Supporting Information

Efficient synthesis of 3-sulfolenes from allylic alcohols and 1,3-dienes enabled by sodium metabisulfite as a sulfur dioxide equivalent

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General procedures

Materials and methods

3,4-Dimethyleneoctane,[1] 5,6-dimethylenedecane,[2] (*E*)-(3-methylbuta-1,3-dien-1-yl)cyclohexane,[3] (*E*)-2-butyloct-2-enal,[4] 1-vinylcyclohex-1-ene,[5] 4,5-diethylocta-3*E*,5*E*-diene,[6] 5,6-dipropyldeca-4*E*,6*E*-diene,[6] 4-methyl-3-methylene-1-phenylpent-4-en-1-ol,[7] 3-methylene-1-phenylpent-4-en-1-ol,[7] and (*R*)-2-methyl-6-methyleneoct-7-ene-2,3-diol[8] were prepared according to the literature procedures. All other chemicals and solvents were used as commercially available.

Experimental equipment: The 3-sulfolene syntheses were conducted in heavy wall glass pressure vessels (35–350 mL capacity, Chemglass and Ace Glass). The internal pressure was measured to be 10–20 psi.

Purification: Column chromatography was performed using CombiFlash Rf-200 (Teledyne-Isco) automated flash chromatography system, as well as manually. Thin layer chromatography was carried out on silica gel-coated glass plates (Merck Kieselgel 60 F254). Plates were visualized under ultraviolet light (254 nm) and using a potassium permanganate stain.

Characterization: ^{1}H, and ^{13}C, NMR spectra were recorded at 500 MHz or 300 MHz (^{1}H), 125 MHz or 75 MHz (^{13}C) on an Agilent Inova 500 or 300, and Bruker AVANCE III 500 instruments in $CDCl_3$ or other specified deuterated solvents with and without

tetramethylsilane (TMS) as an internal standard at 25 °C, unless specified otherwise. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (^{1}H and ^{13}C). Coupling constants (*J*) are in Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint.), septet (sept.), multiplet (m), broad (br).

Infrared measurements were carried out neat on a Bruker Vector 22 FT-IR spectrometer fitted with a Specac diamond attenuated total reflectance (ATR) module.

General Procedure 1 (GP1) for the synthesis of sulfolenes in hexafluoroisopropanol (HFIP)

A 75 mL glass pressure vessel was charged with a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL). The stirred mixture was degassed by bubbling argon for 5 min, then 1,3-diene (2 mmol) and sodium metabisulfite (10 mmol, 5 equiv) were added. The vessel was sealed, and the reaction mixture was stirred at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure to remove HFIP. Ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to afford the sulfolene product.

General Procedure 2 (GP2) for the synthesis of sulfolenes in methanol with $KHSO_4$

A 75 mL pressure vessel was charged with a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL). The stirred mixture was degassed by bubbling argon for 5 min, then $KHSO_4$ (4 mmol, 2 equiv.), diene (2 mmol) and sodium metabisulfite (10 mmol, 5 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated. Ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to afford the sulfolene product.

General Procedure 3 (GP3) for the synthesis of allylic alcohols

To a solution of ketone (5 mmol) in tetrahydrofuran (10 mL) was added 1M vinylmagnesium bromide or isopropenylmagnesium bromide solution in THF (8 mmol,

1.6 equiv.) at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Saturated solution of ammonium chloride (3 mL) was added, and the mixture was extracted with ethyl acetate (4 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The purity of the crude allylic alcohol was assayed by means of ^1H NMR spectroscopy with 1,4-dimethoxybenzene as an internal standard, and the crude allylic alcohol was immediately used for the preparation of 3-sulfolenes (GP4).

General Procedure 4 (GP4) for the synthesis of sulfolenes from allylic alcohols

To a 48 mL pressure vessel charged with allylic alcohol (0.6−1 mmol) was added a 2 : 1 or 3 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (3 mmol, 3−5 equiv.) and $KHSO_4$ (4 mmol, 4−7.3 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. The reaction mixture was then allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and purified by flash chromatography (silica gel, ethyl acetate/ hexane) to afford the 3-sulfolene product.

3-Methyl-2,5-dihydrothiophene-1,1-dioxide (2)[9]

Small scale synthesis in HFIP/H_2O: According to GP1, isoprene (136 mg, 200 μL, 2 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **2** (260 mg, 98%) as a colorless solid.

Gram scale synthesis in HFIP/H_2O: According to GP1, isoprene (1.36 g, 2.0 mL, 20 mmol) was reacted with sodium metabisulfite (19.0 g, 100 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (40 mL) and water (10 mL) at 100 °C for 14 h. The reaction mixture

was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **2** (2.5 g, 95%) as a colorless solid.

Small scale synthesis in CH_3OH/H_2O with $KHSO_4$: According to GP2, isoprene (136 mg, 200 µL, 2 mmol), sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.), and $KHSO_4$ (0.545 g, 4 mmol, 2 equiv.) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **2** (260 mg, 98%) as a colorless solid.

Gram scale synthesis in CH_3OH/H_2O with $KHSO_4$: According to GP2, isoprene (1.36 g, 2.0 mL, 20 mmol), sodium metabisulfite (19.0 g, 100 mmol, 5 equiv.), and $KHSO_4$ (5.45 g, 2 equiv., 40 mmol) were reacted in a 4 : 1 v/v mixture of methanol (40 mL) and water (10 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **2** (2.1 g, 78%) as a colorless solid.

From allylic alcohol: According to GP4, to a 48 mL pressure vessel charged with 2-methylbut-3-en-2-ol (86 mg, 1 mmol) was added a 2 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (570 mg, 3 mmol, 3 equiv.) and $KHSO_4$ (544 mg, 4 mmol, 4 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. After that, the reaction mixture was allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography (ethyl acetate/ hexane) to give sulfolene **2** (114 mg, 86%) as a colorless solid. – m.p. 59–62 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): 5.65 (1 H, s), 3.75 (2 H, s), 3.63 (2 H, s), 1.85 (3 H, s) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 134.3, 118.0, 59.0, 57.4, 19.0 ppm. – IR: 3430, 3060, 2962, 2921, 1656, 1436, 1413, 1283, 1265, 1248, 1155, 1114, 1038, 929, 897 cm^{-1}.

3,4-Dimethyl-2,5-dihydrothiophene-1,1-dioxide (3)[9]

Small scale synthesis in HFIP/H_2O: According to GP1, 2,3-dimethyl-1,3-butadiene (164 mg, 226 μL, 2 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **3** (260 mg, 89%) as a colorless solid.

Gram scale synthesis in HFIP/H_2O: According to GP1, 2,3-dimethyl-1,3-butadiene (2.46 g, 3.39 mL, 30 mmol) was reacted with sodium metabisulfite (28.5 g, 150 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (60 mL) and water (15 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **3** (4.3 g, 99%) as a colorless solid.

Small scale synthesis in CH_3OH/H_2O with $KHSO_4$: According to GP2, 2,3-dimethyl-1,3-butadiene (164 mg, 226 μL, 2 mmol), sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.), and $KHSO_4$ (0.545 g, 4 mmol, 2 equiv.) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **3** (284 mg, 97%) as a colorless solid. – m.p. 105–107 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): 3.72 (4 H, d, J = 1.1 Hz), 1.78 (6 H, s) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 125.5, 60.6, 14.5 ppm. – IR: 2983, 2955, 2921, 1443, 1402, 1386, 1290, 1262, 1198, 1175, 1107, 920, 877 cm^{-1}.

2,3-Dimethyl-2,5-dihydrothiophene-1,1-dioxide (4)[10]

Small scale synthesis in HFIP/H_2O: According to GP1, 3-methylhexa-1,3-diene (164 mg, 225 μL, 2 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction

mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **4** (291 mg, 99%) as a colorless liquid.

Gram scale synthesis in HFIP/H_2O: According to GP1, 3-methylhexa-1,3-diene (1.64 g, 2.25 mL, 20 mmol) was reacted with sodium metabisulfite (19.0 g, 100 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (40 mL) and water (10 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **4** (2.6 g, 86%) as a colorless liquid.

Small scale synthesis in CH_3OH/H_2O with $KHSO_4$: According to GP2, 3-methyl-1,3-diene (164 mg, 225 µL, 2 mmol), sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) and $KHSO_4$ (0.545 g, 2 equiv., 4 mmol) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **4** (220 mg, 75%) as a colorless liquid. – ^{1}H NMR (300 MHz, $CDCl_3$): 5.64 (1 H, s), 3.82–3.60 (2 H, m), 3.54 (1 H, q, *J* = 7.2 Hz), 1.82 (3 H, d, *J* = 0.8 Hz), 1.39 (3 H, d, *J* = 7.2 Hz) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 139.4, 116.3, 62.2, 55.2, 17.4, 12.0 ppm. – IR: 2978, 2936, 2256, 1447, 1413, 1383, 1302, 1427, 1231, 1118, 1088, 1058, 909 cm^{-1}.

3,4-Dipropyl-2,5-dihydrothiophene-1,1-dioxide (5)

In HFIP/H_2O: According to GP1, 3,4-dimethyleneoctane (182 mg, 1 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **5** (186 mg, 91%) as a pale yellow liquid.

In CH_3OH/H_2O with $KHSO_4$: According to GP2, 3,4-dimethyleneoctane (182 mg, 1 mmol), sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) and $KHSO_4$ (0.545 g, 2 equiv., 4 mmol) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **5** (130 mg, 64%) as a pale yellow liquid. – ^{1}H NMR (300 MHz, $CDCl_3$): 3.62 (4 H, s), 2.52–1.96 (4 H, m), 1.31 (4 H, dd, *J* = 15.1, 7.5 Hz), 0.80 (2 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 130.1, 58.6, 30.4, 20.7, 13.5 ppm. – IR: 2959, 2931, 2871, 1645, 1464, 1404, 1380, 1308, 1251, 1232, 1169, 1113, 895 cm^{-1}. – HRMS calcd for $C_{10}H_{19}O_2S$: 202.1028, found 202.1027 [$M+H^+$].

3,4-Dibutyl-2,5-dihydrothiophene 1,1-dioxide (6)

In $HFIP/H_2O$: According to GP1, 5,6-dimethylenedecane (322 mg, 2 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **6** (442 mg, 96%) as a colorless liquid.

In CH_3OH/H_2O with $KHSO_4$: According to GP2, 5,6-dimethylenedecane (332 mg, 2 mmol), sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) and $KHSO_4$ (0.545 g, 2 equiv., 4 mmol) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **6** (450 mg, 98%) as a colorless liquid. – ^{1}H NMR (300 MHz, $CDCl_3$): 3.72 (4 H, s), 2.17 (4 H, t, *J* = 7.1 Hz), 1.53–1.06 (8 H, m), 0.89 (6 H, dd, *J* = 9.2, 4.8 Hz) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 130.3, 59.0, 29.9, 28.6, 22.4, 13.9 ppm. – IR: 2955, 2927, 2859, 1466, 1404, 1379, 1308, 1247, 1215, 1168, 1113, 915 cm^{-1}. – HRMS calcd for $C_{12}H_{23}O_2S$: 231.1413, found 231.1419 [$M+H^+$].

3-(4-Methylpent-3-en-1-yl)-2,5-dihydrothiophene-1,1-dioxide (7)[9]

Small scale synthesis in HFIP/H_2O: According to GP1, myrcene (272 mg, 343 μL, 2 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **7** (320 mg, 86%) as a yellow oil.

Gram scale synthesis in HFIP/H_2O: According to GP1, myrcene (2.72 g, 3.43 mL, 20 mmol) was reacted with sodium metabisulfite (19.0 g, 100 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (40 mL) and water (10 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **7** (3.0 g, 99%) as a yellow oil.

Small scale synthesis CH_3OH/H_2O with $KHSO_4$: According to GP2, myrcene (272 mg, 343 μL, 2 mmol), sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) and $KHSO_4$ (0.545 g, 2 equiv., 4 mmol) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **7** (290 mg, 78%) as a yellow oil. – ^{1}H NMR (300 MHz, $CDCl_3$): 5.61 (1 H, d, *J* = 1.5 Hz), 5.15–4.91 (1 H, m), 3.92–3.64 (2 H, m), 3.60 (2 H, m), 2.33–1.95 (4 H, m), 1.61 (3 H, s), 1.53 (3 H, s) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 138.3, 132.9, 122.4, 117.0, 77.6, 77.2, 76.7, 57.7, 56.9, 32.9, 25.5, 25.3, 17.6 ppm. – IR: 2967, 2922, 1646, 1440, 1403, 1377, 2305, 1233, 1180, 1140, 1119, 893 cm^{-1}.

2,2,4-Trimethyl-2,5-dihydrothiophene-1,1-dioxide (8)[11]

Small scale synthesis in HFIP/H_2O: According to GP1, 2,4-dimethylpenta-1,3-diene (192 mg, 259 μL, 2 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced

pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **8** (200 mg, 62%) as a colorless liquid.

Gram scale synthesis in HFIP/H₂O: According to GP1, 4-dimethylpenta-1,3-diene (0.96 g, 1.3 mL, 10 mmol) was reacted with sodium metabisulfite (9.5 g, 50 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (20 mL) and water (5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **8** (1 g, 63%) as a colorless liquid.

In CH₃OH/H₂O with KHSO₄: According to GP2, 2,4-dimethylpenta-1,3-diene (192 mg, 259 μL, 2 mmol), sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) and $KHSO_4$ (0.545 g, 2 equiv., 4 mmol) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **8** (220 mg, 84%) as a colorless liquid. – ^{1}H NMR (300 MHz, $CDCl_3$): 5.54 (1 H, s), 3.60 (2 H, d, *J* = 0.6 Hz), 1.78 (4 H, s), 1.37 (6 H, s) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 131.7, 130.3, 64.1, 57.2, 22.1, 18.8 ppm. – IR: 2972, 2931, 1462, 1440, 1385, 1293, 1260, 1216, 1196, 1180, 1103, 1016, 892 cm^{-1}.

2-Cyclohexyl-4-methyl-2,5-dihydrothiophene 1,1-dioxide (9)

In CH₃OH/H₂O with KHSO₄: According to GP1, (*E*)-(3-methylbuta-1,3-dien-1-yl)cyclohexane (150 mg, 1 mmol) and $KHSO_4$ (0.273 g, 2 equiv., 2 mmol) were reacted with sodium metabisulfite (0.95 g, 5 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (2 mL) and water (0.5 mL) at 100 °C for 24 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **9** (175 mg, 81%) as a colorless solid.

Gram scale synthesis in CH₃OH/H₂O with KHSO₄: According to GP1, (*E*)-(3-methylbuta-1,3-dien-1-yl)cyclohexane (3.0 g, 20 mmol) was reacted with sodium

metabisulfite (19 g, 100 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (40 mL) and water (10 mL) at 100 °C for 24 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **9** (3.2 g, 74%) as a colorless solid. – m.p.: 28–31 °C. – ^{1}H NMR (500 MHz, $CDCl_3$): 5.69 (1 H, s), 3.76–3.43 (3H, m), 2.08–1.88 (2 H, m), 1.86 (3 H, s), 1.74 (3 H, ddd, *J* = 36.8, 32.9, 12.7 Hz), 1.38–1.04 (5 H, m) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 133.1, 122.0, 71.9, 59.4, 37.7, 31.6, 29.5, 26.0, 25.9, 19.1 ppm. – IR: 2924, 2848, 1448, 1406, 1323, 1293, 1274, 1235, 1210, 1101, 975, 898, 847 cm^{-1}. – HRMS calcd for $C_{11}H_{19}O_2S$: 215.1100, found 215.1102 [M+H$^+$].

(*E*)-5-Vinylundec-5-ene

To a 250 mL flask charged with methyltriphenylphosphonium bromide (8.57 g, 24 mmol, 1.2 equiv.) in 60 mL degassed diethyl ether was added potassium *tert*-butoxide (2.92 g, 26 mmol, 1.3 equiv.). The reaction mixture was stirred at room temperature for 1 h before (*E*)-2-butyloct-2-enal (3.65 g, 20 mmol, 1 equiv.) in 20 mL of diethyl ether was added. The reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was then filtered, and the filtrate was concentrated to remove diethyl ether. The crude product was filtered through a layer of silica gel using hexane as an eluent. The solution was concentrated under reduced pressure to give (*E*)-5-vinylundec-5-ene (2.81 g, 78%) as a colorless liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): 6.26 (1 H, dd, *J* = 17.5, 10.8 Hz), 5.45 (1 H, t, *J* = 7.4 Hz), 5.09 (1 H, d, *J* = 17.4 Hz), 4.91 (1 H, d, *J* = 10.8 Hz), 2.22 (2 H, dd, *J* = 8.9, 6.1 Hz), 2.11 (2 H, q, *J* = 7.4 Hz), 1.42–1.25 (10 H, m), 0.91 (6 H, dt, *J* = 13.8, 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 140.7, 138.7, 133.6, 110.2, 31.8, 31.3, 29.5, 28.2, 26.1, 23.2, 22.7, 14.2, 14.2.ppm. – IR: 3088, 2956, 2924, 2857, 1636, 1605, 1466, 988, 880 cm^{-1}.

3-Butyl-2-pentyl-2,5-dihydrothiophene 1,1-dioxide (10)

Small scale synthesis in HFIP/H_2O: According to GP1, (*E*)-5-vinylundec-5-ene (180 mg, 1 mmol) was reacted with sodium metabisulfite (0.95 g, 5 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture

was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **10** (244 mg, 99%) as a colorless liquid.

In CH_3OH/H_2O with $KHSO_4$: According to GP2, (*E*)-5-vinylundec-5-ene (180 mg, 1 mmol), sodium metabisulfite (0.95 g, 5 mmol, 5 equiv.) and $KHSO_4$ (0.273 g, 2 equiv., 2 mmol) were reacted in a 4 : 1 v/v mixture of methanol (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **10** (202 mg, 82%) as a colorless liquid.

Gram scale synthesis in CH_3OH/H_2O with $KHSO_4$: According to GP1, 5-vinylundec-5-ene (5.04 g, 28 mmol) was reacted with sodium metabisulfite (26.6 g, 140 mmol, 5 equiv.) and $KHSO_4$ (7.6 g, 2 equiv., 56 mmol) in a 4 : 1 v/v mixture of methanol (56 mL) and water (14 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **10** (4.7 g, 69%) as a colorless liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): 5.66 (1 H, s), 3.69 (2 H, q, *J* = 16.3 Hz), 3.53 (1 H, d, *J* = 6.5 Hz), 2.13 (2 H, d, *J* = 6.5 Hz), 1.81 (1 H, dddd, *J* = 18.8, 14.4, 9.6, 4.6 Hz), 1.66–1.54 (1 H, m), 1.56–1.17 (9H, m), 0.93 (6 H, dd, *J* = 14.2, 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 143.0, 115.7, 66.4, 55.7, 31.8, 31.4, 28.8, 27.8, 26.3, 22.4, 22.3, 14.1, 13.9 ppm. – IR: 2956, 2926, 2858, 1636, 1466, 1410, 1379, 1303, 1243, 1119, 1003, 908, 877, 843 cm^{-1}. – HRMS calcd for $C_{13}H_{25}O_2S$: 245.1570, found 245.1574 [$M+H^+$].

2,4,5,6,7,7a-Hexahydrobenzo[b]thiophene-1,1-dioxide (11)[12]

In HFIP/H_2O: According to GP1, 1-vinylcyclohexene (108 mg, 1 mmol) was reacted with sodium metabisulfite (0.95 g, 5 mmol, 5 equiv). in a 4 : 1 v/v mixture of HFIP (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the

mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **11** (150 mg, 87%) as a colorless liquid.

In CH_3OH/H_2O with $KHSO_4$: According to GP2, 1-vinylcyclohexene[5] (108 mg, 1 mmol), sodium metabisulfite (0.95 g, 5 equiv) and $KHSO_4$ (0.275 g, 2 equiv) were reacted in a 4 : 1 v/v mixture of methanol (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **11** (172 mg, 99%) as a colorless liquid.

From allylic alcohol: According to GP4, to a 48 mL pressure vessel charged with 1-vinylcyclohexanol (126 mg, 1 mmol) was added a 3 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (570 mg, 3 mmol, 3 equiv.) and $KHSO_4$ (544 mg, 4 mmol, 4 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. After that, the reaction mixture was allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography (mixture of ethyl acetate and hexane) to give sulfolene **11** (109 mg, 63%) as a colorless liquid. – ^{1}H NMR (300 MHz, $CDCl_3$): 5.52 (1 H, s), 3.59 (3 H, dddd, *J* = 21.0, 16.1, 8.0, 3.3 Hz), 2.41 (1 H, dd, *J* = 14.1, 1.5 Hz), 2.07 (2 H, td, *J* = 15.5, 2.2 Hz), 1.82 (2 H, ddd, *J* = 12.9, 9.1, 1.2 Hz), 1.66–1.05 (3 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 140.2, 112.9, 63.8, 56.0, 31.2, 25.6, 25.3, 23.6 ppm. – IR: 2935, 2859, 1448, 1412, 1299, 1245, 1202, 1161, 1117, 1045, 1000, 942, 918, 837 cm^{-1}.

2,3,4,5-Tetraethyl-2,5-dihydrothiophene-1,1-dioxide (12)

Small scale synthesis in HFIP/H_2O: According to GP1, 4,5-diethylocta-3*E*,5*E*-diene (232 mg, 1.4 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 7 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic

phase was concentrated under reduced pressure to give sulfolene **12** (322 mg, 99%) as a colorless liquid.

Gram scale synthesis in HFIP/H_2O: According to GP1, 4,5-diethylocta-3*E*,5*E*-diene (2.49 g, 15 mmol) was reacted with sodium metabisulfite (14.3 g, 75 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (30 mL) and water (7.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **12** (3.45g, 99%) as a colorless liquid.

In CH_3OH/H_2O with $KHSO_4$: According to GP2, 4,5-diethylocta-3*E*,5*E*-diene (232 mg, 1.4 mmol), sodium metabisulfite (1.9 g, 10 mmol, 7 equiv.) and $KHSO_4$ (0.545 g, 4 mmol, 2.8 equiv.) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **12** (306 mg, 95%) as a colorless liquid. – ^{1}H NMR (300 MHz, $CDCl_3$): 3.48 (2 H, dd, *J* = 8.6, 4.0 Hz), 2.30 (2 H, dq, *J* = 15.0, 7.6 Hz), 1.94 (2 H, dq, *J* = 14.9, 7.6 Hz), 1.84–1.64 (4 H, m), 1.07 (6 H, t, *J* = 7.4 Hz), 0.96 (6 H, t, *J* = 7.6 Hz) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 134.3, 68.0, 22.1, 20.5, 12.8, 12.0 ppm. – IR: 2968, 2935, 2877, 1459, 1381, 1308, 1290, 1221, 1164, 1110, 1056, 952, 905, 826 cm^{-1}. – HRMS calcd for $C_{12}H_{21}O_2S$: 231.1419, found 231.1422 [$M+H^+$].

2,3,4,5-Tetrapropyl-2,5-dihydrothiophene-1,1-dioxide (13)

Small scale synthesis in HFIP/H_2O: According to GP1, 5,6-dipropyldeca-4*E*,6*E*-diene (417 mg, 2 mmol) was reacted with sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **13** (560 mg, 97%) as a colorless liquid.

Gram scale synthesis in HFIP/H_2O: According to GP1, 5,6-dipropyldeca-4,6-diene (1.2 g, 5.75 mmol) was reacted with sodium metabisulfite (5.46 g, 28.75 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (11.5 mL) and water (2.9 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **13** (1.64 g, 99%) as a colorless liquid.

In CH_3OH/H_2O with $KHSO_4$: According to GP2, 5,6-dipropyldeca-4*E*,6*E*-diene (417 mg, 2 mmol), sodium metabisulfite (1.9 g, 10 mmol, 5 equiv.) and $KHSO_4$ (0.545 g, 2 equiv., 4 mmol) were reacted in a 4 : 1 v/v mixture of methanol (4 mL) and water (1 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure to give sulfolene **13** (454 mg, 79%) as a colorless liquid. – ^{1}H NMR (300 MHz, $CDCl_3$): 3.54 (2 H, d, *J* = 9.0 Hz), 2.42–2.11 (2 H, m), 2.12–1.88 (2 H, m), 1.88–1.56 (6 H, m), 1.57–1.40 (4 H, m), 1.40–1.20 (2 H, m), 0.95 (12 H, m) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 133.7, 66.4, 31.2, 29.5, 21.3, 20.8, 14.1 ppm. – IR: 2959, 2933, 2872, 1464, 1380, 1294, 1210, 1163, 1110, 892 cm^{-1}. – HRMS calcd for $C_{16}H_{21}O_2S$: 287.2045, found 287.2049 [$M+H^+$].

3-(2-Hydroxy-2-phenylethyl)-2,5-dihydrothiophene-1,1-dioxide (14)

In HFIP/H_2O: According to GP1, 3-methylene-1-phenylpent-4-en-1-ol (161 mg, 1 mmol) was reacted with sodium metabisulfite (0.95 g, 5 mmol, 5 equiv.) in a 4 : 1 v/v mixture of HFIP (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography (1.5 : 1 v/v mixture of ethyl acetate and hexane) to give sulfolene **14** (164 mg, 73%) as a colorless solid.

In CH_3OH/H_2O with $KHSO_4$: According to GP2, 3-methylene-1-phenylpent-4-en-1-ol (161 mg, 1 mmol), sodium metabisulfite (0.95 g, 5 equiv) and $KHSO_4$ (0.275 g, 2 equiv)

were reacted in a 4 : 1 v/v mixture of methanol (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography (1.5 : 1 v/v mixture of ethyl acetate and hexane) to give sulfolene **14** (213 mg, 95%) as a colorless solid. – m.p. 101–104 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): 7.37–7.30 (5 H, m), 5.73 (1 H, s), 4.85–4.81 (1 H, m), 3.73 (4 H, dt, *J* = 8.2, 4.2 Hz), 2.59 (2 H, m), 2.27 (1 H, s) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): 143.4, 135.6, 128.9, 128.3, 125.7, 120.2, 77.6, 77.2, 76.7, 72.9, 58.3, 56.9, 42.8 ppm. – IR: 3486, 2932, 2900, 2837, 1610, 1585, 1514, 1455, 1397, 1289, 1238, 1144, 1100, 1028 cm^{-1}. – HRMS calcd for $C_{12}H_{14}O_2SNa$: 261.0556, found 261.0549 [M+Na$^+$].

