Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

The conversion of [(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]azines into azine fused thiazole-2-carbonitriles

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Electronic Supplementary Information

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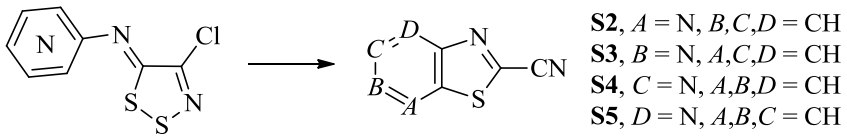
Thermolysis Studies of (Dithiazol-5-ylidene)pyridinamines

Synthesis of thiazolopyridine-2-carbonitriles from N-*(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridinamines* ***S1*** *via thermolysis and via thiophile assisted ring transformations*

Typically the thermolysis of *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)anilines is carried out at 150-160 °C in a preheated Wood's metal bath under an argon atmosphere. To facilitate the present study, the decomposition temperatures of the (dithiazolylidene)pyridinamines **S1a-c** were first determined using differential scanning calorimetry (DSC) (Table S1). Thermolysis of neat *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-2-amine (**S1a**) at *ca.* 210 °C in an argon atmosphere for 10 min gave S_8 and an intractable black residue that could not be resolved. Heating *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S1b**) at *ca.* 155 °C for 10 min under argon atmosphere, however, gave S_8, thiazolo[5,4-*b*]pyridine-2-carbonitrile (**S2** or **10a**) (31%) and thiazolo[4,5-*c*]pyridine-2-carbonitrile (**S4** or **10b**) (35%). Thermolysis of *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-4-amine (**S1c**) at *ca.* 190 °C for 10 min gave S_8 and thiazolo[5,4-*c*]pyridine-2-carbonitrile (**S3**) (30%) (Table S1).

Table S1 Thermolysis of *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridinamines **S1a-c** under argon for 10 min.



S2, *A* = N, *B*,*C*,*D* = CH
S3, *B* = N, *A*,*C*,*D* = CH
S4, *C* = N, *A*,*B*,*D* = CH
S5, *D* = N, *A*,*B*,*C* = CH

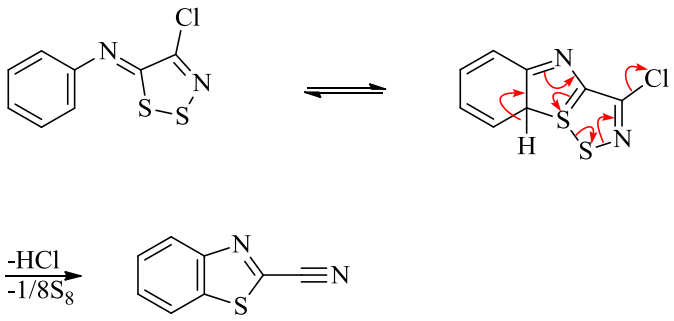
S1a-c

Dithiazole	DSC Decomposition Onset/Peak Temp. (°C)[a]	Reaction Temp. (°C)	Yields (%)
Pyrid-2-yl (**S1a**)	209.7/211.3	210	**S5** (0)
Pyrid-3-yl (**S1b**)	145.3/157.7	155	**S2** (31),[b] **S4** (35),[b] **S1b** (32)
Pyrid-4-yl (**S1c**)	184.0/185.5	190	**S3** (30),[b] **S1c** (8)

[a] Onset/peak decomposition temperatures determined using DSC in hermetically sealed aluminium pans under argon atmosphere with a heating rate of 5 °C/min.
[b] Yields based on recovered (dithiazolylidene)pyridinamines **S1**.

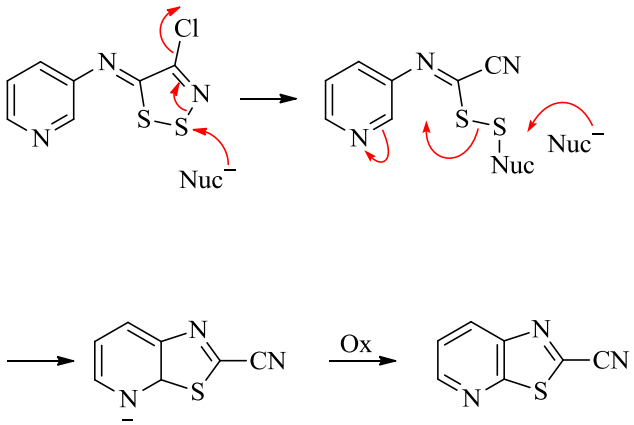
The typical work up involved treating the reaction mixtures (cooled to rt) with water, followed by a DCM extraction and then chromatography. Failure to suspend the reaction mixtures in water

before extraction into the organic phase led to lower product yields. Attempts to dilute the reaction mixtures with Dowtherm® as a high boiling solvent (bp 257 °C), or to use microwave irradiation as a heat source did not simplify the reaction mixtures or lead to improved product yields. Longer reaction times did not lead to complete consumption of the starting material or increased yields on the products formed. The low yields of the desired thiazolopyridines were expected, since the pyridyl substituents were by comparison to the phenyl substituents less electron rich and therefore less likely to form the initial C-S bond required for thiazole formation (Scheme S1).



Scheme S1

In light of the comparative π electron deficiency of pyridine we then considered the thiophile assisted ANRORC style ring transformation of dithiazoles. Tentatively, we postulated that the generation of a nucleophilic S1 atom could be trapped at either of the pyridyls more electrophilic C2 or C4 sites (Scheme S2).



Scheme S2

Initially R_4NHal (Hal = Cl, Br, I) were investigated as thiophiles and the reactions were optimized with respect to the equivalents of the thiophile, the reaction temperature and the solvent (PhH, PhMe, PhCl and xylene). Early studies indicated that benzyltriethylammonium iodide ($BnEt_3NI$) was superior, than the corresponding chloride and bromide that gave slower reactions. Furthermore, the amount of $BnEt_3NI$ could be reduced to only 5 mol% without loss of product yield. In the case of *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-2-amine (**S1a**) the complexity of the reaction prohibited the isolation of any products. When *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S1b**) was treated with $BnEt_3NI$ (0.05 or 1 equiv.) the two expected thiazolopyridine-2-carbonitriles **S2** and **S4** were formed in similar to slightly improved yields than in the case of the thermolysis. In the case whereas chloride or bromide were used (1 equiv.) in PhCl for 24 h, the two products were obtained only in traces and the starting material was recovered in 78-85% (Table S2).

Table S2. Reaction of *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-pyridin-3-amine **S1b** (0.22 mmol) with $BnEt_3NI$ (1 equiv.) in dry solvent (2 ml) under anhydrous conditions, at reflux temperatures.

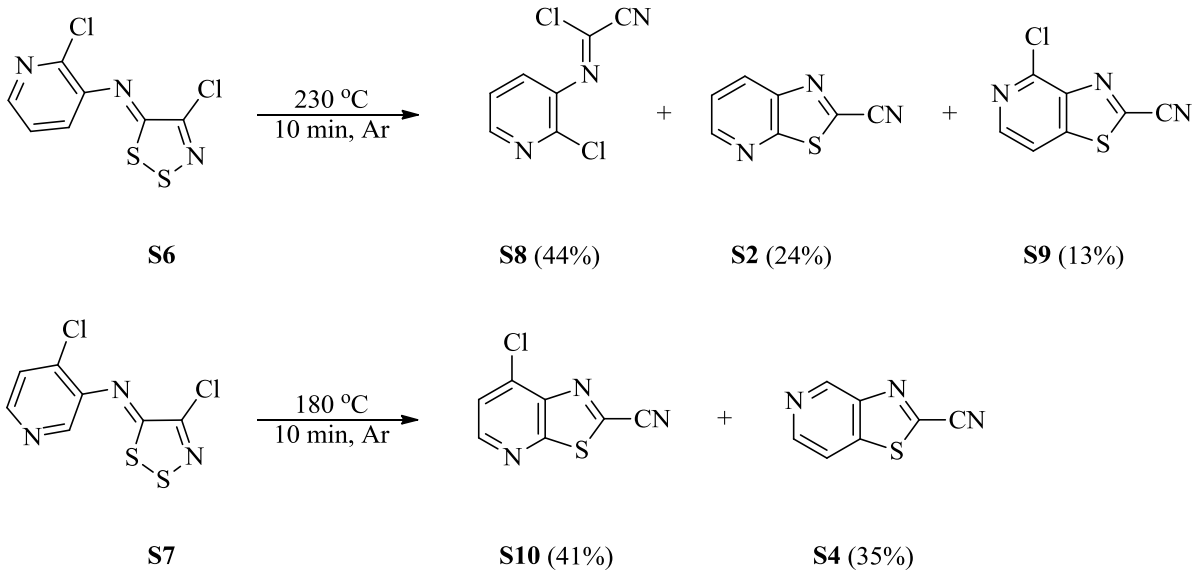
Solvent	Temp. (°C)	Time (h)	Yields (%)	
			S2	**S4**
PhH	80	24	46	22
PhMe	110	2.3	32	17
PhCl	132	0.67	29	25
PhCl[a]	132	20	40	37
xylene	145	0.67	42	35

[a] $BnEt_3NI$ (5 mol%) was used.

When *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-4-amine (**S1c**) was treated with $BnEt_3NI$ (1 equiv.) in PhCl at *ca.* 132 °C only S_8 and traces of the expected thiazolo[5,4-*c*]pyridine **S3** were observed by TLC, however, using a catalytic amount of $BnEt_3NI$ (5 mol%) in PhCl at *ca.* 132 °C for 20 h afforded the desired thiazole[5,4-*c*]pyridine **S3** in a modest 11% yield. The use of chloride or bromide failed to give a complete reaction or improve the product yield.

*Synthesis of thiazolopyridine-2-carbonitriles from 2-chloro- or 4-chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amines **S6** and **S7** via thermolysis and via thiophile assisted ANRORC*

DSC studies indicated the decomposition temperatures of dithiazolylidenamines **S6** and **S7** to be *ca.* 210 and 160 ºC, respectively. Thermolysis of 2-chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S6**) at 230 ºC for 10 min under an argon atmosphere gave S_8 and three other products, while a similar thermolysis of 4-chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S7**) at *ca.* 180 °C for 10 min gave S_8 and two other products (Scheme S4).

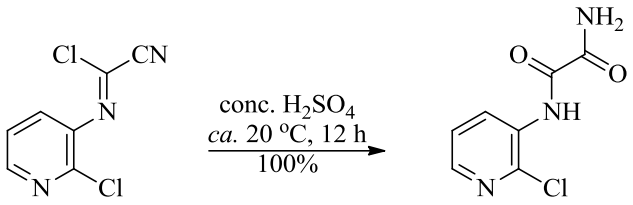


S6 **S8** (44%) **S2** (24%) **S9** (13%)

S7 **S10** (41%) **S4** (35%)

Scheme S4

The first product from the thermolysis of **S6** was that expected from the thermolysis of dithiazolylidenamines bearing electron poor aromatic rings, 2-chloropyridin-3-yl)carboncyanid-imidic chloride (**S8**). The second product was the desired thiazolo[5,4-*b*]pyridine **S2** and the third product was 4-chlorothiazolo[4,5-*c*]pyridine-2-carbonitrile (**S9**). Interestingly, during the chromatographic (silica) isolation of the products, some of the carbonocyanidimidic chloride **S8** converted into *N*′-(2-chloropyridin-3-yl)oxalamide (**S11**). Treatment of the carbonocyanidimidic chloride **S8** with conc. H_2SO_4 gave the oxalamide **S11** in quantitative yield (Scheme S5).



S8 **S11**

Scheme S5

N'-(2-Chloropyridin-3-yl)oxalamide (**S11**) was obtained as colorless needles, mp 221-222 °C (from cyclohexane/EtOH). Microanalysis and mass spectrometry supported the formula $C_7H_6ClN_3O_2$, which indicated that both a hydrolysis and hydration had occurred. The ^{13}C NMR spectrum showed seven carbon resonances of which four were quaternaries. IR bands at 3370, 3291 and 3229 cm^{-1} and at 1721 and 1697 cm^{-1} indicated the presence of NH/NH_2 and carbonyl functionality, respectively. The presence of amino groups was also supported by ^1H NMR spectroscopy that showed three deuterium exchangeable resonances: A singlet at 10.19 ppm and two broad singlets at 8.48 and 8.18 ppm, integrating for one hydrogen each. Furthermore, the ^1H NMR spectrum identified three double-doublet resonances at δ_H 8.33 (*J* 8.0, 1.5 Hz), 8.27 (*J* 5.0, 1.5 Hz) and 7.51 ppm (*J* 8.0, 5.0 Hz), which supported a 2,3-disubstituted pyridine. A mass spectrometry fragment at *m/z* 128, which gave a chlorine isotope pattern, tentatively supported the remaining chlorine atom to be attached to the pyridine ring.

4-Chlorothiazolo[4,5-*c*]pyridine-2-carbonitrile (**S9**) was obtained as colorless needles, mp 161-162 °C (from cyclohexane). High resolution mass spectrometry supported the formula $C_7H_2ClN_3S$. The presence of a cyano group was supported by an IR band at ν(C≡N) 2241 cm^{-1} and a signal in the ^{13}C NMR at δ_C 111.8 ppm. The ^1H NMR spectrum identified two aromatic hydrogen resonances observed as doublets at δ_H 8.52 (*J* 5.5 Hz) and 7.90 ppm (*J* 6.6 Hz) which supported substitution had occurred onto the pyridyl C4 position. This was also supported by the ^{13}C NMR spectrum which showed seven separate carbon resonances of which only two were tertiary.

From the thermolysis of 4-chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S7**) 7-chlorothiazolo[5,4-*b*]pyridine-2-carbonitrile (**S10**) and the expected thiazolo[4,5-*c*]pyridine **S4** were obtained. 7-Chlorothiazolo[5,4-*b*]pyridine-2-carbonitrile (**S10**) was obtained as colorless cotton fibers, mp 177-178 ^{o}C (from cyclohexane). Microanalysis and mass spectrometry supported the formula $C_7H_2ClN_3S$. The presence of a cyano group was supported by an IR band at ν(C≡N) 2234 cm^{-1} and a signal in the ^{13}C NMR at δ_C 112.1 ppm. The ^{1}H NMR spectrum identified two aromatic hydrogen resonances observed as doublets at δ_H 8.70 (*J* 5.0 Hz) and 7.66 ppm (*J* 5.0 Hz) which supported substitution had occurred onto the pyridyl C2 position. This was also supported by the ^{13}C NMR spectrum that showed seven separate carbon resonances of which only two were tertiary.

Experimental Procedures for Thermolysis Study

*Thermolysis of (Z)-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine* ***(S1b)*** *(Typical procedure).*

A dry one-neck round bottom flask (5 ml) was charged with (*Z*)-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S1b**) (50.5 mg, 0.22 mmol), fitted with an air condenser, de-aired under vacuum and then flooded with argon. The reaction flask was then immersed into a preheated Wood's metal bath at *ca.* 155 °C for 10 min and then left to cool to *ca.* 20 °C and partitioned between DCM (10 ml) and water (10 ml). The organic layer was collected and the aqueous phase was extracted with DCM (2 × 10 ml). Then the aqueous layer was neutralized (sat. $NaHCO_3$) and extracted with DCM (3 × 10 ml). The organic layers were combined, dried (anhyd. Na_2SO_4), concentrated under vacuum and adsorbed onto silica. Chromatography (hexane) gave S_8 (4.9 mg, 70%), further elution (hexane/DCM, 2:8) gave thiazolo[5,4-*b*]pyridine-2-carbonitrile (**S2** or **10a**) (7.4 mg, 21%) as colorless cotton fibers, mp (DSC) onset: 133.6 °C, peak max: 134.3 °C (from cyclohexane) identical to an authentic sample. Further elution (hexane/*t*-BuOMe, 1:9) gave (*Z*)-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S1b**) (16.2 mg, 32%) as yellow cotton fibers, mp 126–127 °C (from cyclohexane/EtOH) identical to an authentic sample. Further elution (hexane/*t*-BuOMe, 1:9) gave thiazolo[4,5-*c*]pyridine-2-carbonitrile (**S4** or **10b**) (8.5 mg, 24%) as colorless needles, mp (DSC) onset: 187.2 °C, peak max: 187.8 °C (from cyclohexane) identical to an authentic sample.

*Thermolysis of (Z)-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-4-amine* ***(S1c).***

Similar treatment of (*Z*)-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-4-amine (**S1c**) (50.5 mg, 0.22 mmol) gave after chromatography (hexane) S_8 (5.7 mg, 81%), further elution (DCM/*t*-BuOMe, 9:1) gave *thiazolo[5,4-*c*]pyridine-2-carbonitrile* (**S3**) (10.1 mg, 28%) as colorless needles, mp 95-97 °C (from cyclohexane) identical to an authentic sample. Further elution (DCM/*t*-BuOMe, 9:1) gave

unreacted (*Z*)-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-4-amine (**S1c**) (4 mg, 8%) as yellow prisms, mp 166–167 °C (from cyclohexane/EtOH) identical to an authentic sample.

*Thermolysis of (Z)-2-chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S6**).*

Similar treatment of (*Z*)-2-chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S6**) (50.2 mg, 0.19 mmol) gave after chromatography (hexane) S_8, further elution (hexane/DCM, 2:8) gave *(2-chloropyridin-3-yl)carbonocyanidimidic chloride* (**S8**) (16.7 mg, 44%) as colorless needles, mp 24.3-26.0 ^{o}C (from pentane), R_f 0.69 (hexane/DCM, 2:8); λ_{max}(DCM) 230 (log ε 3.00), 273 (2.65), 325 (2.41); ν_{max}/cm^{-1} 3069w (Ar CH), 2241w (C≡N), 1638s, 1568w, 1443w, 1406s, 1204m, 1130m, 1080m, 1061m, 1047s, 1011w, 943w, 843m, 810s; δ_H(500 MHz; $CDCl_3$) 8.38 (1H, dd, *J* 3.3, 3.3), 7.37-7.34 (2H, m); δ_C(125 MHz; $CDCl_3$) 148.3 (d), 142.0 (s), 138.2 (s), 128.6 (d), 122.7 (d), 120.7 (s), 111.6 (s); *m/z* (EI) 203 (M^++4, 5%), 201 (M^++2, 29), 199 (M^+, 44), 166 (33), 164 (98), 114 (33), 112 (100), 103 (5), 85 (15), 76 (59), 64 (7), 50 (25); HRMS (EI) (Found M^+, 198.9719, $C_7H_3Cl_2N_3$ requires *M*, 198.9704). Further elution (hexane/Et_2O, 6:4) gave thiazolo[5,4-*b*]pyridine-2-carbonitrile (**S2** or **10a**) (7.3 mg, 24%) as colorless cotton fibers, mp (DSC) onset: 133.6 ^{o}C, peak max: 134.3 ^{o}C (from cyclohexane) identical to an authentic sample. Further elution (hexane/Et_2O, 1:1) gave *4-chlorothiazolo[4,5-c]pyridine-2-carbonitrile* (**S9**) (4.8 mg, 13%) as colorless needles, mp 161-162 ^{o}C (from cyclohexane), R_f 0.41 (hexane/DCM, 2:8); λ_{max}(DCM) 241 inf (log ε 2.73), 246 (2.76), 273 (2.96), 302 (2.84); ν_{max}/cm^{-1} 3086w (Ar CH), 2241w (C≡N), 1566s, 1514m, 1460m, 1423s, 1383m, 1287m, 1234m, 1215m, 1159m, 1119s, 1105m, 1069w, 835s, 822s, 715w; δ_H(500 MHz; $CDCl_3$) 8.53 (1H, d, *J* 5.5), 7.90 (1H, d, *J* 5.5); δ_C(125 MHz; $CDCl_3$) 148.1 (s), 145.9 (s), 145.9 (d), 144.6 (s), 138.2 (s), 115.8 (d), 111.8 (s); HRMS (EI) (Found M^+, 194.9680, $C_7H_2ClN_3S$ requires *M*, 194.9658).

*Thermolysis of (Z)-4-chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S7**).*

Similar treatment of (*Z*)-4-chloro-*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (**S7**) (50.2 mg, 0.19 mmol) gave after chromatography (hexane) S_8 (4.7 mg, 81%), further elution (DCM)

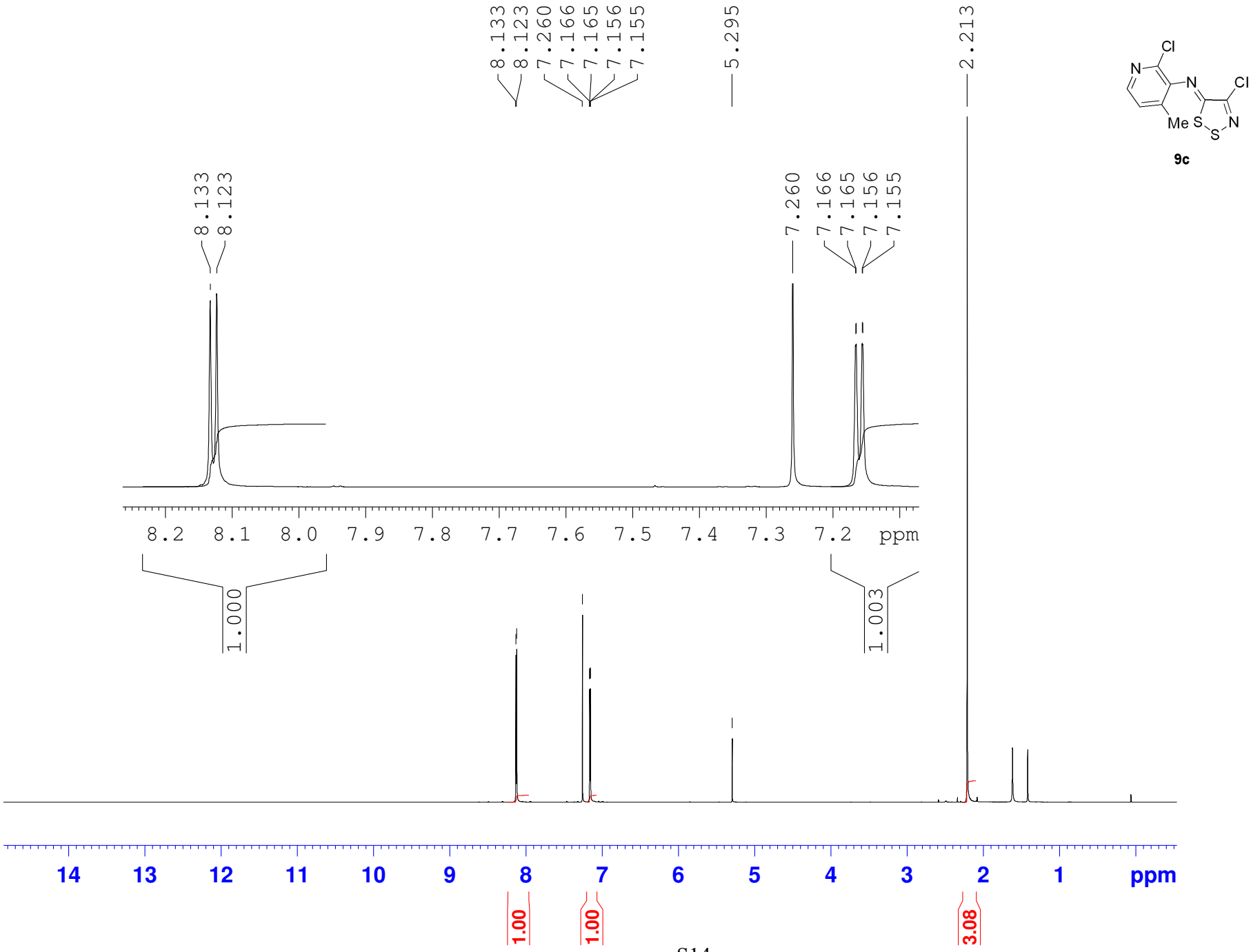
gave *7-chlorothiazolo[5,4-*b*]pyridine-2-carbonitrile* (**S10**) as colorless cotton fibers (15.2 mg, 41%), mp (DSC) onset: 187.2 °C, peak max: 188.3 °C (from cyclohexane); R_f 0.63 (hexane/DCM, 2:8); (found: C, 42.92; H, 1.00; N, 21.57. $C_7H_2ClN_3S$ requires: C, 42.98; H, 1.03; N, 21.48%); λ_{max}(DCM) 230 (log ε 3.10), 241 (3.01), 245 inf (2.99), 282 (3.26), 300 inf (3.09), 311 inf (2.91); ν_{max}/cm^{-1} 3090w and 3049w (Ar CH), 2234w (C≡N), 1566m, 1537m, 1530m, 1462m, 1439m, 1340m, 1288m, 1252m, 1167m, 1121s, 870w, 839s; δ_H(500 MHz; $CDCl_3$) 8.70 (1H, d, *J* 5.5), 7.66 (1H, d, *J* 5.0); δ_C(125 MHz; $CDCl_3$) 158.4 (s), 151.1 (d), 143.3 (s), 140.4 (s), 138.2 (s), 123.4 (d), 112.1 (s); *m/z* (EI) 197 (M^++2, 37%), 195 (M^+, 100%), 160 (23), 145 (5), 143 (13), 137 (8), 108 (16), 83 (21), 81 (28), 70 (35), 64 (18), 50 (12). Further elution (DCM/*t*-BuOMe, 9:1) gave thiazolo[4,5-*c*]pyridine-2-carbonitrile (**S4** or **10b**) (10.7 mg, 35%) as colorless needles, mp (DSC) onset: 187.2 °C, peak max: 187.8 °C (from cyclohexane) identical to an authentic sample.

*Hydrolysis of (2-chloropyridin-3-yl)carbonocyanidimidic chloride (**S8**).*

A solution of (2-chloropyridin-3-yl)carbonocyanidimidic chloride (**S8**) (30 mg, 0.15 mmol) in conc. H_2SO_4 (0.5 ml) was left standing for 12 h at *ca.* 20 ºC. The reaction mixture was then poured onto ice and left to warm to *ca.* 20 ºC. Then the aqueous layer was extracted with DCM (5 × 15 ml). The organic extracts were combined, dried (Na_2SO_4) and concentrated to give N'-*(2-chloropyridin-3-yl)oxalamide* (**S11**) (29.9 mg, 100%) as colorless needles, mp (DSC) onset: 221.2 °C, peak max: 222.1 ºC (from cyclohexane/EtOH); R_f 0.38 (DCM/*t*-BuOMe, 8:2); (found: C, 41.97; H, 2.95; N, 20.88. $C_7H_6ClN_3O_2$ requires: C, 42.12; H, 3.03; N, 21.05%); λ_{max}(DCM) 272 (log ε 3.63), 279 inf (3.58); ν_{max}/cm^{-1} 3370w, 3291w and 3229w (NH), 1721m (C=O), 1697s (C=O), 1584s, 1520s, 1456m, 1414s, 1381s, 1339w, 1306w, 1207m, 1180m, 1082s, 1055w, 920m, 860w, 800s; δ_H(500 MHz; $CDCl_3$) 10.19 (1H, s), 8.48 (1H, br s), 8.33 (1H, dd, *J* 8.0, 1.5), 8.27 (1H, dd, *J* 5.0, 1.5), 8.18 (1H, br s), 7.51 (1H, dd, *J* 8.0, 5.0); δ_C(125 MHz; $CDCl_3$) 161.0 (s), 158.8 (s), 145.8 (d), 142.8 (s), 132.0 (d), 130.8 (s), 123.7 (d); *m/z* (EI) 201 (M^++2, 3%), 199 (M^+, 11), 179 (3), 164 (100), 155 (22),

149 (10), 130 (7), 128 (22), 119 (33), 113 (5), 111 (10), 97 (12), 92 (23), 85 (11), 83 (10), 81 (6), 76 (4), 71 (14), 69 (10), 65 (8), 57 (18), 55 (10).

(Z)-2-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-4-methylpyridin-3-amine (9c)



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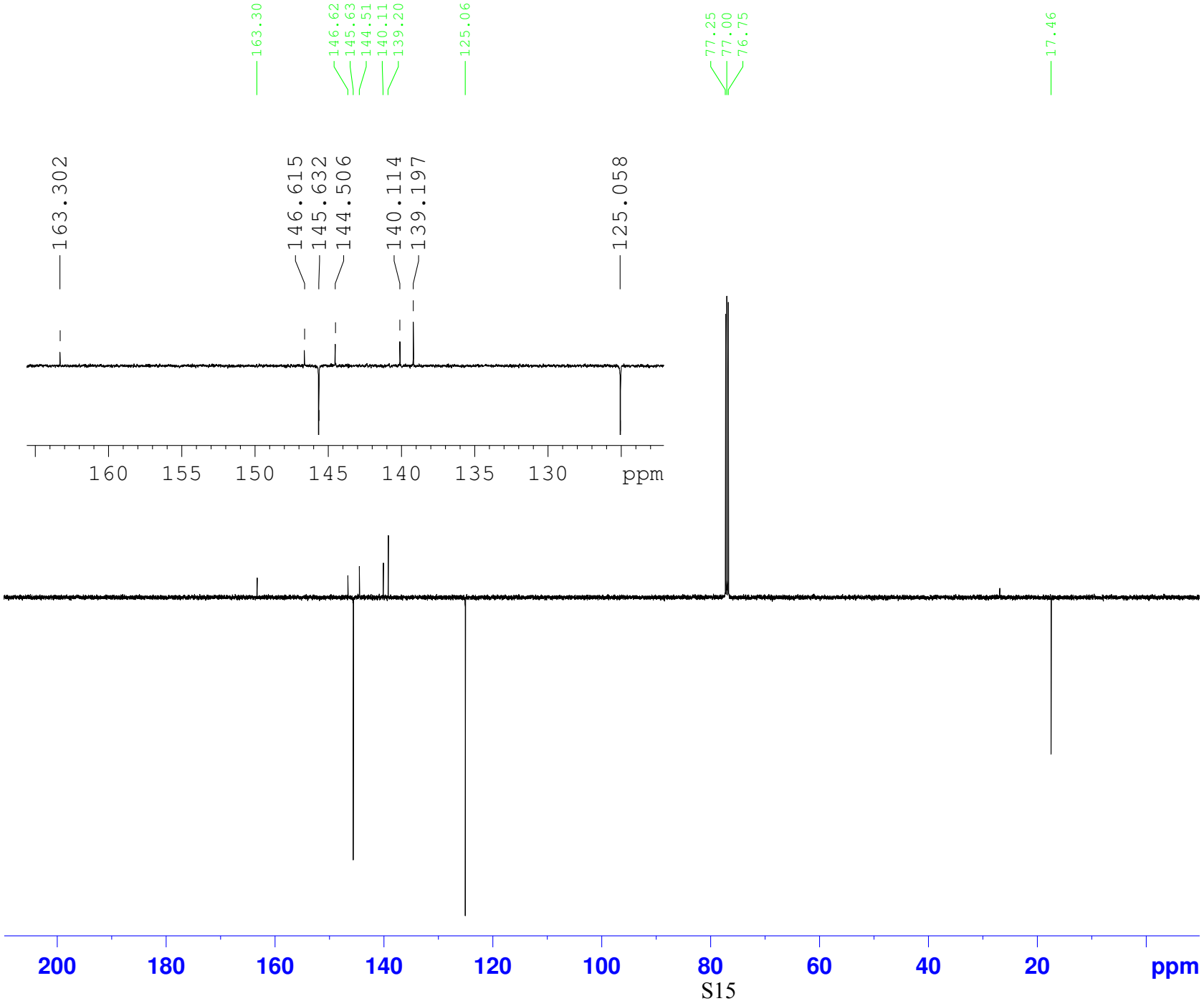
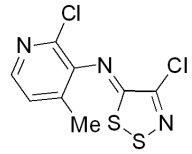
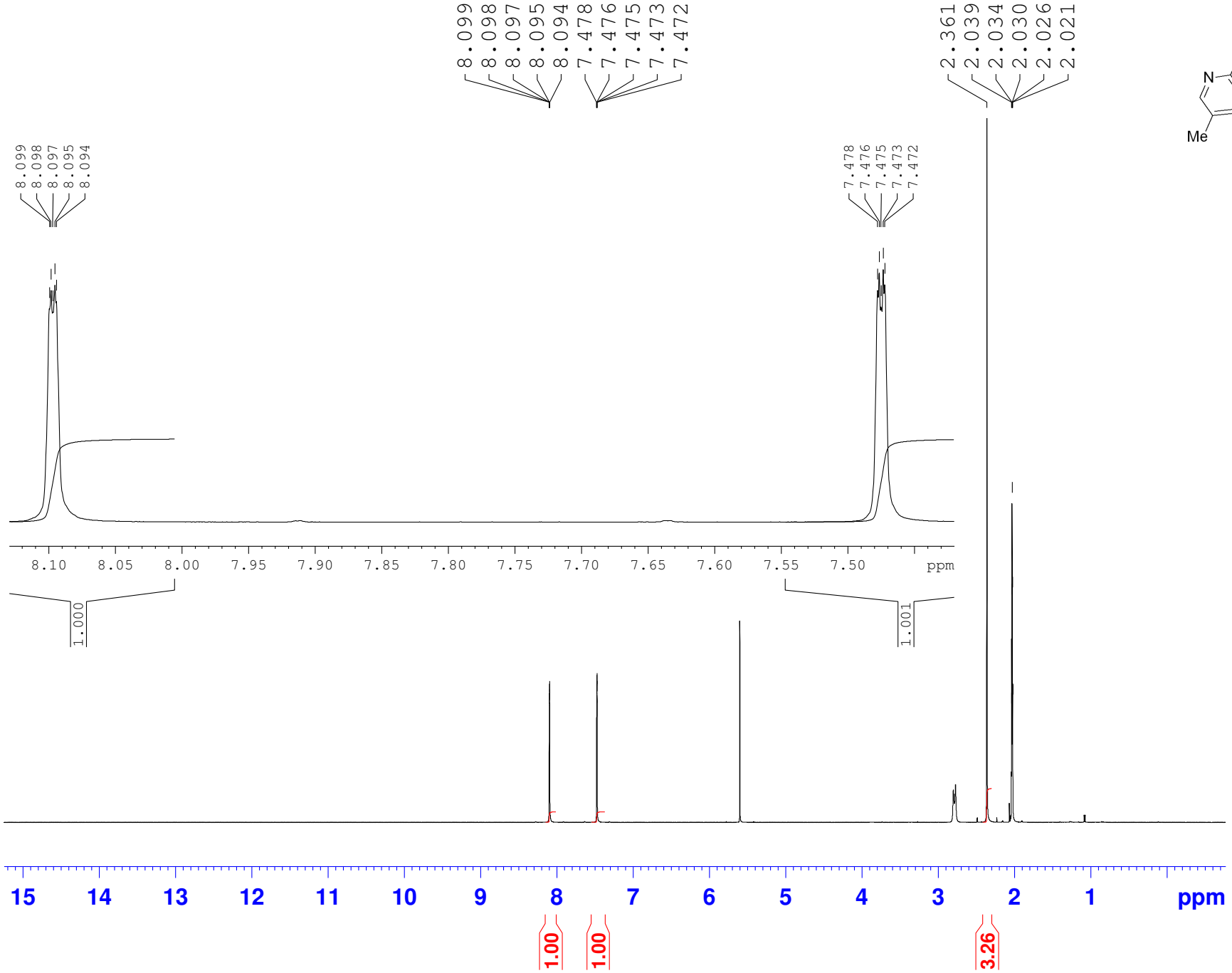




