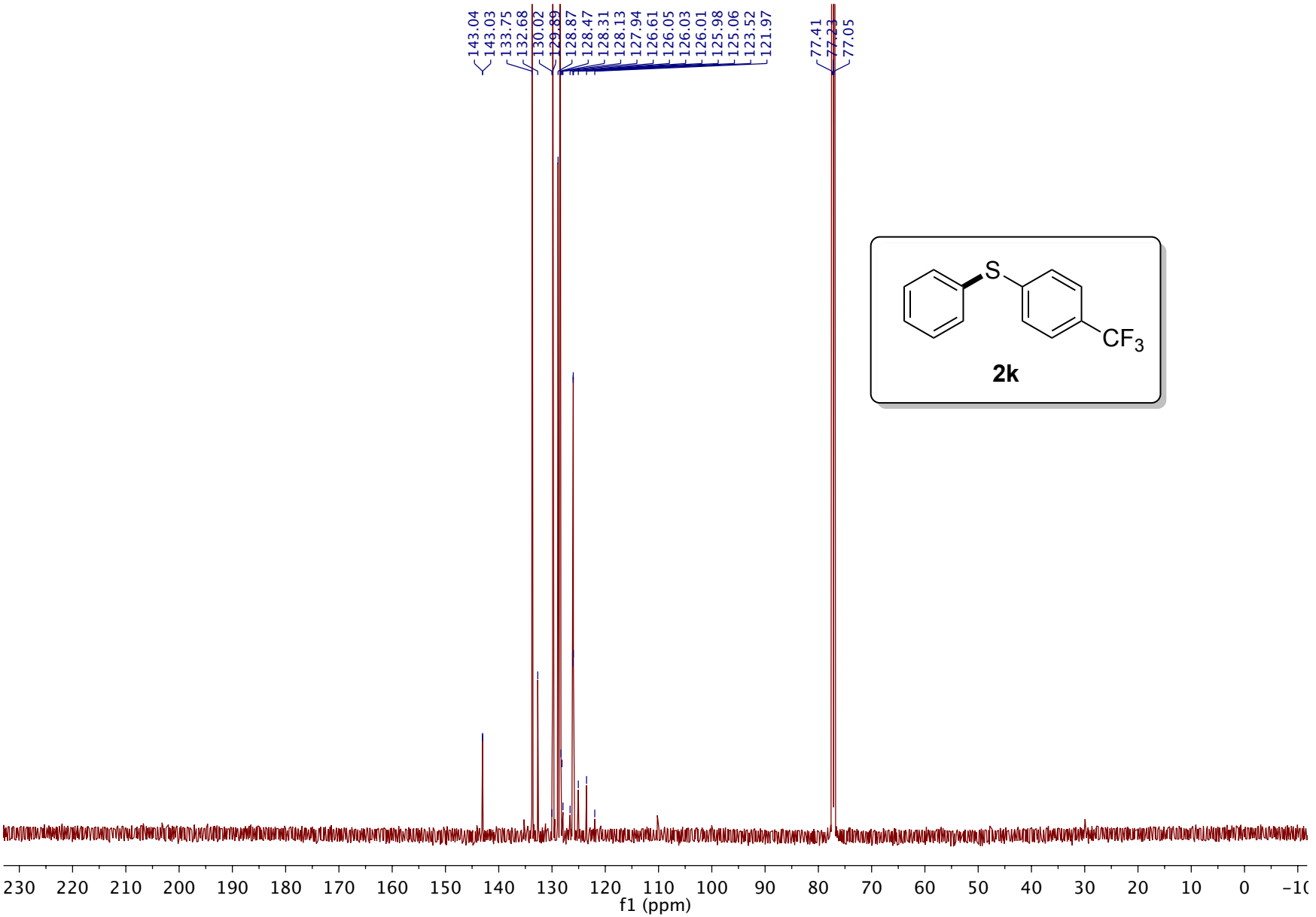

159.80
138.58
135.36
128.90
128.16
125.73
124.26
114.96
77.18 cdcl3
77.00 cdcl3
76.82 cdcl3
55.36
S
OMe
2i
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

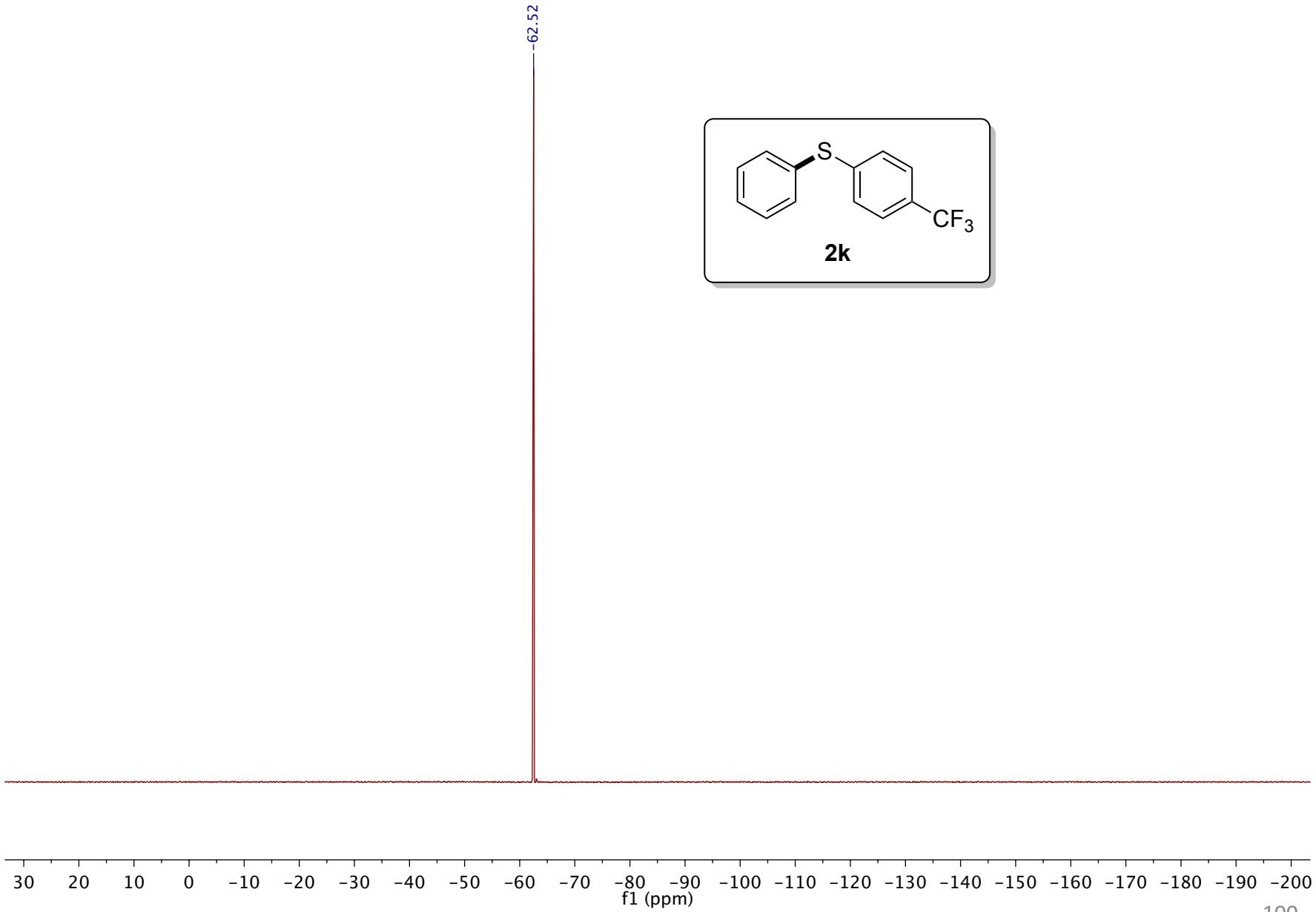

7.40
7.39
7.38
7.31
7.30
7.28
7.27
7.26
7.24
7.23
7.22
7.05
7.04
7.02
S
F
2j
2.00
5.05
2.00
f1 (ppm)

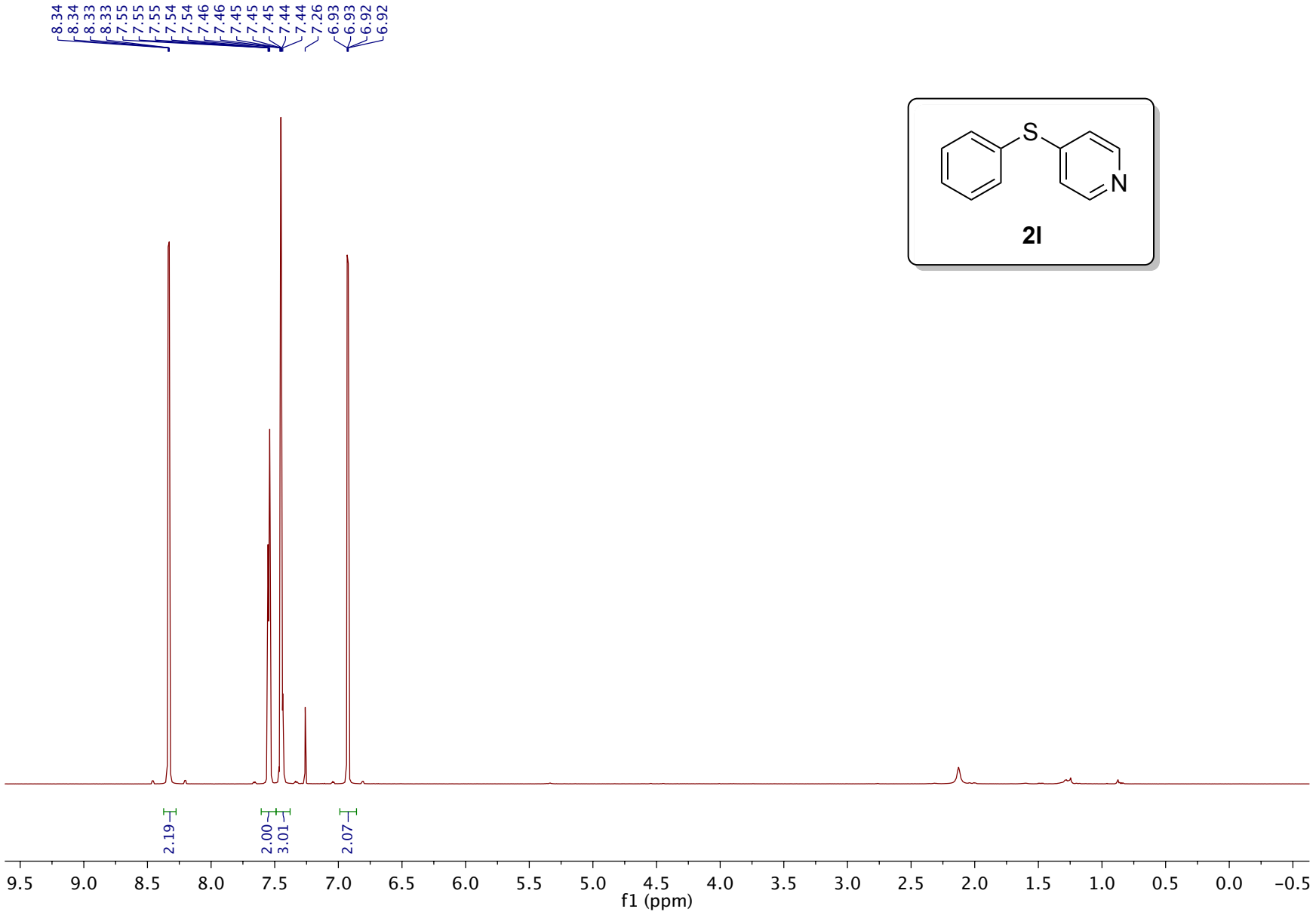

163.28
161.87
136.83
134.31
134.26
130.38
130.36
130.12
129.38
126.95
116.67
116.54
77.41
77.23
77.05
S
F
2j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

