Supporting Information

Copper-Catalyzed Sequential Alkyl/Aryl or Vinyl Esterification of Dicarboxylic Acid Anhydrides with Trialkoxysilanes

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Experimental

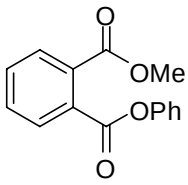
1. General experimental details

Chemicals were either purchased or purified by standard techniques without special instructions. ^{1}H NMR and ^{13}C NMR spectra were measured on a 300 or 500 MHz spectrometer (^{1}H 300 MHz, ^{13}C 75 or 125 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz.

Typical experimental procedure for the reaction of aryl or vinyl trimethoxysilanes with anhydrides to esters： Under air, a reaction tube was charged with anhydride (0.2 mmol), silane reagent (0.3 mmol), CuBr (5.7 mg, 20 mol %), AgF (75.5 mg, 0.6 mmol) and dry toluene (2 mL). The mixture was stirred at 130 ^{o}C. After the mixture was refluxed for 30 h, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel to give the product.

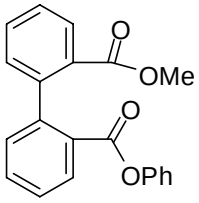
2. Experimental characterization data for compounds

methyl phenyl phthalate (**3aa**)[1]



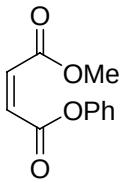
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.90-7.80 (m, 2H), 7.63-7.60 (m, 2H), 7.46-7.41 (m, 2H), 7.29-7.26 (m, 3H), 3.92 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.7, 166.1, 150.8, 132.0, 131.57, 131.51, 131.2, 129.5, 129.2, 129.1, 126.0, 121.3, 52.7.

2-methyl 2'-phenyl biphenyl-2,2'-dicarboxylate (**3ba**)[2]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.21 (d, *J* = 7.7 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.62-7.52 (m, 4H), 7.50-7.10 (m, 5H), 6.90 (d, *J* = 7.7 Hz, 2H), 3.66 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 165.5, 150.6, 143.6, 143.1, 131.9, 131.6, 130.3, 130.29, 130.24, 130.0, 129.2, 129.1, 129.0, 127.33, 127.30, 125.5, 121.3, 51.8.

methyl phenyl maleate (**3ca**)[3]



1H NMR ($CDCl_3$, 300 MHz): δ 7.43-7.38 (m, 2H), 7.28-7.18 (m, 3H), 6.47 (d, *J* = 12.0 Hz, 1H), 6.39 (d, *J* = 12.0 Hz, 1H), 3.82 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.4, 163.6, 150.2, 130.4, 129.6, 129.5, 126.1, 121.3, 52.3.

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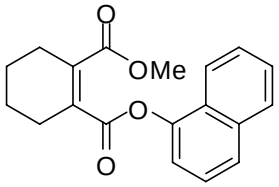
[1] Subramanian, L. R. *Sci. Synth.* **2006**, *20a*, 307.

[2] Kulev, L. P.; Gireva, R. N.; Stepnova, G. M. *Zh. Obshch. Khim.* **1962**, *32*, 2812.

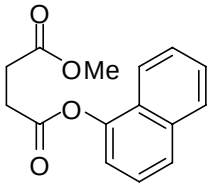
[3] Otsu, T.; Yasuhara, T.; Matsumoto, A. *J. Macromol. Sci., Chem.* **1988**, A25, 537.

1-methyl 2-naphthalen-1-yl cyclohex-1-ene-1,2-dicarboxylate (**3db**)



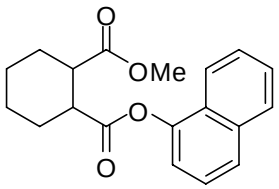
1H NMR (CDCl3, 300 MHz): δ 7.95-7.85 (m, 2H), 7.76-7.74 (m, 1H), 7.53-7.36 (m, 4H), 3.75 (s, 3H), 2.67-2.64 (m, 2H), 2.49-2.46 (m, 2H), 1.81-1.78 (m, 4H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.6, 166.7, 146.3, 137.2, 134.6, 134.3, 127.9, 126.7, 126.4, 126.0, 125.4, 121.2, 117.9, 52.3, 26.54, 26.50, 21.2, 21.1.
IR (prism, cm^{-1}): 2924, 2159, 1733, 1264, 1219.
HRMS Calcd. for $C_{19}H_{19}O_4$ $(M+H)^+$ 311.1283, found 311.1286.

methyl naphthalen-1-yl succinate (**3eb**)



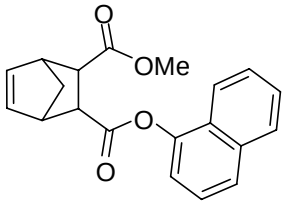
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.93-7.86 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.54-7.44 (m, 3H), 7.27-7.24 (m, 1H), 3.75 (s, 3H), 3.08 (t, J = 6.9 Hz, 2H), 2.83 (t, J = 6.9 Hz, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.5, 170.9, 146.5, 134.6, 127.9, 126.7, 126.47, 126.42, 126.0, 125.3, 121.1, 117.9, 51.9, 29.2, 28.9
IR (prism, cm^{-1}): ν 2930, 2159, 1734, 1265.
HRMS (EI) Calcd for $C_{15}H_{14}O_4$ (M^+) 258.0892, found 258.0892.

1-methyl 2-naphthalen-1-yl cyclohexane-1,2-dicarboxylate (**3fb**)



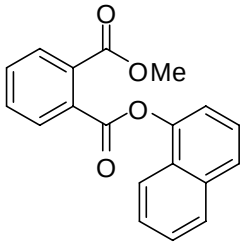
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.95-7.85 (m, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.52-7.43 (m, 3H), 7.24 (d, J = 7.5 Hz, 1H), 3.72 (s, 3H), 3.27-3.25 (m, 1H), 3.11-3.09 (m, 1H), 2.30-1.54 (m, 8H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0, 172.4, 146.7, 134.6, 127.9, 127.0, 126.3, 125.8, 125.4, 121.3, 118.0, 51.8, 42.9, 42.8, 26.4, 26.3, 23.8, 23.7.
IR (prism, cm^{-1}): ν 2924, 2159, 1733, 1224, 1149.
HRMS (EI) Calcd for $C_{19}H_{20}O_4$ (M^+) 312.1362, found 312.1360.

2-methyl 3-naphthalen-1-yl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**3gb**)



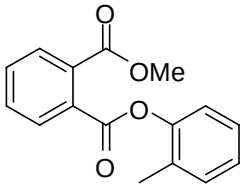
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.96-7.84 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.54-7.42 (m, 3H), 7.32-7.26 (m, 1H), 6.42-6.36 (m, 2H), 3.77-3.73 (m, 1H), 3.60 (s, 3H), 3.53-3.20 (m, 3H), 1.60 (d, *J* = 8.5 Hz, 1H) , 1.48 (d, *J* = 8.5 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.6, 170.9, 146.6, 135.4, 134.8, 134.6, 127.9, 126.8, 126.2, 126.2, 125.6, 125.4, 121.2, 118.0, 51.7, 48.8, 48.5, 48.3, 46.7, 46.5.
IR (prism, cm^{-1}): ν 2922, 2159, 1734, 1224, 1133.
HRMS (EI) Calcd for $C_{20}H_{18}O_4$ (M^+) 322.1205, found 322.1206.

methyl naphthalen-1-yl phthalate (**3ab**)



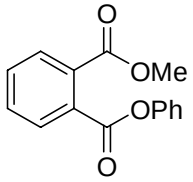
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.10-8.00 (m, 2H), 7.91-7.89 (m, 3H), 7.86-7.79 (m, 2H), 7.69-7.52 (m, 4H), 3.90 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.9, 165.9, 146.8, 134.7, 132.6, 131.8, 131.3, 131.2, 129.4, 129.2, 128.0, 126.8, 126.53, 126.50, 126.2, 125.5, 121.3, 117.9, 52.8.
IR (prism, cm^{-1}): ν 2930, 2159, 1727, 1223, 1110, 1054.
HRMS (EI) Calcd for $C_{19}H_{15}O_4$ $(M+H)^+$ 307.0970, found 307.0962.

methyl *o*-tolyl phthalate (**3ac**)



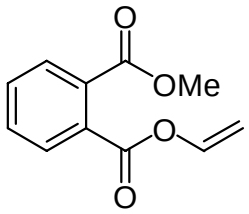
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98-7.95 (m, 1H), 7.81-7.78 (m, 1H), 7.64-7.61 (m, 2H), 7.29-7.19 (m, 4H), 3.92 (s, 3H), 2.27 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.9, 165.5, 149.4, 132.6, 131.6, 131.2, 131.1, 130.2, 129.3, 129.0, 127.0, 126.2, 121.7, 52.7, 16.1.
IR (prism, cm^{-1}): ν 2930, 2159, 1730, 1221, 1113.
HRMS Calcd. for $C_{16}H_{15}O_4$ $(M+H)^+$ 271.0970, found 271.0959.

methyl phenyl phthalate (**3ad**)[1]



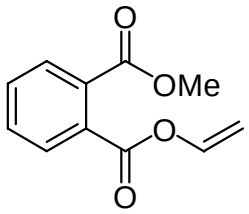
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.91-7.82 (m, 2H), 7.64-7.61 (m, 2H), 7.47-7.42 (m, 2H), 7.30-7.26 (m, 3H), 3.93 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.7, 166.1, 150.9, 132.0, 131.6, 131.5, 131.3, 129.5, 129.3, 129.1, 126.1, 121.4, 52.8.

methyl vinyl phthalate (**3ae**)[4]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.83-7.74 (m, 2H), 7.60-7.57 (m, 2H), 7.47 (dd, J_1 = 13.9 Hz, J_2 = 6.2 Hz, 1H), 5.01 (dd, J_1 = 13.9 Hz, J_2 = 1.7 Hz, 1H), 4.71 (dd, J_1 = 6.2 Hz, J_2 = 1.7 Hz, 1H), 3.91 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.9, 164.5, 141.4, 132.4, 131.7, 131.1, 130.5, 129.3, 129.2, 129.0, 52.7.

methyl vinyl phthalate (**3af**)[4]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82-7.73 (m, 2H), 7.60-7.57 (m, 2H), 7.47 (dd, J_1 = 13.9 Hz, J_2 = 6.2 Hz, 1H), 5.01 (dd, J_1 = 13.9 Hz, J_2 = 1.7 Hz, 1H), 4.71 (dd, J_1 = 6.2, J_2 = 1.7 Hz, 1H), 3.91 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.9, 164.5, 141.4, 132.4, 131.7, 131.1, 130.5, 129.3, 129.2, 129.0, 52.7.

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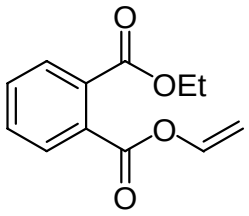
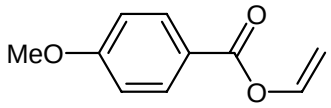
[4] Tomoda, Y.; Fukushima, M. *Jpn. Tokkyo Koho*. JP42020777, 1967; *Chem. Abstr.* **1967**, *68*, 30401.

ethyl vinyl phthalate (**3ag**)[5]



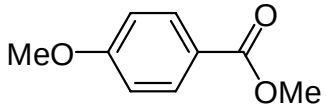
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80-7.75 (m, 2H), 7.60-7.56 (m, 2H), 7.47 (dd, J_1 = 13.9 Hz, J_2 = 6.2 Hz, 1H), 5.00 (dd, J_1 = 13.9 Hz, J_2 = 1.7 Hz, 1H), 4.71 (dd, J_1 = 6.2, J_2 = 1.7 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.3, 164.6, 141.3, 132.5, 131.6, 131.1, 130.7, 129.15, 129.09, 98.6, 61.9, 14.0.

vinyl 4-methoxybenzoate[6]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.06 (d, J = 8.8 Hz, 2H), 7.50 (dd, J_1 = 14.0, J_2 = 6.2 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 5.03 (dd, J_1 = 14.0 Hz, J_2 = 1.1 Hz, 1H), 4.67 (dd, J_1 = 6.2 Hz, J_2 = 1.1 Hz, 1H), 3.88 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.9, 163.3, 141.5, 132.1, 121.2, 113.8, 97.6, 55.4.

methyl 4-methoxybenzoate[7]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.00 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 163.3, 131.6, 122.7, 113.6, 55.4, 51.8.

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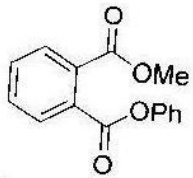
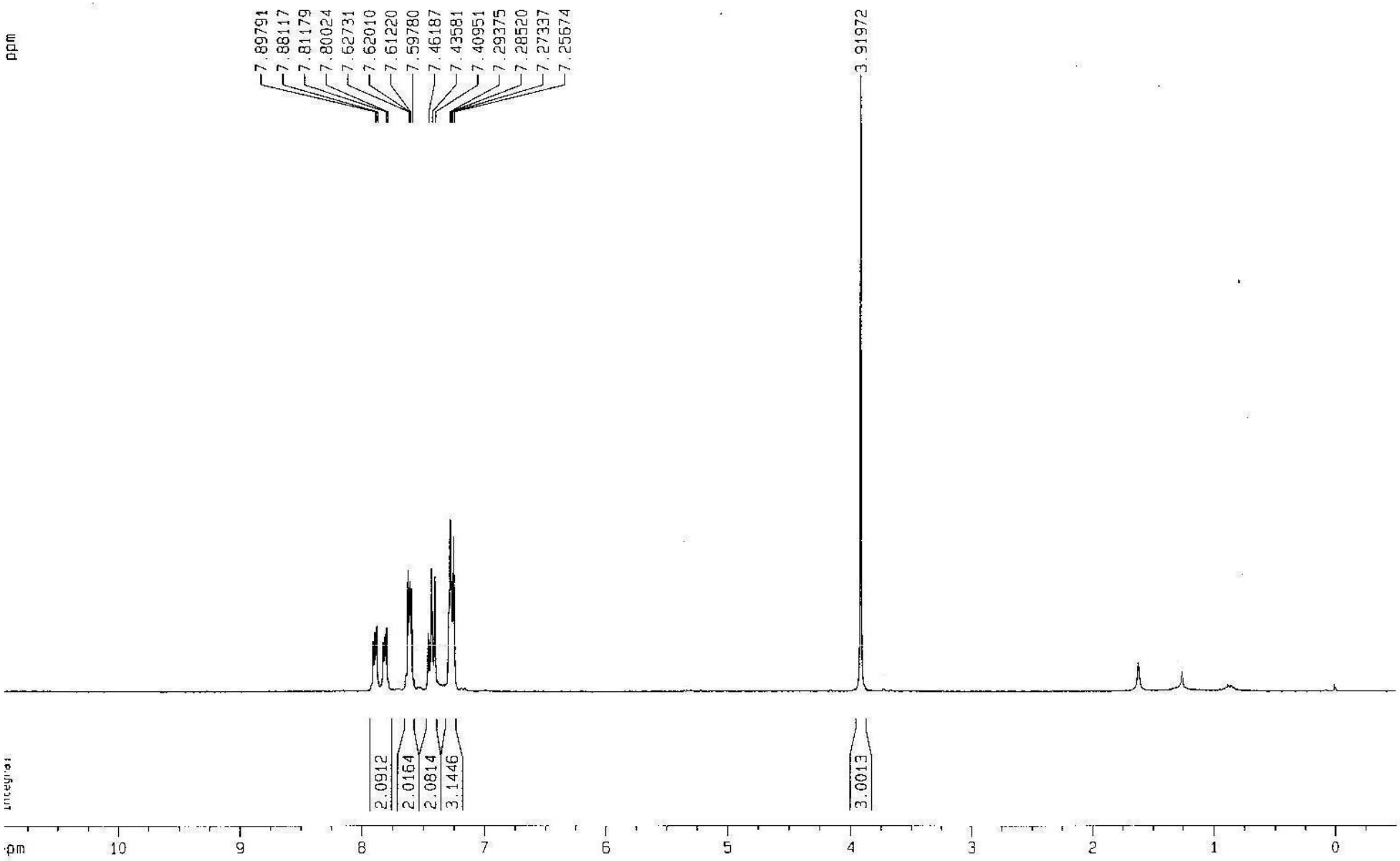
[5] Botts, M. F.; Kohn, F. C.; Miller, M. L. WO9900013, 1999; *Chem. Abstr.* **1999**, *130*, 91677.

