

Synthesis of N-vinyl isothiocyanates and carbamates by the cleavage of NH-1,2,3-triazoles with one-carbon electrophiles

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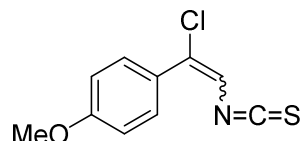
General

All solvents were dried by activated molecular sieves (3 and 4 Å) and stored under nitrogen. All commercially available chemicals were used as received, unless stated otherwise. Starting NH-1,2,3-triazoles were prepared according to procedures published in literature.¹⁻⁴ Flash column chromatography was performed using silica gel 60 (0.040–0.063 mm). ^1H , ^{13}C and ^{19}F NMR spectra were measured at ambient temperature using 5 mm diameter NMR tubes. ^{13}C NMR spectra were proton decoupled. The chemical shift values (δ) are reported in ppm relative to internal Me_4Si (0 ppm for ^1H , ^{13}C NMR) or residual solvents (CDCl_3 , 7.26 ppm for ^1H , 77.0 ppm for ^{13}C NMR) and internal CFCl_3 (0 ppm for ^{19}F NMR). Coupling constants (J) are reported in Hertz. High resolution MS spectra (HRMS) were recorded on Agilent 7250 GC/Q-TOF using electron impact (EI) or chemical (CI) ionizations or on an LTQ Orbitrap XL using electrospray (ESI) or atmospheric pressure chemical (APCI) ionizations.

General procedure 1 for the synthesis of vinyl isothiocyanates from NH-triazoles and thiophosgene

To the suspension of NH-1,2,3-triazole **1** (0.2 mmol) in dry DCE (6 ml) in a 10 ml vial thiophosgene (1.5 equiv., 0.3 mmol, 23 μ l) was added. The vial was sealed, and the resulting mixture was heated at 70 °C for 12-24 hours. After the reaction was complete (NMR monitoring), it was evaporated under reduced pressure and purified by silica gel column chromatography (cyclohexane or cyclohexane/EtOAc) to afford vinyl isothiocyanates **4**.

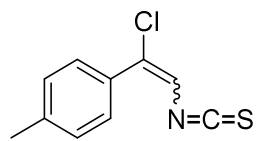
1-(1-chloro-2-isothiocyanatovinyl)-4-methoxybenzene (**4a**)



Vinyl isothiocyanate **4a** was obtained from NH-triazole **1** (35 mg, 0.2 mmol) and thiophosgene according to general procedure 1. Column chromatography (cyclohexane/EtOAc, 19:1) afforded product **4a** (29 mg, 65%, *E/Z* = 2.5:1) as a yellow oil. *E*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.68-7.63 (m, 2H, Ar), 6.98-6.93 (m, 2H, Ar), 6.45 (s, 1H, CH-NCS), 3.85 (s, 3H, OMe); ^{13}C NMR (101 MHz, CDCl_3) δ 160.7, 135.6 (br s, NCS), 135.2, 129.7, 125.9, 113.8, 111.7 (CH-NCS), 55.4 (OMe); *Z*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.46 (m, 2H, Ar), 6.91-6.89 (m, 2H, Ar), 6.46 (s, 1H, CH-NCS), 3.83 (s, 3H, OMe); ^{13}C NMR (101 MHz, CDCl_3) δ 161.0, 137.1 (br s, NCS), 135.2, 127.7, 126.6, 114.1, 111.1 (CH-NCS), 55.4 (OMe); HRMS (Cl^+) *m/z* calcd for $\text{C}_{10}\text{H}_9\text{ClNOS}$ [$\text{M}+\text{H}$] $^+$: 226.0088, found 226.0087.

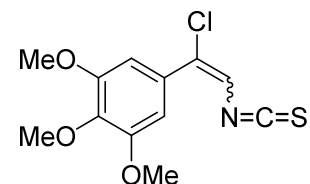
For 1 mmol scale synthesis, vinyl isothiocyanate **4a** was obtained from NH-triazole **1** (175 mg, 1 mmol) and thiophosgene according to general procedure 1 (reaction time 24 hours). Column chromatography (cyclohexane/EtOAc, 19:1) afforded product **4a** (160 mg, 71%, *E/Z* = 2.5:1) as a yellow oil.

1-(1-chloro-2-isothiocyanatovinyl)-4-methylbenzene (**4b**)



Vinyl isothiocyanate **4b** was obtained from NH-triazole **1** (31.8 mg, 0.2 mmol) and thiophosgene (2 equiv.) according to general procedure 1. Column chromatography (cyclohexane) afforded product **4b** (22 mg, 53%, *E/Z* = 1.7:1) as a pale-yellow oil. *E*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.58 (m, 2H, Ar), 7.26-7.24 (m, 2H, Ar), 6.49 (s, 1H, CH-NCS), 2.40 (s, 3H, Me); ^{13}C NMR (101 MHz, CDCl_3) δ 140.4, 135.8 (br s, NCS), 135.4, 130.7, 129.1, 128.0, 112.6 (CH-NCS), 21.4 (Me); *Z*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.42 (m, 2H, Ar), 7.20-7.18 (m, 2H, Ar), 6.52 (s, 1H, CH-NCS), 2.38 (s, 3H, Me); ^{13}C NMR (101 MHz, CDCl_3) δ 140.3, 137.4 (br s, NCS), 135.6, 131.4, 129.4, 126.1, 112.1 (CH-NCS), 21.3 (Me); HRMS (Cl^+) *m/z* calcd for $\text{C}_{10}\text{H}_9\text{ClNS}$ [$\text{M}+\text{H}$] $^+$: 210.0139, found 210.0136.

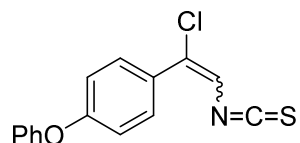
5-(1-chloro-2-isothiocyanatovinyl)-1,2,3-trimethoxybenzene (**4c**)



Vinyl isothiocyanate **4c** was obtained from NH-triazole **1** (47 mg, 0.2 mmol) and thiophosgene according to general procedure 1. Column chromatography (cyclohexane/EtOAc, 9:1) afforded product **4c** (31 mg of *E*-isomer and 14 mg of *Z*-isomer, total yield 79%, *E/Z* = 2.2:1) as a yellow solid. *E*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.93 (s, 2H, Ar), 6.44 (s, 1H, CH-NCS), 3.90 (s, 6H, 2 \times OMe), 3.89 (s, 3H, OMe); ^{13}C NMR (101 MHz, CDCl_3) δ 152.9, 139.5, 135.5, 135.0 (br s, NCS), 128.6, 112.5, 105.5 (CH_{Ar}), 60.9 (OMe), 56.2 (2 \times OMe); *Z*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 6.77 (s, 2H, Ar), 6.54 (s, 1H, CH-NCS), 3.88 (s, 6H, 2 \times OMe), 3.87 (s, 3H, OMe); ^{13}C NMR (101 MHz, CDCl_3) δ 153.2, 139.8, 137.9 (br s, NCS),

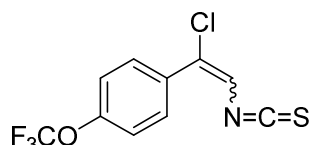
135.1, 129.7, 112.6, 103.8 (CH_{Ar}), 60.9 (OMe), 56.3 (2×OMe); HRMS (ESI⁺) *m/z* calcd for C₁₂H₁₃ClNO₃S [M+H]⁺: 286.0299, found 286.0295.

1-(1-chloro-2-isothiocyanatovinyl)-4-(phenoxy)benzene (4d)



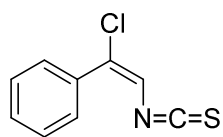
Vinyl isothiocyanate **4d** was obtained from NH-triazole **1** (50 mg, 0.21 mmol) and thiophosgene according to general procedure 1. Column chromatography (cyclohexane/EtOAc, 49:1) afforded product **4d** (37 mg, 61%, *E/Z* = 2.5:1) as a yellow oil. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.58 (m, 2H, Ar), 7.42-7.36 (m, 2H, Ph), 7.20-7.15 (m, 1H, Ph), 7.09-7.06 (m, 2H, Ph), 7.04-7.01 (m, 2H, Ar), 6.50 (s, 1H, CH-NCS); ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 155.9, 136.2 (br s, NCS), 134.6, 130.0, 128.7, 127.8, 124.3, 119.9, 117.7, 112.5 (CH-NCS); *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.48 (m, 2H, Ar), 7.42-7.36 (m, 2H, Ph), 7.20-7.15 (m, 1H, Ph), 7.08-7.06 (m, 2H, Ph), 6.99-6.96 (m, 2H, Ar), 6.49 (s, 1H, CH-NCS); ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 156.0, 137.6 (br s, NCS), 134.8, 131.0, 129.9, 128.0, 124.2, 119.7, 118.2, 112.0 (CH-NCS); HRMS (ESI⁺) *m/z* calcd for C₁₅H₁₁NOClS [M+H]⁺: 288.0244, found 288.0246.

1-(1-chloro-2-isothiocyanatovinyl)-4-(trifluoromethoxy)benzene (4e)



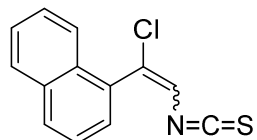
Vinyl isothiocyanate **4e** was obtained from NH-triazole **1** (46 mg, 0.2 mmol) and thiophosgene according to general procedure 1. Column chromatography (cyclohexane) afforded product **4e** (28 mg, 50%, *E/Z* = 1:1.5) as a yellow oil. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.75-7.72 (m, 2H, Ar), 7.28 (dq, *J* = 8.9, 1.0 Hz, 2H, Ar), 6.60 (s, 1H, CH-NCS); ¹³C NMR (101 MHz, CDCl₃) δ 150.2 (q, *J* = 1.8 Hz), 137.3 (br s, NCS), 133.6, 132.8, 129.9, 129.8, 120.6, 120.4 (q, *J* = 258.2 Hz, CF₃), 114.4 (CH-NCS); *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.56 (m, 2H, Ar), 7.24 (dq, *J* = 8.9, 1.0 Hz, 2H, Ar), 6.56 (s, 1H, CH-NCS); ¹³C NMR (101 MHz, CDCl₃) δ 150.0 (q, *J* = 1.8 Hz), 138.5 (br s, NCS), 133.1, 132.1, 129.5, 127.8, 121.0, 120.3 (q, *J* = 258.2 Hz, CF₃), 113.8 (CH-NCS); HRMS (APCI⁺) *m/z* calcd for C₁₀H₅NOClF₃S [M]⁺: 278.9727, found 278.9729.

(E)-(1-chloro-2-isothiocyanatovinyl)benzene (4f)



Vinyl isothiocyanate **4f** was obtained from NH-triazole **1** (29 mg, 0.2 mmol) and thiophosgene according to general procedure 1. Column chromatography (cyclohexane) afforded product **4f** (8.5 mg, 22%, only *E*-isomer) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.53 (m, 2H, Ar), 7.41-7.38 (m, 3H, Ar), 6.56 (s, 1H, CH-NCS); ¹³C NMR (101 MHz, CDCl₃) δ 137.8 (br s, NCS), 135.4, 134.2, 130.0, 128.8, 126.2, 113.0 (CH-NCS); HRMS (EI⁺) *m/z* calcd for C₉H₆ClNS [M]⁺: 194.9904, found 194.9905.

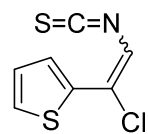
1-(1-chloro-2-isothiocyanatovinyl)naphthalene (4g)



Vinyl isothiocyanate **4g** was obtained from NH-triazole **1** (39 mg, 0.2 mmol) and thiophosgene according to modified general procedure 1 (temperature 45°C, reaction time 24 hours). Column chromatography (cyclohexane) afforded product **4g** (20 mg, 41%, *E/Z* = 2.2:1) as a slightly yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.09-8.06 (m, 1H, CH_{Ar} *Z*-isomer), 7.97-7.88 (m, 9H, CH_{Ar}), 7.61-7.52 (m, 12H, Ar), 7.49-7.44 (m, 2H, CH_{Ar} *Z*-isomer), 6.65 (s, 1H, CH-NCS *E*-isomer), 6.37 (s, 1H, CH-NCS *Z*-isomer); ¹³C NMR (101 MHz, CDCl₃) δ 138.2 (br s, NCS, *Z*-isomer), 137.4 (br s, NCS, *E*-isomer), 134.7, 133.7, 133.63, 133.59, 132.5, 132.1, 131.6, 130.9, 130.6, 130.0, 129.6, 128.7, 128.6, 127.7, 127.6, 127.1, 126.52, 126.48, 125.1, 125.0, 124.9, 124.7, 117.2

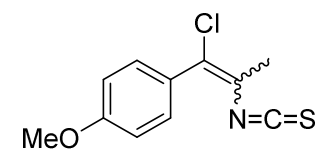
(CH-NCS, *E*-isomer), 116.8 (CH-NCS, *Z*-isomer); HRMS (EI⁺) *m/z* calcd for C₁₃H₈ClNS [M]⁺: 245.0060, found 245.0062.

2-(1-chloro-2-isothiocyanatovinyl)thiophene (**4h**)



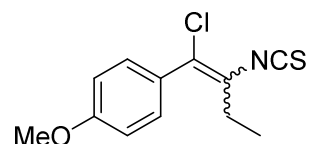
Vinyl isothiocyanate **4h** was obtained from NH-triazole **1** (30.2 mg, 0.2 mmol) and thiophosgene according to modified general procedure 1 (temperature 45°C, reaction time 24 hours). Column chromatography (cyclohexane) afforded product **4h** (19 mg, 48%, *E/Z* = 1.5:1) as a yellow oil. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.30 (m, 2H), 7.03 (dd, *J* = 5.1, 3.8 Hz, 1H), 6.58 (s, 1H, CH-NCS); ¹³C NMR (101 MHz, CDCl₃) δ 138.3-138.0 (br s, NCS), 137.4, 128.7, 127.9, 127.6, 127.1, 111.4 (CH-NCS); *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.47 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.8 Hz, 1H), 6.44 (s, 1H, CH-NCS); ¹³C NMR (101 MHz, CDCl₃) δ 138.3-138.0 (br s, NCS), 135.9, 129.8, 128.8, 128.5, 126.9, 110.7 (CH-NCS); HRMS (EI⁺) *m/z* calcd for C₇H₄ClNS₂ [M]⁺: 200.9468, found 200.9468.

1-(1-chloro-2-isothiocyanatoprop-1-en-1-yl)-4-methoxybenzene (**4i**)



Vinyl isothiocyanate **4i** was obtained from NH-triazole **1** (19 mg, 0.1 mmol) and thiophosgene according to general procedure 1. Column chromatography (pentane/EtOAc, 19:1 to 9:1) afforded product **4i** (11.5 mg of *E*-isomer and 7.5 mg of *Z*-isomer, total yield 19 mg, 79%, *E/Z* = 1.5:1) as a yellow oil. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.48 (m, 2H, Ar), 6.93-6.90 (m, 2H, Ar), 3.84 (s, 3H, OMe), 2.30 (s, 3H, Me); ¹³C NMR (101 MHz, CDCl₃) δ 160.1, 136.4 (br s, NCS), 130.7, 130.0, 128.1, 121.9, 113.6 (C(Me)-NCS), 55.3 (OMe), 21.1 (Me); *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.25 (m, 2H, Ar), 6.91-6.89 (m, 2H, Ar), 3.83 (s, 3H, OMe), 2.38 (s, 3H, Me); ¹³C NMR (101 MHz, CDCl₃) δ 160.1, 137.0 (br s, NCS), 130.6, 130.5, 127.9, 123.0, 113.8 (C(Me)-NCS), 55.4 (OMe), 20.2 (Me); HRMS (EI⁺) *m/z* calcd for C₁₁H₁₀ClNOS [M]⁺: 231.0166, found 231.0168.

1-(1-chloro-2-isothiocyanatobut-1-en-1-yl)-4-methoxybenzene (**4j**)

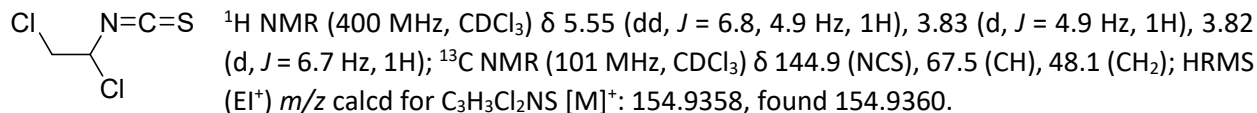


Vinyl isothiocyanate **4j** was obtained from NH-triazole **1** (40.5 mg, 0.2 mmol) and thiophosgene according to general procedure 1. Column chromatography (cyclohexane/EtOAc, 29:1) afforded product **4j** (19 mg, 37%, *E/Z* = 1:1.4) as a yellow oil. *E*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.48 (m, 2H, Ar), 6.93-6.90 (m, 2H, Ar), 3.84 (s, 3H, OMe), 2.68 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.1, 135.5 (br s, NCS), 130.4, 130.0, 128.2, 127.4, 113.6, 55.3 (OMe), 28.2, 11.1; *Z*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.27 (m, 2H, Ar), 6.91-6.89 (m, 2H, Ar), 3.83 (s, 3H, OMe), 2.35 (q, *J* = 7.4 Hz, 2H), 1.16 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.2, 136.6 (br s, NCS), 129.4, 130.2, 128.9, 128.0, 113.9, 55.3 (OMe), 27.0, 12.2; HRMS (ESI⁺) *m/z* calcd for C₁₂H₁₃ClNOS [M+H]⁺: 254.0401, found 254.0397.

Synthesis of 1,2-dichloroethyl isothiocyanate **5**

To the suspension of NH-1,2,3-triazole **1** (34.5 mg, 0.5 mmol) in dry DCE (7 ml) in a 10 ml vial thiophosgene (2 equiv., 1 mmol, 76.5 μl) was added. The vial was sealed, and the resulting mixture was heated at 70 °C for 16 hours. After the reaction was complete (NMR monitoring), it was subjected to silica gel column chromatography (pentane) without evaporation of the initial DCE solution to afford 1,2-dichloroethyl

isothiocyanate **5** as yellow oil (44 mg, 57%). To avoid loss of product during evaporation, the solvent was removed at 300 Torr pressure.

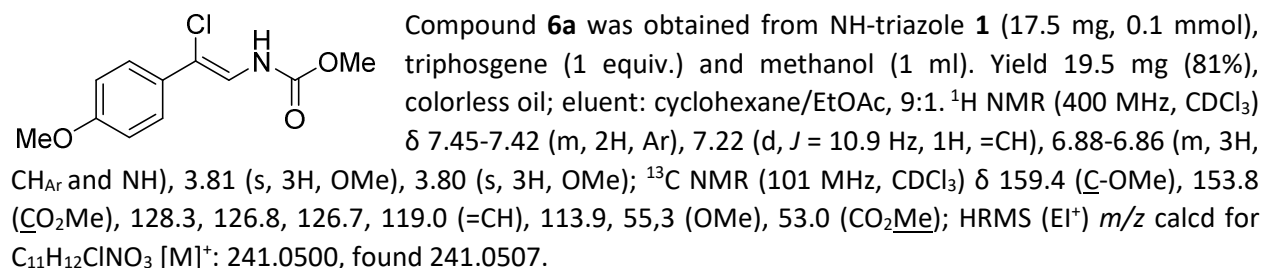


General procedure 2 for the synthesis of N-(chlorovinyl) compounds from NH-triazoles, triphosgene and nucleophiles

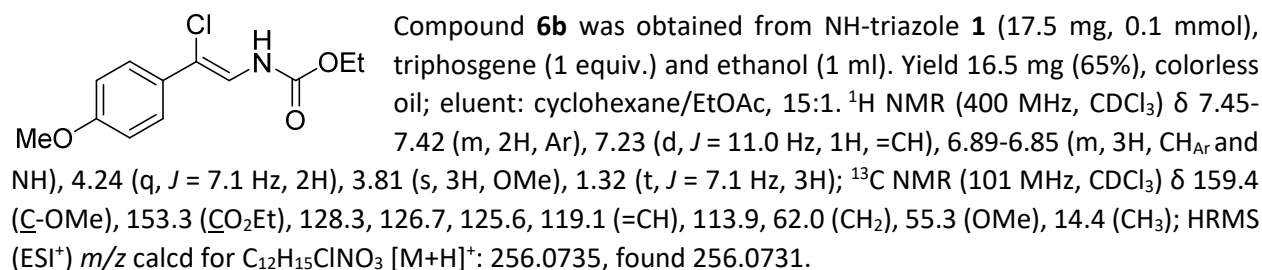
To the suspension of NH-triazole **1** (0.1 mmol) in dry DCE (0.5 ml) triphosgene (30 mg, 0.1 mmol, 1 equiv.) was added, and the resulting mixture was heated in a closed vial at 60°C for 30 min. Then excess of nucleophile (exact amount is specified for each case) was added directly to the reaction mixture and it was stirred at r.t. for 1 hour, then evaporated under reduced pressure. Crude products **6** were purified by column chromatography (cyclohexane/EtOAc).

CAUTION: Triphosgene and phosgene are highly toxic. In the cases when stoichiometric amount of nucleophile (preparation of compounds **6d-6g**) was used, evaporation of the reaction mixture containing residual triphosgene and phosgene should be carried out under well-ventilated fume hood to avoid exposure.

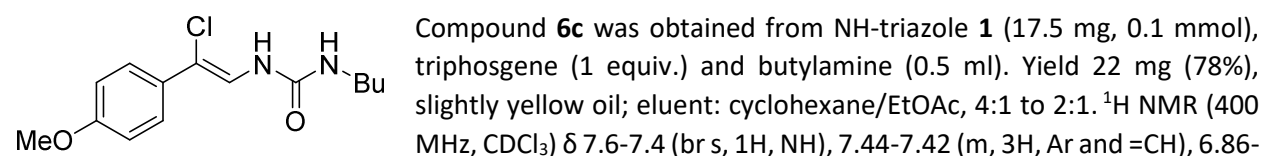
Methyl (Z)-(2-chloro-2-(4-methoxyphenyl)vinyl)carbamate (**6a**)



Ethyl (Z)-(2-chloro-2-(4-methoxyphenyl)vinyl)carbamate (**6b**)

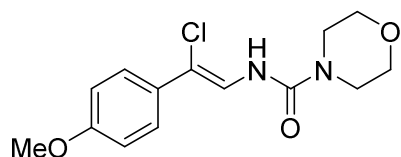


(Z)-1-butyl-3-(2-chloro-2-(4-methoxyphenyl)vinyl)urea (**6c**)



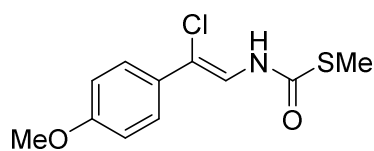
6.83 (m, 2H, Ar), 5.92 (br s, 1H, NH), 3.80 (s, 3H, OMe), 3.29 (t, $J = 7.1$ Hz, 2H), 1.57-1.50 (m, 2H, CH₂), 1.42-1.33 (m, 2H, CH₂), 0.93 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.9 (C-OMe), 154.7 (C=O), 129.0, 126.4, 119.9, 114.7, 113.8, 110.9, 55.3 (OMe), 40.2 (CH₂), 32.1 (CH₂), 20.0 (CH₂), 14.4 (CH₃); HRMS (APCI⁺) m/z calcd for C₁₄H₂₀ClN₂O₂ [M+H]⁺: 283.1208, found 283.1209.

(Z)-*N*-(2-chloro-2-(4-methoxyphenyl)vinyl)morpholine-4-carboxamide (**6d**)



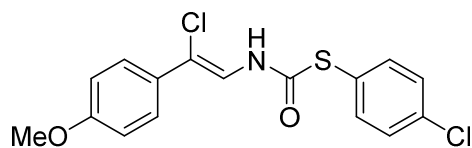
Compound **6d** was obtained from NH-triazole **1** (17.5 mg, 0.1 mmol), triphosgene (1 equiv.) and morpholine (1 equiv.) by modified general procedure 2: Solution of NH-triazole and triphosgene in DCE (0.8 ml) was heated at 60°C for 30 min, then the mixture was evaporated to dryness. A solution of morpholine (9 μl, 0.1 mmol, 1 equiv.) and triethylamine (15 μl, 0.1 mmol, 1.1 equiv.) in DCE (1 ml) was added, and the resulting mixture was stirred for 1 h at r.t. Then it was evaporated under reduced pressure and crude product was purified by column chromatography (eluent: cyclohexane/EtOAc, 3:1 to 1:1). Yield 25 mg (86%), yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, $J = 10.4$ Hz, 1H, =CH), 7.45-7.42 (m, 2H, Ar), 6.89-6.85 (m, 2H, Ar), 6.80 (br d, $J = 10.4$ Hz, 1H, NH), 3.81 (s, 3H, OMe), 3.76-3.73 (m, 2H, CH₂), 3.49-3.47 (m, 2H, CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 159.2 (C-OMe), 153.1 (C=O), 128.5, 126.7, 119.7, 113.9, 112.8, 66.3 (CH₂), 55.3 (OMe), 44.1 (CH₂); HRMS (APCI⁺) m/z calcd for C₁₄H₁₈ClN₂O₃ [M+H]⁺: 297.1001, found 297.0996.

S-methyl (*Z*)-(2-chloro-2-(4-methoxyphenyl)vinyl)carbamothioate (**6e**)



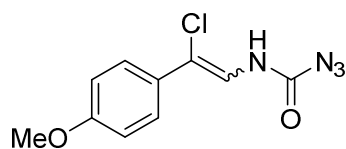
Compound **6e** was obtained from NH-triazole **1** (35 mg, 0.1 mmol), triphosgene (1 equiv.) and sodium methanethiolate (1.3 equiv.) by modified procedure: Solution of NH-triazole and triphosgene in DCE (1 ml) was heated at 60°C for 30 min, then the mixture was evaporated to dryness. Crude product was redissolved in 1 ml of MeCN, and MeSNa (18 mg, 0.26 mmol, 1.3 equiv.) was added. The solution was stirred for 15 min at r.t., then evaporated under reduced pressure. Crude product was purified by column chromatography (eluent: cyclohexane/EtOAc, 4:1). Yield 30 mg (58%), pale yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.42 (m, 4H), 6.90-6.86 (m, 2H, Ar), 3.81 (s, 3H, OMe), 2.45 (s, 3H, SMe); ¹³C NMR (101 MHz, CDCl₃) δ 159.6 (C-OMe), 127.9, 126.9, 125.6, 117.5, 115.0, 113.9, 55.3 (OMe), 12.6 (SMe); HRMS (ESI⁻) m/z calcd for C₁₁H₁₁ClNO₂S [M-H]⁻: 256.0205, found 256.0202.

S-(4-chlorophenyl) (*Z*)-(2-chloro-2-(4-methoxyphenyl)vinyl)carbamothioate (**6f**)



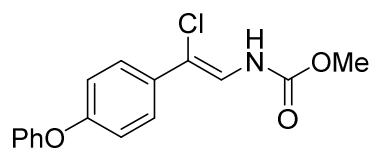
Compound **6f** was obtained from NH-triazole **1** (17.5 mg, 0.1 mmol), triphosgene (1 equiv.) and 4-chlorothiophenol (1 equiv.) by modified procedure: Solution of NH-triazole and triphosgene in DCE (0.8 ml) was heated at 60°C for 30 min, then the mixture was evaporated to dryness. A solution of 4-chlorothiophenol (14.4 mg, 0.1 mmol, 1 equiv.) and triethylamine (15 μl, 0.1 mmol, 1.1 equiv.) in DCE (1 ml) was added, and the resulting mixture was stirred for 1 h at r.t. Then it was evaporated under reduced pressure and crude product was purified by column chromatography (eluent: cyclohexane/EtOAc 9:1 to 4:1). Yield 17.5 mg (49%), pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.51 (m, 2H, Ar), 7.46-7.40 (m, 5H, Ar and =CH), 7.34 (br d, $J = 10.3$ Hz, 1H, NH), 6.89-6.85 (m, 2H, Ar), 3.81 (s, 3H, OMe); ¹³C NMR (101 MHz, CDCl₃) δ 163.6 (C=O), 159.8 (C-OMe), 136.8, 136.7, 129.9, 127.6, 127.0, 125.5, 117.1, 116.4, 114.0, 55.4 (OMe); HRMS (ESI⁺) m/z calcd for C₁₆H₁₃Cl₂NO₂SNa [M+Na]⁺: 375.9936, found 375.9937.

(2-chloro-2-(4-methoxyphenyl)vinyl)carbamoyl azide (6g)



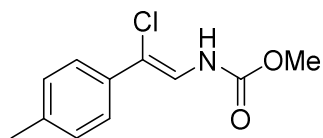
Compound **6g** was obtained from NH-triazole **1** (17.5 mg, 0.1 mmol), triphosgene (1 equiv.) and sodium azide (5 equiv.) according to modified general procedure 2: Solution of NH-triazole and triphosgene in DCE (0.8 ml) was heated at 60°C for 30 min, then the mixture was evaporated to dryness. Yield 8 mg (32%), *Z/E*-mixture (9:1), yellow amorphous solid; eluent: cyclohexane/EtOAc, 9:1. ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.43 (m, 2H, Ar), 7.26 (d, *J* = 11 Hz, 1H, =CH), 7.13 (d, *J* = 11 Hz, 1H, NH), 6.90-6.87 (m, 2H, Ar), 3.82 (s, 3H, OMe); ¹³C NMR (101 MHz, CDCl₃) δ 159.8 (C-OMe), 153.8 (CO₂Me), 127.6, 127.0, 117.5, 116.9, 114.0, 53.4 (OMe); HRMS (APCI⁺) *m/z* calcd for C₁₀H₁₀ClN₂O₂ [M-N₂+H]⁺: 225.0425, found 225.0427.

Methyl (Z)-(2-chloro-2-(4-phenoxyphenyl)vinyl)carbamate (6h)



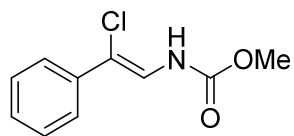
Compound **6h** was obtained from NH-triazole **1** (24.3 mg, 0.1 mmol), triphosgene (1 equiv.) and methanol (1 ml). Yield 25.5 mg (84%), slightly yellow oil, which solidifies upon storage; eluent: cyclohexane/EtOAc, 9:1. ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.45 (m, 2H, Ar), 7.38-7.33 (m, 2H, Ar), 7.27 (d, *J* = 10.5 Hz, 1H), 7.13 (ddt, *J* = 8.5, 7.1, 1.1 Hz, 1H), 7.04-7.01 (m, 2H), 6.99-6.96 (m, 2H), 6.90 (d, *J* = 10.5 Hz, 1H), 3.81 (s, 3H, CO₂Me); ¹³C NMR (101 MHz, CDCl₃) δ 157.2, 156.8, 153.7 (CO₂Me), 130.6, 129.8, 126.9, 123.6, 119.8, 119.1, 118.6, 113.4, 53.1 (CO₂Me); HRMS (ESI⁺) *m/z* calcd for C₁₆H₁₃ClNO₃ [M+H]⁺: 302.0589, found 302.0589.

Methyl (Z)-(2-chloro-2-(p-tolyl)vinyl)carbamate (6i)



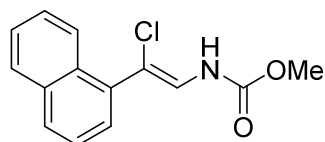
Compound **6i** was obtained from NH-triazole **1** (15.9 mg, 0.1 mmol), triphosgene (1 equiv.) and methanol (1 ml) according to modified general procedure 2; reaction conditions 70°C, 30 min for the first step. Yield 16 mg (70%), colorless oil; eluent: cyclohexane/EtOAc, 9:1. ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.42 (m, 2H, Ar), 7.34 (d, *J* = 10 Hz, 1H, =CH), 7.19-7.17 (m, 2H, Ar), 6.96 (br d, *J* = 10 Hz, 1H, NH), 3.83 (s, 3H, OMe), 2.38 (s, 3H, Me); ¹³C NMR (101 MHz, CDCl₃) δ 153.7 (CO₂Me), 137.7, 132.8, 129.1, 125.2, 119.6 (=CH), 114.0, 53.0 (CO₂Me), 21.0 (Me); HRMS (ESI⁺) *m/z* calcd for C₁₁H₁₃ClNO₂ [M+H]⁺: 226.0629, found 226.0626.

Methyl (Z)-(2-chloro-2-phenylvinyl)carbamate (6j)



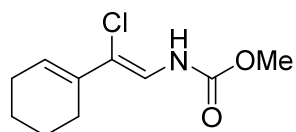
Compound **6j** was obtained from NH-triazole **1** (29 mg, 0.2 mmol), triphosgene (1 equiv.) and methanol (1 ml) according to modified general procedure 2; reaction conditions 70°C, 20 h for the first step. Yield 26 mg (62%), colorless oil, which solidifies upon storage; eluent: cyclohexane/EtOAc, 9:1. ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.51 (m, 2H, Ph), 7.39-7.32 (m, 3H, CH_{Ar} and NH), 7.30-7.25 (m, 1H, Ph), 6.95 (br d, *J* = 8.2 Hz, 1H, NH), 3.81 (s, 3H, OMe); ¹³C NMR (101 MHz, CDCl₃) δ 153.7 (CO₂Me), 135.6, 128.5, 127.8, 125.3, 120.4 (=CH), 113.8, 53.1 (CO₂Me); HRMS (EI⁺) *m/z* calcd for C₁₀H₁₀ClNO₂ [M]⁺: 211.0395, found 211.0397.

Methyl (Z)-(2-chloro-2-(naphthalen-1-yl)vinyl)carbamate (6k)

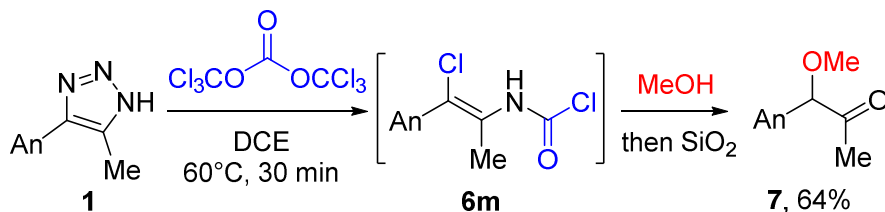


Compound **6k** was obtained from NH-triazole **1** (39 mg, 0.2 mmol), triphosgene (1 equiv.) and methanol (2 ml) according to modified general procedure 2; reaction conditions 70°C, 30 min for the first step. Yield 26.5 mg (51%), slightly brown oil, which solidifies upon storage; eluent: cyclohexane/EtOAc, 14:1. ¹H NMR (400 MHz, CDCl₃) δ 8.13-8.10 (m, 1H, Ar), 7.89-7.85 (m, 2H, Ar), 7.57-7.49 (m, 3H, Ar), 7.44 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.13 (d, *J* = 10.4 Hz, 1H), 7.04 (d, *J* = 10.4 Hz, 1H), 3.82 (s, 3H, OMe); ¹³C NMR (101 MHz, CDCl₃) δ 153.8 (C=O₂Me), 134.0, 133.7, 131.7, 129.7, 128.4, 128.3, 126.5, 126.1, 125.3, 125.1, 123.6, 111.2, 53.1 (CO₂Me); HRMS (EI⁺) *m/z* calcd for C₁₄H₁₂ClNO₂ [M]⁺: 261.0551, found 261.0551.

Methyl (Z)-(2-chloro-2-(cyclohex-1-en-1-yl)vinyl)carbamate (**6l**)



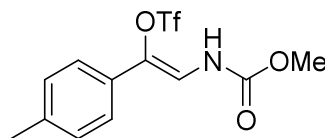
Compound **6l** was obtained from NH-triazole **1** (29.8 mg, 0.2 mmol), triphosgene (1 equiv.) and methanol (1 ml). Yield 31.5 mg (73%), colorless oil; eluent: cyclohexane/EtOAc, 19:1 to 9:1. ¹H NMR (400 MHz, CDCl₃) δ 6.92 (d, *J* = 11.2 Hz, 1H), 6.85 (d, *J* = 11.2 Hz, 1H), 6.12 (t, *J* = 4.0 Hz, 1H), 3.77 (s, 3H, CO₂Me), 2.21-2.15 (m, 2H), 1.72-1.66 (m, 2H), 1.61-1.56 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 153.8 (C=O₂Me), 130.8, 125.7, 117.8, 116.8, 52.9 (CO₂Me), 25.62, 25.60, 22.5, 22.1; HRMS (APCI⁺) *m/z* calcd for C₁₀H₁₅ClNO₂ [M+H]⁺: 216.0786, found 216.0783.



