Supporting Information:

Ni-Catalyzed Sonogashira Coupling of Non-activated Alkyl Halides: Orthogonal Functionalization of Alkyl Iodides, Bromides, and Chlorides

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Chemicals and Reagents

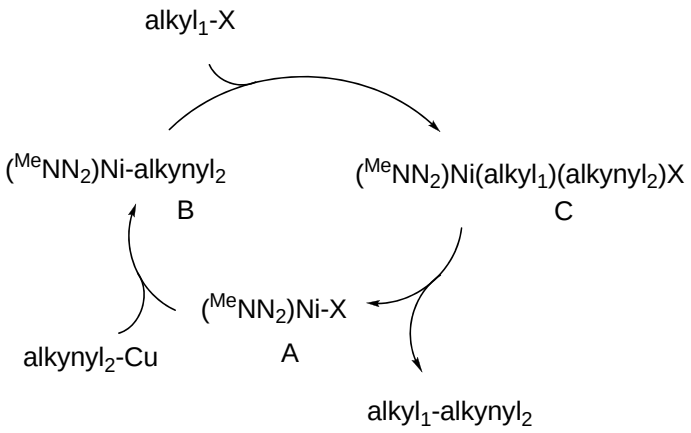
All manipulations were carried out under an inert N_2(g) atmosphere using glovebox techniques. Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Deuterated solvents were purchased from Cambridge 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 [($^{Me}NN_2$)NiCl] and [($^{Me}NN_2$)$_2$Li$_2$] was prepared as described previously.[1] The following starting materials were prepared according to literature procedures: ethyl 4-iodobutanoate (table **1**, entry **4**) from ethyl 4-chlorobutanoate and NaI in acetone by a standard method, N,N-diethyl-6-iodohexanamide (table **1**, entry **5**) from 6-bromo-*N*,*N*-diethylhexanamide[2] and NaI in acetone by a standard method, 1-[1-(3-iodopropyl)-1*H*-pyrrol-2-yl]ethanone (table **1**, entry **6**),[3] 2-(3-iodopropyl)furan (table **1**, entry **7**),[4] 6-chlorohexyl benzoate (table **2**, entry **4**),[5] 1-chloro-4-(2-chloroethyl)benzene (table **2**, entry **14**),[6] 9-(3-chloropropyl)-9H-carbazole (table **2**, entry **12**).[7] In two step reactions the first steps in Eq. 2-4 were done according to procedure described in our previous work. [8,9]

Physical methods

[1] Z. Csok, O. Vechorkin, S. B. Harkins, R. Scopelliti, X. L. Hu, *J. Am. Chem. Soc.* **2008**, *130*, 8156-8157.
[2] J. Zhou, F. C. Fu, *J. Am. Chem. Soc.* **2003**, 125(41), 12527-12530.
[3] D. R. Artis, I. Cho, S. Jaime-Figueroa, J. M. Muchowski, *J. Org. Chem.* **1994**, 59 (9), 2456-2466.
[4] G. Gomez, H. Rivera, I. Garcia, L. Estevez, Y. Fall, *Tetrahedron Letters* **2005**, 46(35), 5819-5822.
[5] Ian H. Gilbert et al., *J. Med. Chem.* **2006**, 49, 4183-4195.
[6] M. Yus et al., *Journal of Organometallic Chemistry* **2002**, 663, 21-31.
[7] J. W. Hulshof et al., *Bioorg. Med. Chem.* **2006**, 14, 7213-7230.
[8] O. Vechorkin, X. L. Hu, *Angew. Chem. Int. Ed.* **2009**, *48*, 2937-2940.
[9] O. Vechorkin, V. Proust, and X. L. Hu, *J. Am. Chem. Soc.* **2009**, 131, 9756-9766.

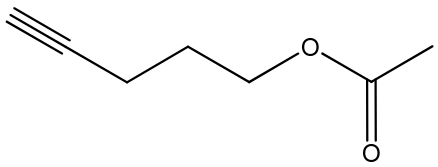
The ^{1}H and ^{13}C NMR spectra were recorded at 293 K on a Bruker Avance 400 spectrometer. ^{1}H NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si ($\delta = 0$ ppm). The $^{13}C\{^{1}H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (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. The temperature of reactions below room temperature was regulated by a Julabo FT-902 chiller.

Figure S1. A possible catalytic cycle for the Sonogashira reactions.



Note: There might be additional steps going from C to A and the coupling product, as suggested for our previously reported Ni-catalyzed Kumada-Corriu-Tamao coupling with sp^2-Grignard reagents (JACS, 2009, 131, 9756-9766). The formal oxidation state of C is Ni^{IV}, but it might also be a Ni^{III}-ligand radical. Alternative pathways exist and more detailed study is warranted.

Synthesis of substrates



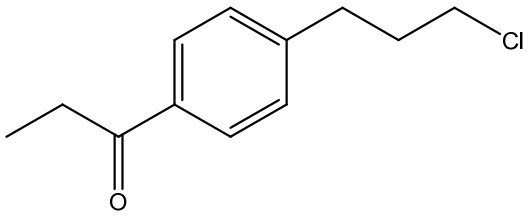
pent-4-ynyl acetate

This compound was synthesized according to a general method described in the literature[10] starting from pent-4-yn-1-ol and acetic anhydride.

^{1}H NMR (400MHz, $CDCl_3$): 4.16 (t, J = 6.2 Hz, 2H), 2.29 (td, J_1 = 7.0 Hz, J_2 = 2.6 Hz, 2H), 2.05 (s, 3H), 1.97 (t, J = 2.6 Hz, 1H), 1.85 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 170.9, 82.9, 68.9, 62.8, 27.4, 20.8, 15.1.

HRCI-MS: calculated for ($C_7H_{11}O_2$, M+H), 127.0759; found, 127.0755.



1-(4-(3-chloropropyl)phenyl)propan-1-one

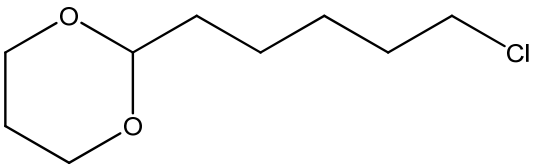
This compound was synthesized by the same way as 1-(4-(2-chloroethyl)phenyl)propan-1-one[11] from (3-chloropropyl)benzene and propionyl chloride.

[10] B. C. Ranu, S. S. Dey and A. Hajra, *Green Chemistry*, **2003**, 5, 44-46.
[11] Lowe et al., *Journal of Medicinal Chemistry* **1991**, Vol. 34, No. 6, 1860-1866.

^{1}H NMR (400MHz, $CDCl_3$): 7.90 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 2.98 (q, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.09 (m, 2H), 1.21 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 200.3, 146.1, 135.0, 128.6, 128.2, 43.9, 33.5, 32.6, 31.6, 8.2.

HRCI-MS: calculated for ($C_{12}H_{16}ClO$, M+H), 211.0890; found, 211.0880.



2-(5-chloropentyl)-1,3-dioxane

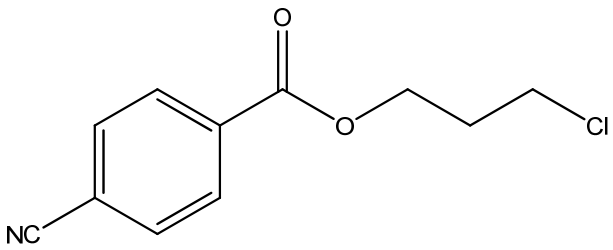
6-chlorohexanal[12] (5.1 g, 37.7 mmol) and propane-1,3-diol (6.0 mL, 83.02 mmol) in dry toluene (50 mL) were placed in a round-bottom flask equipped with a Dean-Stark under nitrogen. The reaction mixture was refluxed in presence of catalytic amount of $TsOH*H_2O$ (200mg) for 3h. The reaction was quenched at room temperature by the addition of aqueous saturated solution of $NaHCO_3$. The organic layer was washed with water, dried over Na_2SO_4 and solvent was removed in vacuum to give the desired protected aldehyde in quantitative yield.

^{1}H NMR (400MHz, $CDCl_3$): 4.50 (t, *J* = 5.3 Hz, 1H), 4.08 (dd, J_1 = 10.9 Hz, J_2 = 5.0 Hz, 2H), 3.74 (m, 2H), 3.51 (t, *J* = 6.7 Hz, 2H), 2.04 (m, 1H), 1.75 (m, 2H), 1.58 (m, 2H), 1.41 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): 102.0, 66.8, 44.9, 34.9, 32.4, 26.6, 25.7, 23.1.

HRCI-MS: calculated for ($C_9H_{18}ClO_2$, M+H), 193.0995; found, 193.0996.

[12] R. J. Fox, G. Lalic and R. G. Bergman, *J. Am. Chem. Soc.* **2007**, 129, 14144-14145.



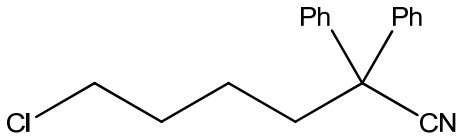
3-chloropropyl 4-cyanobenzoate

4-cyanobenzoyl chloride (4g, 24.1 mmol) was added slowly to a solution of 3-chloropropan-1-ol (2.04 g, 21.58 mmol) in dry pyridine (20 mL) cooled to 0^0C. The reaction was stirred at 0^0C for 1h and then at r.t. overnight. The crude solution was partitioned between saturated aqueous $NaHCO_3$ (60 mL) and EtOAc (50 mL). The organic layer was further washed with water (30 mL) and 1M aqueous HCl (2 x 30 mL), dried over Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by flash chromatography to give a white solid in 75% yield.

^{1}H NMR (400MHz, $CDCl_3$): 8.13 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 4.51 (t, *J* = 6.2 Hz, 2H), 3.69 (t, *J* = 6.2 Hz, 2H), 2.25 (quint, *J* = 5.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 164.6, 133.7, 132.1, 130.0, 117.8, 116.4, 62.4, 41.0, 31.4.

HRCI-MS: calculated for ($C_{11}H_{11}ClNO_2$, M+H), 224.0478; found, 224.0475.



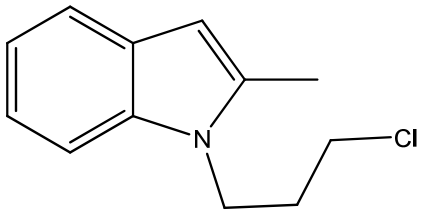
6-chloro-2,2-diphenylhexanenitrile

To a solution of diphenylacetonitrile (2.0 g, 10.3 mmol) in 100 ml of *N*,*N*-dimethylformamide was carefully added sodium hydride (0.5 g, 12.4 mmol, 60% in oil) in small portions. The mixture was stirred at ambient temperature for 15 min, and then 1-chloro-4-iodobutane (3.28 g, 15 mmol) was added in one portion. The mixture was stirred at ambient temperature. After 20 h, the reaction was quenched with 200 ml of water and extracted with two portions of ethyl acetate (200 mL). The combined organic extracts were washed with water (2 x 400 mL) and then brine (400 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yellow oil. Purification by flash column chromatography on silica gel afforded 1.9 g of 6-chloro-2,2-diphenylhexanenitrile as a viscous liquid.

^{1}H NMR (400MHz, $CDCl_3$): 7.40 (m, 8H), 7.31 (m, 2H), 3.51 (t, J = 6.7 Hz, 2H), 2.41 (m, 2H), 1.85 (m, 2H), 1.58 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 139.9, 128.8, 127.8, 126.7, 122.1, 51.6, 44.2, 38.9, 32.2, 23.1.

HRCI-MS: calculated for ($C_{18}H_{19}ClN$, M+H), 284.1206; found, 284.1219.



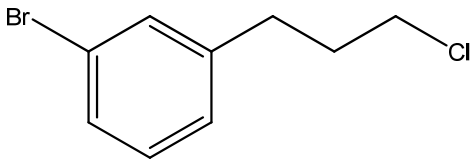
1-(3-chloropropyl)-2-methyl-1H-indole

This compound was synthesized according to a general method described in the literature[3] starting from 2-methyl-1H-indole.

^{1}H NMR (400MHz, $CDCl_3$): 7.57 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.19 (m, 1H), 7.12 (m, 1H), 6.30 (s, 1H), 4.28 (t, *J* = 7.0 Hz, 2H), 3.55 (t, *J* = 6.2 Hz, 2H), 2.49 (s, 3H), 2.25 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 136.5, 136.3, 128.1, 120.5, 119.7, 119.3, 108.8, 100.3, 42.0, 39.9, 32.7, 12.7.

HRCI-MS: calculated for ($C_{12}H_{15}NCl$, M+H), 208.0893; found, 208.0888.



1-bromo-3-(3-chloropropyl)benzene

This compound was synthesized from 3-(3-bromophenyl)propan-1-ol[13] by the same procedure as 1-chloro-4-(2-chloroethyl)benzene.[6]

^{1}H NMR (400MHz, $CDCl_3$): 7.35 (m, 2H), 7.16 (m, 2H), 3.53 (t, *J* = 6.2 Hz, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.07 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 143.0, 131.5, 130.0, 129.2, 127.2, 122.5, 43.9, 33.6, 32.3.

Elemental analysis: Anal. Calcd for $C_9H_{10}BrCl$: C, 46.29; H, 4.32. Found: C, 46.33; H, 4.45.

[13] A. Minami, R. Uchida, T. Eguchi and K. Kakinuma, *J. Am. Chem. Soc.* **2005**, 127, 6148-6149.

General procedure for Sonogashira coupling

[($^{Me}NN_2$)Ni-Cl] (26 mg, 0.075 mmol), CuI (9 mg, 0.045mmol), Cs_2CO_3 (684mg, 2.1mmol), Alkyl-X (1.5 mmol) and alkyne (1.95 mmol) were placed in a vial and 6 mL of dioxane was added. NaI (45 mg, 0.3 mmol) was added in case of Alkyl-Br or NBu_4I (120 mg, 0.3 mmol) was added in case of Alkyl-Cl. After addition the mixture was heated in absence of oxygen during 16h at 100^0C for Alkyl-I and Alkyl-Br and at 140^0C for Alkyl-Cl. After this time reaction was cooled to r.t., quenched with 15 mL of water and 1 mL of 1M HCl, extracted with ether (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.

Choice of the best conditions

Table S1. Choice of the best conditions for Alkyl-I and control experiments[a]

Entry	CuI	Base	Solvent	Cat.	Temp.	Time	Yield
1	7.5mol%	Cs_2CO_3	NMP	[($^{Me}NN_2$)Ni-Cl]	80	16h	21
2	7.5mol%	Cs_2CO_3	DMA	[($^{Me}NN_2$)Ni-Cl]	80	16h	36
3	7.5mol%	Cs_2CO_3	Toluene	[($^{Me}NN_2$)Ni-Cl]	80	16h	46
4	7.5mol%	Cs_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	80	16h	79
5	7.5mol%	K_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	120	16h	23
6	7.5mol%	Na_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	120	16h	10
7	7.5mol%	Cs_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	120	16h	83
8	7.5mol%	Cs_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	60	16h	67

9	7.5mol%	Cs_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	120	2h	34
10	7.5mol%	Cs_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	120	8h	59
11	3mol%	Cs_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	100	16h	75
12	3mol%	Cs_2CO_3	Dioxane	[($^{Me}NN_2$)$_2$Li$_2$]	100	16h	0
13	3mol%	Cs_2CO_3	Dioxane	H$^{Me}NN_2$	100	16h	0
14	3mol%	Cs_2CO_3	Dioxane	Ni(dme)Cl_2	100	16h	0
15	3 mol%	Cs_2CO_3	Dioxane	-	100	16h	4.1
16	-	Cs_2CO_3	Dioxane	-	100	16h	0
17	3 mol%	Cs_2CO_3	Dioxane	[($^{Me}NN_2$)Ni-Cl]	100	16h	12.9

[a] Reactions were performed with 0.5 mmol of octyl-I, 1.3eq. of octyne, 5mol% of cat. in absence of oxygen.

Table S2. Choice of the best conditions for Alkyl-Br[a]

Entry	Additive	Solvent	Temp.	Yield
1	-	Dioxane	120	0
2	20% NaI	Dioxane	120	79
3	20% NaI	Dioxane	100	78

[a] Reactions were performed with 0.5 mmol of octyl-Br, 1.3 equiv. of octyne, 5 mol% of cat [($^{Me}NN_2$)Ni-Cl], 1.4 equiv. of Cs_2CO_3, 3 mol% of CuI in absence of oxygen.

Table S3. Choice of the best conditions for Alkyl-Cl and control experiments[a]

Entry	Additive	Solvent	Temp.	Yield

1	20% NaI	Dioxane	120	5
2	100%NaI	Dioxane	120	5
3	20% KI	Dioxane	120	4
4	20% LiI	Dioxane	120	6
5	20% NBu_4I	Dioxane	120	39
6	20% NBu_4I	Dioxane	100	35
7	20% NBu_4I	Dioxane	140	76
8	20% NBu_4I	Dioxane	140	3.1[b]
9	20% NBu_4I	Dioxane	140	22.5[c]
10	20% NBu_4I	Dioxane	140	14[d]

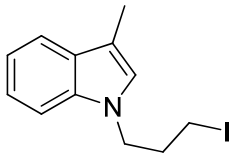
[a] Reactions were performed with 0.5 mmol of octyl-Cl, 1.3 equiv. of octyne, 5 mol% of cat [($^{Me}NN_2$)Ni-Cl], 1.4 equiv. of Cs_2CO_3, 3 mol% of CuI in absence of oxygen. [b]Without Ni catalyst nor Cu-I. [c]With Ni catalyst but not Cu-I. [d]Without Ni catalyst but with Cu-I.

Table S4. Sonogashira coupling of alkyl iodides and bromides, additional entries.[a]

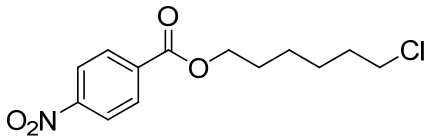
Entry	Alkyl[1]-X	$\equiv$—R[2]	Yield (%)[b]
1	Octyl-I	$\equiv$—Ph	69
2	Octyl-Br	$\equiv$—*n*-C_6H_{13}	79
3	Cl, I	$\equiv$—*n*-C_6H_{13}	82
4	Cl, I	$\equiv$—Si(*i*-Pr)$_3$	80
5	Octyl-Br	$\equiv$—*n*-C_6H_{13}	79
6	Cl, Br	$\equiv$—Ph	64
7	Cl, Br	$\equiv$—*n*-C_6H_{13}	83
8	NC, I	$\equiv$—Ph	41

[a]For coupling of iodides, no NaI was added as additive; for coupling of bromides, 20 mol% of NaI was added as additive. [b]Isolated yields relative to alkyl halide.

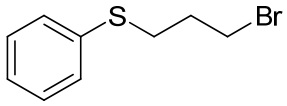
Substrates that cannot be coupled using the current protocols and brief comments:



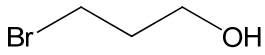
Comments: 2-H is too reactive. If the 2-position is methylated, then coupling occurs (see main text, entry 12, Table 2)



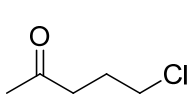
Comments: NO2 group is not tolerated.

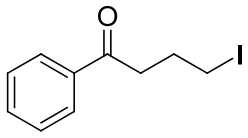


Comments: thioether group is not tolerated.

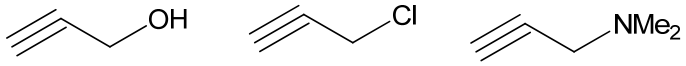


Comments: alcohol group is not tolerated.

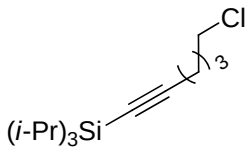




Comments: Substrates with only alkyl groups between keto and halide groups could not be coupled. However, if there is an aryl group between keto and halide groups, then coupling occurs (see entry 5, Table 2, main text).

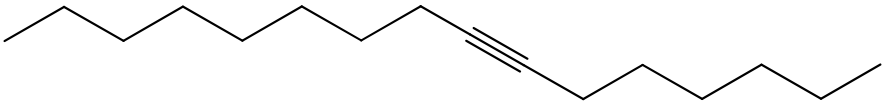


Comments: These alkyne substrates could not be coupled. Electronically they are different from normal alkynes.



Comments: Alkyne-containing alkyl halides could not be coupled, possibly due to the formation of 5- or 6-member rings. If there are 6 CH2 groups between the alkyne and Cl groups, then coupling occurs (see equation 1, main text). In that case, formation of 7- or 8-member rings are not very favorable.

Detailed descriptions for products

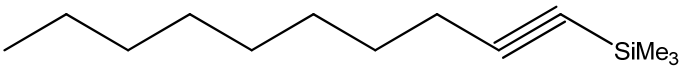


hexadec-7-yne (table 1, entry 1 and table 2, entry 1):[14]

Eluated from the column with hexane-diethyl ether (60:1) in 83% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 2.13 (t, *J* = 6.2 Hz, 4H), 1.47 (m, 4H), 1.22-1.40 (m, 16H), 0.89 (t, *J* = 6.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 80.2, 31.8, 31.3, 29.2, 29.19, 29.16, 28.8, 28.5, 22.6, 22.5, 18.7, 14.08, 14.03.

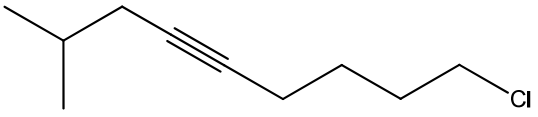


dec-1-ynyltrimethylsilane (table 1, entry 2) :[15]

Eluated from the column with hexane-diethyl ether (100:1) in 74% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 2.21 (t, *J* = 7.0 Hz, 2H), 1.51 (m, 2H), 1.23-1.40 (m, 10H), 0.88 (t, *J* = 6.5 Hz, 3H), 0.14 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): 107.7, 84.2, 31.8, 29.1, 29.0, 28.7, 28.6, 22.6, 19.8, 14.1, 0.1.



[14] N. Kambe et al., *Chem. Commun*. **2007**, 855–857.
[15] T. Stiidemann et al., *Tetrahedron* **1998**, 54, 1299-1316.

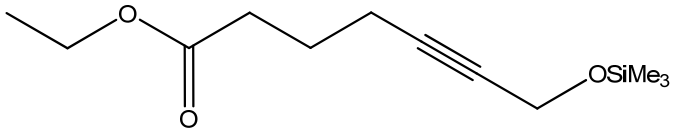
9-chloro-2-methylnon-4-yne (table 1, entry 3):

Eluated from the column with hexane-diethyl ether (60:1) in 84% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 3.56 (t, J = 6.7 Hz, 2H), 2.21 (m, 2H), 2.03 (m, 2H), 1.89 (m, 2H), 1.75 (m, 1H), 1.63 (m, 2H), 0.95 (d, J = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 80.0, 79.8, 44.6, 31.5, 28.2, 27.9, 26.2, 21.9, 18.0.

Elemental analysis: Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.55; H, 9.92. Found: C, 69.41; H, 9.96.



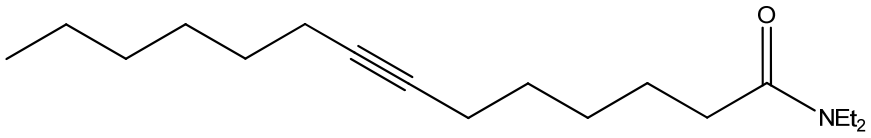
ethyl 7-(trimethylsilyloxy)hept-5-ynoate (table 1, entry 4):

Eluated from the column with hexane-diethyl ether (15:1) in 73% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 4.25 (t, J = 2.3 Hz, 2H), 4.12 (q, J = 7.3 Hz, 2H), 2.41 (t, J = 7.3 Hz, 2H), 2.27 (tt, J_1 = 7.0 Hz, J_2 = 2.1 Hz, 2H), 1.81 (quint, J = 7.3 Hz, 2H), 1.24 (t, J = 7.3 Hz, 3H), 0.15 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): 173.0, 84.2, 79.1, 60.3, 51.1, 33.0, 23.7, 18.2, 14.1, -0.3.

HRCI-MS: calculated for ($C_{12}H_{23}SiO_3$, M+H), 243.1416; found, 243.1419.



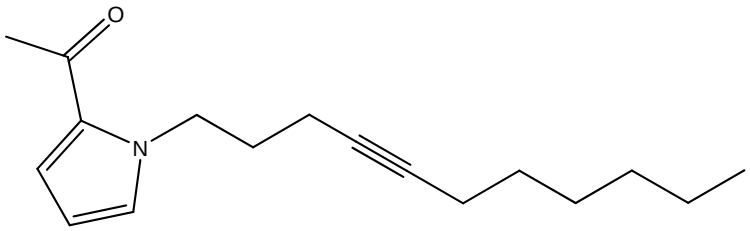
N,N-diethyltetradec-7-ynamide (table 1, entry 5):

Eluated from the column with hexane-diethyl ether (1:1) in 68% yield as a yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 3.35 (q, J = 7.0 Hz, 2H), 3.28 (q, J = 7.0 Hz, 2H), 2.28 (m, 2H), 2.13 (m, 4H), 1.64 (m, 2H), 1.22-1.54 (m, 12H), 1.15 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 7.3 Hz, 3H), 0.87 (t, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 172.0, 80.3, 79.9, 41.8, 39.9, 33.0, 31.3, 29.0, 28.9, 28.7, 28.5, 25.0, 22.5, 18.7, 18.6, 14.3, 14.0, 13.0.

HRCI-MS: calculated for ($C_{18}H_{34}NO$, M+H), 280.2640; found, 280.2648.



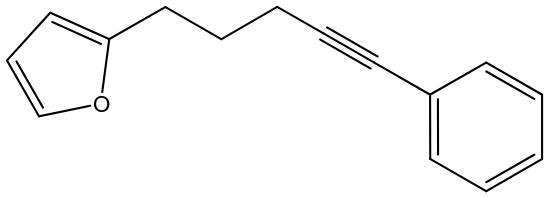
1-(1-(undec-4-ynyl)-1H-pyrrol-2-yl)ethanone (table 1, entry 6):

Eluated from the column with hexane-diethyl ether (20:1) in 61% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 6.97 (dd, J_1 = 4.1 Hz, J_2 = 1.5 Hz, 1H), 6.92 (m, 1H), 6.13 (m, 1H), 4.42 (t, J = 6.7 Hz, 2H), 2.43 (s, 3H), 2.17 (t, J = 7.3 Hz, 2H), 2.10 (t, J = 6.7 Hz, 2H), 1.90 (m, 2H), 1.50 (m, 2H), 1.24-1.42 (m, 6H), 0.90 (t, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 188.0, 130.7, 129.9, 120.3, 107.7, 81.4, 78.7, 48.3, 31.3, 30.1, 29.0, 28.5, 27.2, 22.5, 18.7, 15.7, 14.0.

HRCI-MS: calculated for ($C_{17}H_{26}NO$, M+H), 260.2014; found, 260.1991.



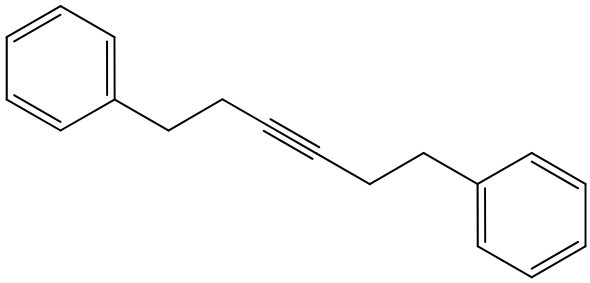
2-(5-phenylpent-4-ynyl)furan (table 1, entry 7):

Eluated from the column with hexane-diethyl ether (60:1) in 84% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.41 (m, 2H), 7.29 (m, 4H), 6.30 (m, 1H), 6.05 (m, 1H), 2.82 (t, J = 7.6 Hz, 2H), 2.47 (t, J = 7.0 Hz, 2H), 1.96 (quint, J = 7.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 155.3, 140.9, 131.5, 128.1, 127.5, 123.8, 110.0, 105.2, 89.4, 81.1, 27.1, 27.0, 18.8.

HRCI-MS: calculated for ($C_{15}H_{15}O$, M+H), 211.1123; found, 211.1124.



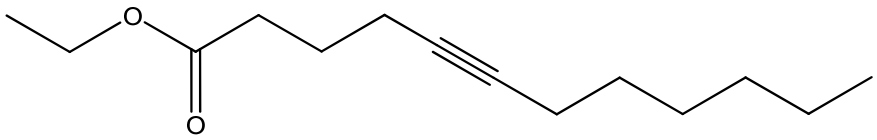
1,6-diphenylhex-3-yne (table 1, entry 8) :[16]

Eluated from the column with hexane-diethyl ether (60:1) in 89% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.32 (m, 4H), 7.23 (m, 6H), 2.81 (t, J = 7.3 Hz, 4H), 2.46 (t, J = 7.6 Hz,4H).

[16] T. Satoh et al., *Tetrahedron* **1995**, 51(34), 9327-9338.

^{13}C NMR (100 MHz, $CDCl_3$): 140.9, 128.4, 128.2, 126.1, 80.2, 35.4, 20.9.



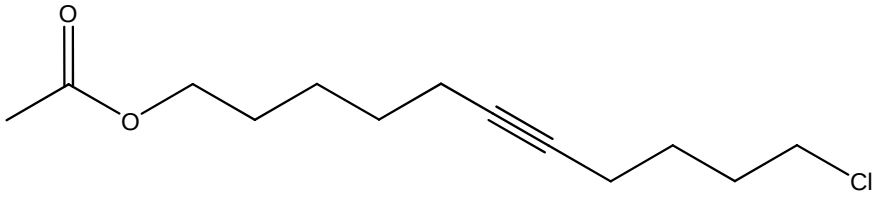
ethyl dodec-5-ynoate (table 1, entry 9):

Eluated from the column with hexane-diethyl ether (30:1) in 73% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 4.09 (q, J = 7.0 Hz, 2H), 2.38 (t, J = 7.6 Hz, 2H), 2.18 (tt, J_1 = 6.9 Hz, J_2 = 2.4 Hz, 2H), 2.09 (tt, J_1 = 6.9 Hz, J_2 = 2.2 Hz, 2H), 1.76 (quint, J = 7.0 Hz, 2H), 1.43 (m, 2H), 1.27 (m, 9H), 0.85 (t, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 173.2, 81.1, 78.6, 60.1, 33.0, 31.2, 28.9, 28.4, 24.2, 22.4, 18.6, 18.1, 14.1, 13.9.

HRCI-MS: calculated for ($C_{14}H_{25}O_2$, M+H), 225.1855; found, 225.1846.



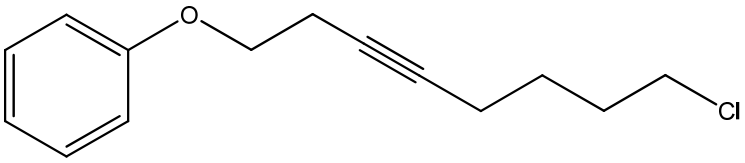
11-chloroundec-6-ynyl acetate (table 1, entry 10):

Eluated from the column with hexane-diethyl ether (15:1) in 70% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 4.05 (t, J = 7.0 Hz, 2H), 3.55 (t, J = 6.7 Hz, 2H), 2.16 (m, 4H), 2.03 (s, 3H), 1.87 (m, 2H), 1.62 (m, 4H), 1.47 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 171.1, 80.4, 79.4, 64.3, 44.5, 31.5, 28.5, 28.0, 26.1, 25.0, 20.9, 18.5, 17.9.

HRCI-MS: calculated for ($C_{13}H_{22}ClO_2$, M+H), 245.1308; found, 245.1309.



