DABCO-Catalyzed Reaction of α-Halo Carbonyl Compounds with Dimethyl Acetylenedicarboxylate: A Novel Method for the Preparation of Polysubstituted Furans and Highly Functionalized 2*H*-Pyrans

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Supporting Information

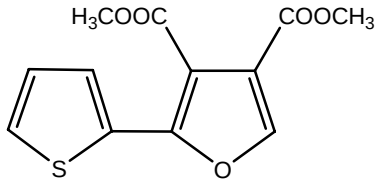
(I). Experimental section.

General Comments. Column chromatography was carried out on silica gel. Melting points were determined on a microscopic apparatus and were uncorrected. Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded at 300MHz in $CDCl_3$ and ^{13}C NMR spectra was recorded at 75MHz in $CDCl_3$ using TMS as internal standard. IR spectra were obtained using an FT IR spectrometer and only major peaks are reported in cm^{-1}. Mass spectra were recorded by the EI method. All solvents used were dried without further purification.

General procedure for the reactions of dimethyl acetylenedicarboxylate with *α*-halo carbonyl compounds. DABCO (0.1 mmol) was added to a stirred solution of *α*-halo carbonyl compound (1.5mmol for *α*-chloroketones, 1.0mmol for *α*-bromoketones) in 6ml of $MeCN/Et_2O$ (1:1) and stirred at room temperature (25-30 $^{\circ}C$) for 30min. Anhydrous K_2CO_3 (1.5 mmol for *α*-chloroketones, 1.0mmol for *α*-bromoketones)) was added, followed by dimethyl acetylenedicarboxylate (0.5 mmol). The reaction was stirred at room temperature until thin layer chromatographic analysis showed complete consumption of the dimethyl acetylenedicarboxylate. H_2O (10ml) was added to the mixture and extracted thrice with 15ml CH_2Cl_2. The combined extracts were washed with H_2O and brine, and then dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica column to give furans **3** and 2*H*-pyrans **4**.

(II). Spectroscopic Data for polySubstituted Furans and highly functionalized 2*H*-pyrans.

3a Dimethyl 2-(thiophen-2-yl) furan-3, 4-dicarboxylate



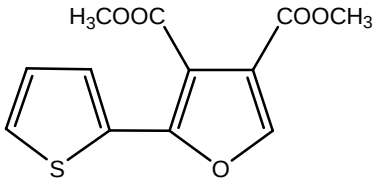
^{1}H NMR (300MHz, $CDCl_3$) δ=3.88(s, 3H), 3.95(s, 3H), 7.11(dd, J=4.2, 4.8Hz, 1H), 7.44 (d, J=5.1Hz, 1H), 7.68 (d, J=3.6Hz, 1H), 7.89(s, 1H).

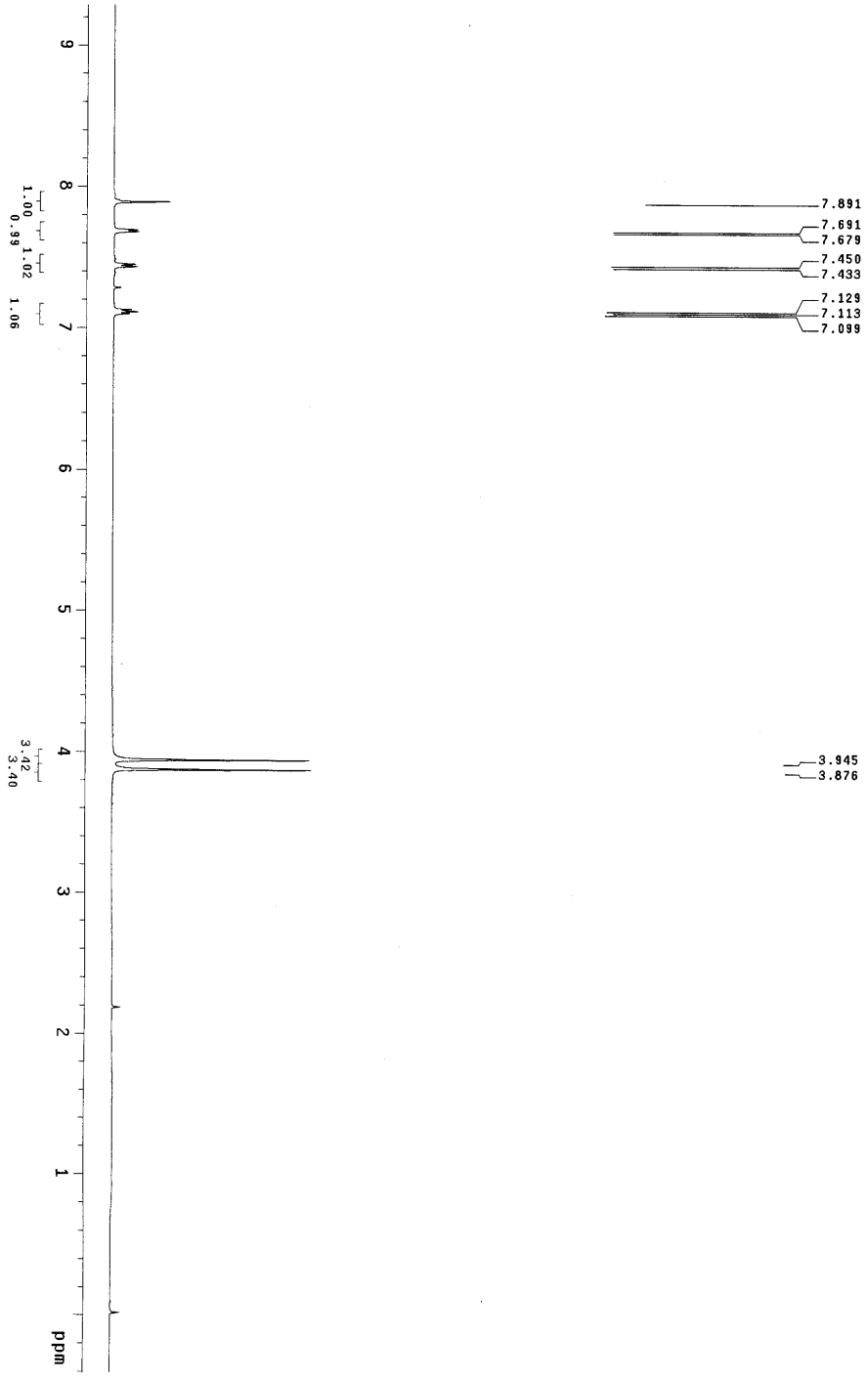
^{13}C NMR (75MHz, $CDCl_3$) δ=23.0, 30.0, 52.3, 52.7, 112.0, 120.0, 128.0, 128.2, 130.4, 146.0, 151.6, 162.4, 164.0.

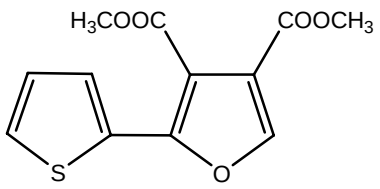
IR (KBr): v=3106, 2921, 1723, 1554, 1441, 1279, 1066, 707cm^{-1}.

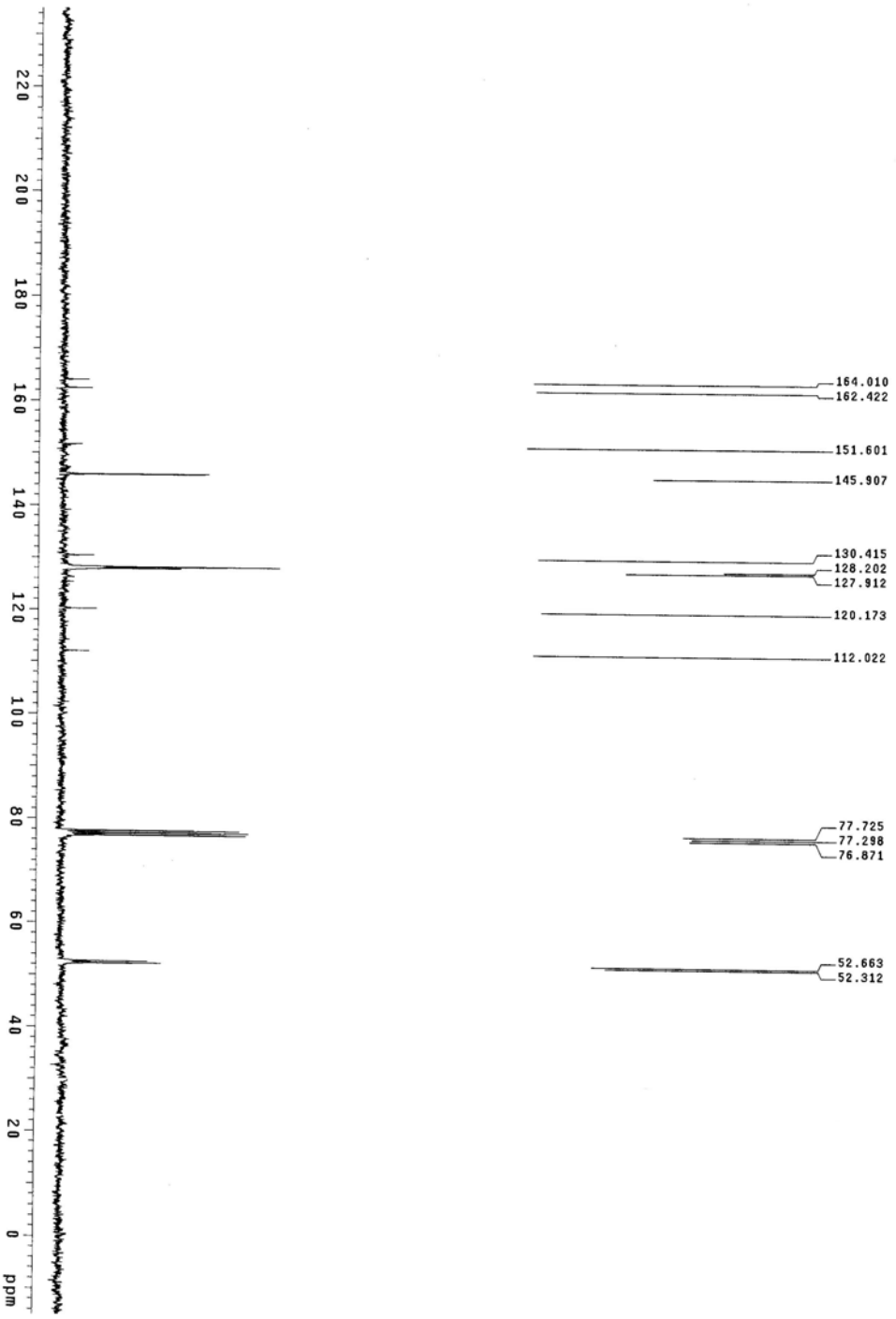
MS: m/z (%)=266(M^+, 50), 235(76.13), 111(13.45), 83(4.32).

HRMS calcd for $C_{12}H_{10}O_5S$: (M+Na) 289.0141, Found: 289.0147.

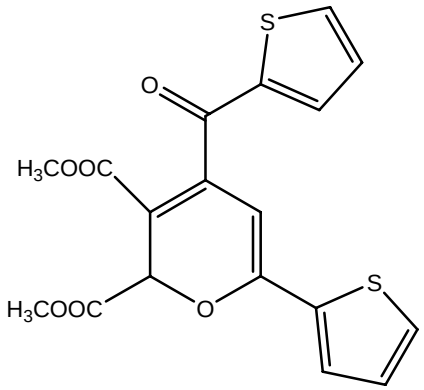

H3COOC
COOCH3
S
O


7.891
7.691
7.679
7.450
7.433
7.129
7.113
7.099
3.945
3.876
1.00
0.99
1.02
1.06
3.42
3.40
9
8
7
6
5
4
3
2
1
ppm


H3COOC
COOCH3
S
O


220
200
180
160
140
120
100
80
60
40
20
0
ppm
164.010
162.422
151.601
145.907
130.415
128.202
127.912
120.173
112.022
77.725
77.298
76.871
52.663
52.312

4a



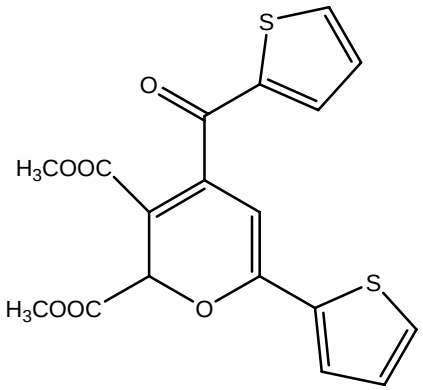
^{1}H NMR (300MHz, $CDCl_3$) δ=3.59(s, 3H), 3.78(s, 3H), 5.94(s, 1H), 6.01(s, 1H), 7.07-7.13(m, 2H), 7.47(d, J=4.8Hz, 1H), 7.53(d, J=2.7Hz, 1H), 7.61(d, J=3.9Hz, 1H), 7.72(d, J=4.8Hz, 1H).