[6] Trost, B. M.; Malhotra, S.; Mino, T.; Rajapaksa, N. S. *Chem.—Eur. J.* **2008**, *14*, 7648.

[7] Wu, X-F.; Darcel, C. *Eur. J. Org. Chem*. **2009**, 1144.


OMe
OPh

^{1}H NMR of 3aa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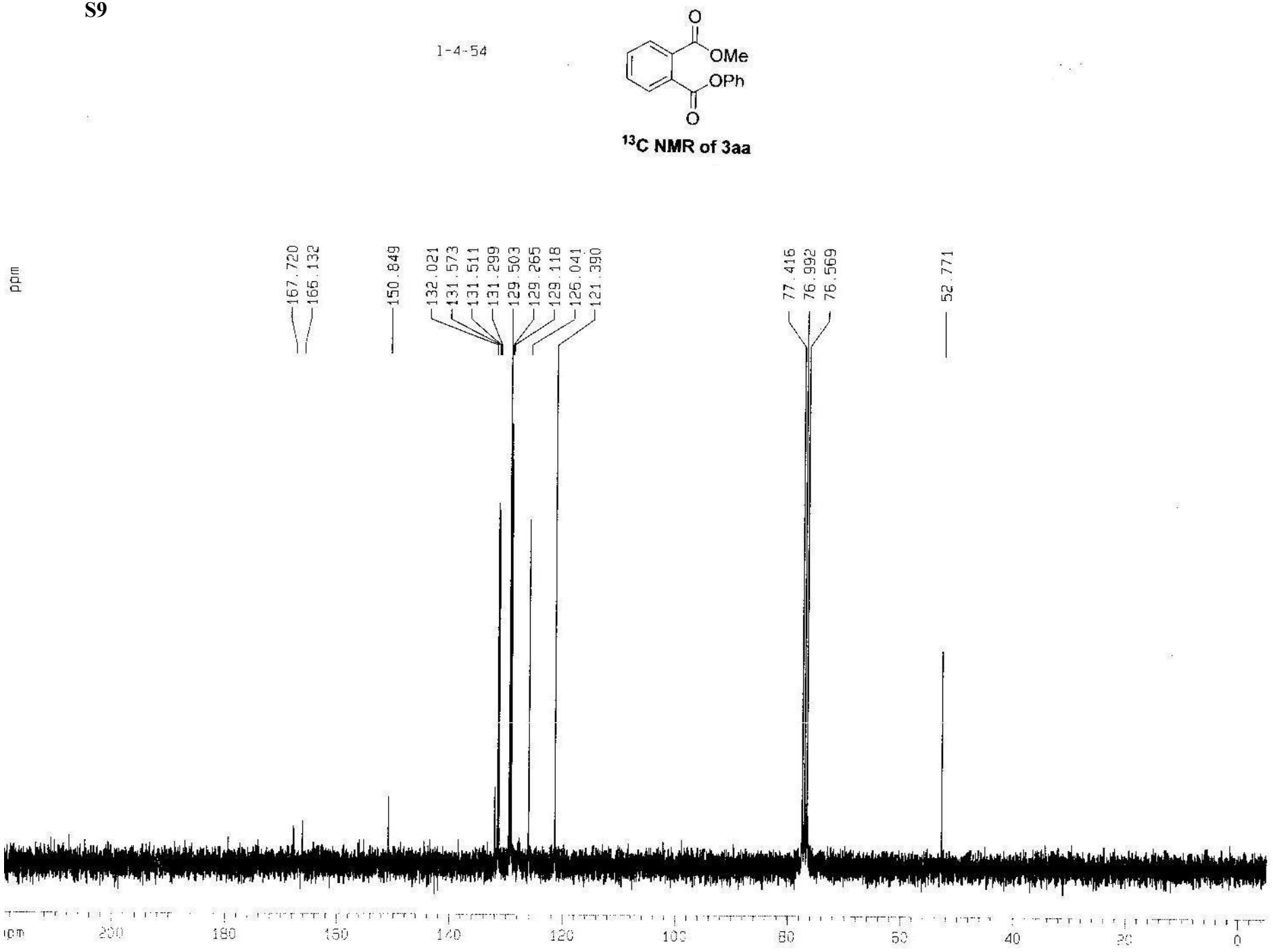
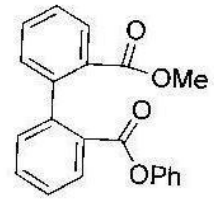
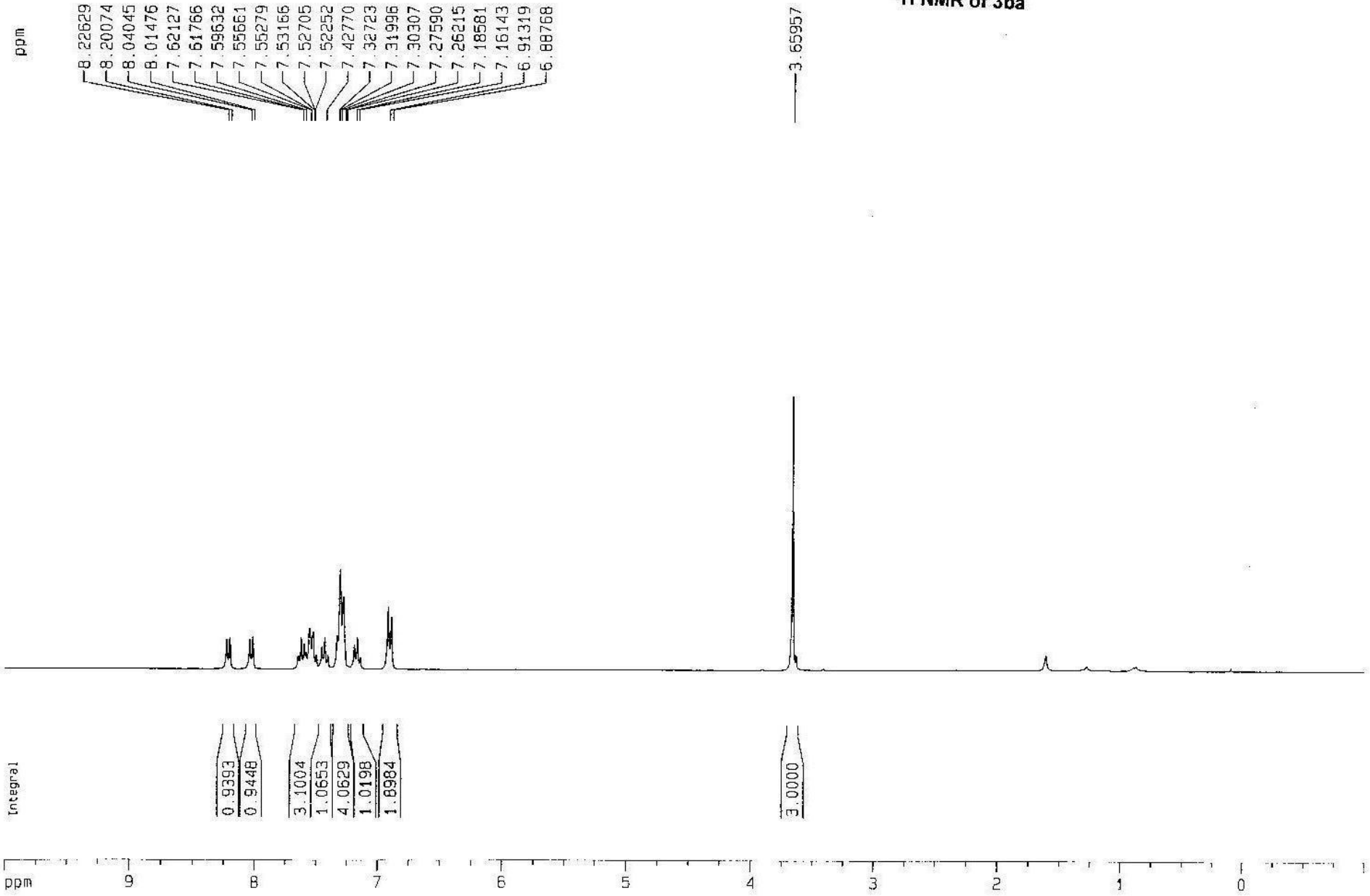


^{13}C NMR of 3aa


O
OMe
O
OPh

^{1}H NMR of 3ba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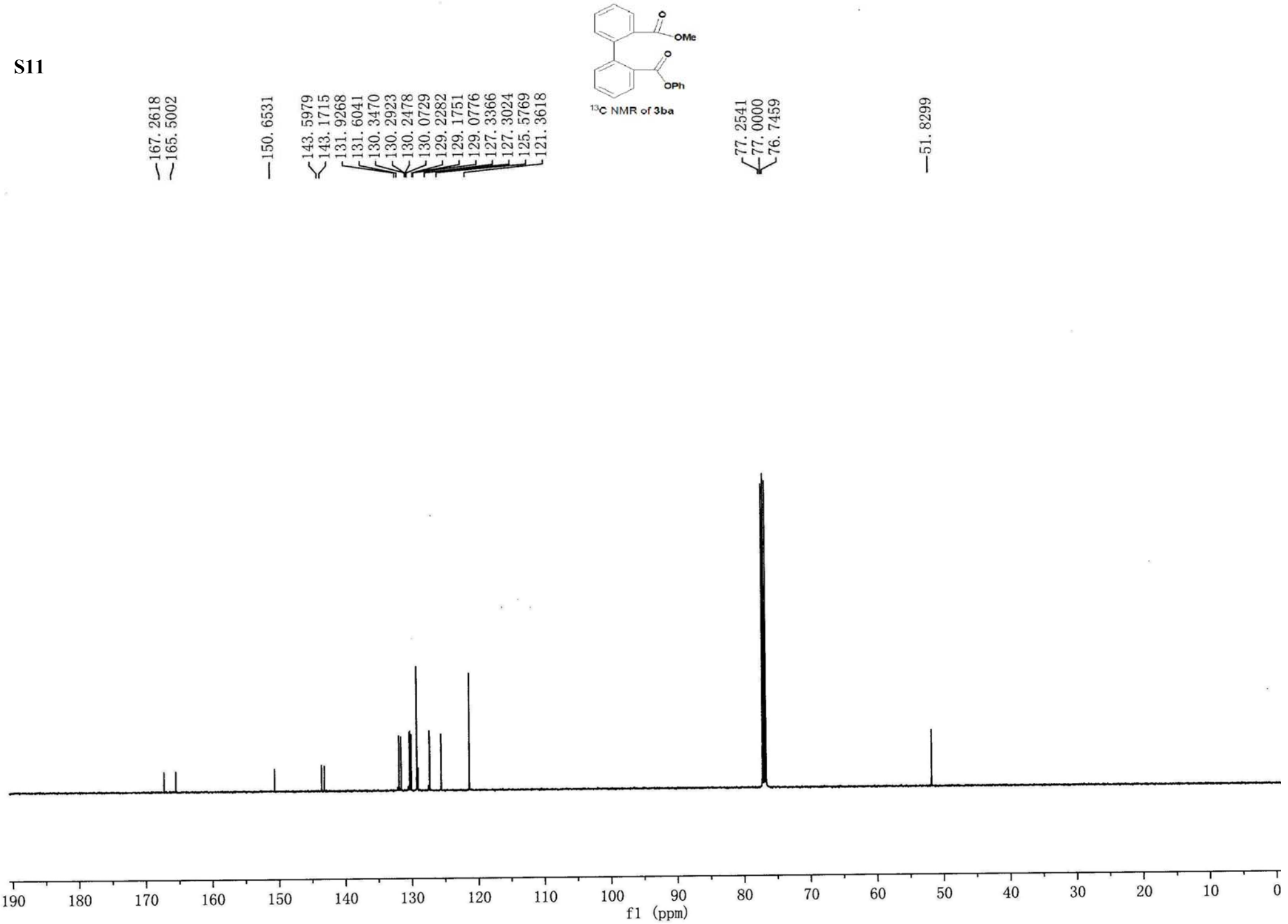
OMe
OPh
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129.2282
129.1751
129.0776
127.3366
127.3024
125.5769
121.3618
77.2541
77.0000
76.7459
51.8299
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180
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160
150
140
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100
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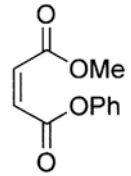
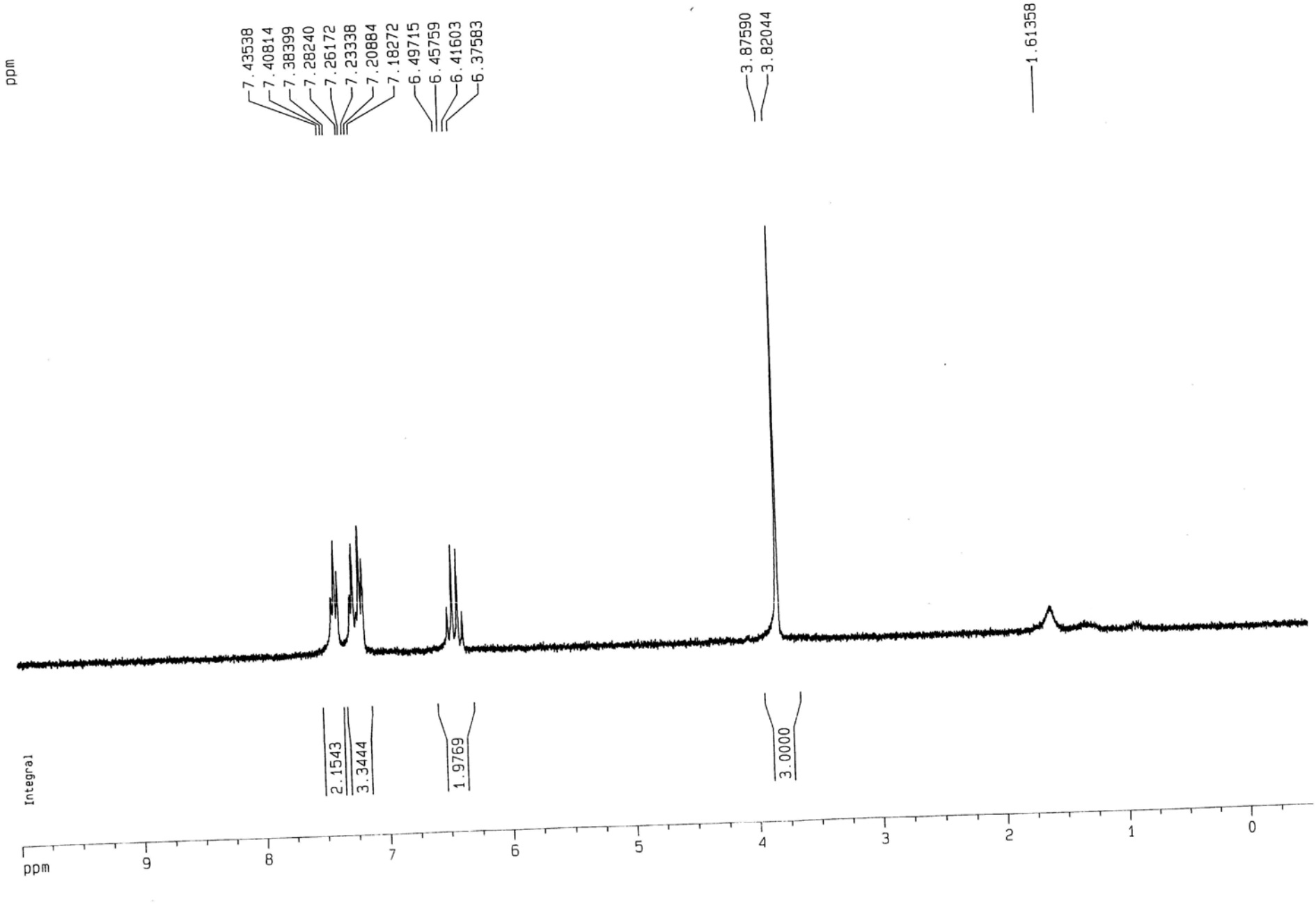
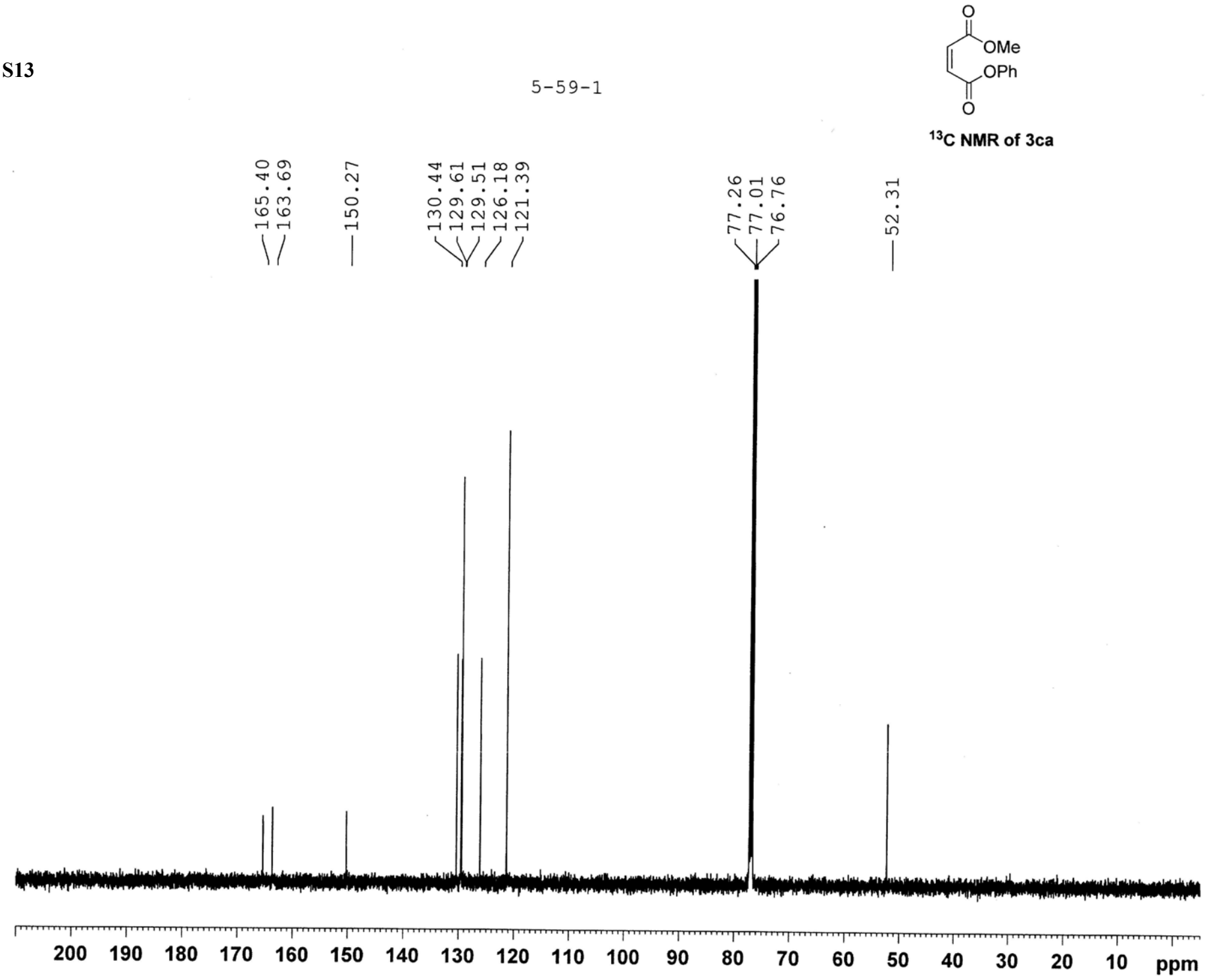
1-5-59-1

