Supporting Information

Gold-Catalyzed Regioselective Dimerization of Terminal Alkynes

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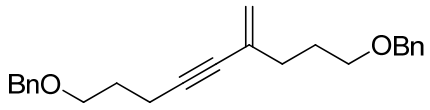
General. Ethyl acetate (ACS grade), hexanes (ACS grade), diethyl ether (ACS grade), NH_4OH (29.4% in H_2O, ACS reagent) were purchased from Fisher Scientific and used without further purification. Anhydrous dichloromethane (HPLC grade) was purified by distillation over calcium hydride. Tetrahydrofuran was distilled over sodium/benzophenone. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates. Flash column chromatography was performed over Silicycle silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 500 MHz Unity plus spectrometer and a Varian 400 MHz spectrometer using residue solvent peaks as internal standards ($CHCl_3$, ^{1}H: 7.26 ppm; ^{13}C: 77.2 ppm). Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Waters micromass ZQ detector using electrospray method.

General procedure: preparation of enynes via gold-catalyzed dimerization of alkynes

A flame-dried Schlenk tube was charged with 1-alkyne (0.1 mmol), anhydrous sodium acetate (16 mg, 0.2 mmol), tButyl-XphosAuNTf$_2$ (4 mg, 5% mol or indicated amount of catalysts) and toluene (0.5 ml) under nitrogen atmosphere. The reaction mixture was stirred at 110 ℃ for 24 h or the indicated reaction time. The reaction was cooled down at room temperature and concentrated under *vacuum*. The residue was purified through silica gel flash chromatography using hexanes/ethyl acetate as the eluent.

(6-Methylenenon-4-yne-1,9-diyl)bis(oxy)bis(methylene)dibenzene

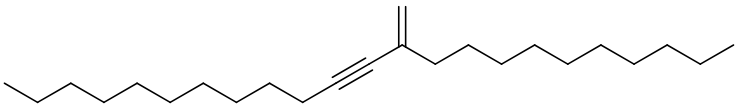


4a

Compound **4a** was prepared in 83% yield according to the general procedure (eluents: ethyl acetate: hexanes = 1: 20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 8H), 7.31 – 7.27 (m, 2H), 5.22 (d, J = 1.9 Hz, 1H), 5.15 (d, J = 1.8 Hz, 1H), 4.53 – 4.50 (m, 4H), 3.58 (t, J = 6.2 Hz, 2H), 3.49 (t, J = 6.4 Hz, 2H), 2.44 (t, J = 7.1 Hz, 2H), 2.23 (t, J = 7.5

Hz, 2H), 1.88 – 1.80 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.59, 138.47, 131.42, 128.35, 128.33, 127.62, 127.58, 127.52, 127.49, 120.09, 89.50, 81.04, 72.96, 72.88, 69.42, 68.85, 34.10, 28.93, 28.18, 16.15.; IR (neat): 3087, 3063, 3030, 2924, 2856, 2221, 1611, 1496, 1454; MS (ES^+) Calculated for $[C_{24}H_{28}O_2Na]^+$: 371.2; Found: 371.2.

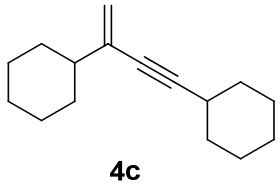
13-Methylenetricos-11-yne



4b

Compound **4b** was prepared in 72% yield according to the general procedure (eluents: hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 (d, *J* = 1.7 Hz, 1H), 5.12 (d, *J* = 1.2 Hz, 1H), 2.30 (t, *J* = 7.1 Hz, 2H), 2.11 (t, *J* = 7.5 Hz, 2H), 1.58 – 1.46 (m, 2H), 1.35 – 1.18 (m, 30H), 0.88 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.43, 119.25, 90.11, 81.02, 37.60, 31.92, 31.91, 29.70, 29.63, 29.61, 29.58, 29.55, 29.47, 29.35, 29.33, 29.14, 28.95, 28.87, 28.78, 28.12, 22.68, 19.28, 14.10. IR (neat): 2956, 2925, 2854, 2220, 1467; GC-MS Calculated for $[C_{24}H_{44}]^+$: 332.3; Found: 332.

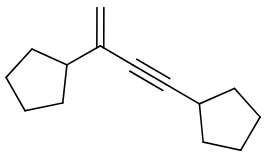
But-3-en-1-yne-1,3-diyldicyclohexane



4c

Compound **4c** was prepared in 69% yield according to the general procedure (eluents: hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (d, *J* = 2.0 Hz, 1H), 5.11 (dd, *J* = 2.0, 1.1 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.05 – 1.97 (m, 1H), 1.88 – 1.62 (m, 8H), 1.58 – 1.41 (m, 4H), 1.41 – 1.04 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.03, 117.06, 94.68, 80.31, 45.28, 32.77, 31.95, 29.56, 26.28, 26.09, 25.94, 24.80. IR (neat): 2927, 2853, 2220, 1457, 1450; GC-MS Calculated for $[C_{16}H_{24}]^+$: 216.2; Found: 216.

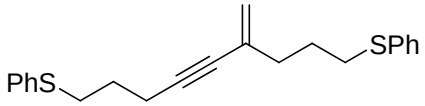
But-3-en-1-yne-1,3-diyldicyclopentane



4d

Compound **4d** was prepared in 85% yield according to the modified procedure. This reaction was carried out at 110 ℃ for 48 h with 10 mol % catalyst loading (eluents: hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.15 (d, *J* = 2.2 Hz, 1H), 5.14 (dd, *J* = 2.1, 0.9 Hz, 1H), 2.73 (p, *J* = 7.4 Hz, 1H), 2.58 – 2.48 (m, 1H), 1.96 – 1.87 (m, 2H), 1.81 – 1.51 (m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.42, 117.69, 94.84, 79.31, 47.12, 33.98, 31.93, 30.72, 25.54, 24.92. IR (neat): 2956, 2868, 2220, 1451, 1341, 1301; GC-MS Calculated for $[C_{14}H_{20}]^{+}$: 188.2; Found: 188.

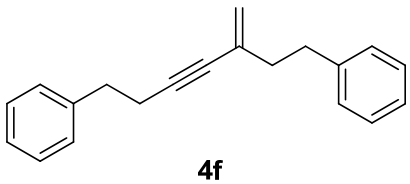
(6-Methylenenon-4-yne-1,9-diyl)bis(phenylsulfane)



4e

Compound **4e** was prepared in 61% yield according to the modified procedure. This reaction was carried out at 110 ℃ for 48 h with 10 mol % catalyst loading (eluents: ethyl acetate: hexanes = 1: 20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.25 (m, 4H), 7.21 – 7.15 (m, 2H), 5.28 (s, 1H), 5.20 (s, 1H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.92 – 1.82 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.63, 136.29, 130.69, 129.18, 129.12, 128.93, 128.85, 125.95, 125.81, 120.89, 89.11, 81.38, 36.30, 32.66, 32.57, 28.13, 27.40, 18.37. IR (neat): 3074, 3058, 3019, 2925, 2851, 2223, 1609, 1584, 1573, 1481, 1438, 1346, 1330, 1280; MS (ES^{+}) Calculated for $[C_{22}H_{24}S_2+H]^{+}$: 353.1; Found: 353.1.

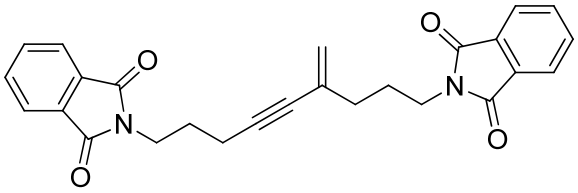
(5-Methylenehept-3-yne-1,7-diyl)dibenzene



4f

Compound **4f** was prepared in 61% yield according to the general procedure (eluents: ethyl acetate: hexanes = 1: 20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 10H), 5.24 (s, 1H), 5.13 (s, 1H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.82 – 2.79 (m, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.45 – 2.41 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.59, 140.66, 131.25, 128.51, 128.49, 128.37, 128.25, 126.30, 125.84, 120.39, 89.71, 81.51, 39.44, 35.17, 34.56, 21.54. IR (neat): 3084, 3063, 3026, 2928, 2857, 2223, 1604, 1497, 1453, 1429, 1340; GC-MS Calculated for $[C_{20}H_{20}]^{+}$: 260.2; Found: 260.