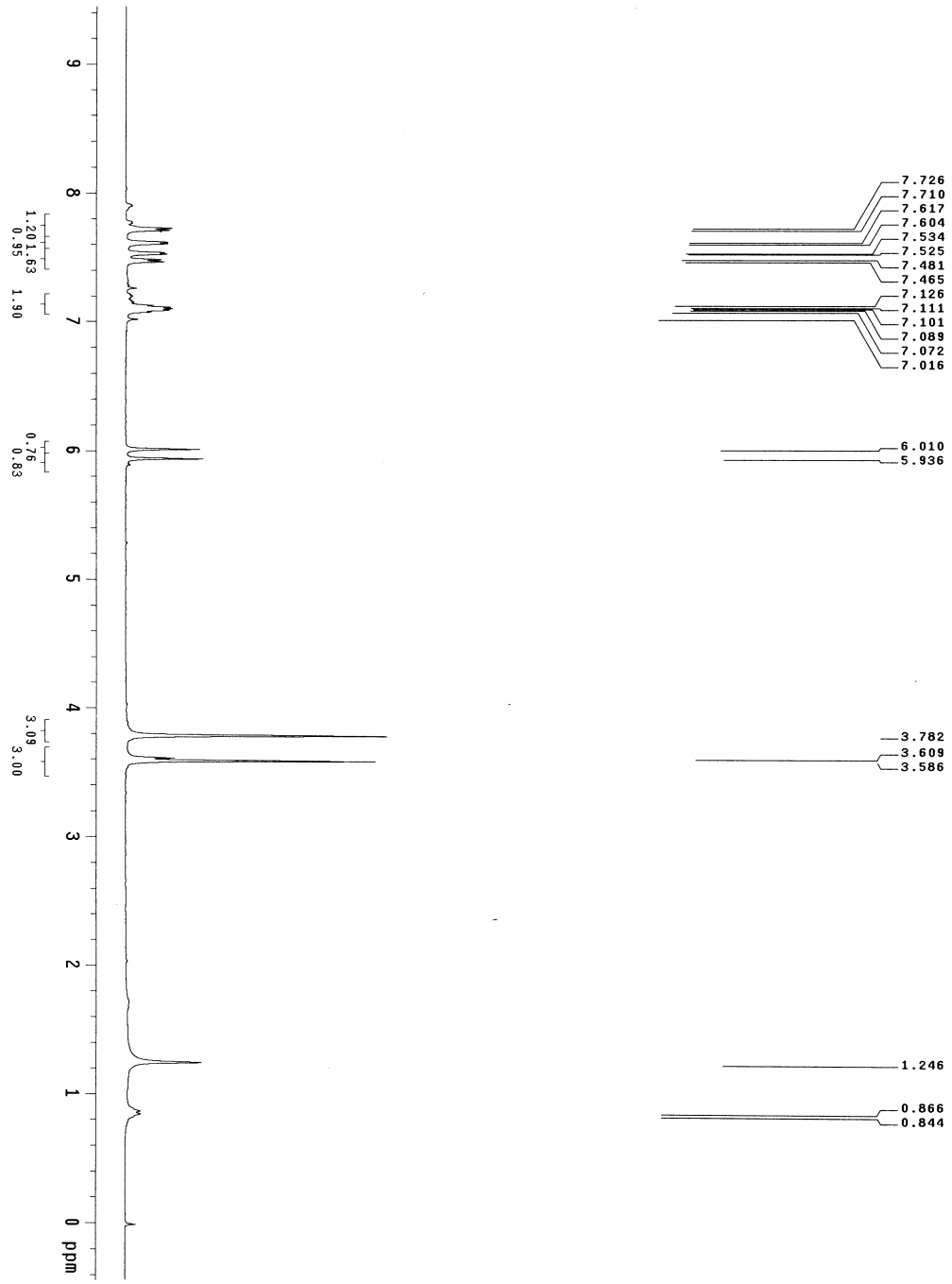
^{13}C NMR (75MHz, $CDCl_3$) δ= 52.3, 53.2, 72.5, 97.6, 110.8, 128.5, 128.7, 128.8, 130.2, 134.6, 135.3, 136.0, 142.8, 144.6, 154.6, 164.0, 169.8, 187.0.

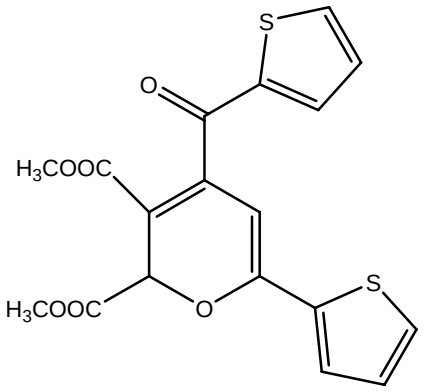
IR (KBr): v=2953, 1741, 1710, 1658, 1412, 1254, 1086, 756cm^{-1}.

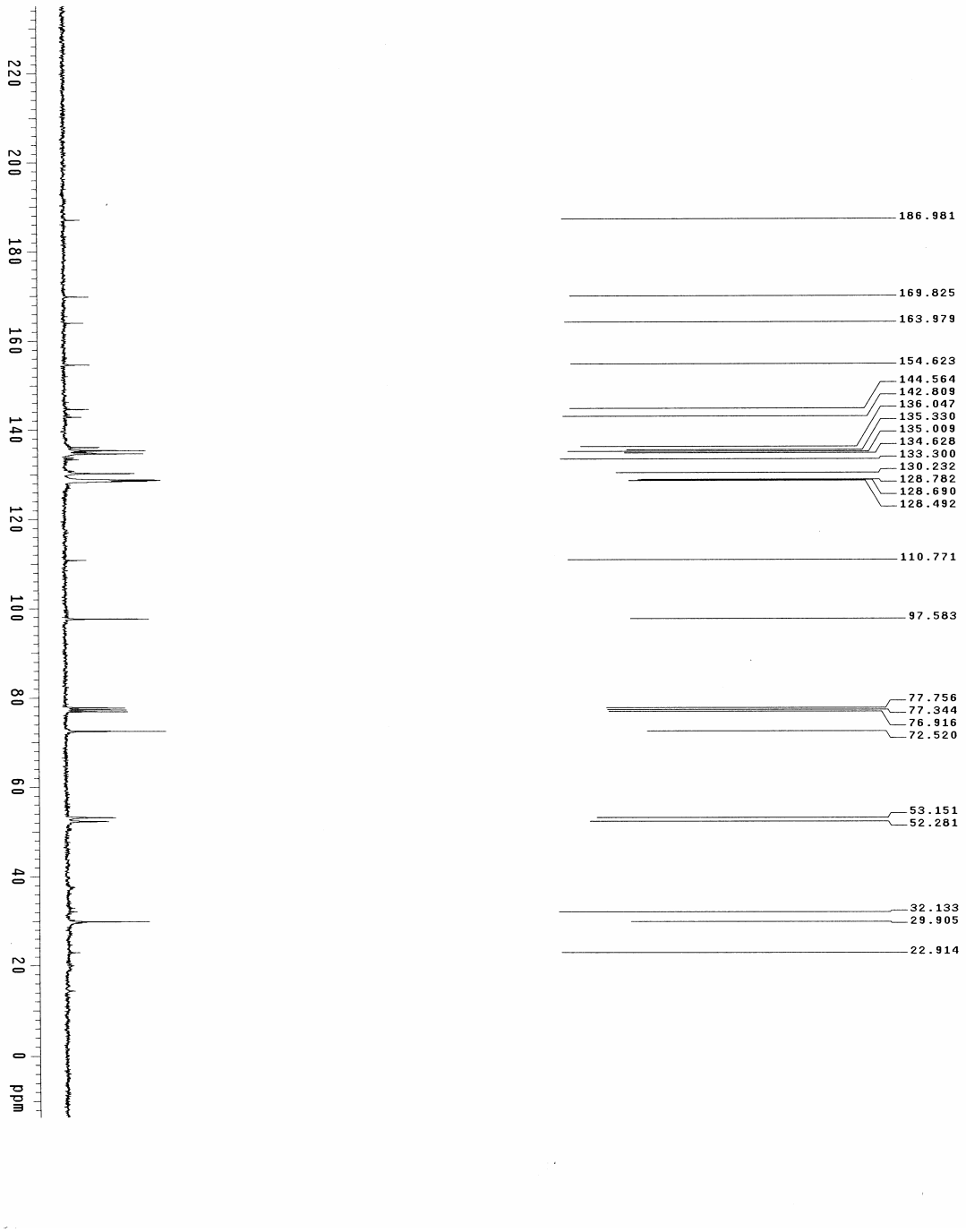
MS: m/z (%)=390(M^+, 2.92), 359(0.79), 331(52.84), 111(100).

HRMS calcd for $C_{18}H_{14}O_6S_2$: (M+NH4) 408.0570, Found: 408.0567.

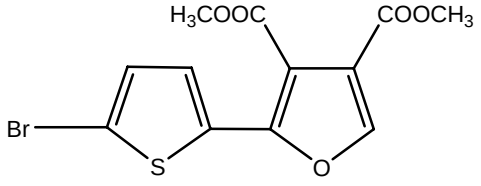

S
O
H3COOC
H3COOC
O
S


7.726
7.710
7.617
7.604
7.534
7.525
7.481
7.465
7.126
7.111
7.101
7.089
7.072
7.016
6.010
5.936
3.782
3.609
3.586
1.246
0.866
0.844
1.20
1.63
0.95
1.90
0.76
0.83
3.09
3.00
9
8
7
6
5
4
3
2
1
0 ppm


S
O
H3COOC
H3COOC
O
S



3b Dimethyl 2-(5-bromothiopen-2-yl) furan-3, 4-dicarboxylate



mp 68-70°C.

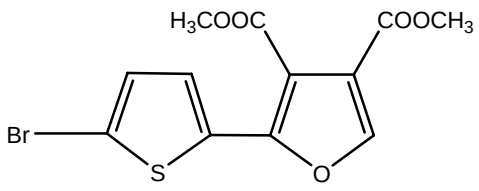
^{1}H NMR (300MHz, $CDCl_3$) δ=3.86(s, 3H), 3.92(s, 3H), 7.06(d, J=3.9Hz, 1H), 7.44(d, J=3.9 Hz, 1H), 7.86(s, 1H).

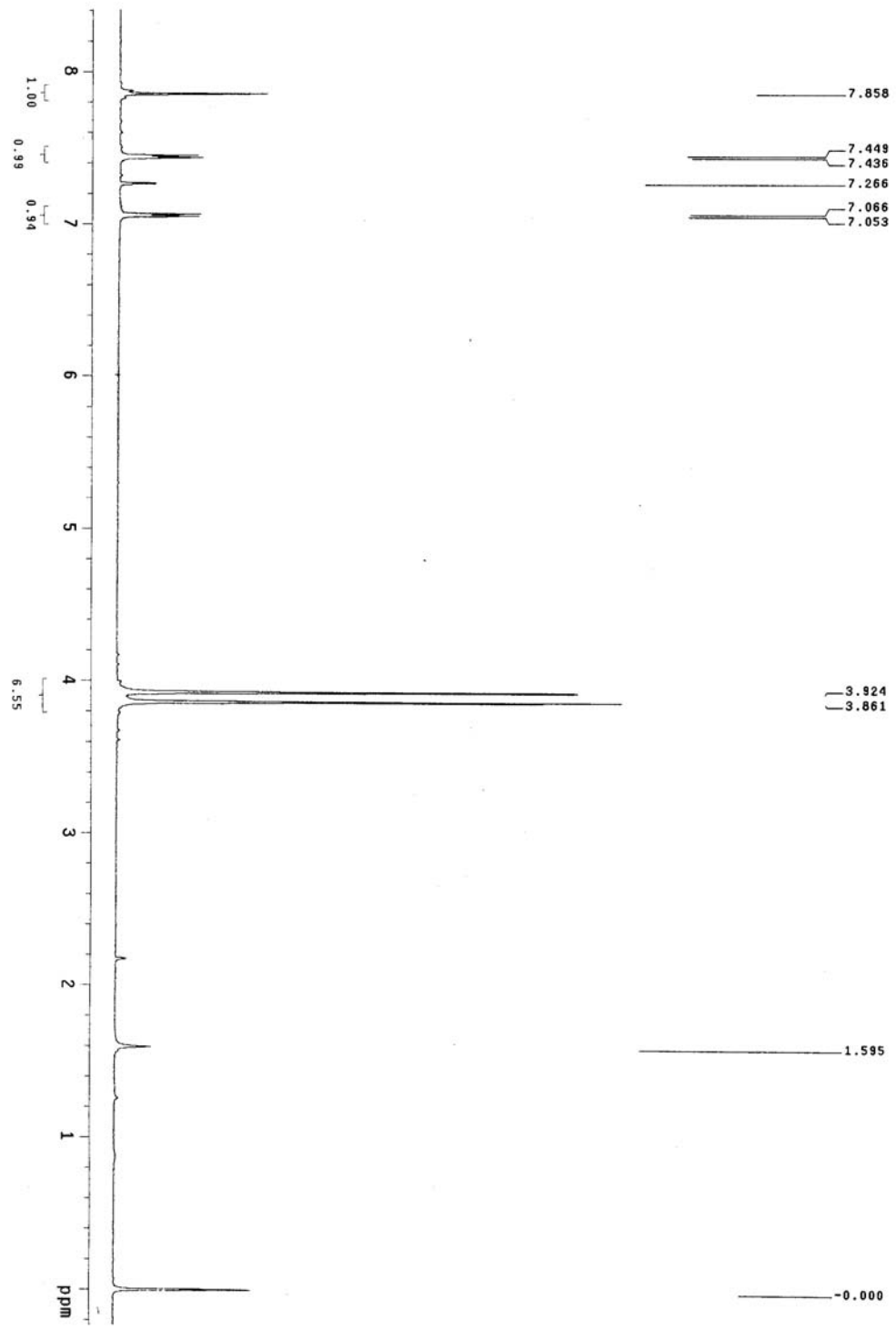
^{13}C NMR (75MHz, $CDCl_3$) δ= 52.0, 52.4, 111.7, 116.0, 120.0, 128.2, 130.3, 131.4, 145.7, 150.7, 161.9, 163.4.

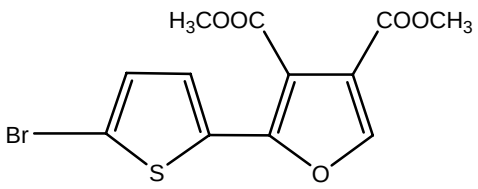
MS: m/z (%)=344(M^+, 5.48), 346(5.69), 313(7.92), 315(8.07), 265(100), 250(27.85), 191(6.63), 59(6.62), 45(7.92).