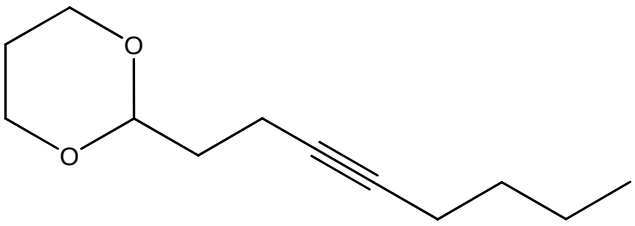
(8-chlorooct-3-ynyloxy)benzene (table 1, entry 11):

Eluated from the column with hexane-diethyl ether (60:1) in 79% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.29 (t, *J* = 8.2 Hz, 2H), 6.94 (m, 3H), 4.06 (t, *J* = 7.3 Hz, 2H), 3.56 (t, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 1.89 (m, 2H), 1.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 158.4, 129.4, 120.8, 114.6, 81.0, 76.6, 66.4, 44.5, 31.5, 25.9, 19.8, 18.0.

HRCI-MS: calculated for ($C_{14}H_{18}ClO$, M+H), 237.1046; found, 237.1054.



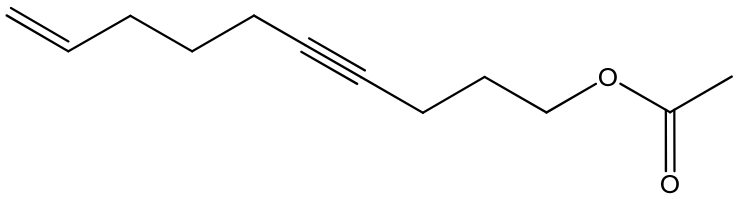
2-(oct-3-ynyl)-1,3-dioxane (table 1, entry 12):

Eluated from the column with hexane-diethyl ether (20:1) in 76% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 4.94 (t, J = 4.6 Hz, 1H), 4.47 (dd, J_1 = 9.5 Hz, J_2 = 4.4 Hz, 2H), 4.17 (td, J_1 = 10.8 Hz, J_2 = 2.1 Hz, 2H), 2.83 (m, 2H), 2.71 (m, 3H), 2.42 (m, 2H), 2.11 (m, 5H), 1.66 (t, J = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 100.9, 80.3, 79.0, 66.8, 34.4, 31.1, 25.8, 21.8, 18.3, 13.6, 13.5.

HRCI-MS: calculated for ($C_{12}H_{21}O_2$, M+H), 197.1542; found, 197.1547.



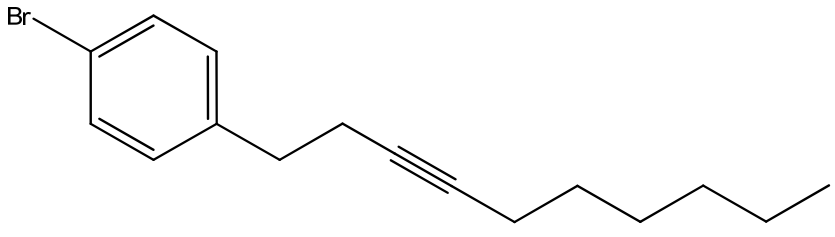
dec-9-en-4-ynyl acetate (table 1, entry 13):

Eluated from the column with hexane-diethyl ether (20:1) in 59% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 5.78 (m, 1H), 5.00 (m, 2H), 4.15 (t, J = 6.5 Hz, 2H), 2.24 (t, J = 7.0 Hz, 2H), 2.14 (m, 4H), 2.04 (s, 3H), 1.80 (m, 2H), 1.56 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 137.9, 114.9, 80.6, 78.7, 63.2, 32.7, 28.1, 28.0, 20.9, 18.0, 15.4.

HRCI-MS: calculated for ($C_{12}H_{19}O_2$, M+H), 195.1385; found, 195.1392.



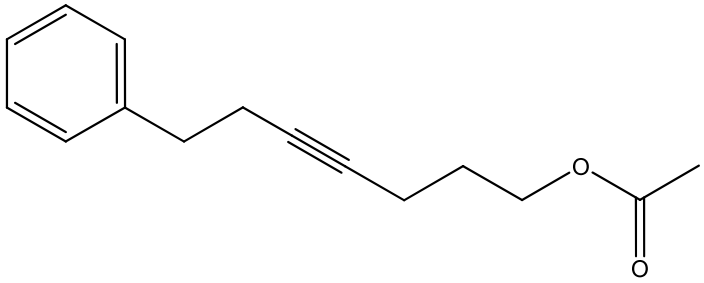
1-bromo-4-(dec-3-ynyl)benzene (table 1, entry 14):

Eluated from the column with hexane-diethyl ether (60:1) in 69% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.40 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.12 (t, *J* = 6.7 Hz, 2H), 1.45 (m, 2H), 1.22-1.38 (m, 6H), 0.90 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 139.8, 131.2, 130.2, 119.9, 81.4, 78.8, 34.8, 31.3, 28.9, 28.5, 22.5, 20.7, 18.6, 14.0.

Elemental analysis: Anal. Calcd for $C_{16}H_{21}Br$: C, 65.53; H, 7.22. Found: C, 65.44; H, 7.33.



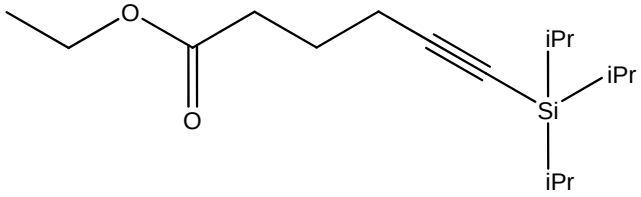
7-phenylhept-4-ynyl acetate (table 2, entry 2):

Eluated from the column with hexane-diethyl ether (9:1) in 66% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.26 (m, 5H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.44 (t, *J* = 7.6 Hz, 2H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 1.78 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 140.8, 128.3, 128.2, 126.1, 80.2, 79.3, 63.1, 35.4, 27.9, 20.95, 20.91, 15.4.

HRCI-MS: calculated for ($C_{15}H_{19}O_2$, M+H), 231.1385; found, 231.1386.



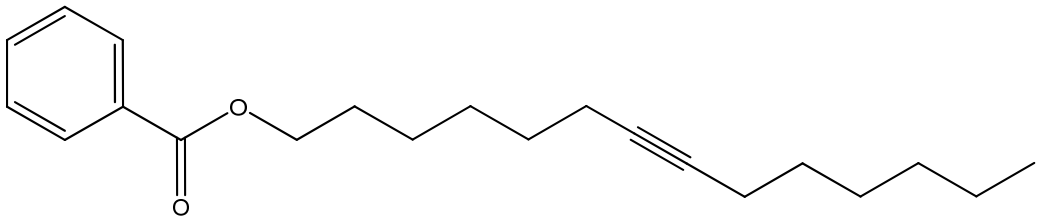
ethyl 6-(triisopropylsilyl)hex-5-ynoate (table 2, entry 3):

Eluated from the column with hexane-diethyl ether (30:1) in 62% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 4.12 (q, *J* = 7.0 Hz, 2H), 2.45 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 6.5 Hz, 2H), 1.83 (m, 2H), 1.24 (t, *J* = 7.3 Hz, 3H), 1.05 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): 173.1, 107.6, 81.1, 60.2, 32.8, 24.0, 19.2, 18.5, 14.1, 11.2.

HRCI-MS: calculated for ($C_{17}H_{33}O_2Si$, M+H), 297.2250; found, 297.2255.



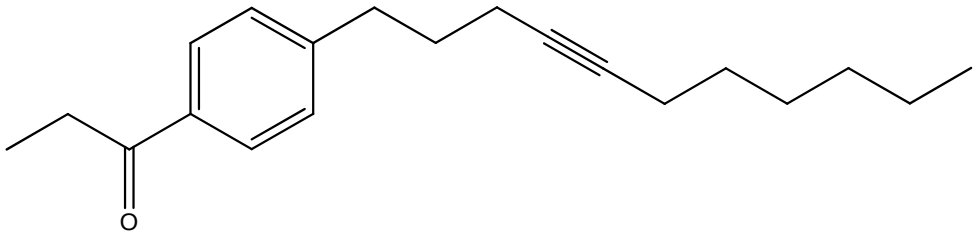
tetradec-7-ynyl benzoate (table 2, entry 4):

Eluated from the column with hexane-diethyl ether (30:1) in 70% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 8.04 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 2.14 (m, 4H), 1.78 (m, 2H), 1.40 (m, 14H), 0.88 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 132.7, 130.4, 129.4, 128.2, 80.4, 79.8, 65.0, 31.3, 29.1, 28.9, 28.6, 28.5, 28.4, 25.6, 22.5, 18.7, 18.6, 14.0.

HRCI-MS: calculated for ($C_{21}H_{31}O_2$, M+H), 315.2324; found, 315.2309.



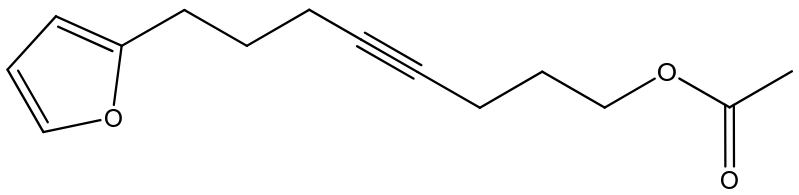
1-(4-(undec-4-ynyl)phenyl)propan-1-one (table 2, entry 5):

Eluated from the column with hexane-diethyl ether (30:1) in 57% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.89 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 2.98 (q, *J* = 7.3 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.16 (t, *J* = 5.6 Hz, 4H), 1.80 (m, 2H), 1.49 (m, 2H), 1.36 (m, 6H), 1.22 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 200.4, 147.4, 134.8, 128.6, 128.1, 81.1, 79.2, 34.7, 31.6, 31.3, 30.3, 29.0, 28.5, 22.5, 18.7, 18.1, 14.0, 8.3.

HRCI-MS: calculated for ($C_{20}H_{29}O$, M+H), 285.2218; found, 285.2223.



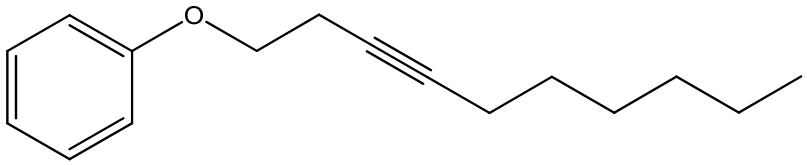
8-(furan-2-yl)oct-4-ynyl acetate (table 2, entry 6):

Eluated from the column with hexane-diethyl ether (20:1) in 64% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.29 (m, 1H), 6.27 (m, 1H), 6.00 (m, 1H), 4.15 (t, *J* = 6.2 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.25 (m, 2H), 2.18 (m, 2H), 2.05 (s, 3H), 1.80 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 155.4, 140.8, 110.0, 105.0, 80.1, 79.1, 63.2, 28.0, 27.3, 26.9, 20.9, 18.1, 15.4.

HRCI-MS: calculated for ($C_{14}H_{19}O_3$, M+H), 235.1334; found, 235.1328.



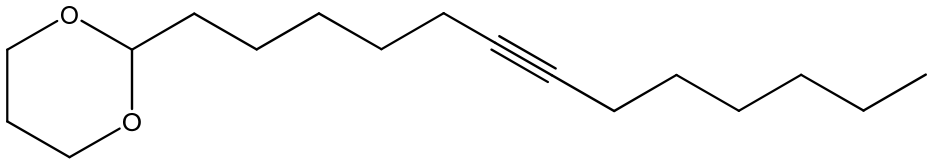
(dec-3-ynyloxy)benzene (table 2, entry 7):

Eluated from the column with hexane-diethyl ether (60:1) in 88% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.29 (m, 2H), 6.95 (m, 3H), 4.07 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.17 (t, *J* = 7.0 Hz, 2H), 1.50 (m, 2H), 1.25-1.42 (m, 6H), 0.91 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 158.5, 129.4, 120.8, 114.6, 82.0, 75.7, 66.5, 31.3, 28.8, 28.5, 22.5, 19.8, 18.7, 14.0.

HRCI-MS: calculated for ($C_{16}H_{23}O$, M+H), 231.1749; found, 231.1758.



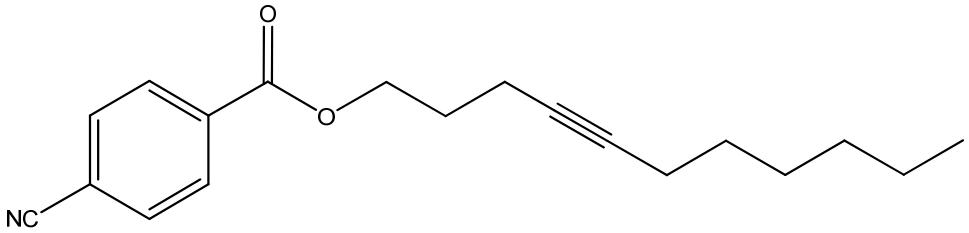
2-(tridec-6-ynyl)-1,3-dioxane (table 2, entry 8):

Eluated from the column with hexane-diethyl ether (20:1 to 9:1) in 73% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 4.50 (t, J = 5.3 Hz, 1H), 4.09 (dd, J_1 = 11.2 Hz, J_2 = 5.3 Hz, 2H), 3.75 (m, 2H), 2.08 (m, 4H), 1.43 (m, 18H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 102.3, 80.2, 80.0, 66.8, 35.1, 31.3, 29.1, 29.0, 28.6, 28.5, 25.8, 23.5, 22.5, 18.7, 18.6, 14.0.

HRCI-MS: calculated for ($C_{17}H_{31}O_2$, M+H), 267.2324; found, 267.2314.



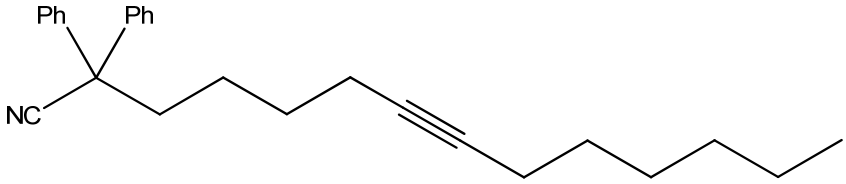
undec-4-ynyl 4-cyanobenzoate (table 2, entry 9):

Eluated from the column with hexane-diethyl ether (15:1) in 63% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 8.14 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 4.45 (t, J = 6.5 Hz, 2H), 2.34 (t, J = 6.7 Hz, 2H), 2.11 (t, J = 6.7 Hz, 2H), 1.95 (quint, J = 6.7 Hz, 2H), 1.45 (m, 2H), 1.30 (m, 6H), 0.87 (t, J = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 164.8, 134.1, 132.1, 130.0, 117.9, 116.3, 81.4, 78.1, 64.6, 31.3, 28.9, 28.5, 28.0, 22.5, 18.6, 15.6, 14.0.

HRCI-MS: calculated for ($C_{19}H_{24}NO_2$, M+H), 298.1807; found, 298.1819.



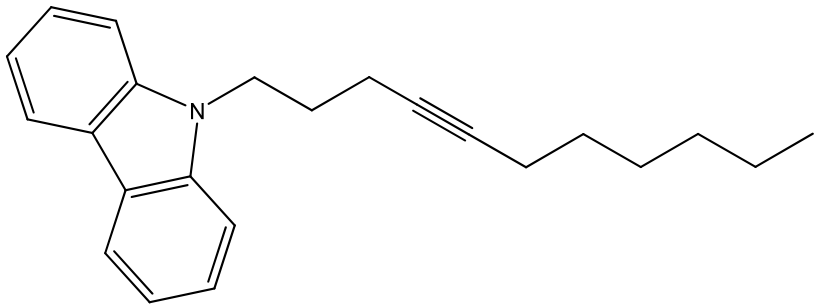
2,2-diphenyltetradec-7-ynenitrile (table 2, entry 10):

Eluated from the column with hexane-diethyl ether (30:1) in 66% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.37 (m, 8H), 7.29 (m, 2H), 2.39 (t, J = 7.6 Hz, 2H), 2.16 (m, 2H), 2.10 (t, J = 7.3 Hz, 2H), 1.57 (m, 4H), 1.43 (m, 2H), 1.22-1.38 (m, 6H), 0.89 (t, J = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 140.2, 128.7, 127.7, 126.8, 122.3, 80.8, 79.2, 51.7, 39.1, 31.3, 29.0, 28.8, 28.5, 24.7, 22.5, 18.6, 18.4, 14.0.

HRCI-MS: calculated for ($C_{26}H_{32}N$, M+H), 358.2535; found, 358.2540.



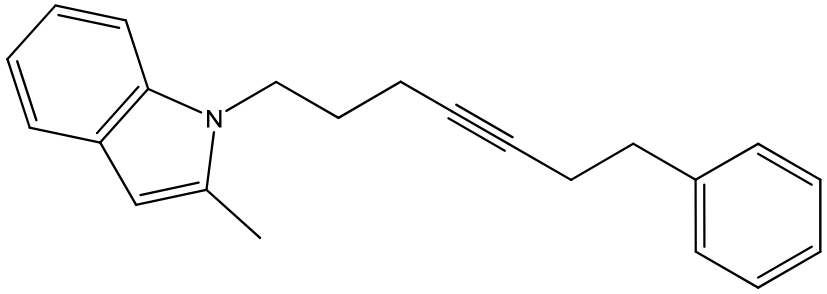
9-(undec-4-ynyl)-9H-carbazole (table 2, entry 11):

Eluated from the column with hexane-diethyl ether (30:1) in 85% yield as a slightly yellow liquid:

^{1}H NMR (400MHz, $CDCl_3$): 8.12 (d, *J* = 7.9 Hz, 2H), 7.50 (m, 4H), 7.26 (m, 2H), 4.46 (t, *J* = 7.0 Hz, 2H), 2.24 (m, 4H), 2.07 (m, 2H), 1.58 (m, 2H), 1.46 (m, 2H), 1.34 (m, 4H), 0.93 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 140.4, 125.5, 122.8, 120.2, 118.8, 108.6, 81.5, 78.9, 41.6, 31.4, 29.1, 28.6, 28.2, 22.5, 18.8, 16.5, 14.0.

HRCI-MS: calculated for ($C_{23}H_{28}N$, M+H), 318.2222; found, 318.2232.



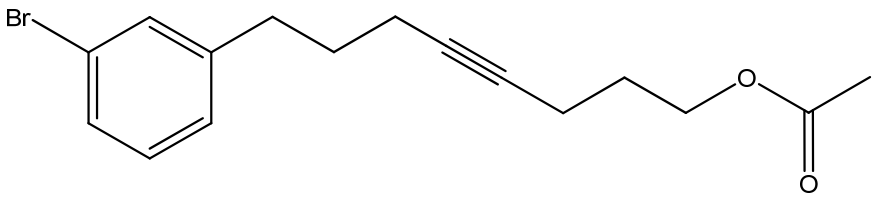
2-methyl-1-(7-phenylhept-4-ynyl)-1H-indole (table 2, entry 12):

Eluated from the column with hexane-diethyl ether (30:1) in 75% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.56 (d, *J* = 8.5 Hz, 1H), 7.31 (m, 6H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.11 (m, 1H), 6.28 (s, 1H), 4.16 (t, *J* = 7.0 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.3 Hz, 2H), 2.44 (s, 3H), 2.21 (t, *J* = 6.5 Hz, 2H), 1.94 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 140.7, 136.5, 136.4, 128.38, 128.33, 128.0, 126.2, 120.3, 119.5, 119.1, 108.9, 99.9, 80.6, 79.6, 41.7, 35.3, 29.1, 20.8, 16.2, 12.6.

HRCI-MS: calculated for ($C_{22}H_{24}N$, M+H), 302.1909; found, 302.1899.



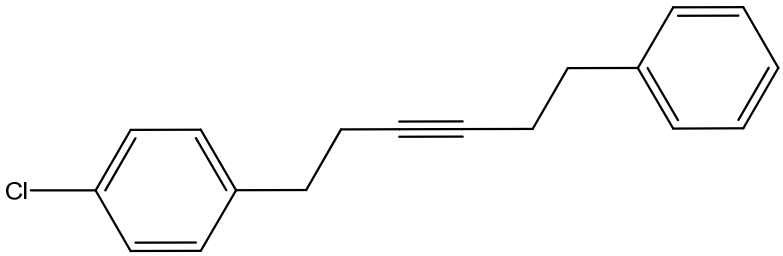
8-(3-bromophenyl)oct-4-ynyl acetate (table 2, entry 13):

Eluated from the column with hexane-diethyl ether (15:1) in 58% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.32 (m, 2H), 7.12 (m, 2H), 4.17 (t, *J* = 6.5 Hz, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.27 (t, *J* = 6.7 Hz, 2H), 2.15 (t, *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 1.80 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 171.0, 144.0, 131.4, 129.8, 128.9, 127.1, 122.3, 80.2, 79.3, 63.2, 34.3, 30.2, 28.0, 20.9, 18.0, 15.4.

HRCI-MS: calculated for ($C_{16}H_{20}BrO_2$, M+H), 323.0647 and 325.0628; found, 323.0659 and 325.0643.



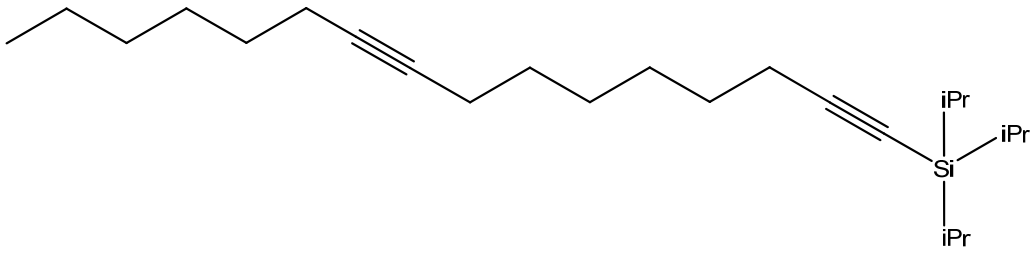
1-chloro-4-(6-phenylhex-3-ynyl)benzene (table 2, entry 14):

Eluated from the column with hexane-diethyl ether (60:1) in 72% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.30 (m, 2H), 7.23 (m, 5H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.77 (m, 4H), 2.43 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 140.8, 139.2, 131.8, 129.8, 128.4, 128.3, 128.2, 126.1, 80.5, 79.7, 35.3, 34.6, 20.85, 20.82.

Elemental analysis: Anal. Calcd for $C_{18}H_{17}Cl$: C, 80.43; H, 6.38. Found: C, 80.46; H, 6.57.



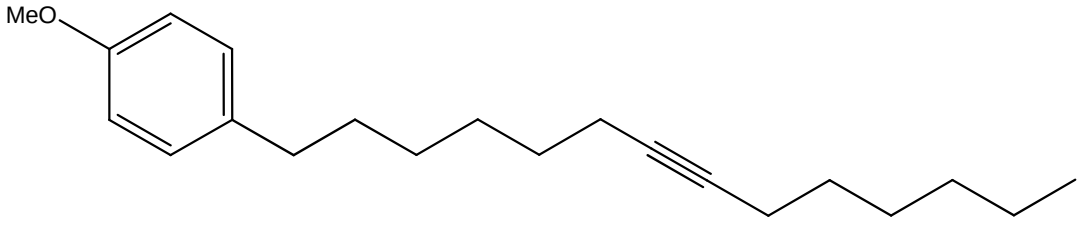
hexadeca-1,9-diynyltriisopropylsilane (2 steps experiments, entry 1):

Eluated from the column with hexane-diethyl ether (100:1) in 69% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 2.25 (t, *J* = 7.0 Hz, 2H), 2.14 (m, 4H), 1.41 (m, 16H), 1.06 (m, 21H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 109.1, 80.3, 80.05, 80.02, 31.3, 29.1, 29.0, 28.7, 28.5, 28.28, 28.21, 22.5, 19.7, 18.76, 18.70, 18.62, 14.0, 11.2.

HRCI-MS: calculated for ($C_{25}H_{47}Si$, M+H), 375.3447; found, 375.3449.



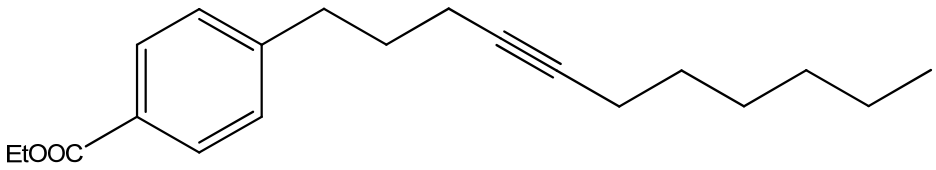
1-methoxy-4-(tetradec-7-ynyl)benzene (2 steps experiments, entry 2):

Eluated from the column with hexane-diethyl ether (30:1) in 86% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.09 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.14 (t, *J* = 6.5 Hz, 4H), 1.59 (m, 2H), 1.24-1.52 (m, 14H), 0.89 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 157.5, 134.8, 129.1, 113.6, 80.2, 80.1, 55.2, 34.9, 31.6, 31.3, 29.1, 29.0, 28.7, 28.6, 28.5, 22.5, 18.75, 18.73, 14.0.

HRCI-MS: calculated for ($C_{21}H_{33}O$, M+H), 301.2531; found, 301.2523.

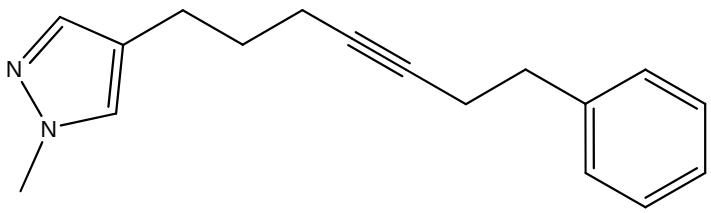


ethyl 4-(undec-4-ynyl)benzoate (2 steps experiments, entry 3):

Eluated from the column with hexane-diethyl ether (60:1) in 77% yield as a colorless liquid:

^{1}H NMR (400MHz, $CDCl_3$): 7.95 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.36 (q, *J* = 7.0 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.16 (t, *J* = 6.7 Hz, 4H), 1.80 (quint, *J* = 6.7 Hz, 2H), 1.49 (m, 2H), 1.38 (t, *J* = 7.3 Hz, 3H), 1.26-1.44 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 147.2, 129.5, 128.4, 128.1, 81.1, 79.2, 60.7, 34.7, 31.3, 30.3, 29.0, 28.5, 22.5, 18.7, 18.1, 14.3, 14.0. **HRCI-MS:** calculated for ($C_{20}H_{29}O_2$, M+H), 301.2168; found, 301.2159.



1-methyl-4-(7-phenylhept-4-ynyl)-1H-pyrazole (2 steps experiments, entry 4):

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

^{1}H NMR (400MHz, $CDCl_3$): 7.26 (m, 6H), 7.10 (s, 1H), 3.85 (s, 3H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.49 (m, 4H), 2.16 (t, *J* = 7.3 Hz, 2H), 1.69 (quint, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 140.8, 138.6, 128.4, 128.2, 126.0, 120.9, 80.3, 79.9, 38.7, 35.4, 30.0, 22.9, 20.8, 18.0. **HRCI-MS:** calculated for ($C_{17}H_{21}N_2$, M+H), 253.1705; found, 253.1695.

