Supporting information

General: Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich and Alfa Aesar.

Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR were recorded on a Varian AV600 spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), p (pentelet) m (multiplet); coupling constants (J) are in Hertz (Hz).

EI MS data were recorded on a Shimadzu GCMS sytem (QP 2010 SE and GC2010plus, CP@Sil@8@MS column, 30m, 0.25µm ID, method: 60°C 5min, 20K/min to 300°C and keep for 20min). HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization.

IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

Syringe pump: Chemyx Inc. Model Fusion 710.

Important safety note:

Safety hazards of diazo acetonitrile, described within this manuscript, have not been investigated. However, it should be noted this particular diazo compound was reported to be highly explosive.[1]

Handling of diazo acetonitrile should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling all diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein diazo acetonitrile. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

General procedure for the synthesis of styrenes

Methyl triphenylphosphonium bromide (1.25 eq) was suspended in THF and n-butyl lithium (1.2 eq) is added slowly at 0 °C. The resulting suspension was stirred at 0 °C for another 60 minutes, then it is cooled to -78 °C and the respective aldehyde was added slowly. The cold bath was removed and the reaction was allowed to warm to rt. Then sat. NH_4Cl was added,

and the resulting mixture was extracted three times with diethyl ether. The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography with pentane as eluent to afford the styrene derivative.

General procedure for the synthesis of α-methyl-styrenes

Methyl triphenylphosphonium bromide (1.2 eq) was suspended in THF and potassium t-butoxide (1.2 eq) is added slowly at 0 °C. The resulting suspension was stirred at 0 °C for another 60 minutes, then the respective aldehyde was added slowly. The cold bath was removed and the reaction was allowed to warm to rt over night. Then sat. NH_4Cl was added, and the resulting mixture was extracted three times with diethyl ether. The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography with pentane as eluent to afford the α-methyl-styrene derivative.

General procedure for catalyst screening using the slow-release protocol

Catalyst, additives (0.1 eq, if used) and amino acetonitrile hydrochloride (2 eq) were dissolved in degassed water (1 mL) and styrene (0.2 or 0.4 mmol, 1 eq) was added under argon atmosphere. $NaNO_2$ (3 eq) was dissolved in 0.5 or 1 mL degassed water, the solution was purged with argon for a minute und was then added via syringe pump over 10 h. After complete addition the resulting reaction mixture was stirred for 4 h. The crude mixture was analysed by NMR to determine the diastereoselectivity. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified on silica gel (hexanes / ethyl acetate 20/1) to afford the cyclopropane.

General procedure for biphasic reaction to nitrile substituted cyclopropanes using the slow-release protocol

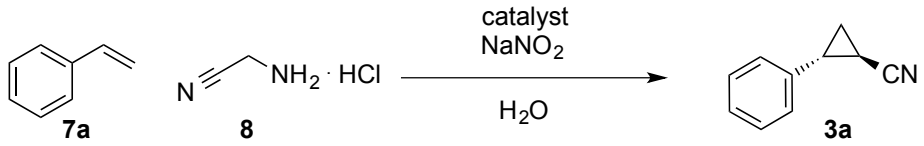
FeTPPCl (1 or 3 mol%), amino acetonitrile hydrochloride (2 eq) and styrene derivative (0.4 mmol, 1 eq) were dissolved in 0.1 mL degassed dichloromethane and 1 mL degassed water under argon atmosphere. $NaNO_2$ (3 eq) was dissolved in 1 mL degassed water. The solution was purged with argon for a minute and was added via syringe pump over 10 h. After complete addition the resulting reaction mixture was stirred for 4 h. The crude mixture was analysed by NMR to determine the diastereoselectivity. The aqueous phase was extracted three times with dichloromethane; the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified on silica gel (hexanes / ethyl acetate 20:1) to afford the desired cyclopropane.

Proceure for cyclopropanation reaction in gram-scale using the slow-release protocol

FeTPPCl (0.1 mol%), amino acetonitrile hydrochloride (2 eq) and styrene derivative (0.4 mmol, 1 eq) were dissolved in 1 mL degassed dichloromethane and 10 mL degassed water under argon atmosphere. $NaNO_2$ (3 eq) was dissolved in 25 mL degassed water. The solution was purged with argon for a minute and was added via syringe pump over 10 h. After complete addition the resulting reaction mixture was stirred for 4 h. The aqueous phase was extracted three times with dichloromethane; the combined organic layers were dried over

$MgSO_4$ and concentrated under reduced pressure. The residue was purified on silica gel (hexanes / ethyl acetate 20:1) to afford the desired cyclopropane.

Table 1. Survey of different catalysts using the slow-release protocol



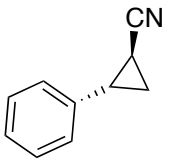
#	catalyst	mol-%	changes from above	d.r.	%yield
1	Ru(TPP)CO	3		2.5:1	23[a]
2	Co(salen)	3		1.3:1	14[a]
3	Rh_2OAc_4	3		1:1	9[a]
4	Fe(TPP)Cl	3		6:1	56

[a] 0.2 mmol styrene, 3 mol-% of catalyst, 2 eq aminoacetontrile hydrochloride were dissolved in the solvent indicated. $NaNO_2$ (3 eq) dissolved in 1 mL water was added over a period of 10 h at rt; the resulting mixture was stirred for another 4 h at rt; yields refer to the trans product after column chromatography; the d.r. was determined from the crude reaction mixture by ^{1}H-NMR; [a] NMR yield using dichloroethane as internal standard.

Physical data

Cyclopropanes

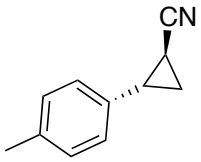
trans-2-phenylcyclopropane-1-carbonitrile



colorless solid (46 mg, 81%); m.p. = 29°C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.12 – 7.08 (m, 2H), 2.63 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.62 (dt, *J* = 9.2, 5.4 Hz, 1H), 1.55 (ddd, *J* = 8.7, 5.5, 4.8 Hz, 1H), 1.45 (ddd, *J* = 8.8, 6.7, 5.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 137.55, 128.76, 127.41, 126.31, 121.05, 24.90, 15.24, 6.63; HRMS (ESI): m/z calc. for [$C_{10}H_9NNa$]: 166.06272, found 166.06276; IR (KBr): ν_{max}/cm^{-1} = 3044, 2235, 2098, 1761, 1600, 1461, 1220, 1051, 920, 705.

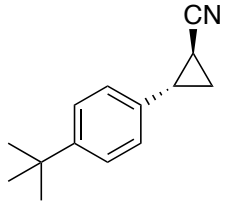
The analytical data is in correspondence with the literature [2]

trans-2-(*p*-tolyl)cyclopropane-1-carbonitrile



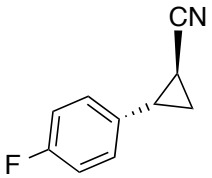
colorless solid (52 mg, 84%); m.p. = 84 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.14 – 7.08 (m, 2H), 7.01 – 6.96 (m, 2H), 2.60 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 2.32 (s, 3H), 1.59 (dt, *J* = 9.2, 5.4 Hz, 1H), 1.50 (ddd, *J* = 8.7, 5.5, 4.7 Hz, 1H), 1.42 (ddd, *J* = 8.8, 6.7, 5.2 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 137.17, 134.51, 129.40, 126.23, 121.19, 24.67, 21.03, 15.12, 6.48; HRMS (ESI): m/z calc. for [$C_{11}H_{12}N$]: 158.09643, found 158.09636; IR (KBr): ν_{max}/cm^{-1} = 3850, 3028, 2919, 2230, 2087, 1912, 1791, 1516, 1452, 1039, 931, 796, 715.

trans-2-(4-(_tert_-butyl)phenyl)cyclopropane-1-carbonitrile



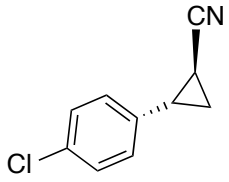
colorless solid (60 mg, 76%); m.p. = 37 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.35 – 7.32 (m, 2H), 7.07 – 7.03 (m, 2H), 2.61 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.60 (dt, *J* = 9.2, 5.4 Hz, 1H), 1.55 – 1.50 (m, 1H), 1.44 (ddd, *J* = 8.8, 6.7, 5.2 Hz, 1H), 1.31 – 1.30 (m, 9H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 50.52, 134.54, 126.04, 125.67, 121.19, 34.51, 31.27, 24.57, 15.14, 6.49; HRMS (ESI): m/z calc. for [$C_{14}H_{17}NNa$]: 222.12532, found 222.12558; IR (KBr): ν_{max}/cm^{-1} = 3032, 2959, 2237, 2106, 1908, 1741, 1516, 1460, 1365, 1269, 1122, 1028, 938, 829, 791.

trans-2-(4-fluorophenyl)cyclopropane-1-carbonitrile



colorless solid (49 mg, 76%); m.p. = 66 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.11 – 7.05 (m, 2H), 7.03 – 6.97 (m, 2H), 2.62 (ddd, *J* = 9.2, 6.6, 4.7 Hz, 1H), 1.62 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.51 (ddd, *J* = 8.9, 5.6, 4.7 Hz, 1H), 1.41 (ddd, *J* = 8.9, 6.7, 5.4 Hz, 1H); ^{19}F-NMR (564 MHz, $CDCl_3$): δ = -114.62 – -114.71 (m); ^{13}C-NMR (151 MHz, $CDCl_3$): δ =162.84, 161.21, 133.21 (d, *J* = 3.5 Hz), 128.10 (d, *J* = 8.5 Hz), 120.86, 115.68 (d, *J* = 21.3 Hz), 24.26, 15.07, 6.54; HRMS (ESI): m/z calc. for [$C_{10}H_8NF$]: 161.06353, found 161.06383; IR (KBr): ν_{max}/cm^{-1} = 3809, 3458, 3036, 2935, 2672, 2326, 2090, 1882, 1751, 1504, 1371, 1215, 1052, 926, 820.

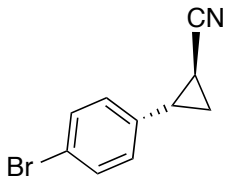
trans-2-(4-chlorophenyl)cyclopropane-1-carbonitrile



colorless solid (58 mg, 82%); m.p. = 86 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.32 – 7.24 (m, 2H), 7.07 – 6.98 (m, 2H), 2.60 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.63 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.53 (ddd, *J* = 8.9, 5.6, 4.7 Hz, 1H), 1.42 (ddd, *J* = 8.8, 6.7, 5.4 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 136.03, 133.25, 128.91, 127.74, 120.71, 24.33, 15.19, 6.73; HRMS (ESI): m/z calc. for

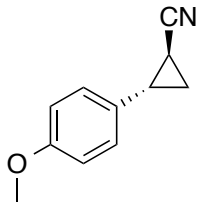
[$C_{10}H_8NClNa$]: 200.02374, found 200.02388; IR (KBr): ν_{max}/cm^{-1} = 3046, 2927, 2232, 2093, 1909, 1740, 1488, 1221, 1086, 917, 792.

trans-2-(4-bromophenyl)cyclopropane-1-carbonitrile



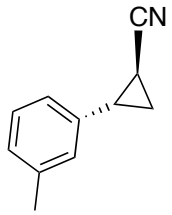
yellowish solid (75 mg, 84%); m.p. = 87 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.49 – 7.40 (m, 2H), 7.03 – 6.93 (m, 2H), 2.59 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.63 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.53 (ddd, *J* = 8.8, 5.6, 4.7 Hz, 1H), 1.42 (ddd, *J* = 8.9, 6.7, 5.5 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 136.57, 131.86, 128.07, 121.25, 120.68, 24.39, 15.18, 6.71; HRMS (ESI): m/z calc. for [$C_{10}H_8NBrNa$]: 243.97323, found 243.97345; IR (KBr): ν_{max}/cm^{-1} = 3840, 3032, 2926, 2673, 2335, 2228, 2094, 1751, 1471, 1218, 1034, 928, 789.

trans-2-(4-methoxyphenyl)cyclopropane-1-carbonitrile



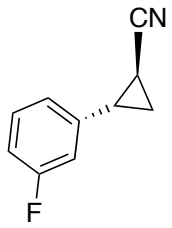
colorless solid (51 mg,74%); m.p. = 76 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.09 – 6.97 (m, 2H), 6.88 – 6.77 (m, 2H), 3.79 (s, 3H), 2.59 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.57 (dt, *J* = 9.2, 5.3 Hz, 1H), 1.46 (ddd, *J* = 8.8, 5.4, 4.7 Hz, 1H), 1.39 (ddd, *J* = 8.8, 6.7, 5.2 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 158.90, 129.49, 127.62, 121.26, 114.13, 55.33, 24.40, 14.92, 6.31; HRMS (ESI): m/z calc. for [$C_{11}H_{11}ONNa$]: 196.07329, found 196.07353; IR (KBr): ν_{max}/cm^{-1} = 3012, 2949, 2241, 1605, 1506, 1461, 1239, 1179, 1021, 934, 826, 705.

trans-2-(_m_-tolyl)cyclopropane-1-carbonitrile



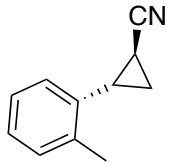
yellowish solid (50 mg, 80%); m.p. = 42 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.6 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.94 – 6.87 (m, 2H), 2.59 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.60 (dt, *J* = 9.1, 5.4 Hz, 1H), 1.56 – 1.50 (m, 1H), 1.44 (ddd, *J* = 8.7, 6.7, 5.2 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 138.50, 137.50, 128.65, 128.15, 127.09, 123.26, 121.12, 24.87, 21.35, 15.20, 6.54; HRMS (ESI): m/z calc. for [$C_{11}H_{12}N$]: 158.09634, found 158.09645; IR (KBr): ν_{max}/cm^{-1} = 3839, 3537, 2922, 2338, 2229, 2100, 1875, 1746, 1598, 1459, 1163, 1040, 955, 891, 778, 697.

***trans*-2-(3-fluorophenyl)cyclopropane-1-carbonitrile**



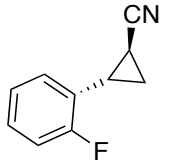
yellowish oil (52 mg, 81%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.30 – 7.24 (m, 1H), 6.98 – 6.93 (m, 1H), 6.92 – 6.89 (m, 1H), 6.81 – 6.77 (m, 1H), 2.62 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.65 (dt, *J* = 9.2, 5.6 Hz, 1H), 1.59 – 1.54 (m, 2H), 1.44 (ddd, *J* = 8.9, 6.6, 5.5 Hz, 1H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = -112.39 – -112.46 (m); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 163.77, 162.14, 140.12 (d, *J* = 7.8 Hz), 130.34 (d, *J* = 8.6 Hz), 122.13 (d, *J* = 3.0 Hz), 120.61, 114.41 (d, *J* = 21.2 Hz), 113.27 (d, *J* = 22.1 Hz), 24.52 (d, *J* = 2.4 Hz), 15.34, 6.89; HRMS (ESI): m/z calc. for [$C_{10}H_9NF$]: 162.07135, found 162.07114; IR (KBr): ν_{max}/cm^{-1} = 3842, 3392, 3051, 2661, 2334, 240, 2095, 1796, 1590, 1457, 1244, 1143, 1054, 974, 875, 779, 687.

***trans*-2-(*o*-tolyl)cyclopropane-1-carbonitrile**



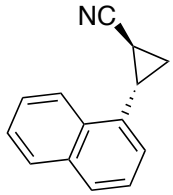
yellowish oil (51 mg, 74%) ; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.22 – 7.18 (m, 2H), 7.17 – 7.12 (m, 1H), 6.98 – 6.94 (m, 1H), 2.61 (dt, *J* = 9.1, 6.0 Hz, 1H), 2.46 (s, 3H), 1.66 – 1.59 (m, 1H), 1.48 – 1.42 (m, 2H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 138.21, 135.62, 130.16, 127.60, 126.10, 125.91, 121.41, 23.62, 19.58, 13.95, 5.11; HRMS (ESI): m/z calc. for [$C_{11}H_{11}NNa$]: 180.07837, found 180.07820; IR (KBr): ν_{max}/cm^{-1} = 3033, 2236, 2100, 1902, 1747, 1456, 1037, 934, 747.

***trans*-2-(2-fluorophenyl)cyclopropane-1-carbonitrile**



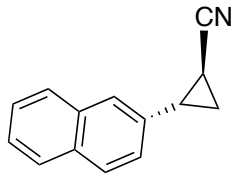
yellowish oil (44 mg, 68%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.27 – 7.21 (m, 1H), 7.11 – 7.02 (m, 2H), 6.97 (td, *J* = 7.6, 1.7 Hz, 1H), 2.76 – 2.64 (m, 1H), 1.67 – 1.61 (m, 2H), 1.52 – 1.46 (m, 1H); ^{19}F NMR (564 MHz, Chloroform-*d*) δ -118.01 – -118.18 (m); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 162.48, 160.84, 128.99 (d, *J* = 8.4 Hz), 127.24 (d, *J* = 3.5 Hz), 124.71 (d, *J* = 14.1 Hz), 124.27 (d, *J* = 3.6 Hz), 120.85, 115.65 (d, *J* = 21.9 Hz), 19.24 (d, *J* = 4.0 Hz), 14.19 (d, *J* = 2.2 Hz), 5.48 (d, *J* = 2.4 Hz); HRMS (ESI): m/z calc. for [$C_{10}H_8NFNa$]: 184.05330, found 184.05356; IR (KBr): ν_{max}/cm^{-1} = 3049, 2239, 1495, 1452, 1238, 1203, 1096, 1033, 942, 816, 755.

***trans*-2-(naphthalen-1-yl)cyclopropane-1-carbonitrile**



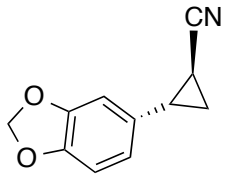
colorless solid (40 mg, 51%); m.p. = 87 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.25 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.89 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.64 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.39 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.24 (dt, *J* = 7.1, 1.2 Hz, 1H), 3.09 – 3.02 (m, 1H), 1.78 (dt, *J* = 9.0, 5.0 Hz, 1H), 1.64 – 1.53 (m, 2H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 33.50 (d, *J* = 6.2 Hz), 132.70, 128.74, 128.47, 126.84, 126.26, 125.17, 124.40, 123.60, 121.46, 23.33, 13.74, 5.18; HRMS (ESI): m/z calc. for [$C_{14}H_{11}NK$]: 232.05231, found 232.05228; IR (KBr): ν_{max}/cm^{-1} = 3055, 2924, 2235, 2111, 1816, 1675, 1507, 1259, 1034, 795, 772, 705.

***trans*-2-(naphthalen-2-yl)cyclopropane-1-carbonitrile**



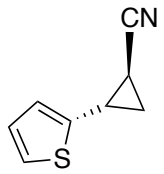
colorless solid (45 mg, 58%); m.p. = 154 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.84 – 7.73 (m, 3H), 7.60 – 7.55 (m, 1H), 7.53 – 7.42 (m, 2H), 7.21 (dd, *J* = 8.5, 1.9 Hz, 1H), 2.80 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.70 (dt, *J* = 9.1, 5.3 Hz, 1H), 1.65 (dt, *J* = 8.5, 5.1 Hz, 1H), 1.58 (ddd, *J* = 8.7, 6.7, 5.1 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 134.90, 133.21, 132.58, 128.62, 127.68, 127.48, 126.59, 126.05, 125.18, 124.29, 121.06, 25.19, 15.21, 6.63; HRMS (ESI): m/z calc. for [$C_{14}H_{11}NNa$]: 216.07837, found 216.07834; IR (KBr): ν_{max}/cm^{-1} = 3741, 3035, 2927, 2662, 2327, 2234, 2092, 1741, 1618, 1506, 1446, 1220, 1035, 955, 798.

***trans*-2-(benzo[*d*][1,3]dioxol-5-yl)cyclopropane-1-carbonitrile**



yellowish solid (51%, 68%); m.p. = 90 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.73 (d, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.56 (d, *J* = 1.8 Hz, 1H), 5.94 (s, 2H), 2.57 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.56 (dt, *J* = 9.2, 5.4 Hz, 1H), 1.46 (ddd, *J* = 8.8, 5.5, 4.7 Hz, 1H), 1.37 (ddd, *J* = 8.8, 6.7, 5.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 48.00, 146.93, 131.29, 121.08, 120.01, 108.38, 106.79, 101.21, 24.84, 15.00, 6.42; HRMS (ESI): m/z calc. for [$C_{11}H_9NO_2Na$]: 210.05255, found 210.05211; IR (KBr): ν_{max}/cm^{-1} = 3020, 2896, 2324, 2236, 2102, 1852, 1495, 1449, 1242, 1109, 1035, 930, 803.

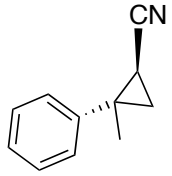
***trans*-2-(thiophen-2-yl)cyclopropane-1-carbonitrile**



yellowish oil (53 mg, 88%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.16 (dt, *J* = 5.1, 1.3 Hz, 1H), 6.92 (ddd, *J* = 5.0, 3.5, 1.3 Hz, 1H), 6.86 (dq, *J* = 3.5, 1.2 Hz, 1H), 2.79 (dddt, *J* = 9.0, 6.6, 4.6, 1.1 Hz, 1H), 1.66 (dtd, *J* = 9.1, 5.5, 1.3 Hz, 1H), 1.60 (dddd, *J* = 8.8, 5.7, 4.5, 1.3 Hz, 1H), 1.46 (dddd, *J* = 8.8, 6.5, 5.3, 1.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 141.32, 127.07, 124.98, 124.27, 120.49, 20.29, 16.18, 7.63; HRMS (ESI): m/z calc. for [C_8H_7NNaS]: 172. 01914, found 172.01872; IR (KBr): ν_{max}/cm^{-1} = 3105, 30442329, 2238, 2114, 1441, 1385, 1239, 1043, 914, 846, 790, 702.

Alpha methylated Cyclopropanes

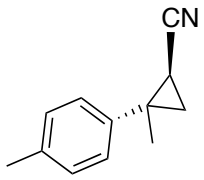
***trans*-2-phenyl-2-methyl-cyclopropane-1-carbonitrile**



colorless oil (44 mg, 71%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.35 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 1.70 – 1.64 (m, 4H), 1.57 (dd, *J* = 9.1, 5.0 Hz, 1H), 1.31 (t, *J* = 5.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 142.67, 128.74, 127.37, 127.32, 120.27, 28.71, 23.48, 21.27, 11.25; HRMS (ESI): m/z calc. for [$C_{11}H_{11}NNa$]: 180.07837, found 1807832; IR (KBr): ν_{max}/cm^{-1} = 3846, 3517, 2947, 2677, 2253, 2093, 1865, 1447, 1254, 1075, 912, 727.

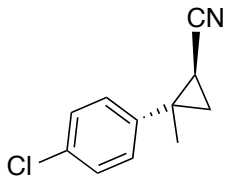
The analytical data is in correspondence with the literature [3]

***trans*-2-(*p*-tolyl)-2-methylcyclopropane-1-carbonitrile**



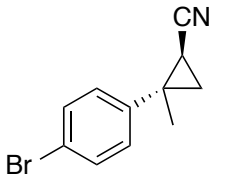
colorless solid (61 mg, 89%); m.p. = 35 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.19 – 7.08 (m, 4H), 2.33 (s, 3H), 1.66 – 1.61 (m, 4H), 1.54 (dd, *J* = 9.1, 5.0 Hz, 1H), 1.29 (t, *J* = 5.2 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ =139.74, 137.07, 129.37, 127.24, 120.38, 28.40, 23.53, 21.29, 21.00, 11.23; HRMS (ESI): m/z calc. for [$C_{12}H_{13}NNa$]: 194.09402, found 194.09398; IR (KBr): ν_{max}/cm^{-1} = 3025, 2966, 2234, 2102, 1902, 1746, 1516, 1445, 1369, 1259, 1075, 901, 817, 721.

***trans*-2-(4-chlorophenyl)-2-methylcyclopropane-1-carbonitrile**



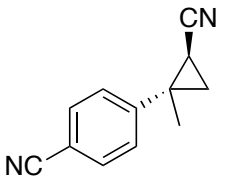
colorless oil (65 mg, 85%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.30 – 7.27 (m, 2H), 7.22 – 7.18 (m, 2H), 1.67 – 1.60 (m, 4H), 1.53 (dd, *J* = 9.3, 5.2 Hz, 1H), 1.32 (td, *J* = 5.3, 1.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 141.15, 133.18, 128.86 (d, *J* = 13.0 Hz), 119.91, 28.17, 23.38, 21.22, 11.35; HRMS (ESI): m/z calc. for [$C_{11}H_{10}NClNa$]: 214.03940, found 214.03879, IR (KBr): ν_{max}/cm^{-1} = 2971, 2237, 2112, 1494, 1443, 1399, 1090, 1012, 949, 897 830, 778, 728.

***trans*-2-(4-bromophenyl)-2-methylcyclopropane-1-carbonitrile**



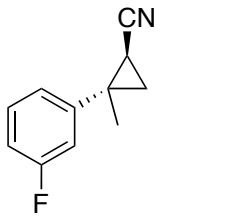
yellowish solid (62 mg, 65%); m.p. = 53 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.49 – 7.37 (m, 2H), 7.18 – 7.09 (m, 2H), 1.66 – 1.61 (m, 4H), 1.53 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.32 (t, *J* = 5.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 141.67, 131.87, 129.16, 121.25, 119.88, 28.24, 23.33, 21.17, 11.31; HRMS (ESI): m/z calc. for [$C_{11}H_{10}NBrNa$]: 257.9888, found 257.98871; IR (KBr): ν_{max}/cm^{-1} = 3042, 2968, 2236, 2106, 1488, 1448, 1388, 1076, 1007, 825, 713.

***trans*-2-(4-cyanophenyl)-2-methylcyclopropyl-1-carbonitrile**



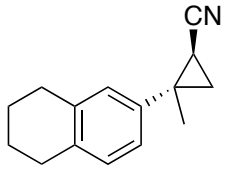
cololess solid (62 mg, 85%); m.p. = 59 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.66 – 7.59 (m, 2H), 7.41 – 7.34 (m, 2H), 1.71 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.67 (s, 3H), 1.59 (dd, *J* = 9.2, 5.4 Hz, 1H) 1.40 (t, *J* = 5.5 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 147.73, 132.64, 128.14, 119.33, 118.35, 111.38, 28.40, 22.88, 21.31, 11.75; HRMS (ESI): m/z calc. for [$C_{12}H_{10}N_2Na$]: 205.07429, found 205.07321; IR (KBr): ν_{max}/cm^{-1} = 3046, 2974, 2231, 2097, 1811, 1692, 1608, 1508, 1445, 1403, 1284, 1109, 1079, 842, 774.

***trans*-2-(3-fluorophenyl)-2-methylcyclopropane-1-carbonitrile**



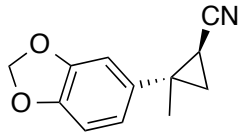
yellowish oil (39 mg, 56%) ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 1H), 7.07 – 7.02 (m, 1H), 6.99 – 6.91 (m, 2H), 1.68 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.65 (s, 3H), 1.56 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.33 (t, *J* = 5.4 Hz, 1H); ^{19}F NMR (564 MHz, Chloroform-*d*) δ -112.23 – -112.32 (m); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 163.62, 161.98, 145.09 (d, *J* = 7.3 Hz), 130.35 (d, *J* = 8.4 Hz), 122.85 (d, *J* = 3.0 Hz), 119.82, 114.41 (dd, *J* = 21.0, 16.4 Hz), 28.24, 23.13, 21.36, 11.57; ^{19}F NMR (564 MHz,$CDCl_3$) δ = -112.28 (ddd, *J* = 10.0, 8.5, 6.0 Hz); HRMS (ESI): m/z calc. for [$C_{11}H_{10}NFN$]: 198.06895, found 198.06897; IR (KBr): ν_{max}/cm^{-1} = 3048, 2972, 2237, 2115, 1613, 1587, 1490, 1440, 1267, 1201, 1074, 959, 922, 870, 785, 694.

***trans*-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-2-methylcyclopropane-1-carbonitrile**



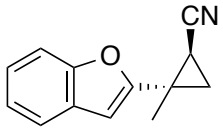
colorless solid (64mg, 76%); m.p. = 86 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.03 – 6.95 (m, 3H), 2.77 – 2.68 (m, 4H), 1.78 (p, *J* = 3.4 Hz, 4H), 1.66 – 1.61 (m, 4H), 1.53 (dd, *J* = 9.1, 5.0 Hz, 1H), 1.27 (t, *J* = 5.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 139.81, 137.52, 136.39, 129.49, 128.07, 124.45, 120.46, 29.39, 29.01, 28.47, 23.58, 23.08 (d, *J* = 3.0 Hz), 21.26, 11.14; HRMS (ESI): m/z calc. for [$C_{15}H_{17}NNa$]: 234.12532, found 234.12526; IR (KBr): ν_{max}/cm^{-1} = 3038, 2929, 2858, 2231, 1802, 1698, 1501, 1435, 1248, 1183, 1081, 917, 807, 712.

***trans*-2-(benzo[*d*][1,3]dioxol-5-yl)-2-methylcyclopropane-1-carbonitrile**



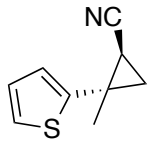
yellowish solid (53 mg, 66%); m.p. = 72 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.77 – 6.71 (m, 3H), 5.94 (s, 2H), 1.63 – 1.59 (m, 4H), 1.50 (dd, *J* = 9.1, 5.0 Hz, 1H), 1.26 (t, *J* = 5.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 147.80, 146.73, 136.69, 120.64, 120.23, 108.28, 108.17, 101.19, 28.75, 23.86, 21.40, 11.30; HRMS (ESI): m/z calc. for [$C_{12}H_{11}O_2NK$]: 240.0414, found 240.04204; IR (KBr): ν_{max}/cm^{-1} = 2972, 2897, 2231, 1490, 1457, 1434, 1349, 1226, 1080, 1033, 924, 869, 808, 728.

***trans*-2-(benzofuran-2-yl)-2-methylcyclopropane-1-carbonitrile**



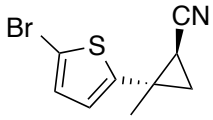
yellowish solid (65 mg, 82%); m.p. = 54°C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.52 – 7.46 (m, 1H), 7.36 – 7.34 (m, 1H), 7.26 – 7.19 (m, 2H), 6.58 – 6.55 (m, 1H), 2.11 (dd, *J* = 9.3, 6.0 Hz, 1H), 1.90 (dd, *J* = 9.4, 5.2 Hz, 1H), 1.77 (s, 3H), 1.39 (dd, *J* = 6.0, 5.2 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 157.05, 154.18, 128.40, 124.16, 123.01, 120.57, 119.23, 110.84, 102.85, 22.35, 21.21, 18.36, 11.77; HRMS (ESI): m/z calc. for [$C_{13}H_{11}ONNa$]: 220.07329, found 220.07317; IR (KBr): ν_{max}/cm^{-1} = 2976, 2238, 2112, 1597, 1454, 1253, 1169, 1090, 960, 938, 807, 747, 673.

