Reagents for Diverse Iodosilane-Mediated Transformations

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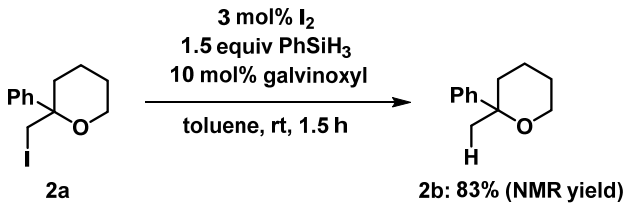
Electronic Supplementary Information

1. General considerations

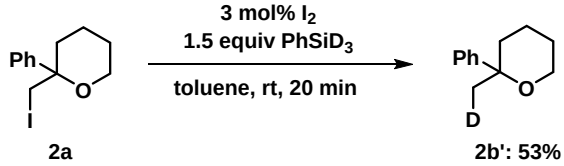
Reagents were purchased from commercial suppliers and used without purification. Column Chromatography was performed on silica gel (Cica silica gel 60N) with solvents specified below. ^{1}H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ or CD_2Cl_2 or toluene-d_8 solution at 25 °C. ^{1}H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ 7.26 ppm for chloroform or δ 0.00 ppm for tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ 77.0 ppm for $CDCl_3$.

2. Deiodination in the presence of galvinoxyl



Scheme S1 Deiodination of **2a** in the presence of galvinoxyl

3. Deuterium labeling study



Scheme S2 Deiodination of **2a** using I_2 and $PhSiD_3$

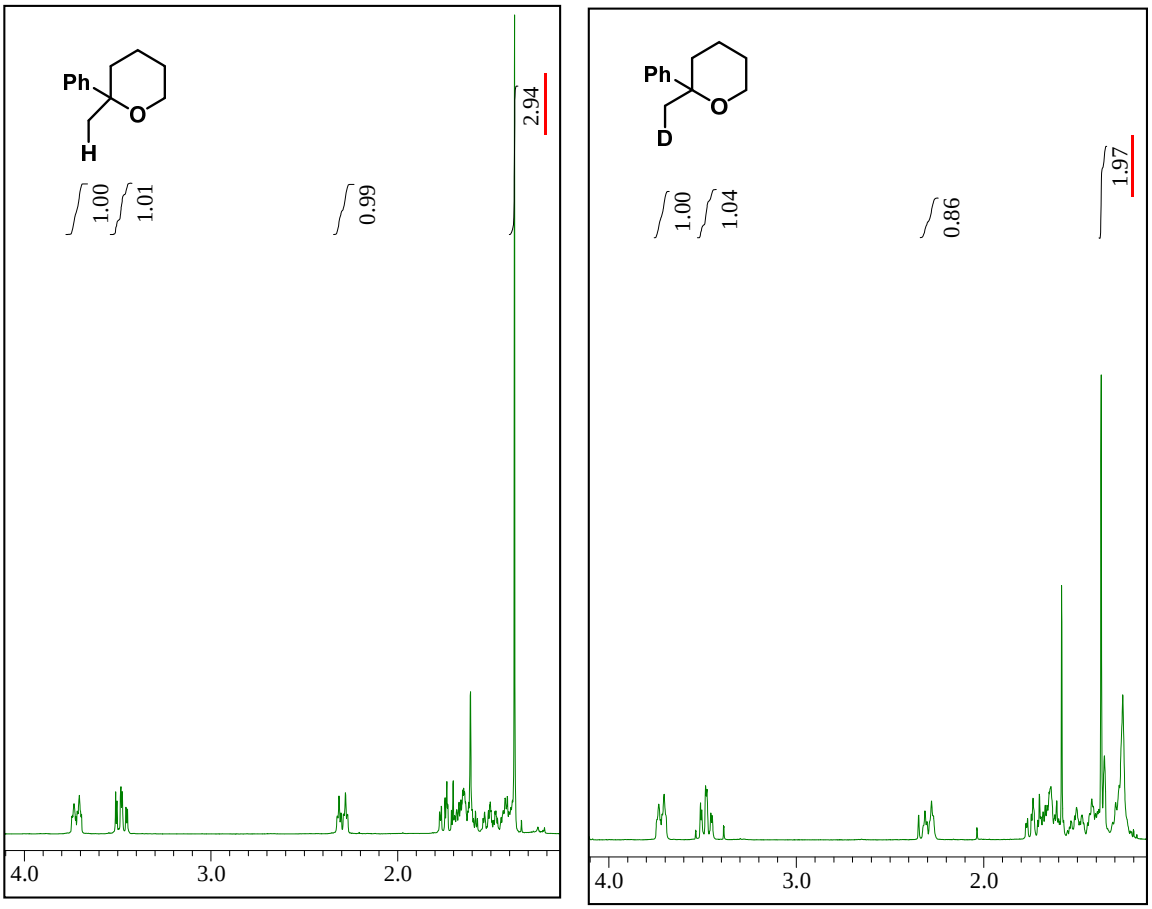


Figure S1 ^{1}H NMR charts of **2b** and **2b'**

4. Reaction of $PhSiH_3$ with I_2 in toluene-d_8 and CD_2Cl_2

$$I_2 + PhSiH_3 \xrightarrow[\text{rt, 30 min}]{} PhSiH_2I$$

	$PhSiH_3$		$PhSiH_2I$
in toluene-d_8	1	:	0.19
in CD_2Cl_2	1	:	1.6

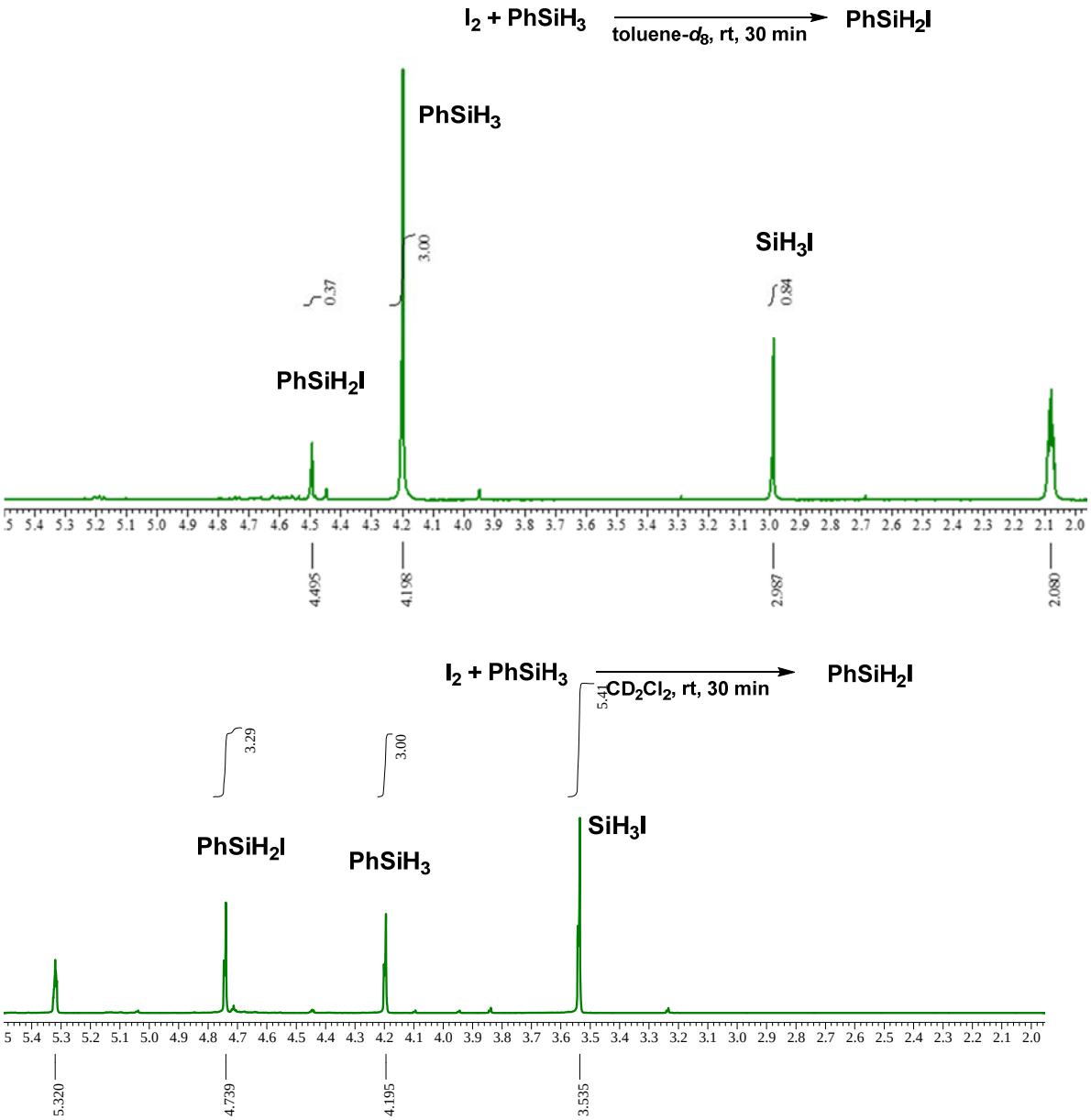
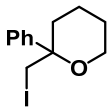


Figure S2 ^{1}H NMR charts of the reaction of $PhSiH_3$ with I_2 in toluene-d_8 and CD_2Cl_2

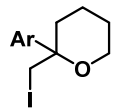
5. Analytical Data of Iodoethers

2-Iodomethyl-2-phenyltetrahydropyran (2a)



colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.37 (m, 4H), 7.33-7.29 (m, 1H), 3.82-3.76 (m, 1H), 3.50 (td, 1H, J = 11.4, 2.4 Hz), 3.39 (d, 1H, J = 10.4 Hz), 3.35 (d, 1H, J = 10.4 Hz), 2.37-2.29 (m, 1H), 2.02 (ddd, 1H, J = 13.6, 12.0, 3.2 Hz), 1.75-1.60 (m, 2H), 1.55-1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 128.6, 127.5, 126.9, 75.8, 63.4, 32.4, 25.4, 21.4, 19.9; IR (neat, cm^{-1}): 2939; HRMS (ESI, m/z) Calcd. for $C_{12}H_{15}INaO$ $[M+Na]^+$: 325.0065, found 325.0045.

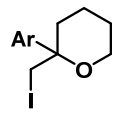
2-Iodomethyl-2-(4-methylphenyl)tetrahydrofuran (4a)



Ar = 4-Me-C_6H_4

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (d, 2H, J = 8.4 Hz), 7.20-7.18 (d, 2H, J = 8.4 Hz), 3.80-3.74 (m, 1H), 3.48 (td, 1H, J = 11.6, 2.4 Hz), 3.37 (d, 1H, J = 10.0 Hz), 3.31 (d, 1H, J = 10.0 Hz), 2.35 (s, 3H), 2.33-2.27 (m, 1H), 2.00 (ddd, 1H, J = 14.0, 12.0, 3.2 Hz), 1.73-1.59 (m, 2H), 1.51-1.44 (m, 1H), 1.39-1.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 137.0, 129.3, 126.8, 75.7, 63.4, 32.3, 25.5, 21.8, 21.0, 20.0; IR (neat, cm^{-1}): 2939; HRMS (ESI, m/z) Calcd. for $C_{13}H_{17}INaO$ $[M+Na]^+$: 339.0222, found 339.0196.

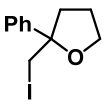
2-Iodomethyl-2-(4-fluorophenyl)tetrahydrofuran (5a)



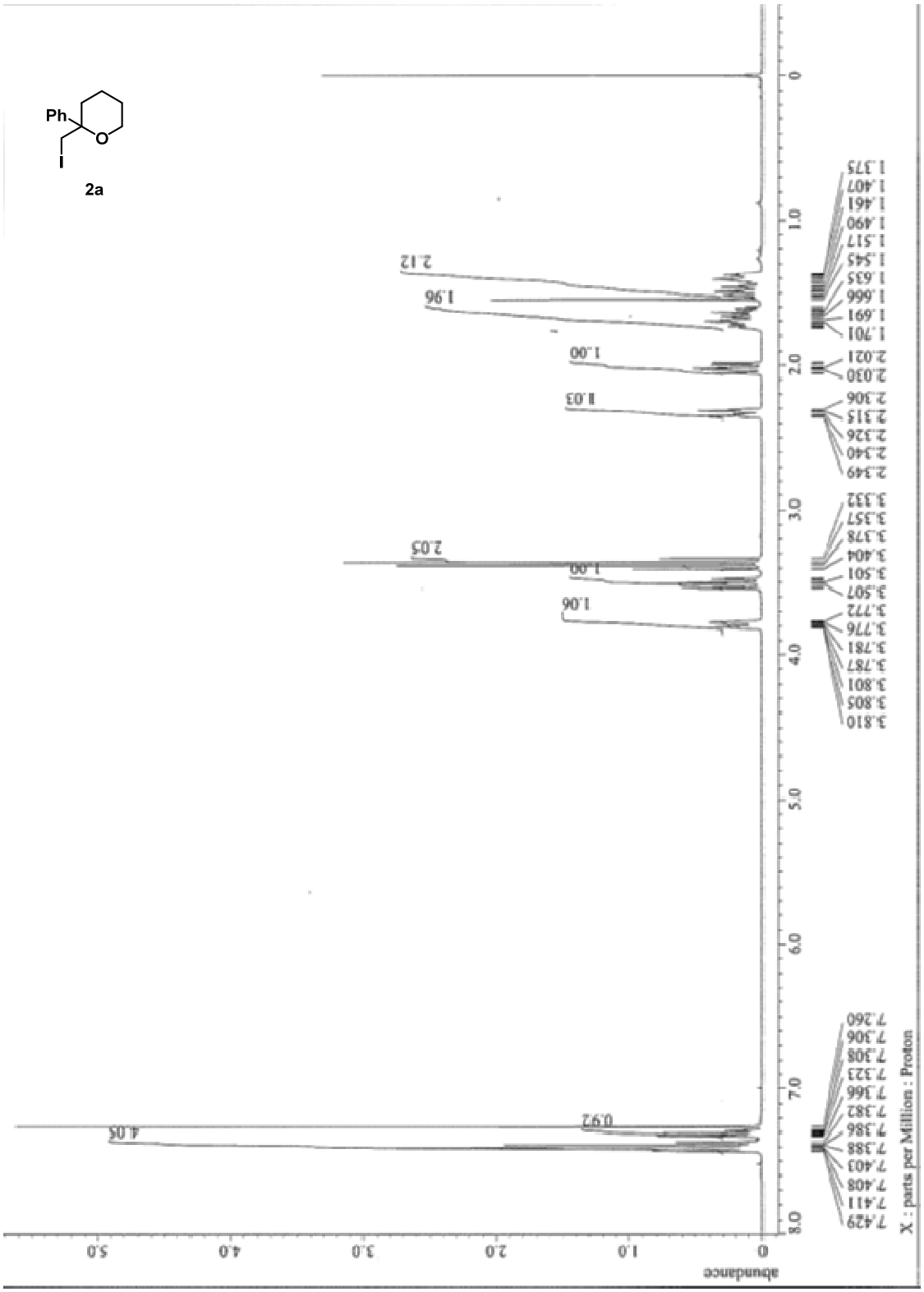
Ar = 4-F-C_6H_4

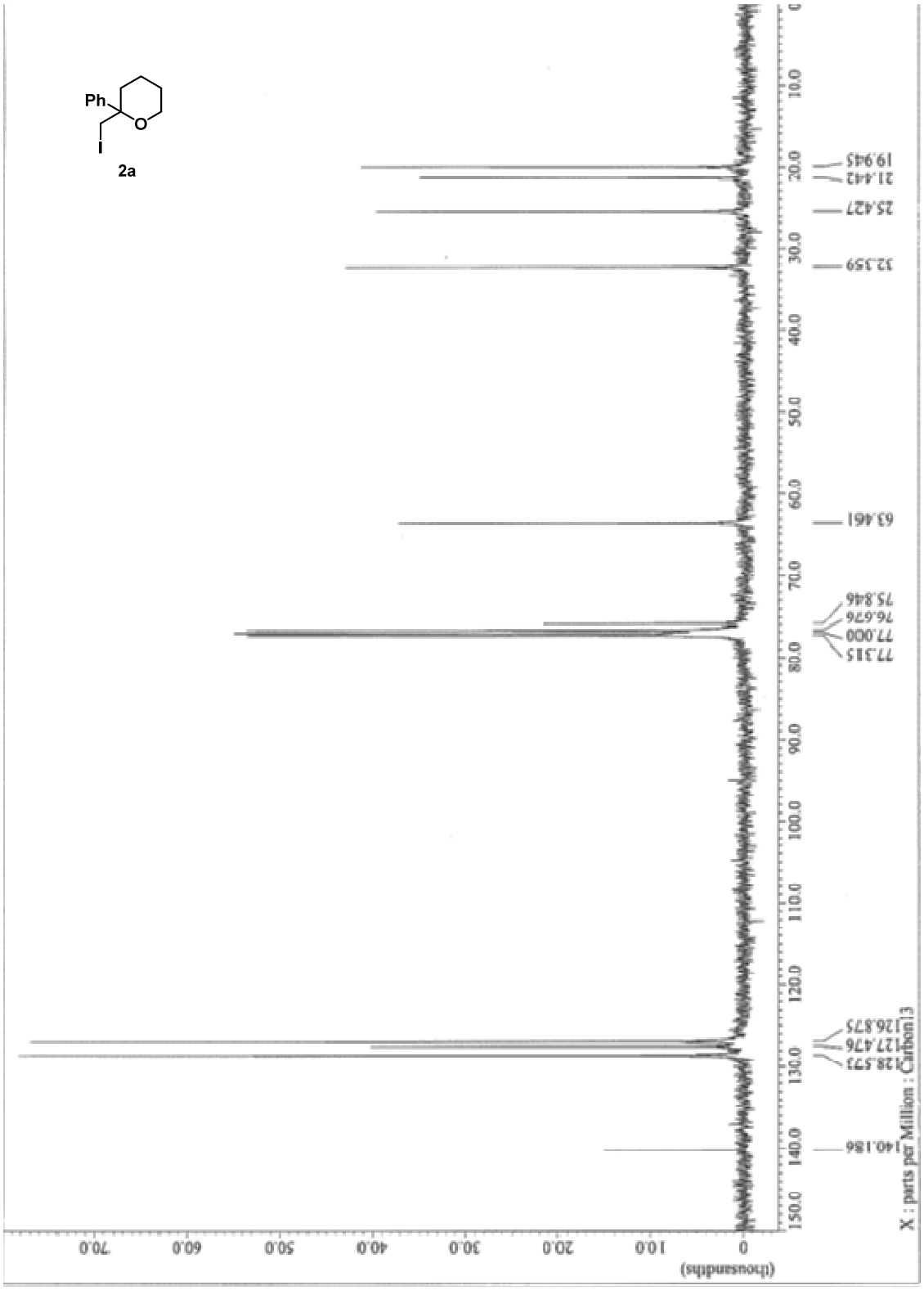
colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.36 (m, 2H), 7.01-7.05 (m, 2H), 3.81-3.75 (m, 1H), 3.46 (td, 1H, J = 13.2, 4.4 Hz), 3.36 (d, 1H, J = 11.2 Hz), 3.34 (d, 1H, J = 11.2 Hz), 2.30 (dt, 1H, J = 13.6, 3.8 Hz), 2.00 (ddd, 1H, J = 14.0, 12.0, 4.8 Hz), 1.76-1.59 (m, 2H), 1.51-1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, J = 246.4 Hz), 136.1 (d, J = 3.8 Hz), 128.7 (d, J = 8.6 Hz), 115.4 (d, J = 21.0 Hz), 75.5, 63.4, 32.5, 25.4, 21.1, 20.0; IR (neat, cm^{-1}): 2940; HRMS (DART, m/z) Calcd. for $C_{12}H_{18}FINO$ $[M+NH_4]^+$: 338.0417, found 338.0427.