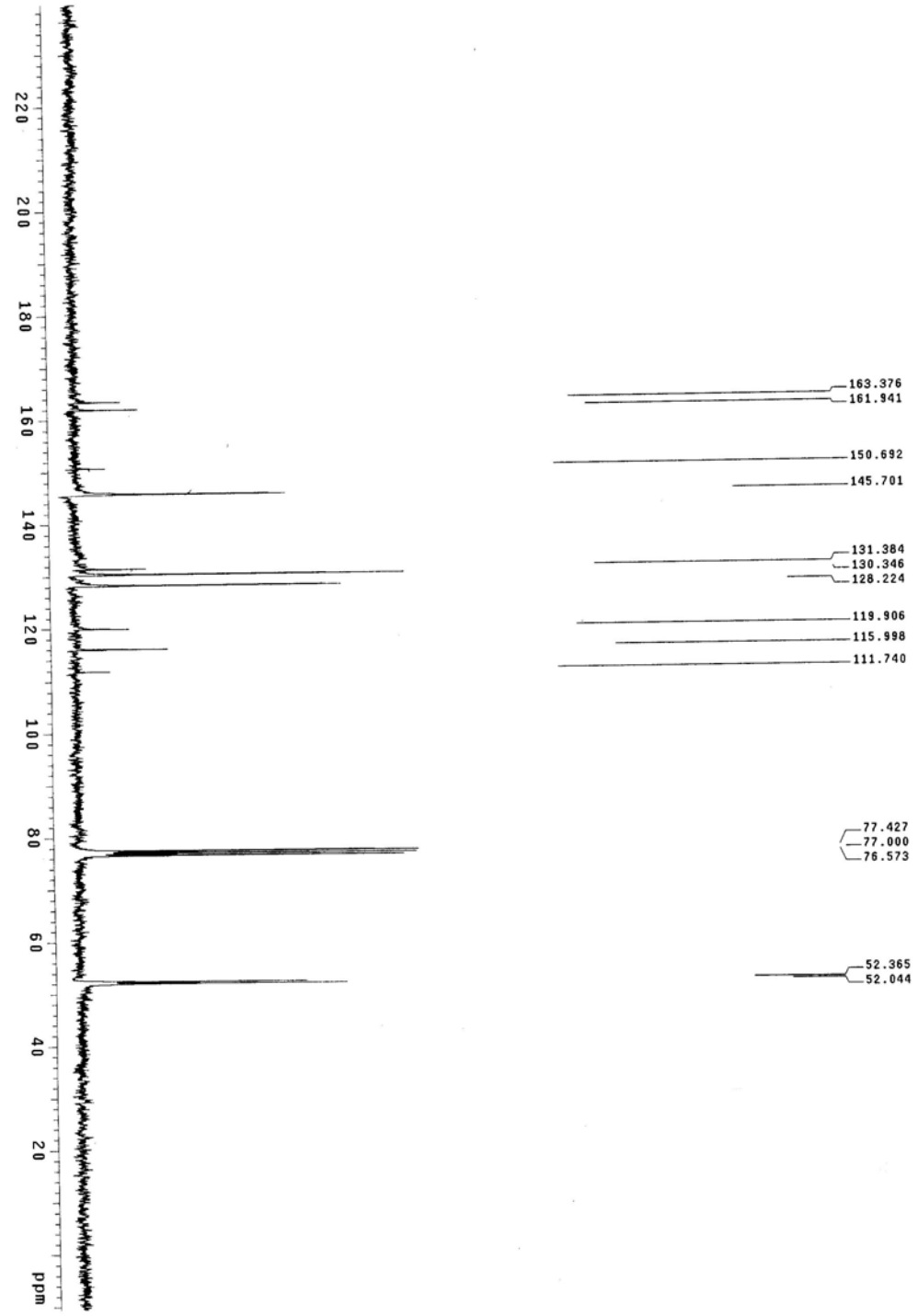
IR (KBr): v=2951, 1728, 1556, 1443, 1277, 1068, 812, 762 cm^{-1}.

HRMS calcd for $C_{12}H_9BrO_5S$: (M+H) 344.9427, Found: 344.9434.

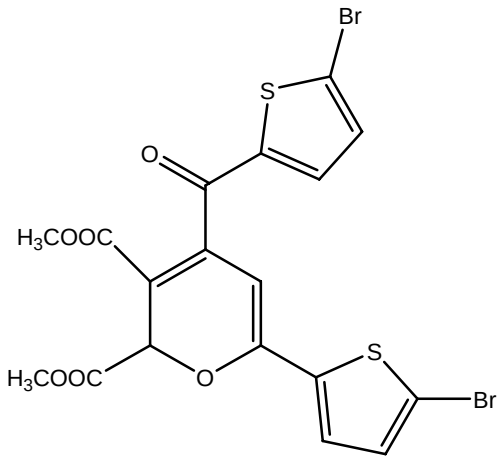

H3COOC
COOCH3
Br
S
O


7.858
7.449
7.436
7.266
7.066
7.053
3.924
3.861
1.595
-0.000
1.00
0.99
0.94
6.55
ppm


H3COOC
COOCH3
Br
S
O


220
200
180
160
140
120
100
80
60
40
20
ppm
163.376
161.941
150.692
145.701
131.384
130.346
128.224
119.906
115.998
111.740
77.427
77.000
76.573
52.365
52.044

4b



mp 136-138°C.

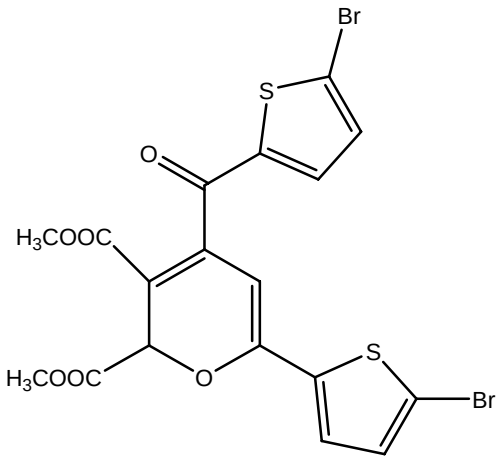
^{1}H NMR (300MHz, $CDCl_3$) δ=3.64(s, 3H), 3.79(s, 3H), 5.83(s, 1H), 5.96(s, 1H), 7.05-7.35 (m, 4H).

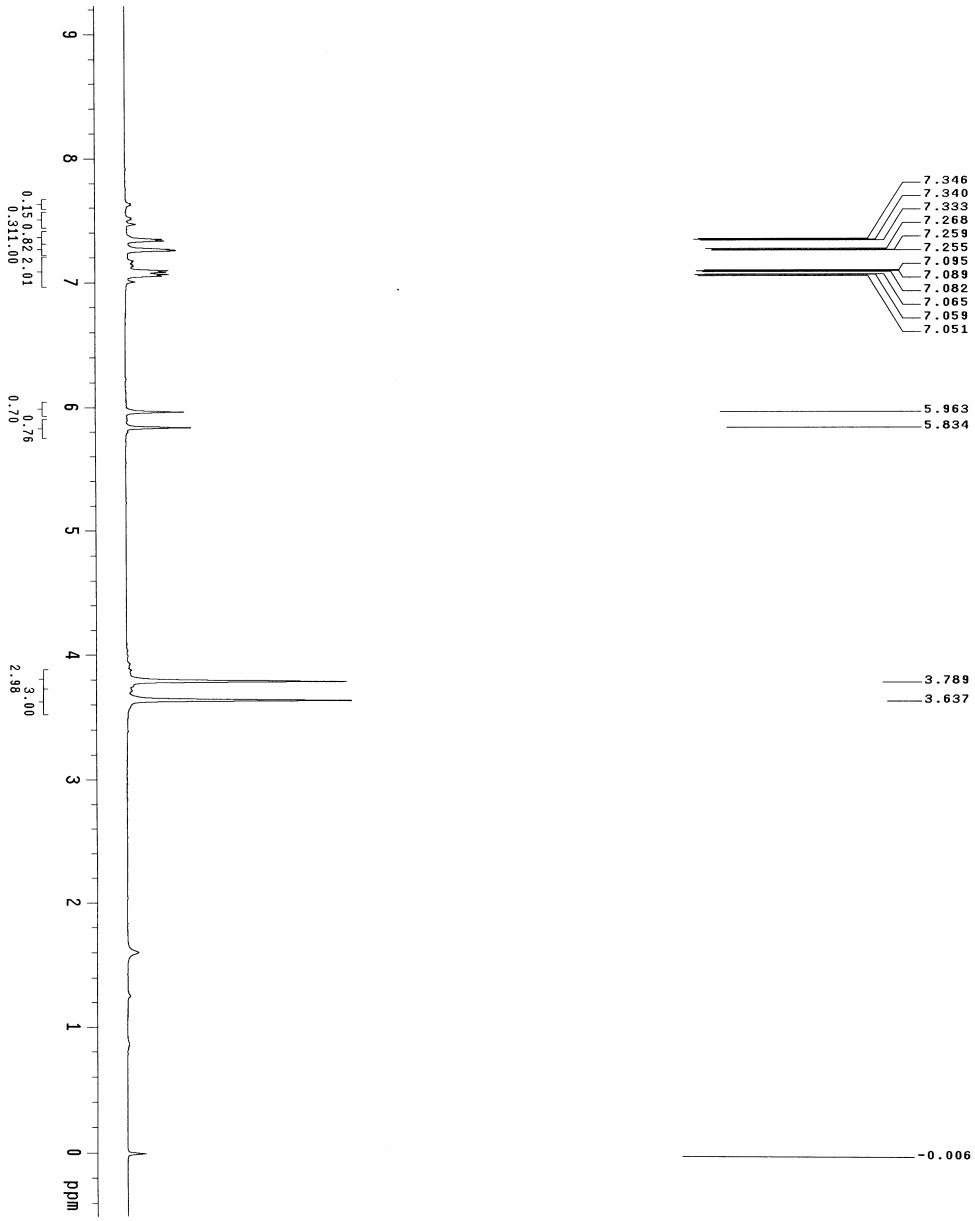
^{13}C NMR (75MHz, $CDCl_3$) δ= 52.5, 53.3, 72.5, 97.5, 111.6, 118.2, 124.5, 128.7, 131.5, 131.9, 134.7, 137.2, 143.5, 144.0, 153.5, 163.7, 169.6, 185.6.

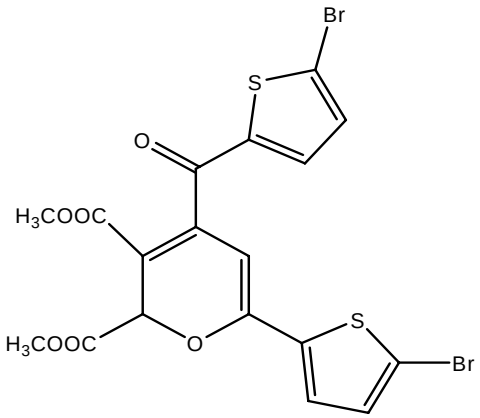
MS: m/z (%)=546(M^+, 2.57), 548(5.88), 550(3.84), 487(47.56), 489(100), 491(56.96) 189(87.74), 191(84.84).

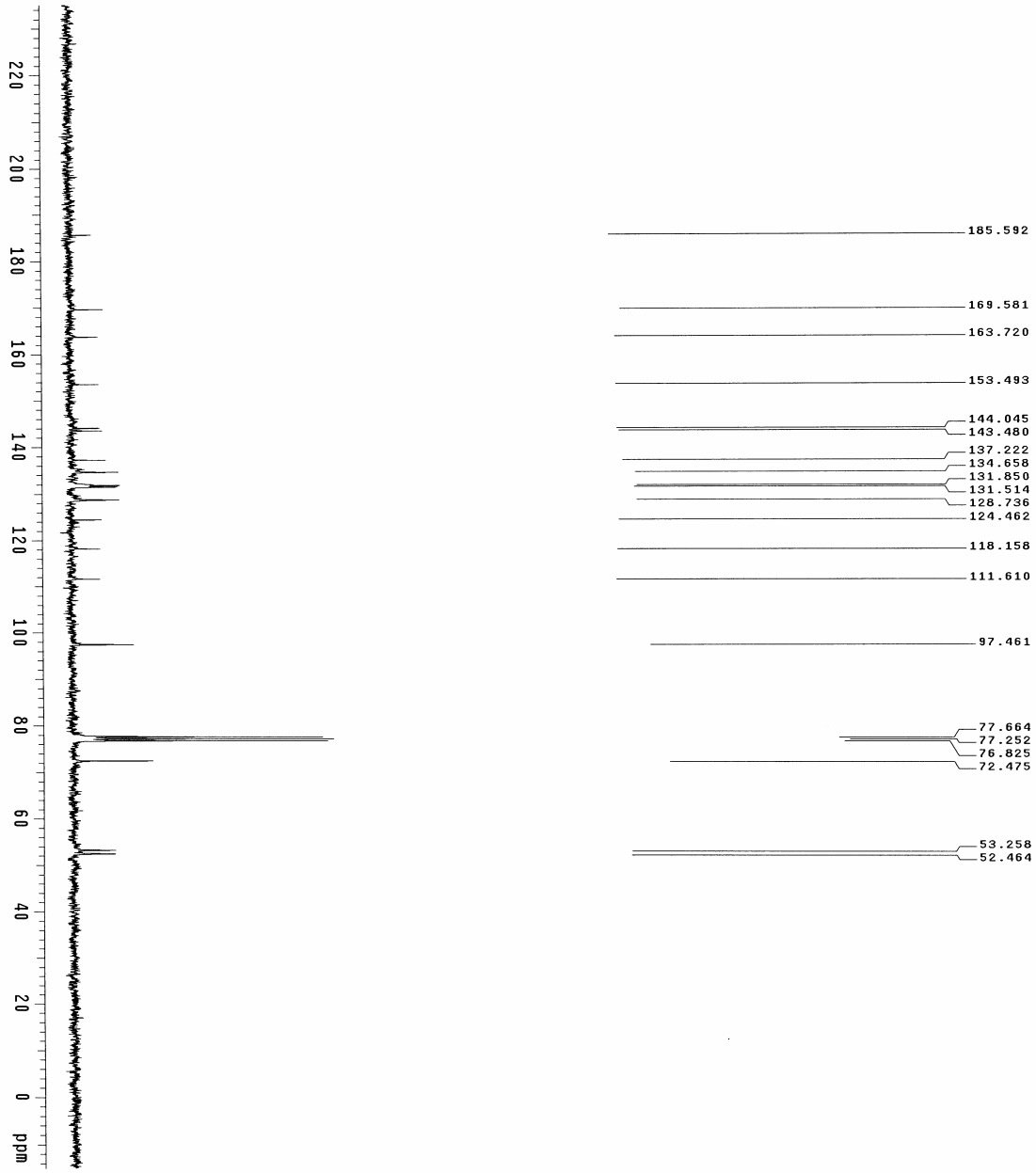
IR (KBr): v = 2952, 1746, 1710, 1655, 1409, 1243, 1079, 731cm^{-1}.