Methoxyketone **7** (An = 4-methoxyphenyl) was obtained from NH-triazole **1** (19 mg, 0.1 mmol), triphosgene (1 equiv.) and MeOH (1 ml) according to general procedure 2. Yield 12.5 mg (64%), colorless oil. NMR matches previously reported data.⁵

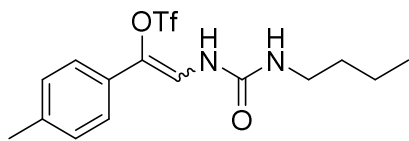
Synthesis of functionalized β-enamido triflates **8**

(Z)-2-((methoxycarbonyl)amino)-1-(p-tolyl)vinyl trifluoromethanesulfonate (**8a**)



To the suspension of NH-triazole **1** (31.8 mg, 0.2 mmol) in dry CHCl₃ (1.5 ml) sodium triflate (38 mg, 0.22 mmol, 1.1 equiv.) and triphosgene (59 mg, 0.2 mmol, 1 equiv.) were added. The vial was sealed and resulting mixture was heated at 50°C for 16 hours. After cooling to r.t. MeOH (0.5 ml) was added, and the mixture was stirred for 10 min, then evaporated under reduced pressure. Crude product was purified by column chromatography (cyclohexane/EtOAc, 19:1 to 9:1) to give product **7a** (32 mg, 47%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.29 (m, 2H, Ar), 7.20-7.17 (m, 2H, Ar), 7.10 (d, *J* = 11.3 Hz, 1H), 6.88 (d, *J* = 11.3 Hz, 1H), 3.82 (s, 3H, CO₂Me), 2.36 (s, 3H, Me); ¹³C NMR (101 MHz, CDCl₃) δ 153.4 (C=O₂Me), 139.1, 131.8, 129.5, 128.7, 124.6, 118.3 (q, *J* = 320.6 Hz), 116.3, 53.4 (CO₂Me), 21.2 (Me); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.2 (s, 3F); HRMS (APCI⁺) *m/z* calcd for C₁₂H₁₃NO₅F₃S [M+H]⁺: 340.0461, found 340.0465.

2-(3-butylureido)-1-(p-tolyl)vinyl trifluoromethanesulfonate (**8b**)



To the suspension of NH-triazole **1** (31.8 mg, 0.2 mmol) in dry CHCl_3 (2 ml) sodium triflate (38 mg, 0.22 mmol, 1.1 equiv.) and triphosgene (59 mg, 0.2 mmol, 1 equiv.) were added. The vial was sealed and resulting mixture was heated at 50°C for 16 hours. After cooling to r.t. BuNH_2 (0.5 ml) was added, and the mixture was stirred for 10 min, then evaporated under reduced pressure. Crude product was purified by column chromatography (cyclohexane/EtOAc, 9:1 to 6:1) to give product **8b** (33.5 mg, 44%, *E/Z* = 1:1) as a colorless oil, which solidified upon storage. ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, *J* = 10.7 Hz, 1H), 7.51-7.46 (br, 1H, NH), 7.40 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 11.0 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 5.86 (br s, 1H, NH), 3.30-3.25 (m, 2 \times 2H, N- CH_2), 2.35 (s, 3H, Me), 2.34 (s, 3H, Me), 1.57-1.50 (m, 2 \times 2H), 1.42-1.35 (m, 2 \times 2H), 0.96-0.92 (m, 2 \times 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.7 (C=O), 154.0 (C=O), 133.4, 130.2, 129.9, 129.4, 129.1, 128.2, 124.9, 124.4, 119.9, 118.9 (q, *J* = 305.5 Hz, CF_3), 118.3 (q, *J* = 320.6 Hz, CF_3), 111.3, 40.4, 40.2, 32.0, 31.9, 21.2, 21.0, 20.0, 19.9, 13.7, 13.6; ^{19}F NMR (376 MHz, CDCl_3) δ -74.1 (s, 3F); HRMS (APCI $^+$) *m/z* calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_4\text{F}_3\text{S}$ [$\text{M}+\text{H}$] $^+$: 381.1090, found 381.1087.

Half-gram scale one-pot three component synthesis of N-vinylurea **6d**

To the suspension of NH-triazole **1** (525 mg, 3 mmol) in DCE (10 ml) triphosgene (890 mg, 3 mmol) was added, and the resulting mixture was heated at 60°C for 30 min in a closed vial. Then it was evaporated to dryness (1 mbar), then redissolved in DCE (10 ml). A solution of morpholine (0.28 ml, 3.3 mmol, 1.1 equiv.) and triethylamine (0.46 ml, 3.3 mmol, 1.1 equiv.) in DCE (5 ml) was added, and the mixture was stirred for 1 h at room temperature. Then it was evaporated under reduced pressure and crude product was purified by column chromatography (eluent: cyclohexane/EtOAc, 3:1 to 1:1). Yield 735 mg (83%), yellow solid.

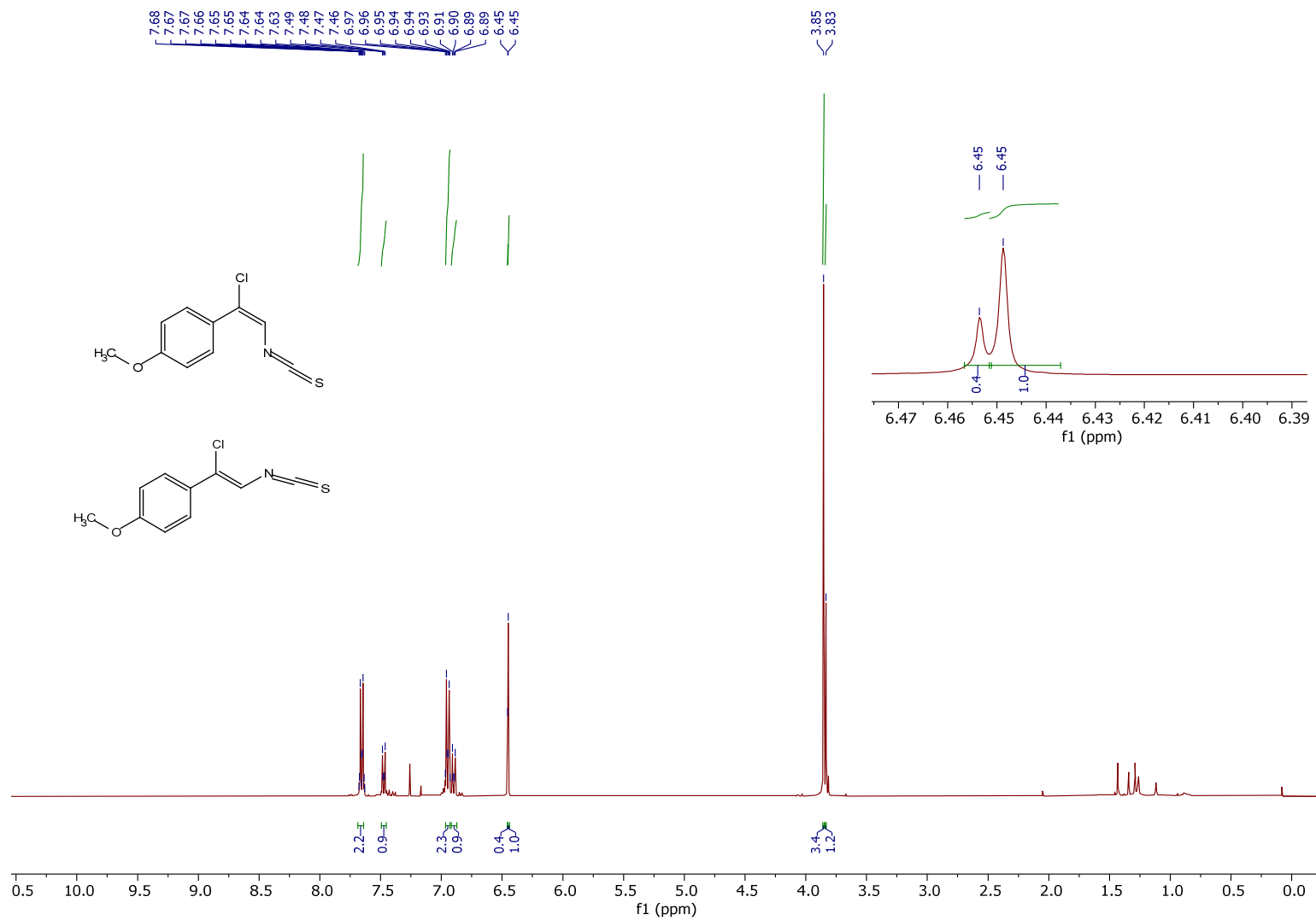
References

1. Hui, R.; Zhao, M.; Chen, M.; Ren, Z.; Guan, Z. *Chin. J. Chem.* **2017**, *35*, 1808.
2. Jin, T.; Kamijo, S.; Yamamoto, Y. *Eur. J. Org. Chem.* **2004**, 3789.
3. Patent WO2012/138877, **2012**, A1.
4. Van Rooden, E. J.; Kreekel, R.; Hansen, T.; Janssen, A. P. A.; van Esbroeck, A. C. M.; den Dulk, H.; van den Berg, R. J. B. H. N.; Codee, J. D. C.; van der Stelt, M. *Org. Biomol. Chem.*, **2018**, *16*, 5250.
5. M. N. Pennell, P. G. Turner, T. D. Sheppard, *Chem. Eur. J.*, **2012**, *18*, 4748.

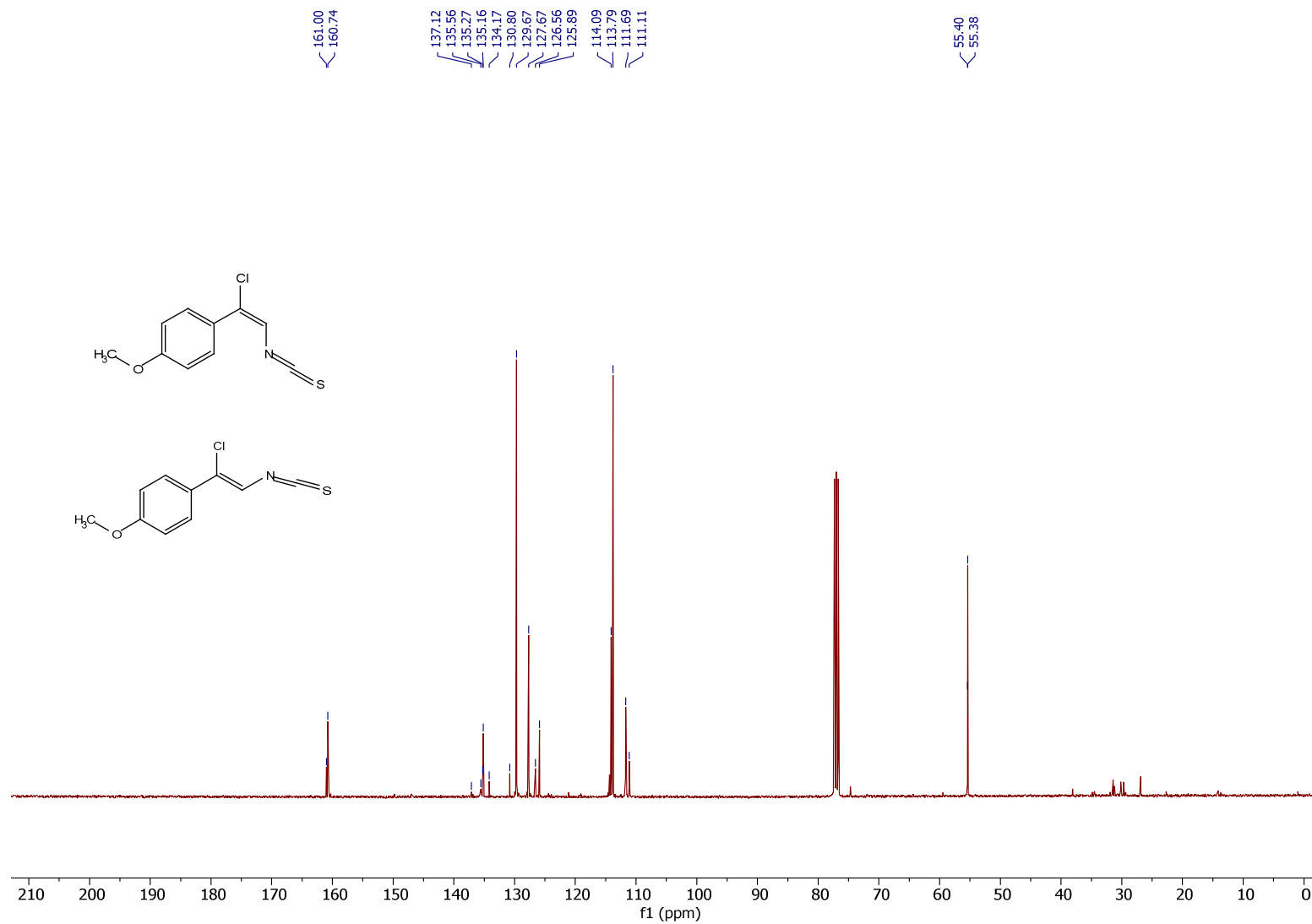
Copies of ^1H , ^{13}C and ^{19}F NMR spectra

1-(1-chloro-2-isothiocyanatovinyl)-4-methoxybenzene (**4a**)

^1H NMR

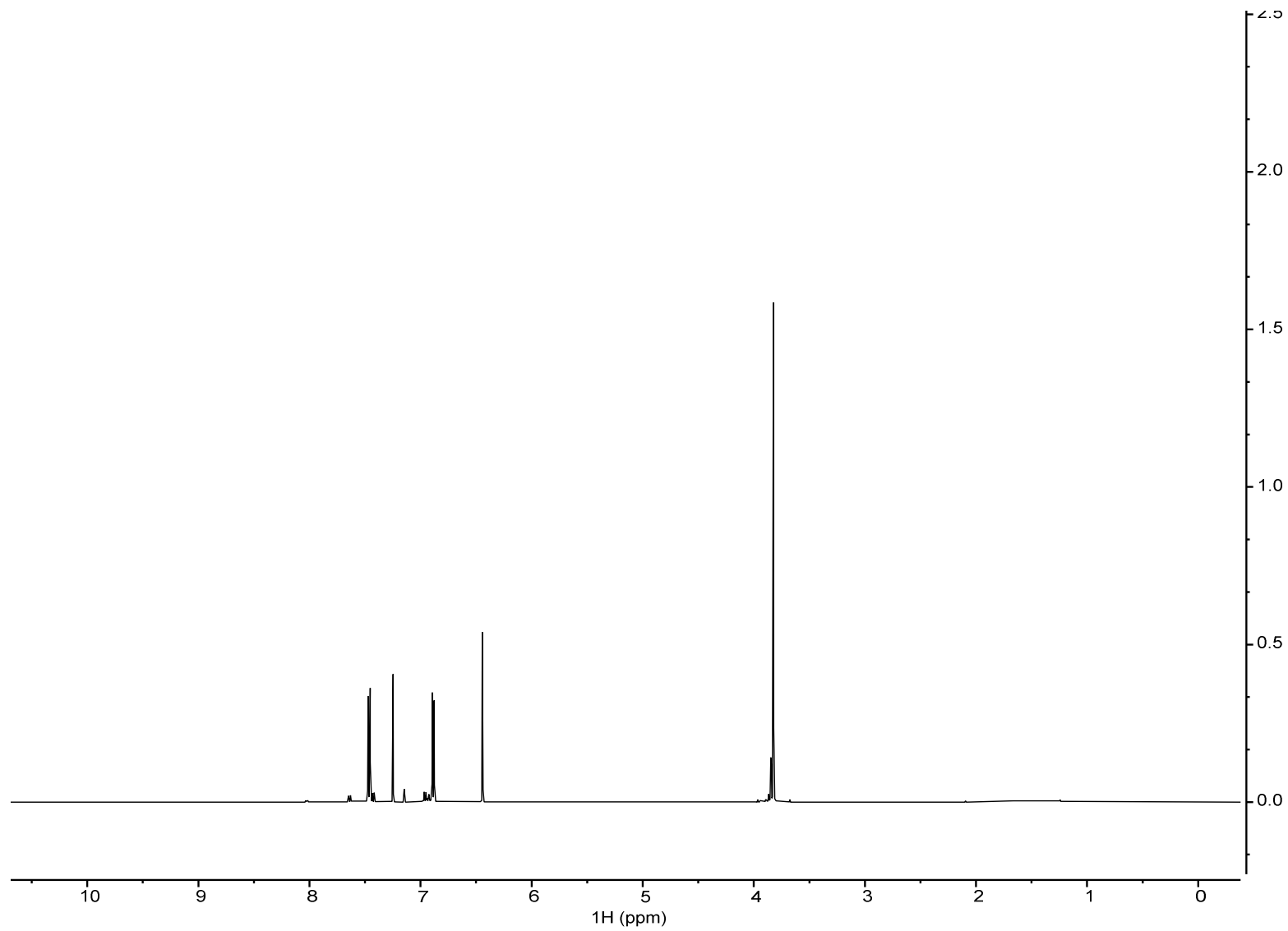


¹³C NMR



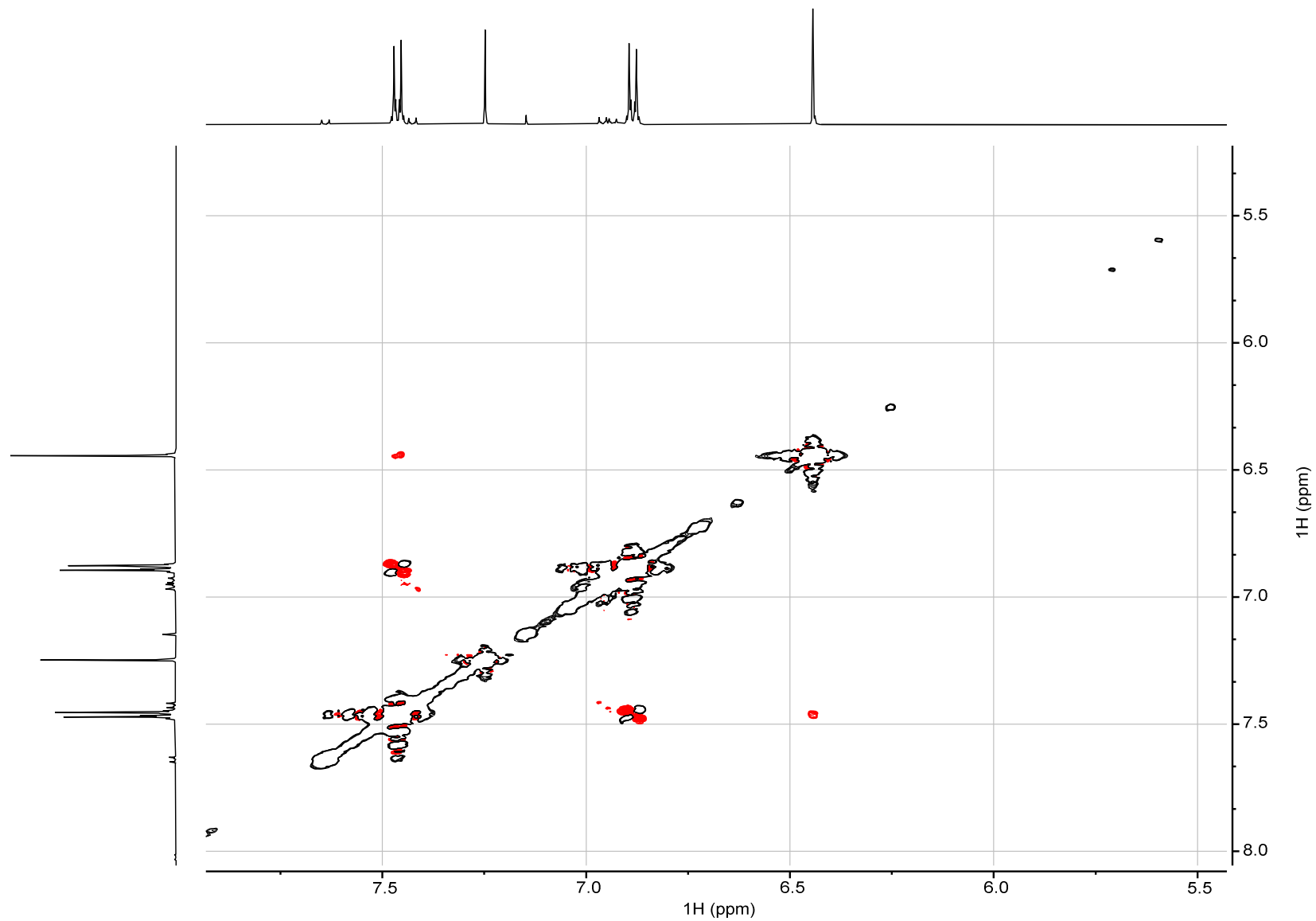
(Z)-1-(1-chloro-2-isothiocyanatovinyl)-4-methoxybenzene (**4a**) (minor isomer)

^1H NMR



SI12

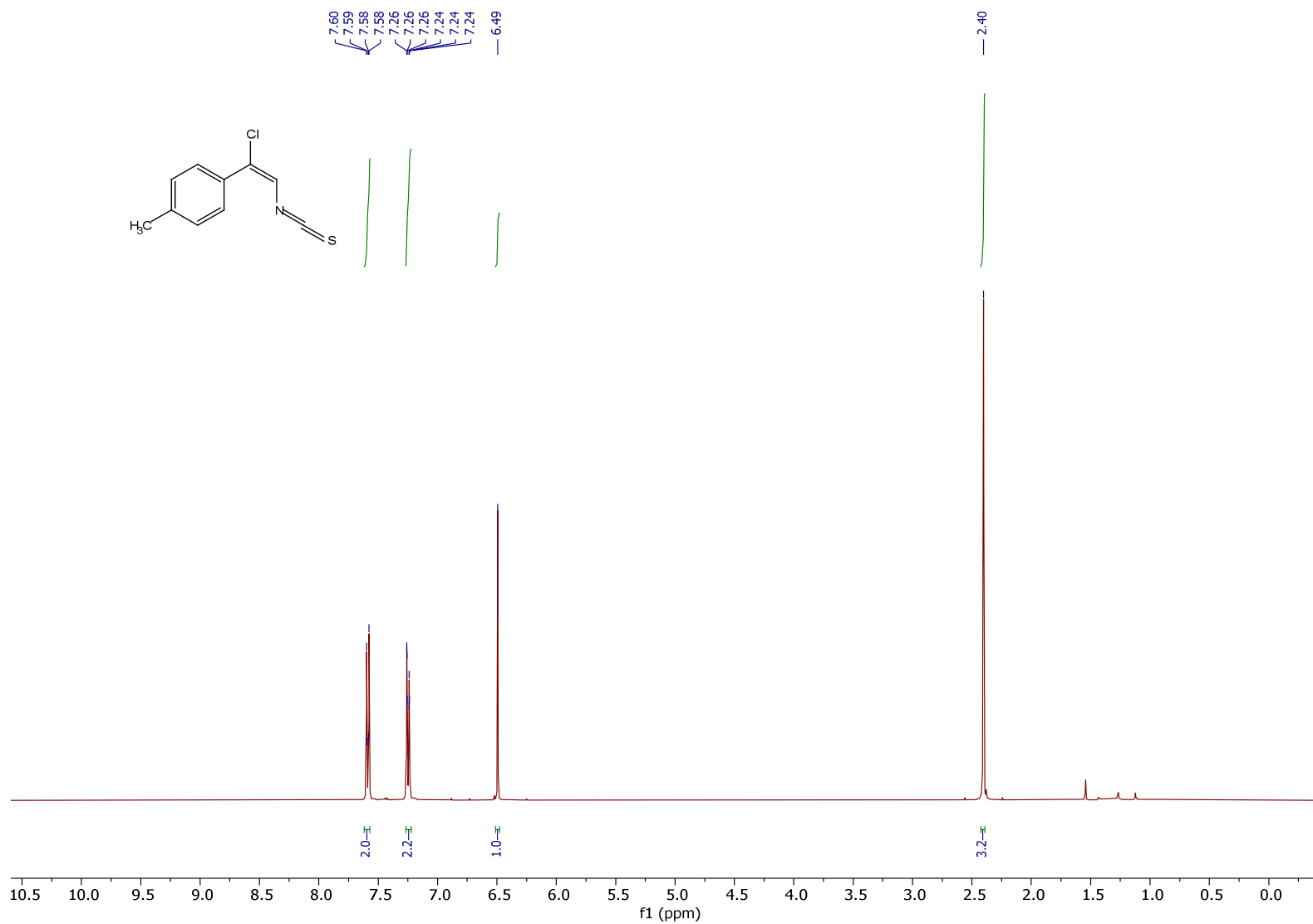
^1H - ^1H ROESY NMR



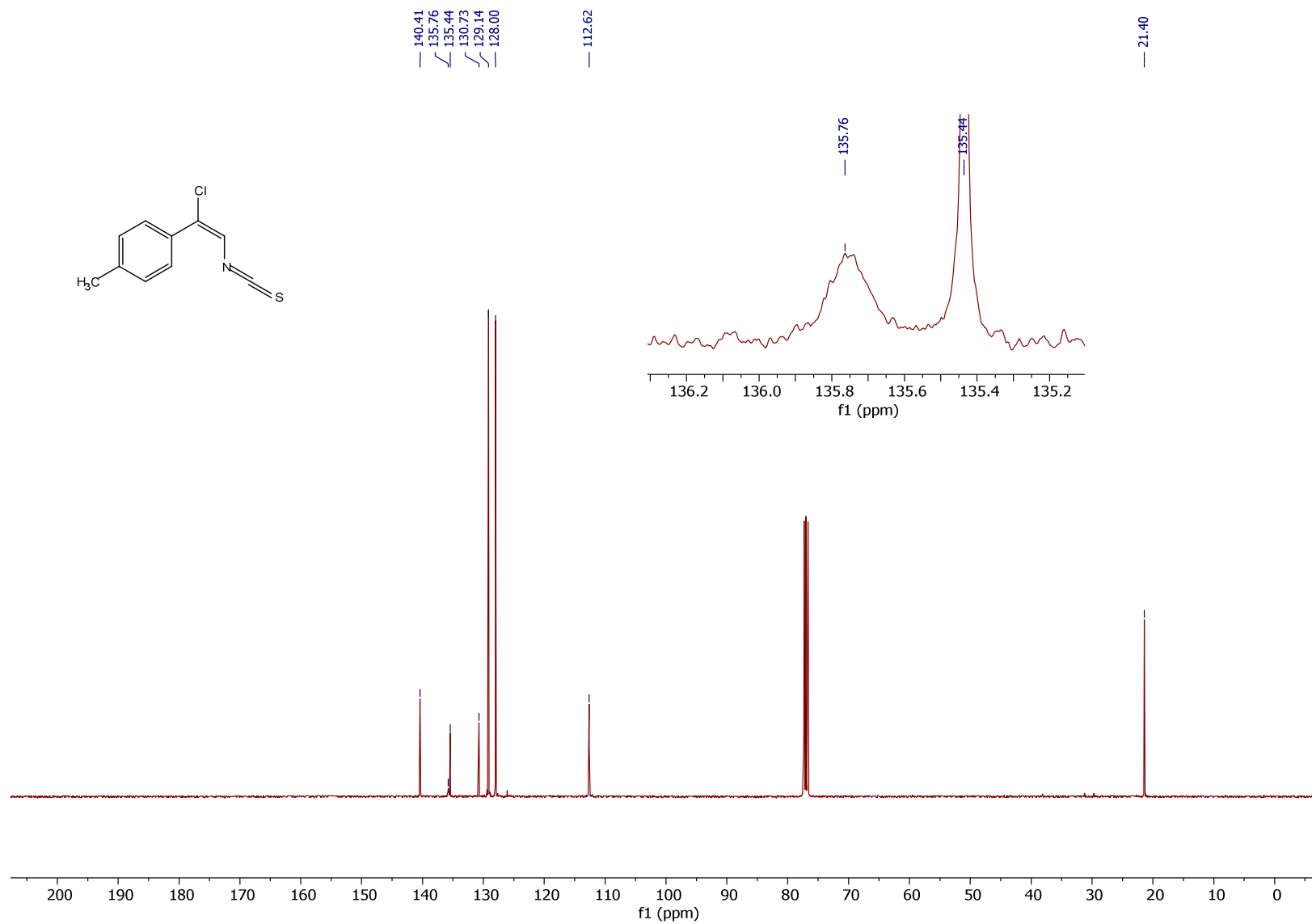
SI13

(E)-1-(1-chloro-2-isothiocyanatovinyl)-4-methylbenzene (**4b**)

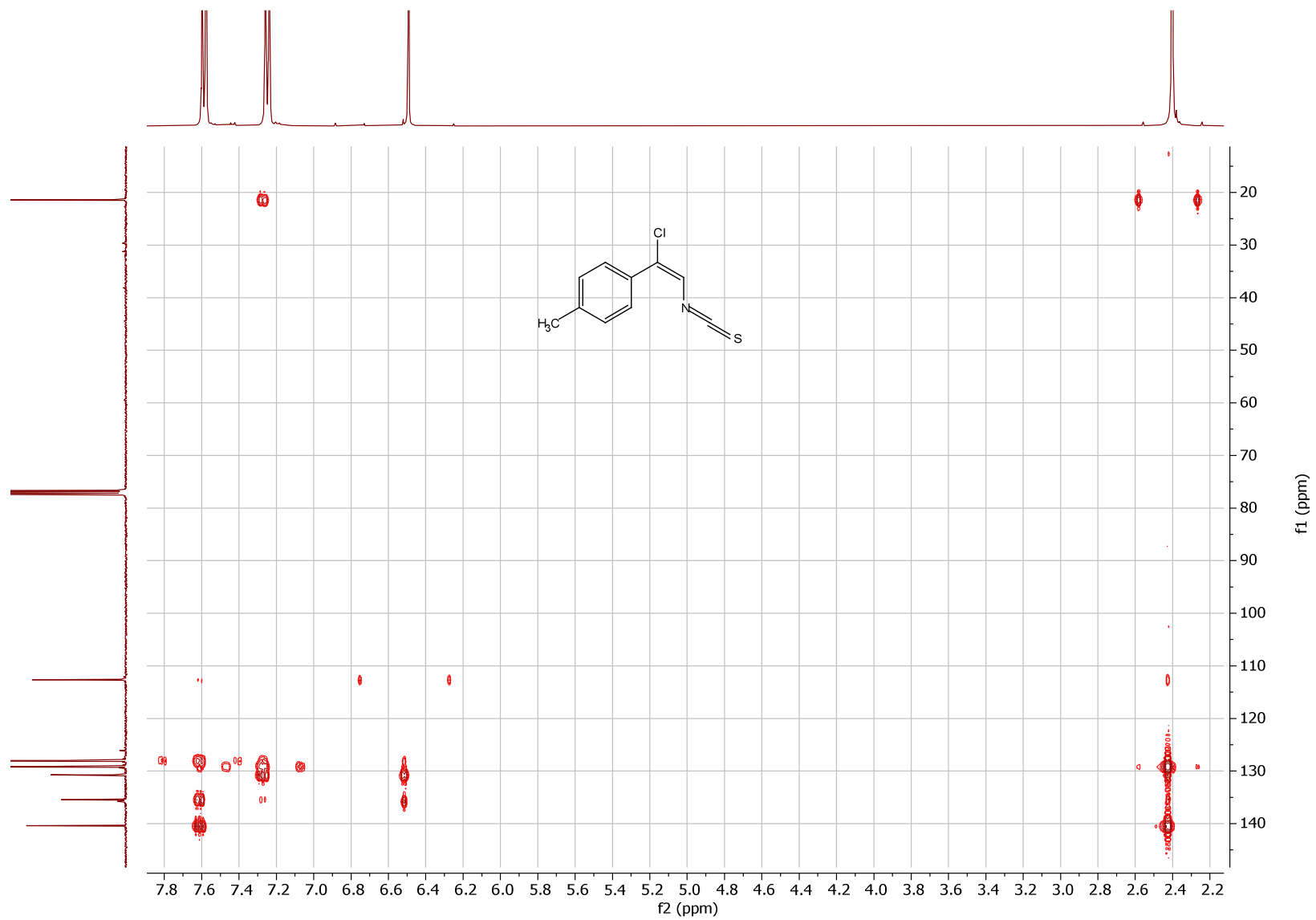
¹H NMR



¹³C NMR

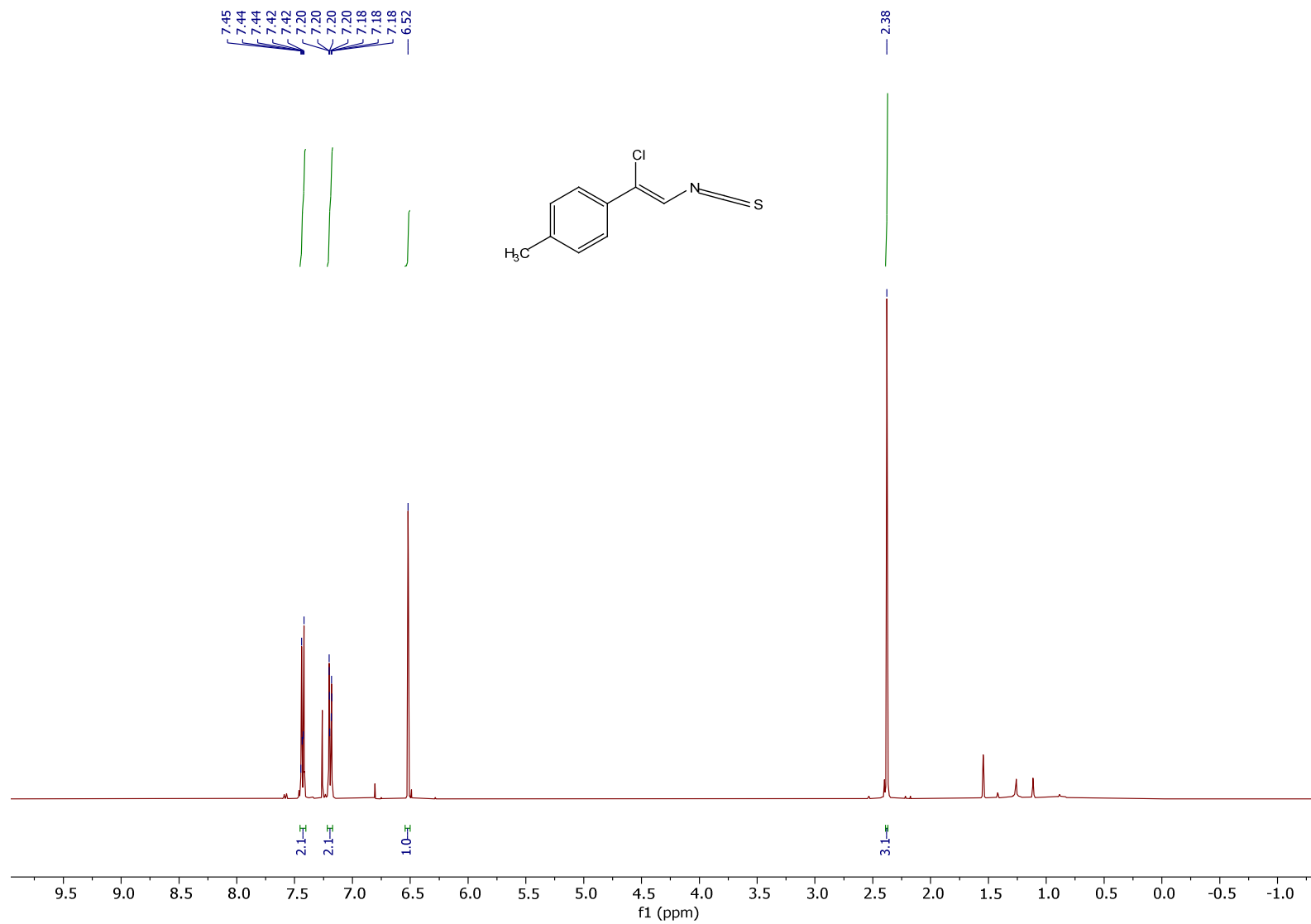


^1H - ^{13}C HMBC NMR

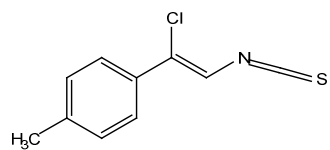


(Z)-1-(1-chloro-2-isothiocyanatovinyl)-4-methylbenzene (**4b**)