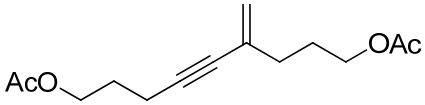
2,2'-(6-Methylenenon-4-yne-1,9-diyl)diisoindoline-1,3-dione



4g

Compound **4g** was prepared in 78% yield according to the general procedure (eluents: ethyl acetate: hexanes = 1: 10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 4H), 7.72 – 7.67 (m, 4H), 5.15 (s, 1H), 5.13 (d, *J* = 1.4 Hz, 1H), 3.79 (t, *J* = 7.1 Hz, 2H), 3.69 (t, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.0 Hz, 2H), 2.14 (t, *J* = 7.6 Hz, 2H), 1.97 – 1.87 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.35, 168.28, 133.82, 133.77, 132.19, 132.15, 130.38, 123.17, 123.10, 120.56, 88.97, 81.13, 37.47, 37.31, 34.66, 27.45, 26.89, 17.14. IR (neat): 2930, 2860, 2219, 1771, 1711, 1615, 1469, 1438, 1395, 1370, 1336; MS (ES^{+}) Calculated for $[C_{26}H_{22}N_2O_4Na]^{+}$: 449.2; Found: 449.1.

6-Methylenenon-4-yne-1,9-diyl diacetate

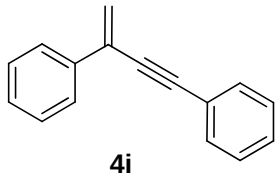


4h

Compound **4h** was prepared in 81% yield according to the general procedure (eluents: ethyl acetate: hexanes = 1: 10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (s, 1H), 5.18 (d, *J* = 1.5 Hz, 1H), 4.17 (t, *J* = 6.4 Hz, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.20 (t, *J* = 7.5 Hz, 2H), 2.06 (s, 3H), 2.06 (s, 3H), 1.91 – 1.83 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.13, 171.04, 130.58, 120.76, 88.76, 81.15, 63.64, 63.14, 33.79, 27.79,

27.04, 20.97, 20.94, 16.04. IR (neat): 2959, 2927, 2852, 2221, 1742, 1612, 1448, 1387, 1365; MS (ES^+) Calculated for $[C_{14}H_{20}O_4Na]^+$: 275.1; Found: 275.1.

But-3-en-1-yne-1,3-diyldibenzene

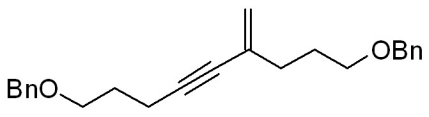


4i

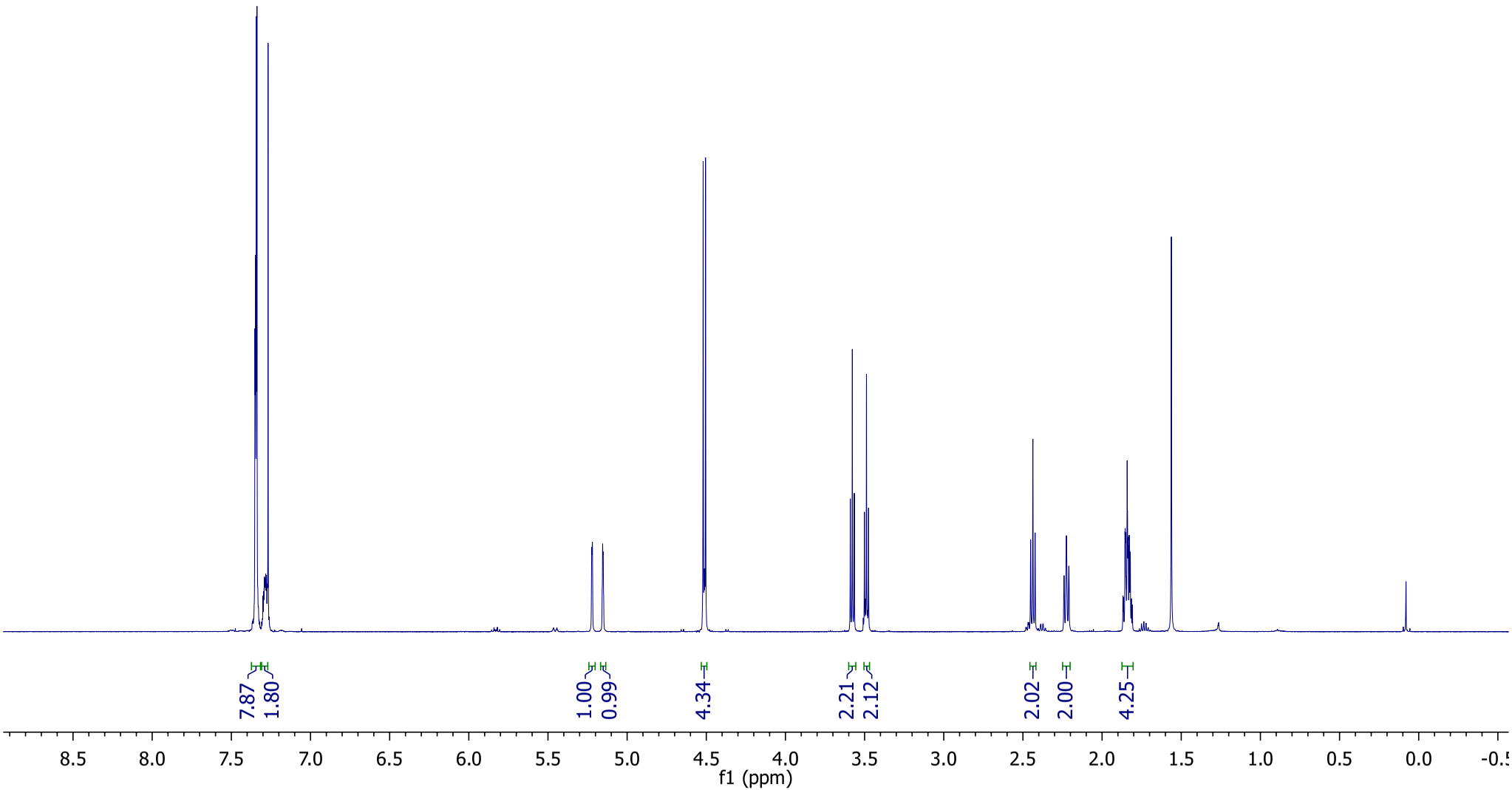
The known compound **4i** was prepared in 8% yield according to the general procedure (eluents: ethyl acetate: hexanes = 1: 20). This is a known compound, and its NMR chemical shifts are consitstent with those reported.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.56 – 7.51 (m, 2H), 7.42 – 7.31 (m, 6H), 5.99 (d, J = 0.9 Hz, 1H), 5.77 (t, J = 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.25, 131.66, 131.44, 130.60, 128.75, 128.40, 128.33, 126.09, 123.09, 120.66, 90.75, 88.53.

References:

1. Wang, T.; Hu, Y.; Zhang, S. *Organic and Biomolecular Chemistry*, **2010**, *8*, 2312 - 2315


BnO
OBn

4a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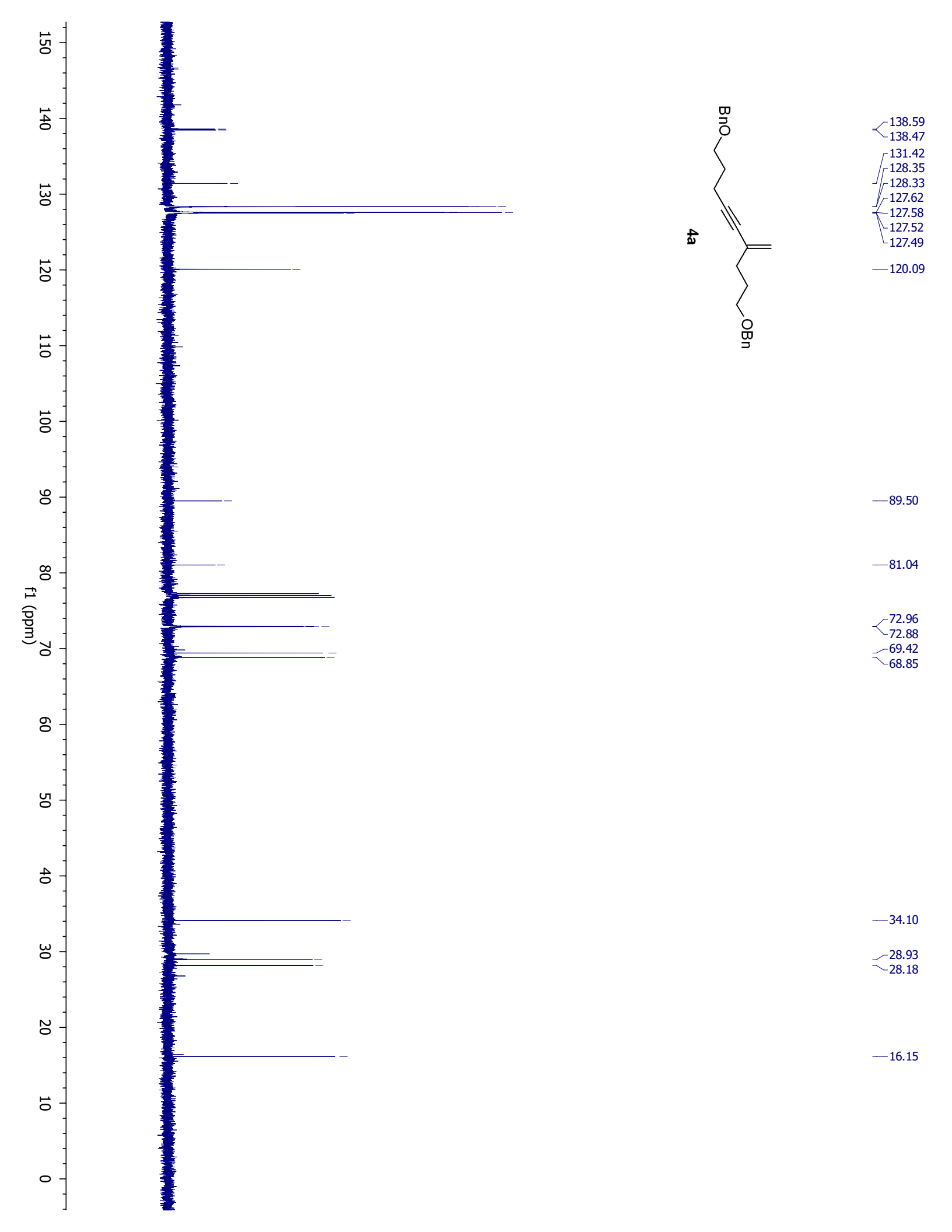
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20
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OBn
4a
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138.47
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128.35
128.33
127.62
127.58
127.52
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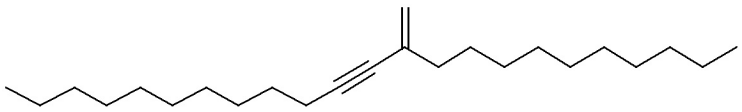
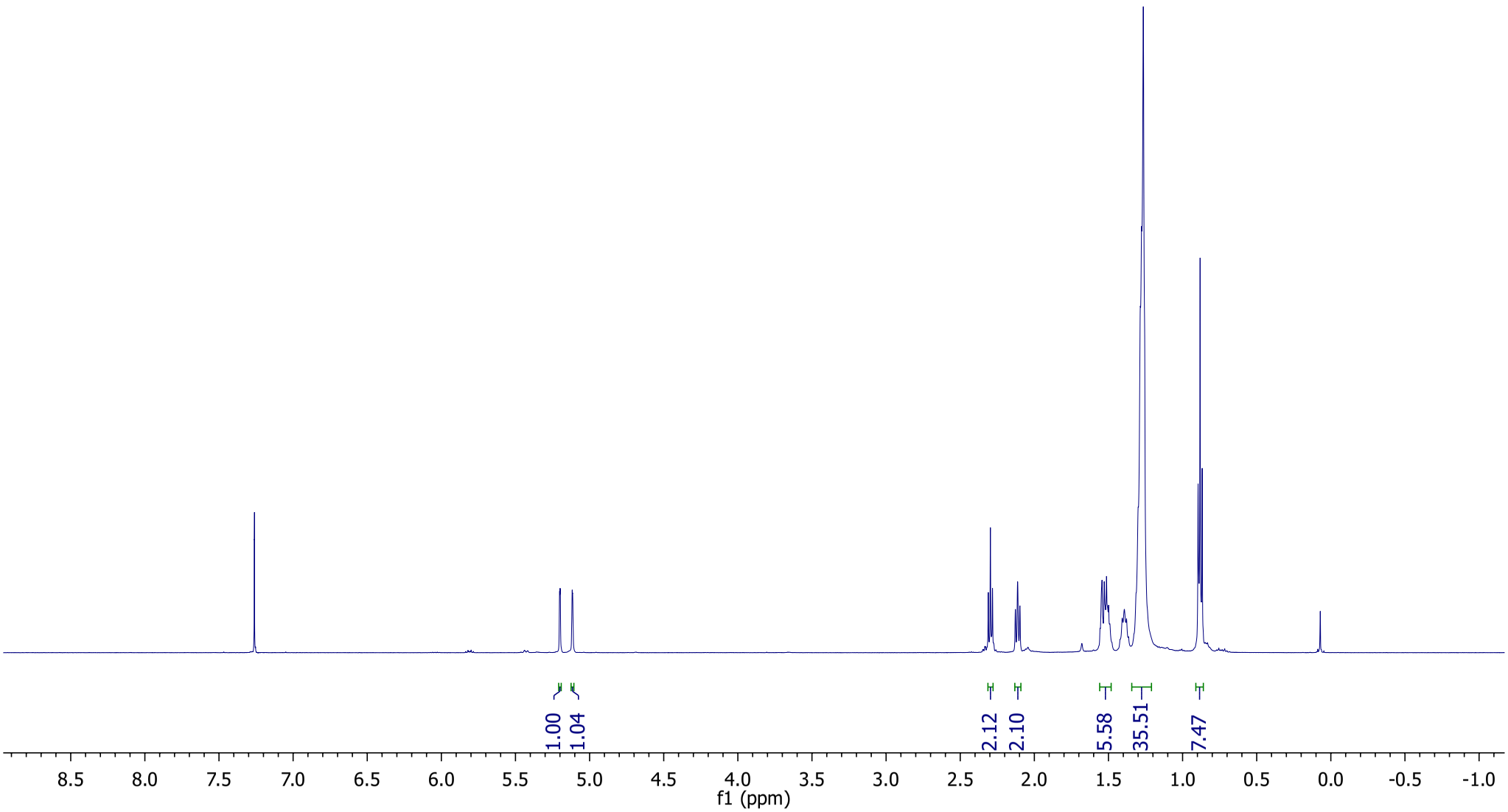
16.15