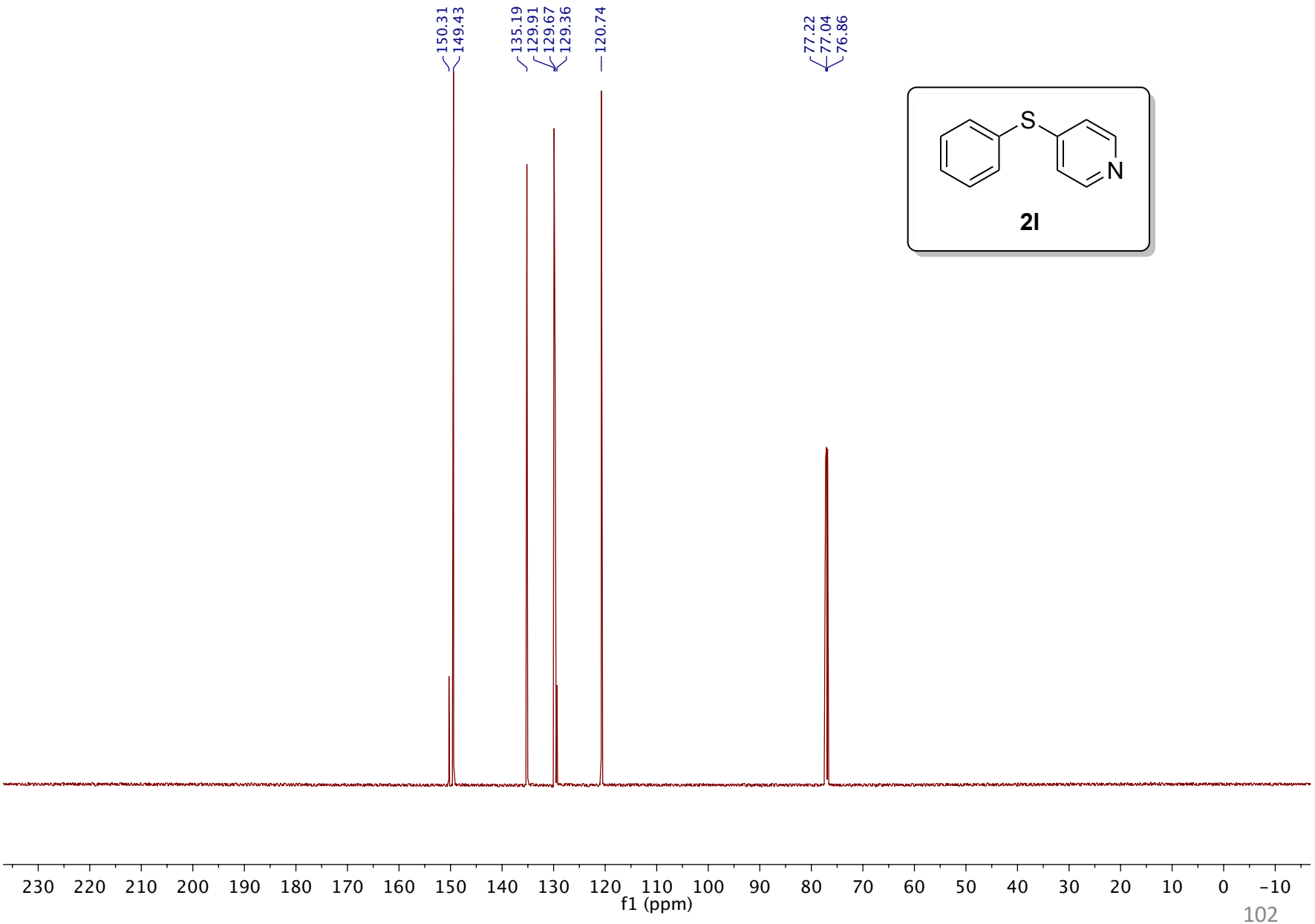

-114.03
S
F
2j
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

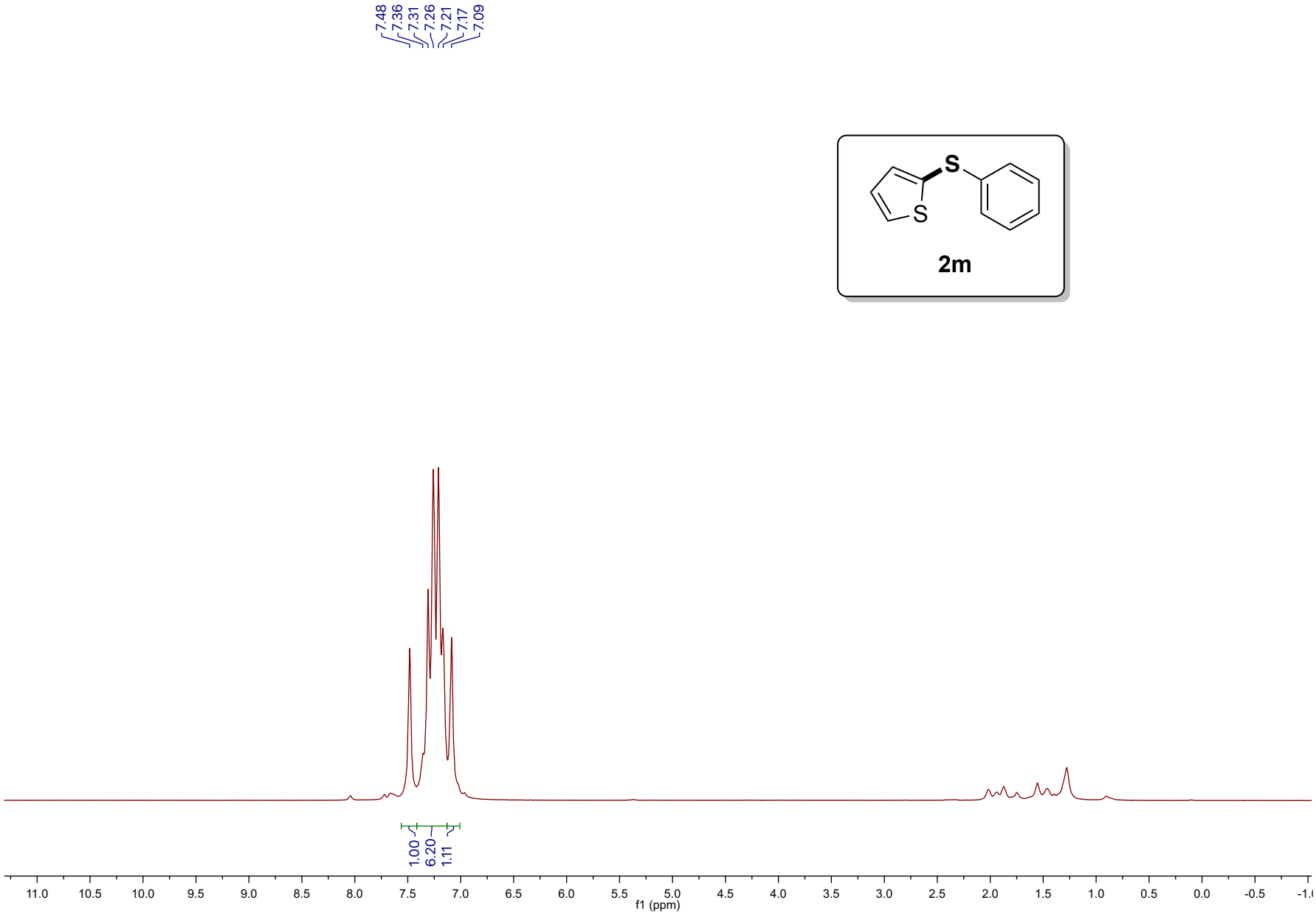

7.49
7.48
7.48
7.47
7.47
7.47
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.27
7.26
7.26
S
CF3
2k
4.04
3.00
2.29
f1 (ppm)

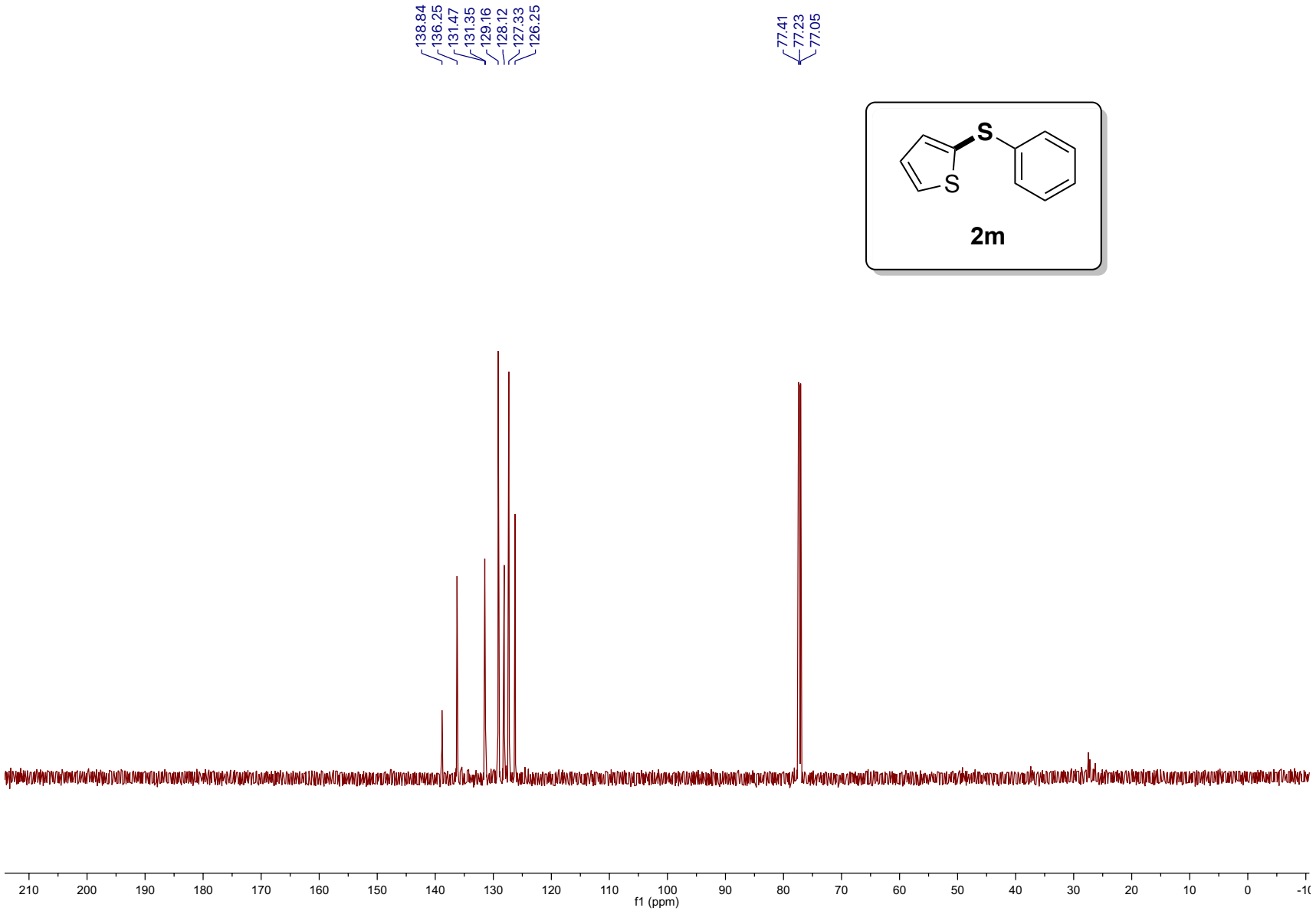

143.04
143.03
133.75
132.68
130.02
129.89
128.87
128.47
128.31
128.13
127.94
126.61
126.05
126.03
126.01
125.98
125.06
123.52
121.97
77.41
77.23
77.05
S
CF3
2k
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