^1H NMR



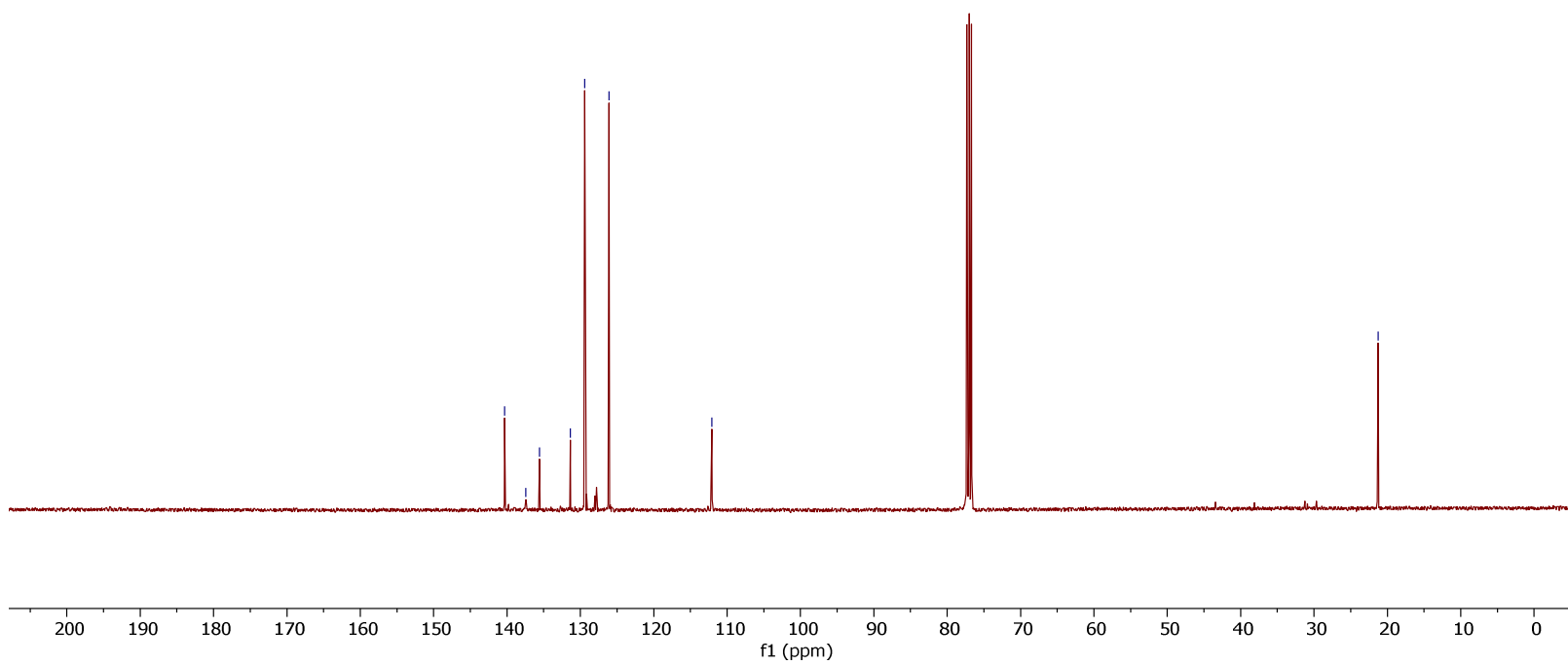
¹³C NMR



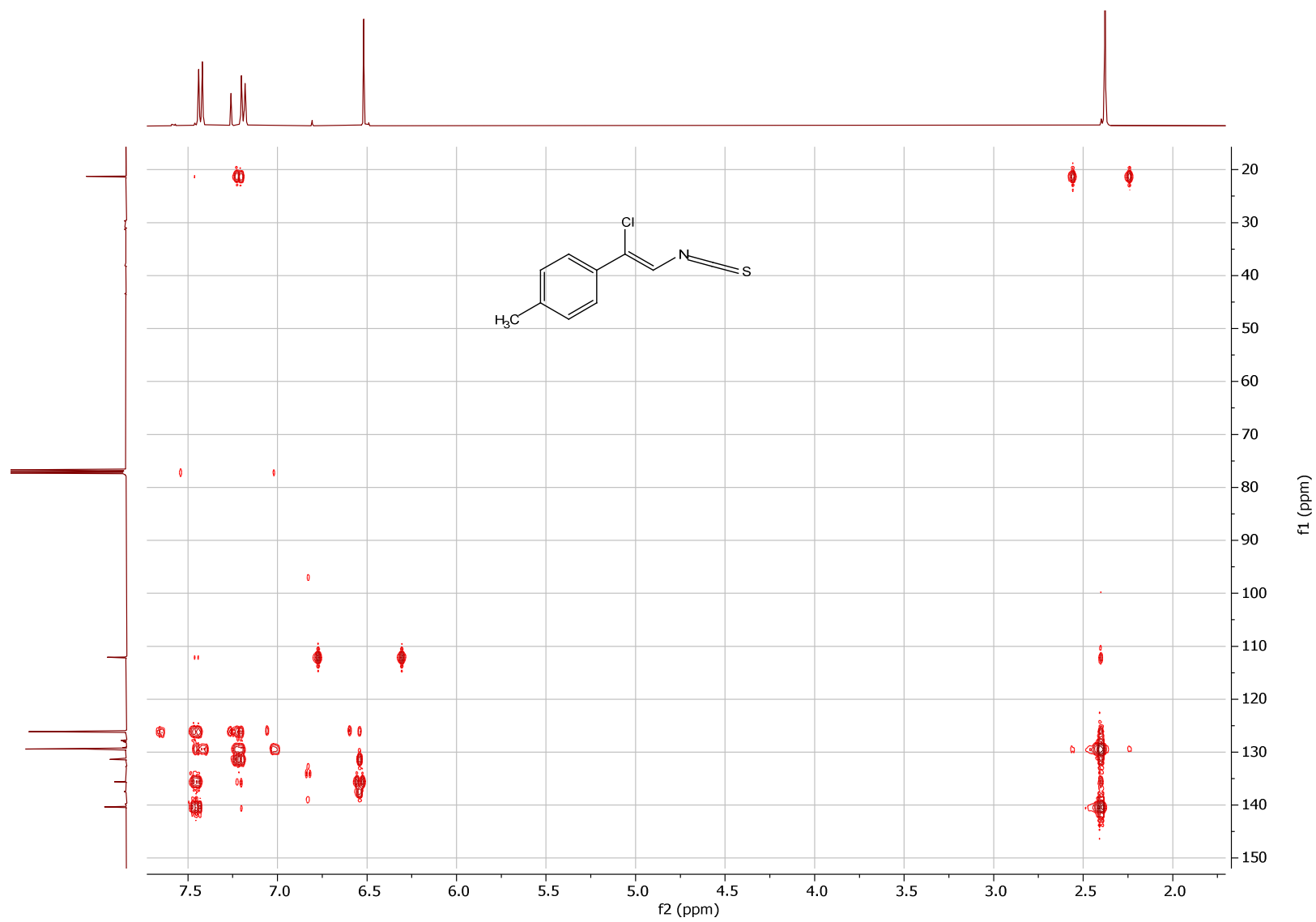
140.33
137.42
135.56
131.35
129.43
126.11

112.08

21.26

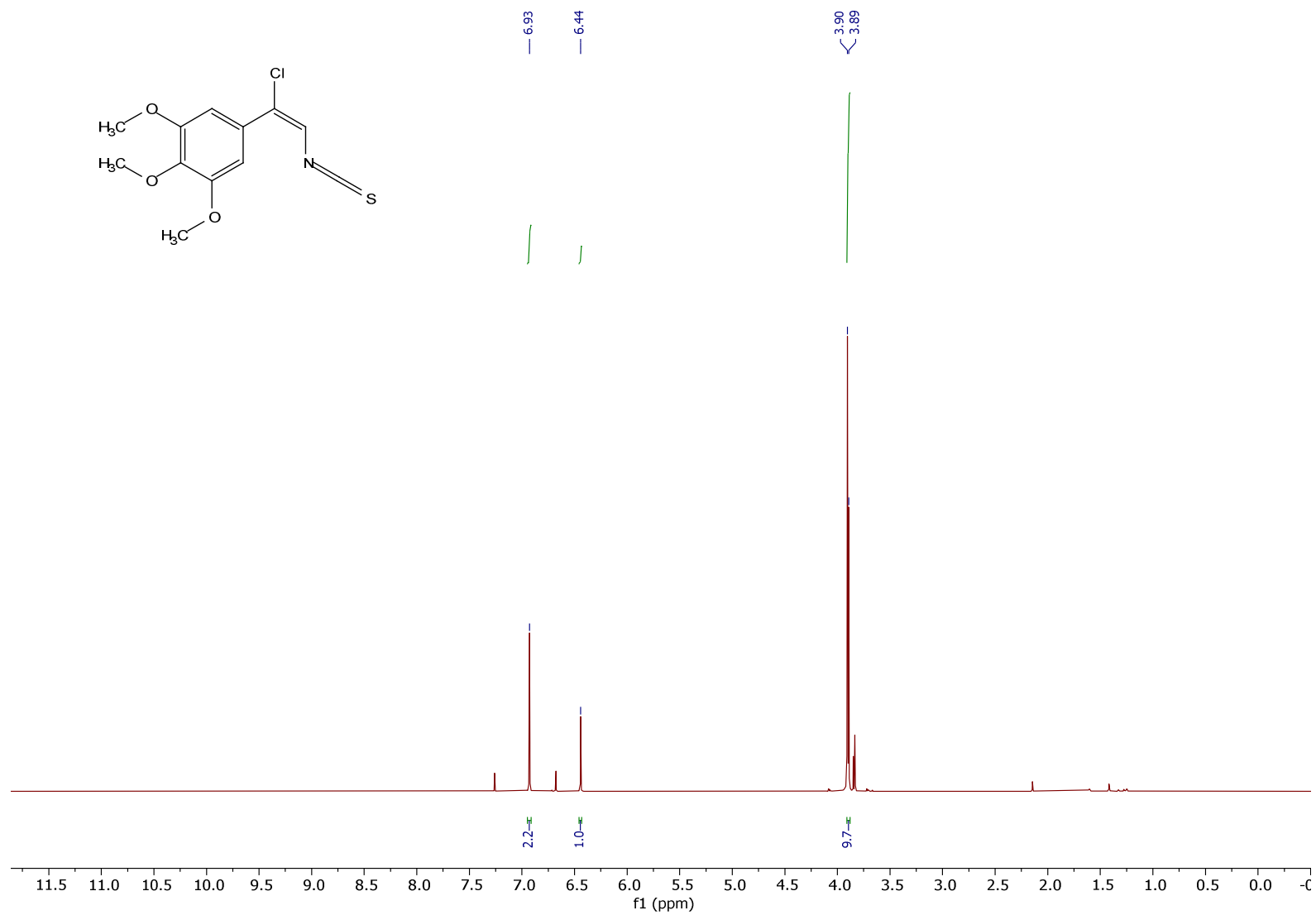


^1H - ^{13}C HMBC NMR

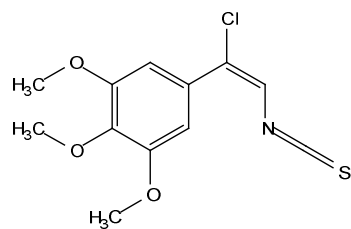


(E)-5-(1-chloro-2-isothiocyanatovinyl)-1,2,3-trimethoxybenzene (**4c**)

¹H NMR



¹³C NMR



— 152.86

— 139.49

— 135.49

— 134.99

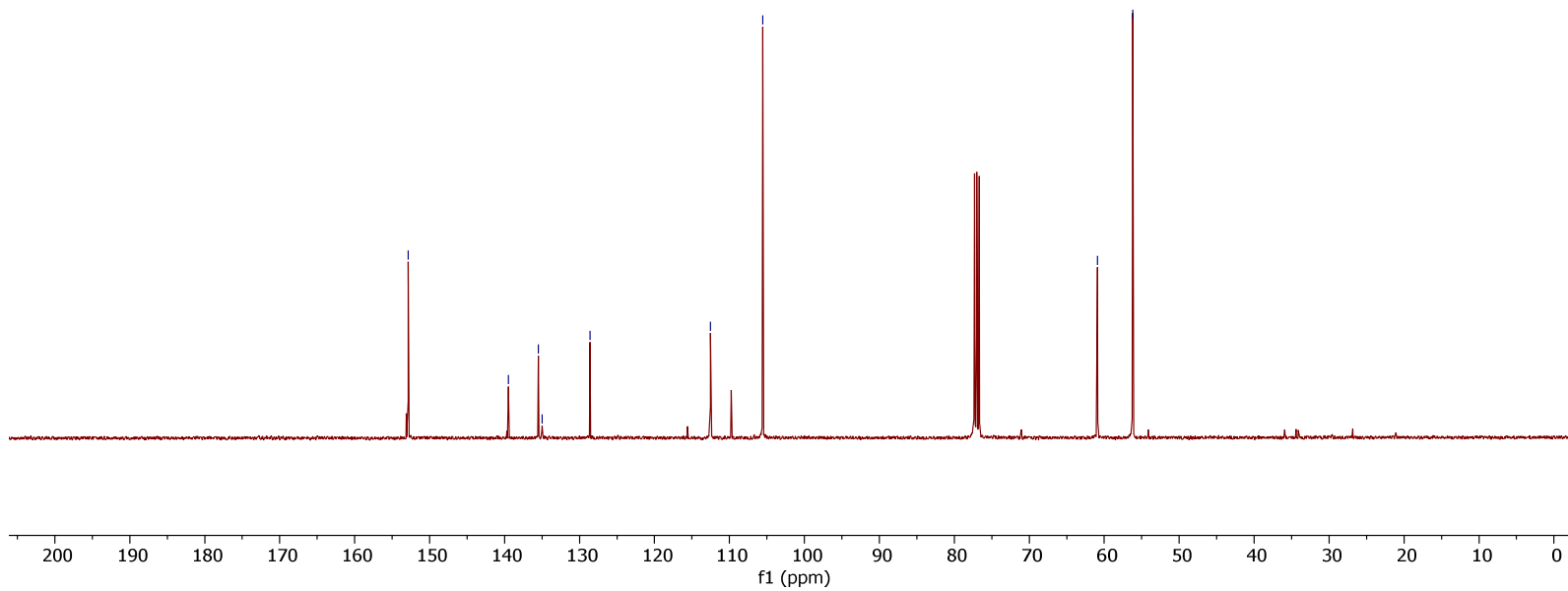
— 128.59

— 112.52

— 105.54

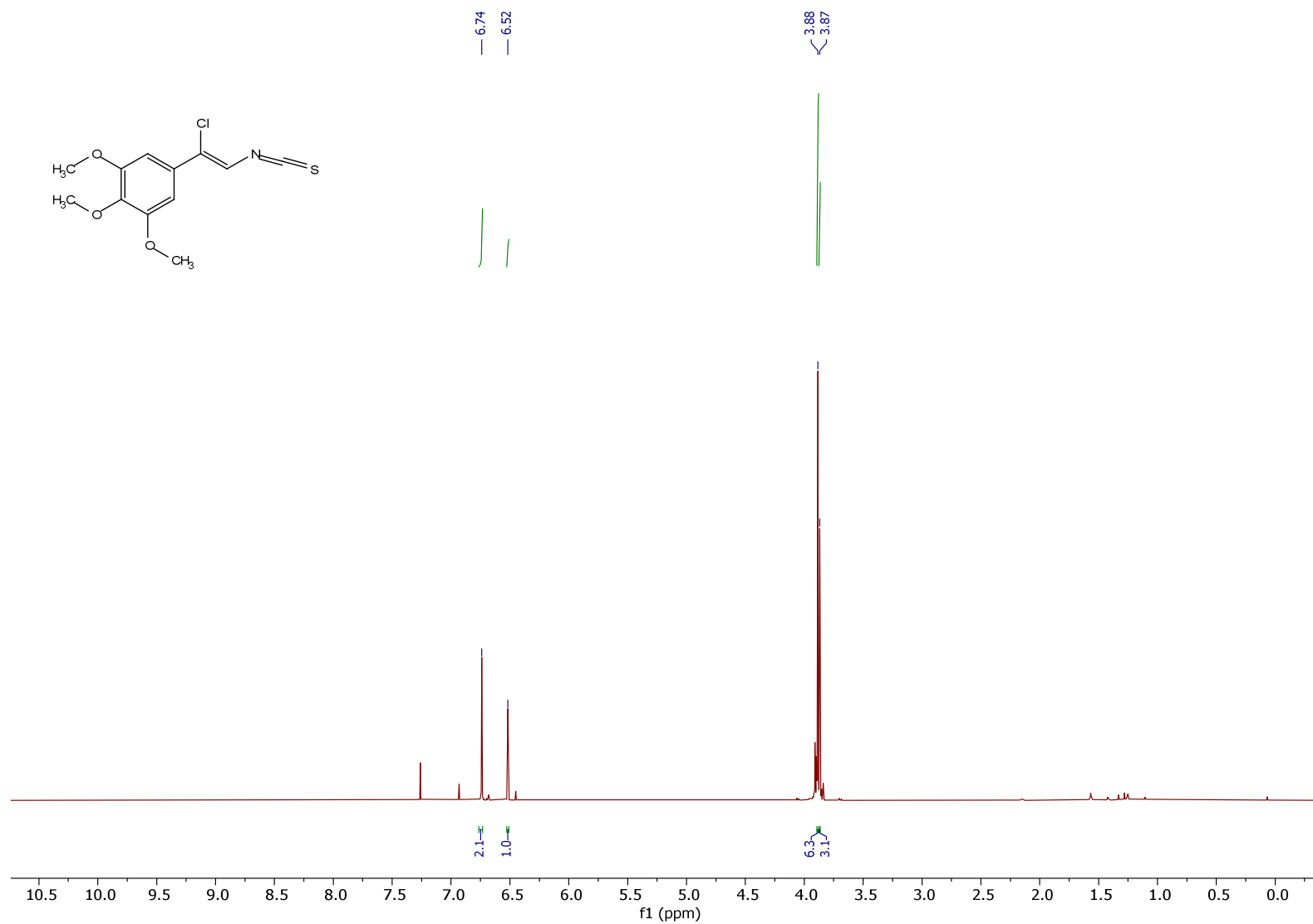
— 60.90

— 56.21

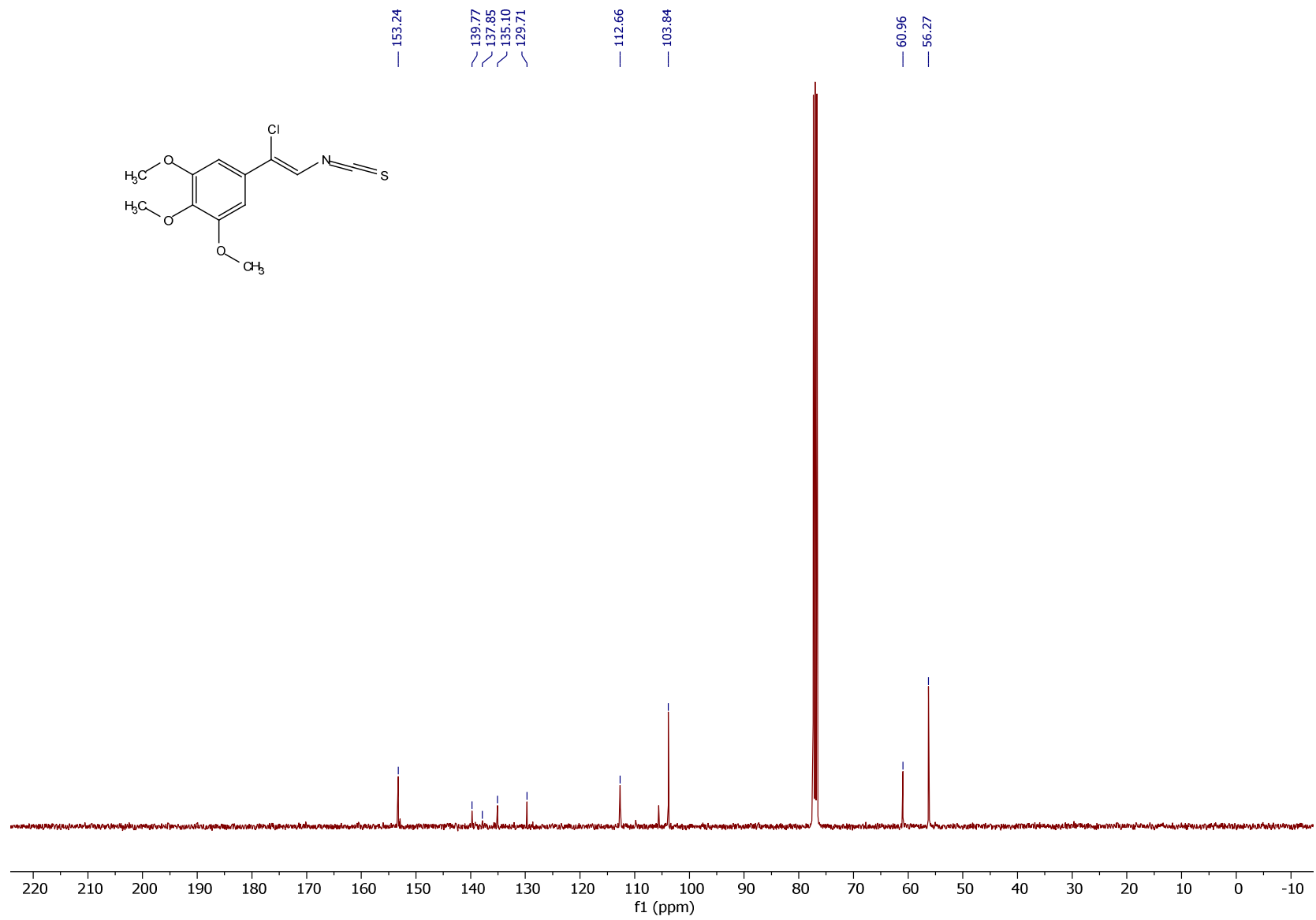
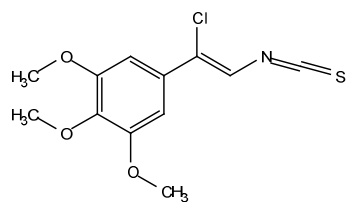


(Z)-5-(1-chloro-2-isothiocyanatovinyl)-1,2,3-trimethoxybenzene (**4c**)

^1H NMR

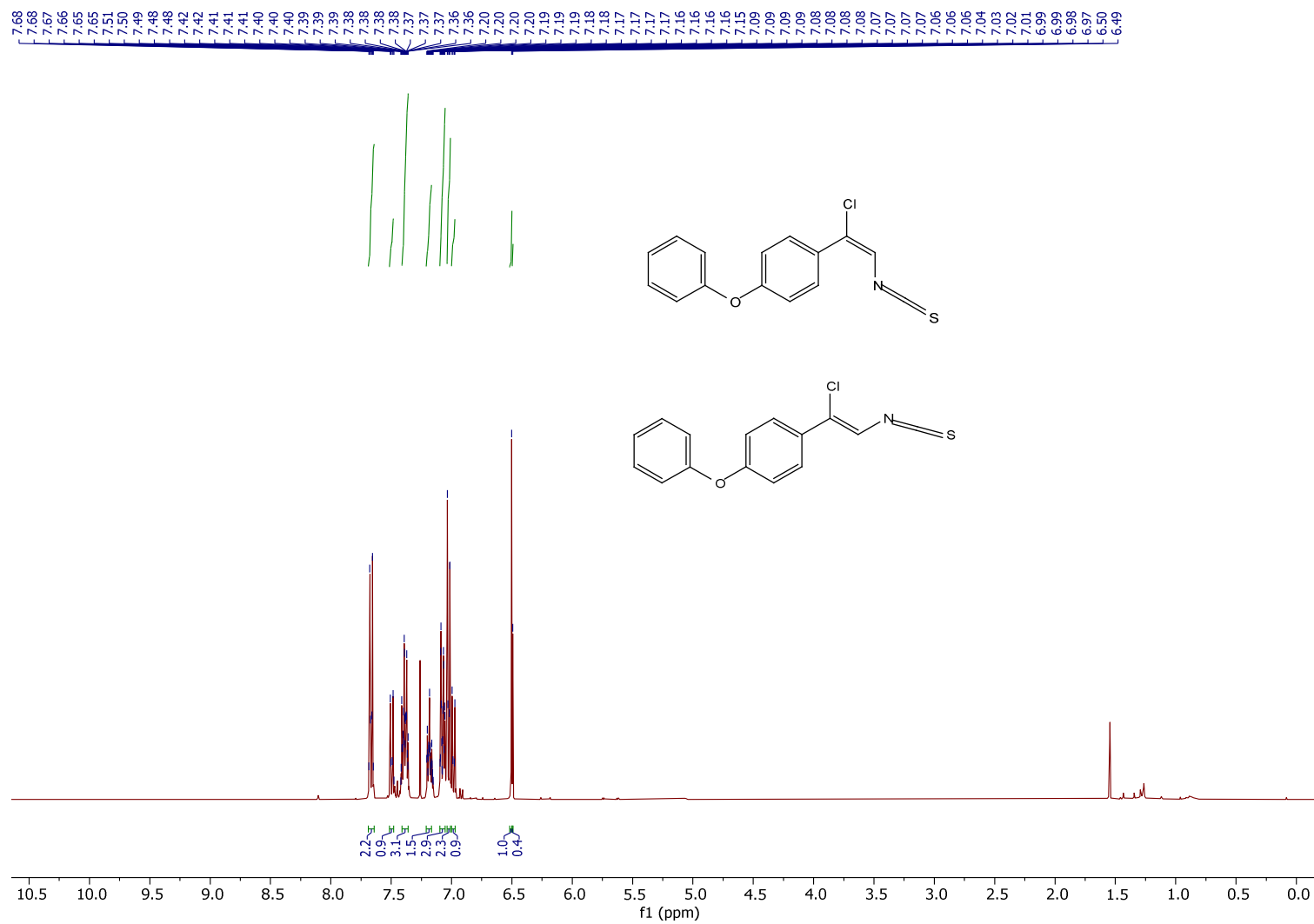


¹³C NMR



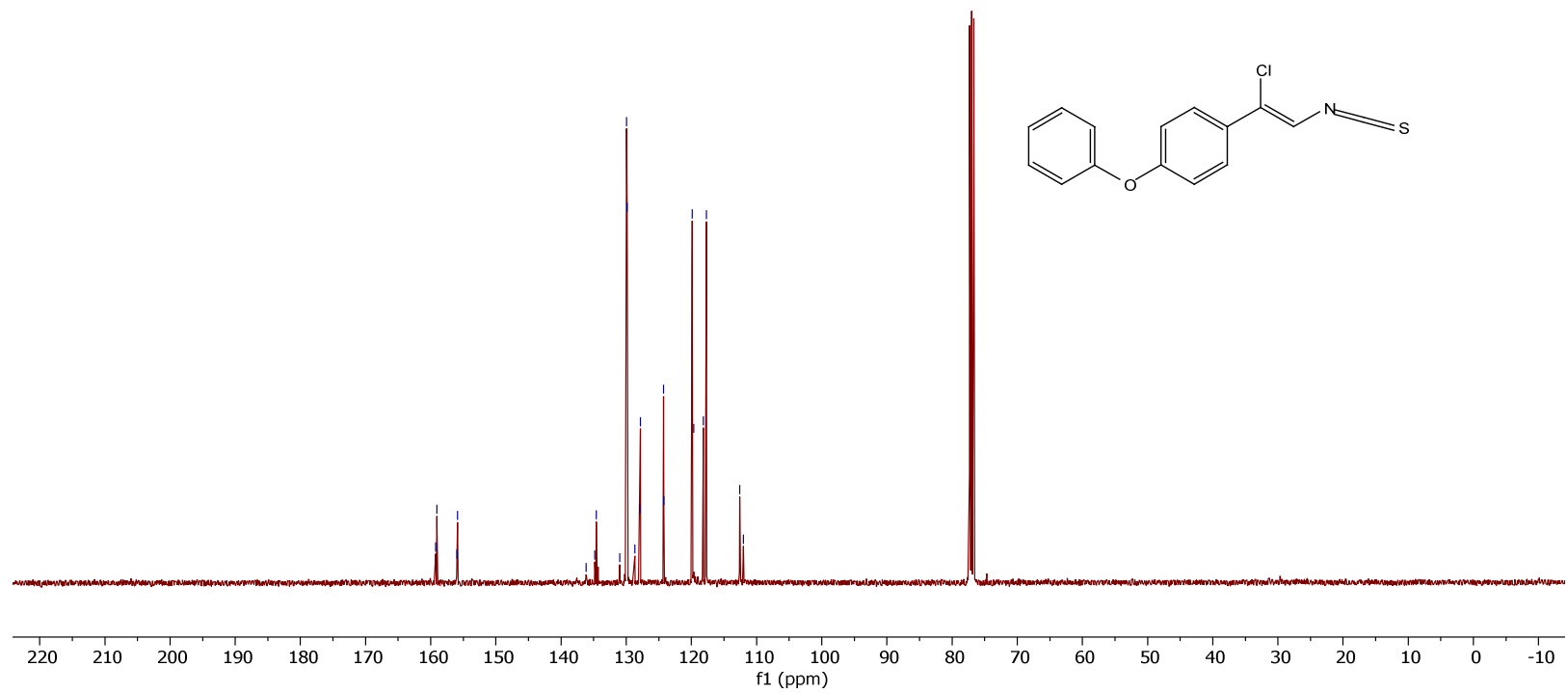
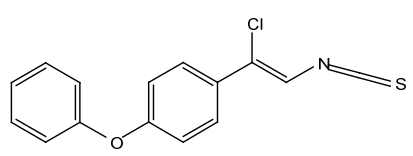
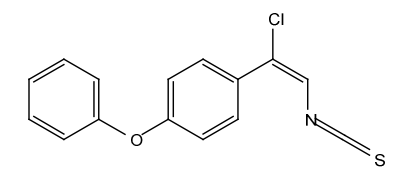
1-(1-chloro-2-isothiocyanatovinyl)-4-(phenoxy)benzene (**4d**)

^1H NMR

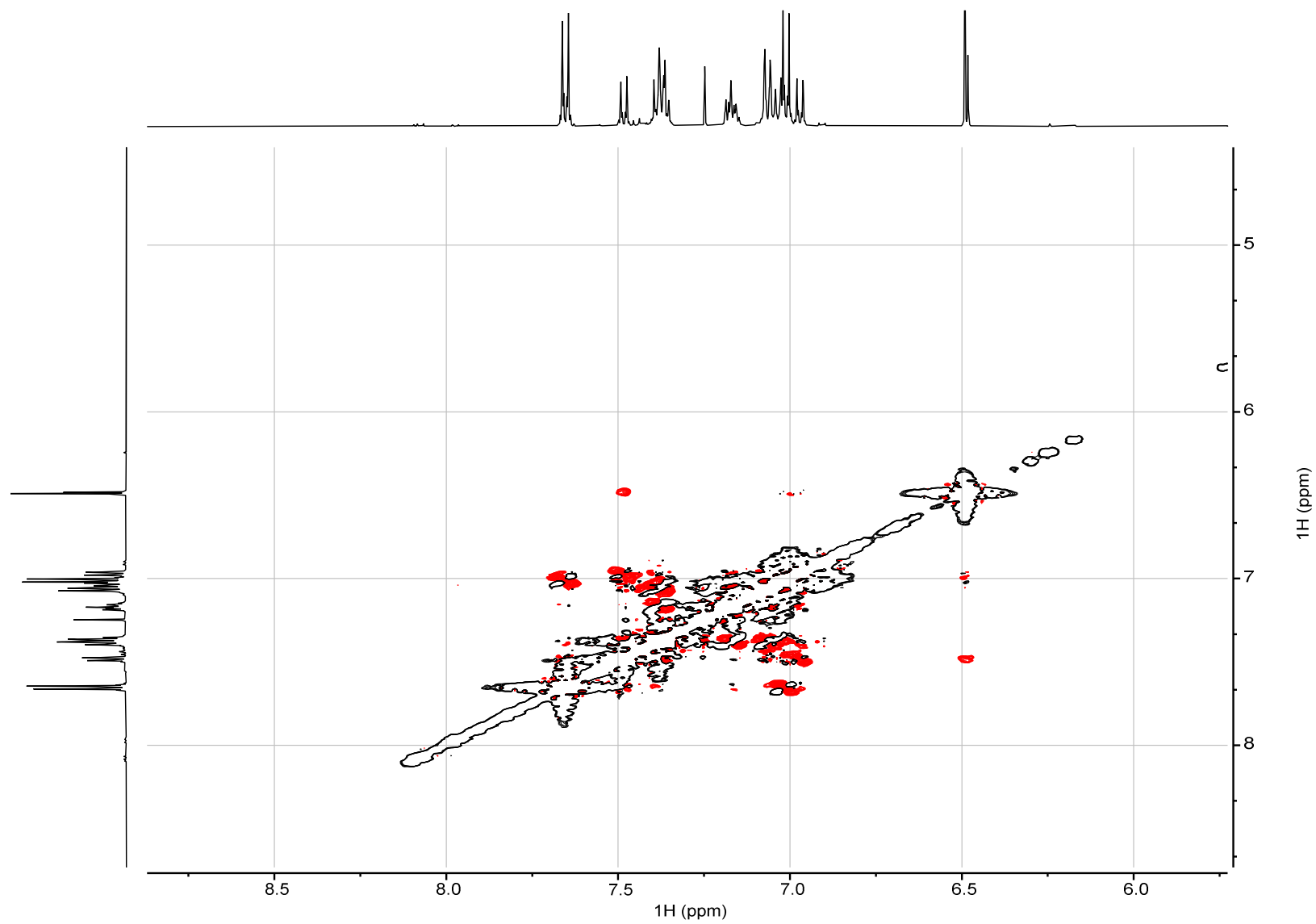


¹³C NMR

159.23
159.04
156.00
155.88
136.16
134.83
134.58
130.98
129.97
129.85
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127.84
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124.21
119.86
119.66
118.18
117.72
112.58
112.02