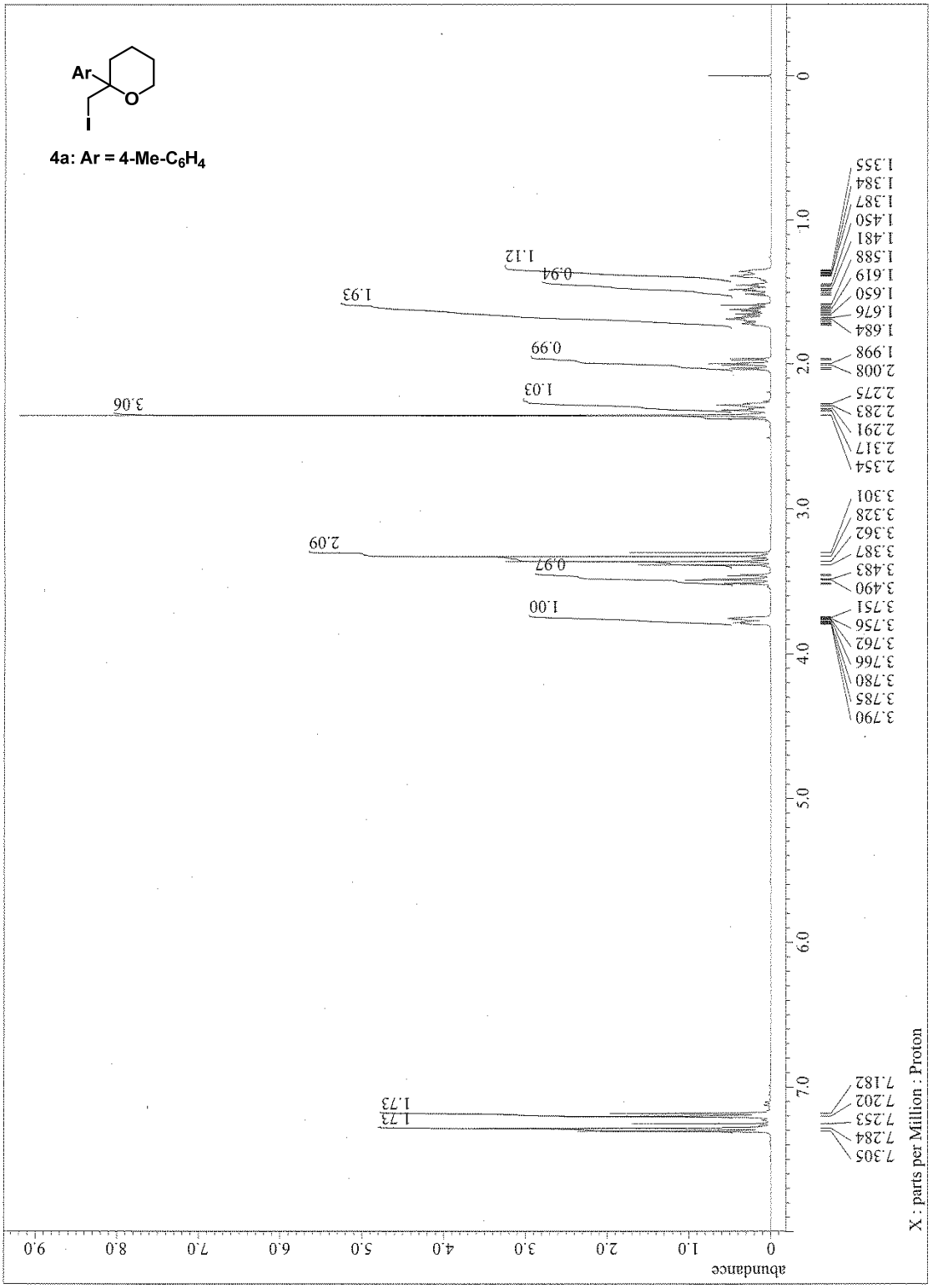
2-Iodomethyl-2-phenyltetrahydrofuran (1a)

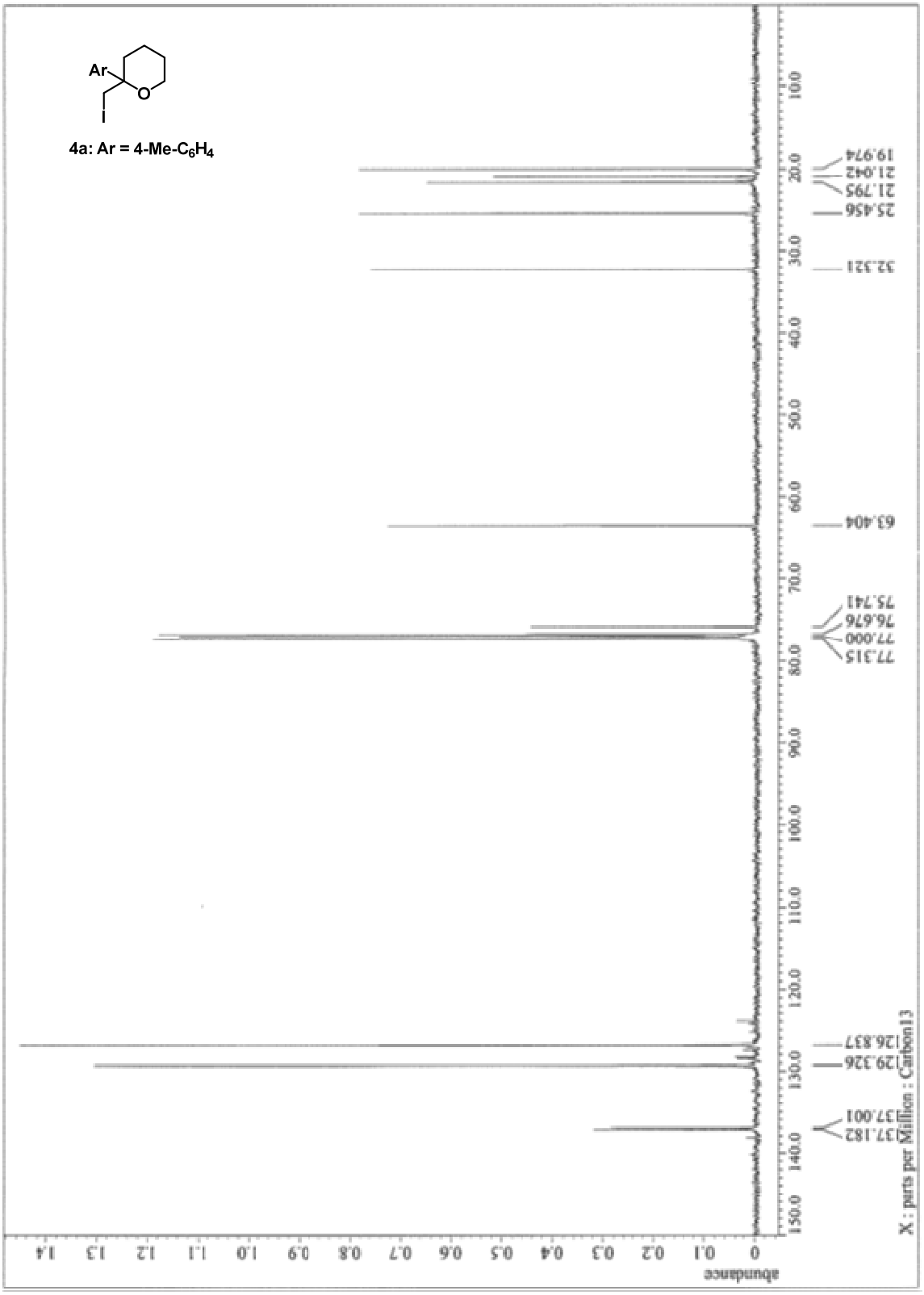


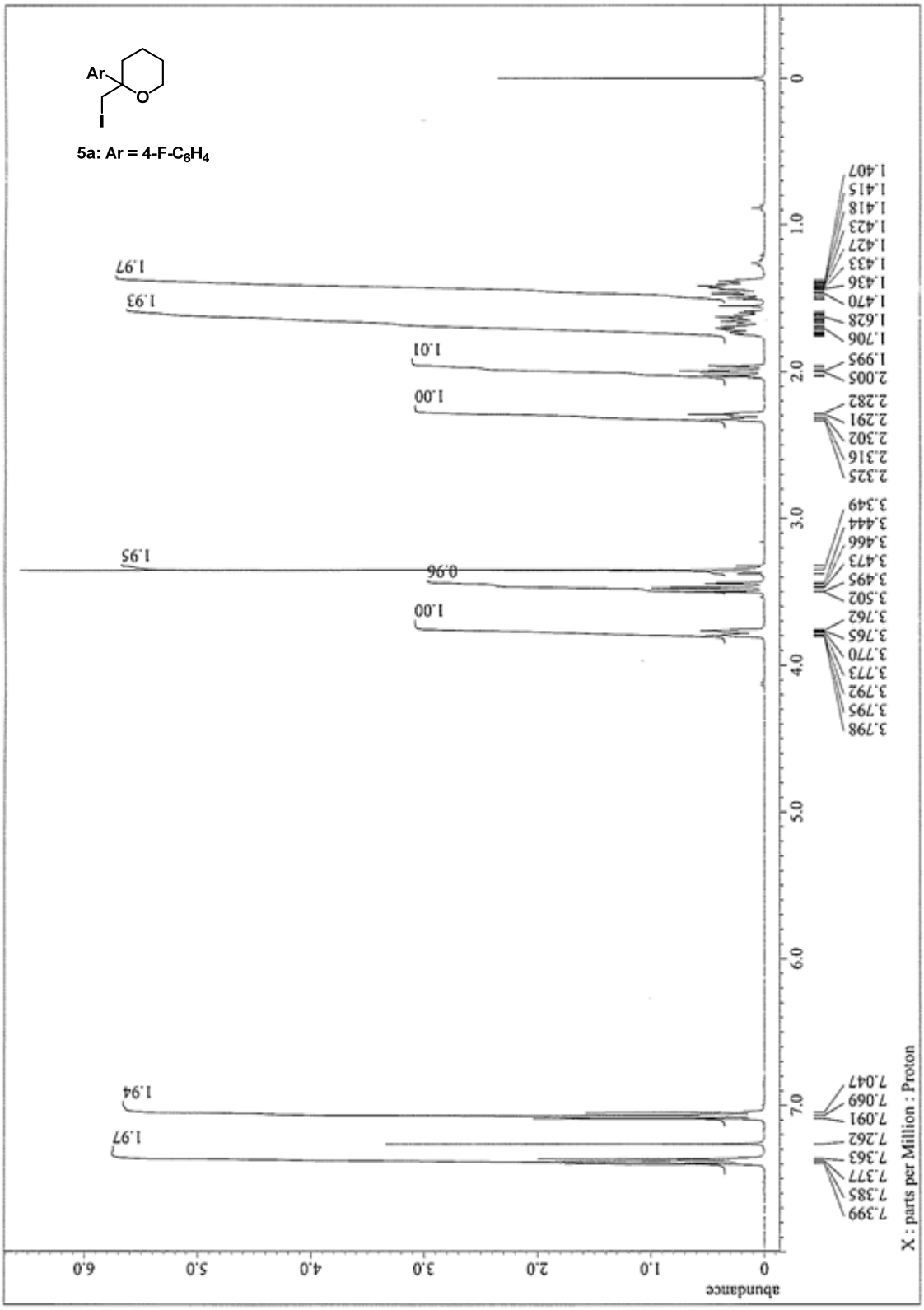
colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.38 (m, 2H), 7.36-7.32 (m, 2H), 7.28-7.24 (m, 1H), 4.07 (dt, 1H, J = 8.0, 7.2 Hz), 3.92 (td, 1H, J = 8.0, 6.0 Hz), 3.57 (d, 1H, J = 10.4 Hz), 3.54 (d, 1H, J = 10.4 Hz), 2.39-2.27 (m, 2H), 2.11-2.02 (m, 1H), 1.89-1.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 128.2, 127.2, 125.3, 84.5, 68.4, 37.6, 26.2, 19.1; IR(neat, cm^{-1}): 2976; HRMS (ESI, m/z) Calcd. for $C_{11}H_{13}INaO$ $[M+Na]^+$: 310.9909, found 310.9889.

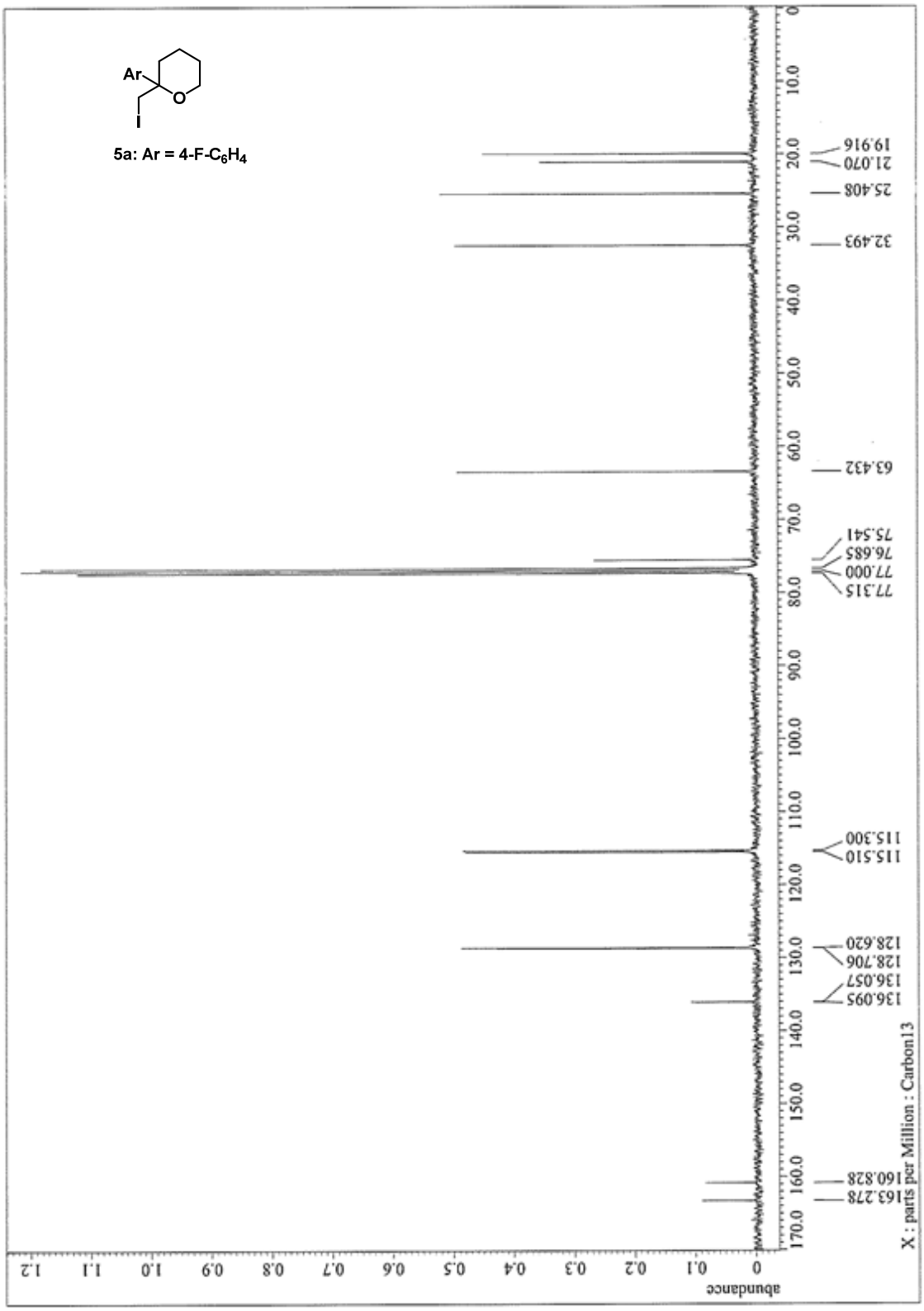

Ph
O
I
2a
7.429
7.411
7.408
7.403
7.388
7.386
7.382
7.366
7.323
7.308
7.306
7.260
3.810
3.805
3.801
3.787
3.781
3.776
3.772
3.507
3.501
3.404
3.378
3.357
3.332
2.349
2.340
2.326
2.315
2.306
2.030
2.021
1.701
1.691
1.666
1.635
1.545
1.517
1.490
1.461
1.407
1.375
4.05
0.92
2.12
1.96
1.00
1.03
2.05
1.00
1.06
abundance
X : parts per Million : Proton

