

Efficient synthesis of 3-arylbutadiene sulfones using the Heck–Matsuda reaction

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General information. 3-Sulfolene was purchased from Aldrich was purified by double recrystallization from MeOH and was finely ground (with a mortar and pestle) prior to use. Pd(OAc)₂ was purchased from Aldrich. Aryldiazonium salts were synthesized according to the literature procedure from corresponding anilines and were well-dried before use.^{S1} Silica gel chromatography purifications were performed by flash chromatography using EM Science silica gel 60 (230-400 mesh). All other reagents were commercially available and were used without further purification. All new compounds were characterized by ¹H and ¹³C NMR spectroscopy and HRMS. Chemicals and solvents were obtained from commercial sources and used without further purification. NMR spectra were obtained on a Bruker “Ascend™ 400” (400 MHz ¹H, 101 MHz ¹³C). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as “s”, “d”, “t” or “m” for singlet, doublet, triplet or multiplet, respectively. The abbreviation “br” is given for broadened signals. HRMS spectra were carried out using AB Sciex TripleTOF 5600+ supported TurboV ESI ionization source.

General Procedure An oven-dried screw-cap tube was cooled to room temperature under argon pressure and charged with aryl diazonium salt (1.0 mmol), 3-sulfolene (1.3 mmol), Pd(OAc)₂ (6.7 mg, 3 mol%) and CH₃OH or THF (2 or 5 ml/mmol respectively). The tube was sealed and placed in a preheated oil bath at 50 °C and stirred for 1h. The reaction mixture was allowed to cool to room temperature followed by evacuation of solvent. Then crude was dissolved in CH₂Cl₂ (5 ml/mmol) and Et₃N (1 ml/mmol) was added followed by refluxed with stirring for 6-24h. The resulting solution was washed with 10% citric acid, dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. The crude product was purified by flash chromatography on silica gel (eluent: CH₂Cl₂/petroleum ether).

Table S1 Optimization of catalytic system and reaction conditions in the Heck-Matsuda reaction between 3-sulfolene and aryldiazonium salts

Entry	Catalyst/base	Solvent	Aryldiazonium salt	<i>T</i> /°C	Yield %
1	Pd ₂ (dba) ₃ /NaOAc	MeCN	PhN ₂ ⁺ BF ₄ ⁻	50	1%
2	Pd(OAc) ₂ 1%/ -	MeOH	PhN ₂ ⁺ BF ₄ ⁻	50	40%
3	Pd(OAc) ₂ 2%/ -	MeOH	PhN ₂ ⁺ BF ₄ ⁻	50	70%
4	Pd(OAc) ₂ 3%/ -	MeOH	PhN ₂ ⁺ BF ₄ ⁻	50	95%
5	Pd ₂ (dba) ₃ ·CHCl ₃ 3%/ -	MeOH	PhN ₂ ⁺ BF ₄ ⁻	50	95%
6	Pd(OAc) ₂ 3%/ -	THF	PhN ₂ ⁺ BF ₄ ⁻	50	65%
7	Pd(OAc) ₂ 3%/ -	MeCN/MeOH 1:1	PhN ₂ ⁺ BF ₄ ⁻	50	1%
8	Pd(OAc) ₂ 3%/ -	Acetone	PhN ₂ ⁺ BF ₄ ⁻	50	7%
9	Pd(OAc) ₂ 3%/ -	NMP	PhN ₂ ⁺ BF ₄ ⁻	50	13%
10	Pd(OAc) ₂ 3%/ -	EtOH	PhN ₂ ⁺ BF ₄ ⁻	50	35%
11	Pd(OAc) ₂ 3%/ -	1,4-dioxane	PhN ₂ ⁺ BF ₄ ⁻	50	27%
12	Pd(OAc) ₂ 3%/ -	MeOH	PhN ₂ ⁺ BF ₄ ⁻	rt	82%
13	Pd(OAc) ₂ 3%/ -	MeOH	4-O ₂ NC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻	50	56%
14	Pd(OAc) ₂ 3%/ -	THF	4-O ₂ NC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻	50	90%
15	Pd ₂ (dba) ₃ ·CHCl ₃ , Ph ₃ P/AcONa	MeCN/H ₂ O	4-O ₂ NC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻	50	0%
16	Pd(OAc) ₂ 3%/ -	1,4-dioxane	4-O ₂ NC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻	50	25%
17	Pd(OAc) ₂ 3%/ -	THF	4-O ₂ NC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻	~20	51%

^a Reaction conditions: 3-sulfolene (1.3 mmol), aryldiazonium salt (1 mmol), 1 h.

3-Phenyl-2,3-dihydrothiophene 1,1-dioxide (**1**)

Yield 184 mg (95%), white solid, m.p. 83-84 °C, lit. data: m.p. 90 °C.^{S2}

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.31 (m, 3H), 7.28 – 7.23 (m, 2H), 6.81 – 6.72 (m, 2H), 4.42 – 4.30 (m, 1H), 3.73 (dd, *J* = 13.9, 8.7 Hz, 1H), 3.19 (dd, *J* = 13.9, 4.9 Hz, 1H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 142.1, 139.1, 131.8, 129.5, 128.3, 127.4, 56.0, 45.0.

NMR is in agreement with lit. data.²

3-Phenyl-2,5-dihydrothiophene 1,1-dioxide (**2a**)

Yield 184 mg (95%) in CH₃OH, 126 mg (65%) in THF; white solid, m.p. 132-134 °C (from CH₂Cl₂); lit. data: m.p. 134 °C.^{S2}

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.29 (m, 5H, Ar), 6.35 (s, 1H, =CH), 4.14 (s, 2H, CH₂), 4.03 (s, 2H, CH₂).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 136.4 (Ar), 134.1 (=C-Ph), 129.4(=C-CH₃), 129.1 (Ar), 125.6 (Ar), 117.3(CH₂-CH=C), 57.8(CH₂), 56.8(CH₂).

NMR is in agreement with lit. data.^{S2}

3-p-Tolyl-2,5-dihydrothiophene 1,1-dioxide (2b)

Yield 206 mg (99%) in CH₃OH, 148 mg (71%) in THF; yellow solid, m.p. 145-146 °C (from CH₂Cl₂); lit. data: m.p. 148 °C.^{S2}

¹H NMR (400 MHz, CDCl₃) δ 7.25(d, *J* = 8.2 Hz, 2H, Ar), 7.19 (d, *J* = 8.1 Hz, 2H, Ar), 6.29 (s, 1H, C, =CH), 4.12 (s, 2H, CH₂), 4.01 (s, 2H, CH₂), 2.37 (s, 3H, CH₃).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 139.5 (Ar), 136.2(=C-Ar), 131.3 (Ar), 129.7(=C-CH₃), 125.4 (Ar), 116.2 (CH₂-CH=C), 57.8 (CH₂), 56.8(CH₂), 21.4 (CH₃).

HRMS calc. for C₁₁H₁₂NaO₂S [M+Na]⁺ 231.0450; found 231.0453.

3-(4-tert-Butylphenyl)-2,5-dihydrothiophene 1,1-dioxide (2c)

Yield 163 mg (65%) in CH₃OH, 180 mg (72%) in THF; white solid, m.p. 175-177 °C (from CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.3 Hz, 2H, Ar), 7.30 (d, *J* = 8.3 Hz, 2H, Ar), 6.30 (s, 1H, =CH), 4.13 (d, *J* = 2.1 Hz, 2H, CH₂), 4.05 – 3.99 (m, 2H, CH₂), 1.33 (s, 9H, t-Bu).

¹³C {¹H} DEPT-135-Q (101 MHz, CDCl₃) δ 152.7(=C-C(CH₃)₃), 136.2 (=C-Ar), 131.3 (Ar), 126.0 (Ar), 125.3(Ar), 116.4 (CH₂-CH=C), 59.2 (CH₂), 56.8 (CH₂), 34.9(-C-(CH₃)₃), 31.3(CH₃).

HRMS calc. for C₁₄H₁₉O₂S [M+H]⁺ 251.1100; found 251.1100.

3-(4-Methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (2d)

Yield 161 mg (72%) in CH₃OH, 90 mg (40%) in THF; white solid, m.p. 130 °C (from CH₂Cl₂); lit. data: m.p. 148 131 °C.^{S2}

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.8 Hz, 2H, Ar), 6.91 (d, *J* = 8.9 Hz, 2H, Ar), 6.20 (s, 1H, =CH), 4.10 (s, 2H, CH₂), 4.00 (s, 2H, CH₂), 3.83 (s, 3H, -OCH₃).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 160.5(=C-OMe), 135.8(Ar), 126.9(Ar), 126.7(=C-Ar), 115.0 (CH₂-CH=C), 114.4 (Ar), 57.8 (CH₂), 56.8 (CH₂), 55.5 (-OCH₃).

HRMS calc. for C₁₁H₁₂NaO₃S [M+Na]⁺ 247.0399; found 247.0401.

3-(Naphthalen-2-yl)-2,5-dihydrothiophene 1,1-dioxide (2e)

Yield 154 mg (63%) in CH₃OH, 51 mg (21%) in THF; white solid, m.p. 194-196 °C (from CH₂Cl₂).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.96–7.89 (m, 4H, Ar), 7.83 (dd, *J* = 8.6, 1.6 Hz, 1H, Ar), 7.58 – 7.51 (m, 2H, Ar), 6.78 (s, 1H, =CH), 4.44 (s, 2H, CH₂), 4.15 (s, 2H, CH₂).

¹³C {¹H} NMR (101 MHz, DMSO-*d*₆) δ 135.3 (=C-Ar), 132.8 (Ar), 132.8 (CH₂-CH=C), 131.4 (Ar), 128.2 (Ar), 128.2 (Ar), 127.6 (Ar), 126.7 (Ar), 125.5 (Ar), 122.8 (Ar), 119.1 (Ar), 57.2 (CH₂), 55.8 (CH₂).

HRMS calc. for C₁₄H₁₃O₂S [M+H]⁺ 245.0631; found 245.0630.

3-(4-Chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (2f)

Yield 187.5 mg (82%) in CH₃OH, 215 mg (94%) in THF; white solid, m.p. 152 °C (from CH₂Cl₂); lit. data: m.p. 148-164 °C.^{S2}

¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 7.4 Hz, 2H, Ar), 7.29 (d, *J* = 7.3 Hz, 2H, Ar), 6.34 (s, 1H, =CH), 4.11 (s, 2H, CH₂), 4.03 (s, 2H, CH₂).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 135.4 (Ar), 132.5 (=C-Ar), 129.3 (Ar), 126.8 (Ar), 118.0 (CH₂-CH=C), 57.8 (CH₂), 56.6 (CH₂).

NMR is in agreement with lit. data.^{S2}

HRMS calc. for C₁₀H₉ClNaO₂S [M+Na]⁺ 250.9904; found 250.9911.

3-(4-Bromophenyl)-2,5-dihydrothiophene 1,1-dioxide (2g)

Yield 210 mg (77%) in CH₃OH, 240 mg (88%) in THF; white solid, m.p. 174-175 °C (from CH₂Cl₂); lit. data: m.p. 148-161 °C.^{S2}

¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.6 Hz, 2H, Ar), 7.22 (d, *J* = 8.6 Hz, 2H, Ar), 6.35 (s, 1H, =CH), 4.14 – 4.07 (m, 2H, CH₂), 4.05 – 3.97 (m, 2H, CH₂).

¹³C {¹H} DEPT-135-Q (101 MHz, CDCl₃) δ 135.4 (Ar), 132.9 (=C-Ar), 132.3 (Ar), 127.1(Ar), 123.5 (C-Br), 118.1 (CH₂-CH=C), 57.8 (CH₂), 56.5 (CH₂).

3-(3-Chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (2h)

Yield 210 mg (92%) in CH₃OH, 215 mg (94%) in THF; white solid, m.p. 130 °C (lit. data: m.p. 120-121 °C).^{S2}

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.32 (m, 3H, Ar), 7.25 – 7.21 (m, 1H, Ar), 6.38 (s, 1H, =CH), 4.11 (d, *J* = 1.7 Hz, 2H, CH₂), 4.04 – 4.02 (m, 2H, CH₂).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 135.8 (Ar), 135.2 (=C-Ar), 135.3 (Ar), 130.4 (Ar), 129.4 (Ar), 125.8 (Ar), 123.7 (Ar), 118.8 (CH₂-CH=C), 57.7 (CH₂), 56.6 (CH₂).

NMR is in agreement with lit. data.^{S2}

HRMS calc. for C₁₀H₉ClNaOS [M+Na]⁺ 250.9904; found 250.9912.

3-(3-Trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (2i)

Yield 207 mg (79%) in CH₃OH, 215 mg (82%) in THF; white solid, m.p. 83-85 °C (from CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.58 (m, 2H, Ar), 7.54 (d, *J* = 5.2 Hz, 2H, Ar), 6.49 – 6.42 (m, 1H, =CH), 4.16 (s, 2H, CH₂), 4.05 (s, 2H, CH₂).

¹³C {¹H} DEPT-135-Q (101 MHz, CDCl₃) 135.3 (Ar), 134.9 (=C-Ar), 131.7 (d, *J* = 32.6 Hz, C-CF₃), 129.7 (Ar), 128.8 (Ar), 126.0 (q, *J* = 3.7 Hz, Ar), 123.84 (q, *J* = 272.5 Hz, CF₃), 122.40 (q, *J* = 3.8 Hz, Ar), 119.4 (CH₂-CH=C), 57.8 (CH₂), 56.6 (CH₂).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.8.

HRMS calc. for C₁₁H₉F₃NaO₂S [M+Na]⁺ 285.0168; found 285.0172.

3-(4-Trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (2j)

Yield 204 mg (78%) in THF; yellow solid, m.p. 153 °C (from CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.2 Hz, 2H, Ar), 7.48 (d, *J* = 8.2 Hz, 2H, Ar), 6.47 (s, 1H, =CH), 4.16 (s, 2H, CH₂), 4.06 (s, 2H, CH₂).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 137.4 (Ar), 135.3 (=C-Ar), 131.25 (q, *J* = 32.7 Hz, C-CF₃), 126.10 (q, *J* = 3.8 Hz, Ar), 126.0 (Ar), 123.9 (q, *J* = 272.2 Hz, C-CF₃), 119.9 (CH₂-CH=C), 57.8 (CH₂), 56.6 (CH₂).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.8.

HRMS calc. for C₁₁H₉F₃NaO₂S [M+Na]⁺ 285.0168; found 285.0172.

3-(4-Nitrophenyl)-2,5-dihydrothiophene 1,1-dioxide (2k)

Yield 134 mg (56%) in CH₃OH, 215 mg (90%) in THF; yellow solid, m.p. 194-195 °C (from CH₂Cl₂).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (d, *J* = 9.0 Hz, 2H, Ar), 7.81 (d, *J* = 8.9 Hz, 2H, Ar), 6.95 – 6.88 (m, 1H, =CH), 4.41 (d, *J* = 1.7 Hz, 2H, CH₂), 4.21 – 4.12 (m, 2H, CH₂).

¹³C {¹H} DEPT-135-Q (101 MHz, DMSO-*d*₆) δ 147.1 (C-NO₂), 140.3 (Ar), 133.9 (=C-Ar), 126.9 (Ar), 123.8 (Ar), 123.4 (CH₂-CH=C), 57.2 (CH₂), 55.5 (CH₂).

HRMS calc. for C₁₀H₉NNaO₄S [M+Na]⁺ 262.0144; found 262.0150.

4-(1,1-Dioxido-2,5-dihydrothiophen-3-yl)benzotrile(2l)

Yield 99 mg (45%) in CH₃OH, 127 mg (58%) in THF; white solid, m.p. 179-180 °C (from CH₂Cl₂).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.89 (d, *J* = 8.3 Hz, 2H, Ar), 7.74 (d, *J* = 8.4 Hz, 2H, Ar), 6.86 (s, 1H, =CH), 4.38 (s, 2H, -CH₂), 4.15 (s, 2H, -CH₂).

¹³C {¹H} NMR (101 MHz, DMSO-*d*₆) δ 138.4 (Ar), 134.2 (=C-Ar), 132.6 (Ar), 126.5 (Ar), 122.5 (CH₂-CH=C), 118.7 (C≡N), 110.9 (C-C≡N), 57.2 (CH₂), 55.4 (CH₂).

HRMS calc. for C₁₁H₉NNaO₂S [M+Na]⁺ 242.0246; found 242.0251.

3-(2-Methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (2m)

Yield 157 mg (70%) in THF; white solid, m.p. 99-100 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.32 (m, 1H, Ar), 7.24 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar), 6.97 (t, *J* = 7.5 Hz, 1H, Ar), 6.92 (d, *J* = 8.3 Hz, 1H, Ar), 6.25 (s, 1H, =CH), 4.22 – 4.18 (m, 2H, CH₂), 3.96 – 3.92 (m, 2H, CH₂), 3.85 (s, 3H, OCH₃).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 157.2 (Ar), 135.7 (=C-Ar), 130.4 (Ar), 129.1 (Ar), 124.3 (CH₂-CH=C), 121.0 (Ar), 120.4 (Ar), 111.2 (C-OMe), 58.0 (CH₂), 56.8 (CH₂), 55.5 (OCH₃).

HRMS calc. for C₁₁H₁₂NaO₃S [M+Na]⁺ 247.0399; found 247.0400.

3-(Naphthalen-1-yl)-2,5-dihydrothiophene 1,1-dioxide (2n)

Yield 107.5 mg (44%) in CH₃OH, 149 mg (61%) in THF; white solid, m.p. 154 °C (from CH₂Cl₂)

¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.84 (m, 3H, Ar), 7.59 – 7.51 (m, 2H, Ar), 7.50 – 7.45 (m, 1H, Ar), 7.35 (d, *J* = 7.0 Hz, 1H, Ar), 6.20 – 6.12 (m, 1H, =CH), 4.20 – 4.13 (m, 2H, CH₂), 4.13 – 4.08 (m, 2H, CH₂).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 137.4, 133.8, 133.6, 130.8, 129.4, 128.9, 127.1, 126.5, 125.9, 125.4, 124.6, 122.7, 59.3 (CH₂), 57.5 (CH₂).

HRMS calc. for C₁₄H₁₂NaO₂S [M+Na]⁺267.0450; found 267.0448.

3-(2-Fluorophenyl)-2,5-dihydrothiophene 1,1-dioxide (2o)

Yield 102 mg (48%) in CH₃OH, 204 mg (96%) in THF; white solid, m.p. 110 °C (from CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.27 (m, 2H, Ar), 7.17 (dd, *J* = 7.6, 1.0 Hz, 1H, Ar), 7.11 (ddd, *J* = 11.6, 8.3, 1.0 Hz, 1H, Ar), 6.42 (s, 1H, =CH), 4.17 (s, 2H, CH₂), 4.00 (s, 2H, CH₂).

¹³C DEPT-135-Q (101 MHz CDCl₃) δ 160.35 (d, *J* = 250.9 Hz, C-F), 132.1 (=C-Ar), 130.8 (d, *J* = 8.8 Hz, Ar), 128.6 (d, *J* = 3.5 Hz, Ar), 124.7 (d, *J* = 3.5 Hz, Ar), 122.4 (d, *J* = 11.8 Hz, Ar), 121.9 (d, *J* = 7.3 Hz, Ar), 116.59 (d, *J* = 22.5 Hz, (CH₂-CH=C) 57.44 (d, *J* = 4.4 Hz, CH₂), 57.4 (CH₂).

¹⁹F NMR (376 MHz, CDCl₃) δ -113.1.

HRMS calc. for C₁₀H₉FN₂O₂S [M+Na]⁺; 235.0199found 235.0202.

3-(2-Bromophenyl)-2,5-dihydrothiophene 1,1-dioxide (2p)

Yield 99 mg (34%) in CH₃OH, 210 mg (77%) in THF; white solid, m.p. 92 °C (from CH₂Cl₂).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.9 Hz, 1H, Ar), 7.35 (t, *J* = 7.5 Hz, 1H, Ar), 7.29 – 7.21 (m, 2H, Ar), 6.07 (s, 1H, =CH), 4.17 (s, 2H, CH₂), 3.99 (s, 2H, CH₂).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 137.9 (Ar), 136.9 (=C-Ar), 133.5 (Ar), 130.5 (Ar), 127.9 (Ar), 123.0 (CH₂-CH=C), 122.0 (C-Br), 57.9 (CH₂), 57.1 (CH₂).

HRMS calc. for C₁₀H₉BrNaO₂S [M+Na]⁺ 296.9399; found 296.9398.

References

- [S1] Griбанov, P. S.; Topchiy, M. A.; Golenko, Y. D.; Lichtenstein, Y. I.; Eshtukov, A. V.; Terekhov, V. E.; Asachenko, A. F.; Nechaev, M. S., An unprecedentedly simple method of synthesis of aryl azides and 3-hydroxytriazenes. *Green Chem.*, **2016**, *18* (22), 5984-5988.
- [S2] Sengupta, S.; Bhattacharyya, S., A Facile Synthesis of 3-Arylbutadiene Sulfones. *Synth. Commun.*, **1996**, *26* (2), 231-236.

NMR and HRMS spectra pictures

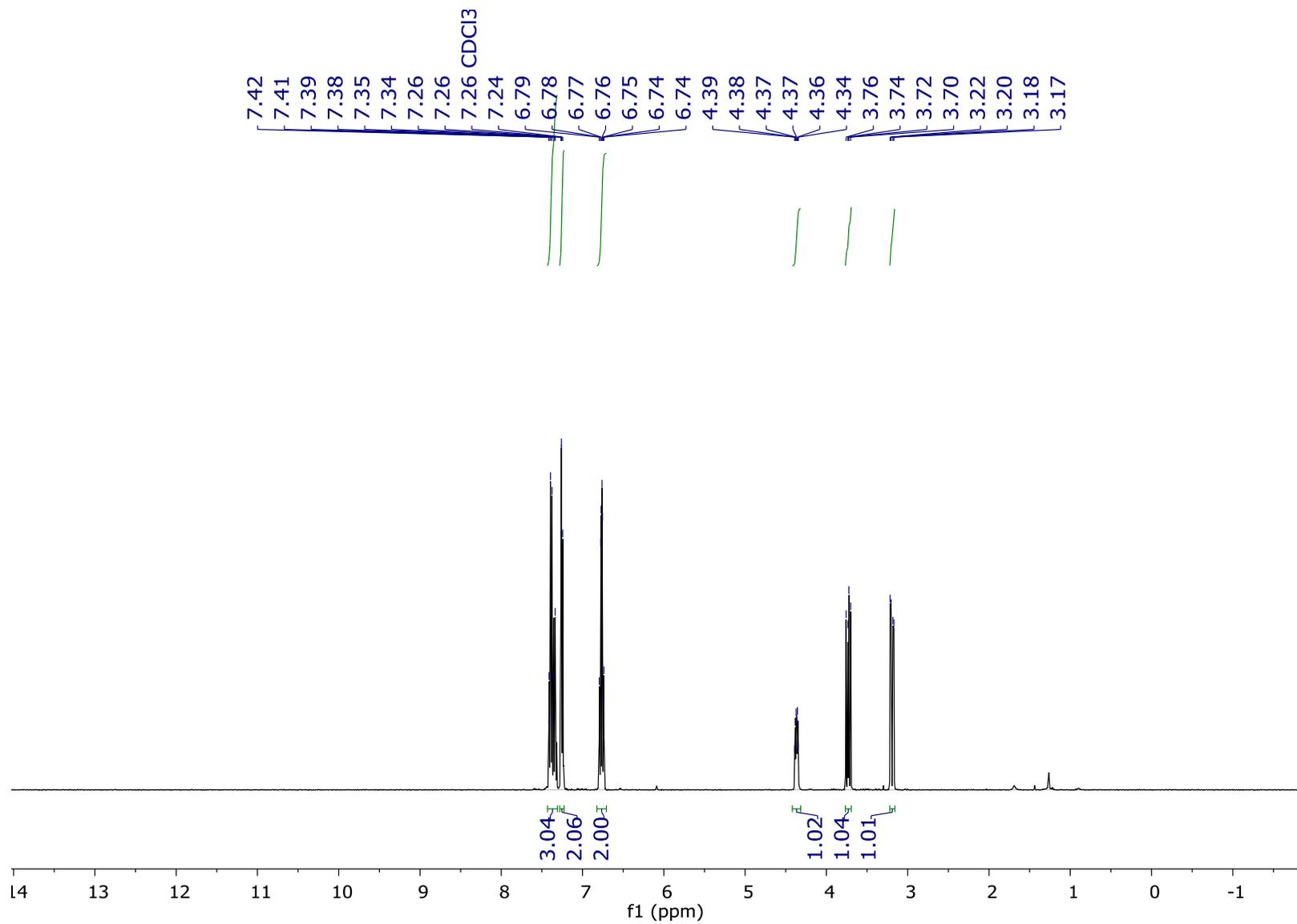


Figure S1. ¹H NMR (400MHz, CDCl₃) of 3-phenyl-2,3-dihydrothiophene 1,1-dioxide (**1**).