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6.0
5.0
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1.95
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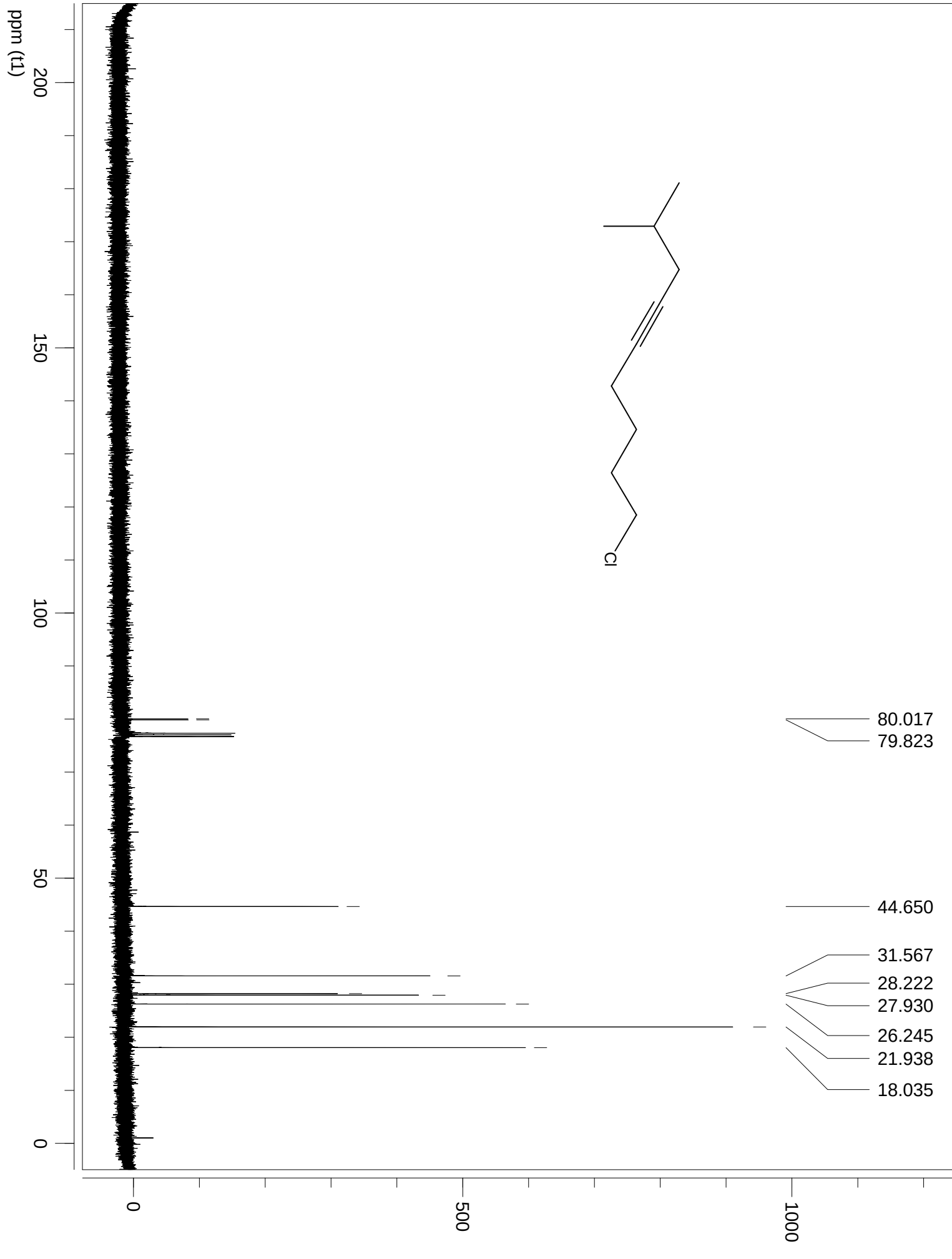
Cl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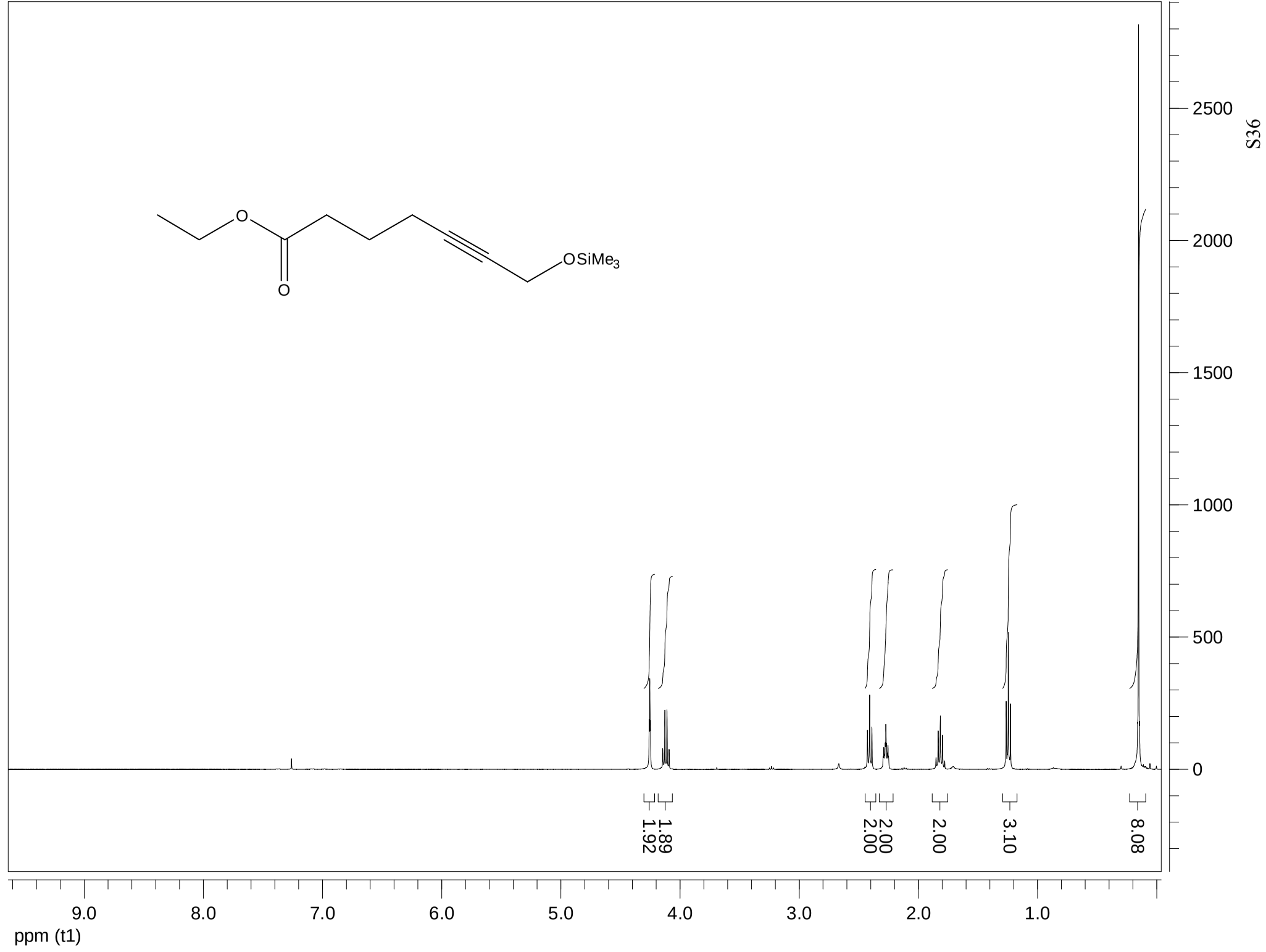
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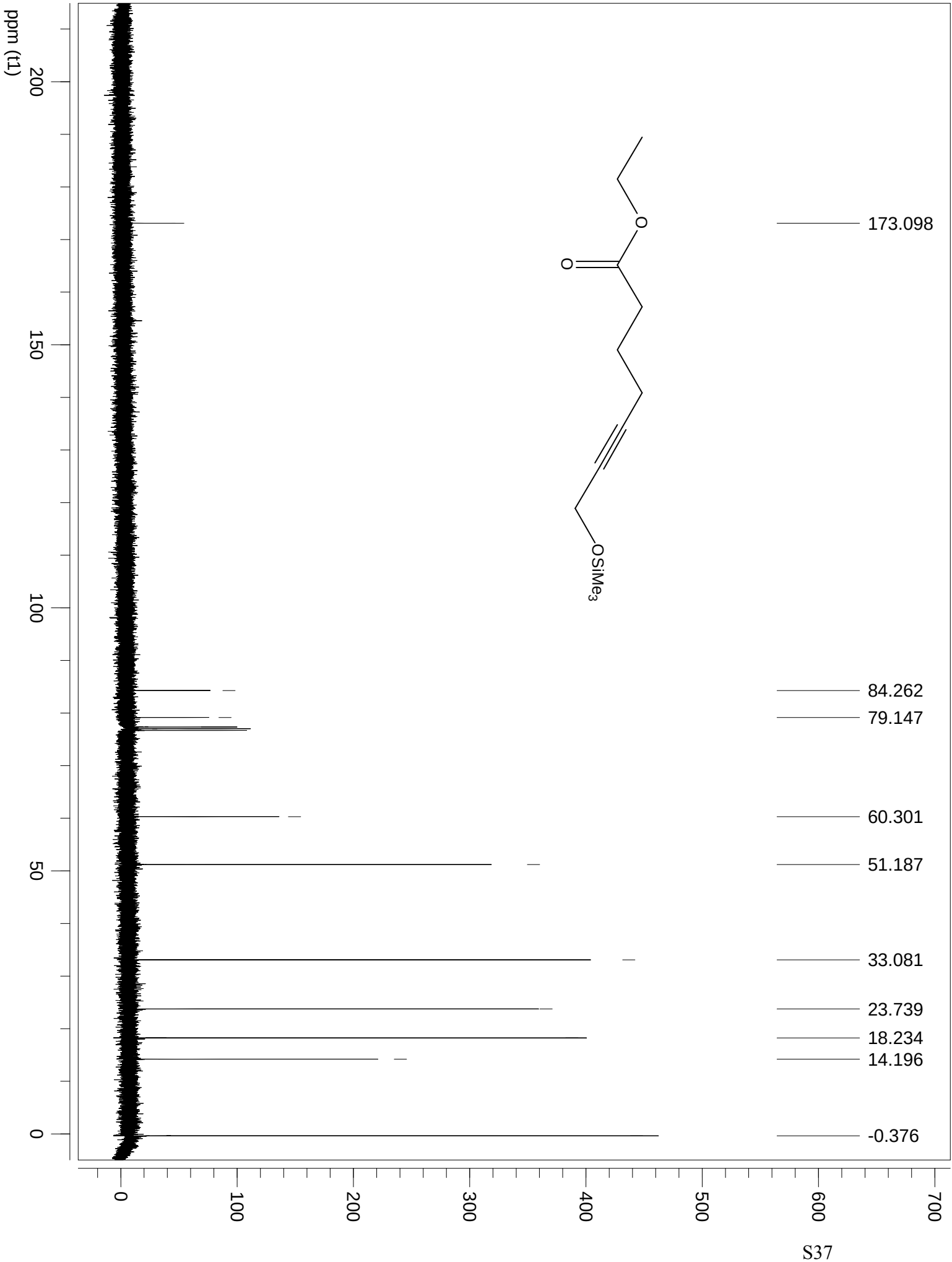
ppm (t1)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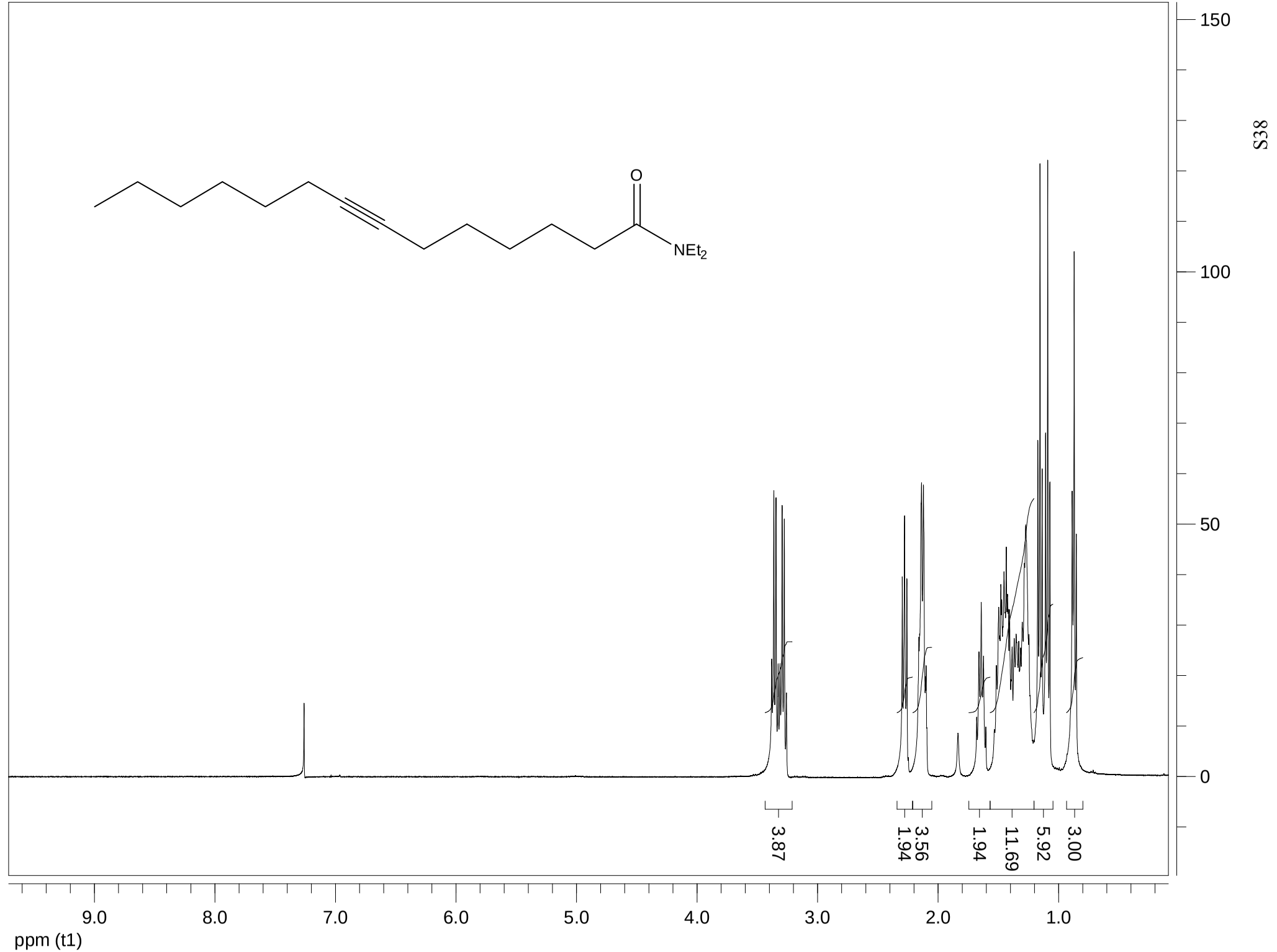
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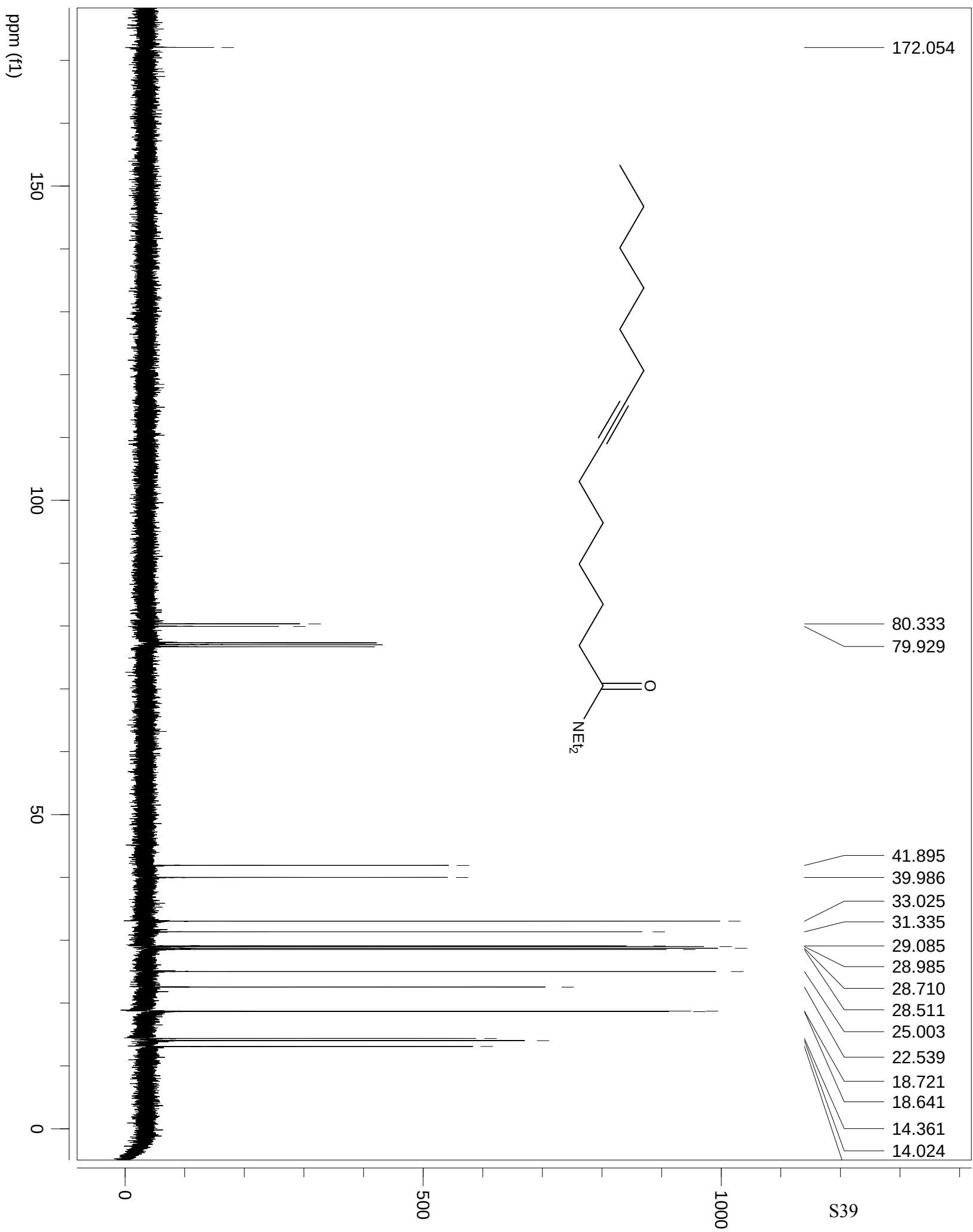
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NEt2