***trans*-2-(thiophen-2-yl)-2-methylcyclopropane-1-carbonitrile**



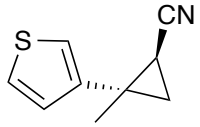
colorless oil (44 mg, 67%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.04 (dd, *J* = 3.0, 1.4 Hz, 1H), 6.87 (dd, *J* = 5.1, 1.4 Hz, 1H), 1.69 (s, 3H), 1.66 (dd, *J* = 9.1, 5.7 Hz, 1H), 1.57 (dd, *J* = 9.1, 5.2 Hz, 1H), 1.33 (t, *J* = 5.4 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 143.70, 126.67, 125.41, 120.70, 119.87, 24.15, 22.34, 21.78, 12.49; HRMS (ESI): m/z calc. for [C_9H_9NKS]: 202.00873, found 202.00871; IR (KBr): ν_{max}/cm^{-1} = 3102, 2971, 2237, 1442, 1263, 1070, 841, 780, 701.

***trans*-2-(5-bromothiophen-2-yl)-2-methylcyclopropane-1-carbonitrile**



yellow oil (62 mg, 64%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 3.8 Hz, 1H), 6.59 (d, *J* = 3.8 Hz, 1H), 1.75 – 1.68 (m, 4H), 1.60 (dd, *J* = 9.2, 5.4 Hz, 1H), 1.38 (t, *J* = 5.6 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 148.51, 129.63, 124.33, 119.08, 110.42, 24.39, 22.95, 22.60, 13.78; HRMS (ESI): m/z calc. for [$C_9H_8NBrNaS$] 263.94530:, found 263.94537; IR (KBr): υ = 3093, 2969, 2325, 2238, 1903, 1741 1442, 1044, 960, 790, 666.

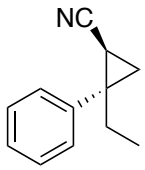
***trans*-2-(thiophen-3-yl))-2-methylcyclopropane-1-carbonitrile**



off-white solid (45 mg, 69%); m.p. = 99 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = .28 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.03 (dd, *J* = 3.0, 1.4 Hz, 1H), 6.87 (dd, *J* = 5.1, 1.4 Hz, 1H), 1.69 (s, 3H), 1.66 (dd, *J* = 9.1, 5.7 Hz, 1H), 1.57 (dd, *J* = 9.1, 5.2 Hz, 1H), 1.33 (t, *J* = 5.4 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 143.70, 126.67, 125.41, 120.71, 119.87, 24.15, 22.35, 21.78, 12.49; HRMS (ESI): m/z calc. for [C_9H_9NNaS]: 186.0379, found 186.03477; IR (KBr): ν_{max}/cm^{-1} = 3103, 2966, 2236, 1445, 1381, 1261, 1205, 1076, 935, 862, 771, 676.

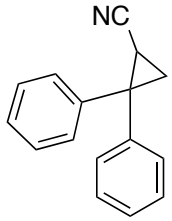
Other Cyclopropanes and Cyclopropene

***trans*-phenyl-2-ethylcyclopropane-1-carbonitrile**



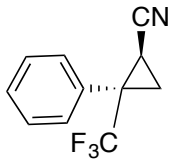
yellow oil (47 mg, 69%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 3H), 1.93 (dqd, *J* = 14.7, 7.3, 1.2 Hz, 1H), 1.82 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.68 (dd, *J* = 9.0, 5.4 Hz, 1H), 1.48 (ddd, *J* = 9.0, 4.9, 1.2 Hz, 1H), 1.28 (t, *J* = 5.2 Hz, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 140.78, 129.03, 128.52, 127.43, 120.44, 34.83, 30.55, 20.19, 10.82, 10.25; HRMS (ESI): m/z calc. for [$C_{12}H_{13}NK$]: 210.06796, found 210.06786; IR (KBr): ν_{max}/cm^{-1} = 3035, 2965, 2876, 2234, 2102, 1896, 1751, 1600, 1449, 1377, 1075, 910, 761, 698.

2,2-diphenylcyclopropane-1-carbonitrile



off-white solid (44 mg, 50%); m.p. = 91 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.47 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.19 (m, 6H), 2.23 (dd, *J* = 9.1, 5.7 Hz, 1H), 2.03 (t, *J* = 5.5 Hz, 1H), 1.81 (dd, *J* = 9.2, 5.2 Hz, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 142.29, 138.89, 129.36, 128.84, 128.78, 127.92, 127.77, 127.39, 119.48, 38.28, 21.02, 12.22; HRMS (ESI): m/z calc. for [$C_{16}H_{13}NNa$]: 242.09402, found 242.09387; IR (KBr): ν_{max}/cm^{-1} = 3028, 2926, 229, 2099, 1882, 1735, 1592, 1492, 1444, 756, 697.

2-phenyl-2-(trifluoromethyl)cyclopropane-1-carbonitrile



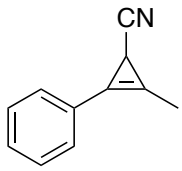
trans-Isomer

yellowish solid (48 mg, 57%); m.p. = 58 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.53 – 7.48 (m, 2H), 7.47 – 7.42 (m, 3H), 2.29 (dd, *J* = 9.6, 6.1 Hz, 1H), 1.94 (dd, *J* = 9.6, 5.8 Hz, 1H), 1.74 (tq, *J* = 6.0, 1.6 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 131.38, 129.97, 129.67, 128.97, 125.05 (q, *J* = 275.6 Hz), 116.96, 34.75 (q, *J* = 34.2 Hz), 16.21 (q, *J* = 2.4 Hz), 8.26 (d, *J* = 3.7 Hz), ^{19}F NMR (564 MHz,$CDCl_3$) δ = -71.19 (d, *J* = 1.5 Hz); HRMS (ESI): m/z calc. for [$C_{11}H_8NF_3Na$]: 234.05011, found 234.04968; IR (KBr): ν_{max}/cm^{-1} = 3049, 2250, 1380, 1341 1288, 1154, 1069, 764, 700, 670.

Cis-Isomer

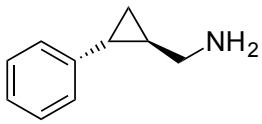
yellowish solid; m.p. = 58 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.46 – 7.36 (m, 5H), 2.07 – 1.99 (m, 2H), 1.73 (ddq, *J* = 9.1, 5.4, 2.0 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 132.75, 130.57, 129.69, 128.94, 123.99 (q, *J* = 275.6 Hz), 116.59, 35.68 (q, *J* = 34.3 Hz), 16.47 (q, *J* = 3.1 Hz), 8.84; ^{19}F-NMR (564 MHz, $CDCl_3$) δ = -67.49 (d, *J* = 1.9 Hz); HRMS (ESI): m/z calc. for [$C_{11}H_8NF_3Na$]: 234.05011, found 234.05008; IR (KBr): ν_{max}/cm^{-1} = 3038, 2247, 1452, 1352, 1286, 1150, 1076, 761, 696.

2-methyl-3-phenylcycloprop-2-ene-1-carbonitrile



yellow oil (44 mg, 71%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.57 – 7.51 (m, 2H), 7.48 – 7.43 (m, 2H), 7.43 – 7.38 (m, 1H), 2.39 (s, 3H), 2.14 (s, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 129.57, 129.26, 128.89, 125.61, 122.58, 104.71 (d, *J* = 5.6 Hz), 10.54, 5.33; HRMS (ESI): m/z calc. for [$C_{11}H_9NNa$]: 178.06272, found 178.06293; IR (KBr): ν_{max}/cm^{-1} = 3054, 2959, 2328, 2220, 2097, 1706, 1594, 1436, 1365, 1165, 1005, 760, 695.

***trans*-2-phenylcyclopropylmethanamine**



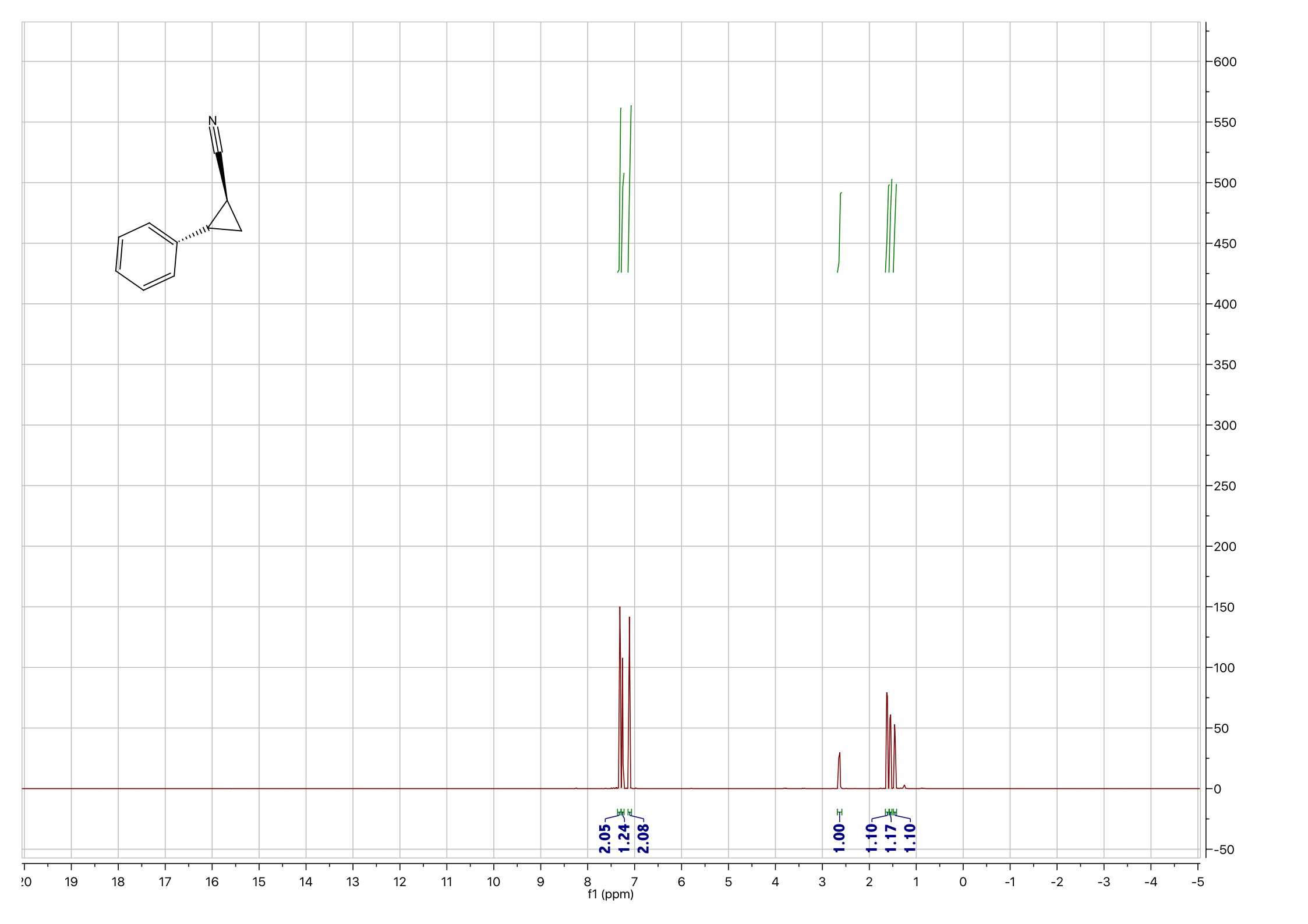
red oil (234 mg, 91%); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.27 – 7.21 (m, 2H), 7.17 – 7.12 (m, 1H), 7.08 – 7.02 (m, 2H), 1.72 (dt, *J* = 9.2, 4.8 Hz, 1H), 1.41 (brs, 2H), 1.31 – 1.25 (m, 1H), 0.91 (dt, *J* = 8.4, 5.0 Hz, 1H), 0.85 (dt, *J* = 8.7, 5.3 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 143.10, 128.27, 125.67, 125.42, 46.61, 26.83, 21.82, 14.61; MS (EI): m/z (%): 147.1 ([M], 5%), 106.1 ([M-C_2H_3N], 100%), 115.0 ([M-CH_6N], 36%), 129.0 ([M-H_4N] 12%), 78.0 ([M-C_6H_6] 9%); IR (KBr): ν_{max}/cm^{-1} = 3026, 3001, 2875, 2109, 1805, 1601, 1495, 1456, 1086, 1031, 876, 744, 696.

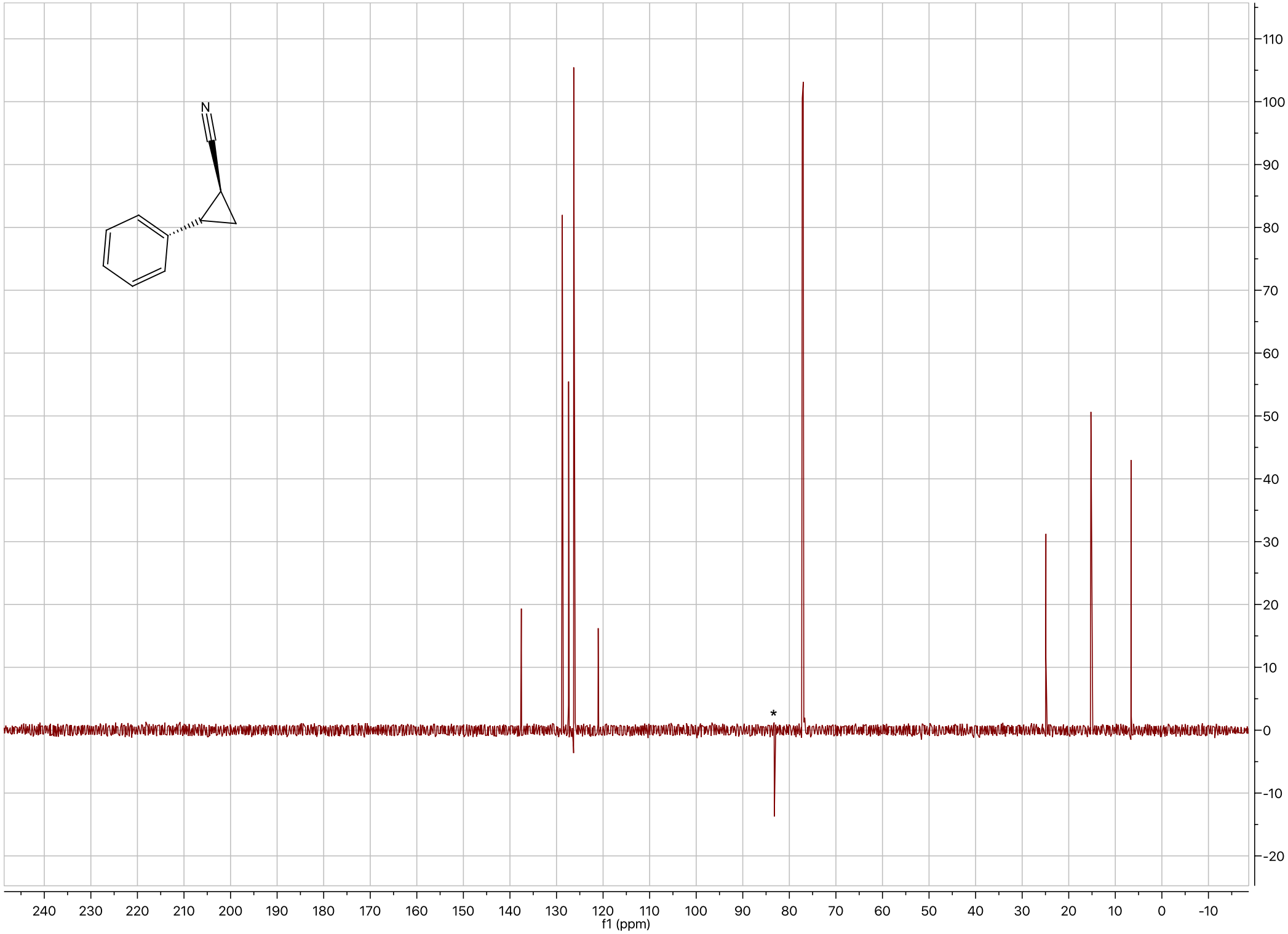
References:

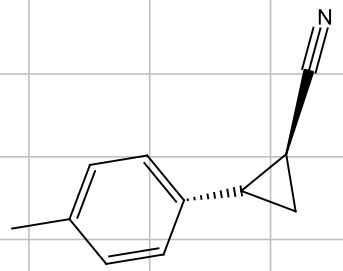
[1] T. Curtius, *Chem. Ber.*, **1898**, *31*, 2489-2492.

[2] M. Gao, N. N. Patwardhan, P. R. Carlier, *J. Am. Chem. Soc.*, **2013**, *135* (38), 14390–14400

[3] K. Thommes, G. Kiefer, R. Scopelliti, K. Severin, Angew. Chem. Int. Ed **2009**, *48*, 8115–8119

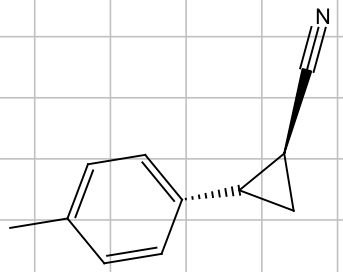

N
2.05
1.24
2.08
1.00
1.10
1.17
1.10
f1 (ppm)


N
*
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

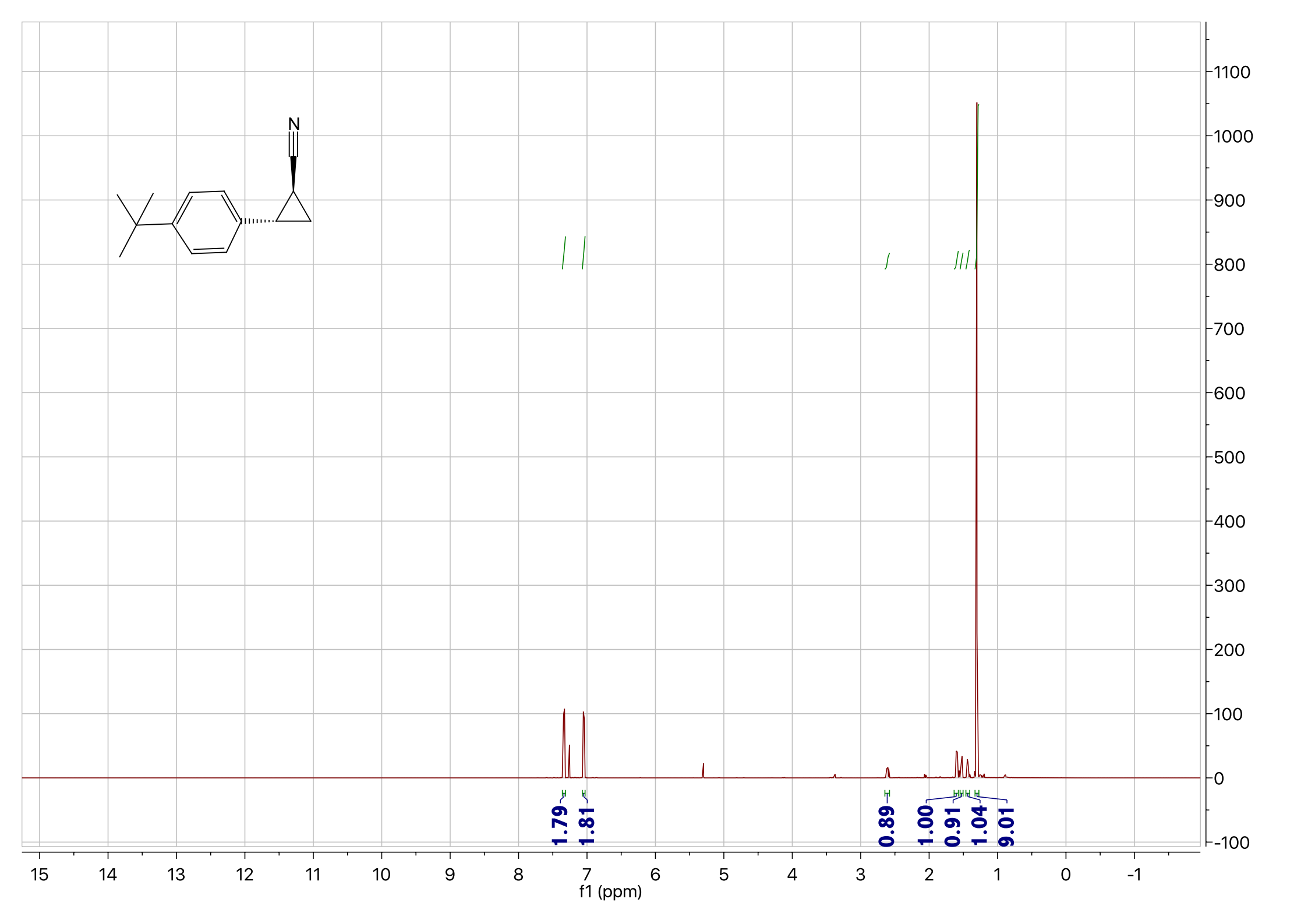


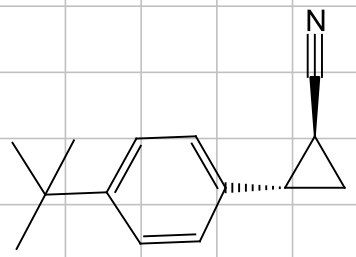
2.04
2.06
1.00
3.31
1.09
1.02
1.11

f1 (ppm)

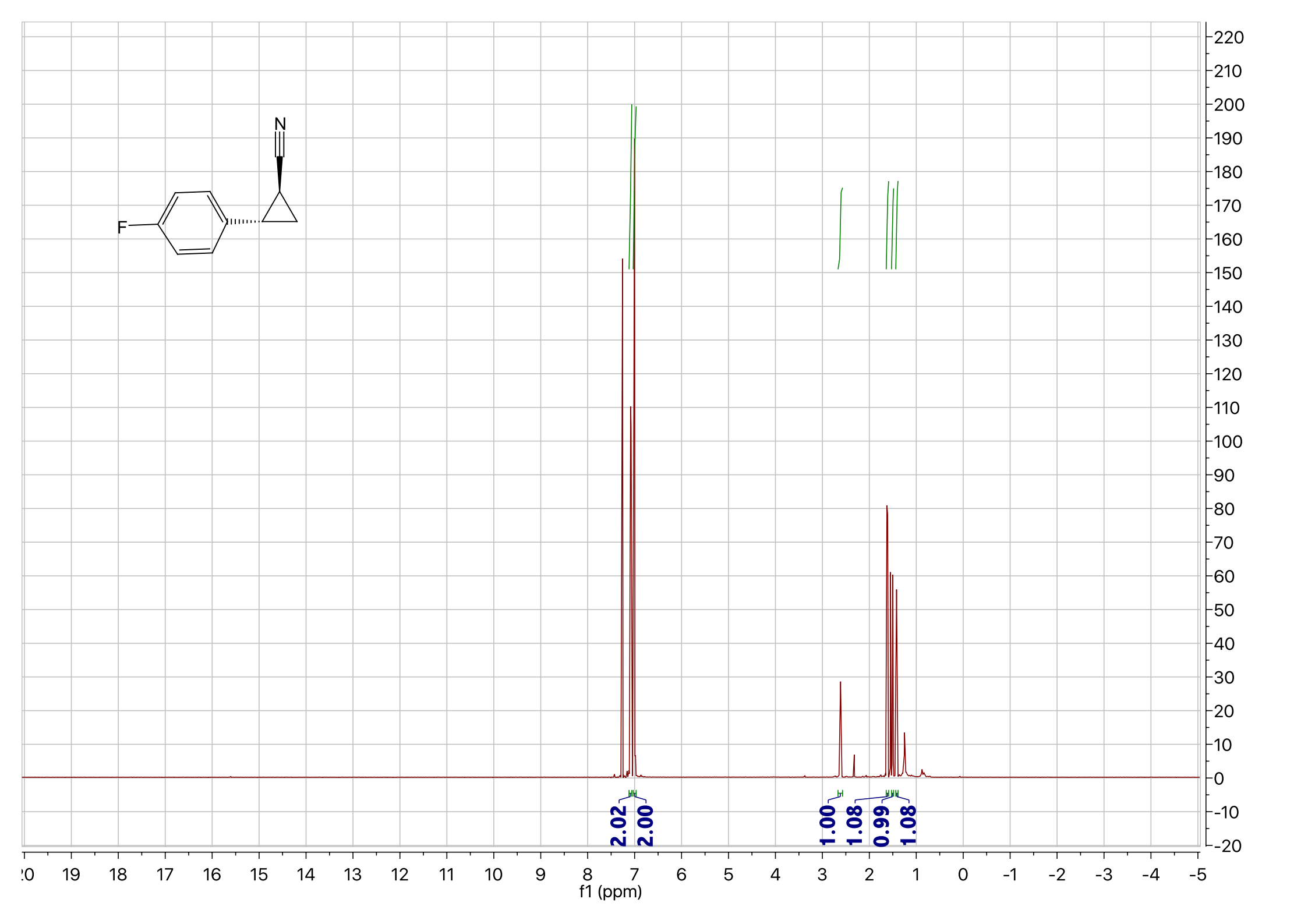

N

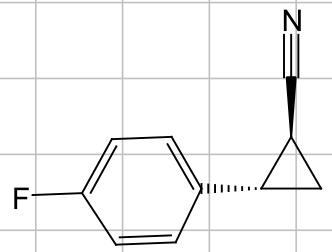
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
*
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
1.79
1.81
0.89
1.00
0.91
1.04
9.01
f1 (ppm)

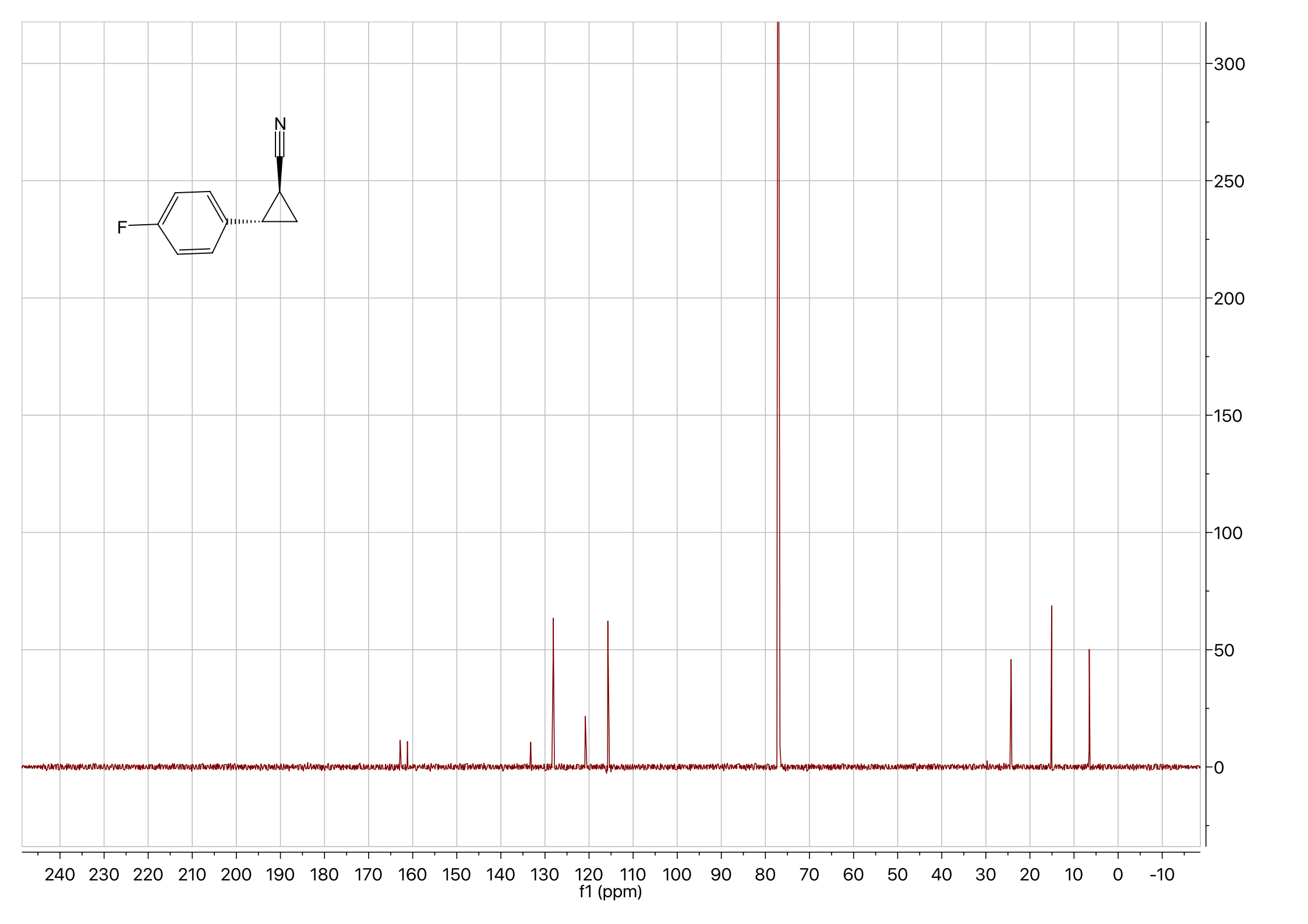


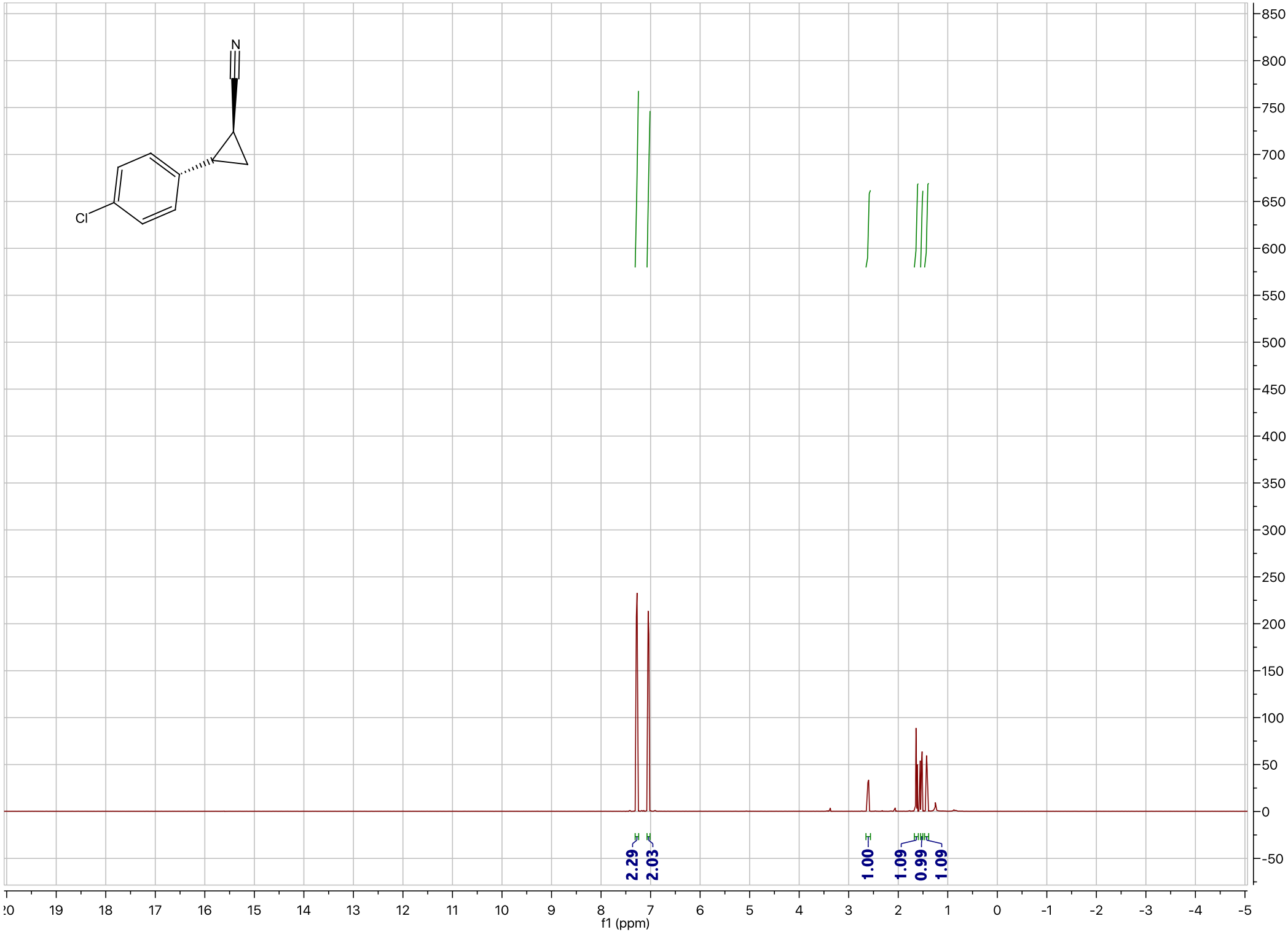
f1 (ppm)