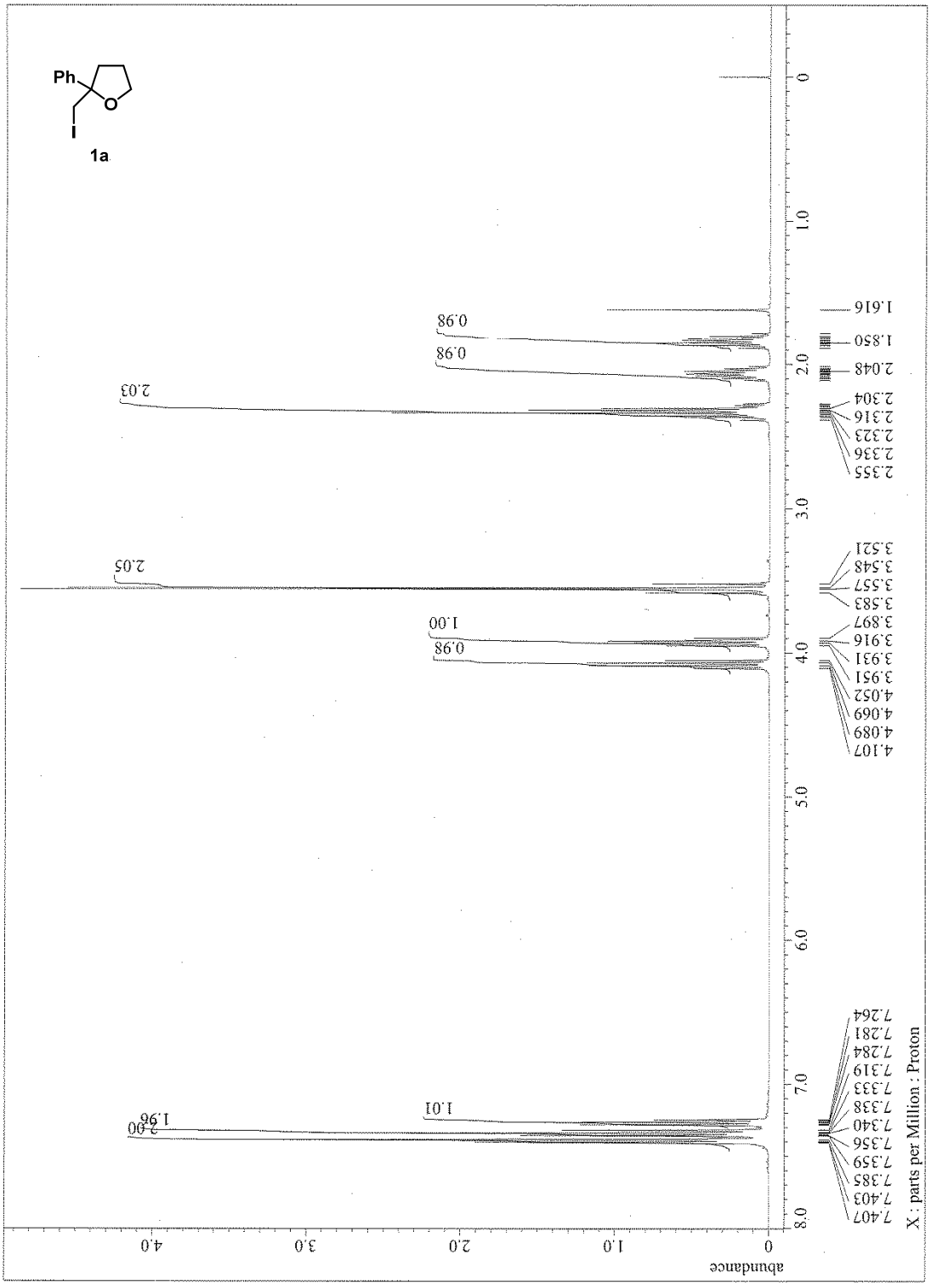

Ph
O
I
2a
19.945
21.442
25.427
32.359
63.461
75.846
76.676
77.000
77.315
126.875
127.476
128.573
140.186
X : parts per Million : Carbon13
(thousandths)

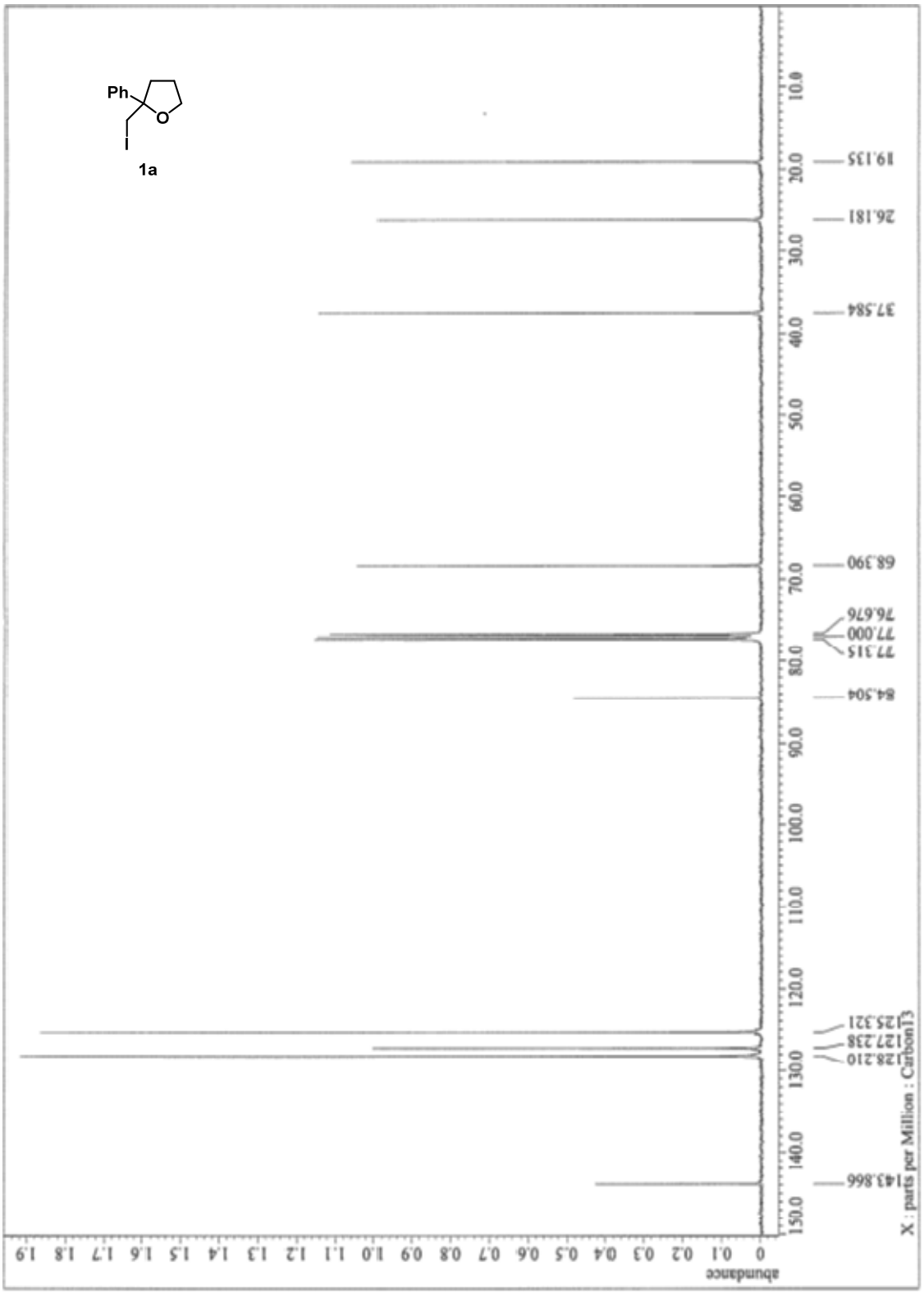

Ar
O
I
4a: Ar = 4-Me-C6H4
7.305
7.284
7.253
7.202
7.182
3.790
3.785
3.780
3.766
3.762
3.756
3.751
3.490
3.483
3.387
3.362
3.328
3.301
2.354
2.317
2.291
2.283
2.275
2.008
1.998
1.684
1.676
1.650
1.619
1.588
1.481
1.450
1.387
1.384
1.355
1.73
1.73
1.00
0.97
2.09
1.03
0.99
1.93
0.94
1.12
3.06
X : parts per Million : Proton
abundance

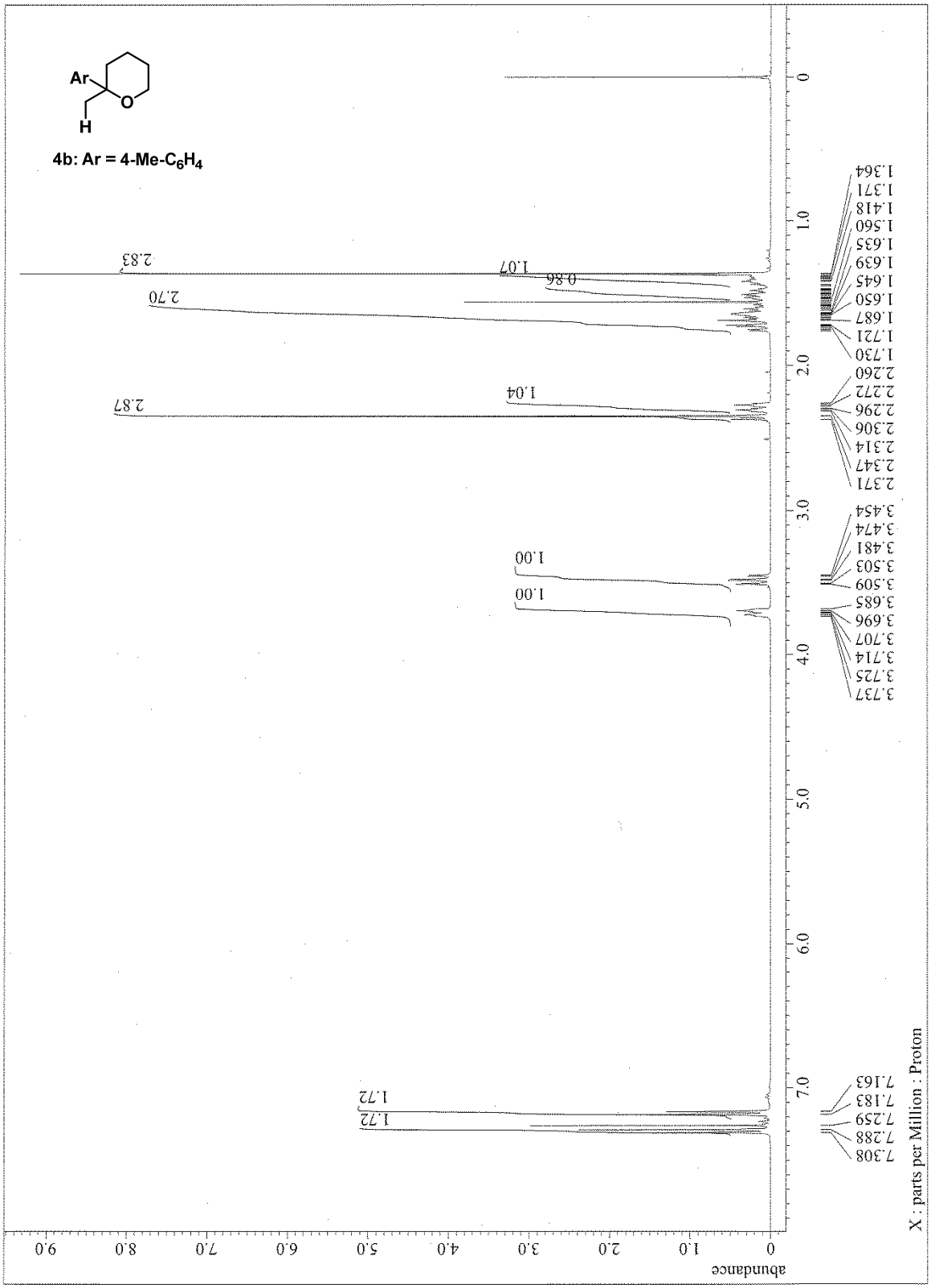

Ar
O
I
4a: Ar = 4-Me-C6H4
19.974
21.042
21.795
25.456
32.321
63.404
75.741
76.676
77.000
77.315
126.837
129.326
137.001
137.182
X : parts per Million : Carbon13
abundance

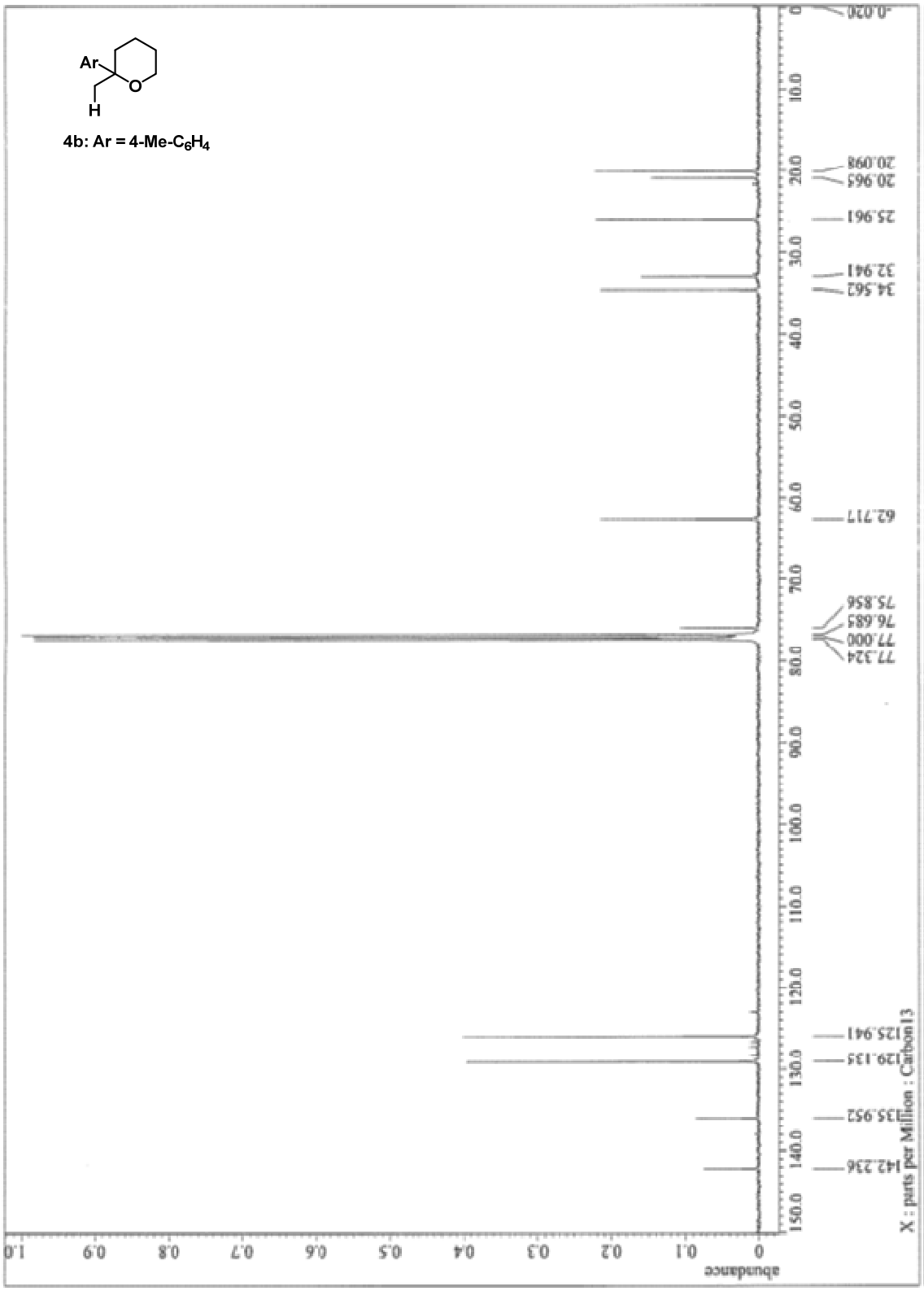

Ar
O
I
5a: Ar = 4-F-C6H4
1.97
1.93
1.01
1.00
1.95
0.96
1.00
1.94
1.97
7.399
7.385
7.377
7.363
7.262
7.091
7.069
7.047
3.798
3.795
3.792
3.773
3.770
3.765
3.762
3.502
3.495
3.473
3.466
3.444
3.349
2.325
2.316
2.302
2.291
2.282
2.005
1.995
1.706
1.628
1.470
1.436
1.433
1.427
1.423
1.418
1.415
1.407
X : parts per Million : Proton
abundance