4b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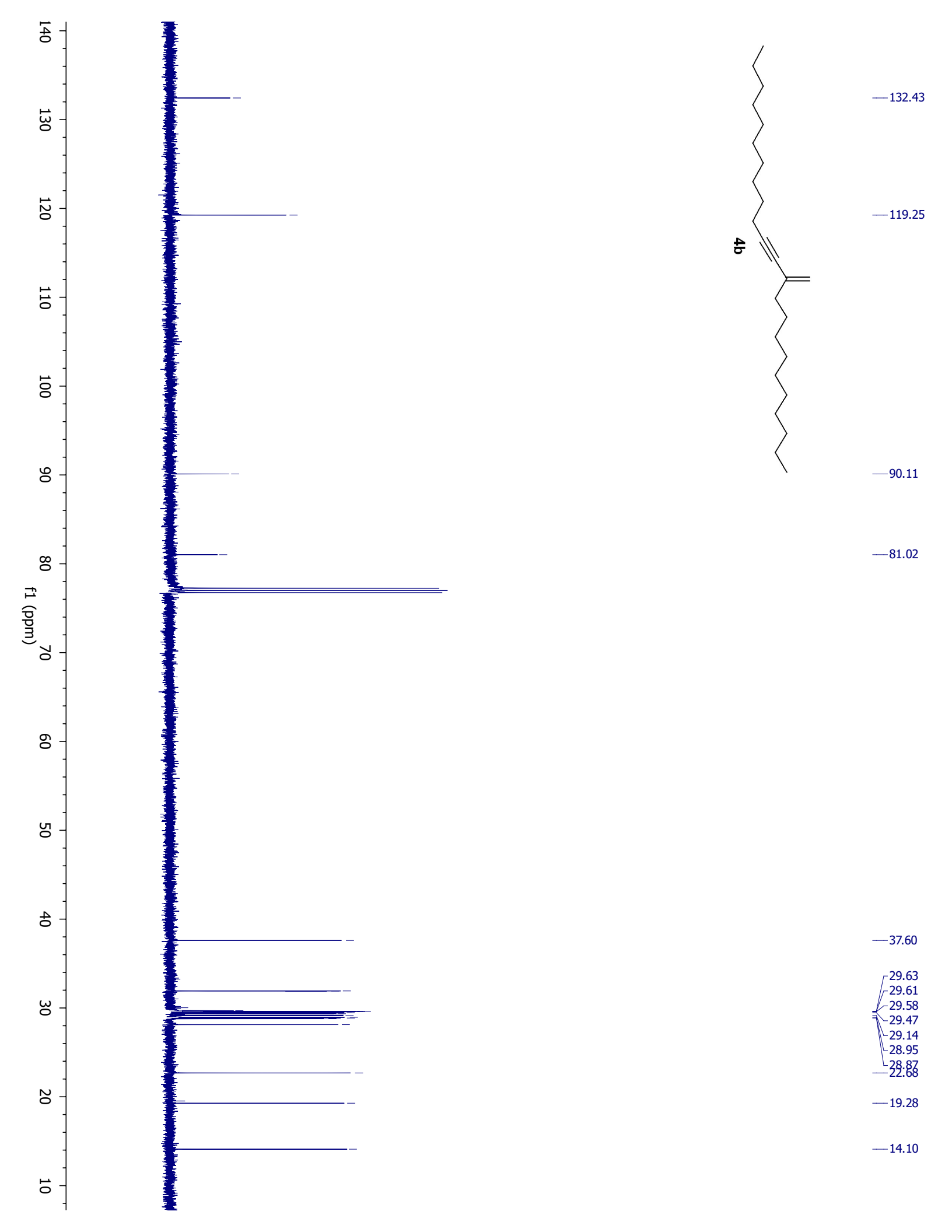
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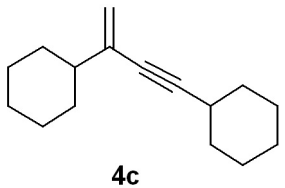
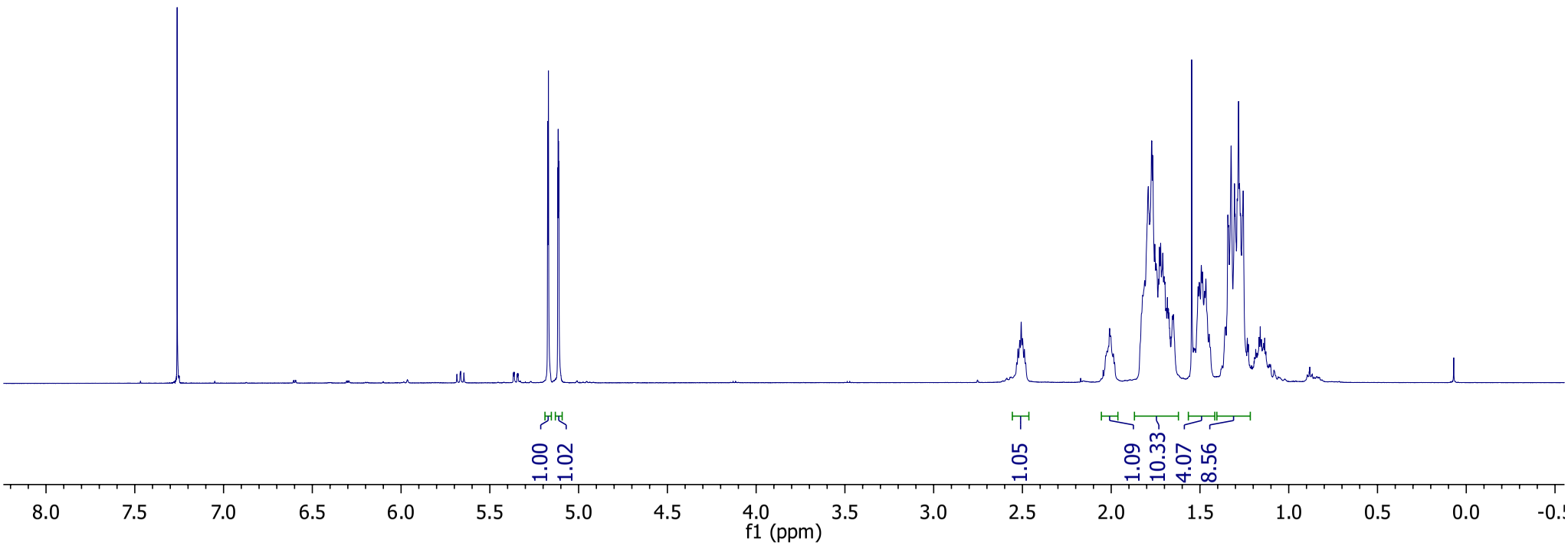
14.10