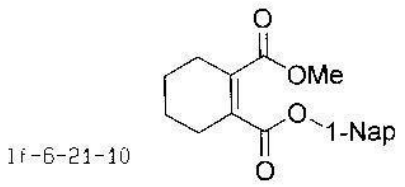


^{1}H NMR of 3ca



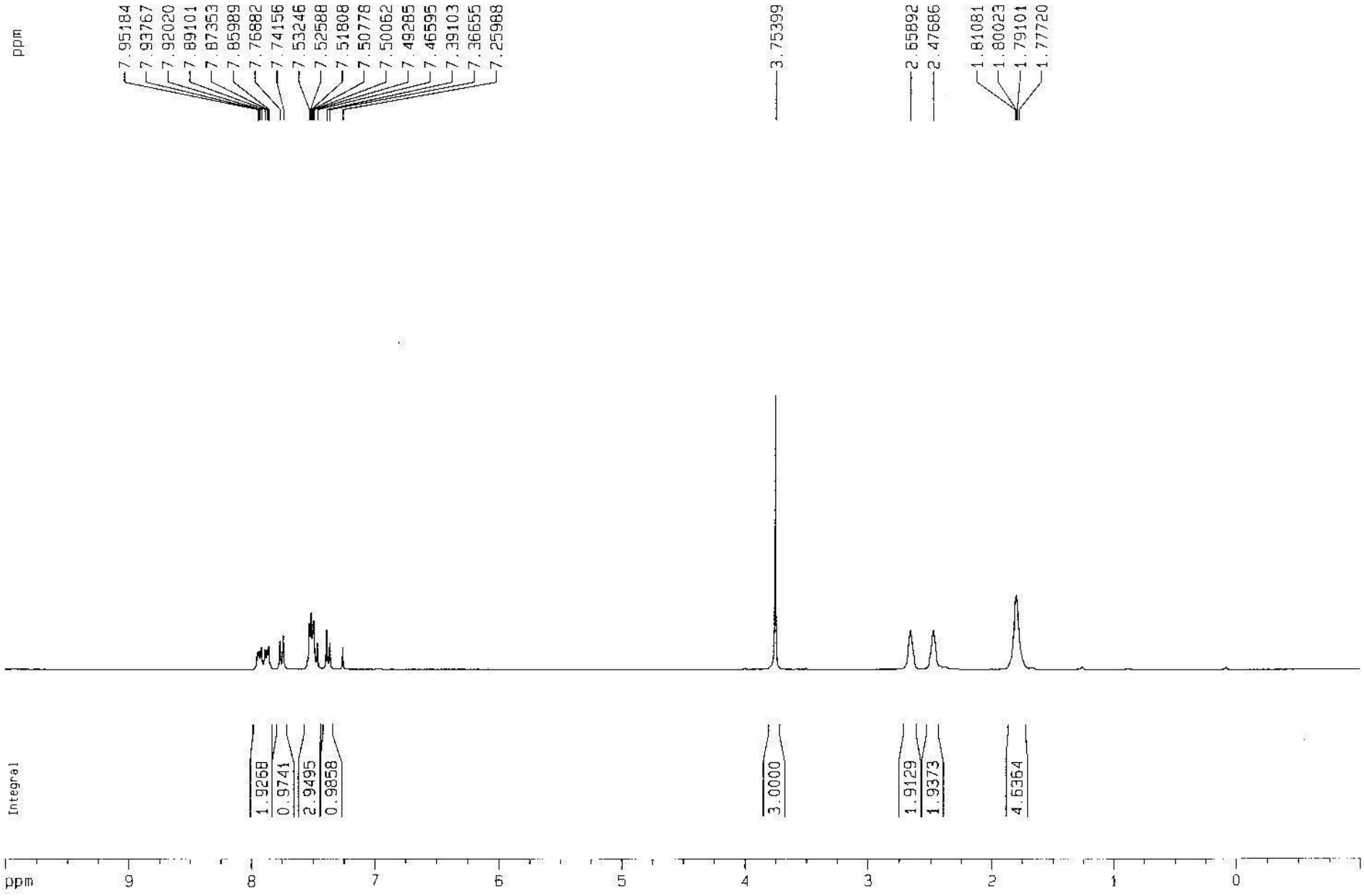


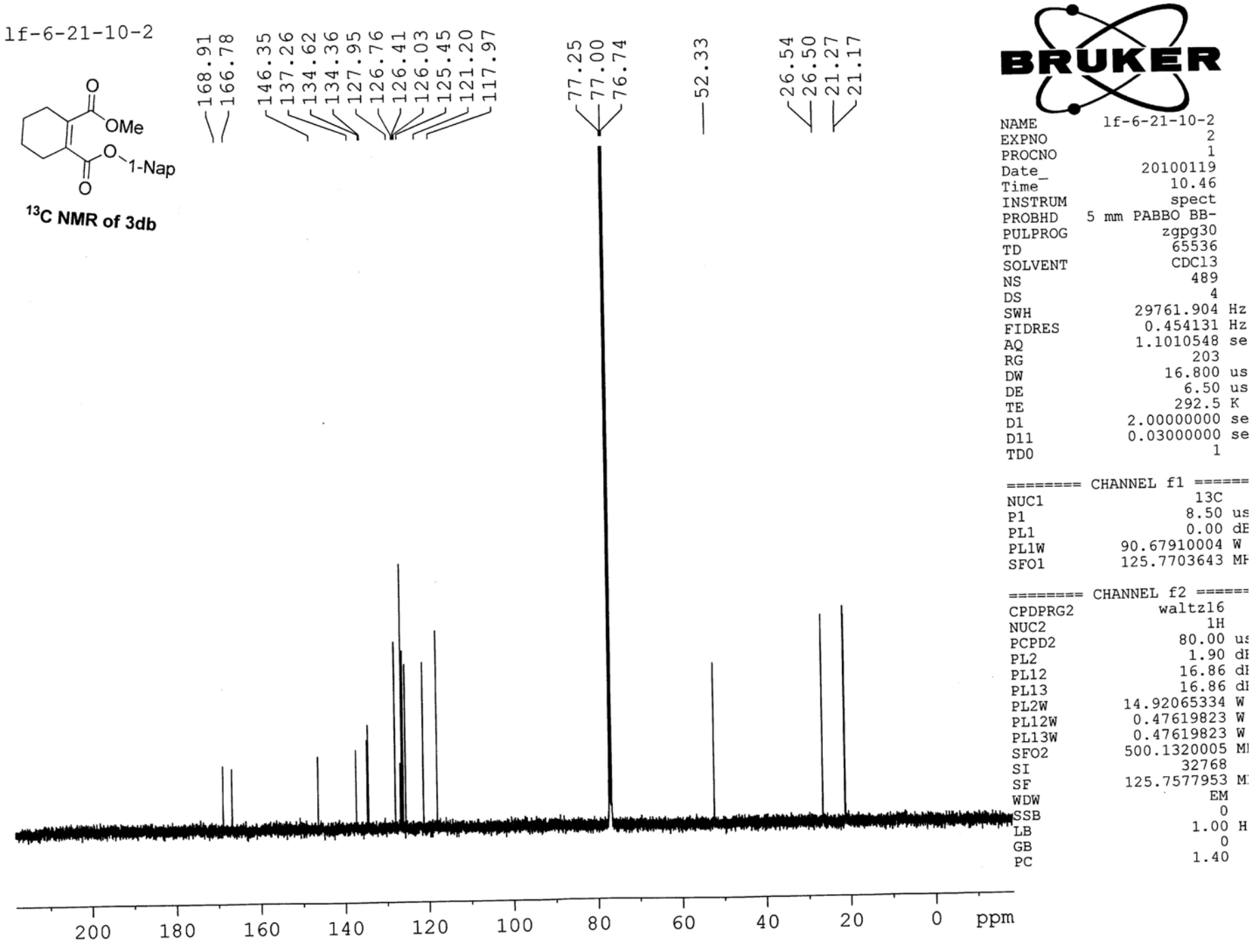
^{13}C NMR of 3ca

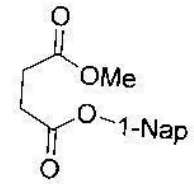


1f-6-21-10

^{1}H NMR of 3db

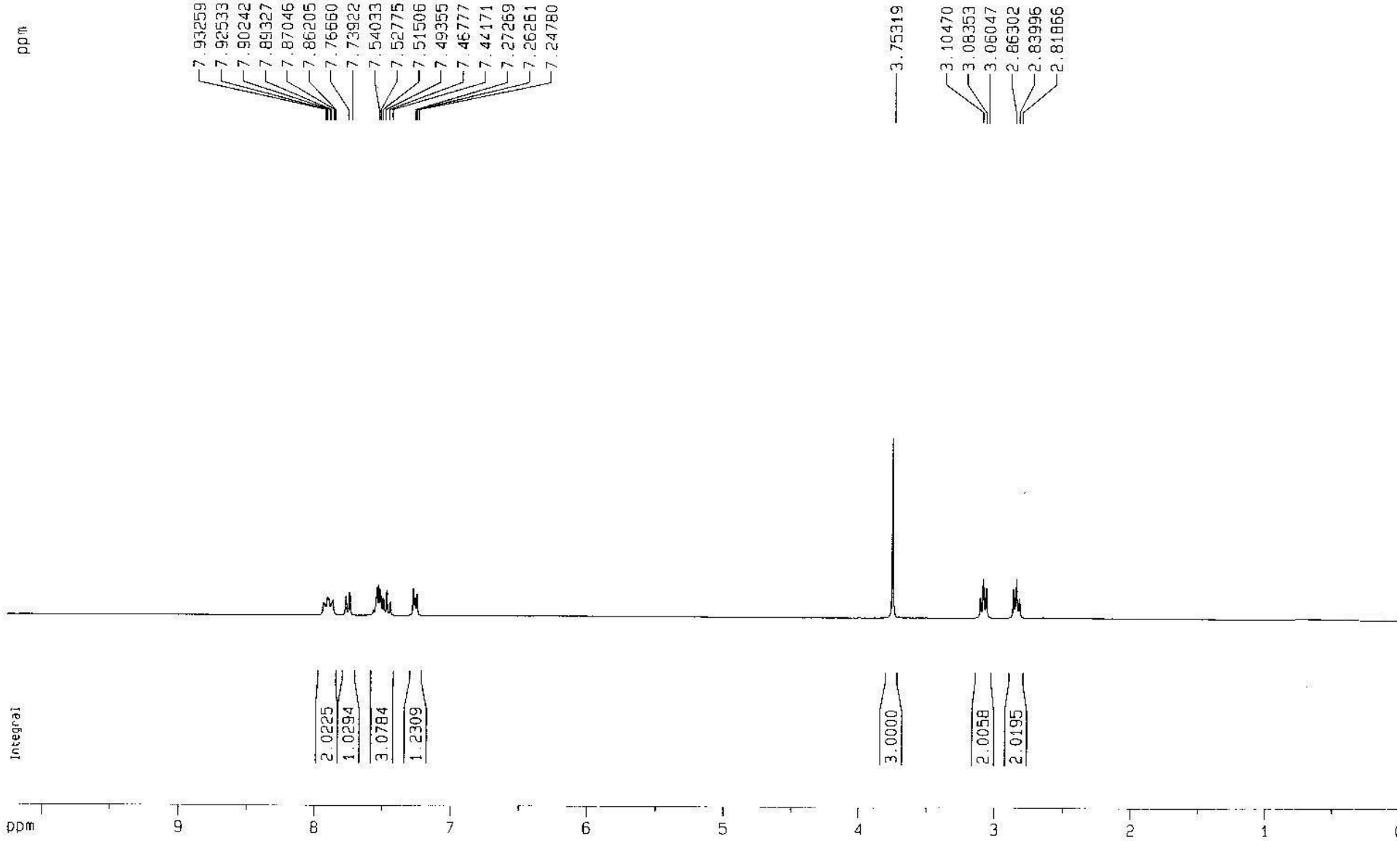


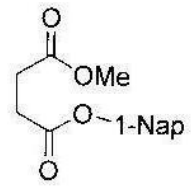

lf-6-21-10-2
OMe
O
1-Nap
O
O
^{13}C NMR of 3db
168.91
166.78
146.35
137.26
134.62
134.36
127.95
126.76
126.41
126.03
125.45
121.20
117.97
77.25
77.00
76.74
52.33
26.54
26.50
21.27
21.17
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
NAME lf-6-21-10-2
EXPNO 2
PROCNO 1
Date_ 20100119
Time 10.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 489
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 se
RG 203
DW 16.800 us
DE 6.50 us
TE 292.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 0.00 dB
PL1W 90.67910004 W
SFO1 125.7703643 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 1.90 dB
PL12 16.86 dB
PL13 16.86 dB
PL2W 14.92065334 W
PL12W 0.47619823 W
PL13W 0.47619823 W
SFO2 500.1320005 MH
SI 32768
SF 125.7577953 MH
WDW EM
SSB 0
LB 1.00 H
GB 0
PC 1.40