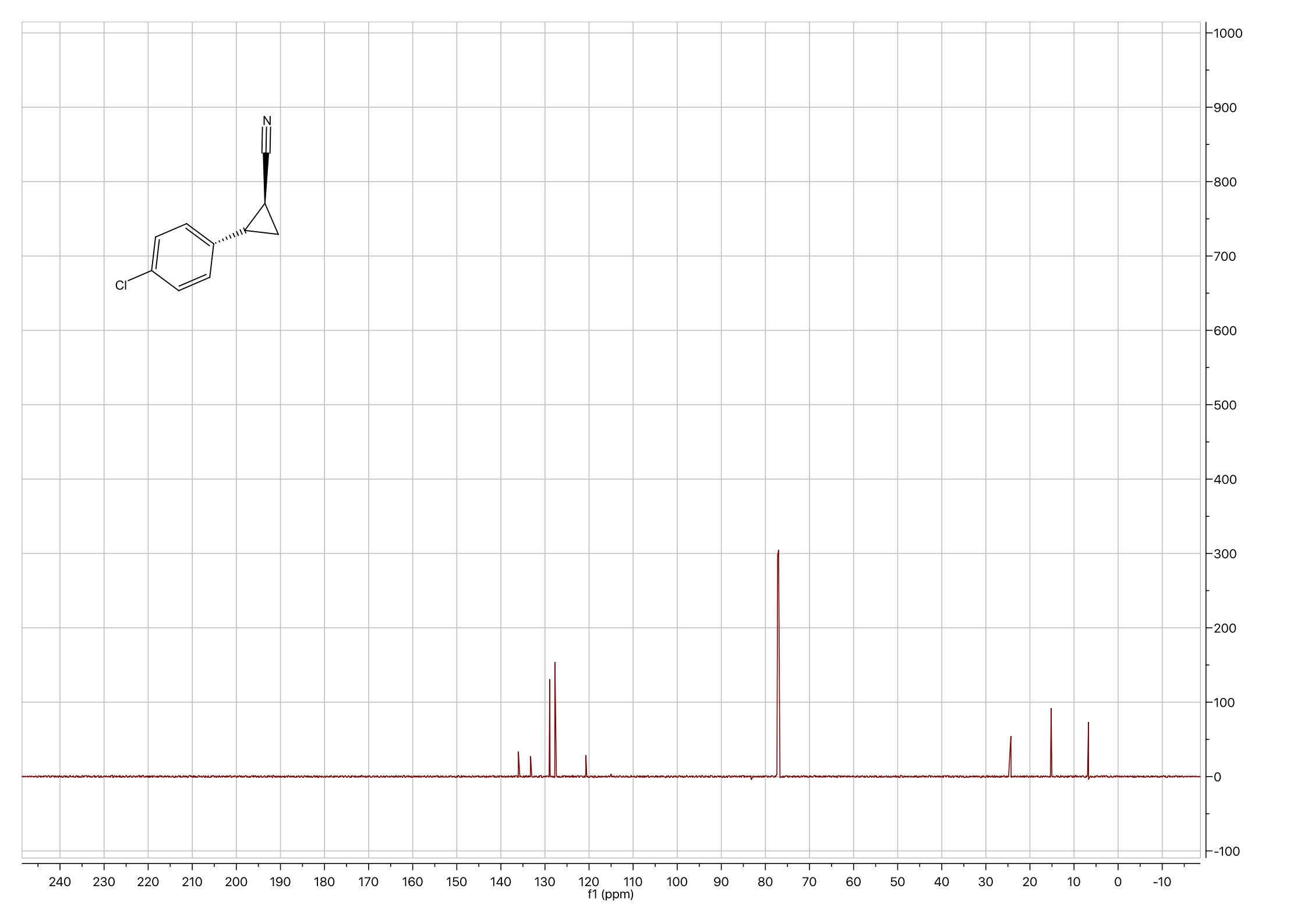

N
F
2.02
2.00
1.00
1.08
0.99
1.08
f1 (ppm)

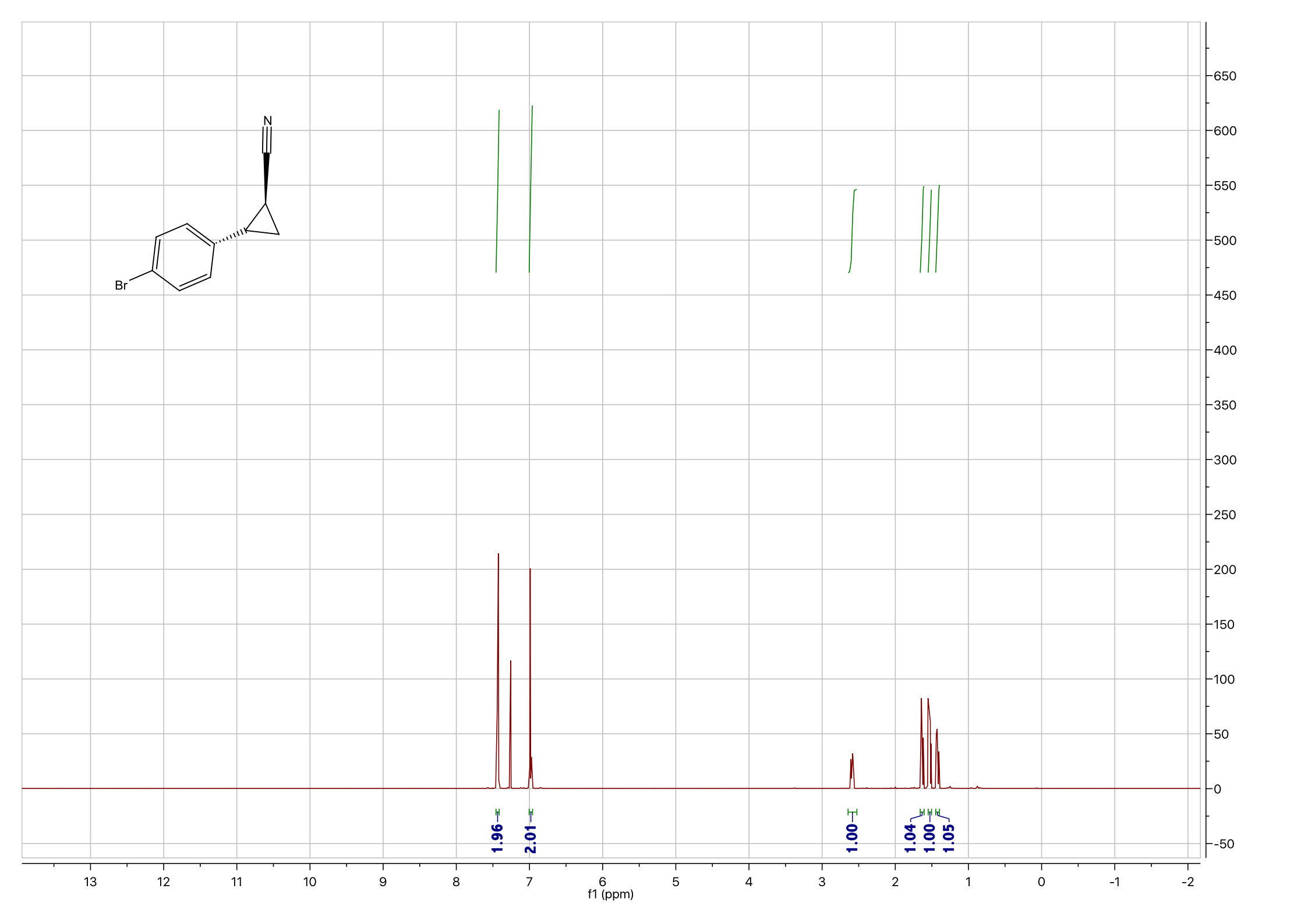

N
F

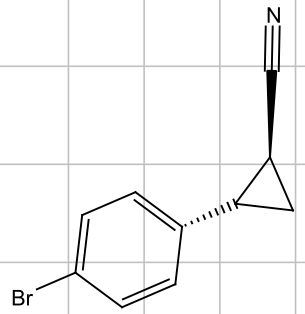
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


N
F
300
250
200
150
100
50
0
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

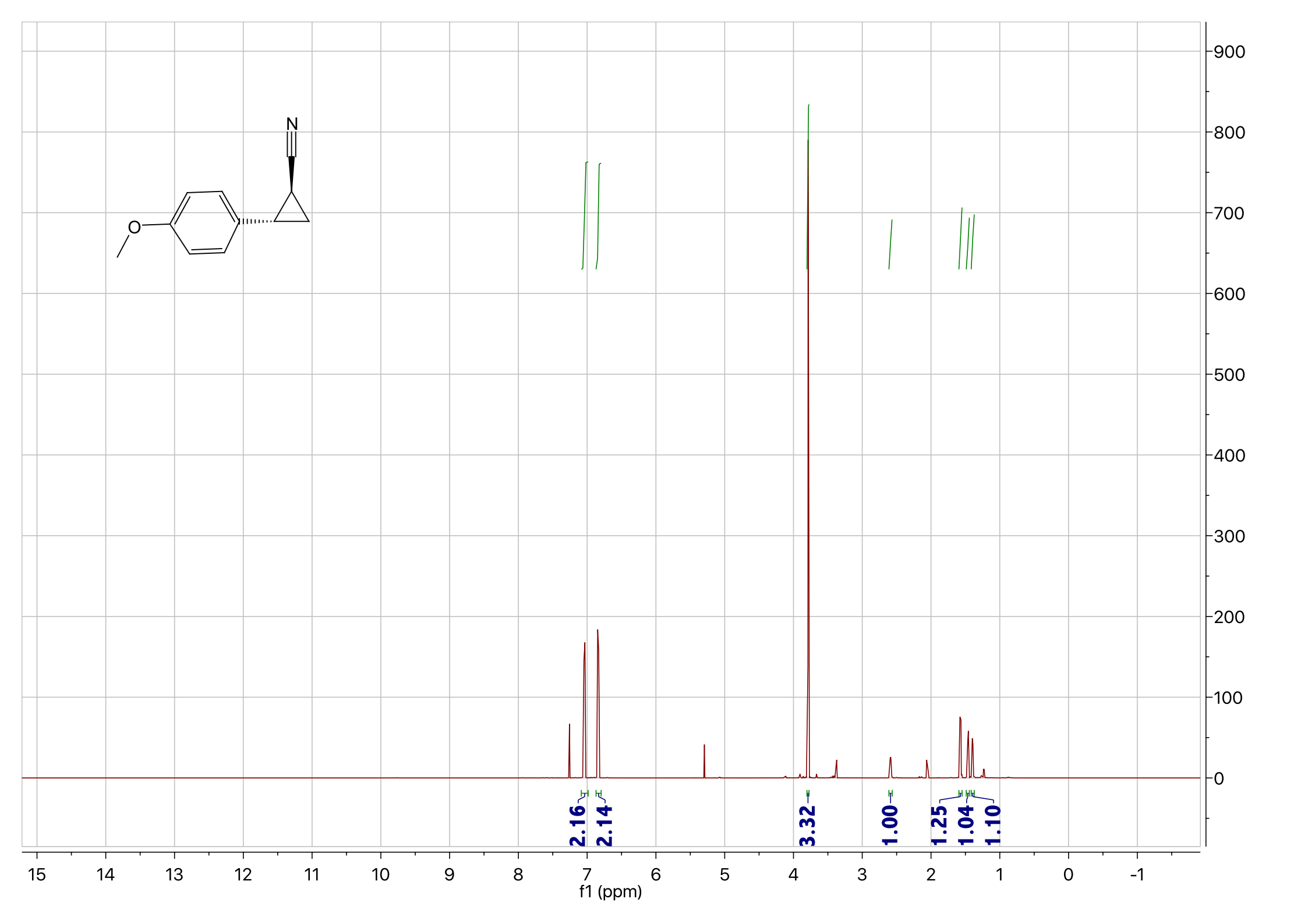

N
Cl
2.29
2.03
1.00
1.09
0.99
1.09
f1 (ppm)

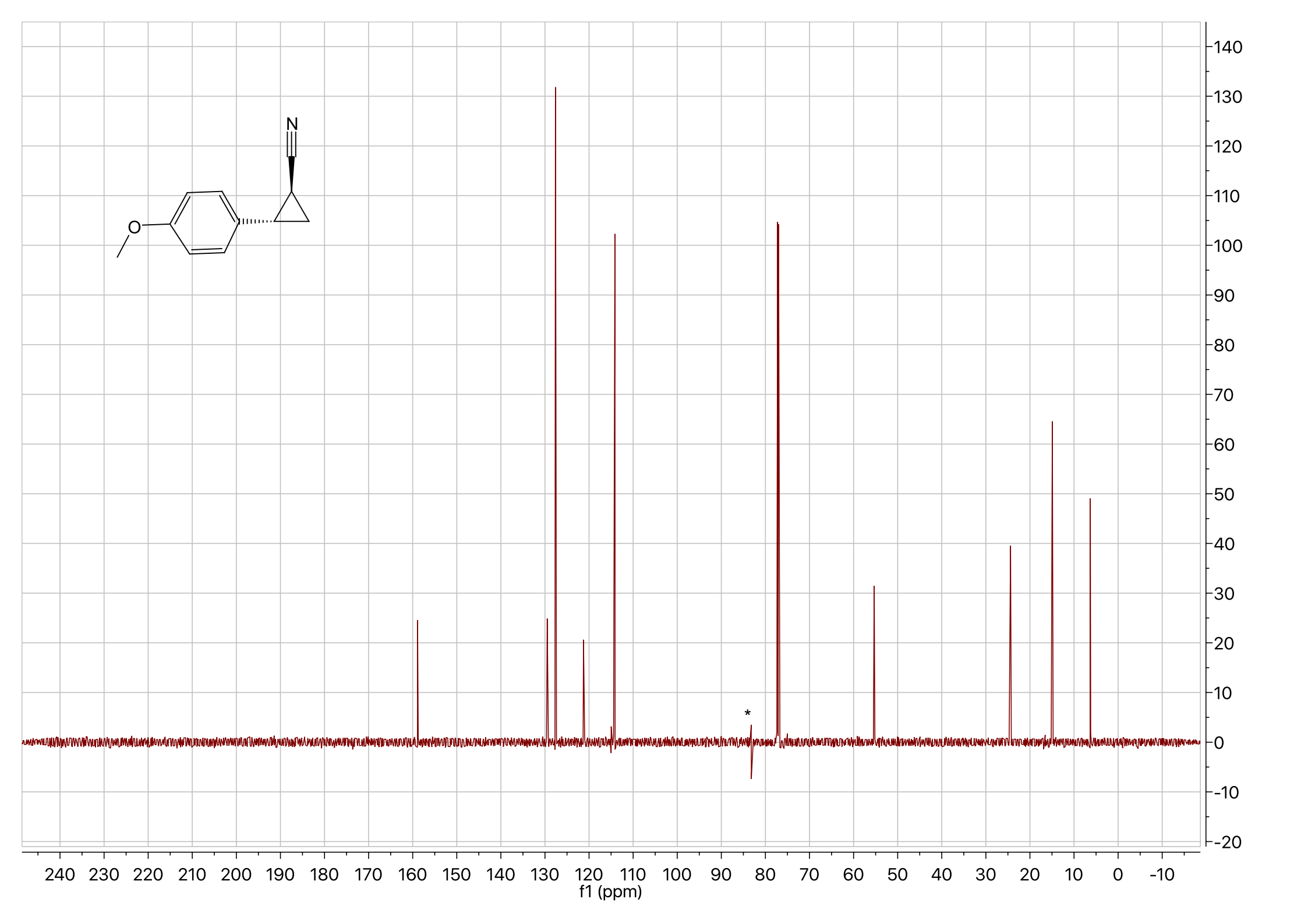

N
Cl
1000
900
800
700
600
500
400
300
200
100
0
-100
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

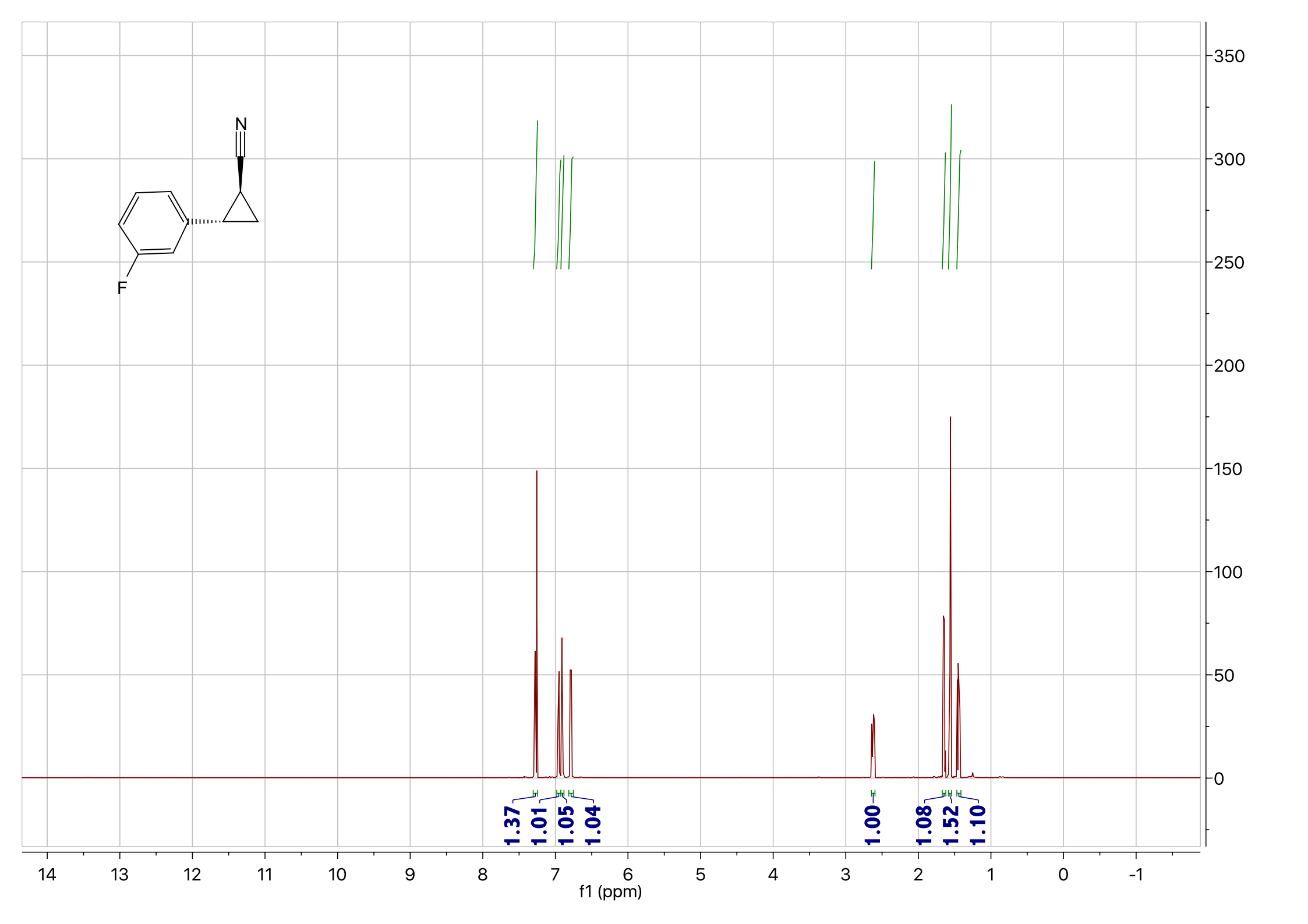

N
Br
1.96
2.01
1.00
1.04
1.00
1.05
f1 (ppm)

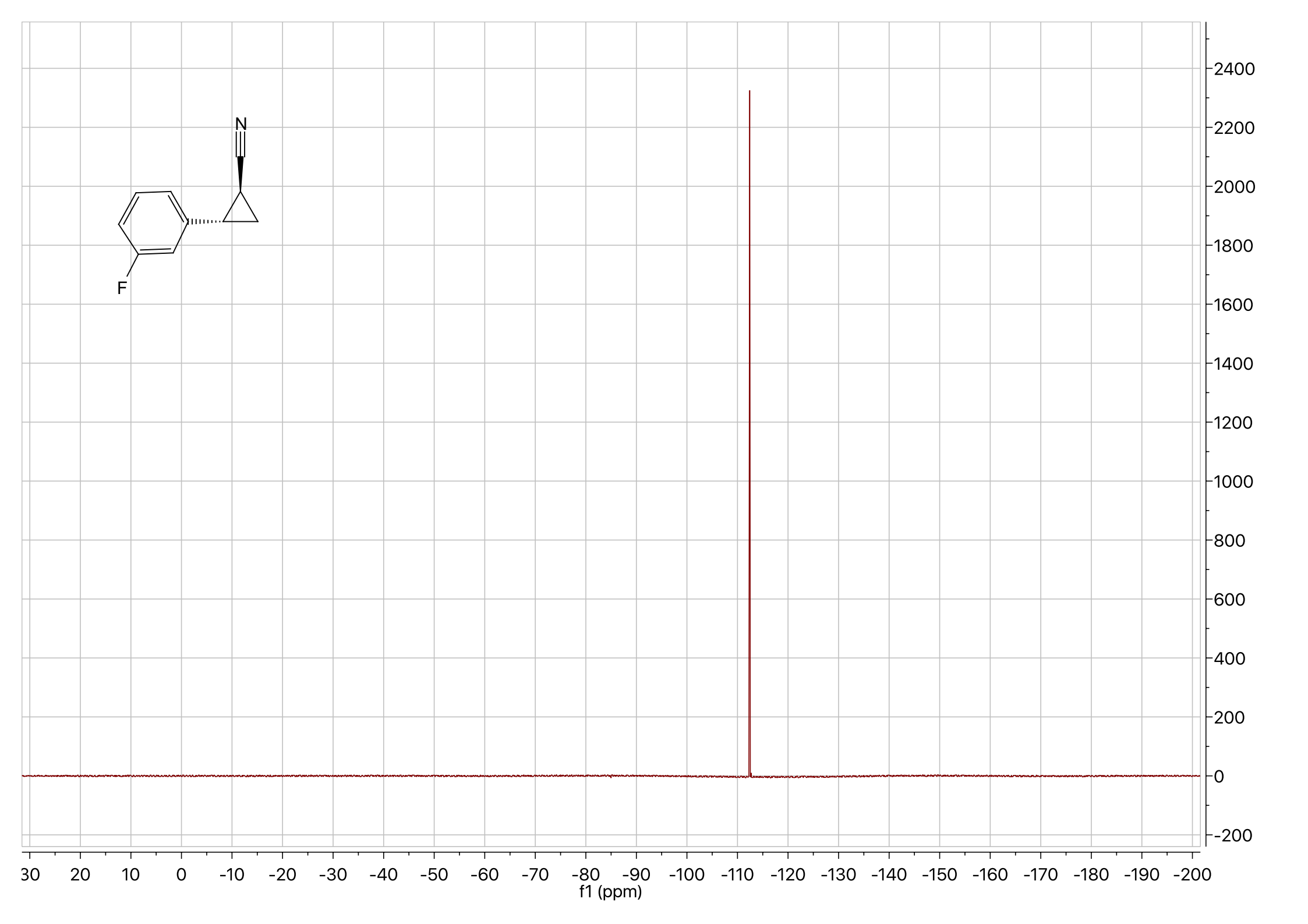


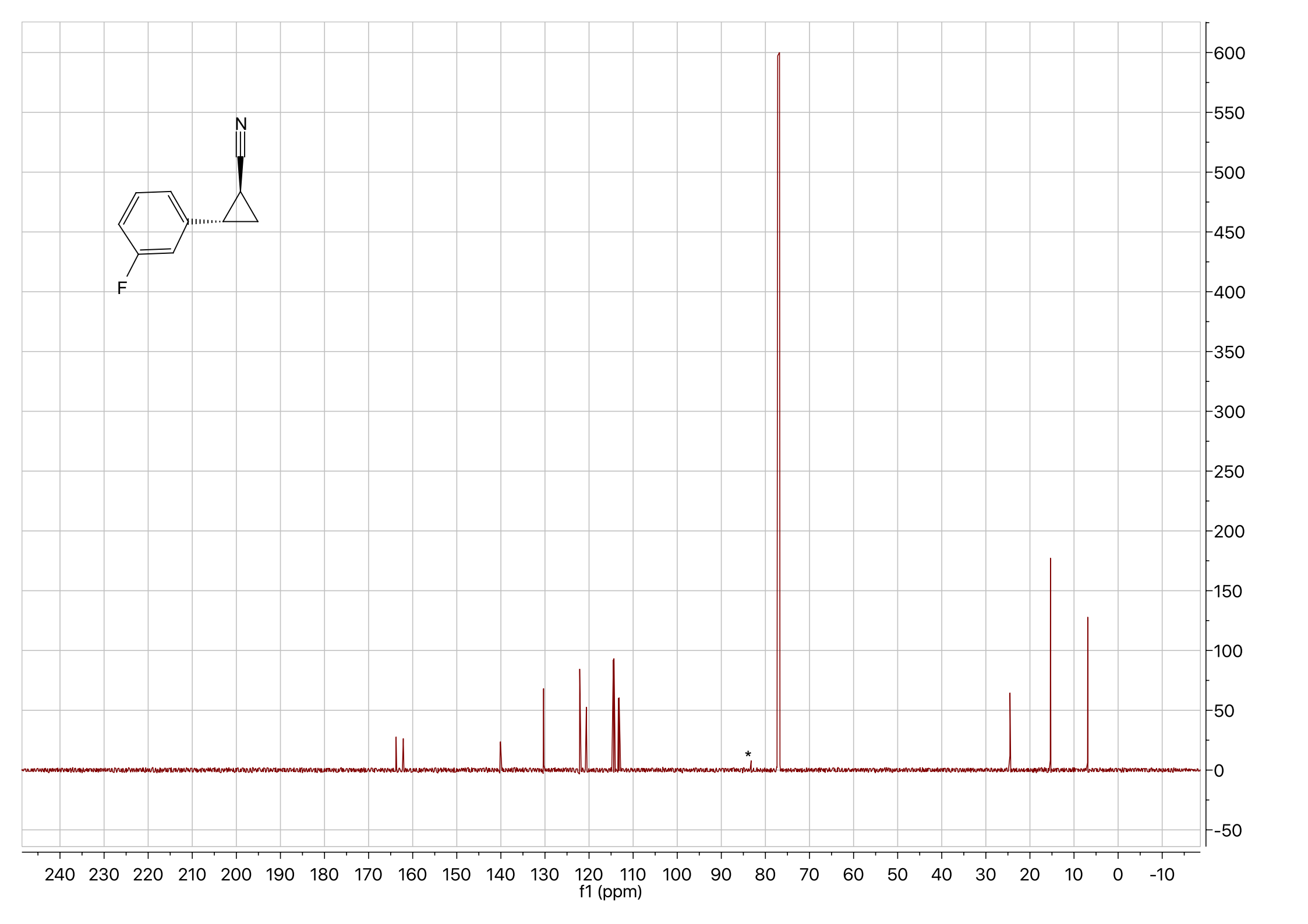
f1 (ppm)

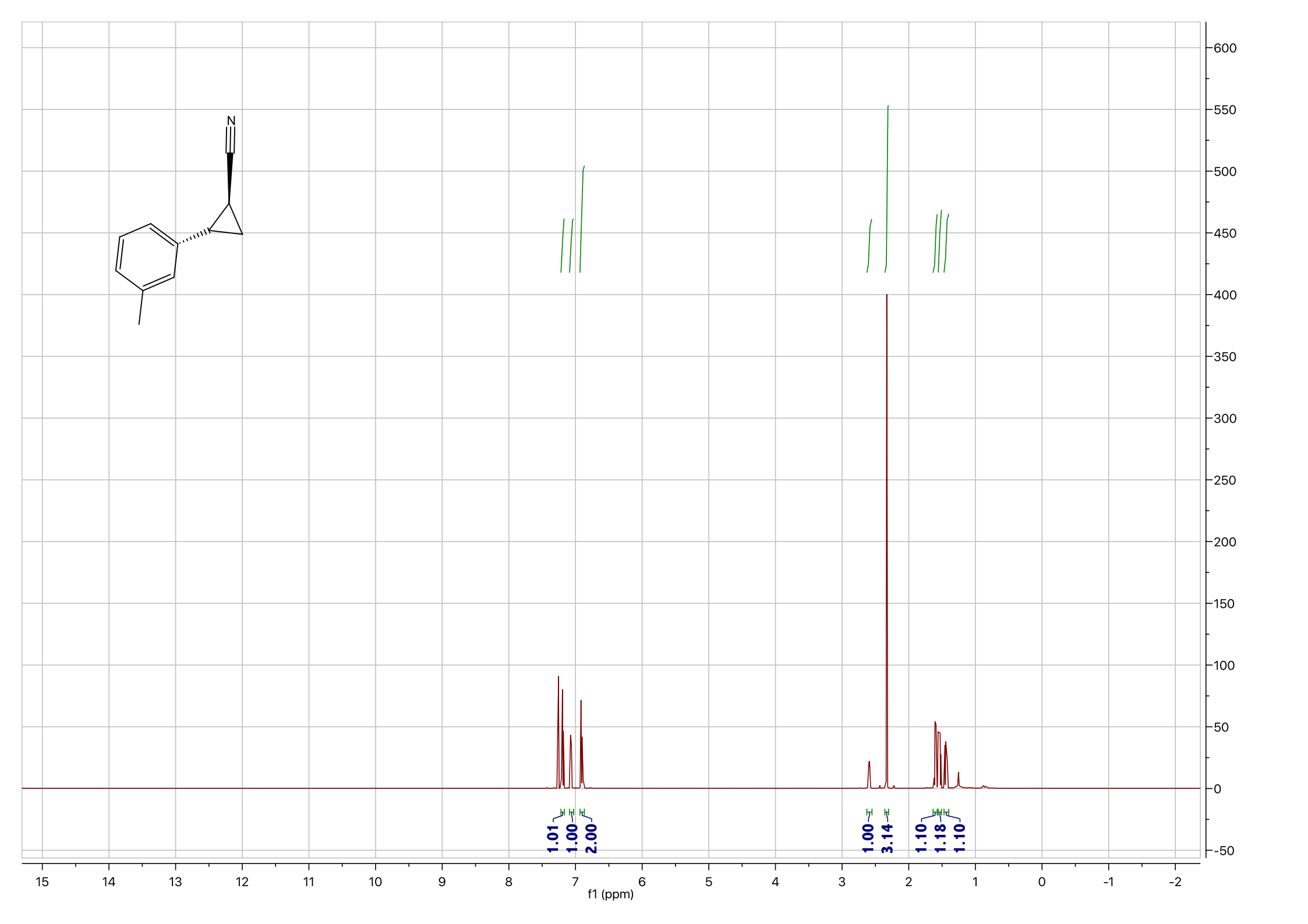

N
O
900
800
700
600
500
400
300
200
100
0
2.16
2.14
3.32
1.00
1.25
1.04
1.10
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