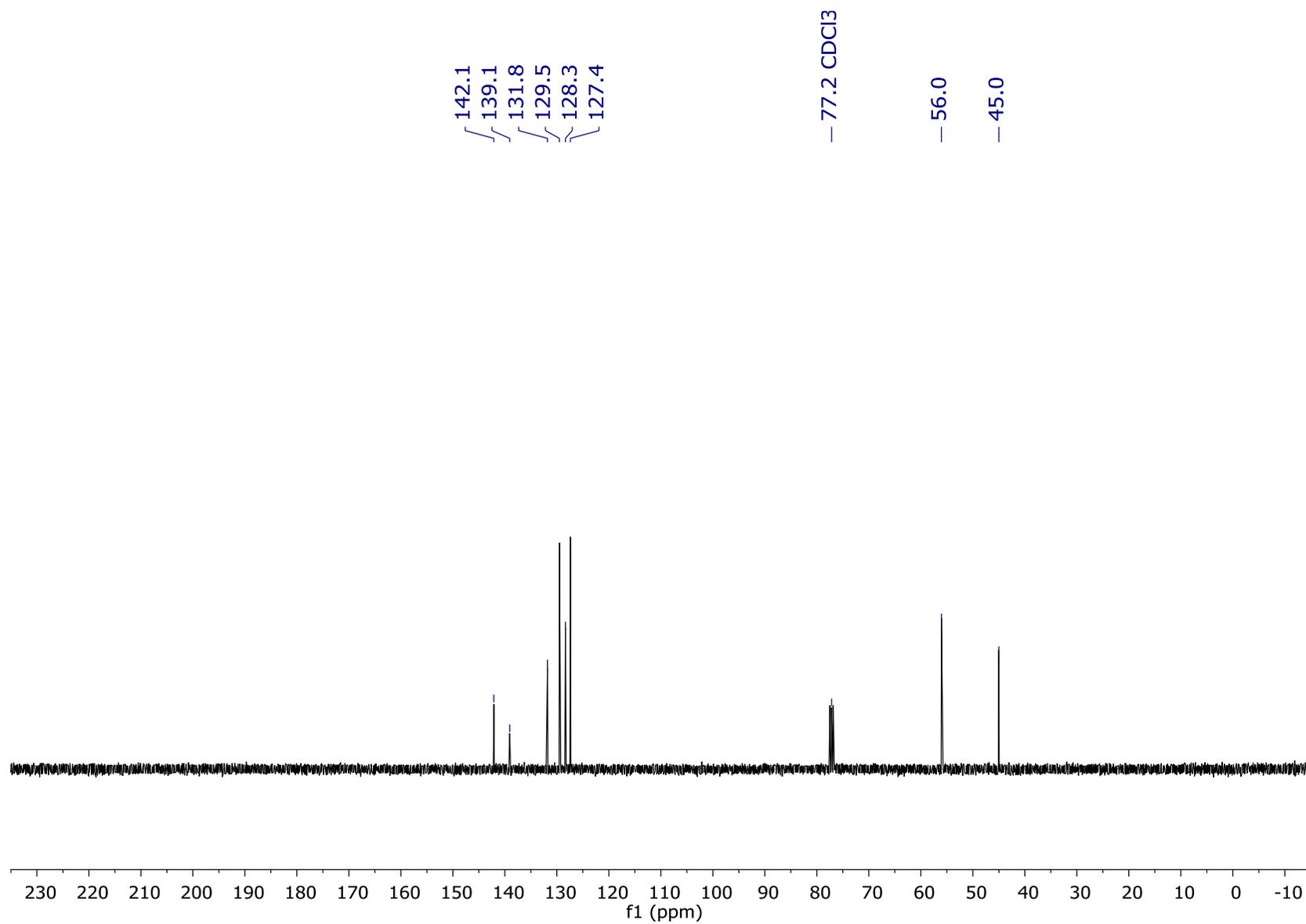


Figure S2. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl_3) of 3-phenyl-2,3-dihydrothiophene 1,1-dioxide (**1**).

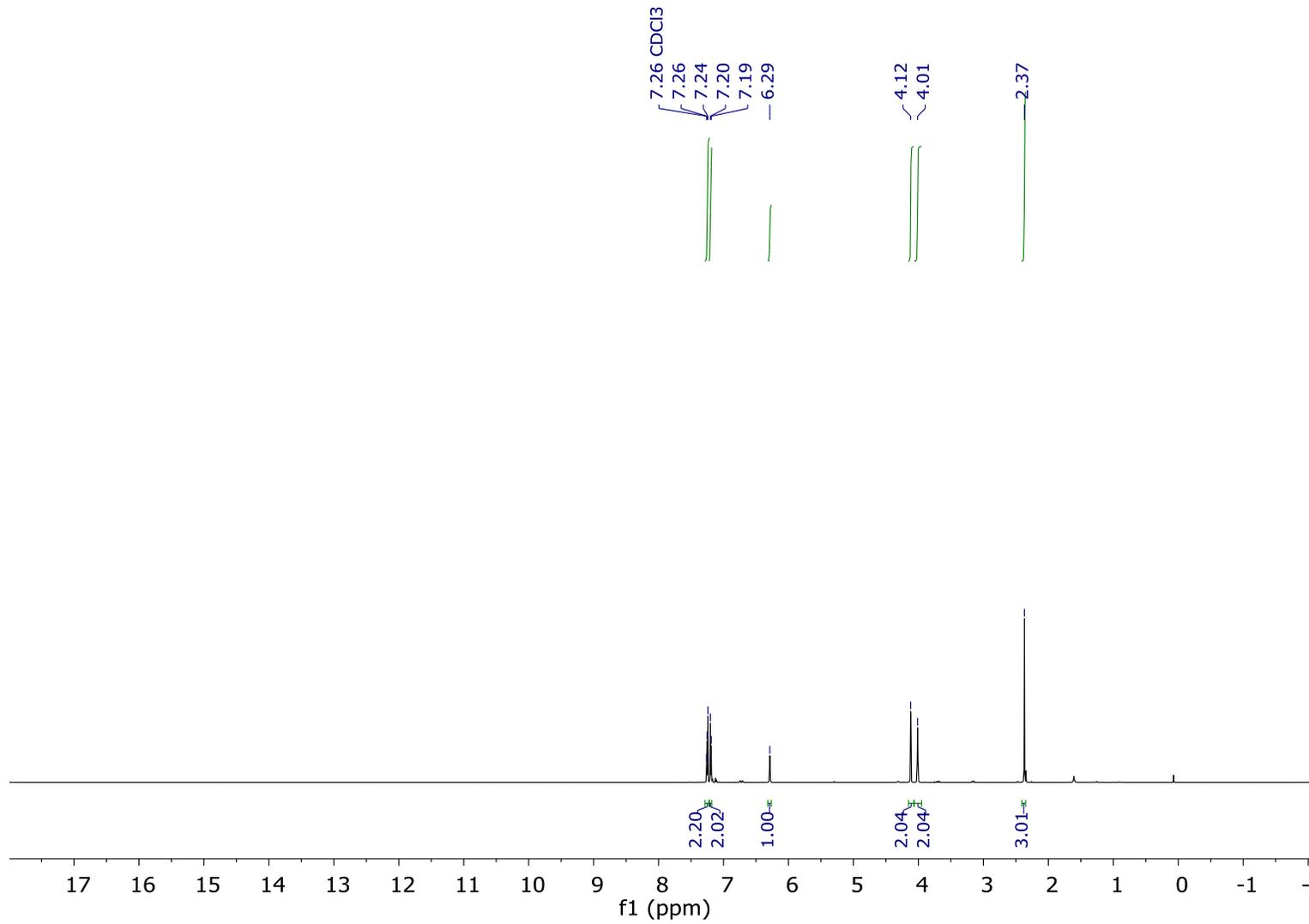


Figure S3. ^1H NMR (400MHz, CDCl_3) of 3-*p*-tolyl-2,5-dihydrothiophene 1,1-dioxide (**2b**).

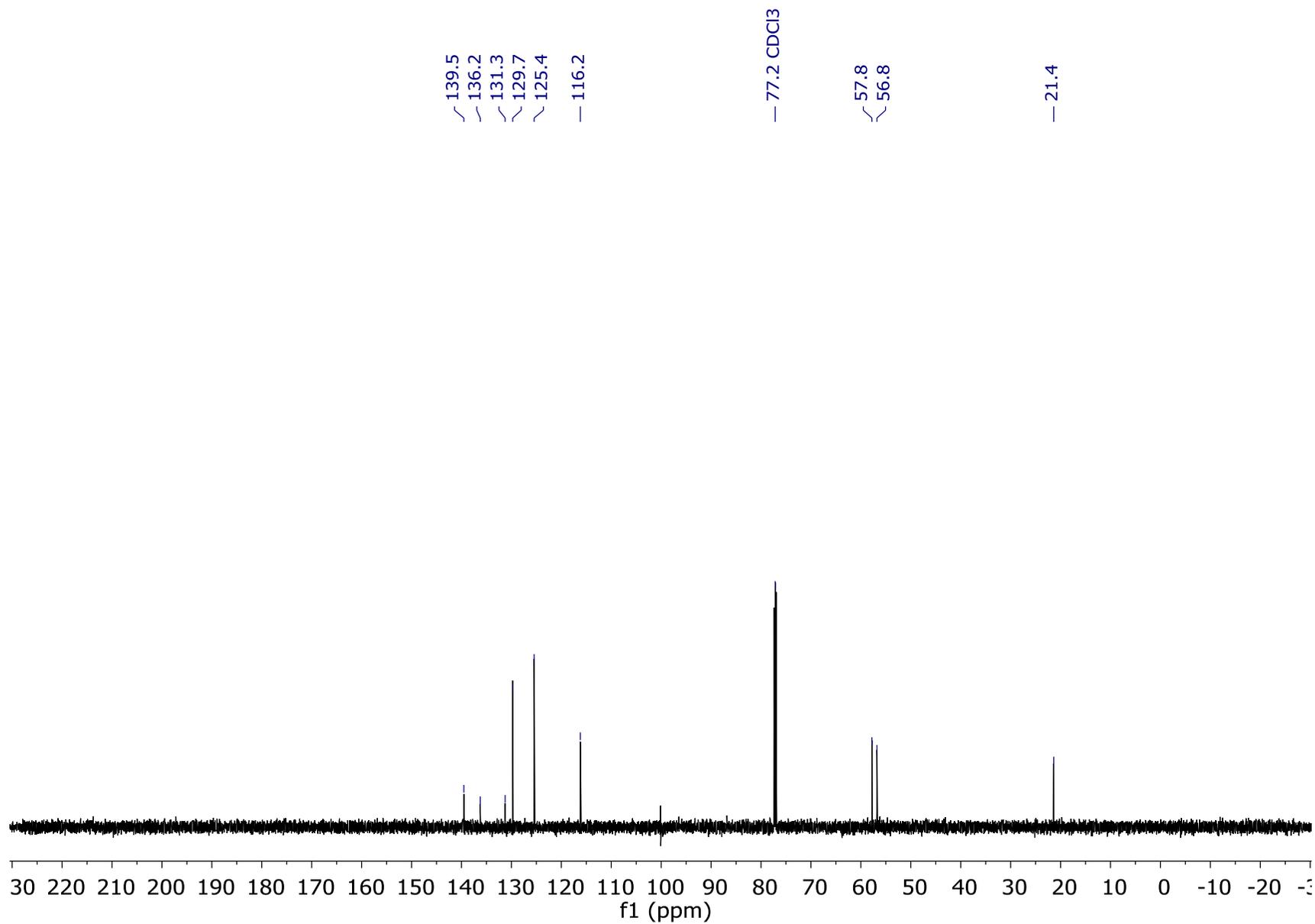


Figure S4. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl_3) of 3-*p*-tolyl-2,5-dihydrothiophene 1,1-dioxide (2b).

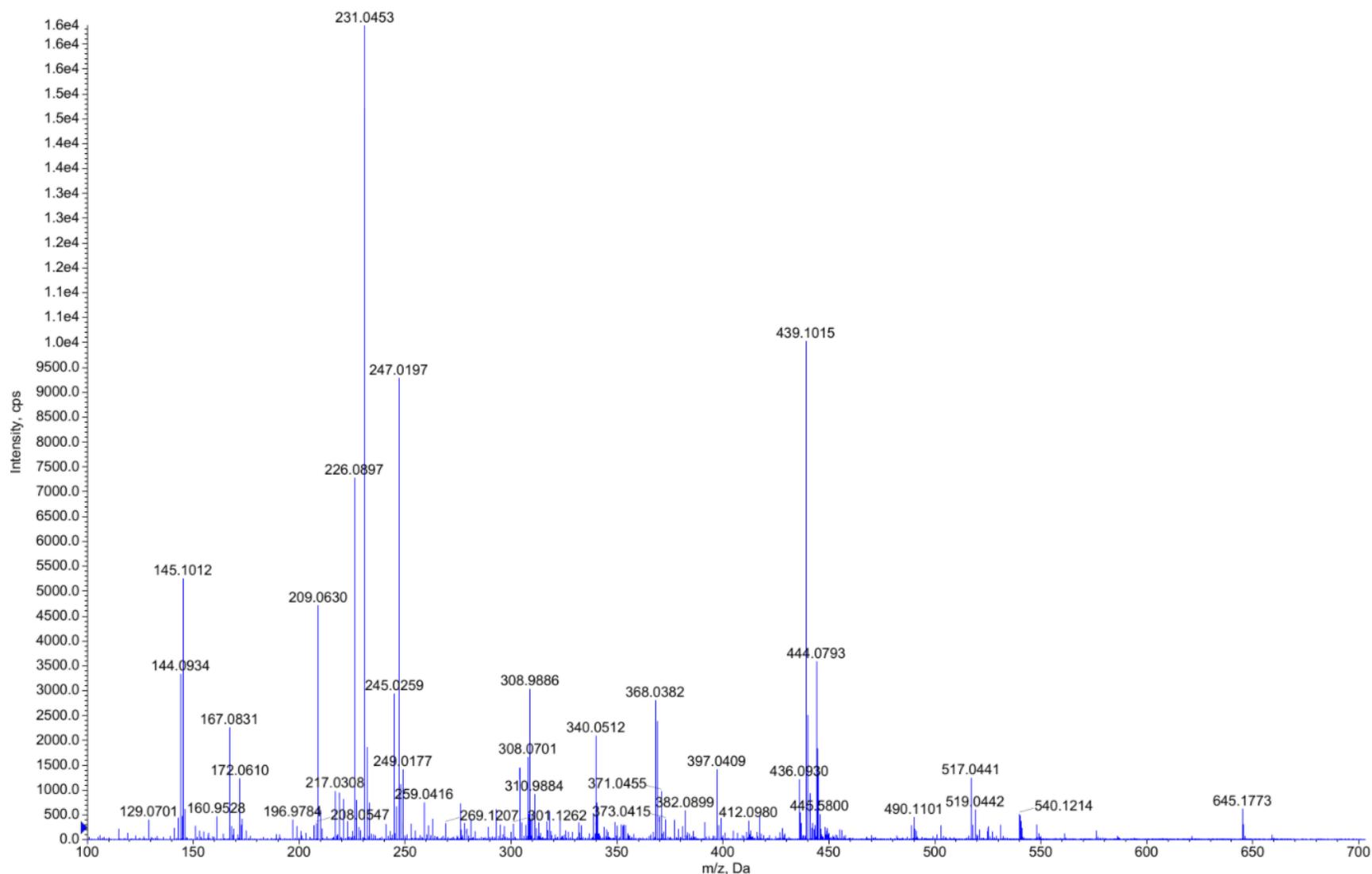


Figure S5. HRMS spectra of 3-*p*-tolyl-2,5-dihydrothiophene 1,1-dioxide (**2b**).

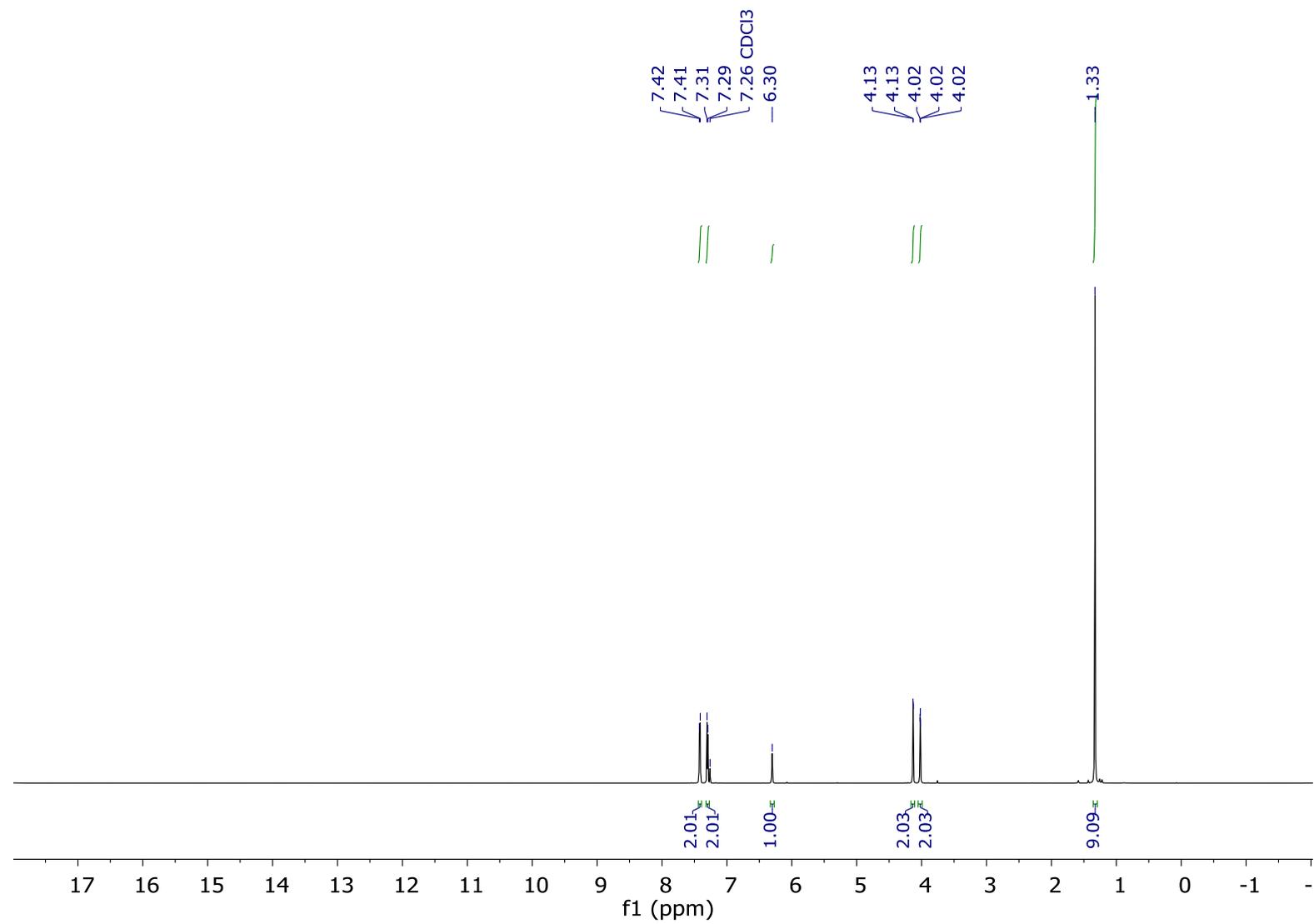


Figure S6. ¹H NMR (400MHz, CDCl₃) of 3-(4-*tert*-butylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2c**).

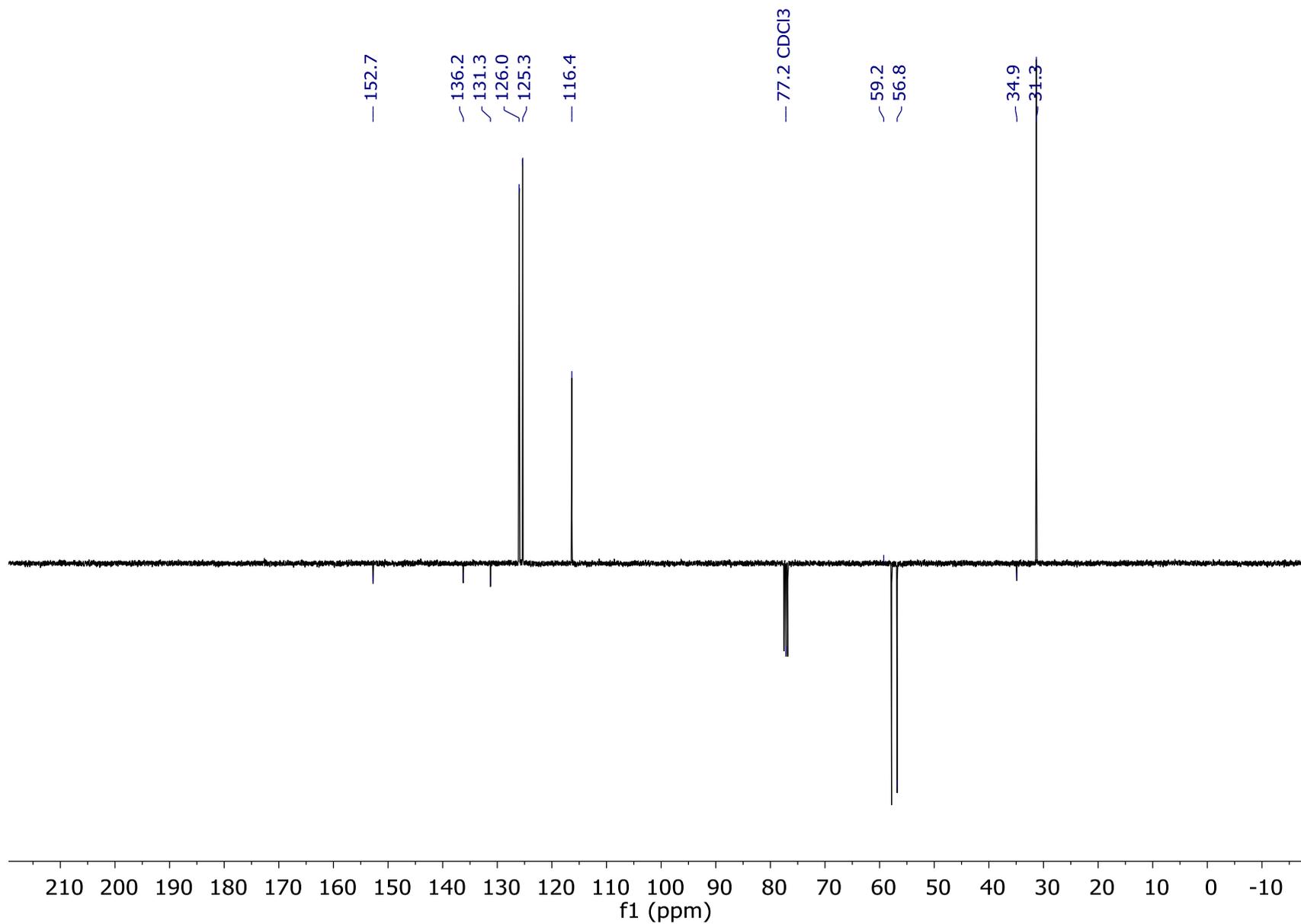


Figure S7. ^{13}C $\{^1\text{H}\}$ DEPT-135-Q NMR (101MHz, CDCl_3) of 3-(4-*tert*-butylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2c**).
S13

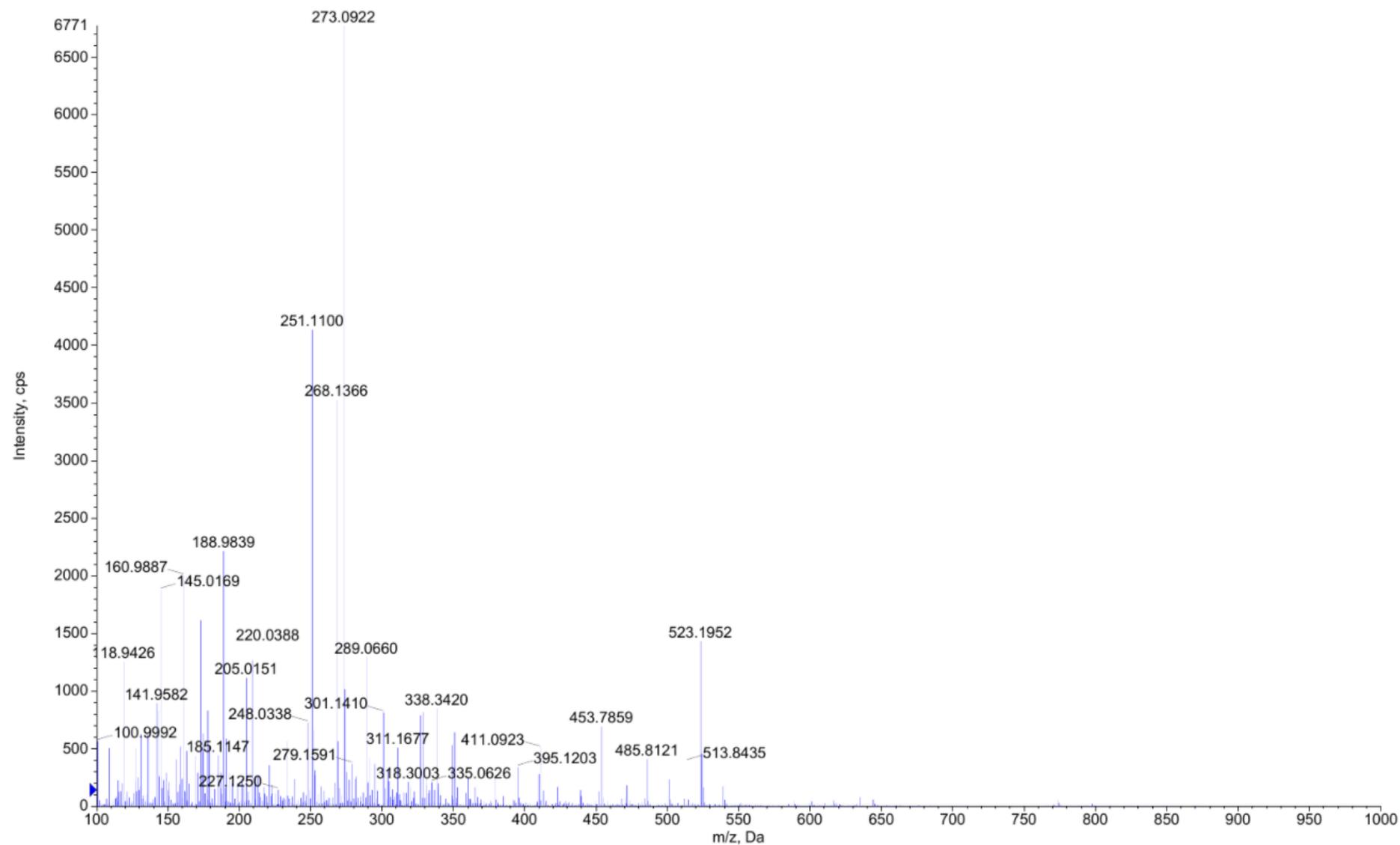


Figure S8. HRMS spectra of 3-(4-*tert*-butylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2c**).