9c

(Z)-2-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-5-methylpyridin-3-amine (9d)



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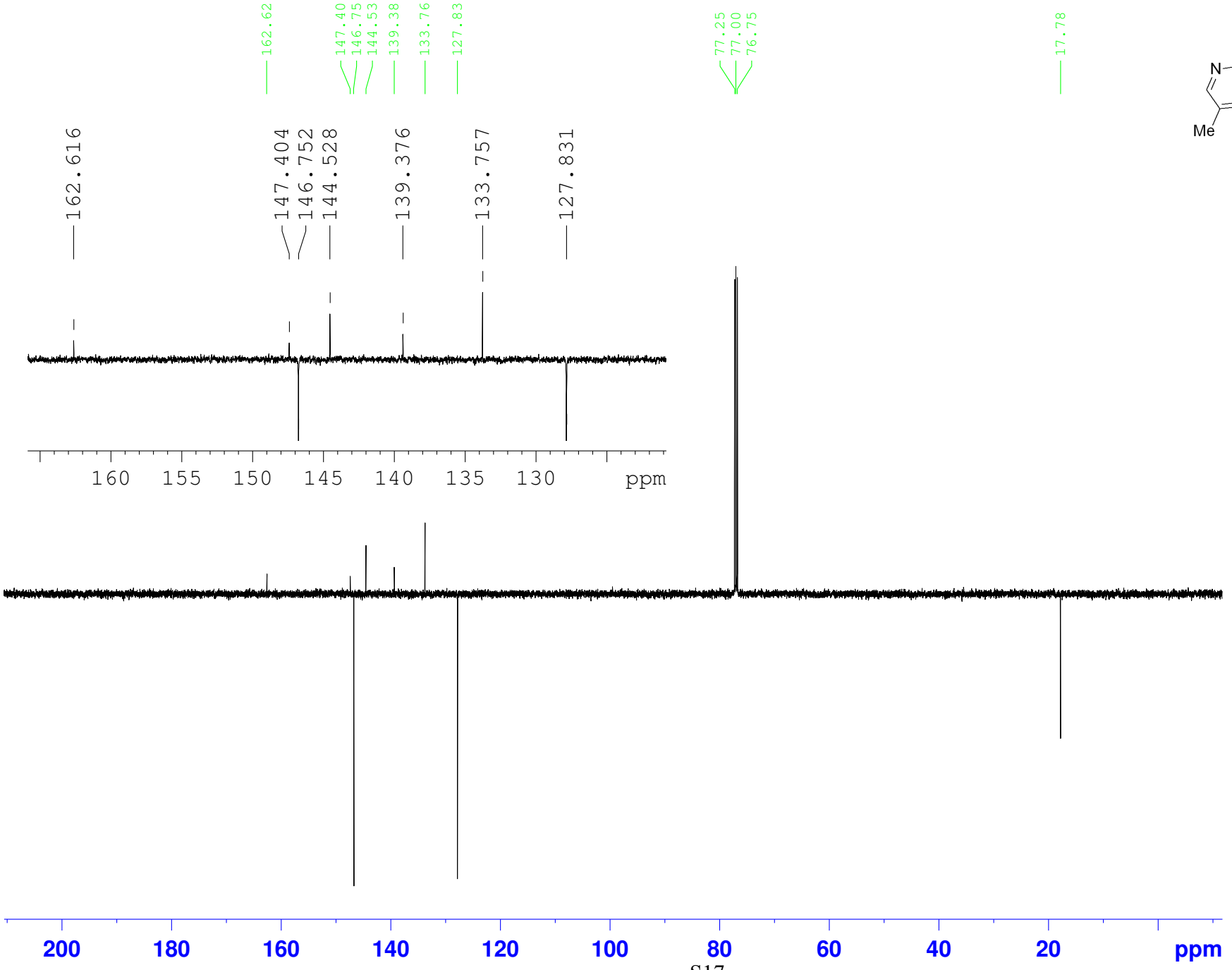
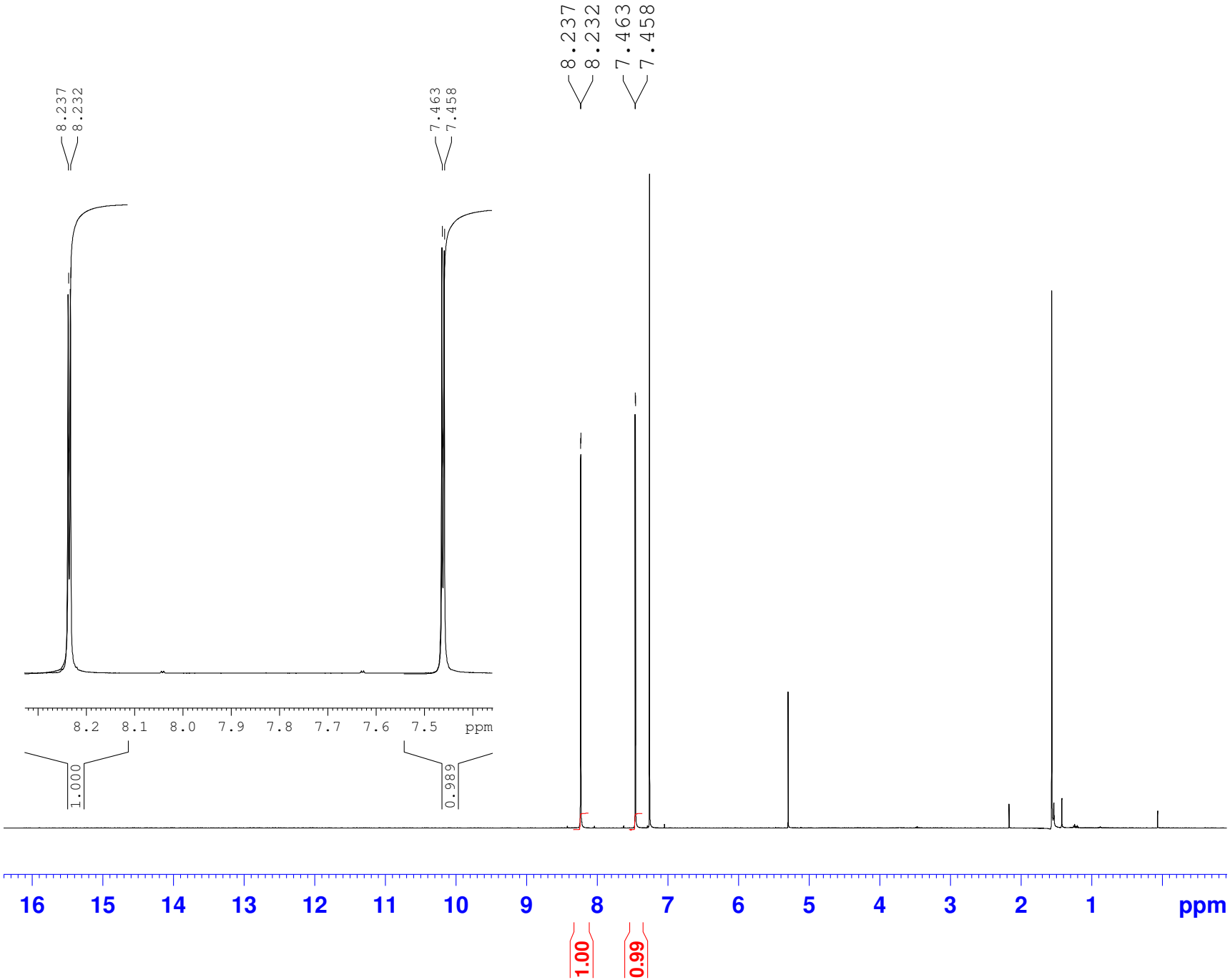
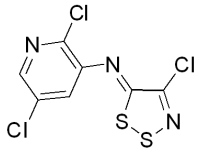


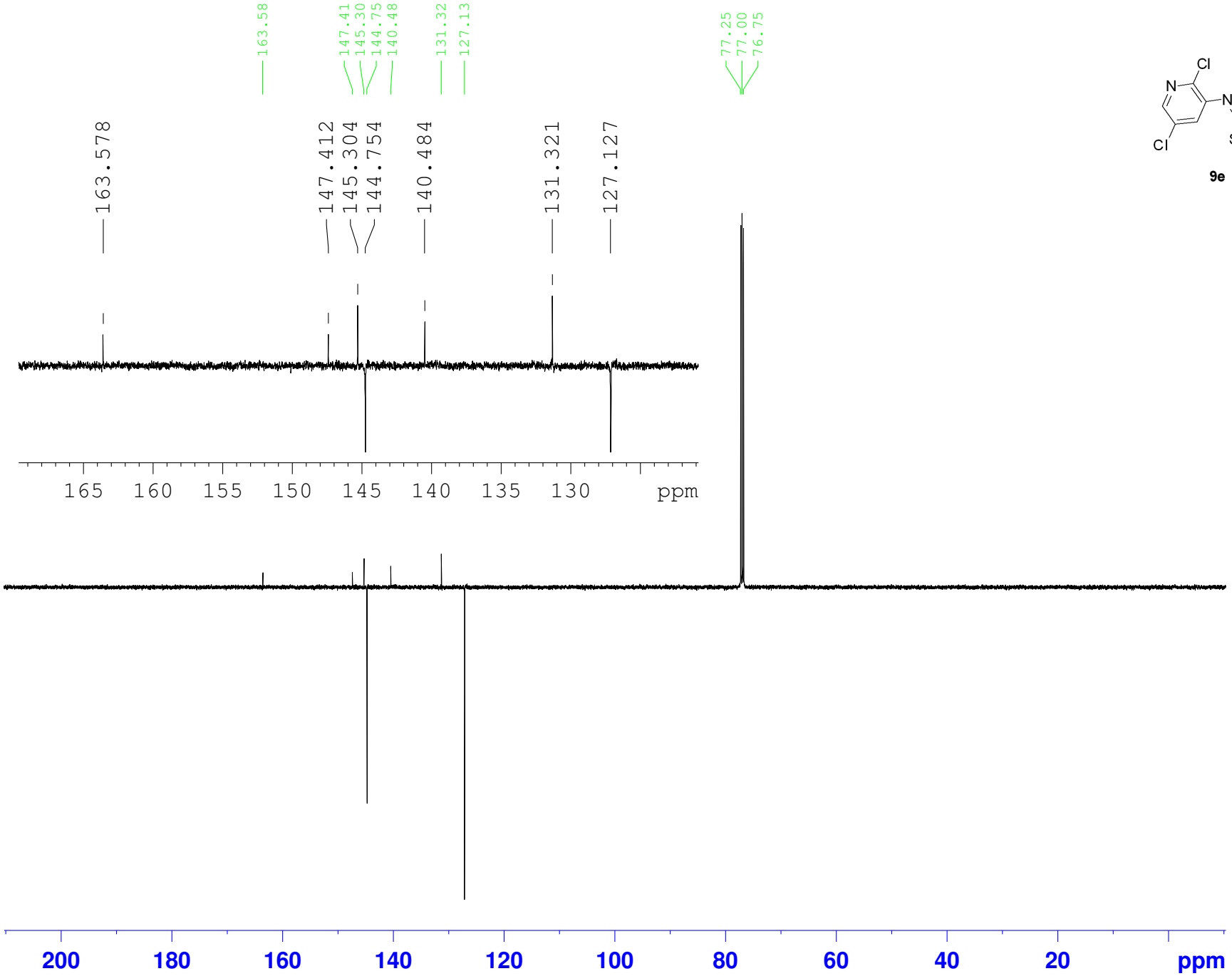
(Z)-2,5-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (9e)





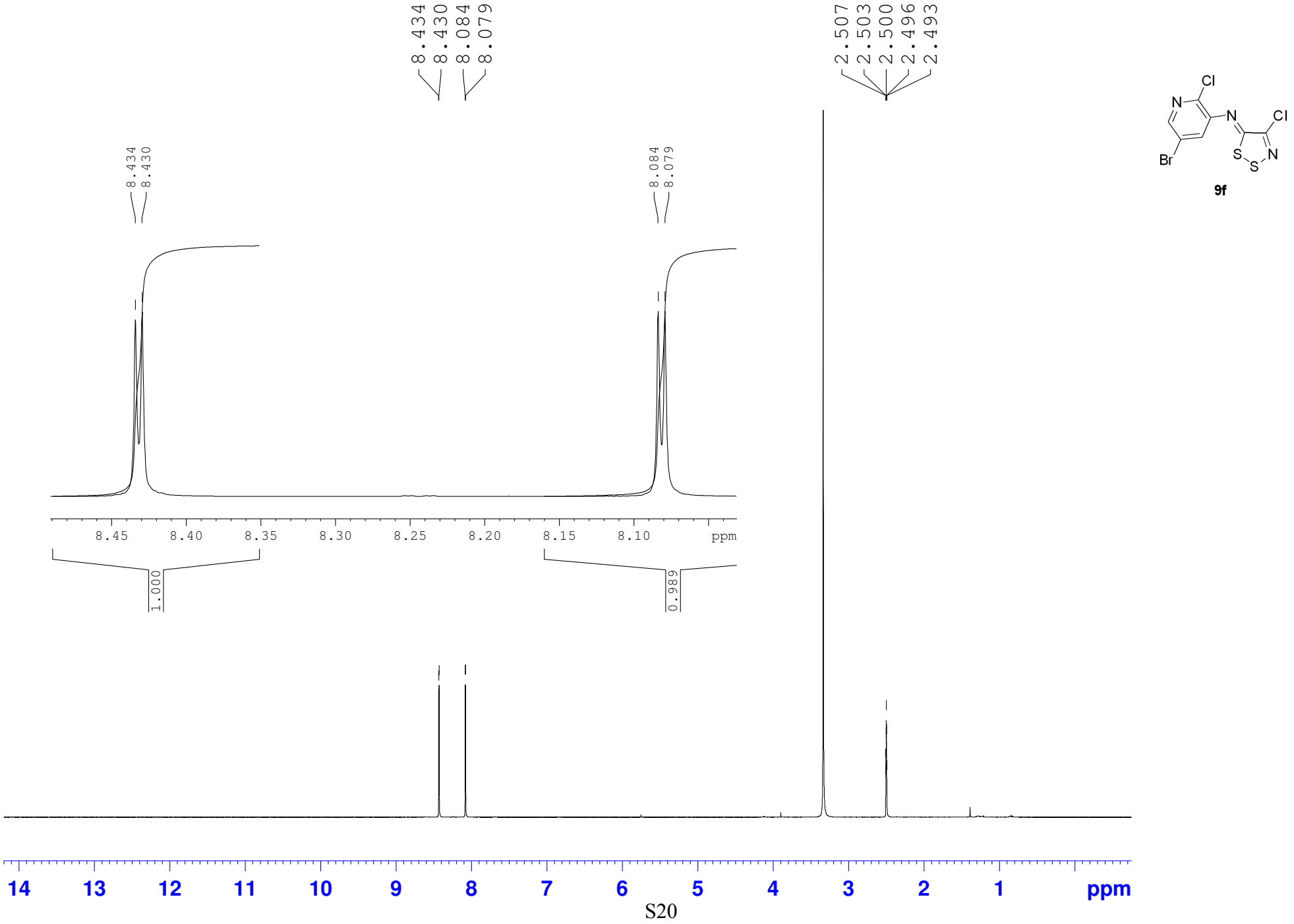
9e

(Z)-2,5-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (9e)

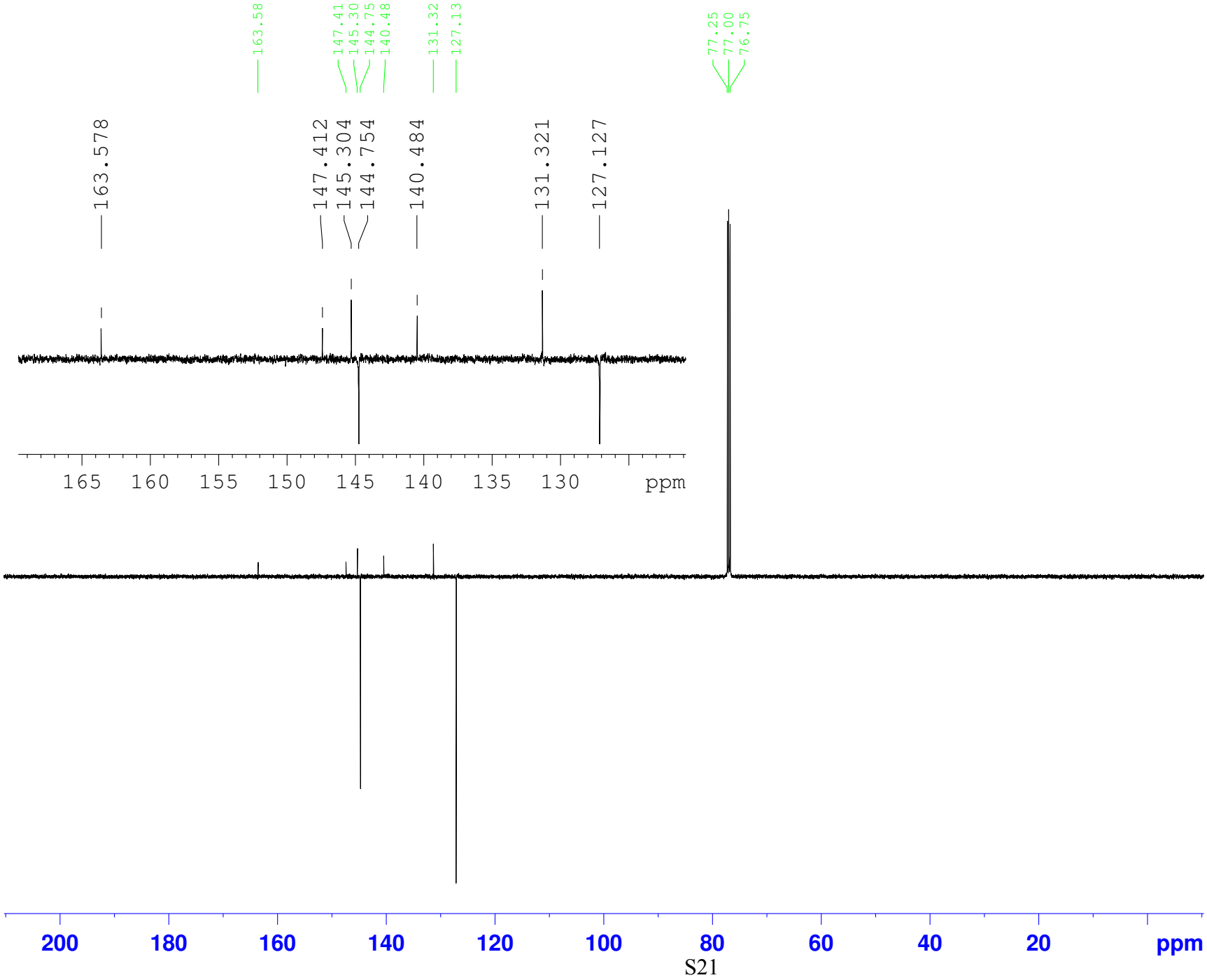


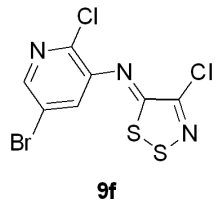
9e

(Z)-5-Bromo-2-chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (9f)



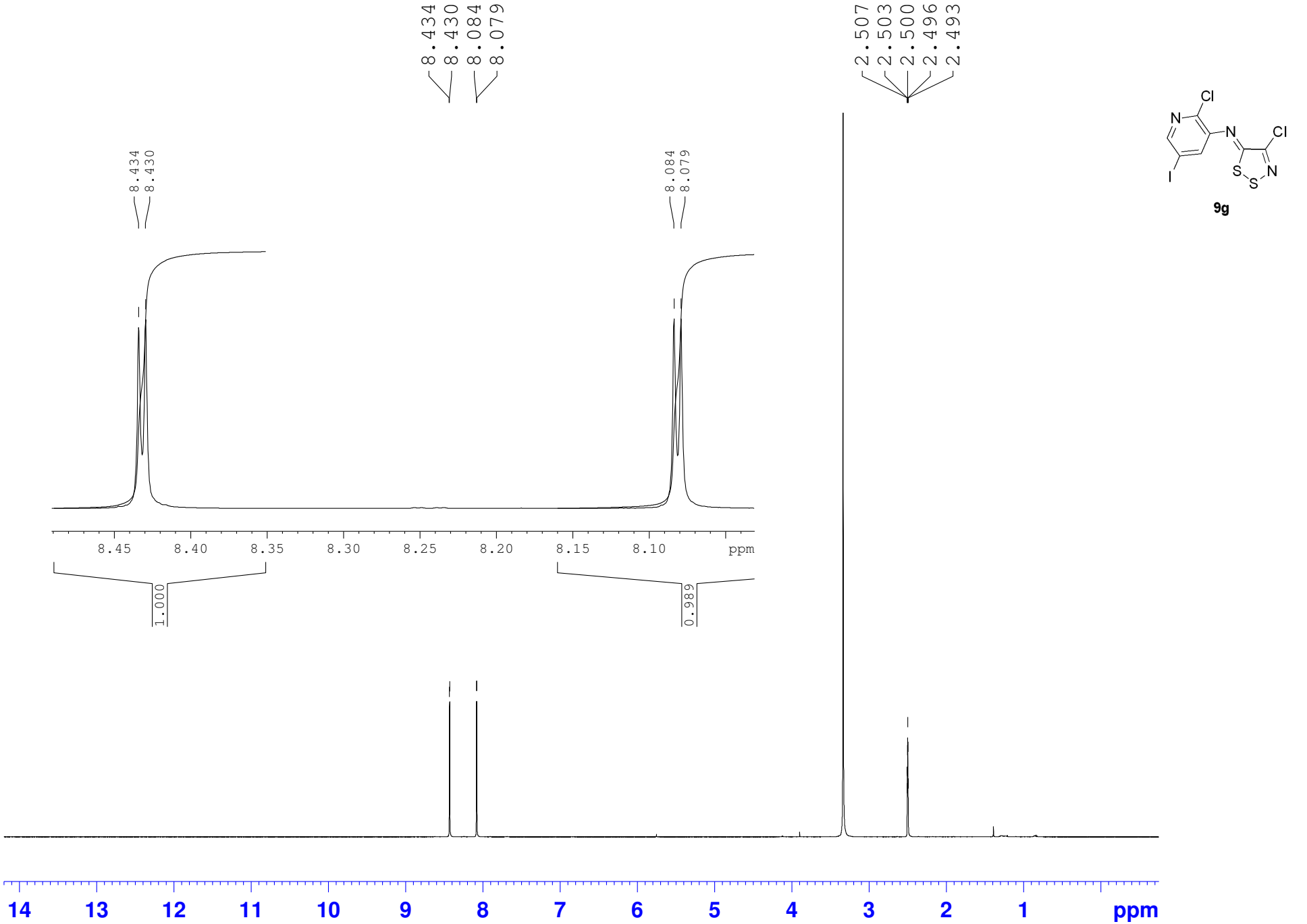
(Z)-5-Bromo-2-chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (9f)



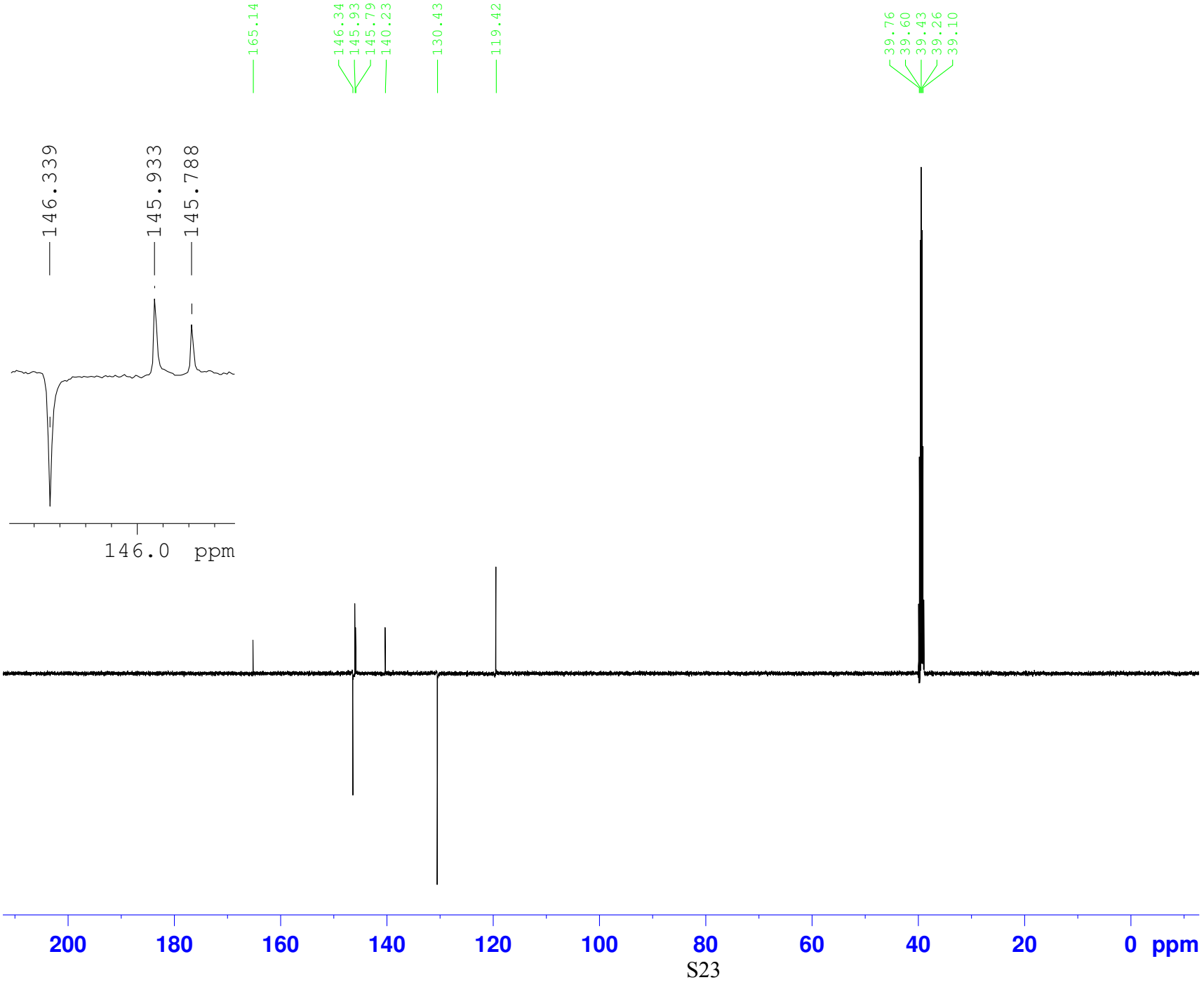


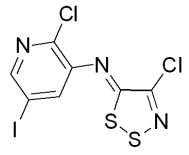
9f

(Z)-2-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-5-iodopyridin-3-amine (9g)



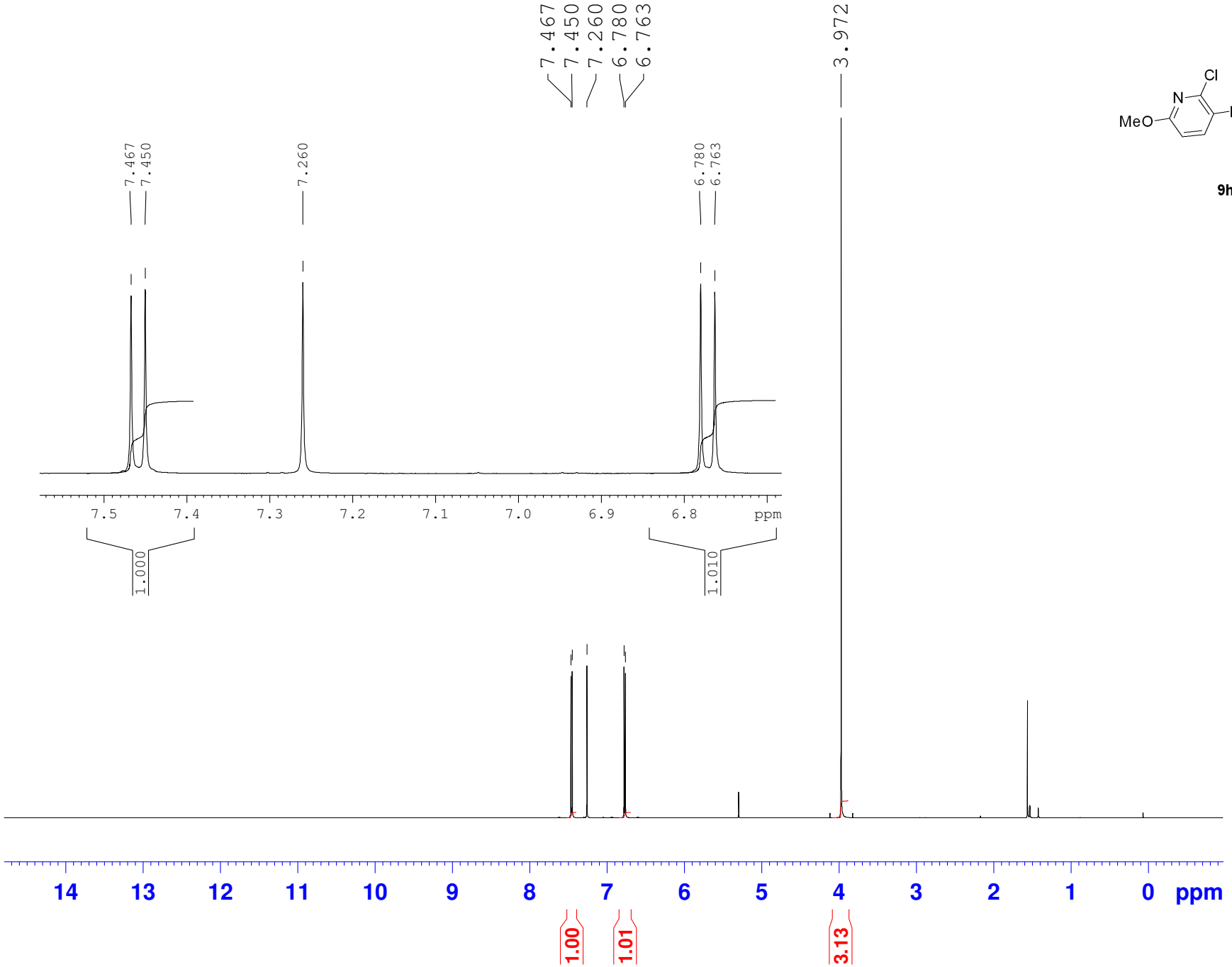
(Z)-2-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-5-iodopyridin-3-amine (9g)



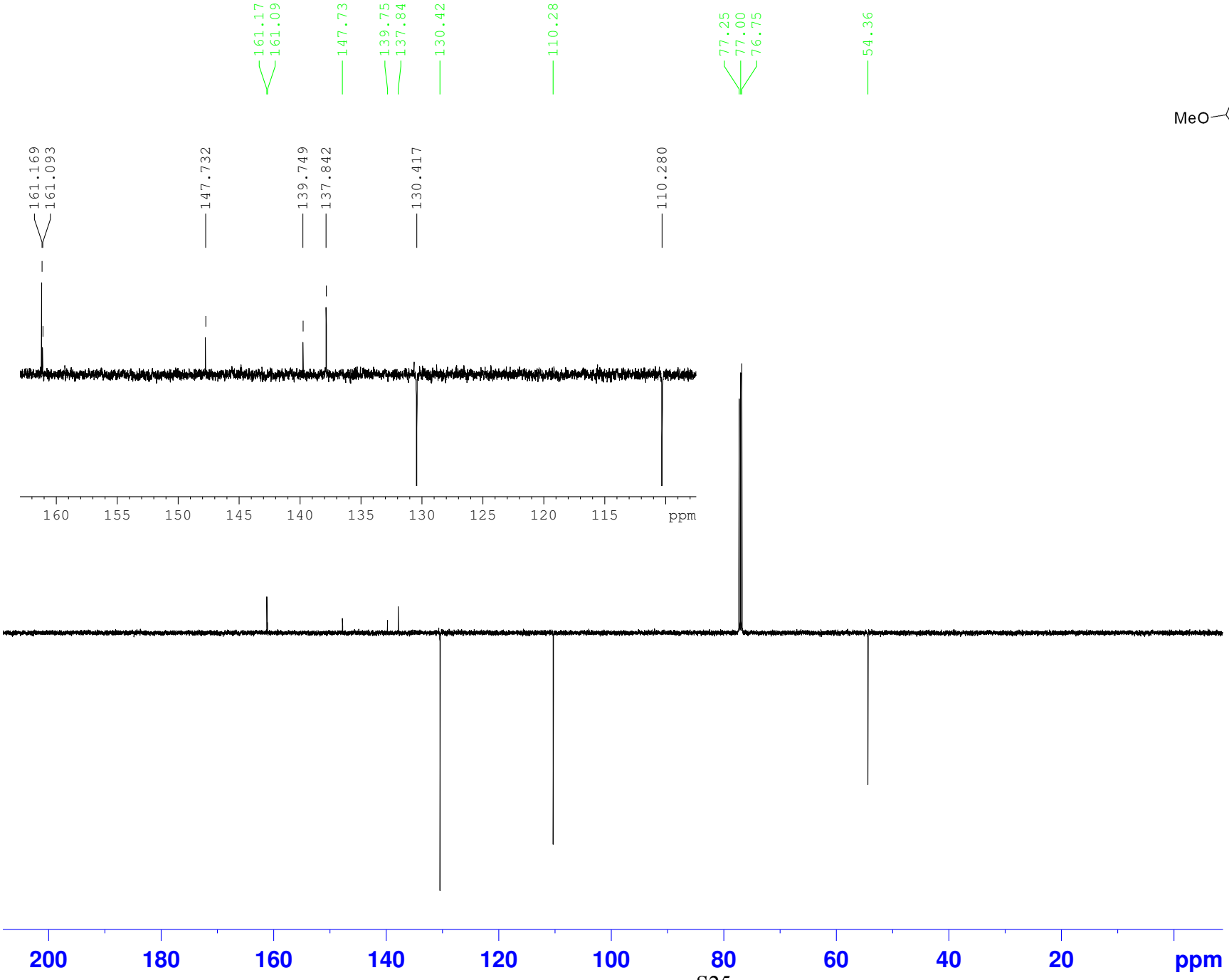


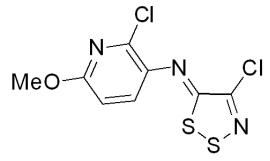
9g

(Z)-2-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-6-methoxypyridin-3-amine (9h)