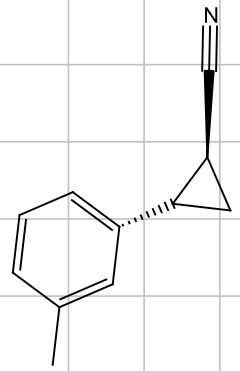

N
O
*
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
F
1.37
1.01
1.05
1.04
1.00
1.08
1.52
1.10
350
300
250
200
150
100
50
0
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

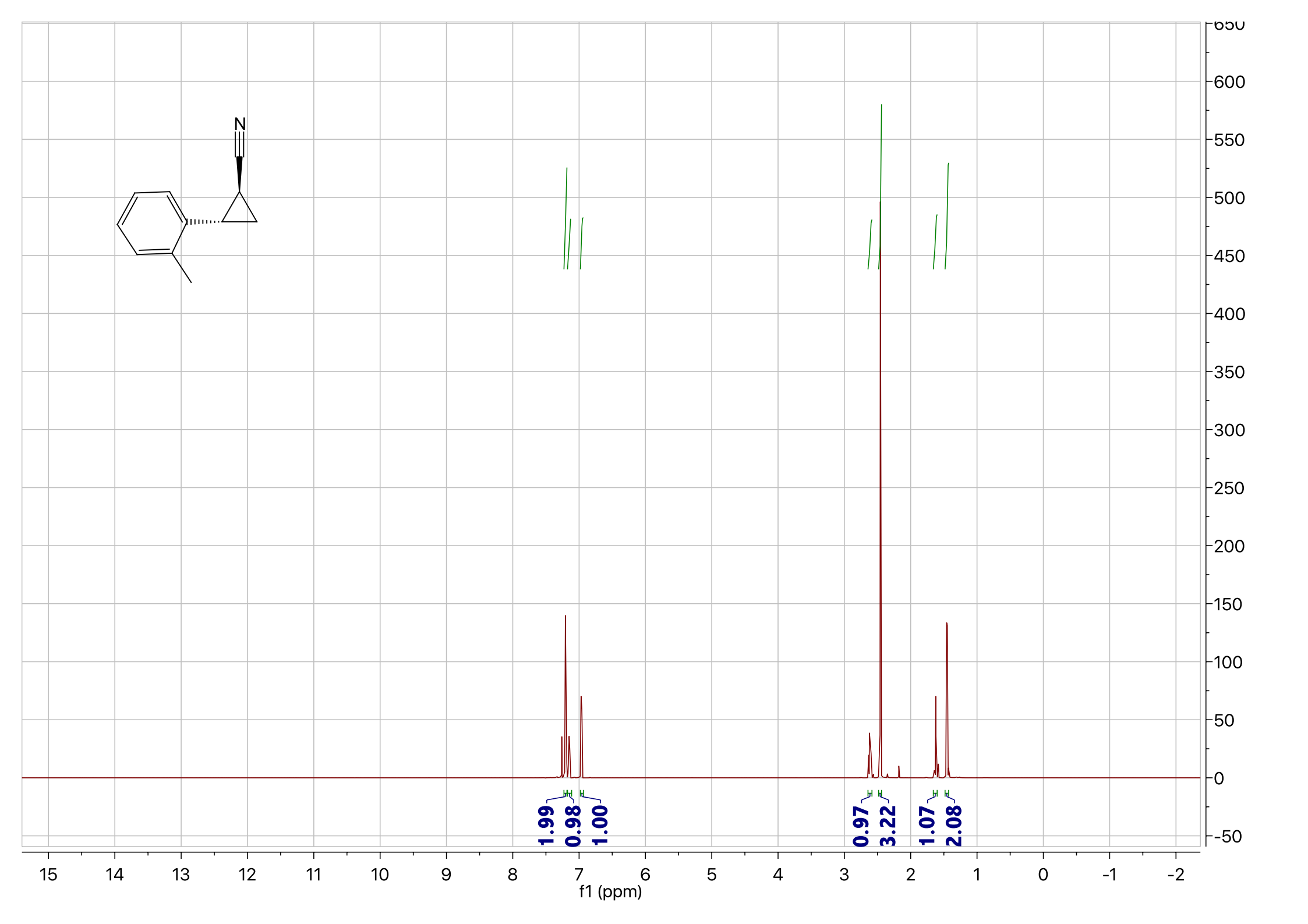

N
F
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

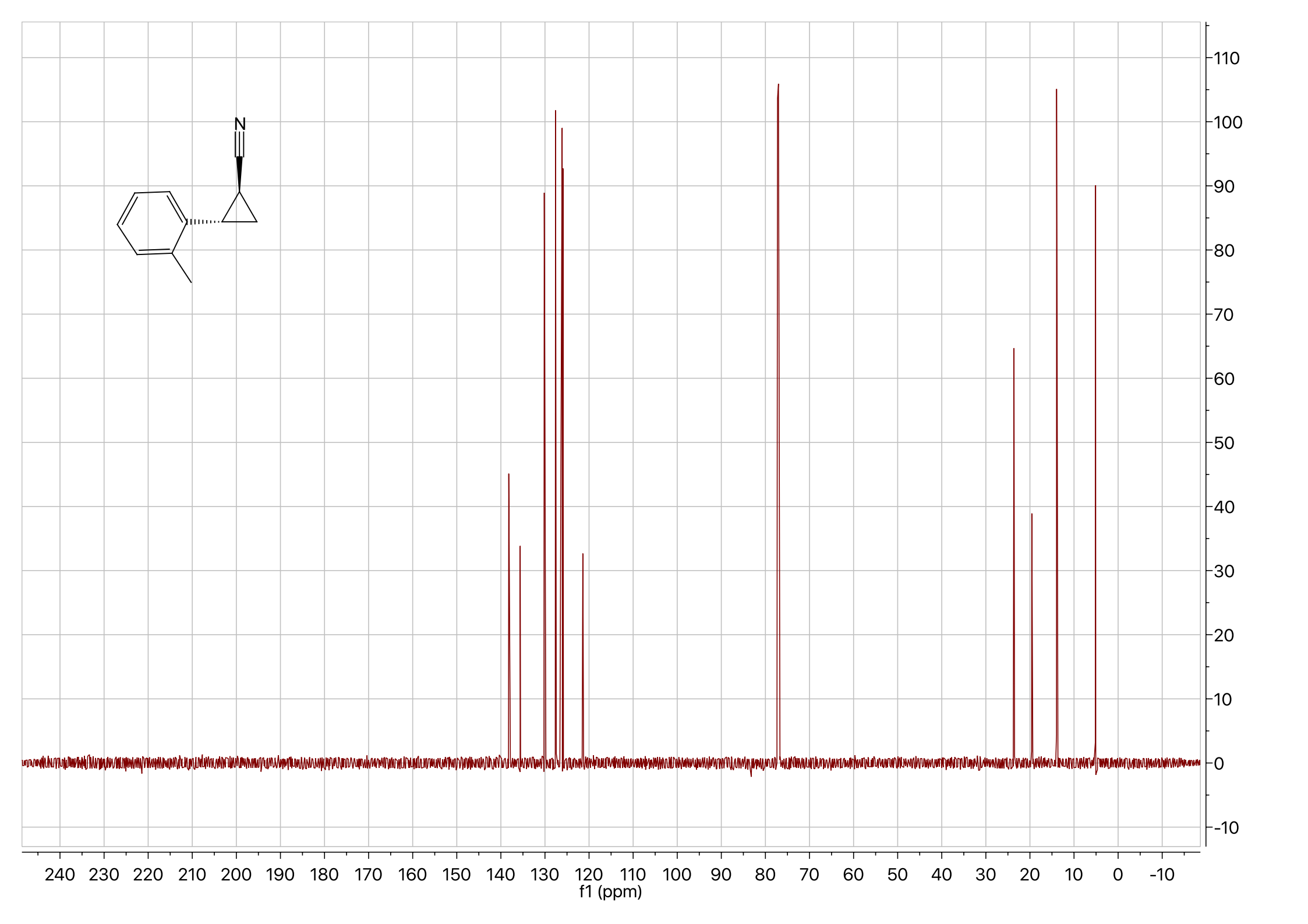

N
F
*
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

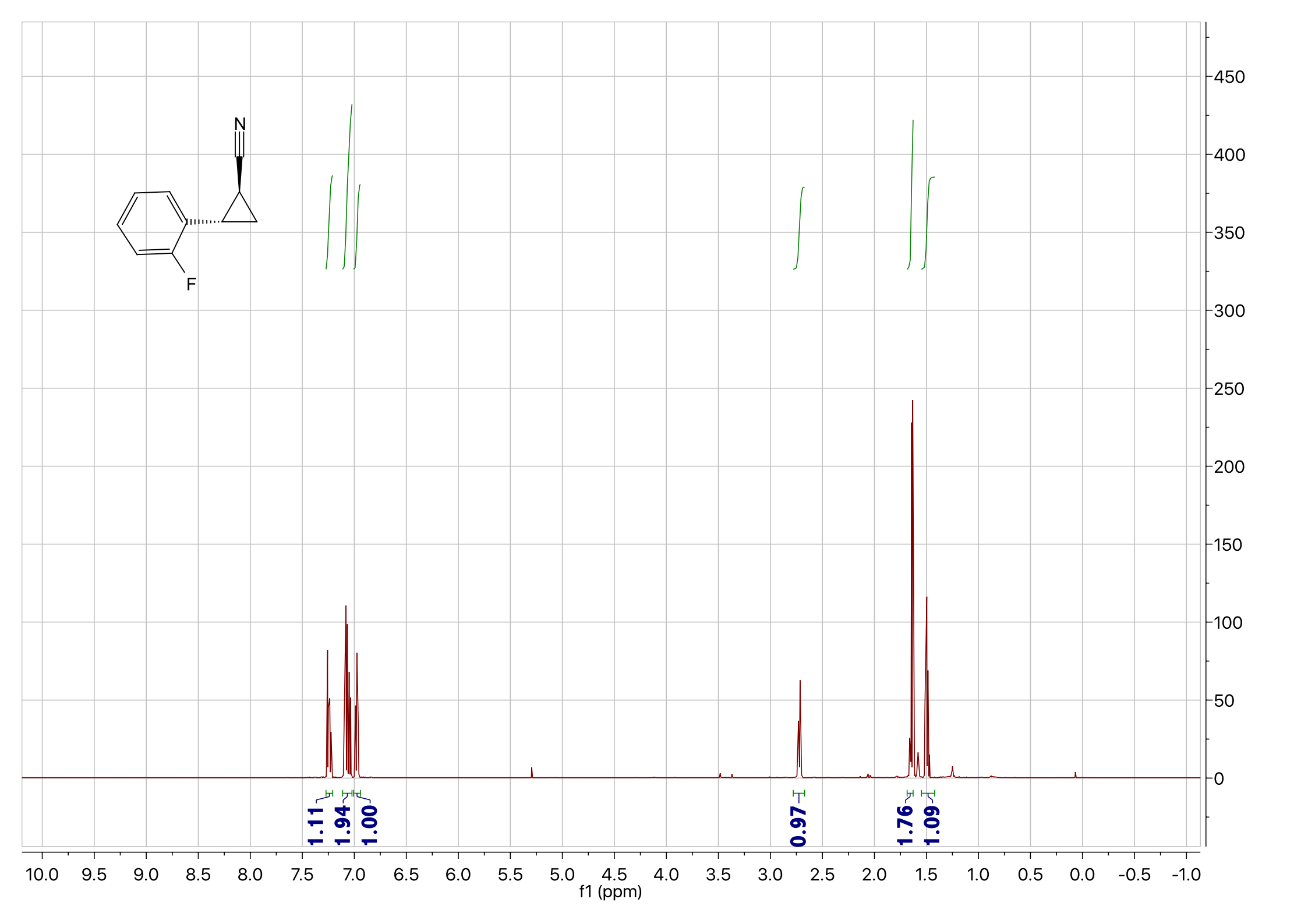

N
1.01
1.00
2.00
1.00
3.14
1.10
1.18
1.10
f1 (ppm)

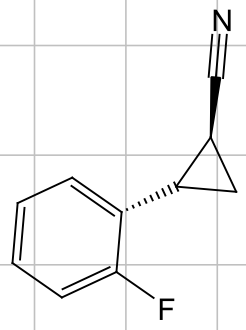

N

800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
1.99
0.98
1.00
0.97
3.22
1.07
2.08
f1 (ppm)


N
110
100
90
80
70
60
50
40
30
20
10
0
-10
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

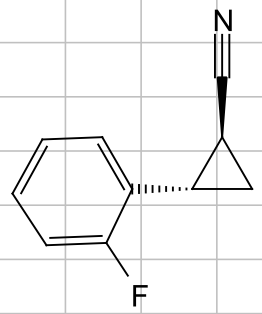

N
F
1.11
1.94
1.00
0.97
1.76
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
450
400
350
300
250
200
150
100
50
0



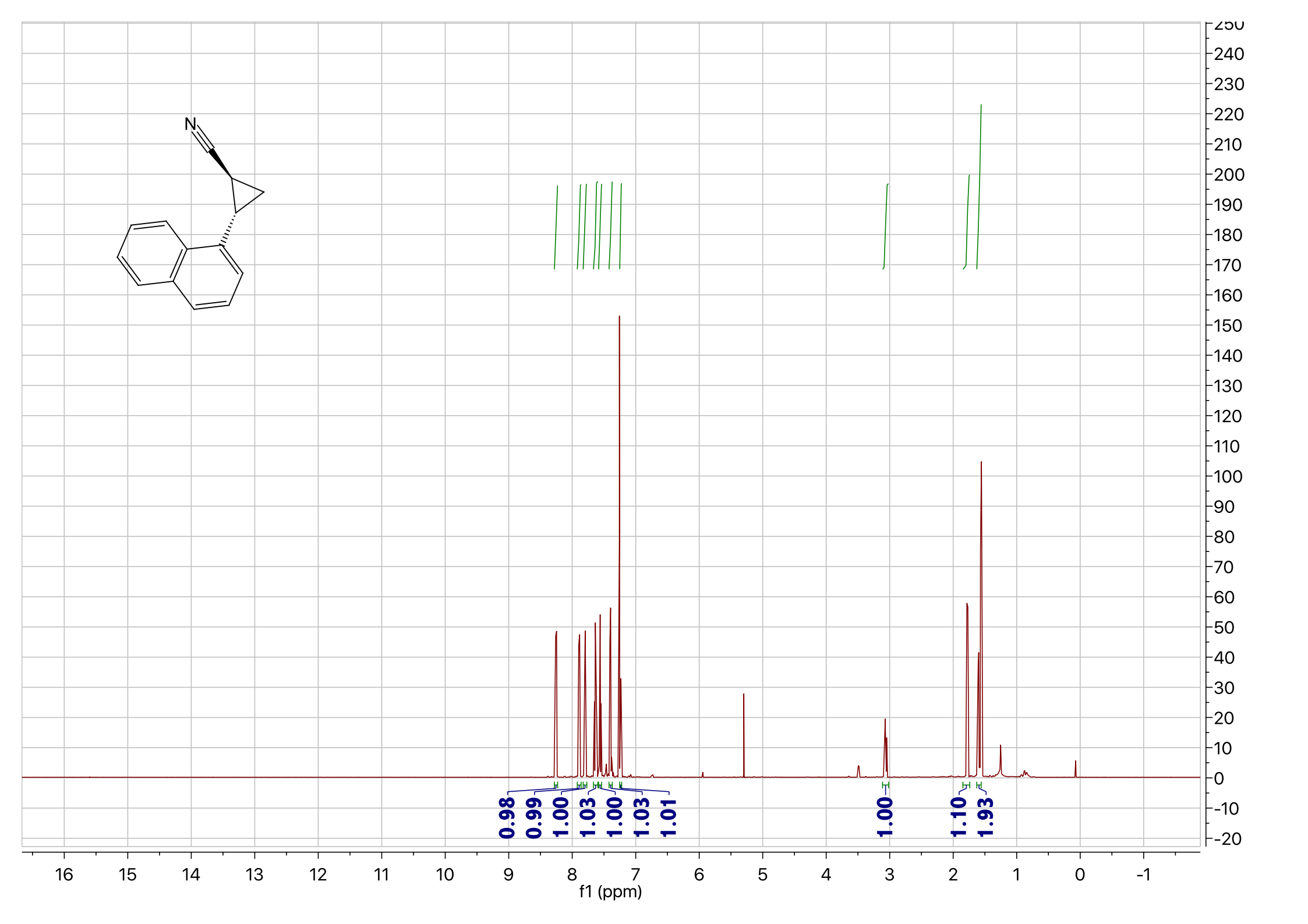
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

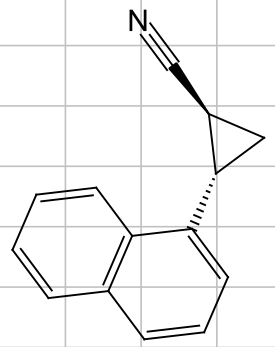
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170

f1 (ppm)

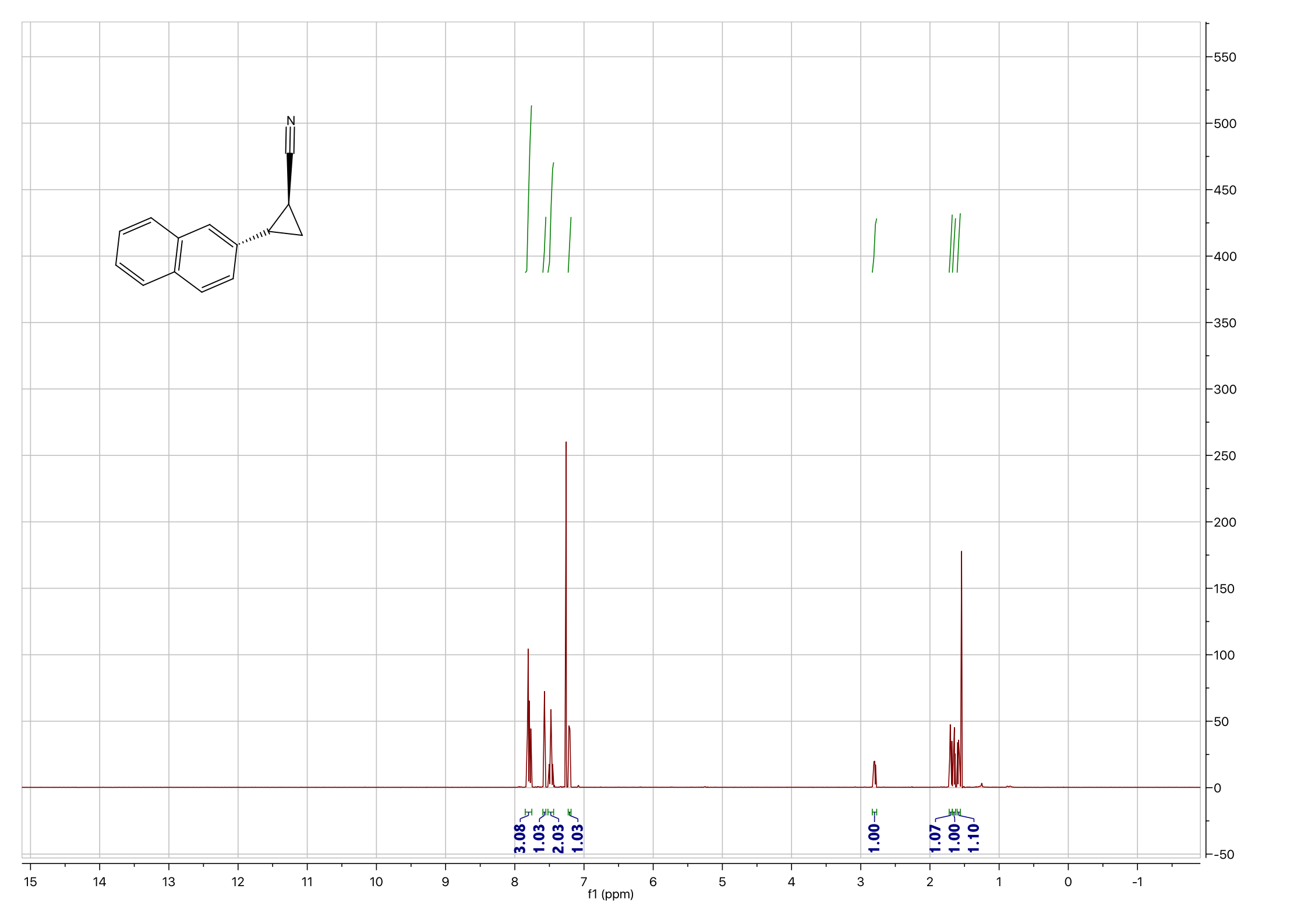


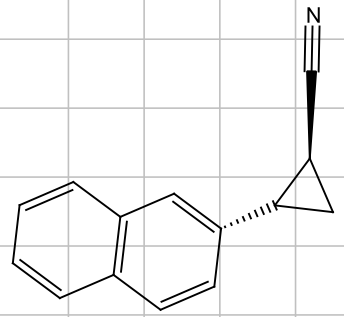
f1 (ppm)


N
0.98
0.99
1.00
1.03
1.00
1.03
1.01
1.00
1.10
1.93
f1 (ppm)

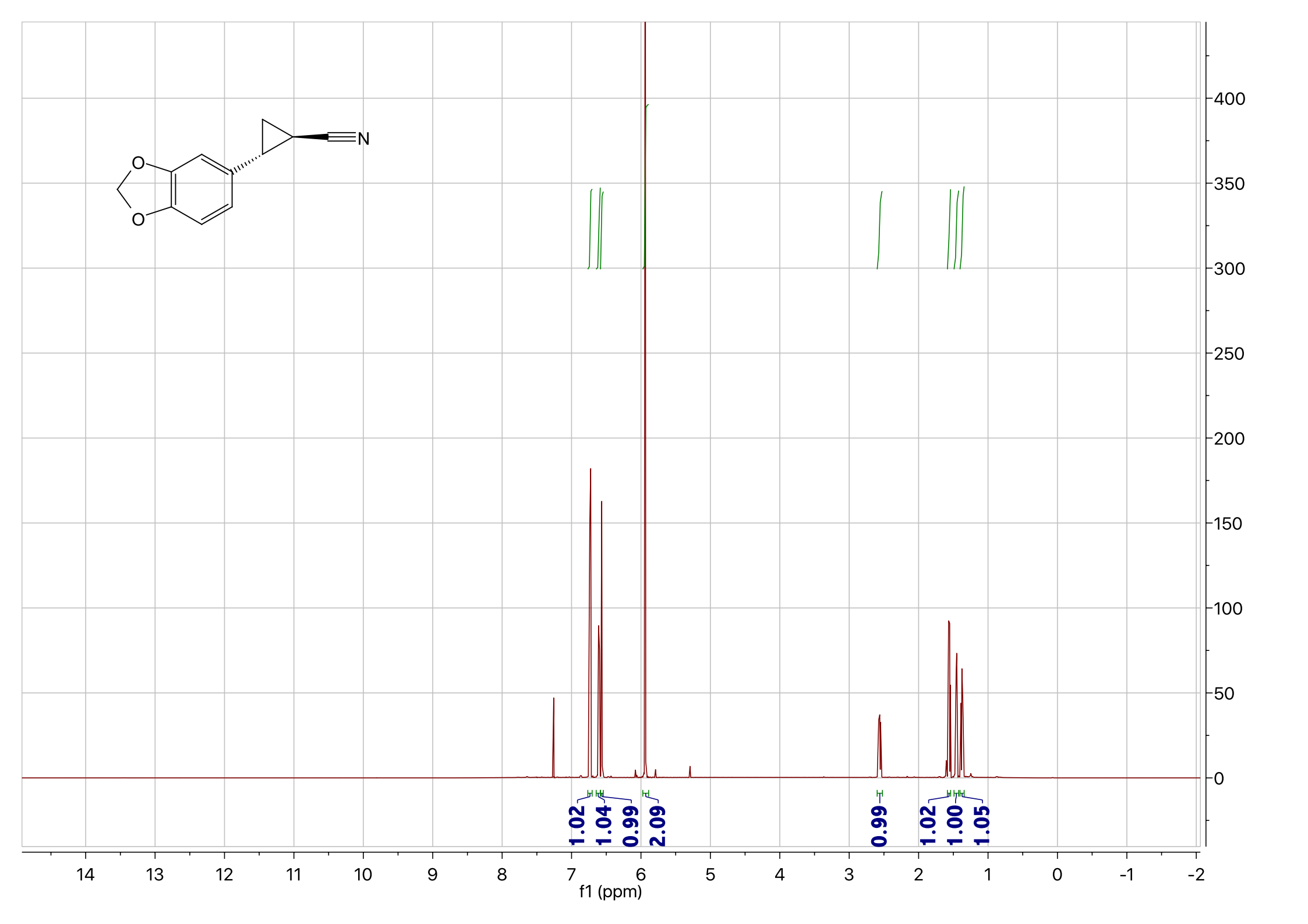

N

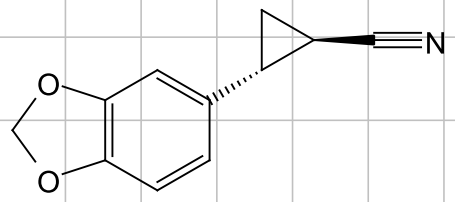
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
3.08
1.03
2.03
1.03
1.00
1.07
1.00
1.10
f1 (ppm)

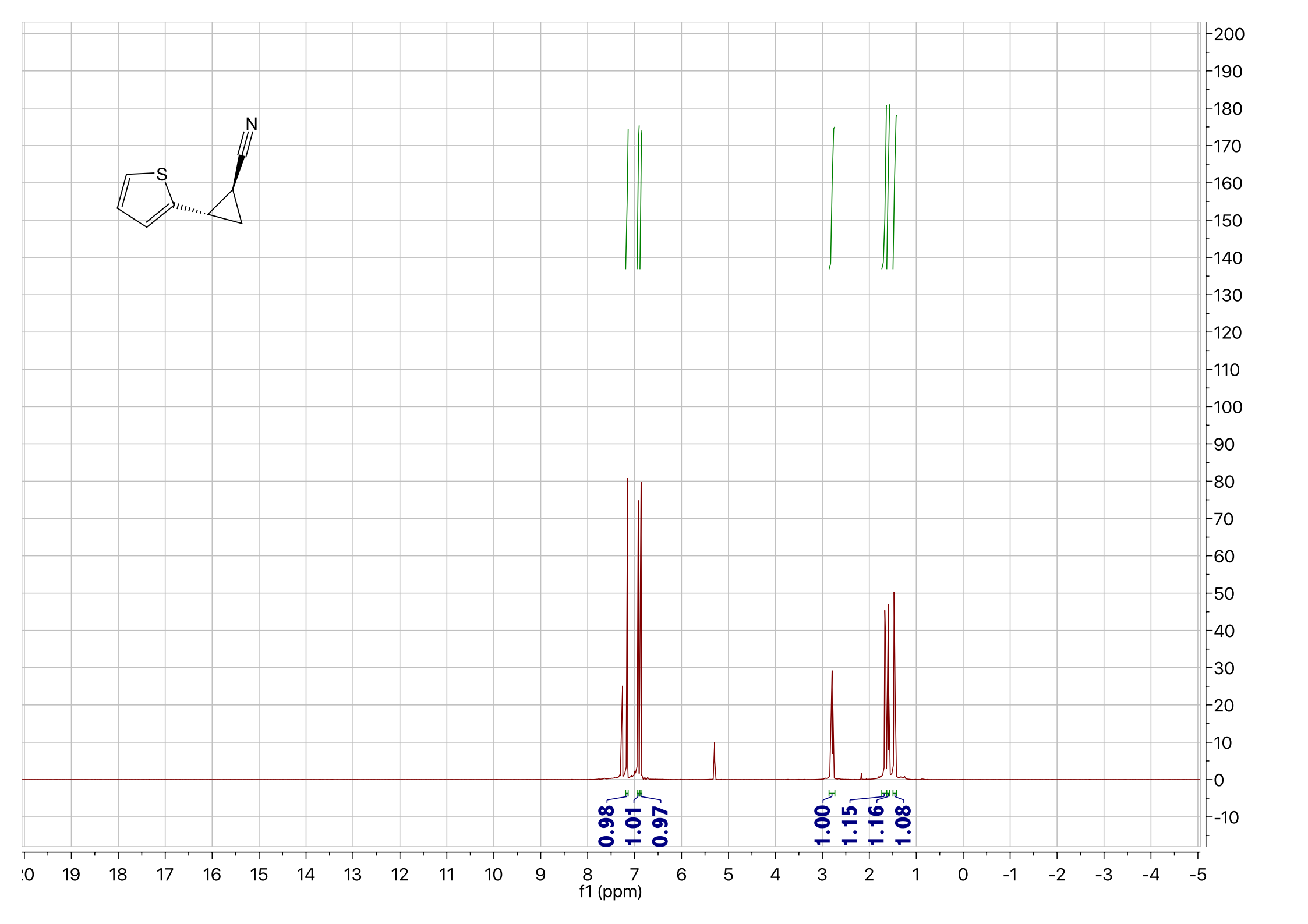


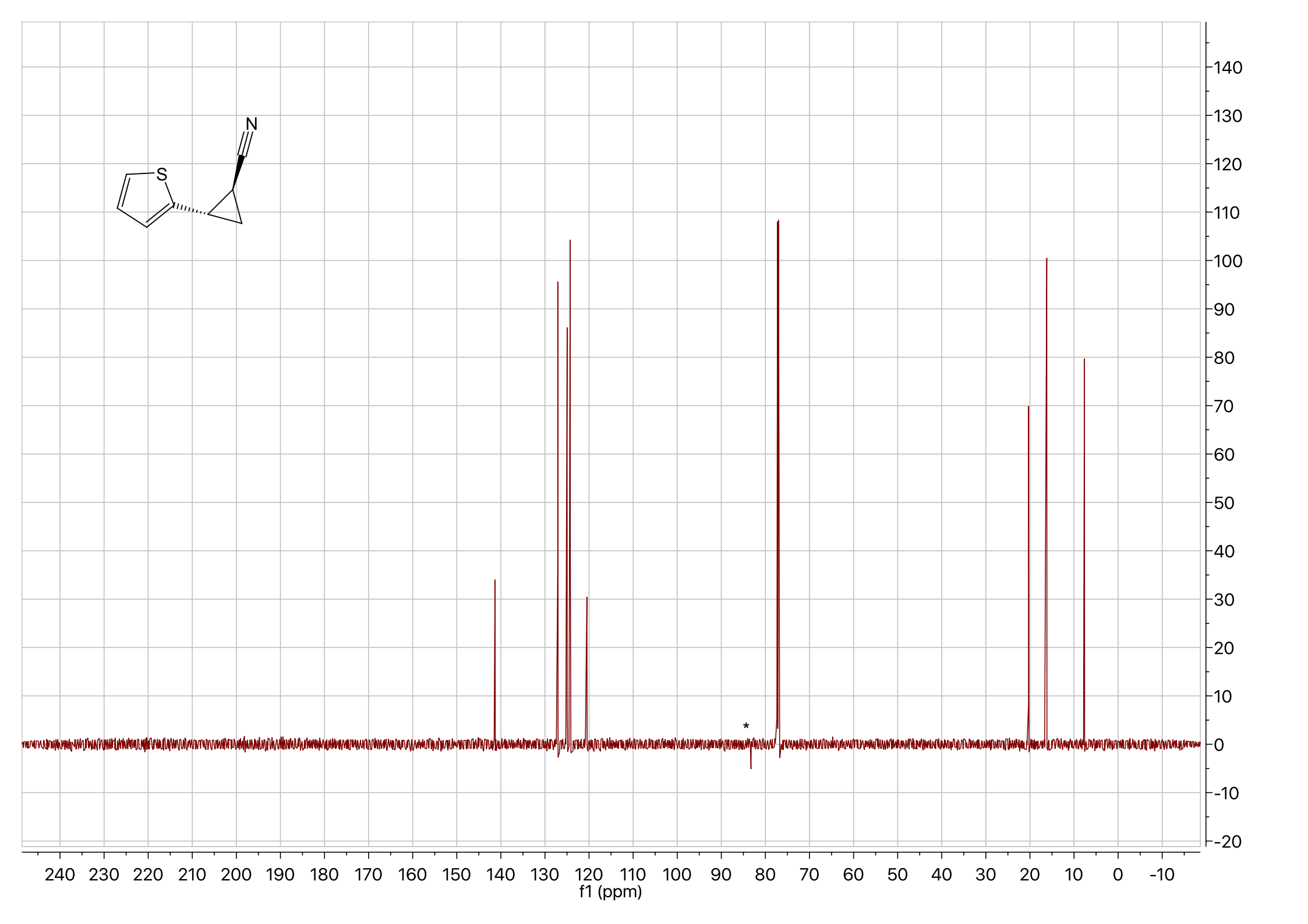
f1 (ppm)

