Supporting information

Novel and efficient methodology of thio-Michael addition to produce cis-β-thio-α-aminoacid derivatives using Zn[(*L*)-Pro]$_2$ as heterogeneous catalyst‡

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1. GENERAL METHODS

All the reaction was carried out via ultrasound device (UltraCleaner 1400A and 40 Hz with heating). All the temperature described for all the reactions by using of US was determined outside of flask (bath temperature). To obtain the US at 0 °C, we filled the US bath with crushed ice and water and maintain the temperature display off. Besides, to obtain US bath at 80 °C turned on the temperature display.

The azlactones were synthesized as described by The respective reactions were monitored by Thin Layer Chromatography (TLC) MACHEREY-NAGEL (SIL G / UV_{254}) and were visualized by fluorescence quenching with UV light at 254 nm. The purification of the compounds was performed through recrystallization using solvent EtOH.

For all the compounds the ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO on Varian Inova (400 MHz or 300 MHz and 100 MHz or 75 MHz, respectively) spectrometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.26 ppm, DMSO δ 2.5 for proton NMR, $CDCl_3$ δ 77.00 ppm and DMSO δ 39.43 ppm for carbon NMR). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t =triplet, m = multiplet), coupling constants (J) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The infrared spectra were recorded on Jasco 4000 spectrometer. Elemental analysis was performed using a Carlo-Erba EA-1110 instrument. The theory calculations were performed at B3LYP/6-311G^{++}(d,p) using GAUSSIAN 09 package. All calculations for compounds **2a**, **2e** and **2h** were carried out (at 298 K) using methods and basis sets implemented in the Gaussian package of programs (G03.E01) [1]. The hybrid Hartree–Fock density functional B3LYP method [2] with the 6-311G^{++}(d,p) basis set was used [3]. Full geometry optimizations were performed for the three compounds allowing complete relaxation of all internal parameters.

References:

1. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G.

Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, 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, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision E.01, Wallingford CT, 2004.

2. A.D. Becke, Phys. Rev. A 38 (1988) 3098; C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785; A.D. Becke, J. Chem. Phys. 98 (1993) 5648; P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
3. W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.

2. EXPERIMENTAL PROCEDURE

2.1 Catalyst – Synthesis of the chiral zinc (II) bis-*L*-prolinate or Zn[(*L*)-Pro]$_2$

First we carried out the synthesis of zinc (II) bis-*L*-prolinate catalyst, following the methodology described by the literature[4] in order to use it in the catalytic process for the β-thio-α amino acids derivatives production.

The zinc amino complex was prepared by adding NaOH (4.34 mmol) to the amino acid (4.34 mmol) in MeOH (10 ml) medium, followed, after 10 min, by zinc acetate (2.17 mmol). After stirring for 45 min, a white precipitate was collected by filtration (95% yield).

FTIR (ν/cm^{-1}): 3443, 2958, 1626, 1597, 1415, 1208, 937, 844, and 522.

Elem. anal. calculated for $C_{10}H_{16}N_2O_4Zn$. Calc: C, 40.91; H, 5.49; N, 9.54; Found: C, 40.70; H, 5.73; N, 9.32.

References

4. (a) M. Kidwai, A. Jain, *Appl. Organometal. Chem.* 2011, **25**, 620-625, (b) Z. N. Siddiqui, T. N. M. Musthafa, *Tetrahedron Letters* 2011, **52**, 4008–4013; (c) Z. N. Siddiqui, F. Farooq, Catal. *Sci. Technol*., 2011, 1, 810–816, (d) Z. N. Siddiqui, *Comptes Rendus Chimie*. 2013, **16**, 183–188, (e) V. Sivamurugan, K. Deepa, M. Palanichamy, V. Murugesan, Synth. Comm. 2004, **34**(21), 3833–3846, V. Sivamurugan, R. Suresh kumar, M. Palanichamy, V. Murugesan, J. *Heterocyclic Chem.*, 2005, **42**, 969-974.

2.2 Synthesis of benzoyl glycine.[5]

Glycine (1.0 mol) was dissolved in 750 ml of 10% sodium hydroxide solution. Posteriorly, was added benzoyl chloride (1.15 mol) in five portions with stirring until the reaction was completed. The solution was transferred to a beaker with a few grams of ice in the ice-bath and hydrochloric acid added. The precipitated product was filtered and washed with ice water. The solid was collected and recrystallized from hot water. Yield (95%)

2.3 General synthesis of azlactones.[5]

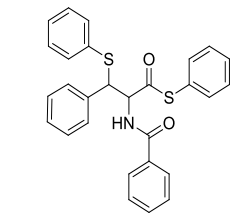
A mixture of aldehyde (1.0 mol), benzoyl glycine (1.0 mol), acetic anhydride (3.0 mol) and sodium acetate (1.0 mol) was heated in a water bath via magnetic stirring until the mixture is liquefied for 2 hours. After the end of the reaction was added 100 mL of ethanol and the mixture was allowed to stand overnight. The product was separated by filtration, washed with 25 ml of boiling water and recrystallized from acetone/water.(Yellow solid) Yield (97%)

Reference

5. Mocake, S. N, Lokwani, D, Shide, D. B, *Bioorg. Med. Chem*., 2012, **20**, 3119-3127.

3. EXPERIMENTAL PROCEDURE FOR ASYMMETRIC SYNTHESIS OF β-THIO- α- AMINO ACIDS

The azlactone **2** (0.22 mmol) was added with the catalyst **3** (0.043 mmol) in ethanol (5 mL) at room temperature and/or 80 ºC/ 0ºC, then thiophenol (1.084 mmol) was added and the mixture was inserted into the tube in the ultrasound up to 2 hours. The reaction product was purified by recrystallization with ketone/water to obtain products **4a**-**4u**.



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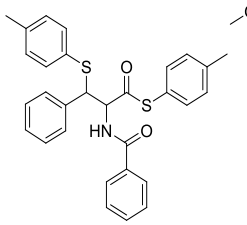

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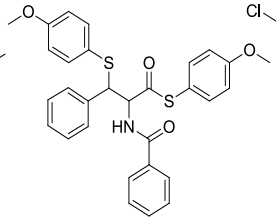

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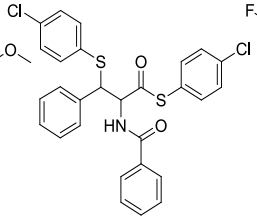

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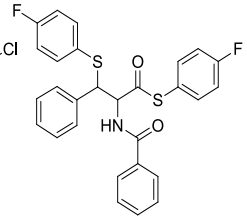

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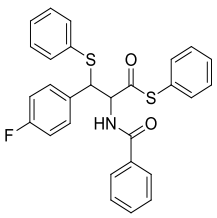

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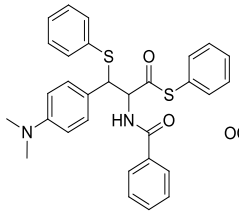

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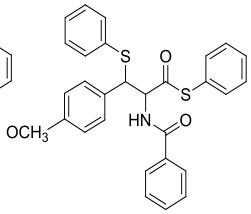

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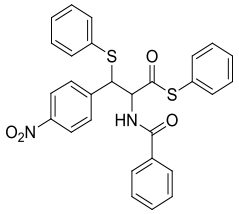

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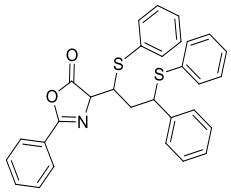

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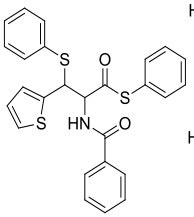

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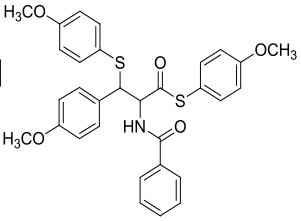

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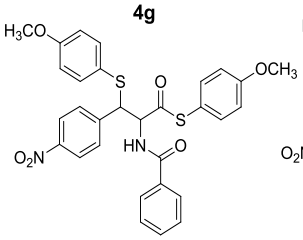

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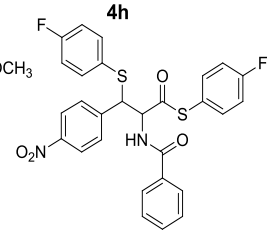

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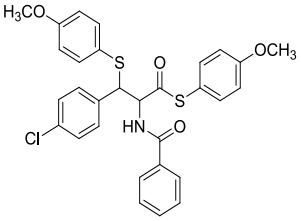

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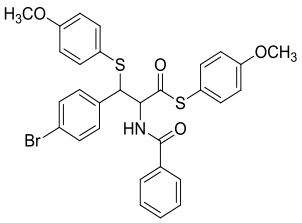

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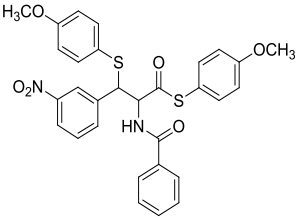

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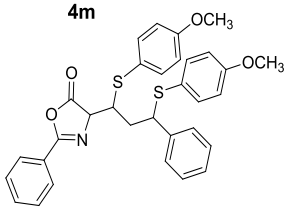

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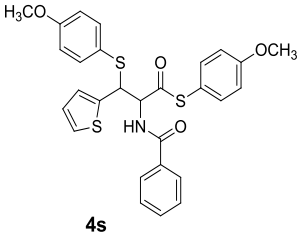

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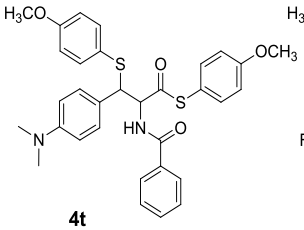

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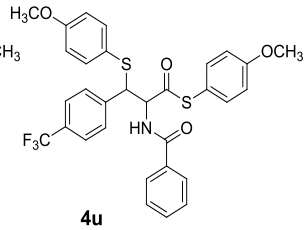
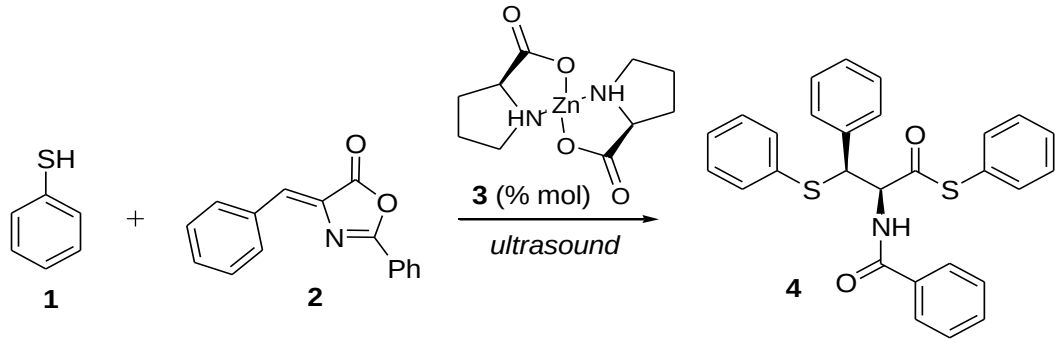


4u

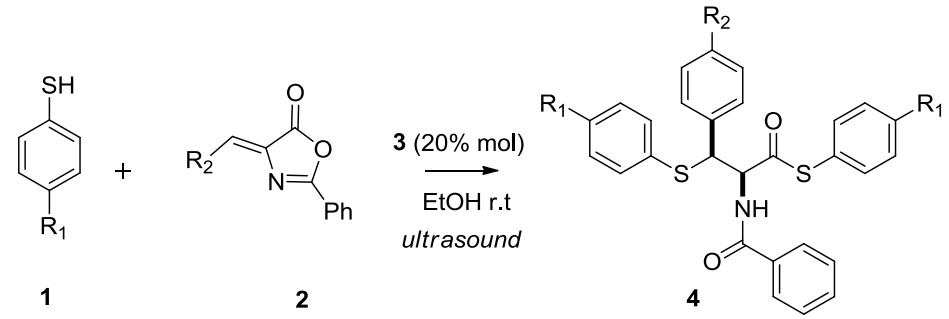
Table 1- Optimization of reactions conditions



Entry[a]	Thiol (eq mol)	Solv.	Catal(%mol)	Yields (%)	d.r.[b]
1	2	$CHCl_3$	10	49	64/36
2	2	$CHCl_3$	20	44	64/36
3	2	$CHCl_3$	30	53	64/36
4	2	THF	10	50	66/34
5	2	THF	20	52	66/34
6	5	THF	10	56	66/34
7	5	THF	20	65	66/34
8	5	EtOH[c]	20	100	70:30

[a]All the reactions were performed with (5 mL) of solvent at room temperature for 5 hours using U.S 40 Hz frequency, [b]isolated yield, ratio syn/anti which was determined by ^{1}H NMR, [c] This reaction was carried out in 2h using U.S (frequency 40 Hz).

Table 2- Asymmetric thio-Michael of 4-substituted azlactones and 4-substituted thiophenol.



R_1= H, OCH_3, CH_3, Cl, F

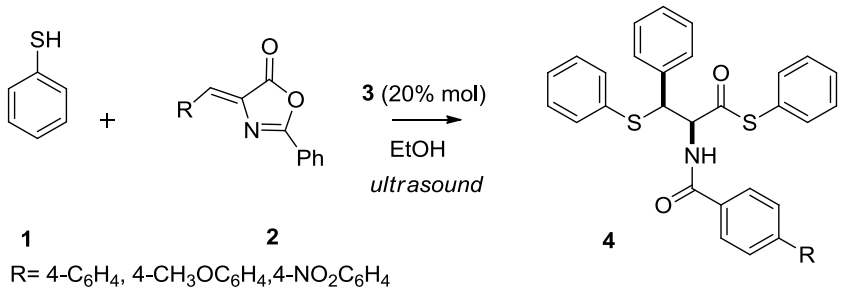
R_2= 4-C_6H_4, 4-$(CH_3)_2NC_6H_4$, 4-$CH_3OC_6H_4$, 4-ClC_6H_4, F-C_6H_4, 4-BrC_6H_4, 4-$NO_2C_6H_4$,3-$NO_2C_6H_4$, SC_5H_4, -CH=CHC_6H_4, 4-$CF_3C_6H_4$

Entry	R_1/R_2	Yields (%)[a]	d.r. (%)[b]
1	H **(1a)** /Ph **(2a)**	**(4a)**/100	70:30
2	4-OCH_3**(1b)**/Ph **(2b)**	**(4b)**/100	100:0
3	4-CH_3 **(1c)** /Ph **(2b)**	**(4c)**/100	100:0

4	4-Cl **(1d)** /Ph **(2b)**	**(4d)**/100	100:0
5	4-F **(1e)** /Ph **(2b)**	**(4e)**/100	40:60
6	H **(1a)** /4-FC_6H_4 **(2c)**	(**4f**)/100	[c]
7	H **(1a)**/4-$(CH_3)_2NC_6H_4$ **(2d)**	**(4g)**/	[d,e]
8	H **(1a)**/ 4-OCH_3 C_6H_4 **(2e)**	**(4h)**/60	[e] 40:60
9	H **(1a)** / 4-NO_2 C_6H_4 **(2f)**	**(4i)**100	100:0
10	H **(1a)** / C_6H_4CH=CH- **(2g)**	**(4j)**/100	[e,f]
11	H **(1a)** / C_4H_3S **(2h)**	**(4k)**/100	[e,f]
12	4-OCH_3 **(1b)** /4-OCH_3 C_6H_4 **(2e)**	**(4l)**/100	100:0
13	4-OCH_3 **(1b)** /4-$NO_2C_6H_4$ **(2f)**	**(4m)**/100	30:70
14	4-F **(1e)** /4-$NO_2C_6H_4$ **(2f)**	**(4n)**/100	100:0
15	4-OCH_3 **(1b)** /4-ClC_6H_4 **(2i)**	**(4o)**/100	100:0
16	4-OCH_3 **(1b)** /4-Br C_6H_4 **(2j)**	**(4p)**/100	100:0
17	4-OCH_3 **(1b)**/ 3-$NO_2C_6H_4$**(2k)**	**(4q)**/100	100:0
18	4-OCH_3 **(1b)** /C_6H_4CH=CH- **(2g)**	**(4r)**/100	[e,f]
20	4-OCH_3 **(1b)**/4-$(CH_3)_2NC_6H_4$ **(2d)**	**(4s)**/	[d,e]
21	4-OCH_3 **(1b)**/ C_4H_3S **(2h)**	**(4t)**/100	[e,f]
22	4-OCH_3**(1b)** / 4-$CF_3C_6H_4$ **(2m)**	**4(u)**/100	100:0

[a]Isolated yields for reactions carried out with **1** (1.08 mmol), **2** (0.22 mmol), 2h (0.044 mmol) catalyst in ethanol (5 ml) at room temperature; [b]diastereomeric ratio described by ^{1}H NMR analysis; [c]d.r. was impossible to be determined by ^{1}H NMR; [d]no reaction; [e]Reaction performed in 5h; [f]only the compound from carbonyl attack was obtained (ring open).

Table 3- Yields and d.r. for thio-Michael between of 4-substituted azlactones and 4-substituted thiophenol at 0º C, r.t. and 80º C



1 **2** **4**

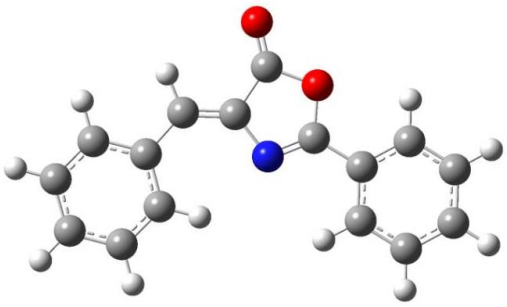
R= 4-C_6H_4, 4-$CH_3OC_6H_4$,4-$NO_2C_6H_4$

Azlactone[a] 4-substituted	**Yield at 0° C**	**Yield at r.t.**	**Yield at 80 °C**
NO_2	**(4i)**/100	**(4i)**/100	**(4i)**/100
H	**(4a)**/100	**(4a)**/100	**(4a)**/100
OCH_3	**(4h)**/60	**(4h)**/60	**(4h)**/50

[a]Isolated yields for reactions performed with **1** (1.08 mmol), **2**(0.22 mmol), 2h (0.044 mmol) catalyst in ethanol (5 ml).

