Supporting Information

The Reaction of DABCO with 4-Chloro-5*H*-1,2,3-dithiazoles:

Synthesis and Chemistry of 4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazoles

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S1. Optimization Study

S1.1. Reaction of N-*(4-chloro-5*H-*1,2,3-dithiazol-5-ylidene)aniline (**2aa**) with DABCO to give* N-*{4-[*N-*(2-chloroethyl)piperazin-1-yl]-5*H-*1,2,3-dithiazol-5-ylidene}aniline (**13aa**)*

For the optimization of the reaction, the simplest *N*-aryl-1,2,3-dithiazolimine, *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)aniline (**2aa**) was chosen. The reaction was optimized with respect to the reaction solvent, reagent concentrations, reaction time and temperature. Initial studies showed that in polar solvents (DCM, THF, 1,4-dioxane or MeCN) the dithiazolimine **2aa** reacted with DABCO even at *ca.* 20 °C to give S_8 and multiple unidentified colorless products while no formation of the desired product was observed. In less polar solvents (*c*-hexane, PhMe, xylene or PhCl) predominately unreacted starting material was observed at *ca.* 20 °C but on heating these reactions at reflux the formation of the desired product, *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**), was observed (by TLC). The reactions performed in PhCl at 131 °C gave the cleanest and fasted reactions. Nevertheless, even in hot PhCl three side products were also formed. Based on spectroscopic data these side products were identified as: *N*-{4-[*N*-(2-thiocyanatoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16ah**), *N*-(2-chloroethyl)-*N*-phenylpiperazine-1-carbimidoyl cyanide (**17a**) and *N*-(2-{*N*-[5-(phenylimino)-5*H*-1,2,3-dithiazol-4-yl]piperazin-1-yl}ethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride (**18**).

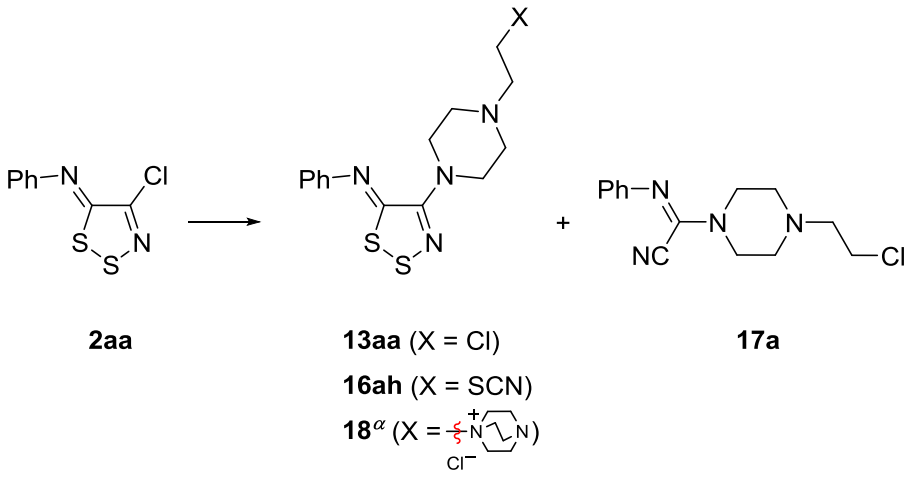
The concentration of the reaction mixtrure was critical: irrespective of the equivalents of DABCO used, when the concentration of the dithiazolimine **2aa** was high (0.2 mmol in 2 mL PhCl) the desired product **13aa** was obtained in moderate 53-63% yields (Table S1, entries 1-3). In these reactions the carbimidoyl cyanide **17a** was also formed in significant quantities (10-16%) together with brown intractable polar materials (baseline on TLC). By diluting the reaction

(0.2 mmol of **2aa** in 4, 8 and 12 mL of PhCl) the yield of the desired product **13aa** increased (65-79%), reaching a plato in 8 mL of PhCl. Under these conditions the formation of the side products **16ah** and **17a** was minimized and the reactions were less complex. Under these "dilute" conditions it was also necessary to increase the quantity of DABCO to achieve a good reaction rate and limit side reactions. With less than 2 equivalents of DABCO the reactions needed prolonged heating (>8 h) and led to lower product yields (65-70%) (Table S1, entries 4 & 7). The best yields were obtained with 2 or 3 equiv of DABCO (79-81%) but even in these cases 3-5% starting material remained unreacted (Table S1, entries 9 & 11). Extending the reaction time to consume all the starting material had a detrimental effect on product yield without complete consumption of the starting material (Table S1, entry 10). As such, we selected as our optimized reaction conditions the use of DABCO (2 equiv) in PhCl (8 mL) heated at *ca.* 131 °C for 4 h (Table S1, entry 9).

The optimized reaction conditions from the reaction of DABCO (2 equiv) with dithiazolimine **2aa** (Table S1, entry 9) also worked well with 4-chloro-5*H*-1,2,3-dithiazol-5-one (**2b**) and 4-chloro-5*H*-1,2,3-dithiazole-5-thione (**2c**) to give the analogous 2-chloroethylpiperazinyl products **13b** and **13c** in high yields, 85% and 76%, respectively. Nevertheless, these reactions were also partially re-optimized and, interestingly, alternative reaction conditions were identified that gave comparable product yields. These were: for 4-chloro-5*H*-1,2,3-dithiazol-5-one (**2b**) the use of PhCl (6 mL) and DABCO (1.2 equiv) for 1.25 h which gave the product **13b** in 85% yield and for the 4-chloro-5*H*-1,2,3-dithiazole-5-thione (**2c**) the use of PhCl (8 mL) and DABCO (1.5 equiv) for 4 h which gave the product **13c** in 71% yield. In the latter case only a subtle decrease on product yield was observed in comparison with the best conditions from the dithiazolimine

2aa study. As demonstrated for those two dithiazoles the reaction was scalable (up to 1.6 mmol) without significant loss on product yield.

Table S1. The Reaction of *N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)aniline (2aa) (0.2 mmol) with DABCO (x equiv) in PhCl (x mL) at *ca.* 131 °C



2aa **13aa** (X = Cl) **17a**

16ah (X = SCN)

18[α] (X =)

entry	PhCl (mL)	DABCO (equiv)	time (h)	yields (%)			
				2aa[b]	**13aa**	**16ah**	**17a**
1	2	1	24	traces	53	4	10
2	2	1.2	3	traces	63	8	16
3	2	2	1.5	traces	54	3	16
4	4	1.2	6	4	65	5	8
5	4	2	2.2	4	74	2	4
6	4	2	4	traces	69	6	5
7	8	1.2	23	5	65	5	5
8	8	1.5	8	traces	70	2	7
9	8	2	4	5	79	2	2
10	8	2	7	2	71	4	5
11	8	3	2.2	3	81	2	3
12	12	2	7	3	79	3	3

[a] Product **18** in most cases was not isolated sufficiently pure to calculate a yield. [b] Recovered starting material.

S2. Structure Elucidation of Compounds 13aa, 16ah, 17a and 18

S2.1. N-*{4-[*N-*(2-Chloroethyl)piperazin-1-yl]-5*H-*1,2,3-dithiazol-5-ylidene}aniline* ***(13aa)***. Obtained as yellow plates, mp 73-74 °C (from *n*-hexane/*t*-BuOMe at *ca.* -20 °C). Mass spectrometry gave a parent ion of *m/z* 343 with an isotope pattern typical for the presence of one chlorine atom. Combined with elemental analysis data this supported a molecular formula of $C_{14}H_{17}ClN_4S_2$. UV/vis data showed a lowest energy absorption at 379 nm [λ_{max}(EtOH)/nm 379 (log ε 3.83); λ_{max}(DCM)/nm 382 (log ε 3.90)] which was similar to that of the starting *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)aniline (**2aa**) [λ_{max}(EtOH)/nm 373 (log ε 3.77)][1] suggesting the presence of the dithiazole ring. ^{1}H NMR spectroscopy revealed the presence of three aromatic sp^2 CH resonances integrating for 5 H with a splitting pattern typical for a mono-substituted phenyl. In addition, four aliphatic sp^3 CH_2 resonances, were observed, two of which were triplets, with a *J* coupling of 7.0 Hz, each integrating for 2 H [δ_H 3.62 (2H, t, *J* 7.0, C*H*$_2$) & 2.79 (2H, t, *J* 7.0, C*H*$_2$)] and two were doublet of doublets, with *J* couplings of 5.0 and 5.0 Hz, each integrating for 4 H [δ_H 3.79 (4H, dd, *J* 5.0, 5.0, C*H*$_2$) & 2.67 (4H, dd, *J* 5.0, 5.0, C*H*$_2$)]; these data were characteristic for a *N*-[(2-substituted)ethyl]piperazine group.[2] In addition to the three sp^2 CH and the four aliphatic sp^3 CH_2 resonances, ^{13}C NMR spectroscopy showed the presence of three C (s) resonances in the range 153-161 ppm [δ_C 160.6 (s), 158.3 (s), 152.5 (s)]. These are in the range typical for the C (s) resonances of 1,2,3-dithiazolimines.[1] Based on these spectroscopic data the compound was tentatively identified as *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**).

*S2.2. N-{4-[*N-*(2-Thiocyanatoethyl)piperazin-1-yl]-5*H-*1,2,3-dithiazol-5-ylidene}aniline* ***(16ah)***. Obtained as yellow plates, mp 86-87 °C (from *n*-hexane/*t*-BuOMe at *ca.* -20 °C). Mass

spectrometry gave a parent ion of *m/z* 364 which in combination with microanalysis supported a molecular formula of $C_{15}H_{17}N_5S_3$. UV/vis data showed a lowest energy absorption at 382 nm [λ_{max}(DCM)/nm 382 (3.74)] which was identical with *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**). ^{1}H NMR spectroscopy revealed the presence of three aromatic sp^2 CH resonances integrating for 5 H with a splitting pattern typical for a mono-substituted phenyl, and also four aliphatic sp^3 CH_2 resonances two of which were triplets, with *J* coupling of 7.0 Hz, each integrating for 2 H [δ_H 3.22 (2H, t, *J* 6.5, C*H*$_2$) & 2.80 (2H, t, *J* 6.5, C*H*$_2$)] and two were doublet of doublets, with *J* couplings of 4.8-5.0 Hz, each integrating for 4 H [δ_H 3.78 (4H, dd, *J* 4.8, 4.8, C*H*$_2$) & 2.64 (4H, dd, *J* 5.0, 5.0, *CH*$_2$)]. These data were very similar with *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**); the only difference observed was the upfield shift of one of the sp^3 CH_2 resonances (3.22 ppm for **16ah** *vs* 3.62 ppm for **13aa**), which for dithiazolimine **13aa** must correspond to the CH_2 next to the chlorine atom. The upfield shift, tentatively indicated the substitution of the chlorine atom with a less electron withdrawing substituent. In addition to these resonances, ^{13}C NMR spectroscopy showed the presence of four C (s) resonances [δ_C 160.5 (s), 158.2 (s), 152.5 (s), 113.0 (s)], three of which were identical with **13aa**, further supporting the presence of the dithiazole ring, while the fourth fitted for X-*C*≡N (δ_C 113 ppm). FTIR spectroscopy gave a stretching frequency characteristic for thiocyanates [ν(C≡N) 2145 cm^{-1}]. Based on these spectroscopic data the compound was tentatively identified as *N*-{4-[*N*-(2-thiocyanatoethyl)-piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16ah**). This compound was also independently synthesized by reaction of *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**) with KSCN (see main manuscript Section 2.3.1.).

S2.3. N-*(2-Chloroethyl)*-N-*phenylpiperazine-1-carbimidoyl cyanide (**17a**)*. Obtained as colorless plates, mp 45-46.5 °C (from *n*-hexane/Et_2O at *ca.* -40 °C). Mass spectrometry gave a parent ion of *m/z* 277 with an isotope pattern typical for the presence of one chlorine. In combination with elemental analysis data, this supported a molecular formula of $C_{14}H_{17}ClN_4$. UV/vis data showed a lowest energy absorption at 311 nm [λ_{max}(DCM)/nm 311 (log ε 3.79)] which suggested the presence of a conjugation but owing to the absence of any significant color we tentatively dismissed the presence of a dithiazole ring. ^{1}H NMR spectroscopy showed three aromatic sp^2 CH resonances integrating for 5 H typical for the presence of a mono-substituted phenyl, and also four aliphatic sp^3 CH_2 resonances [δ_H 3.73 (4H, br *s*, CH_2), 3.63 (2H, t, *J* 6.5, CH_2), 2.83 (2H, t, *J* 6.0, CH_2), 2.65 (4H, br s, CH_2)] for which integrals, chemical shifts and splitting patterns were very similar with *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**), suggesting that both the phenylimine and the *N*-[(2-chloro)ethyl]piperazinyl moieties were intact. In addition to these resonances, ^{13}C NMR spectroscopy revealed the presence of three C (s) resonances which differed significantly from those of dithiazolimine **13aa** further supporting the absence of the dithiazole ring. In addition, one of the C (s) resonances fitted for C≡N (δ_C 108.2 ppm). The presence of the C≡N was further supported by FTIR spectroscopy [ν(C≡N) 2228 cm^{-1}]. Based on these spectroscopic data the compound was tentatively identified as *N*-(2-chloroethyl)-*N*-phenylpiperazine-1-carbimidoyl cyanide (**17a**). This compound was also independently synthesized by reaction of *N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)aniline (**2aa**) with *N*-[(2-chloro)ethyl]piperazine **21a** (see main manuscript Section 2.2.).

S2.4. N-*(2-{*N-*[5-(Phenylimino)-5*H-*1,2,3-dithiazol-4-yl]piperazin-1-yl}ethyl)-1,4-diazabicyclo[2.2.2]-octan-1-ium chloride (**18**).* Obtained as yellow glassy plates, decomp. (DSC) onset: 184.4 °C, peak max: 194.2 °C (precipitated from DCM with *n*-pentane/Et_2O). MALDI-TOF analysis on a ground steel plate with 2,5-dihydroxybenzoic acid (DHB) as matrix gave a parent ion of *m/z* 417 which on MS/MS showed the loss of *m/z* 112 equivalent to one molecule of DABCO. When the same sample was analyzed on a PAC II 384/96 HCCA plate a parent ion of *m/z* 453 (5%) with a chlorine isotope pattern was observed, together with fragments that corresponded to the loss of a chlorine atom [*m/z* 417 (60%), M^+-Cl] and subsequent loss of a DABCO molecule [*m/z* 305 (100%), M^+-Cl-DABCO]. Furthermore, on the spectrum, peaks corresponding to an *N*-ethylpiperazine fragment (*m/z* 175) and a DABCO molecule (*m/z* 112) were found. UV/vis data showed a lowest energy absorption at 380 nm [λ_{max}(DCM)/nm 380 (log ε 3.75)] similar to *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**) indicating the presence of the dithiazole ring. ^{1}H NMR spectroscopy showed the presence of three aromatic sp^2 CH resonances, supporting the presence of a mono-substituted phenyl, and six aliphatic sp^3 CH_2 resonances. Two of the sp^3 CH_2 resonances were doublet of doublets, with *J* couplings of 7.2 Hz, each integrated for 6 H and with chemical shifts in the range of 3-4 ppm [δ_H 3.83 (6H, dd, *J* 7.2, 7.2, CH_2) & 3.19 (6H, dd, *J* 7.2, 7.2, CH_2)]; these data were typical for the presence of a quaternized DABCO moiety.[3] The remaining four sp^3 CH_2 resonances [δ_H 3.90 (2H, dd, *J* 5.1, 5.1, CH_2), 3.71 (4H, br s, CH_2), 2.89 (2H, dd, *J* 4.8, 4.8, CH_2), 2.68 (4H, dd, *J* 4.5, 4.5, CH_2)] were very similar with those of *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**) except from the downfield movement for one of the sp^3 CH_2 resonances (3.90 ppm for **18** *vs* 3.62 for **13aa**). As mentioned above, this signal for dithiazolimine **13aa** must correspond to the CH_2 next to the chlorine atom, and the downfield

shift, tentatively, indicates the substitution of the chlorine atom with a more electron withdrawing substituent, this probably been the quaternized DABCO. In addition to these resonances, ^{13}C NMR spectroscopy showed the presence of three C (s) resonances [δ_C 160.4 (s), 158.1 (s), 152.4 (s)] which were identical with the dithiazolimine **13aa**. Furthermore, the compound was highly hygroscopic and water soluble which further supported the presence of a quaternized moiety. Based on these spectroscopic data and observations, the compound was tentatively identified as *N*-(2-{*N*-[5-(phenylimino)-5*H*-1,2,3-dithiazol-4-yl]piperazin-1-yl}ethyl)-1,4-diazabicyclo-[2.2.2]octan-1-ium chloride (**18**). This compound was also obtained by the reaction of clean and recrystallized *N*-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**) with DABCO in PhCl (see main manuscript Section 2.2.).

S2.5. Section References

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S3. N···S Interaction – Computational Study

S3.1. Computational Methods

The geometry of molecules **2aa, 2au, 2as** and **2aq** was optimized at the DFT RB3LYP/6-31g+(d,p) level of theory. For the Mulliken population analyses,[1] single-point calculations were performed on the optimized structures of **2aa, 2au, 2as** and **2aq** by employing the MP2/6-31g(d) level of theory with additional keyword "Density = MP2". All the computations were performed using the Gaussian 03[2] or the Gaussian 09[3] suite of programs.

S3.2. Discussion

The reactivity of the *N*-azin-2-yl- (**2as** and **2aq**) and *N*-azol-2-yl (**2au**) substituted dithiazolimines was intriguing as these dithiazoles were more resistant to nucleophilic attack by DABCO than the corresponding *N*-phenyl dithiazolimine **2aa**. The relative order of reactivity decreased accordingly: phenyl > thiazol-2-yl > pyrazin-2-yl > pyrid-2-yl. A common feature in these *N*-hetaryl analogues was the *ortho* nitrogen atom to the dithiazole ring that can participate in a N···S interaction with the dithiazole S-1 atom. For comparison, the reactivity of the pyrid-3-yl analogue **2ar**, which is isomeric to the pyrid-2-yl **2aq** but has no possible intramolecular N···S interaction, was comparable with the *N*-phenyl dithiazolimine **2aa**.

Non-bonded X···E-Y interactions (where X = N, O or S and E = S, Se or Te) attracted considerable interest,[4] and their nature as well as the factors influencing their strength have been studied experimentally,[5] and computationally.[6]

From computational studies has been suggested that two major factors influence these X···E-Y interactions: (a) an electrostatic interaction and b) a molecular orbital interaction which involves electron donation from the lone pair heteroatom X (n_X orbital) to the antibonding orbital of the E-Y bond (in our case the S-S bond) ($\sigma^*_{E\text{-}Y}$ orbital).

The major characteristics of X···E-Y interactions are that: (a) the molecules adapt a planar conformation where the X···E-Y atoms essentially align (150-180°); (b) the distance of X···E is longer than a typical covalent X-E bond but smaller than the sum of the van der Waals radii of the two atoms; and (c) the E-Y bond is lengthened. The strength of the interaction depends both on the electronegativity of Y and X. More electronegative Ys and/or less electronegative Xs lead to stronger X···E interactions and *vice versa*.

To investigate the strength of the N···S interaction in dithiazoles **2a** and the effect on their reactivity, the structures of the dithiazoles **2aa, 2au, 2as** and **2aq** were optimized at the DFT RB3LYP/6-31g+(d,p) level of theory and their geometric parameters and Mulliken atomic charges, calculated at the MP2/6-31g(d) level of theory for the optimized structures, were analyzed.

As can be observed from Figure S1 and Table S3 the N···S distance decreases in the order thiazol-2-yl (2.656 Å) > pyrazin-2-yl (2.574 Å) > pyrid-2-yl (2.519 Å) with concomitant lengthening of the S-S bond, thiazol-2-yl (2.147 Å) < pyrazin-2-yl (2.154 Å) < pyrid-2-yl (2.163 Å). Compared with the *N*-phenyl dithiazolimine **2aa**, where there is no N···S interaction, the lengthening of the S-S bond in the *N*-hetaryl dithiazolimines **2au, 2as** and **2aq** is in the order of 0.15-0.3 Å. The above geometric data supported that the strength of the N···S interaction

increased in the order thiazol-2-yl < pyrazin-2-yl < pyrid-2-yl, which can be explained in terms of both steric and electronic effects. The weakened N···S interaction in the pyrazin-2-yl **2as** compared to the pyrid-2-yl analogue **2aq** can be attributed to the presence of the additional sp^2 nitrogen of the pyrazin-2-yl which makes this azine more electronegative than the pyrid-2-yl analogue leading to a weaker orbital interaction.[5a] While the thiazol-2-yl moiety is more electron rich than the pyrid-2-yl and pyrazin-2-yl moieties which could lead to stronger N···S interaction, this was not observed for steric reasons since the geometry of the five membered thiazol-2-yl ring prevented the sp^2 nitrogen atom from attaining an optimum alignment of its lone pair (n_N) with the antibonding orbital $\sigma^*_{S\text{-}S}$. This decrease on the strength of the X···E interaction imposed by the exchange of a 6-membered for a 5-membered ring was also observed on a recent study on N···Se interactions.[6e]

By comparing the experimentally observed order of reactivity with the N···S interaction strength, as measured by the N···S distance, it was evident that as the N···S interaction increased the dithiazole became less reactive towards DABCO. This can now be attributed to a decrease on the electrophilicity of the S2 atom caused by an increase of its electronic population as a result of the $n_N \rightarrow \sigma^*_{S\text{-}S}$ interaction. Furthermore, this was supported by Mulliken population analysis which showed an increase on the electronic population of S2 and a decrease in the electronic population of S1 on dithiazoles **2au**, **2as** and **2aq** in comparison with the "parent" dithiazole **2aa**.

Table S3. **Geometric Parameters of Optimized Dithiazoles at the DFT RB3LYP/6-31g+(d,p) Level of Theory and Mulliken Atomic Charges Computed at the MP2/6-31g(d) Level of Theory.**

distance (Å)	phenyl **2aa**	thiazol-2-yl **2au**	pyrazin-2-yl **2as**	pyrid-2-yl **2aq**
S-S	2.133	2.147	2.154	2.163
N···S	-	2.656	2.574	2.519
Angle (°)				
S1-C5-N6	128.17	126.14	126.58	126.33
C5-N6-C7	127.39	119.83	120.52	120.07
N6-C7-X8	124.48	126.03	120.36	118.89
Mulliken charge				
S1	0.074	0.196	0.193	0.190
S2	0.301	0.279	0.272	0.252
C4	0.078	0.087	0.081	0.083

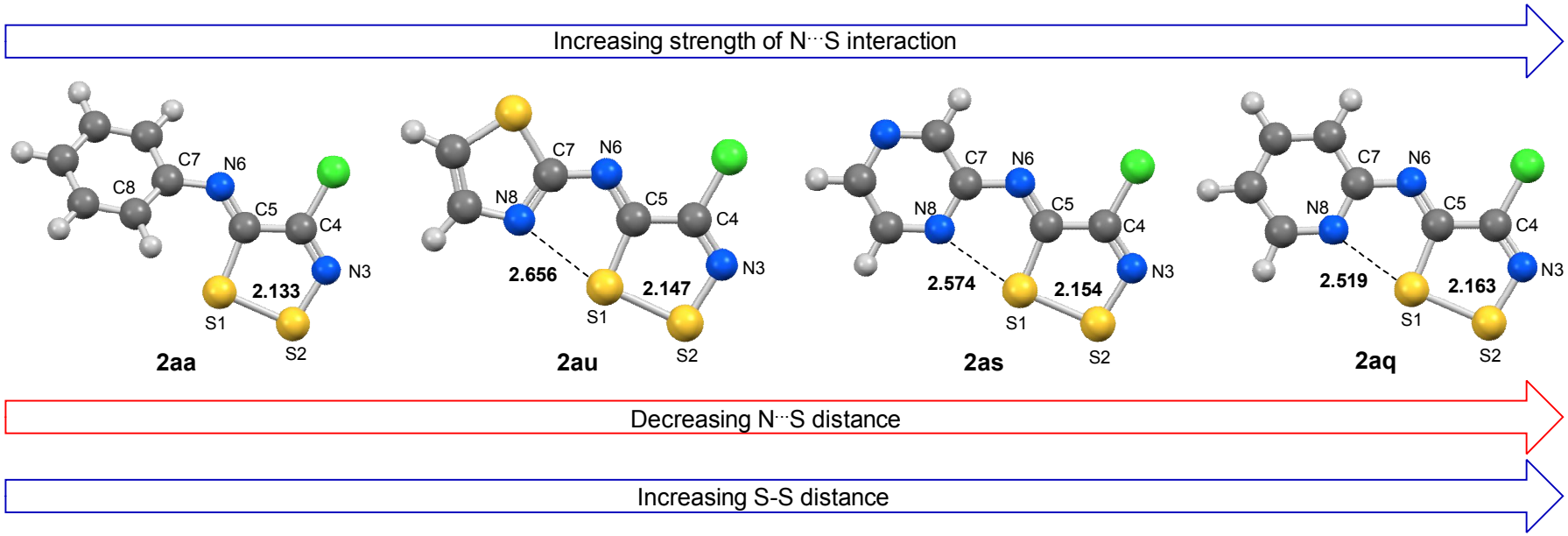

Figure S1. Optimized Structures at the DFT RB3LYP/6-31g+(d,p) Level of Theory of Dithiazoles 2aa, 2au, 2as and 2aq with Partial Atom Labeling. The *N*-Hetaryl Dithiazolimines 2au, 2as and 2aq are Planar (the Maximum Deviation from Planarity is 0.2°) in Contrast with the *N*-Phenyl Dithiazolimine 2aa Which has a Torsion Angle C5-N6-C7-C8 of 33.69°.

S3.3. Section References

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Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

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S4. Crystal Structure of 4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazole-5-thione (13c).

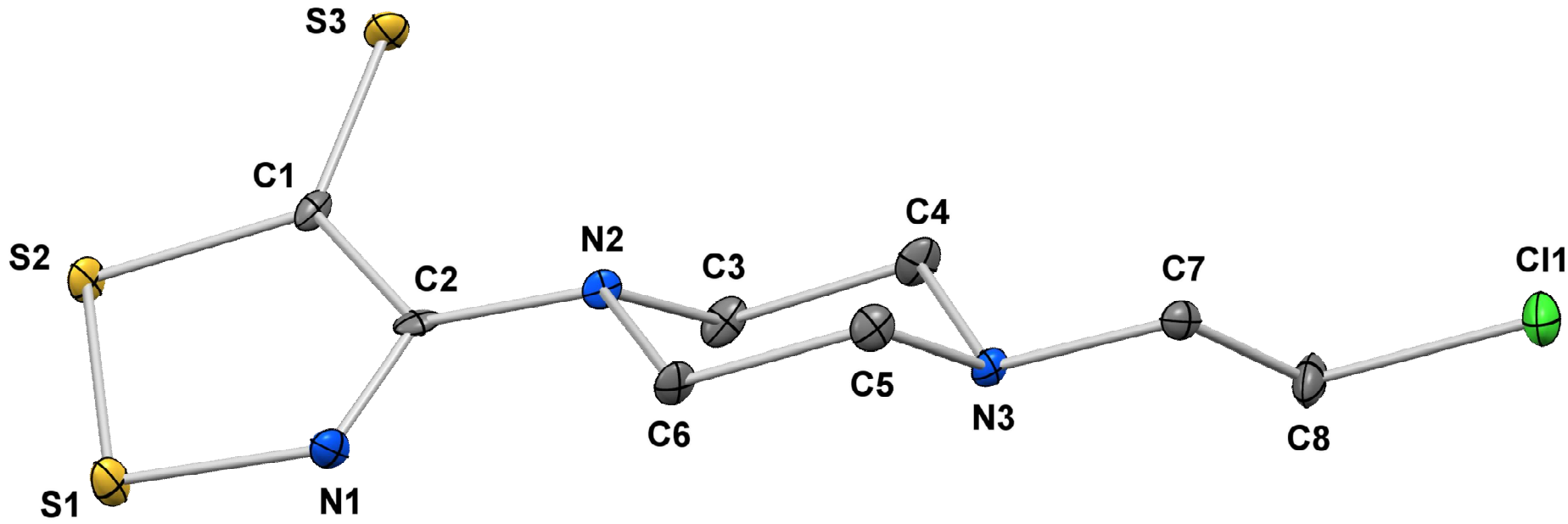
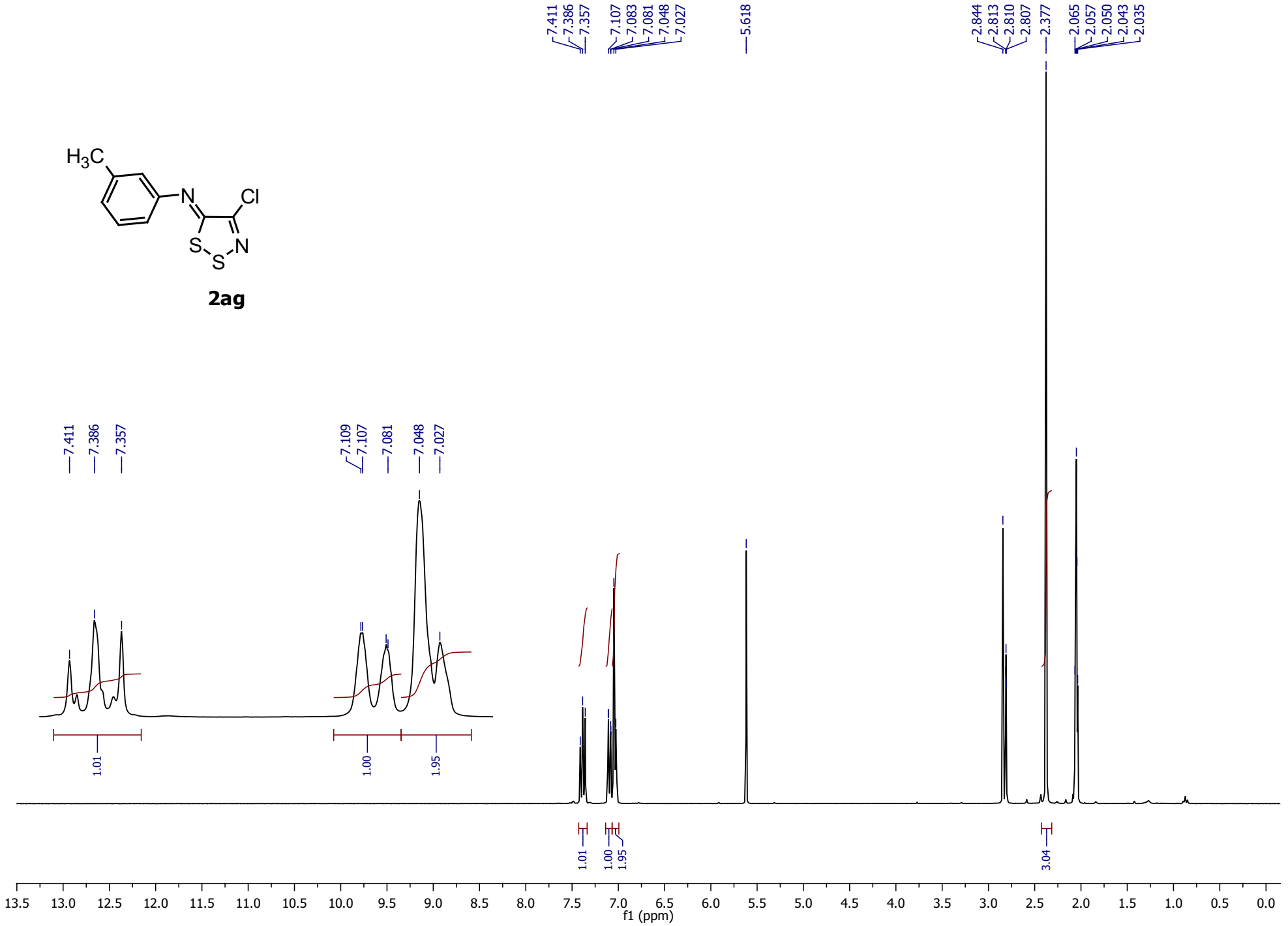


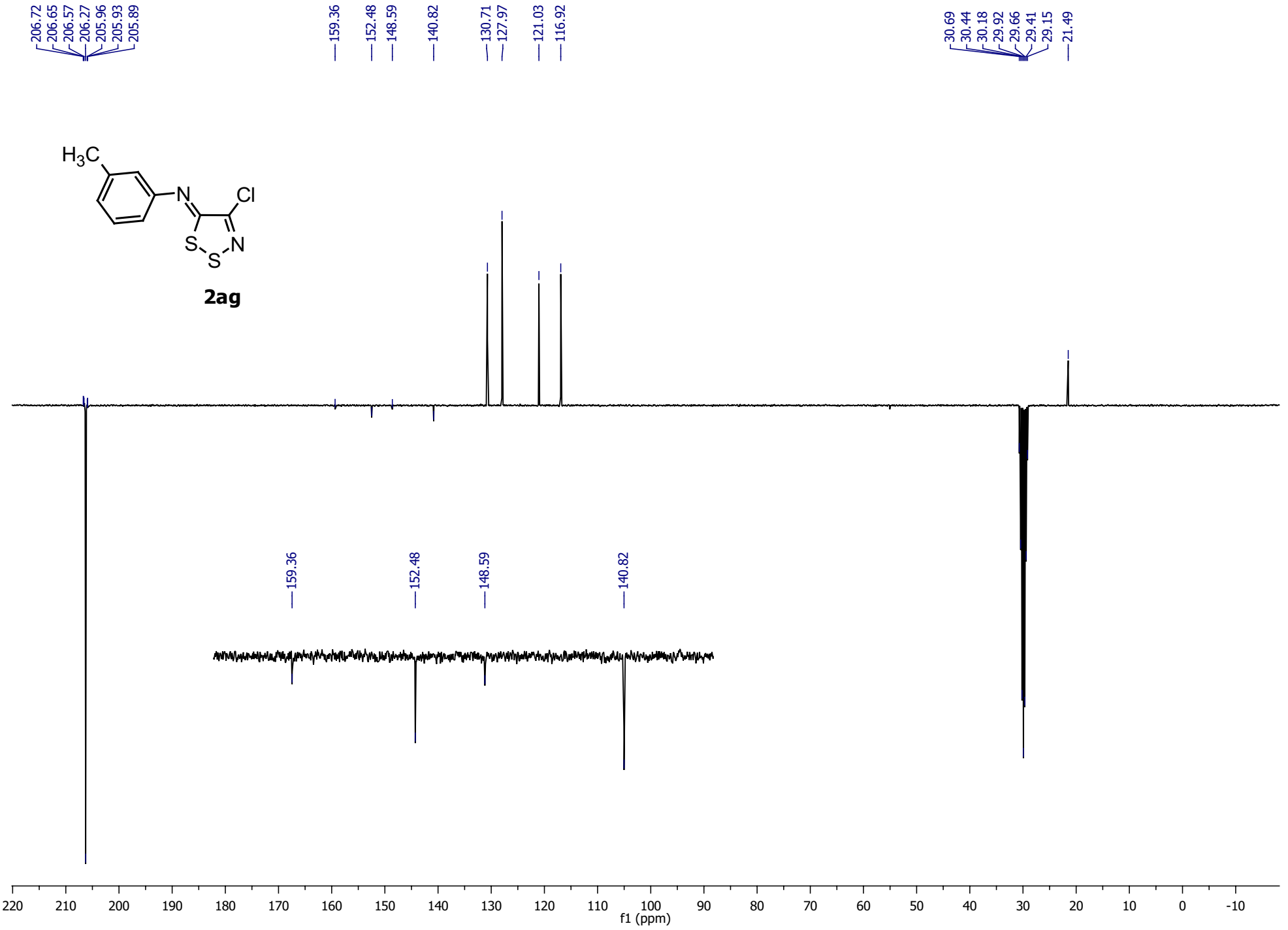
Figure S2. Ellipsoid (Probability Level of 50%) Representation of the Crystal Structure 4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazole-5-thione (13c) with Crystallographic Atom Labeling. The H Atoms were Omitted for Clarity.

S5. ^{1}H and ^{13}C NMR Spectra

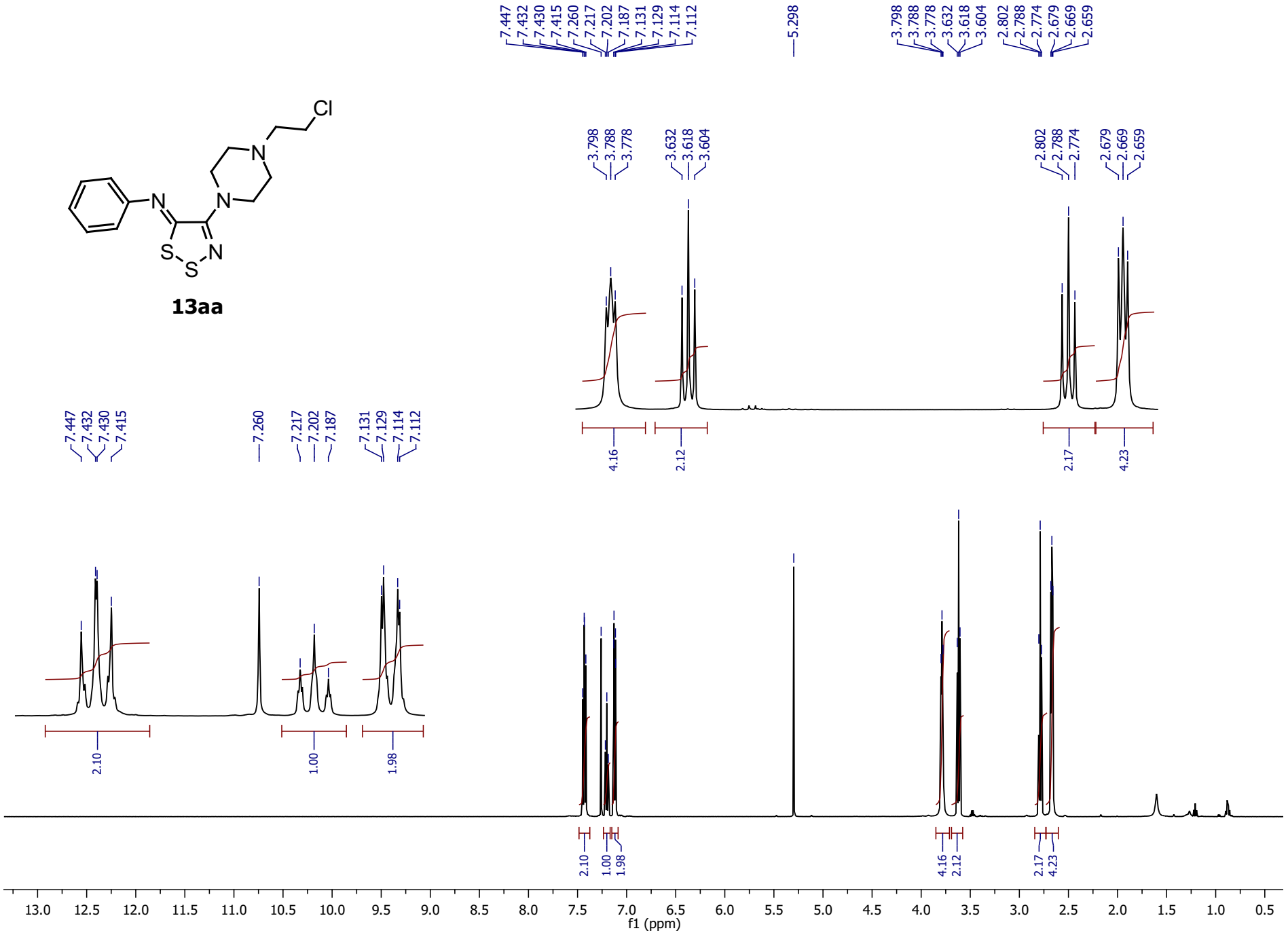
N-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-methylaniline (**2ag**) (^{1}H-NMR, 300 MHz, acetone-d_6)



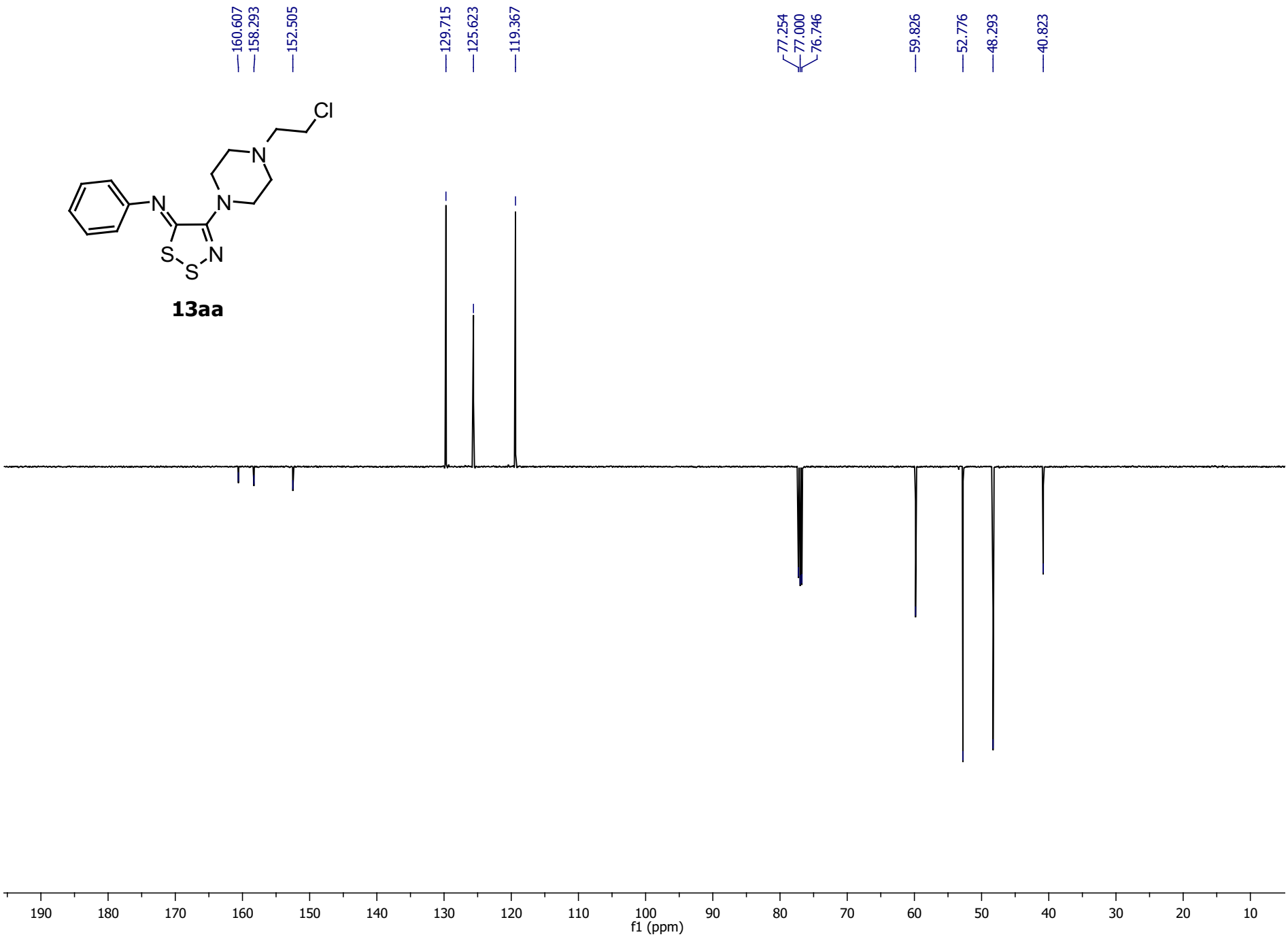
N-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-methylaniline (**2ag**) (13C-NMR, 75 MHz, acetone-d_6)



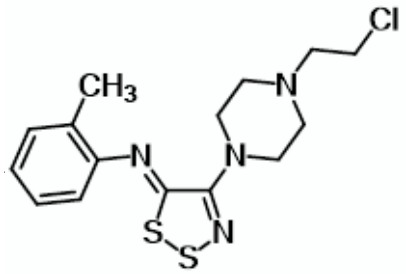
N-{4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



N-{4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13aa**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

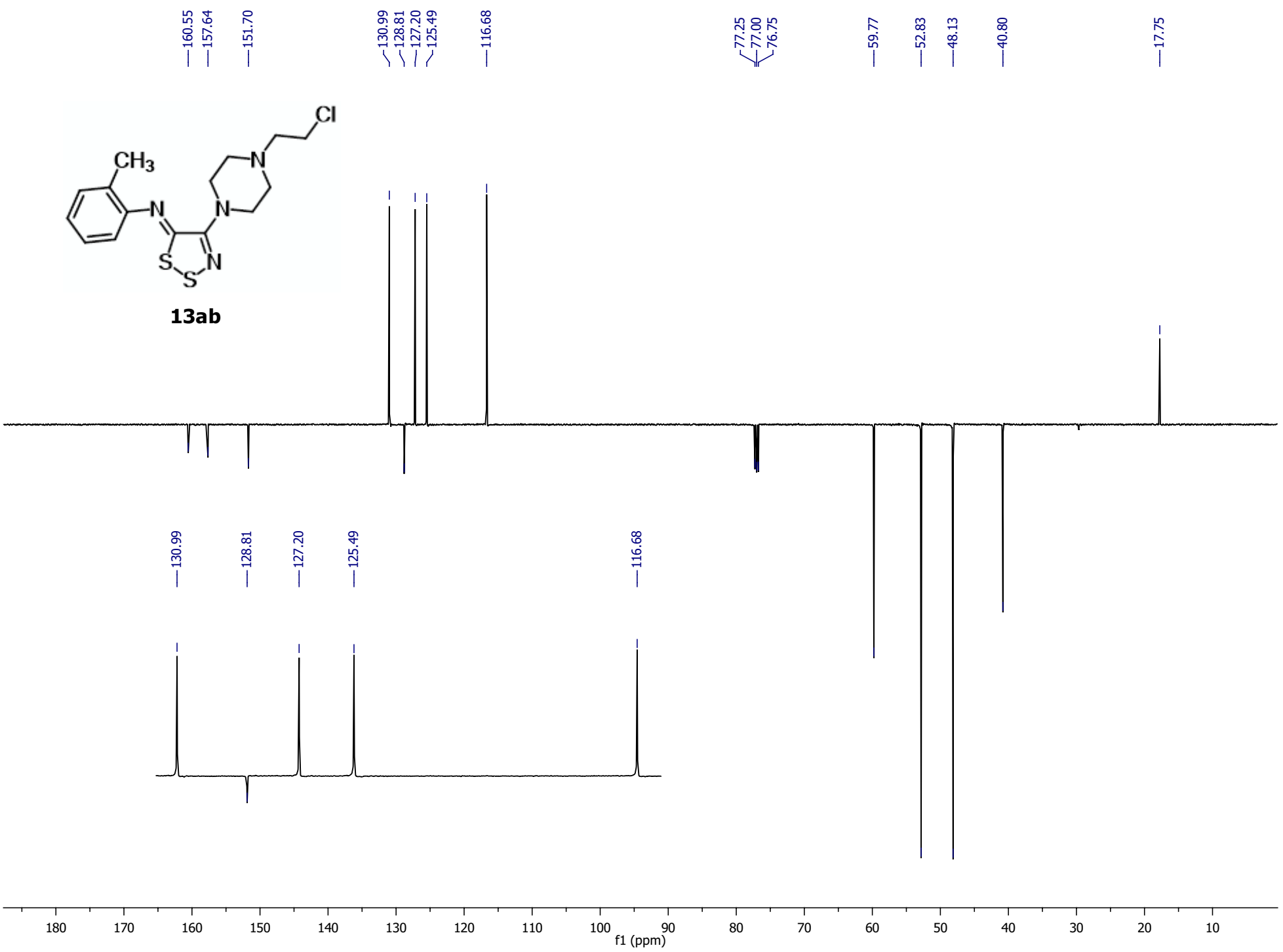


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-methylaniline (**13ab**) (^{1}H-NMR, 500 MHz, acetone-d_6)