lr-6-21-1

^{1}H NMR of 3eb

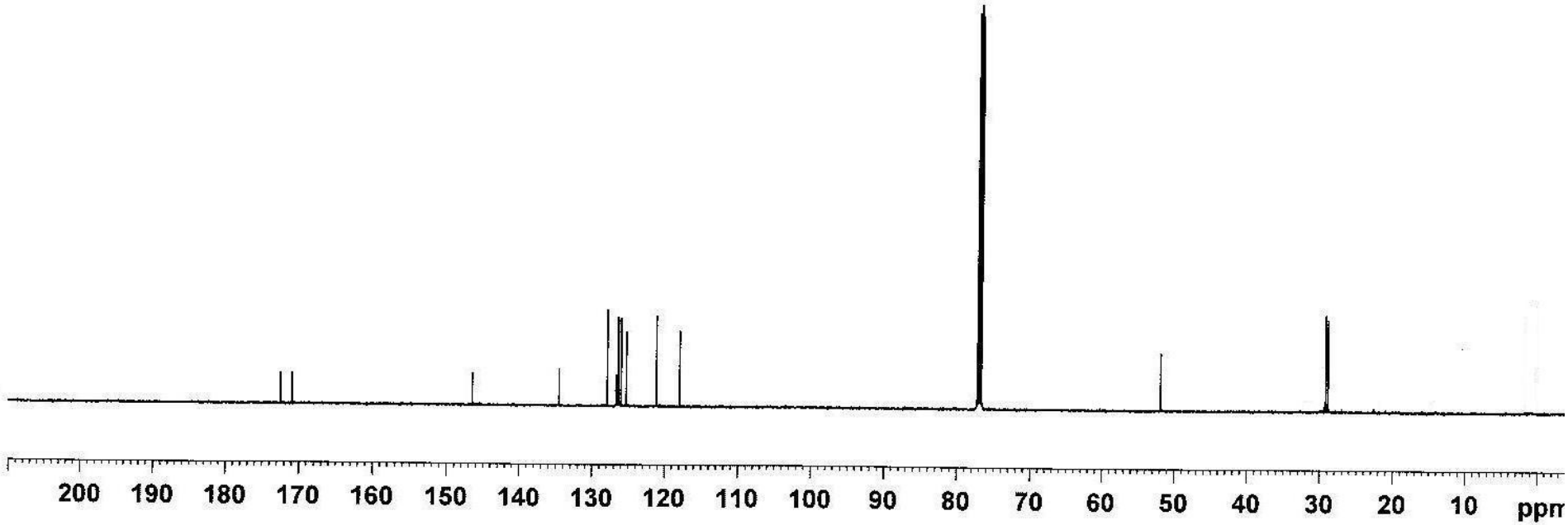


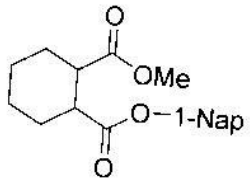


lf-6-21-1

^{13}C NMR of 3eb

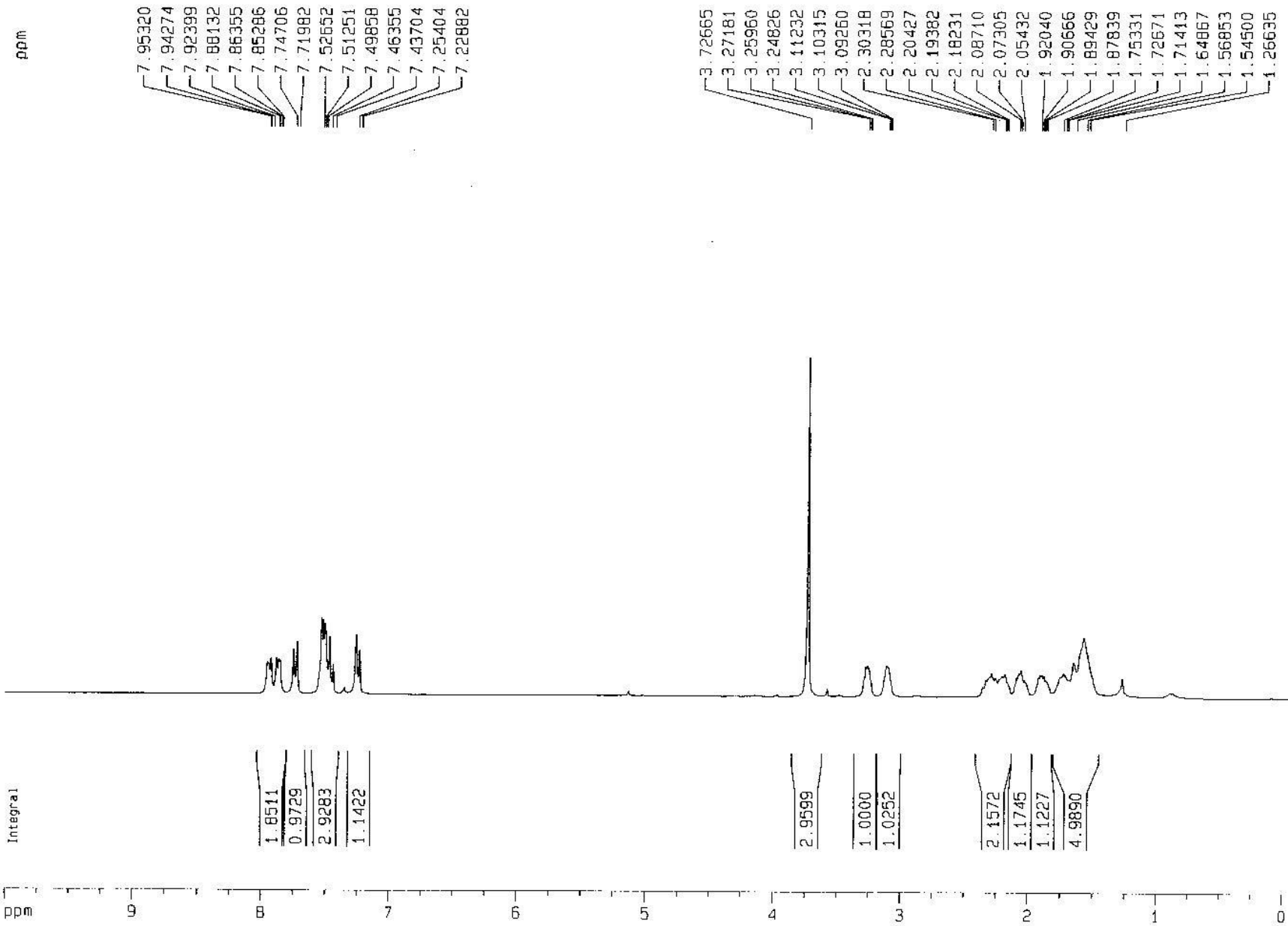
172.53
170.93
146.53
134.62
127.95
126.77
126.47
126.42
126.05
125.33
121.17
117.97
77.25
77.00
76.75
51.96
29.25
28.93



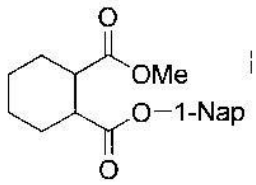


1f-6-21-2

^{1}H NMR of 3fb

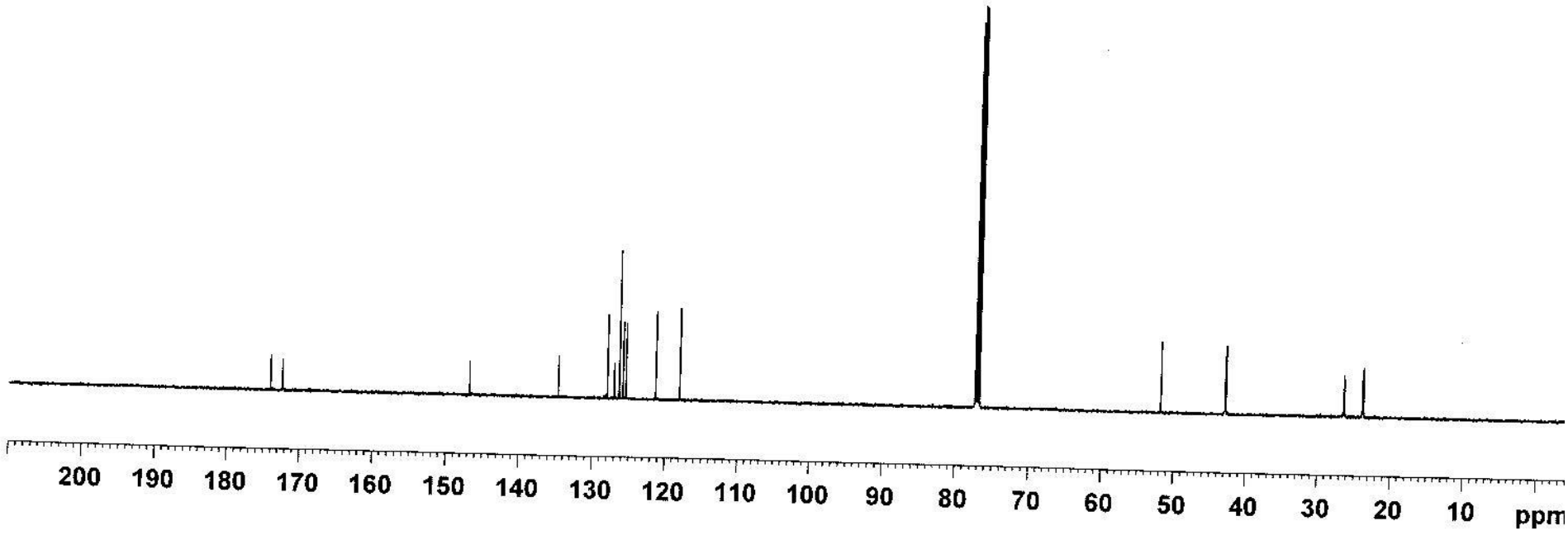


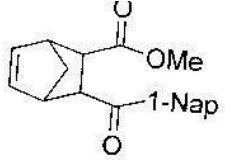
lf-6-21-2



^{13}C NMR of 3fb

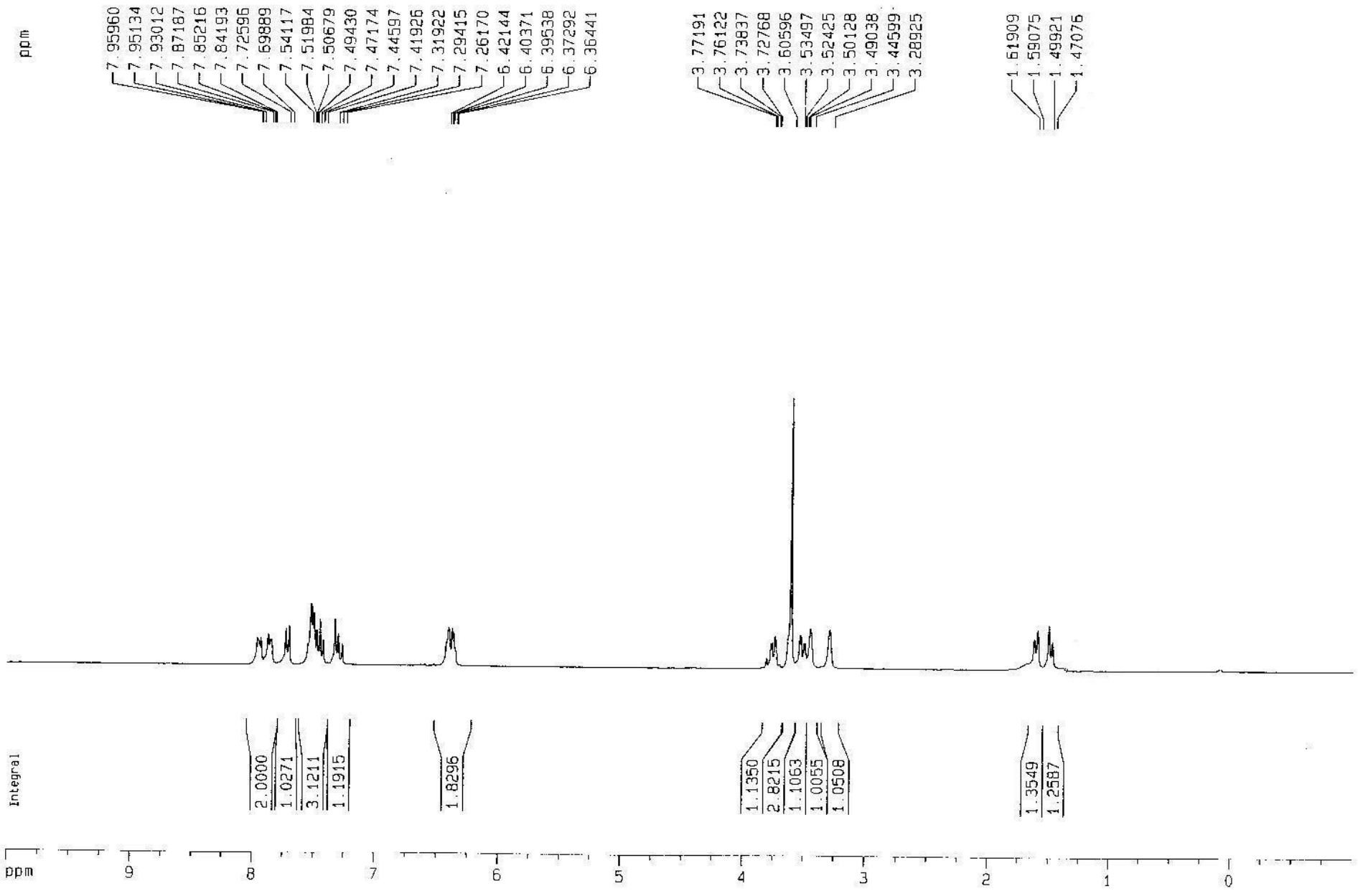
174.03
172.40
146.78
134.67
127.96
127.05
126.35
125.83
125.42
121.32
118.03
77.30
77.04
76.79
51.82
42.94
42.82
26.45
26.39
23.88
23.76