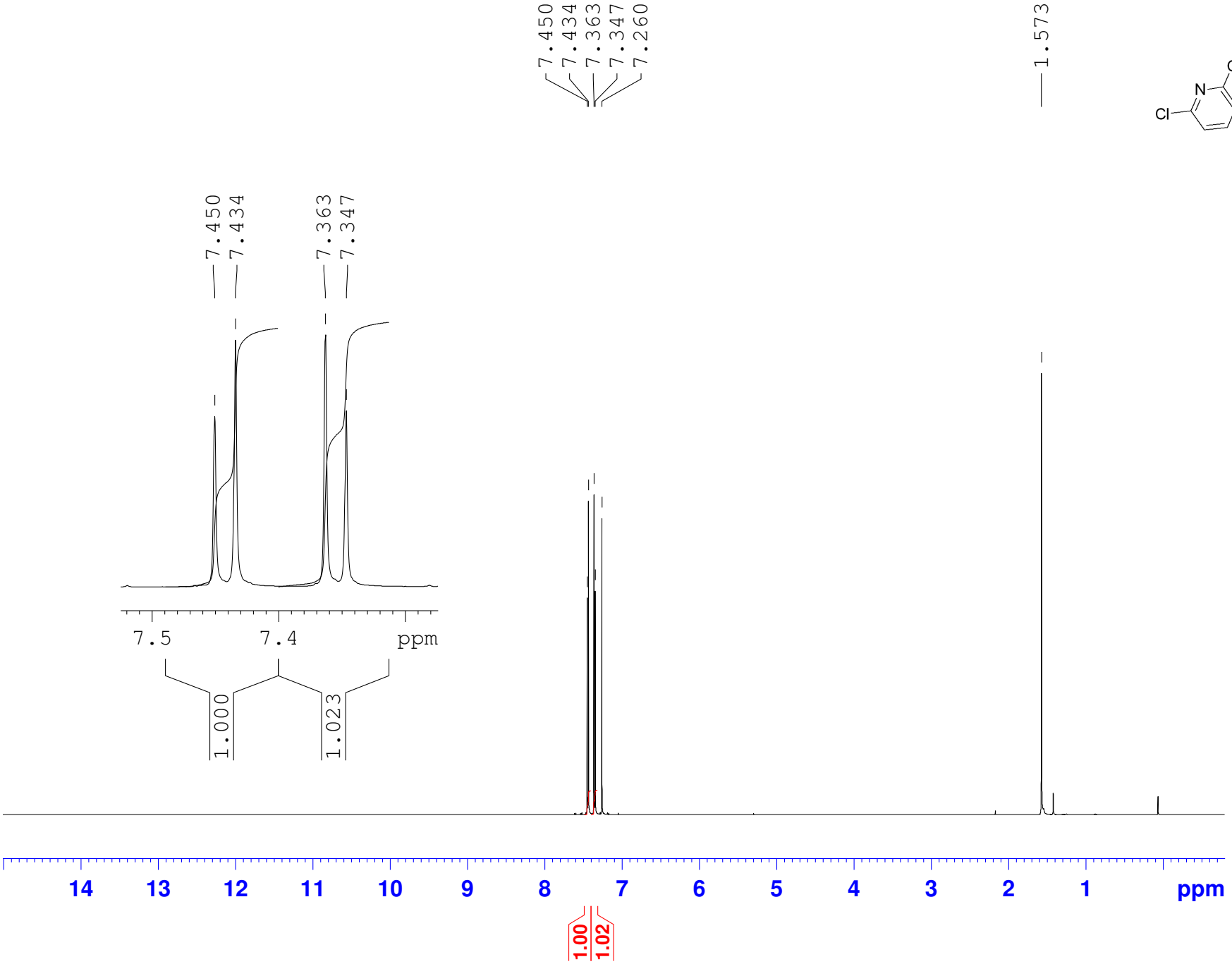
(Z)-2-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-6-methoxypyridin-3-amine (9h)



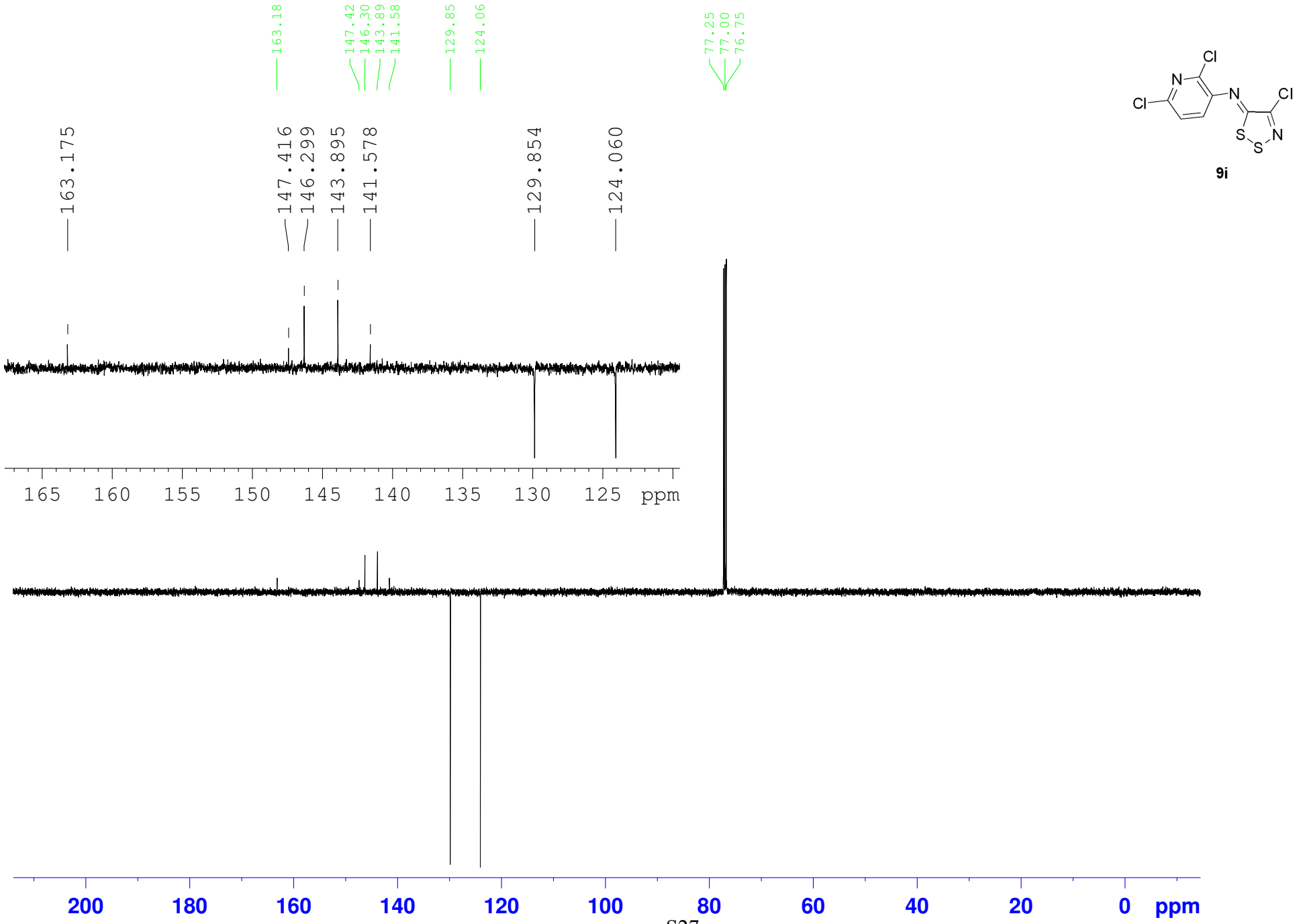


9h

(Z)-2,6-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (9i)

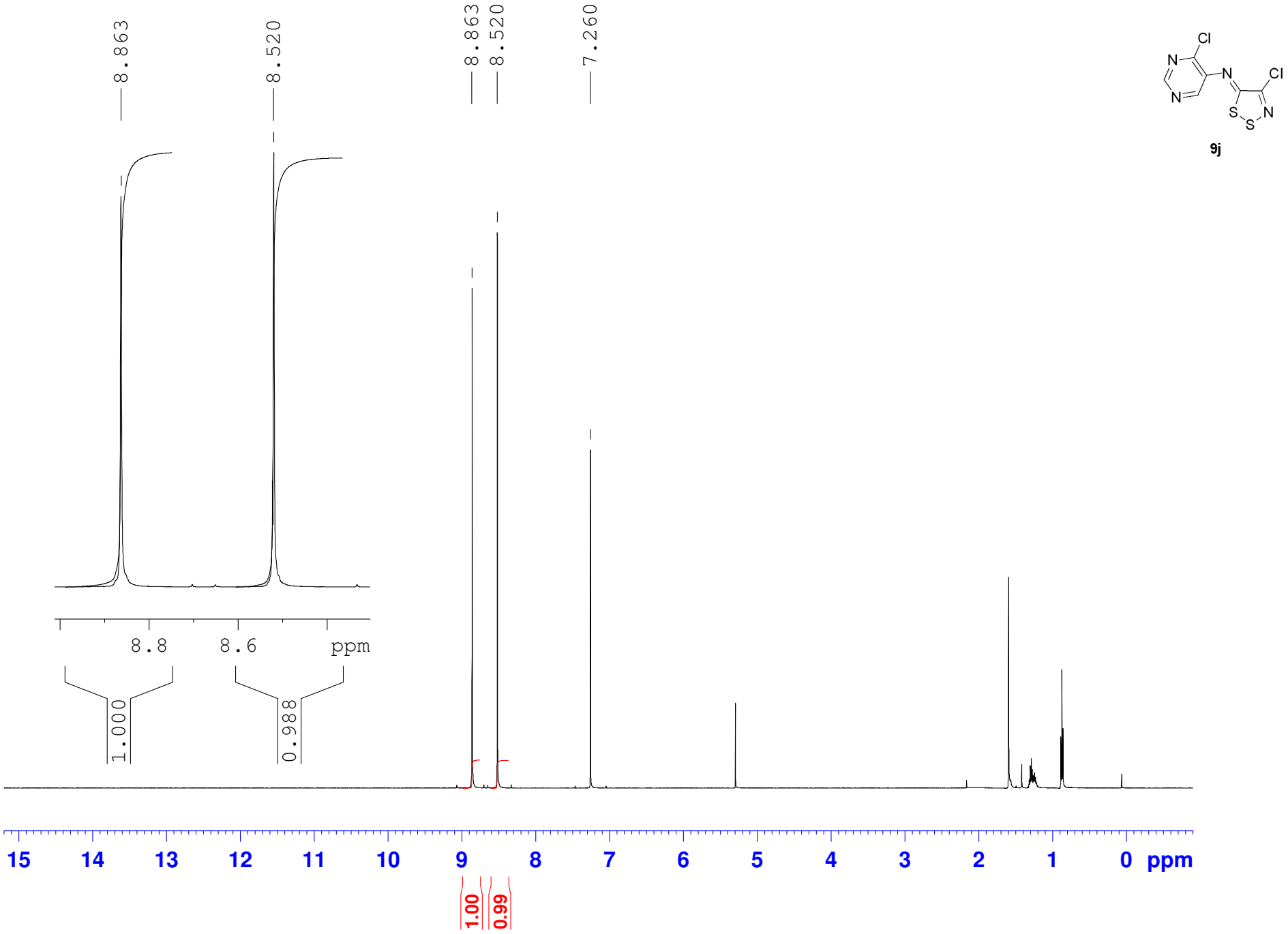


(Z)-2,6-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyridin-3-amine (9i)



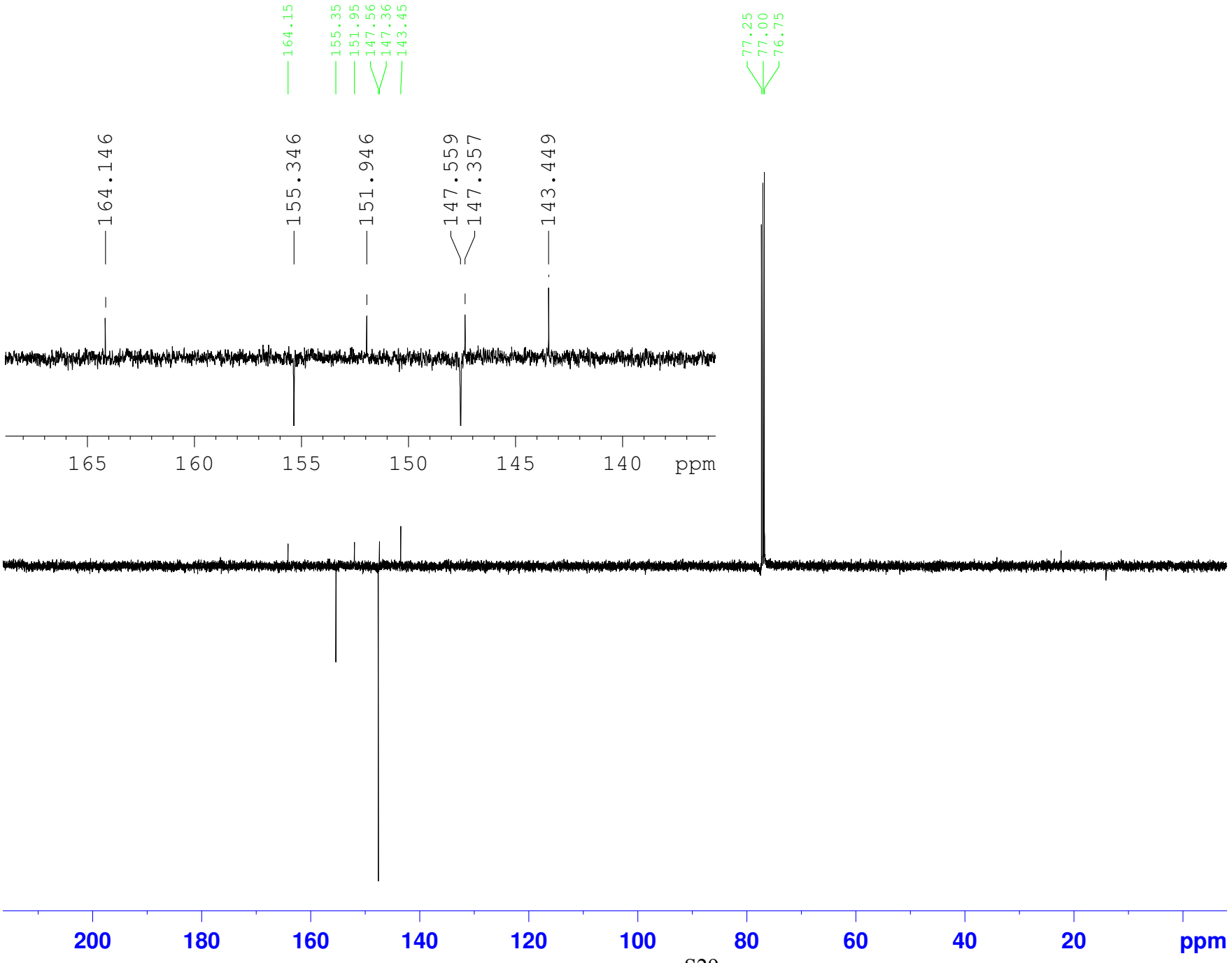
9i

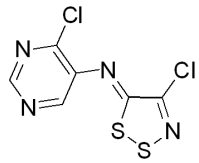
(Z)-4-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyrimidin-5-amine (9j)



9j

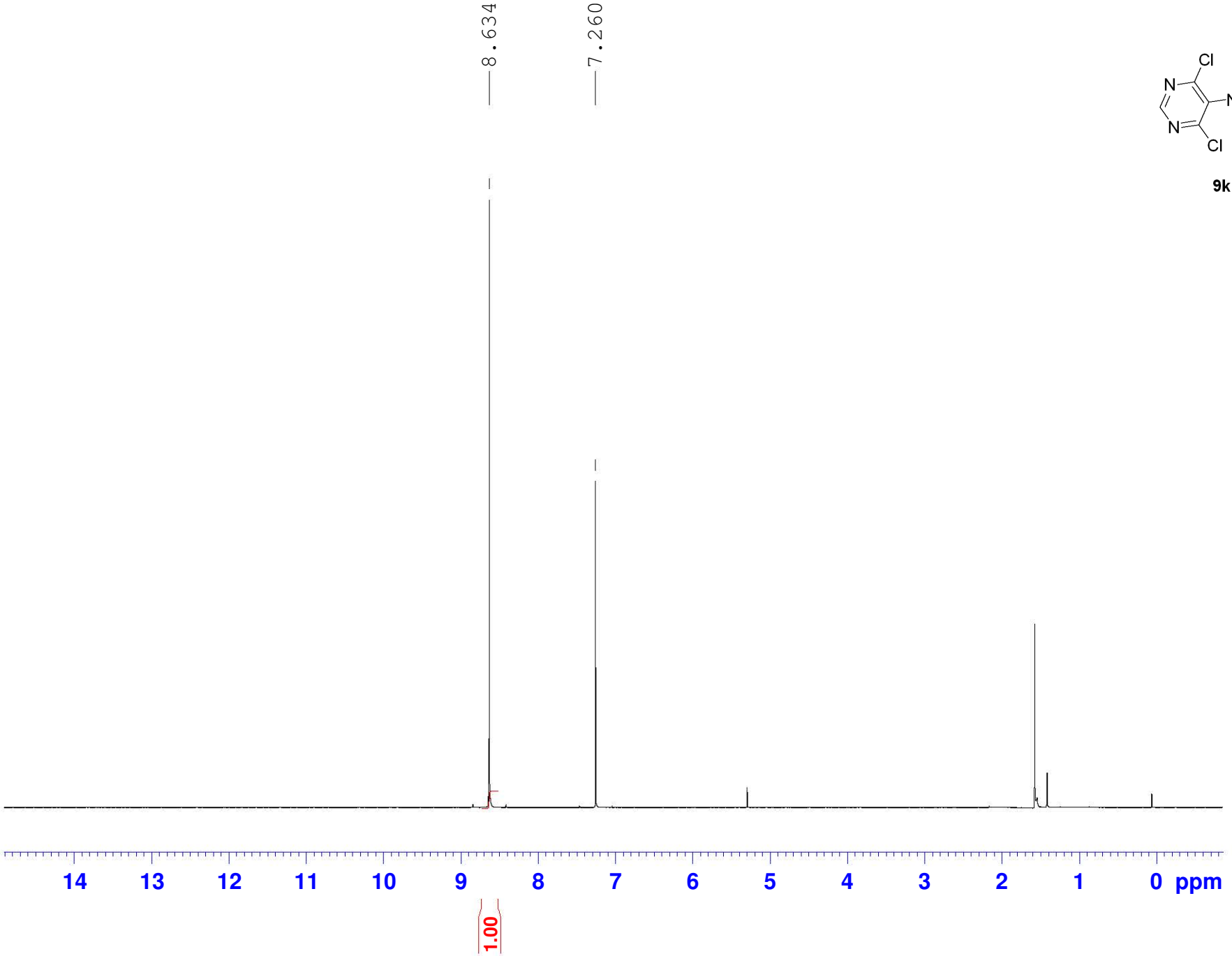
(Z)-4-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyrimidin-5-amine (9j)



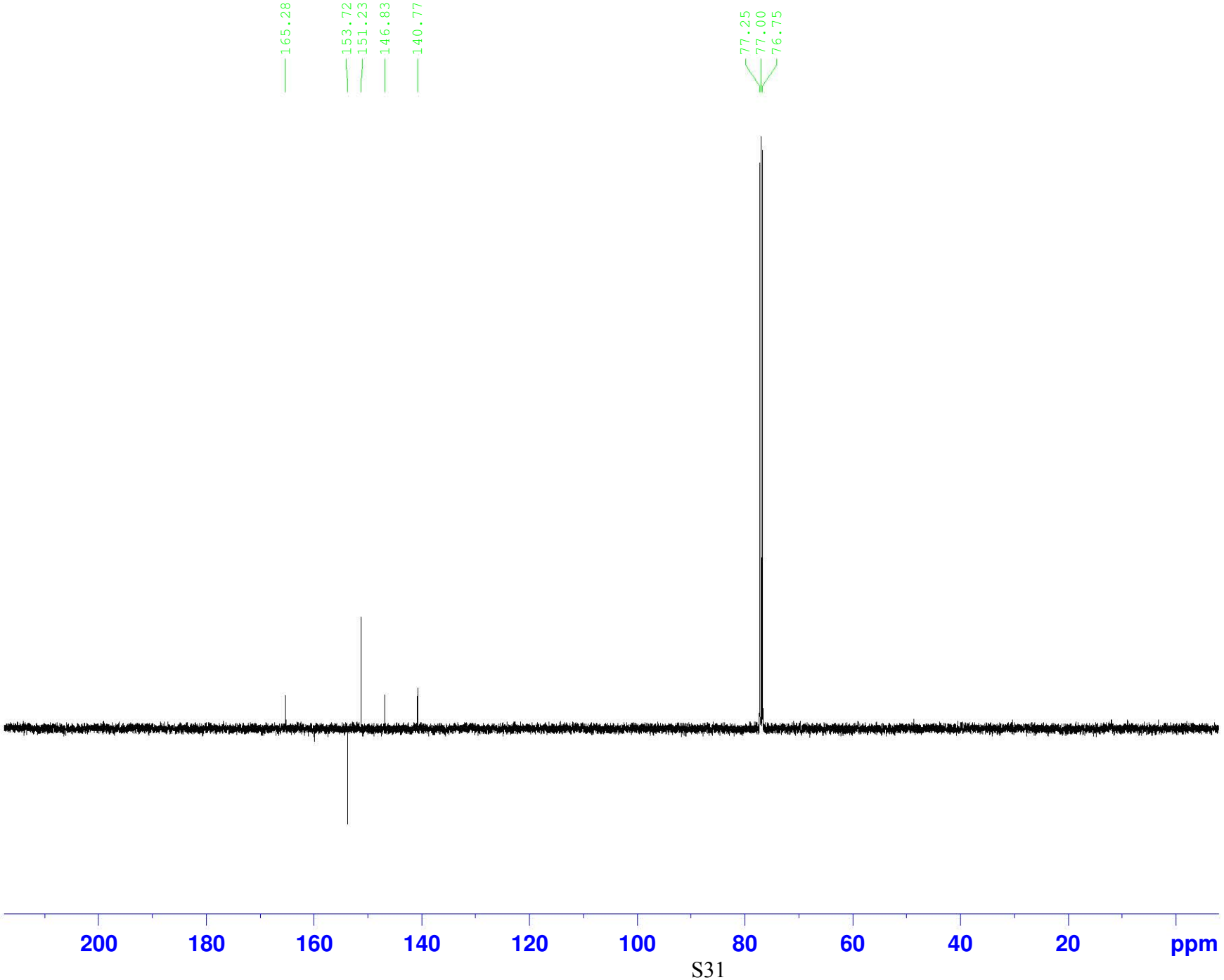


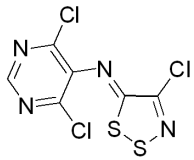
9j

(Z)-4,6-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyrimidin-5-amine (9k)



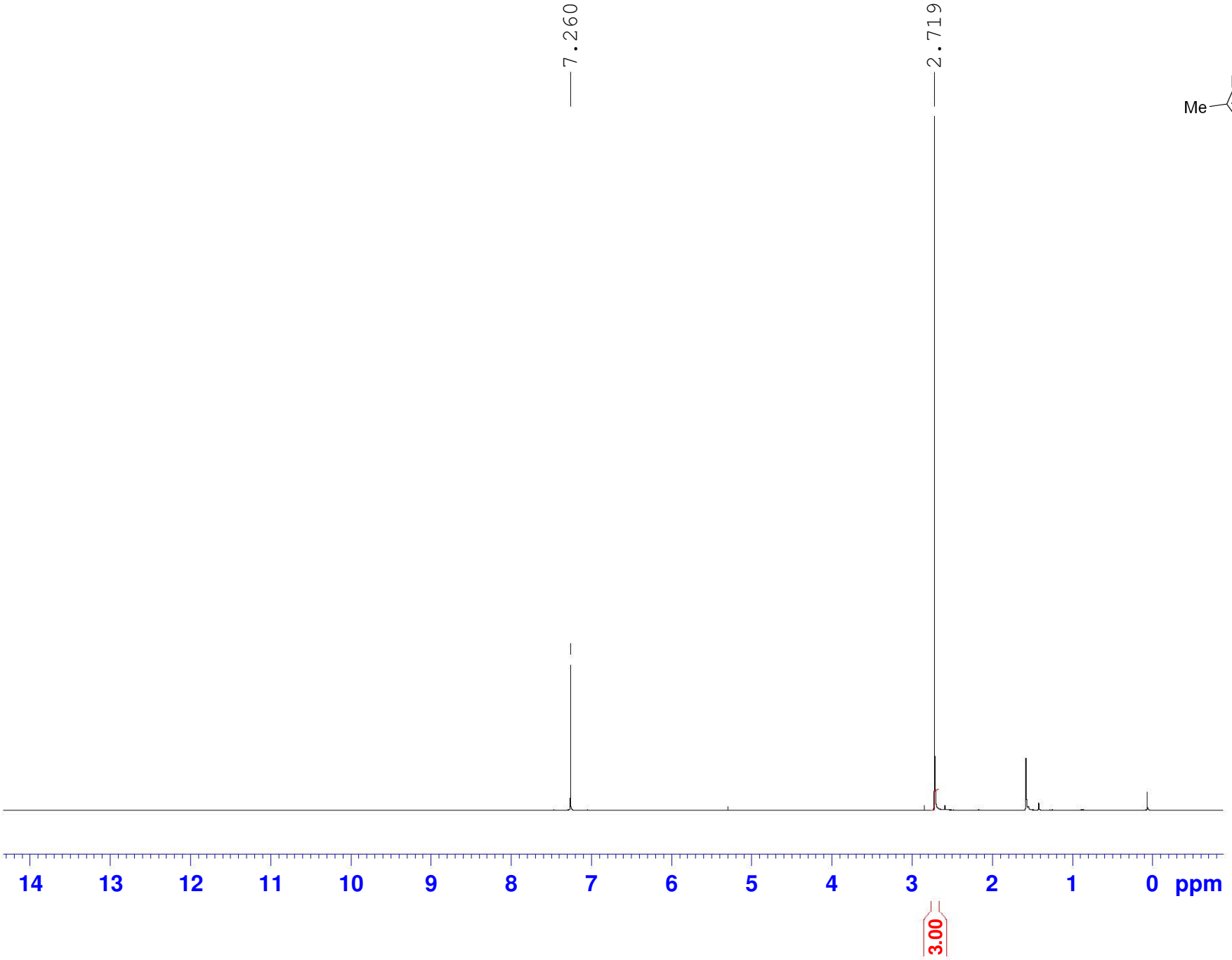
(Z)-4,6-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyrimidin-5-amine (9k)

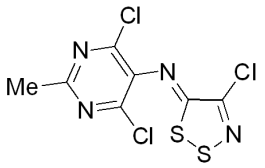




9k

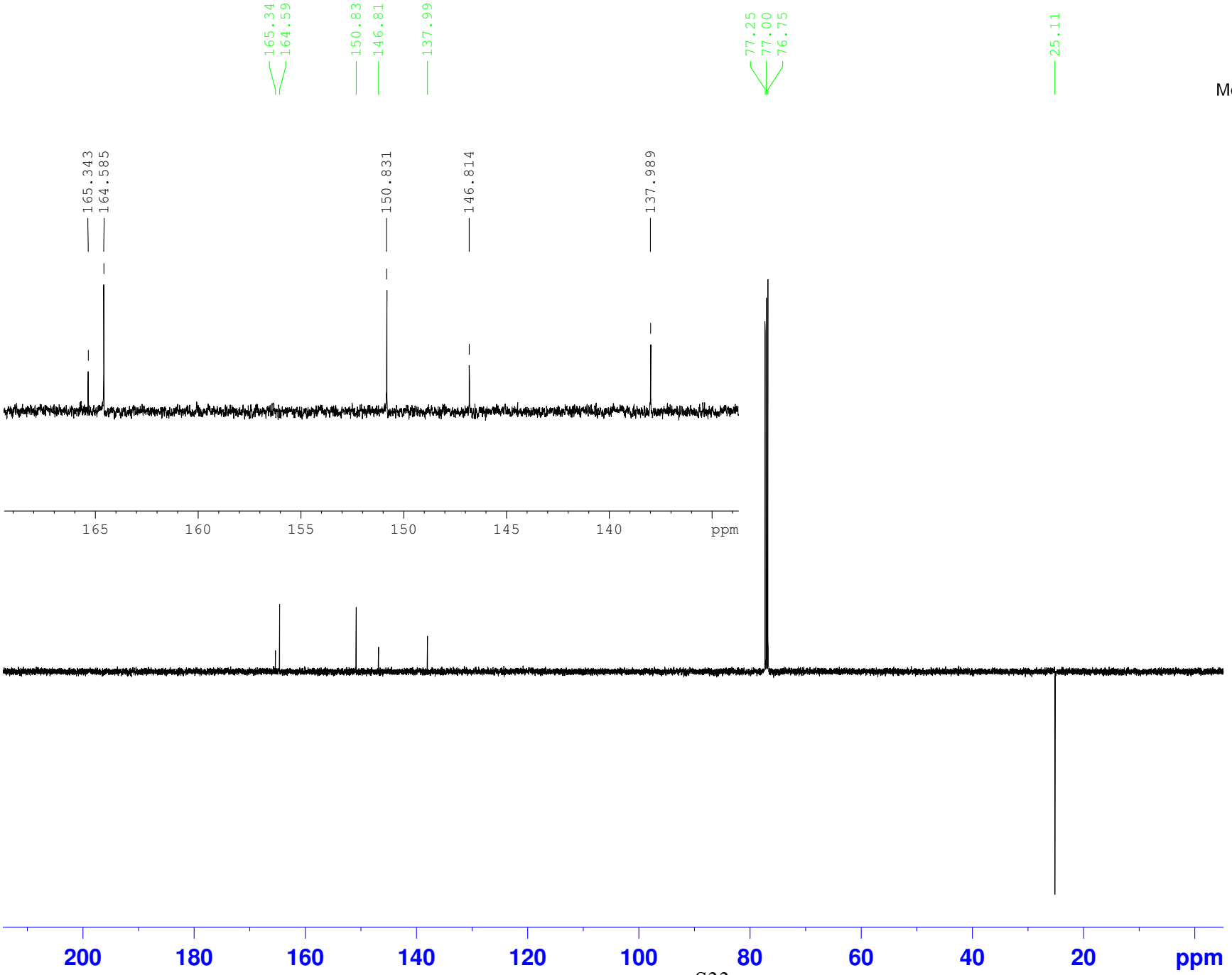
(Z)-4,6-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-2-methylpyrimidin-5-amine (9l)

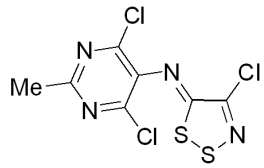




9l

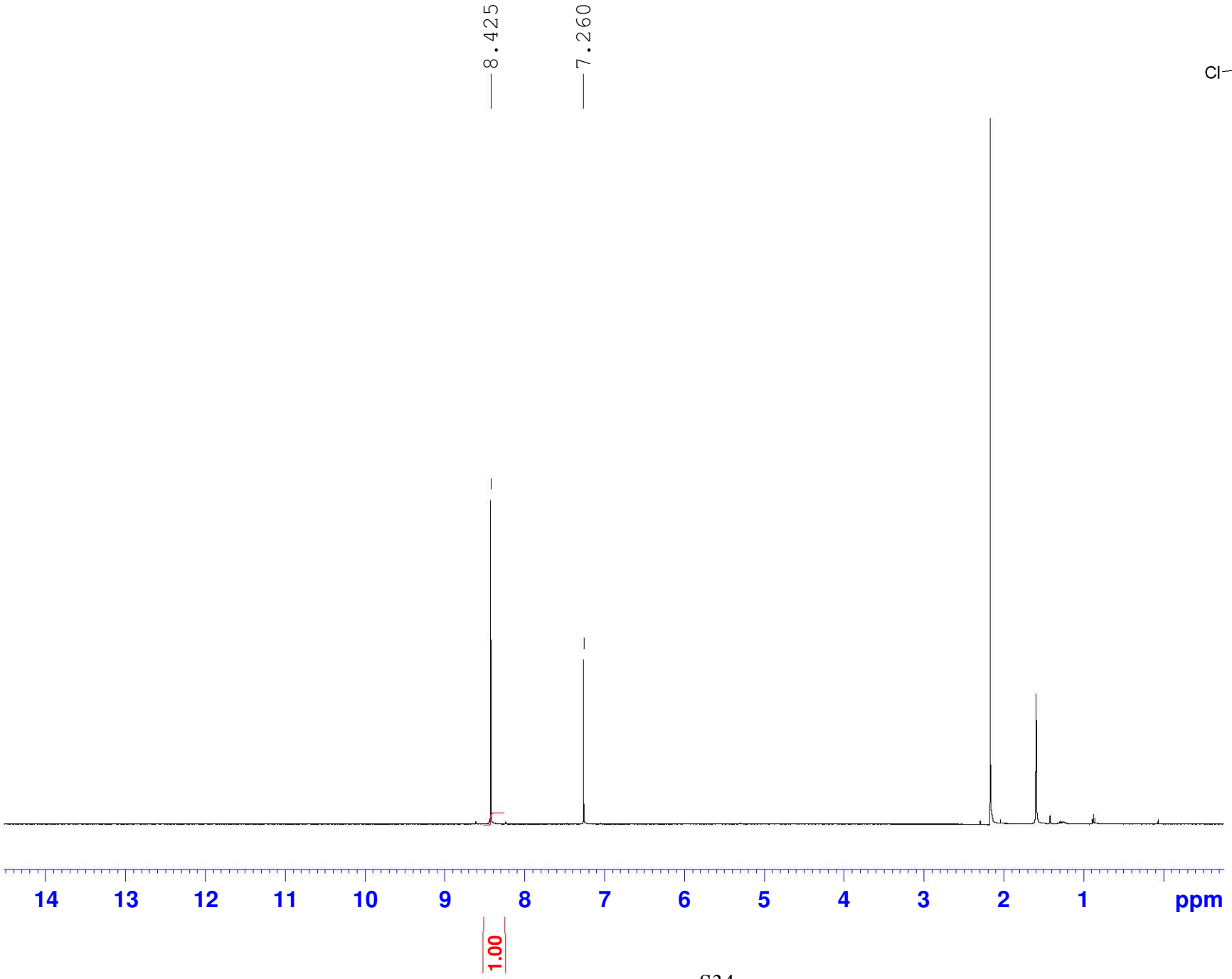
(Z)-4,6-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)-2-methylpyrimidin-5-amine (9l)