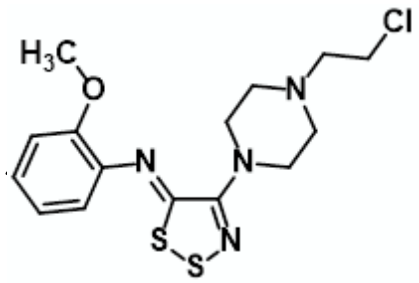


13ab

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-methylaniline (**13ab**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

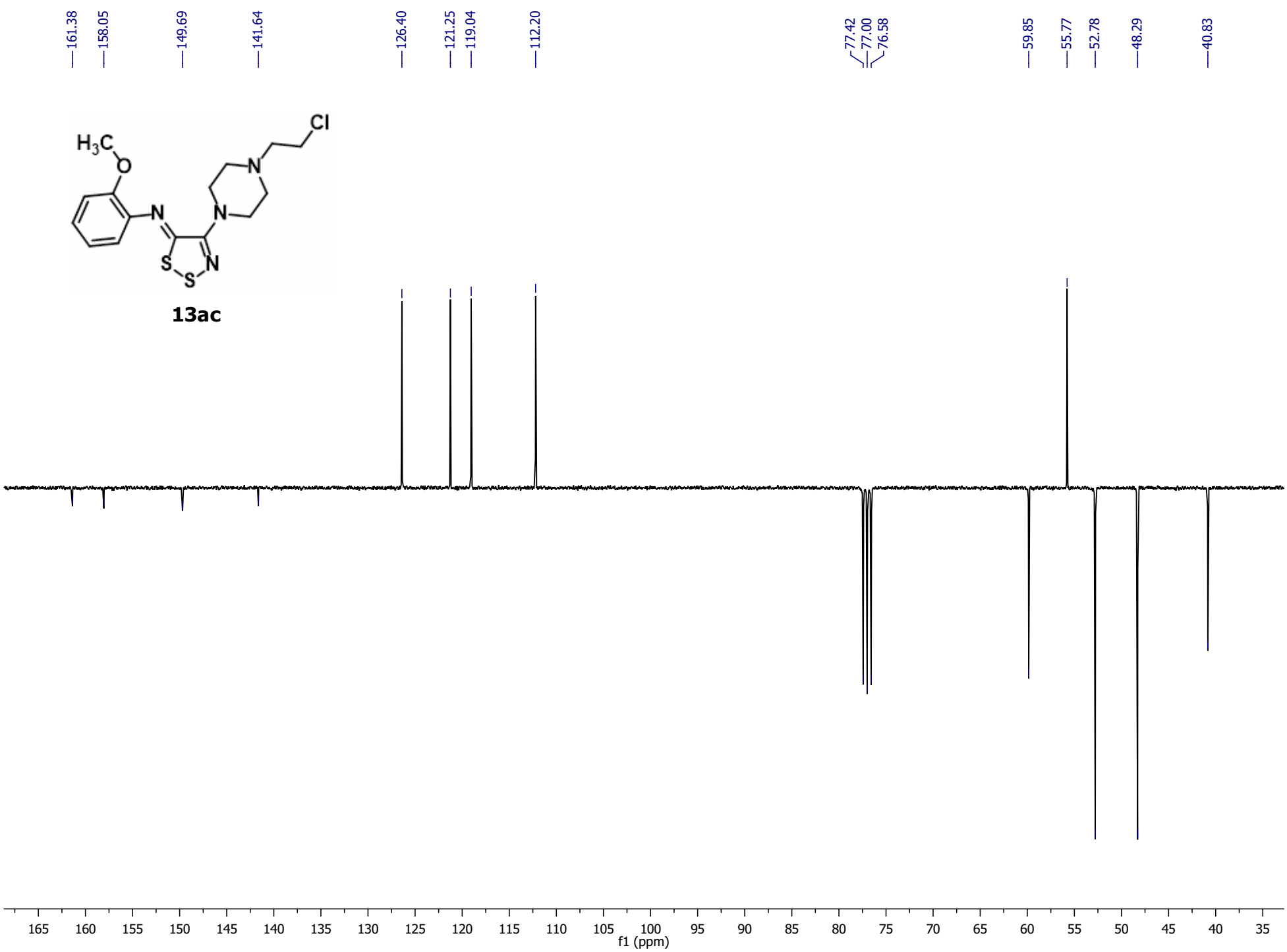


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-methoxyaniline (**13ac**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

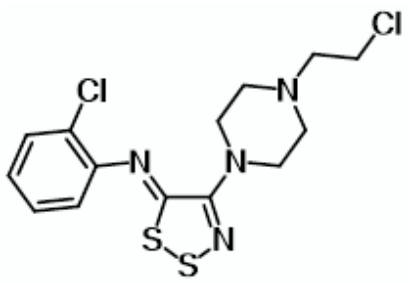


13ac

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-methoxyaniline (**13ac**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

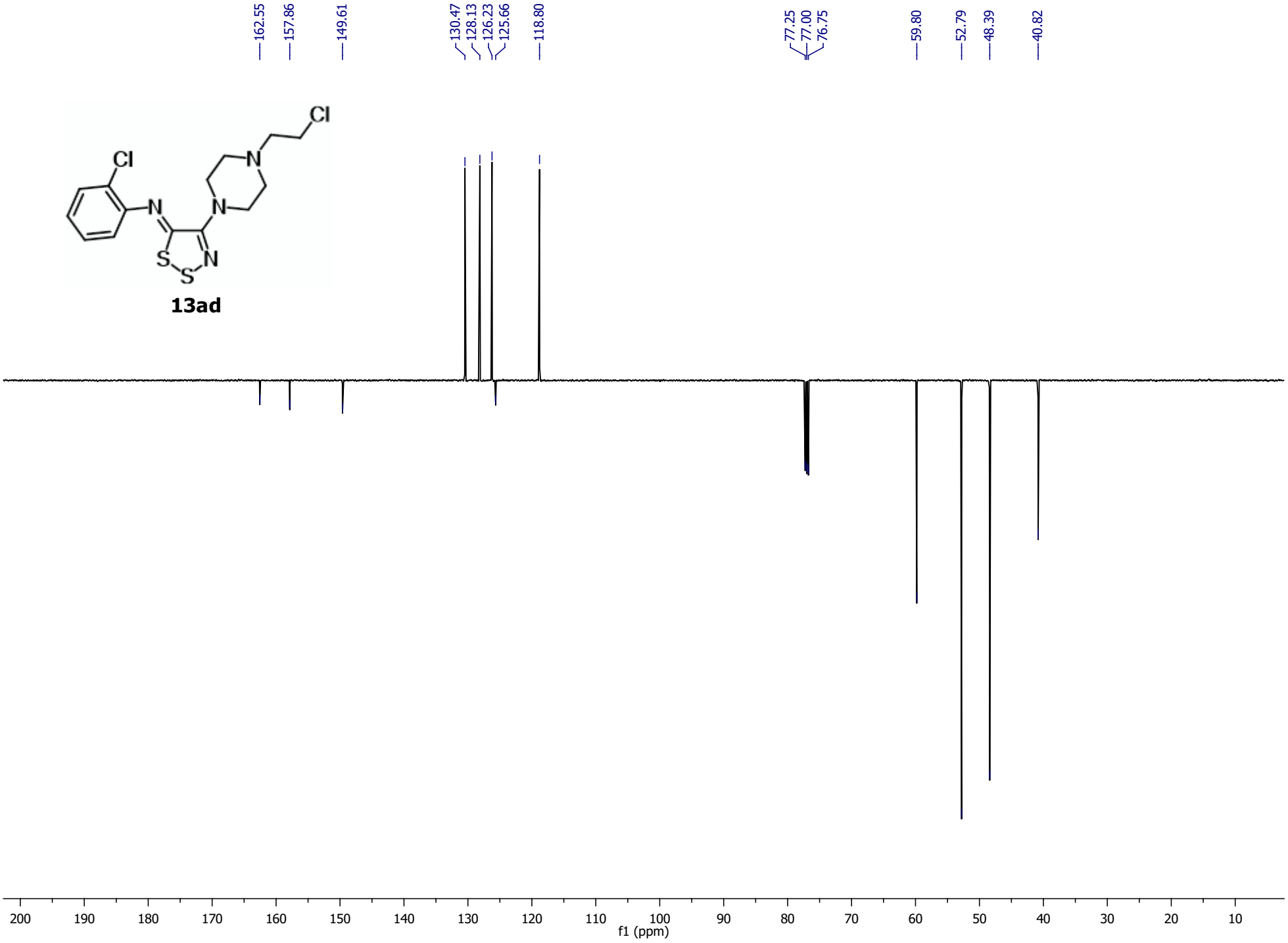


2-Chloro-*N*-{[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13ad**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

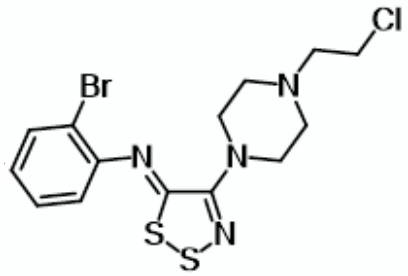


13ad

2-Chloro-*N*-{[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13ad**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

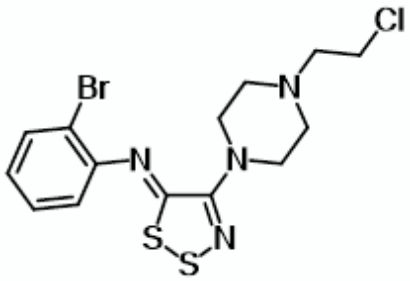


2-Bromo-*N*-{[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13ae**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



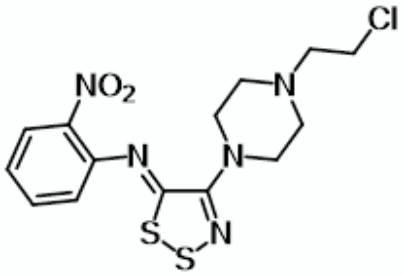
13ae

2-Bromo-*N*-{[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13ae**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



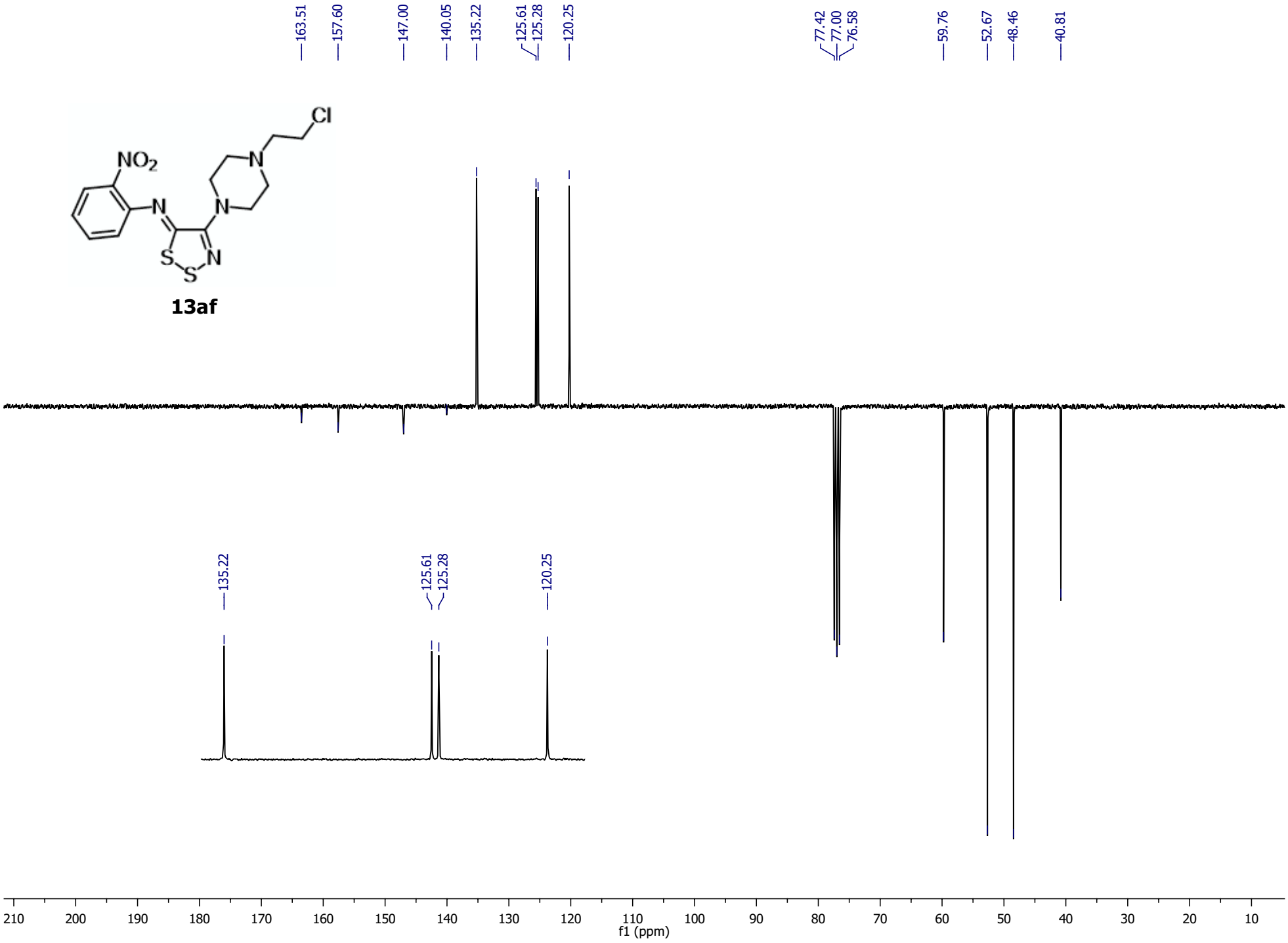
13ae

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-nitroaniline (**13af**) (^{1}H-NMR, 300 MHz, $CDCl_3$)

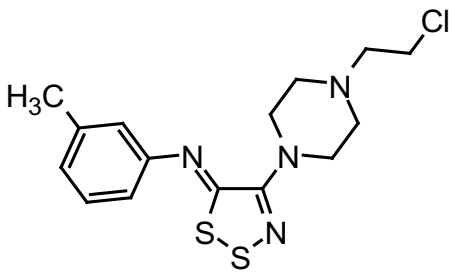


13af

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-nitroaniline (**13af**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

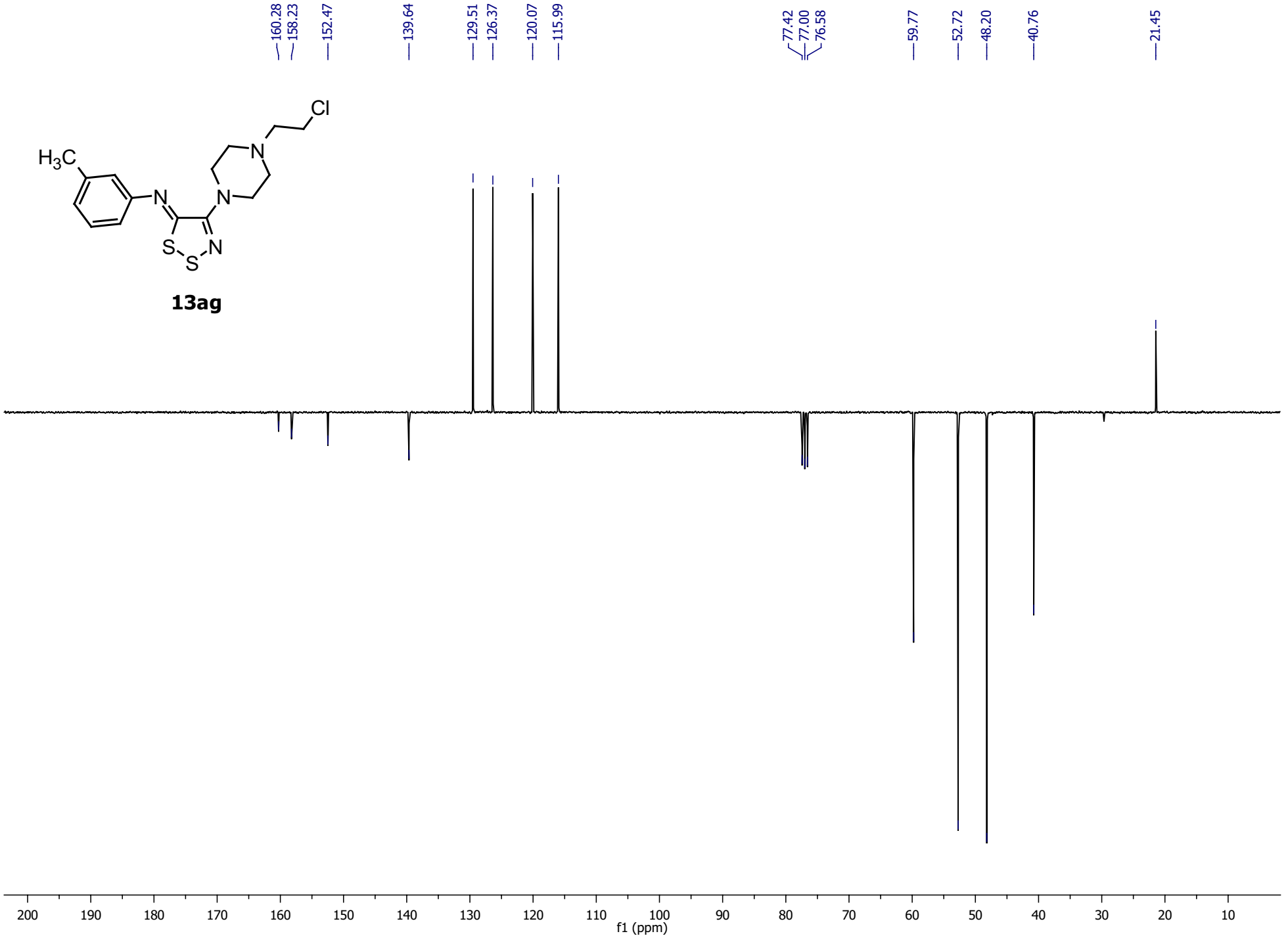


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-3-methylaniline (**13ag**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

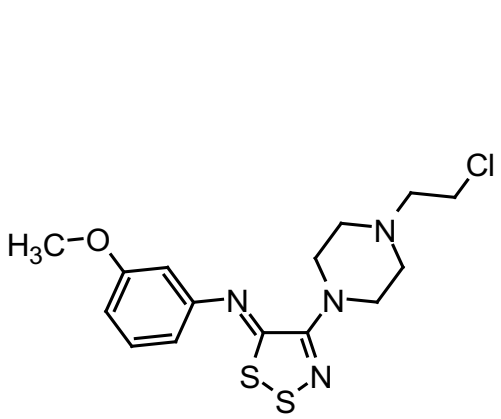


13ag

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-3-methylaniline (**13ag**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

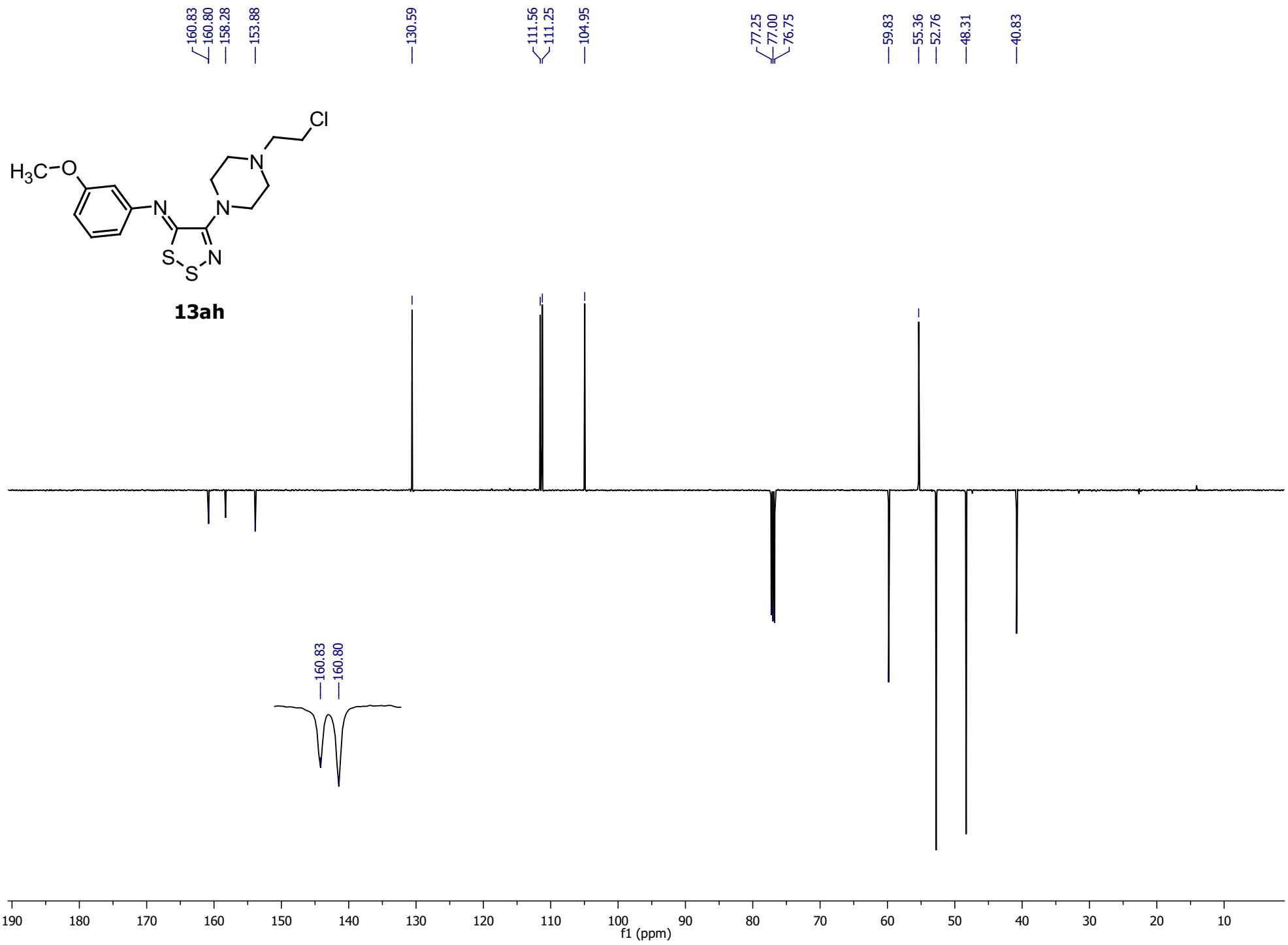


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-3-methoxyaniline (**13ah**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

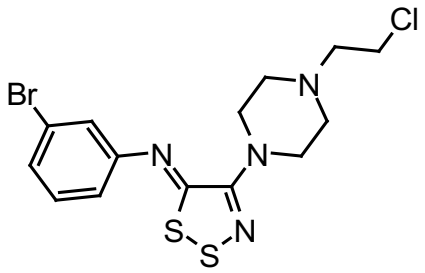


13ah

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-3-methoxyaniline (**13ah**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

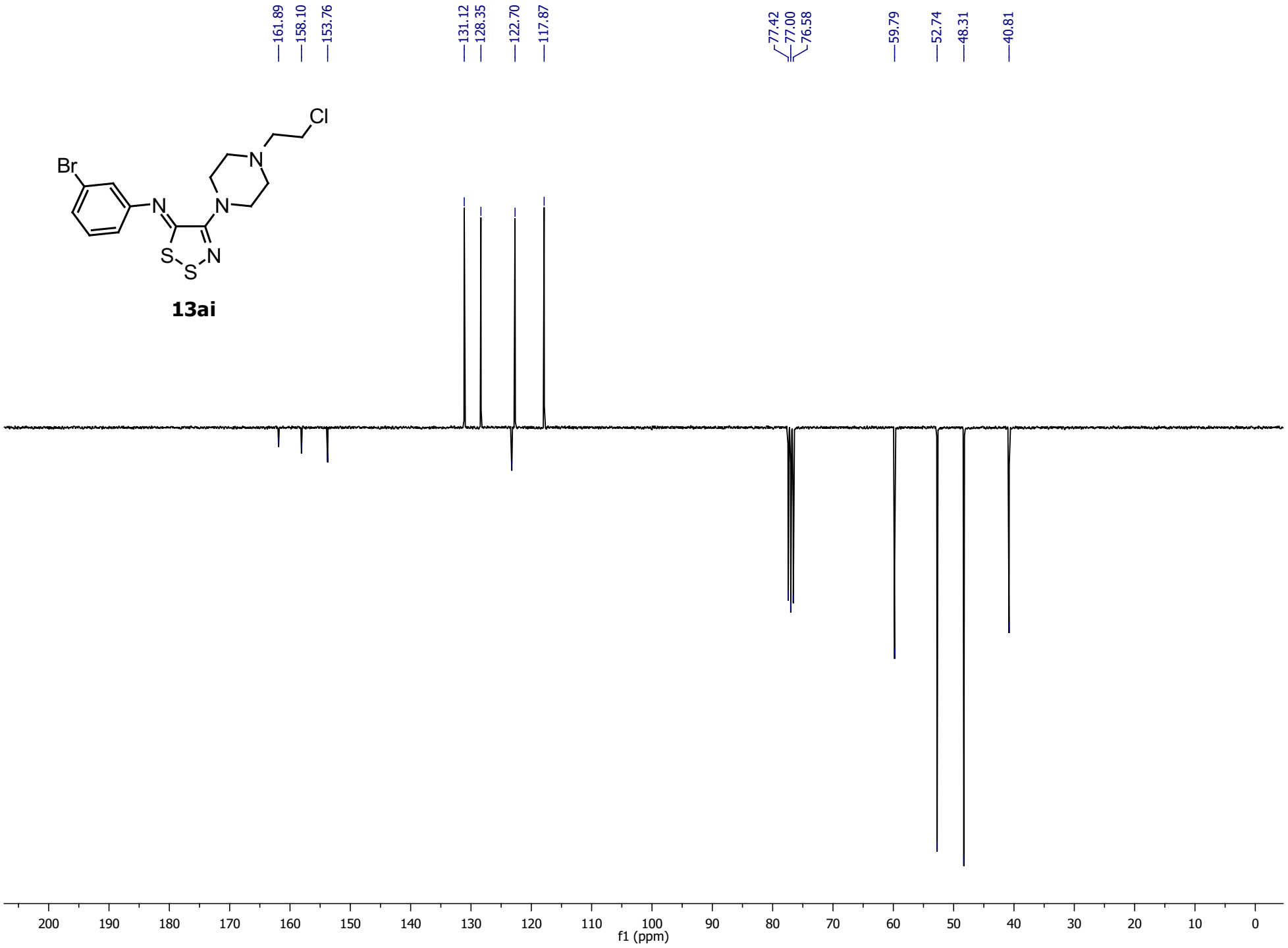


3-Bromo-*N*-{[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13ai**) (^{1}H-NMR, 500 MHz, acetone-d_6)

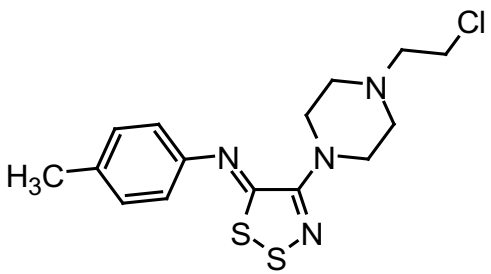


13ai

3-Bromo-*N*-{[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13ai**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

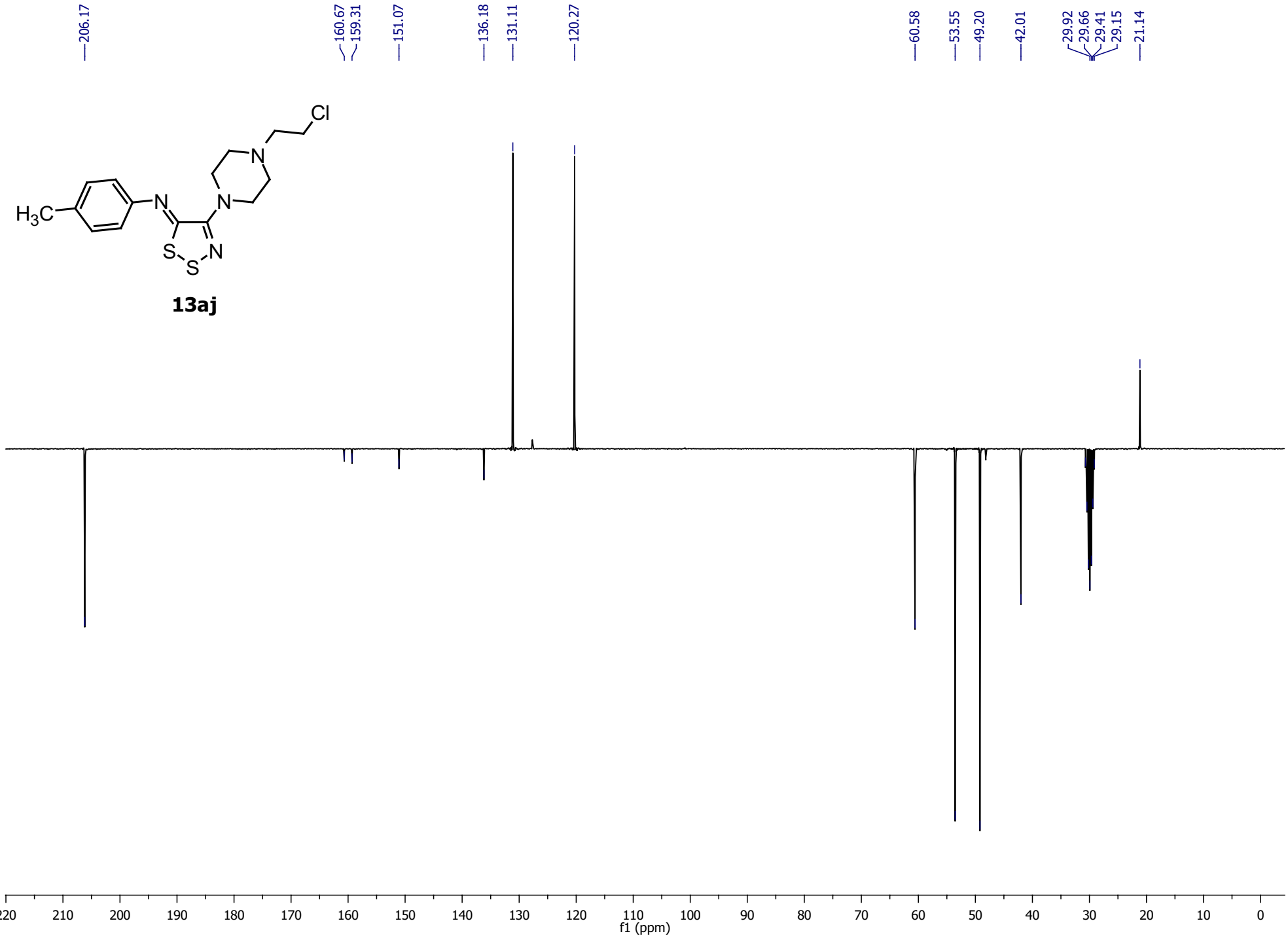


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-4-methylaniline (**13aj**) (^{1}H-NMR, 300 MHz, acetone-d_6)

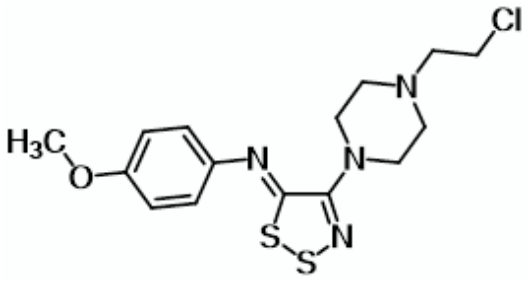


13aj

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-4-methylaniline (**13aj**) (^{13}C-NMR, 75 MHz, acetone-d_6)

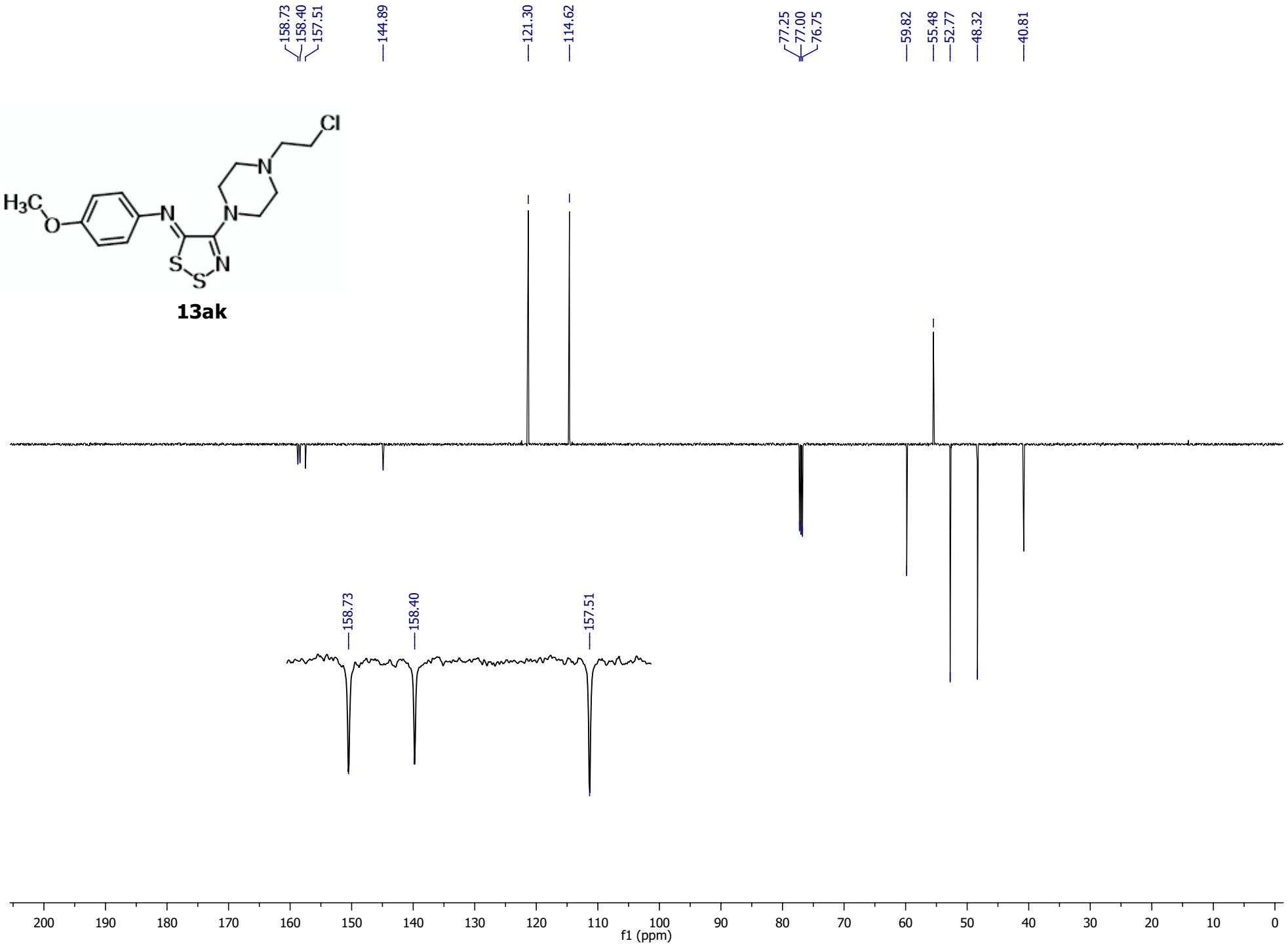


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-4-methoxyaniline (**13ak**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

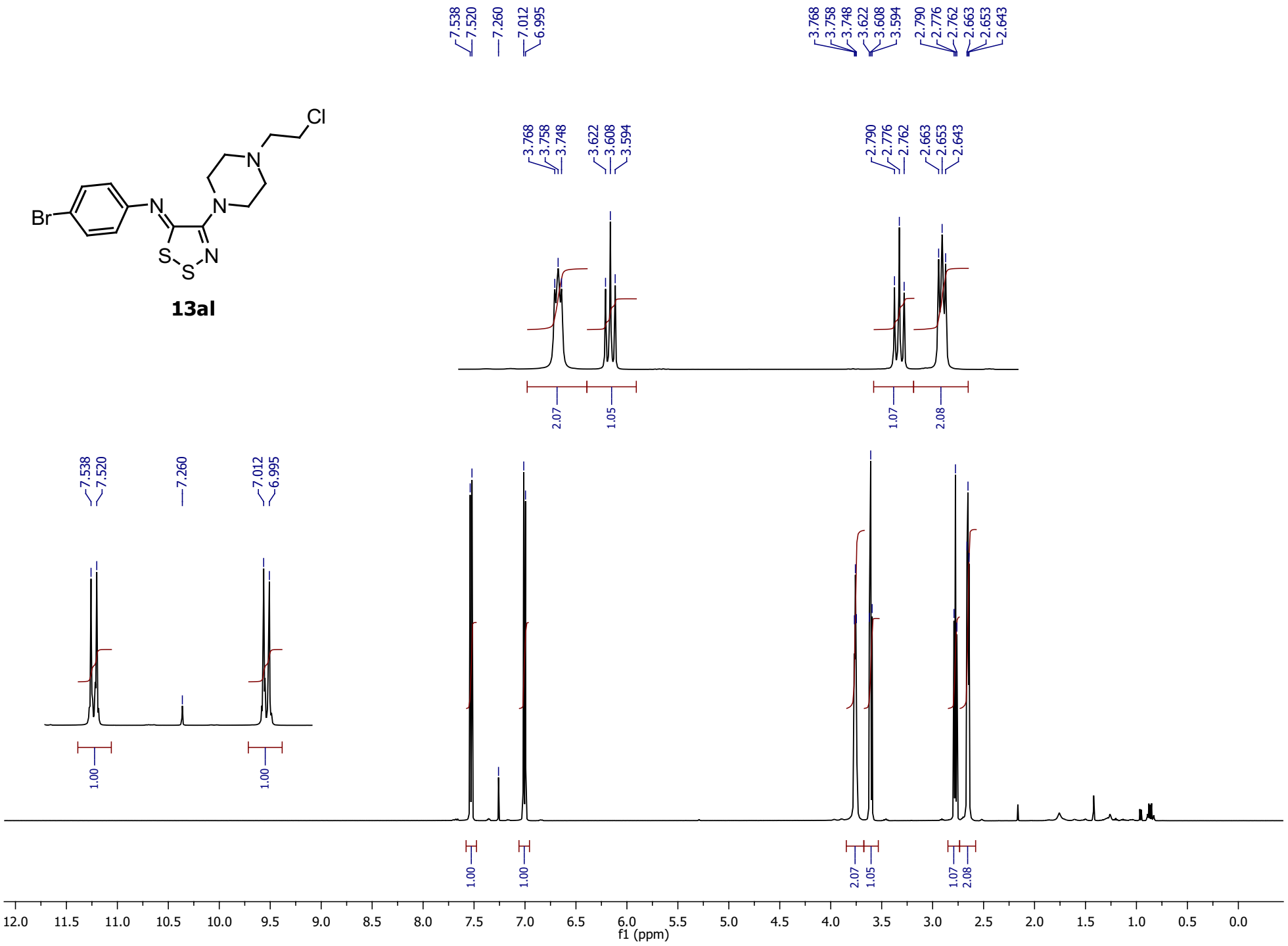


13ak

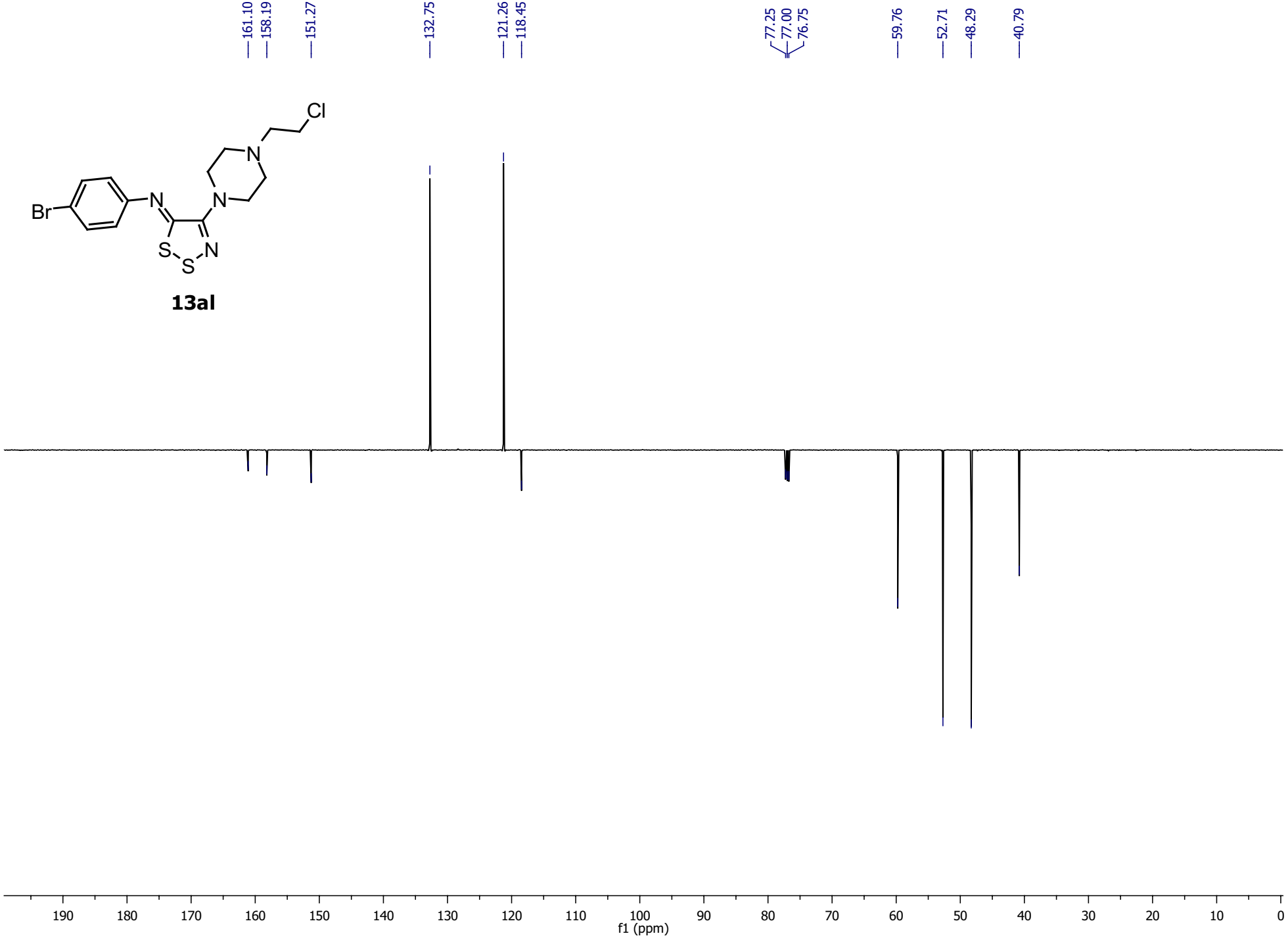
N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-4-methoxyaniline (**13ak**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