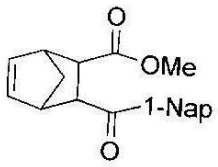


1f-6-21-3

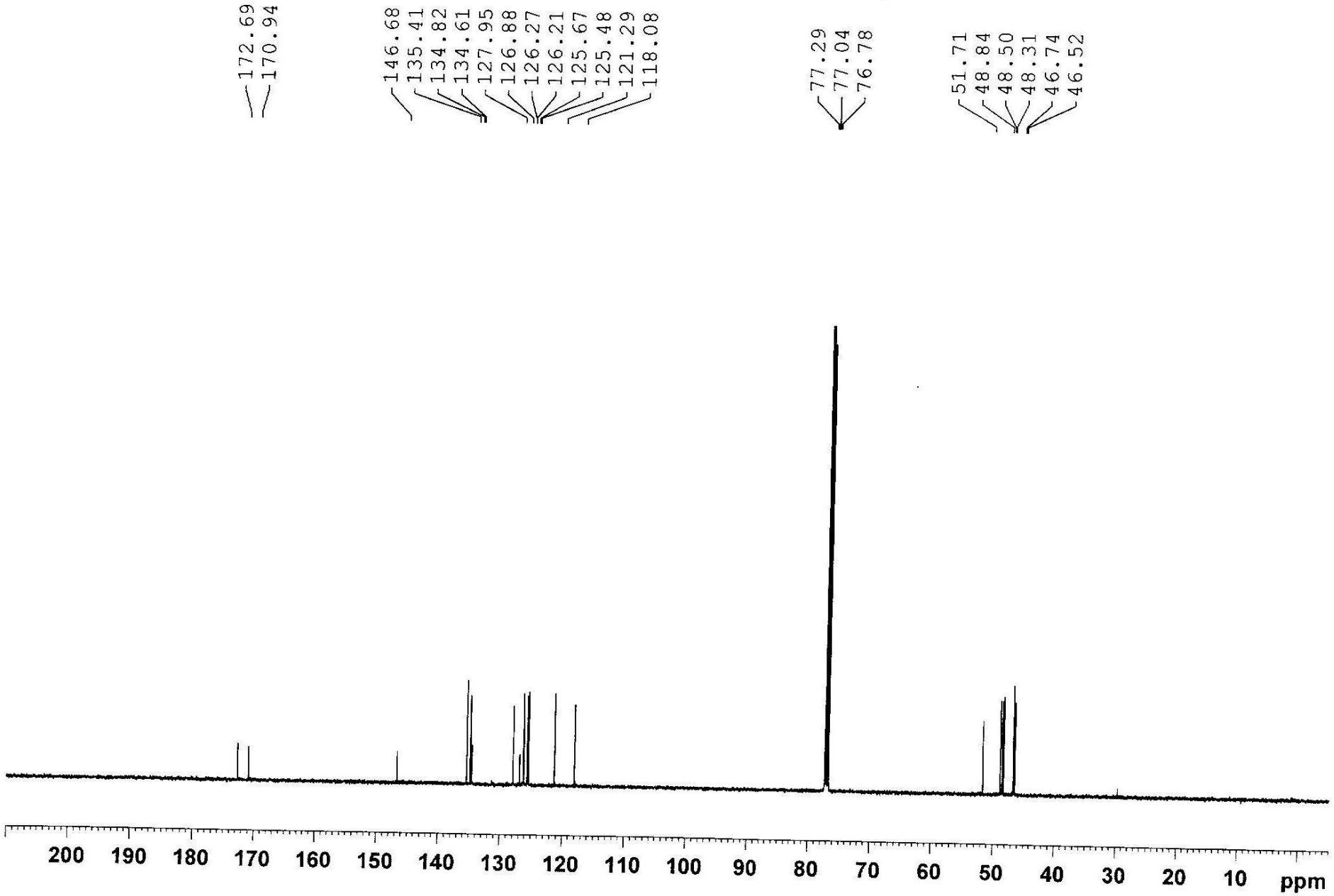
^{1}H NMR of 3gb

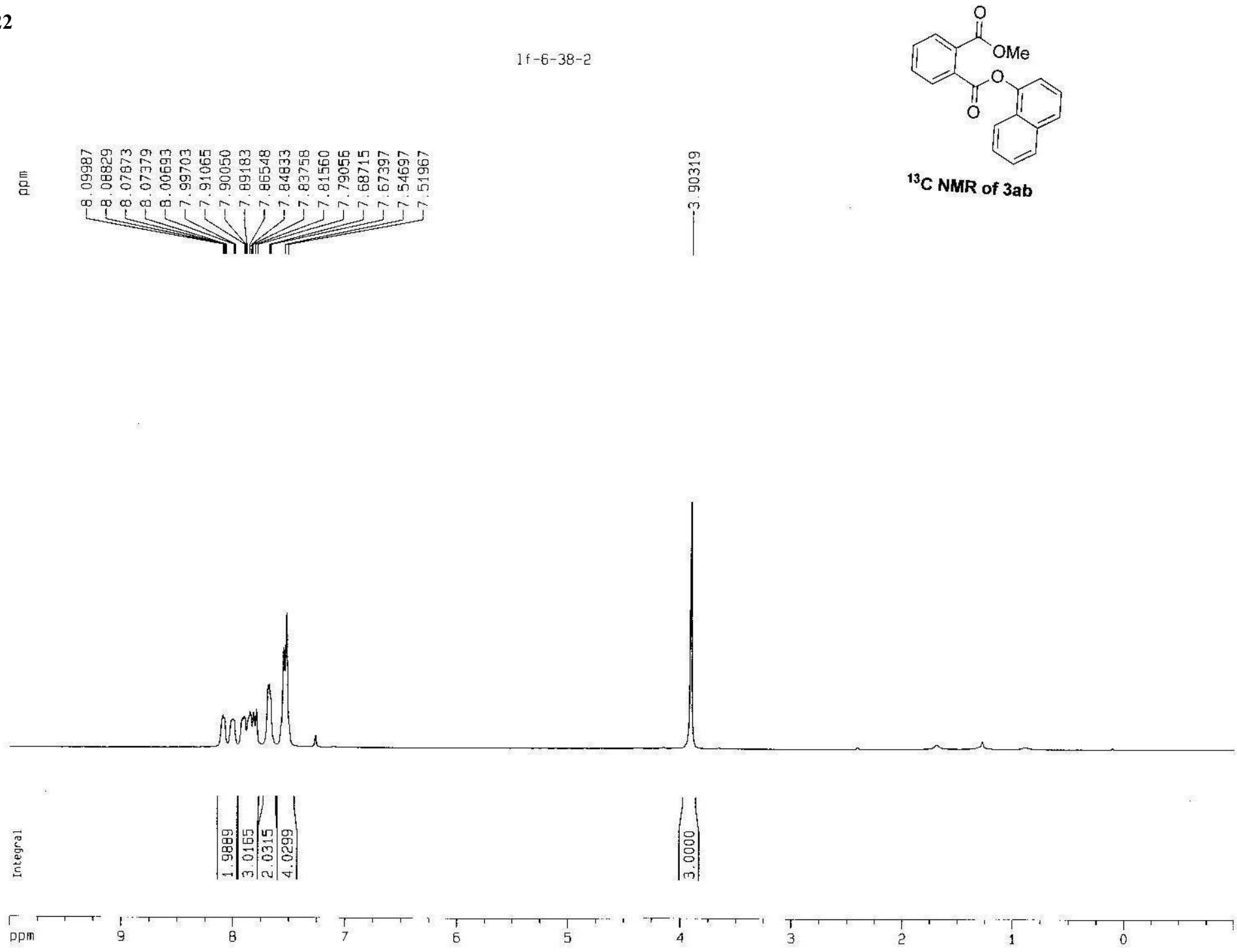


lf-6-21-3

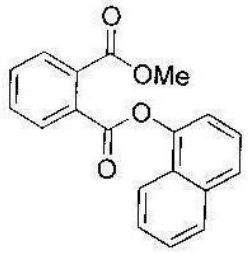


^{13}C NMR of 3gb





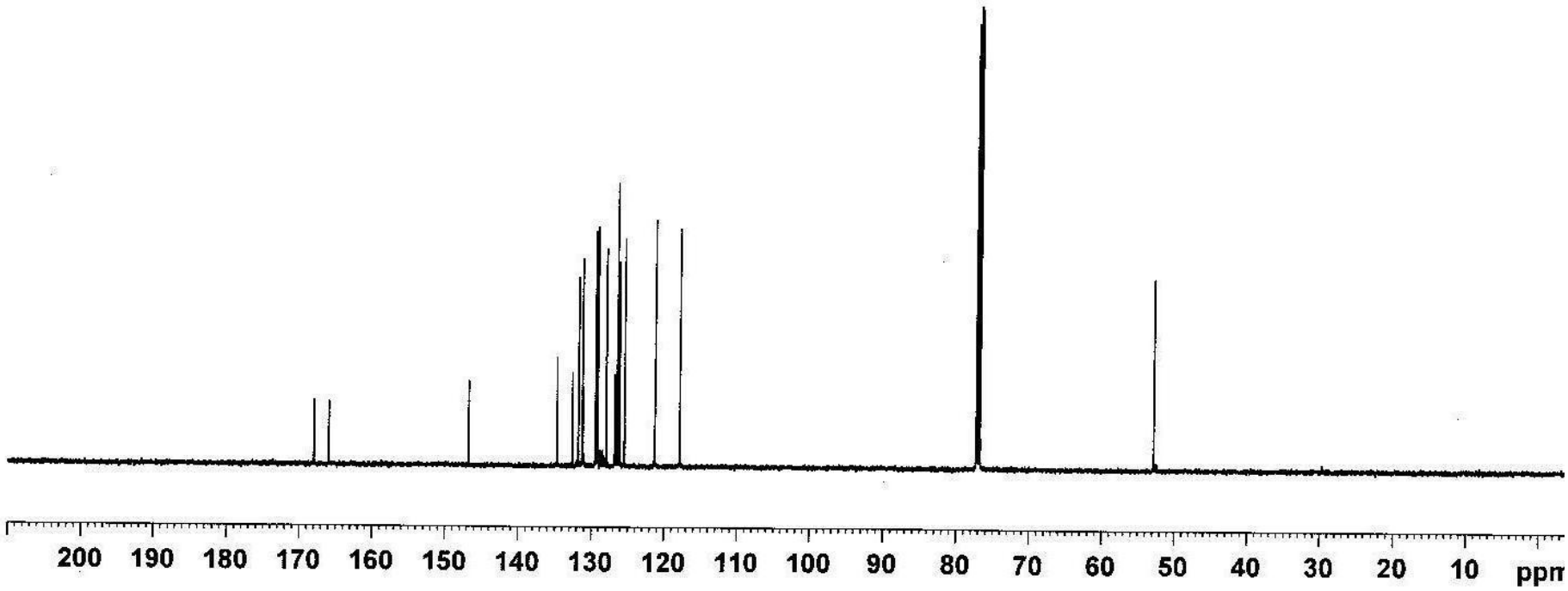
^{13}C NMR of 3ab

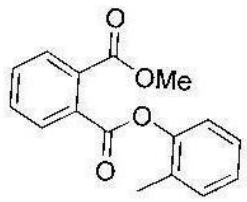


^{1}H NMR of 3ab

5-62-2

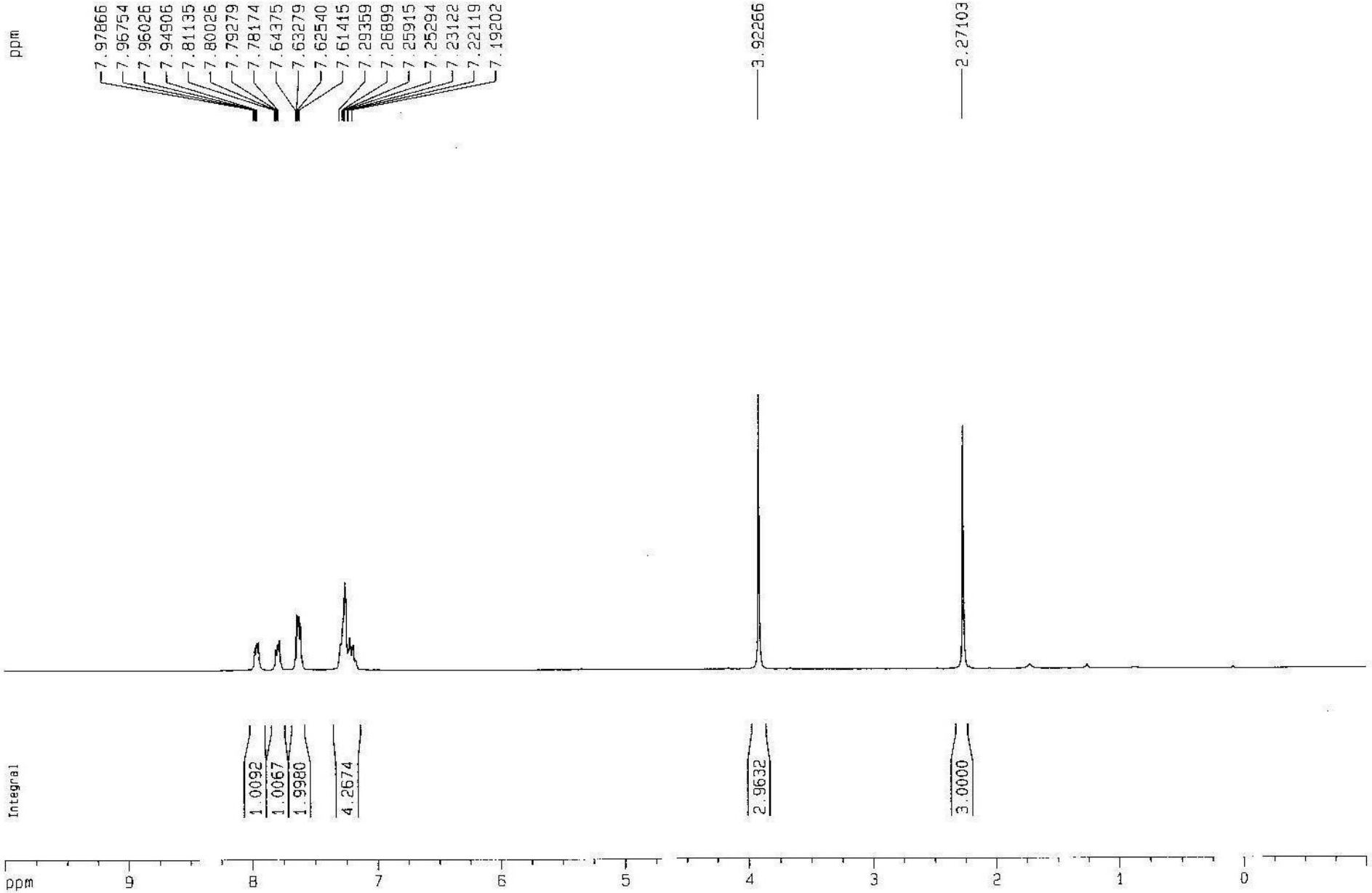
167.95
165.92
146.81
134.76
132.66
131.82
131.30
131.23
129.49
129.21
128.03
126.85
126.53
126.52
126.23
125.51
121.33
117.95
77.32
77.06
76.81
52.82