4c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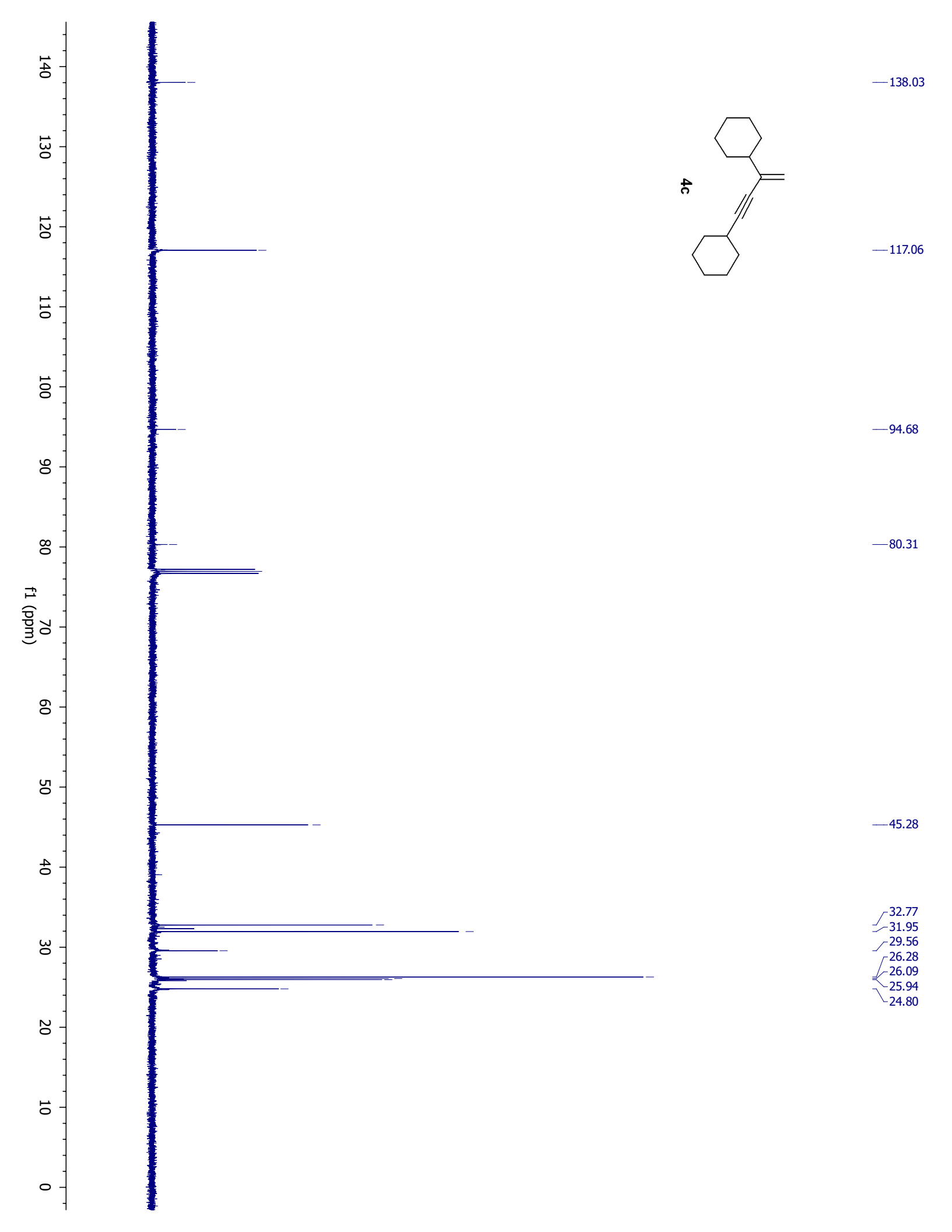
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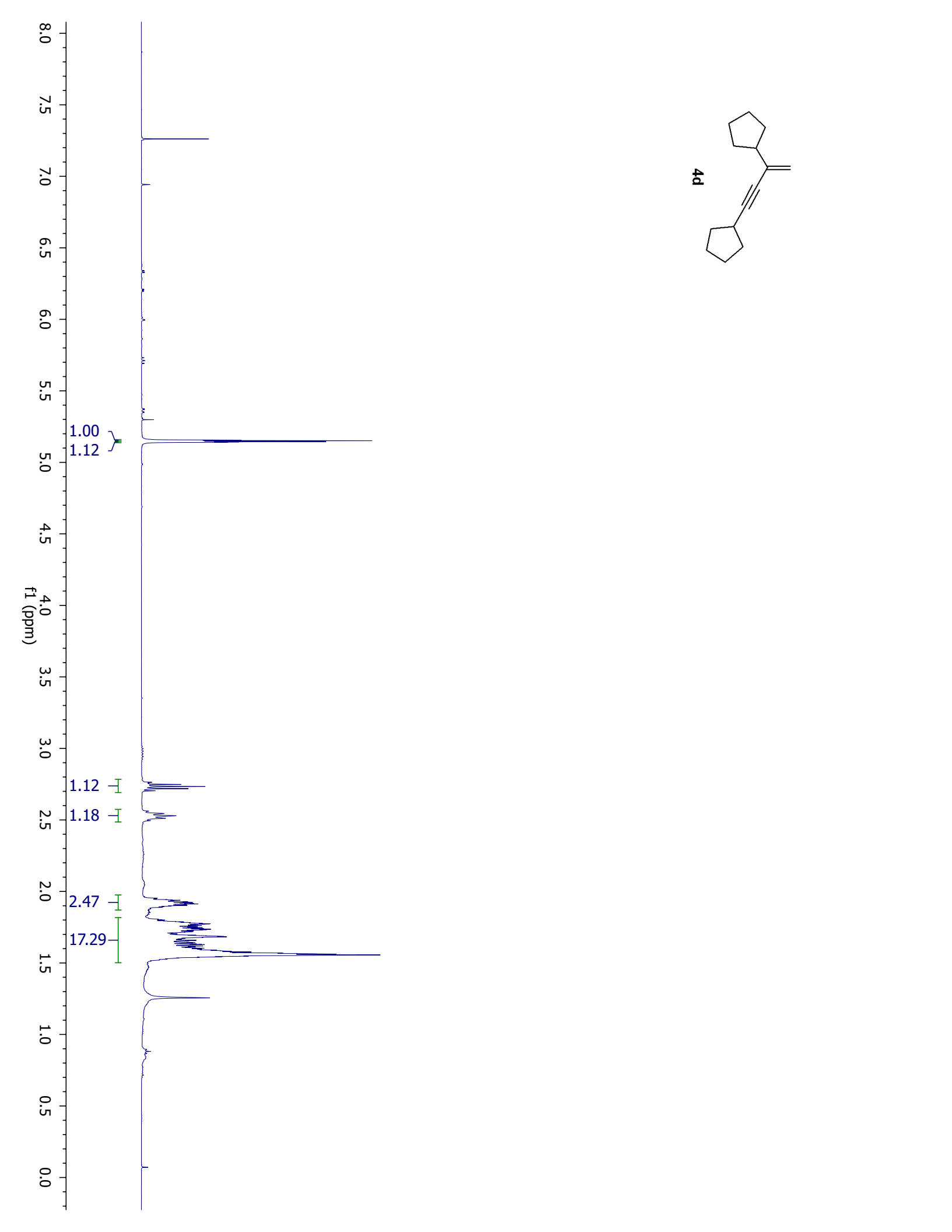
24.80
4c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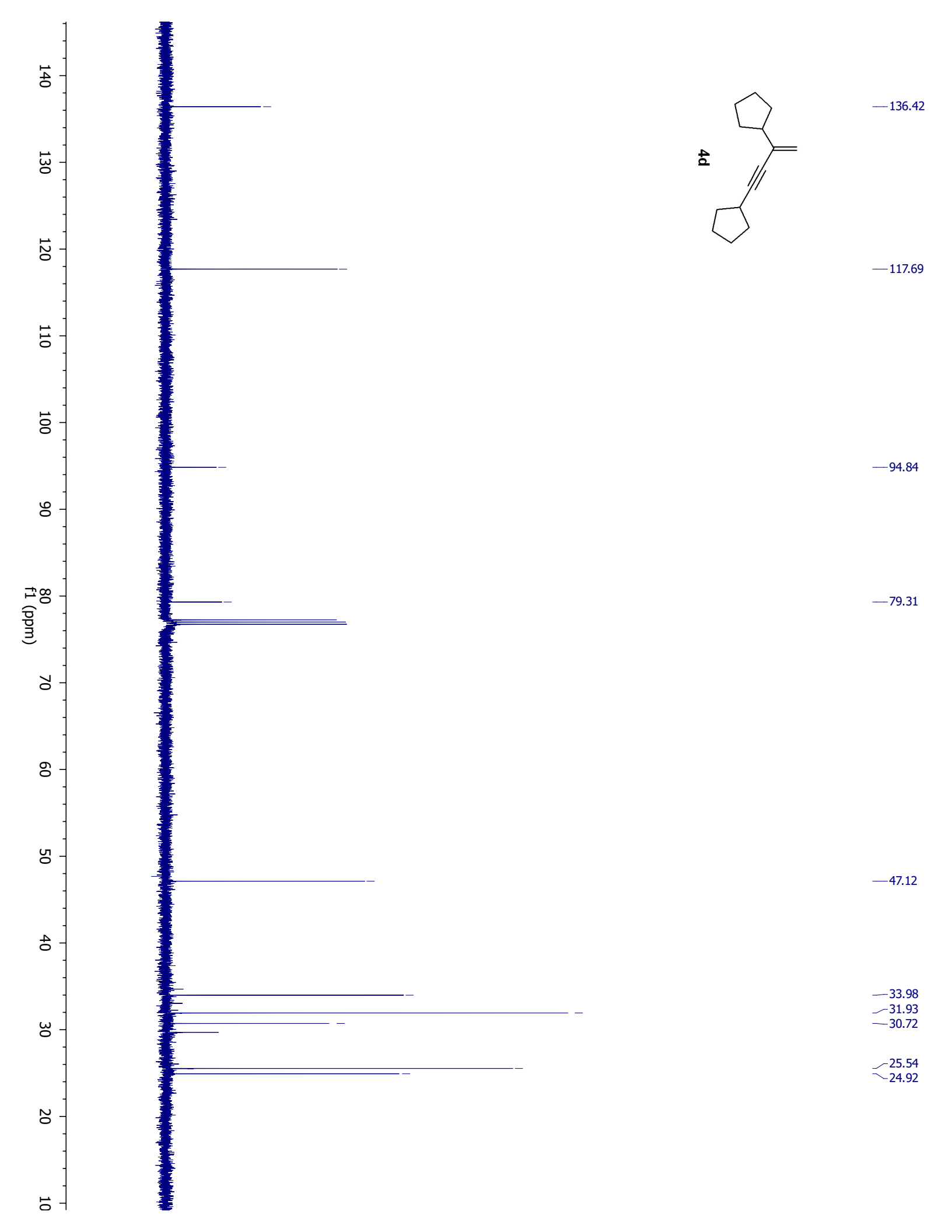
4d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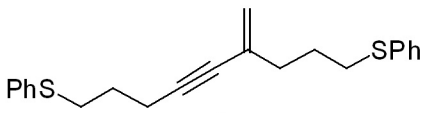
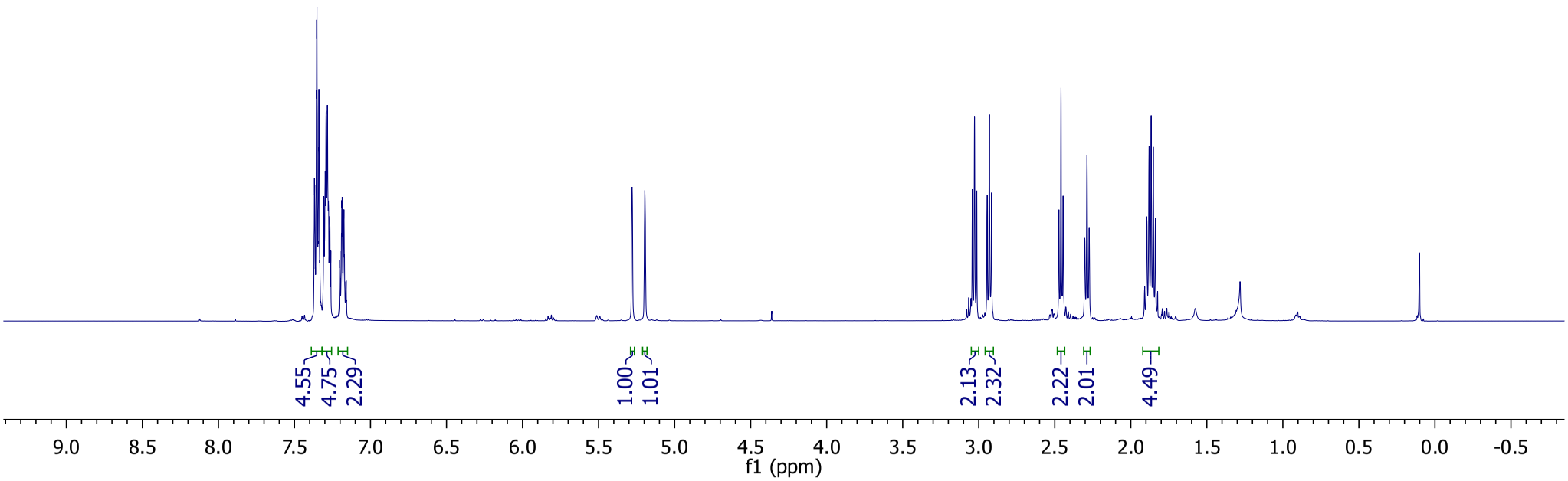