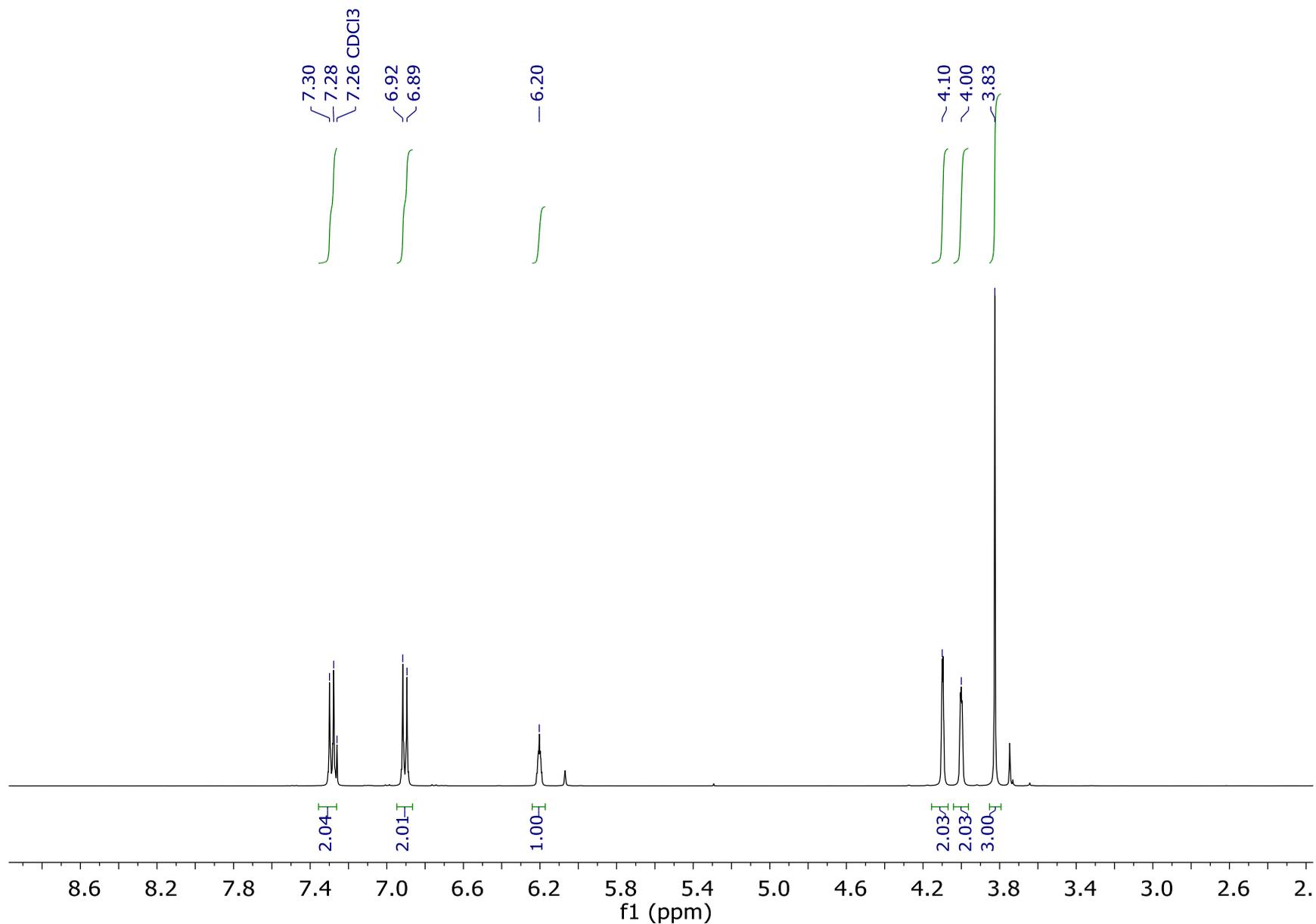


Figure S9. ¹H NMR (400MHz, CDCl₃) of 3-(4-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2d**).

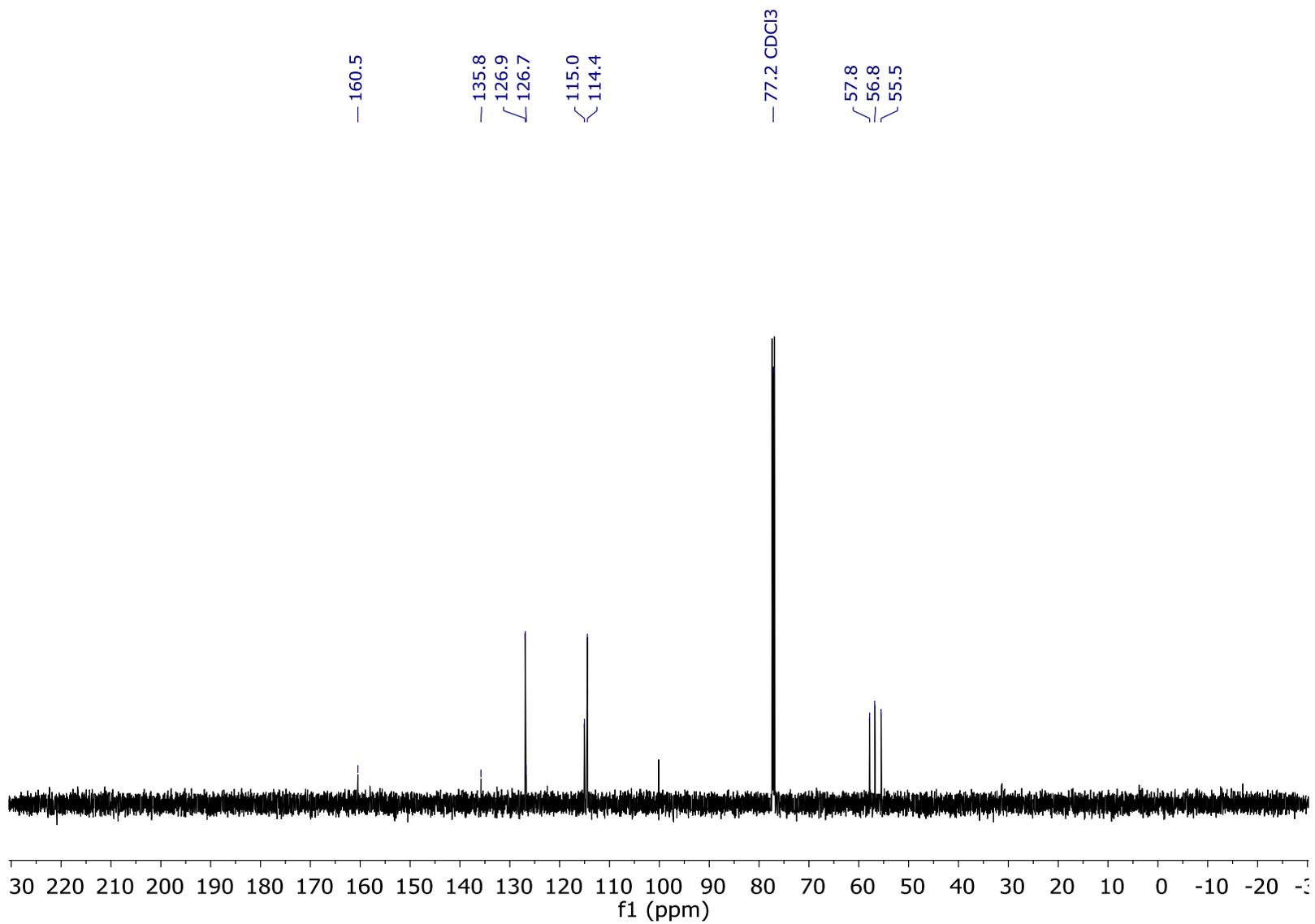


Figure S10. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl₃) of 3-(4-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2d**).

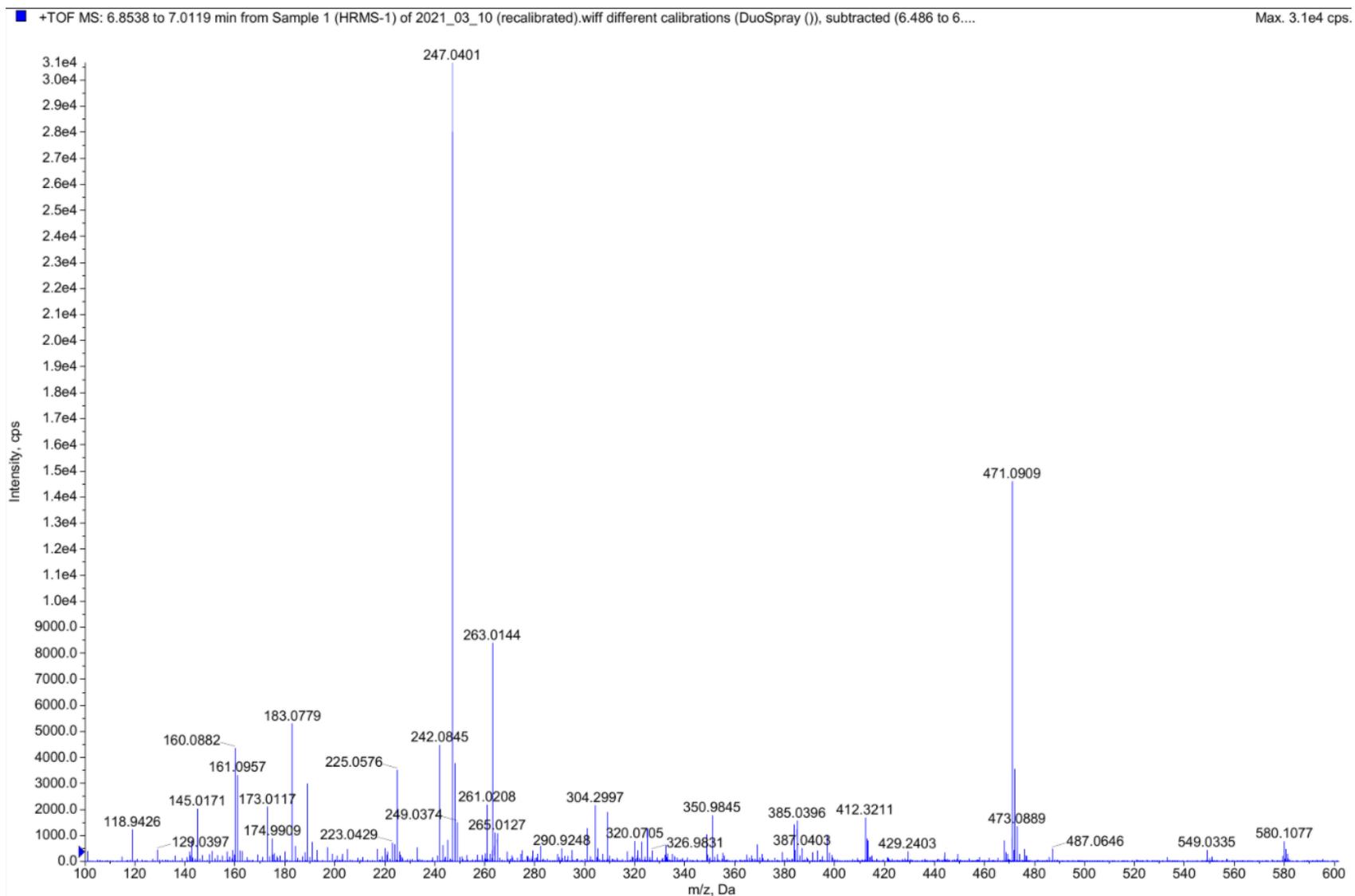


Figure S11. HRMS spectra of 3-(4-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2d**)

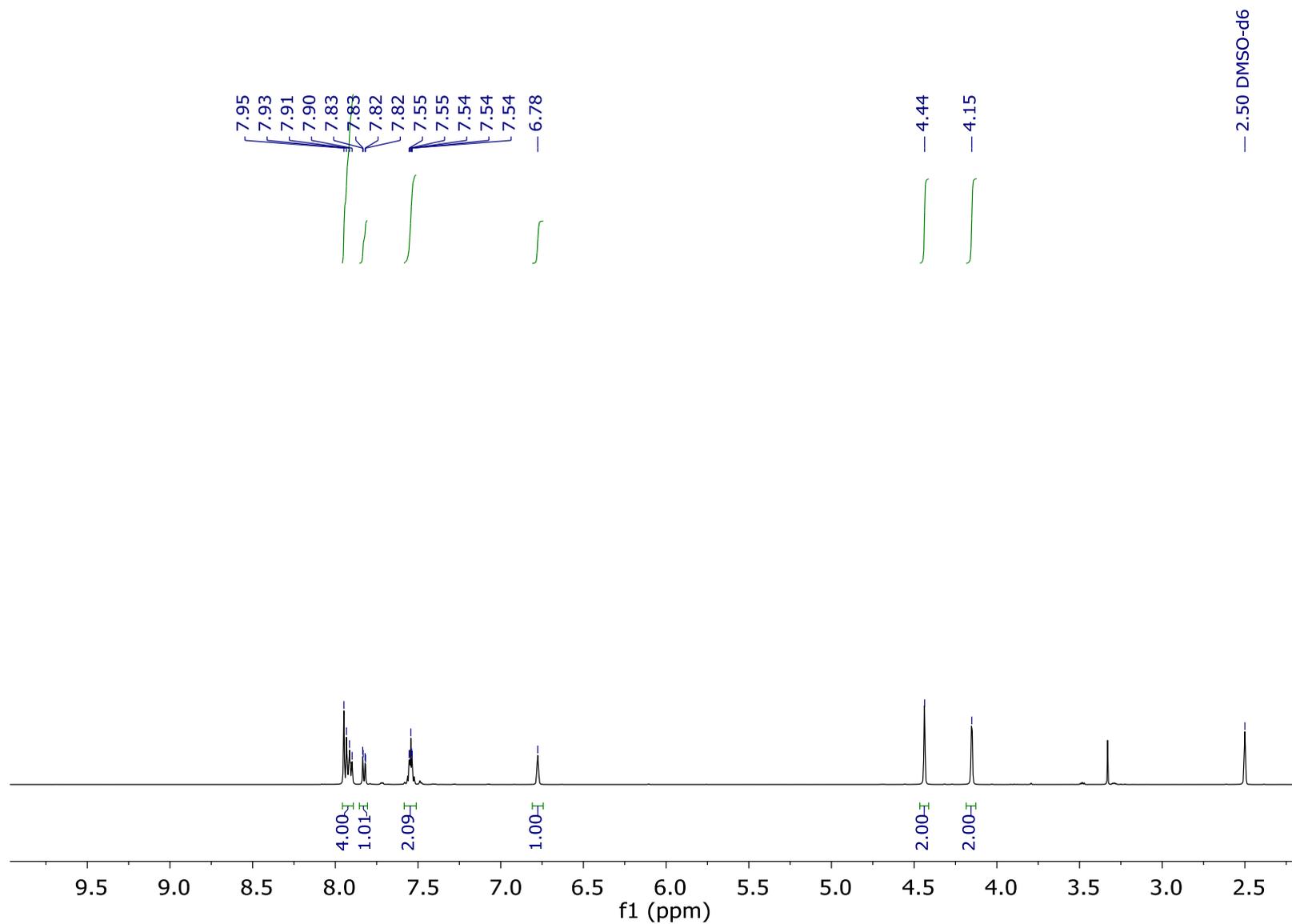


Figure S12. ¹H NMR (400MHz, CDCl₃) of 3-(naphthalen-2-yl)-2,5-dihydrothiophene 1,1-dioxide (**2e**).

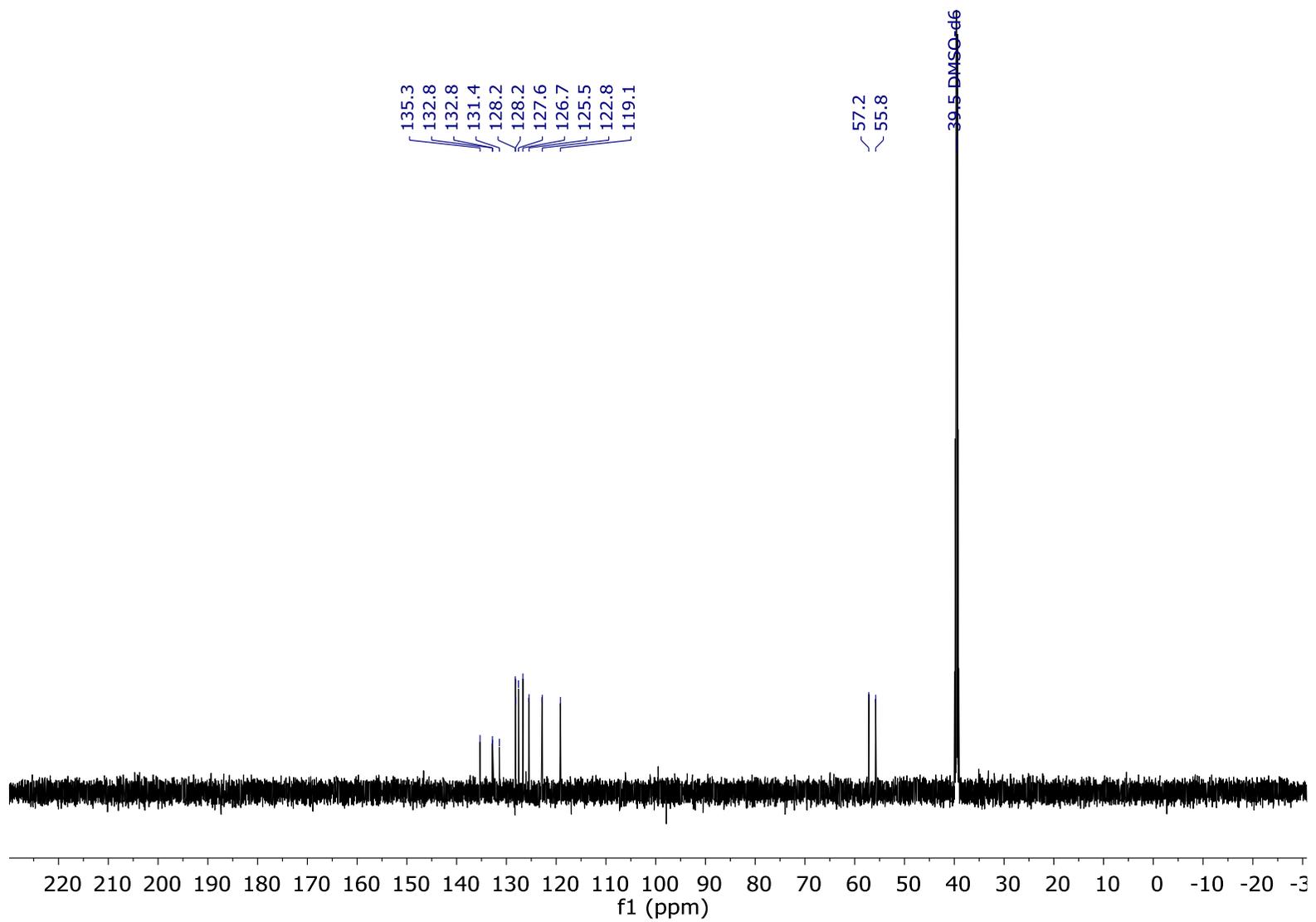


Figure S13. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl_3) of 3-(naphthalen-2-yl)-2,5-dihydrothiophene 1,1-dioxide (**2e**).

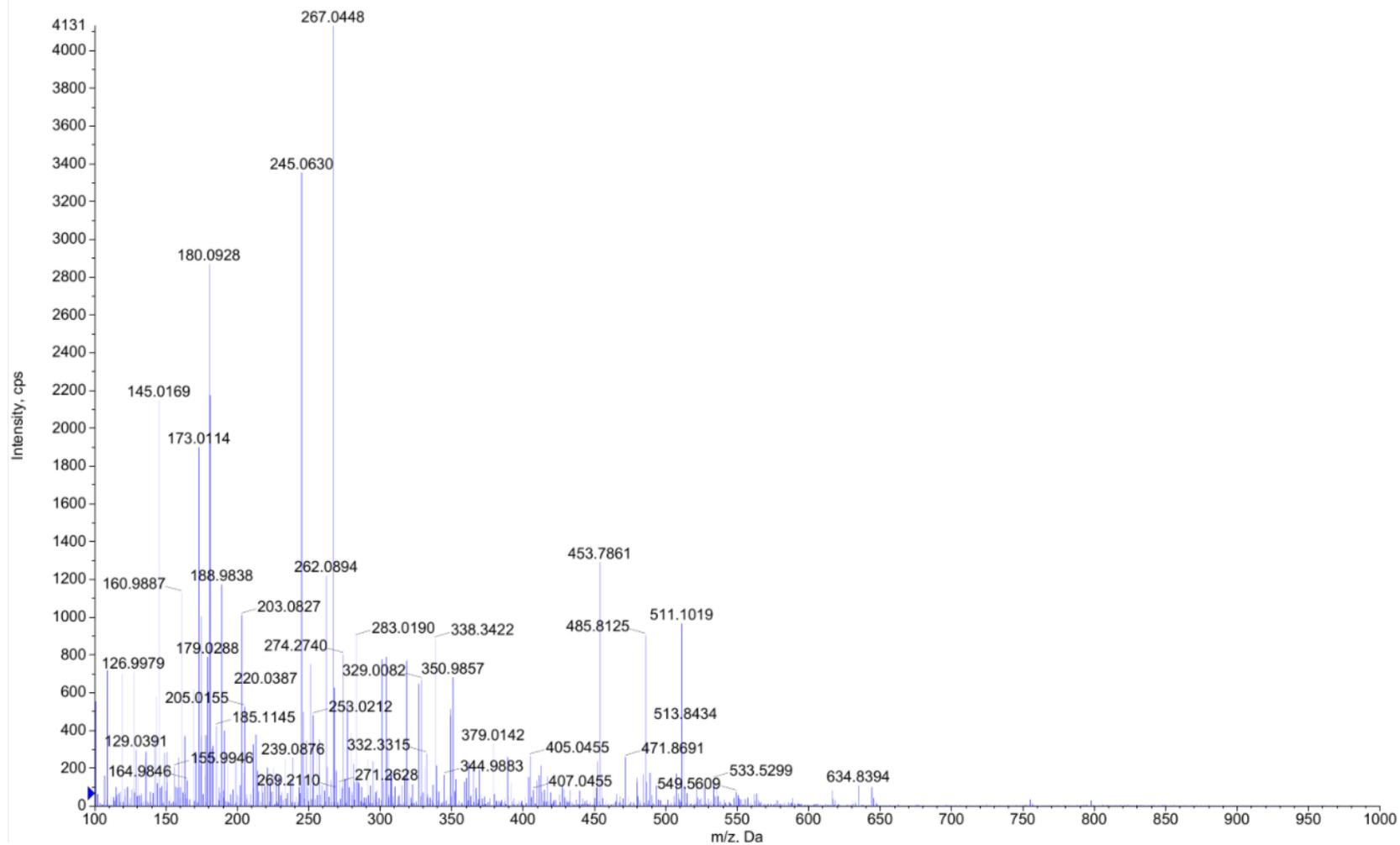


Figure S14. HRMS spectra of 3-(naphthalen-2-yl)-2,5-dihydrothiophene 1,1-dioxide (**2e**).

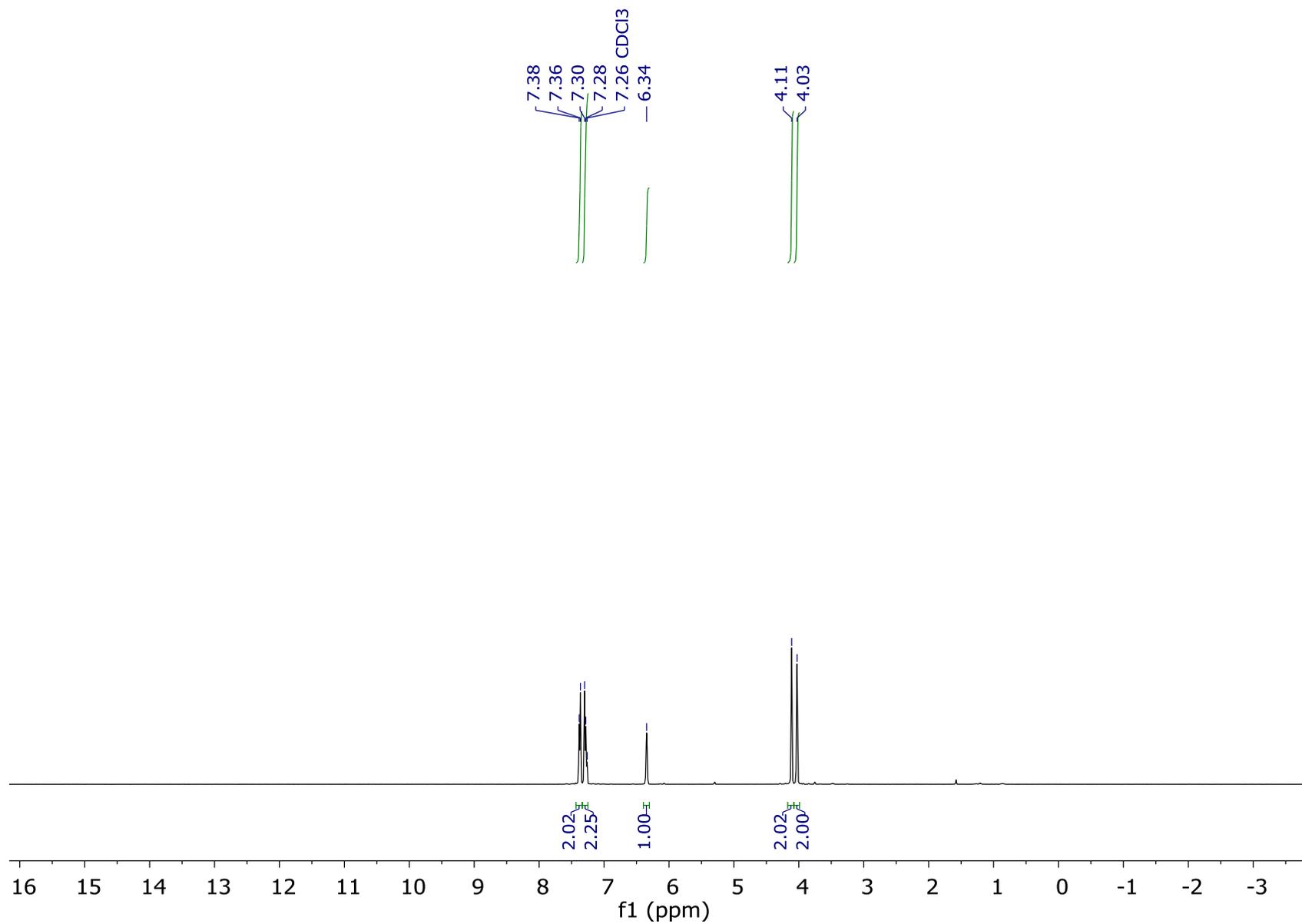


Figure S15. ^1H NMR (400MHz, CDCl_3) of 3-(4-chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2f**).