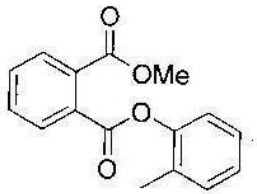




1f-6-38-3

^{1}H NMR of 3ac

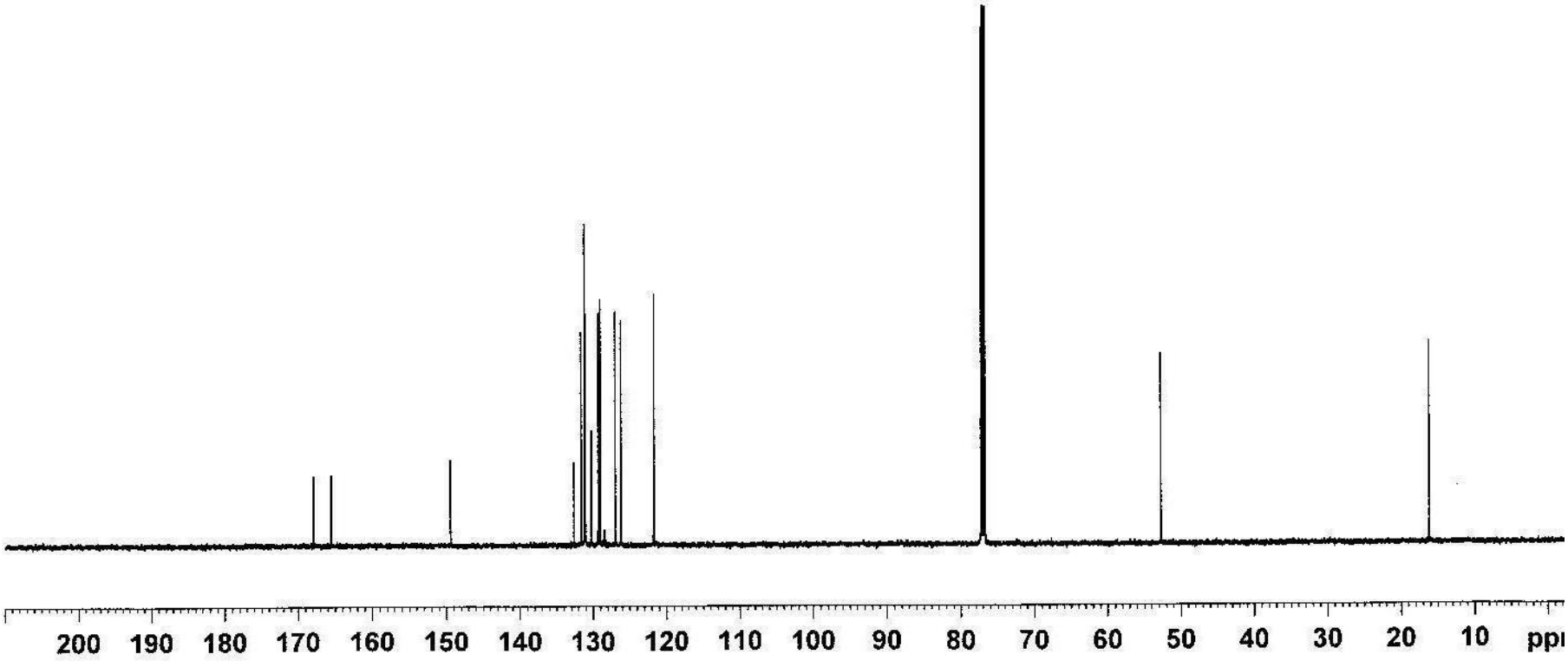


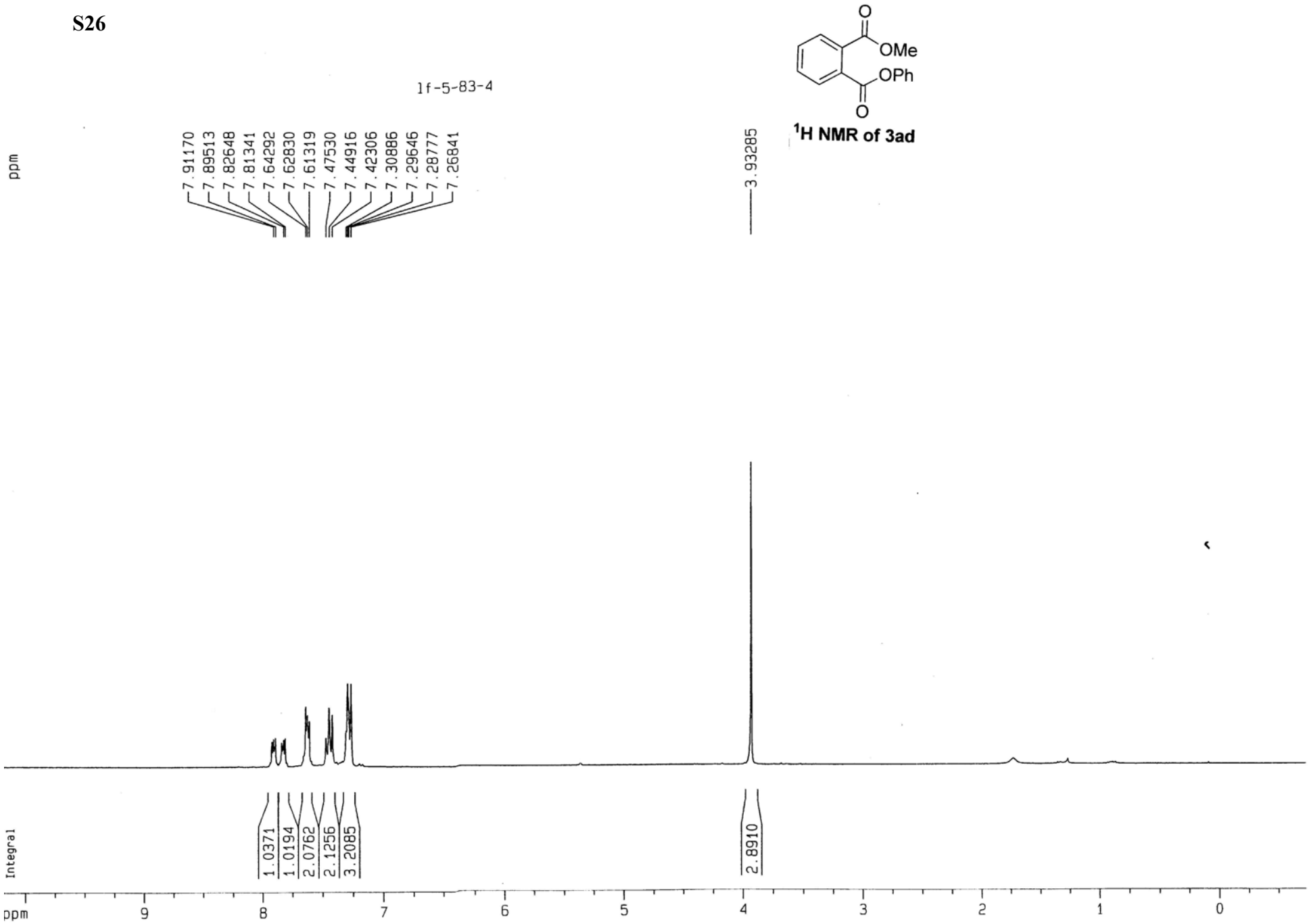


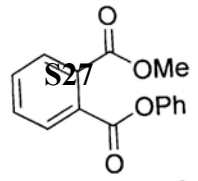
5-58-2

^{13}C NMR of 3ac

167.94
165.54
149.46
132.65
131.67
131.21
131.14
130.25
129.33
129.07
127.04
126.24
121.73
77.30
77.05
76.80
52.75
16.16



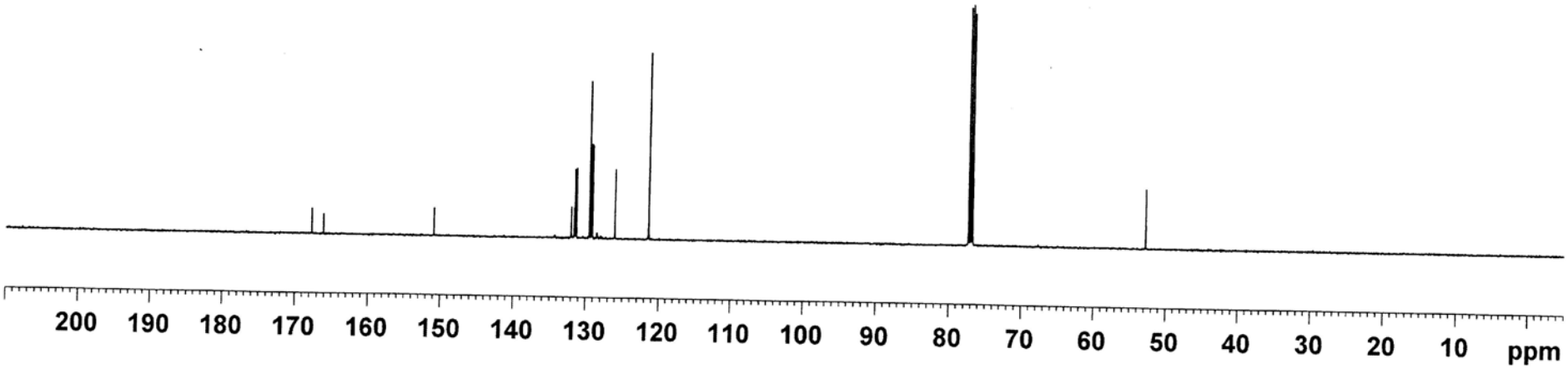

1f-5-83-4
ppm
7.91170
7.89513
7.82648
7.81341
7.64292
7.62830
7.61319
7.47530
7.44916
7.42306
7.30886
7.29646
7.28777
7.26841
3.93285
OMe
OPh
O
O
O
1H NMR of 3ad
Integral
1.0371
1.0194
2.0762
2.1256
3.2085
2.8910
ppm
9
8
7
6
5
4
3
2
1
0

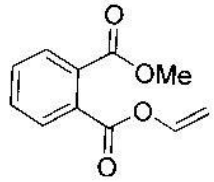


^{13}C NMR of 3ad

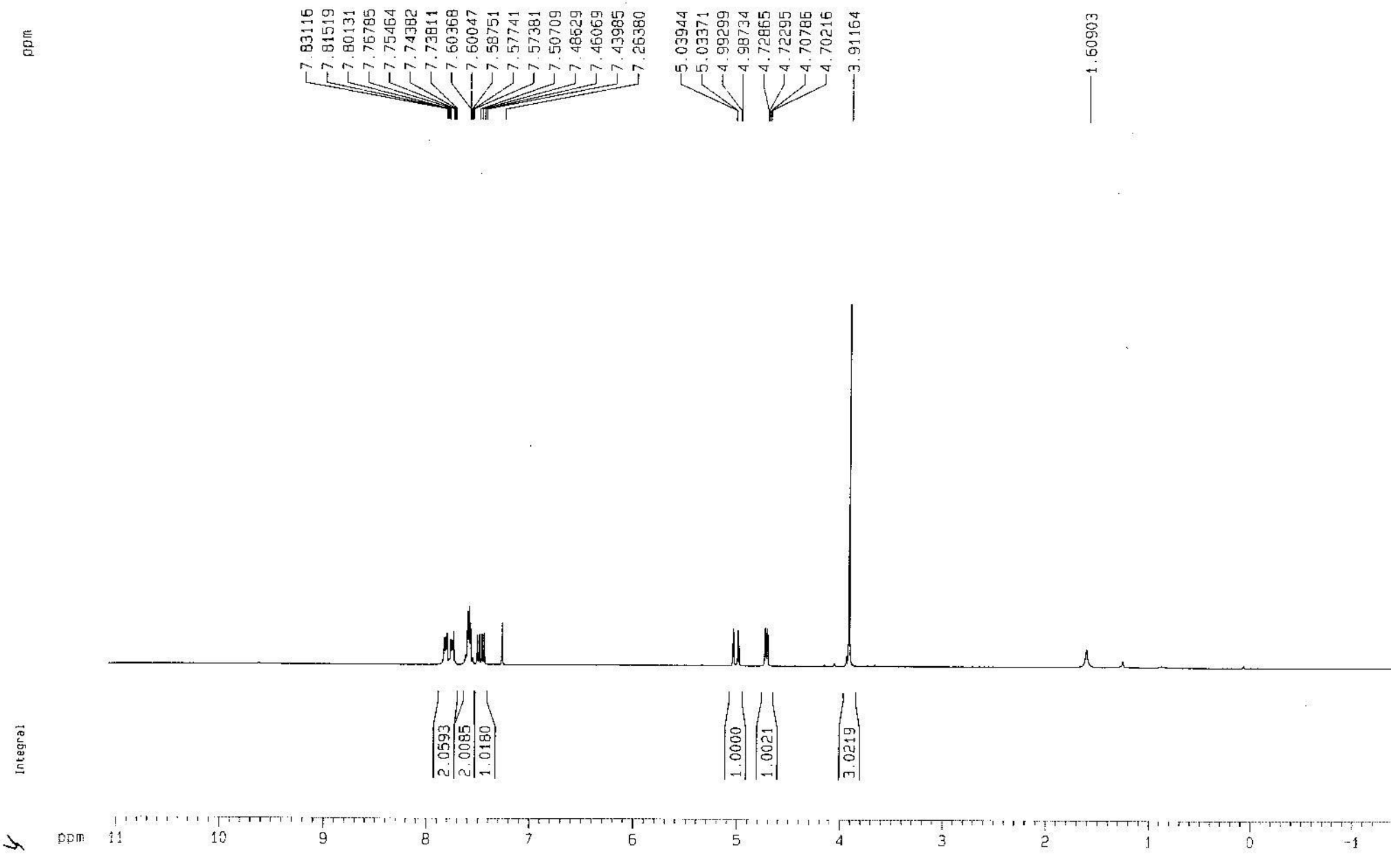
lf-5-83-4

167.74
166.16
150.91
132.07
131.64
131.54
131.34
129.54
129.30
129.16
126.08
121.44
77.31
77.05
76.80
52.80

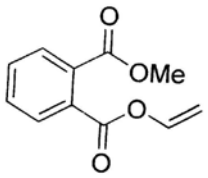



OMe
O
O
O

^{1}H NMR of 3ae

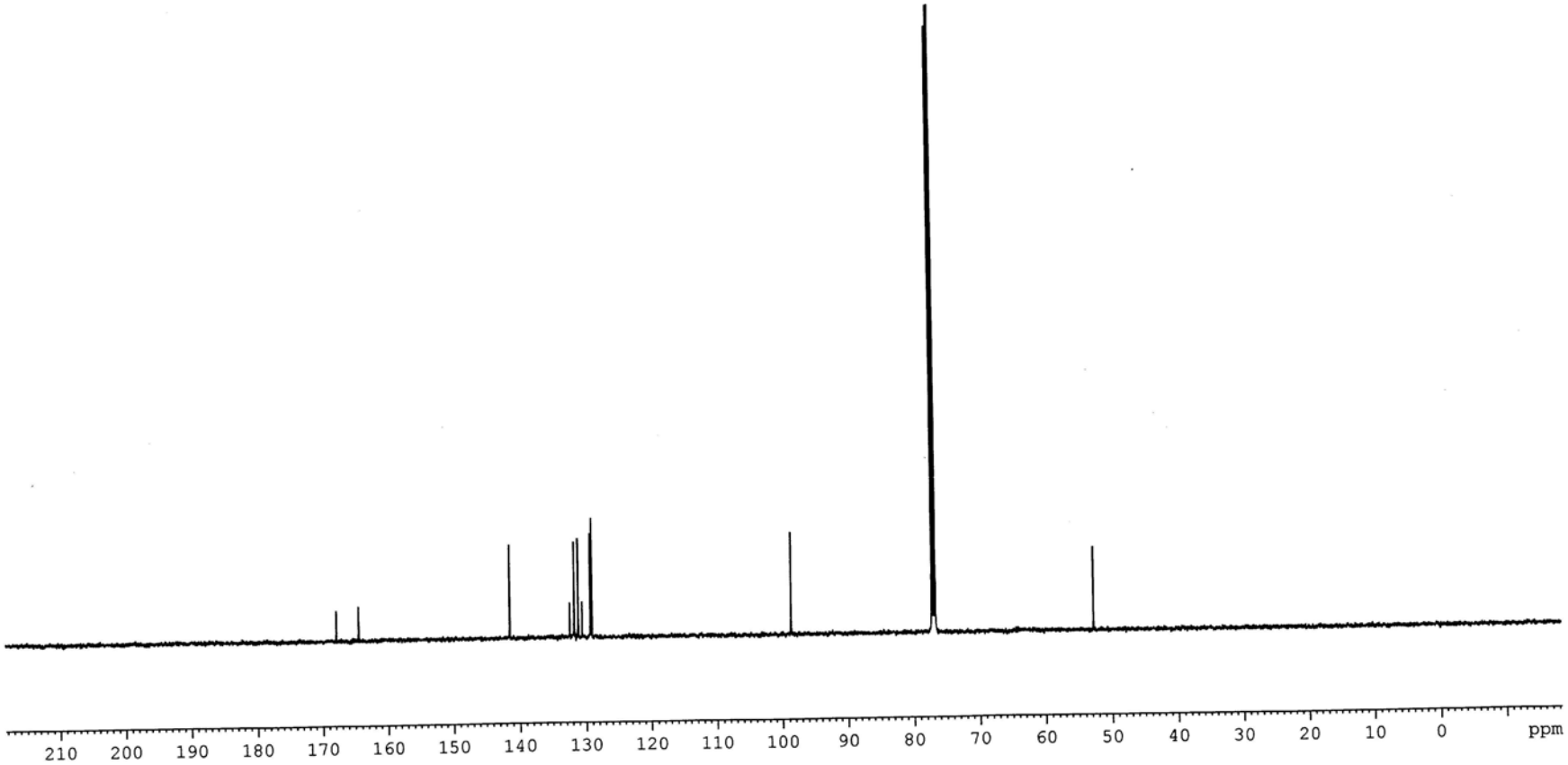

1f-6-6-3
ppm
7.83116
7.81519
7.80131
7.76785
7.75464
7.74382
7.73811
7.60368
7.60047
7.58751
7.57741
7.57381
7.50709
7.48629
7.46069
7.43985
7.26380
5.03944
5.03371
4.99299
4.98734
4.72865
4.72295
4.70786
4.70216
3.91164
1.60903
Integral
2.0593
2.0085
1.0180
1.0000
1.0021
3.0219
ppm
11
10
9
8
7
6
5
4
3
2
1
0
-1