4. THEORETIC CALCULATION B3LYP 6-311G^{++} (d,p) LEVEL

4.1 Optimized structure for compound **2a**



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# RB3LYP/6-311++G(d,p) Opt Test
```

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C	1.40992600	0.53819600	-0.00005400
N	0.21097400	0.05707600	-0.00023500
C	-0.64420400	1.15925700	-0.00028500
C	0.18089700	2.39002100	-0.00003000
O	-0.07518100	3.55717500	0.00016500
C	-1.99957100	1.20025100	-0.00018000
C	-2.96556600	0.11820400	-0.00006200
C	2.65962100	-0.21152900	-0.00012600
C	2.62428400	-1.61474400	-0.00023300
C	3.80876300	-2.33867200	-0.00023800
C	5.03752500	-1.67416800	0.00008900
C	5.07696900	-0.28069800	0.00032700
C	3.89471800	0.45278300	0.00011500
C	-4.33448700	0.45325900	-0.00008600
C	-5.31372500	-0.53220300	0.00003100
C	-4.94592200	-1.87743500	0.00019400
C	-3.59365800	-2.22681700	0.00023800
C	-2.61002800	-1.24636200	0.00009600
H	-2.41335100	2.20518000	-0.00017100
H	1.66493700	-2.11642400	-0.00037300
H	3.77795600	-3.42214100	-0.00041500
H	5.96071400	-2.24260200	0.00018300
H	6.02963300	0.23609700	0.00071000
H	3.91931400	1.53485100	0.00013200
H	-4.62229500	1.49933100	-0.00020300
H	-6.36126400	-0.25343000	-0.00000100
H	-5.70719100	-2.64938600	0.00028000
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```
1 2 1.0 5 1.0
2 3 2.0 9 1.0
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```
 3 4 1.0
 4 5 1.0 7 2.0
 5 6 2.0
 6
 7 8 1.0 20 1.0
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 9 10 1.5 14 1.5
 10 11 1.5 21 1.0
 11 12 1.5 22 1.0
 12 13 1.5 23 1.0
 13 14 1.5 24 1.0
 14 25 1.0
 15 16 1.5 26 1.0
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 17 18 1.5 28 1.0
 18 19 1.5 29 1.0
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 30
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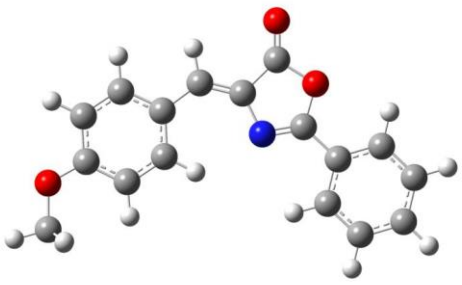
4.2 Optimized structure for compound **2e**



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# RB3LYP/6-311++G(d,p) Opt Test

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 N                  0.92201900    0.27651100    0.00010400
 C                  0.31347200    1.53273400   -0.00009000
 C                  1.37055200    2.56485400   -0.00011100
 O                  2.56863800    1.82220000   -0.00014100
 O                  1.36345500    3.76105300   -0.00012800
```

```
C                  3.26266600   -0.49288000   -0.00006100
C                 -1.00803400    1.84761700   -0.00000700
C                 -2.16957900    0.98905700    0.00010800
C                  2.93874500   -1.85863500    0.00011600
C                  3.94770800   -2.81217000    0.00018600
C                  5.28754800   -2.41693800    0.00009200
C                  5.61373100   -1.06167200   -0.00006600
C                  4.60859600   -0.09931000   -0.00013700
C                 -3.45013200    1.58729700    0.00033300
C                 -4.60364400    0.82850000    0.00032100
C                 -4.51925500   -0.57156900    0.00004600
C                 -3.26128700   -1.18978500    0.00000300
C                 -2.10709500   -0.41734200    0.00002700
O                 -5.70304100   -1.23502900   -0.00022200
C                 -5.69714100   -2.65957400   -0.00026800
H                 -1.20811200    2.91599700   -0.00007800
H                  1.89630700   -2.15092700    0.00021300
H                  3.69316400   -3.86586000    0.00033500
H                  6.07314200   -3.16409100    0.00015600
H                  6.65264500   -0.75272800   -0.00011100
H                  4.85655700    0.95426900   -0.00021400
H                 -3.52733900    2.66943300    0.00045300
H                 -5.58335900    1.29024200    0.00044200
H                 -3.17321900   -2.26789000    0.00013000
H                 -1.13901600   -0.89939400   -0.00008700
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H                 -5.20530100   -3.05477600   -0.89477100
H                 -5.20653200   -3.05475500    0.89492900

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2 3 1.0
3 4 1.0 8 2.0
4 5 1.0 6 2.0
5
6
7 10 1.5 14 1.5
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19 31 1.0
20 21 1.0
21 32 1.0 33 1.0 34 1.0
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23
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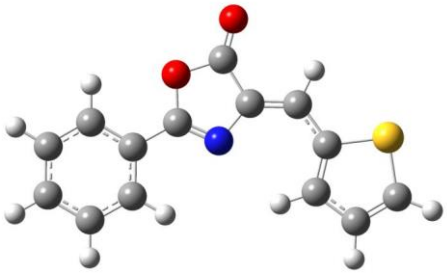
4.3.Optimized structure for compound **2h**



RB3LYP/6-311++G(d,p) Opt Test

