Supporting Information

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The Nickel/Copper-Catalyzed Direct Alkylation of Heterocyclic C–H Bonds**

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Experimental Section

Chemicals and Reagents

All manipulations were carried out under an inert N_2(g) atmosphere using glovebox techniques. Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over activated 3 Å molecular sieves. Unless noted, all other reagents were purchased from commercial sources and used without further purification. Liquid compounds were degassed by standard freeze-pump-thaw procedures prior to use in the glovebox. Complex [($^{Me}NN_2$)Ni-Cl] was prepared as described previously.[1] The following starting materials were prepared according to literature procedures: 2-(3-iodopropyl)furan[2], 6-iodohexyl benzoate from 6-chlorohexyl benzoate[3] and NaI in acetone by standard method, 1-chloro-4-(2-chloroethyl)benzene[4], 9-(3-chloropropyl)-9H-carbazole[5], [(3-bromopropyl)sulfanyl]benzene[6], (3-bromopropoxy)benzene[7], tert-butyl 4-(iodomethyl)piperidine-1-carboxylate[8], lithium 3-ethylpentan-3-olate[9]. Substrates 5-phenyloxazole, 5-(4-methoxyphenyl)oxazole and 5-(4-bromophenyl)oxazole were prepared according to a general procedure[10]. Synthesis of 1-(4-(3-chloropropyl)phenyl)propan-1-one, 1-

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[1] Z. Csok, O. Vechorkin, S. B. Harkins, R. Scopelliti, X. L. Hu, *J. Am. Chem. Soc.* **2008**, *130*, 8156-8157.

[2] G. Gomez, H. Rivera, I. Garcia, L. Estevez, Y. Fall, *Tetrahedron Letters* **2005**, 46(35), 5819-5822.

[3] Ian H. Gilbert et al., *J. Med. Chem.* **2006**, 49, 4183-4195.

[4] M. Yus et al., *Journal of Organometallic Chemistry* **2002**, 663, 21-31.

[5] J. W. Hulshof et al., *Bioorg. Med. Chem.* **2006**, 14, 7213-7230.

[6] X. Zhou, R. G. Carter, *Angew. Chem., Int. Ed.* **2006**, 45(11), 1787-1790.

[7] A. Kakefuda et al., *J. Med. Chem.* **2003**, 46, 4728-4740.

[8] J. C. Sutton et al., *Bioorg. Med. Chem. Lett.* **2004**, 14, 2233–2239.

[9] H. Do, R. M. Kashif Khan, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 15185–15192.

[10] F. Besselievre, F. Mahuteau-Betzer, D. Grierson, S. Pigue, *J. Org. Chem.***2008**, *73*, 3278-3280.

(3-chloropropyl)-2-methyl-1H-indole, 2-(5-chloropentyl)-1,3-dioxane and 6-chloro-2,2-diphenylhexanenitrile was described in our previous work. [11] 2-Deuteriobenzoxazole was made following literature method.[12]

Physical methods

The ^{1}H and ^{13}C NMR spectra were recorded at 293 K on a Bruker Avance 400 spectrometer. ^{1}H NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si ($\delta = 0$ ppm). The $^{13}C\{^1H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm). GC-MS measurements were conducted on a Perkin-Elmer Clarus 600 GC equipped with Clarus 600T MS. GC measurement was conducted on a Perkin-Elmer Clarus 400 GC with a FID detector. HRESI-MS measurements were conducted at the EPFL ISIC Mass Spectrometry Service at Micro Mass QTOF Ultima. Elemental analyses were performed on a Carlo Erba EA 1110 CHN instrument at EPFL.

General procedure for coupling reactions

A mixture of [($^{Me}NN_2$)Ni-Cl] (26 mg, 0.075 mmol), CuI (14 mg, 0.075mmol), ^{t}BuOLi (168mg, 2.1mmol) or Et_3COLi (256mg, 2.1mmol), Alkyl-X (1.8 mmol) and heteroarene (1.5 mmol) was placed in a vial and 5 mL of dioxane was added. Additional NaI (45 mg, 0.3 mmol) was added for coupling of Alkyl-Br or Alkyl-Cl. The mixture was heated under N_2 during 16h at 140^{0}C.

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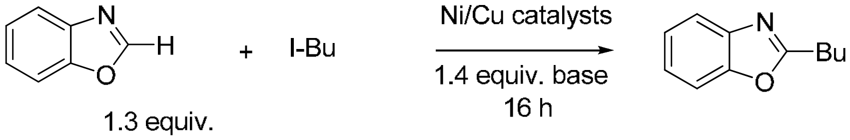
[11] O. Vechorkin, D. Barmaz, V. Proust, X. L. Hu, *J. Am. Chem. Soc.* **2009**, *131*, 12078–12079.

[12] F. Mongin et al., *J. Org. Chem.***2005**, *70*, 5190-5196.

The reaction mixture was then cooled to room temperature, quenched with 15 mL of water and 1 mL of 1M HCl, extracted with CH_2Cl_2 (3 times, 20 mL each), dried over Na_2SO_4, filtered, and finally evaporated under a reduced pressure. The residue was purified by flash chromatography on silica-gel.

Exploration of reaction conditions

Table S1. Investigation of conditions for coupling of Alkyl-I[a]



Entry	CuI	Base	Solvent	Catalyst	Temp.	Time	Yield[b]
1	7.5mol%	Cs_2CO_3	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	100	16h	12
2	7.5mol%	Cs_2CO_3	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	140	16h	20
3	7.5mol%	tBuOK	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	100	16h	22
4	7.5mol%	tBuOK	Toluene	$[(^{Me}NN_2)Ni\text{-}Cl]$	100	16h	29
5	7.5mol%	tBuONa	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	120	16h	68
6	7.5mol%	tBuONa	Toluene	$[(^{Me}NN_2)Ni\text{-}Cl]$	120	16h	67

7	**7.5mol%**	**tBuONa**	**Toluene**	**$[(^{Me}NN_2)Ni\text{-}Cl]$**	**140**	**16h**	**75**
8	7.5mol%	tBuOLi	Toluene	$[(^{Me}NN_2)Ni\text{-}Cl]$	120	16h	29
9	7.5mol%	tBuOLi	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	120	16h	76
10	**7.5mol%**	**tBuOLi**	**Dioxane**	**$[(^{Me}NN_2)Ni\text{-}Cl]$**	**140**	**16h**	**78**
11	7.5mol%	MeONa	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	140	16h	65
12	7.5mol%	K_3PO_4	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	140	16h	35
13	0 mol%	tBuONa	Toluene	$[(^{Me}NN_2)Ni\text{-}Cl]$	140	16h	54
14	0 mol%	tBuONa	Toluene	-	140	16h	0
15	0 mol%	tBuOLi	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	140	16h	18
16	7.5mol%	Et_3N	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	140	16h	0
17	7.5mol%	DBU	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	140	16h	0
18	7.5mol%	4Me-guanidine	Dioxane	$[(^{Me}NN_2)Ni\text{-}Cl]$	140	16h	0
19	7.5mol%	tBuONa	Toluene	$Ni(dme)Cl_2$	140	16h	36
20	7.5mol%	tBuONa	Toluene	$Ni(PPh_3)_2Cl_2$	140	16h	37

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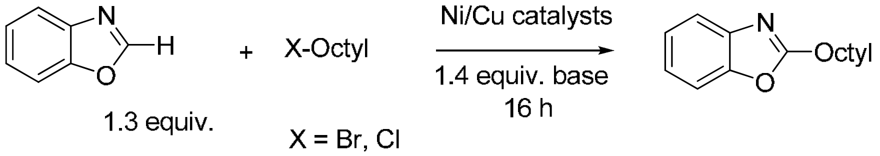
[a] Reactions were performed with 0.5 mmol of butyl-I. [b] GC yields relative to butyl iodide

Table S2. Investigation of conditions for coupling of Alkyl-Br and Alkyl-Cl[a]

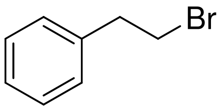


Entry	X	Additive	Base	Solvent	Temp.	Time	Yield[b]
1	Br	-	tBuONa	Toluene	140	16h	22
2	Br	0.2 equiv. NaI	tBuONa	Toluene	140	16h	35
3	Br	0.2 equiv. Bu_4NI	tBuONa	Toluene	140	16h	27
4	Br	0.2 equiv. NaI	tBuOLi	Dioxane	140	16h	85
5	Br	-	tBuOLi	Dioxane	140	16h	83
6	Cl	0.2 equiv. NaI	tBuOLi	Dioxane	140	16h	72
7	Cl	-	tBuOLi	Dioxane	140	16h	66
8	Cl	0.2 equiv. Bu_4NI	tBuOLi	Dioxane	140	16h	68
9	Cl	-	tBuONa	Toluene	140	16h	0
10	Cl	0.2 equiv. NaI	tBuONa	Toluene	140	16h	0
11	Cl	0.2 equiv. Bu_4NI	tBuONa	Toluene	140	16h	5

[a] Reactions were performed with 0.5 mmol of octyl-X, 0.65 mmol benzoxazole, 5 mol% $[(^{Me}NN_2)Ni\text{-}Cl]$ catalyst, 7.5 mol% CuI. [b] GC yields relative to octyl halides

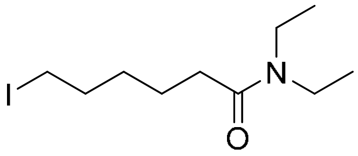
Examples of substrates that suffer from elimination:

(a)

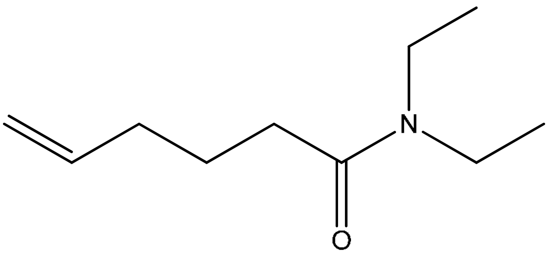


Comments: Styrene could be detected by GC (17%) in addition to 47% coupling product.

(b)



Comments: some elimination product can be isolated and characterized.



N,N-diethylhex-5-enamide (elimination product):

Eluated from the column with hexane-diethyl ether (1:1) in 71% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 5.84 – 5.68 (m, 1H), 4.95 (m, 2H), 3.33 (q, *J* = 7.1 Hz, 2H), 3.25 (q, *J* = 7.1 Hz, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 2.06 (q, *J* = 7.0 Hz, 2H), 1.71 (p, *J* = 7.4 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 171.83, 138.14, 114.90, 41.81, 39.93, 33.23, 32.09, 24.35, 14.26, 12.99.

HR-MS: calculated for ($C_{10}H_{20}NO$, M+H), 170.1545; found, 170.1550.

Mechanistic investigations

1. Hg-test experiment

Conditions: [($^{Me}NN_2$)Ni-Cl] (9 mg, 0.025 mmol), CuI (5 mg, 0.025mmol), ^{t}BuOLi (56mg, 0.7mmol), Hg (501mg, 2.5mmol), Bu-I (57.1µl, 0.5 mmol) and Benzoxazole (77mg, 0.65 mmol) were placed in a vial and 2 mL of dioxane was added. After addition the mixture was heated in absence of oxygen during 16h at 140^{0}C. After this time the reaction mixture was cooled to r.t., quenched with 10 mL of water and 1 mL of 1M HCl. The resulting solution mixture was then extracted with CH_2Cl_2 (3 times, 10 mL each), dried over Na_2SO_4, filtered, and subjected to GC analysis. 60 µL of dodecane was used as an internal standard. The yield of coupling product is 19% (instead of ca. 80% in the absence of Hg).

Comments: Hg poisoned the active catalyst, suggesting that metal particles are responsible for the catalysis.

2. Filtration experiment

Conditions: [(^{Me}NN$_2$)Ni-Cl] (9 mg, 0.025 mmol), CuI (5 mg, 0.025mmol), ^{t}BuOLi (56mg, 0.7mmol), Bu-I (57.1μl, 0.5 mmol) and Benzoxazole (77mg, 0.65 mmol) were placed in a vial and 2 mL of dioxane was added. After addition the mixture was heated in absence of oxygen during 1h at 140^{0}C. Then the reaction mixture was cooled to r.t. and filtered in absence of oxygen to a new vial. CuI (5 mg, 0.025mmol) and ^{t}BuOLi (56mg, 0.7mmol) were added again and the mixture was heated during 16h at 140^{0}C. After this time the reaction mixture was cooled to r.t., quenched with 10 mL of water and 1 mL of 1M HCl. The resulting solution mixture was then extracted with CH_2Cl_2 (3 times, 10 mL each), dried over Na_2SO_4, filtered, and subjected to GC analysis. 60 μL of dodecane was used as an internal standard. The yield of coupling product is ca. 30% (instead of ca. 80% in without filtration of heterogeneous mixture after 1 h).

Comments: Filtration of insoluble solids during the reaction decreased the yield of coupling, suggesting that the active catalyst is insoluble.

3. D_2O quenching experiment

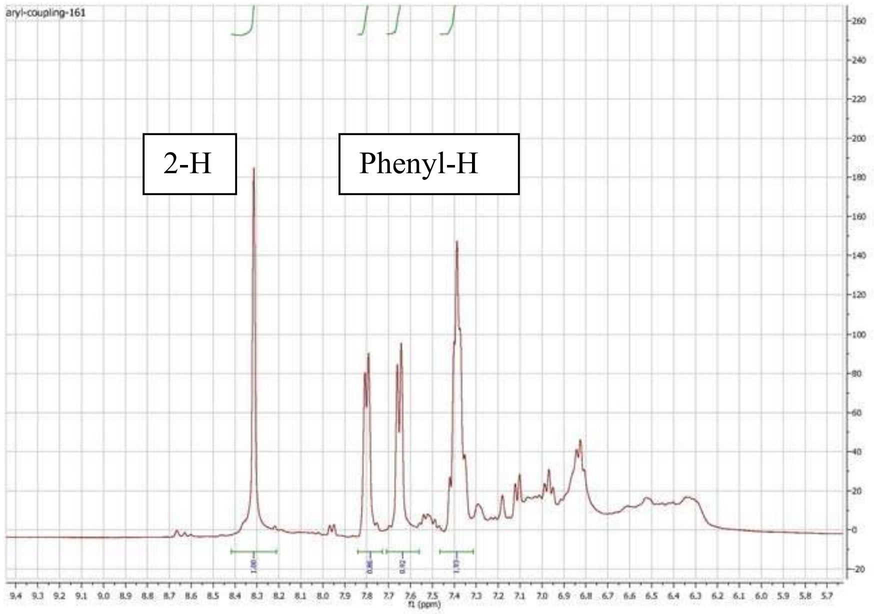
Conditions: [(^{Me}NN$_2$)Ni-Cl] (9 mg, 0.025 mmol), CuI (5 mg, 0.025mmol), ^{t}BuOLi (56mg, 0.7mmol), Bu-I (57.1μl, 0.5 mmol) and Benzoxazole (77mg, 0.65 mmol) were placed in a vial and 1.5 mL of dioxane-D8 was added. After addition the mixture was heated in absence of oxygen during 1h at 140^{0}C. After this time the reaction mixture was cooled to r.t., filtered and its NMR-spectrum was recorded. Then D_2O (91μl, 5mmol, 99.9% D) was added and the NMR-spectrum was recorded again after 15 minutes and overnight (ca. 12h).

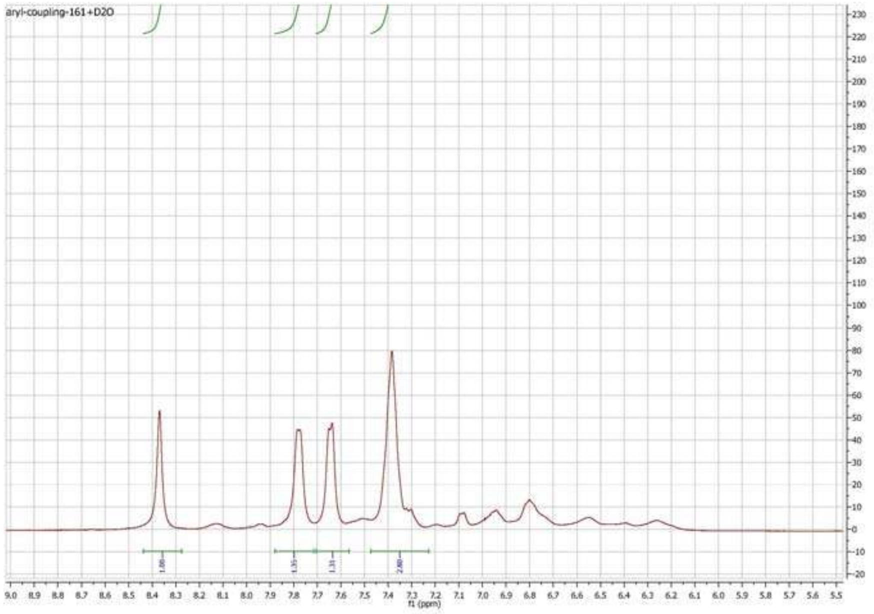
Results: 2-D-benzoxazole was produced. This can be seen from the relative intensities of the ^{1}H NMR signals corresponding to the 2-H and the protons on the phenyl ring. As shown in Figure

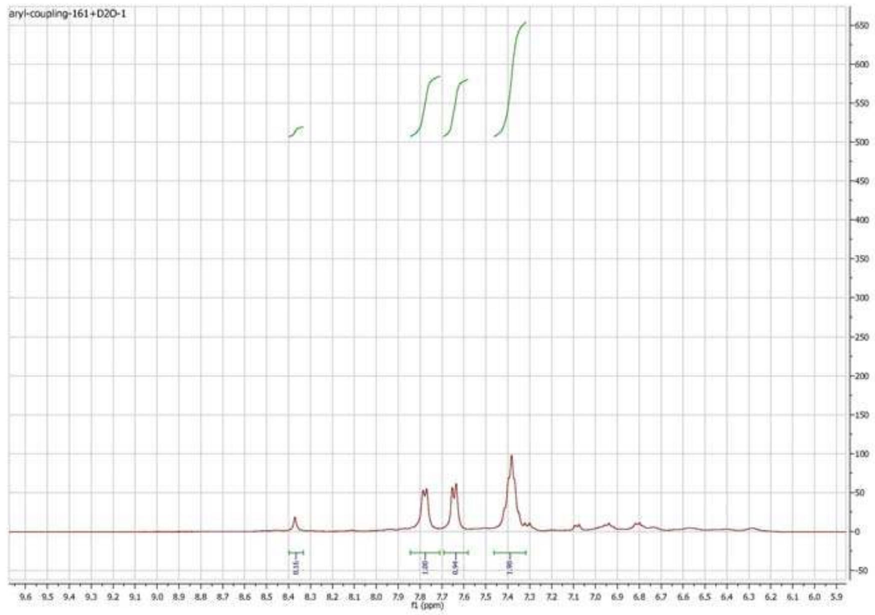
S2, after 1 hour of reaction and before D_2O quenching, the ratio of integrations is ca. 1 to 3.7, which is close to the theoretical ratio of 1 to 4 within experimental errors (Figure S1, top). 15 minute after D_2O quenching, the ratio turned into ca. 1 to 5.5 (Figure S1, middle), which was due to the formation of 2-D-benzoxazole (ca. 40% relative to unreacted starting materials). When compared to an internal standard (e.g., from proton residue of d8-dioxane), the intensity of the ^1H signal from 2-H remained the same after D_2O quenching, suggesting that 2-H-benzoxazole did not undergo H/D exchange during the 15-minute time period. This H/D exchange did occur when the same mixture was allowed to stay at room temperature overnight, as shown in Figure S1, bottom.

Comments: These results suggest that anionic azole intermediates exist during the catalysis. These intermediates might exist in the 2-metallated cyclic azole form, or in the ring-opened isocyano phenolate/enolate form, or as an equilibrium mixture. Addition of D_2O converted these anionic species back to 2-D-azoles. For a discussion of equilibrium between metallated oxazole(thiazole) derivatives and their acyclic isomers, see Hiff et al. Chem. Ber./Recueil 1997, 130, 1213-1221.

Figure S1. NMR spectra before, 15 minutes after, and 12 hours after the D2O quenching experiment as described in the previous paragraphs.


aryl-coupling-161
2-H
Phenyl-H
1.00
0.86
0.92
1.93
f1 (ppm)


aryl-coupling-161+D2O
1.00
1.35
1.31
2.80
f1 (ppm)



4. H/D isotopic effect measurement

Conditions: Identical reactions conditions including the reaction scale and time were employed. Two independent runs were carried out. To ensure a relatively high conversion in 1 hour, 20% catalyst loading was used. [(^{Me}NN$_2$)Ni-Cl] (36 mg, 0.1 mmol), CuI (5 mg, 0.025mmol), ^{t}BuOLi (56mg, 0.7mmol), Bu-I (68.6µl, 0.6 mmol) and Benzoxazole-H (60mg, 0.5 mmol) or Benzoxazole-D (60mg, 0.5 mmol, contains 89.4% D) were placed in a vial and 1.5 mL of dioxane was added. After addition the mixture was heated in absence of oxygen during 1h at 140^{0}C. After this time the reaction mixture was cooled to r.t., quenched with 10 mL of water and 1 mL of 1M HCl. The resulting solution mixture was then extracted with CH_2Cl_2 (3 times, 10 mL each), dried over Na_2SO_4, filtered, and subjected to GC analysis. 60 µL of dodecane was used as an internal standard.

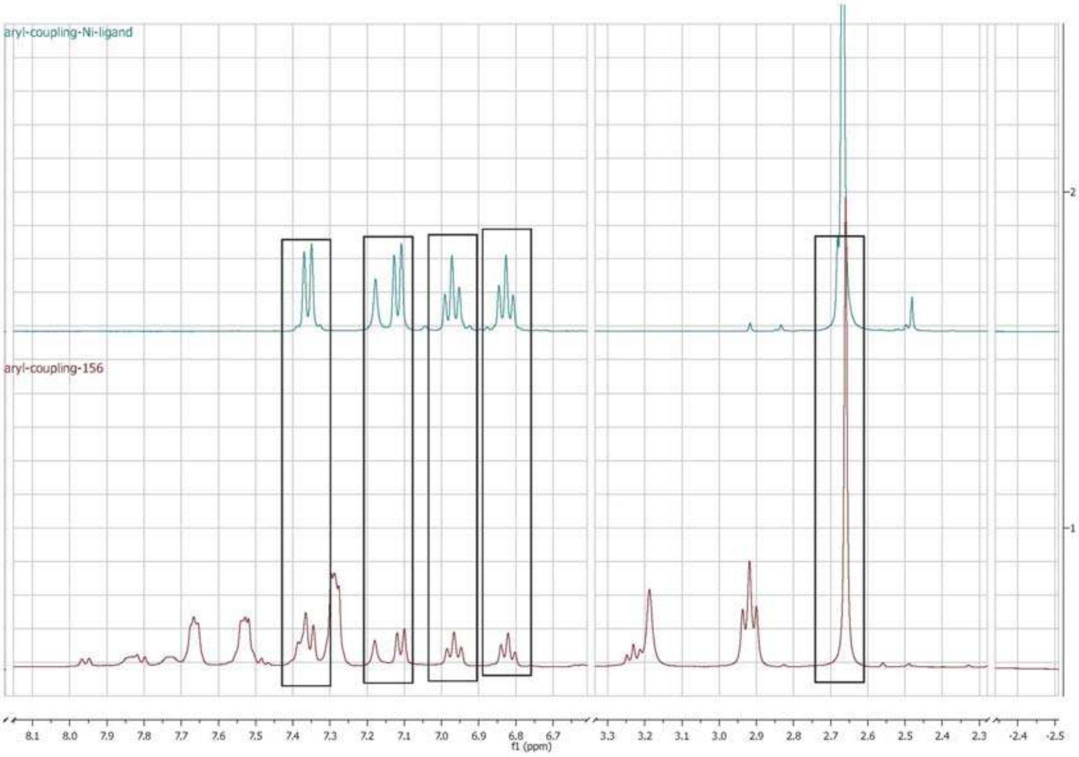
Results: Two trials were made. For the coupling of 2-H benzoxazole, the yields were 49% and 50%, respectively. For the coupling of 2-D benzoxale, the yields were 46% and 44%, respectively. The difference in yields is very small and almost no isotopic effect is detected.

5. Following the catalysis by NMR

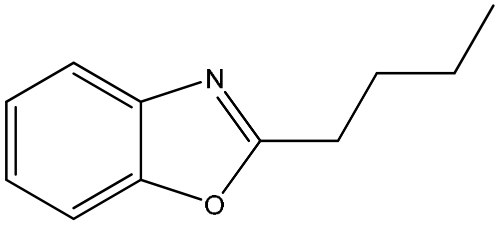
Experimental conditions: $[(^{Me}NN_2)Ni\text{-}Cl]$ (36 mg, 0.1 mmol), CuI (5 mg, 0.025mmol), ^{t}BuOLi (56mg, 0.7mmol), Bu-I (57.1µl, 0.5 mmol) and Benzoxazole (77mg, 0.65 mmol) were placed in a vial and 1.5 mL of dioxane-D8 was added. After addition the mixture was heated in absence of oxygen during 1h or 16h at 140^0C. After this time the reaction mixture was cooled to r.t., filtered and its NMR-spectrum was measured.

Results: free ligand $H^{Me}NN_2$ was the only ligand-containing species observed after 1h (ca. 50% conversion) and after completion of reaction (16h).

Figure S2. Comparison of NMR spectra of ligand $H^{Me}NN_2$ (top) and catalysis mixture (bottom).



Detail descriptions for products



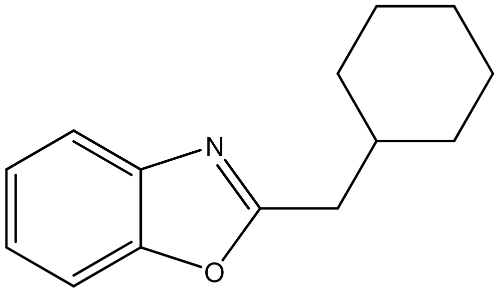
2-butylbenzo[d]oxazole:

Eluated from the column with hexane-diethyl ether (20:1) in 78% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.67 (m, 1H), 7.47 (m, 1H), 7.29 (m, 2H), 2.93 (t, J = 7.6 Hz, 2H), 1.87 (m, 2H), 1.46 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 167.3, 150.7, 141.3, 124.3, 123.9, 119.4, 110.2, 28.8, 28.3, 22.2, 13.6.

HR-MS: calculated for ($C_{11}H_{14}NO$, M+H), 176.1075; found, 176.1067.



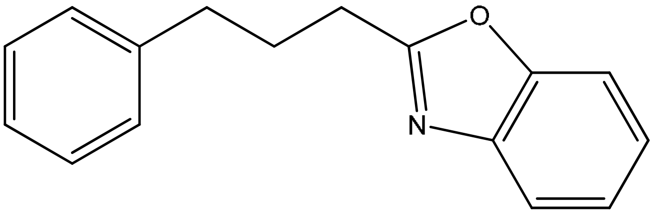
2-(cyclohexylmethyl)benzo[d]oxazole (table 1, entry 1):

Eluated from the column with hexane-diethyl ether (10:1) in 79% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.67 (m, 1H), 7.47 (m, 1H), 7.29 (m, 2H), 2.81 (d, *J* = 7.0 Hz, 2H), 1.97 (m, 1H), 1.72 (m, 5H), 1.15 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 150.7, 141.3, 124.2, 123.9, 119.4, 110.1, 36.5, 36.2, 33.0, 26.0, 25.9.

HR-MS: calculated for ($C_{14}H_{18}NO$, M+H), 216.1388; found, 216.1386.



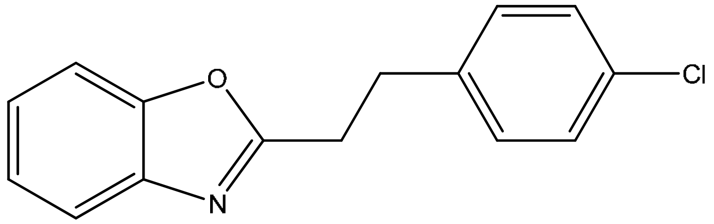
2-(3-phenylpropyl)benzo[d]oxazole (table 1, entry 2):

Eluated from the column with hexane-diethyl ether (10:1) in 70% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.70 (m, 1H), 7.49 (m, 1H), 7.26 (m, 7H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 7.3 Hz, 2H), 2.24 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.9, 150.7, 141.1, 141.0, 128.4, 128.3, 126.0, 124.4, 124.0, 119.4, 110.2, 35.0, 28.1, 27.9.

HR-MS: calculated for ($C_{16}H_{16}NO$, M+H), 238.1232; found, 238.1241.



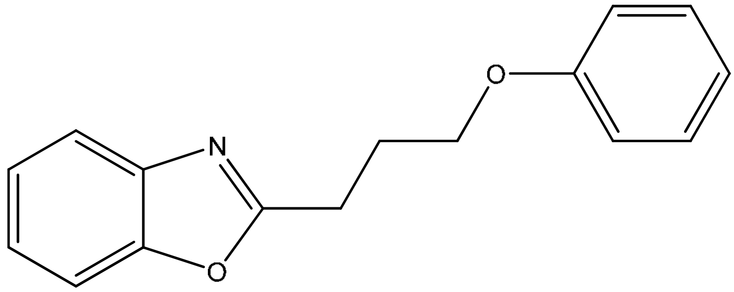
2-(4-chlorophenethyl)benzo[d]oxazole (table 1, entry 3):

Eluated from the column with hexane-diethyl ether (10:1) in 75% yield as a white solid:

^{1}**H NMR** (400MHz, $CDCl_3$): 7.68 (m 1H), 7.48 (m 1H), 7.31 (m 2H), 7.25 (m 2H), 7.17 (m 2H), 3.20 (s 4H).

^{13}**C NMR** (100 MHz, $CDCl_3$): 165.7, 150.6, 141.1, 138.4, 132.2, 129.5, 128.6, 124.5, 124.1, 119.5, 110.2, 32.0, 30.2.

HR-MS: calculated for ($C_{15}H_{13}NOCl$, M+H), 258.0686; found, 258.0695.



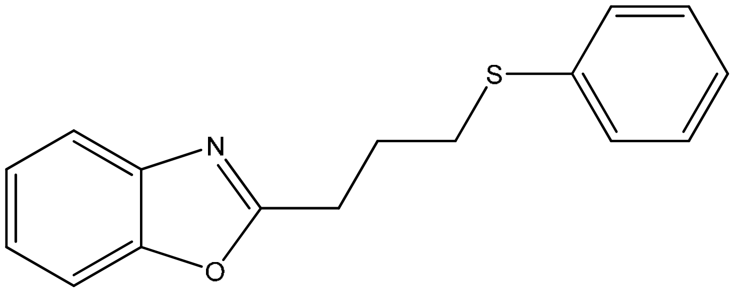
2-(3-phenoxypropyl)benzo[d]oxazole (table 1, entry 4):

Eluated from the column with hexane-diethyl ether (4:1) in 84% yield as a slightly yellow liquid:

^{1}**H NMR** (400MHz, $CDCl_3$): 7.70 (m, 1H), 7.50 (m, 1H), 7.28 (m, 4H), 6.92 (m, 3H), 4.12 (t, J = 5.9 Hz, 2H), 3.17 (t, J = 7.3 Hz, 2H), 2.40 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 158.6, 150.7, 141.2, 129.4, 124.5, 124.0, 120.7, 119.5, 114.4, 110.2, 66.3, 26.3, 25.3.

HR-MS: calculated for ($C_{16}H_{16}NO_2$, M+H), 254.1181; found, 254.1169.



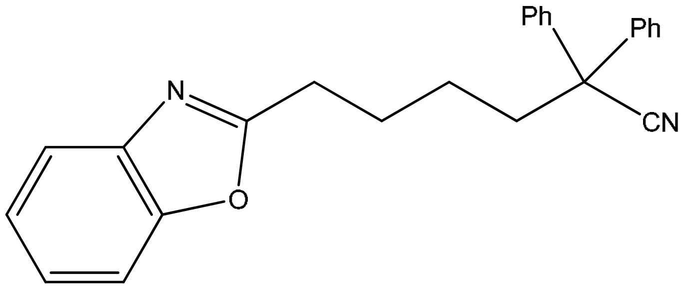
2-(3-(phenylthio)propyl)benzo[d]oxazole (table 1, entry 5):

Eluated from the column with hexane-diethyl ether (4:1) in 65% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.68 (m, 1H), 7.48 (m, 1H), 7.31 (m, 6H), 7.18 (m, 1H), 3.08 (q, J = 7.3 Hz, 4H), 2.23 (quint, J = 7.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.0, 150.6, 141.1, 135.7, 129.3, 128.8, 126.0, 124.5, 124.0, 119.4, 110.2, 32.8, 27.2, 25.9.

HR-MS: calculated for ($C_{16}H_{16}NOS$, M+H), 270.0953; found, 270.0953.



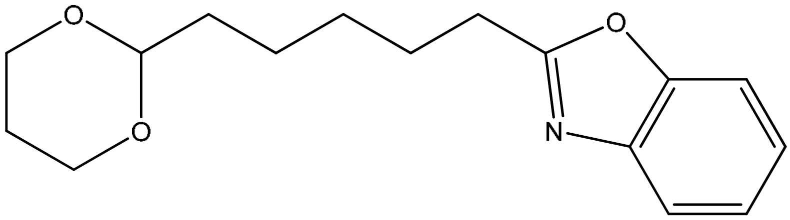
6-(benzo[d]oxazol-2-yl)-2,2-diphenylhexanenitrile (table 1, entry 6):

Eluated from the column with hexane-diethyl ether (2:1) in 56% yield as a yellow oil:

^{1}H NMR (400MHz, CDCl$_3$): 7.67 (m, 1H), 7.37 (m, 13H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.46 (m, 2H), 1.98 (m, 2H), 1.60 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): 166.4, 150.6, 141.1, 139.9, 128.8, 127.8, 126.7, 124.4, 124.0, 122.2, 119.4, 110.2, 51.5, 39.1, 28.1, 26.4, 25.1.

HR-MS: calculated for ($C_{25}H_{23}N_2O$, M+H), 367.1810; found, 367.1794.



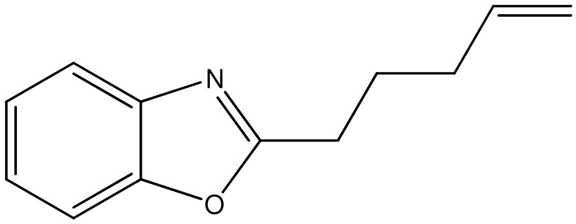
2-(5-(1,3-dioxan-2-yl)pentyl)benzo[d]oxazole (table 1, entry 7):

Eluated from the column with hexane-diethyl ether (2:1) in 86% yield as a yellow oil:

^{1}H NMR (400MHz, CDCl$_3$): 7.65 (m, 1H), 7.46 (m, 1H), 7.28 (m, 2H), 4.49 (t, *J* = 5.0 Hz, 1H), 4.07 (dd, J_1 = 11.7 Hz, J_2 = 5.0 Hz, 2H), 3.73 (m, 2H), 2.92 (t, *J* = 7.9 Hz, 2H), 2.06 (m, 1H), 1.88 (m, 2H), 1.59 (m, 2H), 1.40 (m, 5H).

^{13}C NMR (100 MHz, CDCl$_3$): 167.1, 150.7, 141.3, 124.3, 123.9, 119.4, 110.1, 102.1, 66.8, 34.9, 28.9, 28.4, 26.6, 25.7, 23.5.

HR-MS: calculated for ($C_{16}H_{22}NO_3$, M+H), 276.1600; found, 276.1601.