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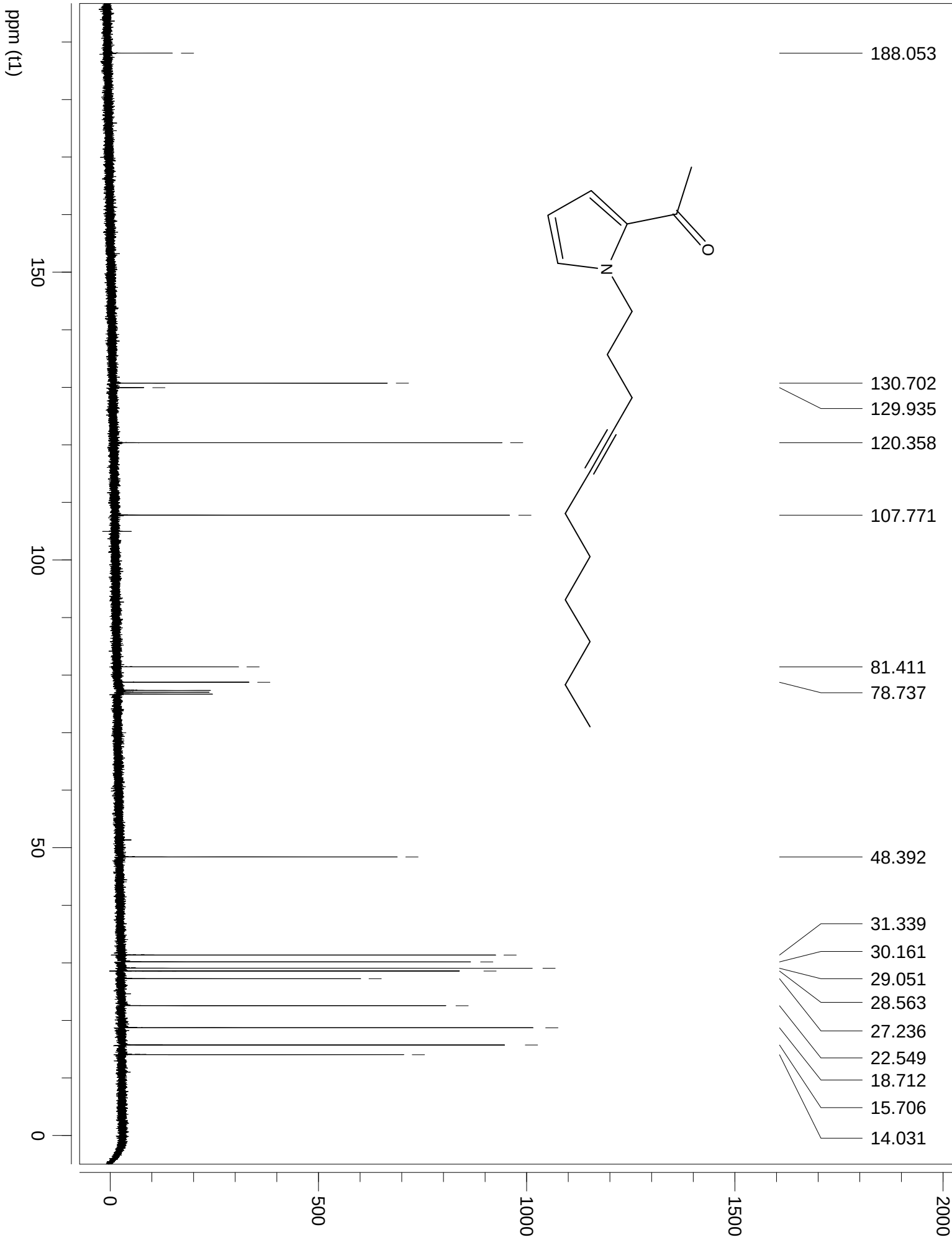
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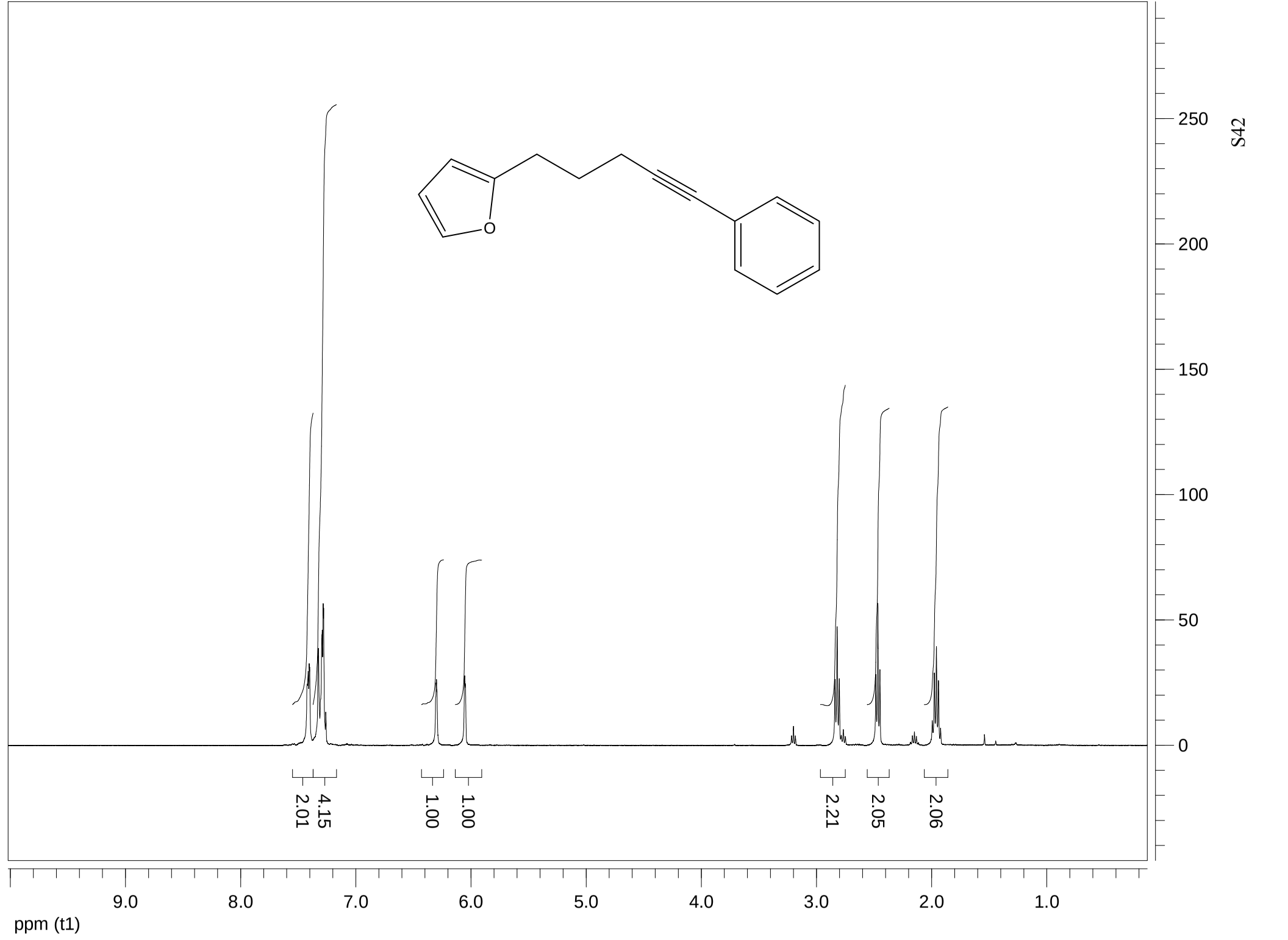
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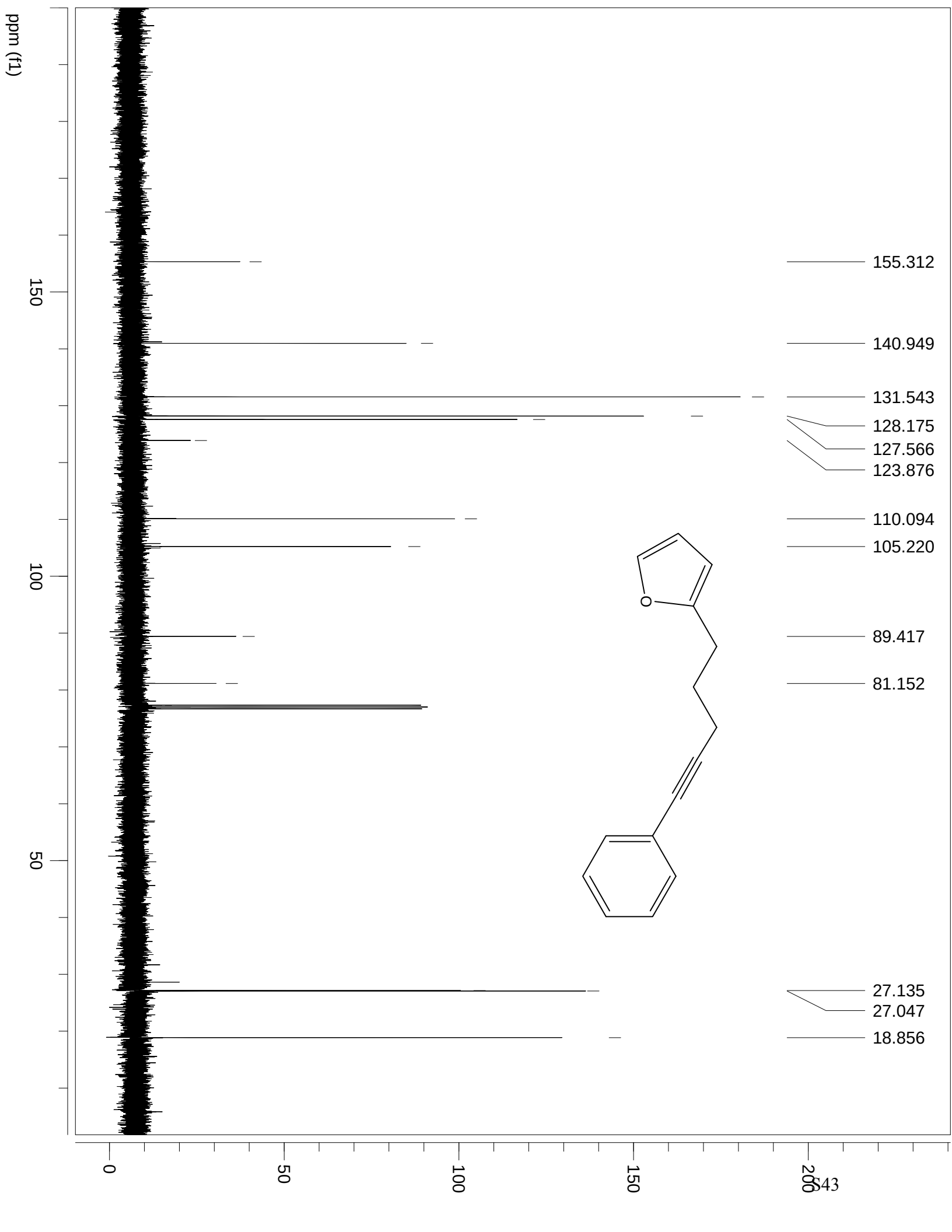
ppm (t1)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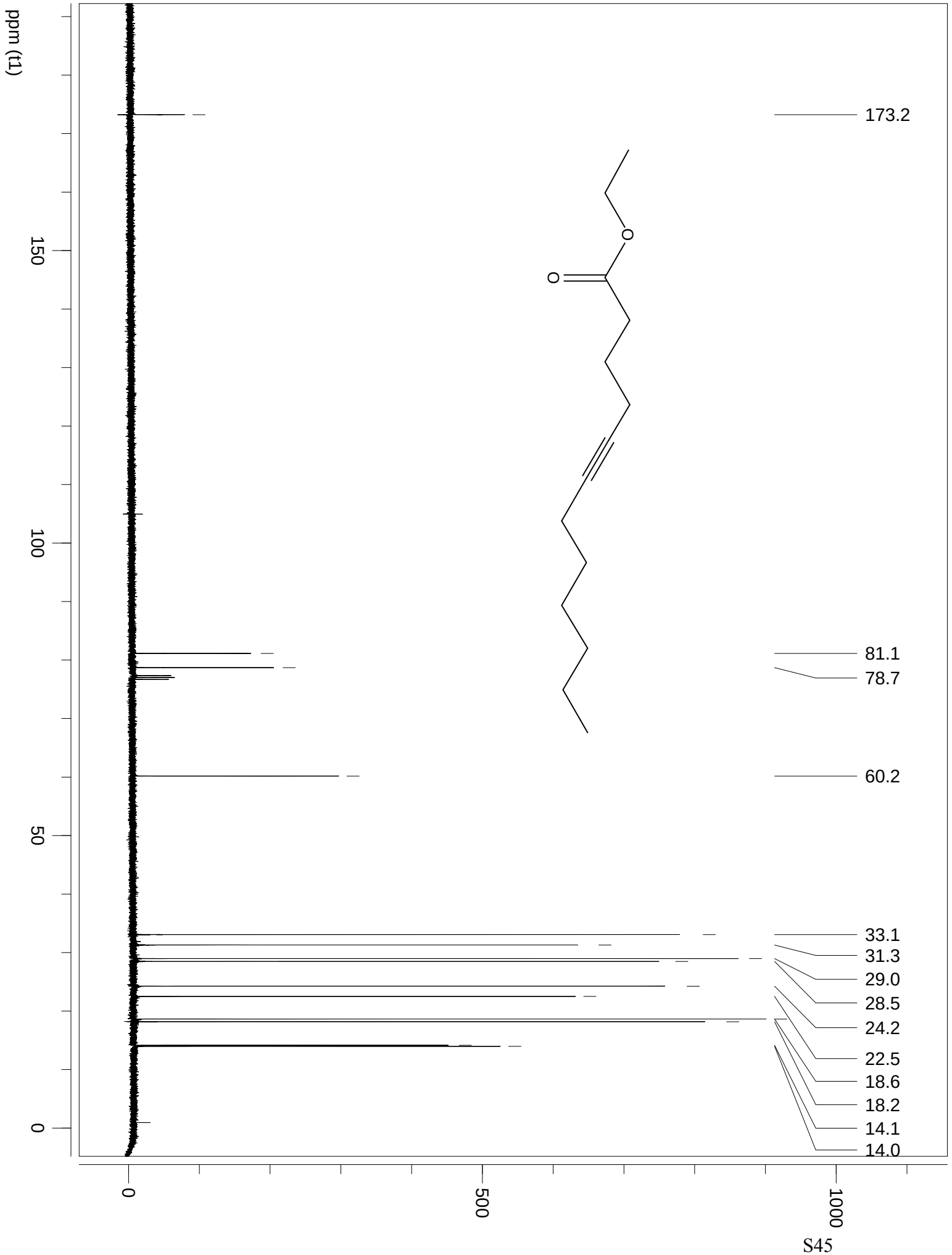
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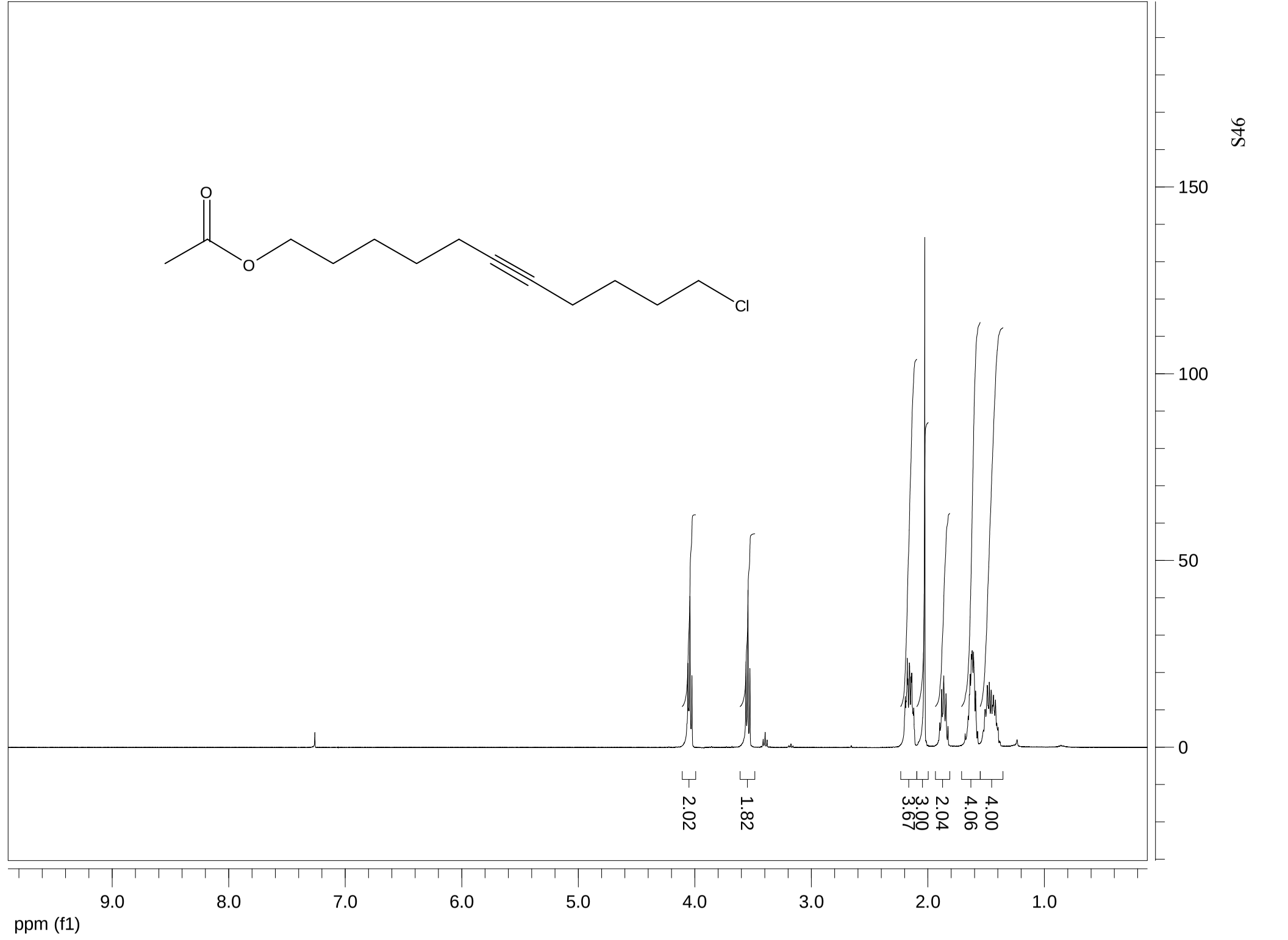
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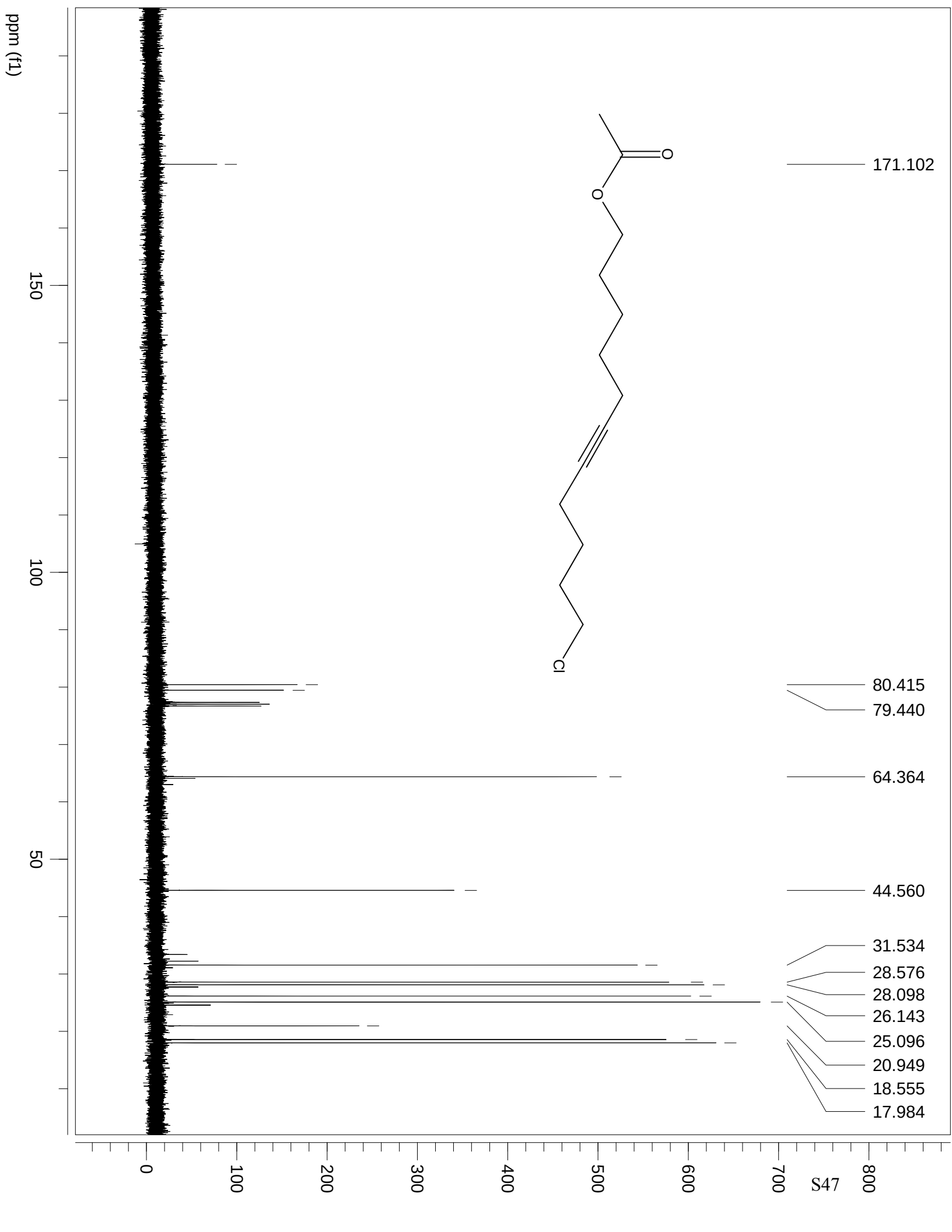
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2.02
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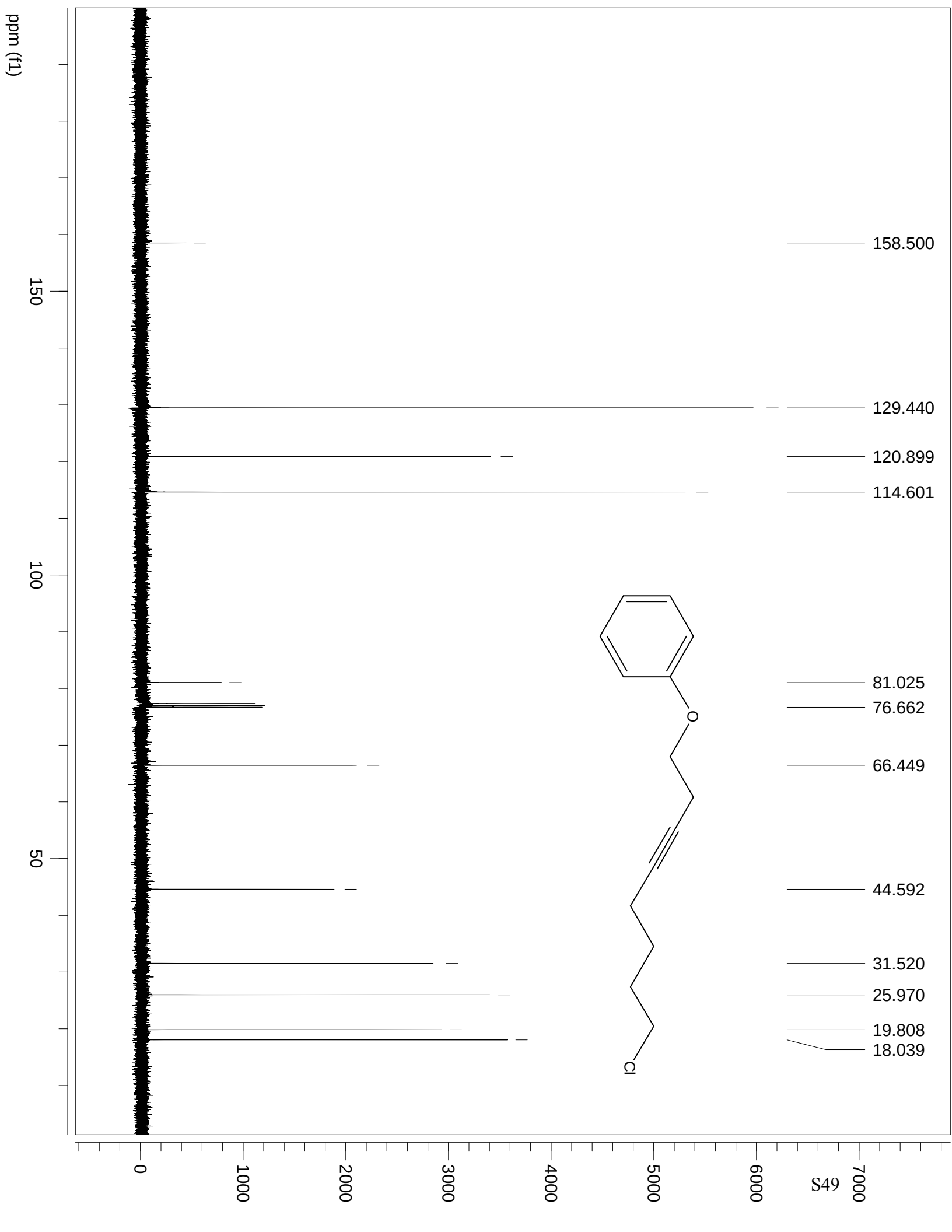
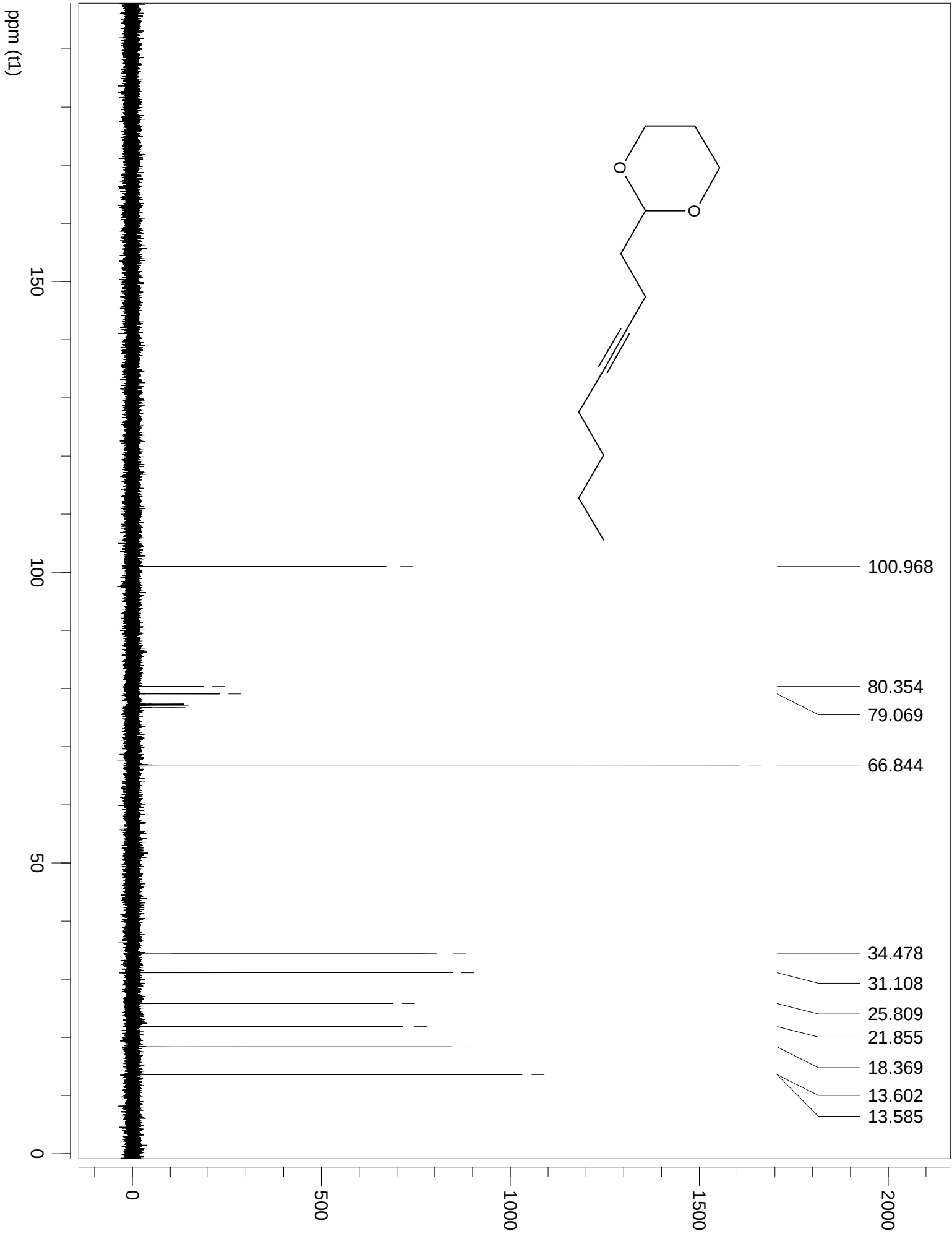
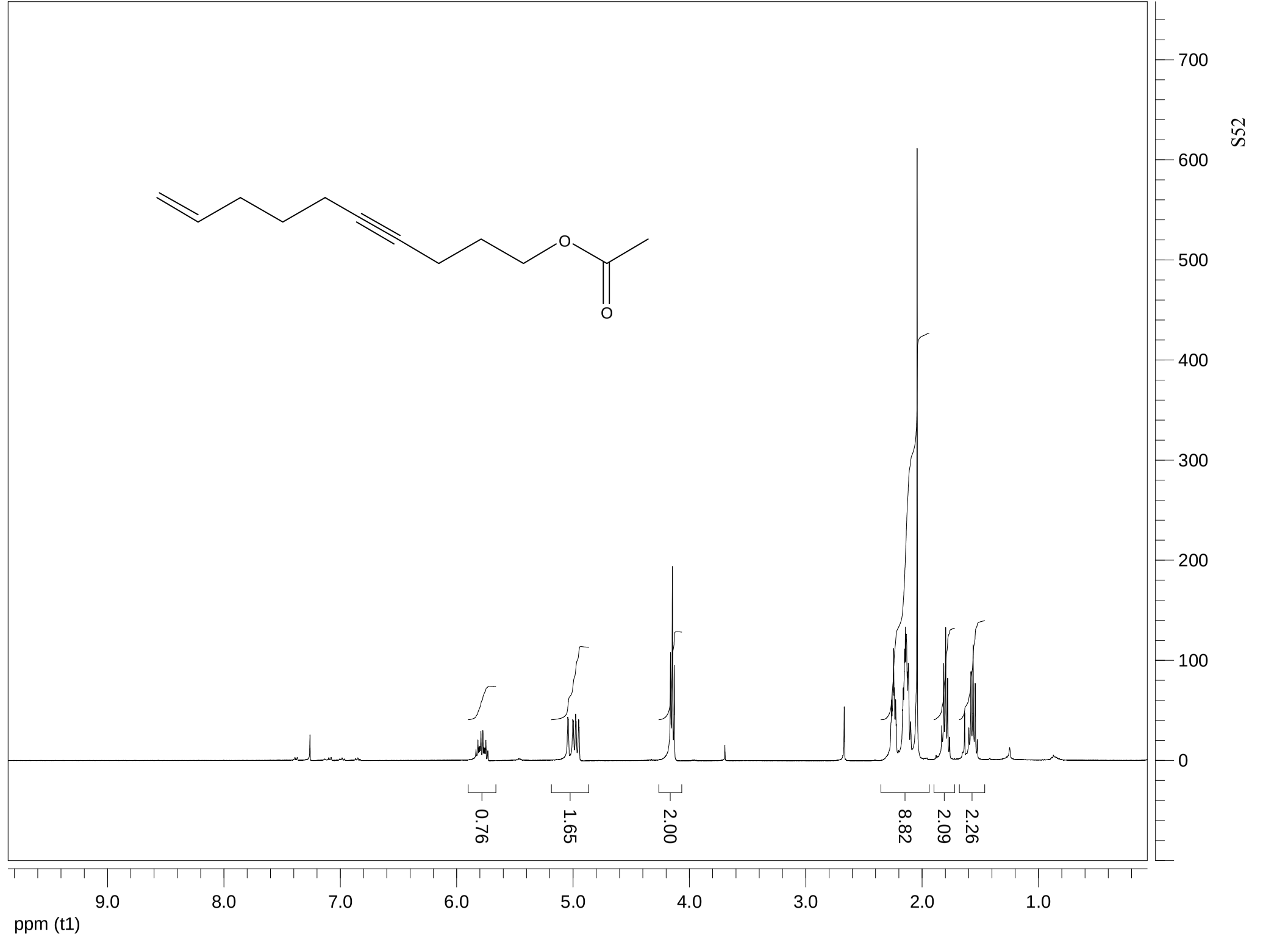
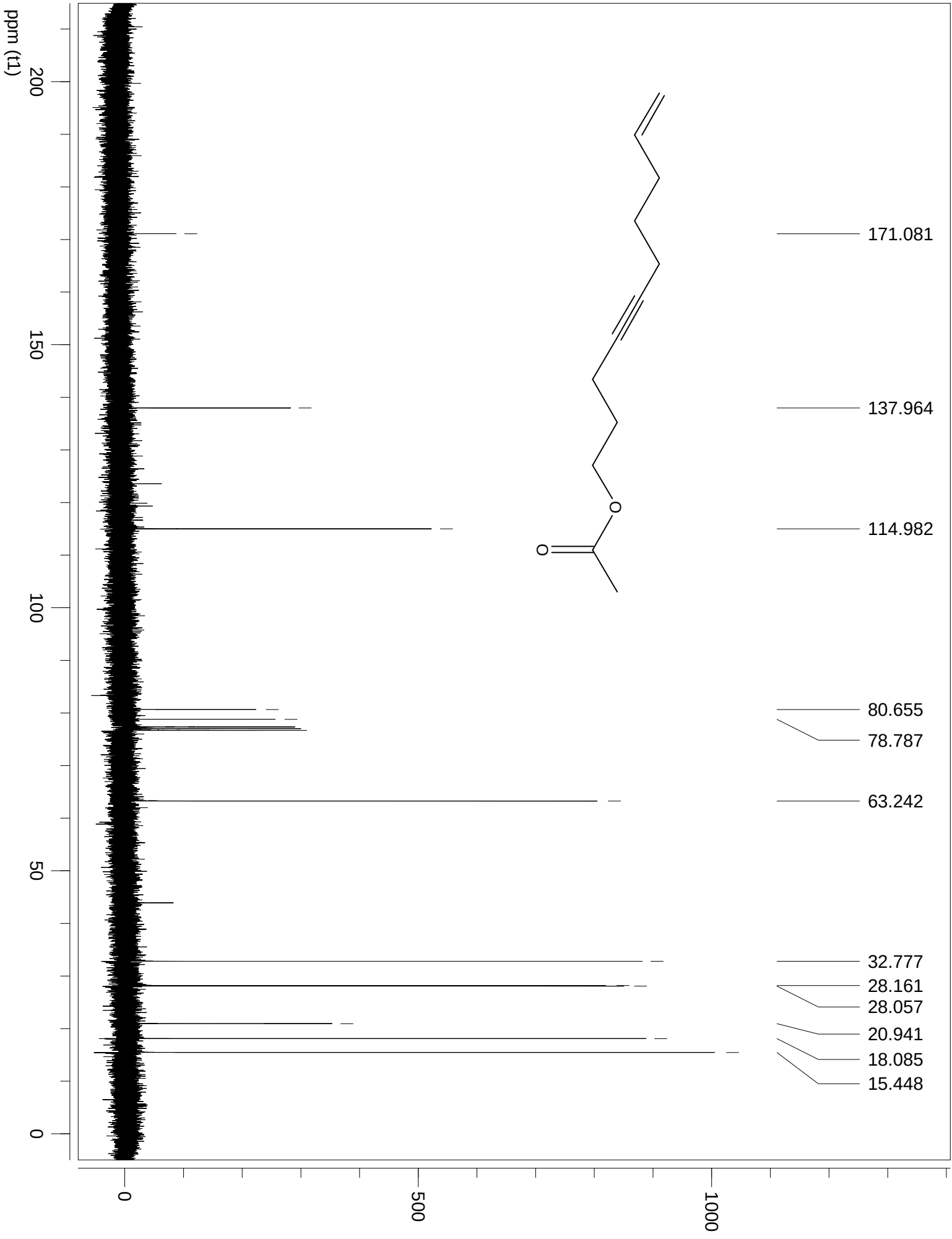
O
Cl


ppm (f1)
150
100
50
0
1000
2000
3000
4000
5000
6000
7000
158.500
129.440
120.899
114.601
81.025
76.662
66.449
44.592
31.520
25.970
19.808
18.039
O
Cl

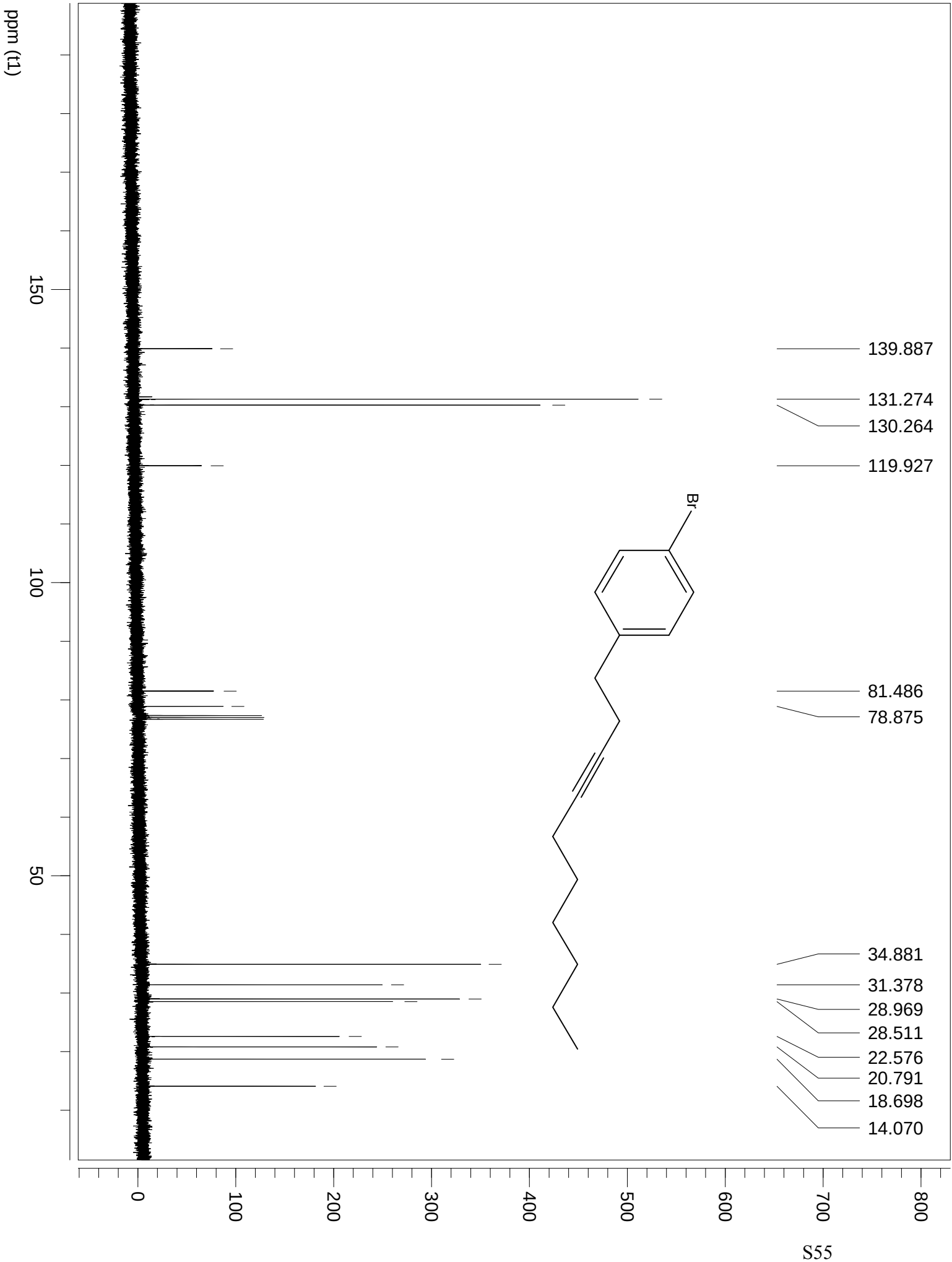
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
50
100
0.90
1.97
1.99
1.89
3.00
1.90
4.98
3.00
O
O


ppm (t1)
150
100
50
0
0
500
1000
1500
2000
O
O
100.968
80.354
79.069
66.844
34.478
31.108
25.809
21.855
18.369
13.602
13.585

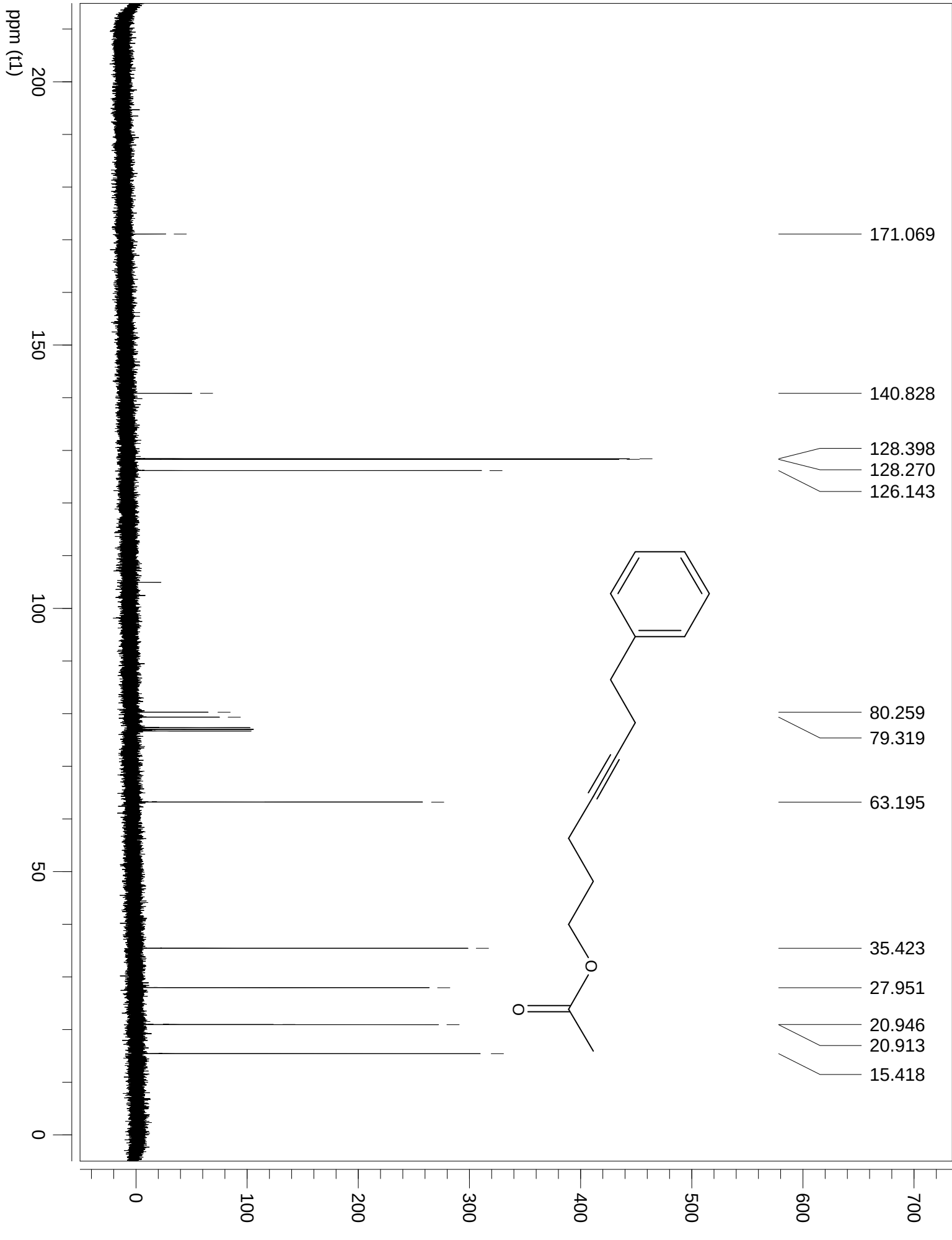

O
O
0.76
1.65
2.00
8.82
2.09
2.26
700
600
500
400
300
200
100
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

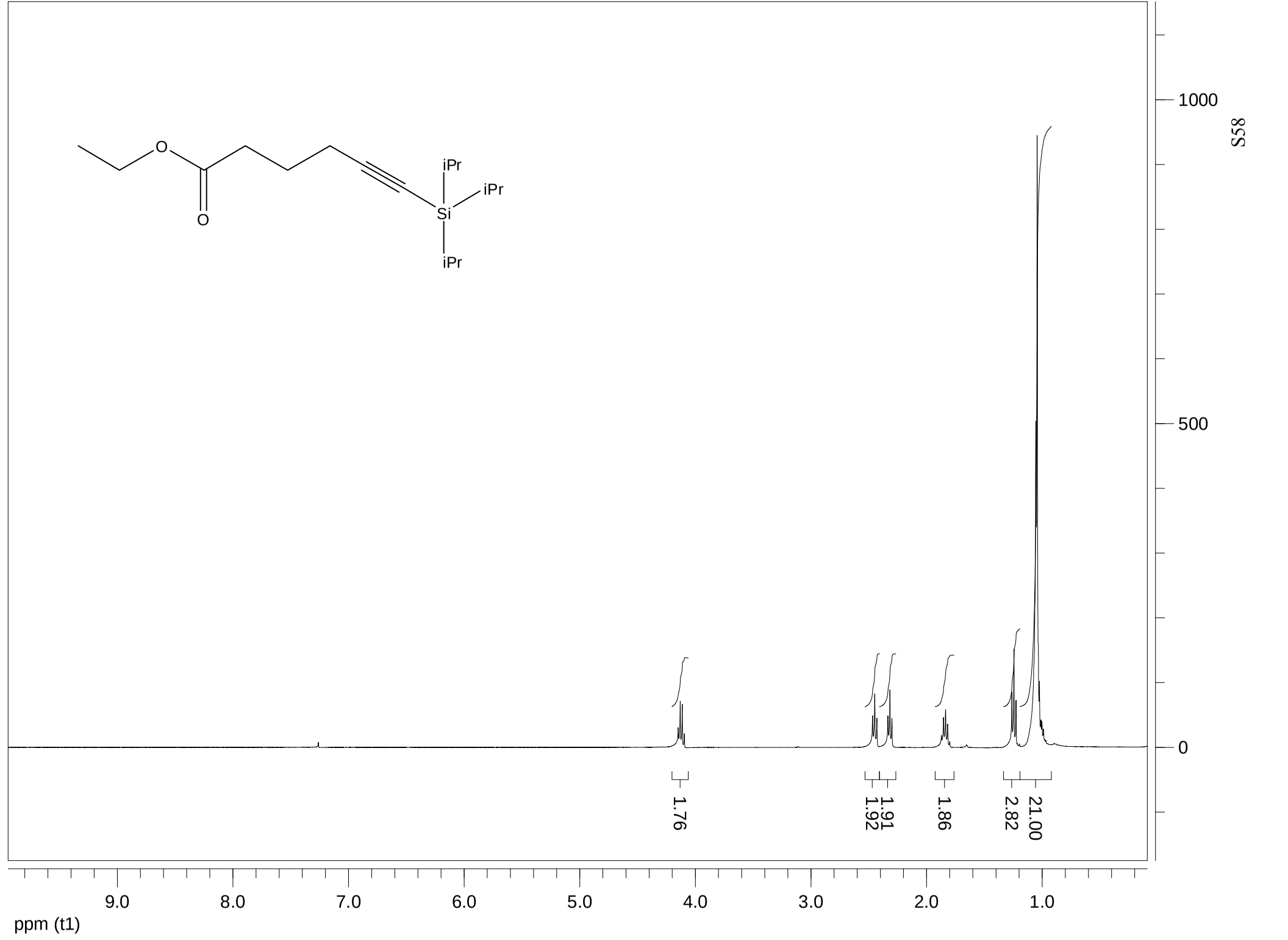

ppm (t1)
200
150
100
50
0
0
500
1000
O
O
171.081
137.964
114.982
80.655
78.787
63.242
32.777
28.161
28.057
20.941
18.085
15.448

