Supporting information

A new synthesis of allyl sulfoxides via nucleophilic addition of sulfinyl carbanions to Group 6 Fischer carbene complexes

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General: ^{1}H NMR spectra were recorded on a Bruker AMX-400 (400 MHz) or Bruker DPX-300 (300 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, dd: double doublet, td: triplet of doublets, t: triplet, q: quarter, br: broad, m: multiplet), coupling constants (*J* in Hz), integration and assignment. ^{13}C NMR spectra were recorded on a Bruker AMX-400 (100 MHz) or Bruker DPX-300 (75 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 76.95). Bidimensional NMR experiments (COSY, HMQC, HMBC and NOESY) were recorded on a Bruker AMX-400 (400 MHz). High-resolution mass spectrometry was carried out on a Finnigan-Mat 95 spectrometer.
All reactions were carried out under nitrogen atmosphere. THF was distilled over benzophenone/sodium under nitrogen atmosphere. DMSO was dried by distillation from calcium hydride under reduced presure. Methyl lithium (1.5 M in pentane) and sulfoxides were purchased from Aldrich.

All Fischer carbenes complexes **1** were prepared according to literature procedures.[1]

General procedure for the preparation of allyl sulfoxides 4 and enol ethers 5.
To a solution of the sulfoxide **2** (2.5 mmol) in THF (15 mL) cooled to -20ºC, MeLi 1.5 M in pentane (2.6 mmol) is added. The resulting mixture is allowed to warm to room temperature and then is added dropwise to a solution of carbene complexe **1** (1 mmol) in THF (20 mL) at -78ºC. The mixture is stirred during 30 minutes and then is warmed to room temperature. Silica gel is added and, after evaporating solvents under reduced presure, the allyl sulfoxide **4** or enol ether **5** was obtained by cromatography as an oil.

Methyl 2-phenylallyl sulfoxide (4a). Yellow oil. R_f 0.12 (ethyl acetate). ^{1}H NMR (300 MHz, CDCl3) δ 7.50-7.32 (m, 5H), 5.70 (s, 1H), 5.43 (s, 1H), 4.12 (d, *J* = 12.9 Hz, 1H), 3.83 (d, *J* = 12.9 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 137.6, 128.7, 128.5, 125.9, 119.6, 60.8, 37.8. HRMS calcd. for $C_{10}H_{12}OS$: 180.0603, found 180.0599.

2-(4-Methoxyphenyl)allyl methyl sulfoxide (4b). Yellow oil. R_f 0.15 (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 7.7 Hz, 2H), 5.55 (s, 1H), 5.30 (s, 1H), 4.06 (d, *J* = 12.9 Hz, 1H), 3.80 (s, 3H), 3.73 (d, *J* = 12.9 Hz), 2.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 137.1, 130.9, 127.1, 117.4, 113.9, 61.2, 55.2, 37.9. HRMS calcd. for $C_{11}H_{14}O_2S$: 210.0715, found 210.0718.

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[1] (a) E. O. Fischer, A. Maasböl, *Angew. Chem. Int. Ed. Engl.*, **1964**, *76*, 645. (b) E. O. Fischer, A. Maasböl, *Angew. Chem. Int. Ed. Engl.*, **1964**, *3*, 580. R. Aumann, H. Heinen, *Chem. Ber.*, **1987**, *120*, 537.

2-(2-Furyl)allyl methyl sulfoxide (4c). Orange oil. R_f 0.15 (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (bs, 1H), 6.48 (bs, 1H), 6.43 (bs, 1H), 5.80 (s, 1H), 5.26 (s, 1H), 3.92 (d, *J* = 12.8 Hz, 1H), 3.67 (d, *J* = 12.8 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 142.8, 127.3, 115.5, 111.5, 107.8, 58.8, 38.0. HRMS calcd. for $C_8H_{10}O_2S$: 170.0396, found 170.0398.

Methyl 2-methylene-4-phenyl-3-butynyl sulfoxide (4d). Yellow oil. R_f 0.11 (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.30 (m, 3H), 5.71 (s, 1H), 5.60 (s, 1H), 3.72 (d, *J* = 12.5 Hz, 1H), 3.55 (d, *J* = 12.5 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5, 128.8, 128.3, 127.8, 122.1, 120.4, 91.1, 87.8, 61.6, 37.9. HRMS calcd. for $C_{12}H_{12}OS$: 204.0609, found 204.0601.

(*E*)-4-(2-Furyl)-2-methylene-3-butenyl methyl sulfoxide (4e). Yellow oil. R_f 0.10 (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (bs, 1H), 6.78 (d, *J* = 16.4 Hz, 1H), 6.51 (d, *J* = 16.4 Hz, 1H), 6.40 (m, 2H), 5.52 (s, 1H), 5.31 (s, 1H), 3.89 (d, *J* = 12.6 Hz, 1H), 3.56 (d, *J* = 12.6 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 146.3, 145.0, 131.9, 128.8, 112.7, 111.8, 108.9, 61.8, 36.5. HRMS calcd. for $C_{10}H_{12}O_2S$: 196.0558, found 196.0564.

4-(1-Cyclopentenyl)-2-methylene-3-butynyl methyl sulfoxide (4f). Orange oil. R_f 0.17 (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (bs, 1H), 5.64 (d, *J* = 1.0 Hz, 1H), 5.53 (d, *J* = 1.0 Hz, 1H), 3.69 (d, *J* = 12.5 Hz, 1H), 3.48 (d, *J* = 12.5 Hz, 1H), 2.66 (s, 3H), 2.50-2.44 (m, 4H), 1.97-1.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 127.1, 123.6, 120.5, 89.0, 88.6, 61.6, 37.9, 36.1, 33.3, 23.2. HRMS calcd. for $C_{11}H_{14}OS$: 179.0525, found 179.0529.

2-(4-Methoxyphenyl)allyl *p*-tolyl sulfoxide (4g). Colorless oil. R_f 0.11 (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.38-7.26 (m, 4H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.45 (s, 1H), 4.99 (s, 1H), 4.07 (d, *J* = 12.8 Hz, 1H), 3.83 (s, 3H), 3.79 (d, *J* = 12.8 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 141.6, 140.3, 136.8, 131.3, 129.6, 127.2, 124.4, 117.9, 113.8, 65.0, 55.2, 21.3. HRMS calcd. for $C_{17}H_{18}O_2S$: 286.1022, found 286.1022.

2-(2-Furyl)allyl *p*-tolyl sulfoxide (4h). Orange oil. R_f 0.08 (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.45 (s, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.38 (s, 2H), 5.69 (s, 1H), 4.96 (s, 1H), 3.91 (d, *J* = 12.6 Hz, 1H), 3.68 (d, *J* = 12.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 142.5, 141.7, 140.3, 129.6, 127.0, 124.3, 116.0, 111.3, 107.4, 62.7, 21.3. HRMS calcd. for $C_{14}H_{14}O_2S$: 246.0709, found 246.0720.

4-Phenyl-2-methylene-3-butynyl *p*-tolyl sulfoxide (4i). Yellow oil. R_f 0.12 (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.26 (m, 9H), 5.65 (d, *J* = 1.1 Hz, 1H), 5.37 (d, *J* = 1.1 Hz, 1H), 3.76 (d, *J* = 12.3 Hz, 1H), 3.57 (d, *J* = 12.3 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 139.6, 131.5, 129.6, 128.5, 128.2, 128.0, 124.3, 122.3, 120.2, 90.6, 87.8, 64.9, 21.3. HRMS calcd. for $C_{18}H_{16}OS$: 280.0922, found 280.0927.

1-Methoxy-4-(1-methoxy-2-phenylvinyl)benzene (5a). Orange oil. R_f 0.45 (HxH/AcOEt 5/1).

Mayor diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6-7.0 (m, 9H), 5.9 (s, 1H), 3.9 (s, 3H), 3.8 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 156.8, 137.1, 130.4, 128.6, 128.2, 127.8, 124.9, 113.3, 100.6, 55.2, 54.9.

Minor diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.9-7.1 (m, 9H), 6.2 (s, 1H), 3.9 (s, 3H), 3.7 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 157.0, 136.0, 130.3, 128.3, 128.2, 127.7, 126.1, 113.7, 111.1, 57.6, 55.0.

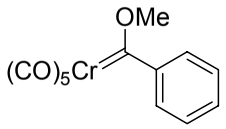
2-(1-Methoxy-2-phenylvinyl)furan (5b). Colorless oil. R_f 0.45 (HxH/AcOEt 5/1).

Mayor diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (bs, 1H), 7.50-7.20 (m, 5H), 6.62 (bs, 1H), 6.54 (bs, 1H), 6.01 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 142.5, 137.1, 135.0, 128.5, 127.8, 126.7 111.6, 110.7, 107.6, 55.4,

(1-Methoxy-3-methyl-1-butenyl)benzene (5c). Yellow oil. R_f 0.69 (HxH/AcOEt 10/1).

Mayor diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.25 (m, 5H), 4.60 (d, J = 9.9 Hz, 1H), 3.66 (s, 3H), 2.50 (m, 1H), 1.06 (d, J = 6.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 136.9,128.7, 127.5, 125.8, 108.2, 54.8, 26.8, 24.5.