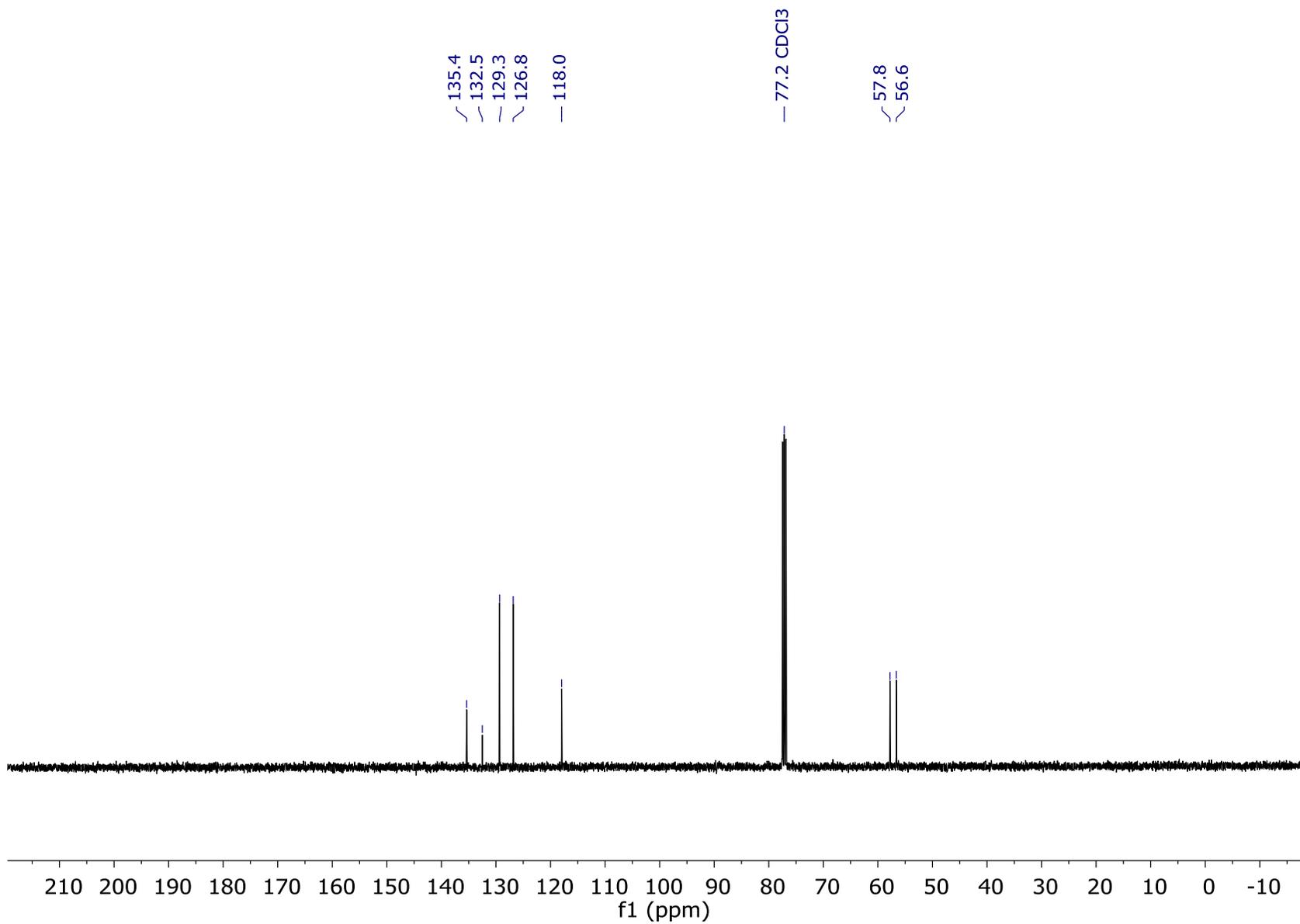


Figure S16. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl_3) of 3-(4-chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2f**).

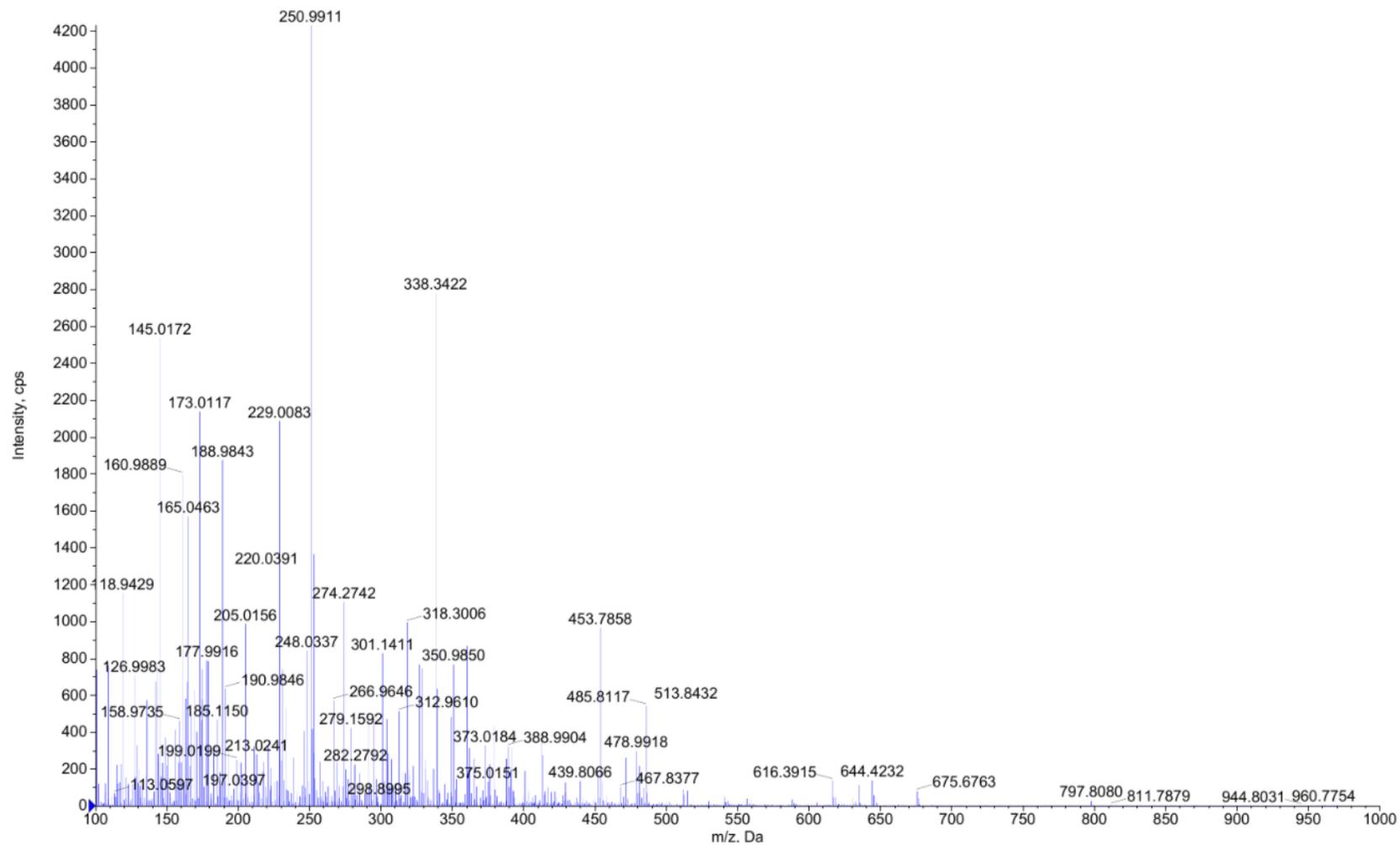


Figure S17. HRMS spectra of 3-(4-chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2f**).

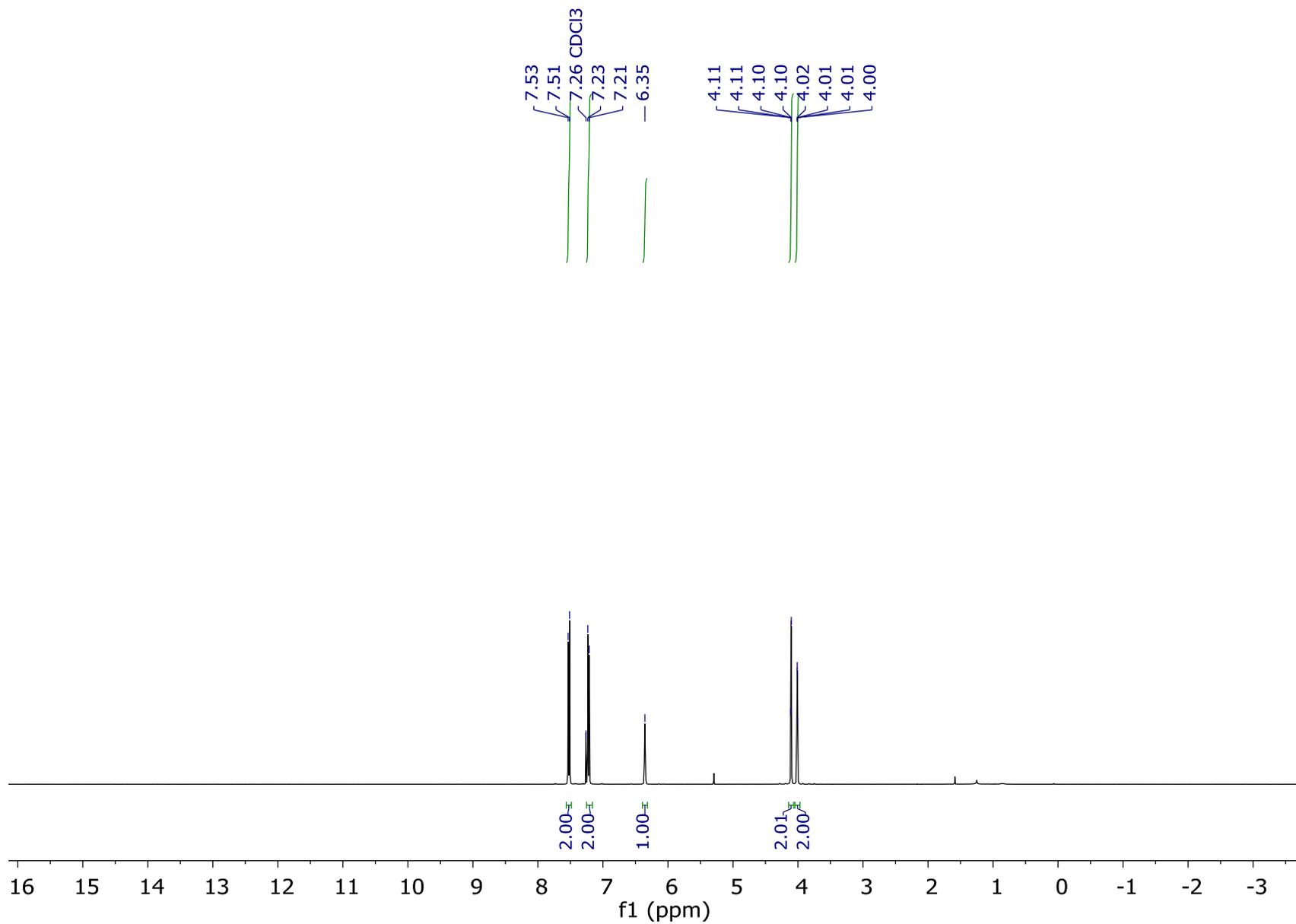


Figure S18. ¹H NMR (400MHz, CDCl₃) of 3-(4-bromophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2g**).

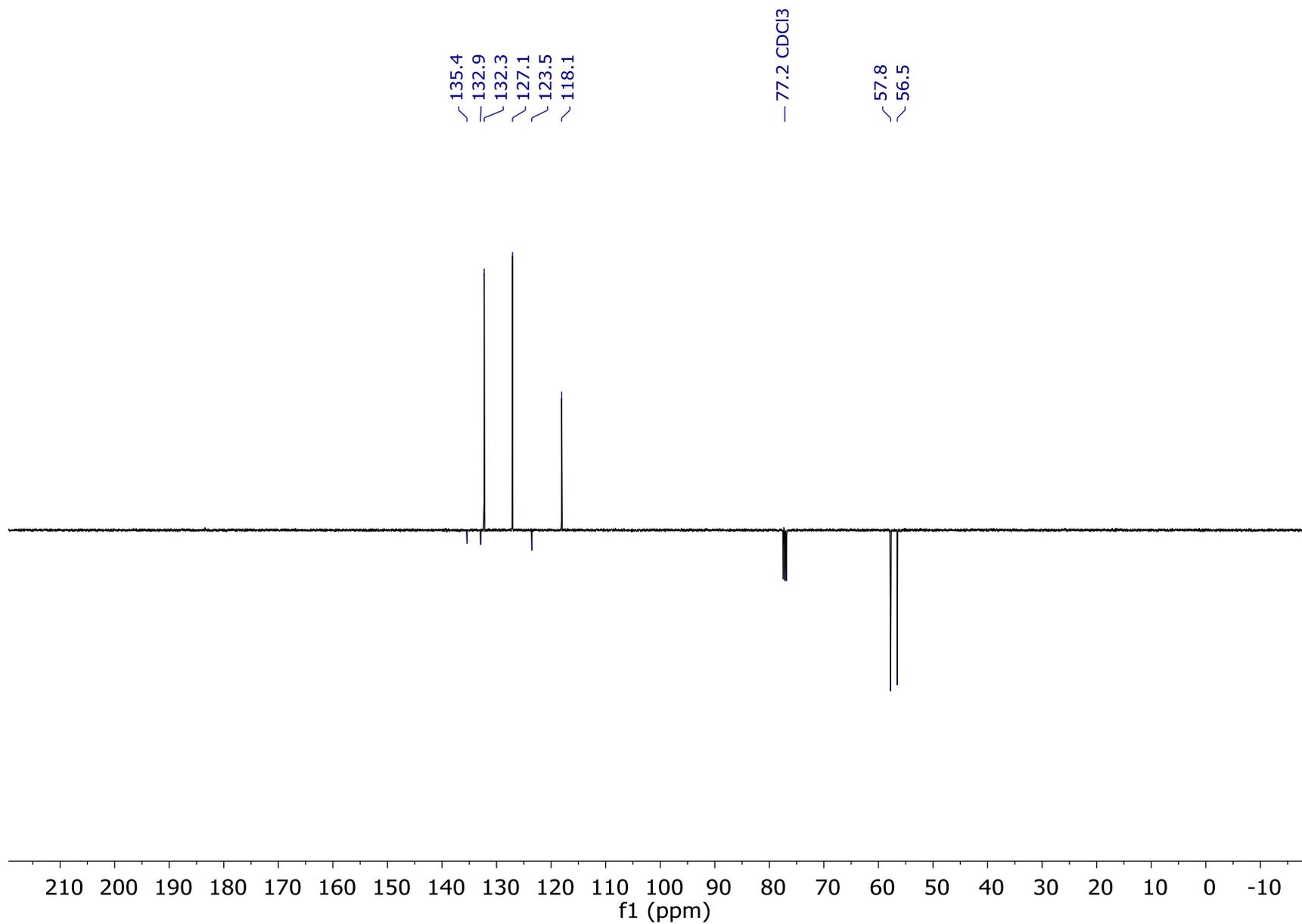


Figure S19. ¹³C {¹H} DEPT-135-Q (101 MHz, CDCl₃) of 3-(4-bromophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2g**).

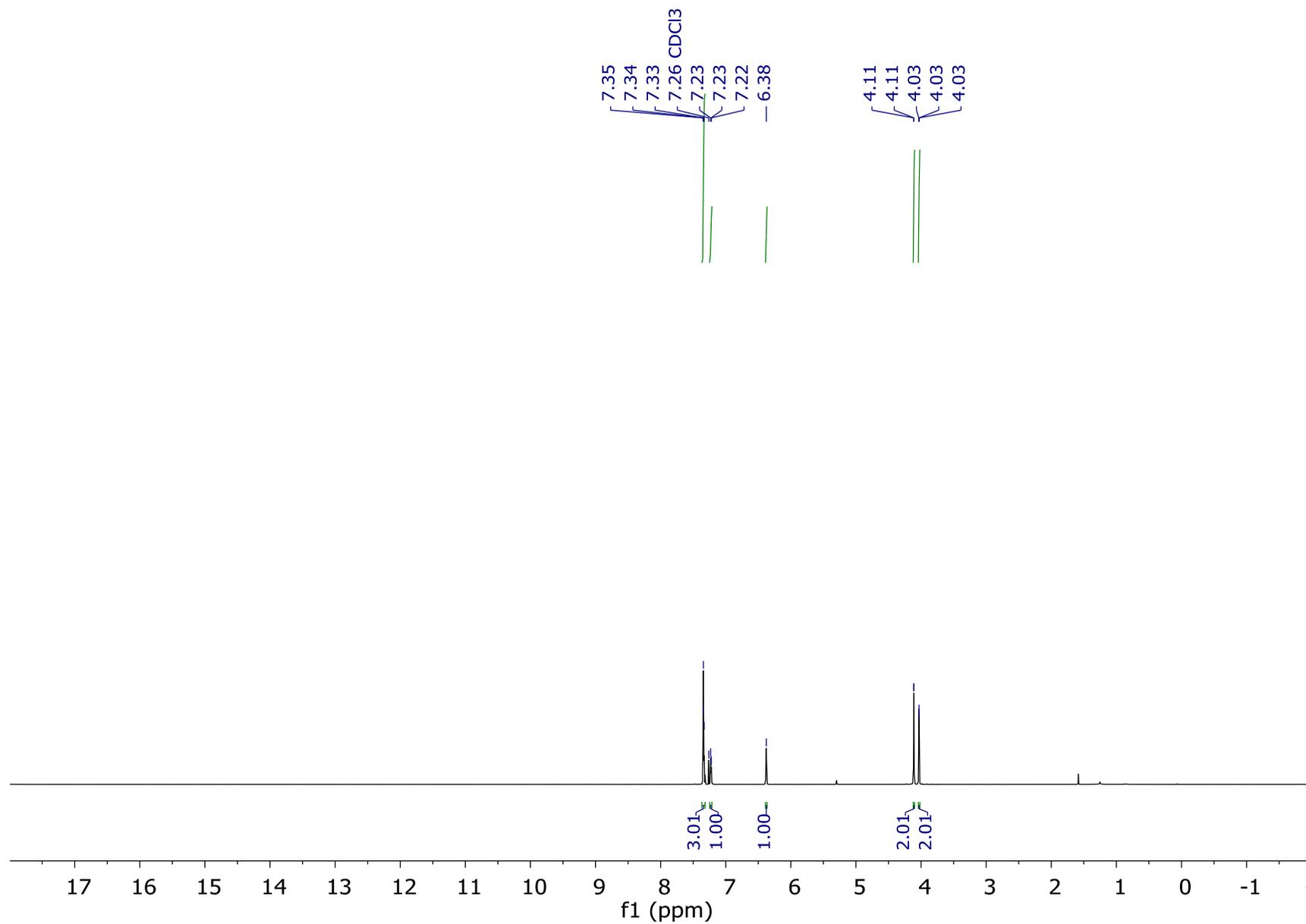


Figure S20. ^1H NMR (400MHz, CDCl_3) of 3-(3-chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2h**).

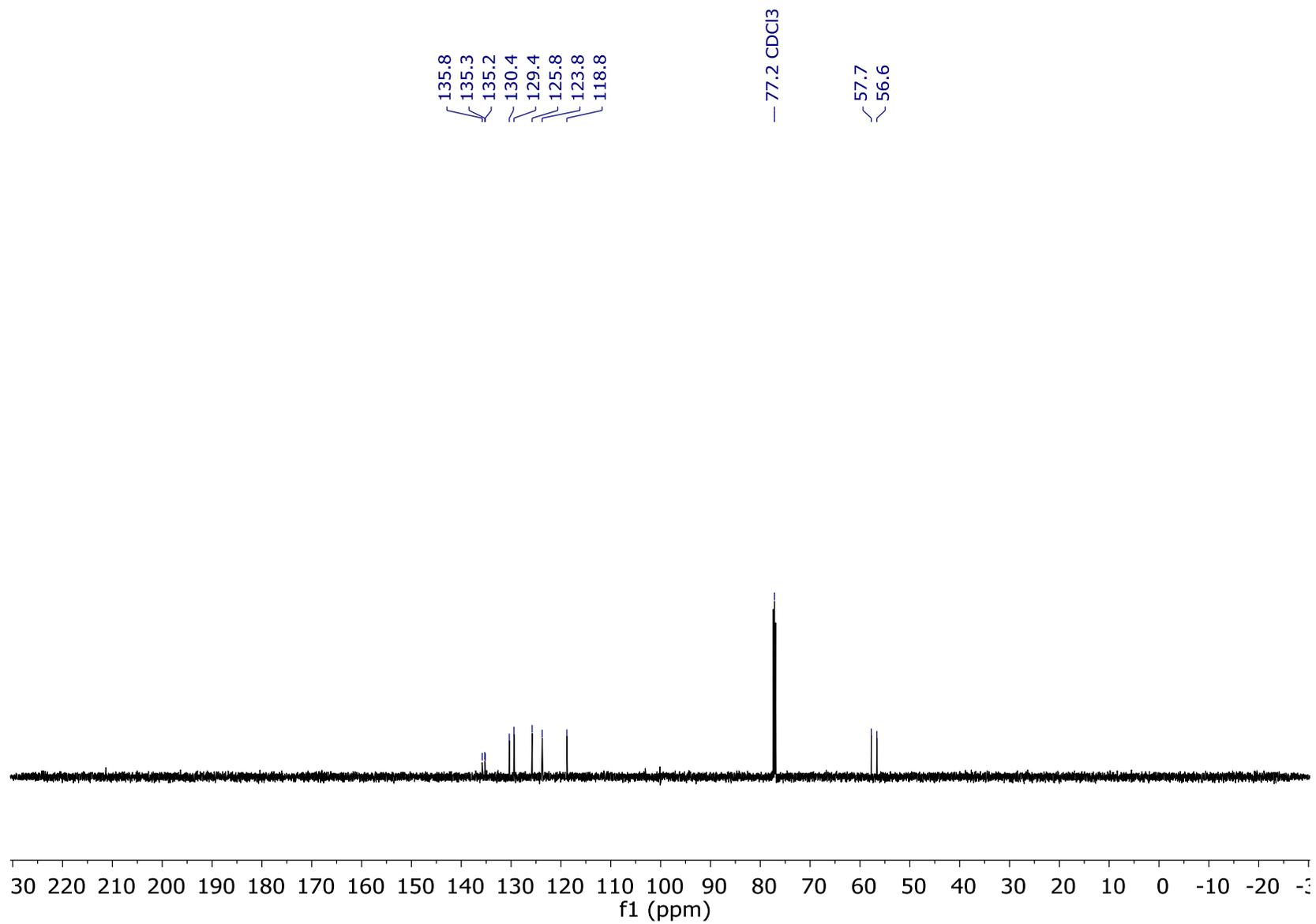


Figure S21. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl_3) of 3-(3-chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2h**).

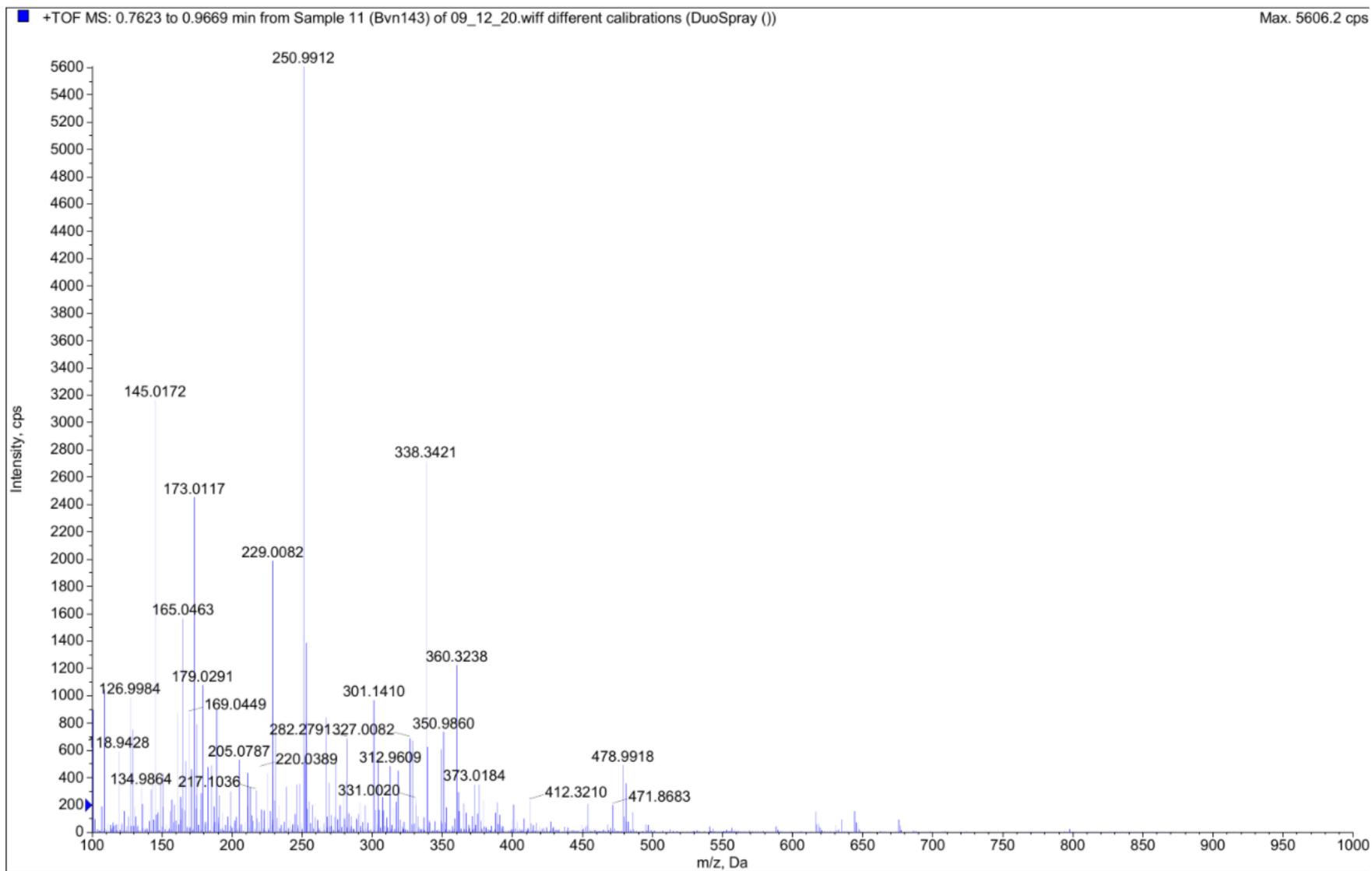


Figure S22. HRMS spectra of 3-(3-chlorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2h**).