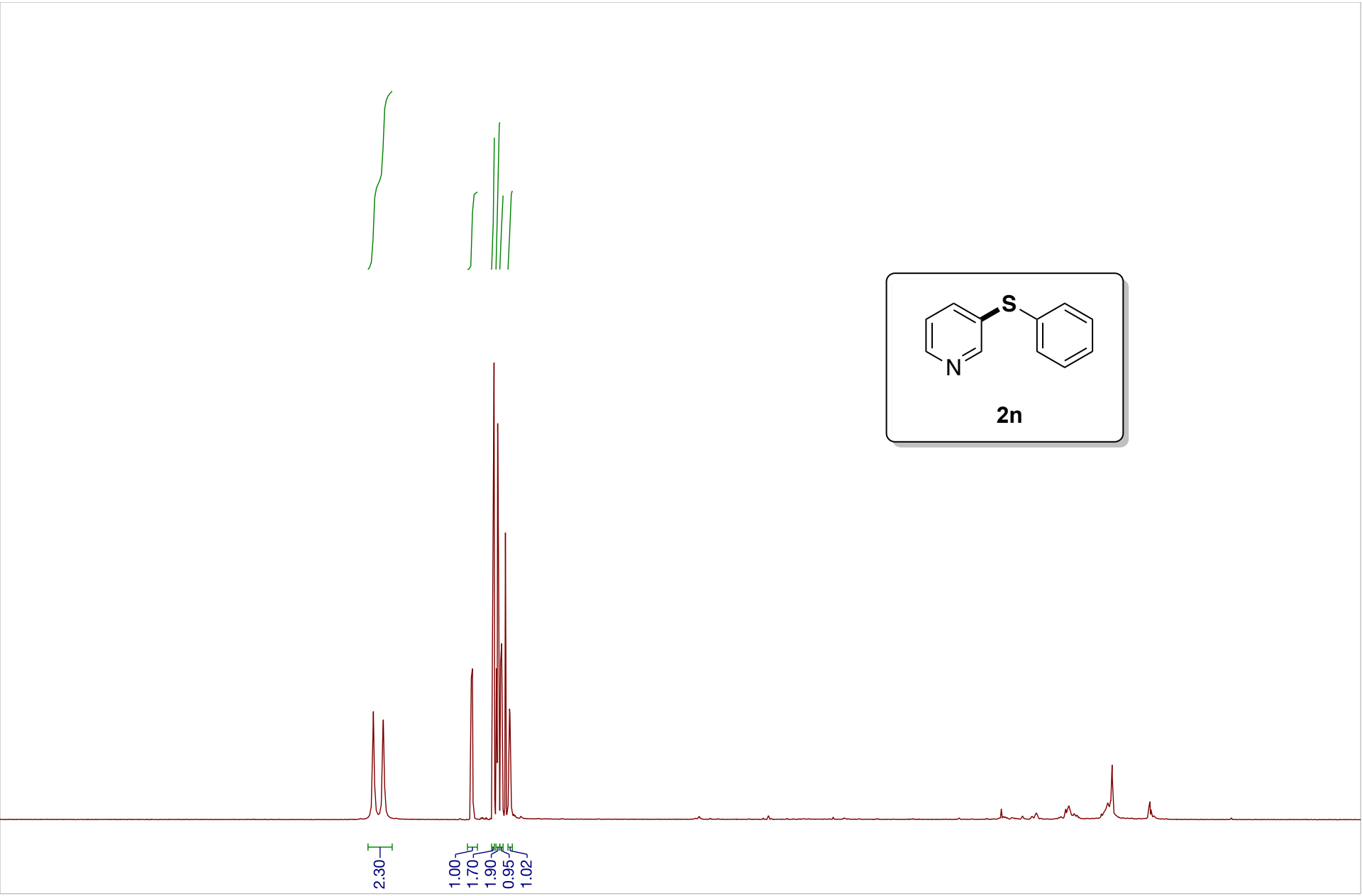

-62.52
S
CF3
2k
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

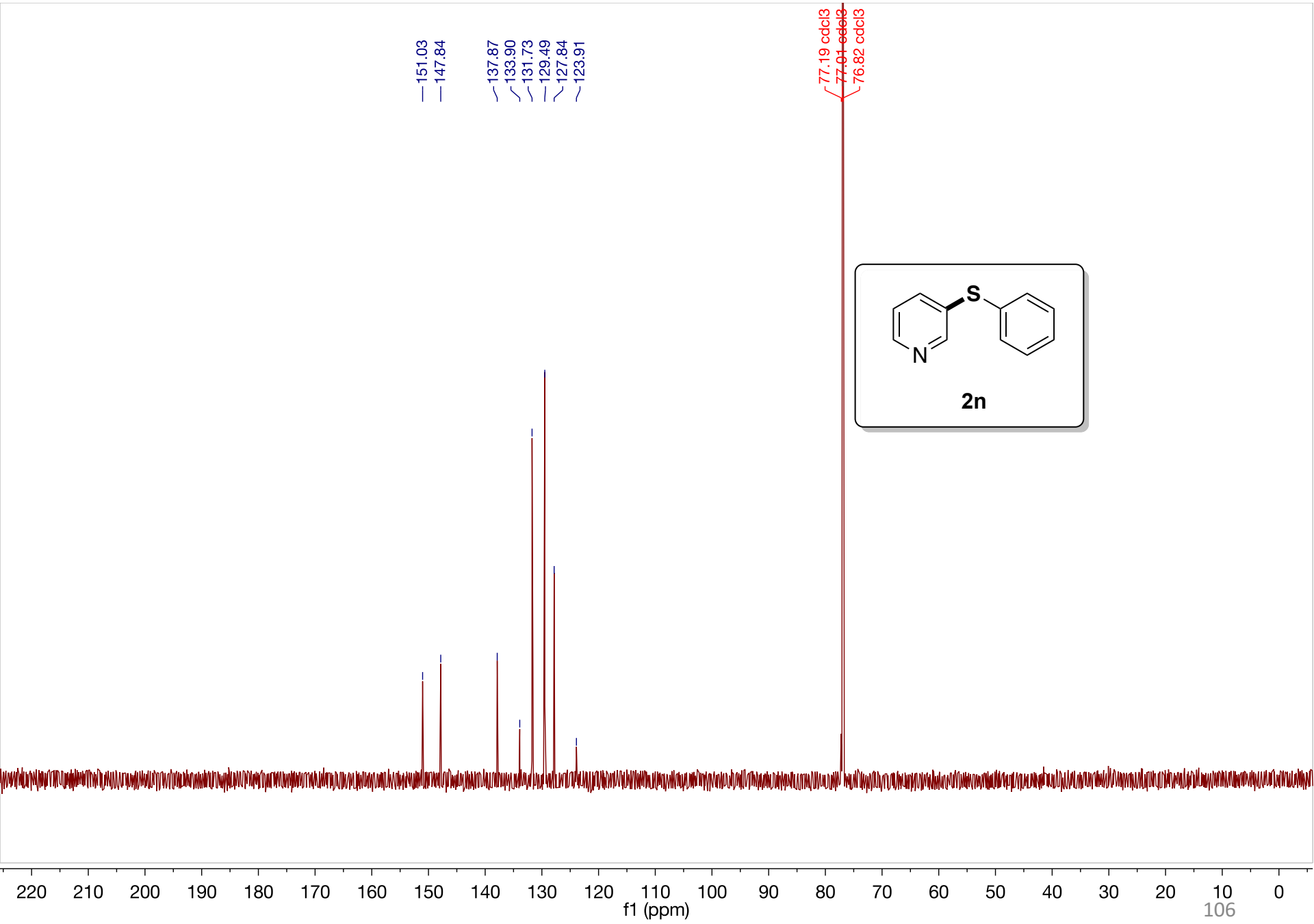

8.34
8.34
8.33
8.33
7.55
7.55
7.55
7.54
7.54
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.26
6.93
6.93
6.92
6.92
S
N
2l
2.19
2.00
3.01
2.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


150.31
149.43
135.19
129.91
129.67
129.36
120.74
77.22
77.04
76.86
S
N
2l
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

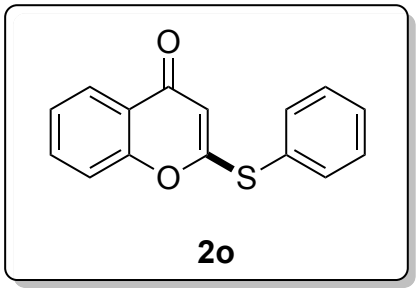

7.48
7.36
7.31
7.26
7.21
7.17
7.09
S
S
2m
1.00
6.20
1.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


138.84
136.25
131.47
131.35
129.16
128.12
127.33
126.25
77.41
77.23
77.05
S
S
2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

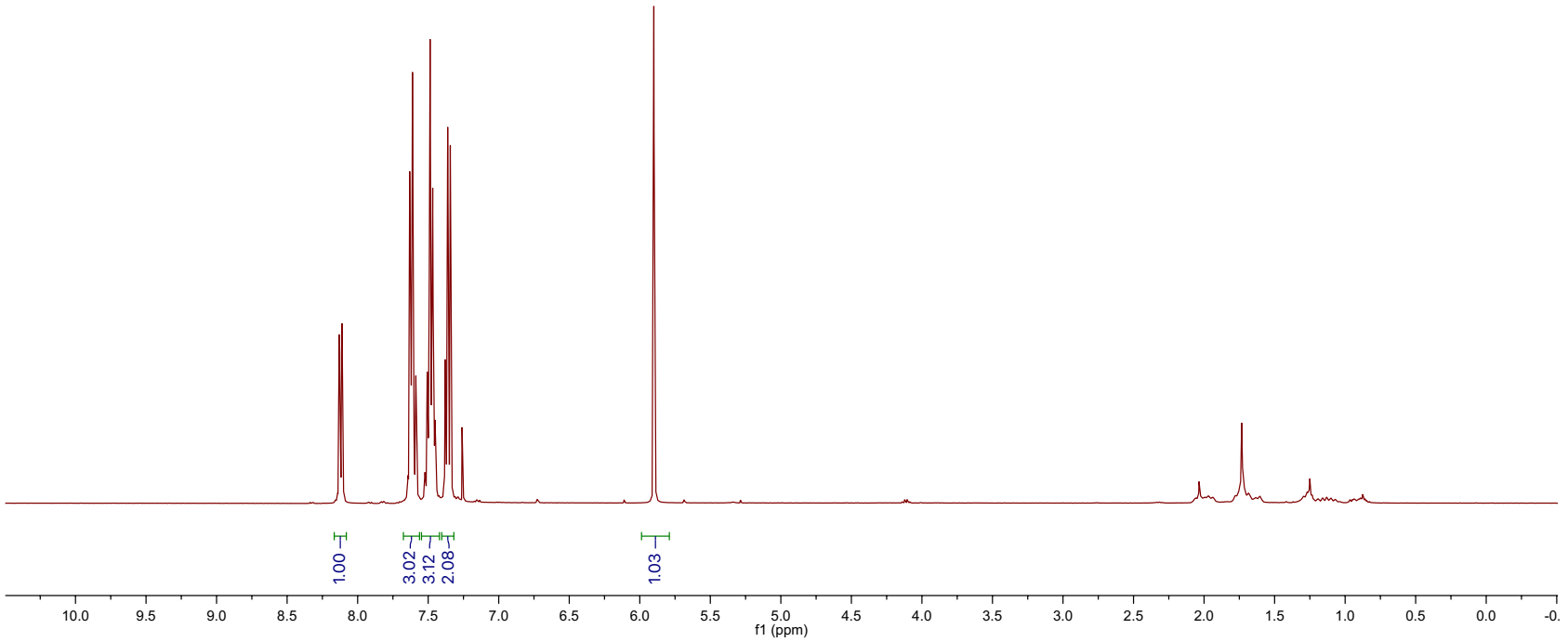

S
N
2n
2.30
1.00
1.70
1.90
0.95
1.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