Minor diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.25 (m, 5H), 5.22 (d, J = 9.4 Hz, 1H), 3.58 (s, 3H), 3.01 (m, 1H), 1.11 (d, J = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 135.9, 128.4, 127.3 122.3, 115.1, 58.7, 25.2, 23.3.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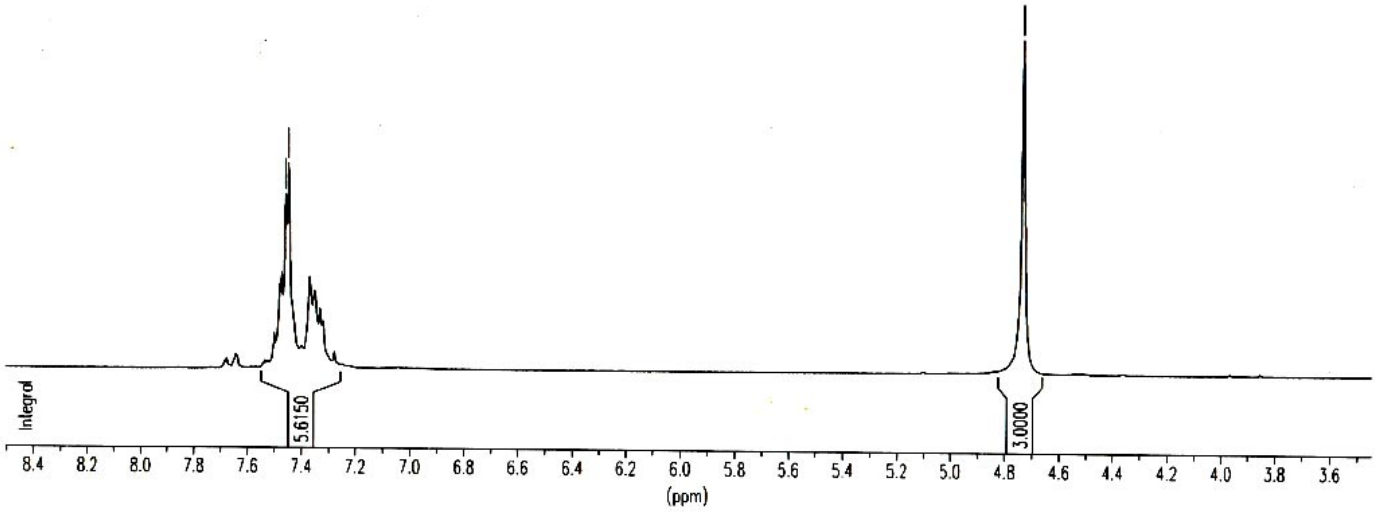
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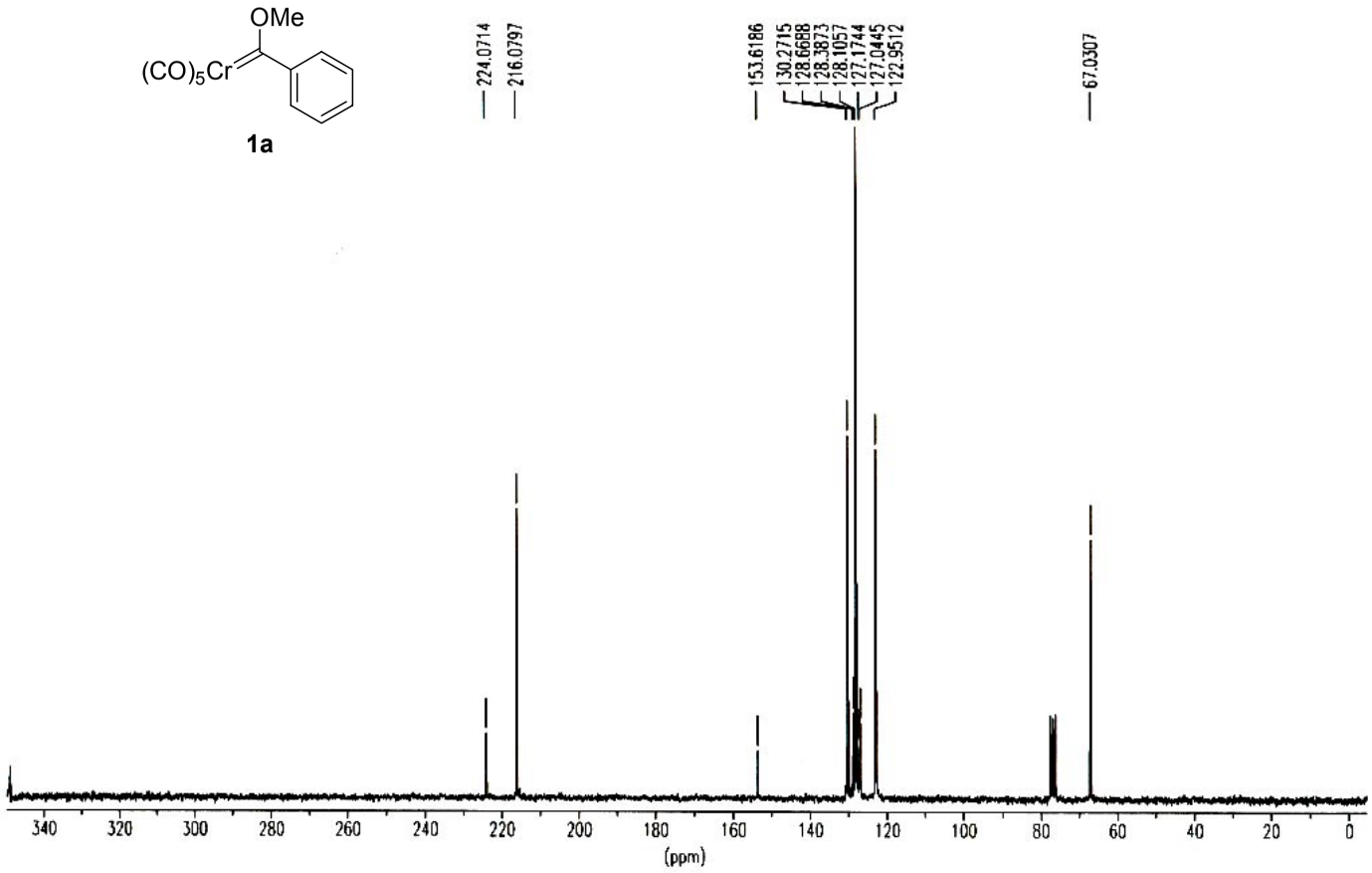
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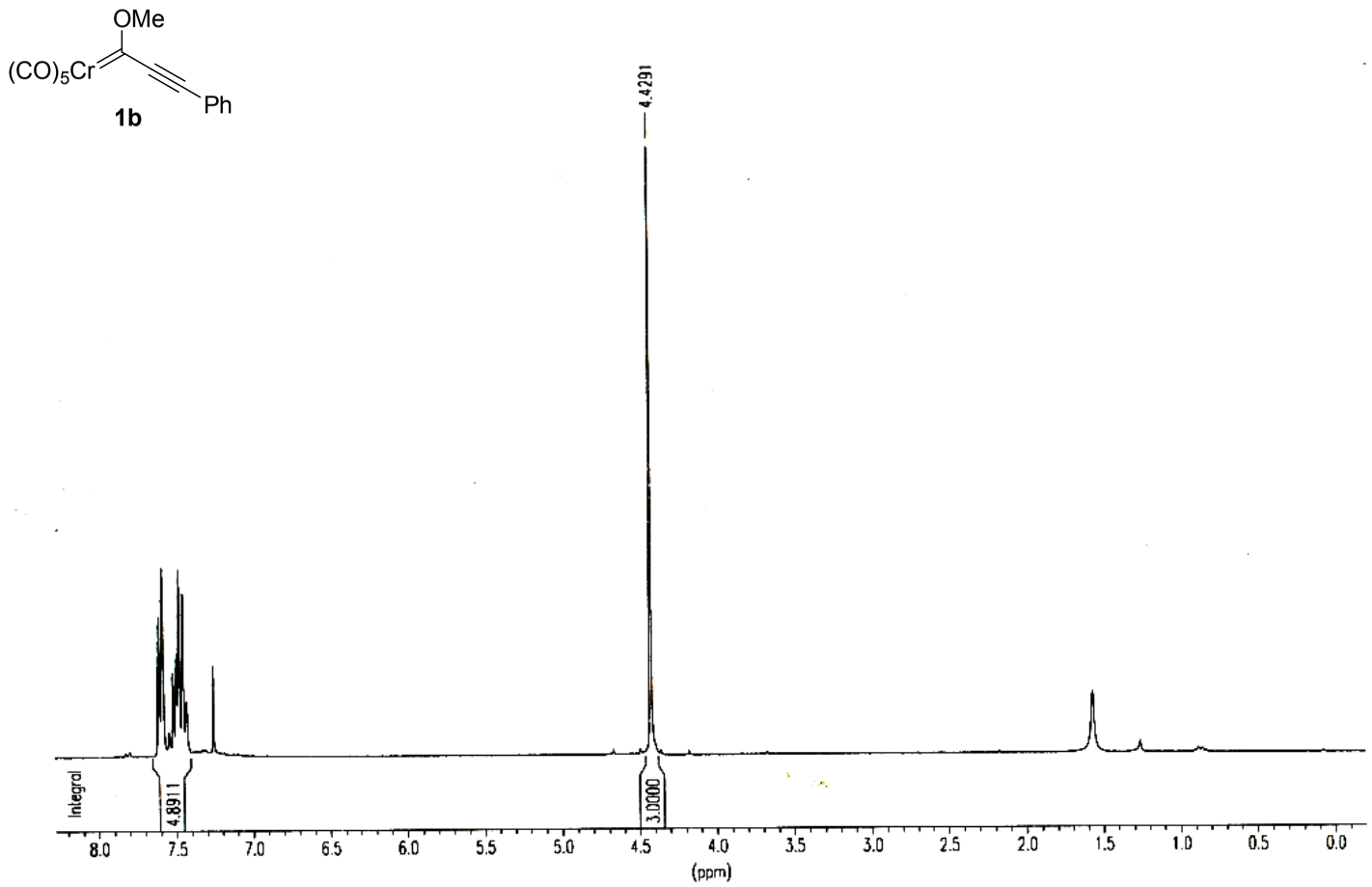
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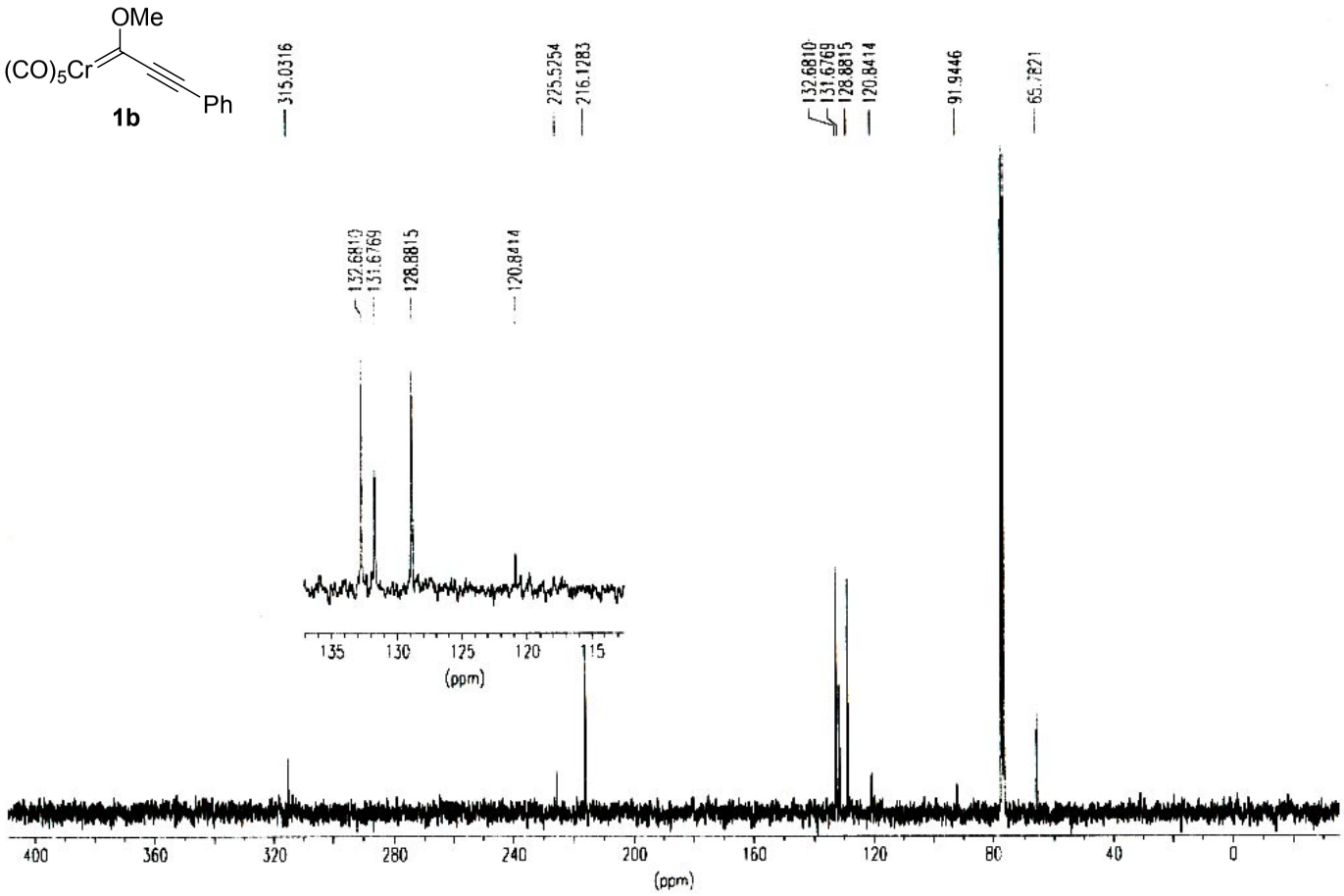
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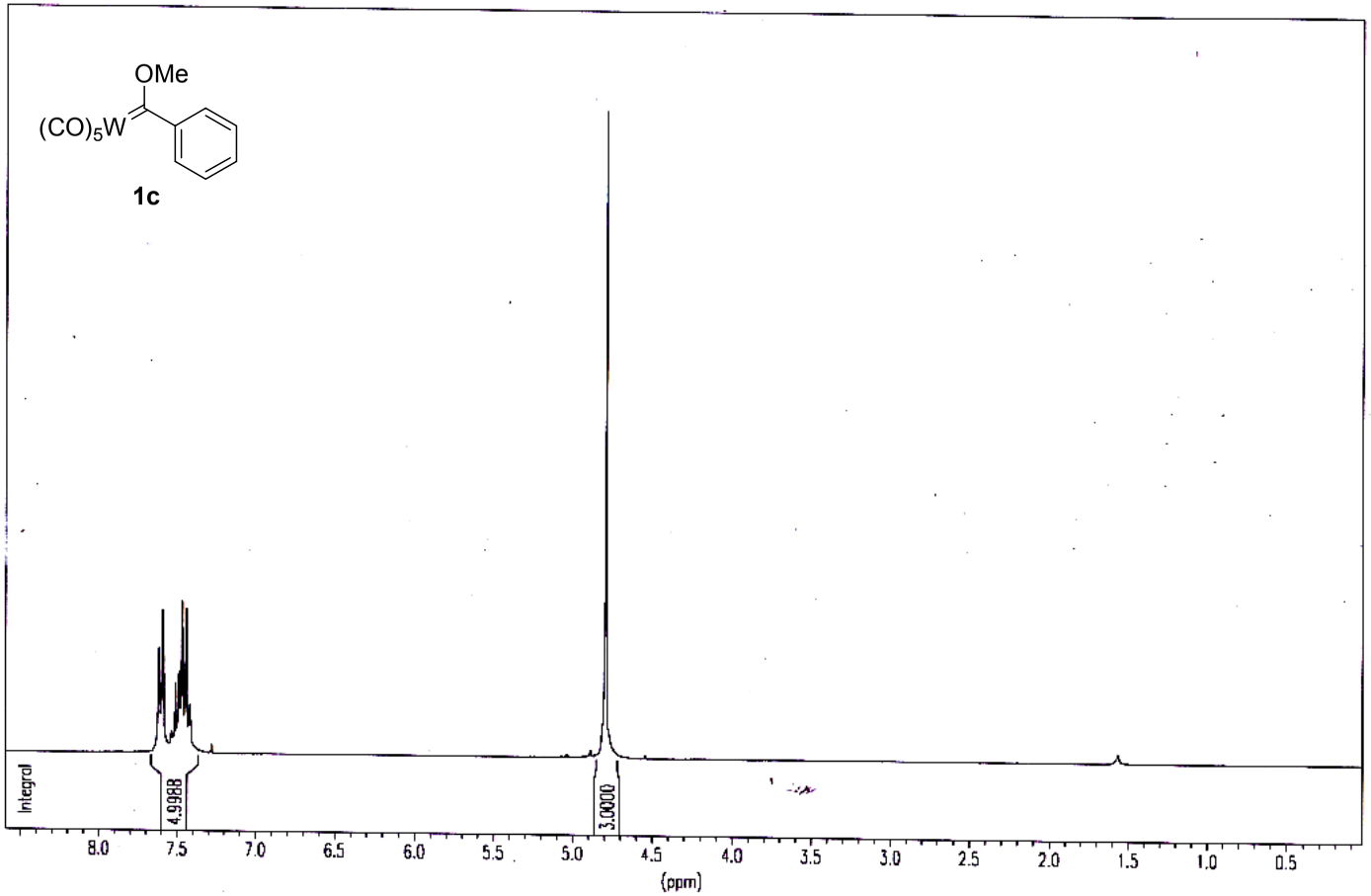
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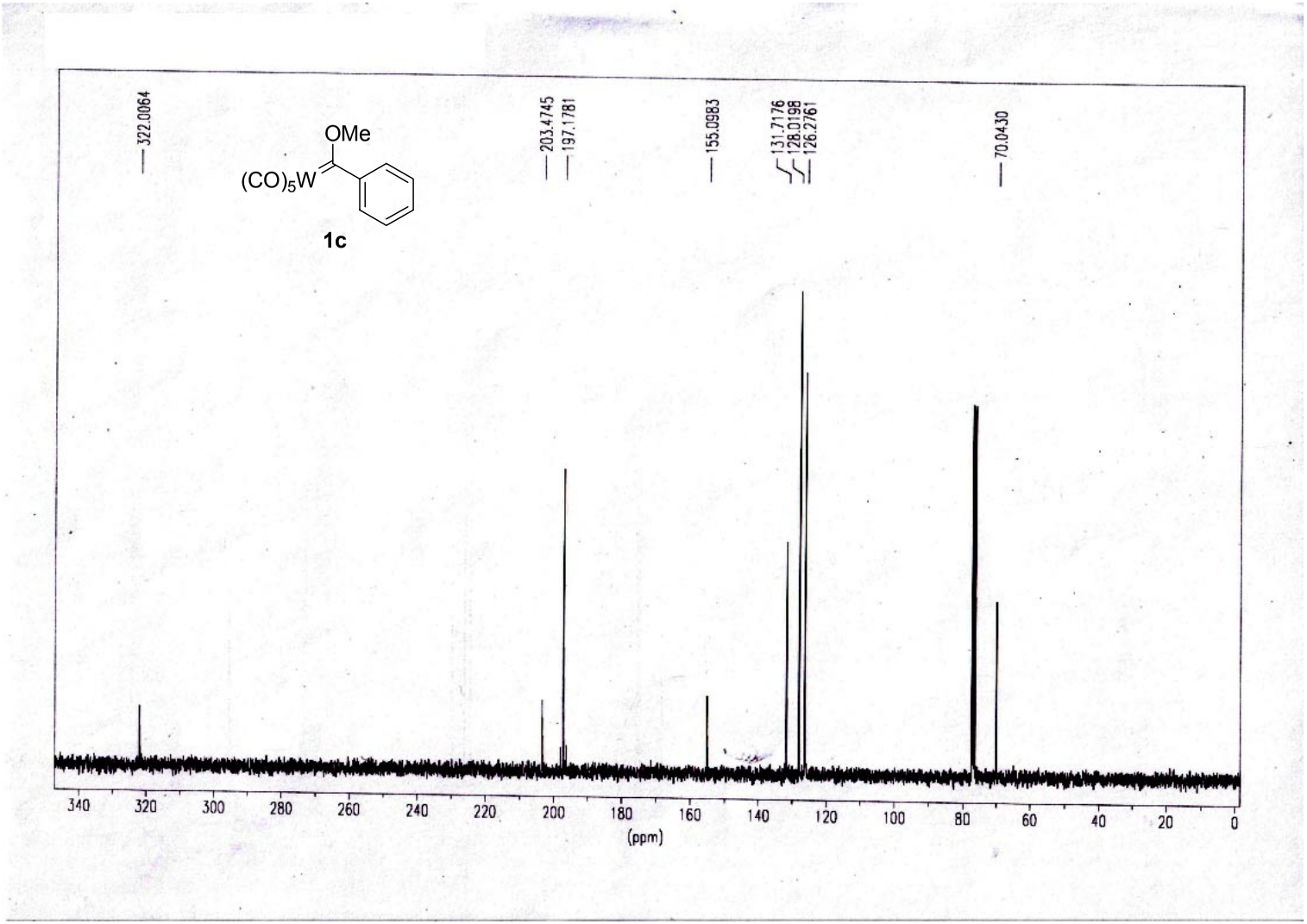
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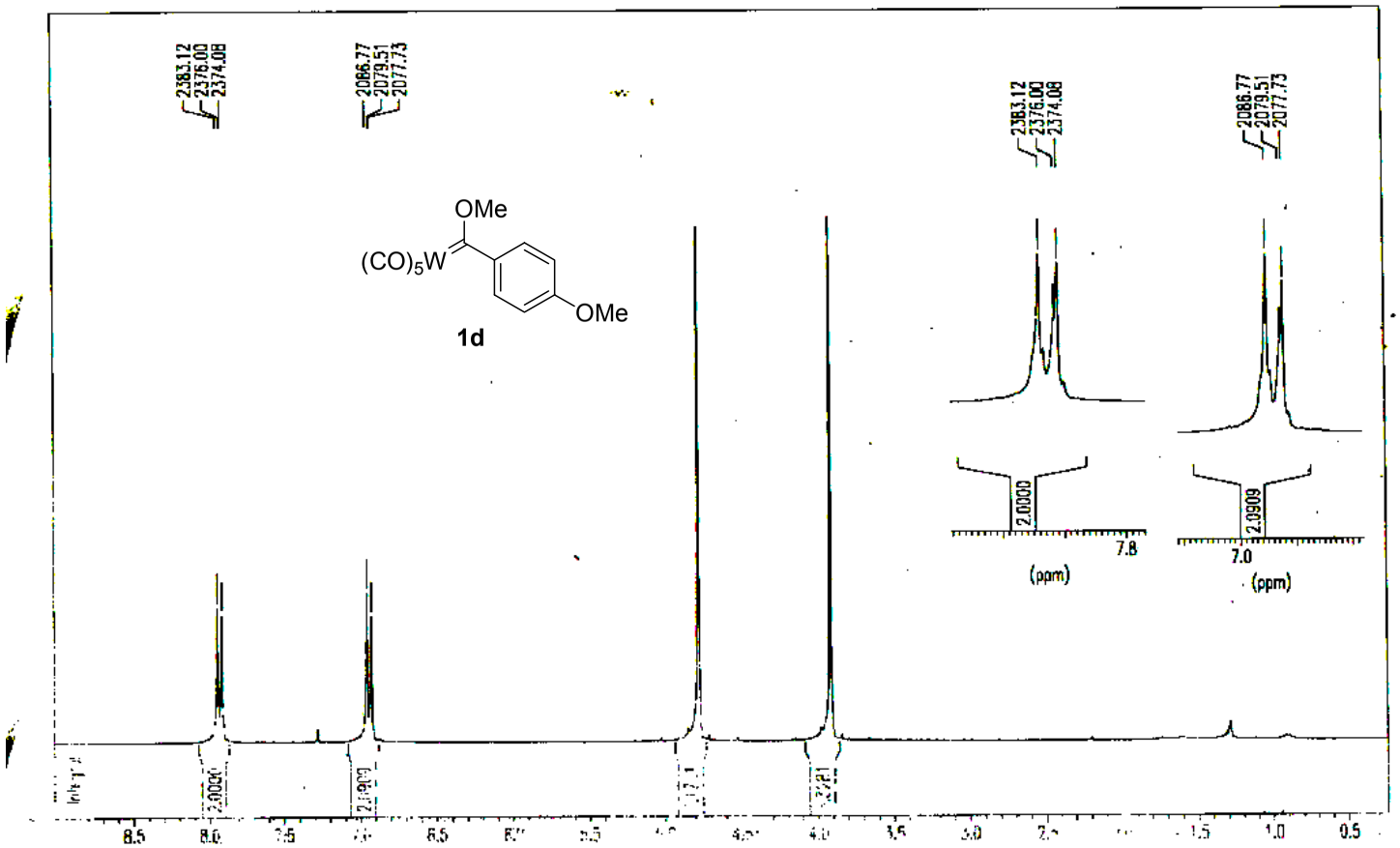
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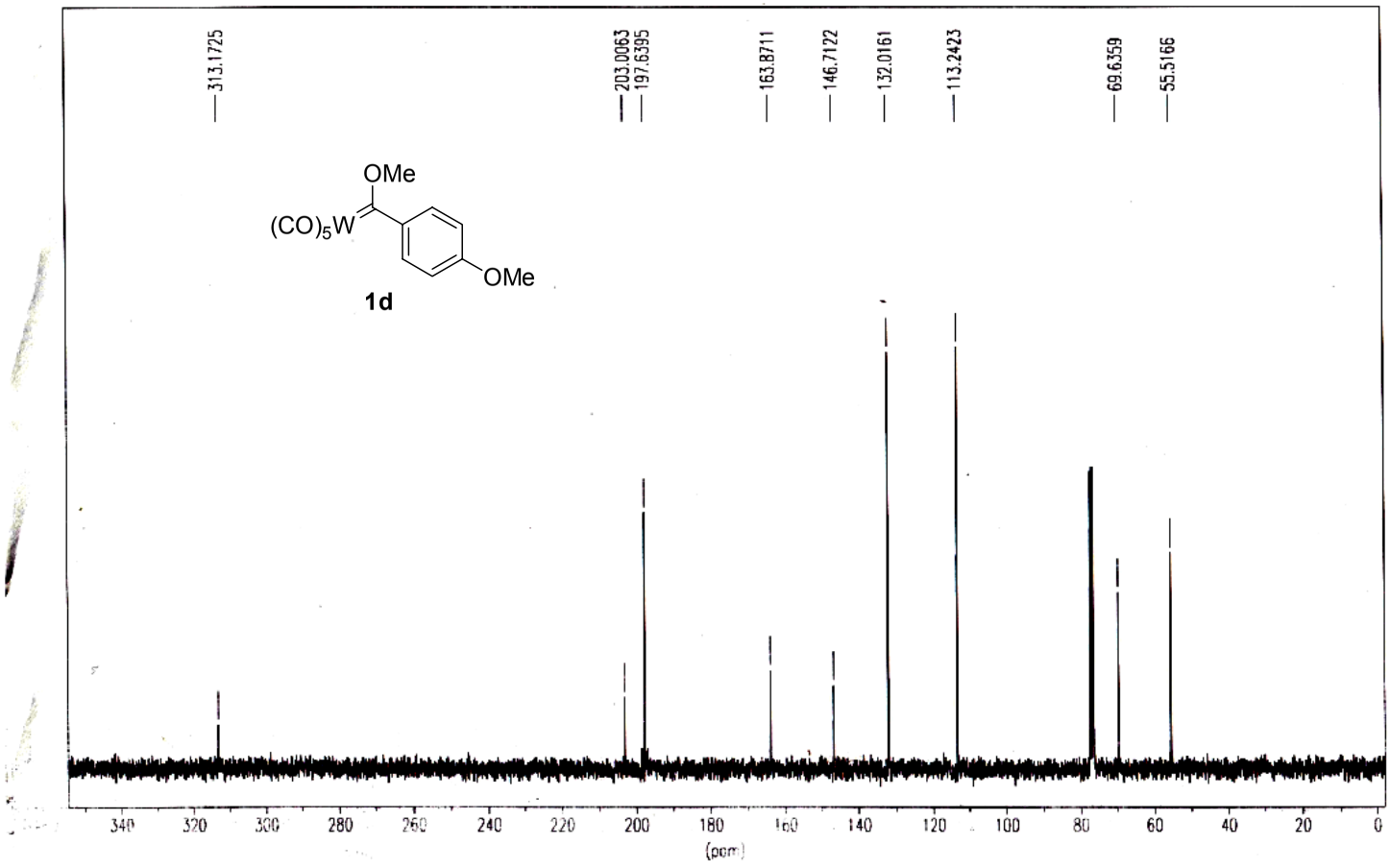
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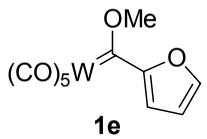
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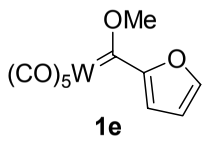