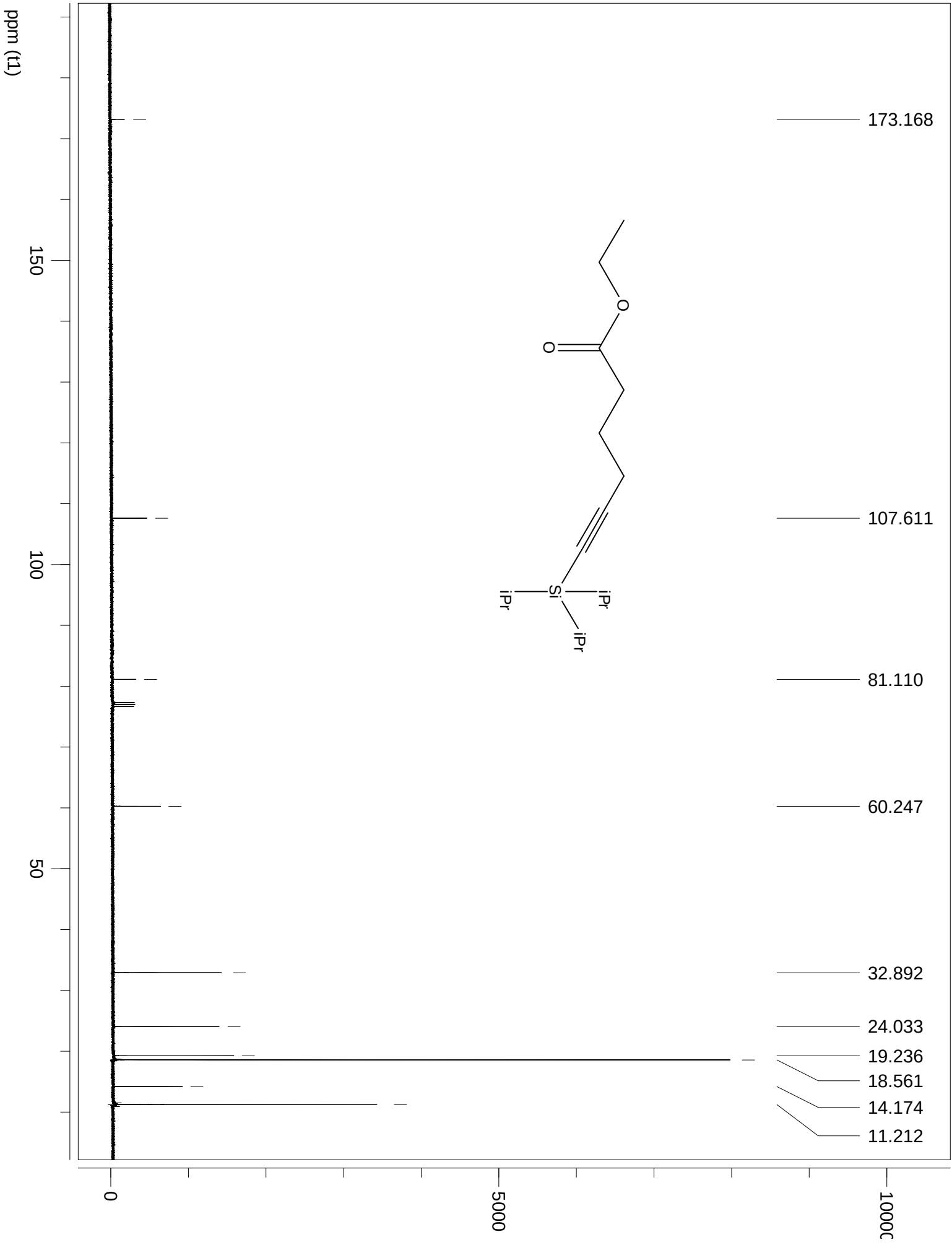
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
50
100
1.72
1.83
1.84
1.87
1.91
1.96
6.08
3.00
Br


ppm (t1)
150
100
50
0
100
200
300
400
500
600
700
800
139.887
131.274
130.264
119.927
Br
81.486
78.875
34.881
31.378
28.969
28.511
22.576
20.791
18.698
14.070

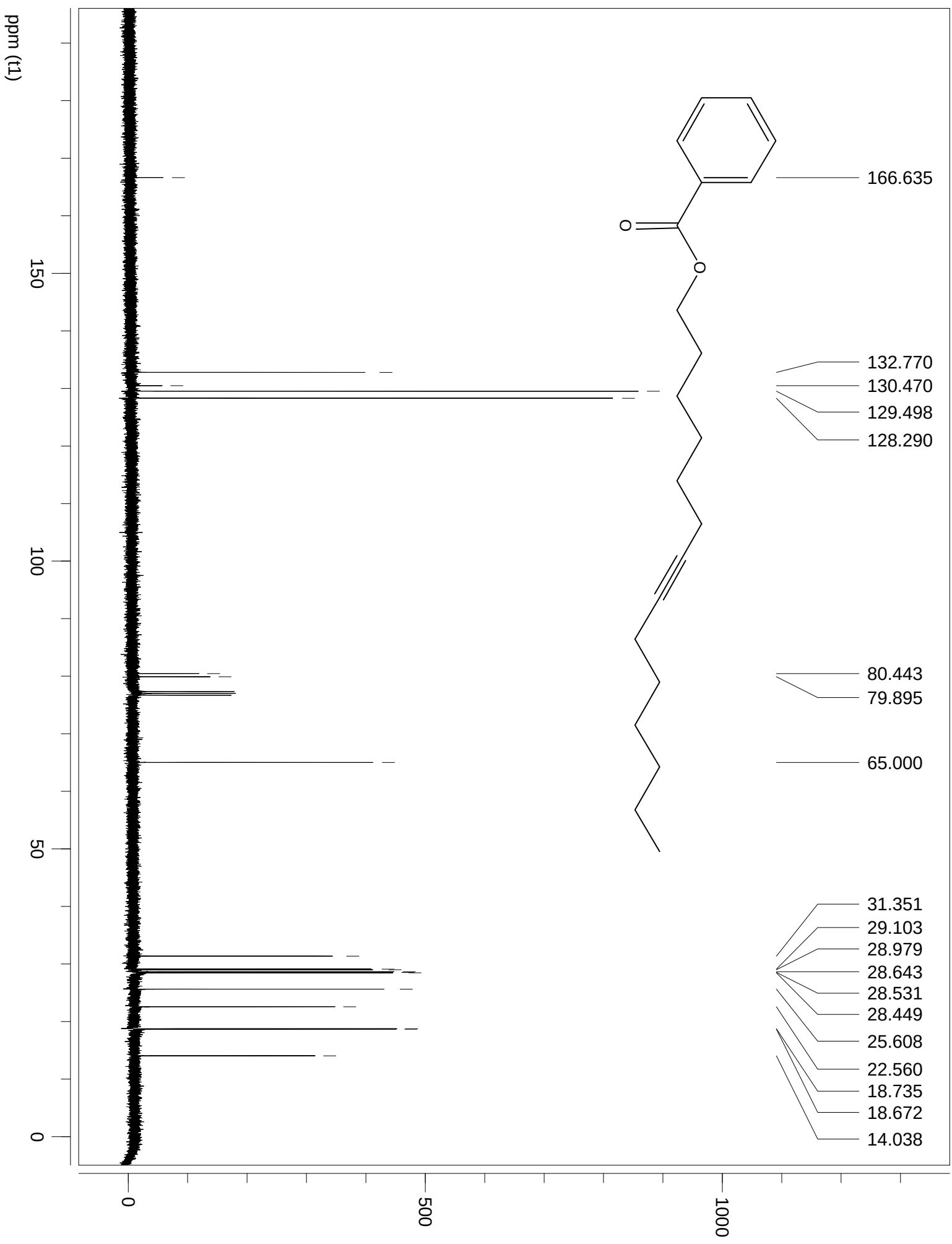
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
100
200
300
400
500
600
4.50
2.00
1.94
1.98
2.06
2.82
2.07
O
O


ppm (t1)
200
150
100
50
0
171.069
140.828
128.398
128.270
126.143
80.259
79.319
63.195
35.423
27.951
20.946
20.913
15.418
O
O
0
100
200
300
400
500
600
700

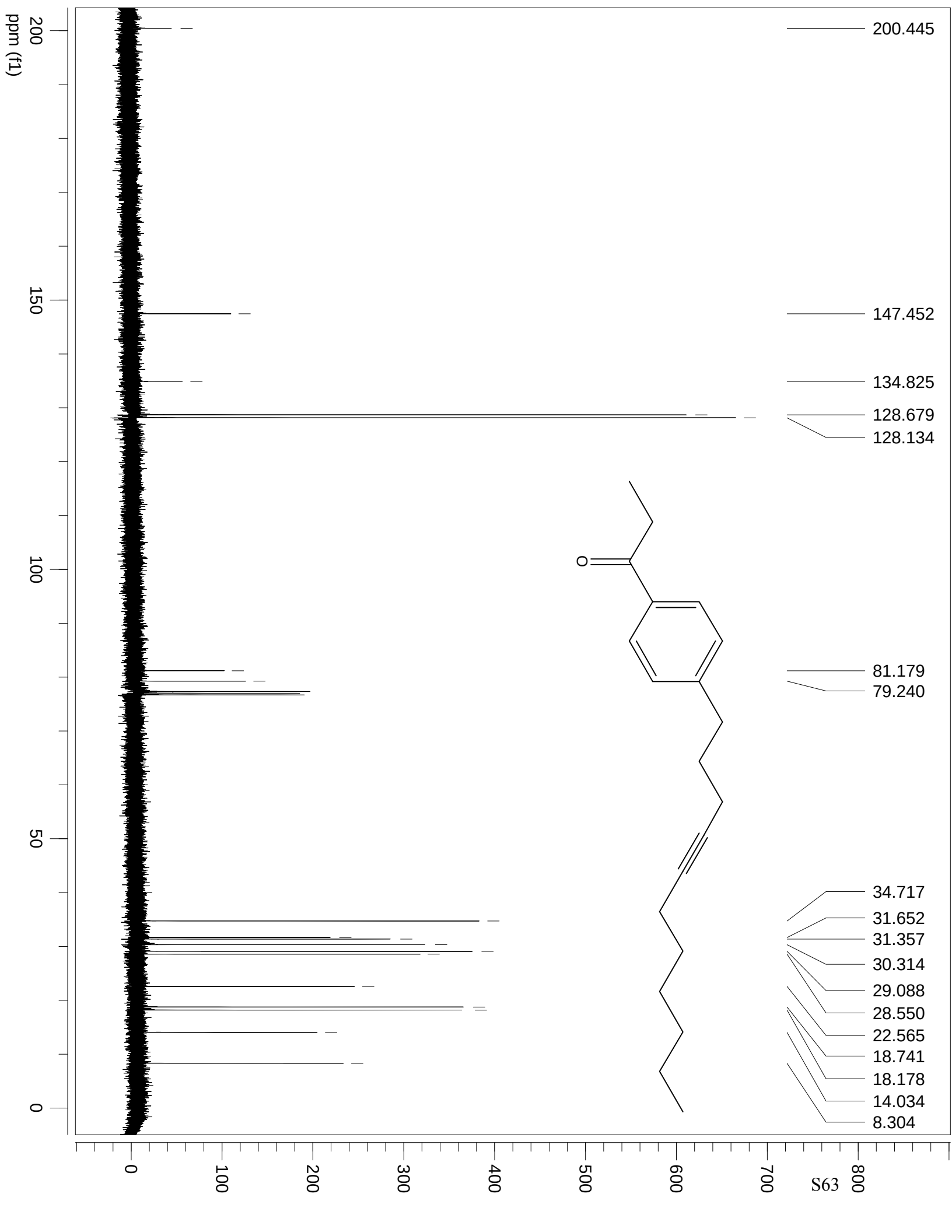

O
O
Si
iPr
iPr
iPr
1000
500
0
1.76
1.92
1.91
1.86
2.82
21.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


ppm (t1)
150
100
50
0
5000
1000
O
O
Si
iPr
iPr
iPr
173.168
107.611
81.110
60.247
32.892
24.033
19.236
18.561
14.174
11.212

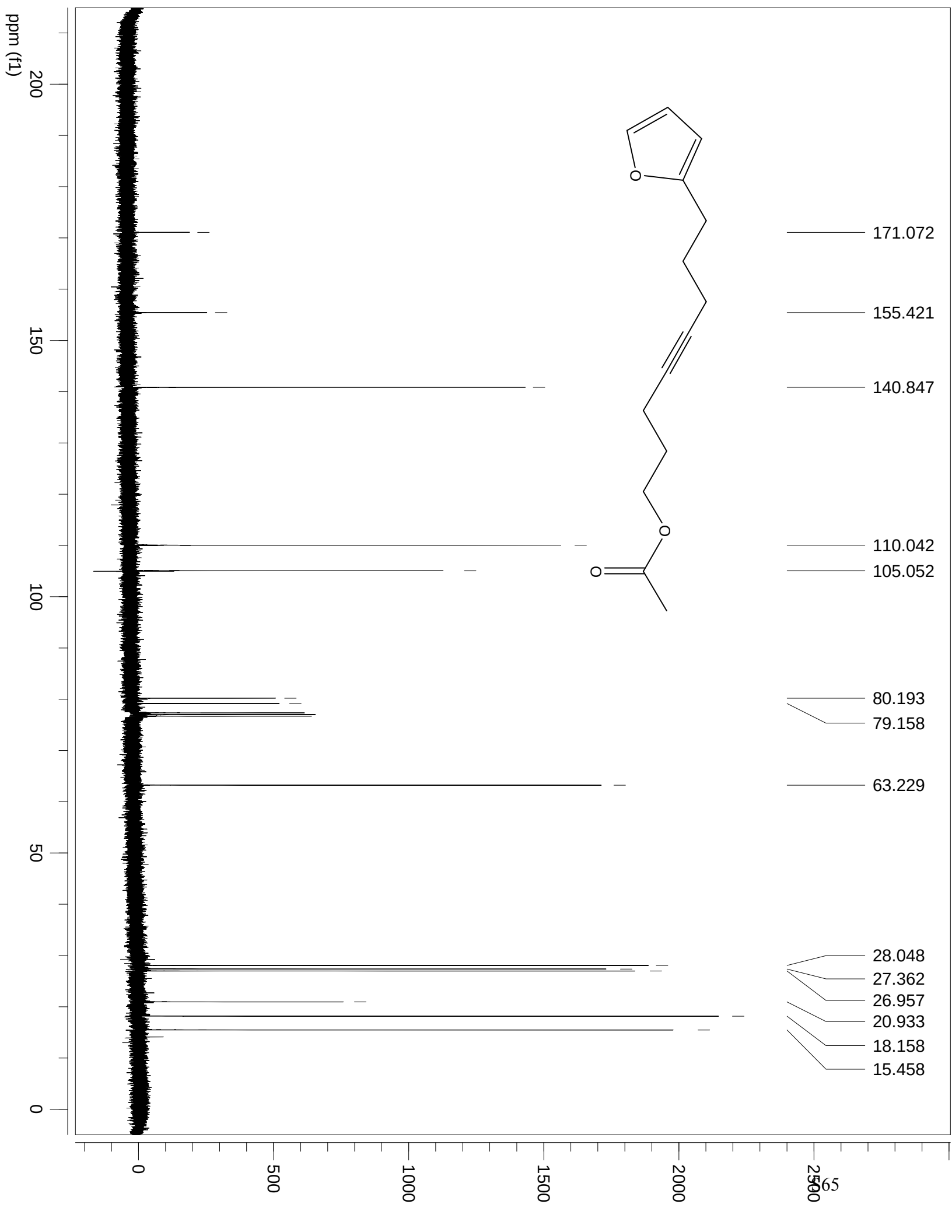
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1.69
0.88
1.84
2.00
4.03
2.09
14.86
2.98
0
50
100
150
200
O
O


ppm (t1)
150
100
50
0
0
500
1000
O
O
166.635
132.770
130.470
129.498
128.290
80.443
79.895
65.000
31.351
29.103
28.979
28.643
28.531
28.449
25.608
22.560
18.735
18.672
14.038

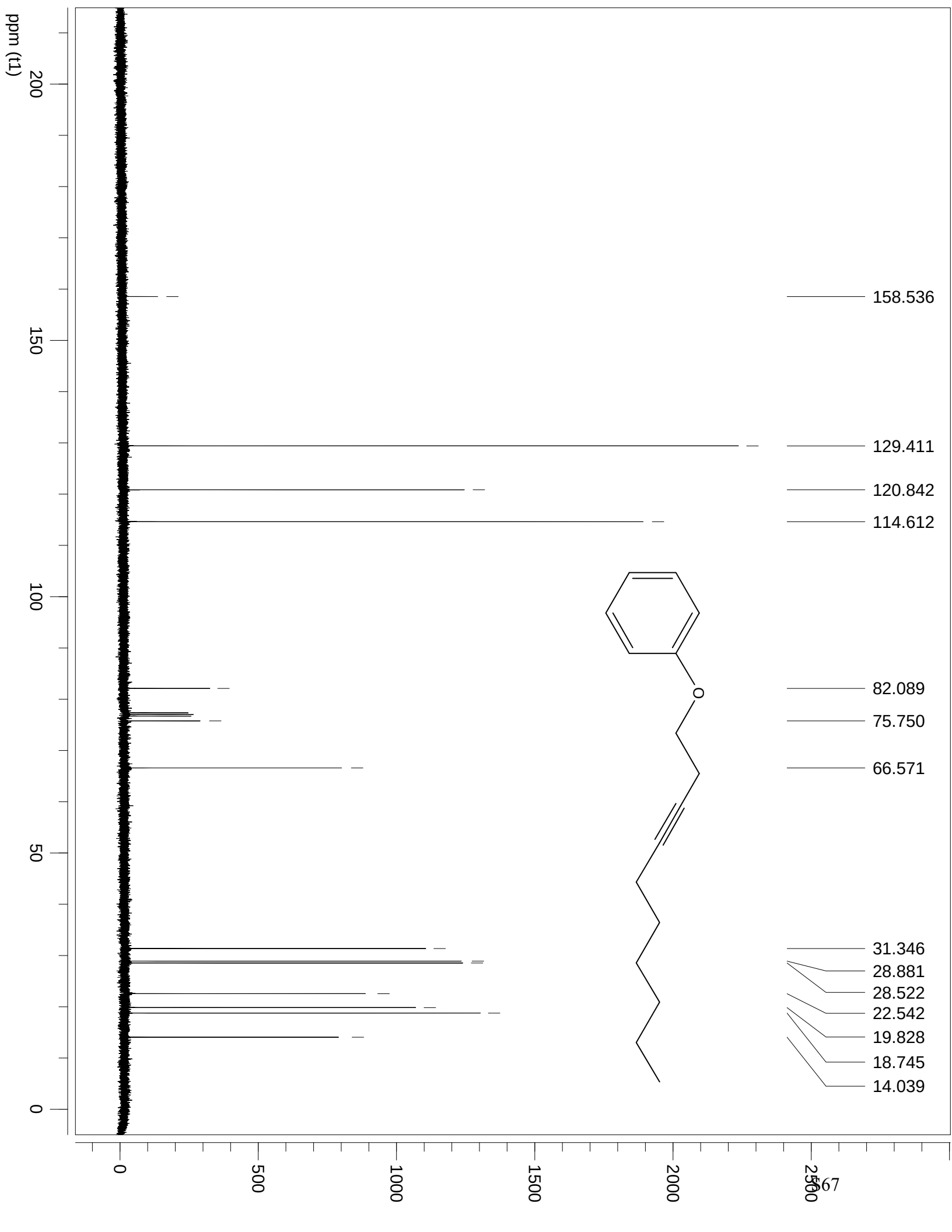
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1.89
1.98
2.03
1.98
3.95
1.96
11.21
3.00
0
50
100
150
O

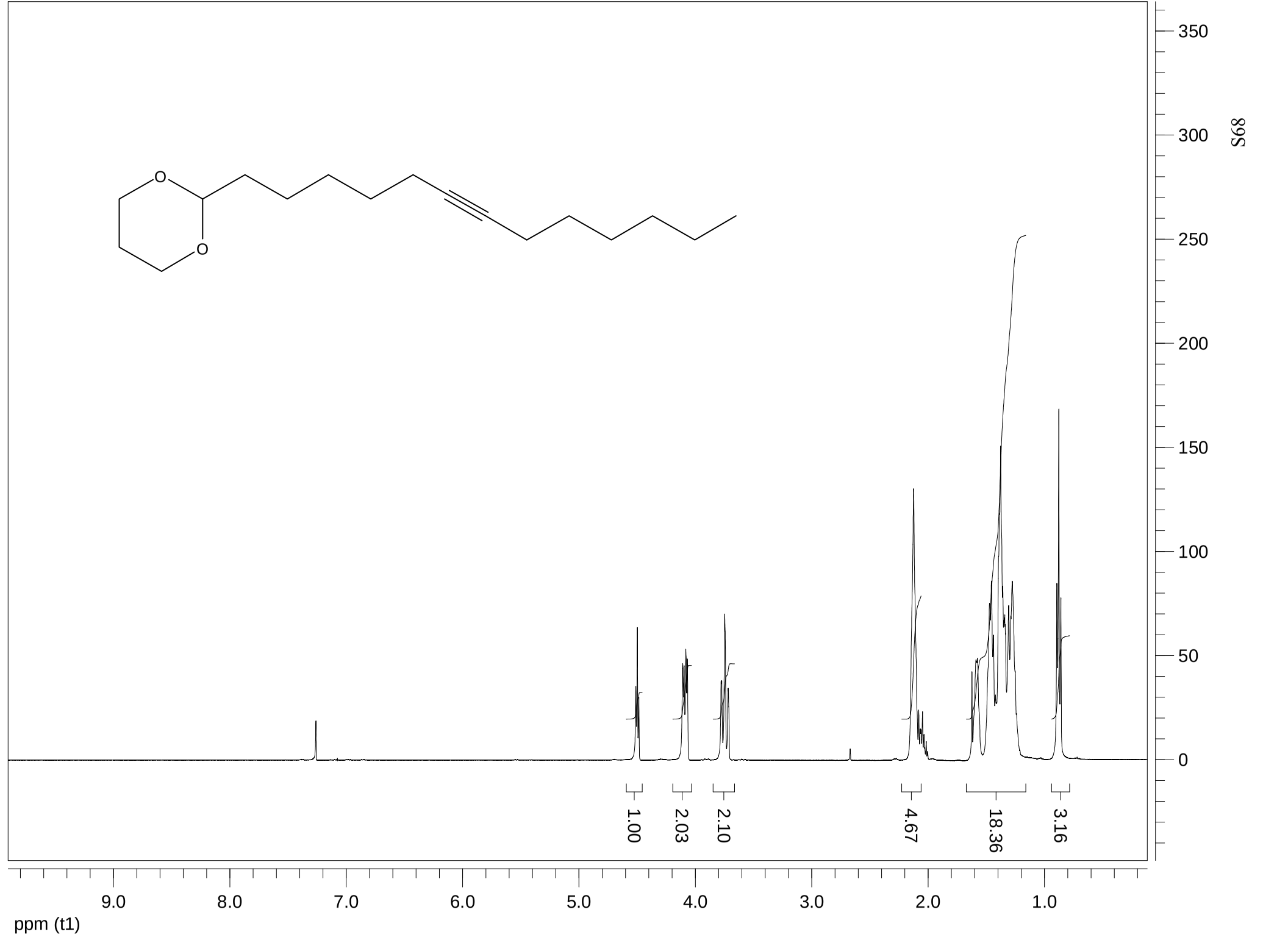

ppm (f1)
200
150
100
50
0
200.445
147.452
134.825
128.679
128.134
81.179
79.240
34.717
31.652
31.357
30.314
29.088
28.550
22.565
18.741
18.178
14.034
8.304
O
0
100
200
300
400
500
600
700
800

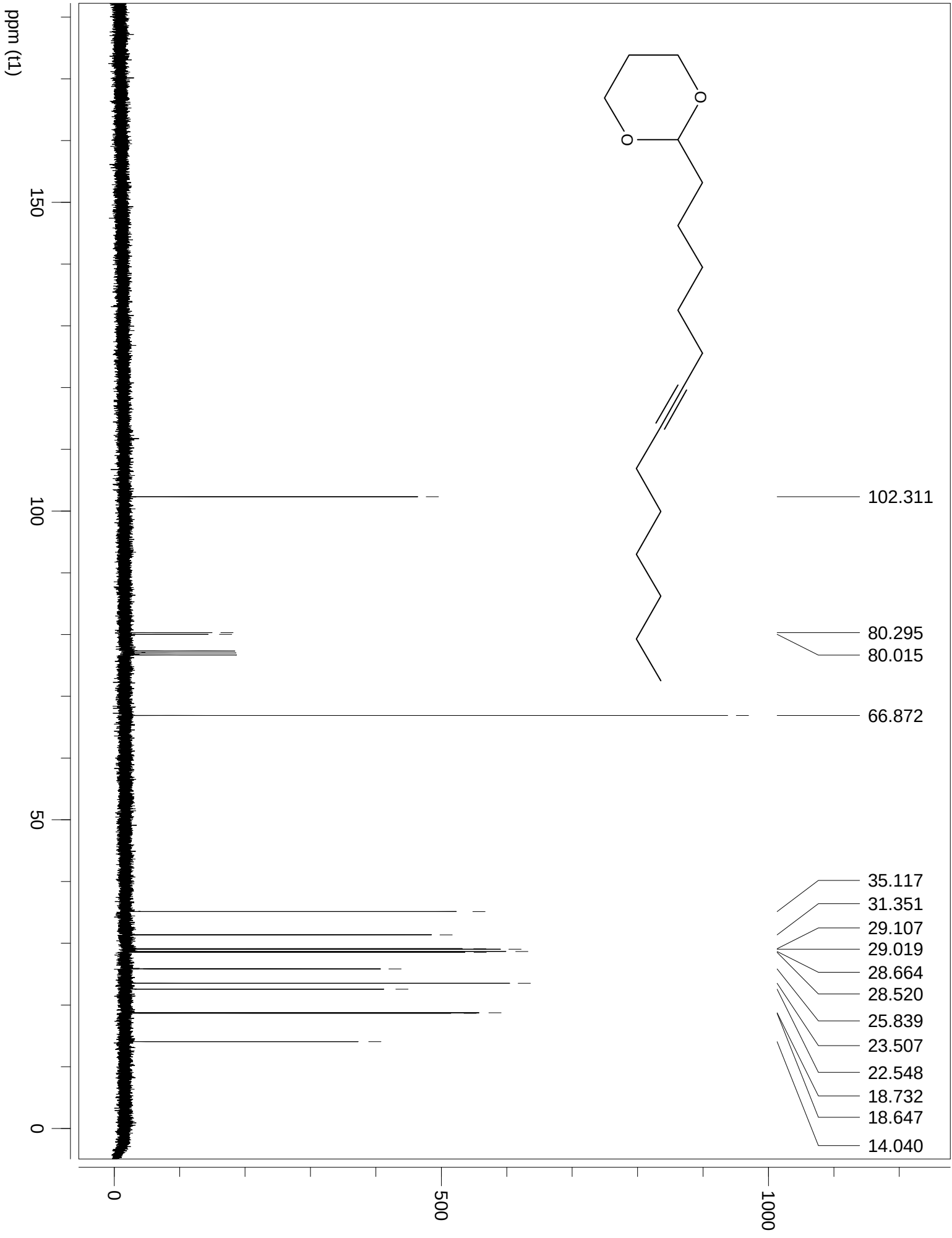
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
500
0.78
0.80
0.80
2.13
2.13
4.38
3.00
4.39
O
O
O

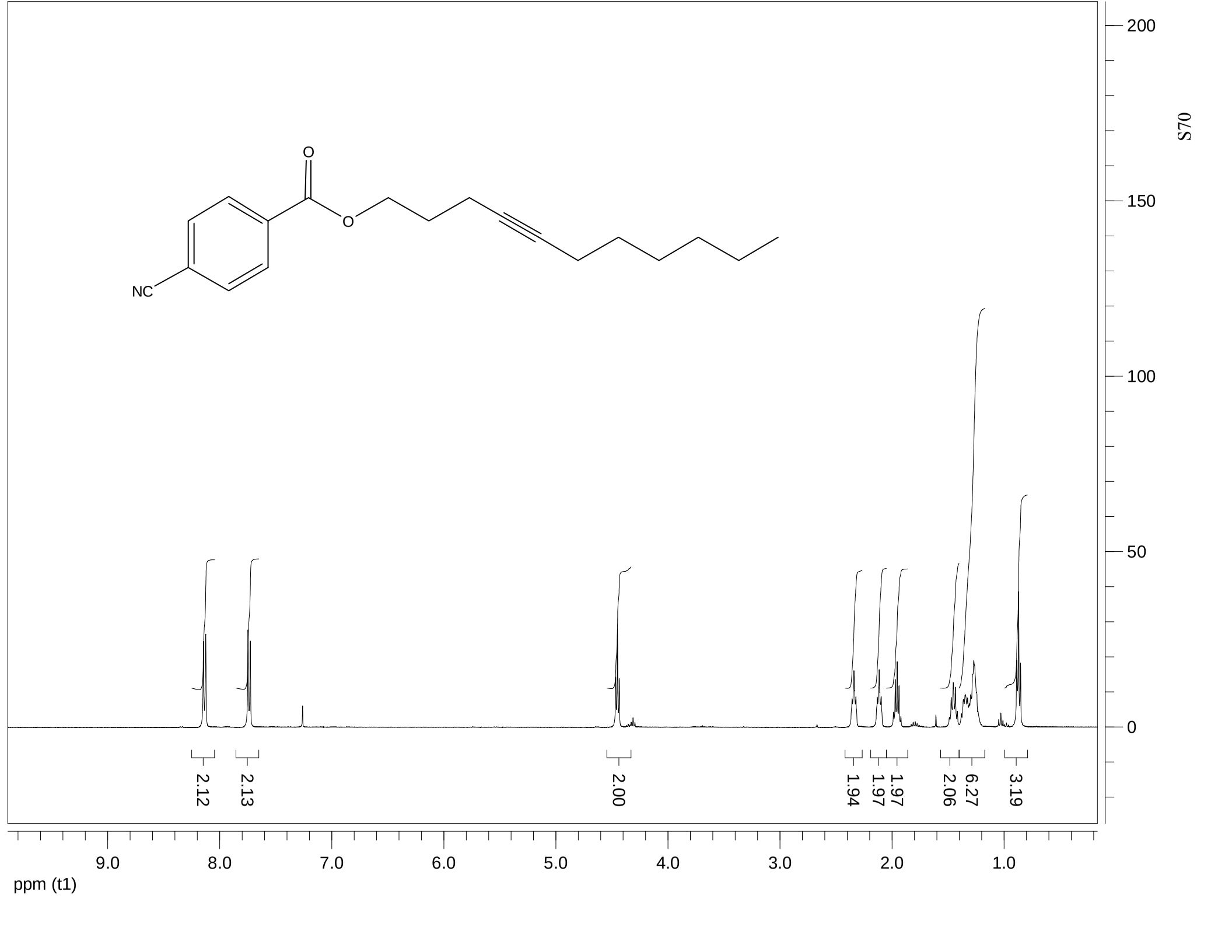

ppm (f1)
200
150
100
50
0
0
500
1000
1500
2000
2500
O
O
O
171.072
155.421
140.847
110.042
105.052
80.193
79.158
63.229
28.048
27.362
26.957
20.933
18.158
15.458