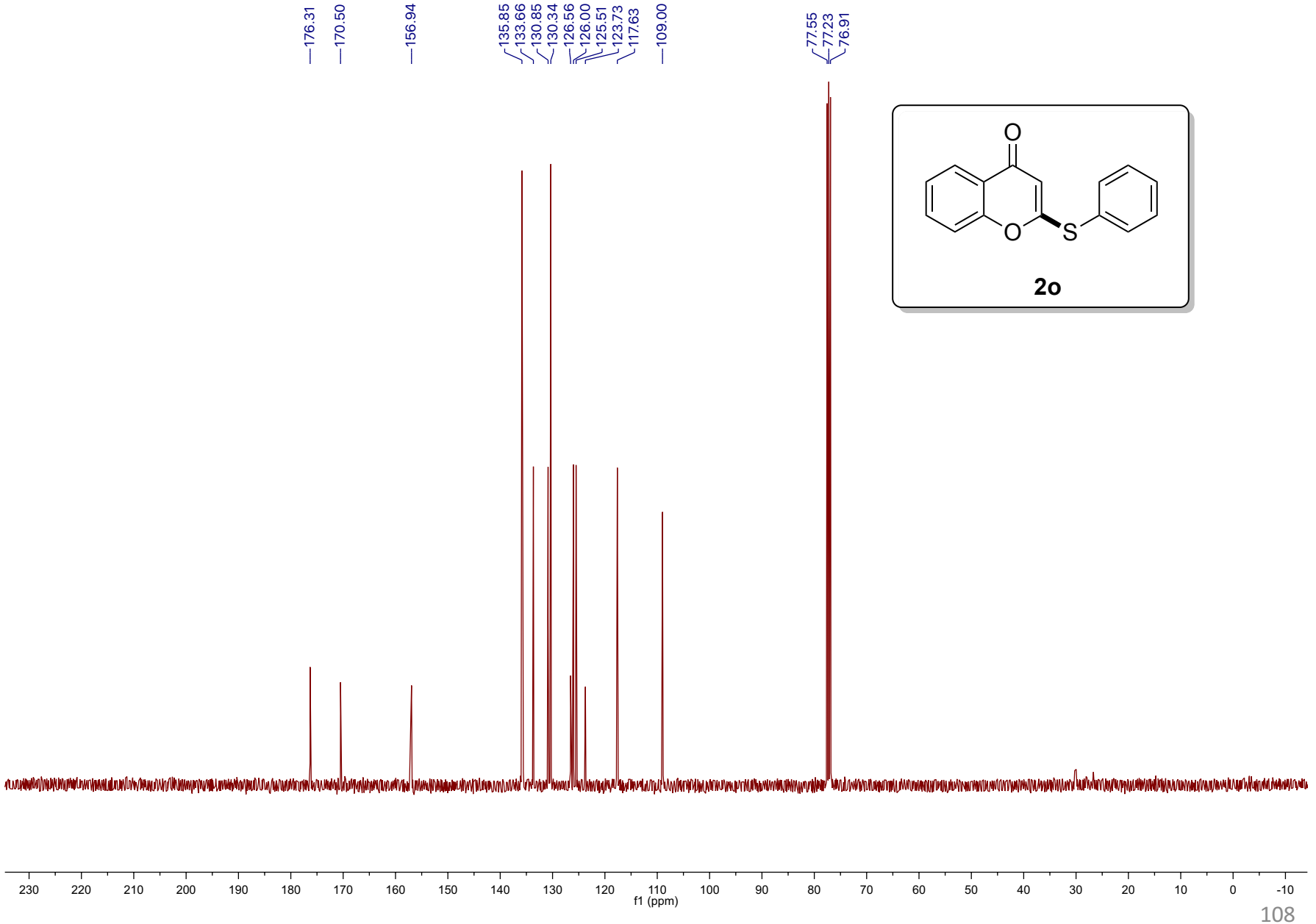

151.03
147.84
137.87
133.90
131.73
129.49
127.84
123.91
77.19 cdcl3
77.01 cdcl3
76.82 cdcl3
S
N
2n
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

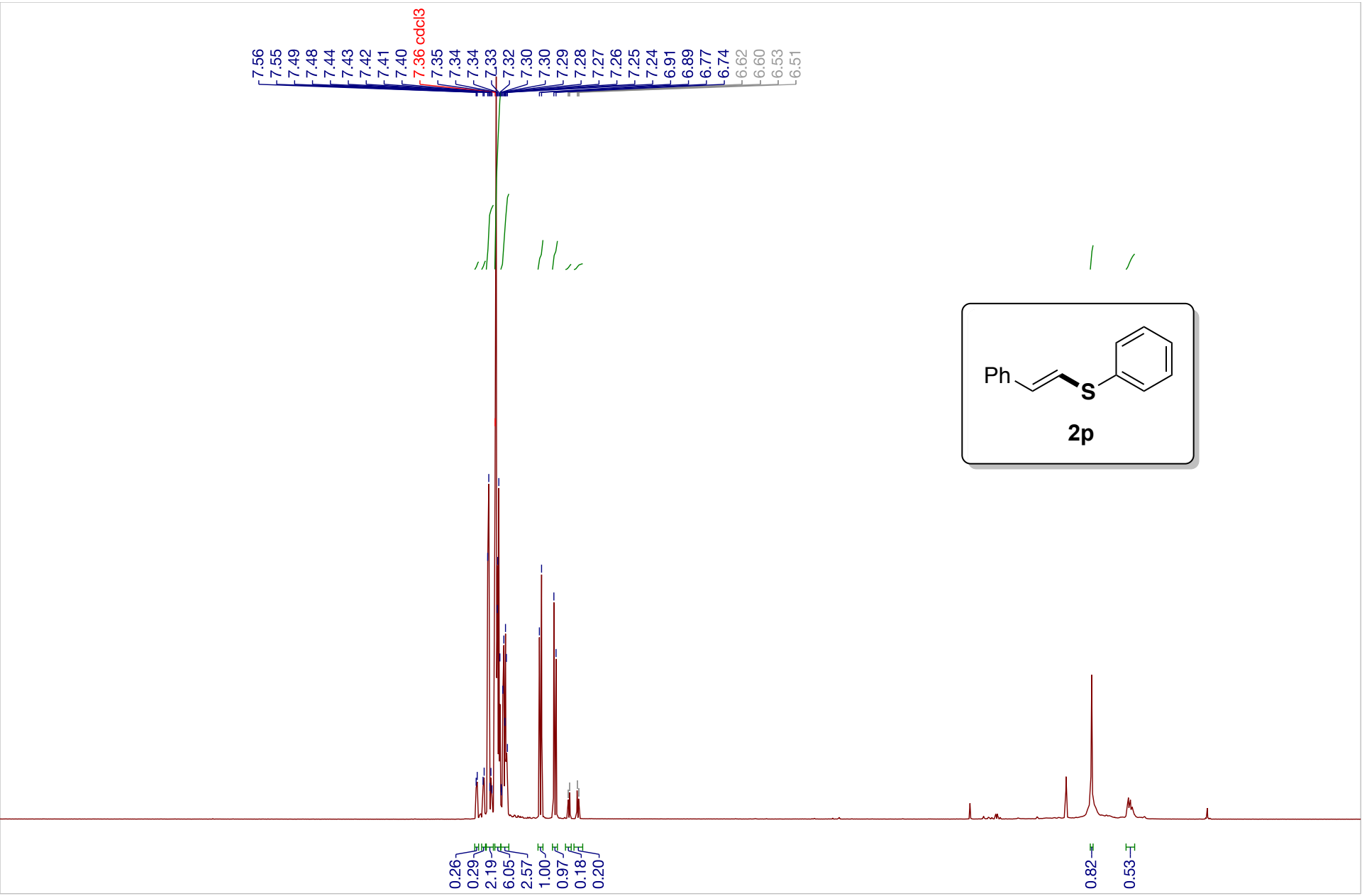

8.14
8.13
8.11
8.11
7.64
7.63
7.63
7.62
7.62
7.61
7.61
7.60
7.59
7.59
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.38
7.37
7.36
7.36
7.34
7.26
5.90