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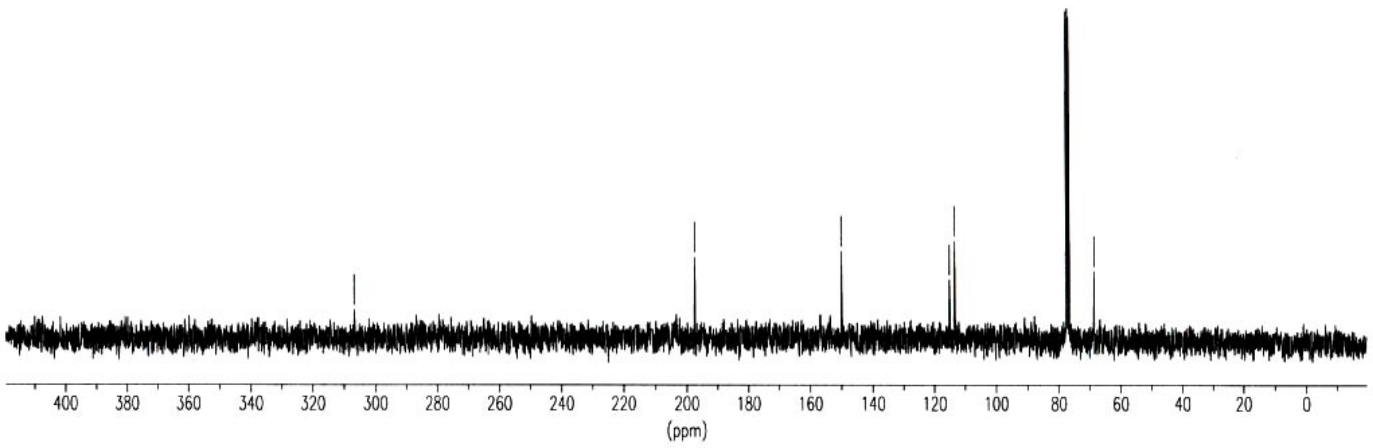

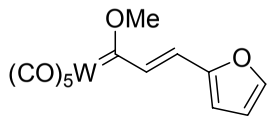

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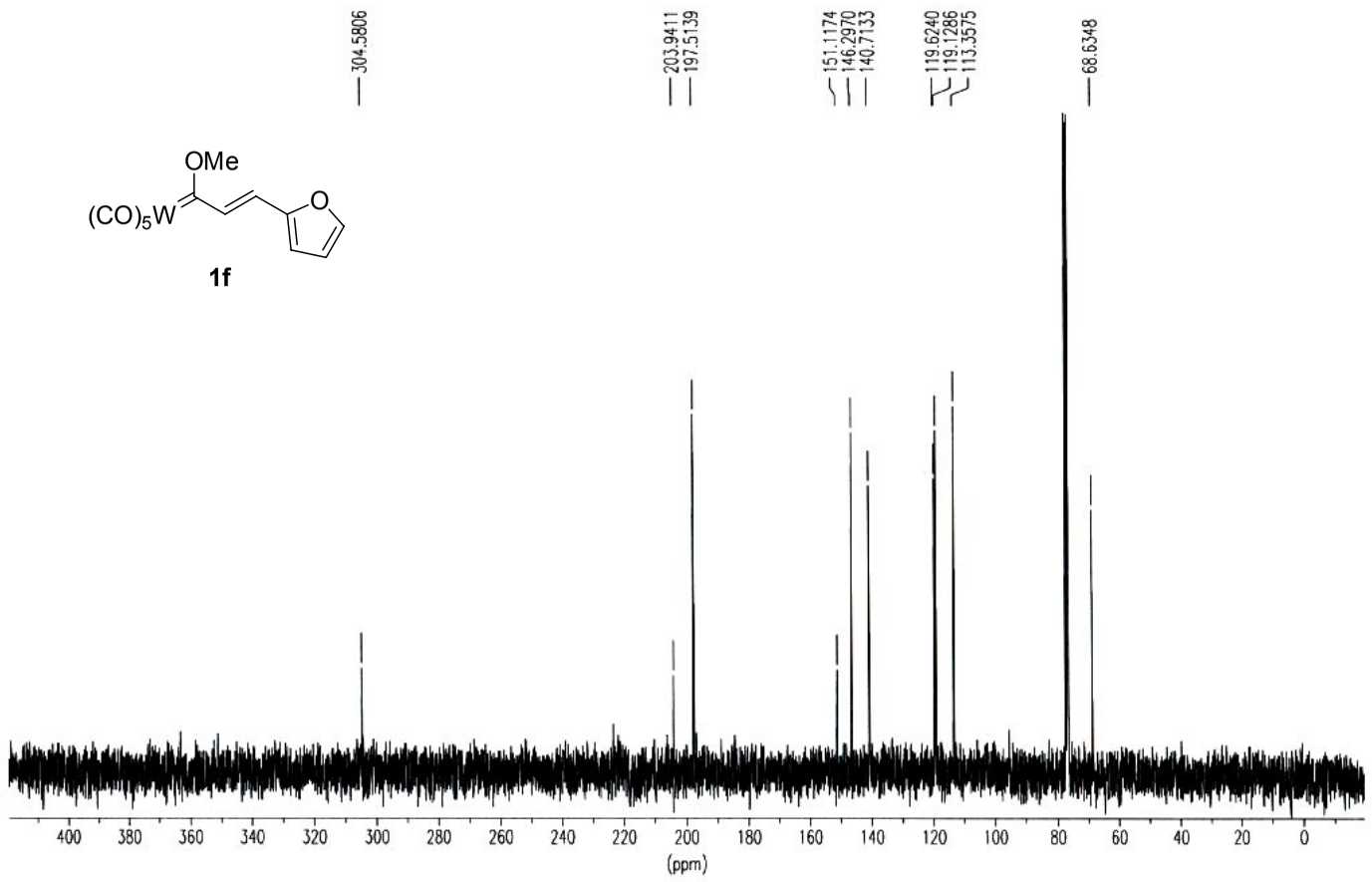
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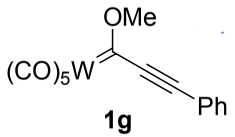

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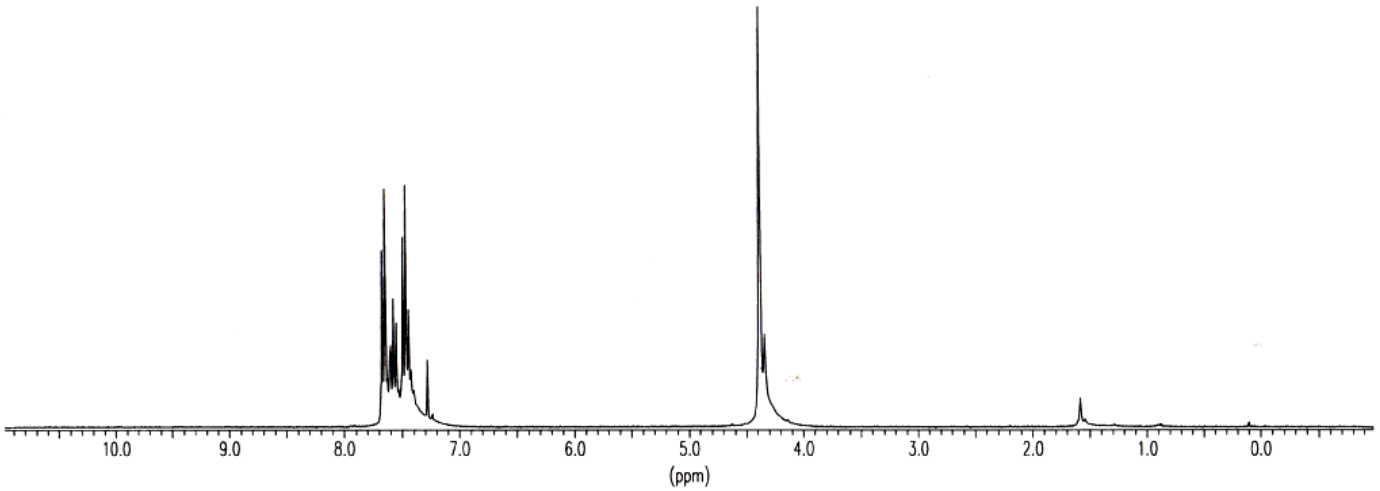