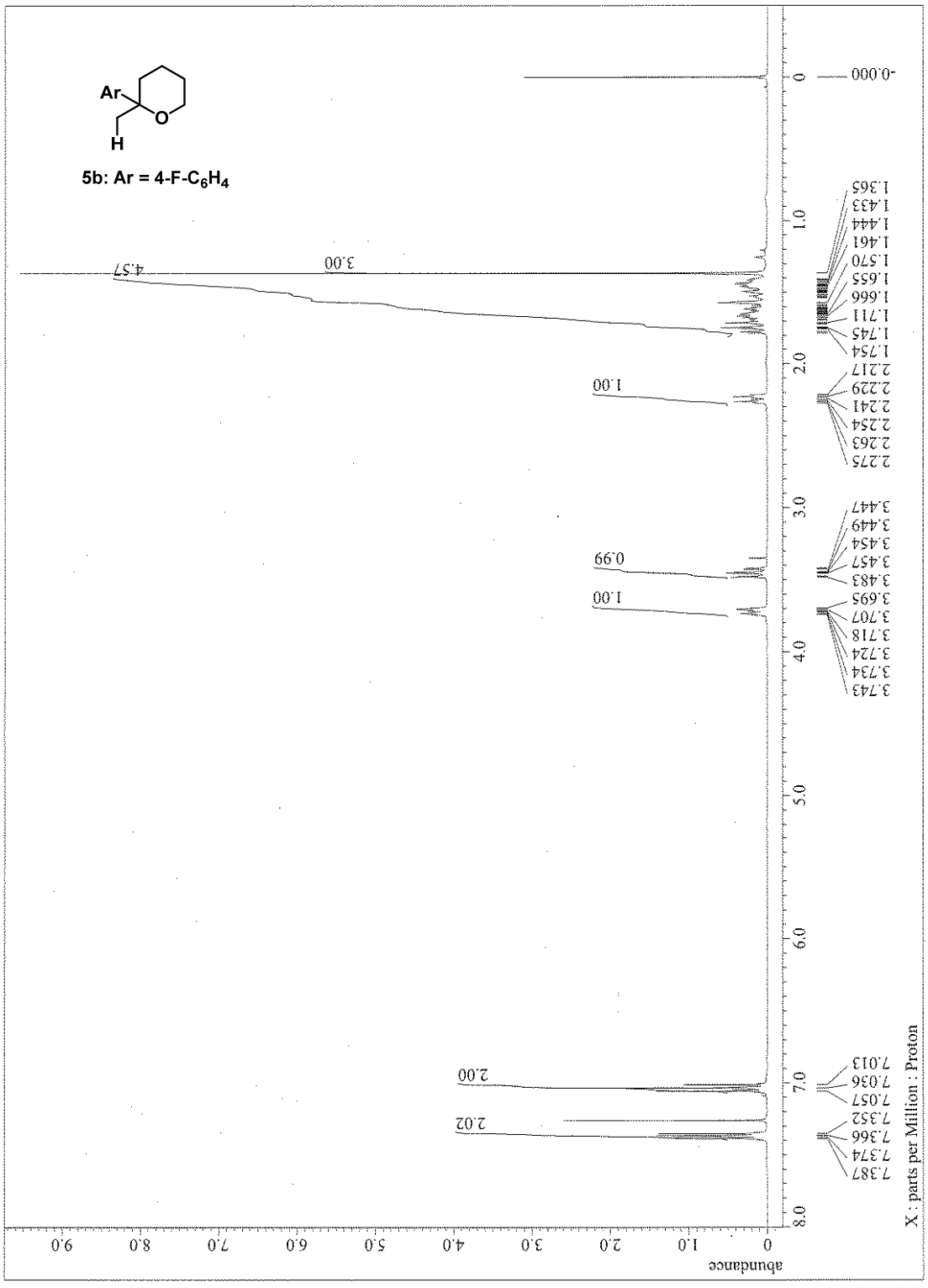

Ar
O
I
5a: Ar = 4-F-C6H4
19.916
21.070
25.408
32.493
63.432
75.541
76.685
77.000
77.315
115.300
115.510
128.620
128.706
136.057
136.095
160.828
163.278
X : parts per Million : Carbon13
abundance

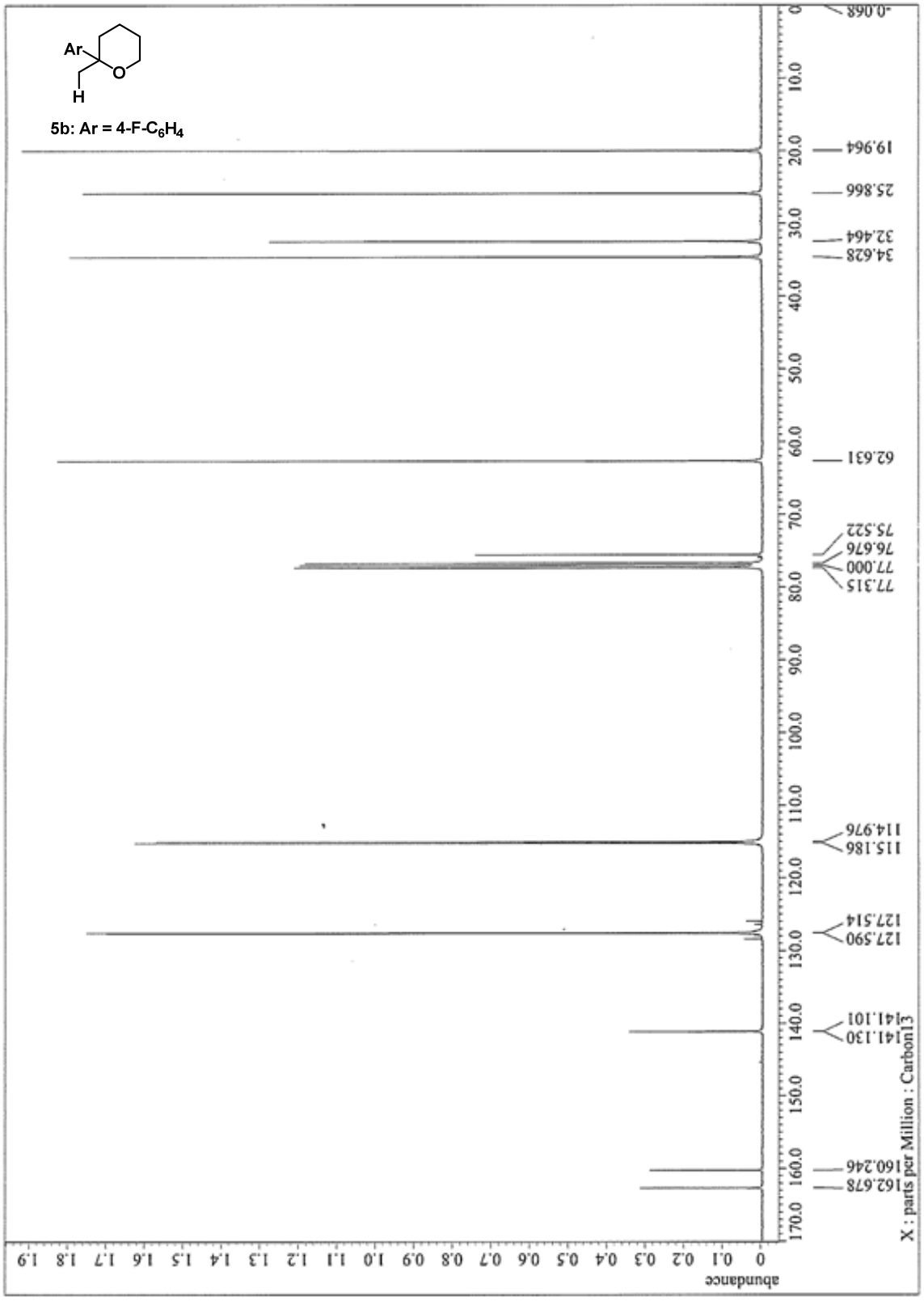

Ph
O
I
1a
X : parts per Million : Proton
abundance
7.407
7.403
7.385
7.359
7.356
7.340
7.338
7.333
7.319
7.284
7.281
7.264
4.107
4.089
4.069
4.052
3.951
3.931
3.916
3.897
3.583
3.557
3.548
3.521
2.355
2.336
2.323
2.316
2.304
2.048
1.850
1.616
1.96
2.00
1.01
0.98
1.00
2.05
0.98
0.98
2.03

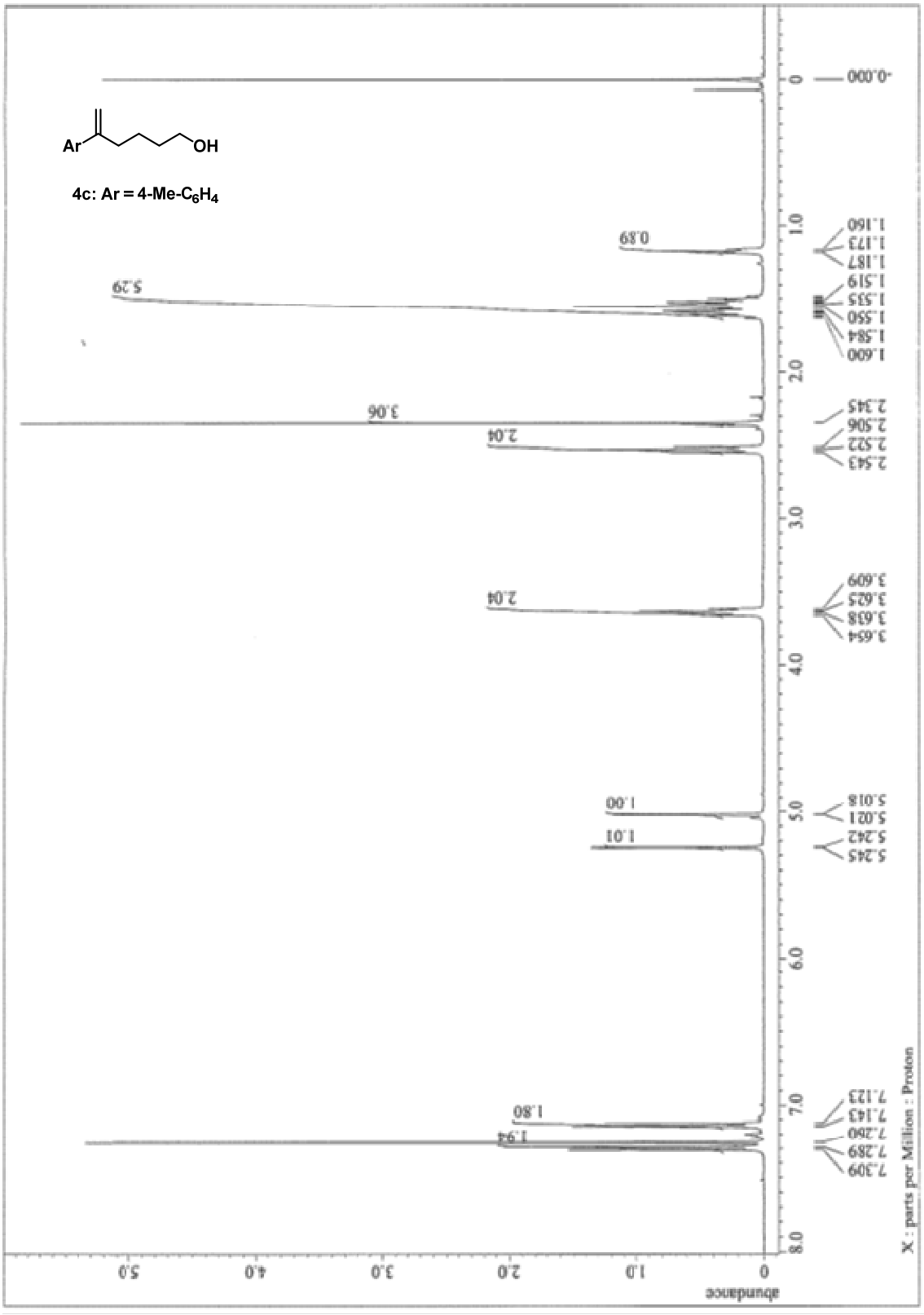

Ph
O
I
1a
19.135
26.181
37.584
68.390
76.676
77.000
77.315
84.504
125.321
127.238
128.210
143.866
X : parts per Million : Carbon13
abundance

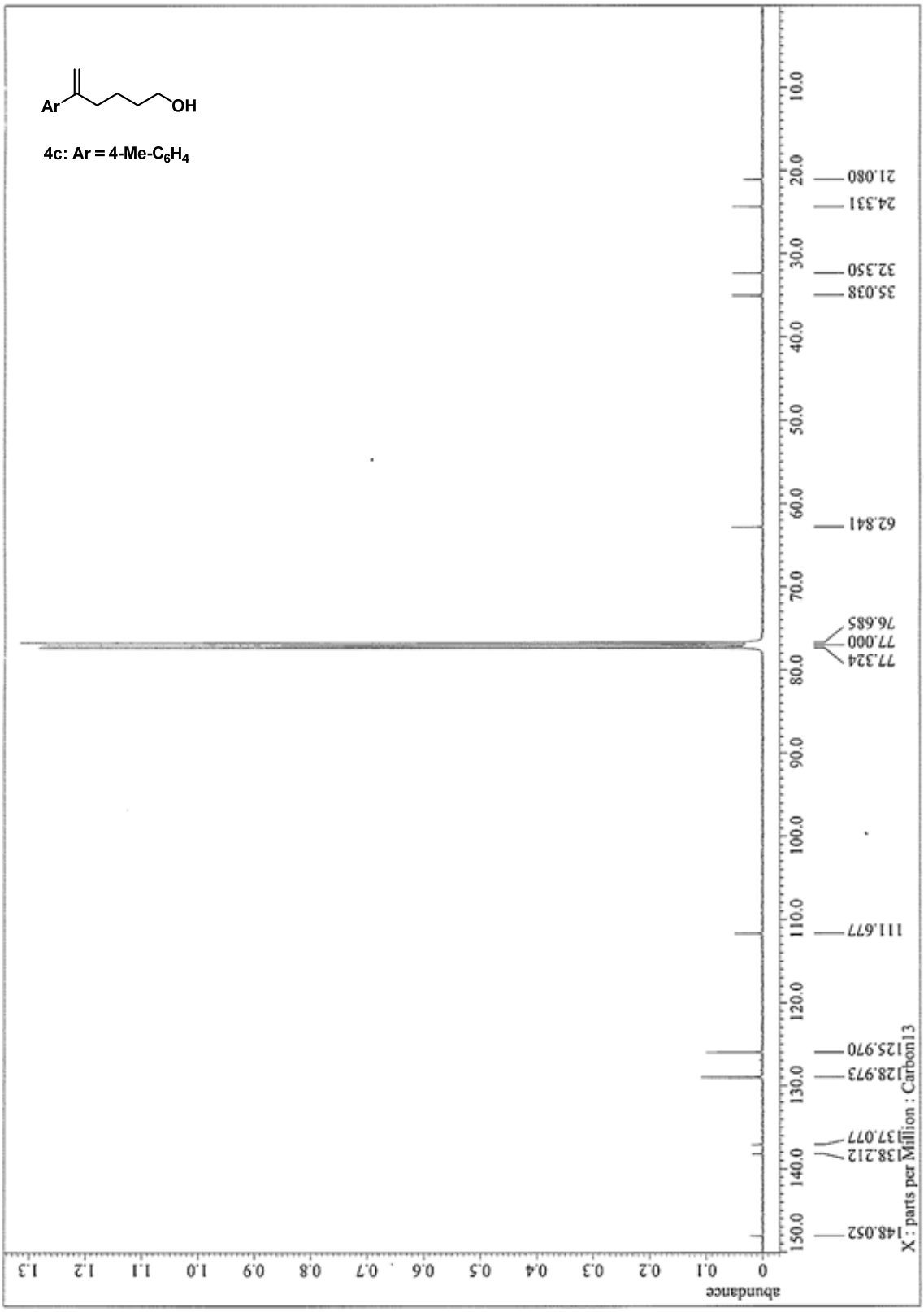

Ar
O
H
4b: Ar = 4-Me-C6H4
abundance
X : parts per Million : Proton

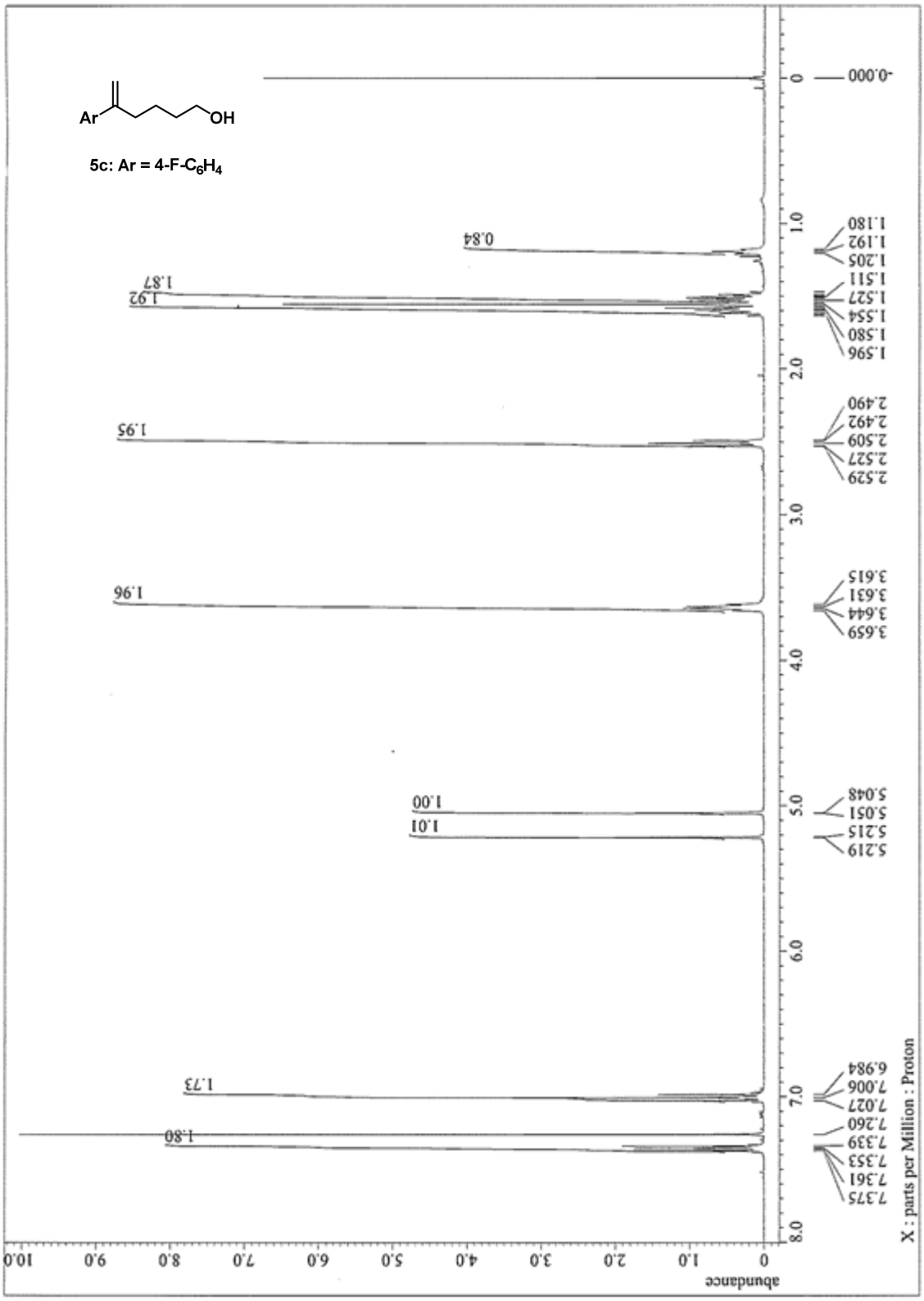

Ar
O
H
4b: Ar = 4-Me-C6H4
-0.020
20.098
20.965
25.961
32.941
34.562
62.717
75.856
76.685
77.000
77.324
125.941
129.135
135.952
142.236
X : parts per Million : Carbon13
abundance