HRMS calcd for $C_{18}H_{12}Br_2O_6S_2$: (M+H) 546.8515, Found: 546.8524.

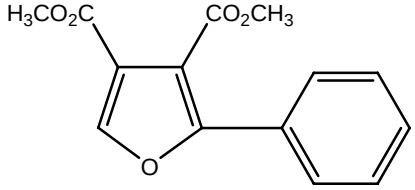

Br
S
O
H3COOC
H3COOC
O
S
Br


7.346
7.340
7.333
7.268
7.259
7.255
7.095
7.089
7.082
7.065
7.059
7.051
5.963
5.834
3.789
3.637
-0.006
0.15
0.82
2.01
0.31
1.00
0.76
0.70
3.00
2.98
ppm


Br
S
O
H3COOC
H3COOC
O
S
Br



3c Dimethyl 2-phenylfuran-3, 4-dicarboxylate



mp 68-70°C.

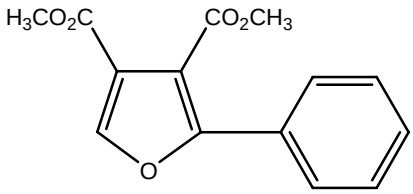
^{1}H NMR (300MHz, $CDCl_3$) δ=3.87(d, J=3.6Hz, 3H), 3.92(d, J=3.6Hz, 3H), 7.40-7.43(m, 3H), 7.69-7.73(m, 2H), 7.98(d, J=3.0Hz, 1H).

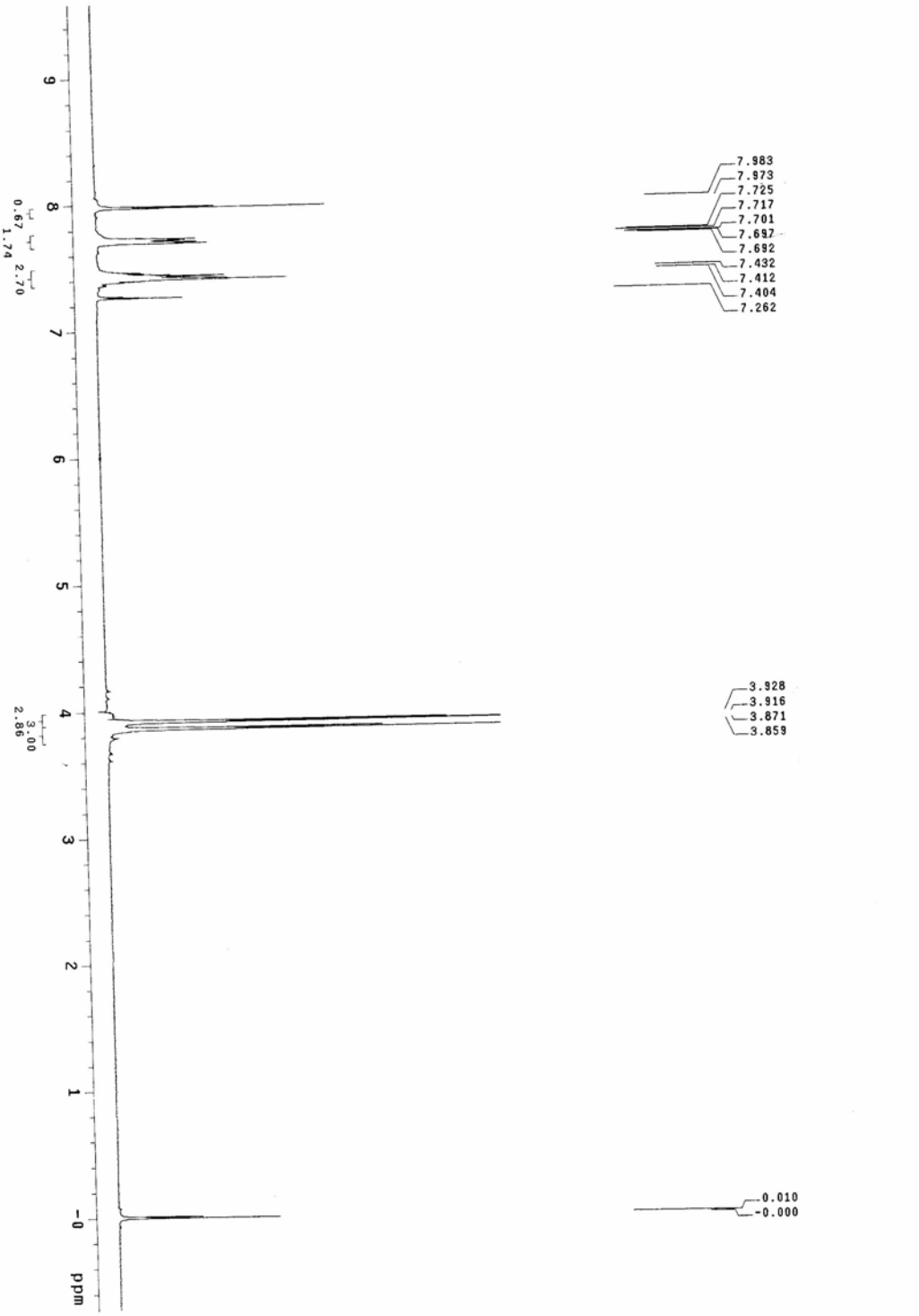
^{13}C NMR (75MHz, $CDCl_3$) δ=52.2, 53.0, 113.8, 120.0, 126.6, 129.0, 129.7, 146.5, 154.3, 162.5, 165.1.

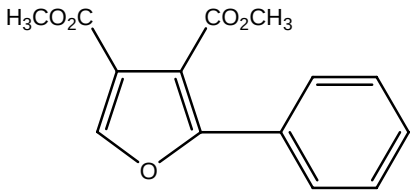
IR (KBr): v=3151, 2955, 1717, 1552, 1441, 1282, 1151, 771, 693 cm^{-1}.

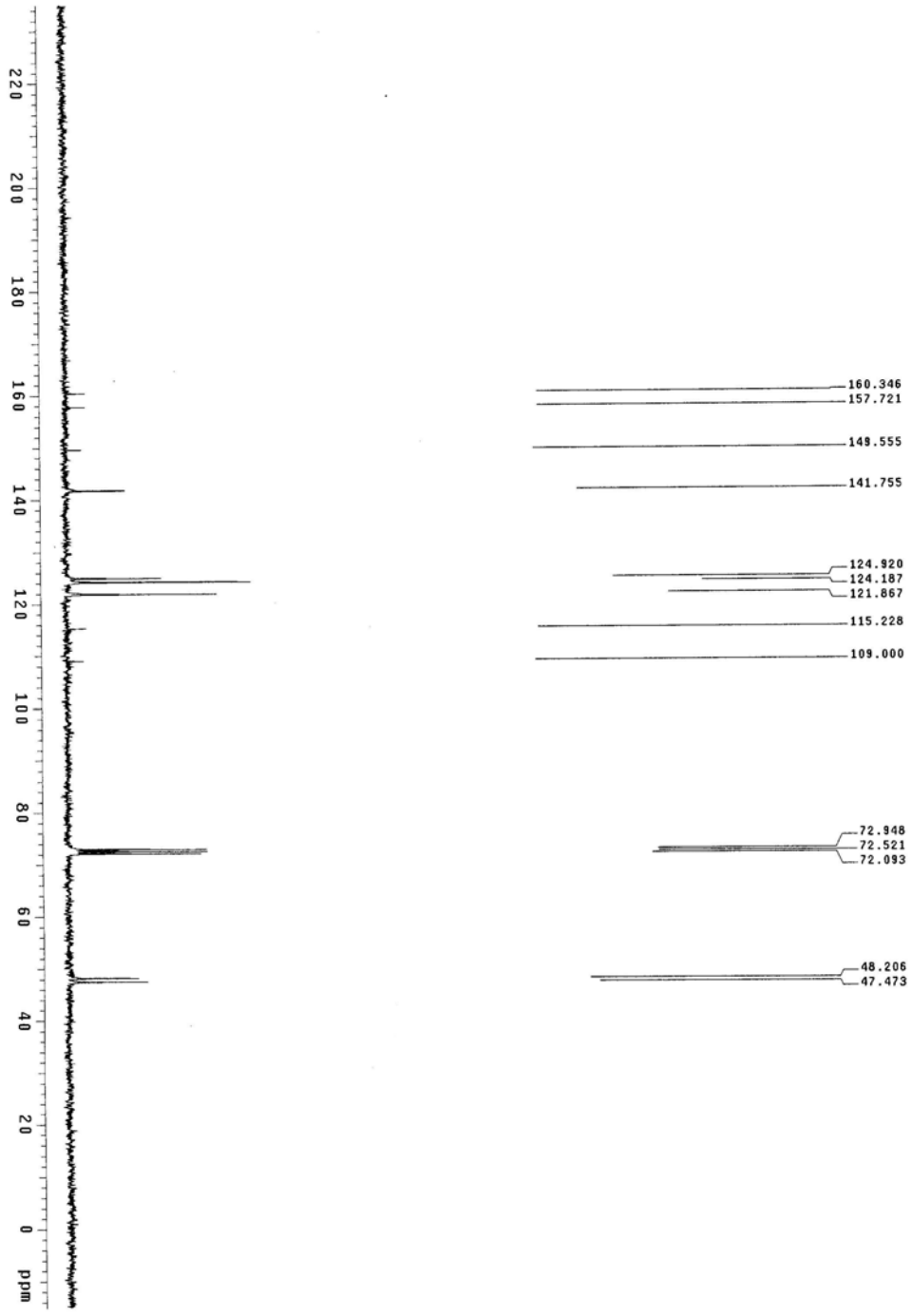
MS: m/z (%)=260(M^+, 70.80), 229(100), 105(16.89), 77(26.31).

HRMS calcd for $C_{14}H_{12}O_5$: (M+Na) 283.0577, Found: 283.0583.

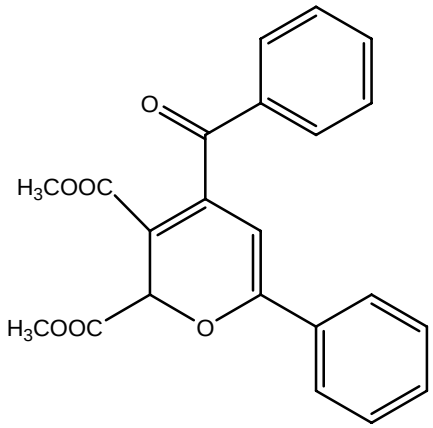

H3CO2C
CO2CH3
O


7.983
7.973
7.725
7.717
7.701
7.697
7.692
7.432
7.412
7.404
7.262
3.928
3.916
3.871
3.859
0.010
-0.000
0.67
1.74
2.70
3.00
2.86
ppm


H3CO2C
CO2CH3
O


160.346
157.721
149.555
141.755
124.920
124.187
121.867
115.228
109.000
72.948
72.521
72.093
48.206
47.473
220
200
180
160
140
120
100
80
60
40
20
0
ppm

4c



mp 99-101°C.

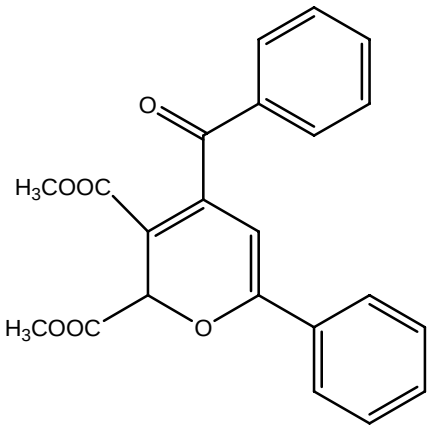
^{1}H NMR (300MHz, $CDCl_3$) δ=3.52(s, 3H), 3.78(s, 3H), 6.01(s, 1H), 6.09(s, 1H), 7.37-7.95(m, 10H).