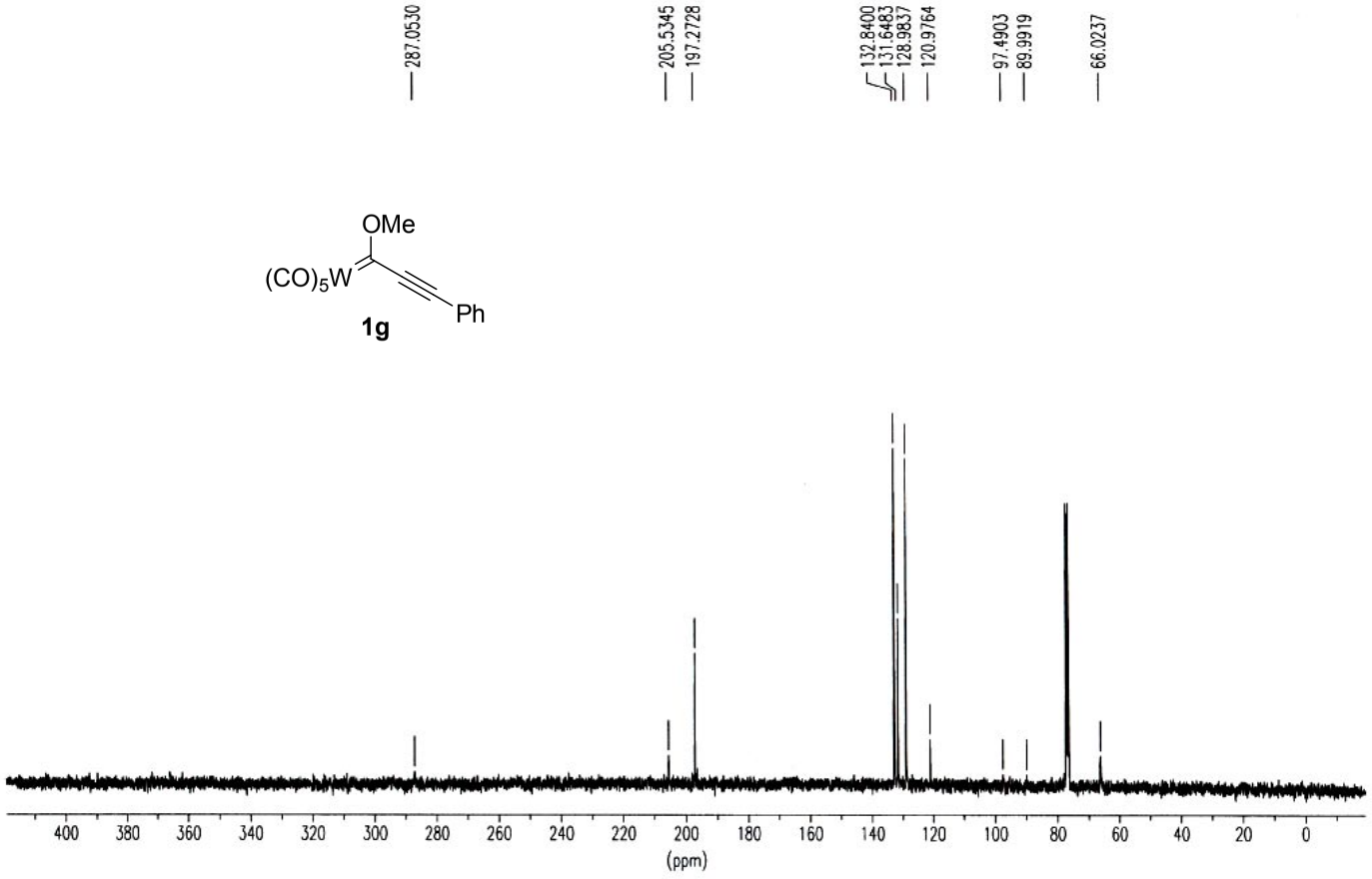
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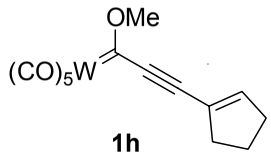
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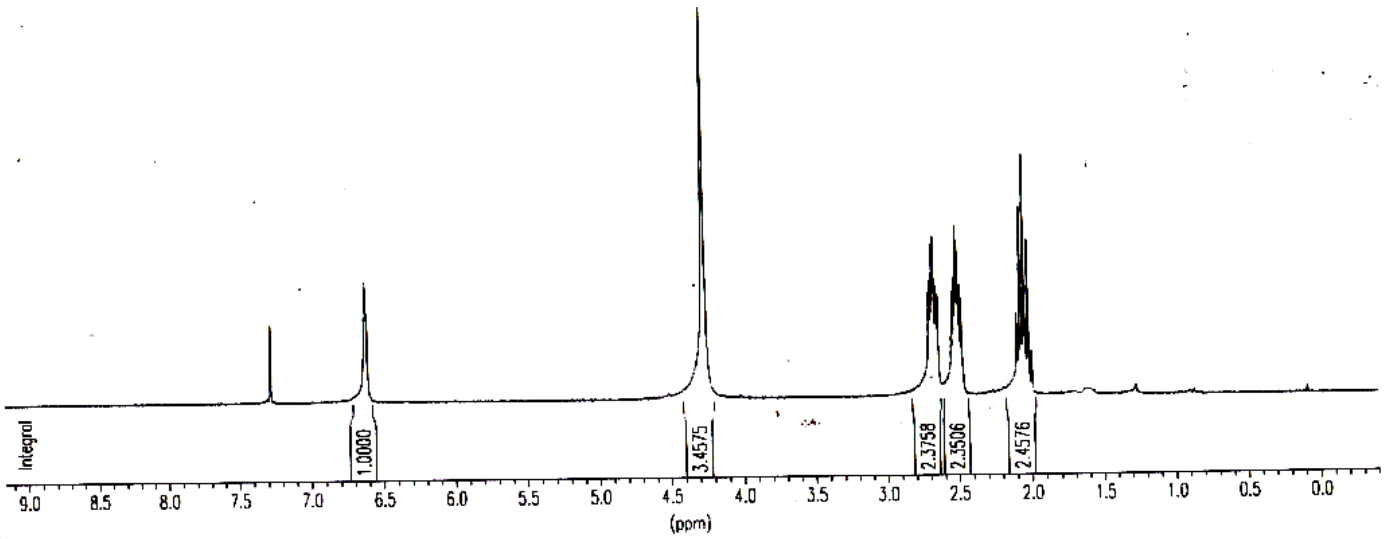
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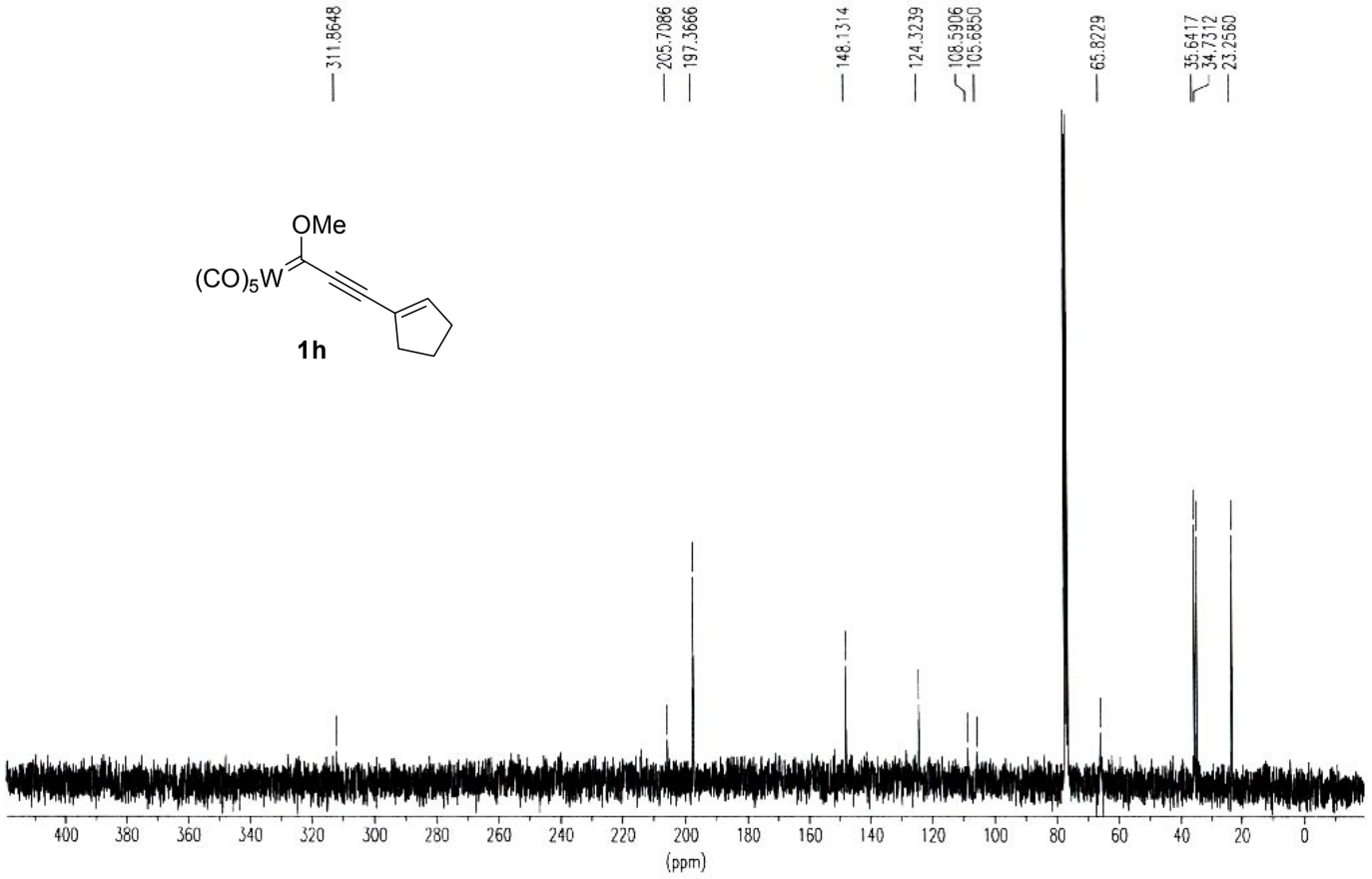
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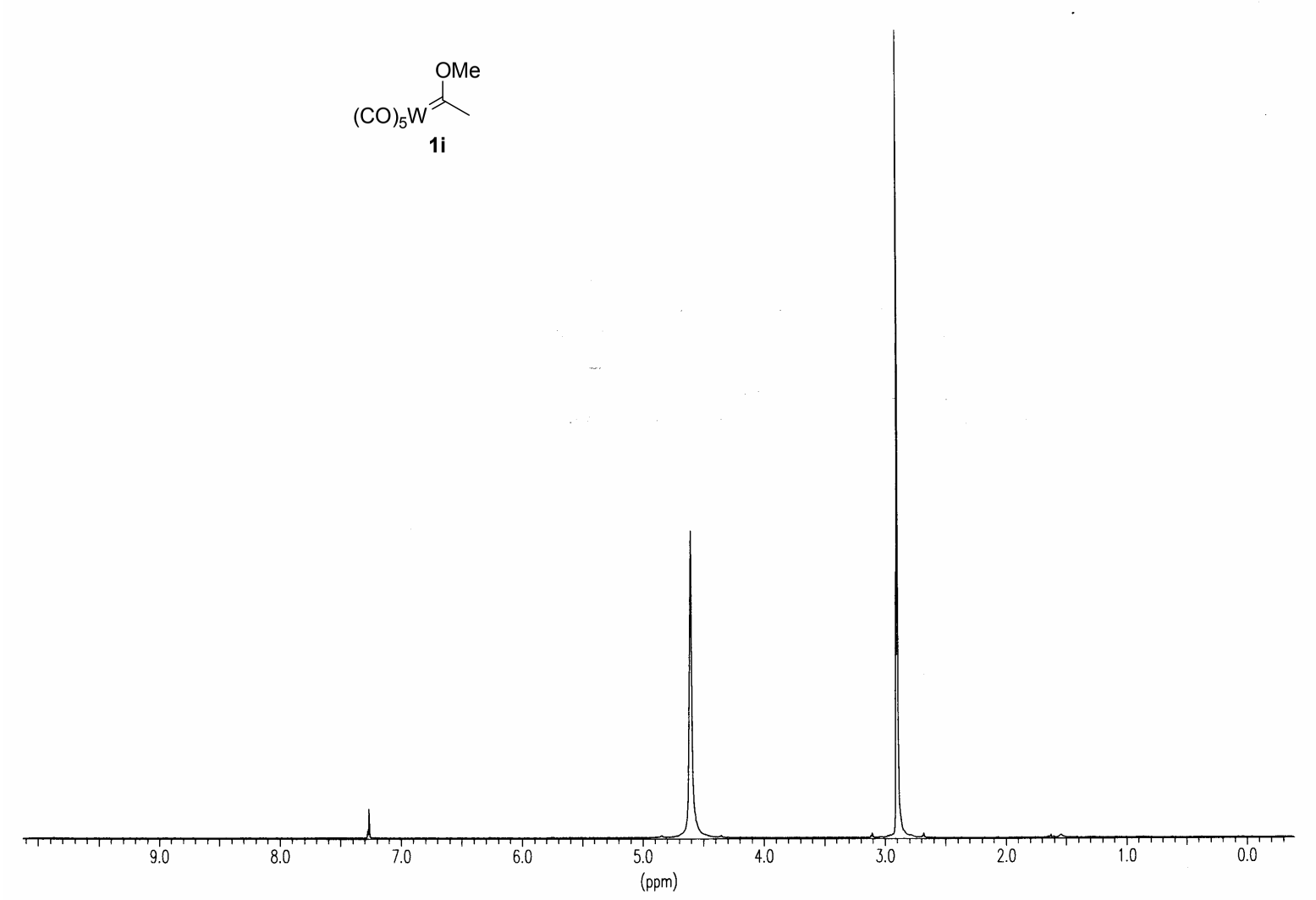
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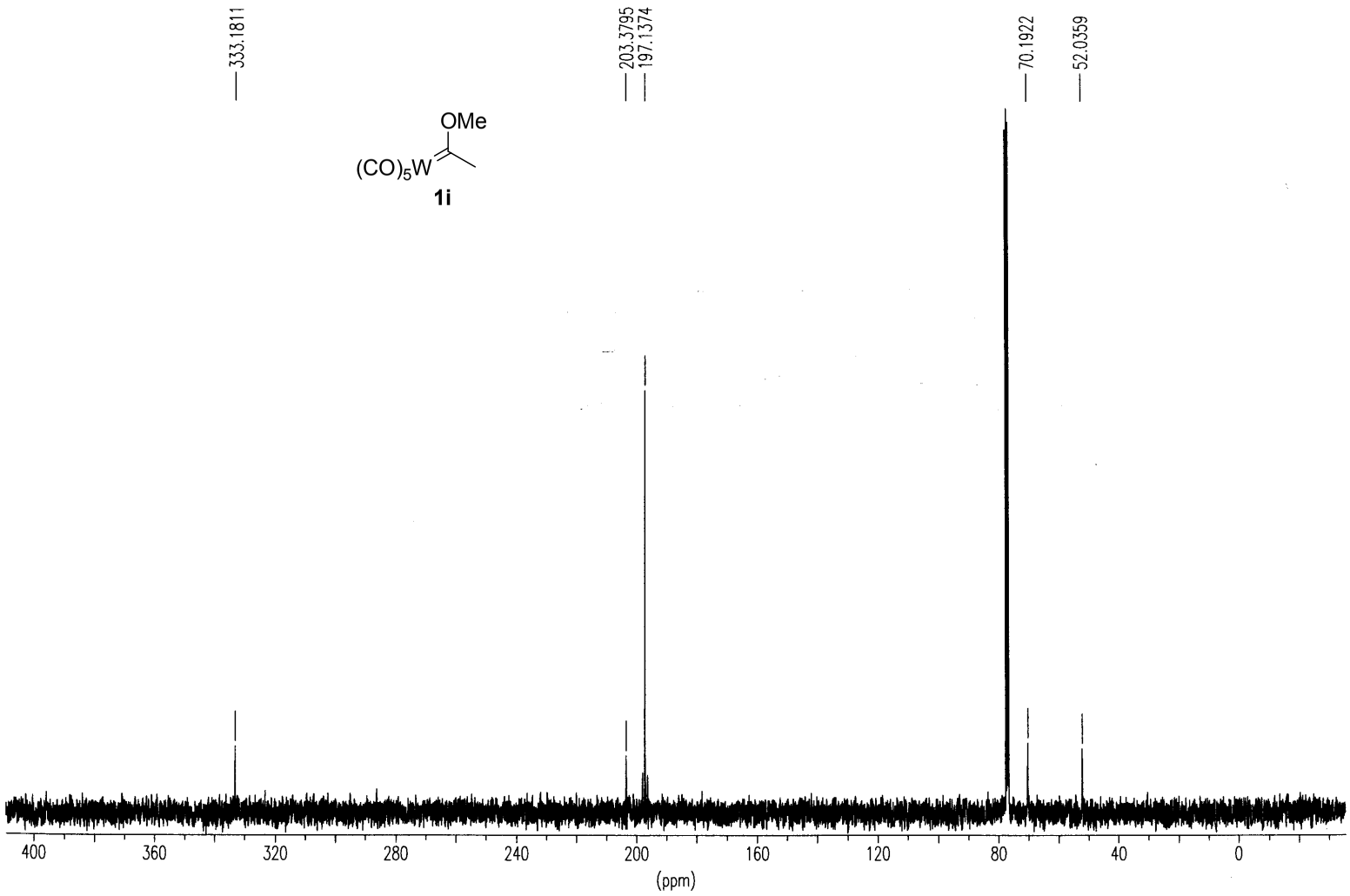
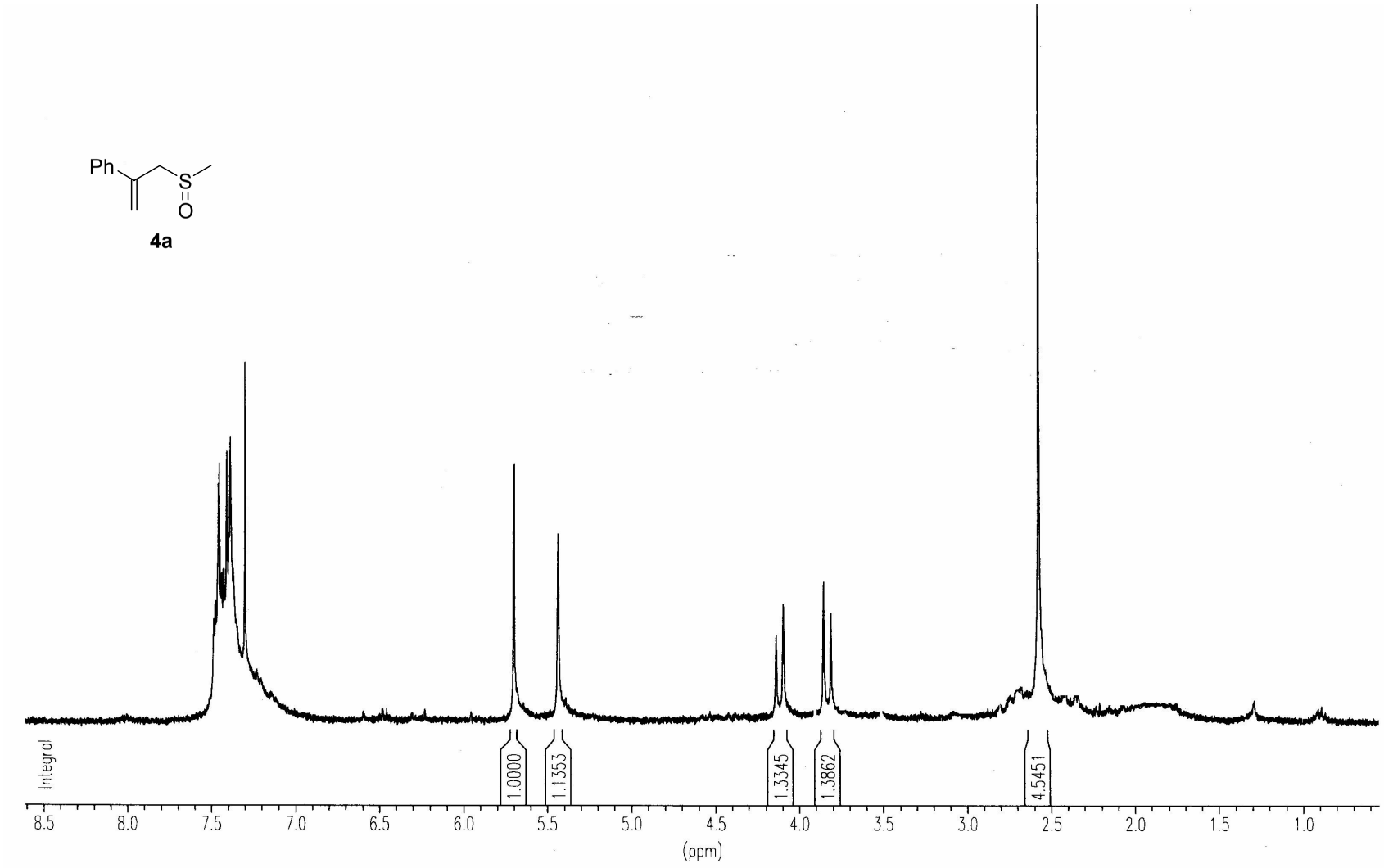
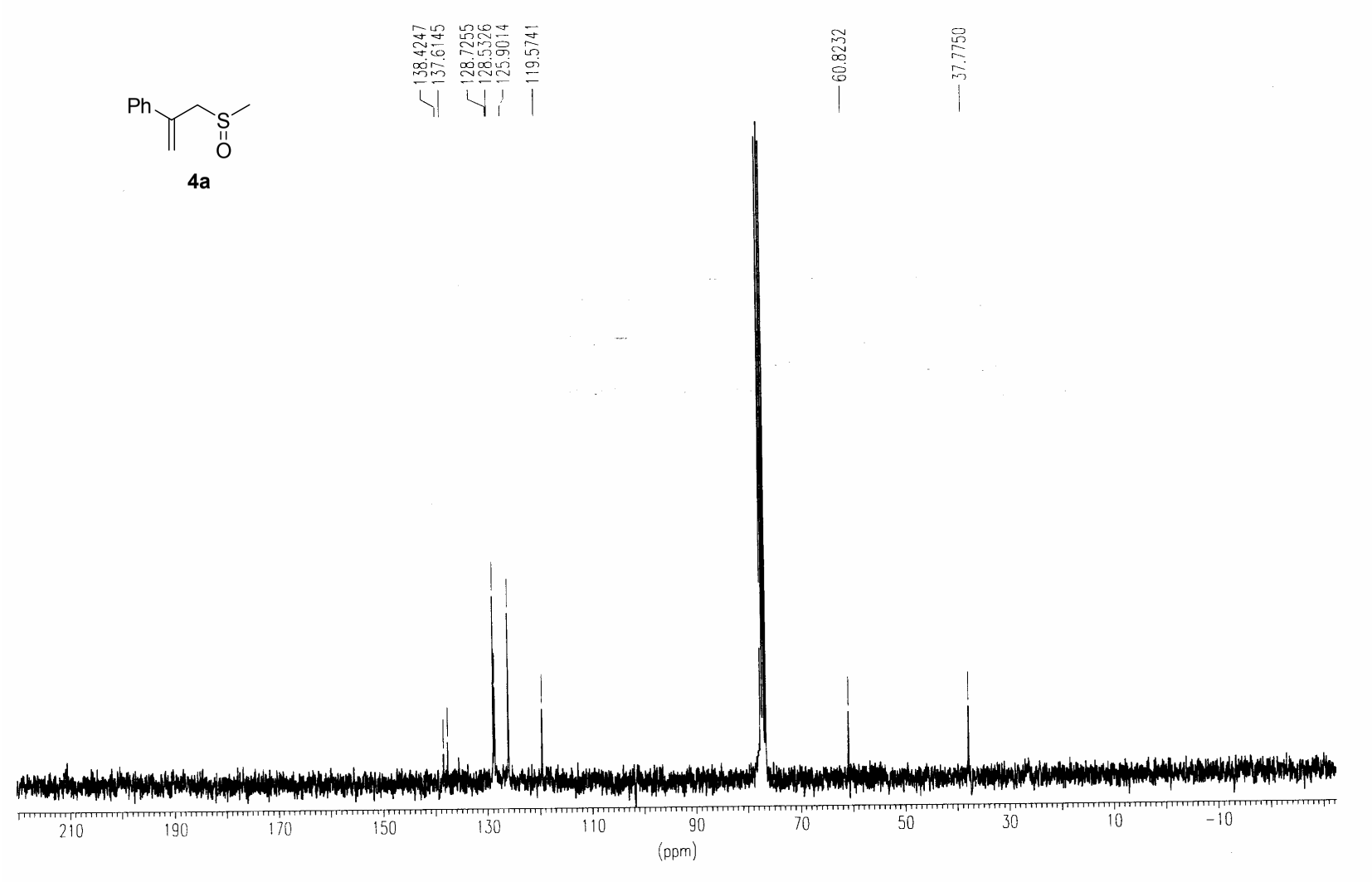
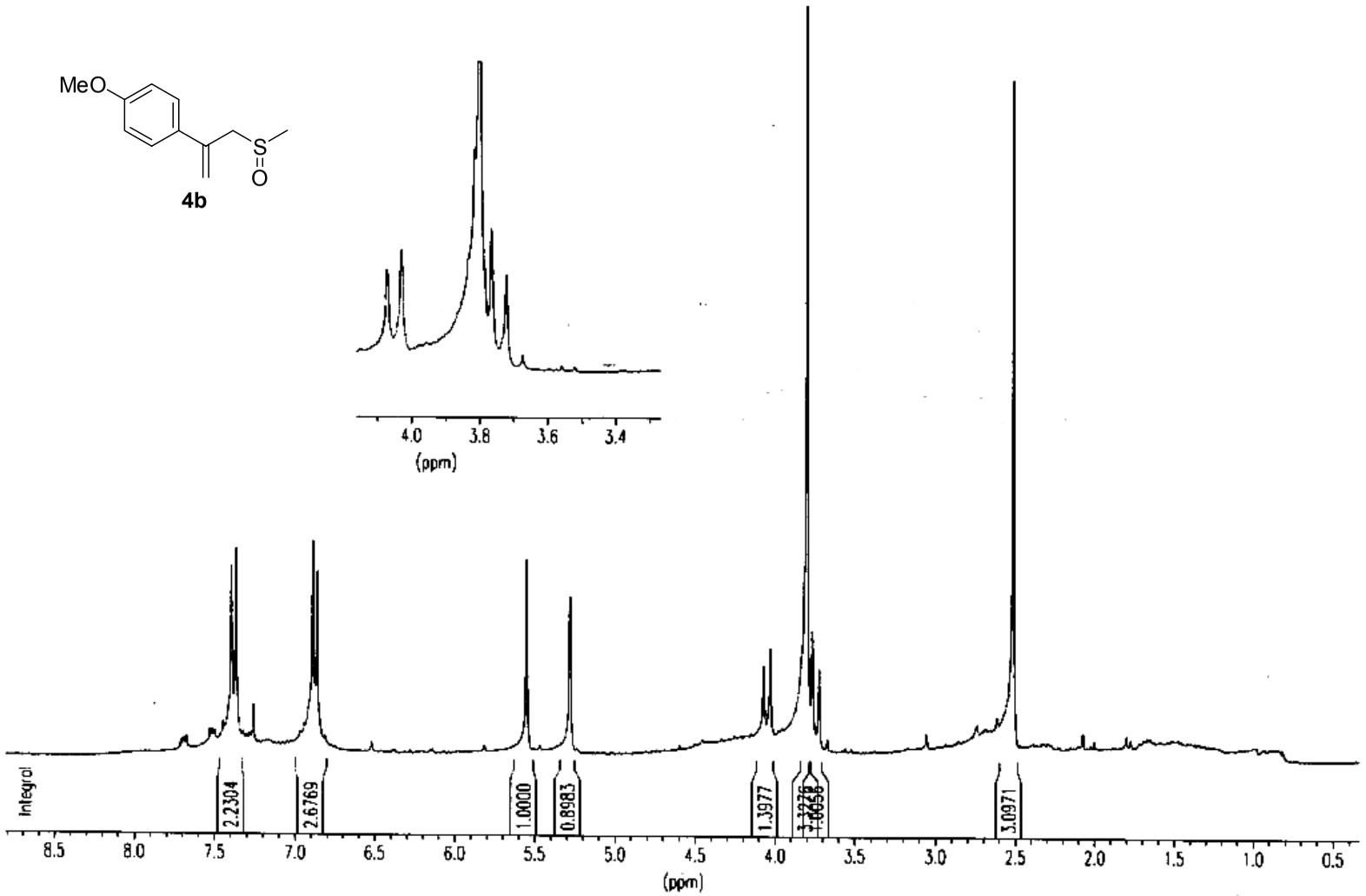
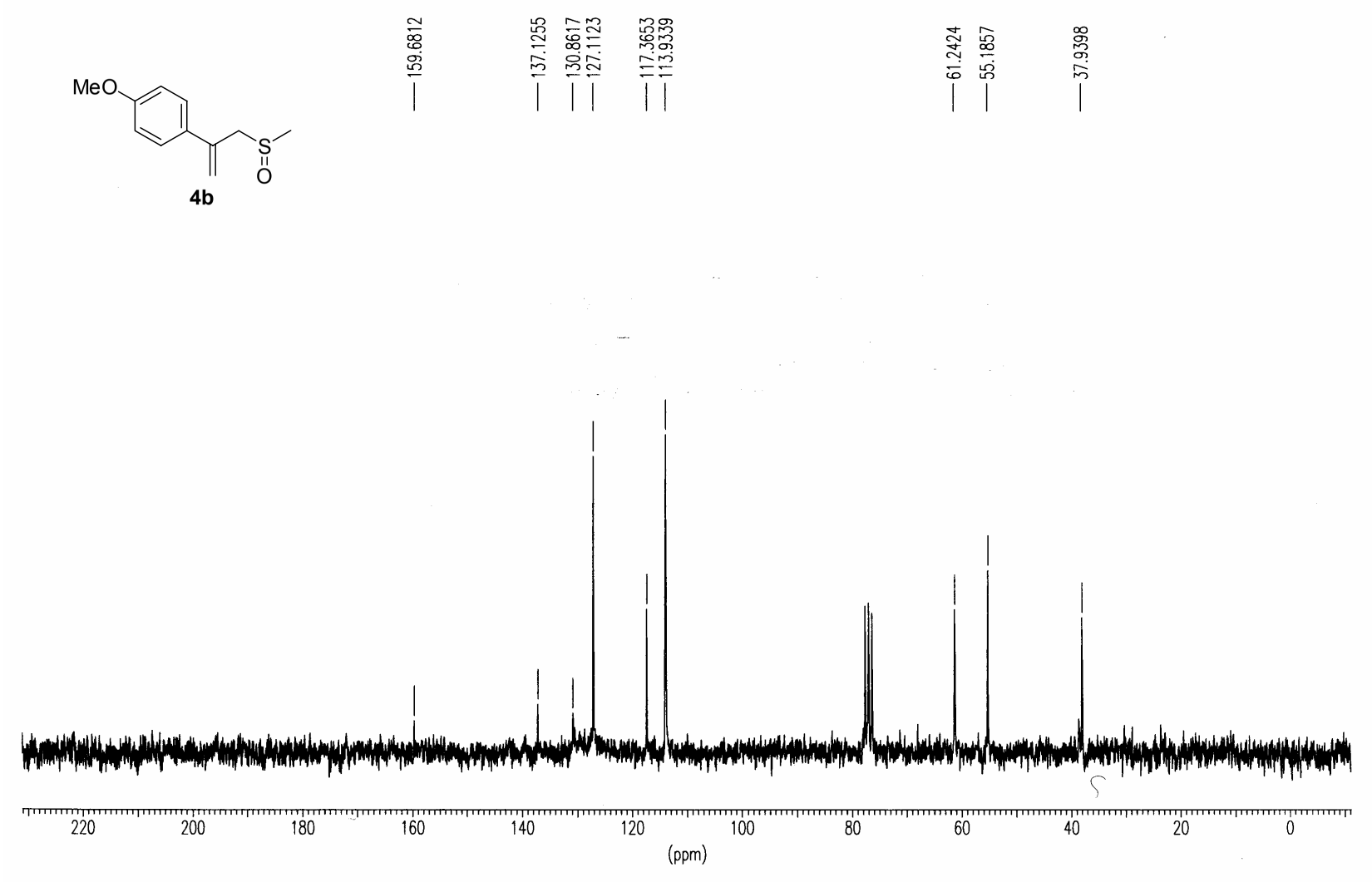
0.0
(ppm)