PhS
SPh

4e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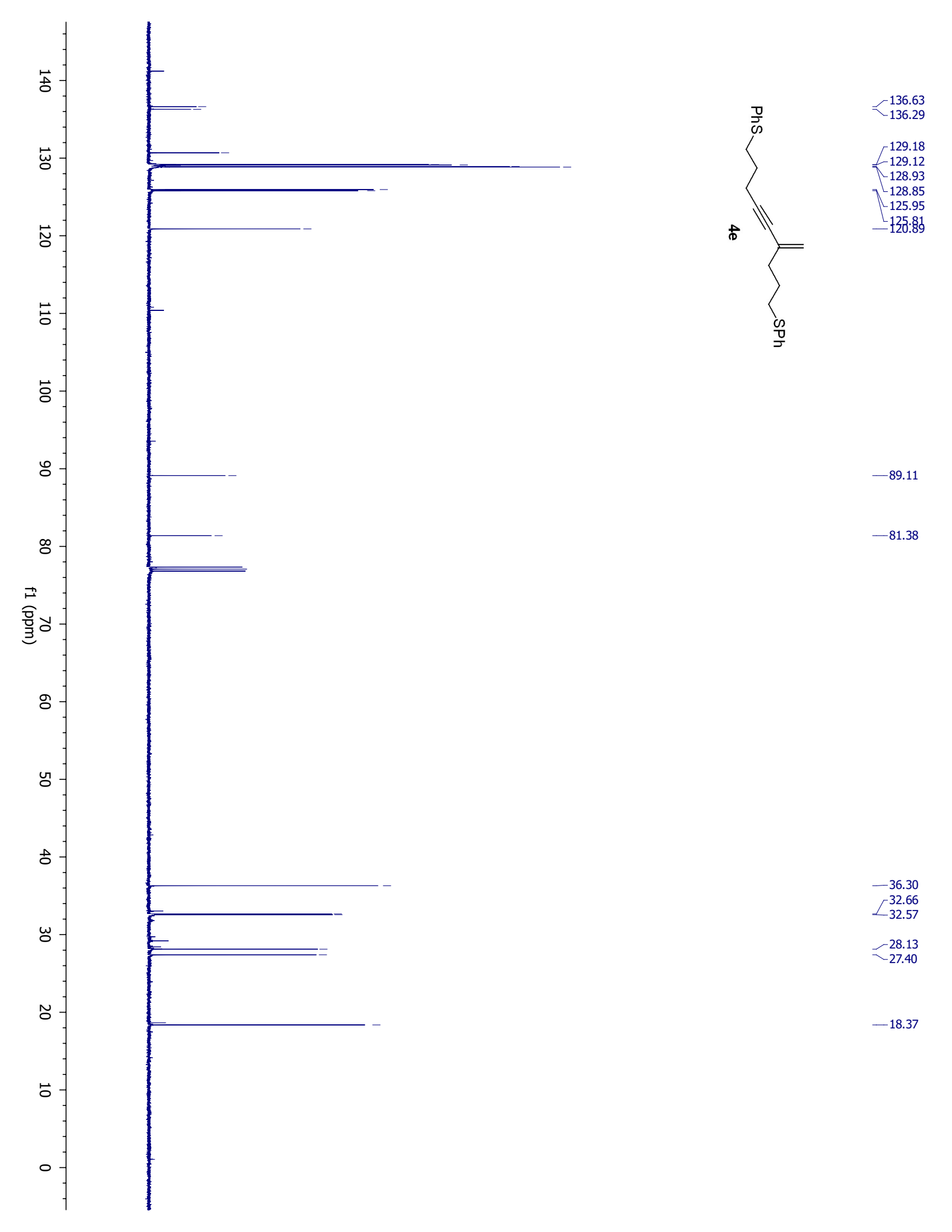
f1 (ppm)


PhS
SPh
4e
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125.95
125.81
120.89
89.11
81.38
36.30
32.66
32.57
28.13
27.40
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120
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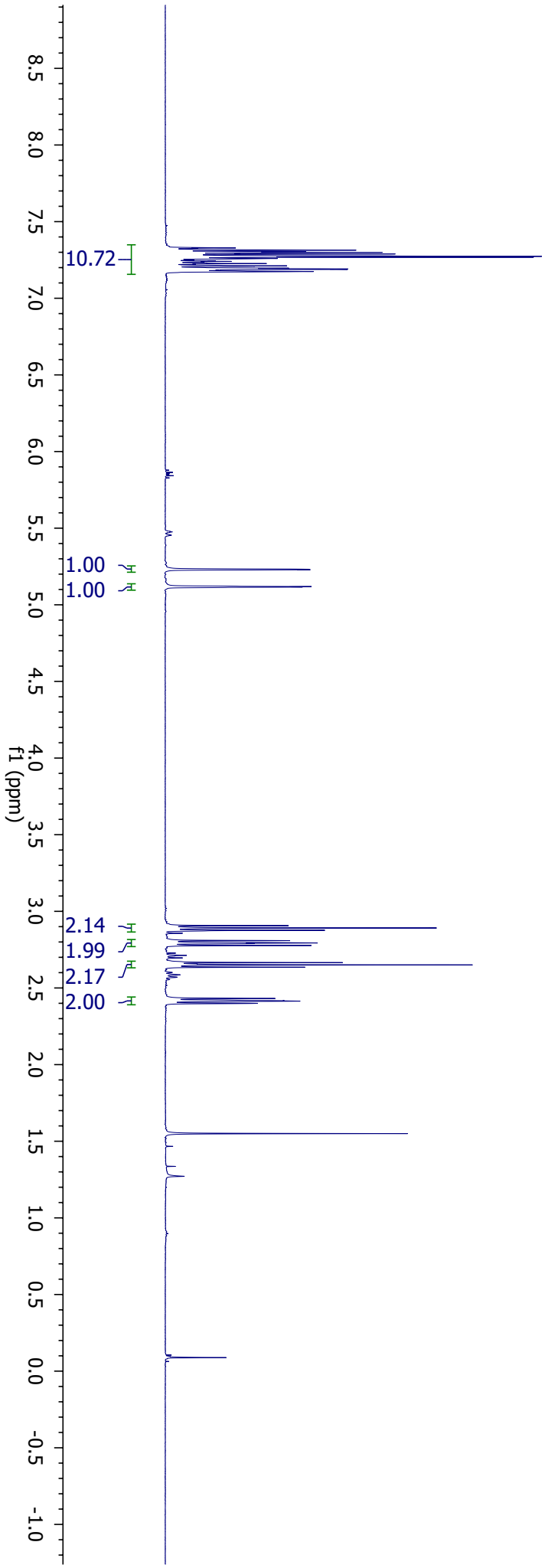
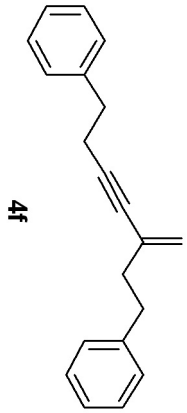
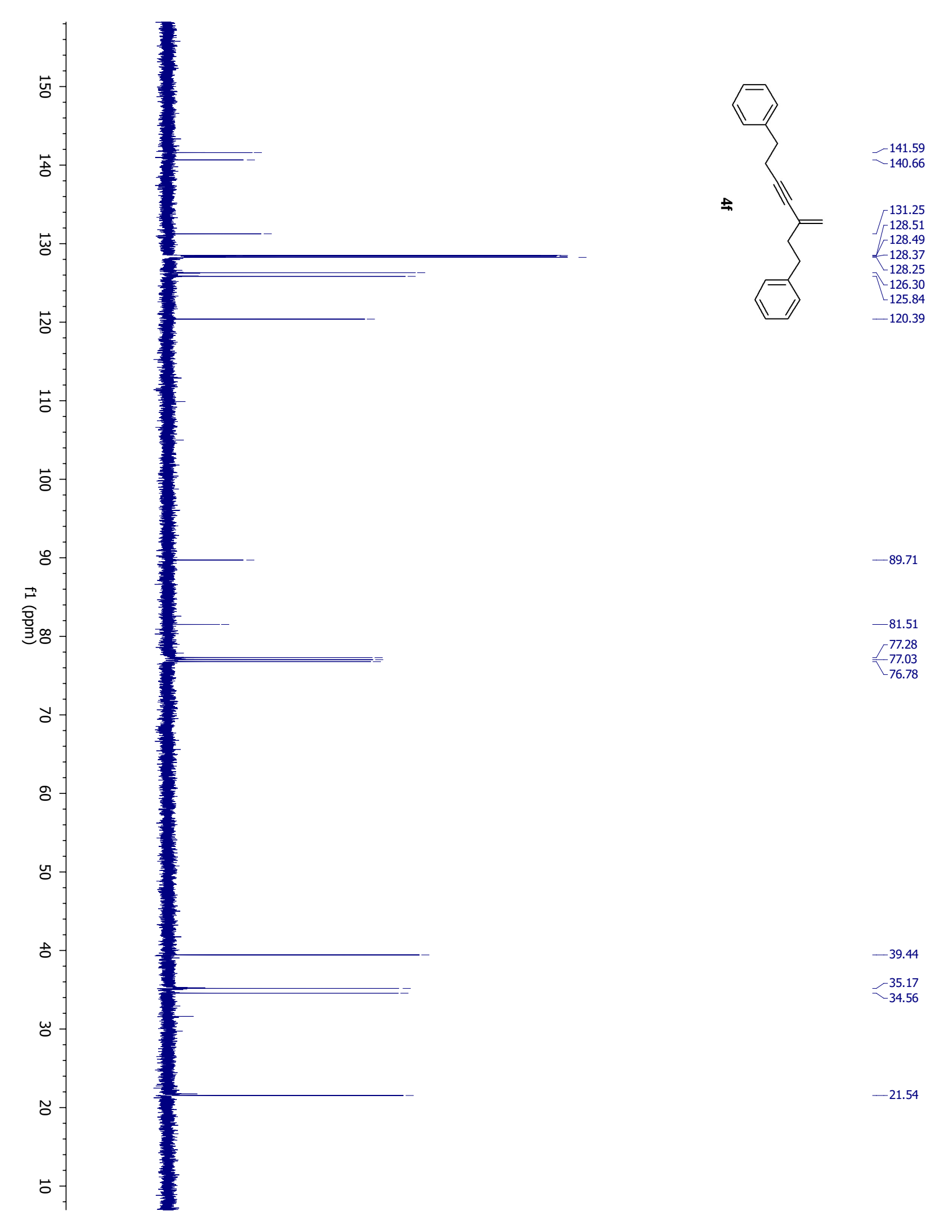
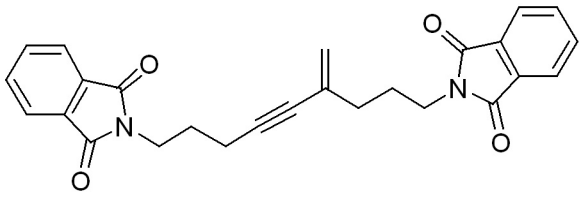


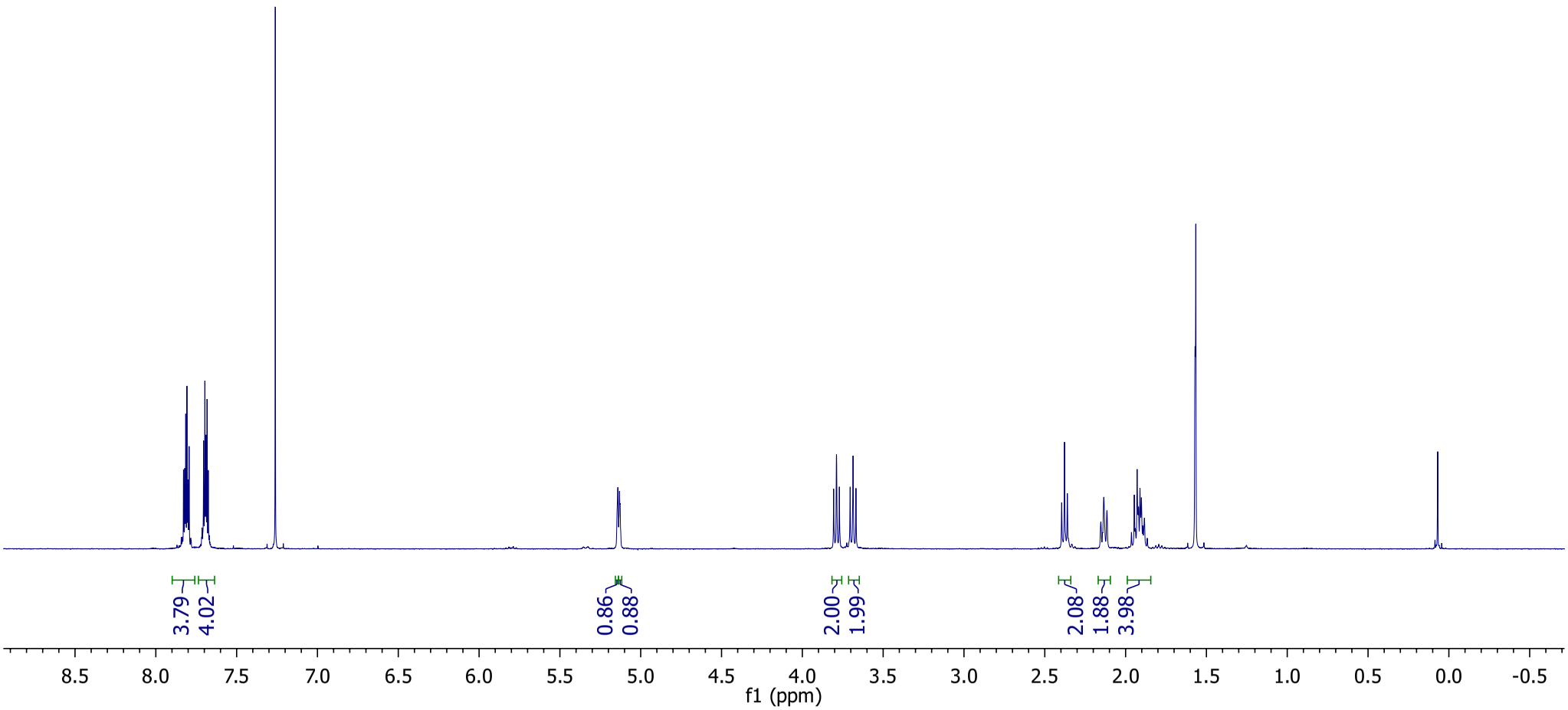


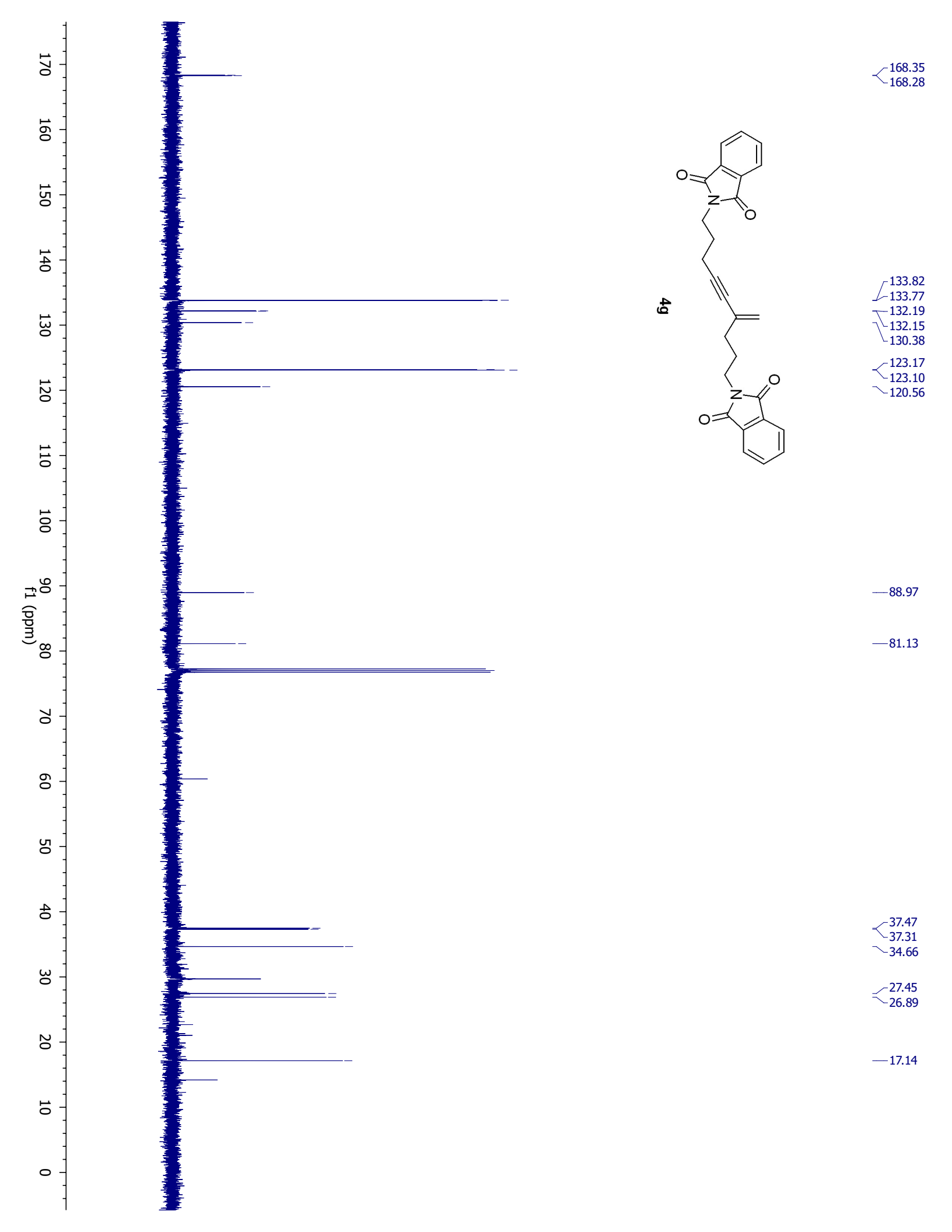
4f

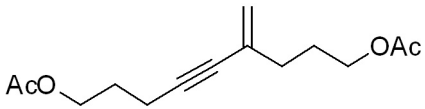

4f
141.59
140.66
131.25
128.51
128.49
128.37
128.25
126.30
125.84
120.39
89.71
81.51
77.28
77.03
76.78
39.44
35.17
34.56
21.54
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