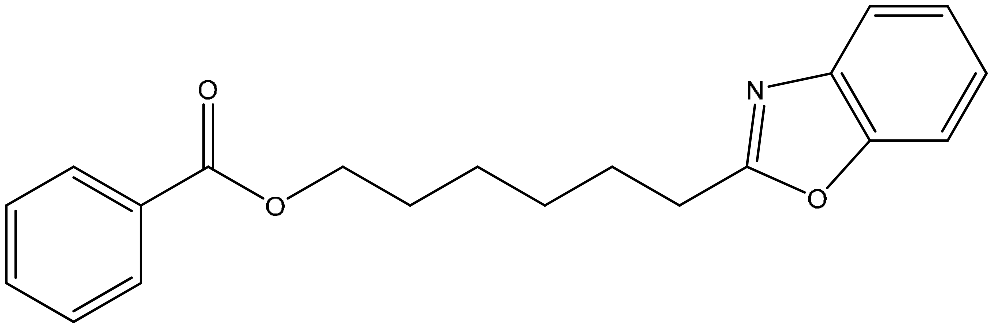
2-(pent-4-enyl)benzo[d]oxazole (table 1, entry 8):

Eluated from the column with hexane-diethyl ether (10:1) in 70% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, CDCl$_3$): 7.67 (m, 1H), 7.47 (m, 1H), 7.28 (m, 2H), 5.82 (m, 1H), 5.04 (m, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.20 (q, *J* = 7.0 Hz, 2H), 1.99 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): 166.9, 150.7, 141.3, 137.3, 124.3, 123.9, 119.4, 115.5, 110.1, 32.9, 27.8, 25.7.

HR-MS: calculated for ($C_{12}H_{14}NO$, M+H), 188.1075; found, 188.1083.



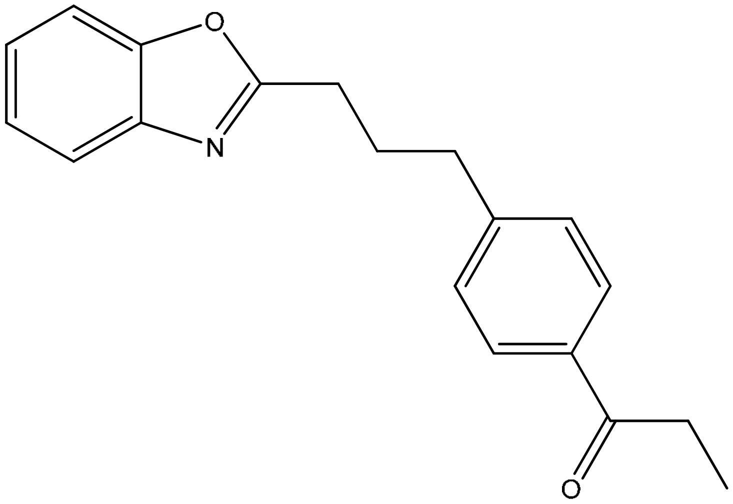
6-(benzo[d]oxazol-2-yl)hexyl benzoate (table 1, entry 9):

Eluated from the column with hexane-diethyl ether (3:1) in 71% yield as a yellow oil:

^{1}H NMR (400MHz, $CDCl_3$): 8.03 (d, *J* = 7.6 Hz, 2H), 7.67 (m, 1H), 7.54 (t, *J* = 6.7 Hz, 1H), 7.44 (m, 3H), 7.29 (m, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 1.93 (m, 2H), 1.79 (m, 2H), 1.54 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 167.0, 166.5, 150.7, 141.3, 132.7, 130.3, 129.4, 128.2, 124.3, 124.0, 119.4, 110.2, 64.8, 28.7, 28.5, 28.4, 26.5, 25.6.

HR-MS: calculated for ($C_{20}H_{22}NO_3$, M+H), 324.1600; found, 324.1588.



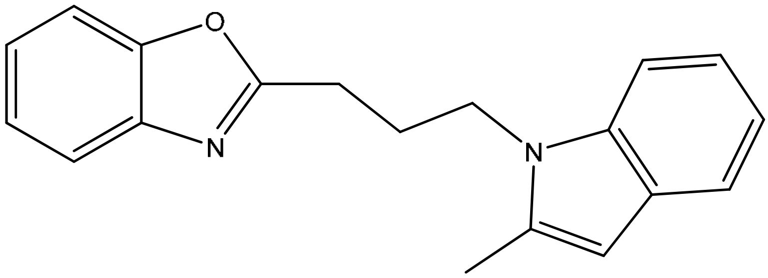
1-(4-(3-(benzo[d]oxazol-2-yl)propyl)phenyl)propan-1-one (table 1, entry 10):

Eluated from the column with hexane-diethyl ether (3:1) in 44% yield as a yellow oil:

^{1}H NMR (400MHz, $CDCl_3$): 7.89 (d, *J* = 8.2 Hz, 2H), 7.67 (m, 1H), 7.47 (m, 1H), 7.30 (m, 4H), 2.97 (m, 4H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.25 (m, 2H), 1.22 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 200.4, 166.4, 150.7, 146.5, 141.2, 135.0, 128.6, 128.2, 124.5, 124.1, 119.5, 110.2, 35.0, 31.6, 27.8, 27.7, 8.2.

HR-MS: calculated for ($C_{19}H_{20}NO_2$, M+H), 294.1494; found, 294.1483.



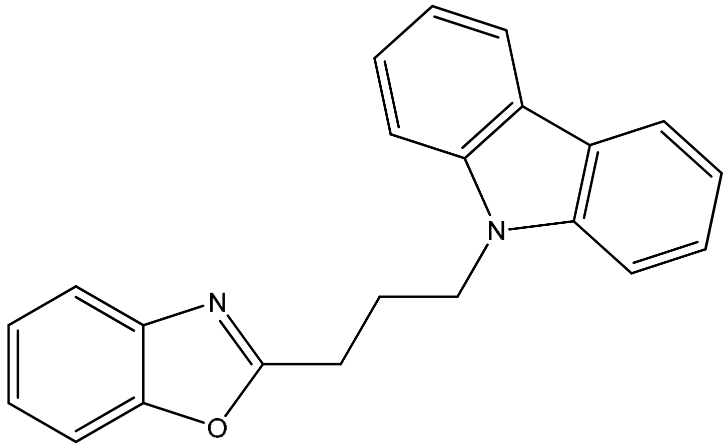
2-(3-(2-methyl-1H-indol-1-yl)propyl)benzo[d]oxazole (table 1, entry 11):

Eluated from the column with hexane-diethyl ether (2:1) in 74% yield as a yellow oil:

^{1}H NMR (400MHz, $CDCl_3$): 7.74 (m, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (m, 1H), 7.34 (m, 3H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.11 (m, 1H), 6.29 (s, 1H), 4.27 (t, *J* = 7.3 Hz, 2H), 2.97 (t, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 2.41 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 150.6, 141.1, 136.5, 136.1, 128.0, 124.6, 124.1, 120.5, 119.6, 119.5, 119.2, 110.2, 108.8, 100.2, 41.9, 26.6, 25.6, 12.6.

HR-MS: calculated for ($C_{19}H_{19}N_2O$, M+H), 291.1497; found, 291.1483.



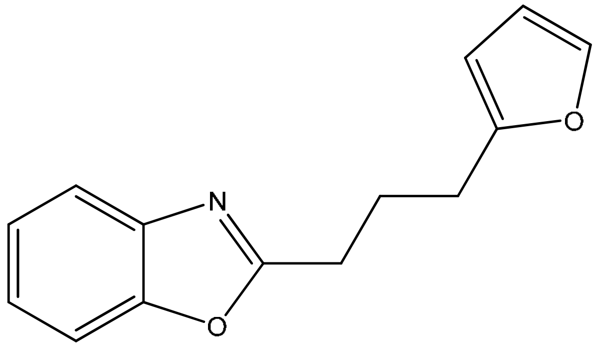
2-(3-(9H-carbazol-9-yl)propyl)benzo[d]oxazole (table 1, entry 12):

Eluated from the column with hexane-diethyl ether (10:1 to 3:1) in 75% yield as a yellow solid:

^{1}H NMR (400MHz, $CDCl_3$): 8.11 (d, *J* = 7.6 Hz, 2H), 7.73 (m, 1H), 7.44 (m, 5H), 7.29 (m, 4H), 4.54 (t, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.53 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 165.9, 150.6, 140.9, 140.2, 125.7, 124.7, 124.2, 122.9, 120.3, 119.5, 118.9, 110.2, 108.5, 41.8, 25.8, 25.6.

HR-MS: calculated for ($C_{22}H_{19}N_2O$, M+H), 327.1497; found, 327.1497.



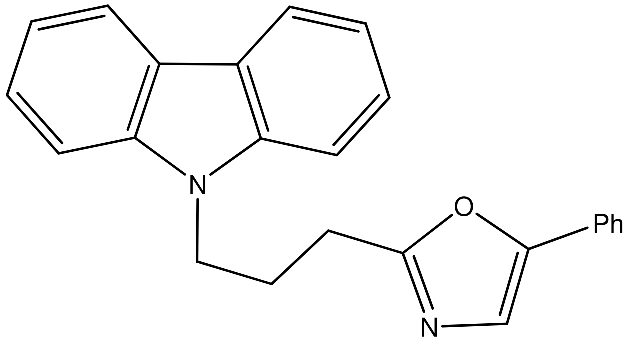
2-(3-(furan-2-yl)propyl)benzo[d]oxazole (table 1, entry 13):

Eluated from the column with hexane-diethyl ether (10:1) in 73% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.68 (m, 1H), 7.48 (m, 1H), 7.30 (m, 3H), 6.28 (m, 1H), 6.05 (m, 1H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.80 (t, *J* = 7.0 Hz, 2H), 2.25 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 154.7, 150.7, 141.0, 124.5, 124.1, 119.4, 110.2, 110.0, 105.4, 27.8, 27.2, 25.0.

HR-MS: calculated for ($C_{14}H_{14}NO_2$, M+H), 228.1024; found, 228.1022.



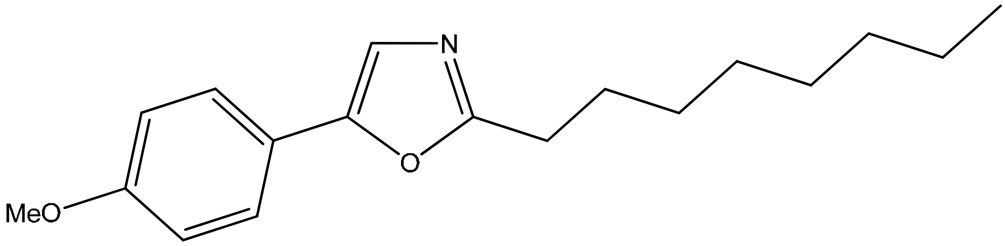
2-(3-(9H-carbazol-9-yl)propyl)-5-phenyloxazole (table 2, entry 1):

Eluated from the column with hexane-diethyl ether (1:1) in 74% yield as a yellow solid:

^{1}H NMR (400MHz, $CDCl_3$): 8.18 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.49 (m, 6H), 7.34 (m, 4H), 4.49 (t, *J* = 6.7 Hz, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 2.47 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 163.0, 151.0, 140.1, 128.7, 128.0, 127.8, 125.6, 123.8, 122.7, 121.6, 120.2, 118.8, 108.4, 41.6, 25.6, 25.3.

HR-MS: calculated for ($C_{24}H_{21}N_2O$, M+H), 353.1654; found, 353.1653.



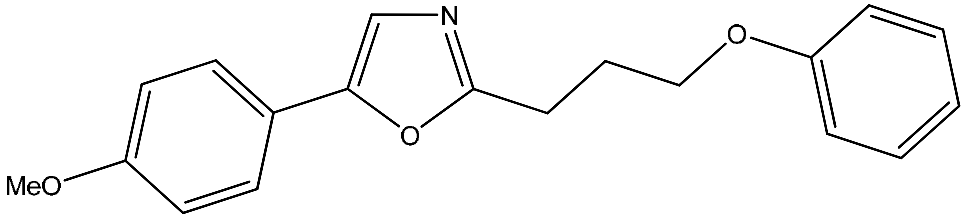
5-(4-methoxyphenyl)-2-octyloxazole (table 2, entry 2):

Eluated from the column with hexane-diethyl ether (2:1) in 86% yield as a yellow solid:

^{1}H NMR (400MHz, $CDCl_3$): 7.51 (d, J = 8.8 Hz, 2H), 7.07 (s, 1H), 6.91 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H), 2.78 (t, J = 7.6 Hz, 2H), 1.79 (m, 2H), 1.22-1.42 (m, 10H), 0.86 (t, J = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 163.9, 159.3, 150.6, 125.3, 121.0, 120.0, 114.1, 55.1, 31.7, 29.1, 29.06, 29.05, 28.1, 26.9, 22.5, 14.0.

HR-MS: calculated for ($C_{18}H_{26}NO_2$, M+H), 288.1964; found, 288.1977.



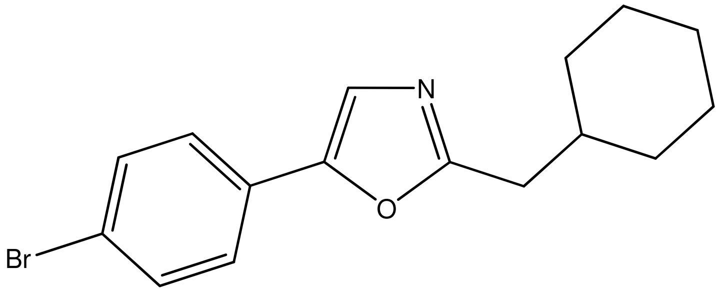
5-(4-methoxyphenyl)-2-(3-phenoxypropyl)oxazole (table 2, entry 3):

Eluated from the column with hexane-diethyl ether (1:1) in 81% yield as a yellow solid:

^{1}H NMR (400MHz, $CDCl_3$): 7.52 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.11 (s, 1H), 6.93 (m, 5H), 4.08 (t, *J* = 6.2 Hz, 2H), 3.82 (s, 3H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.31 (quint, *J* = 7.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 162.9, 159.4, 158.7, 150.9, 129.3, 125.4, 120.9, 120.6, 120.1, 114.3, 114.1, 66.3, 55.2, 26.6, 24.8.

HR-MS: calculated for ($C_{19}H_{20}NO_3$, M+H), 310.1443; found, 310.1427.



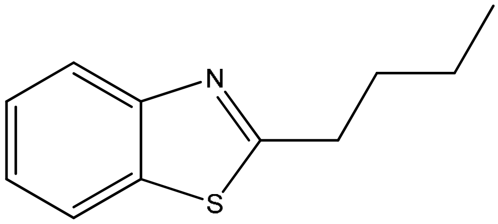
5-(4-bromophenyl)-2-(cyclohexylmethyl)oxazole (table 2, entry 4):

Eluated from the column with hexane-diethyl ether (3:1) in 76% yield as a dark red oil:

^{1}H NMR (400MHz, $CDCl_3$): 7.52 (m, 2H), 7.46 (m, 2H), 7.23 (s, 1H), 2.69 (d, *J* = 7.0 Hz, 2H), 1.75 (m, 6H), 1.24 (m, 3H), 1.04 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 164.3, 149.8, 131.9, 127.1, 125.3, 122.2, 121.7, 36.7, 35.8, 32.9, 26.1, 26.0.

HR-MS: calculated for ($C_{16}H_{19}NOBr$, M+H), 320.0650 and 322.0631; found, 320.0640 and 322.0630.



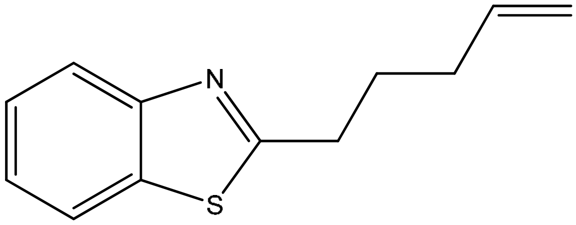
2-butylbenzo[d]thiazole (table 2, entry 5):

Eluated from the column with hexane-diethyl ether (15:1) in 79% yield as a yellow oil:

^{1}H NMR (400MHz, CDCl$_3$): 7.97 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.44 (m, 1H), 7.34 (m, 1H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.87 (m, 2H), 1.47 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): 172.3, 153.2, 135.1, 125.7, 124.5, 122.4, 121.4, 34.0, 31.7, 22.2, 13.7.

HR-MS: calculated for ($C_{11}H_{14}NS$, M+H), 192.0847; found, 192.0844.



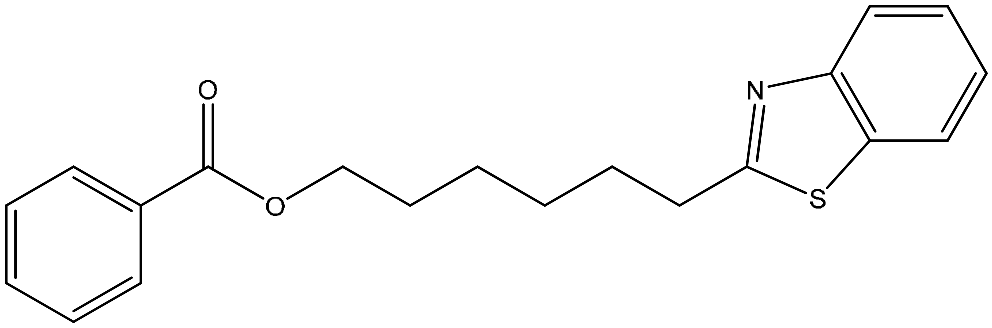
2-(pent-4-enyl)benzo[d]thiazole (table 2, entry 6):

Eluated from the column with hexane-diethyl ether (10:1) in 74% yield as a yellow oil:

^{1}H NMR (400MHz, CDCl$_3$): 7.97 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.33 (m, 1H), 5.82 (m, 1H), 5.05 (m, 2H), 3.11 (m, 2H), 2.20 (q, *J* = 7.0 Hz, 2H), 1.98 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 153.1, 137.4, 135.0, 125.7, 124.5, 122.4, 121.3, 115.4, 33.5, 32.9, 28.6.

HR-MS: calculated for ($C_{12}H_{14}NS$, M+H), 204.0847; found, 204.0842.



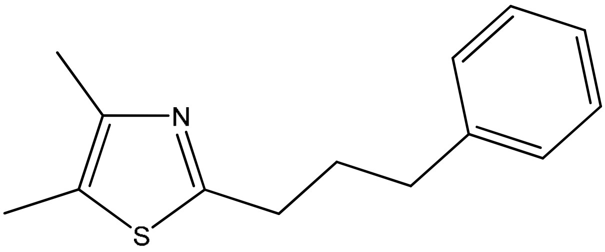
6-(benzo[d]thiazol-2-yl)hexyl benzoate (table 2, entry 7):

Eluated from the column with hexane-diethyl ether (4:1) in 72% yield as a yellow solid:

^{1}H NMR (400MHz, $CDCl_3$): 8.04 (d, J = 7.3 Hz, 2H), 7.97 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.55 (t,J = 7.0 Hz, 1H), 7.44 (m, 3H), 7.34 (m, 1H), 4.32 (t, J = 6.5 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H), 1.92 (m, 2H), 1.79 (m, 2H), 1.53 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 172.0, 166.6, 153.1, 135.0, 132.7, 130.3, 129.4, 128.2, 125.8, 124.6, 122.4, 121.4, 64.8, 34.1, 29.5, 28.7, 28.5, 25.7.

HR-MS: calculated for ($C_{20}H_{22}NO_2S$, M+H), 340.1371; found, 340.1369.



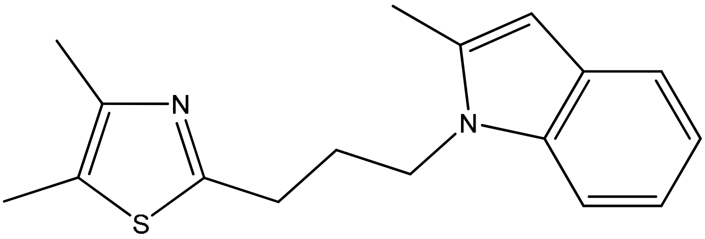
4,5-dimethyl-2-(3-phenylpropyl)thiazole (table 2, entry 8):

Eluated from the column with hexane-diethyl ether (5:1) in 76% yield as a yellow liquid:

^{1}H NMR (400MHz, CDCl$_3$): 7.28 (m, 2H), 7.19 (d, *J* = 7.0 Hz, 3H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 6H), 2.07 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): 166.0, 147.1, 141.4, 128.3, 128.2, 125.7, 124.8, 35.1, 32.7, 31.6, 14.5, 11.1.

HR-MS: calculated for ($C_{14}H_{18}NS$, M+H), 232.1160; found, 232.1161.



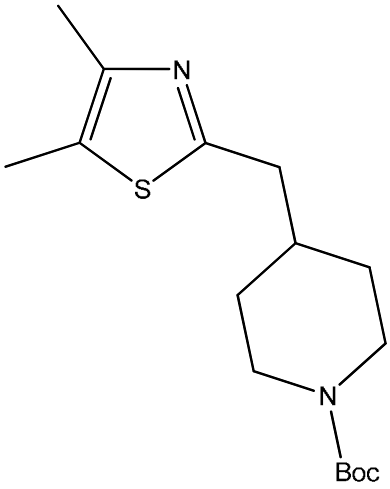
4,5-dimethyl-2-(3-(2-methyl-1H-indol-1-yl)propyl)thiazole (table 2, entry 9):

Eluated from the column with hexane-diethyl ether (2:1) in 85% yield as a yellow oil:

^{1}H NMR (400MHz, CDCl$_3$): 7.53 (d, *J* = 7.6 Hz, 1H), 7.27 (m, 1H), 7.14 (t, *J* = 6.7 Hz, 1H), 7.07 (m, 1H), 6.25 (s, 1H), 4.17 (t, *J* = 7.3 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.32 (m, 6H), 2.22 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): 164.7, 147.4, 136.5, 136.1, 128.0, 125.2, 120.3, 119.6, 119.1, 108.9, 100.0, 42.2, 30.5, 29.9, 14.5, 12.6, 11.2.

HR-MS: calculated for ($C_{17}H_{21}N_2S$, M+H), 285.1425; found, 285.1411.



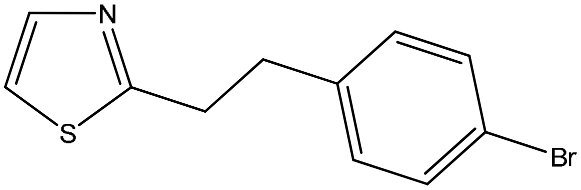
tert-butyl 4-((4,5-dimethylthiazol-2-yl)methyl)piperidine-1-carboxylate (table 2, entry 10):

Eluated from the column with hexane-diethyl ether (1:1) in 79% yield as a yellow oil:

^{1}H NMR (400MHz, CDCl$_3$): 4.06 (br., 2H), 2.78 (d, *J* = 7.0 Hz, 2H), 2.65 (br., 2H), 2.28 (m, 6H), 1.86 (m, 1H), 1.68 (d, *J* = 12.9 Hz, 2H), 1.43 (s, 9H), 1.21 (m, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): 163.9, 154.7, 147.5, 125.1, 79.2, 43.6, 39.8, 37.2, 31.7, 28.3, 14.6, 11.1.

HR-MS: calculated for ($C_{16}H_{27}N_2O_2S$, M+H), 311.1793; found, 311.1798.



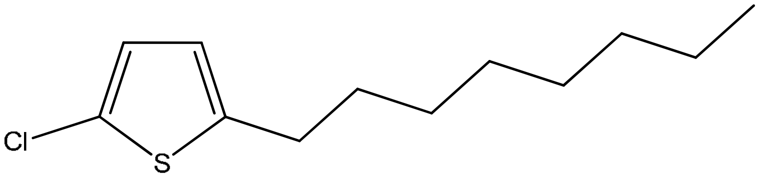
2-(4-bromophenethyl)thiazole (table 2, entry 11):

Eluated from the column with hexane-diethyl ether (3:1) in 60% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.69 (d, *J* = 3.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 3.2 Hz, 1H), 7.07 (d, *J*= 8.2 Hz, 2H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.08 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 169.4, 142.3, 139.2, 131.5, 130.1, 120.1, 118.2, 35.2, 34.6.

HR-MS: calculated for ($C_{11}H_{11}NSBr$, M+H), 267.9796 and 269.9775; found, 267.9779 and 269.9764.



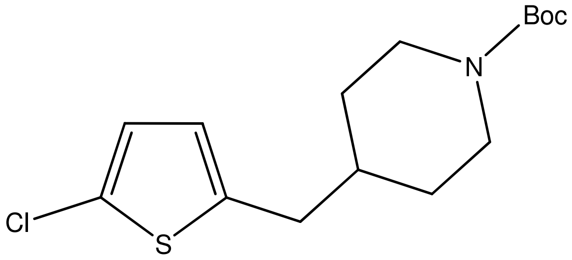
2-chloro-5-octylthiophene (table 2, entry 12):

Eluated from the column with hexane-diethyl ether (30:1) in 81% yield as a colorless oil:

^{1}H NMR (400MHz, $CDCl_3$): 6.70 (d, *J* = 3.8 Hz, 1H), 6.53 (d, *J* = 3.8 Hz, 1H), 2.71 (t, *J* = 7.3 Hz, 2H), 1.62 (m, 2H), 1.30 (m, 10H), 0.88 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 144.7, 126.4, 125.5, 123.1, 31.8, 31.4, 30.3, 29.2, 29.1, 28.9, 22.6, 14.0.

Elemental analysis: Anal. Calcd for $C_{12}H_{19}ClS$: C, 62.45; H, 8.30. Found: C, 62.25; H, 8.43.



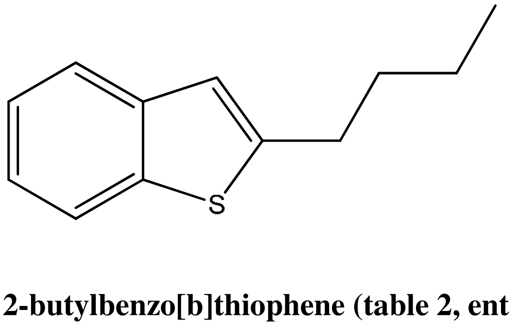
tert-butyl 4-((5-chlorothiophen-2-yl)methyl)piperidine-1-carboxylate (table 2, entry 13):

Eluated from the column with hexane-diethyl ether (10:1) in 62% yield as a colorless oil:

^{1}H NMR (400MHz, $CDCl_3$): 6.71 (d, *J* = 3.5 Hz, 1H), 6.52 (d, *J* = 3.2 Hz, 1H), 4.10 (br., 2H), 2.65 (m, 4H), 1.70 (m, 3H), 1.45 (s, 9H), 1.11 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 154.7, 141.6, 125.6, 124.5, 79.3, 43.1, 38.3, 37.2, 31.7, 28.4.

HR-MS: calculated for ($C_{15}H_{23}ClNO_2S$, M+H), 316.1138; found, 316.1128.



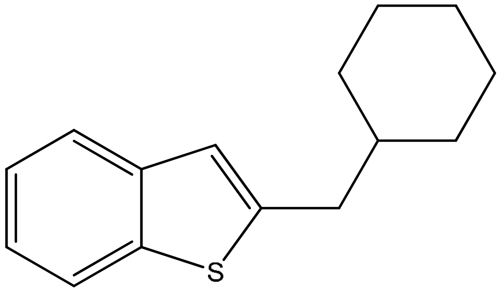
2-butylbenzo[b]thiophene (table 2, entry 14):

Eluated from the column with hexane in 78% yield as a colorless liquid:

^{1}**H NMR** (400MHz, $CDCl_3$): 7.80 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.35 (m, 2H), 7.28 (m, 1H), 2.94 (t, *J* = 7.3 Hz, 2H), 1.78 (m, 2H), 1.47 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H).

^{13}**C NMR** (100 MHz, $CDCl_3$): 146.7, 140.1, 139.2, 123.9, 123.2, 122.5, 122.0, 120.3, 33.1, 30.4, 22.1, 13.8.

Elemental analysis: Anal. Calcd for $C_{12}H_{14}S$: C, 75.45; H, 7.42. Found: C, 75.14; H, 7.43.



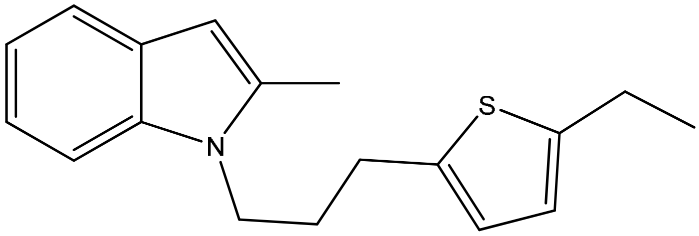
2-(cyclohexylmethyl)benzo[b]thiophene (table 2, entry 15):

Eluated from the column with hexane-diethyl ether (100:1) in 72% yield as a colorless liquid:

^{1}**H NMR** (400MHz, $CDCl_3$): 7.77 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.28 (m, 2H), 6.98 (s, 1H), 2.78 (d, *J* = 7.0 Hz, 2H), 1.73 (m, 6H), 1.23 (m, 3H), 1.00 (m, 2H).

^{13}**C NMR** (100 MHz, $CDCl_3$): 145.2, 140.1, 139.4, 123.9, 123.2, 122.5, 122.0, 121.3, 39.7, 38.6, 33.0, 26.4, 26.1.

Elemental analysis: Anal. Calcd for $C_{15}H_{18}S$: C, 78.21; H, 7.88. Found: C, 77.94; H, 7.59.



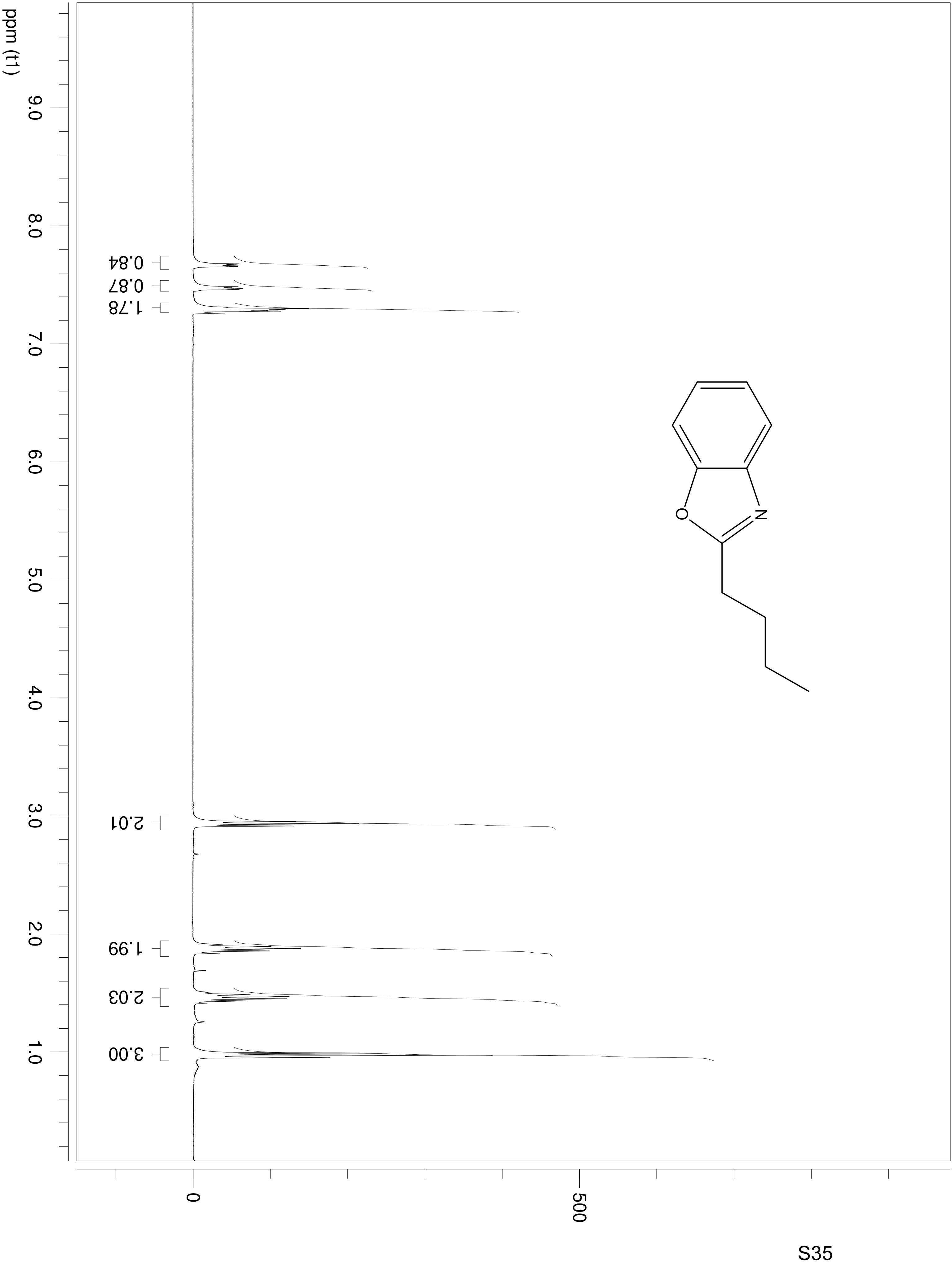
1-(3-(5-ethylthiophen-2-yl)propyl)-2-methyl-1H-indole (table 2, entry 16):

Eluated from the column with hexane-diethyl ether (100:1) in 66% yield as a colorless liquid:

^{1}H NMR (400MHz, CDCl$_3$): 7.53 (d, *J* = 7.3 Hz, 1H), 7.24 (m, 1H), 7.14 (t, *J* = 7.0 Hz, 1H), 7.07 (m, 1H), 6.61 (s, 2H), 6.25 (s, 1H), 4.12 (t, *J* = 7.3 Hz, 2H), 2.83 (m, 4H), 2.41 (s, 3H), 2.13 (m, 2H), 1.30 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): 145.4, 141.1, 136.5, 136.2, 128.0, 123.9, 122.7, 120.3, 119.6, 119.1, 108.9, 99.9, 42.3, 31.6, 27.5, 23.4, 15.9, 12.7.