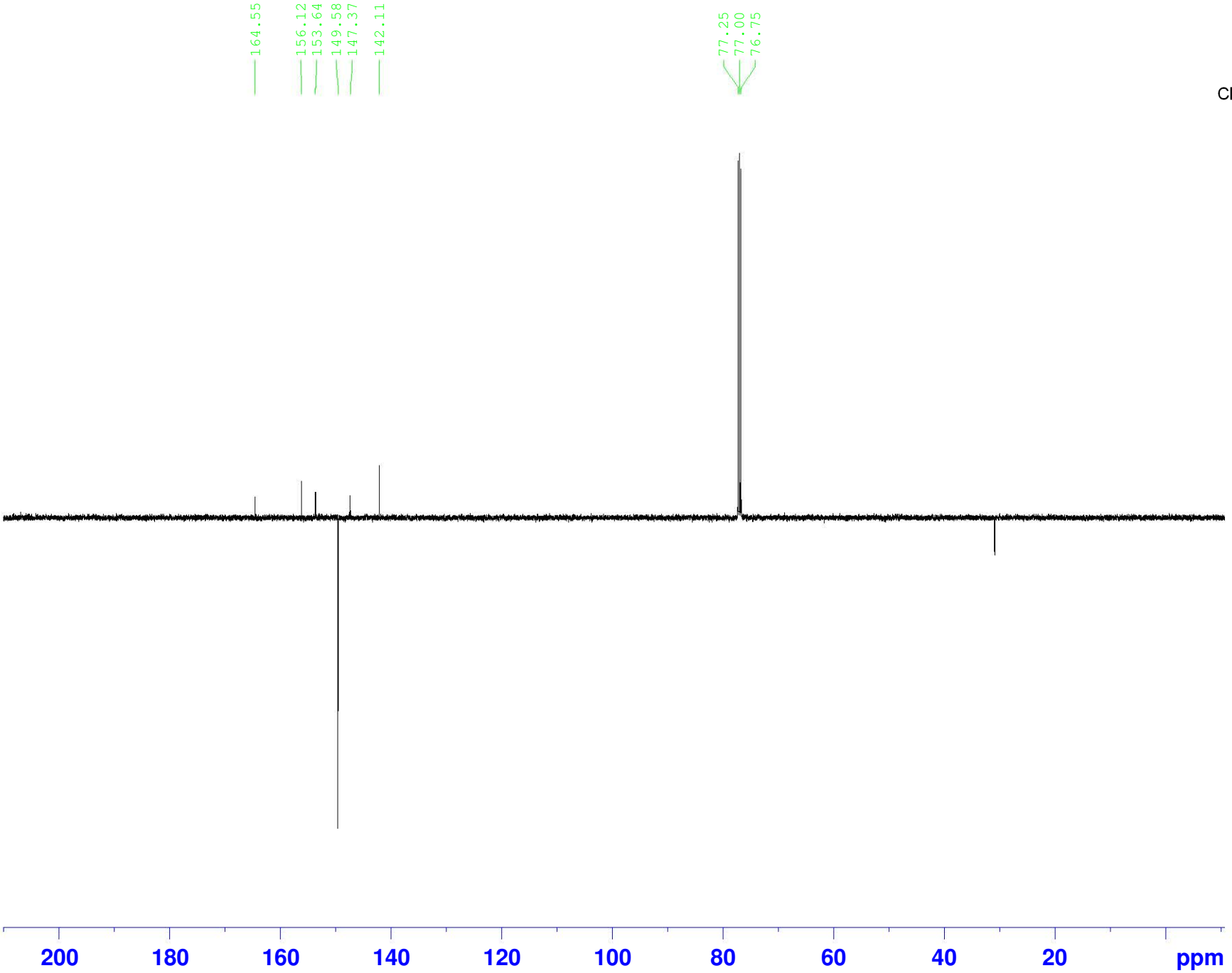


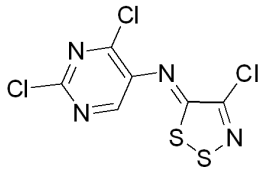
9l

(Z)-2,4-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyrimidin-5-amine (9m)



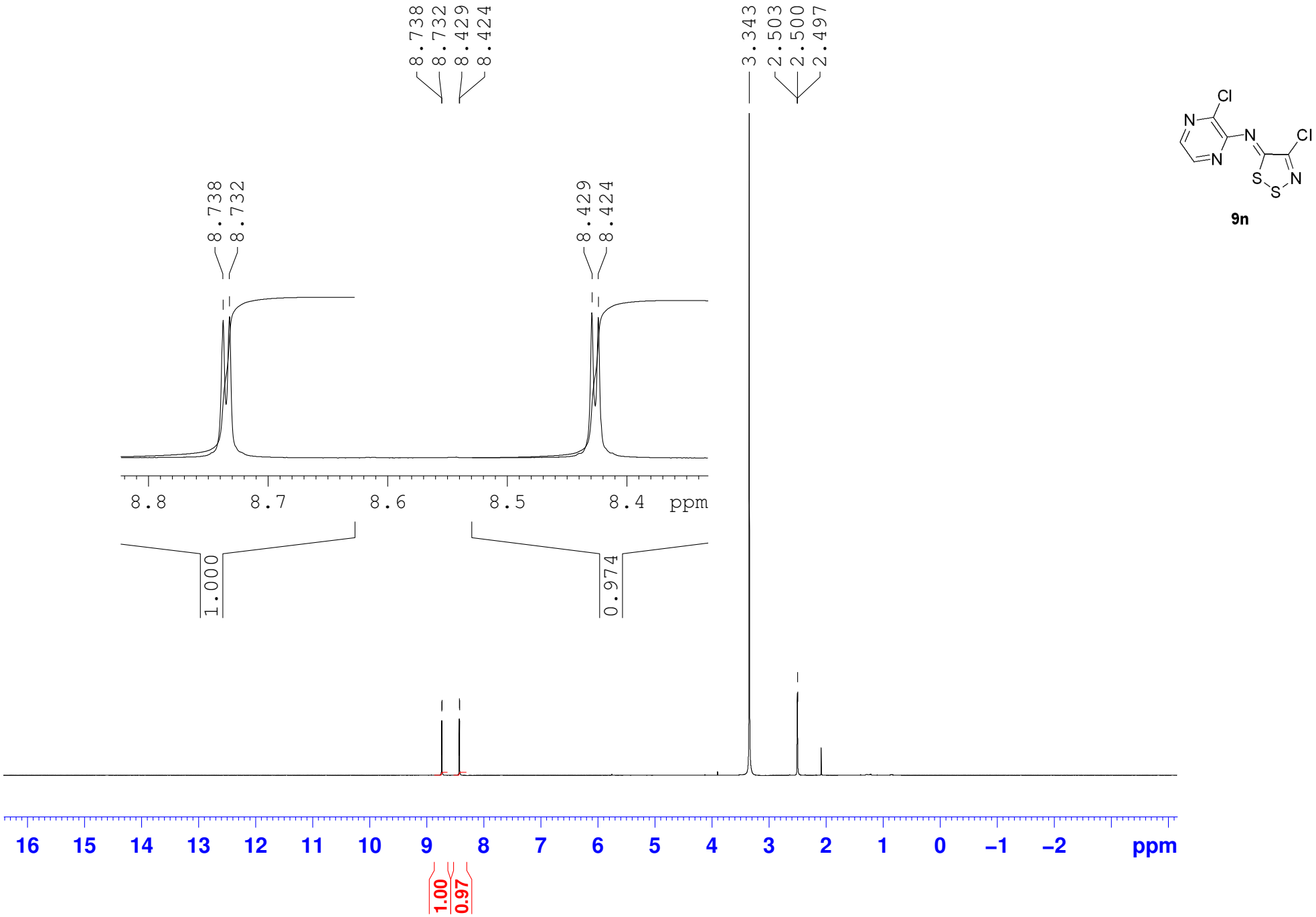
(Z)-2,4-Dichloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyrimidin-5-amine (9m)





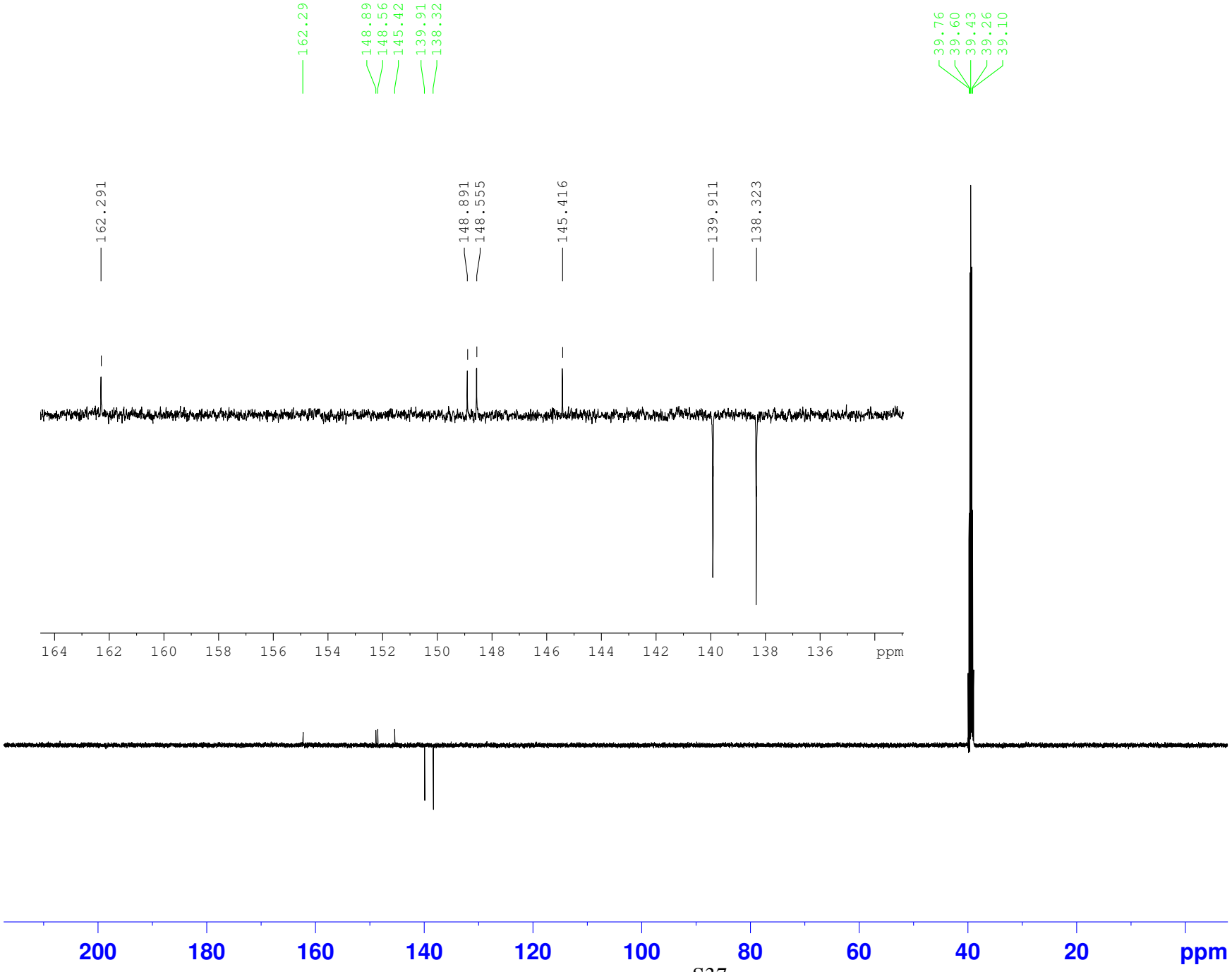
9m

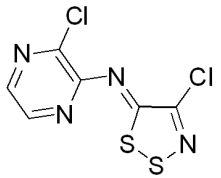
(Z)-3-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyrazin-2-amine (9n)



9n

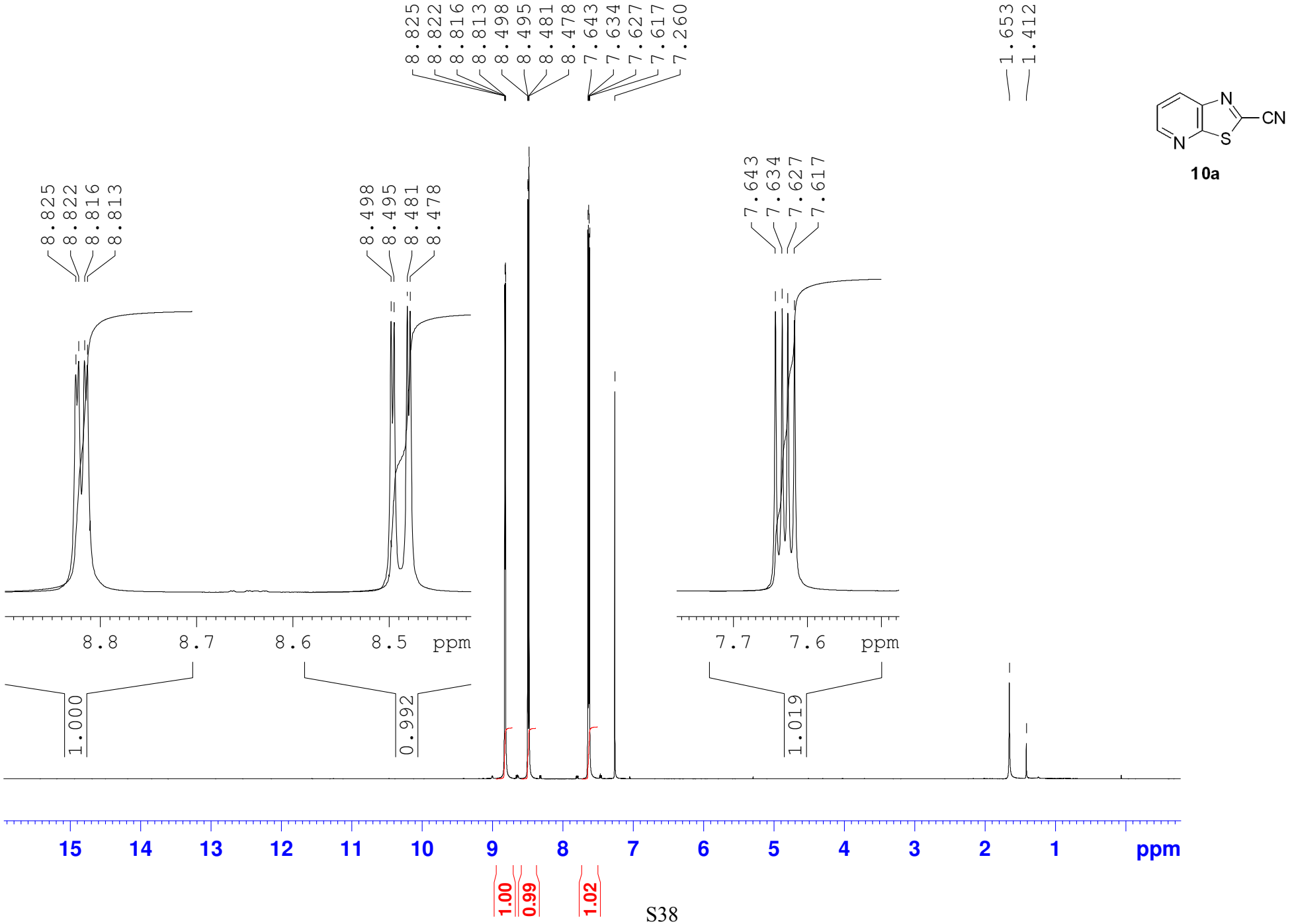
(Z)-3-Chloro-N-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)pyrazin-2-amine (9n)



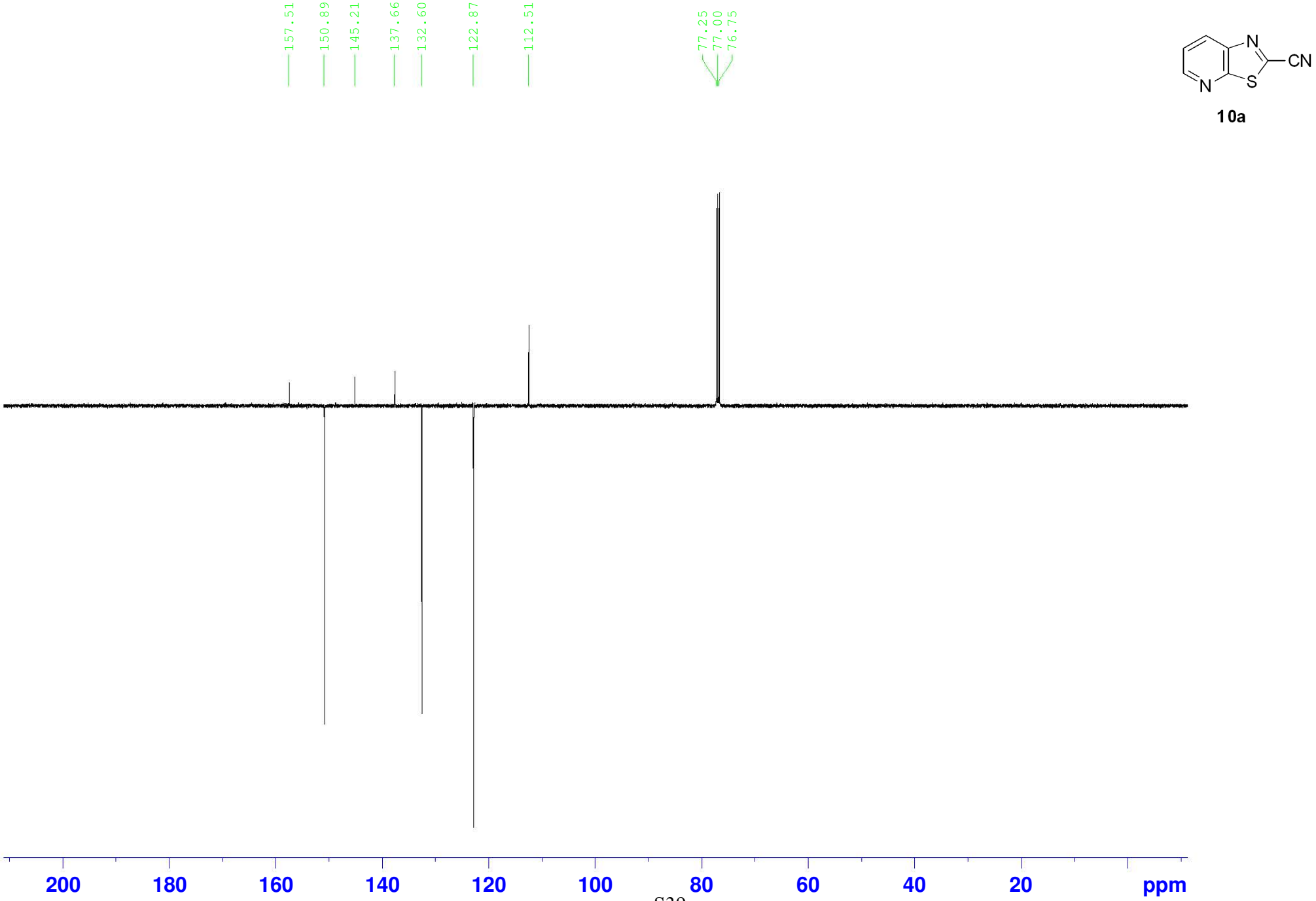


9n

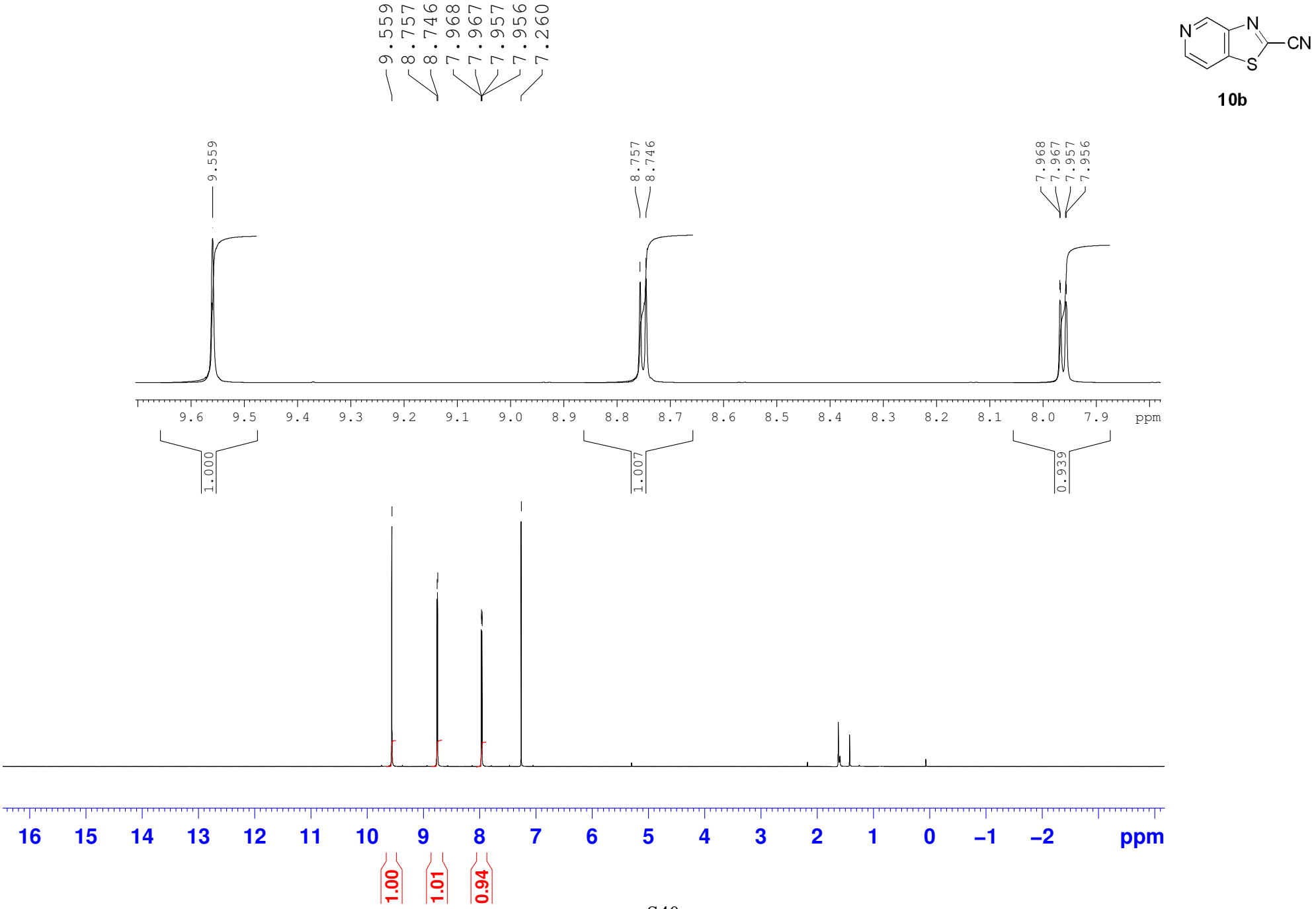
Thiazolo[5,4-b]pyridine-2-carbonitrile (10a)



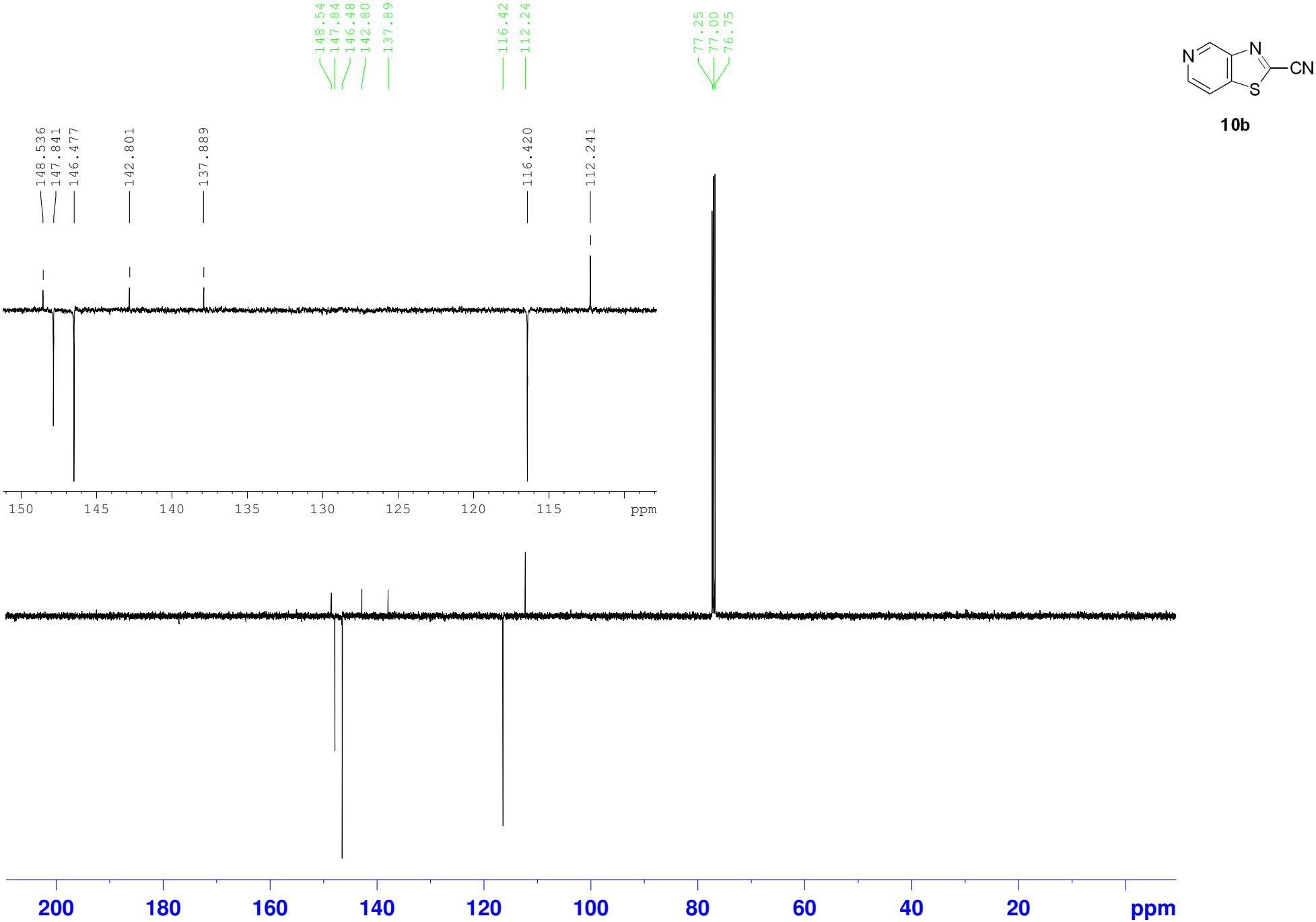
Thiazolo[5,4-b]pyridine-2-carbonitrile (10a)



Thiazolo[4,5-c]pyridine-2-carbonitrile (10b)

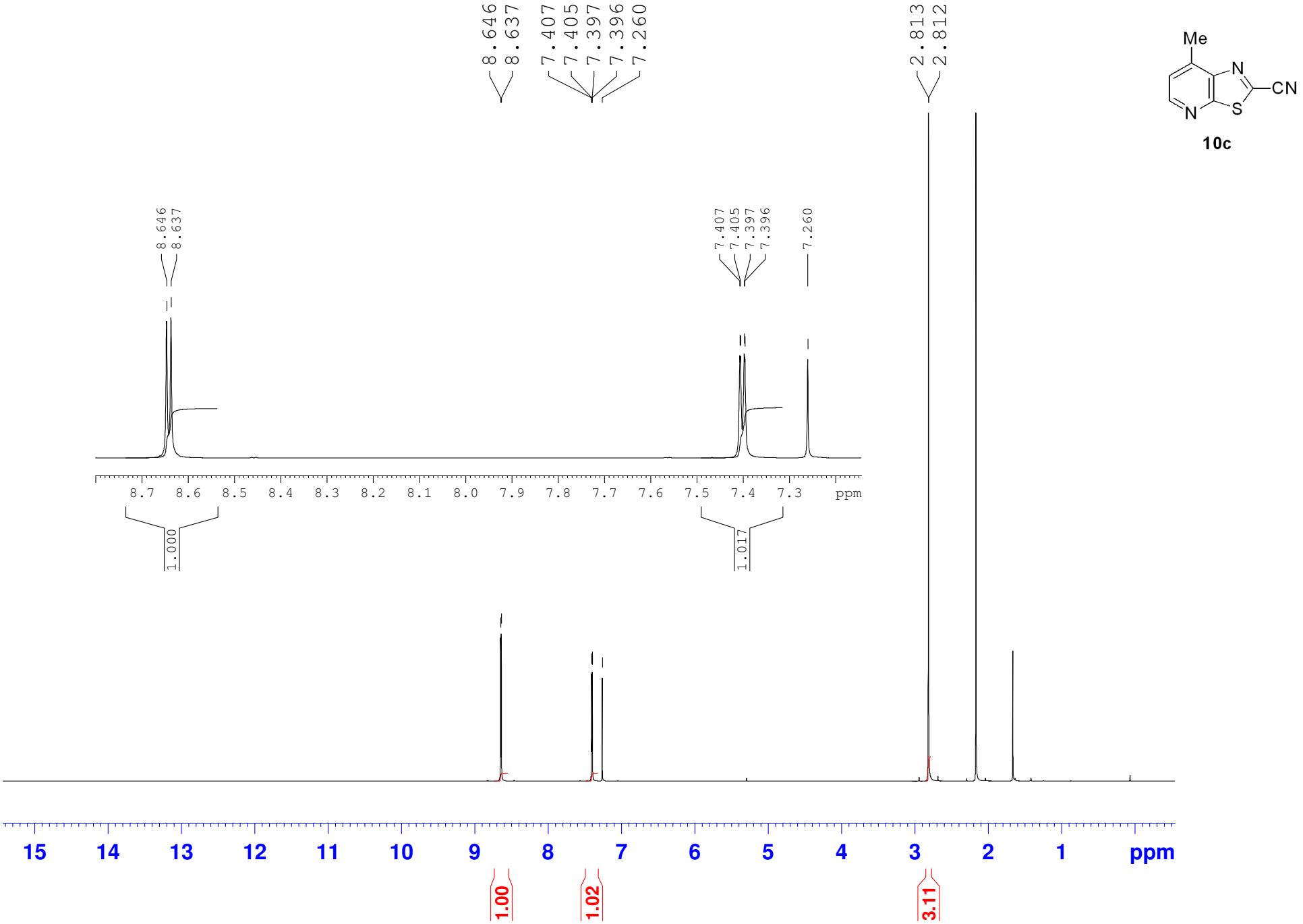


Thiazolo[4,5-c]pyridine-2-carbonitrile (10b)

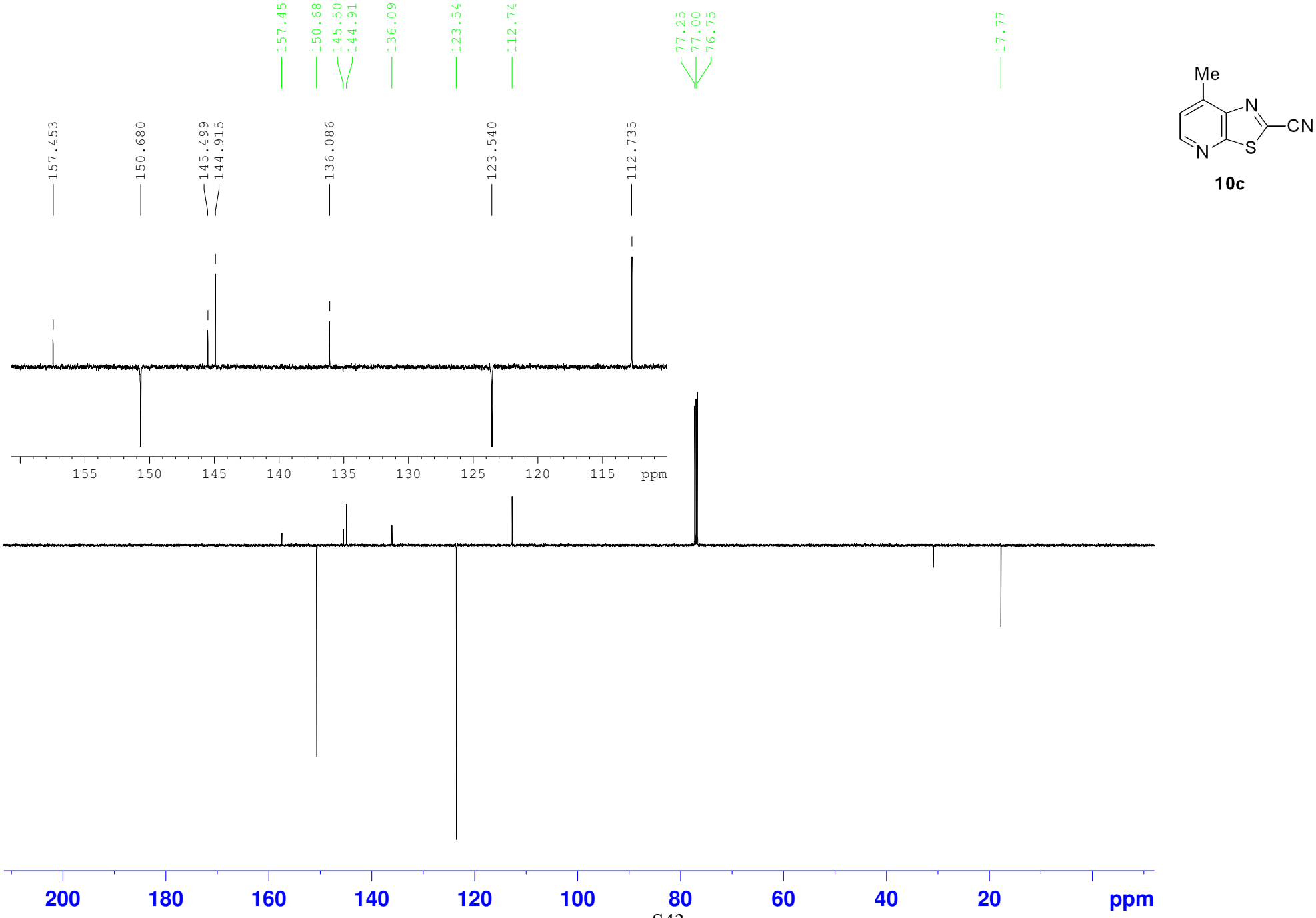


10b

7-Methylthiazolo[5,4-b]pyridine-2-carbonitrile (10c)