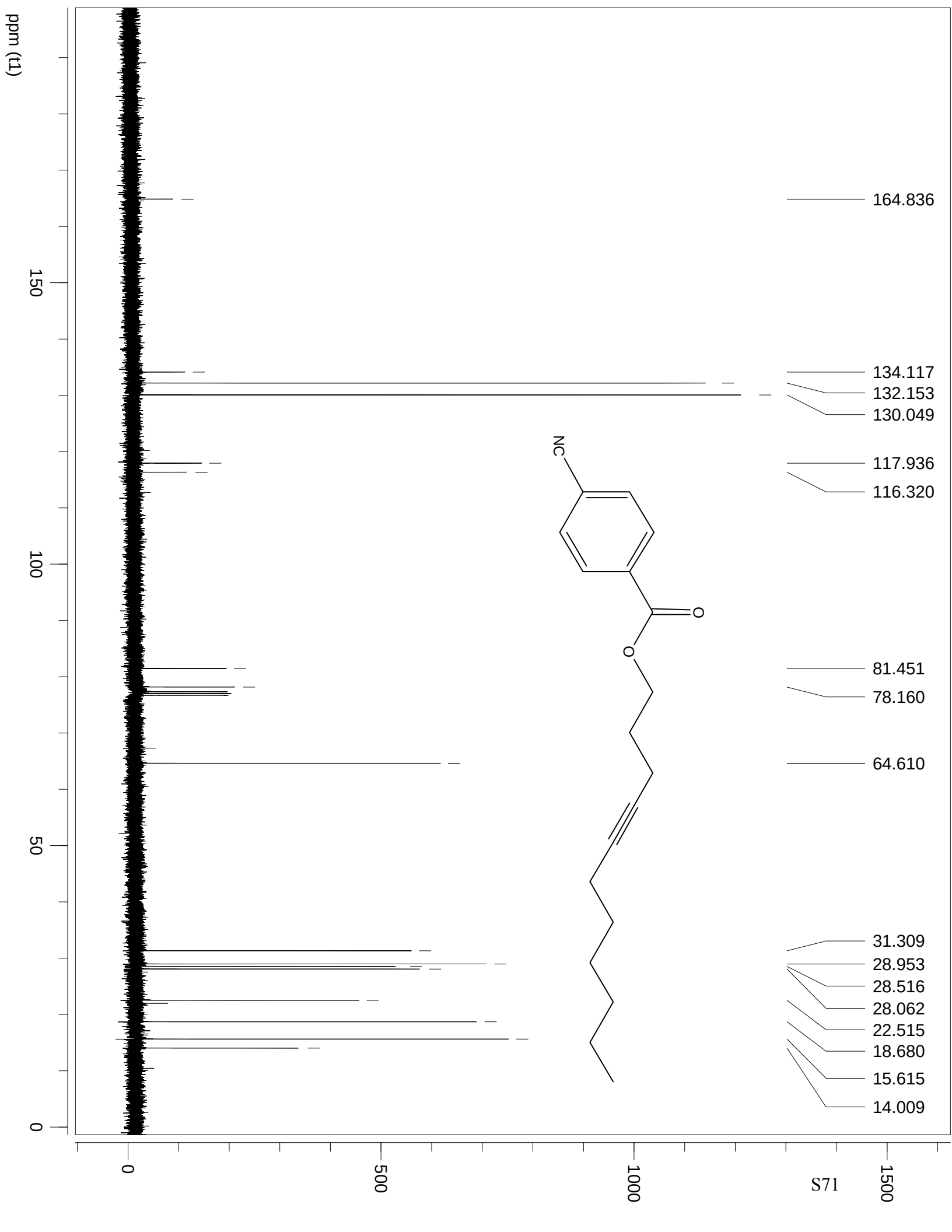
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1.94
2.77
1.85
1.85
1.87
2.00
6.39
3.17
0
10
20
30
40
50
60
O


ppm (t1)
200
150
100
50
0
158.536
129.411
120.842
114.612
82.089
75.750
66.571
31.346
28.881
28.522
22.542
19.828
18.745
14.039
O
0
500
1000
1500
2000
2500

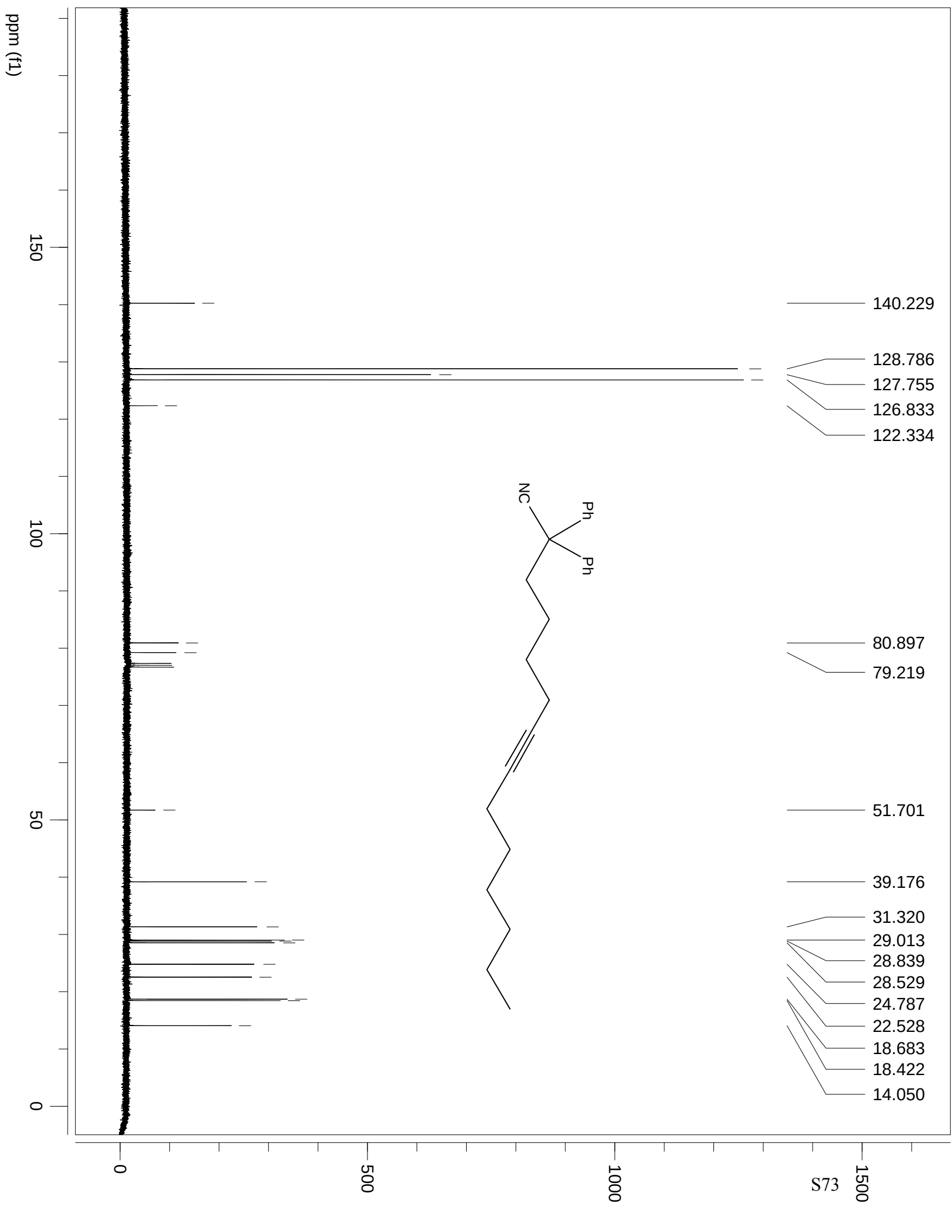

O
O
350
300
250
200
150
100
50
0
1.00
2.03
2.10
4.67
18.36
3.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


ppm (t1)
150
100
50
0
0
500
1000
O
O
102.311
80.295
80.015
66.872
35.117
31.351
29.107
29.019
28.664
28.520
25.839
23.507
22.548
18.732
18.647
14.040

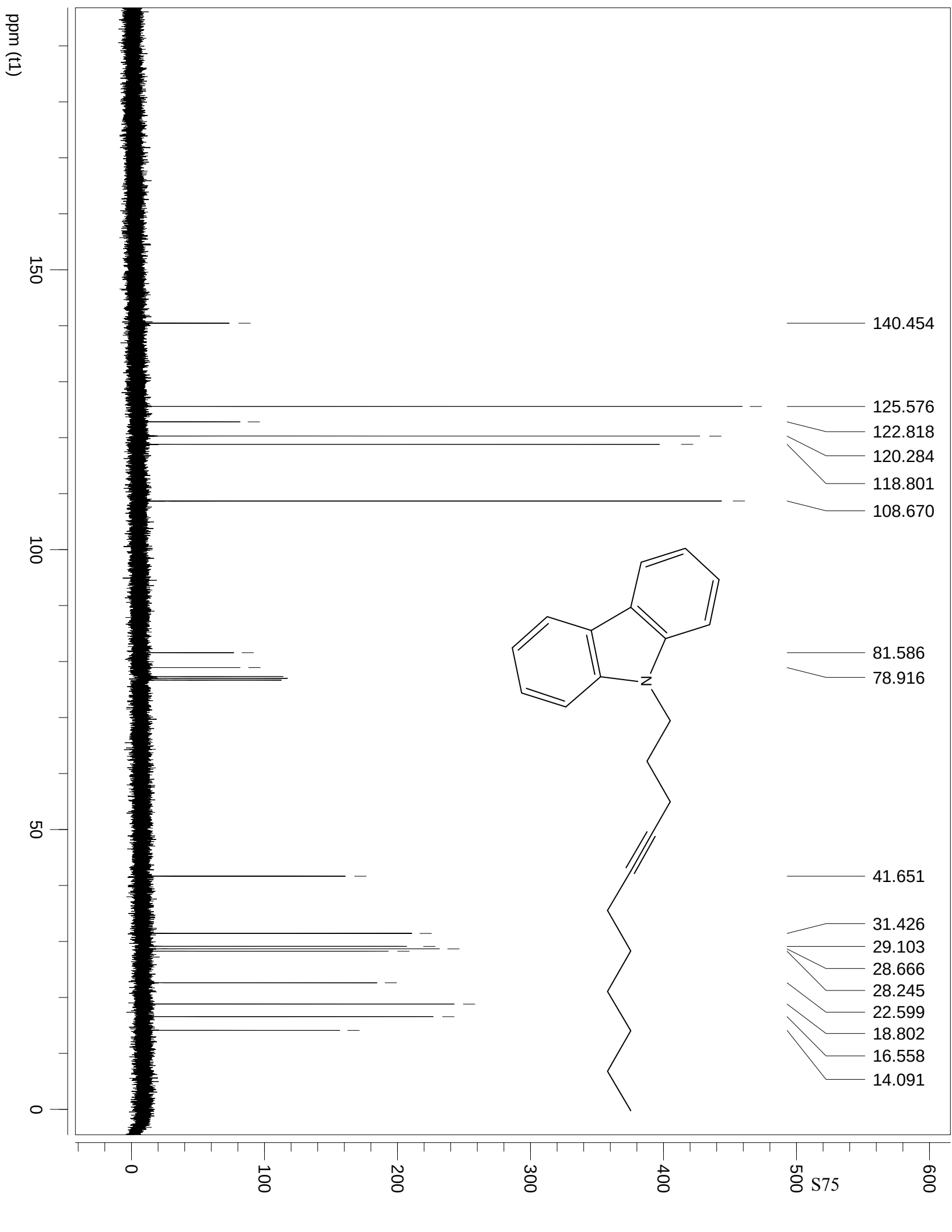

O
O
NC
200
150
100
50
0
2.12
2.13
2.00
1.94
1.97
1.97
2.06
6.27
3.19
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


ppm (t1)
150
100
50
0
0
500
1000
1500
164.836
134.117
132.153
130.049
117.936
116.320
81.451
78.160
64.610
31.309
28.953
28.516
28.062
22.515
18.680
15.615
14.009
NC
O
O

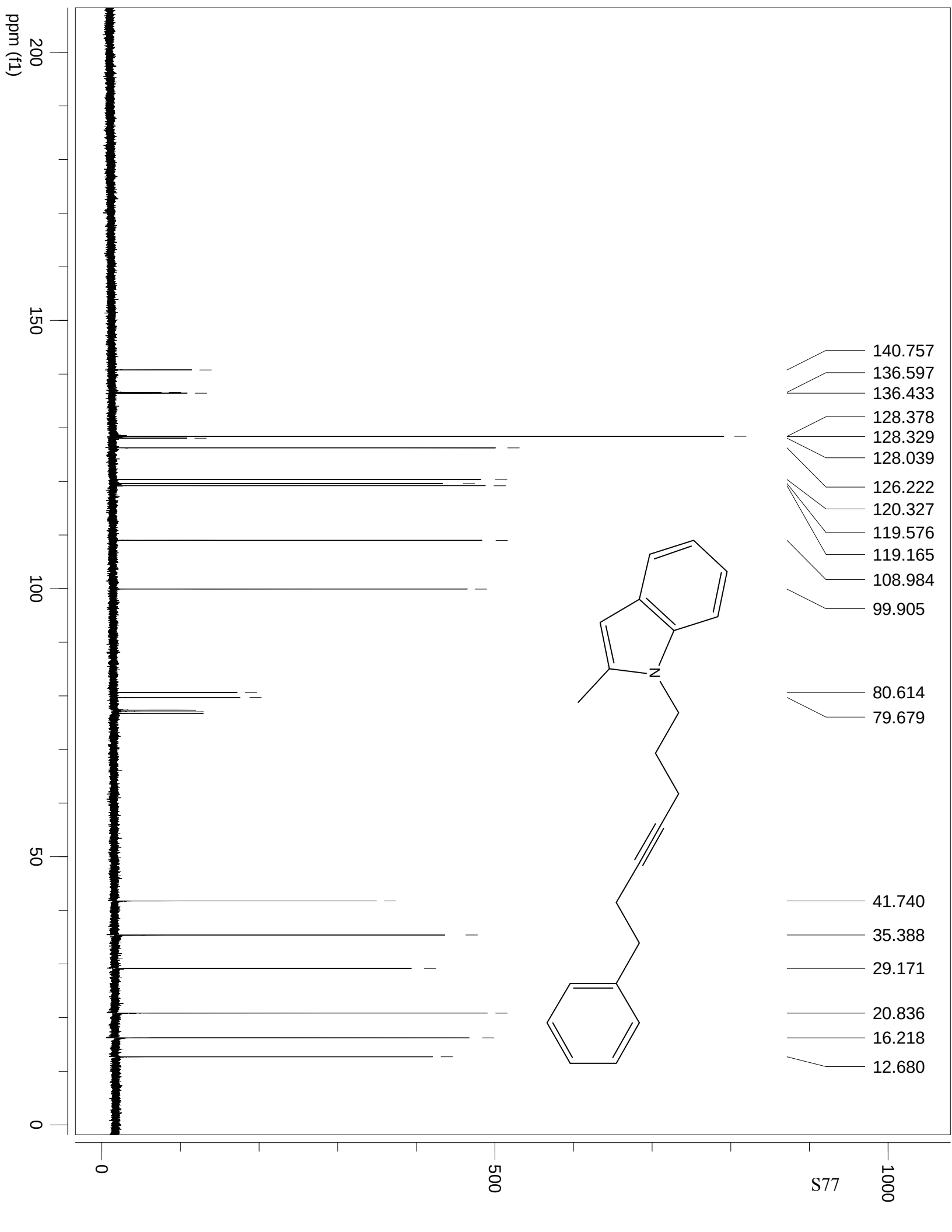
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
50
100
150
200
7.96
1.91
3.20
6.51
2.18
4.15
2.07
1.99
2.00
NC
Ph
Ph

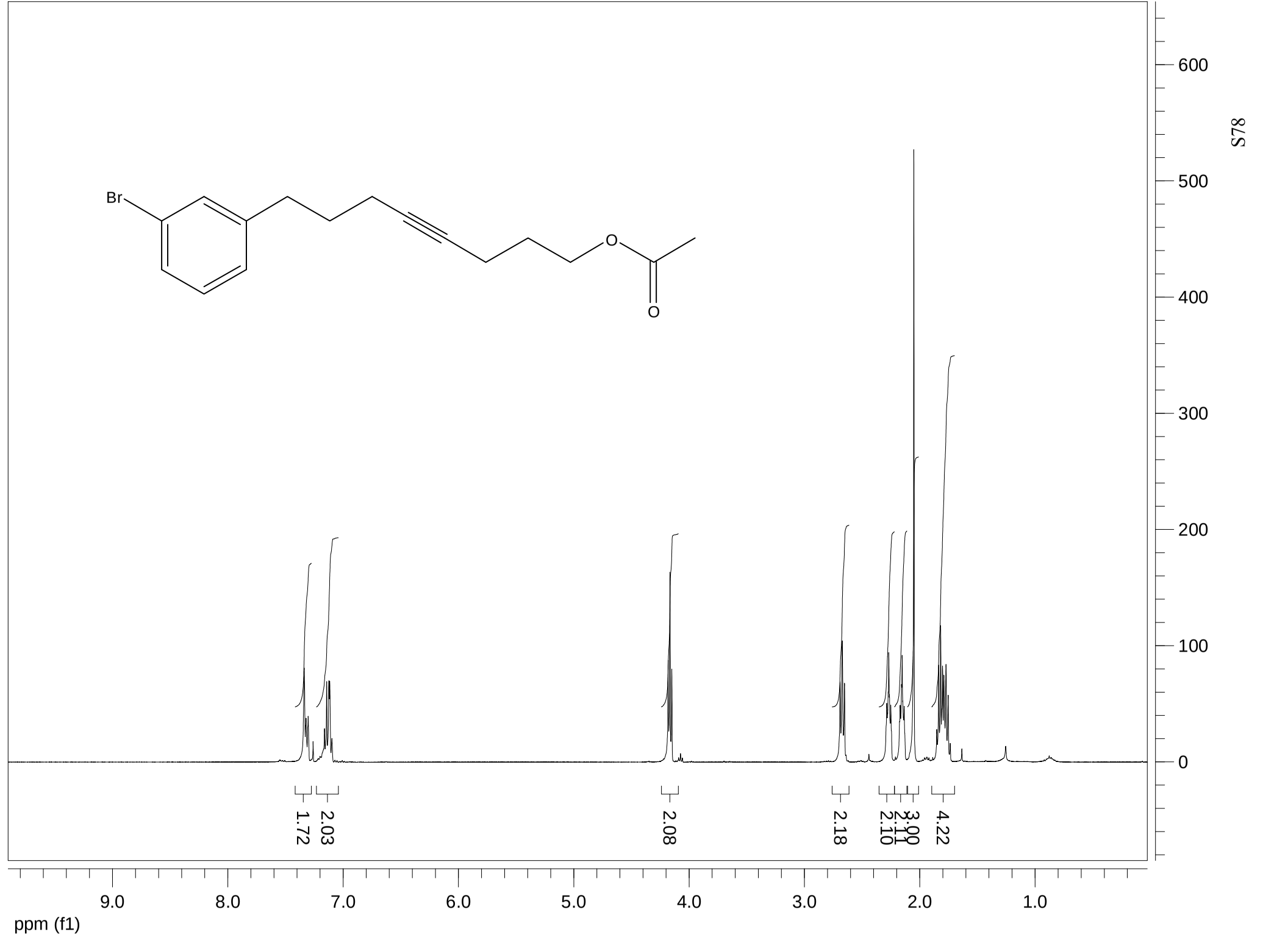

ppm (f1)
150
100
50
0
0
500
1000
1500
140.229
128.786
127.755
126.833
122.334
NC
Ph
Ph
80.897
79.219
51.701
39.176
31.320
29.013
28.839
28.529
24.787
22.528
18.683
18.422
14.050

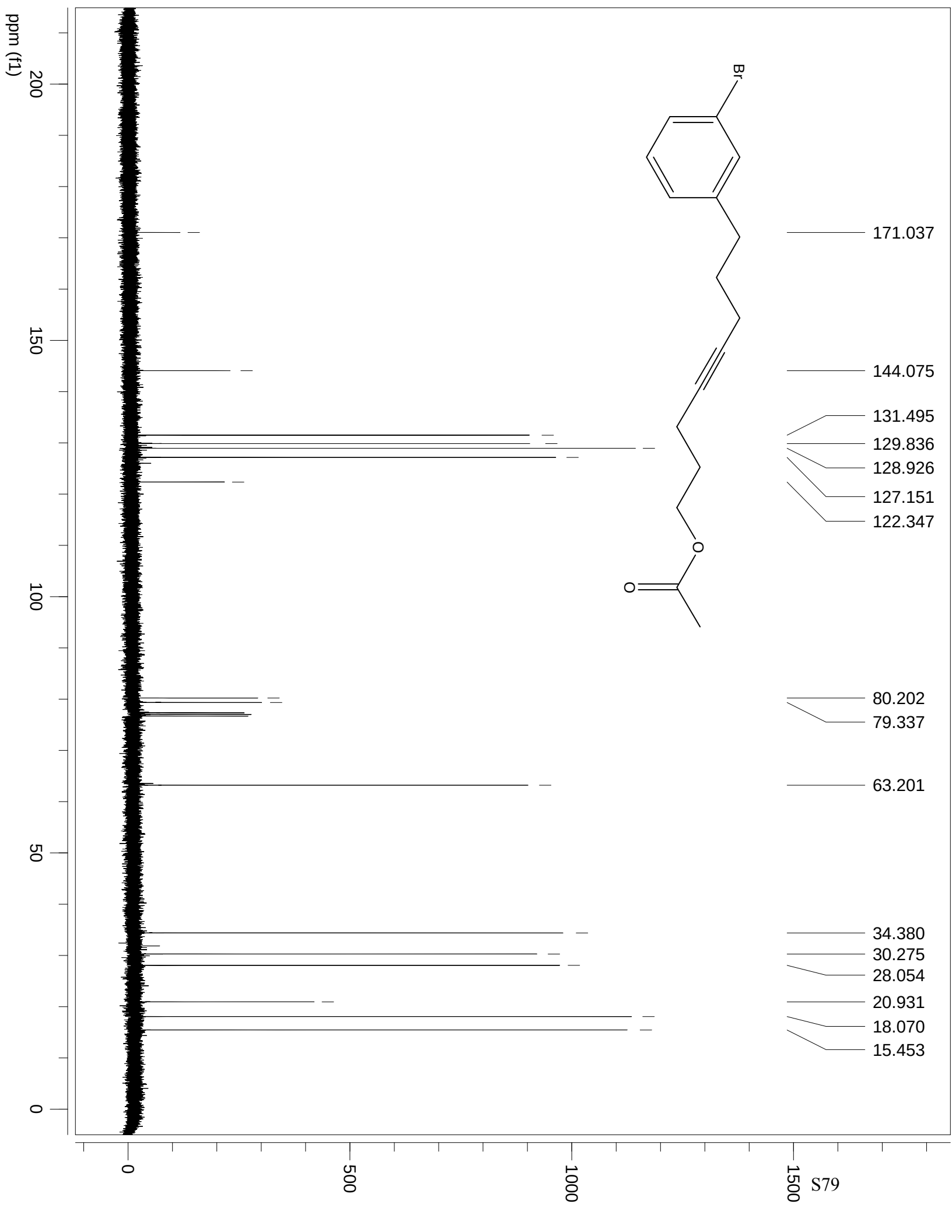
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
50
100
150
200
250
300
350
1.78
3.82
2.18
1.94
3.92
2.00
2.08
2.04
4.47
3.29
N

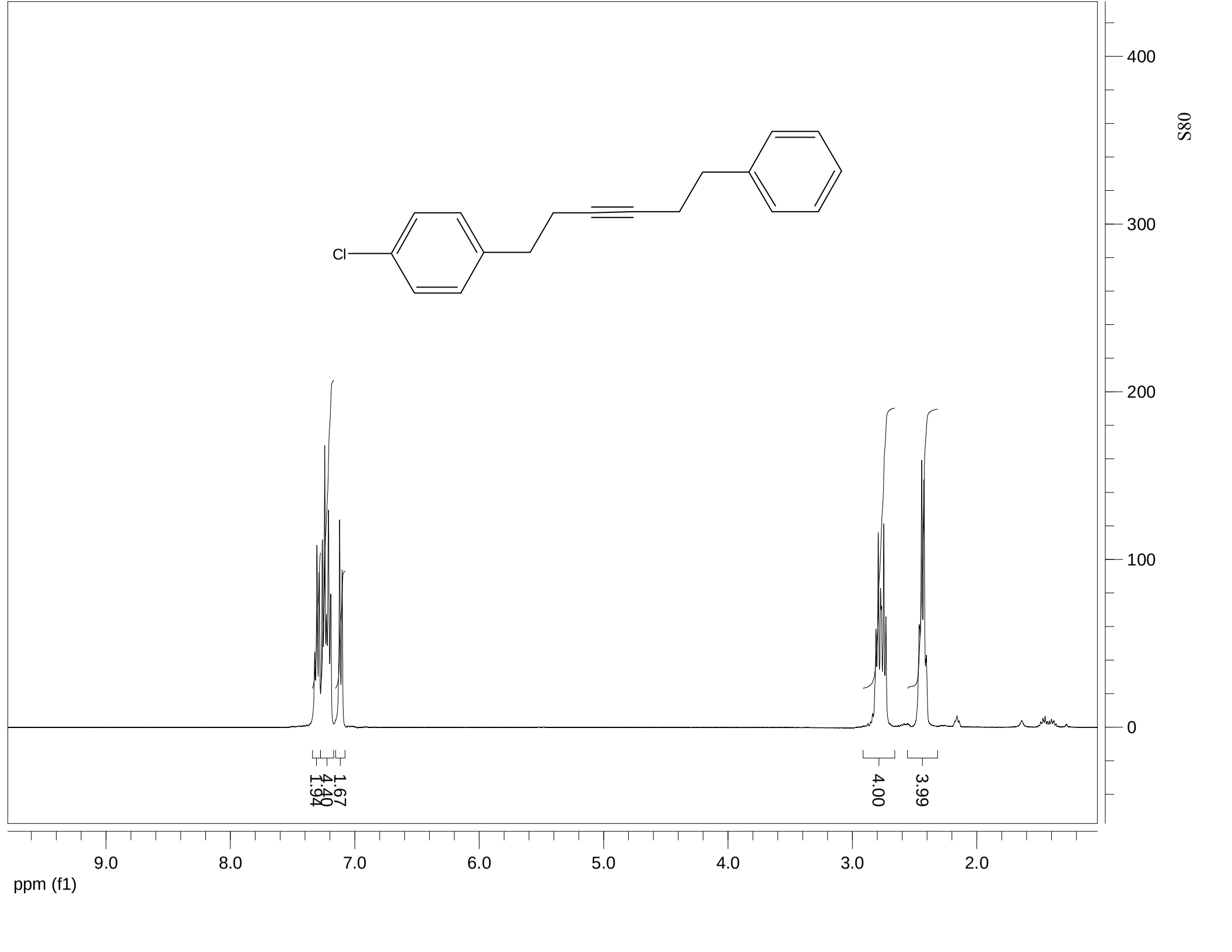

ppm (t1)
0
50
100
150
0
100
200
300
400
500
600
140.454
125.576
122.818
120.284
118.801
108.670
81.586
78.916
41.651
31.426
29.103
28.666
28.245
22.599
18.802
16.558
14.091
N

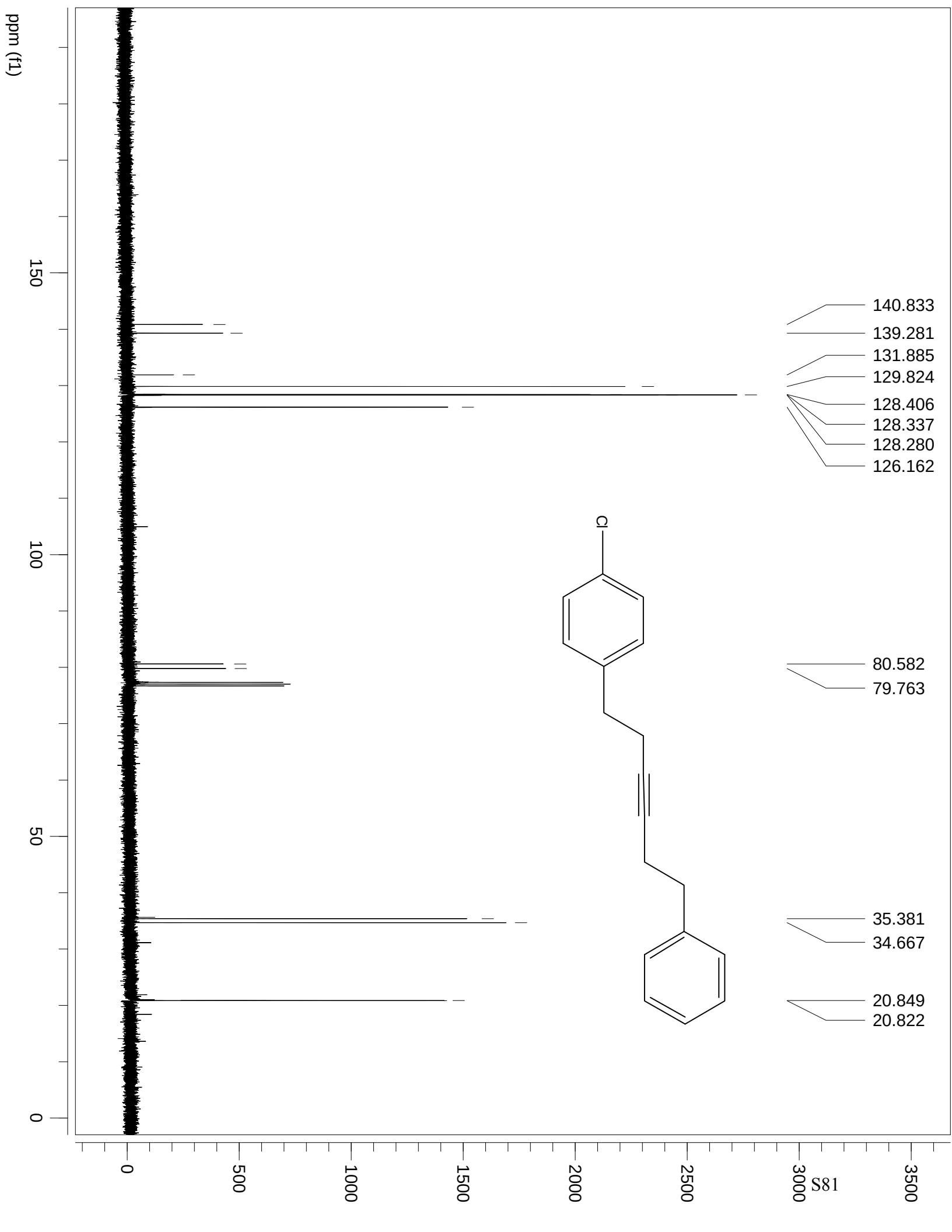
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
50
100
1.00
6.59
1.17
1.04
0.94
2.06
2.27
2.16
3.28
2.19
2.16
N

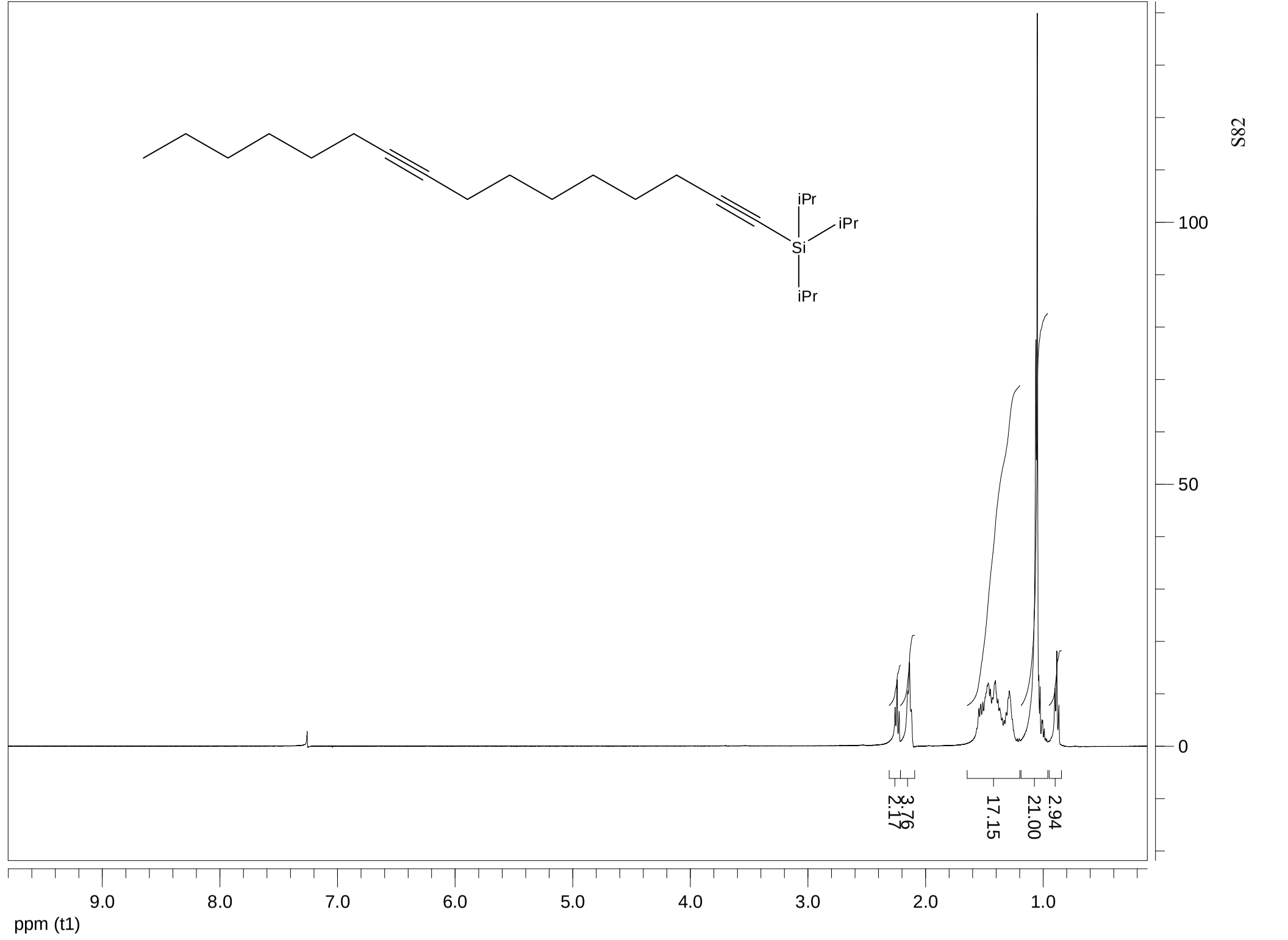

ppm (f1)
200
150
100
50
0
0
500
1000
140.757
136.597
136.433
128.378
128.329
128.039
126.222
120.327
119.576
119.165
108.984
99.905
80.614
79.679
41.740
35.388
29.171
20.836
16.218
12.680
N

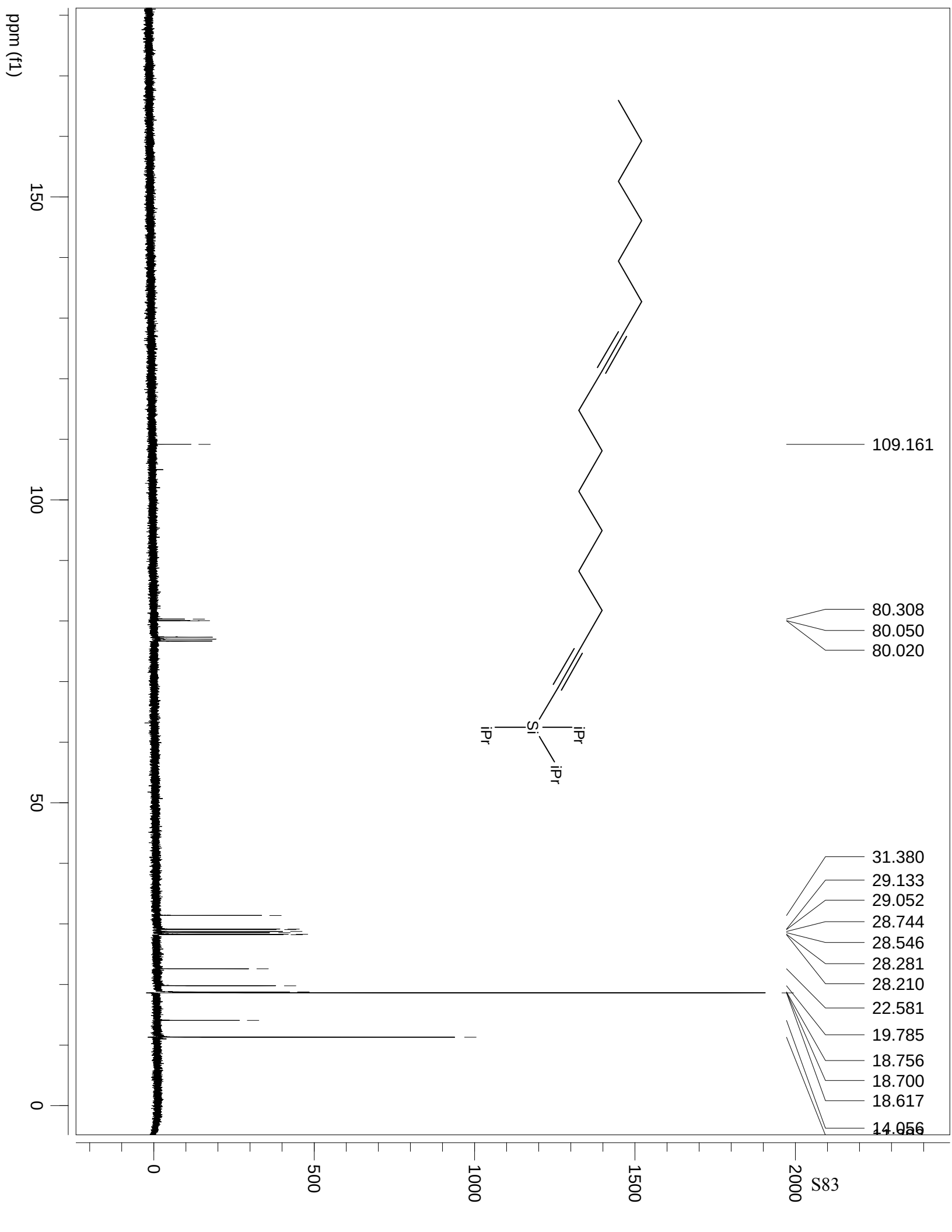

Br
O
O
600
500
400
300
200
100
0
1.72
2.03
2.08
2.18
2.10
2.11
3.00
4.22
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

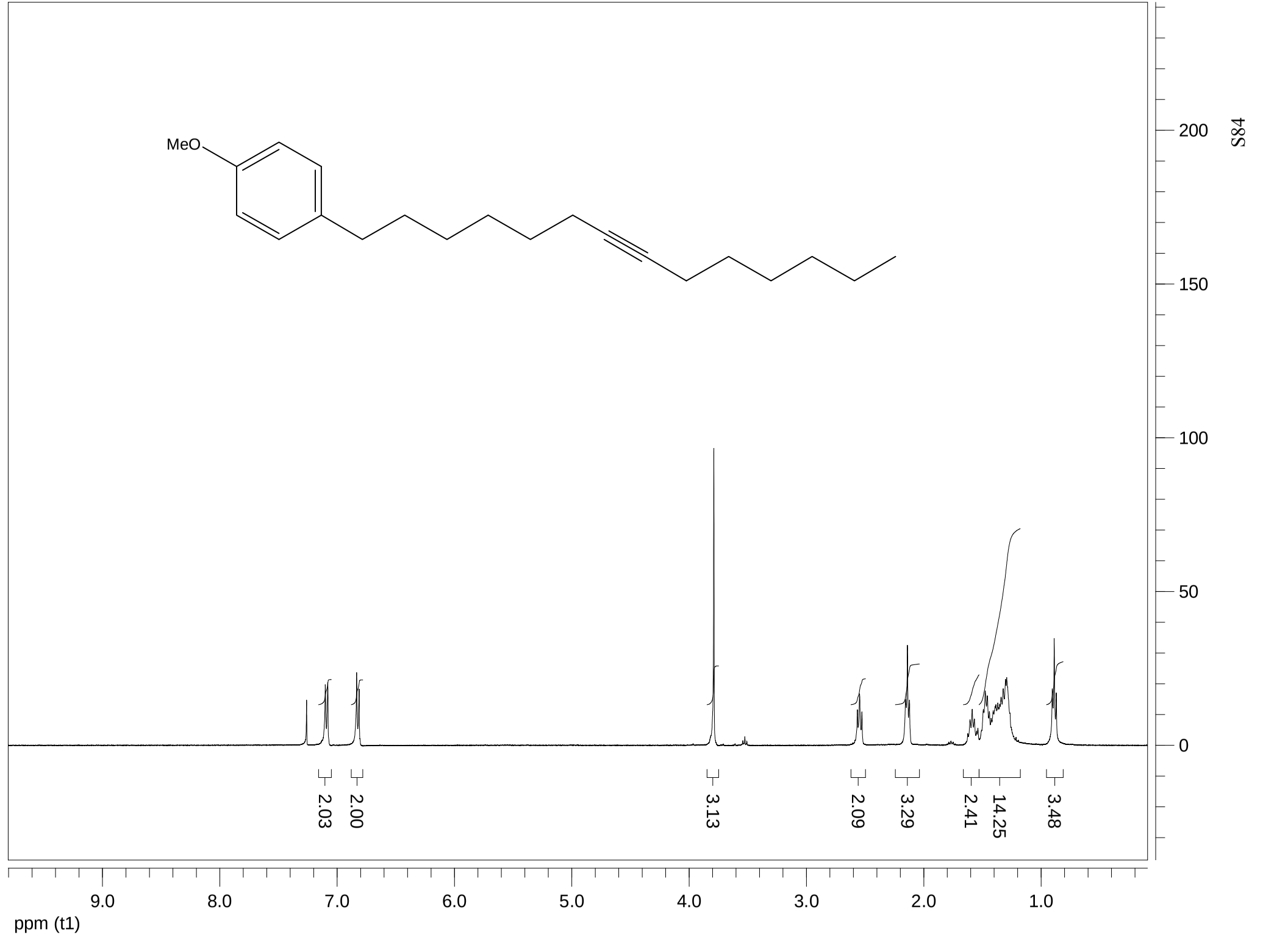

ppm (f1)
200
150
100
50
0
Br
O
O
171.037
144.075
131.495
129.836
128.926
127.151
122.347
80.202
79.337
63.201
34.380
30.275
28.054
20.931
18.070
15.453
0
500
1000
1500

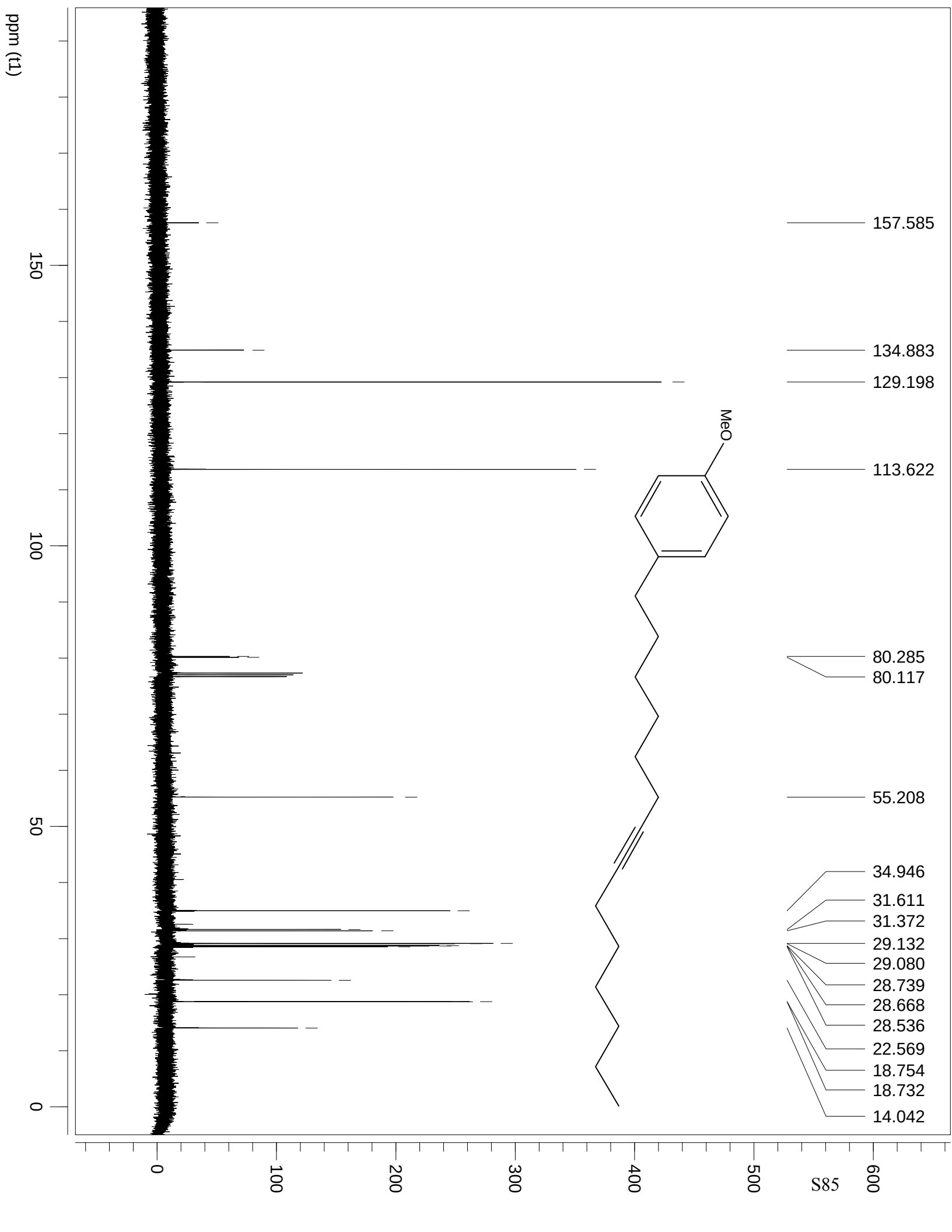

Cl
400
300
200
100
0
1.94
4.40
1.67
4.00
3.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)


ppm (f1)
150
100
50
0
0
500
1000
1500
2000
2500
3000
3500
140.833
139.281
131.885
129.824
128.406
128.337
128.280
126.162
Cl
80.582
79.763
35.381
34.667
20.849
20.822

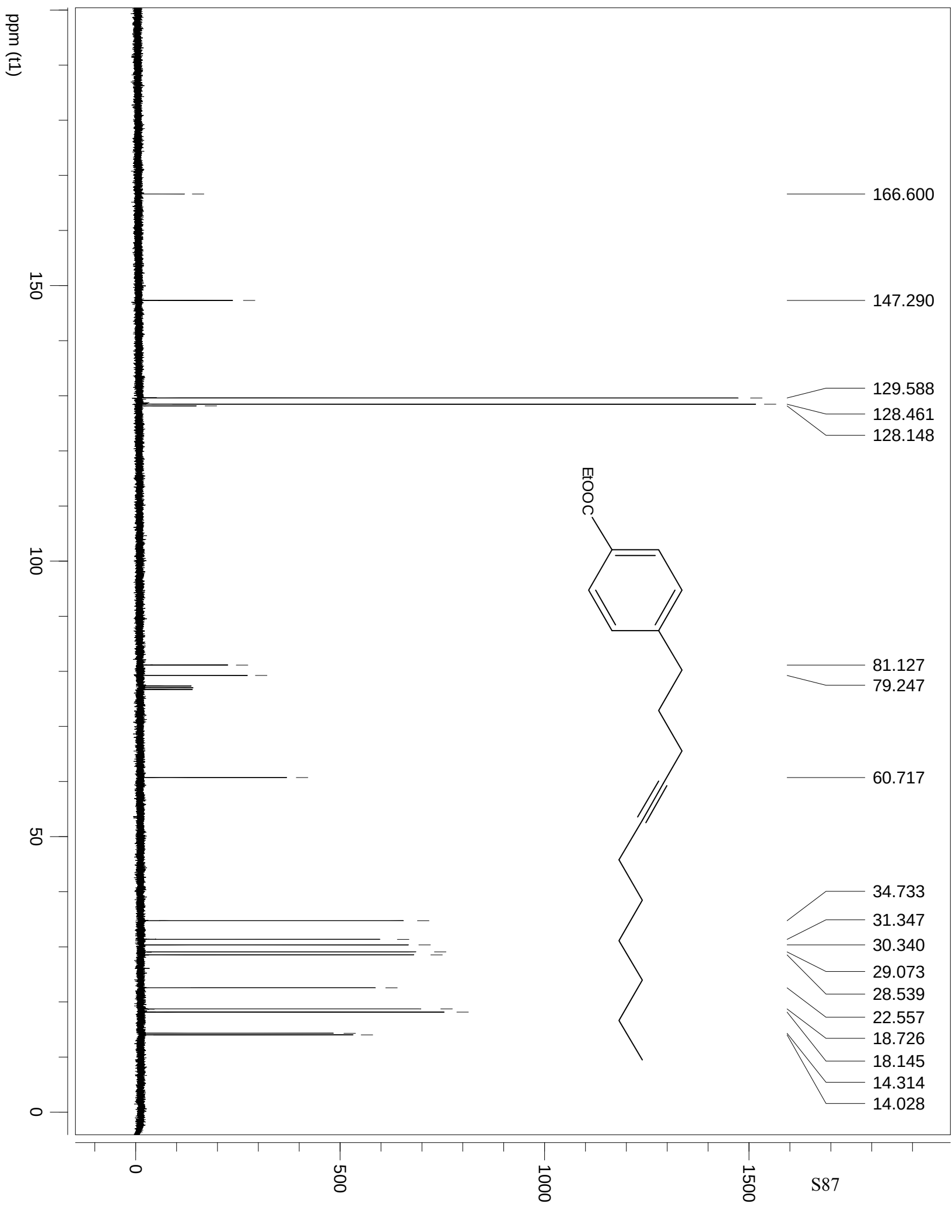

iPr
iPr
Si
iPr
100
50
0
2.17
3.76
17.15
21.00
2.94
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


ppm (f1)
150
100
50
0
0
500
1000
1500
2000
Si
iPr
iPr
iPr
109.161
80.308
80.050
80.020
31.380
29.133
29.052
28.744
28.546
28.281
28.210
22.581
19.785
18.756
18.700
18.617
14.056

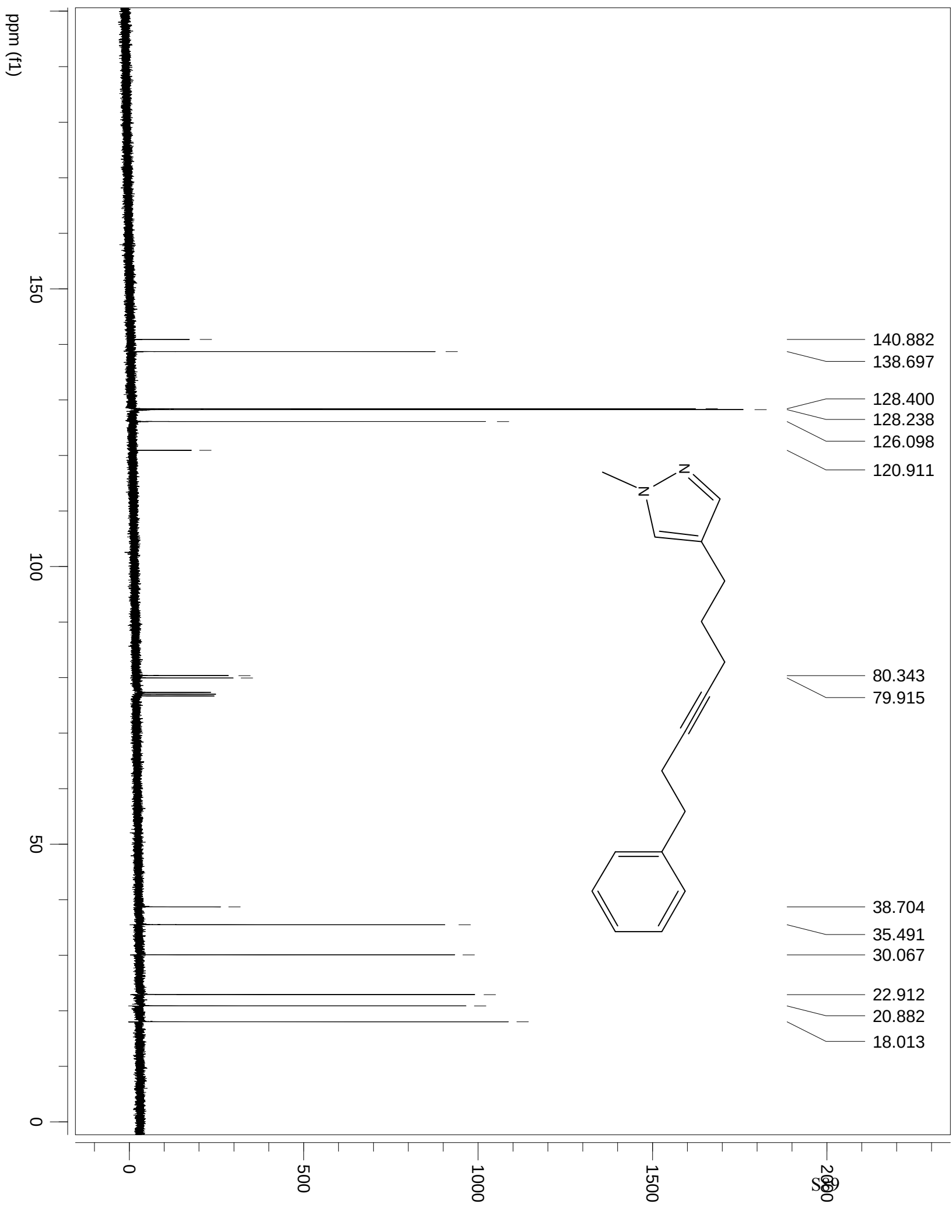

MeO
200
150
100
50
0
2.03
2.00
3.13
2.09
3.29
2.41
14.25
3.48
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


ppm (t1)
150
100
50
0
0
100
200
300
400
500
600
MeO
157.585
134.883
129.198
113.622
80.285
80.117
55.208
34.946
31.611
31.372
29.132
29.080
28.739
28.668
28.536
22.569
18.754
18.732
14.042

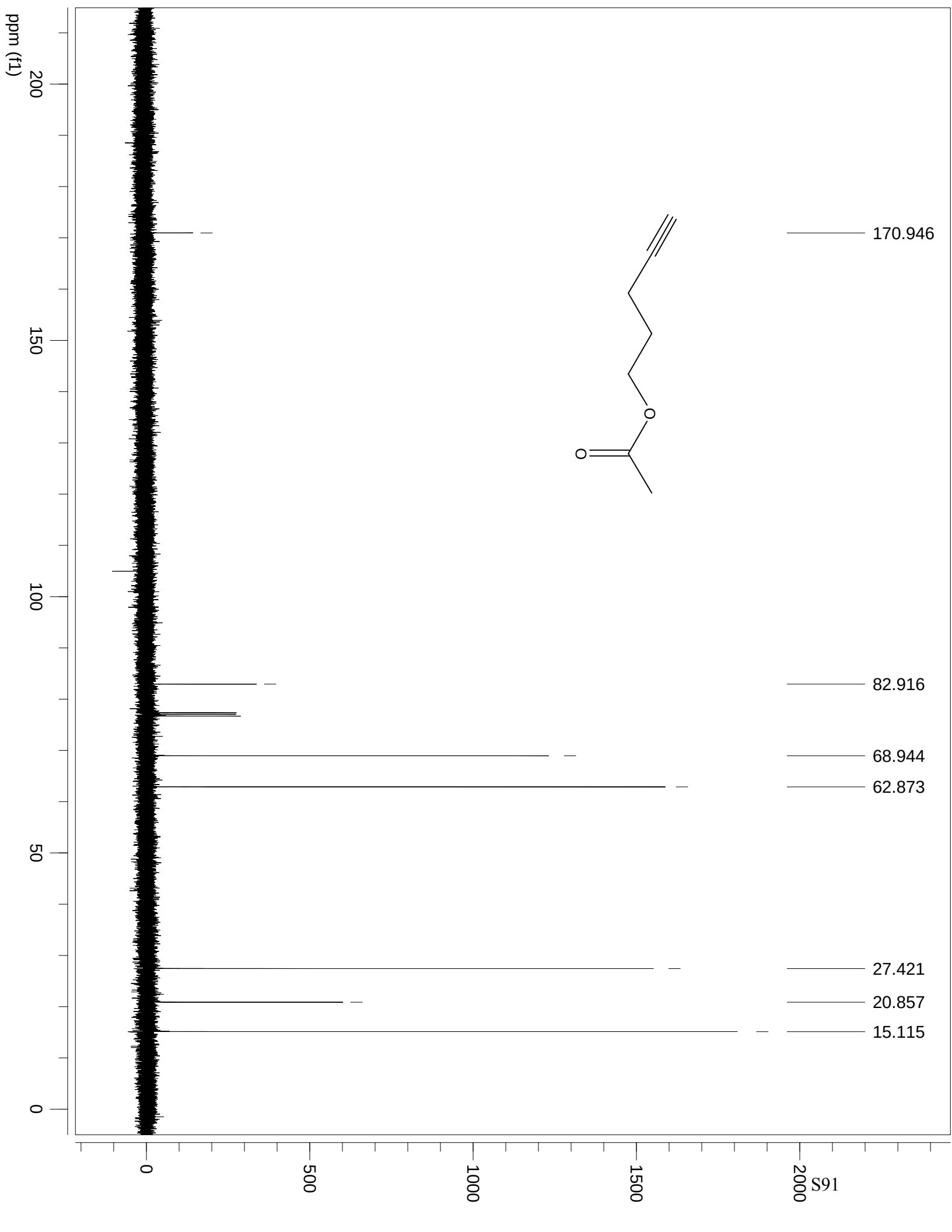
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
50
100
150
200
250
300
1.88
2.08
2.00
2.02
4.10
2.03
2.07
9.43
3.00
EtOOC

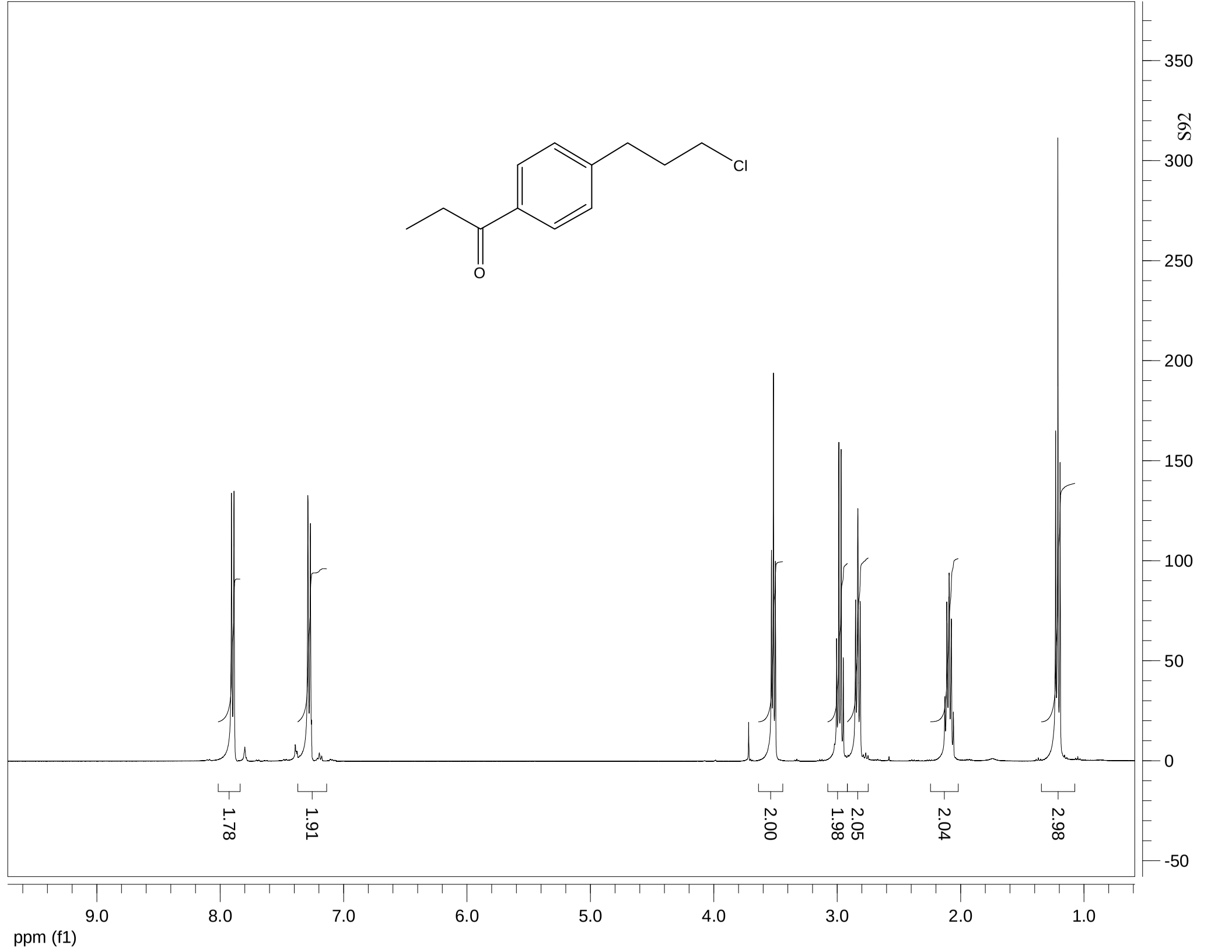

ppm (t1)
150
100
50
0
0
500
1000
1500
166.600
147.290
129.588
128.461
128.148
EtOOC
81.127
79.247
60.717
34.733
31.347
30.340
29.073
28.539
22.557
18.726
18.145
14.314
14.028

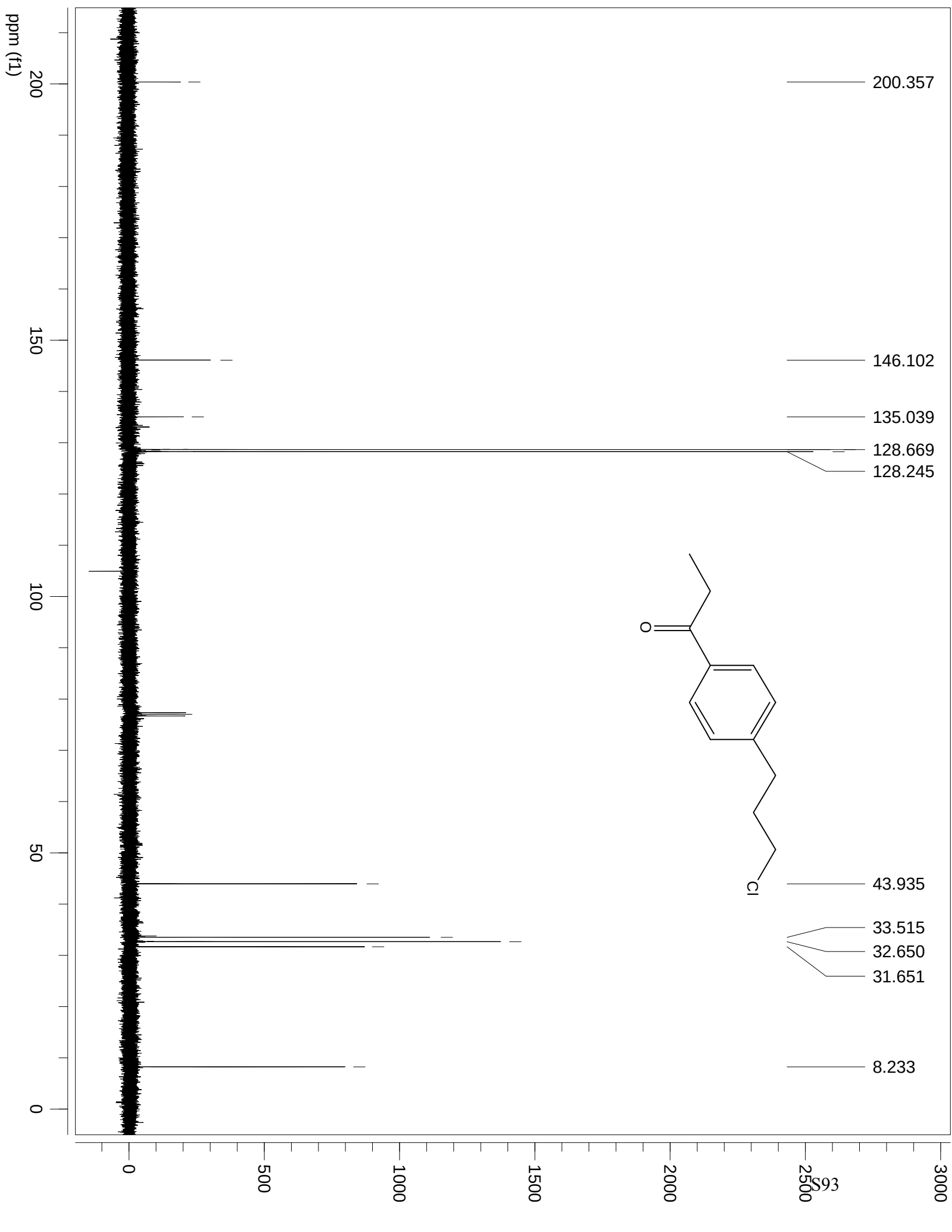
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
100
200
300
400
500
600
5.73
0.84
3.00
2.11
4.27
2.19
2.28
N
N

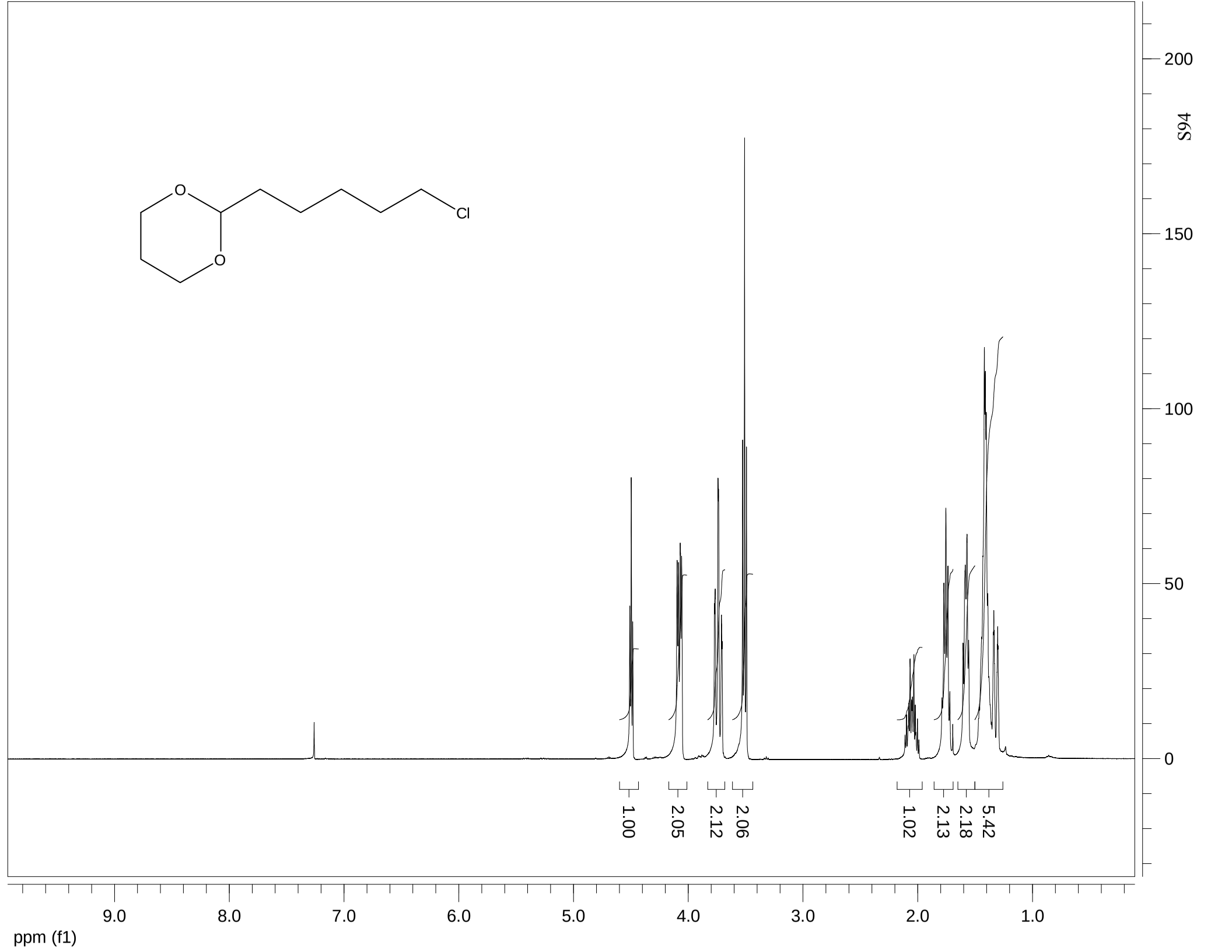

ppm (f1)
150
100
50
0
0
500
1000
1500
2000
140.882
138.697
128.400
128.238
126.098
120.911
80.343
79.915
38.704
35.491
30.067
22.912
20.882
18.013
N
N

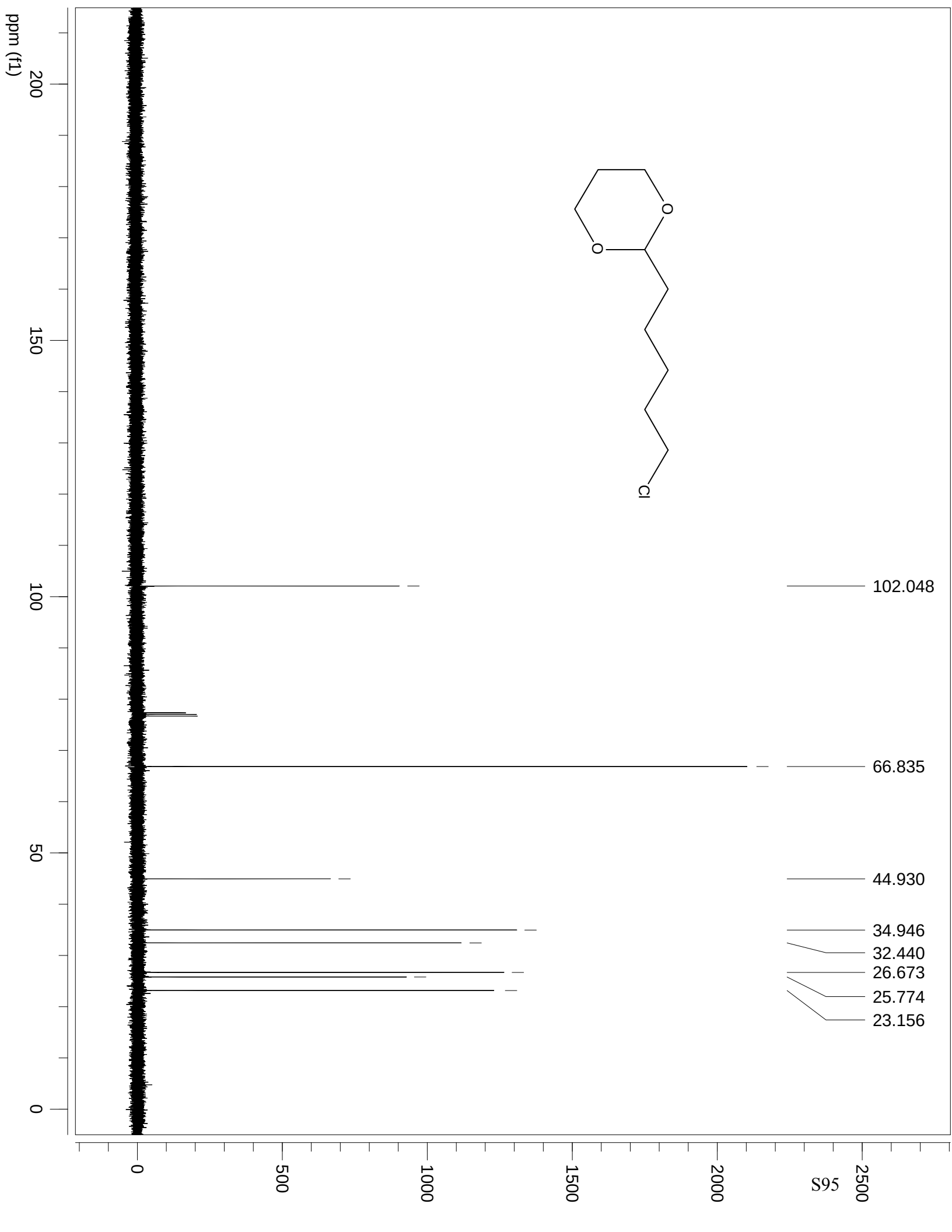
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
500
2.00
2.00
2.90
2.22
2.09
O
O

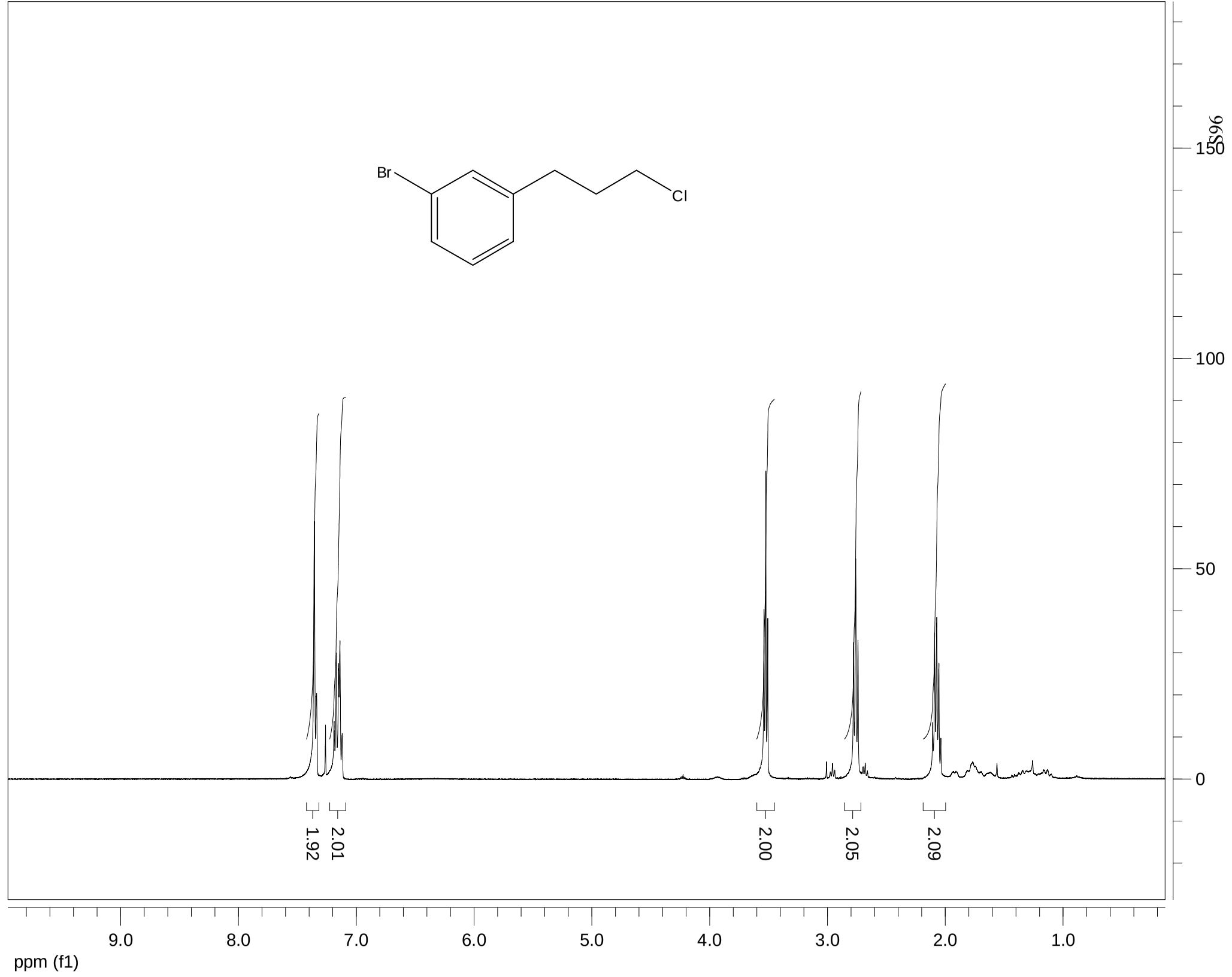

ppm (f1)
200
150
100
50
0
0
500
1000
1500
2000
O
O
170.946
82.916
68.944
62.873
27.421
20.857
15.115

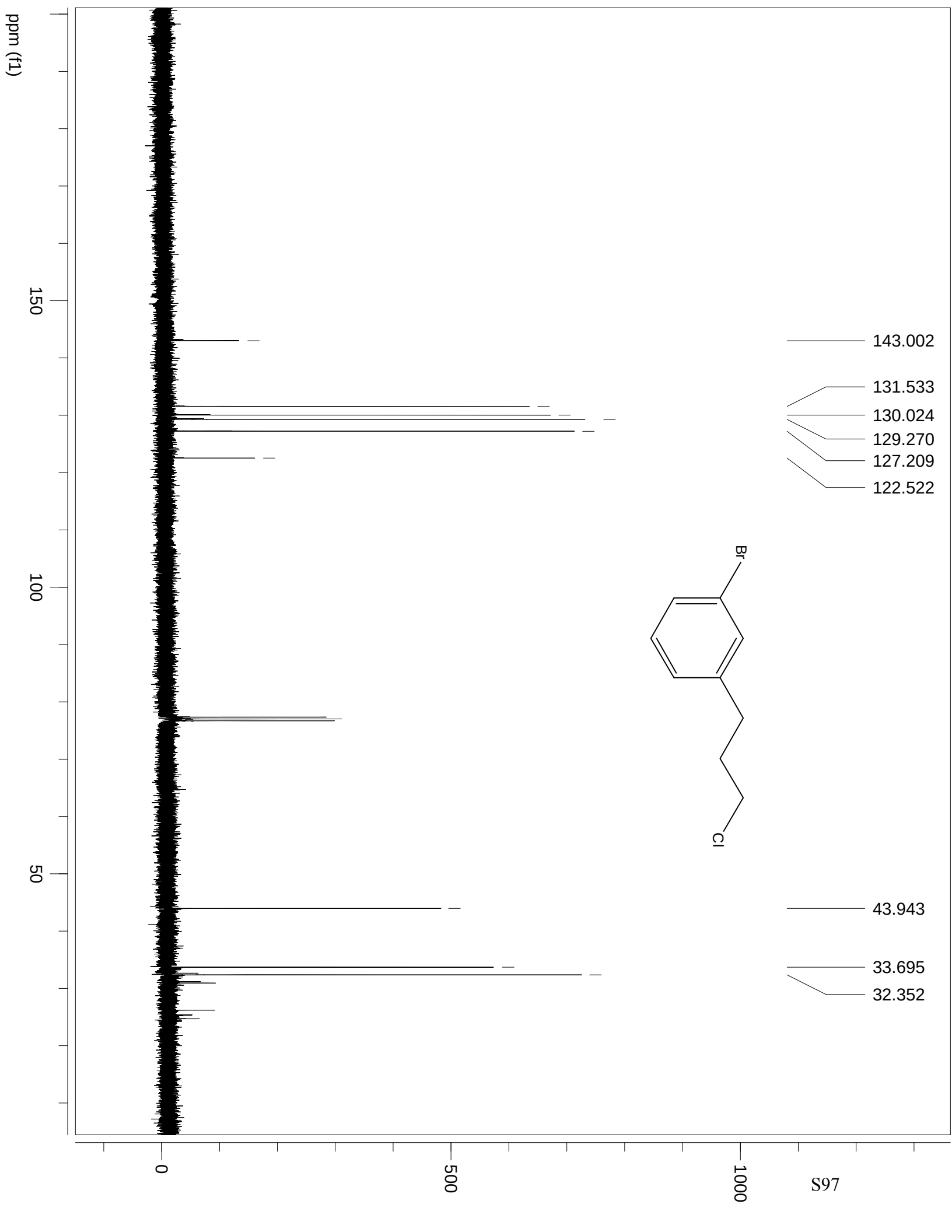

Cl
O
1.78
1.91
2.00
1.98
2.05
2.04
2.98
350
300
250
200
150
100
50
0
-50
S92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


ppm (f1)
200
150
100
50
0
200.357
146.102
135.039
128.669
128.245
43.935
33.515
32.650
31.651
8.233
O
Cl
0
500
1000
1500
2000
2500
3000

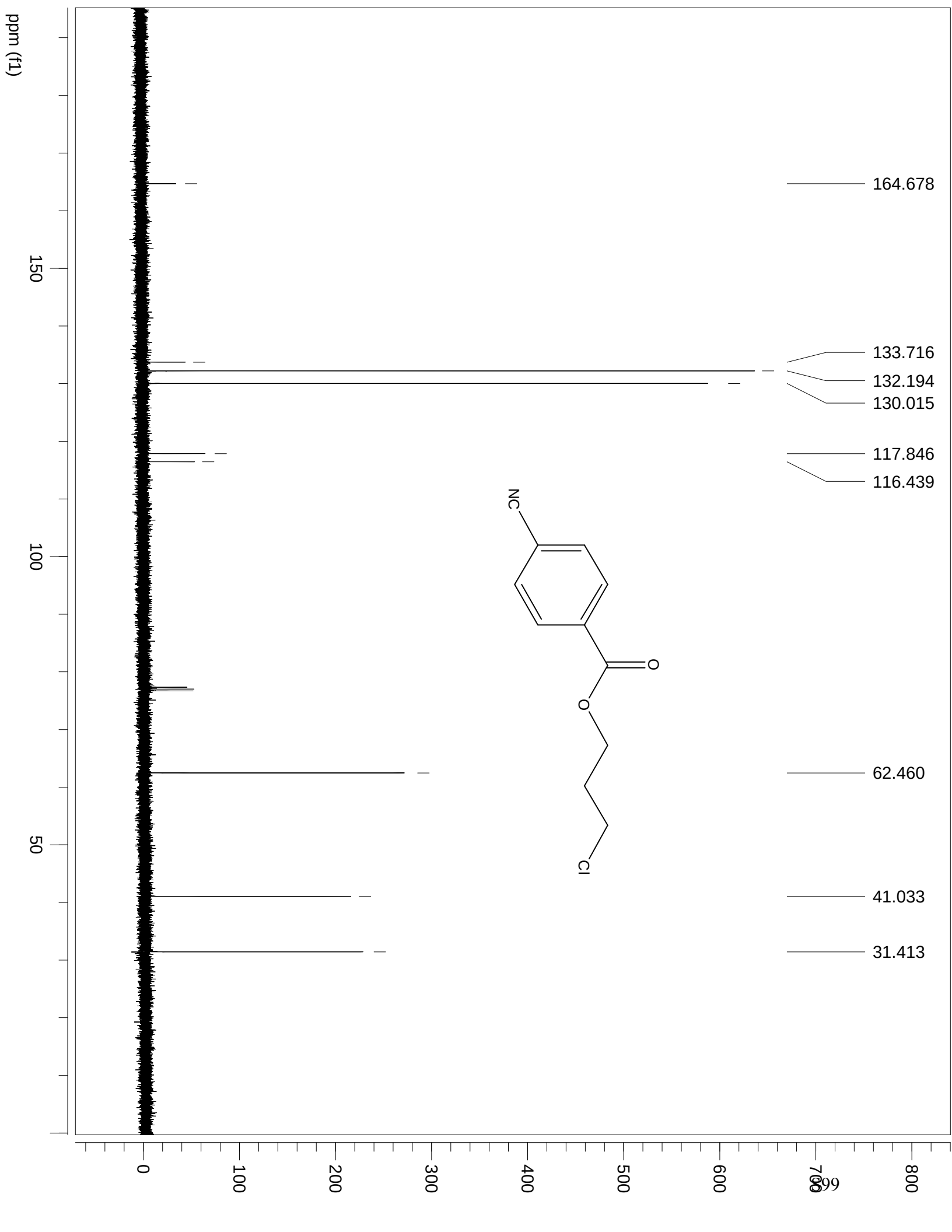

O
O
Cl
1.00
2.05
2.12
2.06
1.02
2.13
2.18
5.42
200
150
100
50
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

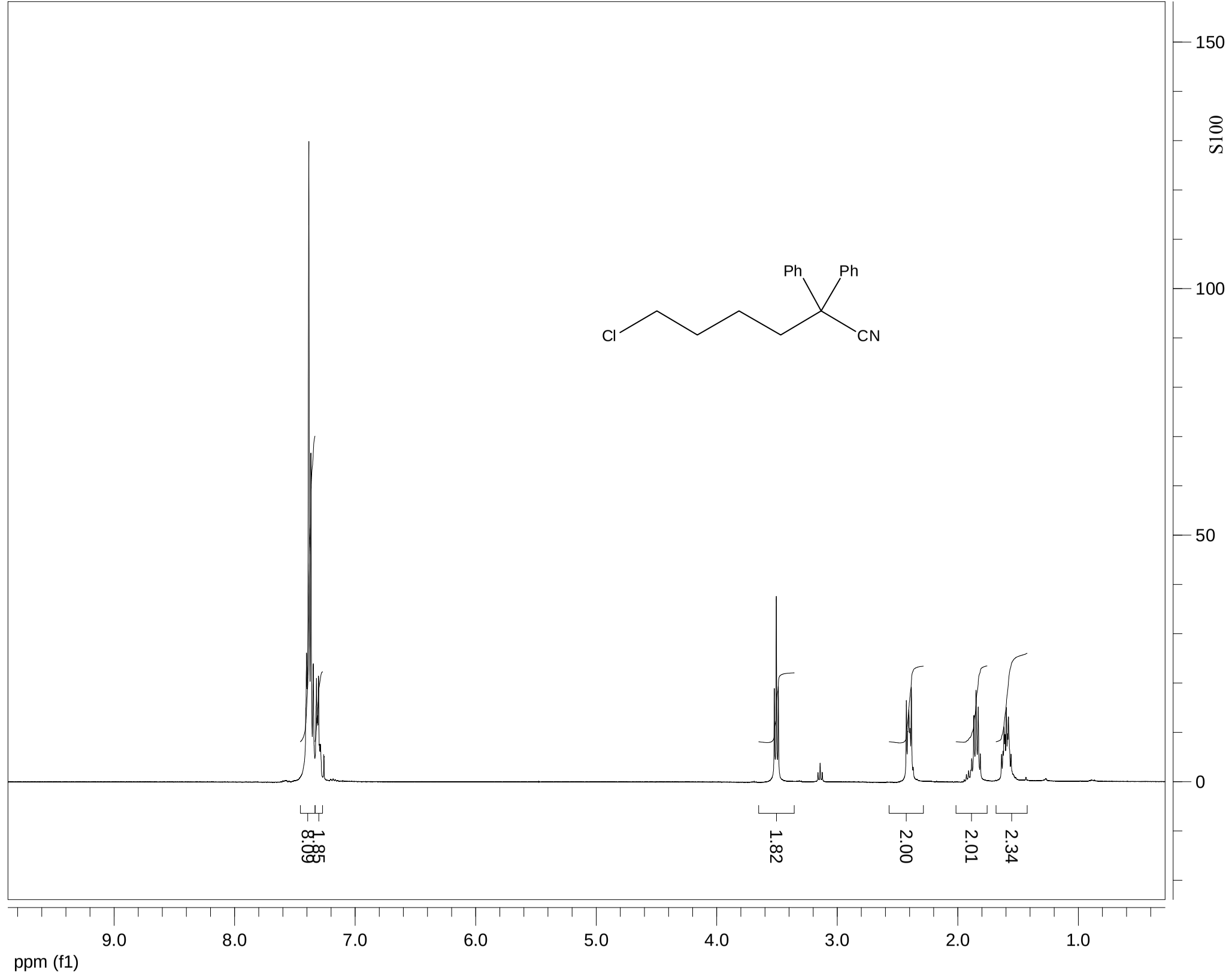

ppm (f1)
200
150
100
50
0
O
O
Cl
102.048
66.835
44.930
34.946
32.440
26.673
25.774
23.156
0
500
1000
1500
2000
2500

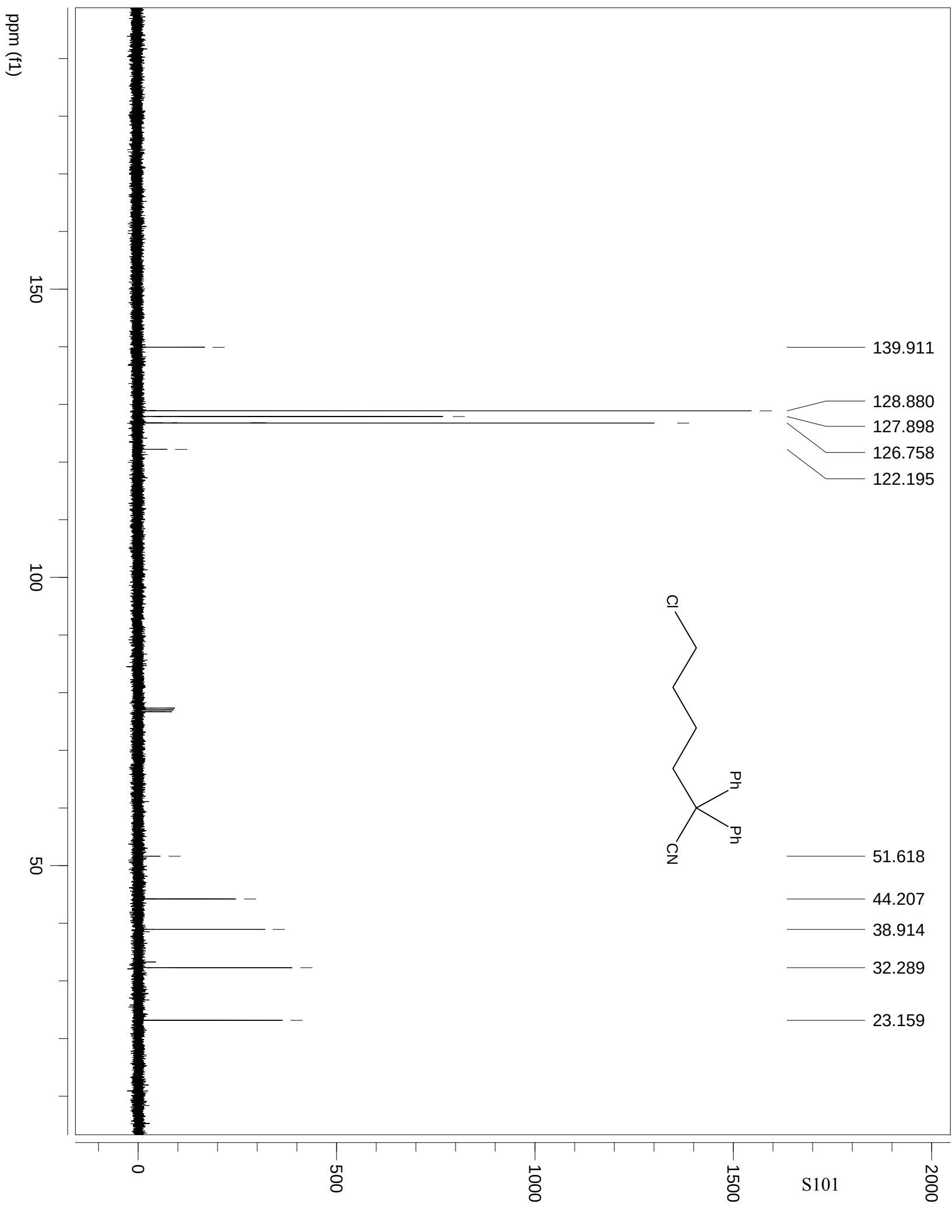

Br
Cl
1.92
2.01
2.00
2.05
2.09
150
100
50
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


ppm (f1)
150
100
50
0
500
1000
143.002
131.533
130.024
129.270
127.209
122.522
Br
Cl
43.943
33.695
32.352

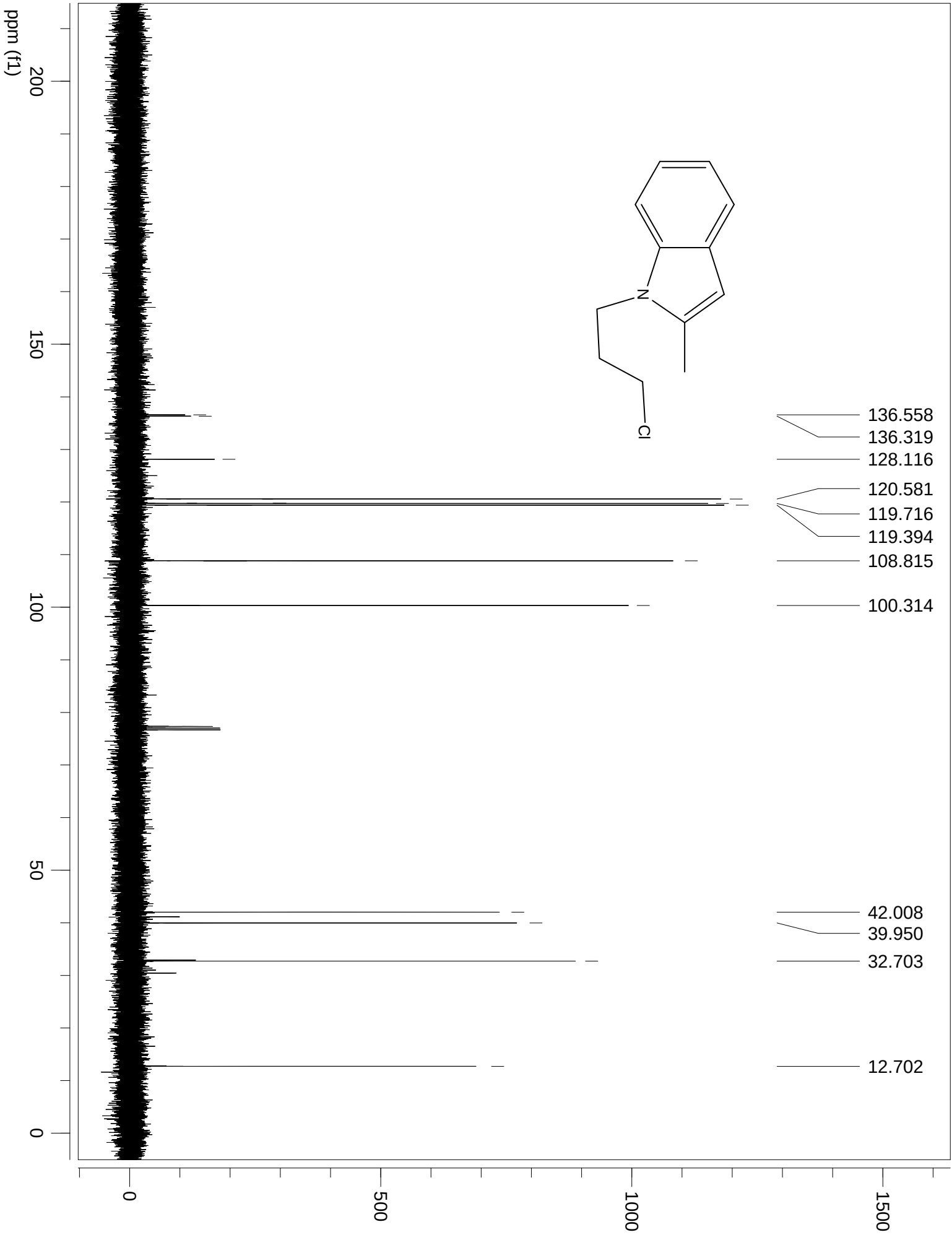

O
O
Cl
NC
1.78
1.78
2.00
2.05
2.08
350
300
250
200
150
100
50
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


ppm (f1)
150
100
50
0
100
200
300
400
500
600
700
800
164.678
133.716
132.194
130.015
117.846
116.439
62.460
41.033
31.413
NC
O
O
Cl


Ph
Ph
Cl
CN
8.09
1.85
1.82
2.00
2.01
2.34
150
100
50
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


ppm (f1)
150
100
50
0
500
1000
1500
2000
139.911
128.880
127.898
126.758
122.195
51.618
44.207
38.914
32.289
23.159
Cl
Ph
Ph
CN

ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1.00
1.11
1.12
1.01
0.93
2.31
2.18
3.50
2.32
0
50
100
150
200
N
Cl


ppm (f1)
200
150
100
50
0
N
Cl
136.558
136.319
128.116
120.581
119.716
119.394
108.815
100.314
42.008
39.950
32.703
12.702
0
500
1000
1500