Copper Catalyzed Three-Component Thiocyanosulfonylation of Allenes

Supporting Information

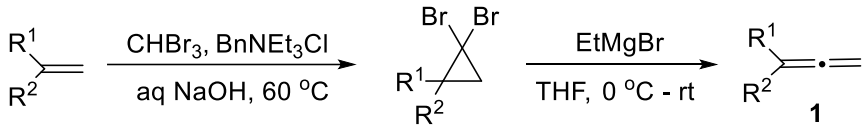
Table of Contents

1.General information.

All commercially available reagents were used without further purification. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (J) were given in Hertz (Hz). Data were reported as s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific Q Exactive ESI (Analyzer: TOF).

2. General procedure for the synthesis of Allenes

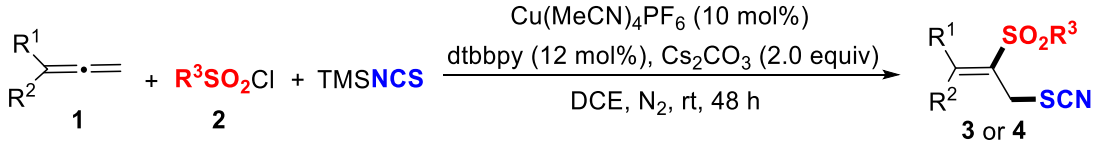
The substrates **1** was synthesized according to the literature.[1]



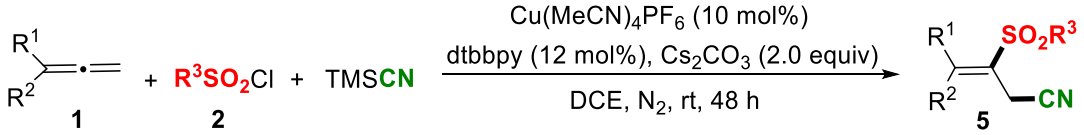
To a solution of alkene (10 mmol), bromoform (15 mmol) and $BnNEt_3Cl$ (0.1 mmol) was added dropwise a solution of 50% NaOH (40 mmol), and the mixture was stirred at room temperature for 1 h, then heated to 60 °C and further stirred until conversion was complete as observed by TLC analysis. Water was added and the aqueous phase was extracted with EA (2 × 50 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography afforded dibromocyclopropane derivatives.

Dibromocyclopropane derivatives (5 mmol) was added in dry THF (5 mL), then the solution cooled to 0 °C. EtMgBr (1.0 M in THF, 7.5 mmol) was added dropwise under nitrogen atmosphere, then the mixture was slowly warmed to room temperature, and stirred at room temperature for 2 hours. Then the reaction was quenched by NH_4Cl solution, and the mixture extracted with EA (2 × 50 mL). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and filtered. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to afford allenes **1**.

3.General procedure for the synthesis of products

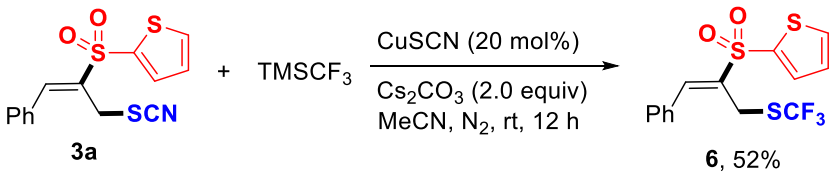


To a reaction tube were added **1** (0.20 mmol), **2** (0.24 mmol), TMSNCS (52.5 mg, 0.40 mmol), $Cu(CH_3CN)_4PF_6$ (7.5 mg, 10 mol%), dtbbpy (6.5 mg, 12 mol%), Cs_2CO_3 (130.3 mg, 0.40 mmol), and DCE (2.0 mL). The solution was degassed and finally backfilled with nitrogen. Then the reaction mixture was stirred at room temperature under nitrogen atmosphere for 48 h. After completion of the reaction, the mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give products **3** or **4**.



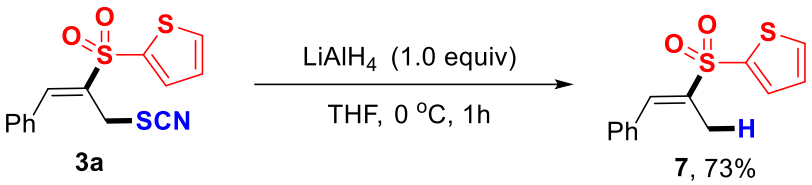
To a reaction tube were added **1** (0.20 mmol), **2** (0.24 mmol), TMSCN (39.7 mg, 0.40 mmol), $Cu(CH_3CN)_4PF_6$ (7.5 mg, 10 mol%), dtbbpy (6.5 mg, 12 mol%), Cs_2CO_3 (130.3 mg, 0.40 mmol), and DCE (2.0 mL). The solution was degassed and finally backfilled with nitrogen. Then the reaction mixture was stirred at room temperature under nitrogen atmosphere for 48 h. After completion of the reaction, the mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give products **5**.

4. Synthetic applications



To a reaction tube were added **3a** (0.20 mmol), $TMSCF_3$ (0.40 mmol), CuSCN (20 mol%), Cs_2CO_3 (0.40 mmol), and MeCN (2.0 mL). The solution was degassed and finally backfilled with nitrogen. Then the reaction mixture was stirred at room temperature for 12 h. After completion of the reaction, the mixture was concentrated

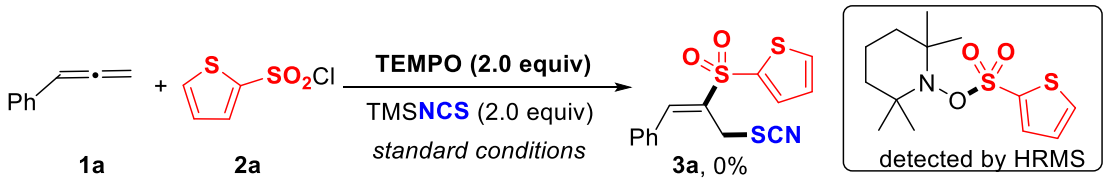
in vacuo. The residue was purified by column chromatography on silica gel to give product **6**.



To a reaction tube were added **3a** (0.20 mmol) and THF (2.0 mL). Then the solution was cooled to 0 °C, and the $LiAlH_4$ (0.20 mmol) was added. The reaction mixture was stirred for 1 h. After completion of the reaction, the mixture was quenched with water, extracted with ethyl acetate (EA), and dried over sodium sulfate. The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel to give product **7**.

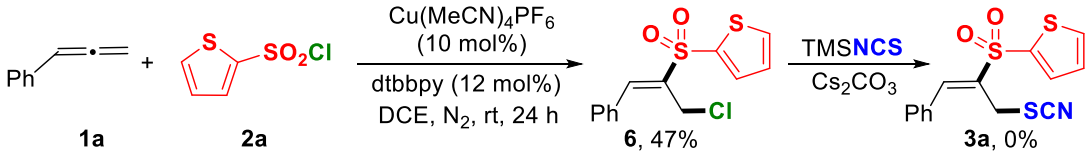
5. Mechanistic studies

5.1 Radical trapping experiment



To a reaction tube were added **1a** (23.2 mg, 0.20 mmol), and **2a** (43.6 mg, 0.24 mmol), TMSNCS (52.5 mg, 0.40 mmol), TEMPO (93.8 mg, 0.60 mmol), $Cu(CH_3CN)_4PF_6$ (7.4 mg, 10 mol%), dtbbpy (6.5 mg, 12 mol%), Cs_2CO_3 (130.3 mg, 0.40 mmol), and DCE (2.0 mL). The mixture was degassed and finally backfilled with nitrogen. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 48 h. The ^{19}F NMR analysis indicated that the formation of product **3a** was not detected and the sulfonyl radical adduct was detected through high-resolution mass spectrometry (HRMS). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{22}NO_3S_2$ 304.1036, found 304.1033.

5.2 Control experiment



To a reaction tube were added **1a** (46.4 mg, 0.40 mmol), **2a** (87.6 mg, 0.48 mmol)，$Cu(MeCN)_4PF_6$ (14.8 mg, 10 mol%), dtbbpy (12.8 mg, 12 mol%), and DCE (4.0 mL). The mixture was degassed and finally backfilled with nitrogen. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 24 h. After completion of the reaction, the mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give product **6**. Then **6** (0.20 mmol), TMSNSC (0.40 mmol), Cs_2CO_3 (0.40 mmol), and DCE (2.0 mL) were added to a reaction tube. The mixture was stirred at room temperature under nitrogen atmosphere for 24 h. **3a** was not detected by TLC.

5.3 Cyclic Voltammetry experiments

Cyclic Voltammetry was performed on a CHI 660E electrochemical analyzer. CV measurement of starting material (0.001 M) was carried out in 0.1 M of Bu_4NPF_6/MeCN at a scan rate of 50 mV/s with the protection of N_2. The working electrode is a glassy carbon, the counter electrode is a Pt wire, and the reference electrode is Ag/AgCl (3.0 M KCl). As showed in Figure S1, the reduction potentials of RSO_2Cl (**2a)**, LCu [$Cu(MeCN)_4PF_6$+dtbbpy], TMSNCS, and the LCu+TMSNCS complex are as follows: -0.907 V (-0.876 V SCE), -0.979 V (-0.948 V SCE), -0.77 V (-0.739 V SCE), -1.053 V (-1.022 V SCE).

These results confirm that the LCu(I) complex possess sufficient reducing power to activate RSO_2Cl via single-electron transfer (SET), supporting the proposed mechanism (path a, Figure S2). On the other hand, the results also indicate that the [LCu(I) + TMSNCS] adduct can reduce the RSO_2Cl, raising the possibility that LCu(I) first binds with TMSNCS to form the adduct, which subsequently undergoes SET with RSO_2Cl (path b, Figure S2).

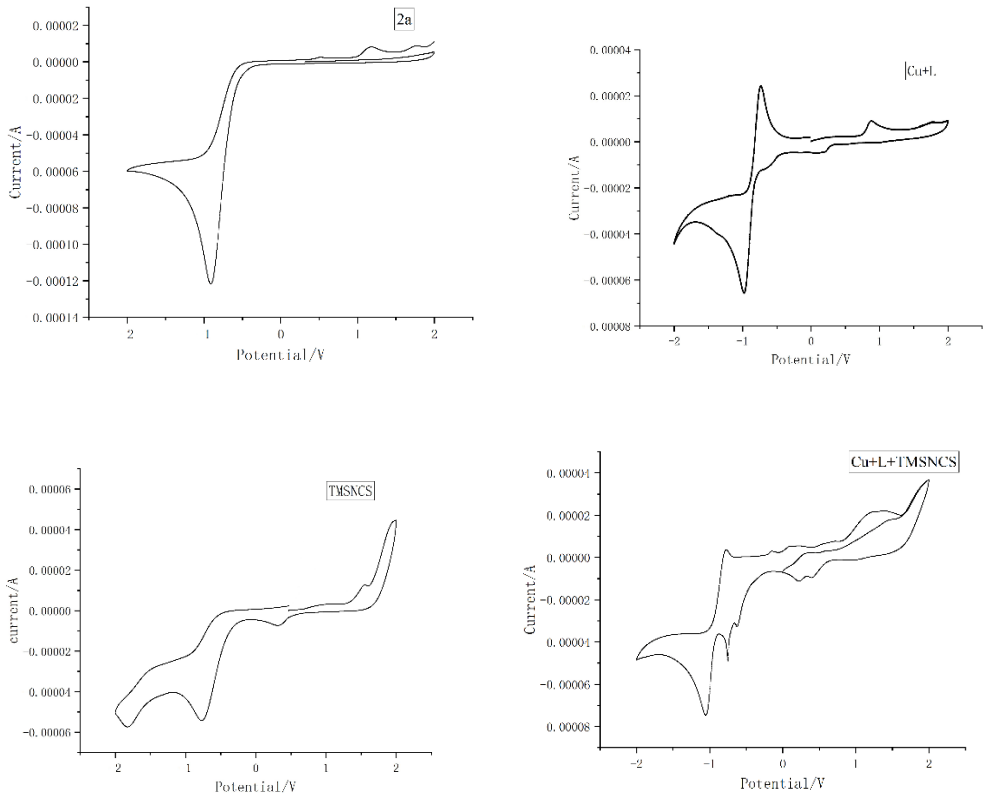


Figure S1. Cyclic voltammograms of **2a**, Cu+L, TMSNCS, and Cu+L+TMSNCS

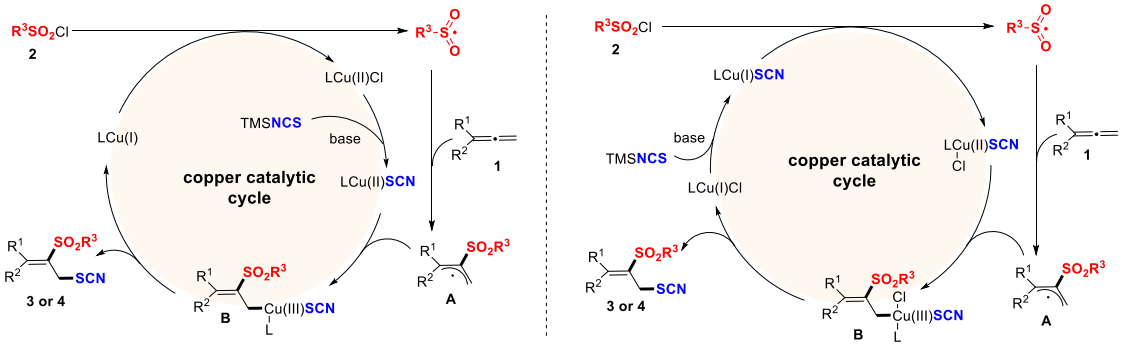
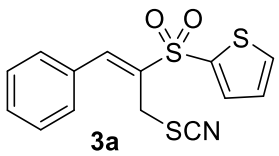


Figure S2. Proposed mechanism

6. Characterization data

(E)-2-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3a)

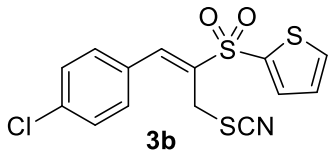


3a

White solid (47.4 mg, 74%); The product is purified with silica gel chromatography

(eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 1H), 7.86 – 7.74 (m, 2H), 7.53 – 7.45 (m, 5H), 7.23 – 7.14 (m, 1H), 4.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 139.8, 135.2, 135.1, 135.0, 131.7, 130.9, 129.5, 129.3, 128.3, 110.9, 30.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}NO_2S_3$ 322.0025, found 322.0032.

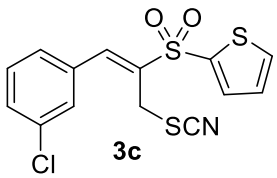
(E)-2-((1-(4-chlorophenyl)-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3b)



3b

White solid (50.8 mg, 71%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.87 – 7.76 (m, 2H), 7.54 – 7.39 (m, 4H), 7.20 (t, J = 4.4 Hz, 1H), 4.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 139.6, 137.3, 135.7, 135.5, 135.3，130.8, 130.2, 129.7, 128.4, 110.8, 30.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}ClNO_2S_3$ 355.9635, found 355.9631.

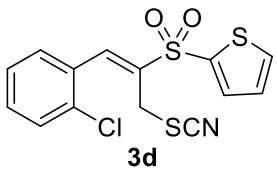
(E)-2-((1-(3-chlorophenyl)-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3c)



3c

White solid (48.2 mg, 68%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.84 – 7.79 (m, 2H), 7.48 – 7.36 (m, 4H), 7.25 – 7.18 (m, 1H), 4.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 139.3, 136.8, 135.6, 135.4, 135.2, 133.4, 130.8, 130.5, 129.3, 128.4, 127.2, 110.6, 29.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}ClNO_2S_3$ 355.9635, found 355.9651.

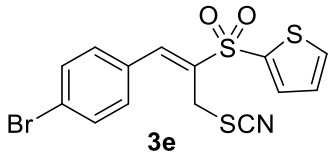
(E)-2-((1-(2-chlorophenyl)-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3d)



3d

White solid (51.4 mg, 72%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.87 – 7.78 (m, 2H), 7.51 – 7.37 (m, 4H), 7.23 – 7.18 (m, 1H), 4.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.5, 138.4, 135.6, 135.3, 134.4, 131.6, 130.6, 130.2, 129.2, 128.3, 127.4, 110.8, 29.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}ClNO_2S_3$ 355.9635, found 355.9639.

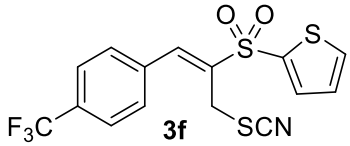
(E)-2-((1-(4-bromophenyl)-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (**3e**)



3e

White solid (60.6 mg, 76%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 1H), 7.84 – 7.75 (m, 2H), 7.68 – 7.56 (m, 2H), 7.43 – 7.31 (m, 2H), 7.24 – 7.16 (m, 1H), 4.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 139.6, 135.8, 135.5, 135.4, 132.7, 131.0, 130.6, 128.4, 125.8, 110.8, 30.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}BrNO_2S_3$ 399.9130, found 399.9155.

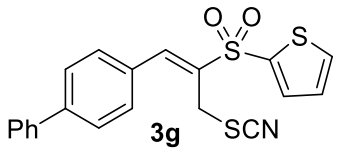
(E)-2-((3-thiocyanato-1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)sulfonyl)thiophene (**3f**)



3f

White solid (56.6 mg, 73%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.83 (d, J = 4.3 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 4.4 Hz, 1H), 4.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.4, 138.0, 135.8, 135.6, 135.3, 132.4 (q, J = 32.9 Hz), 129.6, 128.5, 126.3 (q, J = 3.7 Hz), 123.4 (q, J = 270.9 Hz), 110.6, 29.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{11}F_3NO_2S_3$ 389.9899, found 389.9912.

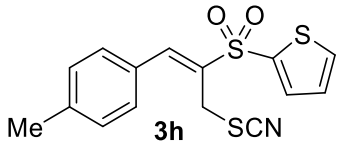
(E)-2-((1-([1,1'-biphenyl]-4-yl)-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (**3g**)



3g

White solid (54.6 mg, 69%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.85 – 7.71 (m, 4H), 7.67 – 7.57 (m, 4H), 7.54 – 7.38 (m, 3H), 7.24 – 7.17 (m, 1H), 4.35 (s, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.5, 139.9, 139.3, 135.2, 135.1, 134.2, 130.5, 130.4, 129.0, 128.3, 128.2, 127.9, 127.0, 111.0, 30.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}NO_2S_3$ 398.0338, found 398.0337.

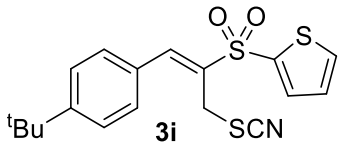
(E)-2-((3-thiocyanato-1-(p-tolyl)prop-1-en-2-yl)sulfonyl)thiophene (3h)



3h

White solid (51.1 mg, 76%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 1H), 7.83 – 7.73 (m, 2H), 7.46 – 7.37 (m, 2H), 7.36 – 7.26 (m, 2H), 7.22 – 7.12 (m, 1H), 4.30 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.9, 140.0, 135.1, 135.0, 133.5, 130.1, 129.8, 128.9, 128.3, 111.1, 30.7, 21.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NO_2S_3$ 336.0181, found 336.0198.

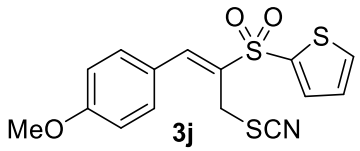
(E)-2-((1-(4-(tert-butyl)phenyl)-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3i)



3i

White solid (52.5 mg, 70%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 1H), 7.82 – 7.73 (m, 2H), 7.57 – 7.44 (m, 4H), 7.22 – 7.14 (m, 1H), 4.31 (s, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 143.9, 140.0, 135.1, 135.0, 133.5, 129.8, 128.8, 128.2, 126.4, 111.1, 35.0, 31.0, 30.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}NO_2S_3$ 378.0651, found 378.0619.

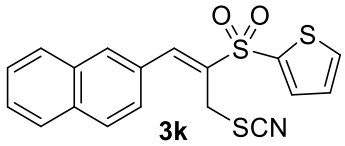
(E)-2-((1-(4-methoxyphenyl)-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3j)



3j

White solid (50.8 mg, 72%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.85 – 7.71 (m, 2H), 7.61 – 7.47 (m, 2H), 7.23 – 7.14 (m, 1H), 7.07 – 6.96 (m, 2H), 4.34 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 143.5, 140.3, 134.9, 134.8, 132.2, 131.4, 128.2, 124.1, 114.9, 111.1, 55.5, 31.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NO_3S_3$ 352.0130, found 352.0133.

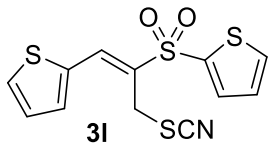
(E)-2-((1-(naphthalen-2-yl)-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3k)



3k

White solid (48.4 mg, 65%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.05 (s, 1H), 8.00 – 7.91 (m, 2H), 7.90 – 7.74 (m, 3H), 7.63 – 7.50 (m, 3H), 7.25 – 7.17 (m, 1H), 4.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 140.0, 135.3, 135.2, 135.0, 134.0, 133.0, 130.8, 129.3, 129.2, 128.9, 128.4, 128.2, 127.8, 127.3, 125.6, 111.2, 30.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{14}NO_2S_3$ 372.0181, found 372.0194.

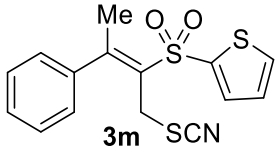
(E)-2-((3-thiocyanato-1-(thiophen-2-yl)prop-1-en-2-yl)sulfonyl)thiophene (3l)



3l

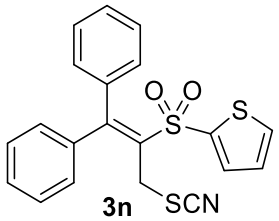
White solid (43.5 mg, 66%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.80 – 7.70 (m, 3H), 7.54 – 7.48 (m, 1H), 7.25 – 7.11 (m, 2H), 4.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 136.1, 135.8, 135.0, 134.8, 134.2, 133.5, 129.6, 128.4, 128.3, 111.1, 30.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{10}NO_2S_4$ 327.9589, found 327.9592.

(E)-2-((3-phenyl-1-thiocyanatobut-2-en-2-yl)sulfonyl)thiophene (3m)



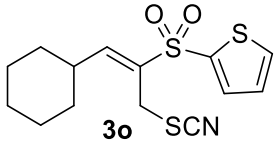
White solid (47.5 mg, 71%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 1H), 7.81 – 7.74 (m, 1H), 7.50 – 7.33 (m, 3H), 7.23 – 7.11 (m, 3H), 3.99 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.5, 140.3, 134.29, 134.25, 129.03, 128.96, 127.7, 126.5, 111.6, 34.2, 24.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NO_2S_3$ 336.0181, found 336.0166.

2-((1,1-diphenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3n)



White solid (55.7 mg, 70%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 1H), 7.40 – 7.29 (m, 3H), 7.25 – 7.22 (m, 1H), 7.19 – 7.12 (m, 4H), 7.08 – 7.01 (m, 2H), 6.92 – 6.85 (m, 1H), 6.77 – 6.68 (m, 1H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 140.7, 139.0, 137.5, 137.2, 135.1, 134.2, 129.3, 129.0, 128.84, 128.81, 128.5, 127.8, 126.8, 110.7, 34.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}NO_2S_3$ 398.0338, found 398.0317.

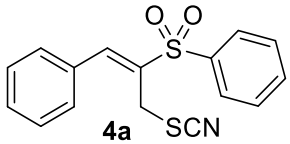
(E)-2-((1-cyclohexyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (3o)



Light yellow oil (37.0 mg, 56%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 5.1 Hz, 1H), 7.69 (d, J = 3.7 Hz, 1H), 7.15 (t, J = 4.7 Hz, 1H), 7.07 (d, J = 10.8 Hz, 1H), 4.01 (s, 2H), 2.45 – 2.32 (m, 1H), 1.83 – 1.64 (m, 5H), 1.39 – 1.19 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 140.6, 134.9, 134.7, 134.1,

128.2, 111.2, 38.9, 31.8, 28.9, 25.3, 24.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{114}H_{18}NO_2S_3$ 328.0494, found 328.0498.

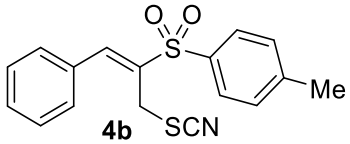
(E)-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)benzene (4a)



4a

White solid (47.8 mg, 76%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 1H), 8.02 – 7.92 (m, 2H), 7.75 – 7.55 (m, 3H), 7.55 – 7.46 (m, 5H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.8, 134.5, 134.2, 131.9, 131.0, 129.63, 129.58, 129.4, 128.4, 110.9, 30.4; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{14}NO_2S_2$ 316.0460, found 316.0443.

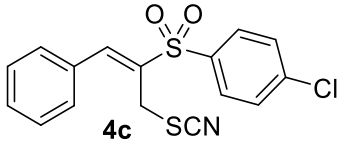
(E)-1-methyl-4-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)benzene (4b)



4b

White solid (51.2 mg, 78%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.51 – 7.48 (m, 5H), 7.38 (d, J = 7.7 Hz, 2H), 4.17 (s, 2H), 2.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 143.8, 135.6, 134.7, 131.9, 130.8, 130.2, 129.4, 129.2, 128.3, 110.0, 30.3, 21.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NO_2S_3$ 336.0181, found 336.0134.

(E)-1-chloro-4-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)benzene (4c)

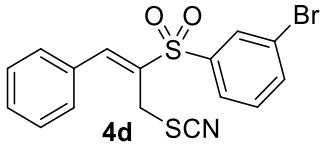


4c

White solid (49.2 mg, 70%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.51 – 7.48 (m, 5H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 140.9, 137.4, 134.1, 131.6, 131.0, 129.8, 129.7, 129.5, 129.3, 110.6, 30.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}ClNO_2S_3$

355.9635, found 355.9657.

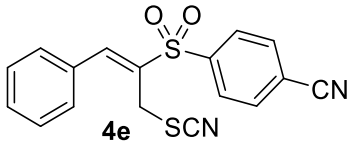
(E)-1-bromo-3-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)benzene (4d)



4d

White solid (57.8 mg, 73%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.02 (m, 2H), 7.96 – 7.88 (m, 1H), 7.86 – 7.73 (m, 1H), 7.55 – 7.43 (m, 6H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 140.8, 137.1, 133.8, 131.6, 131.2, 131.0, 130.9, 129.6, 129.3, 126.8, 123.5 110.6, 30.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}BrNO_2S_3$ 399.9130, found 399.9103.

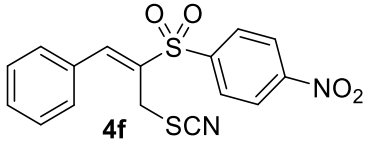
(E)-4-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)benzonitrile (4e)



4e

White solid (47.0 mg, 69%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.15 – 8.07 (m, 2H), 7.96 – 7.84 (m, 2H), 7.58 – 7.47 (m, 5H), 4.22 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 143.6, 133.4, 133.2, 131.5, 131.4, 129.7, 129.5, 128.9, 117.8, 116.9, 110.2, 30.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{13}N_2O_2S_2$ 341.0413, found 341.0446.

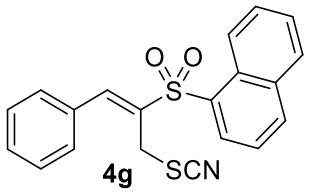
(E)-1-nitro-4-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)benzene (4f)



4f

White solid (47.1 mg, 65%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.36 (m, 2H), 8.26 – 8.13 (m, 3H), 7.63 – 7.38 (m, 5H), 4.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 146.8, 145.2, 133.4, 131.5, 131.4, 129.7, 129.5, 124.7, 110.2, 30.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}F_3N_2O_4S_2$ 361.0311, found 361.0301.

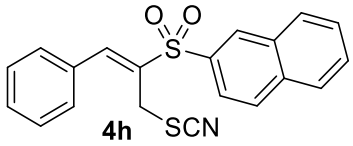
(E)-1-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)naphthalene (4g)



4g

White solid (50.0 mg, 74%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.54 (m, 1H), 8.54 – 8.46 (m, 1H), 8.32 – 8.27 (m, 1H), 8.23 – 8.13 (m, 1H), 8.05 – 7.88 (m, 1H), 7.77 – 7.56 (m, 3H), 7.49 – 7.46 (m, 5H), 4.08 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.1, 134.4, 134.2, 132.1, 131.8, 131.7, 130.8, 129.4, 129.34, 129.26, 128.8, 128.4, 127.2, 124.6, 123.7, 110.9, 30.3; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{16}NO_2S_2$ 366.0617, found 366.0662.

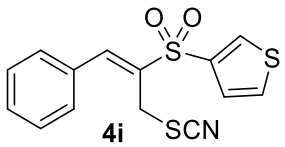
(E)-1-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)naphthalene (4h)



4h

White solid (46.8 mg, 64%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.25 – 8.14 (m, 1H), 8.11 – 7.83 (m, 4H), 7.74 – 7.63 (m, 2H), 7.55 – 7.44 (m, 5H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 135.35, 135.28, 134.4, 132.0, 131.8, 130.9, 130.3, 130.0, 129.6, 129.5, 129.4, 129.3, 127.93, 127.87, 122.5, 110.9, 30.4; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{16}NO_2S_2$ 366.0617, found 366.0655.

(E)-3-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)thiophene (4i)

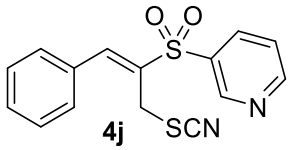


4i

White solid (46.2 mg, 72%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.10 (s, 1H), 7.58 – 7.44 (m, 6H), 7.42 – 7.37 (m, 1H), 4.24 (s, 2H).. ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 138.9, 134.6, 133.7, 131.7, 130.9, 129.5, 129.3, 129.0, 125.9, 110.9, 30.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}NO_2S_3$ 322.0025,

found 322.0042.

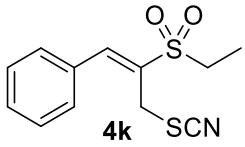
(E)-3-((1-phenyl-3-thiocyanatoprop-1-en-2-yl)sulfonyl)pyridine (4j)



4j

White solid (29.4 mg, 46%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 – 9.16 (m, 1H), 8.98 – 8.75 (m, 1H), 8.34 – 8.23 (m, 1H), 8.21 – 8.12 (m, 1H), 7.60 – 7.33 (m, 5H), 4.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 149.2, 146.0, 136.0, 135.8, 134.0, 131.5, 131.3, 129.6, 129.4, 124.0, 110.3, 30.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}N_2O_2S_2$ 317.0413, found 317.0428.

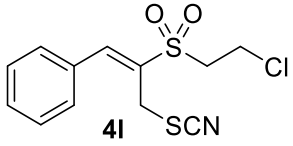
(E)-(2-(ethylsulfonyl)-3-thiocyanatoprop-1-en-1-yl)benzene (4k)



4k

White solid (40.1 mg, 75%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.52 – 7.47 (m, 5H), 4.31 (s, 2H), 3.27 (q, J = 7.2, 6.7 Hz, 2H), 1.45 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 132.8, 131.8, 130.9, 129.4, 129.3, 110.6, 50.2, 30.3, 7.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}NO_2S_2$ 268.0460, found 268.0445.

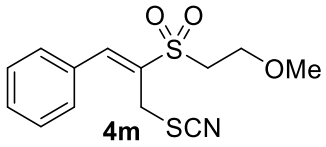
(E)-(2-((2-chloroethyl)sulfonyl)-3-thiocyanatoprop-1-en-1-yl)benzene (4l)



4l

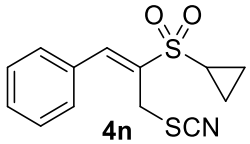
White solid (36.7 mg, 61%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.55 – 7.49 (m, 5H), 4.34 (s, 2H), 3.94 (t, J = 7.2 Hz, 2H), 3.70 (t, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 133.5, 131.6, 131.3, 129.5, 129.4, 110.4, 57.7, 35.5, 30.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}ClNO_2S_2$ 302.0071, found 302.0050.

(E)-(2-((2-methoxyethyl)sulfonyl)-3-thiocyanatoprop-1-en-1-yl)benzene (4m)



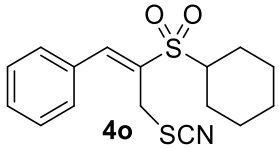
White solid (40.6 mg, 68%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.54 – 7.46 (m, 5H), 4.32 (s, 2H), 3.95 – 3.77 (m, 2H), 3.56 – 3.43 (m, 2H)，3.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 134.3, 131.9, 130.8, 129.28, 129.26, 111.2, 65.7, 58.8, 55.9, 30.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}NO_3S_2$ 298.0566, found 298.0537.

(E)-(2-(cyclopropylsulfonyl)-3-thiocyanatoprop-1-en-1-yl)benzene (4n)



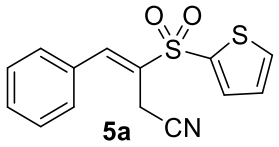
White solid (39.9 mg, 71%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.55 – 7.43 (m, 5H), 4.34 (s, 2H), 2.76 – 2.50 (m, 1H), 1.44 – 1.32 (m, 2H), 1.26 – 1.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.6, 132.0, 130.8, 129.4, 129.3, 110.8, 32.2, 30.4, 6.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}NO_2S_2$ 280.0460, found 280.0487.

(E)-(2-(cyclohexylsulfonyl)-3-thiocyanatoprop-1-en-1-yl)benzene (4o)



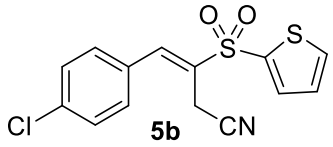
White solid (43.1 mg, 67%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.53 – 7.44 (m, 5H), 4.30 (s, 2H), 3.23 – 2.99 (m, 1H), 2.35 – 2.13 (m, 2H), 2.04 – 1.88 (m, 2H), 1.77 – 1.67 (m, 1H), 1.65 – 1.49 (m, 2H), 1.44 – 1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 131.9, 131.6, 130.8, 129.3, 129.2, 110.8, 62.6，30.6, 24.95, 24.95, 24.90; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NO_2S_2$ 322.0930, found 322.0903.

(E)-4-phenyl-3-(thiophen-2-ylsulfonyl)but-3-enenitrile (5a)



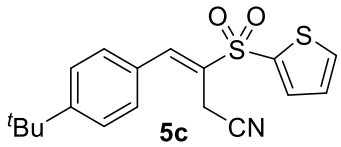
White solid (37.1 mg, 64%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.88 – 7.78 (m, 2H), 7.56 – 7.42 (m, 5H), 7.26 – 7.18 (m, 1H), 3.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 139.3, 135.6, 135.3, 131.8, 131.5, 130.8, 129.4, 129.3, 128.4, 115.1, 16.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}NO_2S_2$ 290.0304, found 290.0336.

(E)-4-(4-chlorophenyl)-3-(thiophen-2-ylsulfonyl)but-3-enenitrile (5b)



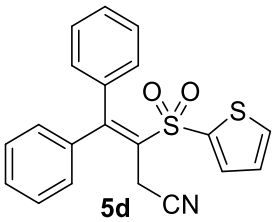
White solid (37.8 mg, 58%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.89 – 7.76 (m, 2H), 7.53 – 7.36 (m, 4H), 7.27 – 7.19 (m, 1H), 3.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 139.0, 137.2, 135.8, 135.5, 132.1, 130.7, 130.2, 129.7, 128.6, 114.9, 16.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}ClNO_2S_2$ 323.9914, found 323.9902.

(E)-4-(4-(tert-butyl)phenyl)-3-(thiophen-2-ylsulfonyl)but-3-enenitrile (5c)



White solid (44.1 mg, 64%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83 – 7.75 (m, 2H), 7.57 – 7.47 (m, 2H), 7.46 – 7.38 (m, 2H), 7.24 – 7.16 (m, 1H), 3.68 (s, 2H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 142.3, 139.5, 135.4, 135.1, 130.3, 129.6, 128.9, 128.4, 126.3, 115.2, 35.0, 31.0, 16.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}NO_2S_2$ 346.0930, found 346.0911.

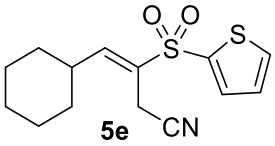
4,4-diphenyl-3-(thiophen-2-ylsulfonyl)but-3-enenitrile (5d)



5d

White solid (44.0 mg, 60%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.42 – 7.34 (m, 3H), 7.33 – 7.18 (m, 5H), 7.19 – 7.12 (m, 1H), 7.10 – 7.03 (m, 2H), 6.94 – 6.83 (m, 1H), 3.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 140.5, 139.5, 137.4, 135.0, 134.5, 132.6, 129.5, 129.0, 128.9, 128.8, 127.8, 127.6, 127.2, 117.0, 20.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}NO_2S_2$ 366.0617, found 366.0654.

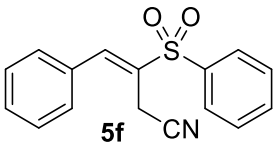
(E)-4-cyclohexyl-3-(thiophen-2-ylsulfonyl)but-3-enenitrile (5e)



5e

Light yellow oil (27.6 mg, 47%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 4.9 Hz, 1H), 7.71 (d, J = 3.7 Hz, 1H), 7.17 (t, J = 4.6 Hz, 1H), 7.01 (d, J = 10.4 Hz, 1H), 3.47 (s, 2H), 2.42 – 2.27 (m, 1H), 1.85 – 1.67 (m, 5H), 1.39 – 1.11 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 139.6, 135.2, 134.9, 130.2, 128.3, 115.1, 38.6, 31.0, 25.4, 25.0, 14.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}NO_2S_2$ 295.0701, found 295.0708.

(E)-4-phenyl-3-(phenylsulfonyl)but-3-enenitrile (5f)

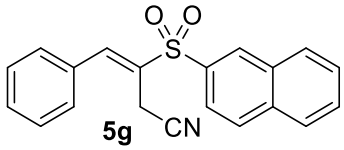


5f

White solid (35.0 mg, 62%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.02 – 7.94 (m, 2H), 7.74 – 7.65 (m, 1H), 7.66 – 7.56 (m, 2H), 7.52 – 7.39 (m, 5H), 3.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 138.3, 134.3, 131.9, 131.0,

130.8, 129.7, 129.4, 129.3, 128.4, 115.1, 16.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NO_2S$ 284.0740, found 284.0791.

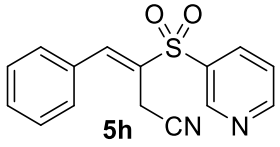
(E)-3-(naphthalen-2-ylsulfonyl)-4-phenylbut-3-enenitrile (5g)



5g

White solid (42.8 mg, 65%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.16 (s, 1H), 8.06 – 7.99 (m, 2H), 7.96 – 7.85 (m, 2H), 7.72 – 7.61 (m, 2H), 7.50 – 7.41 (m, 5H), 3.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 135.4, 134.9, 132.1, 131.9, 130.9, 130.7, 130.5, 130.1, 129.6, 129.4, 129.2, 128.0, 127.8, 122.5, 115.2, 16.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}NO_2S$ 334.0896, found 334.0872.

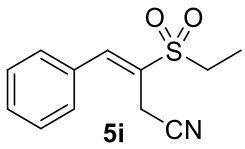
(E)-4-phenyl-3-(pyridin-3-ylsulfonyl)but-3-enenitrile (5h)



5h

White solid (27.7 mg, 49%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.90 (s, 1H), 8.30 – 8.22 (m, 1H), 8.13 (d, J = 2.8 Hz, 1H), 7.59 – 7.41 (m, 6H), 3.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 149.2, 144.3, 136.0, 135.4, 131.5, 131.2, 130.5, 129.5, 129.4, 124.1, 114.9, 16.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}N_2O_2S$ 285.0692, found 285.0637.

(E)-3-(ethylsulfonyl)-4-phenylbut-3-enenitrile (5i)

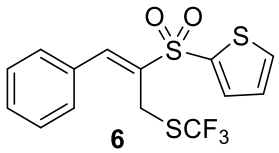


5i

White solid (19.6 mg, 42%); The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.55 – 7.43 (m, 5H), 3.74 (s, 2H), 3.25 (q, J = 7.3 Hz, 2H), 1.43 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 131.9, 130.9, 129.35, 129.35, 128.7, 115.9,

49.2, 16.5, 7.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}NO_2S$ 236.0740, found 236.0748.

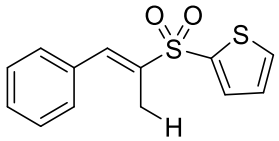
(E)-2-((1-phenyl-3-((trifluoromethyl)thio)prop-1-en-2-yl)sulfonyl)thiophene (**6**)



6

White solid; The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.82 – 7.73 (m, 2H), 7.59 – 7.52 (m, 2H), 7.52 – 7.43 (m, 3H), 7.22 – 7.15 (m, 1H), 4.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.1, 135.1, 135.00, 134.98, 132.2, 130.8, 130.1 (q, J = 305.8 Hz), 129.7, 129.1, 128.1, 26.2 (q, J = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.5; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{11}F_3NaO_2S_3$ 386.9765, found 386.9761.

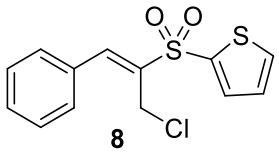
(E)-2-((1-phenylprop-1-en-2-yl)sulfonyl)thiophene (**7**)



7

White solid; The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.73 – 7.69 (m, 2H), 7.43 – 7.37 (m, 5H), 7.17 – 7.12 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 137.9, 137.2, 134.1, 133.9, 133.7, 129.6, 129.4, 128.7, 127.8, 13.2; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{12}NaO_2S_2$ 287.0171, found 287.0170.

(E)-2-((3-chloro-1-phenylprop-1-en-2-yl)sulfonyl)thiophene (**8**)



8

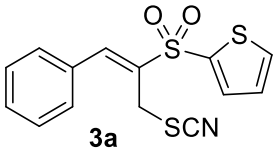
White solid; The product is purified with silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.84

– 7.78 (m, 1H), 7.80 – 7.73 (m, 1H), 7.68 – 7.61 (m, 2H), 7.53 – 7.46 (m, 3H), 7.22 – 7.15 (m, 1H), 4.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 141.0, 137.8, 134.8, 134.6, 132.2, 130.8, 130.0, 129.1, 127.9, 37.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}ClO_2S_2$ 298.9962, found 298.9901.

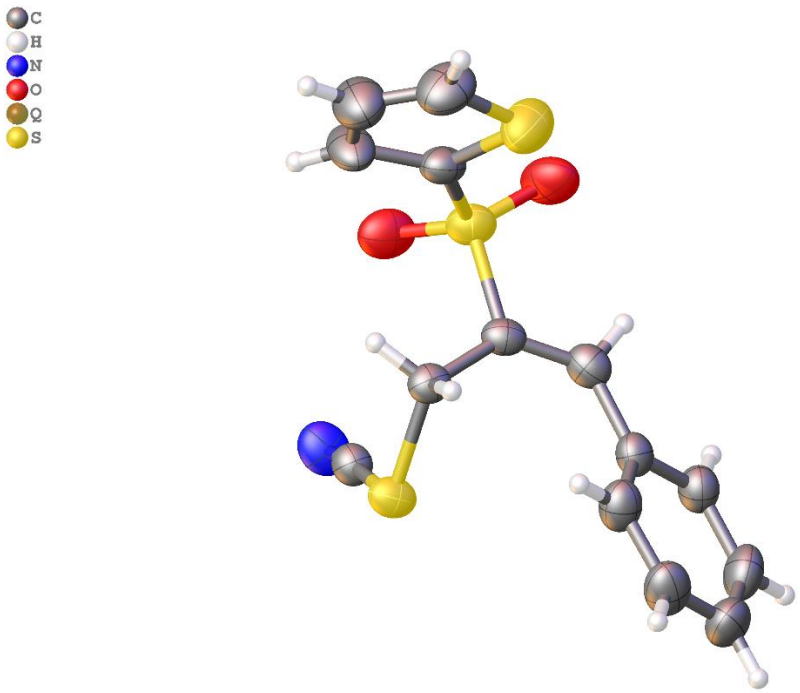
7. X-ray structure of 3a (CCDC 2536775)

The single crystal of compound **3a** was cultivated by slow evaporation technique. **3j** (50 mg) was dissolved in ethyl acetate and the solvent was allowed to evaporate in open air, and the resulting crystals of **3a** were collected for X-ray diffraction analysis. The crystal was tested on a Bruker D8 Quest diffractometer, and the structure was solved with the Superflip structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization.