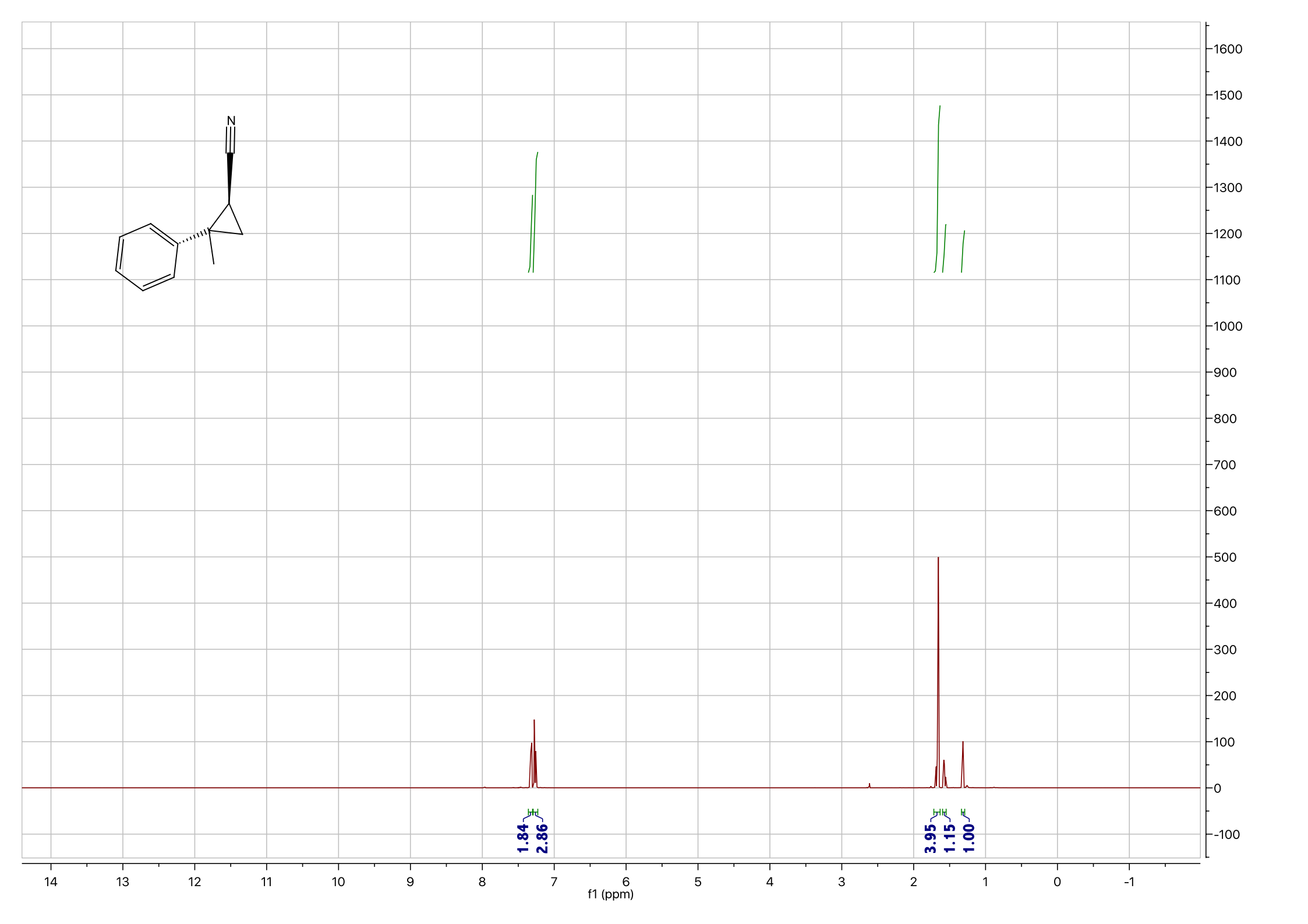

O
O
N
400
350
300
250
200
150
100
50
0
1.02
1.04
0.99
2.09
0.99
1.02
1.00
1.05
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

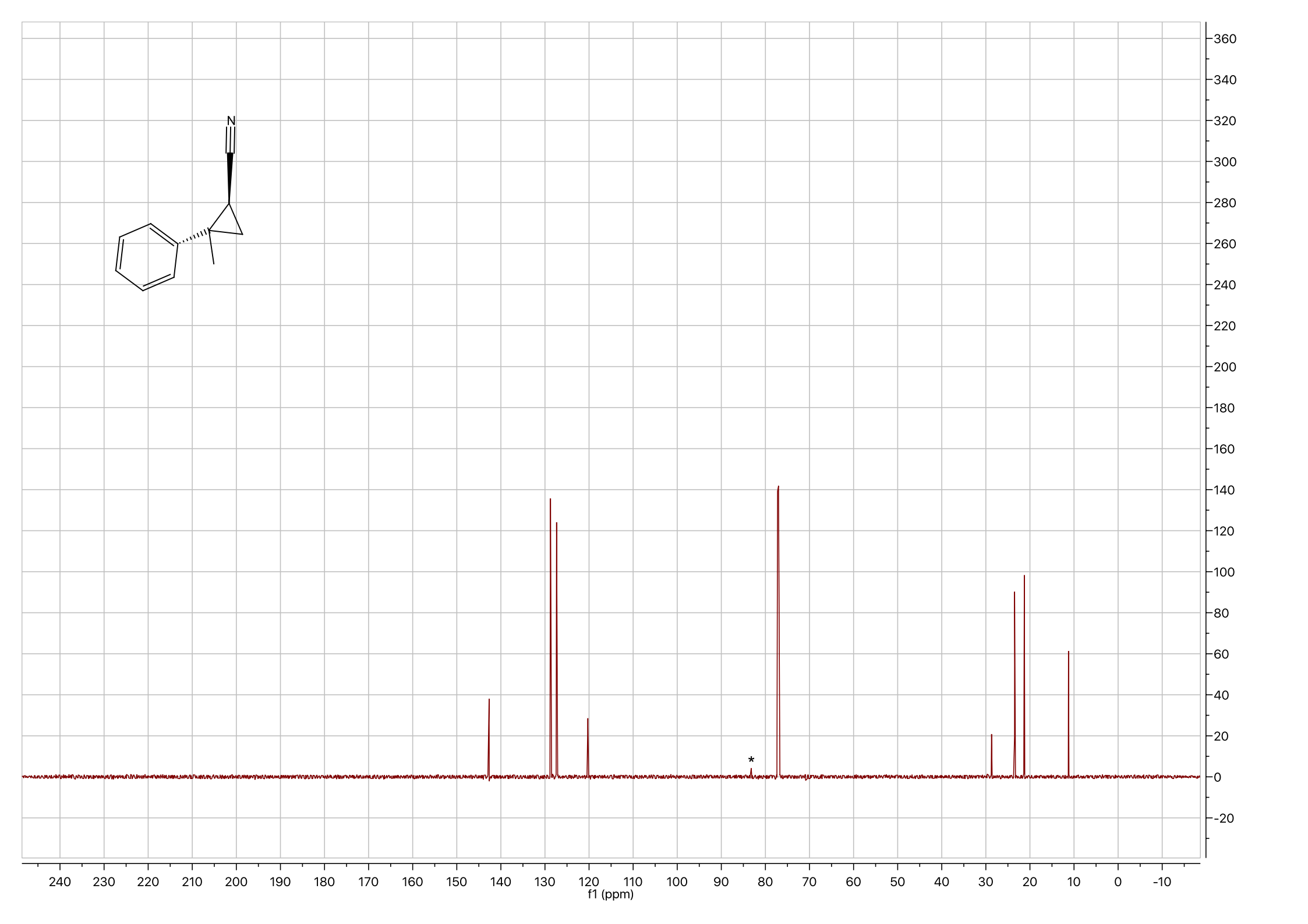


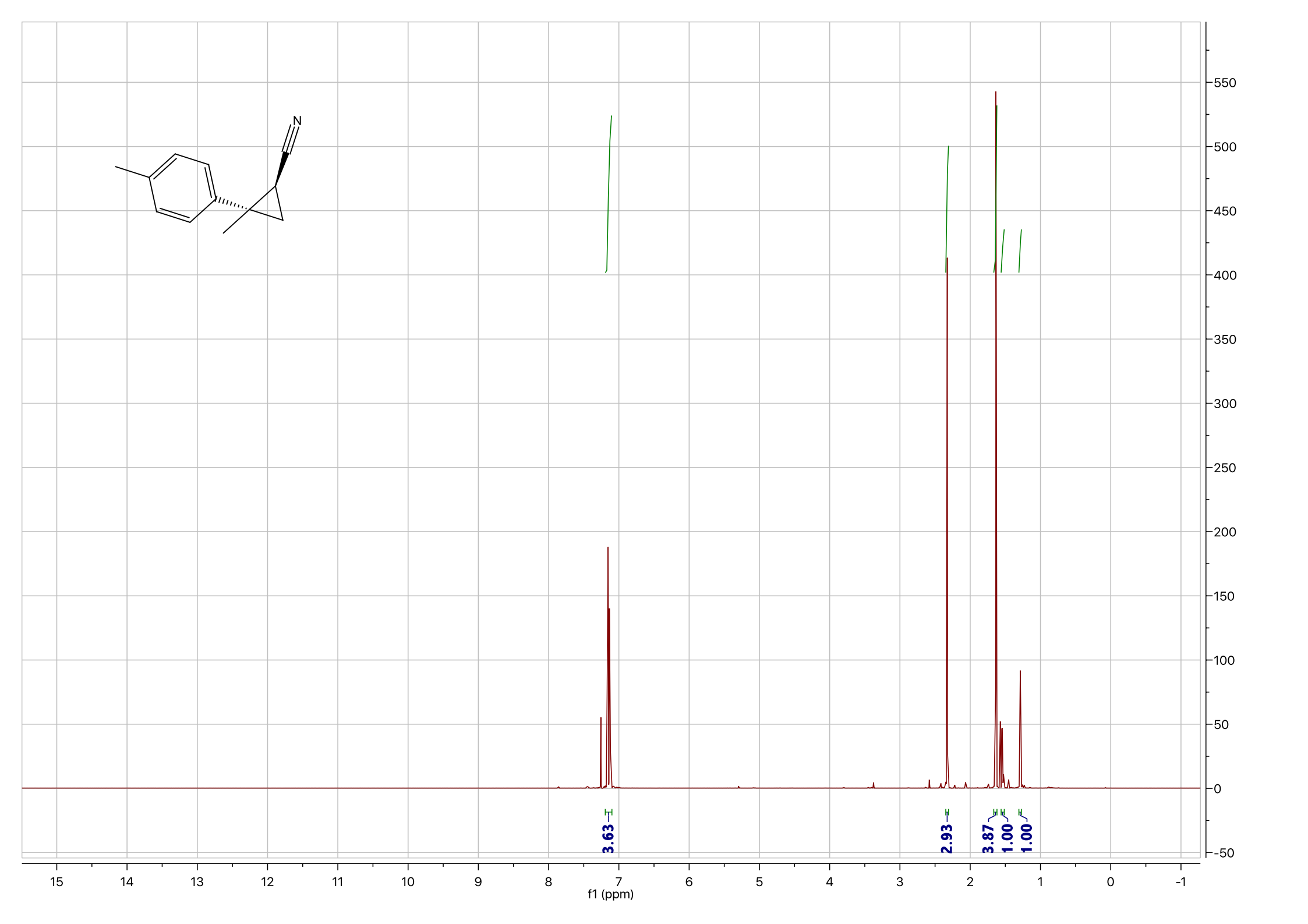
f1 (ppm)

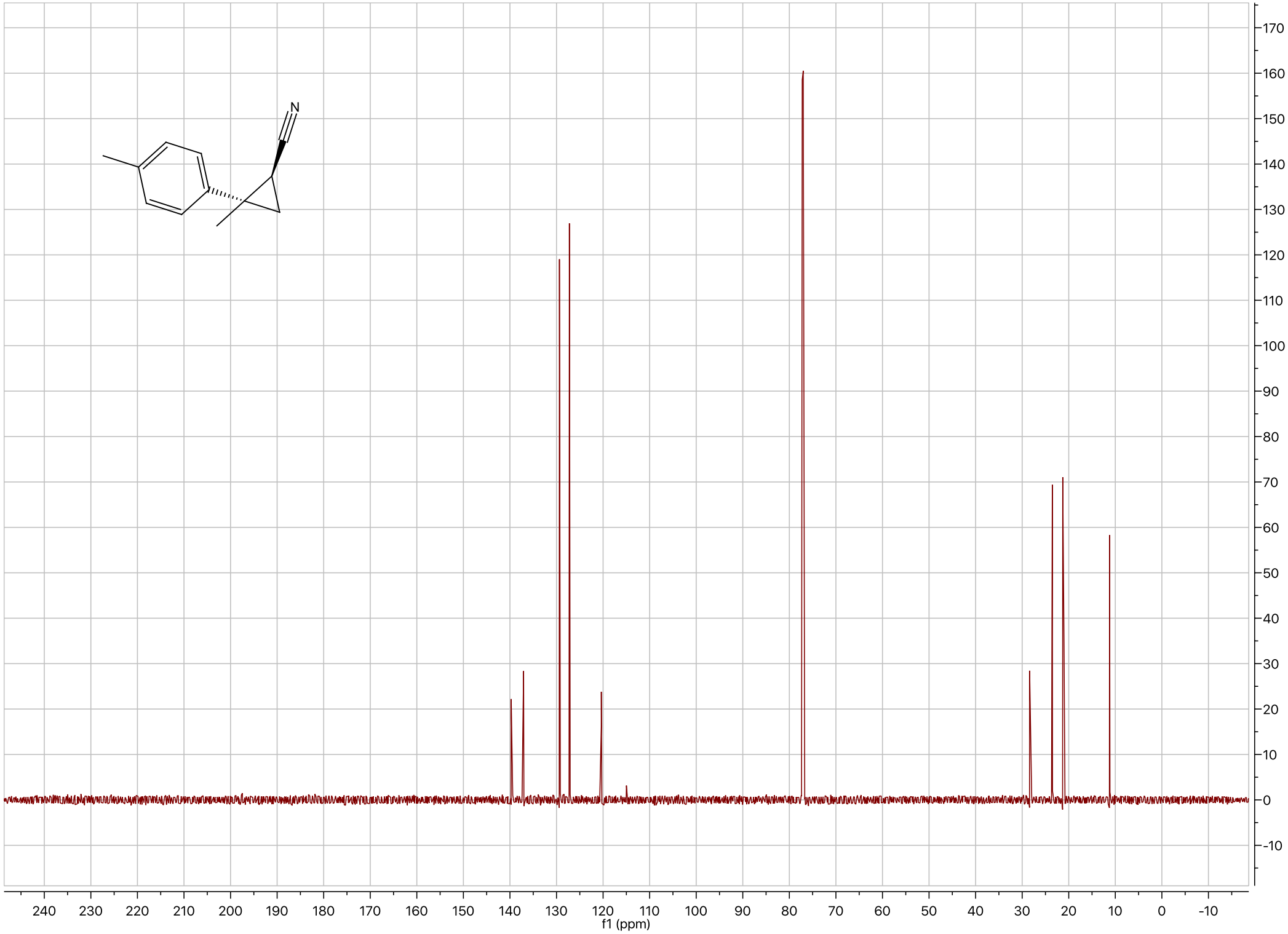

N
S
0.98
1.01
0.97
1.00
1.15
1.16
1.08
f1 (ppm)

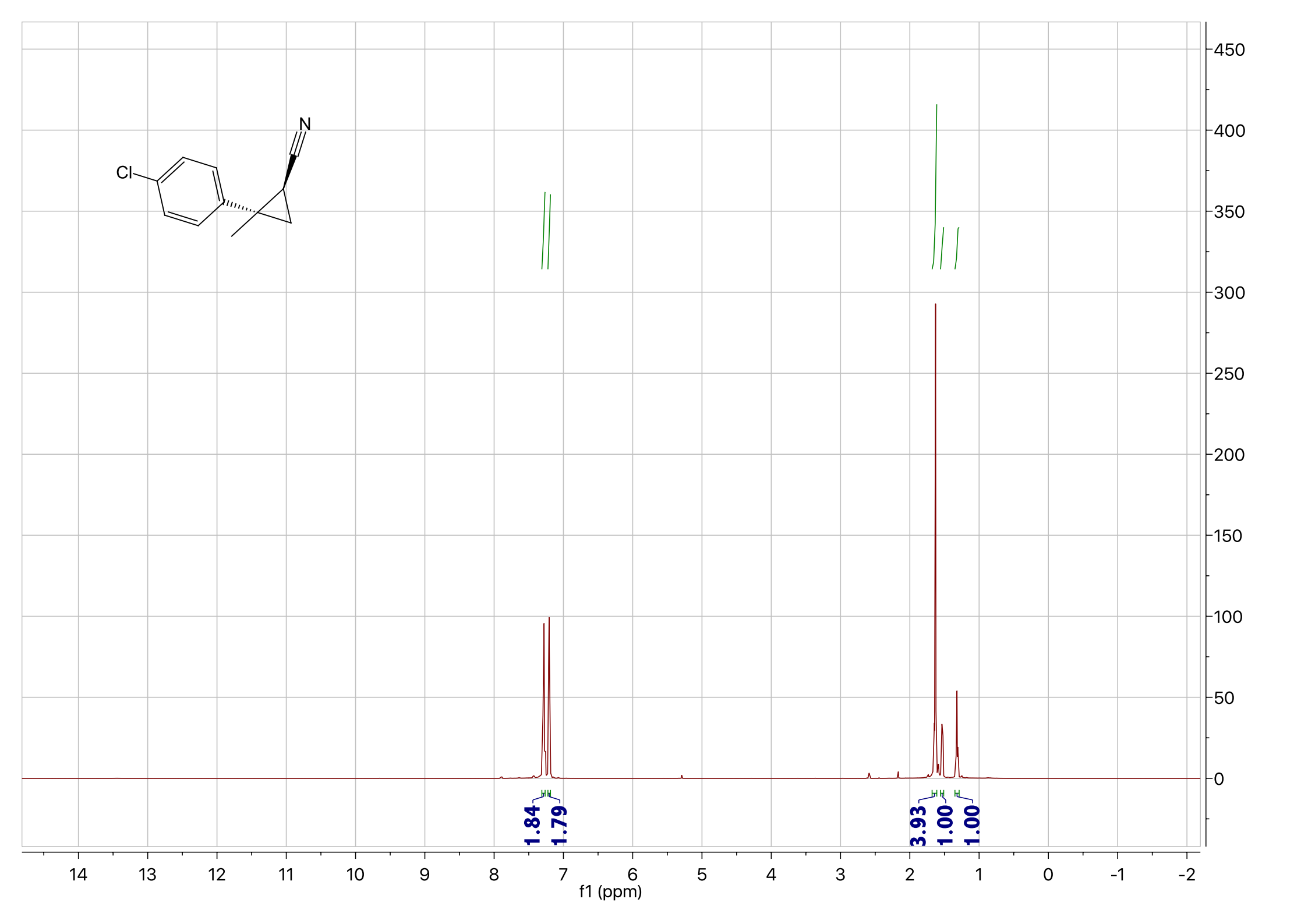

N
S
*
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

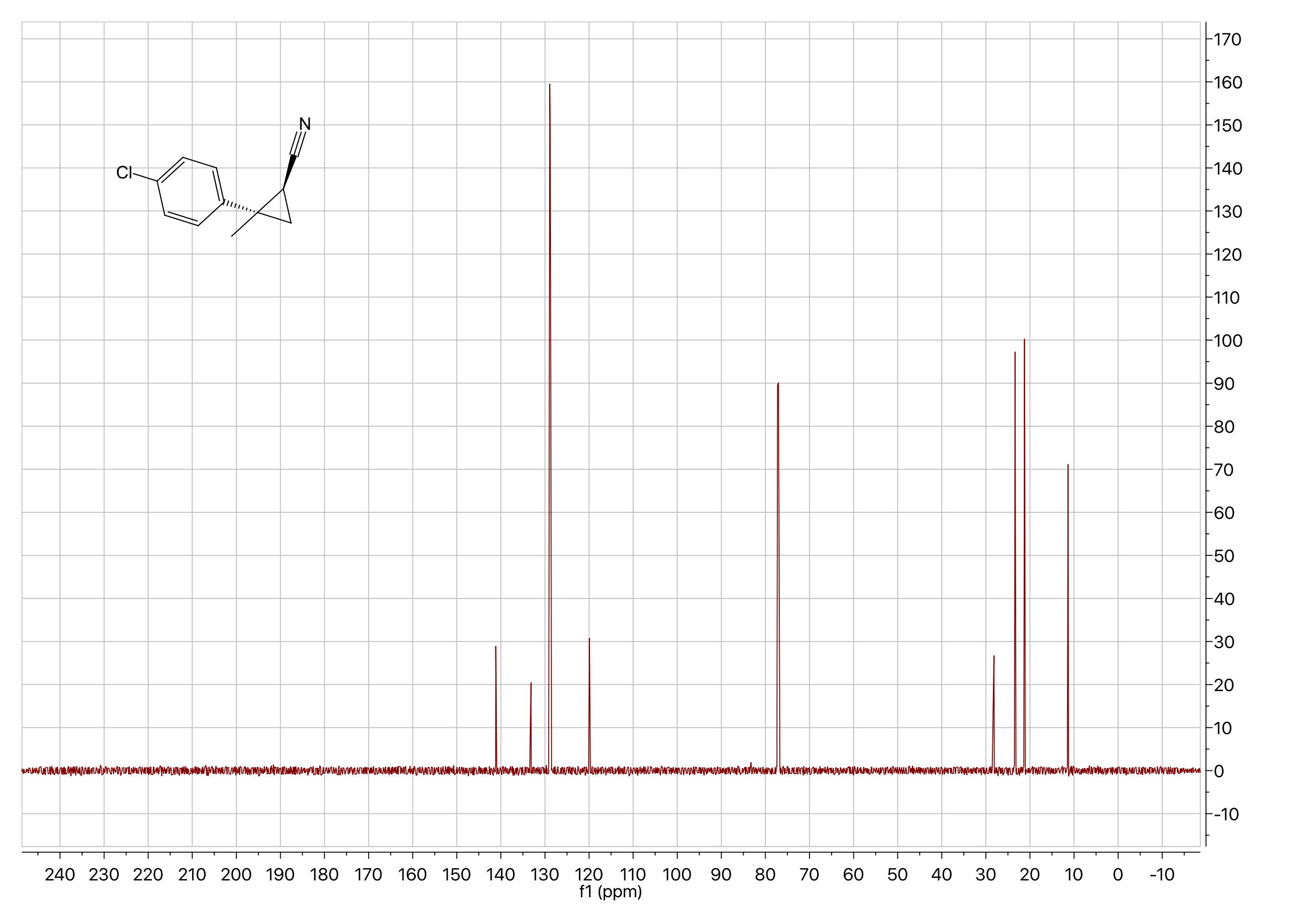

N
1.84
2.86
3.95
1.15
1.00
f1 (ppm)

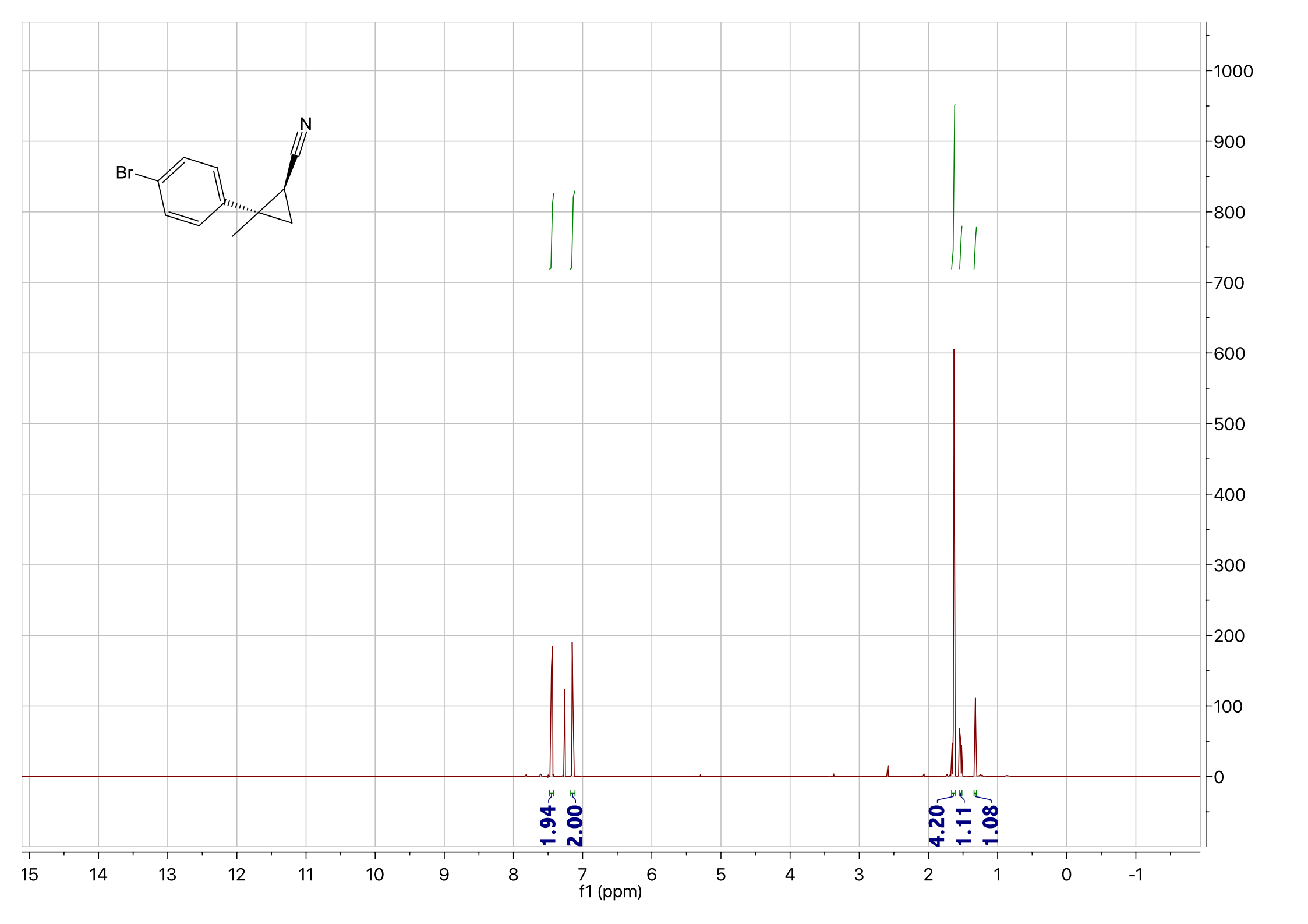

N
*
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

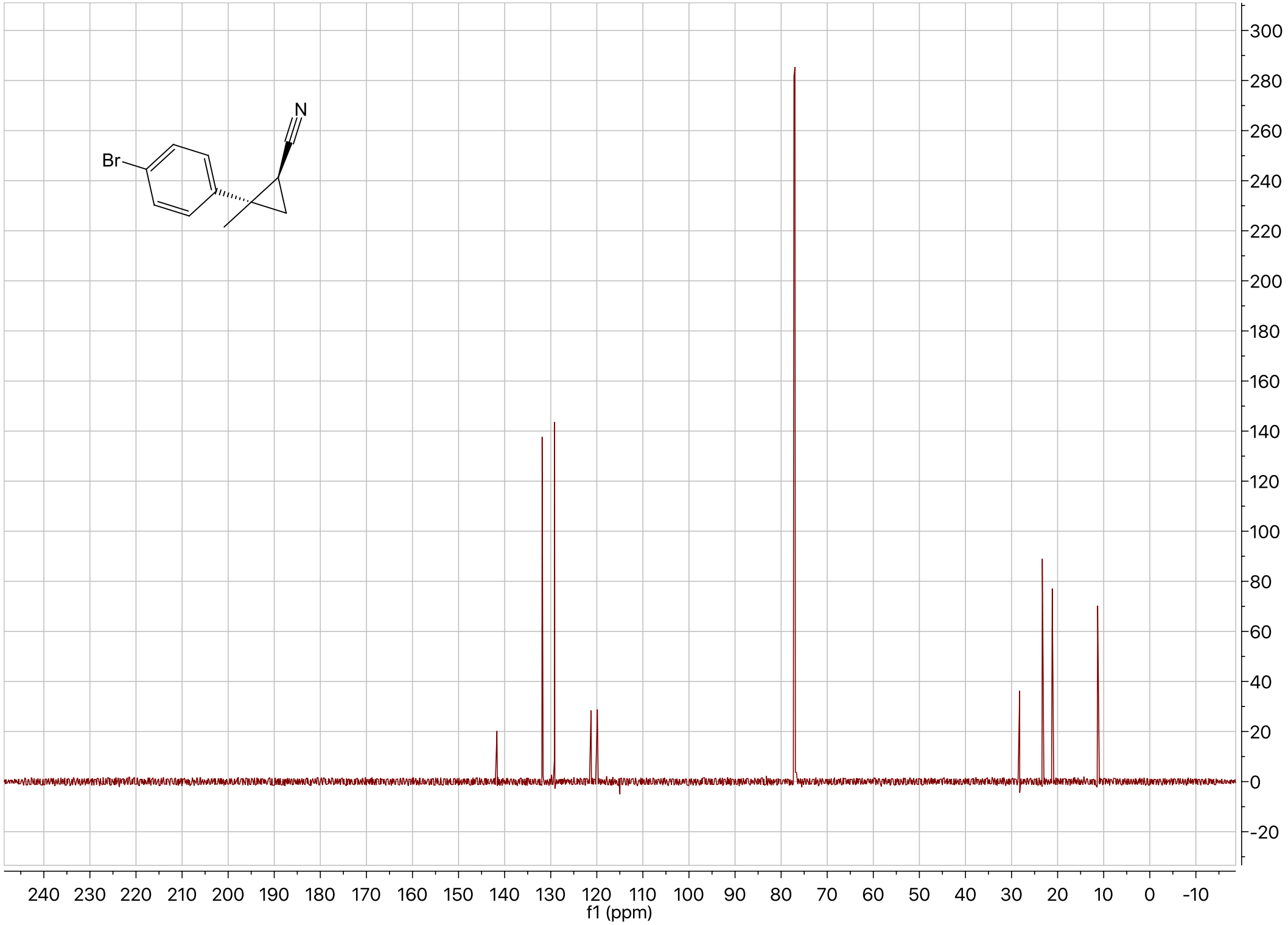

N
3.63
2.93
3.87
1.00
1.00
f1 (ppm)