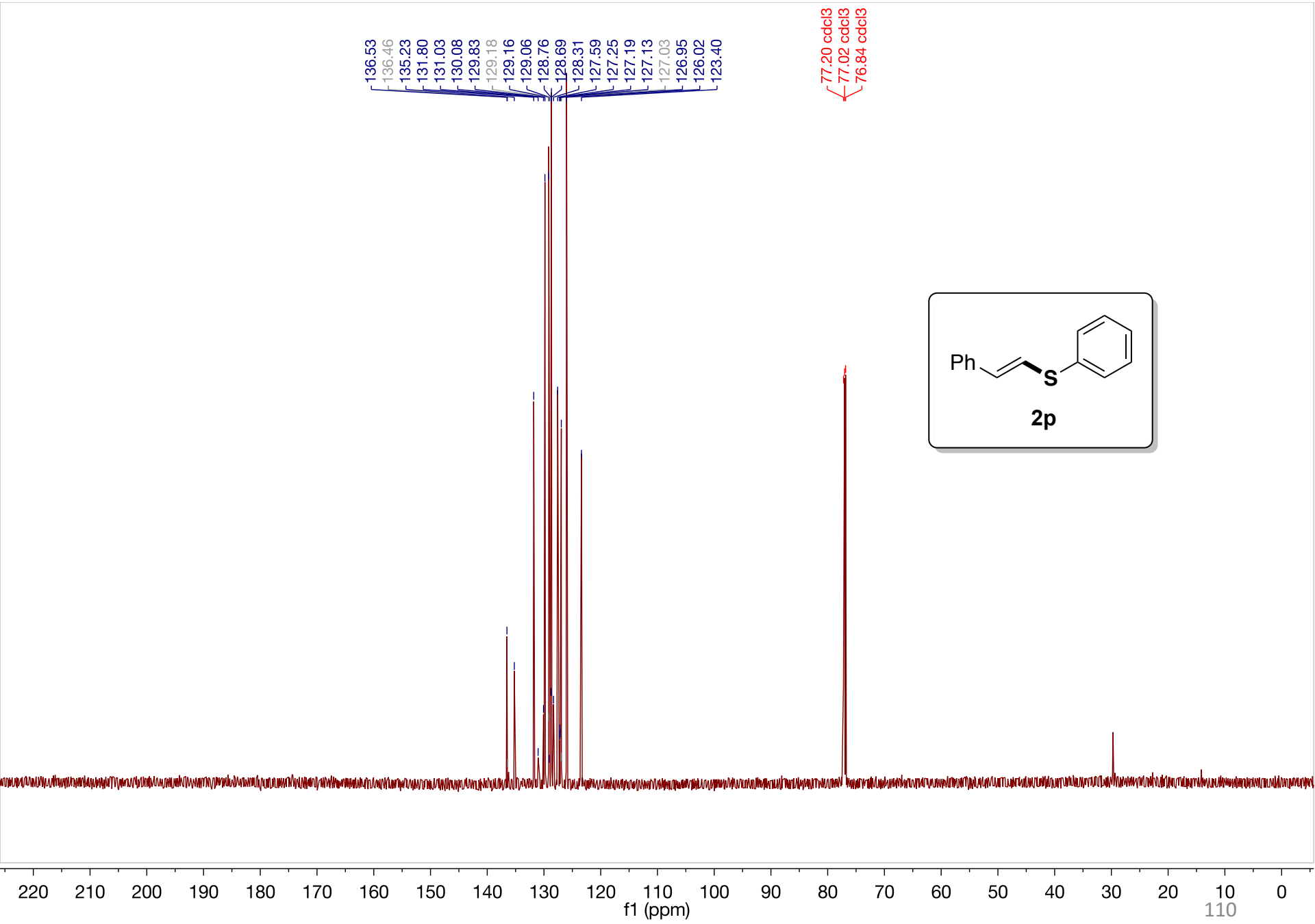

O
O
S

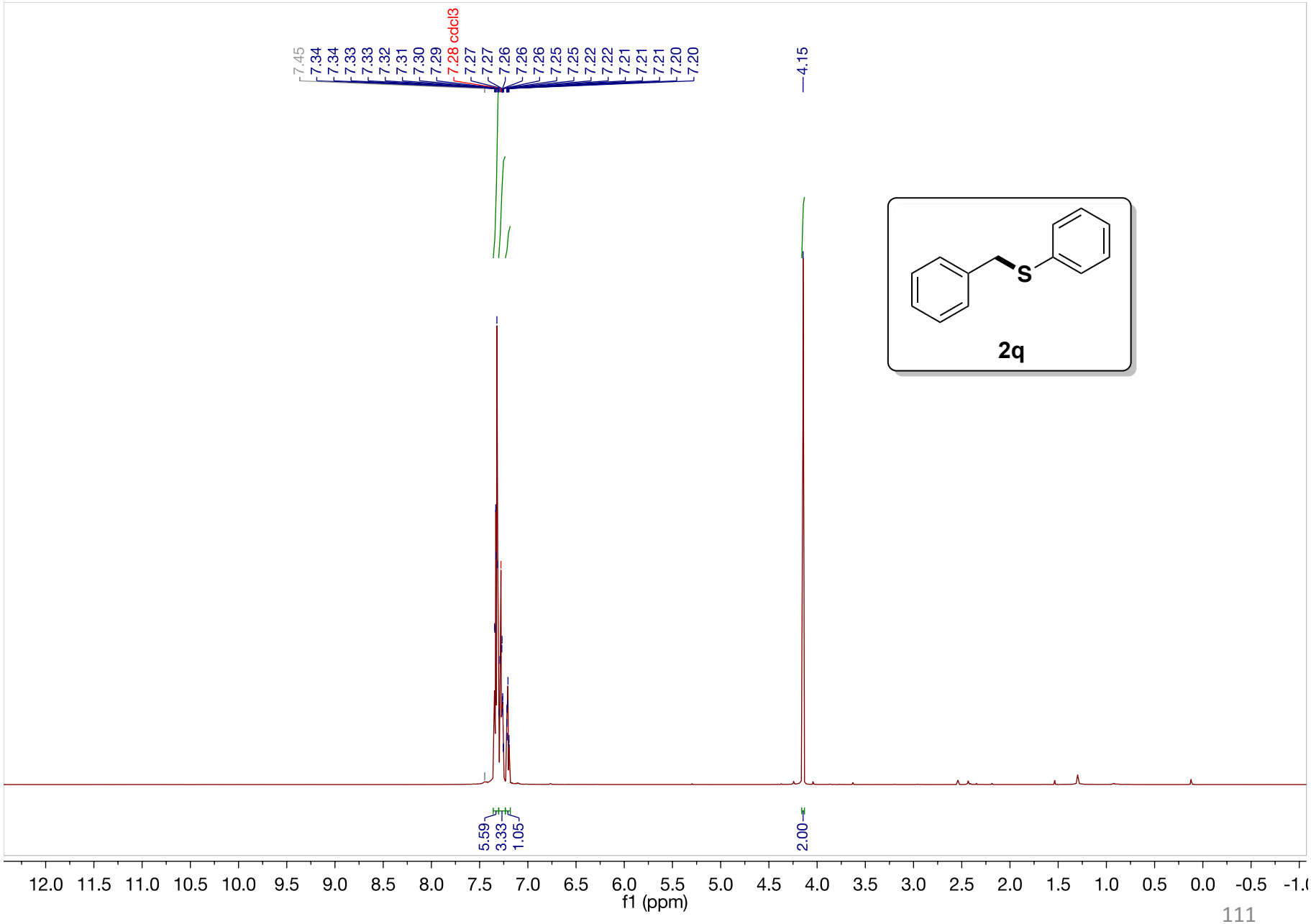
2o

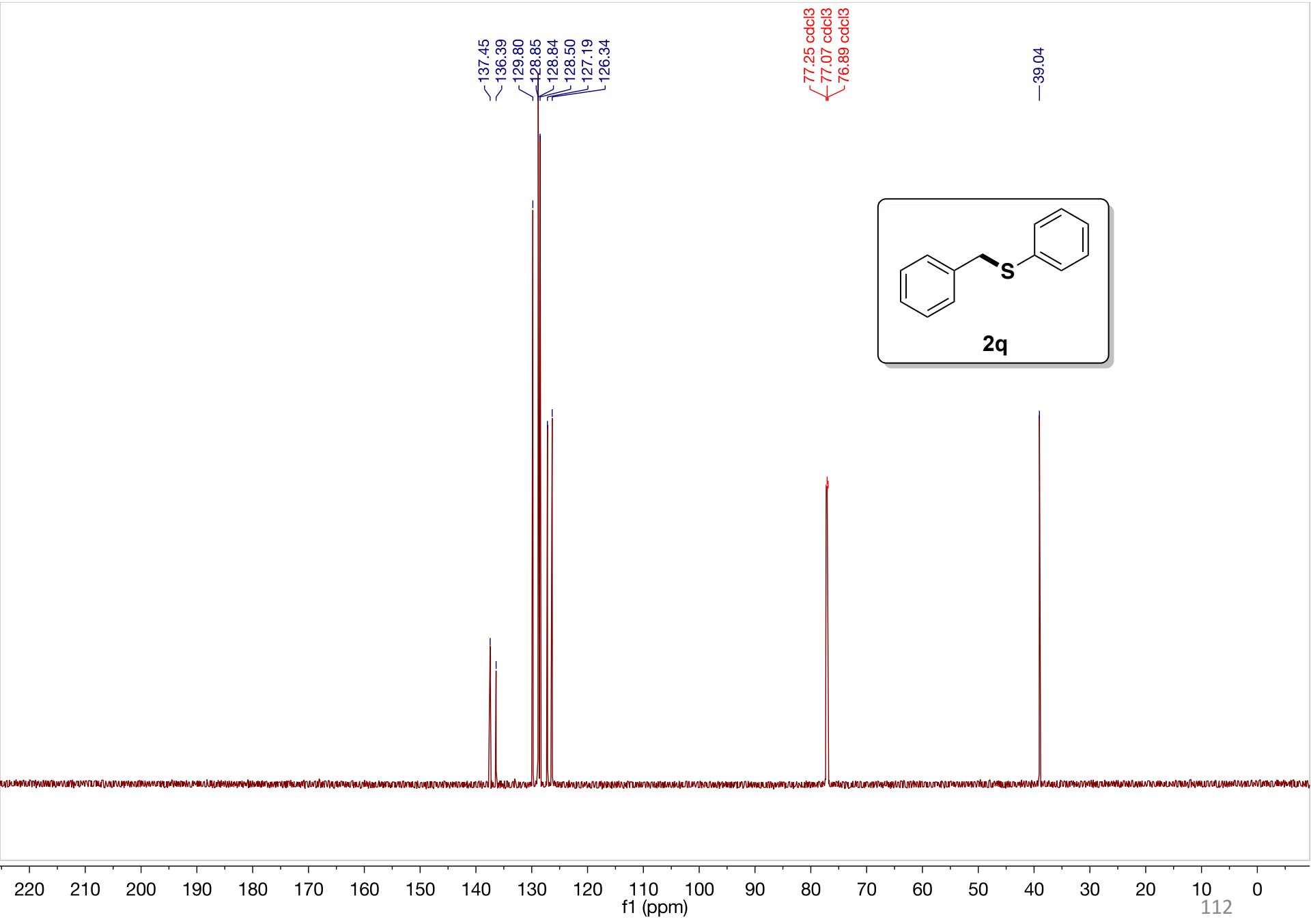

1.00
3.02
3.12
2.08
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

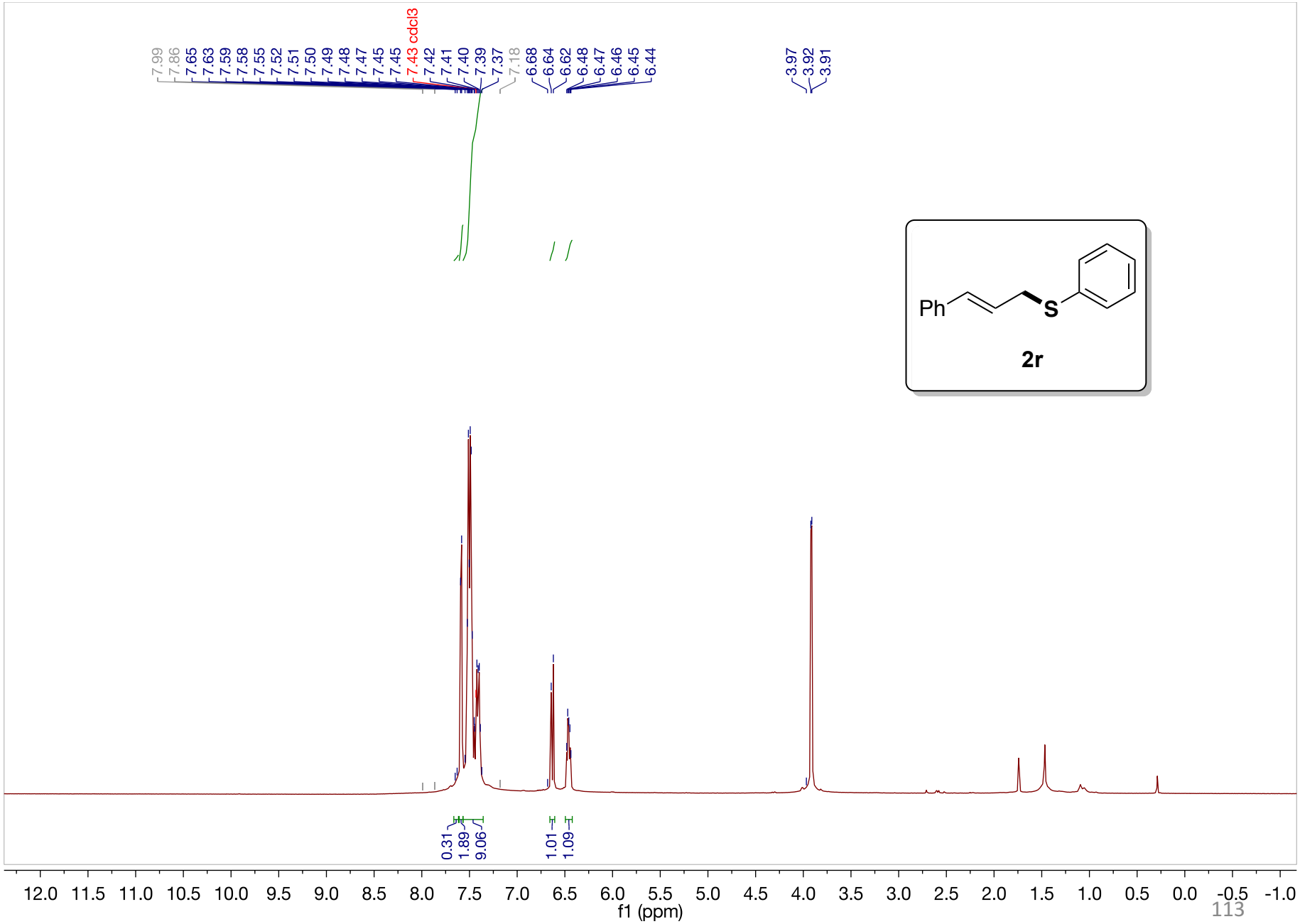

176.31
170.50
156.94
135.85
133.66
130.85
130.34
126.56
126.00
125.51
123.73
117.63
109.00
77.55
77.23
76.91
O
O
S
2o
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