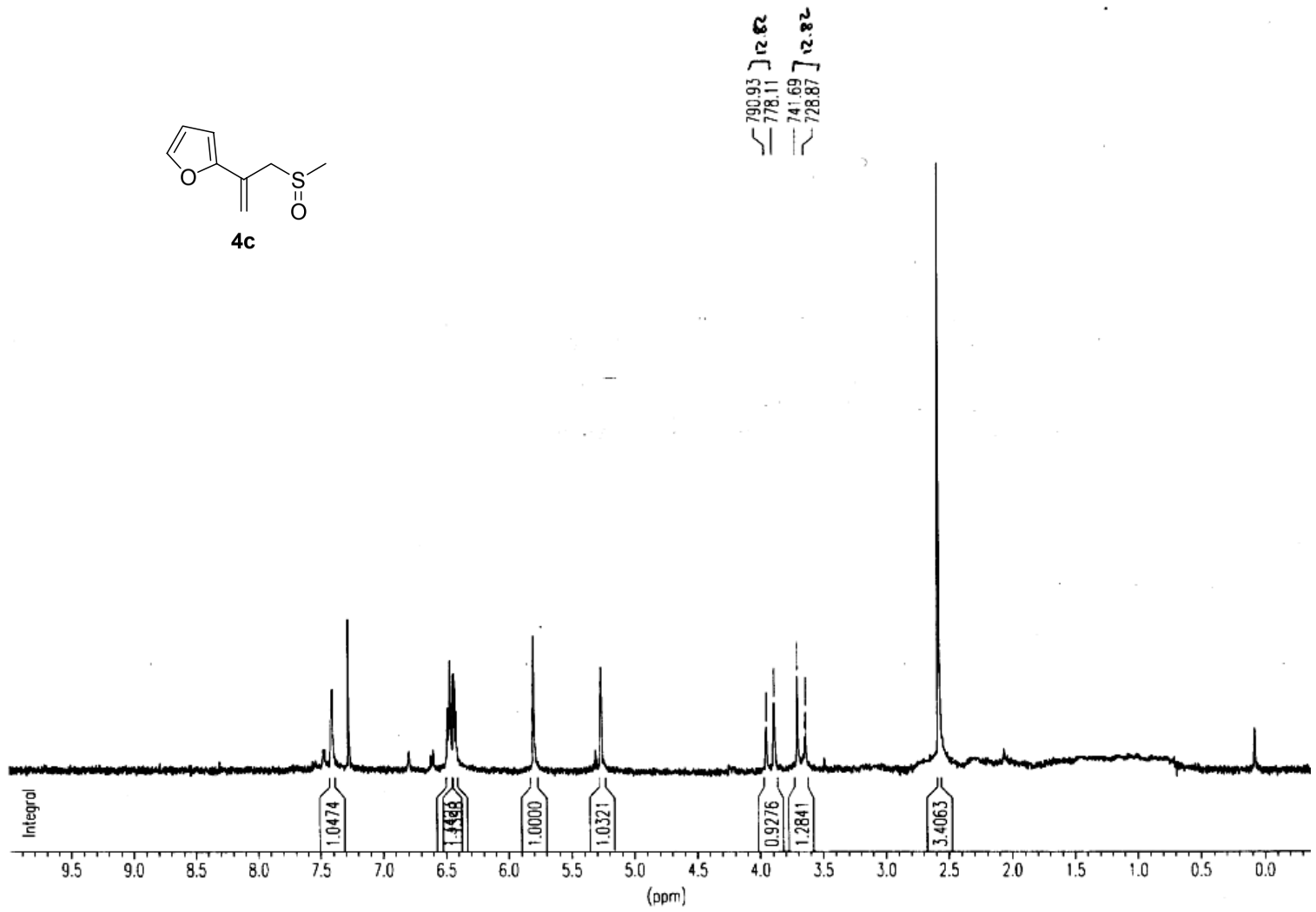

333.1811
203.3795
197.1374
70.1922
52.0359
OMe
(CO)5W
1i
400
360
320
280
240
200
160
120
80
40
0
(ppm)

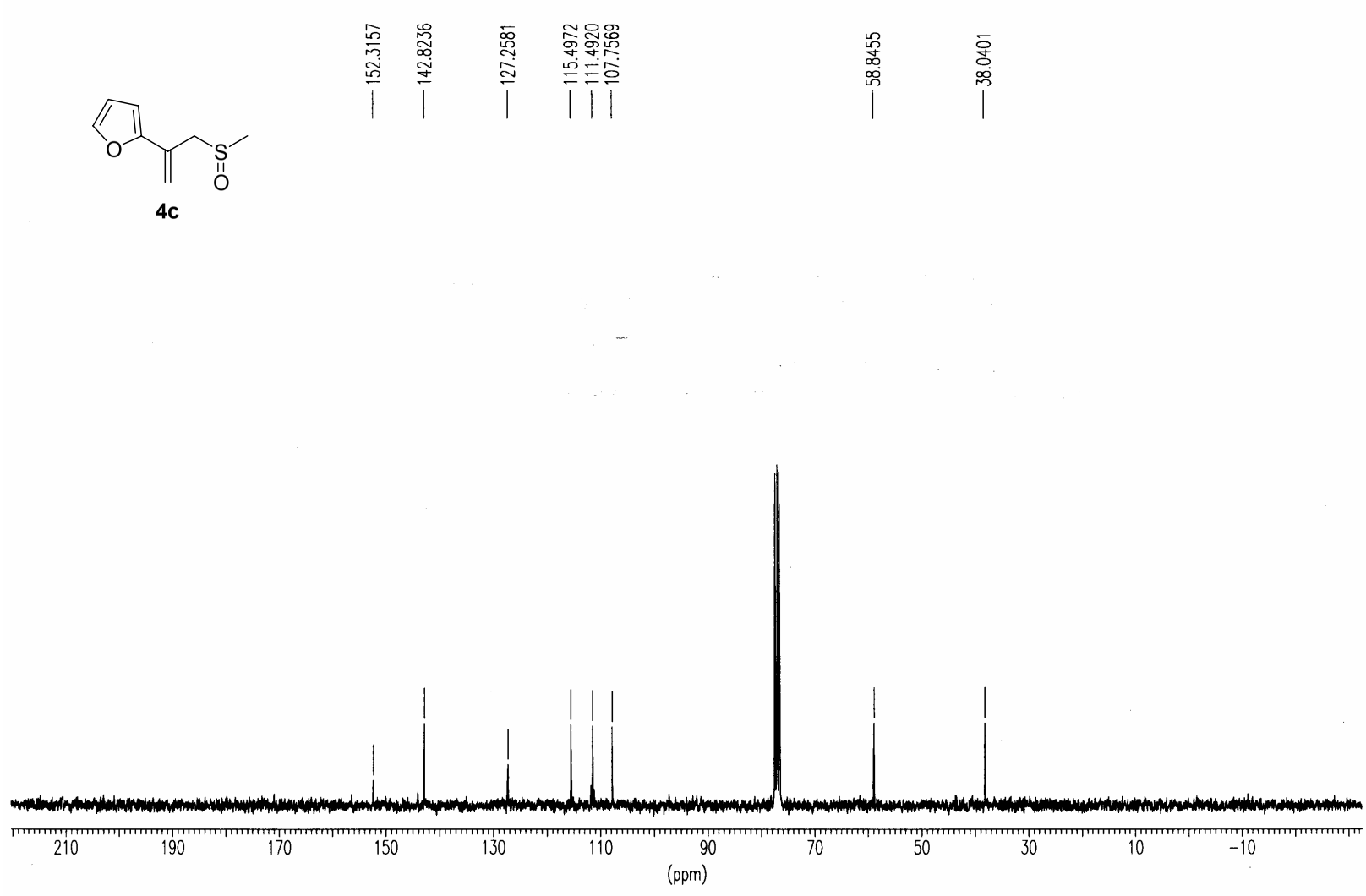

Ph
S
O
4a
Integral
1.0000
1.1353
1.3345
1.3862
4.5451
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

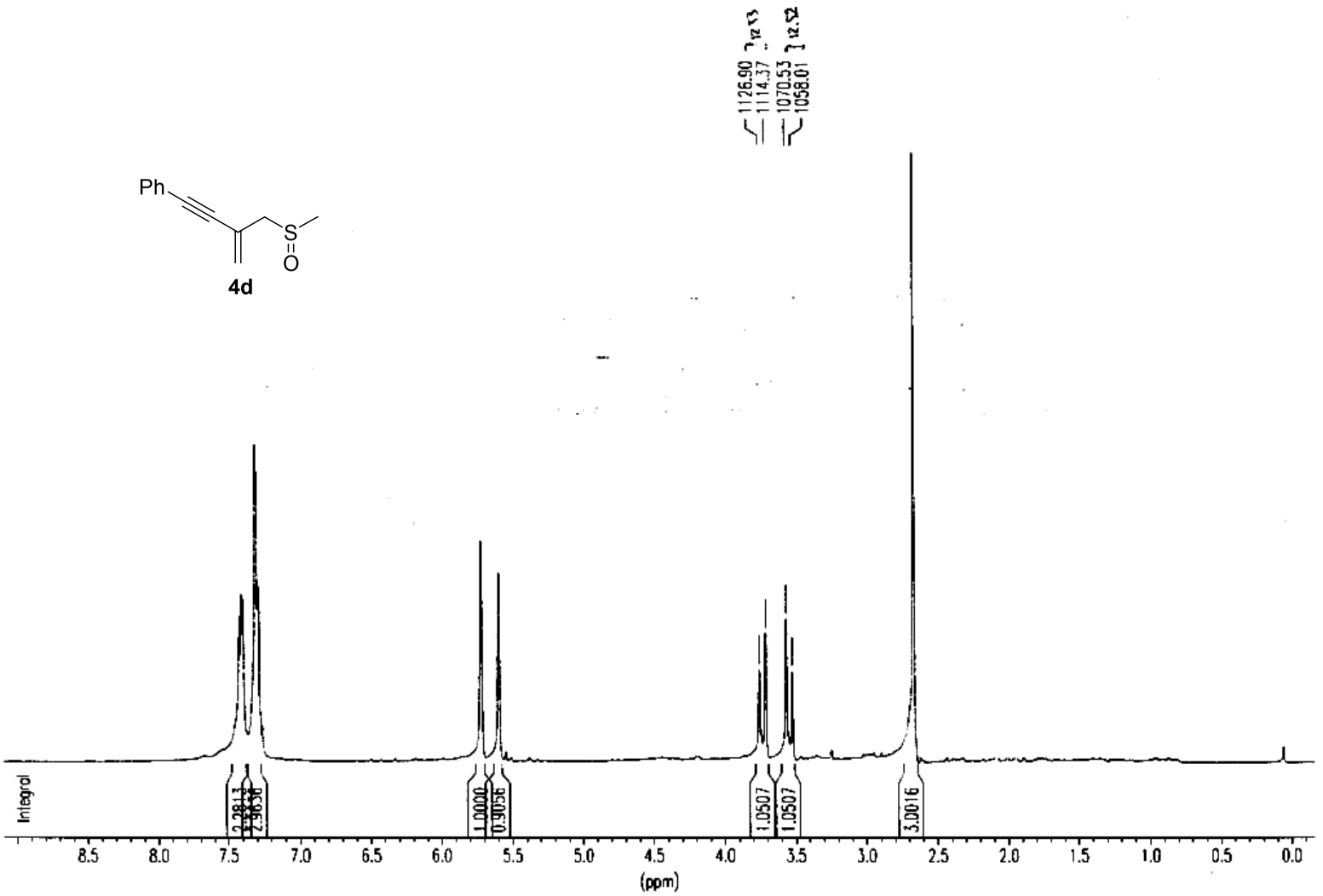

Ph
S
O
4a
138.4247
137.6145
128.7255
128.5326
125.9014
119.5741
60.8232
37.7750
210
190
170
150
130
110
90
70
50
30
10
−10
(ppm)