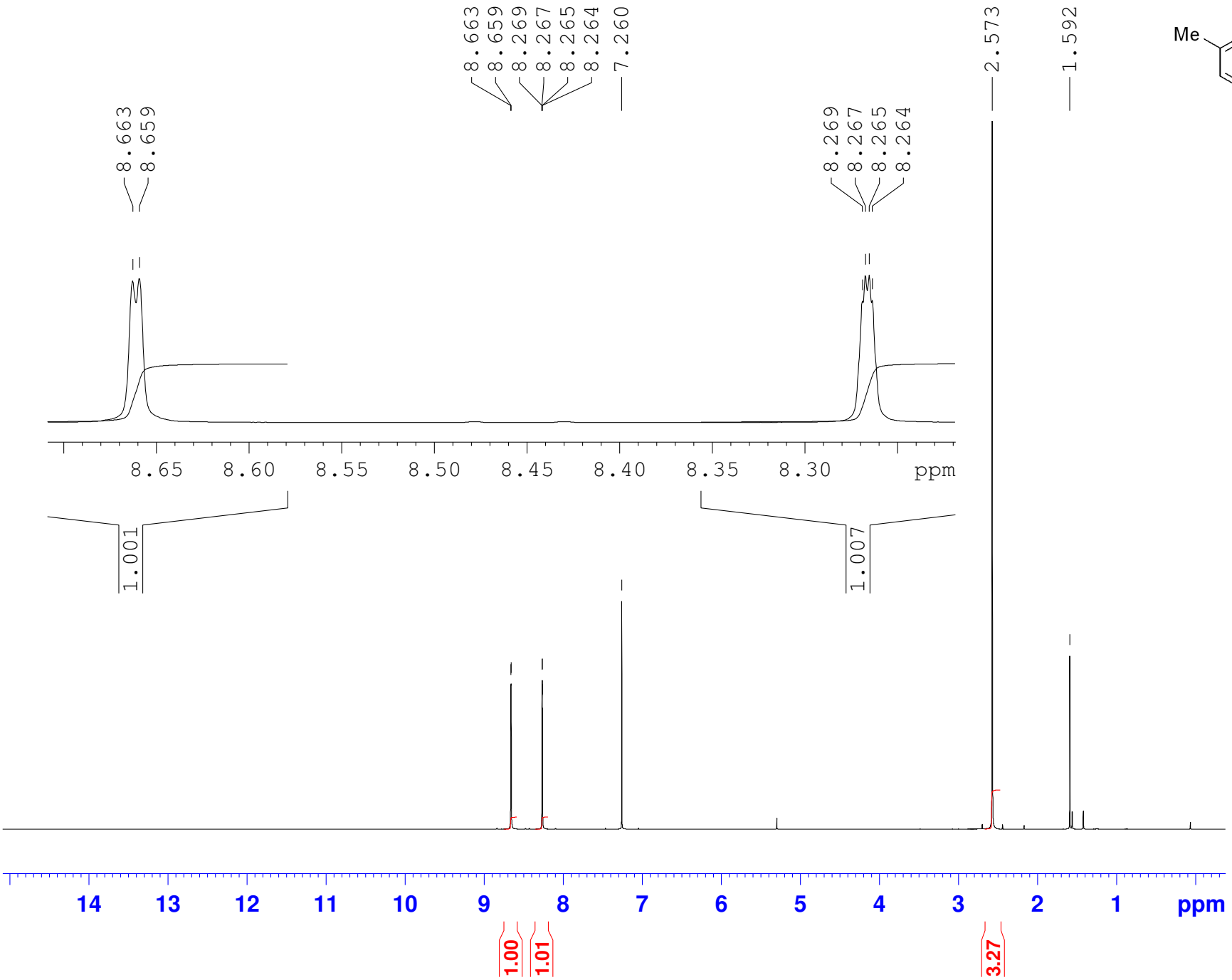


7-Methylthiazolo[5,4-b]pyridine-2-carbonitrile (10c)

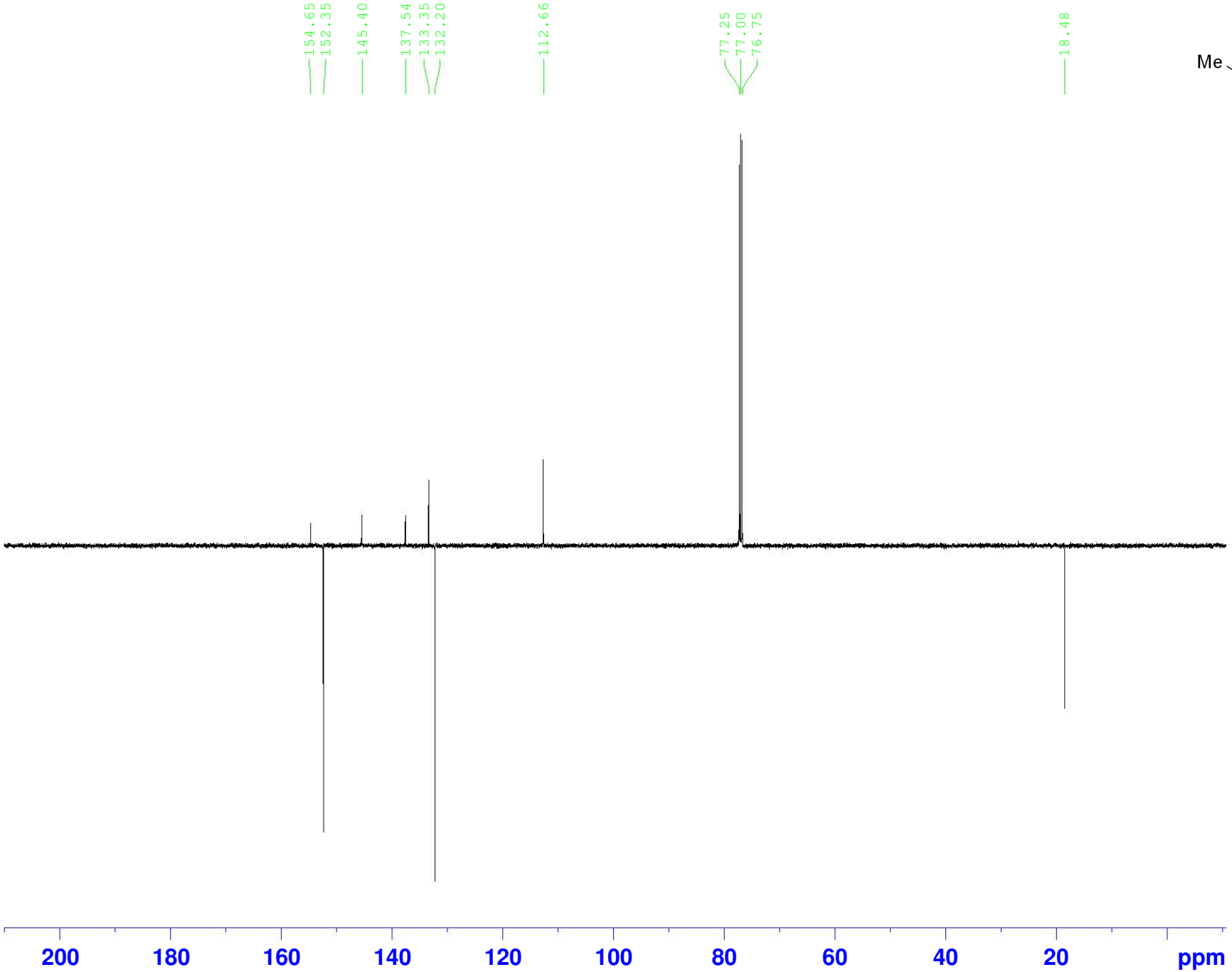


10c

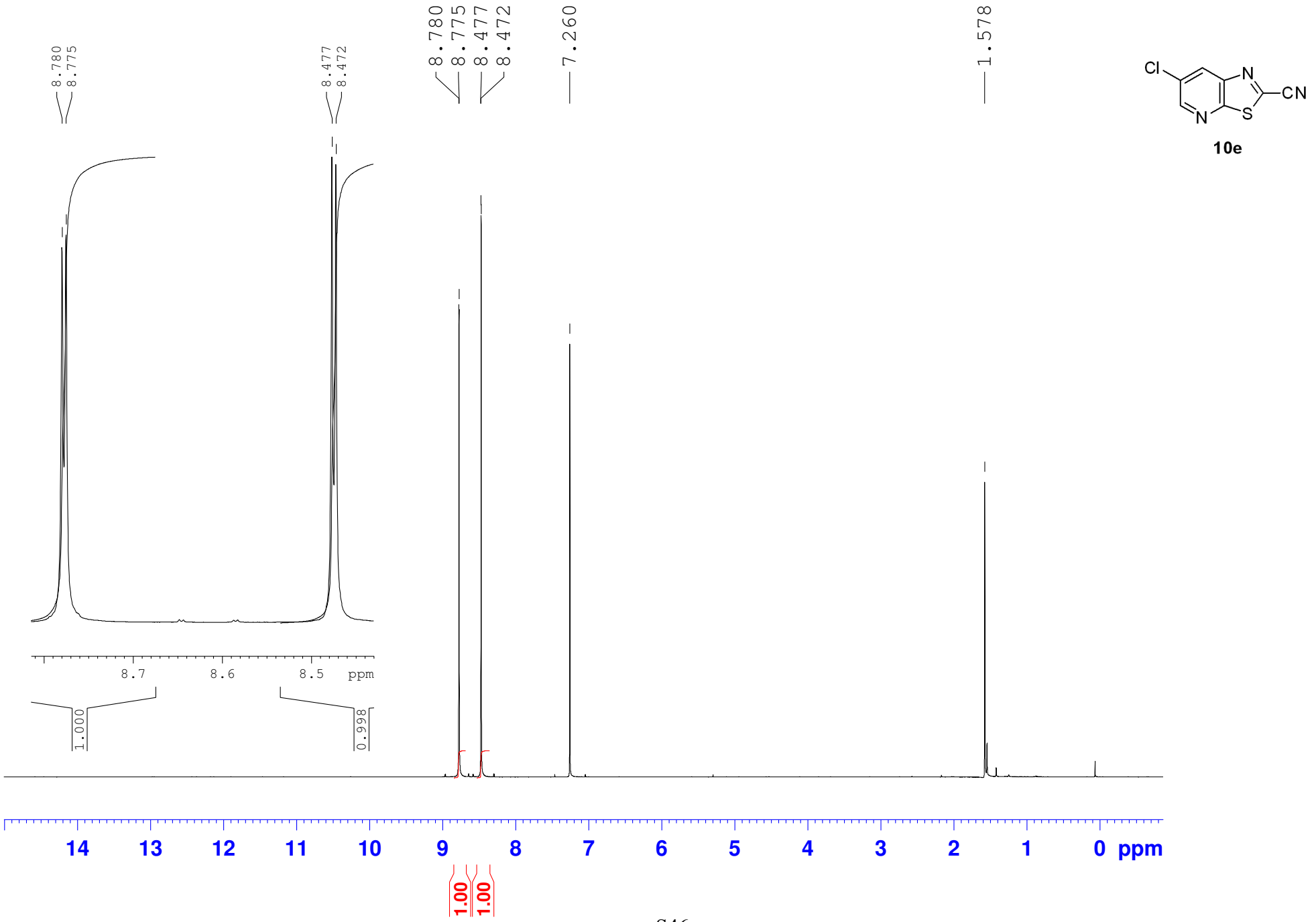
6-Methylthiazolo[5,4-b]pyridine-2-carbonitrile (10d)



6-Methylthiazolo[5,4-b]pyridine-2-carbonitrile (10d)

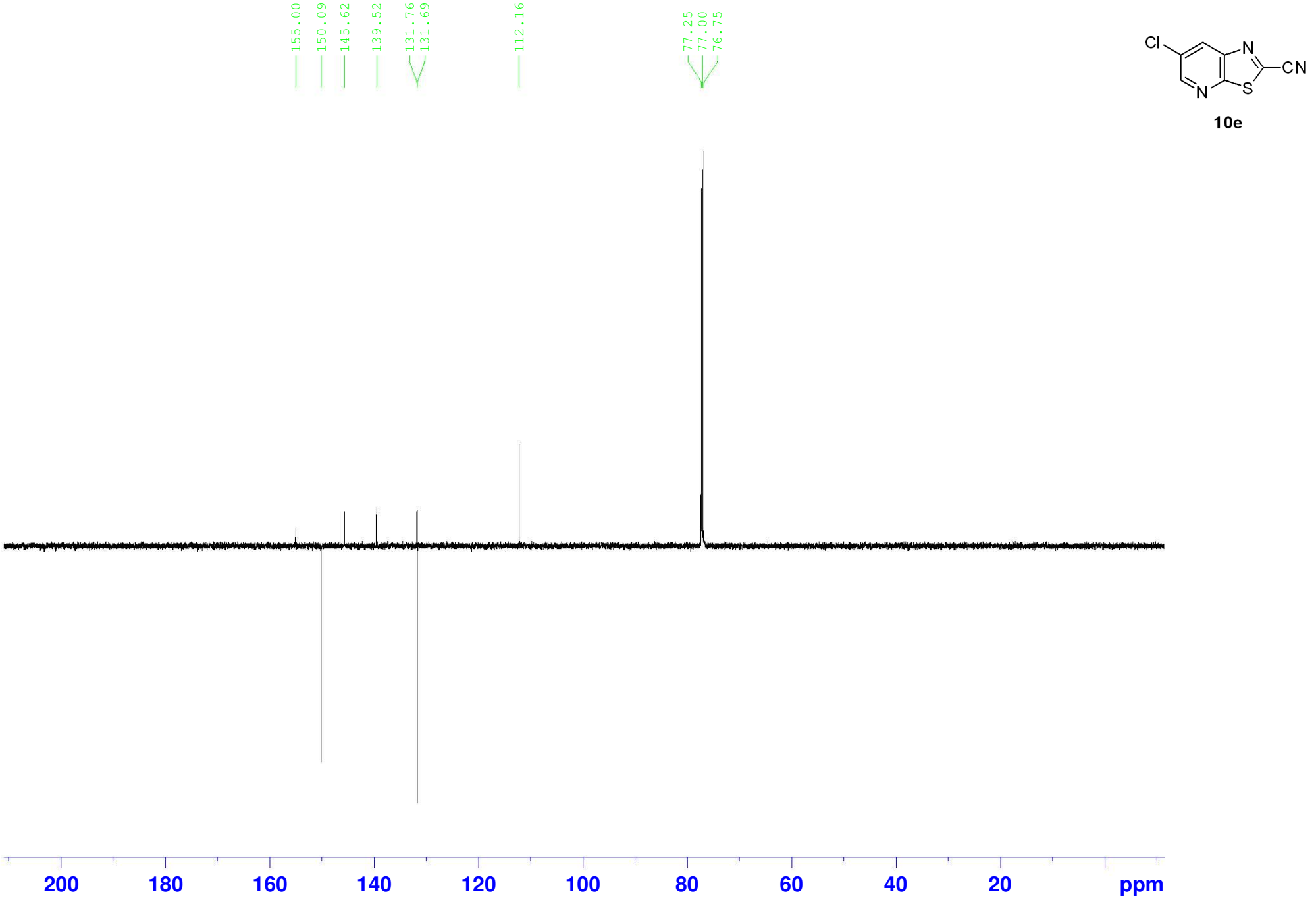


6-Chlorothiazolo[5,4-b]pyridine-2-carbonitrile (10e)

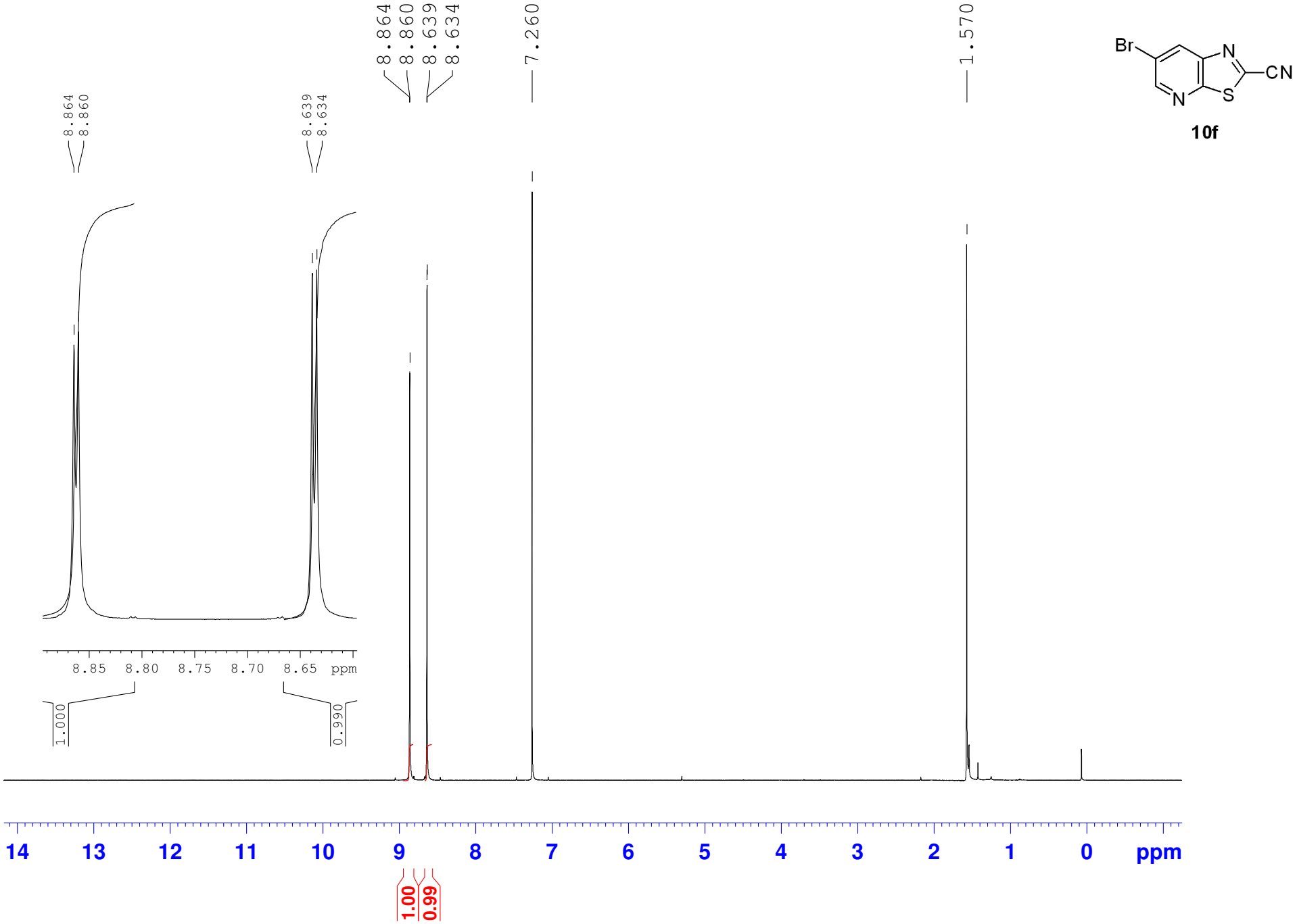


10e

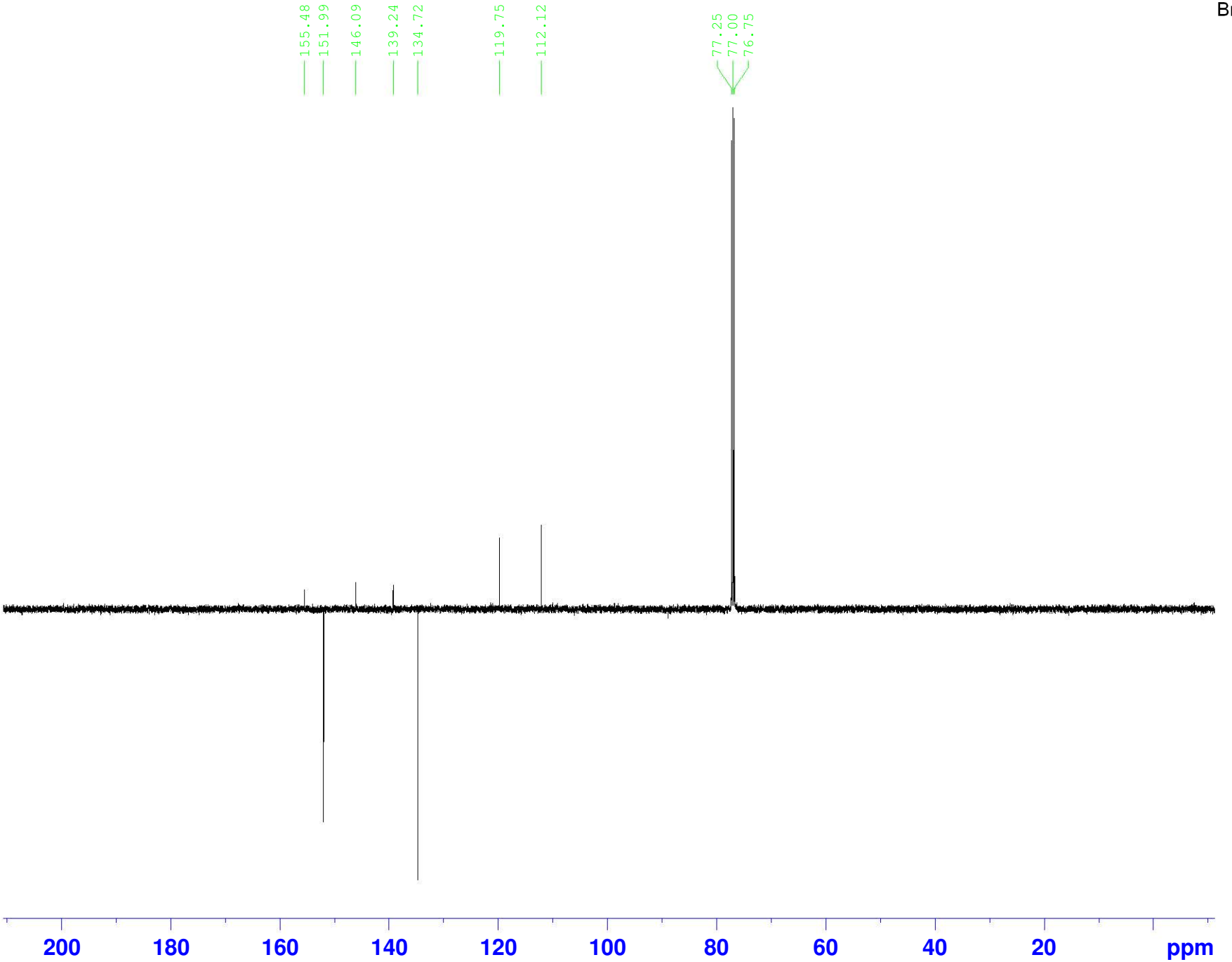
6-Chlorothiazolo[5,4-b]pyridine-2-carbonitrile (10e)

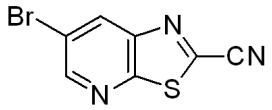


6-Bromothiazolo[5,4-b]pyridine-2-carbonitrile (10f)



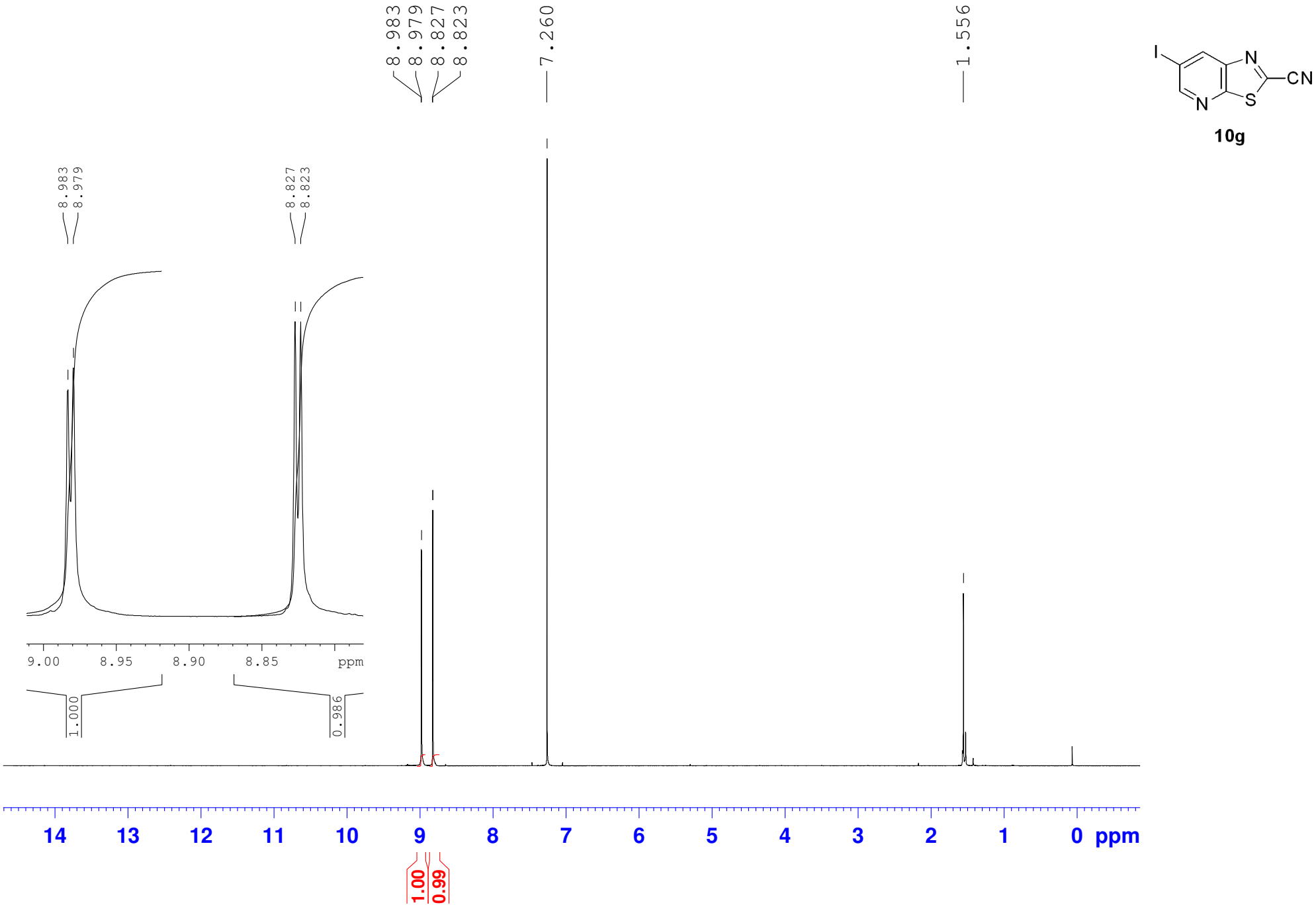
6-Bromothiazolo[5,4-b]pyridine-2-carbonitrile (10f)



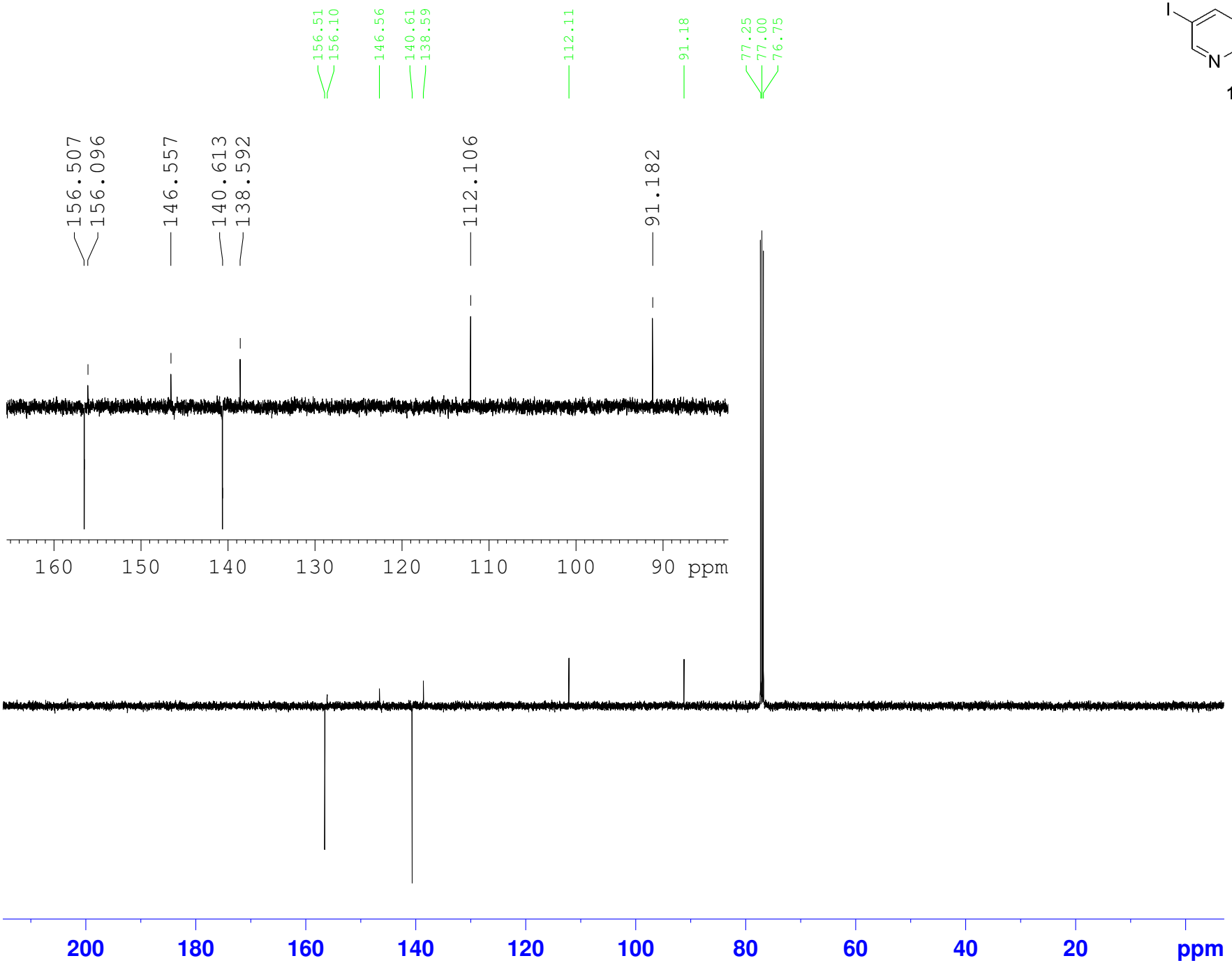


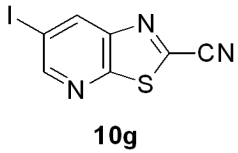
10f

6-Iodothiazolo[5,4-b]pyridine-2-carbonitrile (10g)



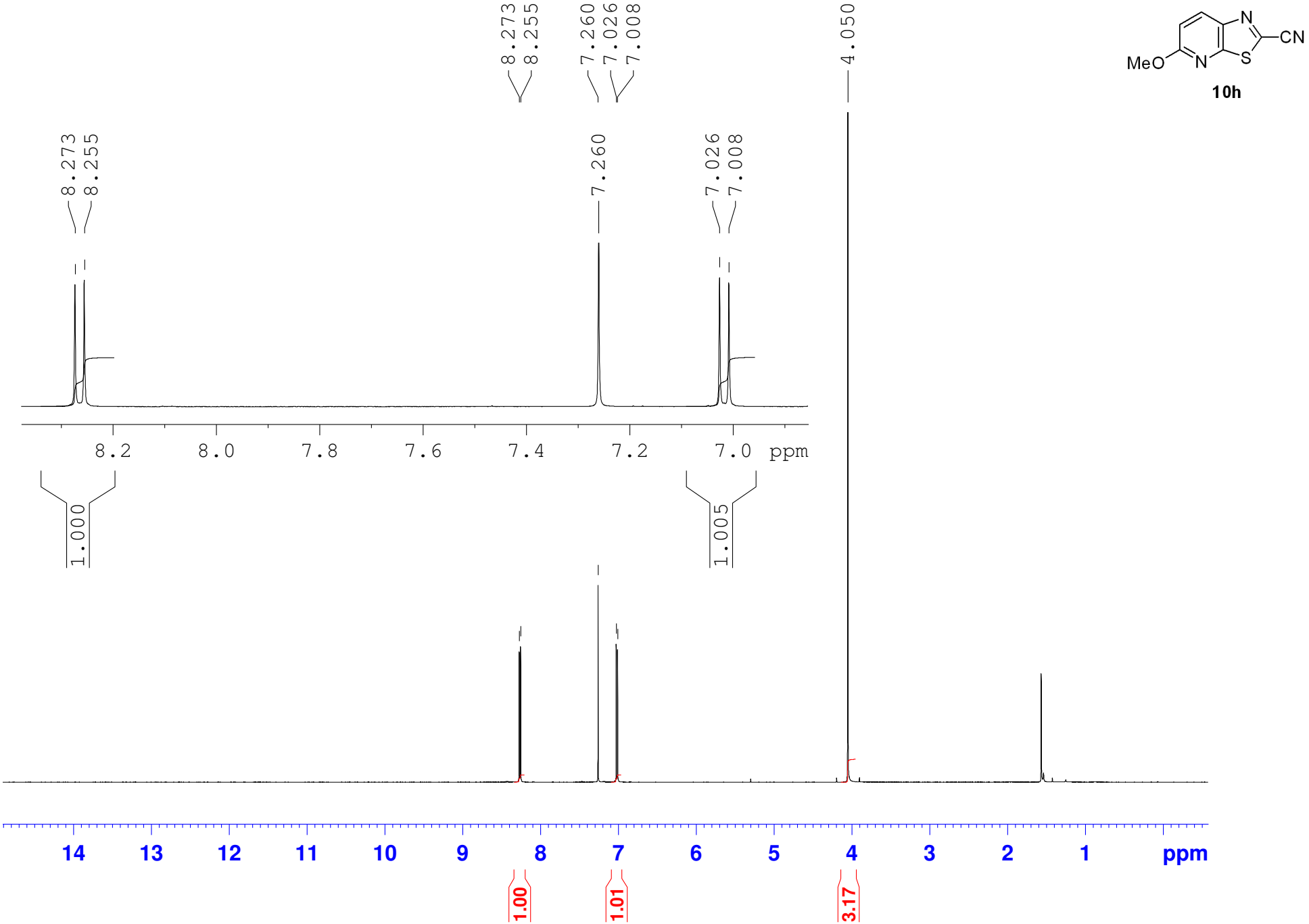
6-Iodothiazolo[5,4-b]pyridine-2-carbonitrile (10g)