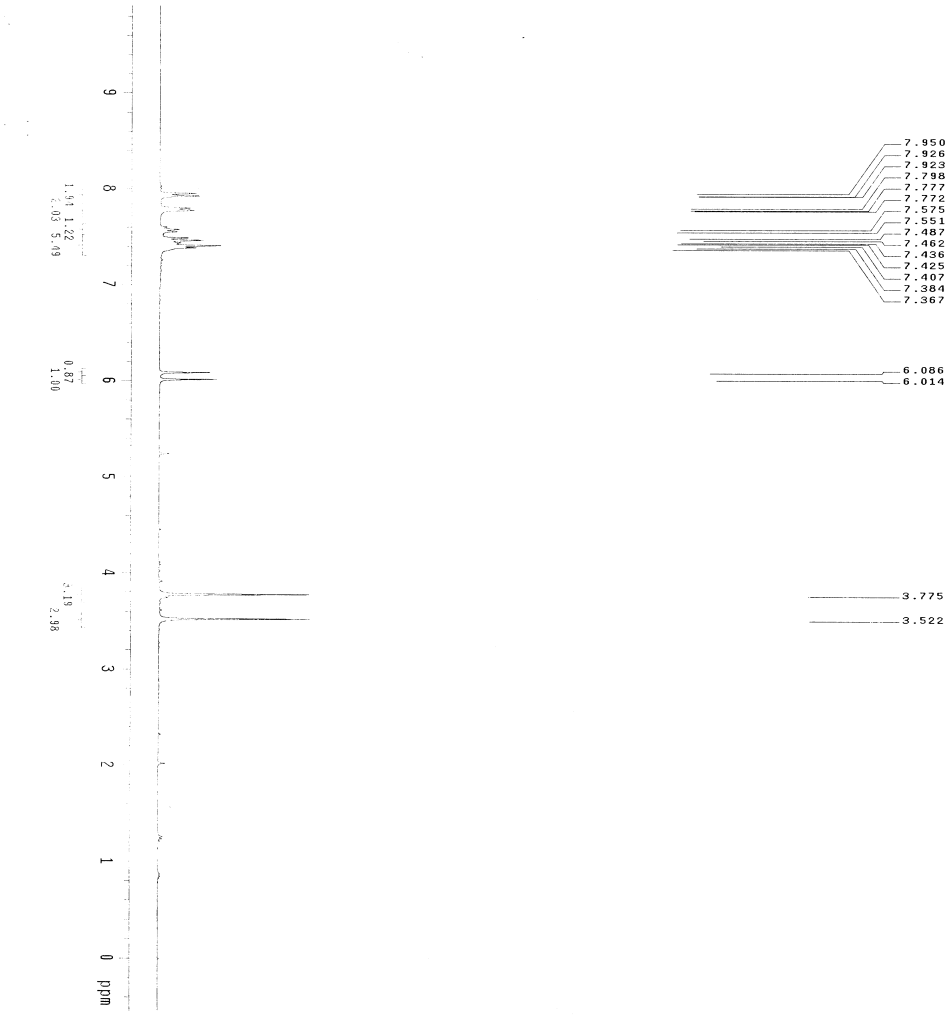
^{13}C NMR (75MHz, $CDCl_3$) δ=51.7, 52.7, 72.0, 97.9, 110.6, 126.8, 128.4, 128.7, 130.9, 131.7, 133.7, 135.0, 144.9, 159.1, 163.7, 169.6, 194.6.

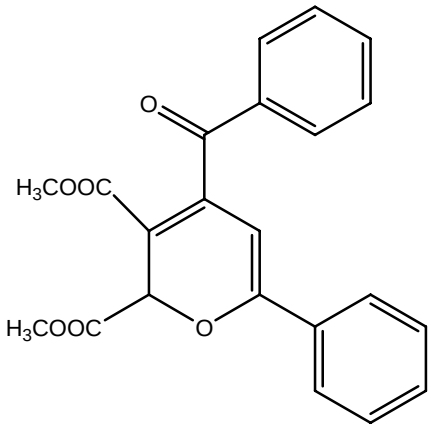
IR (KBr): v= 2954, 1747, 1708, 1679, 1254, 1084, 730, 695cm^{-1}.

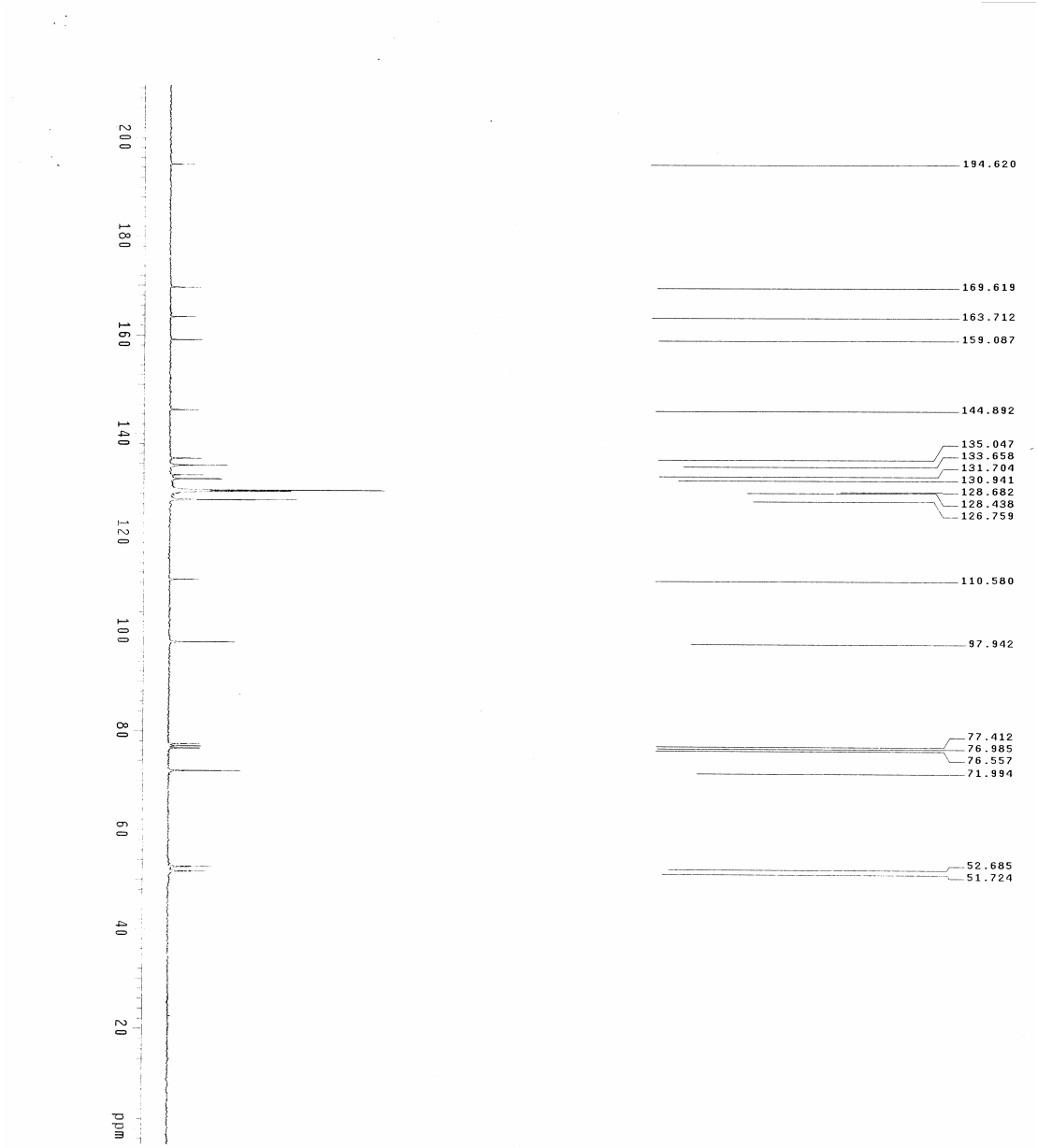
MS: m/z (%)=378(M^+, 1.11), 319(43.14), 105(81.62), 77(100).

HRMS calcd for $C_{22}H_{18}O_6$: (M+Na) 401.0996, Found: 401.0990.

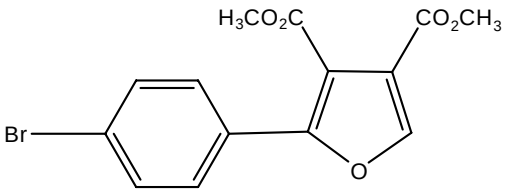

O
H3COOC
H3COOC
O


7.950
7.926
7.923
7.798
7.777
7.772
7.575
7.551
7.487
7.462
7.436
7.425
7.407
7.384
7.367
6.086
6.014
3.775
3.522
1.91 1.42
2.03 5.49
0.87
1.00
3.19
2.96
9
8
7
6
5
4
3
2
1
0 ppm


O
H3COOC
H3COOC
O



3d Dimethyl 2-(4-bromophenyl) furan-3, 4-dicarboxylate



mp 79-81°C.

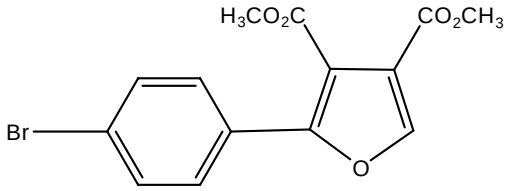
^{1}H NMR (300MHz, $CDCl_3$) δ=3.85(s, 3H), 3.91 (s, 3H), 7.56(m, 4H), 7.96(s, 1H).

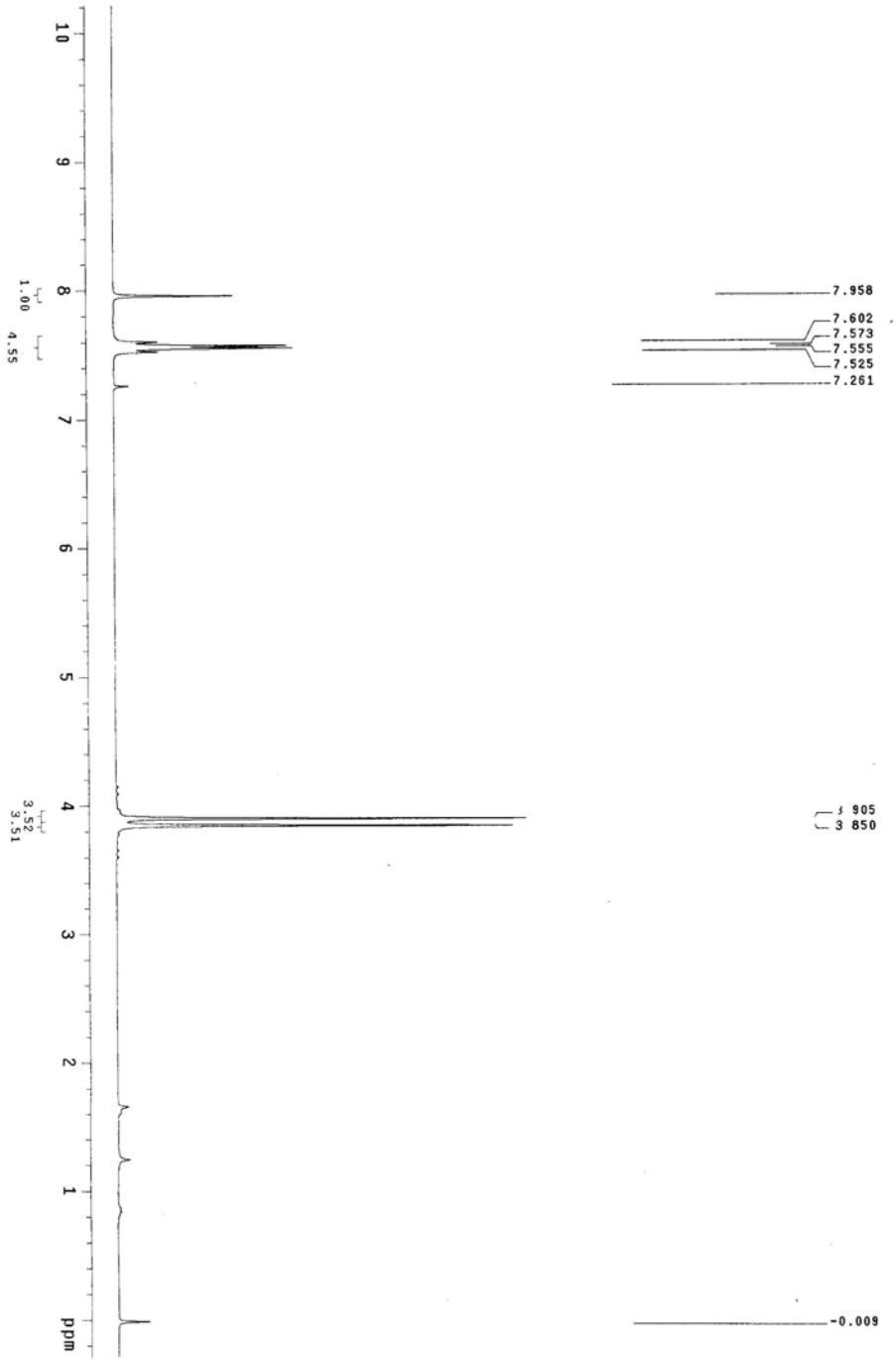
^{13}C NMR (75MHz, $CDCl_3$) δ=52.3, 53.0, 114.2, 120.2, 124.1, 127.8, 128.2, 132.2, 146.7, 153.4, 162.3, 164.8

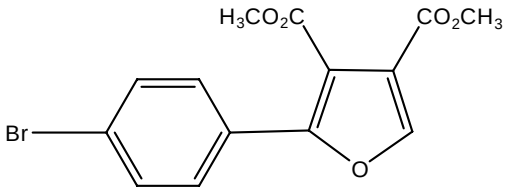
IR (KBr): v=3163, 2951, 1733, 1547, 1487, 1325, 1167, 1059, 816cm^{-1}.