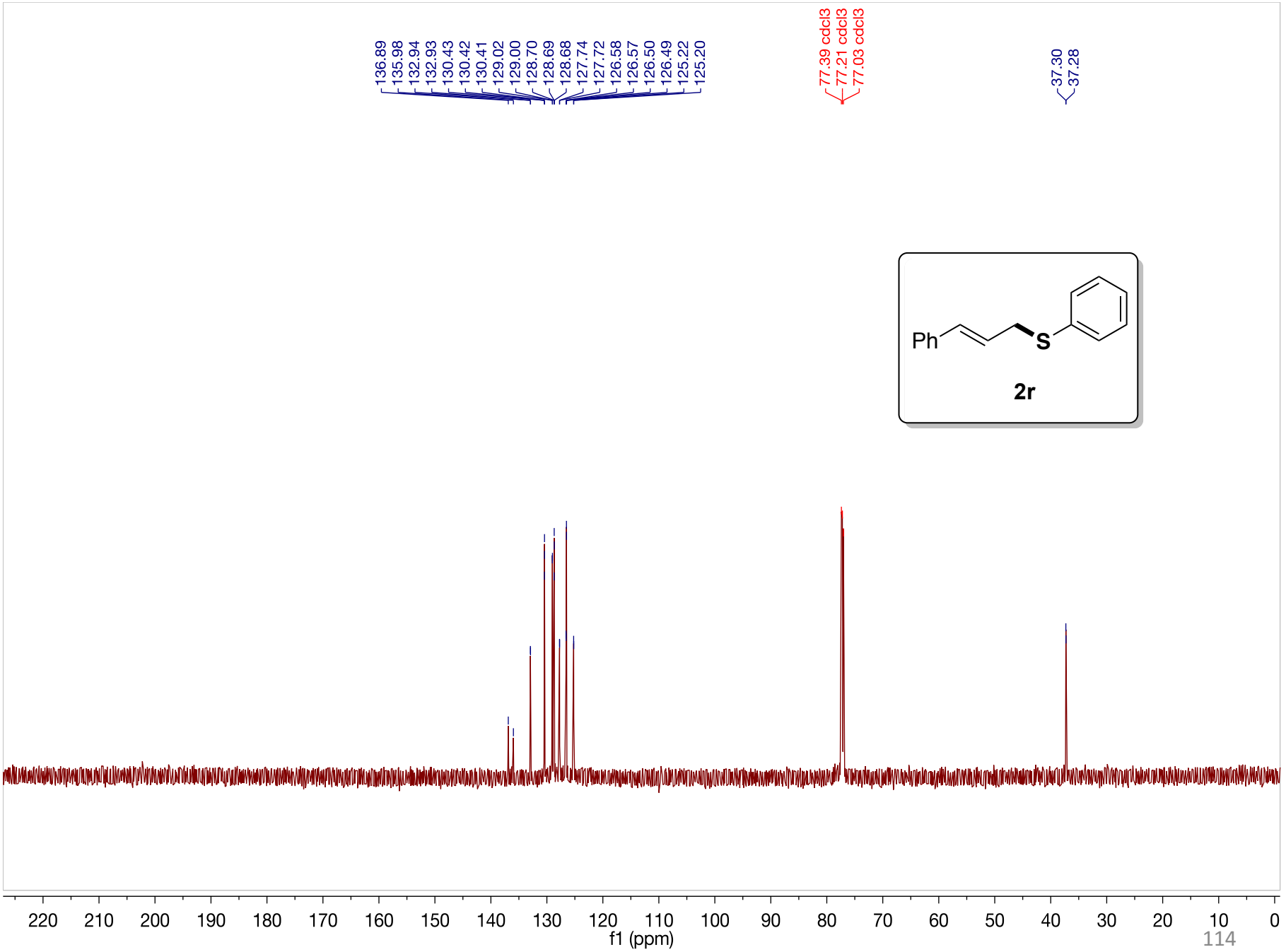

7.56
7.55
7.49
7.48
7.44
7.43
7.42
7.41
7.40
7.36 cdcl3
7.35
7.34
7.34
7.33
7.32
7.30
7.30
7.29
7.28
7.27
7.26
7.25
7.24
6.91
6.89
6.77
6.74
6.62
6.60
6.53
6.51
Ph
S
2p
0.26
0.29
2.19
6.05
2.57
1.00
0.97
0.18
0.20
0.82
0.53
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

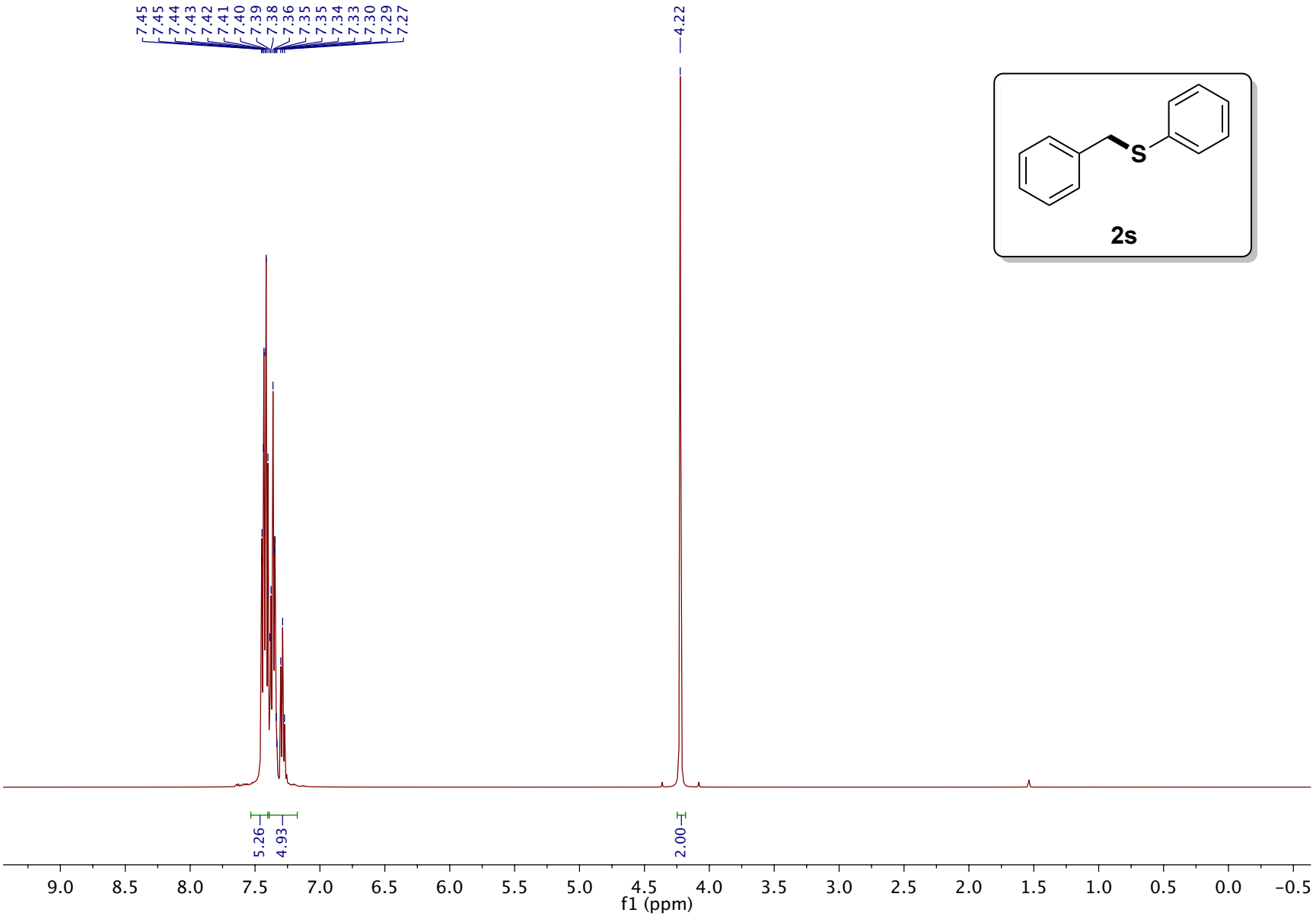

136.53
136.46
135.23
131.80
131.03
130.08
129.83
129.18
129.16
129.06
128.76
128.69
128.31
127.59
127.25
127.19
127.13
127.03
126.95
126.02
123.40
77.20 cdcl3
77.02 cdcl3
76.84 cdcl3
Ph
S
2p
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

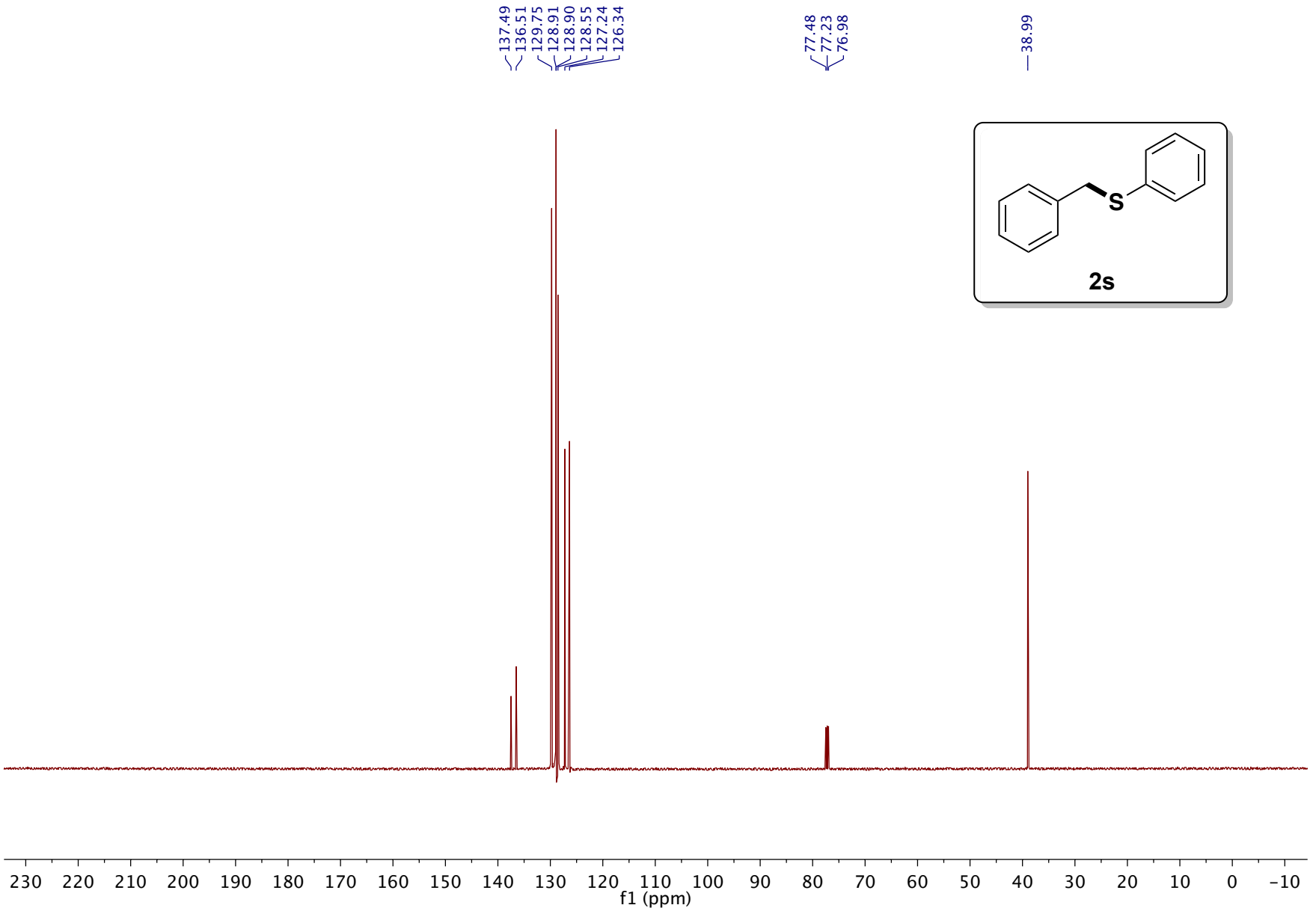

7.45
7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.28 cdcl3
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.22
7.22
7.21
7.21
7.21
7.20
7.20
4.15
S
2q
5.59
3.33
1.05
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

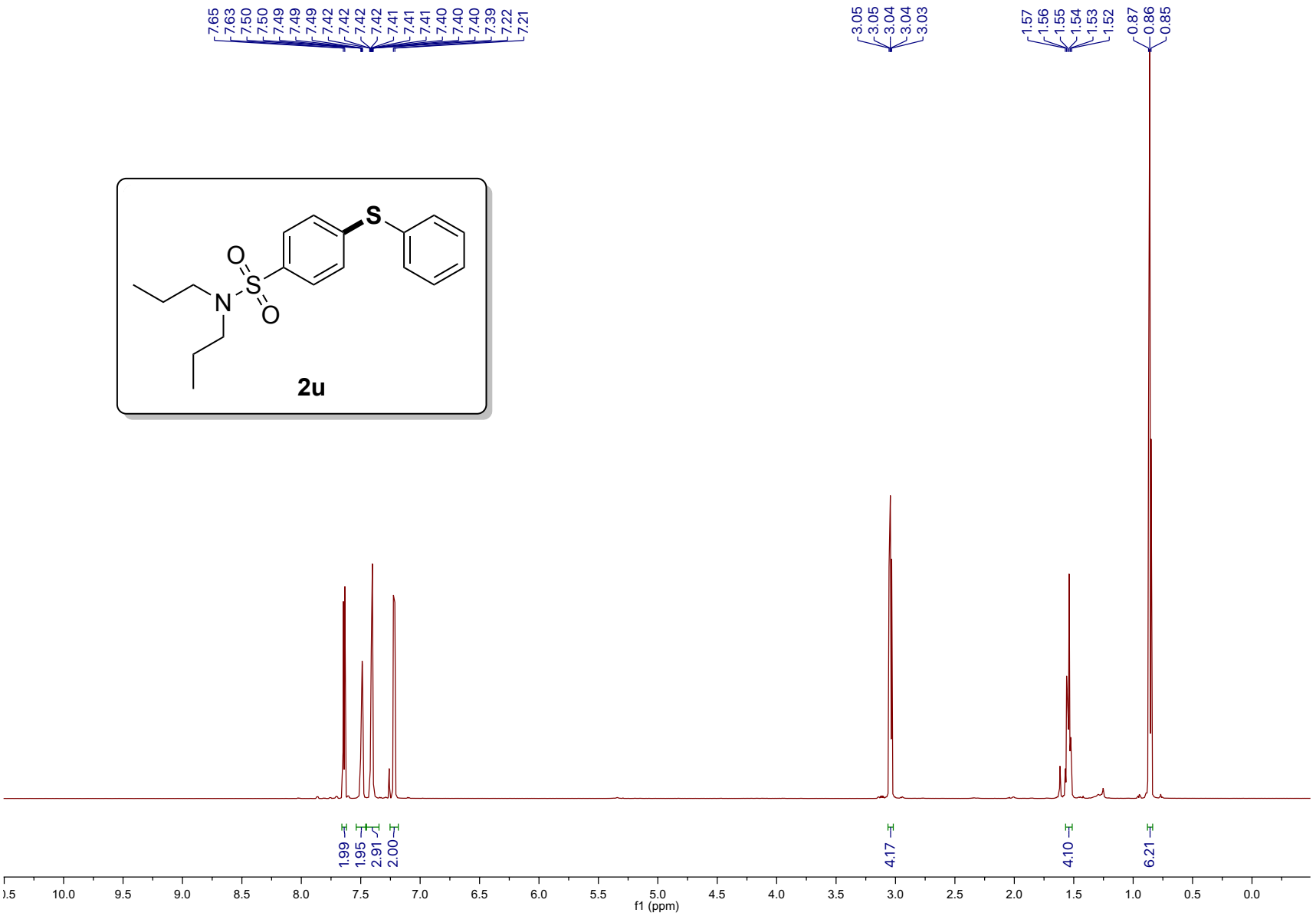

137.45
136.39
129.80
128.85
128.84
128.50
127.19
126.34
77.25 cdcl3
77.07 cdcl3
76.89 cdcl3
39.04
S
2q
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