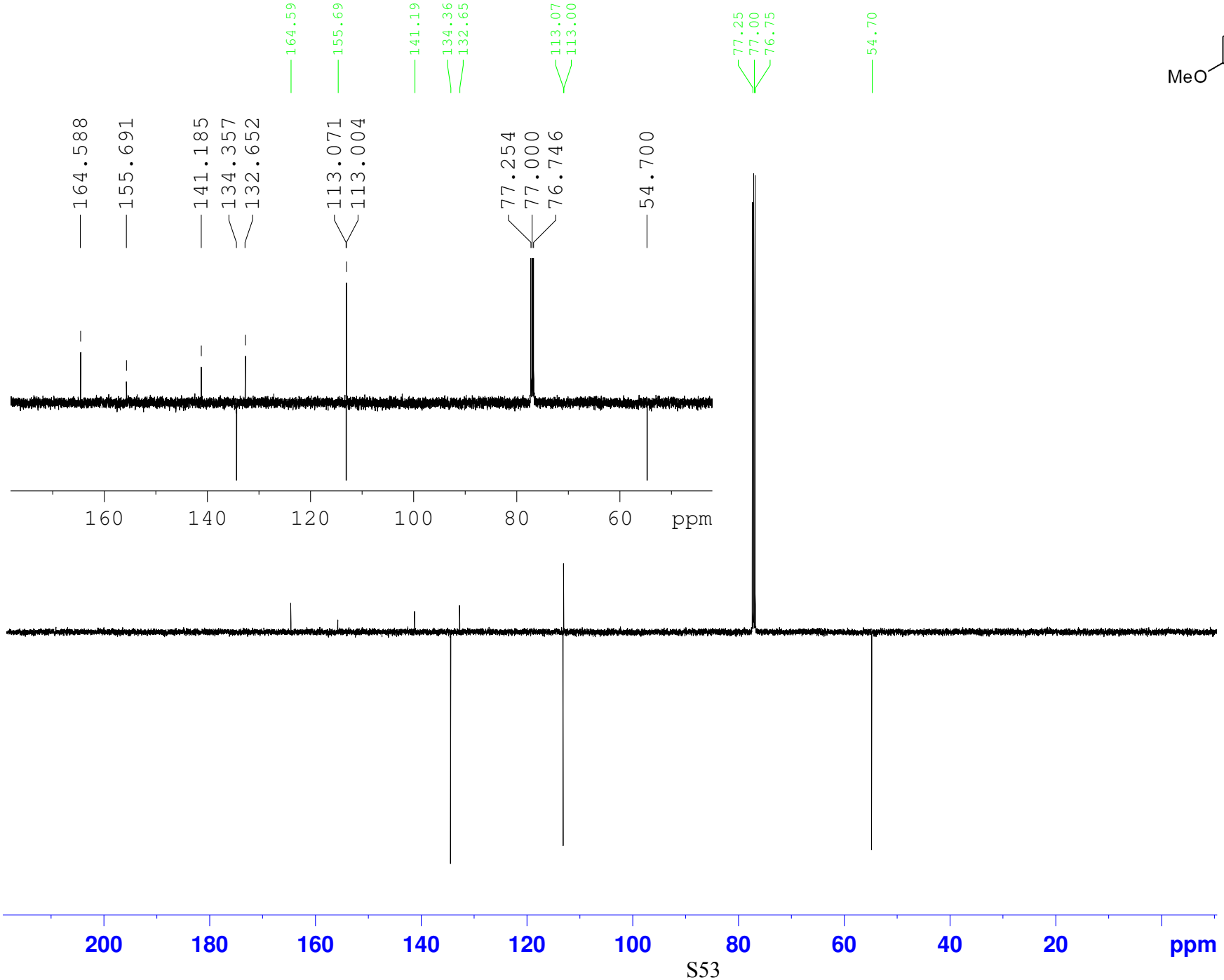


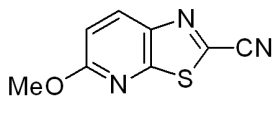
10g

5-Methoxythiazolo-[5,4-b]pyridine-2-carbonitrile (10h)



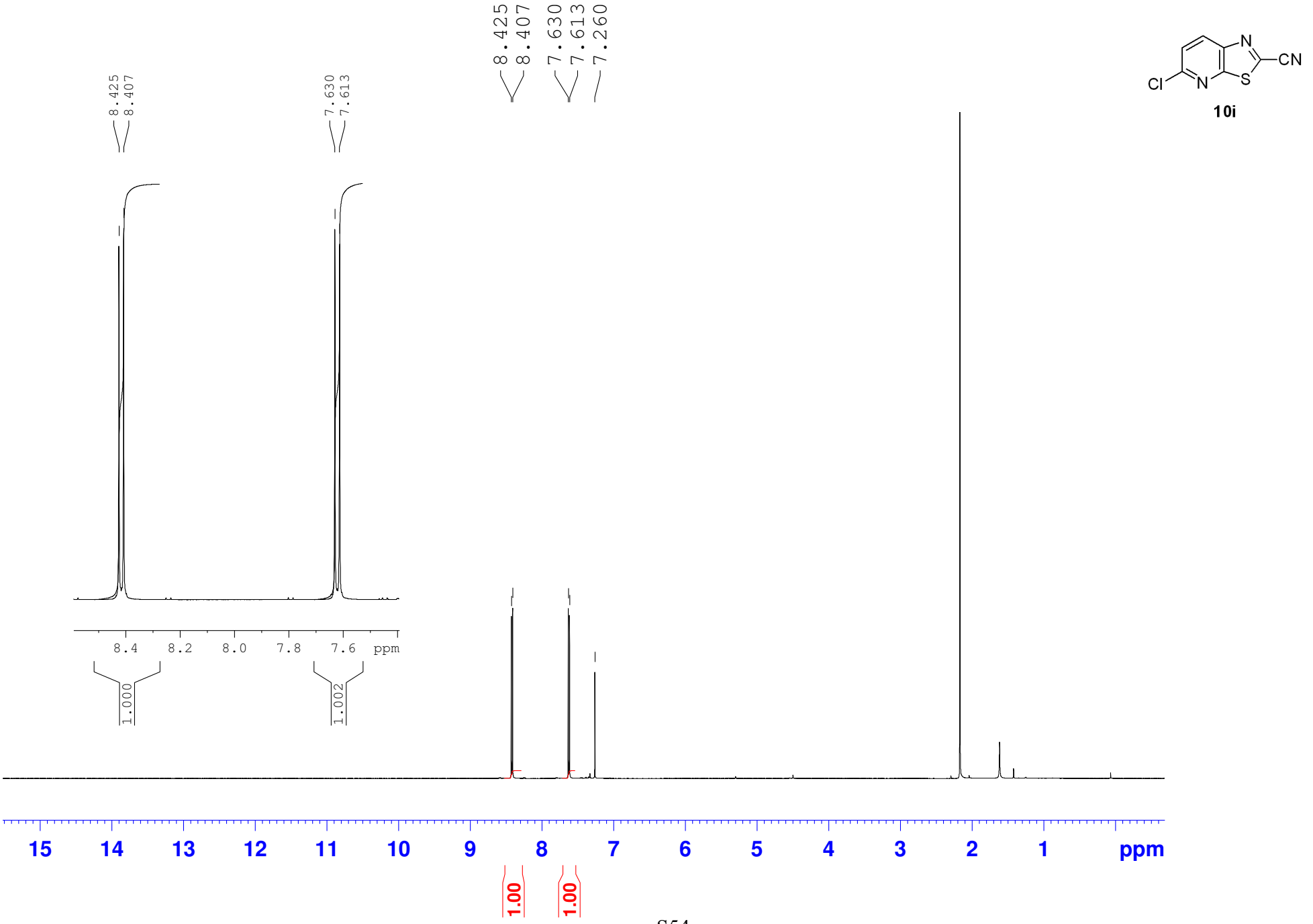
5-Methoxythiazolo-[5,4-b]pyridine-2-carbonitrile (10h)





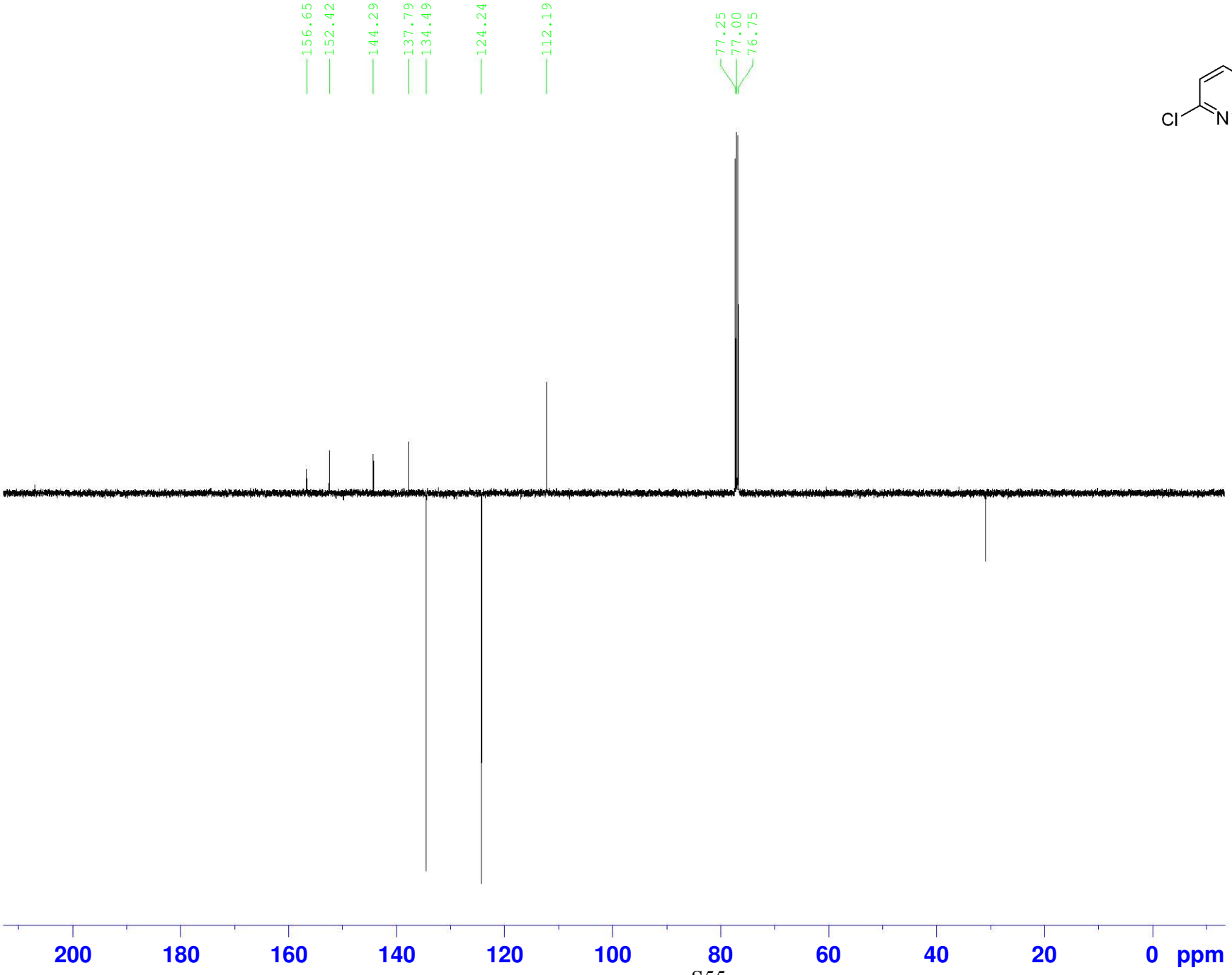
10h

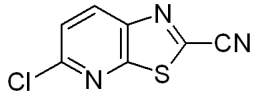
5-Chlorothiazolo[5,4-b]-pyridine-2-carbonitrile (10i)



10i

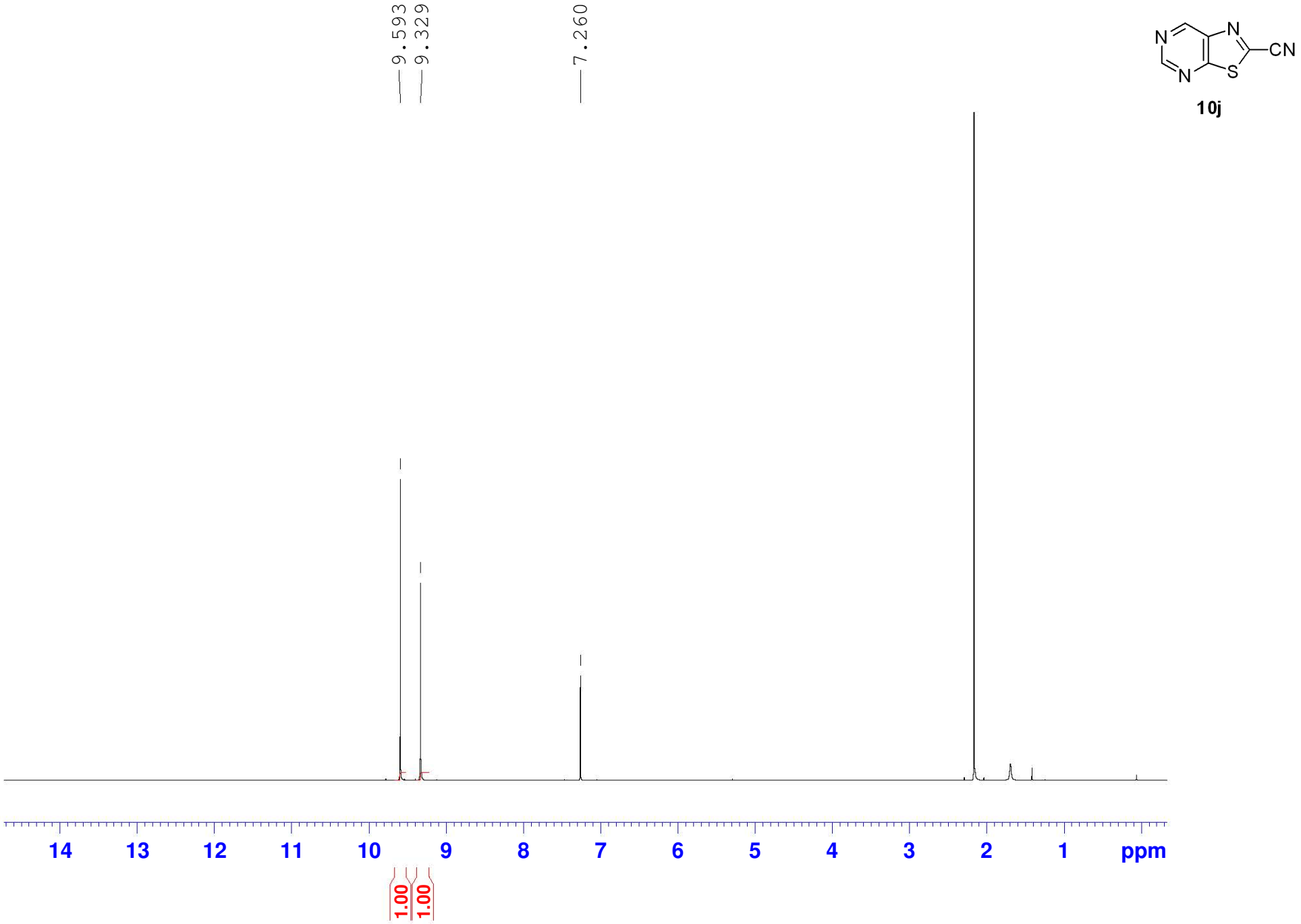
5-Chlorothiazolo[5,4-b]-pyridine-2-carbonitrile (10i)



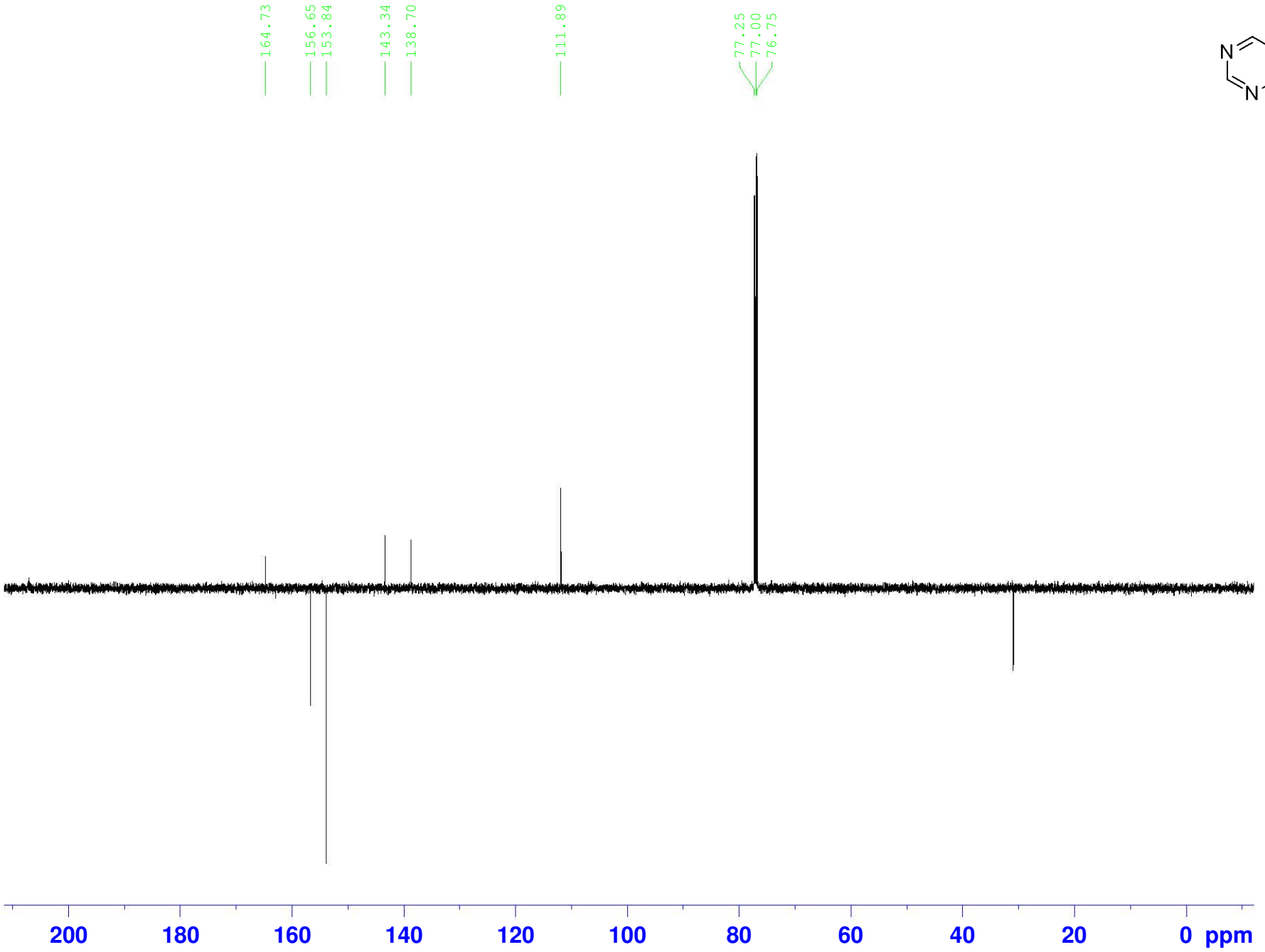


10i

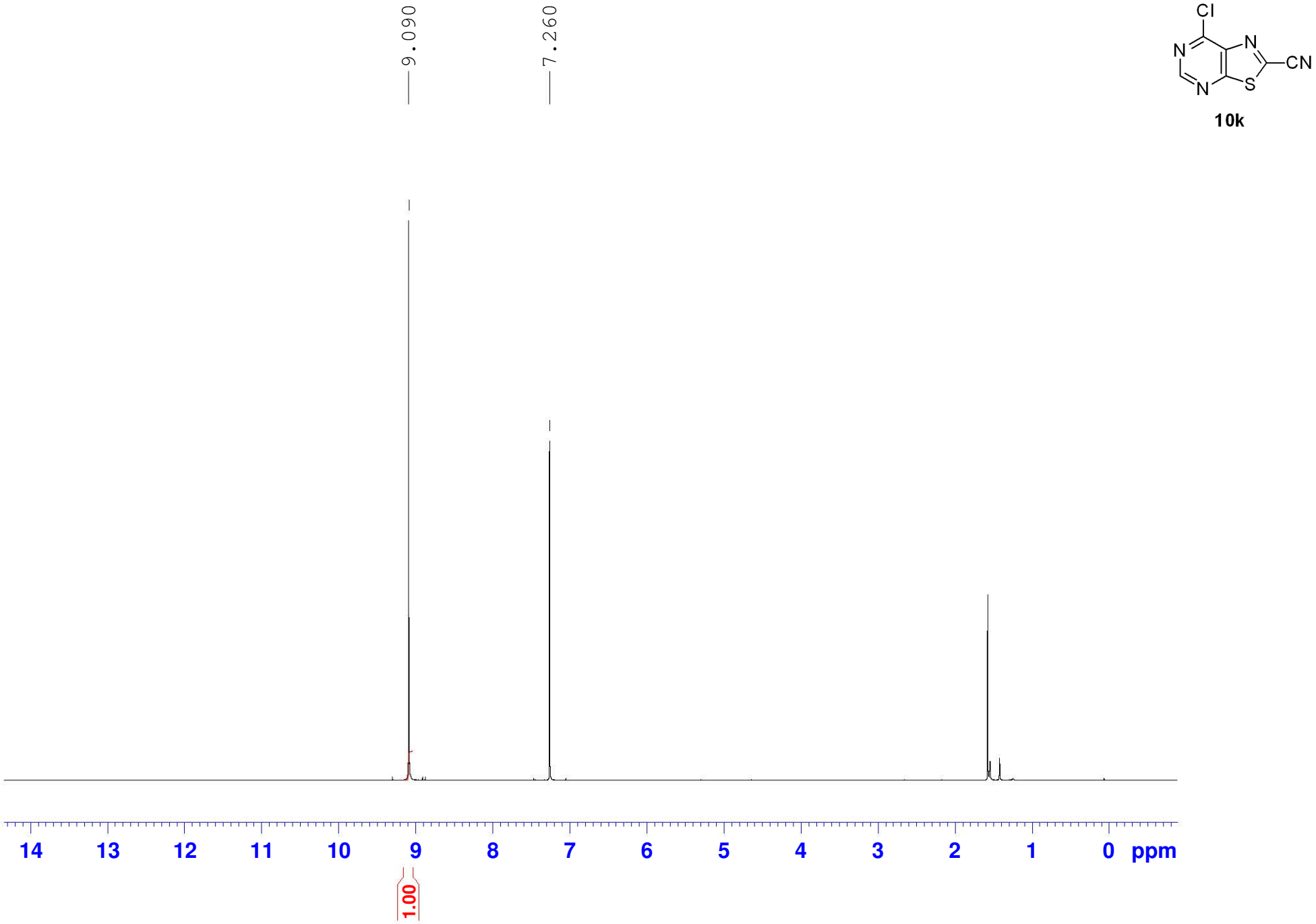
Thiazolo[5,4-d]pyrimidine-2-carbonitrile (10j)



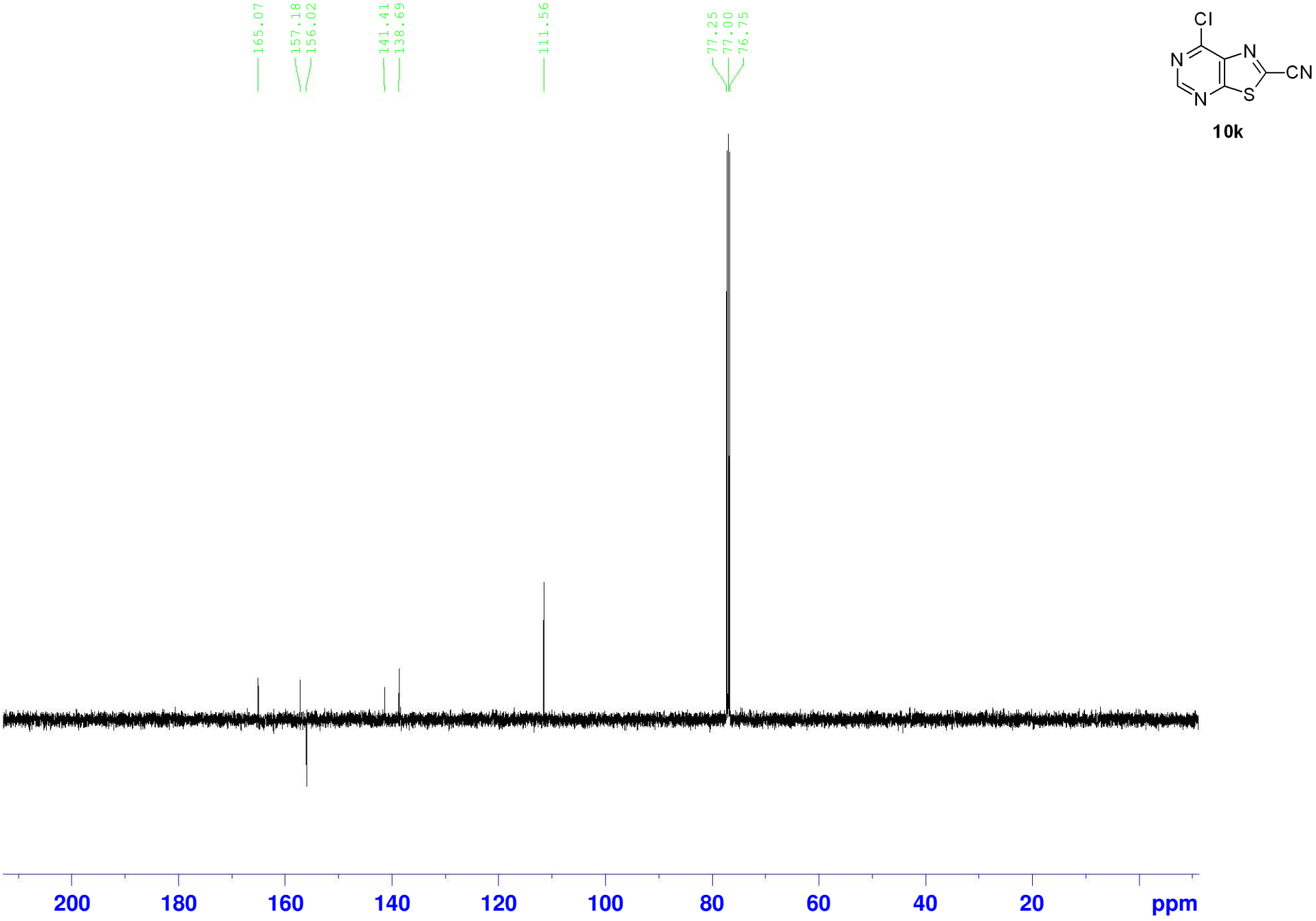
Thiazolo[5,4-d]pyrimidine-2-carbonitrile (10j)



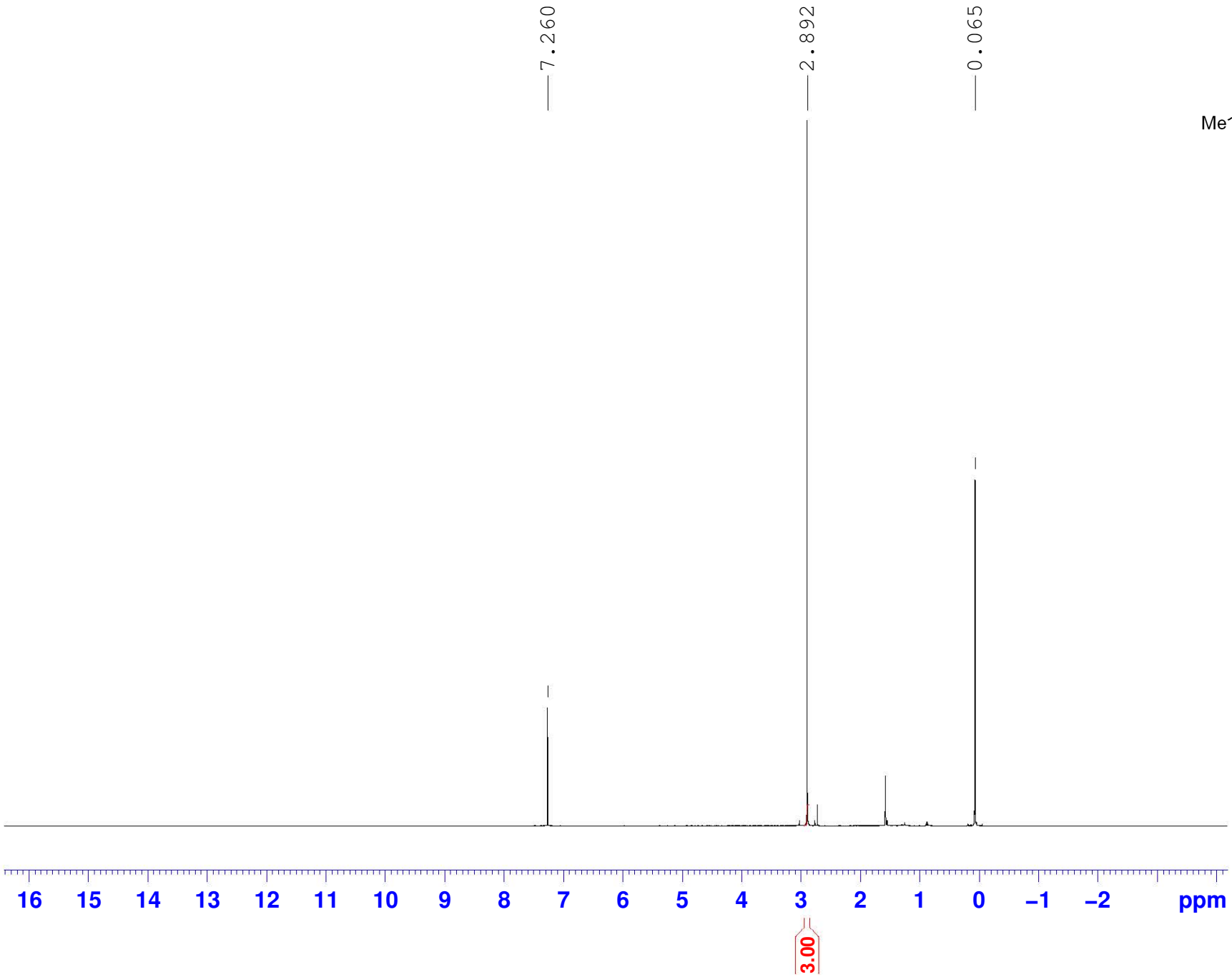
7-Chlorothiazolo[5,4-d]pyrimidine-2-carbonitrile (10k)



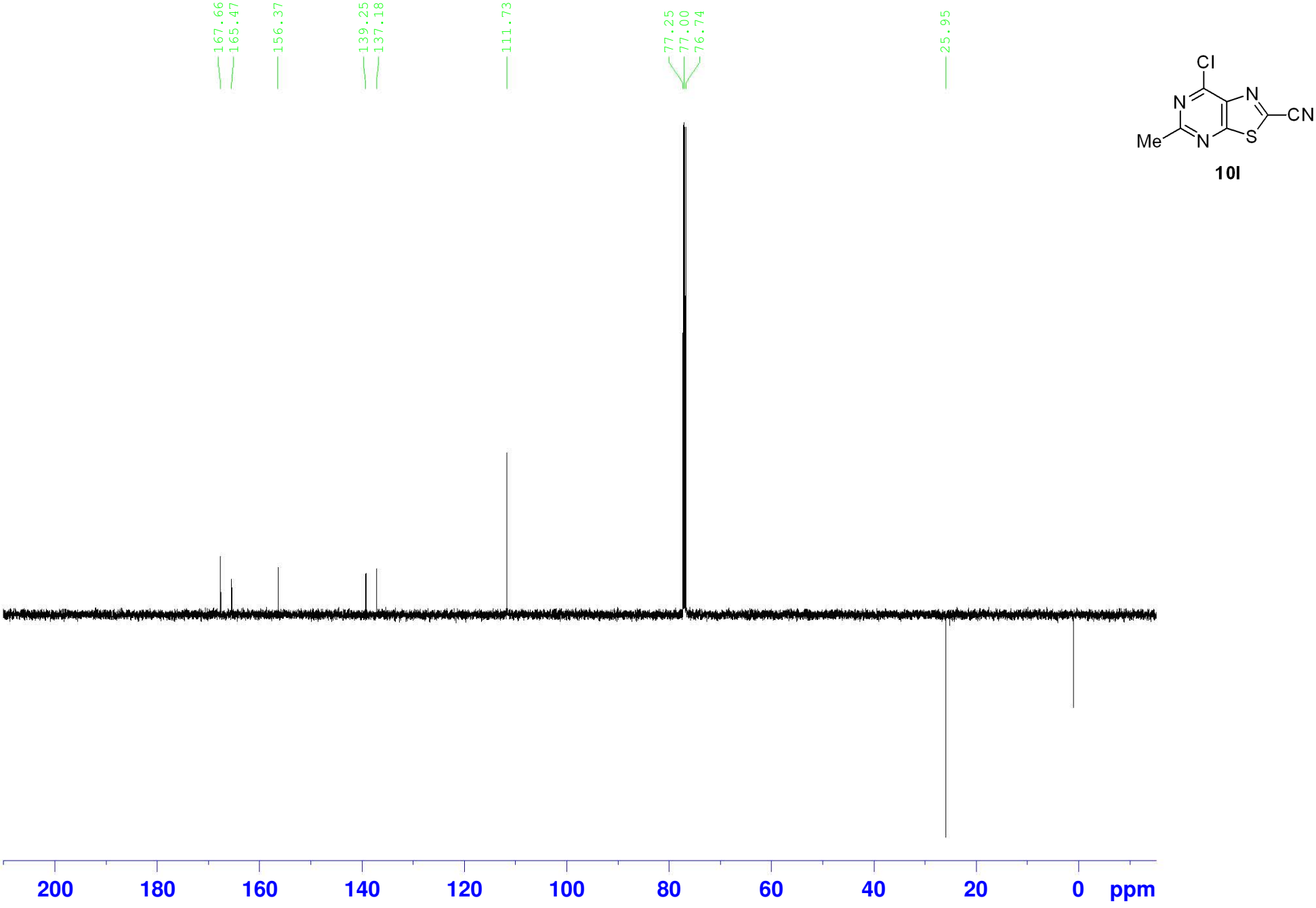
7-Chlorothiazolo[5,4-d]pyrimidine-2-carbonitrile (10k)