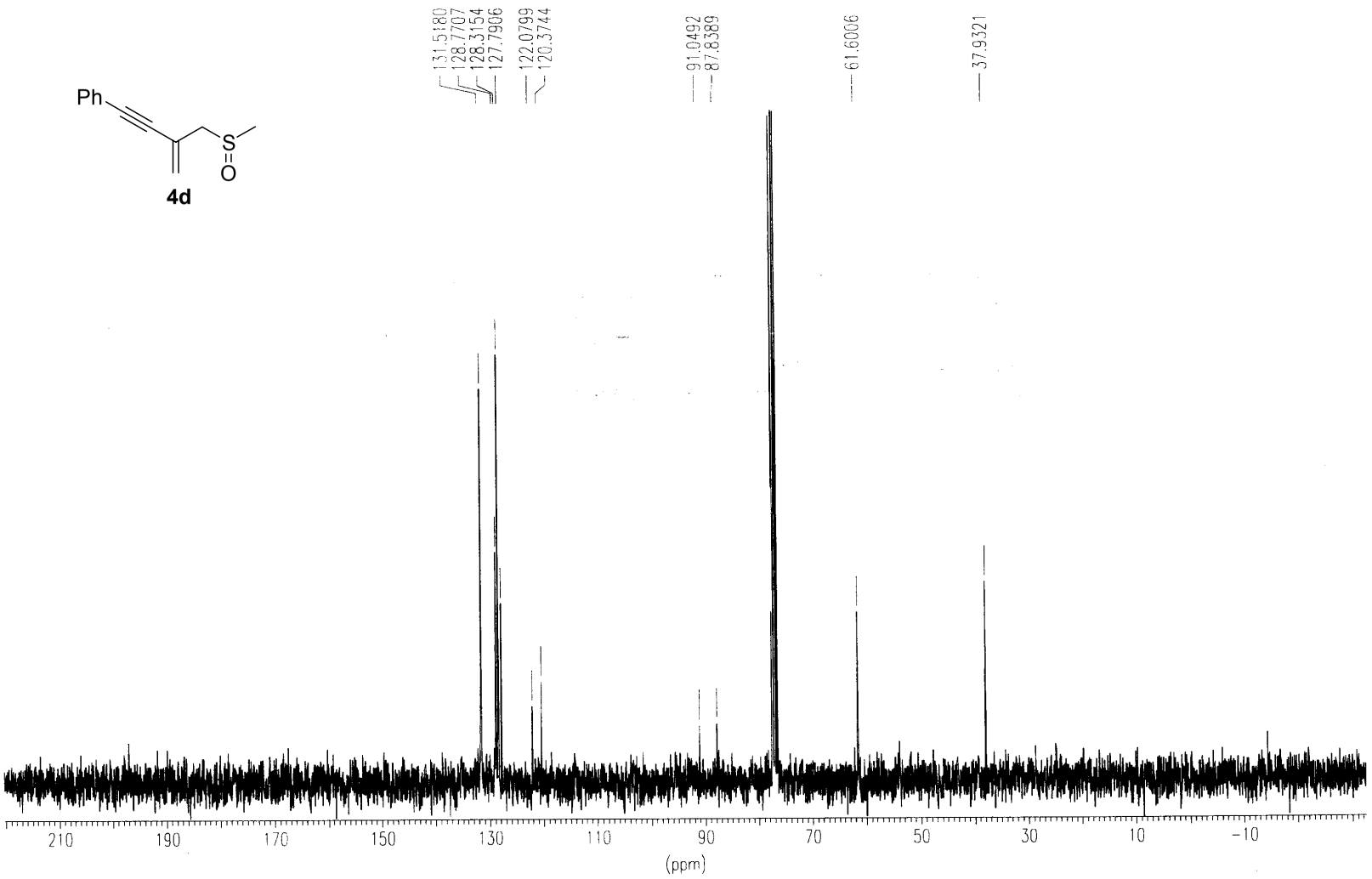

MeO
S
O
4b
4.0
3.8
3.6
3.4
(ppm)
Integral
2.2304
2.6769
1.0000
0.8983
1.3977
3.0971
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

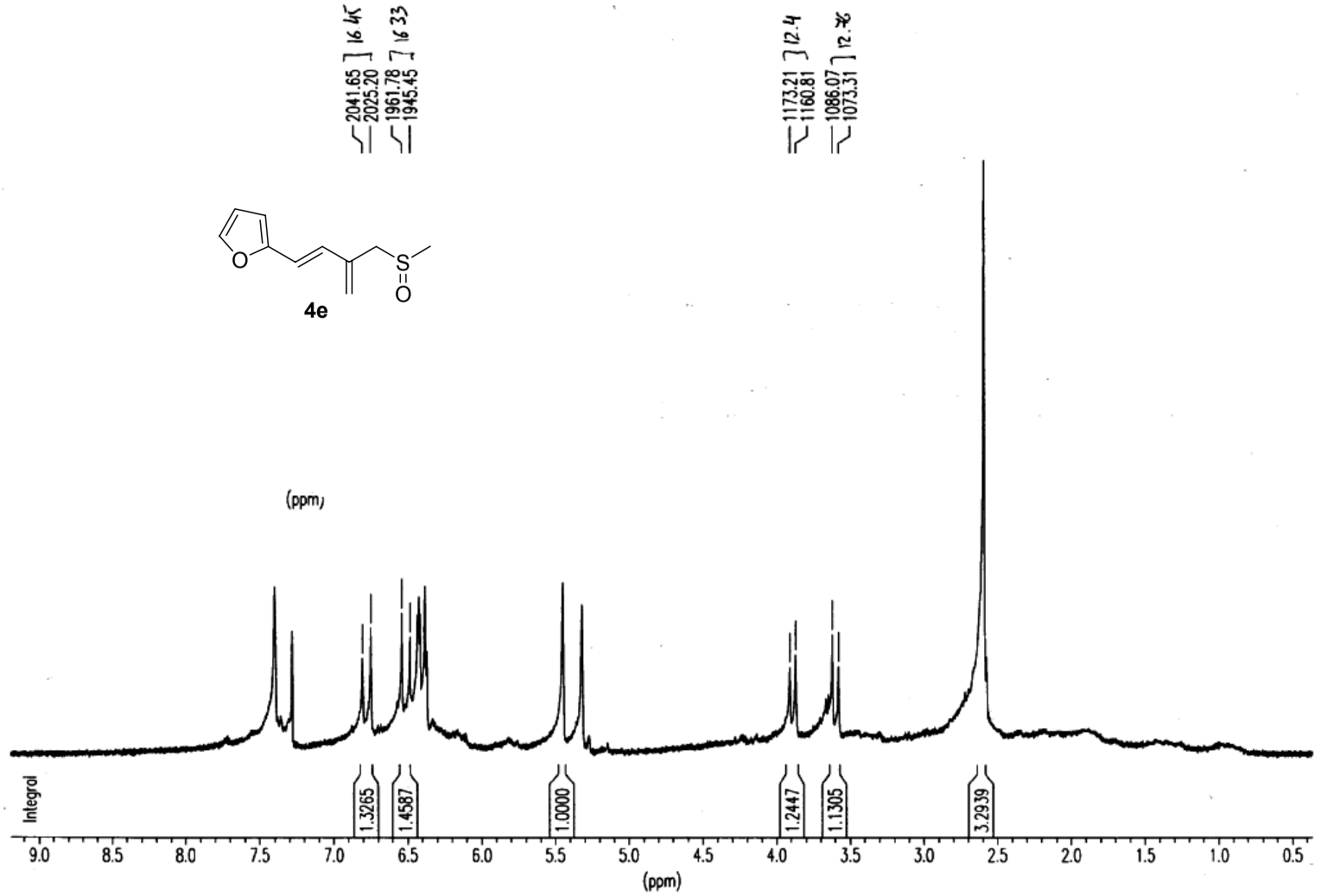

MeO
S
O
4b
159.6812
137.1255
130.8617
127.1123
117.3653
113.9339
61.2424
55.1857
37.9398
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

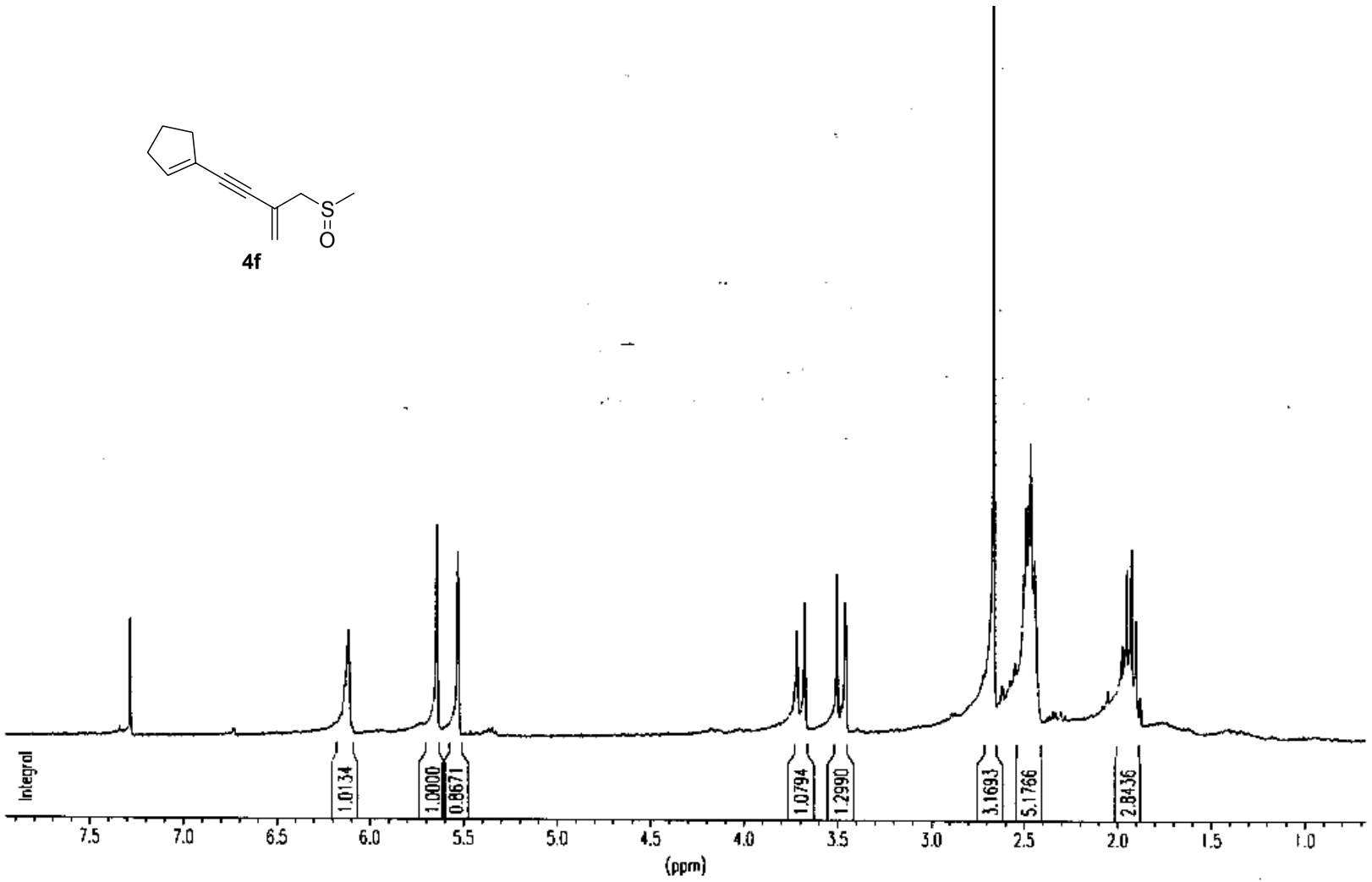

4c
790.93
778.11
741.69
728.87
12.82
12.82
Integral
1.0474
1.0000
1.0321
0.9276
1.2841
3.4063
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

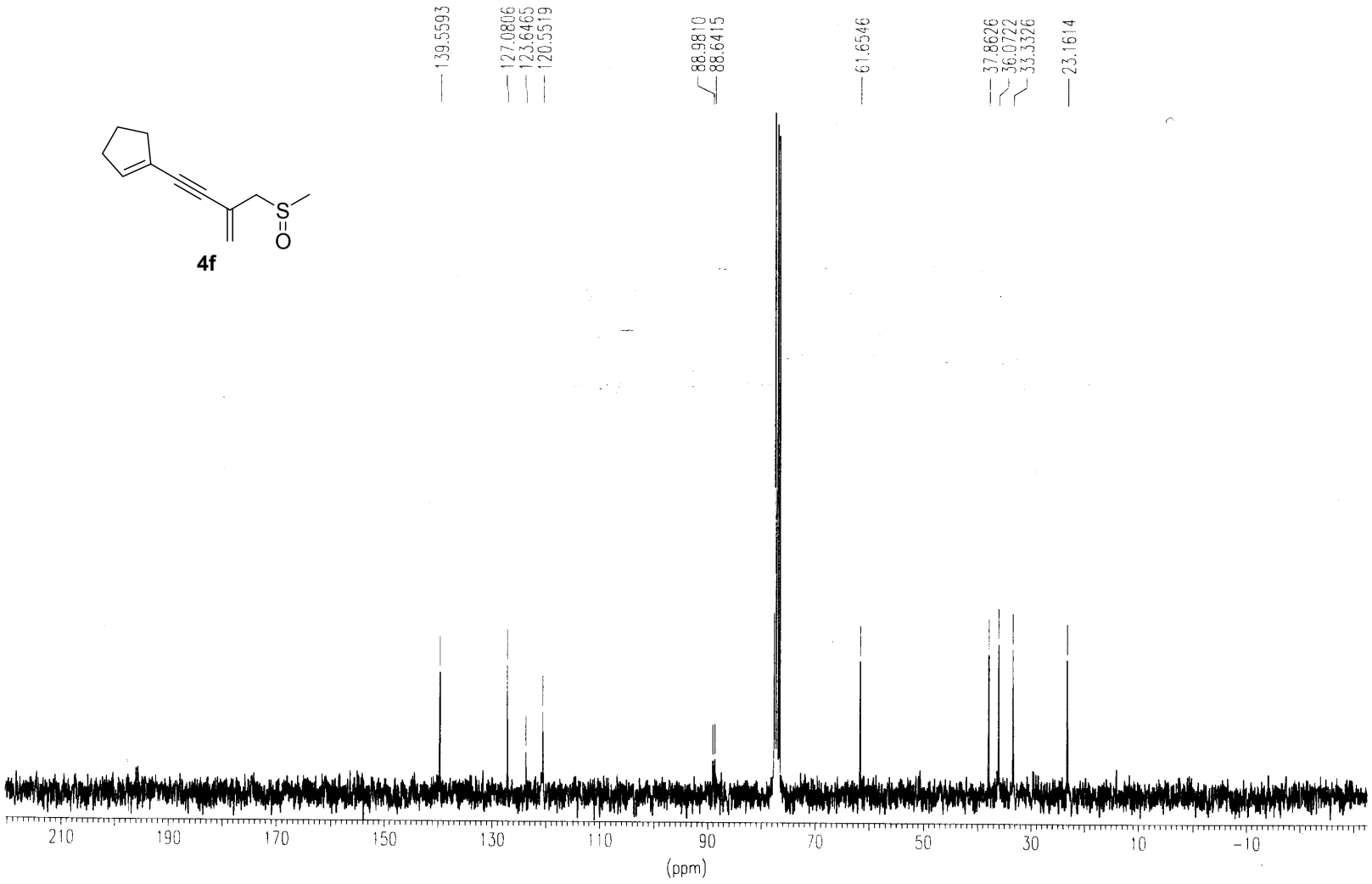

152.3157
142.8236
127.2581
115.4972
111.4920
107.7569
58.8455
38.0401
O
S
O=
4c
210
190
170
150
130
110
90
70
50
30
10
−10
(ppm)

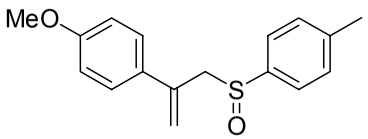

Ph
S
O
4d
1126.90
1114.37
1070.53
1058.01
Integral
2.2813
2.3636
1.0000
0.3056
1.0507
1.0507
3.0016
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


Ph
S
O
4d
131.5180
128.7707
128.3154
127.7906
122.0799
120.3744
91.0492
87.8389
61.6006
37.9321
210
190
170
150
130
110
90
70
50
30
10
-10
(ppm)


2041.65
2025.20
1961.78
1945.45
1173.21
1160.81
1086.07
1073.31
O
S
O=S
O
4e
(ppm)
Integral
1.3265
1.4587
1.0000
1.2447
1.1305
3.2939
9.0
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
(ppm)

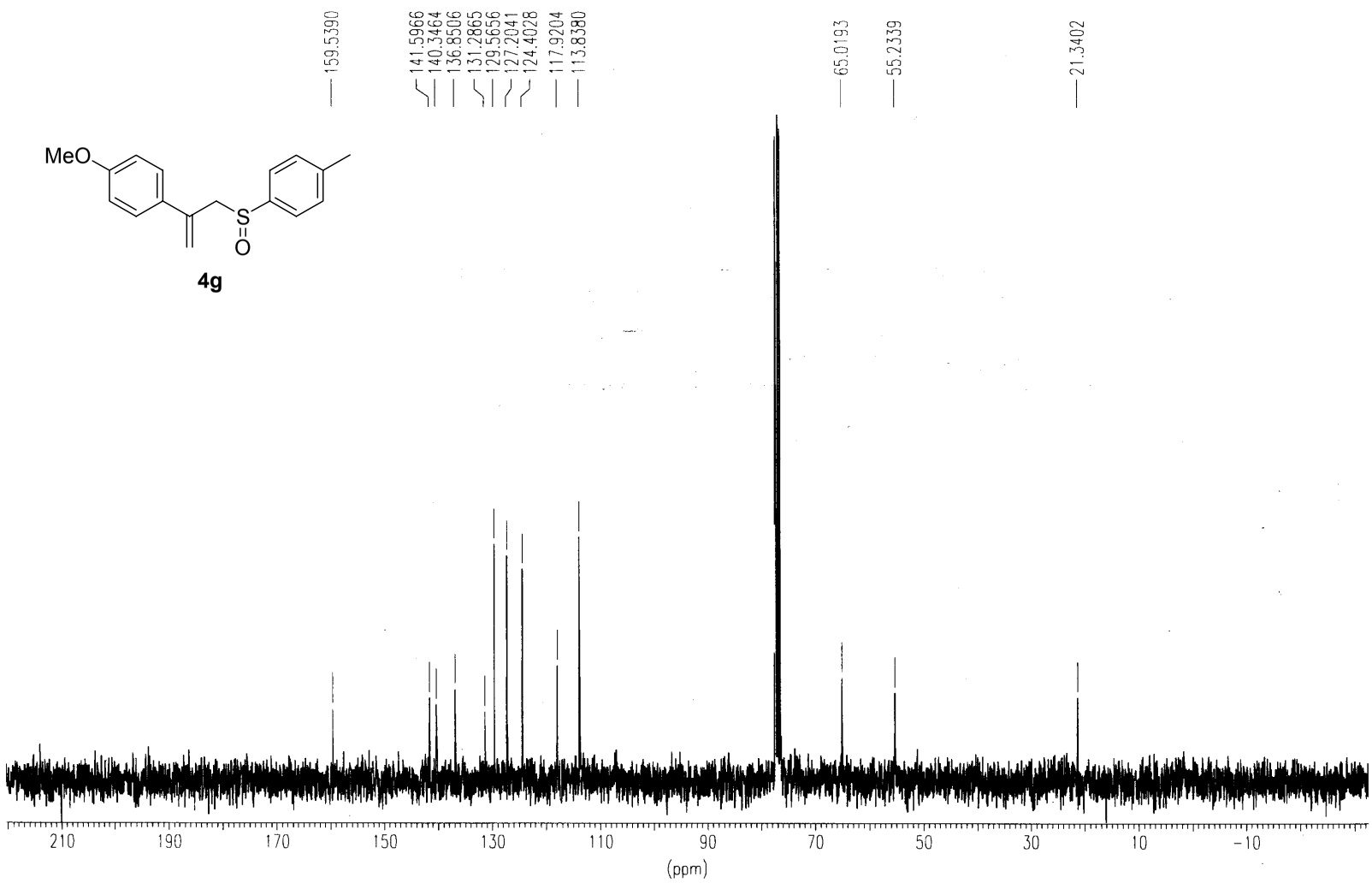

S
O
4f
Integral
1.0134
1.0000
0.8671
1.0794
1.2990
3.1693
5.1766
2.8436
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