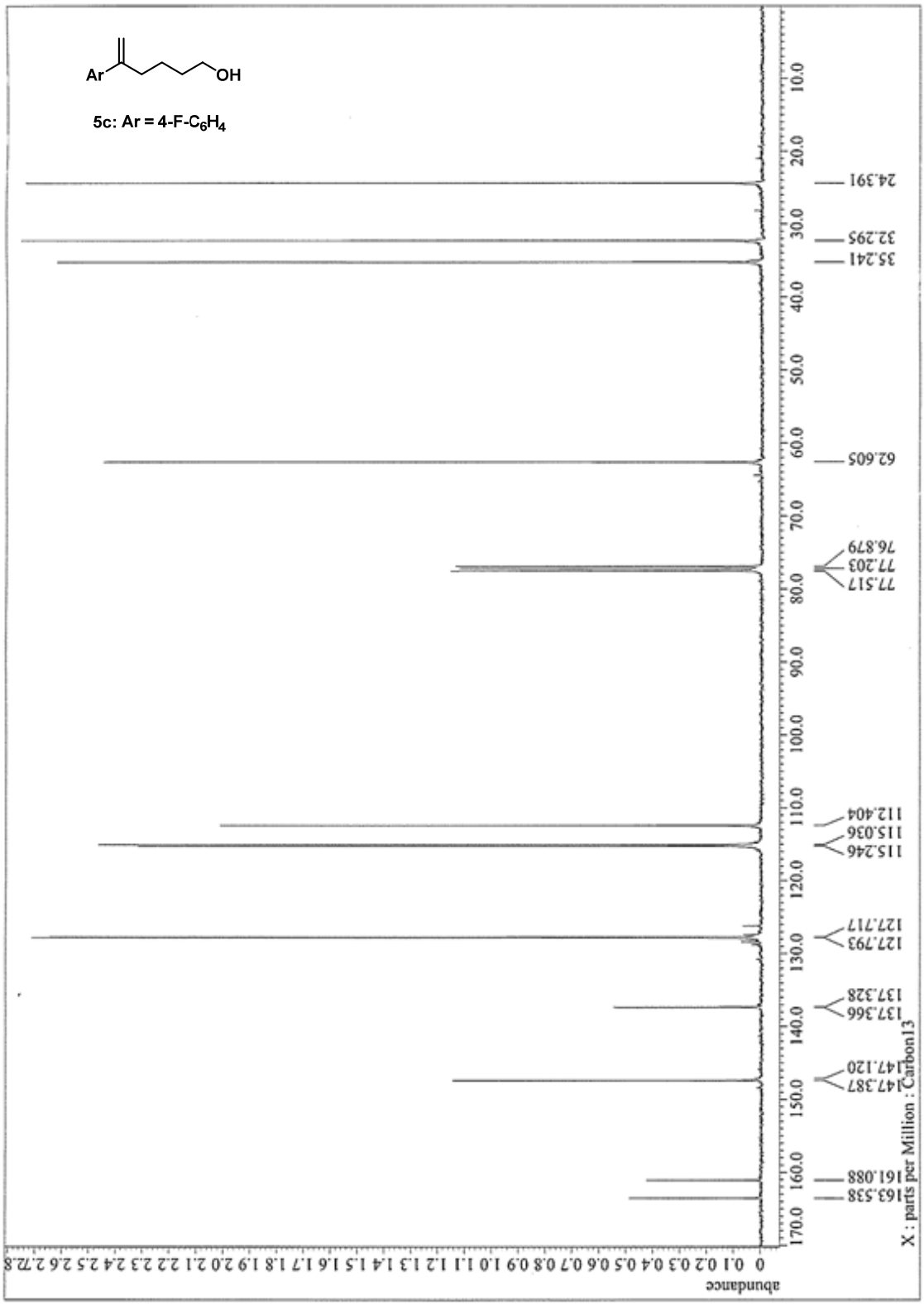

Ar
O
H
5b: Ar = 4-F-C6H4
-0.000
7.387
7.374
7.366
7.352
7.057
7.036
7.013
3.743
3.734
3.724
3.718
3.707
3.695
3.483
3.457
3.454
3.449
3.447
2.275
2.263
2.254
2.241
2.229
2.217
1.754
1.745
1.711
1.666
1.655
1.570
1.461
1.444
1.433
1.365
4.57
3.00
2.00
2.02
1.00
0.99
1.00
abundance
X : parts per Million : Proton

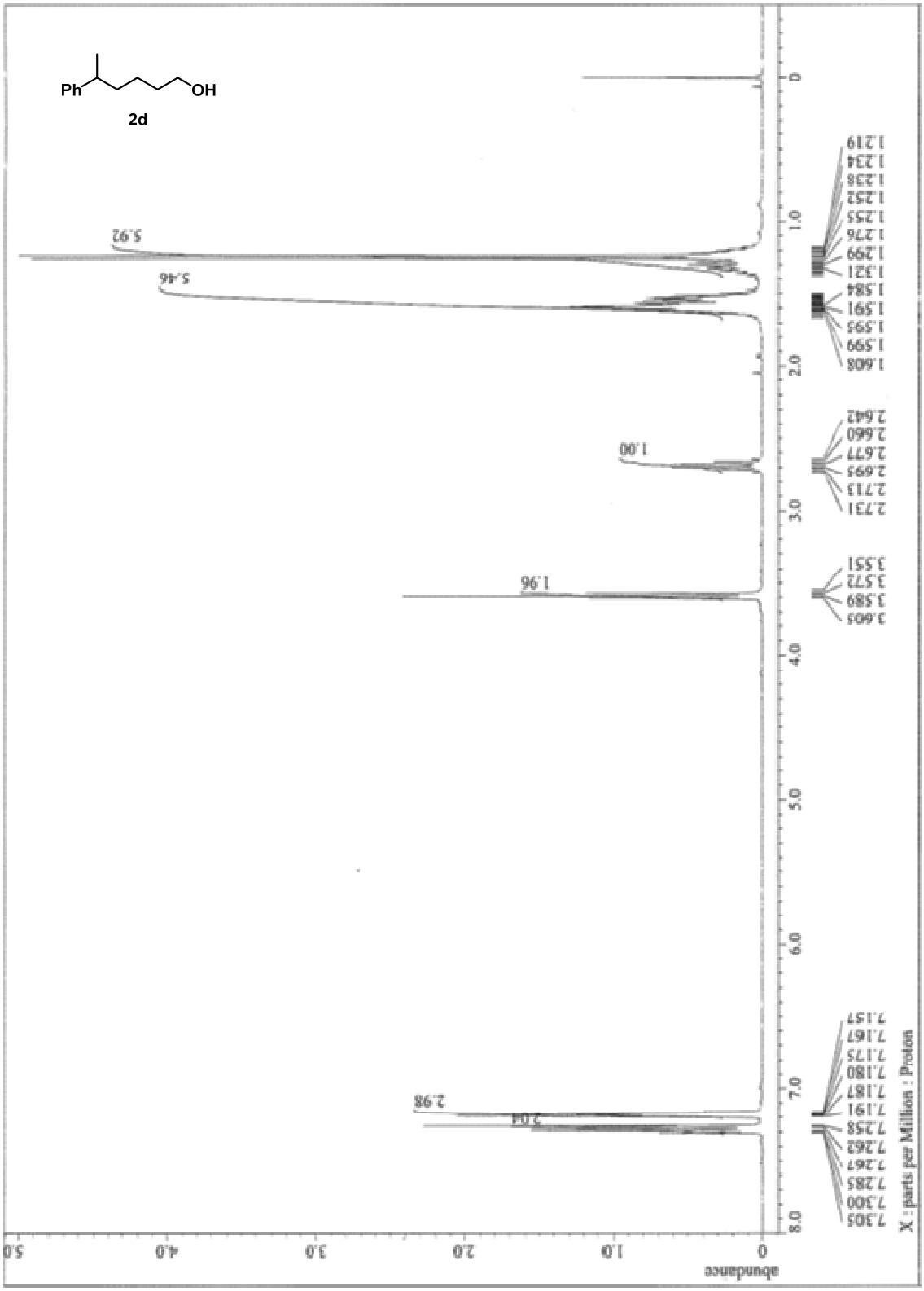

Ar
O
H
5b: Ar = 4-F-C6H4
-0.068
19.964
25.866
32.464
34.628
62.631
75.522
76.676
77.000
77.315
114.976
115.186
127.514
127.590
141.101
141.130
160.246
162.678
X : parts per Million : Carbon13
abundance

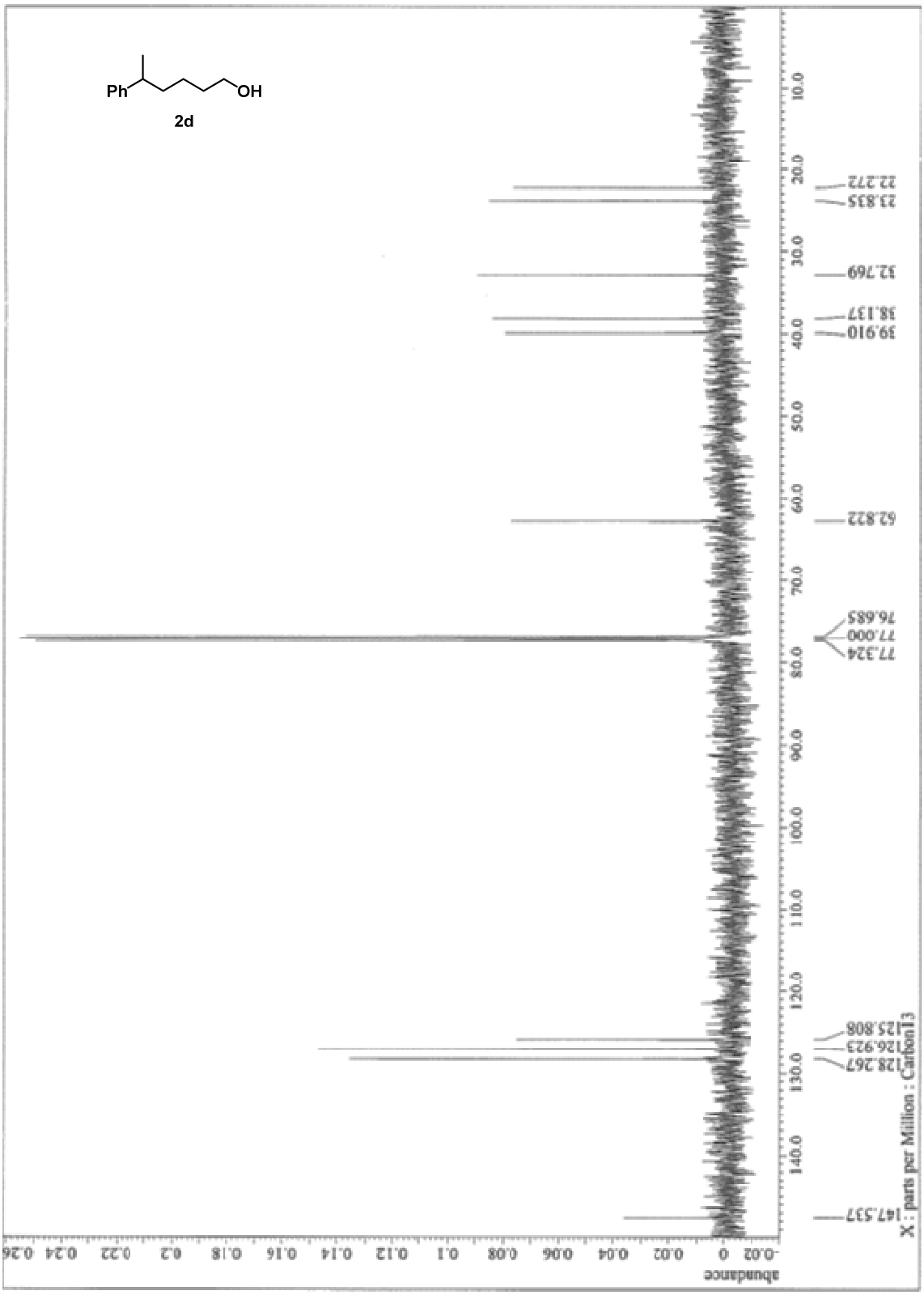

Ar
OH
4c: Ar = 4-Me-C6H4
X : parts per Million : Proton
abundance

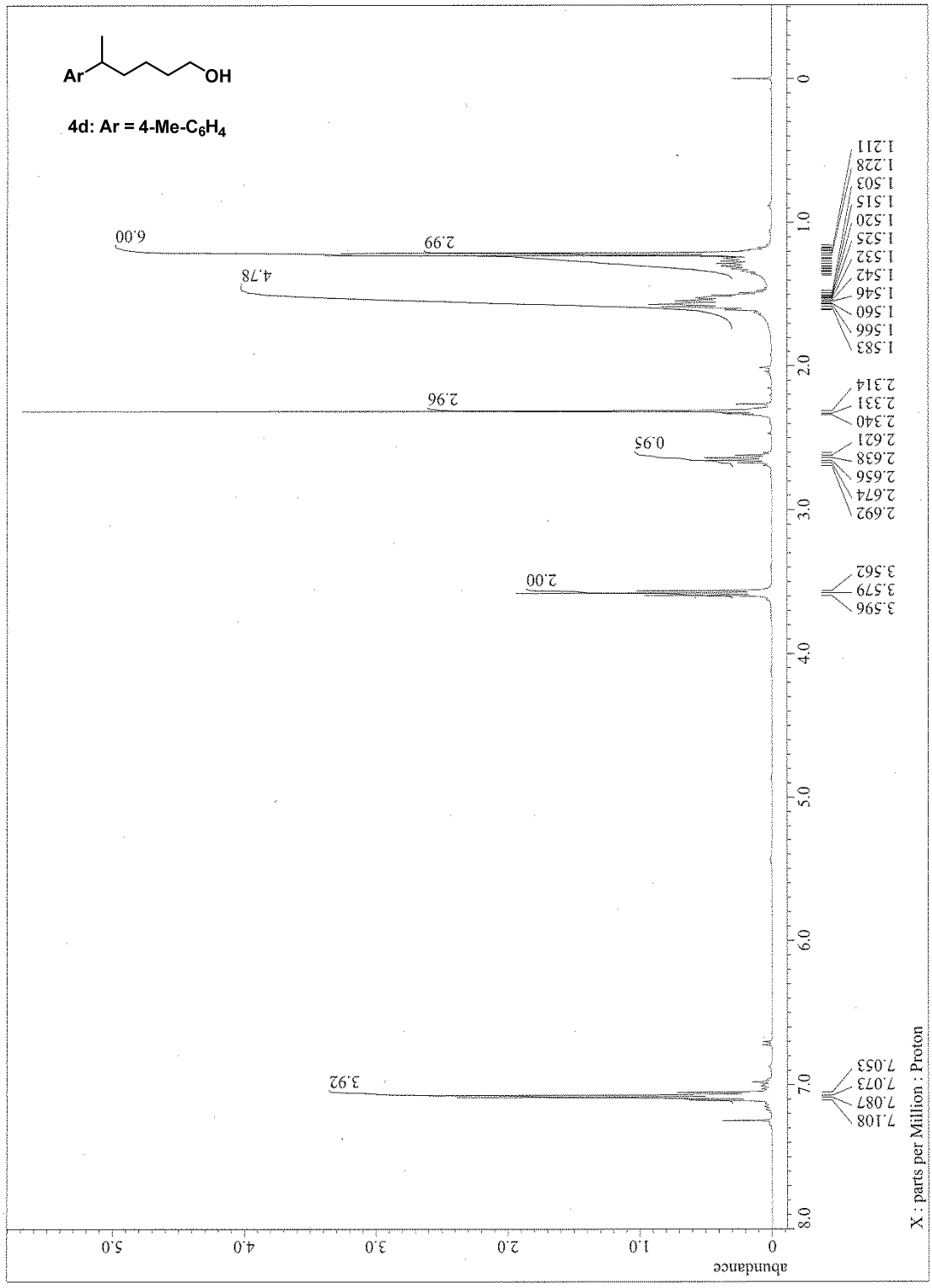

Ar
OH
4c: Ar = 4-Me-C6H4
21.080
24.331
32.350
35.038
62.841
76.685
77.000
77.324
111.677
125.970
128.973
137.077
138.212
148.052
X : parts per Million : Carbon13
abundance

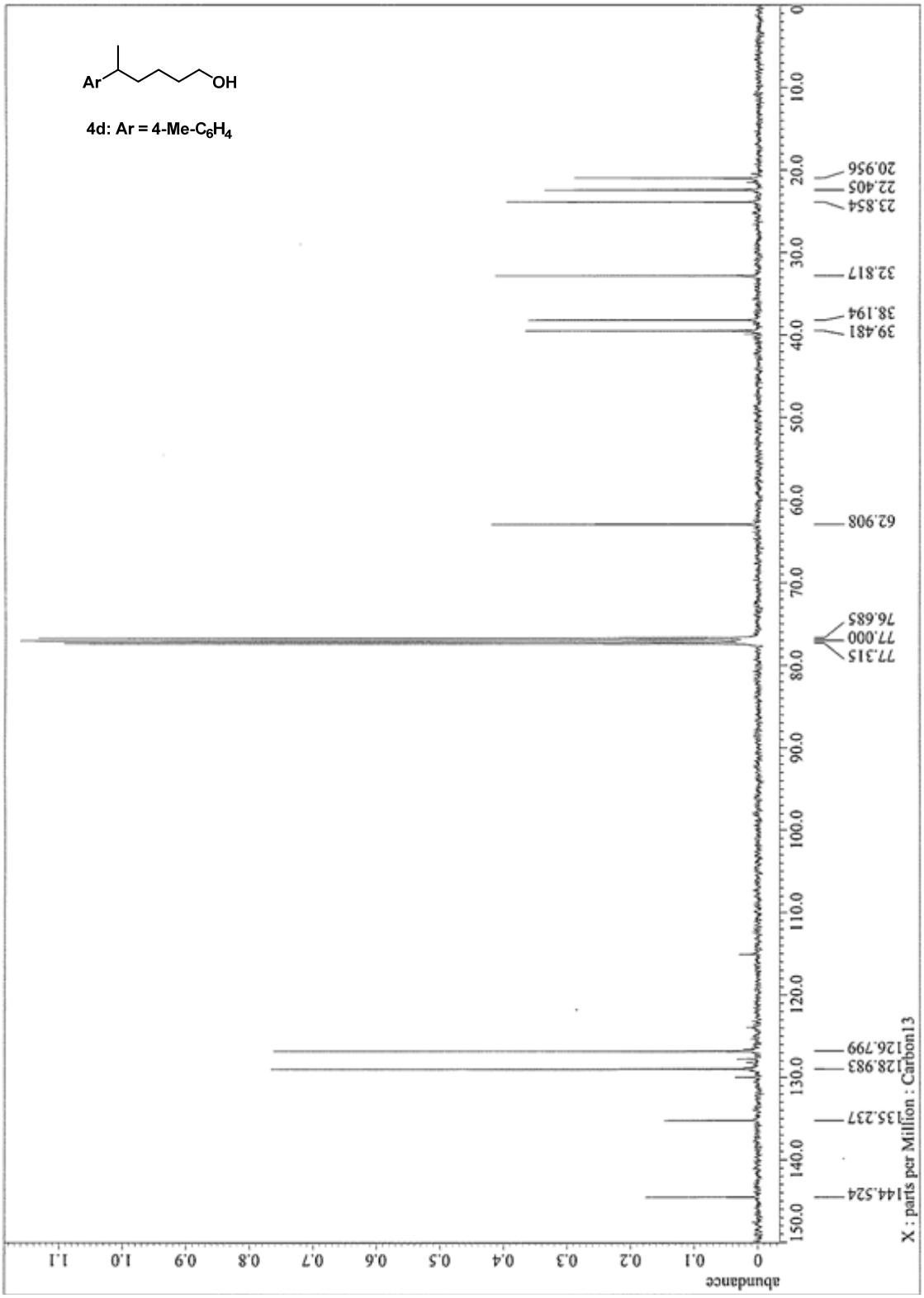

Ar
OH
5c: Ar = 4-F-C6H4
X : parts per Million : Proton
abundance

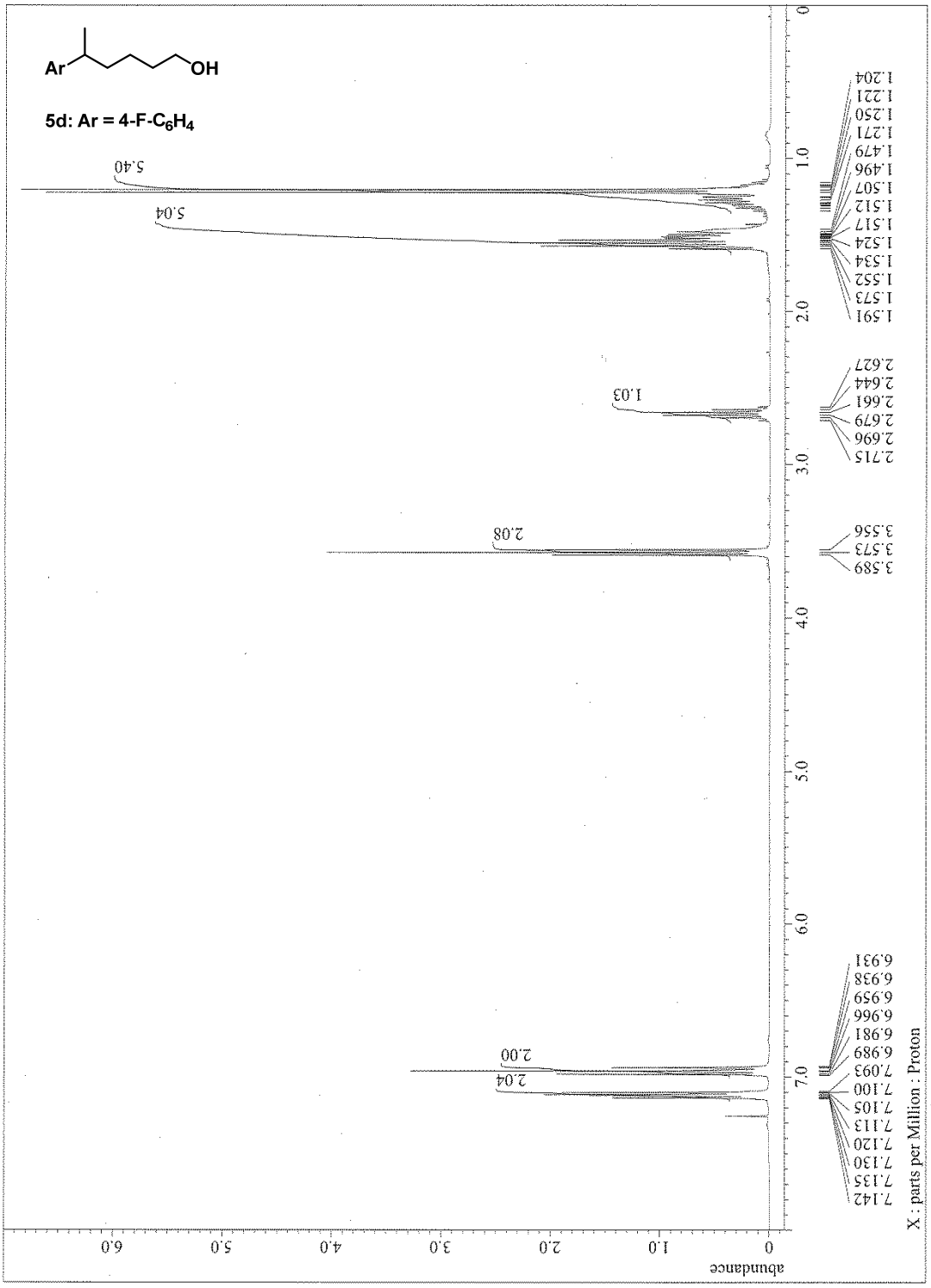

Ar
OH
5c: Ar = 4-F-C6H4
24.391
32.295
35.241
62.605
76.879
77.203
77.517
112.404
115.036
115.246
127.717
127.793
137.328
137.366
147.120
147.387
161.088
163.538
X : parts per Million : Carbon13
abundance

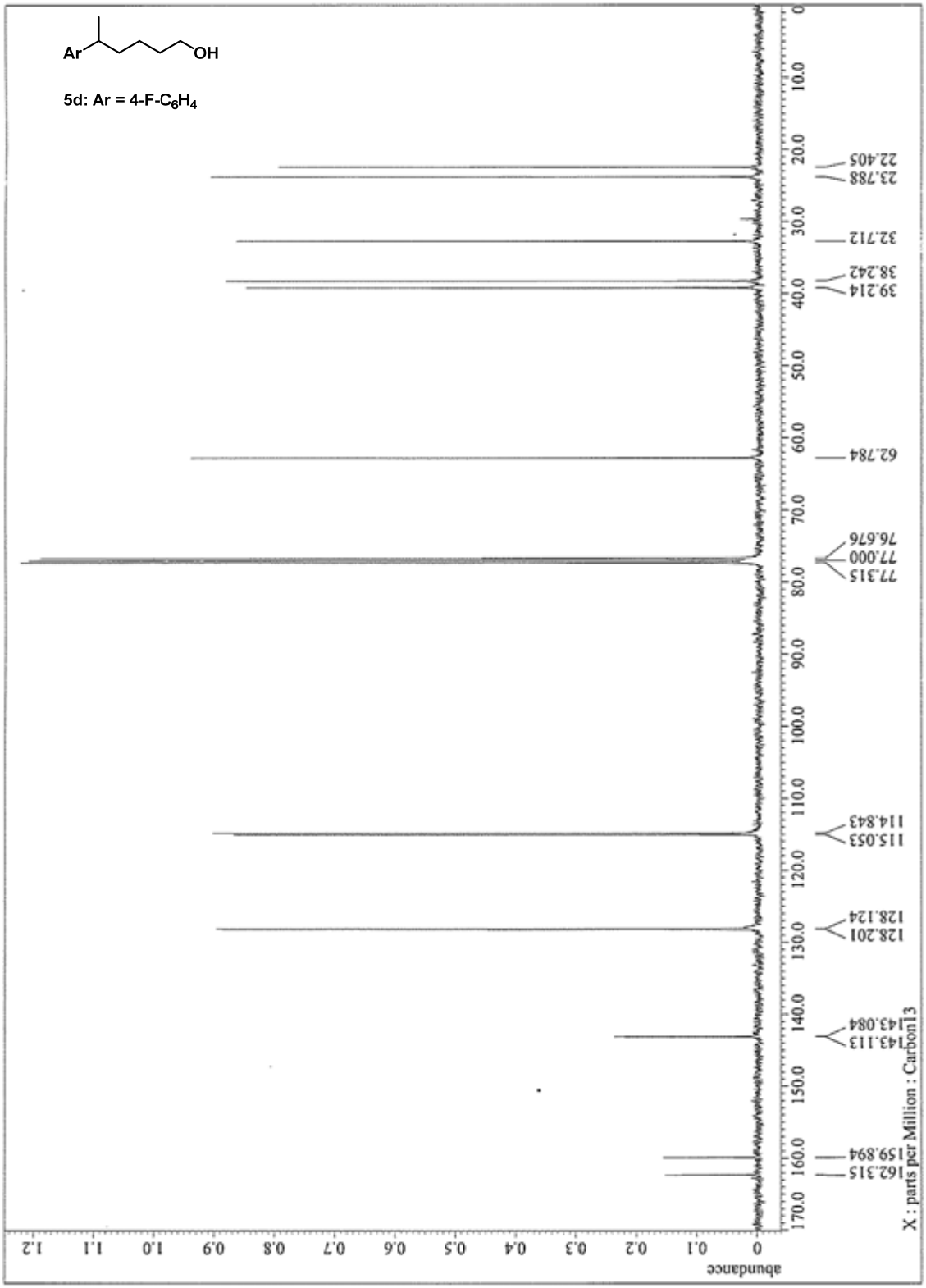

Ph
OH
2d
X : parts per Million : Proton
abundance

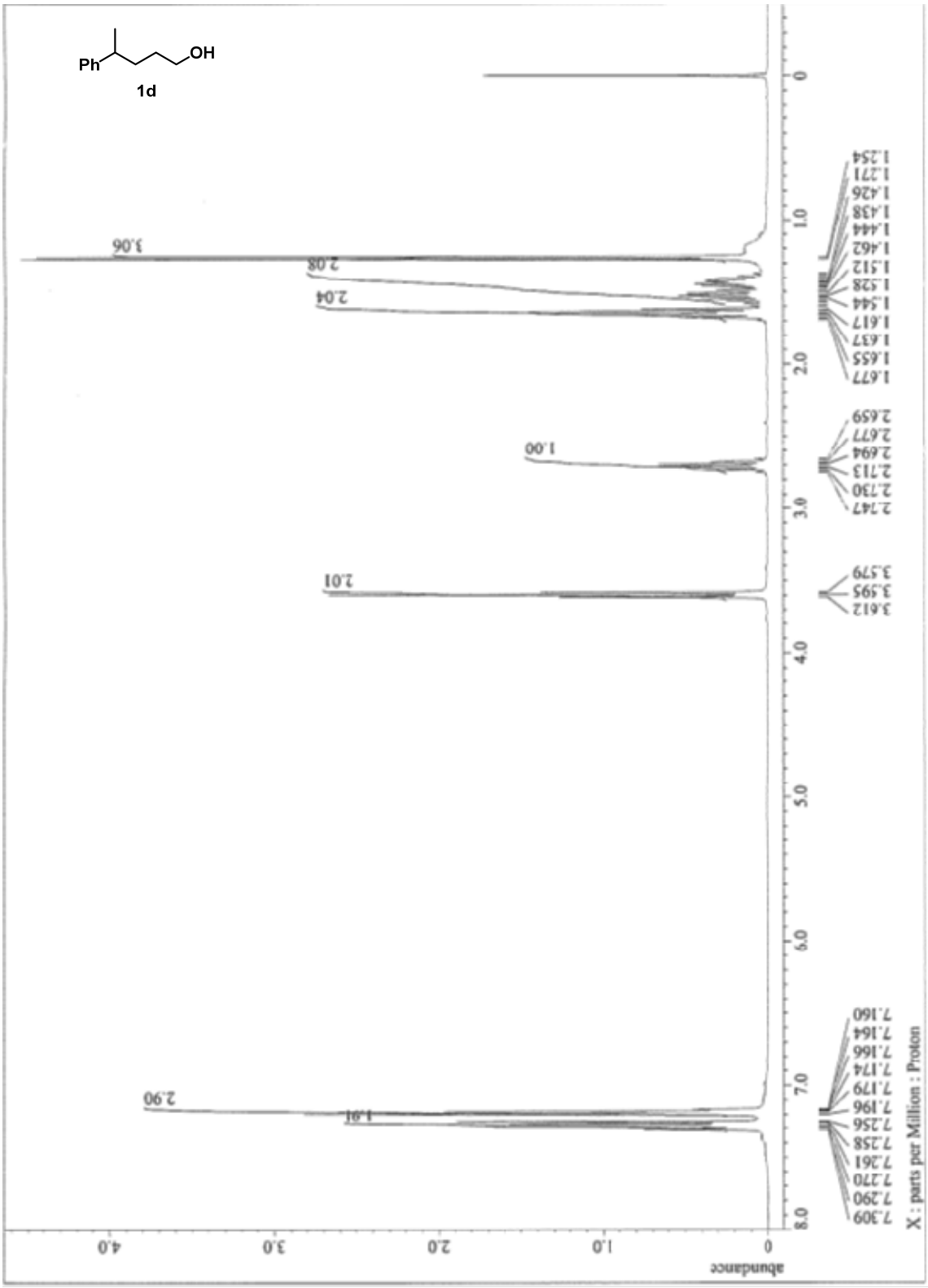

Ph
OH
2d
X : parts per Million : Carbon13
Abundance
22.272
23.835
32.769
38.137
39.910
62.822
76.685
77.000
77.324
125.808
126.923
128.267
147.537

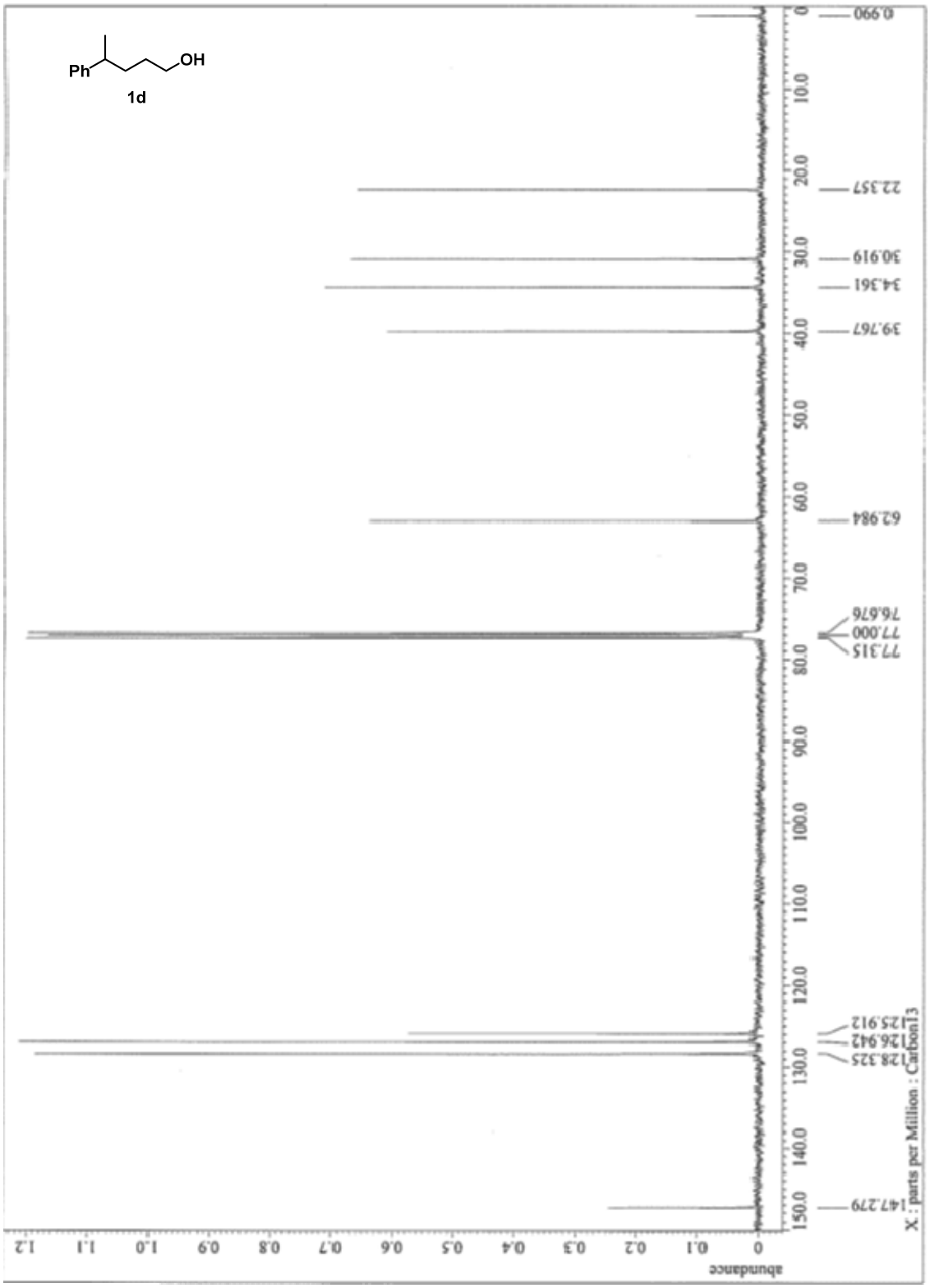

Ar
OH
4d: Ar = 4-Me-C6H4
6.00
2.99
4.78
2.96
0.95
2.00
3.92
7.053
7.073
7.087
7.108
3.562
3.579
3.596
2.314
2.331
2.340
2.621
2.638
2.656
2.674
2.692
1.211
1.228
1.503
1.515
1.520
1.525
1.532
1.542
1.546
1.560
1.566
1.583
abundance
X : parts per Million : Proton

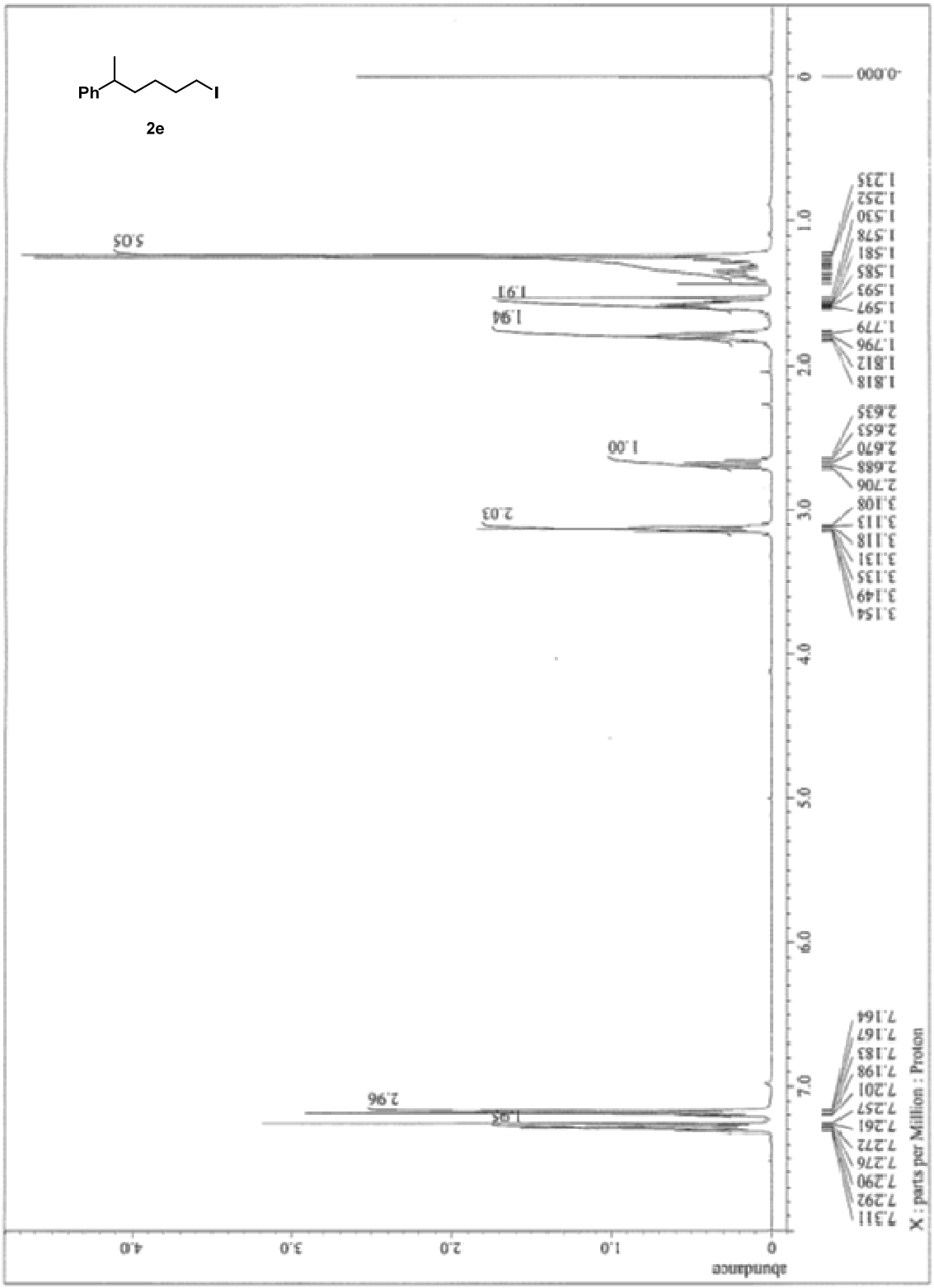

Ar
OH
4d: Ar = 4-Me-C6H4
20.956
22.405
23.854
32.817
38.194
39.481
62.908
76.685
77.000
77.315
126.799
128.983
135.237
144.524
X : parts per Million : Carbon13
abundance

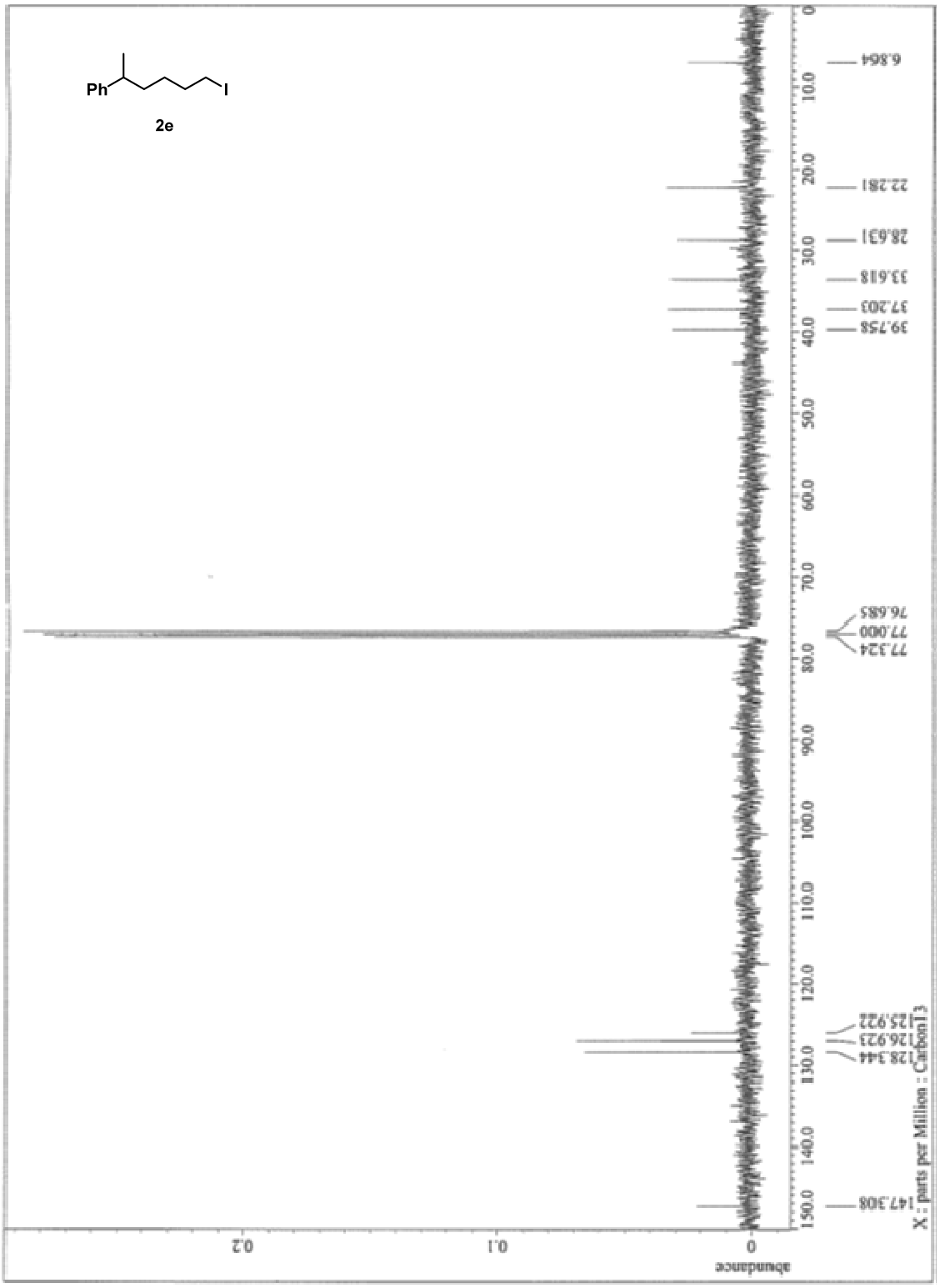

Ar
OH
5d: Ar = 4-F-C6H4
5.40
5.04
1.03
2.08
2.04
2.00
abundance
X : parts per Million : Proton

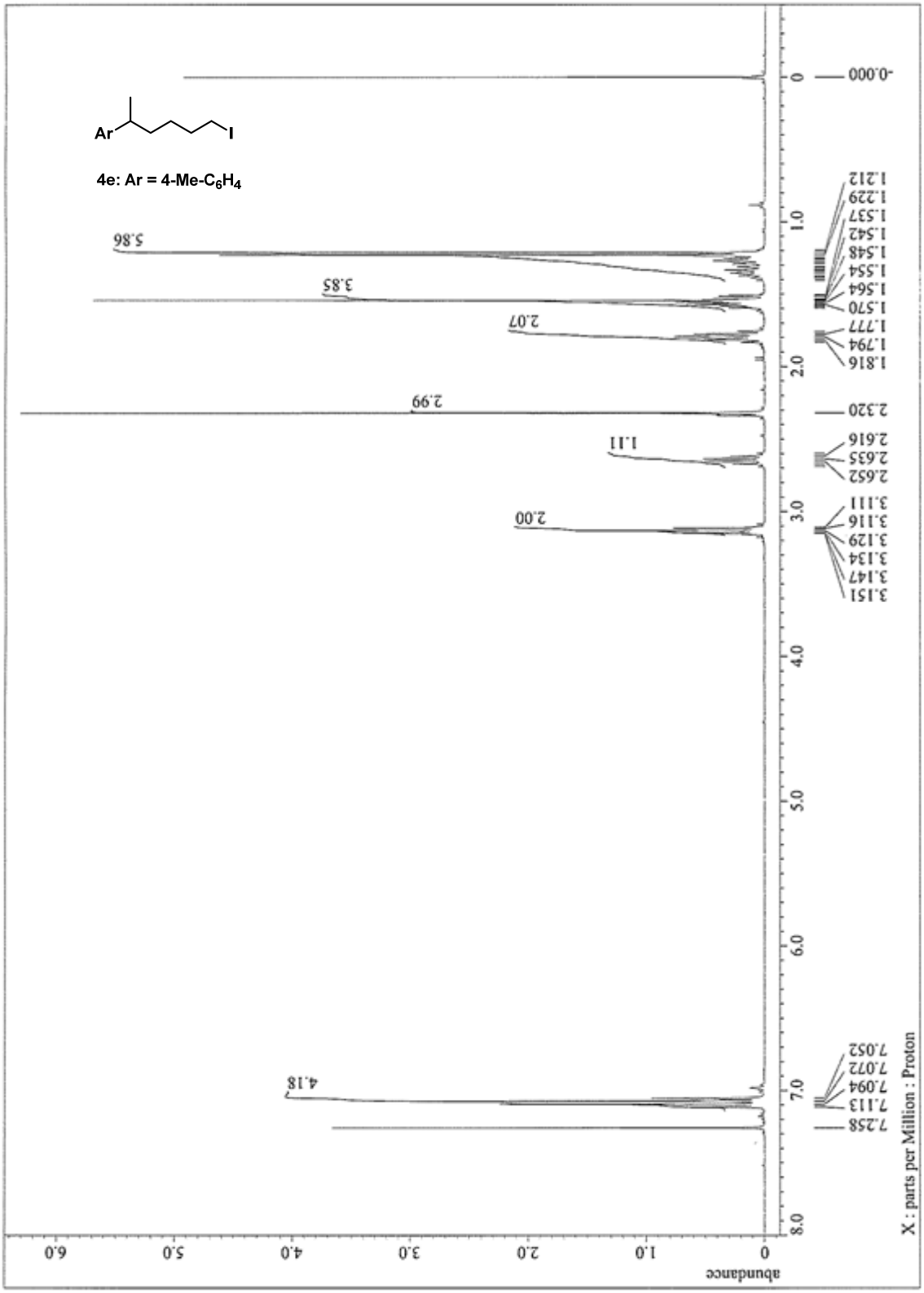

Ar
OH
5d: Ar = 4-F-C6H4
22.405
23.788
32.712
38.242
39.214
62.784
76.676
77.000
77.315
114.843
115.053
128.124
128.201
143.084
143.113
159.894
162.315
X : parts per Million : Carbon13
abundance