HR-MS: calculated for ($C_{18}H_{22}NS$, M+H), 284.1473; found, 284.1468.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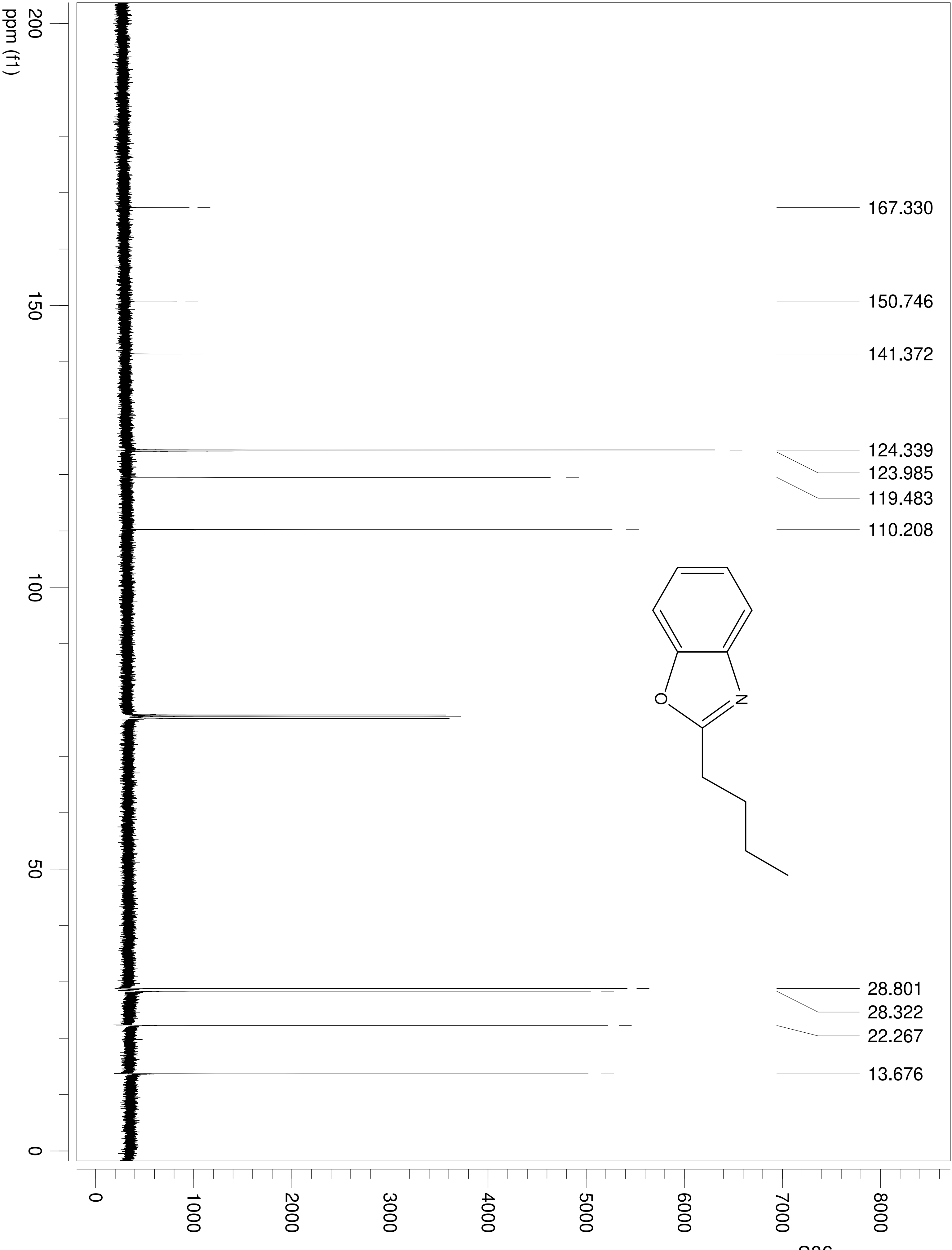
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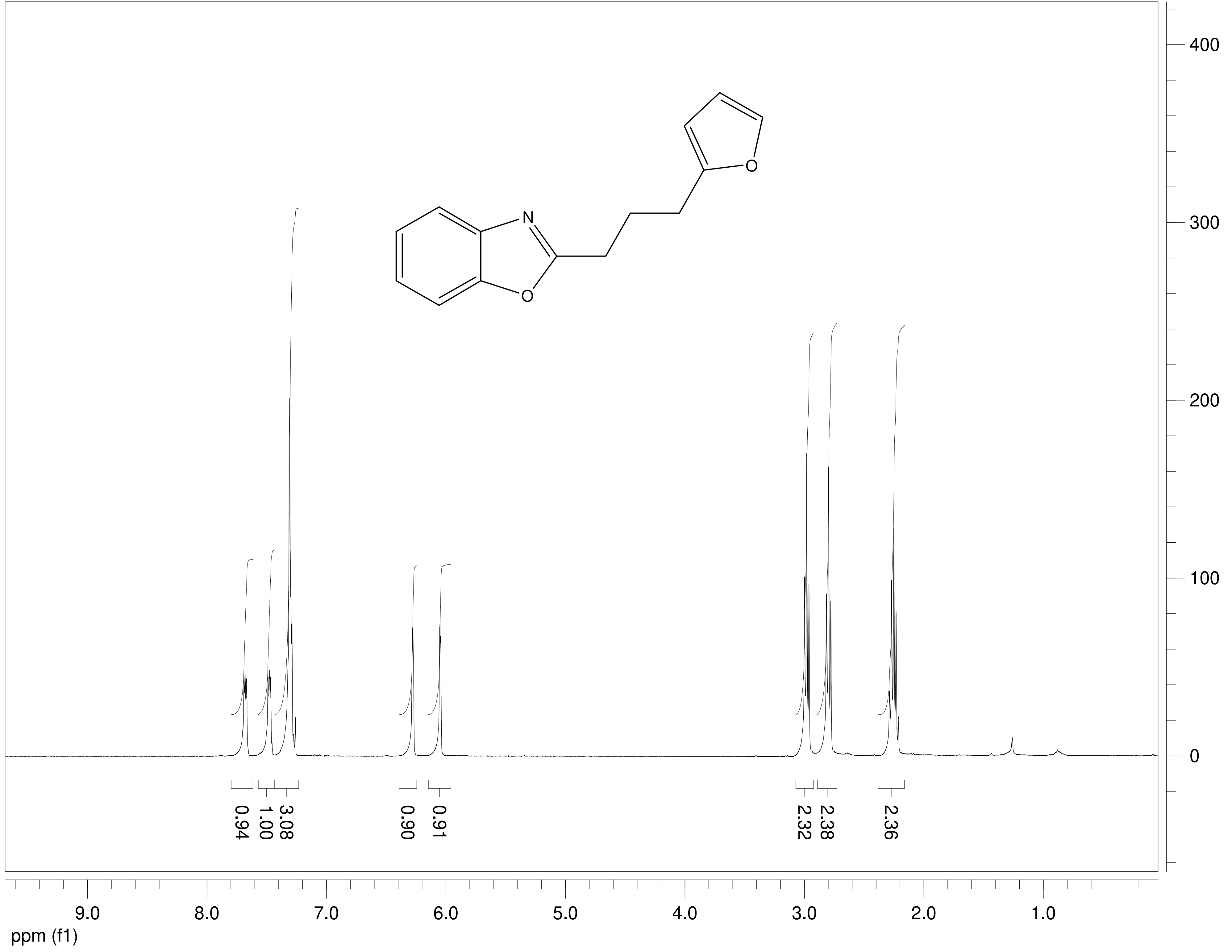
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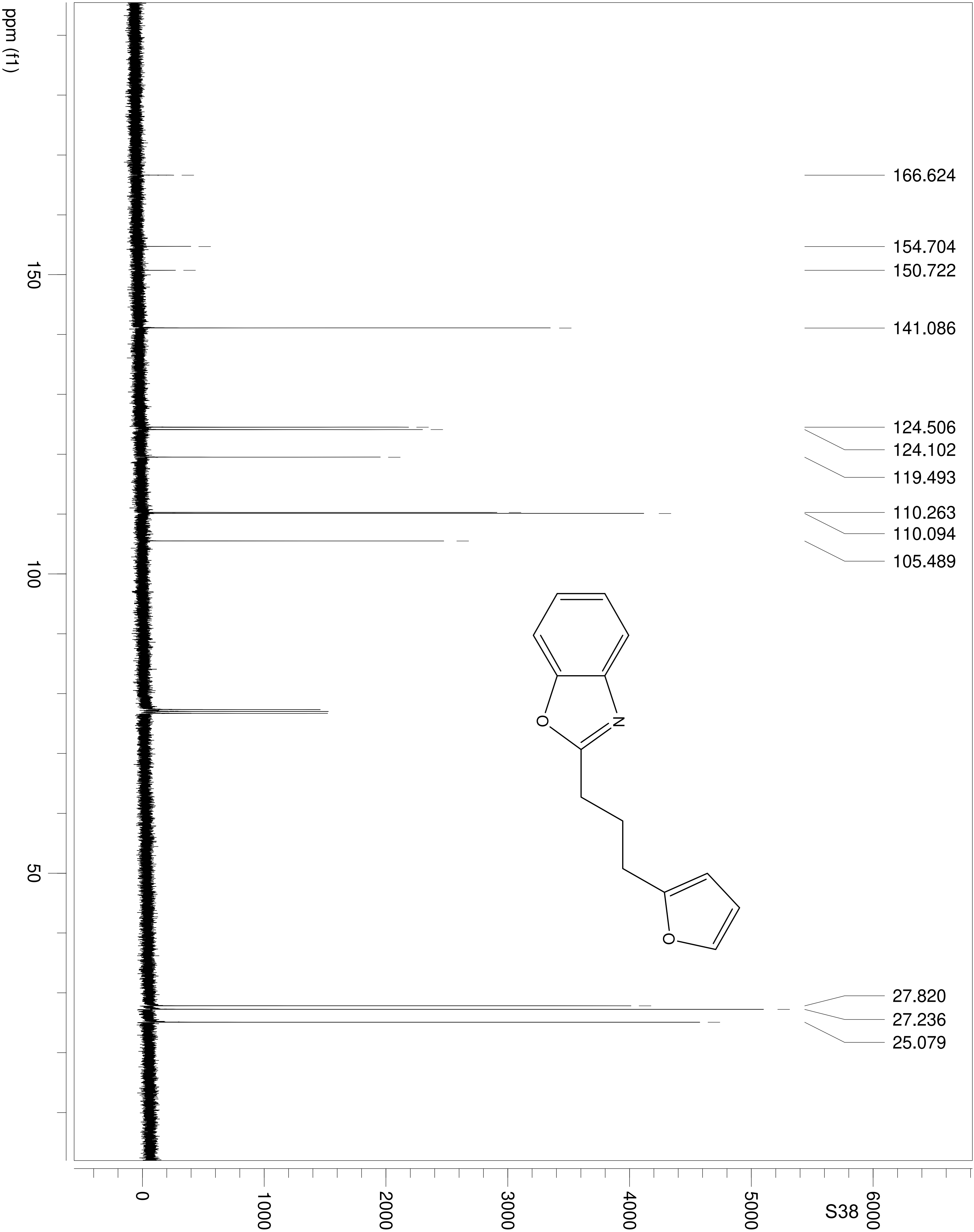
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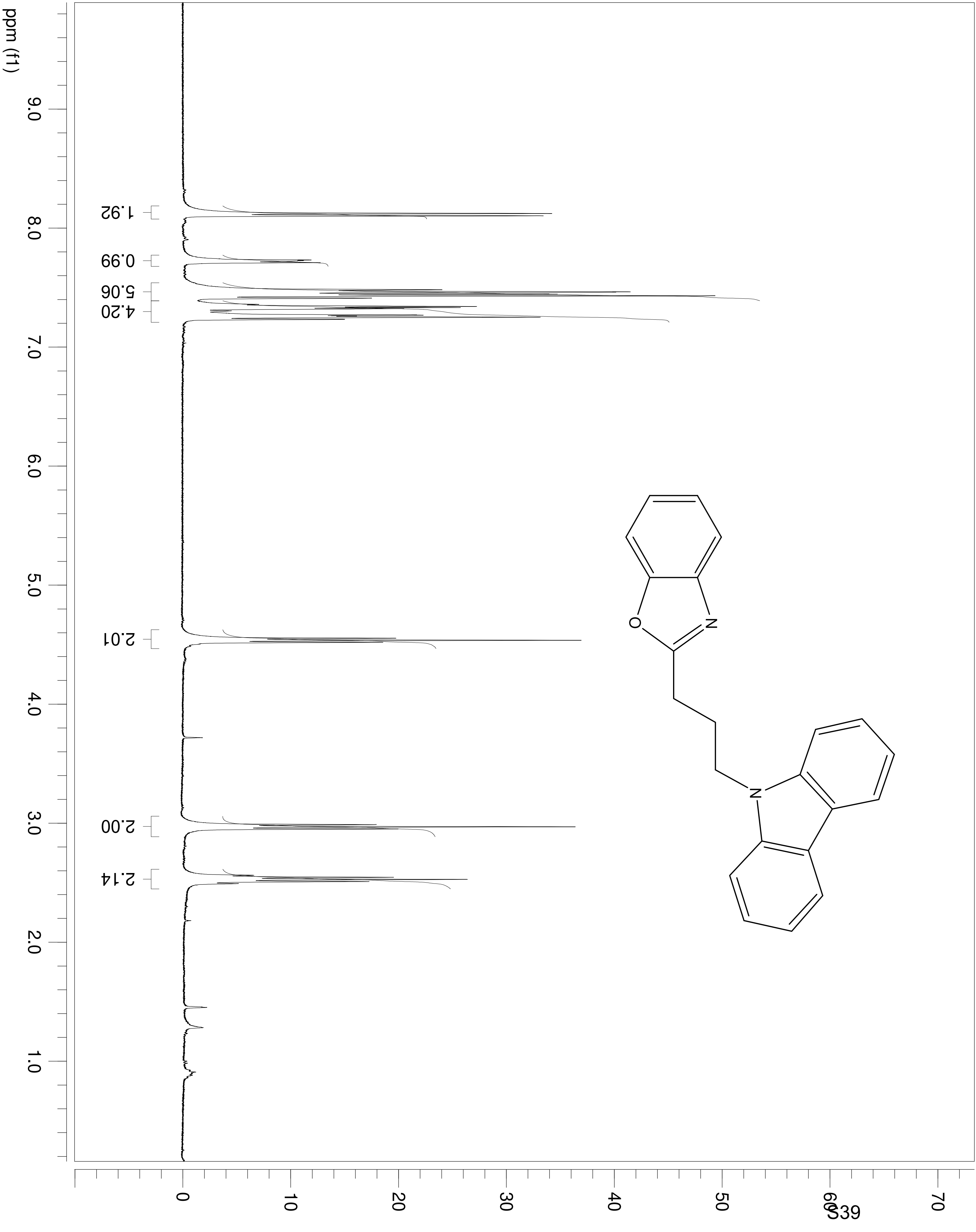
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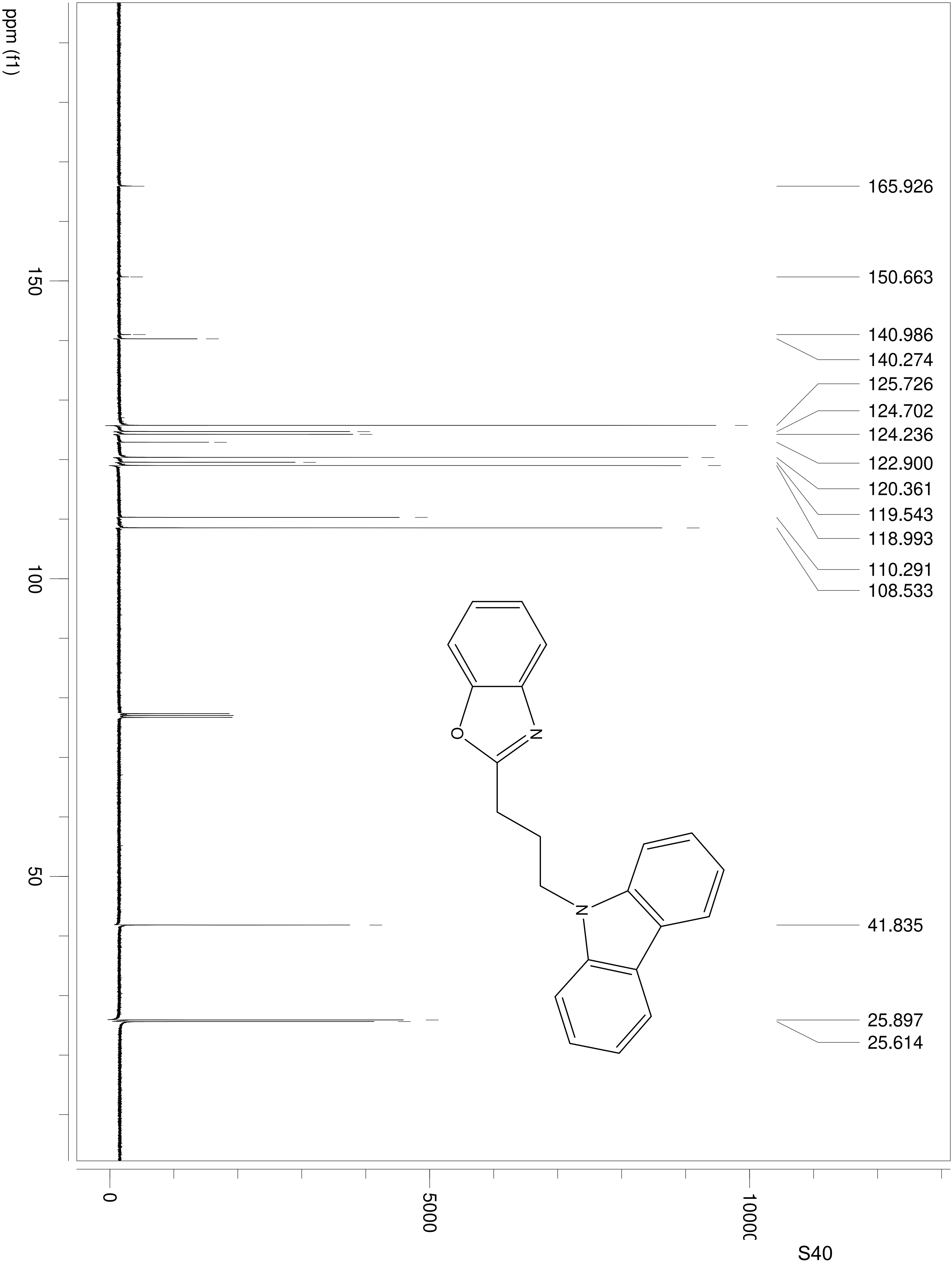

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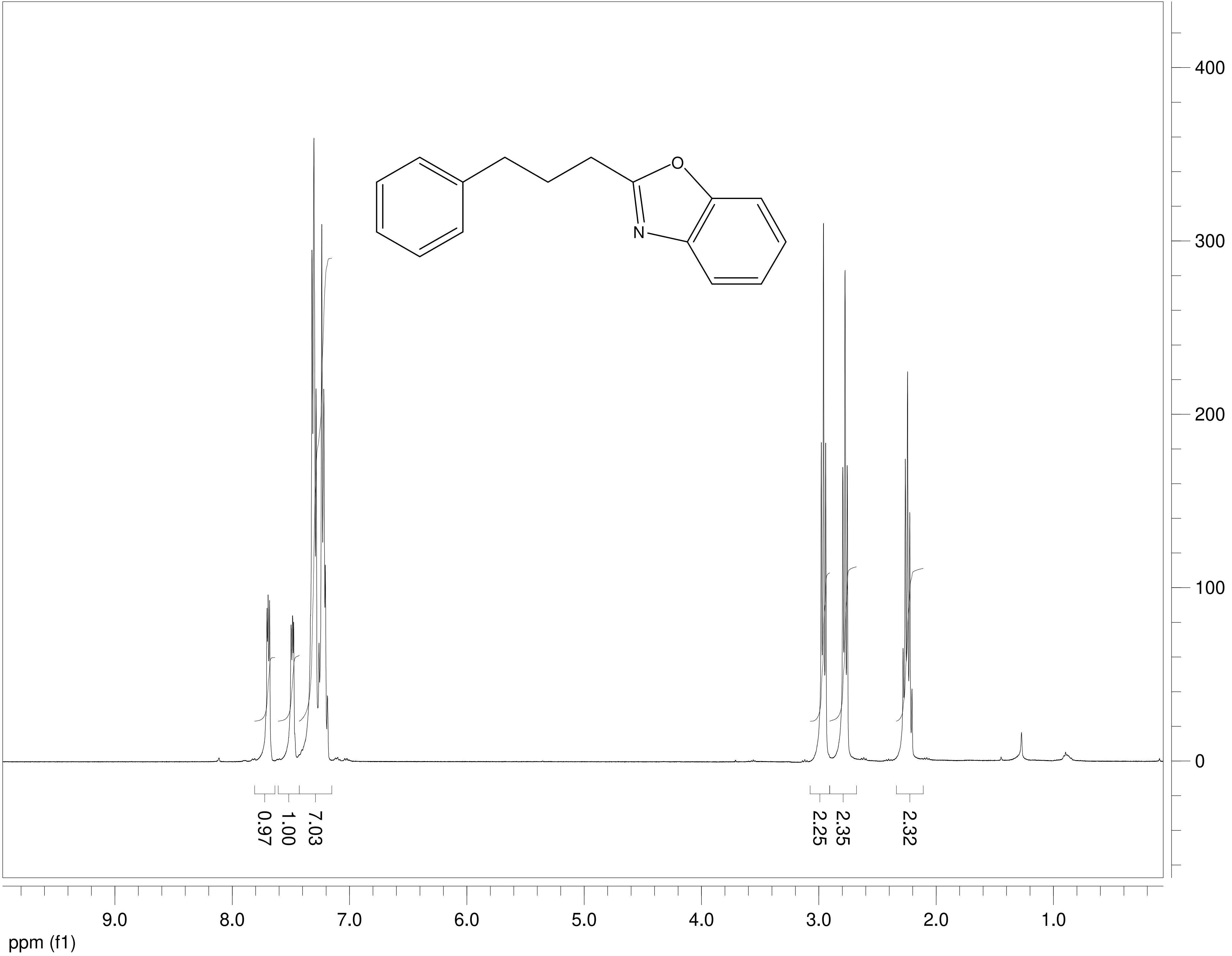
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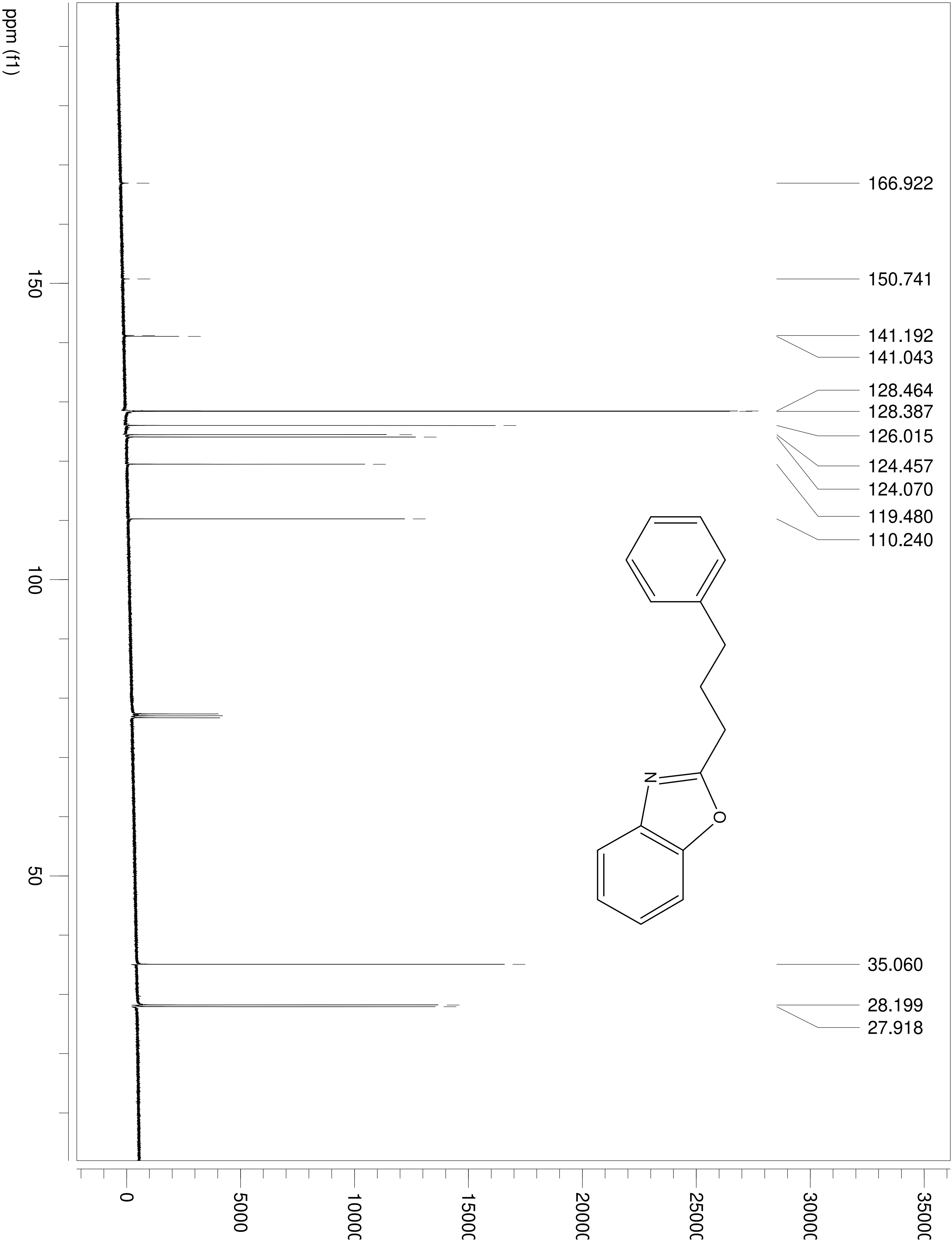
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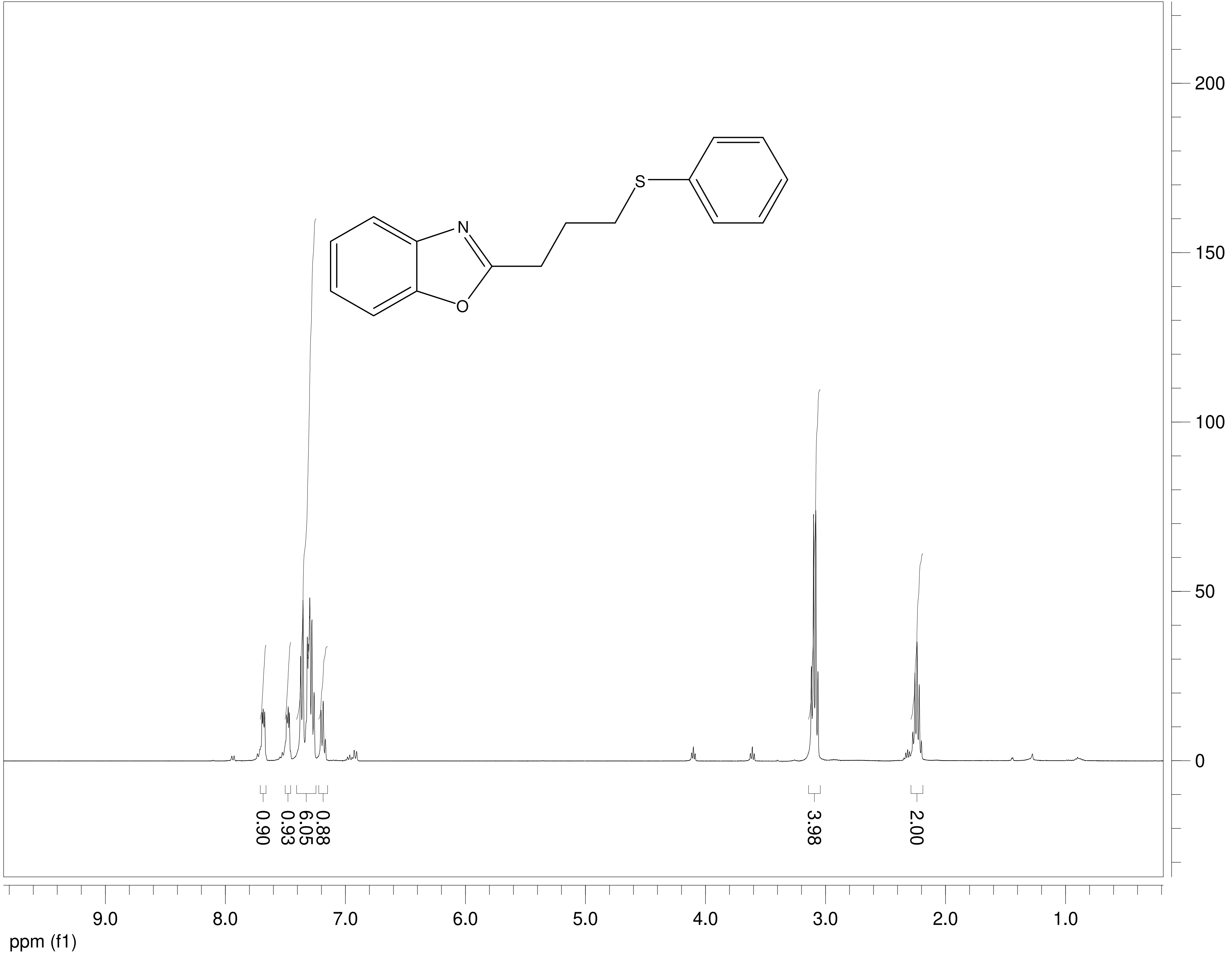
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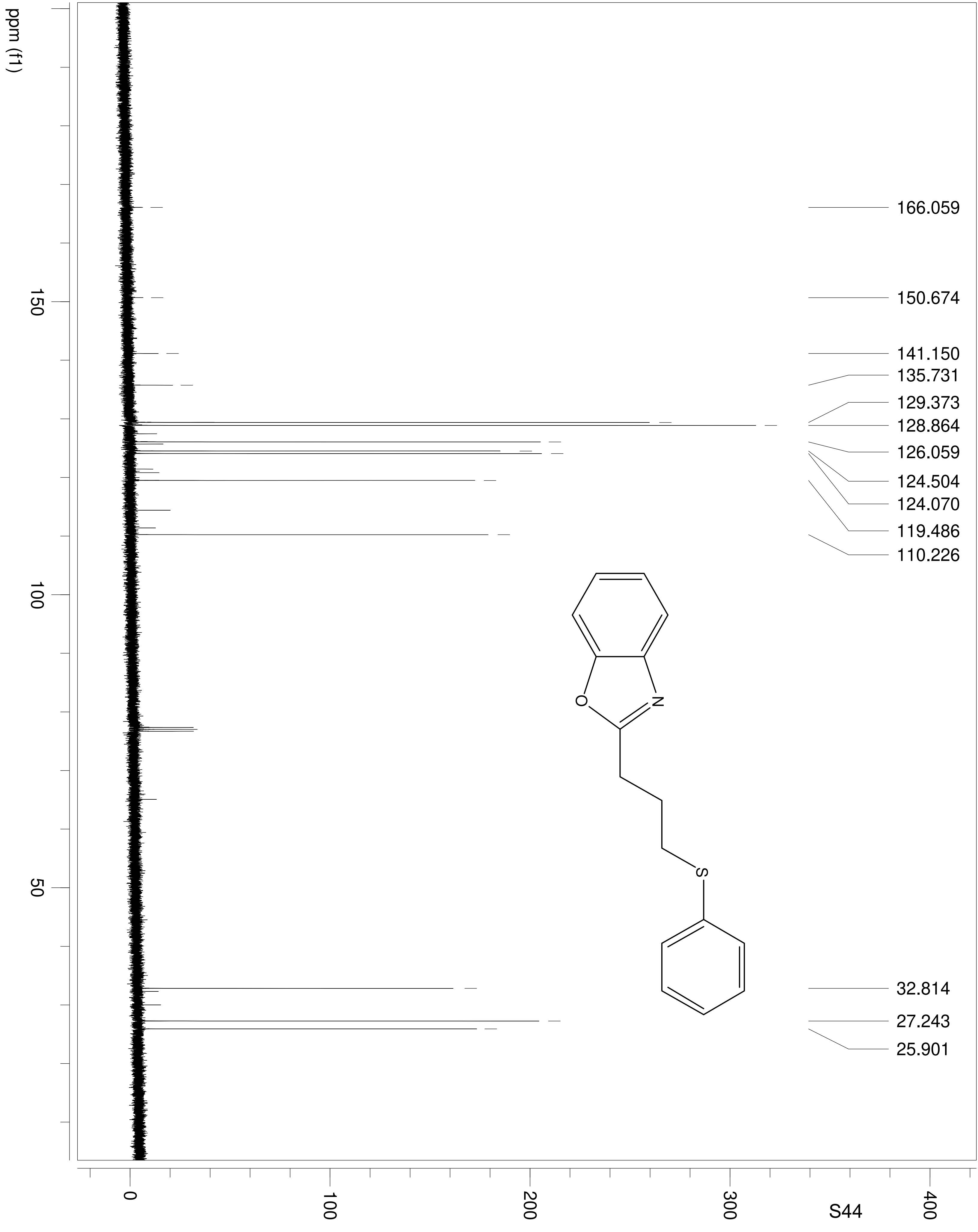
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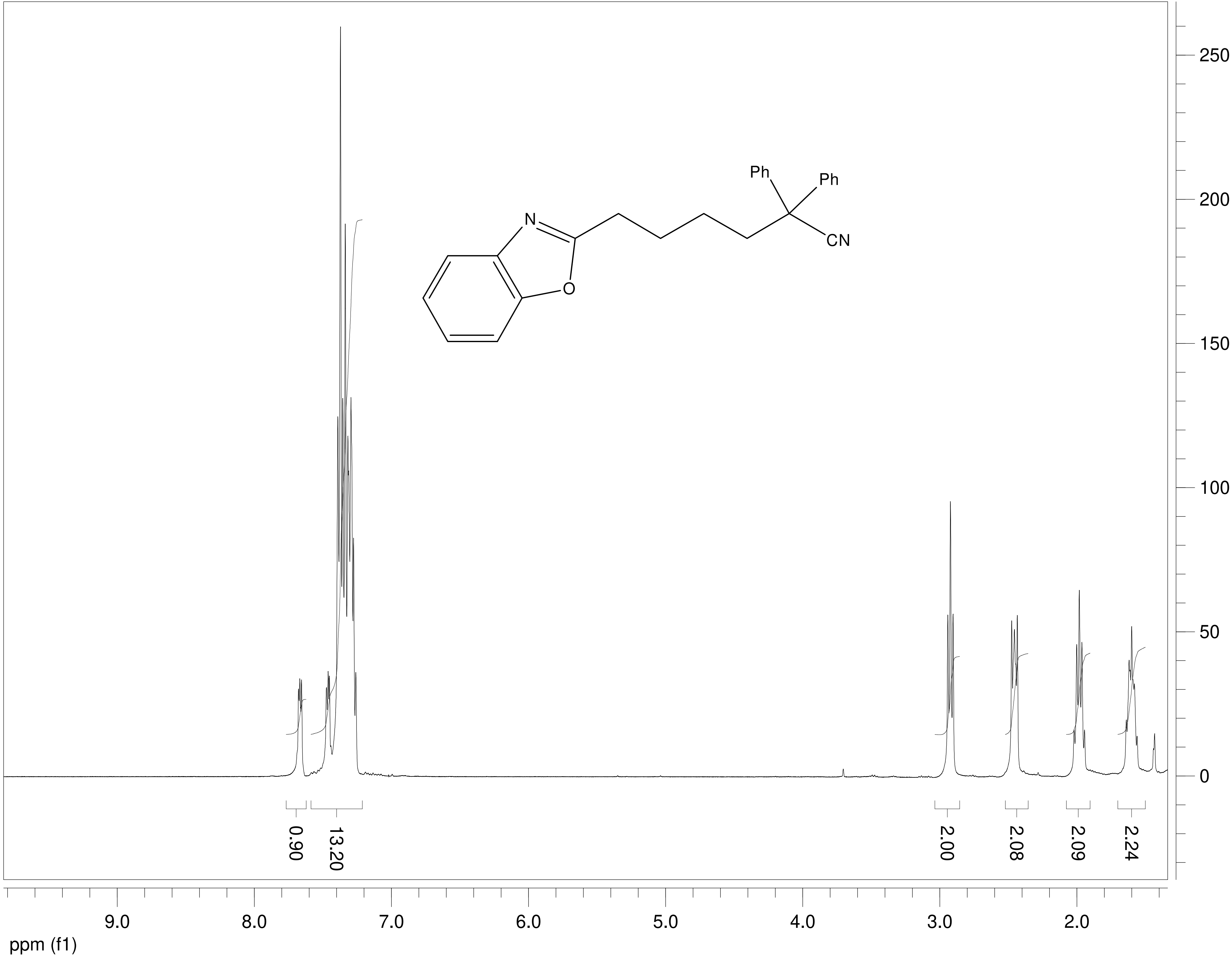
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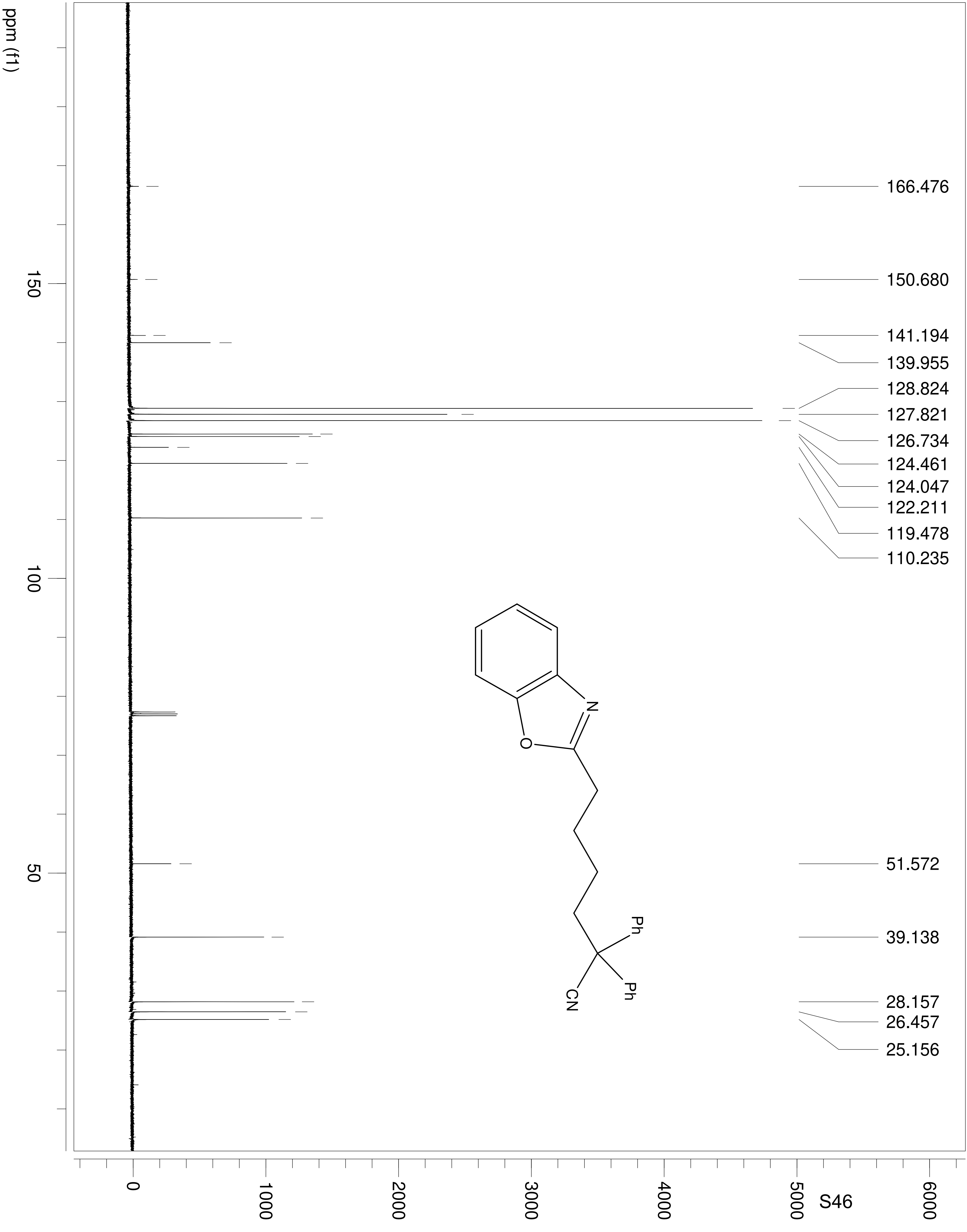
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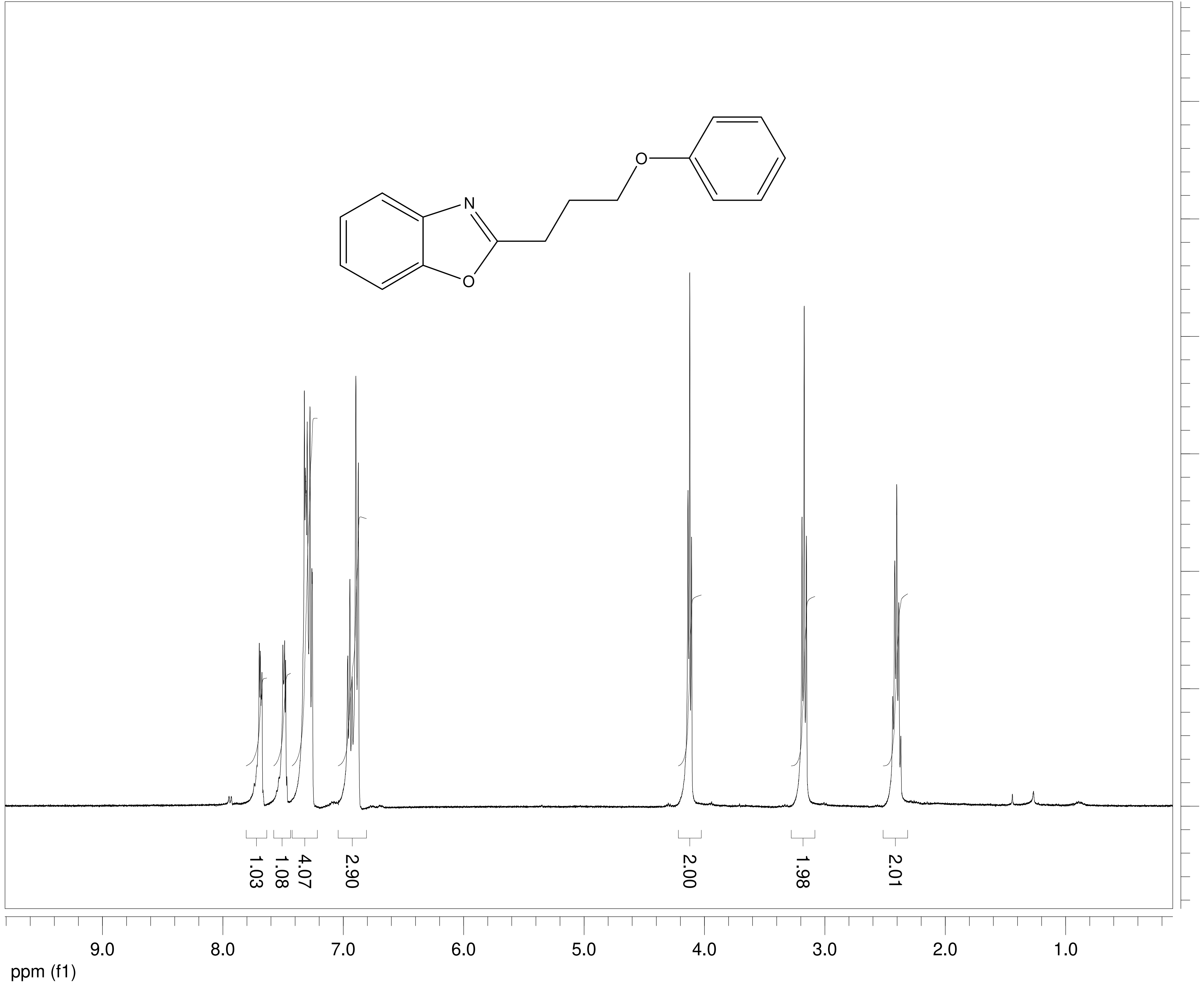
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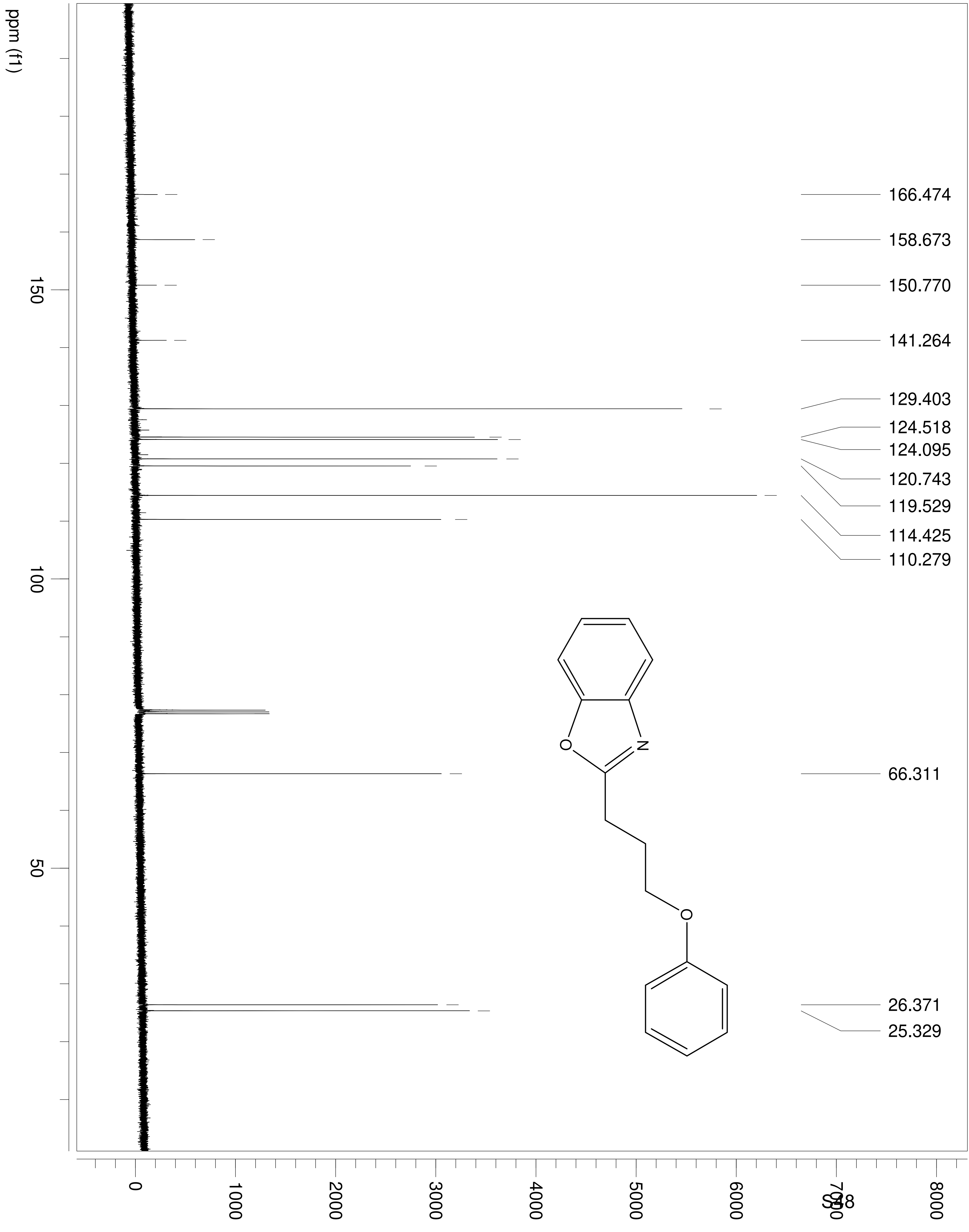
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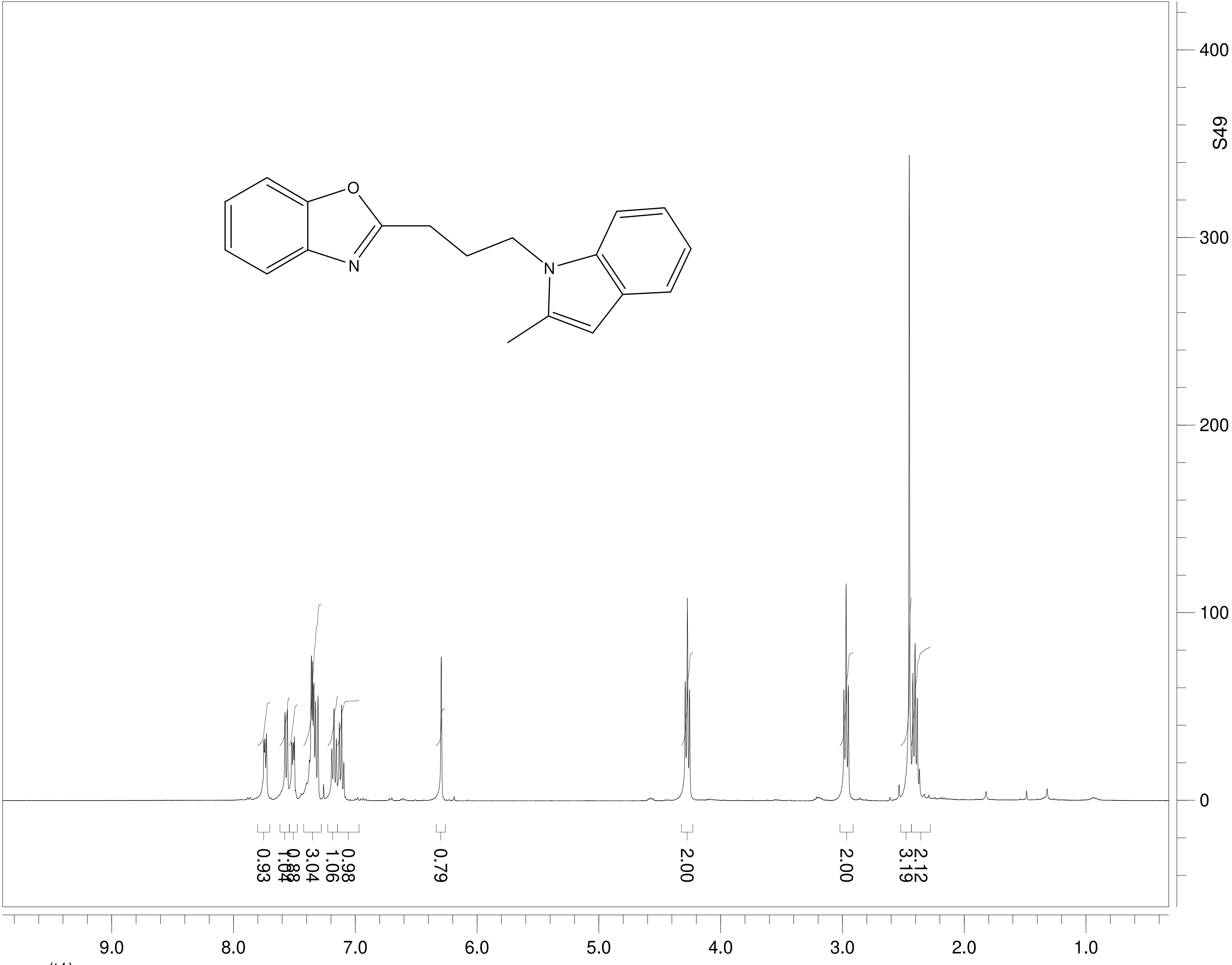
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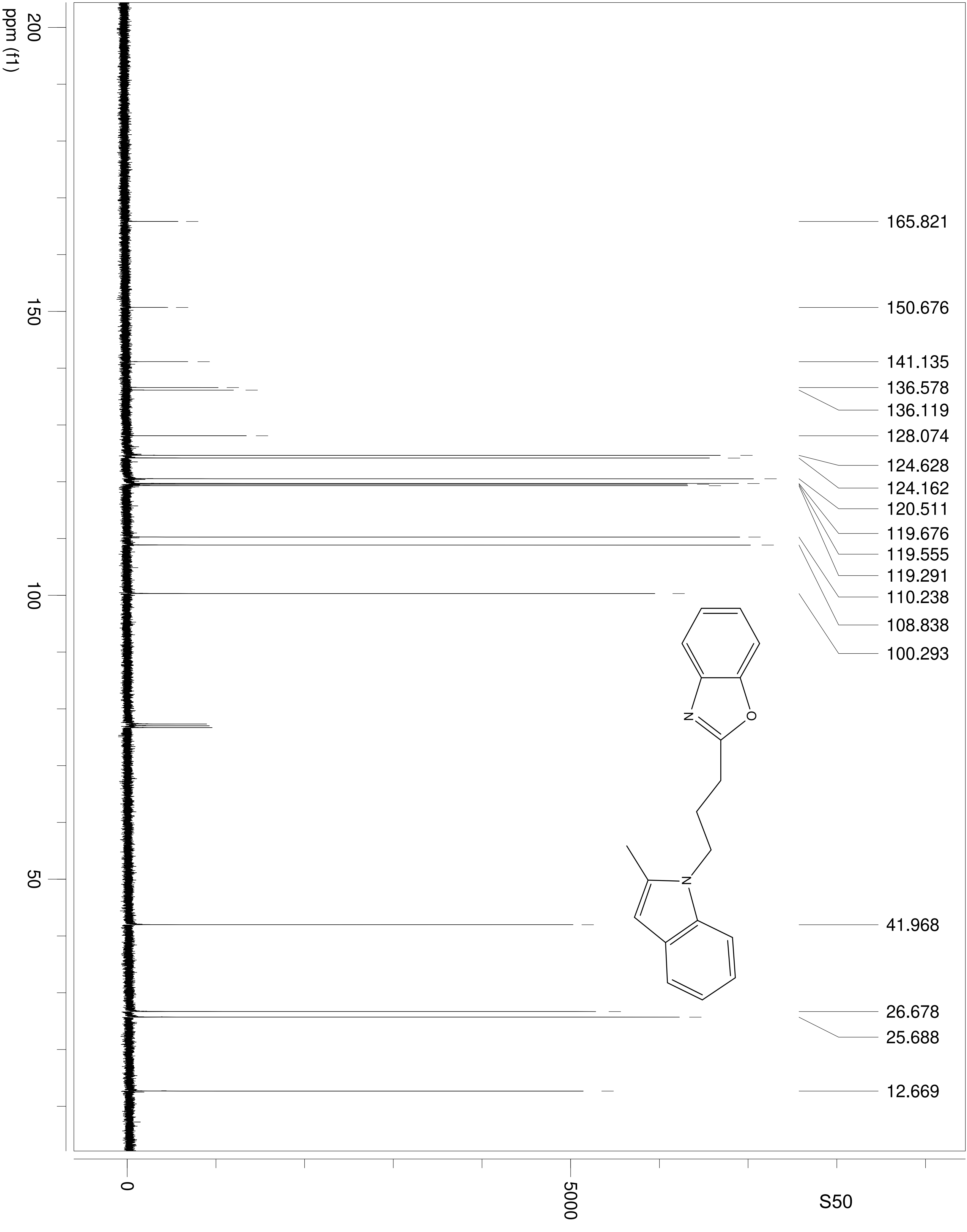
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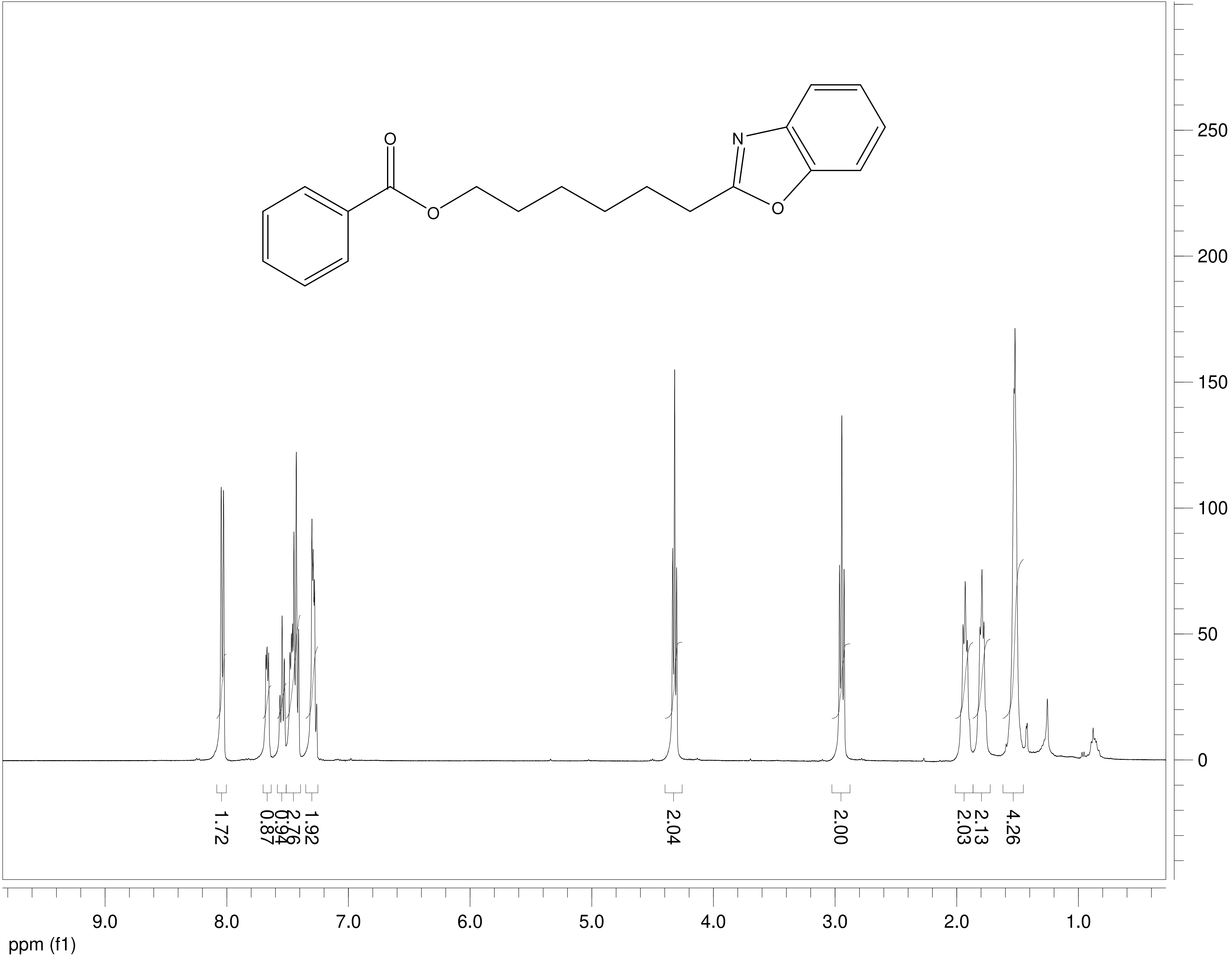
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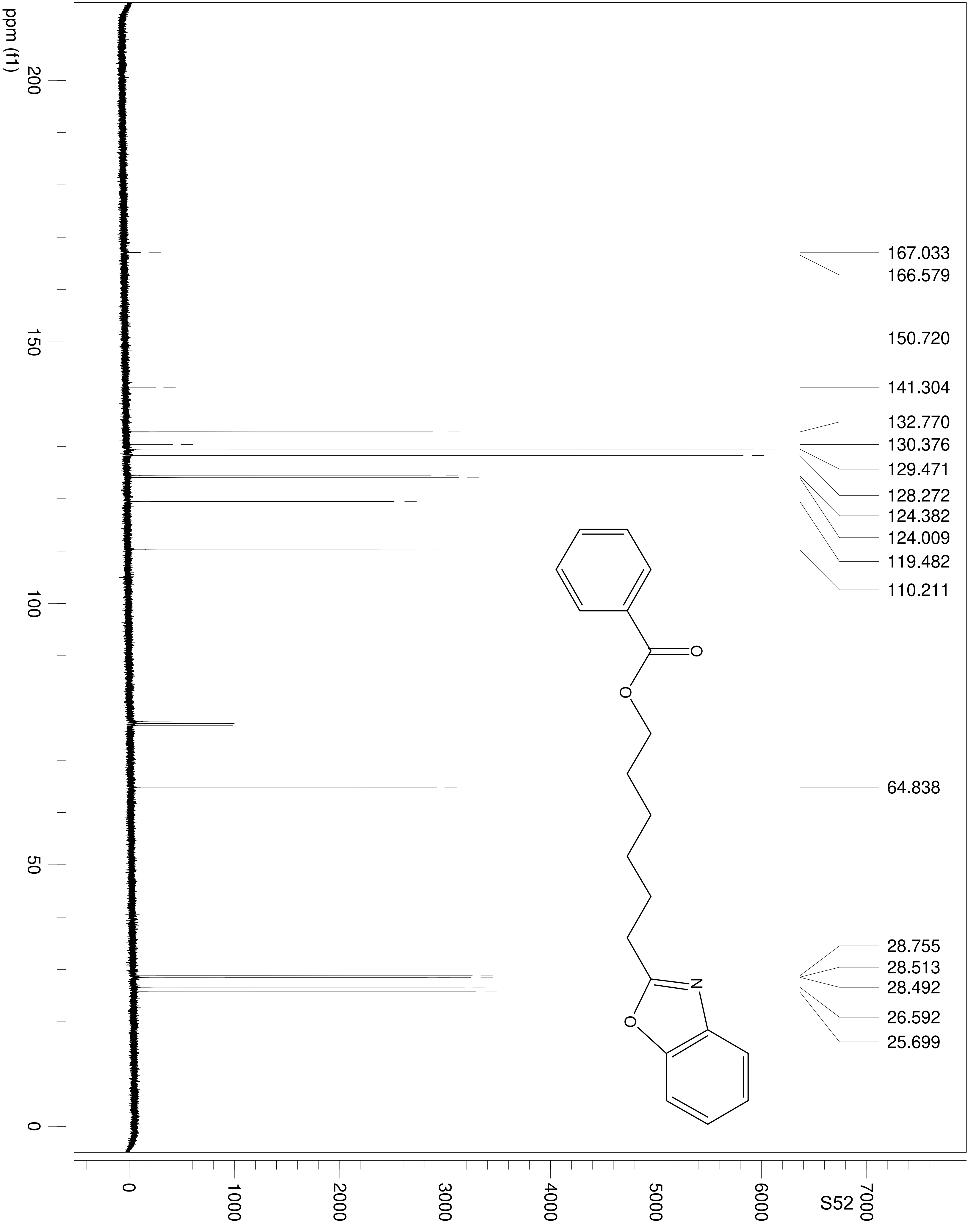
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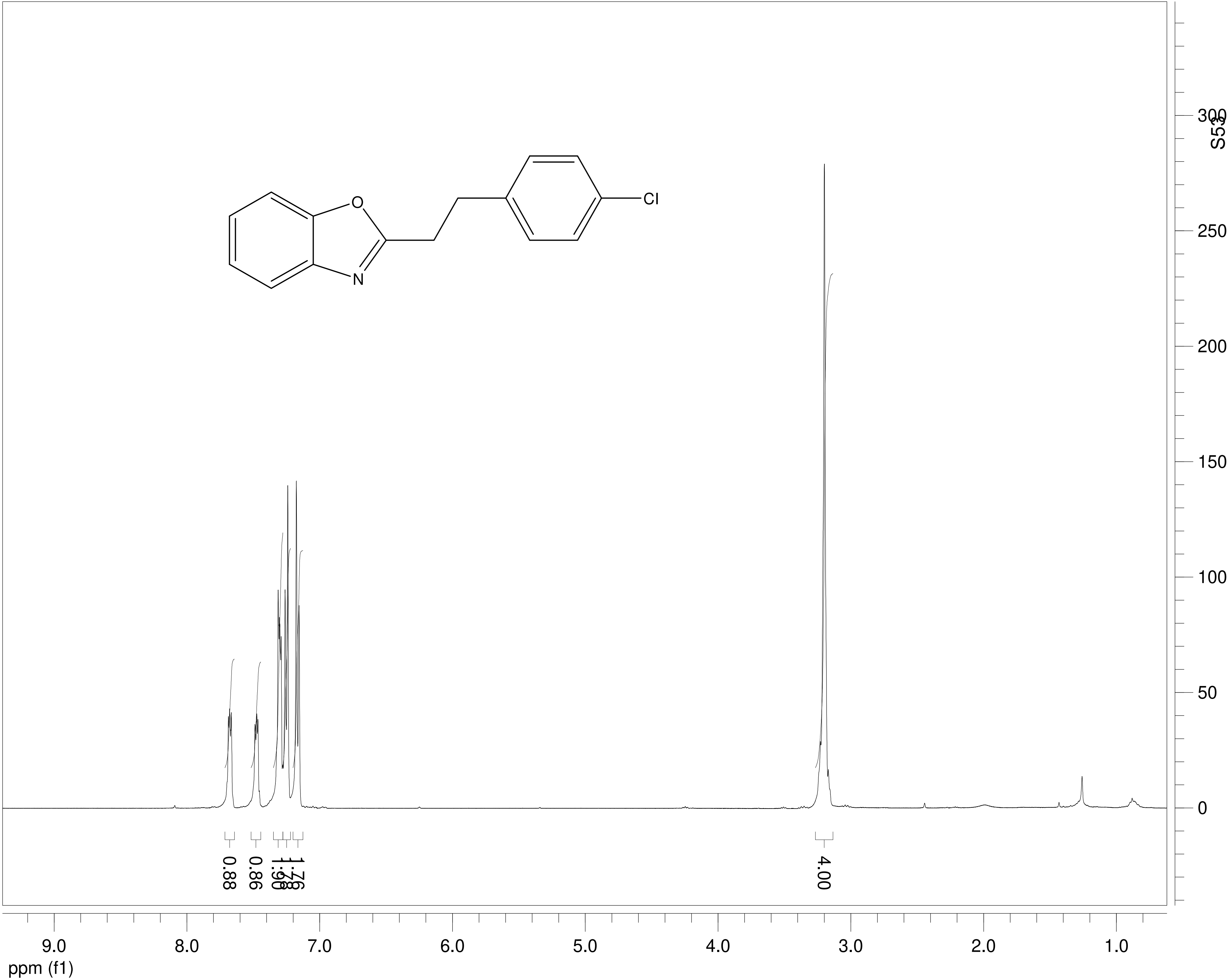
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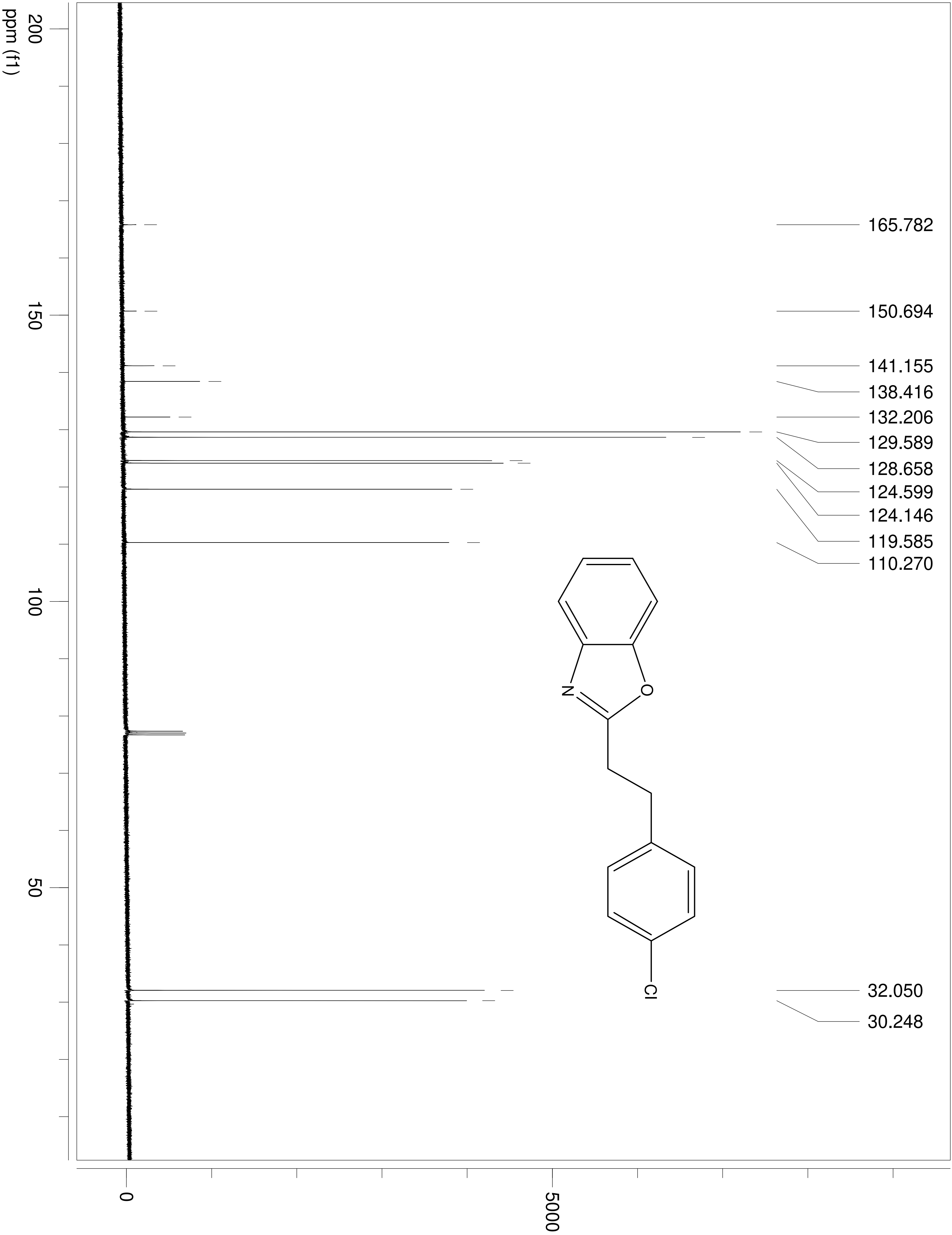
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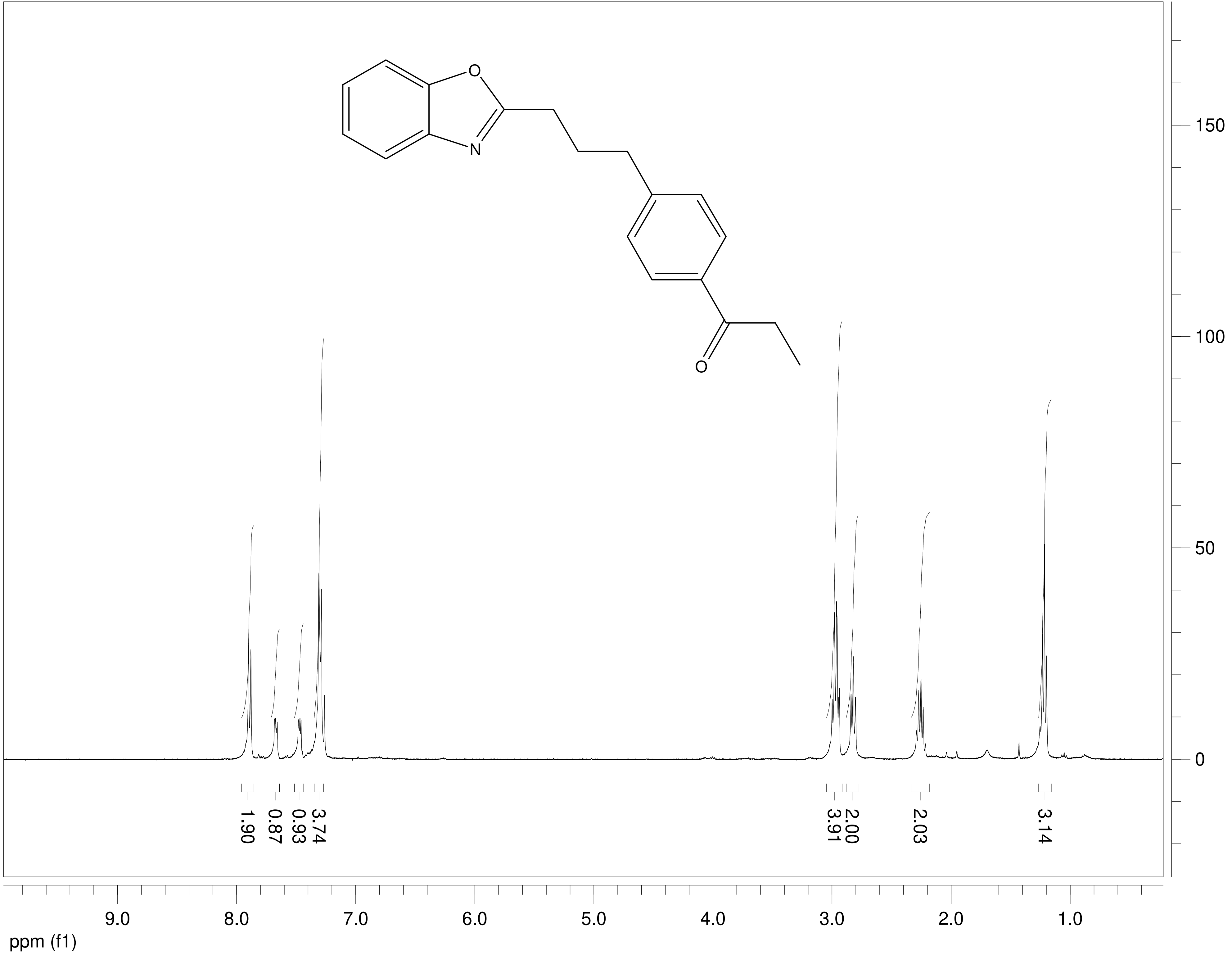

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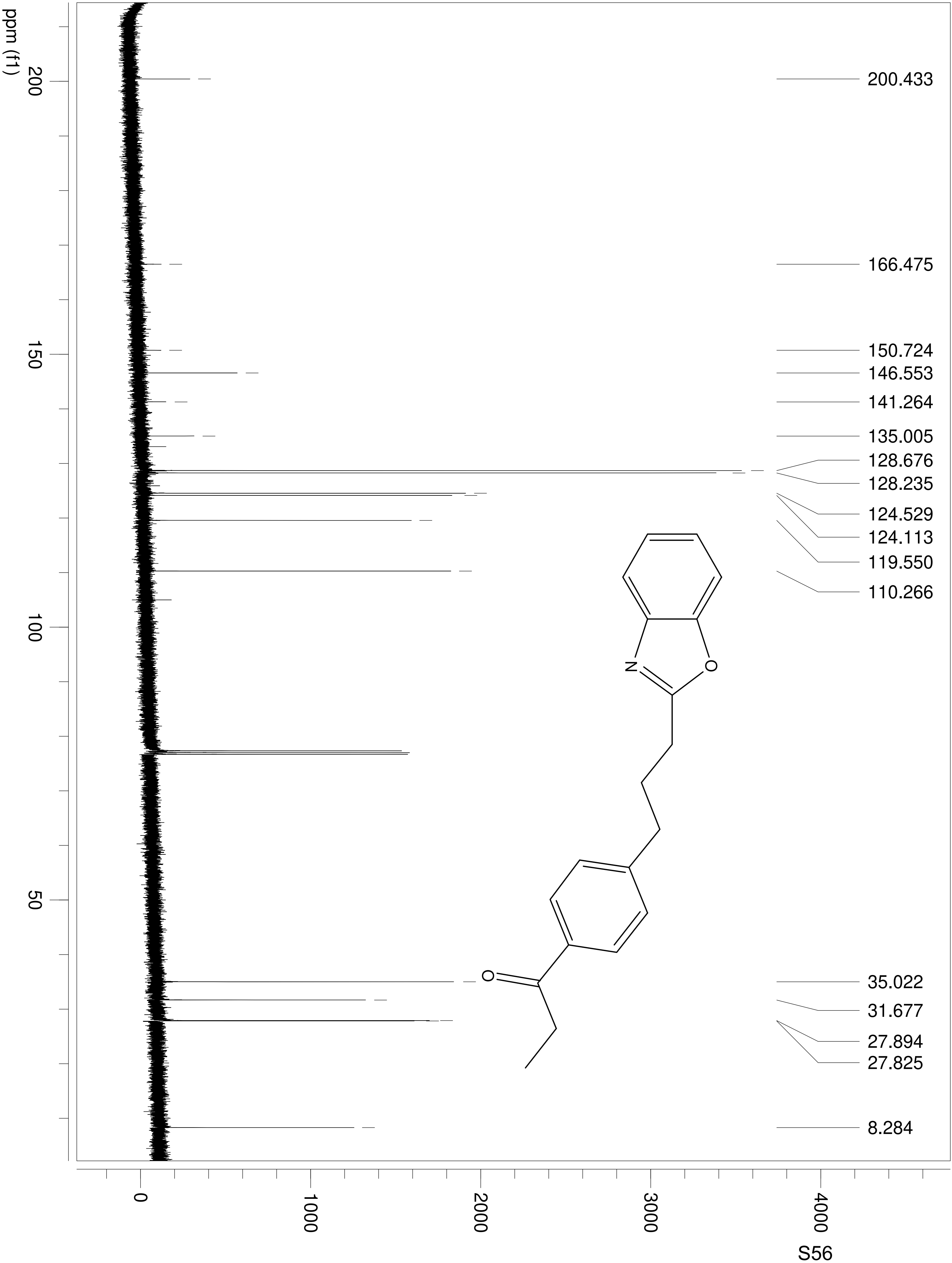
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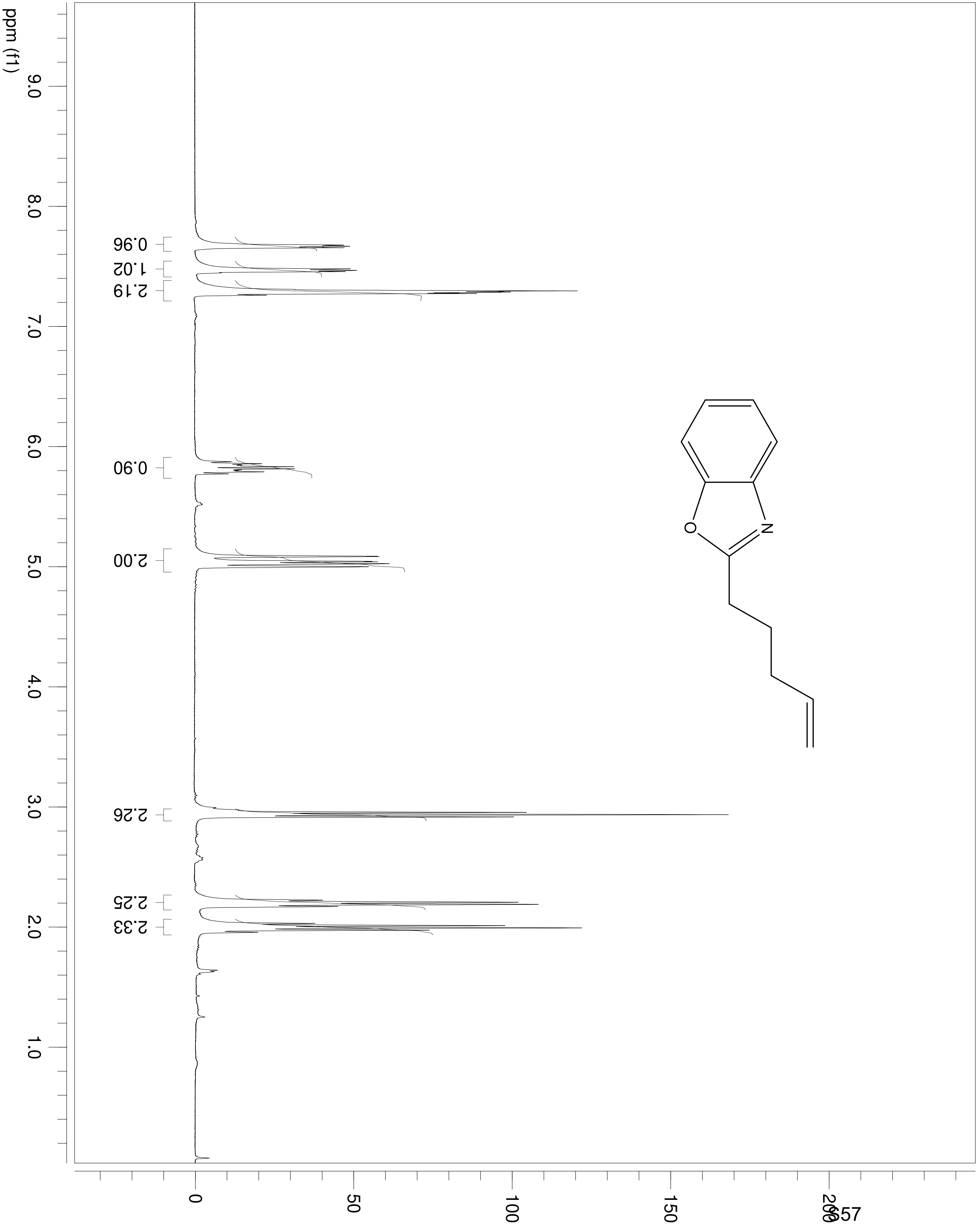
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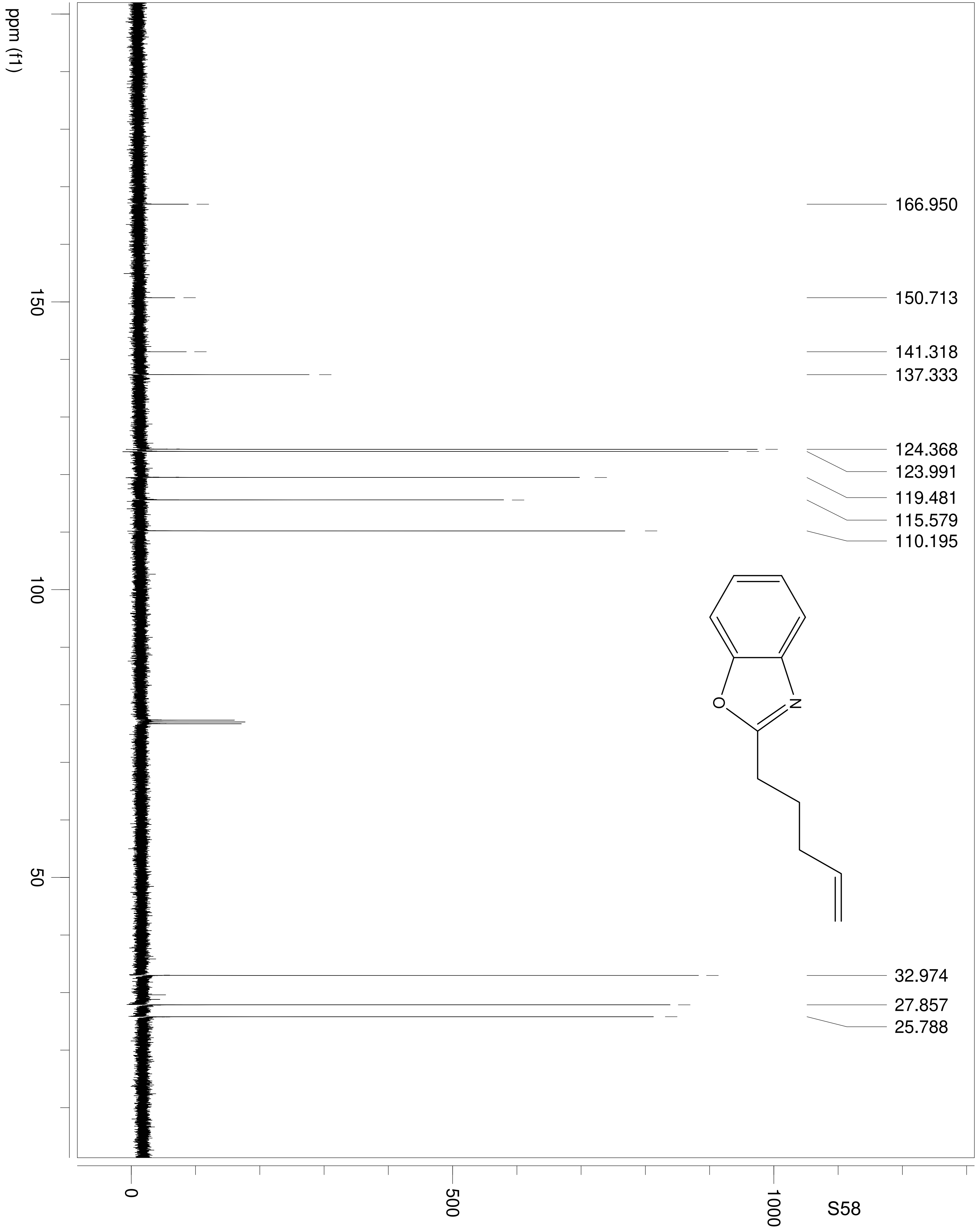
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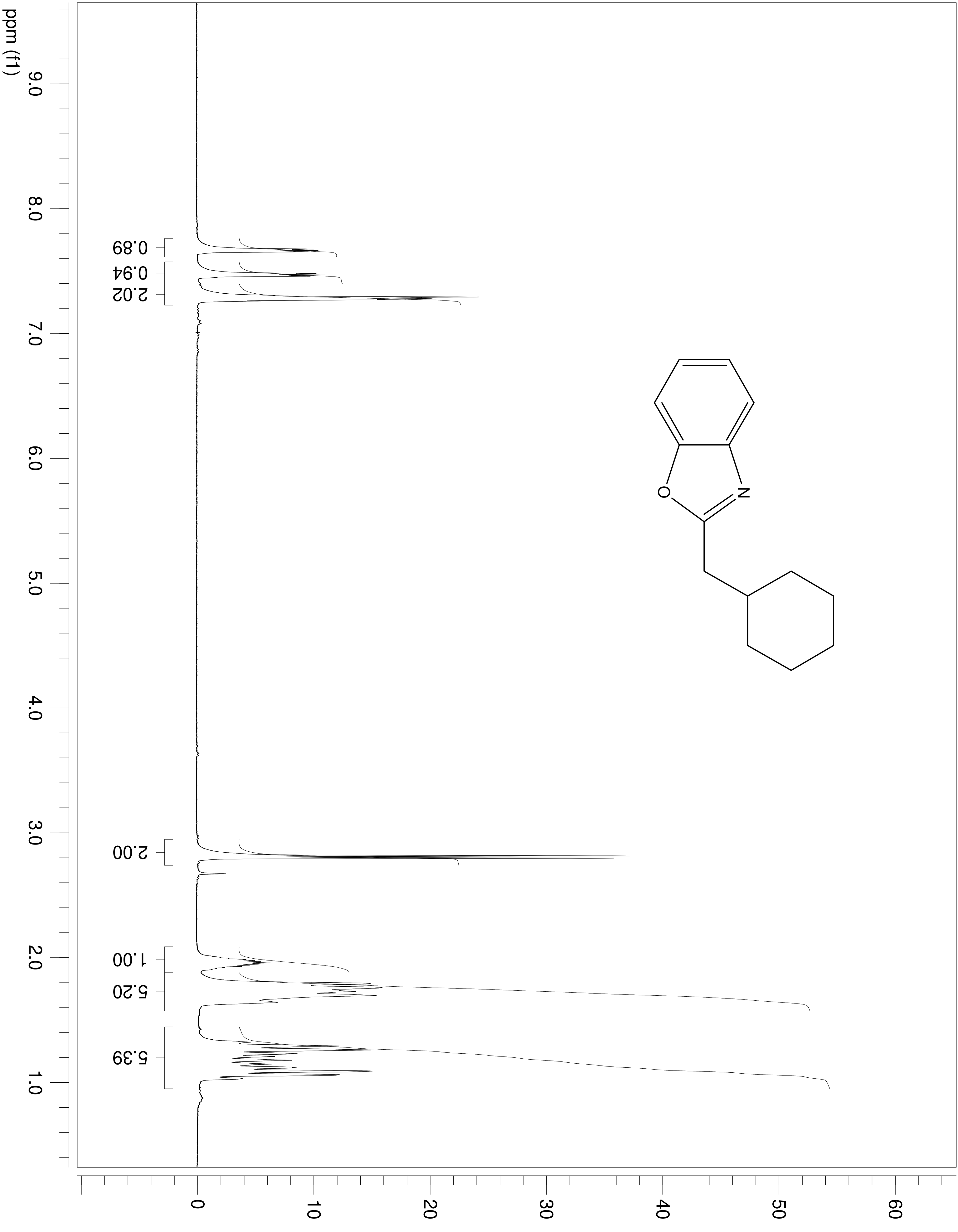
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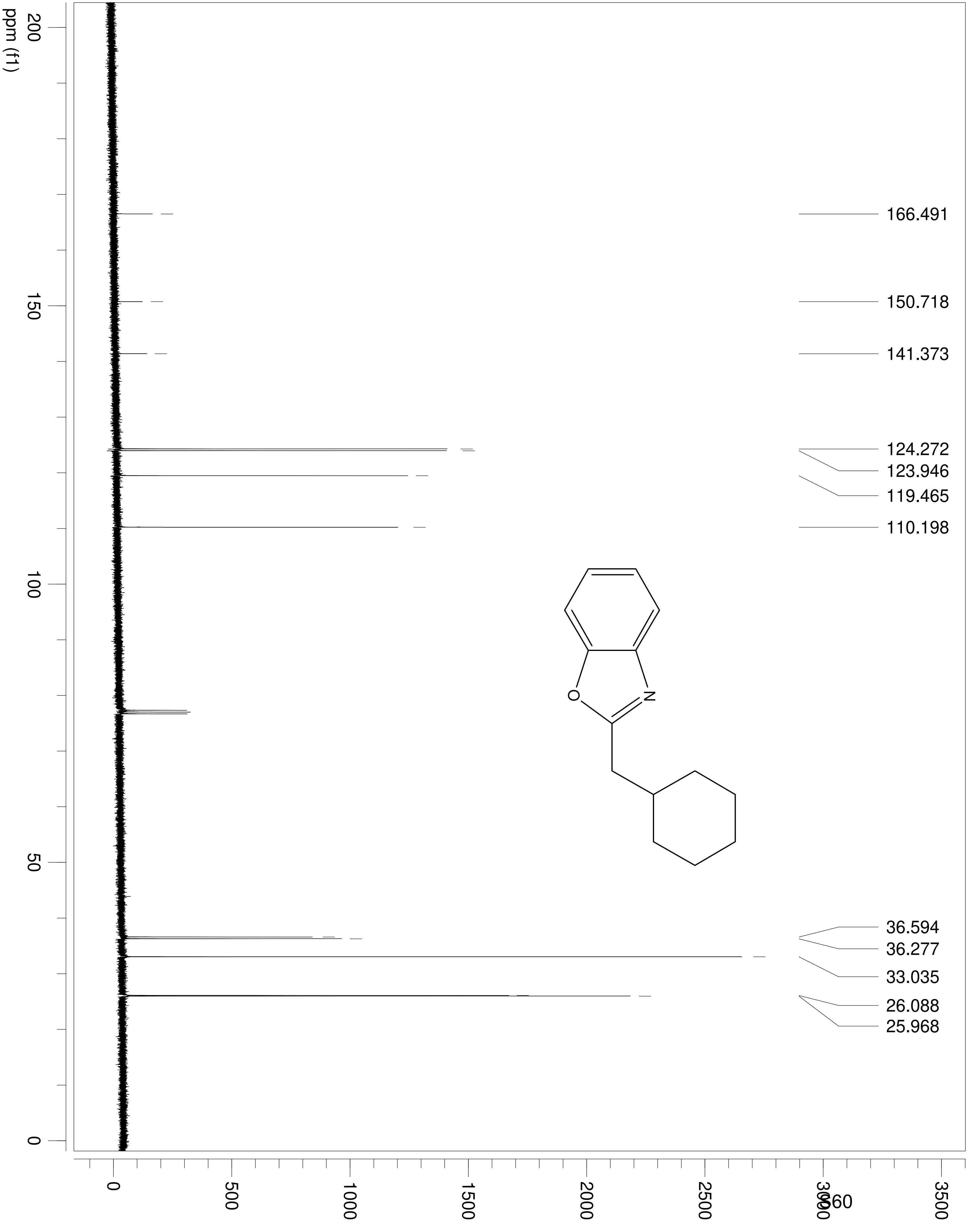
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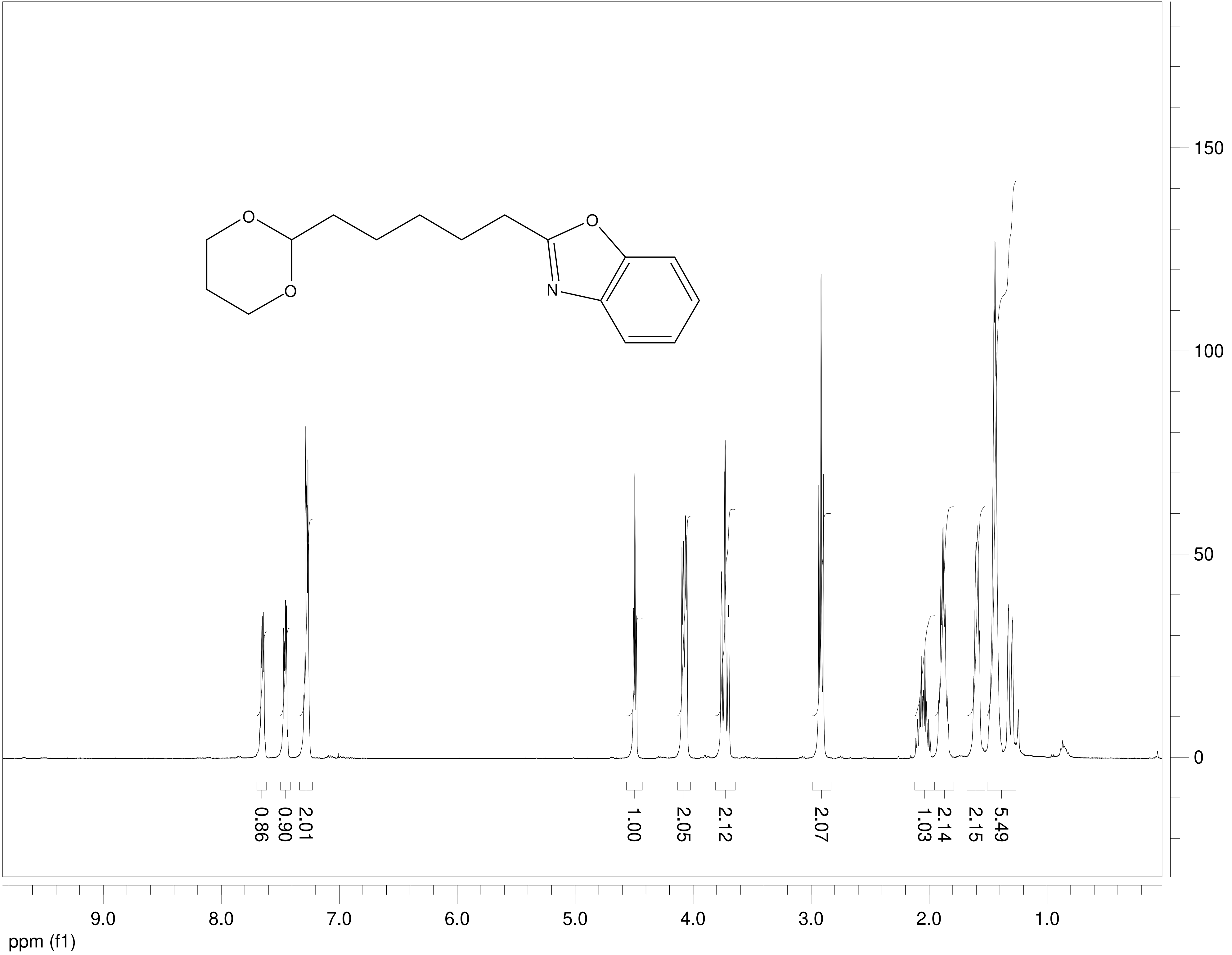
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O
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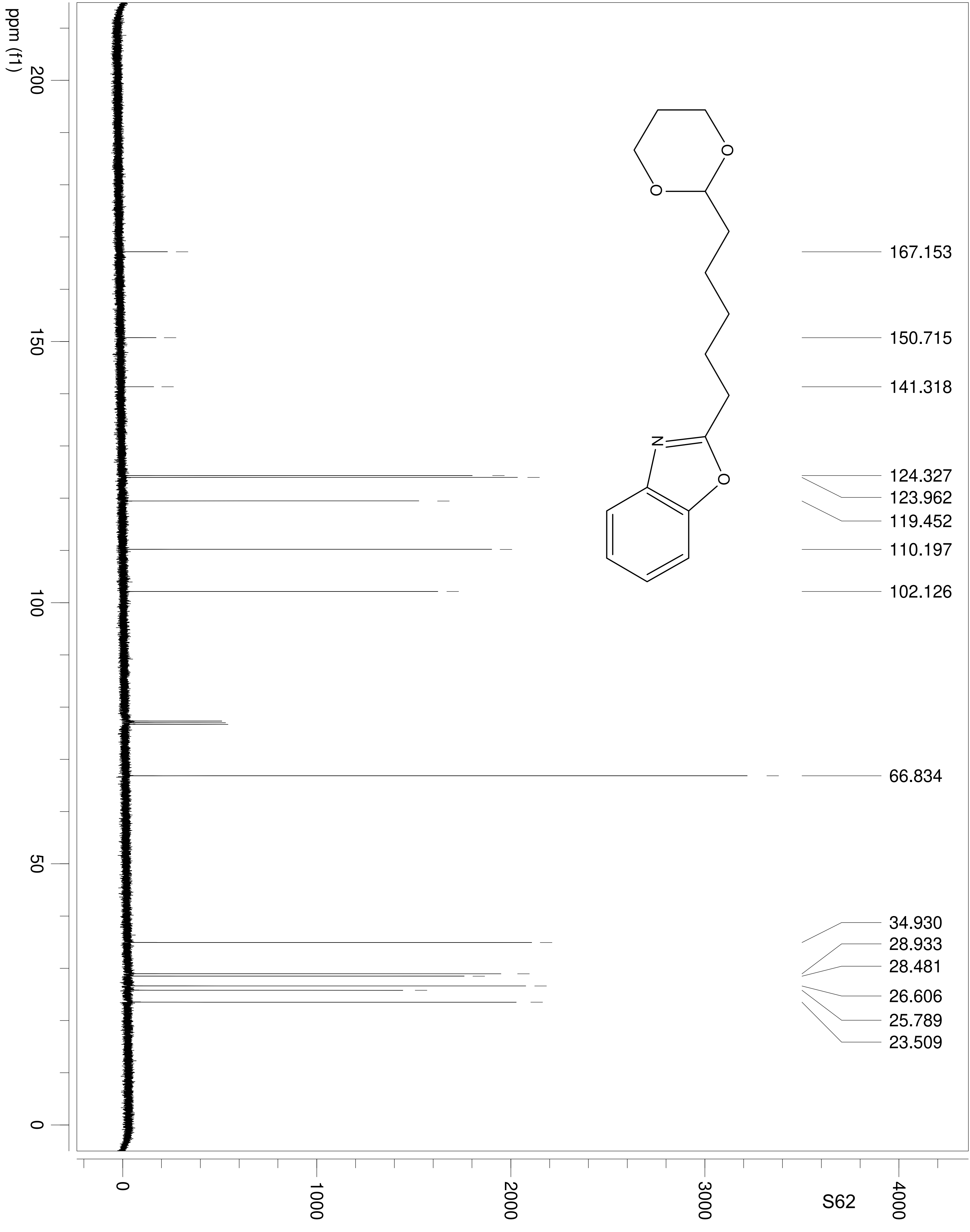
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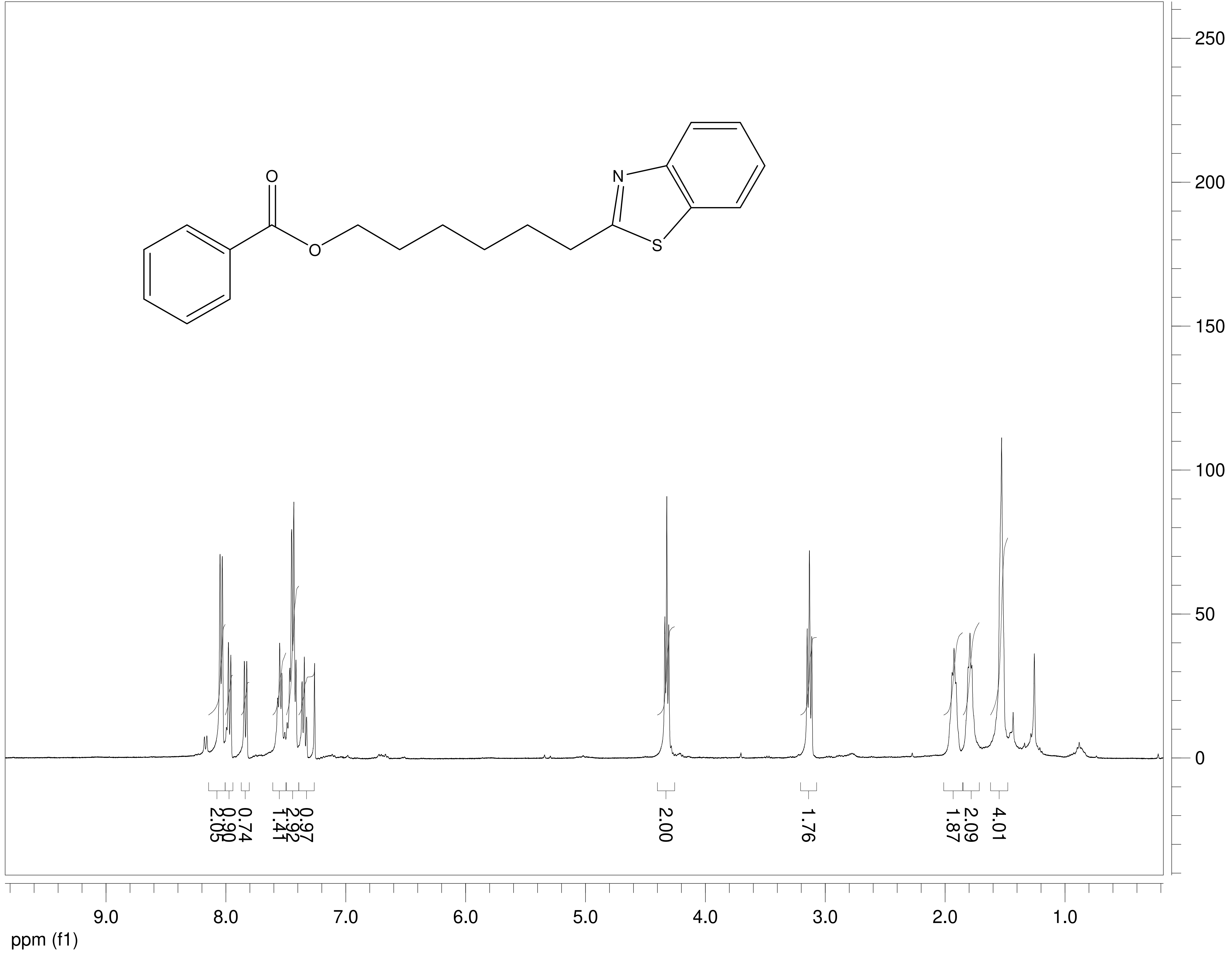
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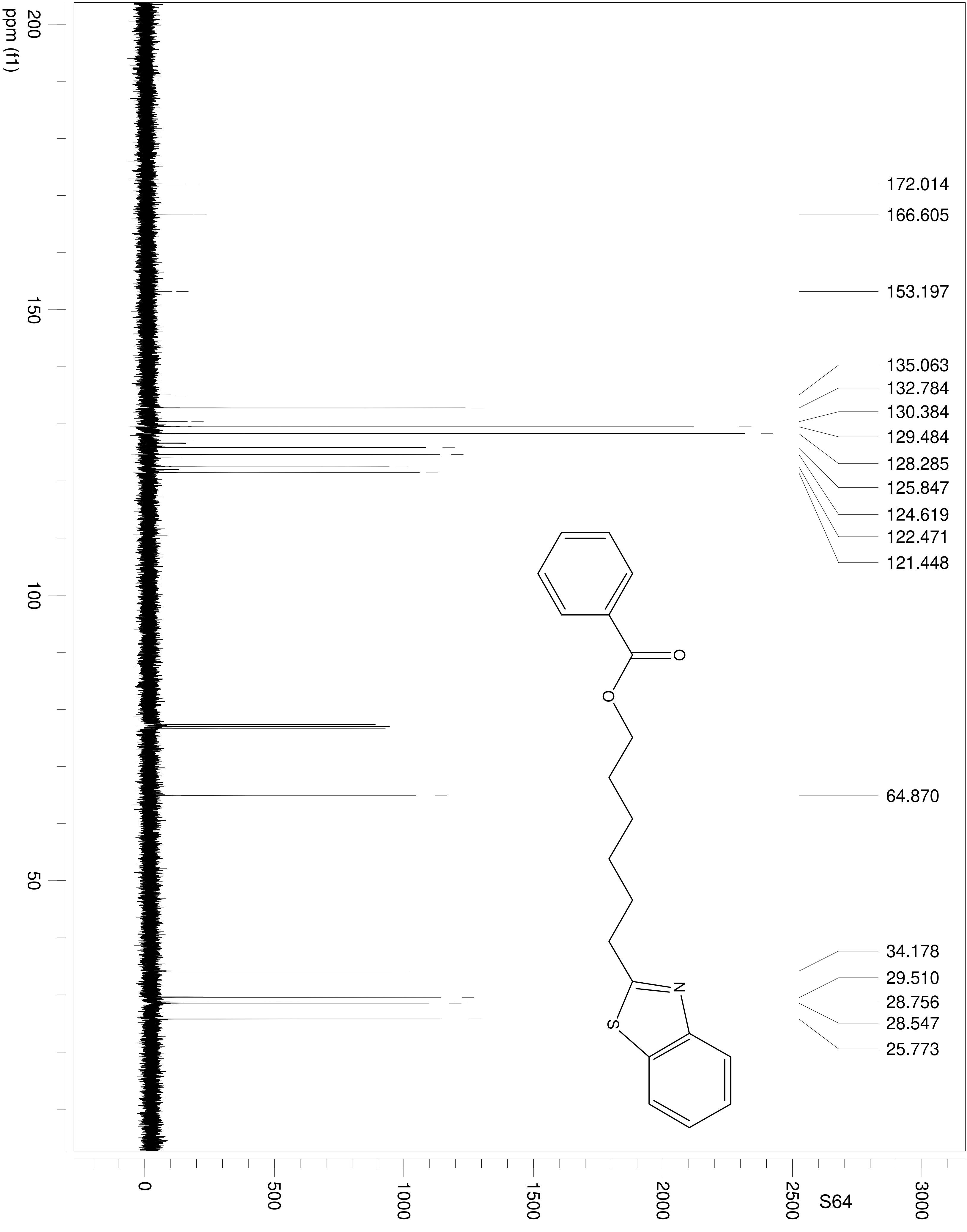
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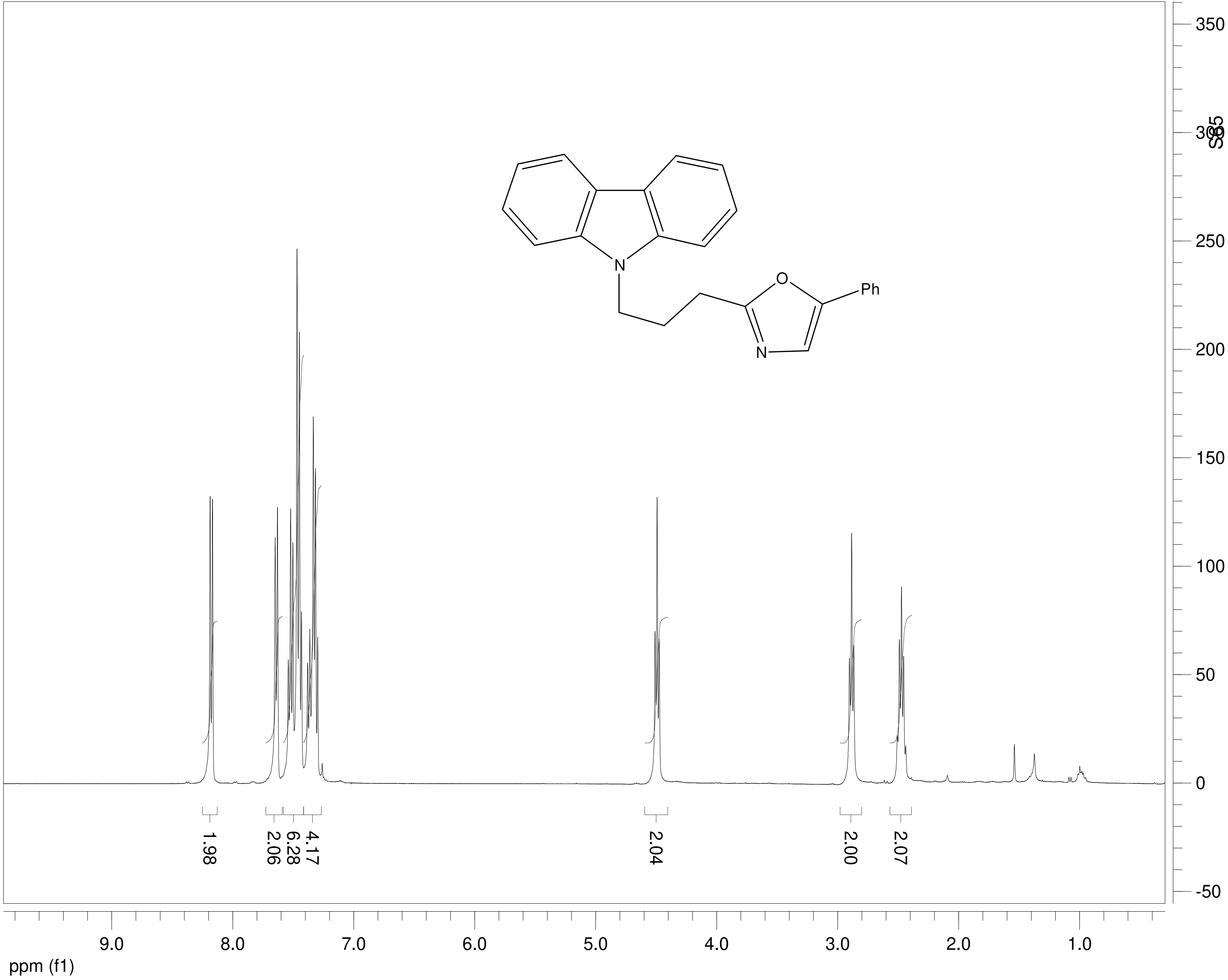
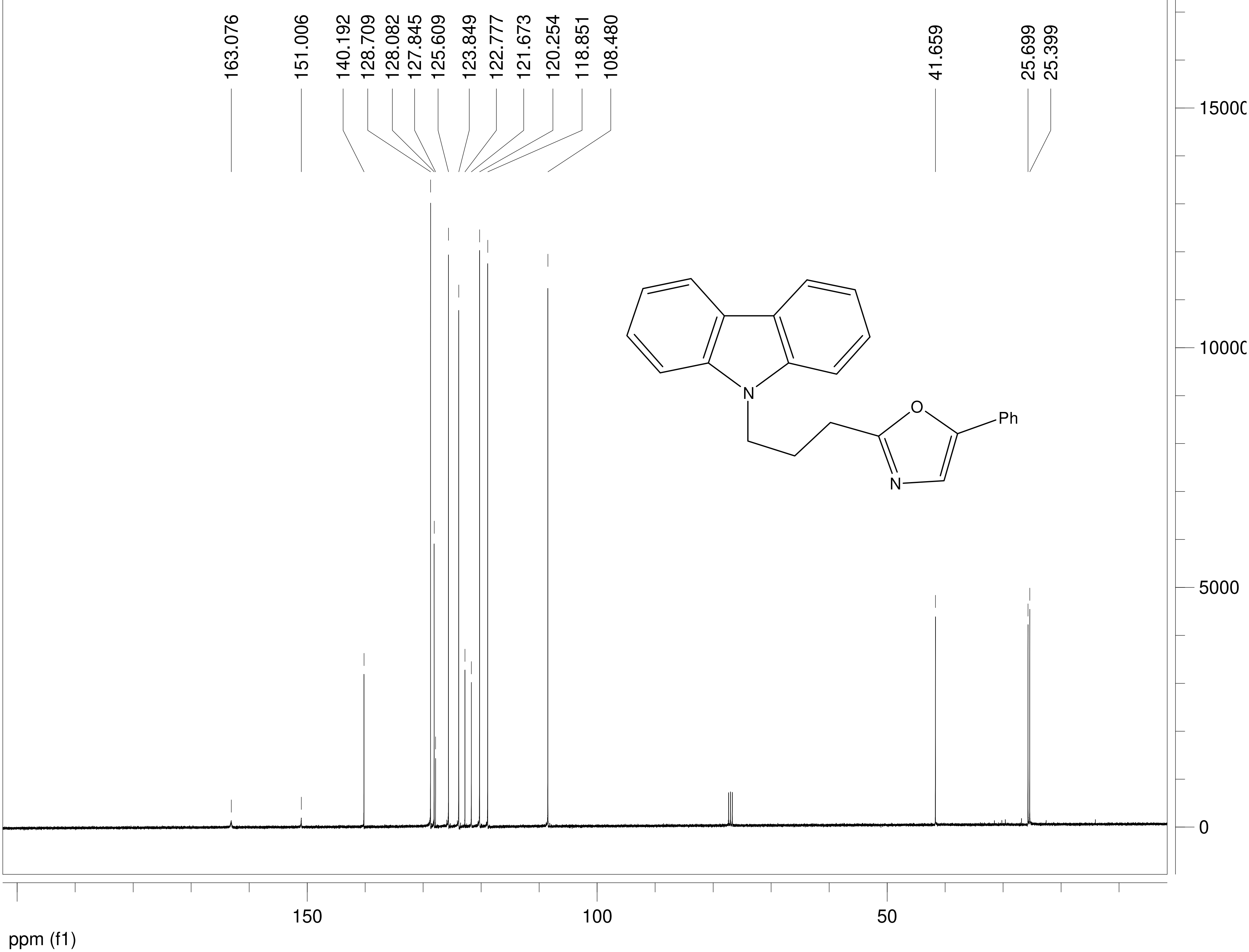
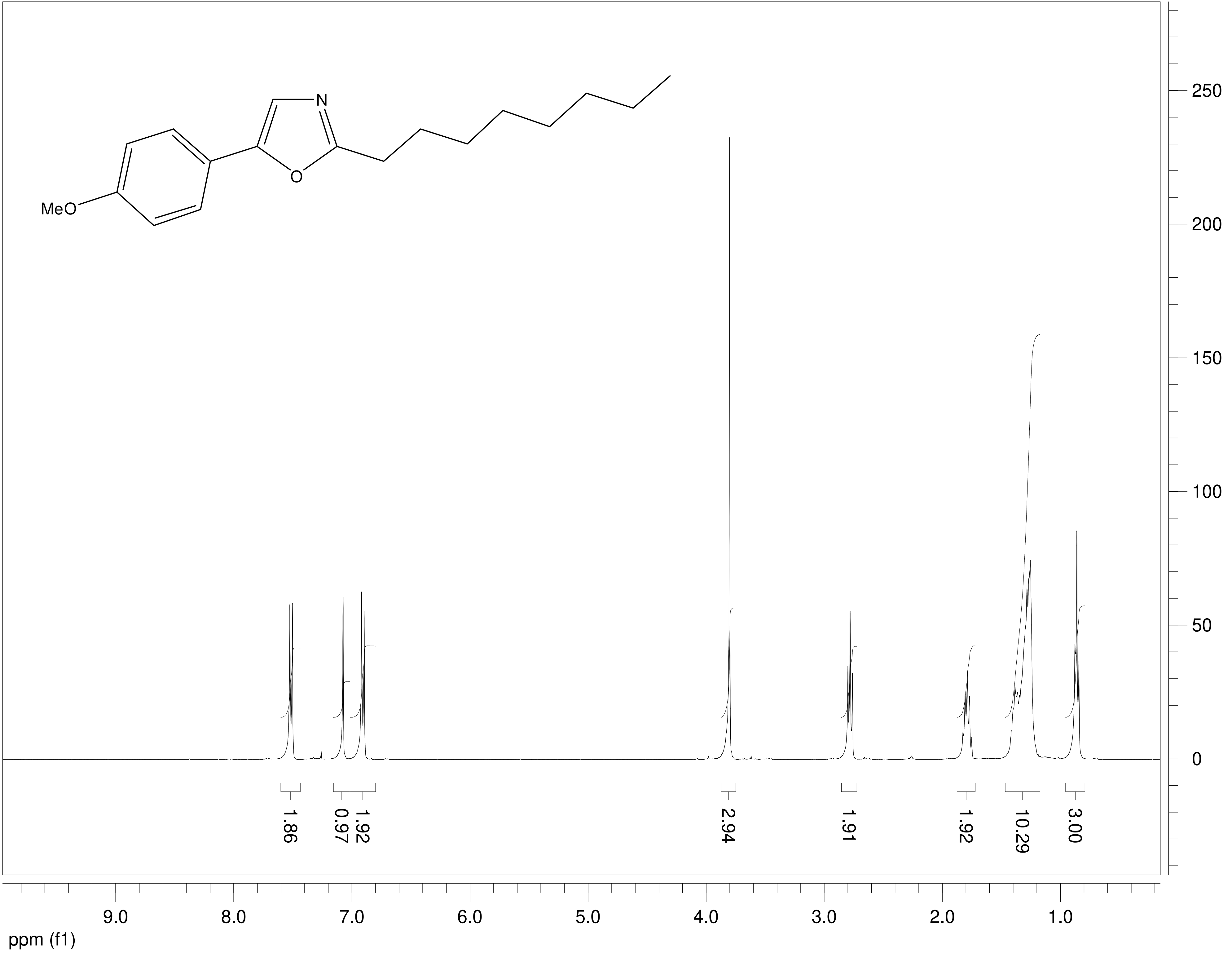
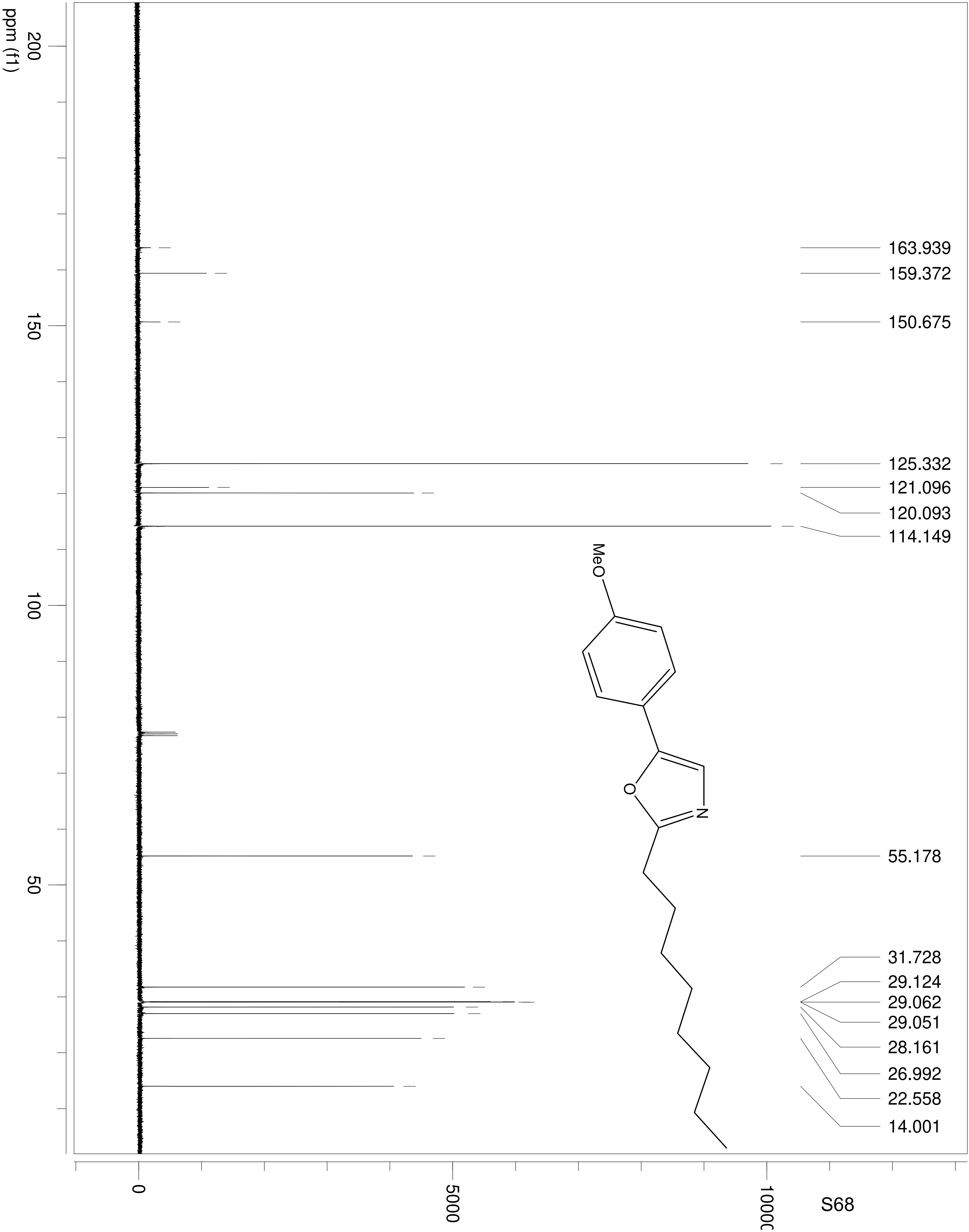
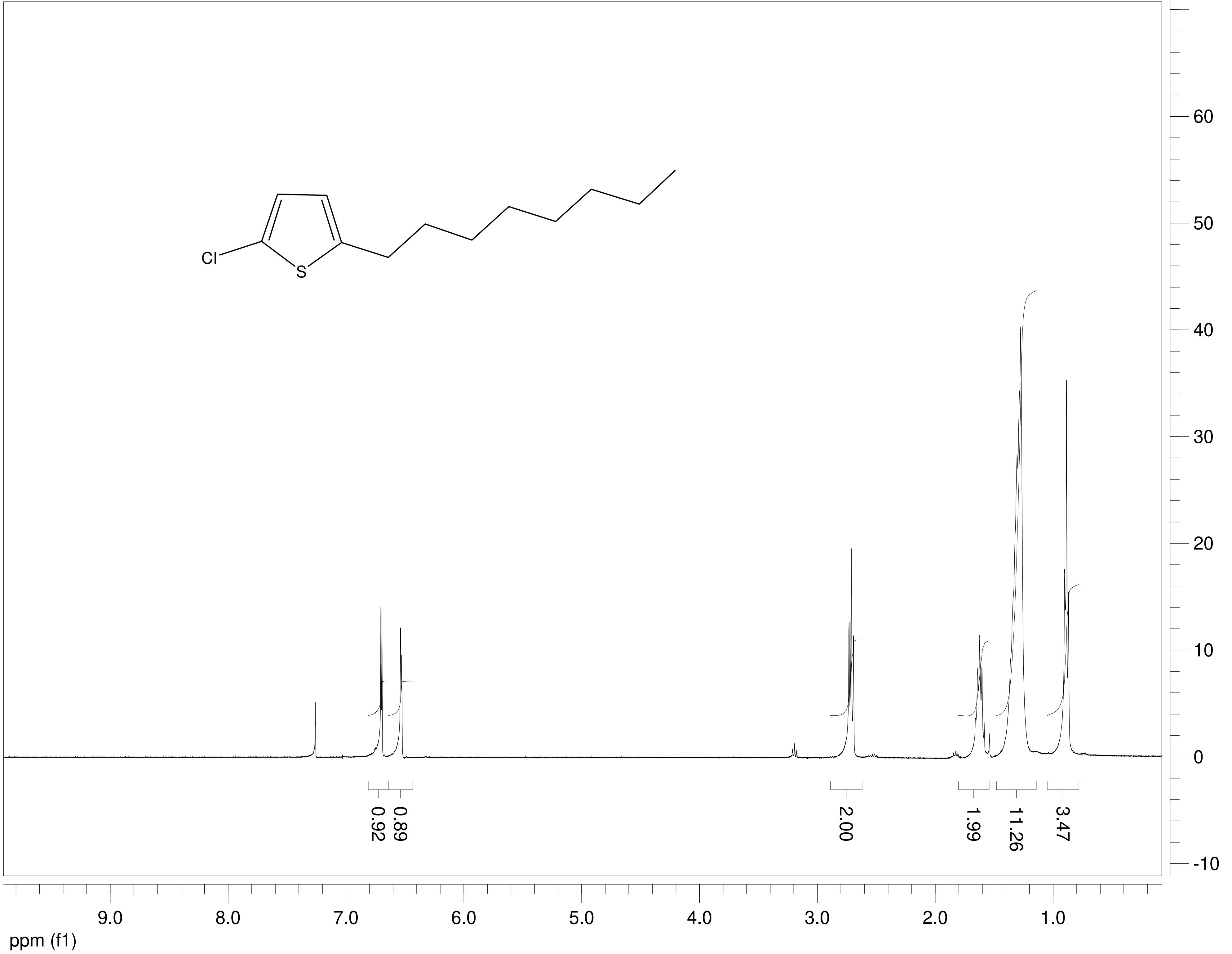
121.448
64.870
34.178
29.510
28.756
28.547
25.773
O
O
N
S
0
500
1000
1500
2000
2500
3000