lf-6-6-3-2

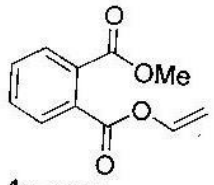


^{13}C NMR of 3ae

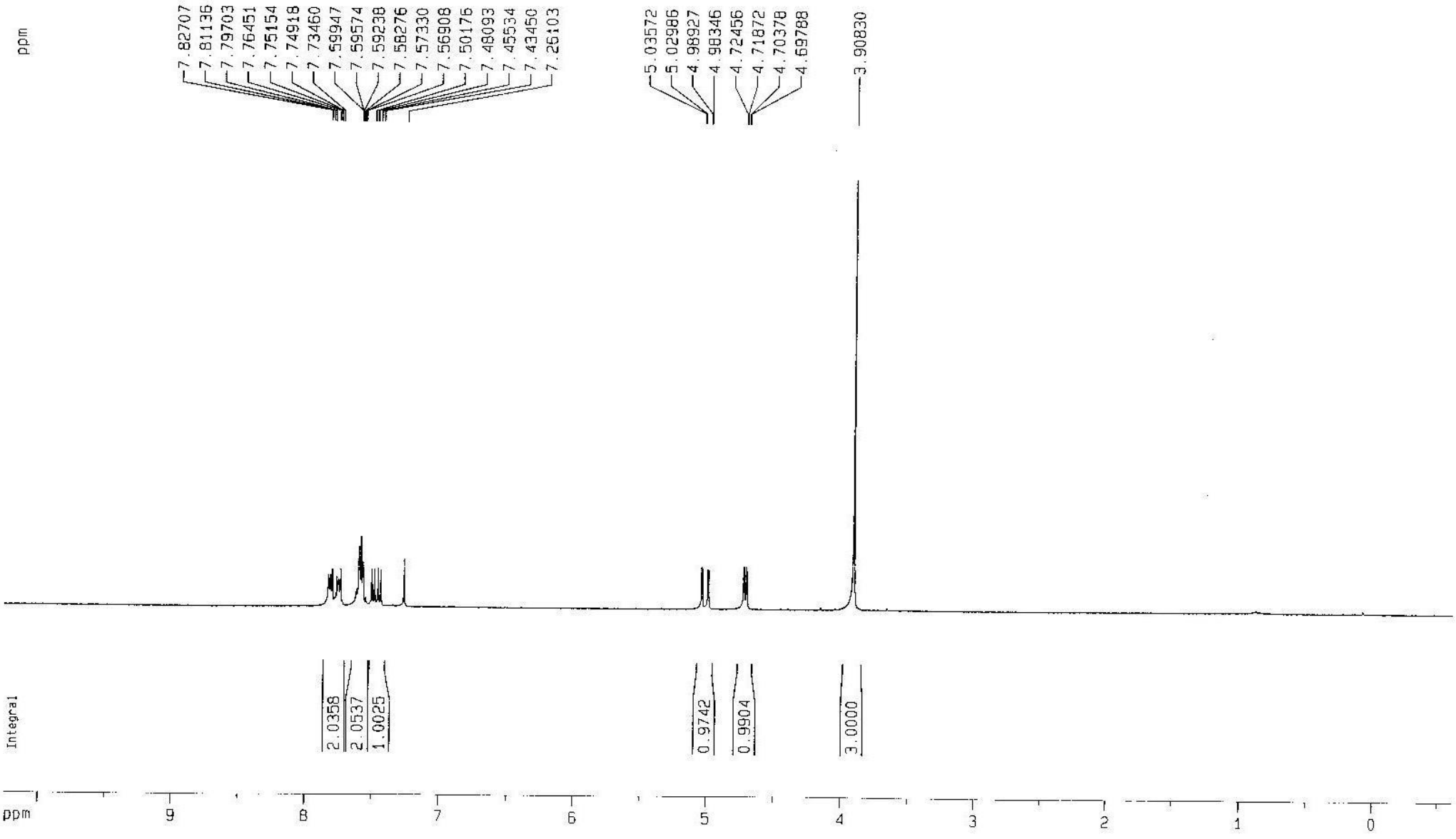
167.92
164.49
141.46
132.45
131.77
131.14
130.55
129.32
129.03
98.70
77.27
77.02
76.77
52.79