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C	-2.73584800	-1.57864700	0.00003200
C	-3.94620200	-2.25826900	-0.00000200
C	-5.14965800	-1.54886800	-0.00011500
C	-5.13749400	-0.15488400	-0.00019700
C	-3.92893800	0.53440000	-0.00016000
H	2.46859600	2.01727200	0.00019100
H	1.49379900	-1.80267600	0.00065000
H	3.60678900	-3.38027100	0.00063500
H	5.84278400	-1.99504600	-0.00016900

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H                 -1.79573300   -2.11545200    0.00010500
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H                 -6.09316100   -2.08288800   -0.00013600
H                 -6.07039300    0.39679100   -0.00029600
H                 -3.91361800    1.61663000   -0.00022600

1 2 1.0 5 1.0
2 3 2.0 7 1.0
3 4 1.0
4 5 1.0 8 2.0
5 6 2.0
6
7 14 1.5 18 1.5
8 9 1.5 19 1.0
9 10 2.0 13 1.0
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18 27 1.0
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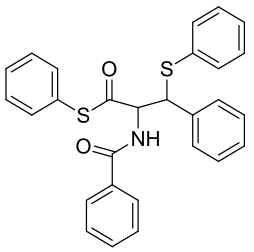
5. ^{1}H and ^{13}C NMR spectra analysis

S-phenyl 2-benzamido-3-phenyl-3-(phenylthio)propanethioate (4a)



Chemical Formula: $C_{28}H_{23}NO_2S_2$
Molecular Weight: 469.62

Ultrasound r. t,100% yield, dr = 70/30, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9-7.7 (m, 3H), 7.6-7.4 (m, 5H), 7.4-7.3 (m, 12H), 7.4–7.3 (m, 9H), 7.3-7.2 (m, 4H), 7.2–7.1 (m, 3H), 7.2–7.1 (m, 3H), 5.5 (m, 2H), 5.1-4.9 (d, J_{anti} = 4.3 Hz, 0.5H, d, J_{syn} = 5.3 Hz, 1H); *Ultrasson 80ºC*, 100% yield, dr = 55/45, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9-7.7 (t, 4H), 7.6-7,1 (m, 41H), 5.5-5.4 (m, 2 H), 5.1-5.0 (d, *J* = 8.0 Hz, 1H), 5.1-5.0 (*J* = 4.3 Hz, 1H);

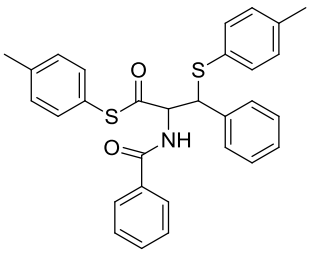
Ultrasound 0ºC, 100% yield, dr = 90/10 ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.8-7.7 (m, 2H), 7.6-7.4 (m, 4H), 7.4-7.1 (m, 15H), 7.2-7.1 (m, 3H), 5.5-5.4 (m, 1H), 5.1-5.0 (dd, *J*= 4.3 Hz, *J* = 9.9 Hz, 1H);

^{13}C NMR *Ultrasound r. t* (75 MHz, $CDCl_3$) δ 197.5, 197.0, 167.1, 137.0, 134.5, 132.7, 134.5, 133.3, 132.7, 132.6, 132.2, 132.1, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 129.05, 129.0, 129.0, 128.9, 128.82, 128.8, 128.7, 128.69, 128.61, 128.23, 128.16, 128.0, 127.9, 127.5, 127.2, 127.1, 126.7, 117.3, 71.5, 63.2, 61.7, 58.7, 55.5, 55.1;

IR (KBr) νmax: 3424, 3294, 3059, 2920, 2849, 1699, 1639, 1538, 1482, 1023, 740, 691 cm^{-1}.

Elem. anal. calculated for $C_{28}H_{23}NO_2S_2$: C 71.61, H 4.94, N 2.98; found: C 71.31, H 4.86, N 3.15.

S-p-tolyl 2-benzamido-3-phenyl-3-(p-tolylthio)propanethioate (4b)



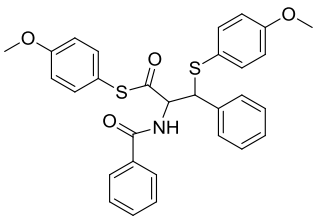
Chemical Formula: $C_{30}H_{27}NO_2S_2$
Molecular Weight: 497.67

100% yield, dr =100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2-8.1 (m, 3H), 7.8-7.7 (m, 2H), 7.5-7.3 (m, 8H), 7.3-7.2 (m, 2H), 7.2 (m, 9H), 7.1 (m, 3H), 7.0 (m, 4H), 5.4-5.3 (dd, *J* = 8.9 Hz, *J* = 5.0 Hz, 1H), 4.9-4.8 (d, J_{syn}= 5.0 Hz, 1H), 2.3 (s, 3H), 2.2 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 167.9, 139.9, 138.3, 138.1, 134.5, 134.0, 133.0, 132.1, 129.9, 128.8, 128.7, 128.6, 128.1, 127.2, 123.2, 128.1, 127.3, 123.4, 63.1, 62.9, 55.8, 21.4.

Elem. anal. calculated for $C_{30}H_{27}NO_2S_2$: C 72.40; H 5.47; N 2.81; found: C 72.15; H 5.38; N 2.63.

S-(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-phenylpropanethioate (4c)

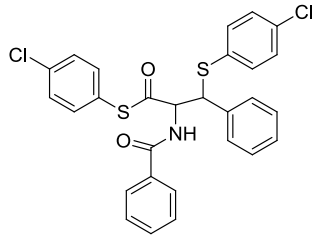


Chemical Formula: $C_{30}H_{27}NO_4S_2$
Molecular Weight: 529.67

100% yield, dr = 100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.8-7.7 (m, 2H), 7.5-7.4 (m, 3H), 7.2-7.1 (m, 9H), 7.0- 6.9 (m, 2H), 6.8-6.6 (m, 4H), 5.4-5.3, (dd, J = 8.8 Hz, J = 5.3 Hz, 1H), 4.8- 4.7 (d, J_{syn} =5.3, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 167.0, 160.6, 160.1, 138.2, 136.0, 135.8, 133.6, 132.1, 128.8, 128.6, 128.3, 128.0, 127.3, 123.0, 117.4, 114.8, 114.7, 77.4, 77.0, 76.6, 62.7, 56.5; IR (KBr) *v*max: 3443.7, 2958.2, 2834.8, 1714.4, 1639.6, 1591.4, 1514.0, 1490.2, 1284.8, 1251.58, 1172.9, 1027.39, 825.9, 713.5 cm^{-1}.

Elem. anal. calculated for $C_{30}H_{27}NO_2S_2$: C, 72.40; H, 5.47; N, 2.81; found: C 72.15; H 5.38; N 2.63.

S-(4-chlorophenyl) 2-benzamido-3-((4-chlorophenyl)thio)-3-phenylpropanethioate (4d)

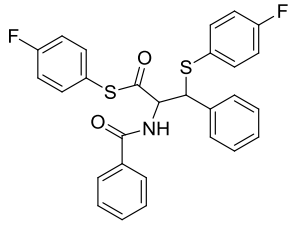


Chemical Formula: $C_{28}H_{21}Cl_2NO_2S_2$
Molecular Weight: 538.51

100% yield, dr = 100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2-8.1 (m, 1H), 7.9-7.8 (m, 2H), 7.6- 7.5 (m, 5H), 7.3-7.2 (m, 9H), 7.2-7.0 (m, 5H), 5.5-5.4 (dd, J = 8.9 Hz, J = 5.2 Hz, 1H), 5.0-4.9 (d, J_{syn} =5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.7, 167.1, 136.3, 136.2, 135.6, 134.5, 134.3, 134.2, 133.1, 133.3, 132.5, 132.4, 131.3, 131.2, 129.6, 129.3, 128.9 128.8, 128.4, 128.2, 127.2, 125.1, 99.9, 77.5, 77.2, 77.0, 76.6, 62.9, 55.6; IR (KBr) *v*max: 3444, 3313, 3062, 2923, 1692, 1646, 1631, 1526, 1472, 1384, 1329, 1094, 1009, 978, 812, 685 cm^{-1}.

Elem. anal. calculated for $C_{28}H_{21}Cl_2NO_2S$: C 62.45; H 3.93; N 2.60; found: C 62.2; H 3.82; N 2.63.

S-(4-fluorophenyl) 2-benzamido-3-((4-fluorophenyl)thio)-3-phenylpropanethioate (4e)



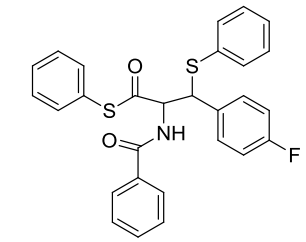
Chemical Formula: $C_{28}H_{21}F_2NO_2S_2$
Molecular Weight: 505.60

100% yield, dr = not determinated, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.8- 7.7(m, 2H), 7.5-7.4 m, 3H), 7.1 (m, 12H), 7.0- 6.9 (m,3H), 5.5-5.3 (dd, J = 9.5 Hz, J_{syn} = 5.4 Hz, 1H) and (dd, J = 9.5 Hz, J_{anti} = 4.6 Hz, 0.4H), 4.90 (dd, J_{syn} = 5.4 Hz, 1H, J_{anti} = 4,49 Hz, 0,4H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 196.7, 166.9, 166.8, 163.5, 163.3, 161.5, 161.3, 134.4, 134.0, 133.8, 133.7, 133.3, 133.4, 132.9, 132.8, 132.7, 132.6, 132.5, 132.3, 132.2, 132.1, 130.3, 130.2, 129.9, 129.8, 129.7, 129.6, 129.3, 129.2, 128.8, 128.2, 128.1, 127.2, 127.1, 115.9, 115.6, 115.7, 115.5, 63.1, 61.6, 54.8, 54.4, 18.4.

Elem. anal. calculated for $C_{28}H_{21}F_2NO_2S_2$: C 66.52; H 4.19; N 2.77; found: C 66.23; H 4.08; N 2.88.

S-phenyl 2-benzamido-3-(4-fluorophenyl)-3-(phenylthio)propanethioate (4f)

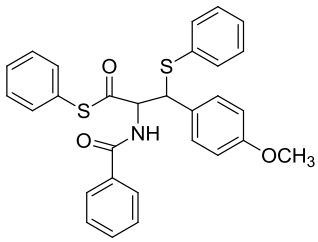


Chemical Formula: $C_{28}H_{22}FNO_2S_2$
Molecular Weight: 487.61

100% yield, d.r = not determinated, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.8-7.7 (m, 2H), 7.6-7.4 (m, 3H), 7.4-7.2 (m, 12H), 7.1-6.9 (m, 3H), 5.5-5.3 (m, 0.45H), 5.5-5.41 (m, 1H), 5.1-4.9 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 137.0, 134.4, 132.8, 132.7, 132.3, 130.0, 129.9, 129.7, 129.6, 129.4, 129.2, 128.9, 128.8, 128.2, 128.1, 127.4, 127.3, 127.2, 127.1, 125.5, 115.7, 115.5, 63.1, 54.8.

Elem. anal. calculated for $C_{28}H_{22}FNO_2S_2$: C 68.97, H 4.55, N 2.87; found: C 68.72, H 4.43, N 2.82.

S-phenyl 2-benzamido-3-(4-methoxyphenyl)-3-(phenylthio)propanethioate (4h)



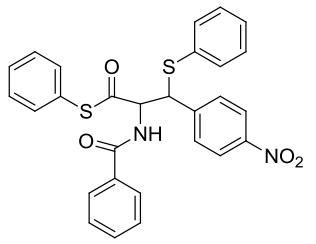
Chemical Formula: $C_{29}H_{25}NO_3S_2$
Molecular Weight: 499.64

Ultrasound r.t, 60% yield, dr =35/65 ^{1}H NMR: δ 7.8-7.7 (m, 3H), 7.5-7.1 (m, 17 H), 6.9- 6.7 (m, 2H), 6.5-6.4 (m, 1H), 5.43-5.3 (m, 1.49 H), 4.9-4.0 (dd, J_{anti}=4.1 Hz, J_{syn}= 5.3Hz, 1.49H), 3.8 (s, 3H); *Ultrasound 80ºC*, 50% yield, d.r 60/40, ^{1}H NMR: δ 7.8-7.7 (m,4H), 7.5-7.1 (m, 4H), 6.8-6.7 (m, 4H), 5.4-5.3 (m, 1.74H), 5.0-4.9 (dd, J_{anti}=4.1 Hz, J_{syn}=5.3Hz, 1.67H),

3.8 (s, 3H), 3.7 (s, 3H); *Ultrasound 0ºC*, 60% yield, dr = 100/0, ^{1}H NMR: δ 8.1 (m, 5H), 7.8 (m, 2H), 7.5 (m, 8H), 7.2-7.1 (m, 15H), 7.0 (m, 2H), 5.5-5.4 (dd, *J*= 8.8 Hz, *J*= 5,3 Hz, 1H), 4.8 (d, J_{syn} = 5.2 Hz, 1H), 3.8 (s, 3H), 3.8 (s, 3H), 3.7 (s, 1.57H); ^{13}C NMR *Ultrasound r. t* (75 MHz, $CDCl_3$): δ 197.7, 197.3, 197.0, 167.1, 159.6, 134.5, 133.7, 133.5, 132.7, 132.2, 129.9, 129.6, 129.5, 129.4, 129.1, 128.9, 127.9, 127.8, 127.3,127.2, 126.9, 114.3, 114.2, 63.4, 63.2, 61.7, 55.4, 54.9, 54.3. IR (KBr) νmax: 3454, 3335, 3055, 2931, 2830, 1696, 1639, 1512, 1479, 1255, 1176, 1031, 982, 747, 691 cm^{-1}.

Elem. anal. calculated for $C_{29}H_{25}NO_3S_2$: C 69.71; H 5.04; N 2.80; found: C 69.43; H 4.96; N 2.87.

S-phenyl 2-benzamido-3-(4-nitrophenyl)-3-(phenylthio)propanethioate (4i)



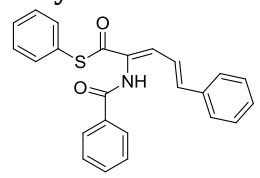
Chemical Formula: $C_{28}H_{22}N_2O_4S_2$
Molecular Weight: 514.62

Ultrasound r.t, 100% yield, dr =100/0 ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0 (d, 2H), 7.8 (d, 2H), 7.5- 7.4 (m, 5H), 7.2-7.0 (m, 6H), 5.5-5.4 (dd, *J* = 9.1 Hz, *J* = 5.3 Hz, 1H), 5.0 (d, J_{syn}= 5.2, 1H); *Ultrasound 80ºC*, 100% yield, dr = 100/0 ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2-8.1 (t, 3H), 7.9-7.8 (d, *J*= 8.1 Hz, 3H), 7.6-7.5 (m, 8H), 7.4-7.3 (m, 5H), 7.3-7.2 (m, 8H), 5.1, 5.0 (d, J_{syn}= 5.1 Hz, 1H), 4.4-4.4 (m, 1H);

Ultrasound 0ºC, 100% yield, dr =40/60 ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.4-8.1 (m, H), 7.9-7.8 (d, *J* = 6.4 Hz, 1H), 7.8-7.0 (d, *J* = 8.2 Hz, 2H), 7.6-7.0 (m, 26H), 5.7-5.6 (m, 1H), 5.6-5.5 (m, 0.60 H), 5.1-5.0 (m, 0.63H), 5.0-4.9 (m,1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 196.2, 167.0, 166.8, 147.6, 147.5, 144.3, 134.4, 134.3, 133.1, 133.0, 132.9, 132.5, 132.4, 132.2, 131.8, 130.0, 129.9, 129.6, 129.5, 129.4, 129.3, 129.2, 129.0, 128.9, 128.8, 128.5, 128.6, 127.5, 127.2, 127.1, 127.0, 126.9, 126.2, 126.0, 123.8, 62.5, 61.2, 55.3, 55.1.

Elem. anal. calculated for $C_{28}H_{22}N_2O_4S_2$: C 65.35; H 4.31; N 5.44; found: C 65.05; H 4.13; N 5.55.

S-phenyl 2-benzamido-5-phenylpenta-2,4-dienethioate (4j)

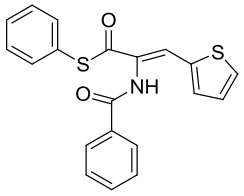


Chemical Formula: $C_{24}H_{19}NO_2S$
Molecular Weight: 385.48

100% yield, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9-7.8 (m, 1H), 7.7 (s,0.41), 7.5-7.3 (m, 6H), 7.3-7.2 (m,1.57H), 7.2 (s, 1H), 7.0-6.8 (m, 1H), 1,5 (s, 2.44H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 166.2, 166.04 161.3, 135.8, 135.6, 134.5, 133.5, 133.3, 133.2, 133.1, 132.3, 132.1, 132.0, 131.6, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.4, 127.9, 127.8, 127.6, 127.4, 127.3, 125.2, 122.5; IR (KBr) *ν*max: 3447, 1785, 1755, 1647, 1636, 1494, 1449, 1333, 1299, 1191, 967, 889, 773, 683 cm^{-1}.

Elem. anal. calculated for $C_{24}H_{19}NO_2S$: C 74.78; H 4.97; N 3.63; found: : C 74.54; H 4.86; N 3.51.

S-phenyl 2-benzamido-3-(thiophen-2-yl)prop-2-enethioate (4k)

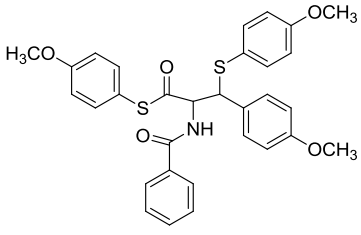


Chemical Formula: $C_{20}H_{15}NO_2S_2$
Molecular Weight: 365.47

100% yield, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0-7.9 (m, 1H), 7.7-7.6 (m, 4H), 7.3-7.1 (m,2), 7.2-7.0 (m,1), 1.6 (s, 4H), 1.3 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 134.9, 134.8, 133.6, 132.4, 131.9, 129.5, 129.2, 128.9, 127.6, 127.5, 127.3; IR (KBr) *ν*max: 3439, 3290, 3077, 3047, 1673, 1602, 1501, 1464, 1277, 1172, 971, 792, 698, 567 cm^{-1}.

Elem. anal. calculated for $C_{20}H_{15}NO_2S_2$: C 65.73; H 4.14; N 3.83; found: C 65.45; H 4.23; N 3.66.

S-(4-methoxyphenyl)2-benzamido-3-(4-methoxyphenyl)-3-((4-methoxyphenyl)thio)propanethioate (4l)



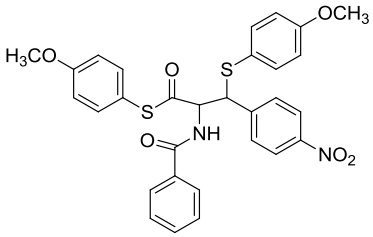
Chemical Formula: $C_{31}H_{29}NO_5S_2$
Molecular Weight: 559.70

100% yield, dr = 100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.1 Hz, 2H), 7.6-7.4 (m, 3H), 7.4-7.2 (m, 6H), 7.1-7.0 (d, *J* = 8.6 Hz, 2H), 6.8-6.7 (m, 7H), 5.4-5.3 (dd, *J* = 8.6 Hz, *J* = 5.4 Hz 1H), 4.9-4.8 (d, J_{syn} = 5.3 Hz, 1H), 3.8 (s, 3H), 3.7 (s, 3H), 3.6 (s, 3H);

^{3}C NMR (75 MHz, $CDCl_3$): δ 197.8, 166.9, 160.7, 159.9, 159.2, 136.0, 135.8, 133.6, 132.1, 129.4, 128.7, 127.2, 117.5, 114.8, 114.6, 113.9, 62.8, 55.8, 55.3, 55.3, 55.2.

Elem. anal. calculated for $C_{31}H_{29}NO_5S_2$: C 66.52; H 5.22; N 2.50; found: C 66.25; H 4.10; N 3.77.

S-(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-(4-nitrophenyl)propanethioate (4m)



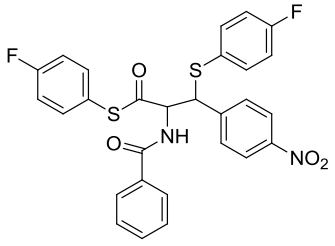
Chemical Formula: $C_{30}H_{26}N_2O_6S_2$
Molecular Weight: 574.67

100% yield, dr = 30/70, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2-8.1 (m, 3H), 7.9 (d, *J* = 6.9 Hz, 2H), 7.7-7.4 (m, 10H), 7.3-7.1 (m, 9H), 6.9-6.7 (m, 7H), 5.6-5.5 (m, 1.48H), 4.9-4.8 (dd, J_{syn}=5.4, J_{anti}= 6.1Hz, 1.46H), 3.8-3.7 (m, 6H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 197.2, 167.0, 166.7, 161.0, 160.9, 160.5, 160.4, 147.5, 147.4, 145.8, 144.5, 136.3, 136.0, 135.9, 135.9, 133.2, 133.1, 132.4, 132.3, 129.6, 129.3, 128.9, 128.8, 127.2, 127.0, 123.7, 122.0, 121.7, 116.8, 116.7, 115.1, 115.0, 114.9, 62.0, 60.6, 56.2, 55.9, 55.4, 55.3.

Elem. anal. calculated for $C_{30}H_{26}N_2O_6S_2$: C 62.70; H 4.56; N 4.87; found: C 62.49; H 4.27; N 4.76.

S-(4-fluorophenyl)2-benzamido-3-((4-fluorophenyl)thio)-3-(4-nitrophenyl)propanethioate (4n)

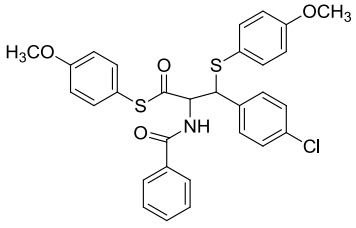


Chemical Formula: $C_{28}H_{20}F_2N_2O_4S_2$
Molecular Weight: 550.60

100% yield, dr = 100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.1 (d, *J* = 8.4 Hz, 2H),7.8 (d, *J* = 7.1 Hz, 2H),7.6-7.4 (m, 6H),7.3-7.1 (m, 6H),7.1 (t, *J* = 8.4 Hz, 3H), 6.9 (t, *J* = 8.5 Hz, 2H), 5.5-5.4 (dd, *J* = 8.8 Hz, *J* = 5.2 Hz, 1H),4.9 (d, J_{syn} = 5.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 167.1, 165.8, 165.0, 161.7, 161.1, 147.6, 145.2, 136.5, 136.4, 135.9, 135.8, 132.9, 132.6, 129.2, 129.0, 127.2, 126.6, 126.5, 123.9, 121.5, 121.4, 116.9, 116.8, 116.5, 116.4, 62.3, 55.9.

Elem. anal. calculated for $C_{28}H_{20}F_2N_2O_4S_2$: C 61.08; H 3.66; N 5.09; found: C 60.85; H 3.46; N 5.2.

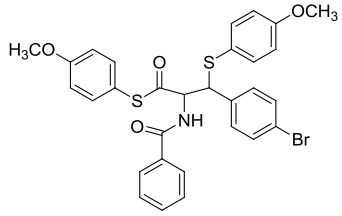
S-(4-methoxyphenyl)2-benzamido-3-(4-chlorophenyl)-3-((4-methoxyphenyl)thio)propanethioate (4o)



Chemical Formula: $C_{30}H_{26}ClNO_4S_2$
Molecular Weight: 564.11

100% yield, x% ee, dr= 100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9 (d, *J* = 6.9 Hz, 2H), 7.6-7.5 (m, 3H), 7.3-7.2 (m, 7H), 7.2-7.1 (m, 3H), 6.9-6.7 (m, 4H), 5.4-5.3 (dd, *J*=8.8 Hz, *J*=5.4 Hz, 1H), 4.8 (d, J_{syn}=5.4 Hz, 1H), 3.8 (s, 3H), 3.7 (s, 3H);
^{13}C NMR (75 MHz, $CDCl_3$): δ 197.0, 135.9, 129.9, 129.6, 128.8, 128.7, 127.7, 127.3, 127.2, 127.2, 123.0, 122.9, 121.3, 114.9, 114.8, 100.0, 98.0, 96.7, 95.8, 62.5, 61.6, 55.3.
Elem. anal. calculated for $C_{30}H_{26}ClNO_4S_2$: C 63.87; H 4.65; N 2.48; found: C 63.60; H 4.48; N, 2.59.

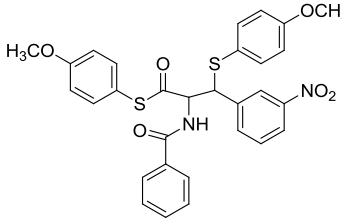
S-(4-methoxyphenyl)2-benzamido-3-(4-bromophenyl)-3-((4-methoxyphenyl)thio)propanethioate (4p)



Chemical Formula: $C_{30}H_{26}BrNO_4S_2$
Molecular Weight: 608.57

100% yield, dr = 100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9-7.8 (d, *J* = 8.2 Hz, 2H), 7.6-7.5 (m, 3H), 7.4-7.3 (d, *J* = 8.2 Hz, 2H), 7.3-7.2 (m, 2H), 7.2-7.1 (d, *J* = 8.2 Hz, 3H), 7.1-7.0 (m, 2.5H),6.9-6.7 (dd, *J* = 29.7 Hz, *J* = 8.8 Hz, 4H), 5.4-5.3 (dd, *J* =8.8 Hz, J_{svn} = 5.4 Hz, 1H), 4.8-4.8 (d, J_{syn} = 5.4 Hz, 1H), 3.8 (s, 3H), 3.7 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5, 166.98 160.8, 160.2, 137.3, 135.9, 135.8, 133.4, 132.2, 131.7, 129.9, 128.8, 127.2, 122.5, 121.9, 114.9, 114.8, 62.4, 55.9, 55.3, 55.3.
Elem. anal. calculated for $C_{30}H_{26}BrNO_4S_2$: C 59.21; H 4.31; N 2.30; found: C 59.01; H 4.29; N 2.41.

S-(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-(3-nitrophenyl)propanethioate (4q)



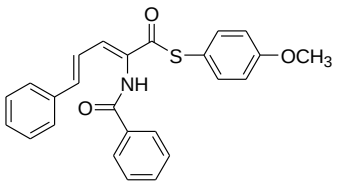
Chemical Formula: $C_{30}H_{26}N_2O_6S_2$
Molecular Weight: 574.67

100% yield, dr = 100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2 (s, 1H), 8.1 (d, *J* = 8.1 Hz, 1H), 7.8 (d, 2H), 7.6-7.4 (m,6H), 7.3-7.1 (m, 6H), 6.9-6.7 (m, 4.5 H), 5.5-5.4 (dd, *J* = 8.9 Hz, *J* = 5.2 Hz, 1H), 4.9-4.8 (d, J_{syn} = 5.2 Hz, 1H), 3.8 (s, 3H), 3.7 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): 197.2, 167.2, 160.9, 160.4, 148.2, 140.6, 136.0, 136.0, 134.3, 133.2, 132.4, 129.5, 128.9, 127.2, 123.5, 122.9, 121.7, 116.8, 115.0, 114.9, 62.3, 56.0, 55.3, 55.3.

Elem. anal. calculated for $C_{30}H_{26}N_2O_6S_2$: C 62.70; H 4.56; N 4.87; found: C 62.40; H 4.48; N 4.75.

S-(4-methoxyphenyl) 2-benzamido-5-phenylpenta-2,4-dienethioate (4r)

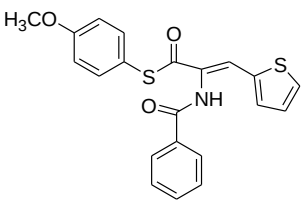


Chemical Formula: $C_{25}H_{21}NO_3S$
Molecular Weight: 415.50

100% yield, ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0-7.8 (m,3H), 7.6-7.2 (m,12H), 7.1- 6.8 (m, 4H), 3.8 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.4, 165.7, 160.9, 141.7, 136.6, 136.2, 133.7, 132.3, 132.2, 129.4, 129.3, 128.8, 128.7, 127.6, 127.5, 123.7, 117.4, 114.9, 114.9, 55.5, 55.4, 55.2.

Elem. anal. calculated for $C_{25}H_{21}NO_3S$: C 72.27; H 5.09; N 3.37; found: C 72.14; H 5.11; N 3.25.

2-Benzoylamino-3-thiophen-2-yl-thioacrylic acid S-(4-methoxy-phenyl) ester (4s)

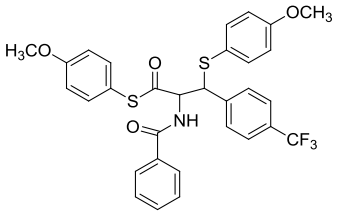


Chemical Formula: $C_{21}H_{17}NO_3S_2$
Molecular Wteigh.: 395,49

100% yield, ^{1}H NMR (300 MHz, $CDCl_3$): 8.0 (d, 2H), 7.9 (s, 1H), 7.6-7.5 (m, 5H),7.4-7.3 (m, 3H), 7.3 (s, 1H), 7.2-7.1(dd, 1H),7.1-6.9 (m, 2H), 3.8 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.3, 166.8, 160.7, 136.5, 135.9, 135.3, 134.9, 134.8, 133.7, 133.2, 132.8, 132.6, 132.4, 131.8, 130.9, 128.8, 128.3, 128.1, 127.9, 127.6, 127.5, 127.0, 125.6, 124.8, 117.8, 114.9, 55.3.

Elem. anal. calculated for $C_{21}H_{17}NO_3S_2$: C 63.77; H 4.33; N 3.54; found C 63.47; H 4.13; N 3.60.

S-(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-(4-(trifluoromethyl)phenyl)propanethioate (4u)



Chemical Formula: $C_{31}H_{26}F_3NO_4S_2$
Molecular Weight: 597.67

100% yield, dr = 100/0, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9-7.8 (m, 2H), 7.6-7.4 (m, 8H), 7.3-7.2 (m, 2H), 7.2-7.1 (d, *J* = 8.9 Hz, 1H), 7.1 (m, 2H), 6.9-6.7 (m, 4H), 5.5-5.4 (dd, *J* = 8.9 Hz, *J* = 5.4 Hz, 1H), 4.9-4.8 (d, *J* = 5.4 Hz, 1H), 3.8 (s,3H), 3.7 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5, 167.0, 160.8, 160.3, 142.4, 135.9, 133.3, 132.6, 132.3, 130.3, 129.9, 128.8, 128.6, 127.2, 125.6, 125.5, 125.5, 125.4, 122.2, 117.0, 114.9, 114.8, 114.5, 62.2, 56.2, 55.3.

Elem. anal. calculated for $C_{31}H_{26}F_3NO_4S_2$: C 62.30; H 4.38; N 2.34; found: C 62.10; H 4.29; N 2.20.

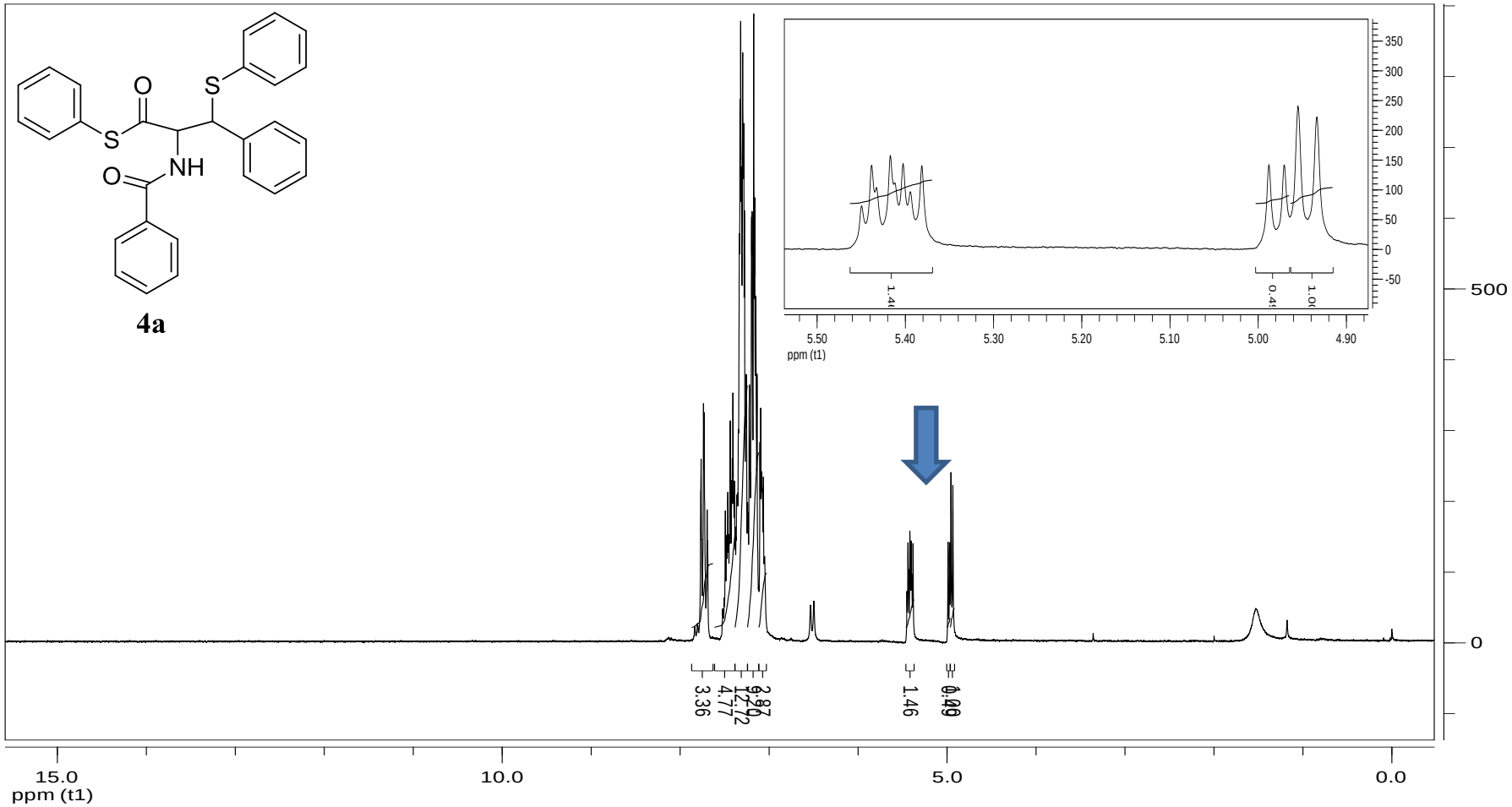


Figure 1. ^{1}H NMR spectra for the **(4a) S-phenyl 2-benzamido-3-phenyl-3-(phenylthio)propanethioate** in $CDCl_3$.

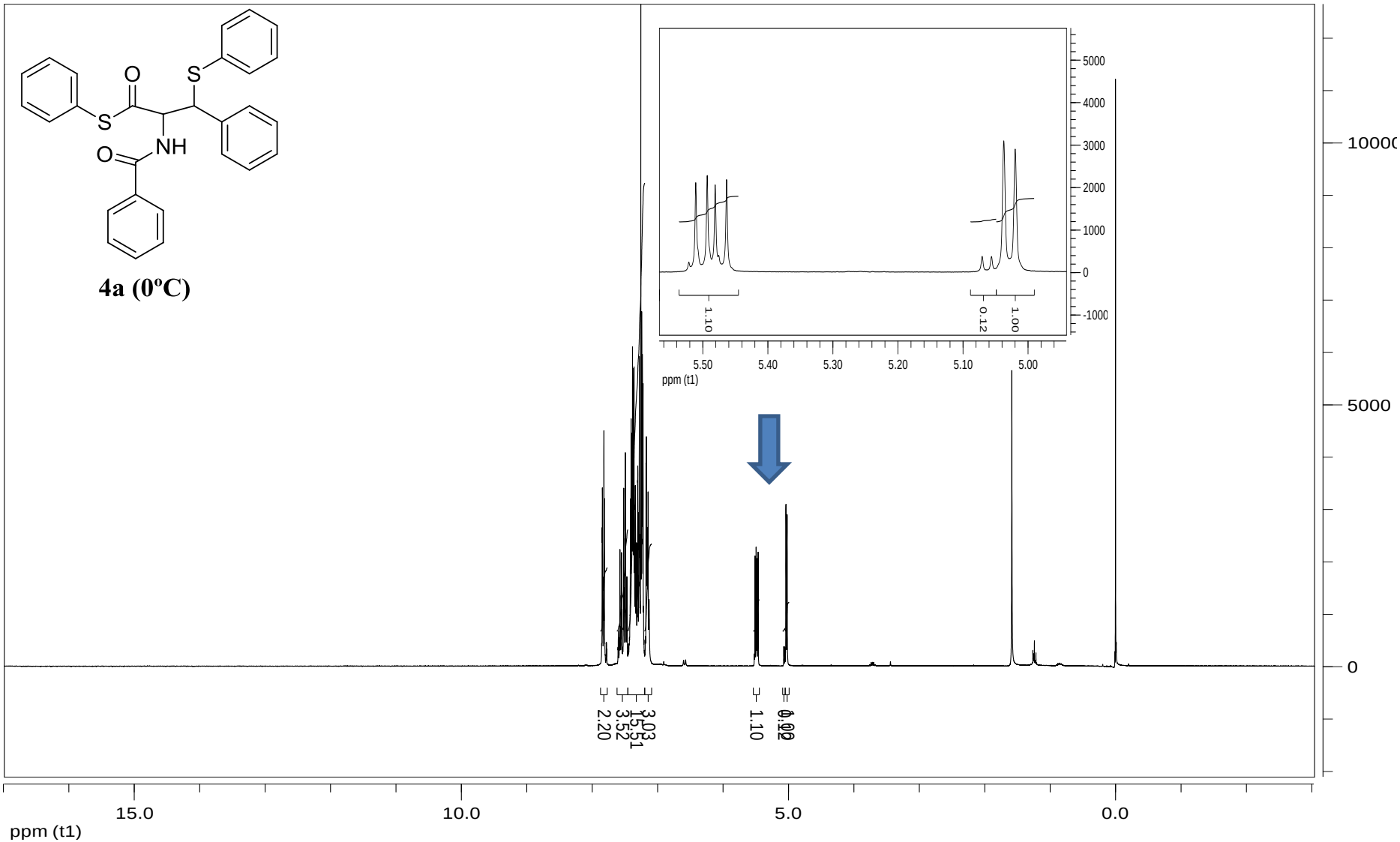


Figure 2. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-3-phenyl-3-(phenylthio)propanethioate** in $CDCl_3$.

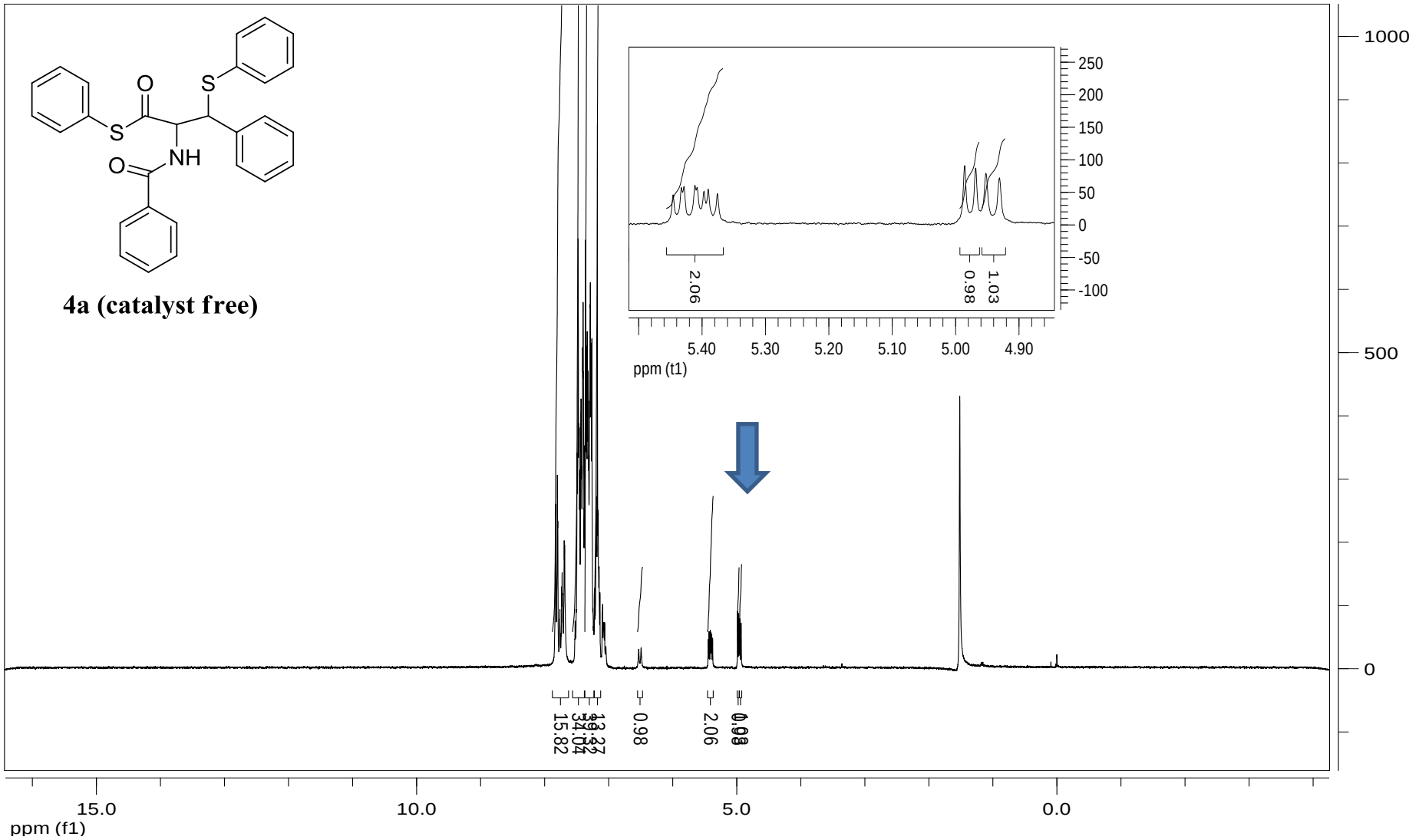


Figure 3. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-3-phenyl-3-(phenylthio)propanethioate** in $CDCl_3$.

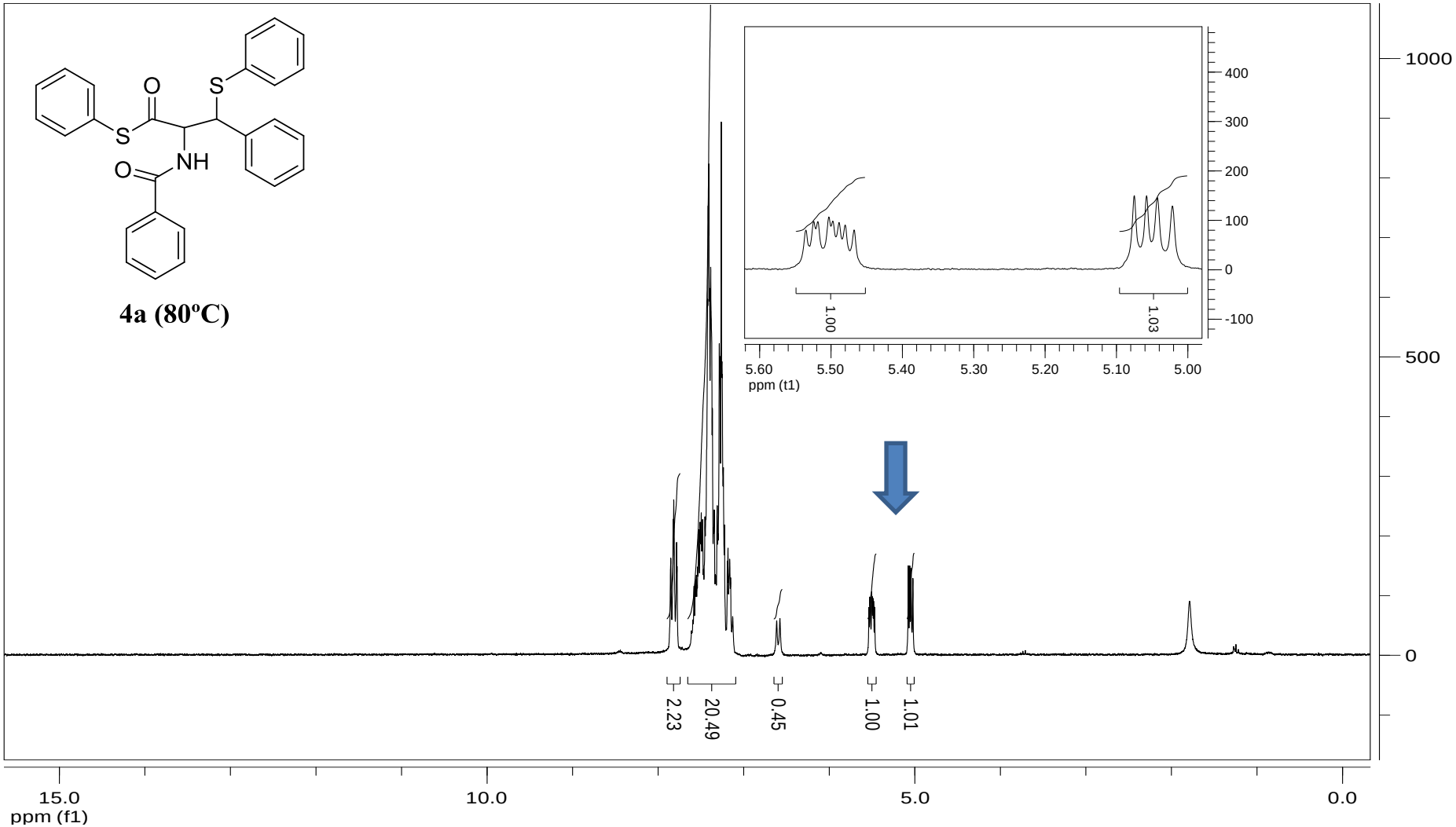


Figure 4. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-3-phenyl-3-(phenylthio)propanethioate** in $CDCl_3$.

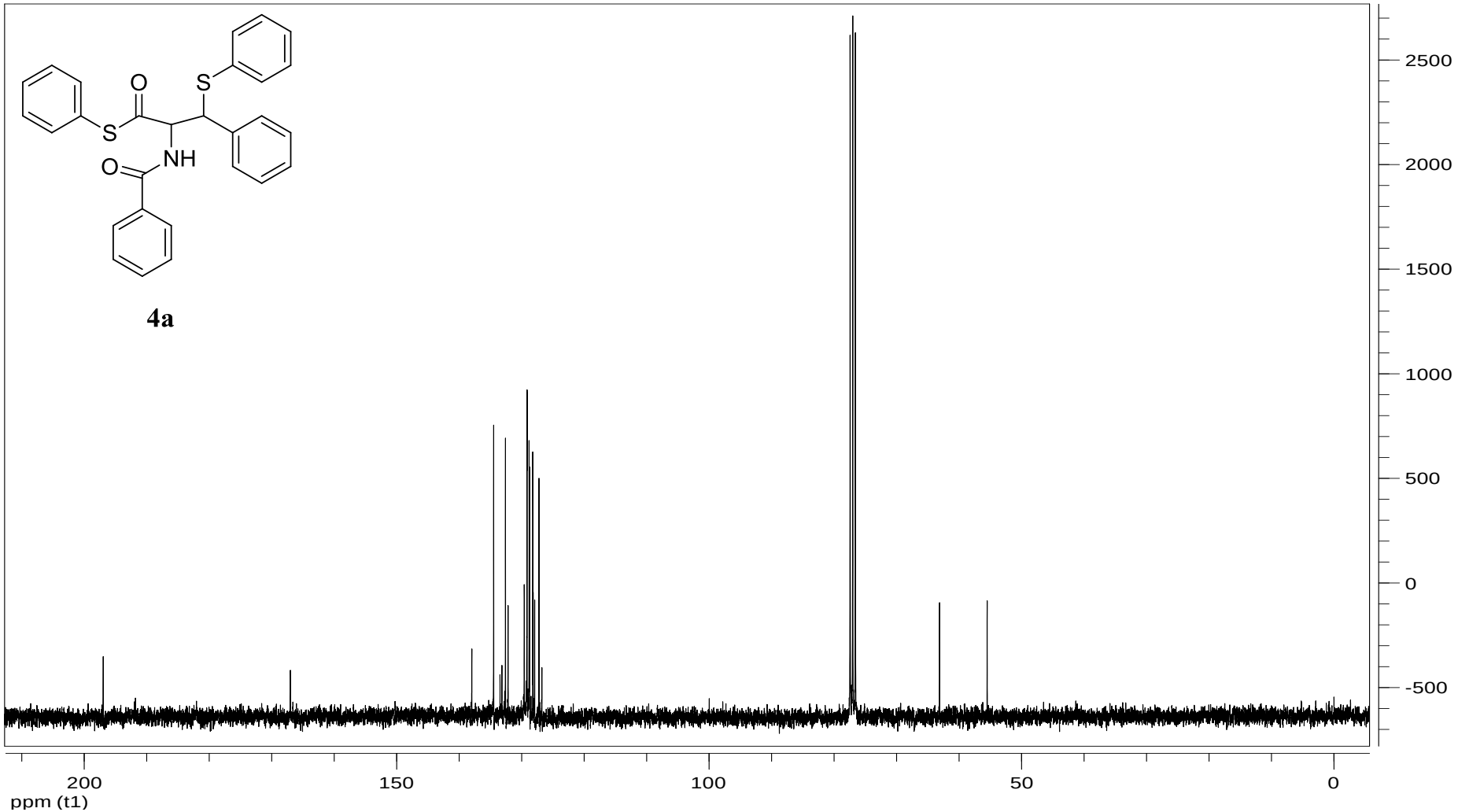


Figure 5. ^{13}C NMR spectra for the **S-phenyl 2-benzamido-3-phenyl-3-(phenylthio)propanethioate** in $CDCl_3$.

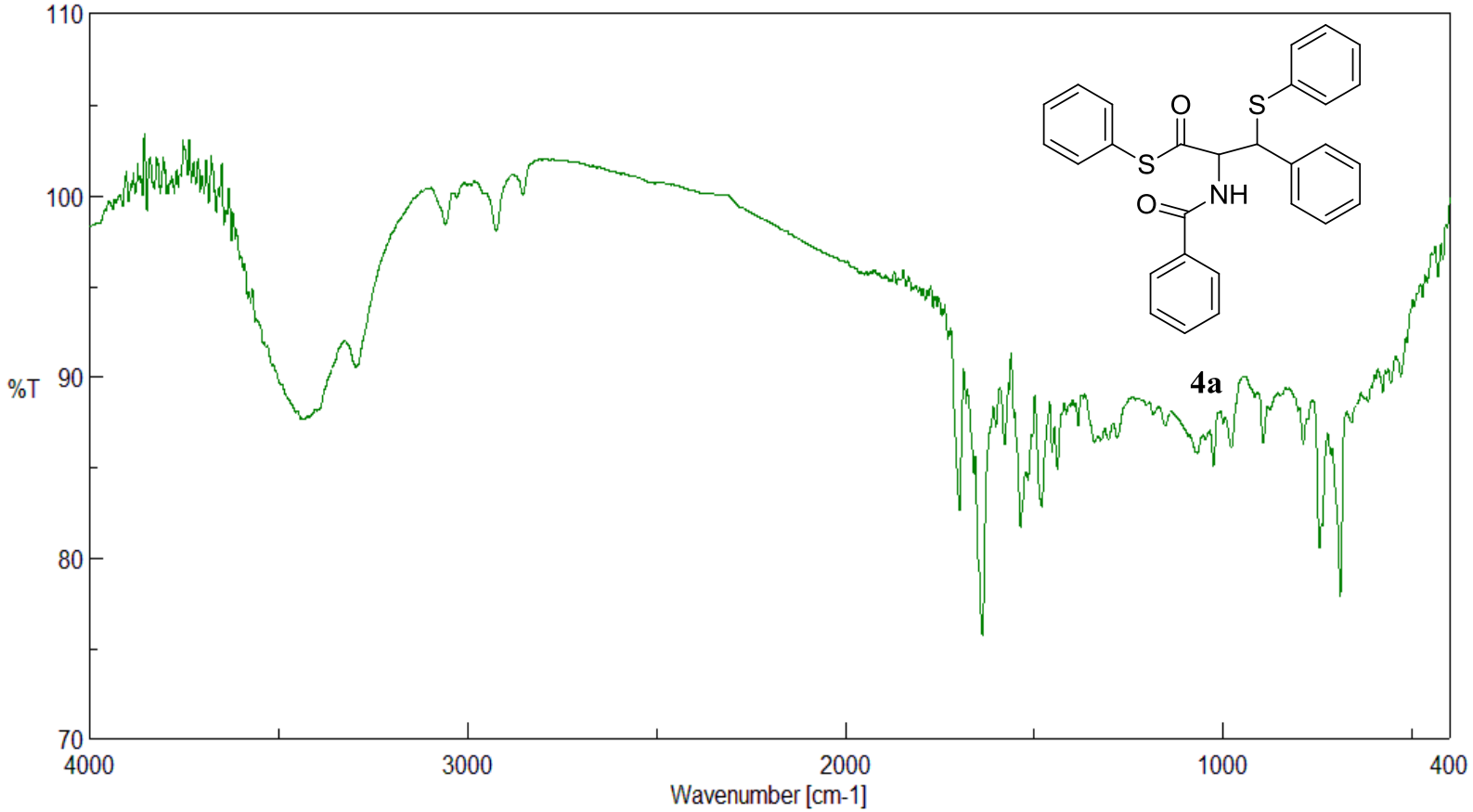


Figure 6. FTIR spectra for the S-phenyl 2-benzamido-3-phenyl-3-(phenylthio)propanethioate in KBr.

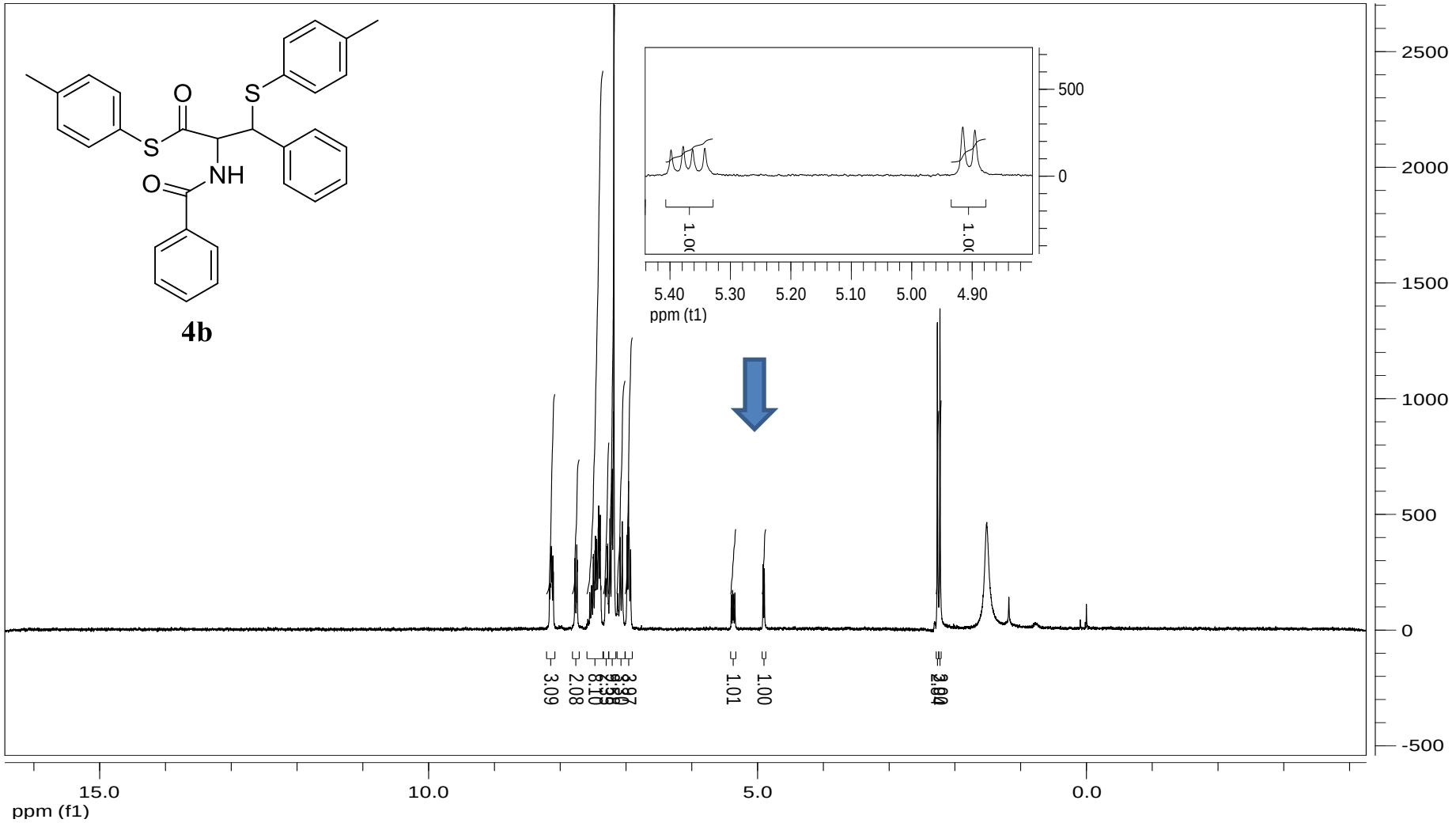


Figure 7. ^{1}H NMR spectra for the **S-p-tolyl 2-benzamido-3-phenyl-3-(p-tolylthio)propanethioate** in $CDCl_3$.

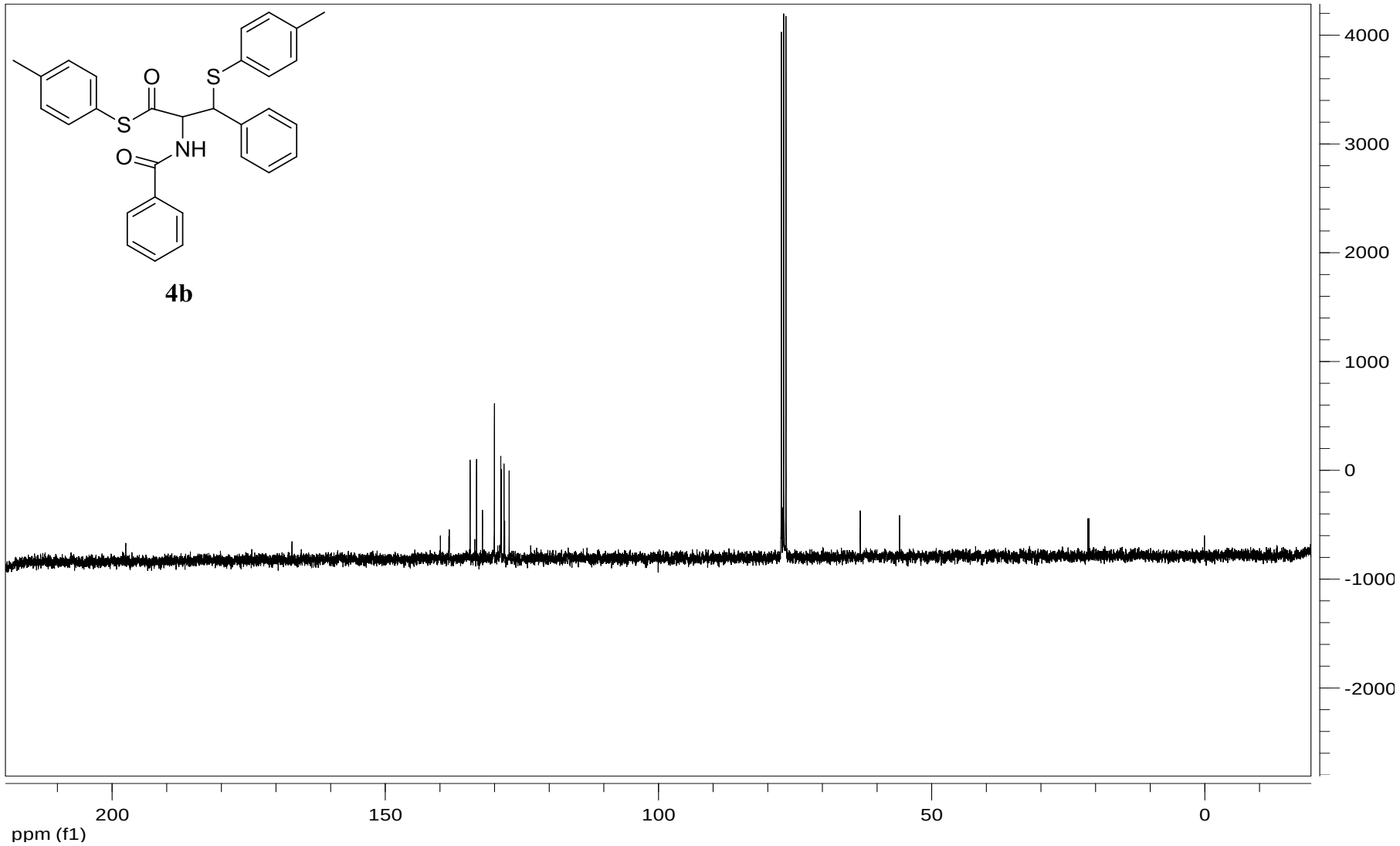


Figure 8. ^{13}C NMR spectra for the **S-p-tolyl 2-benzamido-3-phenyl-3-(p-tolylthio)propanethioate** in $CDCl_3$.

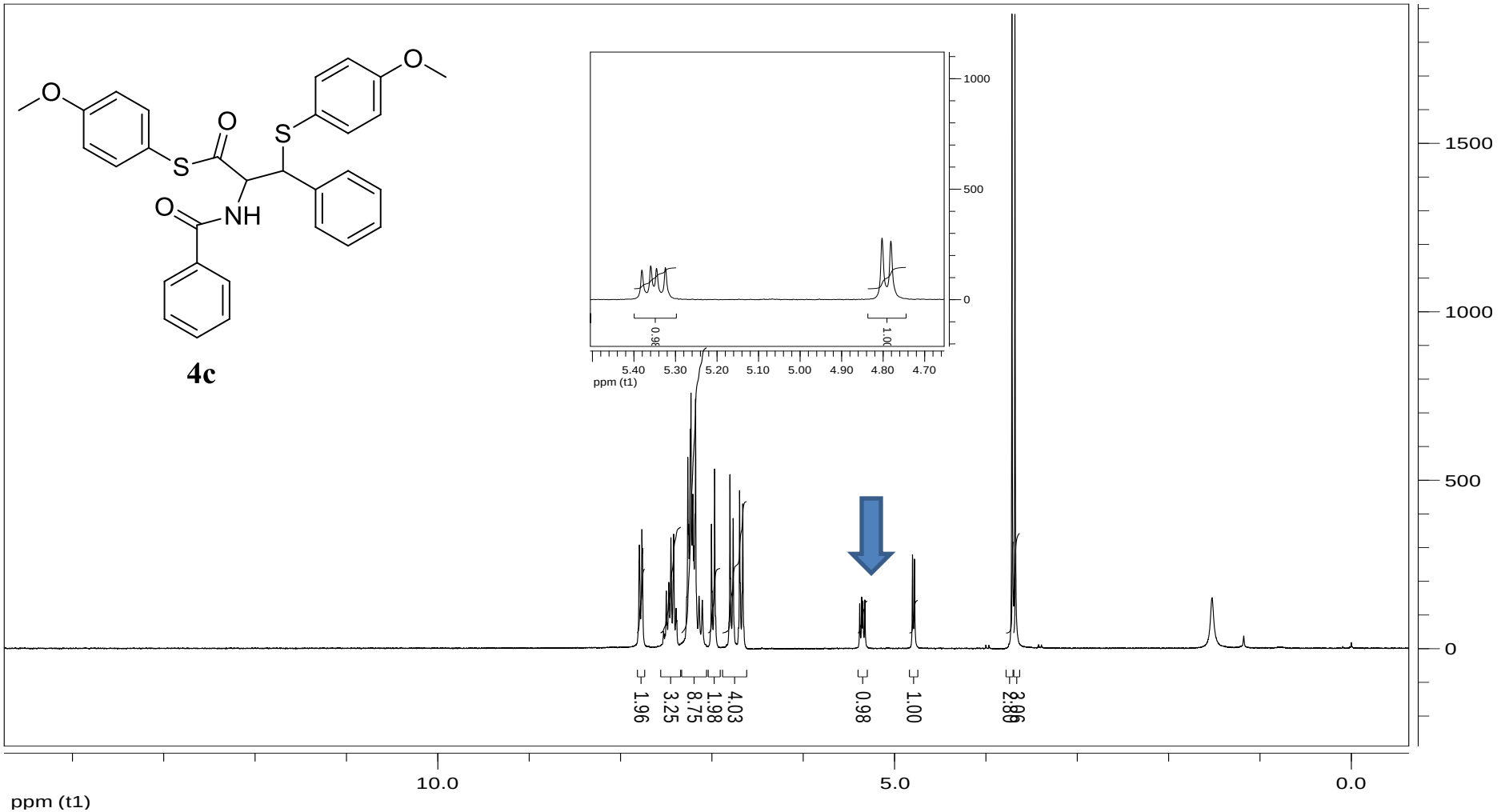


Figure 9. ^{1}H NMR spectra for the **S-(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-phenylpropanethioate** in $CDCl_3$.

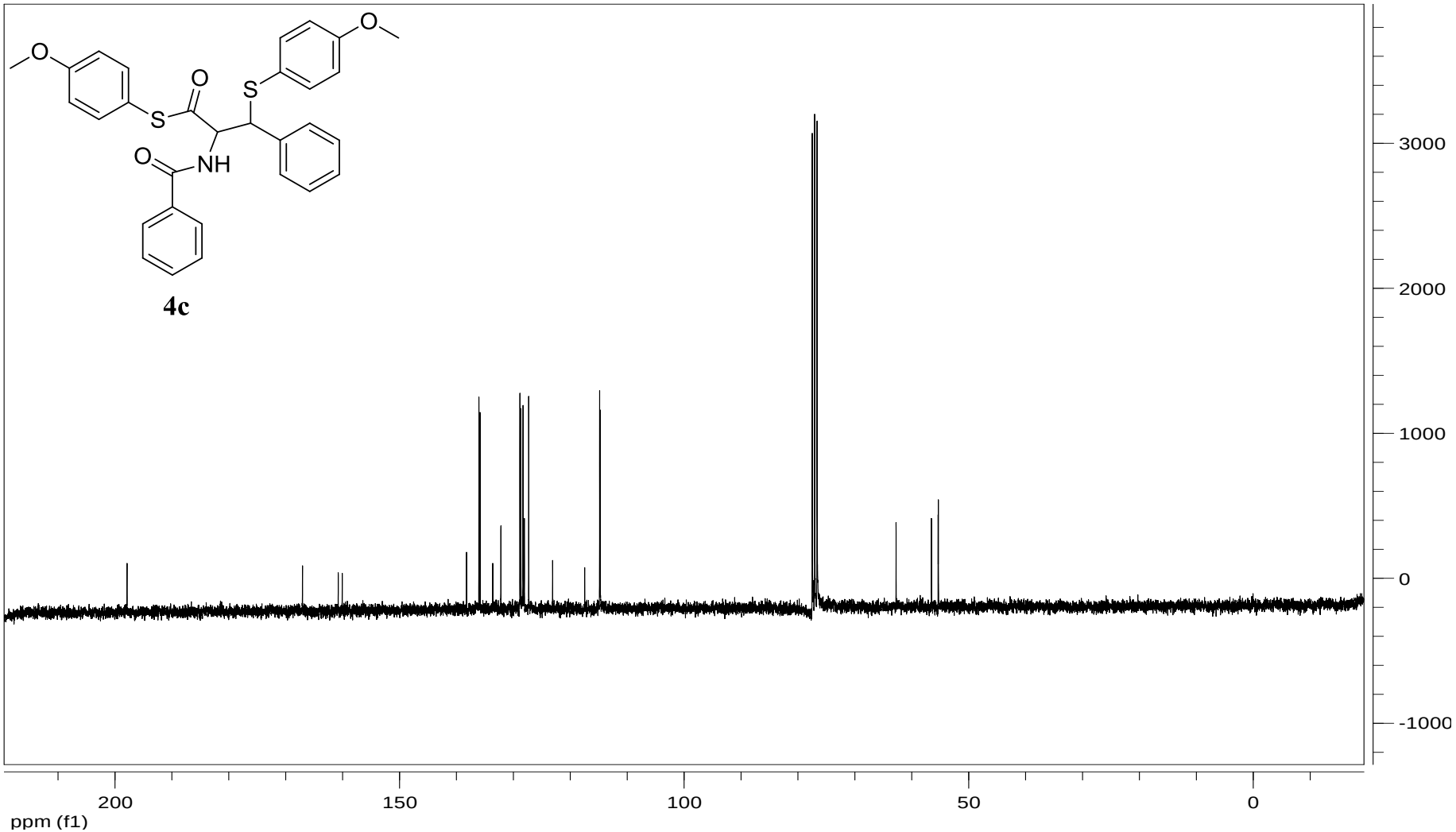


Figure 10. ^{13}C NMR spectra for the **S--(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-phenylpropanethioate** in $CDCl_3$.

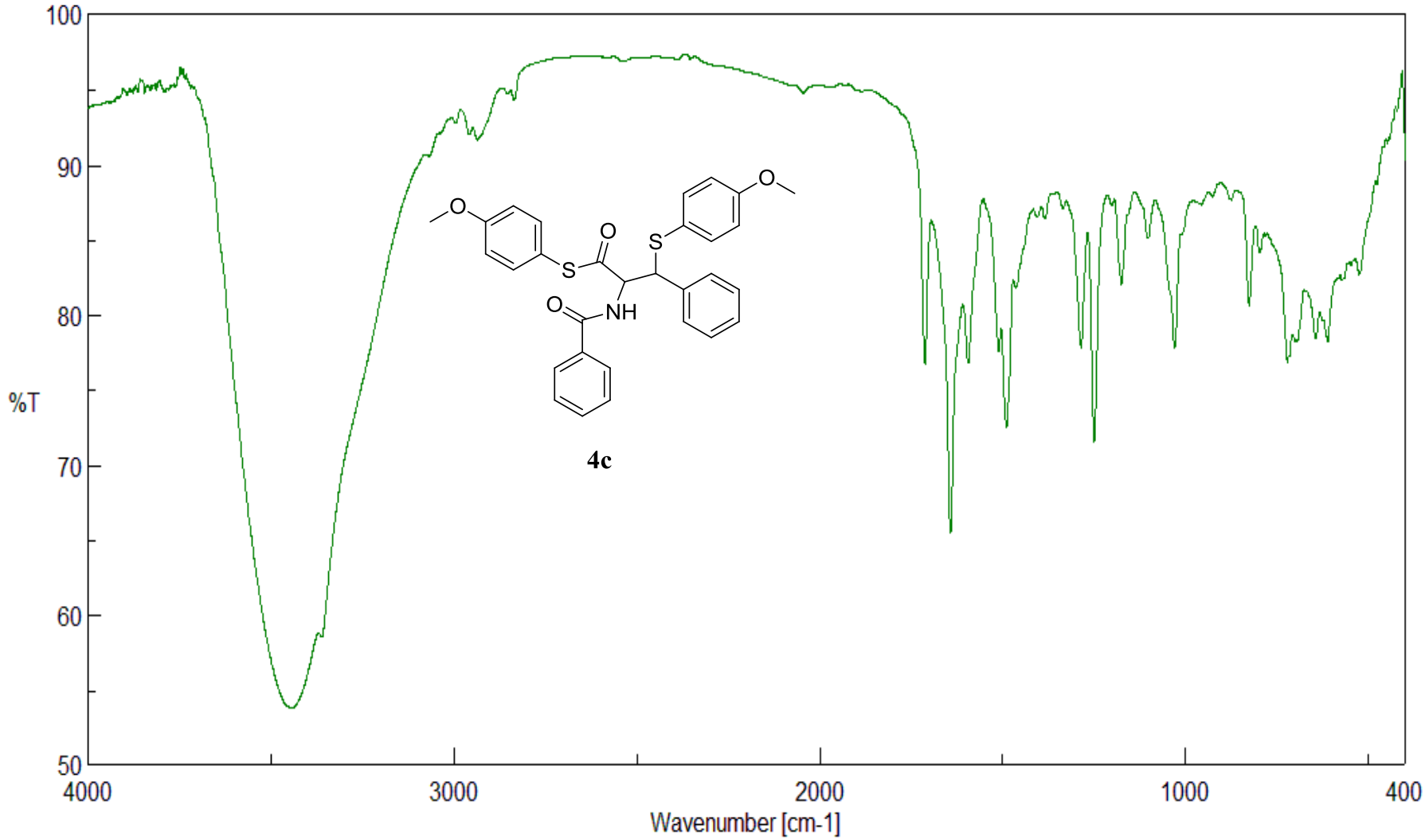


Figure 11. FTIR spectra for the **S--(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-phenylpropanethioate** in KBr.

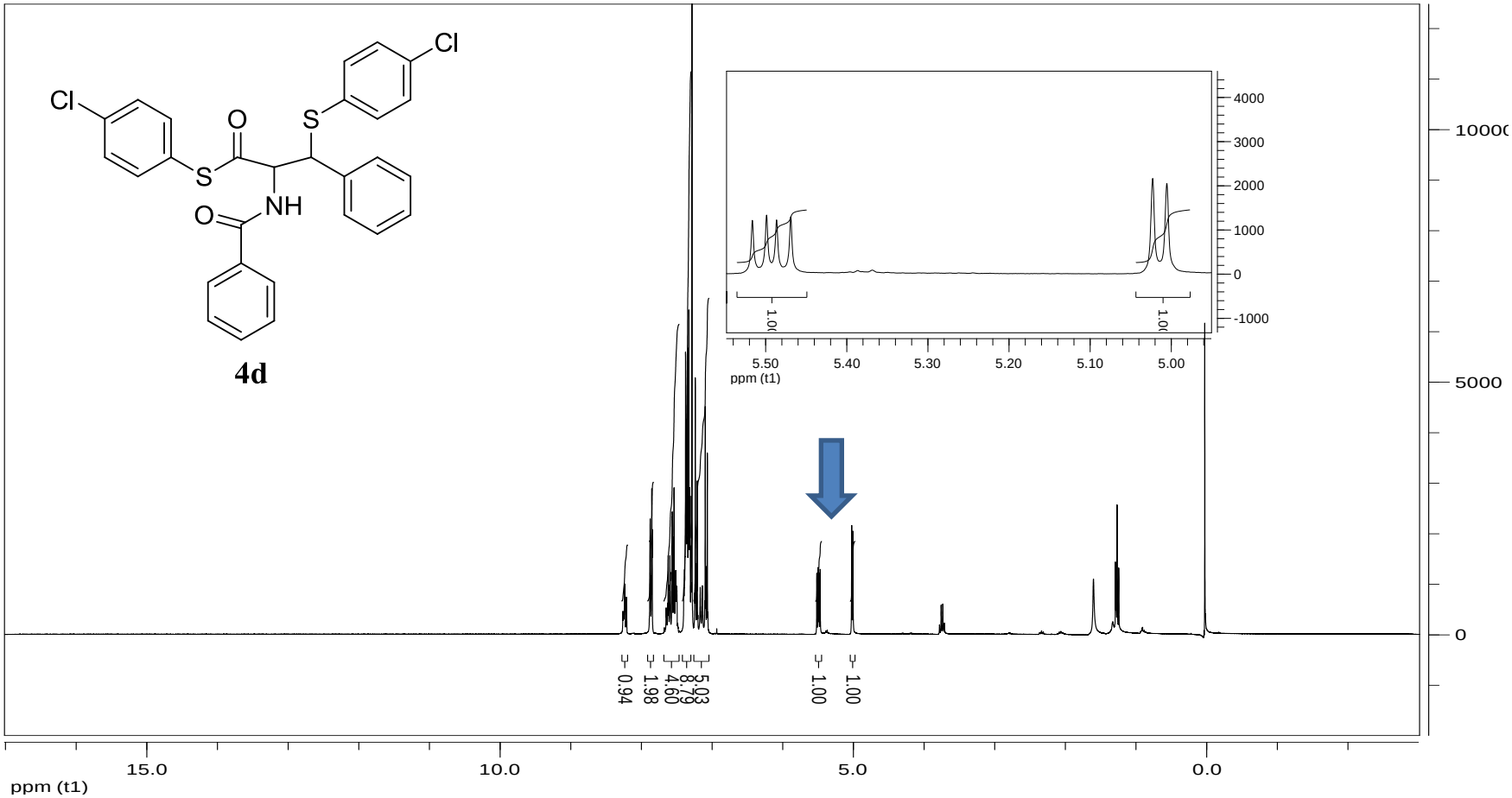


Figure 12. ^{1}H NMR spectra for the **S-(4-chlorophenyl) 2-benzamido-3-((4-chlorophenyl)thio)-3-phenylpropanethioate** in $CDCl_3$.

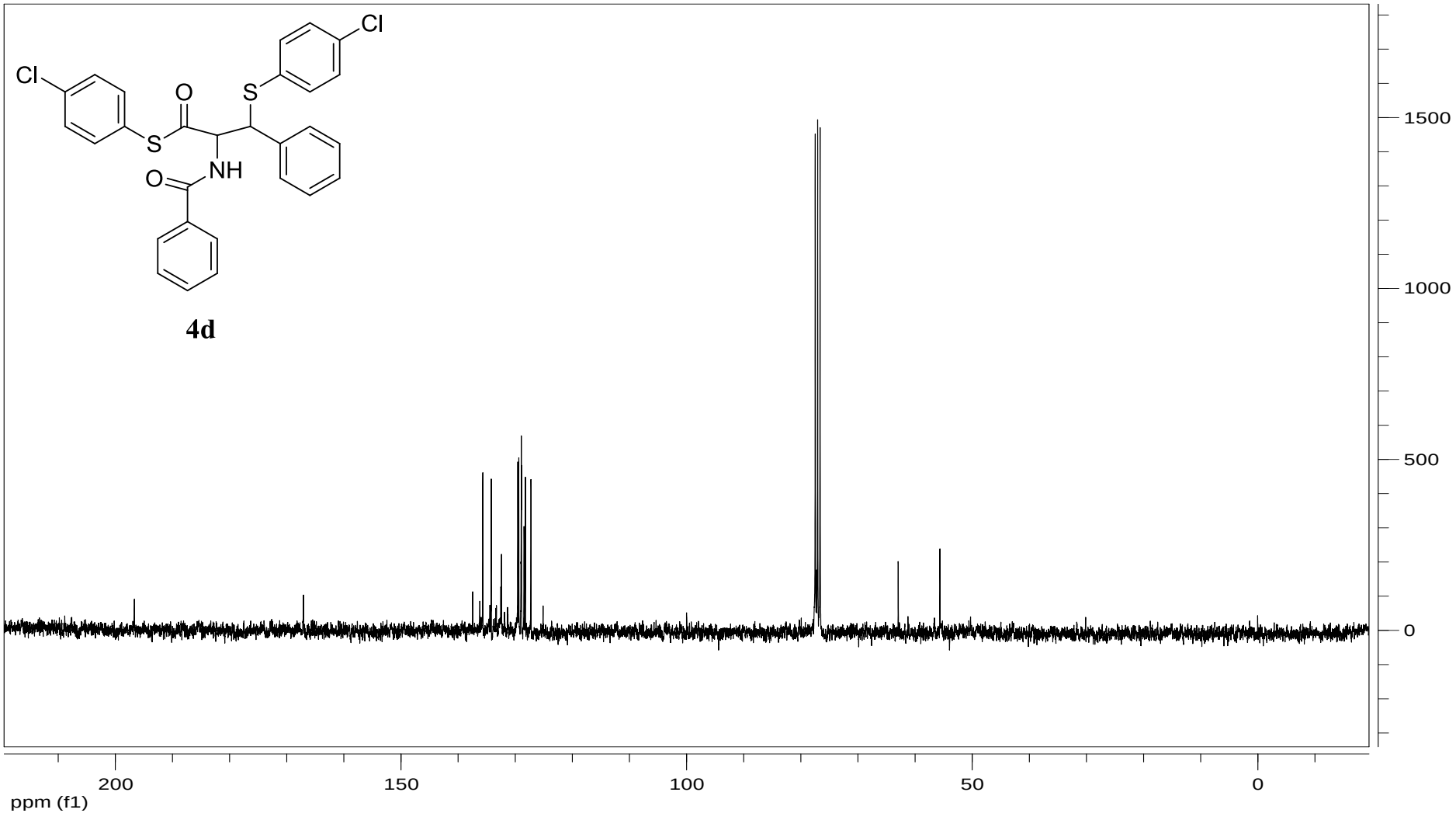


Figure 13. ^{13}C NMR spectra for the **S-(4-chlorophenyl) 2-benzamido-3-((4-chlorophenyl)thio)-3-phenylpropanethioate** in $CDCl_3$.

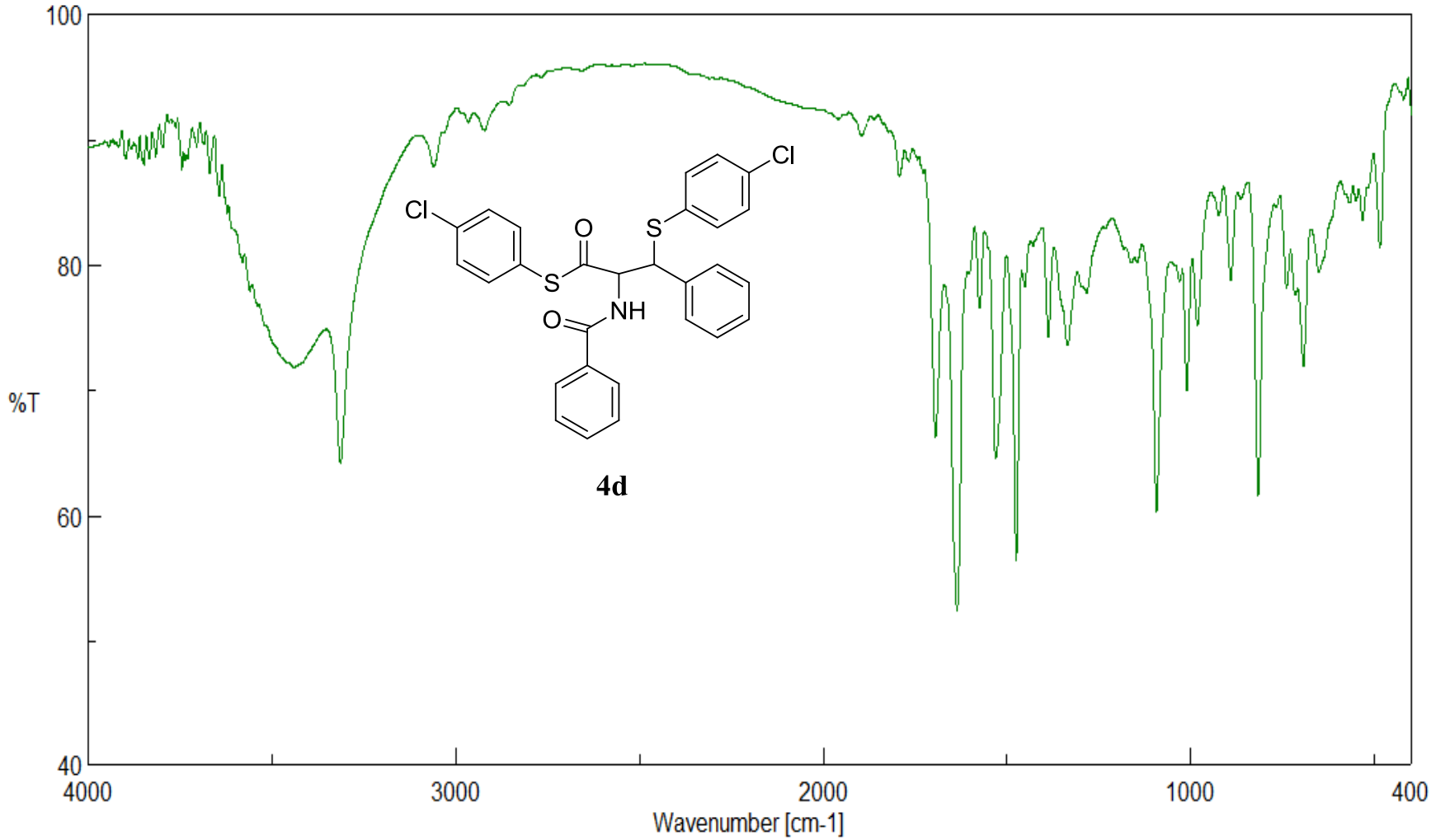


Figure 14. FTIR spectra for the **S-(4-chlorophenyl) 2-benzamido-3-((4-chlorophenyl)thio)-3-phenylpropanethioate** in KBr.

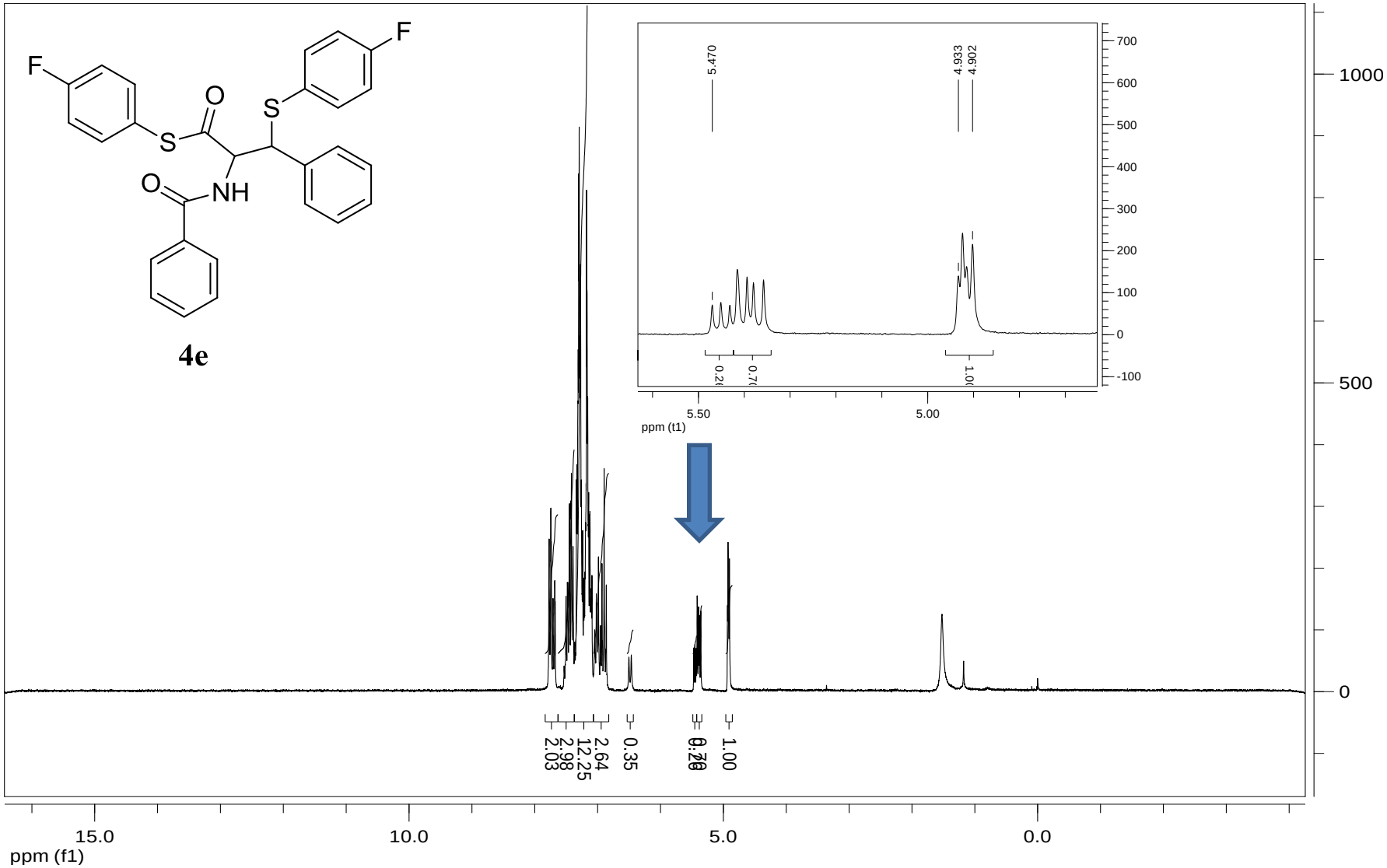


Figure 15. ^{1}H NMR spectra for the **S-(4-fluorophenyl) 2-benzamido-3-((4-fluorophenyl)thio)-3-phenylpropanethioate** in $CDCl_3$.

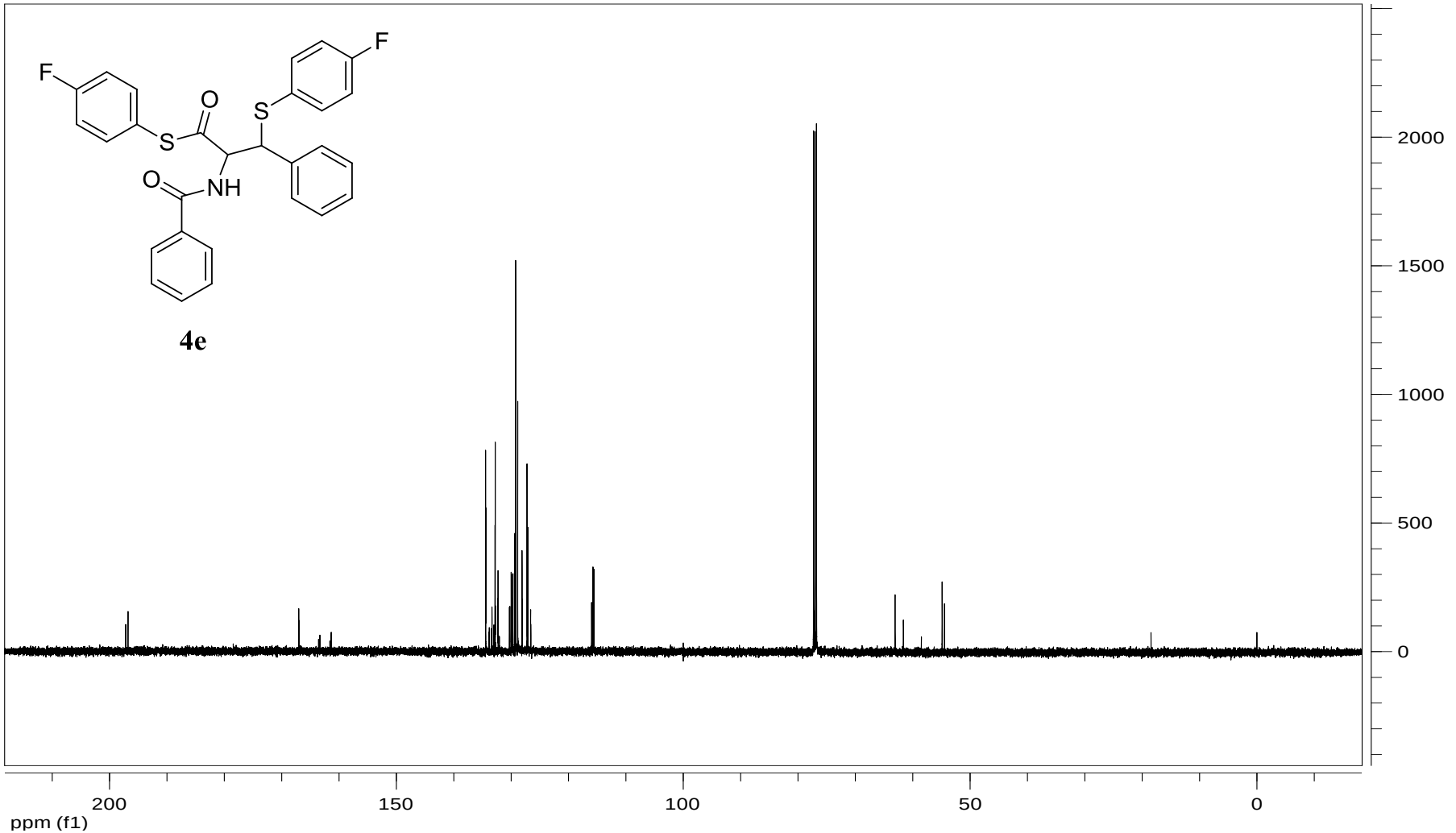


Figure 16. ^{13}C NMR spectra for the **S-(4-fluorophenyl) 2-benzamido-3-((4-fluorophenyl)thio)-3-phenylpropanethioate** in $CDCl_3$.

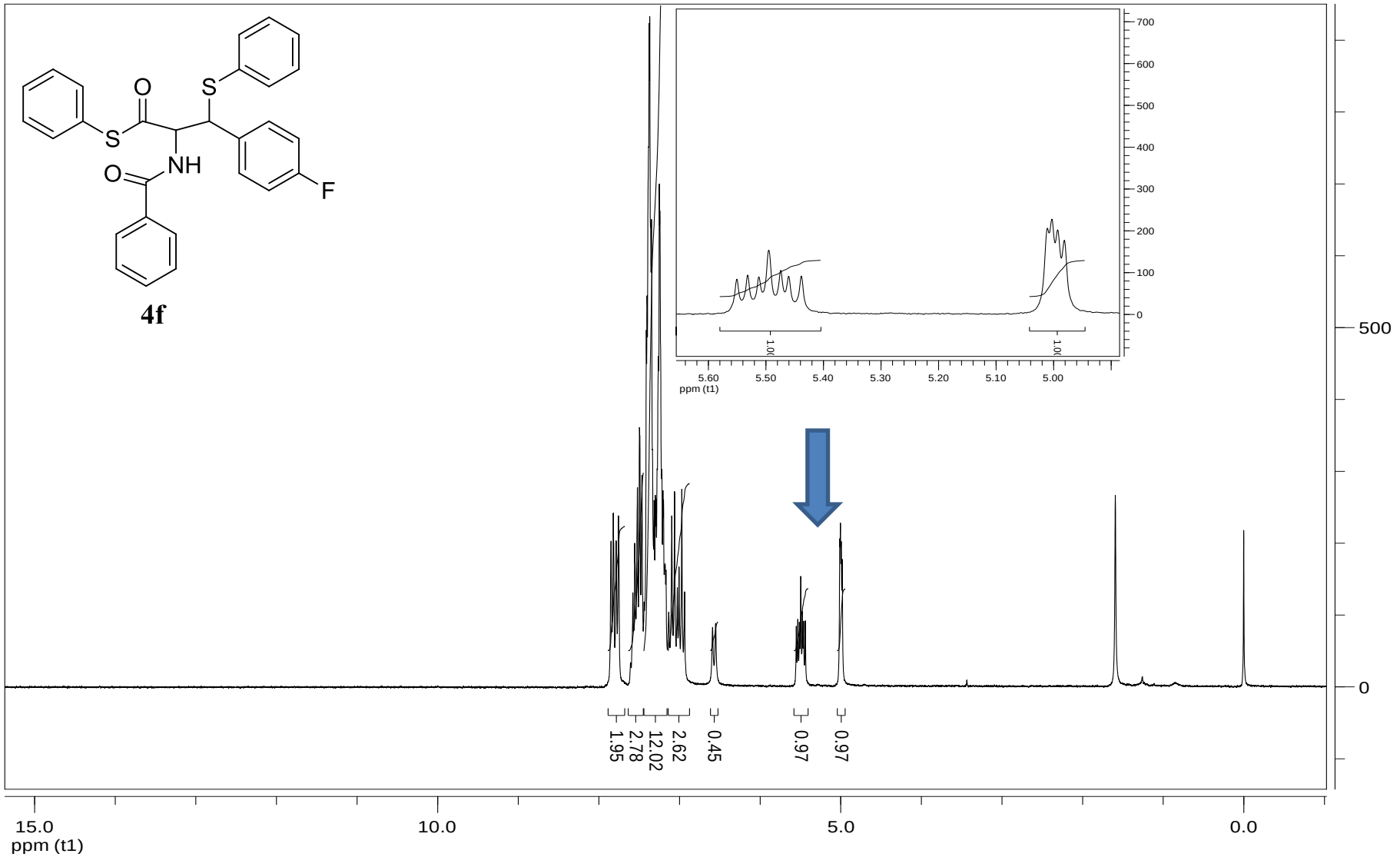


Figure 17. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-3-(4-fluorophenyl)-3-(phenylthio)propanethioate** in DMSO.

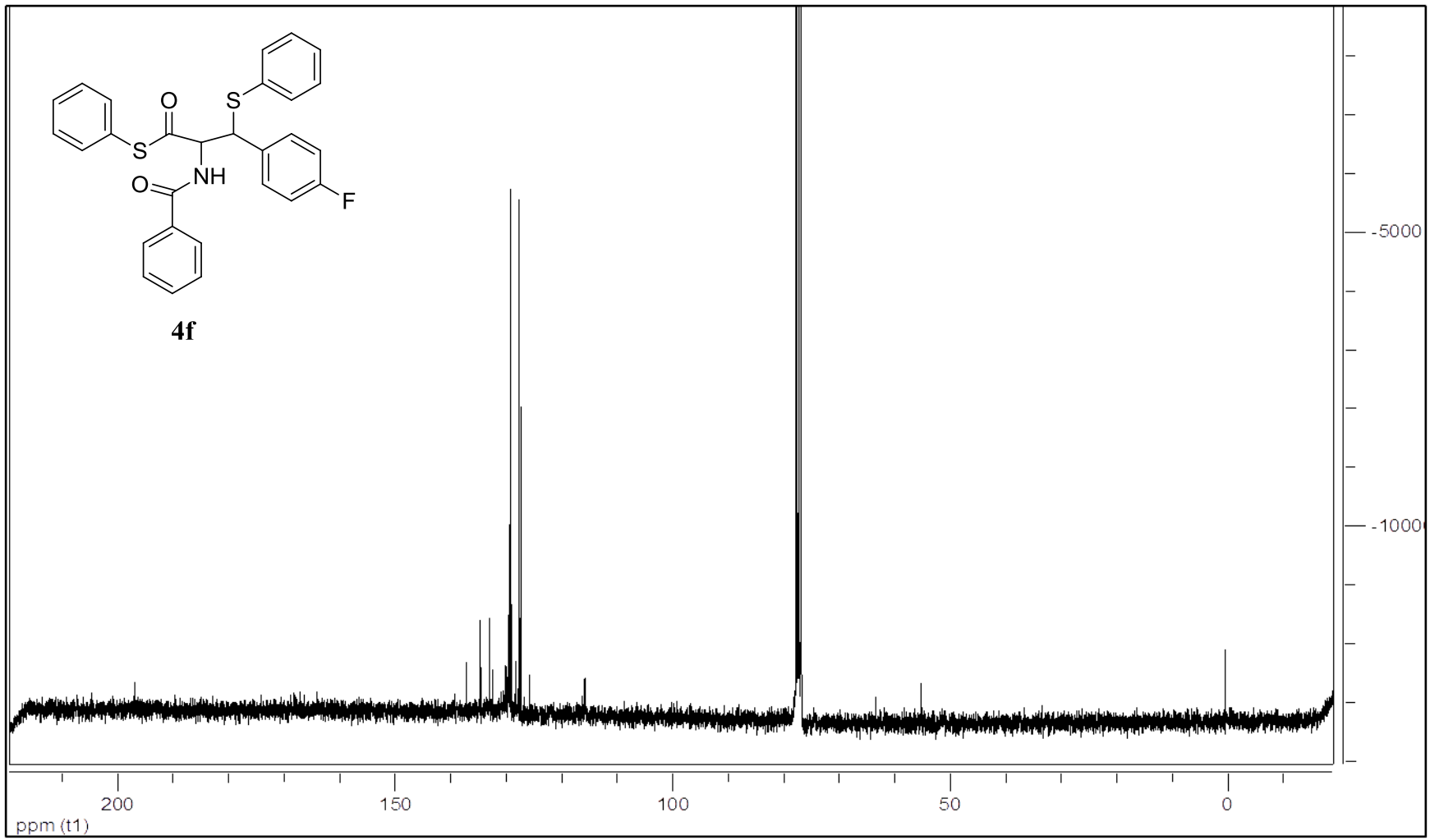


Figure 18. ^{13}C NMR spectra for the ***S*-phenyl 2-benzamido-3-(4-fluorophenyl)-3-(phenylthio)propanethioate** in $CDCl_3$.

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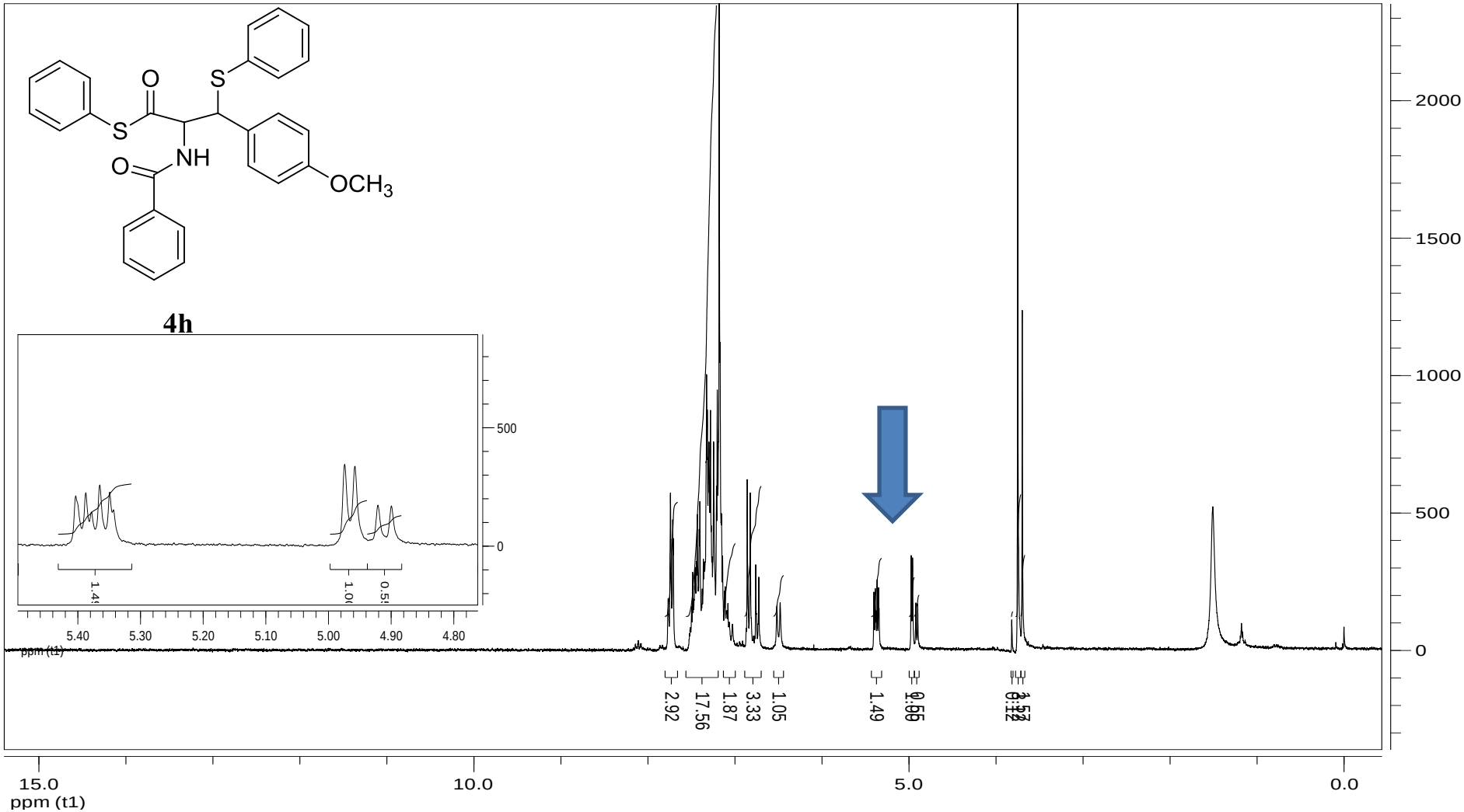

Figure 19. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-3-(4-methoxyphenyl)-3-(phenylthio)propanethioate** in $CDCl_3$.

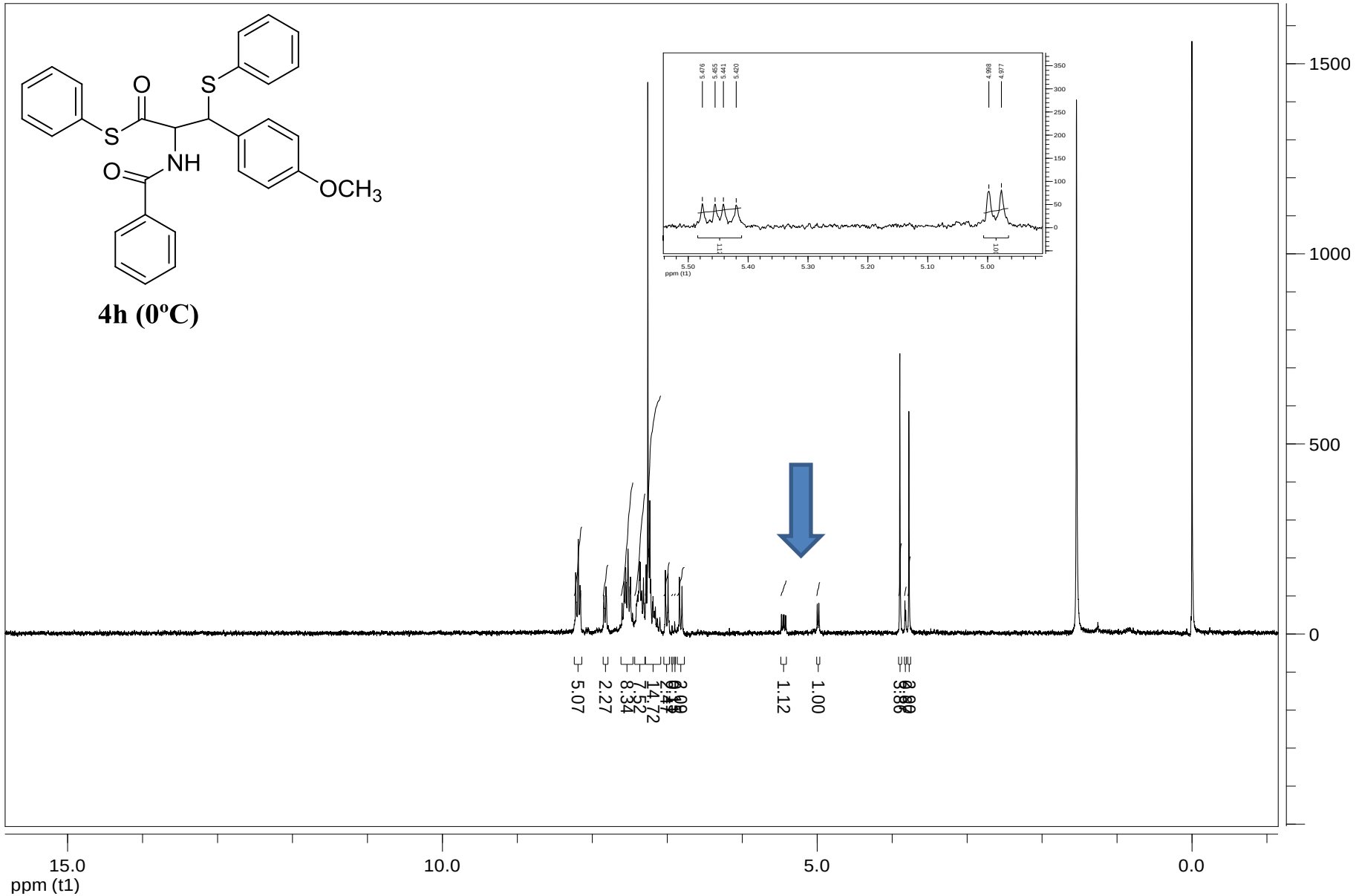

Figure 20. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-3-(4-methoxyphenyl)-3-(phenylthio)propanethioate** in $CDCl_3$.

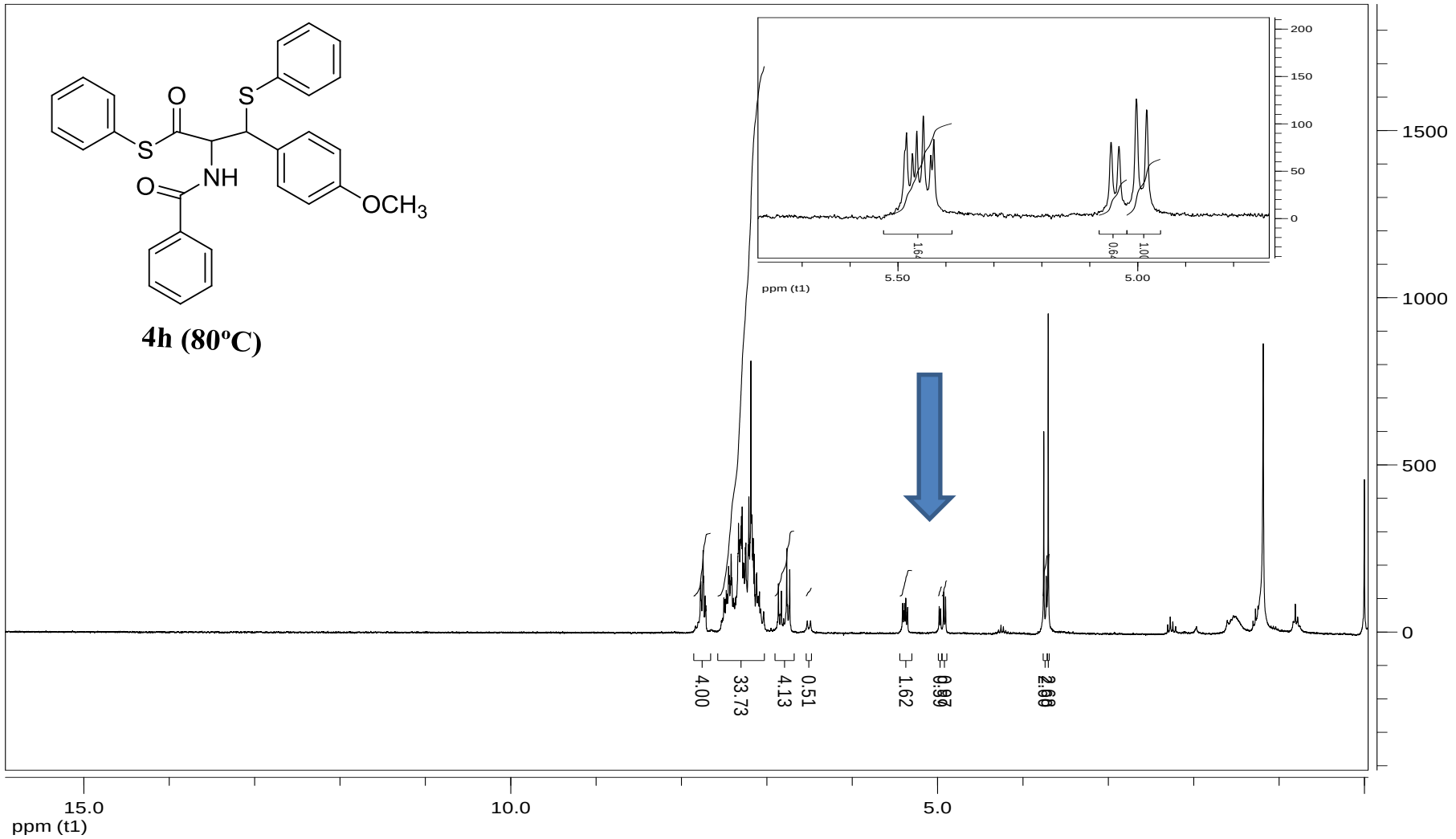

Figure 21. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-3-(4-methoxyphenyl)-3-(phenylthio)propanethioate** in $CDCl_3$.

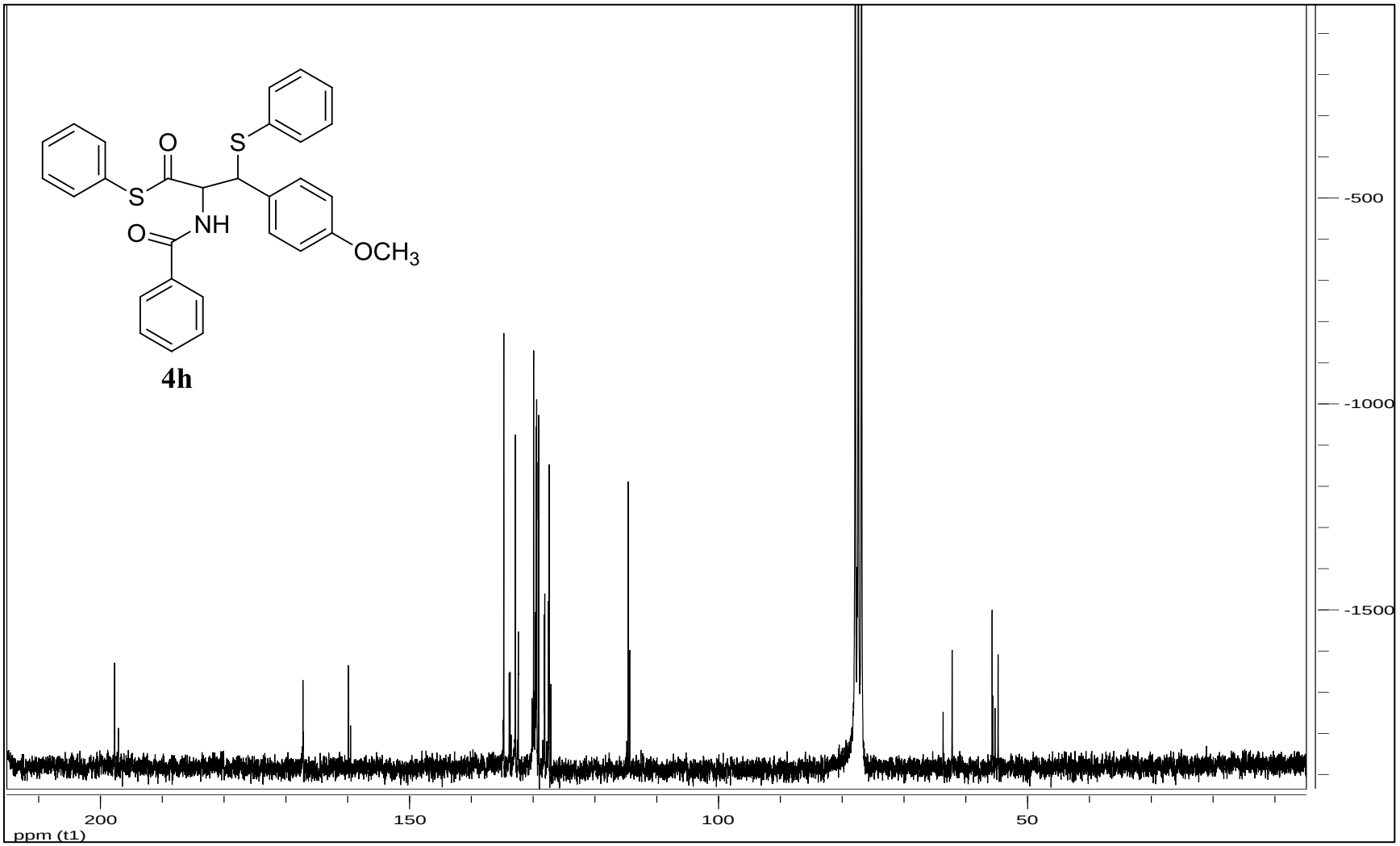

Figure 22. ^{13}C NMR spectra for the **S-phenyl 2-benzamido-3-(4-methoxyphenyl)-3-(phenylthio)propanethioate** in $CDCl_3$

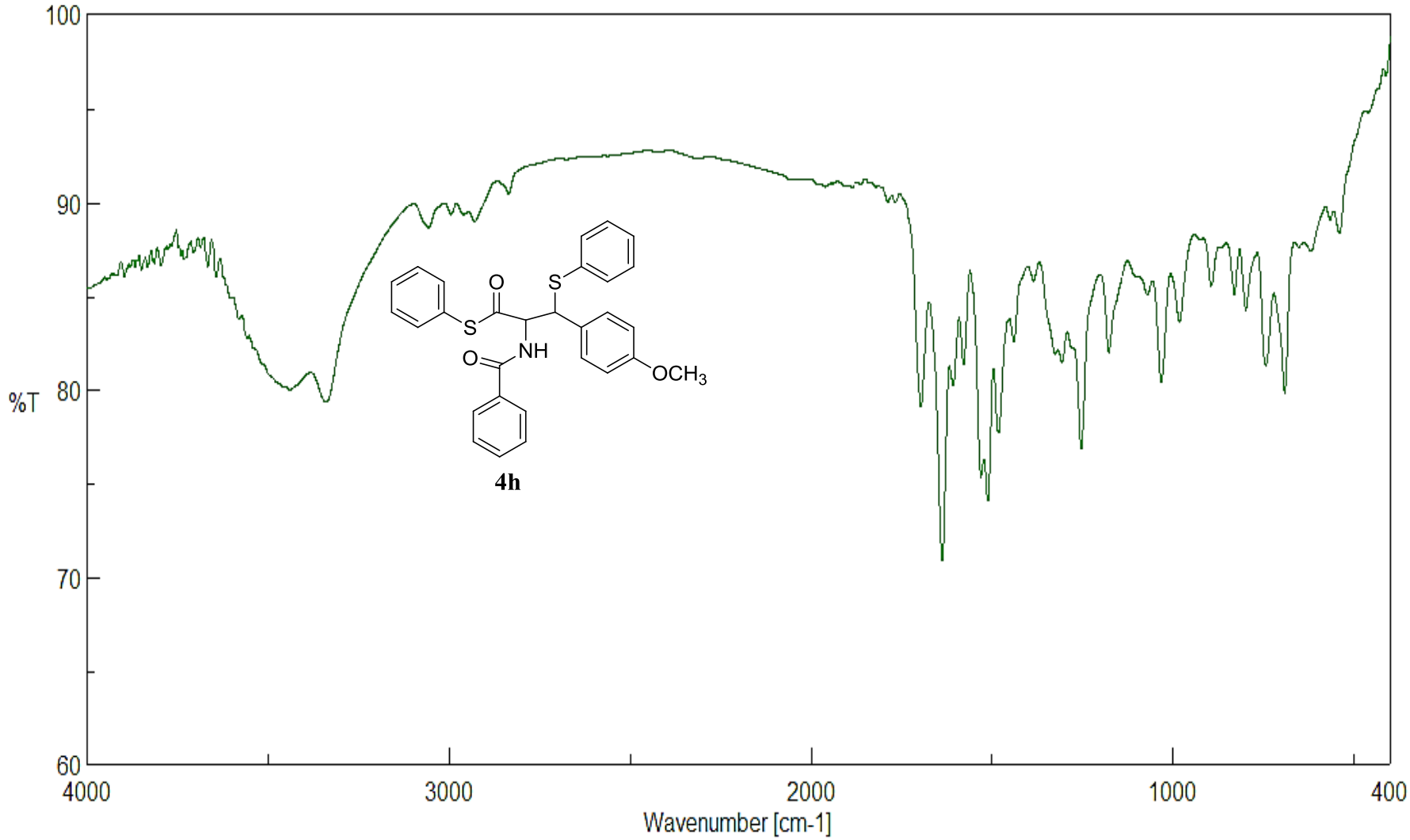

Figure 23. FTIR spectra for the **S-phenyl 2-benzamido-3-(4-methoxyphenyl)-3-(phenylthio)propanethioate** in KBr.

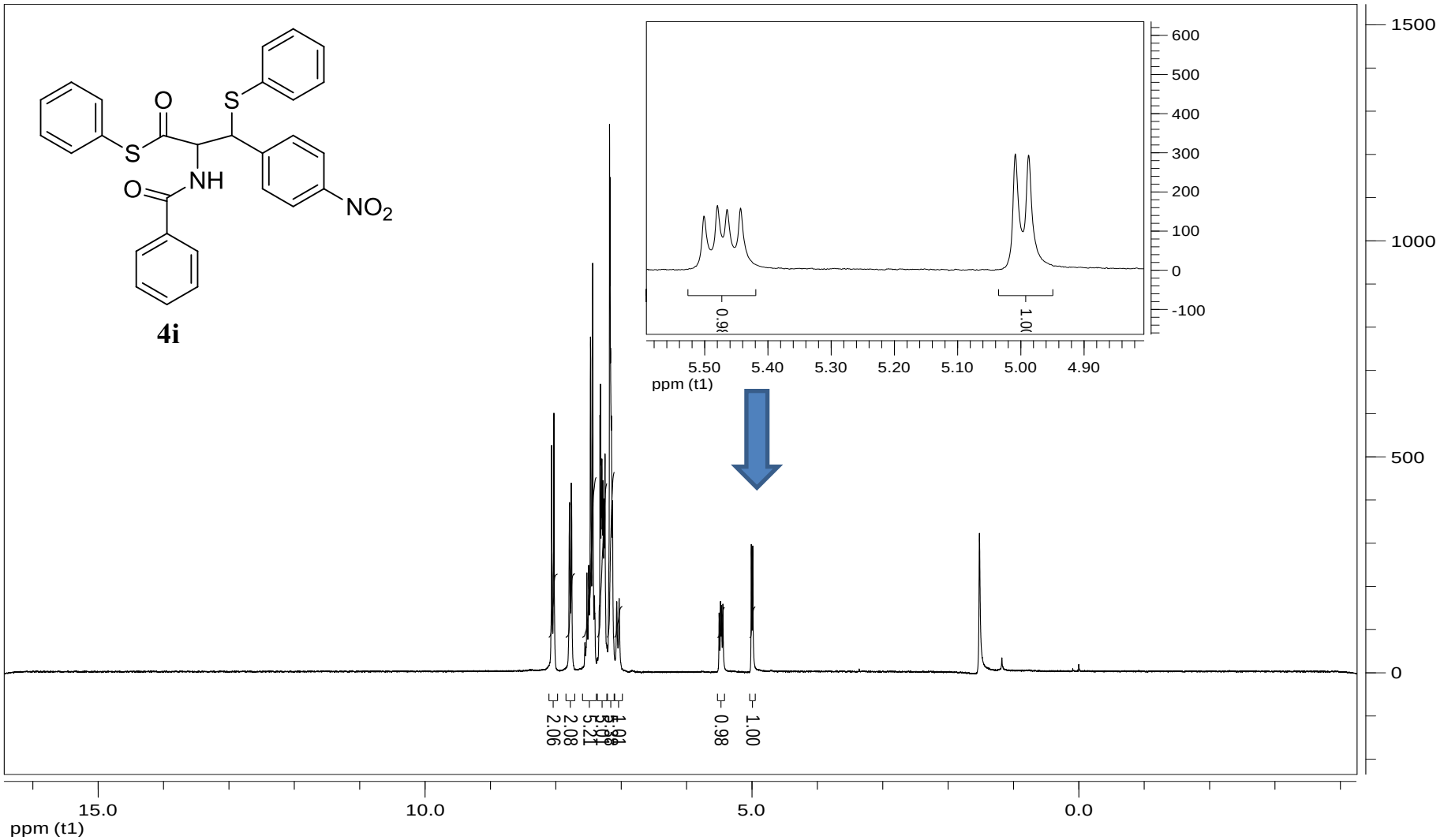

Figure 24. ^{1}H NMR spectra for the ***S*-phenyl 2-benzamido-3-(4-nitrophenyl)-3-(phenylthio)propanethioate** in $CDCl_3$.

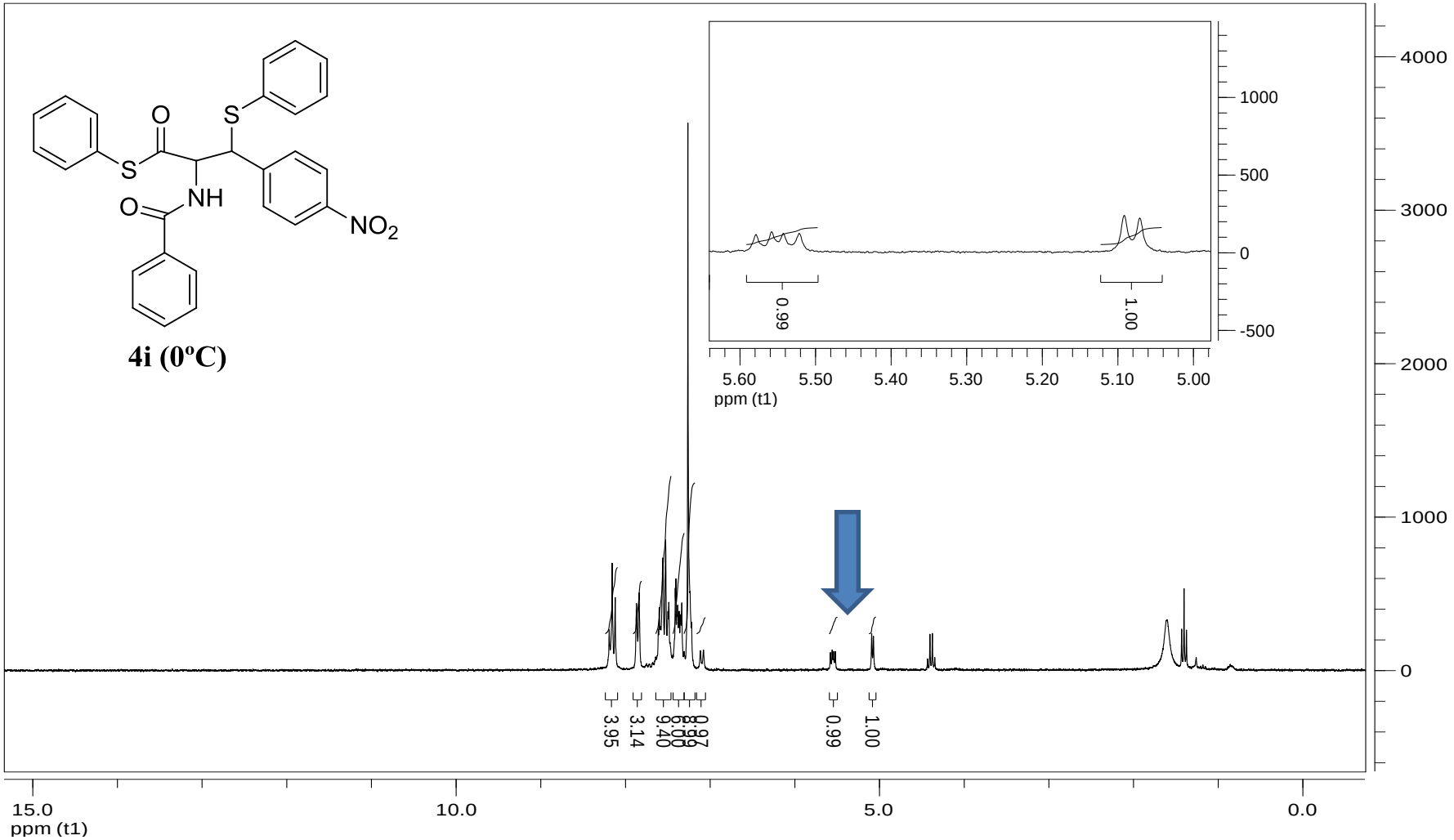

Figure 25. ^{1}H NMR spectra for the ***S*-phenyl 2-benzamido-3-(4-nitrophenyl)-3-(phenylthio)propanethioate** in $CDCl_3$.

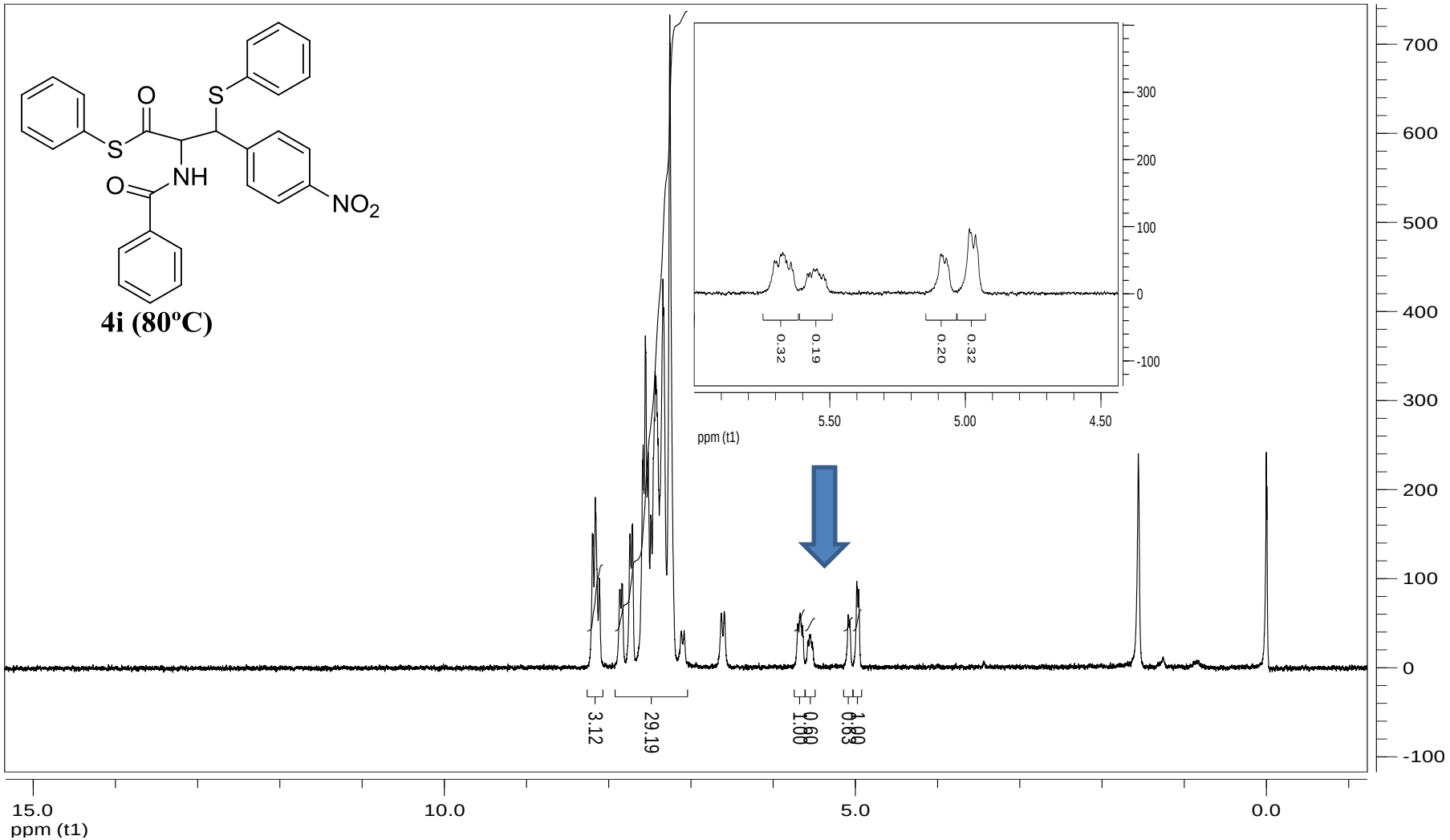

Figure 26. ^{1}H NMR spectra for the ***S*-phenyl 2-benzamido-3-(4-nitrophenyl)-3-(phenylthio)propanethioate** in $CDCl_3$.

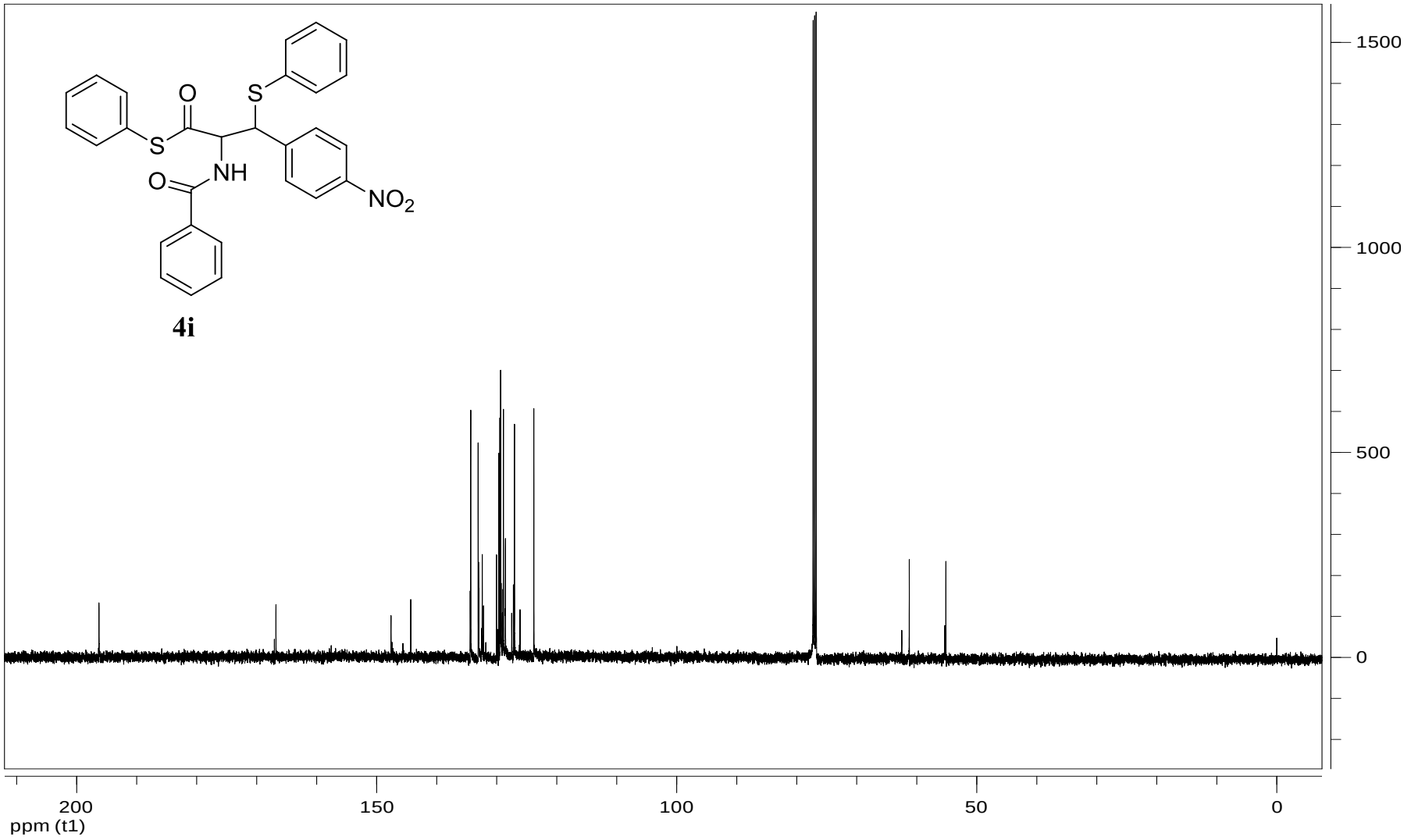

Figure 27 ^{13}C NMR spectra for the ***S*-phenyl 2-benzamido-3-(4-nitrophenyl)-3-(phenylthio)propanethioate** in $CDCl_3$.

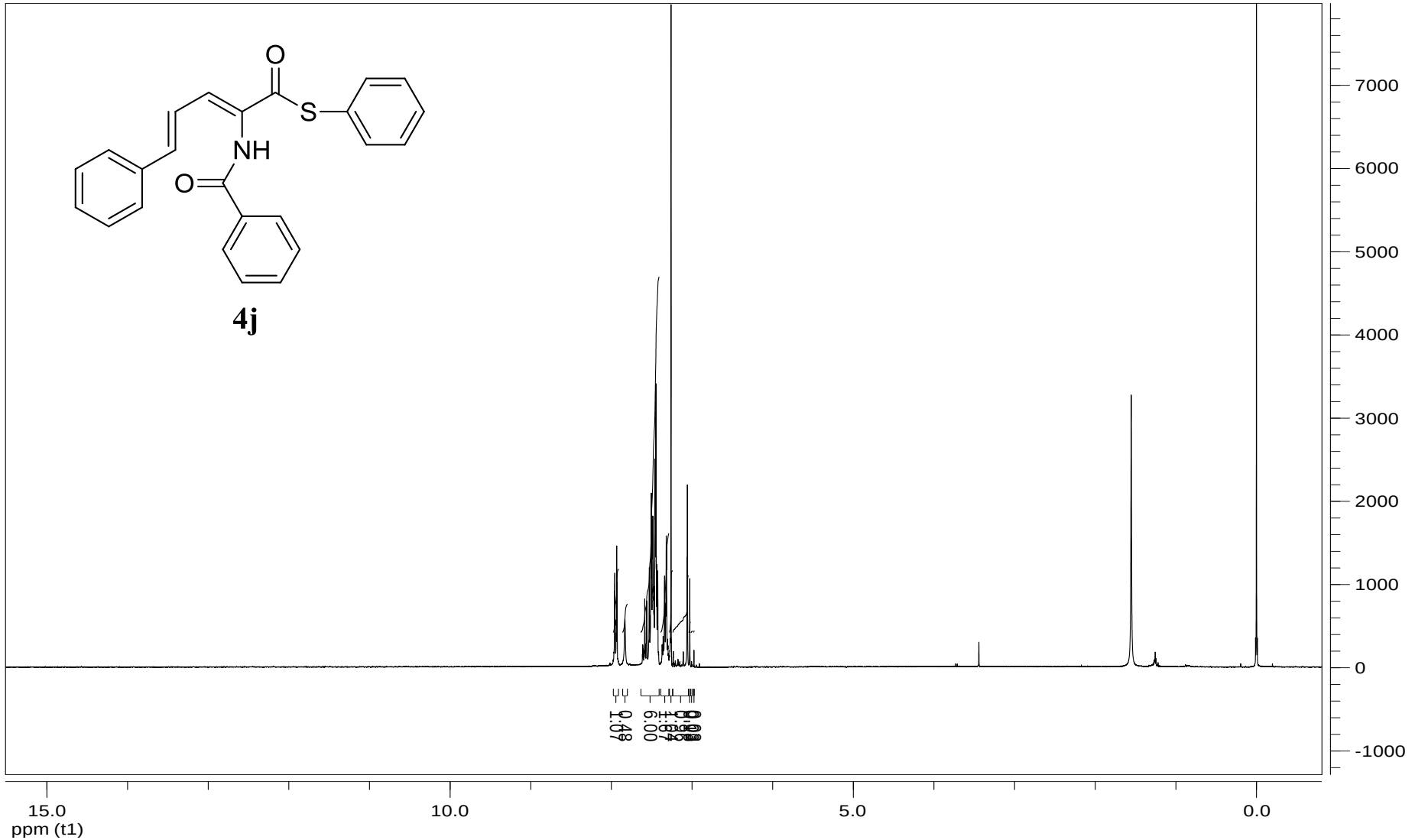

Figure 28. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-5-phenylpenta-2,4-dienethioate** in DMSO.

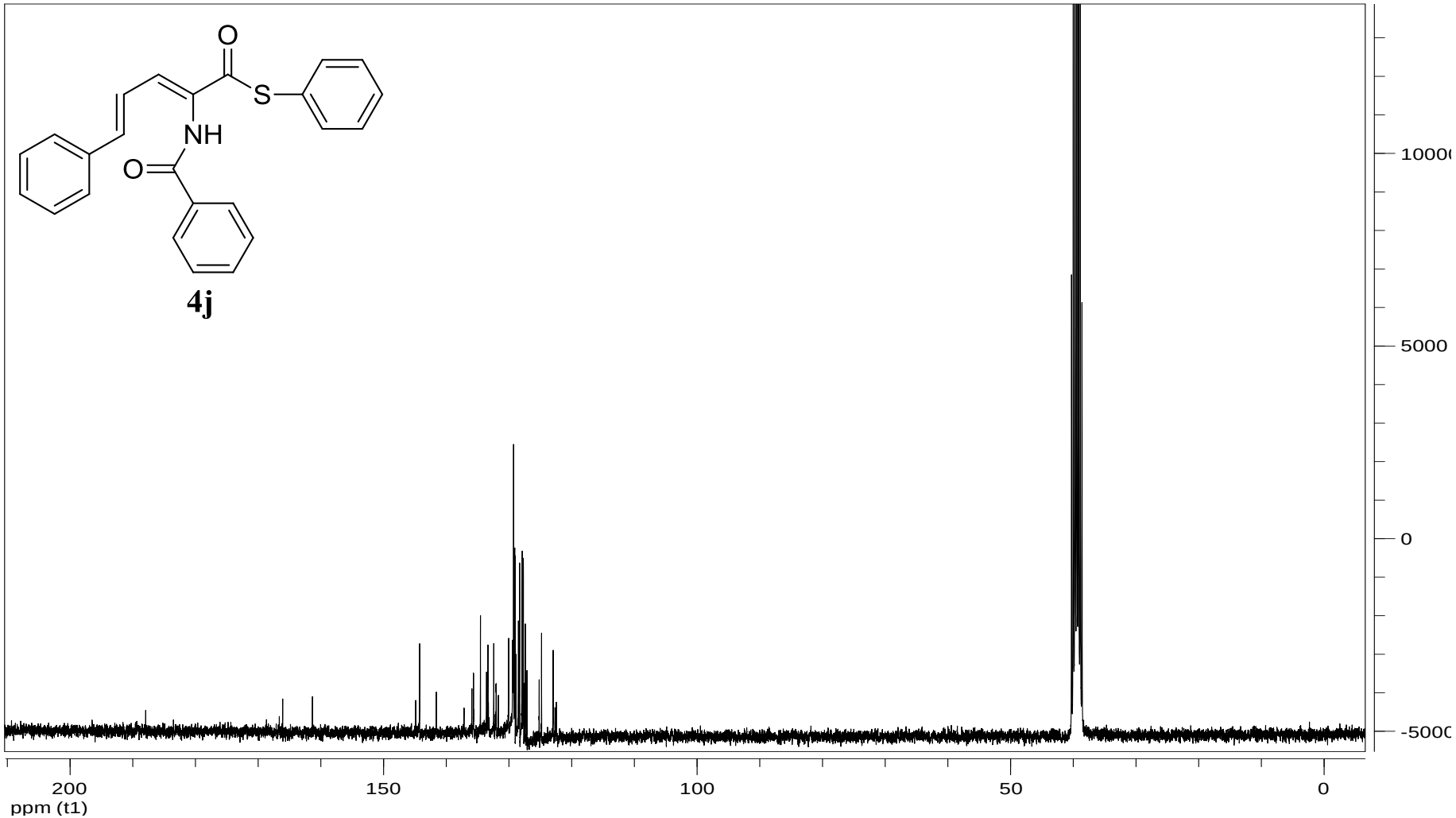

Figure 29. ^{1}H NMR spectra for the **S-phenyl 2-benzamido-5-phenylpenta-2,4-dienethioate** in DMSO.

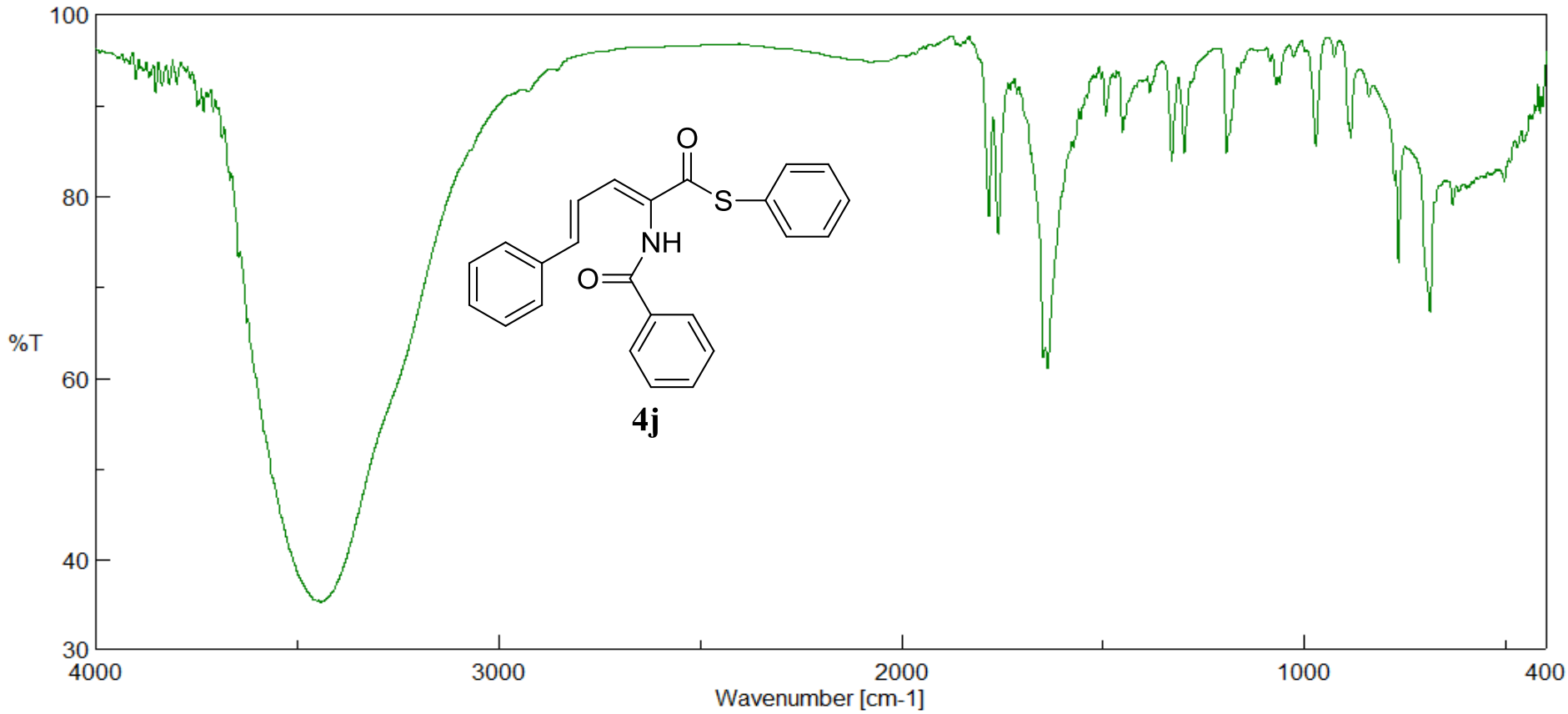

Figure 30. FTIR spectra for the **S-phenyl 2-benzamido-5-phenylpenta-2,4-dienethioate** in KBr.

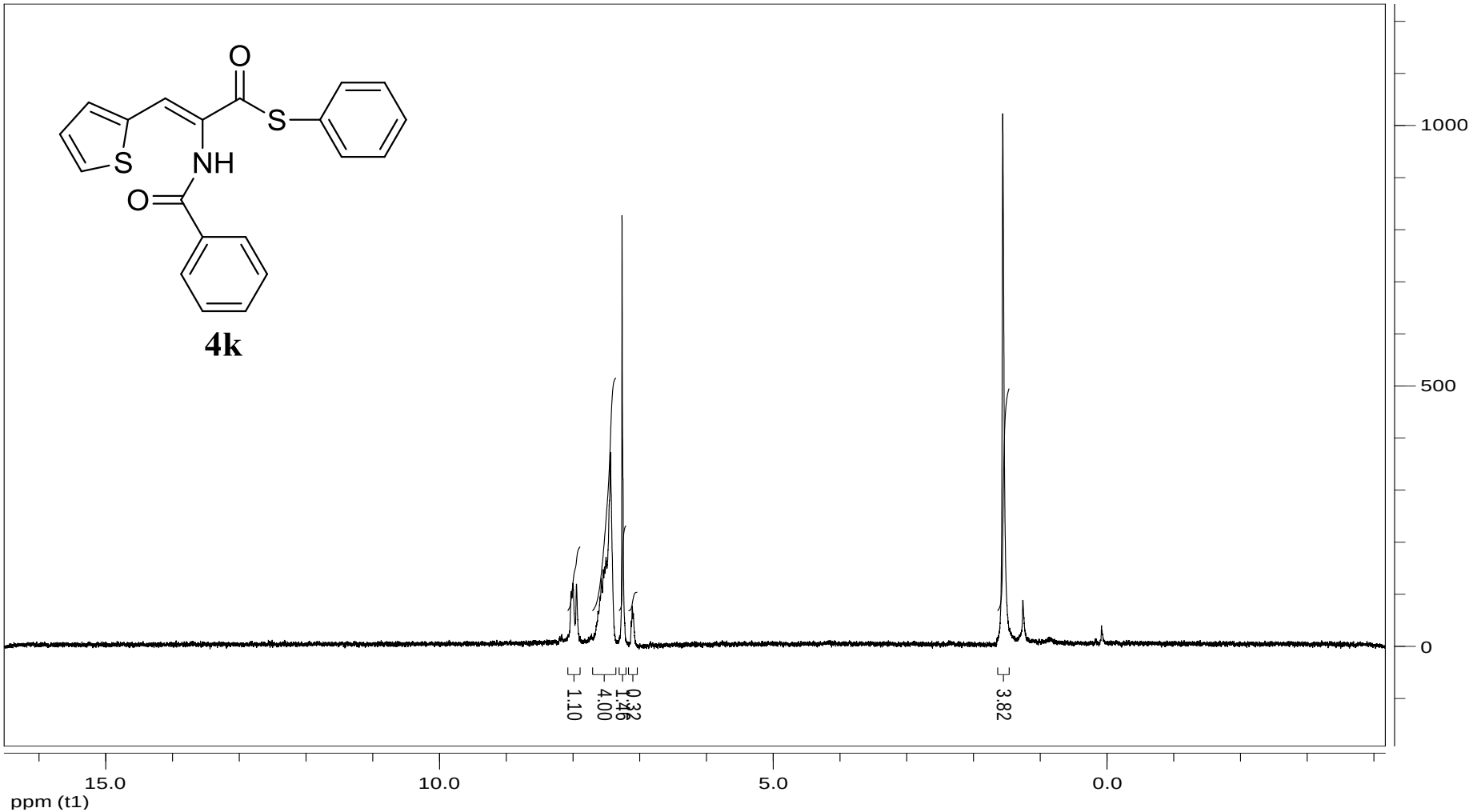

Figure 31. ^{1}H NMR spectra for the ***S*-phenyl 2-benzamido-3-(4-(thiophen-2-yl)phenyl)prop-2-enethioate** in $CDCl_3$.

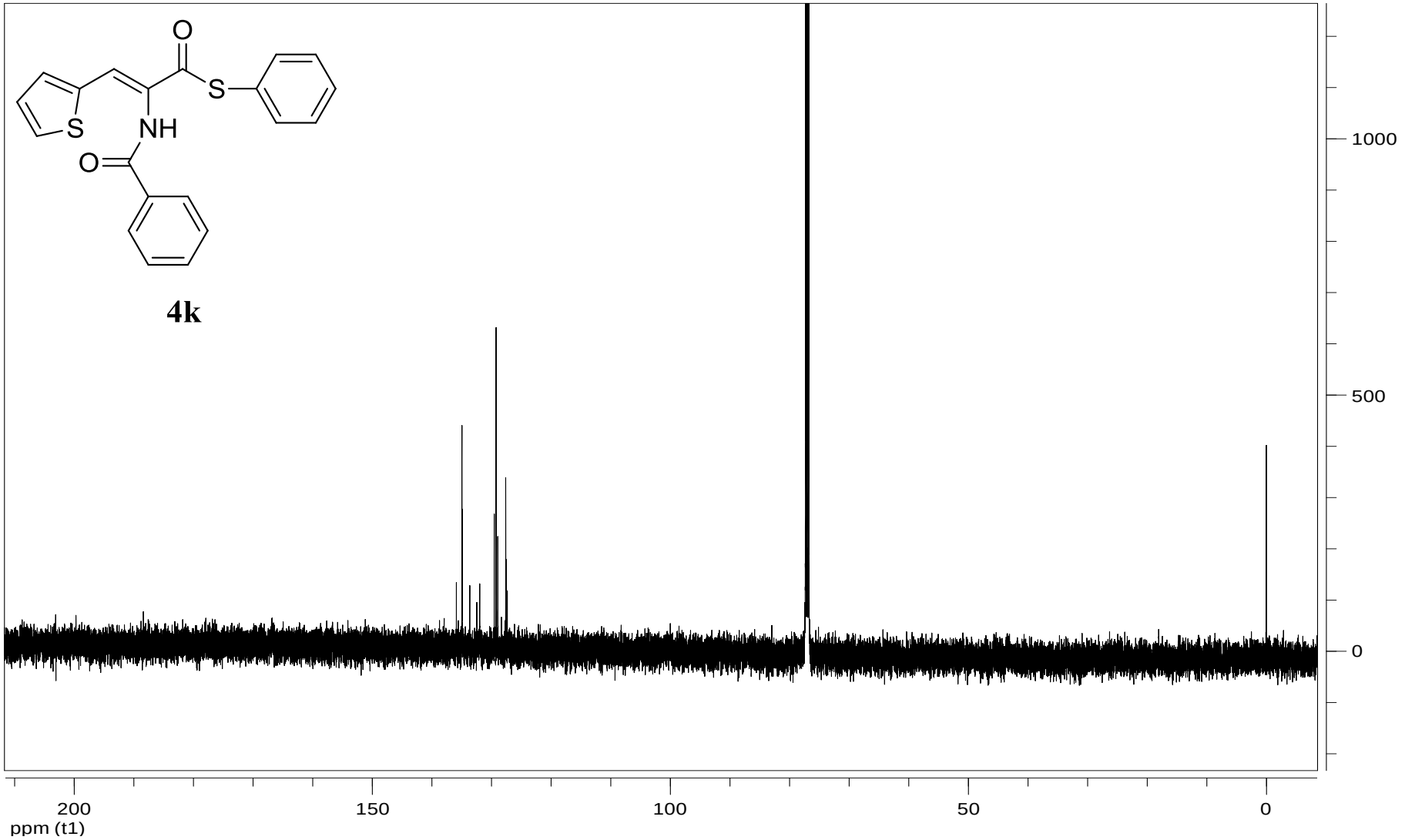

Figure 32. ^{13}C NMR spectra for the **S-phenyl 2-benzamido-5-phenylpenta-2,4-dienethioate** in $CDCl_3$.

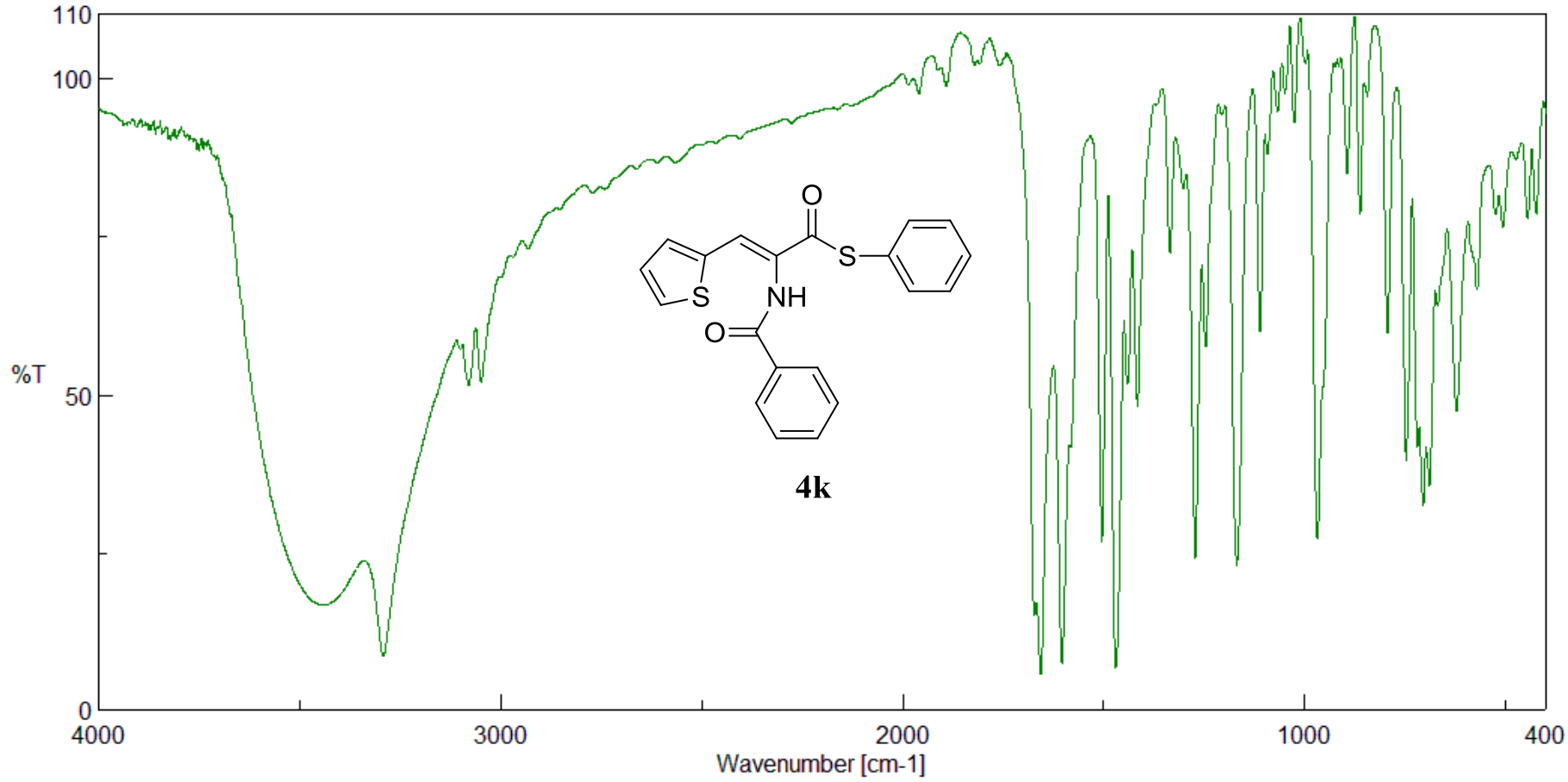

Figure 33. FTIR spectra for the **S-phenyl 2-benzamido-5-phenylpenta-2,4-dienethioate** in KBr.

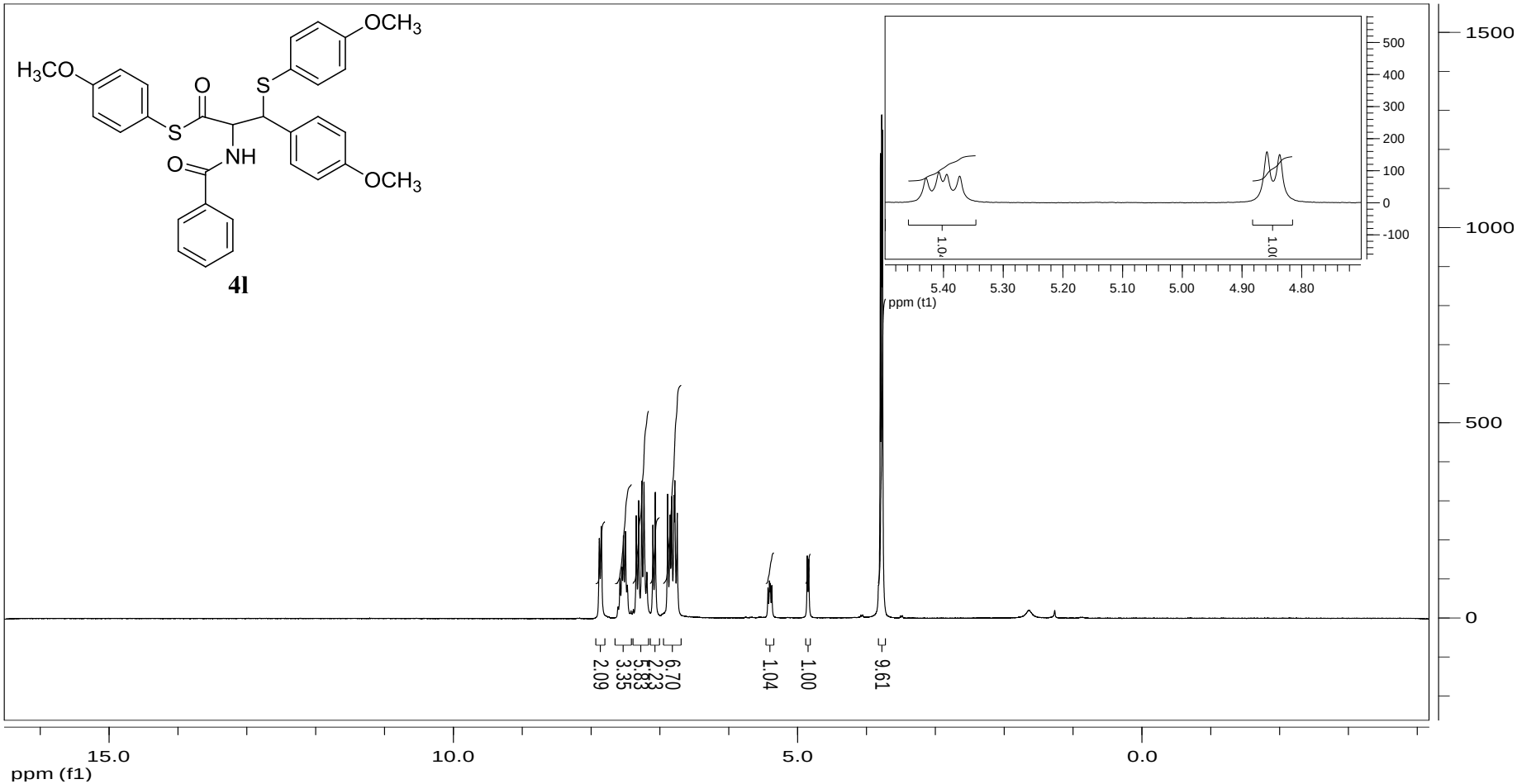

Figure 34. ^{1}H NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-(4-methoxyphenyl)-3-((4-methoxyphenyl)thio)propanethioate** in $CDCl_3$.

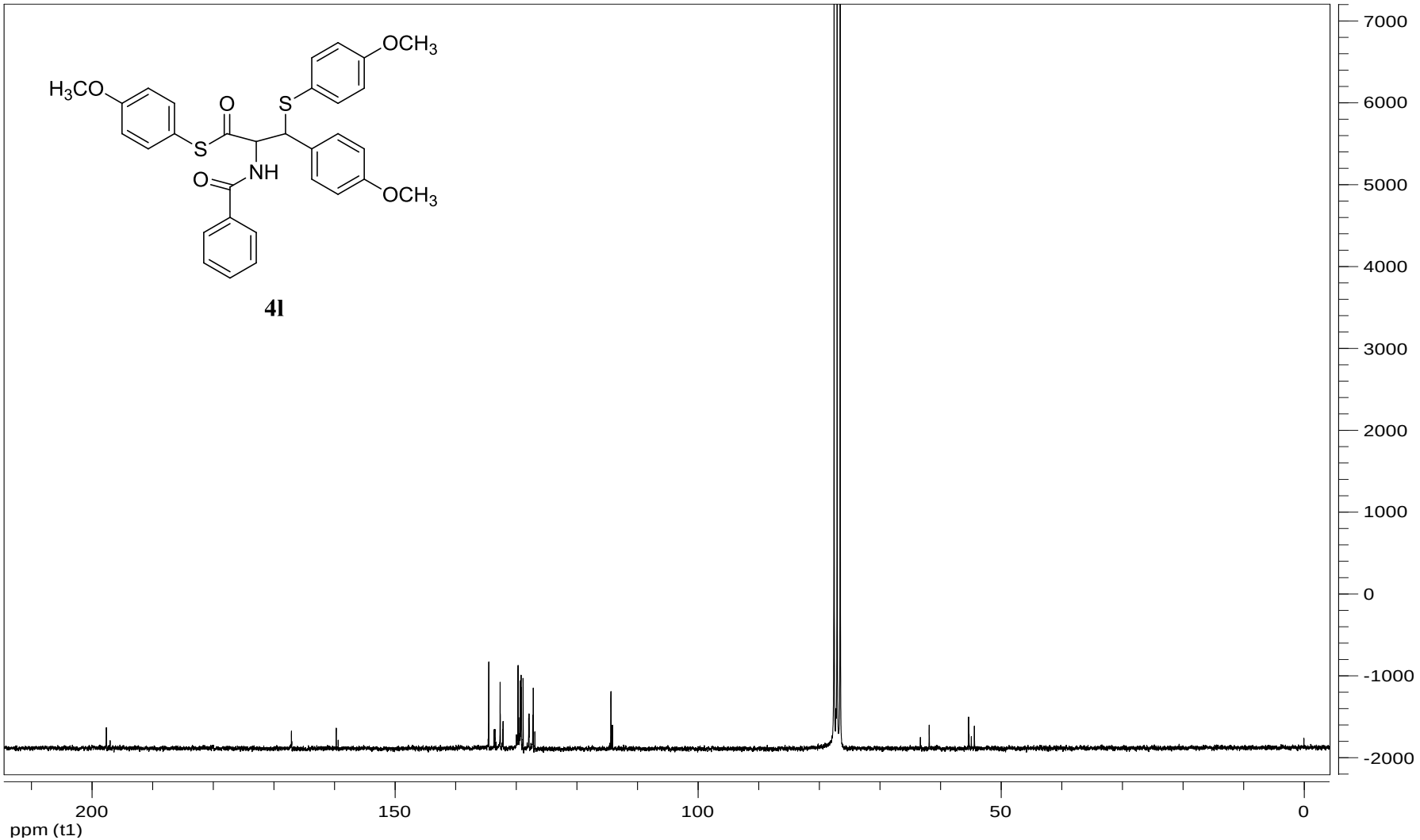

Figure 35. ^{13}C NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-(4-methoxyphenyl)-3-((4-methoxyphenyl)thio)propanethioate** in $CDCl_3$.

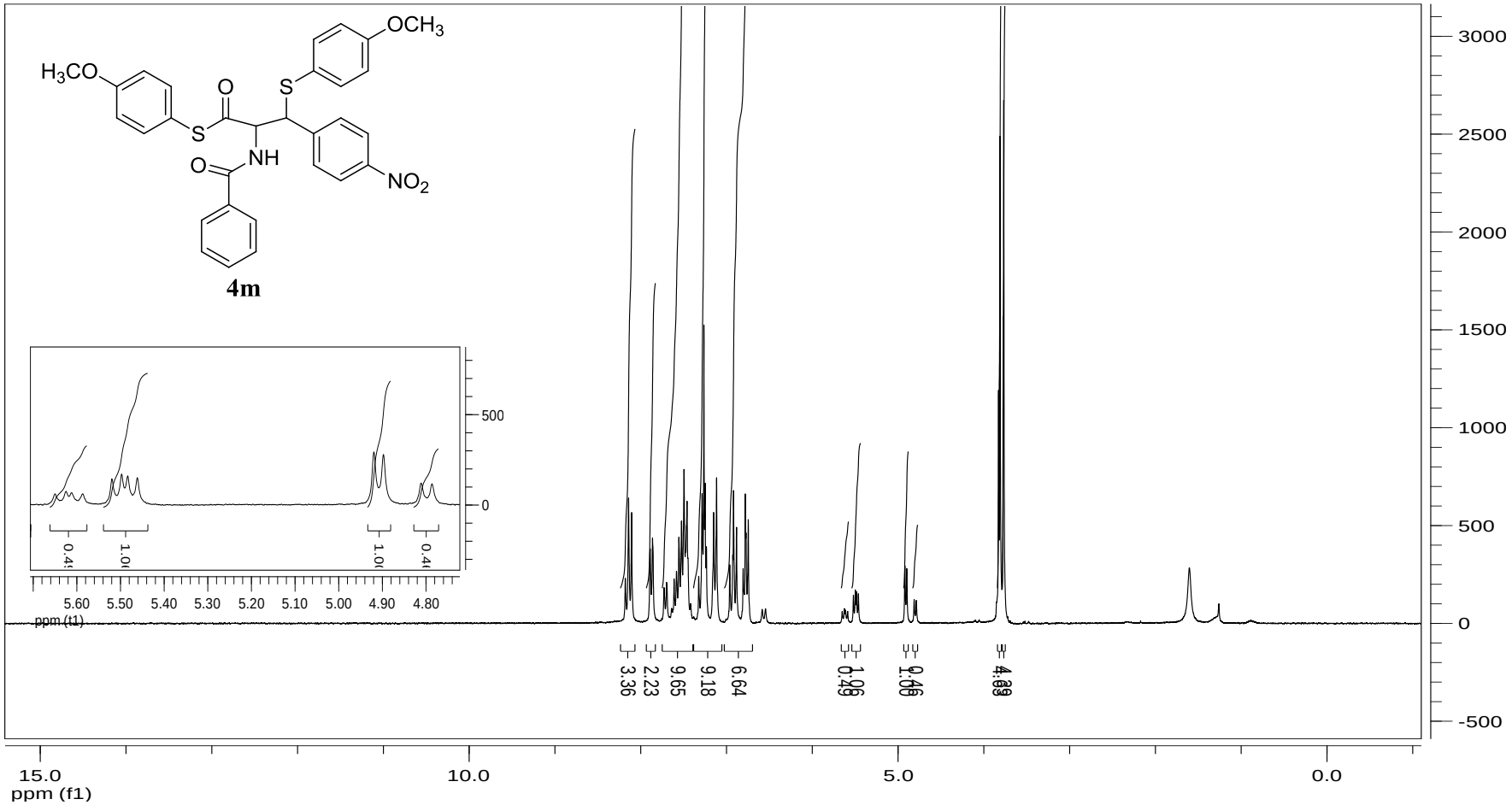

Figure 36. ^{1}H NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-((4-methoxyphenyl)thio)-3-(3-nitrophenyl)propanethioate** in $CDCl_3$.

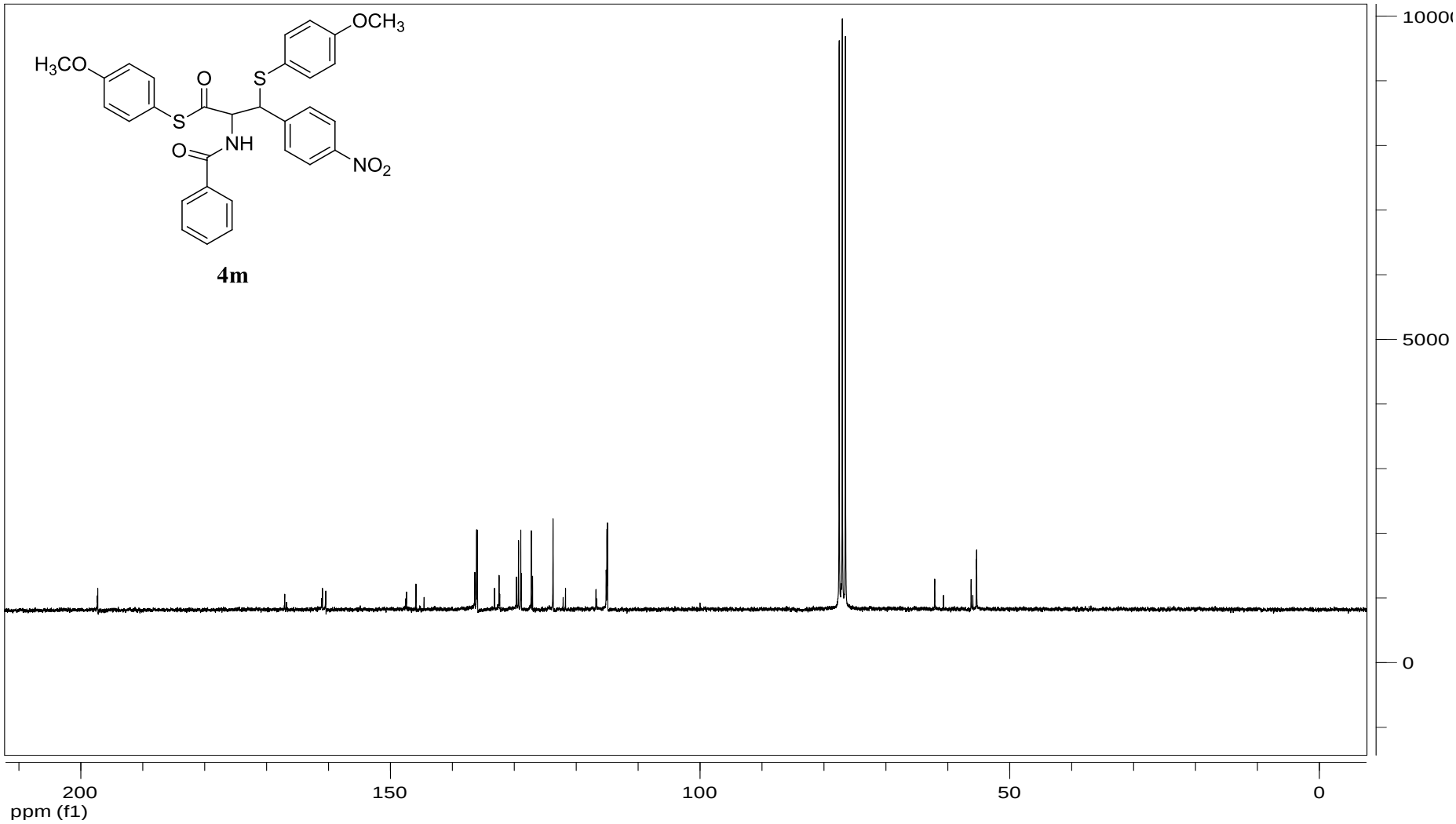

Figure 37. ^{13}C NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-((4-methoxyphenyl)thio)-3-(4-nitrophenyl)propanethioate** in $CDCl_3$.

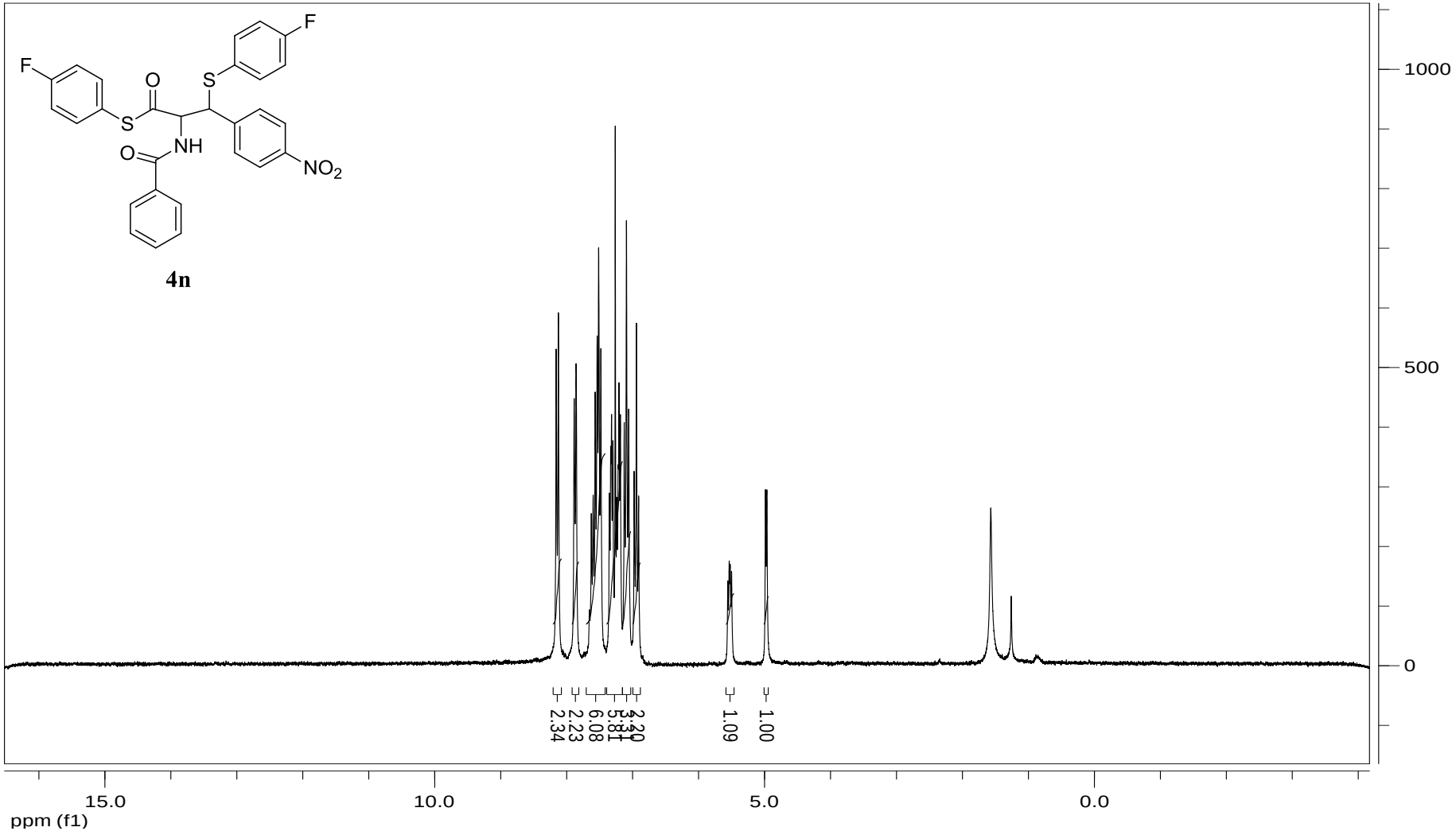

Figure 38. ^{1}H NMR spectra for the **S-(4-fluorophenyl) 2-benzamido-3-((4-fluorophenyl)thio)-3-(4-nitrophenyl)propanethioate** in $CDCl_3$.

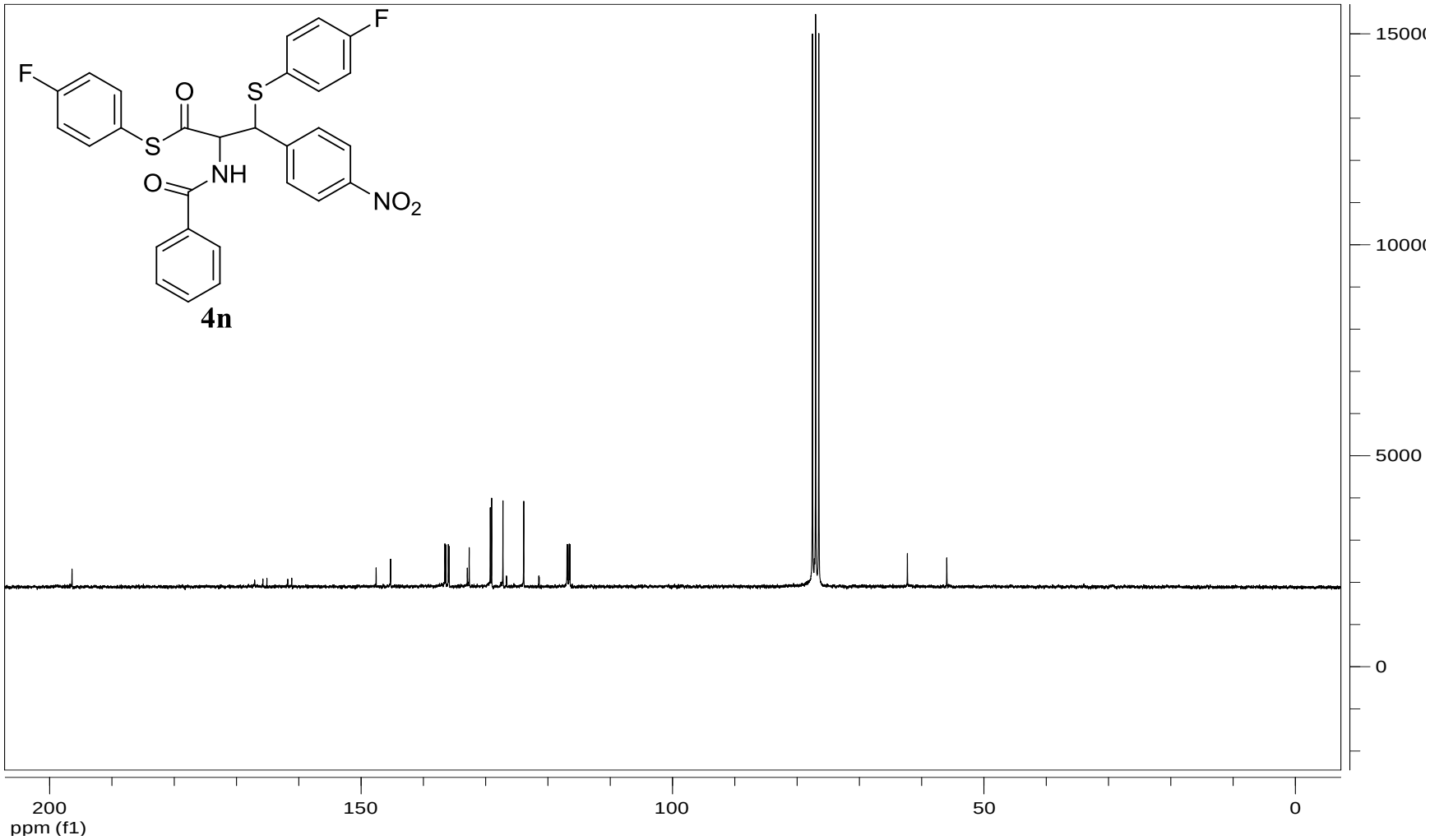

Figure 39. ^{1}H NMR spectra for the **S-(4-fluorophenyl) 2-benzamido-3-((4-fluorophenyl)thio)-3-(4-nitrophenyl)propanethioate** in $CDCl_{3.}$

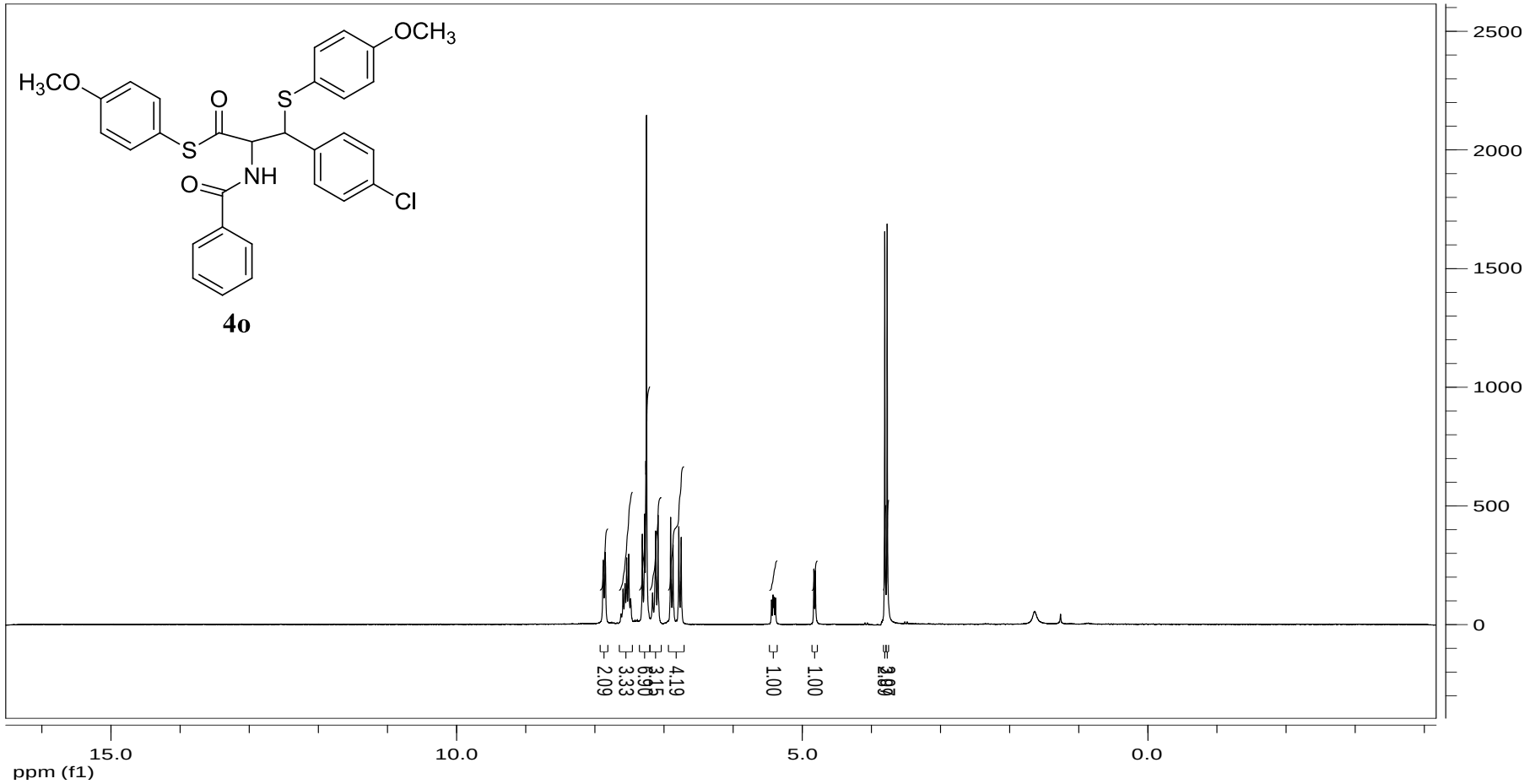

Figure 40. ^{13}H NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-(4-chlorophenyl)-3-((4-methoxyphenyl)thio)propanethioate** in $CDCl_3$.

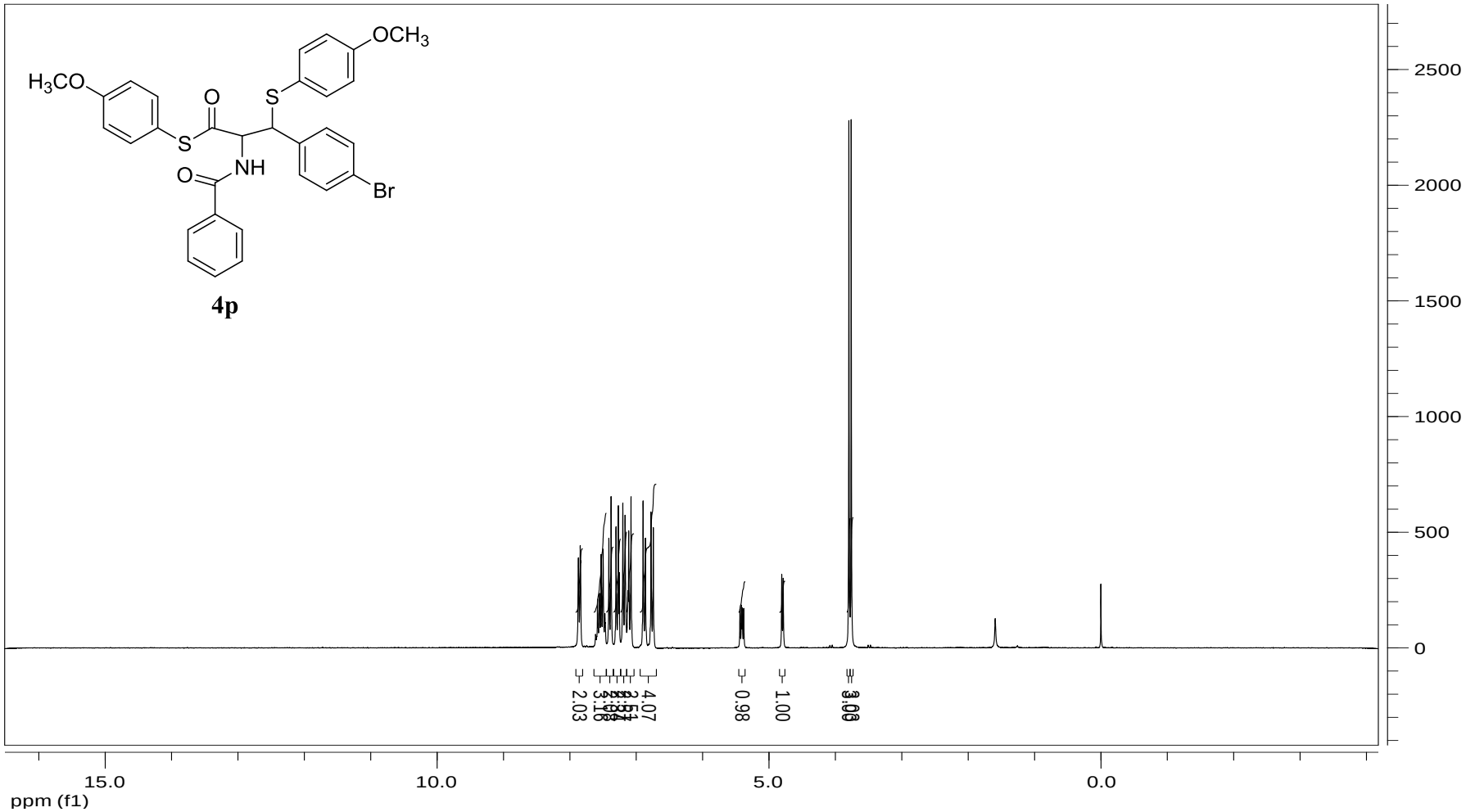

Figure 41. ^{1}H NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-(4-bromophenyl)-3-((4-methoxyphenyl)thio)propanethioate**in $CDCl_3$.

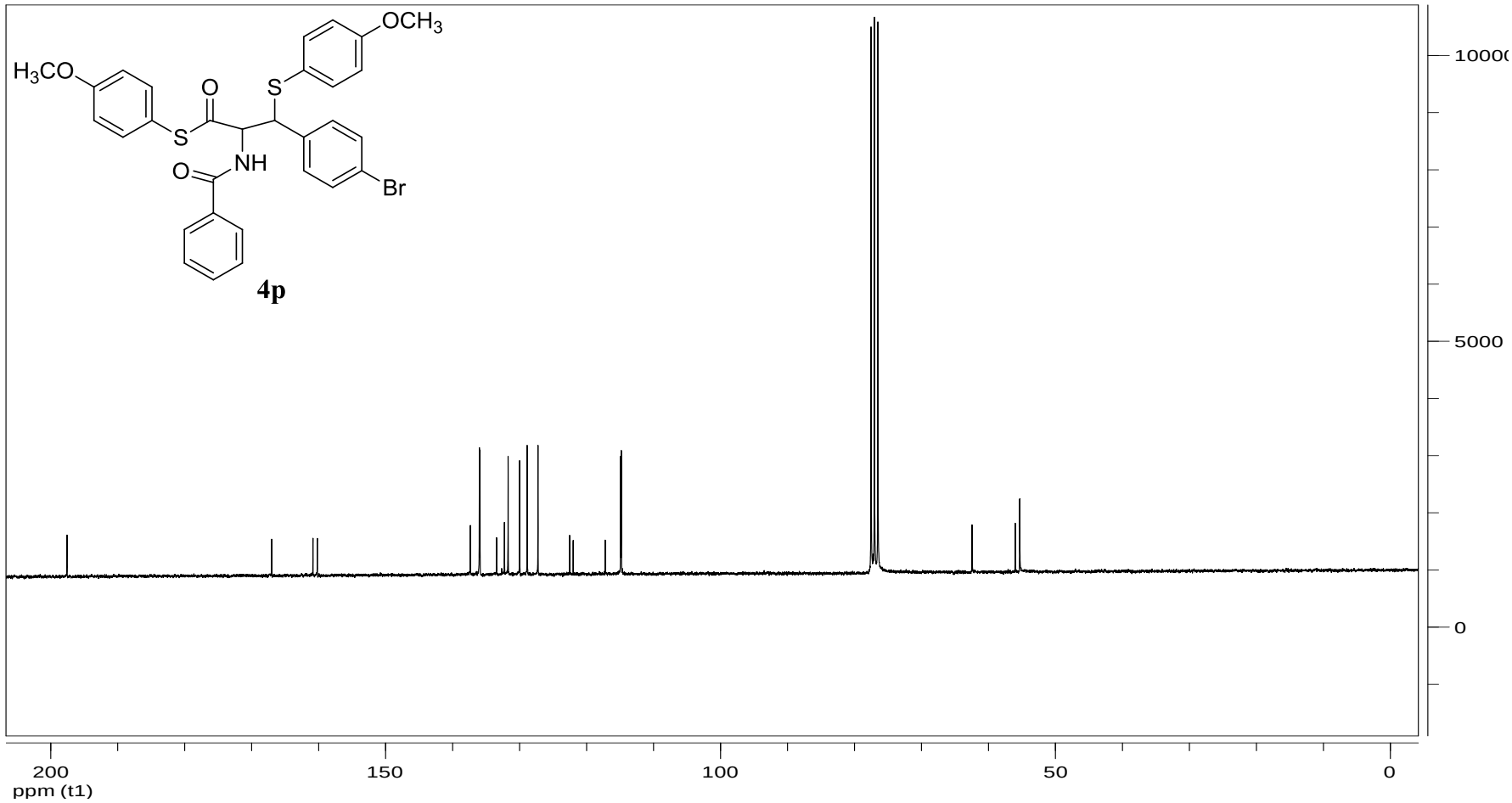

Figure 42. ^{13}C NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-(4-bromophenyl)-3-((4-methoxyphenyl)thio)propanethioate**in $CDCl_3$.

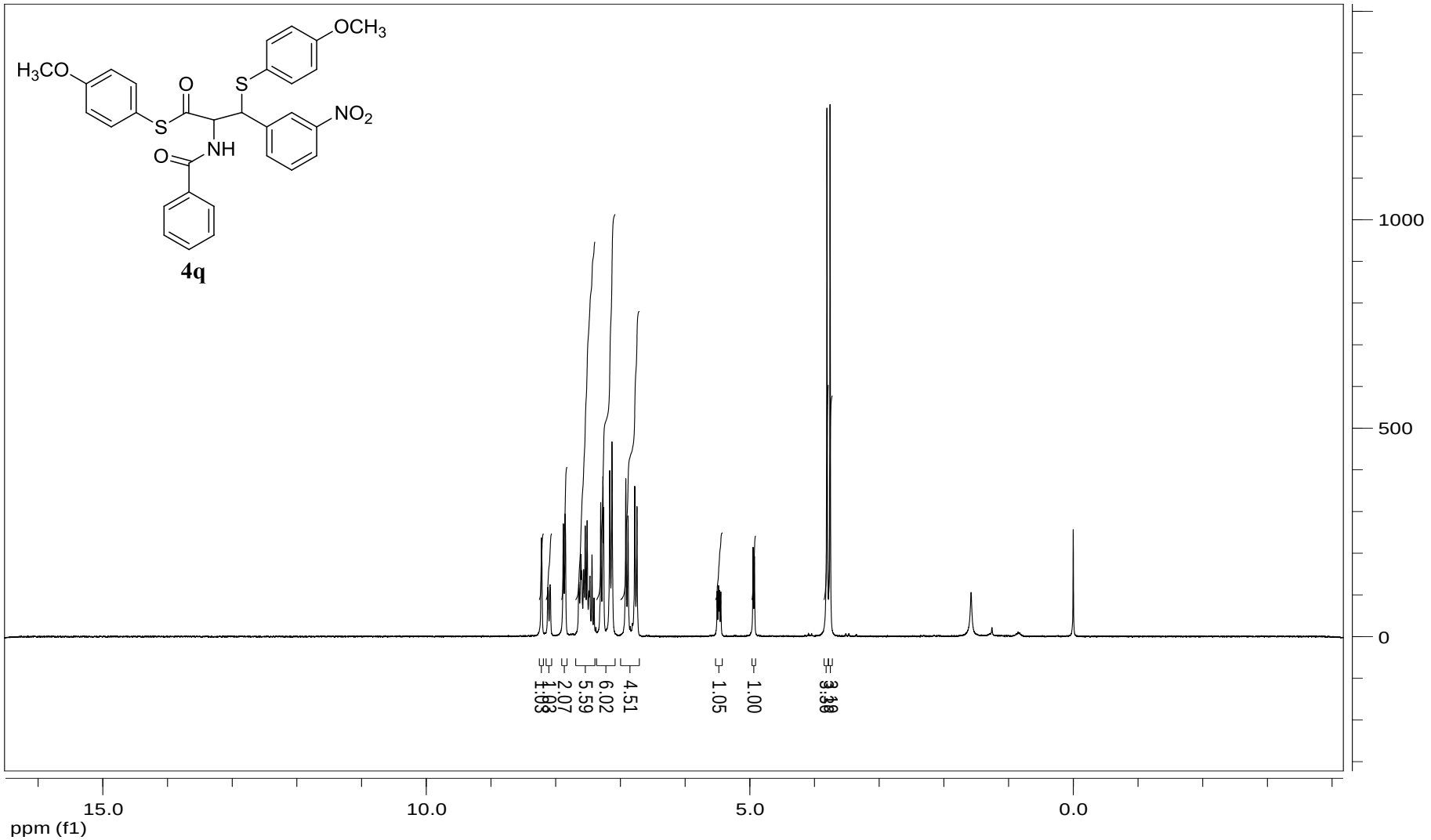

Figure 43. ^{1}H NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-((4-methoxyphenyl)thio)-3-(3-nitrophenyl)propanethioate** in $CDCl_3$.

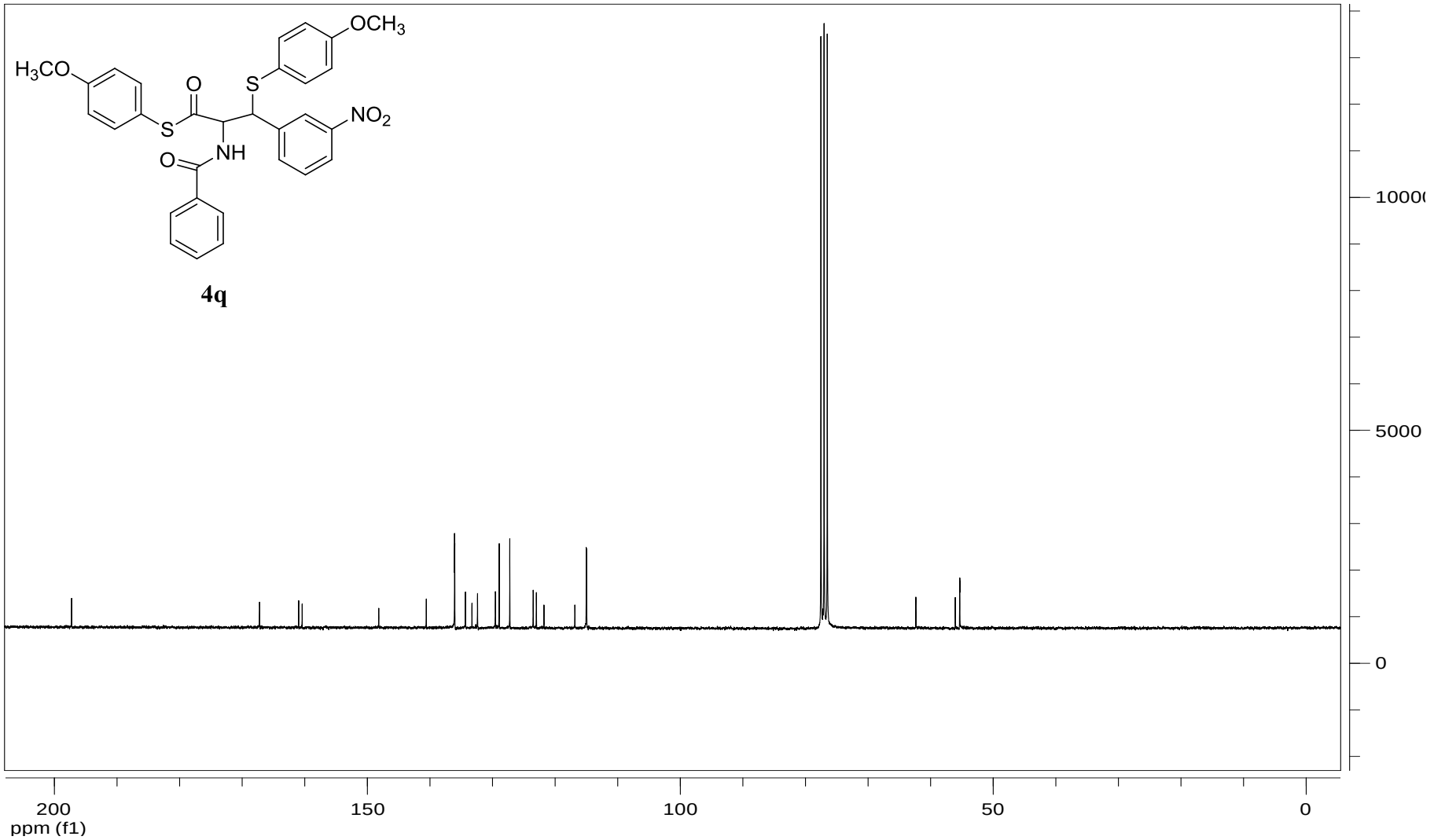

Figure 44. ^{13}C NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-((4-methoxyphenyl)thio)-3-(3-nitrophenyl)propanethioate** in $CDCl_3$.

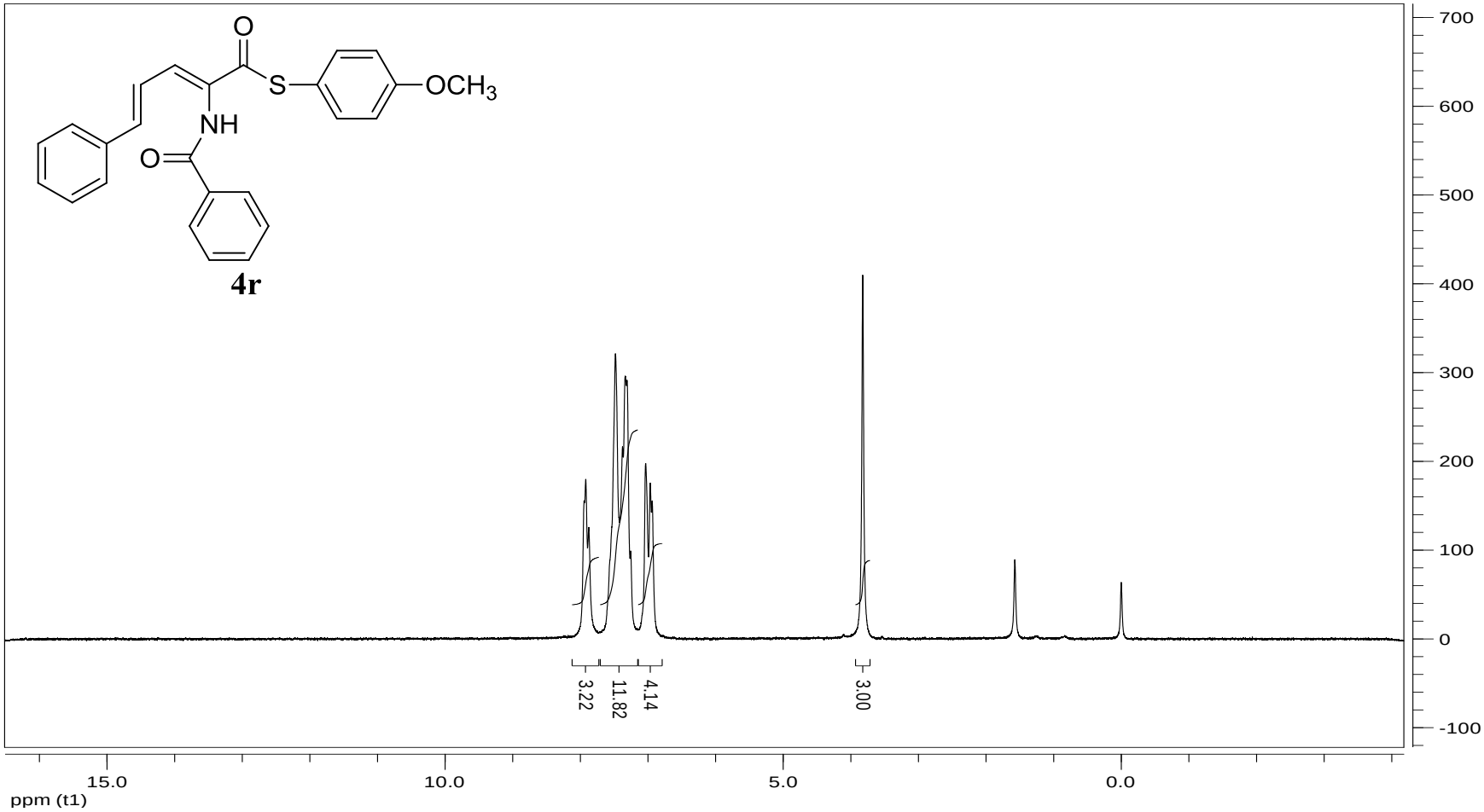

Figure 45. ^{1}H NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-5-phenylpenta-2,4-dienethioate** in $CDCl_3$.

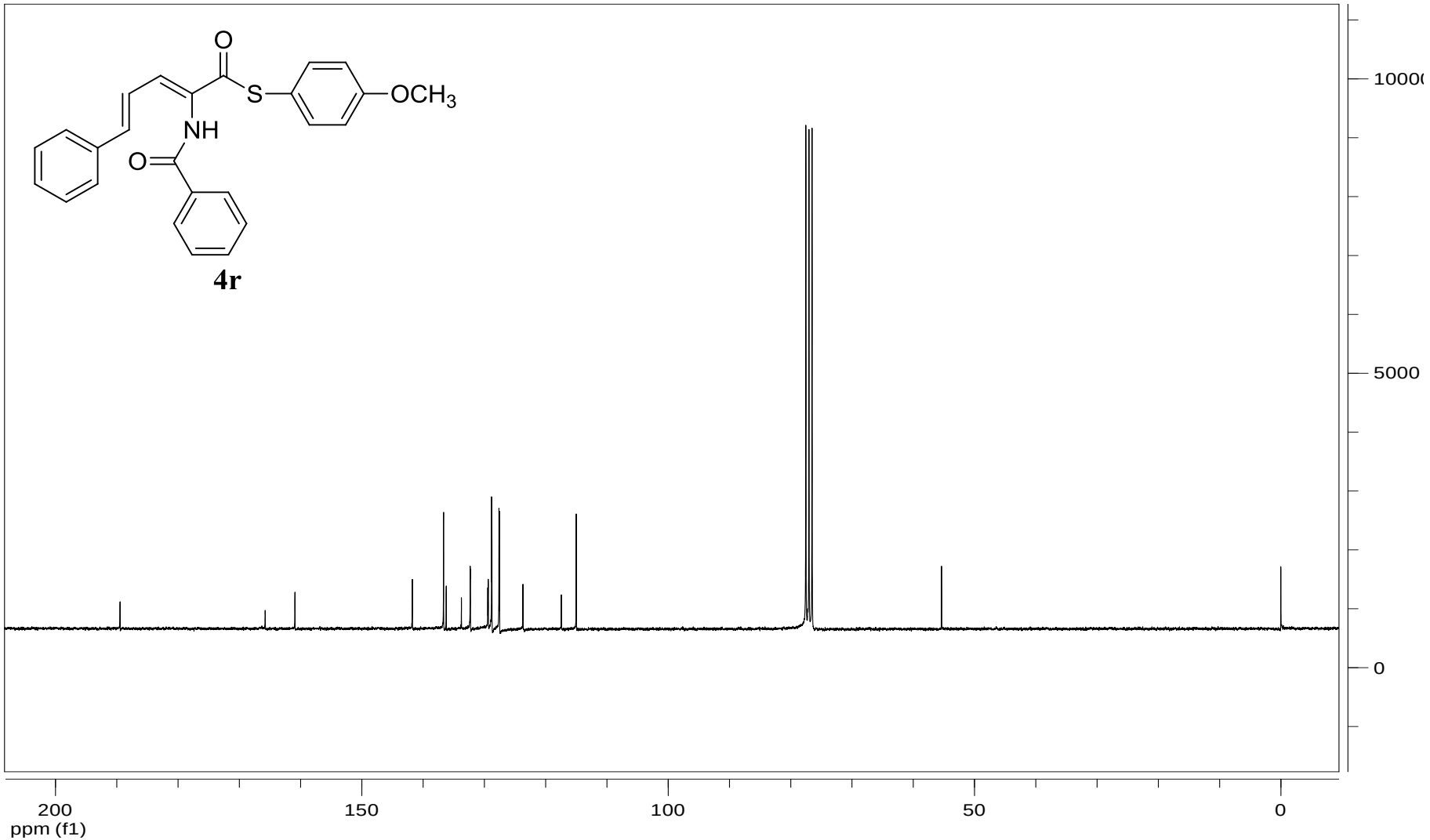

Figure 46. ^{13}C NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-5-phenylpenta-2,4-dienethioate**in $CDCl_3$.

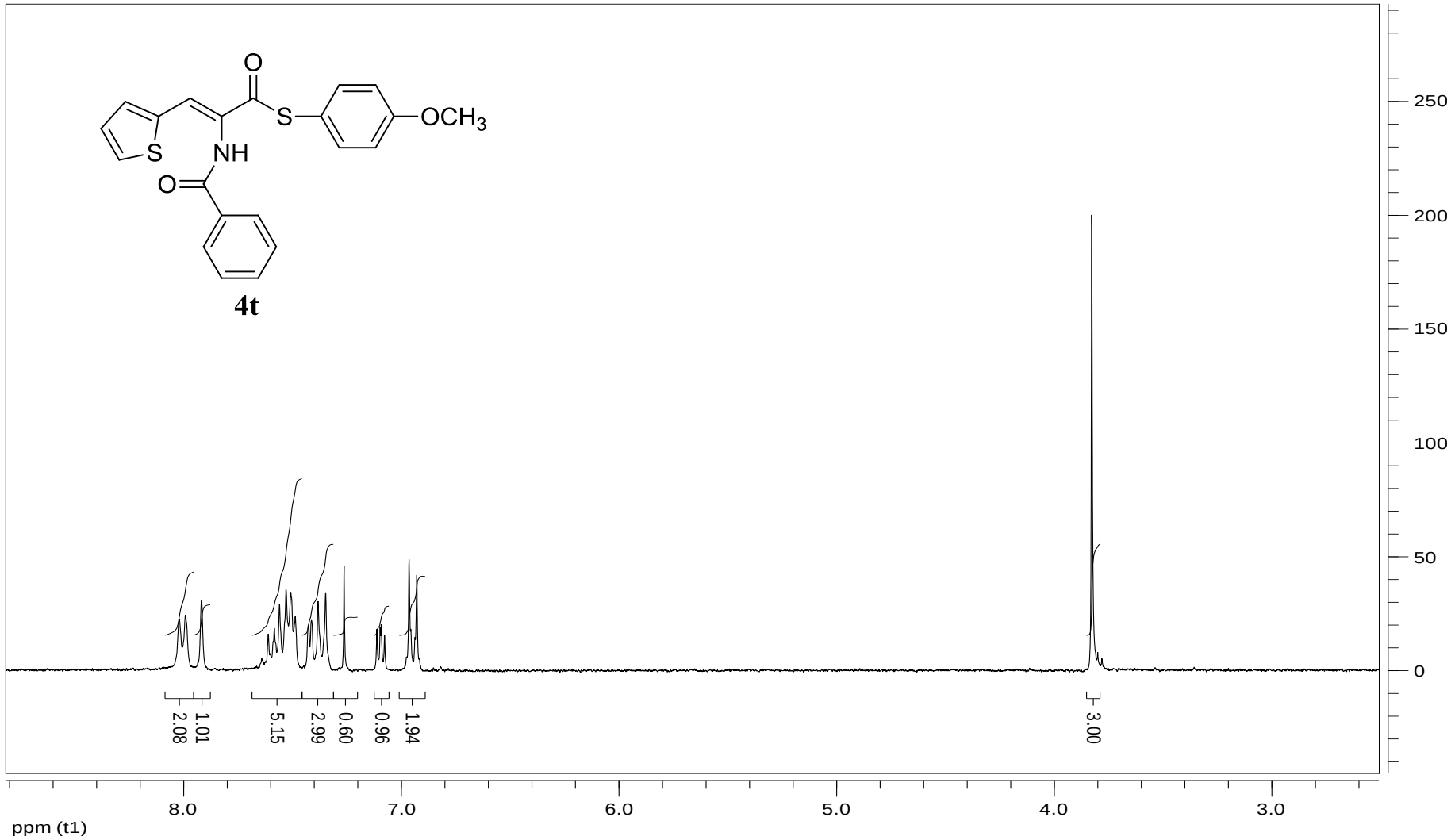

Figure 47. ^{1}H NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-((4-methoxyphenyl)thio)-5-(thiophen-2-yl)pent-4-enethioate** in $CDCl_3$

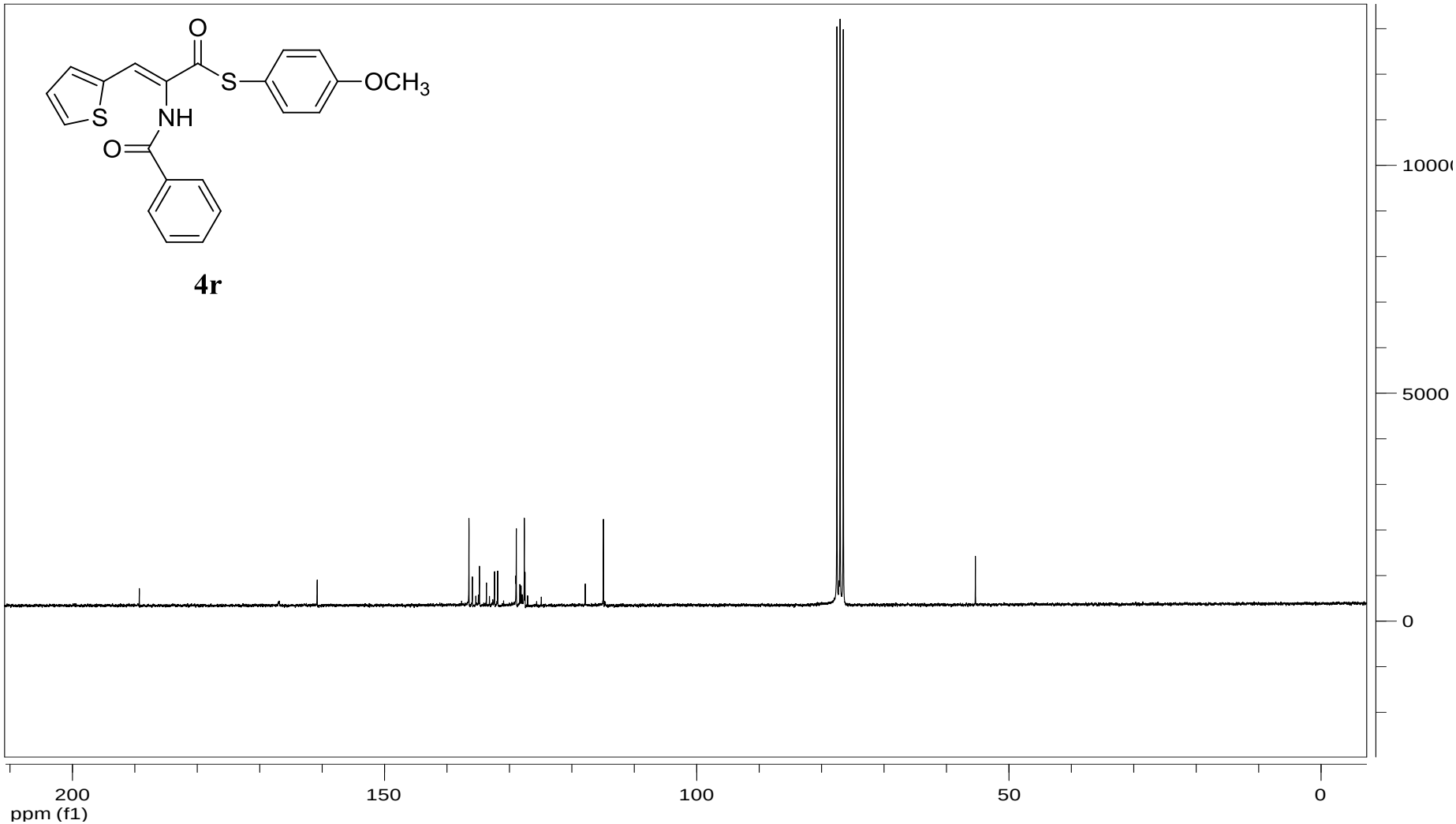

Figure 48. ^{1}H NMR spectra for the **S-(4-methoxyphenyl) 2-benzamido-3-((4-methoxyphenyl)thio)-5-(thiophen-2-yl)pent-4-enethioate** in $CDCl_3$

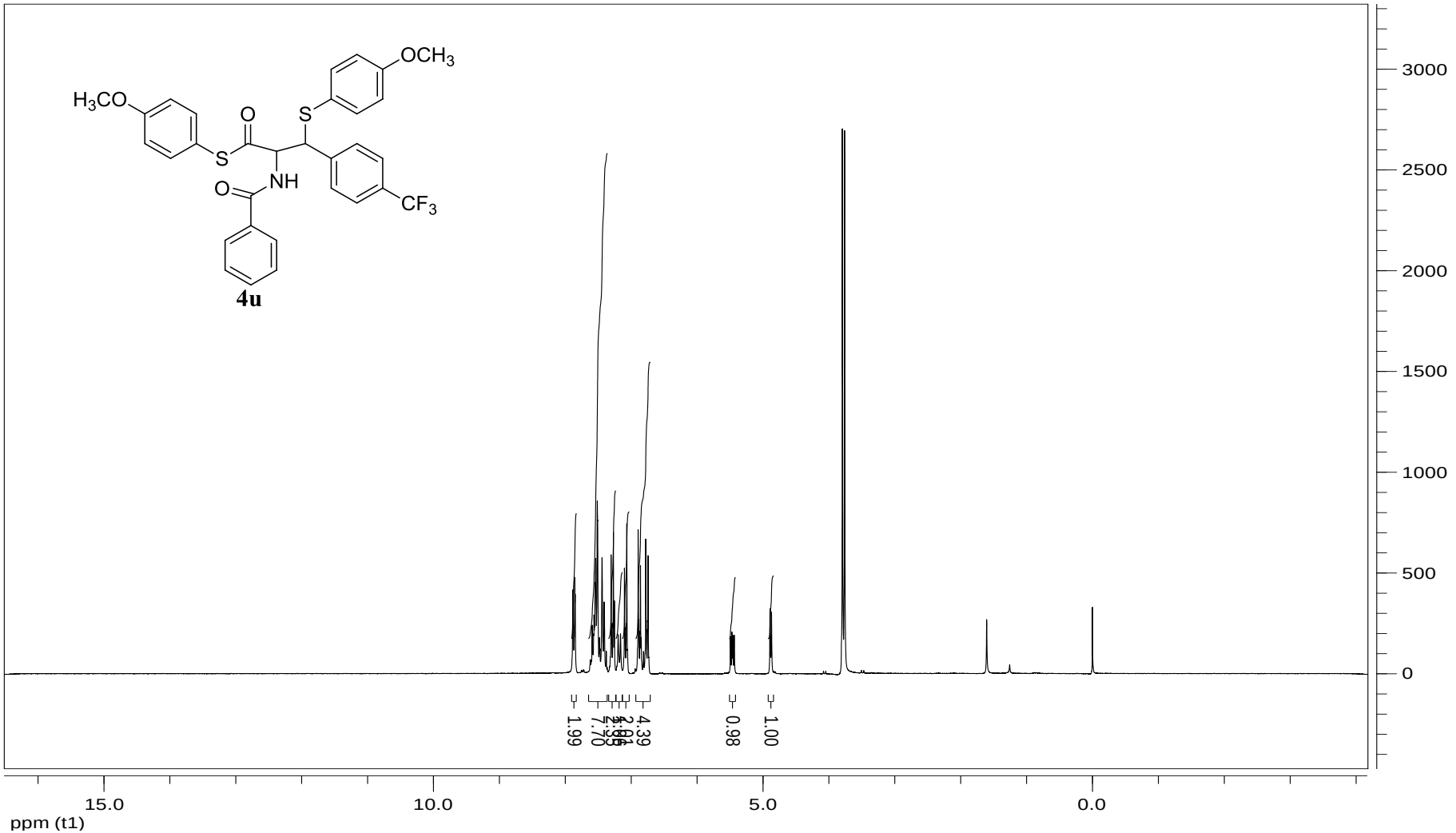

Figure 49. ^{1}H NMR spectra for the **S-(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-(4-(trifluoromethyl)phenyl)propanethioate** in $CDCl_3$.

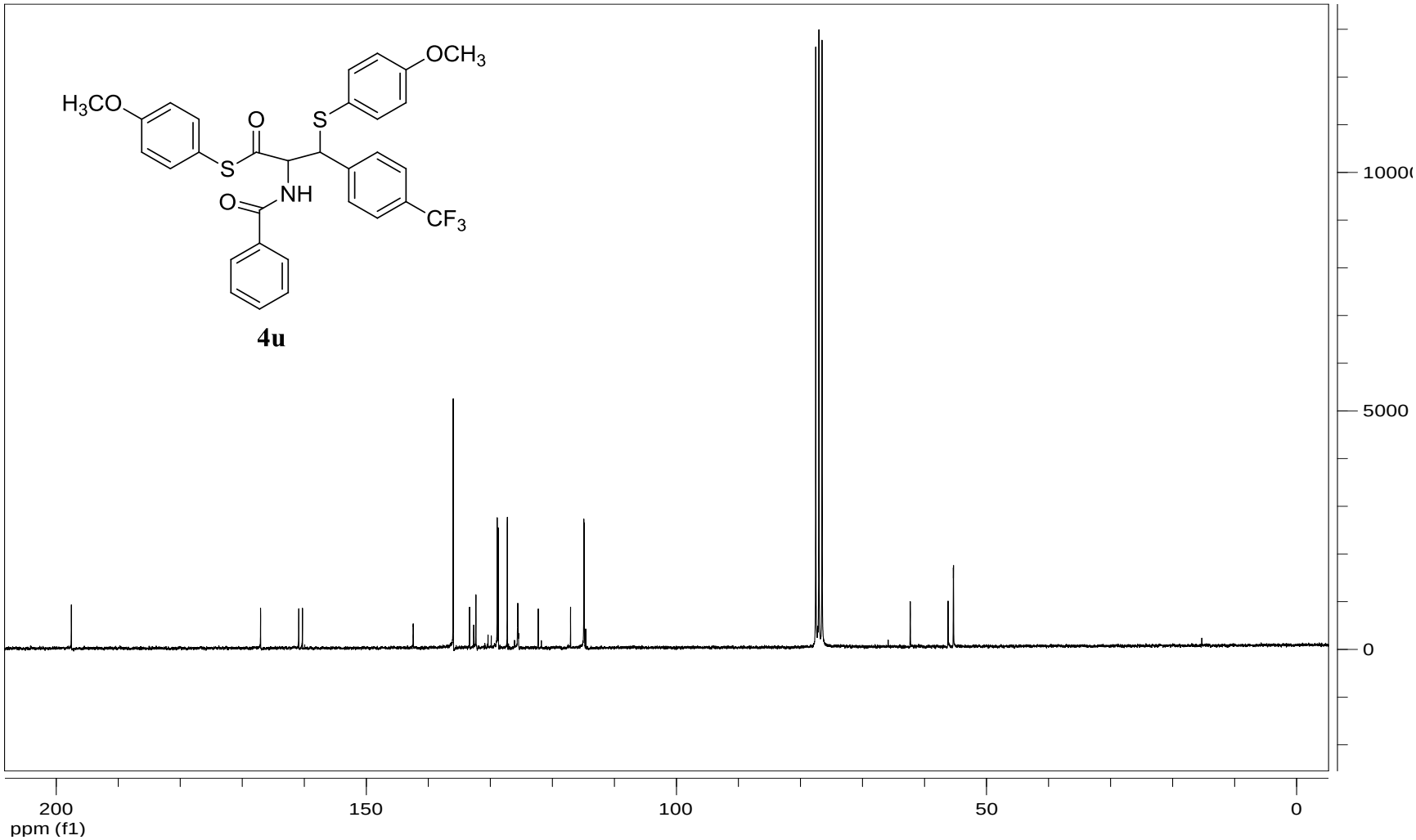

Figure 50. ^{13}C NMR spectra for the **S-(4-methoxyphenyl)2-benzamido-3-((4-methoxyphenyl)thio)-3-(4-(trifluoromethyl)phenyl)propanethioate** in $CDCl_3$.