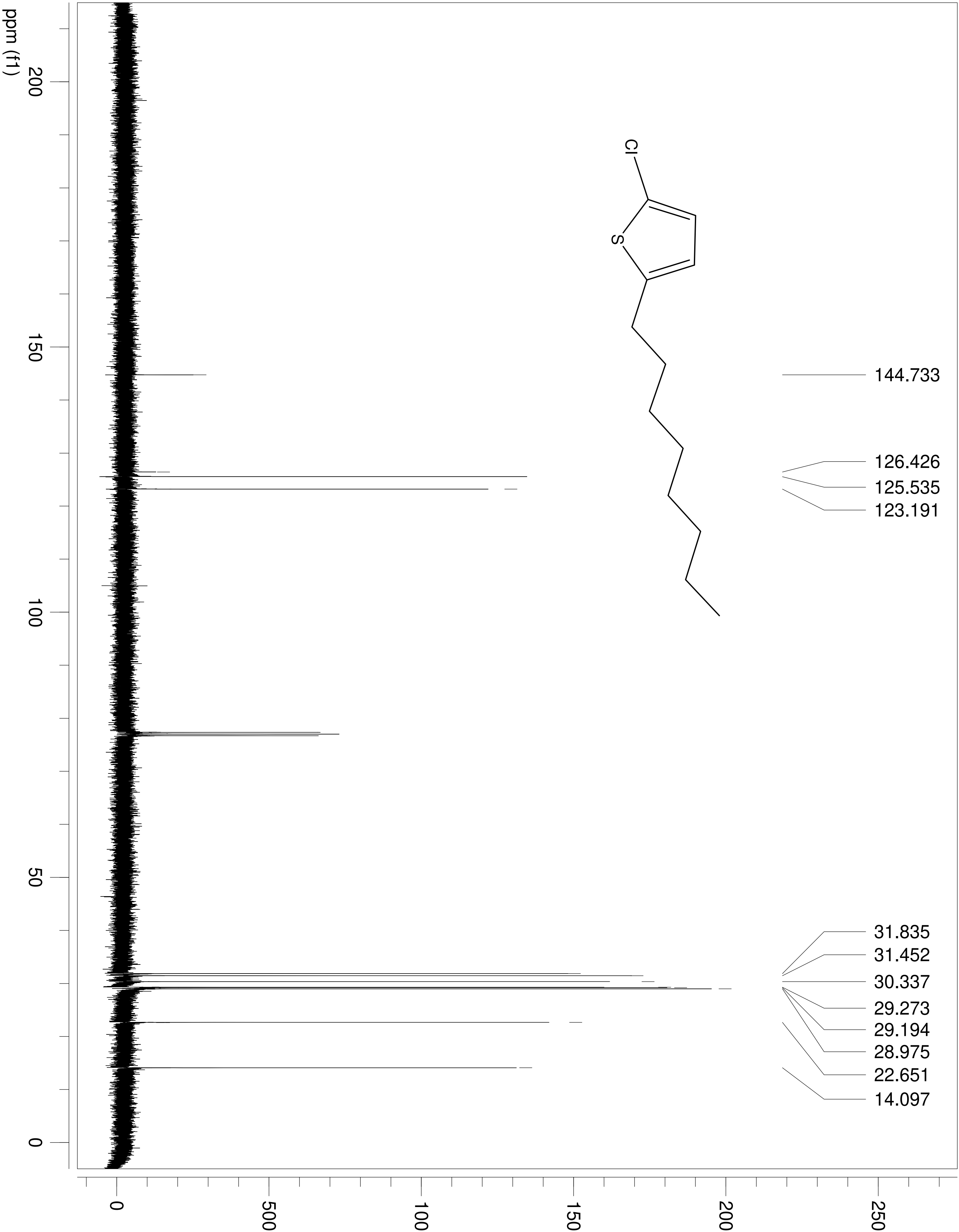

Ph
O
N
N
1.98
2.06
6.28
4.17
2.04
2.00
2.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
350
300
250
200
150
100
50
0
-50

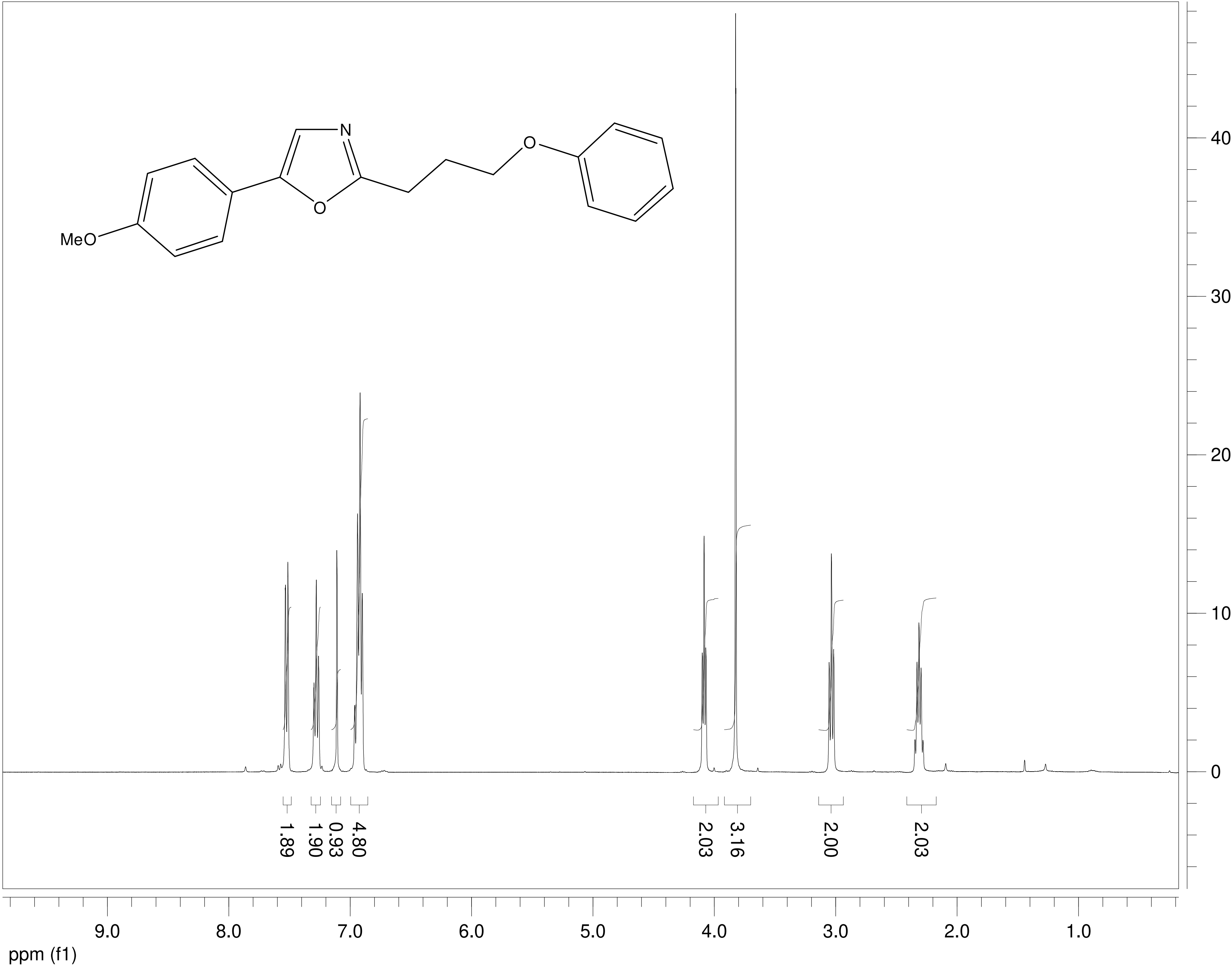

163.076
151.006
140.192
128.709
128.082
127.845
125.609
123.849
122.777
121.673
120.254
118.851
108.480
41.659
25.699
25.399
N
O
N
Ph
15000
10000
5000
0
150
100
50
ppm (f1)

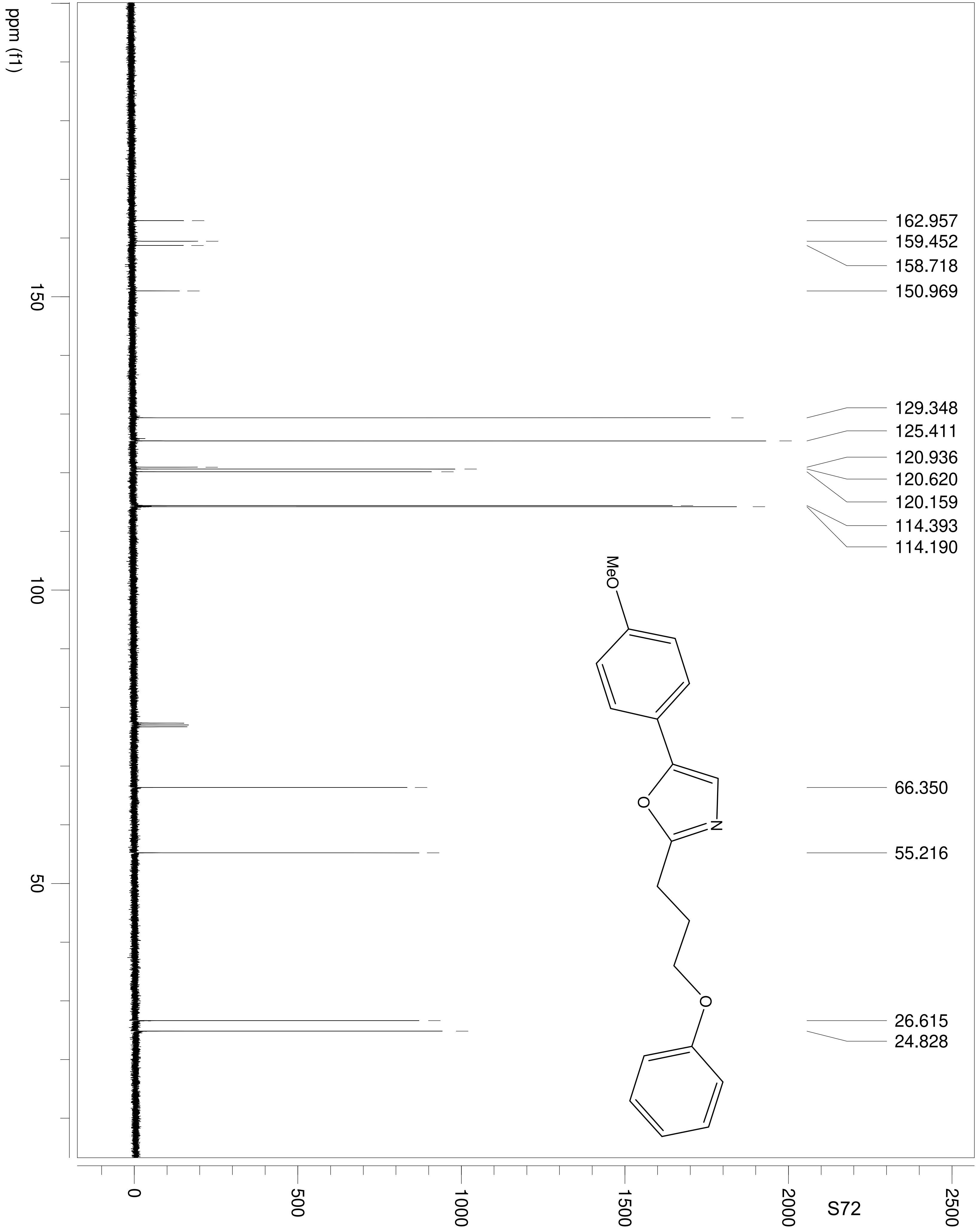

MeO
O
N
1.86
0.97
1.92
2.94
1.91
1.92
10.29
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
0
50
100
150
200
250

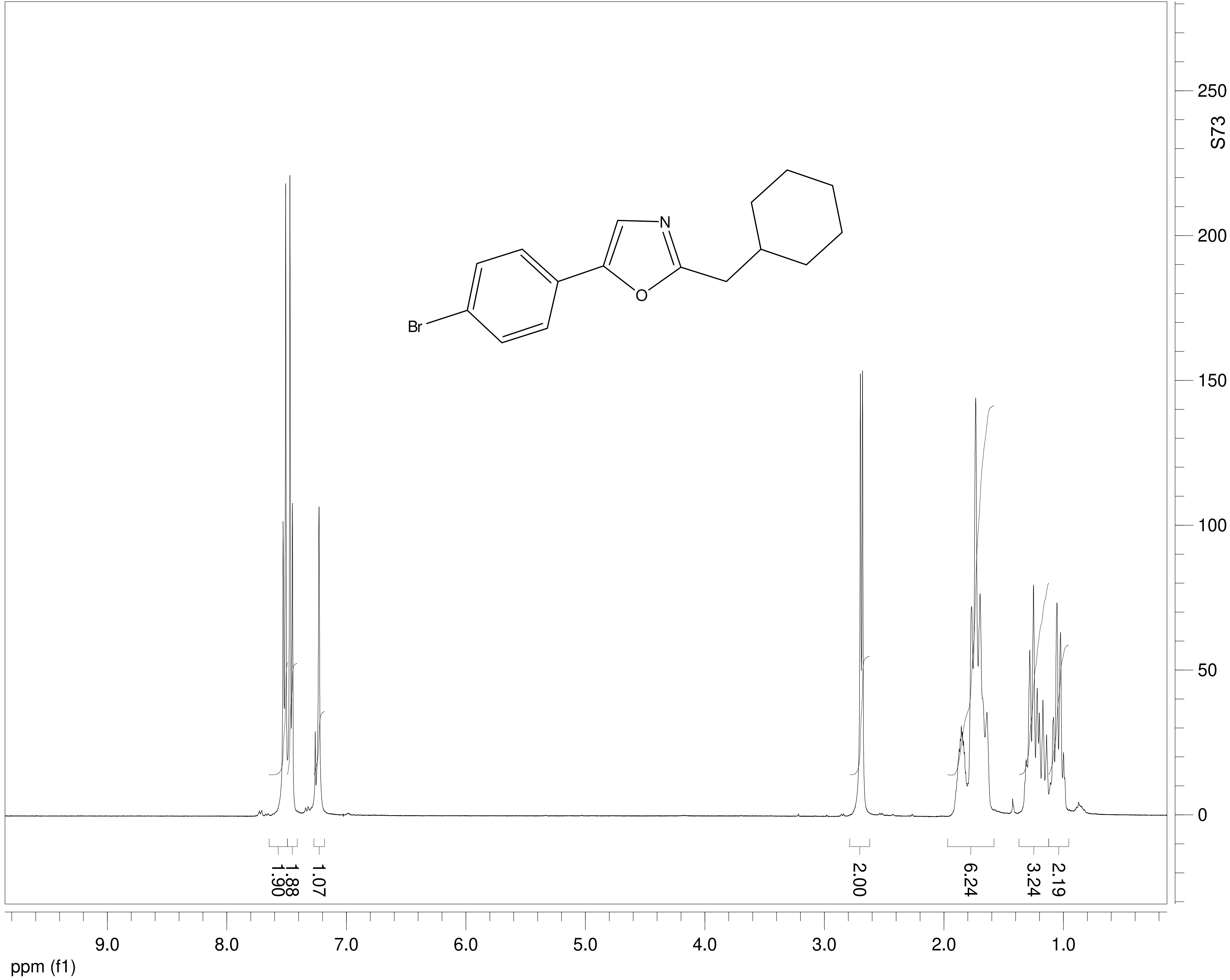

ppm (f1)
200
150
100
50
163.939
159.372
150.675
125.332
121.096
120.093
114.149
55.178
31.728
29.124
29.062
29.051
28.161
26.992
22.558
14.001
MeO
O
N
0
5000
10000

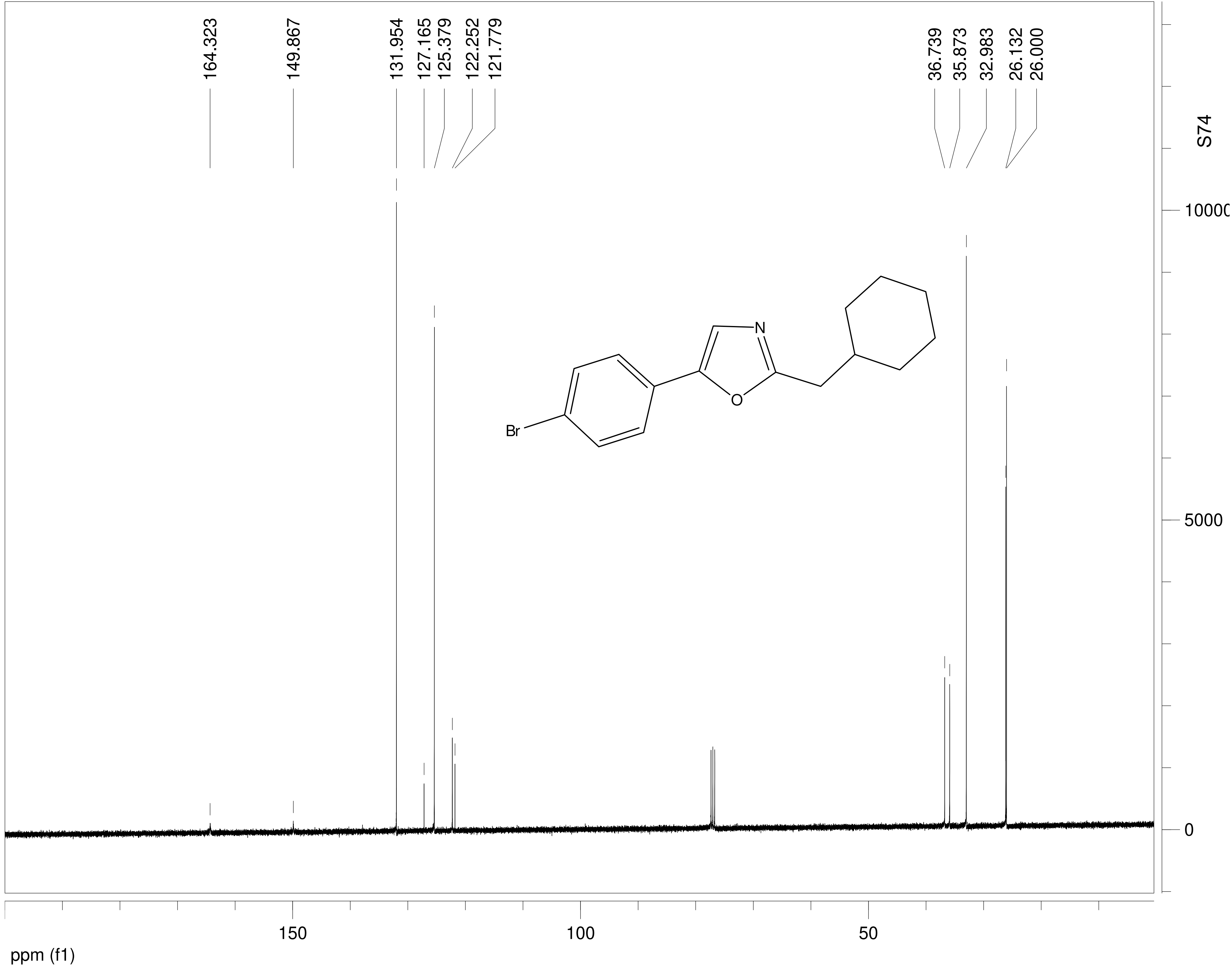

Cl
S
0.92
0.89
2.00
1.99
11.26
3.47
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
60
50
40
30
20
10
0
-10

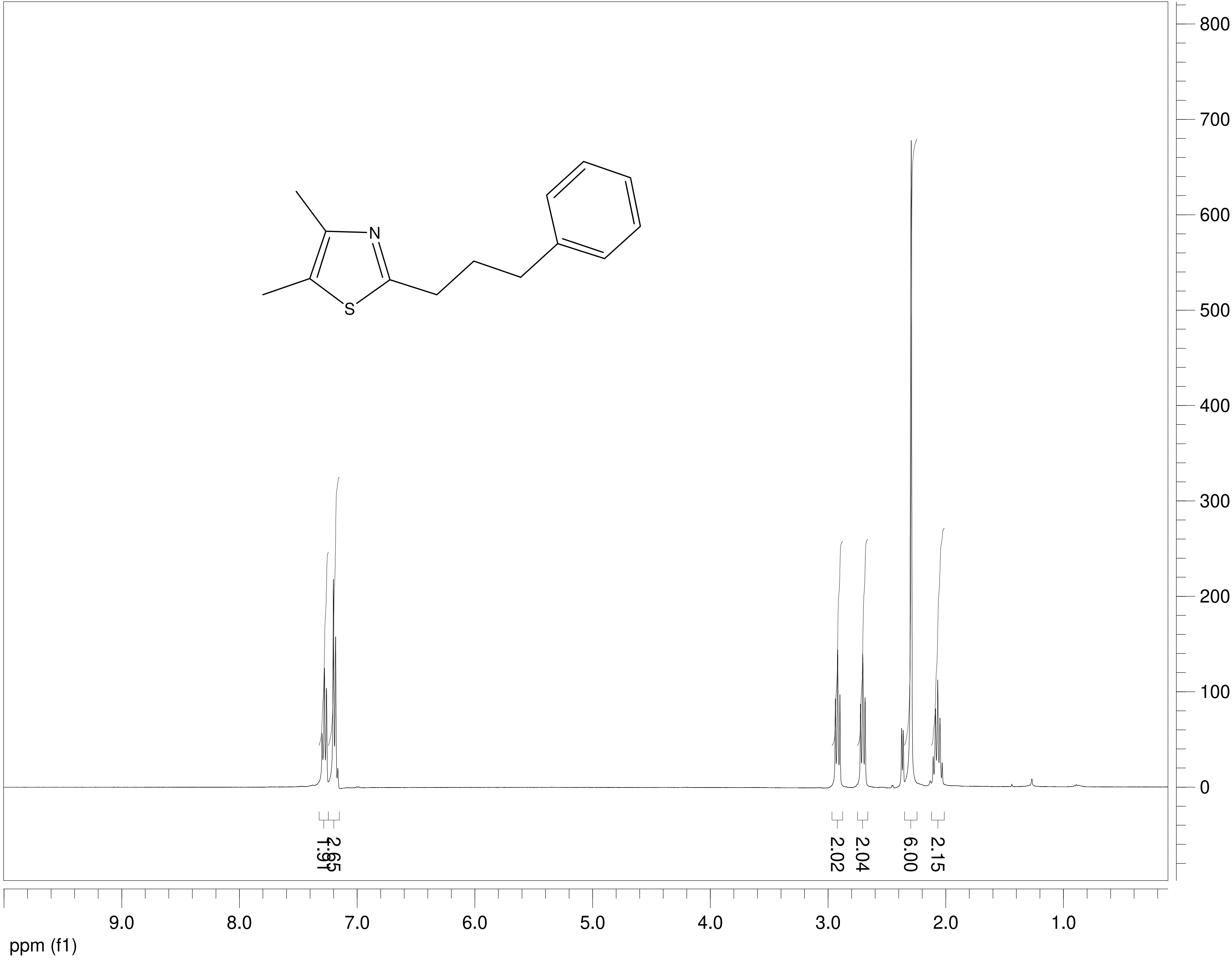

Cl
S
144.733
126.426
125.535
123.191
31.835
31.452
30.337
29.273
29.194
28.975
22.651
14.097
ppm (f1)
200
150
100
50
0
0
500
1000
1500
2000
2500