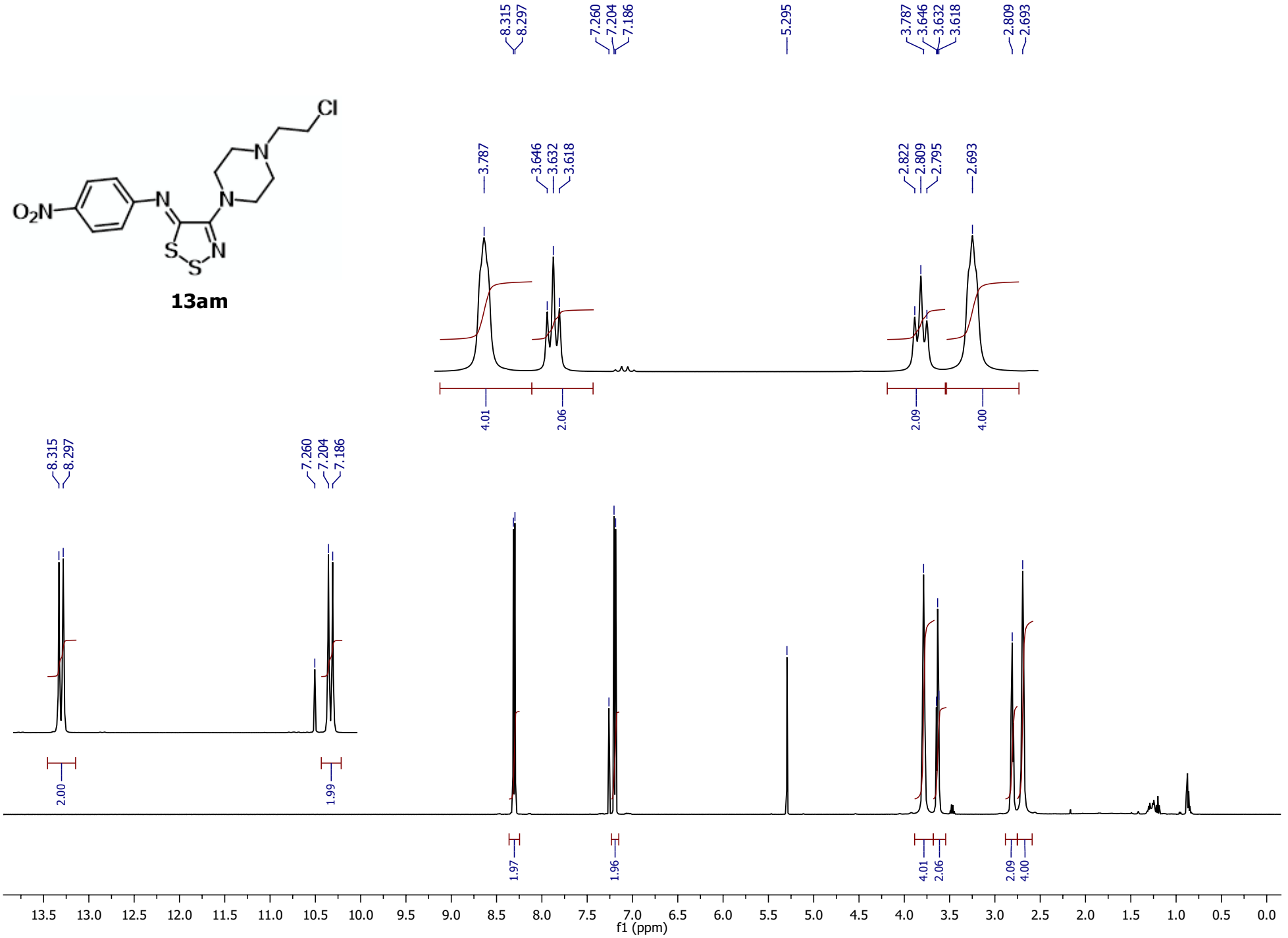
4-Bromo-*N*-{[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13al**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



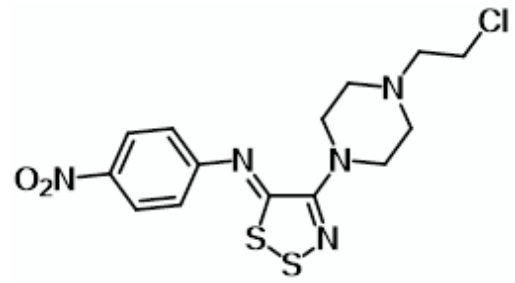
4-Bromo-*N*-{[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**13al**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-4-nitroaniline (**13am**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

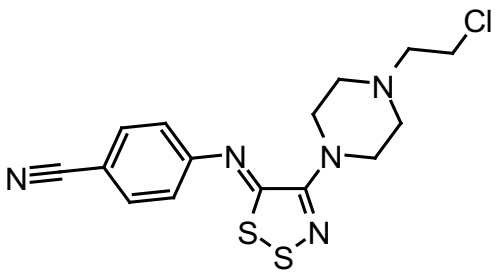


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-4-nitroaniline (**13am**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



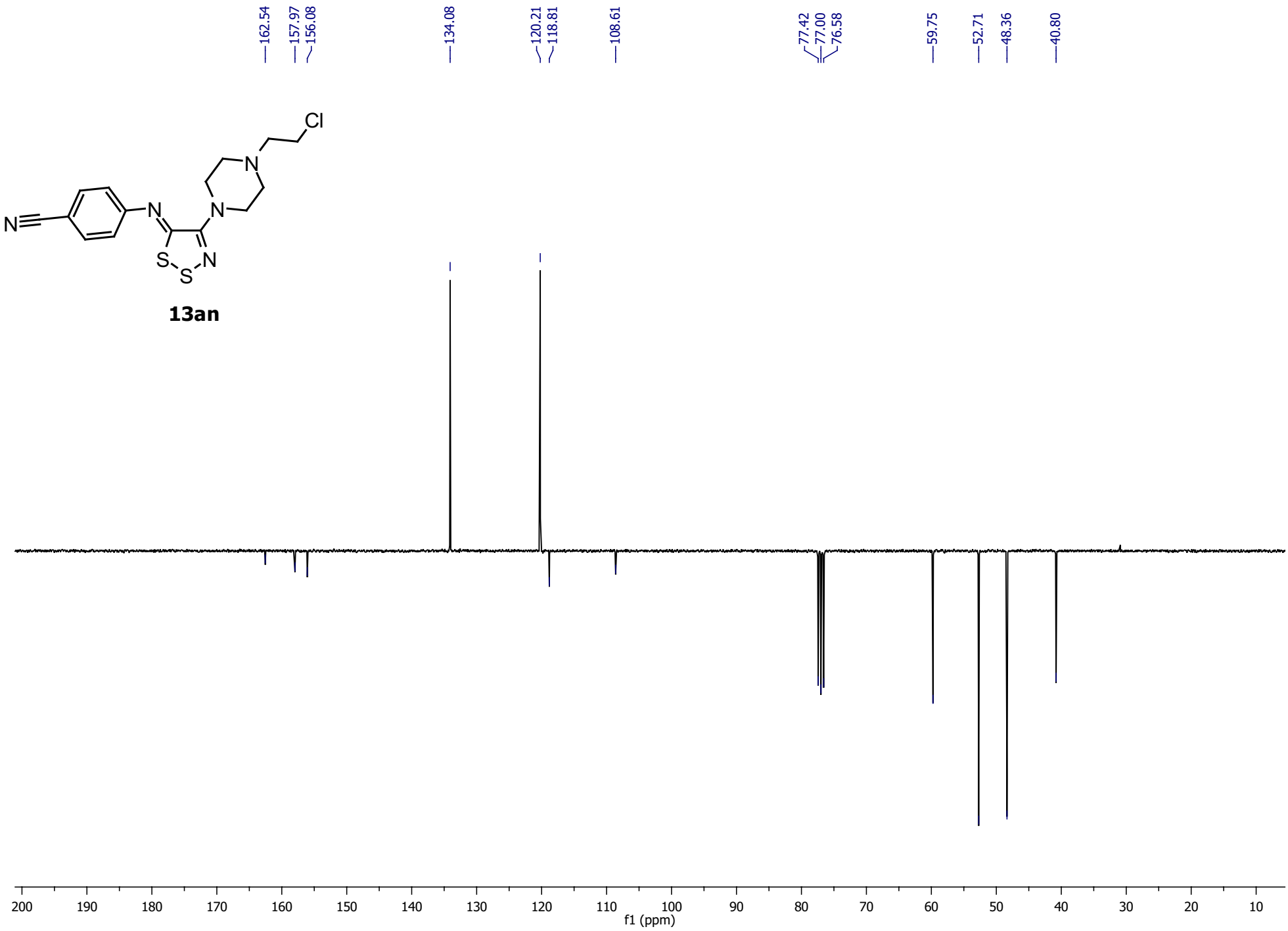
13am

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-4-cyanoaniline (**13an**) (^{1}H-NMR, 300 MHz, $CDCl_3$)

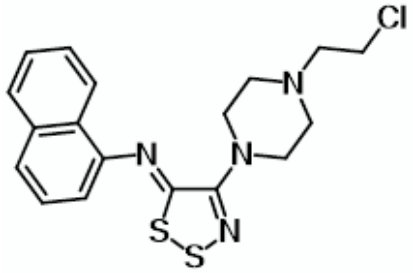


13an

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-4-cyanoaniline (**13an**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

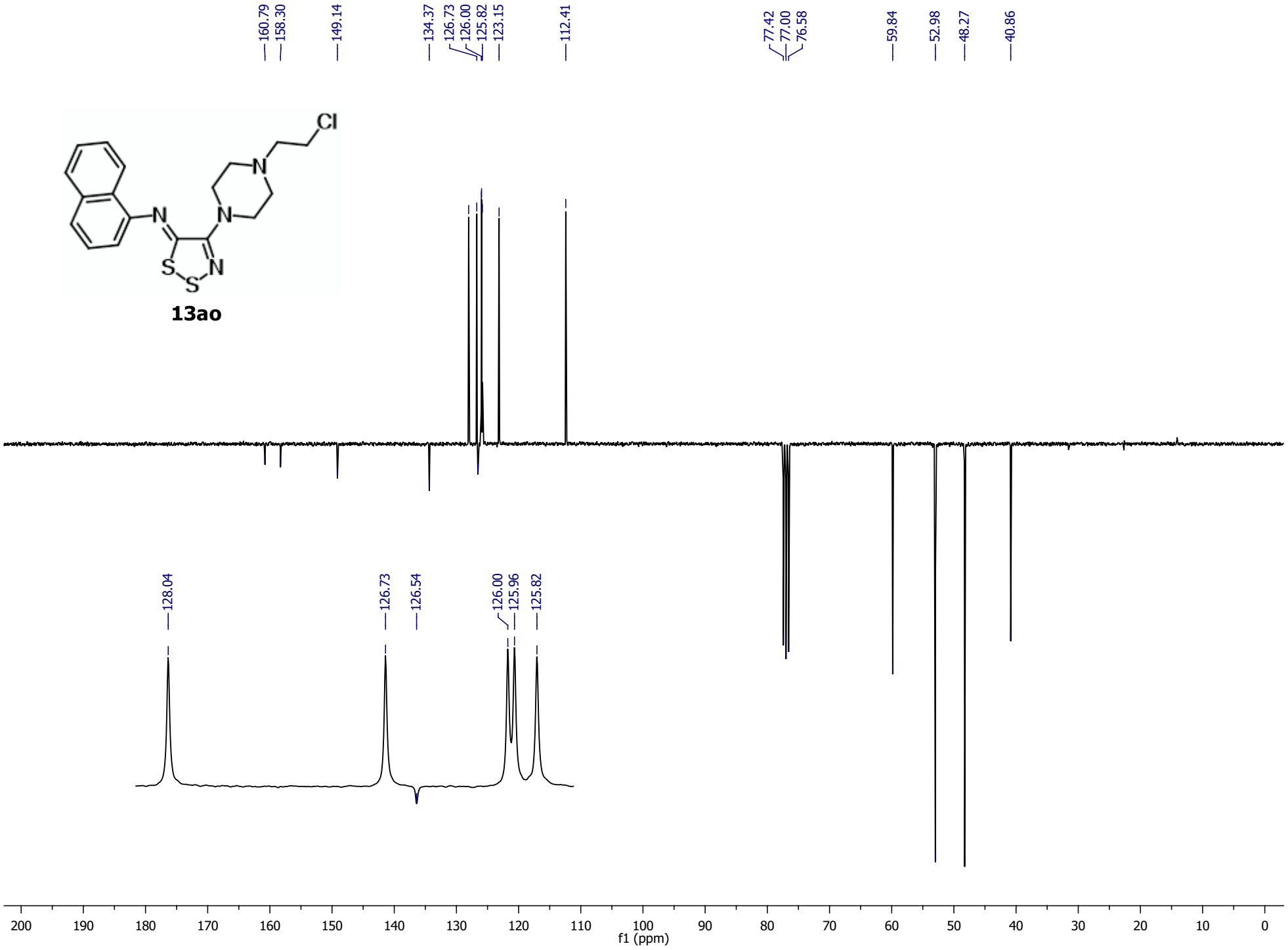


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-1-naphthylamine (**13ao**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

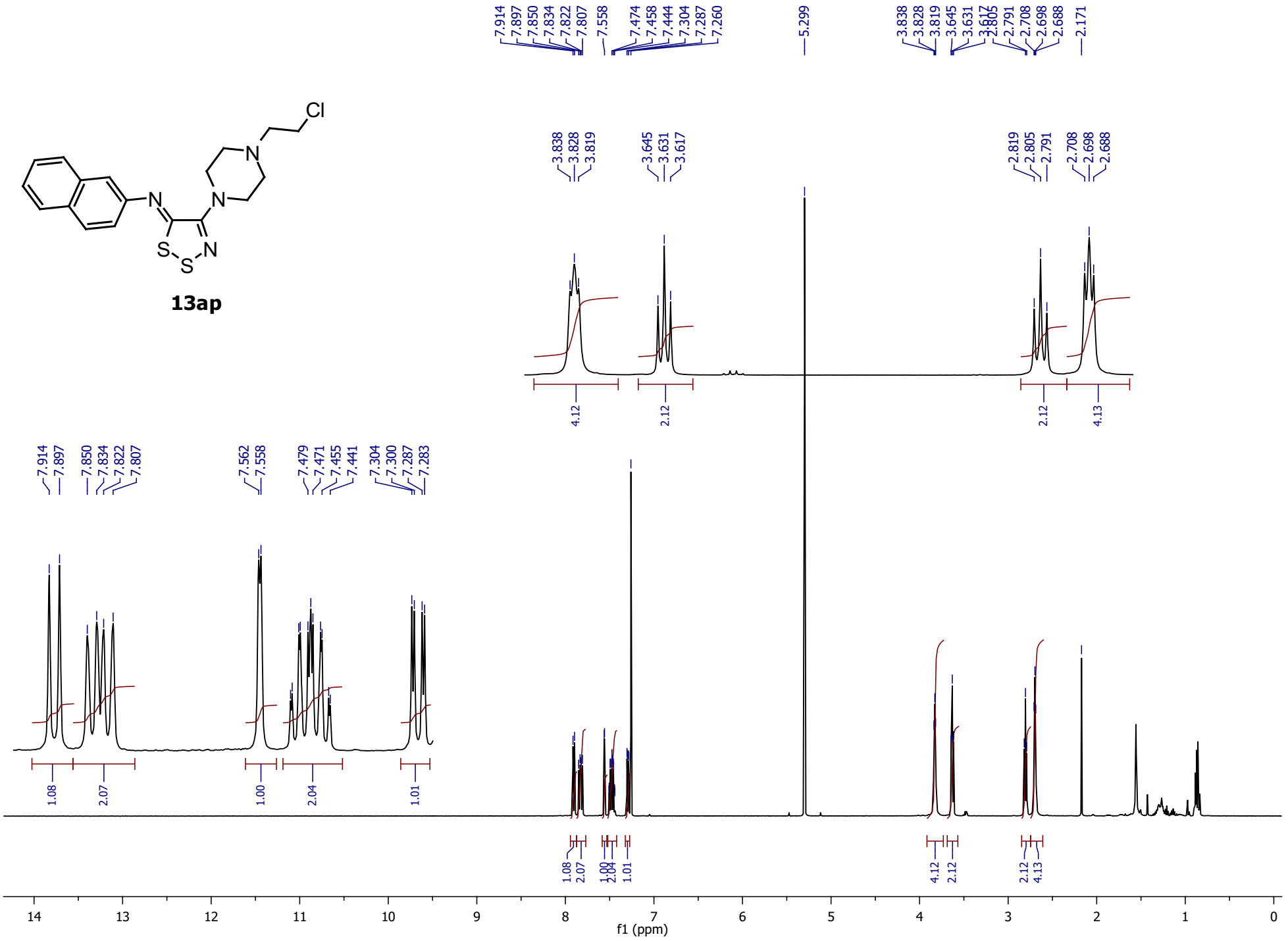


13ao

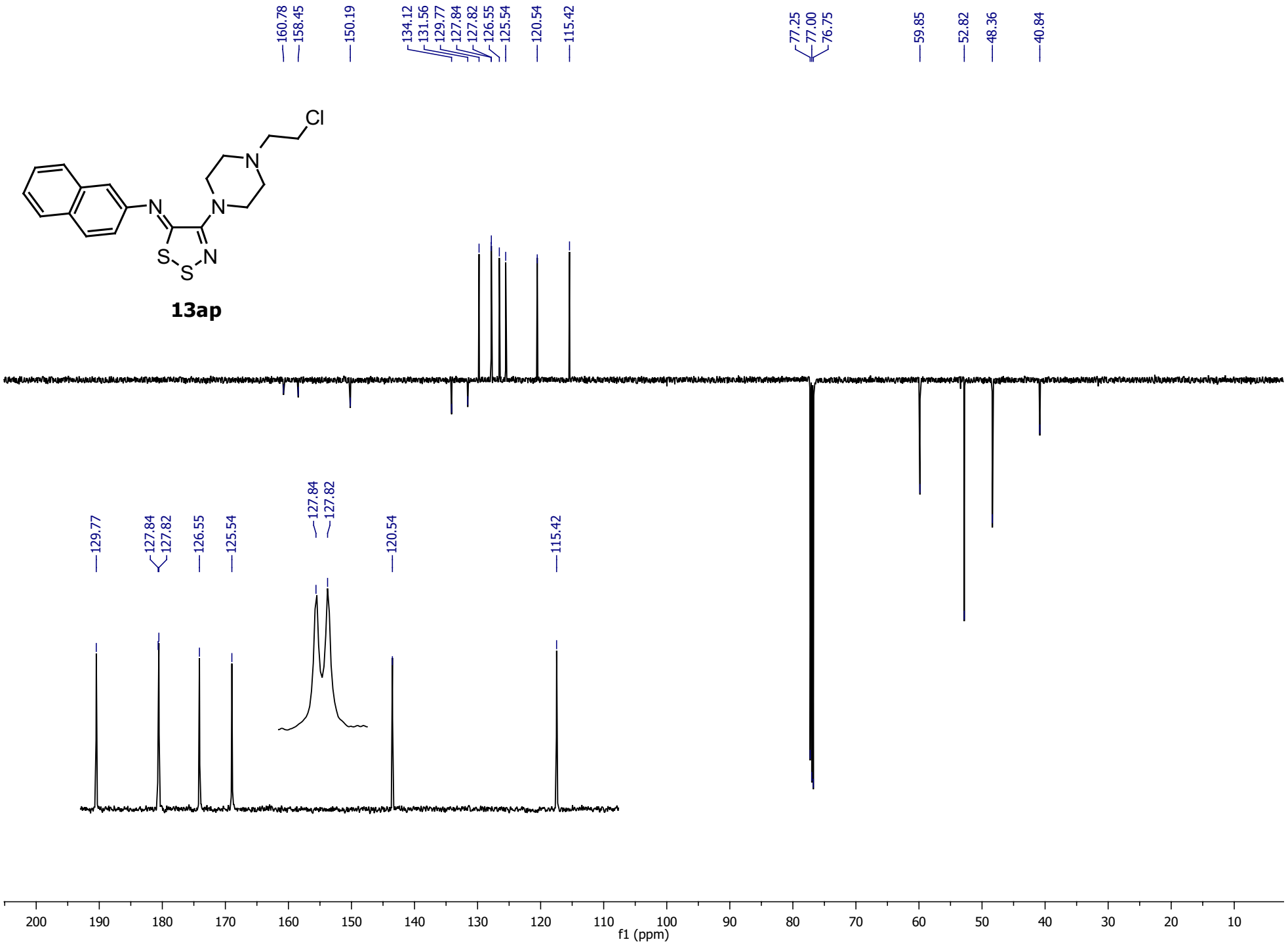
N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-1-naphthylamine (**13ao**) (^{13}C-NMR, 75 MHz, $CDCl_3$)



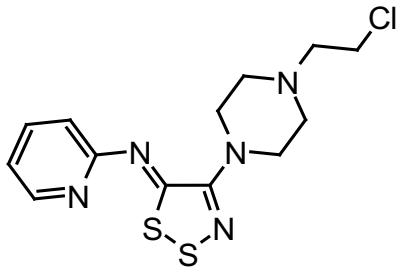
N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-naphthylamine (**13ap**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-naphthylamine (**13ap**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

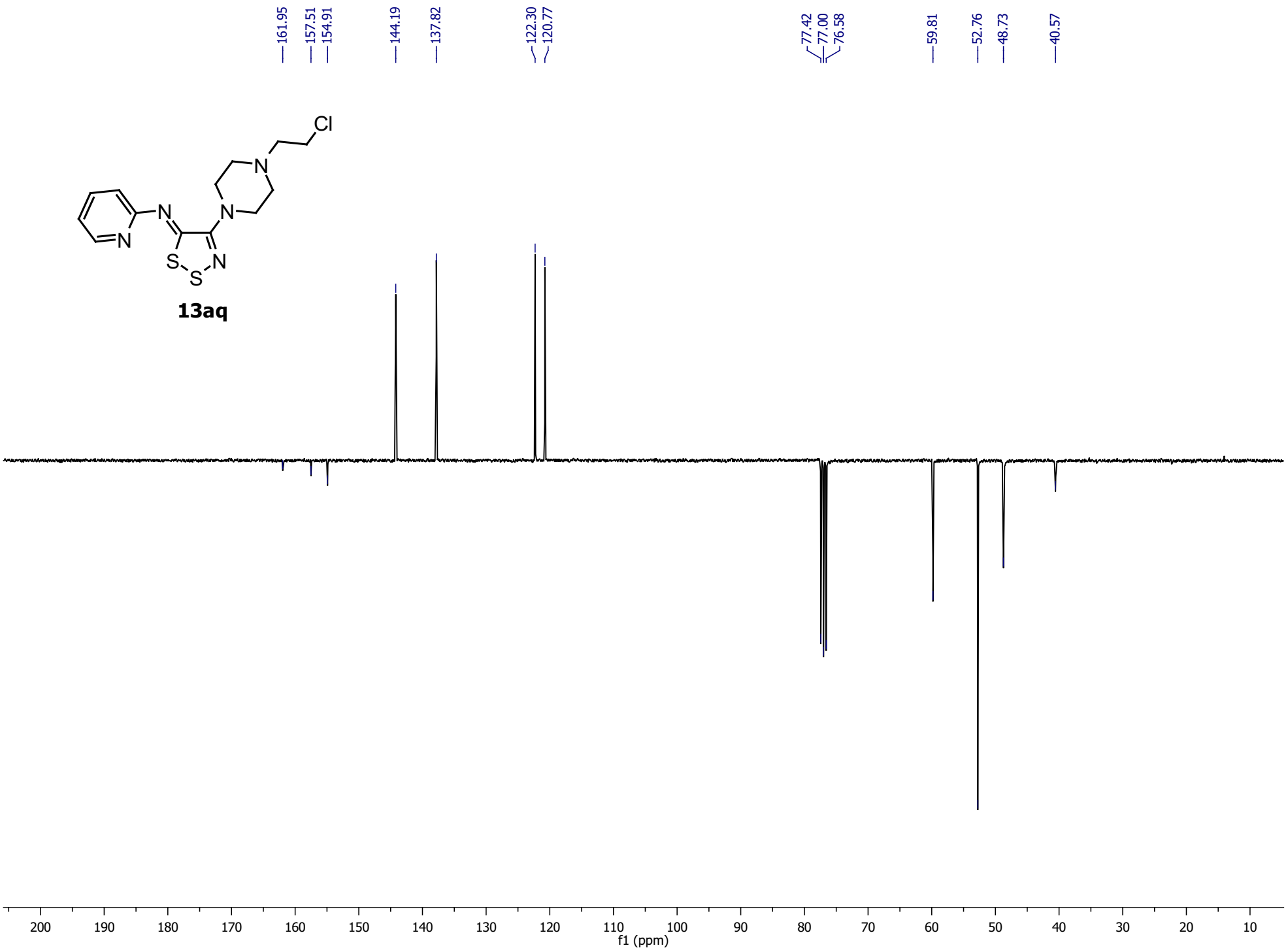


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-pyridylamine (**13aq**) (^{1}H-NMR, 300 MHz, $CDCl_3$)

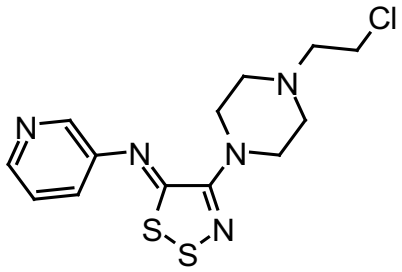


13aq

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-pyridylamine (**13aq**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

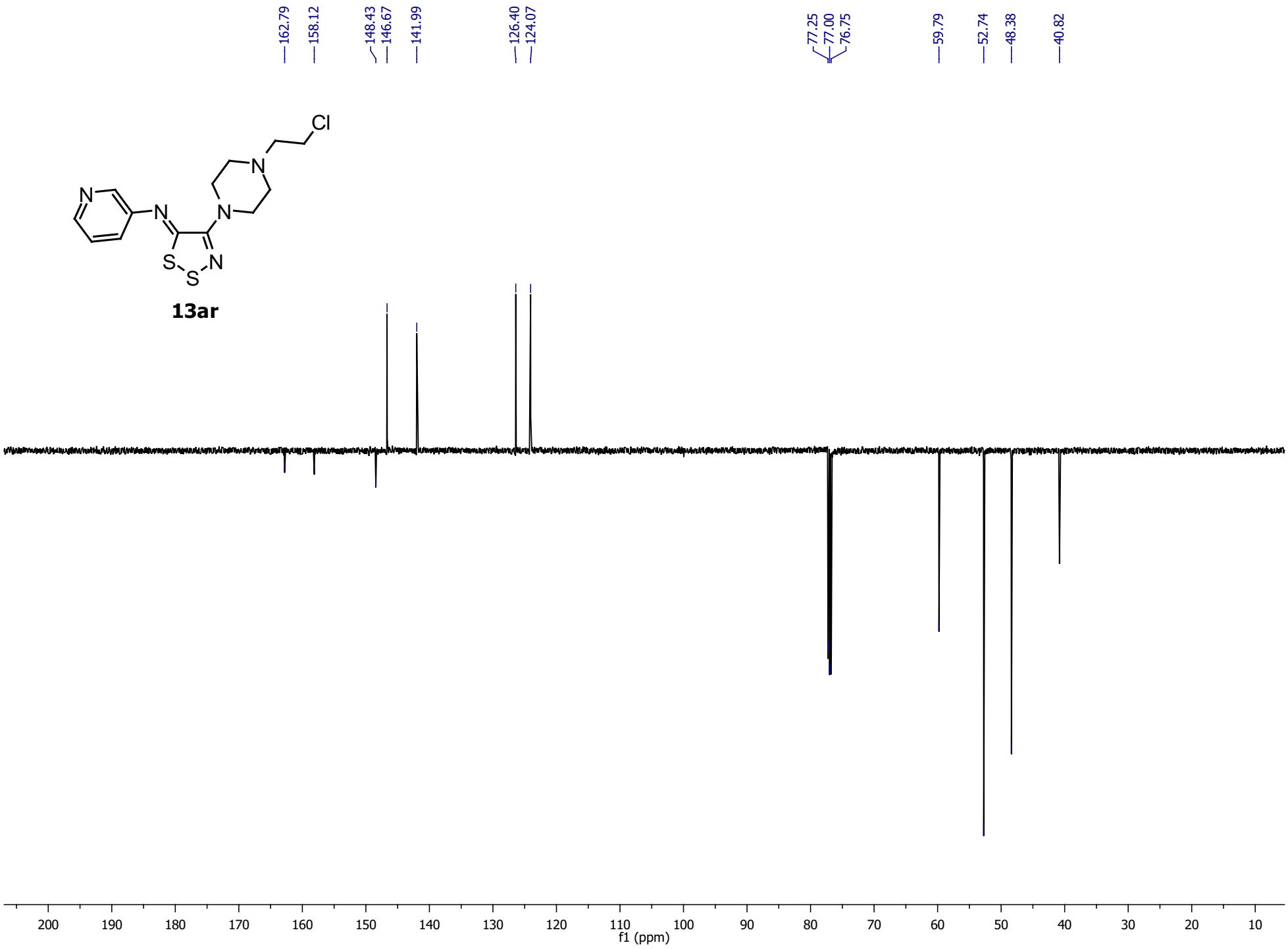


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-3-pyridylamine (**13ar**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

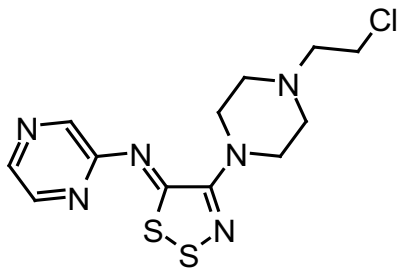


13ar

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-3-pyridylamine (**13ar**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

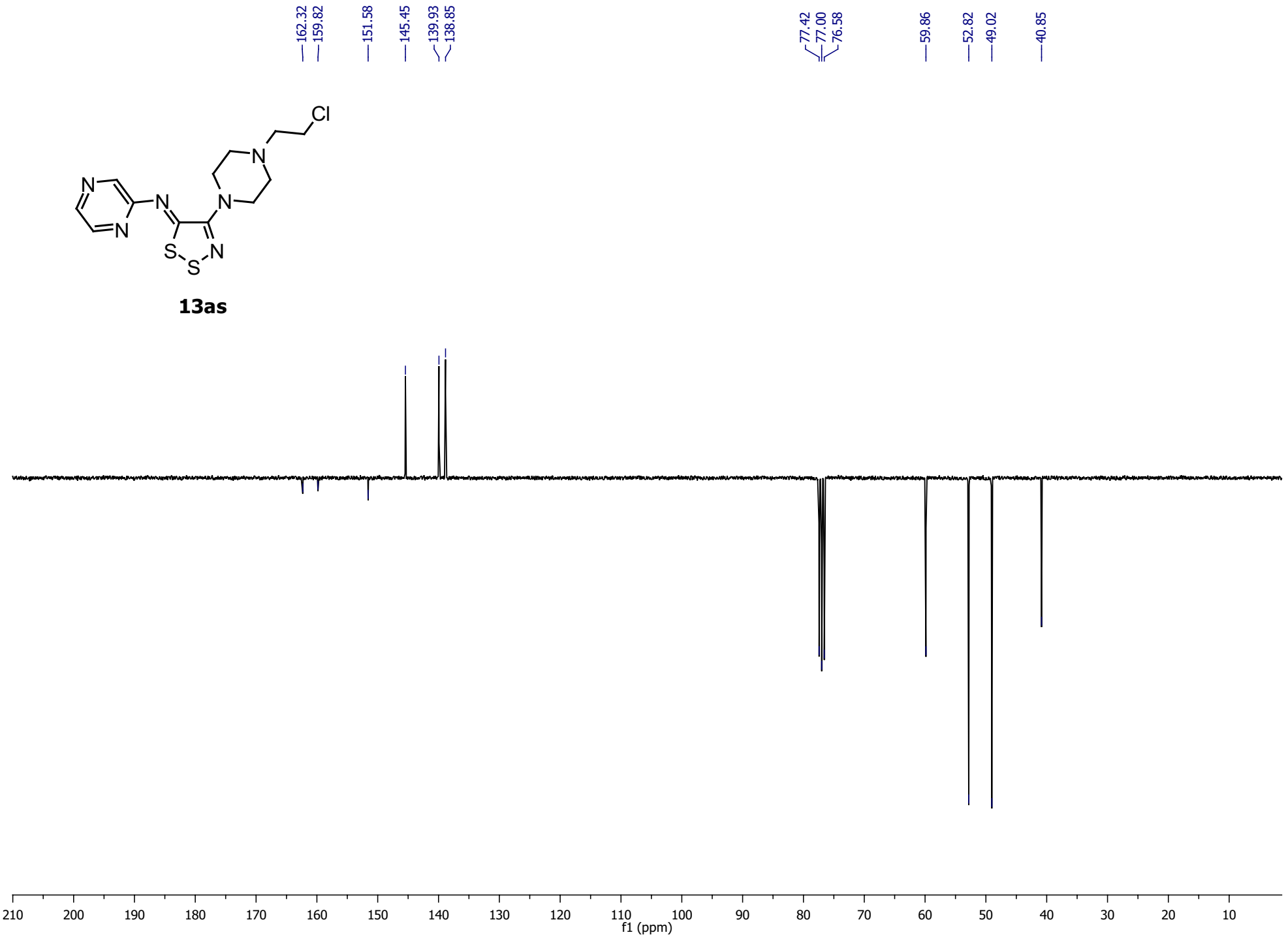


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-pyrazinylamine (**13as**) (^{1}H-NMR, 300 MHz, $CDCl_3$)



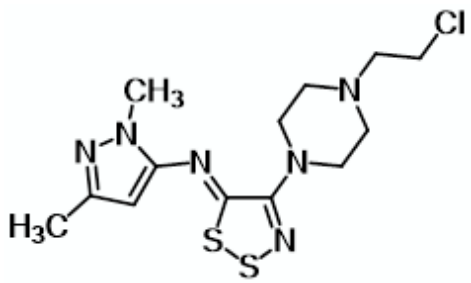
13as

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-2-pyrazinylamine (**13as**) (^{13}C-NMR, 75 MHz, $CDCl_3$)



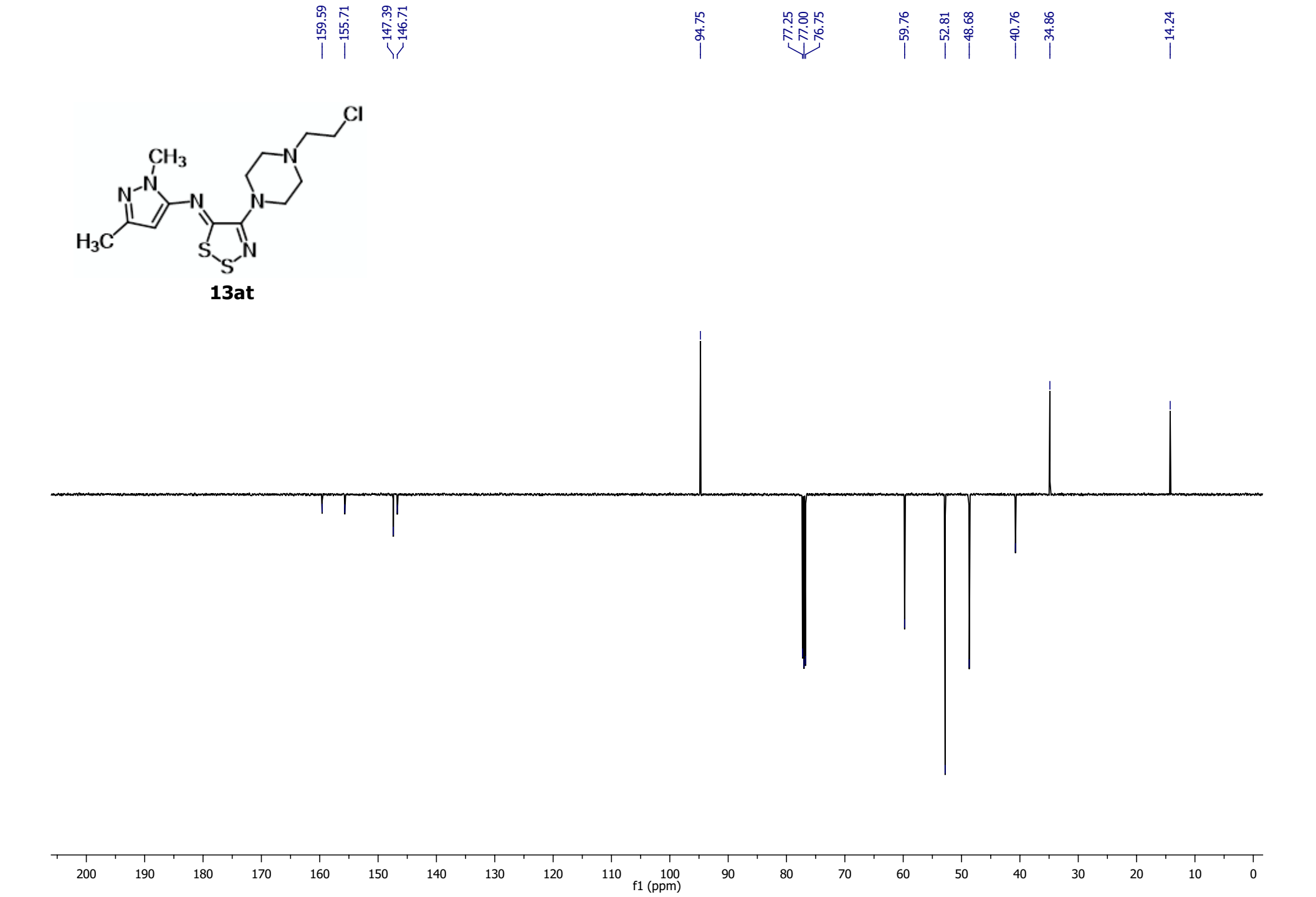
13as

N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-1,3-dimethyl-1*H*-pyrazol-5-amine (**at**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

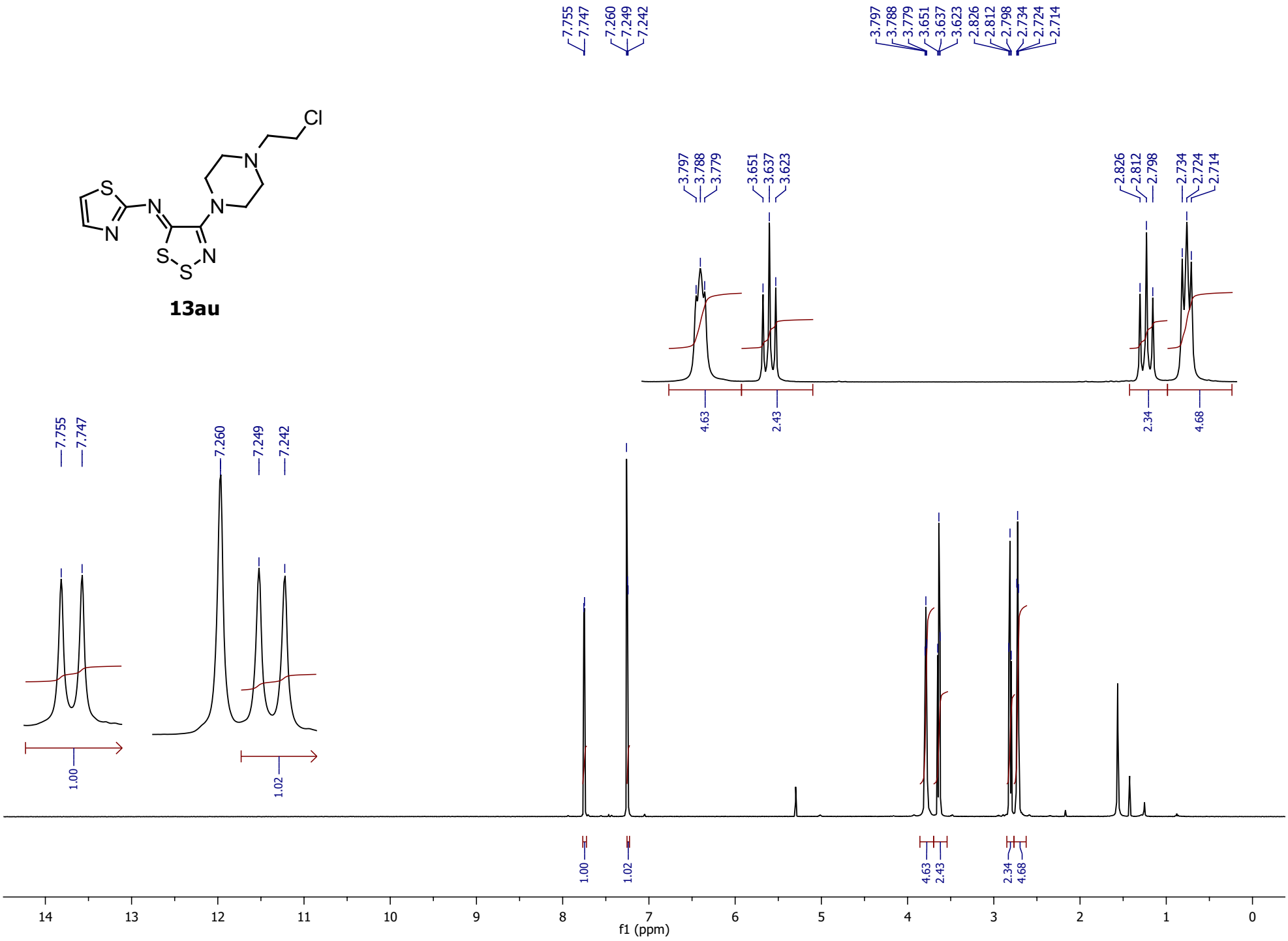


13at

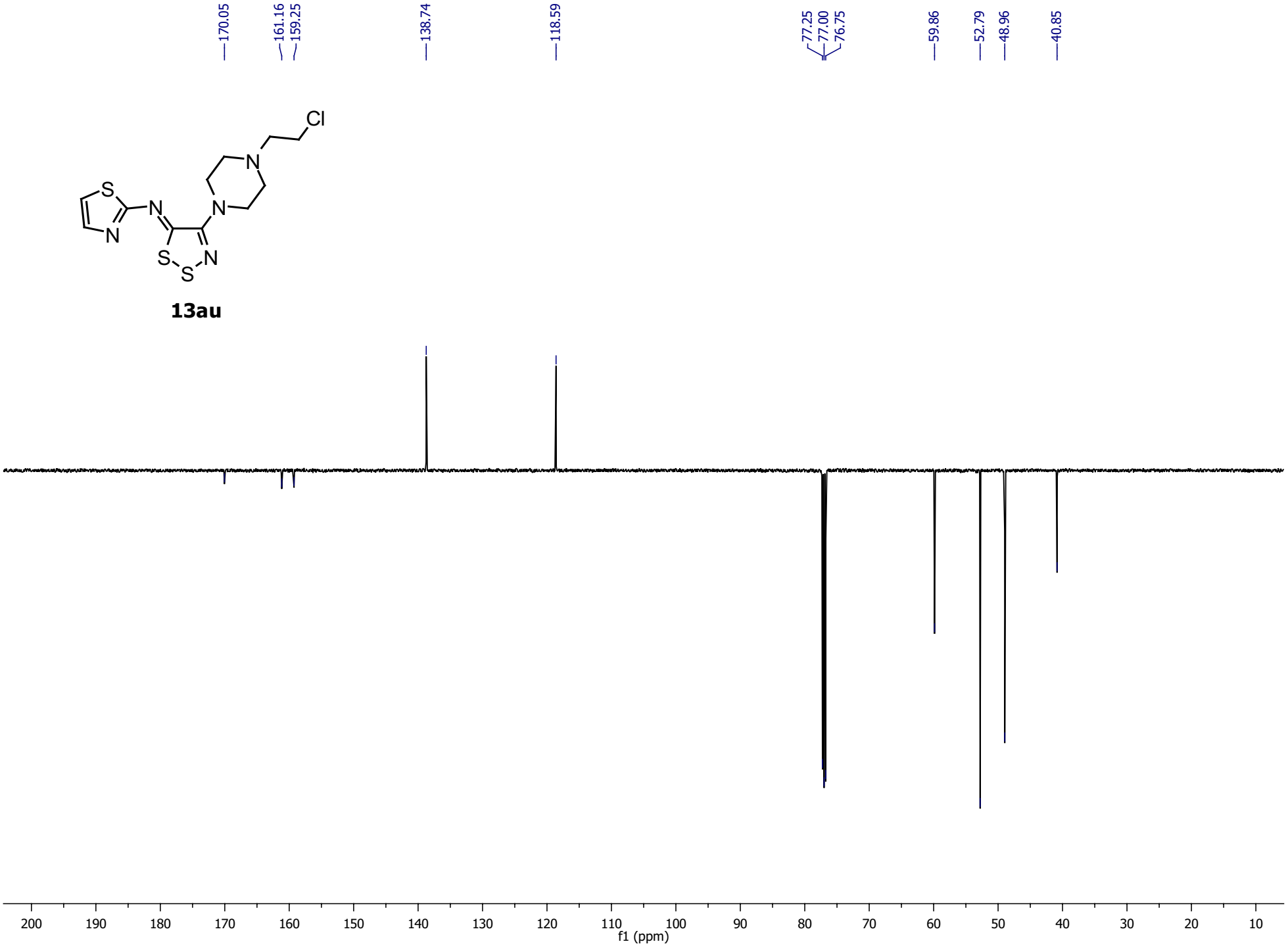
N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}-1,3-dimethyl-1*H*-pyrazol-5-amine (**at**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}thiazol-2-amine (**13au**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

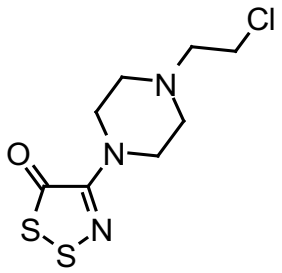


N-{[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}thiazol-2-amine (**13au**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



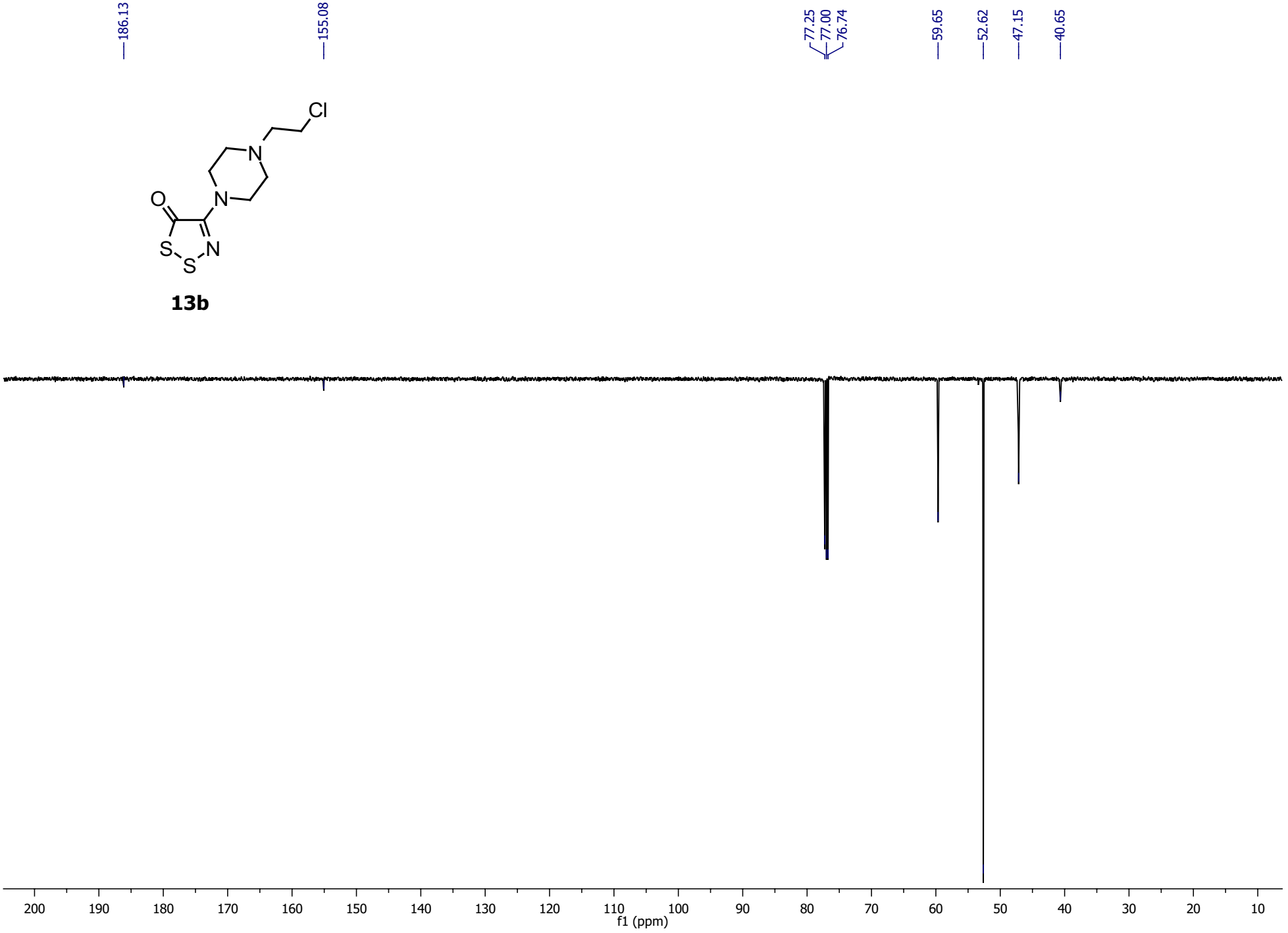
13au

4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**13b**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

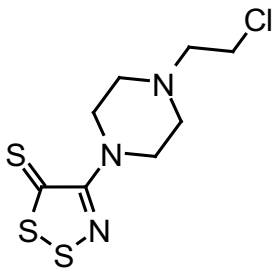


13b

4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**13b**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

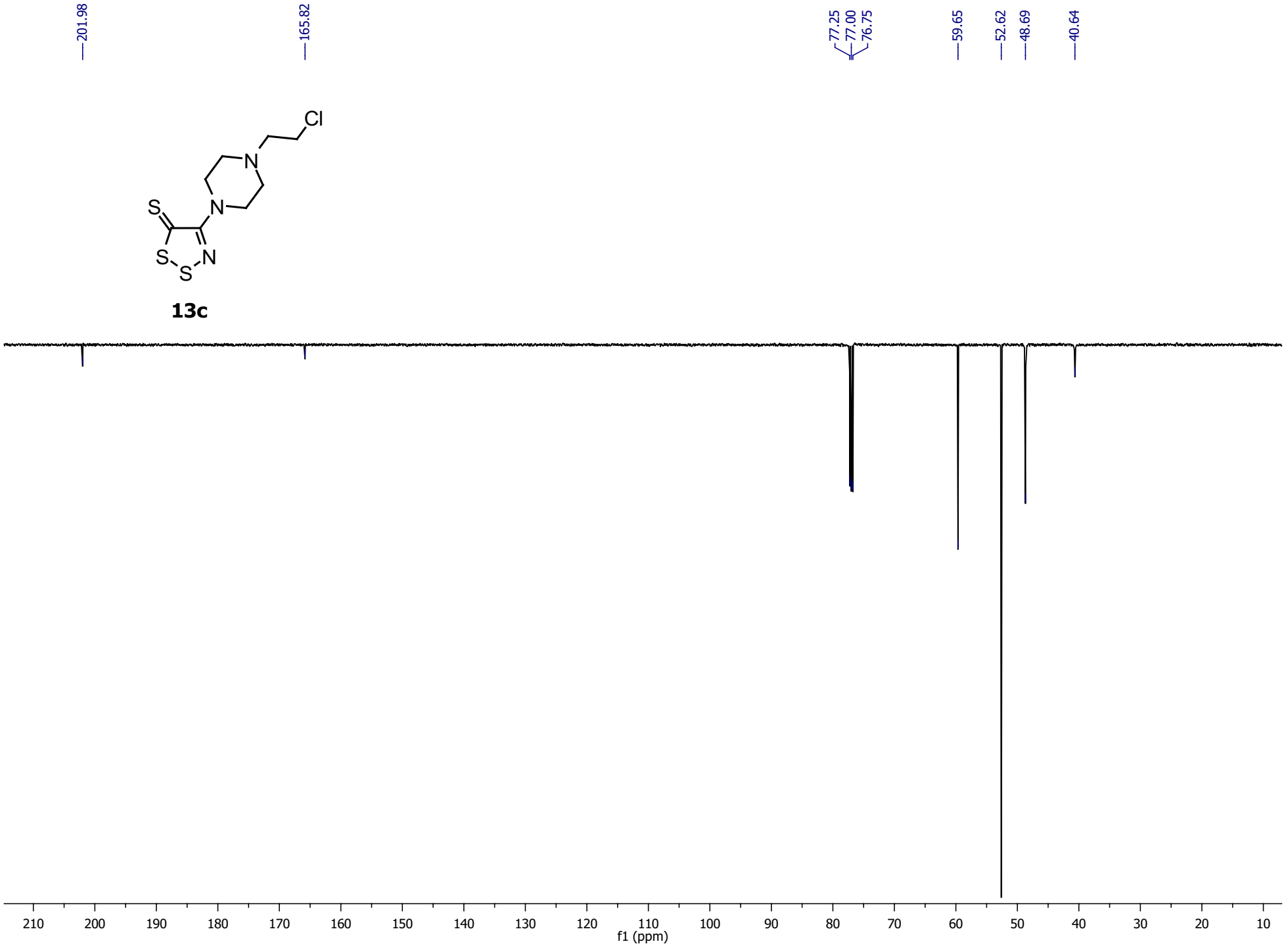


4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazole-5-thione (**13c**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



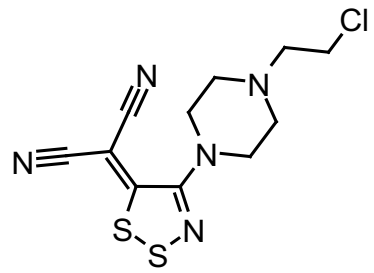
13c

4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazole-5-thione (**13c**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



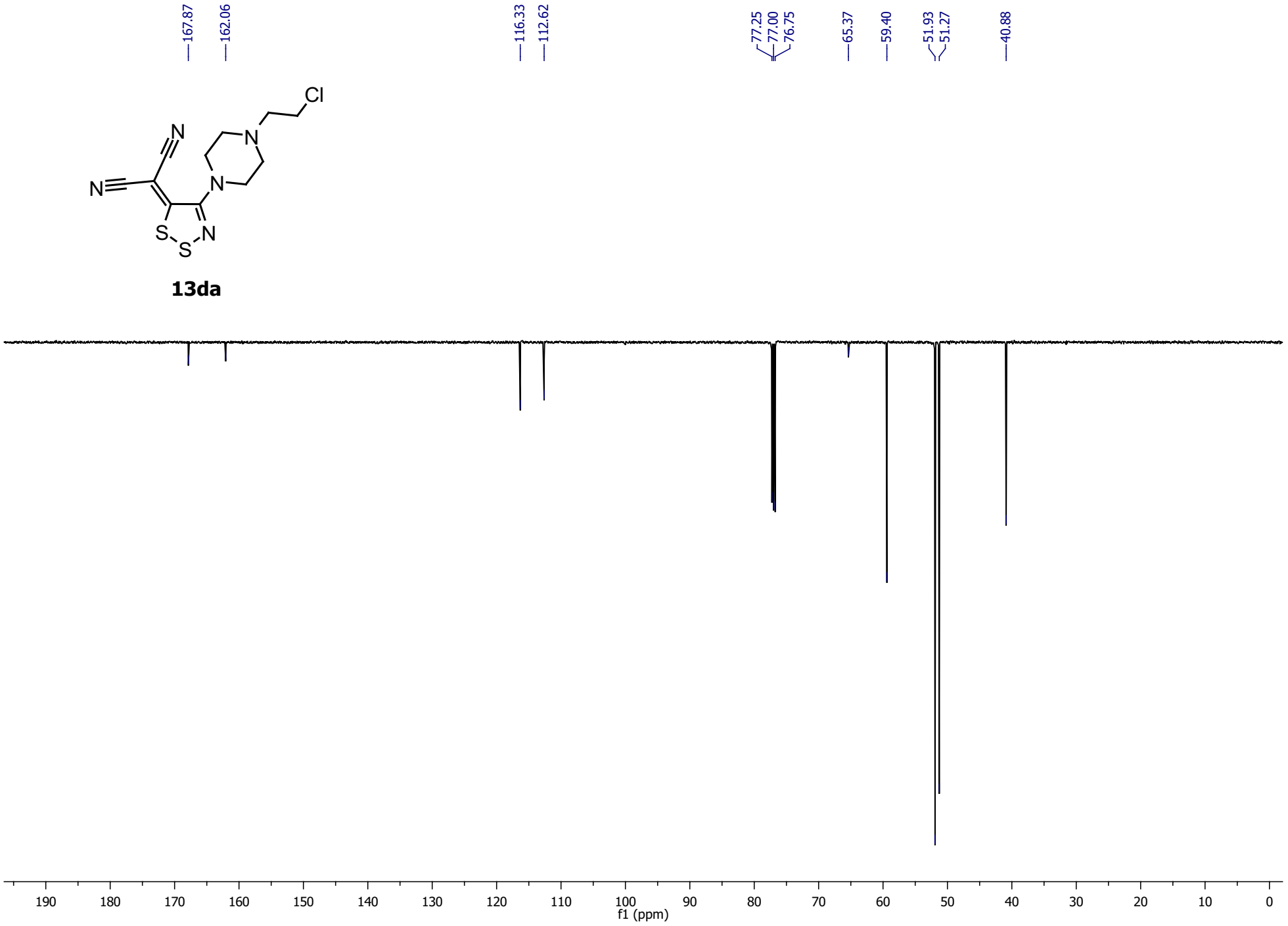
13c

2-{4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}malononitrile (**13da**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

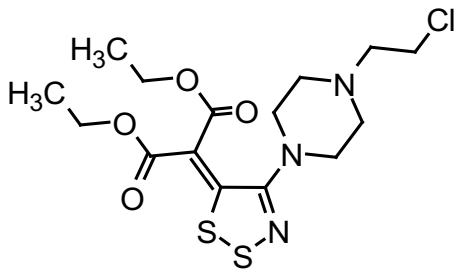


13da

2-{4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}malononitrile (**13da**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

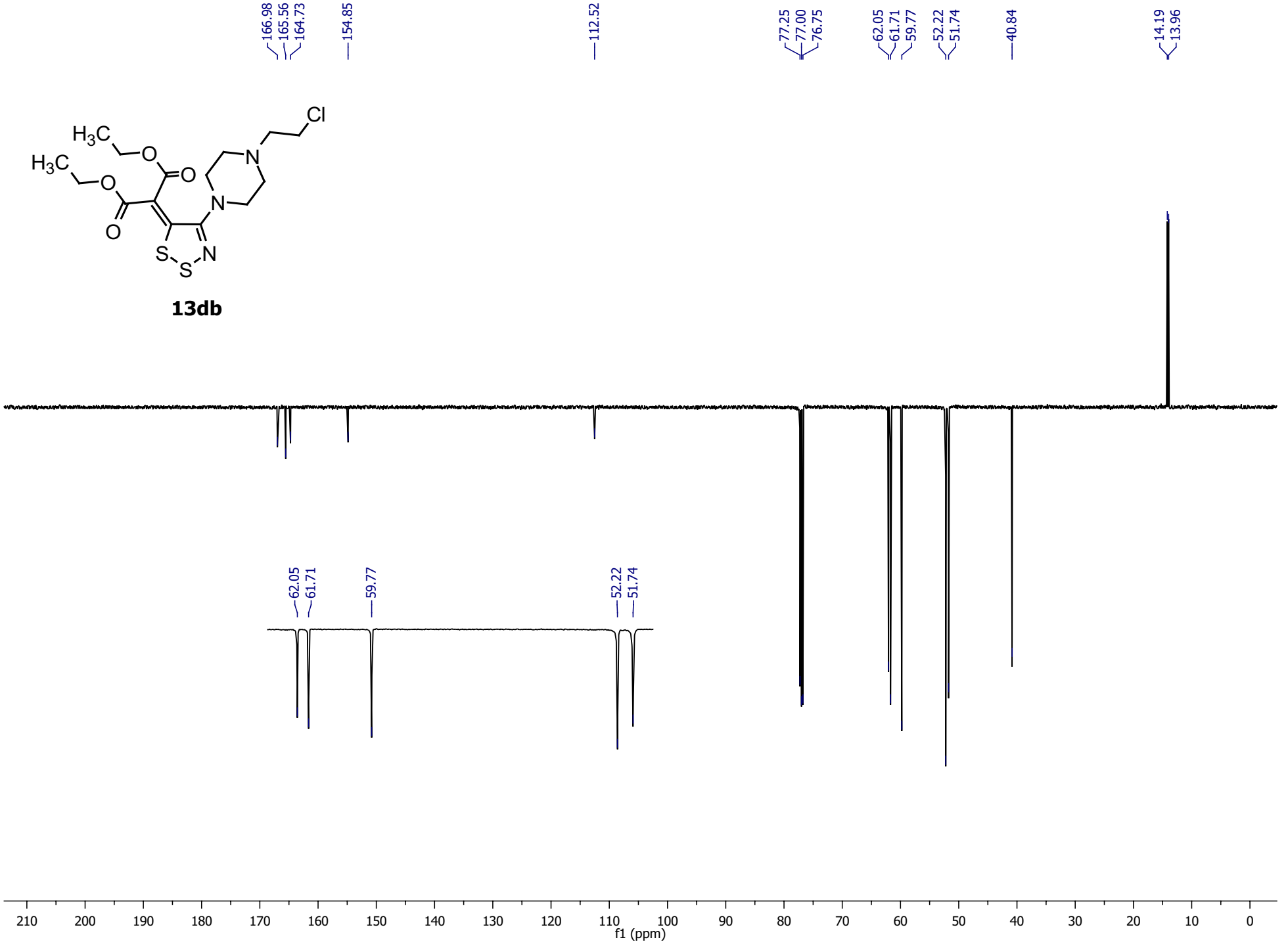


Diethyl 2-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}malonate (**13db**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



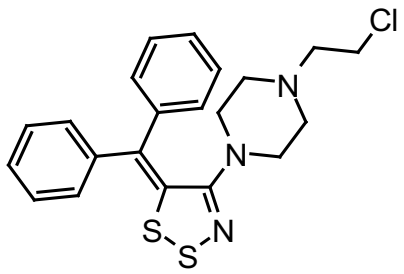
13db

Diethyl 2-{4-[*N*-(2-chloroethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}malonate (**13db**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



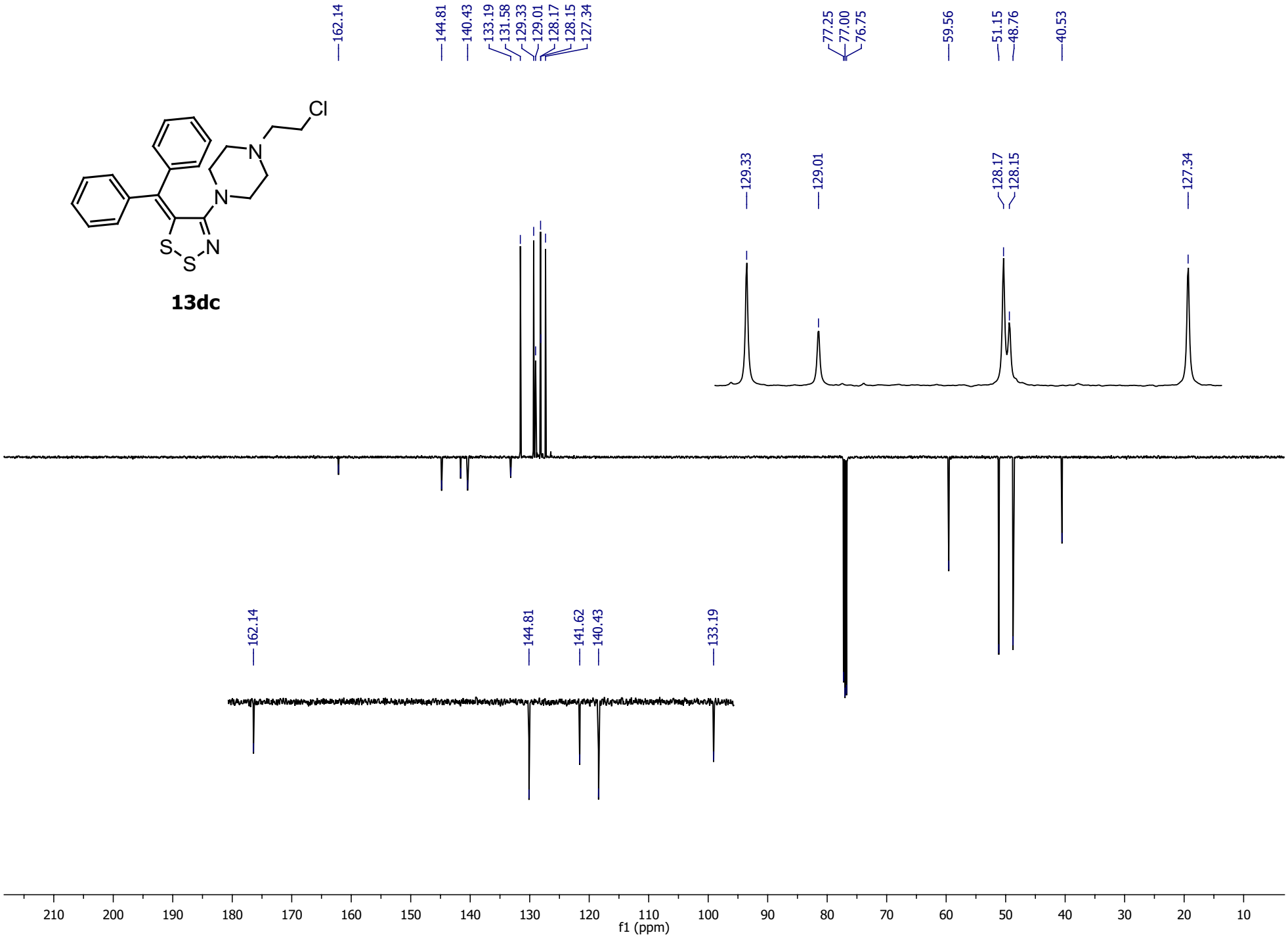
13db

4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5-(diphenylmethylene)-5*H*-1,2,3-dithiazole (**13dc**) (^{1}H-NMR at 65 °C, 500 MHz, CD_3CN)

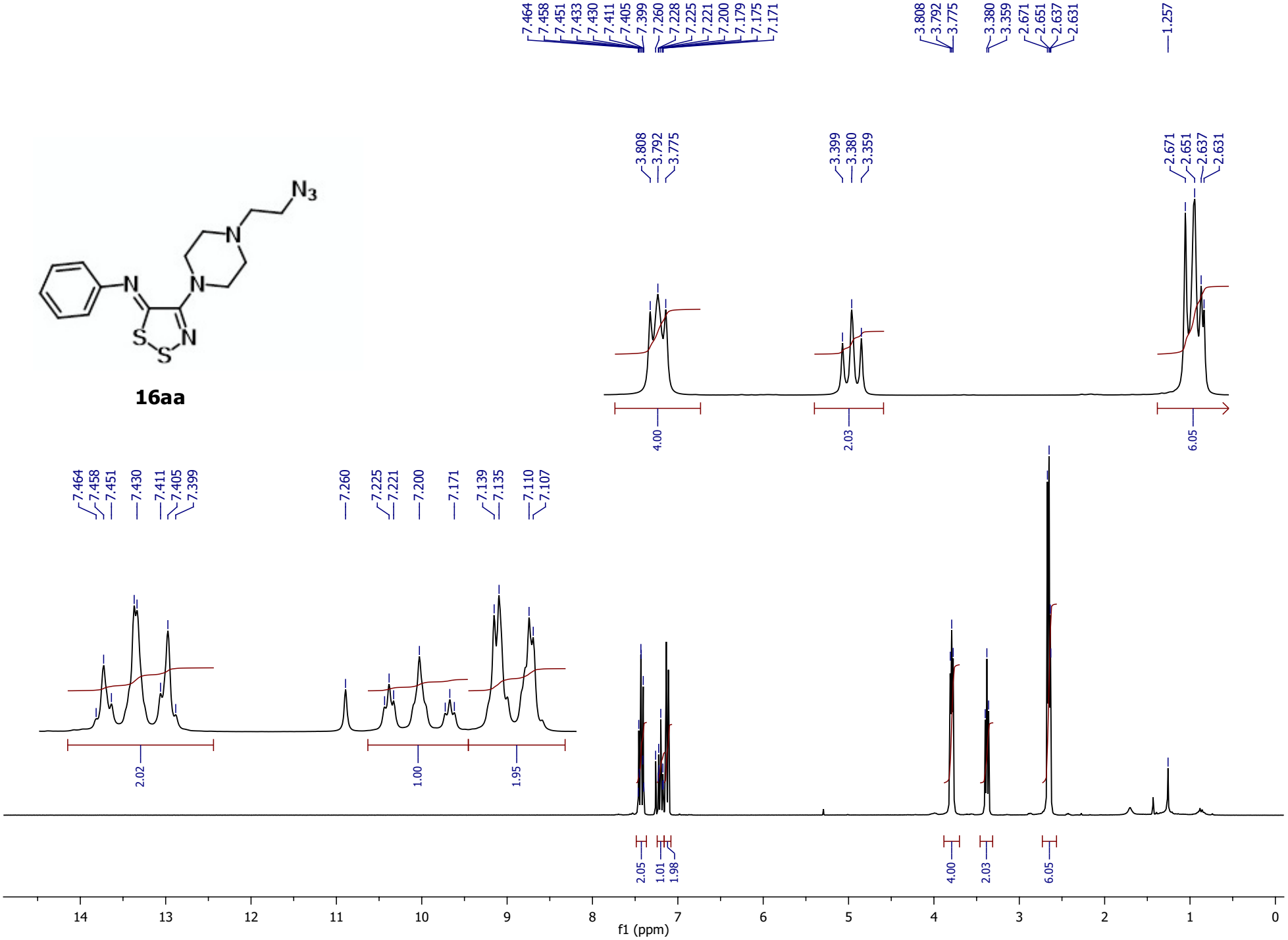


13dc

4-[*N*-(2-Chloroethyl)piperazin-1-yl]-5-(diphenylmethylene)-5*H*-1,2,3-dithiazole (**13dc**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

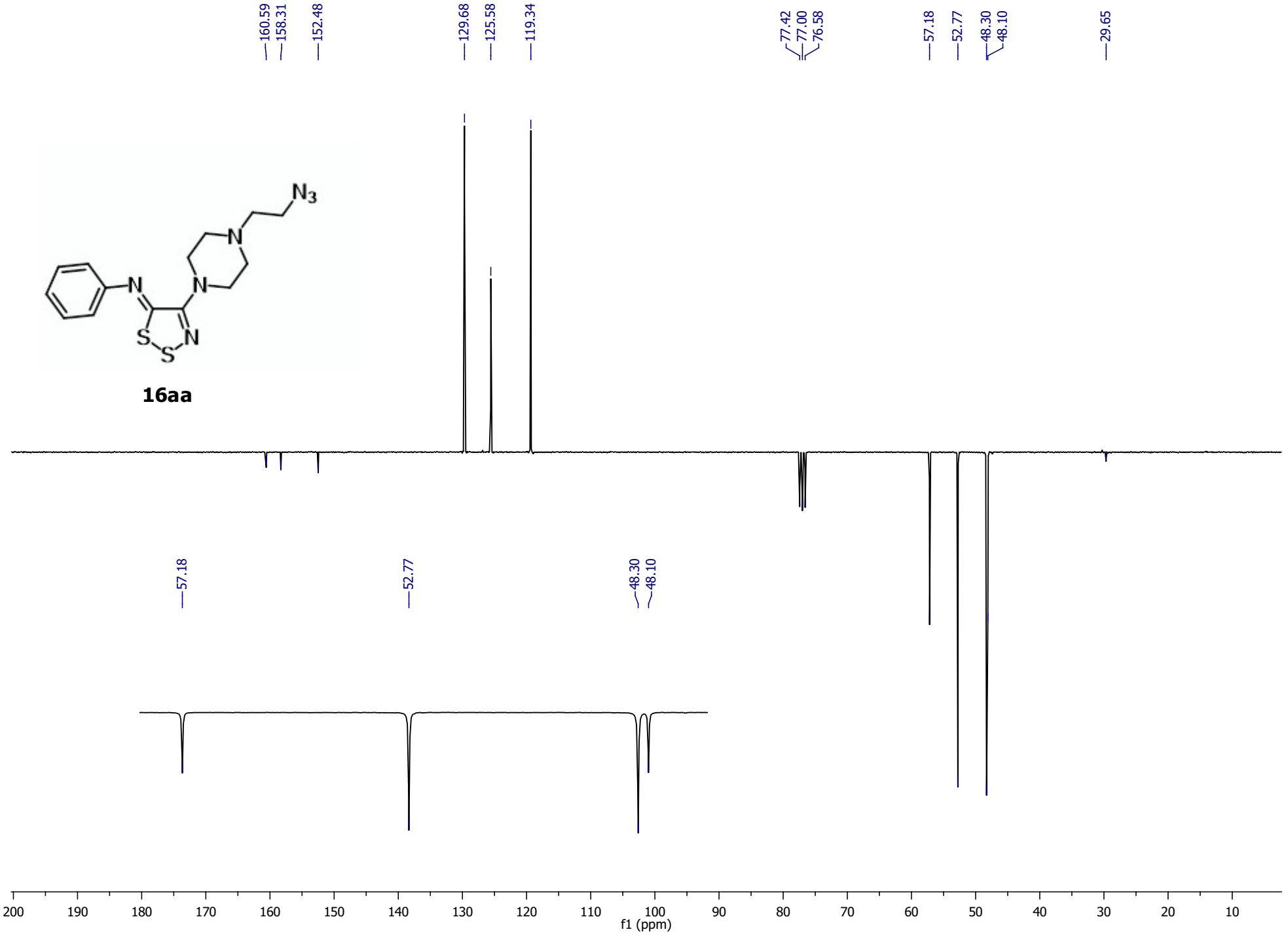


N-{4-[*N*-(2-Azidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16aa**) (^{1}H-NMR, 300 MHz, $CDCl_3$)

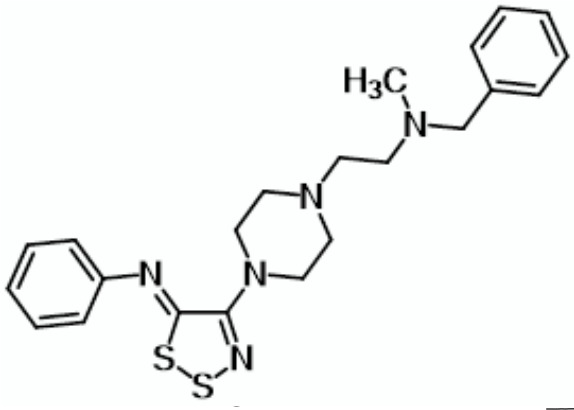


16aa

N-{4-[*N*-(2-Azidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16aa**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

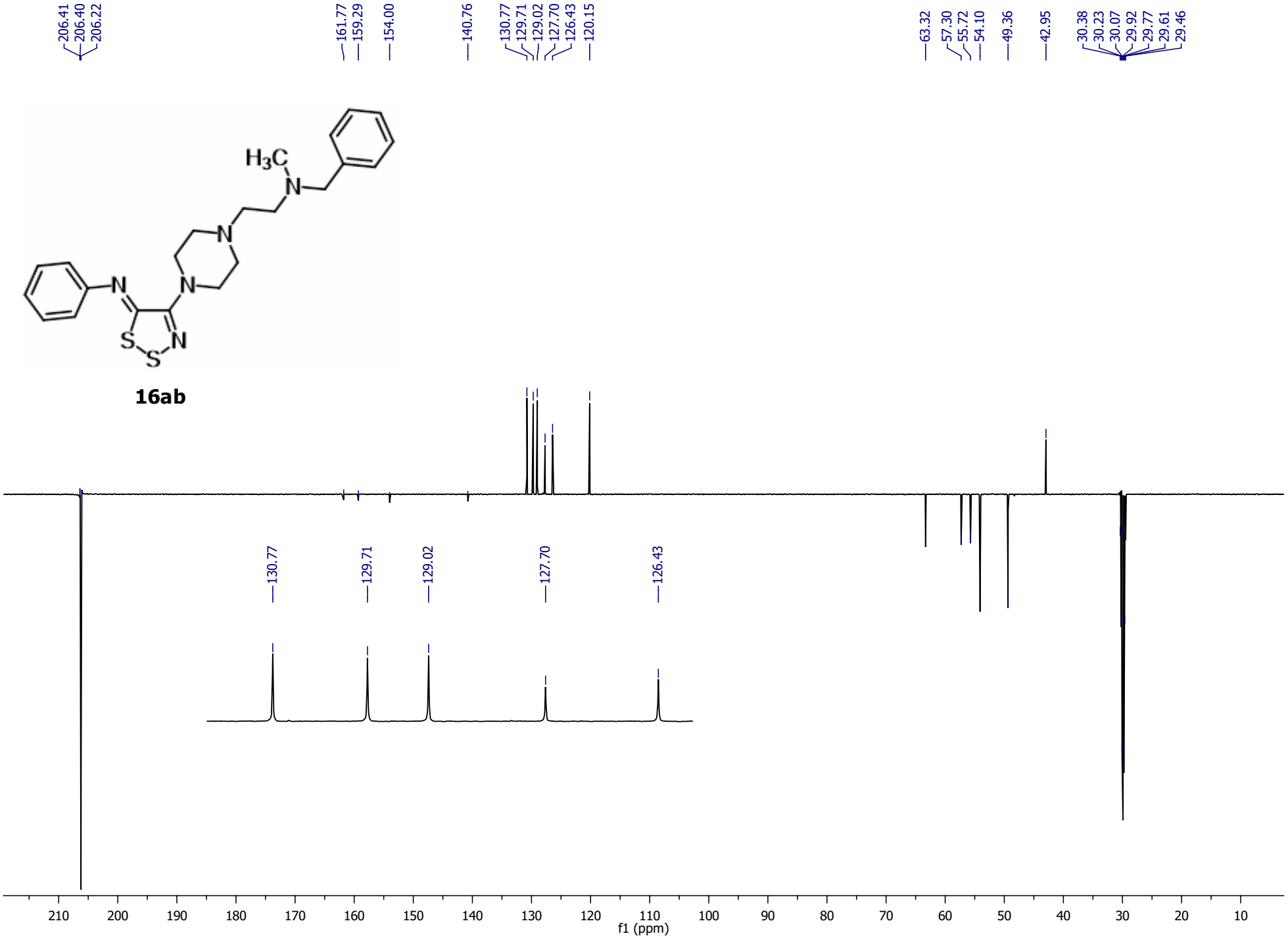


N-[4-(*N*-{2-[Benzyl(methyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-ylidene]aniline (**16ab**) (^{1}H-NMR, 500 MHz, acetone-d_6)

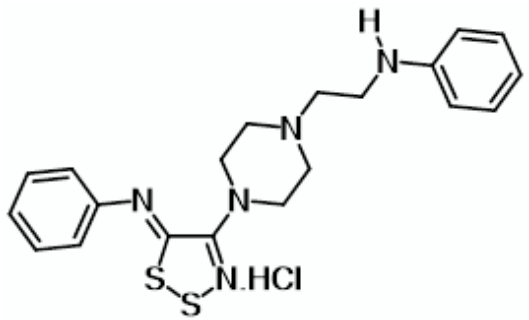


16ab

N-[4-(*N*-{2-[Benzyl(methyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-ylidene]aniline (**16ab**) (^{13}C-NMR, 125 MHz, acetone-d_6)

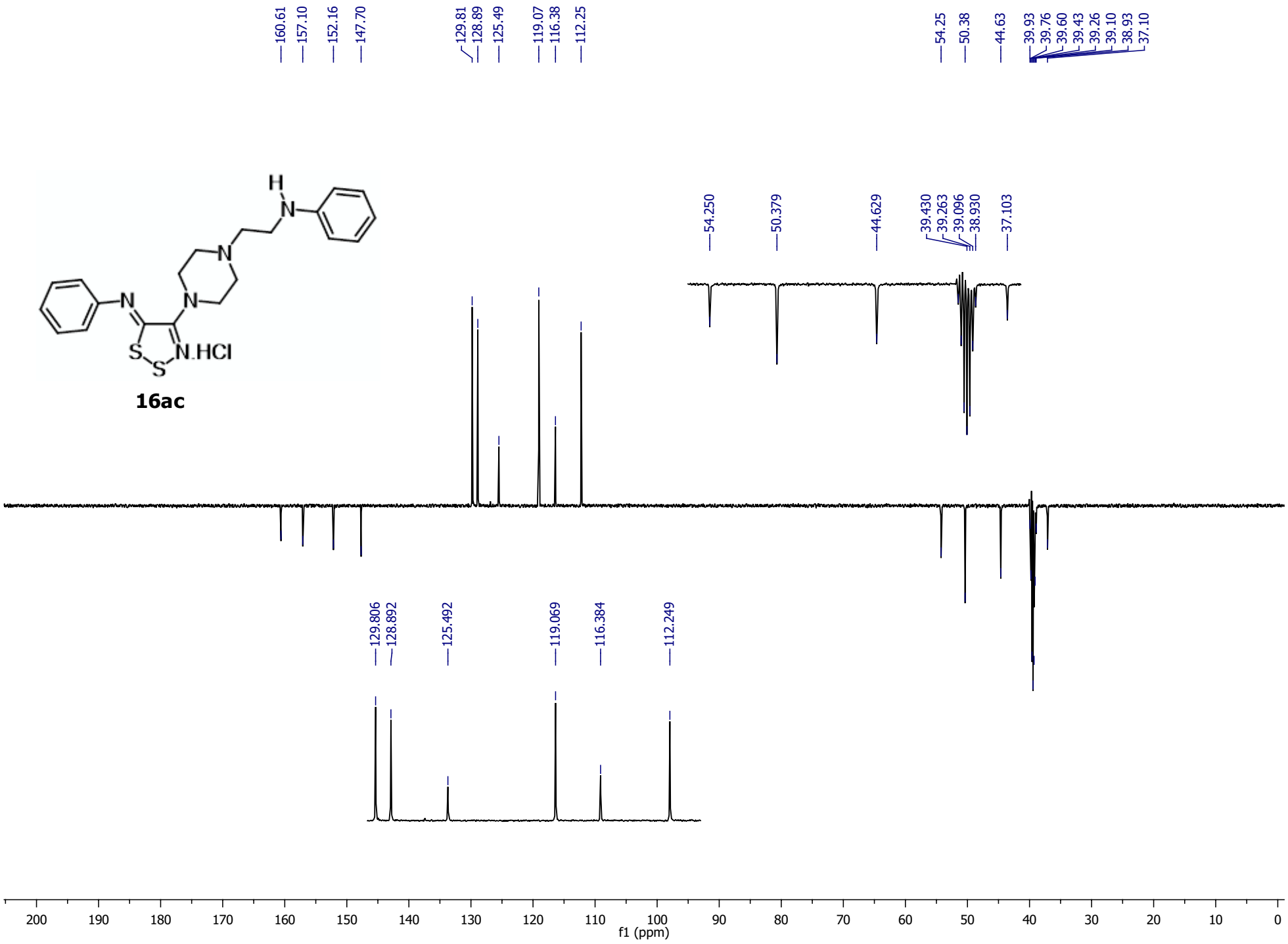


N-(4-{*N*-[2-(Phenylamino)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazol-5-ylidene)aniline hydrochloride (**16ac**)
(^{1}H-NMR at 80 °C, 500 MHz, DMSO-d_6)



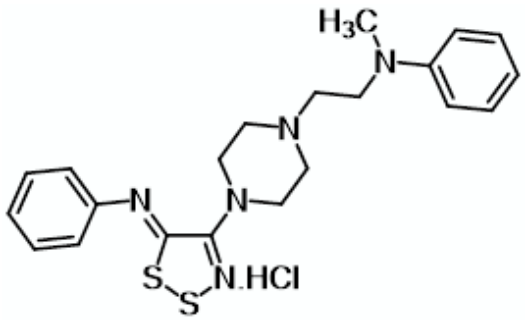
16ac

N-(4-{*N*-[2-(Phenylamino)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazol-5-ylidene)aniline hydrochloride (**16ac**) (^{13}C-NMR, 125 MHz, DMSO-d_6)



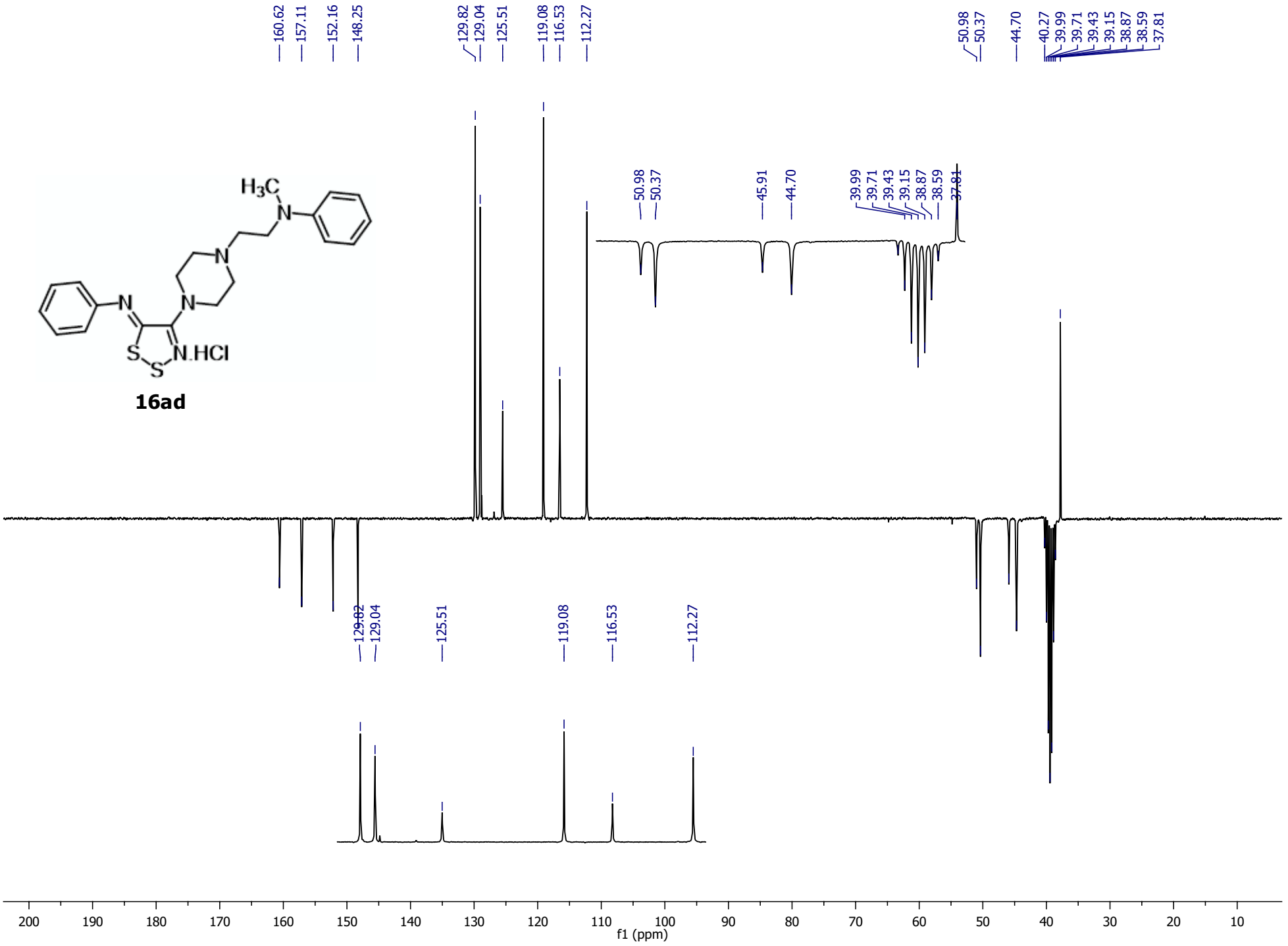
16ac

N-[4-(*N*-{2-[Methyl(phenyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-ylidene]aniline hydrochloride (**16ad**)
(^{1}H-NMR at 80 °C, 500 MHz, DMSO-d_6)



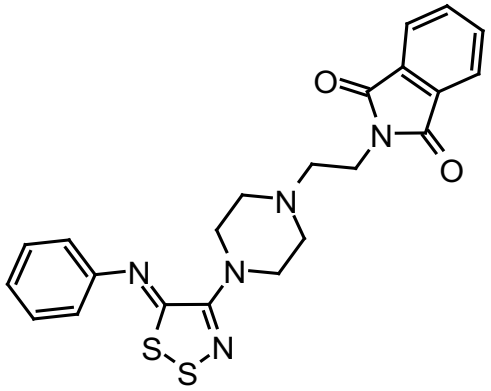
16ad

N-[4-(*N*-{2-[Methyl(phenyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-ylidene]aniline hydrochloride (**16ad**) (^{13}C-NMR, 75 MHz, DMSO-d_6)



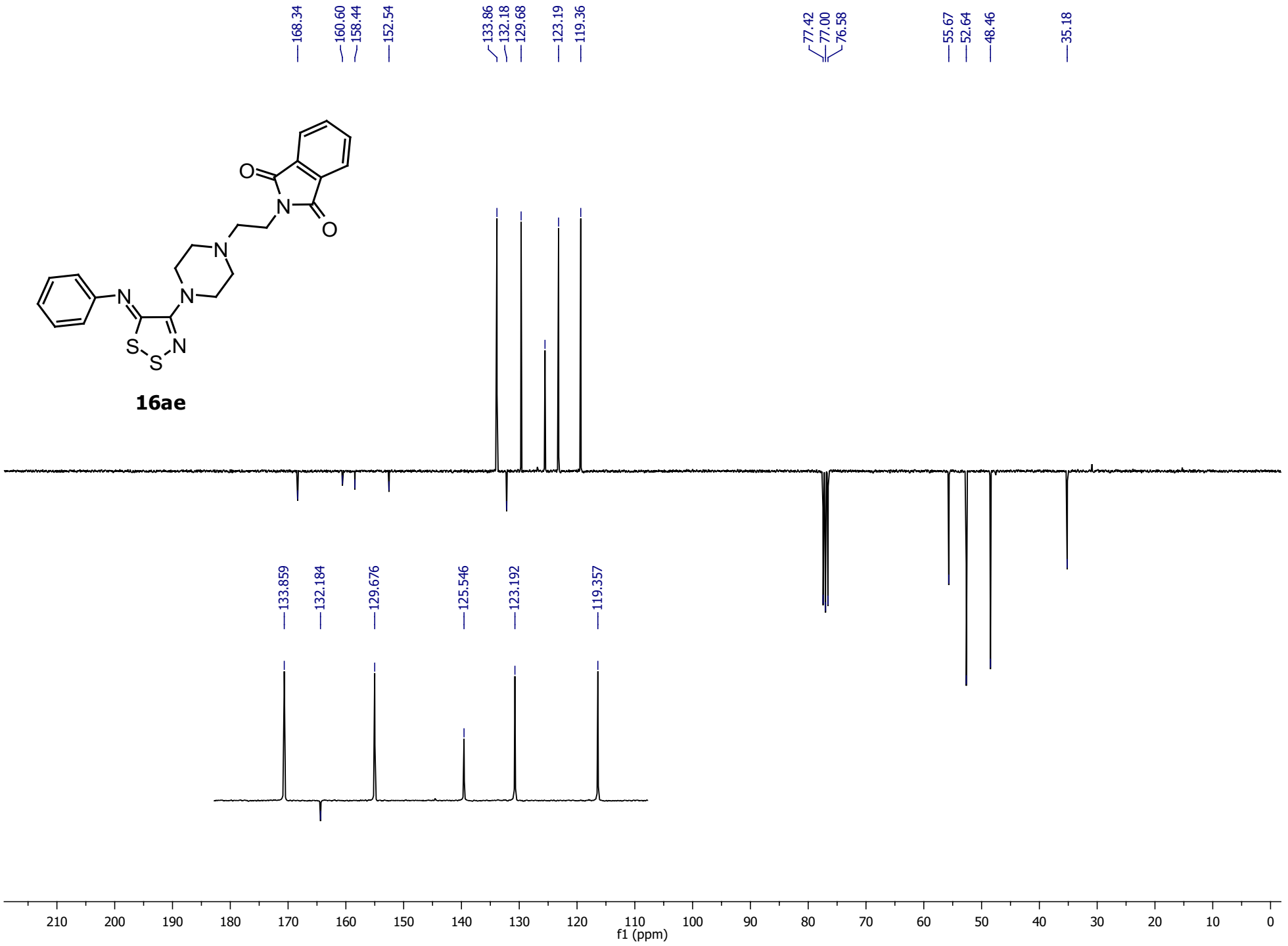
16ad

N-{4-[*N*-(2-Phthalimidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16ae**) (^{1}H-NMR, 300 MHz, $CDCl_3$)



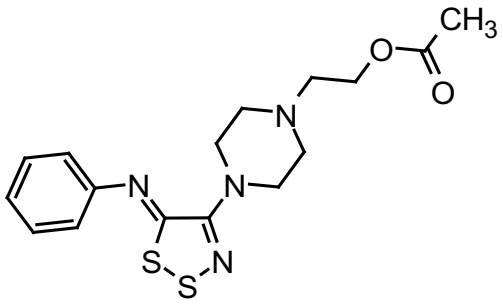
16ae

N-{4-[*N*-(2-Phthalimidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16ae**) (^{13}C-NMR, 75 MHz, $CDCl_3$)



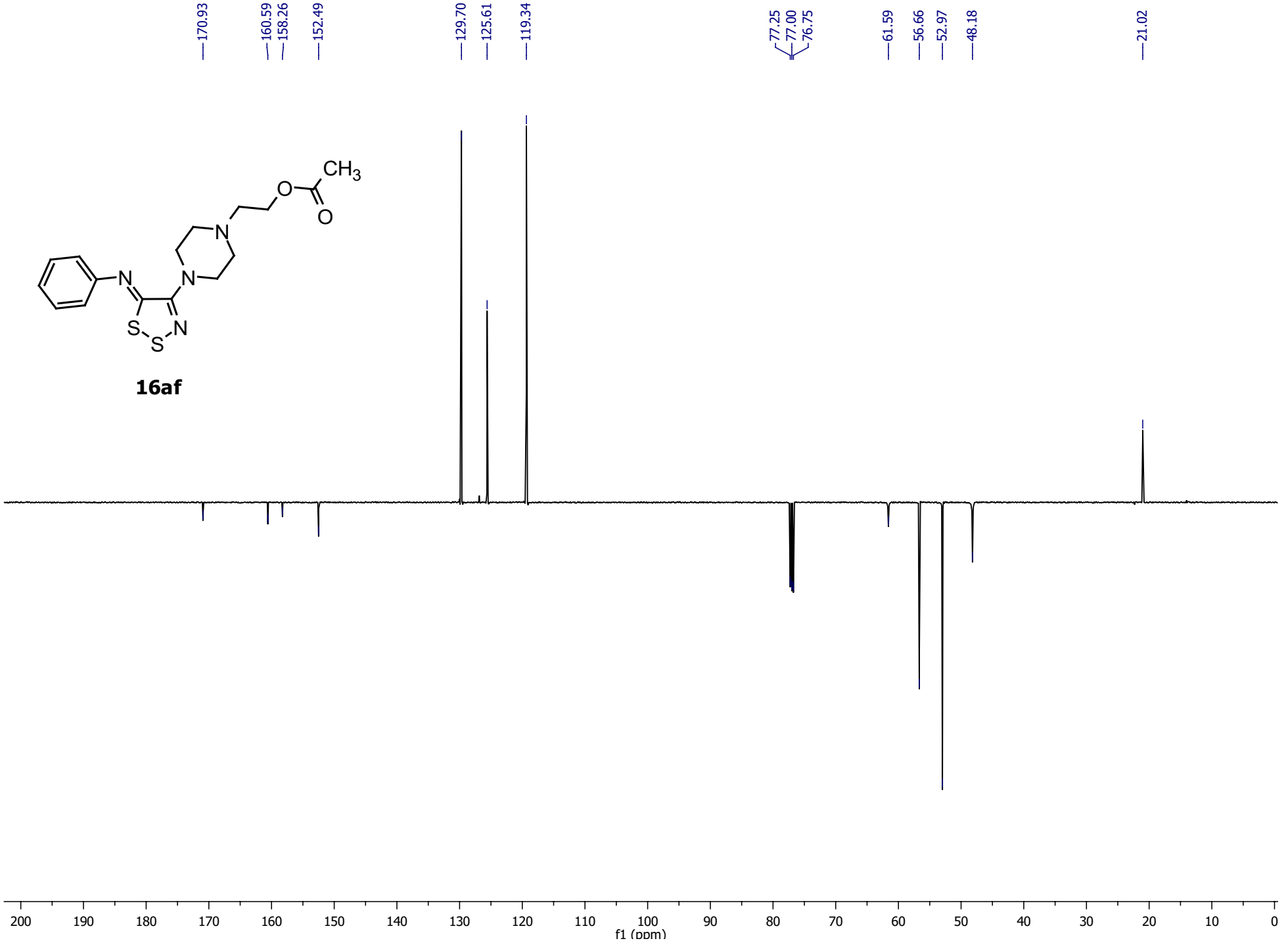
16ae

N-{4-[*N*-(2-Acetoxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16af**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

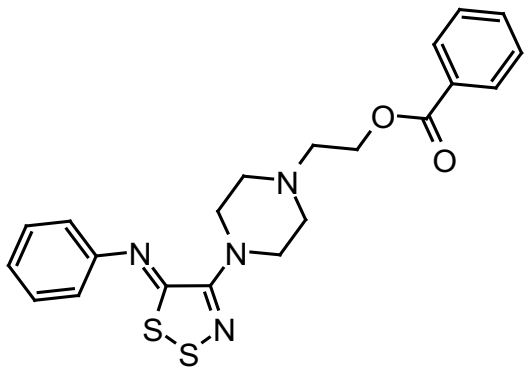


16af

N-{4-[*N*-(2-Acetoxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16af**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

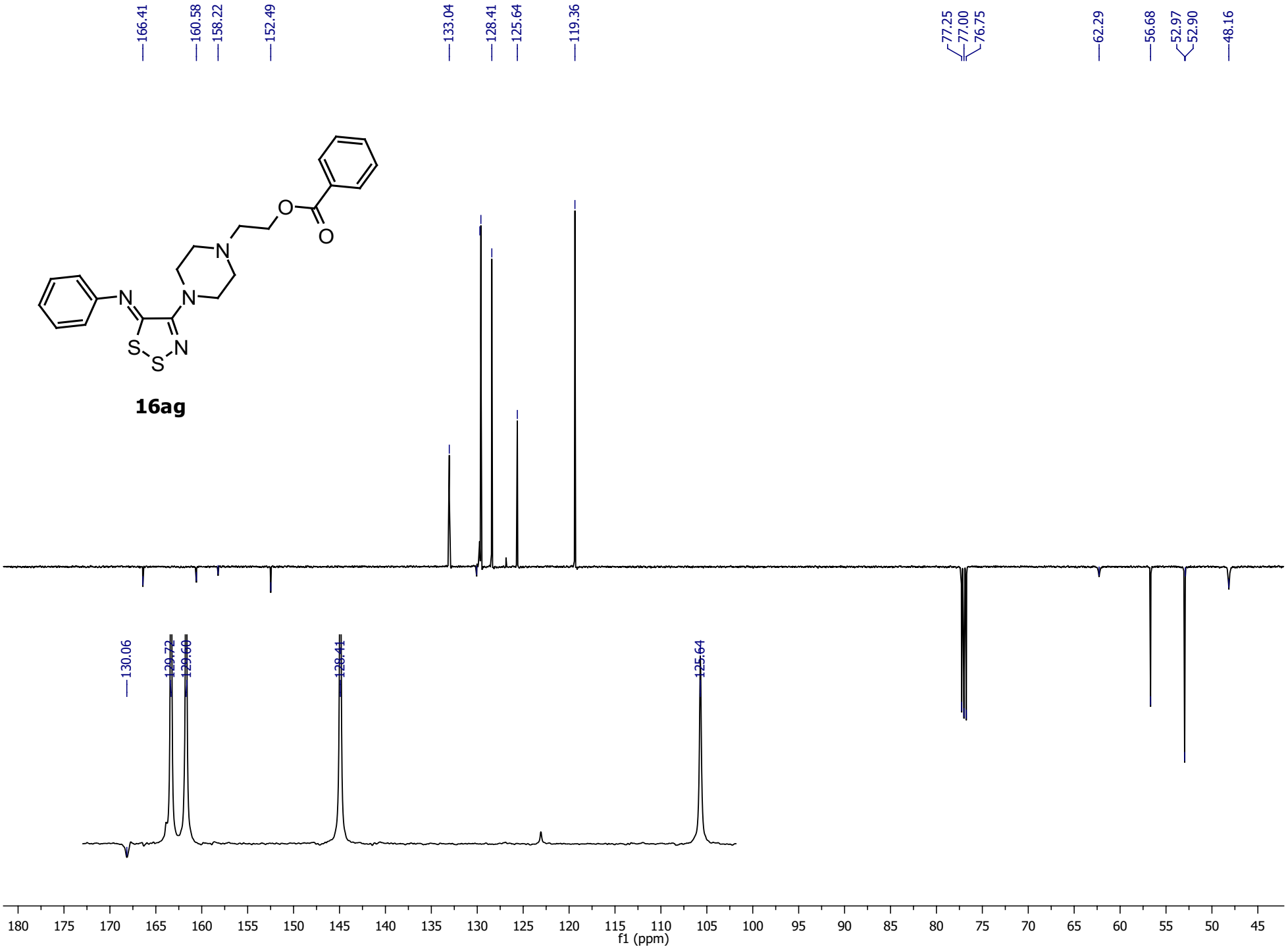


N-{4-[*N*-(2-Benzoyloxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16ag**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



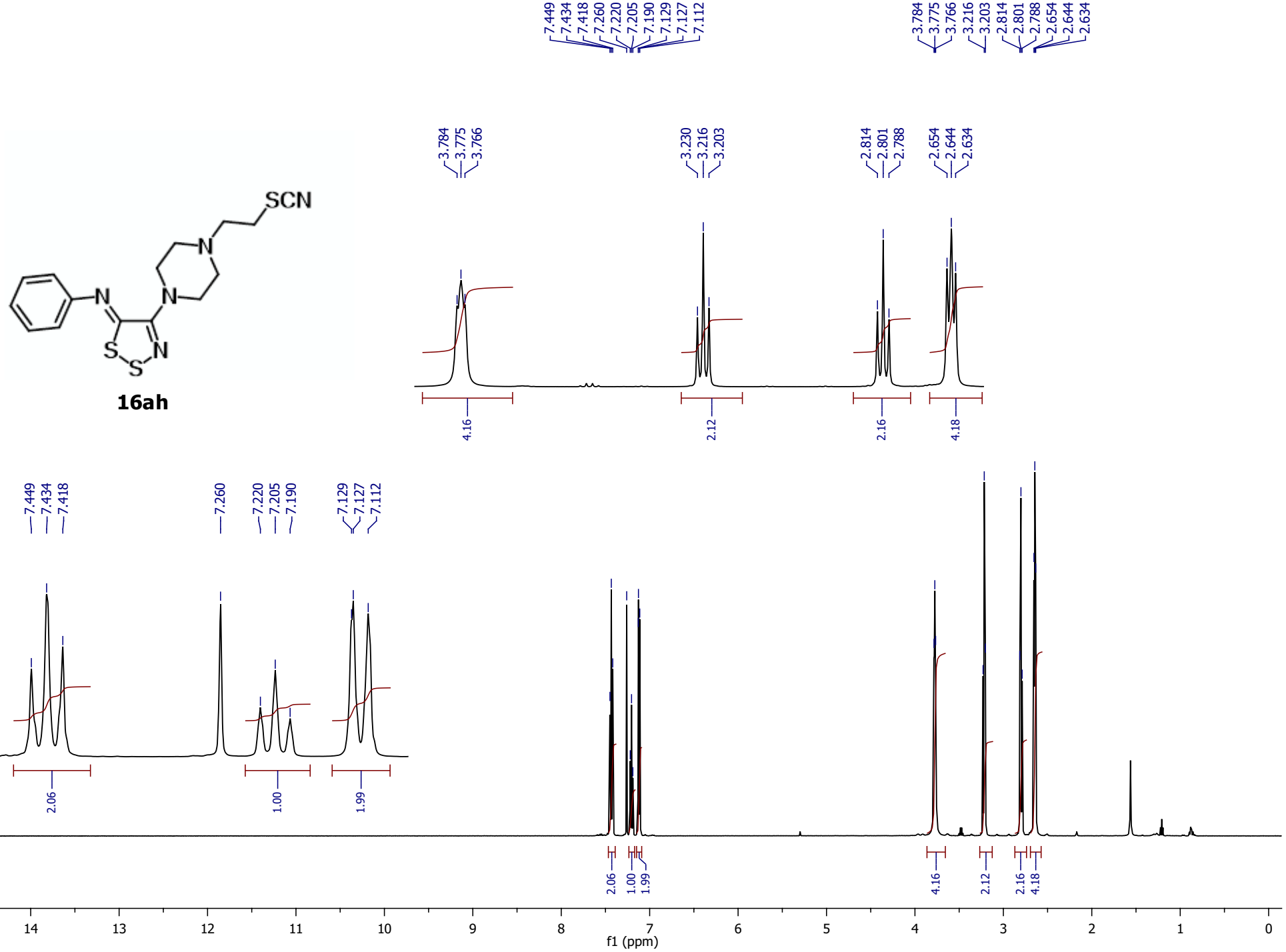
16ag

N-{4-[*N*-(2-Benzoyloxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16ag**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

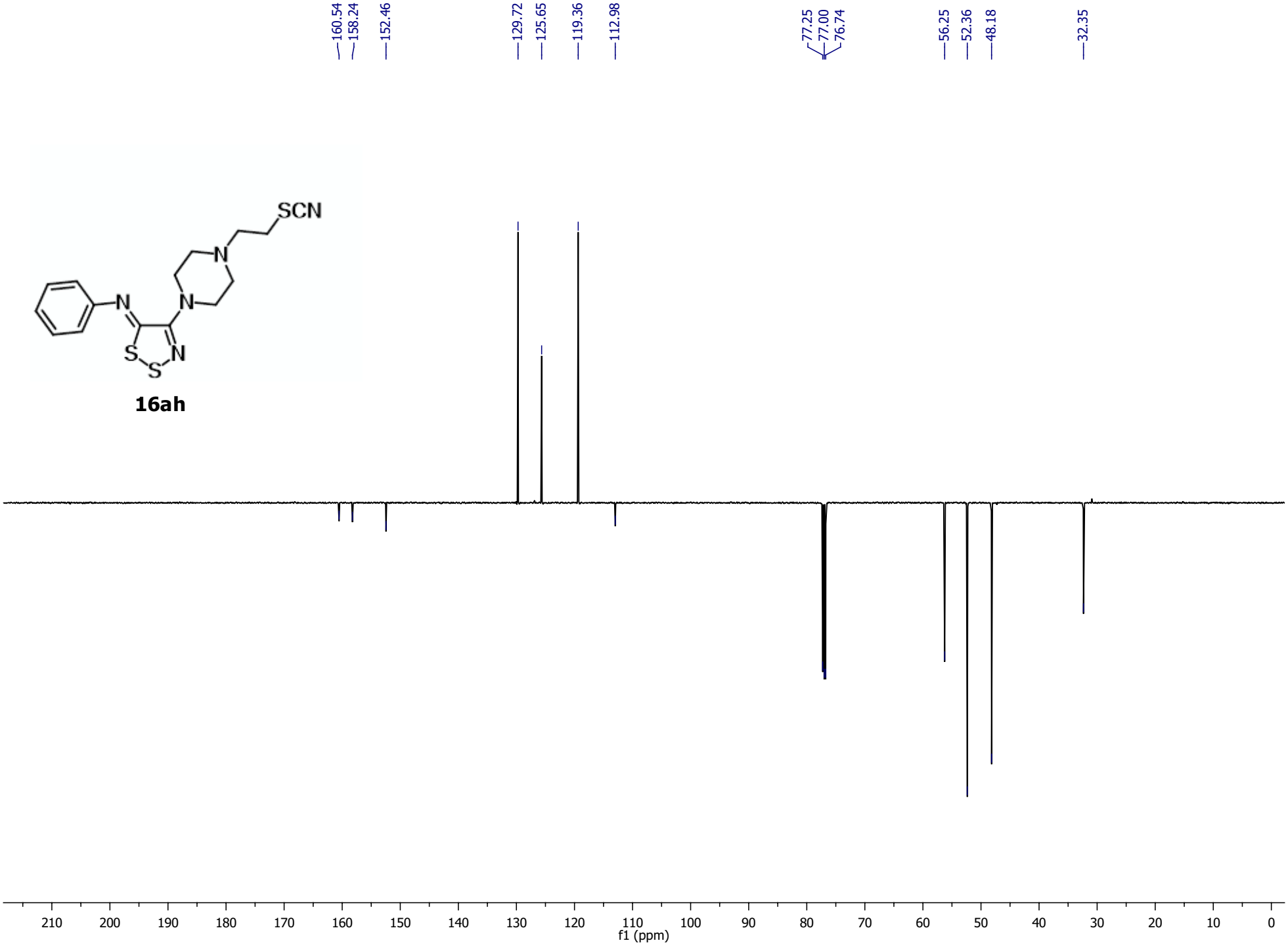


16ag

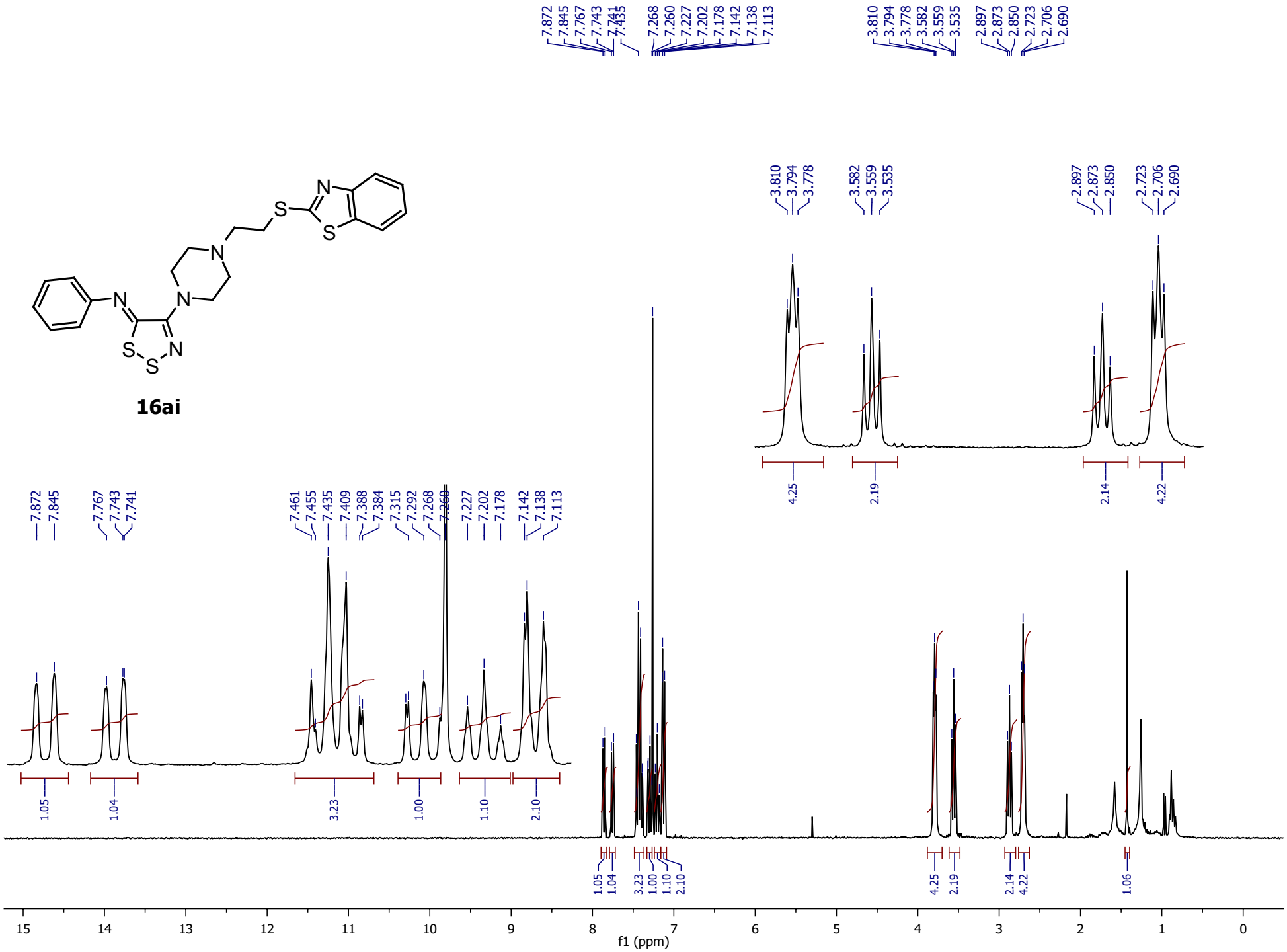
N-{4-[*N*-(2-Thiocyanatoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16ah**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



N-{4-[*N*-(2-Thiocyanatoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-ylidene}aniline (**16ah**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

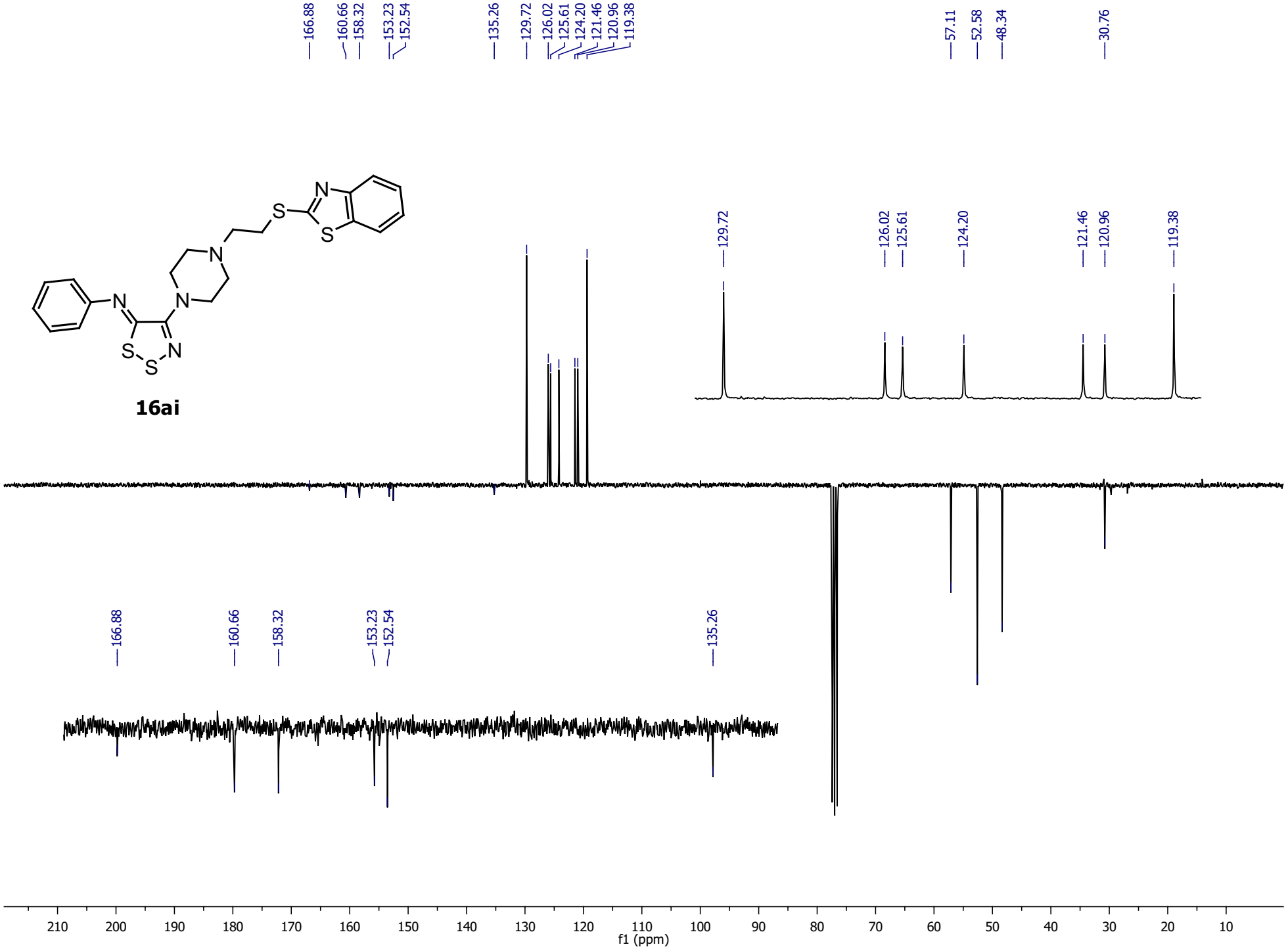


N-(4-{*N*-[2-(Benzo[*d*]thiazol-2-ylthio)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazol-5-ylidene)aniline (**16ai**) (^{1}H-NMR, 300 MHz, $CDCl_3$)

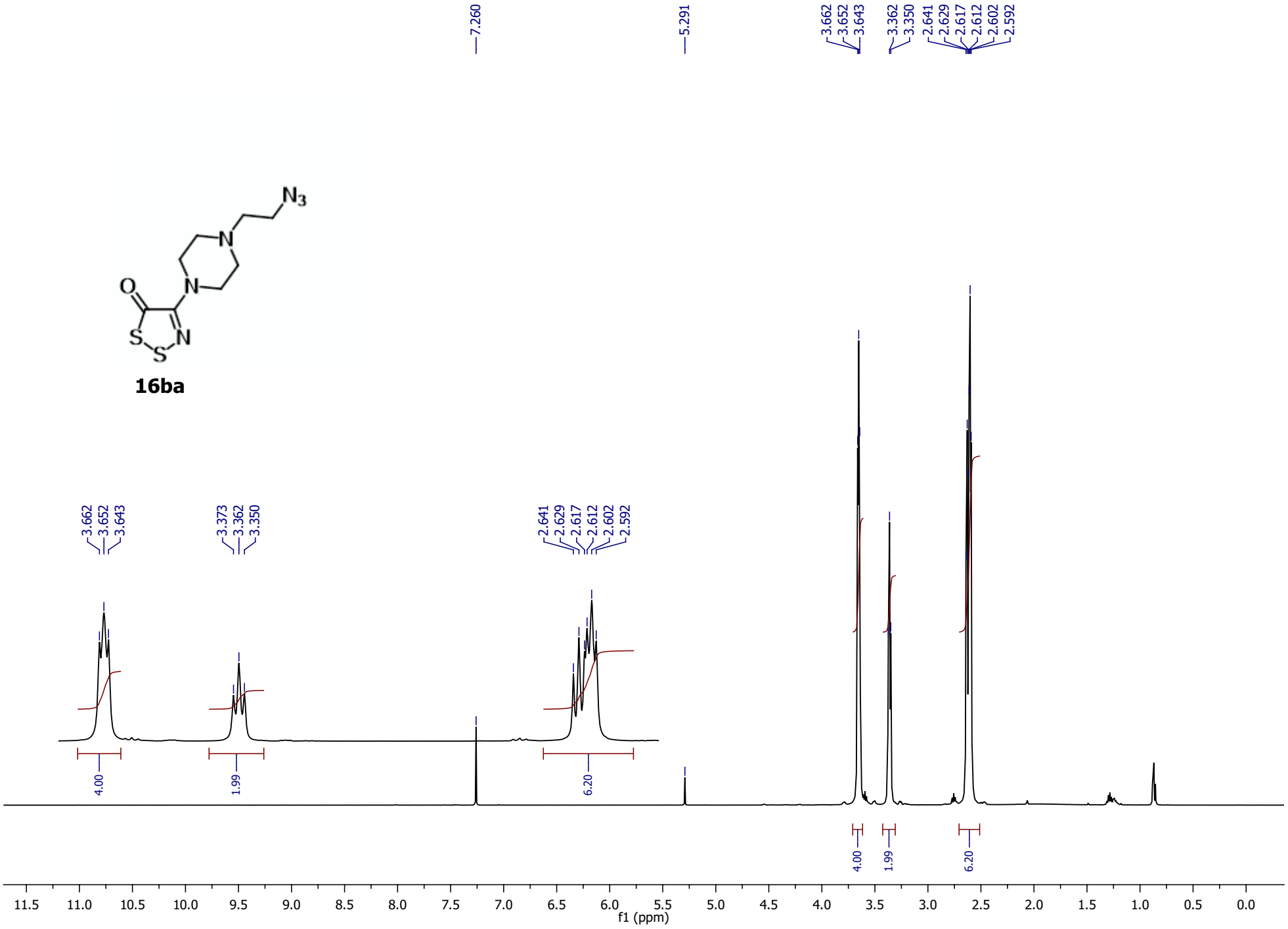


16ai

N-(4-{*N*-[2-(Benzo[*d*]thiazol-2-ylthio)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazol-5-ylidene)aniline (**16ai**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

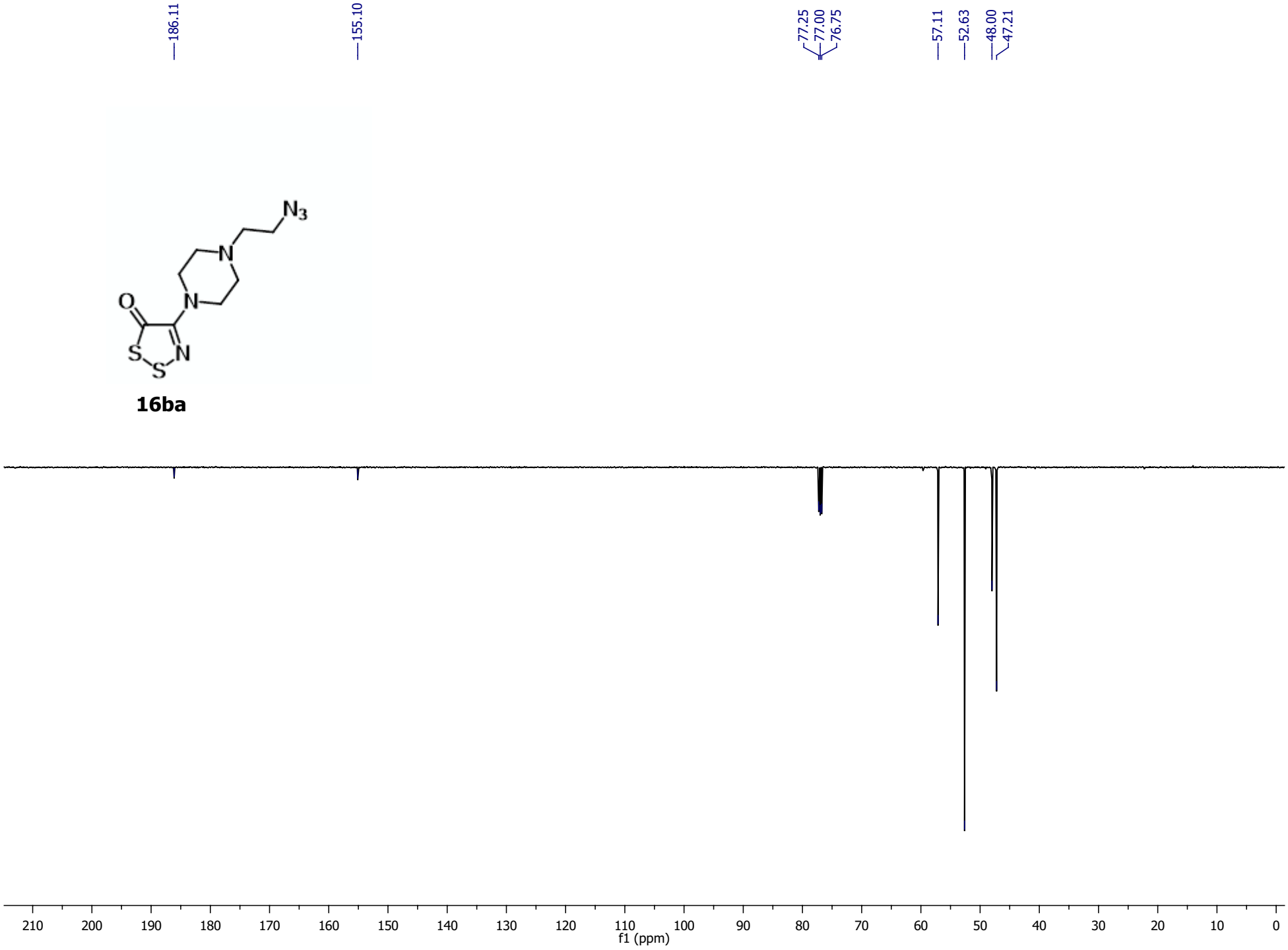


4-[*N*-(2-Azidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16ba**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



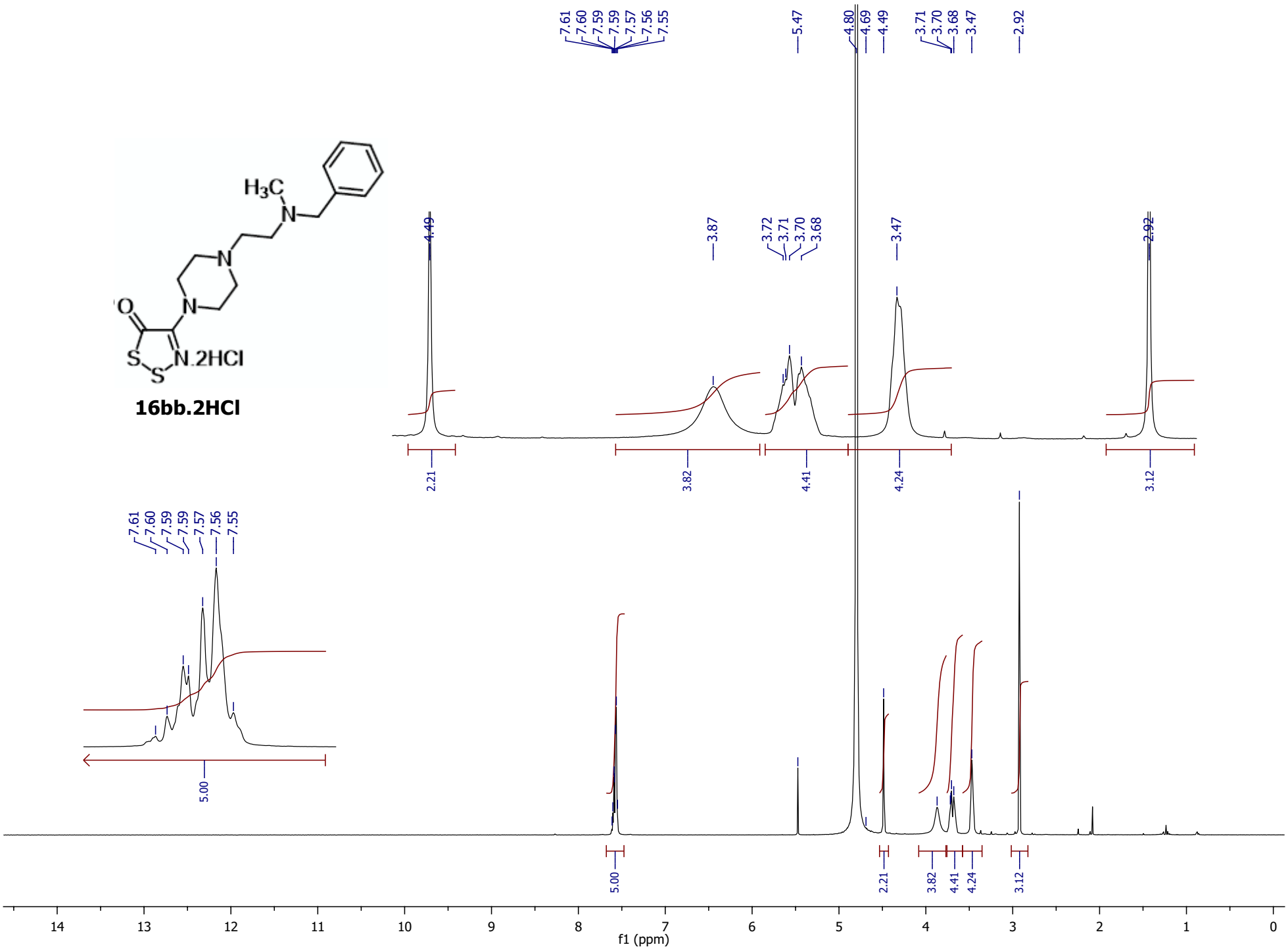
16ba

4-[*N*-(2-Azidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16ba**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



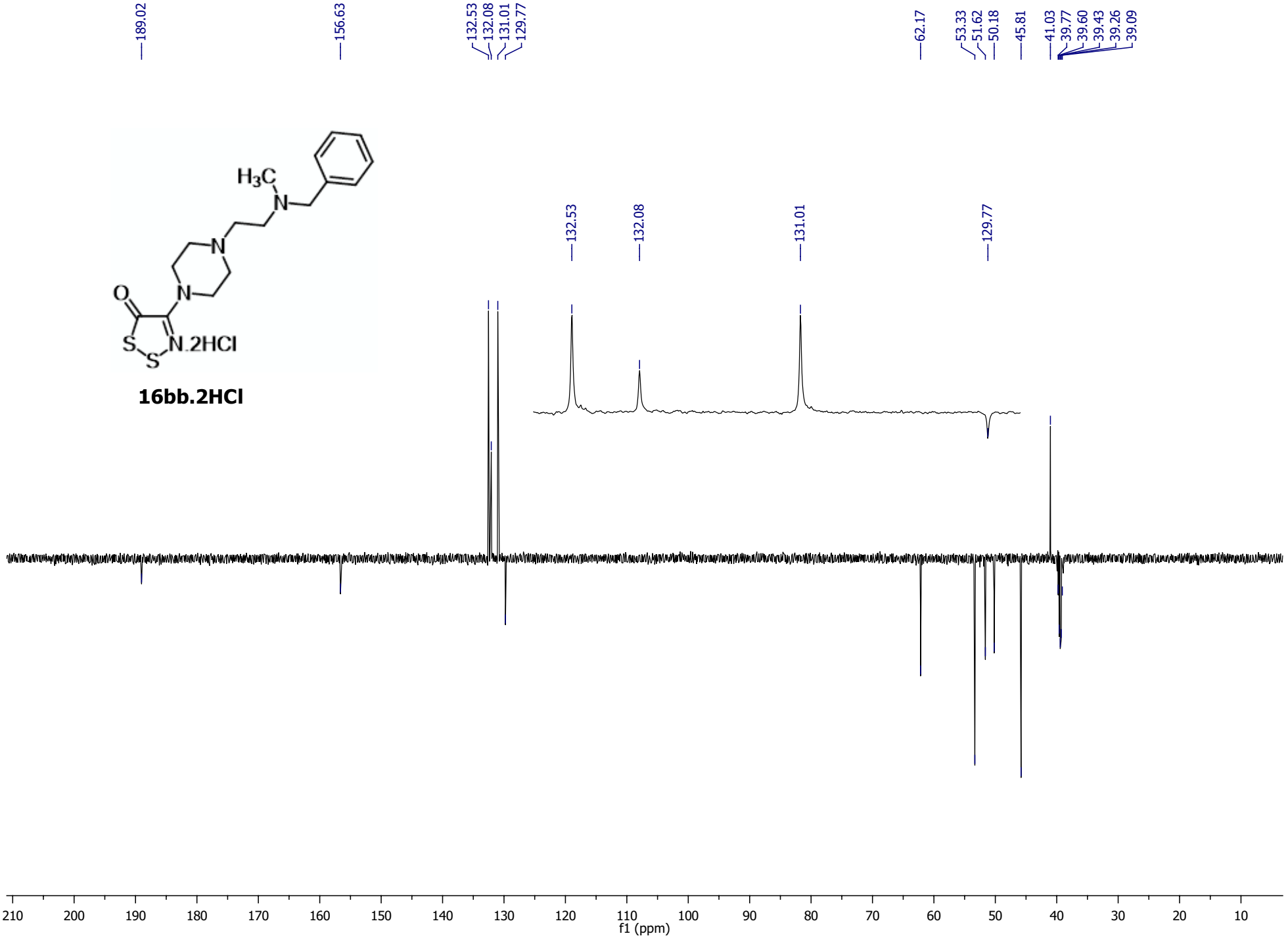
16ba

4-(*N*-{2-[Benzyl(methyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-one diydrochloride (**16bb.2HCl**) (^{1}H-NMR, 500 MHz, D_2O)

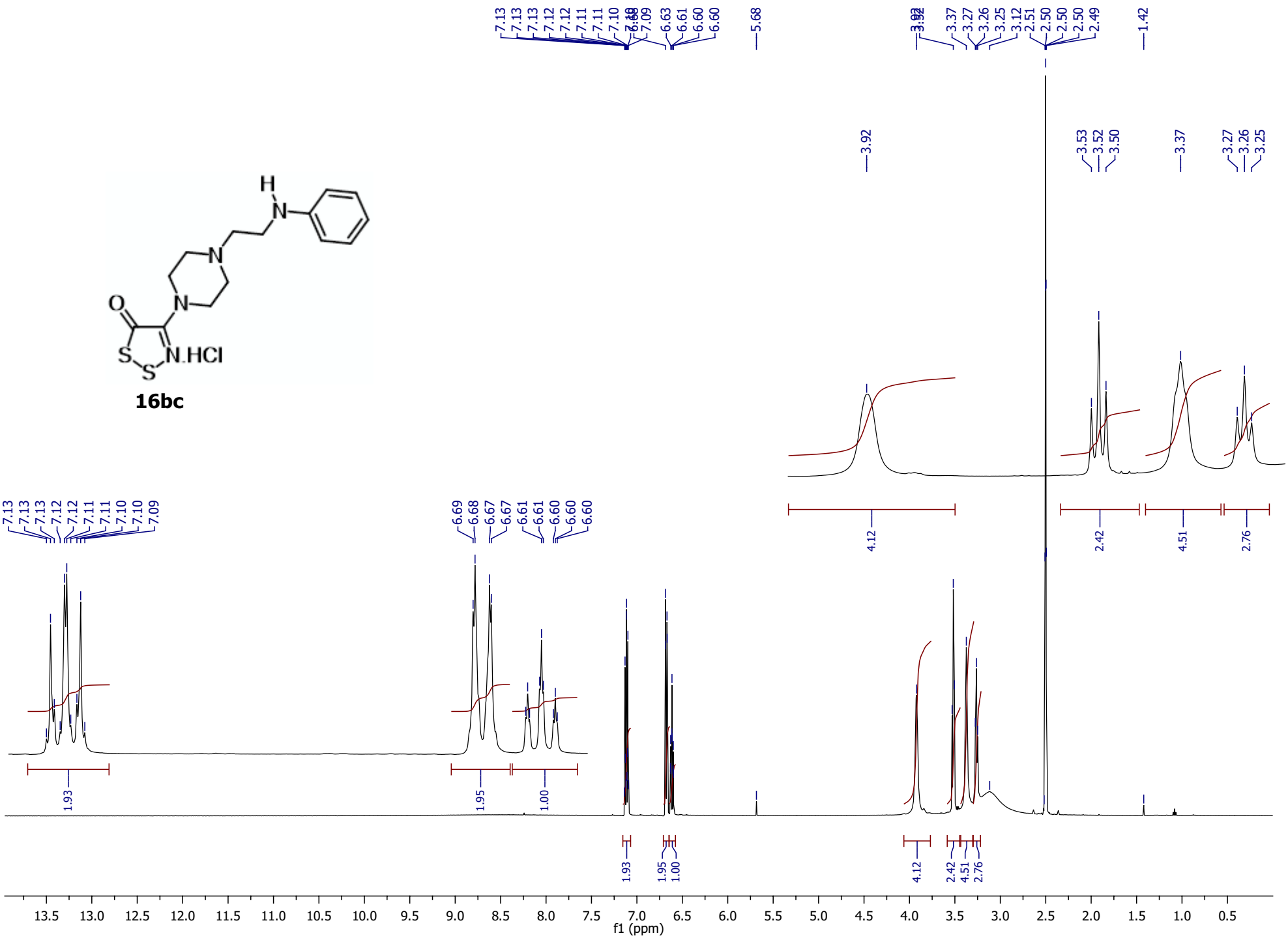


16bb.2HCl

4-(*N*-{2-[Benzyl(methyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-one diydrochloride (**16bb.2HCl**) (^{13}C-NMR, 125 MHz, D_2O + DMSO-d_6)

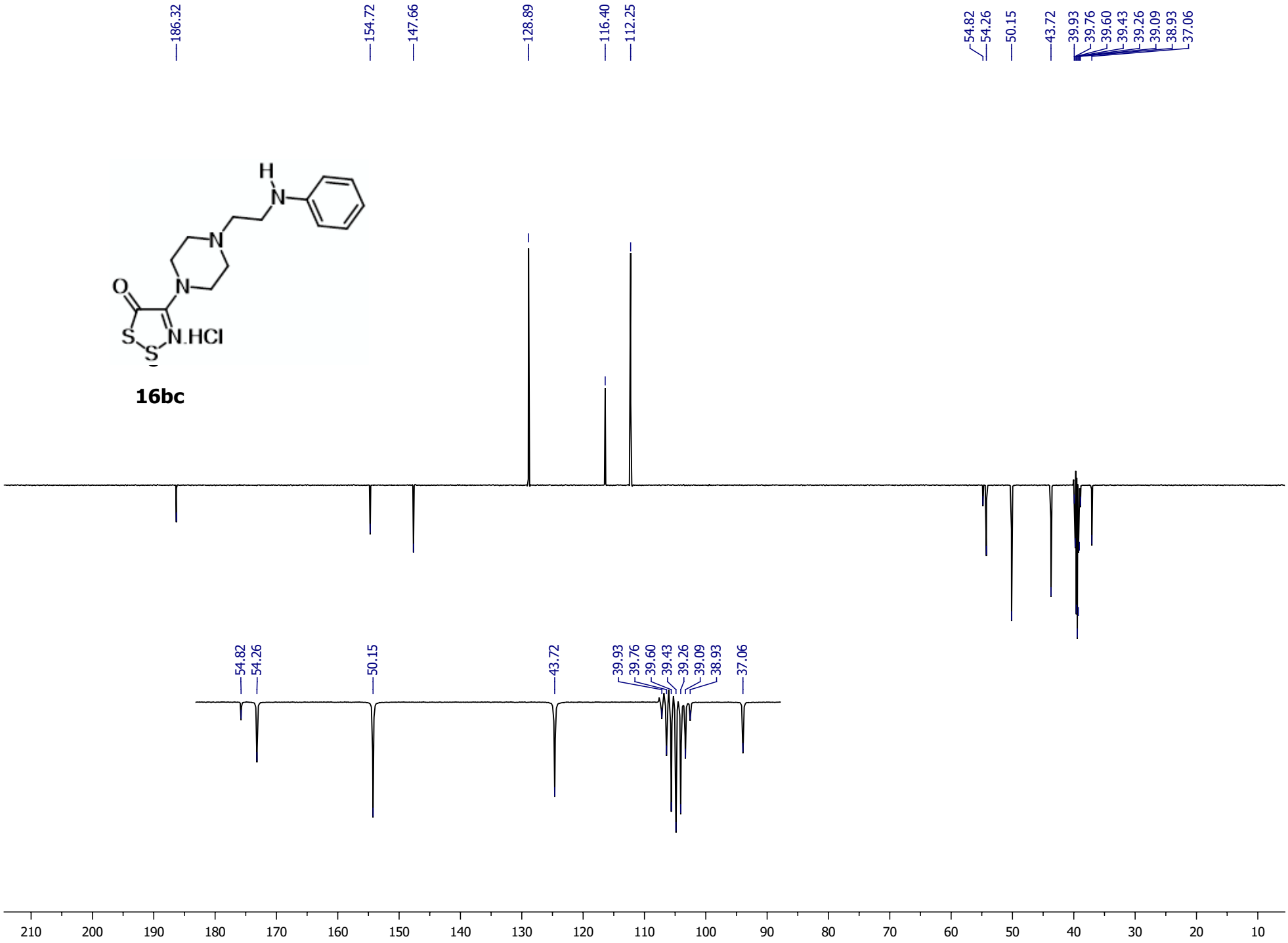


4-{*N*-[2-(Phenylamino)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazol-5-one hydrochloride (**16bc**) (^{1}H-NMR at 80 °C, 500 MHz, DMSO-d_6)

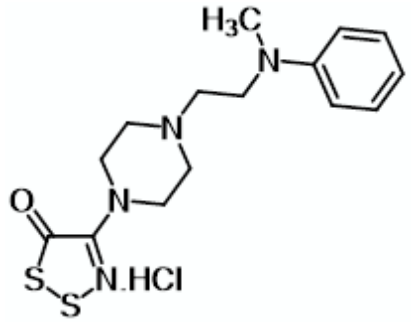


16bc

4-{*N*-[2-(Phenylamino)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazol-5-one hydrochloride (**16bc**) (^{13}C-NMR, 125 MHz, DMSO-d_6)

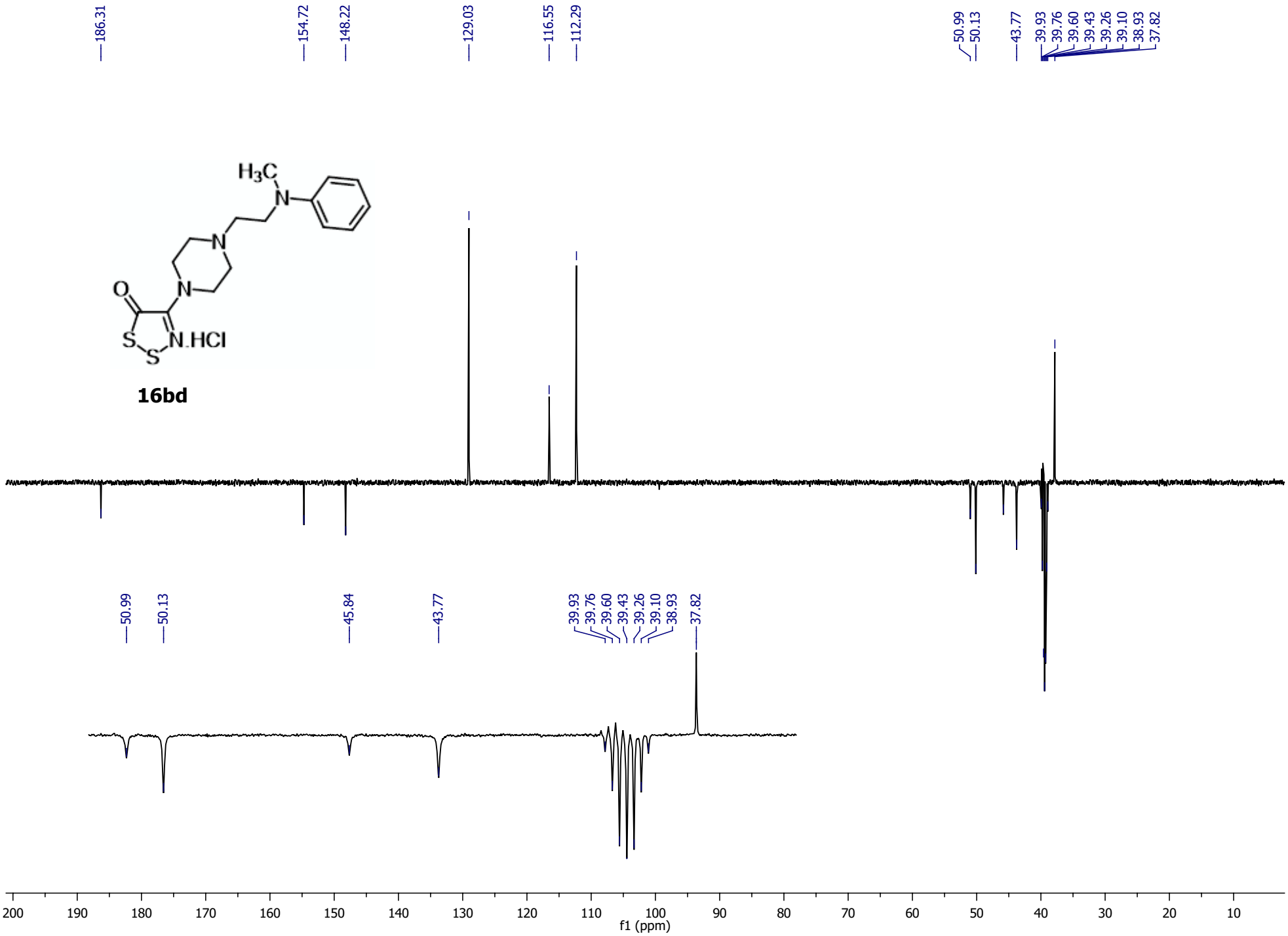


4-(*N*-{2-[Methyl(phenyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-one hydrochloride (**16bd**)
(^{1}H-NMR at 80 °C, 500 MHz, DMSO-d_6)

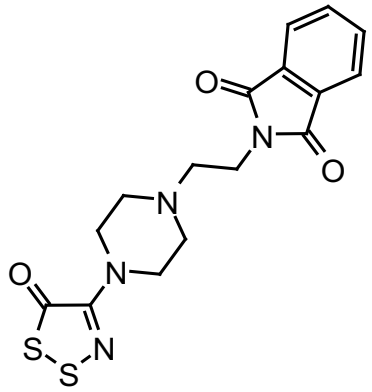


16bd

4-(*N*-{2-[Methyl(phenyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-one hydrochloride (**16bd**) (^{13}C-NMR, 125 MHz, DMSO-d_6)

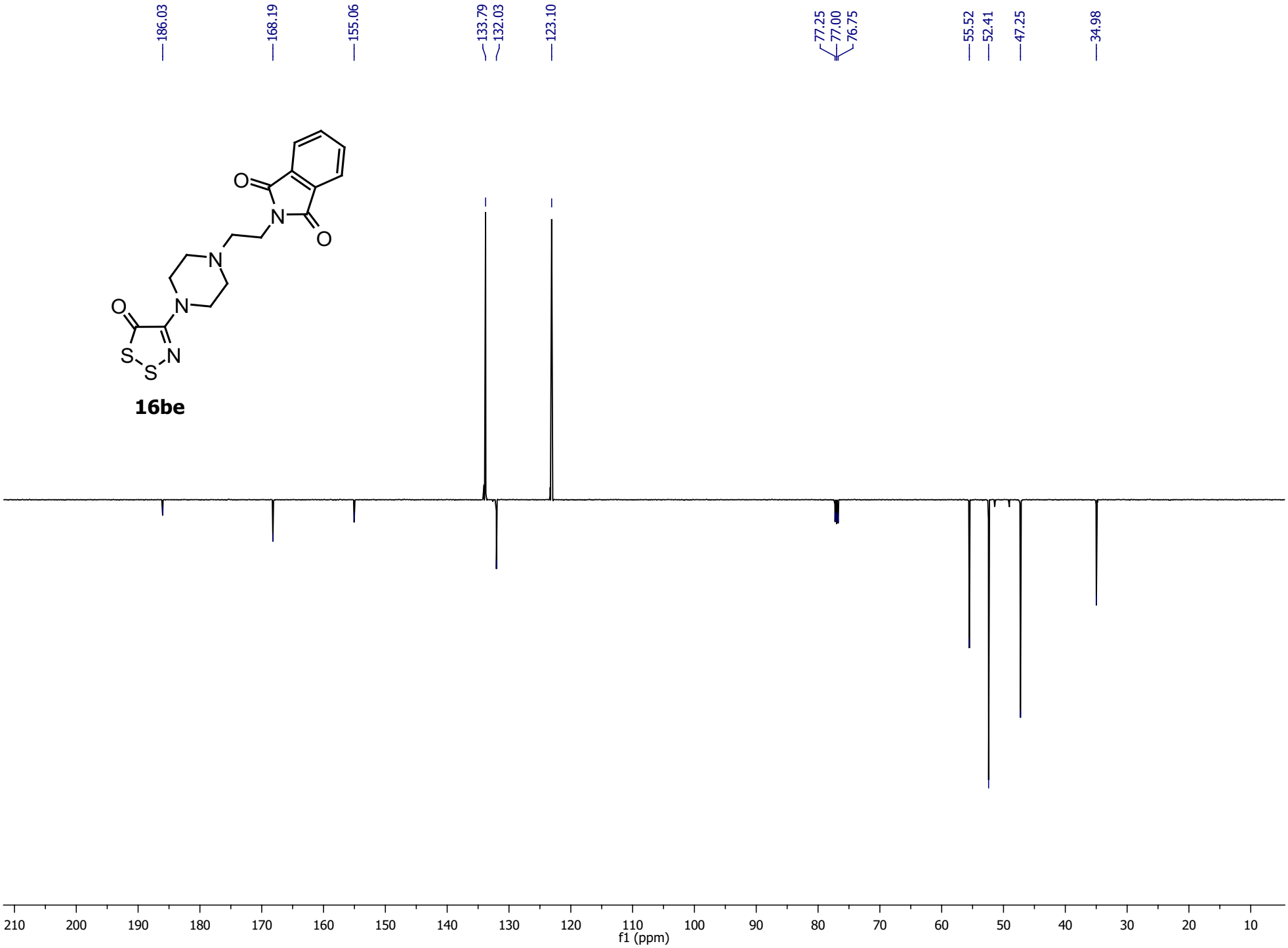


4-[*N*-(2-Phthalimidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16be**) (1H-NMR, 500 MHz, $CDCl_3$)

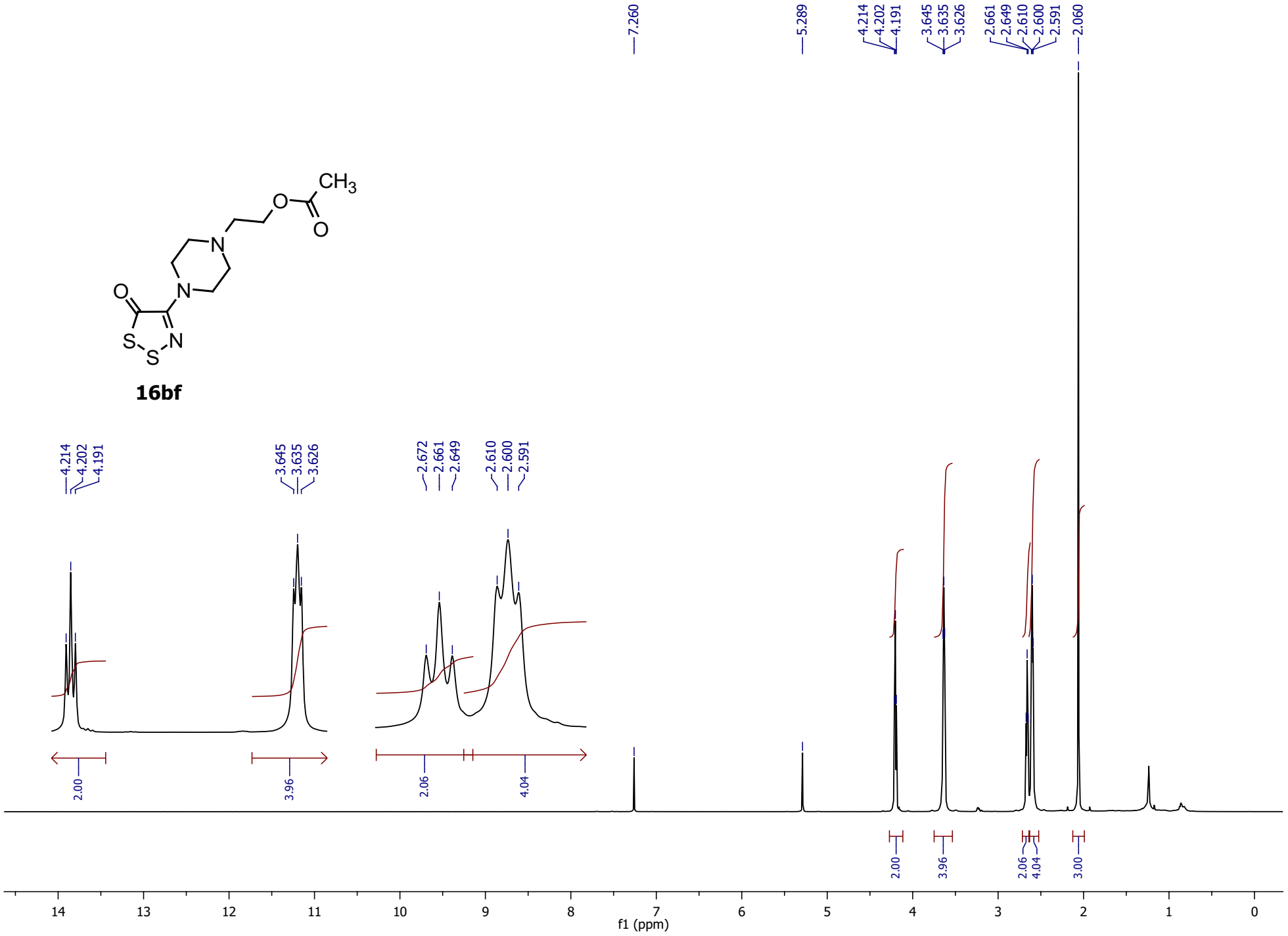


16be

4-[*N*-(2-Phthalimidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16be**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

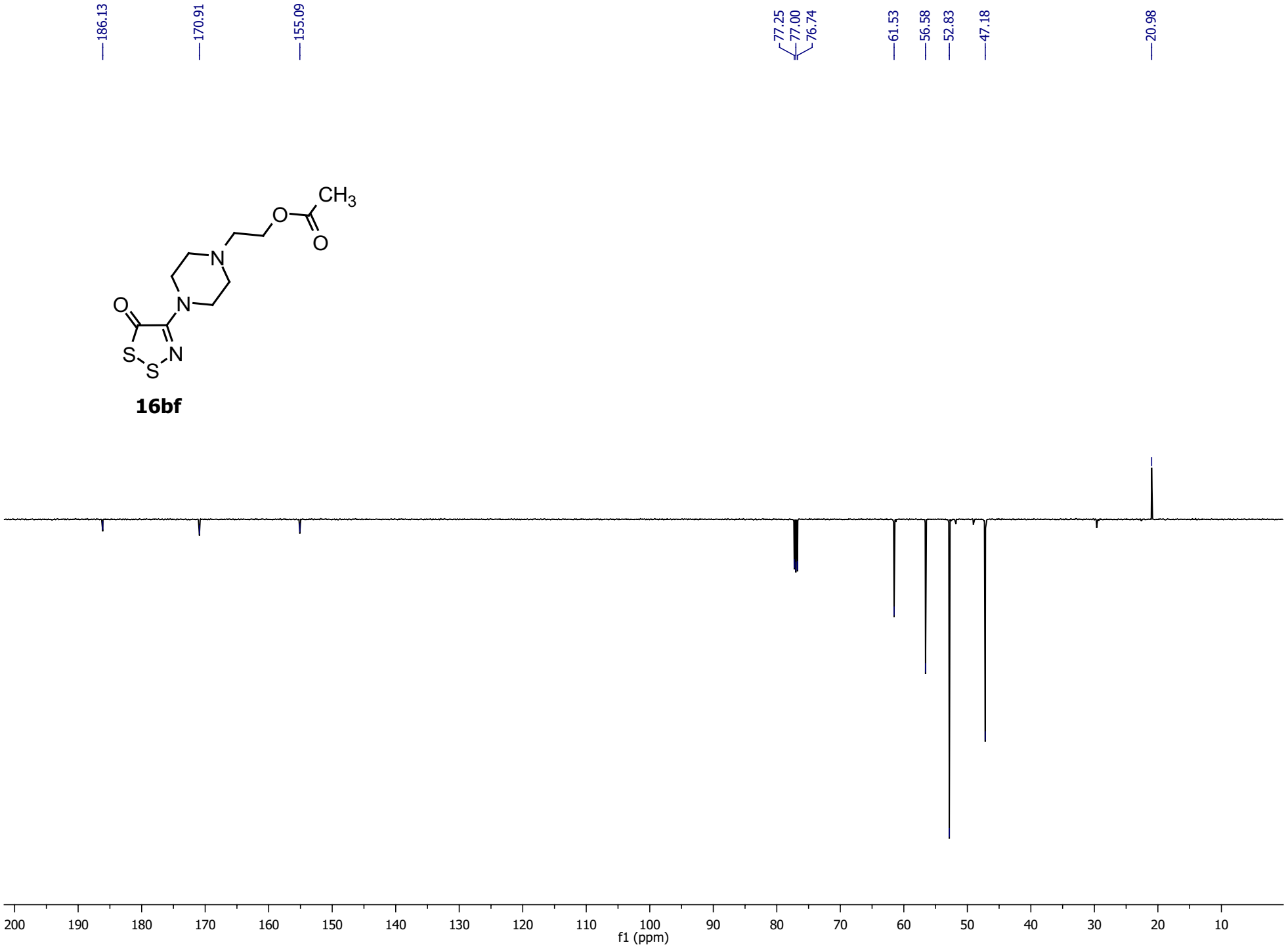


4-[*N*-(2-Acetoxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16bf**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

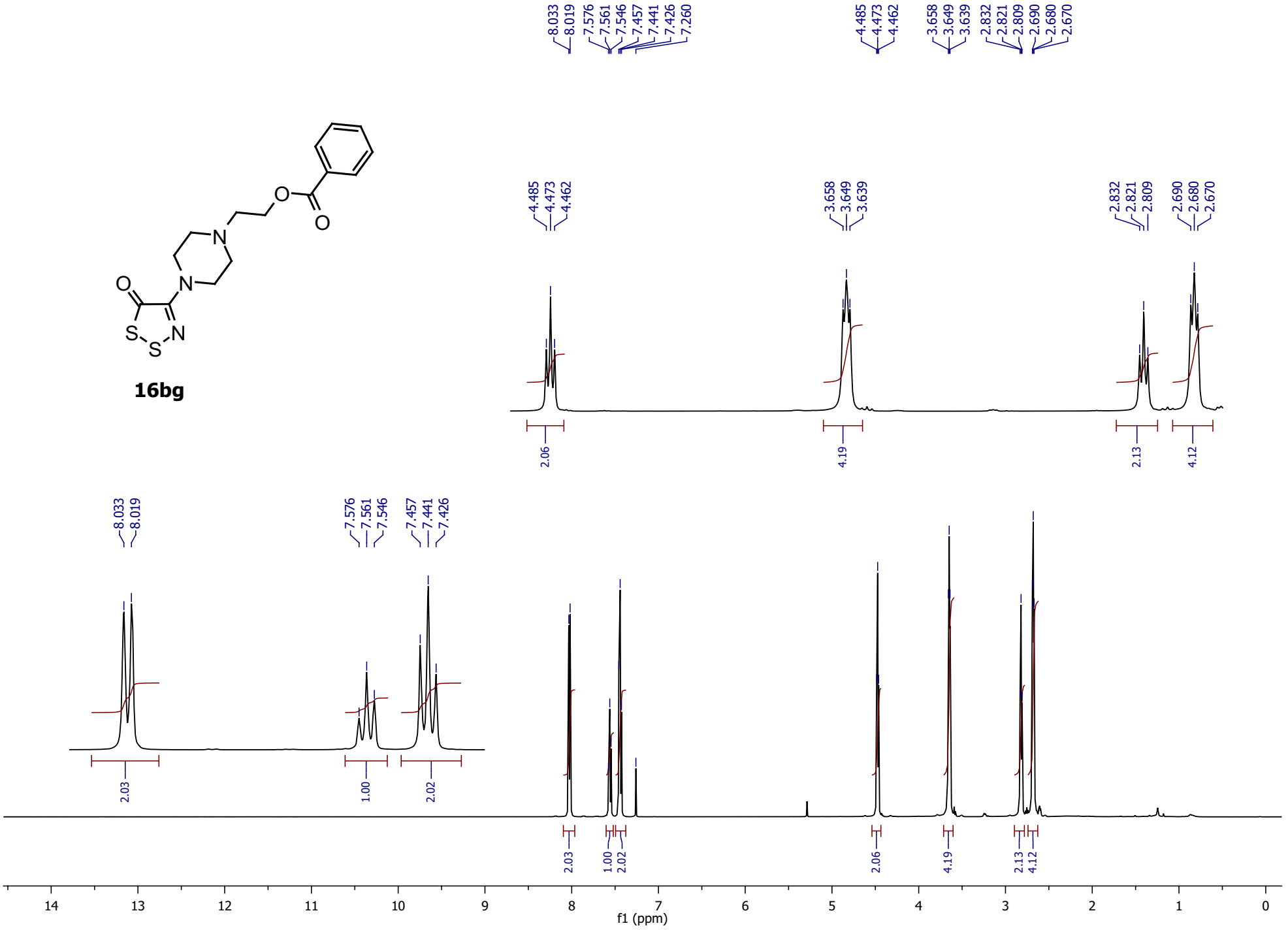


16bf

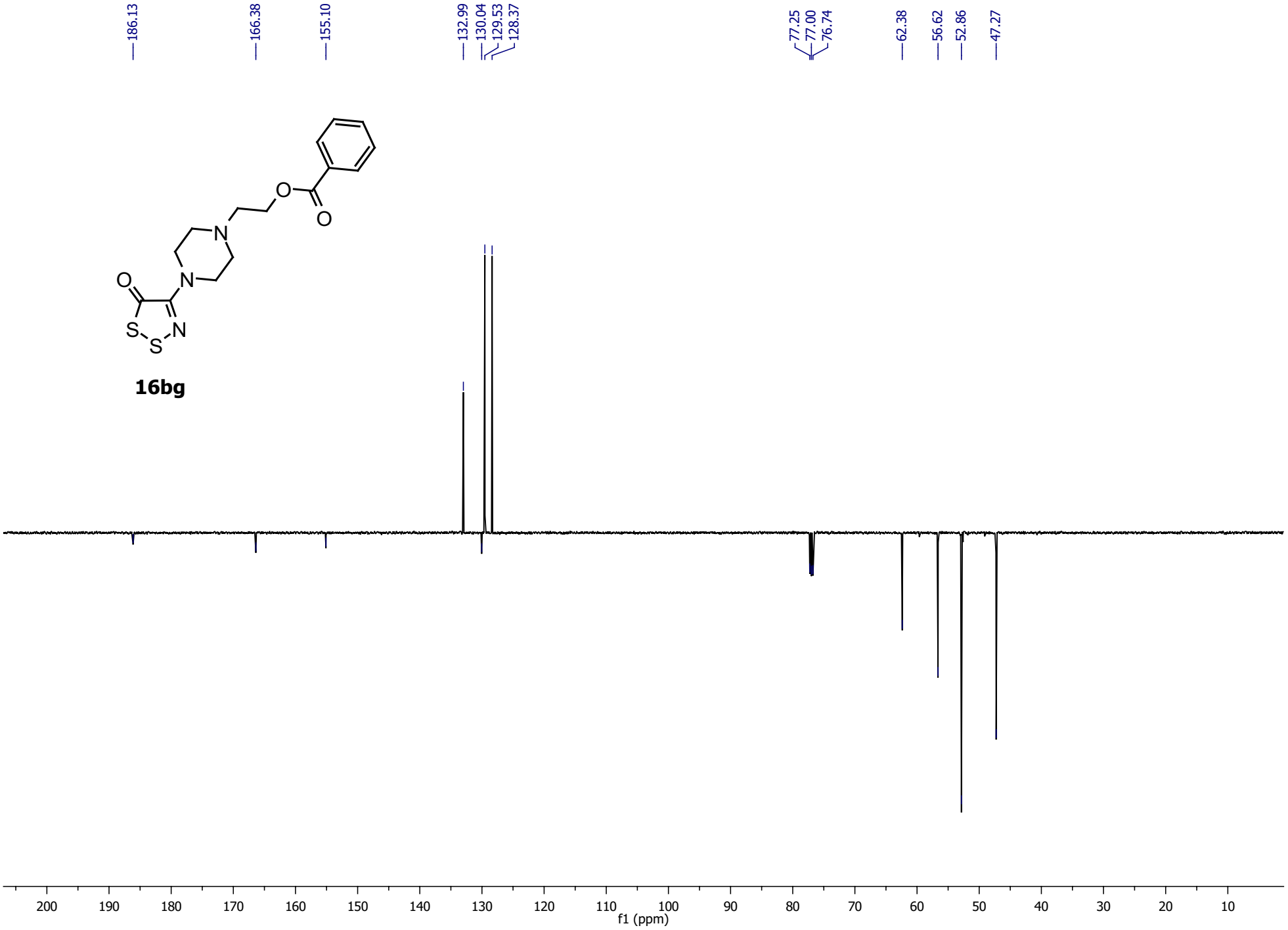
4-[*N*-(2-Acetoxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16bf**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



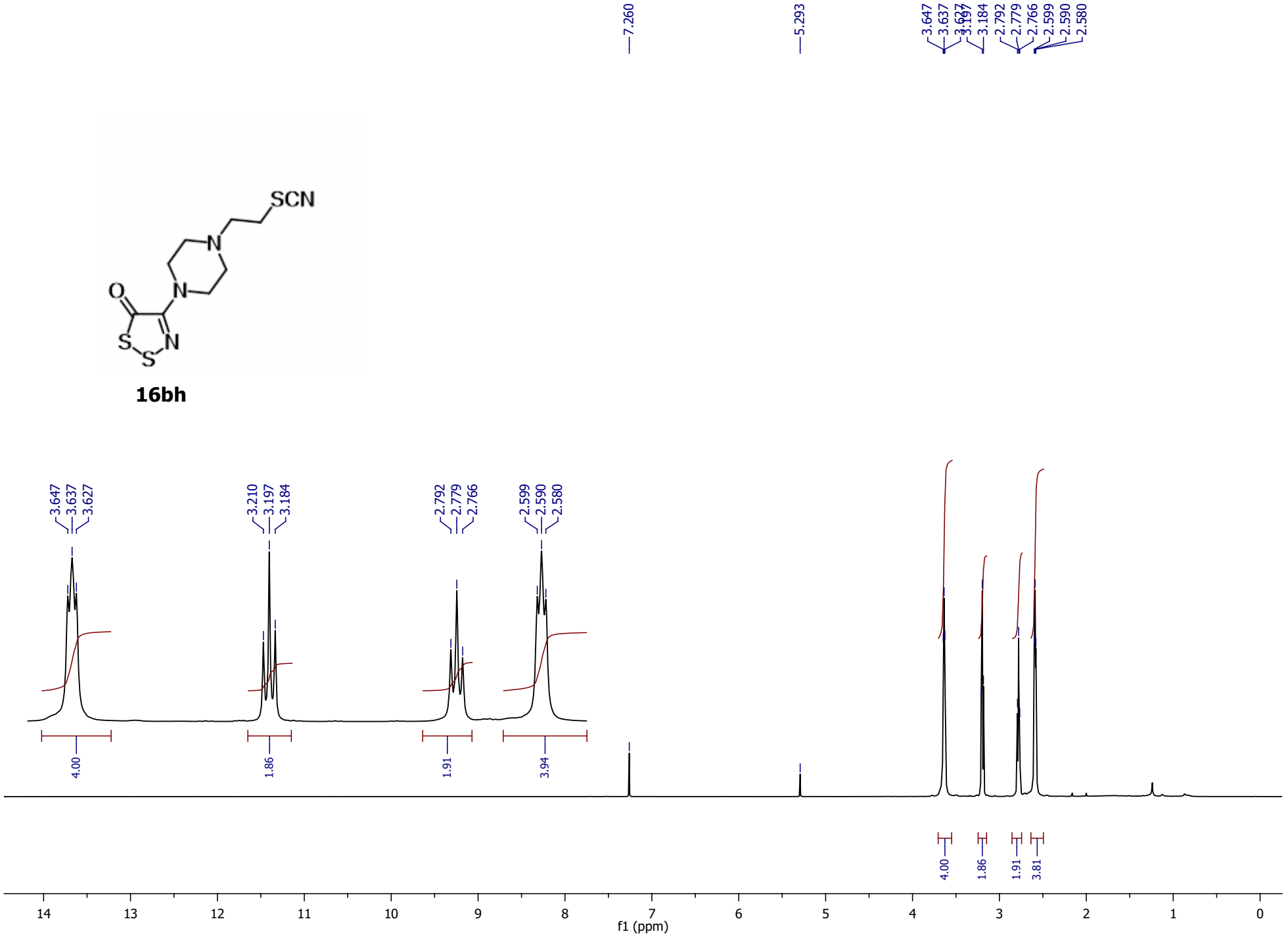
4-[*N*-(2-Benzoyloxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16bg**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



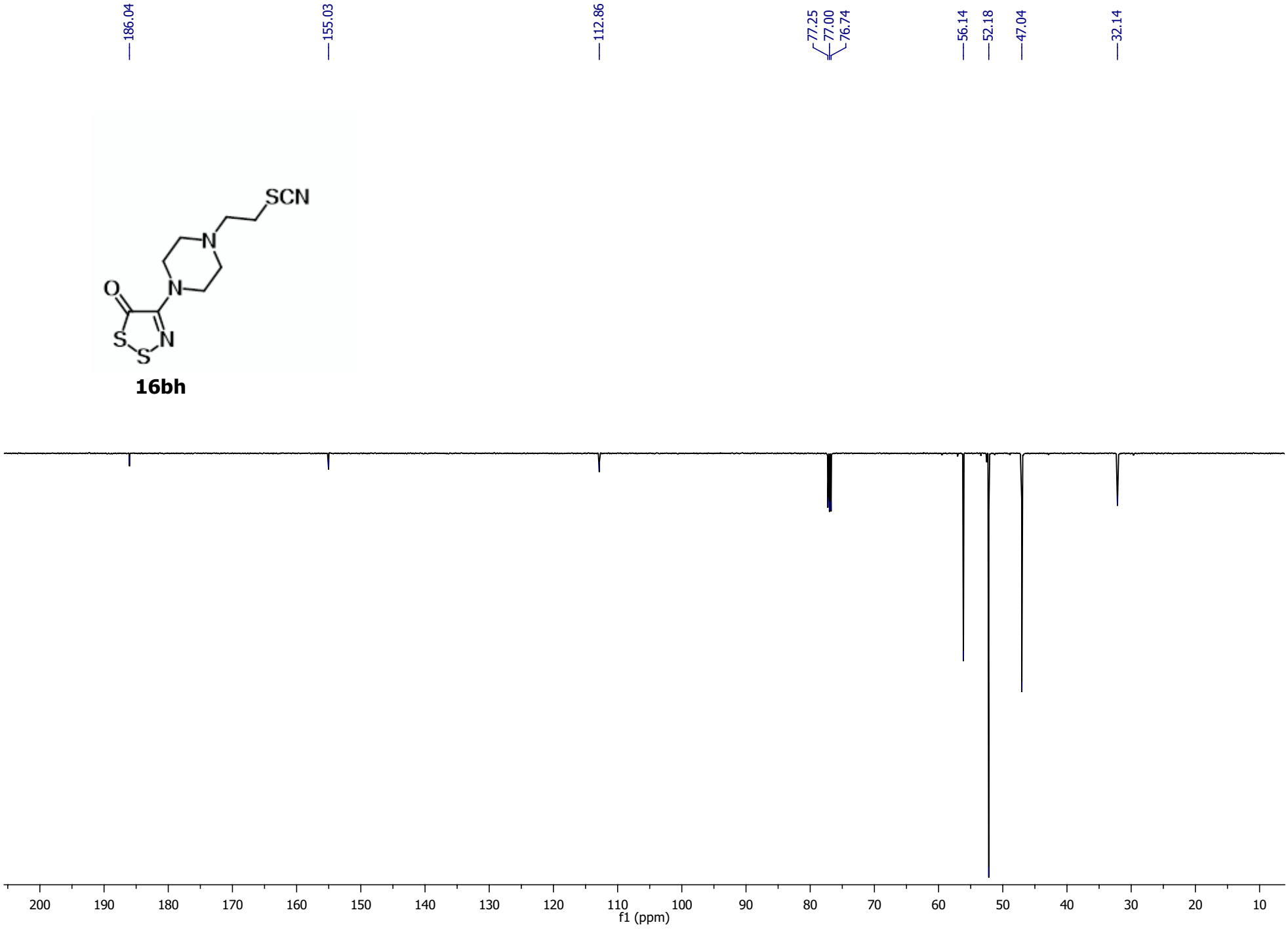
4-[*N*-(2-Benzoyloxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16bg**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



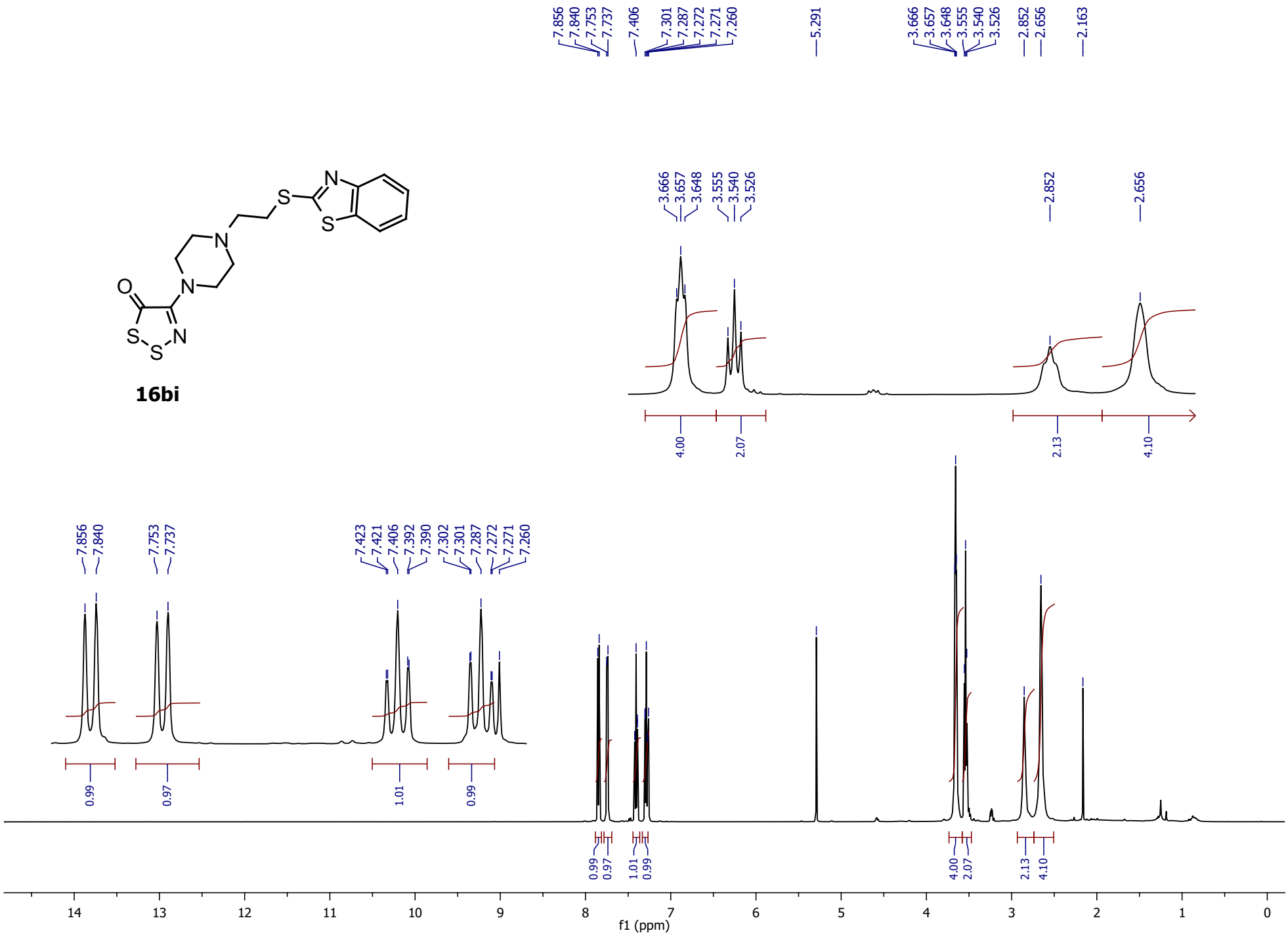
4-[*N*-(2-Thiocyanatoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16bh**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



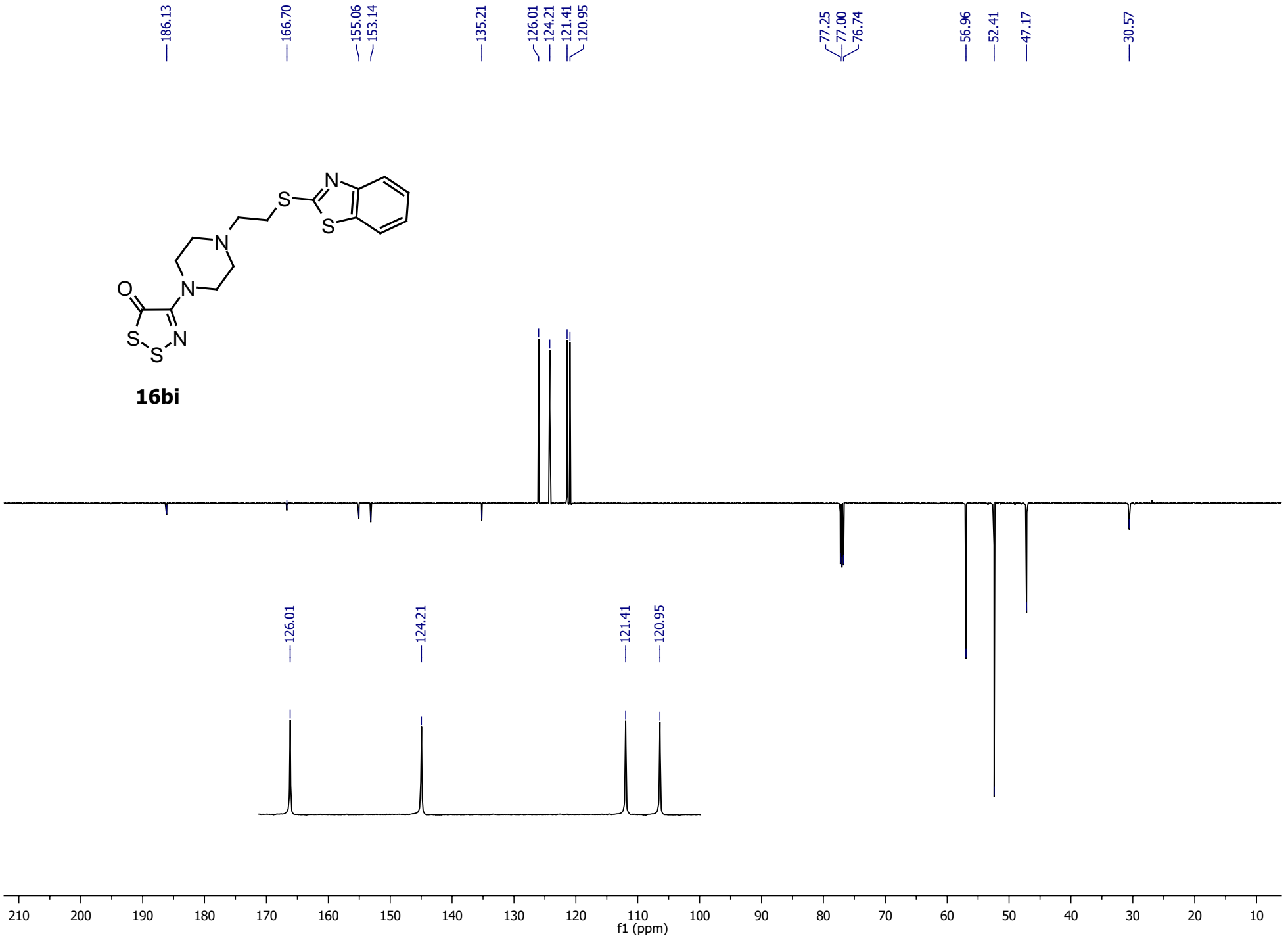
4-[*N*-(2-Thiocyanatoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-one (**16bh**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



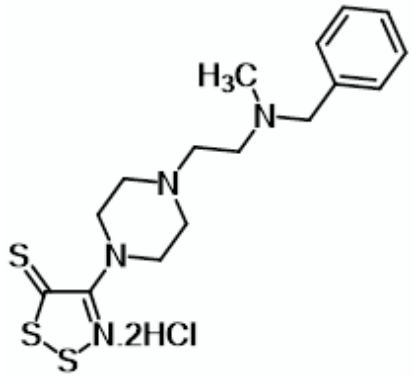
4-{*N*-[2-(Benzo[*d*]thiazol-2-ylthio)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazol-5-one (**16bi**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



4-{*N*-[2-(Benzo[*d*]thiazol-2-ylthio)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazol-5-one (**16bi**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

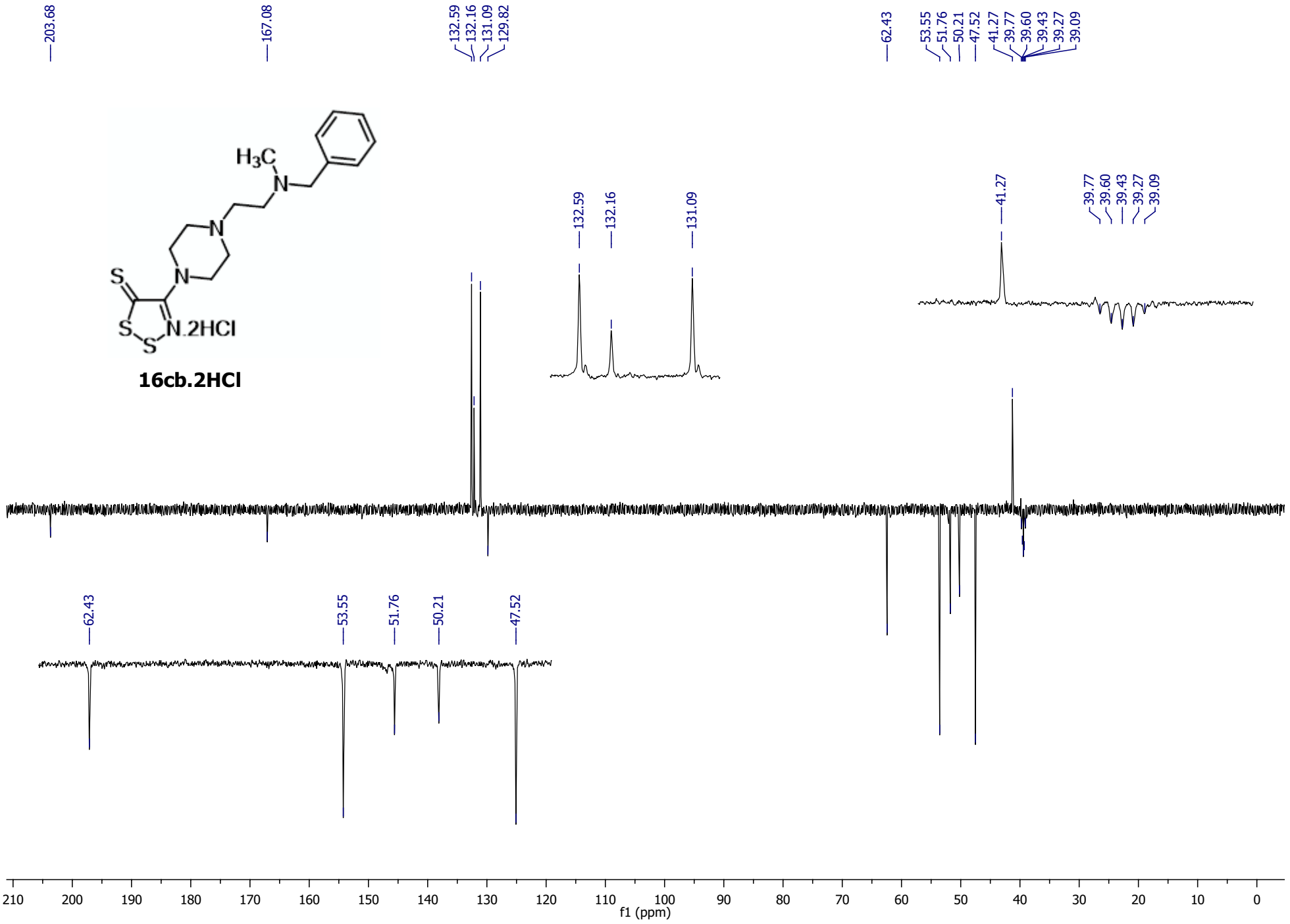


4-(*N*-{2-[Benzyl(methyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-one dihydrochloride (**16cb.2HCl**) (^{1}H-NMR, 500 MHz, D_2O)

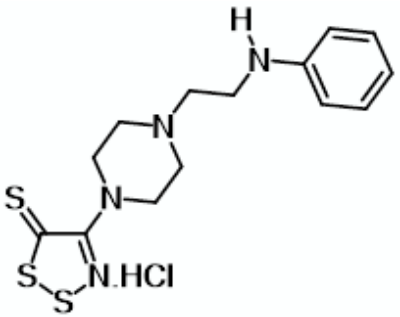


16cb.2HCl

4-(*N*-{2-[Benzyl(methyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazol-5-one dihydrochloride (**16cb.2HCl**)
(^{13}C-NMR, 125 MHz, D_2O + 1 drop DMSO-d_6)