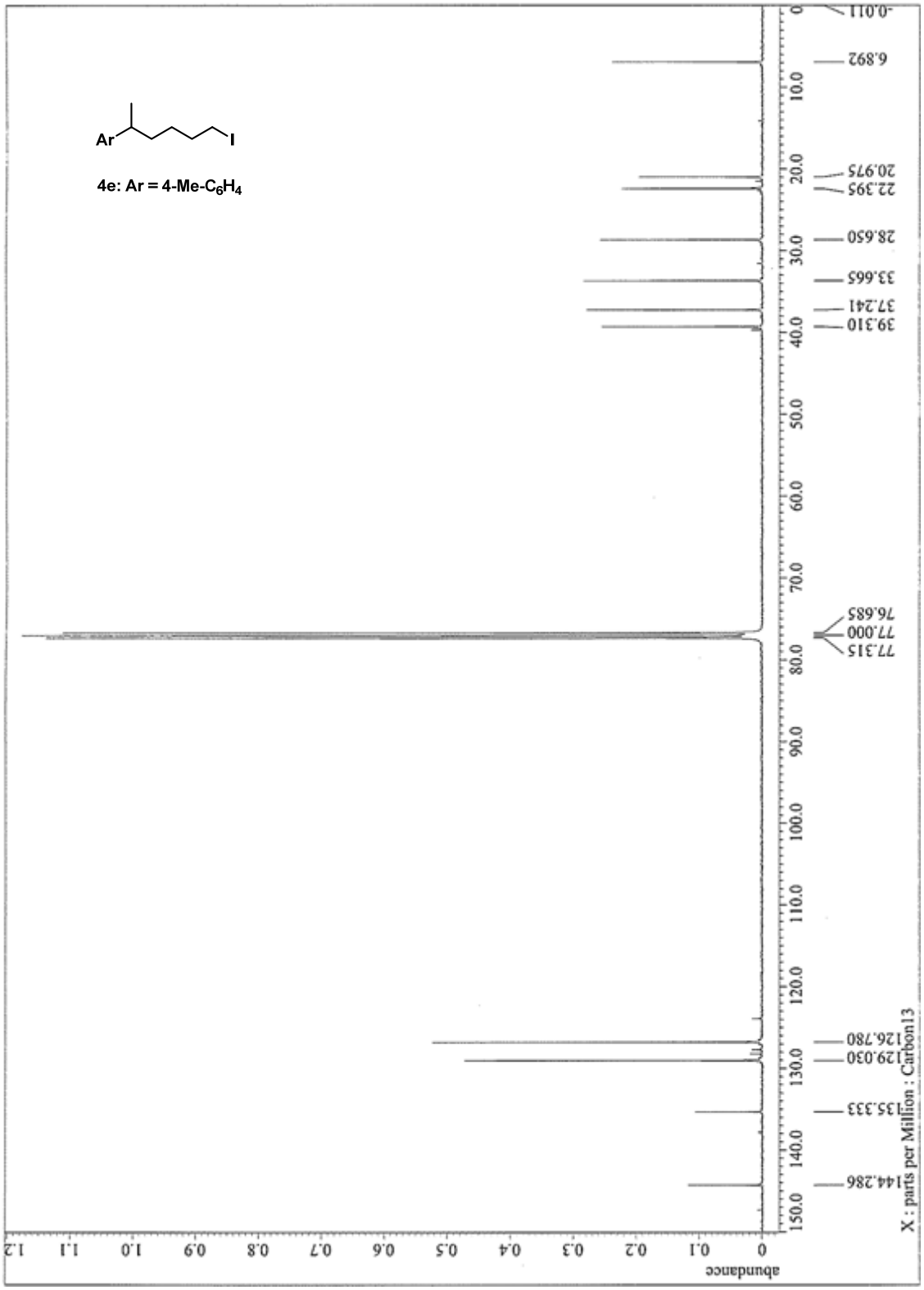

Ph
OH
1d
X : parts per Million : Proton
abundance

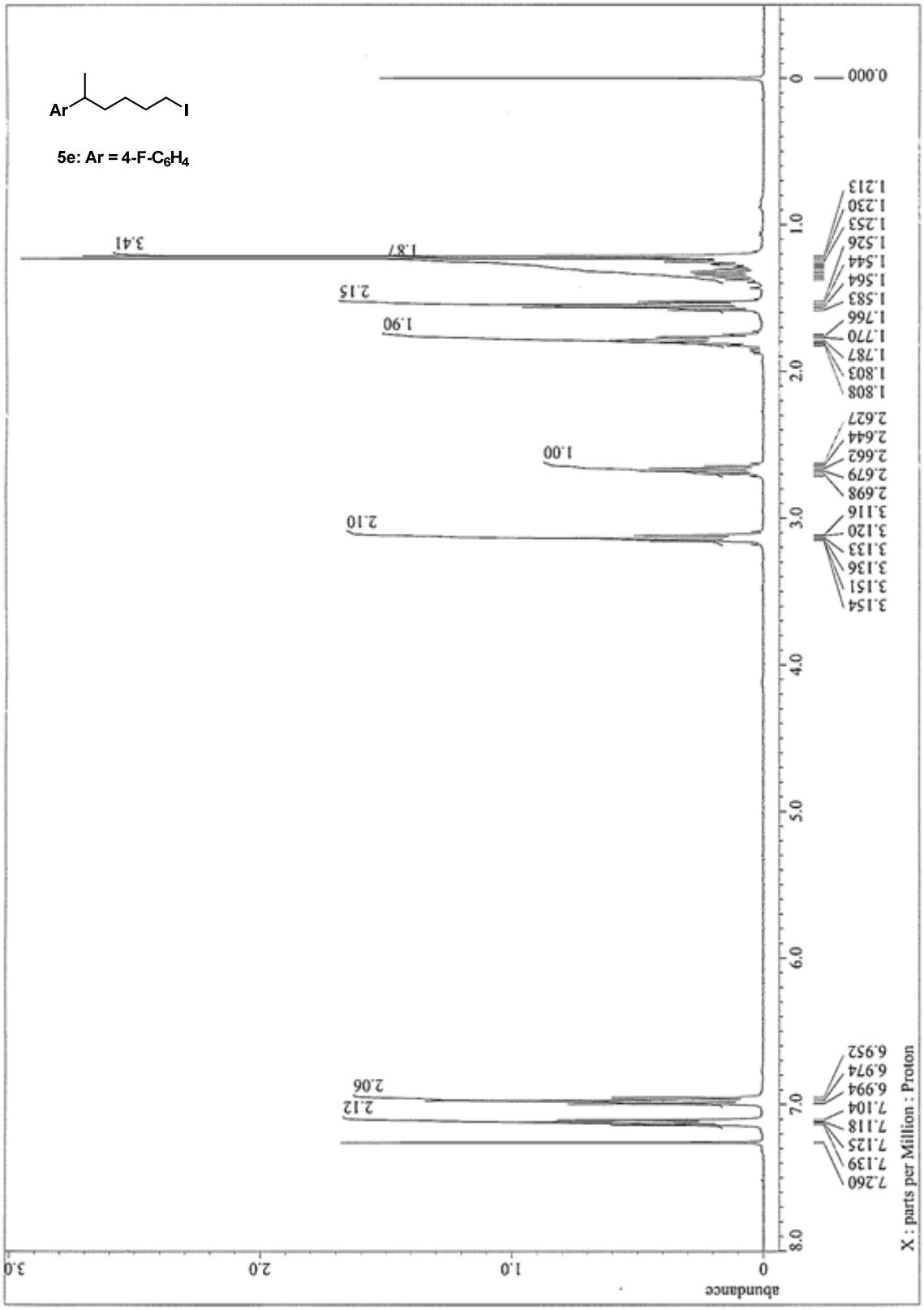

Ph
OH
1d
0.990
22.357
30.919
34.361
39.767
62.984
76.676
77.000
77.315
125.912
126.942
128.325
147.279
X : parts per Million : Carbon13
abundance

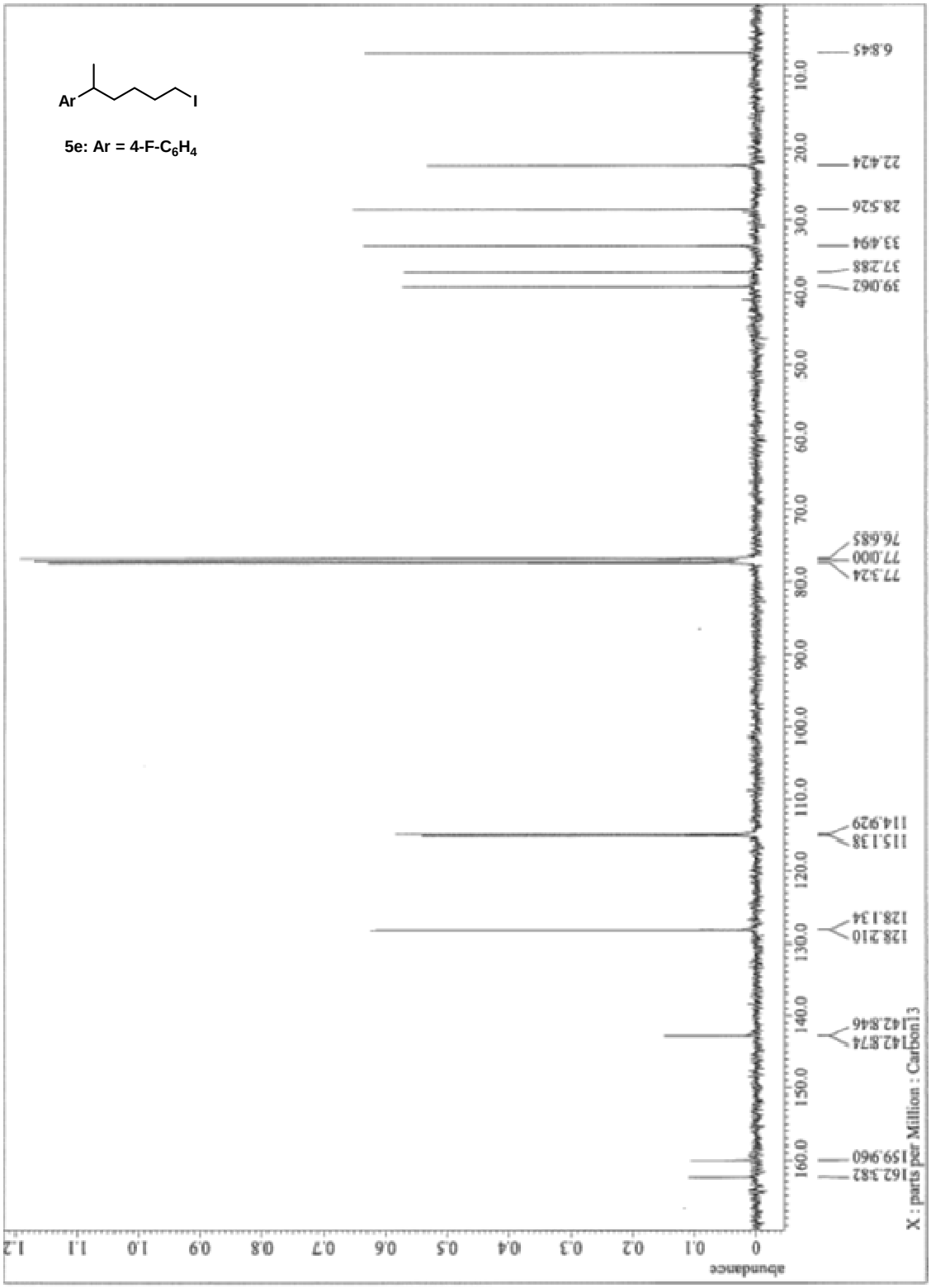

Ph
I
2e
X : parts per Million : Proton
abundance

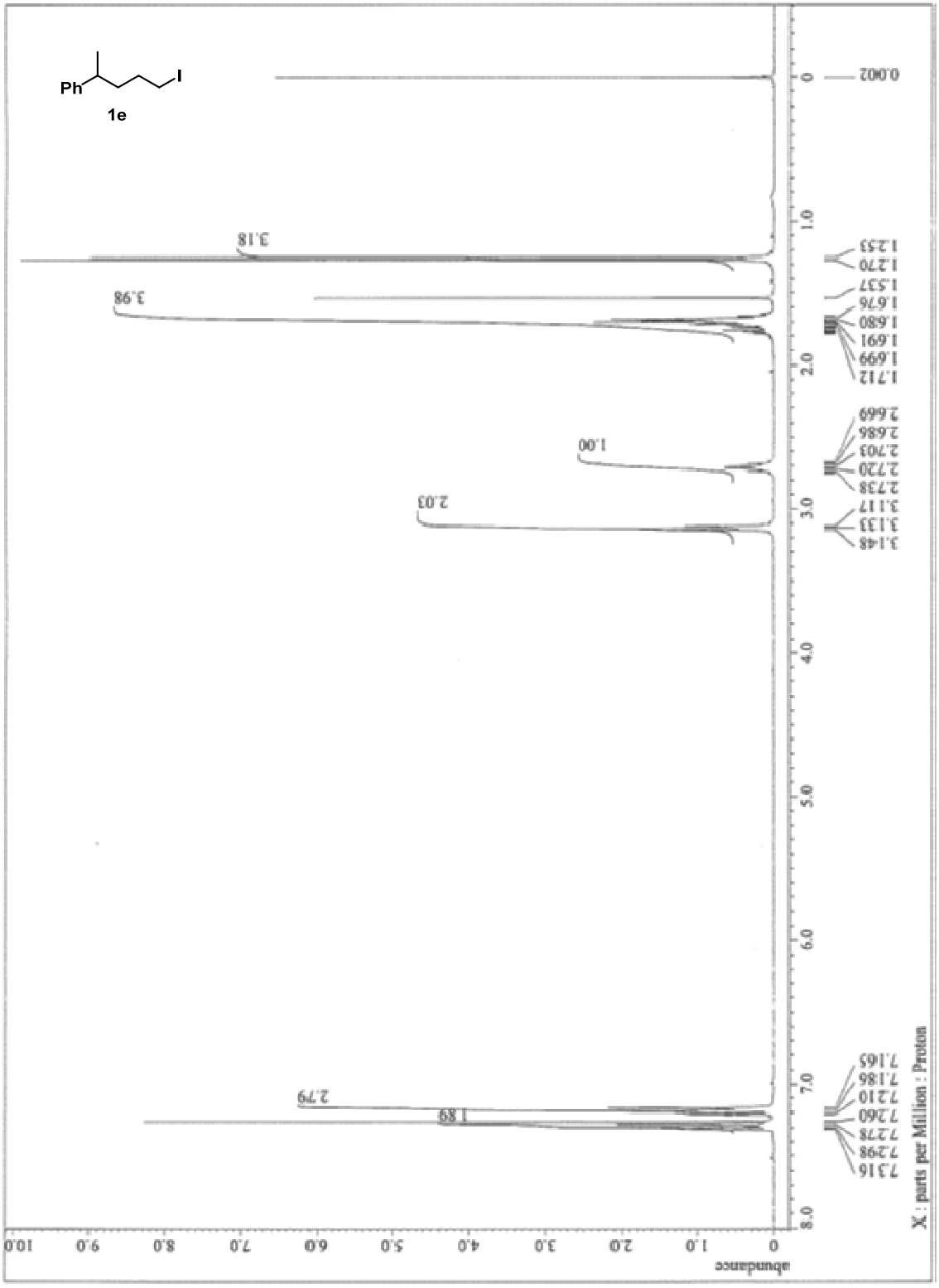

Ph
I
2e
6.864
22.281
28.631
33.618
37.203
39.758
76.685
77.000
77.324
125.922
126.923
128.344
147.308
X : parts per Million : Carbon13
abundance
0
0.1
0.2

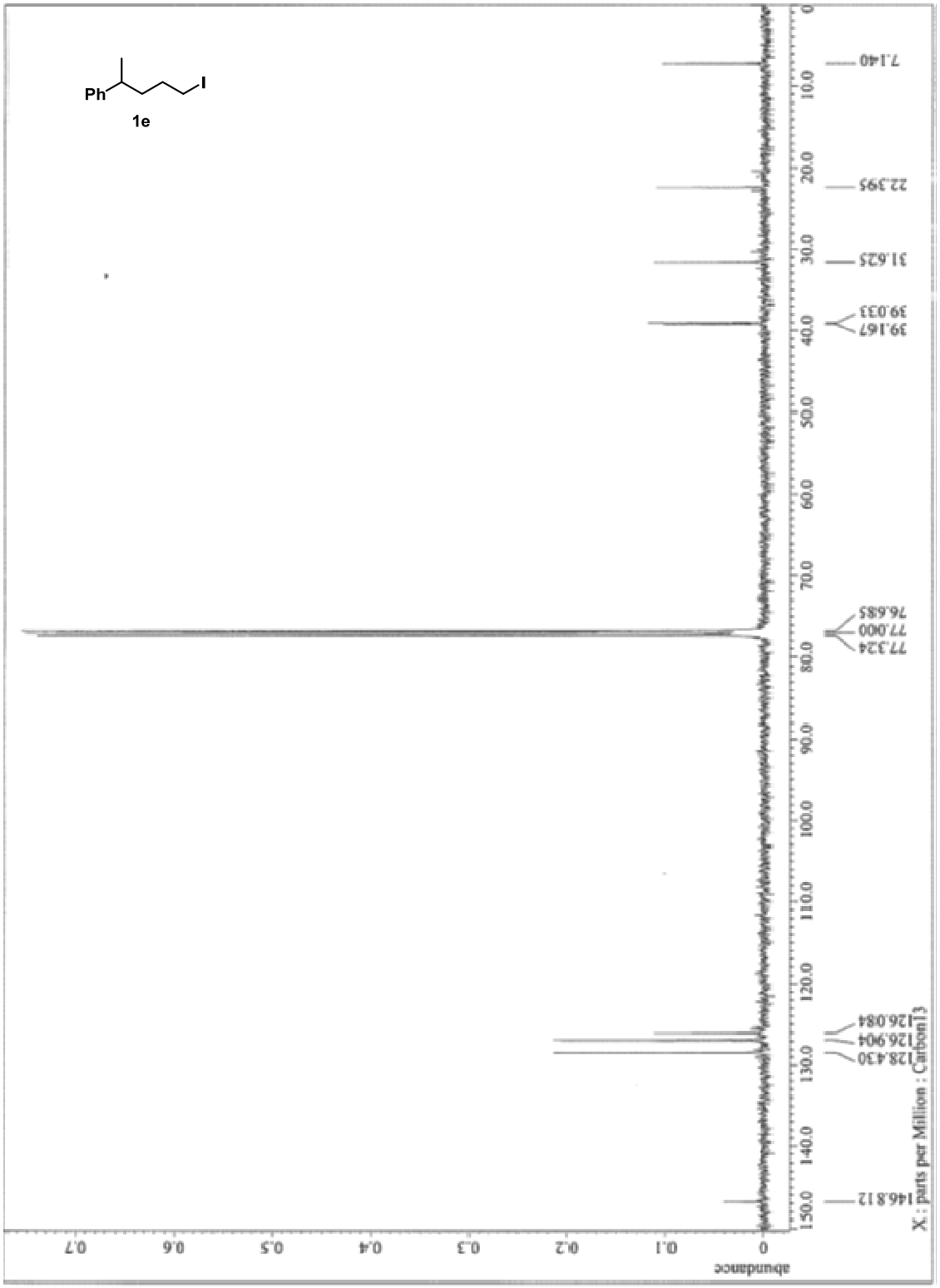

Ar
I
4e: Ar = 4-Me-C6H4
-0.000
1.212
1.229
1.537
1.542
1.548
1.554
1.564
1.570
1.777
1.794
1.816
2.320
2.616
2.635
2.652
3.111
3.116
3.129
3.134
3.147
3.151
7.052
7.072
7.094
7.113
7.258
5.86
3.85
2.07
2.99
1.11
2.00
4.18
X : parts per Million : Proton
abundance


Ar
I
4e: Ar = 4-Me-C6H4
-0.011
6.892
20.975
22.395
28.650
33.665
37.241
39.310
76.685
77.000
77.315
126.780
129.030
135.333
144.286
X : parts per Million : Carbon13
abundance


Ar
I
5e: Ar = 4-F-C6H4
0.000
1.213
1.230
1.253
1.526
1.544
1.564
1.583
1.766
1.770
1.787
1.803
1.808
2.627
2.644
2.662
2.679
2.698
3.116
3.120
3.133
3.136
3.151
3.154
6.952
6.974
6.994
7.104
7.118
7.125
7.139
7.260
3.41
1.87
2.15
1.90
1.00
2.10
2.12
2.06
X : parts per Million : Proton
abundance


Ar
I
5e: Ar = 4-F-C6H4
6.845
22.424
28.526
33.494
37.288
39.062
76.685
77.000
77.324
114.929
115.138
128.210
128.134
142.874
142.846
159.960
162.382
X : parts per Million : Carbon13
abundance


Ph
I
1e
0.002
1.253
1.270
1.537
1.676
1.680
1.691
1.699
1.712
2.669
2.686
2.703
2.720
2.738
3.117
3.133
3.148
3.18
3.98
1.00
2.03
1.89
2.79
7.165
7.186
7.210
7.260
7.278
7.298
7.316
X : parts per Million : Proton
abundance


Ph
I
1e
7.140
22.395
31.625
39.033
39.167
76.685
77.000
77.324
126.084
126.904
128.430
146.812
X : parts per Million : Carbon13
abundance