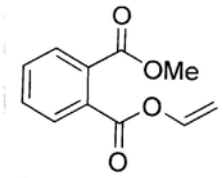
1f-5-62-4



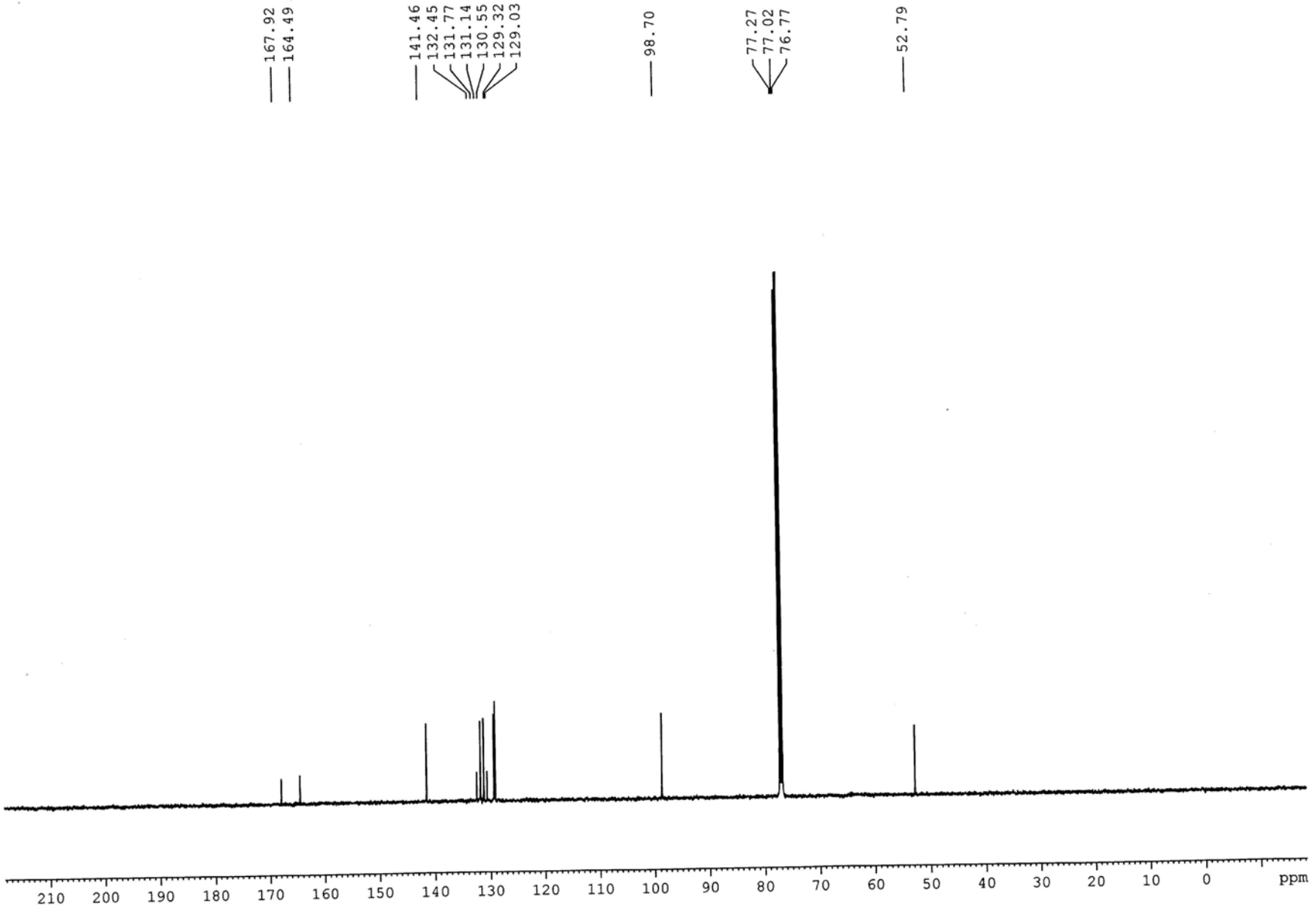
^{1}H NMR of 3af



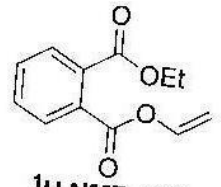
lf-6-6-3-2



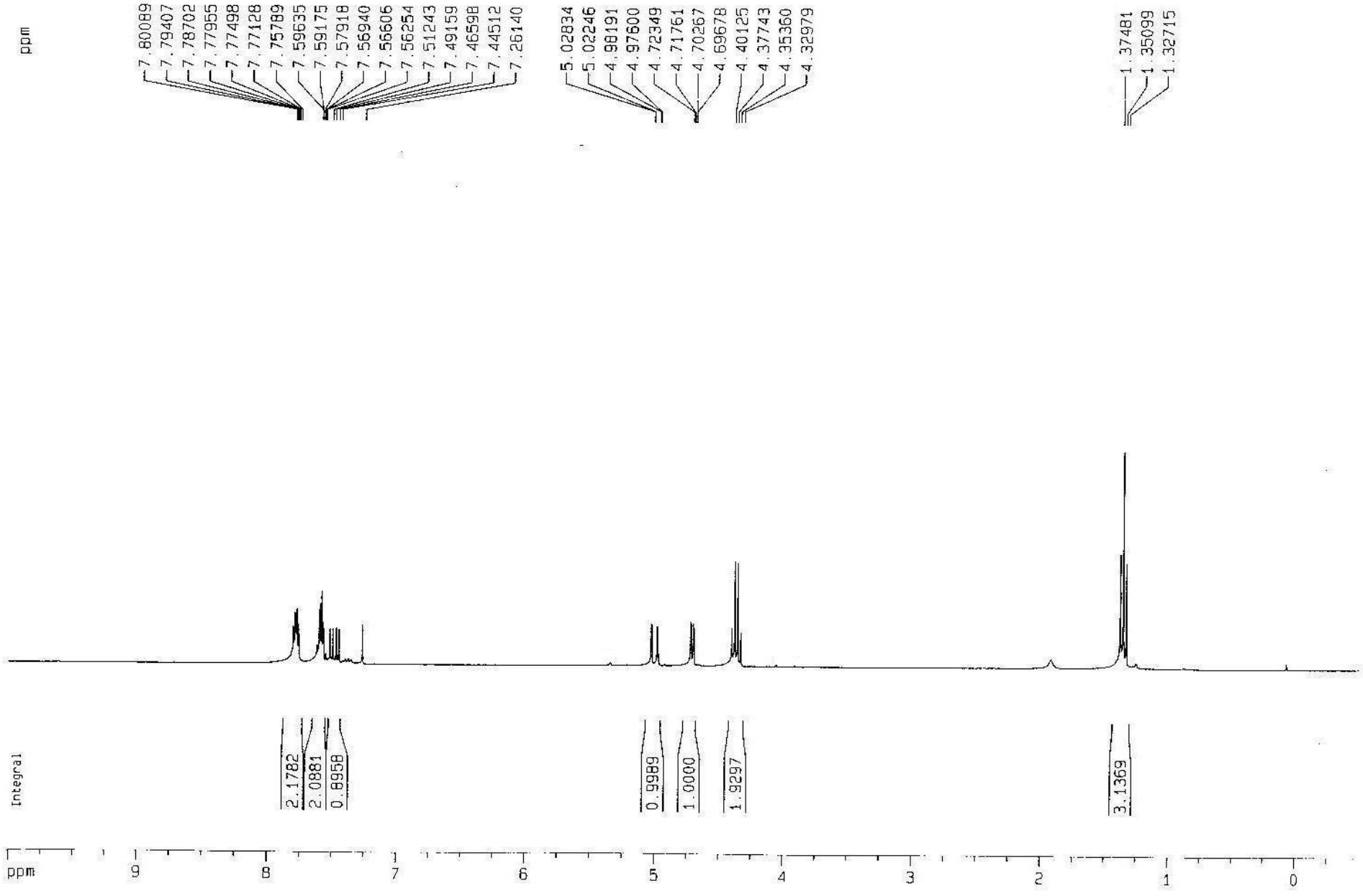
^{13}C NMR of 3af



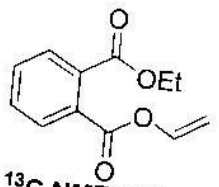
1f-6---1-2



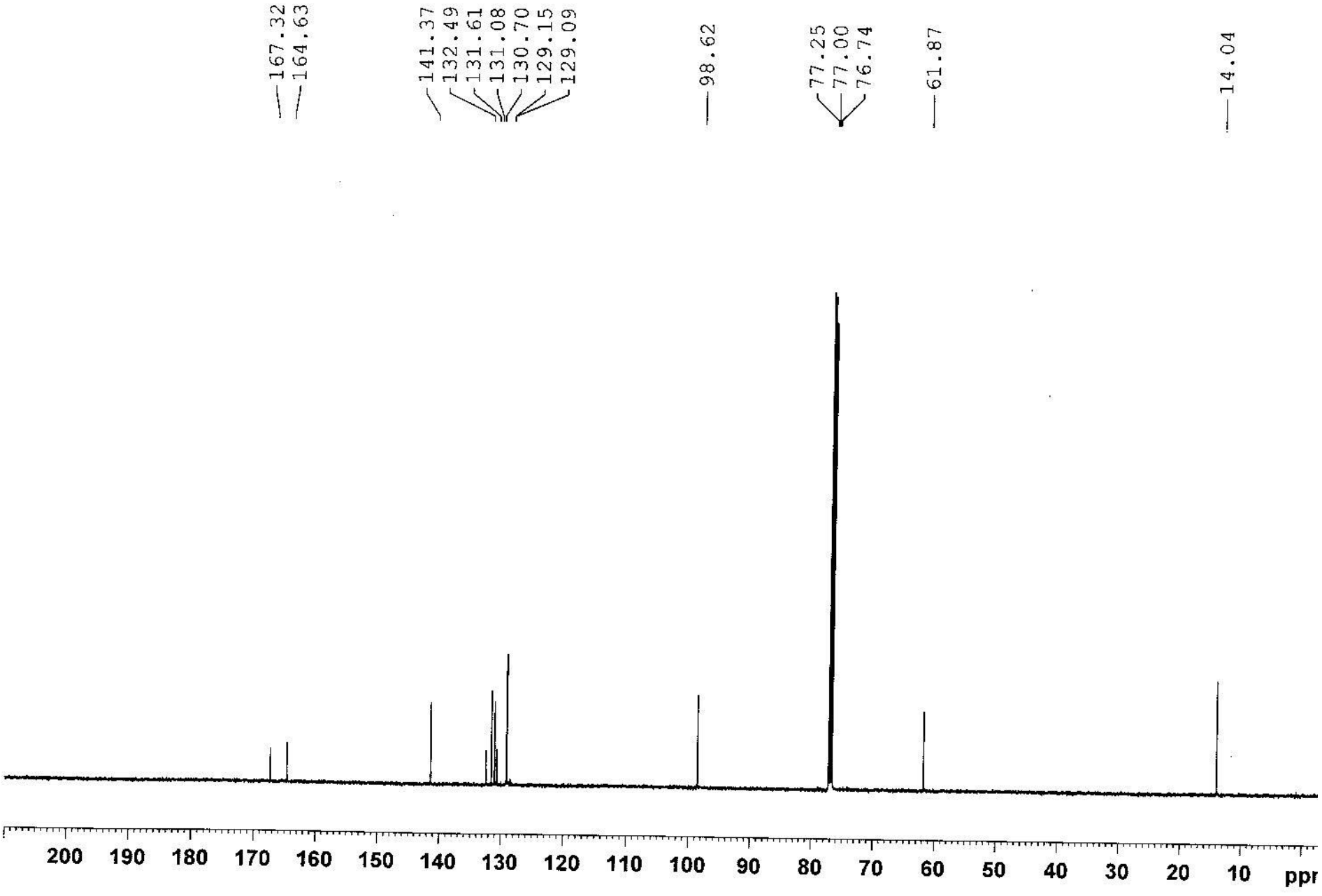
^{1}H NMR of 3ag



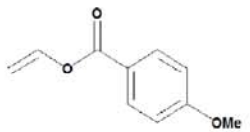
lf-6-6-1



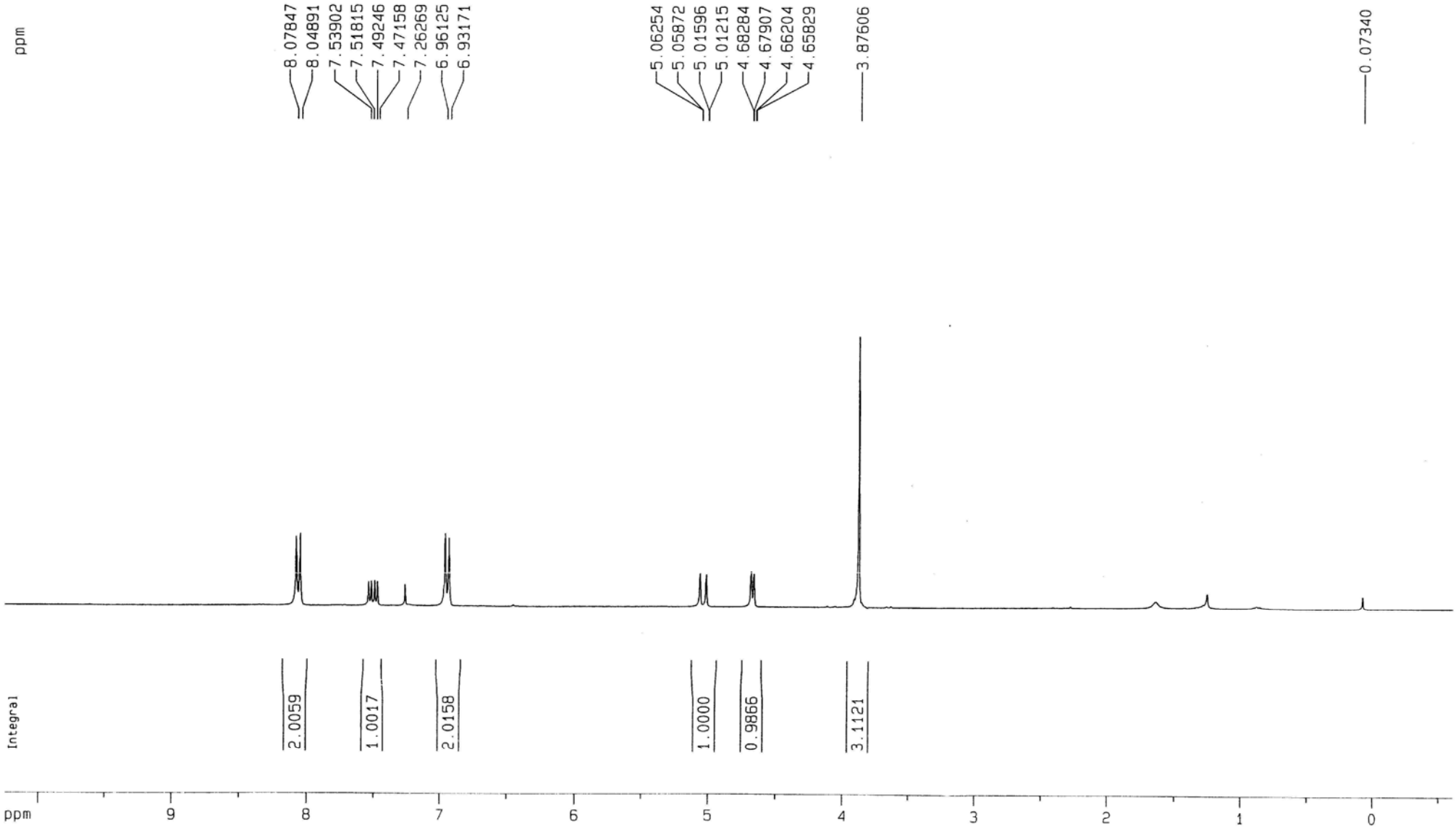
^{13}C NMR of 3ag



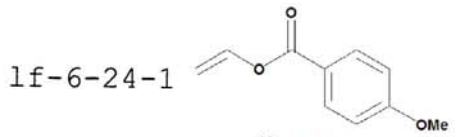
1f-6-24-1



^{1}H NMR

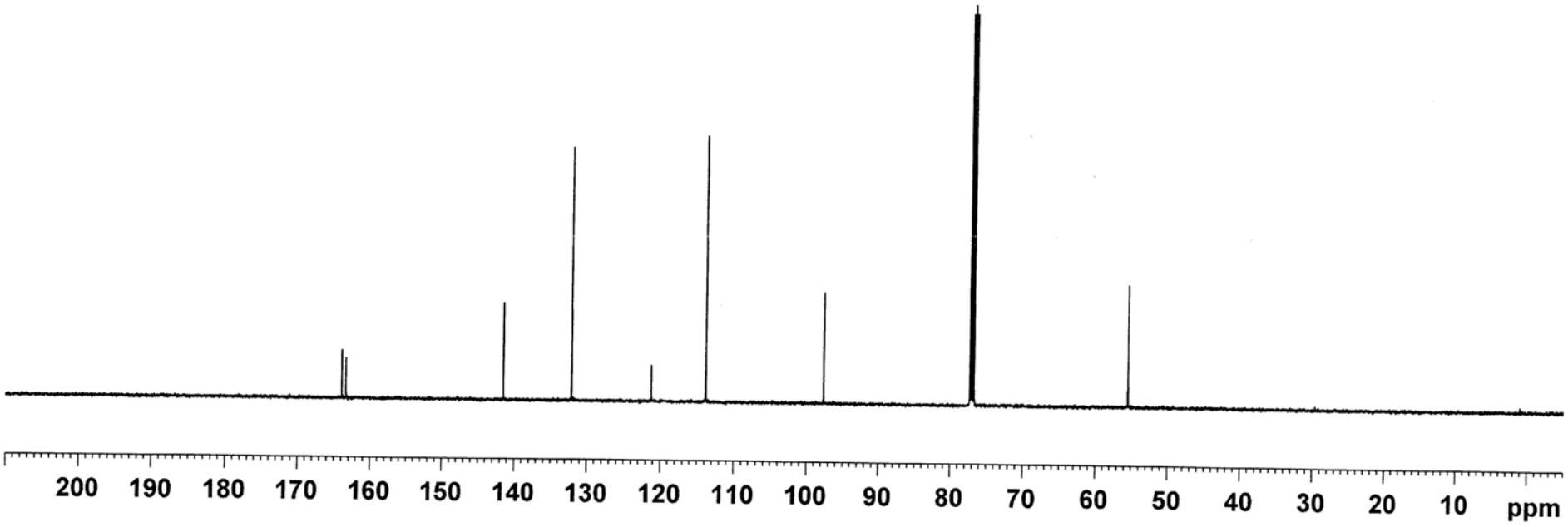


lf-6-24-1

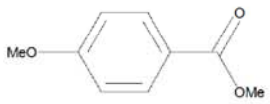


^{13}C NMR

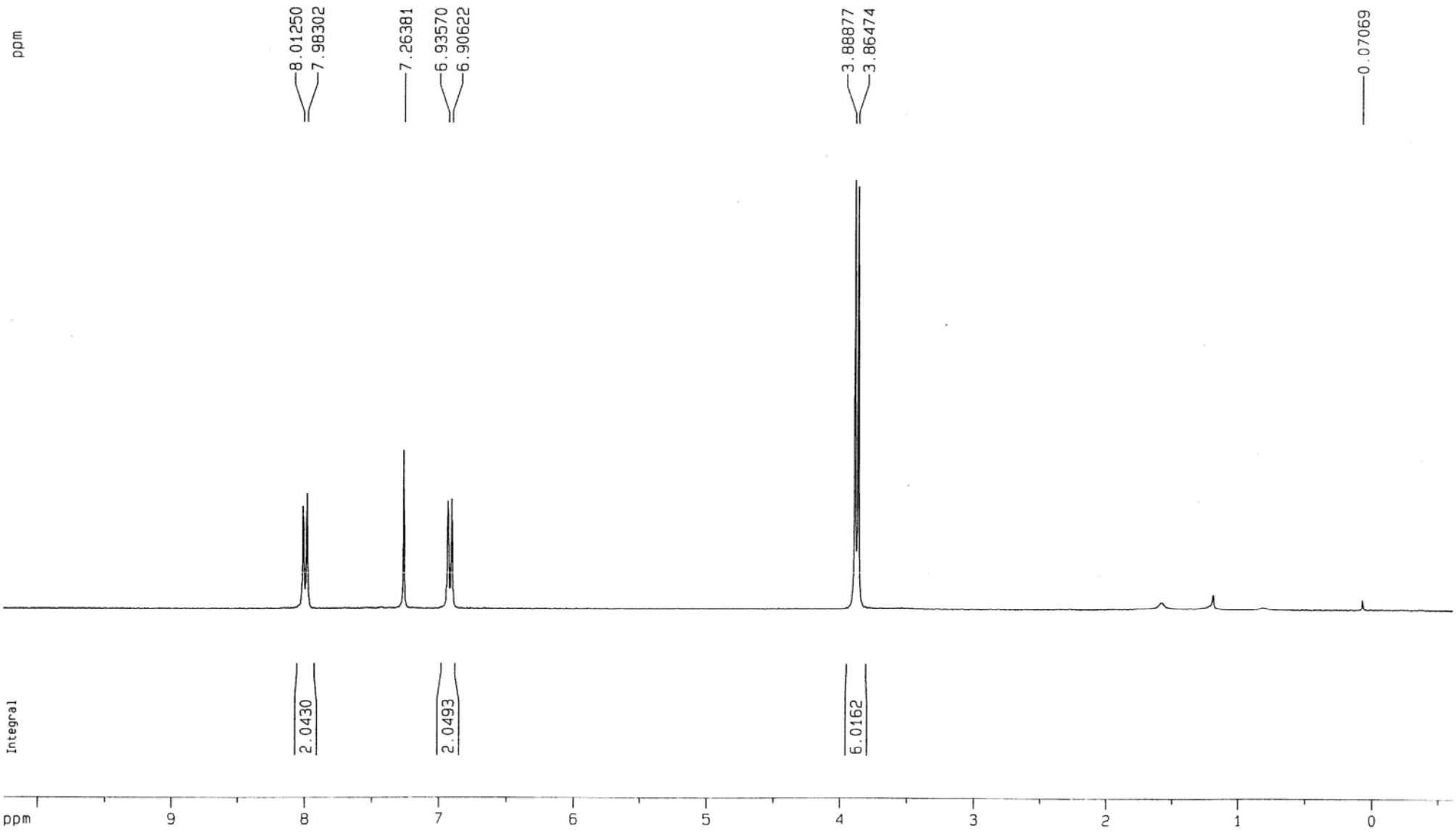
163.93
163.38
141.53
132.13
121.25
113.83
97.66
77.27
77.02
76.76
55.47

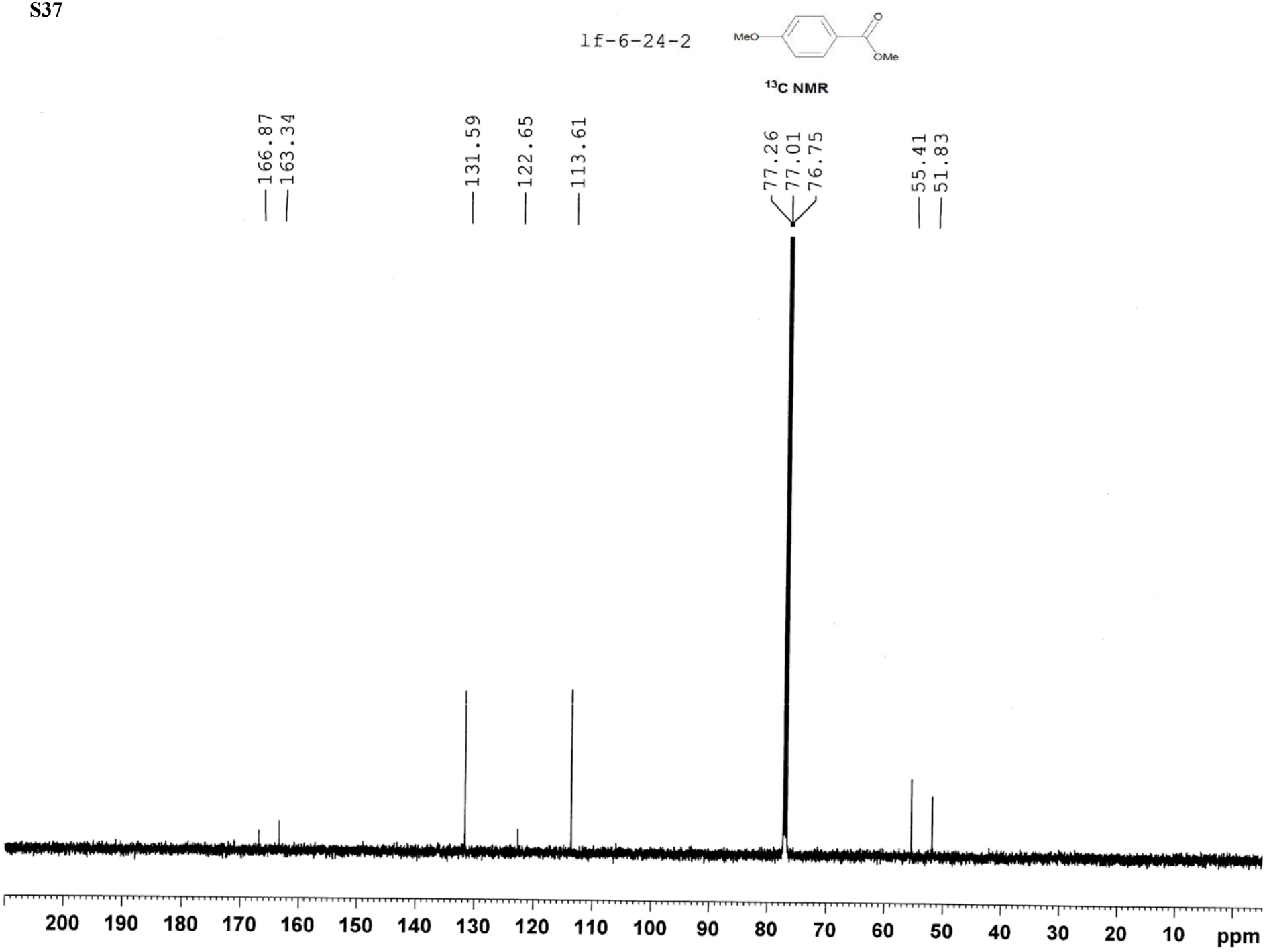


1f-6-24-2



^{1}H NMR




lf-6-24-2
MeO
OMe
O
^{13}C NMR
166.87
163.34
131.59
122.65
113.61
77.26
77.01
76.75
55.41
51.83
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm