Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary information for

Synthesis of vinyl ethers of alcohols using calcium carbide under superbasic catalytic condition (KOH/DMSO)

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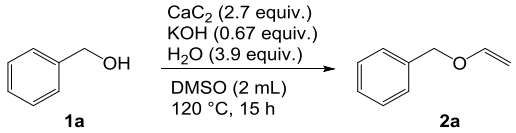
I. General remarks

Products were purified by column chromatography on silica gel (Kanto Chemical Co., Inc., Silica Gel 60N (spherical, neutral), 63-210 mm) or Florisil® (Sigma-Aldrich Japan, Florisil, 100-200 mesh). ^{1}H NMR spectra were recorded with a JEOL-ECP-500 (500 MHz) and a JEOL-ECS-400 (400 MHz) spectrometer in $CDCl_3$. Chemical shifts were reported in parts per million (δ) referenced to the solvent peak at 7.26 ppm ($CDCl_3$). ^{13}C NMR spectra were recorded with a JEOL-ECP-500 (126 MHz) and a JEOL-ECS-400 (100 MHz) spectrometer in $CDCl_3$ and referenced to the solvent peak at 77.16 ppm ($CDCl_3$). ^{19}F NMR spectrum was recorded with a JEOL-ECS-400 (378 MHz) spectrometer in $CDCl_3$ and referenced to $PhCF_3$ at -62.6 ppm. Coupling constants, *J*, were reported in Hertz (Hz), and splitting patterns were designated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet) and m (multiplet). IR spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions were reported in reciprocal centimeters. Conventional mass spectra were recorded with a SHIMADZU GCMS-QP2010Plus spectrometer and high-resolution mass spectra were recorded with a JEOL MS-700 spectrometer.

II. Materials

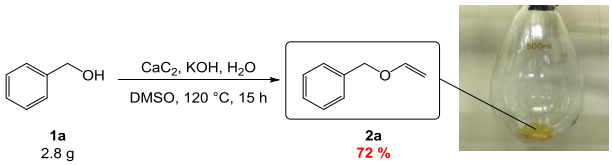
All matelials were purchased from commercially available sources and used without further purification. Calcium carbide was crushed to smaller than 5 mm before using.

III. Typical procedure for the vinylation reaction (Table 2, entry 1)



To a Pyrex reaction tube (20 x 125 mm, with a screw cap) was added a mixture of benzyl alcohol (162 mg, 1.5 mmol), KOH (55 mg, 1.0 mmol), and water (106 mg, 5.9 mmol) in DMSO (2 mL). After stirring at room temperature for 30 min, calcium carbide (262 mg, 4.1 mmol) was added. Then, the tube was sealed, and the mixture was heated to 120 °C with vigorous stirring for 15 h. The mixture was then filtered through a pad of silica gel (20 g) and washed with hexane/ethyl acetate (4/1 v/v, 250 mL). The filtrate was evaporated under vacuum and the residue was purified by column chromatography on Florisil® with pentane to give desired product **2a** (183 mg, 91%) as a pale yellow oil.

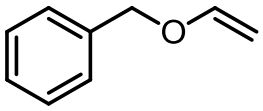
IV. Typical procedure for the vinylation reaction on gram scale



In a 200 mL two-necked round-bottom flask with a reflux condenser, a mixture of benzyl alcohol (2.8 g, 26 mmol), KOH (1.1 g, 20 mmol), and water (2.2 g, 120 mmol) in DMSO (40 mL) was prepared. After stirring at room temperature for 30 min, calcium carbide (5.2 g, 81.4 mmol) was added, the flask was then sealed with a rubber septum and attached to a balloon to avoid excess pressure due to generated acetylene. The mixture was heated to 120 °C with vigorous stirring for 15 h. Then, the mixture was filtered through a pad of silica gel (100 g) and washed with hexane/ethyl acetate (4/1 v/v, 2.5 L). The filtrate was evaporated under vacuum and the residue was purified by column chromatography on silica gel with pentane to give desired product **2a** (2.5 g, 72%) as a pale yellow oil.

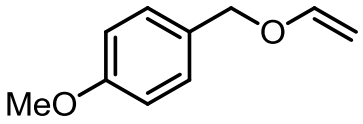
V. Spectroscopic data of vinylation products

Benzyl vinyl ether (2a)[S1]:



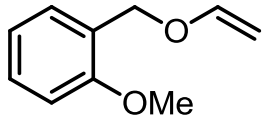
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (5H, m, ArH), 6.58 (1H, dd, *J* = 14.3, 6.7 Hz, OCH), 4.77 (2H, s, OCH_2), 4.32 (1H, dd, *J* = 14.1, 2.6 Hz, $=CH_2$), 4.10-4.09 (1H, m, $=CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.55, 136.88, 128.34, 127.73, 127.39, 87.18, 69.81.

4-Methoxybenzyl vinyl ether (2b)[S2]



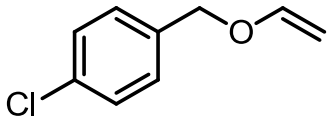
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, d, *J* = 8.3 Hz, ArH), 6.90 (2H, d, *J* = 8.3 Hz, ArH), 6.55 (1H, dd, *J* = 14.3, 6.4 Hz, OCH), 4.69 (2H, s, OCH_2), 4.30 (1H, dd, *J* = 14.5, 2.3 Hz, $=CH_2$), 4.07 (1H, dd, *J* = 6.8, 2.3 Hz, $=CH_2$), 3.81 (3H, s, OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.47, 151.72, 129.34, 128.97, 113.95, 87.22, 69.90.

2-Methoxybenzyl vinyl ether (2c)



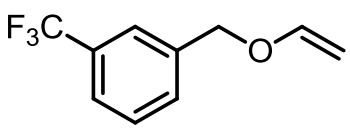
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (1H, dd, *J* = 7.6, 1.8 Hz, ArH), 7.29 (1H, dt, *J* = 8.0, 1.8 Hz, ArH), 6.97 (1H, t, *J* = 6.9 Hz, ArH), 6.89 (1H, d, *J* =8.3 Hz, ArH), 6.58 (1H, dd, *J* = 14.3, 6.4 Hz, OCH), 4.82 (2H, s, OCH_2), 4.33 (1H, dd, *J* = 14.3, 2.3 Hz, $=CH_2$), 4.07 (1H, dd, *J* ＝6.9, 1.8 Hz, $=CH_2$), 3.85 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.96, 151.91, 129.06, 128.90, 125.26, 120.52, 110.25, 87.11, 65.34, 55.34; ν_{max}/cm^{-1} (neat) 1636, 1617, 1246, 1030; GC-MS (EI) m/z (relative intensity) 164 (M^+, 5%), 127 (33), 126 (8), 125 (100), 99 (5), 90 (5), 89 (19), 63 (7); HRMS (EI) Found: [M^+]: 164.0834. $C_{10}H_{12}O_2$ requires 164.0837.

4-Chlorobenzyl vinyl ether (2d)[S2]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (2H, d, *J* = 8.7 Hz, ArH), 7.29 (2H, d, *J* = 8.3 Hz, ArH), 6.55 (1H, dd, *J* = 14.5, 6.9 Hz, OCH), 4.73 (2H, s, OCH_2), 4.29 (1H, dd, *J* = 14.5, 2.3 Hz, $=CH_2$), 4.10 (1H, dd, *J* = 6.9, 2.3 Hz, $=CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.51, 135.48, 133.77, 128.90, 128.76, 87.71, 69.27.

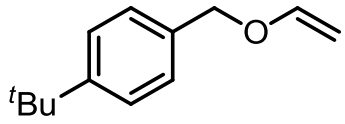
3-Trifluoromethylbenzyl vinyl ether (2e)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, s, ArH), 7.58-7.47 (3H, m, ArH), 6.58 (1H, dd, *J* = 14.5, 6.4 Hz, OCH), 4.81 (2H, s, OCH_2), 4.31(1H, dd, *J* = 14.3, 2.3 Hz, $=CH_2$), 4.13 (1H, dd, *J* = 6.4, 2.3 Hz, $=CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.45, 138.14, 131.01 (q, $J_{C\text{-}F}$

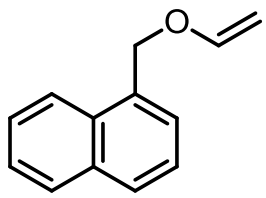
= 31.8 Hz), 130.70, 129.08, 124.76 (d, $J_{C\text{-}F}$ = 3.9 Hz), 124.27 (q, $J_{C\text{-}F}$ = 271.7 Hz), 124.19 (d, $J_{C\text{-}F}$ = 3.9 Hz), 87.82, 69.10; ^{19}F NMR (378 MHz, $CDCl_3$) δ -62.58; ν_{max}/cm^{-1} (neat) 1639, 1619; GC-MS (EI) m/z (relative intensity) 202 (M^+, 2%), 184 (12), 160 (9), 159 (100), 119 (8), 109 (25); HRMS (EI) Found: [M^+]: 202.0601. $C_{10}H_9F_3O$ requires 202.0605.

4-*tert*-Butylbenzyl vinyl ether (2g)[S3]:



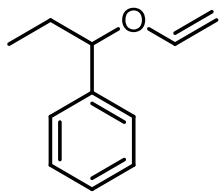
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, *J* = 8.2 Hz, ArH), 7.30 (2H, d, *J* = 8.2 Hz, ArH), 6.57 (1H, dd, *J* = 17.4, 6.7 Hz, OCH), 4.73 (2H, s, OCH_2), 4.31 (1H, dd, *J* = 14.3, 2.1 Hz, $=CH_2$), 4.08 (1H, dd, *J* = 6.7, 2.1 Hz, $=CH_2$), 1.32 (9H, s, ^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.85, 151.02, 133.94, 127.61, 125.54, 87.24, 70.02, 34.66, 31.44.

1-Naphthylmethyl vinyl ether (2h)[S4]:



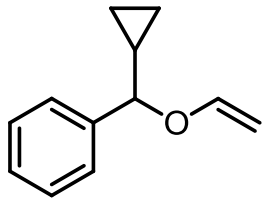
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (1H, d, *J* = 8.3 Hz, ArH), 7.87 (2H, dd, *J* = 15.4, 8.3 Hz, ArH), 7.44-7.58 (4H, m, ArH), 6.66 (1H, dd, *J* = 14.3, 6.43 Hz, OCH), 5.20 (2H, s, OCH_2), 4.44 (1H, dd, *J* = 14.5, 2.3Hz, $=CH_2$), 4.16 (1H, dd, *J* = 7.1, 1.8 Hz, $=CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.72, 133.83, 132.32, 131.64, 129.10, 128.73, 126.74, 126.52, 125.98, 125.33, 123.75, 87.48, 68.62.

1-Phenylpropyl vinyl ether (2i):



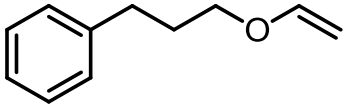
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (2H, m, ArH), 7.26-7.23 (3H, m, ArH), 6.30 (1H, dd, *J* = 13.8, 6.7 Hz, OCH), 4.60 (1H, t, *J* = 6.7 Hz, benzyl-H), 4.21 (1H, dd, *J* = 14.3, 1.5 Hz, $=CH_2$), 3.93 (1H, dd, *J* =6.7, 1.5 Hz, $=CH_2$), 1.88 (1H, dq , *J* = 13.8, 7.2 Hz, C*H*$_2$CH$_3$), 1.75 (1H, dq, *J* = 13.8, 7.2 Hz, C*H*$_2$CH$_3$), 0.90 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.98, 141.74, 128.48, 127.63, 126.41, 89.17, 82.94, 30.87, 10.06; ν_{max}/cm^{-1} (neat) 1635, 1615; GC-MS (EI) m/z (relative intensity) 162 (M^+, 2%), 120 (6), 119 (53), 117 (7), 92 (9), 91 (100), 77 (10), 41 (18); HRMS (EI) Found: [M^+] 162.1050. $C_{11}H_{14}O$ requires 162.1044.

Cyclopropylphenylmethyl vinyl ether (2k)[S5]:



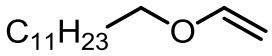
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (5H, m, ArH), 6.33 (1H, dd, *J* = 14.0, 6.4 Hz, OCH), 4.24 (1H, dd, *J* = 14.3, 1.4 Hz, $=CH_2$), 4.17 (1H, d, *J* = 7.8 Hz, O*CH*Ph), 3.96 (1H, dd, *J* = 6.7, 1.4 Hz, $=CH_2$), 1.30-1.22 (1H, m, c-propyl), 0.69-0.63 (1H, m, c-propyl), 0.57-0.46 (2H, m, c-propyl), 0.40-0.35 (1H, m, c-propyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.90, 141.22, 128.54, 127.81, 126.53, 89.50, 85.43, 17.74, 4.09, 2.54.

3-Phenylpropyl vinyl ether (2l)[S6]:



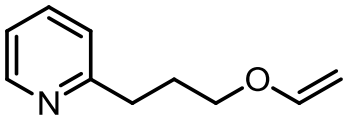
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.32 (2H, m, ArH), 7.21-7.19 (3H, m, ArH), 6.49 (1H, dd, *J* = 14.3, 6.9 Hz, OCH), 4.17 (1H, dd, *J* = 14.3, 1.8 Hz, =CH_2), 3.99 (1H, dd, *J* = 5.8, 1.8 Hz, =CH_2), 3.70 (2H, t, *J* = 6.4 Hz, O*CH*$_2$), 2.73 (2H, t, *J* = 7.4 Hz, *CH*$_2$Ph), 1.99 (2H, quint, *J* = 6.4 Hz, CH_2*CH*$_2$$CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.94, 141.63, 128.58, 128.49, 126.00, 86.49, 67.05, 32.23, 30.78.

n-Dodecyl vinyl ether (2m)[S7]



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (1H, dd, *J* = 14.3, 7.2 Hz, OCH), 4.17 (1H, dd, *J* = 14.3, 2.1 Hz, =CH_2), 3.97 (1H, dd, *J* = 6.7, 2.1 Hz, =CH_2), 3.67 (2H, t, *J* = 6.7 Hz, OCH_2), 1.65 (2H, q, *J* = 6.7 Hz, OCH_2CH_2), 1.31-1.26 (18H, m, alkyl), 0.88 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.07, 86.11, 68.08, 32.09, 29.84, 29.82, 29.77, 29.75, 29.57, 29.53, 29.23, 26.19, 22.84, 14.21.

3-(2-Pyridyl)propyl vinyl ether (2n)[S8]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (1H, d, *J* = 4.1 Hz, ArH), 7.59 (1H, td, *J* = 7.8, 1.8 Hz, ArH), 7.16 (1H, d, *J* = 7.8 Hz, ArH), 7.11 (1H, dd, *J* = 7.4, 5.1 Hz, ArH), 6.48 (1H, dd, *J* = 14.3, 6.9 Hz, OCH), 4.16 (1H, dd, *J* = 14.3, 1.8 Hz, =CH_2), 3.98 (1H, dd, *J* = 6.9, 1.8 Hz, =CH_2), 3.72 (2H, t, *J* = 6.4 Hz, O*CH*$_2$), 2.90 (2H, t, *J* = 7.4 Hz, *CH*$_2$Ph), 2.15-2.08 (2H, m, CH_2*CH*$_2$$CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.15, 151.74, 149.23, 136.25, 122.84, 121.03, 86.31, 66.99, 34.49, 28.86.

References

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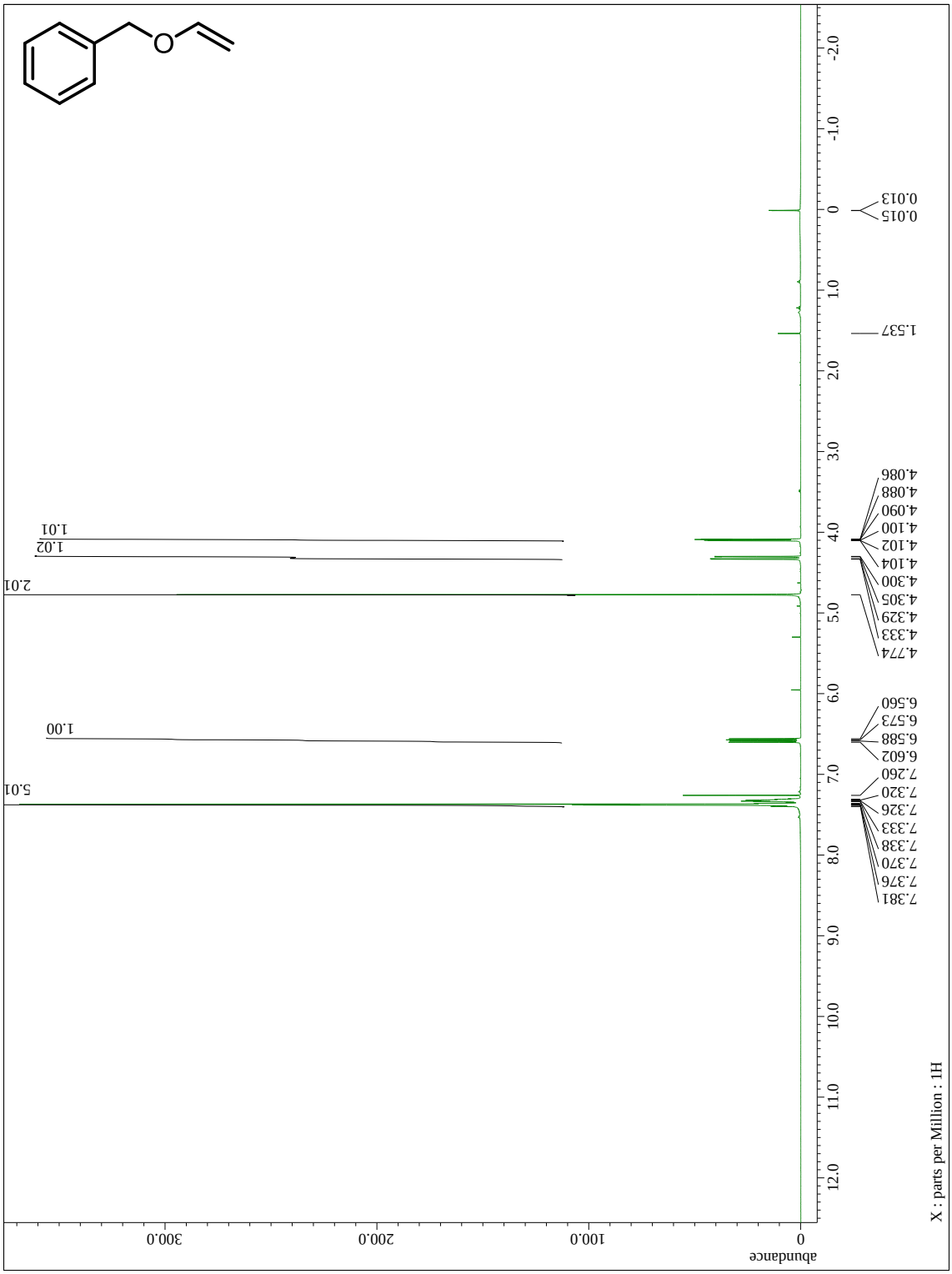
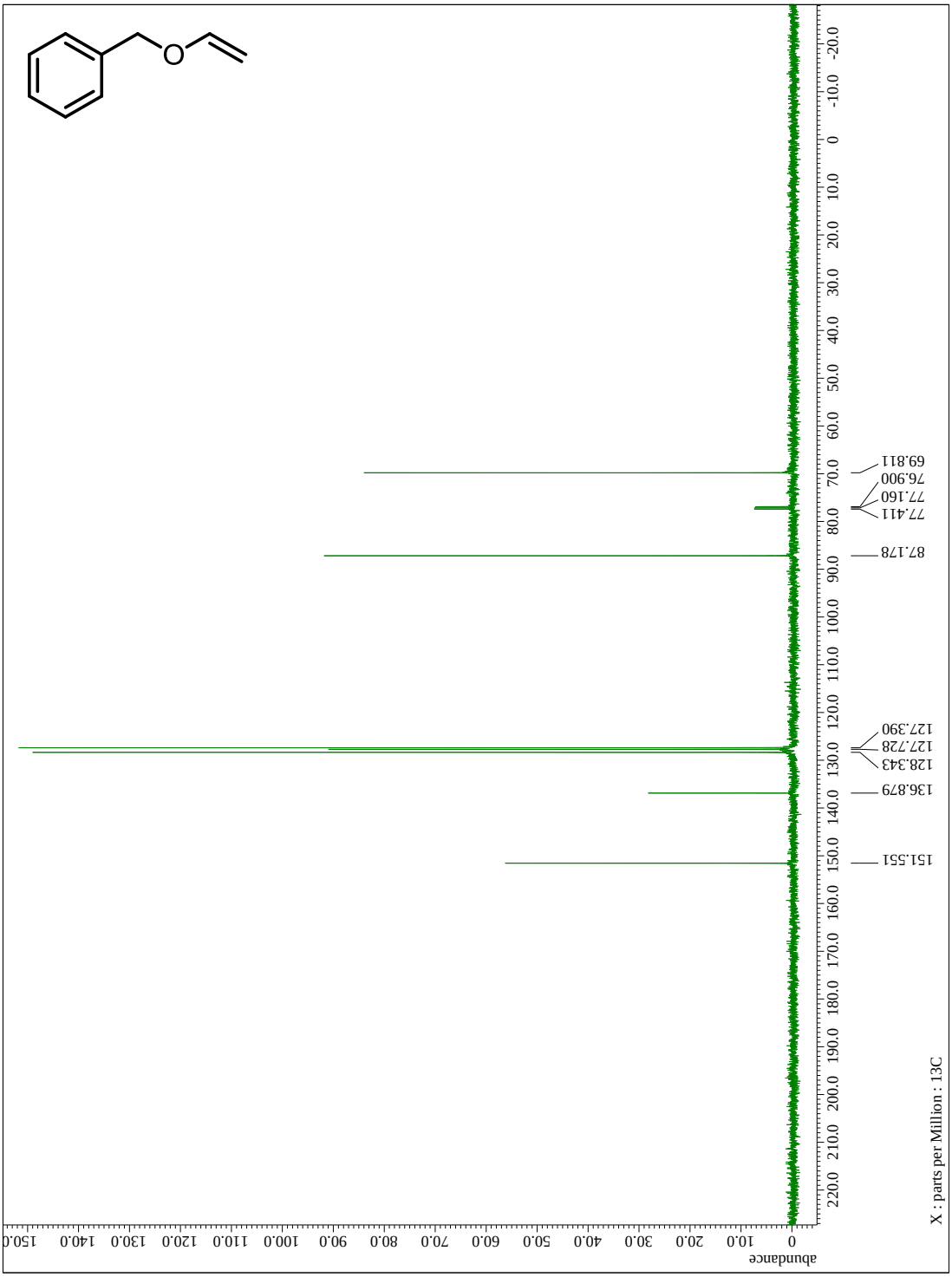
S8. US Pat., 3 651 071, 1969.

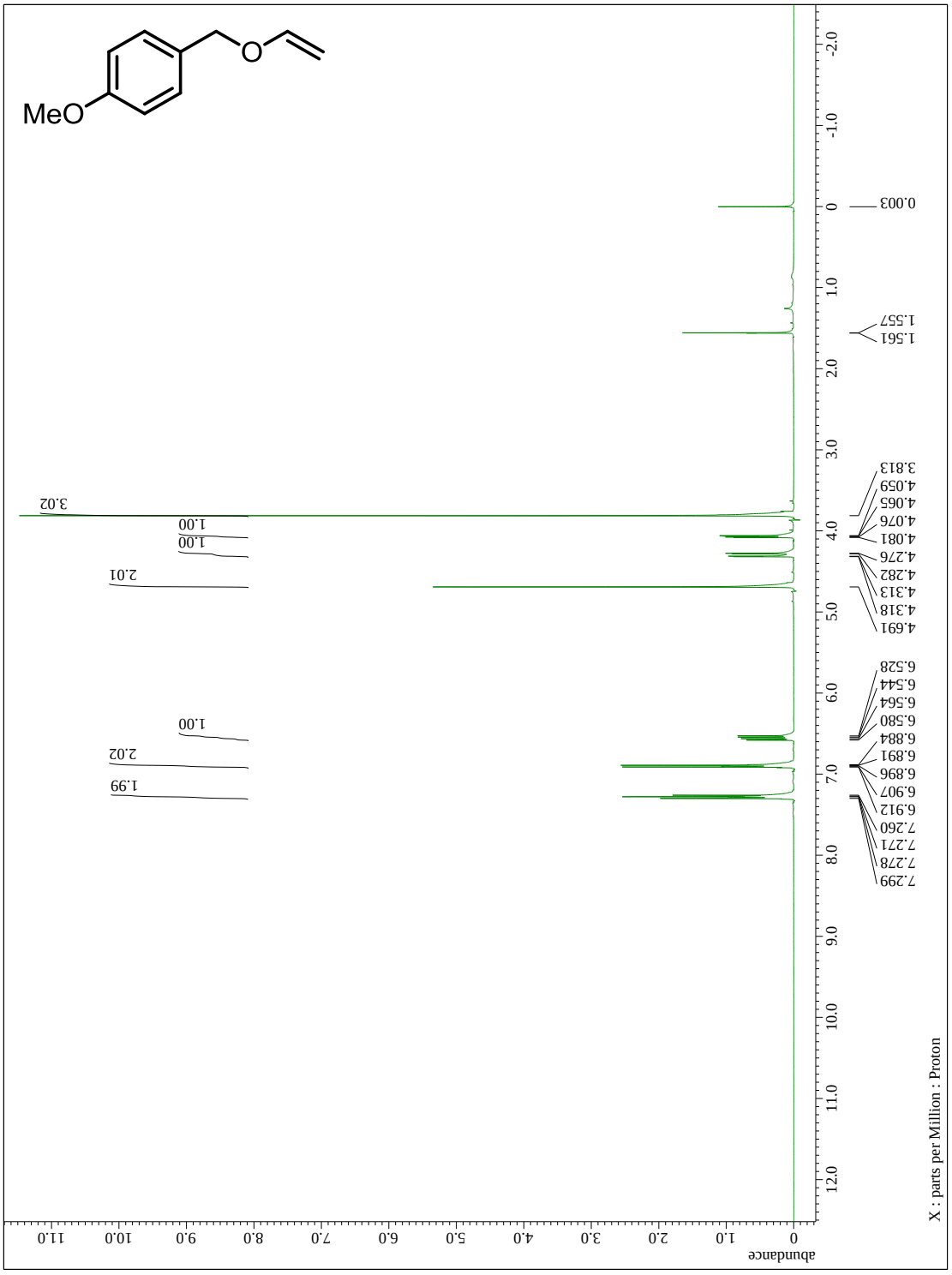
VI. NMR spectra of vinylation products

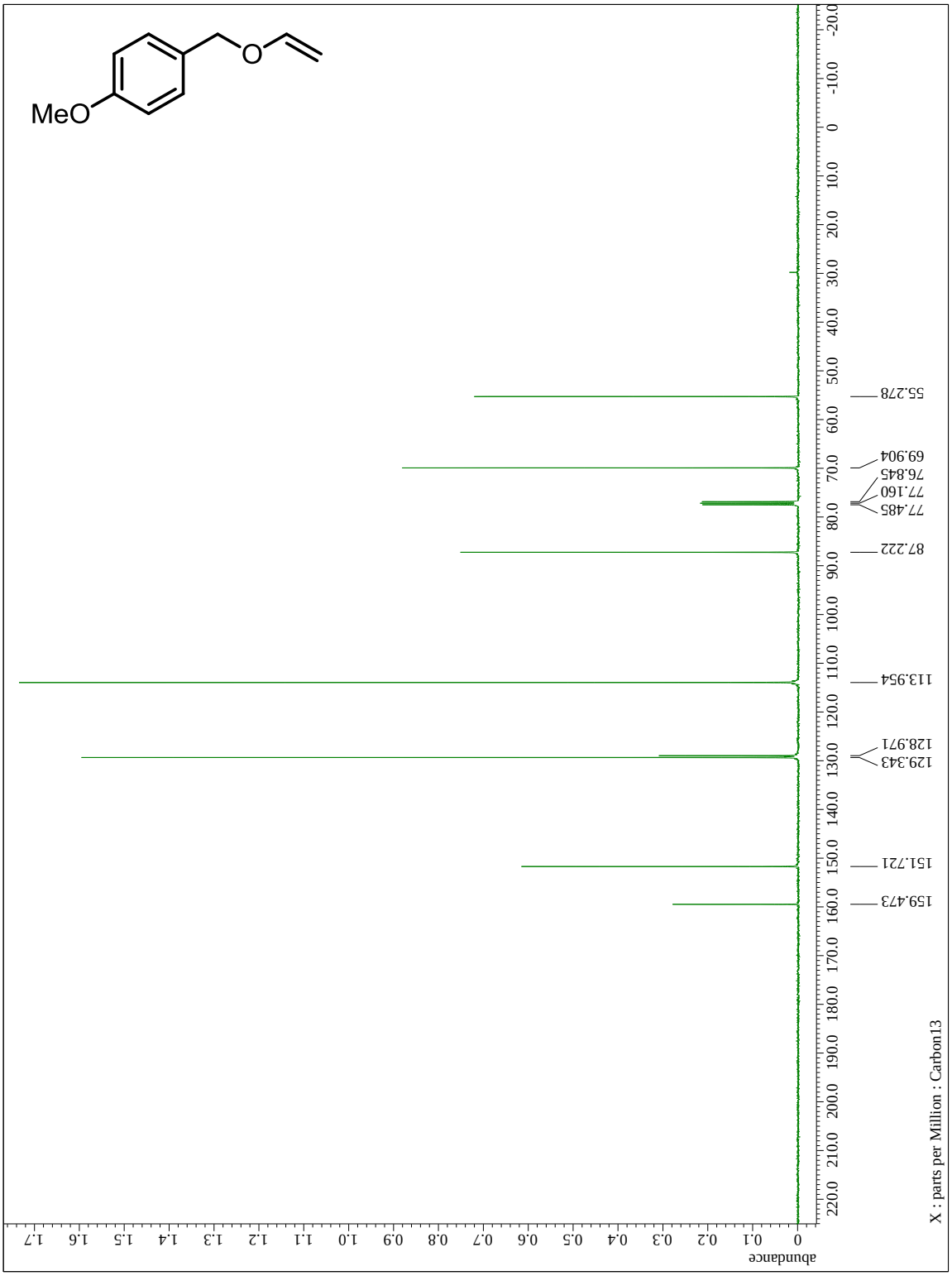
Benzyl vinyl ether (2a)



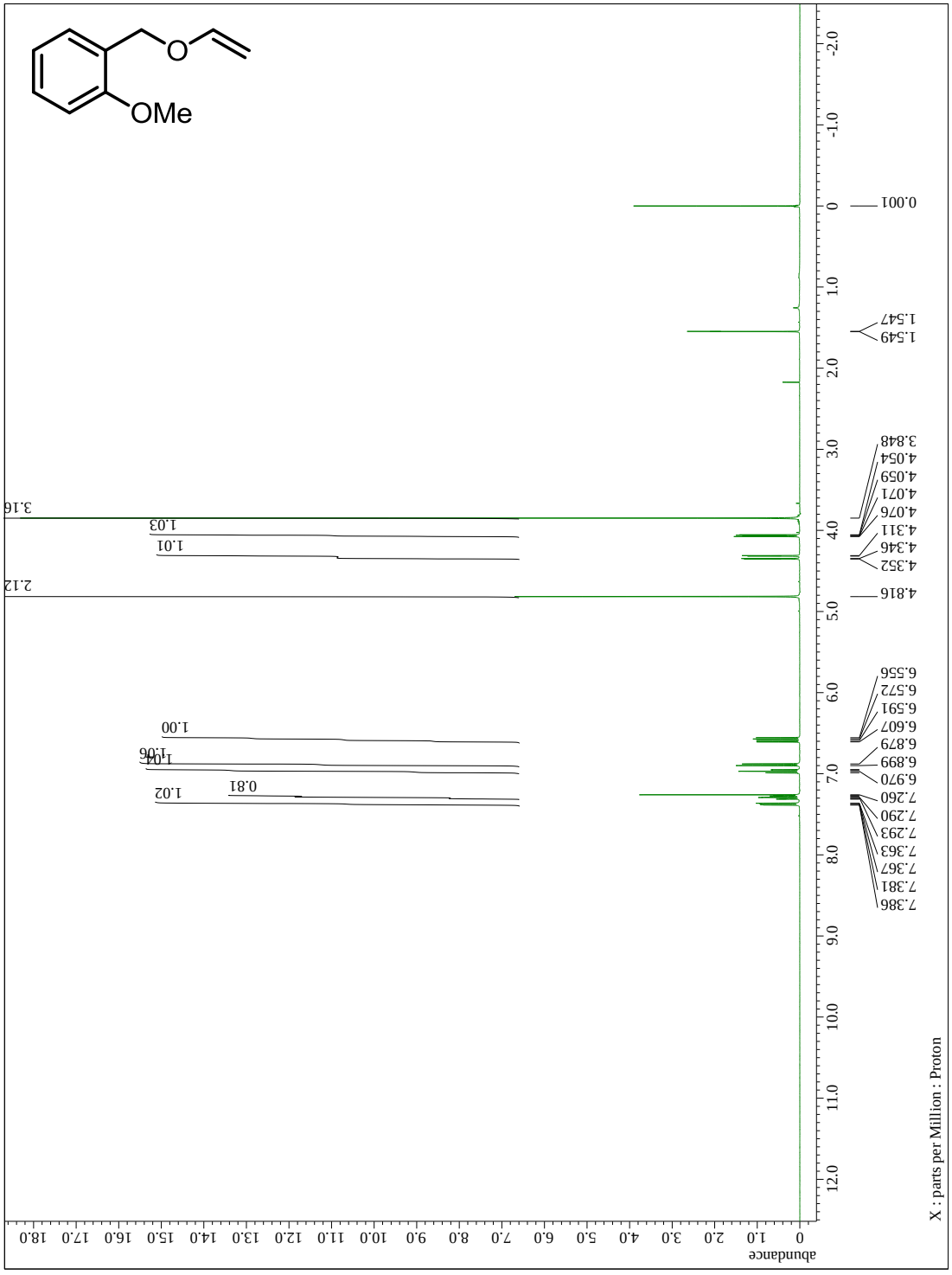

151.551
136.879
128.343
127.728
127.390
87.178
77.411
77.160
76.900
69.811
X : parts per Million : 13C
abundance

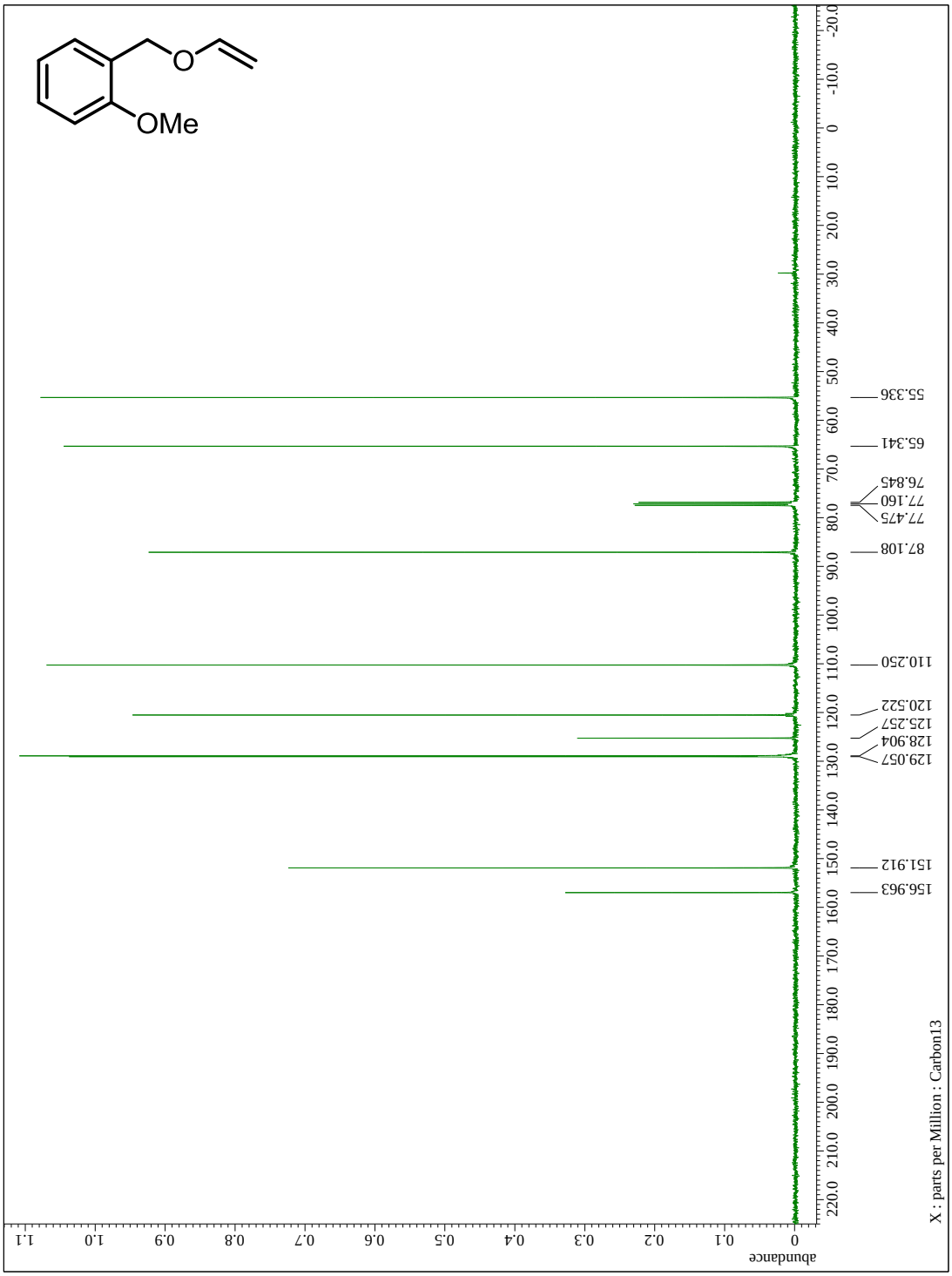
4-Methoxybenzyl vinyl ether (2b)



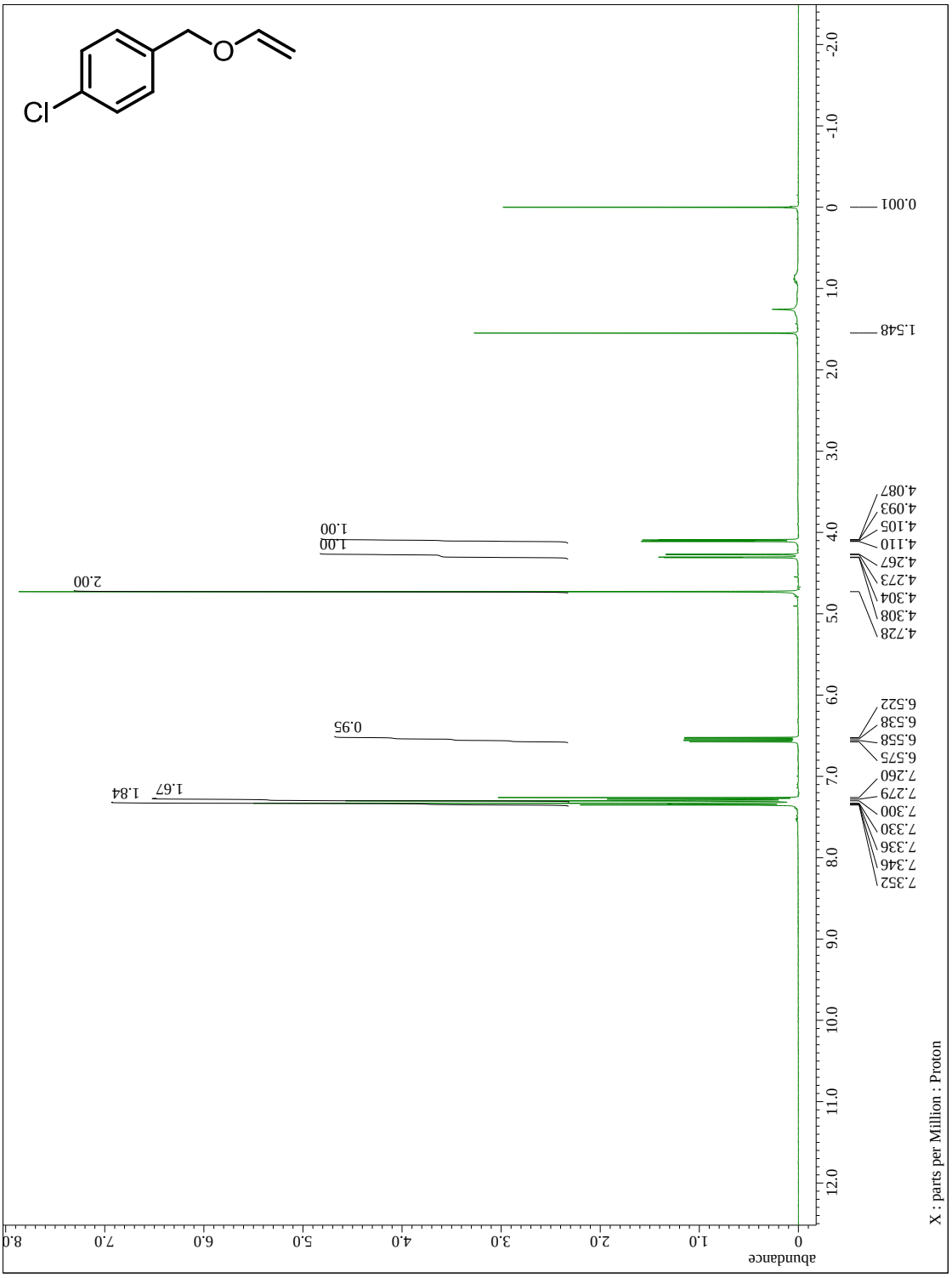

MeO
O
159.473
151.721
129.343
128.971
113.954
87.222
77.485
77.160
76.845
69.904
55.278
X : parts per Million : Carbon13
abundance

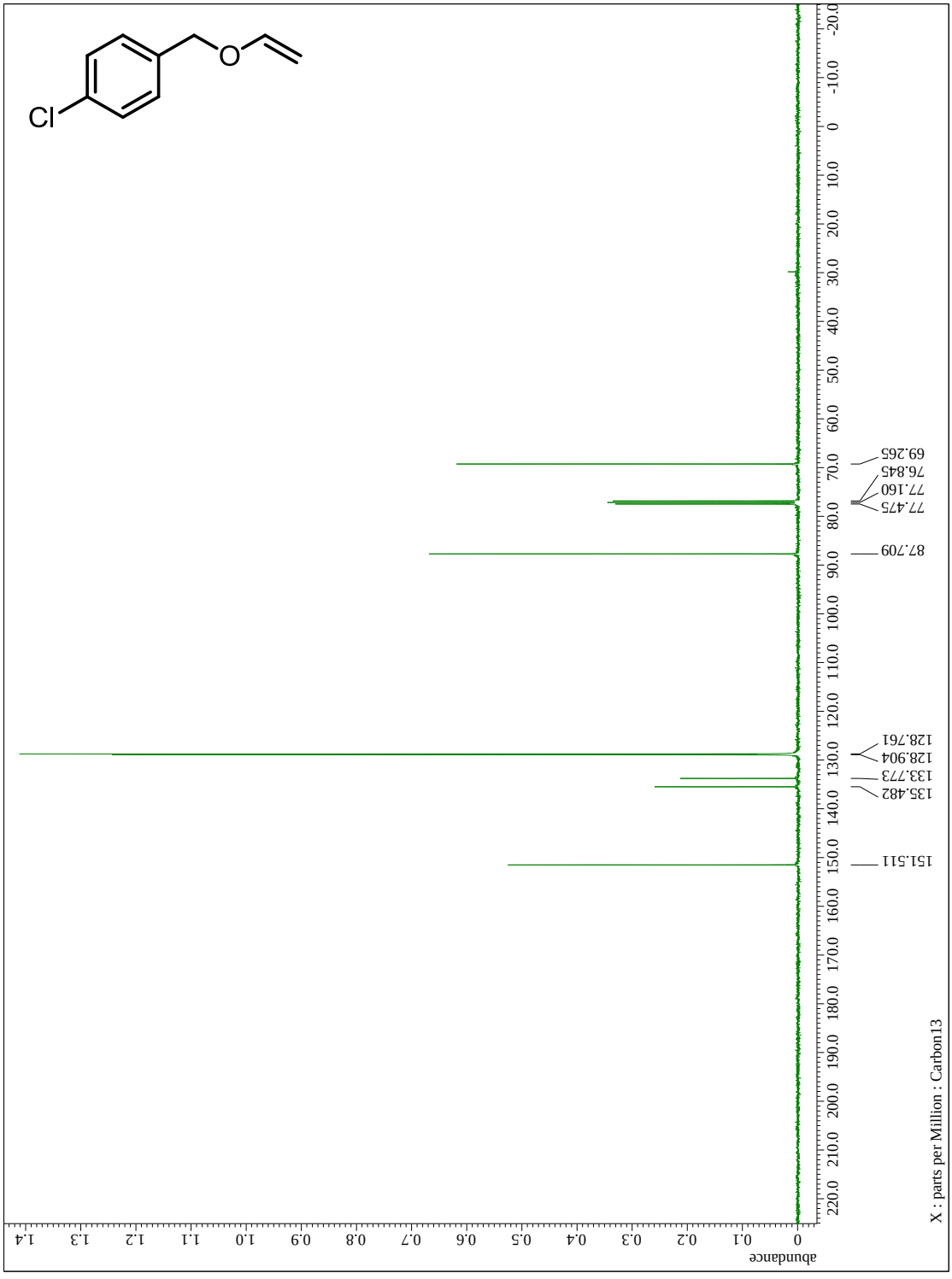
2-Methoxybenzyl vinyl ether (2c)



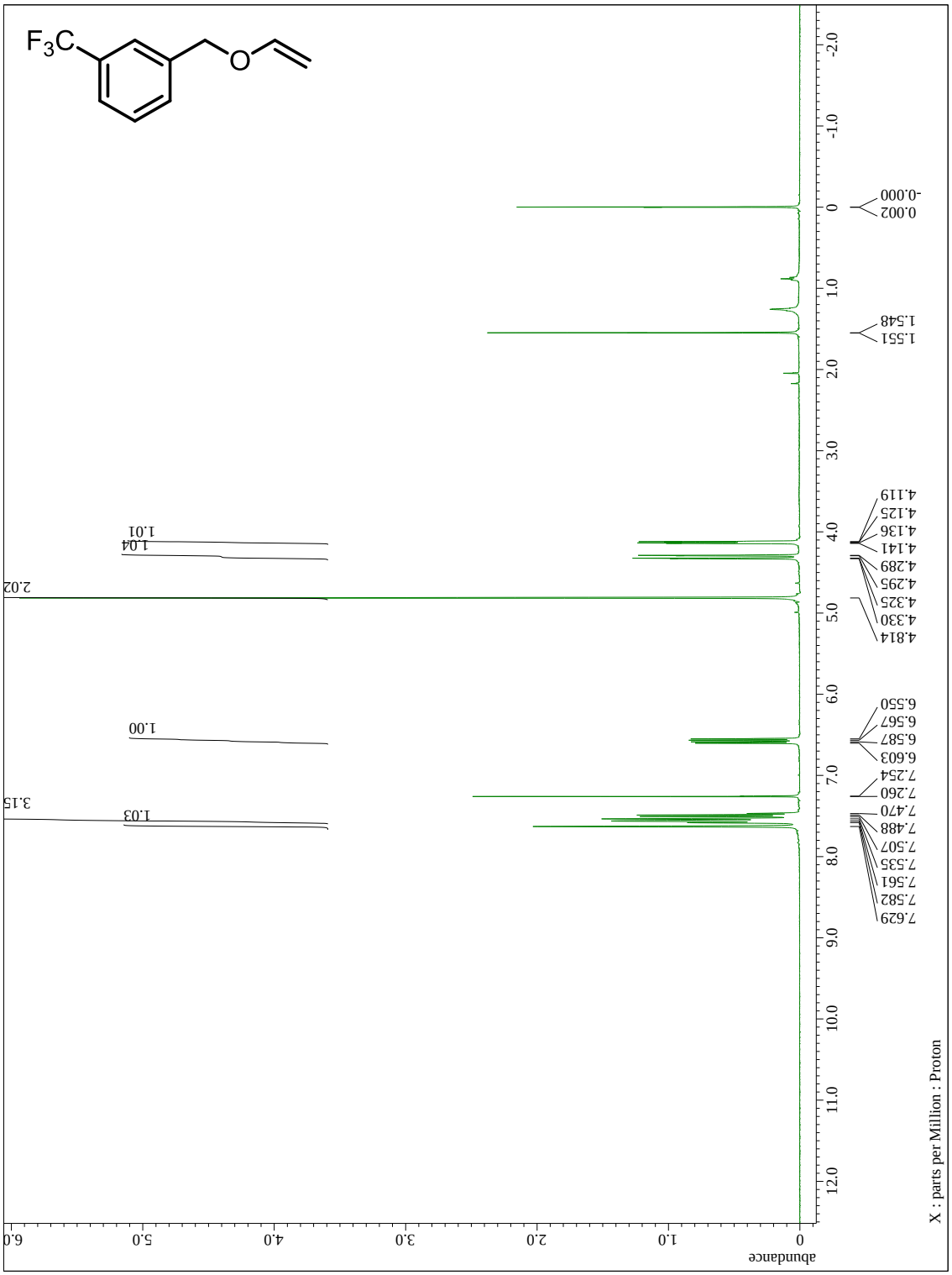

OMe
O
abundance
X : parts per Million : Carbon13
55.336
65.341
76.845
77.160
77.475
87.108
110.250
120.522
125.257
128.904
129.057
151.912
156.963

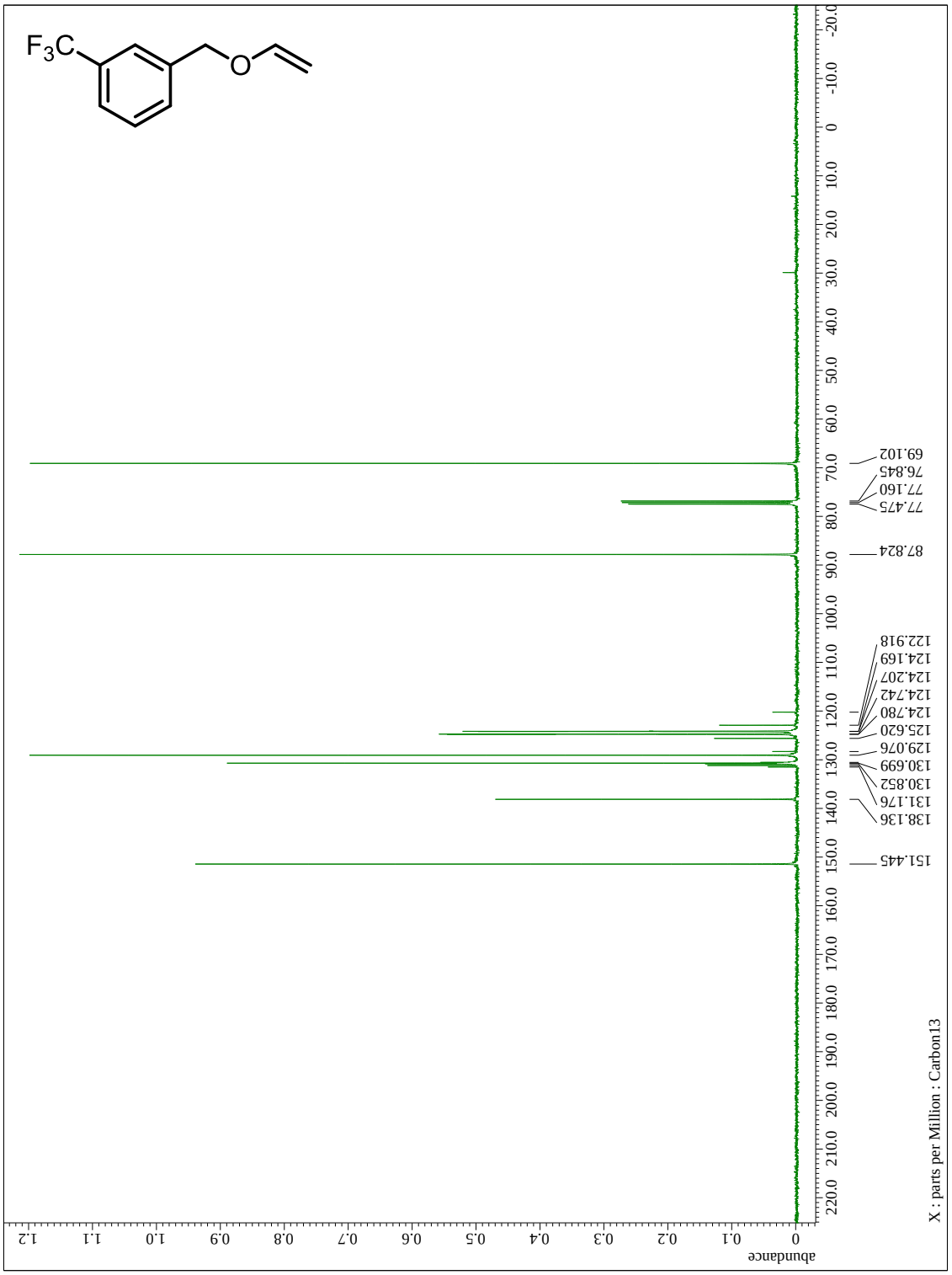
4-Chlorobenzyl vinyl ether (2d)

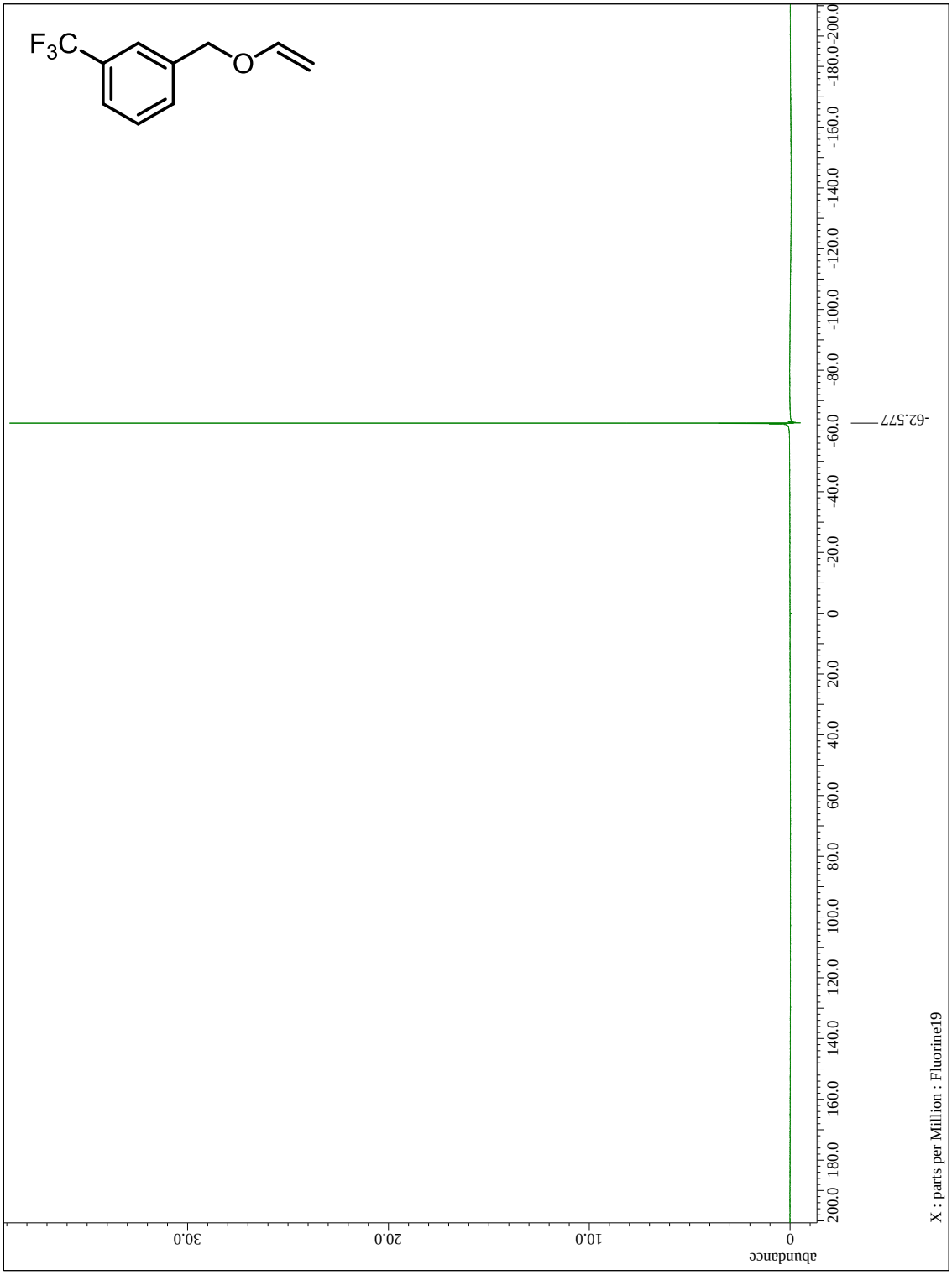



Cl
O
151.511
135.482
133.773
128.904
128.761
87.709
77.475
77.160
76.845
69.265
X : parts per Million : Carbon13
abundance

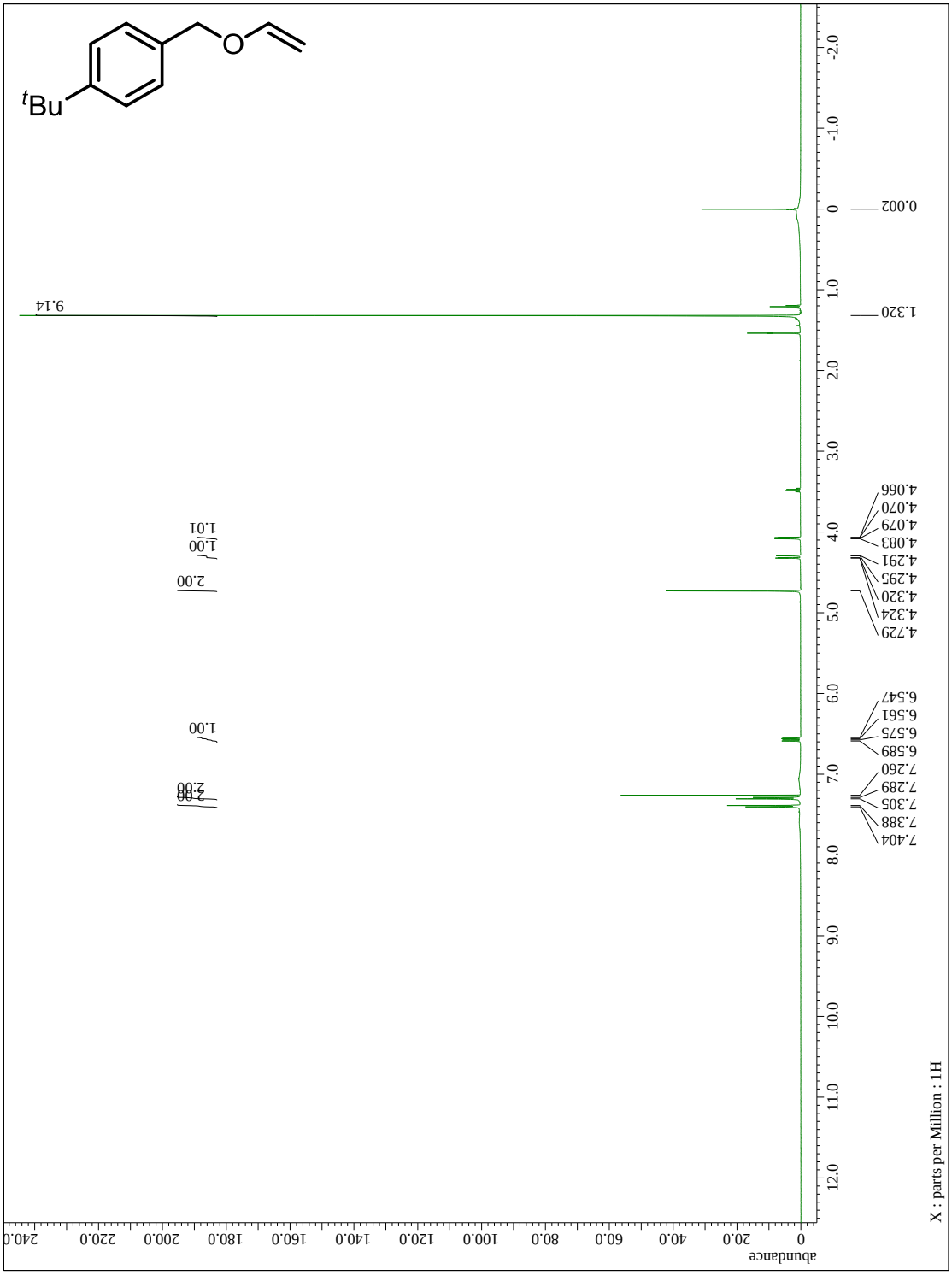
3-Trifluoromethylbenzyl vinyl ether (2e)

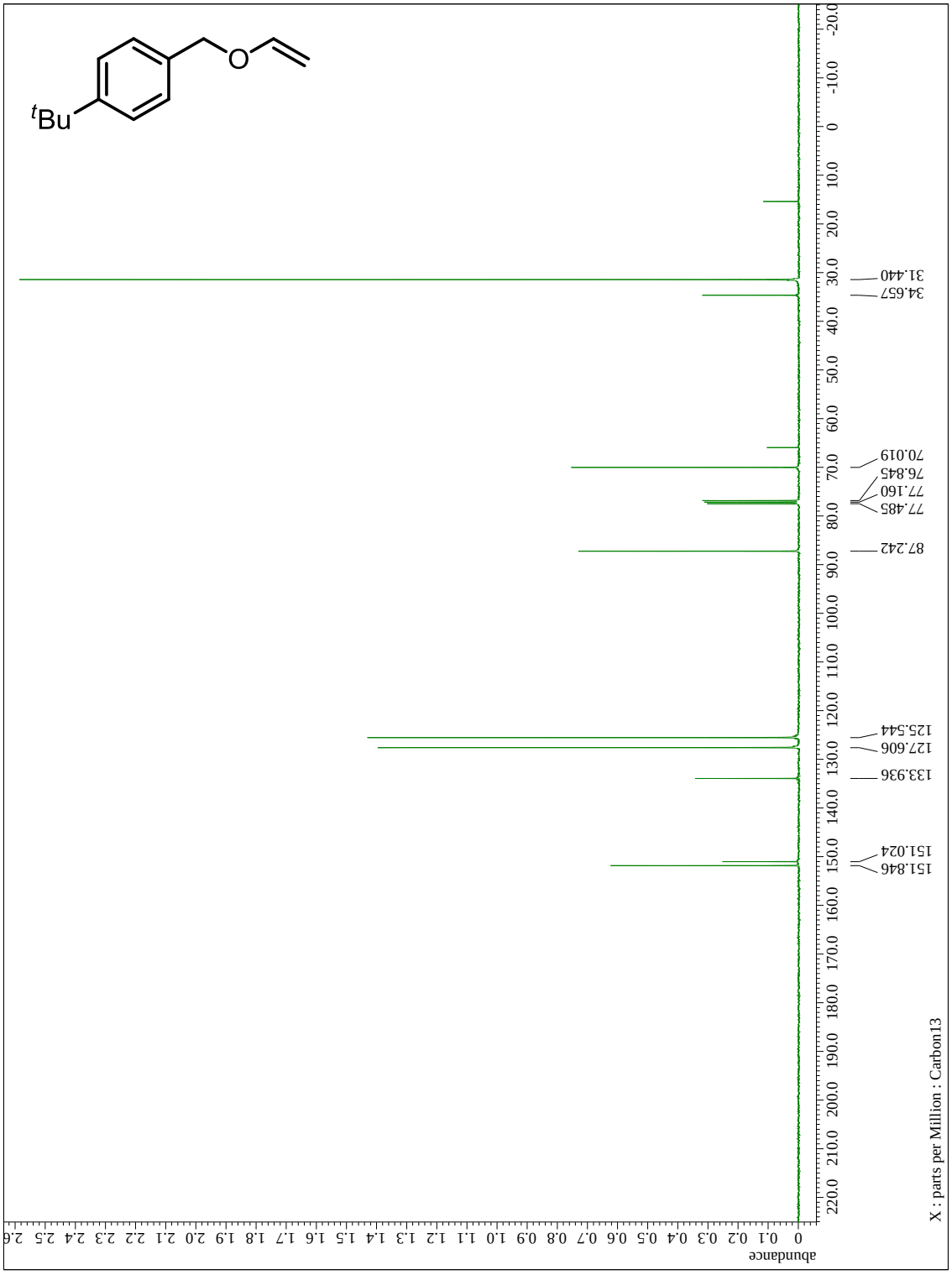



F3C
O
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
X : parts per Million : Carbon13
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
151.445
138.136
131.176
130.852
130.699
129.076
125.620
124.780
124.742
124.207
124.169
122.918
87.824
77.475
77.160
76.845
69.102

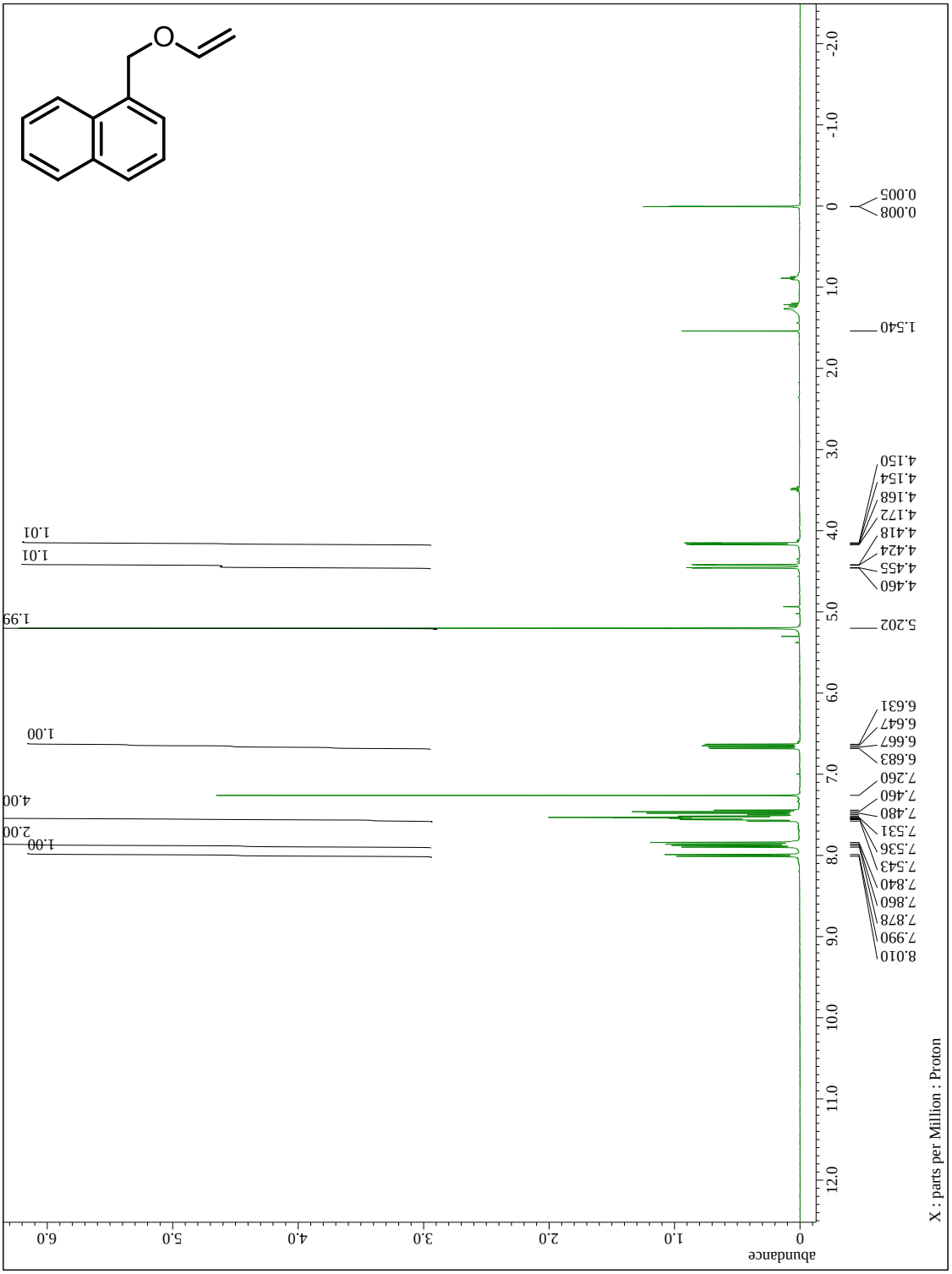

F3C
O
-62.577
X : parts per Million : Fluorine19
abundance

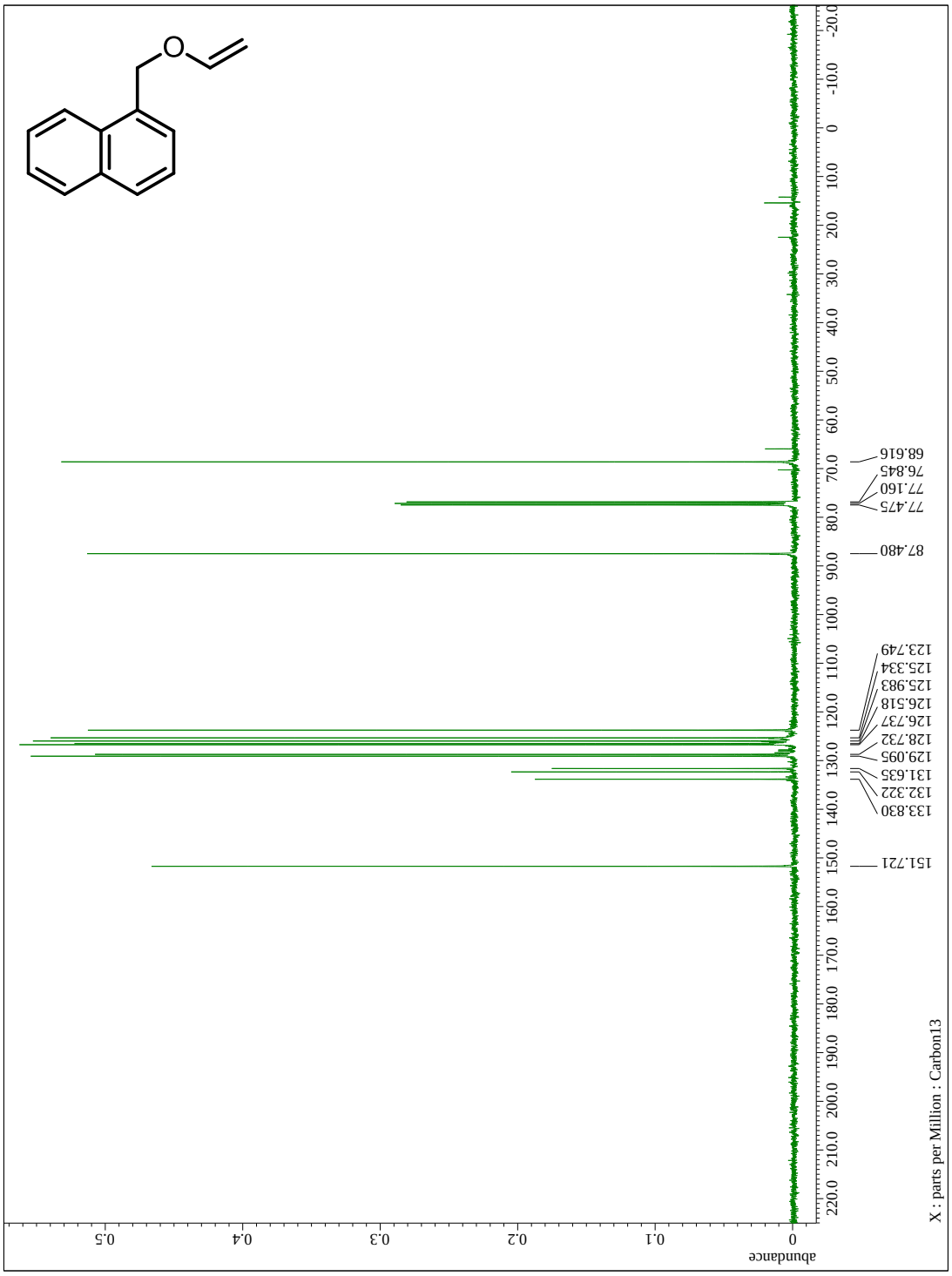
4-*tert*-Butylbenzyl vinyl ether (2g)



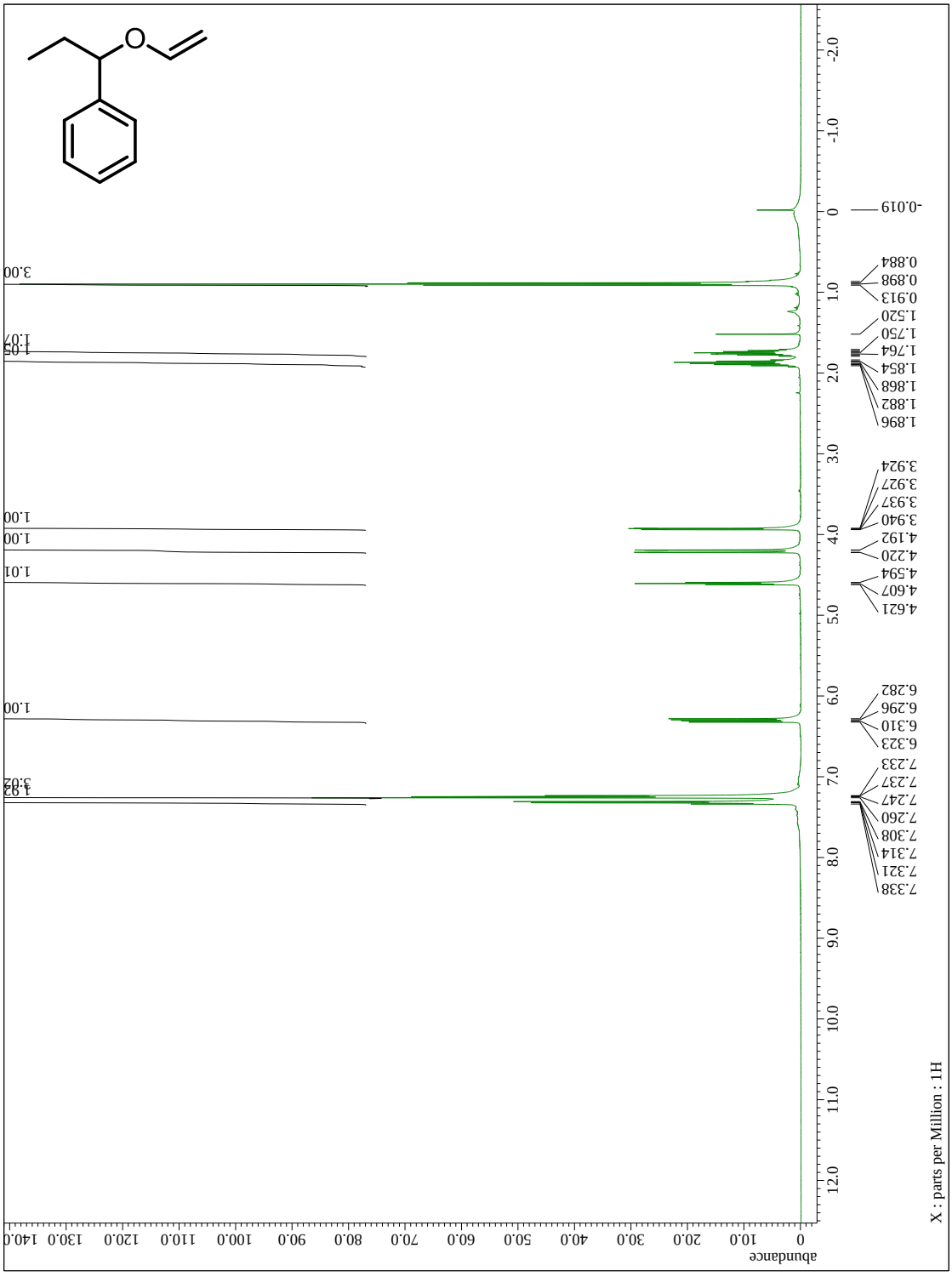

O
tBu
151.846
151.024
133.936
127.606
125.544
87.242
77.485
77.160
76.845
70.019
34.657
31.440
X : parts per Million : Carbon13
abundance

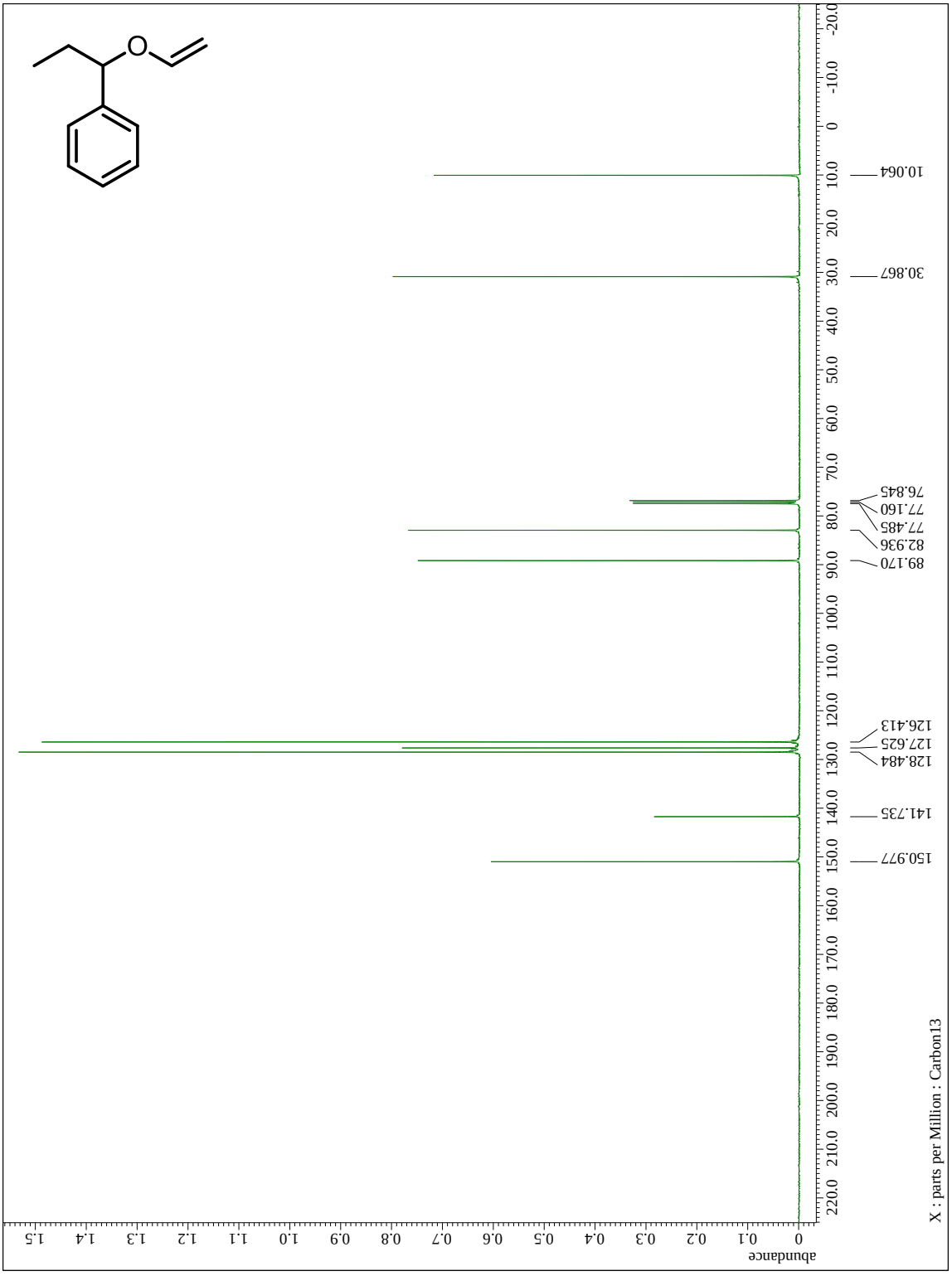
1-Naphthylmethyl vinyl ether (2h)



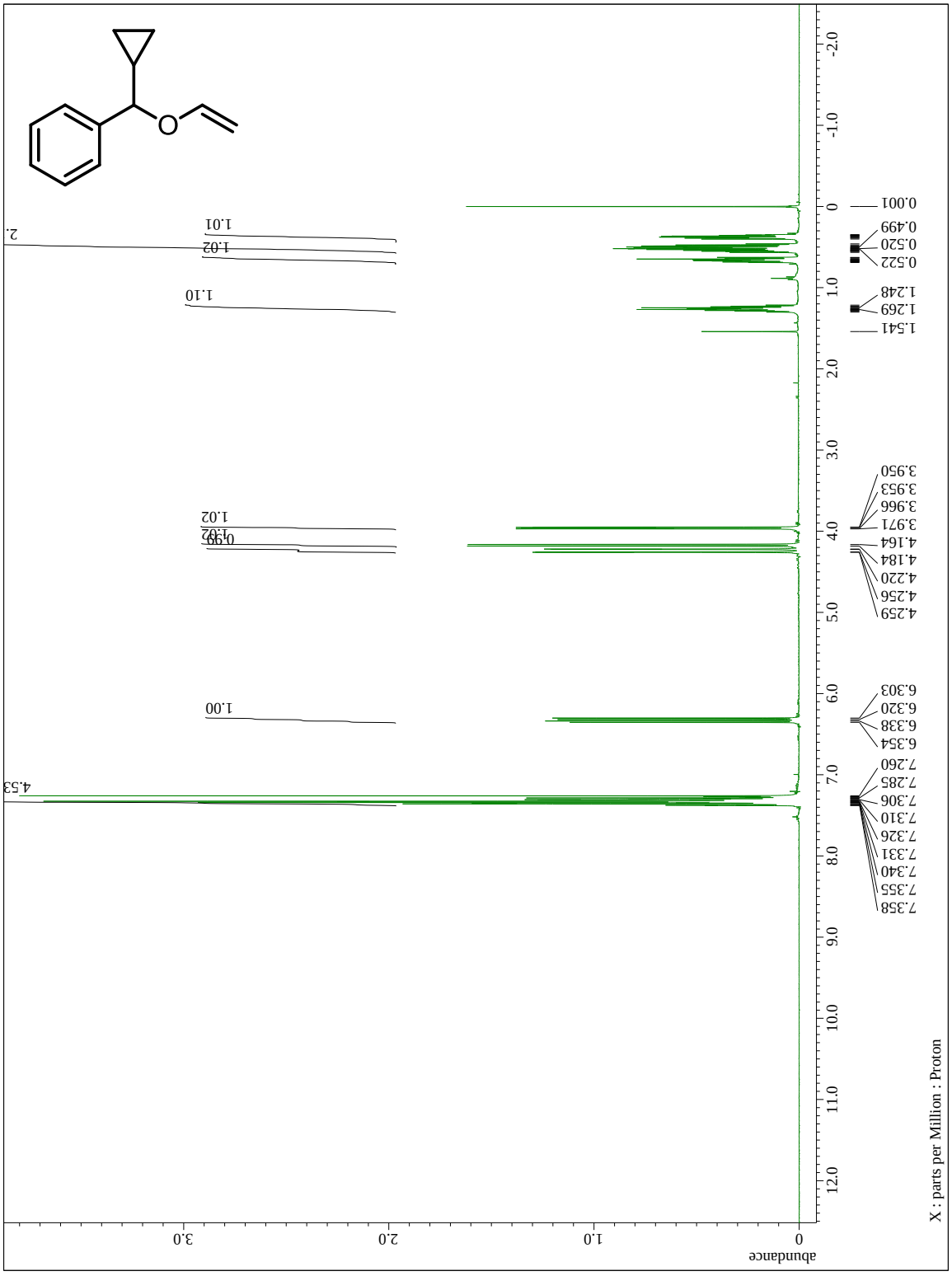

O
abundance
0
0.1
0.2
0.3
0.4
0.5
X : parts per Million : Carbon13
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
151.721
133.830
132.322
131.635
129.095
128.732
126.737
126.518
125.983
125.334
123.749
87.480
77.475
77.160
76.845
68.616

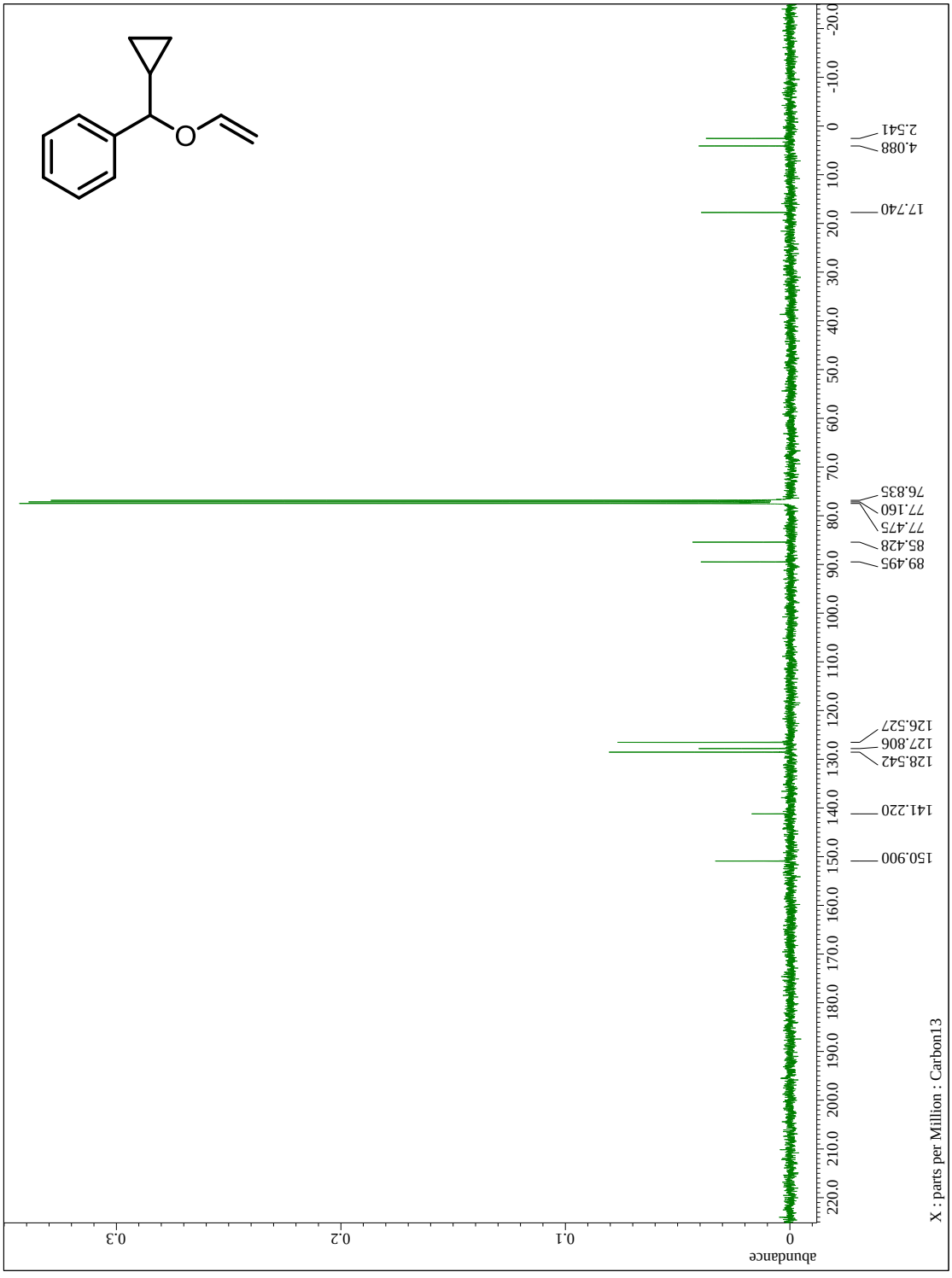
1-Phenylpropyl vinyl ether (2i)



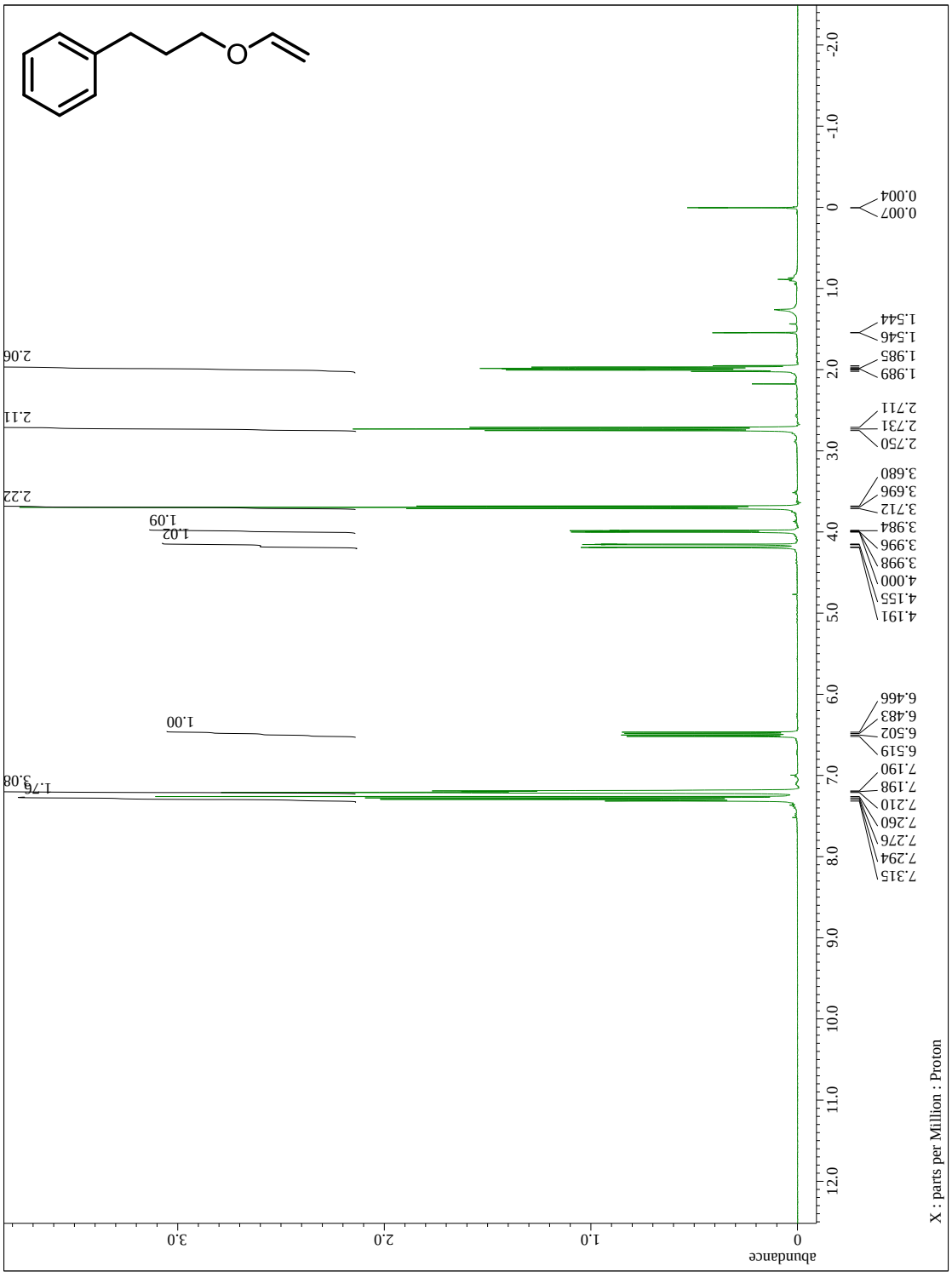

abundance
X : parts per Million : Carbon13
10.064
30.867
76.845
77.160
77.485
82.936
89.170
126.413
127.625
128.484
141.735
150.977

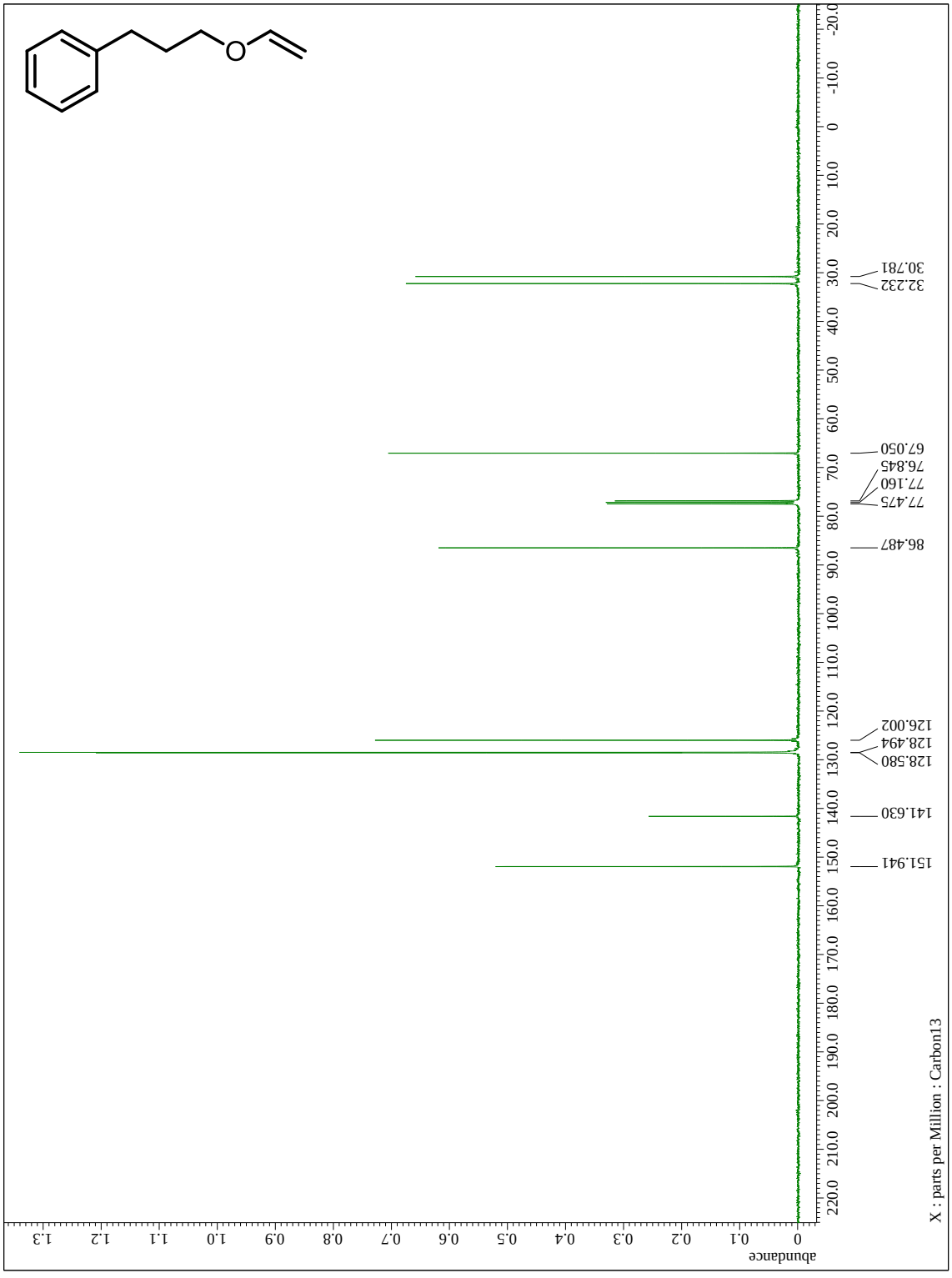
Cyclopropylphenylmethyl vinyl ether (2k)



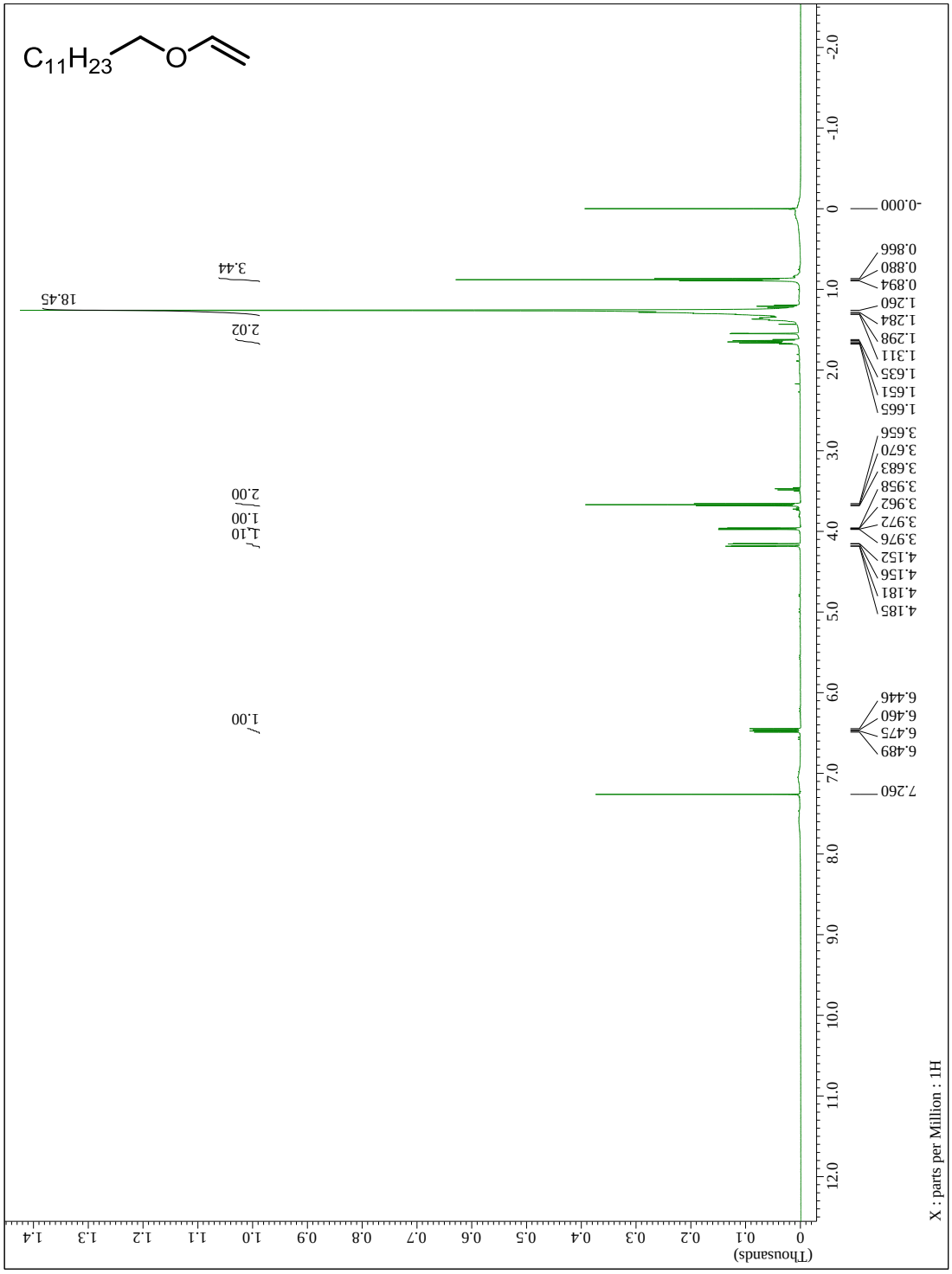

abundance
0
0.1
0.2
0.3
X : parts per Million : Carbon13
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
150.900
141.220
128.542
127.806
126.527
89.495
85.428
77.475
77.160
76.835
17.740
4.088
2.541
O

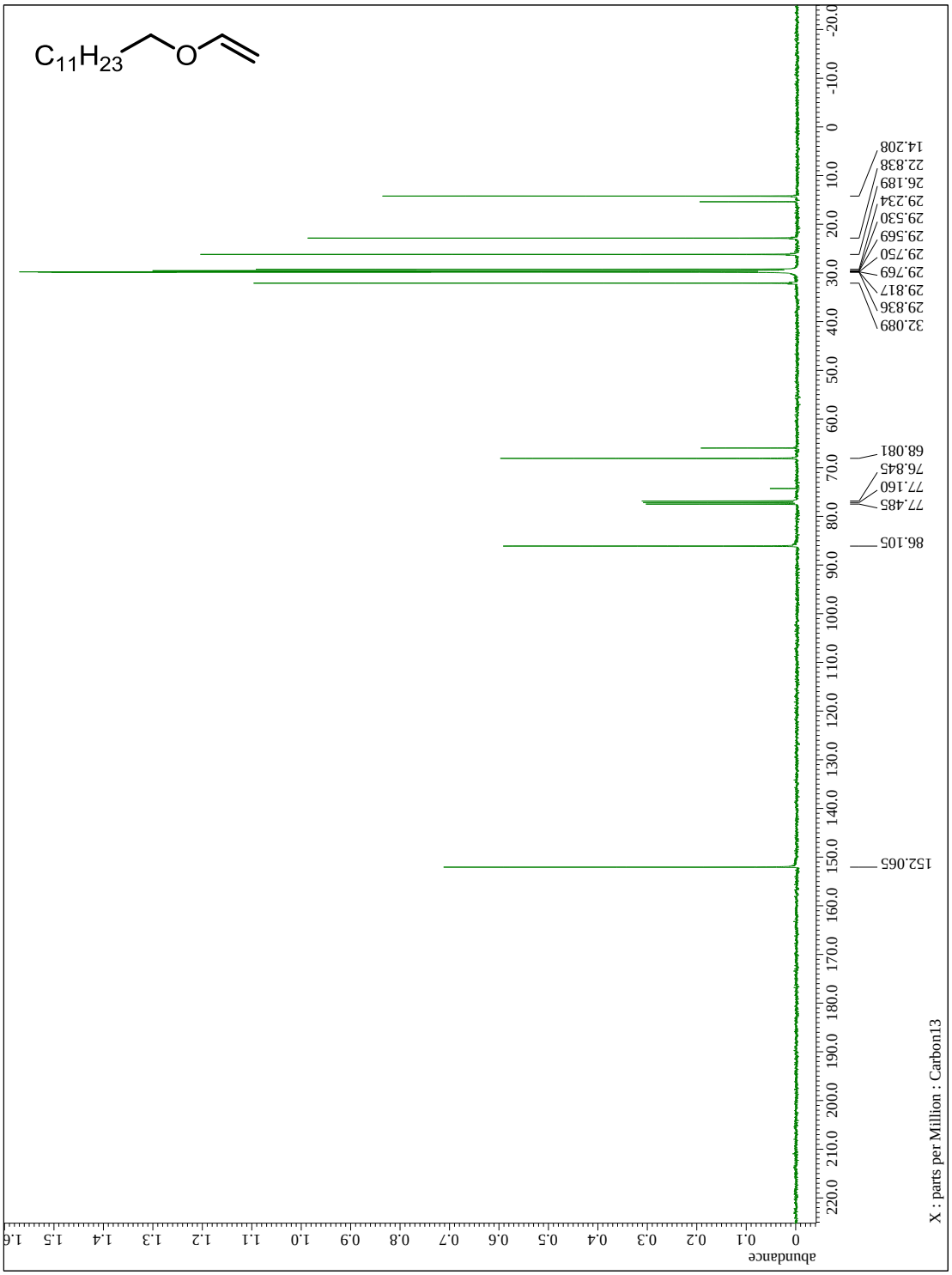
3-Phenylpropyl vinyl ether (2l)



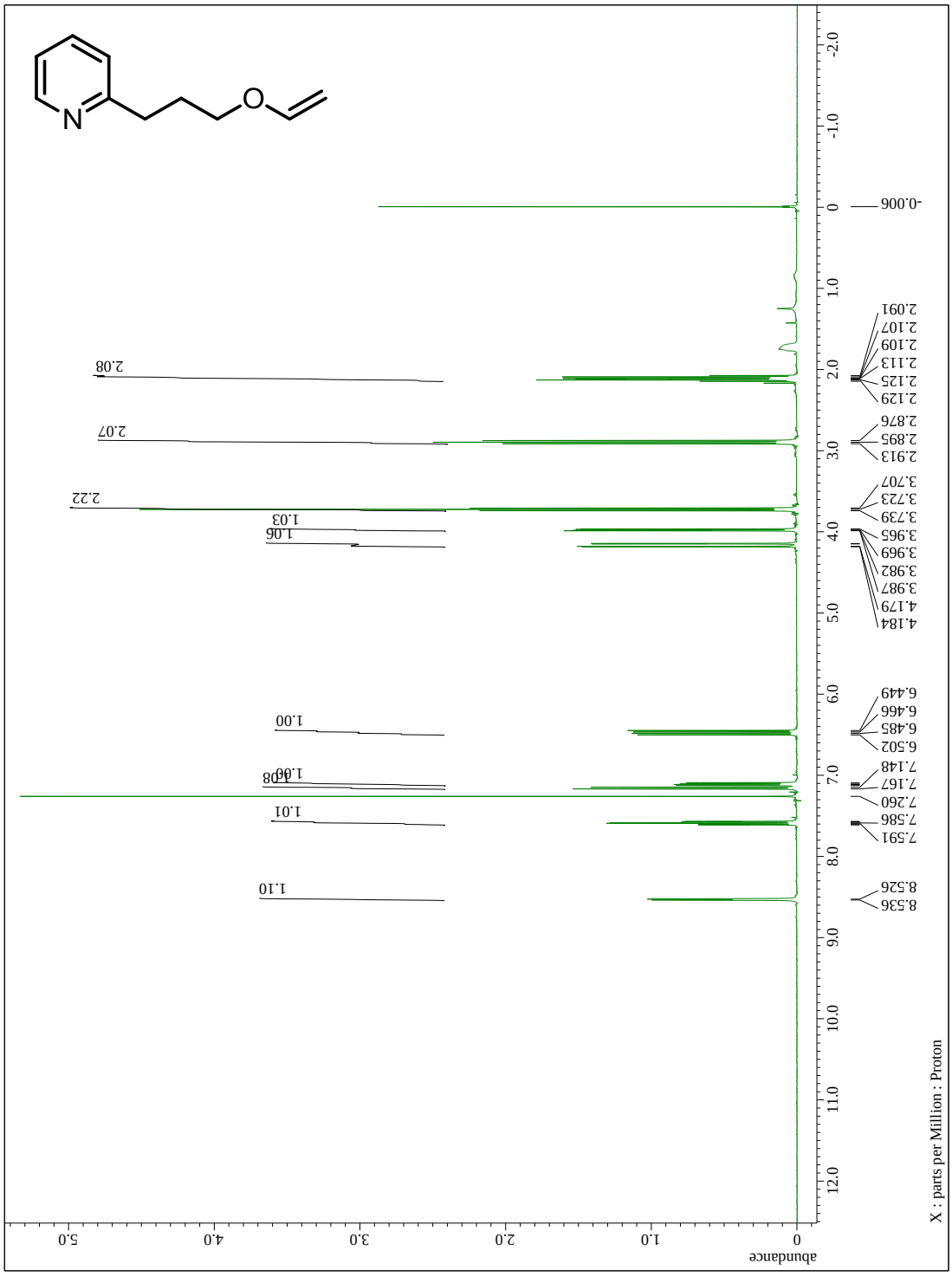

abundance
X : parts per Million : Carbon13
151.941
141.630
128.580
128.494
126.002
86.487
77.475
77.160
76.845
67.050
32.232
30.781

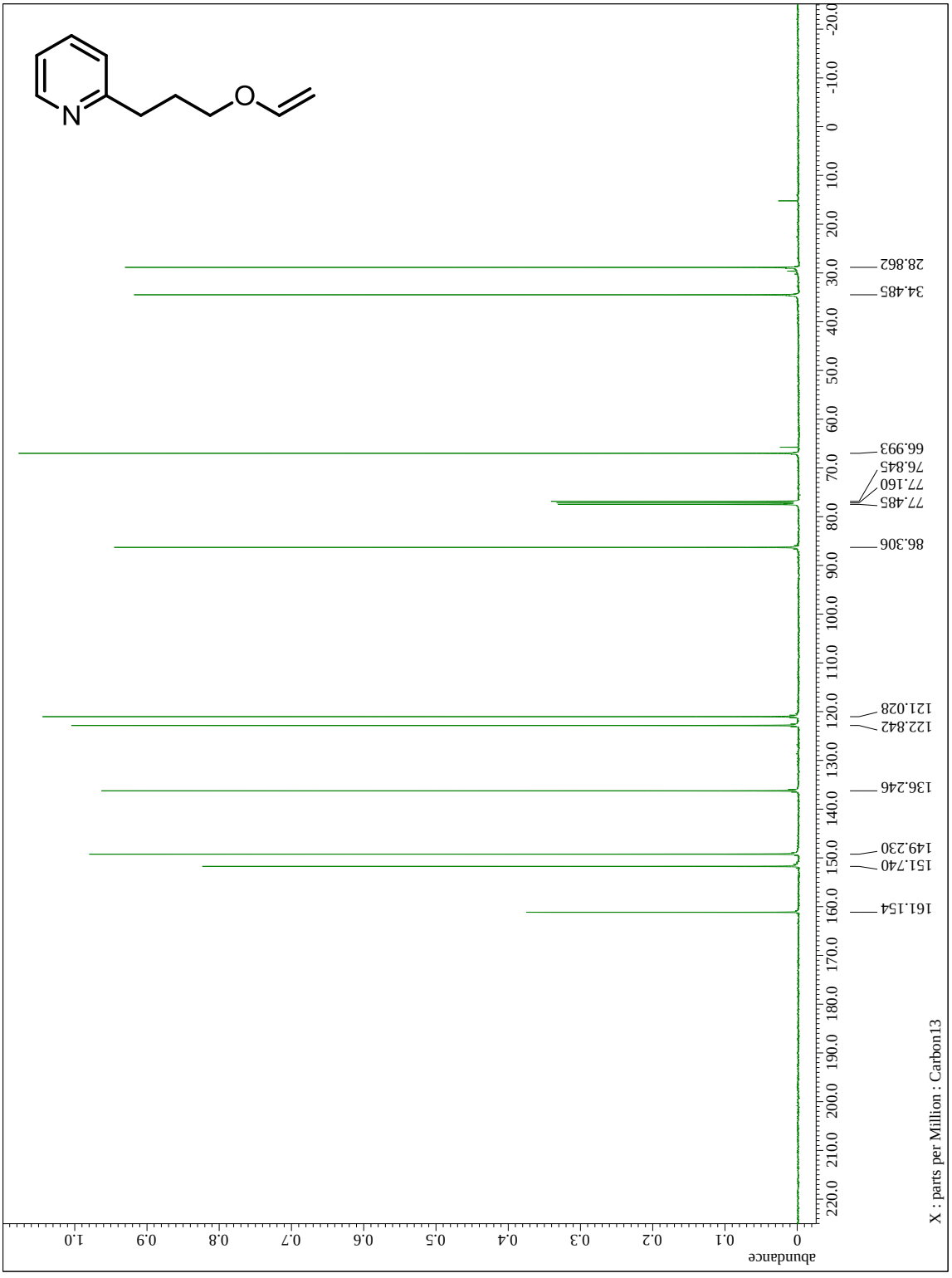
n-Dodecyl vinyl ether (2m)




C11H23
O
14.208
22.838
26.189
29.234
29.530
29.569
29.750
29.769
29.817
29.836
32.089
68.081
76.845
77.160
77.485
86.105
152.065
X : parts per Million : Carbon13
abundance

3-(2-Pyridyl)propyl vinyl ether (2n)




N
O
28.862
34.485
66.993
76.845
77.160
77.485
86.306
121.028
122.842
136.246
149.230
151.740
161.154
X : parts per Million : Carbon13
abundance