7-Chloro-5-methylthiazolo[5,4-d]pyrimidine-2-carbonitrile (10l)

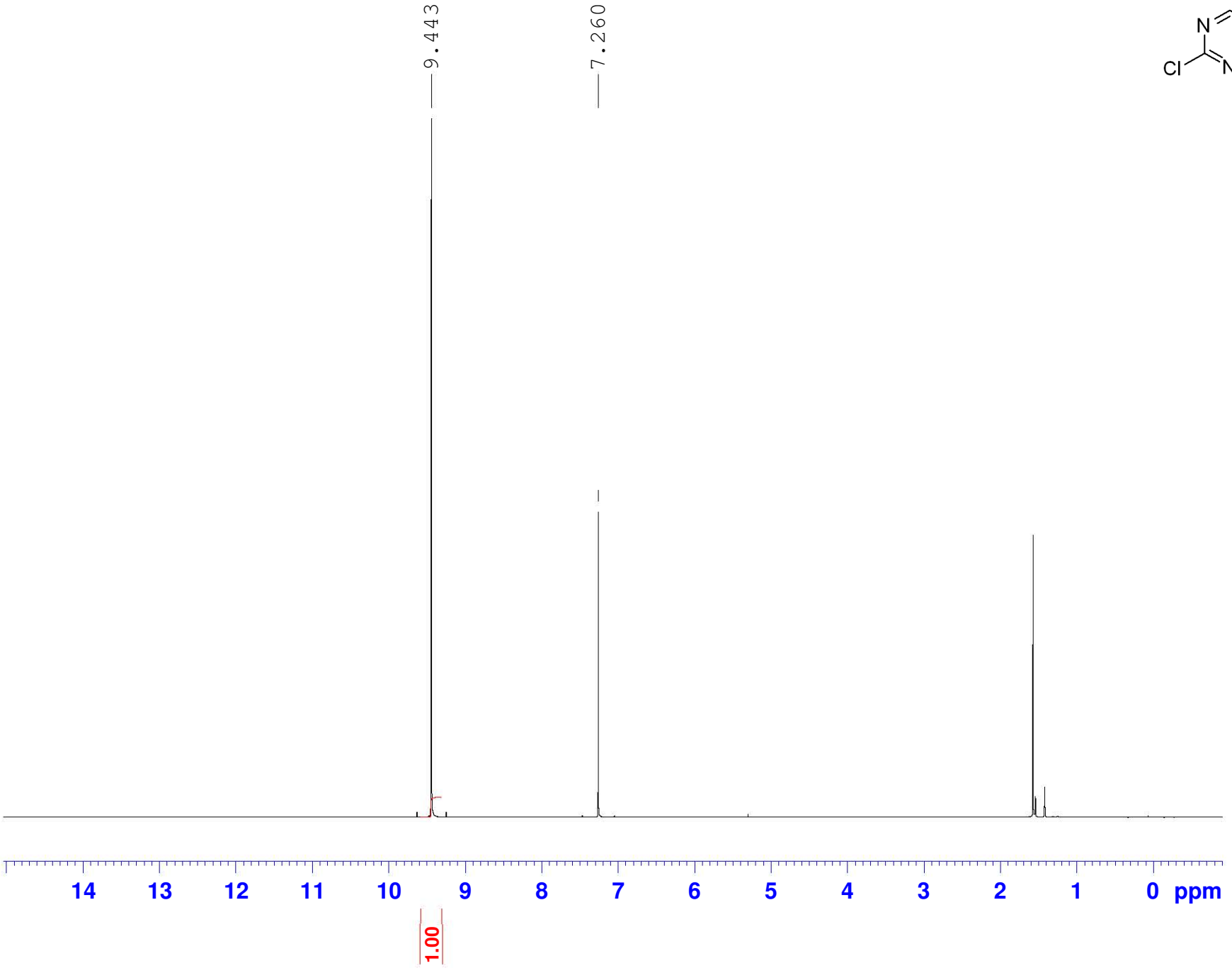


7-Chloro-5-methylthiazolo[5,4-d]pyrimidine-2-carbonitrile (10l)

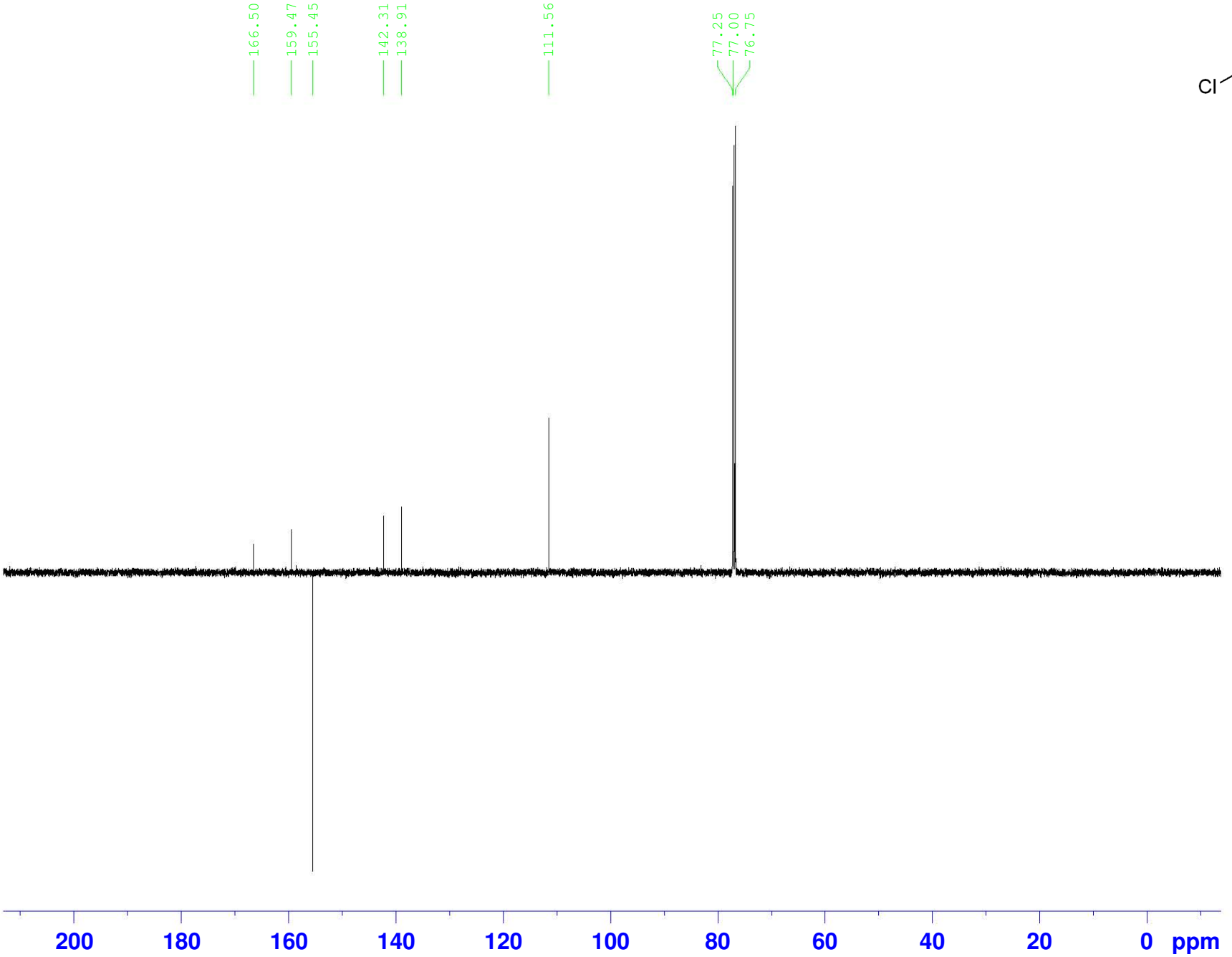


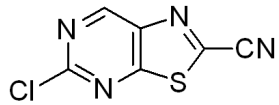
10l

5-Chlorothiazolo[5,4-d]pyrimidine-2-carbonitrile (10m)



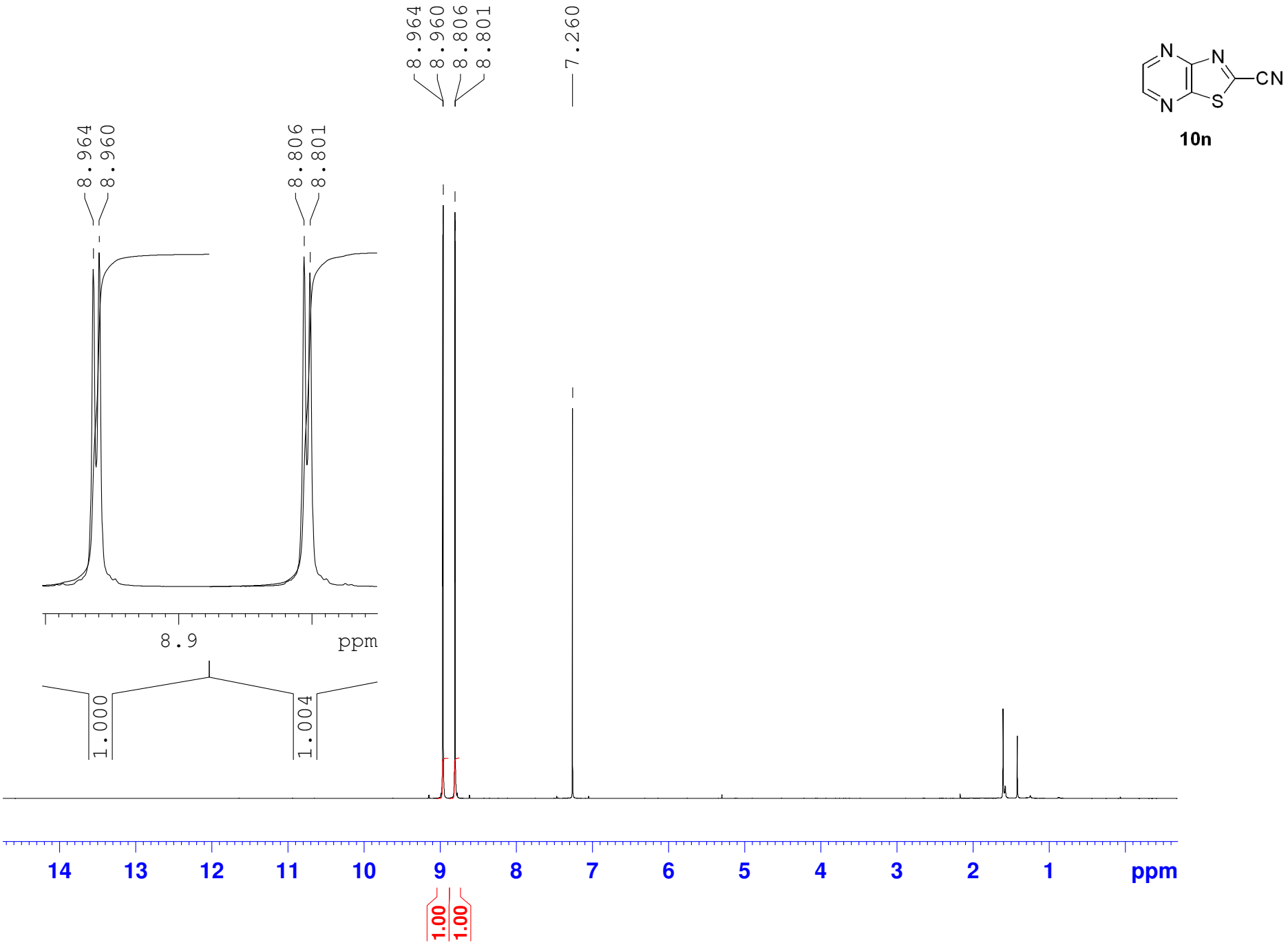
5-Chlorothiazolo[5,4-d]pyrimidine-2-carbonitrile (10m)



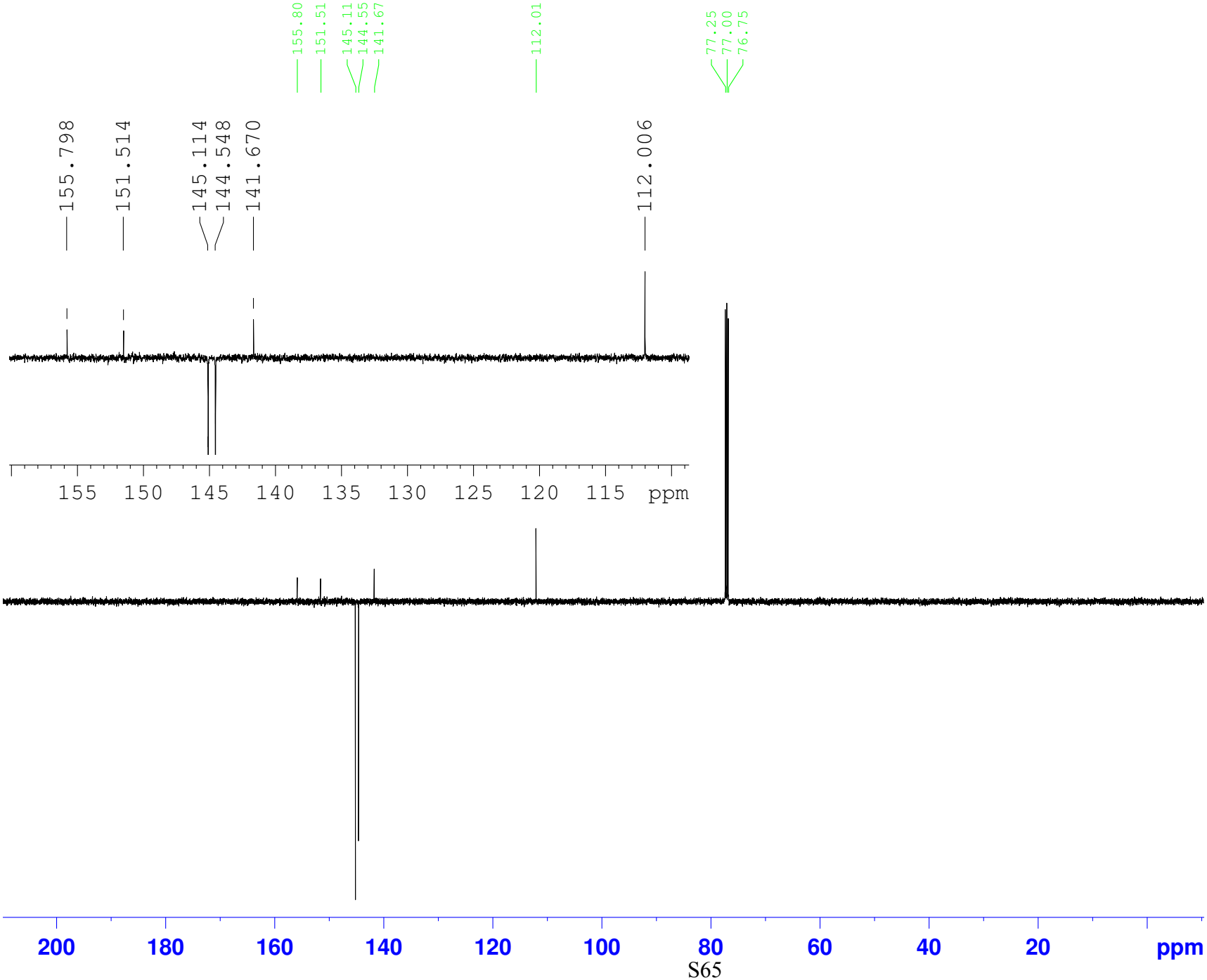


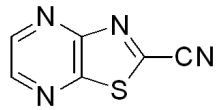
10m

Thiazolo[4,5-b]pyrazine-2-carbonitrile (10n)



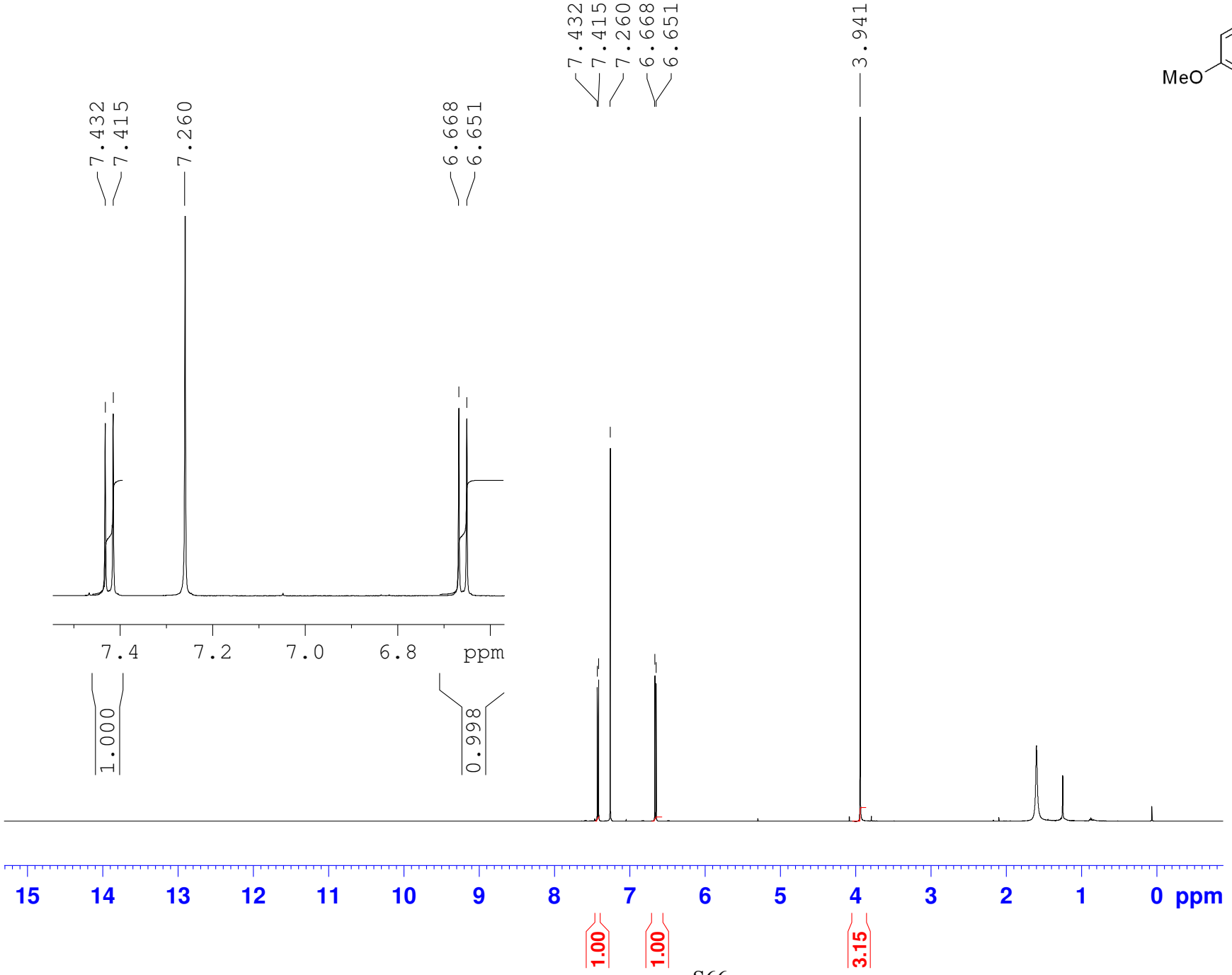
Thiazolo[4,5-b]pyrazine-2-carbonitrile (10n)



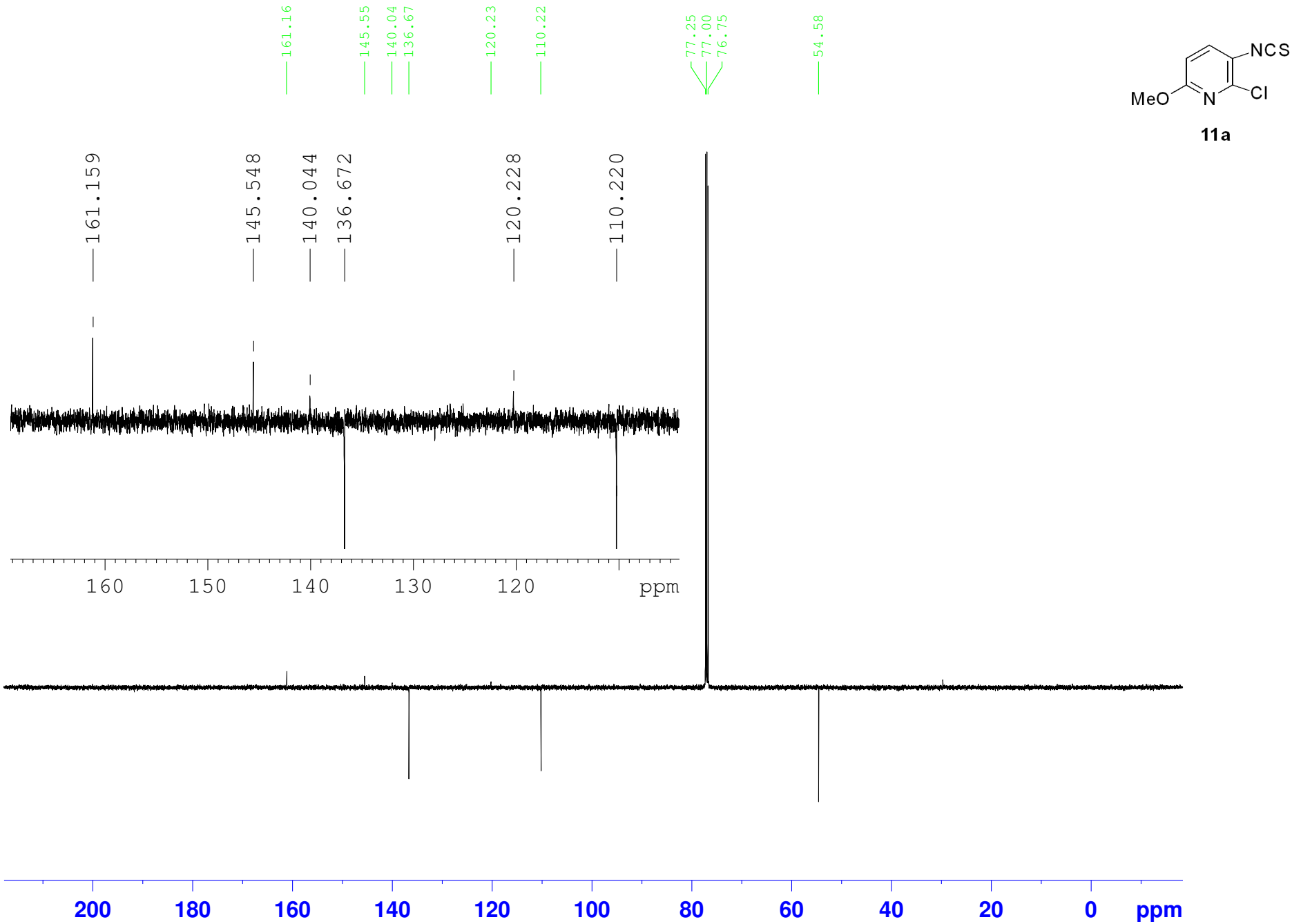


10n

2-Chloro-3-isothiocyanato-6-methoxypyridine (11a)

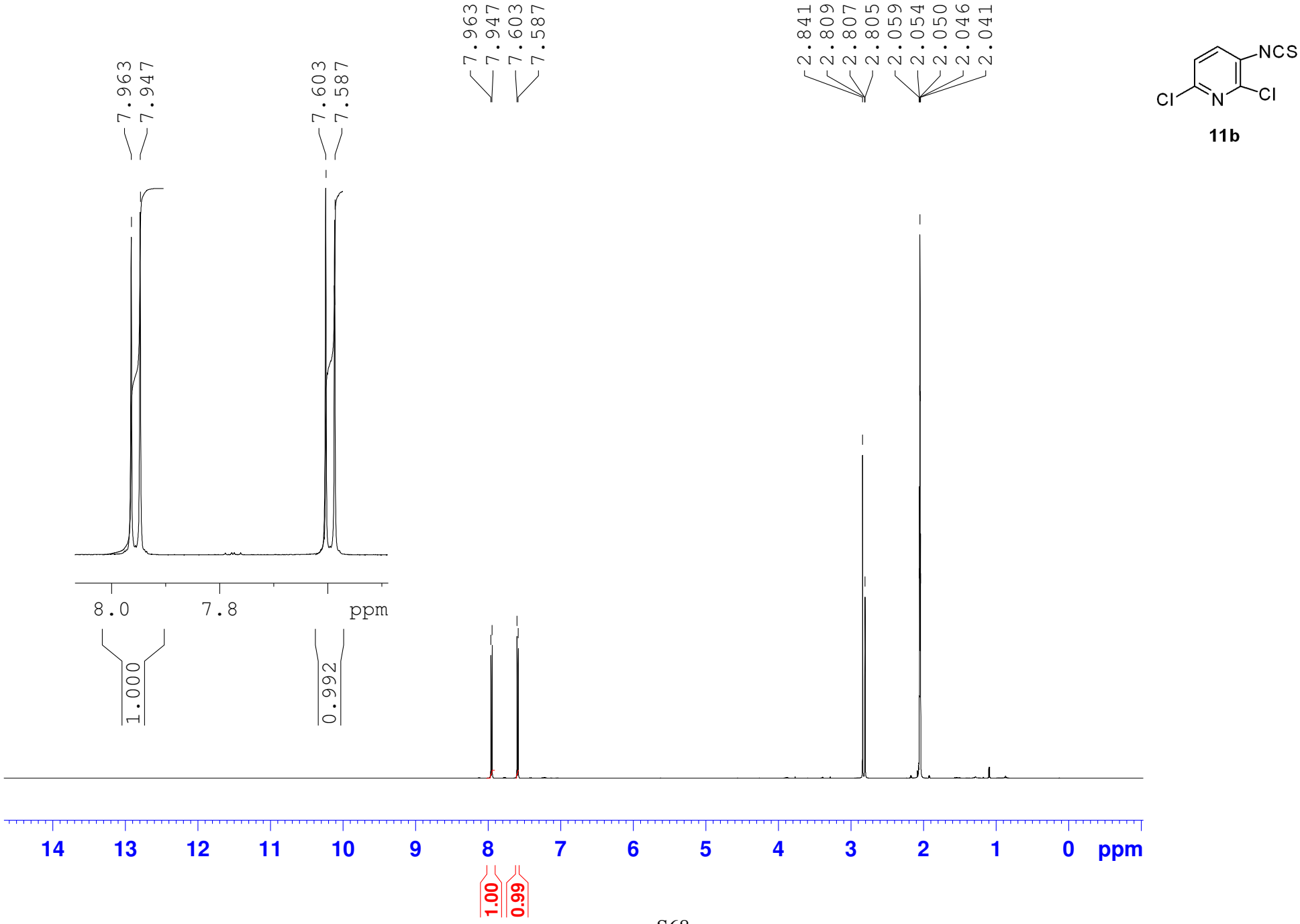


2-Chloro-3-isothiocyanato-6-methoxypyridine (11a)

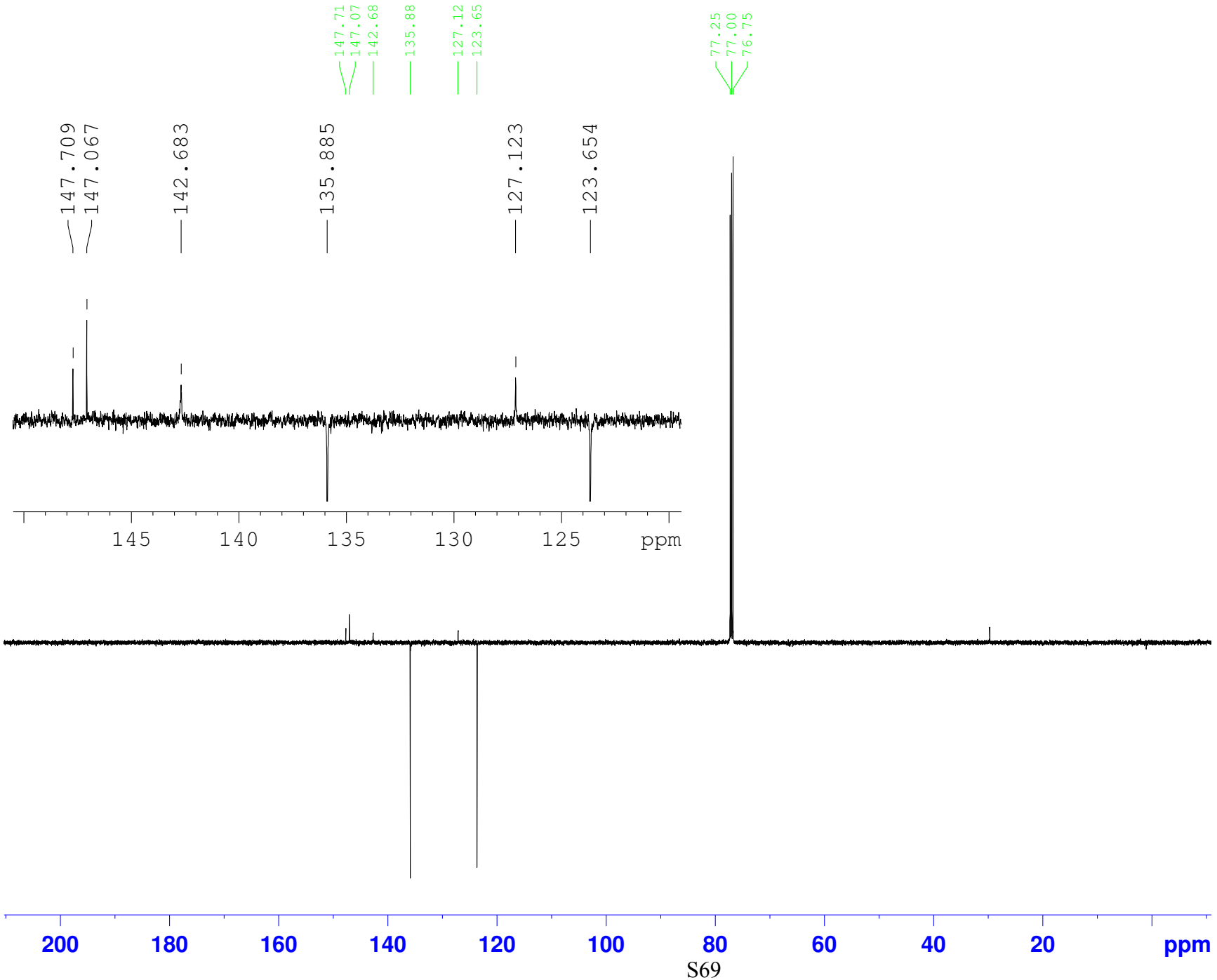


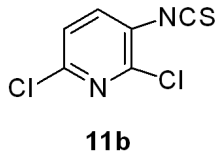
11a

2,6-Dichloro-3-isothiocyanatopyridine (11b)



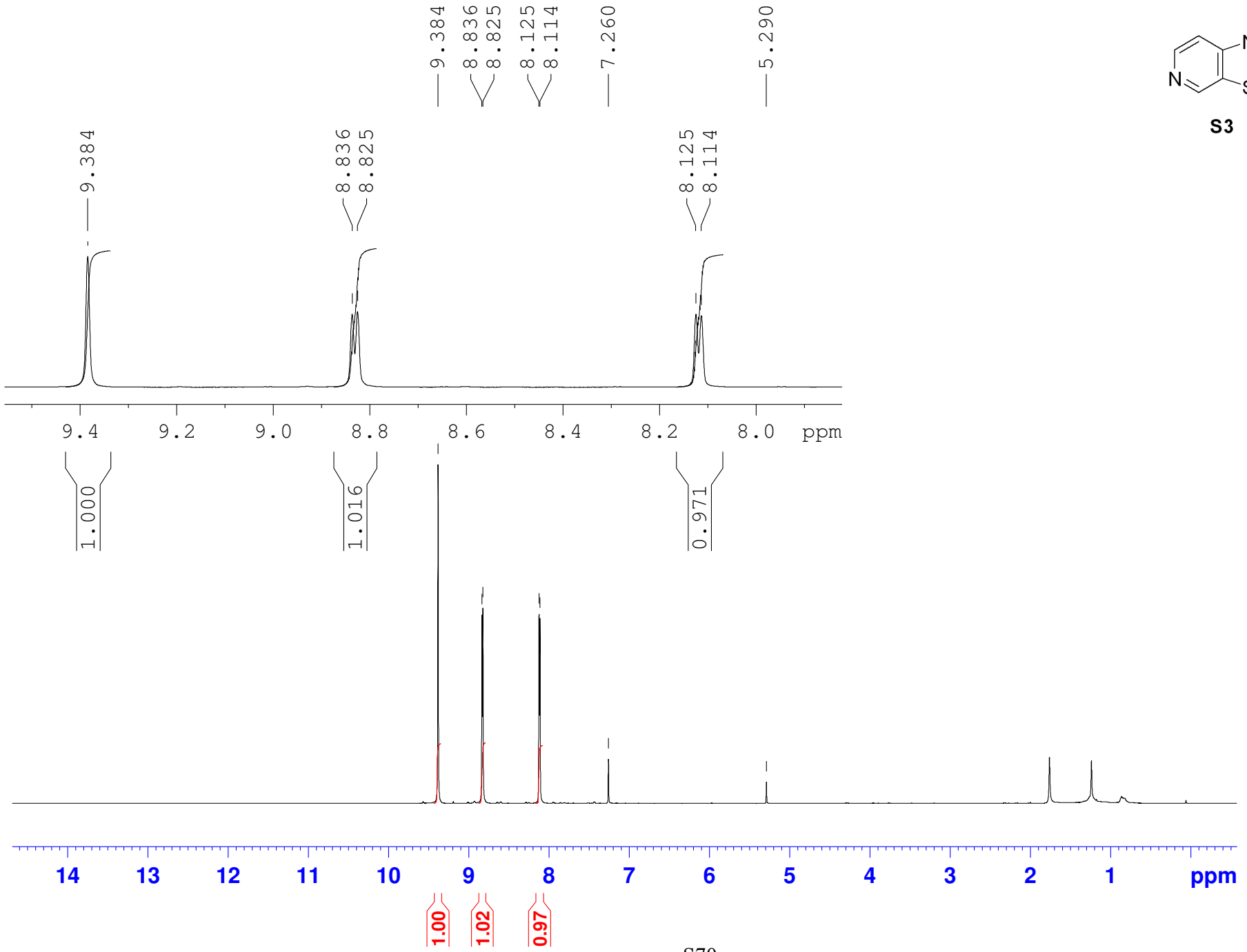
2,6-Dichloro-3-isothiocyanatopyridine (11b)