X-ray structure of **3a** with thermal ellipsoids shown at the 50% probability level



3a

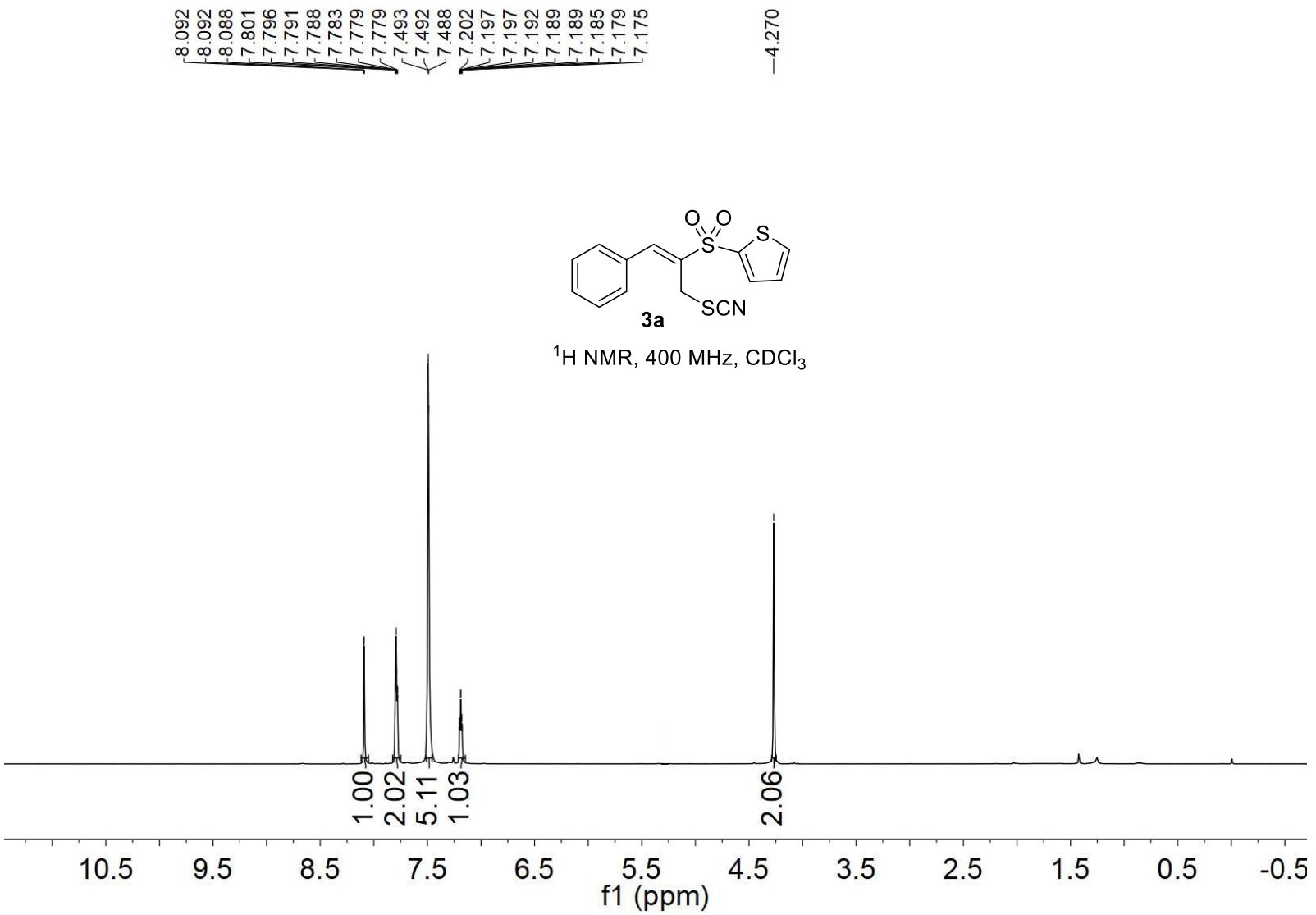


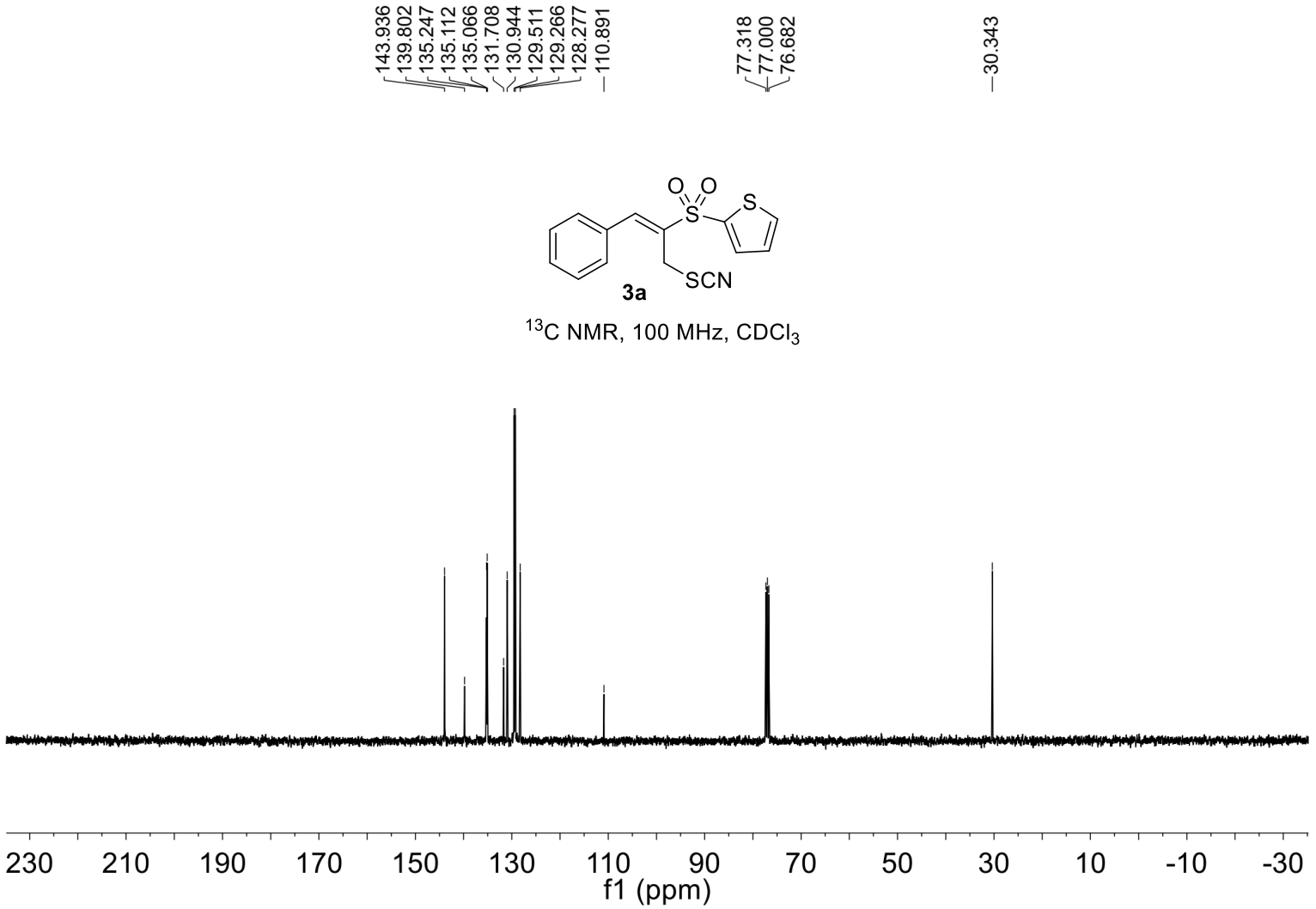
Identification code	3a
Empirical formula	$C_{14}H_{11}NO_2S_3$
Formula weight	321.42

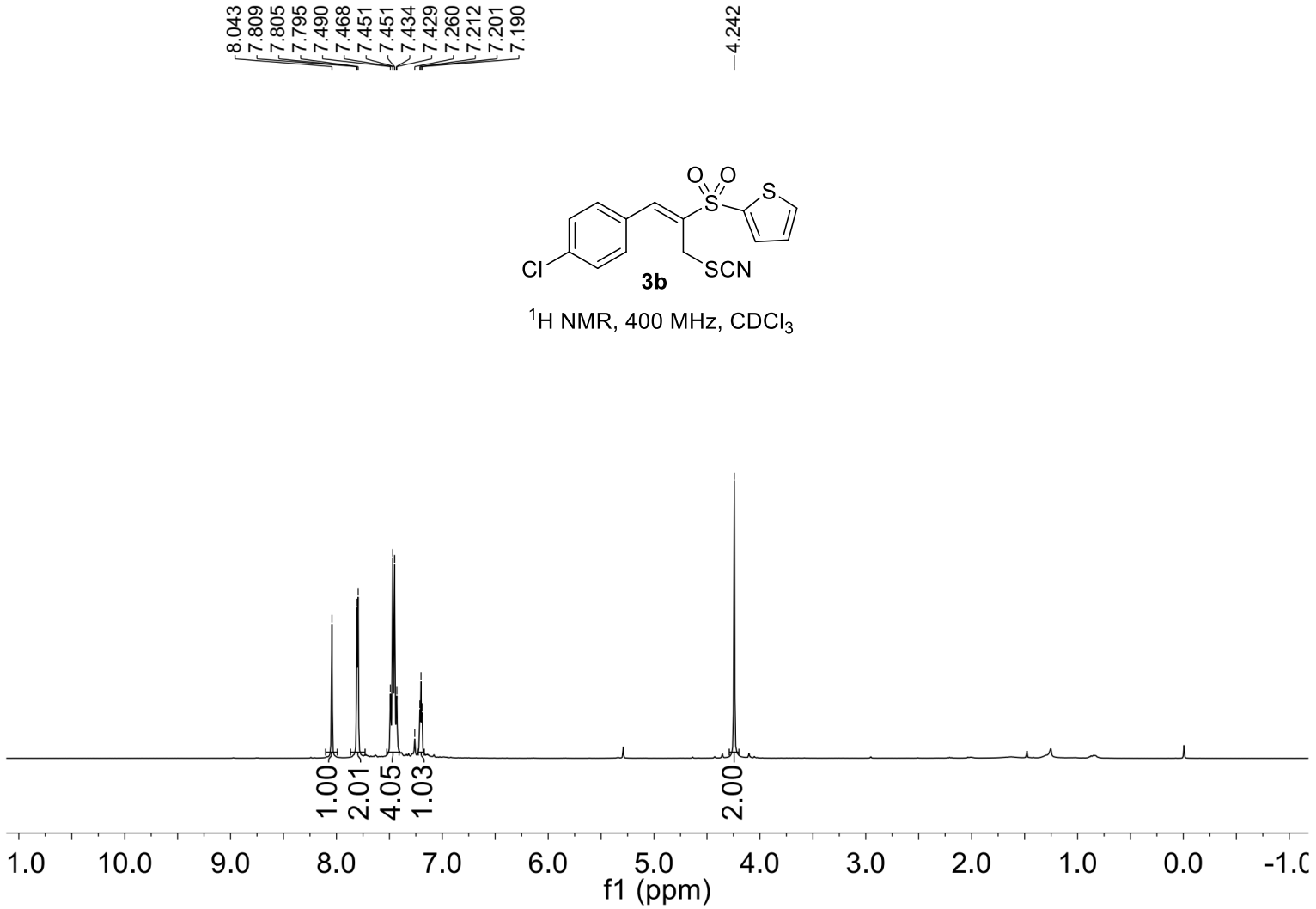
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	5.8621(3)
b/Å	9.7553(6)
c/Å	13.0274(8)
α/°	97.051(2)
β/°	91.909(2)
γ/°	98.638(2)
Volume/Å3	729.95(7)
Z	2
ρcalcg/cm3	1.462
μ/mm-1	0.506
F(000)	332.0
Crystal size/mm3	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.962 to 50.222
Index ranges	-6 ≤ h ≤ 6, -11 ≤ k ≤ 11, -15 ≤ l ≤ 14
Reflections collected	16673
Independent reflections	2554 [Rint = 0.0581, Rsigma = 0.0452]
Data/restraints/parameters	2554/0/181
Goodness-of-fit on F2	1.062
Final R indexes [I>=2σ (I)]	R1 = 0.0540, wR2 = 0.1264
Final R indexes [all data]	R1 = 0.0836, wR2 = 0.1448
Largest diff. peak/hole / e Å-3	0.44/-0.49

8. References

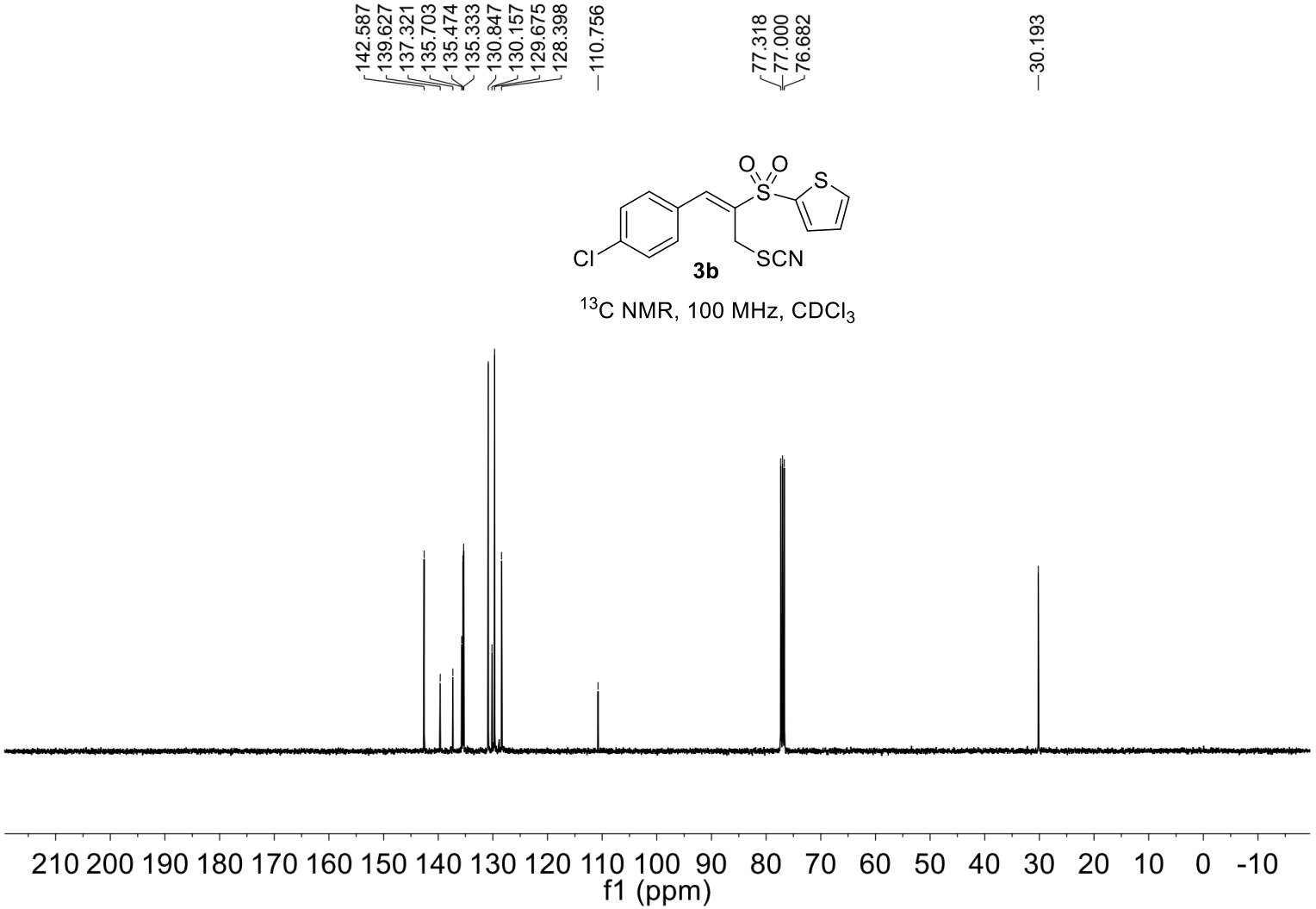
(1) Zhao, Z.; Racicot, L.; Murphy, G. K. Angewandte Chemie International Edition. 2017, 56, 11620–11623.

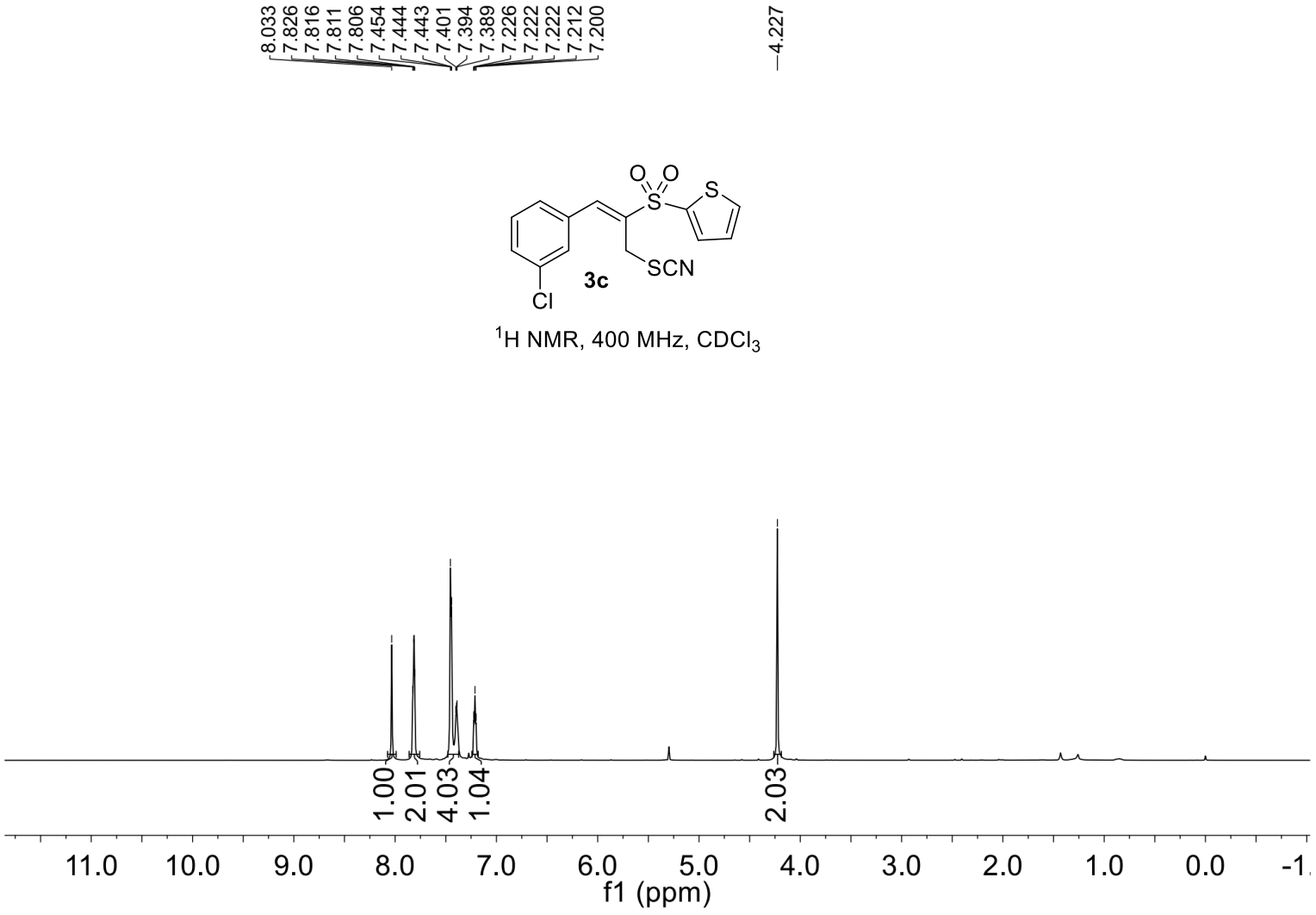

8.092
8.092
8.088
7.801
7.796
7.791
7.788
7.783
7.779
7.779
7.493
7.492
7.488
7.202
7.197
7.197
7.192
7.189
7.189
7.185
7.179
7.175
4.270
O
O
S
S
SCN
3a
1H NMR, 400 MHz, CDCl3
1.00
2.02
5.11
1.03
2.06
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


143.936
139.802
135.247
135.112
135.066
131.708
130.944
129.511
129.266
128.277
110.891
77.318
77.000
76.682
30.343
O
O
S
S
SCN
3a
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

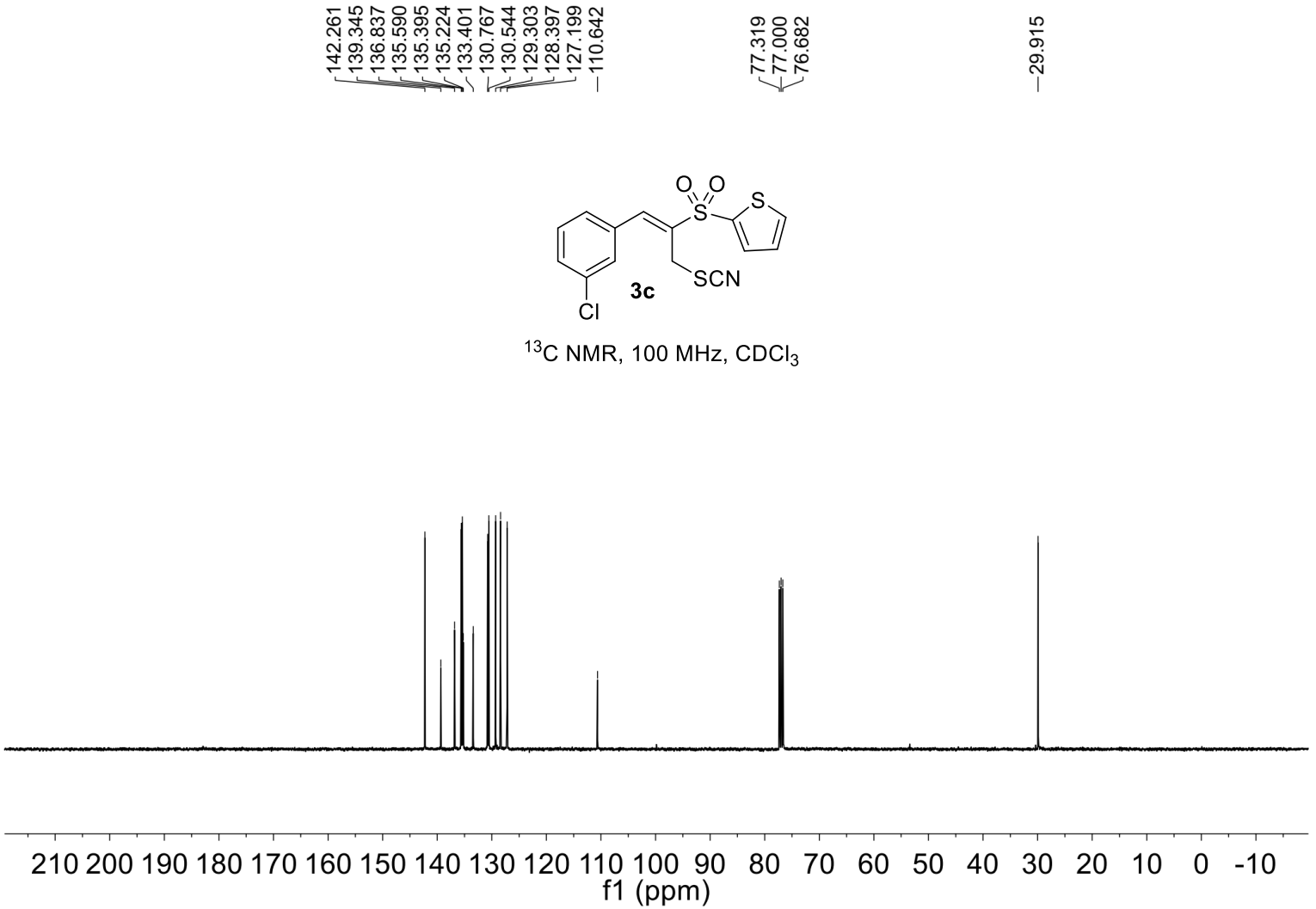


^{1}H NMR, 400 MHz, $CDCl_3$

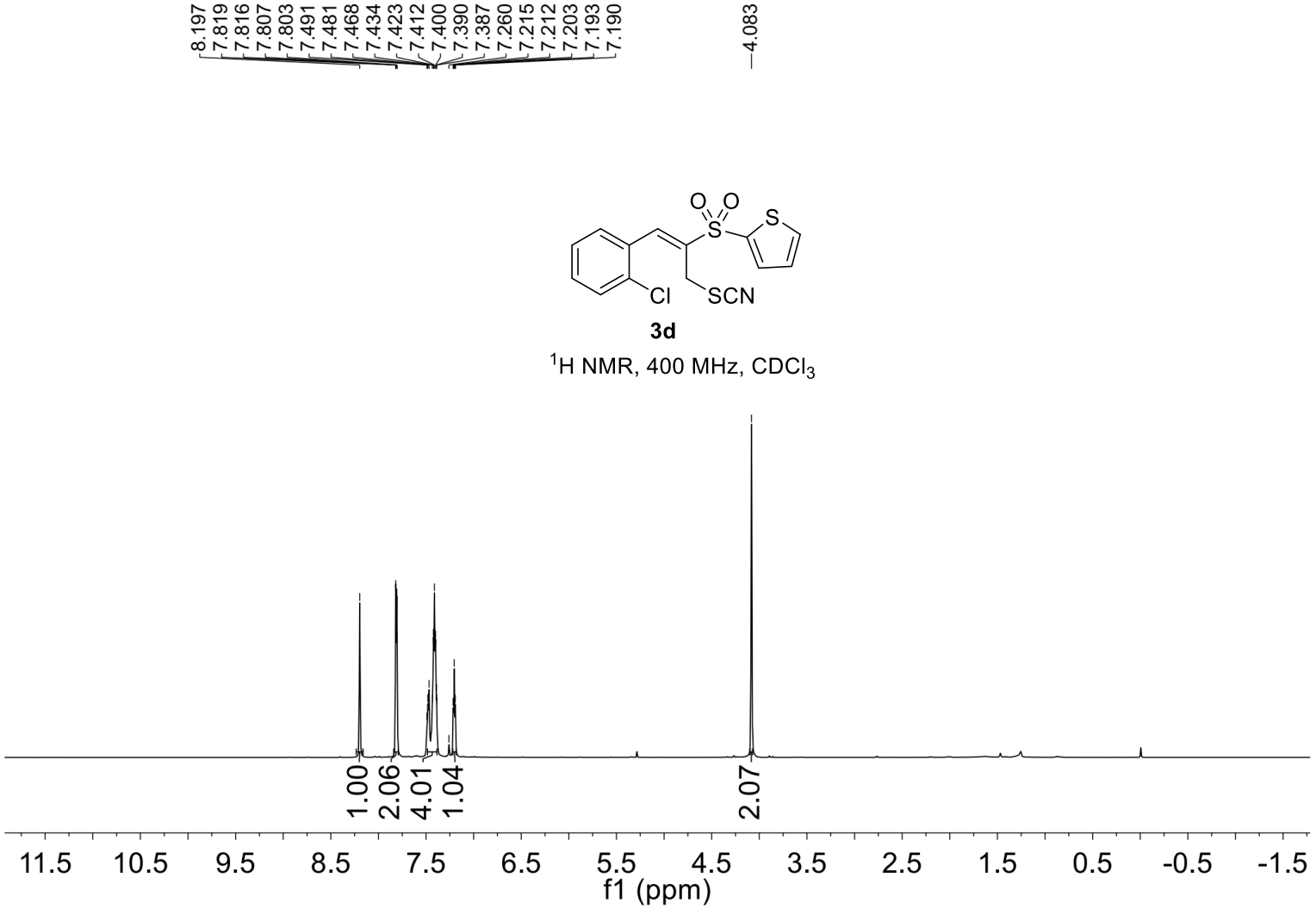

142.587
139.627
137.321
135.703
135.474
135.333
130.847
130.157
129.675
128.398
110.756
77.318
77.000
76.682
30.193
O
O
S
S
Cl
SCN
3b
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



^{1}H NMR, 400 MHz, $CDCl_3$

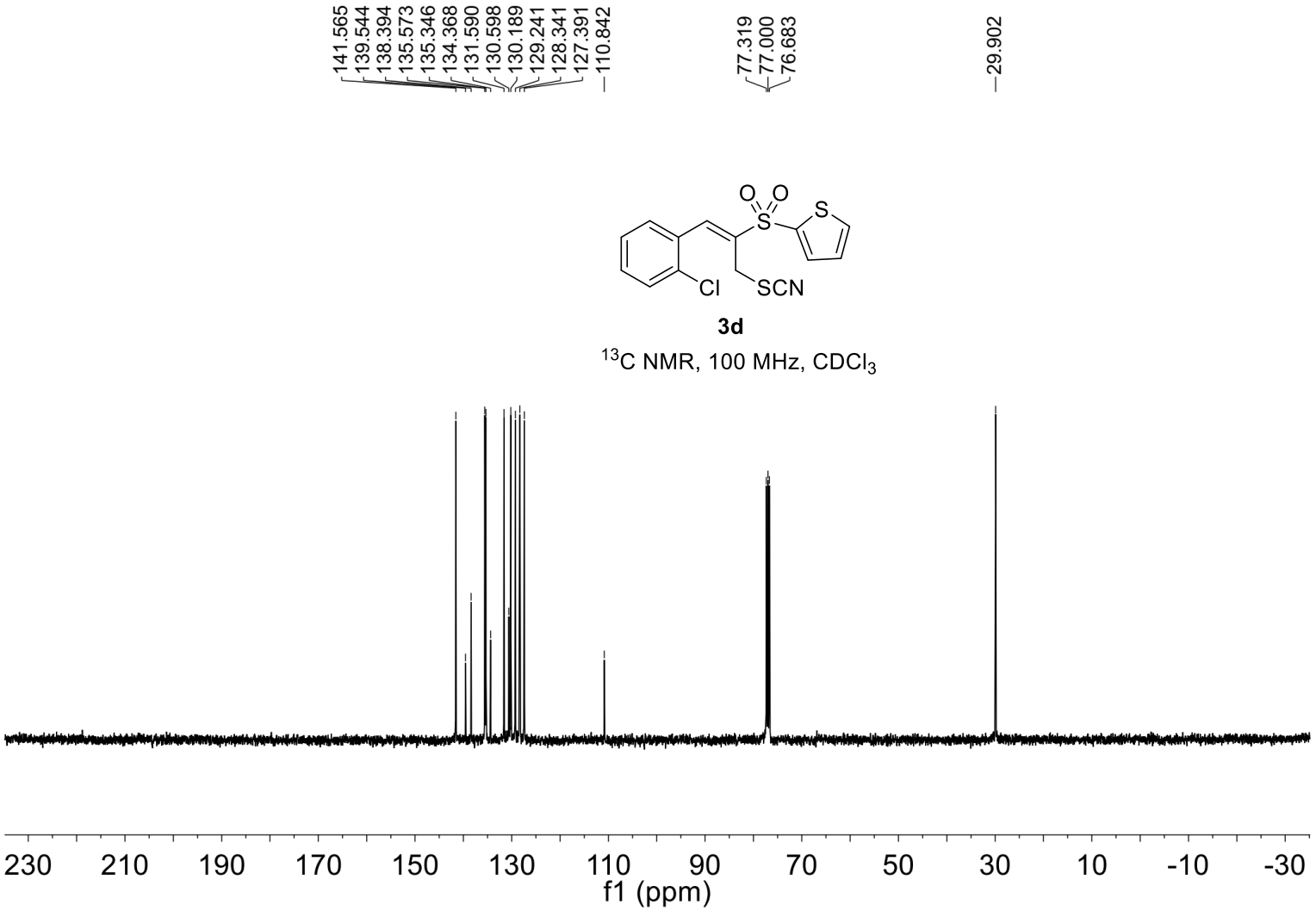


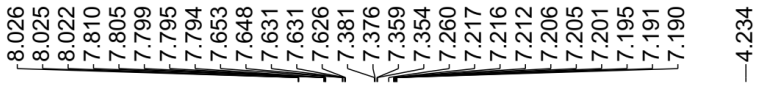
^{13}C NMR, 100 MHz, $CDCl_3$

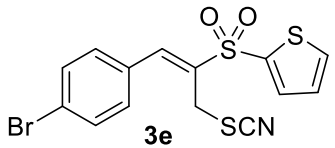


3d

^{1}H NMR, 400 MHz, $CDCl_3$

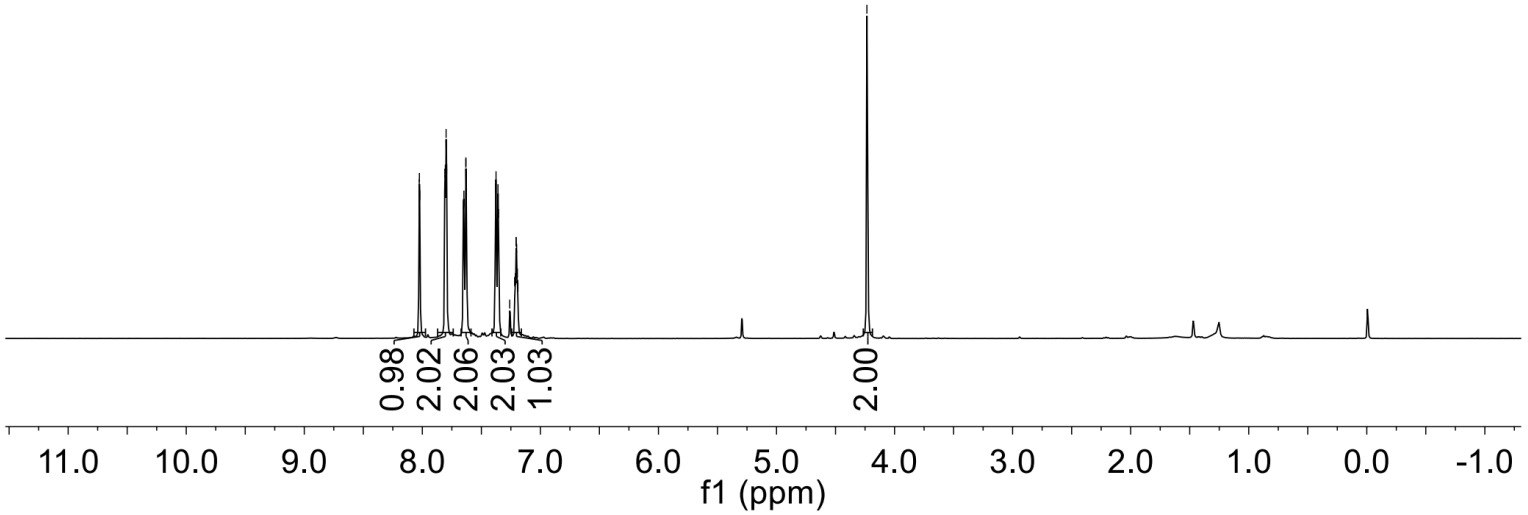

141.565
139.544
138.394
135.573
135.346
134.368
131.590
130.598
130.189
129.241
128.341
127.391
110.842
77.319
77.000
76.683
29.902
O
O
S
S
Cl
SCN
3d
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

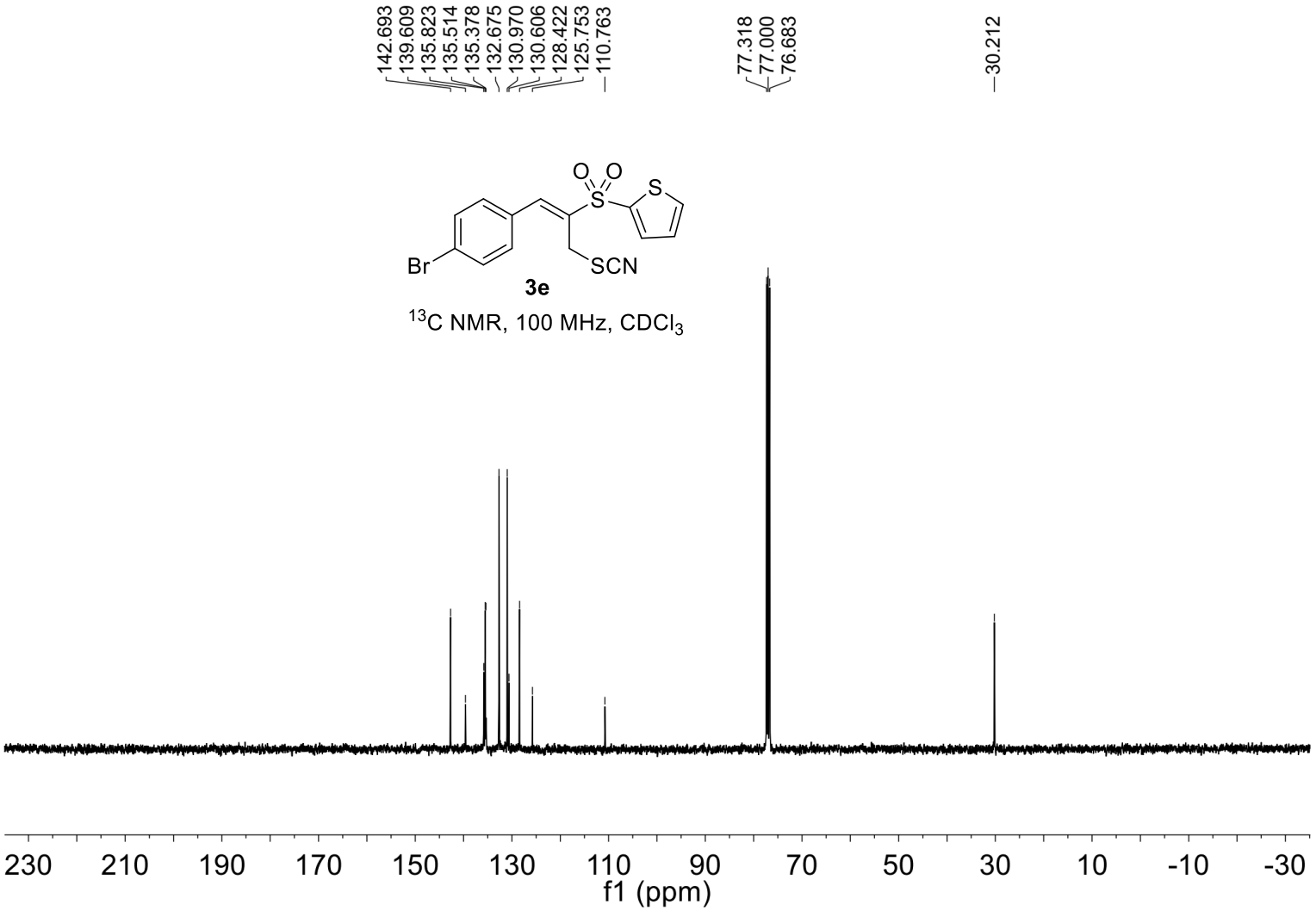


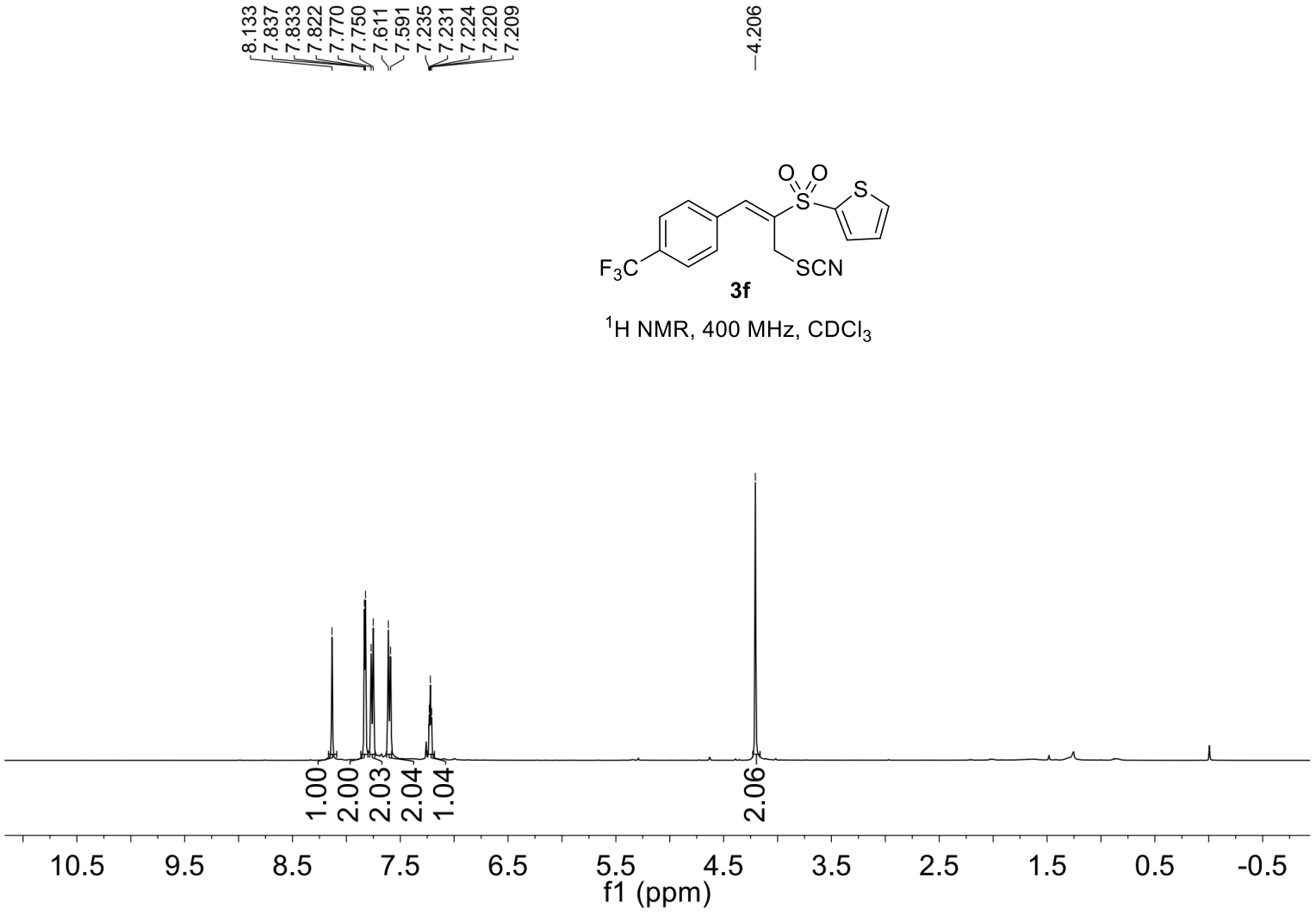


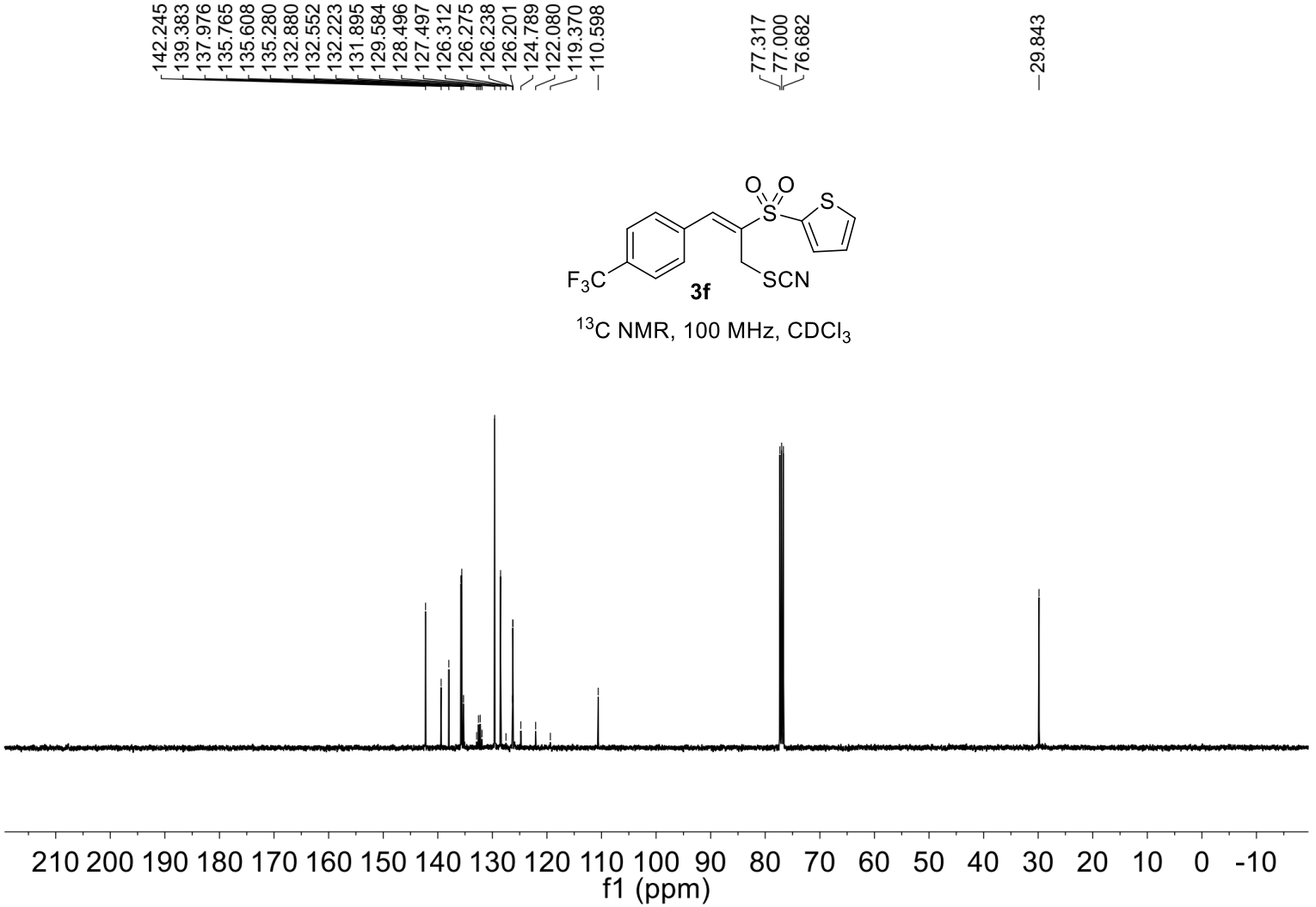
3e

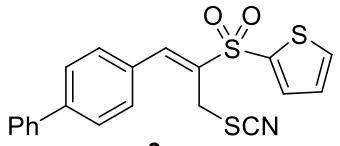
^{1}H NMR, 400 MHz, $CDCl_3$




142.693
139.609
135.823
135.514
135.378
132.675
130.970
130.606
128.422
125.753
110.763
77.318
77.000
76.683
30.212
O
O
S
S
Br
SCN
3e
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

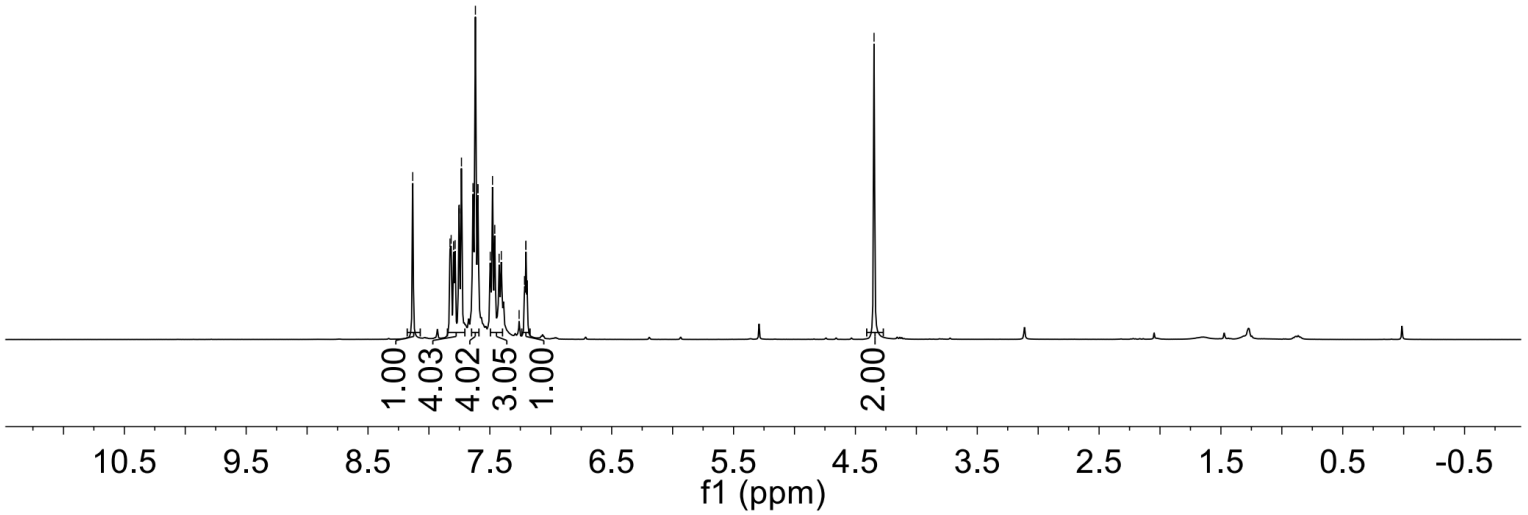

8.133
7.837
7.833
7.822
7.770
7.750
7.611
7.591
7.235
7.231
7.224
7.220
7.209
4.206
O
O
S
S
F3C
SCN
3f
1H NMR, 400 MHz, CDCl3
1.00
2.00
2.03
2.04
1.04
2.06
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

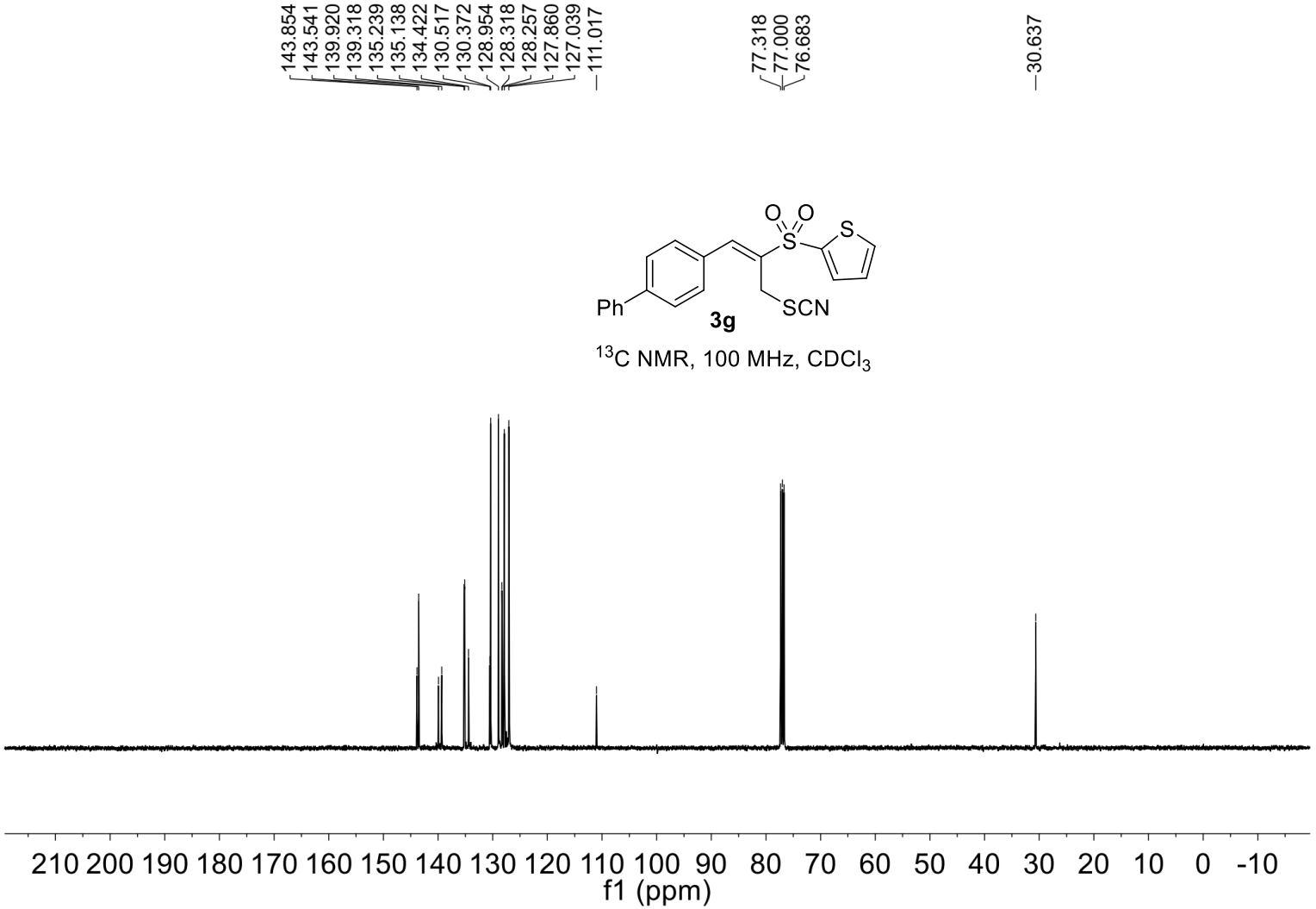

142.245
139.383
137.976
135.765
135.608
135.280
132.880
132.552
132.223
131.895
129.584
128.496
127.497
126.312
126.275
126.238
126.201
124.789
122.080
119.370
110.598
77.317
77.000
76.682
29.843
O
O
S
S
F3C
SCN
3f
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

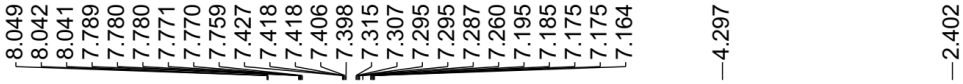


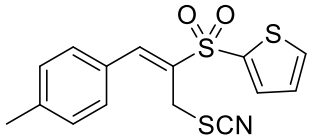
3g

^{1}H NMR, 400 MHz, $CDCl_3$



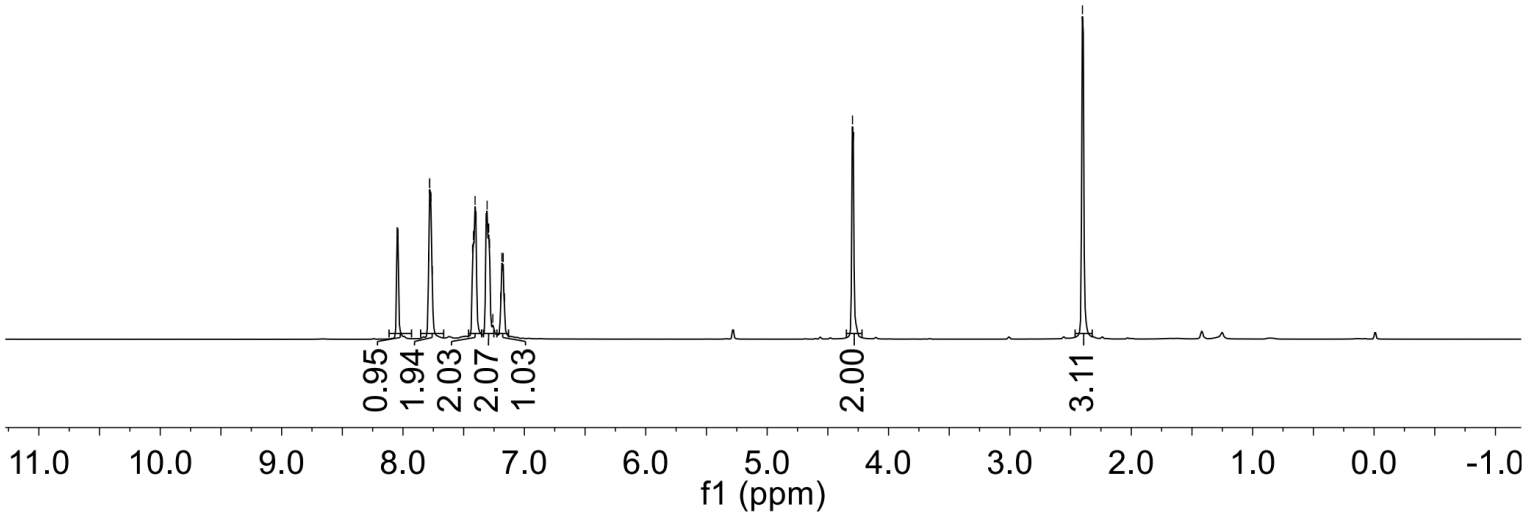

143.854
143.541
139.920
139.318
135.239
135.138
134.422
130.517
130.372
128.954
128.318
128.257
127.860
127.039
111.017
77.318
77.000
76.683
30.637
O
O
S
S
Ph
SCN
3g
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

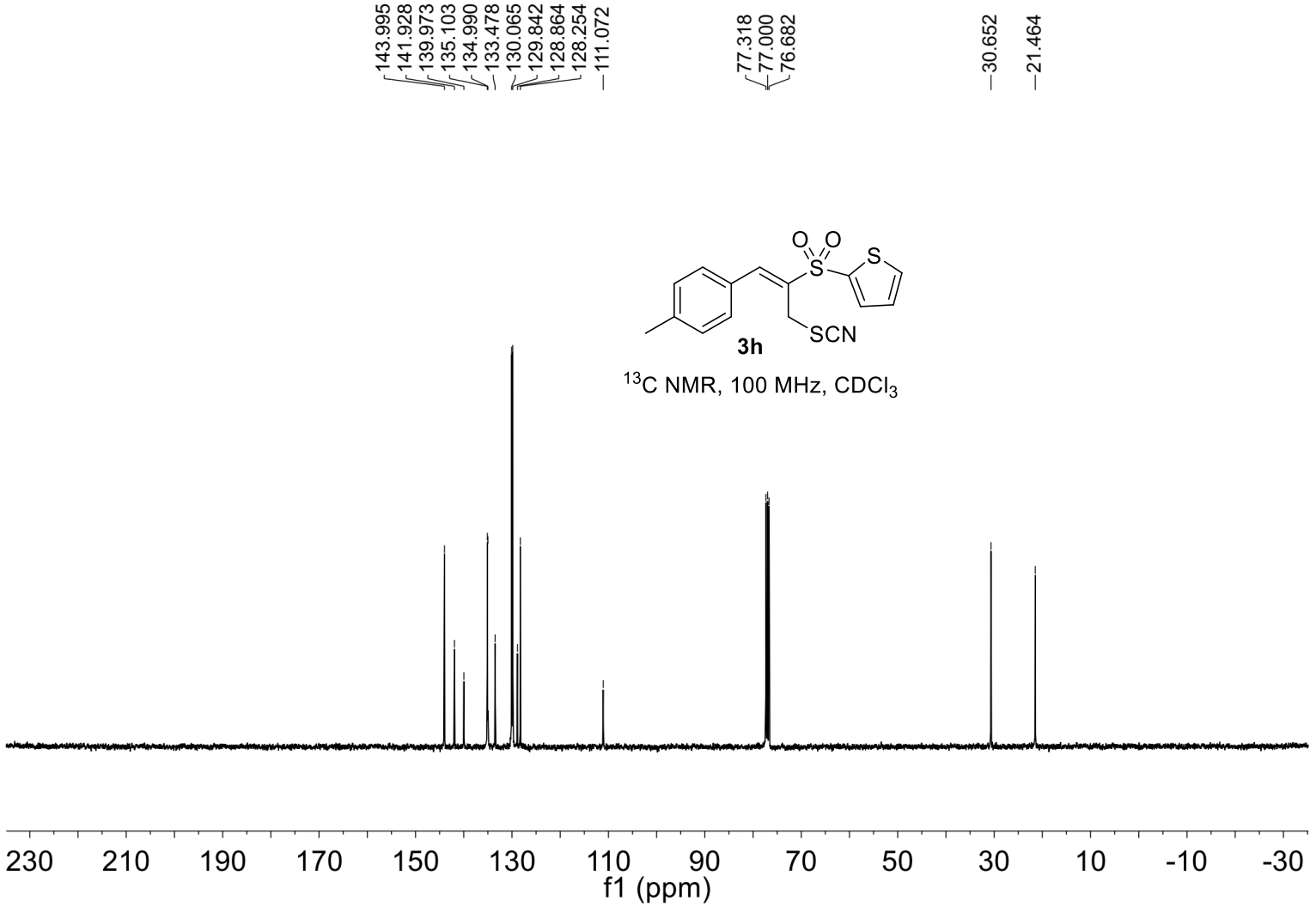


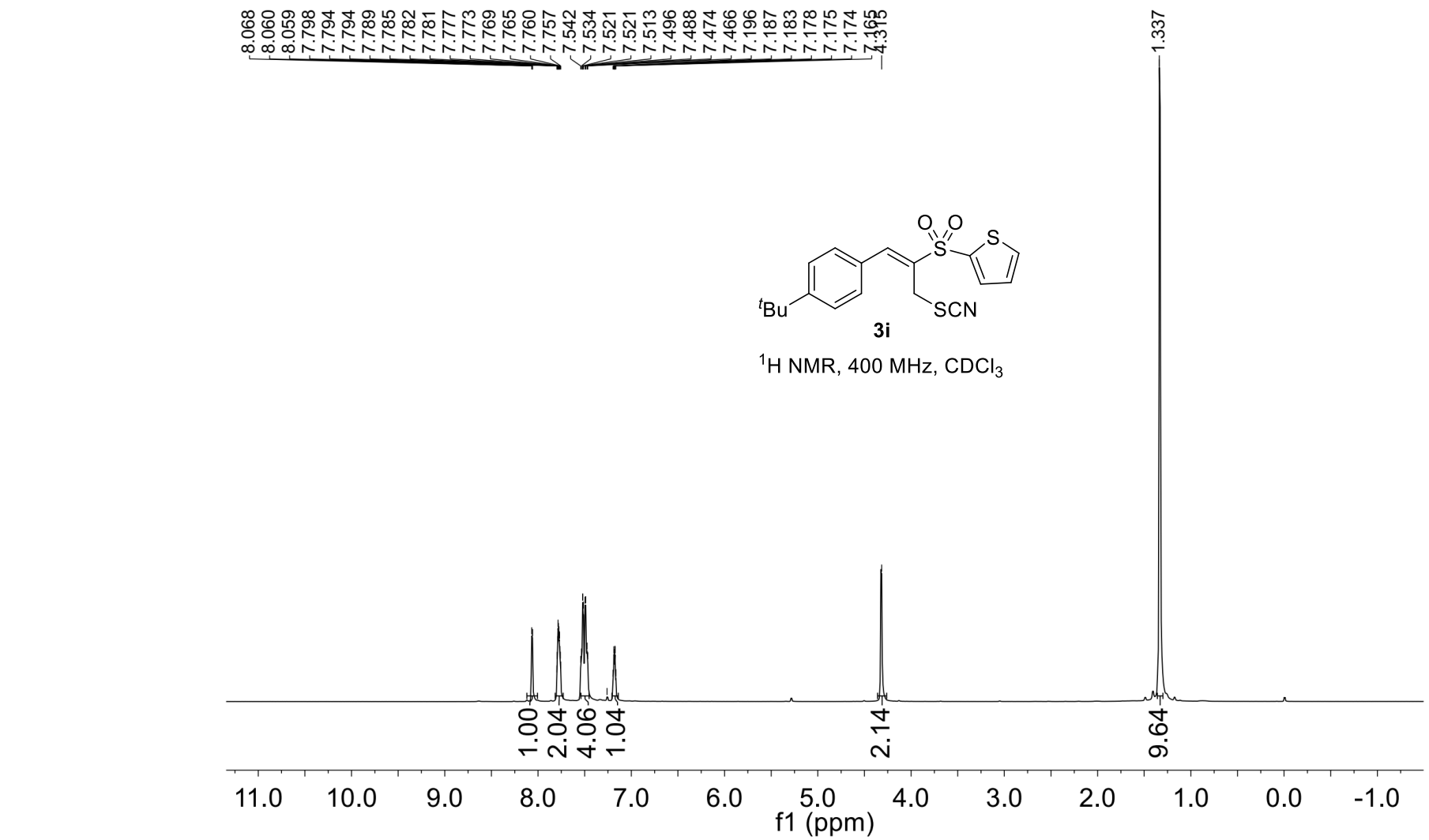


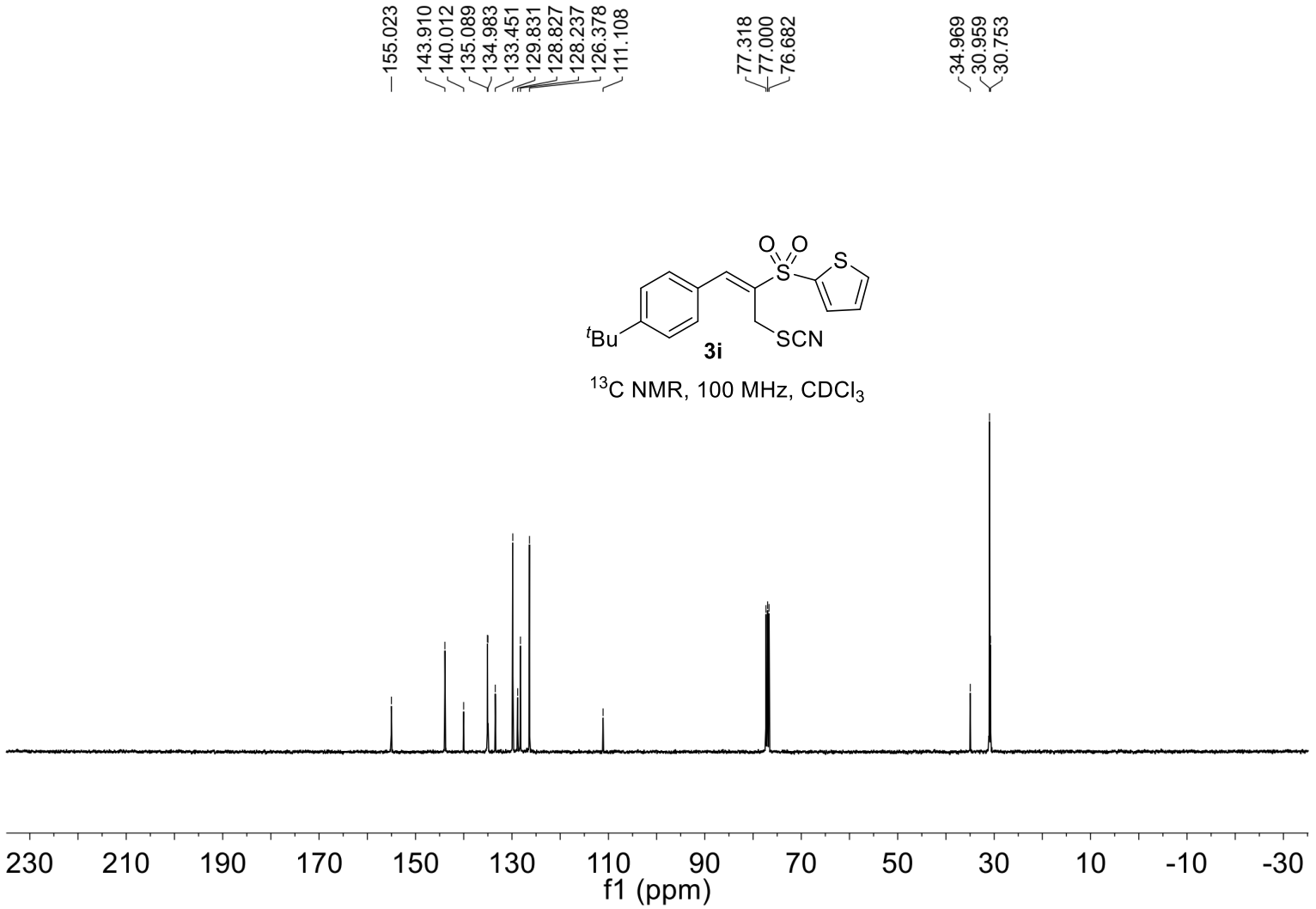
3h

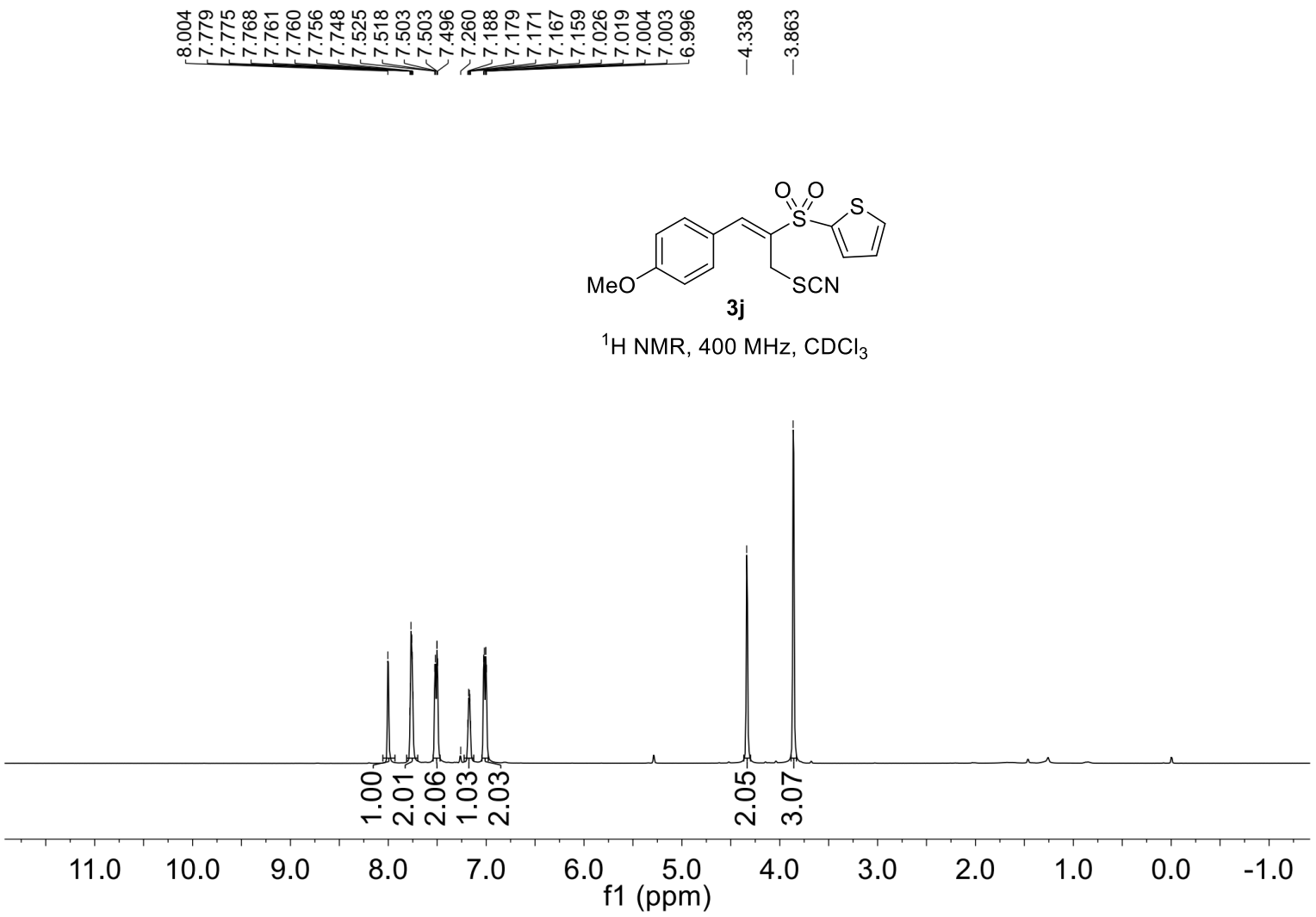
^{1}H NMR, 400 MHz, $CDCl_3$

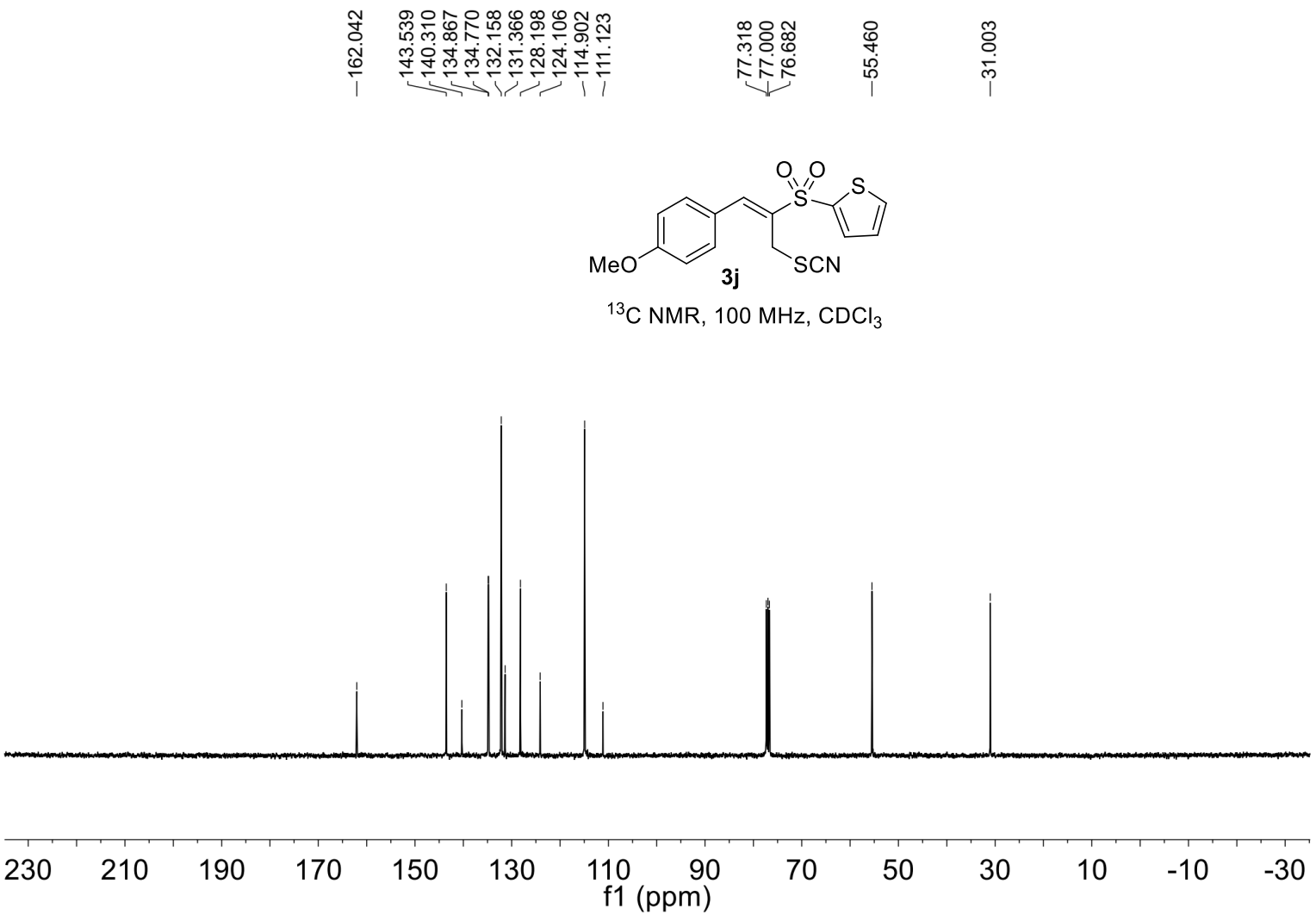


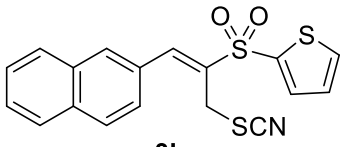

143.995
141.928
139.973
135.103
134.990
133.478
130.065
129.842
128.864
128.254
111.072
77.318
77.000
76.682
30.652
21.464
O
O
S
S
SCN
3h
^{13}C NMR, 100 MHz, $CDCl_3$
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)


8.068
8.060
8.059
7.798
7.794
7.794
7.789
7.785
7.782
7.781
7.777
7.773
7.769
7.765
7.760
7.757
7.542
7.534
7.521
7.521
7.513
7.496
7.488
7.474
7.466
7.196
7.187
7.183
7.178
7.175
7.174
7.165
4.315
1.337
O
O
S
S
tBu
SCN
3i
1H NMR, 400 MHz, CDCl3
1.00
2.04
4.06
1.04
2.14
9.64
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


155.023
143.910
140.012
135.089
134.983
133.451
129.831
128.827
128.237
126.378
111.108
77.318
77.000
76.682
34.969
30.959
30.753
O
O
S
S
tBu
SCN
3i
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

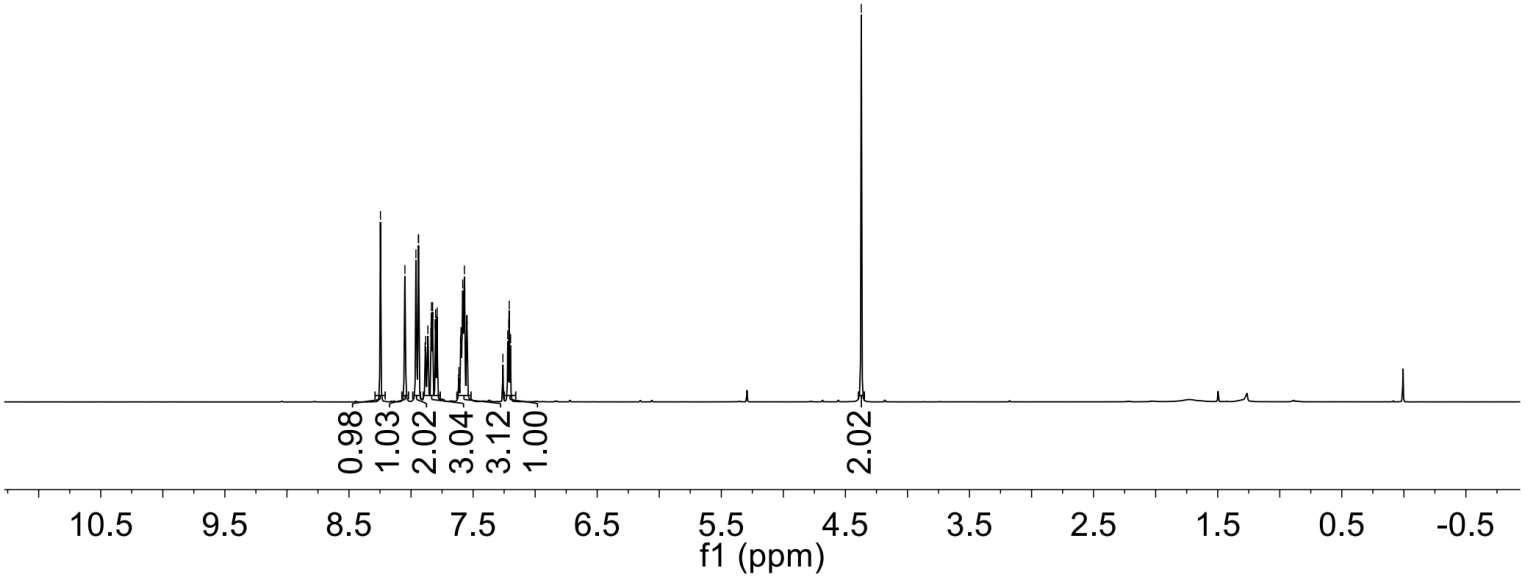

8.004
7.779
7.775
7.768
7.761
7.760
7.756
7.748
7.525
7.518
7.503
7.503
7.496
7.260
7.188
7.179
7.171
7.167
7.159
7.026
7.019
7.004
7.003
6.996
4.338
3.863
O
O
S
S
MeO
SCN
3j
1H NMR, 400 MHz, CDCl3
1.00
2.01
2.06
1.03
2.03
2.05
3.07
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

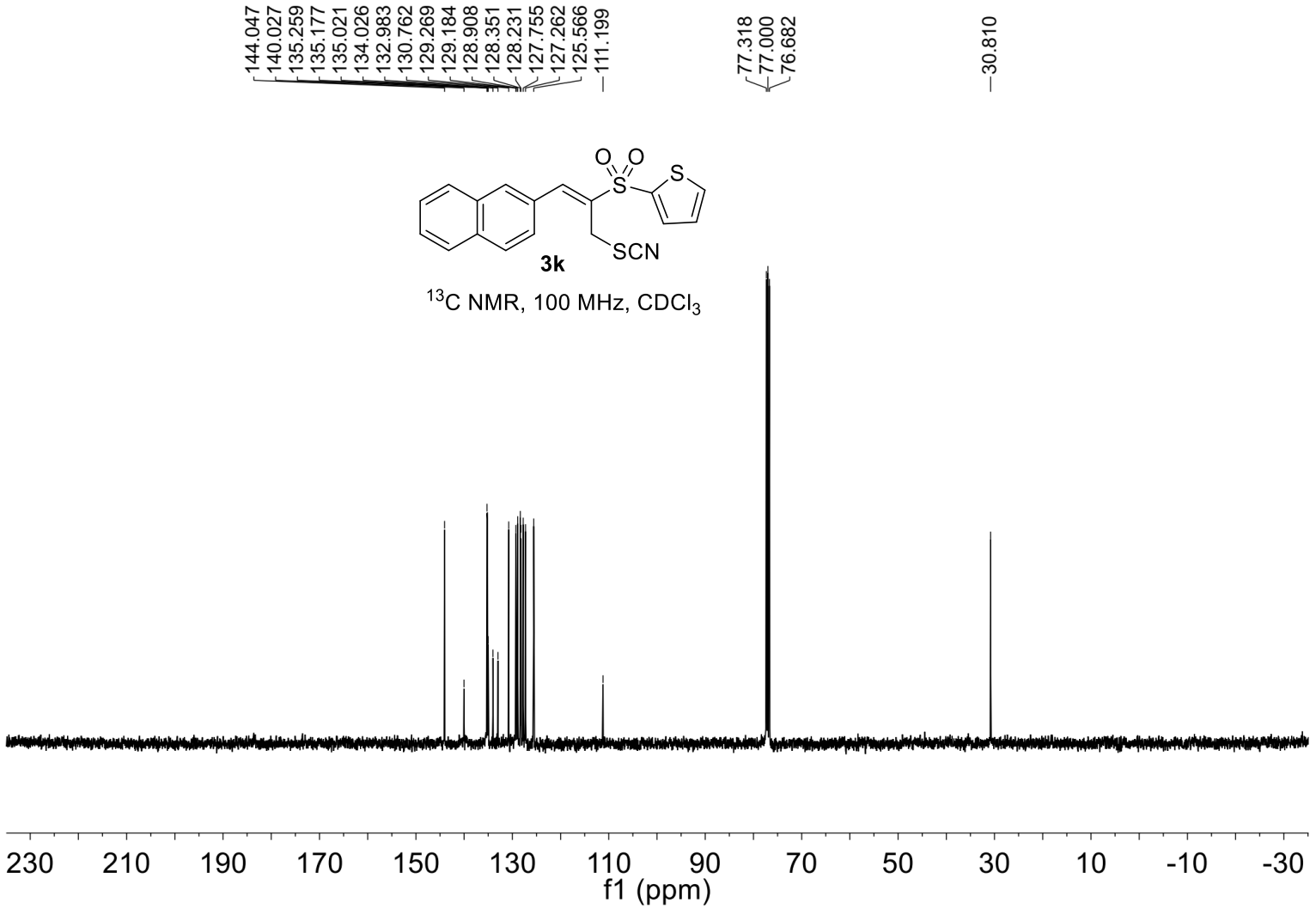

162.042
143.539
140.310
134.867
134.770
132.158
131.366
128.198
124.106
114.902
111.123
77.318
77.000
76.682
55.460
31.003
O
O
S
S
MeO
SCN
3j
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

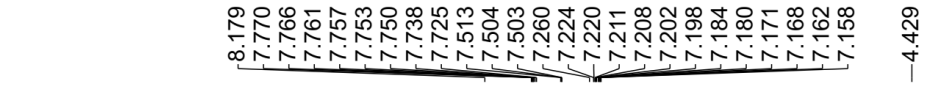


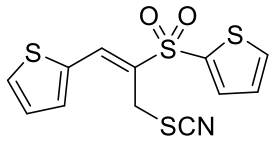
3k

^{1}H NMR, 400 MHz, $CDCl_3$



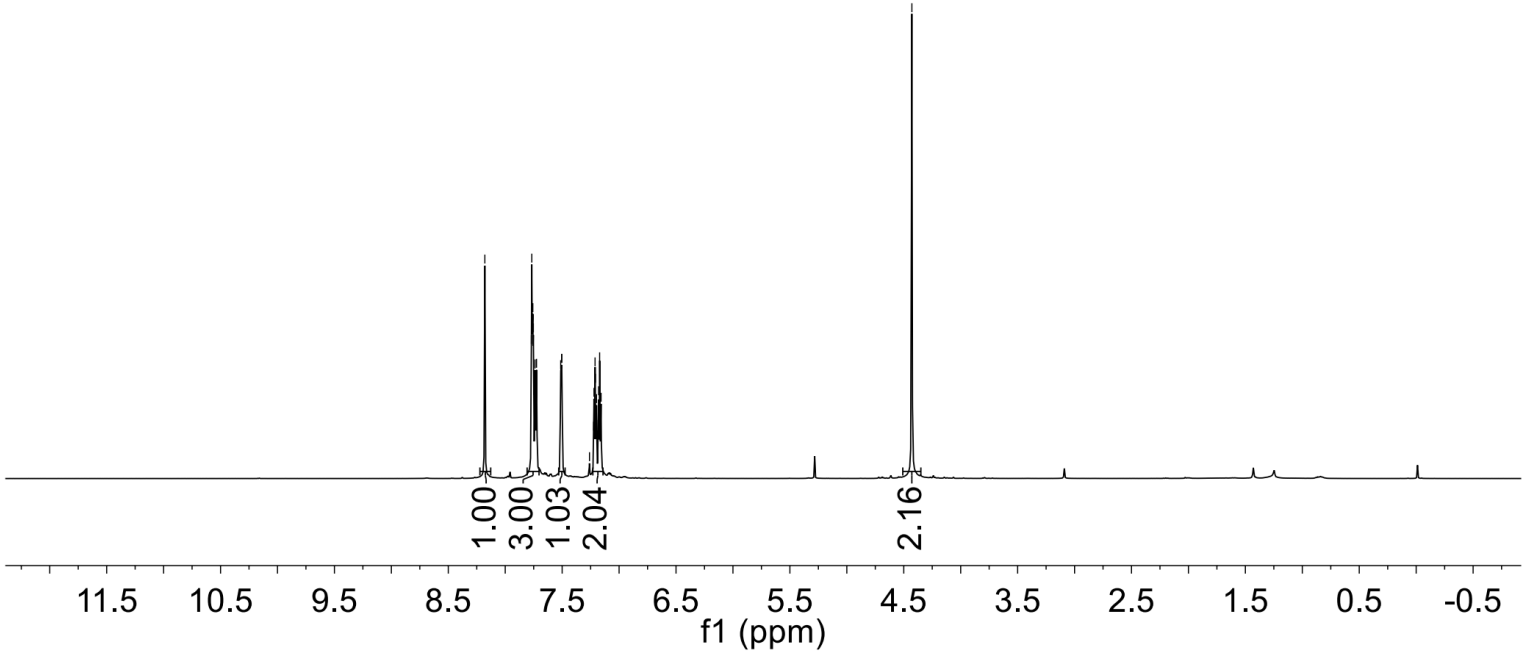

144.047
140.027
135.259
135.177
135.021
134.026
132.983
130.762
129.269
129.184
128.908
128.351
128.231
127.755
127.262
125.566
111.199
77.318
77.000
76.682
30.810
O
O
S
S
SCN
3k
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

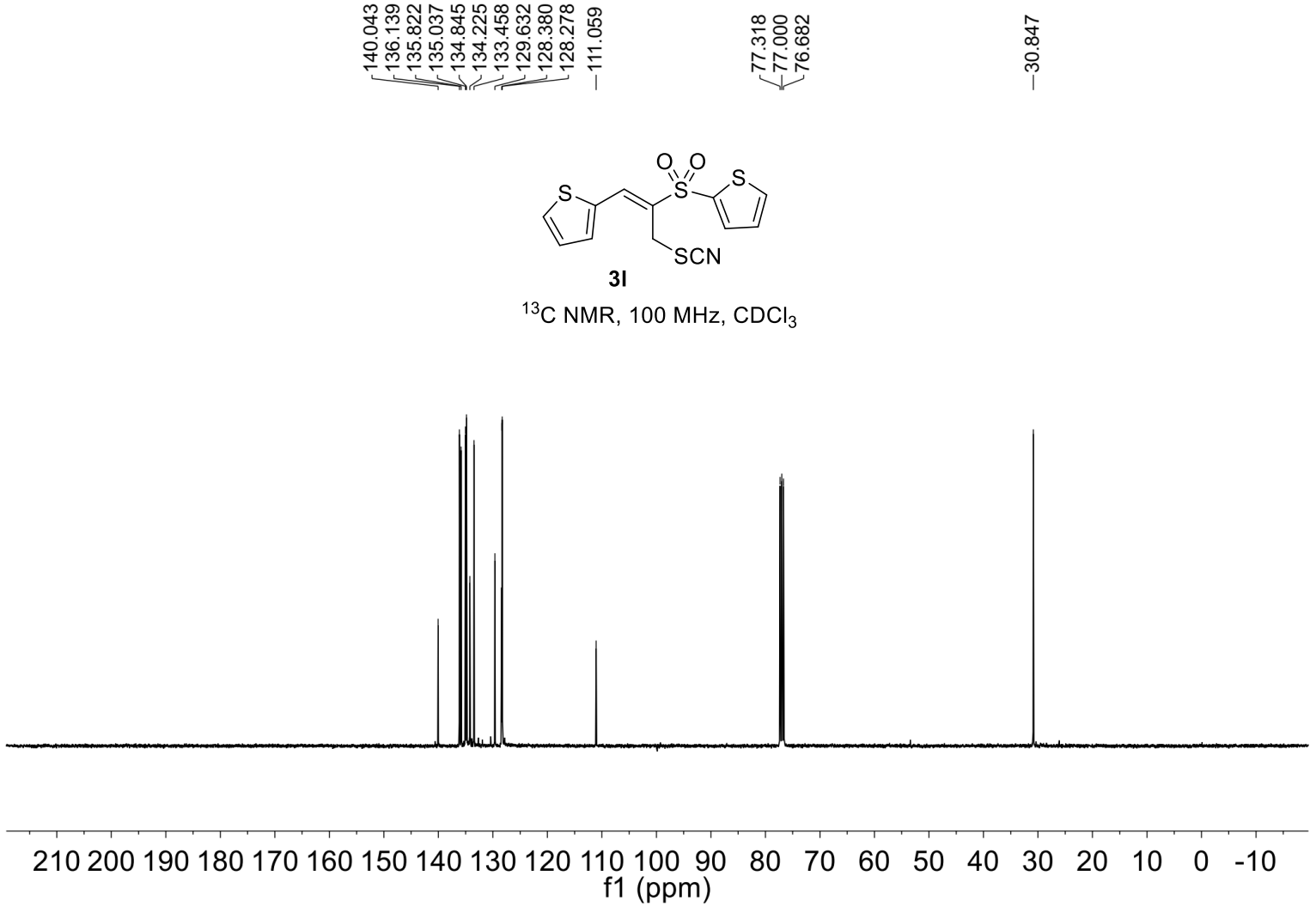




3l

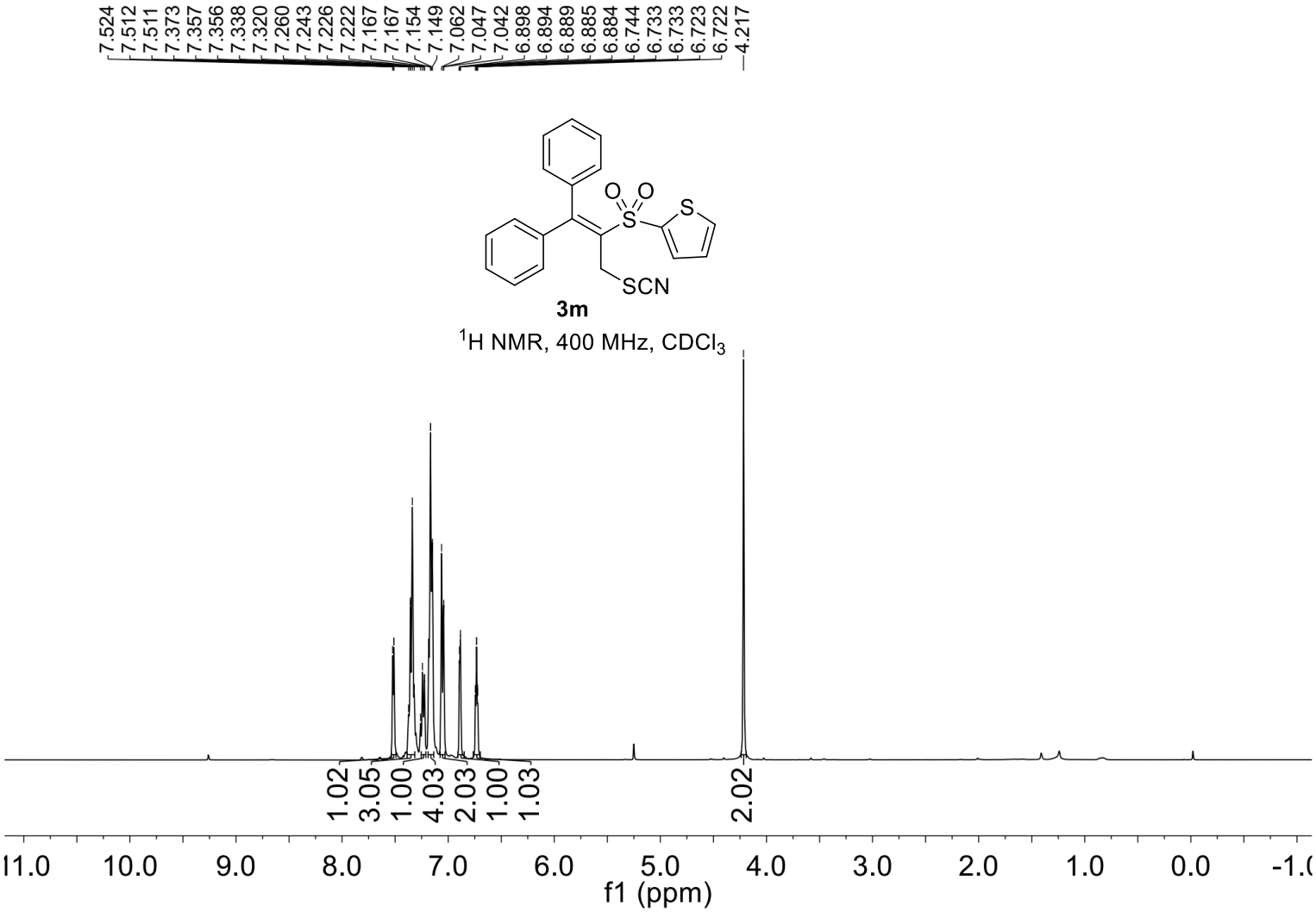
^{1}H NMR, 400 MHz, $CDCl_3$

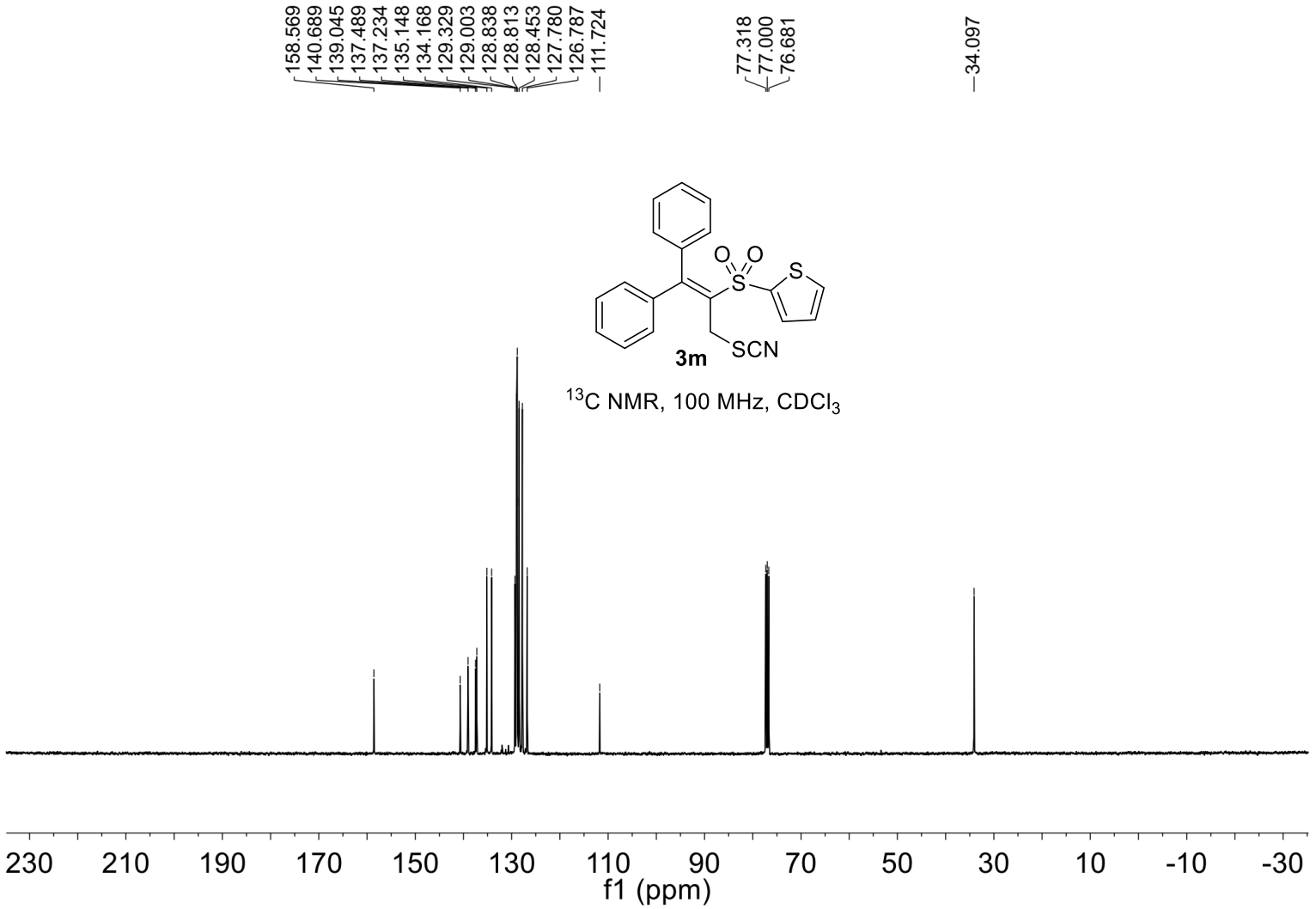


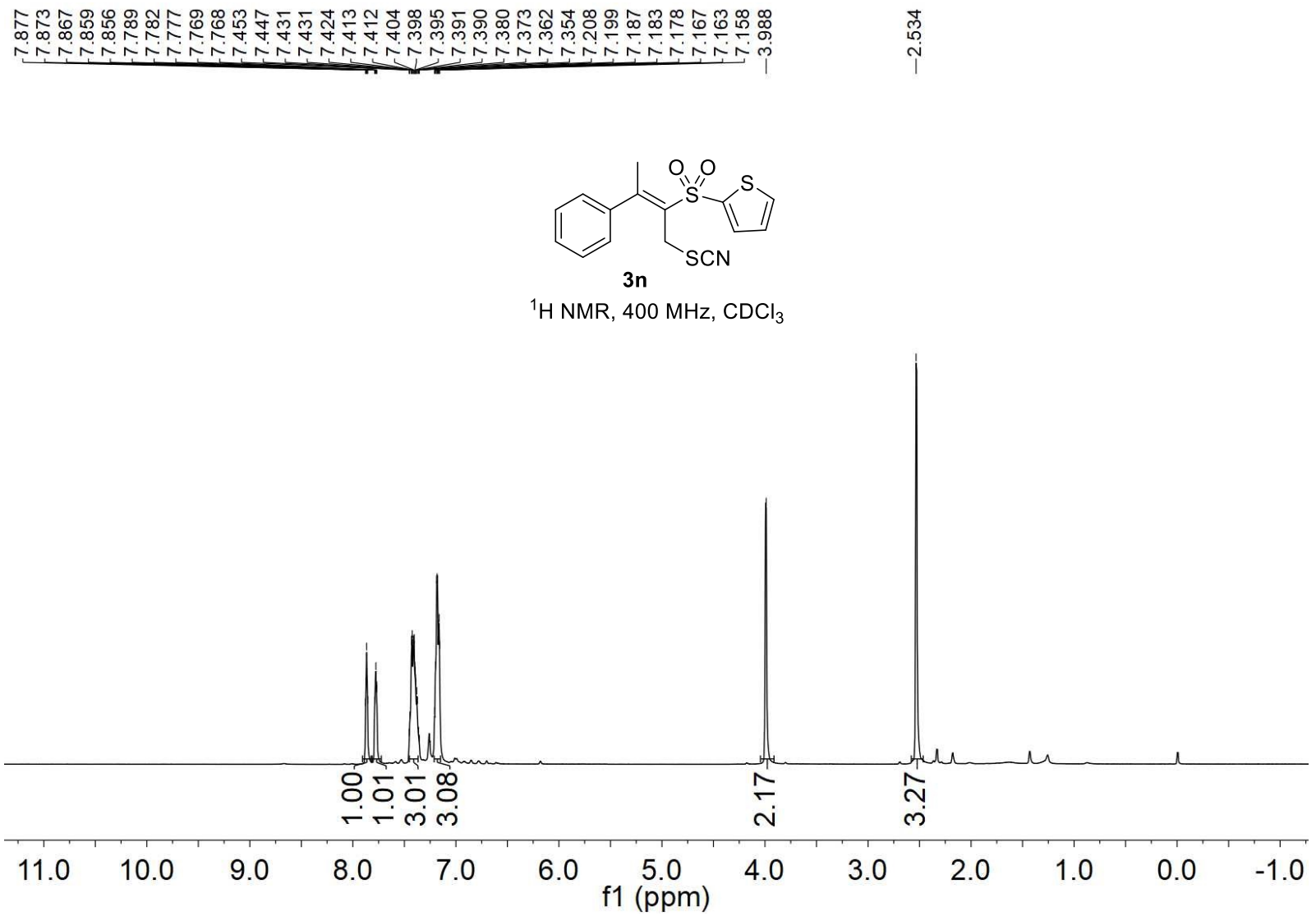


3l

^{13}C NMR, 100 MHz, $CDCl_3$

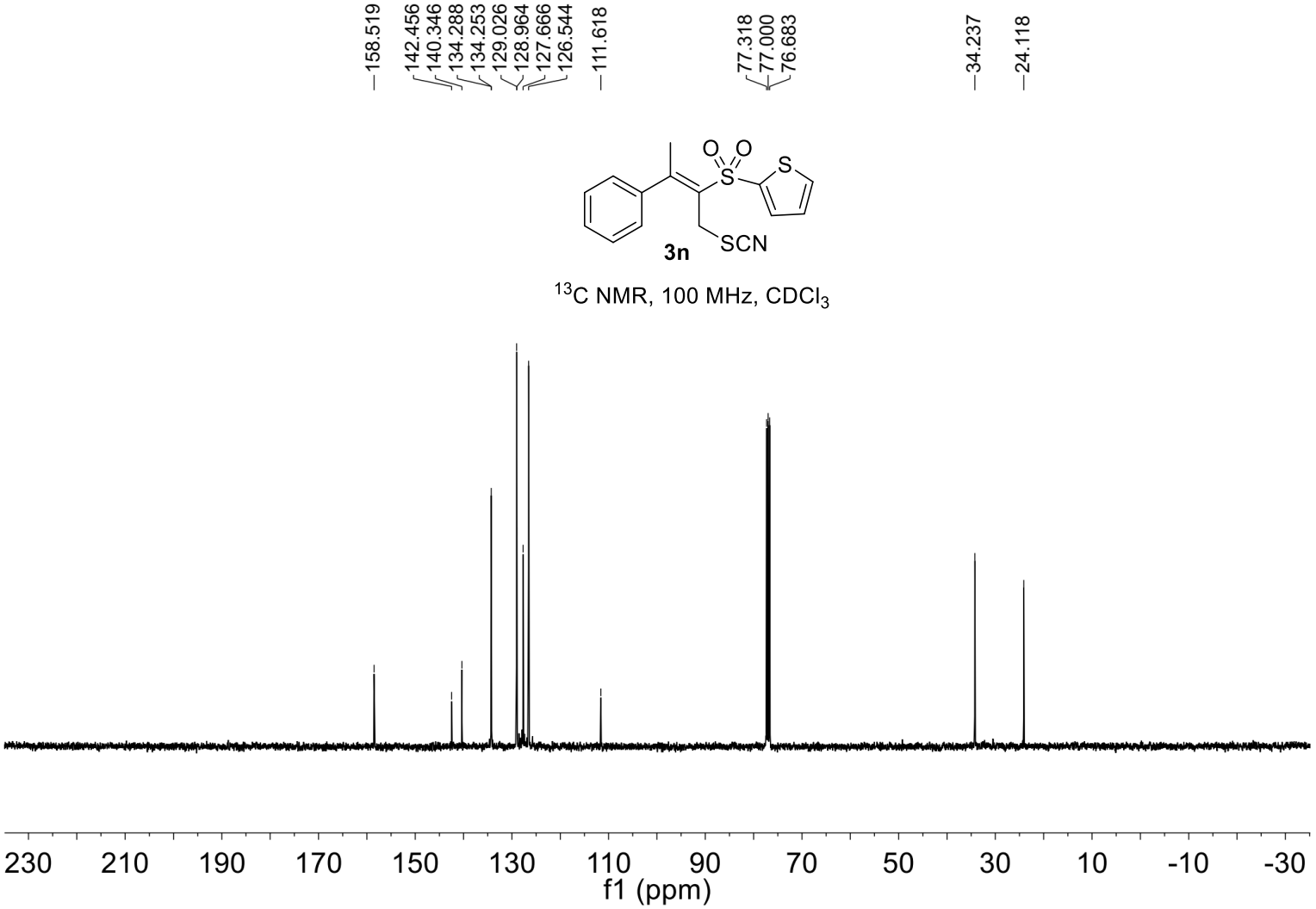

7.524
7.512
7.511
7.373
7.357
7.356
7.338
7.320
7.260
7.243
7.226
7.222
7.167
7.167
7.154
7.149
7.062
7.047
7.042
6.898
6.894
6.889
6.885
6.884
6.744
6.733
6.733
6.723
6.722
4.217
O
O
S
S
SCN
3m
1H NMR, 400 MHz, CDCl3
1.02
3.05
1.00
4.03
2.03
1.00
1.03
2.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

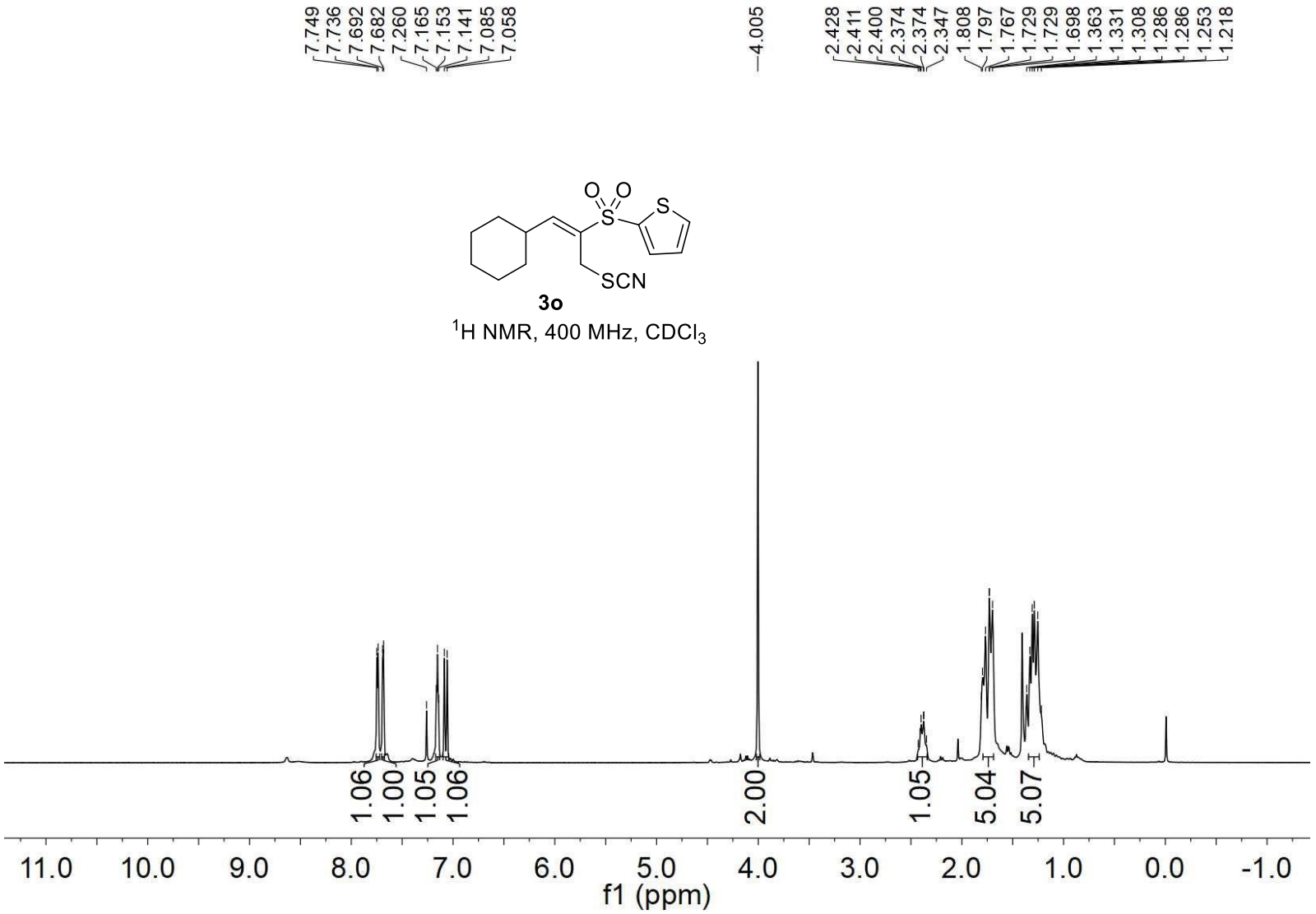

158.569
140.689
139.045
137.489
137.234
135.148
134.168
129.329
129.003
128.838
128.813
128.453
127.780
126.787
111.724
77.318
77.000
76.681
34.097
O
O
S
S
SCN
3m
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

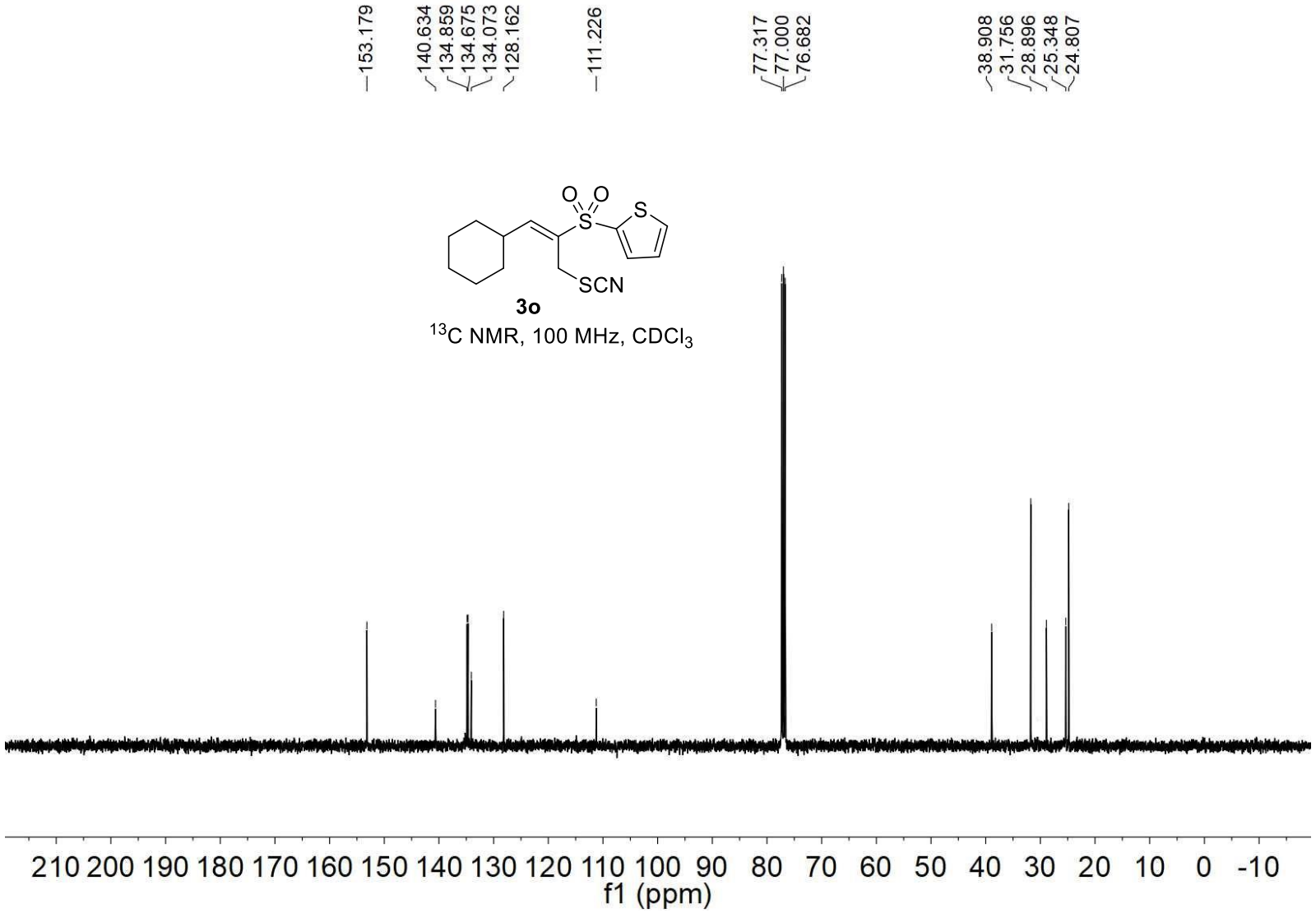


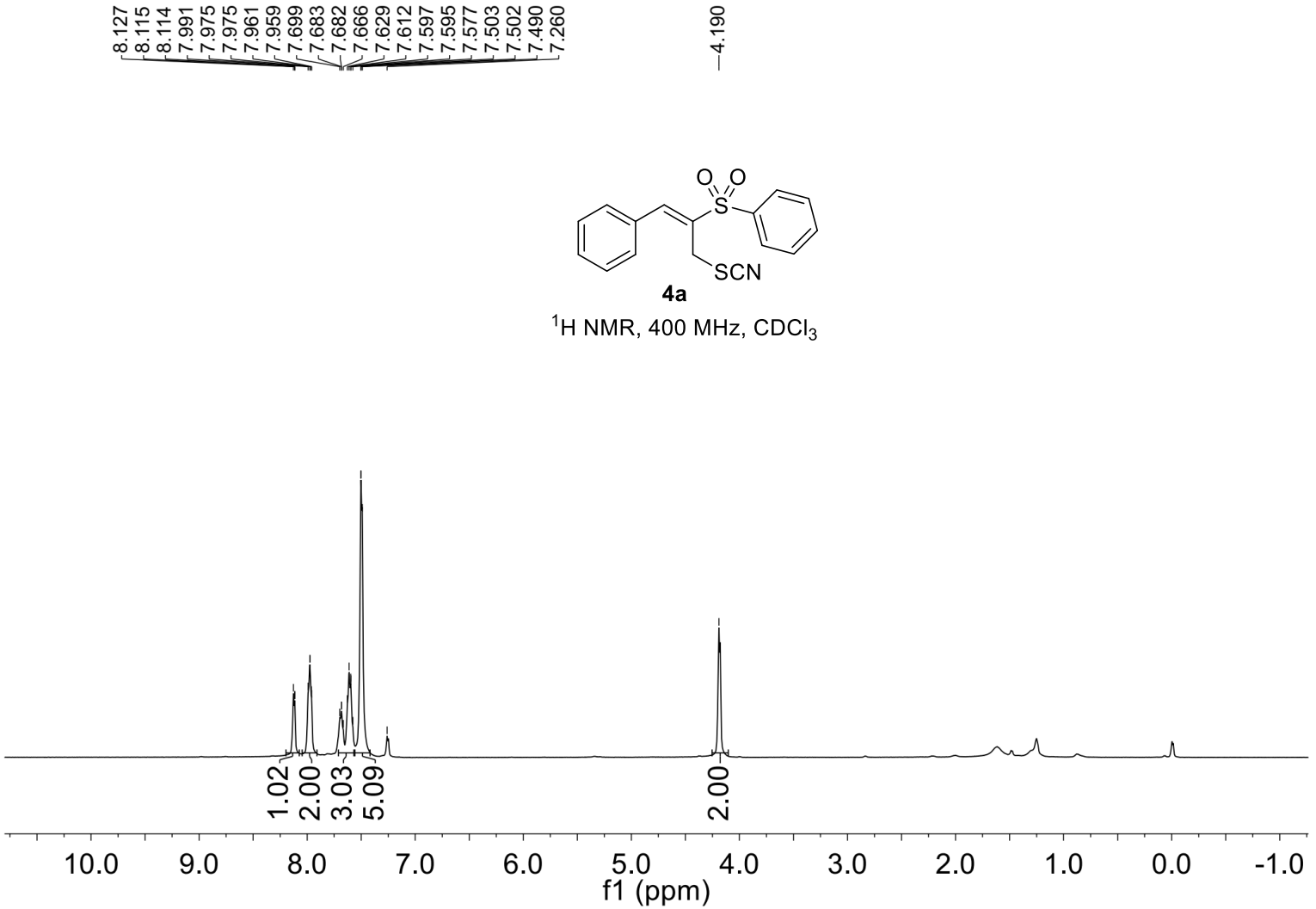
3n

^{1}H NMR, 400 MHz, $CDCl_3$


158.519
142.456
140.346
134.288
134.253
129.026
128.964
127.666
126.544
111.618
77.318
77.000
76.683
34.237
24.118
O
O
S
S
SCN
3n
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

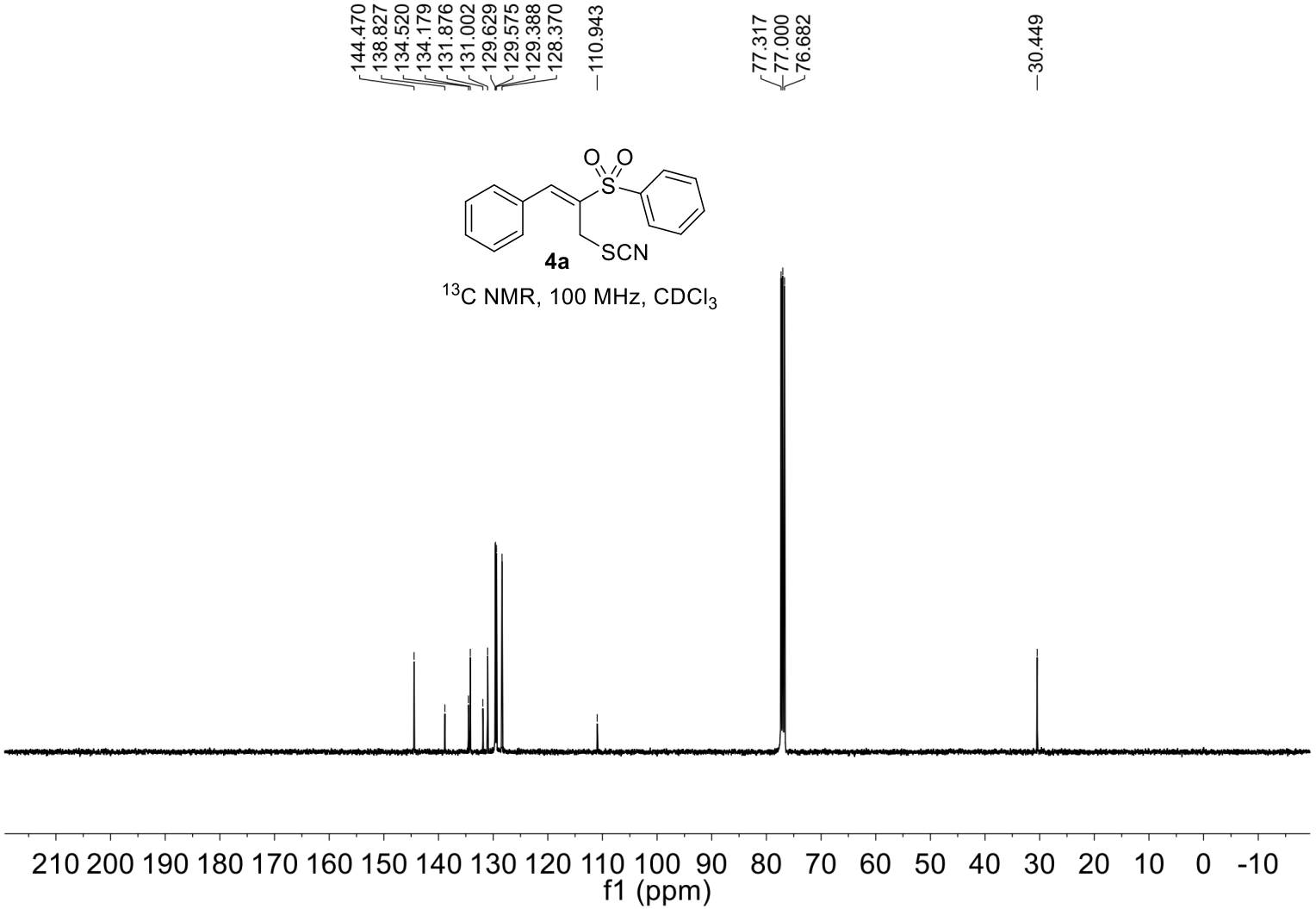

7.749
7.736
7.692
7.682
7.260
7.165
7.153
7.141
7.085
7.058
4.005
2.428
2.411
2.400
2.374
2.374
2.347
1.808
1.797
1.767
1.729
1.729
1.698
1.363
1.331
1.308
1.286
1.286
1.253
1.218
O
O
S
S
SCN
3o
1H NMR, 400 MHz, CDCl3
1.06
1.00
1.05
1.06
2.00
1.05
5.04
5.07
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

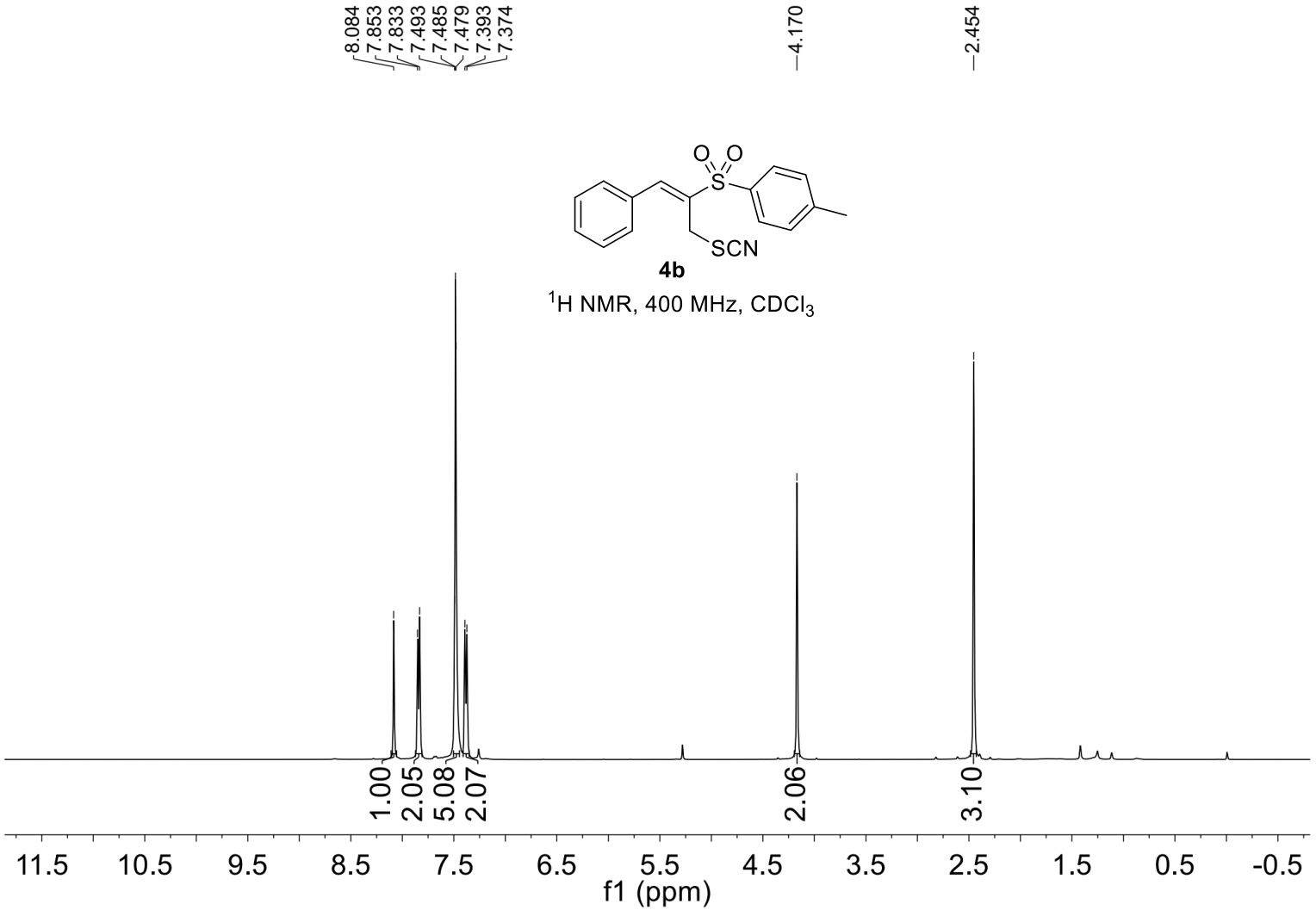

153.179
140.634
134.859
134.675
134.073
128.162
111.226
77.317
77.000
76.682
38.908
31.756
28.896
25.348
24.807
O
O
S
S
SCN
3o
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

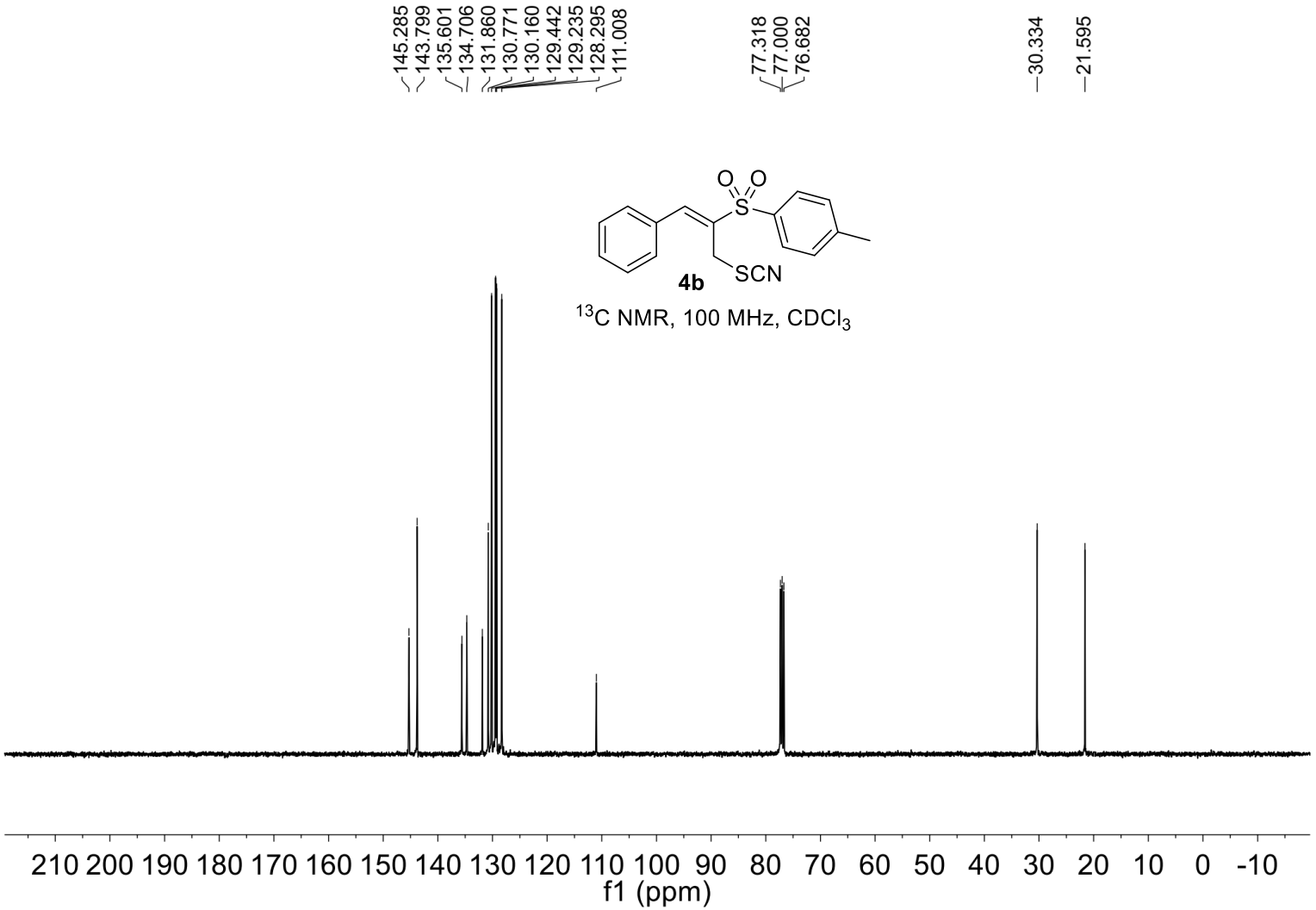


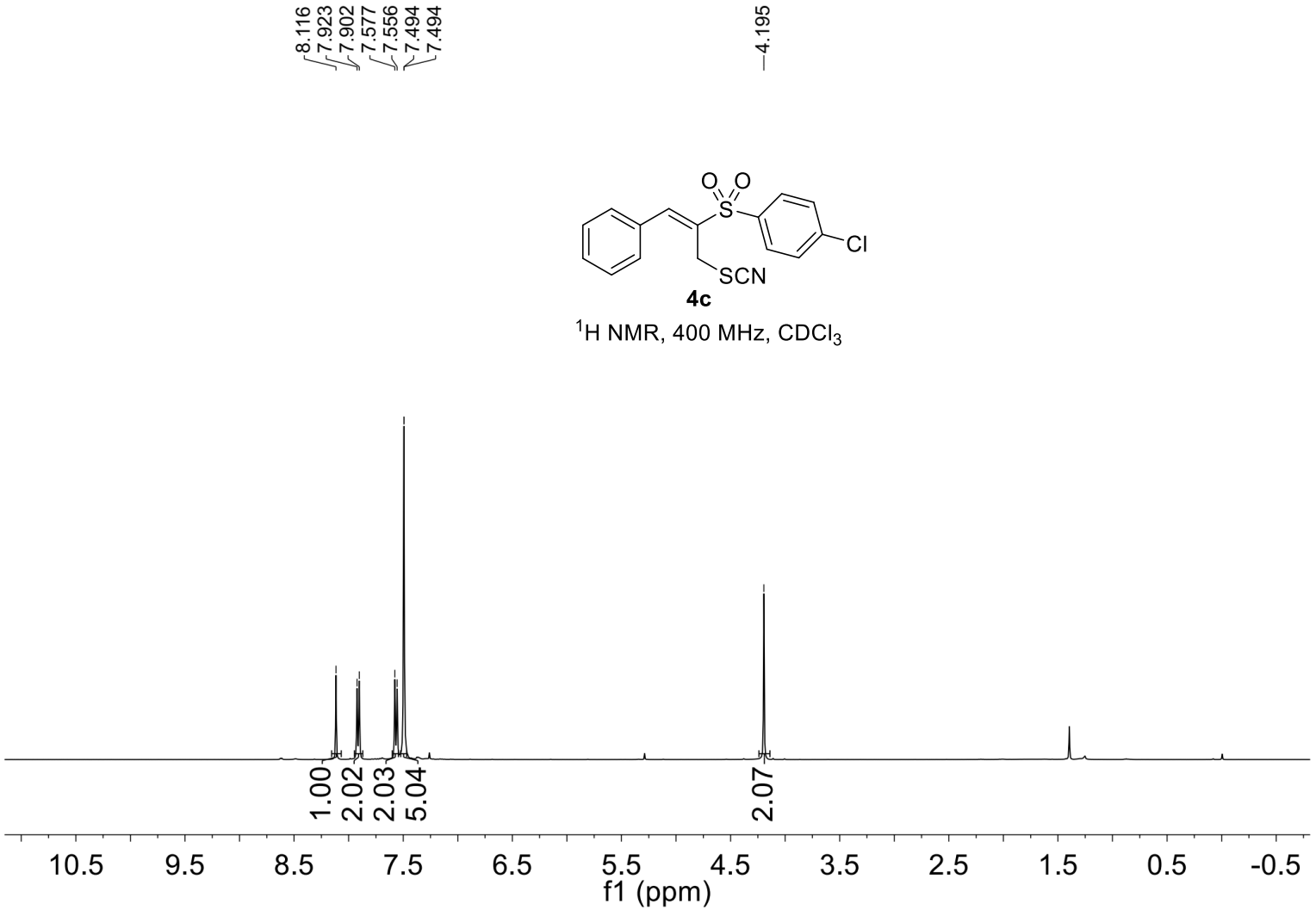
4a

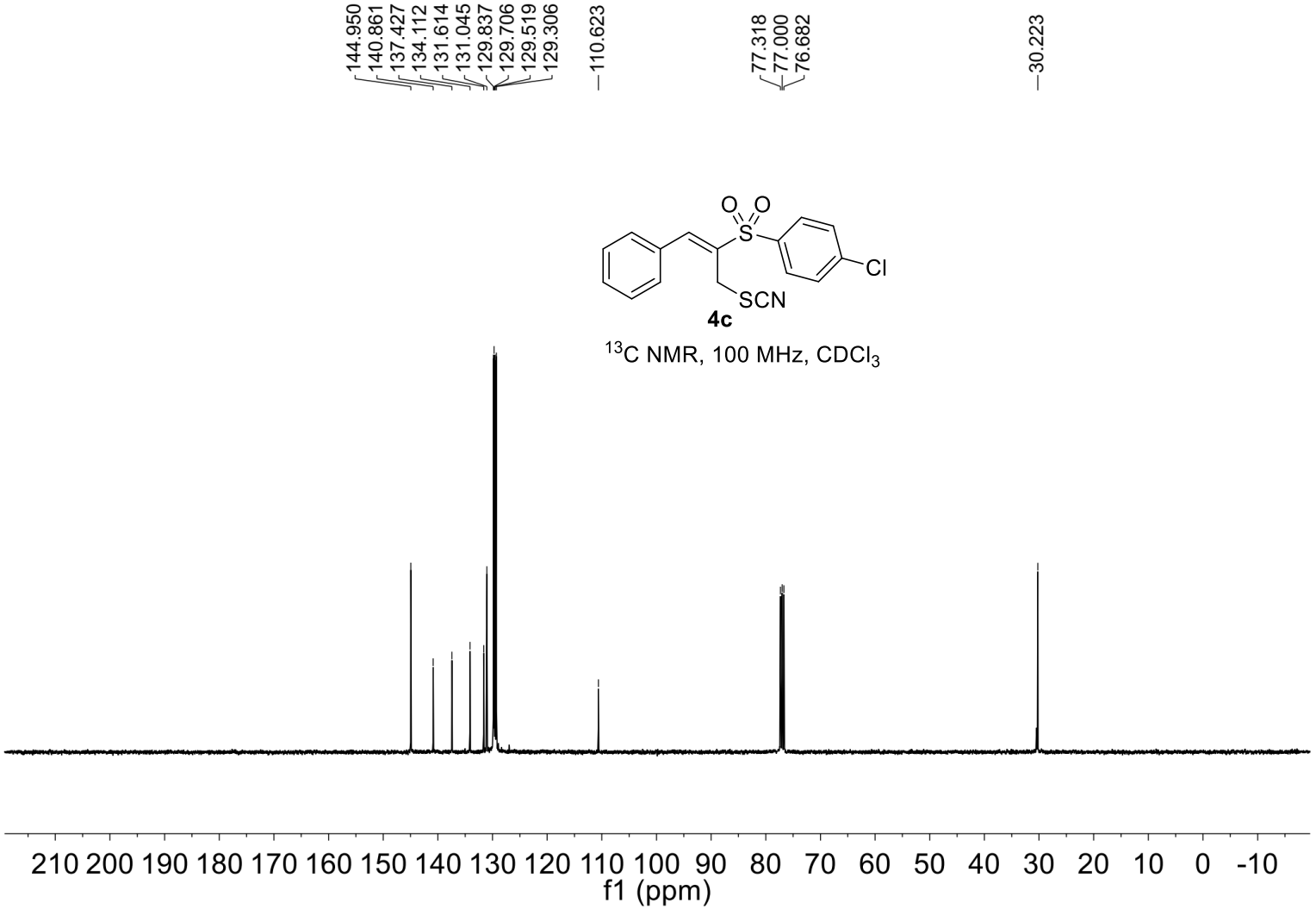
^{1}H NMR, 400 MHz, $CDCl_3$

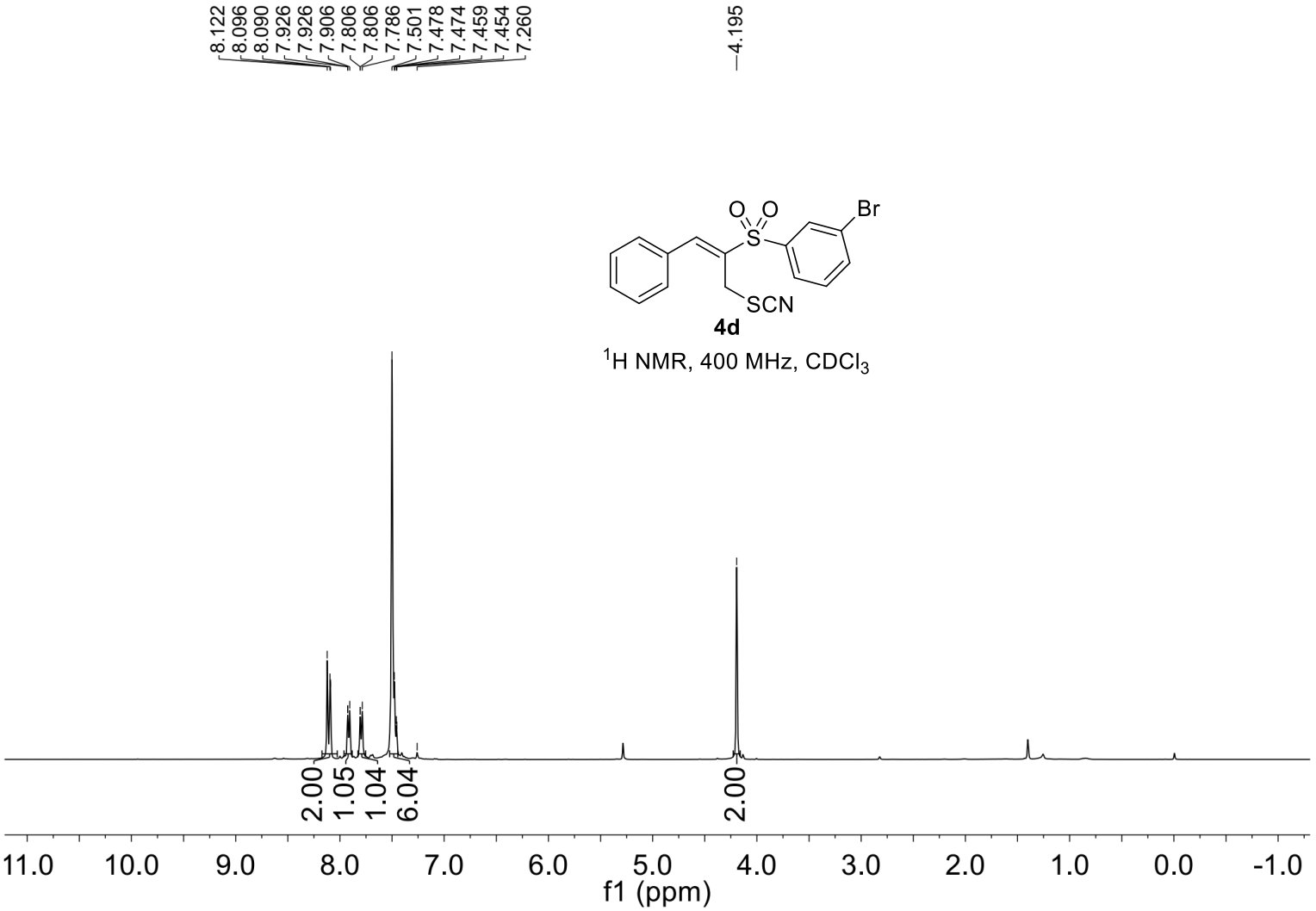

144.470
138.827
134.520
134.179
131.876
131.002
129.629
129.575
129.388
128.370
110.943
77.317
77.000
76.682
30.449
O
O
S
SCN
4a
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

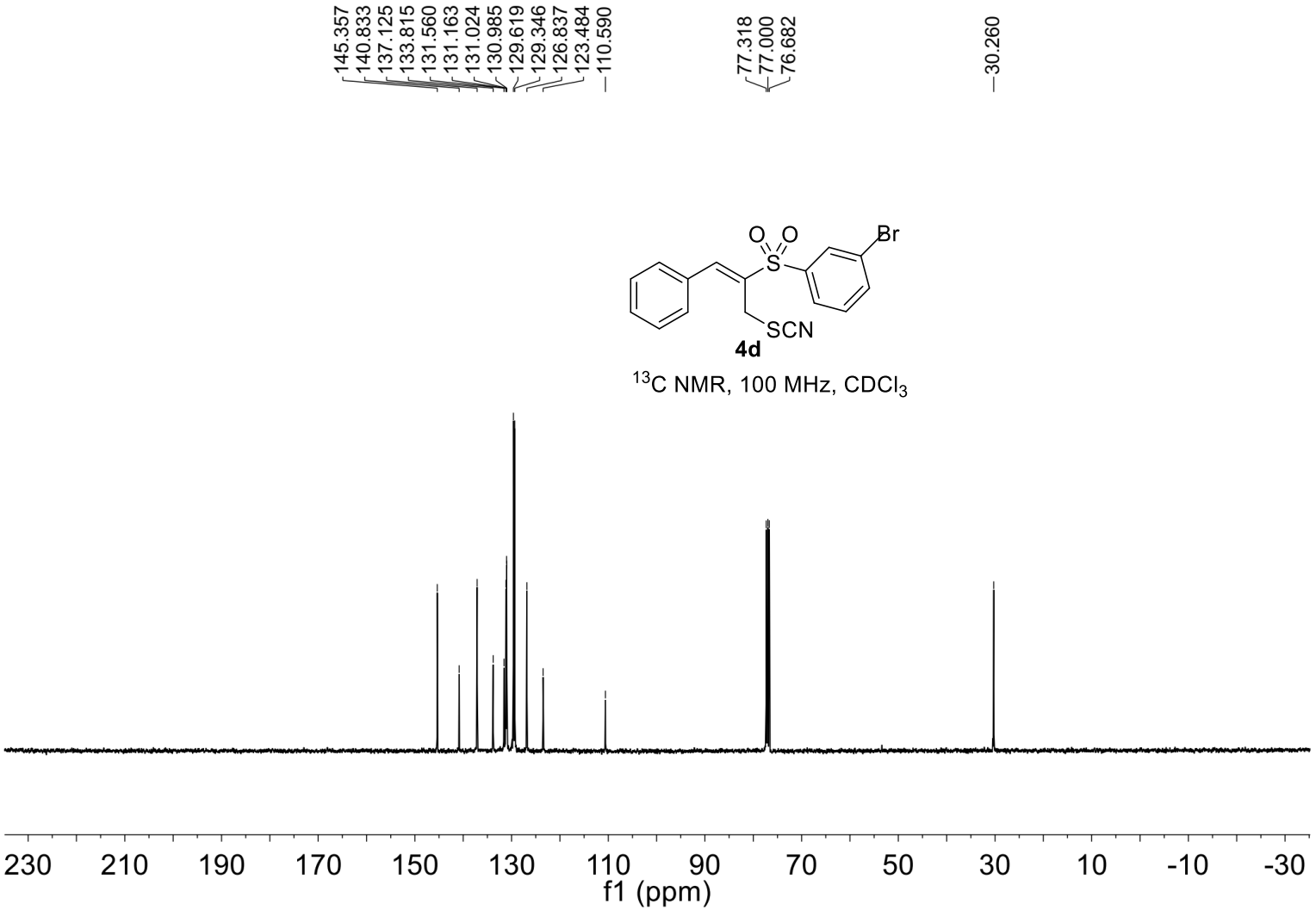

8.084
7.853
7.833
7.493
7.485
7.479
7.393
7.374
4.170
2.454
O
O
S
SCN
4b
^{1}H NMR, 400 MHz, $CDCl_3$
1.00
2.05
5.08
2.07
2.06
3.10
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

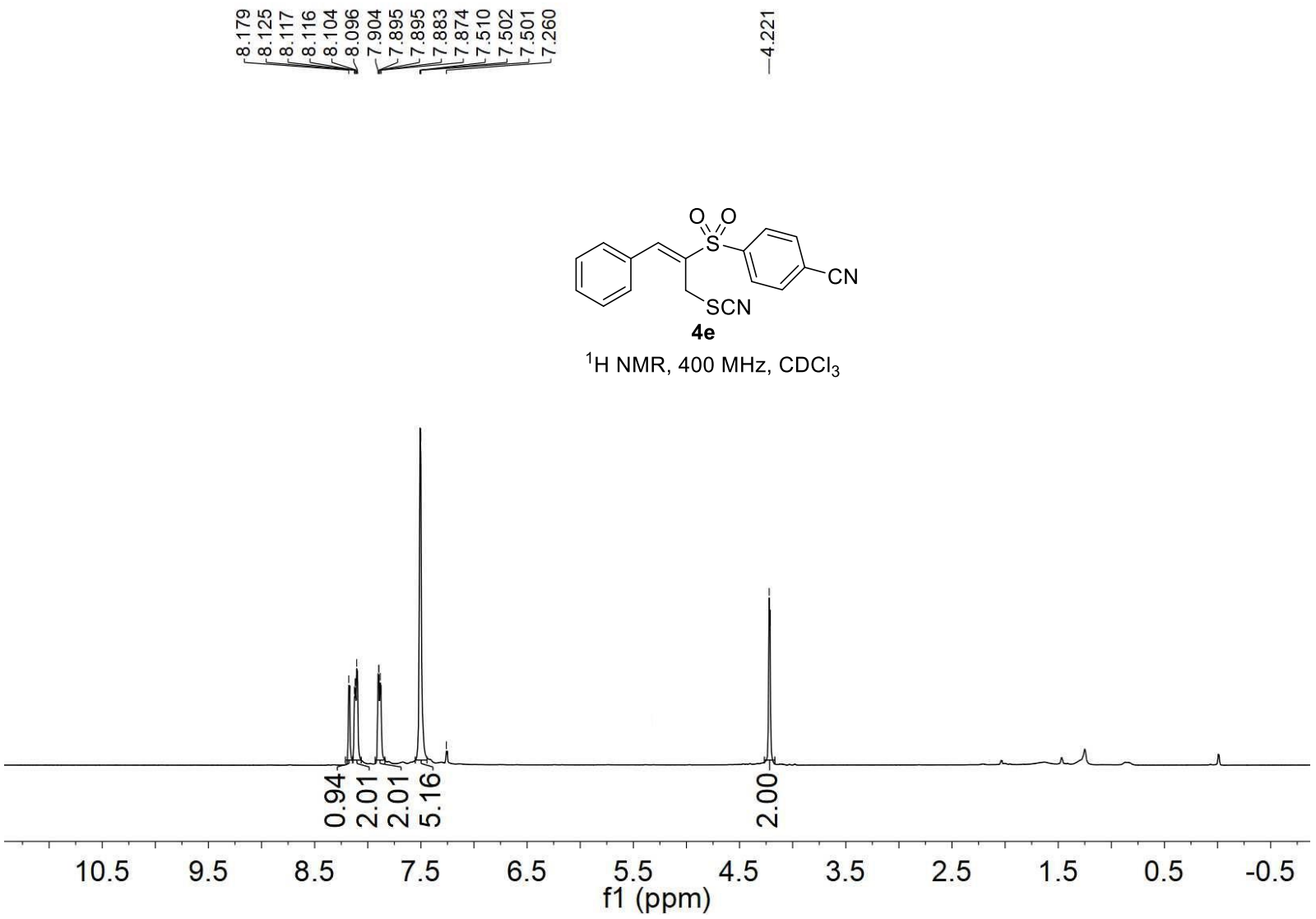

145.285
143.799
135.601
134.706
131.860
130.771
130.160
129.442
129.235
128.295
111.008
77.318
77.000
76.682
30.334
21.595
O
O
S
SCN
4b
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.116
7.923
7.902
7.577
7.556
7.494
7.494
4.195
O
O
S
Cl
SCN
4c
1H NMR, 400 MHz, CDCl3
1.00
2.02
2.03
5.04
2.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


144.950
140.861
137.427
134.112
131.614
131.045
129.837
129.706
129.519
129.306
110.623
77.318
77.000
76.682
30.223
O
O
S
Cl
SCN
4c
^{13}C NMR, 100 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

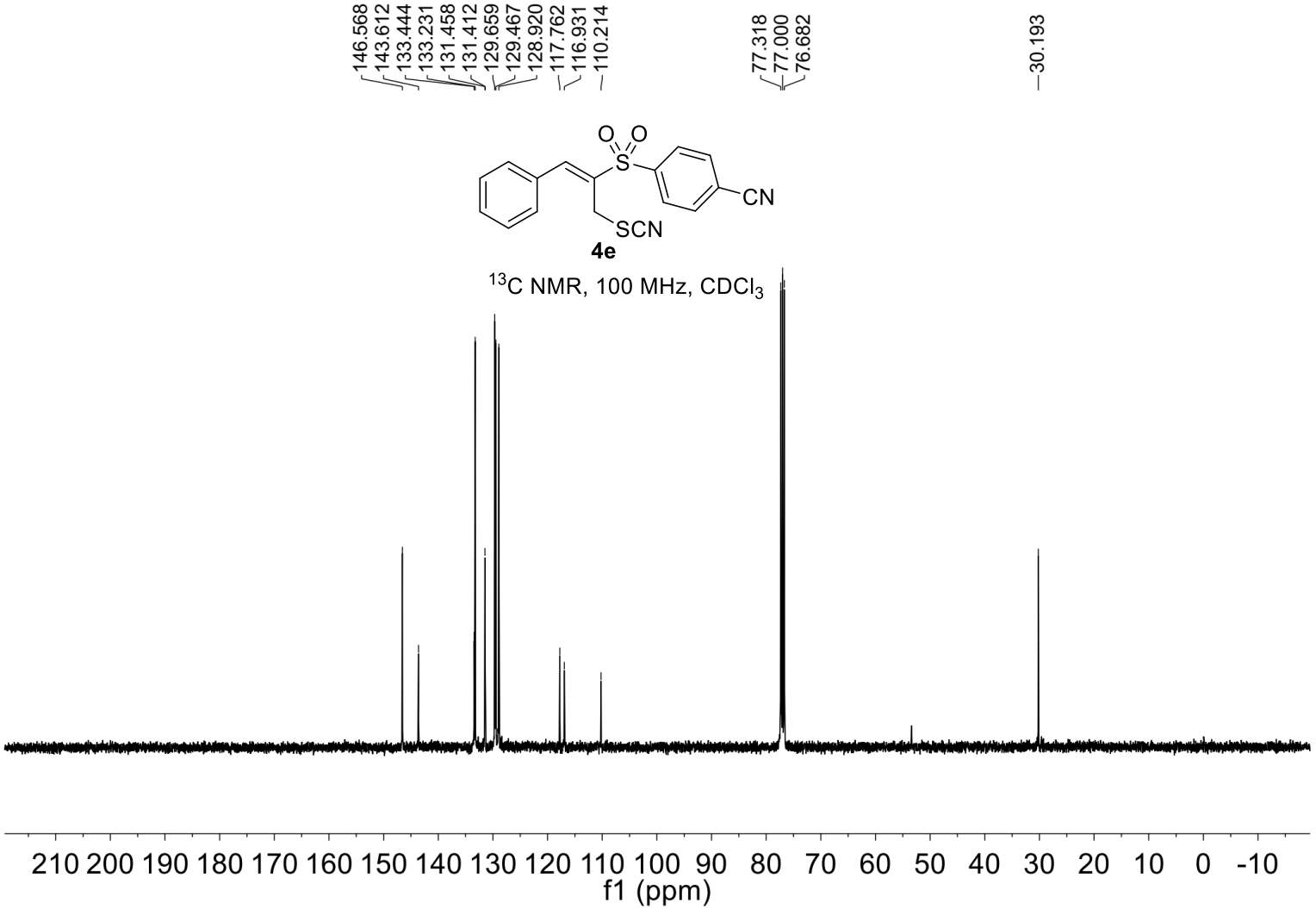

8.122
8.096
8.090
7.926
7.926
7.906
7.806
7.806
7.786
7.501
7.478
7.474
7.459
7.454
7.260
4.195
O
O
S
Br
SCN
4d
1H NMR, 400 MHz, CDCl3
2.00
1.05
1.04
6.04
2.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

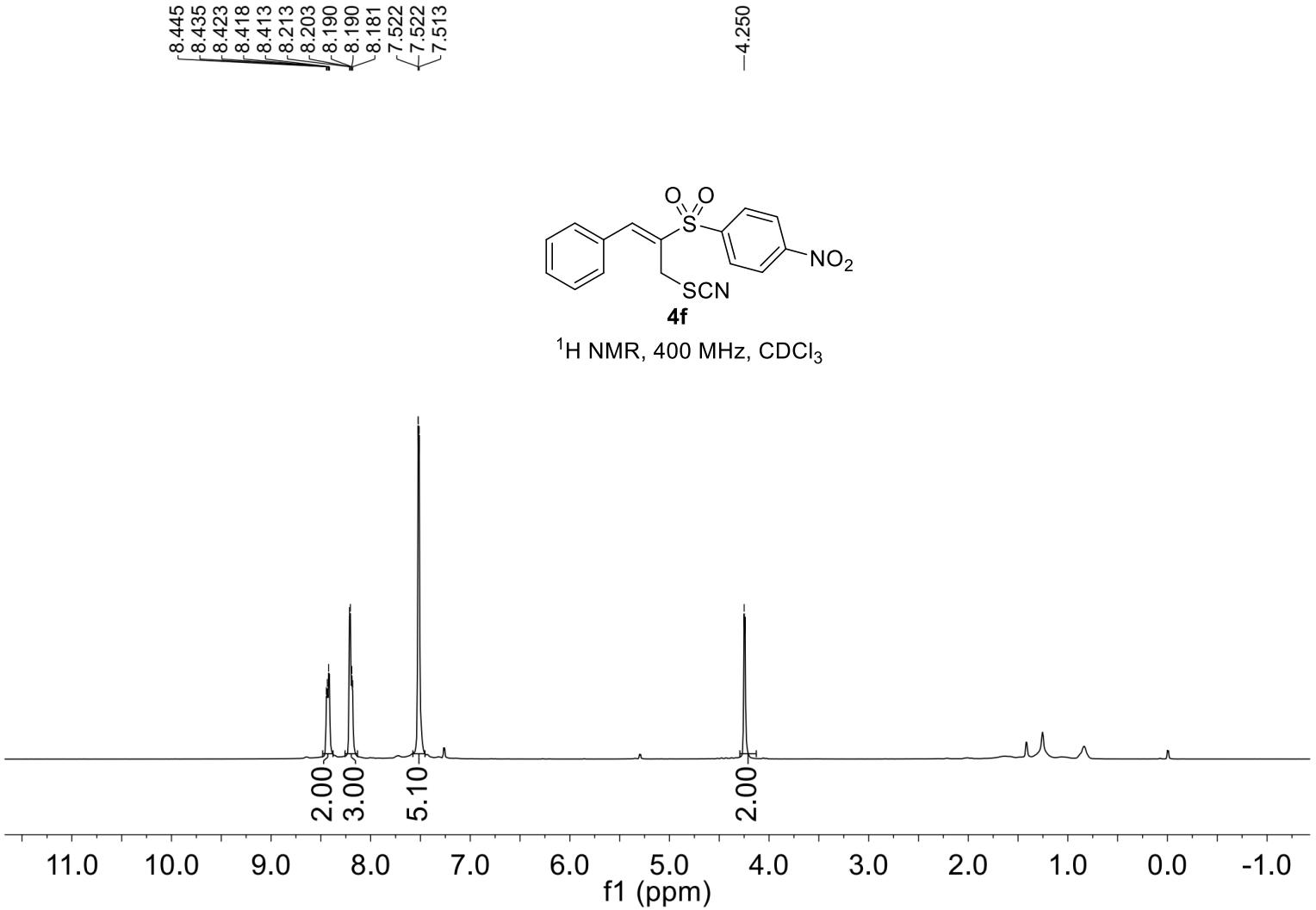

145.357
140.833
137.125
133.815
131.560
131.163
131.024
130.985
129.619
129.346
126.837
123.484
110.590
77.318
77.000
76.682
30.260
O
O
S
Br
SCN
4d
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

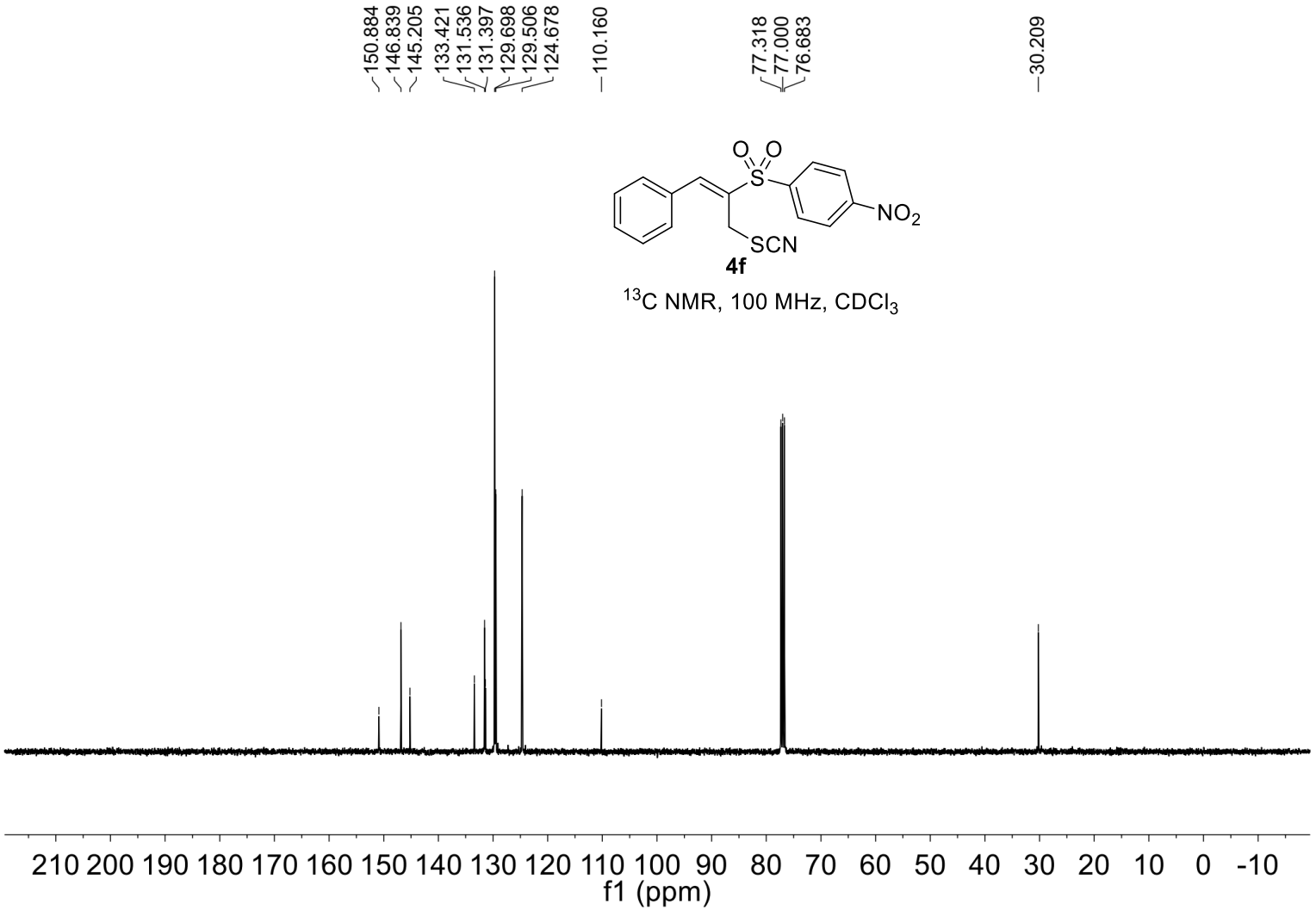


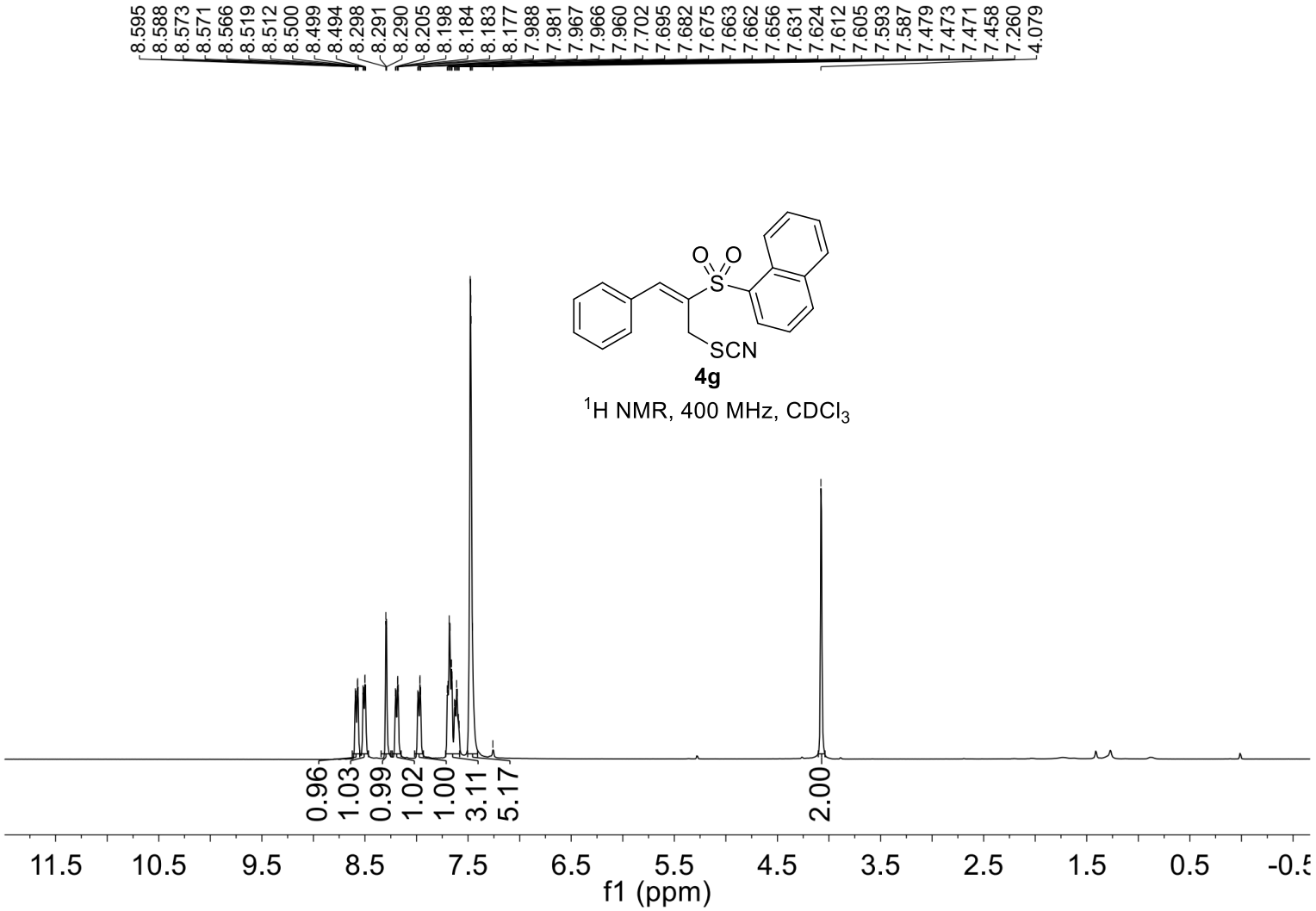
4e

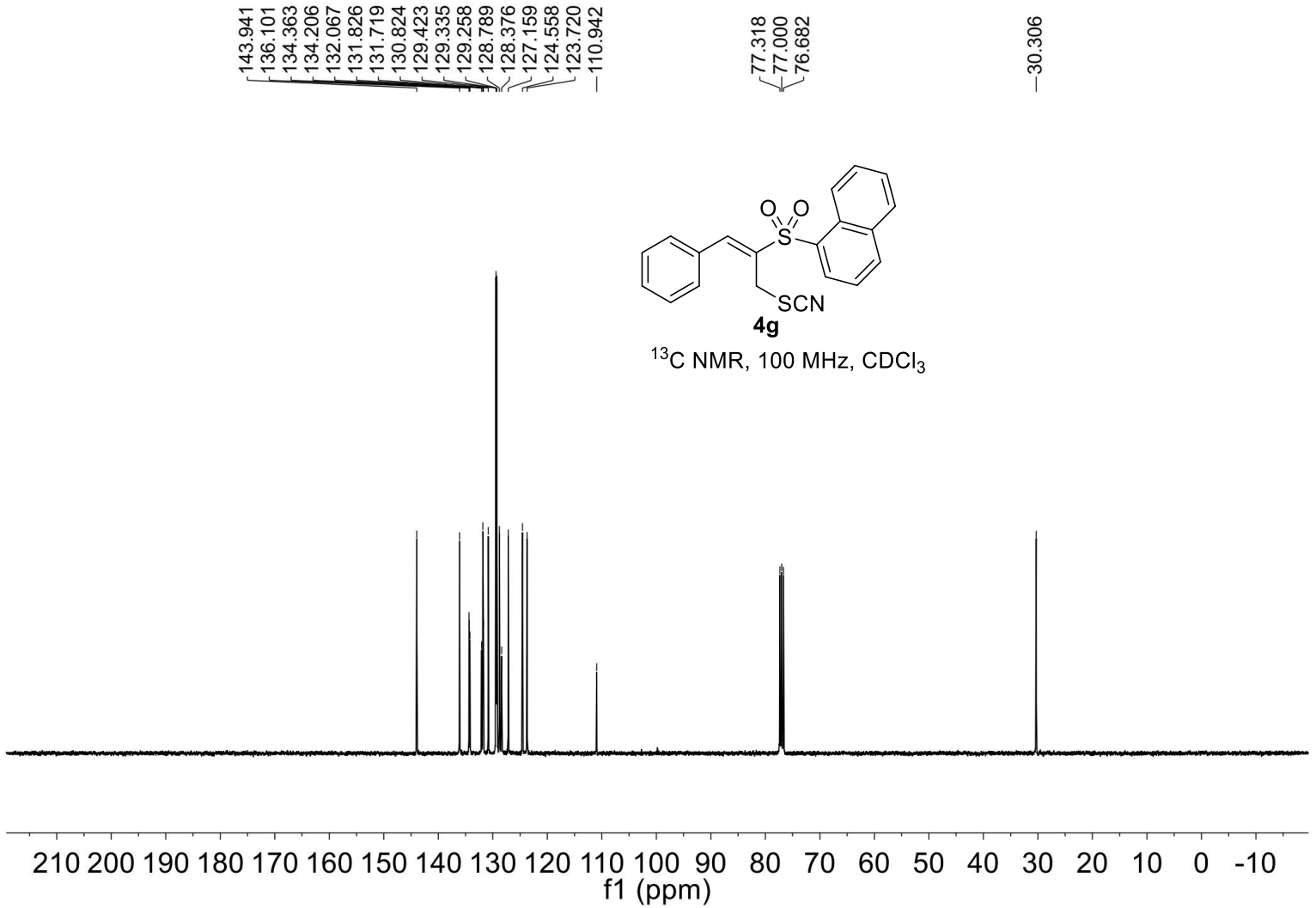
^{1}H NMR, 400 MHz, $CDCl_3$

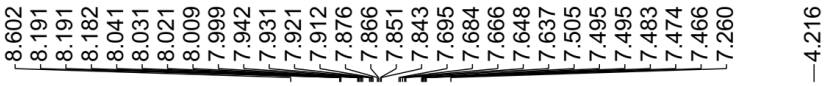

146.568
143.612
133.444
133.231
131.458
131.412
129.659
129.467
128.920
117.762
116.931
110.214
77.318
77.000
76.682
30.193
O
O
S
CN
SCN
4e
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

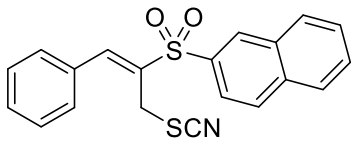

8.445
8.435
8.423
8.418
8.413
8.213
8.203
8.190
8.190
8.181
7.522
7.522
7.513
4.250
O
O
S
NO2
SCN
4f
1H NMR, 400 MHz, CDCl3
2.00
3.00
5.10
2.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


150.884
146.839
145.205
133.421
131.536
131.397
129.698
129.506
124.678
110.160
77.318
77.000
76.683
30.209
O
O
S
NO2
SCN
4f
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.595
8.588
8.573
8.571
8.566
8.519
8.512
8.500
8.499
8.494
8.298
8.291
8.290
8.205
8.198
8.184
8.183
8.177
7.988
7.981
7.967
7.966
7.960
7.702
7.695
7.682
7.675
7.663
7.662
7.656
7.631
7.624
7.612
7.605
7.593
7.587
7.479
7.473
7.471
7.458
7.260
4.079
O
O
S
SCN
4g
1H NMR, 400 MHz, CDCl3
0.96
1.03
0.99
1.02
1.00
3.11
5.17
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

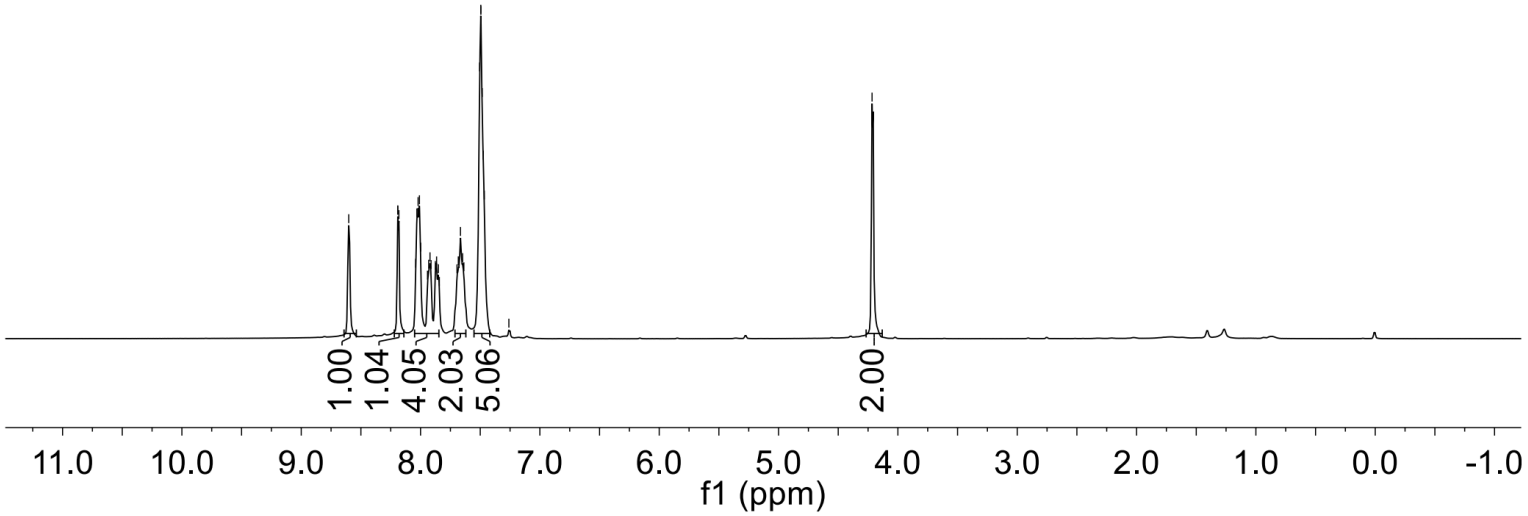

143.941
136.101
134.363
134.206
132.067
131.826
131.719
130.824
129.423
129.335
129.258
128.789
128.376
127.159
124.558
123.720
110.942
77.318
77.000
76.682
30.306
O
O
S
SCN
4g
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

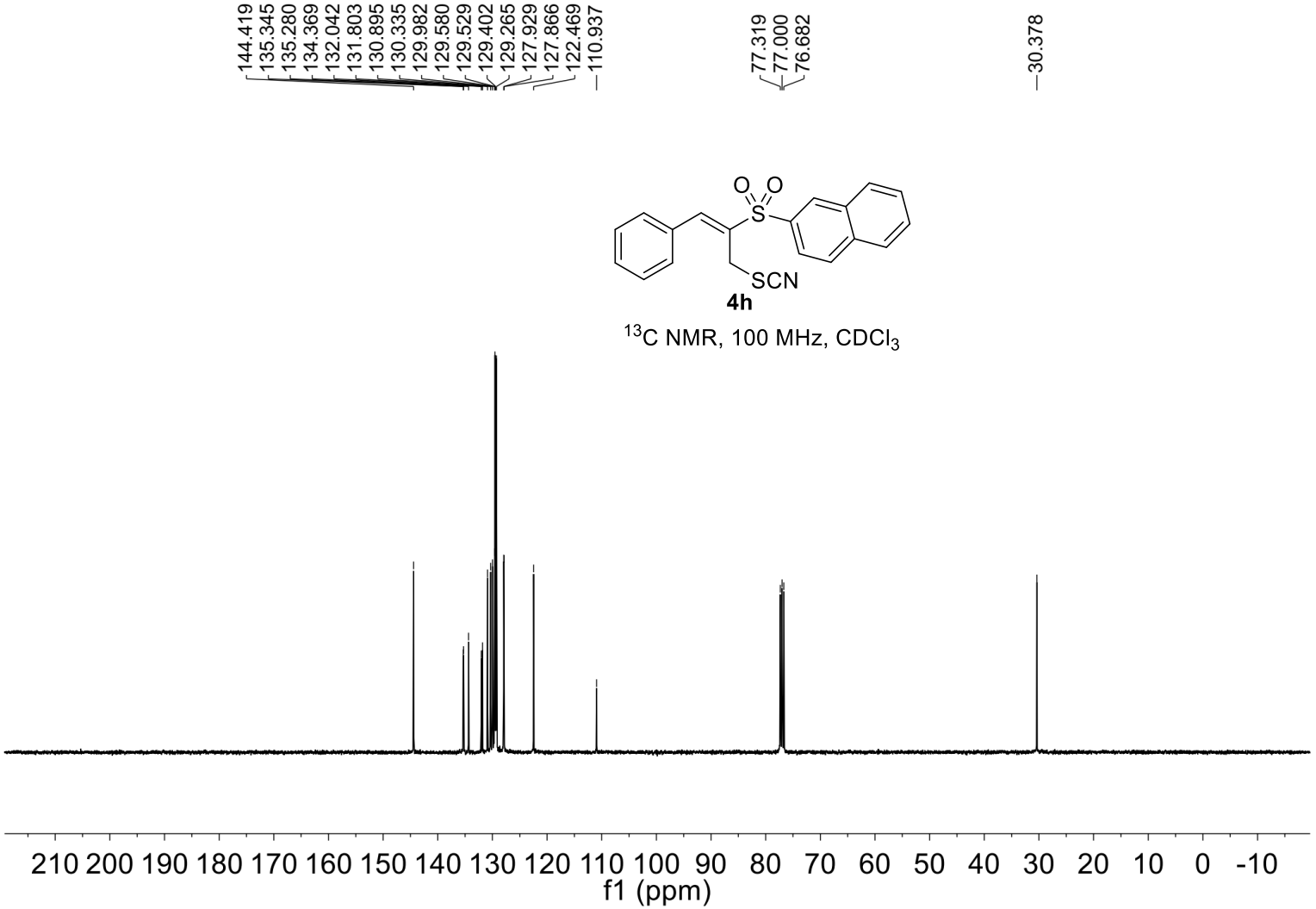


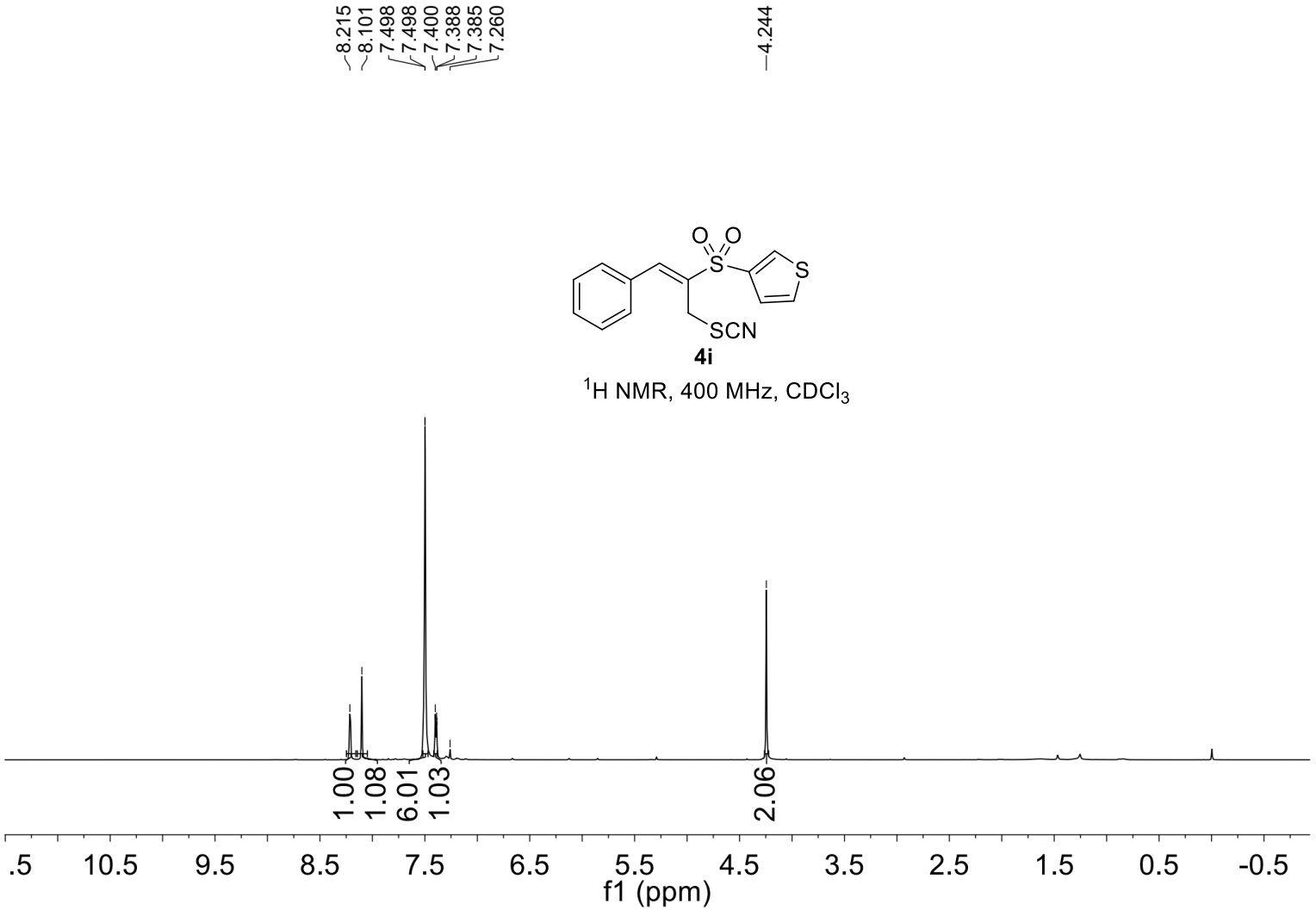


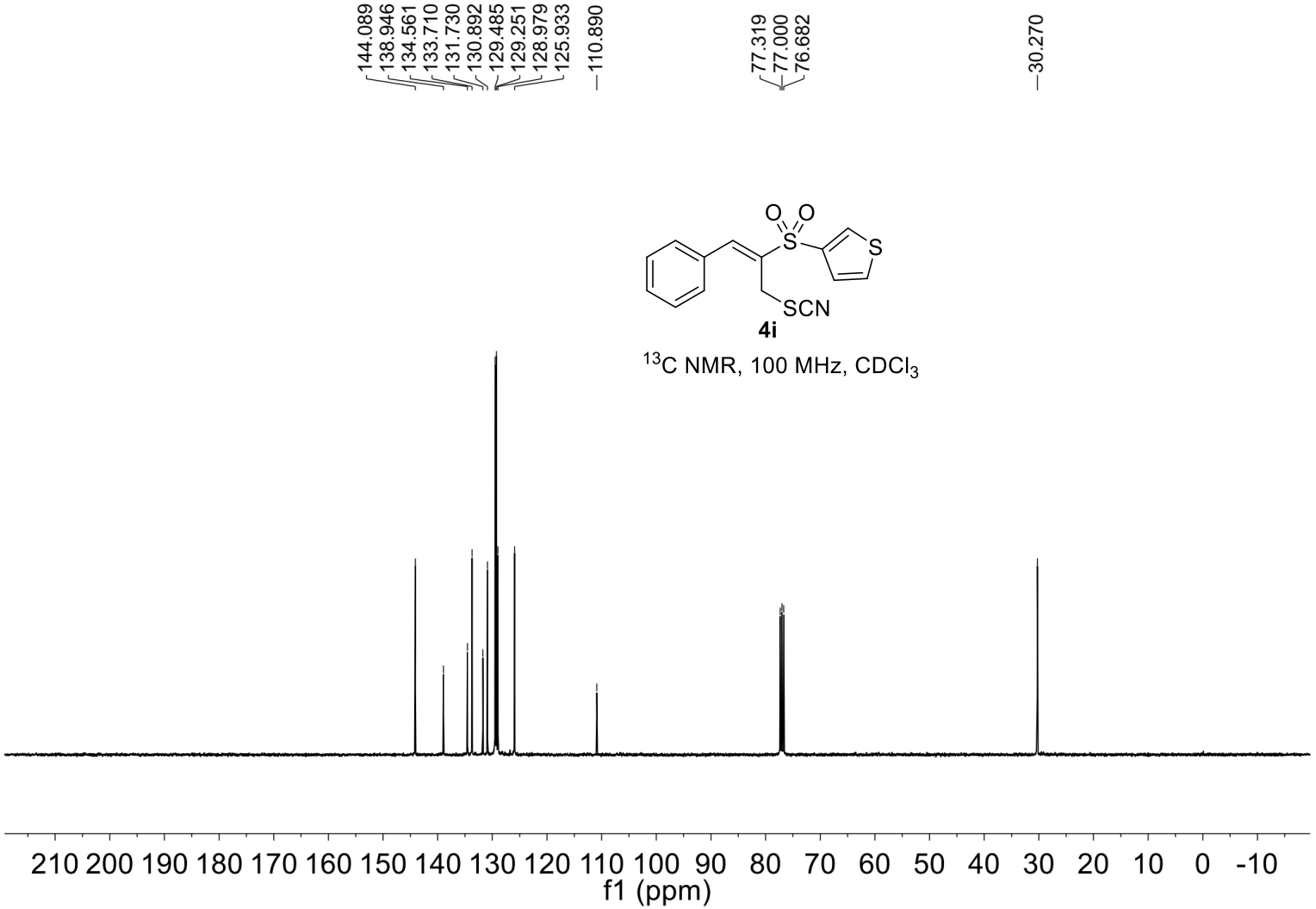
4h

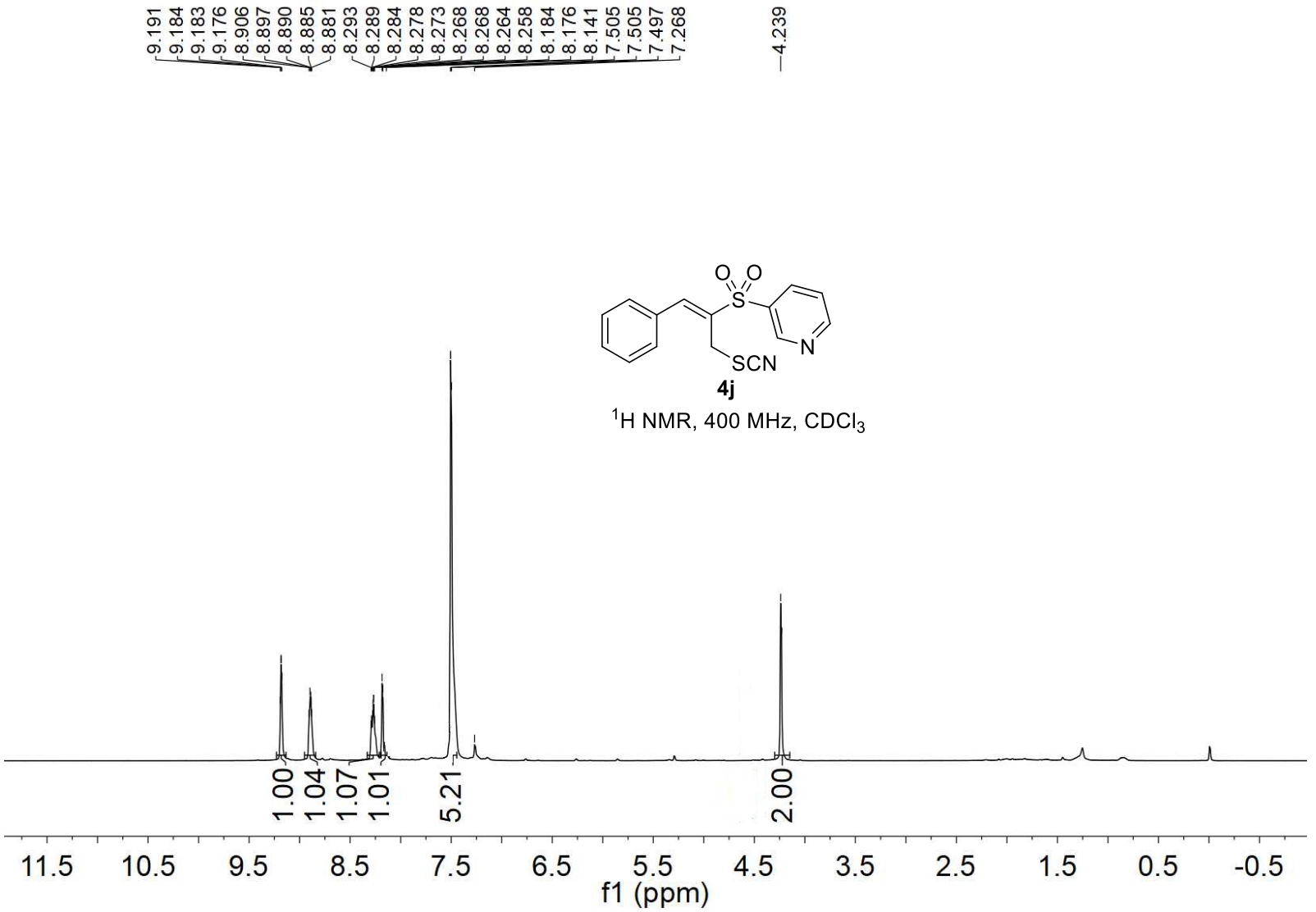
^{1}H NMR, 400 MHz, $CDCl_3$

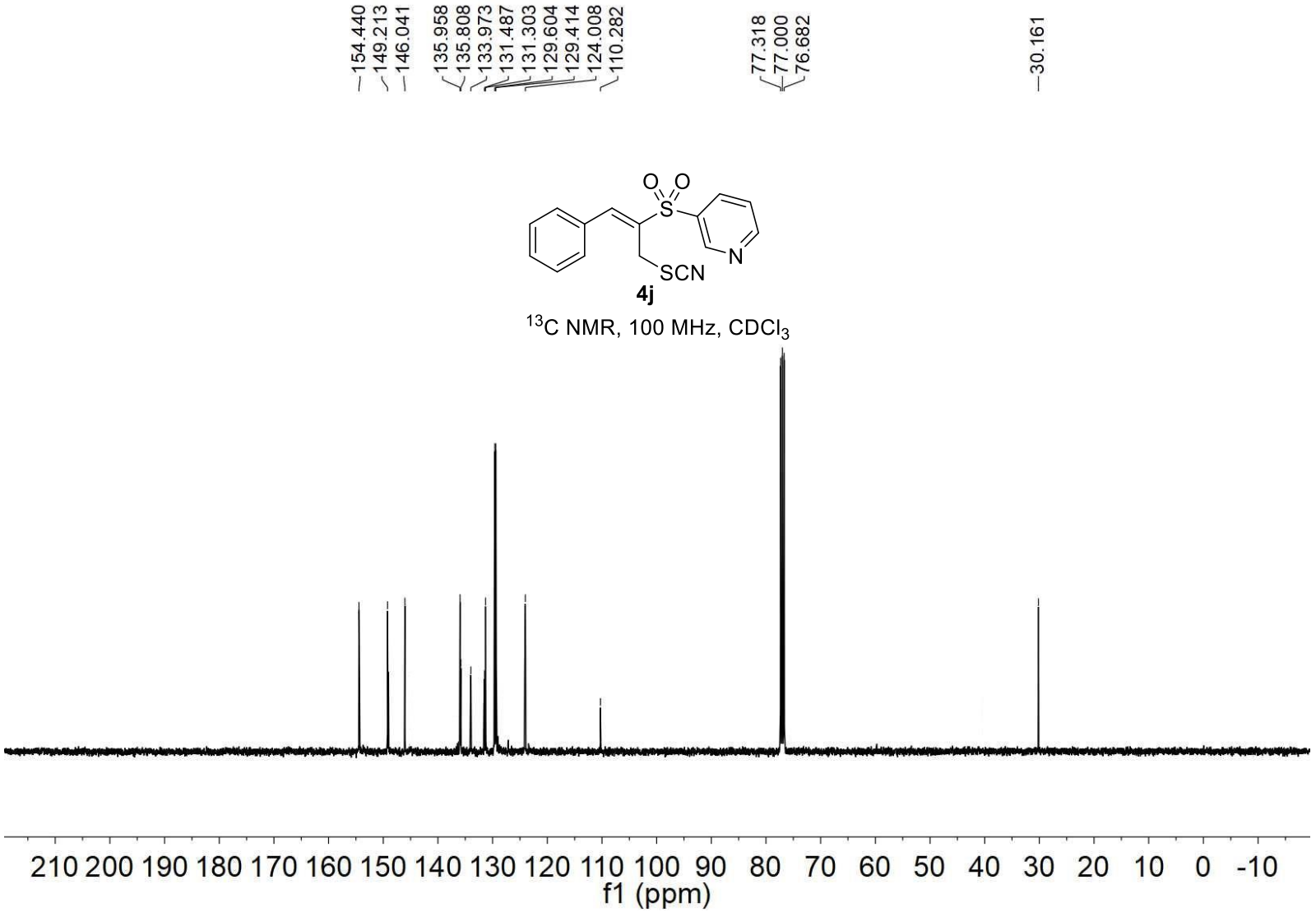


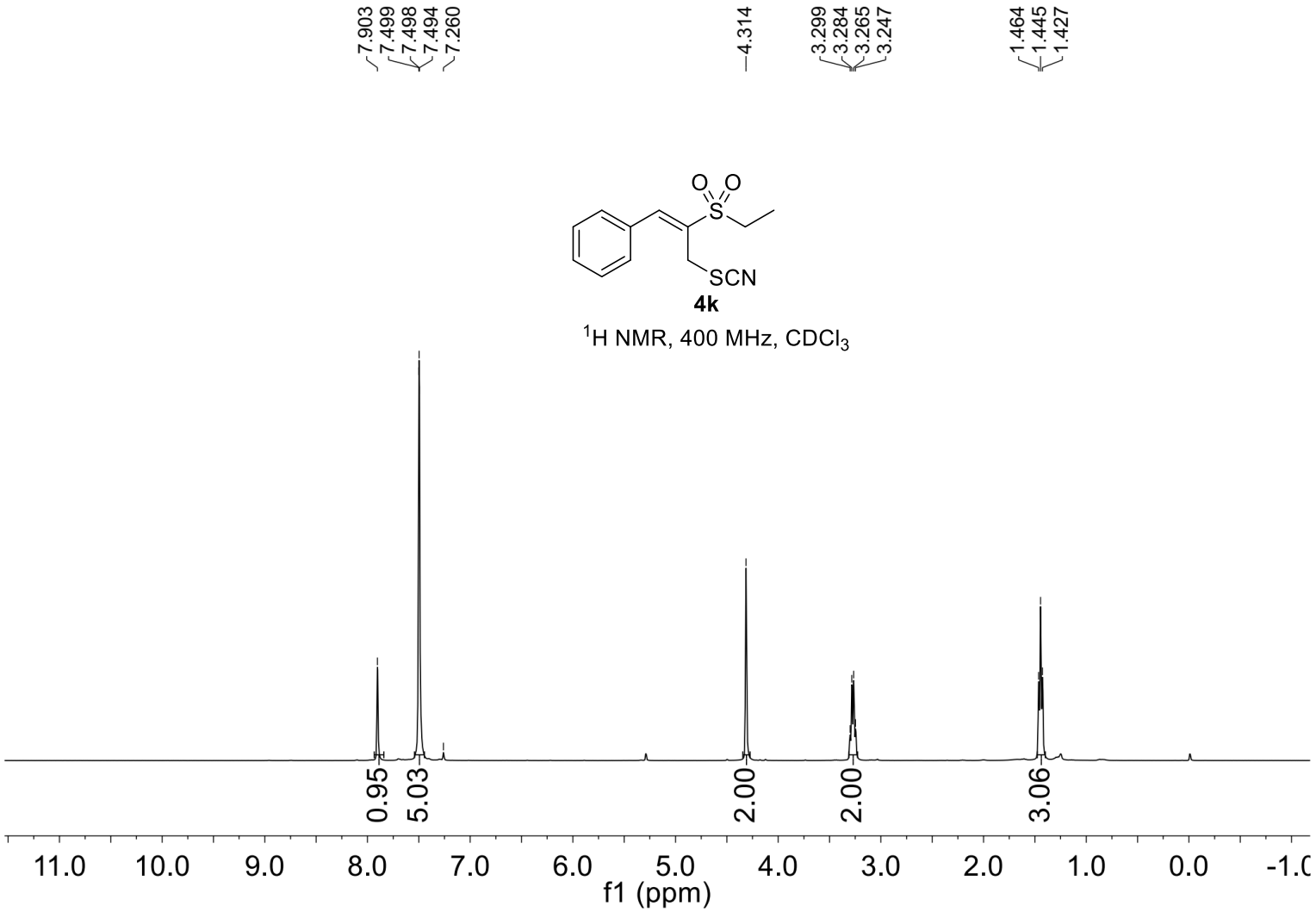

144.419
135.345
135.280
134.369
132.042
131.803
130.895
130.335
129.982
129.580
129.529
129.402
129.265
127.929
127.866
122.469
110.937
77.319
77.000
76.682
30.378
O
O
S
SCN
4h
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

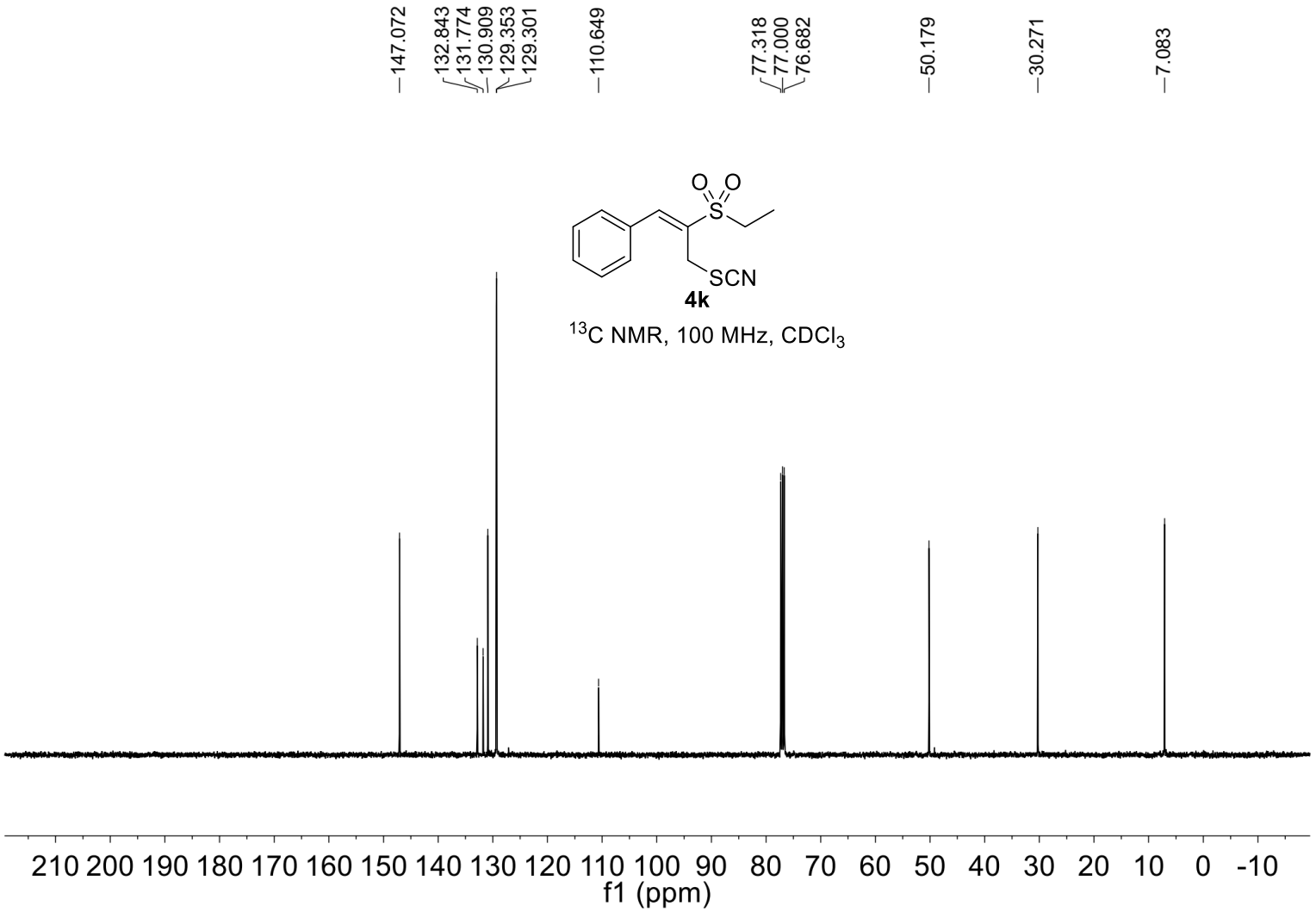

8.215
8.101
7.498
7.498
7.400
7.388
7.385
7.260
4.244
O
O
S
S
SCN
4i
1H NMR, 400 MHz, CDCl3
1.00
1.08
6.01
1.03
2.06
.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

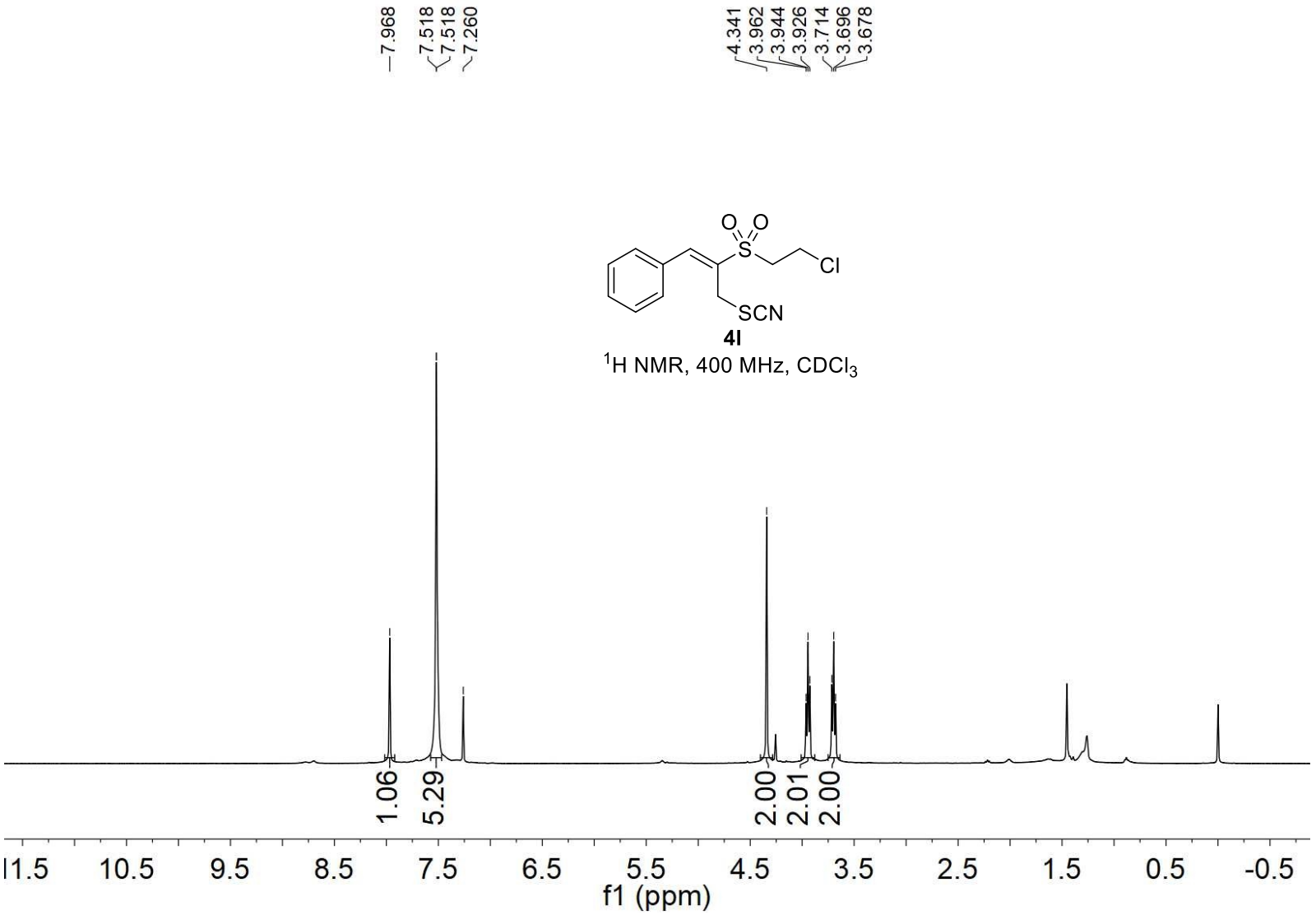

144.089
138.946
134.561
133.710
131.730
130.892
129.485
129.251
128.979
125.933
110.890
77.319
77.000
76.682
30.270
O
O
S
S
SCN
4i
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

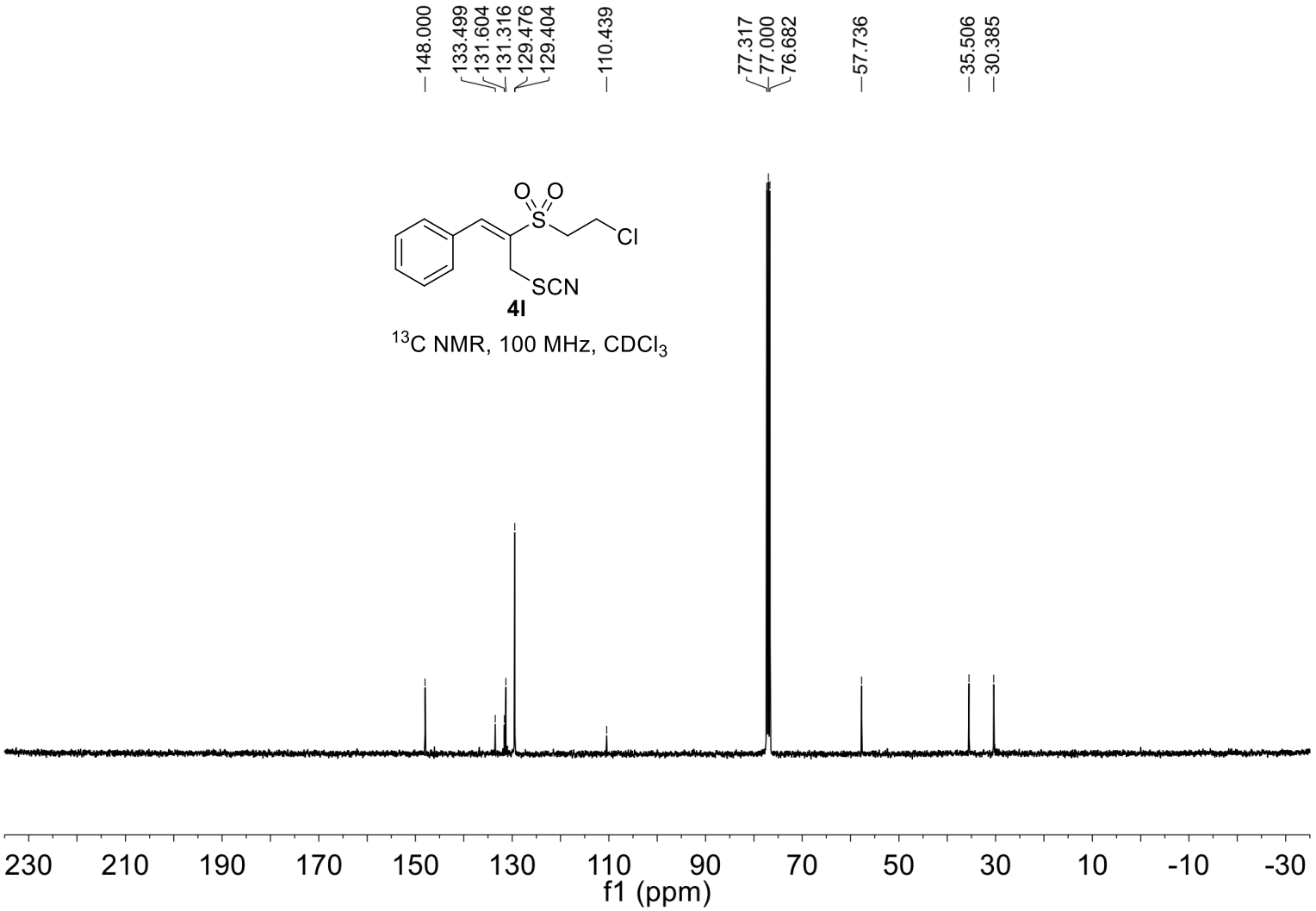

9.191
9.184
9.183
9.176
8.906
8.897
8.890
8.885
8.881
8.293
8.289
8.284
8.278
8.273
8.268
8.268
8.264
8.258
8.184
8.176
8.141
7.505
7.505
7.497
7.268
4.239
O
O
S
N
SCN
4j
1H NMR, 400 MHz, CDCl3
1.00
1.04
1.07
1.01
5.21
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

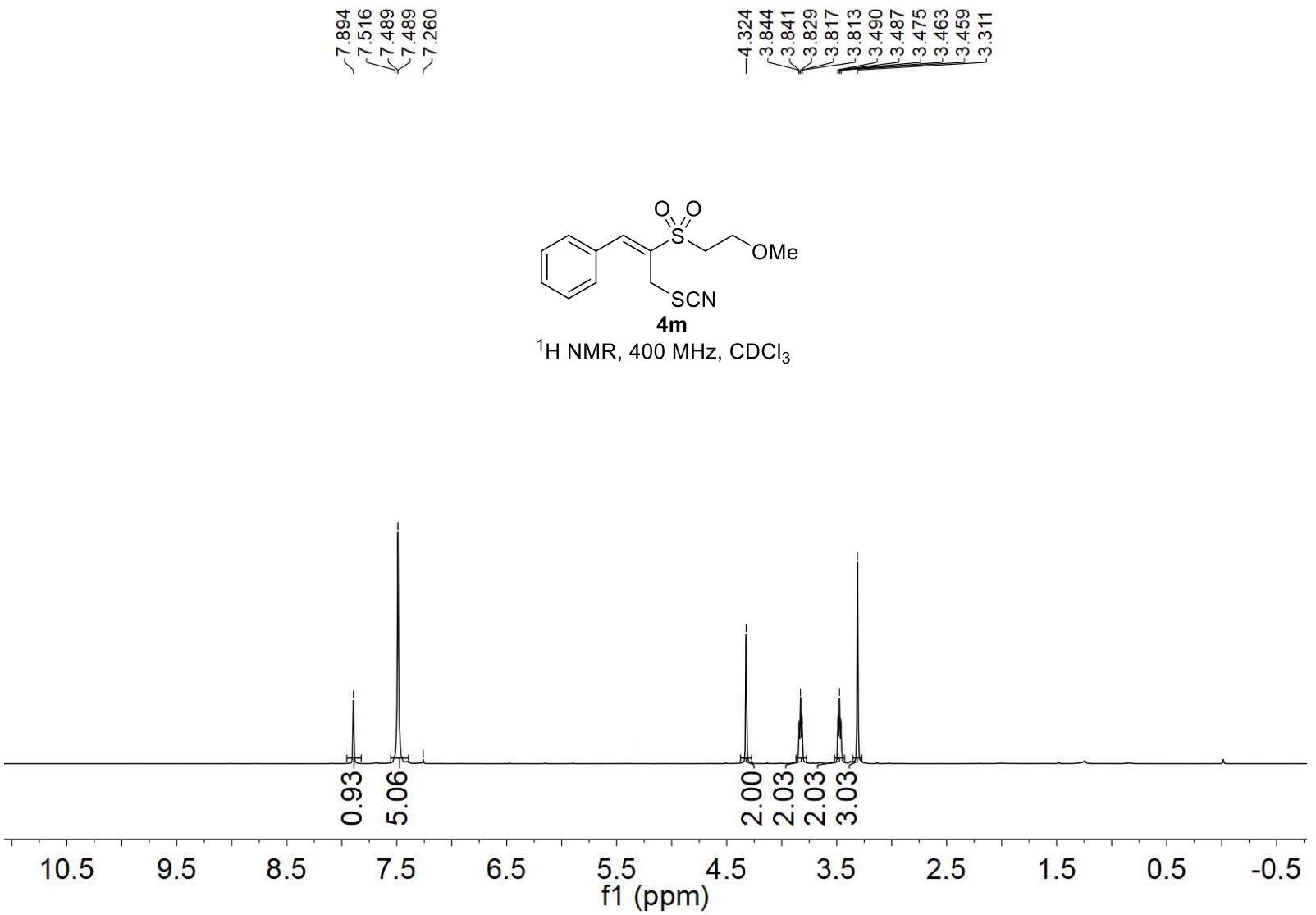

154.440
149.213
146.041
135.958
135.808
133.973
131.487
131.303
129.604
129.414
124.008
110.282
77.318
77.000
76.682
30.161
O
O
S
N
SCN
4j
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

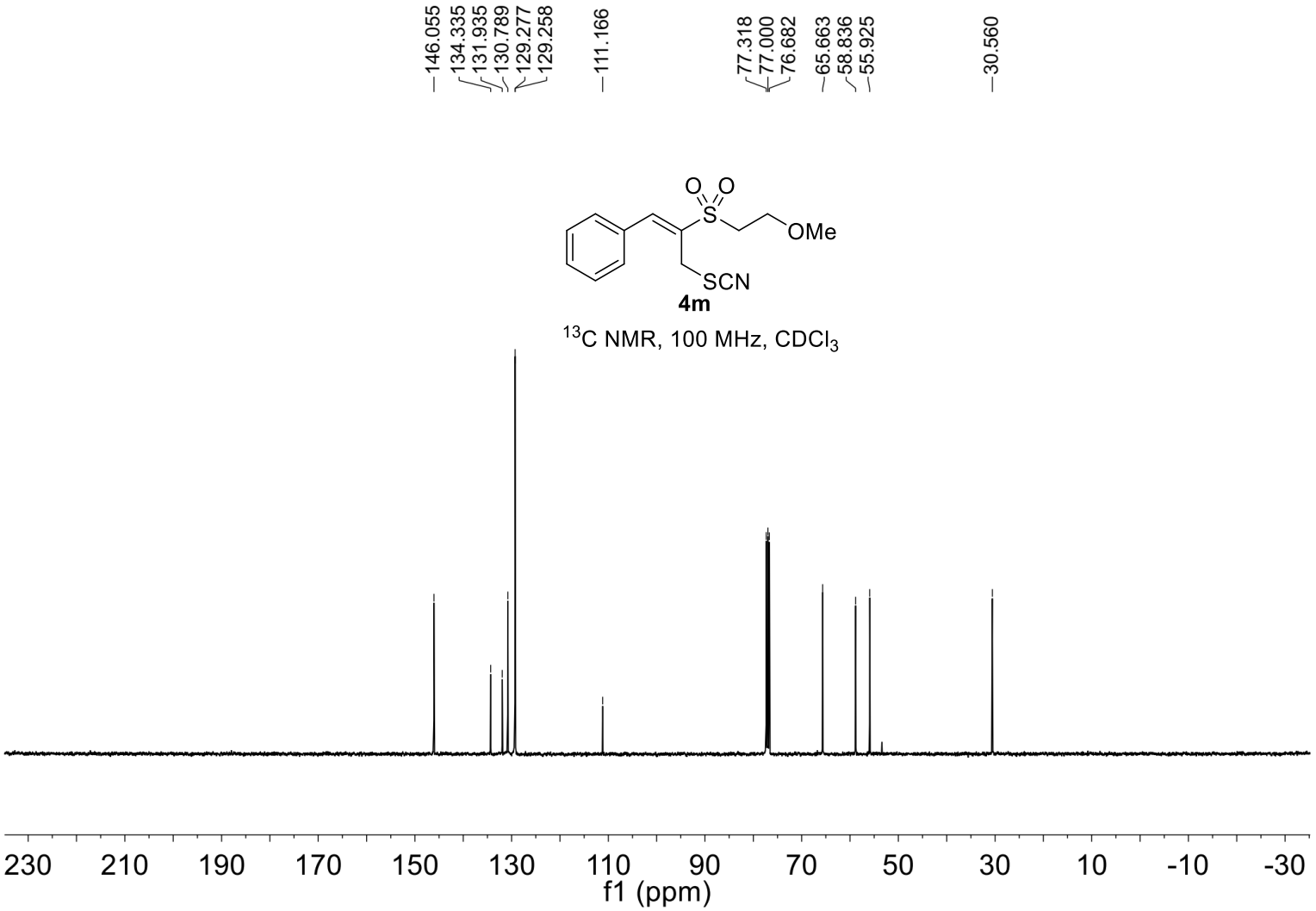

7.903
7.499
7.498
7.494
7.260
4.314
3.299
3.284
3.265
3.247
1.464
1.445
1.427
O
O
S
SCN
4k
1H NMR, 400 MHz, CDCl3
0.95
5.03
2.00
2.00
3.06
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

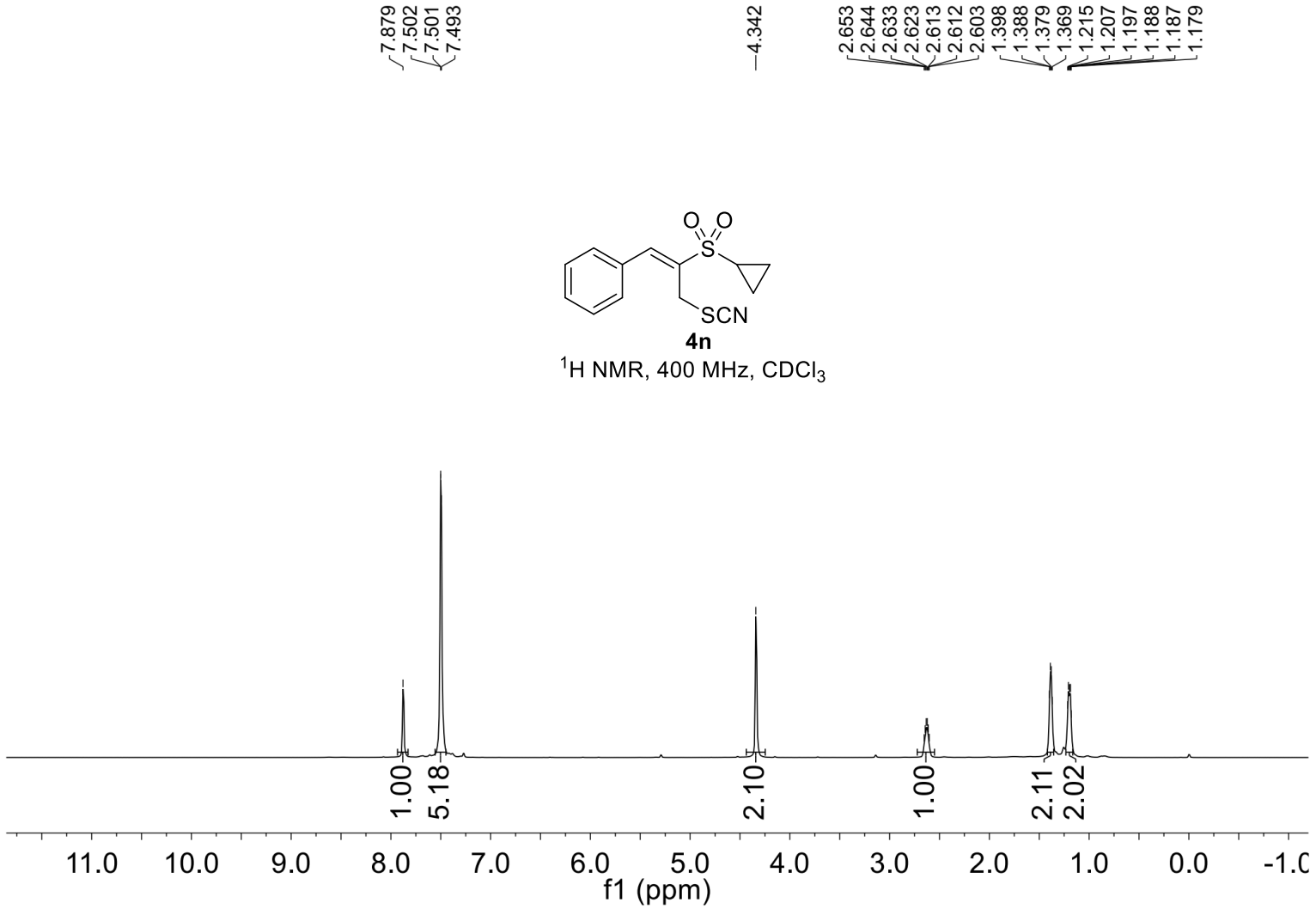

147.072
132.843
131.774
130.909
129.353
129.301
110.649
77.318
77.000
76.682
50.179
30.271
7.083
O
O
S
SCN
4k
^{13}C NMR, 100 MHz, CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

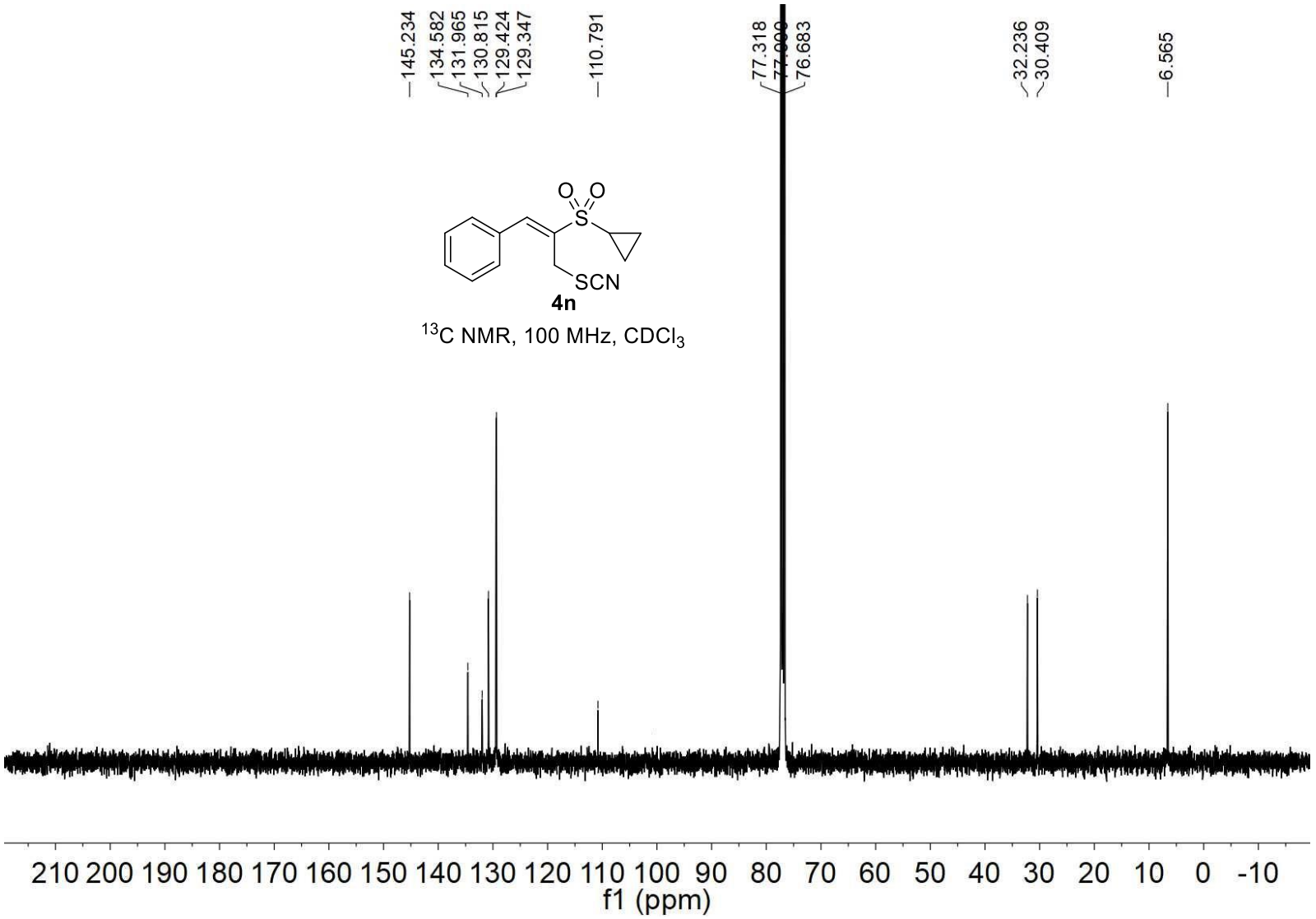

7.968
7.518
7.518
7.260
4.341
3.962
3.944
3.926
3.714
3.696
3.678
O
O
S
Cl
SCN
4l
1H NMR, 400 MHz, CDCl3
1.06
5.29
2.00
2.01
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

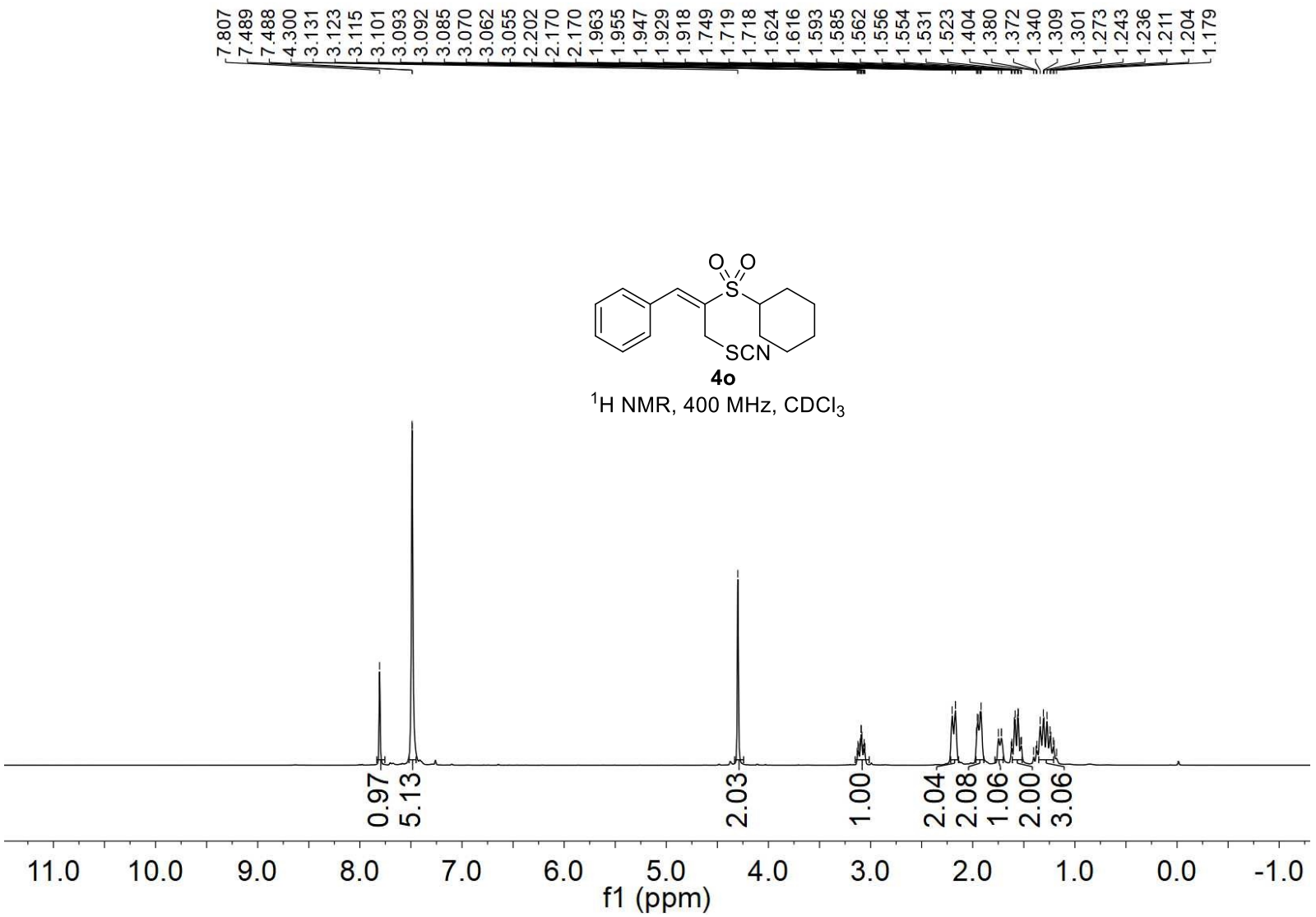

148.000
133.499
131.604
131.316
129.476
129.404
110.439
77.317
77.000
76.682
57.736
35.506
30.385
O
O
S
Cl
SCN
4l
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

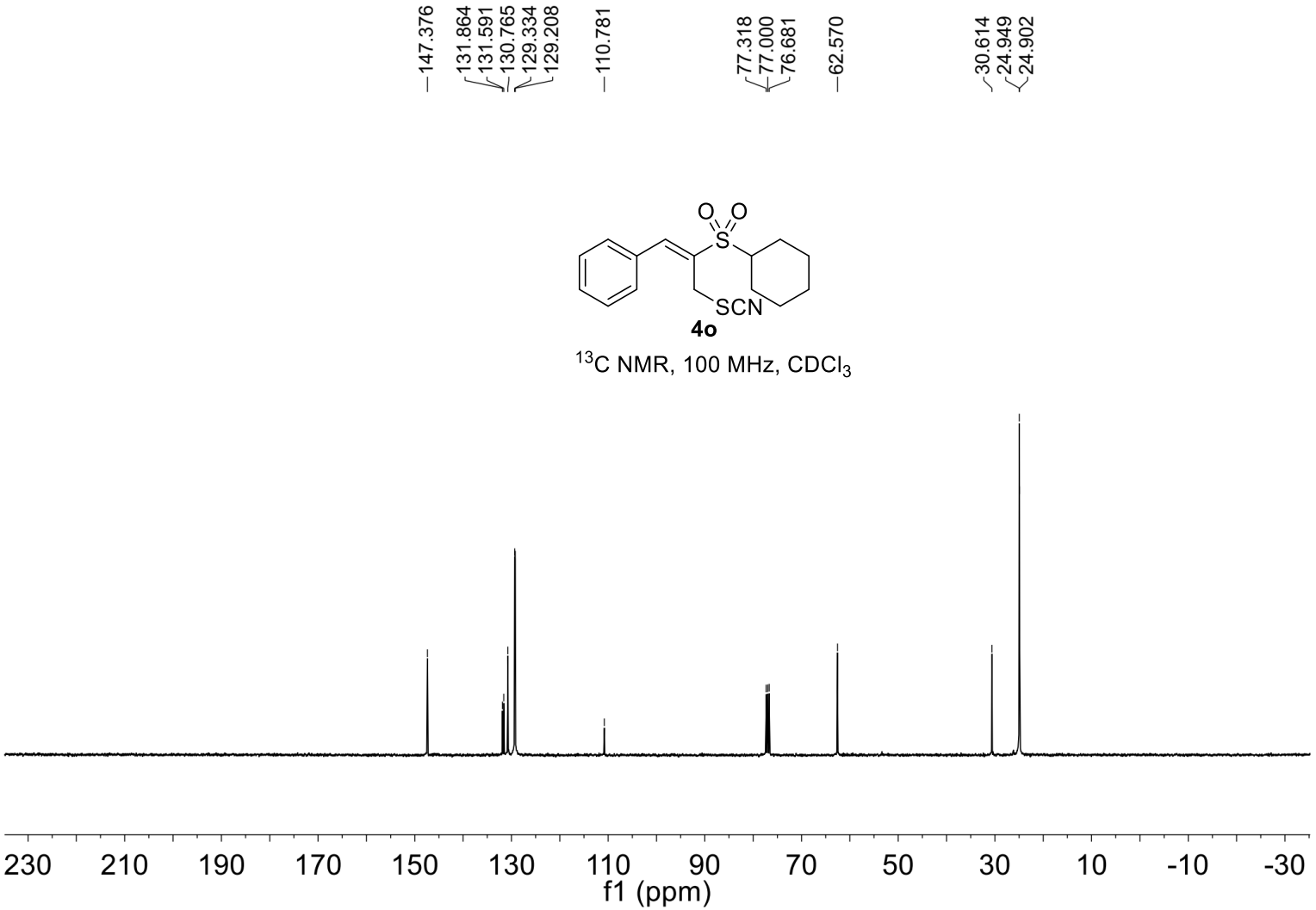

7.894
7.516
7.489
7.489
7.260
4.324
3.844
3.841
3.829
3.817
3.813
3.490
3.487
3.475
3.463
3.459
3.311
O
O
S
OMe
SCN
4m
1H NMR, 400 MHz, CDCl3
0.93
5.06
2.00
2.03
2.03
3.03
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

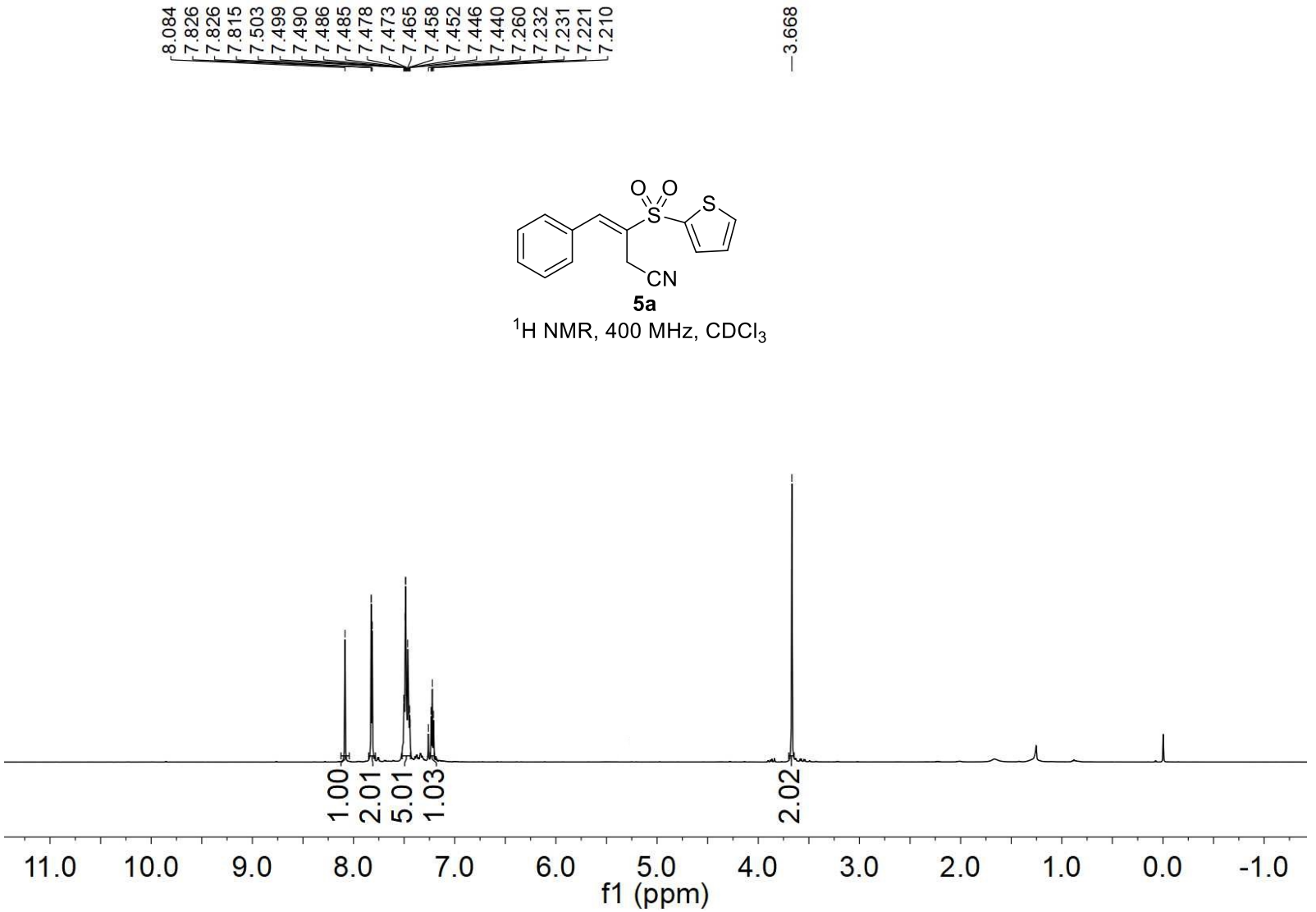

146.055
134.335
131.935
130.789
129.277
129.258
111.166
77.318
77.000
76.682
65.663
58.836
55.925
30.560
O
O
S
OMe
SCN
4m
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)


7.879
7.502
7.501
7.493
4.342
2.653
2.644
2.633
2.623
2.613
2.612
2.603
1.398
1.388
1.379
1.369
1.215
1.207
1.197
1.188
1.187
1.179
O
O
S
SCN
4n
1H NMR, 400 MHz, CDCl3
1.00
5.18
2.10
1.00
2.11
2.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


145.234
134.582
131.965
130.815
129.424
129.347
110.791
77.318
77.000
76.683
32.236
30.409
6.565
O
O
S
SCN
4n
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

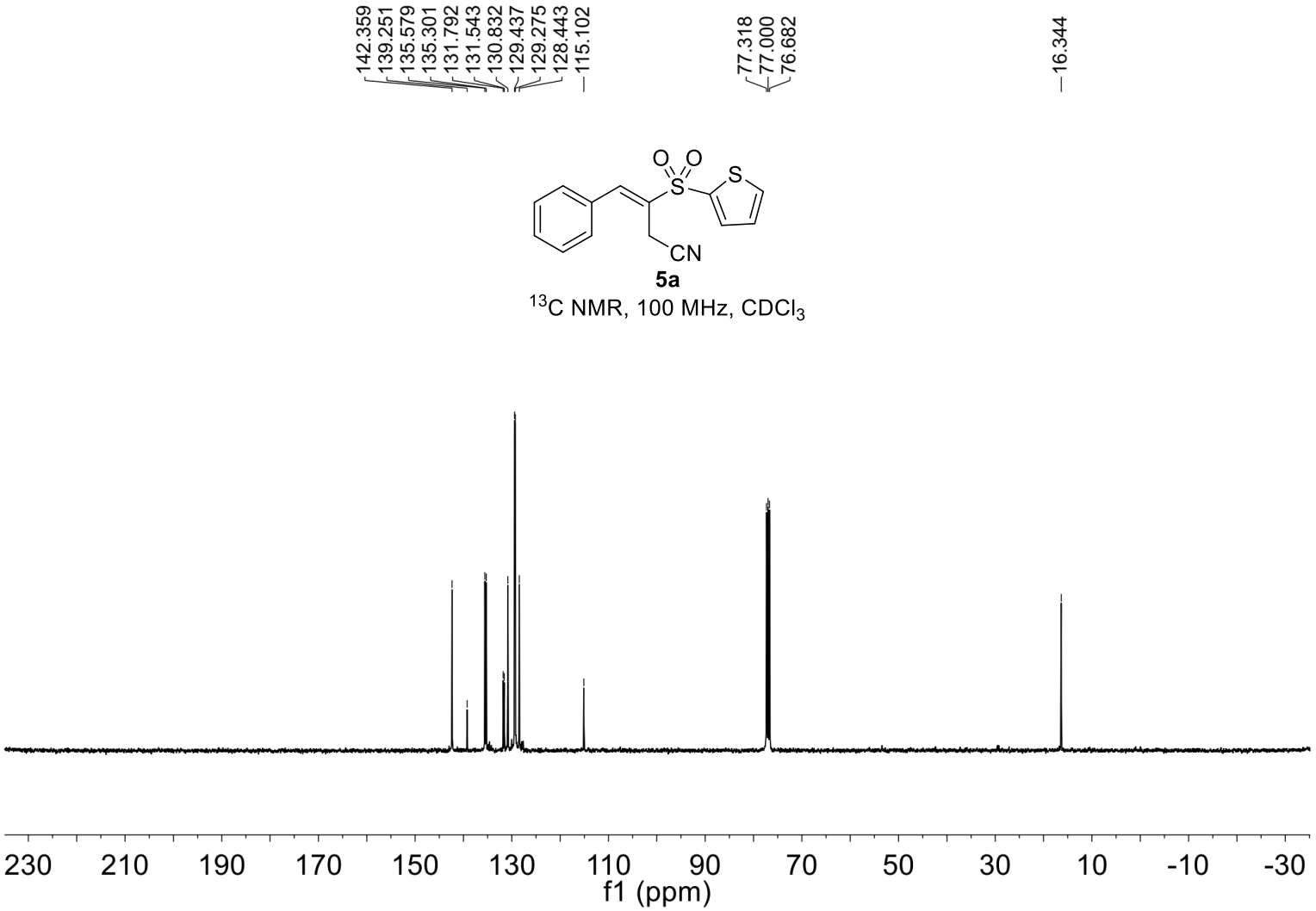

7.807
7.489
7.488
4.300
3.131
3.123
3.115
3.101
3.093
3.092
3.085
3.070
3.062
3.055
2.202
2.170
2.170
1.963
1.955
1.947
1.929
1.918
1.749
1.719
1.718
1.624
1.616
1.593
1.585
1.562
1.556
1.554
1.531
1.523
1.404
1.380
1.372
1.340
1.309
1.301
1.273
1.243
1.236
1.211
1.204
1.179
O
O
S
SCN
4o
1H NMR, 400 MHz, CDCl3
0.97
5.13
2.03
1.00
2.04
2.08
1.06
2.00
3.06
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


147.376
131.864
131.591
130.765
129.334
129.208
110.781
77.318
77.000
76.681
62.570
30.614
24.949
24.902
O
O
S
SCN
4o
^{13}C NMR, 100 MHz, $CDCl_3$
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)



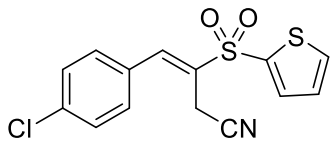
5a

^{1}H NMR, 400 MHz, $CDCl_3$



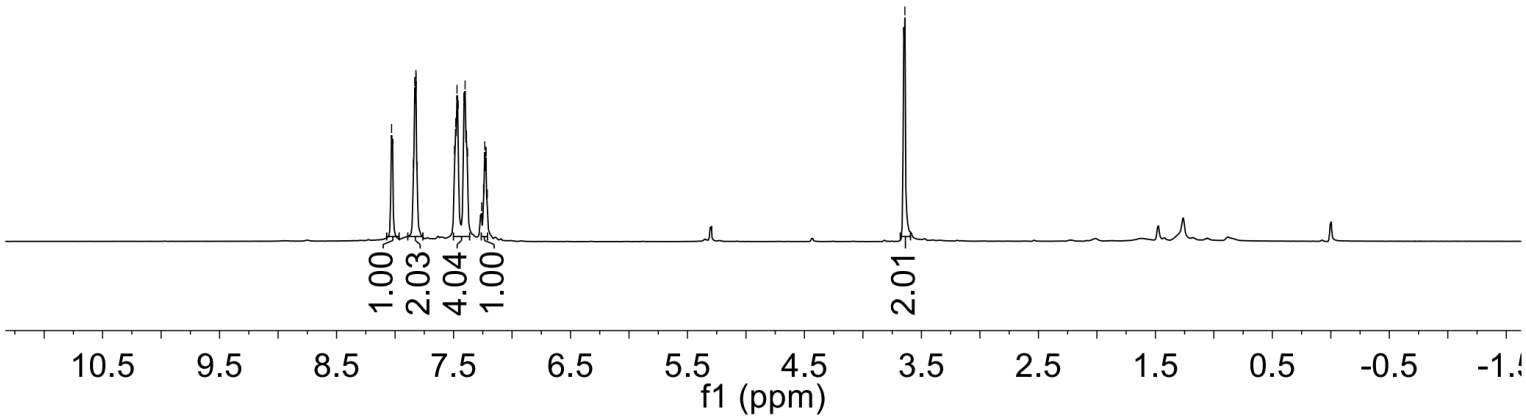
5a

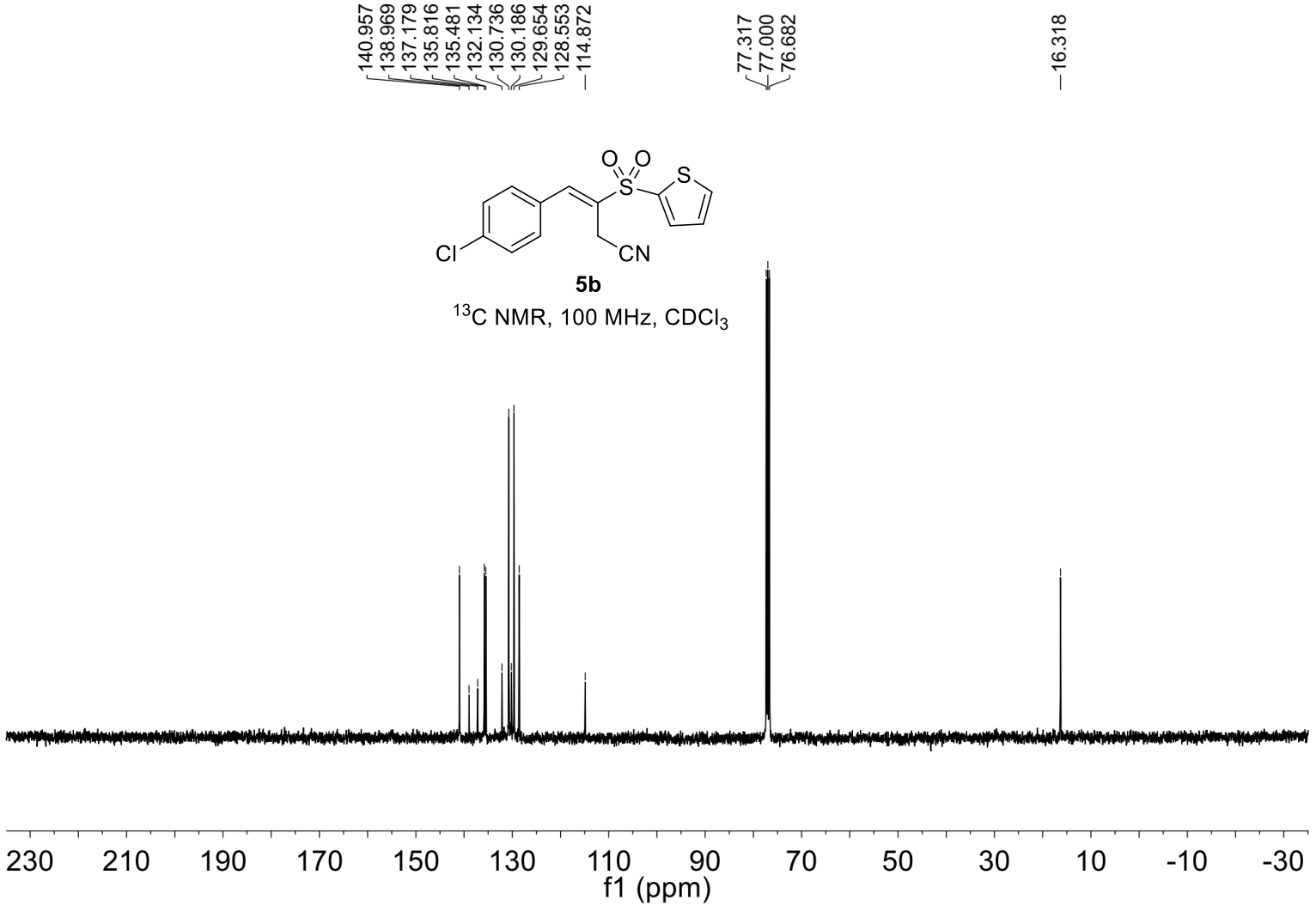
^{13}C NMR, 100 MHz, $CDCl_3$

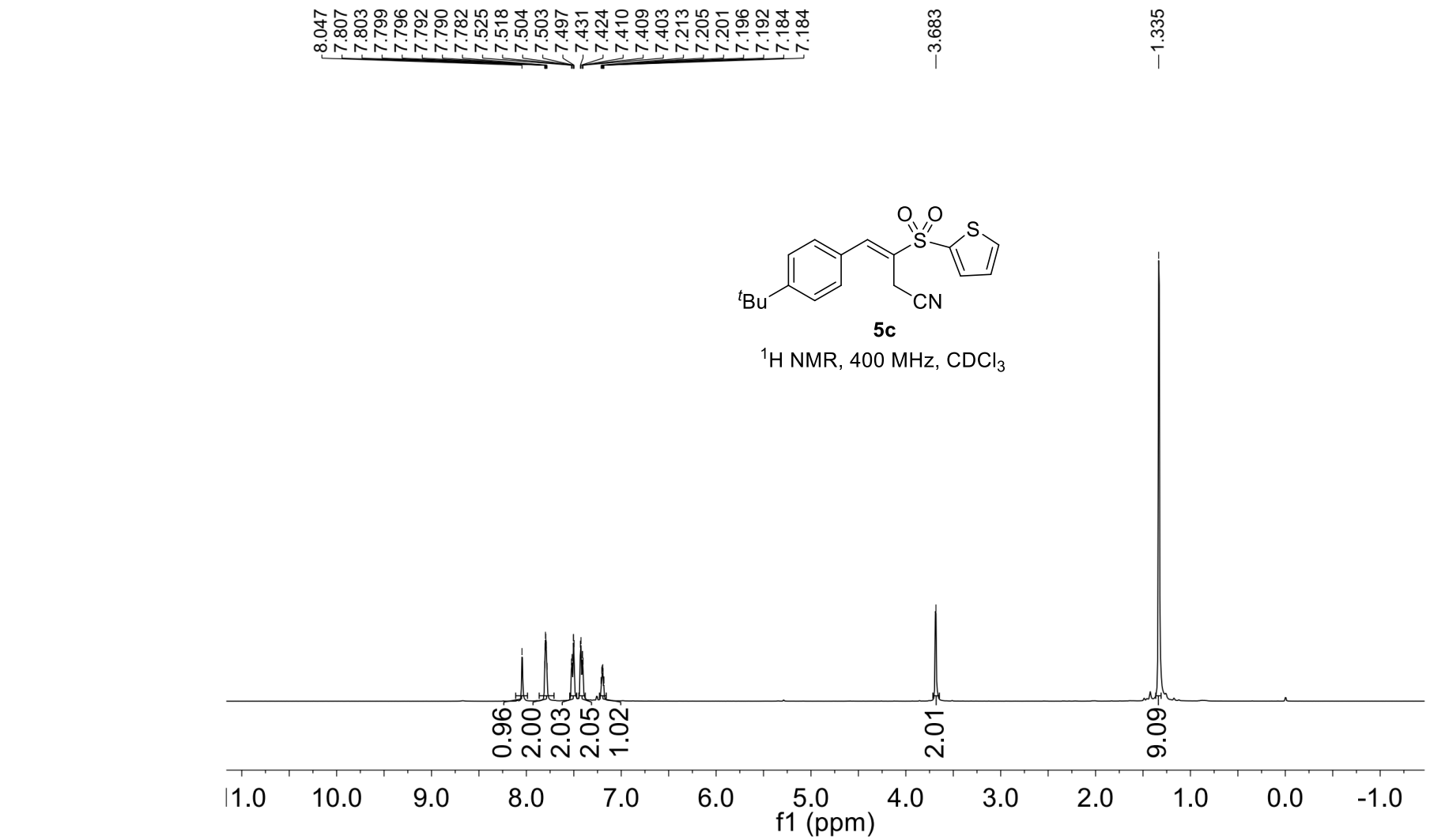


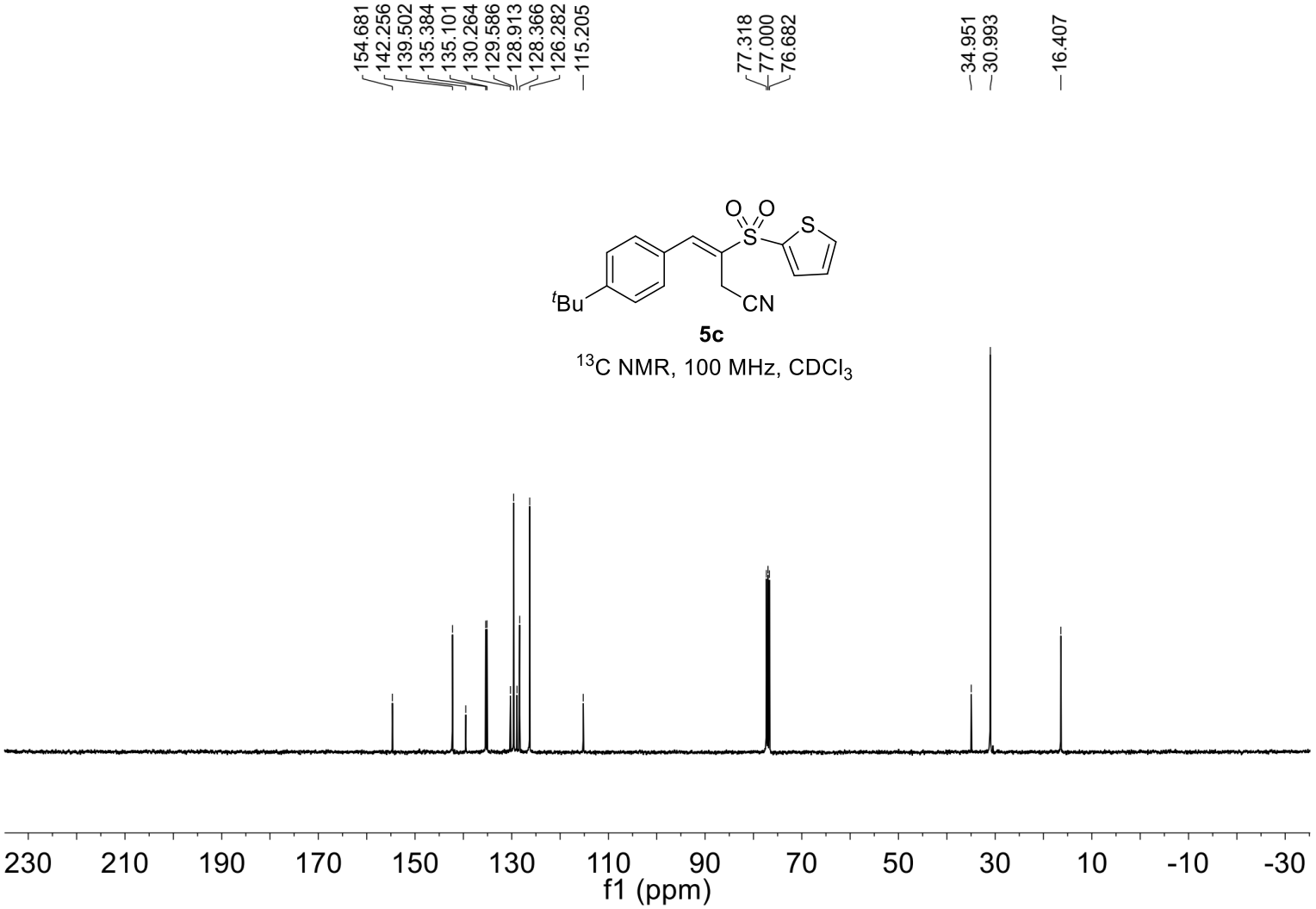
5b

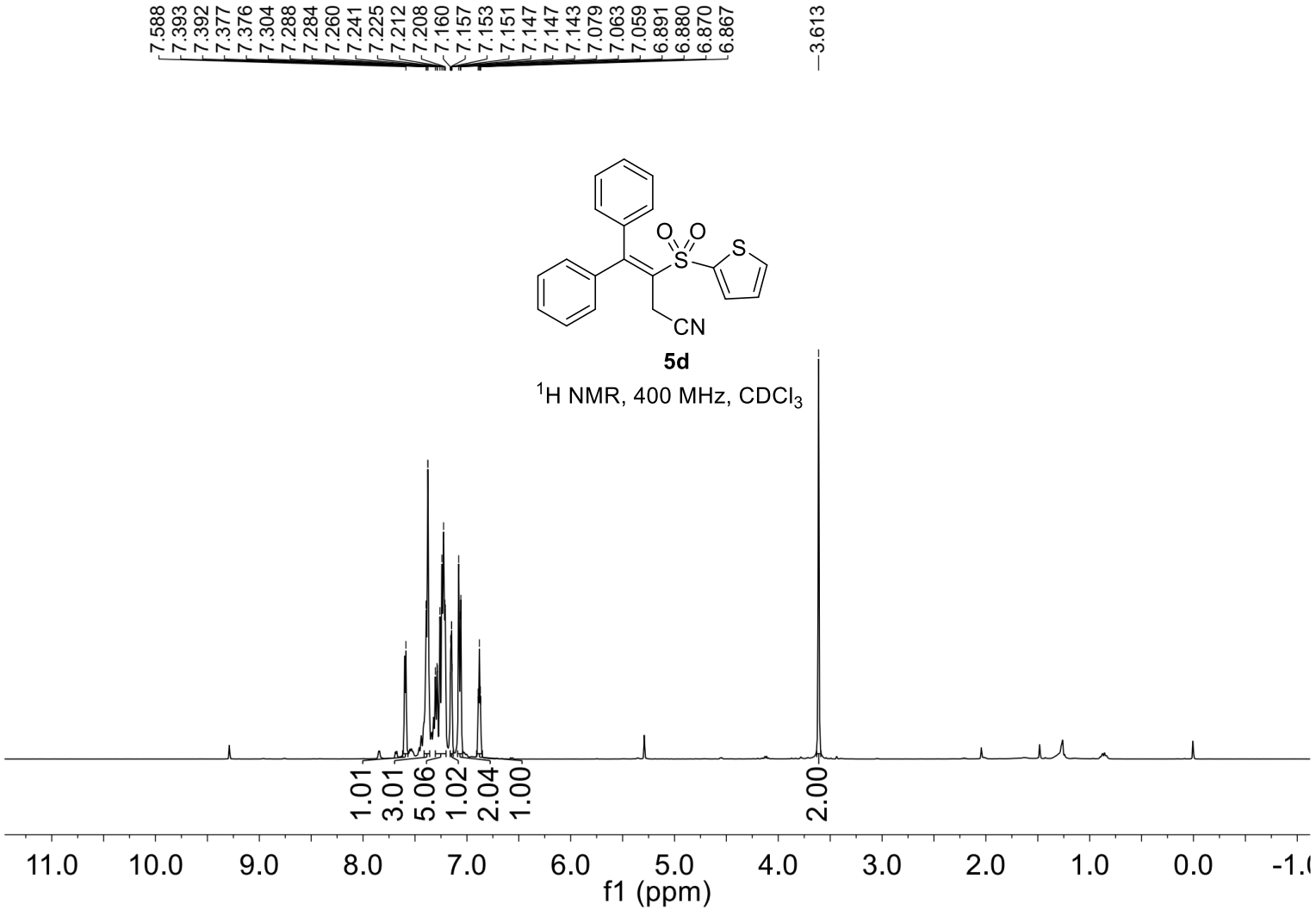
^{1}H NMR, 400 MHz, $CDCl_3$

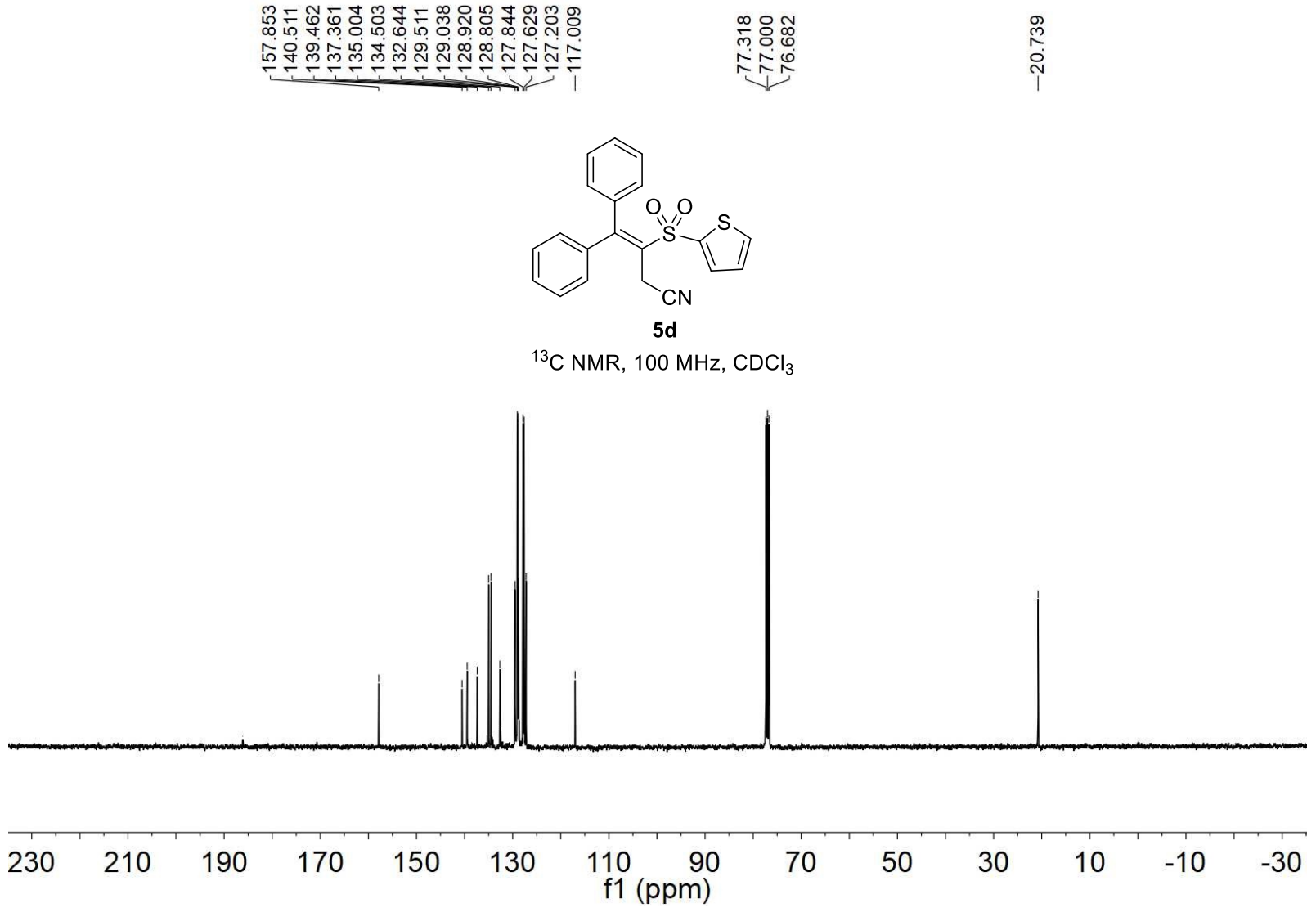



140.957
138.969
137.179
135.816
135.481
132.134
130.736
130.186
129.654
128.553
114.872
77.317
77.000
76.682
16.318
O
O
S
S
Cl
CN
5b
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)


8.047
7.807
7.803
7.799
7.796
7.792
7.790
7.782
7.525
7.518
7.504
7.503
7.497
7.431
7.424
7.410
7.409
7.403
7.213
7.205
7.201
7.196
7.192
7.184
7.184
3.683
1.335
O
O
S
S
tBu
CN
5c
1H NMR, 400 MHz, CDCl3
0.96
2.00
2.03
2.05
1.02
2.01
9.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

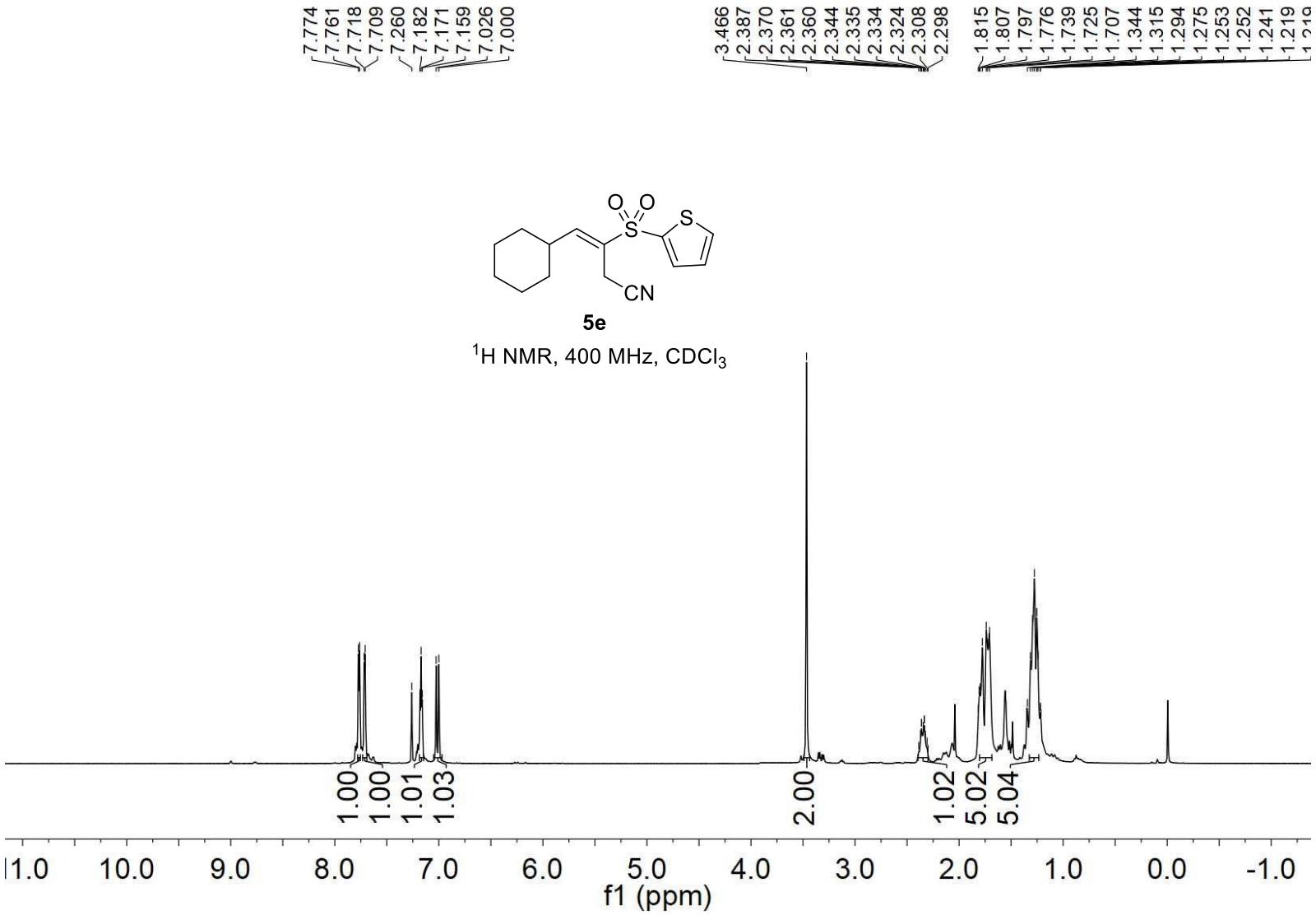

154.681
142.256
139.502
135.384
135.101
130.264
129.586
128.913
128.366
126.282
115.205
77.318
77.000
76.682
34.951
30.993
16.407
O
O
S
S
tBu
CN
5c
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

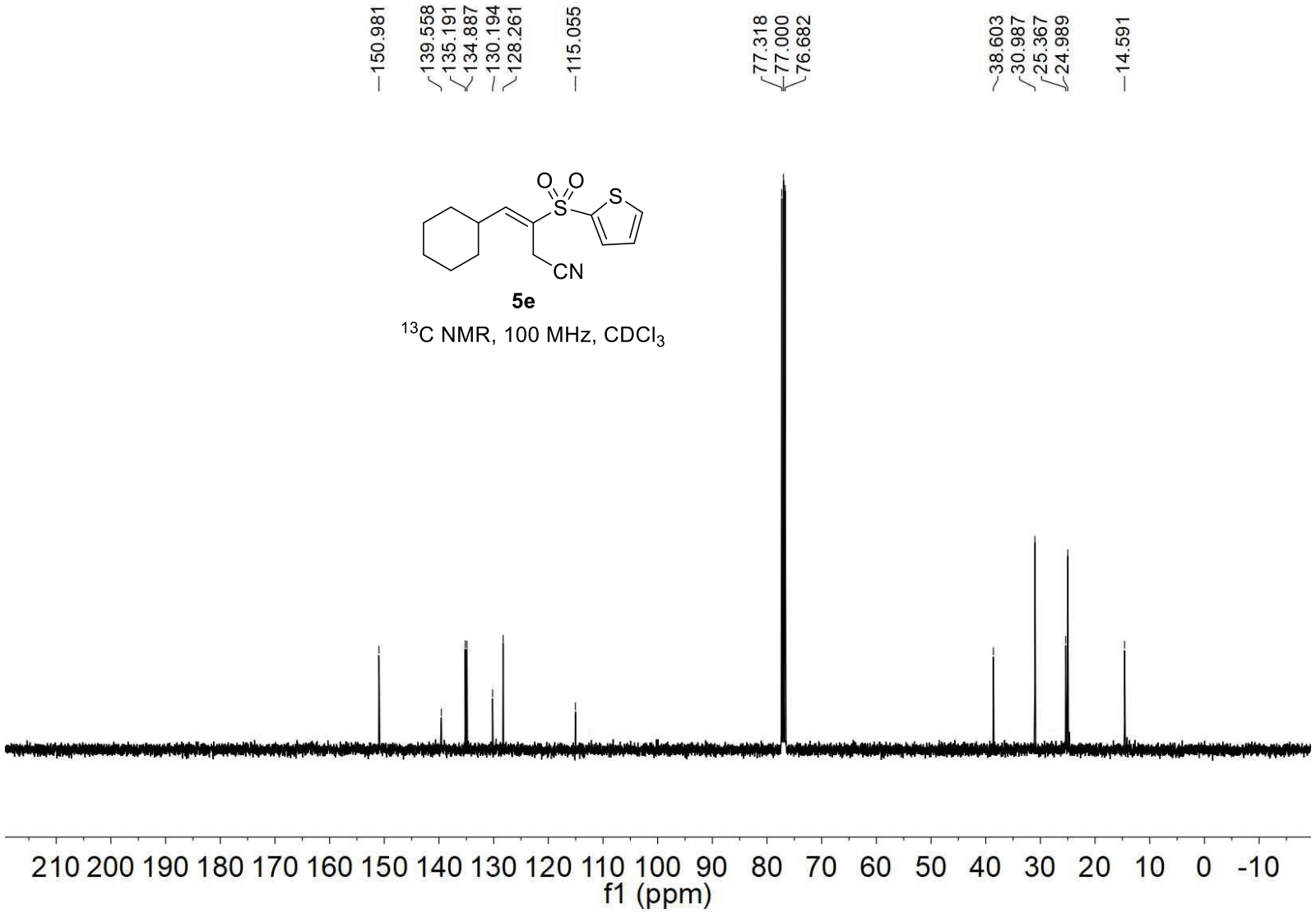

7.588
7.393
7.392
7.377
7.376
7.304
7.288
7.284
7.260
7.241
7.225
7.212
7.208
7.160
7.157
7.153
7.151
7.147
7.147
7.143
7.079
7.063
7.059
6.891
6.880
6.870
6.867
3.613
O
O
S
S
CN
5d
1H NMR, 400 MHz, CDCl3
1.01
3.01
5.06
1.02
2.04
1.00
2.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

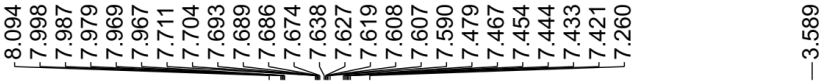


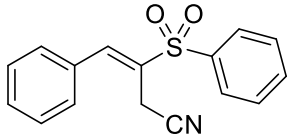
5d

^{13}C NMR, 100 MHz, $CDCl_3$


7.774
7.761
7.718
7.709
7.260
7.182
7.171
7.159
7.026
7.000
3.466
2.387
2.370
2.361
2.360
2.344
2.335
2.334
2.324
2.308
2.298
1.815
1.807
1.797
1.776
1.739
1.725
1.707
1.344
1.315
1.294
1.275
1.253
1.252
1.241
1.219
O
O
S
S
CN
5e
1H NMR, 400 MHz, CDCl3
1.00
1.00
1.01
1.03
2.00
1.02
5.02
5.04
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

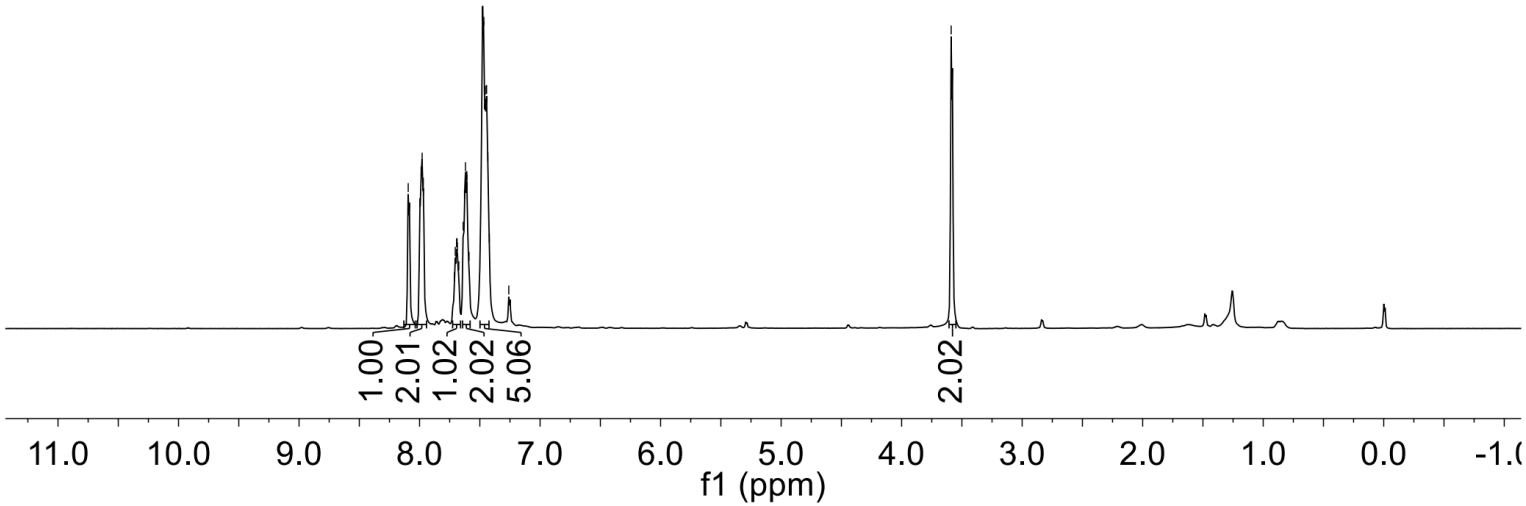

150.981
139.558
135.191
134.887
130.194
128.261
115.055
77.318
77.000
76.682
38.603
30.987
25.367
24.989
14.591
O
O
S
S
CN
5e
13C NMR, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

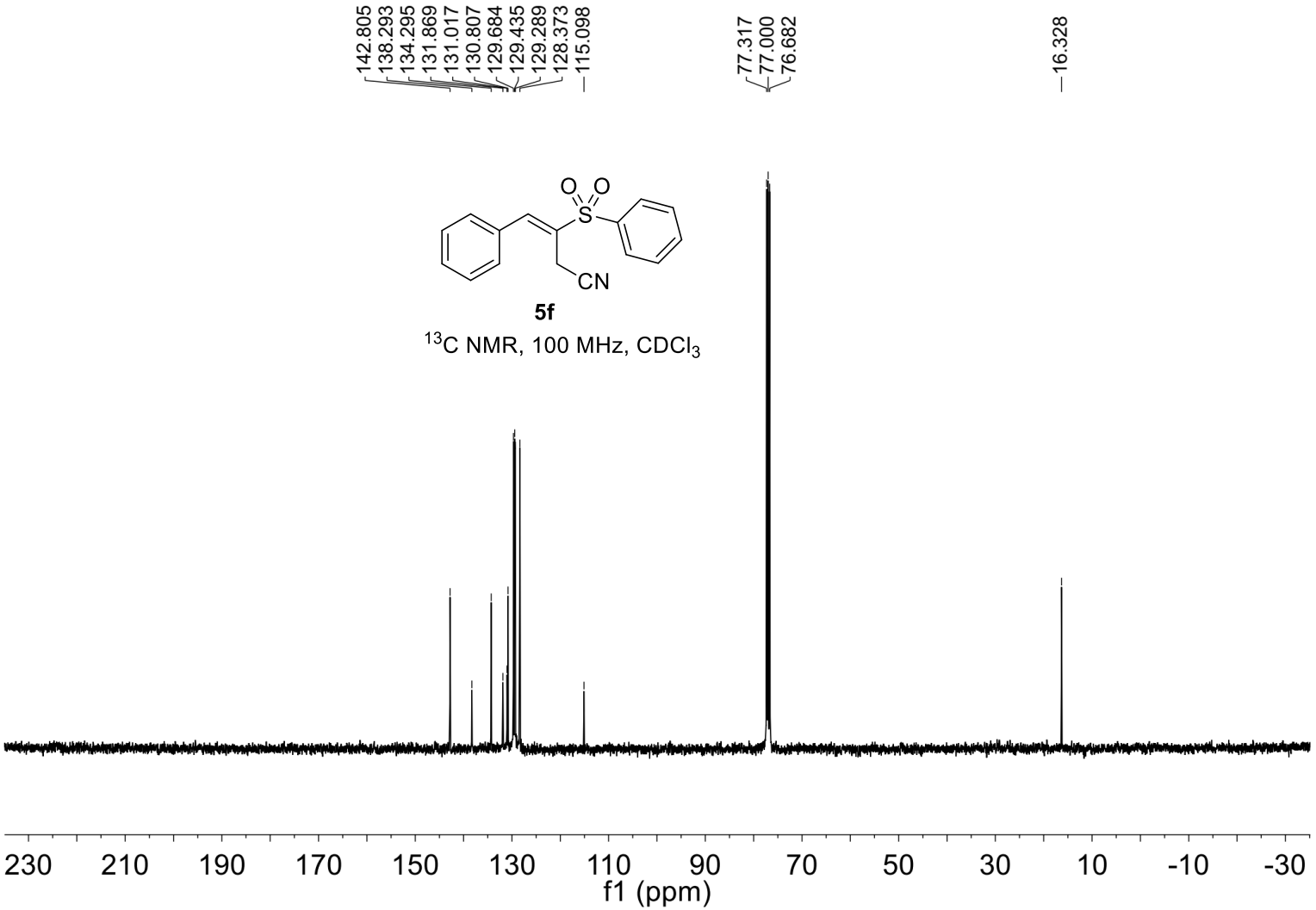




5f

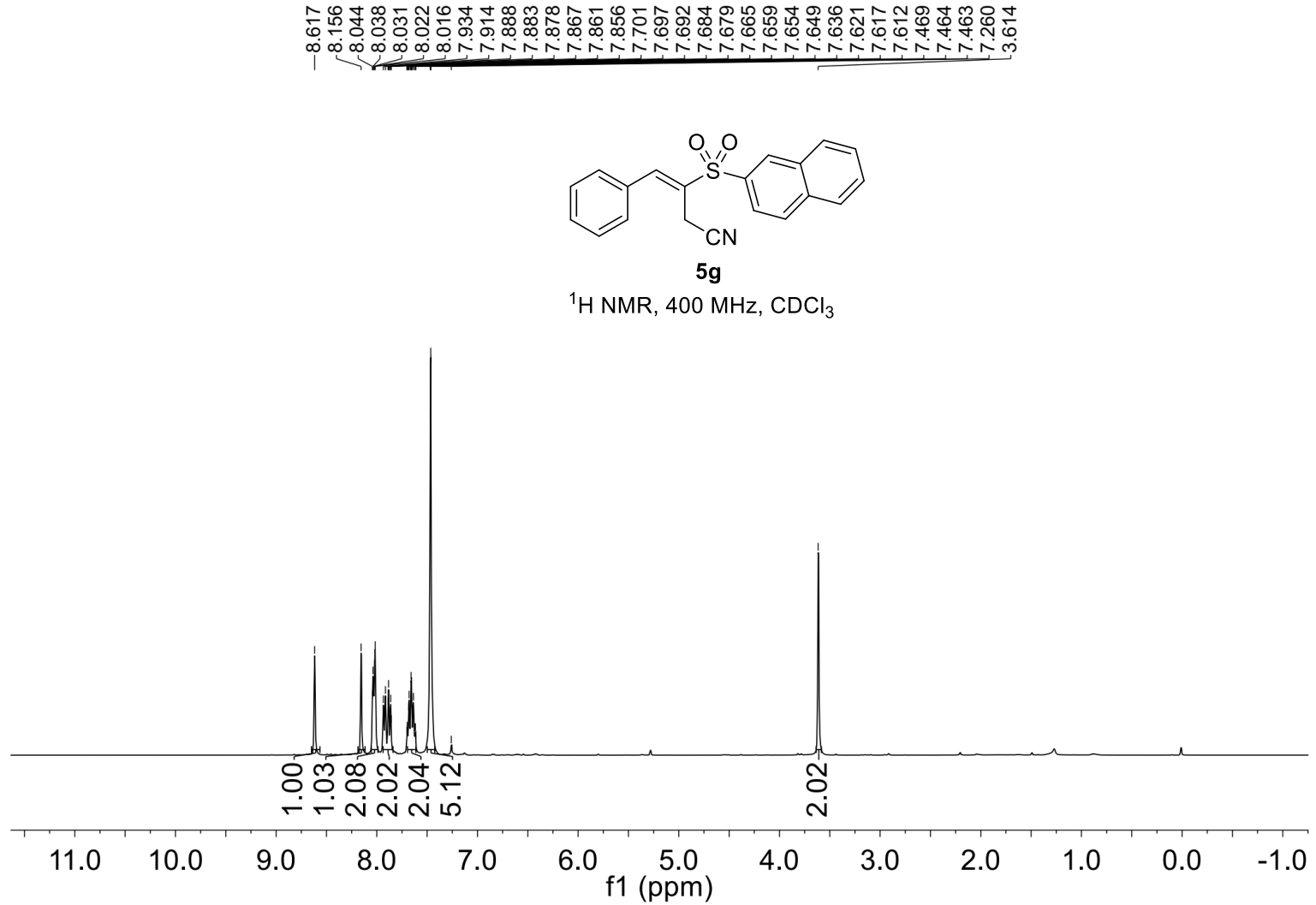
^{1}H NMR, 400 MHz, $CDCl_3$

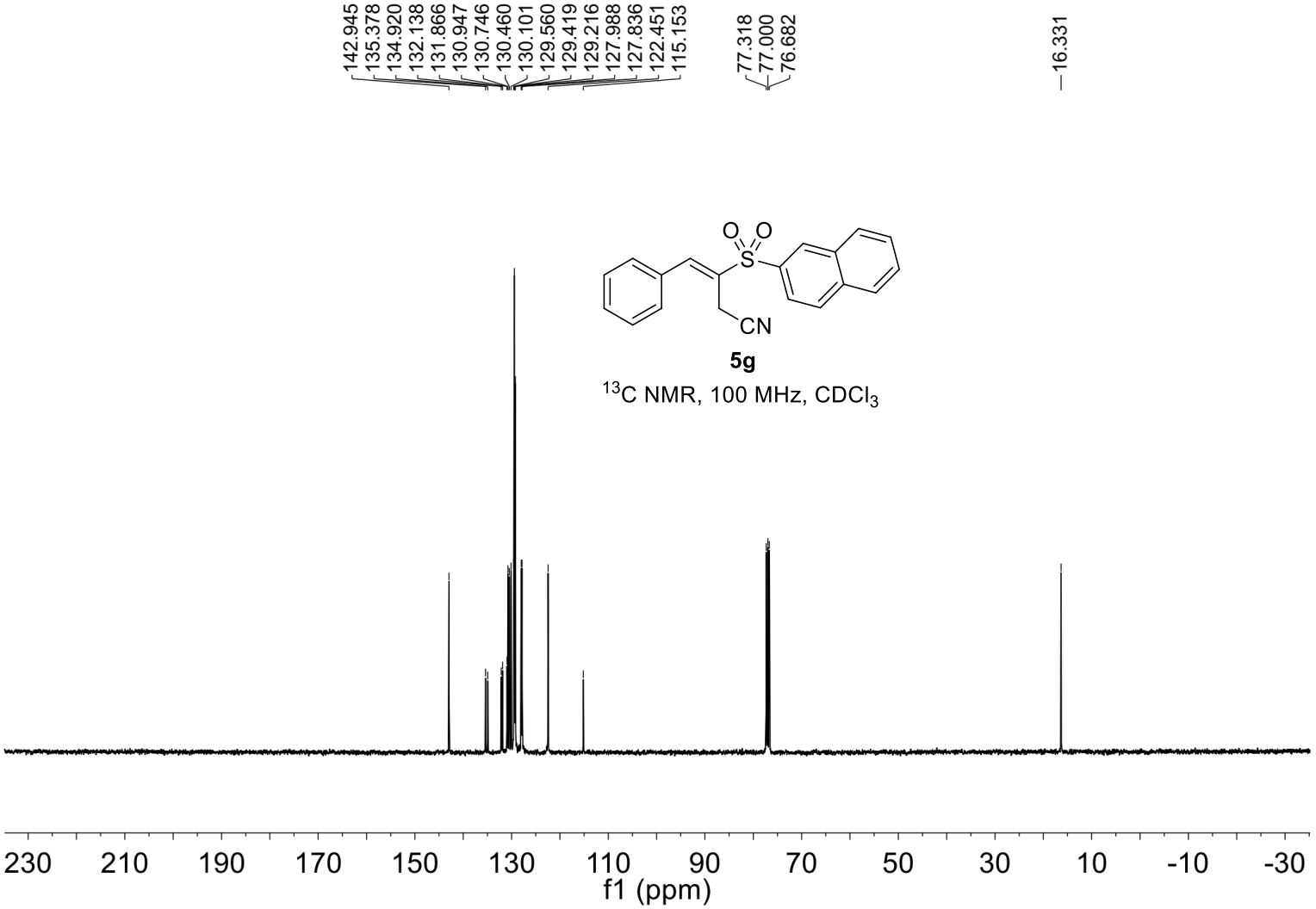


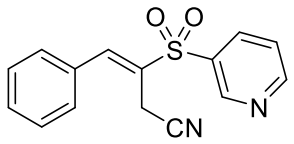


5f

^{13}C NMR, 100 MHz, $CDCl_3$

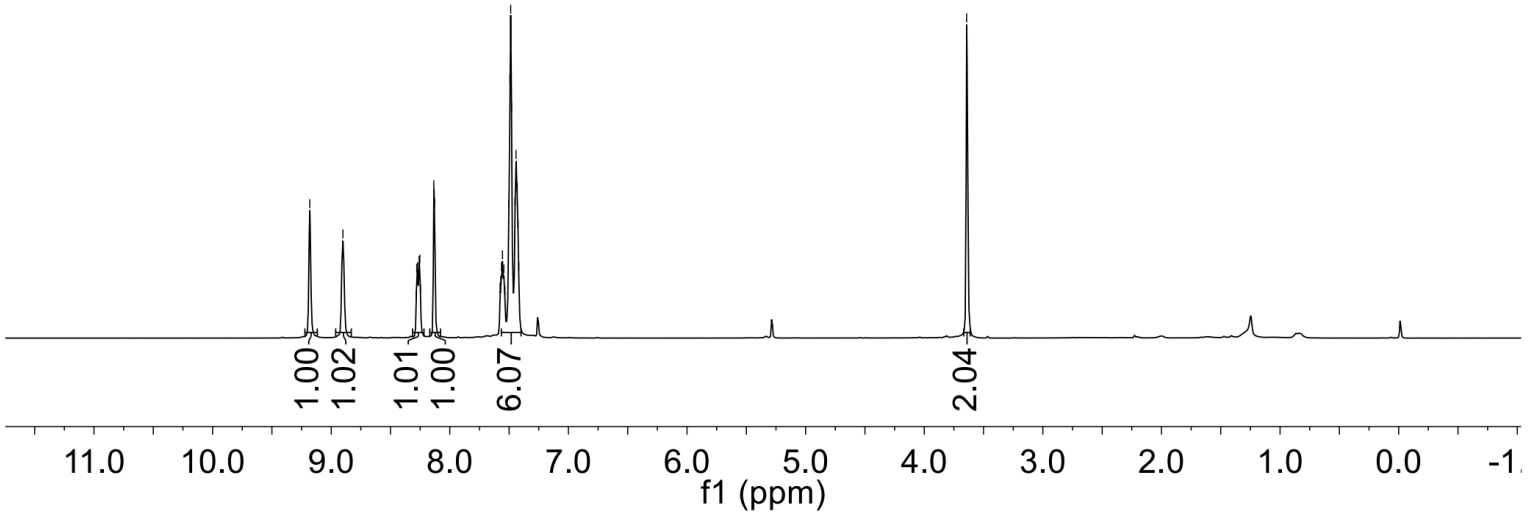

8.617
8.156
8.044
8.038
8.031
8.022
8.016
7.934
7.914
7.888
7.883
7.878
7.867
7.861
7.856
7.701
7.697
7.692
7.684
7.679
7.665
7.659
7.654
7.649
7.636
7.621
7.617
7.612
7.469
7.464
7.463
7.260
3.614
O
O
S
CN
5g
1H NMR, 400 MHz, CDCl3
1.00
1.03
2.08
2.02
2.04
5.12
2.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

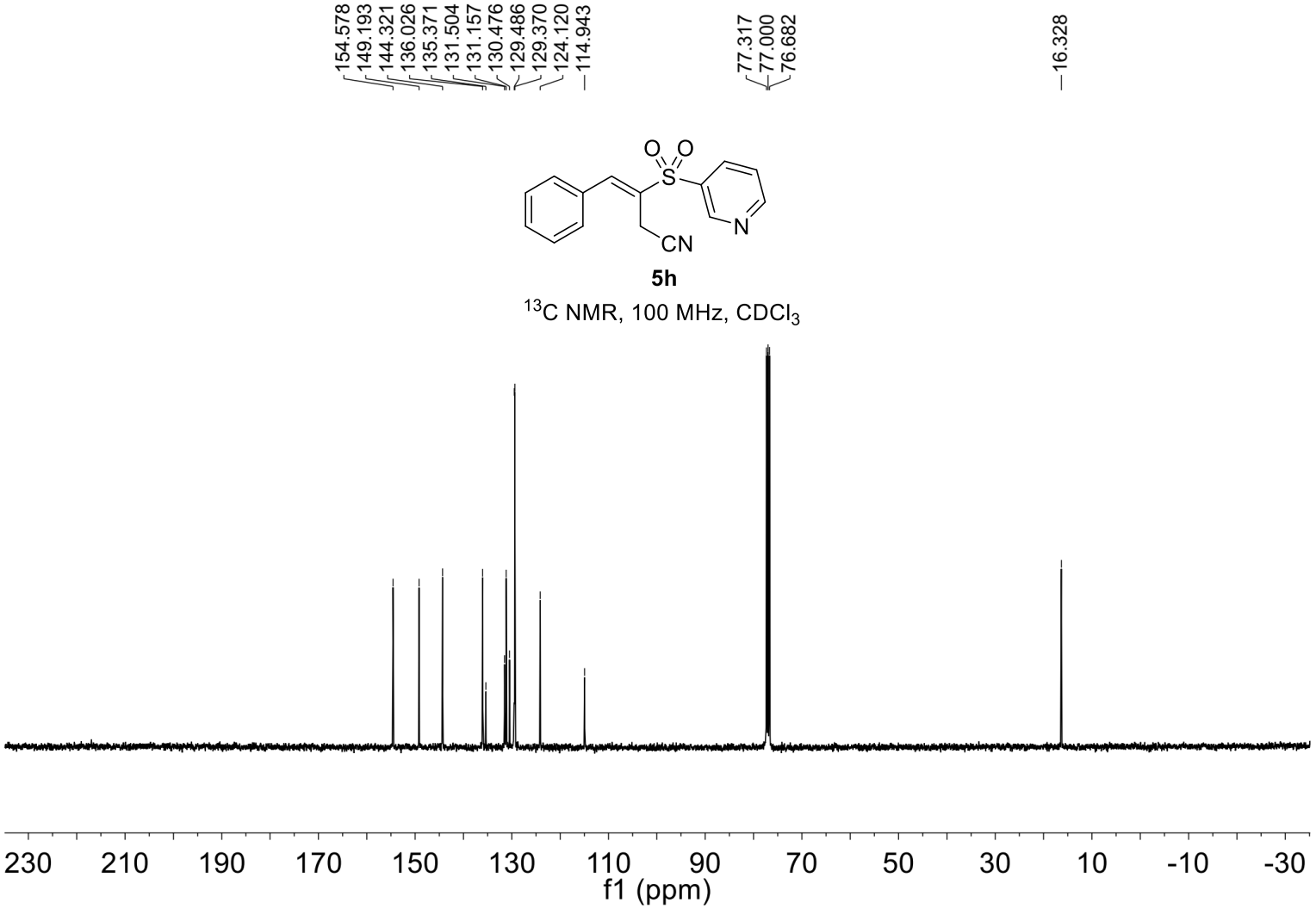

142.945
135.378
134.920
132.138
131.866
130.947
130.746
130.460
130.101
129.560
129.419
129.216
127.988
127.836
122.451
115.153
77.318
77.000
76.682
16.331
O
O
S
CN
5g
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

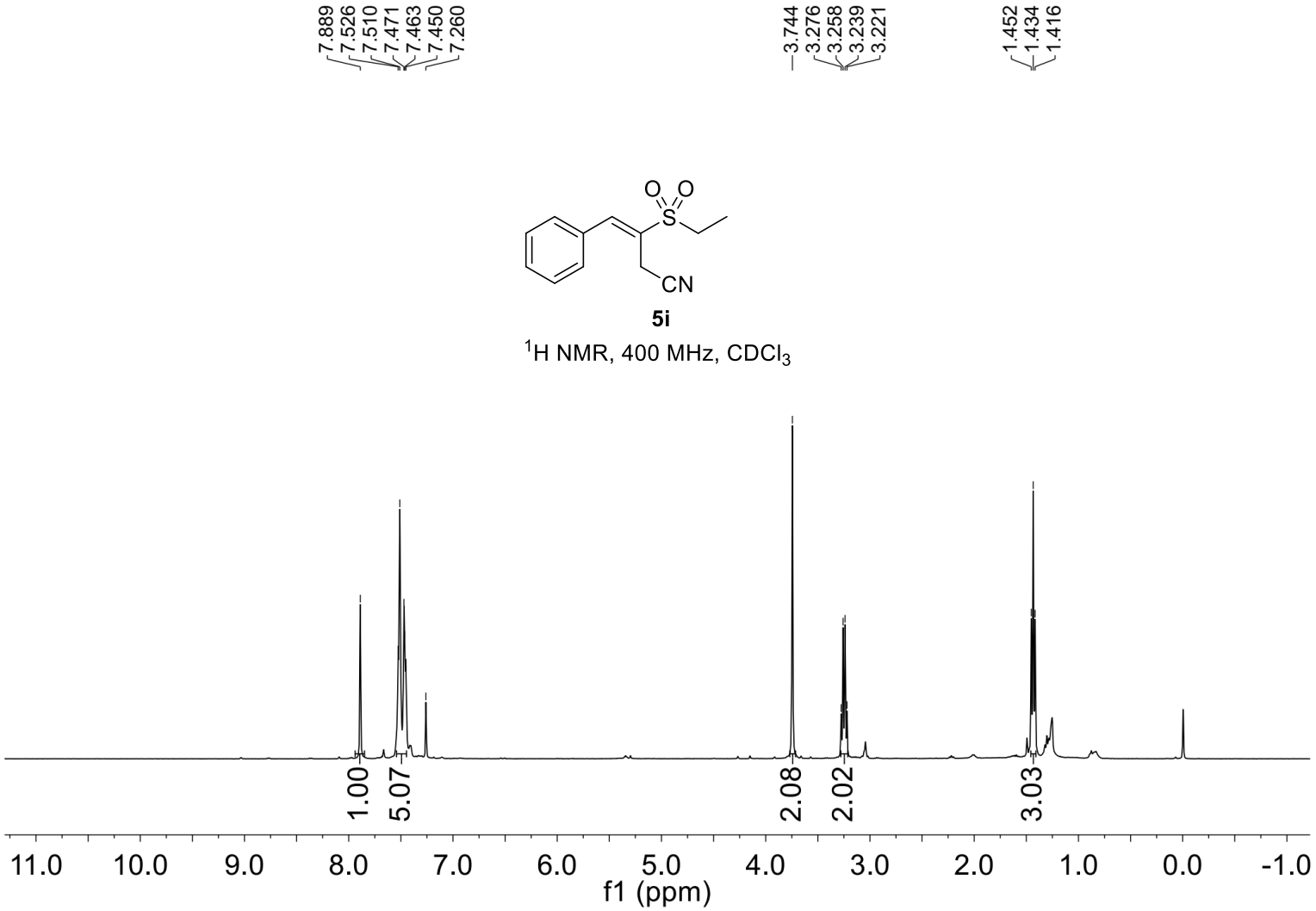


5h

^{1}H NMR, 400 MHz, $CDCl_3$

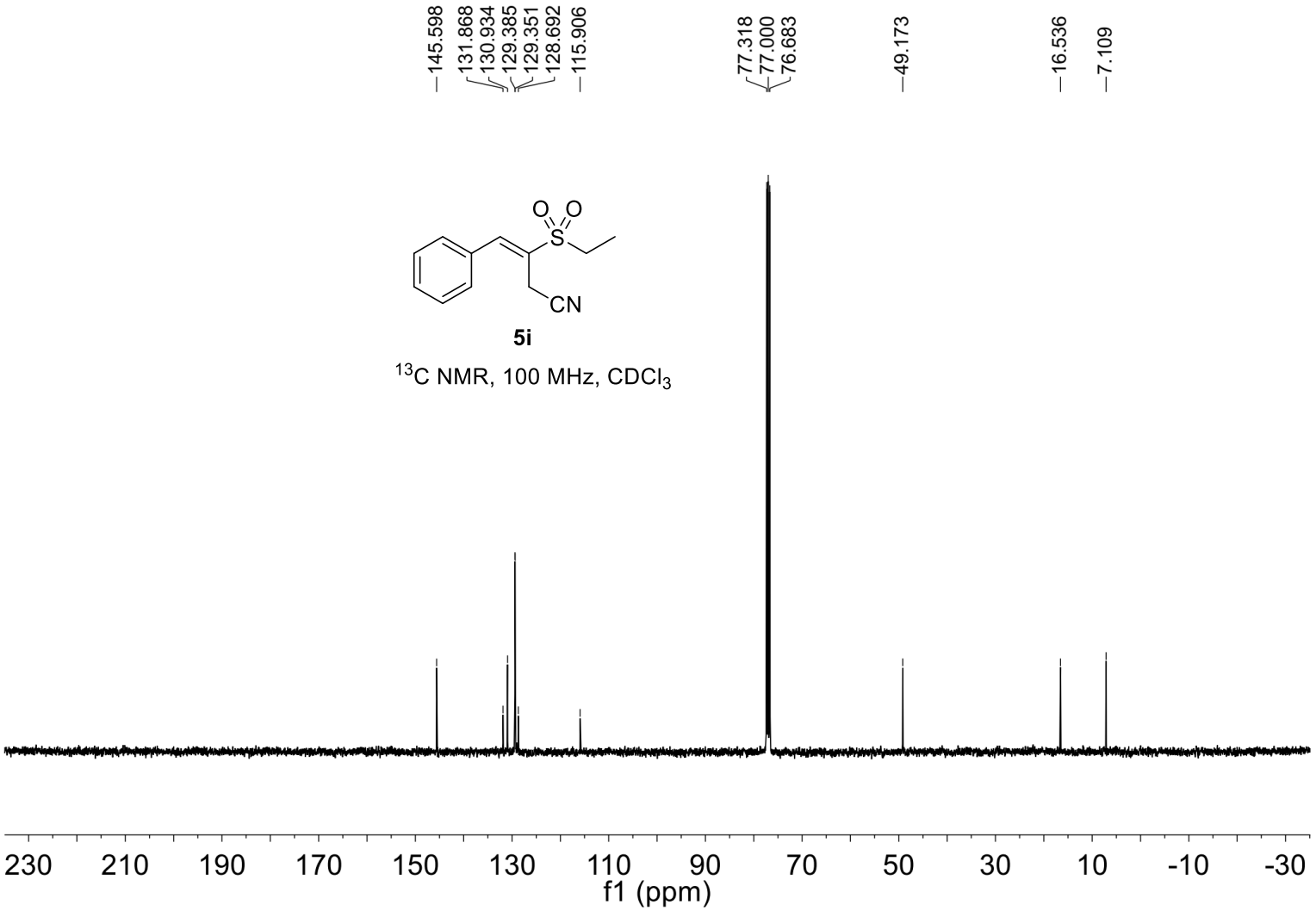


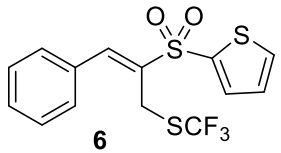

154.578
149.193
144.321
136.026
135.371
131.504
131.157
130.476
129.486
129.370
124.120
114.943
77.317
77.000
76.682
16.328
O
O
S
N
CN
5h
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)



5i

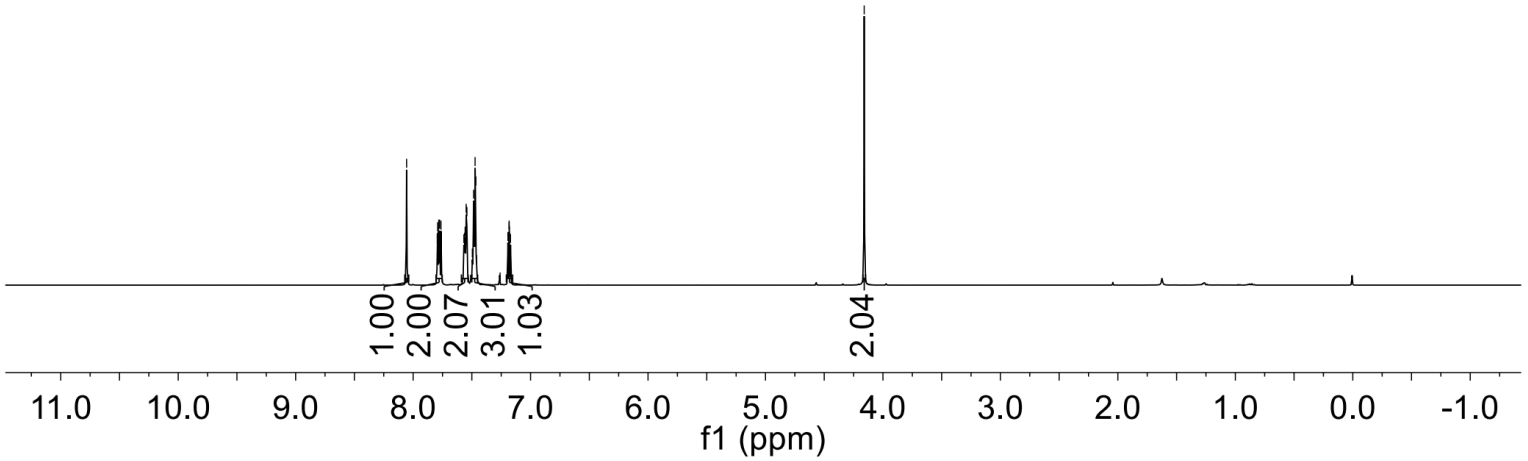
^{1}H NMR, 400 MHz, $CDCl_3$

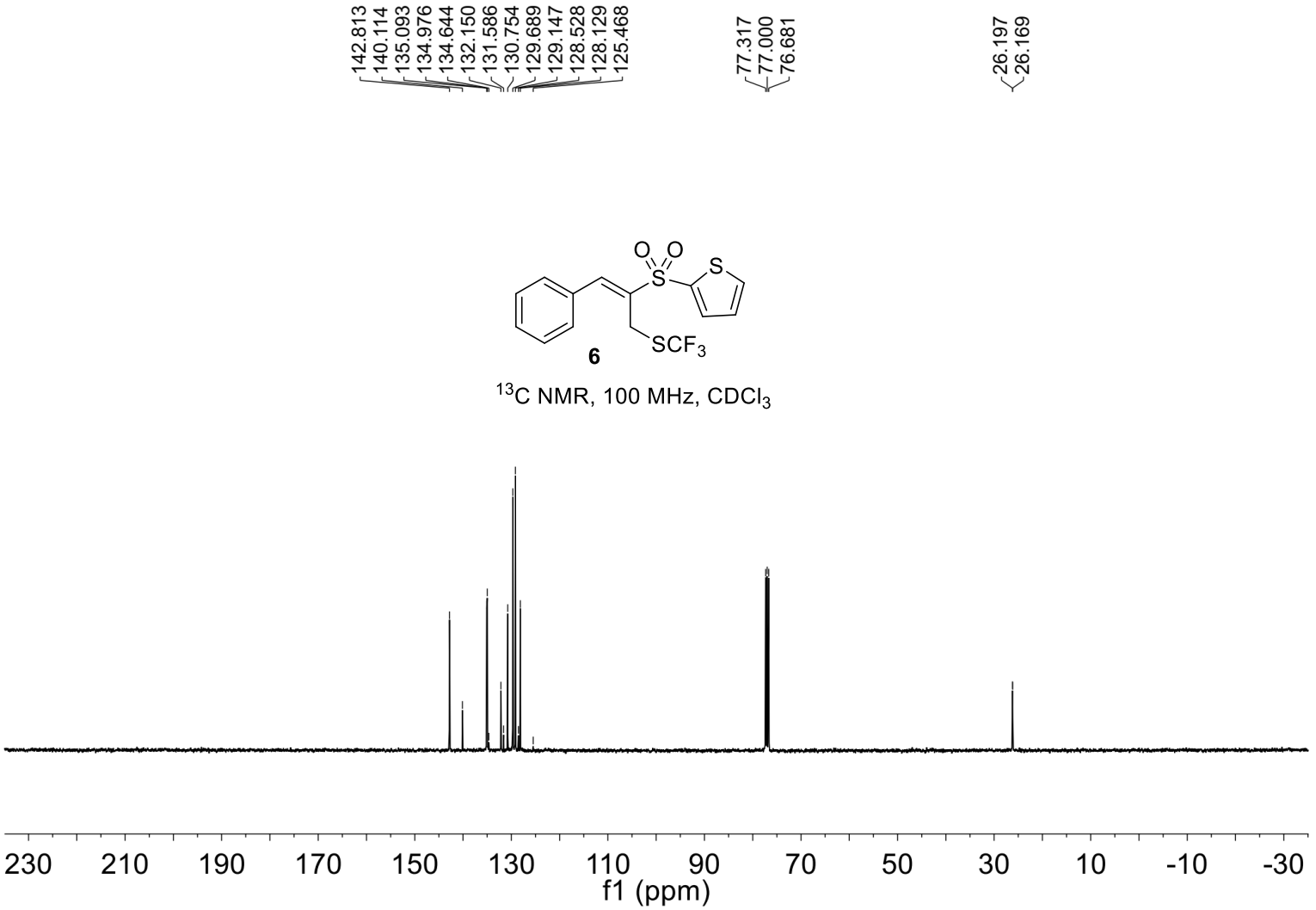

145.598
131.868
130.934
129.385
129.351
128.692
115.906
77.318
77.000
76.683
49.173
16.536
7.109
O
O
S
CN
5i
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)

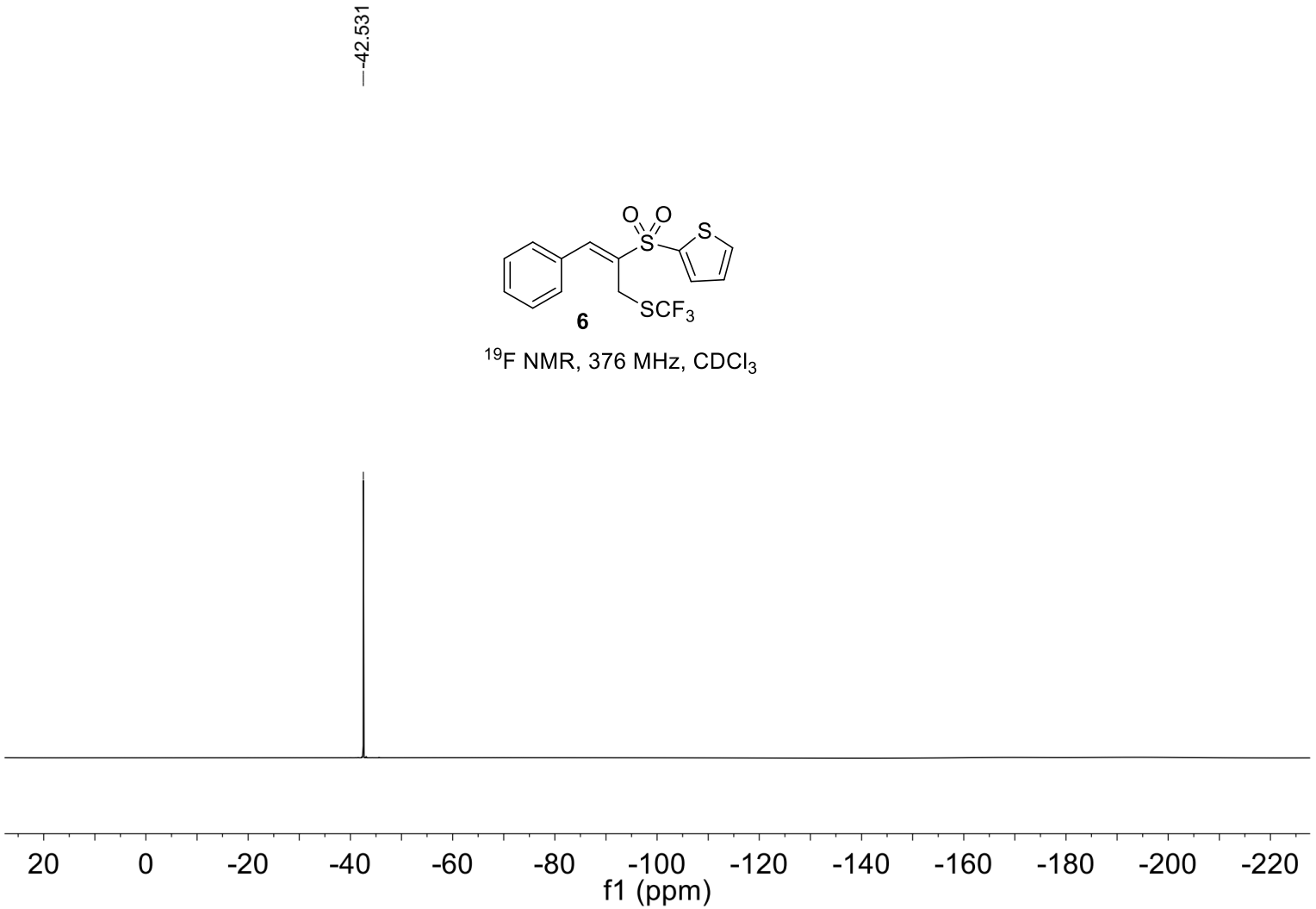


6

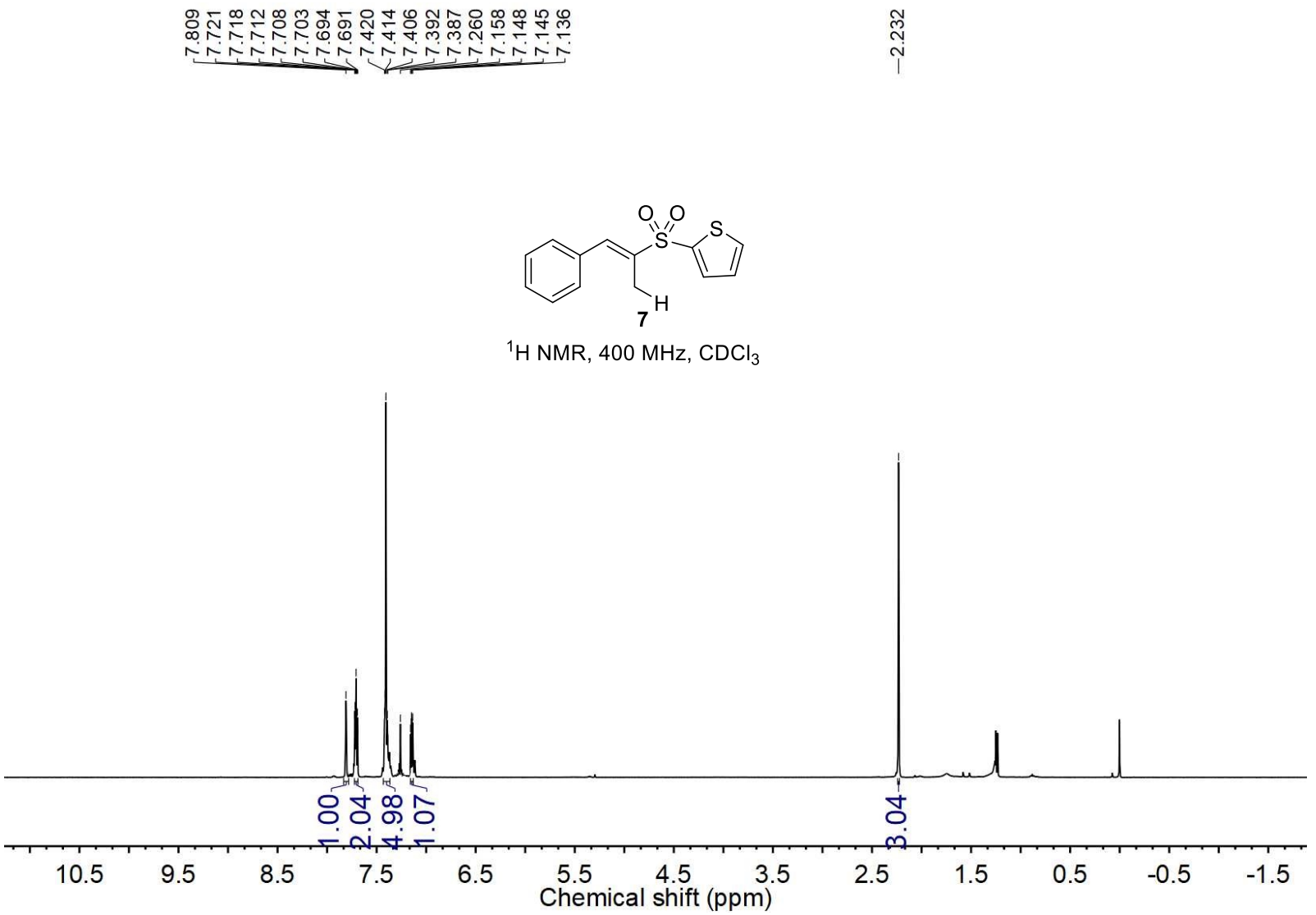
^{1}H NMR, 400 MHz, $CDCl_3$



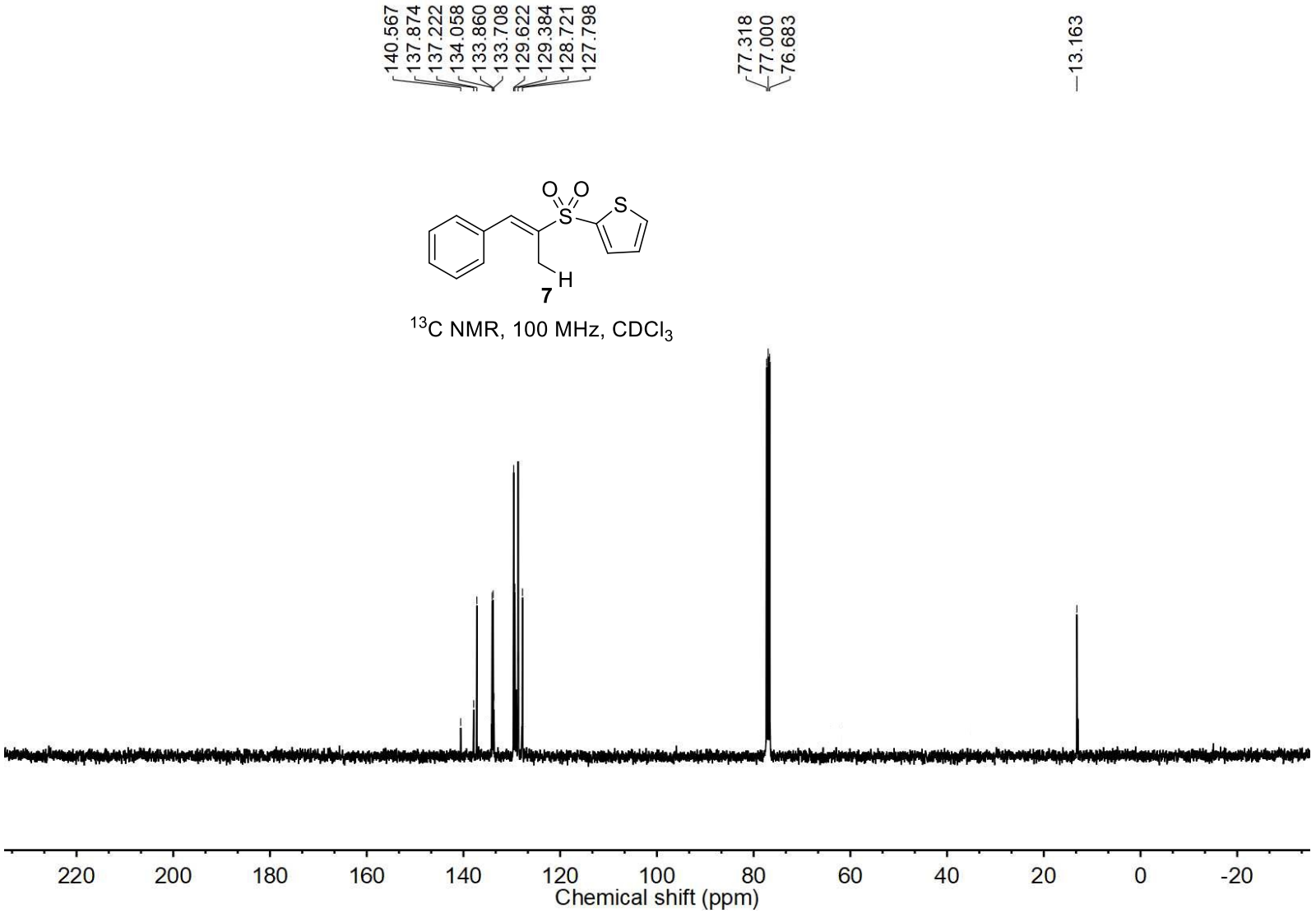

142.813
140.114
135.093
134.976
134.644
132.150
131.586
130.754
129.689
129.147
128.528
128.129
125.468
77.317
77.000
76.681
26.197
26.169
O
O
S
S
SCF3
6
13C NMR, 100 MHz, CDCl3
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
f1 (ppm)



^{19}F NMR, 376 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$


140.567
137.874
137.222
134.058
133.860
133.708
129.622
129.384
128.721
127.798
77.318
77.000
76.683
13.163
O
O
S
S
H
7
13C NMR, 100 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical shift (ppm)