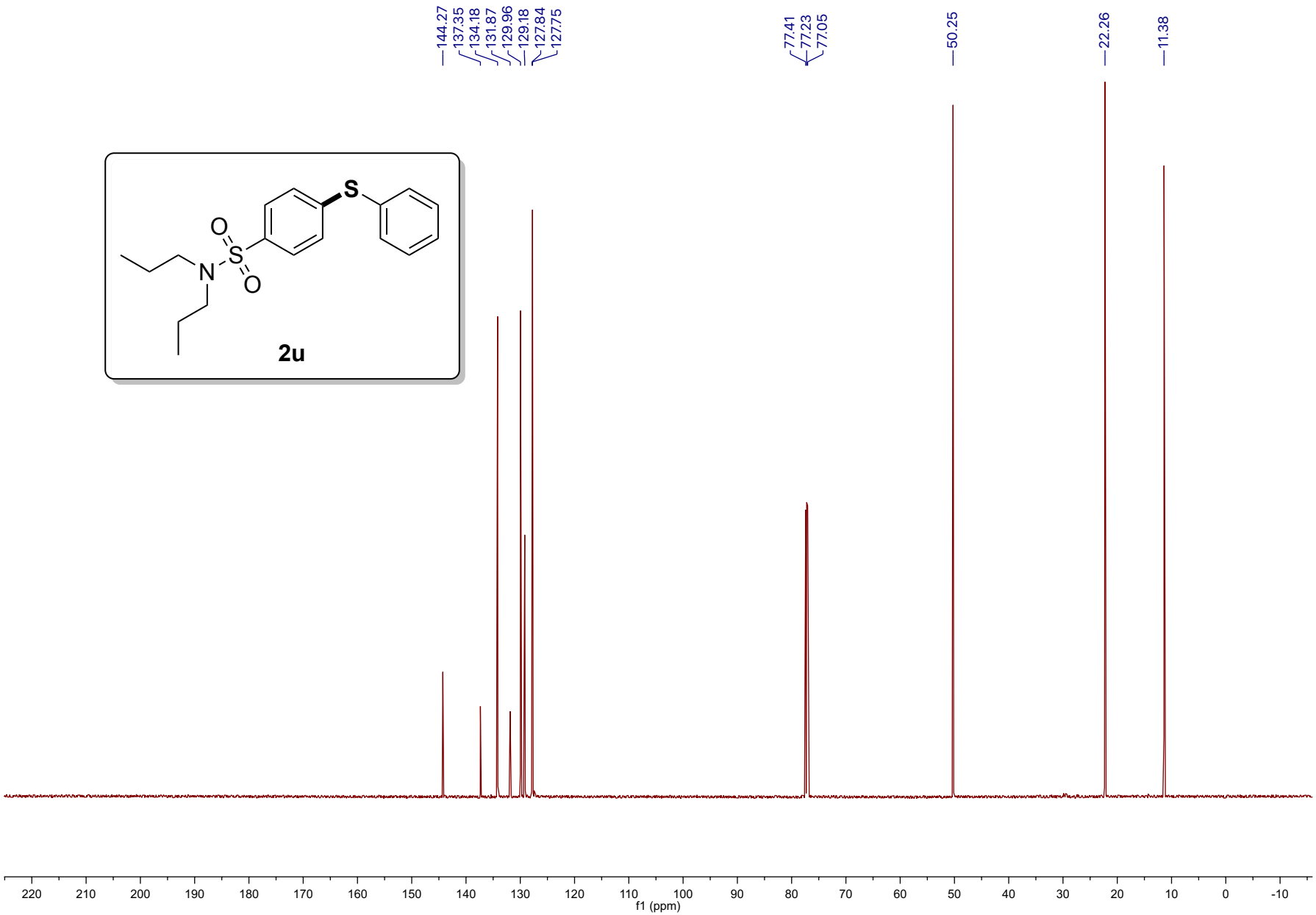

7.99
7.86
7.65
7.63
7.59
7.58
7.55
7.52
7.51
7.50
7.49
7.48
7.47
7.45
7.45
7.43 cdcl3
7.42
7.41
7.40
7.39
7.37
7.18
6.68
6.64
6.62
6.48
6.47
6.46
6.45
6.44
3.97
3.92
3.91
Ph
S
2r
0.31
1.89
9.06
1.01
1.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

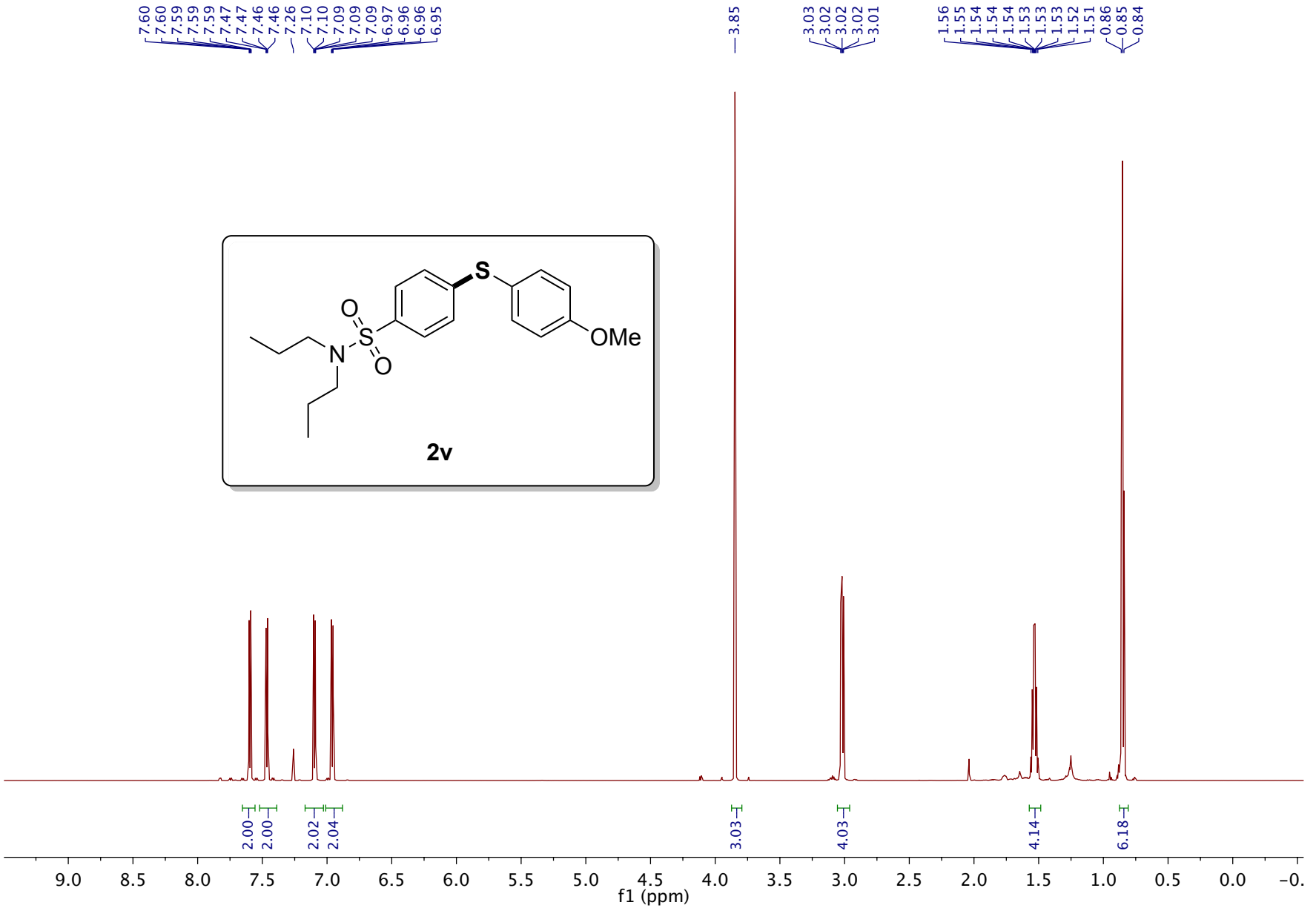

136.89
135.98
132.94
132.93
130.43
130.42
130.41
129.02
129.00
128.70
128.69
128.68
127.74
127.72
126.58
126.57
126.50
126.49
125.22
125.20
77.39 cdcl3
77.21 cdcl3
77.03 cdcl3
37.30
37.28
Ph
S
2r
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

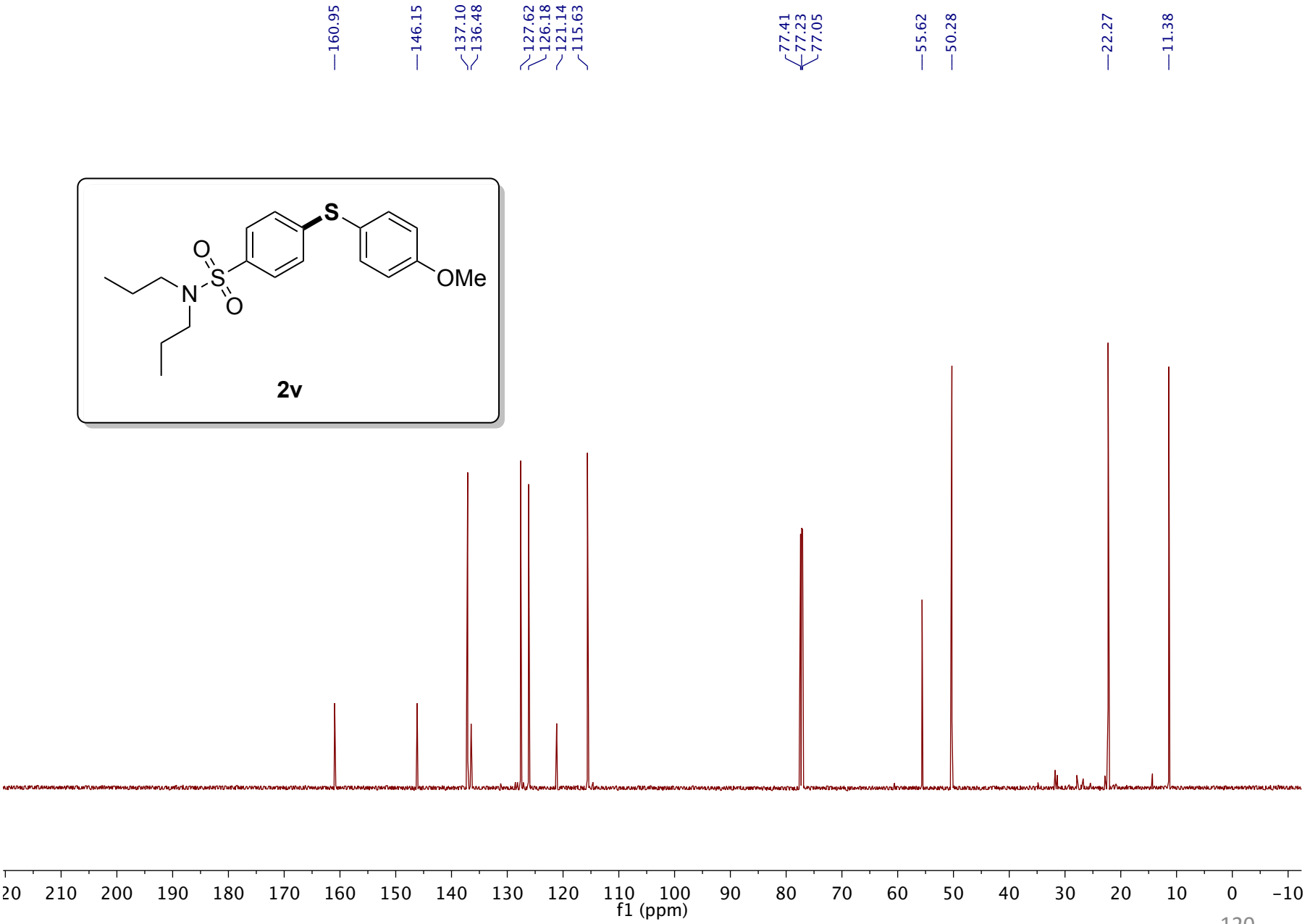

7.45
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.36
7.35
7.35
7.34
7.33
7.30
7.29
7.27
4.22
S
2s
5.26
4.93
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