3-(2-Hydroxy-2-phenylethyl)-4-methyl-2,5-dihydrothiophene-1,1-dioxide (15)

In HFIP/H₂O: According to GP1, 4-methyl-3-methylene-1-phenylpent-4-en-1-ol (174 mg, 1 mmol) was reacted with sodium metabisulfite (0.95 g, 5 mmol, 5 equiv). in a 4 : 1 v/v mixture of HFIP (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography (1.5 : 1 v/v mixture of ethyl acetate and hexane) to give sulfolene **15** (224 mg, 90%) as a colorless solid.

In CH₃OH/H₂O with KHSO₄: According to GP2, 4-methyl-3-methylene-1-phenylpent-4-en-1-ol (174 mg, 1 mmol), sodium metabisulfite (0.95 g, 5 equiv) and $KHSO_4$ (0.275 g, 2 equiv) were reacted in a 4 : 1 v/v mixture of methanol (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography (1.5 : 1 v/v mixture of ethyl acetate and hexane) to give sulfolene **15** (143 mg, 57%) as a colorless solid. – m.p. 70–73 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): 7.40–7.26 (5 H, m), 4.74 (1 H, dd, *J* = 7.4, 5.4 Hz), 3.71 (2 H, s), 3.60 (2 H, s), 2.89 (1 H, br s), 2.74–2.38 (2 H, m), 1.56 (3 H, s) ppm. – ^{13}C NMR

(75 MHz, $CDCl_3$): 143.6, 128.4, 128.3, 127.7, 126.6, 125.5, 72.5, 60.2, 59.6, 38.4, 14.4 ppm. – IR: 3474, 2919, 2255, 1493, 1454, 1402, 1304, 1251, 1179, 1106, 1070, 909 cm^{-1}. – HRMS calcd for $C_{13}H_{16}O_3SNa$: 275.0712, found 275.0705 [$M+Na^+$].

(*R*)-3-(3,4-Dihydroxy-4-methylpentyl)-2,5-dihydrothiophene 1,1-dioxide (16)

In HFIP/H_2O: According to GP1, (*R*)-2-methyl-6-methyleneoct-7-ene-2,3-diol (170 mg, 1 mmol) was reacted with sodium metabisulfite (0.95 g, 5 mmol, 5 equiv). in a 4 : 1 v/v mixture of HFIP (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography (4 : 1 v/v mixture of ethyl acetate and hexane) to give sulfolene **16** (171 mg, 73%) as a colorless liquid.

In CH_3OH/H_2O with $KHSO_4$: According to GP2, 2-methyl-6-methyleneoct-7-ene-2,3-diol (170 mg, 1 mmol) sodium metabisulfite (0.95 g, 5 equiv) and $KHSO_4$ (0.275 g, 2 equiv) were reacted in a 4 : 1 v/v mixture of methanol (2 mL) and water (0.5 mL) at 100 °C for 14 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Ethyl acetate was added, and the mixture was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography (4 : 1 v/v mixture of ethyl acetate and hexane) to give sulfolene **16** (181 mg, 77%) as a colorless liquid. – $[\alpha]_D^{23}$ = +0.16 (*c* 1.0, $CHCl_3$). – ^{1}H NMR (500 MHz, CD_3OD): 5.78 (1 H, s), 3.81 (2 H, s), 3.77 (2 H, s), 3.26 (1 H, d, *J* = 10.3 Hz), 2.43–2.44 (1 H, m), 2.36–2.18 (1 H, m), 1.79 (1 H, dt, *J* = 14.9, 7.8 Hz), 1.55–1.36 (1 H, m), 1.17 (3 H, s), 1.15 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CD_3OD): 139.8, 118.3, 78.3, 73.5, 58.4, 57.8, 31.0, 29.3, 25.7, 24.9 ppm. – IR: 3373, 2972, 2928, 1646, 1403, 1384, 1295, 1236, 1142, 1121, 1078, 997, 937 cm^{-1}. – HRMS calcd for $C_{10}H_{18}O_4SNa$: 257.0818, found 257.0810 [$M+Na^+$].

3-Ethyl-2-methyl-2,5-dihydrothiophene 1,1-dioxide (17)[13]

Small scale synthesis from allylic alcohol: According to GP4, to a 48 mL pressure vessel charged with 3-ethylpent-1-en-3-ol (**25**) (114 mg, 0.8 mmol, 80 % assay by ^{1}H

NMR with 1,4-dimethoxybenzene as an internal standard, prepared according to GP3) was added a 2 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (570 mg, 3 mmol, 3.75 equiv.) and $KHSO_4$ (544 mg, 4 mmol, 5 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. The reaction mixture was then allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and purified by flash chromatography (mixture of ethyl acetate and hexane) to give sulfolene **17** (106 mg, 83%) as a colorless liquid.

Gram scale synthesis from allylic alcohol: According to GP4, to a 300 mL pressure vessel charged with 3-ethylpent-1-en-3-ol (**25**) (2.3 g, 14.2 mmol, 71 % assay by ^{1}H NMR with 1,4-dimethylxybenzene as an internal standard, prepared according to GP3) was added a 2 : 1 v/v mixture of degassed HFIP and water (100 mL). Sodium metabisulfite (10.1 g, 75 mmol, 3.75 equiv.) and $KHSO_4$ (9.7 g, 71 mmol, 5 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. The reaction mixture was then allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and purified by flash chromatography (mixture of ethyl acetate and hexane) to give sulfolene **17** (1.5 g, 67%) as a colorless liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): 5.64 (1 H, d, *J* = 1.3 Hz), 3.72 (2 H, q, *J* = 16.2 Hz), 3.60 (1 H, q, *J* = 7.2 Hz), 2.16 (2 H, m), 1.41 (3 H, d, *J* = 7.3 Hz), 1.11 (3 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 145.3, 114.4, 61.6, 55.1, 24.3, 12.6, 11.0 ppm. – IR: 2985, 1301, 1243, 1118, 1095, 1050, 839, 810 cm^{-1}.

2-Ethyl-3-propyl-2,5-dihydrothiophene 1,1-dioxide (18)

From allylic alcohol: According to GP4, to a 48 mL pressure vessel charged with 4-vinylheptan-4-ol (**26**) (142 mg, 0.72 mmol, 72 % assay by ^{1}H NMR with 1,4-dimethoxybenzene as an internal standard, prepared according to GP3) was added a 2 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (570 mg, 3 mmol, 3.75 equiv.) and $KHSO_4$ (544 mg, 4 mmol, 5 equiv.) were added. The vessel was

sealed, and the reaction mixture was stirred at room temperature for 15 minutes. After that, the reaction mixture was allowed to stir at 100°C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and purified by flash chromatography (mixture of ethyl acetate and hexane) to give sulfolene **18** (100 mg, 74%) as a colorless liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): 5.66 (1 H, s), 3.66 (2 H, dd, *J* = 39.4, 16.3 Hz), 3.46 (1 H, d, *J* = 7.0 Hz), 2.07 (2 H, t, *J* = 7.1 Hz), 1.97–1.77 (2 H, m), 1.61–1.38 (2 H, m), 1.08 (3 H, t, *J* = 7.4 Hz), 0.92 (4 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 142.5, 116.1, 67.6, 55.9, 33.7, 21.1, 19.9, 13.7, 10.9 ppm. – IR: 2961, 2932, 2874, 1738, 1458, 1412, 1381, 1305, 1216, 1119 cm^{-1}. – HRMS calcd for $C_9H_{17}O_2S$: 189.0944, found 189.0947 [$M+H^+$].

3-Butyl-2-propyl-2,5-dihydrothiophene 1,1-dioxide (19)

From allylic alcohol: According to GP4, to a 48 mL pressure vessel charged with 5-vinylnonan-5-ol (**27**) (170 mg, 0.77 mmol, 77 % assay by ^{1}H NMR with 1,4-dimethoxybenzene as an internal standard, prepared according to GP3) was added a 2 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (570 mg, 3 mmol, 3.9 equiv.) and $KHSO_4$ (544 mg, 4 mmol, 5.2 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. The reaction mixture was then allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and purified by flash chromatography (mixture of ethyl acetate and hexane) to give sulfolene **19** (125 mg, 75%) as a colorless liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): 5.63 (1 H, dt, *J* = 3.2, 1.7 Hz), 3.65 (2 H, q, *J* = 16.2 Hz), 3.50 (1 H, d, *J* = 8.7 Hz), 2.17–2.03 (2 H, m), 1.87–1.67 (2 H, m), 1.68–1.53 (1 H, m), 1.54–1.22 (5 H, m), 0.95 (3 H, td, *J* = 7.3, 1.8 Hz), 0.89 (3 H, td, *J* = 7.3, 1.9 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 143.0, 115.7, 66.2, 55.7, 31.3, 29.8, 28.7, 22.3, 19.9, 14.0, 13.9 ppm. – IR: 2935, 2859, 1448, 1324, 1300, 1246, 1203, 1162, 1118, 1000 cm^{-1}. – HRMS calcd for $C_{11}H_{21}O_2S$: 217.1257, found 217.1261 [$M+H^+$].

3-Ethyl-2,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide (20)

From allylic alcohol: According to GP4, to a 48 mL pressure vessel charged with 3-ethyl-2-methylpent-1-en-3-ol (**28**) (128 mg, 0.55 mmol, 55 % assay by ^{1}H NMR with 1,4-dimethoxybenzene as an internal standard, prepared according to GP3) was added a 2 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (570 mg, 3 mmol, 5.45 equiv.) and $KHSO_4$ (544 mg, 4 mmol, 7.3 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. The reaction mixture was then allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and purified by flash chromatography (mixture of ethyl acetate and hexane) to give sulfolene **20** (83 mg, 87%) as a colorless liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): 3.72–3.67 (1 H, m), 3.65 (2 H, s), 2.34 (1 H, dq, *J* = 15.0, 7.6 Hz), 2.01 (1 H, dq, *J* = 15.1, 7.6 Hz), 1.77 (3 H, s), 1.38 (3 H, d, *J* = 7.2 Hz), 1.01 (3 H, t, *J* = 7.6 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 137, 123.8, 62.1, 59, 20.4, 14.7, 13.1, 12.4 ppm. – IR: 2983, 1701, 1447, 1407, 1302, 1242, 1168, 1105, 1015, 900 cm^{-1}. – HRMS calcd for $C_8H_{15}O_2S$: 175.0787, found 175.0792 [$M+H^+$].

2-Ethyl-4-methyl-3-propyl-2,5-dihydrothiophene 1,1-dioxide (21)

From allylic alcohol: According to GP4, to a 48 mL pressure vessel charged with 4-(prop-1-en-2-yl)heptan-4-ol (**29**) (156 mg, 0.81 mmol, 81 % assay by ^{1}H NMR with 1,4-dimethoxybenzene as an internal standard, prepared according to GP3) was added a 2 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (570 mg, 3 mmol, 3.7 equiv.) and $KHSO_4$ (544 mg, 4 mmol, 5 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. After that, the reaction mixture was allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and purified by flash chromatography (mixture of ethyl acetate and hexane) to give sulfolene **21** (118 mg, 72%) as a colorless liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): 3.63 (2 H, s), 3.54 (1 H, d, *J* = 8.1 Hz), 2.33–2.22 (1 H, m), 2.00–1.92 (1 H, m), 1.92–1.79 (2 H,

m), 1.77 (3 H, dd, *J* = 2.2, 1.1 Hz), 1.49 (1 H, ddtd, *J* = 16.4, 14.6, 7.3, 5.3 Hz), 1.41–1.29 (1 H, m), 1.08 (3 H, t, *J* = 7.4 Hz), 0.91 (3 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 134.4, 125.3, 68.5, 59.8, 29.3, 21.6, 20.9, 15.0, 13.9, 11.0 ppm. – IR: 2987, 1700, 1406, 1304, 1225, 1167, 1110, 1048 cm^{-1}. – HRMS calcd for $C_{10}H_{19}O_2S$: 203.1100, found 203.1105 [$M+H^+$].

3-Methyl-2,4,5,6,7,7a-hexahydrobenzo[*b*]thiophene 1,1-dioxide (22)

From allylic alcohol: According to GP4, to a 48 mL pressure vessel charged with 1-(prop-1-en-2-yl)cyclohexanol (**30**) (140 mg, 0.6 mmol, 60 % assay by ^{1}H NMR with 1,4-dimethoxybenzene as an internal standard, prepared according to GP3) was added a 2 : 1 v/v mixture of degassed HFIP and water (5 mL). Sodium metabisulfite (570 mg, 3 mmol, 5 equiv.) and $KHSO_4$ (544 mg, 4 mmol, 6.7 equiv.) were added. The vessel was sealed, and the reaction mixture was stirred at room temperature for 15 minutes. The reaction mixture was then allowed to stir at 100 °C for 36 h. The reaction mixture was cooled to room temperature, ethyl acetate was added, and the solution was dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and purified by flash chromatography (mixture of ethyl acetate and hexane) to give sulfolene **22** (69 mg, 62%) as a colorless liquid. – ^{1}H NMR (500 MHz, $CDCl_3$): 3.74 (1 H, dd, *J* = 15.8, 3.9 Hz), 3.57 (2 H, d, *J* = 15.1 Hz), 2.72 (1 H, dd, *J* = 13.1, 4.2 Hz), 2.23–2.14 (1 H, m), 1.95 (1 H, dt, *J* = 14.4, 3.3 Hz), 1.90–1.79 (2 H, m), 1.74 (3 H, s), 1.61 (1 H, qd, *J* = 12.8, 3.8 Hz), 1.40 (1 H, dtd, *J* = 13.4, 10.8, 3.0 Hz), 1.21 (1 H, dtd, *J* = 13.8, 10.7, 3.8 Hz) ppm. – ^{13}C NMR (126 MHz, $CDCl_3$): 132.1, 121.4, 65.5, 50.0, 26.8, 26.0, 25.2, 23.9, 14.3 ppm. – IR: 2934, 2857, 1698, 1447, 1407, 1336, 1297, 1264, 1245, 1183, 1109 cm^{-1}. – HRMS calcd for $C_9H_{15}O_2S$: 187.0787, found 187.0792 [$M+H^+$].

X-Ray Crystallographic Data

3-(2-Hydroxy-2-phenylethyl)-4-methyl-2,5-dihydrothiophene-1,1-dioxide (15)

CCDC 1833351

Bond precision: C–C = 0.0033 A Wavelength = 0.71073

Cell: a=13.4091(3) b=7.5272(1) c=13.3823(3)

$\alpha = 90$ $\beta = 114.262(3)$ $\gamma = 90$

Temperature: 98 K

	Calculated	Reported
Volume	1231.42(5)	1231.41(5)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{13}H_{16}O_3S$	$C_{13}H_{16}O_3S$
Sum formula	$C_{13}H_{16}O_3S$	$C_{13}H_{16}O_3S$
M_r	252.32	252.32
D_x, g·cm^{-3}	1.361	1.361
Z	4	4
Mu (mm^{-1})	0.256	0.256
F000	536.0	536.0
F000'	536.74	
h,k,l_{max}	16,9,16	16,9,16
N_{ref}	2552	2549

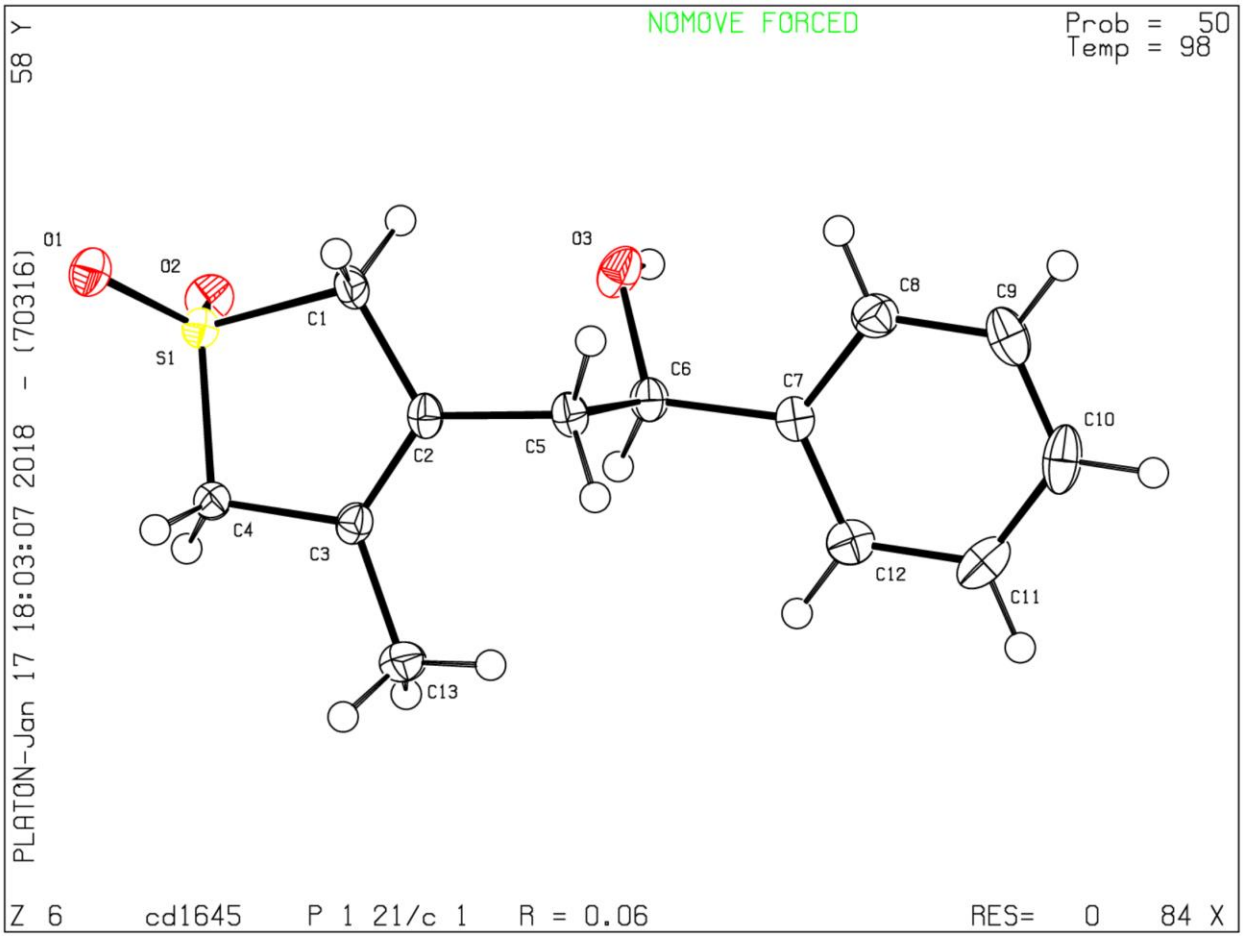
T_{min}, T_{max}	0.950,0.967	0.914,1.000
T_{min}'	0.950	

Correction method= # Reported T Limits: T_{min} = 0.914
T_{max} = 1.000 AbsCorr = MULTI-SCAN

Data completeness = 0.999 Theta(max)= 26.498

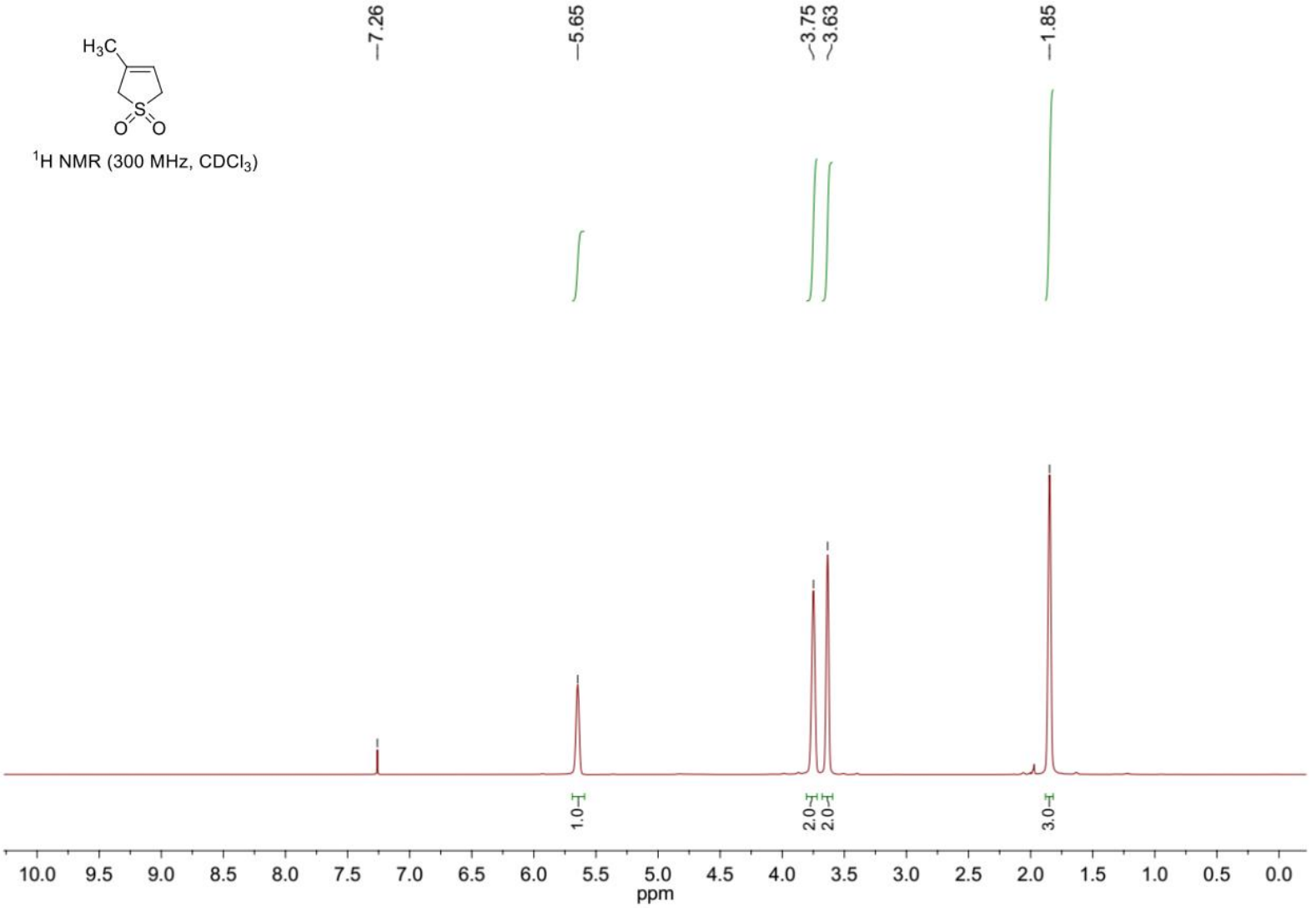
R(reflections)= 0.0601(2397) wR2(reflections)= 0.1292(2549)

S = 1.054 N_{par} = 156

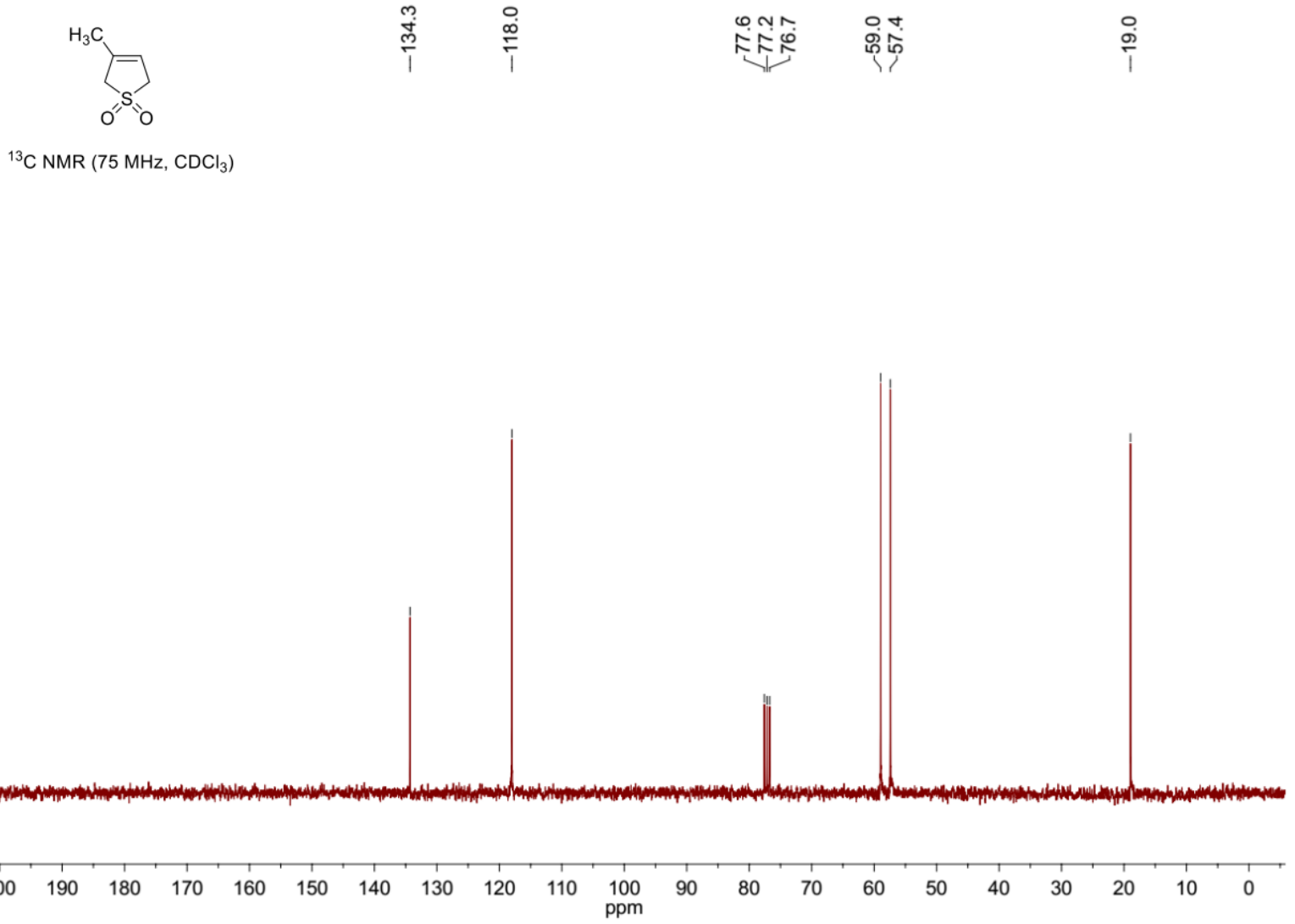


^{1}H and ^{13}C NMR Spectra

3-Methyl-2,5-dihydrothiophene-1,1-dioxide (2)

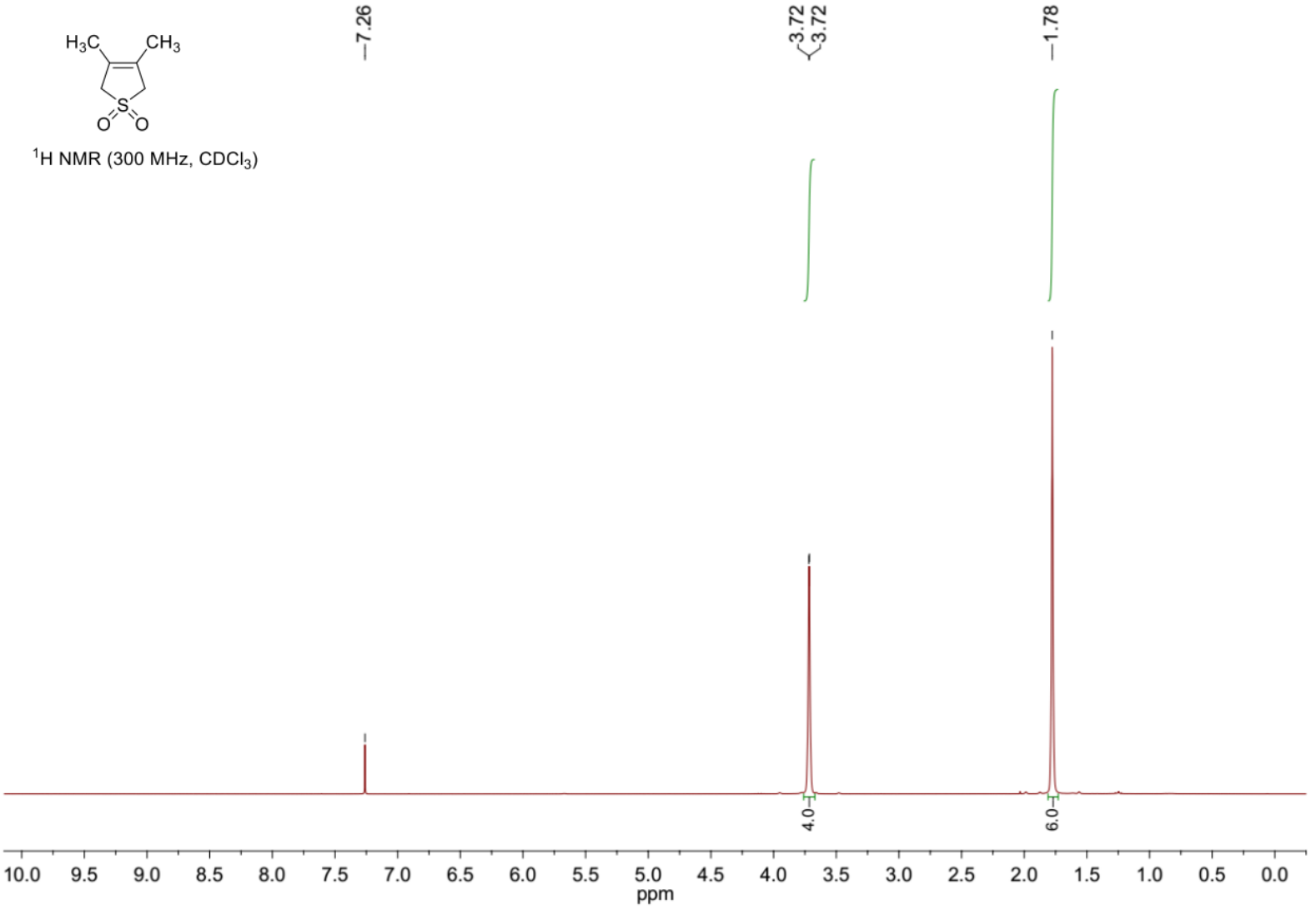


3-Methyl-2,5-dihydrothiophene-1,1-dioxide (2)

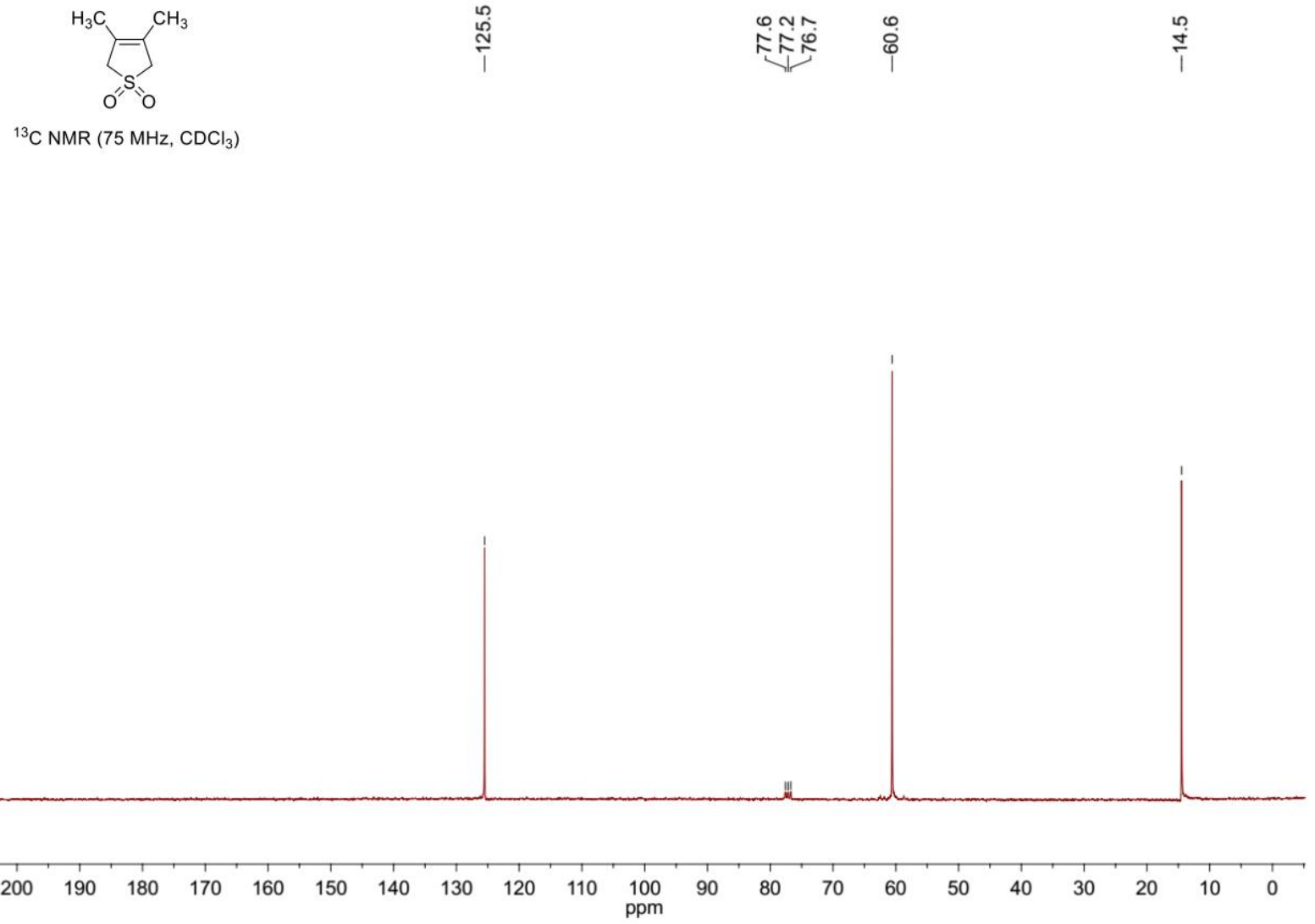


^{13}C NMR (75 MHz, $CDCl_3$)

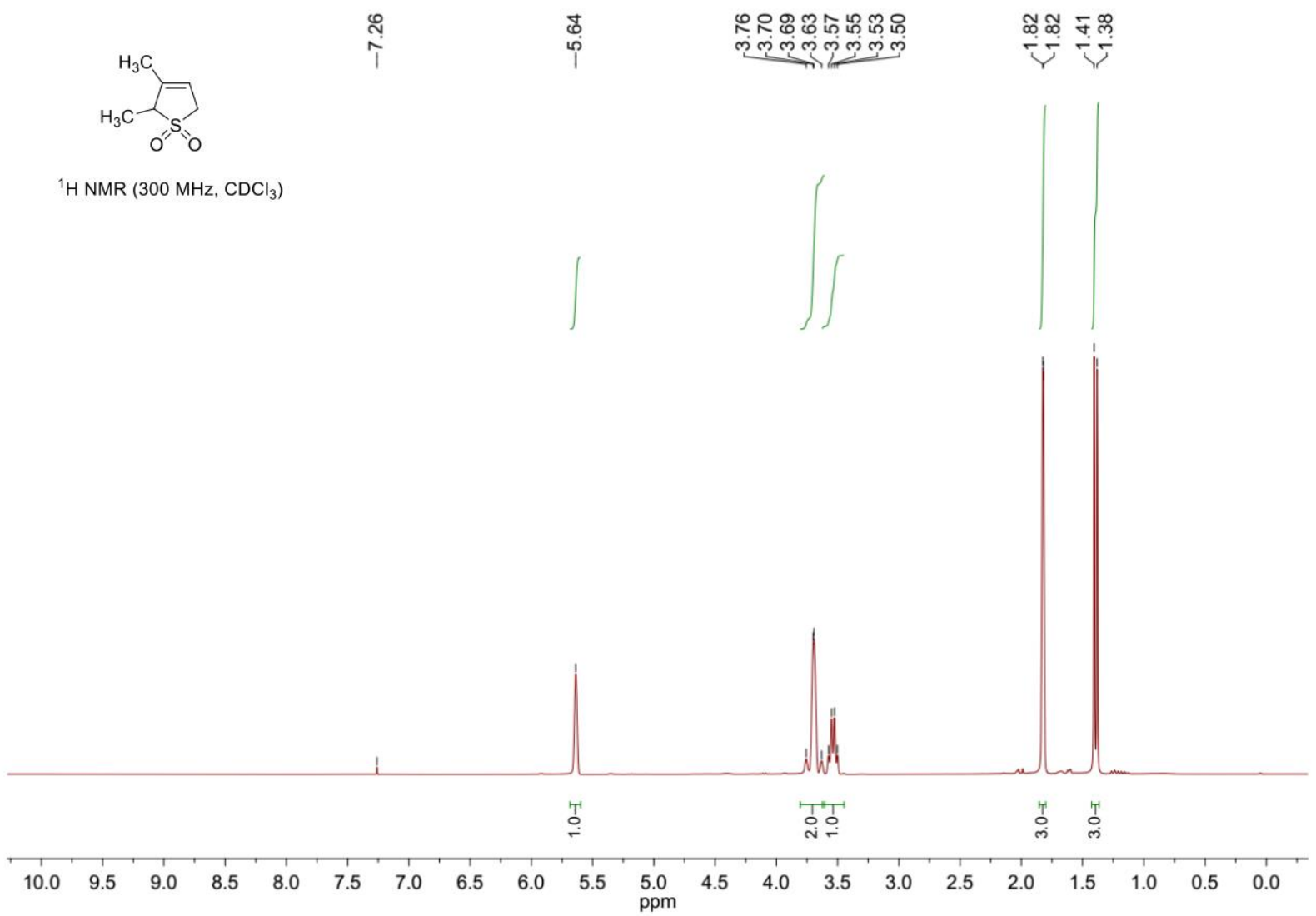
3,4-Dimethyl-2,5-dihydrothiophene-1,1-dioxide (3)



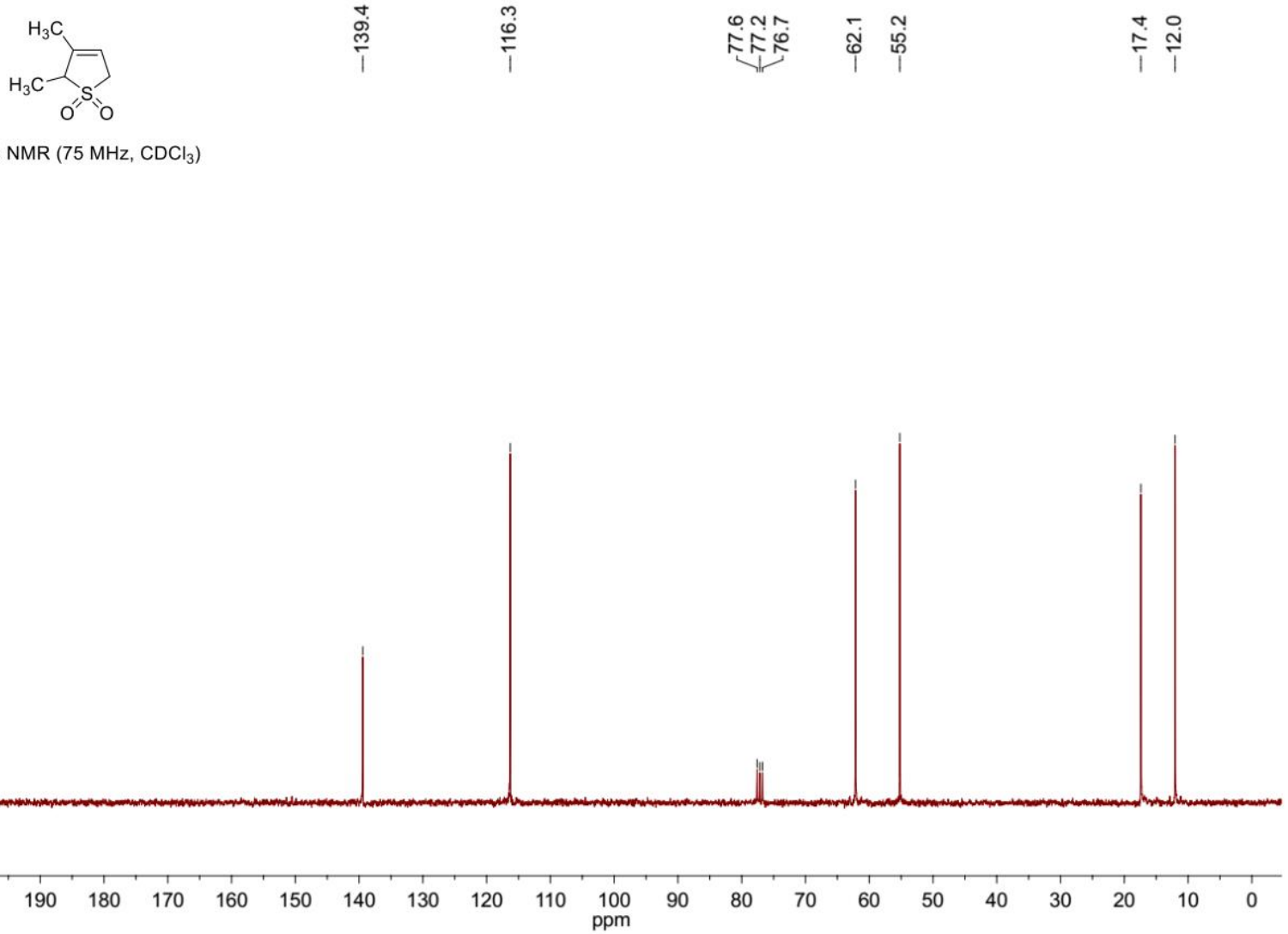
3,4-Dimethyl-2,5-dihydrothiophene-1,1-dioxide (3)



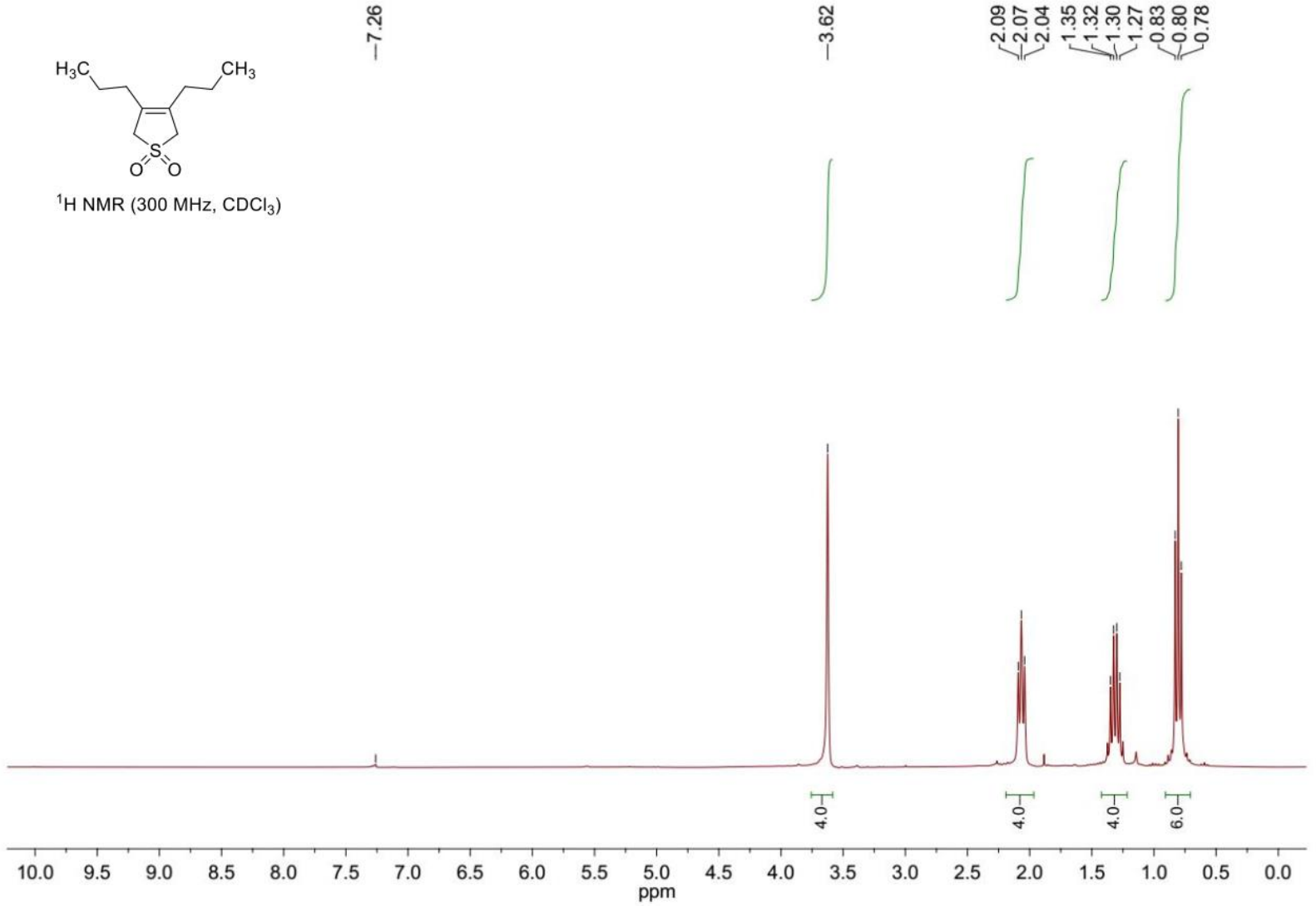
2,3-Dimethyl-2,5-dihydrothiophene-1,1-dioxide (4)



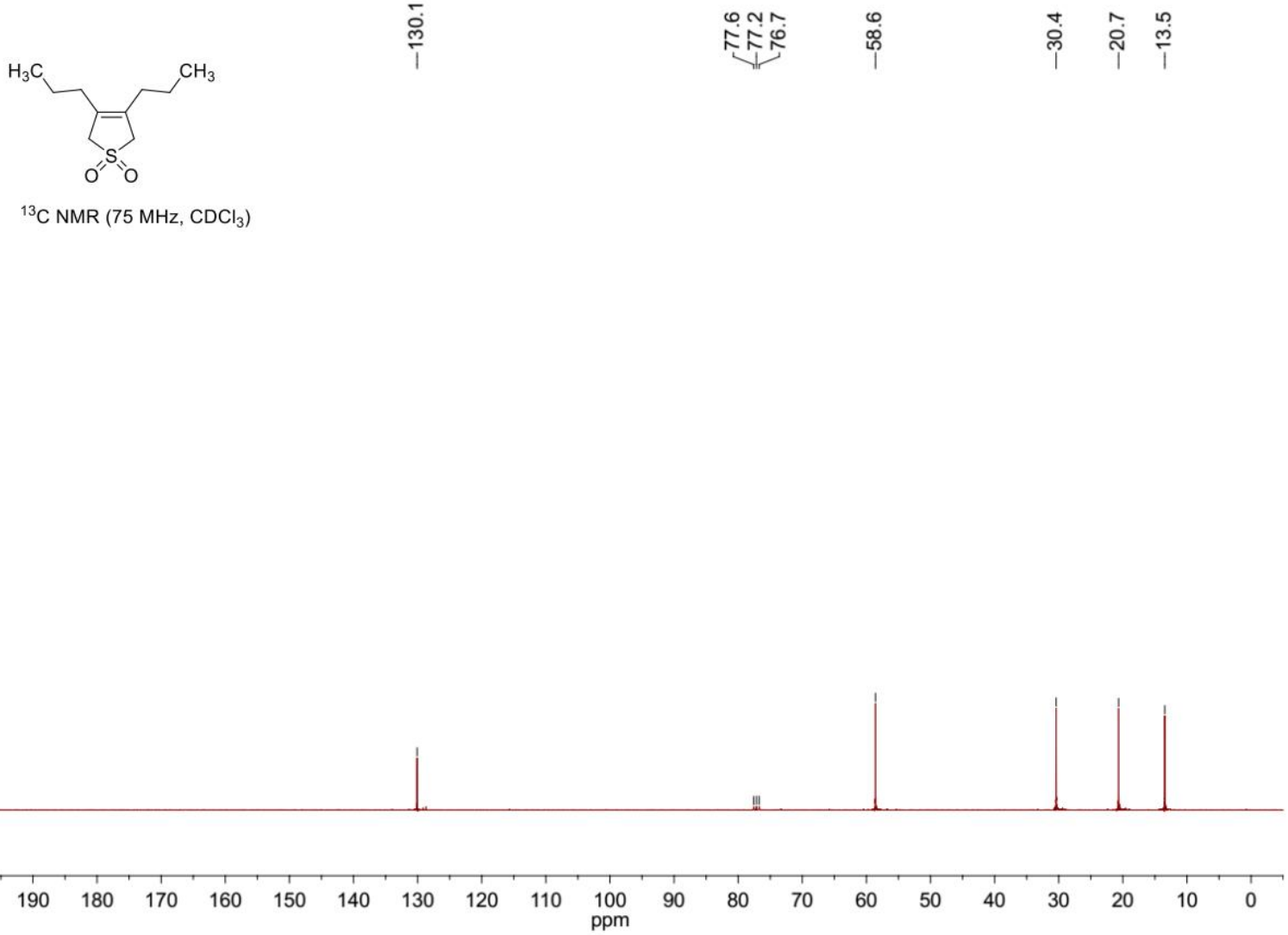
2,3-Dimethyl-2,5-dihydrothiophene-1,1-dioxide (4)



3,4-Dipropyl-2,5-dihy drothiophene-1,1-dioxide (5)

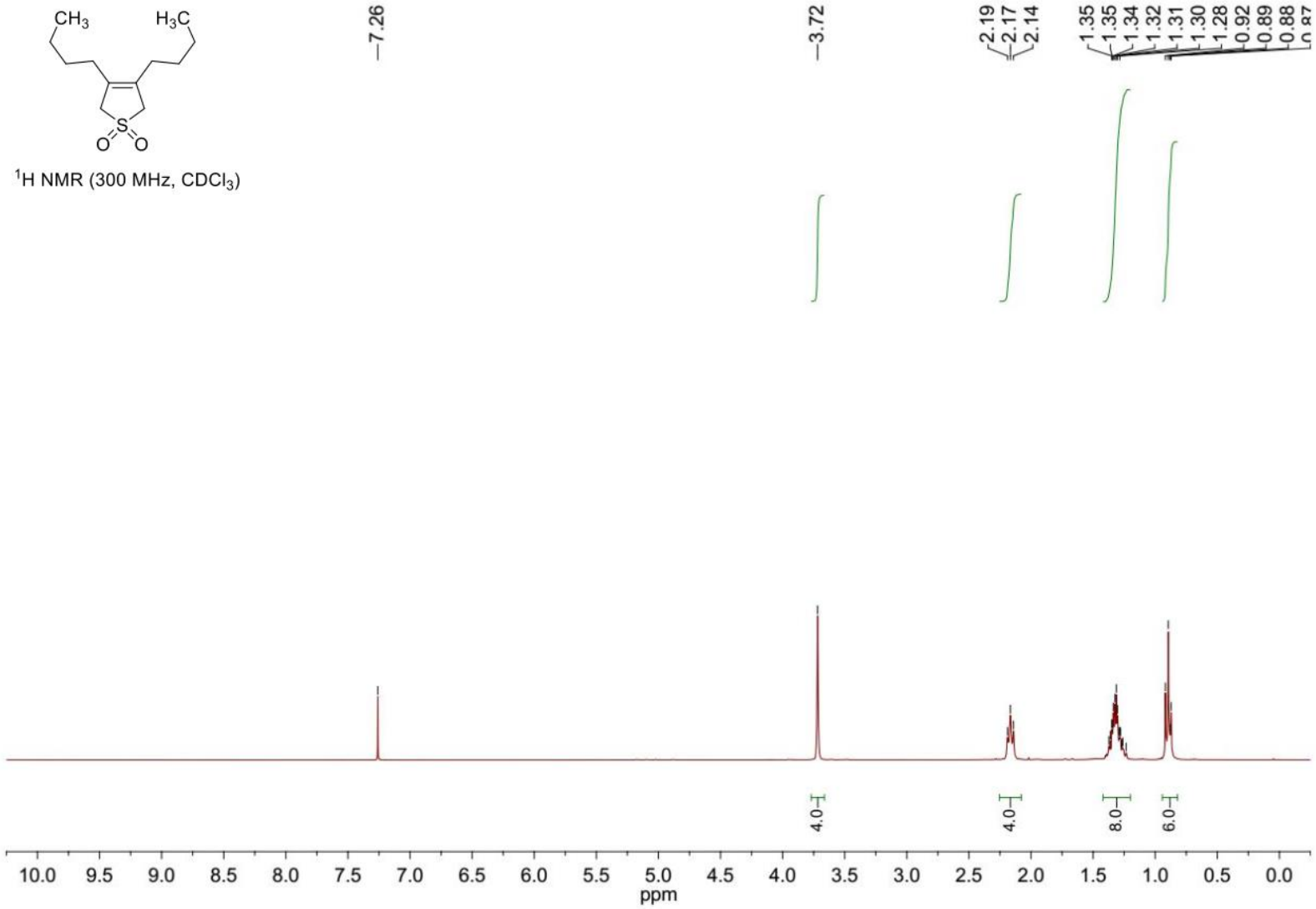


3,4-Dipropyl-2,5-dihydrothiophene-1,1-dioxide (5)

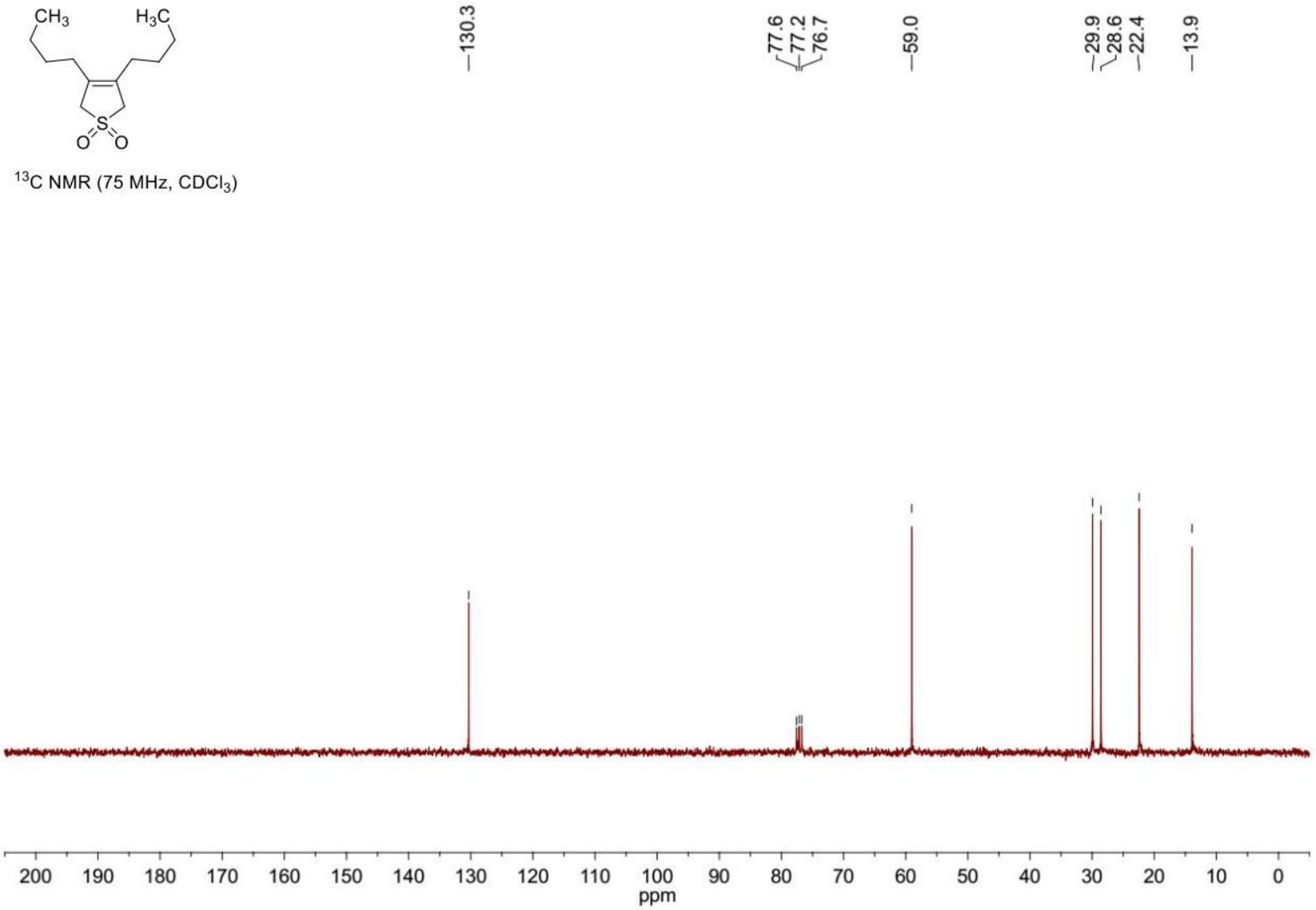


^{13}C NMR (75 MHz, $CDCl_3$)

3,4-Dibutyl-2,5-dihydrothiophene 1,1-dioxide (6)

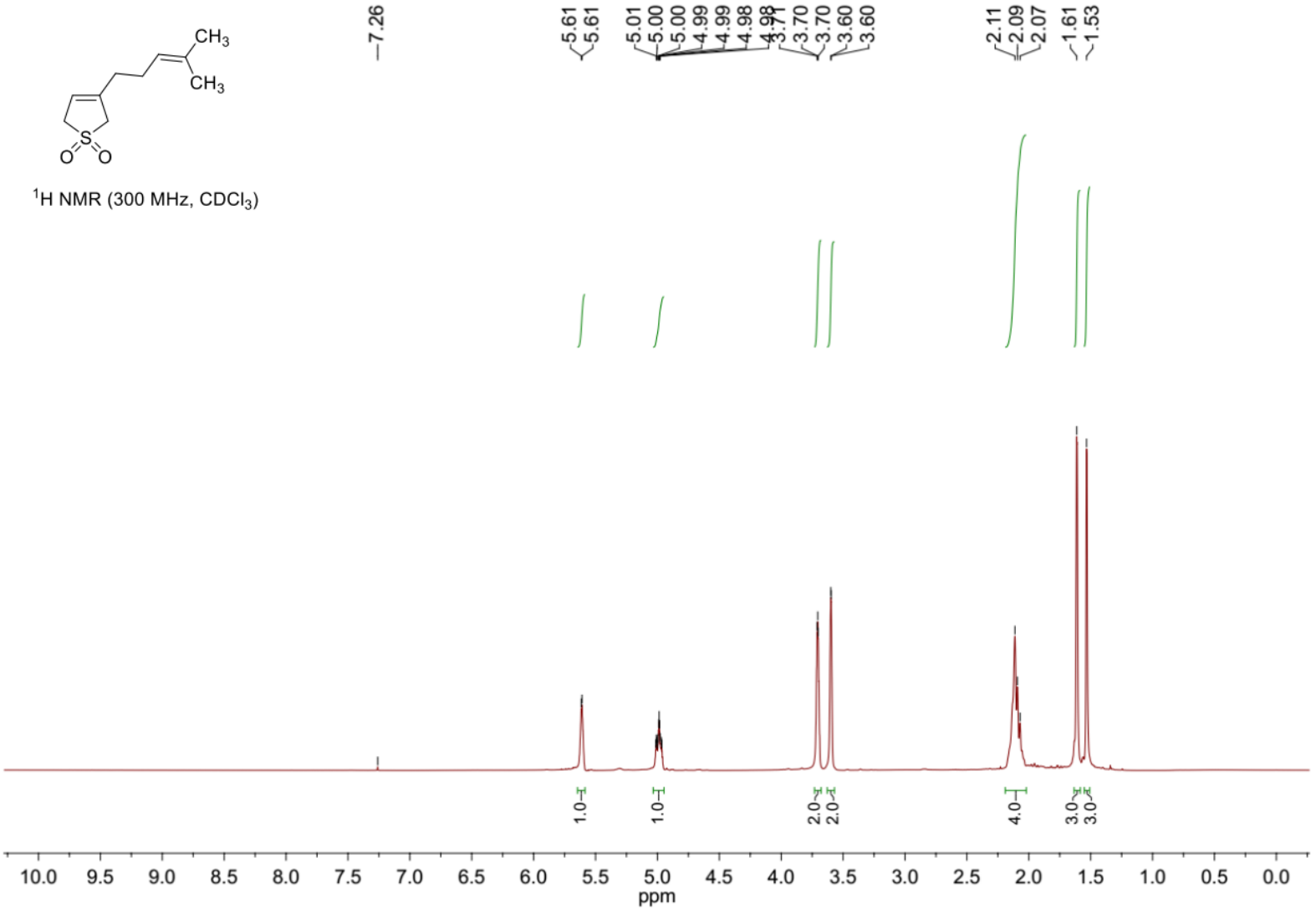


3,4-Dibutyl-2,5-dihydrothiophene 1,1-dioxide (6)

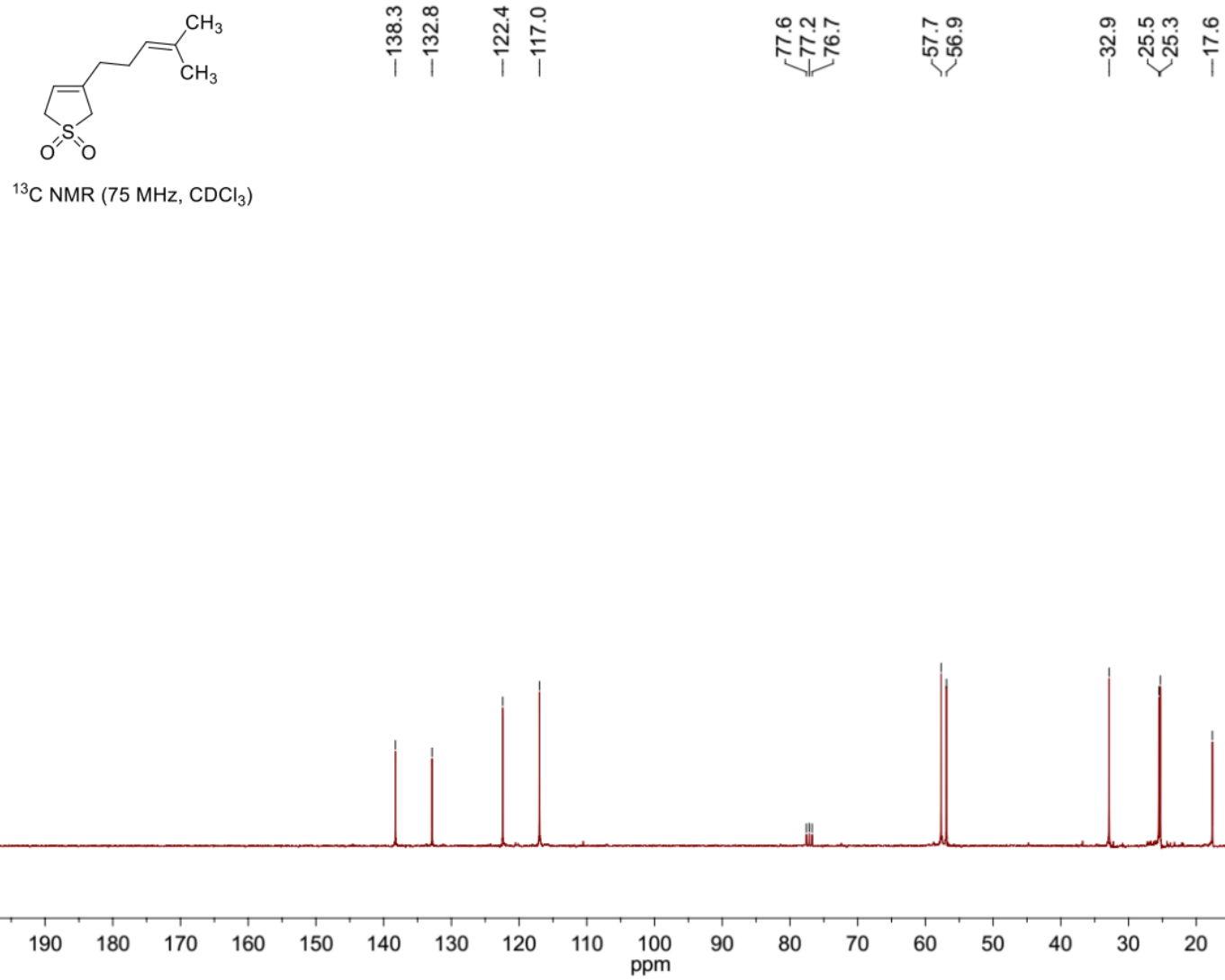


^{13}C NMR (75 MHz, $CDCl_3$)

3-(4-Methylpent-3-en-1-yl)-2,5-dihydrothiophene-1,1-dioxide (7)

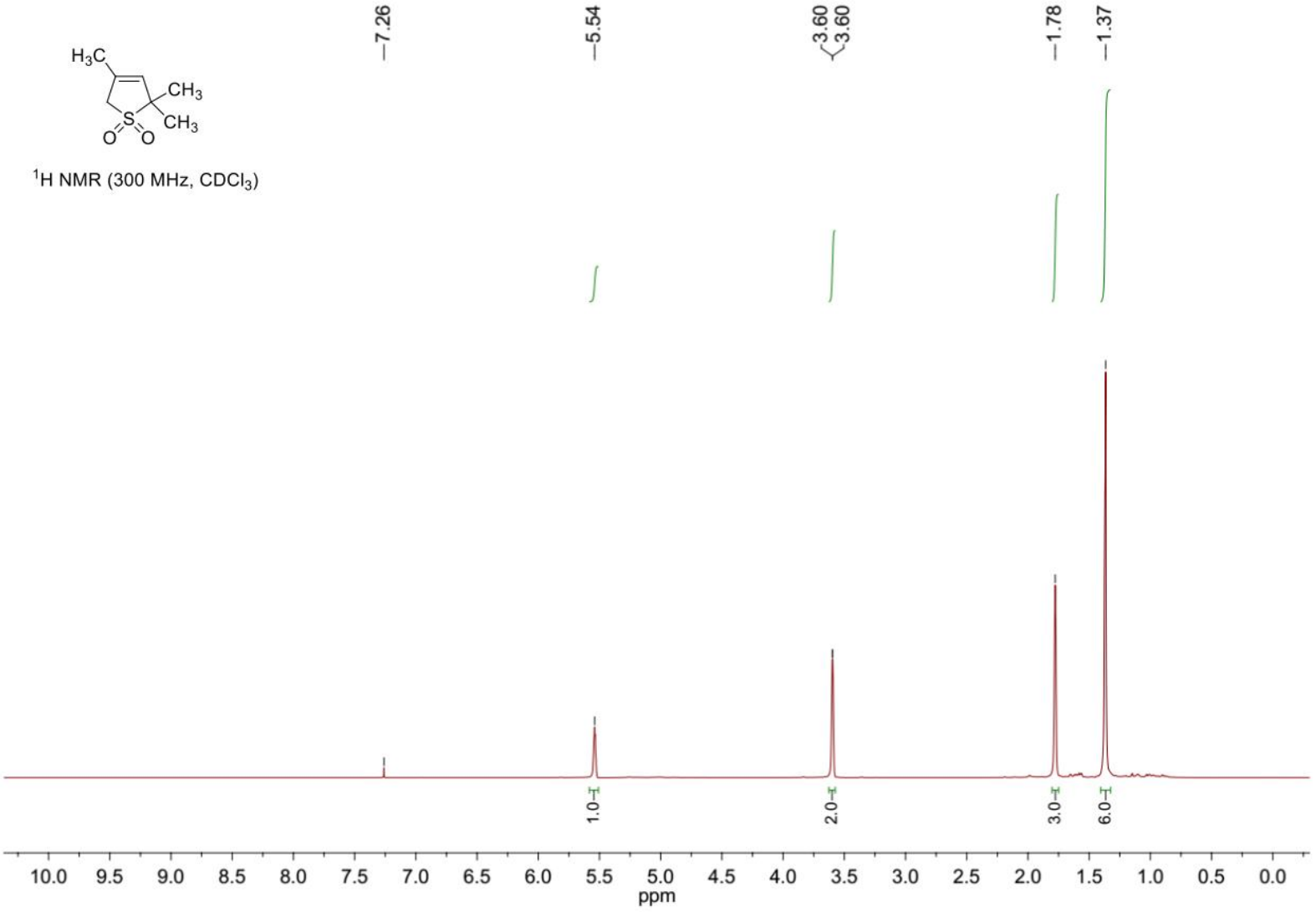


3-(4-Methylpent-3-en-1-yl)-2,5-dihydrothiophene-1,1-dioxide (7)

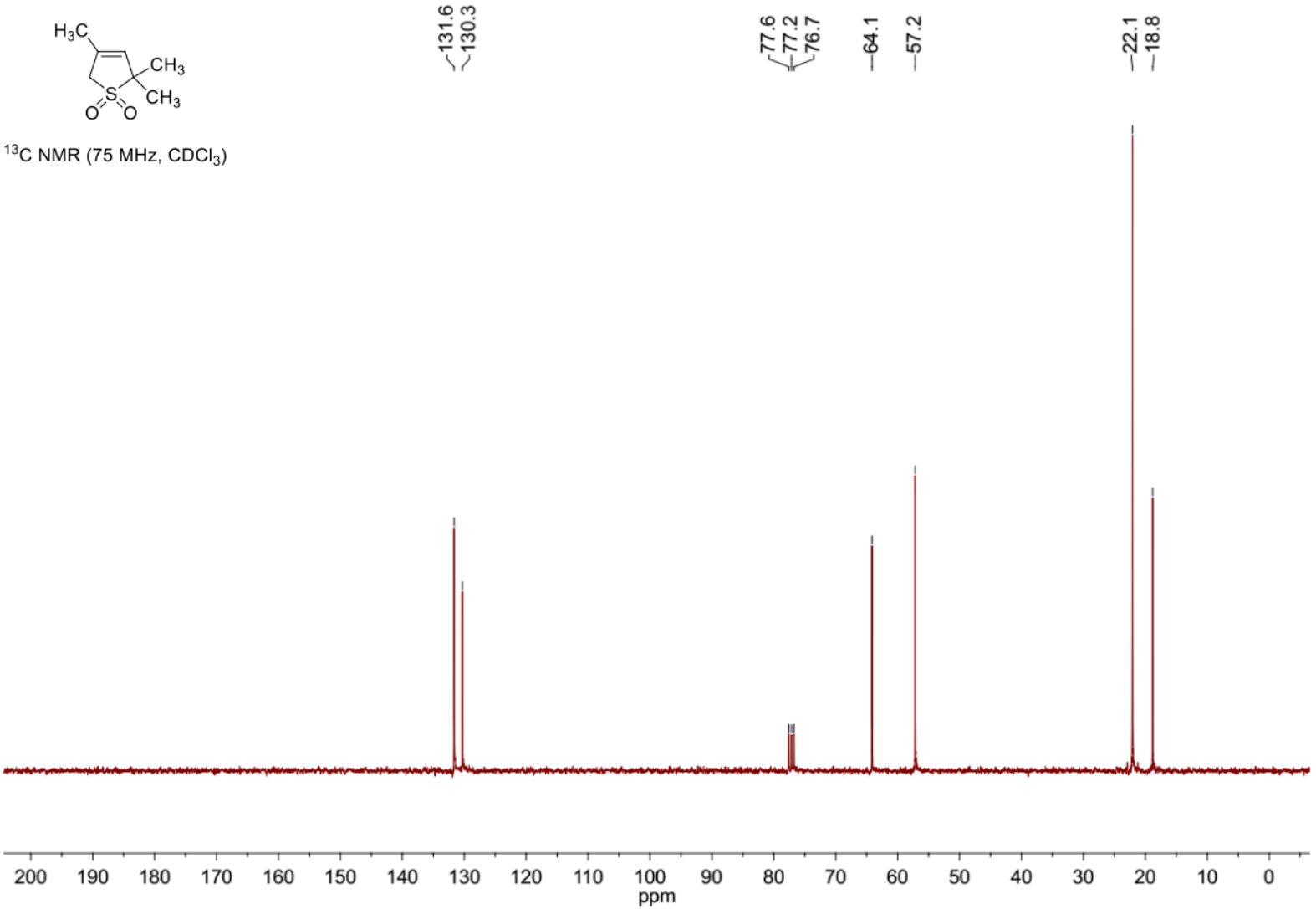


^{13}C NMR (75 MHz, $CDCl_3$)

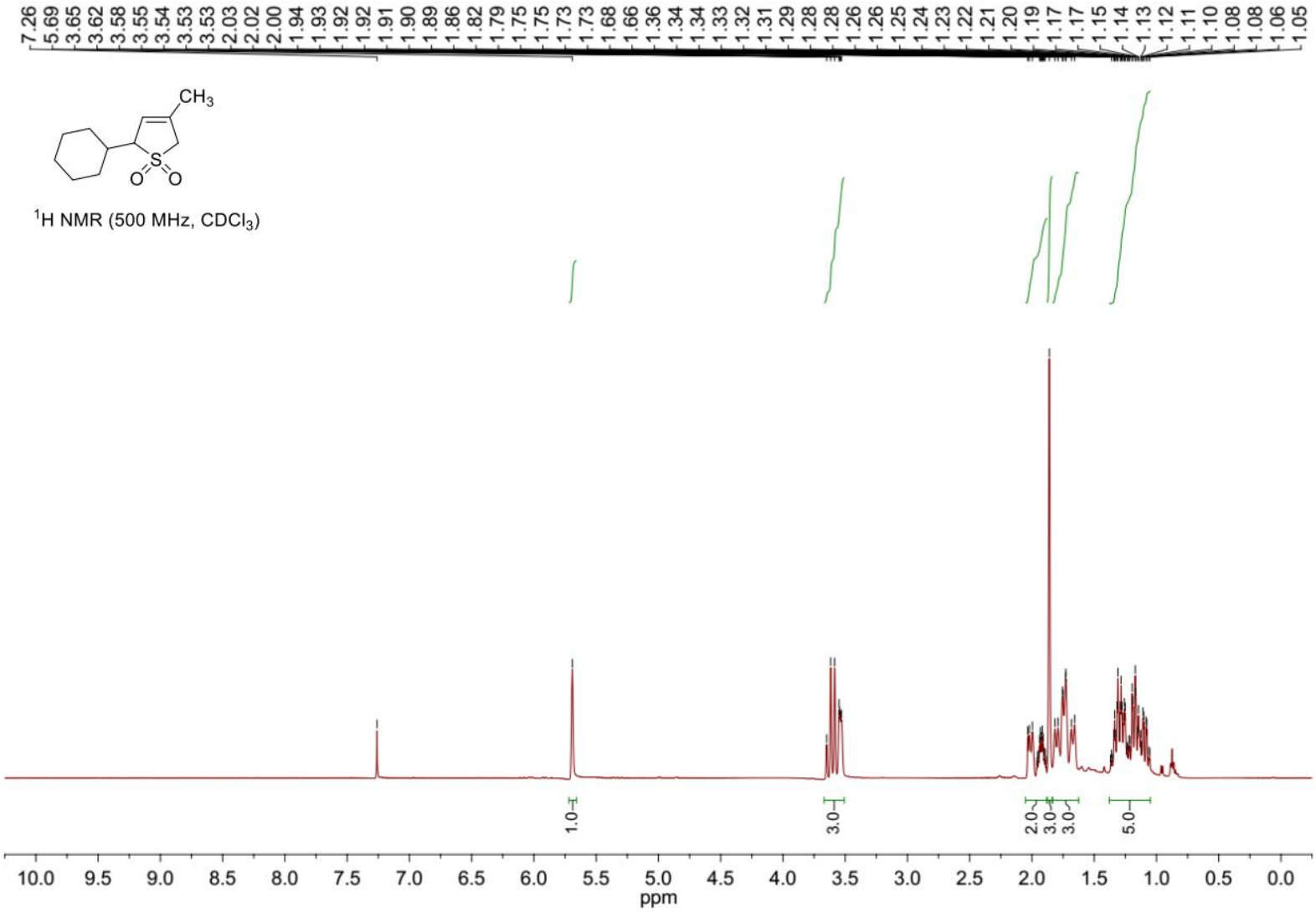
2,2,4-Trimethyl-2,5-dihydrothiophene-1,1-dioxide (8)



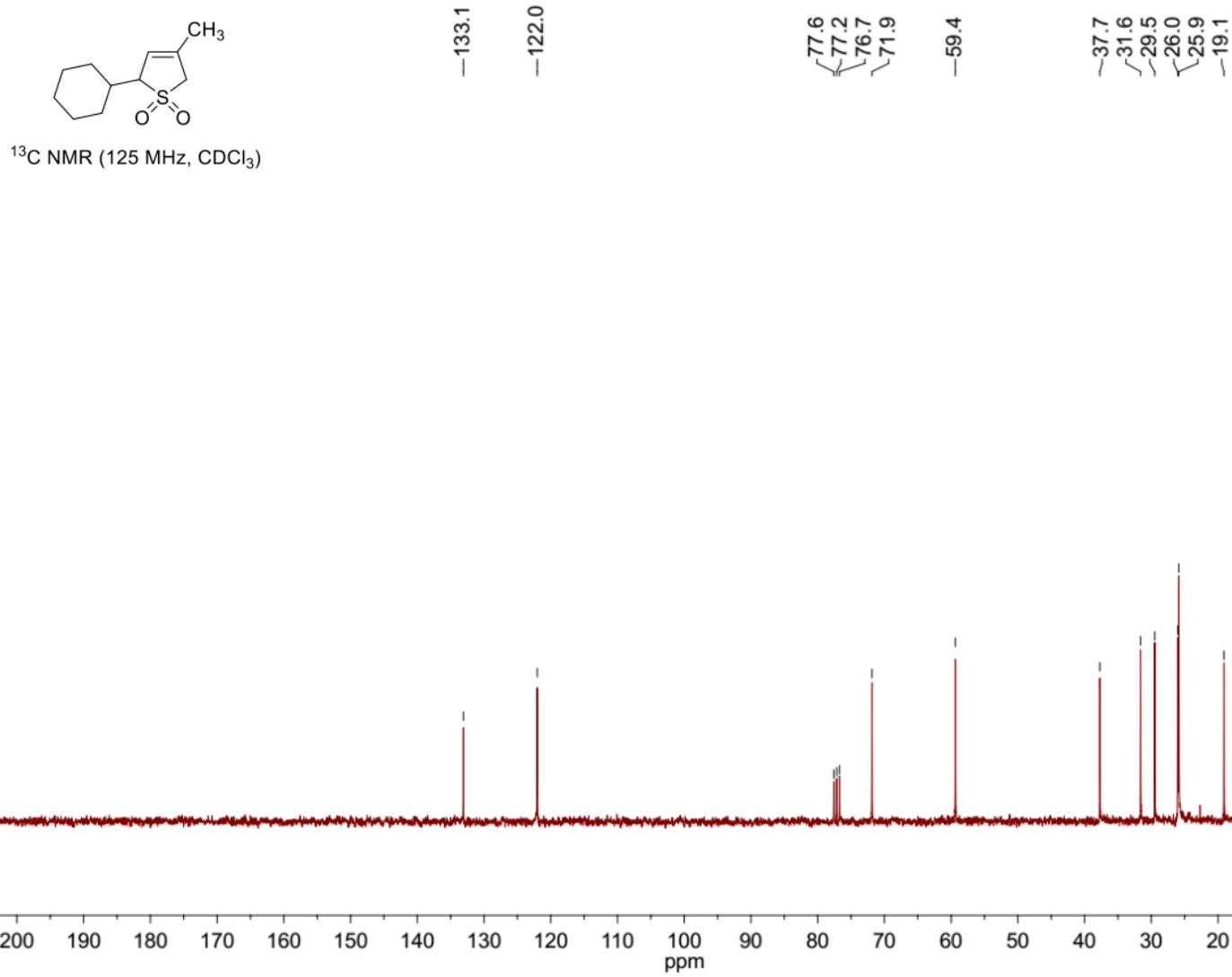
2,2,4-Trimethyl-2,5-dihydrothiophene-1,1-dioxide (8)



2-Cyclohexyl-4-methyl-2,5-dihydrothiophene 1,1-dioxide (9)

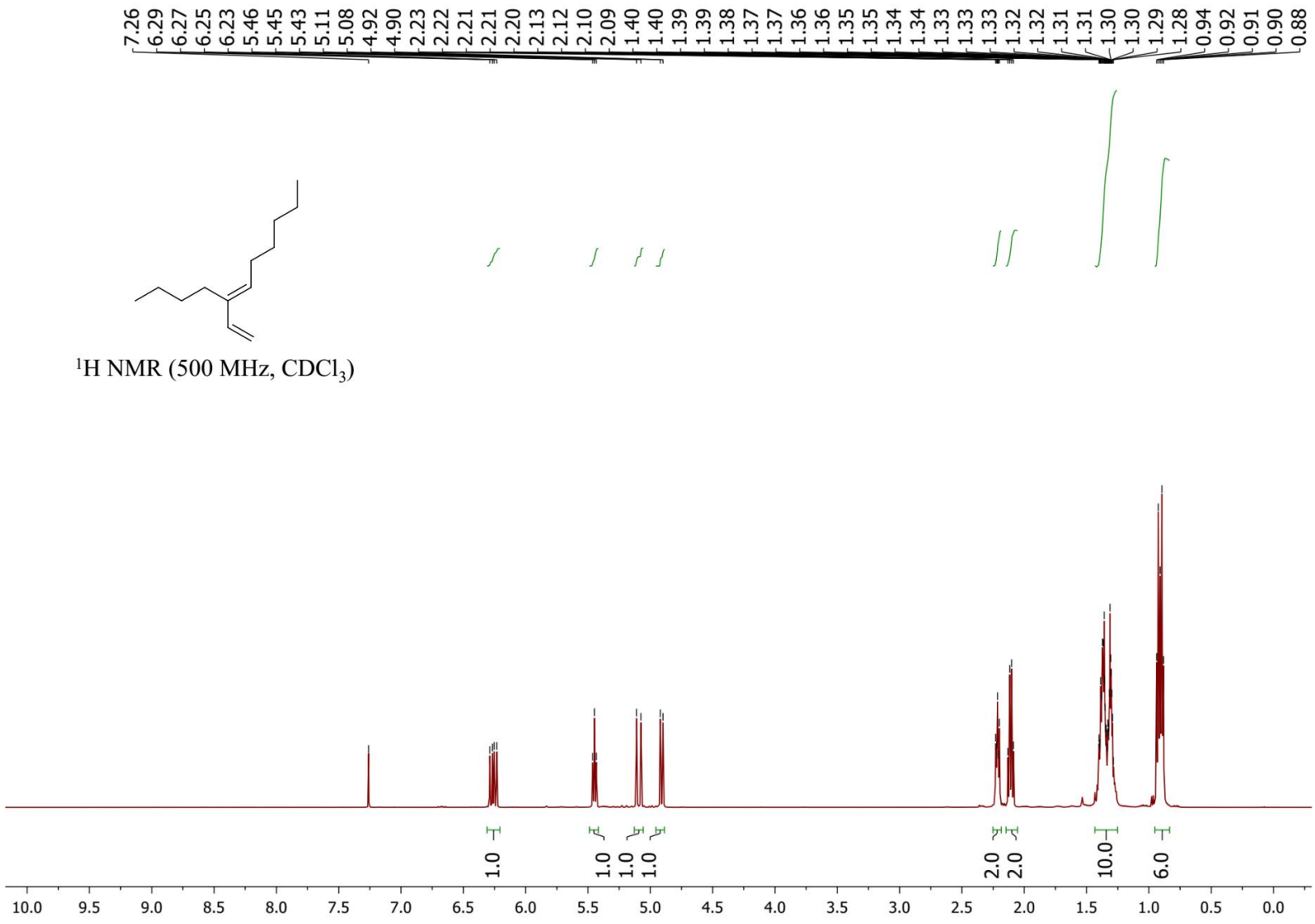


2-Cyclohexyl-4-methyl-2,5-dihydrothiophene 1,1-dioxide (9)



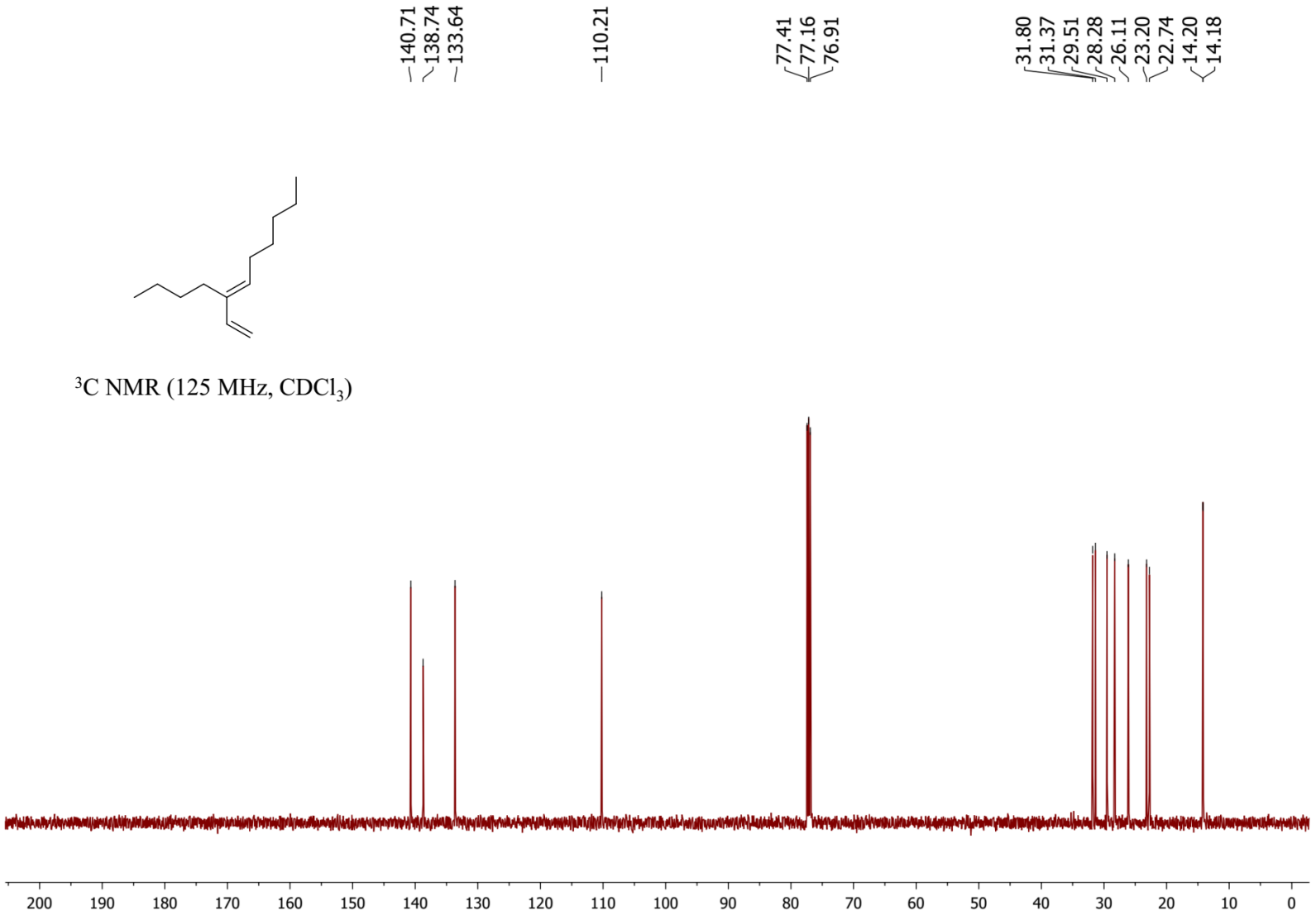
^{13}C NMR (125 MHz, $CDCl_3$)

(*E*)-5-Vinylundec-5-ene



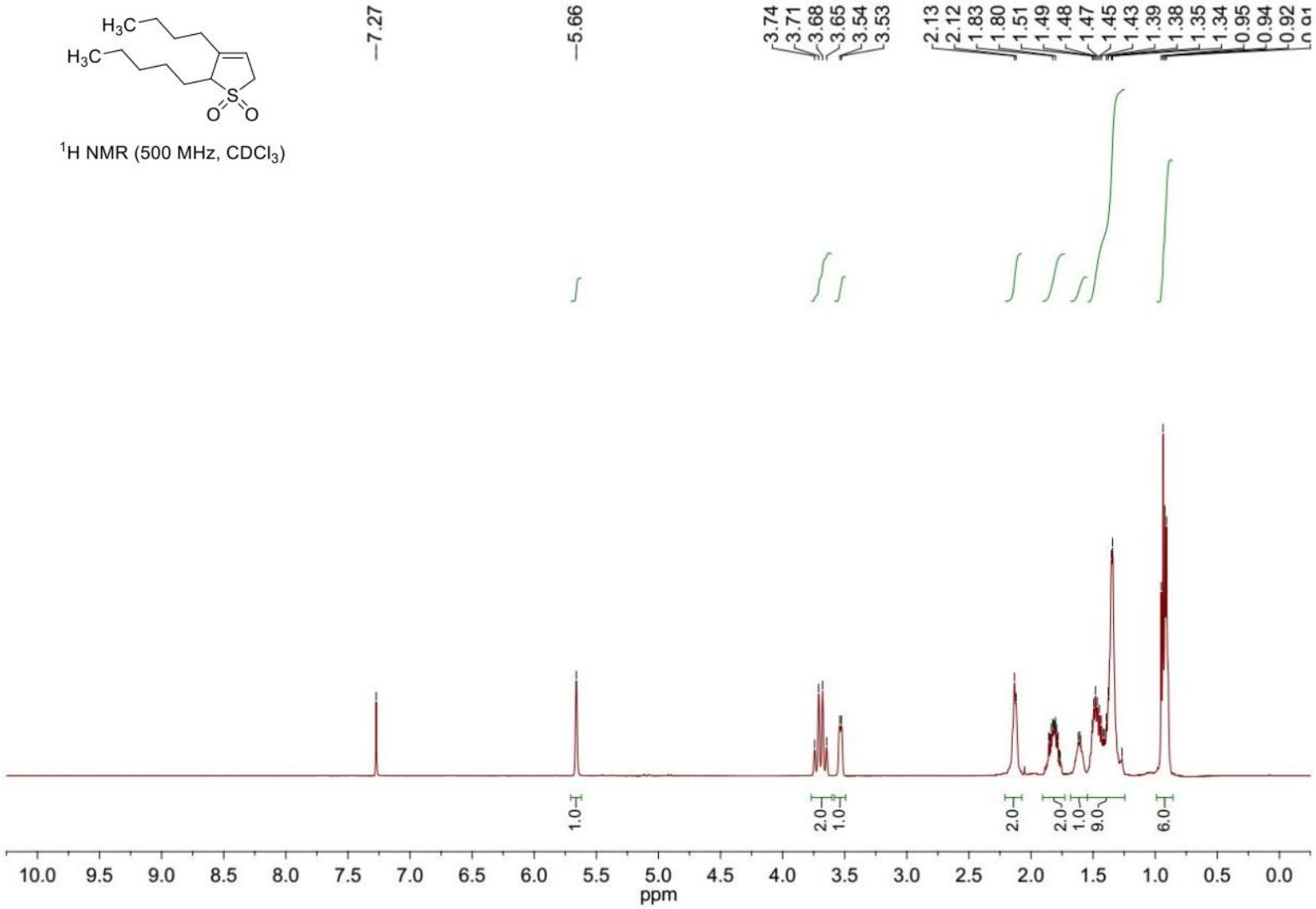
^{1}H NMR (500 MHz, $CDCl_3$)

(*E*)-5-Vinylundec-5-ene

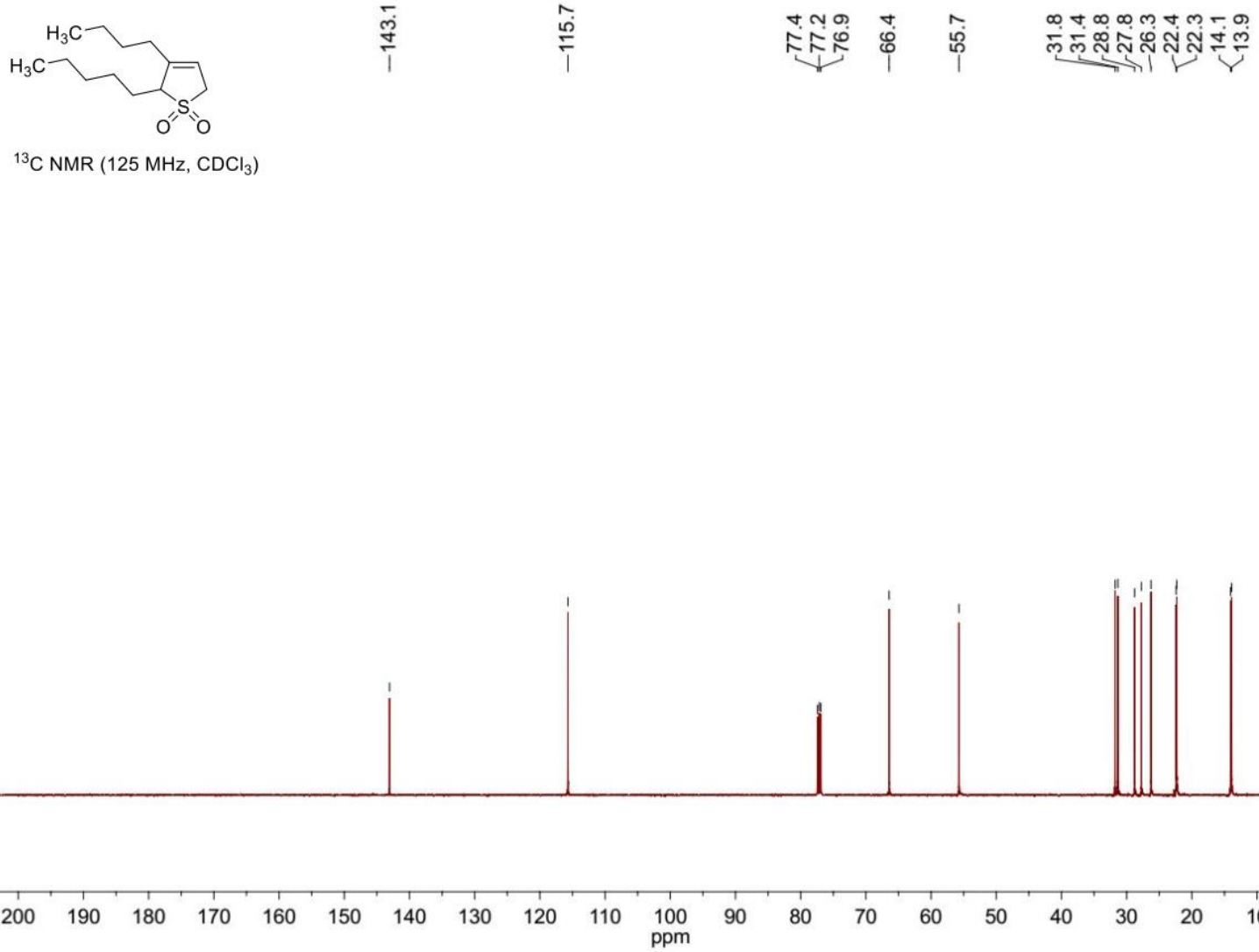


^{3}C NMR (125 MHz, $CDCl_3$)

3-Butyl-2-pentyl-2,5-dihydrothiophene 1,1-dioxide (10)

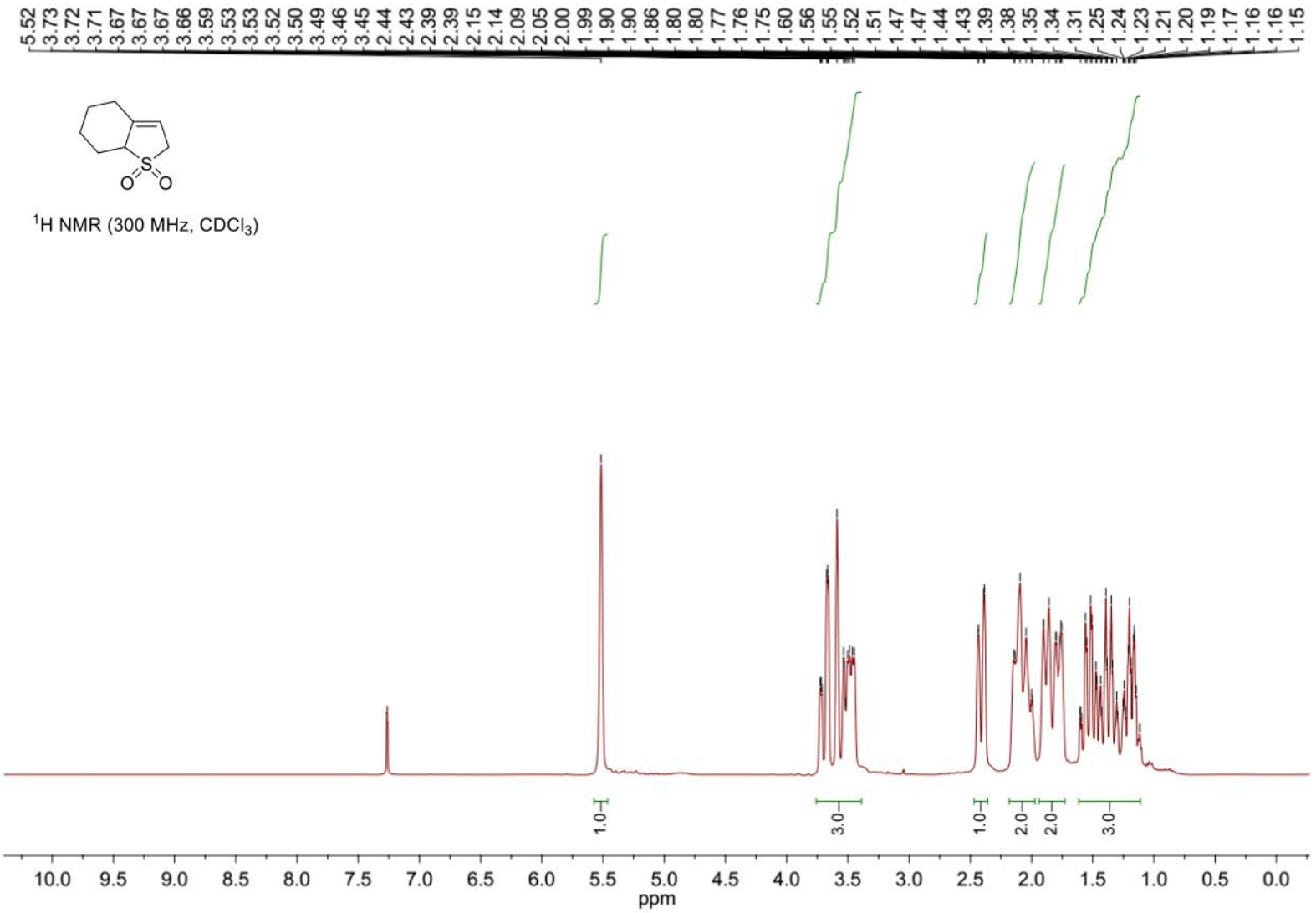


3-Butyl-2-pentyl-2,5-dihydrothiophene 1,1-dioxide (10)

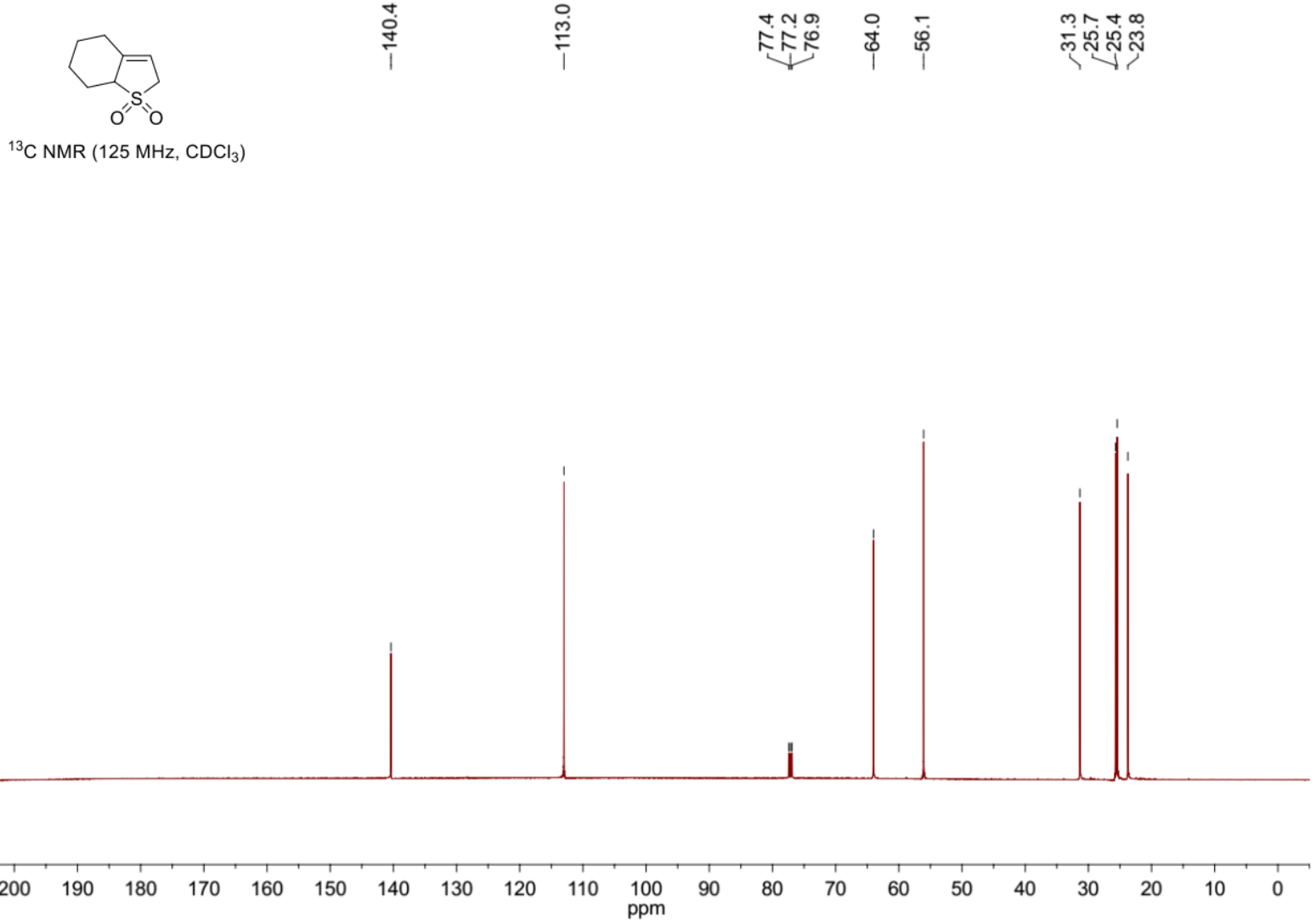


^{13}C NMR (125 MHz, $CDCl_3$)

2,4,5,6,7,7a-Hexahydrobenzo[b]thiophene-1,1-dioxide (11)

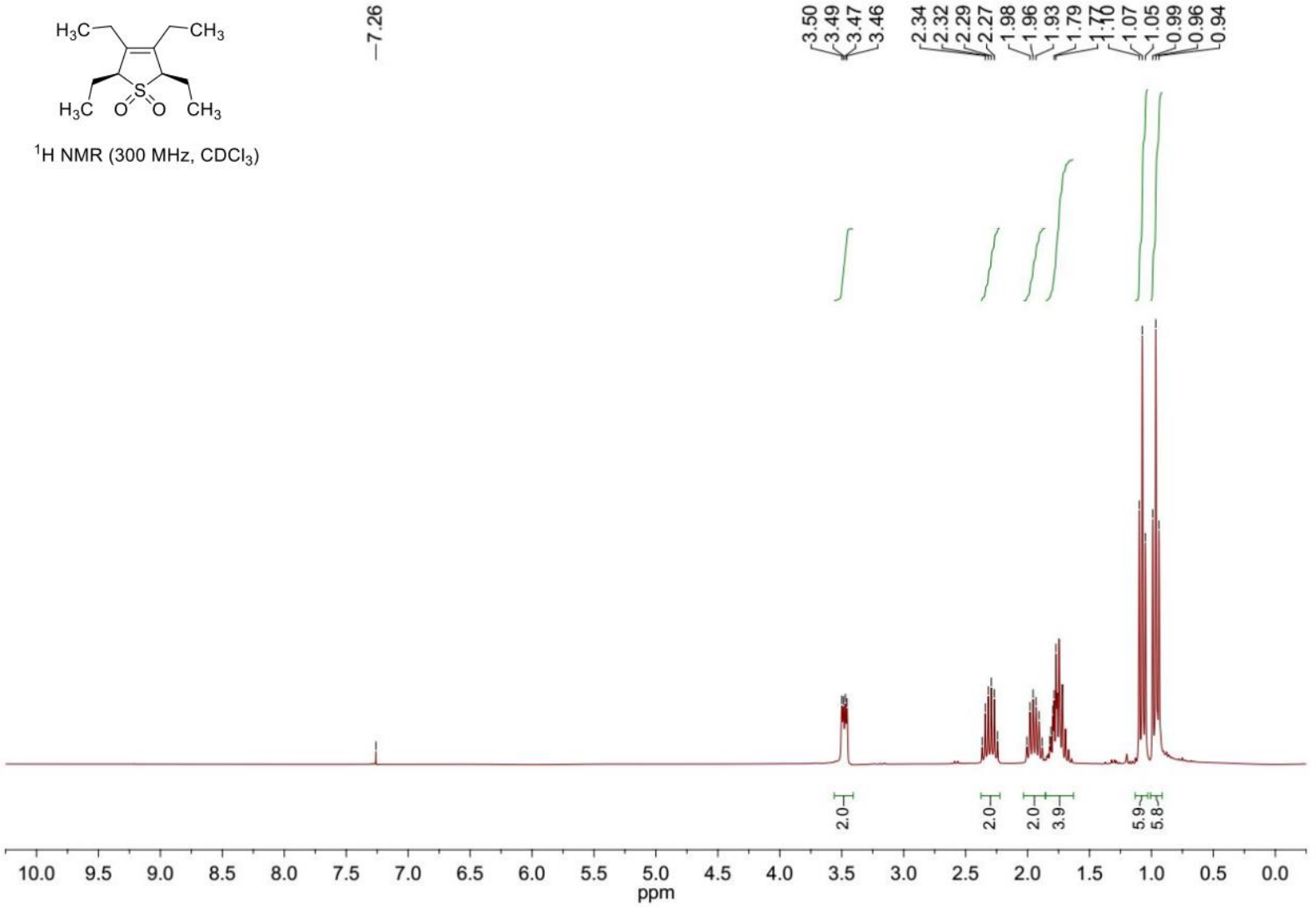


2,4,5,6,7,7a-Hexahydrobenzo[b]thiophene-1,1-dioxide (11)

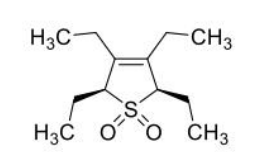


^{13}C NMR (125 MHz, $CDCl_3$)

2,3,4,5-Tetraethyl-2,5-dihydrothiophene-1,1-dioxide (12)

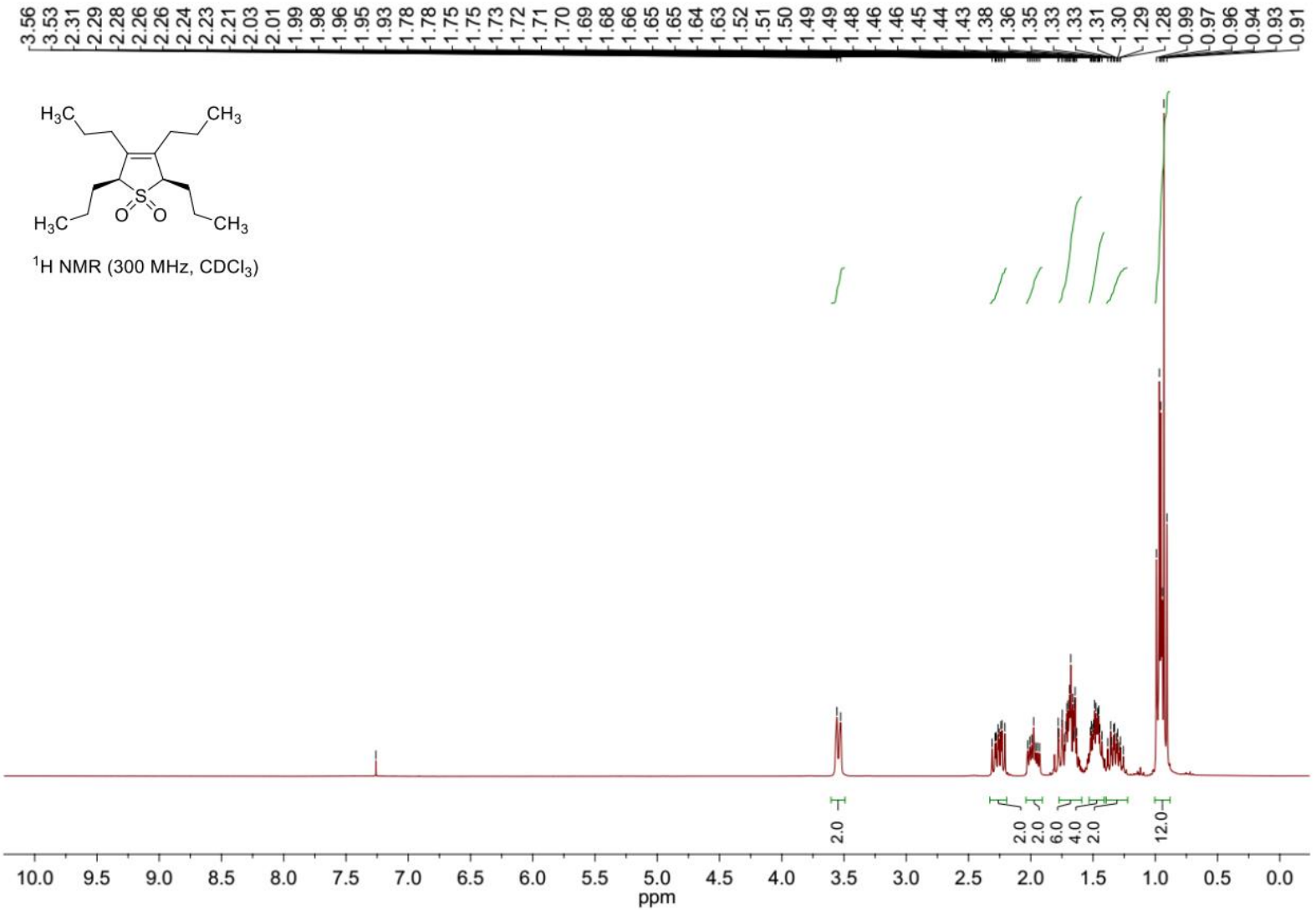


2,3,4,5-Tetraethyl-2,5-dihydrothiophene-1,1-dioxide (12)

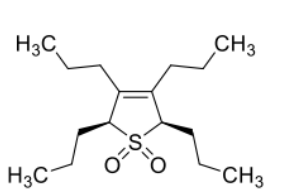


^{13}C NMR (75 MHz, $CDCl_3$)

2,3,4,5-Tetrapropyl-2,5-dihydrothiophene-1,1-dioxide (13)

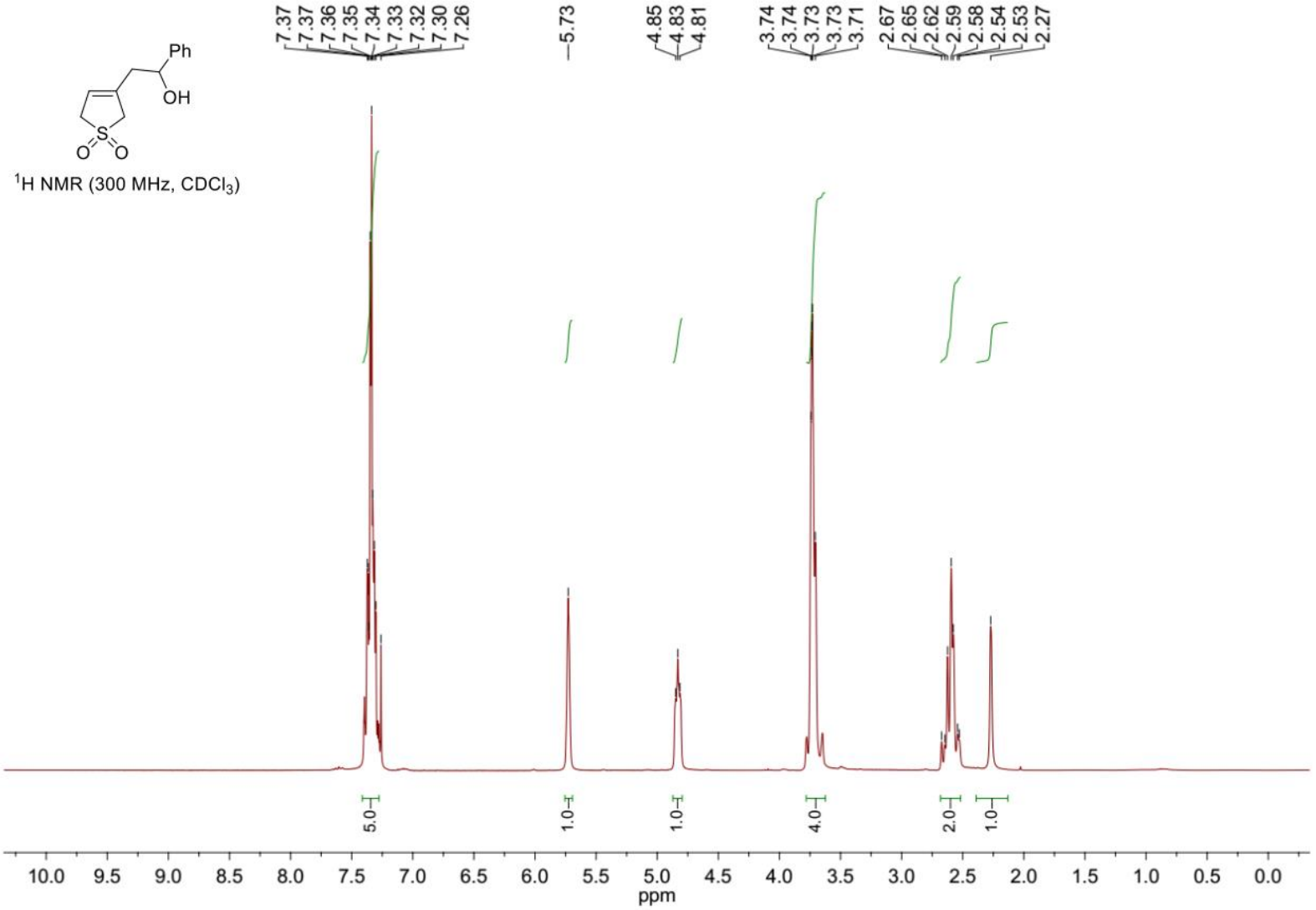


2,3,4,5-Tetrapropyl-2,5-dihydrothiophene-1,1-dioxide (13)

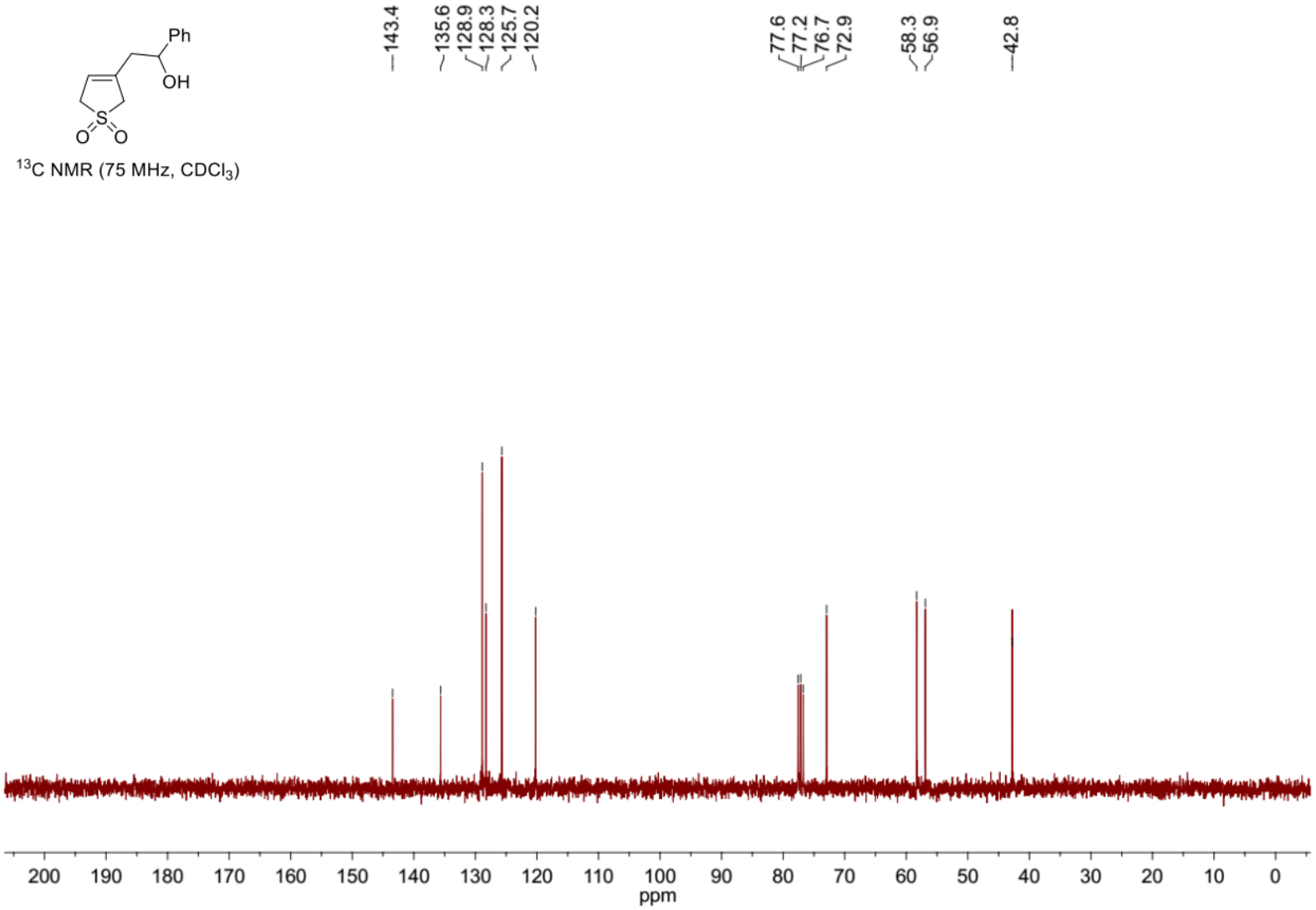


^{13}C NMR (75 MHz, $CDCl_3$)

3-(2-Hydroxy-2-phenylethyl)-2,5-dihydrothiophene-1,1-dioxide (14)

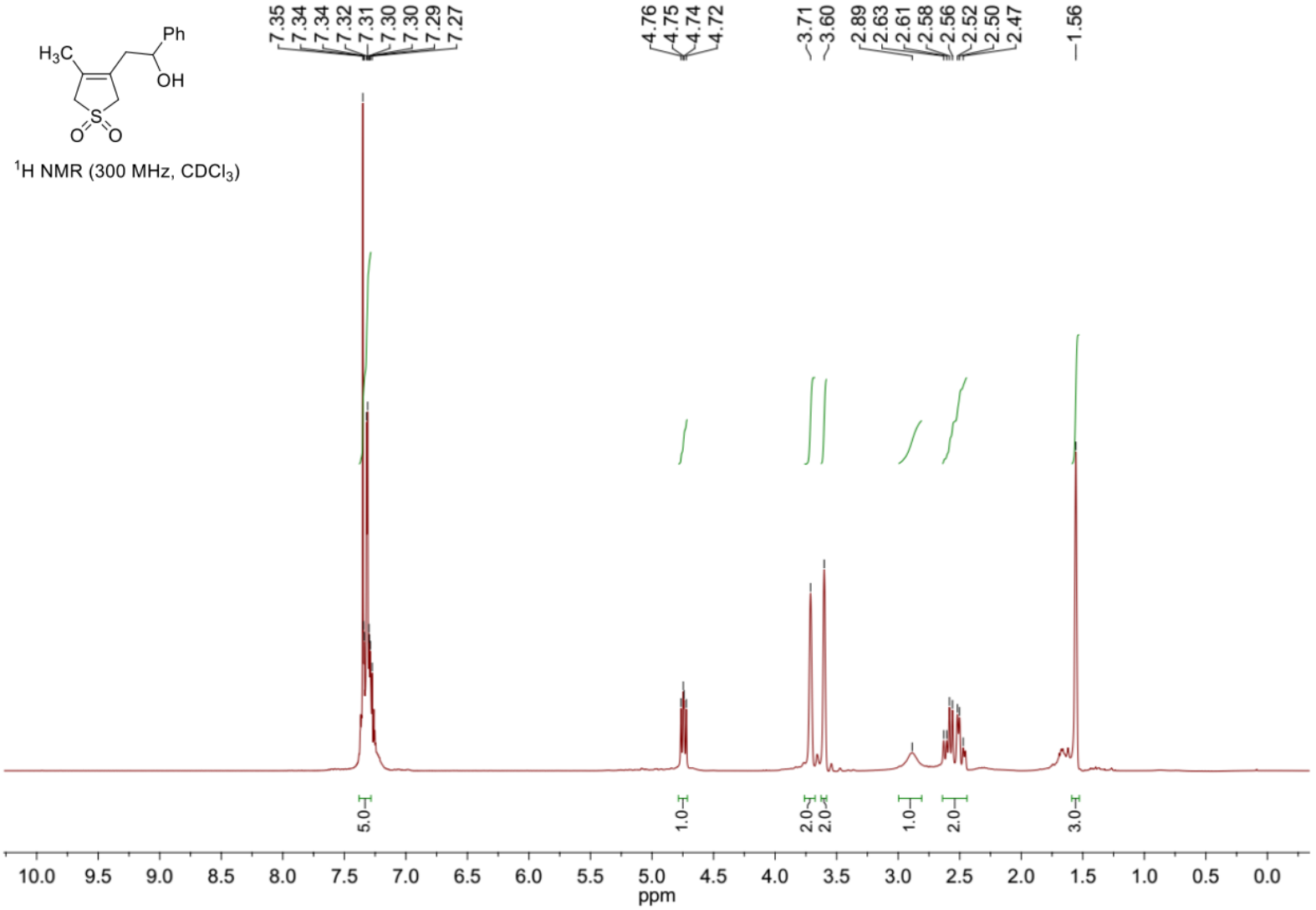


3-(2-Hydroxy-2-phenylethyl)-2,5-dihydrothiophene-1,1-dioxide (14)

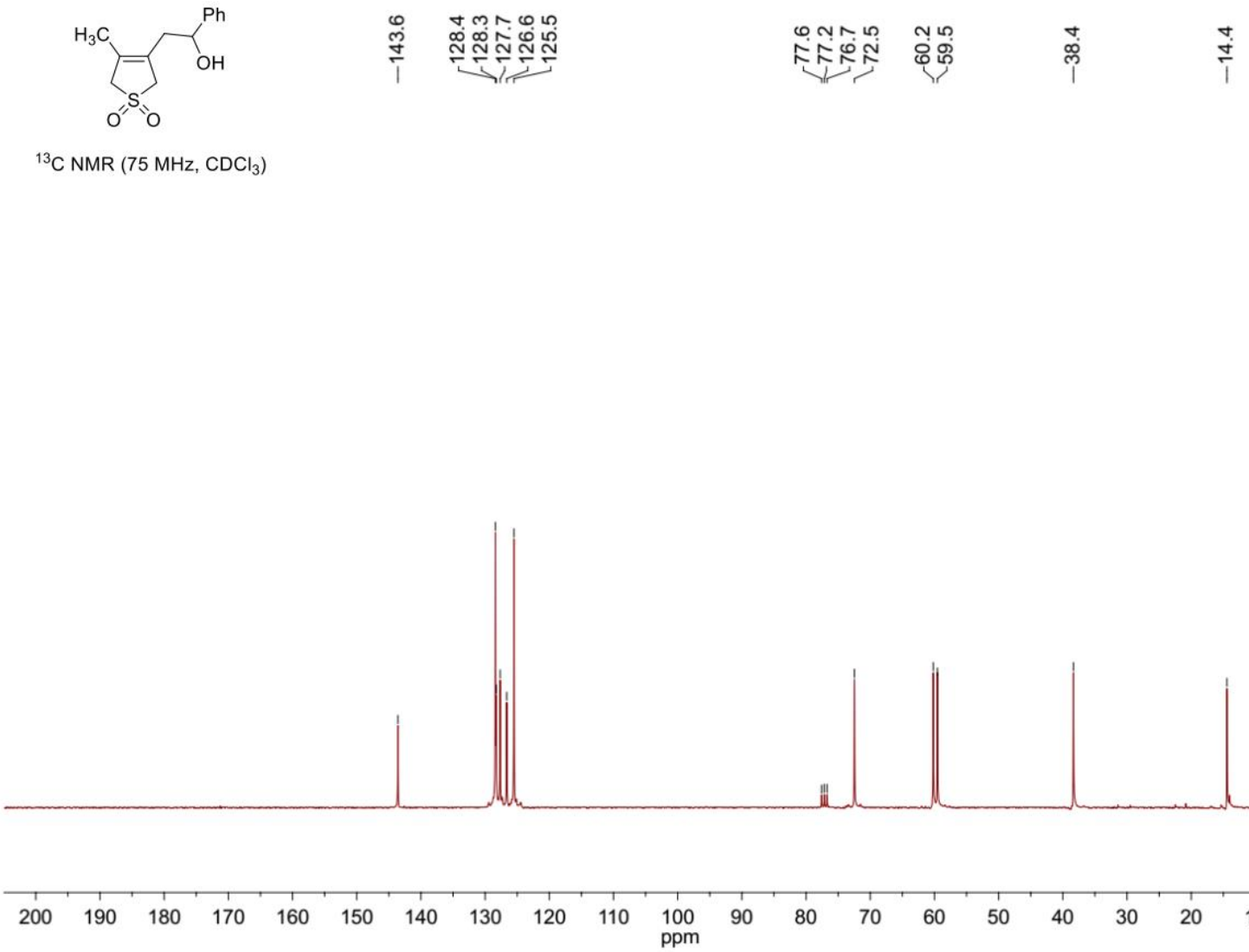


^{13}C NMR (75 MHz, $CDCl_3$)

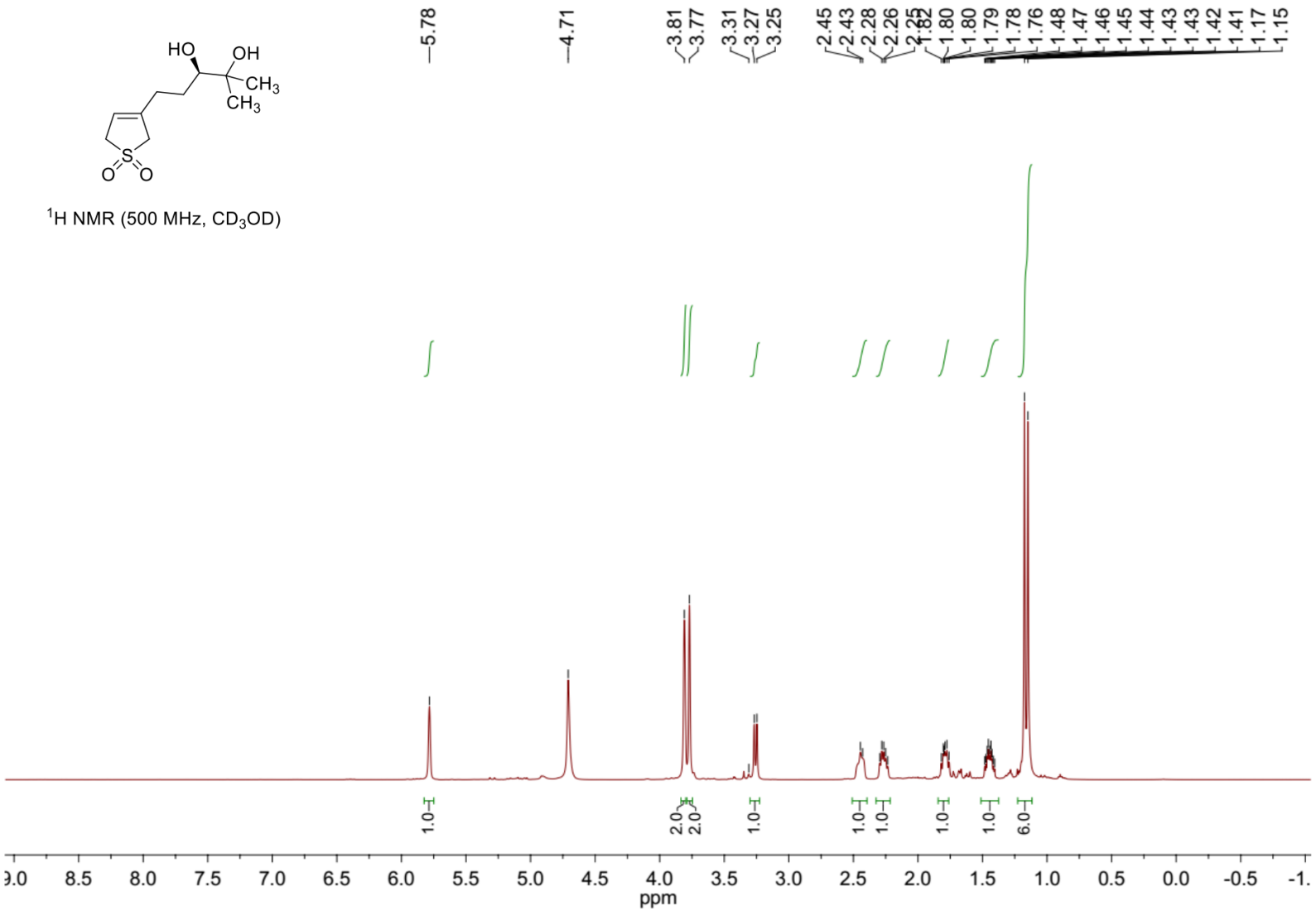
3-(2-Hydroxy-2-phenylethyl)-4-methyl-2,5-dihydrothiophene-1,1-dioxide (15)