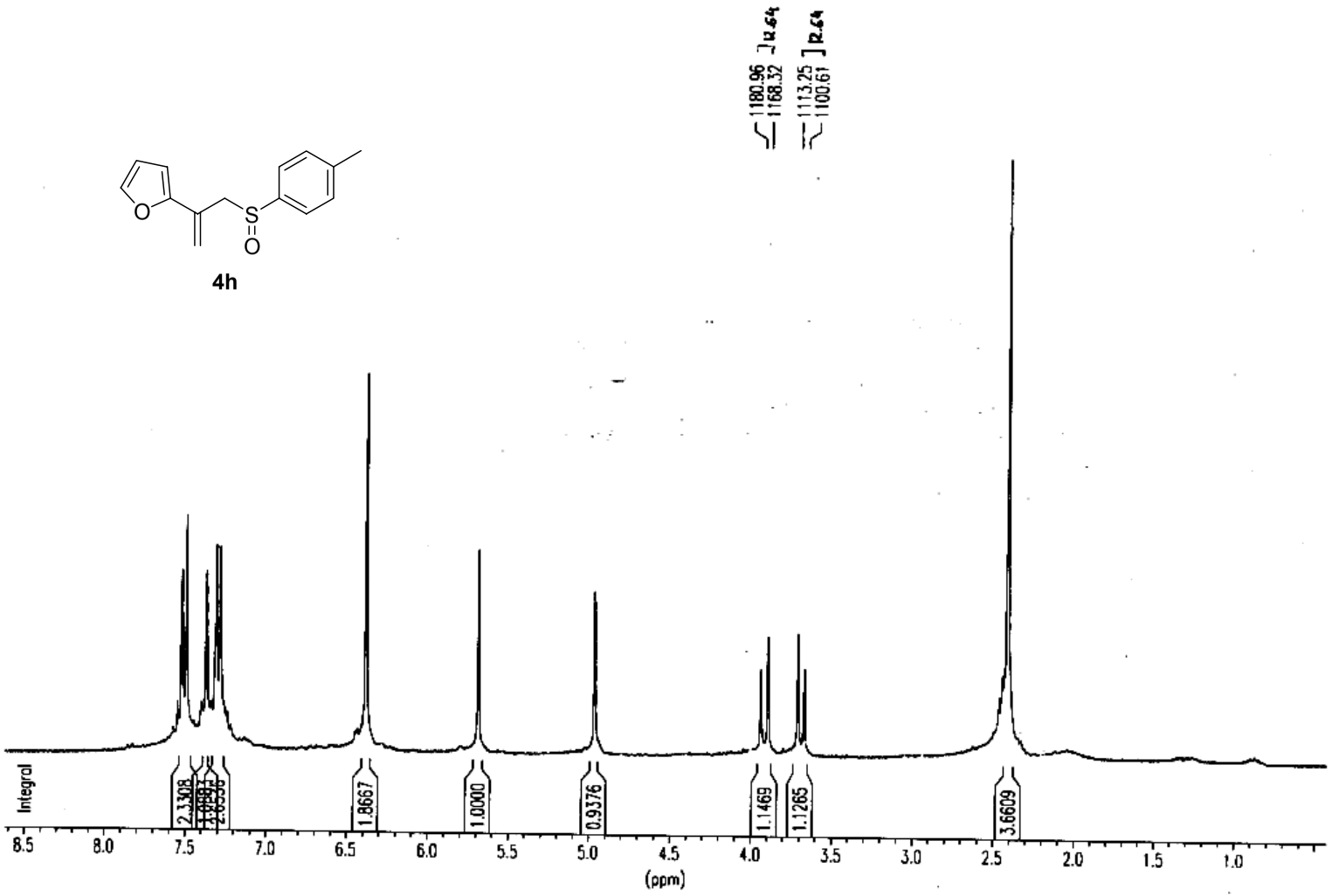

139.5593
127.0806
123.6465
120.5519
88.9810
88.6415
61.6546
37.8626
36.0722
33.3326
23.1614
S
O=
4f
210
190
170
150
130
110
90
70
50
30
10
-10
(ppm)


MeO
S
O

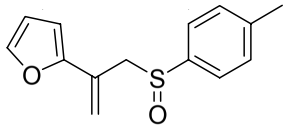
4g

Integral
1.0000
1.0110
0.9796
3.3571
9.5
9.0
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
(ppm)


159.5390
141.5966
140.3464
136.8506
131.2865
129.5656
127.2041
124.4028
117.9204
113.8380
65.0193
55.2339
21.3402
MeO
S
O
4g
210
190
170
150
130
110
90
70
50
30
10
-10
(ppm)

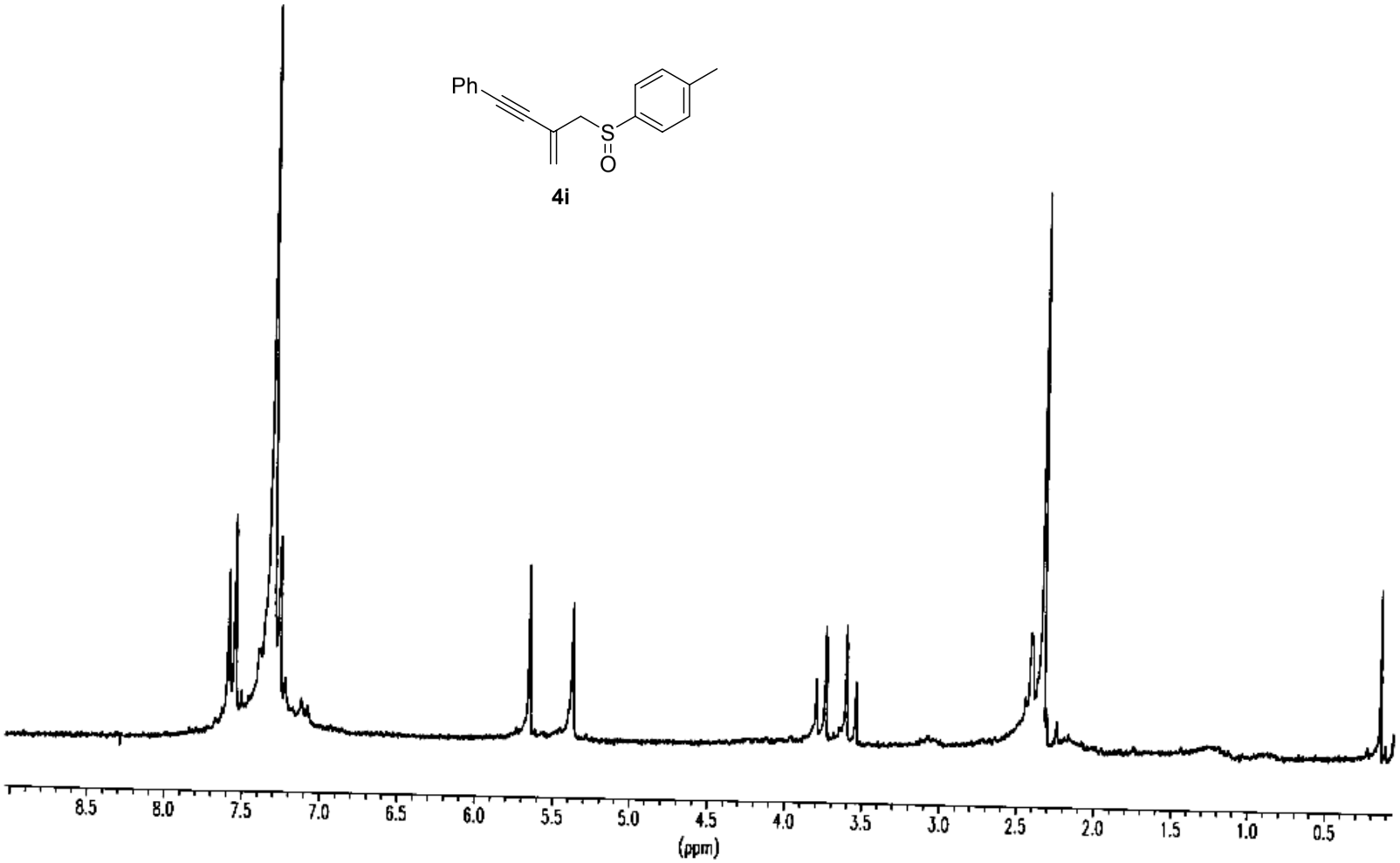

1180.96
1168.32
12.64
1113.25
1100.61
12.64
Integral
1.8667
1.0000
0.9376
1.1469
1.1265
3.6609
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

4h

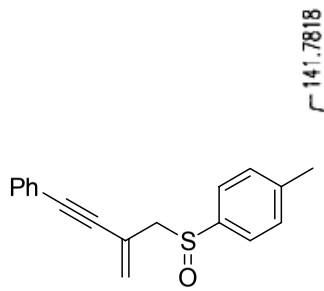


4h

152.5144
142.5440
141.7225
140.2620
129.5965
127.0407
124.3094
116.0031
111.3268
107.4089
62.6685
21.3124
220
200
180
160
140
120
100
80
60
40
20
(ppm)