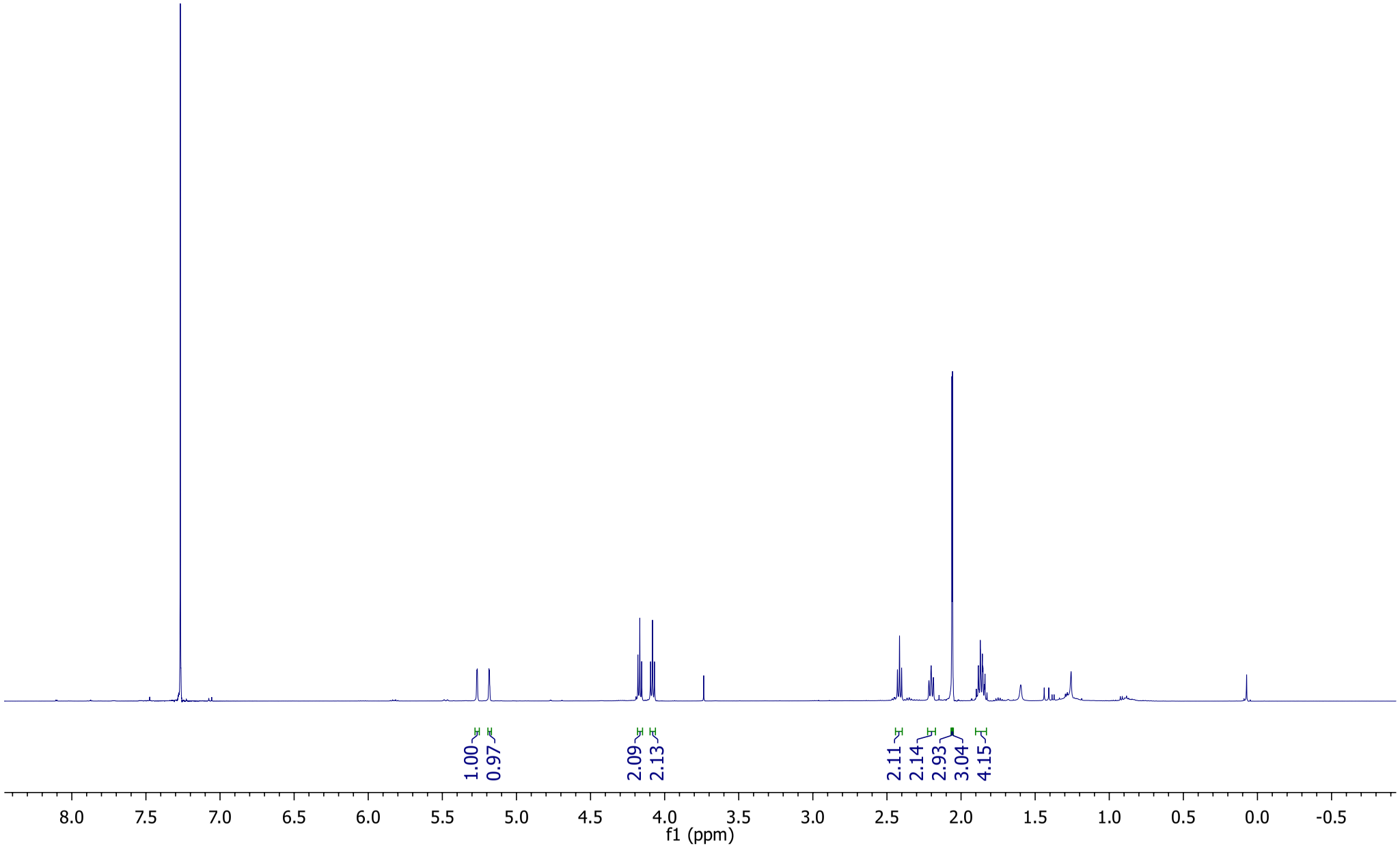
4g

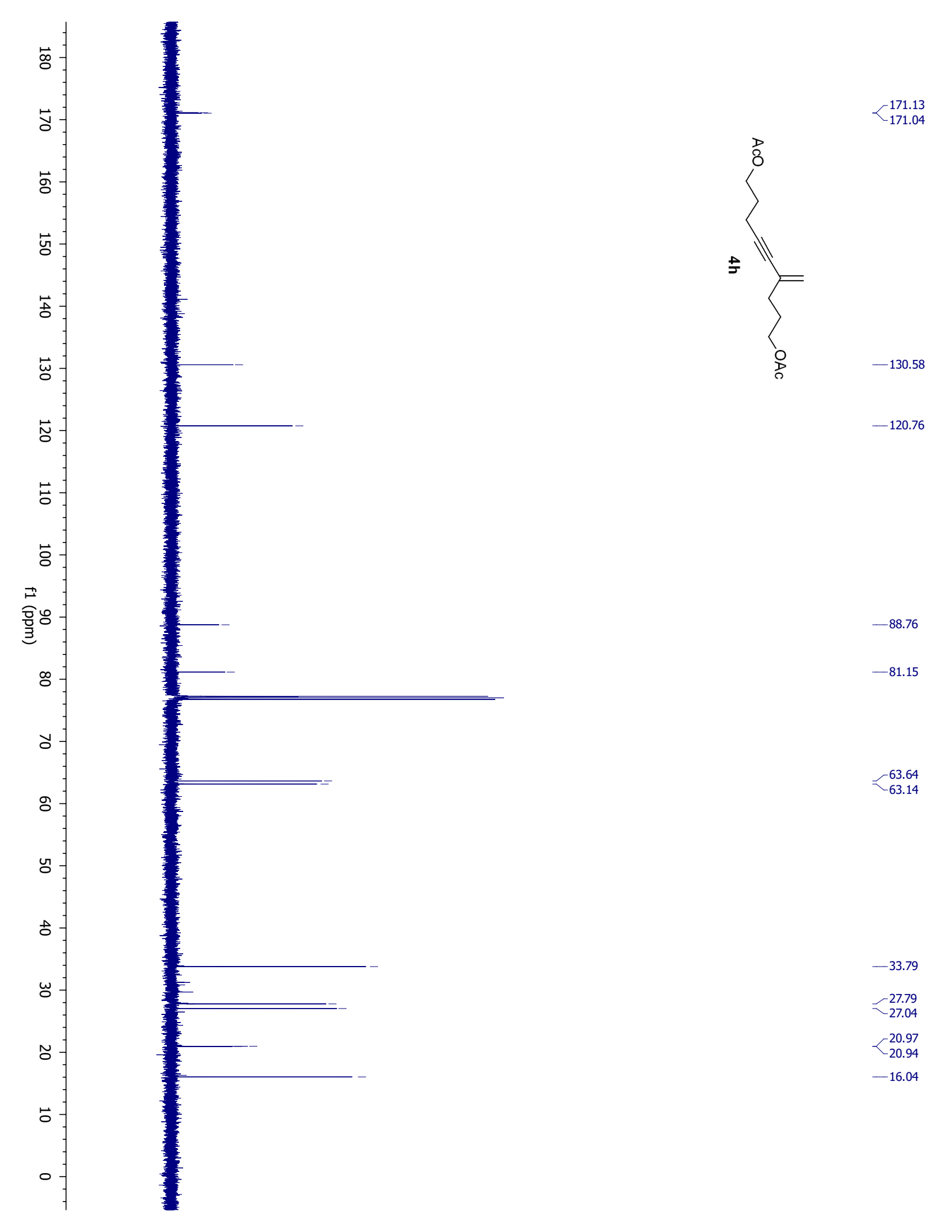

3.79
4.02
0.86
0.88
2.00
1.99
2.08
1.88
3.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
168.35
168.28
133.82
133.77
132.19
132.15
130.38
123.17
123.10
120.56
88.97
81.13
37.47
37.31
34.66
27.45
26.89
17.14
4g
O
N
O
O
N
O
O


AcO
OAc

4h


1.00
0.97
2.09
2.13
2.11
2.14
2.93
3.04
4.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


AcO
OAc
4h
171.13
171.04
130.58
120.76
88.76
81.15
63.64
63.14
33.79
27.79
27.04
20.97
20.94
16.04
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0