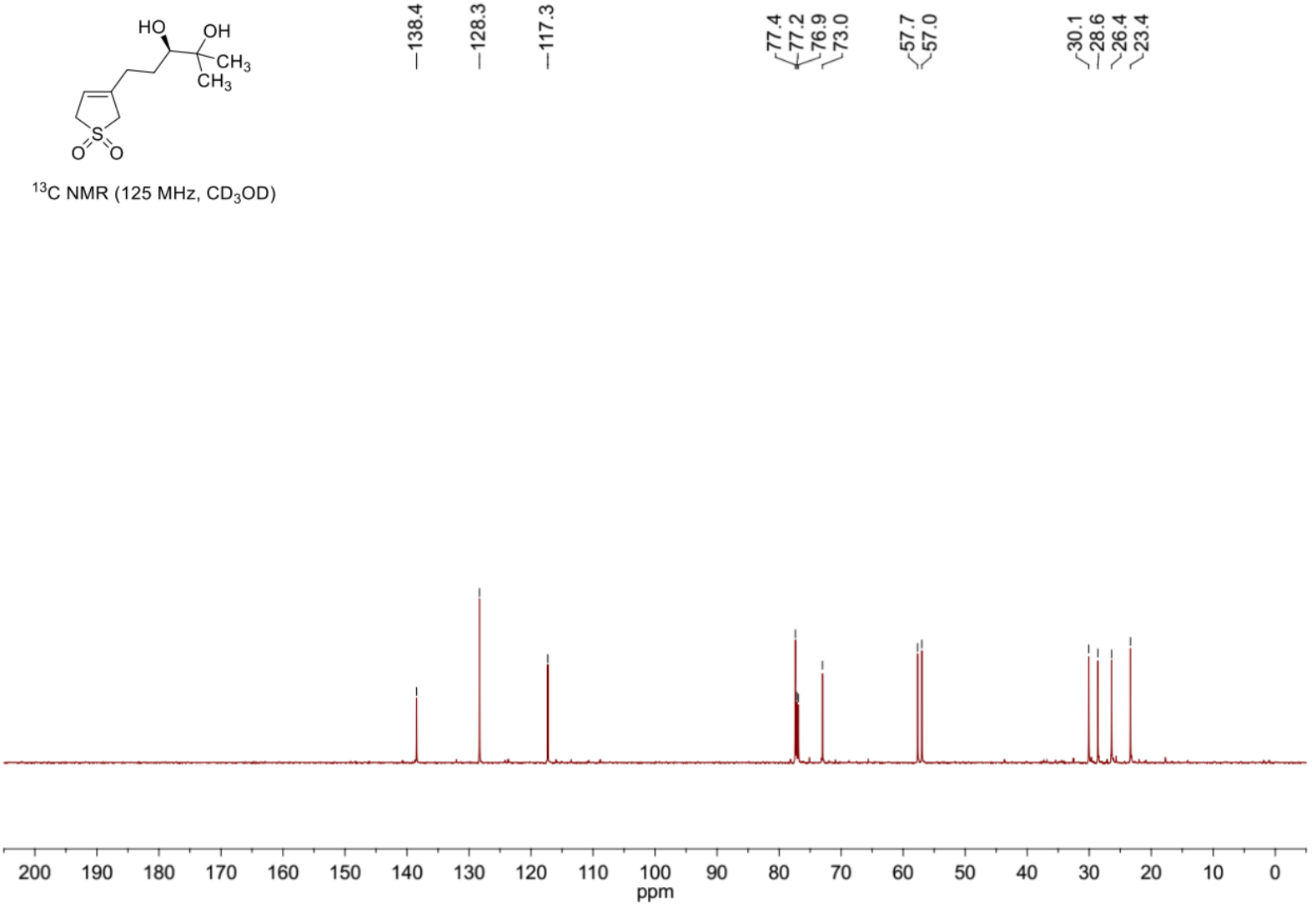
3-(2-Hydroxy-2-phenylethyl)-4-methyl-2,5-dihydrothiophene-1,1-dioxide (15)



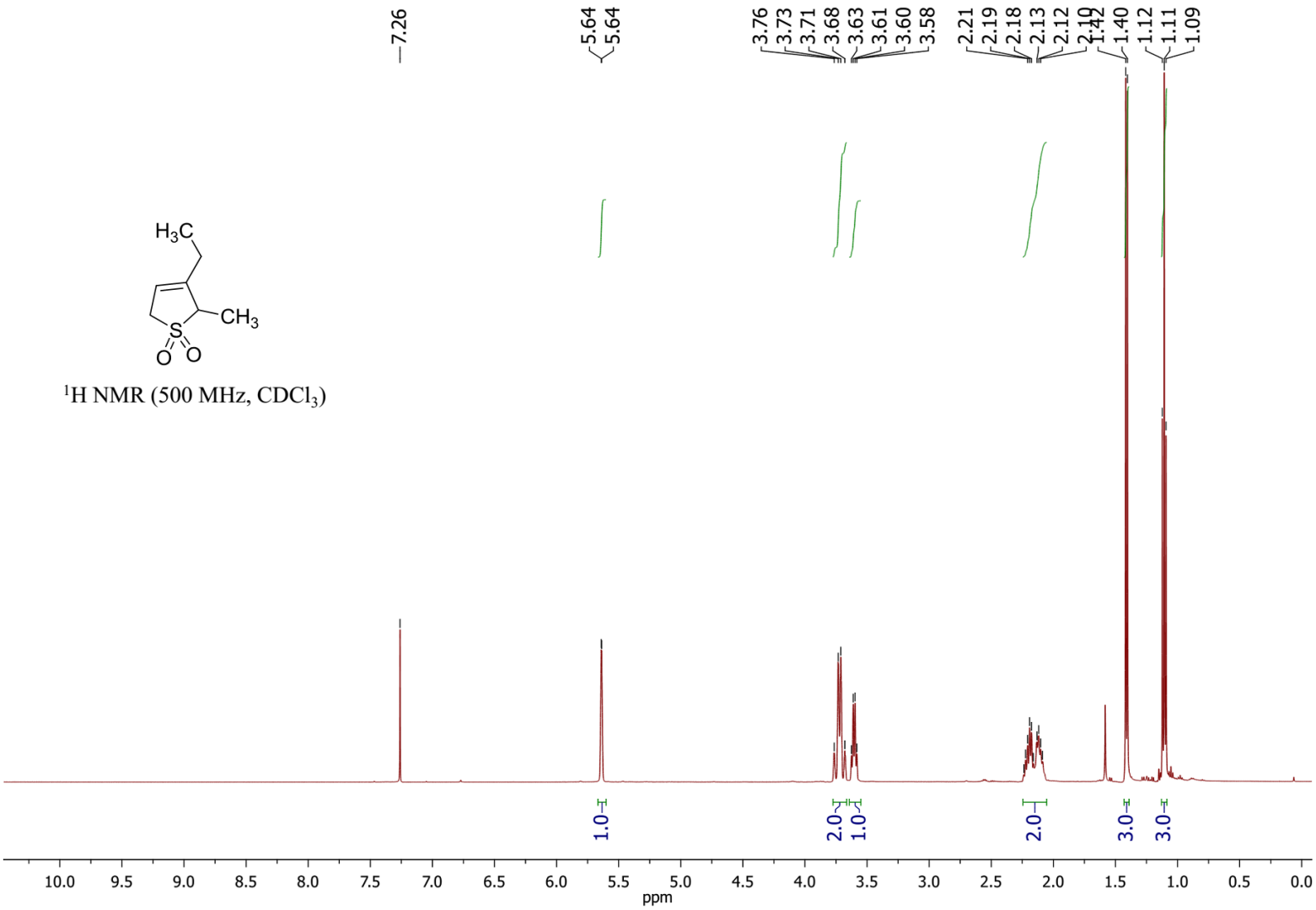
(*R*)-3-(3,4-Dihydroxy-4-methylpentyl)-2,5-dihydrothiophene 1,1-dioxide (16)



(*R*)-3-(3,4-Dihydroxy-4-methylpentyl)-2,5-dihydrothiophene 1,1-dioxide (16)

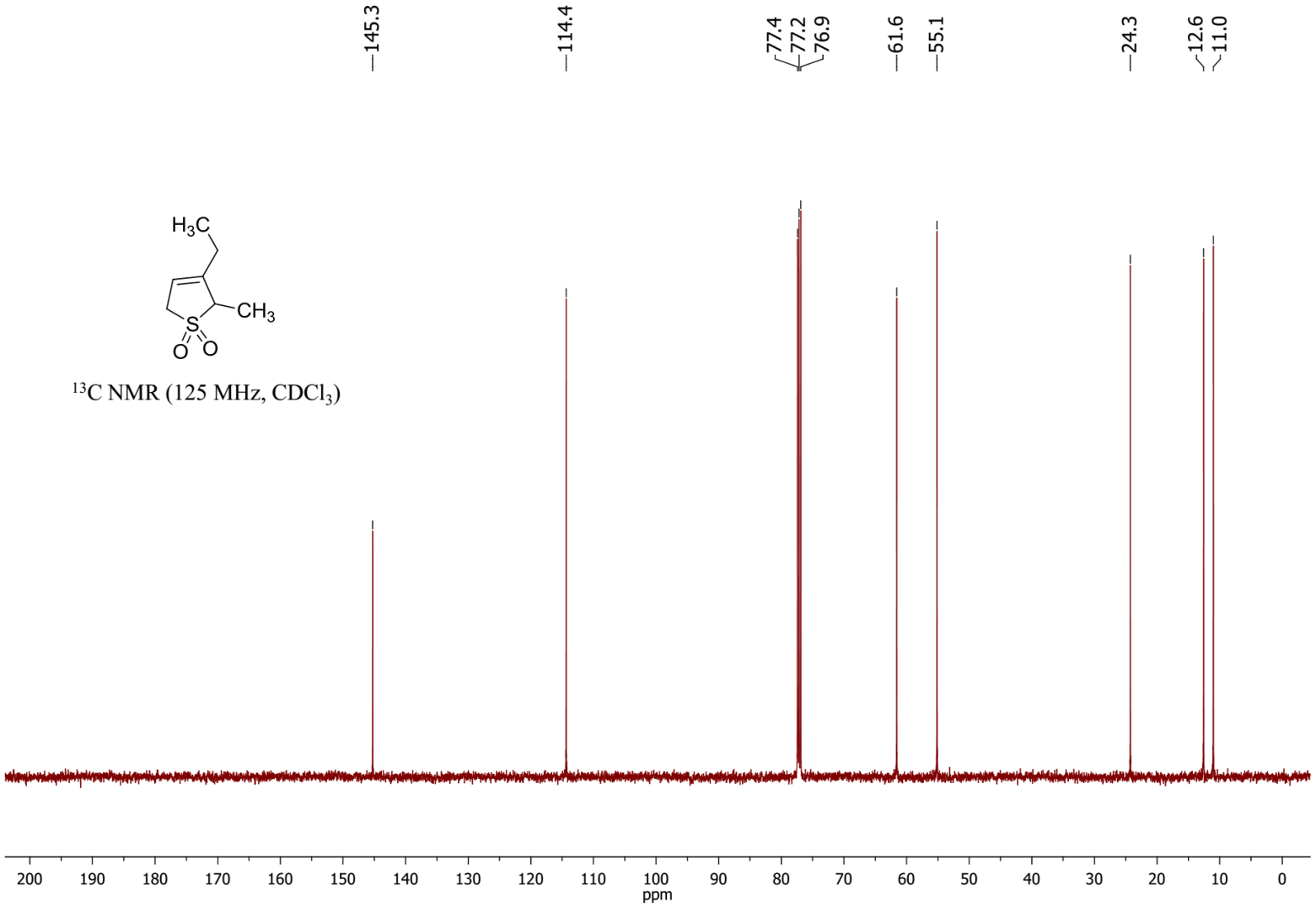


3-Ethyl-2-methyl-2,5-dihydrothiophene 1,1-dioxide (17)



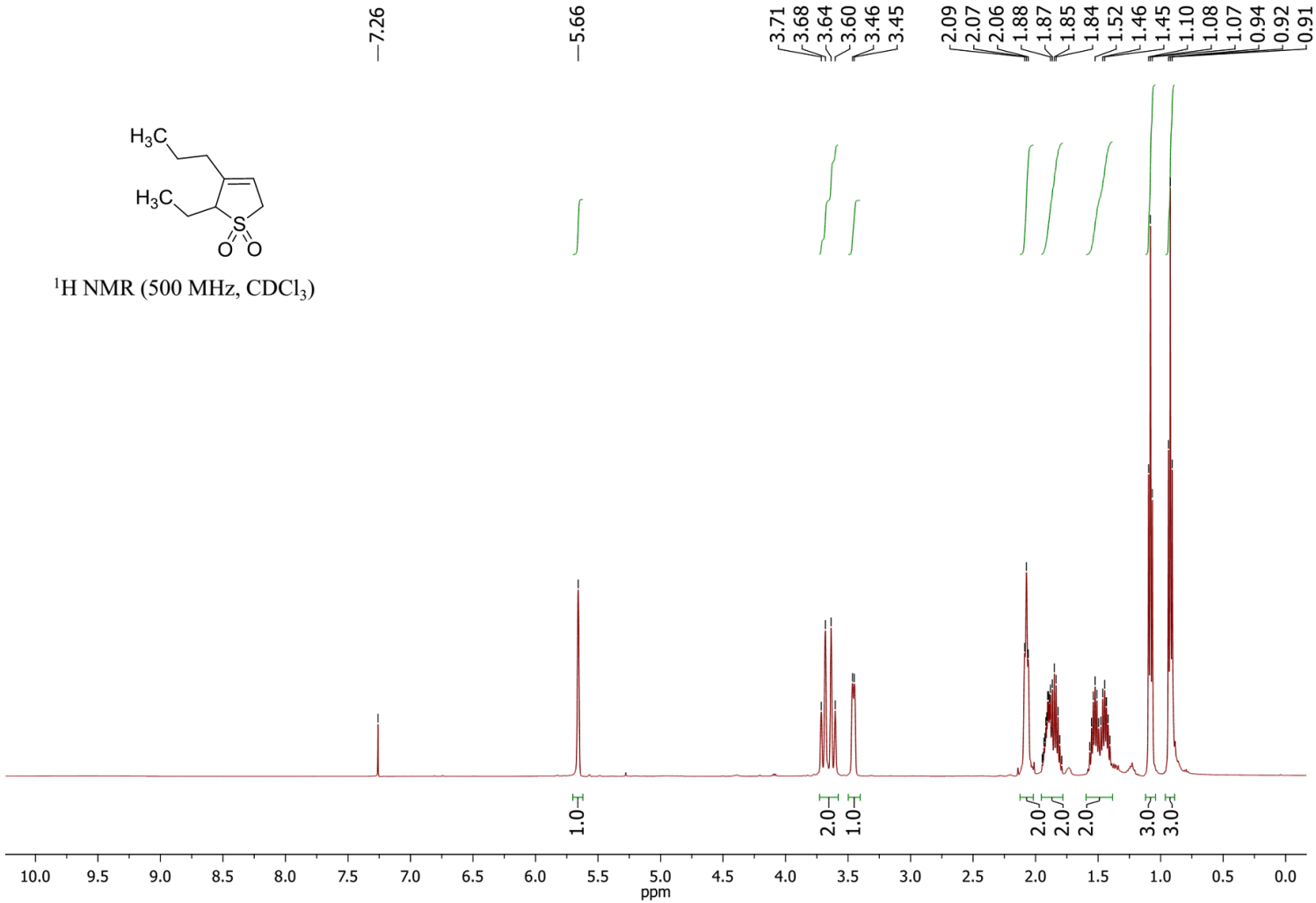
^{1}H NMR (500 MHz, $CDCl_3$)

3-Ethyl-2-methyl-2,5-dihydrothiophene 1,1-dioxide (17)



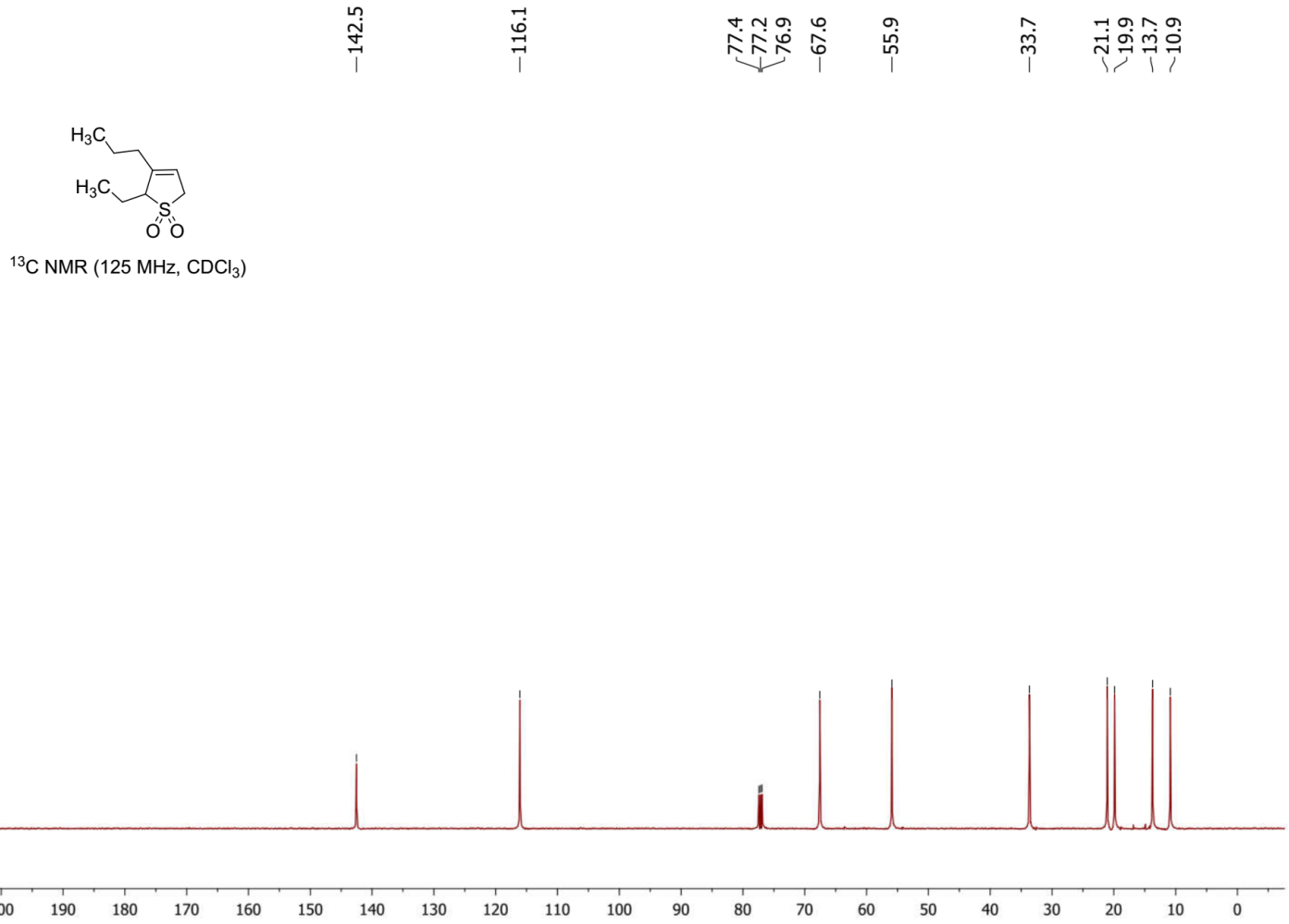
^{13}C NMR (125 MHz, $CDCl_3$)

2-Ethyl-3-propyl-2,5-dihydrothiophene 1,1-dioxide (18)

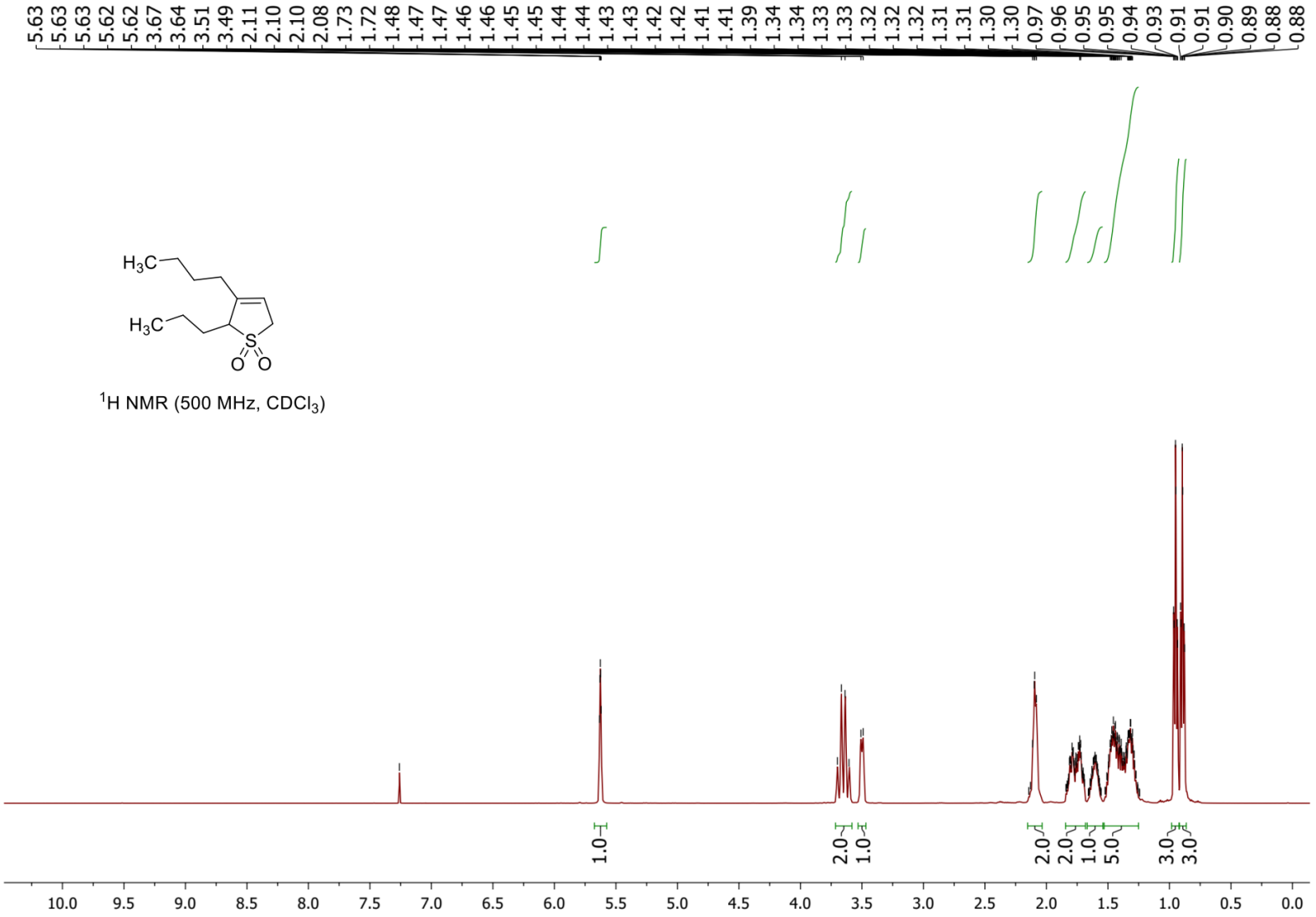


^{1}H NMR (500 MHz, $CDCl_3$)