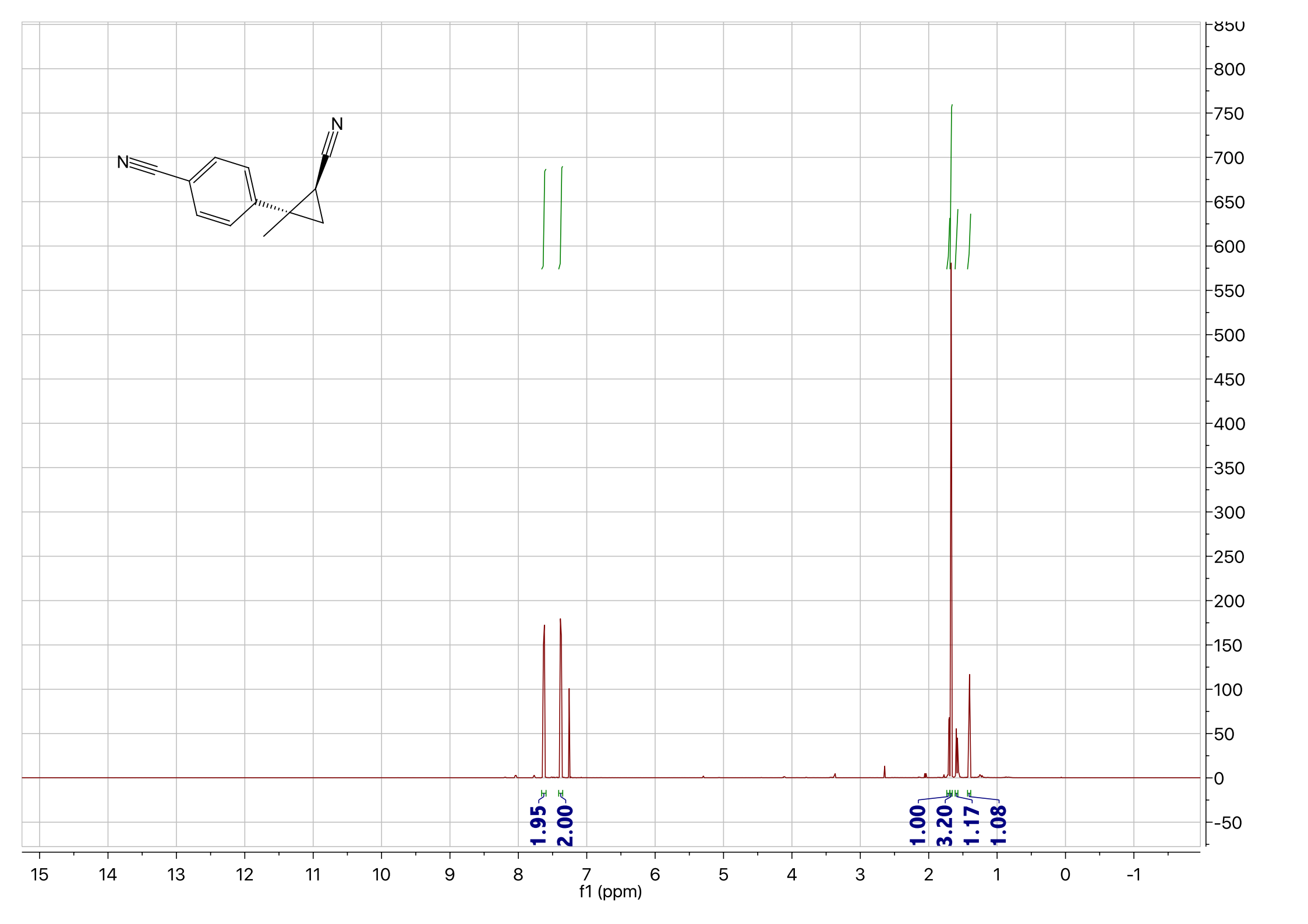

N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

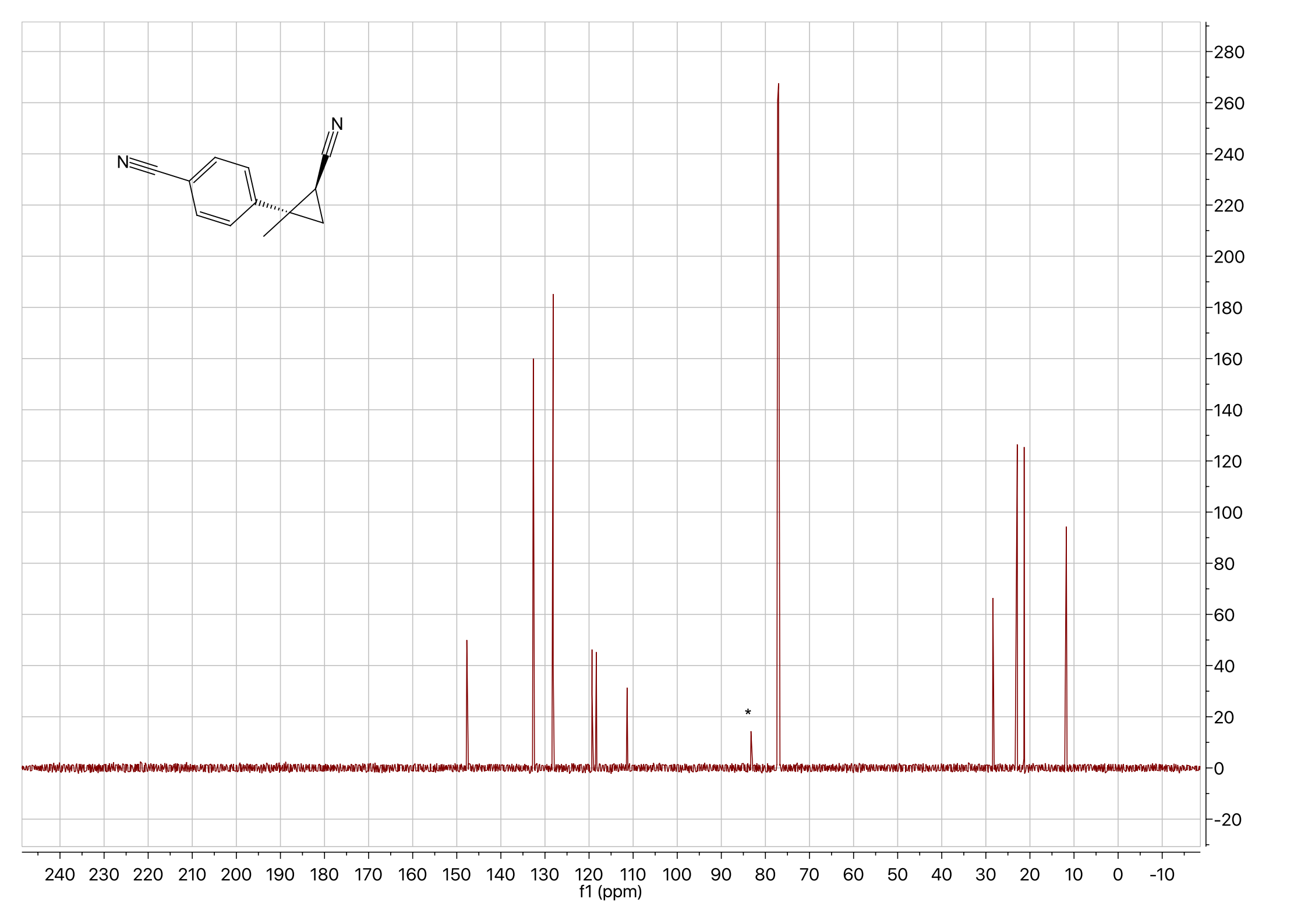

N
Cl
1.84
1.79
3.93
1.00
1.00
f1 (ppm)

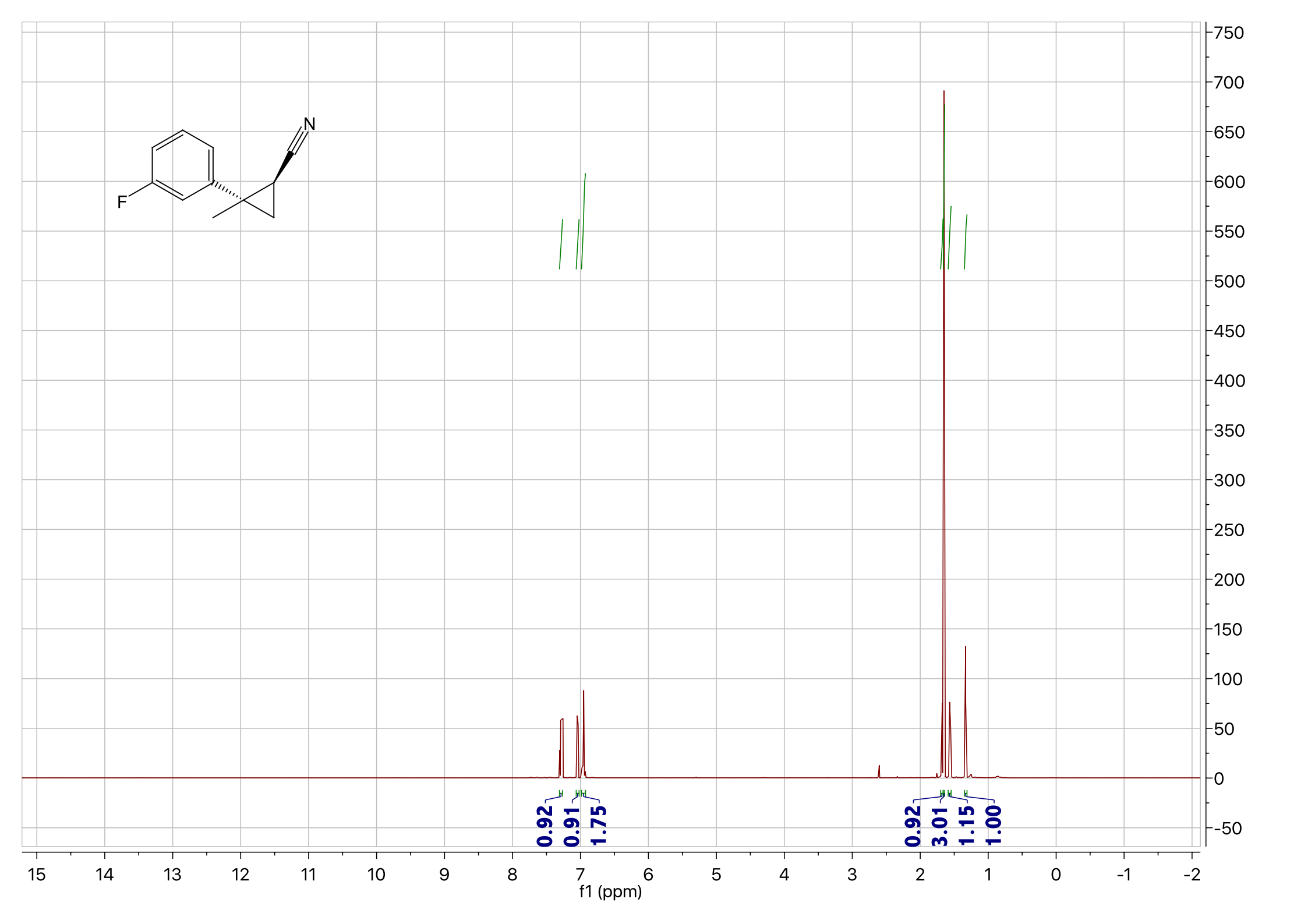

Cl
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

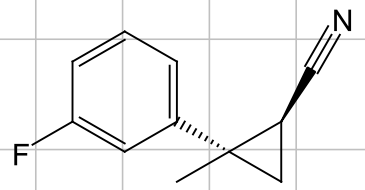

N
Br
1.94
2.00
4.20
1.11
1.08
1000
900
800
700
600
500
400
300
200
100
0
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


Br
N
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N
1.95
2.00
1.00
3.20
1.17
1.08
f1 (ppm)


N
N
*
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

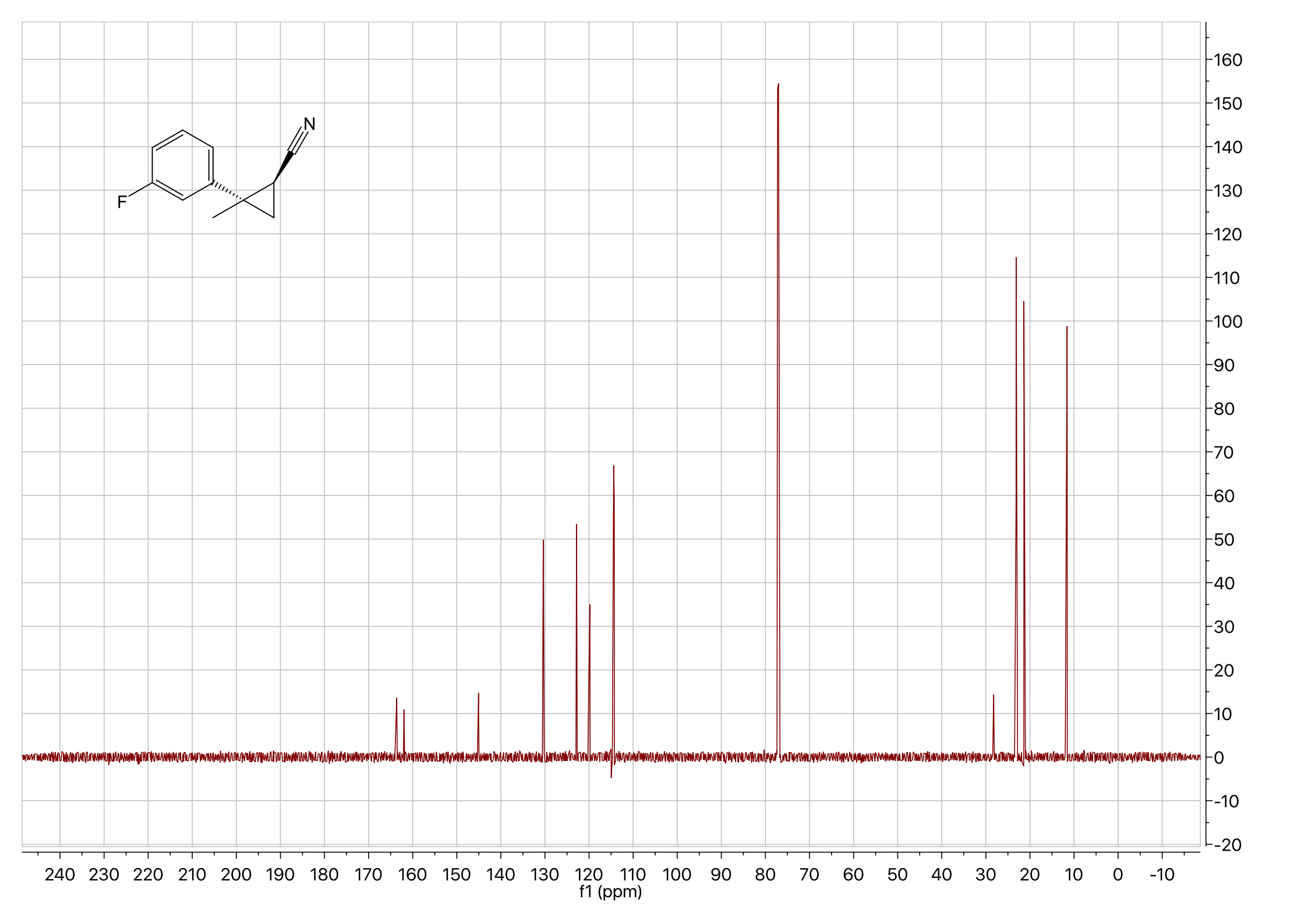

N
F
0.92
0.91
1.75
0.92
3.01
1.15
1.00
f1 (ppm)

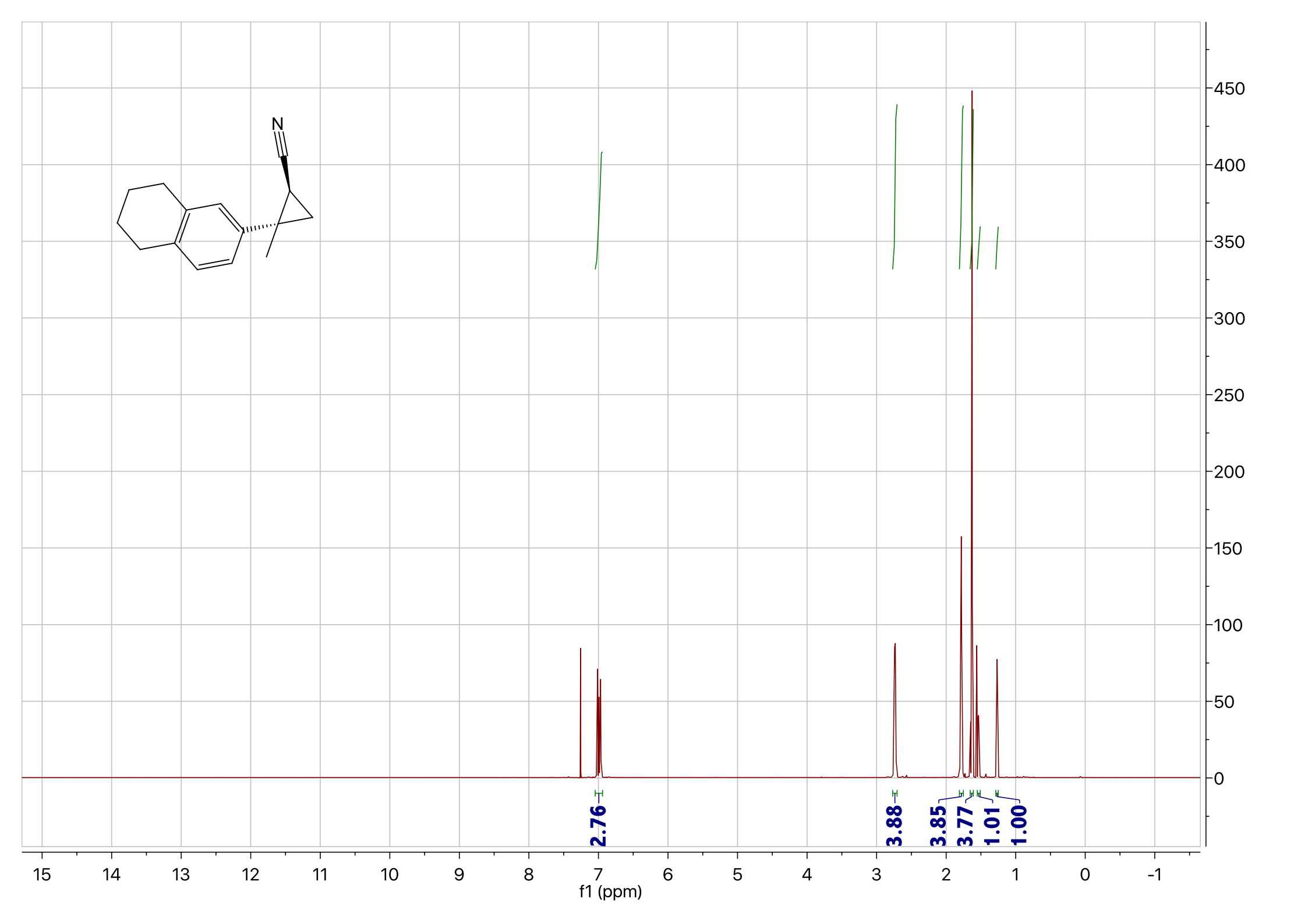


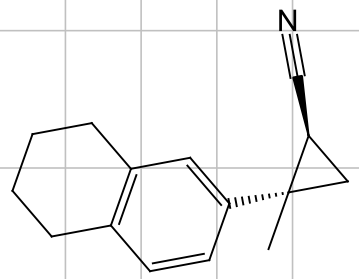
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

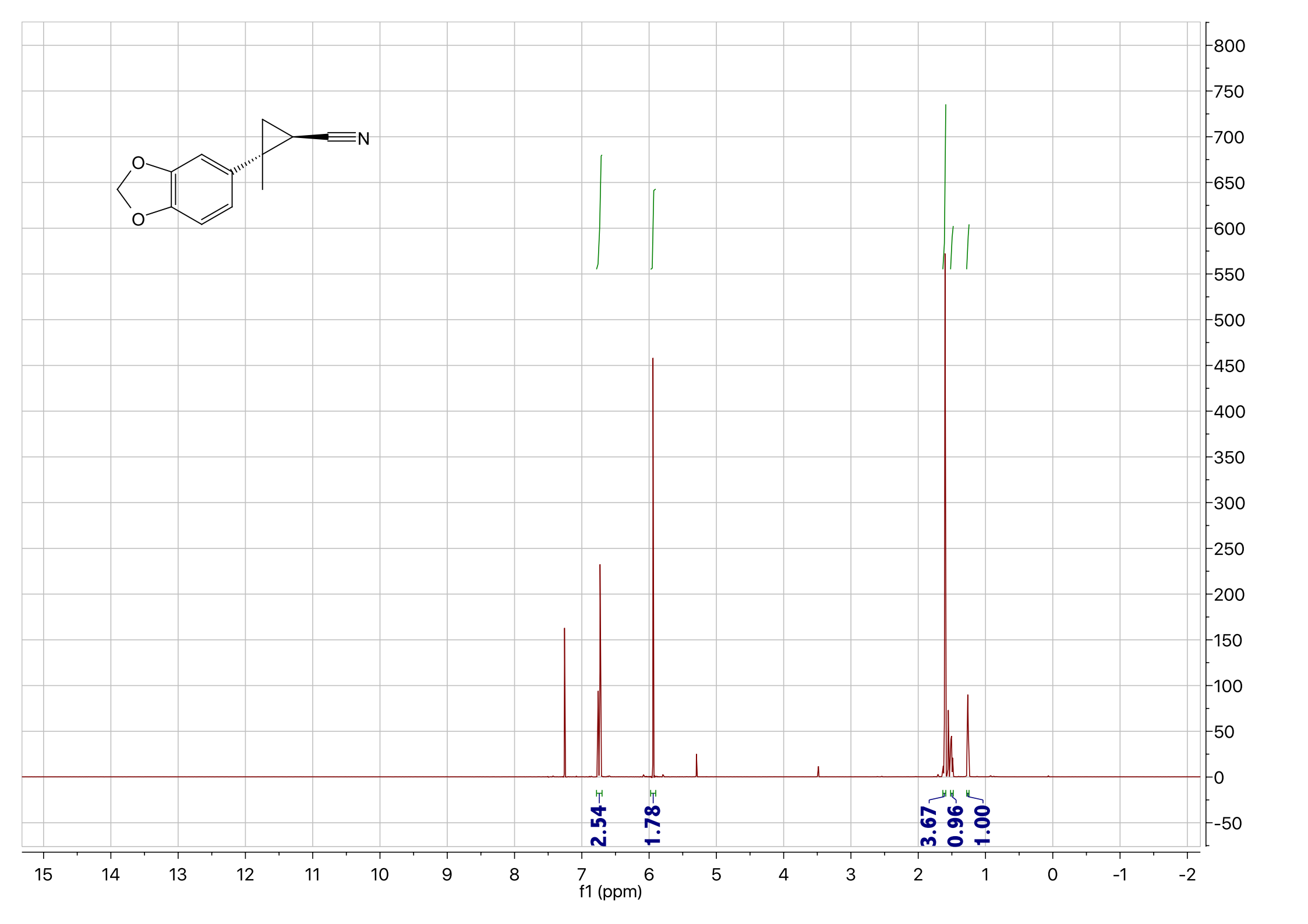
f1 (ppm)

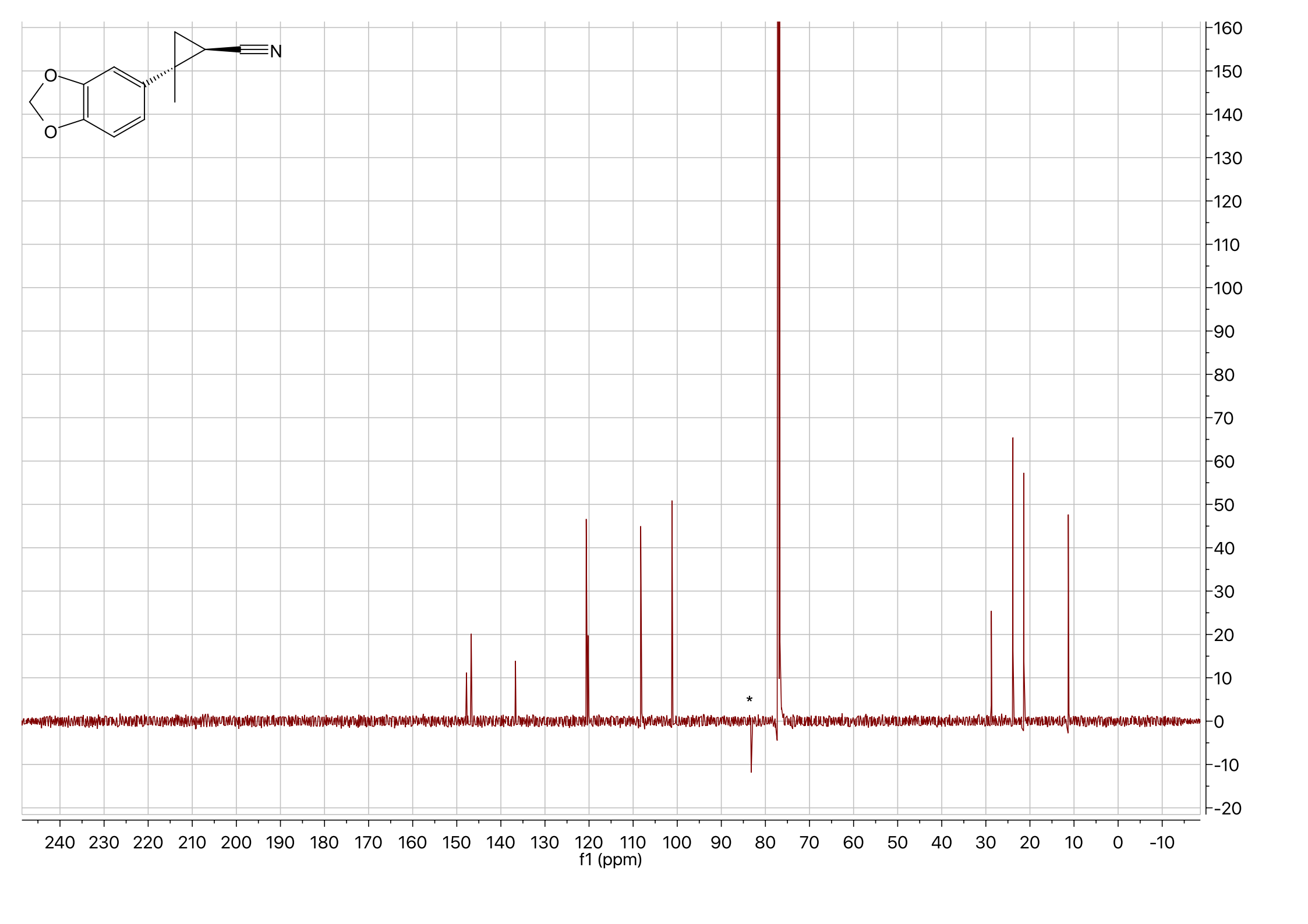

N
F
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

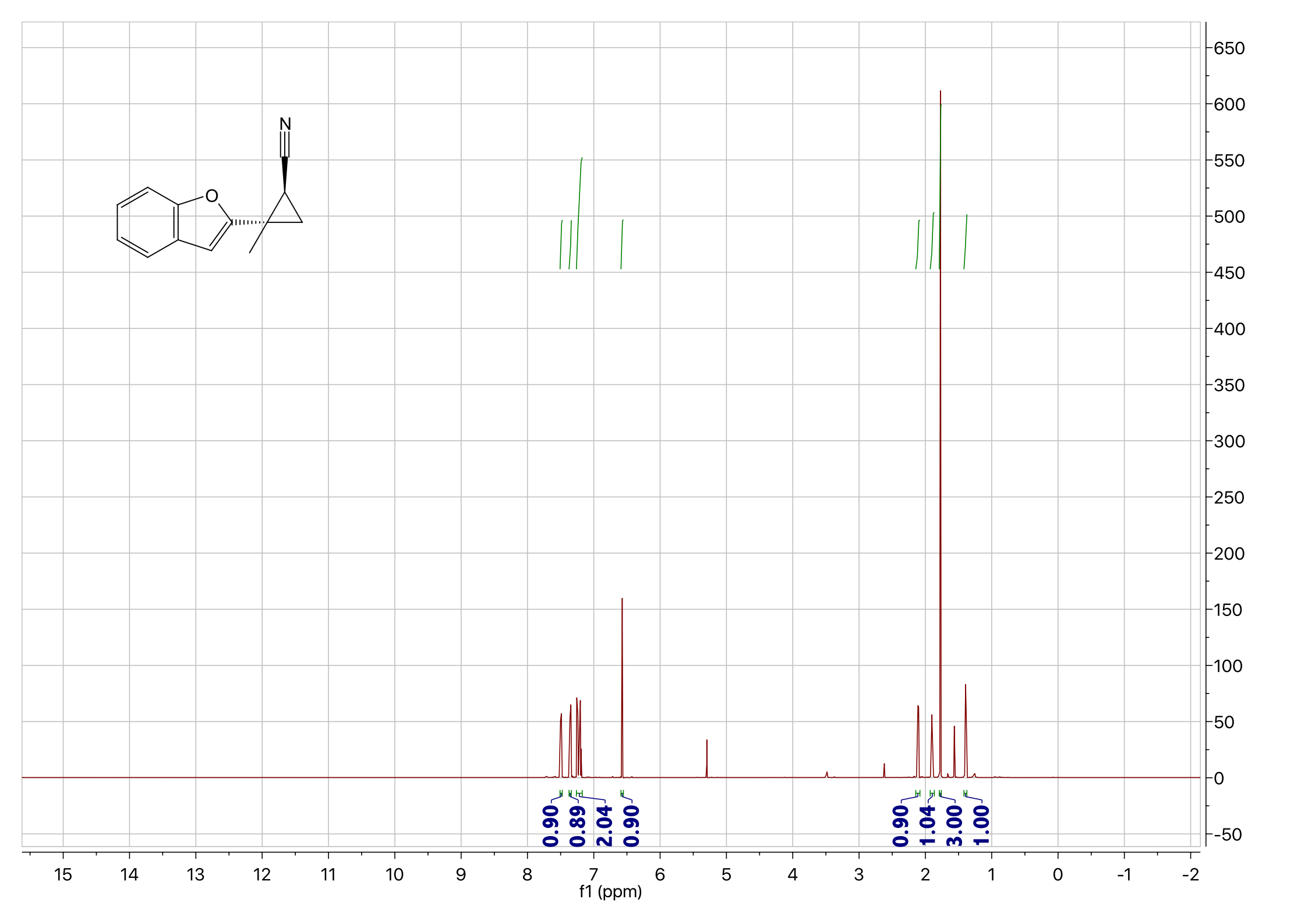

N
2.76
3.88
3.85
3.77
1.01
1.00
f1 (ppm)