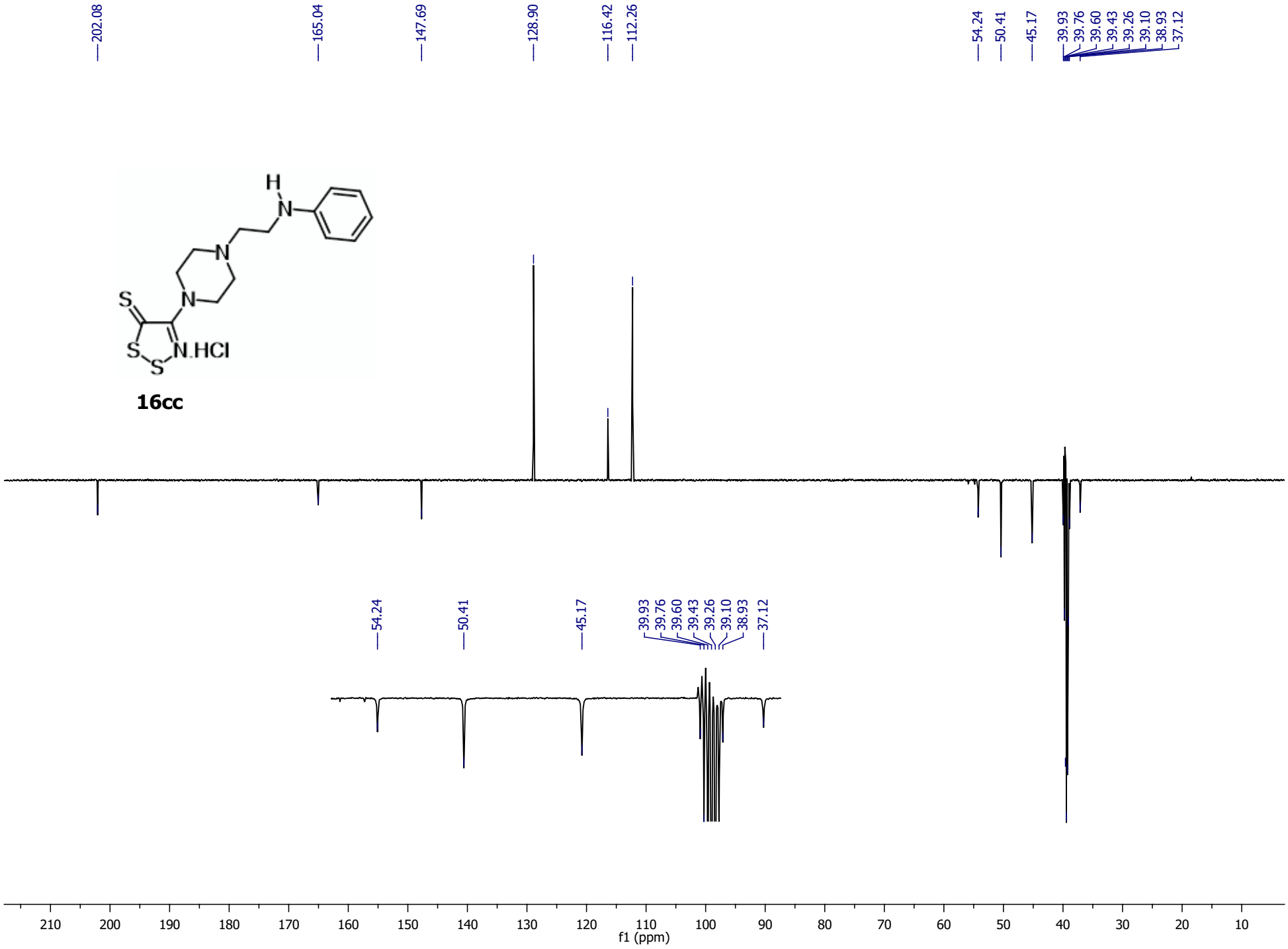


4-{*N*-[2-(Phenylamino)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazole-5-thione hydrochloride (**16cc**) (^{1}H-NMR at 80 °C, 500 MHz, DMSO-d_6)

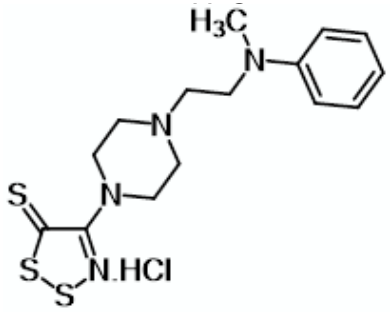


16cc

4-{*N*-[2-(Phenylamino)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazole-5-thione hydrochloride (**16cc**) (^{13}C-NMR, 125 MHz, DMSO-d_6)

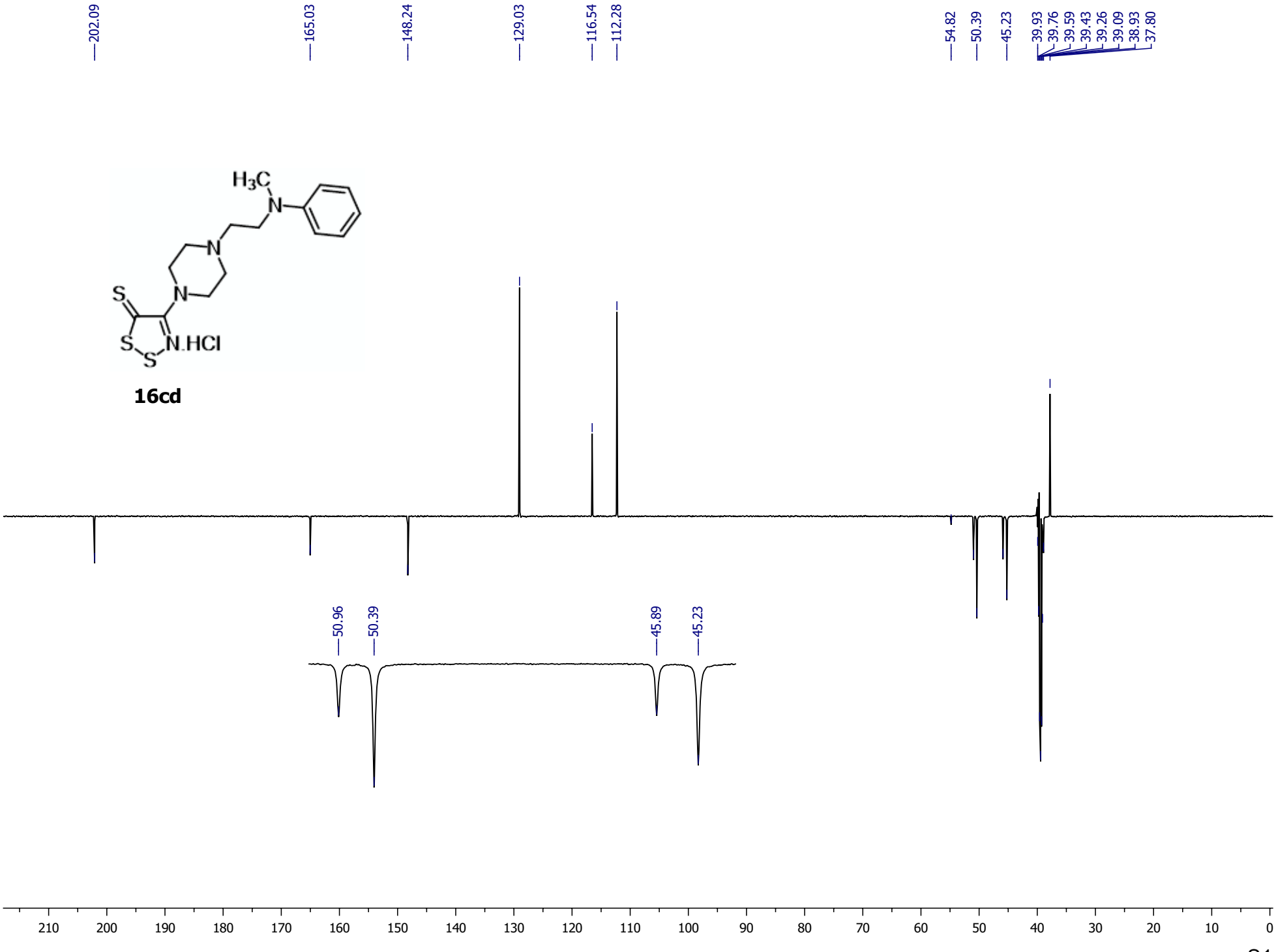


4-(*N*-{2-[Methyl(phenyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazole-5-thione hydrochloride (**16cd**)
(^{1}H-NMR at 80 °C, 500 MHz, DMSO-d_6)



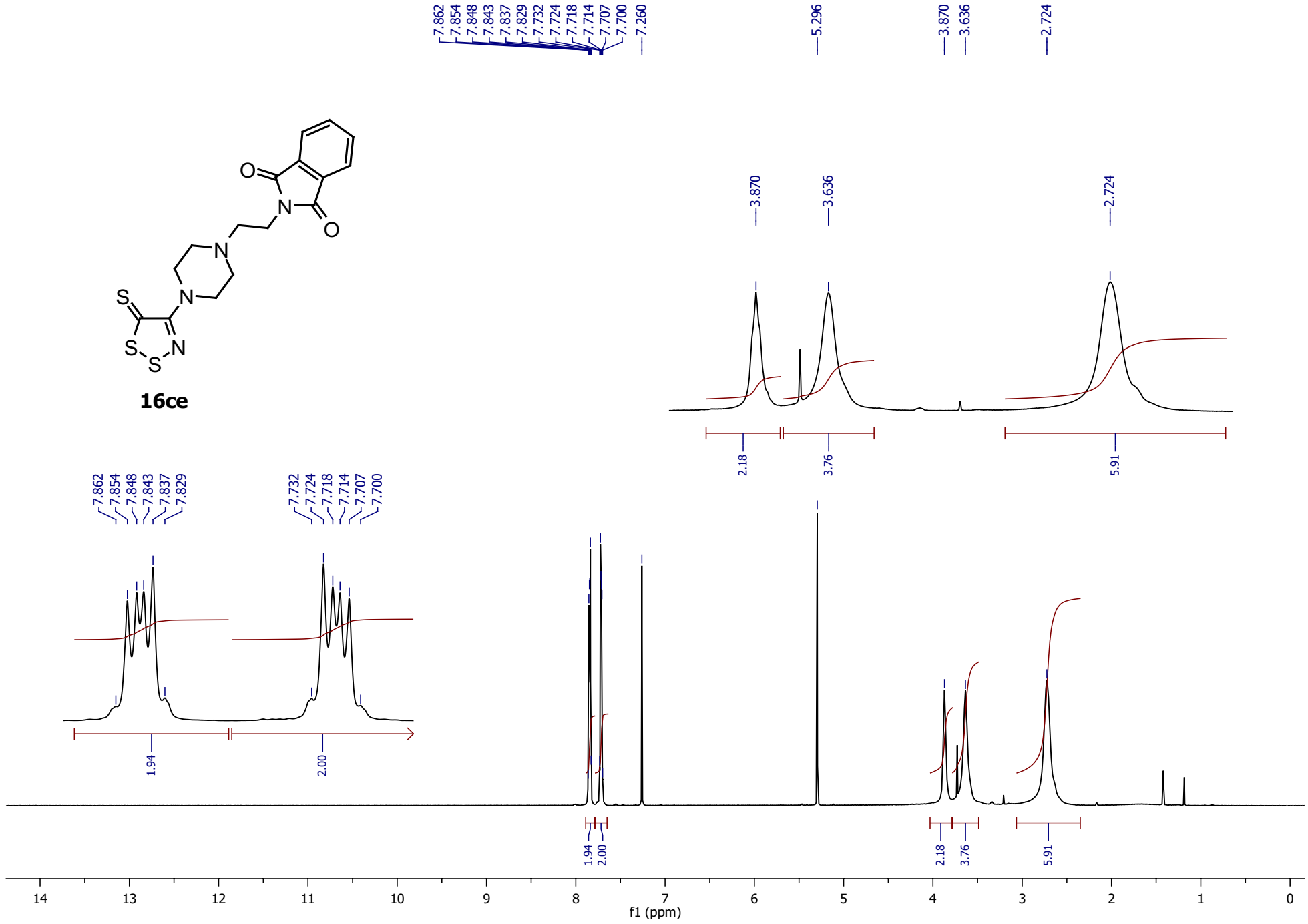
16cd

4-(*N*-{2-[Methyl(phenyl)amino]ethyl}piperazin-1-yl)-5*H*-1,2,3-dithiazole-5-thione hydrochloride (**16cd**) (^{13}C-NMR, 125 MHz, DMSO-d_6)

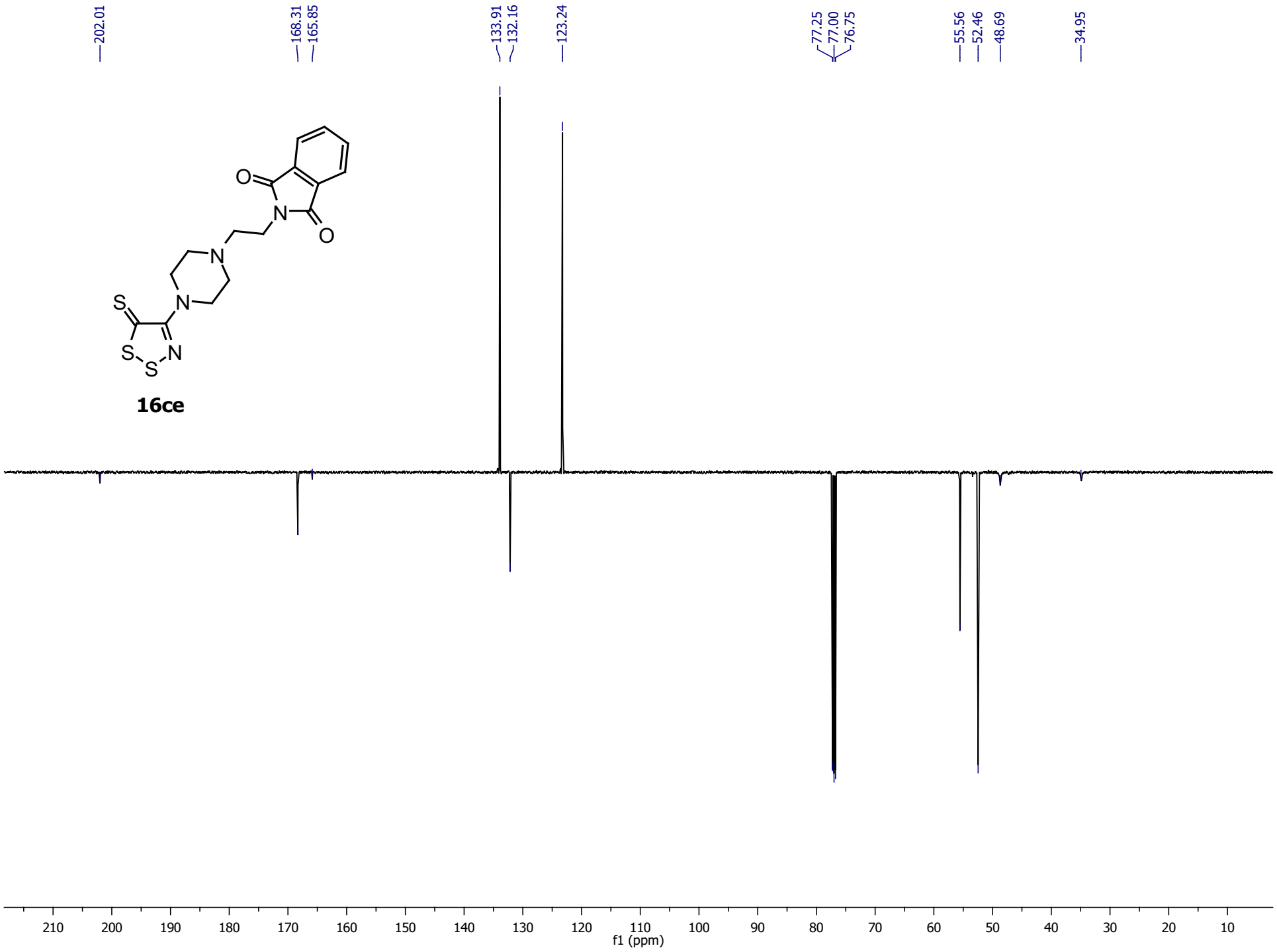


16cd

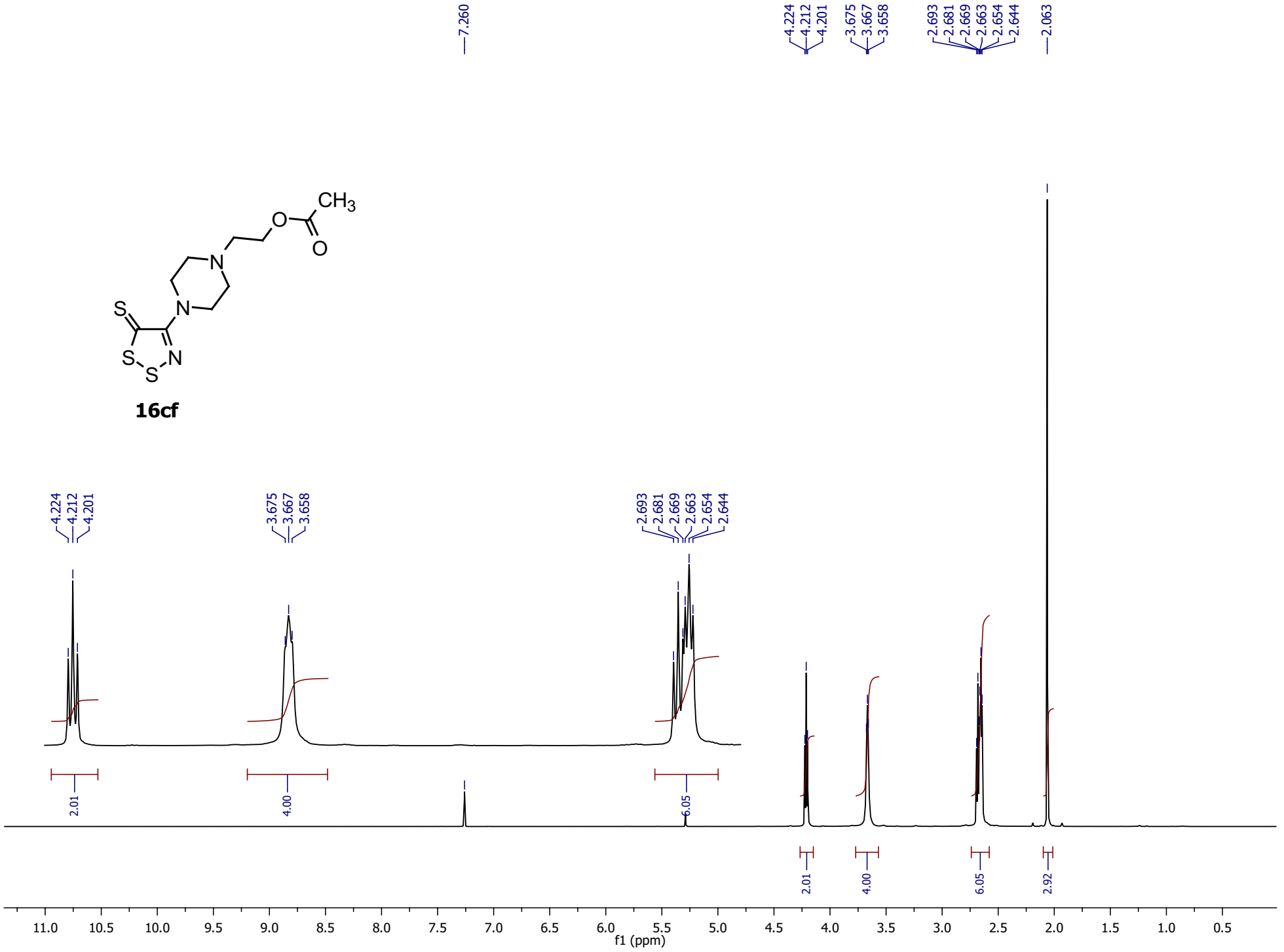
4-[*N*-(2-Phthalimidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-thione (**16ce**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



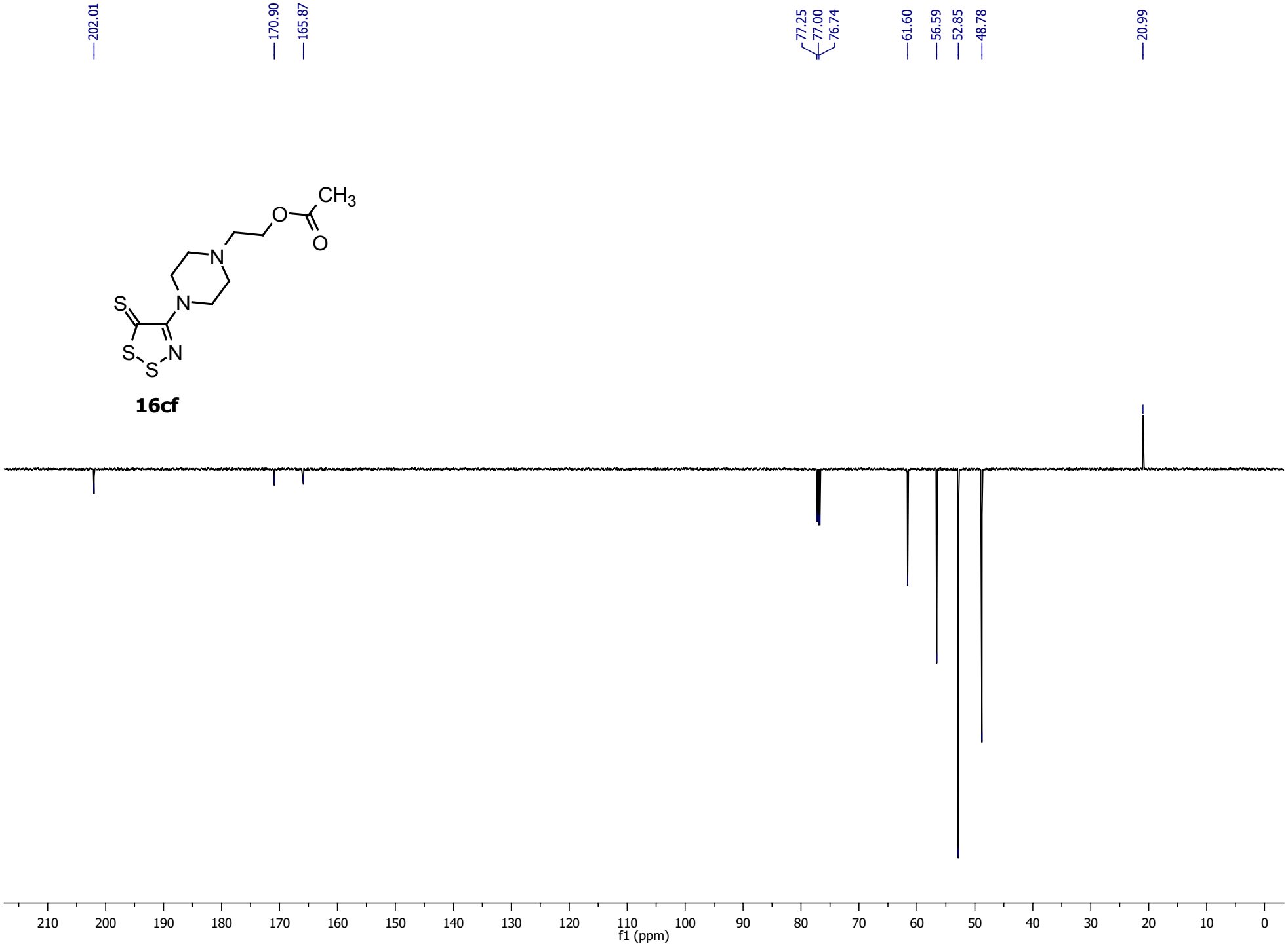
4-[*N*-(2-Phthalimidoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-thione (**16ce**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



4-[*N*-(2-Acetoxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-thione (**16cf**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

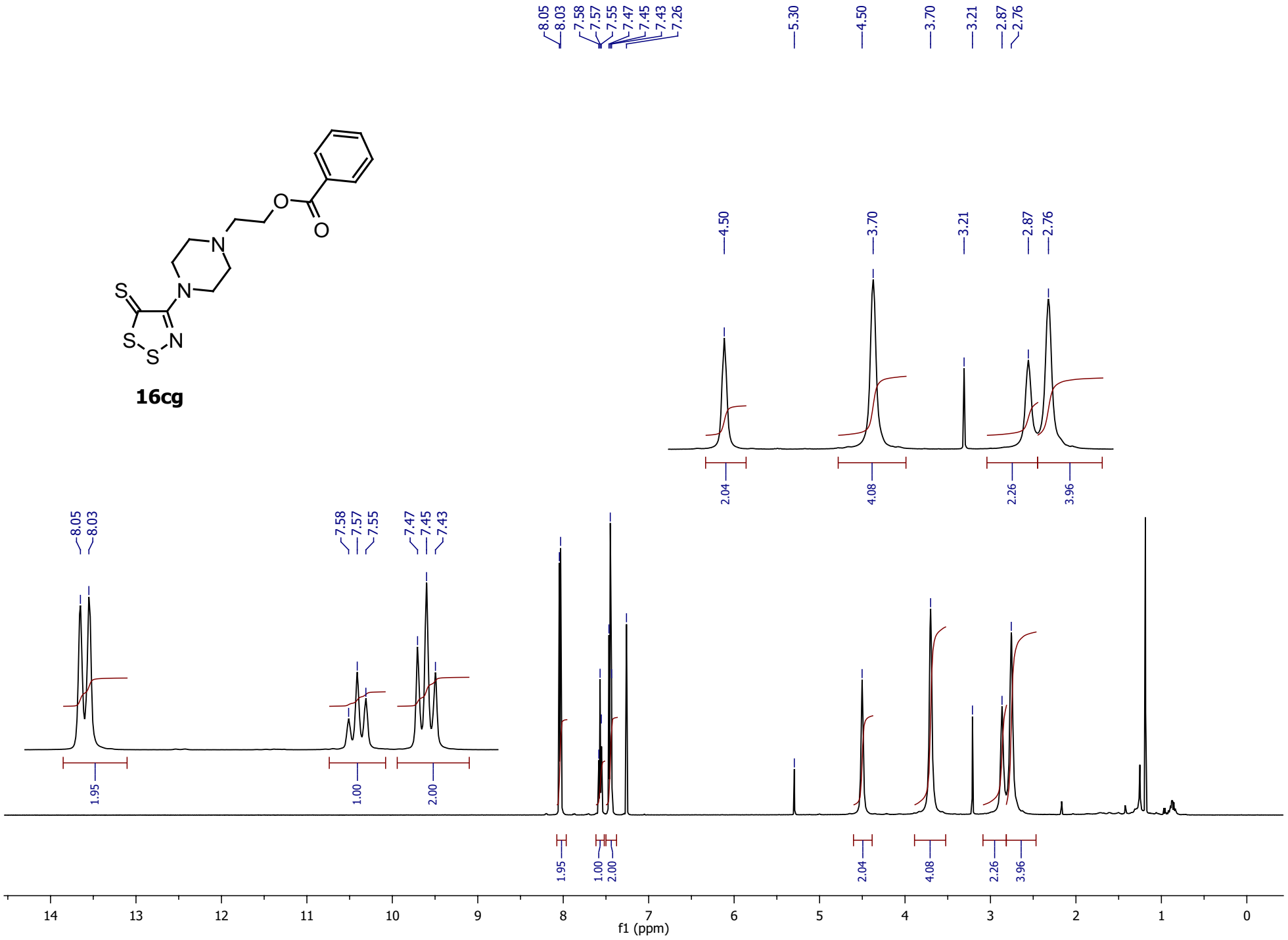


4-[*N*-(2-Acetoxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-thione (**16cf**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



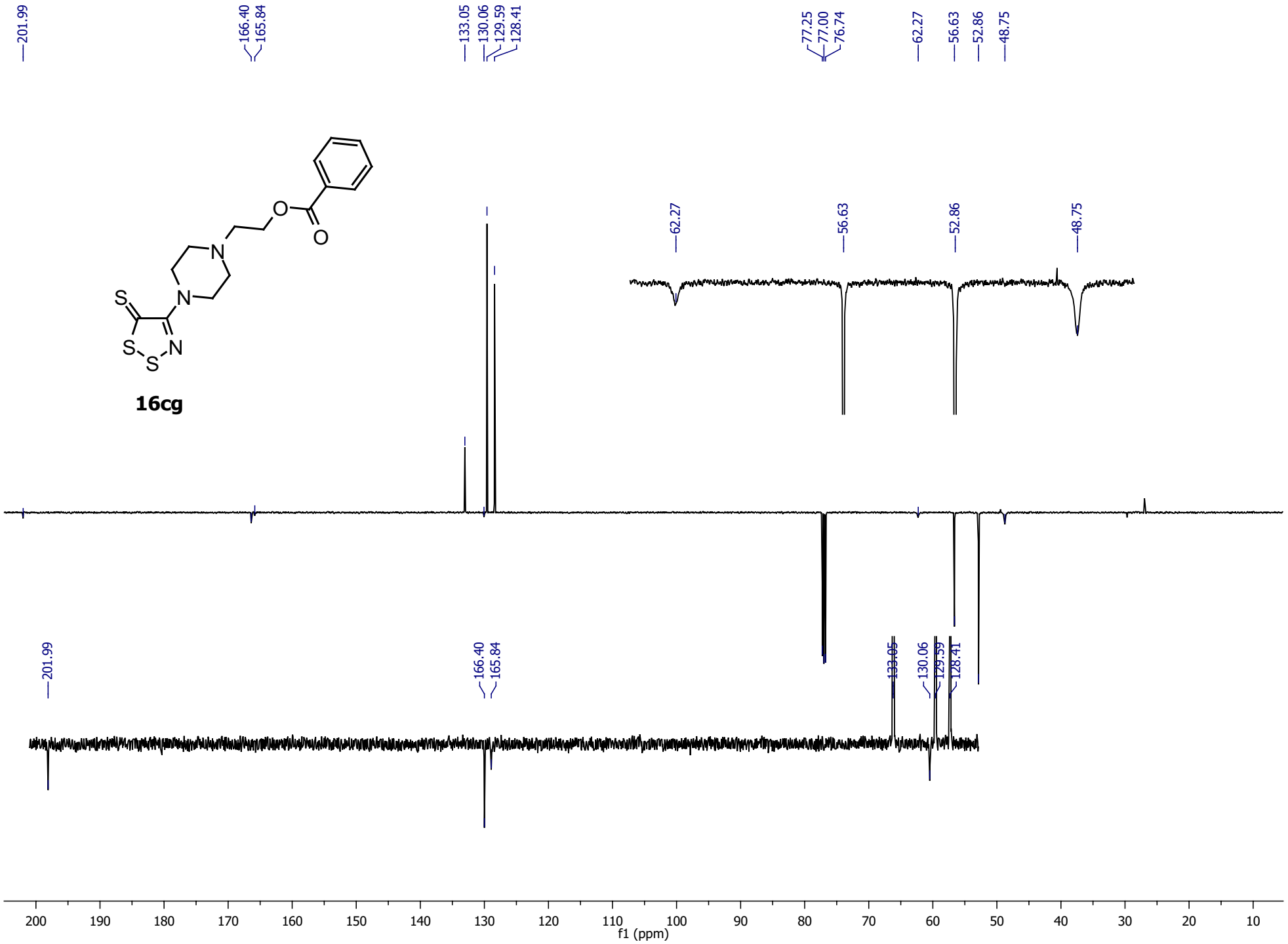
16cf

4-[*N*-(2-Benzoyloxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-thione (**16cg**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

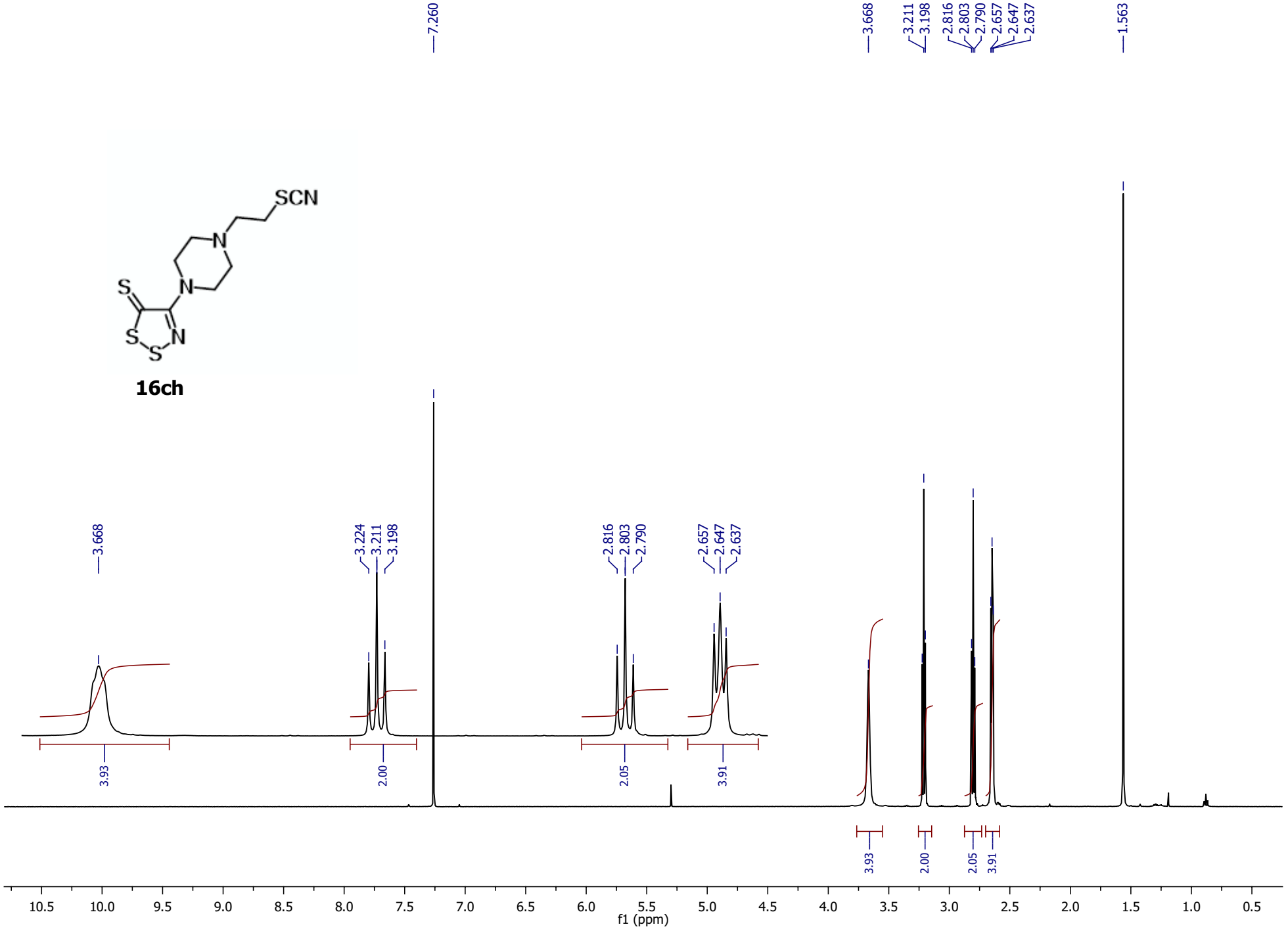


16cg

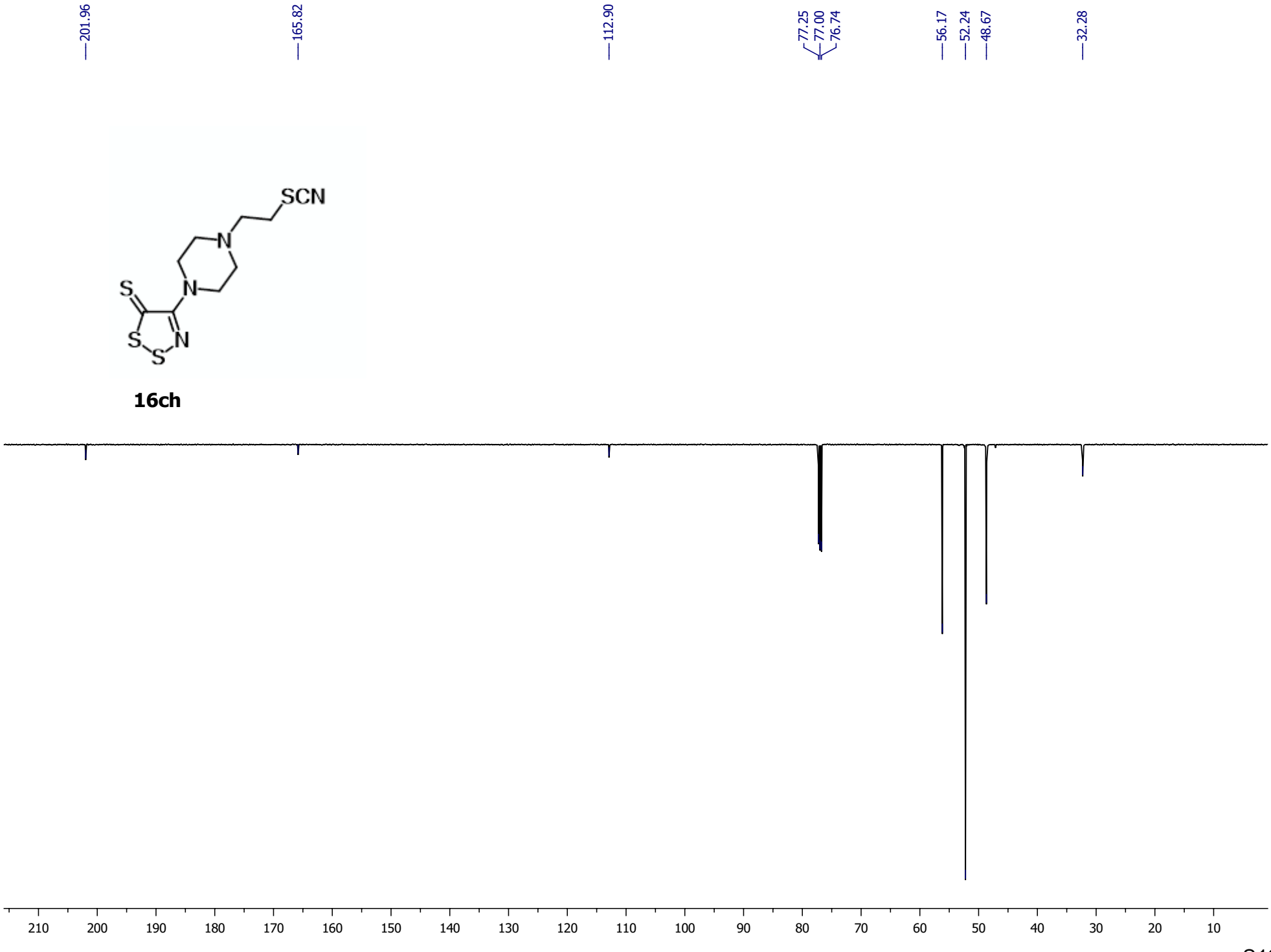
4-[*N*-(2-Benzoyloxyethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazol-5-thione (**16cg**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



4-[*N*-(2-Thiocyanatoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazole-5-thione (**16ch**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

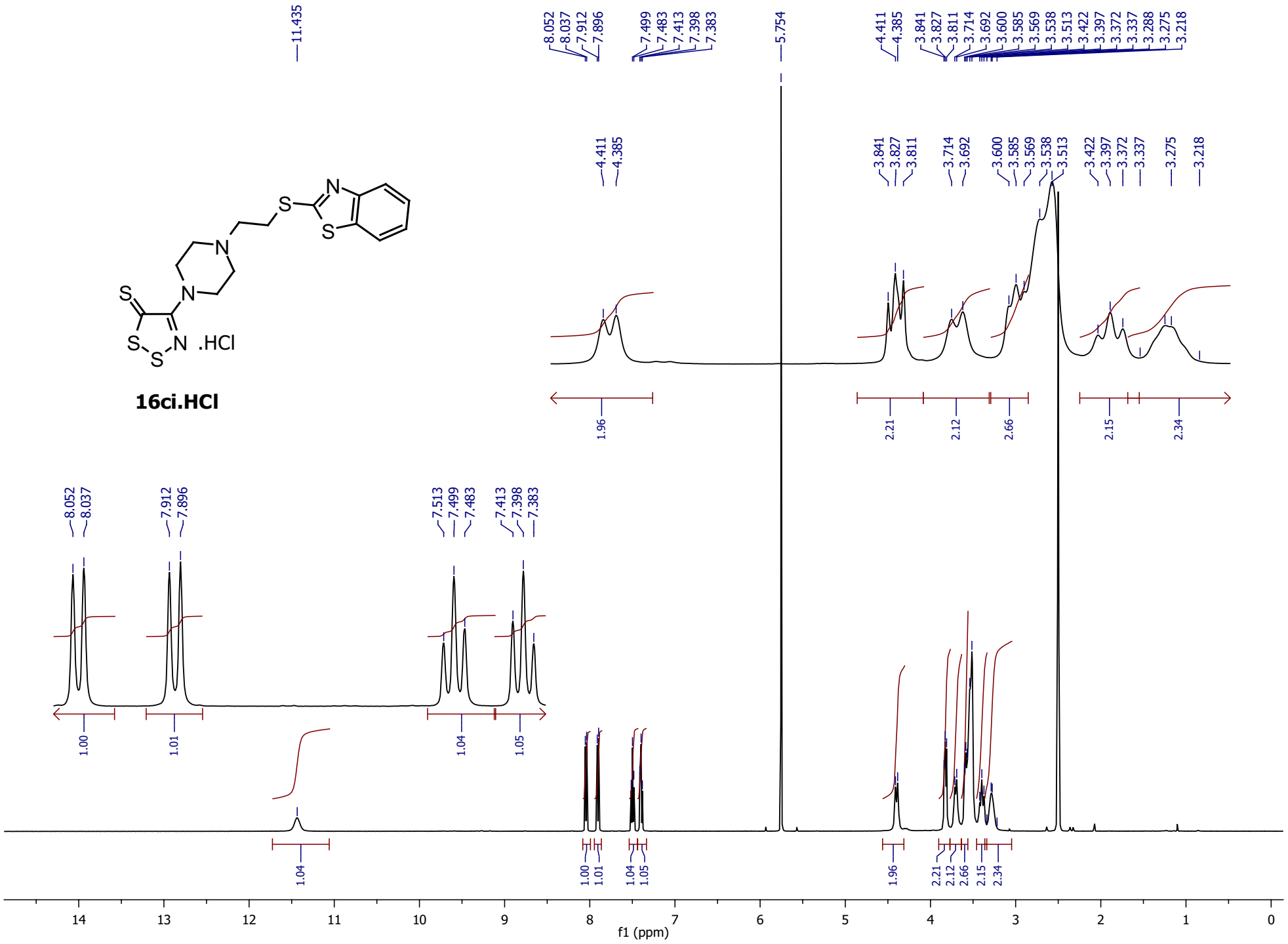


4-[*N*-(2-Thiocyanatoethyl)piperazin-1-yl]-5*H*-1,2,3-dithiazole-5-thione (**16ch**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

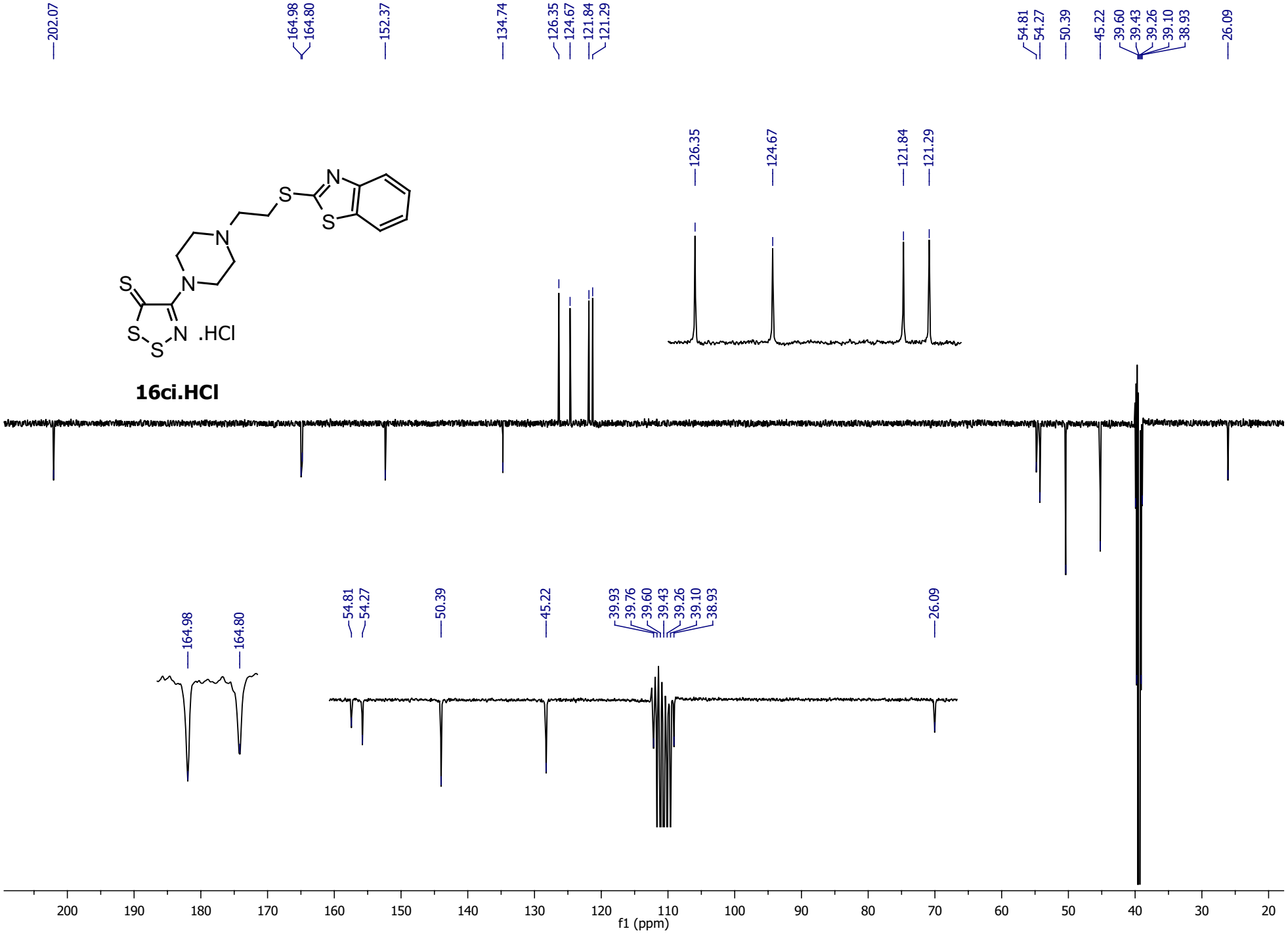


16ch

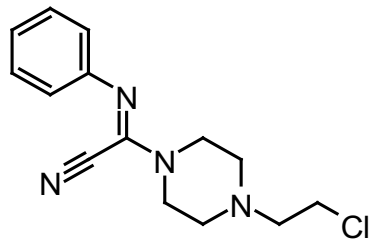
4-{*N*-[2-(Benzo[*d*]thiazol-2-ylthio)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazole-5-thione hydrochloride (**16ci.HCl**) (^{1}H-NMR, 500 MHz, DMSO-d_6)