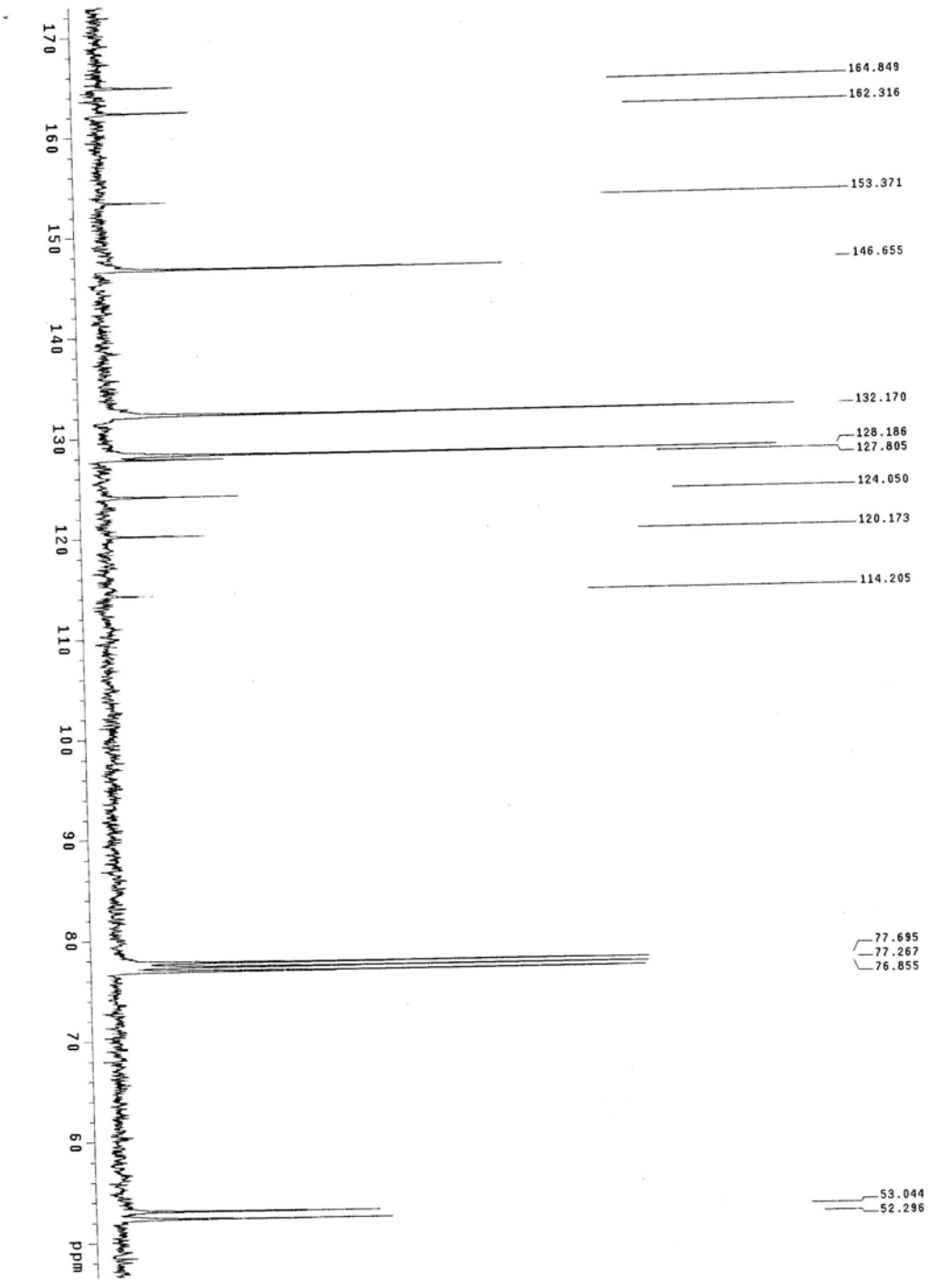
MS: m/z (%)=338(M^+, 100), 340(93.87), 307(85.46), 309(80.56), 183(19.42), 185(19.98) 155(13.95), 157(13.72), 113(43.45), 59(25.64).

HRMS calcd for $C_{14}H_{11}BrO_5$: (M+Na) 360.9682, Found: 360.9677.

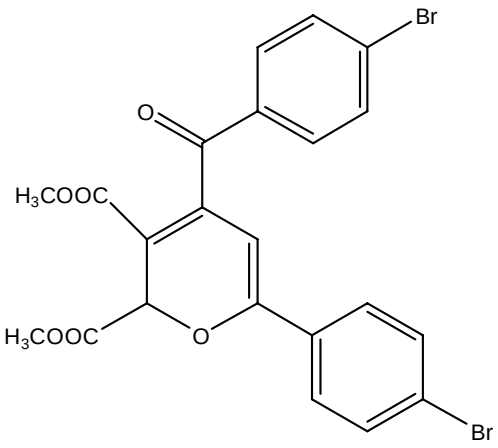



7.958
7.602
7.573
7.555
7.525
7.261
3.905
3.850
-0.009
1.00
4.55
3.52
3.51
ppm


H3CO2C
CO2CH3
Br
O


164.849
162.316
153.371
146.655
132.170
128.186
127.805
124.050
120.173
114.205
77.695
77.267
76.855
53.044
52.296
170
160
150
140
130
120
110
100
90
80
70
60
ppm

4d



mp 142-143°C

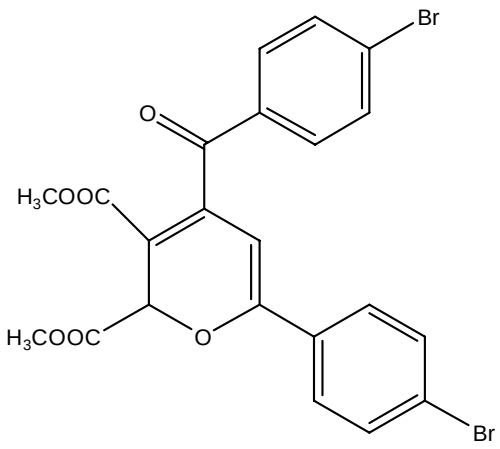
^{1}H NMR (300MHz, $CDCl_3$) δ=3.57(s, 3H), 3.79 (s, 3H), 5.96(s, 1H), 6.04(s, 1H), 7.53-7.80(m, 8H).

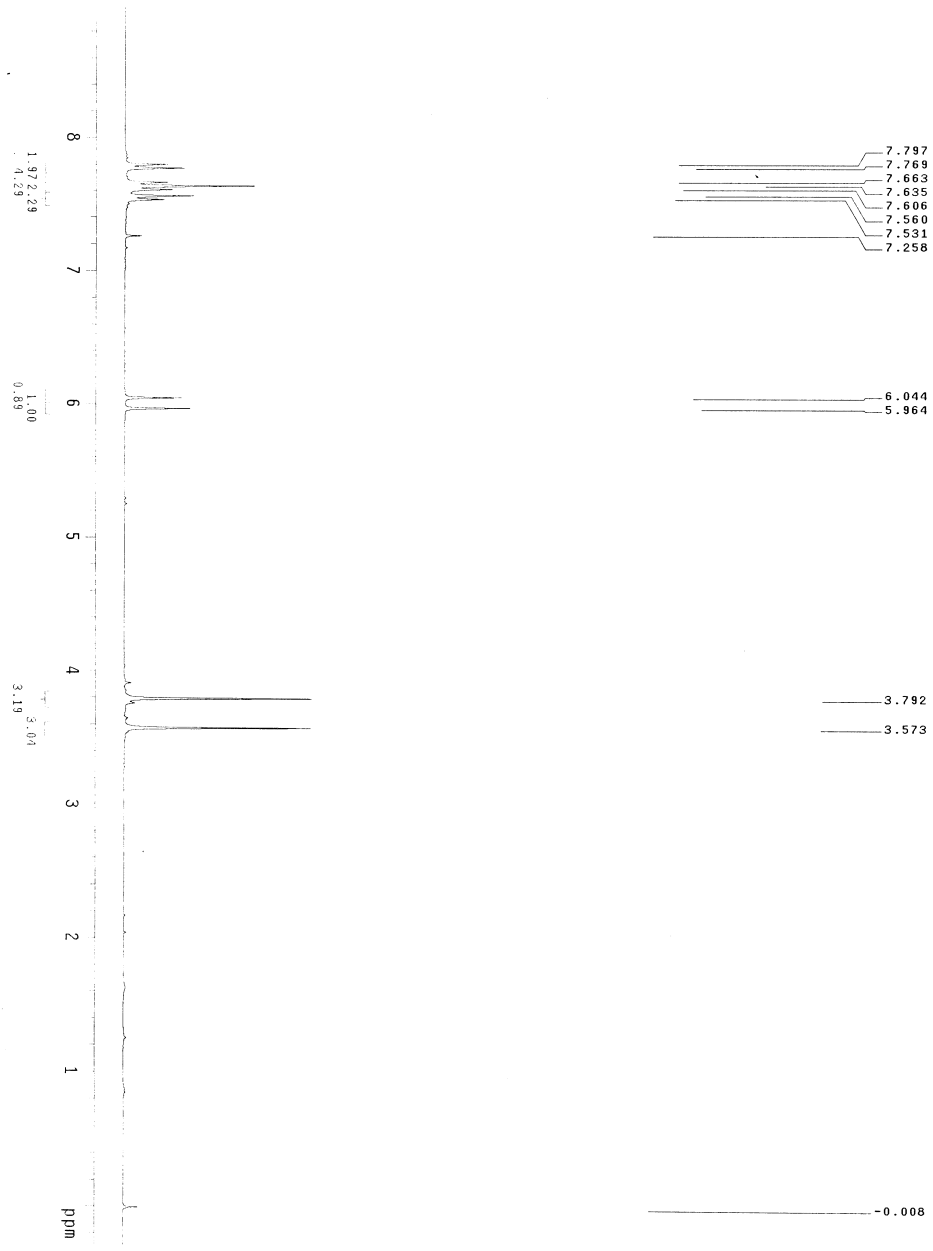
^{13}C NMR (75MHz, $CDCl_3$) δ=52.1, 53.0, 72.1, 98.2, 111.4, 125.8, 128.3, 129.2, 130.3, 130.7, 131.9, 132.2, 134.0, 144.3, 158.4, 163.7, 169.6, 193.6.

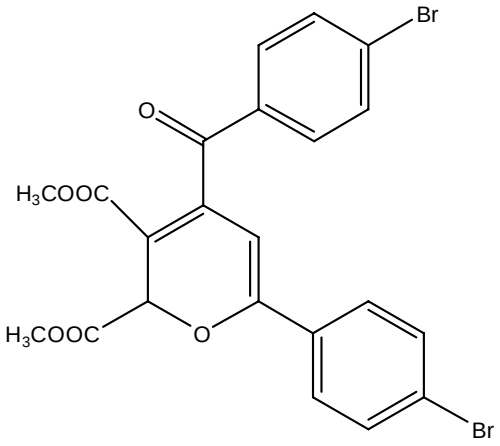
IR (KBr): v=2954, 1747, 1709, 1680, 1254, 1076, 839cm^{-1}.

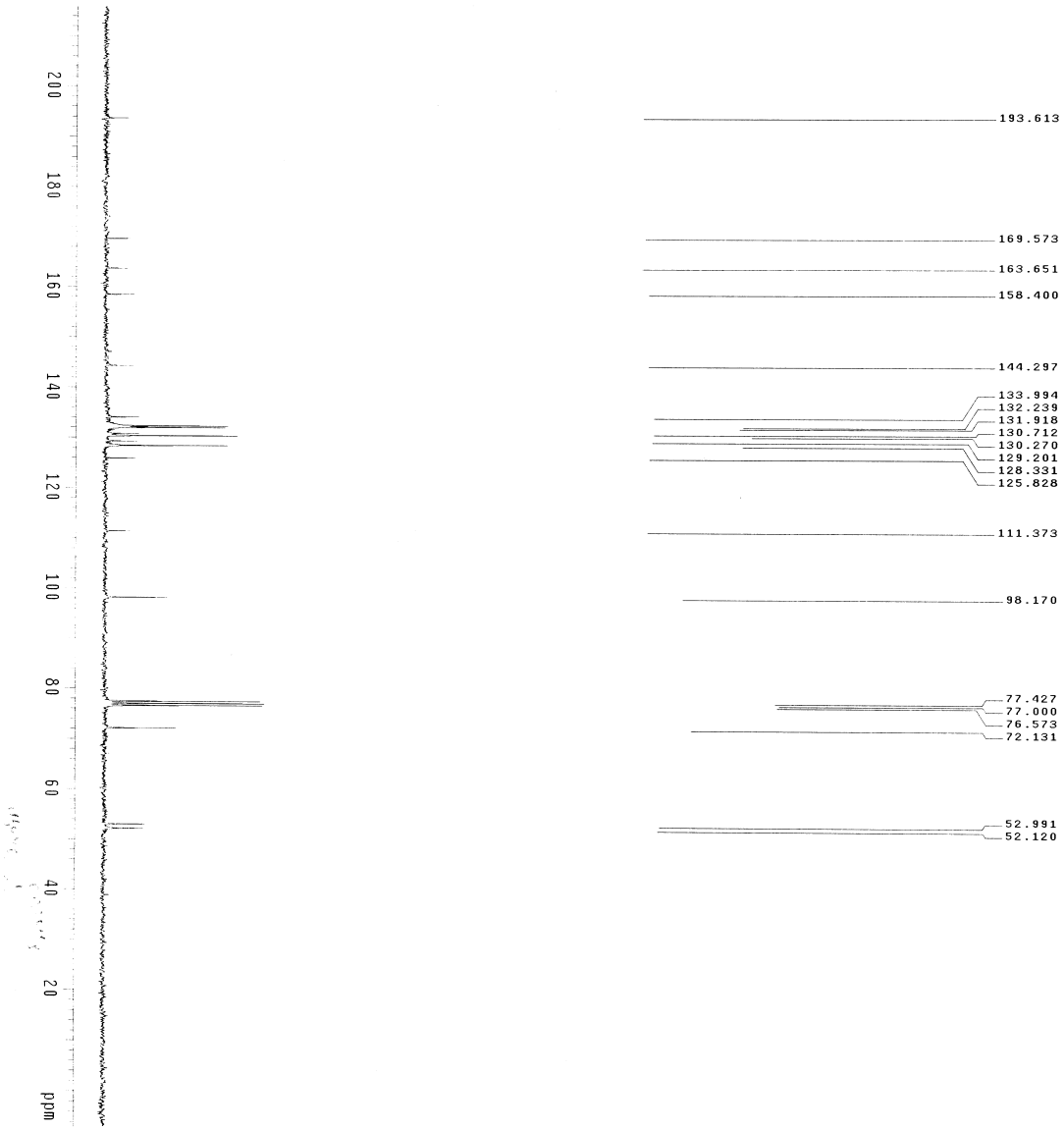
MS: m/z (%)=534(M^+, 0.37), 536(0.76), 475(15.32), 477(29.26), 479(14.98), 183(100), 185(97.86) 155(84.90), 157(78.49).