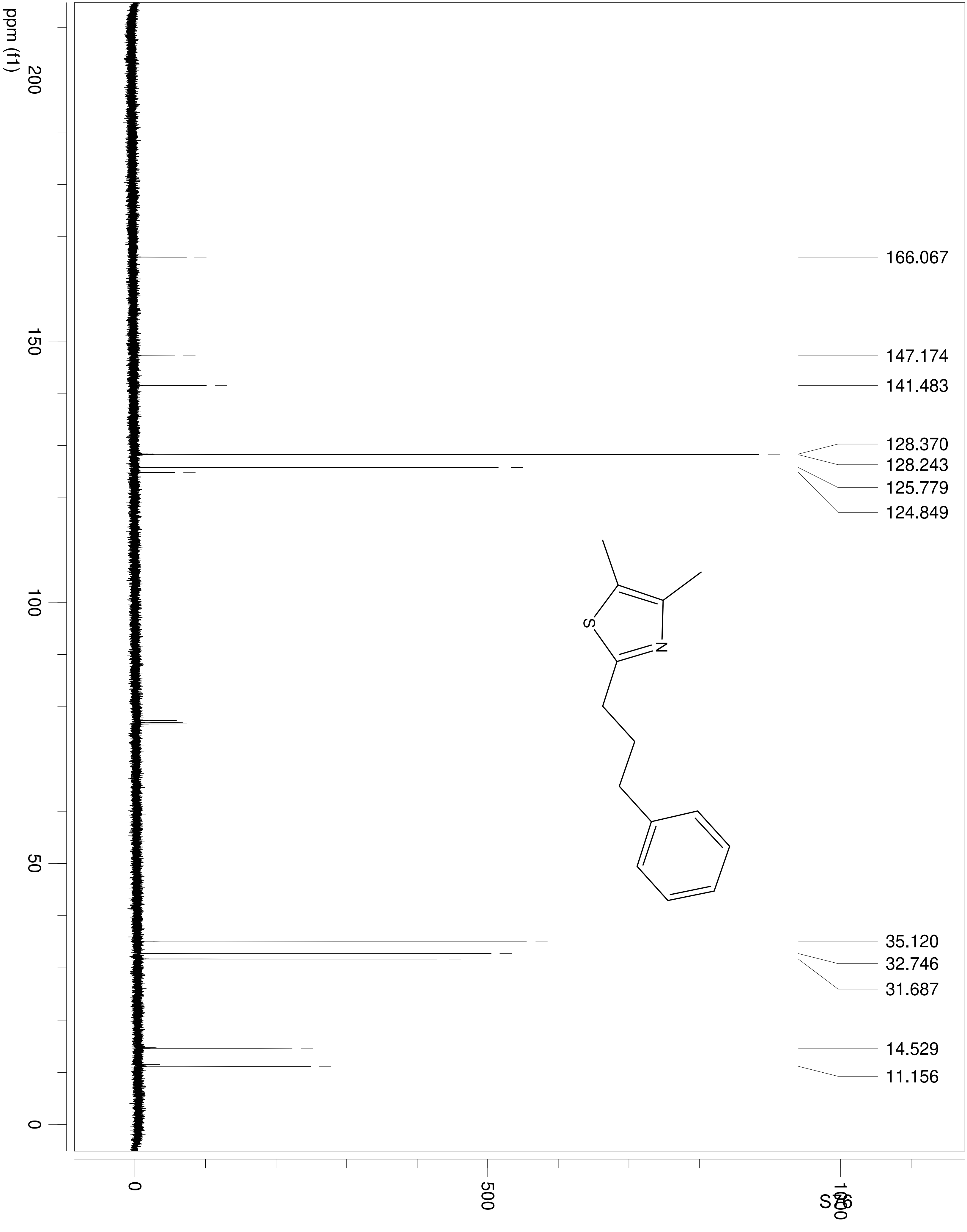

MeO
N
O
O
1.89
1.90
0.93
4.80
2.03
3.16
2.00
2.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
0
100
200
300
400

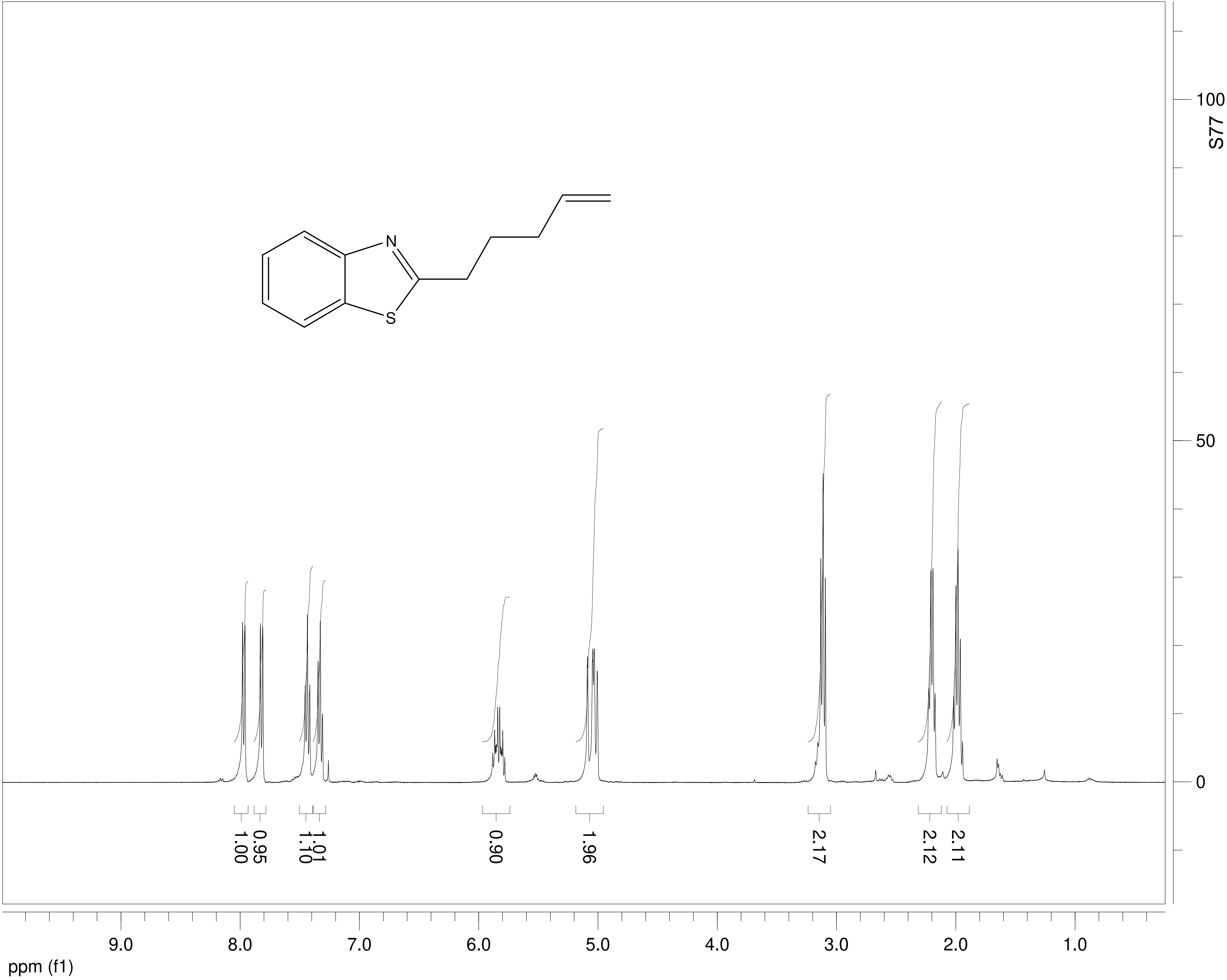

ppm (f1)
150
100
50
0
500
1000
1500
2000
2500
162.957
159.452
158.718
150.969
129.348
125.411
120.936
120.620
120.159
114.393
114.190
66.350
55.216
26.615
24.828
MeO
O
N
O

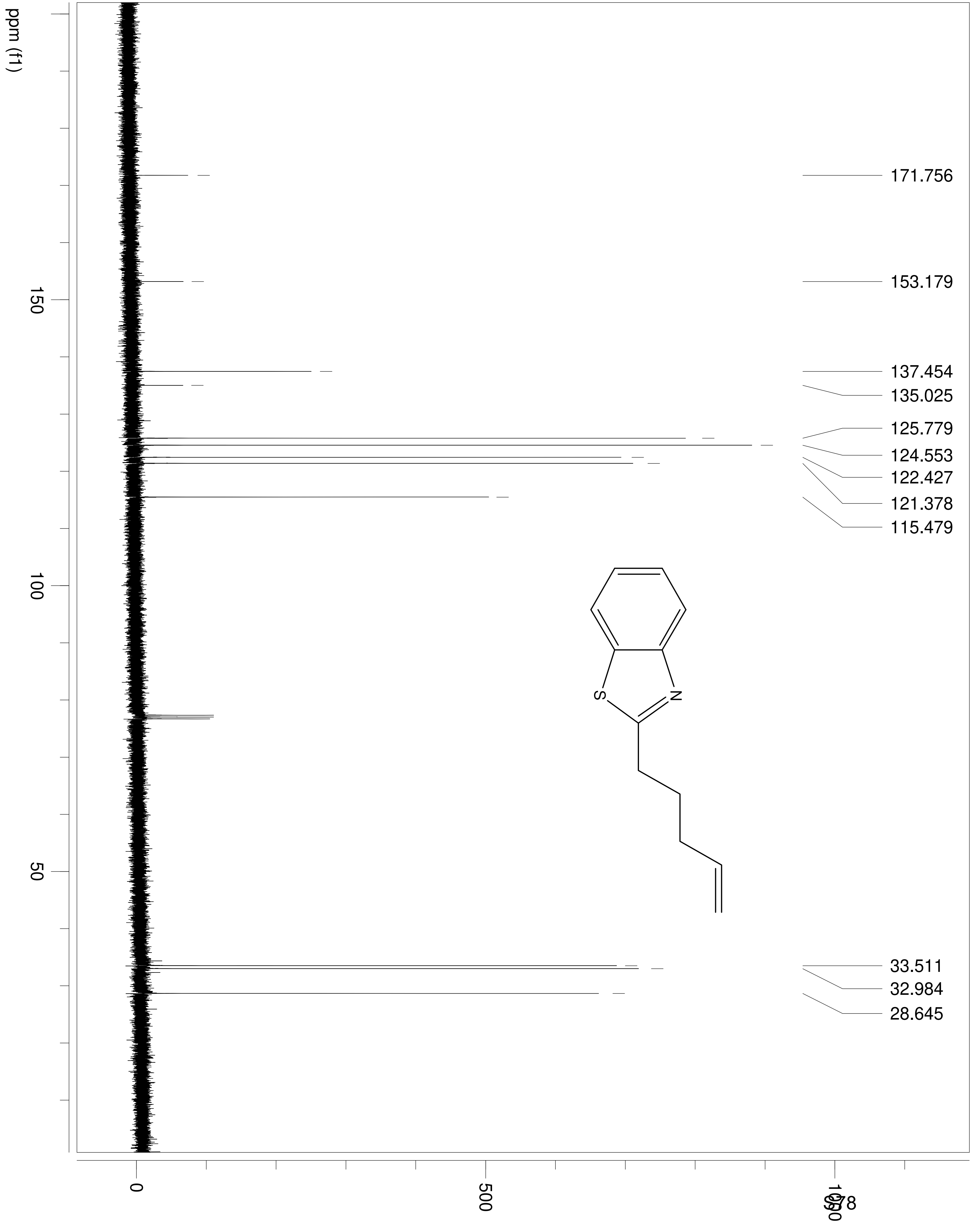

Br
O
N
1.90
1.88
1.07
2.00
6.24
3.24
2.19
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
0
50
100
150
200
250

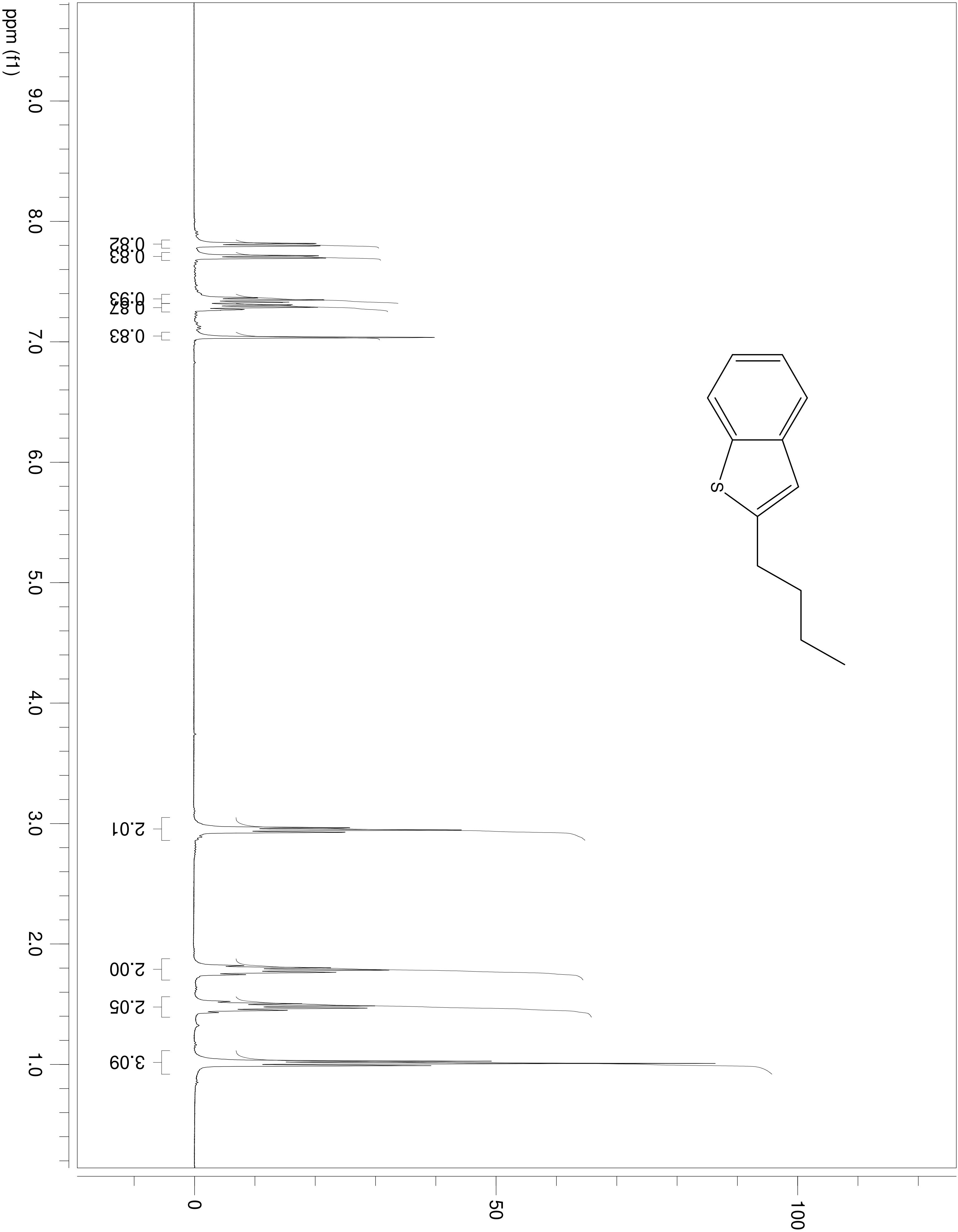

164.323
149.867
131.954
127.165
125.379
122.252
121.779
36.739
35.873
32.983
26.132
26.000
Br
N
O
10000
5000
0
150
100
50
ppm (f1)

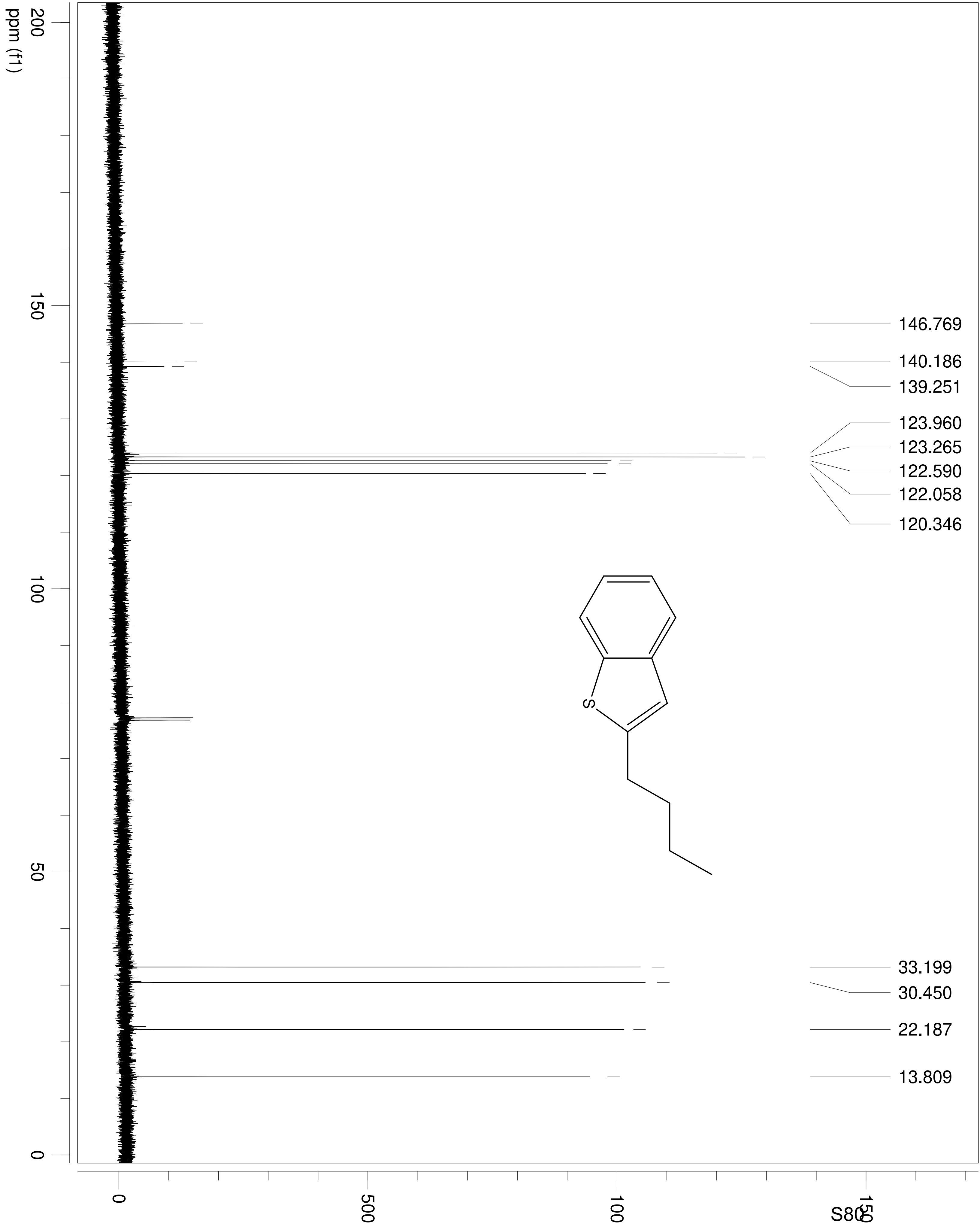

N
S
1.91
2.65
2.02
2.04
6.00
2.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
0
100
200
300
400
500
600
700
800

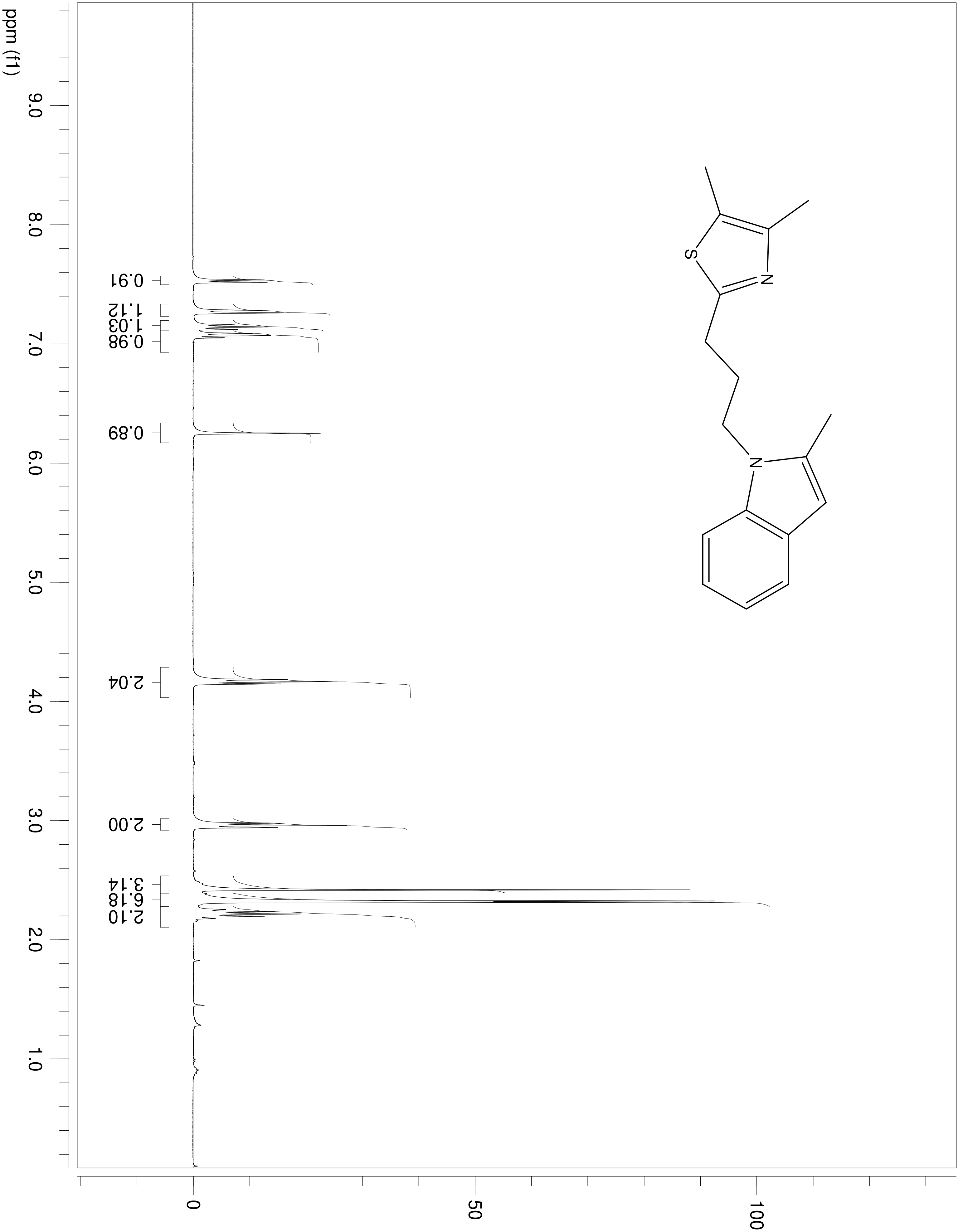

ppm (f1)
200
150
100
50
0
0
500
1000
166.067
147.174
141.483
128.370
128.243
125.779
124.849
35.120
32.746
31.687
14.529
11.156
S
N

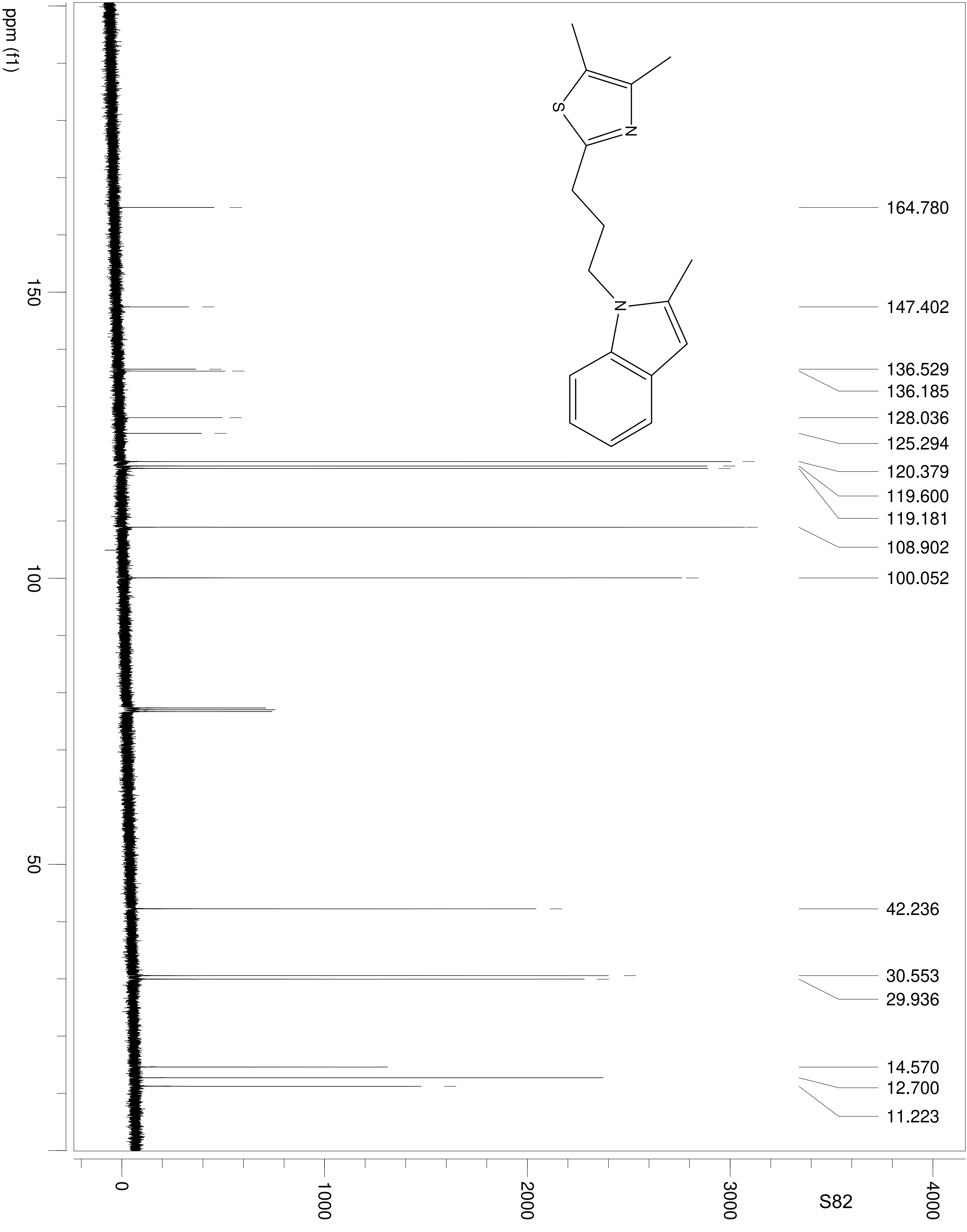

N
S
1.00
0.95
1.10
1.01
0.90
1.96
2.17
2.12
2.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
0
50
100

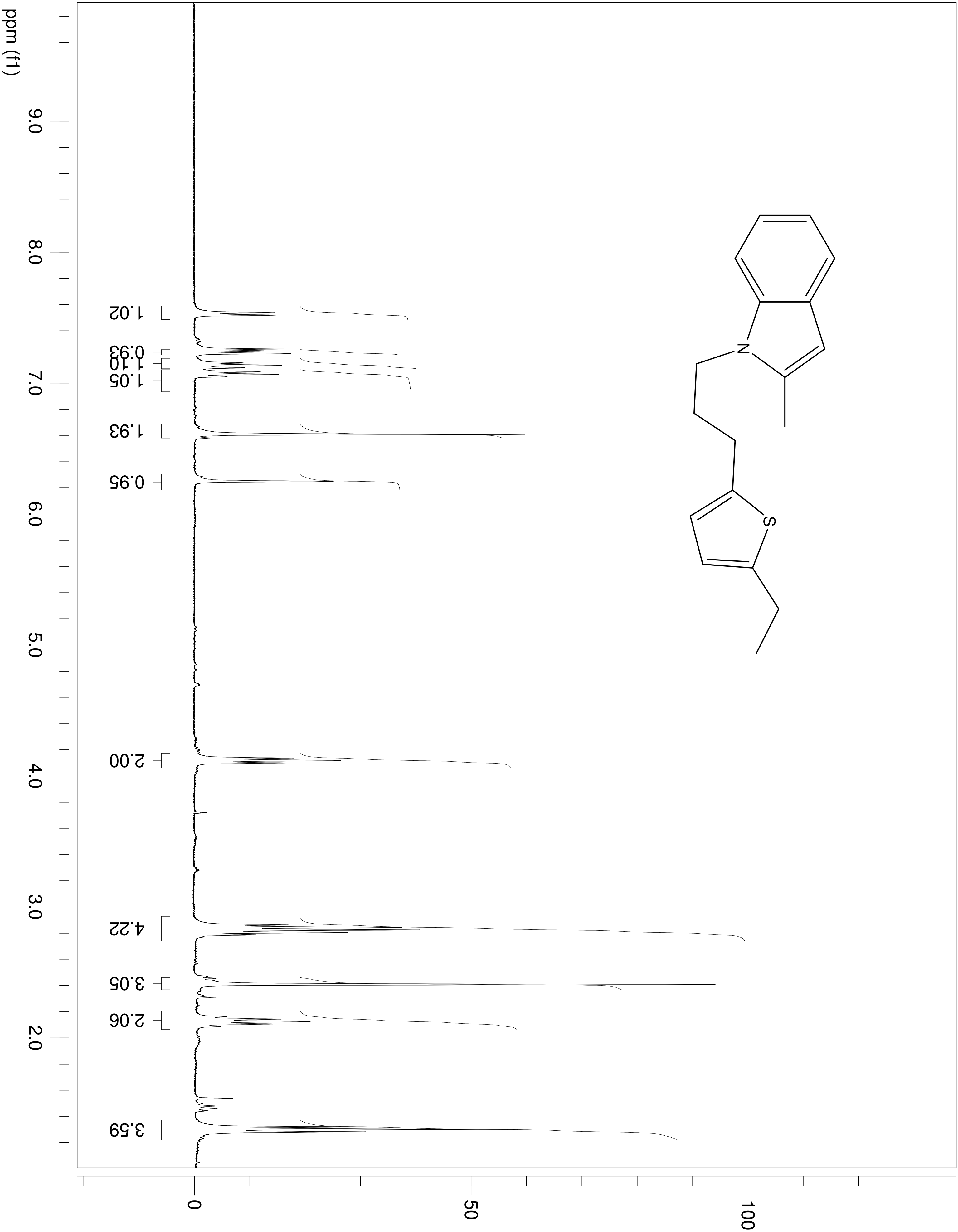

ppm (f1)
150
100
50
0
500
1000
171.756
153.179
137.454
135.025
125.779
124.553
122.427
121.378
115.479
33.511
32.984
28.645
S
N

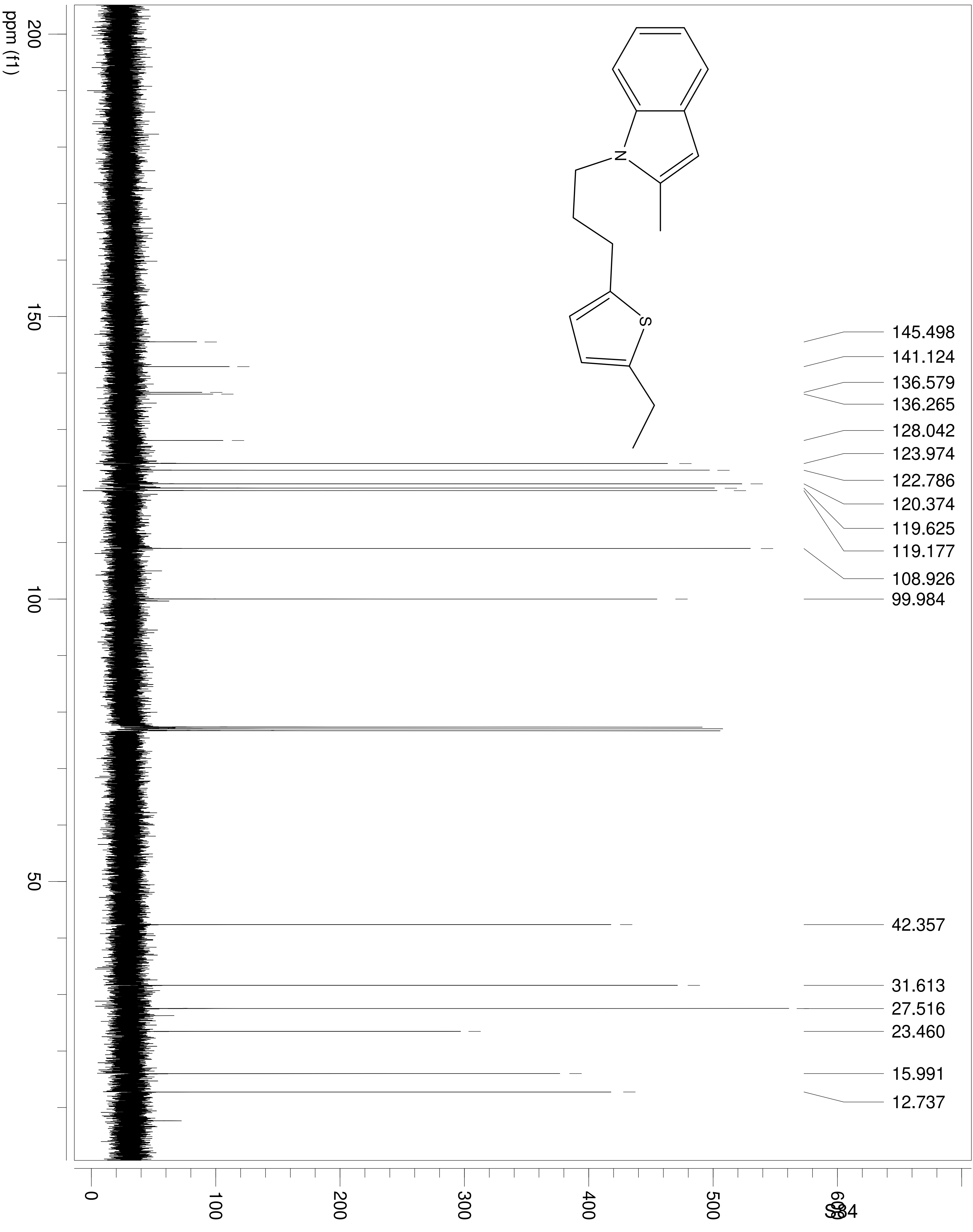

ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.82
0.83
0.93
0.87
0.83
2.01
2.00
2.05
3.09
0
50
100
S