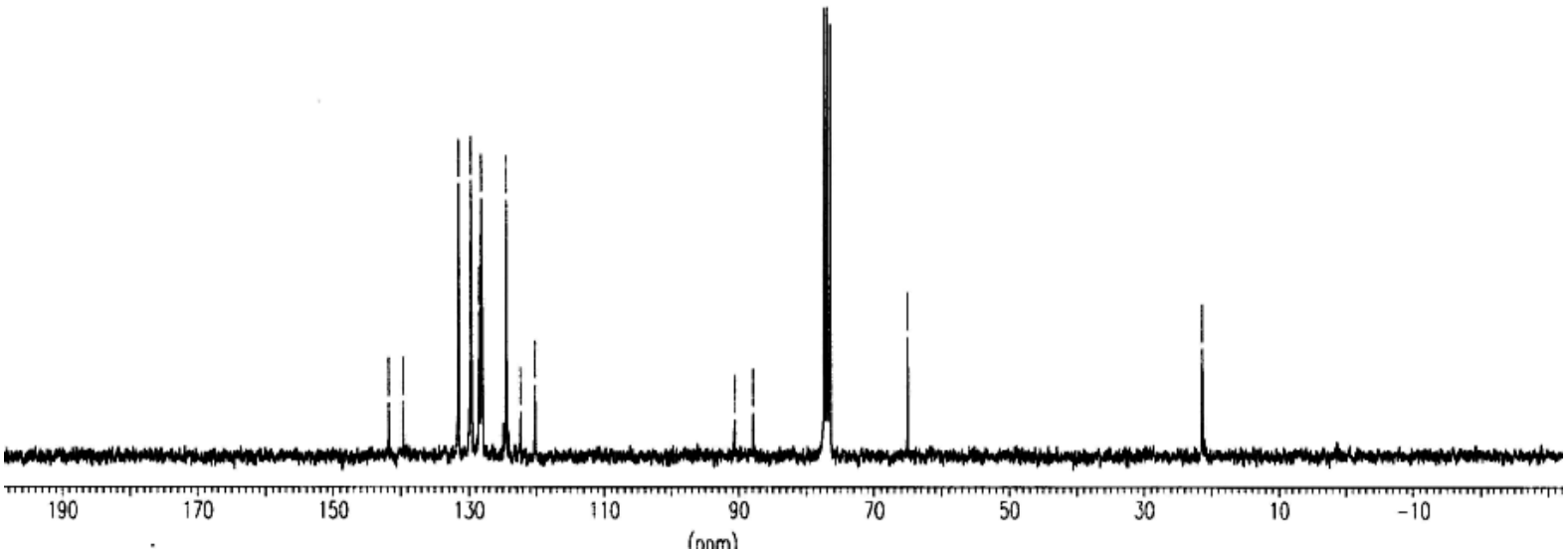


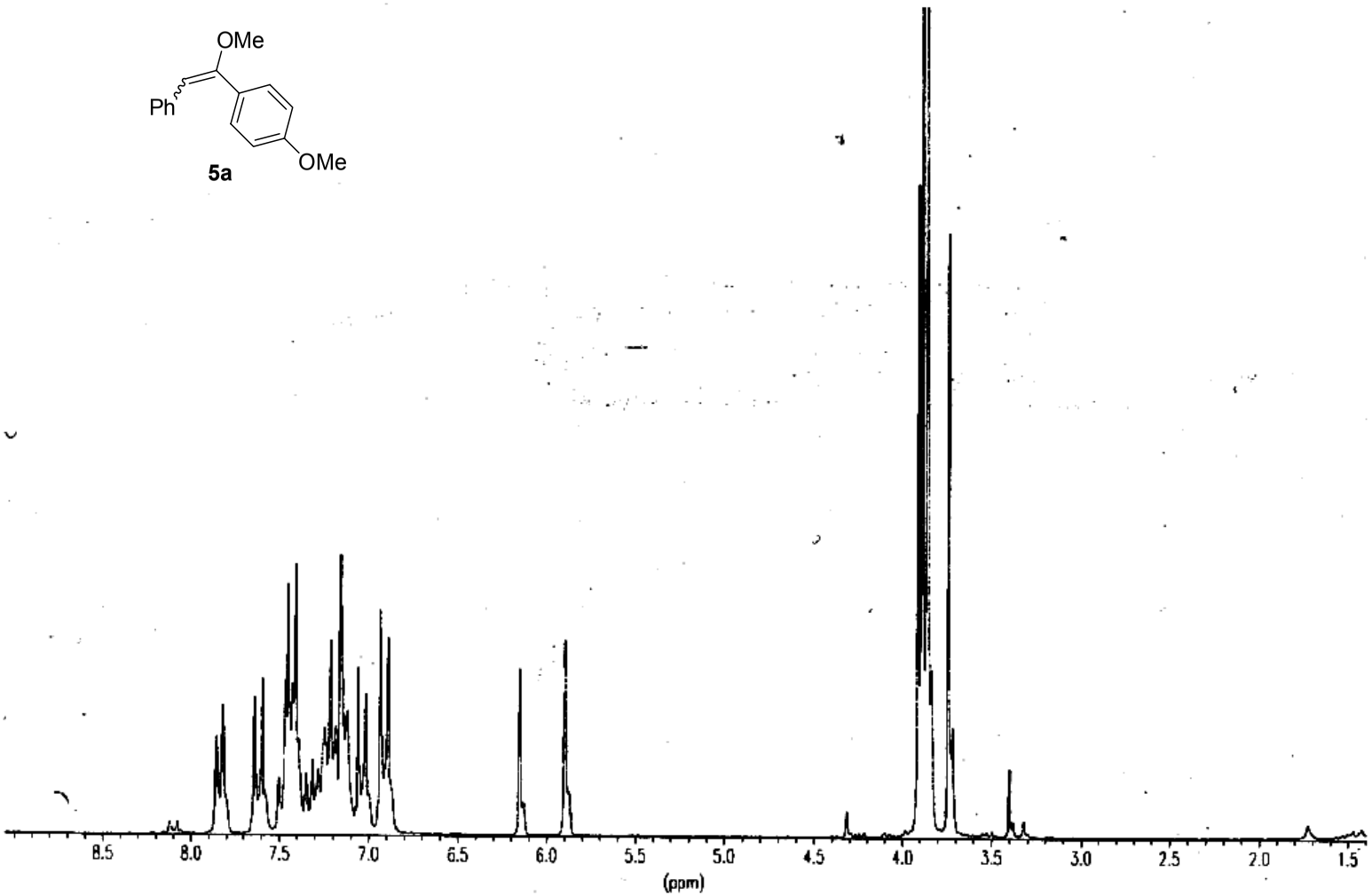
4i

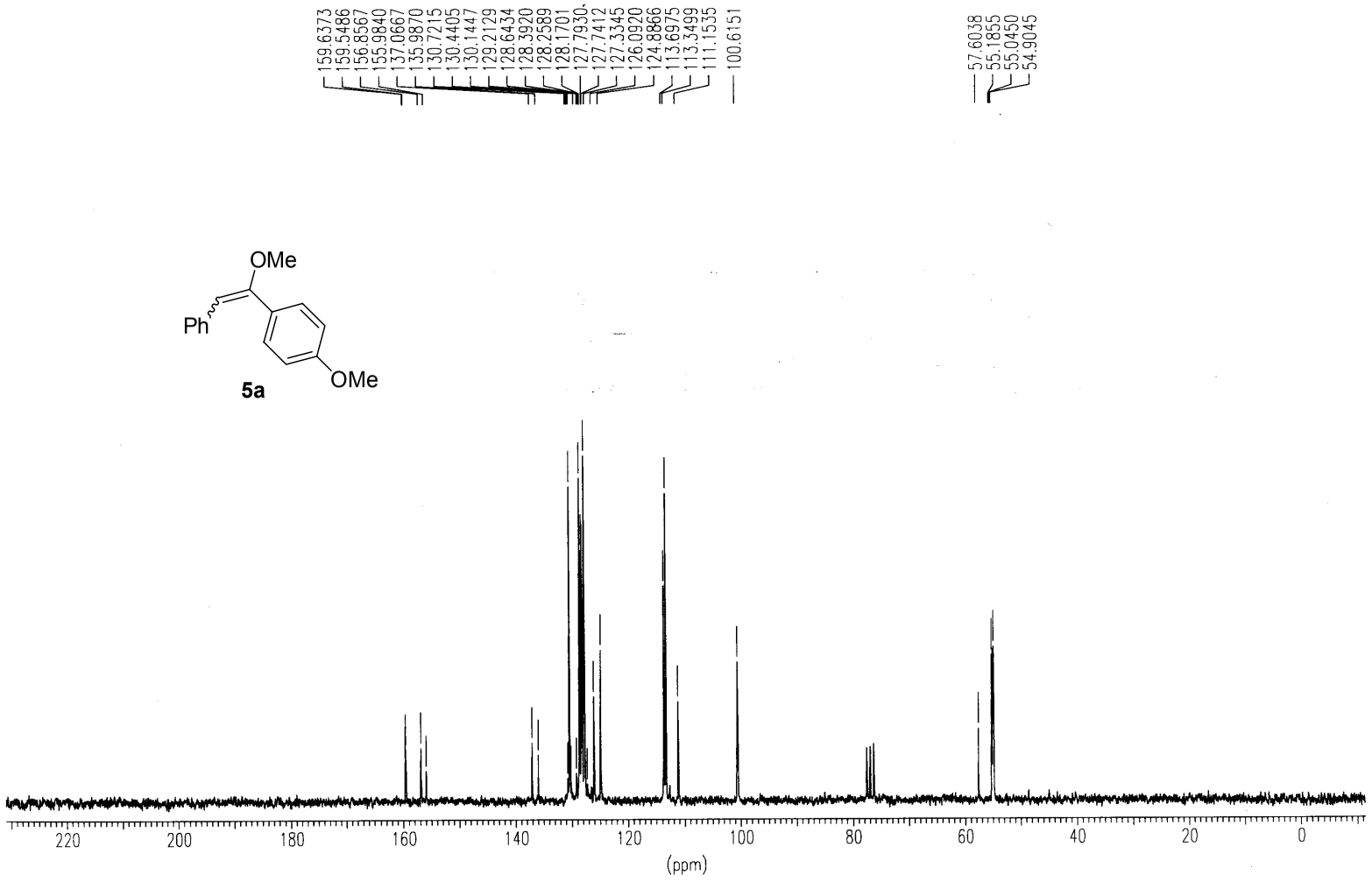


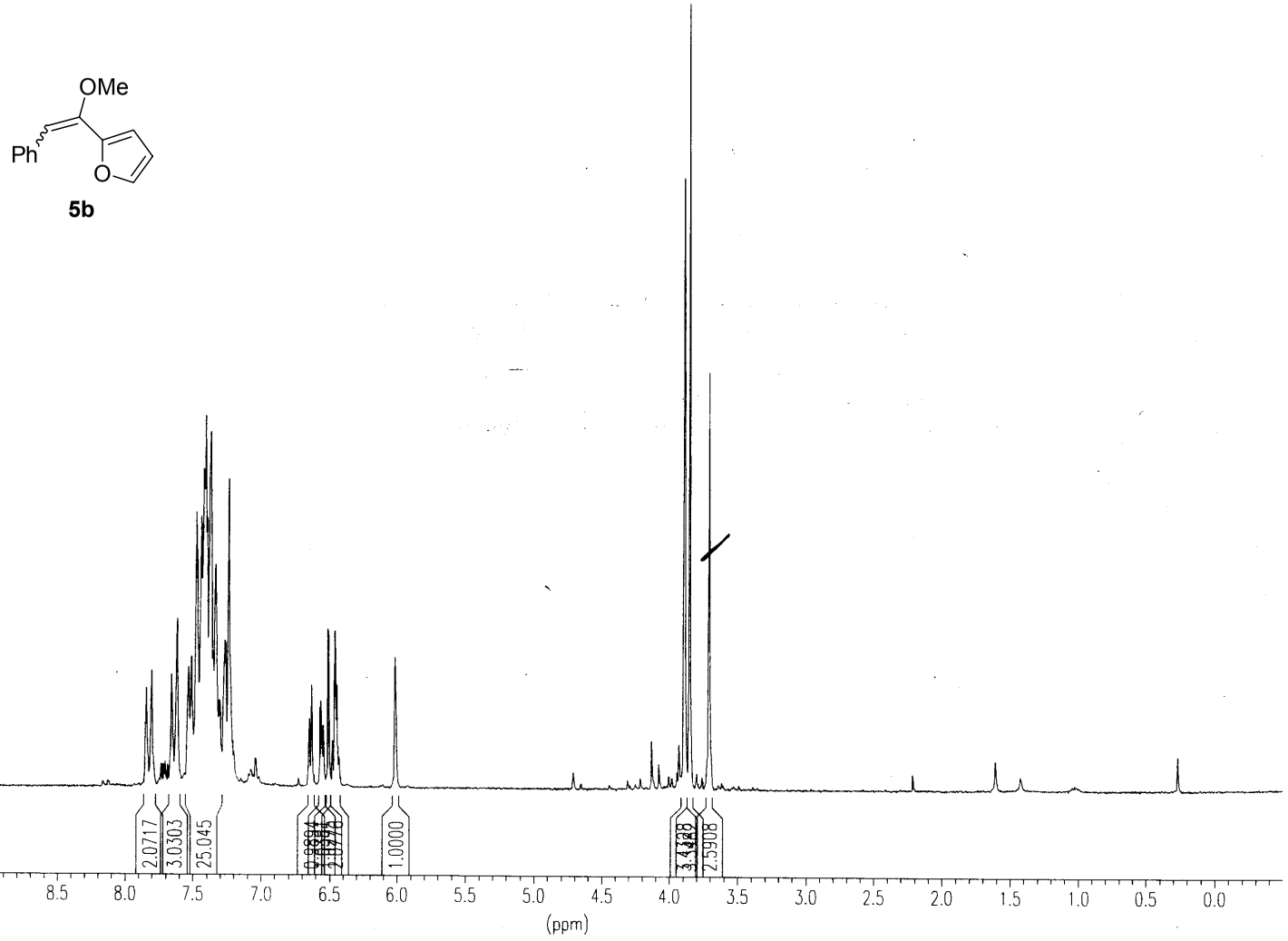
4i

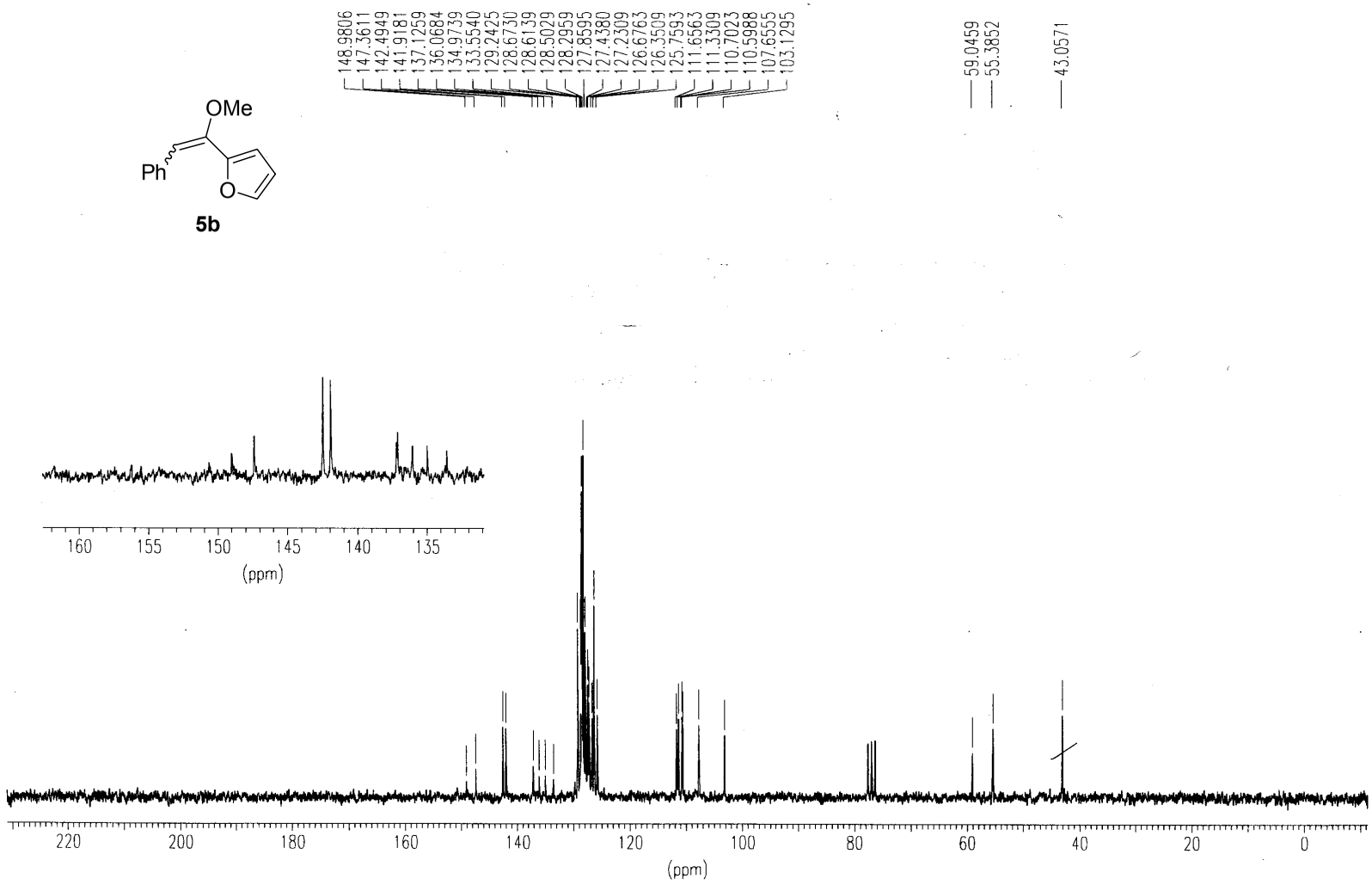
141.7818
139.5670
131.5180
129.6659
128.4852
128.1611
127.9758
124.4877
122.3269
120.1815
90.5785
87.8698
64.9653
21.2707

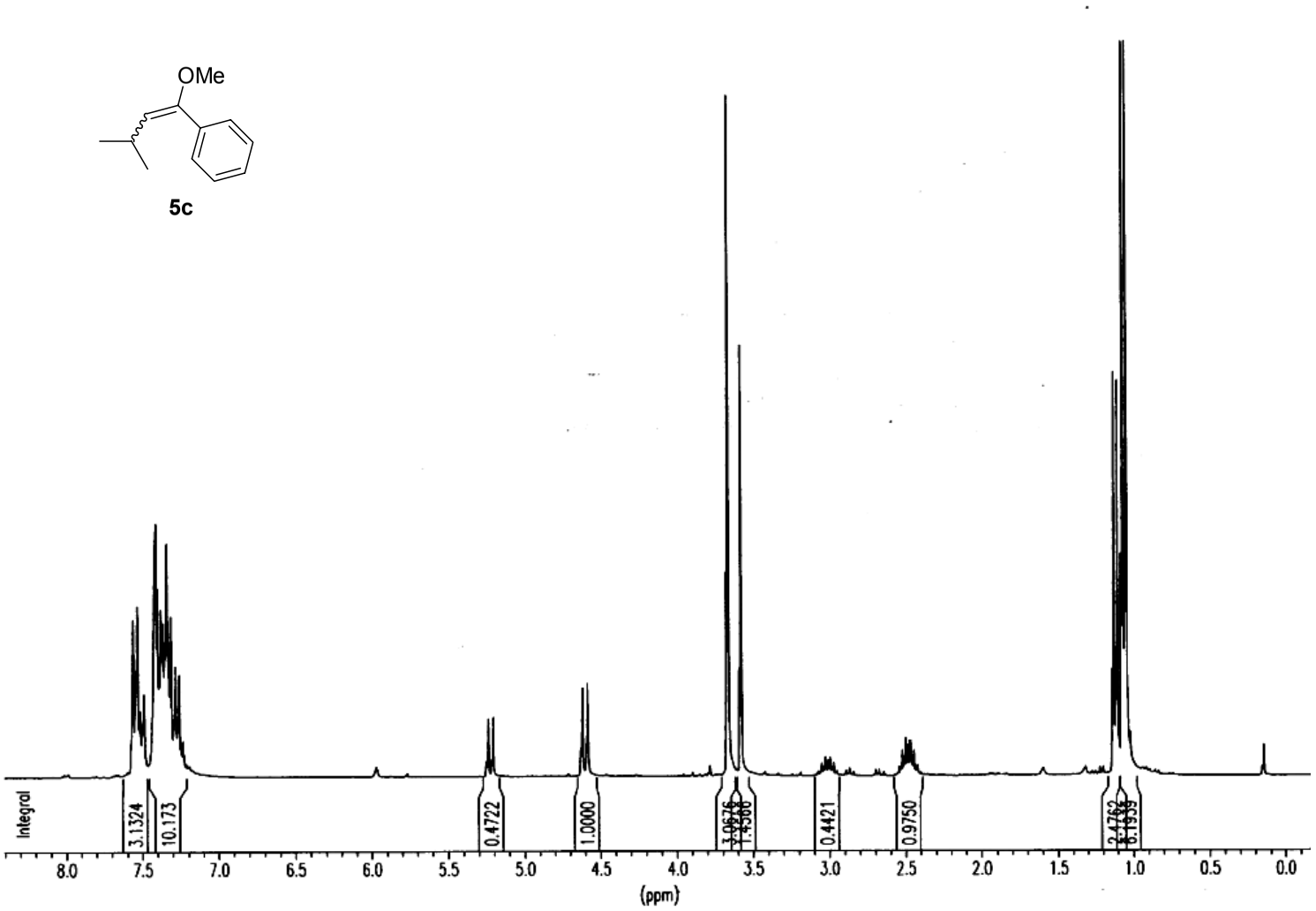


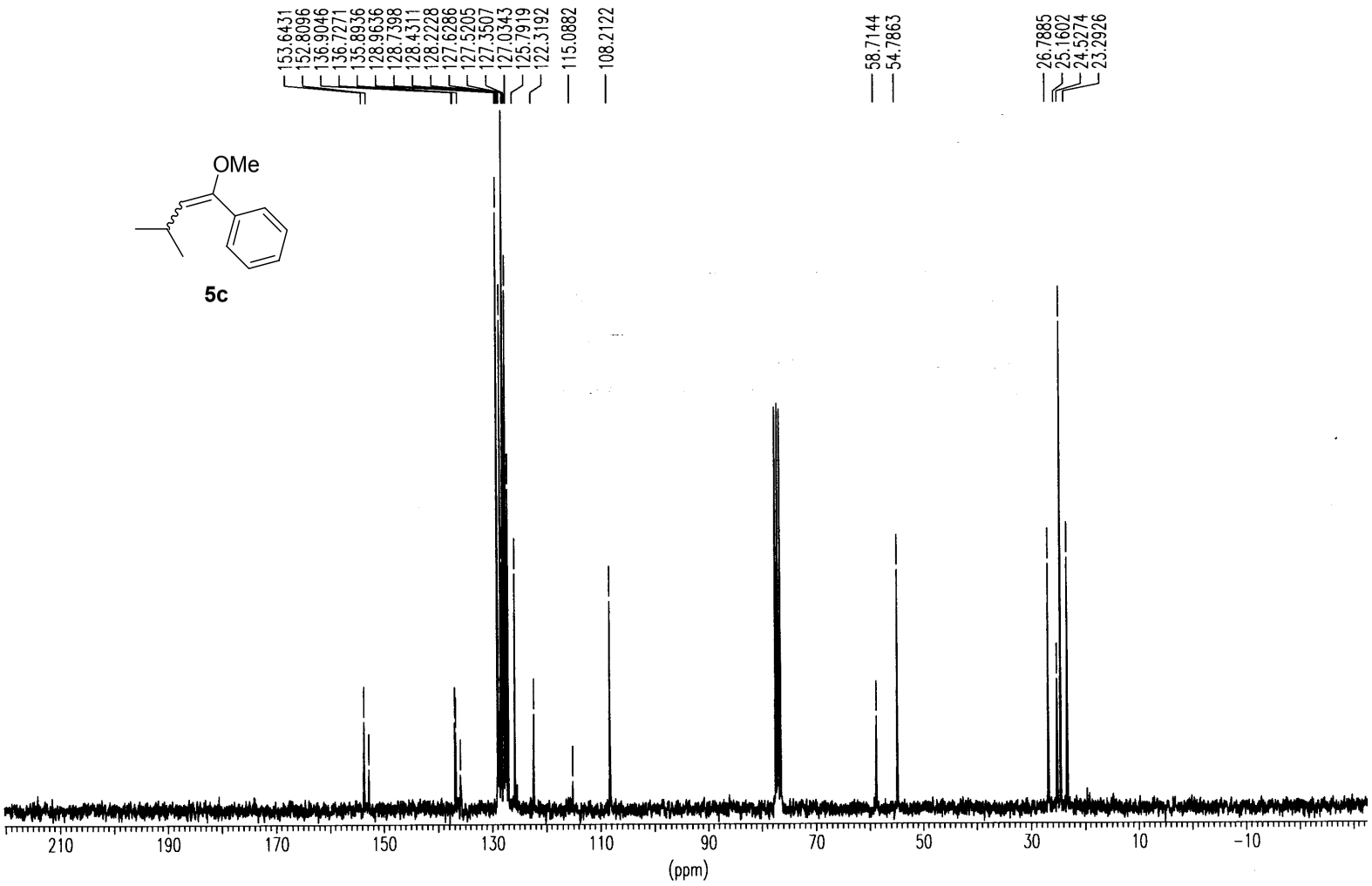

OMe
Ph
OMe
5a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)


159.6373
159.5486
156.8567
155.9840
137.0667
135.9870
130.7215
130.4405
130.1447
129.2129
128.6434
128.3920
128.2589
128.1701
127.7930
127.7412
127.3345
126.0920
124.8866
113.6975
113.3499
111.1535
100.6151
57.6038
55.1855
55.0450
54.9045
OMe
Ph
OMe
5a
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)


OMe
Ph
O
5b
Integral
2.0717
3.0303
25.045
1.0000
2.5908
9.5
9.0
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
(ppm)


148.9806
147.3611
142.4949
141.9181
137.1259
136.0684
134.9739
133.5540
129.2425
128.6730
128.6139
128.5029
128.2959
127.8595
127.4380
127.2309
126.6763
126.3509
125.7593
111.6563
111.3309
110.7023
110.5988
107.6555
103.1295
59.0459
55.3852
43.0571
OMe
Ph
O
5b
160
155
150
145
140
135
(ppm)
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)


OMe
5c
Integral
3.1324
10.173
0.4722
1.0000
3.0676
1.4300
0.4421
0.9750
2.4762
6.1959
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
(ppm)


153.6431
152.8096
136.9046
136.7271
135.8936
128.9636
128.7398
128.4311
128.2228
127.6286
127.5205
127.3507
127.0343
125.7919
122.3192
115.0882
108.2122
58.7144
54.7863
26.7885
25.1602
24.5274
23.2926
OMe
5c
210
190
170
150
130
110
90
70
50
30
10
-10
(ppm)