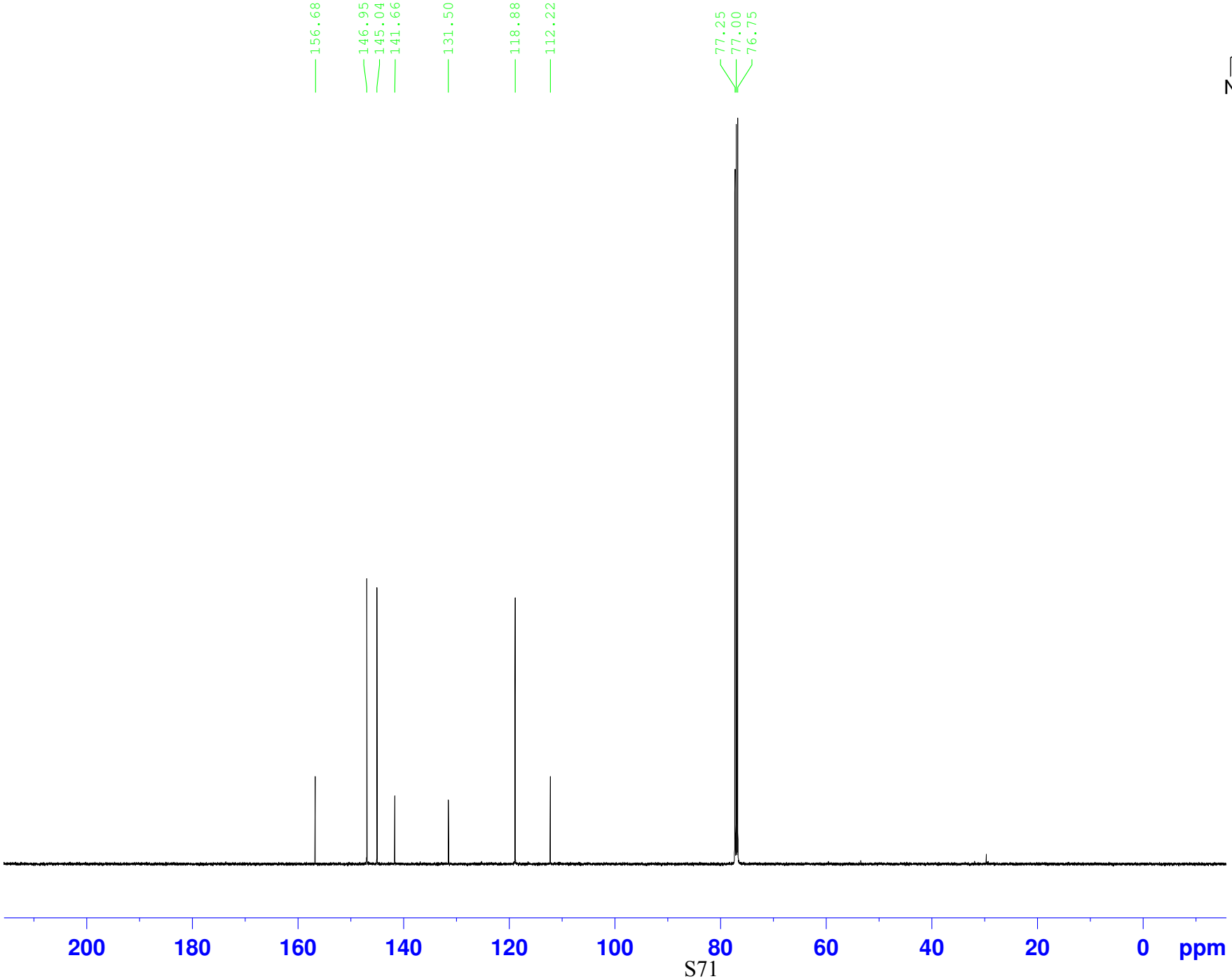


11b

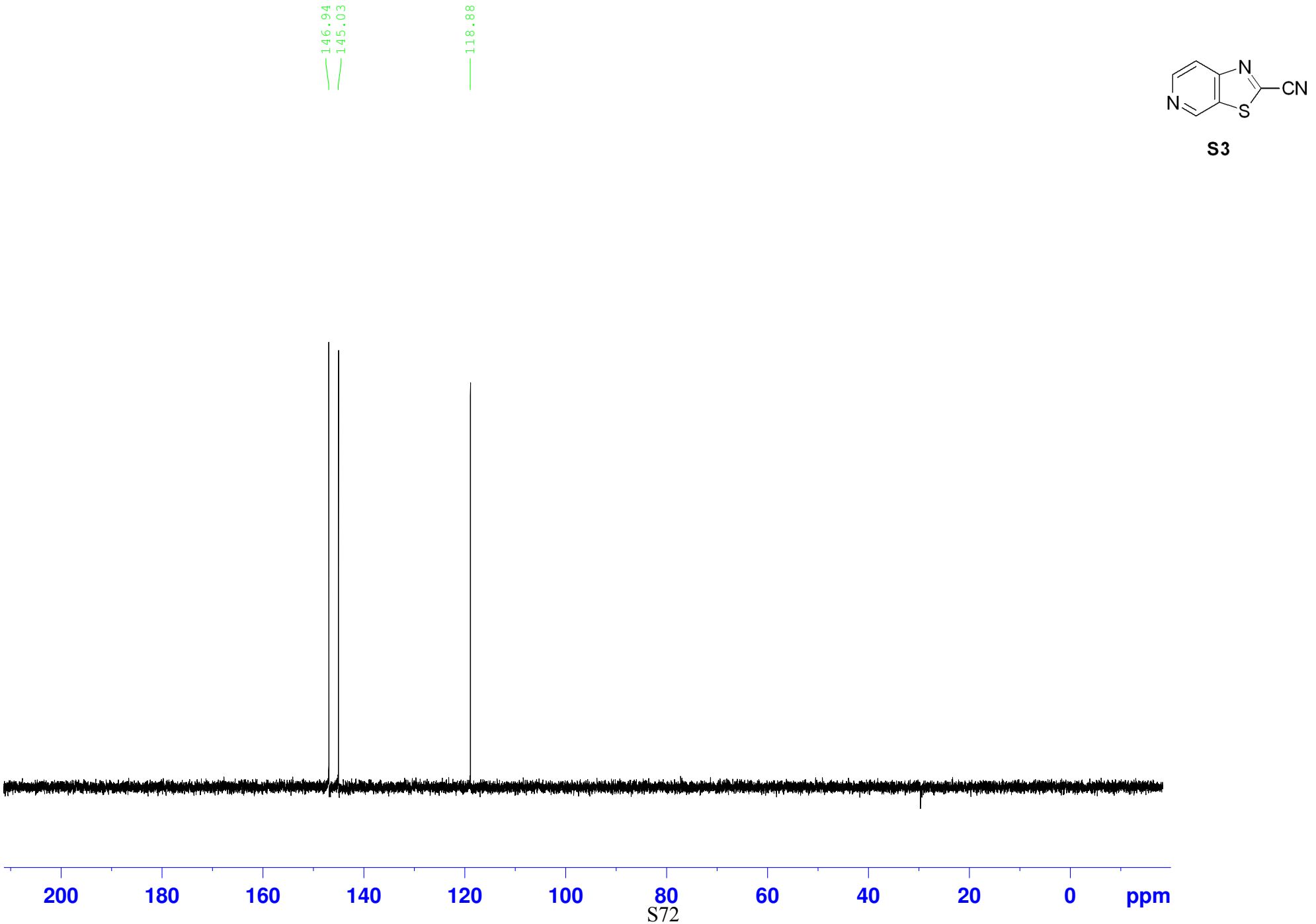
Thiazolo[5,4-c]pyridine-2-carbonitrile (S3)



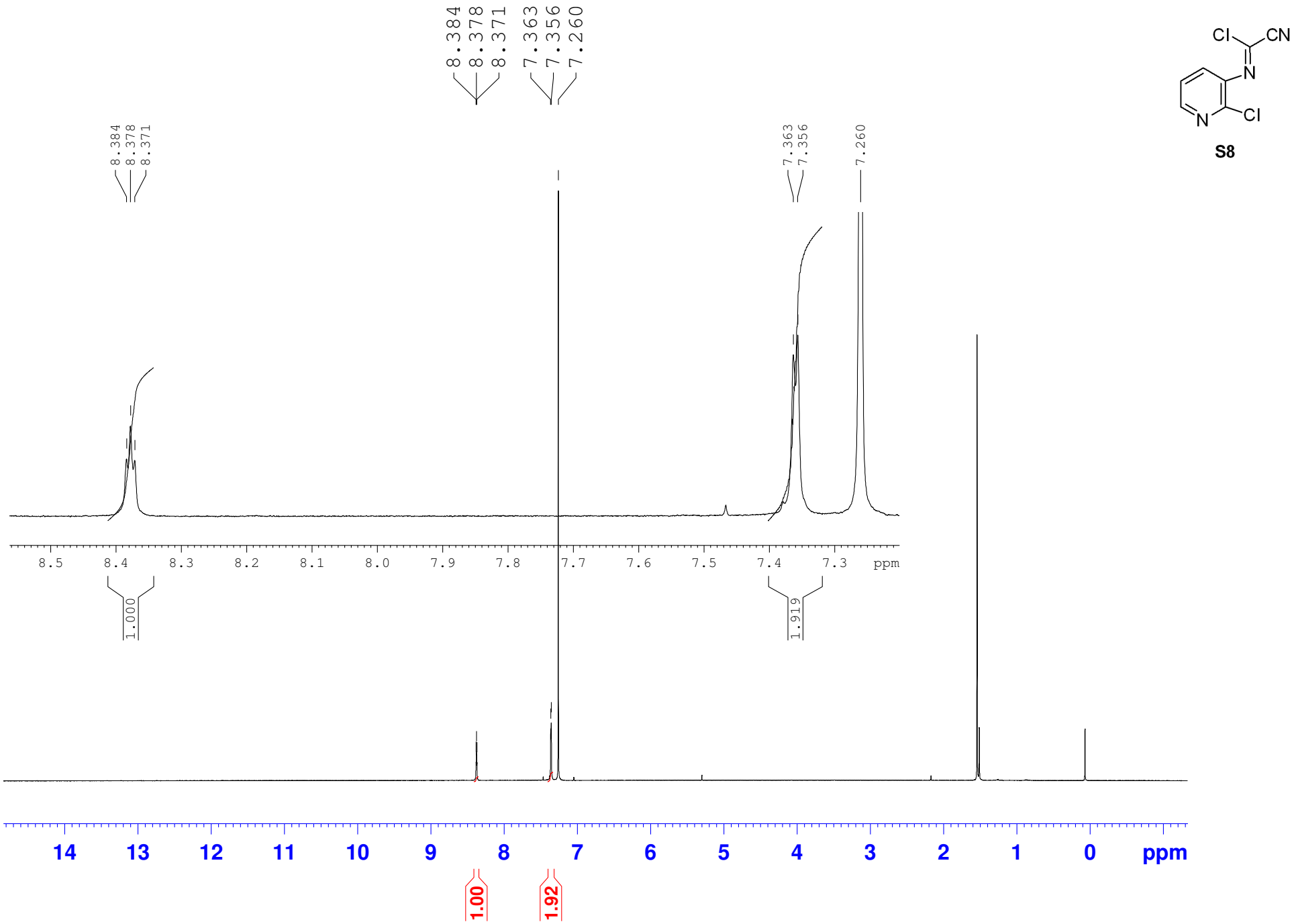
Thiazolo[5,4-c]pyridine-2-carbonitrile (S3)



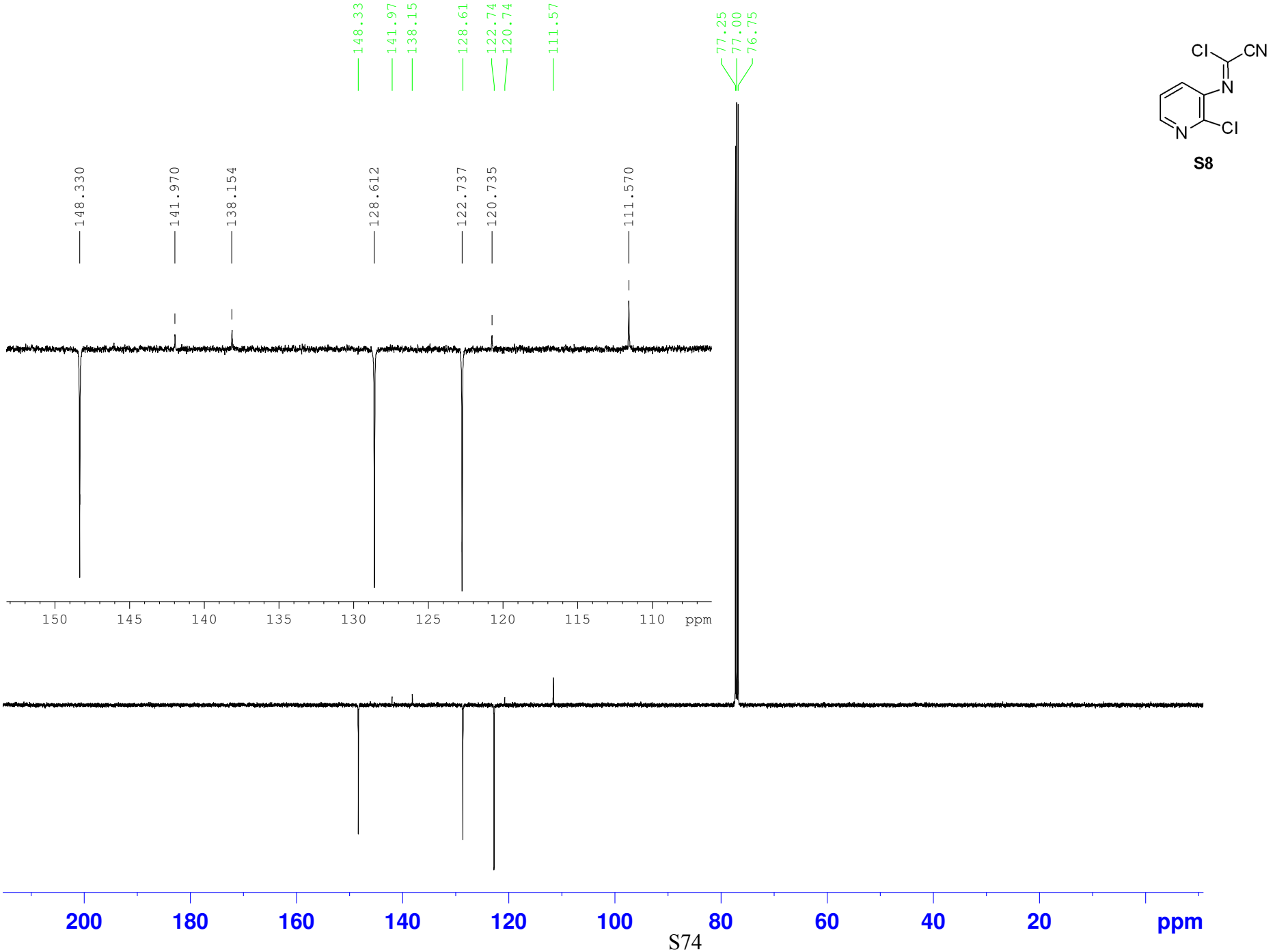
Thiazolo[5,4-c]pyridine-2-carbonitrile (S3)



(2-Chloropyridin-3-yl)carbonocyanidimidic chloride (S8)

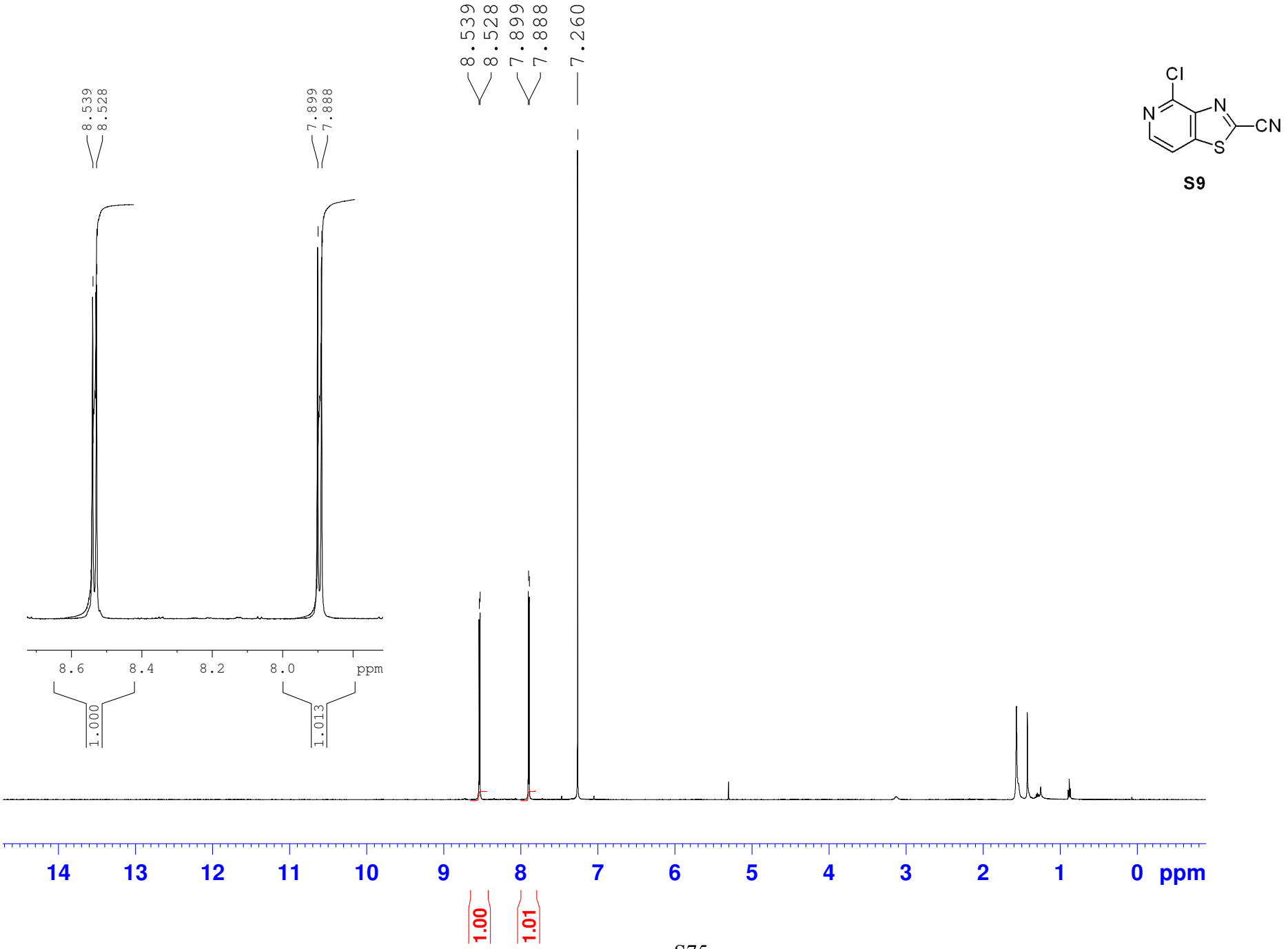


(2-Chloropyridin-3-yl)carbonocyanidimidic chloride (S8)



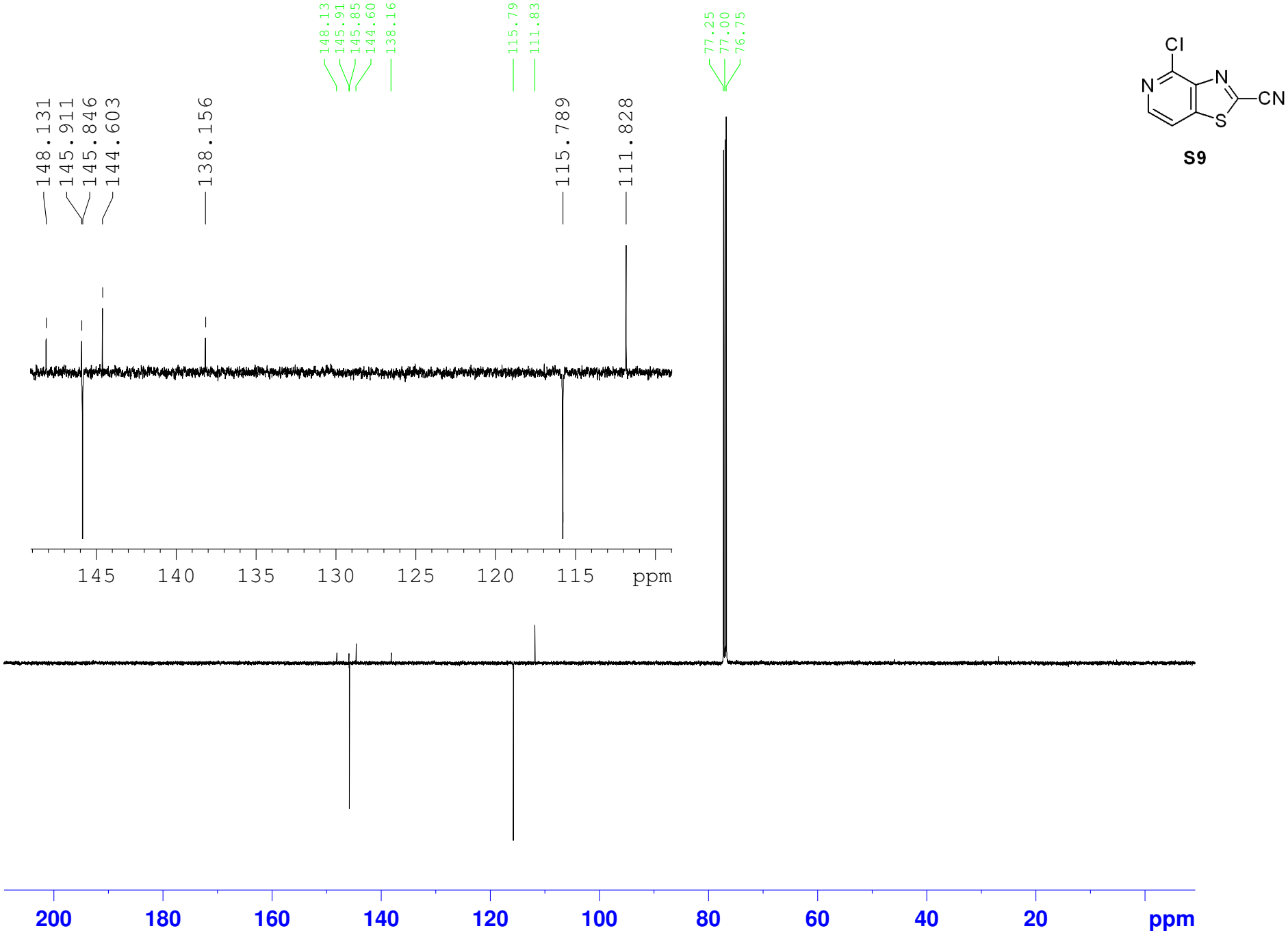
S8

4-Chlorothiazolo[4,5-c]pyridine-2-carbonitrile (S9)



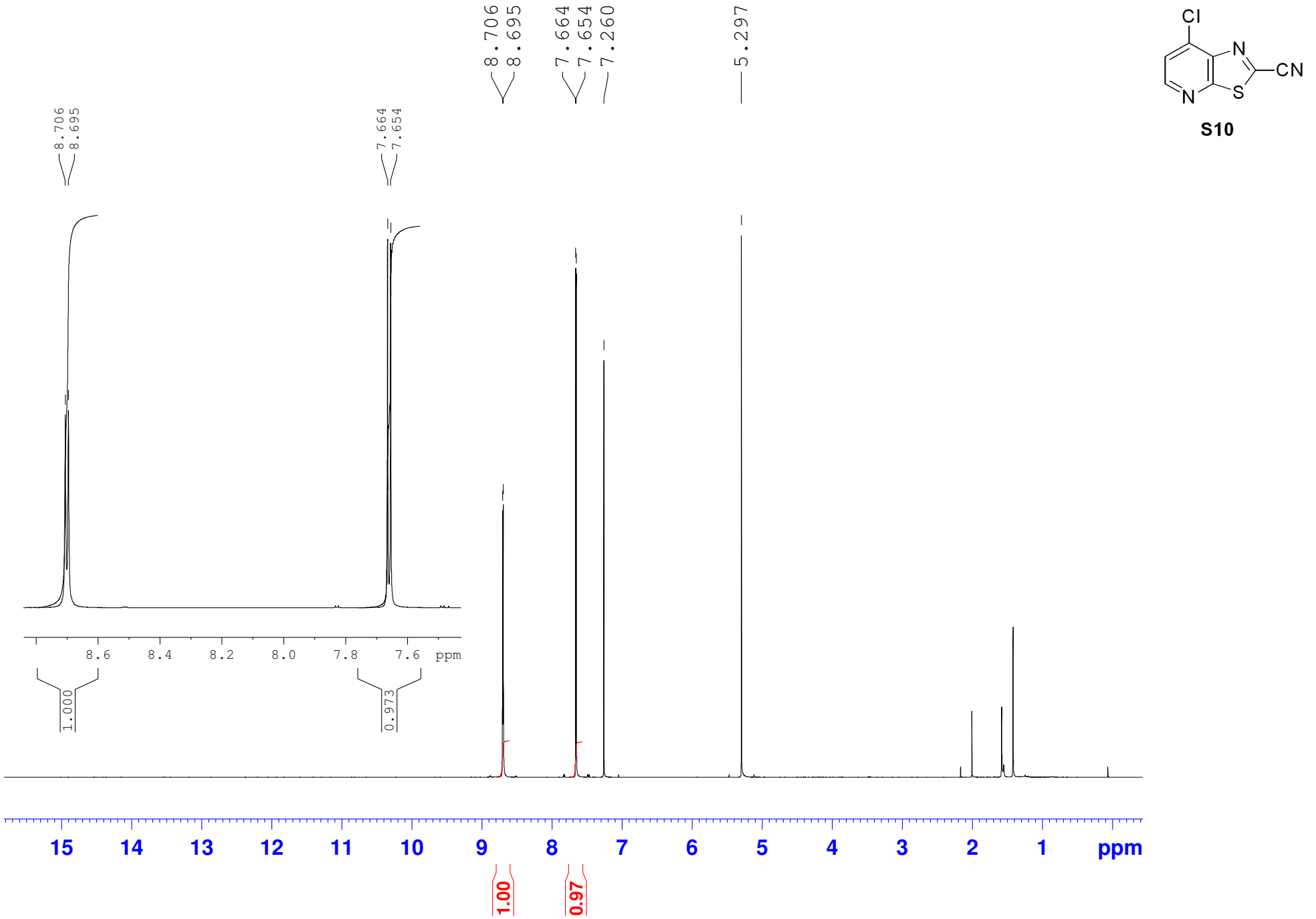
S9

4-Chlorothiazolo[4,5-c]pyridine-2-carbonitrile (S9)

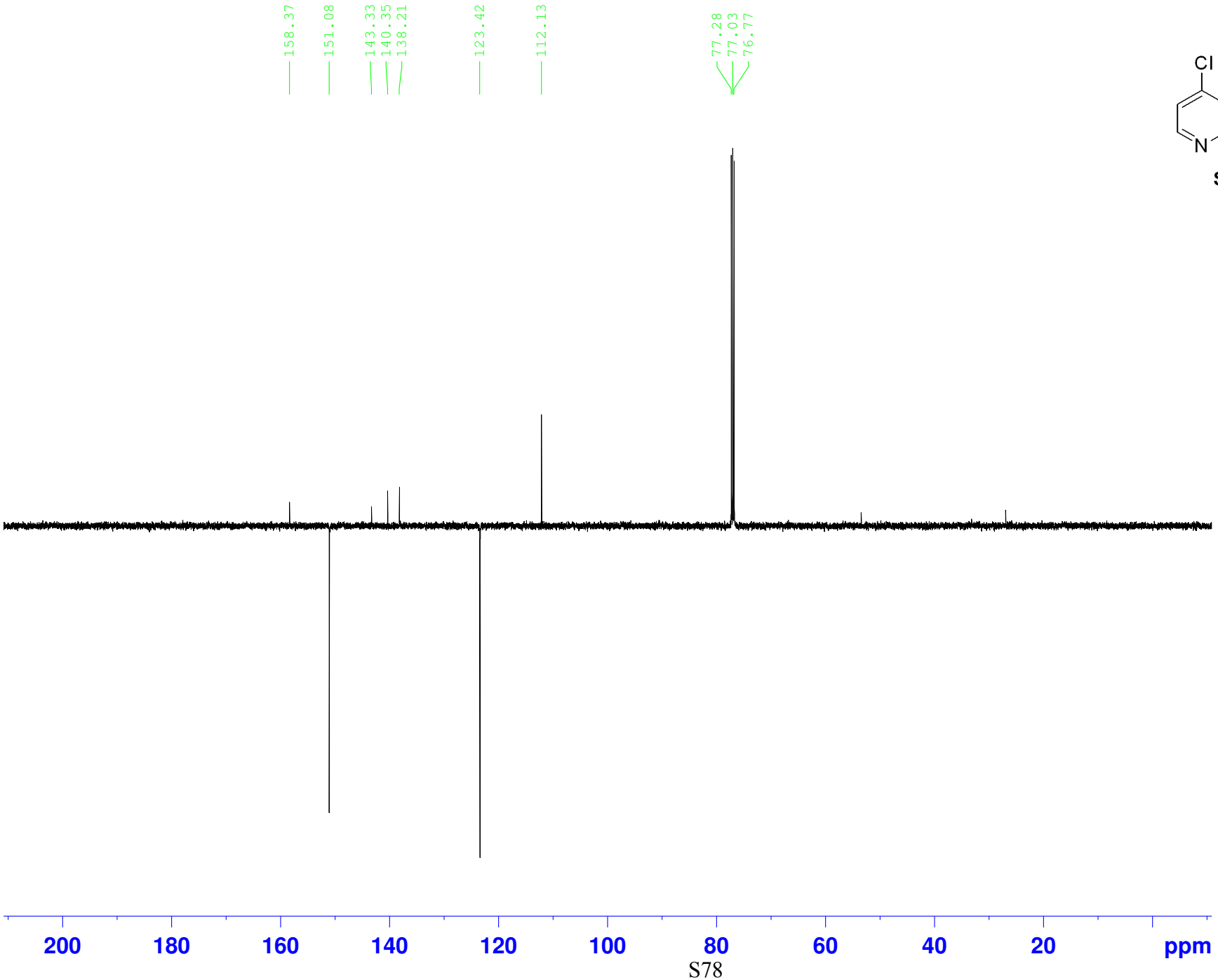


S9

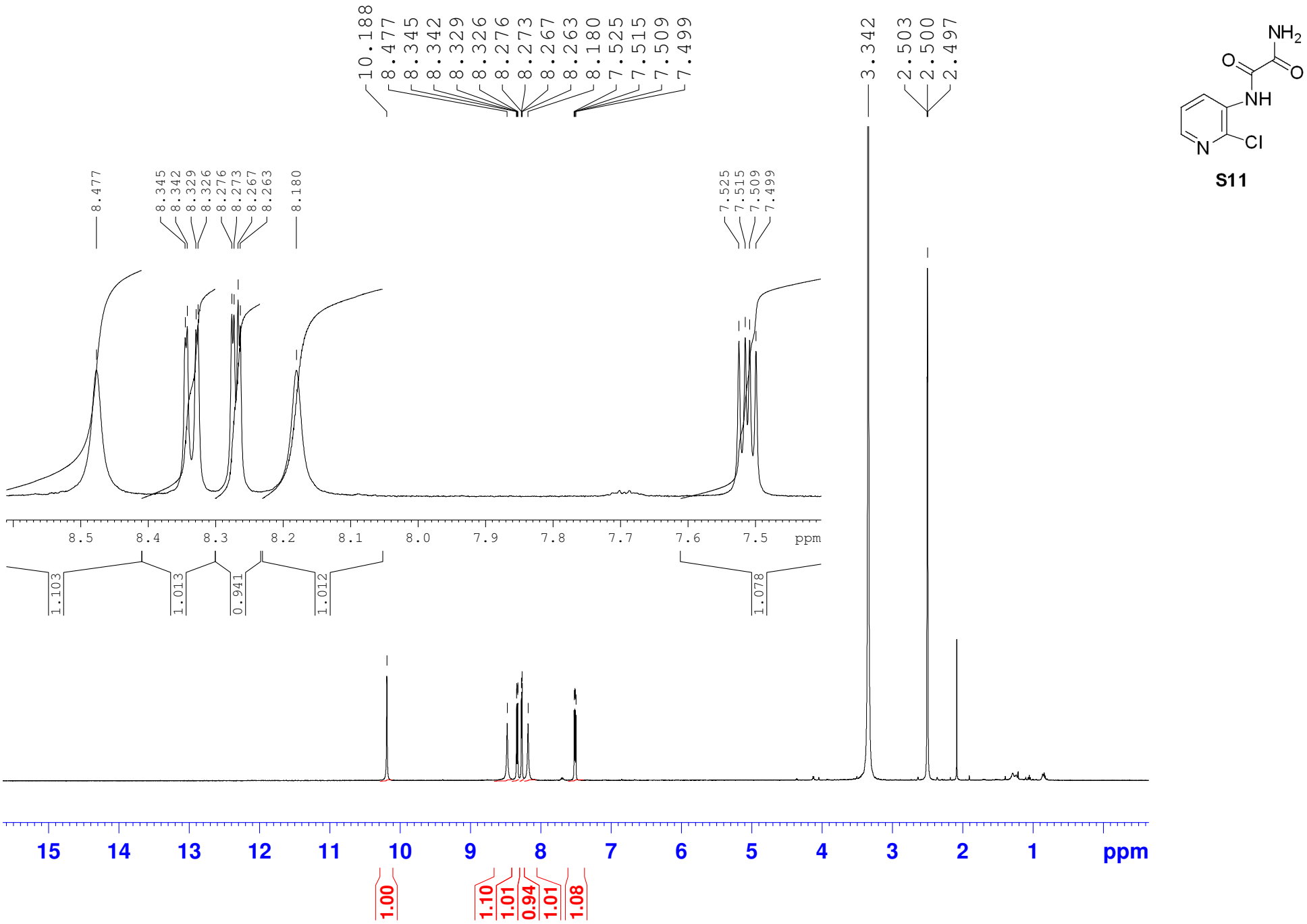
7-Chlorothiazolo[5,4-b]pyridine-2-carbonitrile (S10)



7-Chlorothiazolo[5,4-b]pyridine-2-carbonitrile (S10)



N'-(2-Chloropyridin-3-yl)oxalamide (S11)



N'-(2-Chloropyridin-3-yl)oxalamide (S11)