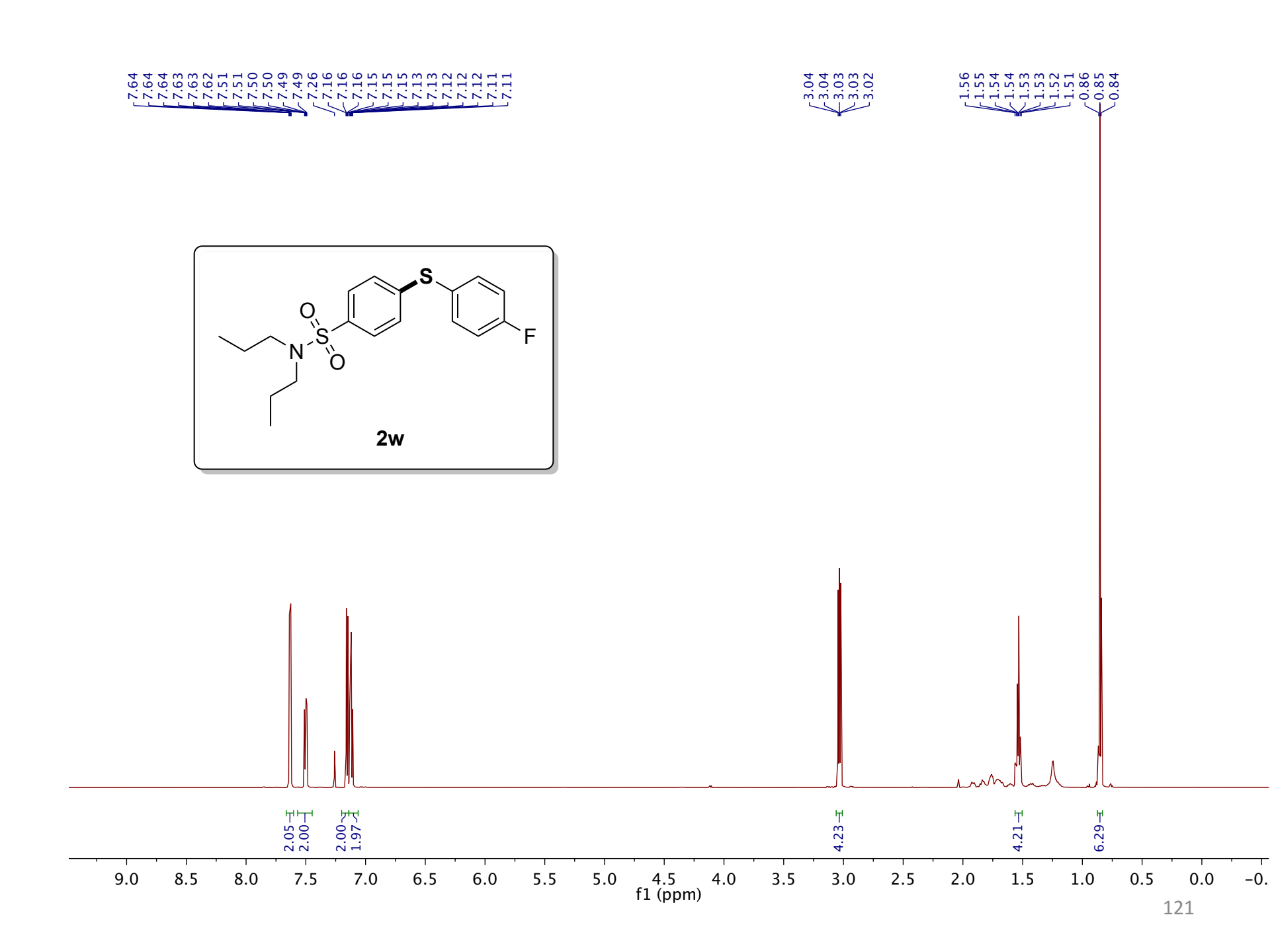

137.49
136.51
129.75
128.91
128.90
128.55
127.24
126.34
77.48
77.23
76.98
38.99
S
2s
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

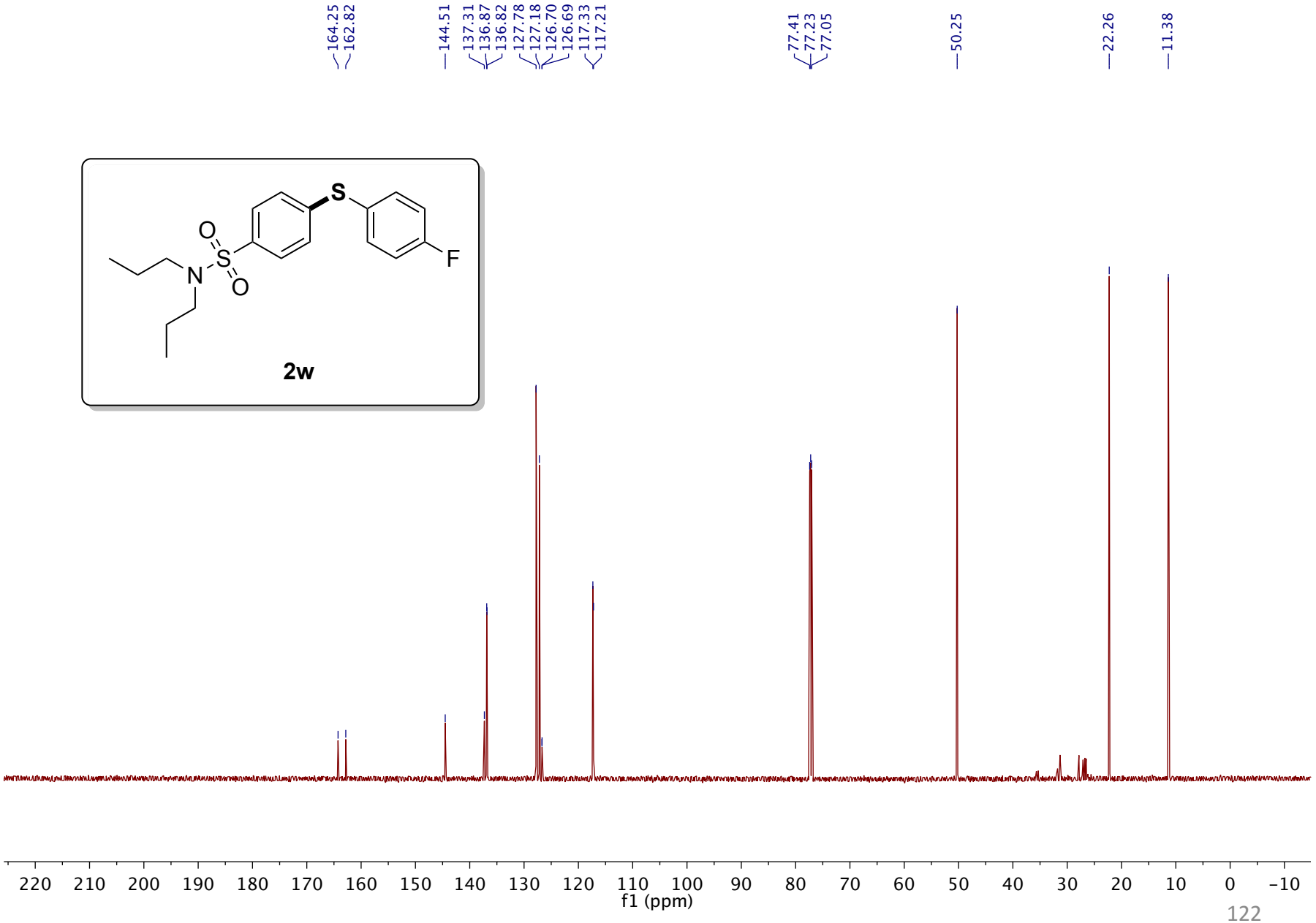

7.65
7.63
7.50
7.50
7.49
7.49
7.49
7.42
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
7.22
7.21
3.05
3.05
3.04
3.04
3.03
1.57
1.56
1.55
1.54
1.53
1.52
0.87
0.86
0.85
O
S
O
N
S
2u
1.99
1.95
2.91
2.00
4.17
4.10
6.21
f1 (ppm)

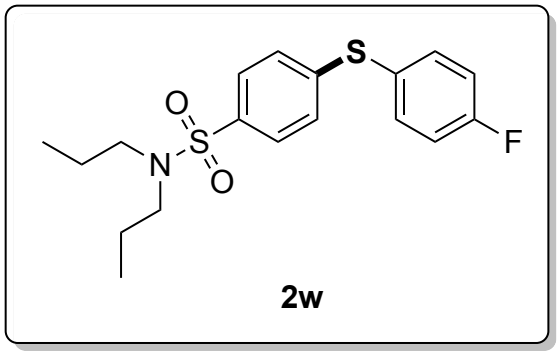

144.27
137.35
134.18
131.87
129.96
129.18
127.84
127.75
77.41
77.23
77.05
50.25
22.26
11.38
O
S
O
N
S
2u
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.60
7.60
7.59
7.59
7.59
7.47
7.47
7.46
7.46
7.26
7.10
7.10
7.09
7.09
7.09
6.97
6.96
6.96
6.95
3.85
3.03
3.02
3.02
3.02
3.01
1.56
1.55
1.54
1.54
1.54
1.53
1.53
1.53
1.52
1.51
0.86
0.85
0.84
S
O
S
O
N
OMe
2v
2.00
2.00
2.02
2.04
3.03
4.03
4.14
6.18
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.
f1 (ppm)


160.95
146.15
137.10
136.48
127.62
126.18
121.14
115.63
77.41
77.23
77.05
55.62
50.28
22.27
11.38
O
S
O
N
S
OMe
2v
f1 (ppm)


7.64 7.64 7.64 7.63 7.63 7.62 7.51 7.51 7.50 7.50 7.49 7.49 7.26 7.16 7.16 7.16 7.15 7.15 7.15 7.13 7.13 7.12 7.12 7.12 7.11 7.11
3.04 3.04 3.03 3.03 3.02
1.56 1.55 1.54 1.54 1.53 1.53 1.52 1.51 0.86 0.85 0.84
O
S
O
N
S
F
2w
2.05 2.00 2.00 1.97 4.23 4.21 6.29
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.
f1 (ppm)


164.25
162.82
144.51
137.31
136.87
136.82
127.78
127.18
126.70
126.69
117.33
117.21
77.41
77.23
77.05
50.25
22.26
11.38
S
O
S
O
N
F
2w
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


S
O
S
O
N
F

2w

-111.29
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)