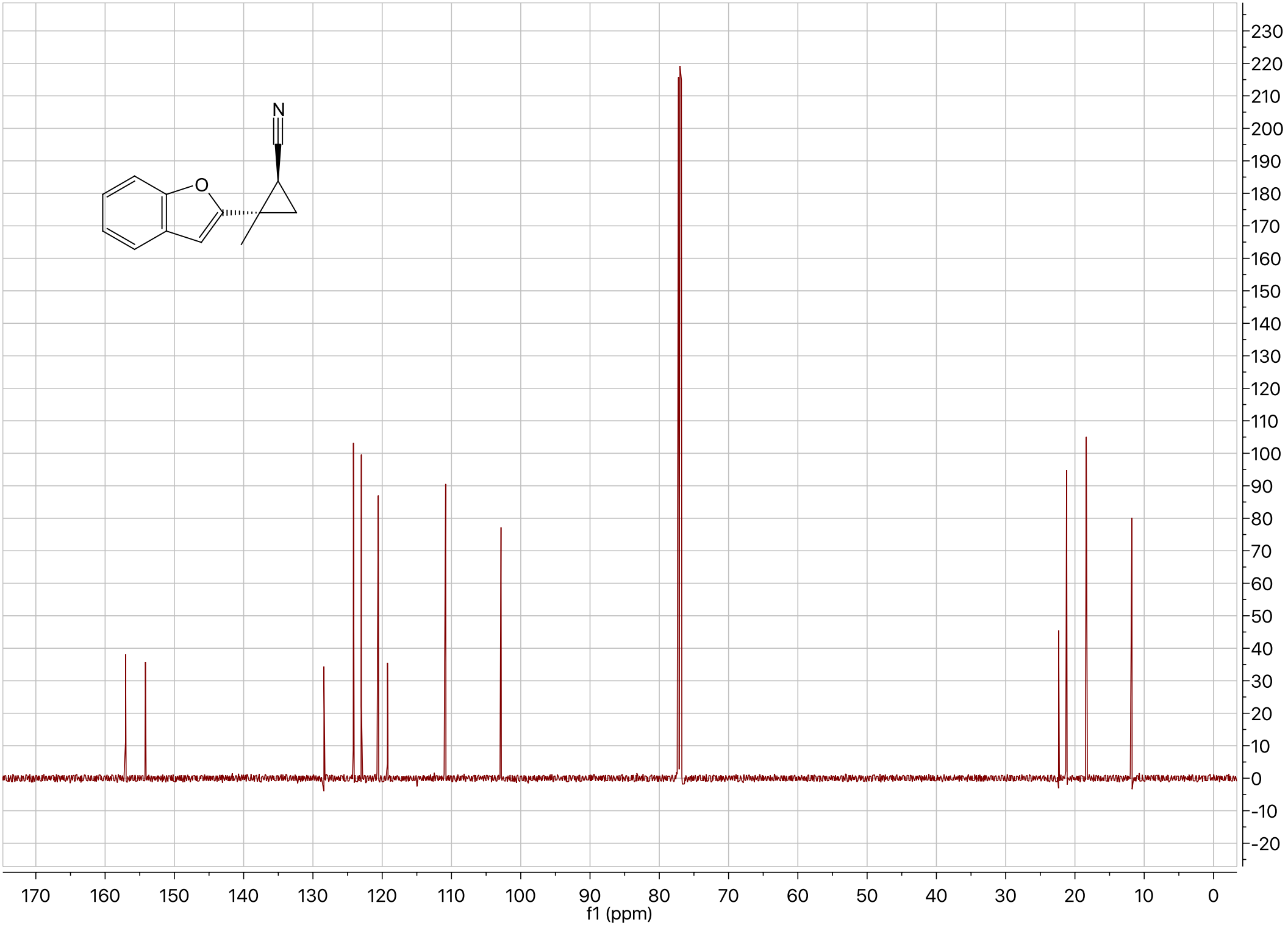

N

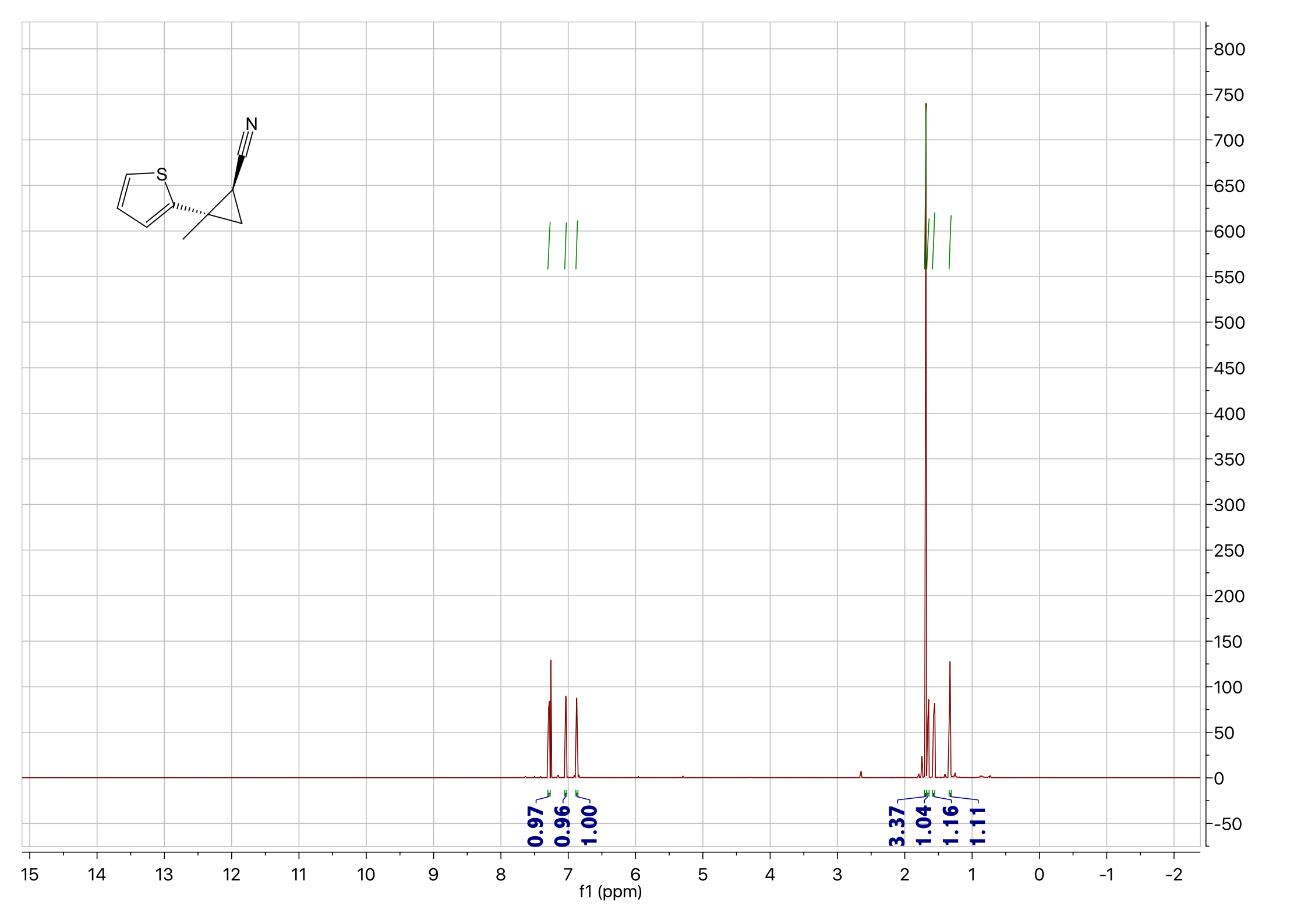
450
400
350
300
250
200
150
100
50
0
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

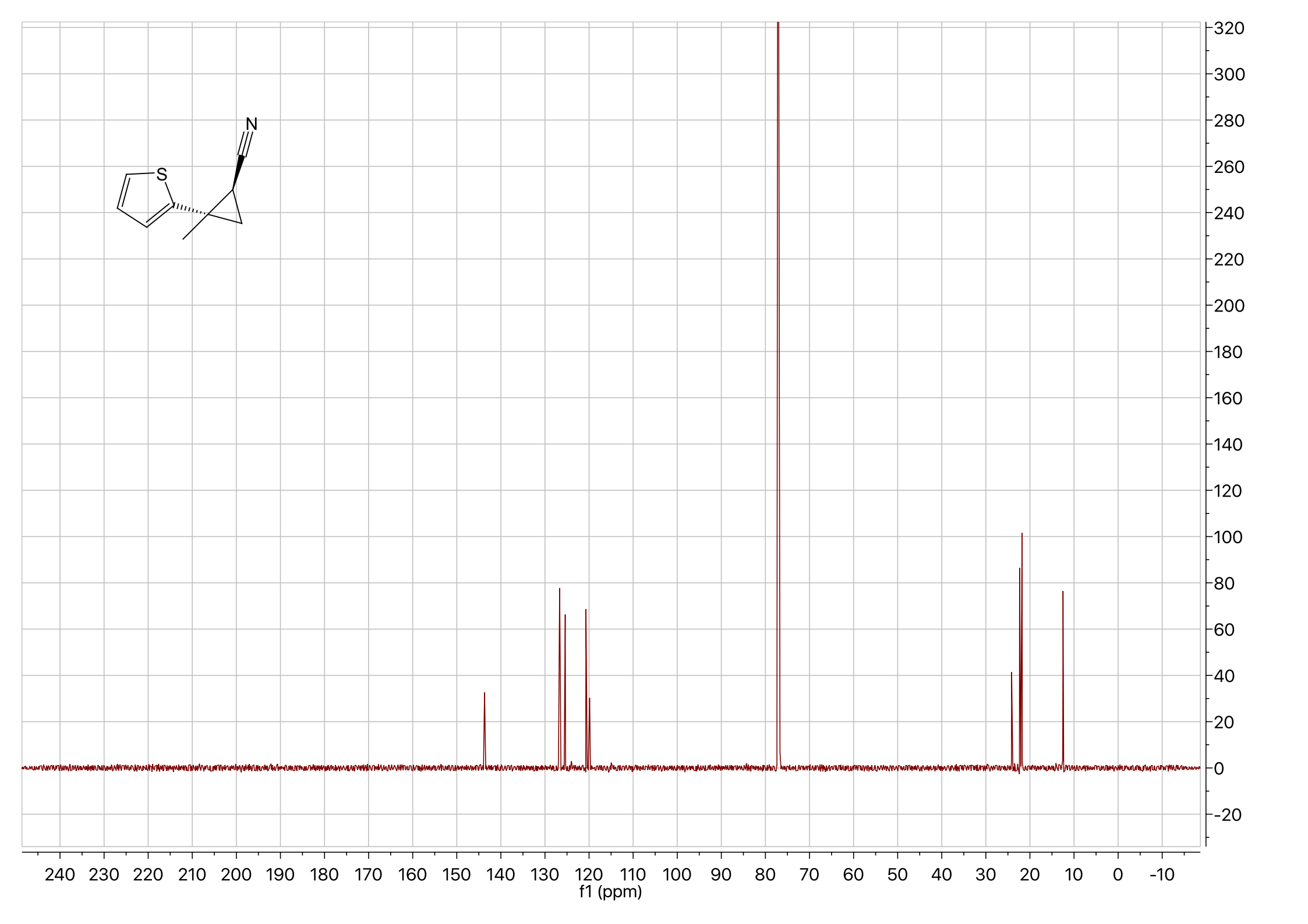

O
O
N
2.54
1.78
3.67
0.96
1.00
f1 (ppm)

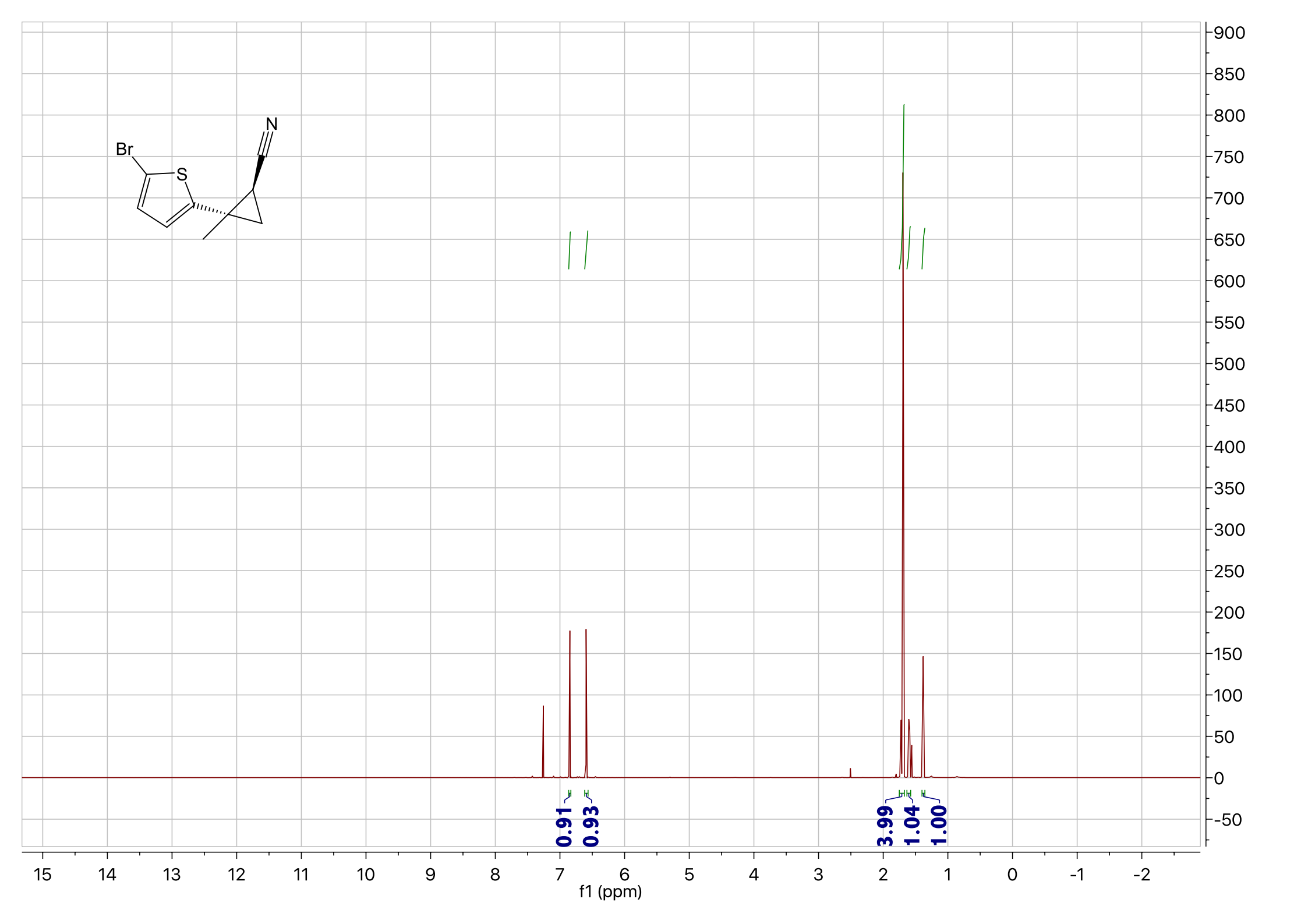

O
O
N
*
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

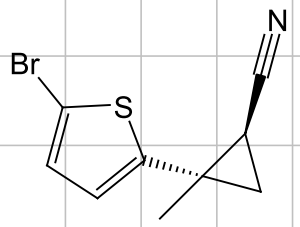

N
O
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
0.90
0.89
2.04
0.90
0.90
1.04
3.00
1.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


N
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

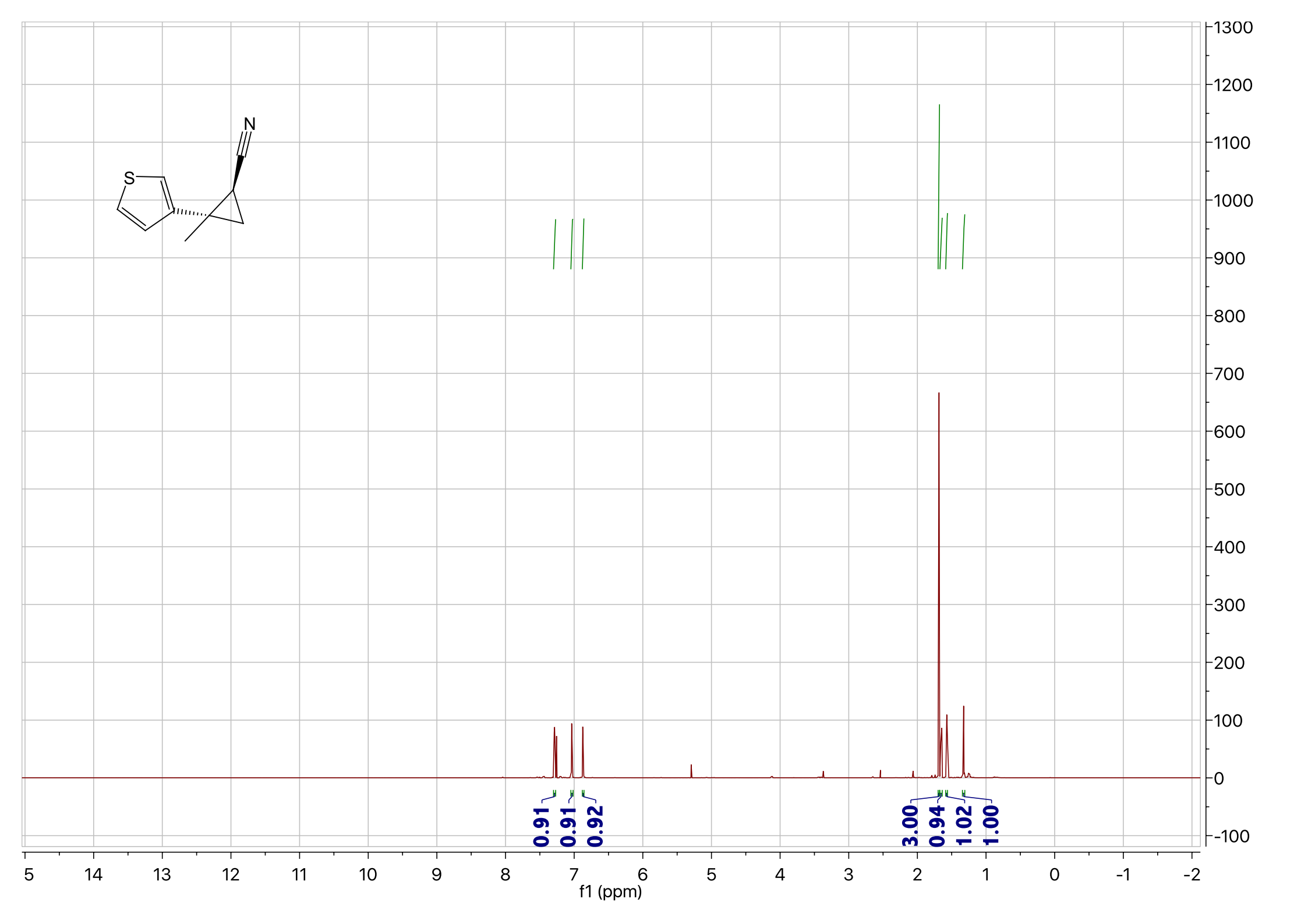

N
S
0.97
0.96
1.00
3.37
1.04
1.16
1.11
f1 (ppm)

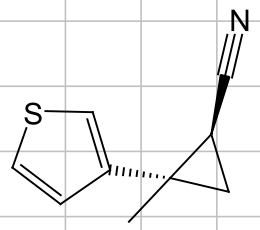

N
S
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Br
S
N
0.91
0.93
3.99
1.04
1.00
f1 (ppm)

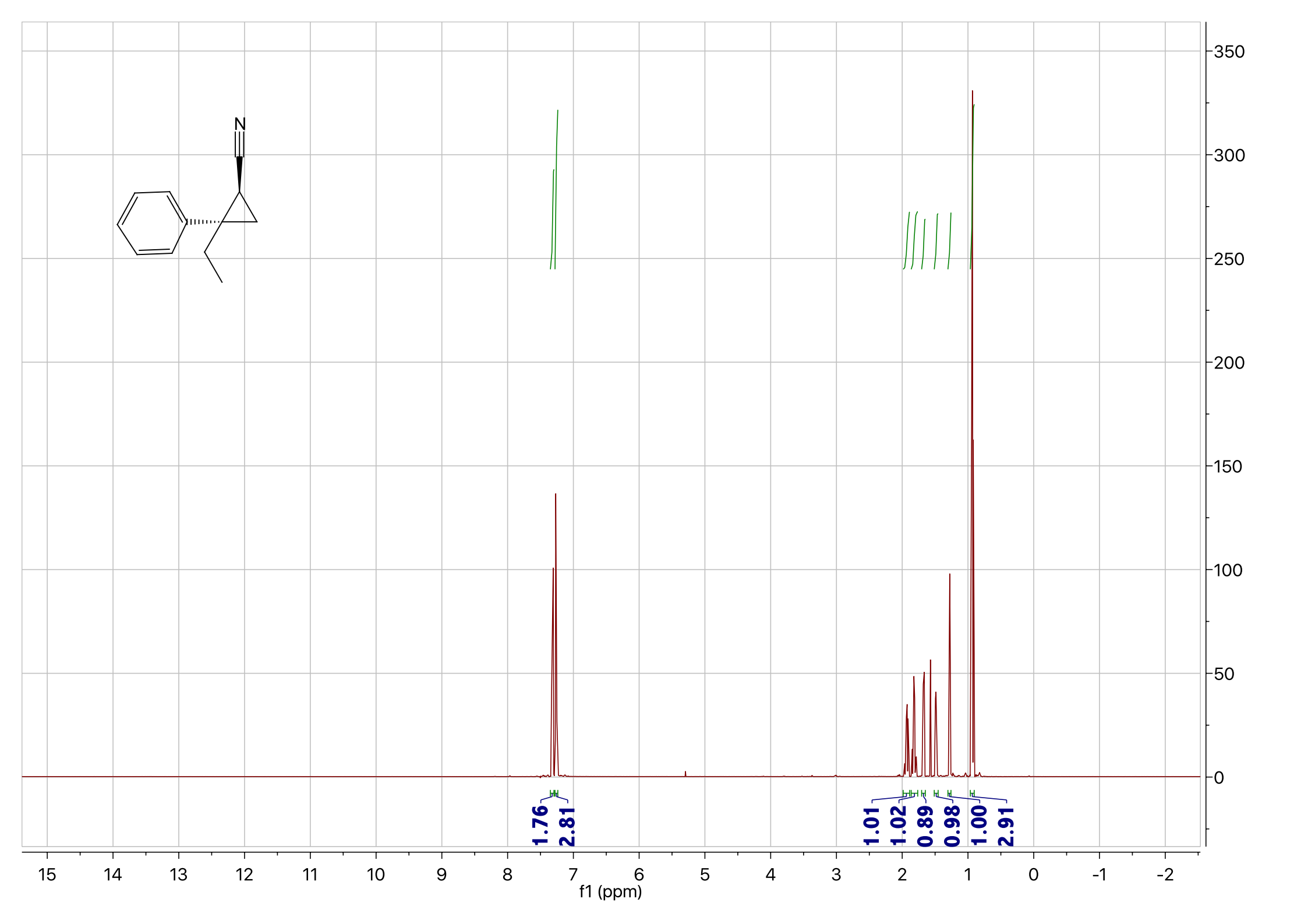


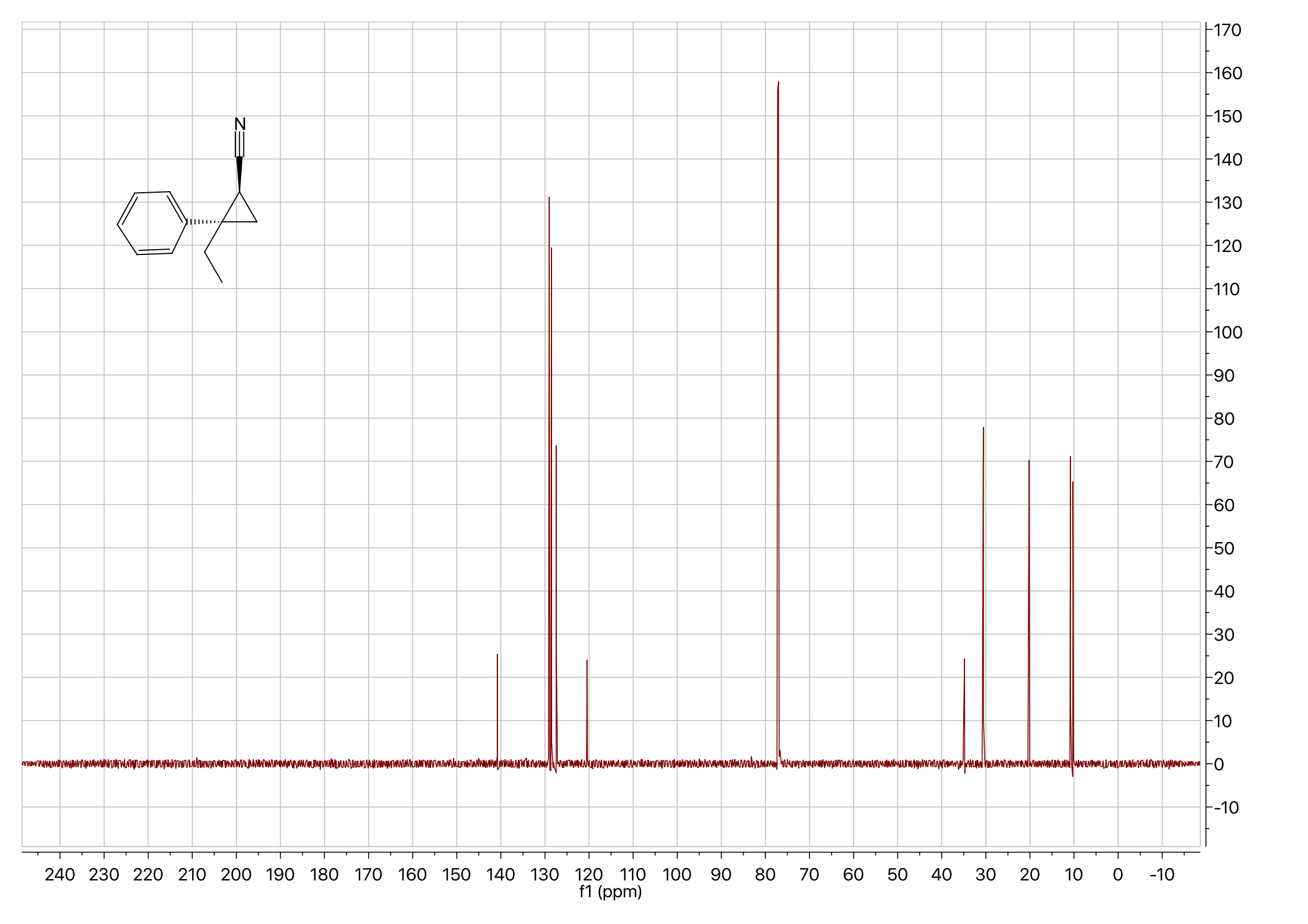
f1 (ppm)

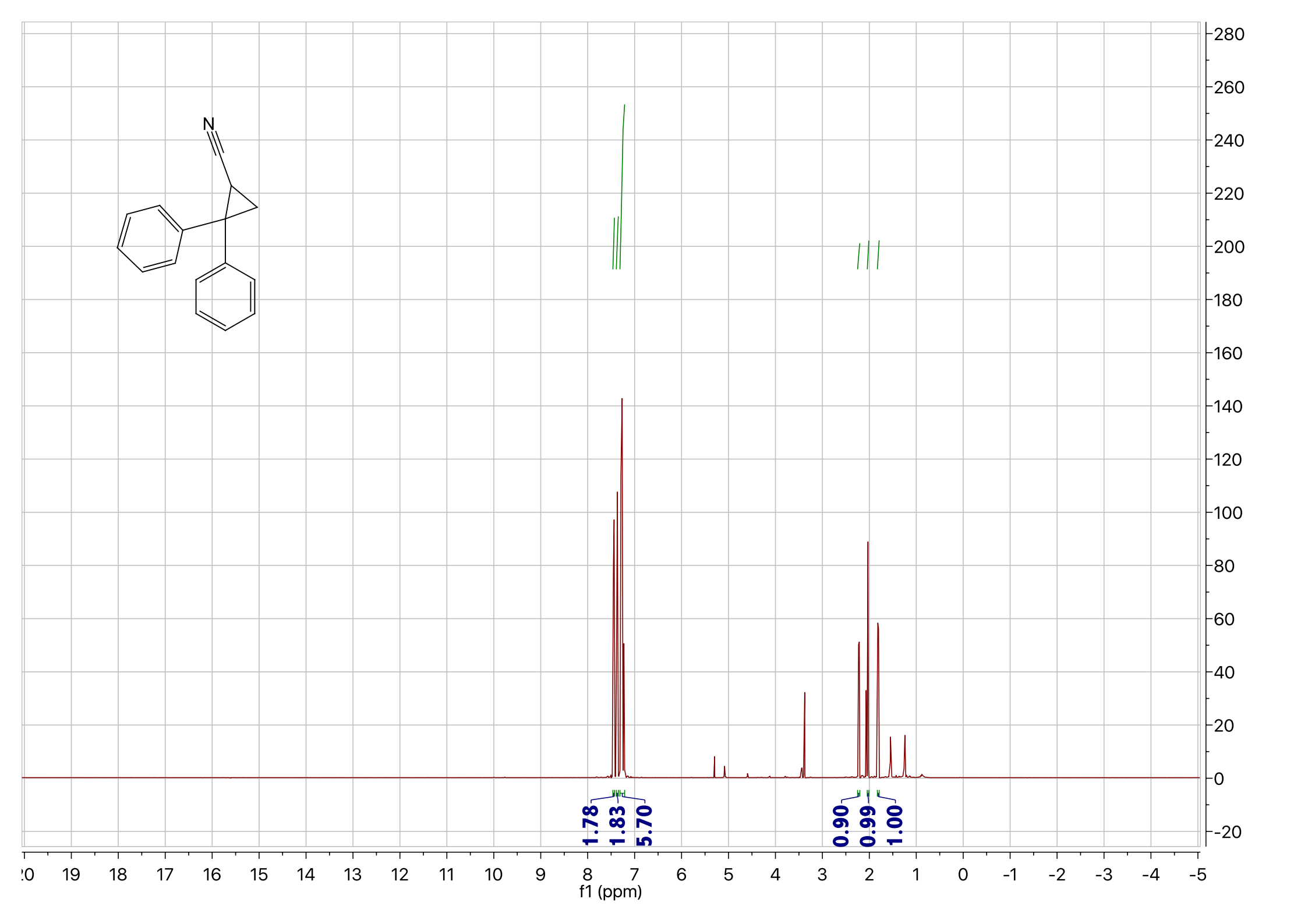

N
S
0.91
0.91
0.92
3.00
0.94
1.02
1.00
f1 (ppm)