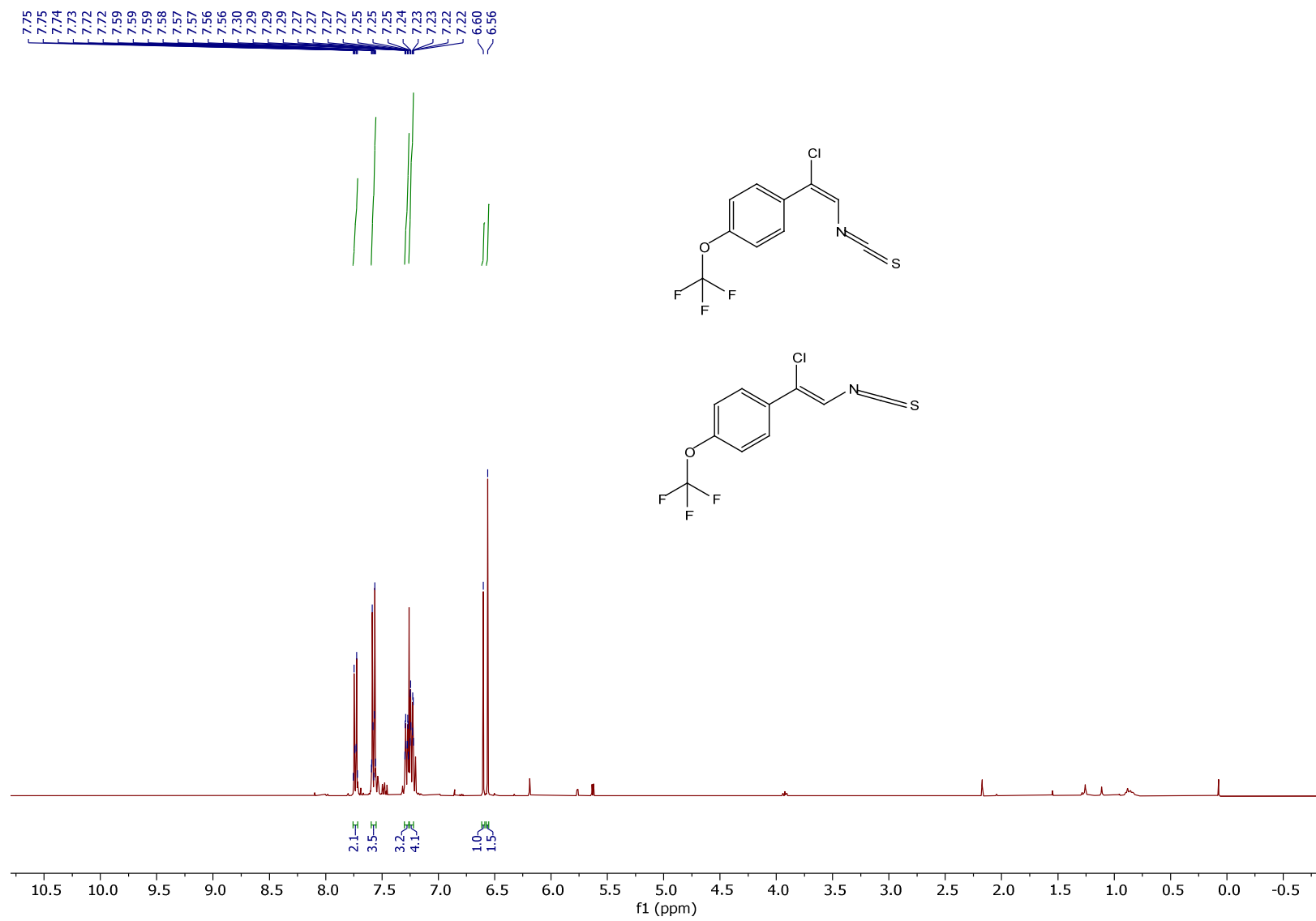


^1H - ^1H ROESY NMR



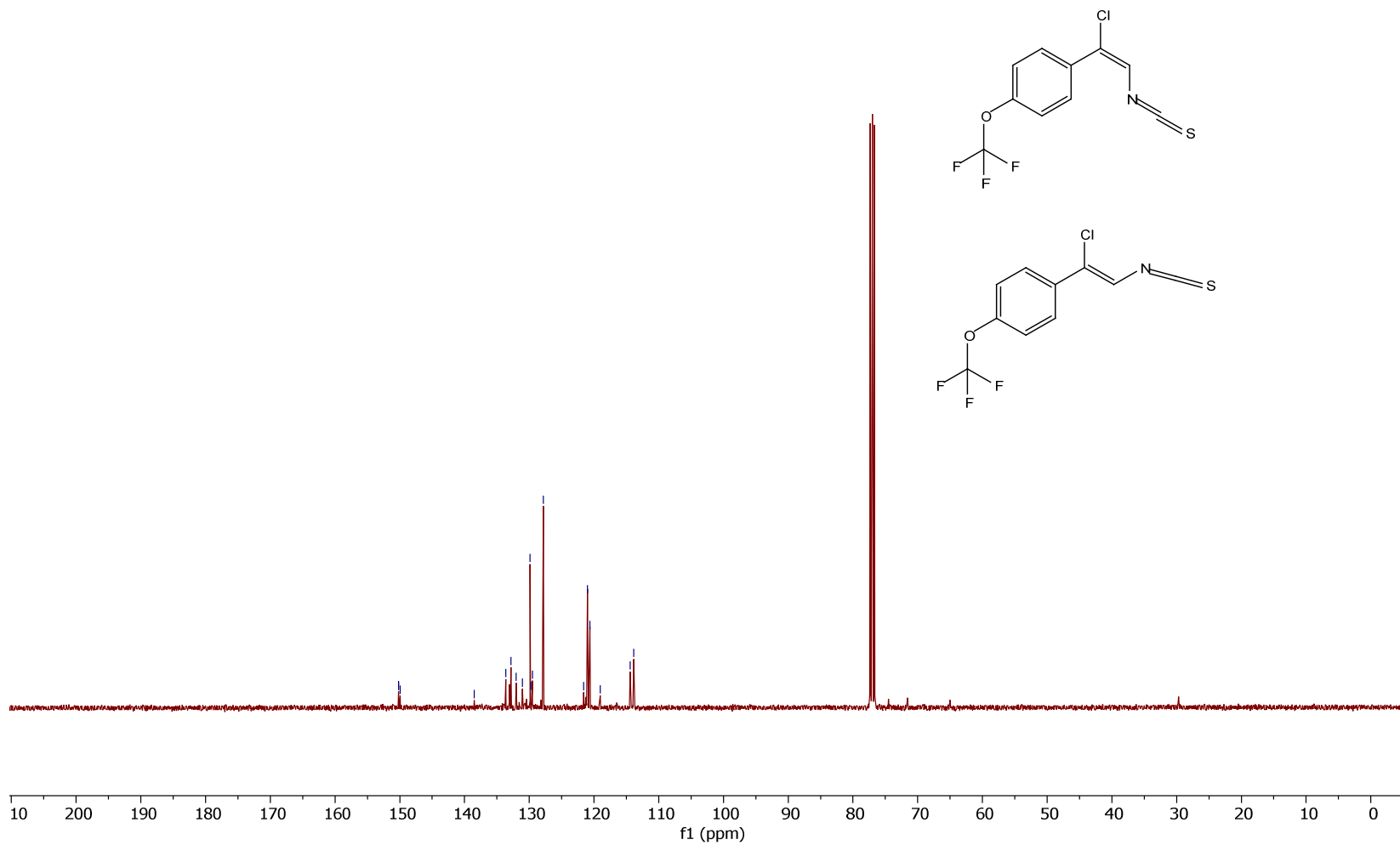
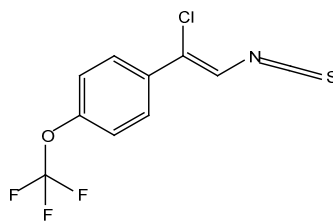
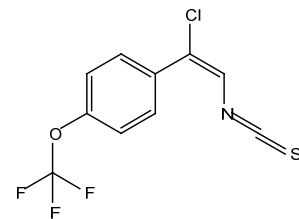
1-(1-chloro-2-isothiocyanatovinyl)-4-(trifluoromethoxy)benzene (**4e**)

^1H NMR

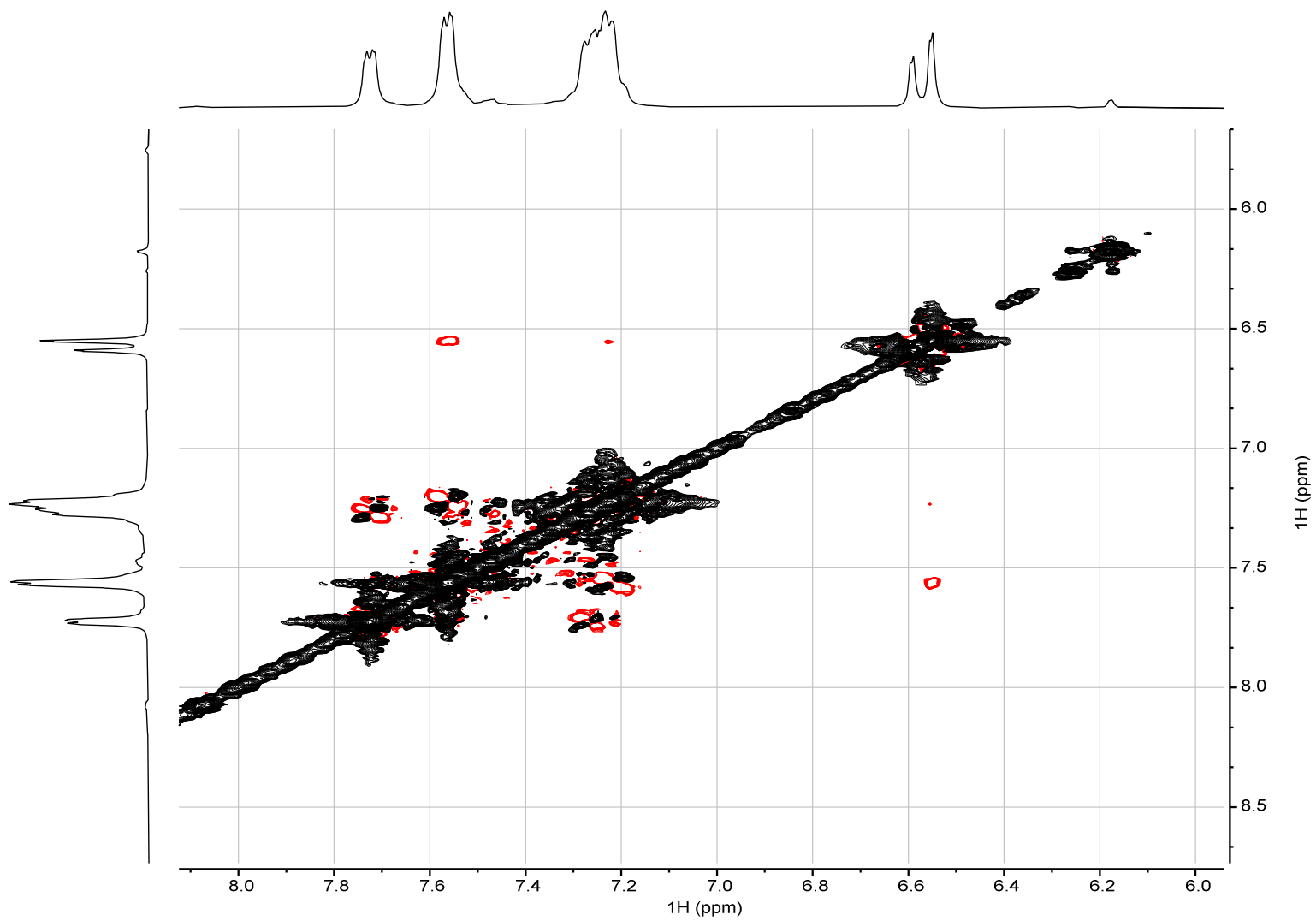


¹³C NMR

150.20
150.18
149.94
138.50
133.64
132.81
132.05
131.05
129.86
129.75
129.52
127.81
121.60
121.02
120.63
119.04
114.40
113.85

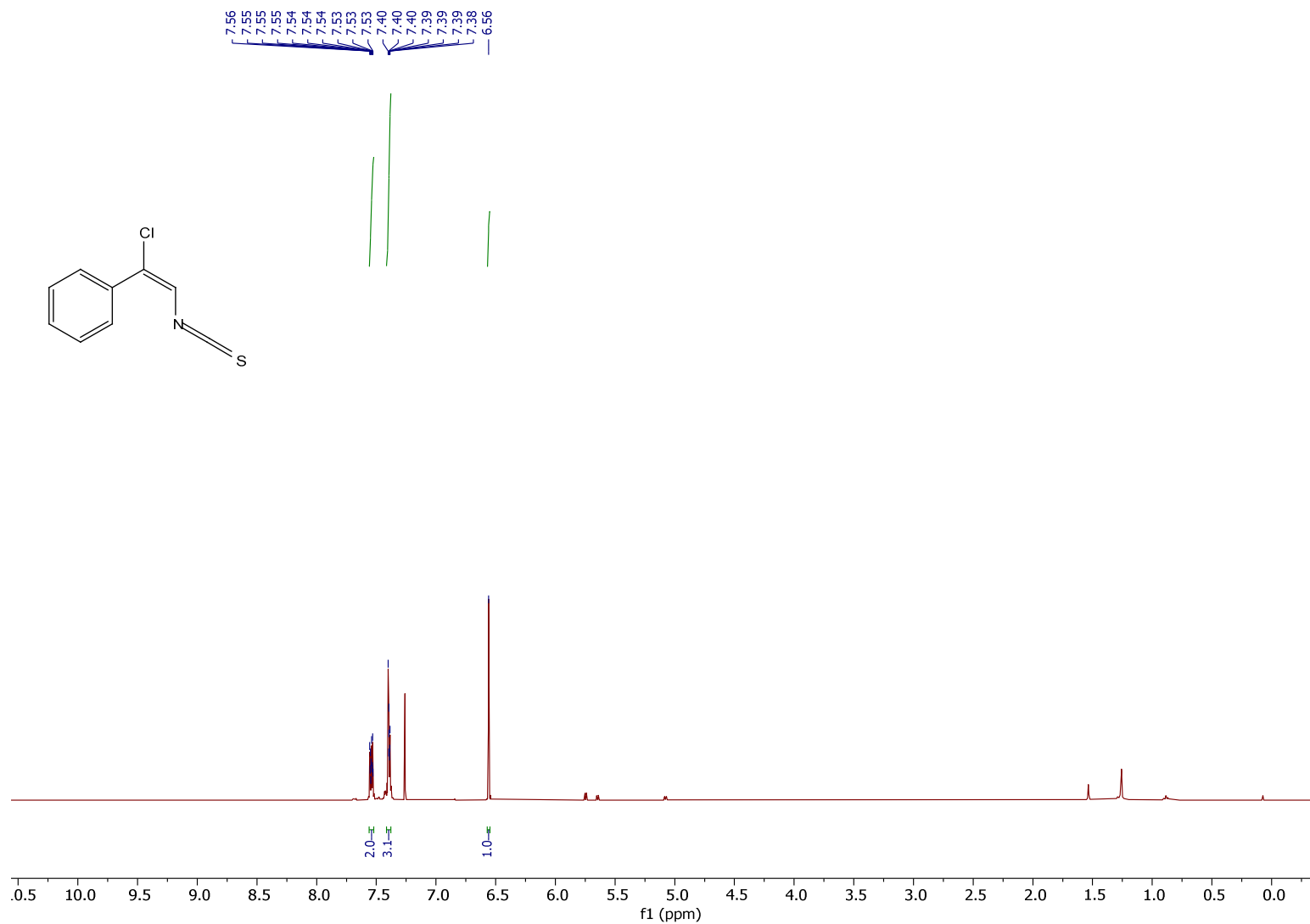


^1H - ^1H ROESY NMR

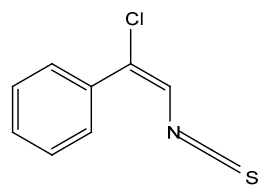


(1-chloro-2-isothiocyanatovinyl)benzene (**4f**)

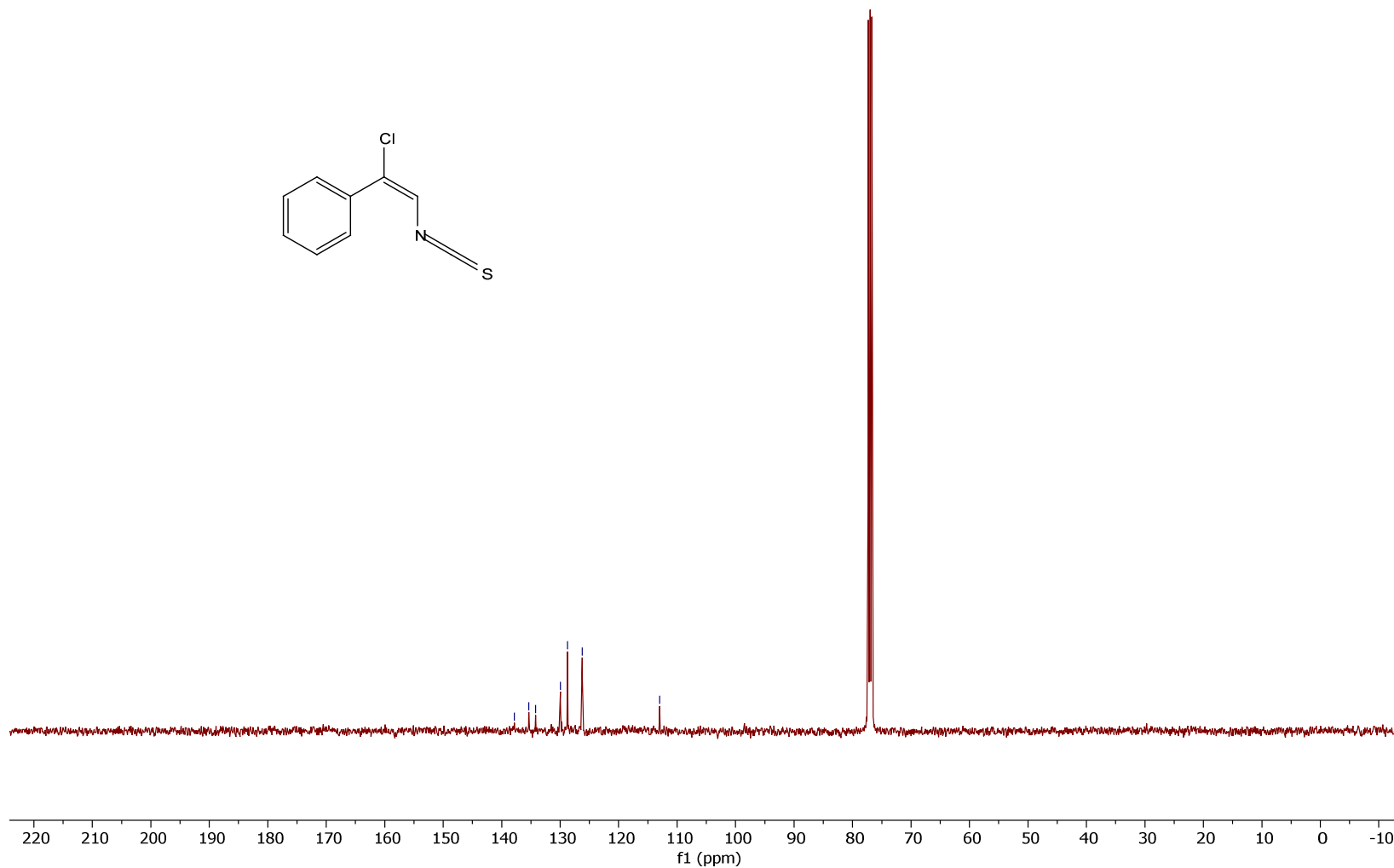
^1H NMR



¹³C NMR

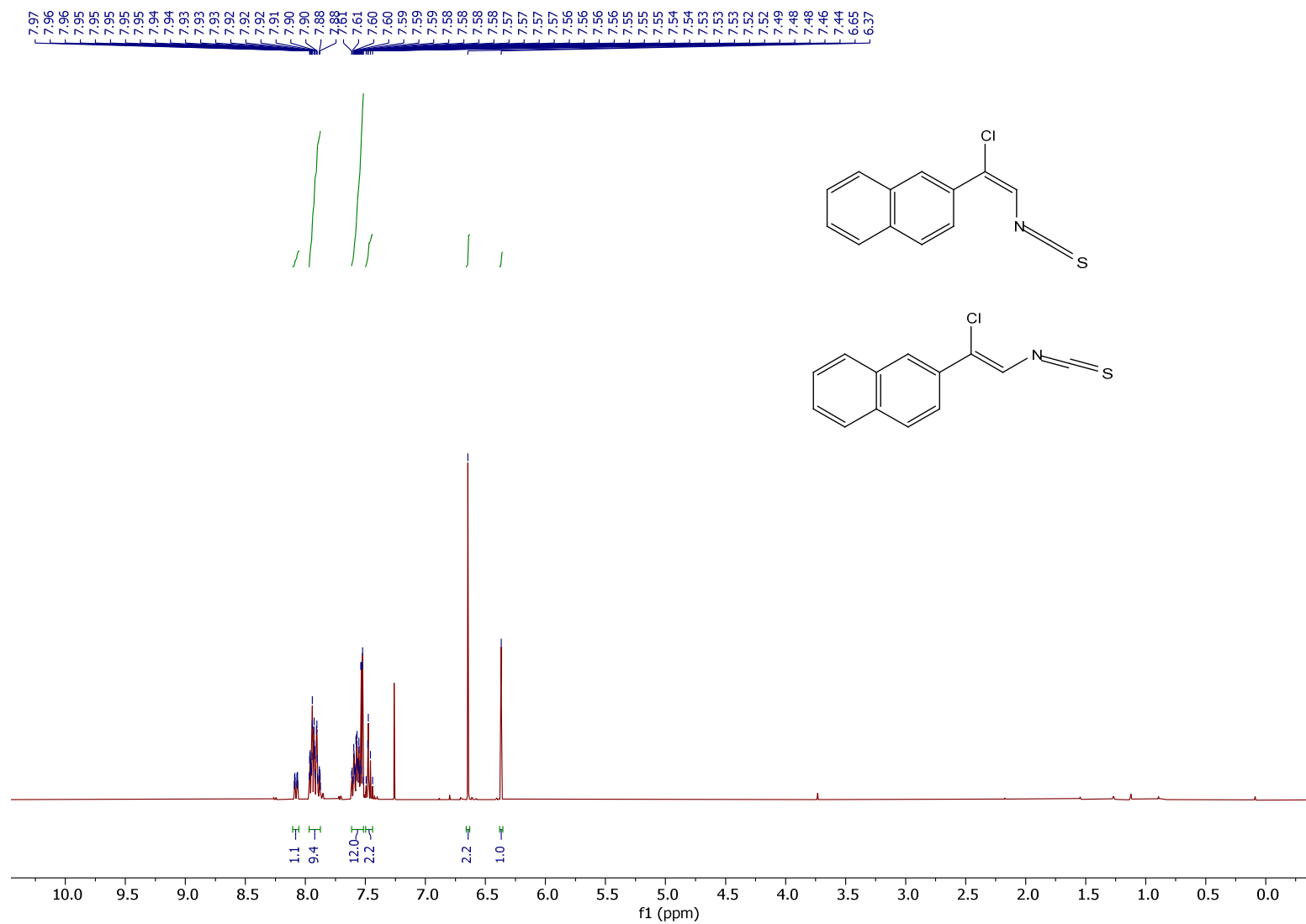


137.82
135.37
134.18
129.96
128.75
126.23
112.98



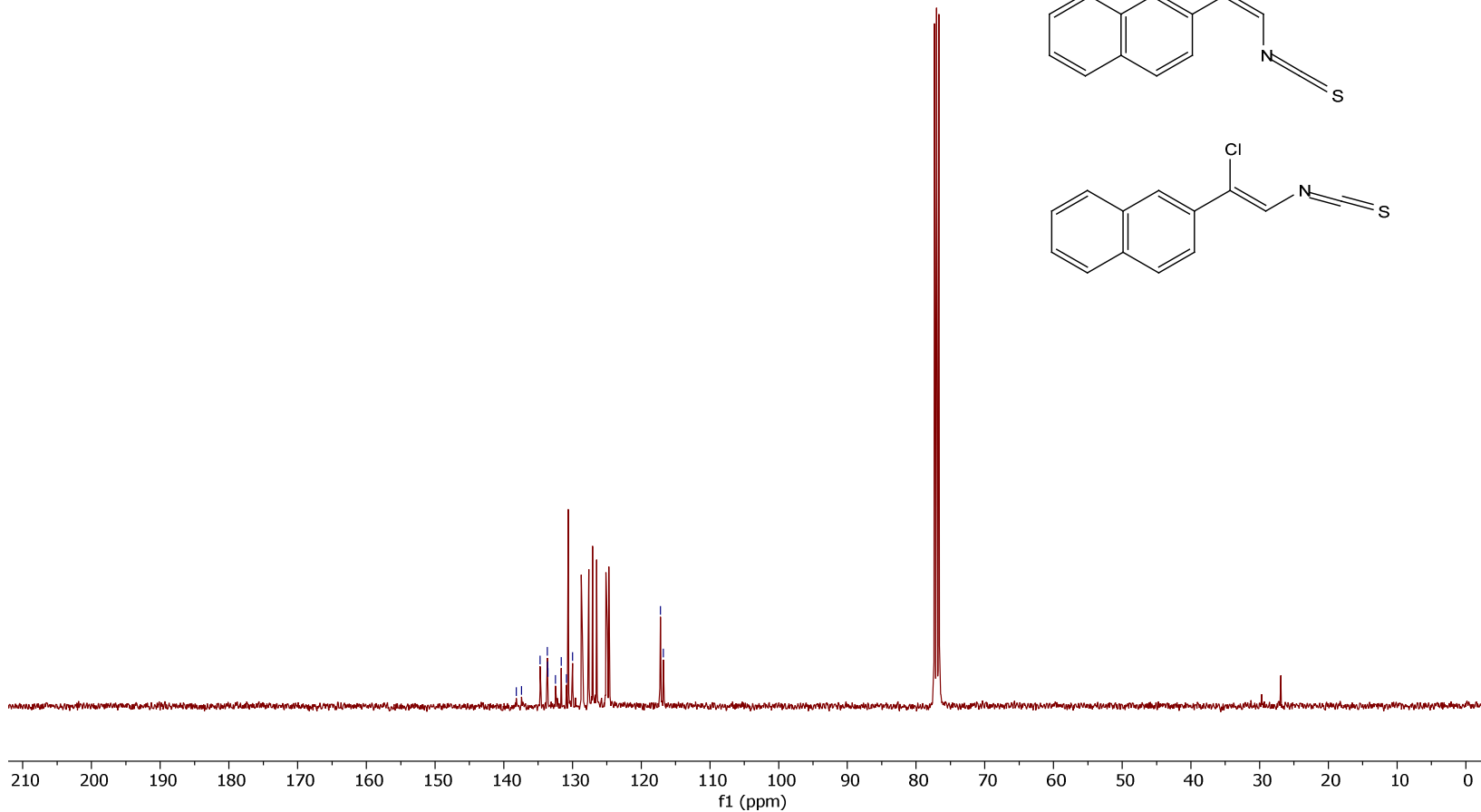
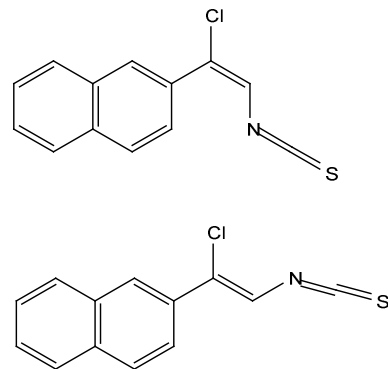
1-(1-chloro-2-isothiocyanatovinyl)naphthalene (**4g**)

¹H NMR



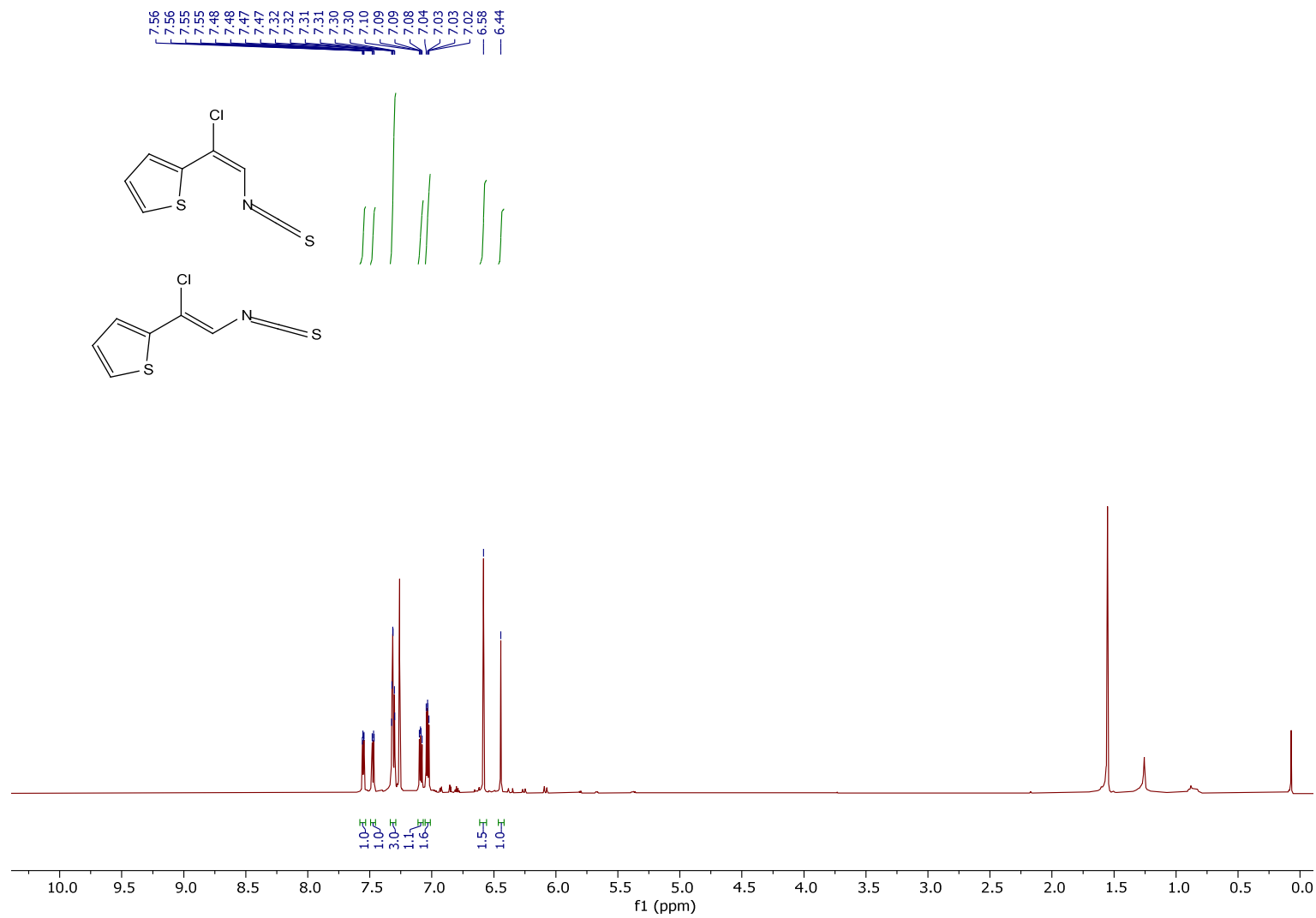
¹³C NMR

138.16
137.42
134.70
133.68
133.63
133.59
132.48
131.64
130.88
129.99
117.22
116.76

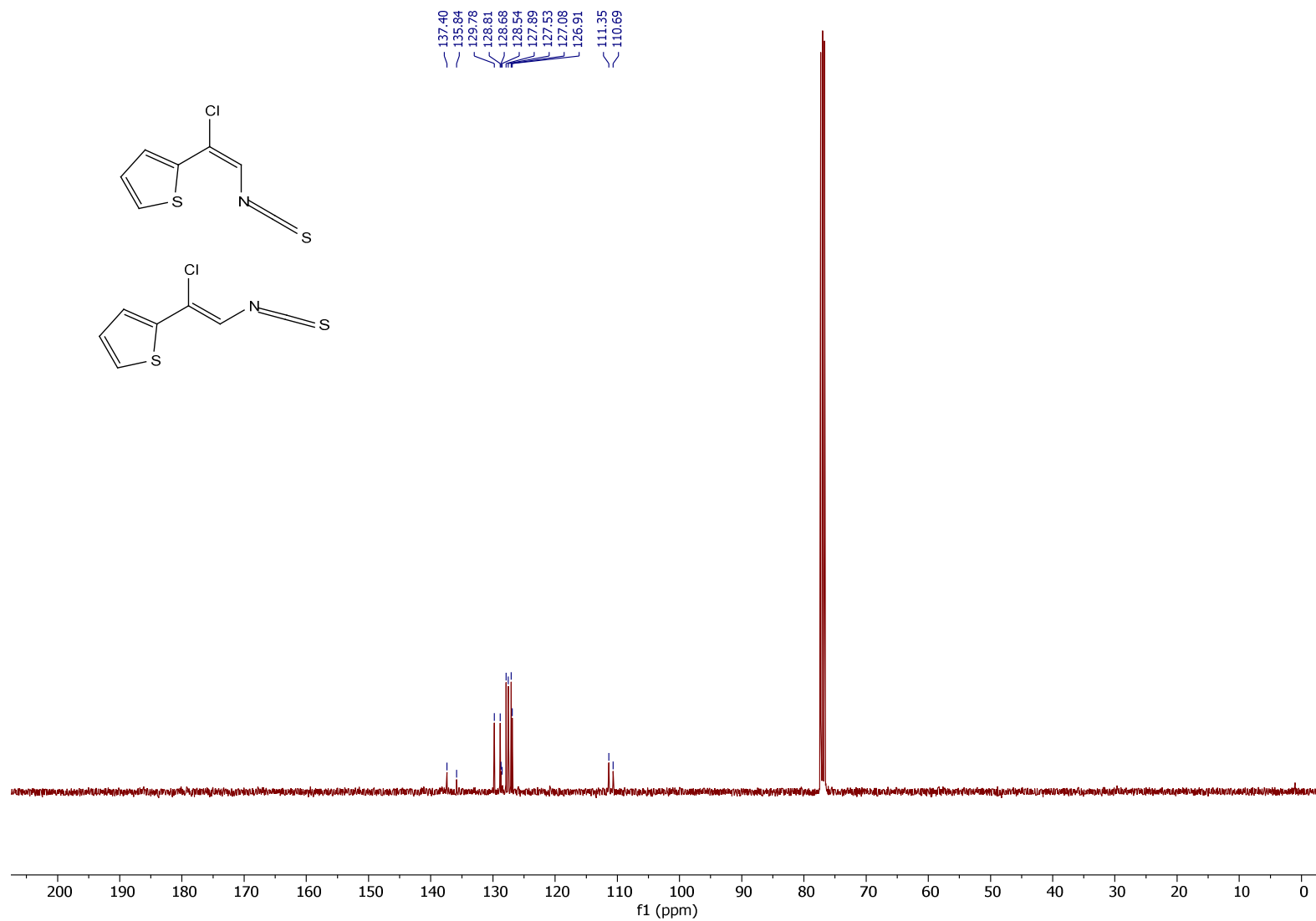


2-(1-chloro-2-isothiocyanatovinyl)thiophene (**4h**)

¹H NMR

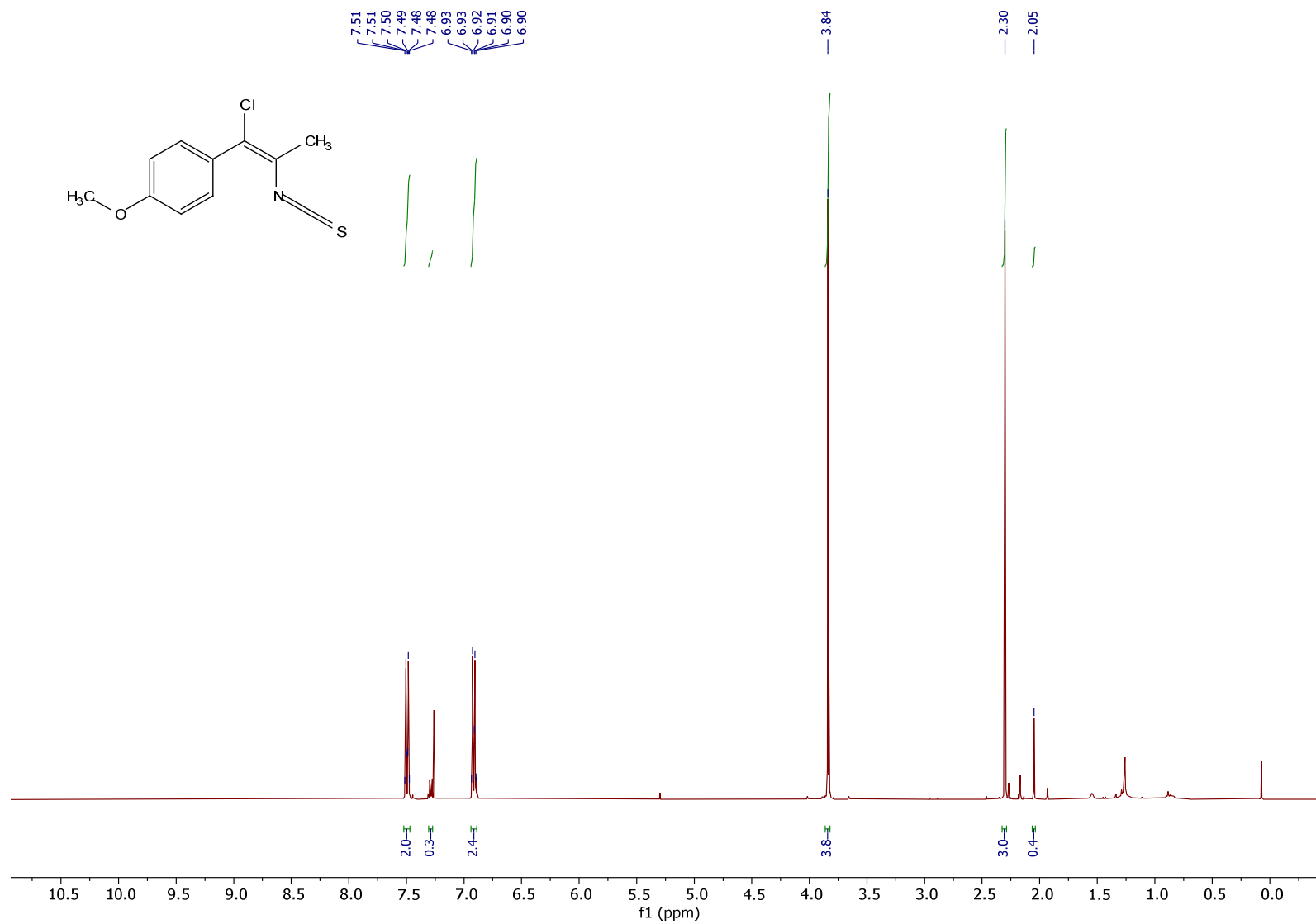


¹³C NMR

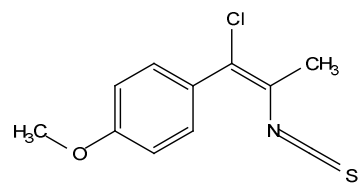


1-(1-chloro-2-isothiocyanatoprop-1-en-1-yl)-4-methoxybenzene (**4i**) (E/Z = 6:1)