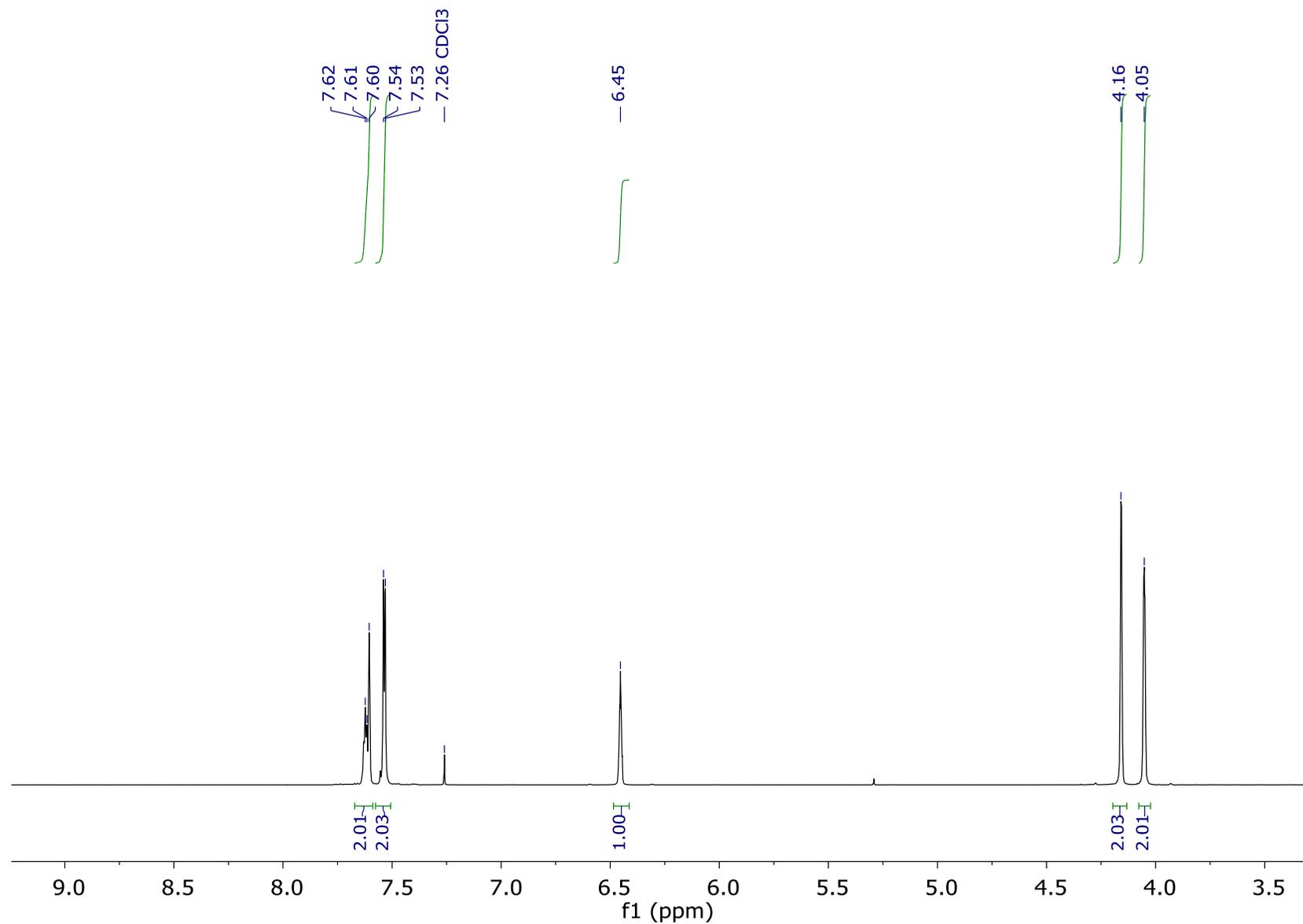


Figure S23. ¹H NMR (400MHz, CDCl₃) of 3-(3-trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2i**).

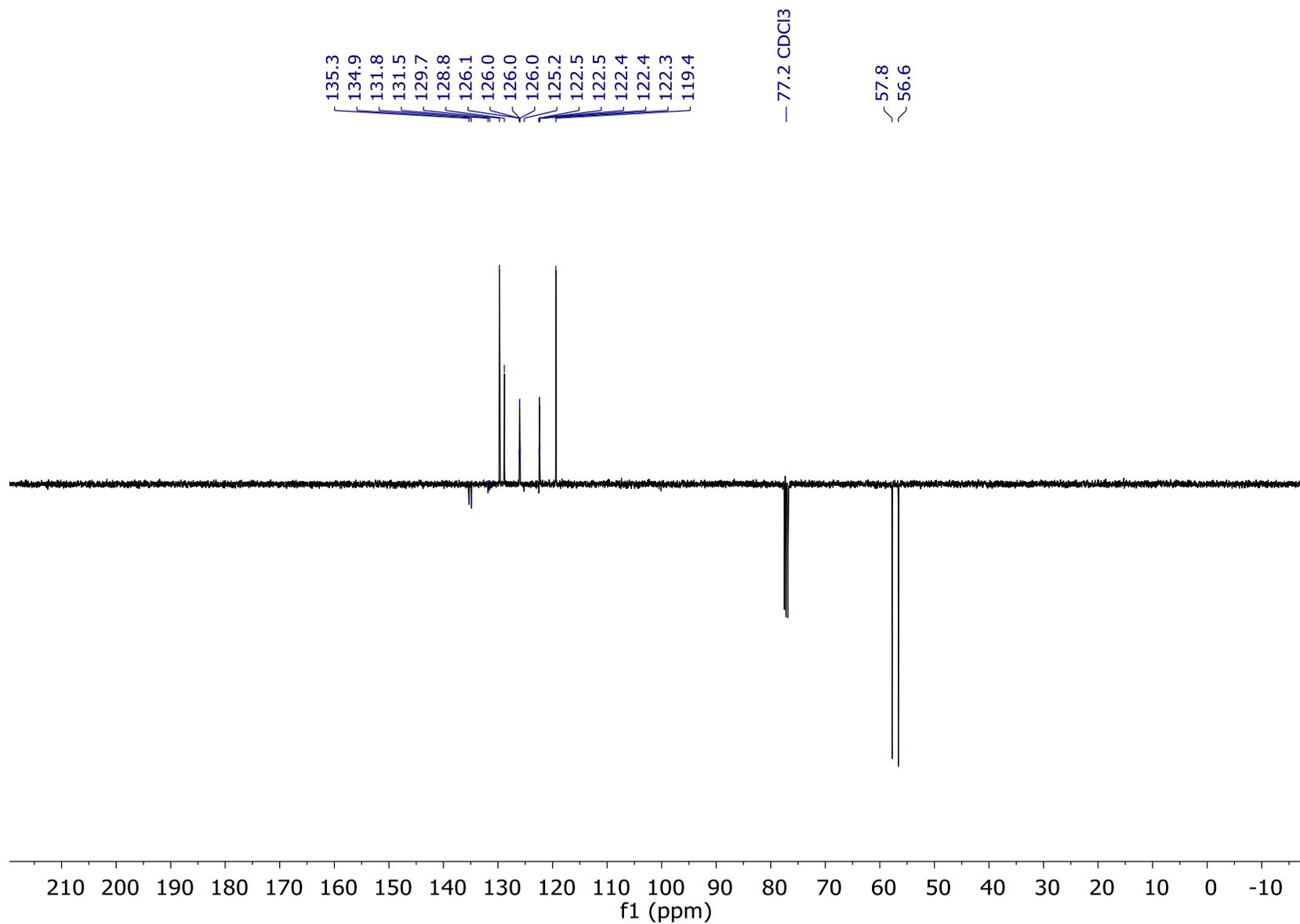


Figure S24. ^{13}C $\{^1\text{H}\}$ DEPT-135-Q (101 MHz, CDCl_3) of 3-(3-trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2i**).

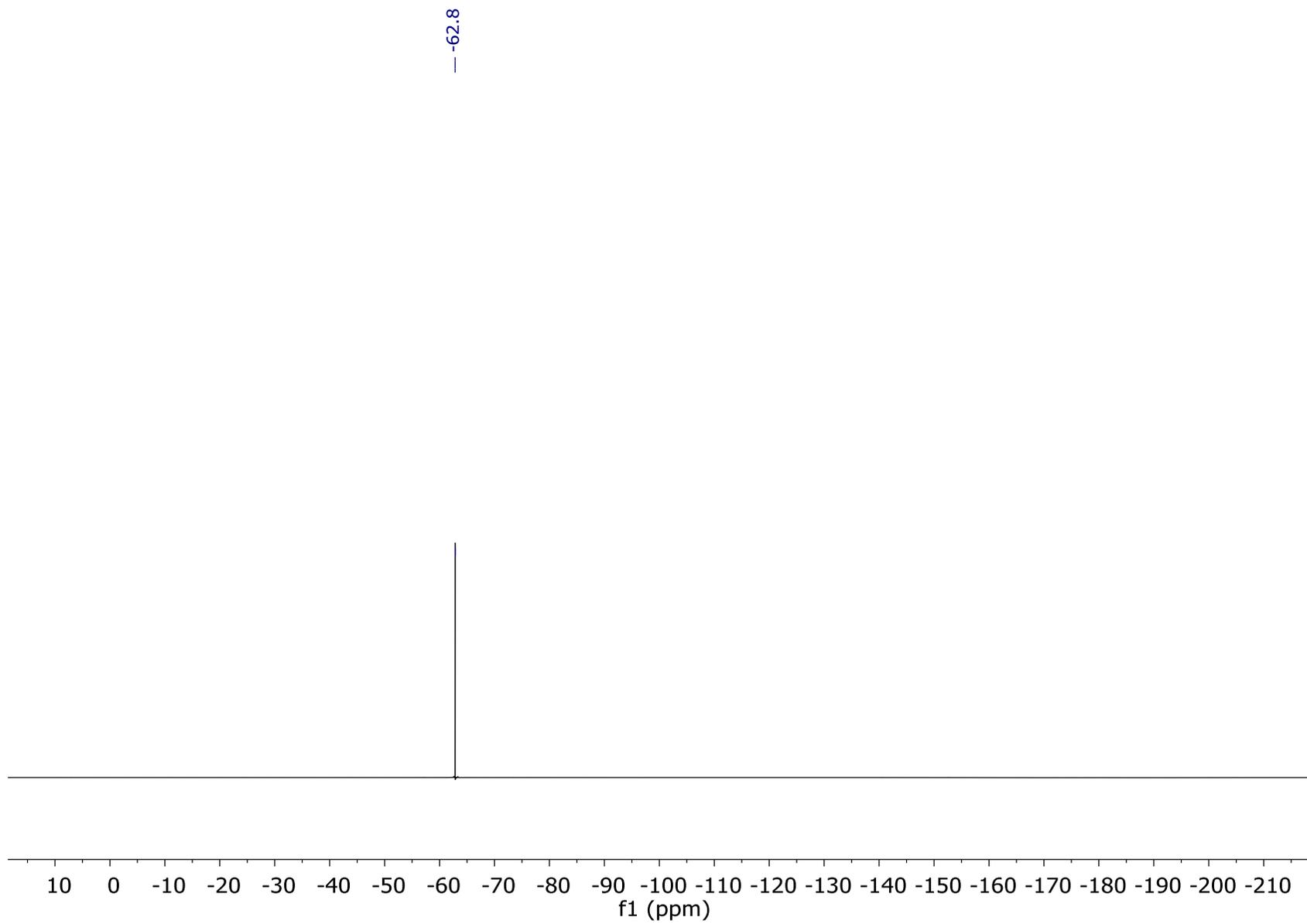


Figure S25. ^{19}F NMR (376 MHz, CDCl_3) of 3-(3-trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2i**).

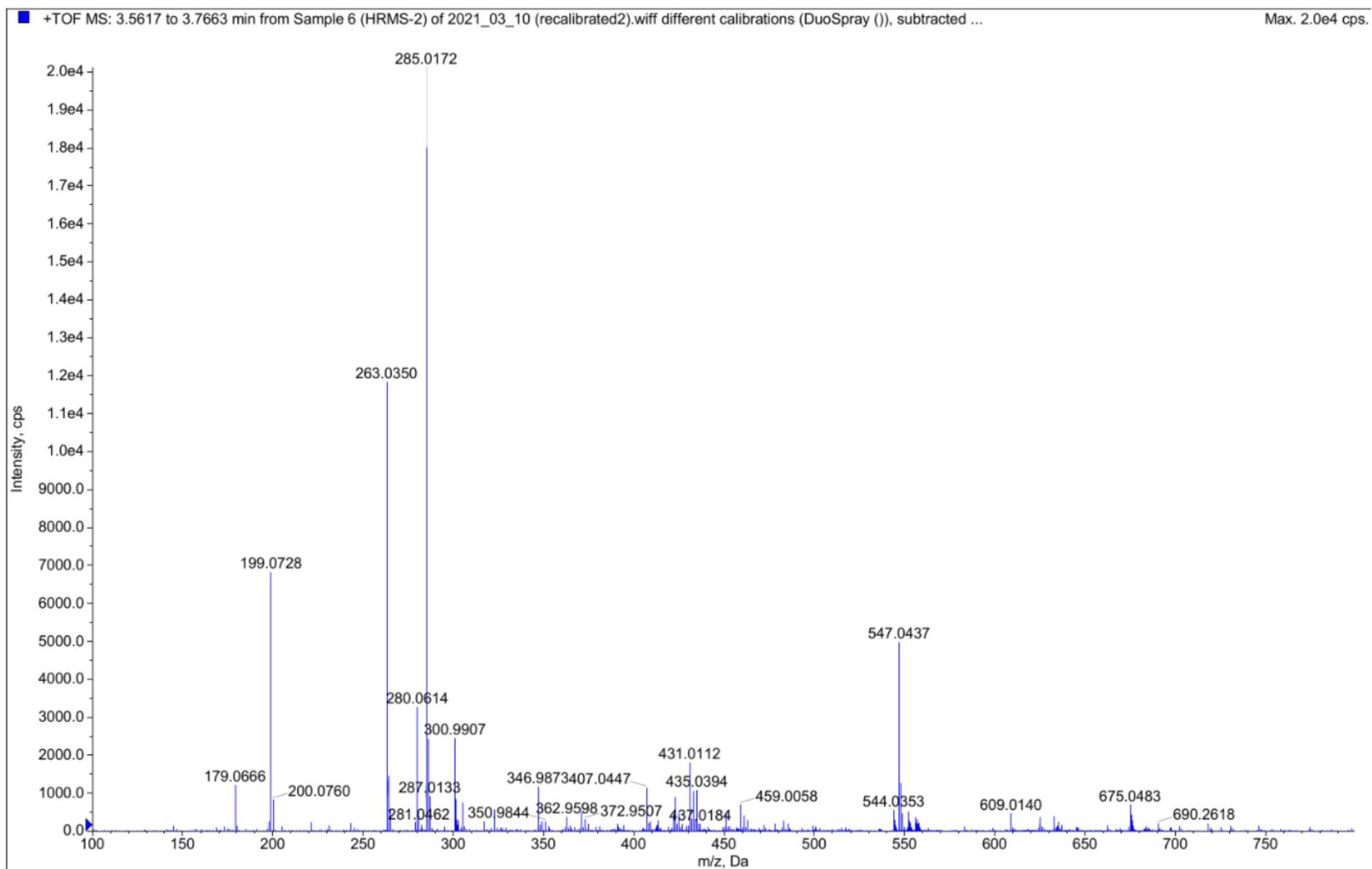


Figure S26. HRMS spectra of 3-(3-trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2i**).

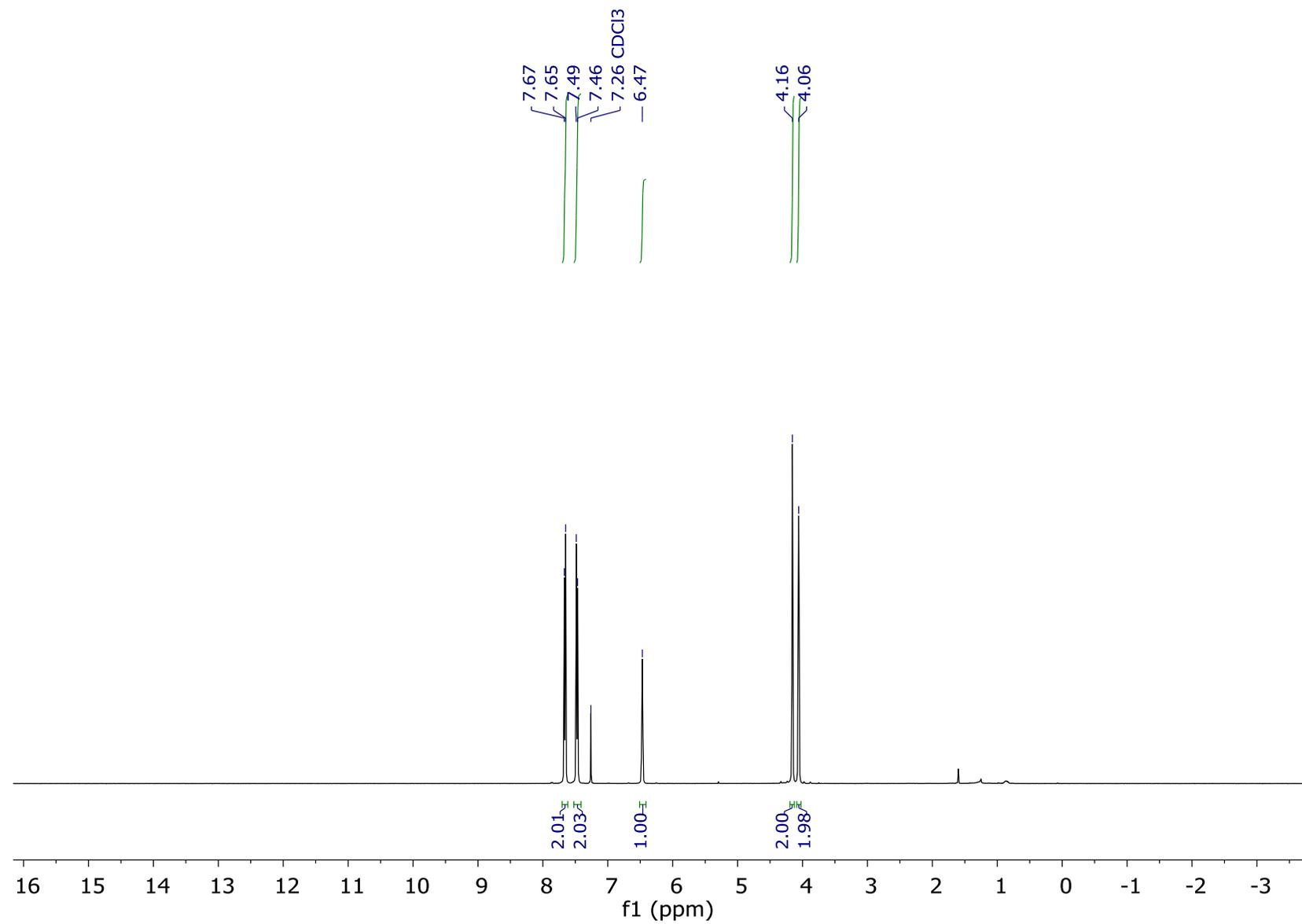


Figure S27. ¹H NMR (400MHz, CDCl₃) of 3-(4-trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2j**).

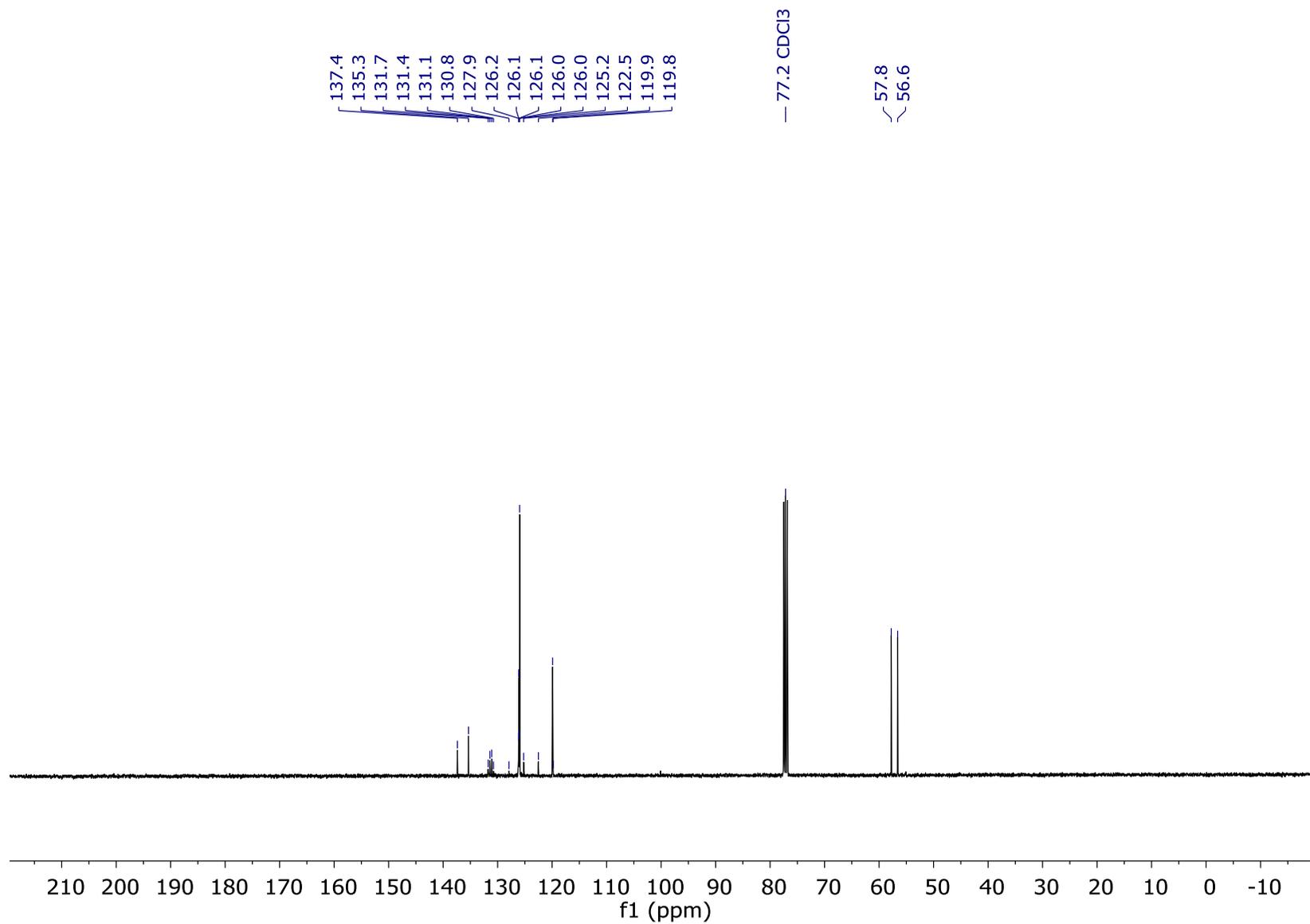


Figure S28. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl_3) of 3-(4-trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2j**).

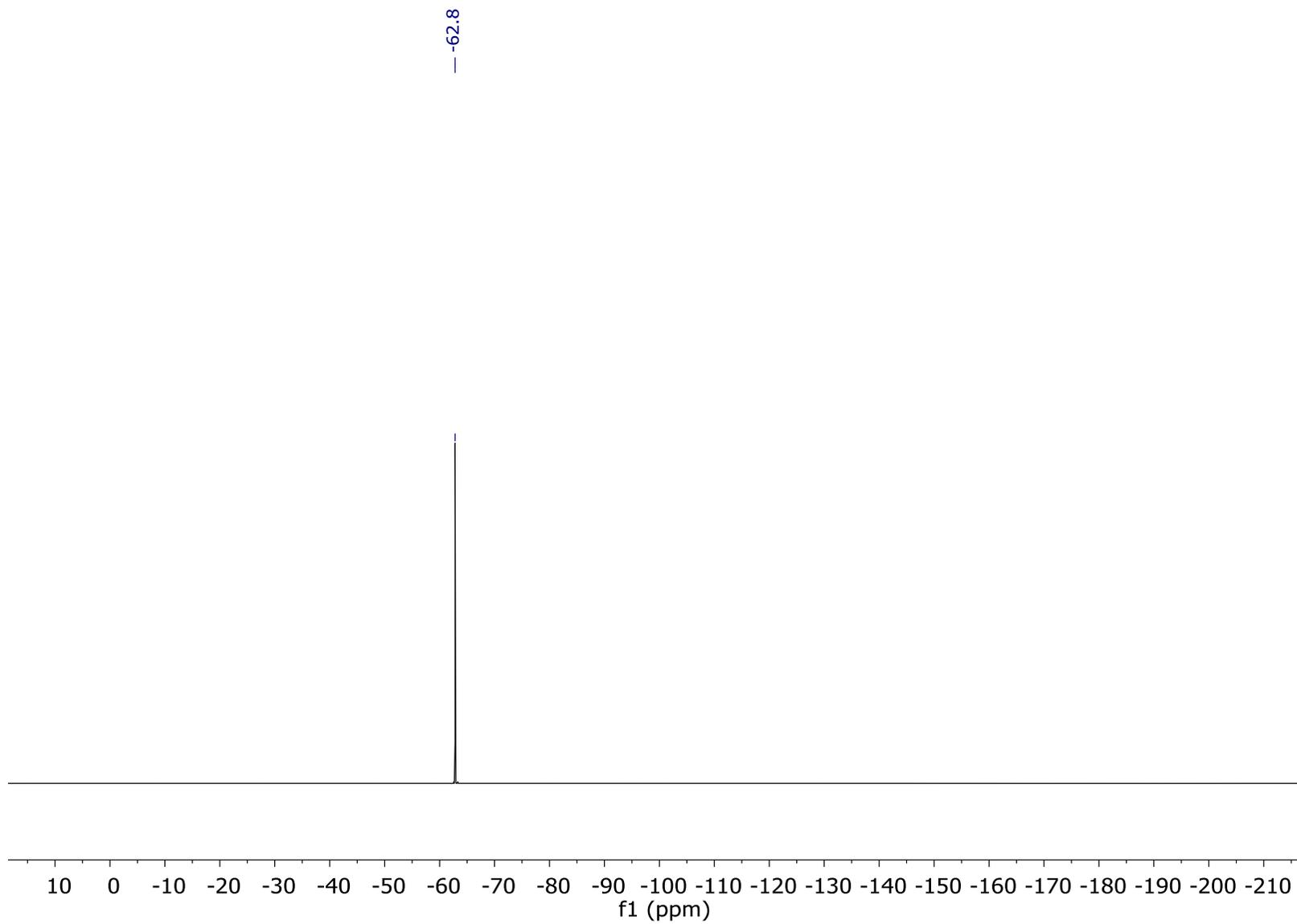


Figure S29. ^{19}F NMR (376 MHz, CDCl_3) of 3-(4-trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2j**).