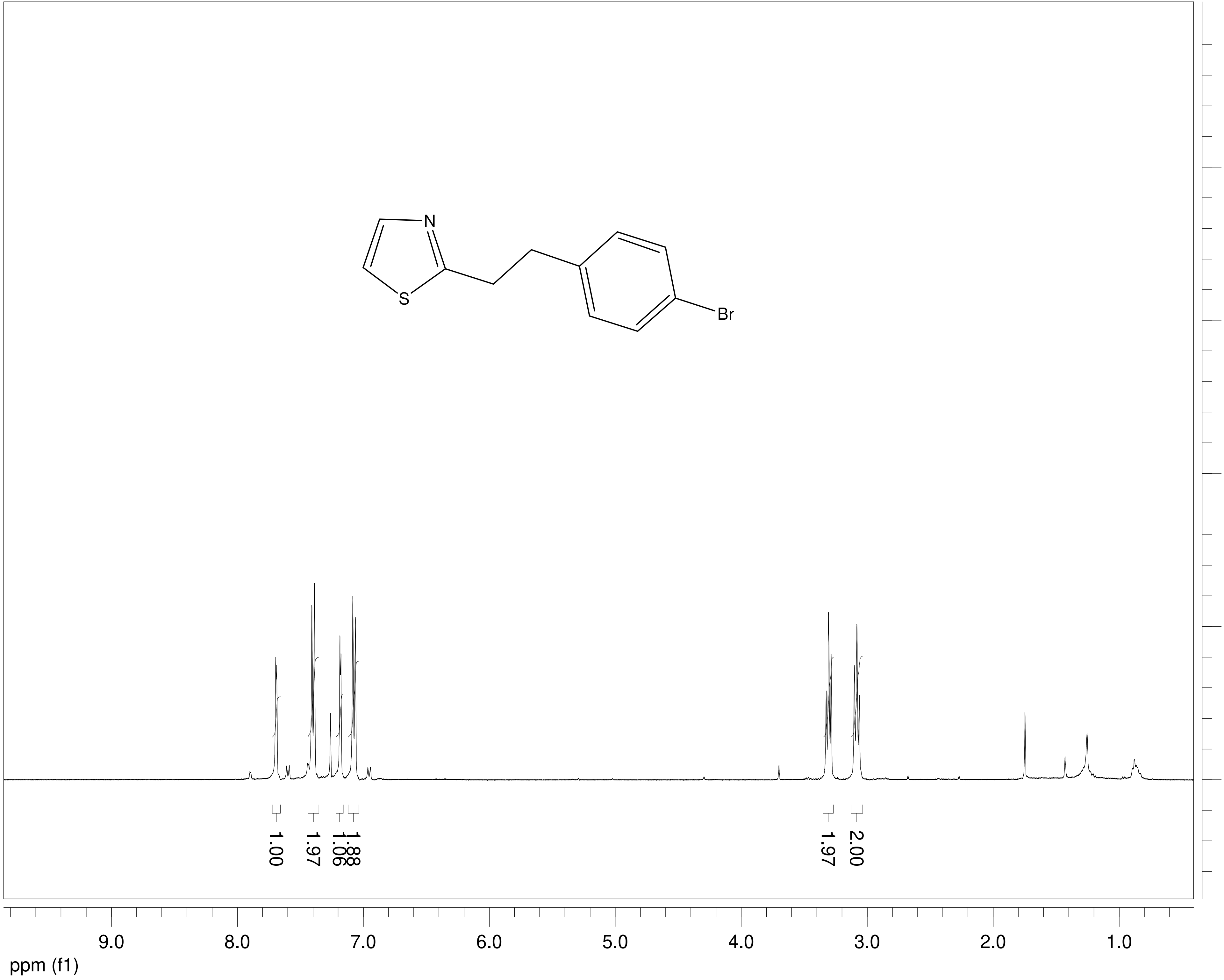

ppm (f1)
200
150
100
50
0
146.769
140.186
139.251
123.960
123.265
122.590
122.058
120.346
33.199
30.450
22.187
13.809
S
0
500
1000
1500

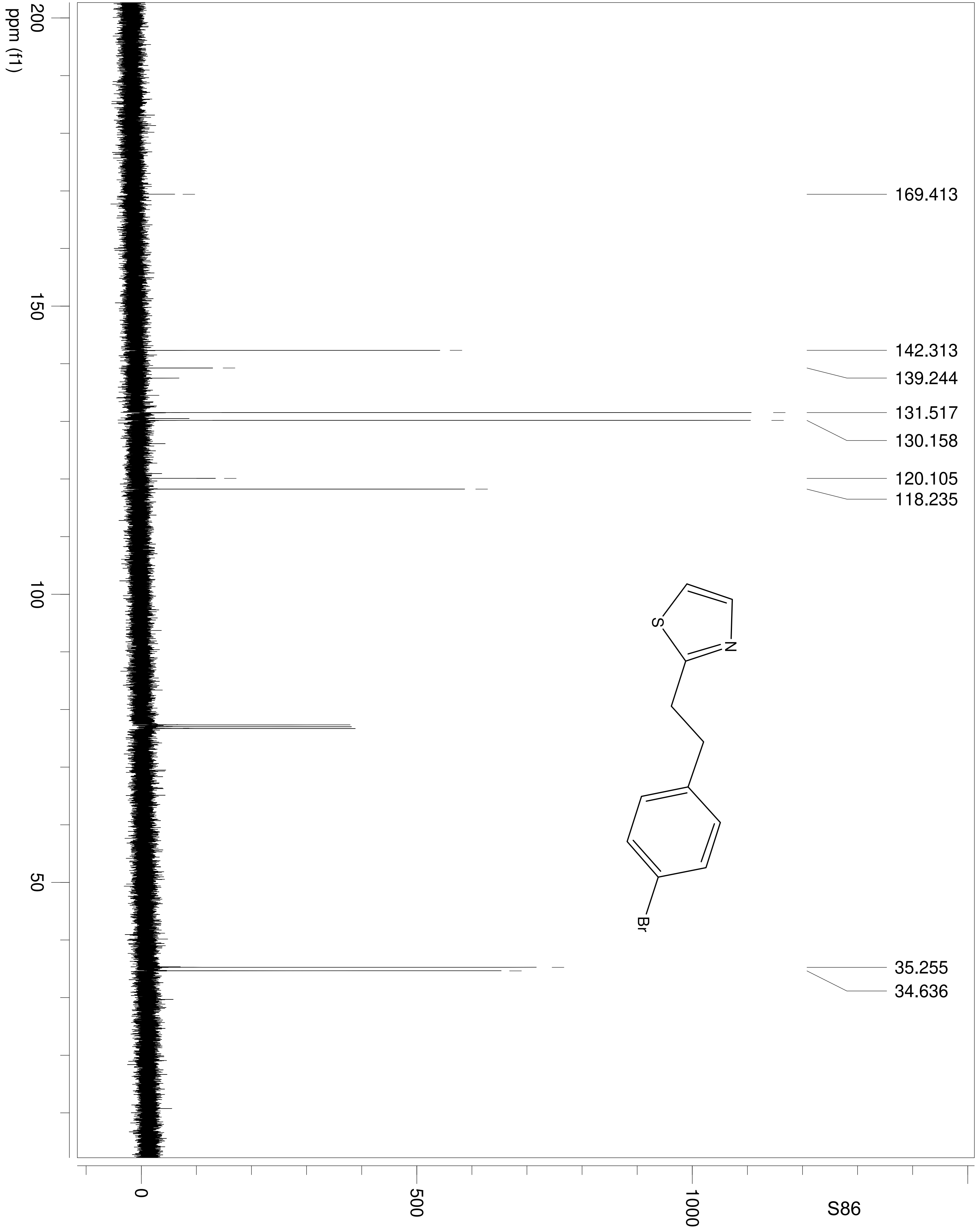

ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.91
1.12
1.03
0.98
0.89
2.04
2.00
3.14
6.18
2.10
0
50
100
S
N
N

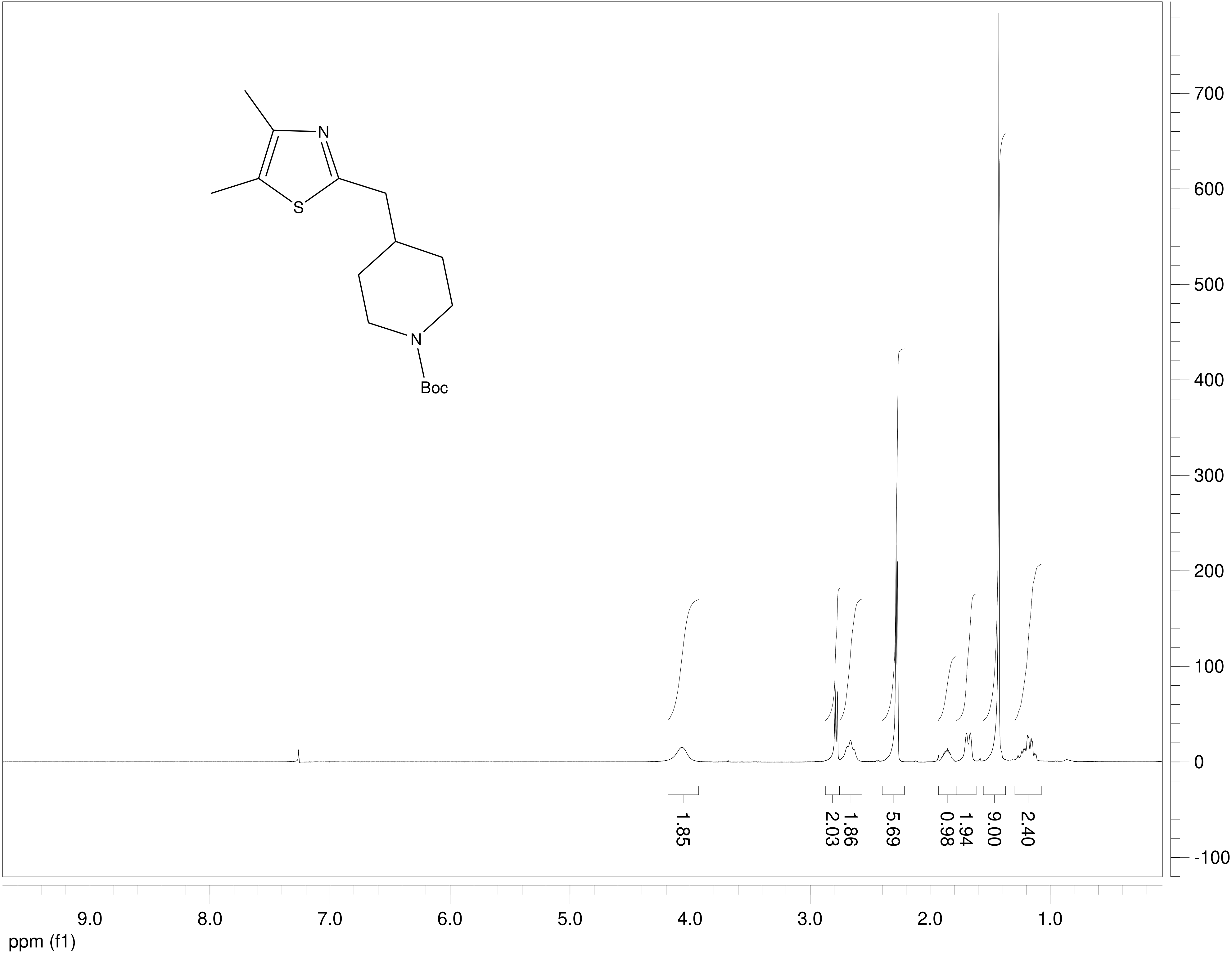

ppm (f1)
150
100
50
0
1000
2000
3000
4000
164.780
147.402
136.529
136.185
128.036
125.294
120.379
119.600
119.181
108.902
100.052
42.236
30.553
29.936
14.570
12.700
11.223
S
N
N

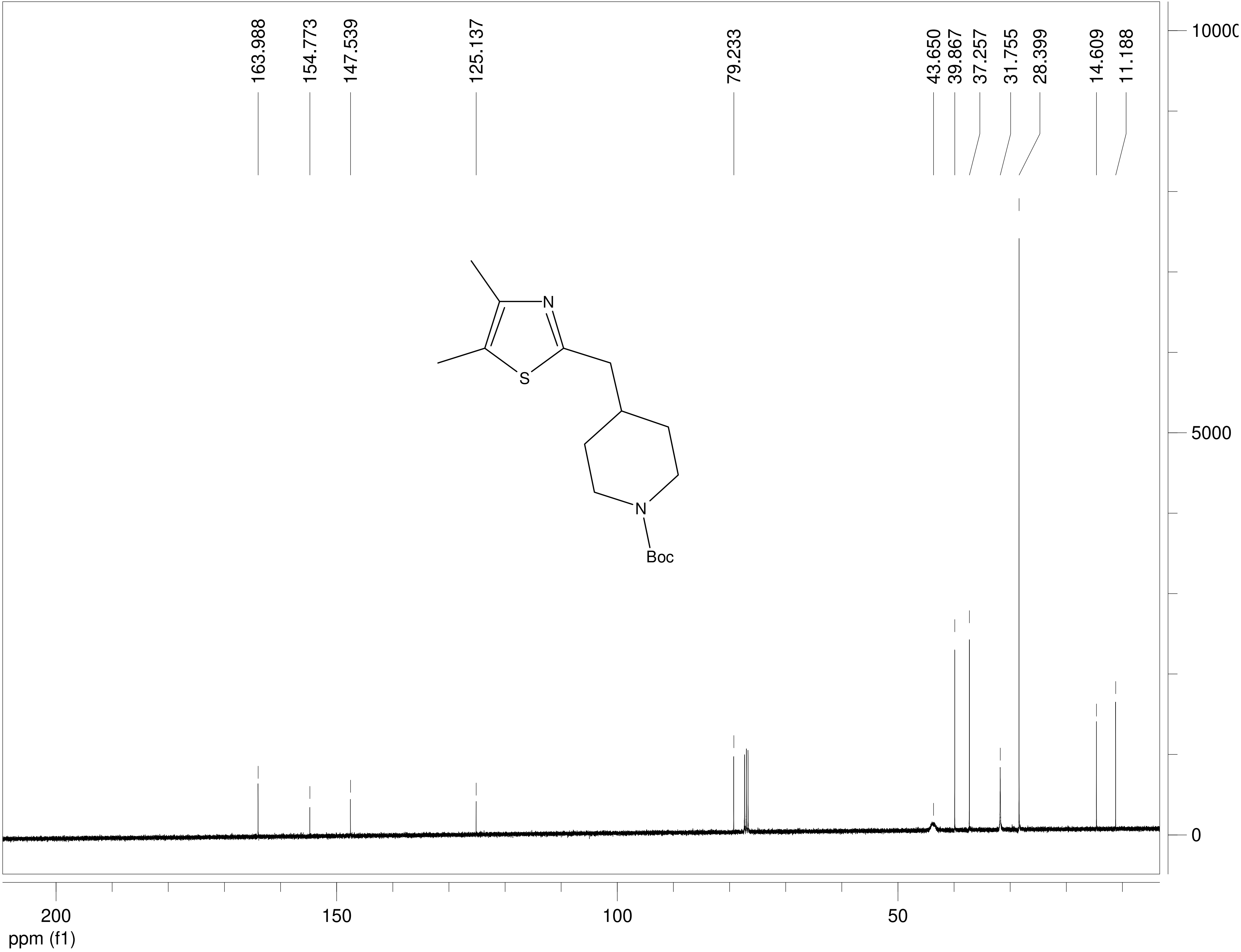

ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.02
0.93
1.10
1.05
1.93
0.95
2.00
4.22
3.05
2.06
3.59
0
50
100
N
S

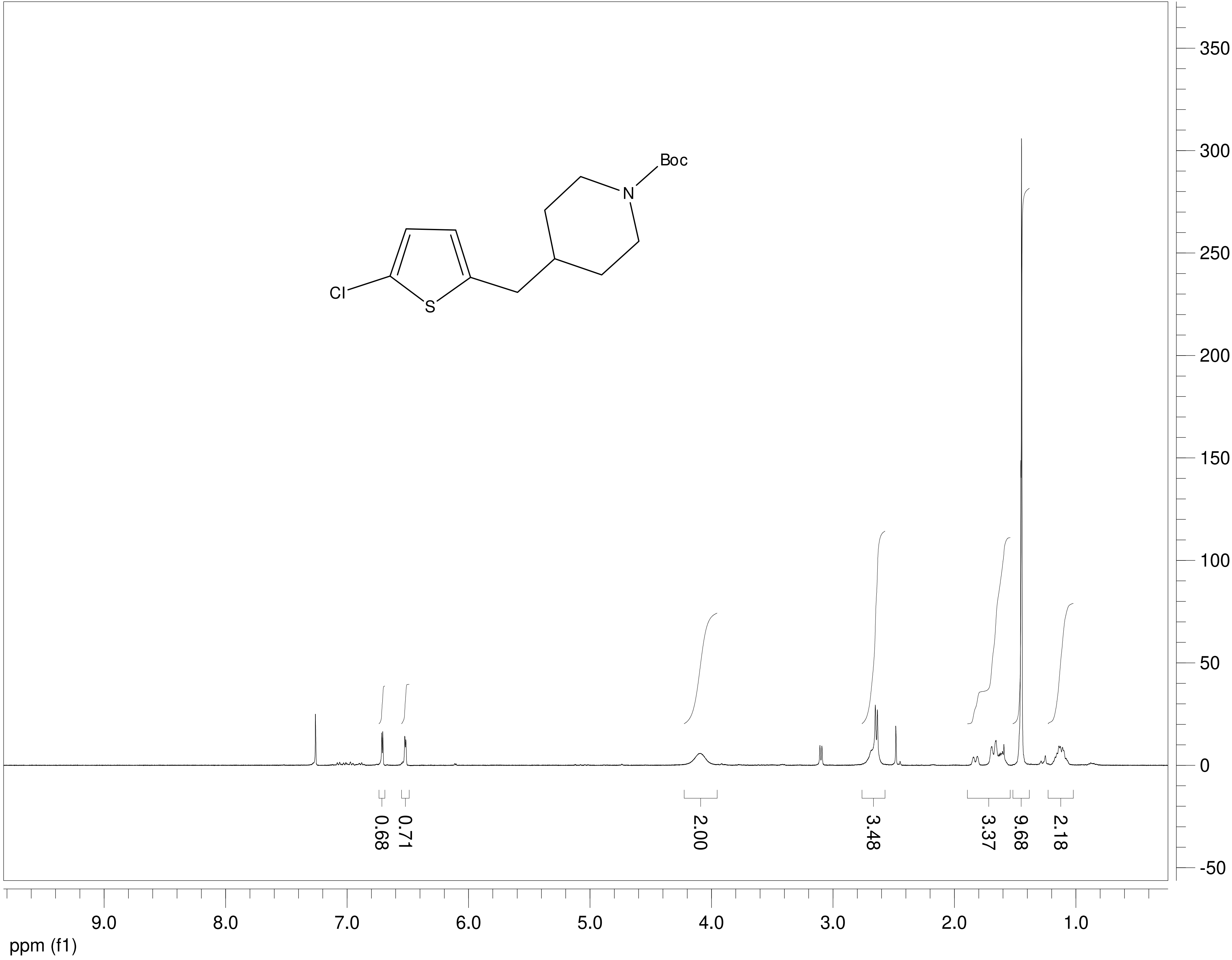

N
S
145.498
141.124
136.579
136.265
128.042
123.974
122.786
120.374
119.625
119.177
108.926
99.984
42.357
31.613
27.516
23.460
15.991
12.737
ppm (f1)
200
150
100
50
0
100
200
300
400
500
600

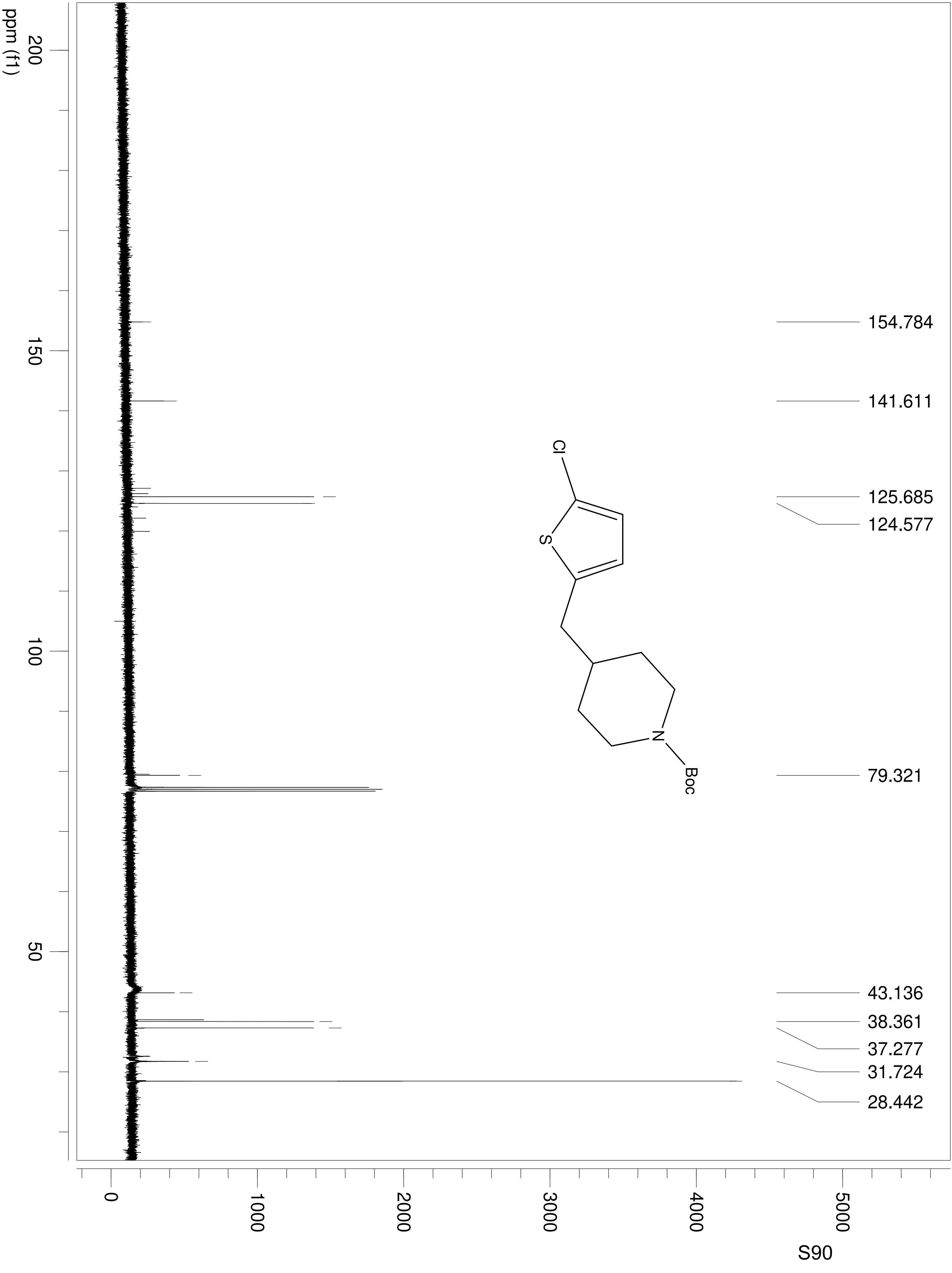

S
N
Br
1.00
1.97
1.06
1.88
1.97
2.00
0
10
20
30
40
50
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


ppm (f1)
200
150
100
50
169.413
142.313
139.244
131.517
130.158
120.105
118.235
35.255
34.636
S
N
Br
0
500
1000

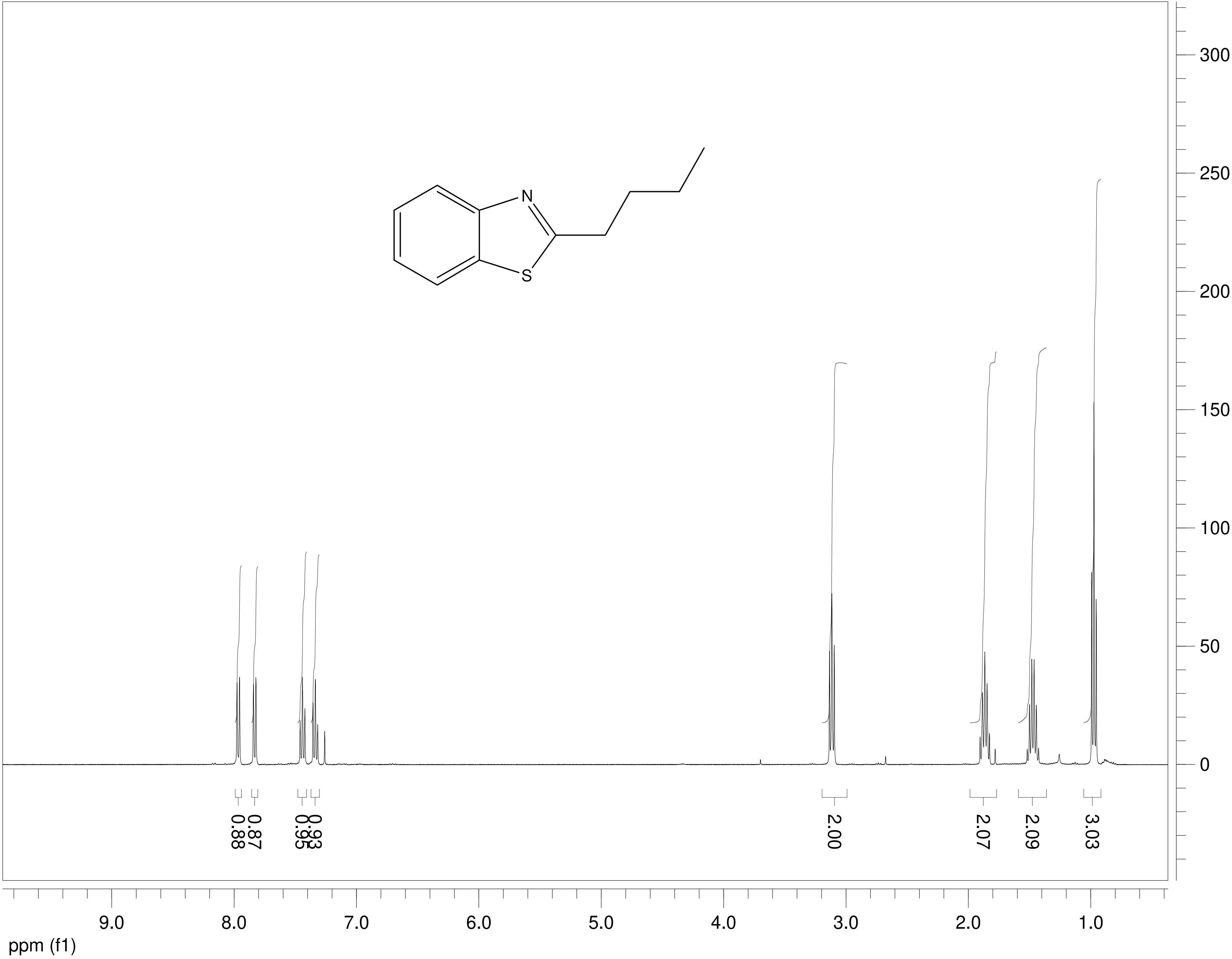

Boc
N
S
N
1.85
2.03
1.86
5.69
0.98
1.94
9.00
2.40
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
700
600
500
400
300
200
100
0
-100

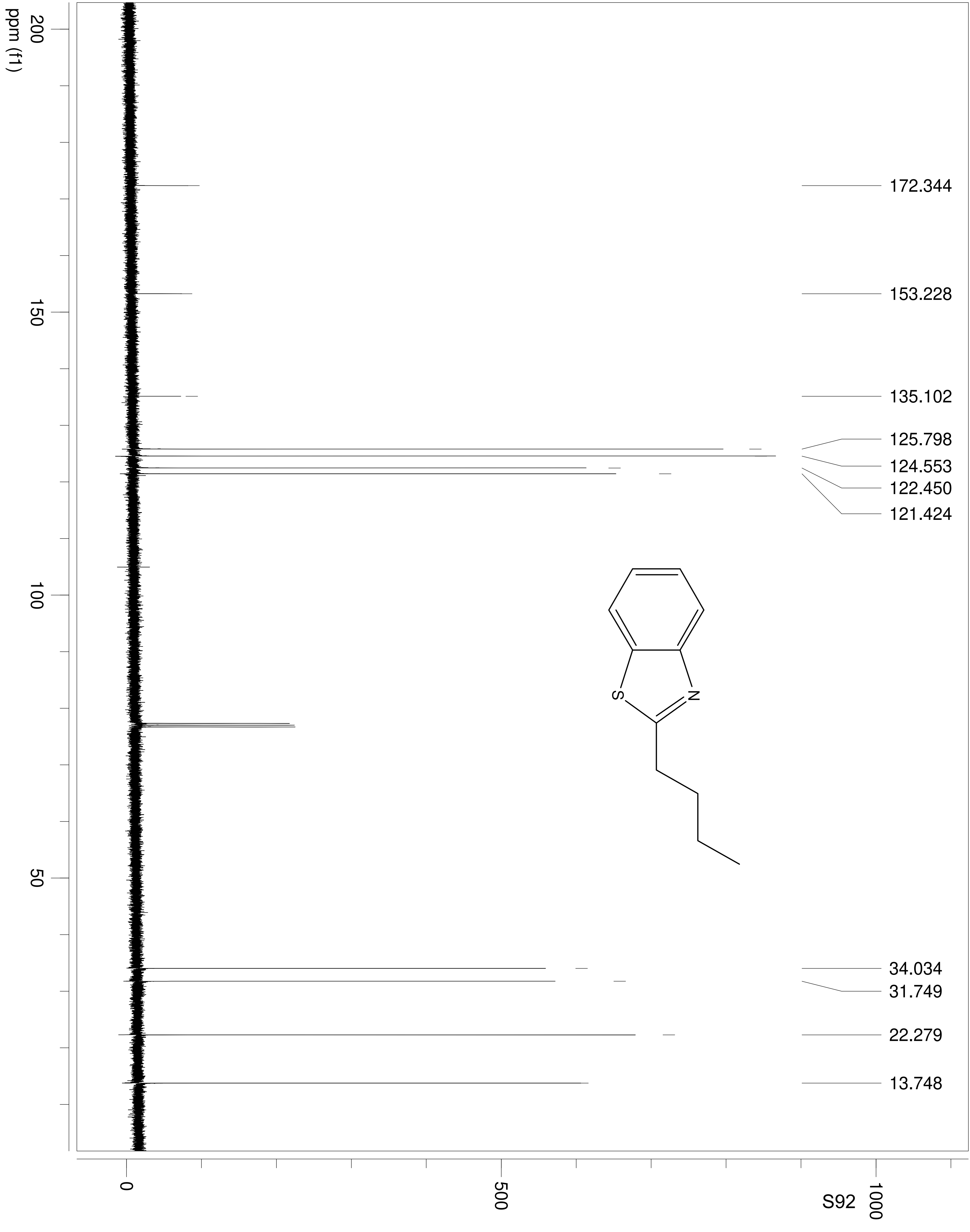

163.988
154.773
147.539
125.137
79.233
43.650
39.867
37.257
31.755
28.399
14.609
11.188
N
S
N
Boc
10000
5000
0
200
150
100
50
ppm (f1)

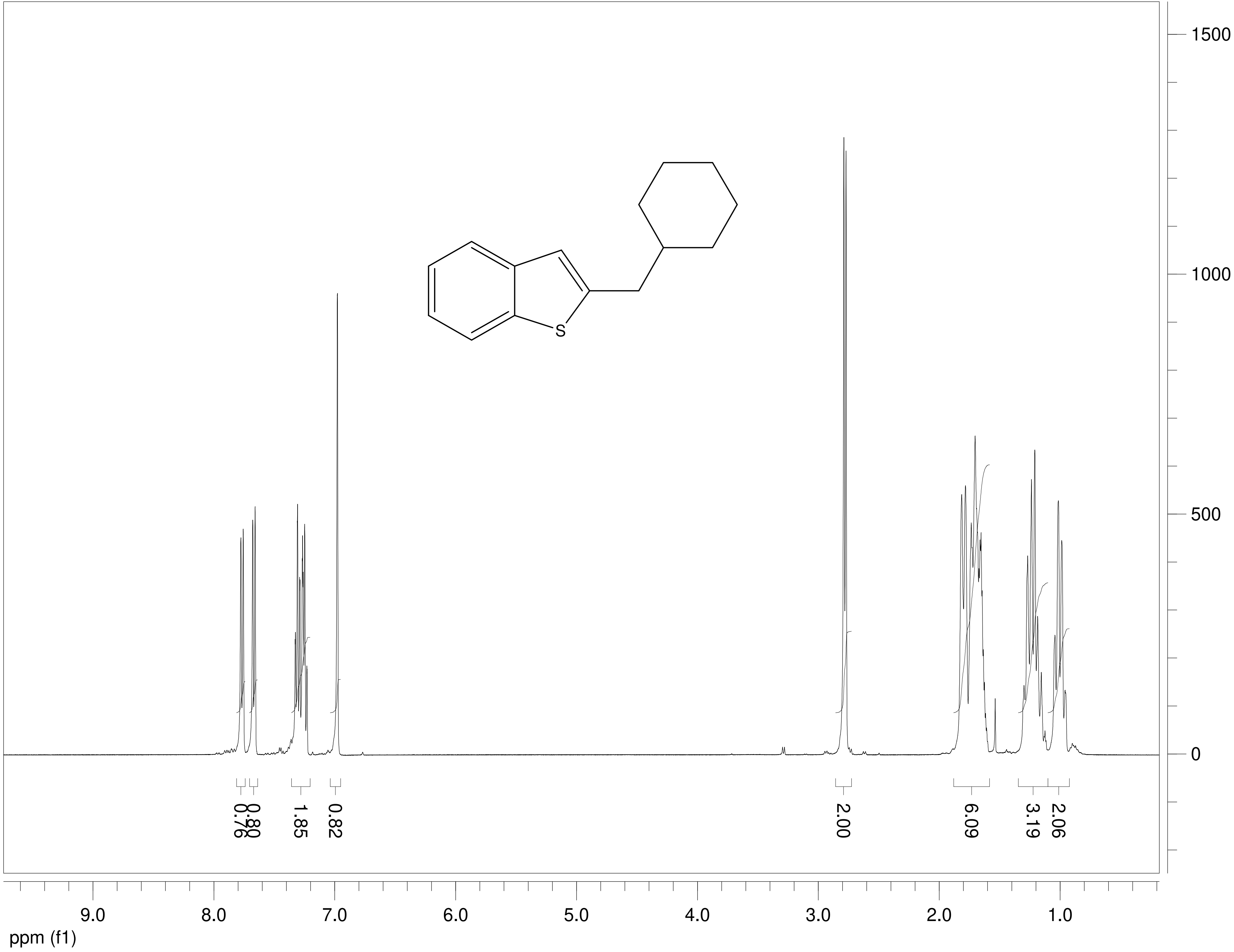

Cl
S
N
Boc
0.68
0.71
2.00
3.48
3.37
9.68
2.18
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
350
300
250
200
150
100
50
0
-50


ppm (f1)
200
150
100
50
154.784
141.611
125.685
124.577
79.321
43.136
38.361
37.277
31.724
28.442
Cl
S
N
Boc
0
1000
2000
3000
4000
5000

S90


N
S
0.88
0.87
0.95
0.93
2.00
2.07
2.09
3.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
0
50
100
150
200
250
300


ppm (f1)
200
150
100
50
172.344
153.228
135.102
125.798
124.553
122.450
121.424
34.034
31.749
22.279
13.748
S
N
0
500
1000


S
0.76
0.80
1.85
0.82
2.00
6.09
3.19
2.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
0
500
1000
1500


ppm (f1)
150
100
50
145.228
140.170
139.460
123.956
123.260
122.573
122.039
121.327
39.743
38.674
33.071
26.422
26.168
S
0
1000
2000
3000
4000
5000