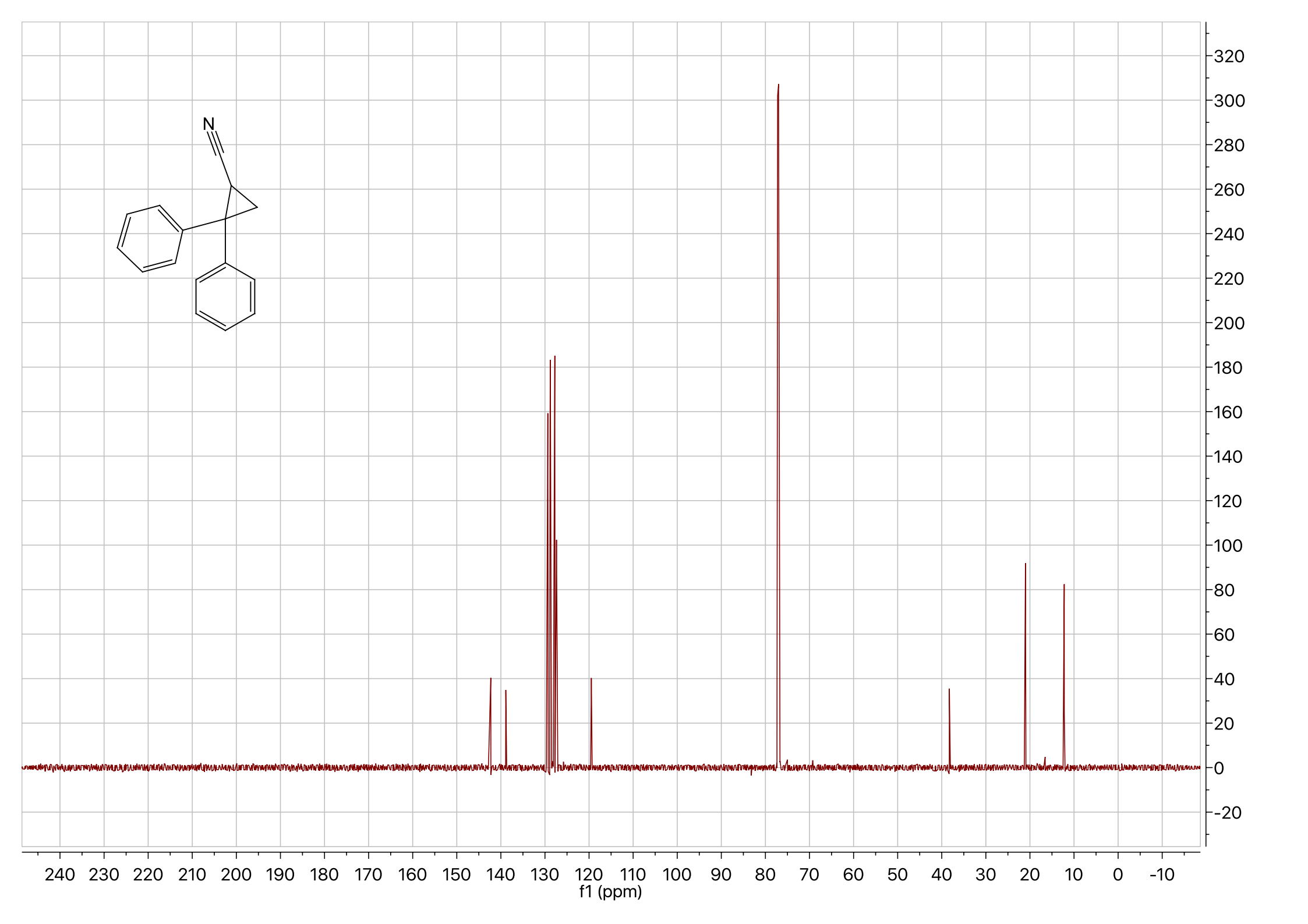

N
S

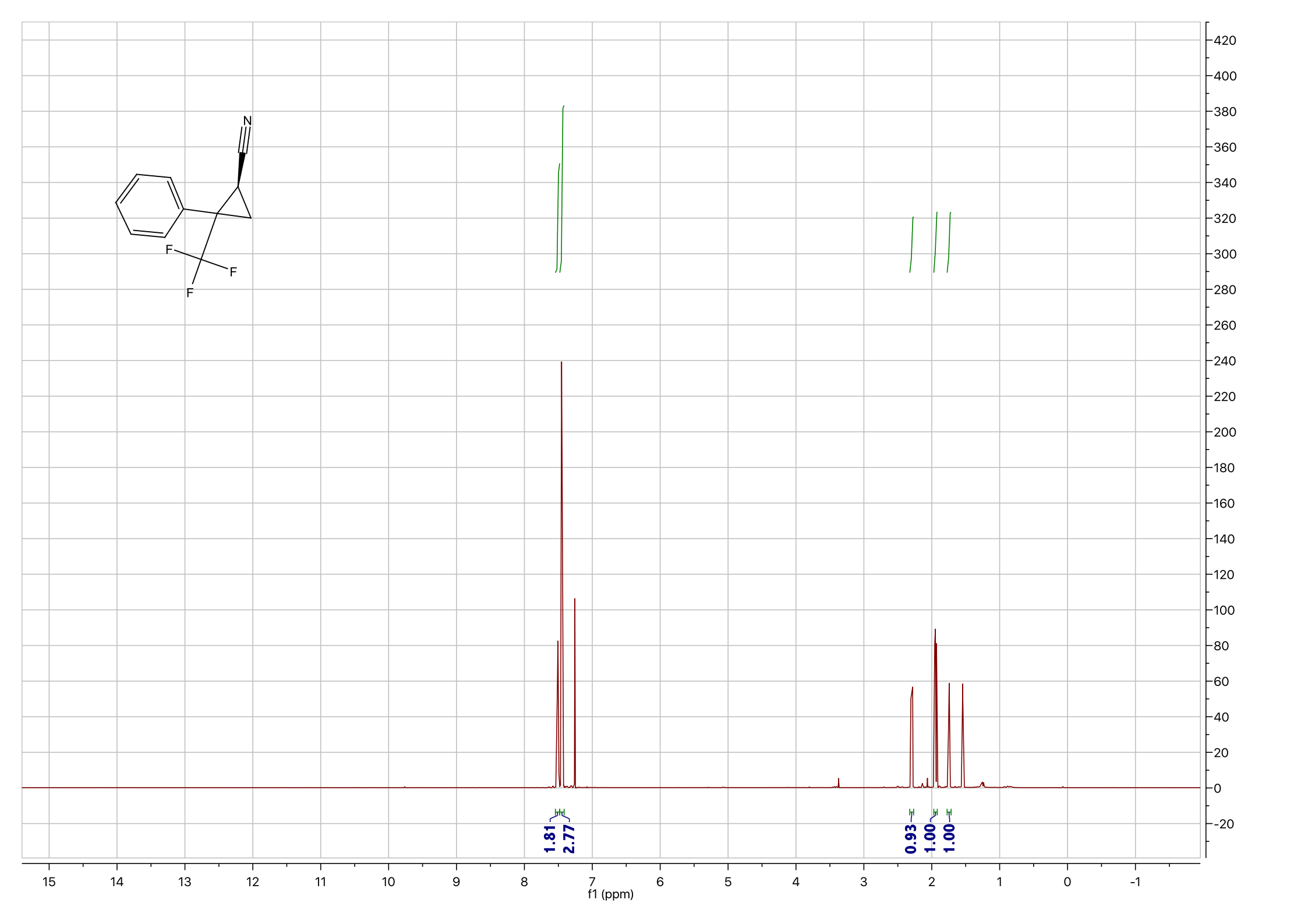
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

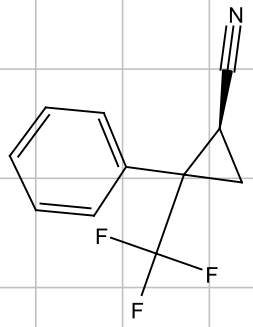

N
350
300
250
200
150
100
50
0
1.76
2.81
1.01
1.02
0.89
0.98
1.00
2.91
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


N
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


N
1.78
1.83
5.70
0.90
0.99
1.00
f1 (ppm)


N
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

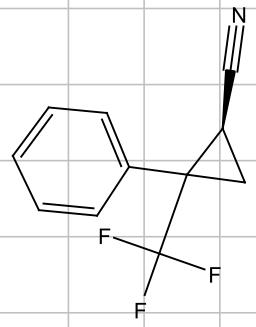

N
F
F
F
1.81
2.77
0.93
1.00
1.00
f1 (ppm)



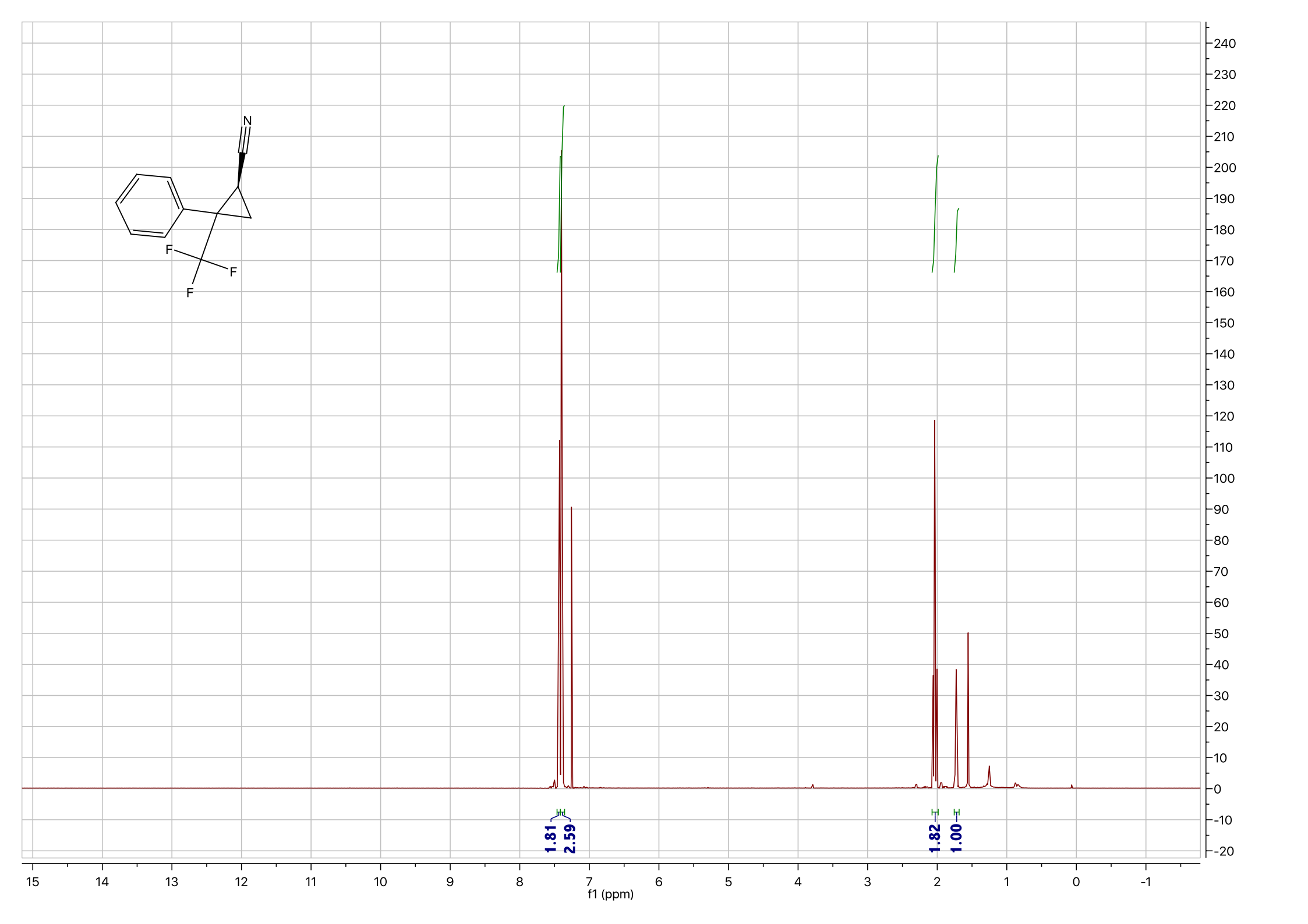
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

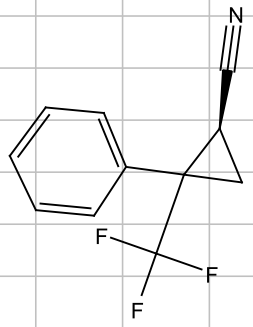
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)

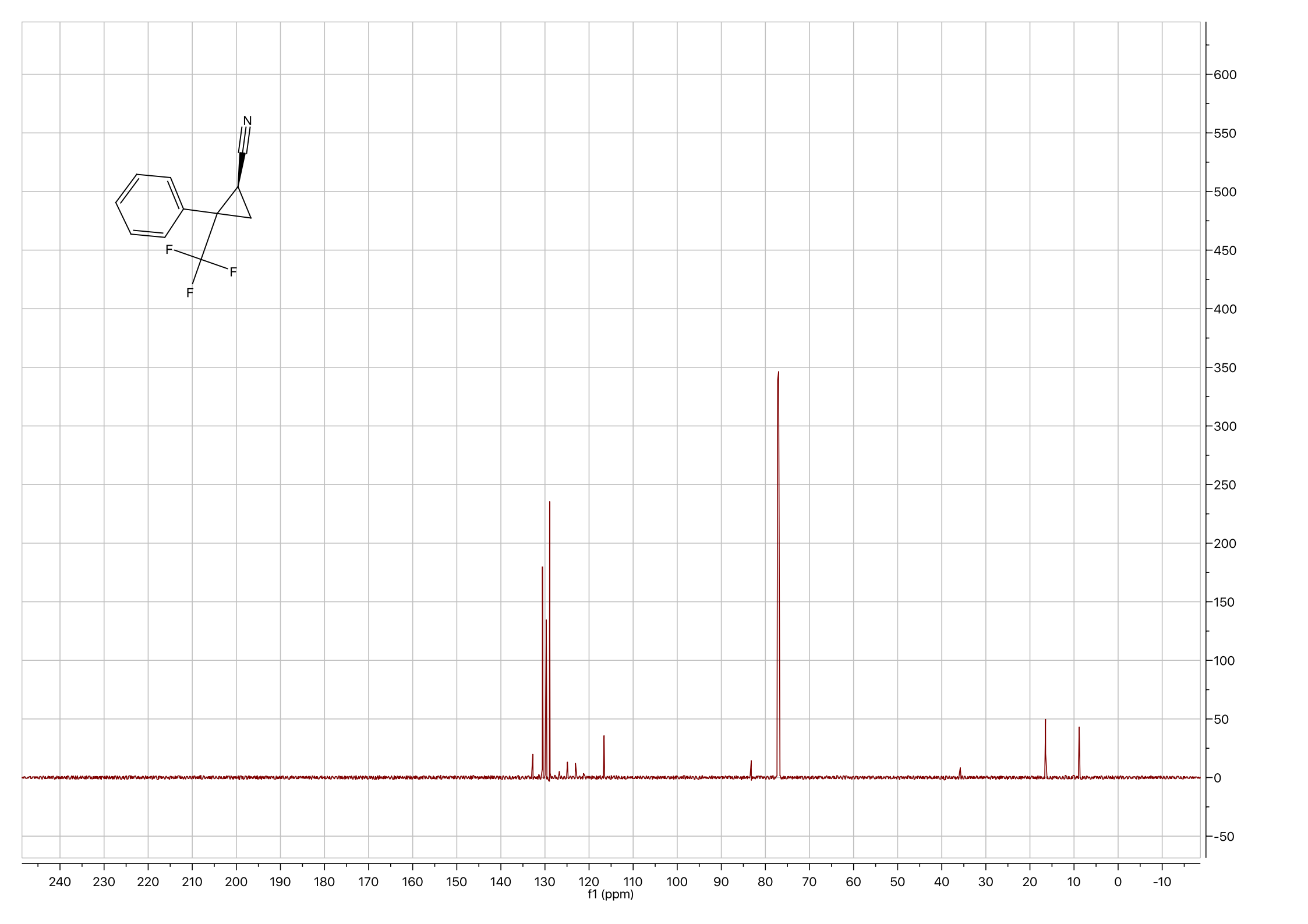


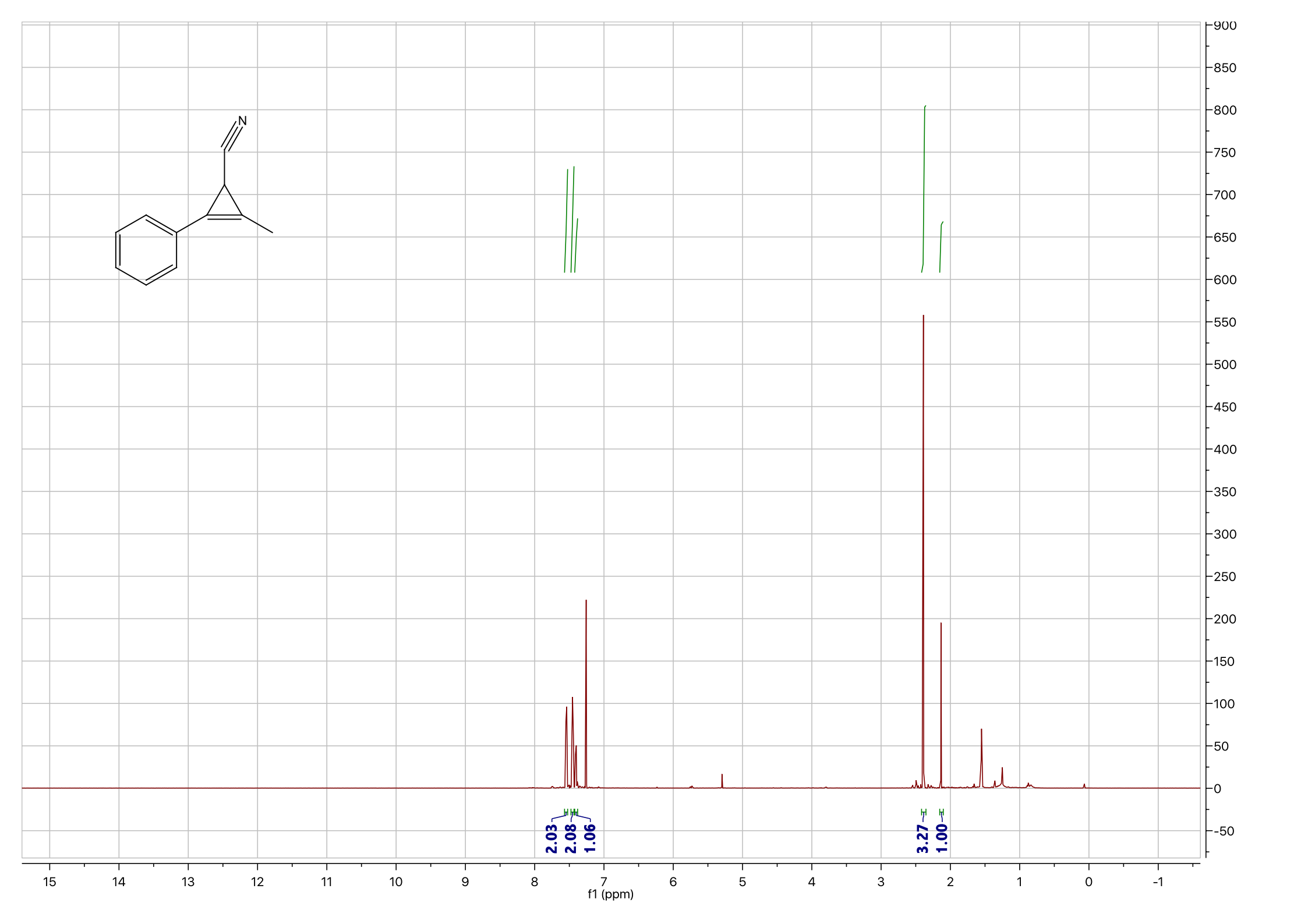
f1 (ppm)

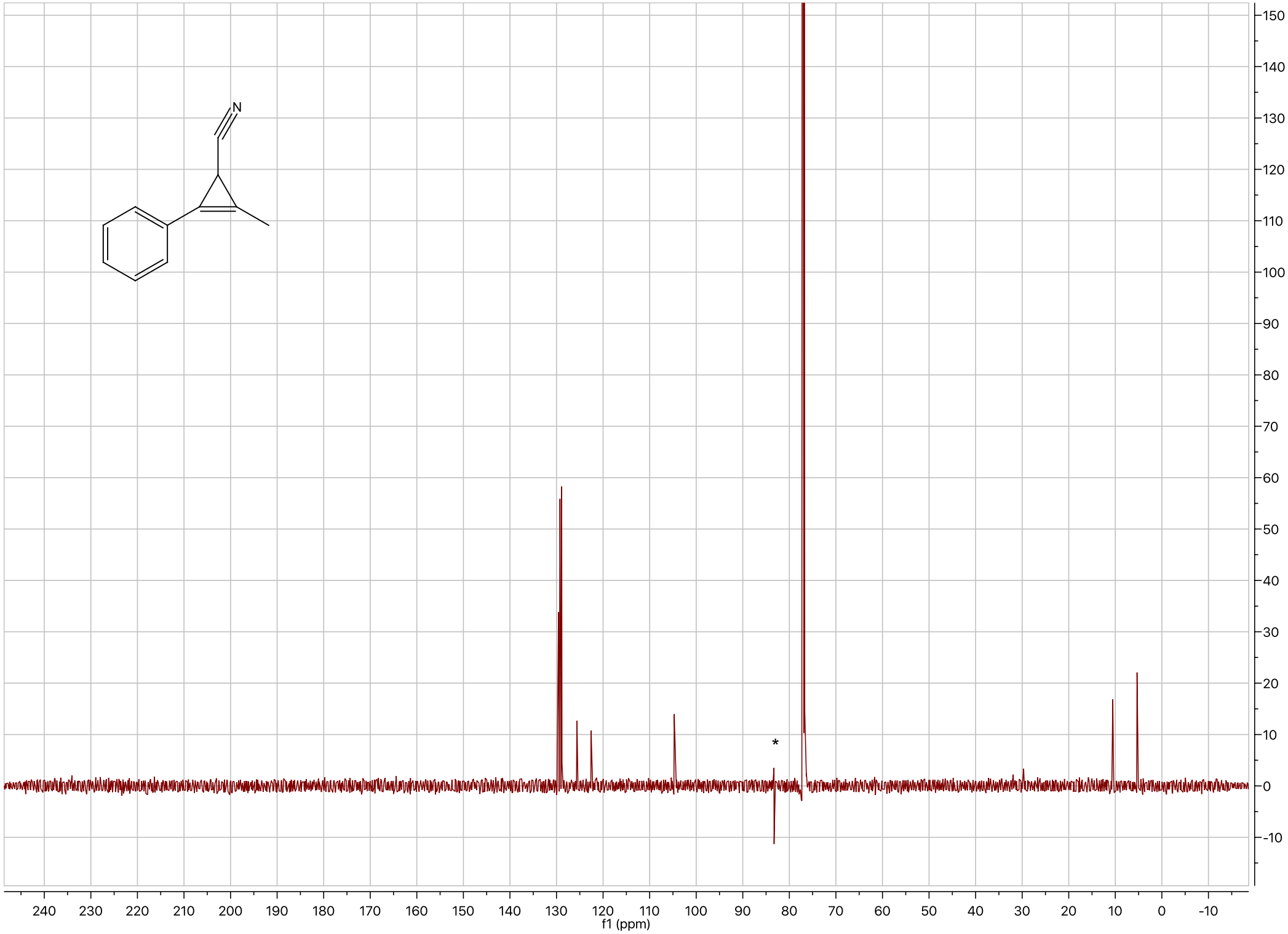

N
F
F
F
1.81
2.59
1.82
1.00
f1 (ppm)

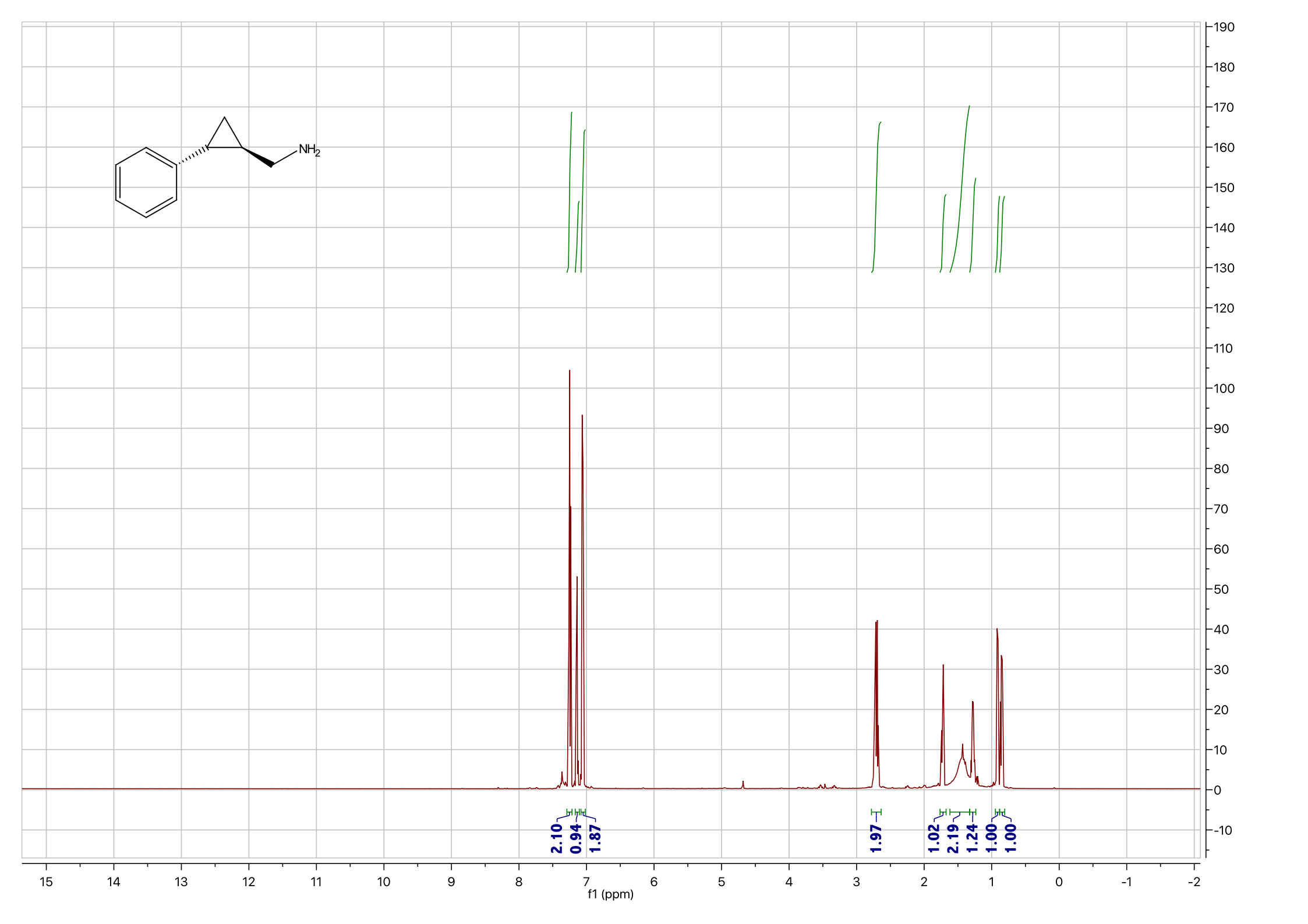


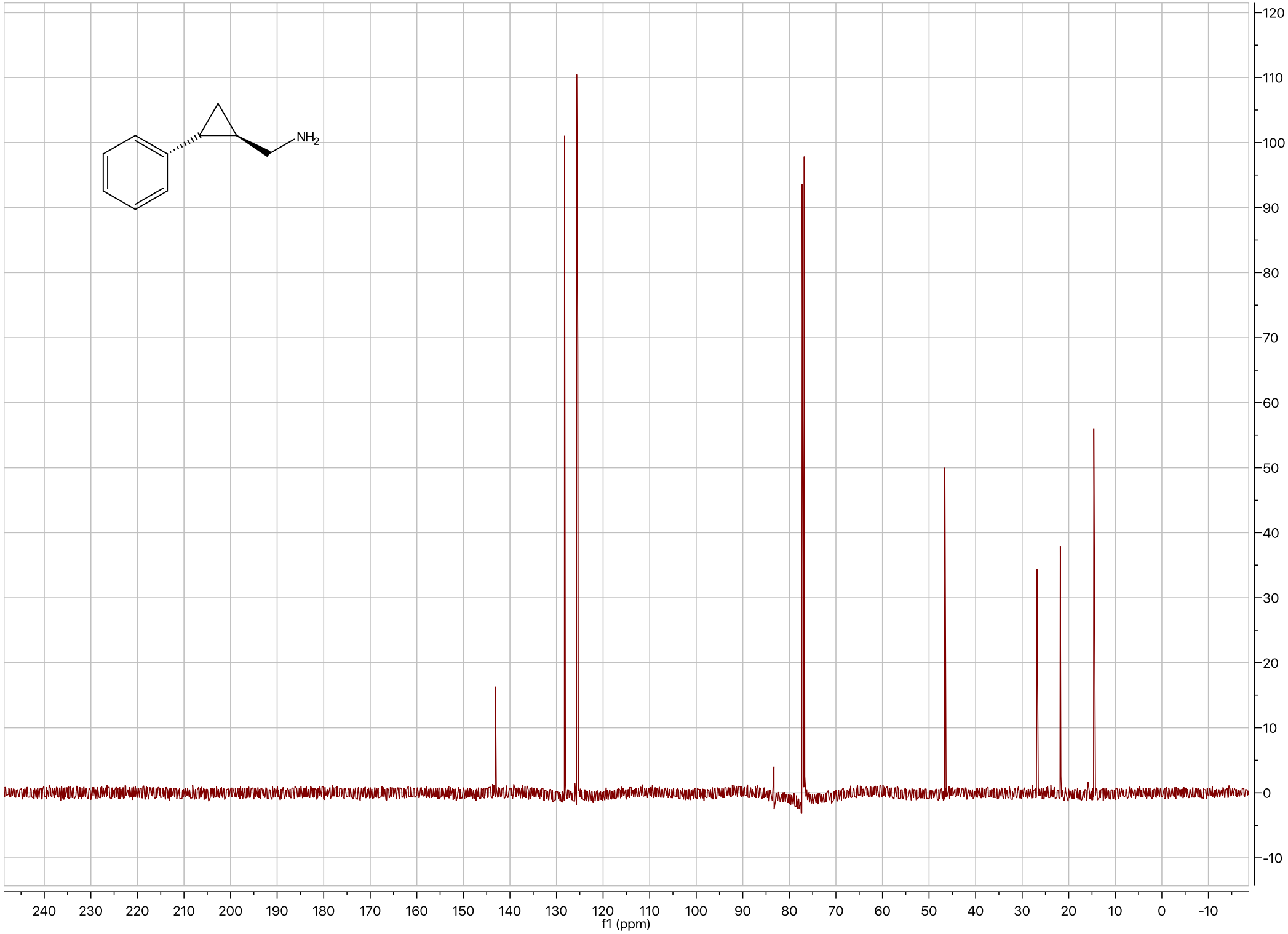
f1 (ppm)


N
F
F
F
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
2.03
2.08
1.06
3.27
1.00
f1 (ppm)


N
*
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


NH2
2.10
0.94
1.87
1.97
1.02
2.19
1.24
1.00
1.00
f1 (ppm)


NH2
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)