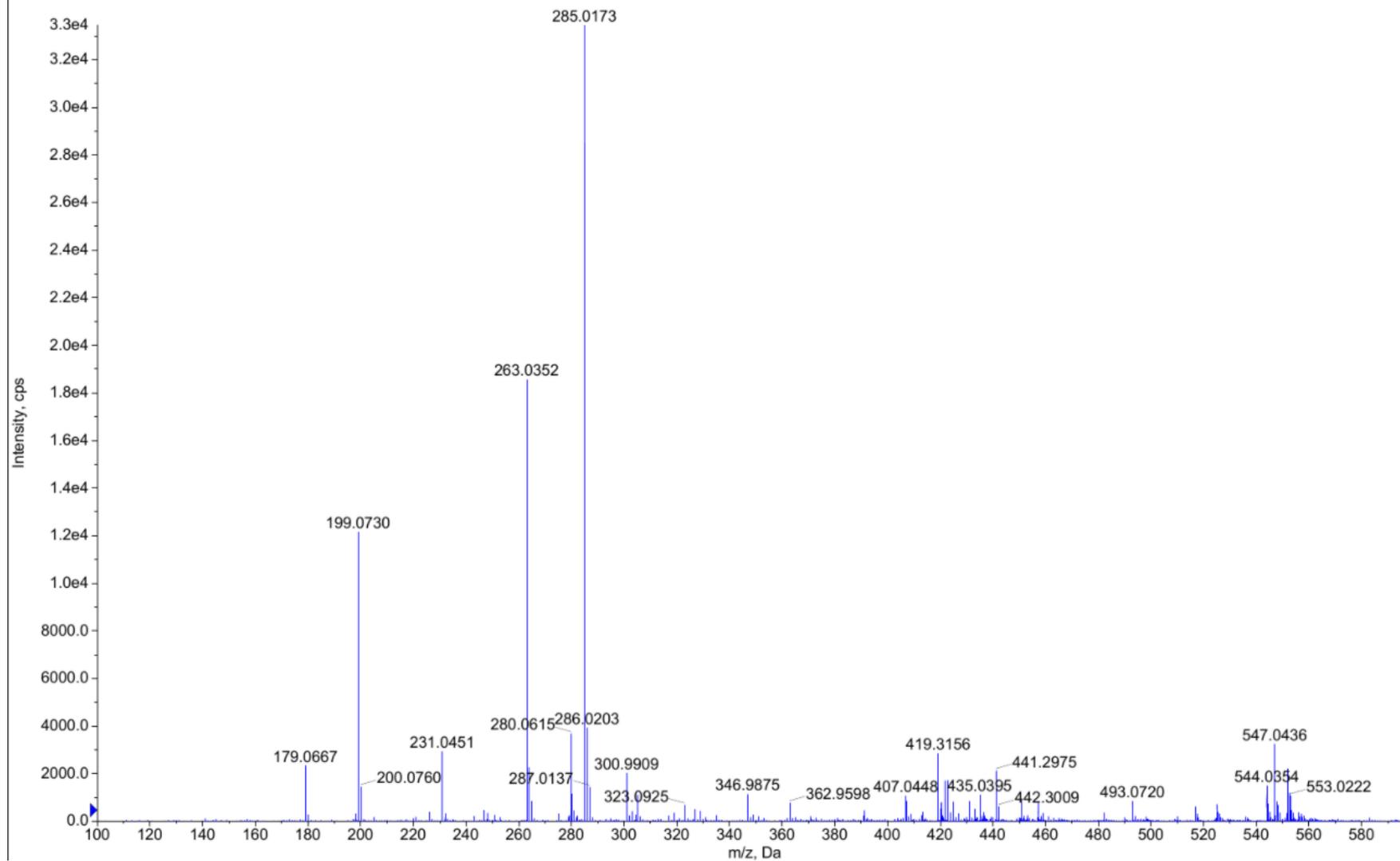


Figure S30. HRMS spectra of 3-(4-trifluoromethylphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2j**).

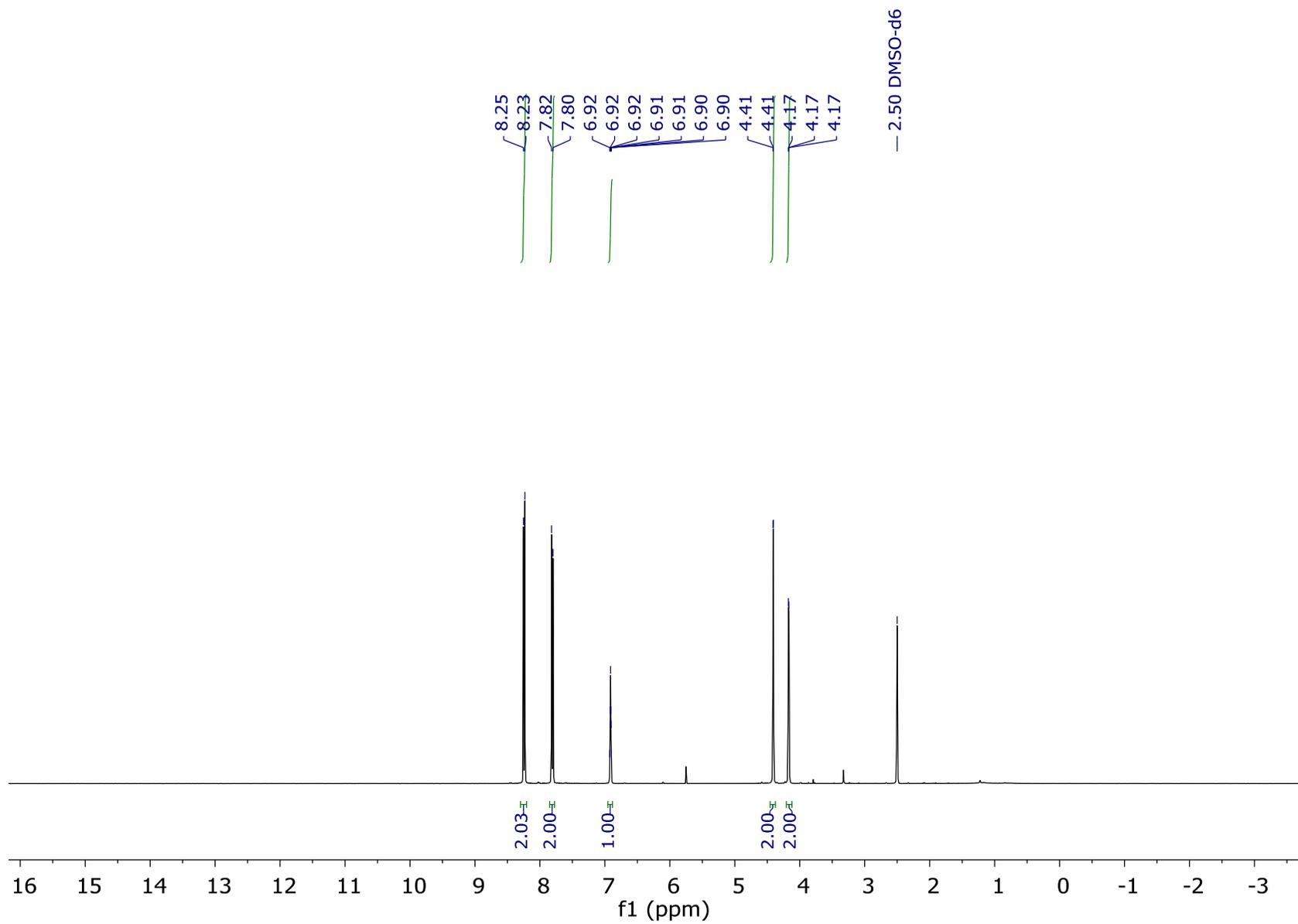


Figure S31. ¹H NMR (400MHz, CDCl₃) of 3-(4-nitrophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2k**).

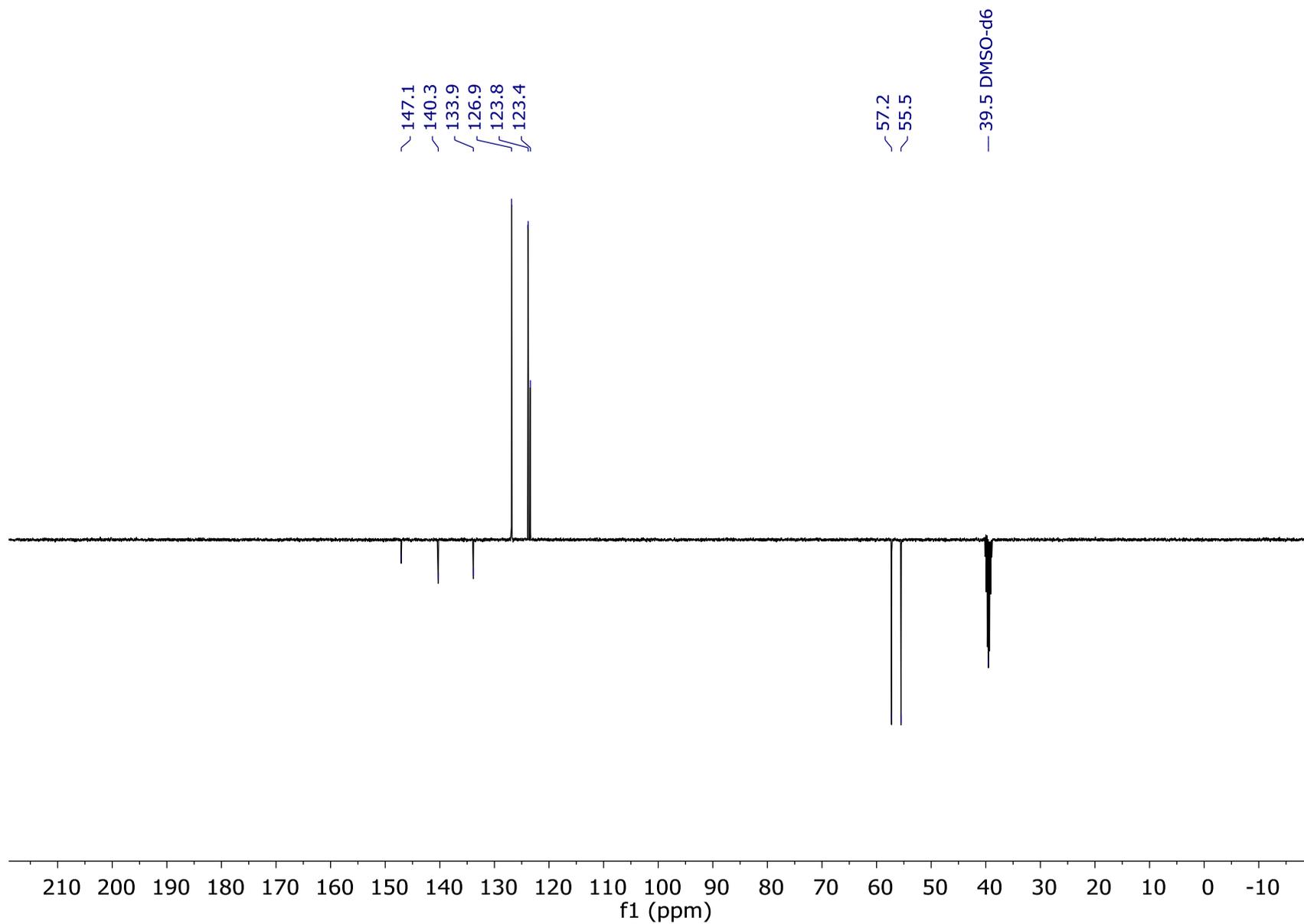


Figure S32. ^{13}C $\{^1\text{H}\}$ DEPT-135-Q (101 MHz, $\text{DMSO-}d_6$) of 3-(4-nitrophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2k**).

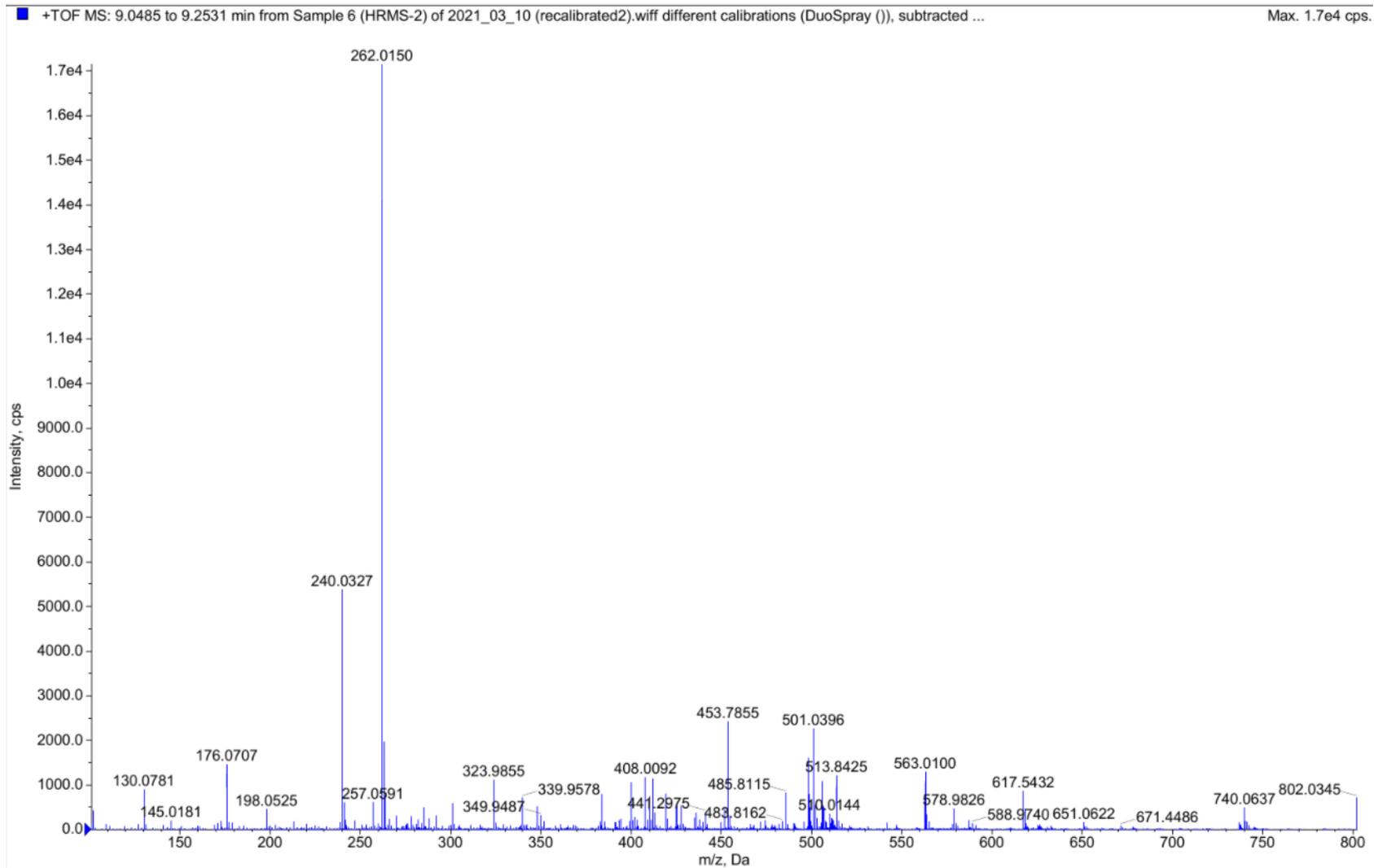


Figure S33. HRMS spectra of 3-(4-nitrophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2k**).

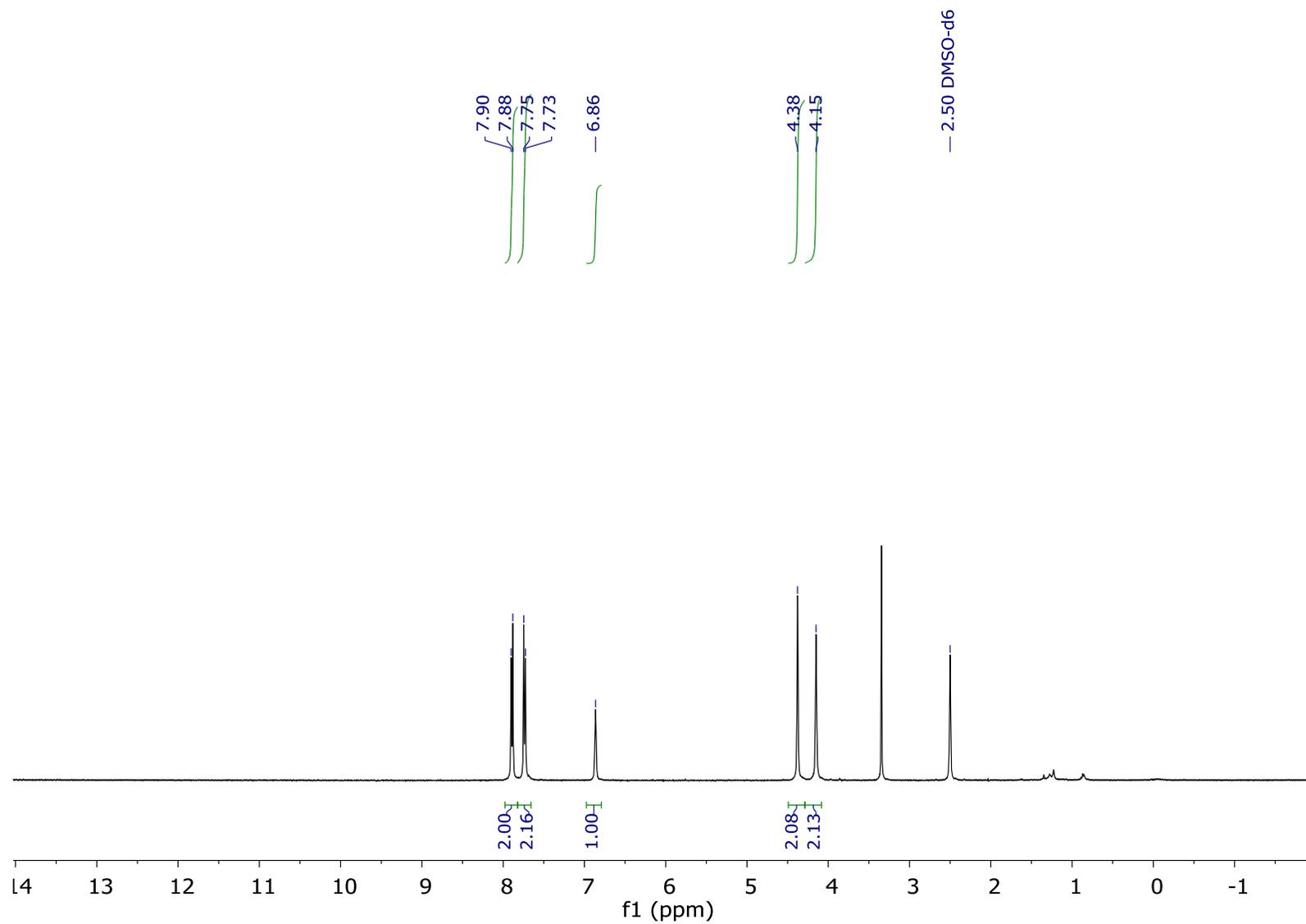


Figure S34. ^1H NMR (400MHz, $\text{DMSO-}d_6$) spectra of 4-(1,1-dioxido-2,5-dihydrothiophen-3-yl)benzonitrile (**2I**).

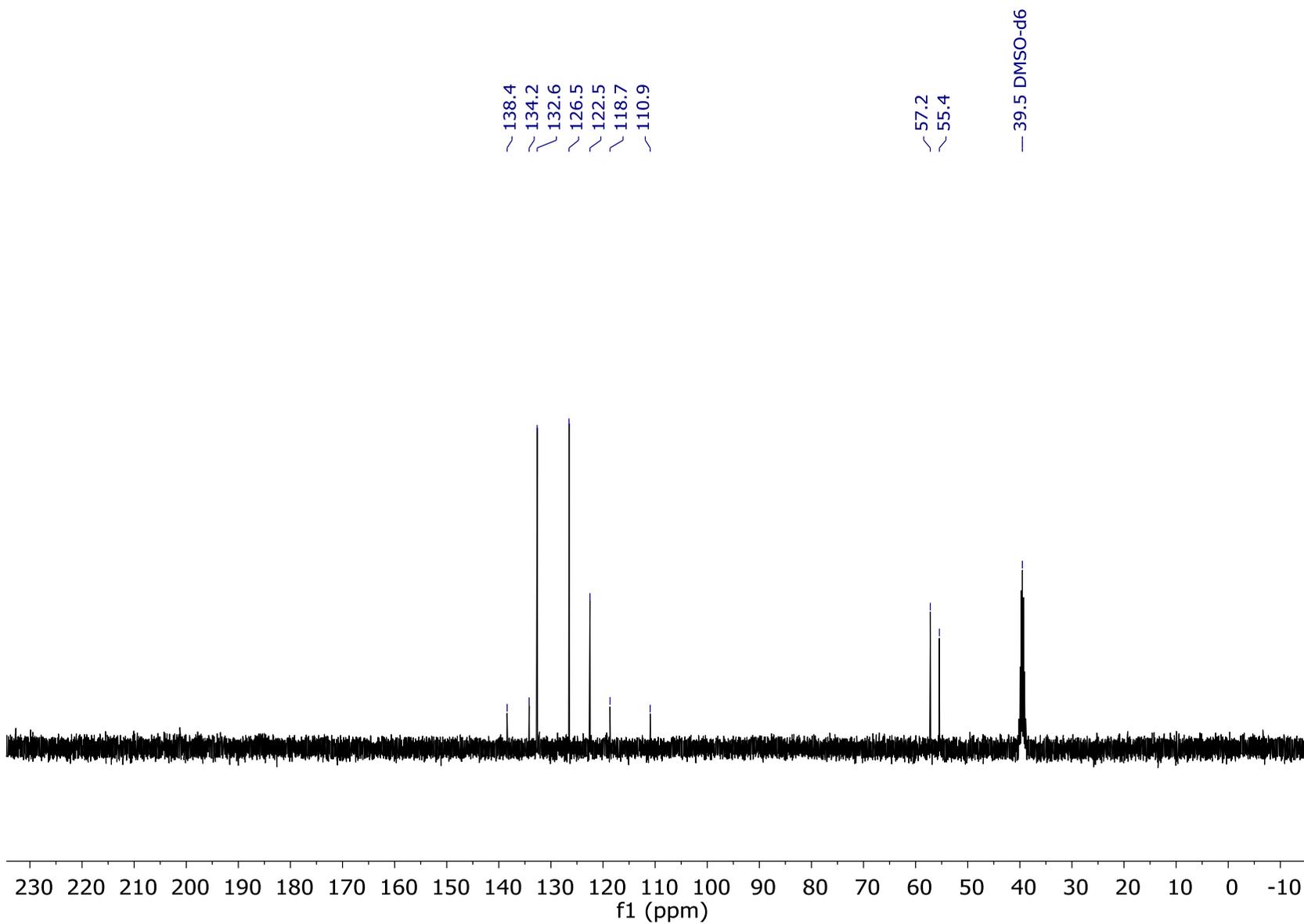


Figure S35. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, DMSO- d_6) of 4-(1,1-dioxido-2,5-dihydrothiophen-3-yl)benzonitrile (**21**).

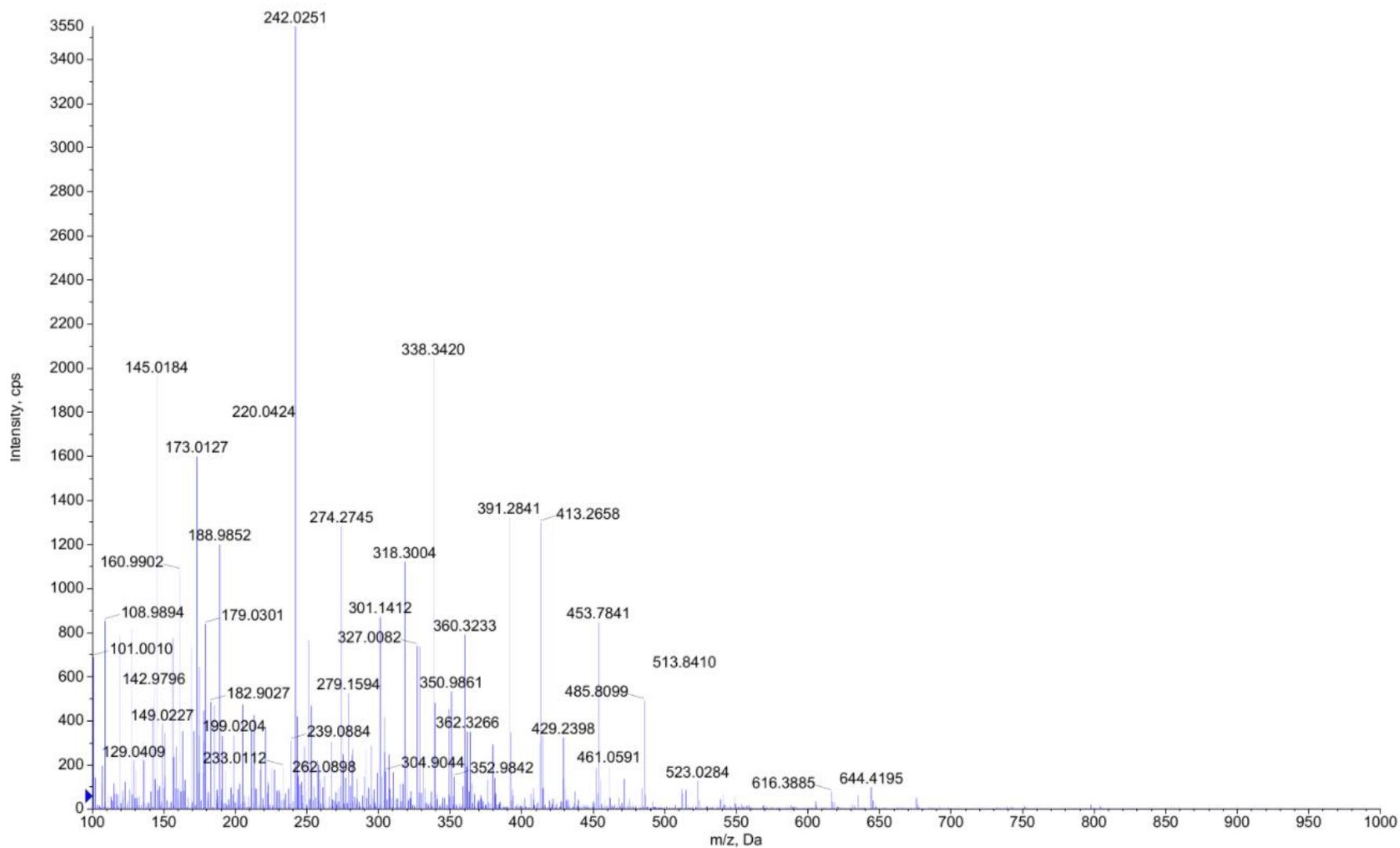


Figure S36. HRMS spectra of 4-(1,1-dioxido-2,5-dihydrothiophen-3-yl)benzotrile (**21**).

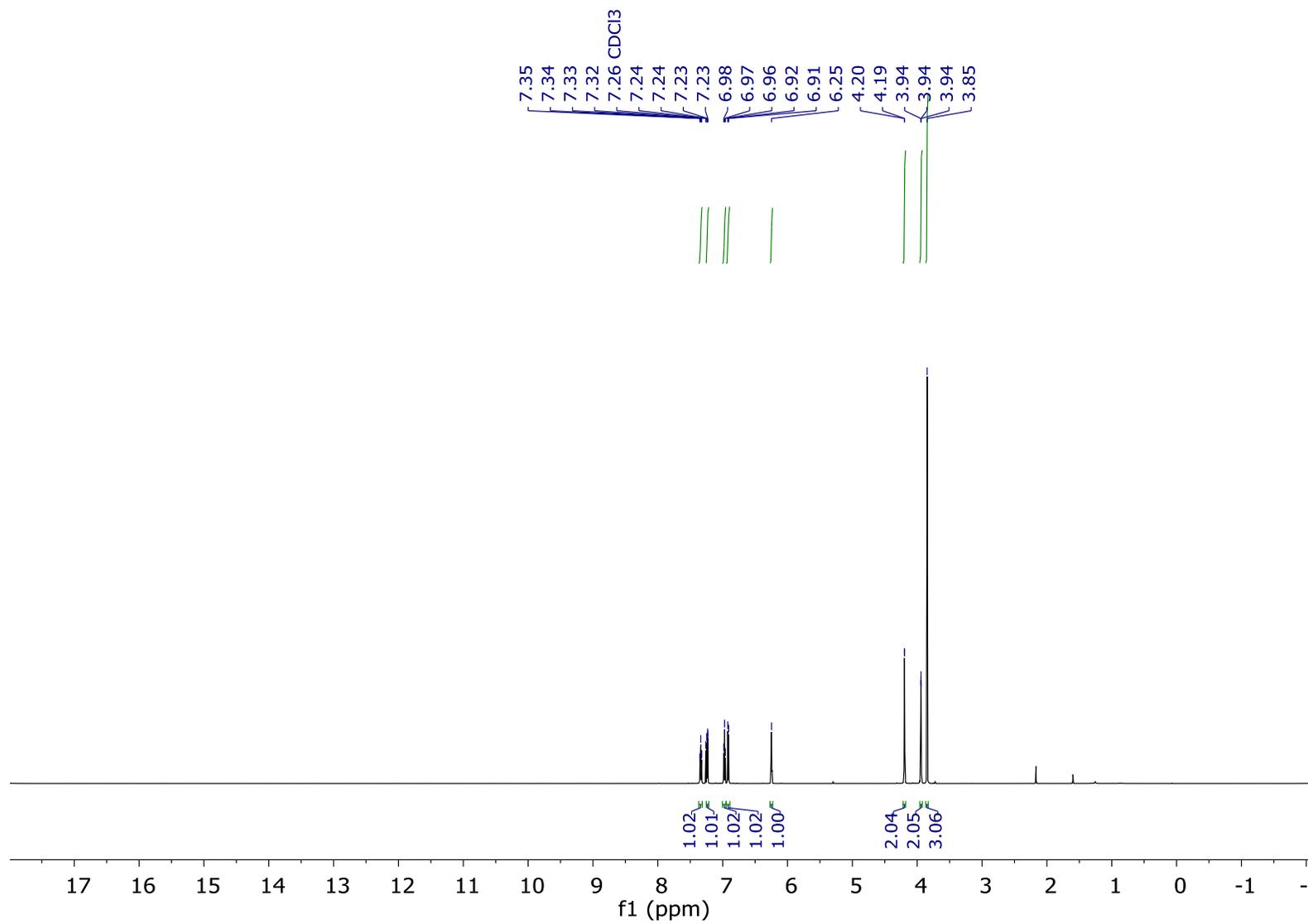


Figure S37. ¹H NMR (400MHz, CDCl₃) of 3-(2-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2m**).

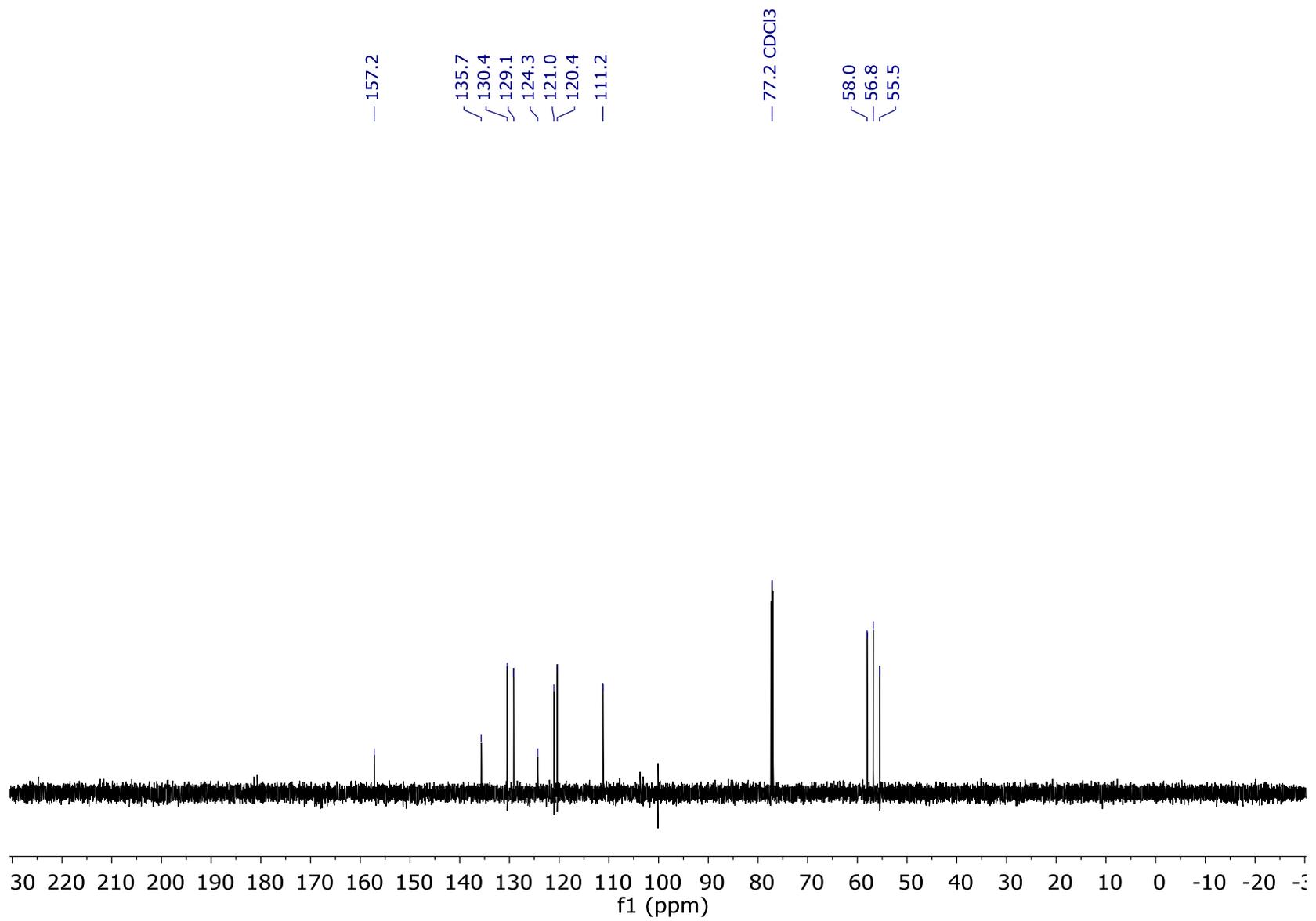


Figure S38. ¹³C {¹H} NMR (101MHz, CDCl₃) of 3-(2-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2m**).

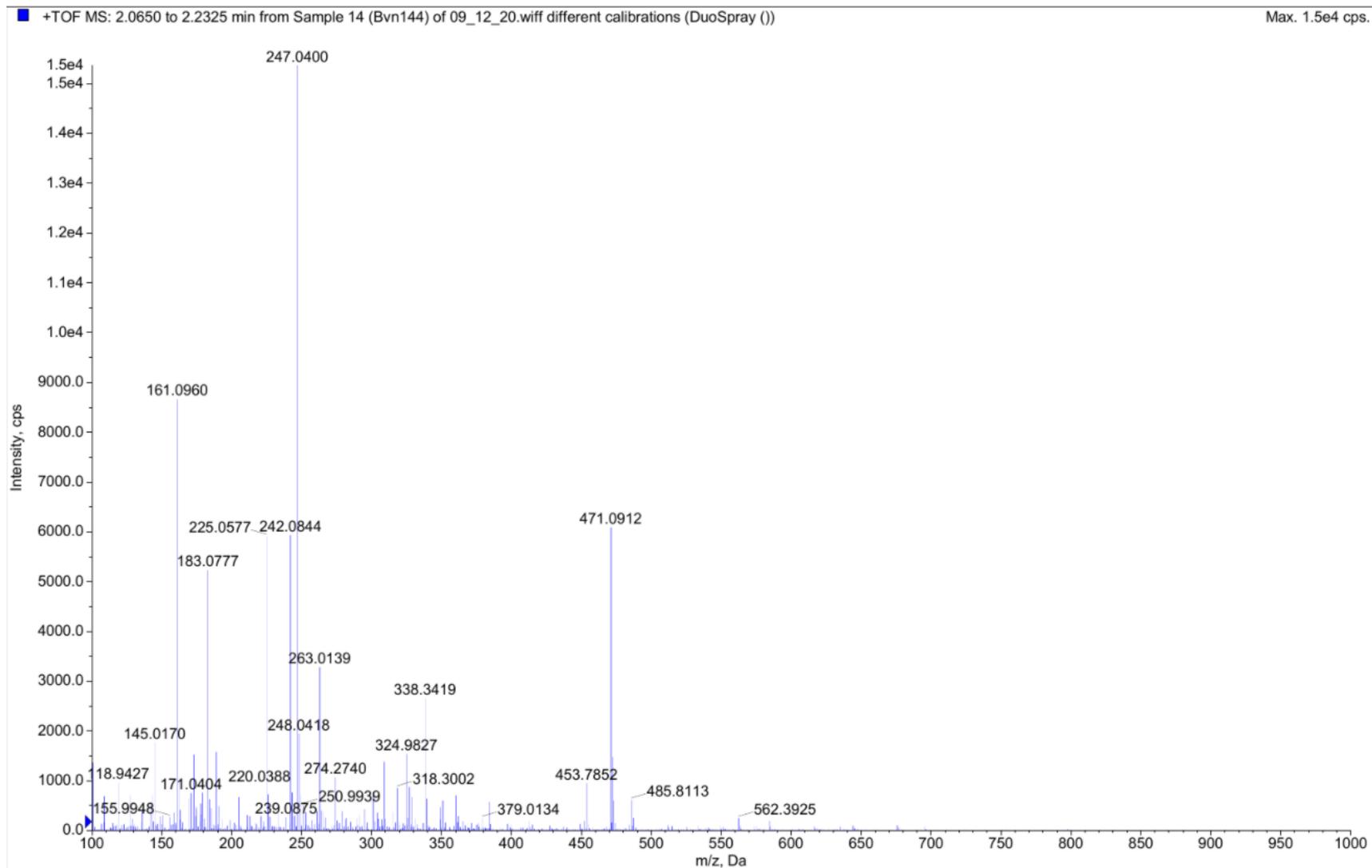


Figure S39. HRMS spectra of 3-(2-methoxyphenyl)-2,5-dihydrothiophene 1,1-dioxide (**2m**).

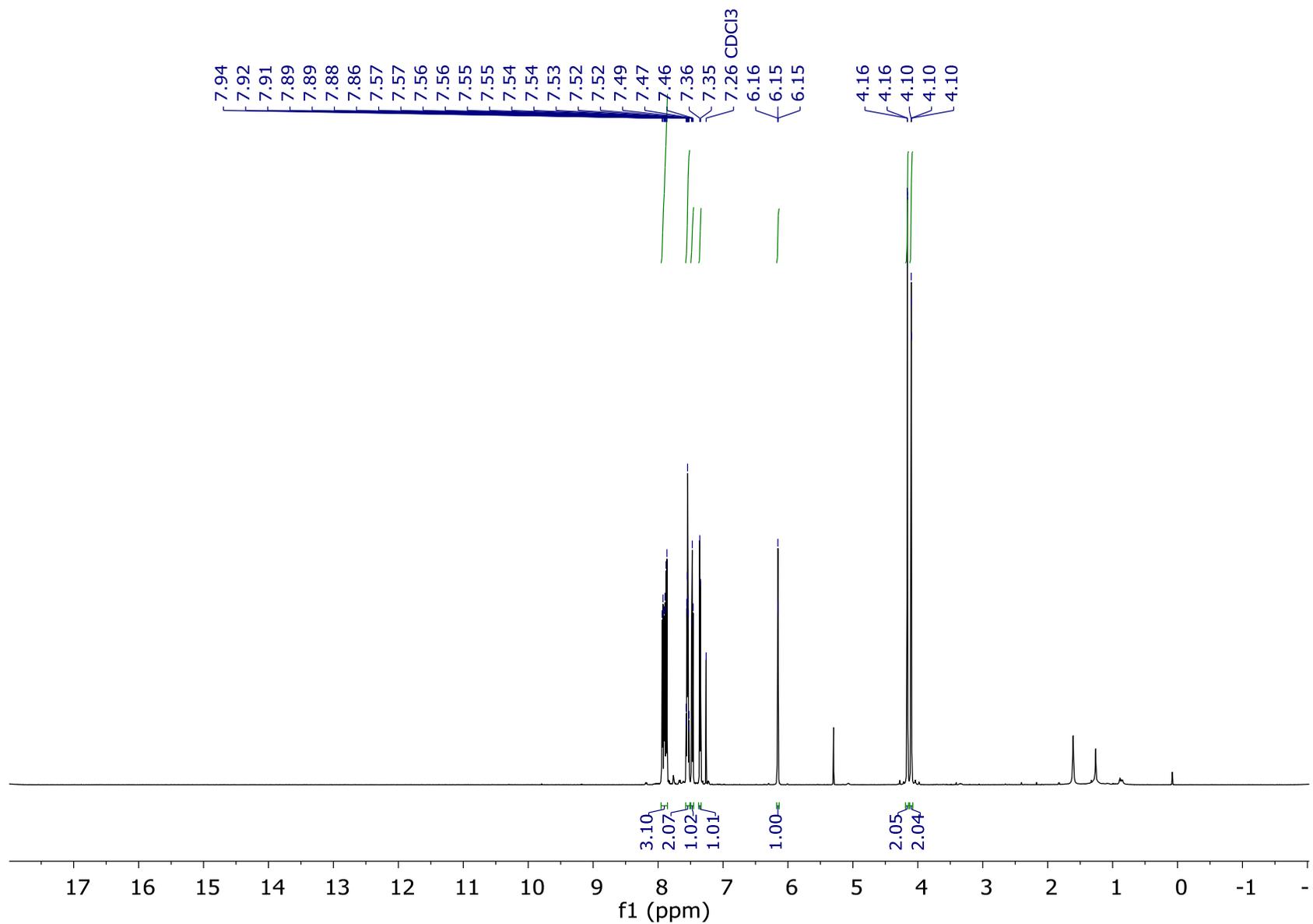


Figure S40. ^1H NMR (400MHz, CDCl_3) of 3-(naphthalen-1-yl)-2,5-dihydrothiophene 1,1-dioxide (**2n**).

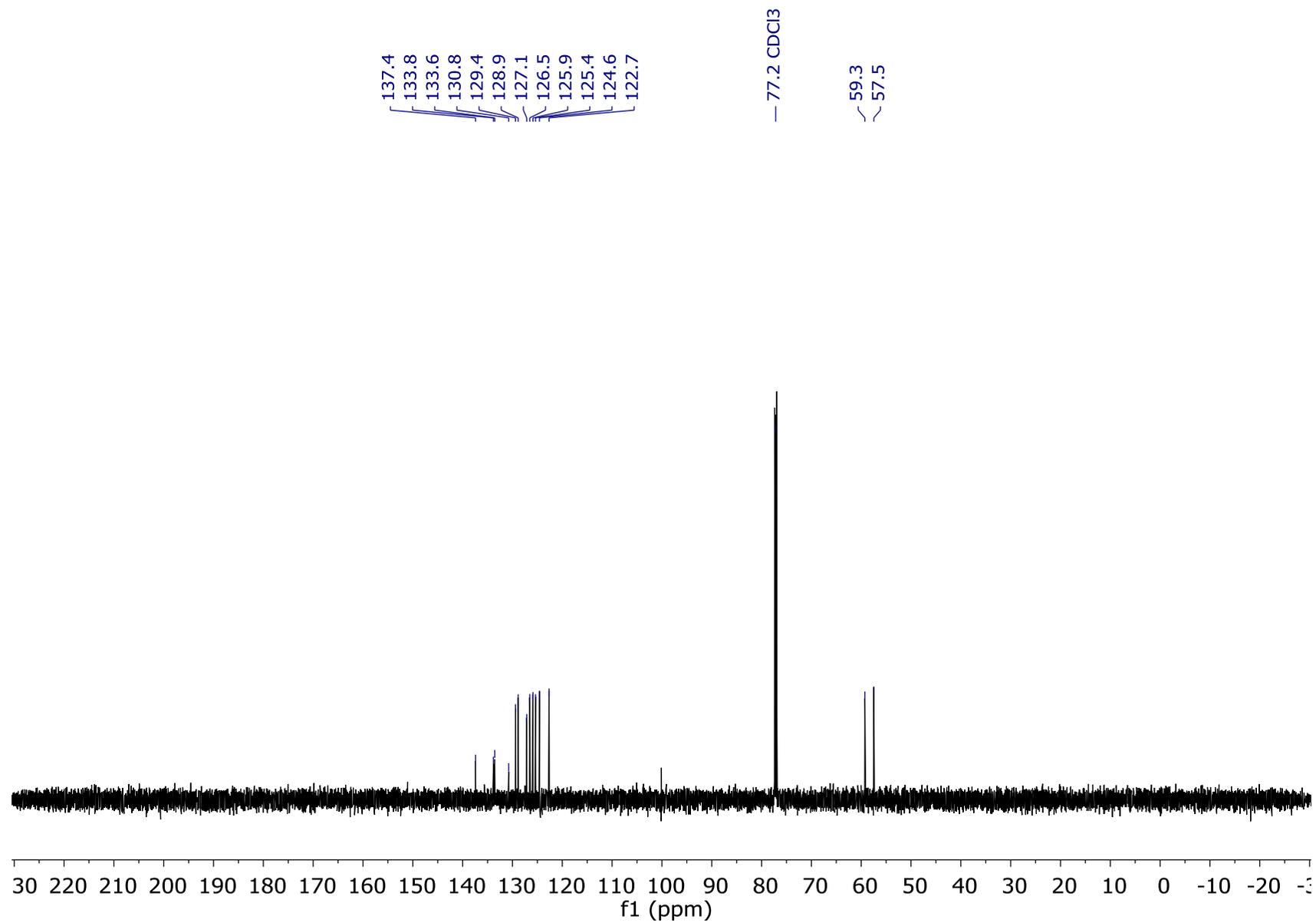


Figure S41. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl_3) of 3-(naphthalen-1-yl)-2,5-dihydrothiophene 1,1-dioxide (**2n**).

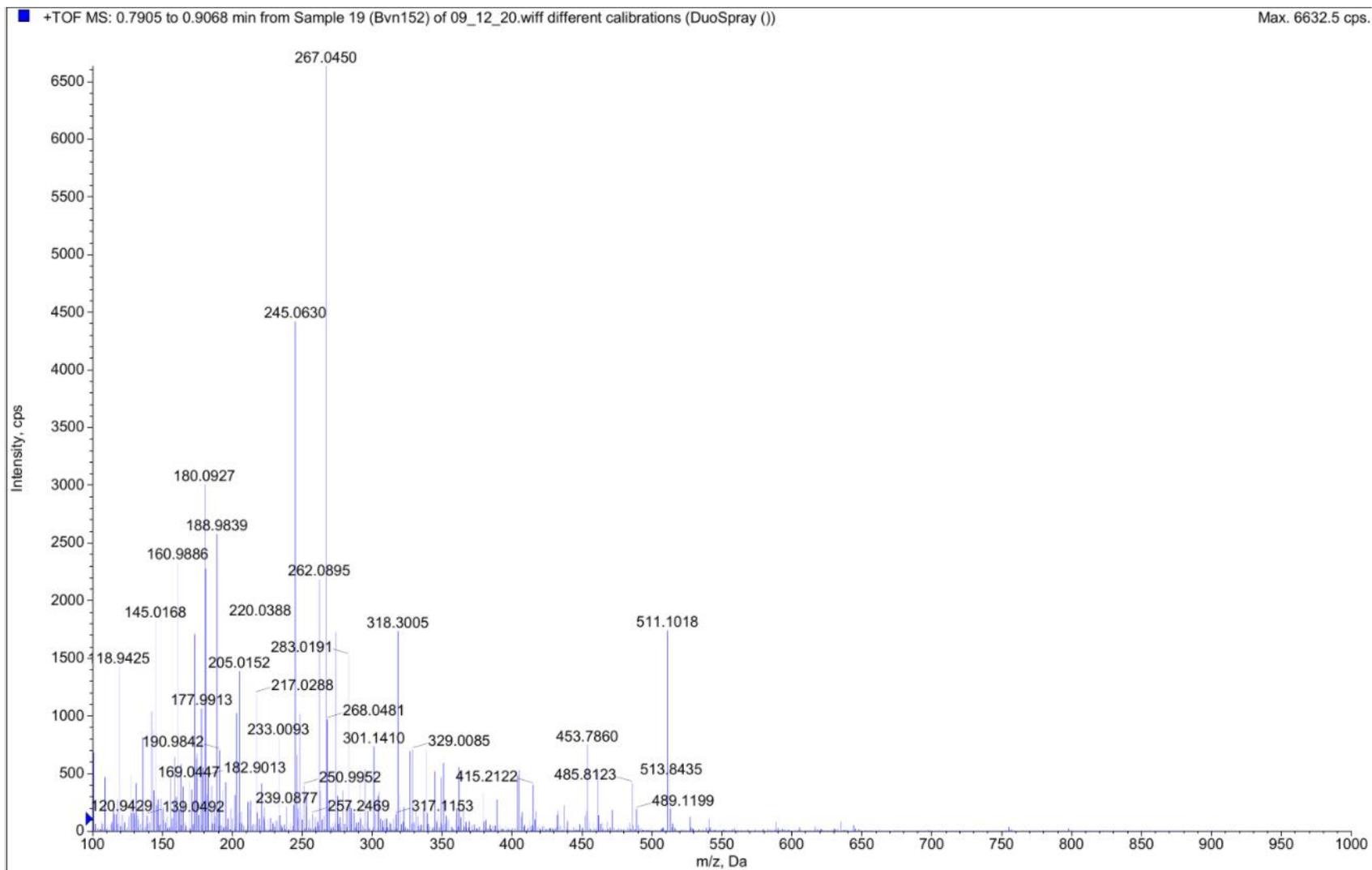


Figure S42. HRMS spectra of 3-(naphthalen-1-yl)-2,5-dihydrothiophene 1,1-dioxide (**2n**).

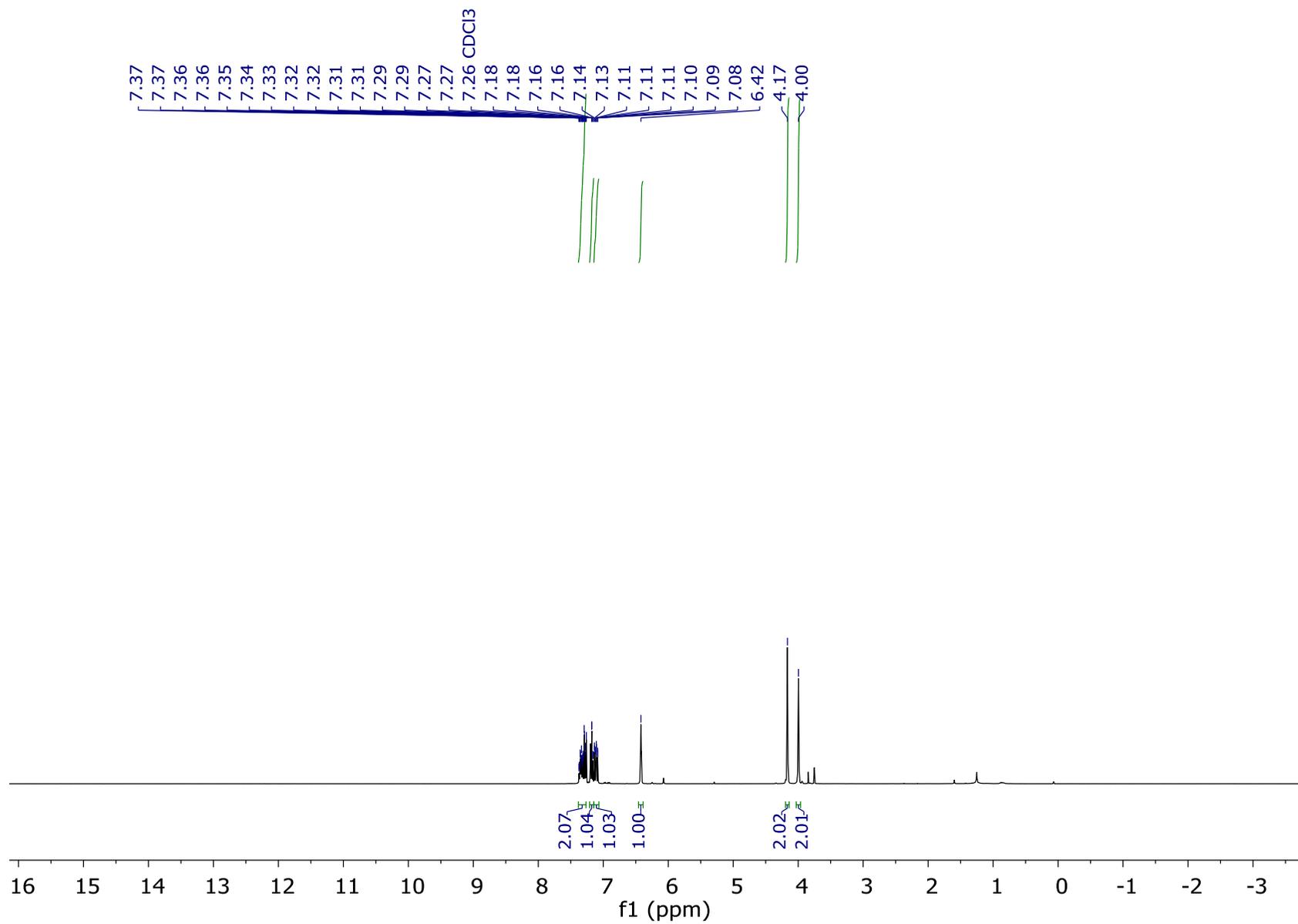


Figure S43. ^1H NMR (400MHz, CDCl_3) of 3-(2-fluorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2o**).

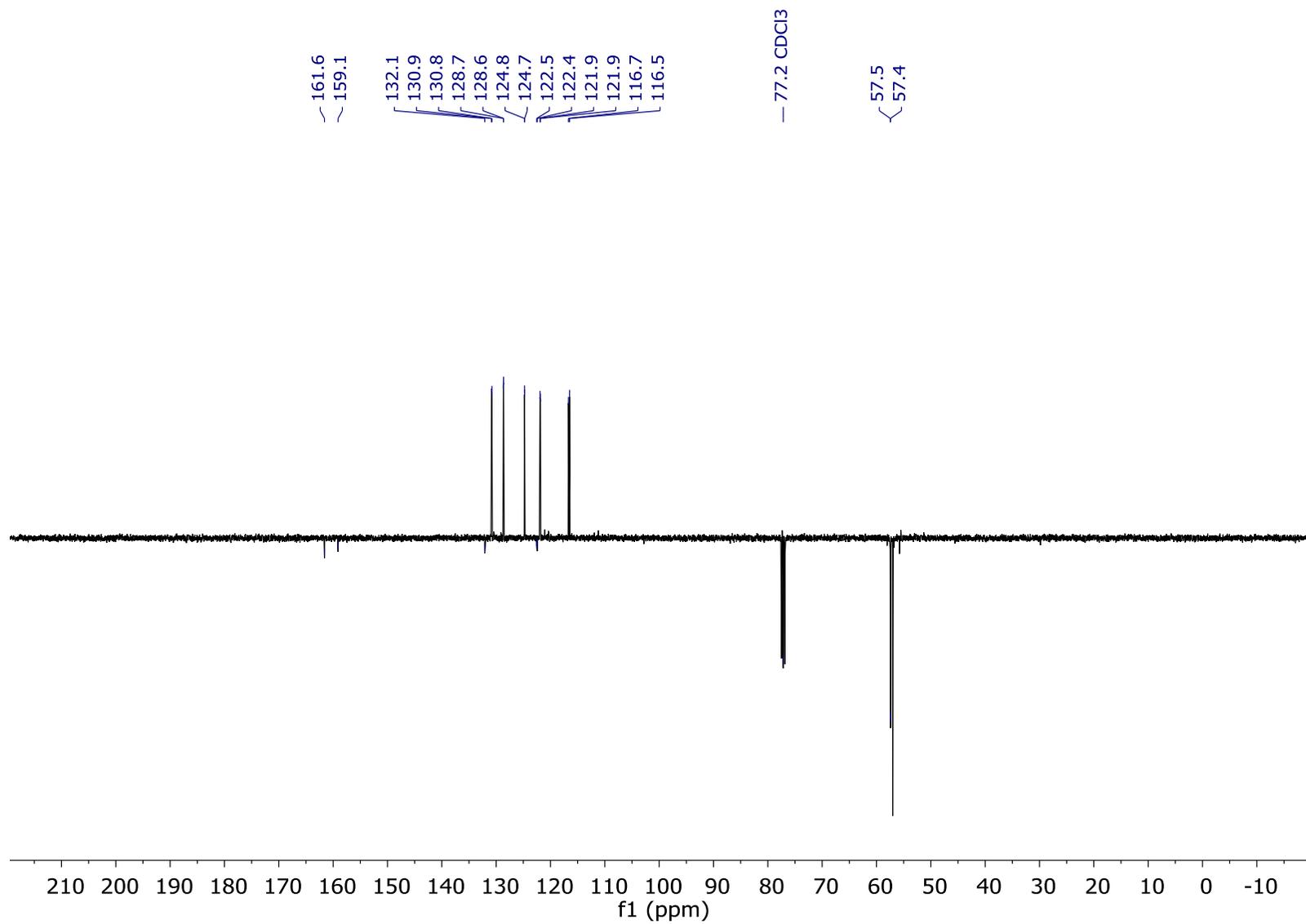


Figure S44. ^{13}C $\{^1\text{H}\}$ DEPT-135-Q (101 MHz, CDCl_3) of 3-(2-fluorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2o**).

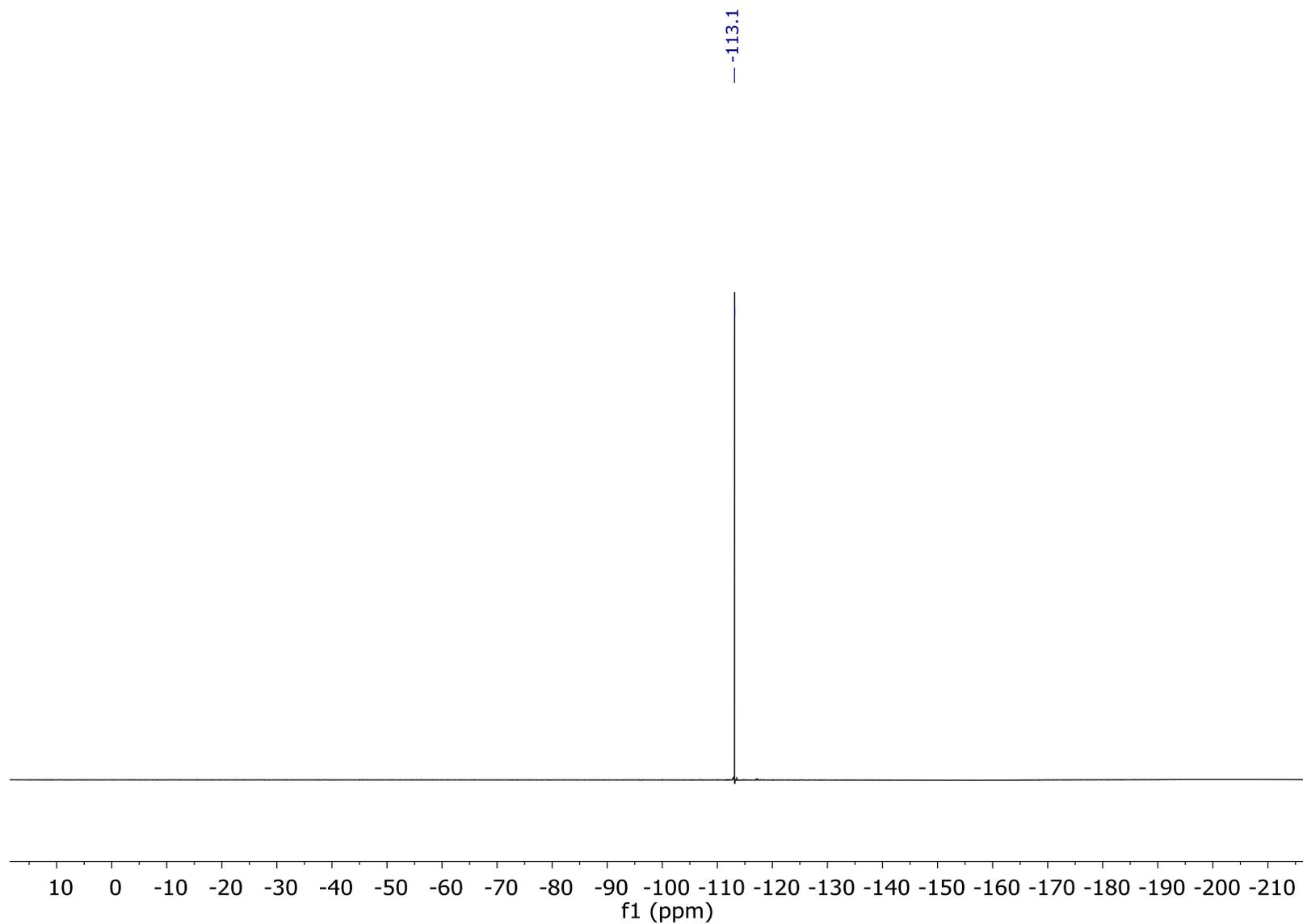


Figure S45. ^{19}F NMR (376 MHz, CDCl_3) of 3-(2-fluorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2o**).

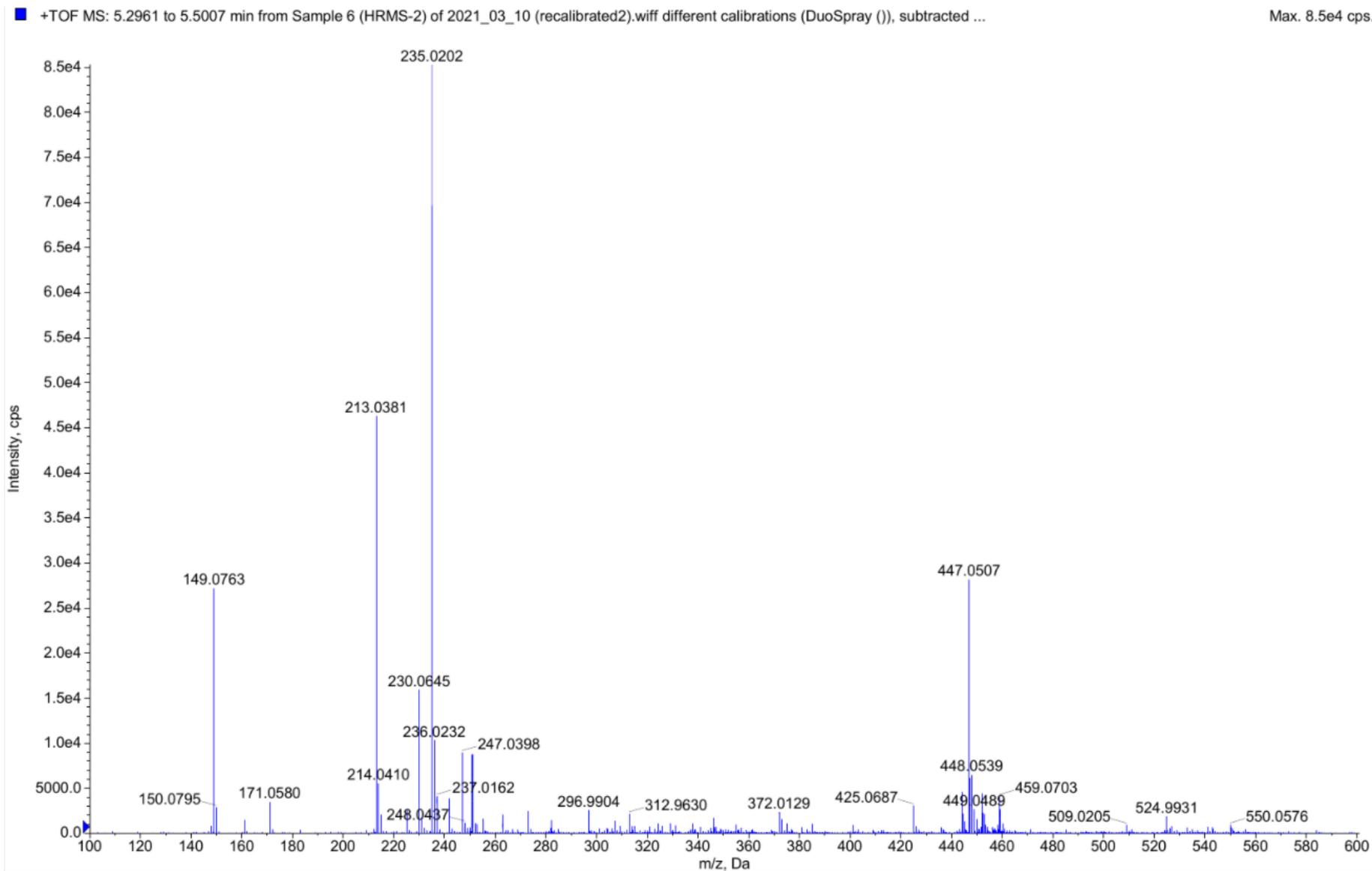


Figure S46. HRMS spectra of 3-(2-fluorophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2o**).

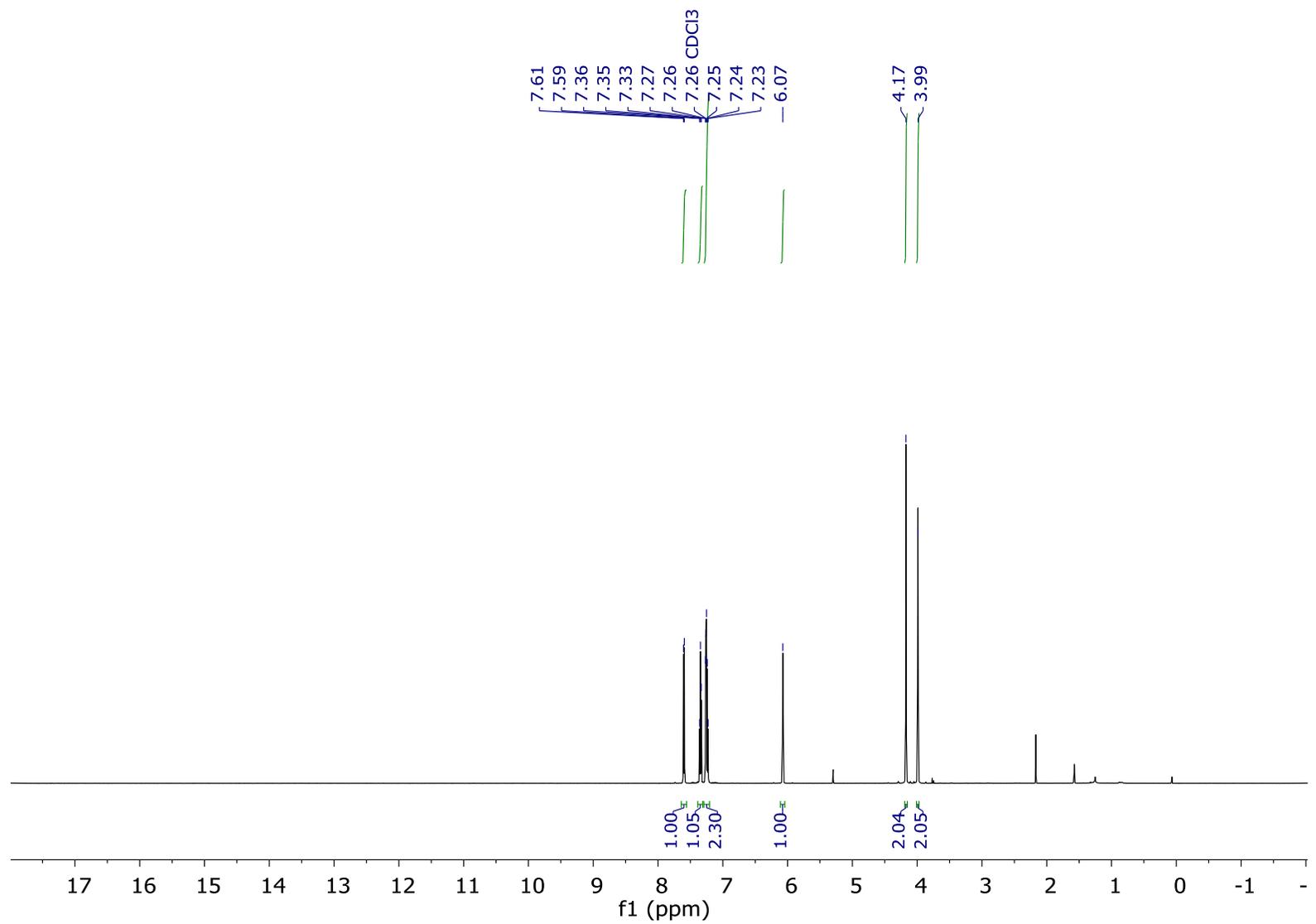


Figure S47. ¹H NMR (400MHz, CDCl₃) 3-(2-bromophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2p**).

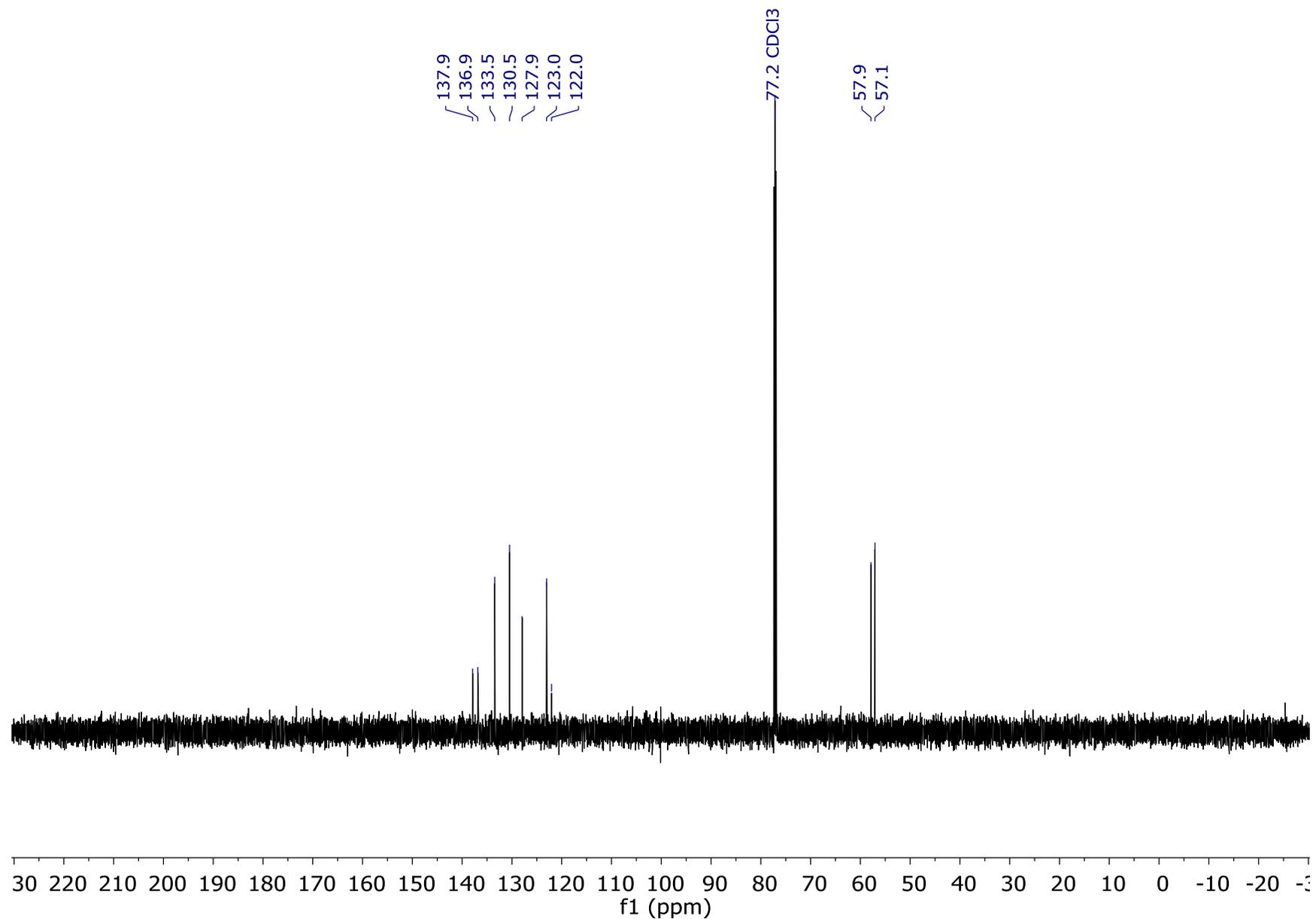


Figure S48. ^{13}C $\{^1\text{H}\}$ NMR (101MHz, CDCl_3) 3-(2-bromophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2p**).

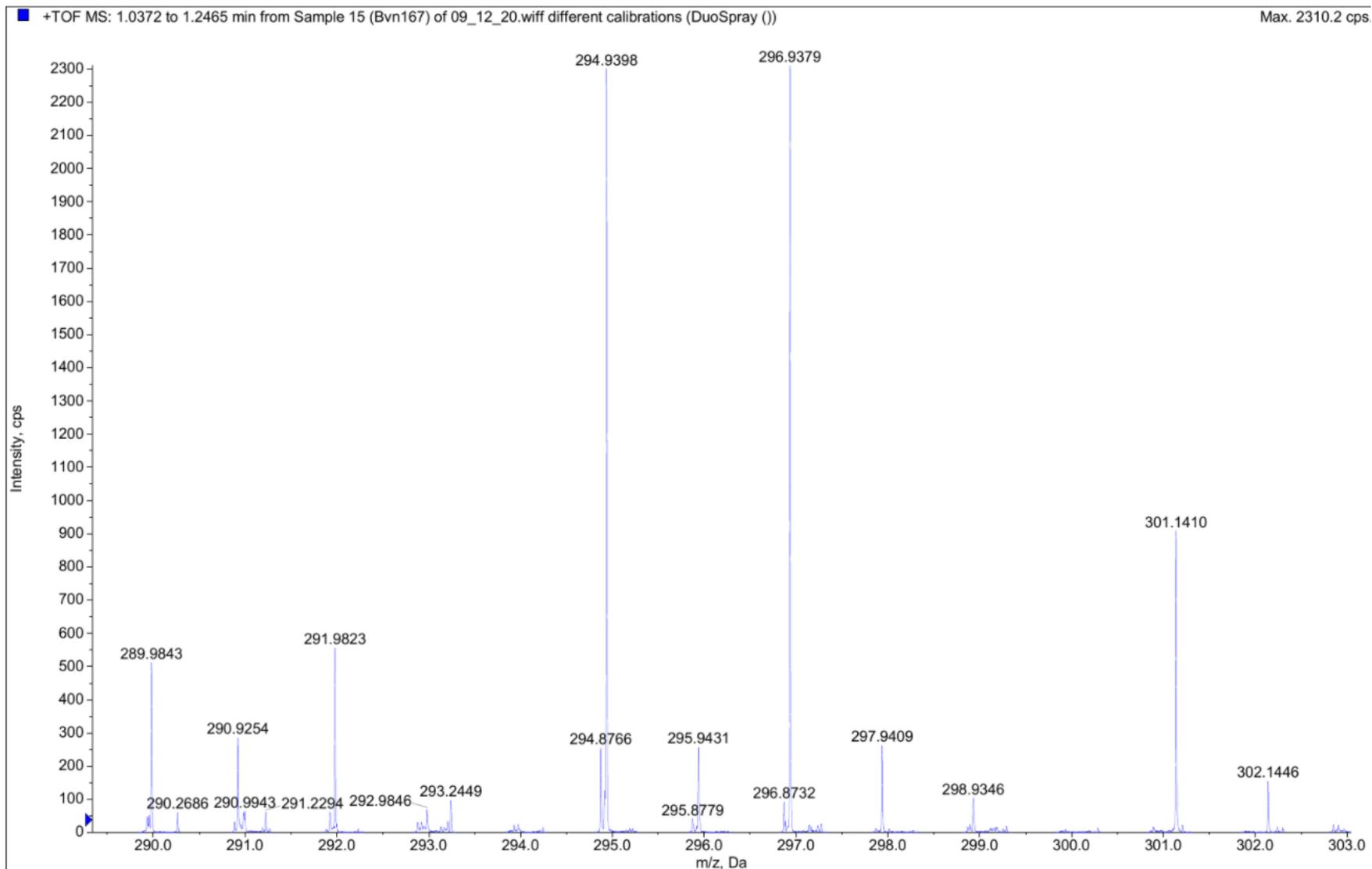


Figure S49. HRMS spectra 33-(2-bromophenyl)-2,5-dihydrothiophene 1,1-dioxide (**2p**).