HRMS calcd for $C_{22}H_{16}Br_2O_6$: (M+H) 534.9386, Found: 534.9376.

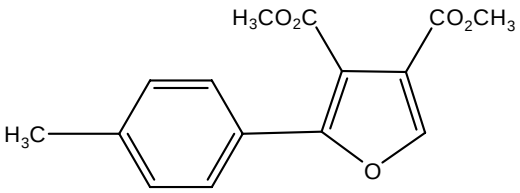

Br
O
H3COOC
H3COOC
O
Br


7.797
7.769
7.663
7.635
7.606
7.560
7.531
7.258
6.044
5.964
3.792
3.573
-0.008
1.97
2.29
1.29
1.00
0.89
3.01
3.19
8
7
6
5
4
3
2
1
ppm


Br
O
H3COOC
H3COOC
O
Br



3e Dimethyl 2-(4-methylphenyl) furan-3, 4-dicarboxylate



mp 95-97°C.

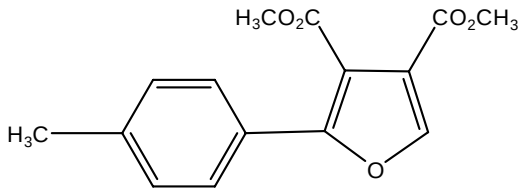
^{1}H NMR (300MHz, $CDCl_3$) δ=2.37(s, 3H), 3.84(s, 3H), 3.90(s, 3H), 7.22(d, J=8.1Hz, 2H), 7.59(d, J=7.8Hz, 2H), 7.93(s, 1H).

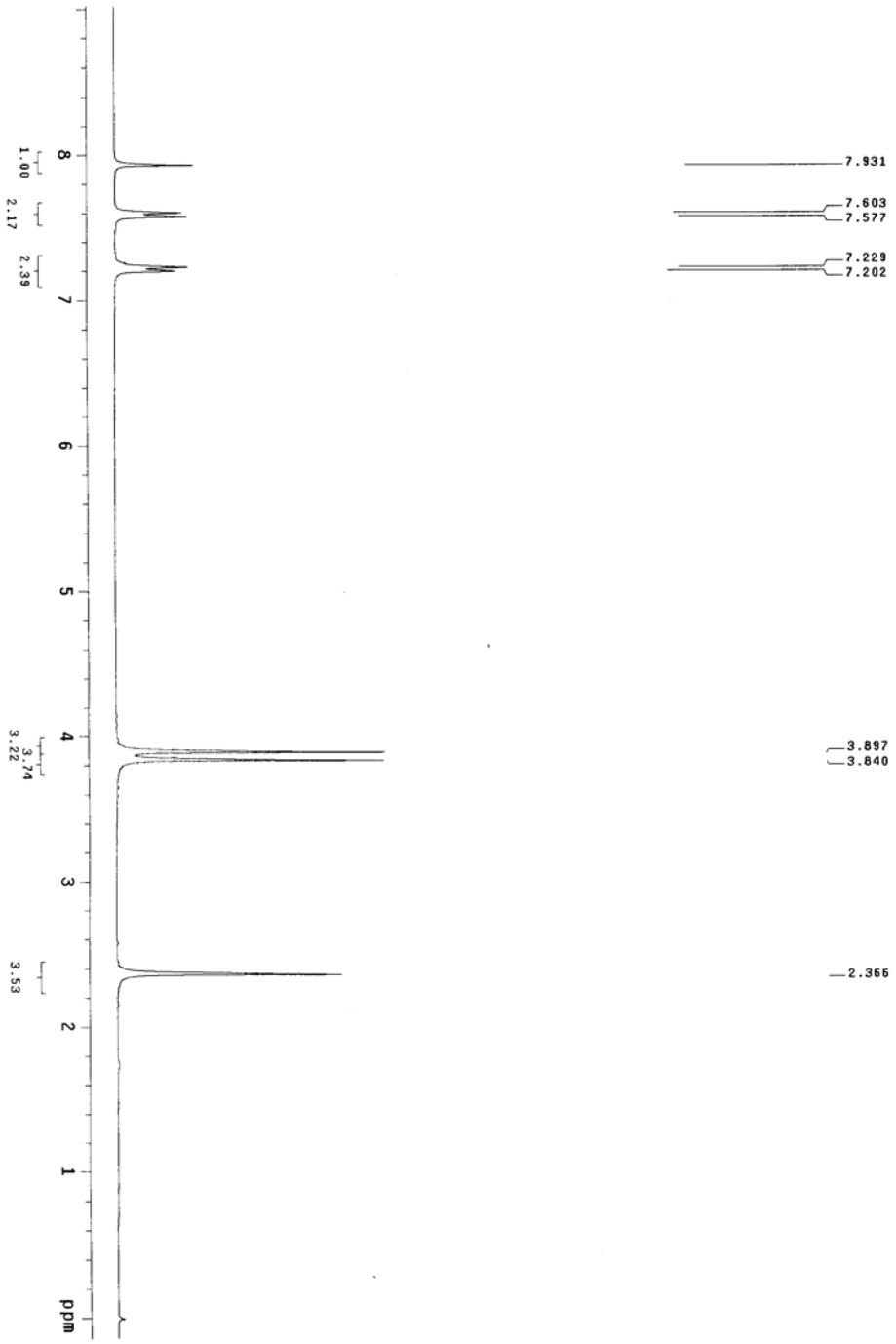
^{13}C NMR (300MHz, $CDCl_3$) δ=21.6, 52.2, 52.9, 113.1, 119.9, 126.2, 126.6, 129.6, 139.9, 146.2, 154.7, 162.5, 165.2.

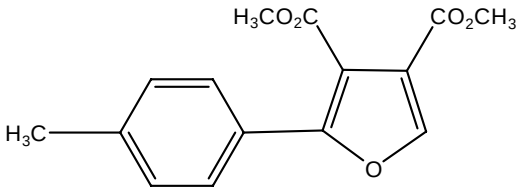
IR (KBr): v=3158, 2954, 1723, 1508, 1441, 1328, 1162, 1060, 821 cm^{-1}.

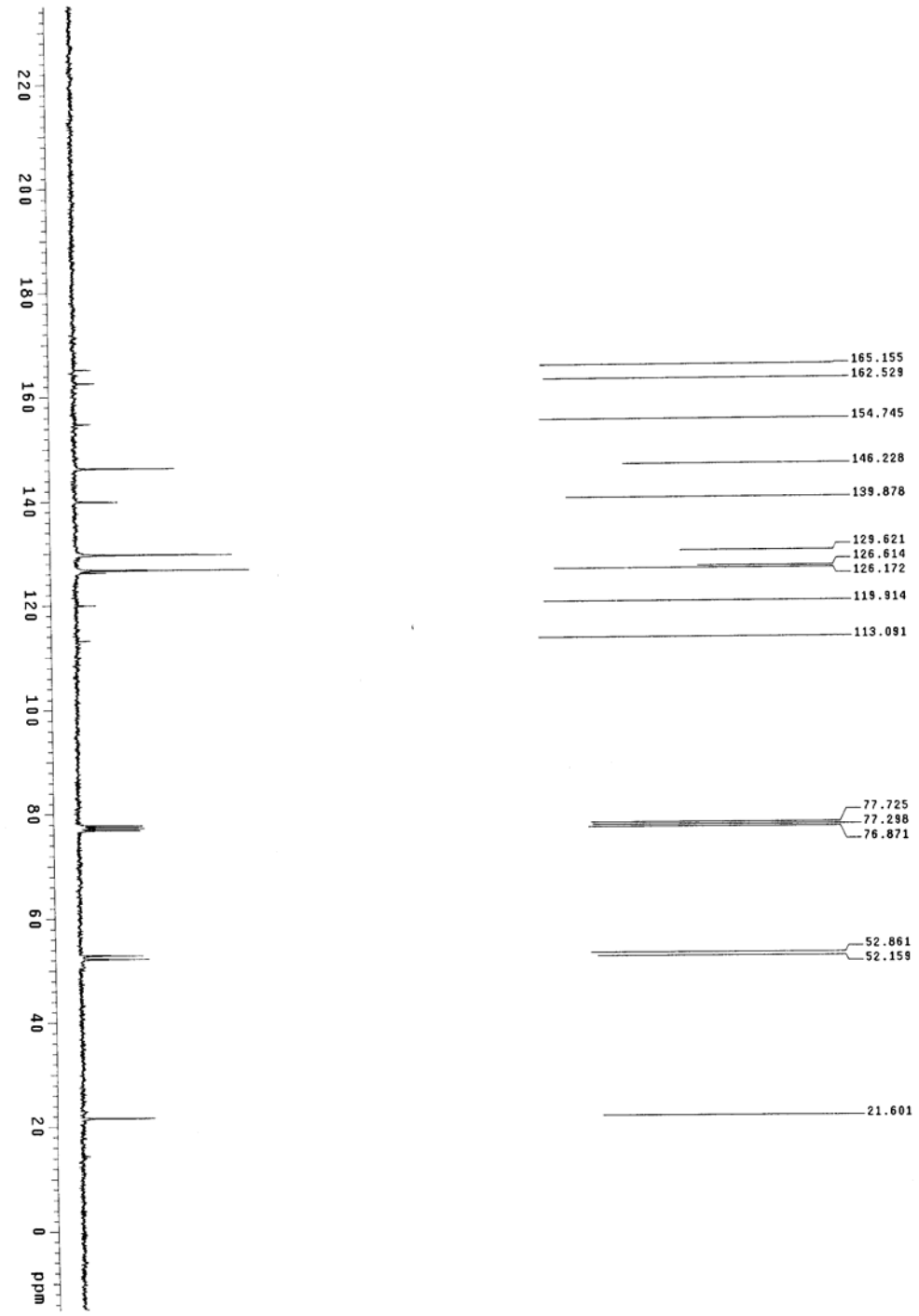
MS: m/z (%)=274(M^+, 100), 243(94.1), 215(6.12), 187(6.04), 119(20.63), 91 (24.47), 43(43.33).

HRMS calcd for $C_{15}H_{14}O_5$: (M+Na) 297.0733, Found: 297.0735.

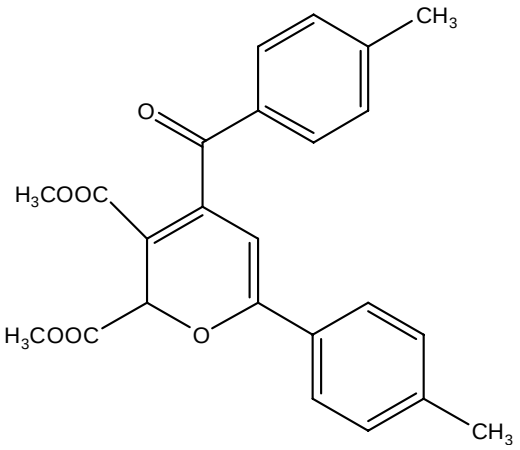



7.931
7.603
7.577
7.229
7.202
3.897
3.840
2.366
1.00
2.17
2.39
3.74
3.22
3.53
8
7
6
5
4
3
2
1
ppm


H3CO2C
CO2CH3
H3C
O


220
200
180
160
140
120
100
80
60
40
20
0
ppm
165.155
162.529
154.745
146.228
139.878
129.621
126.614
126.172
119.914
113.091
77.725
77.298
76.871
52.861
52.159
21.601

4e



mp 148-150°C

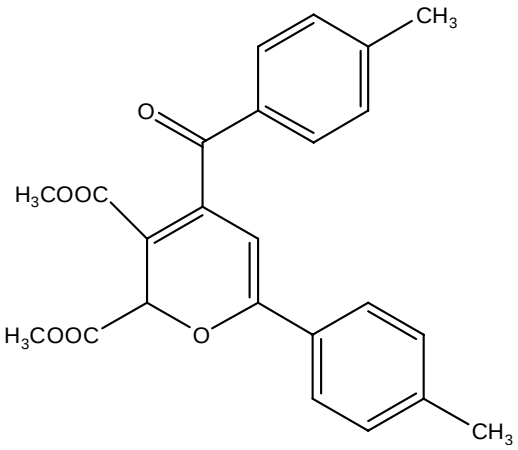
^{1}H NMR (300MHz, $CDCl_3$) δ=2.38(s, 3H), 2.41(s, 3H), 3.55(s, 3H), 3.79(s, 3H), 5.95(s, 1H), 6.07(s, 1H), 7.21(d, J=8.1Hz, 2H), 7.21(d, J=7.8Hz, 4H), 7.68(d, J=8.1Hz, 2H), 7.83(d, J=8.1Hz, 2H).