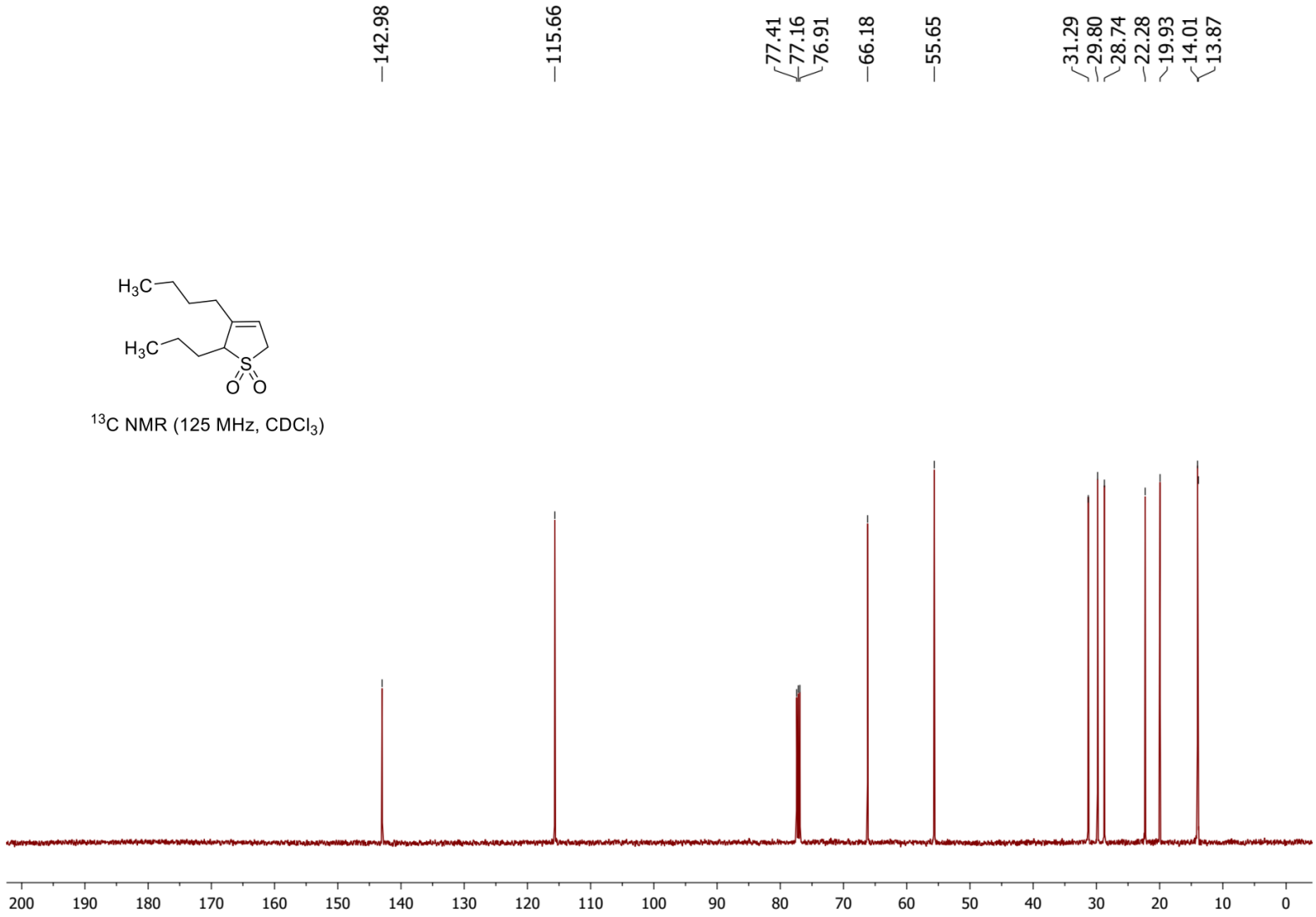
2-Ethyl-3-propyl-2,5-dihydrothiophene 1,1-dioxide (18)



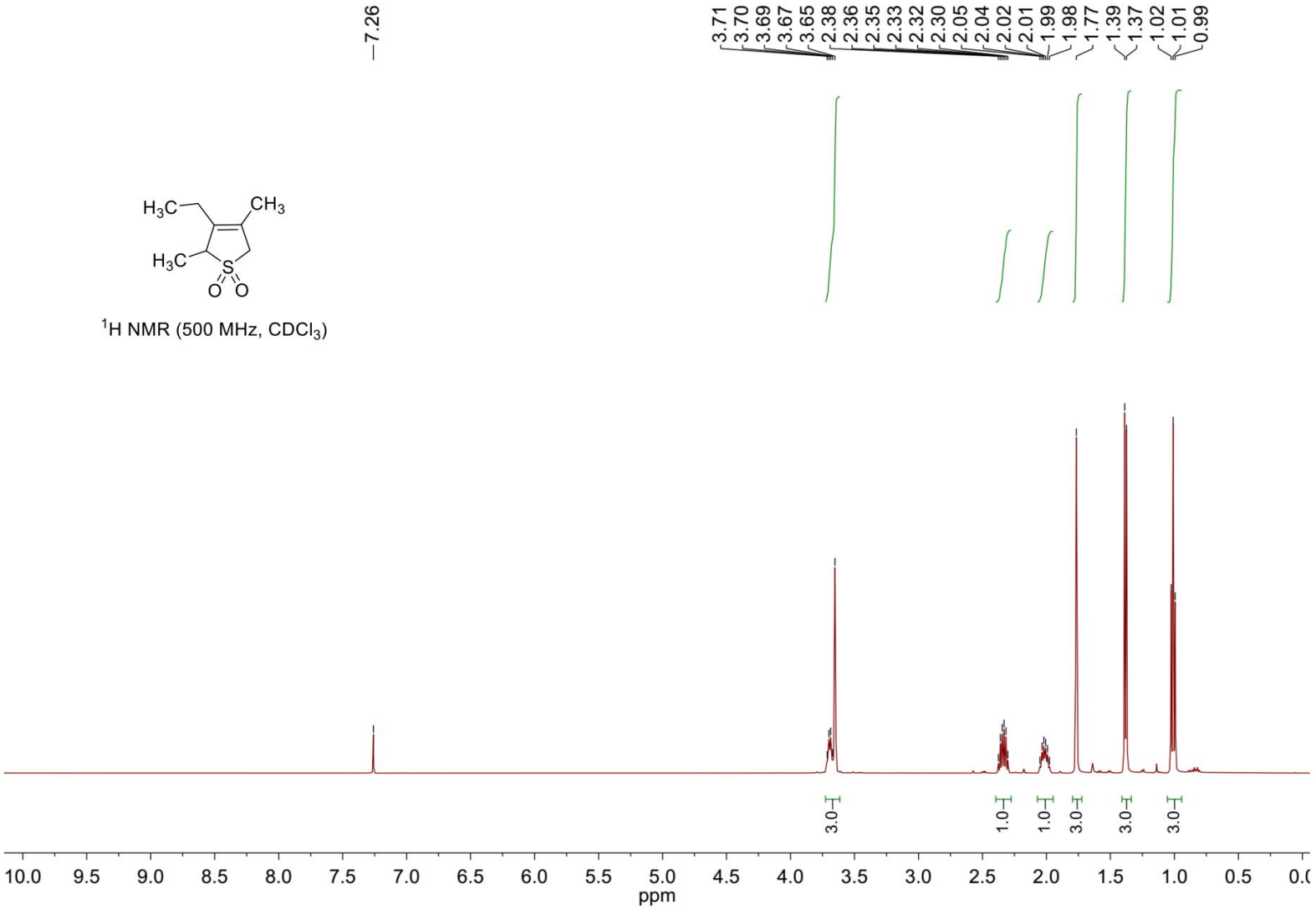
3-Butyl-2-propyl-2,5-dihydrothiophene 1,1-dioxide (19)



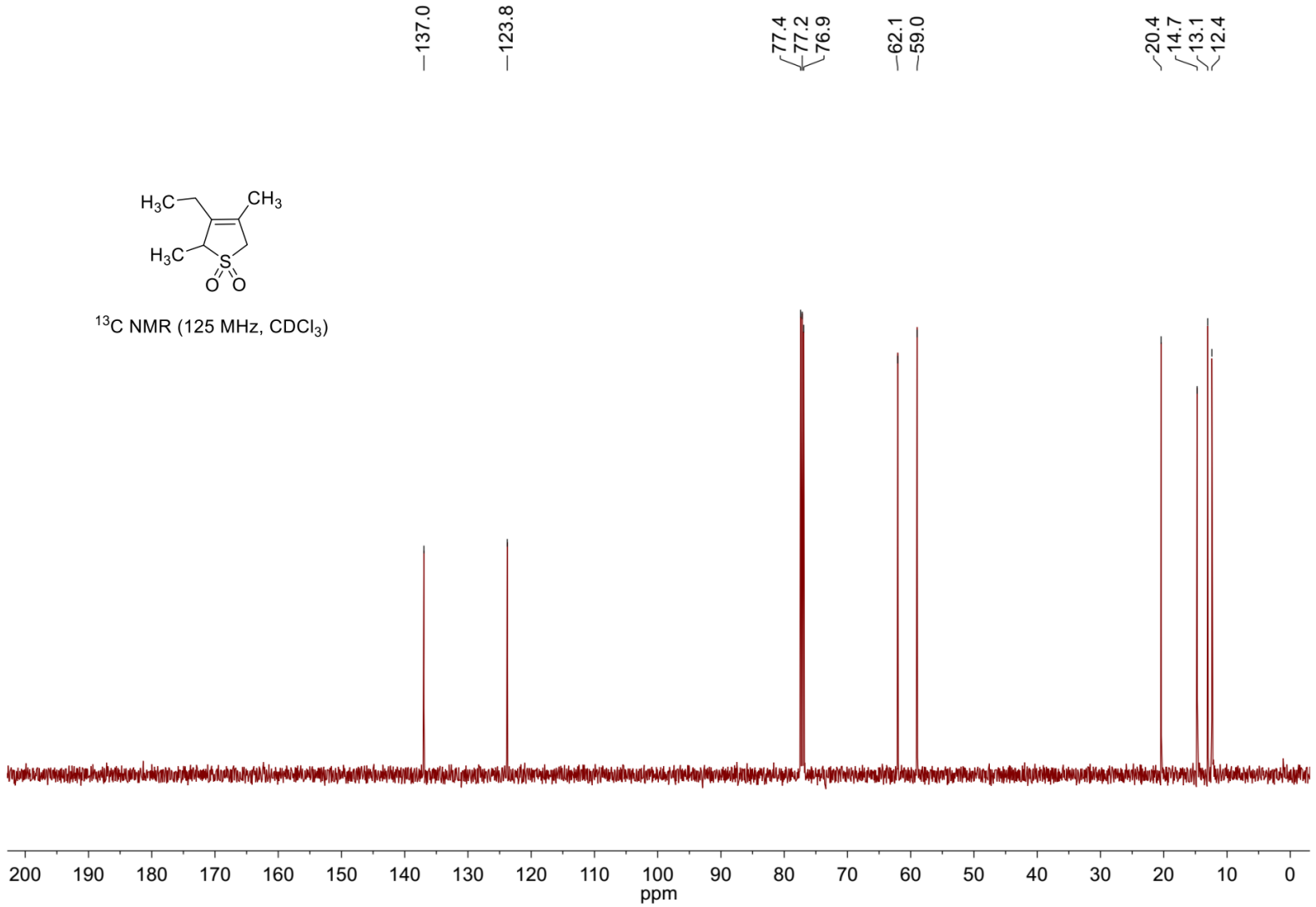
3-Butyl-2-propyl-2,5-dihydrothiophene 1,1-dioxide (19)



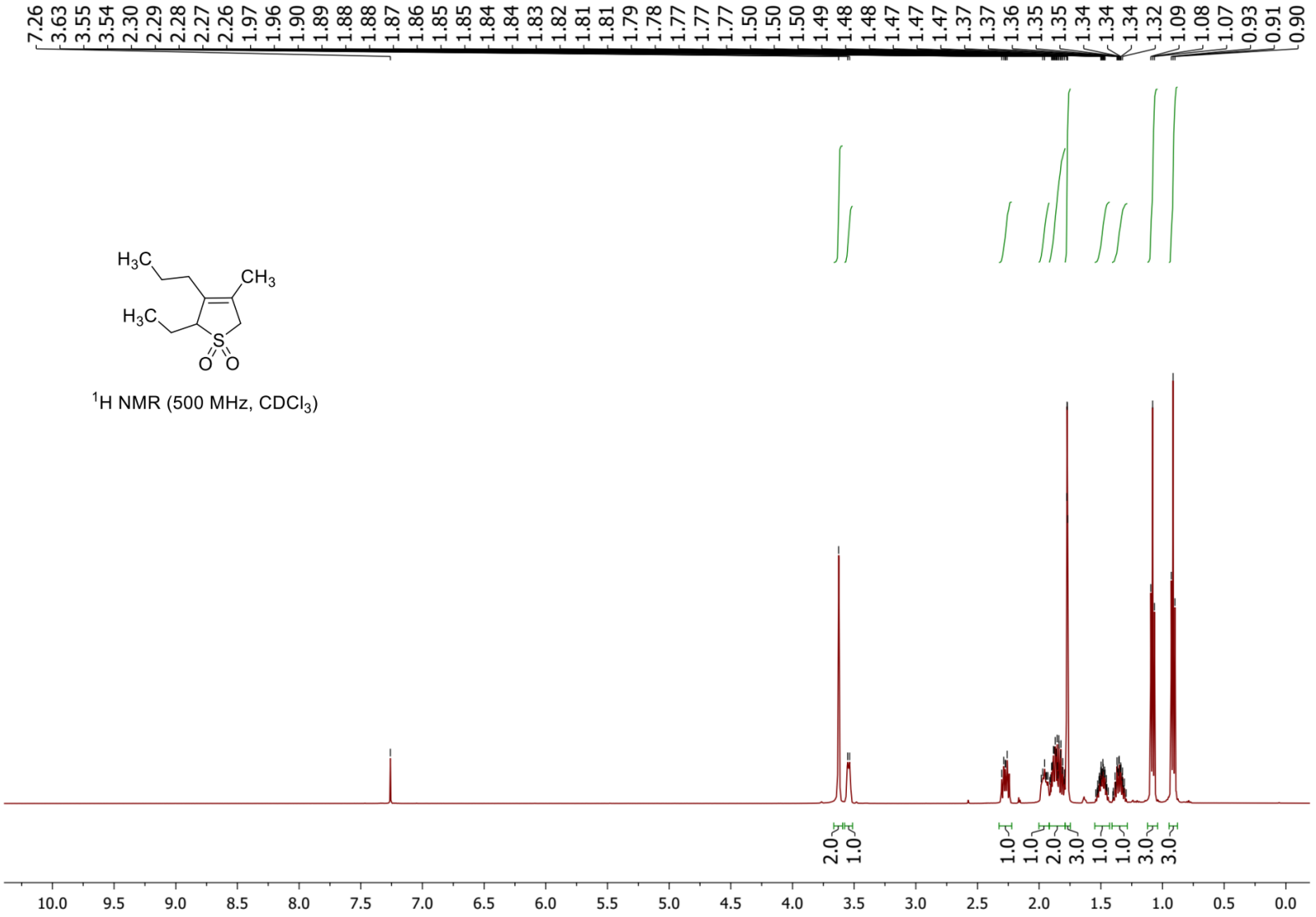
3-Ethyl-2,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide (20)



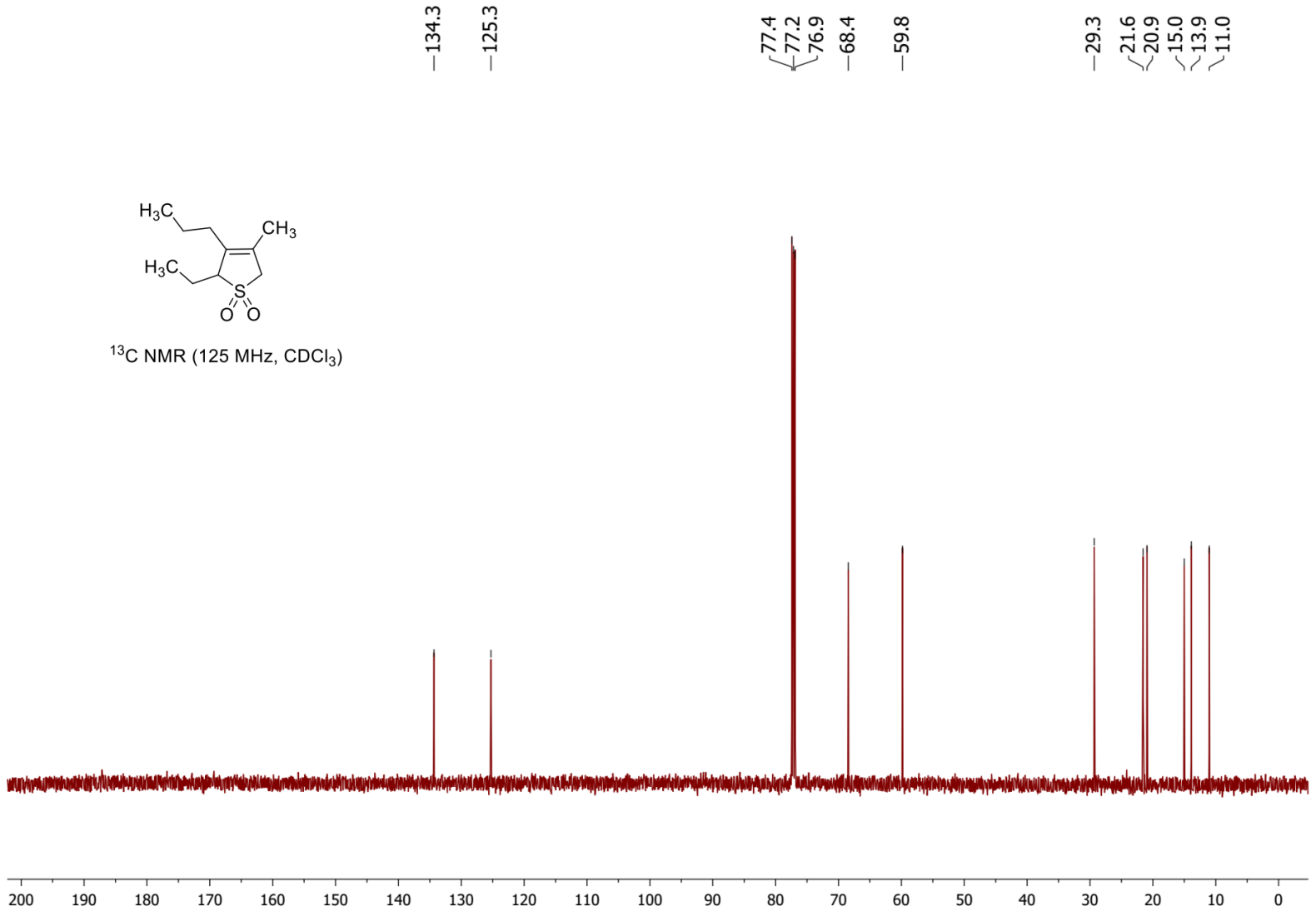
3-Ethyl-2,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide (20)



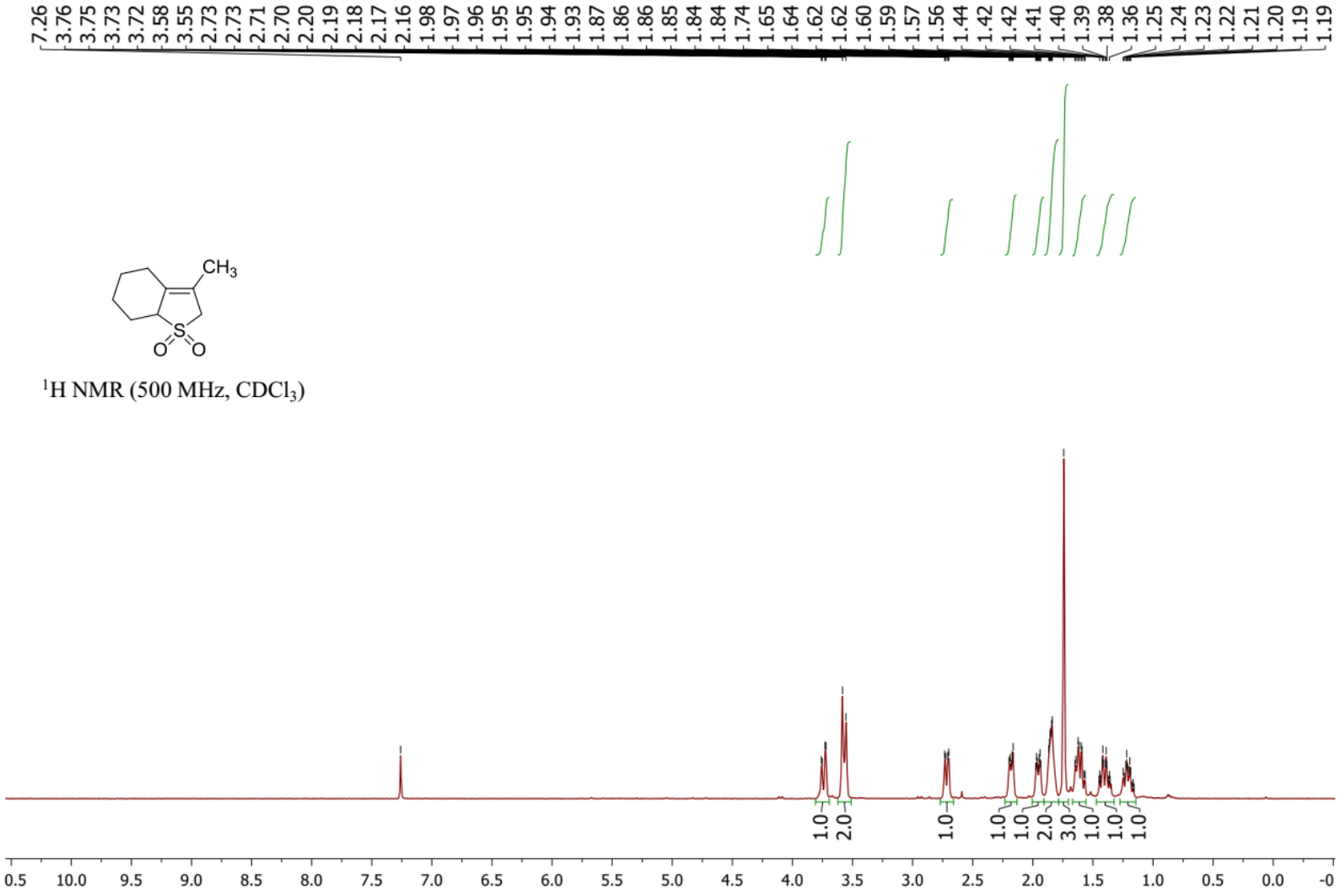
2-Ethyl-4-methyl-3-propyl-2,5-dihydrothiophene 1,1-dioxide (21)



2-Ethyl-4-methyl-3-propyl-2,5-dihydrothiophene 1,1-dioxide (21)

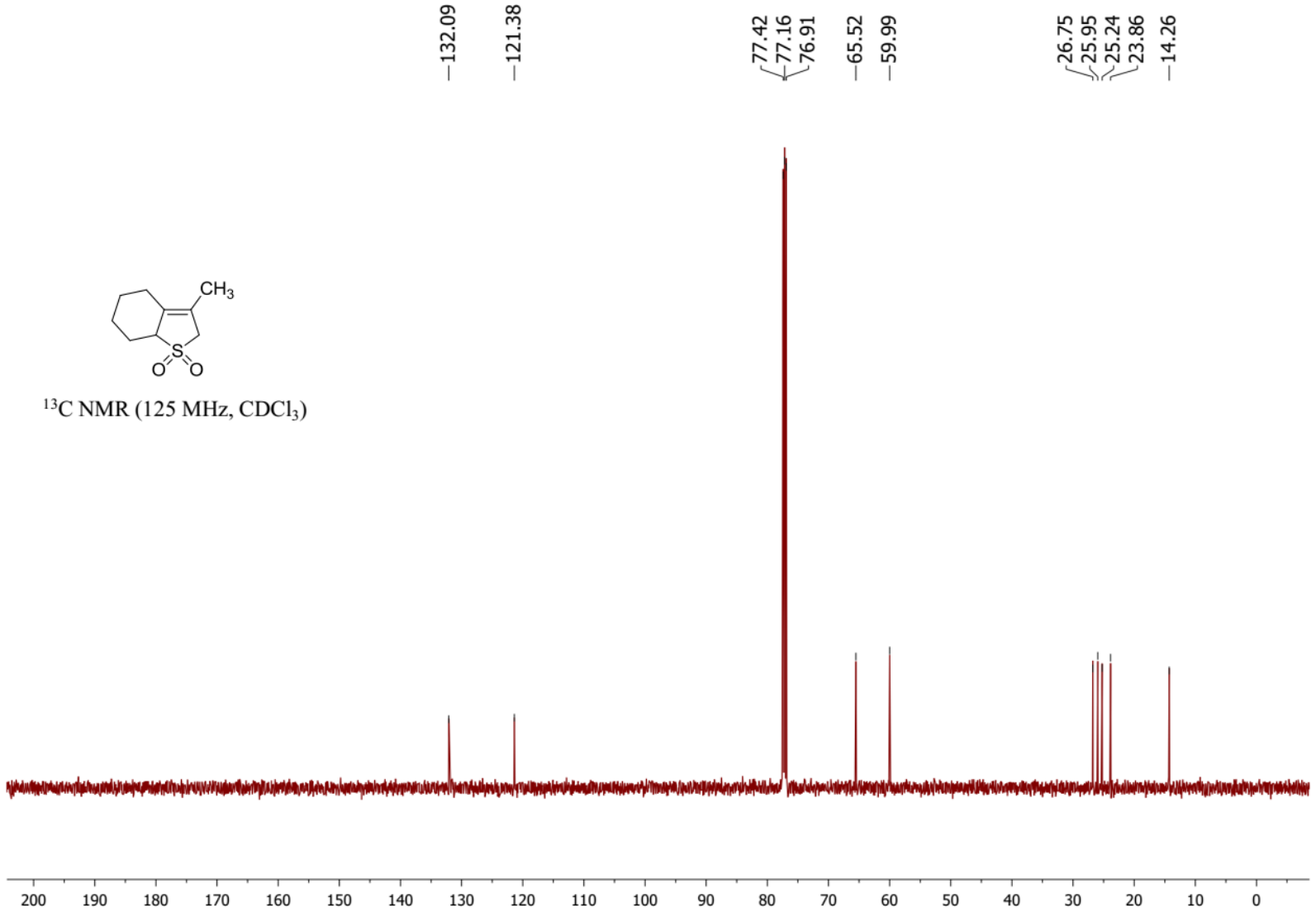


3-Methyl-2,4,5,6,7,7a-hexahydrobenzo[b]thiophene 1,1-dioxide (22)



^{1}H NMR (500 MHz, $CDCl_3$)

3-Methyl-2,4,5,6,7,7a-hexahydrobenzo[b]thiophene 1,1-dioxide (22)



^{13}C NMR (125 MHz, $CDCl_3$)

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