¹H NMR



¹³C NMR



160.08

136.43

130.69

129.95

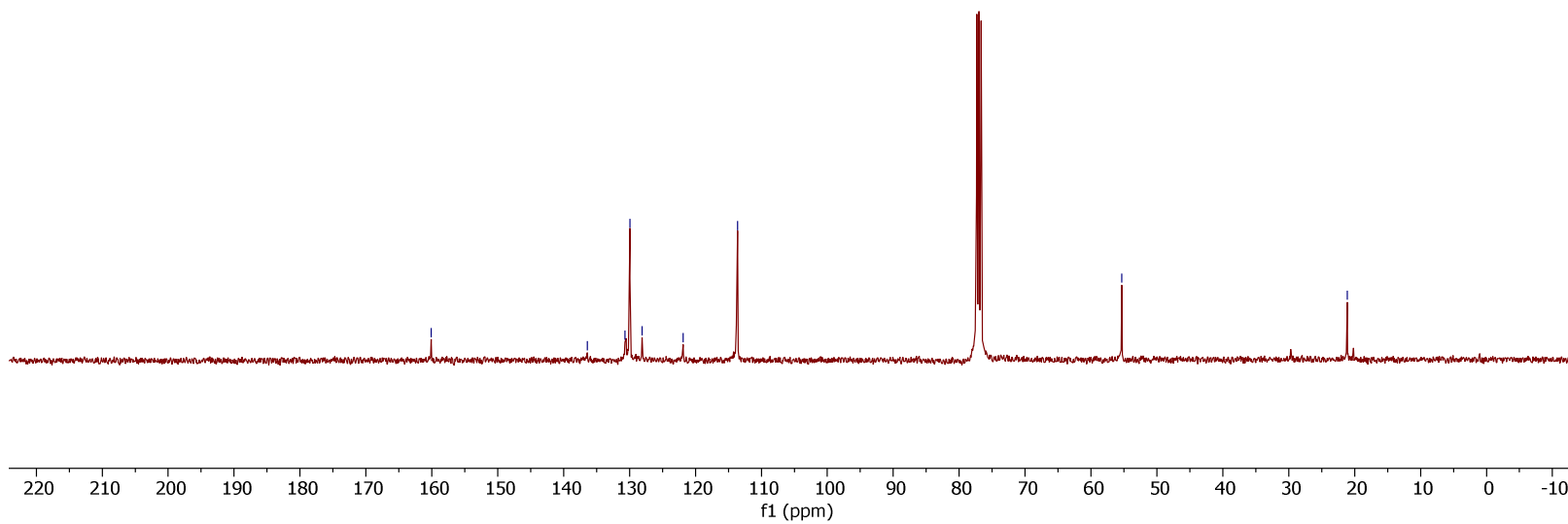
128.08

121.88

113.63

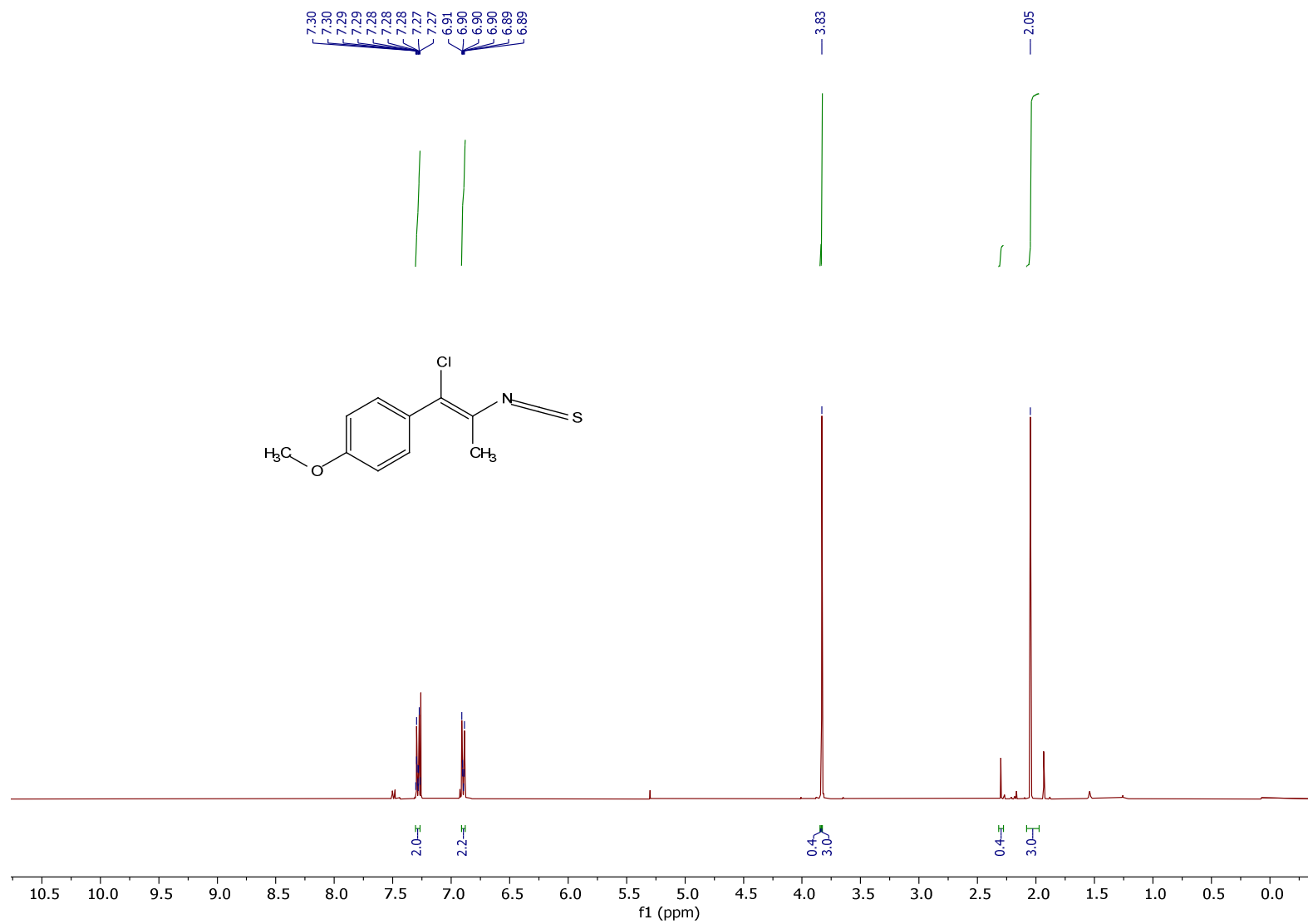
55.34

21.13

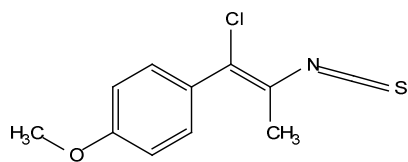


1-(1-chloro-2-isothiocyanatoprop-1-en-1-yl)-4-methoxybenzene (**4i**) (Z/E = 5:1)

^1H NMR



¹³C NMR



160.14

137.03

130.61

130.52

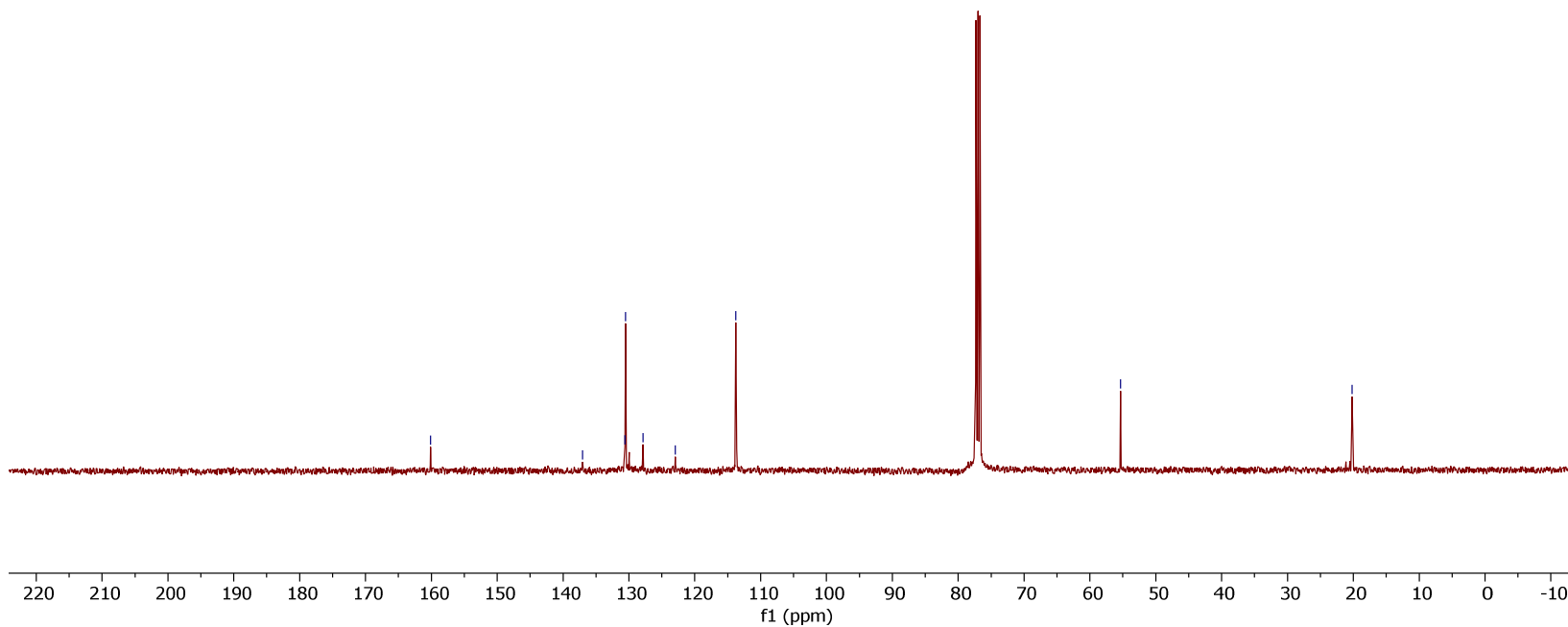
127.87

122.96

113.80

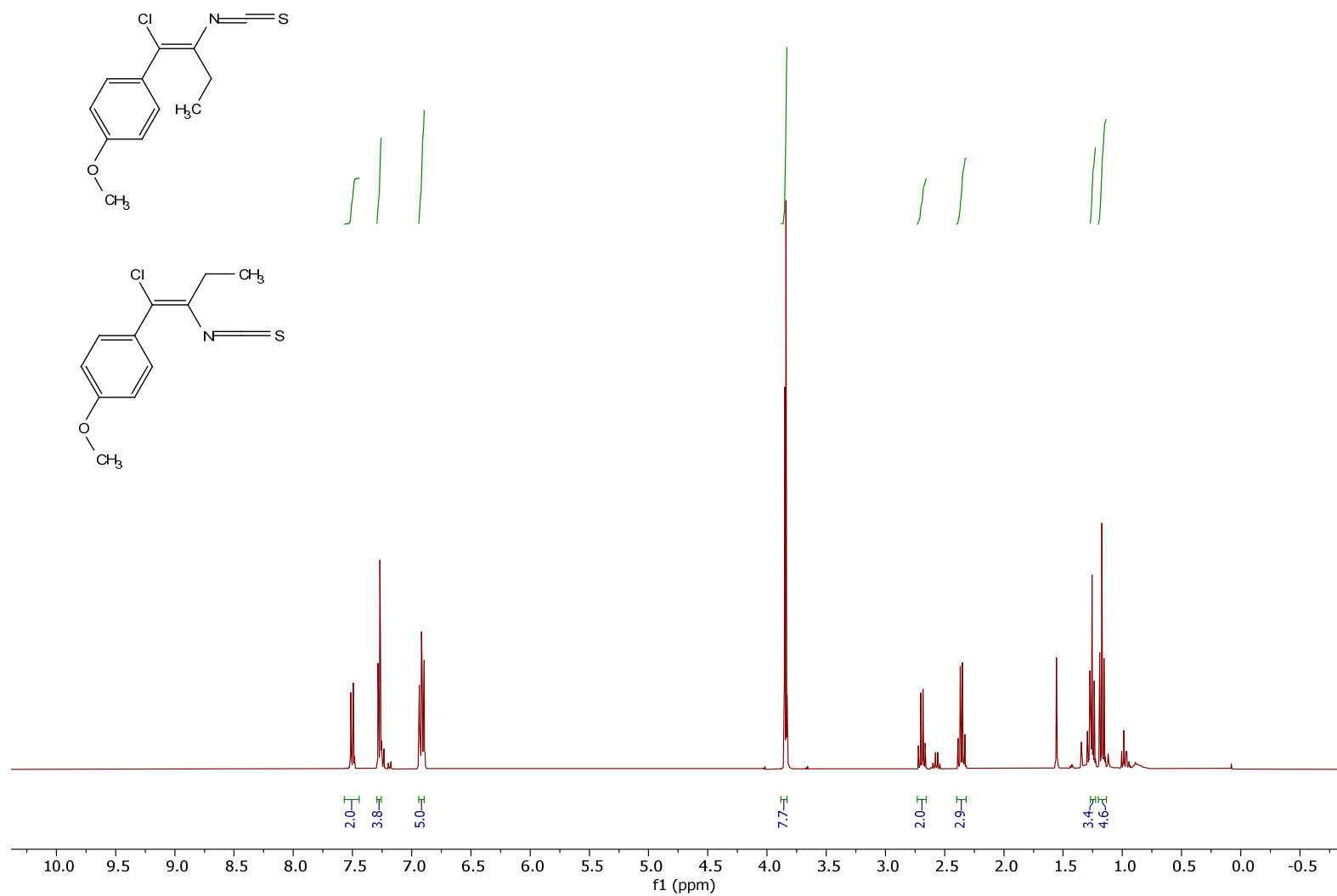
55.36

20.17

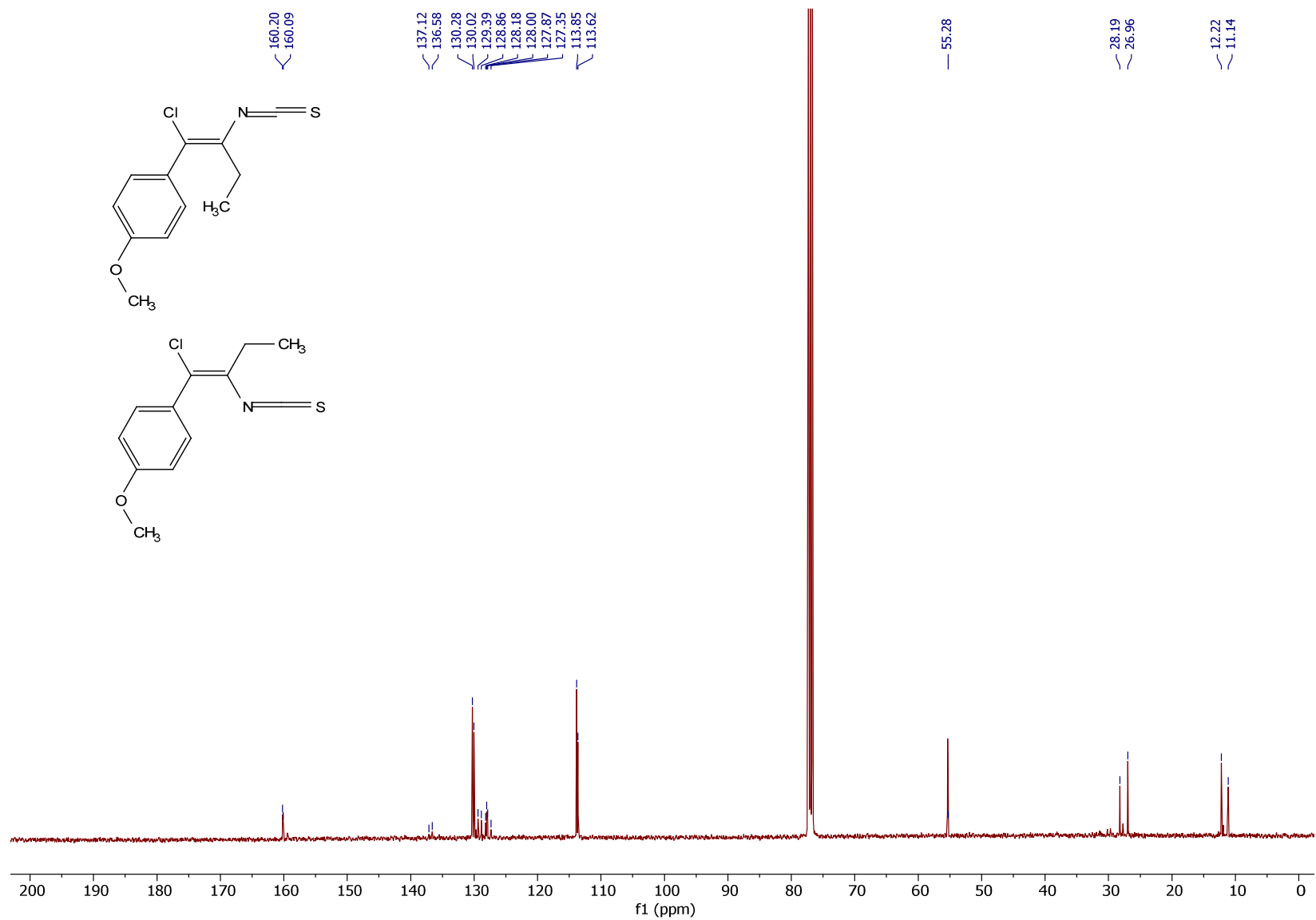


1-(1-chloro-2-isothiocyanatobut-1-en-1-yl)-4-methoxybenzene (4j)

¹H NMR

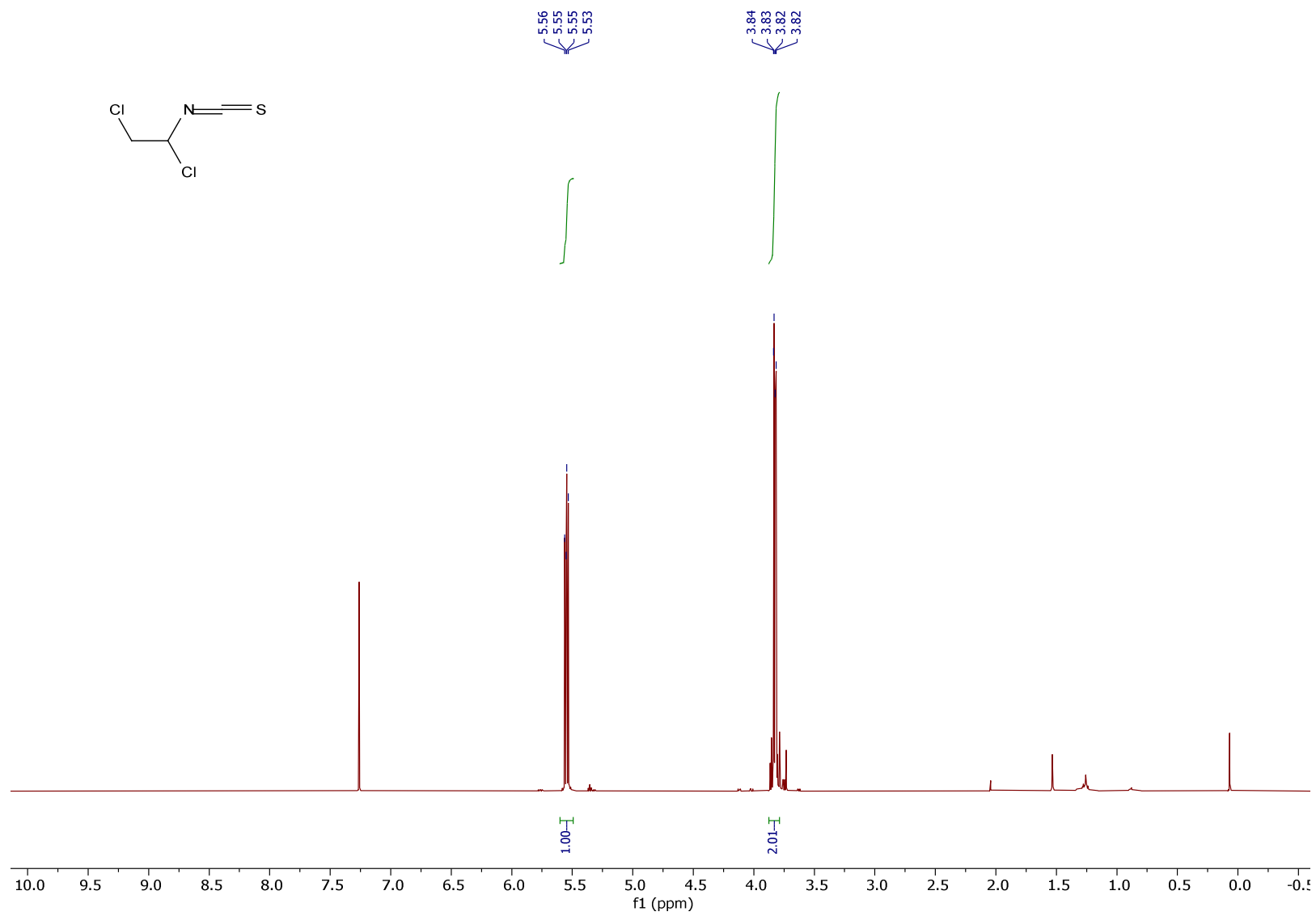
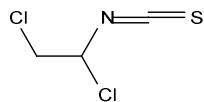


¹³C NMR



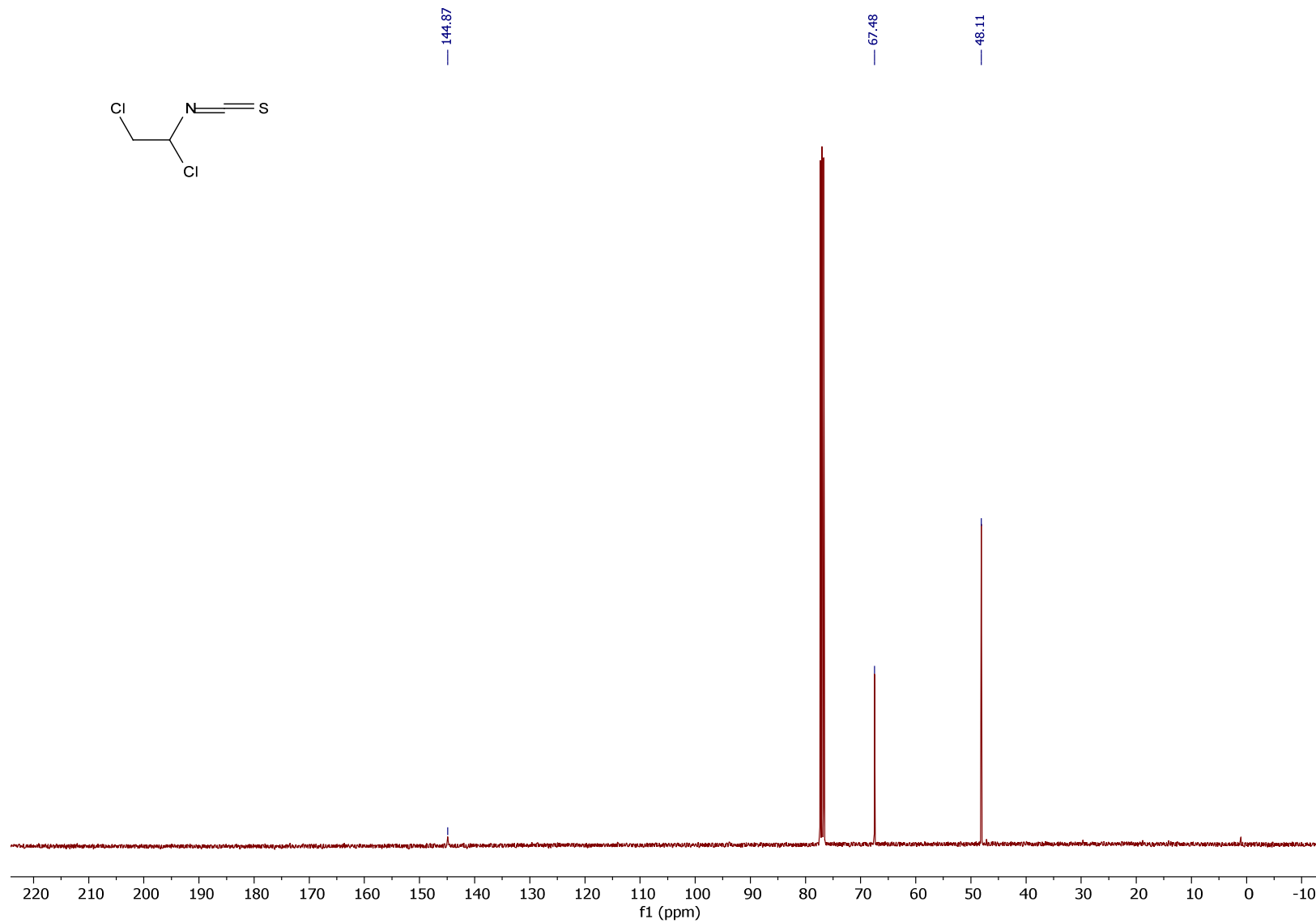
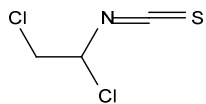
1,2-dichloro-1-isothiocyanatoethane (5)

^1H NMR



SI42

^{13}C NMR

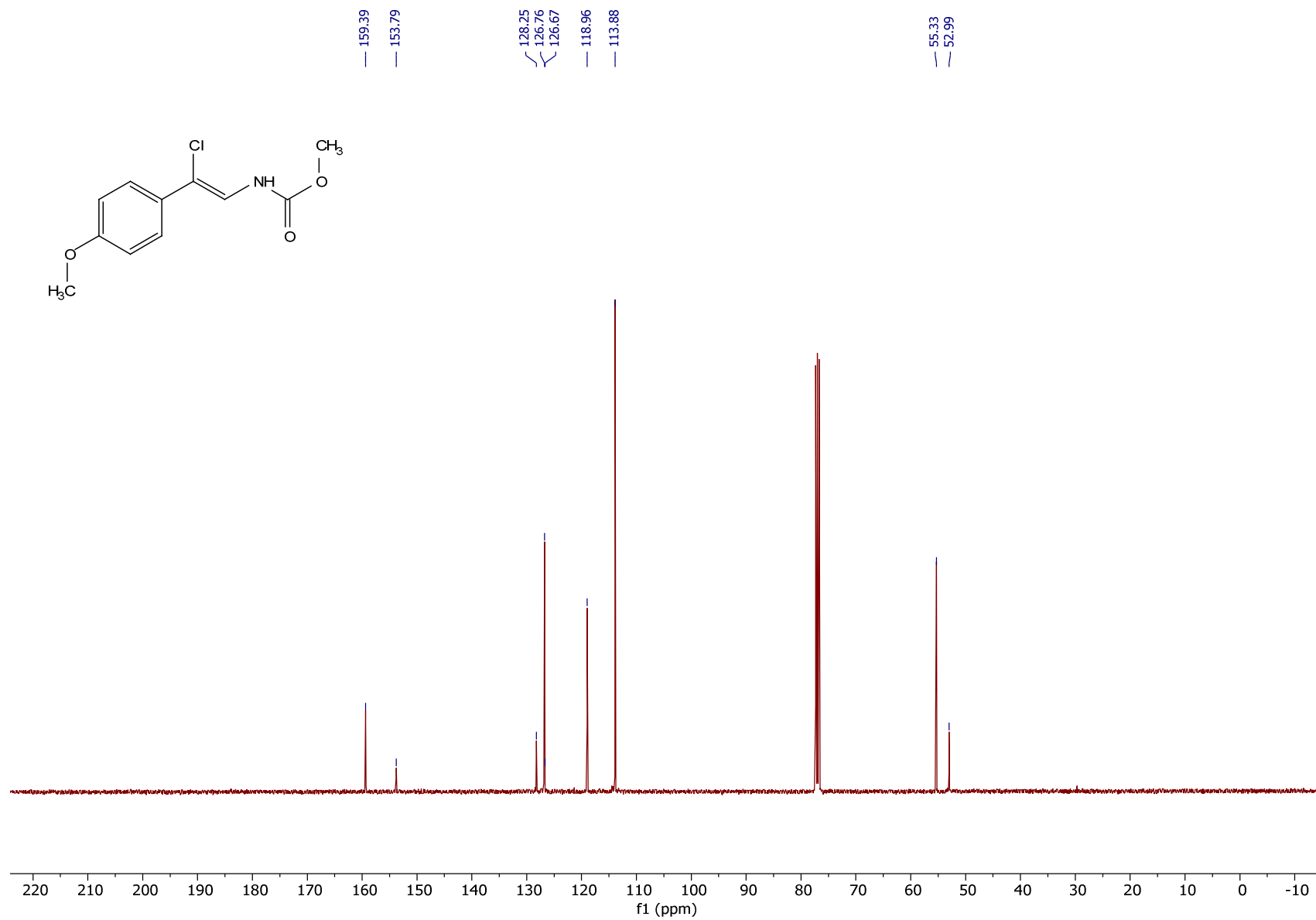


Methyl (Z)-(2-chloro-2-(4-methoxyphenyl)vinyl)carbamate (**6a**)

^1H NMR

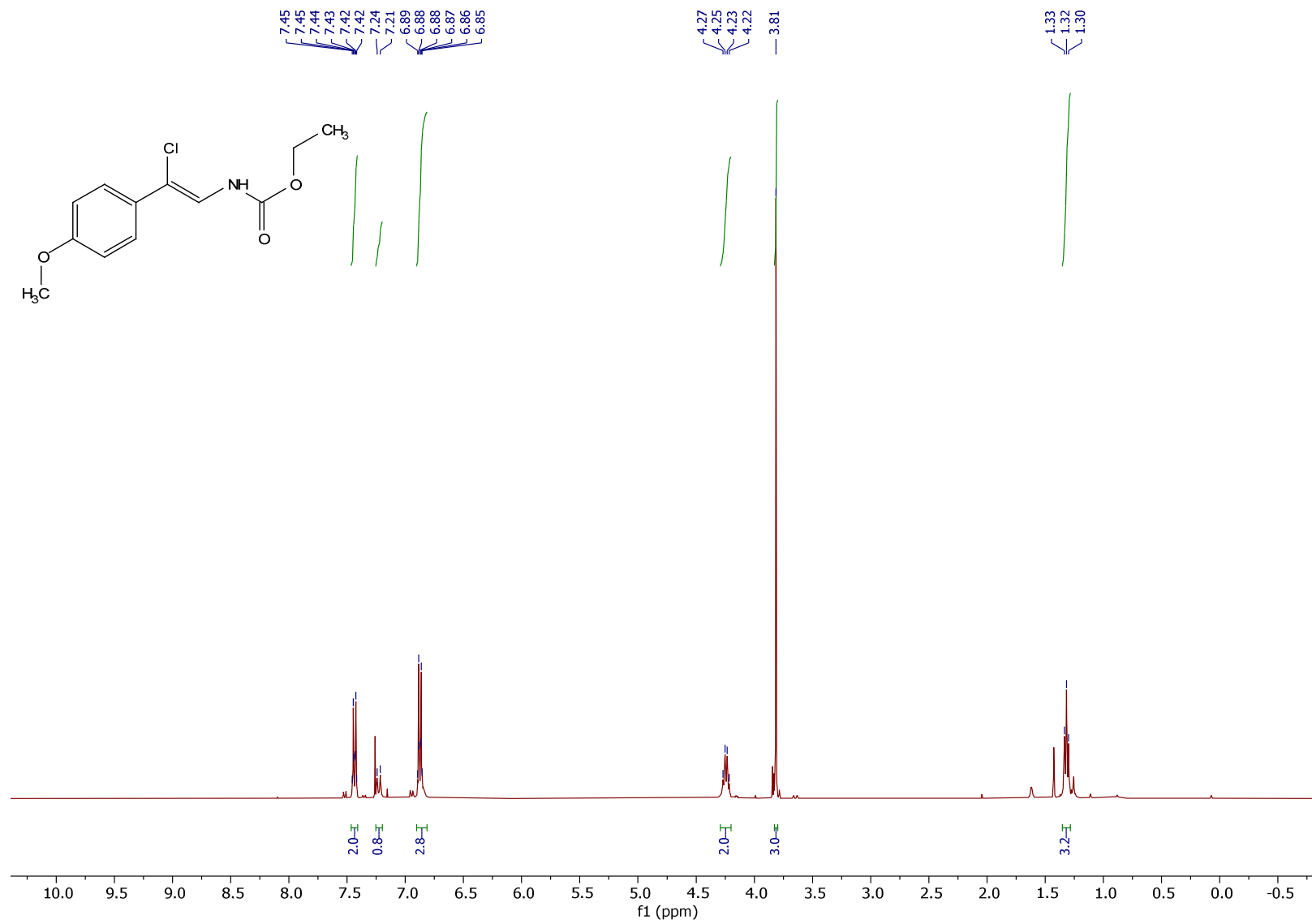


¹³C NMR



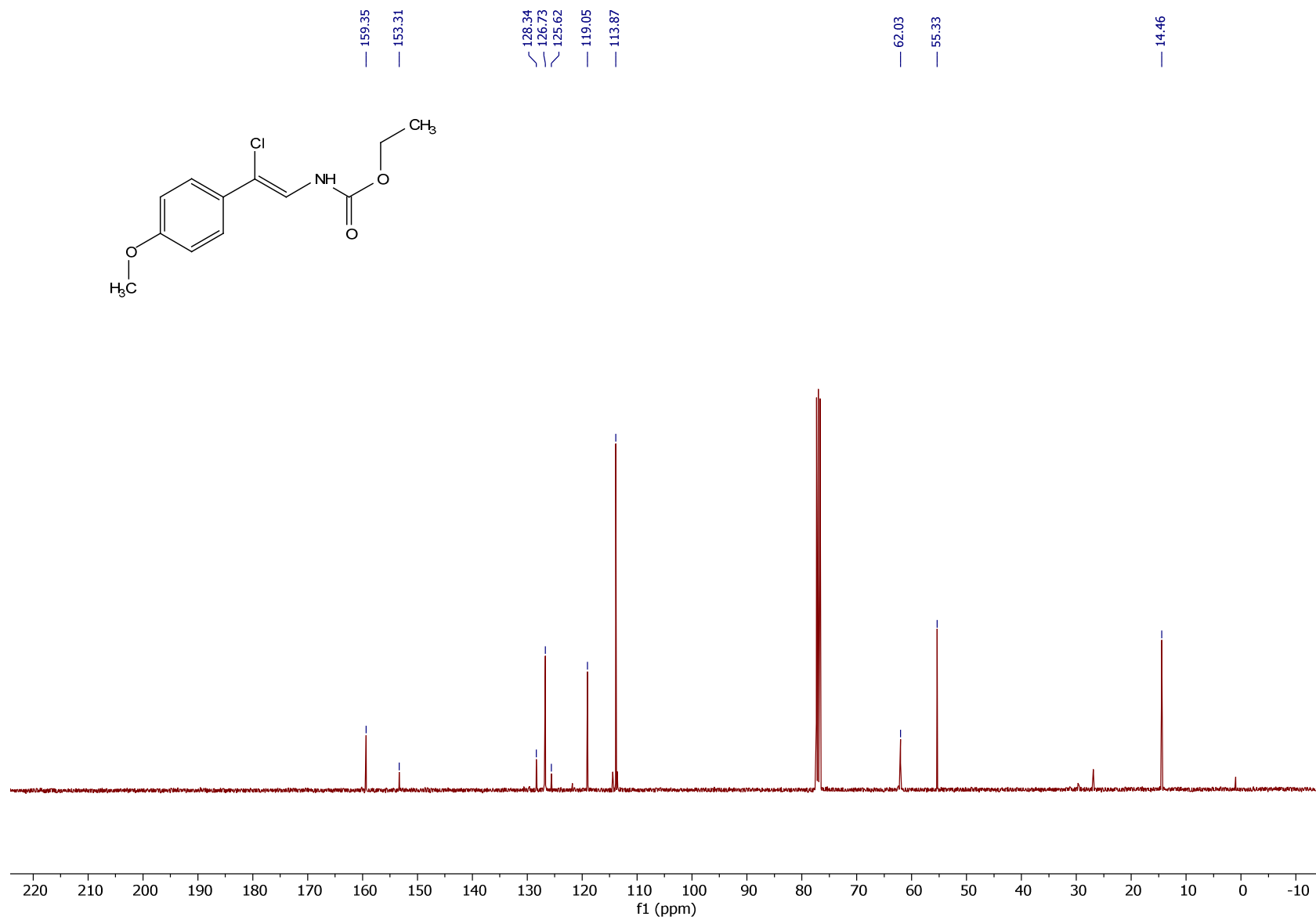
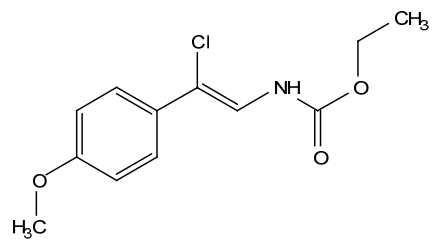
Ethyl (Z)-(2-chloro-2-(4-methoxyphenyl)vinyl)carbamate (**6b**)

^1H NMR



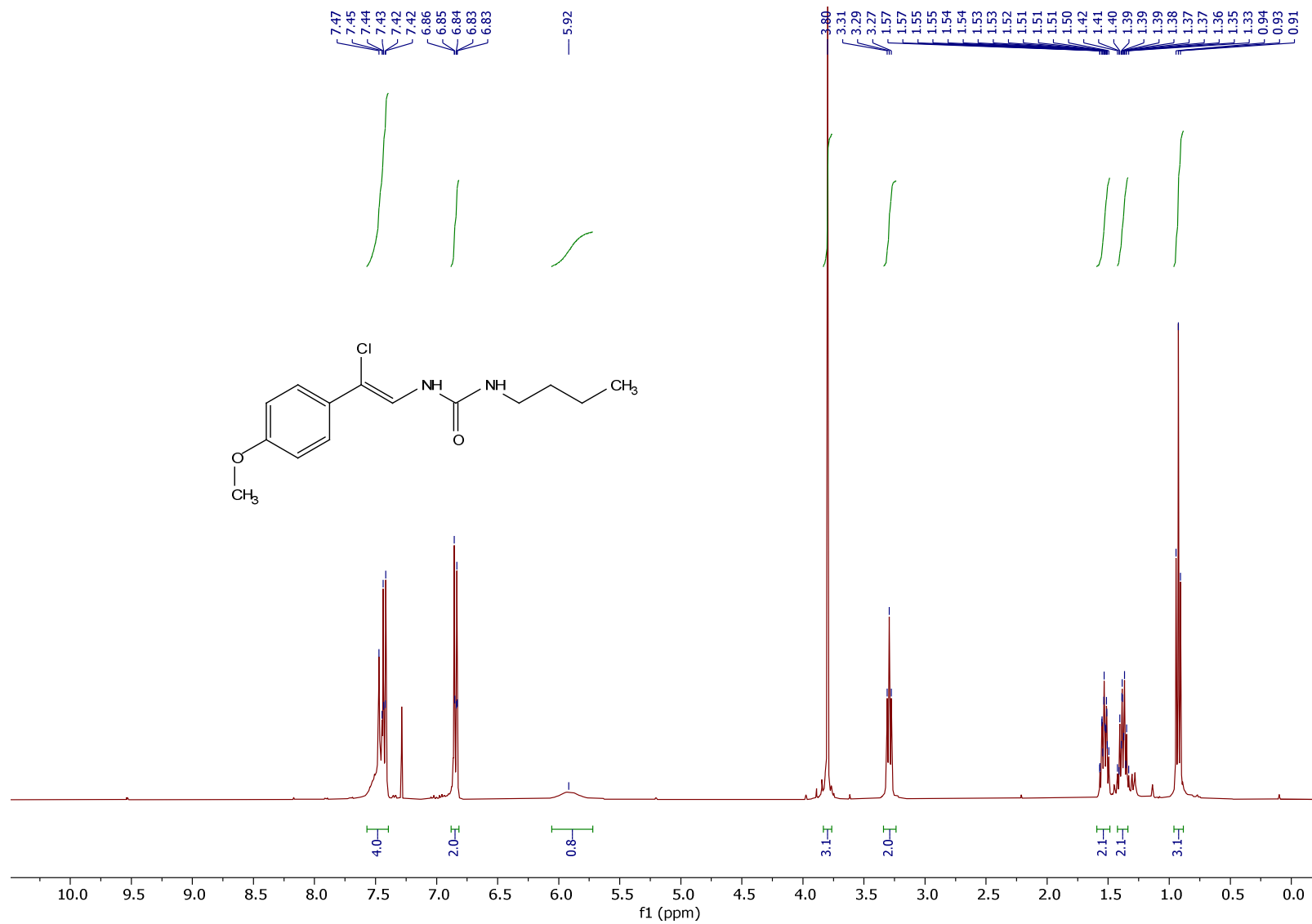
SI46

¹³C NMR

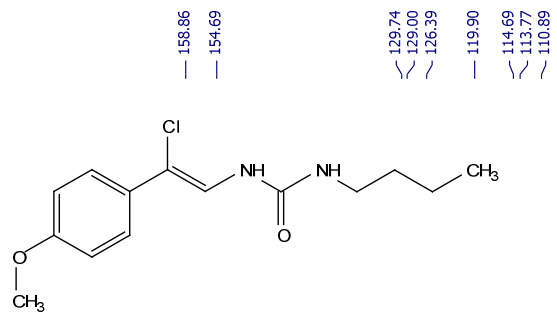


(Z)-1-butyl-3-(2-chloro-2-(4-methoxyphenyl)vinyl)urea (**6c**)

¹H NMR



¹³C NMR



158.86
154.69

129.74
129.00
126.39
119.90
114.69
113.77
110.89

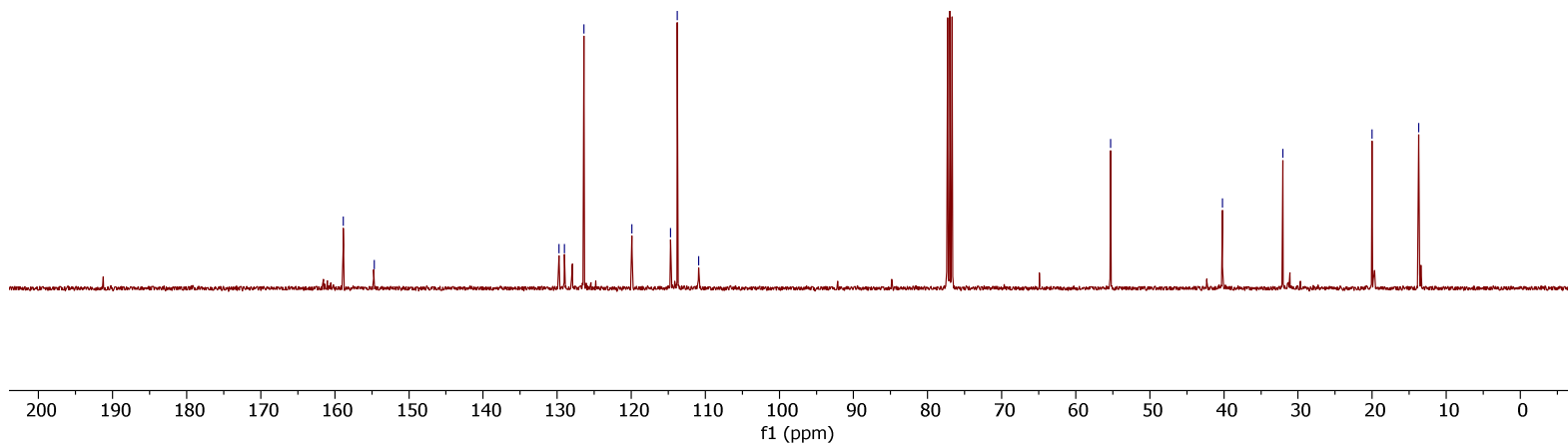
55.29

40.20

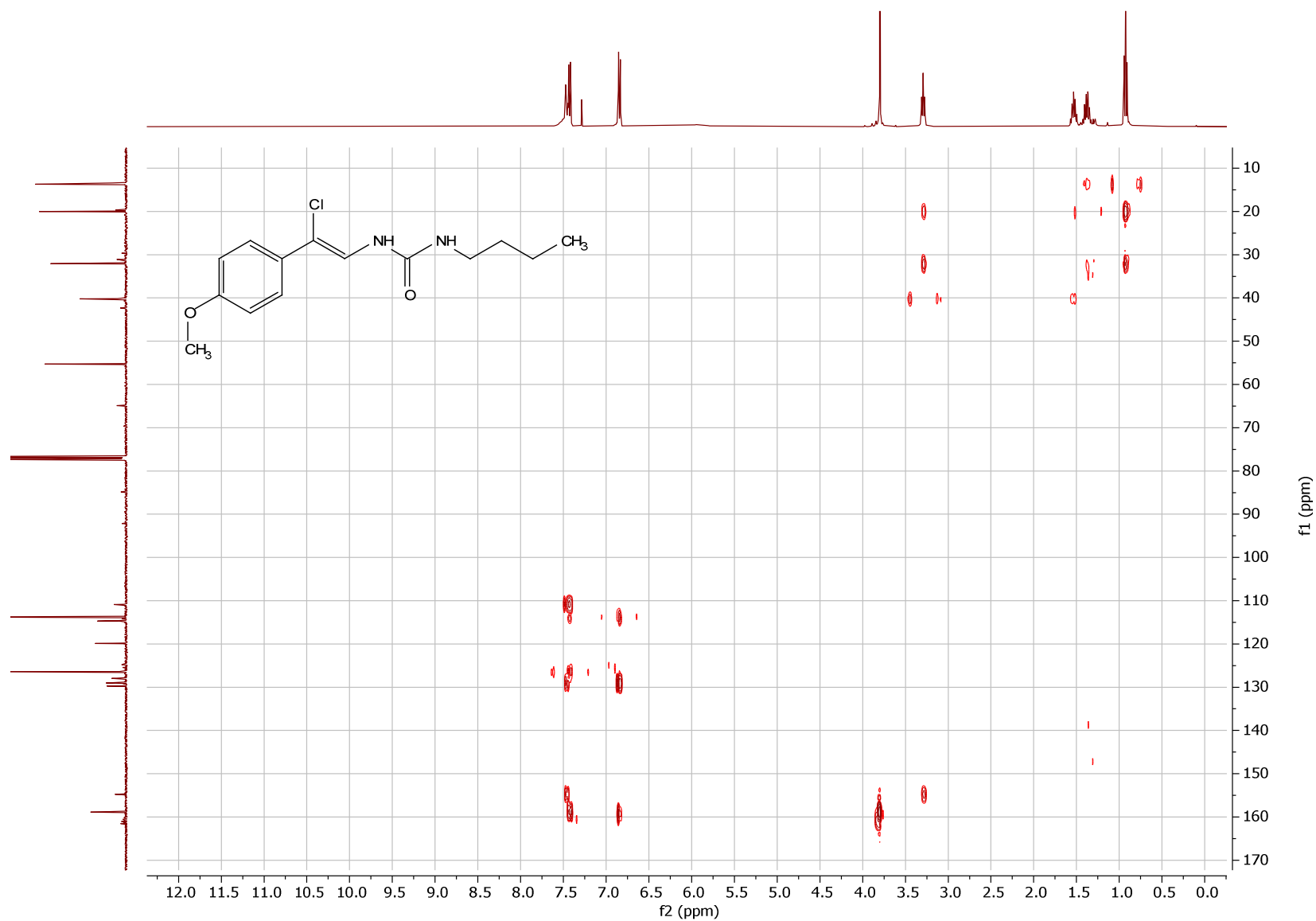
32.06

20.00

13.72

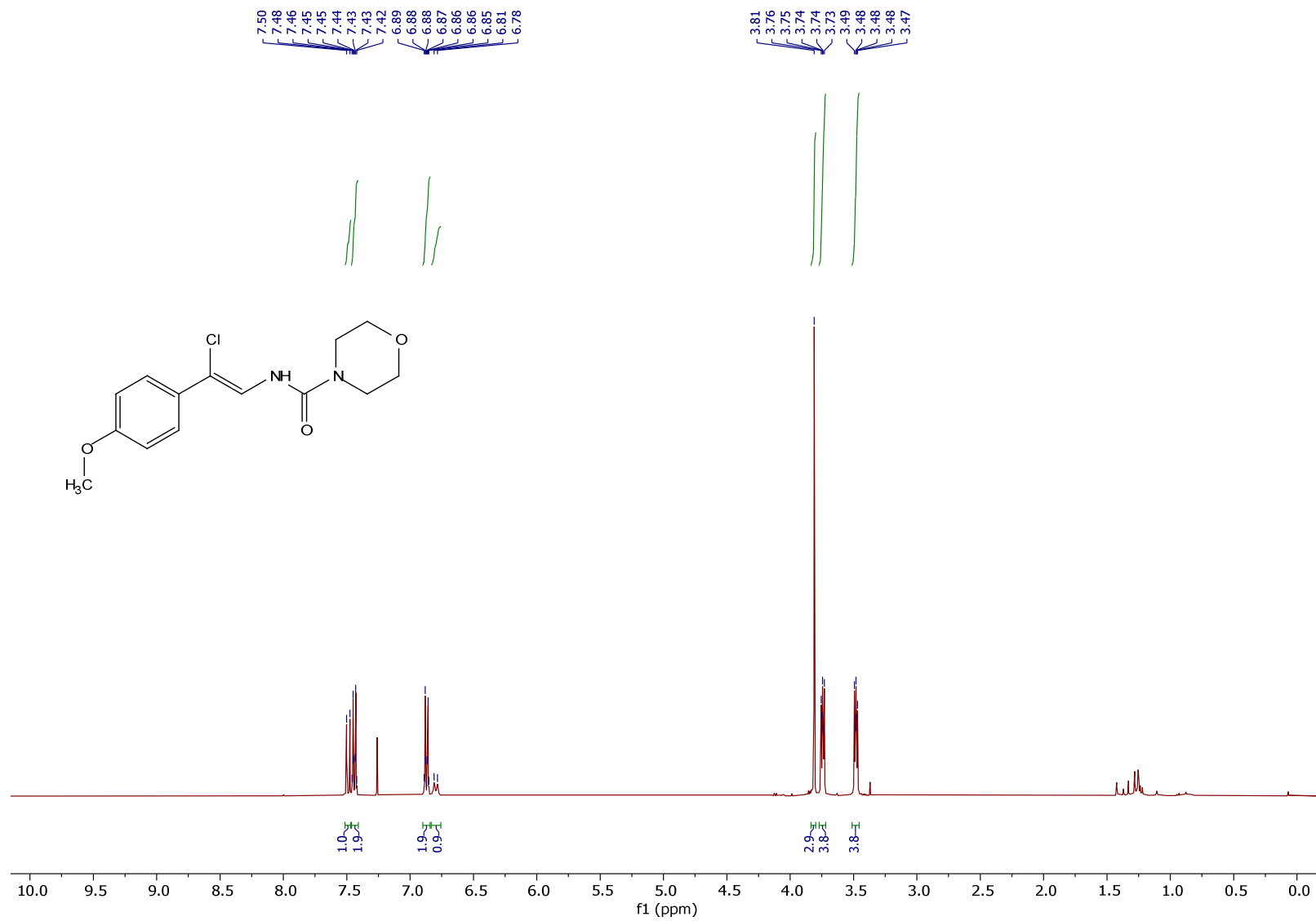


^1H - ^{13}C HMBC NMR

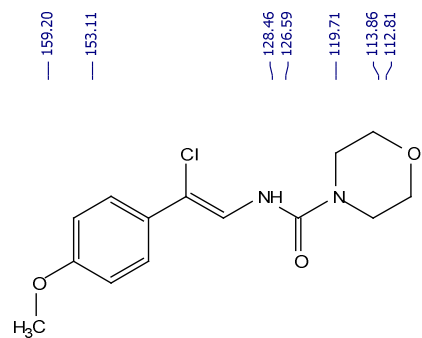


(Z)-N-(2-chloro-2-(4-methoxyphenyl)vinyl)morpholine-4-carboxamide (**6d**)

¹H NMR



¹³C NMR



159.20

153.11

128.46

126.59

119.71

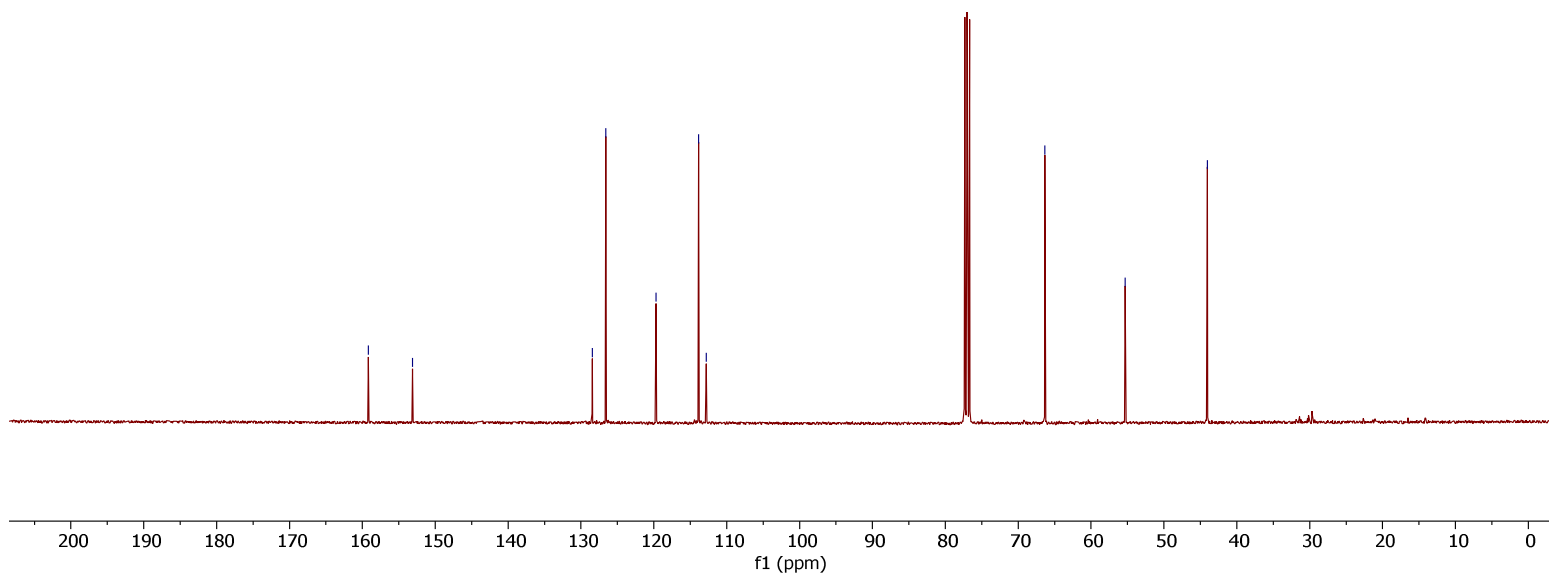
113.86

112.81

66.33

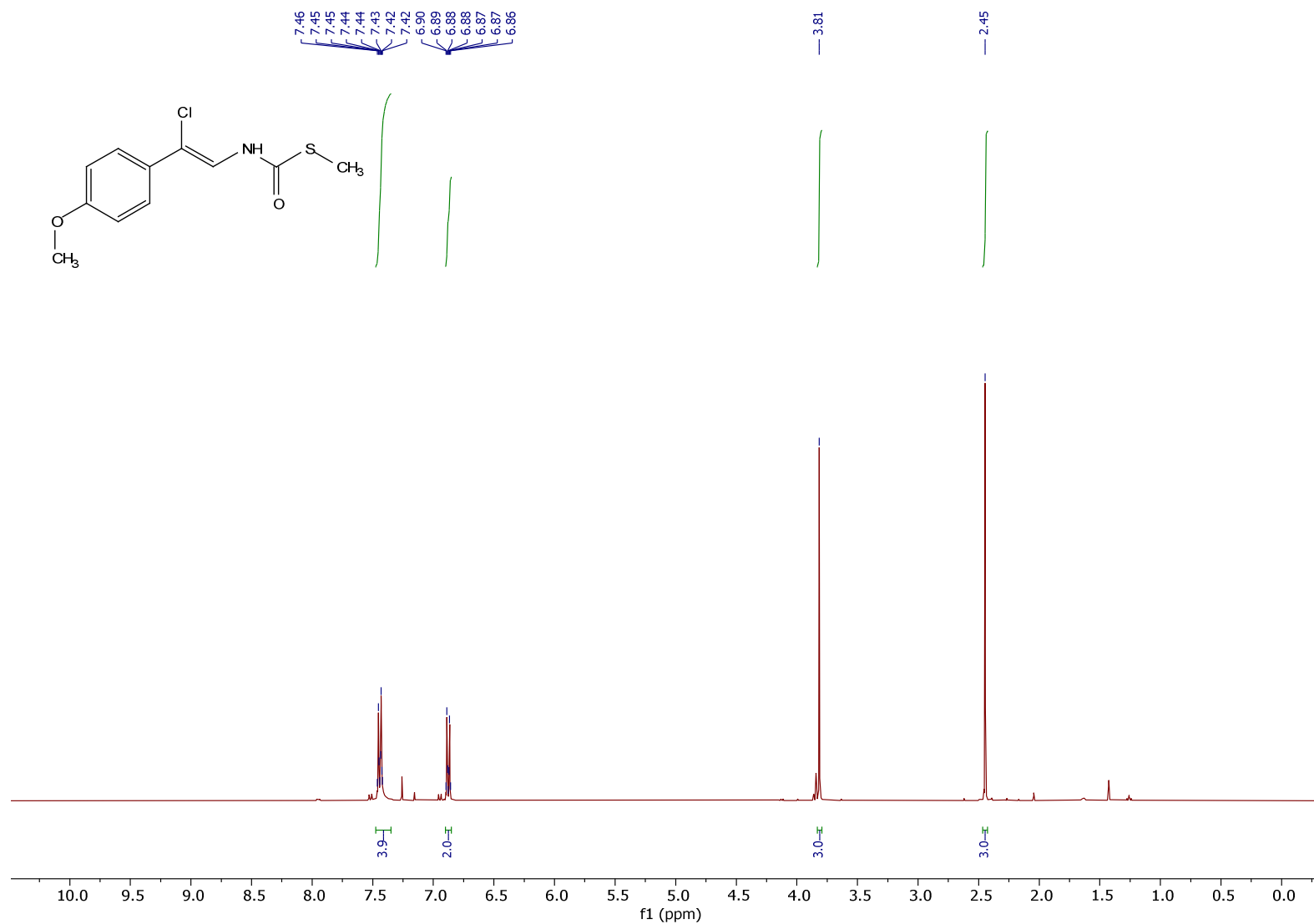
55.33

44.05

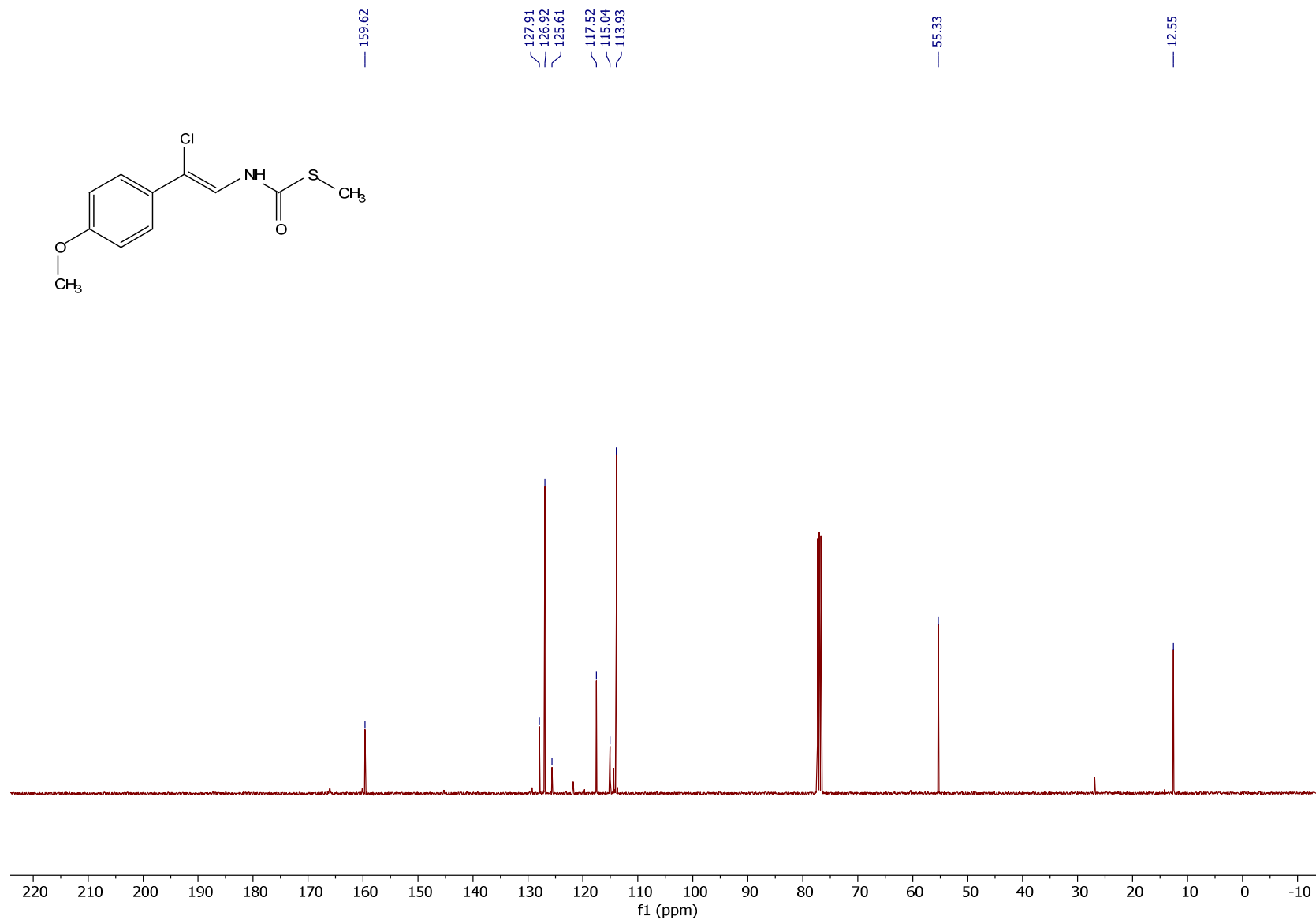


S-methyl (Z)-(2-chloro-2-(4-methoxyphenyl)vinyl)carbamothioate (**6e**)

¹H NMR

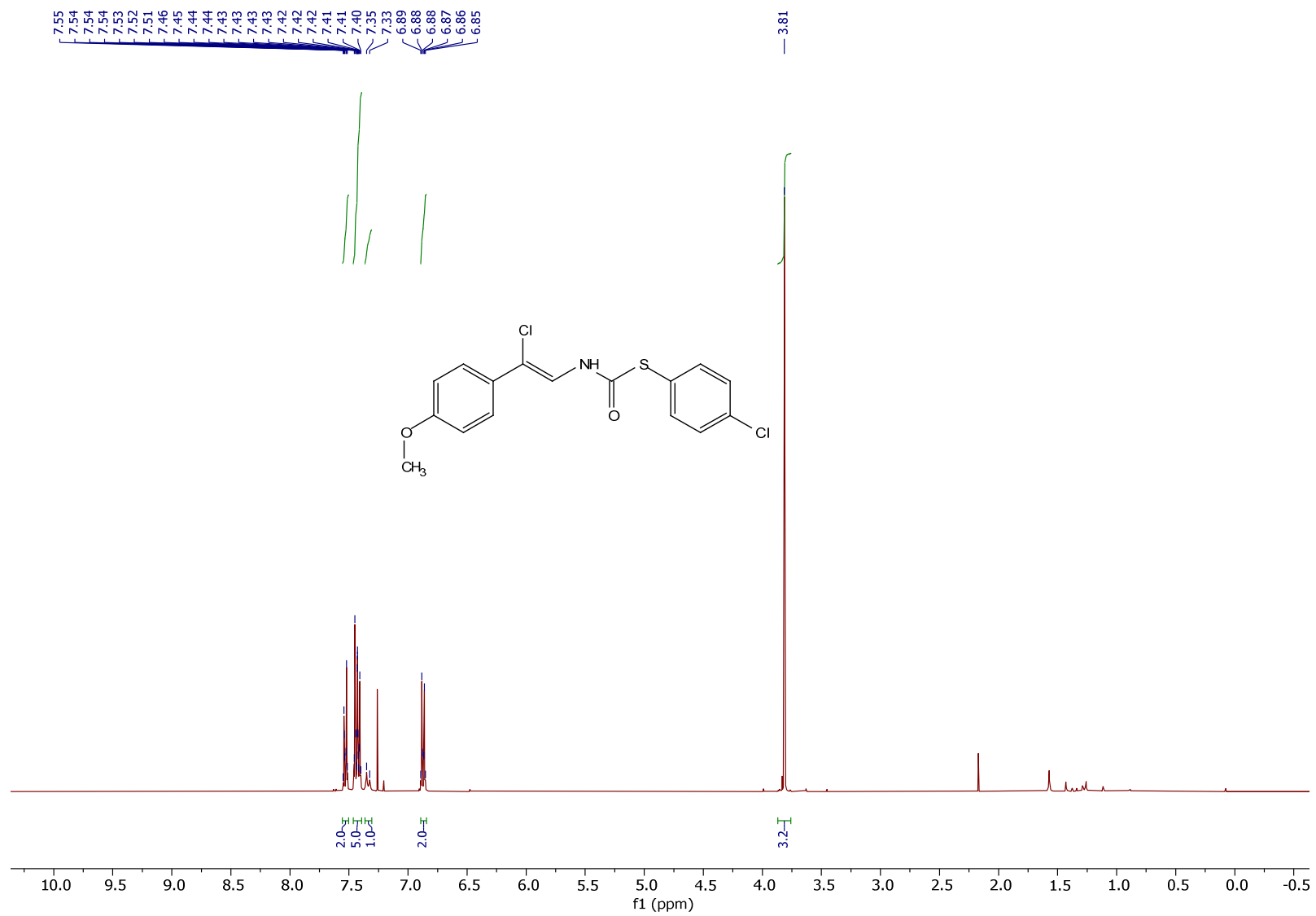


¹³C NMR

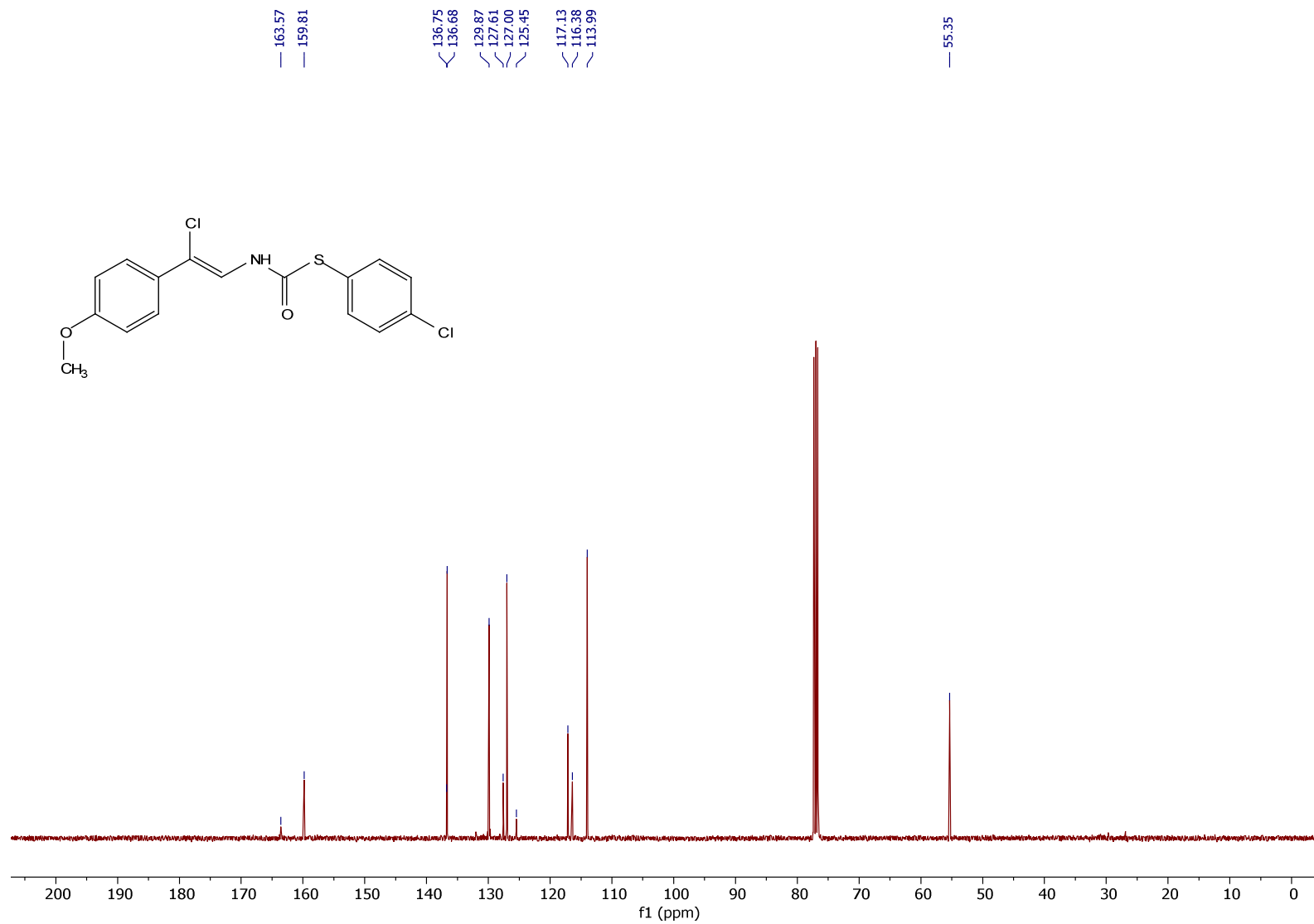


S-(4-chlorophenyl) (Z)-(2-chloro-2-(4-methoxyphenyl)vinyl)carbamothioate (**6f**)

¹H NMR

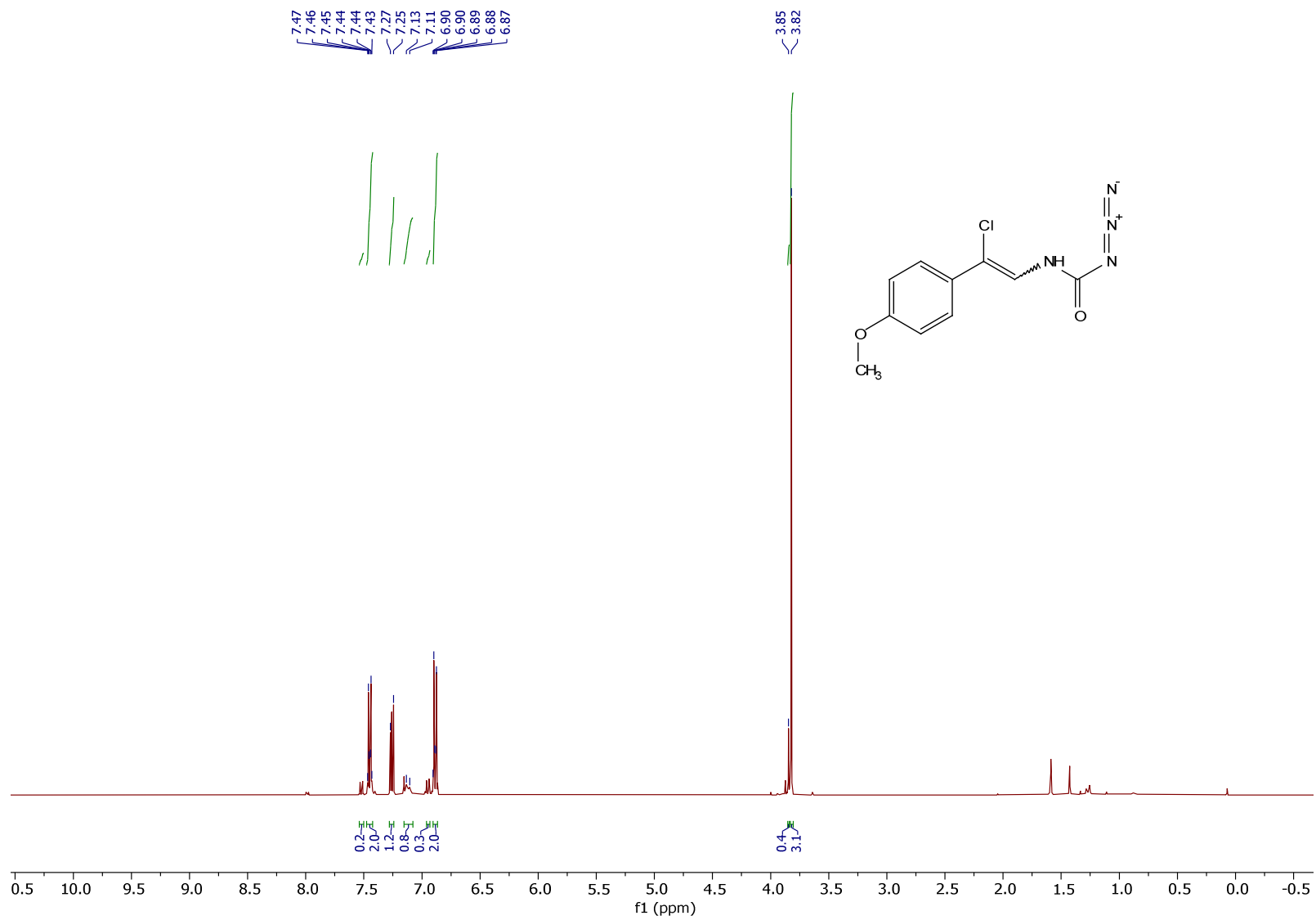


¹³C NMR

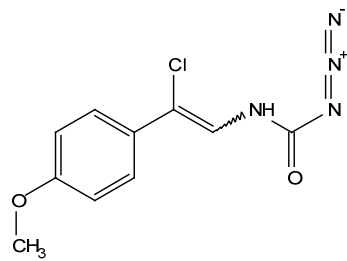


(2-chloro-2-(4-methoxyphenyl)vinyl)carbamoyl azide (**6g**)

^1H NMR



¹³C NMR



159.84

153.82

127.59

127.00

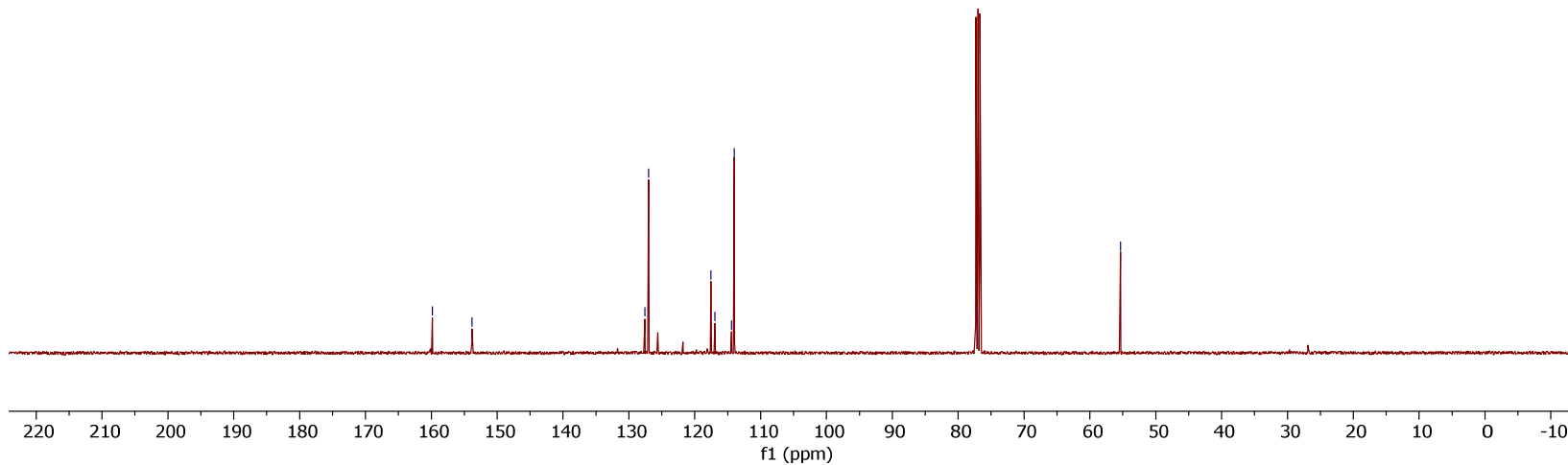
117.54

116.92

114.43

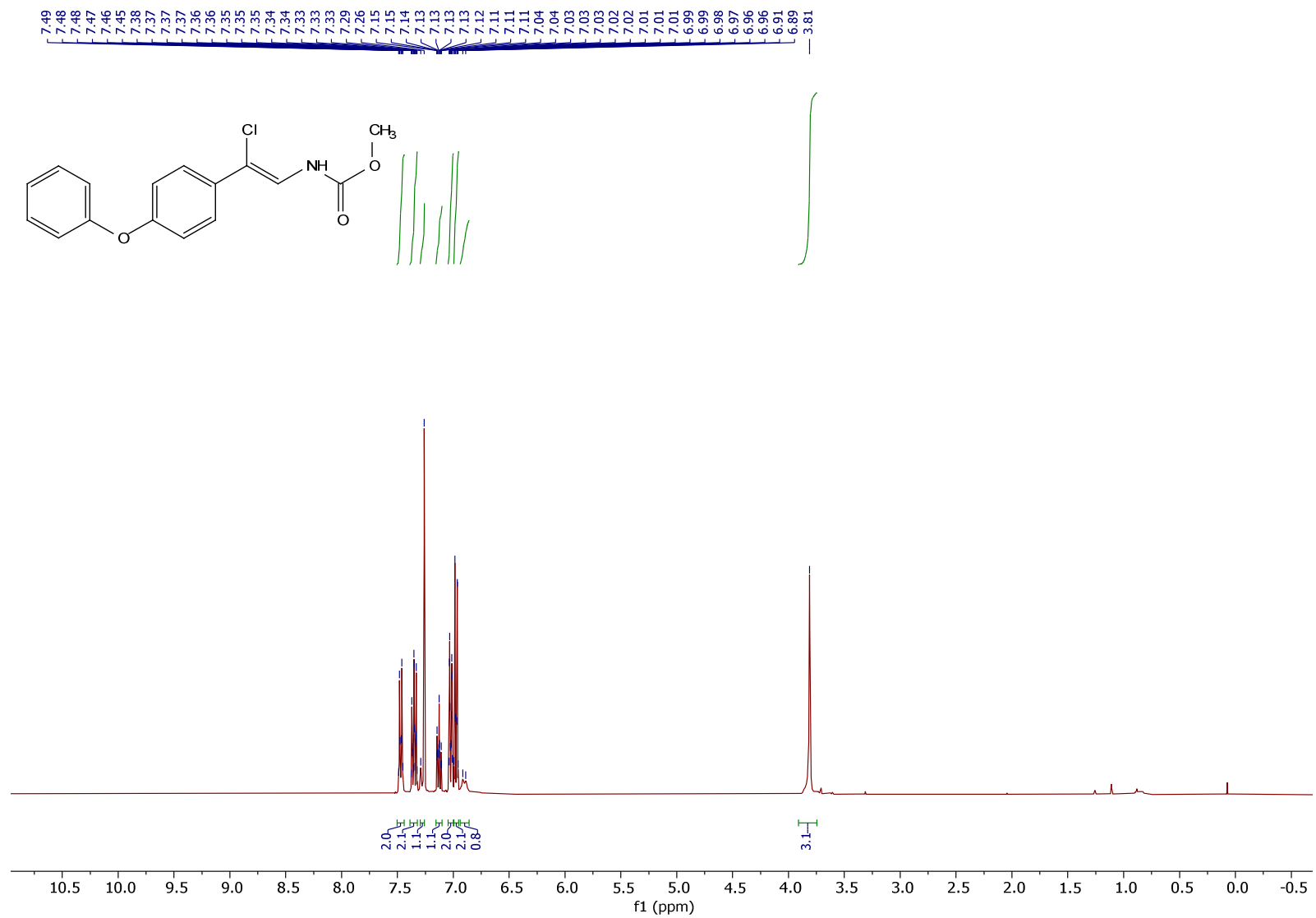
113.98

55.36

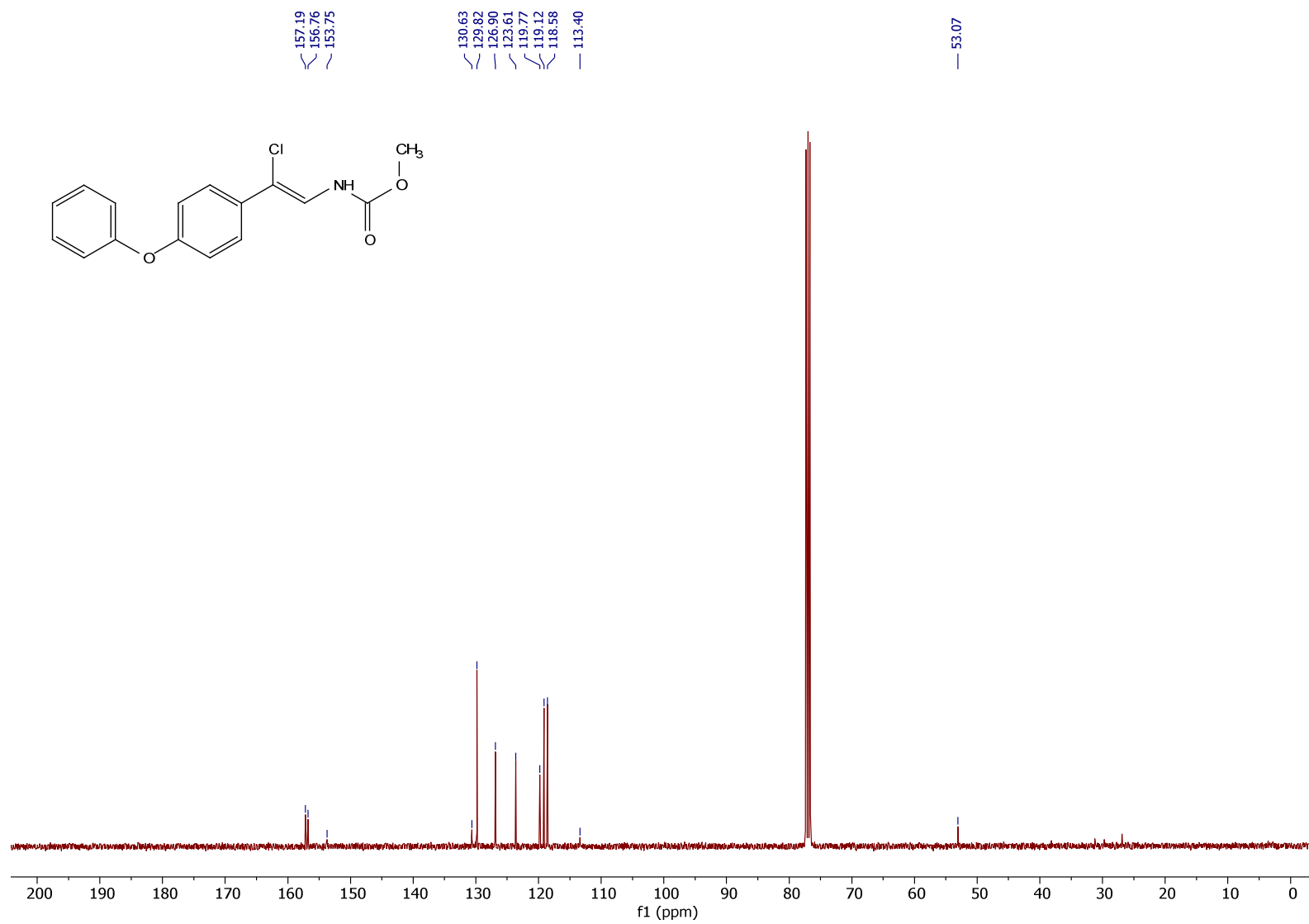


Methyl (Z)-(2-chloro-2-(4-phenoxyphenyl)vinyl)carbamate (**6h**)

^1H NMR

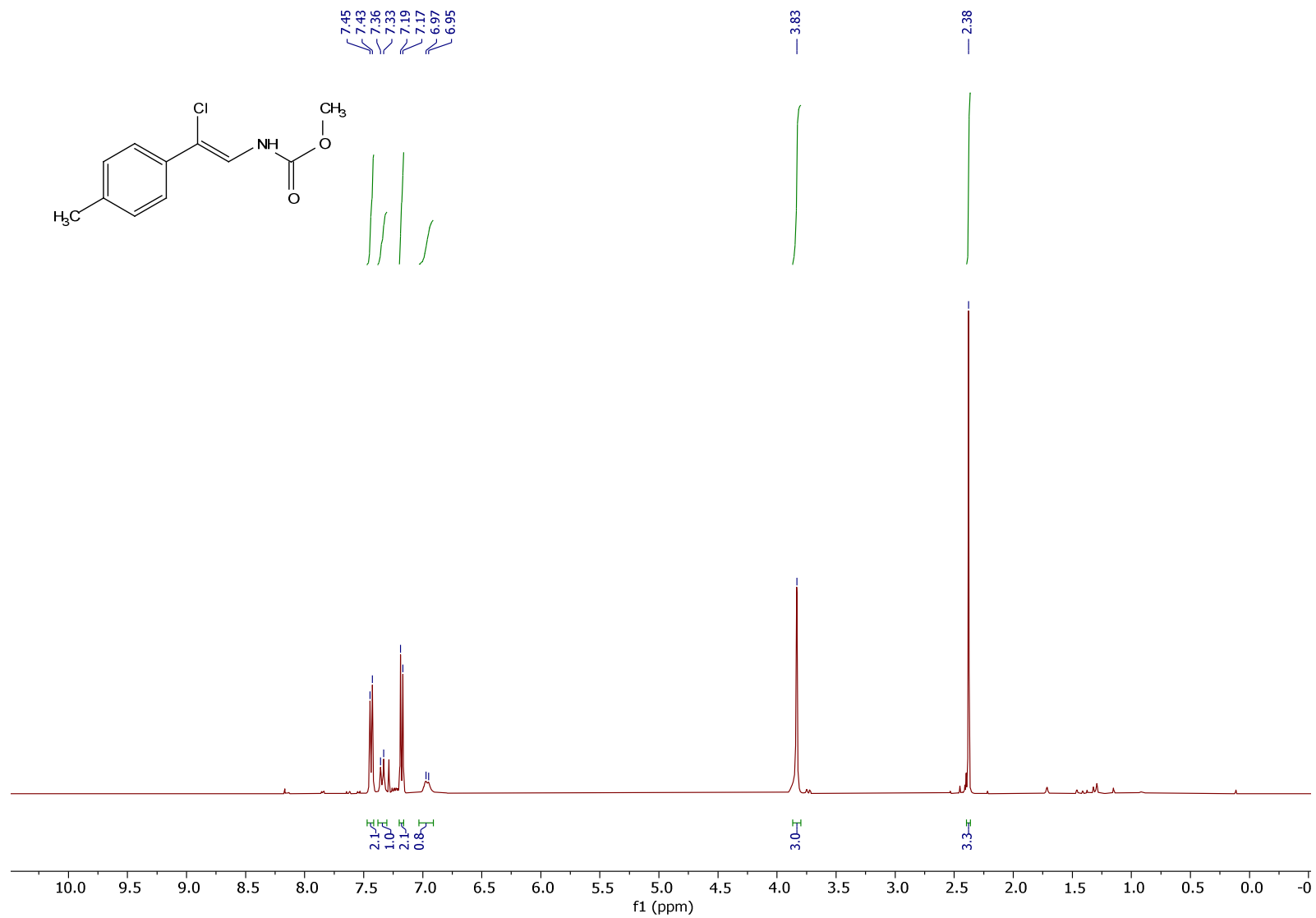


¹³C NMR

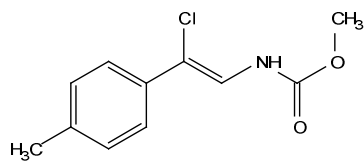


Methyl (Z)-(2-chloro-2-(p-tolyl)vinyl)carbamate (**6i**)

^1H NMR



¹³C NMR



— 153.73

— 137.74

— 132.75

— 129.14

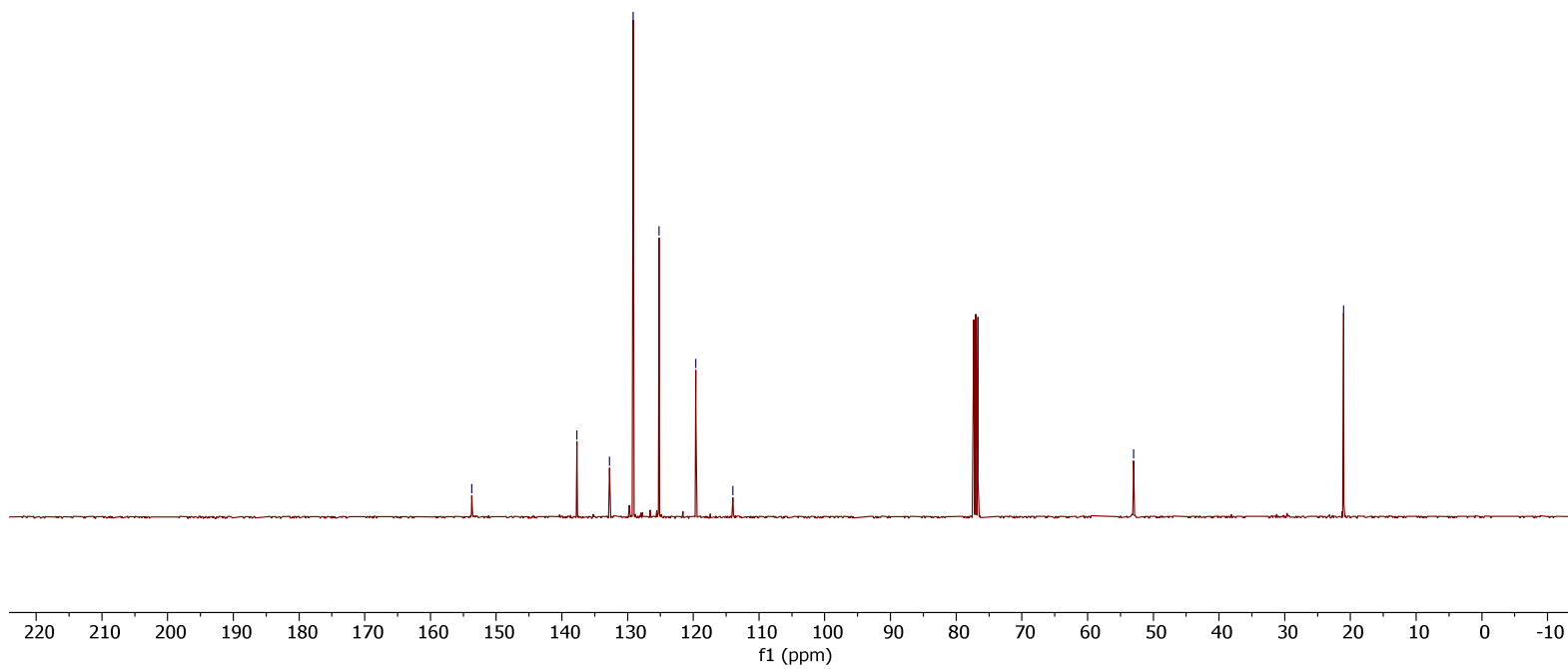
— 125.21

— 119.61

— 114.00

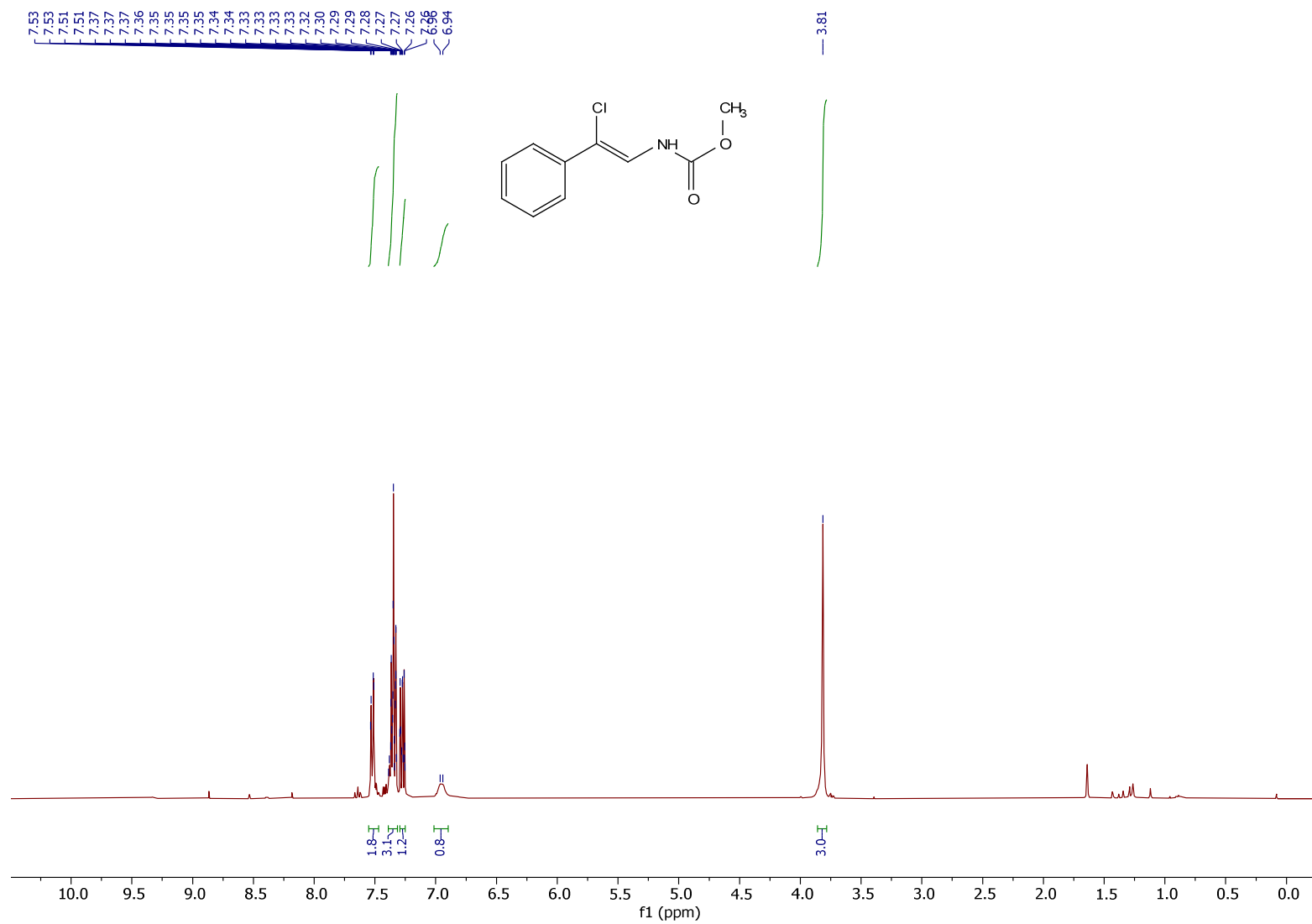
— 52.98

— 21.03



Methyl (Z)-(2-chloro-2-phenylvinyl)carbamate (**6j**)

^1H NMR



¹³C NMR

— 153.72

— 135.56

— 128.48

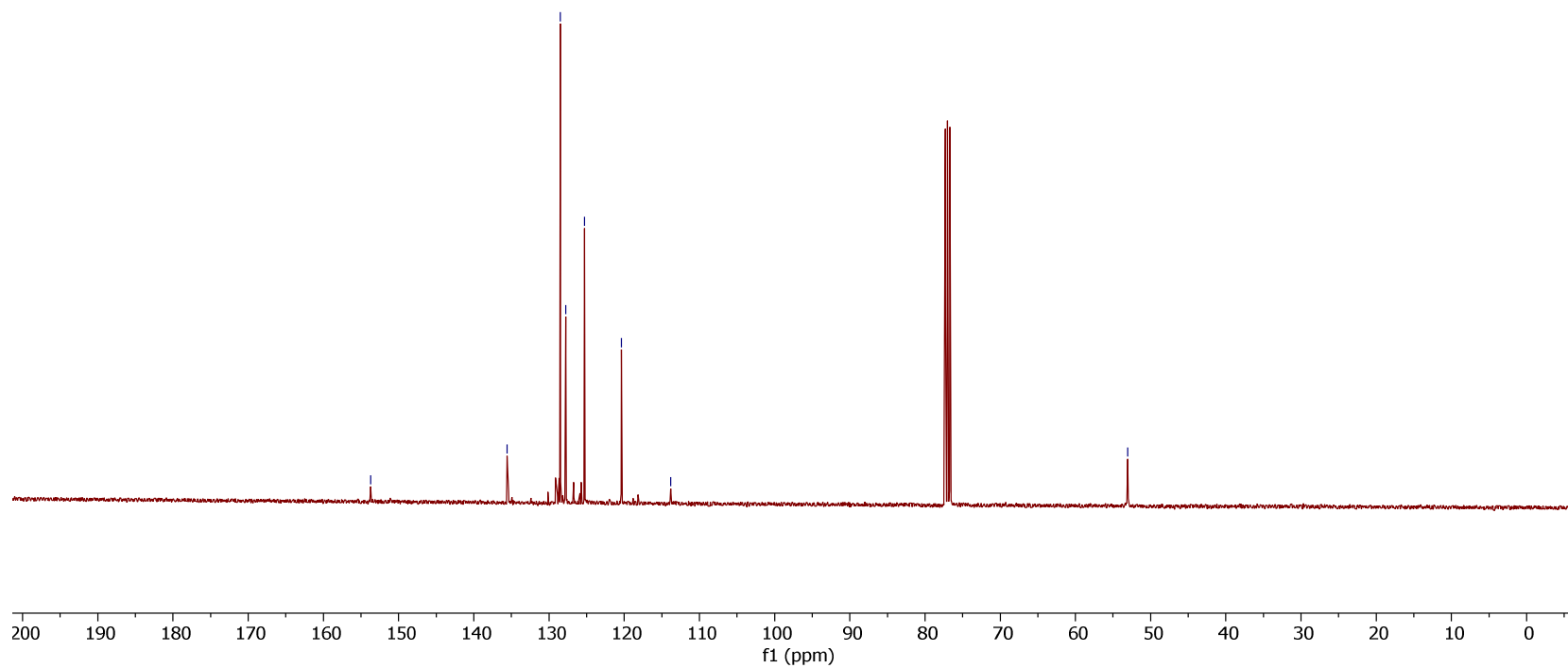
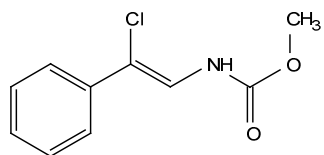
— 127.79

— 125.28

— 120.36

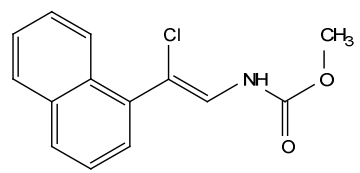
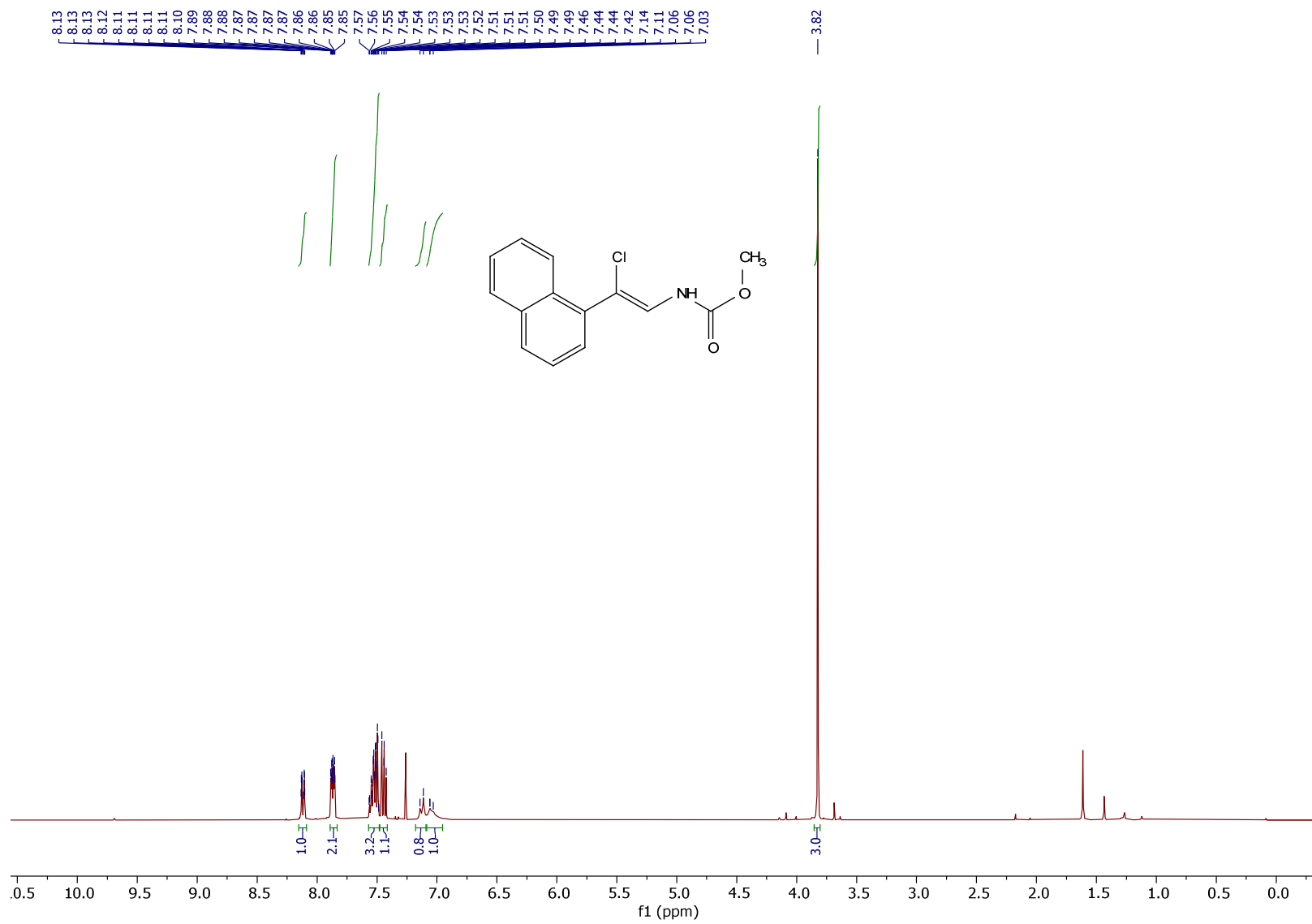
— 113.82

— 53.05

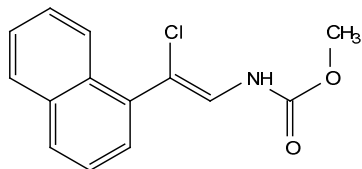


Methyl (Z)-(2-chloro-2-(naphthalen-1-yl)vinyl)carbamate (**6k**)

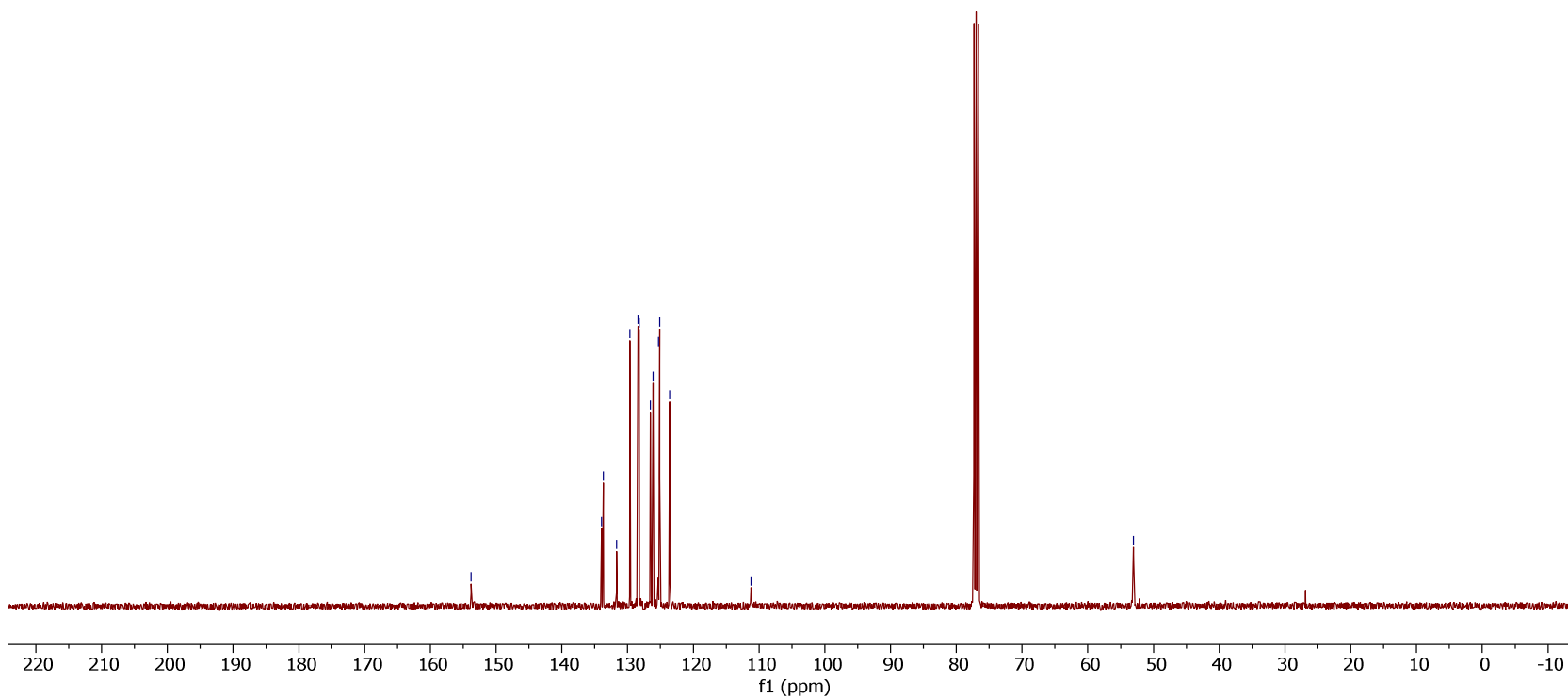
^1H NMR



^{13}C NMR

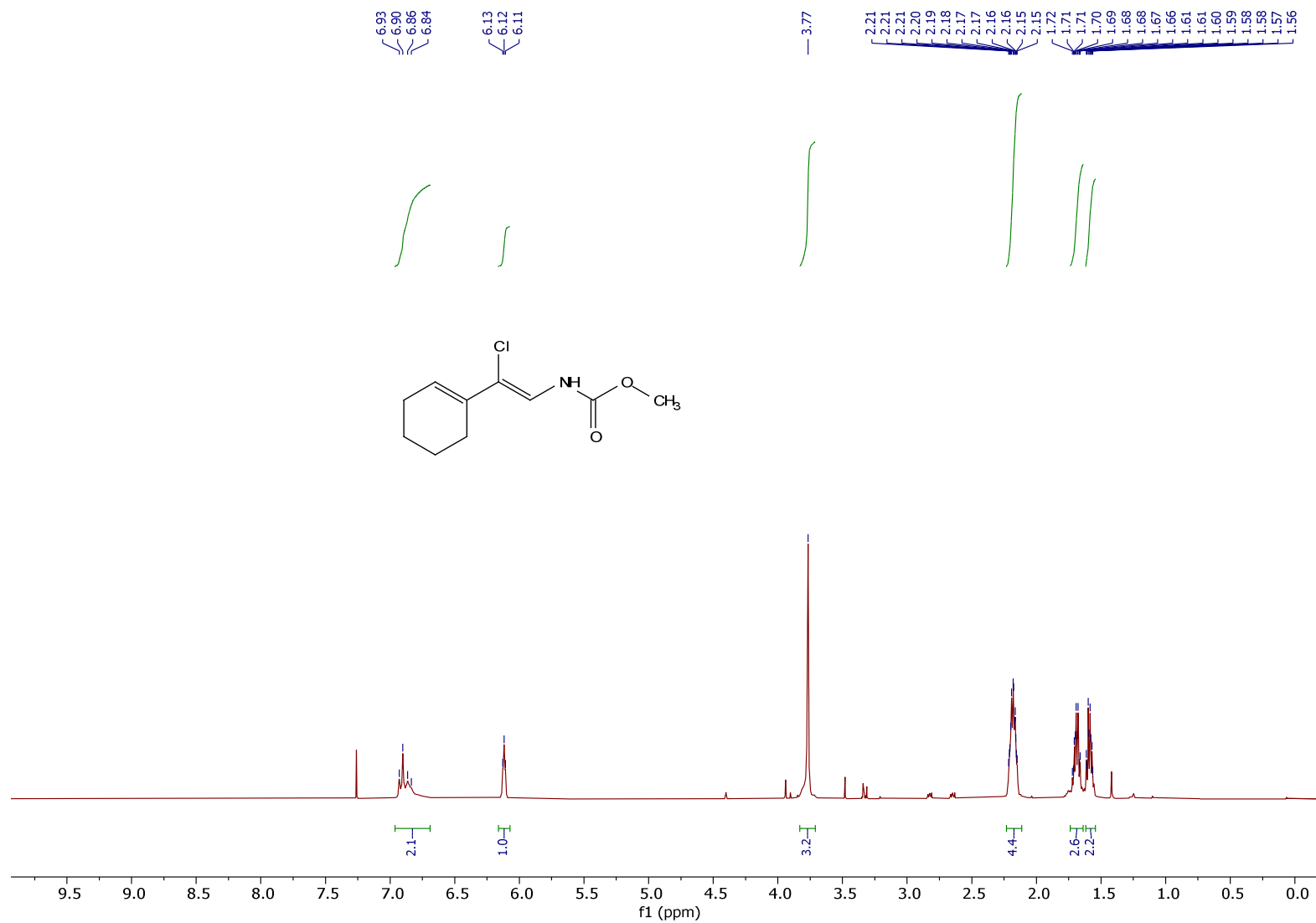


153.79
133.95
133.70
131.66
129.65
128.43
128.25
126.54
126.14
125.50
125.12
123.61
111.22
53.04

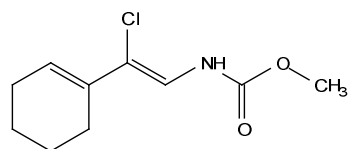


Methyl (Z)-(2-chloro-2-(cyclohex-1-en-1-yl)vinyl)carbamate (**6I**)

^1H NMR



¹³C NMR



— 153.75

— 130.78

— 125.72

— 117.80

— 116.75

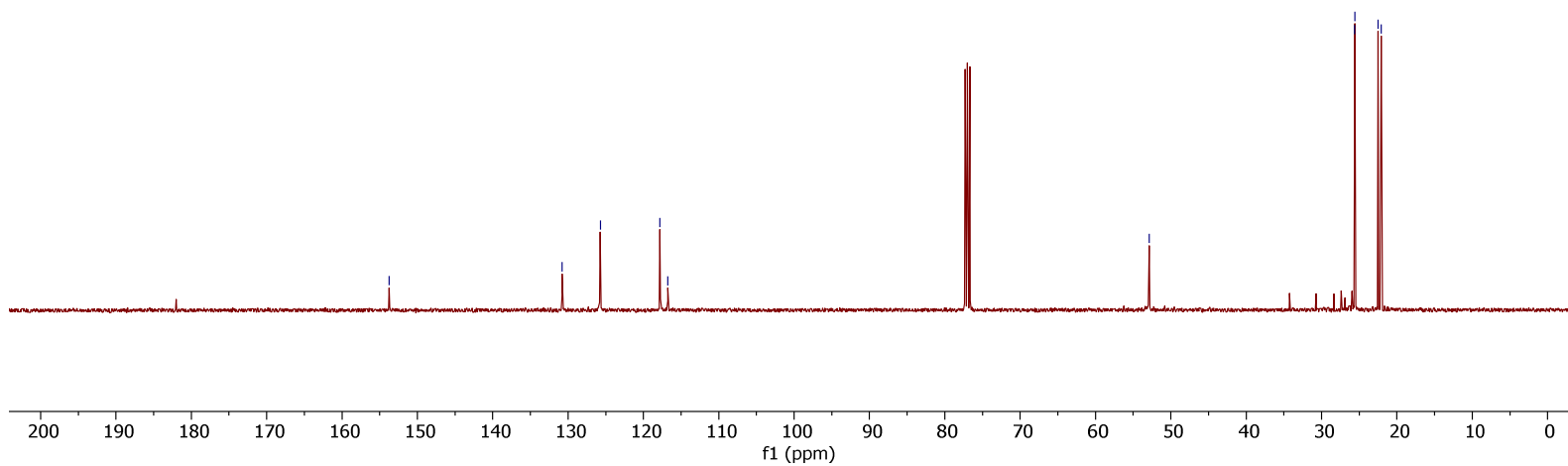
— 52.89

— 25.62

— 25.60

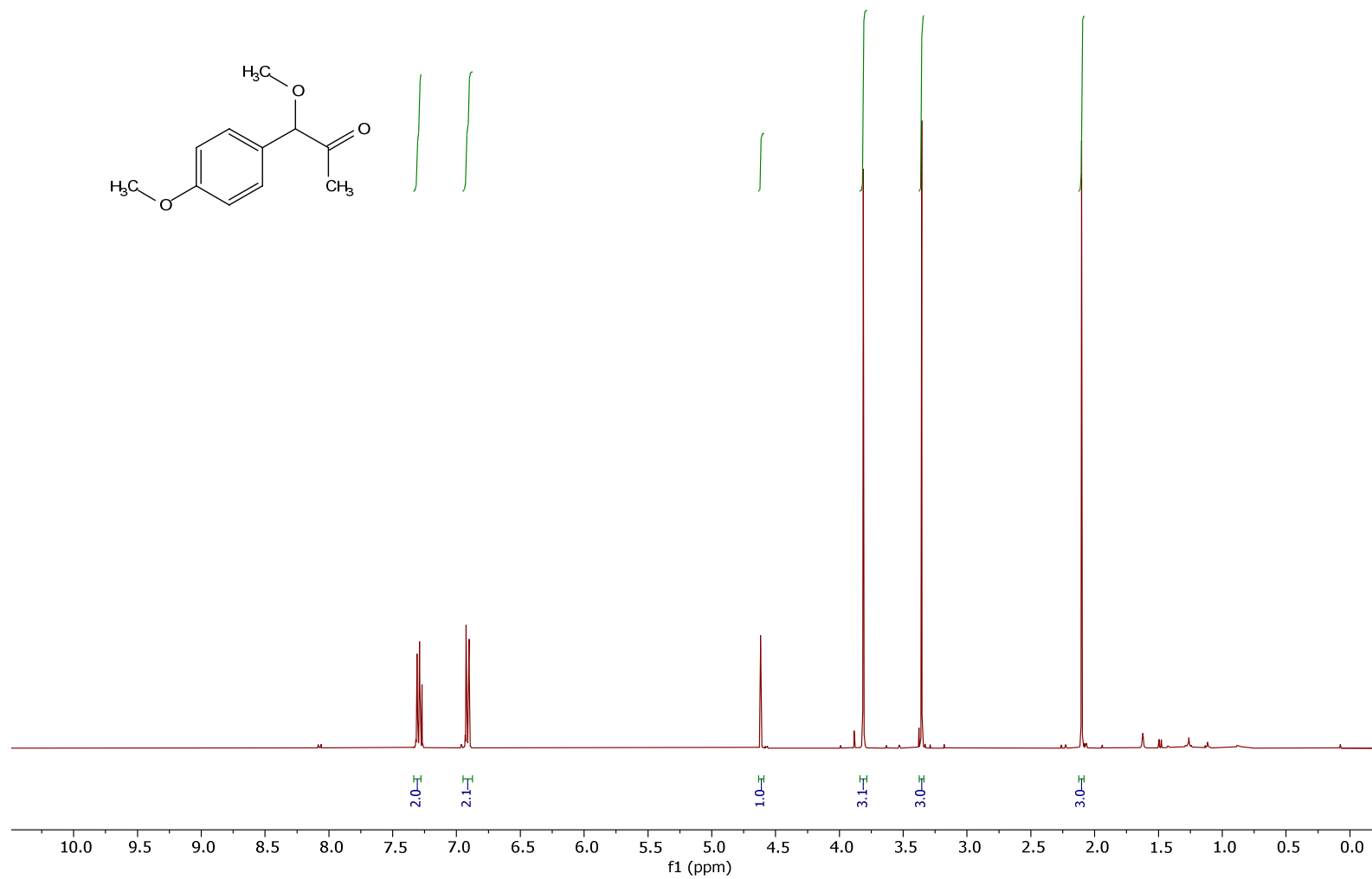
— 22.50

— 22.06

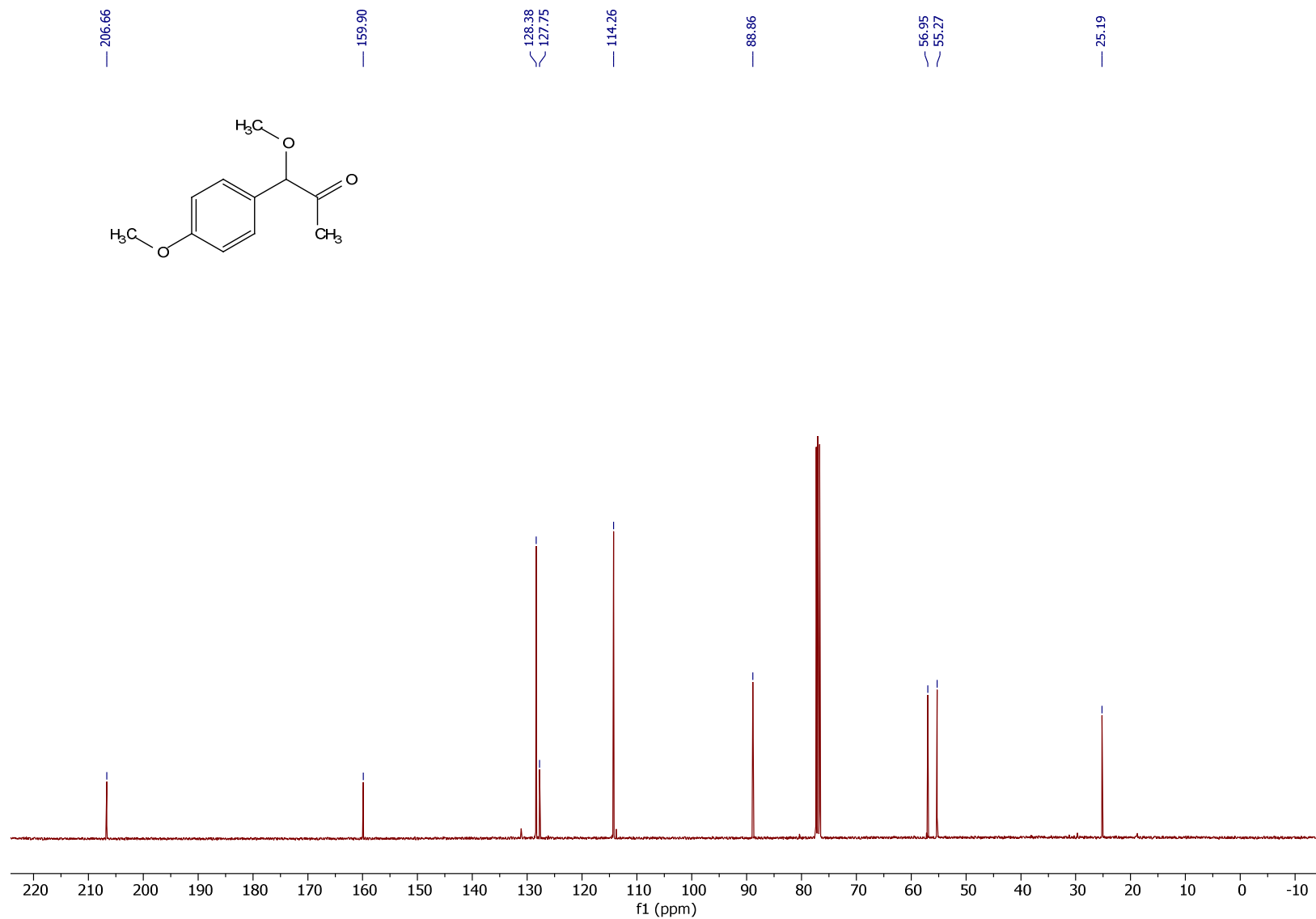
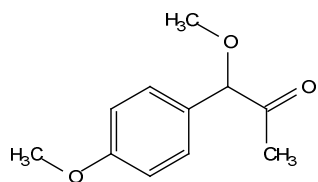


1-methoxy-1-(4-methoxyphenyl)propan-2-one (**7**)

^1H NMR

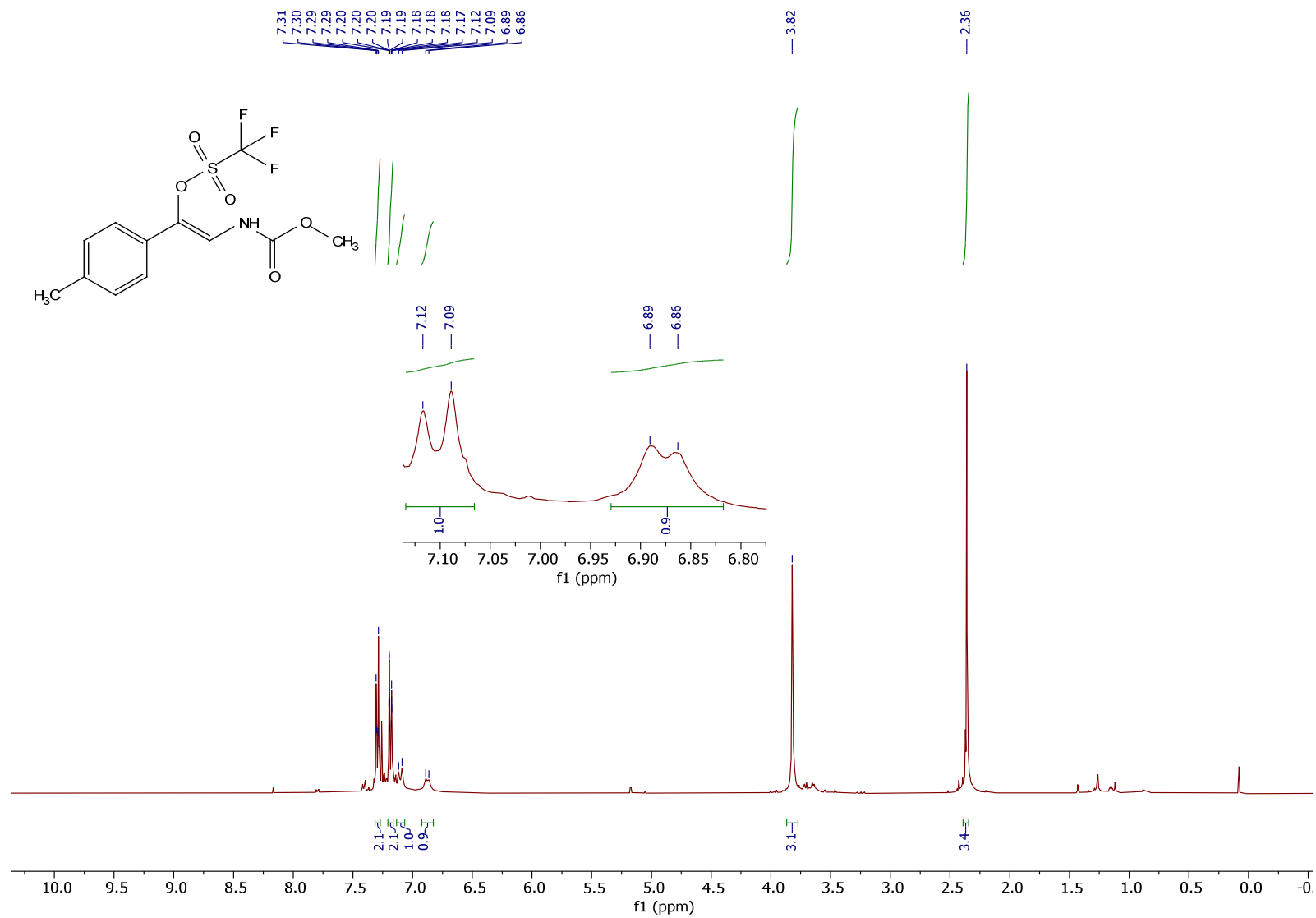


¹³C NMR



(Z)-2-((methoxycarbonyl)amino)-1-(p-tolyl)vinyl trifluoromethanesulfonate (**8a**)

¹H NMR



^{13}C NMR

— 153.38

— 139.07

— 131.80

— 129.53

— 128.71

— 124.56

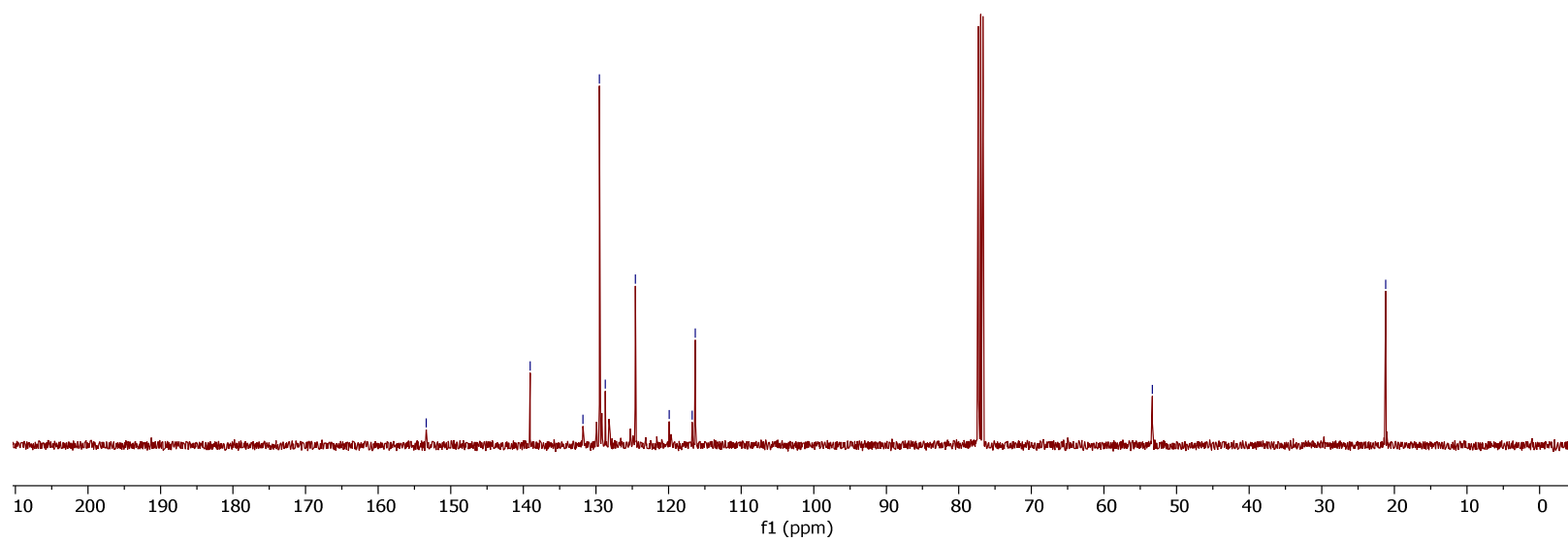
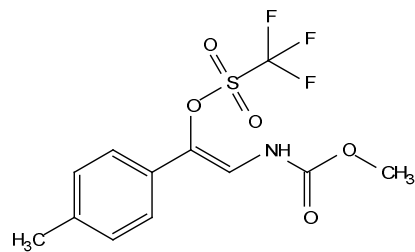
— 119.92

— 116.73

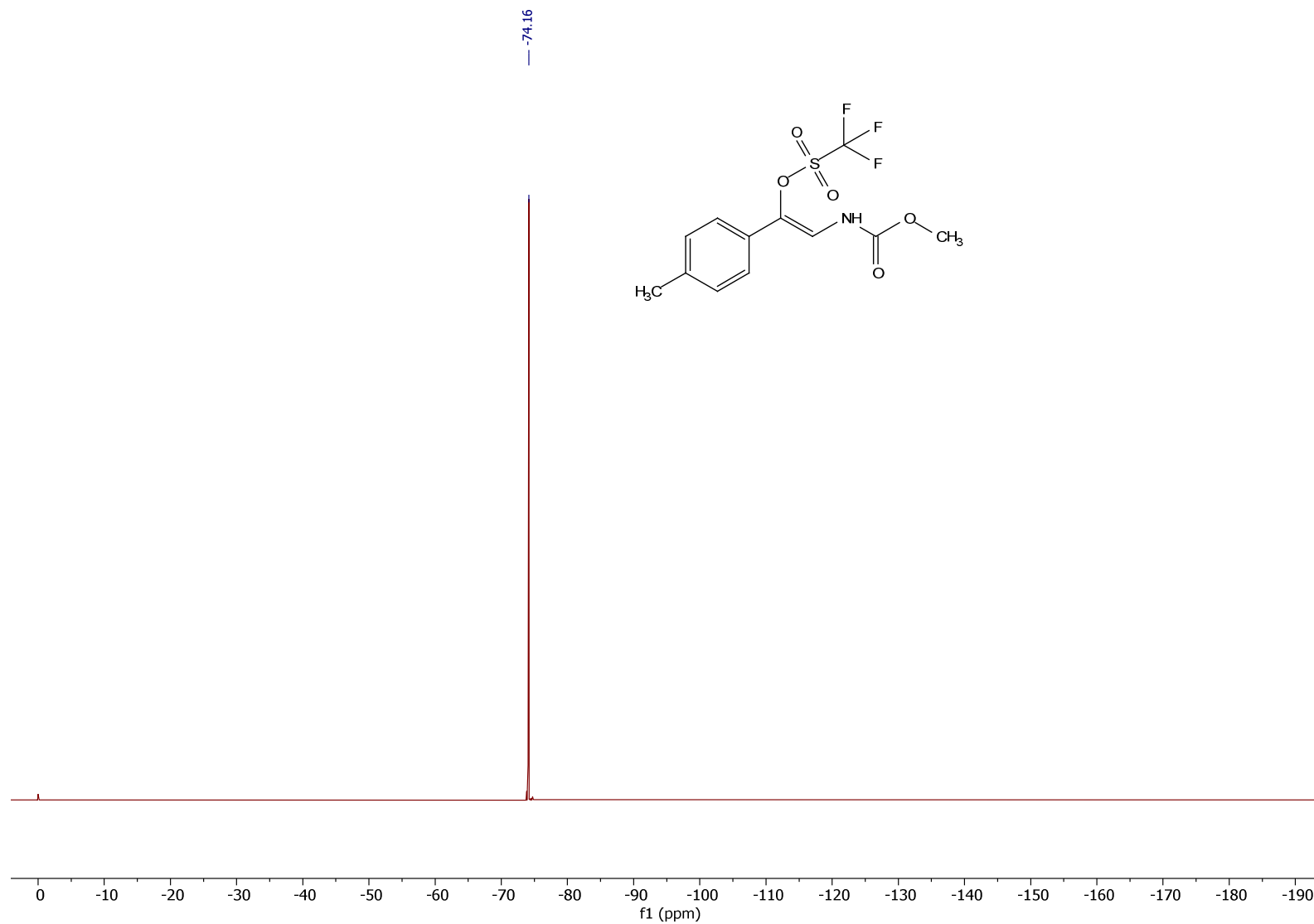
— 116.31

— 53.35

— 21.20



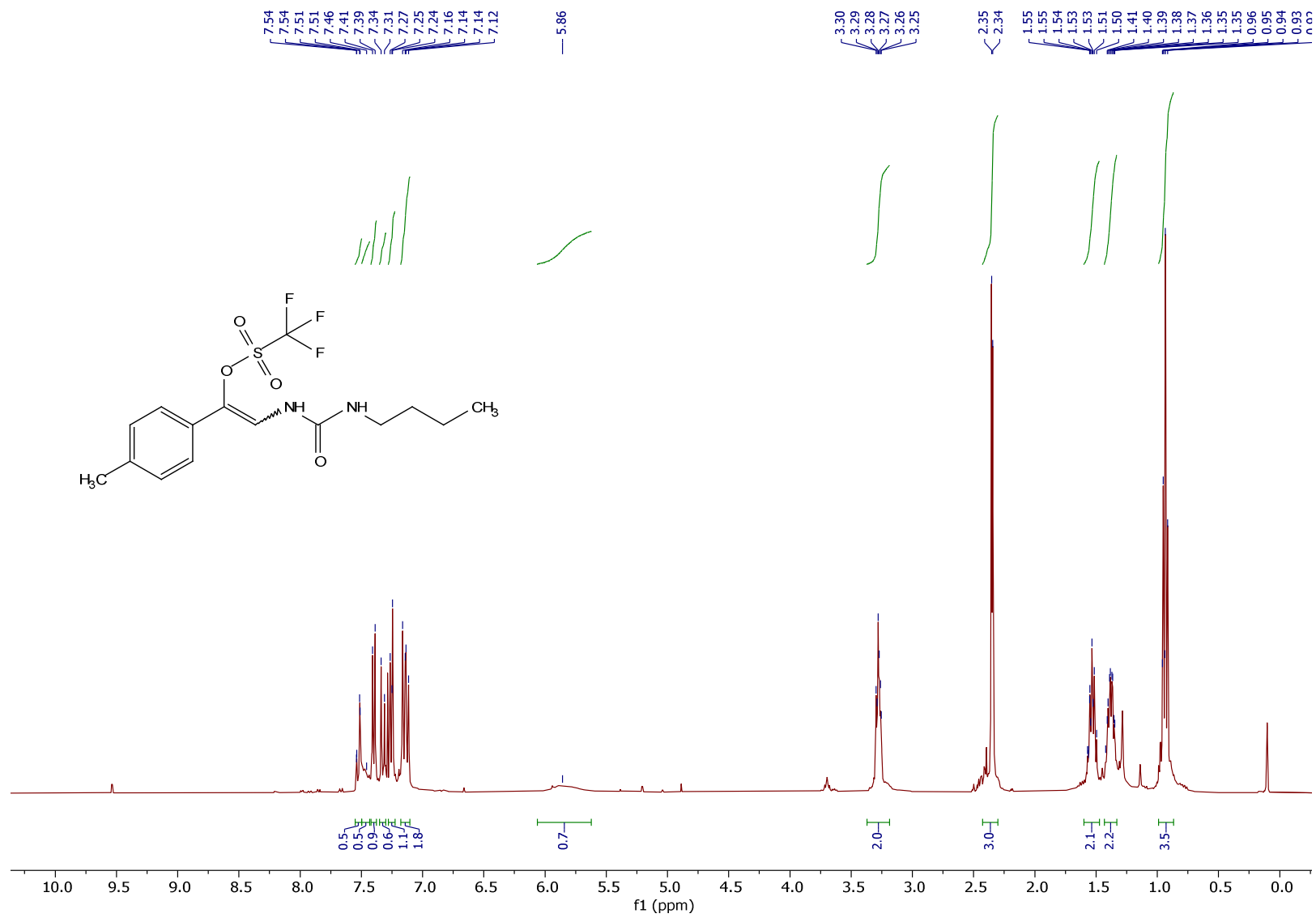
^{19}F NMR



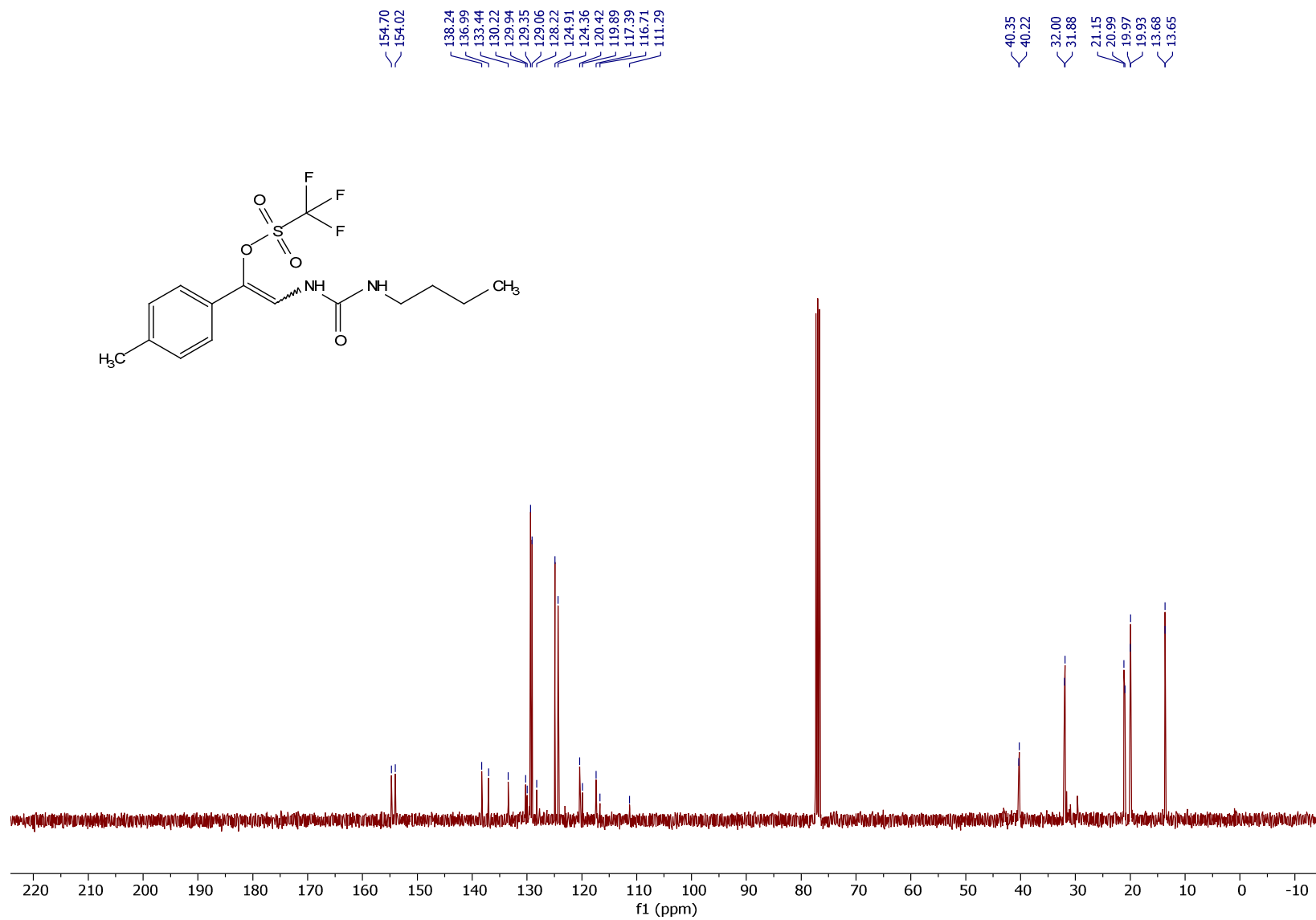
SI73

2-(3-butylureido)-1-(p-tolyl)vinyl trifluoromethanesulfonate (**8b**)

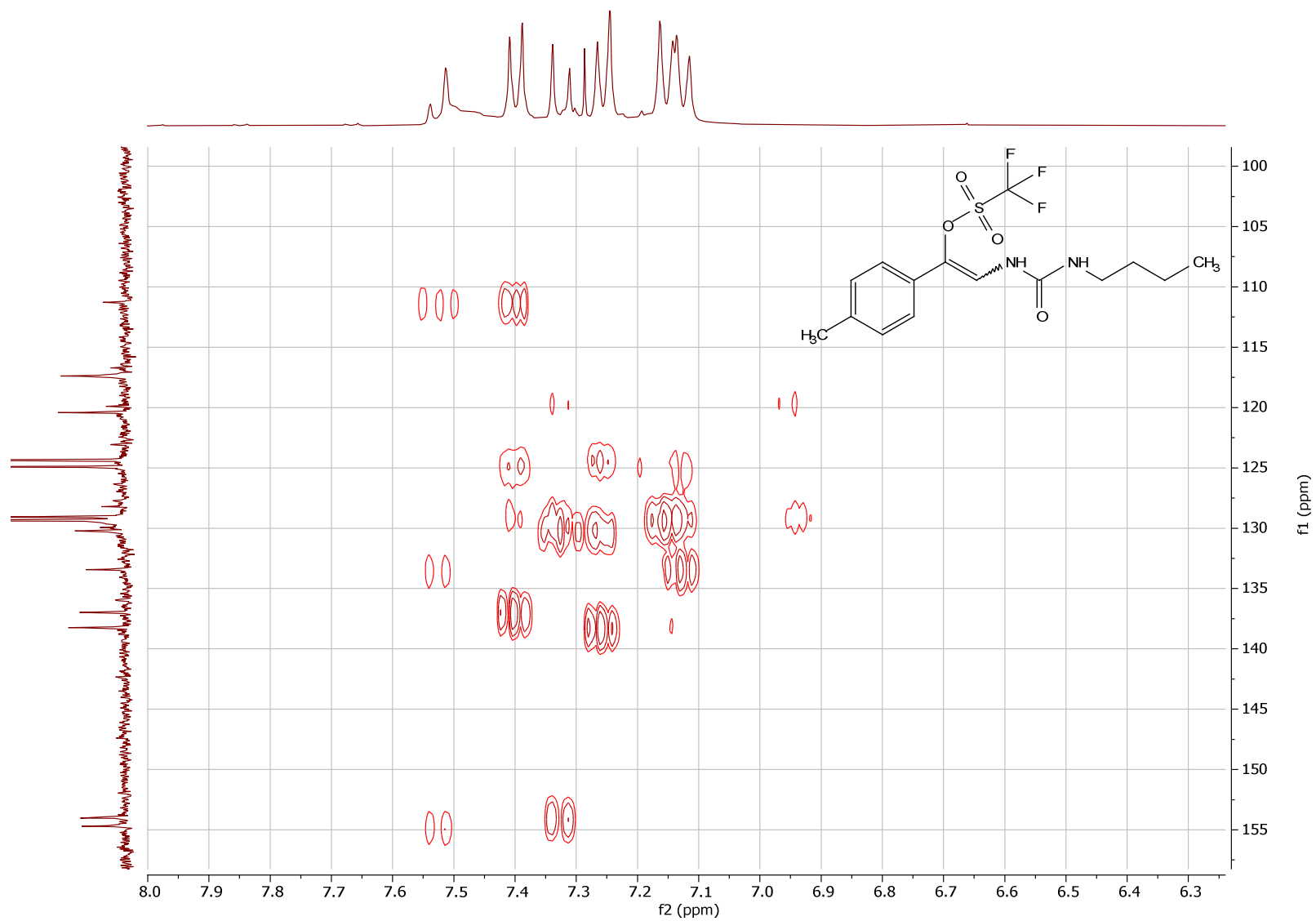
¹H NMR



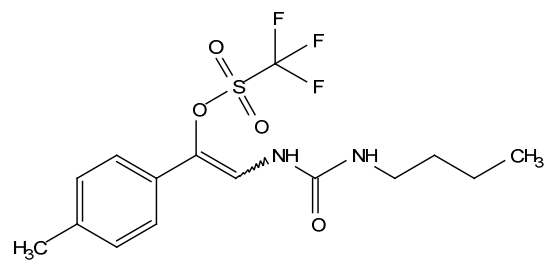
¹³C NMR



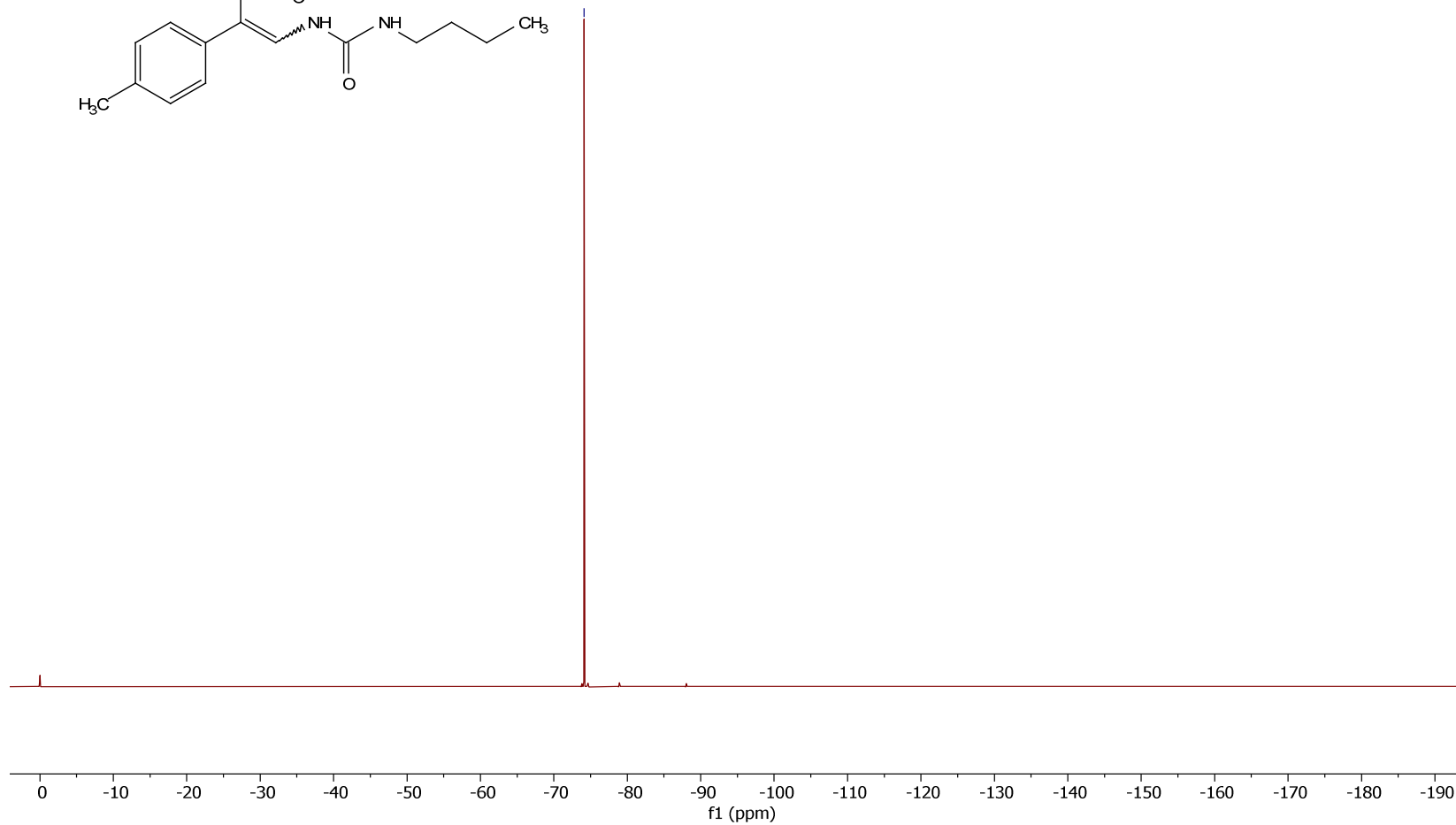
^1H - ^{13}C HMBC NMR



^{19}F NMR



-74.11



SI77