4-{*N*-[2-(Benzo[*d*]thiazol-2-ylthio)ethyl]piperazin-1-yl}-5*H*-1,2,3-dithiazole-5-thione hydrochloride (**16ci.HCl**) (^{13}C-NMR, 125 MHz, DMSO-d_6)

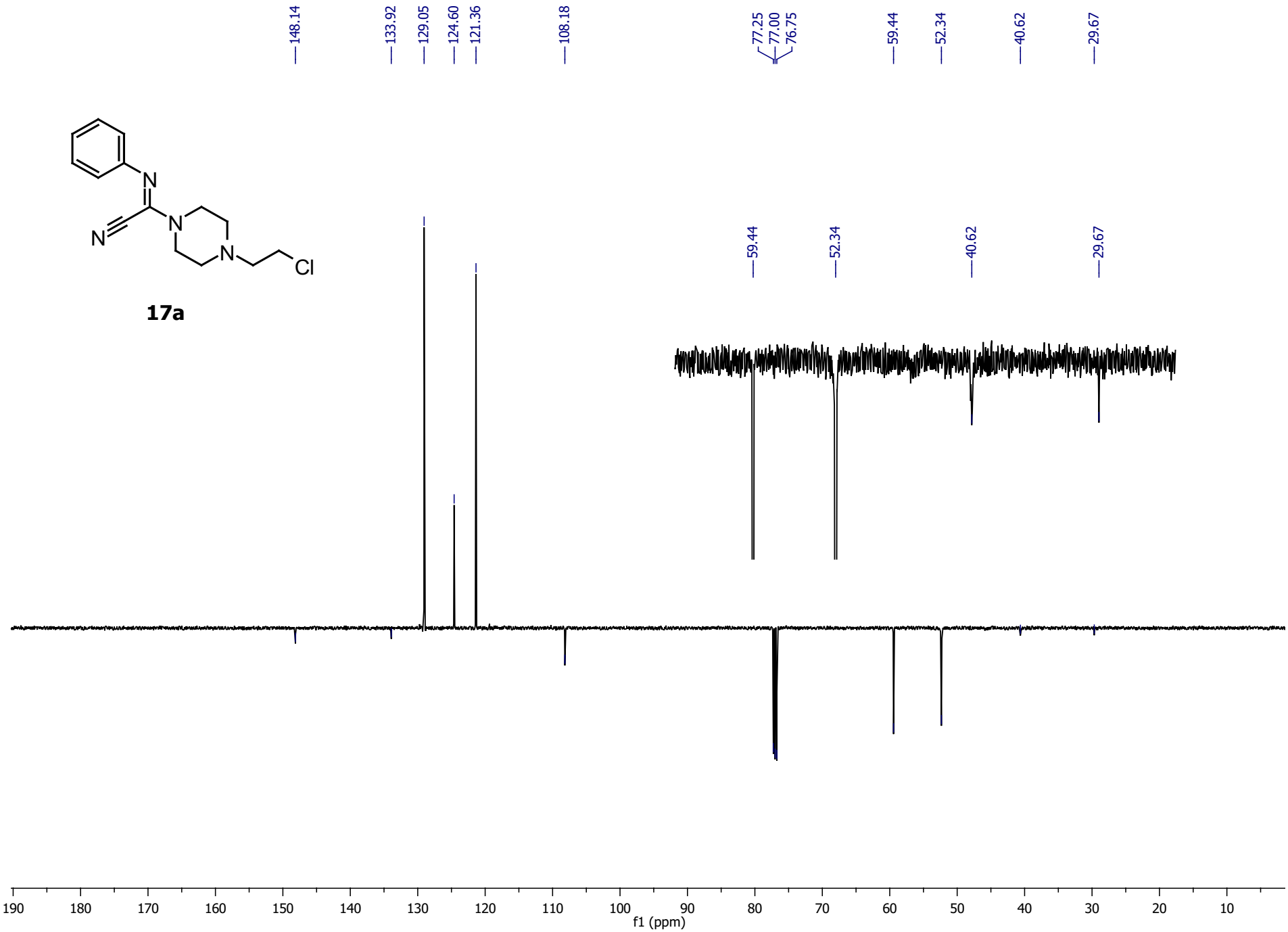


4-(2-Chloroethyl)-*N*-phenylpiperazine-1-carbimidoyl cyanide (**17a**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

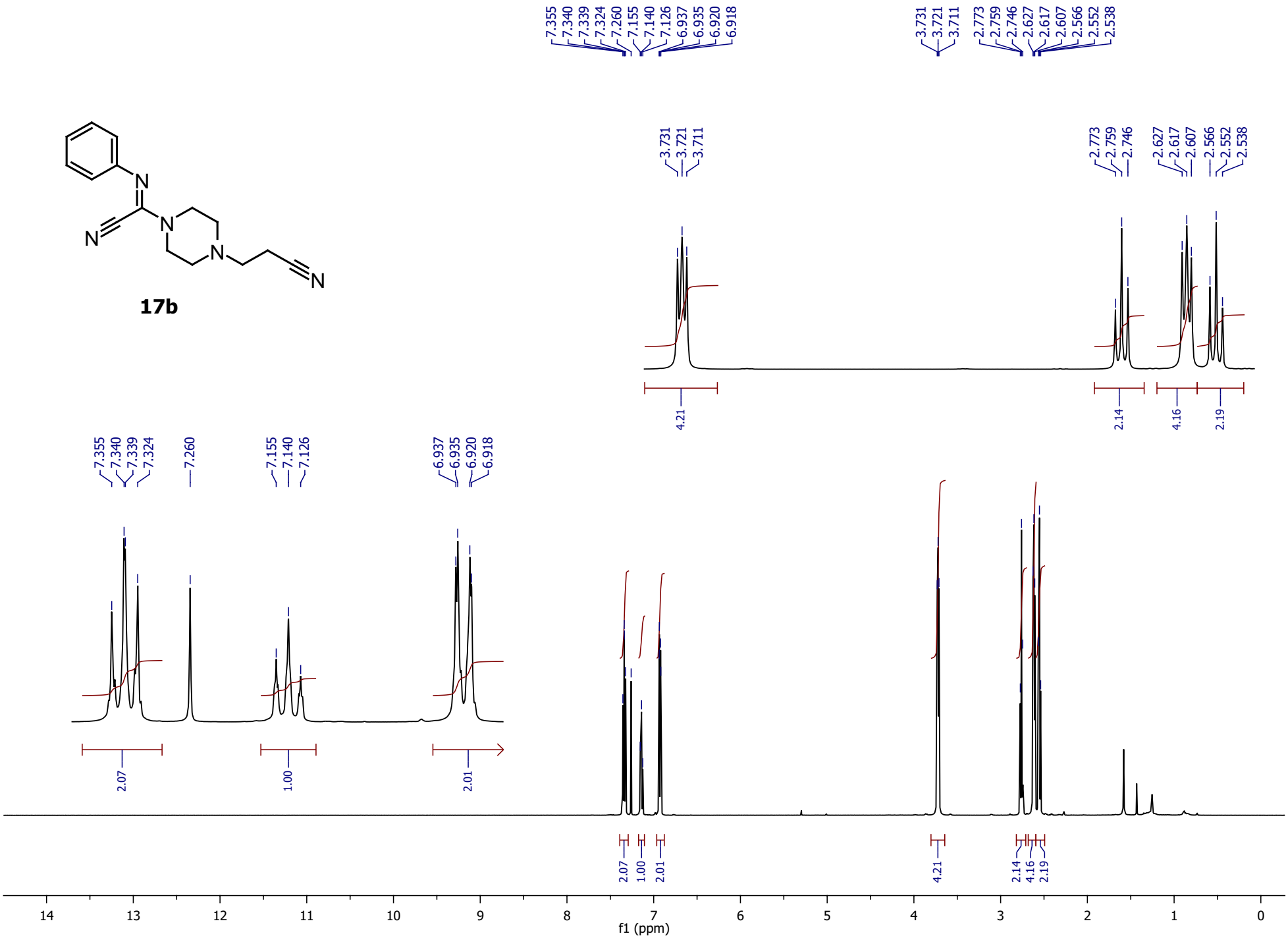


17a

4-(2-Chloroethyl)-*N*-phenylpiperazine-1-carbimidoyl cyanide (**17a**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

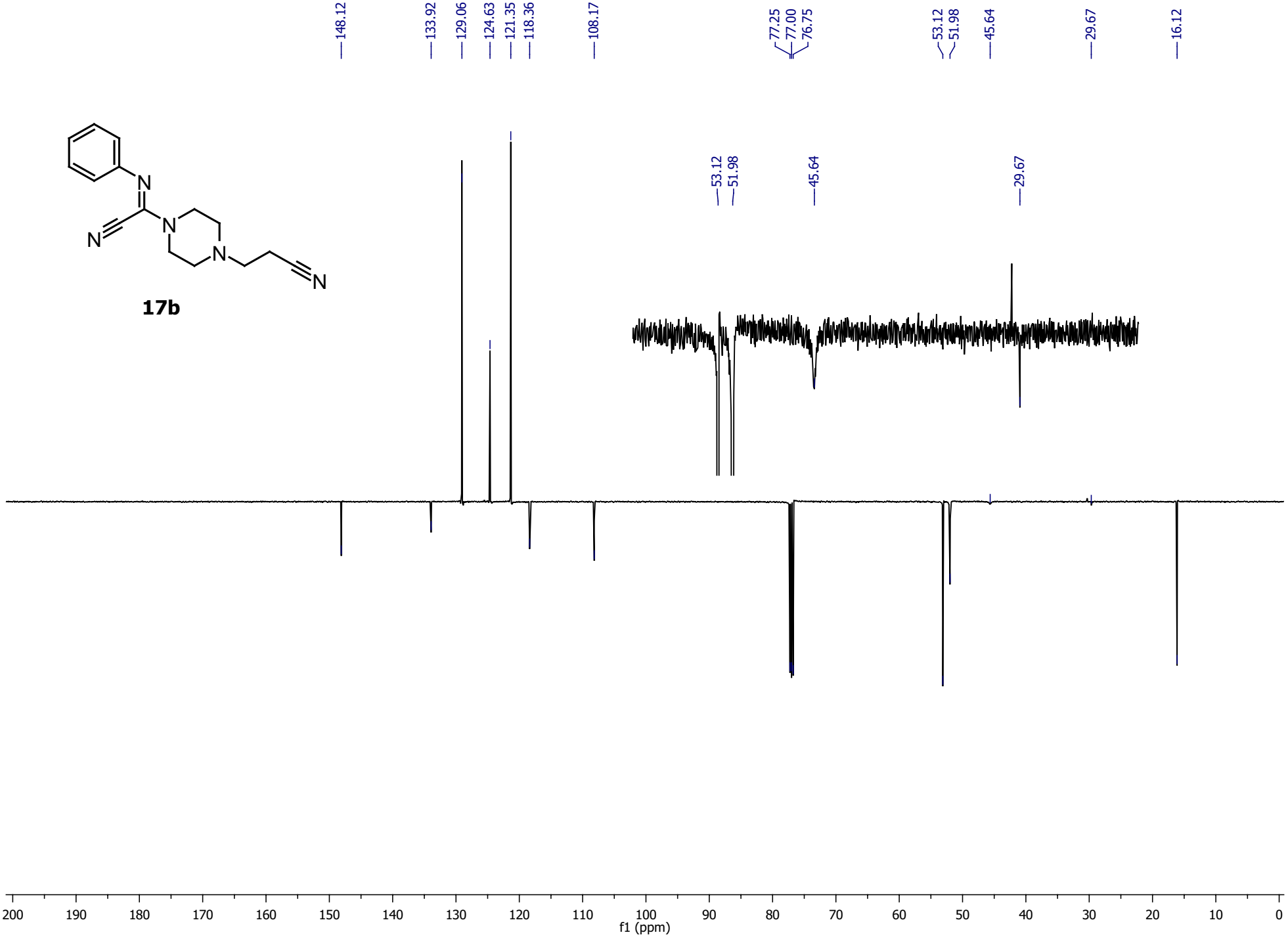


N-(2-Chloroethyl)-*N*-phenylpiperazine-1-carbimidoyl cyanide (**17b**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

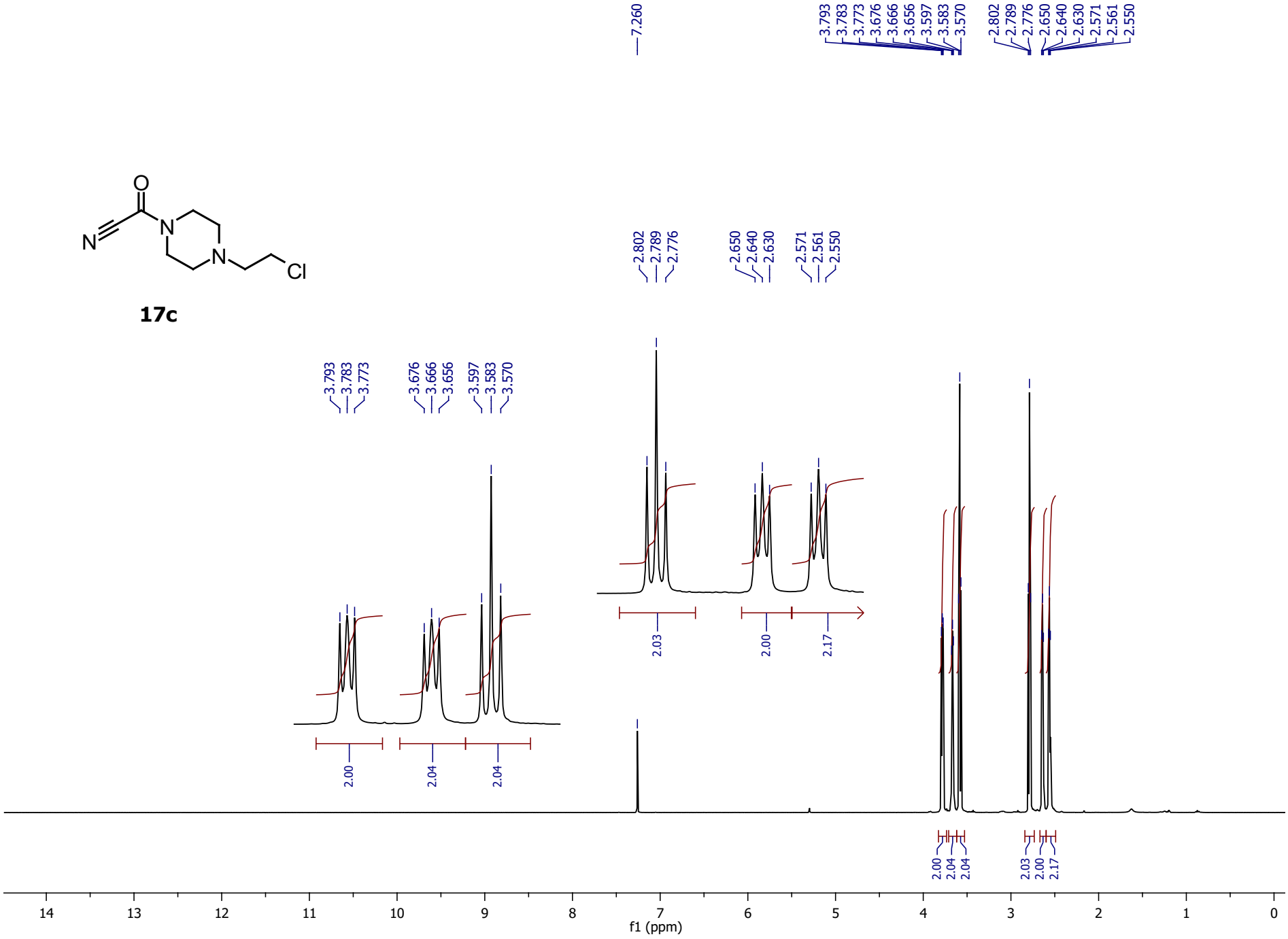


17b

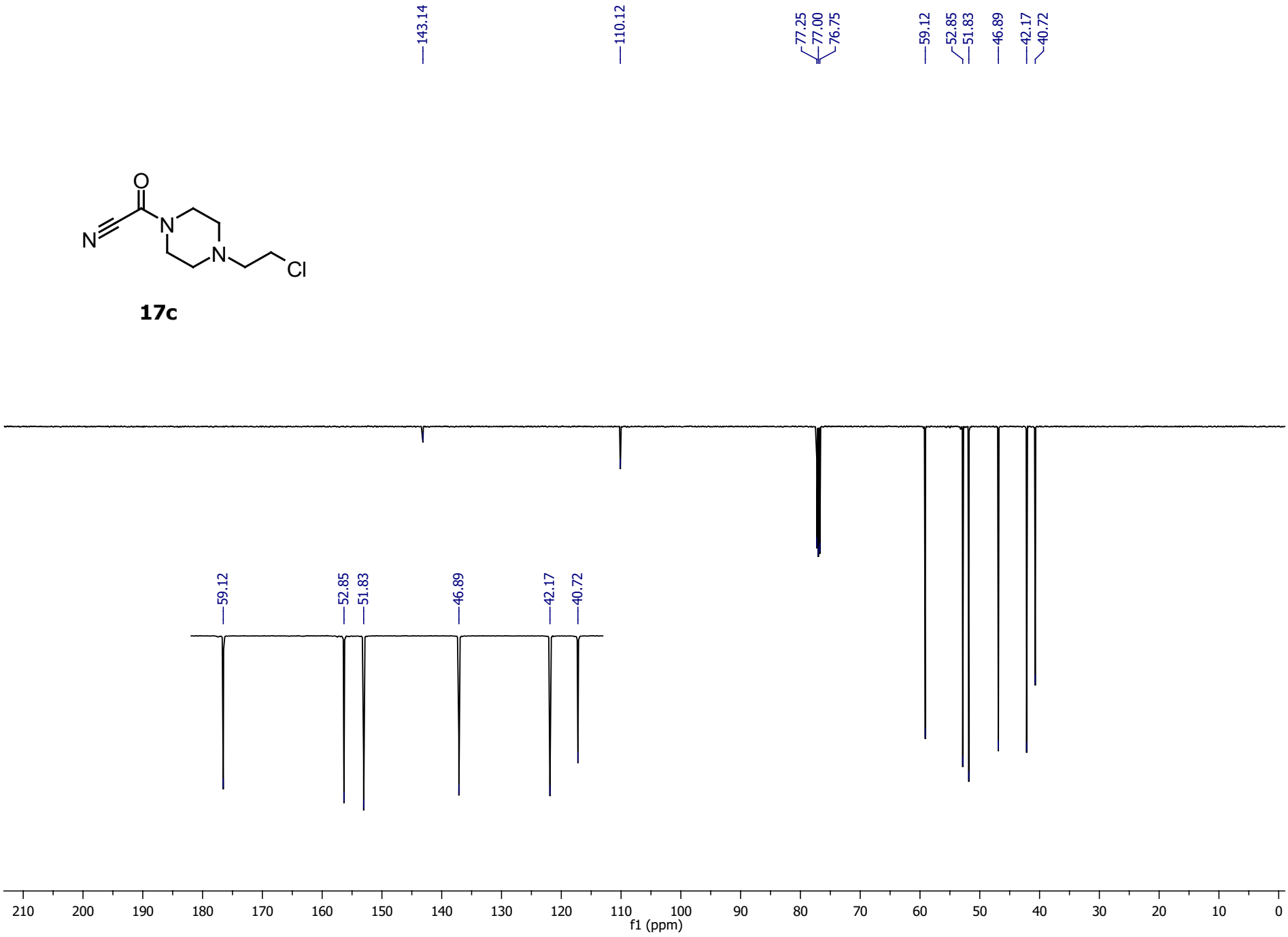
N-(2-Chloroethyl)-*N*-phenylpiperazine-1-carbimidoyl cyanide (**17b**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



4-(2-Chloroethyl)piperazine-1-carbonyl cyanide (**17c**) (^{1}H-NMR, 500 MHz, $CDCl_3$)

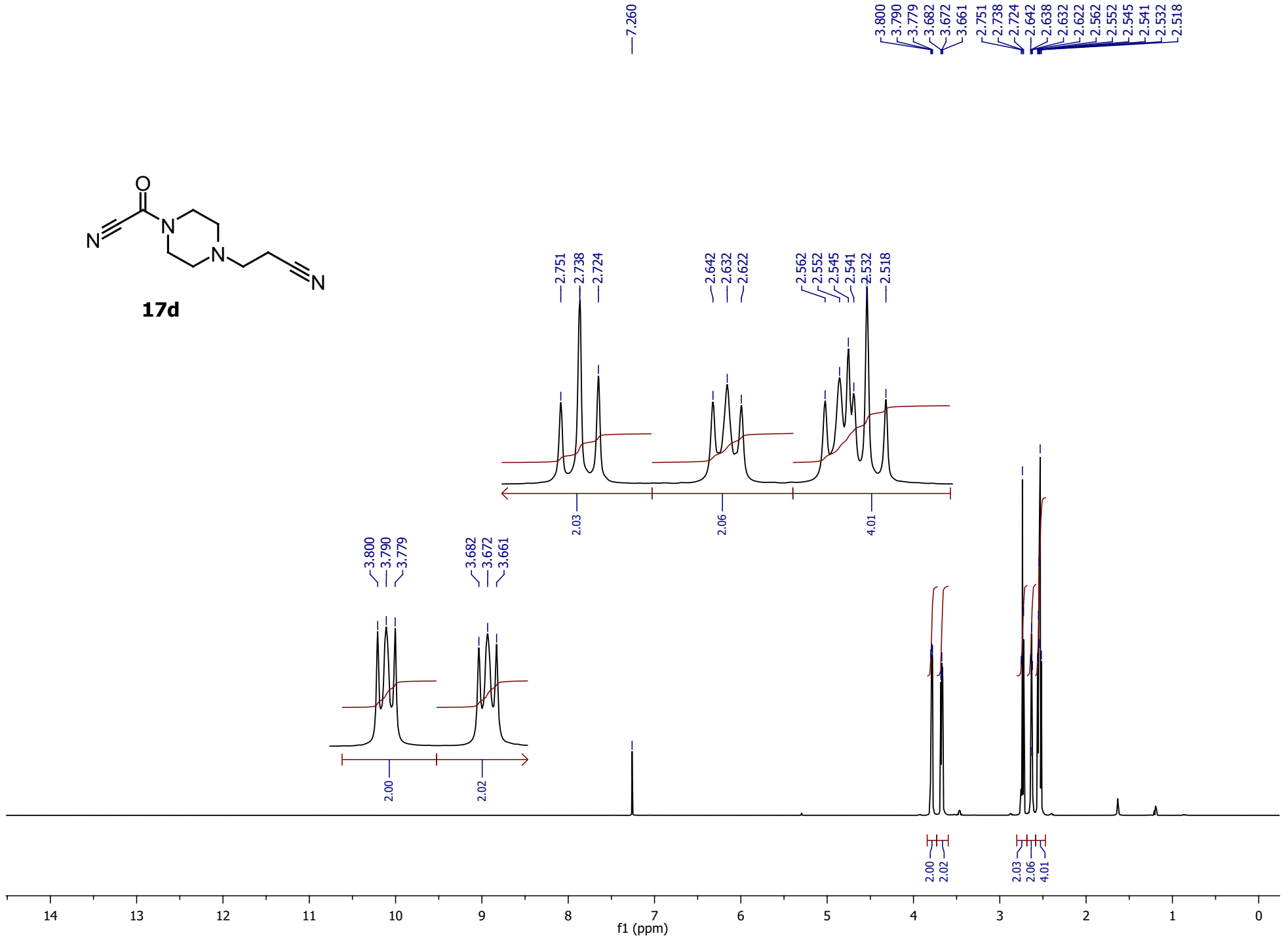


4-(2-Chloroethyl)piperazine-1-carbonyl cyanide (**17c**) (^{13}C-NMR, 125 MHz, $CDCl_3$)



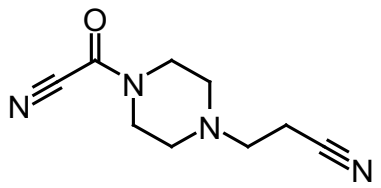
17c

N-(2-Cyanoethyl)piperazine-1-carbonyl cyanide (**17d**) (^{1}H-NMR, 500 MHz, $CDCl_3$)



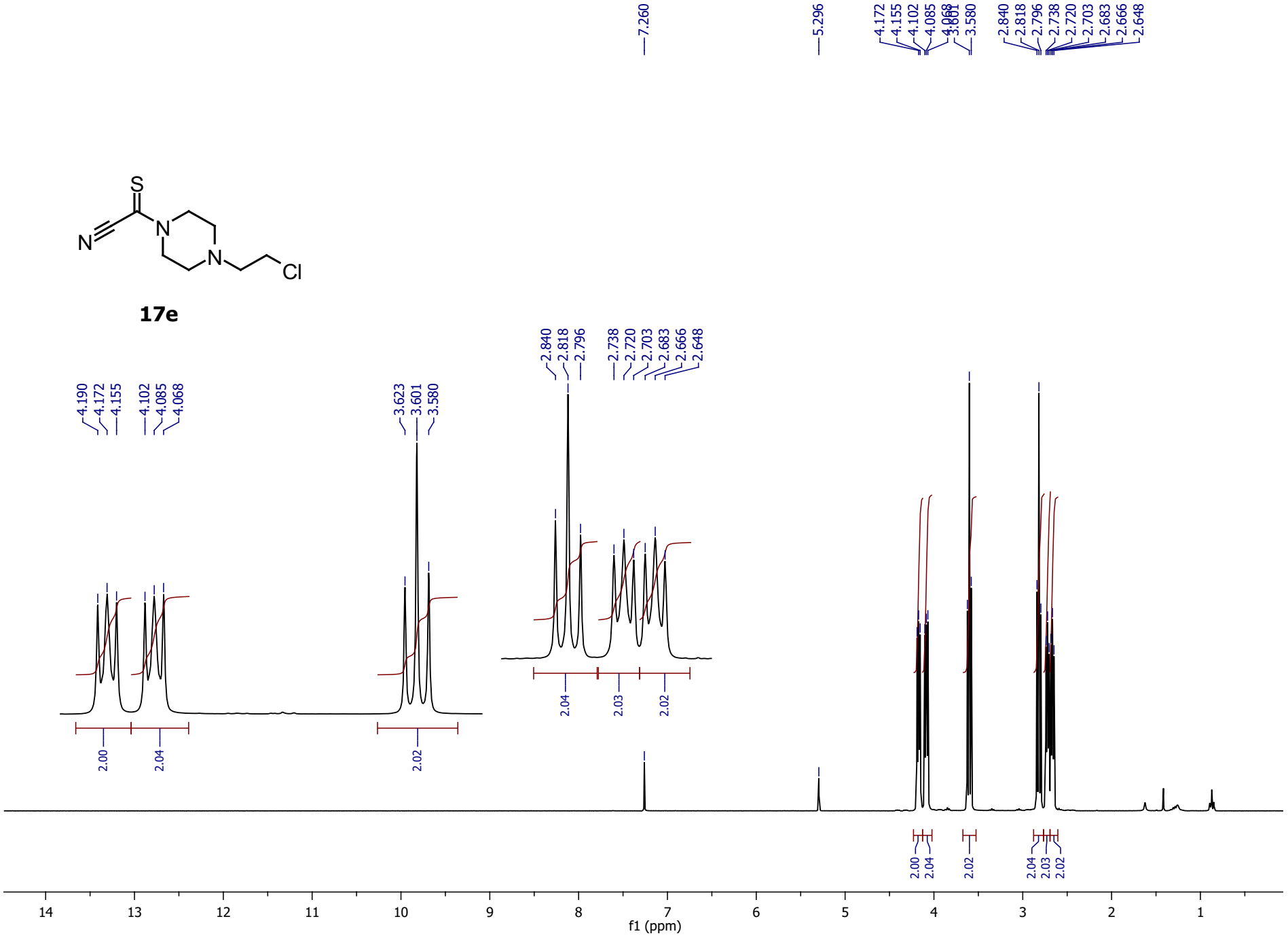
17d

N-(2-Cyanoethyl)piperazine-1-carbonyl cyanide (**17d**) (^{13}C-NMR, 125 MHz, $CDCl_3$)

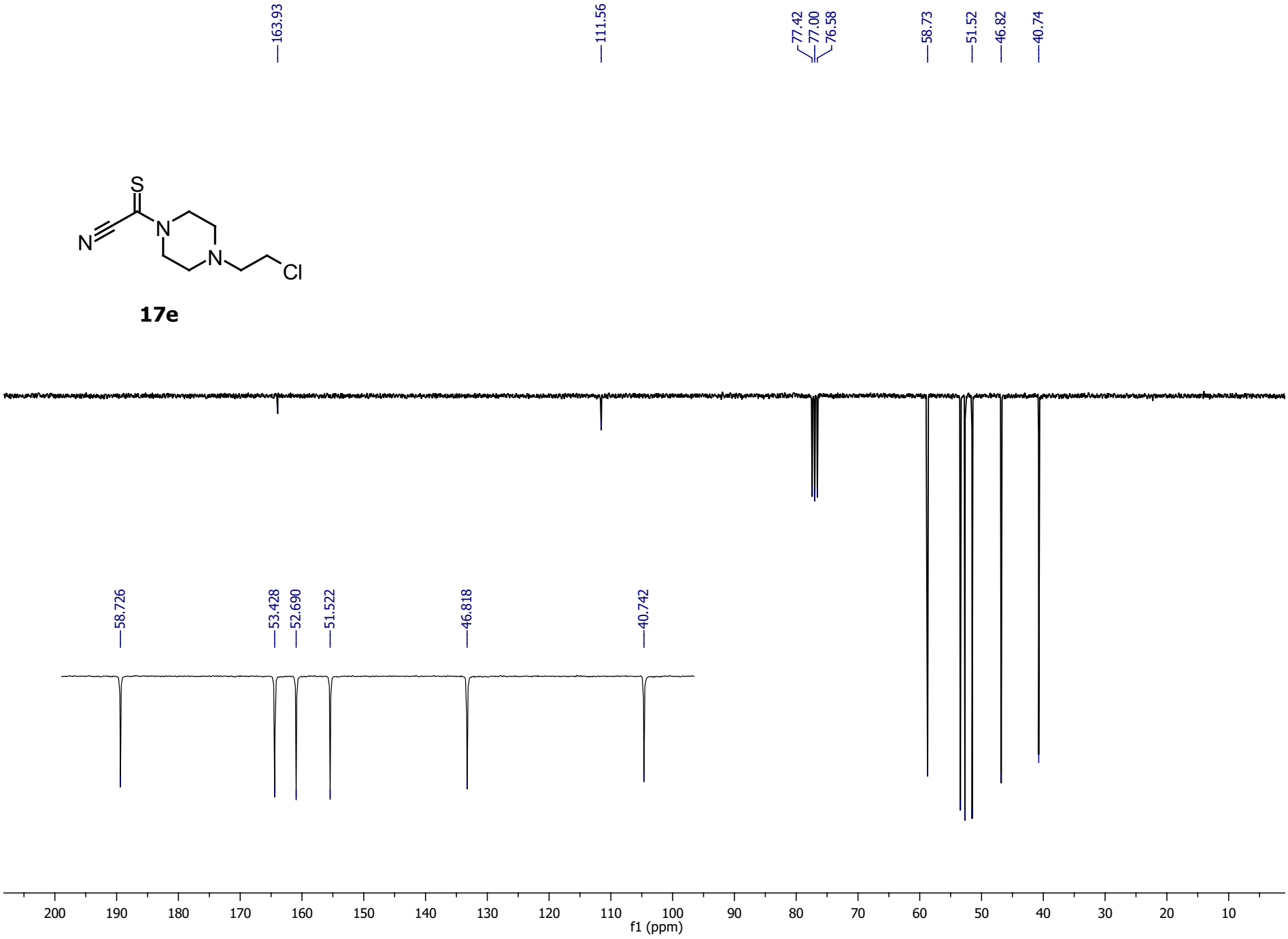


17d

4-(2-Chloroethyl)piperazine-1-carbothioyl cyanide **(17e)** (^{1}H-NMR, 300 MHz, $CDCl_3$)

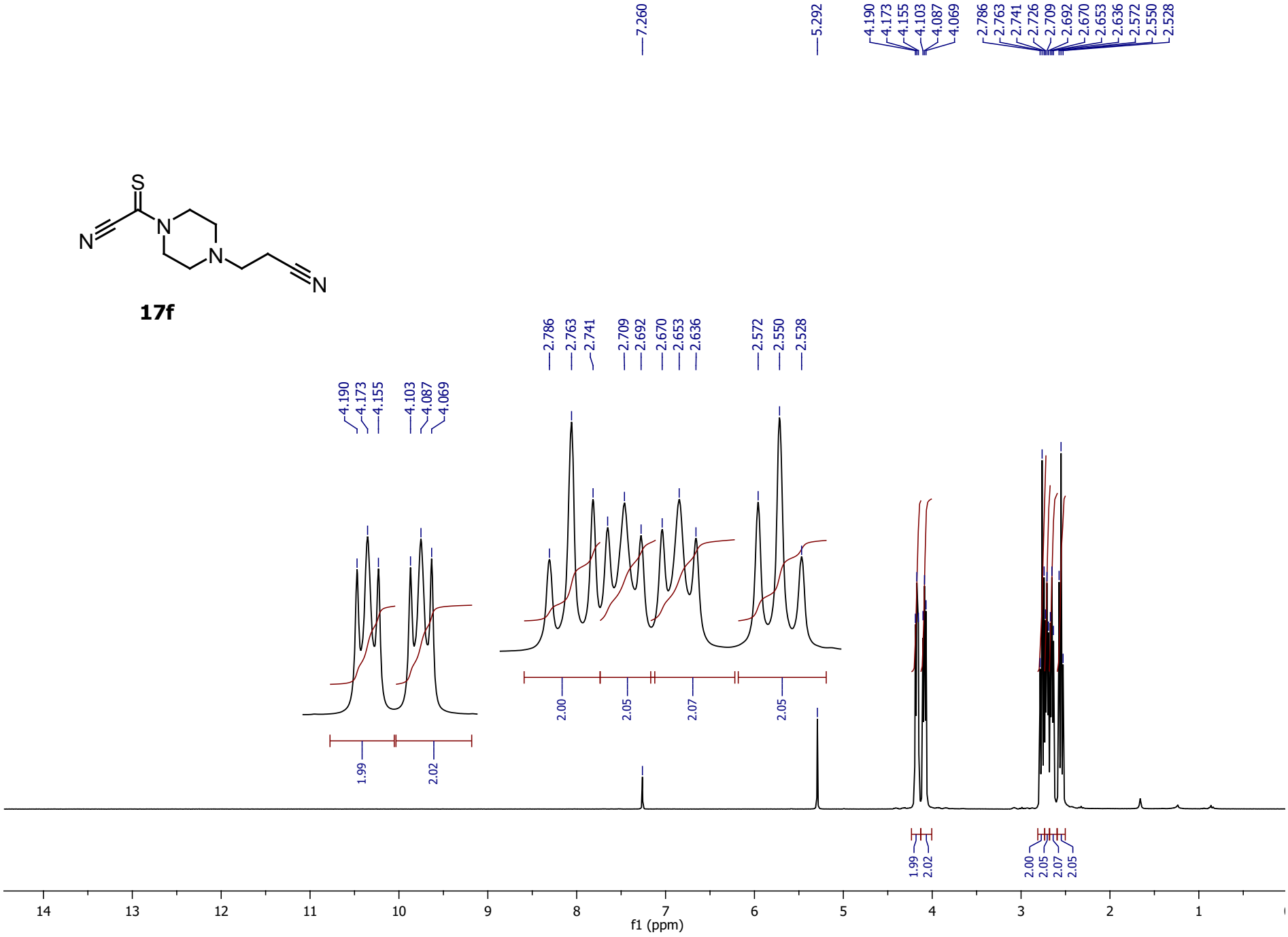


4-(2-Chloroethyl)piperazine-1-carbothioyl cyanide (**17e**) (^{13}C-NMR, 75 MHz, $CDCl_3$)



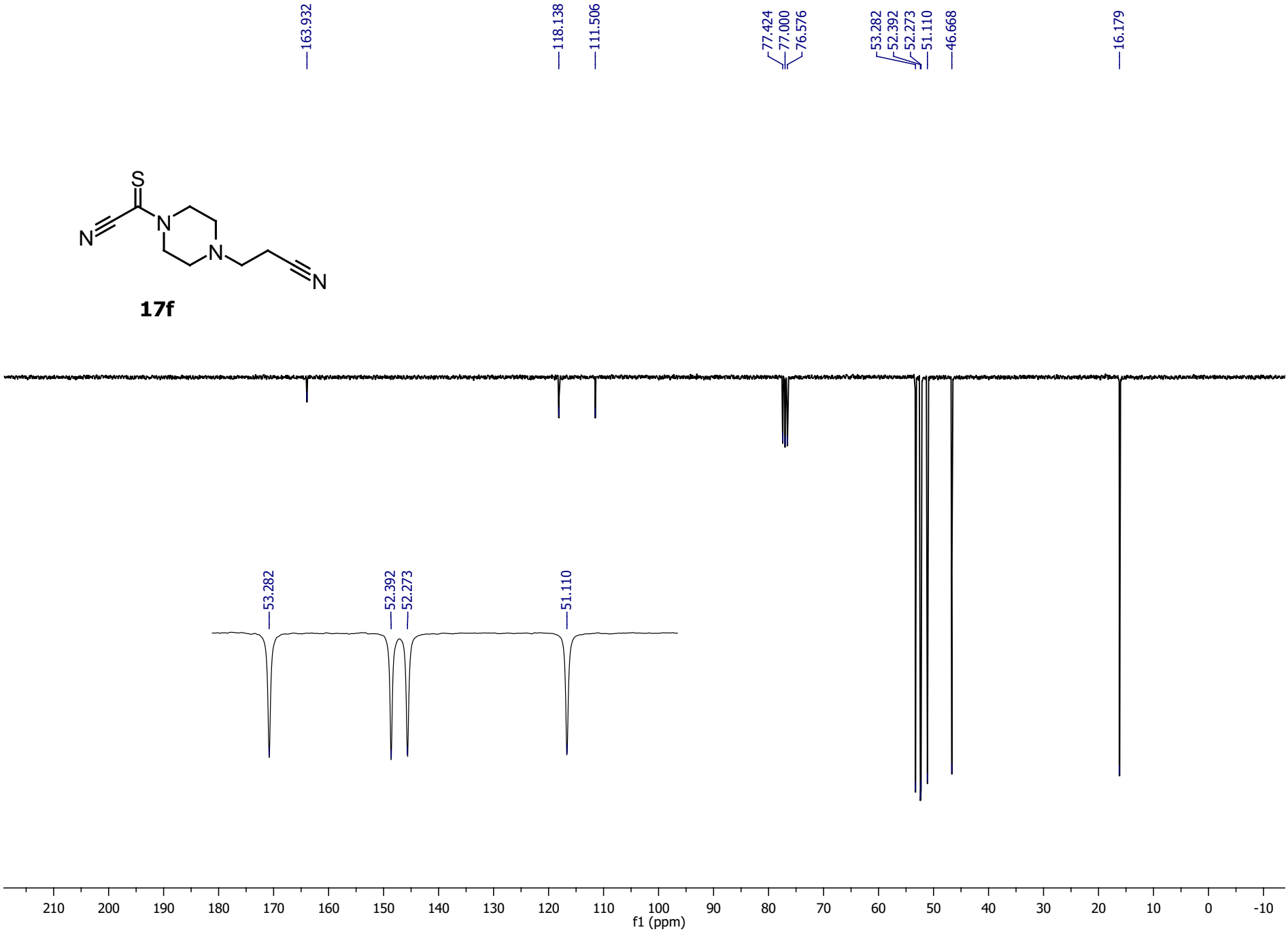
17e

4-(2-Cyanoethyl)piperazine-1-carbothioyl cyanide (**17f**) (^{1}H-NMR, 300 MHz, $CDCl_3$)

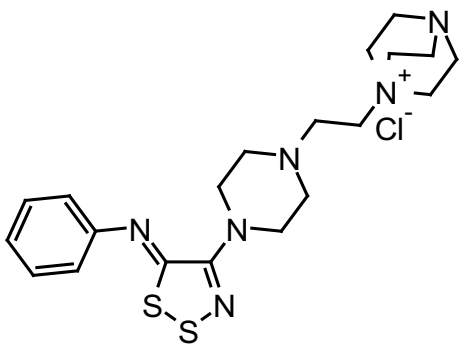


17f

4-(2-Cyanoethyl)piperazine-1-carbothioyl cyanide (**17f**) (^{13}C-NMR, 75 MHz, $CDCl_3$)

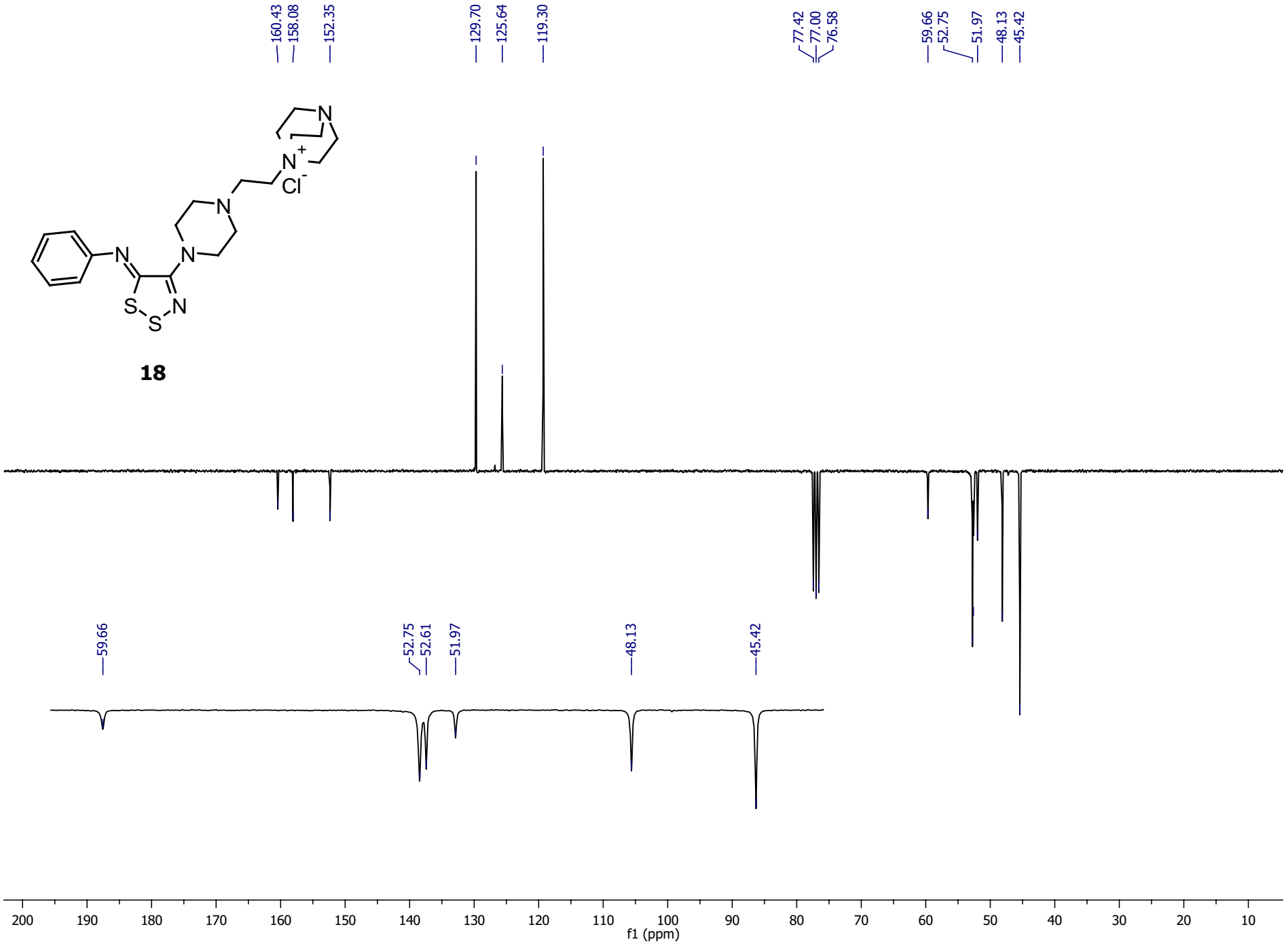


N-(2-{*N*-[5-(Phenylimino)-5*H*-1,2,3-dithiazol-4-yl]piperazin-1-yl}ethyl)-1,4-diazabicyclo[2.2.2]octan-1-iumchloride (**18**) (^{1}H-NMR, 300 MHz, $CDCl_3$)



18

N-(2-{*N*-[5-(Phenylimino)-5*H*-1,2,3-dithiazol-4-yl]piperazin-1-yl}ethyl)-1,4-diazabicyclo[2.2.2]octan-1-iumchloride (**18**) (^{13}C-NMR, 75 MHz, $CDCl_3$)



18