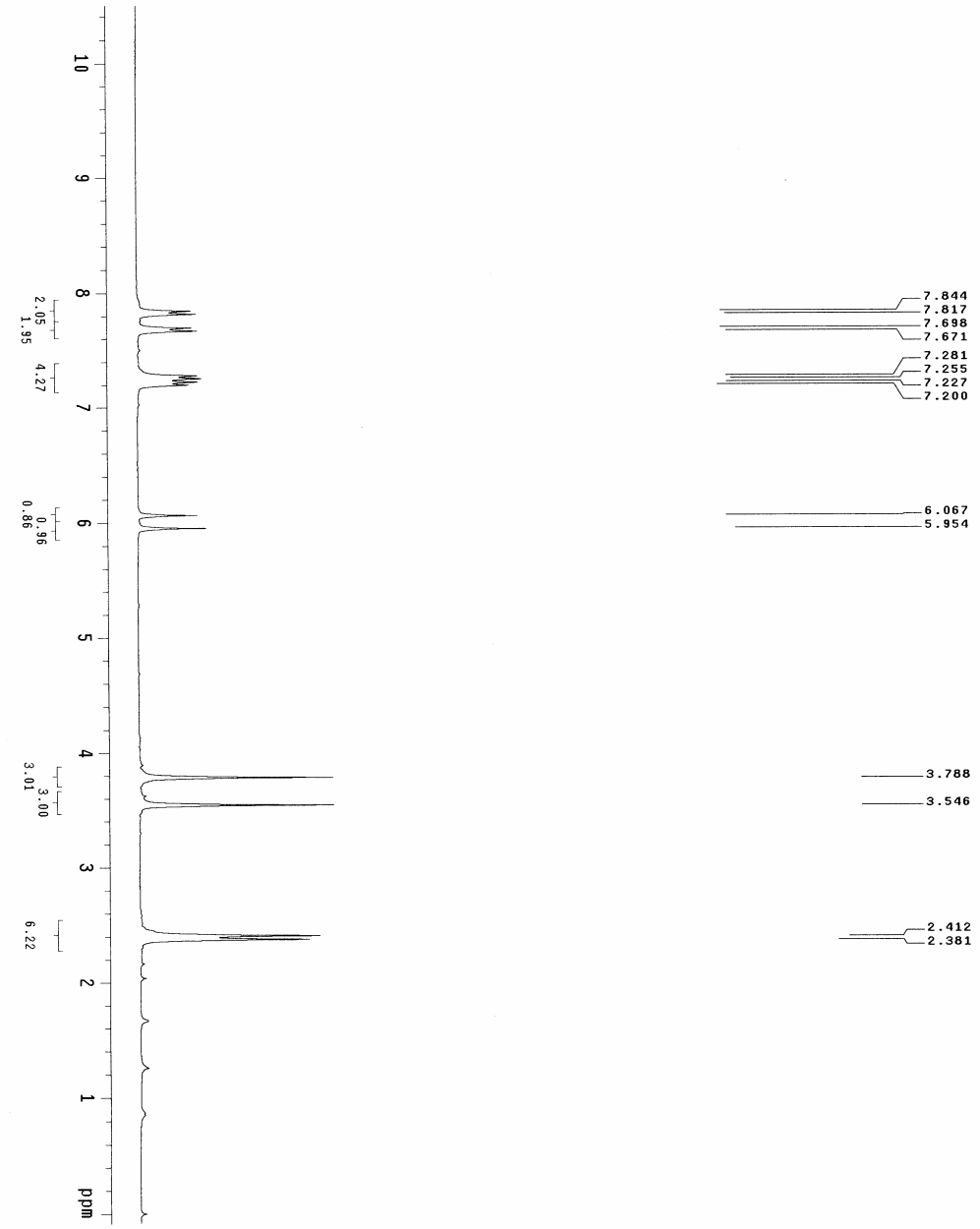
^{13}C NMR (75MHz, $CDCl_3$) δ=21.7, 22.0, 52.1, 53.0, 72.5, 97.8, 110.3, 127.2, 129.3, 129.6, 129.8, 133.1, 141.9, 145.0, 145.7, 159.7, 164.3, 170.2, 194.8.

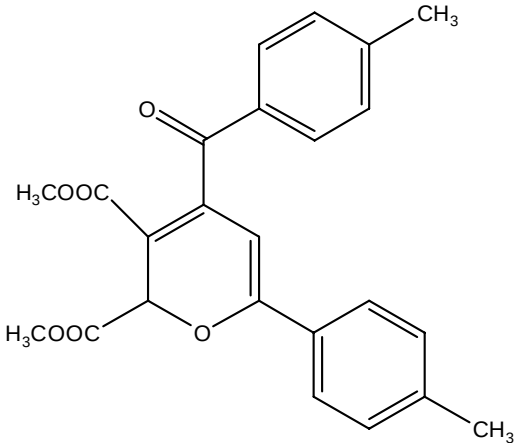
IR (KBr): v=2953, 1750, 1709, 1675, 1255, 1087, 804cm^{-1}.

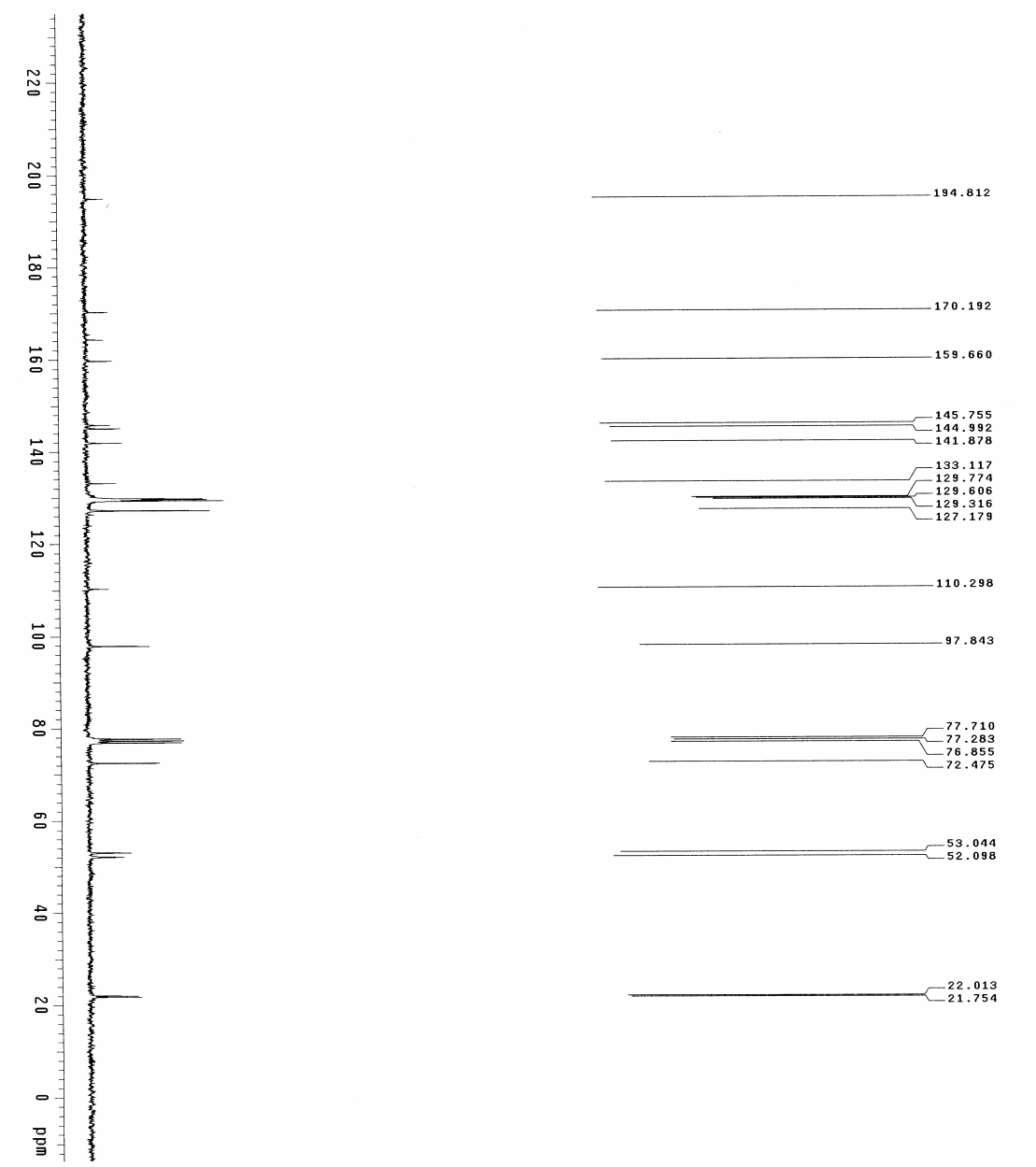
MS: m/z (%)=406(M^+, 4.13), 347(100), 119(56.98), 91(44.05).

HRMS calcd for $C_{24}H_{22}O_6$: (M+Na) 429.1306, Found: 429.1313.

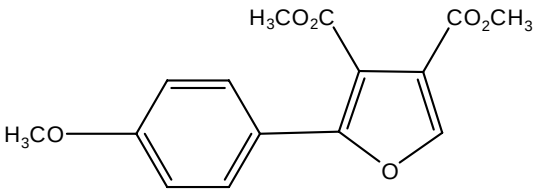

CH3
O
H3COOC
H3COOC
O
CH3


7.844
7.817
7.698
7.671
7.281
7.255
7.227
7.200
6.067
5.954
3.788
3.546
2.412
2.381
2.05
1.95
4.27
0.96
0.86
3.00
3.01
6.22
10
9
8
7
6
5
4
3
2
1
ppm


CH3
O
H3COOC
H3COOC
O
CH3



3f Dimethyl 2-(4-methoxylphenyl) furan-3, 4-dicarboxylate



^{1}H NMR (300MHz, $CDCl_3$) δ=3.83(s, 3H), 3.84(s, 3H), 3.89(s, 3H), 6.94(d, J=8.4Hz, 2H), 7.67 (d,

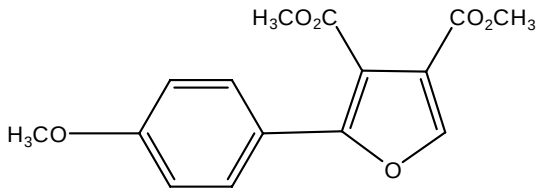
J=8.7Hz, 2H), 7.91(s, 1H).

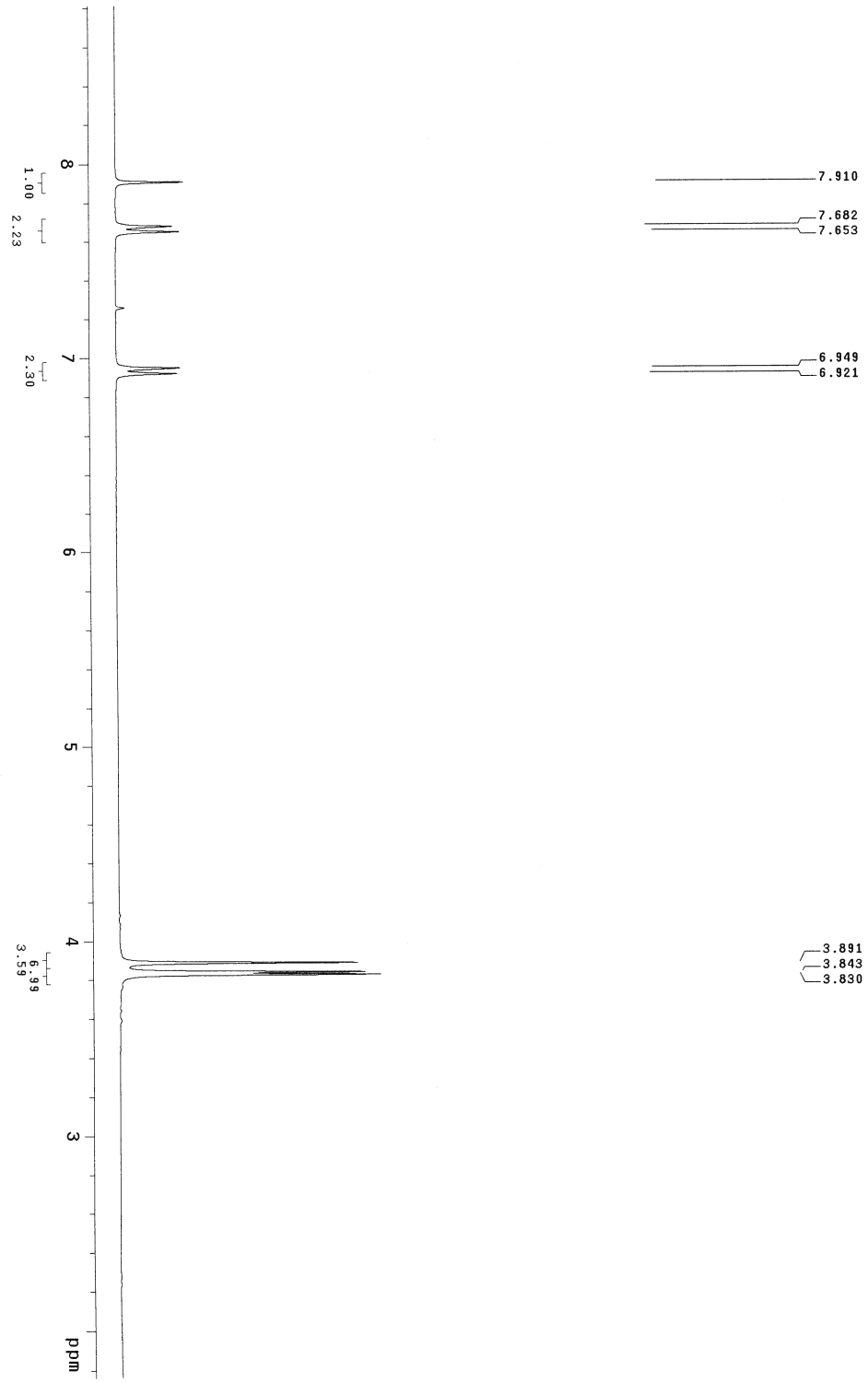
^{13}C NMR (75MHz, $CDCl_3$) δ=52.1, 52.8, 55.5, 112.3, 114.3, 120.0, 121.6, 128.4, 145.9, 155.0, 1160.8, 162.6, 165.1.

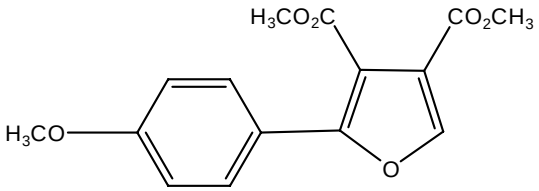
IR (KBr): v=2953, 2919, 1728, 1506, 1256, 1165, 1066, 733 cm^{-1}.

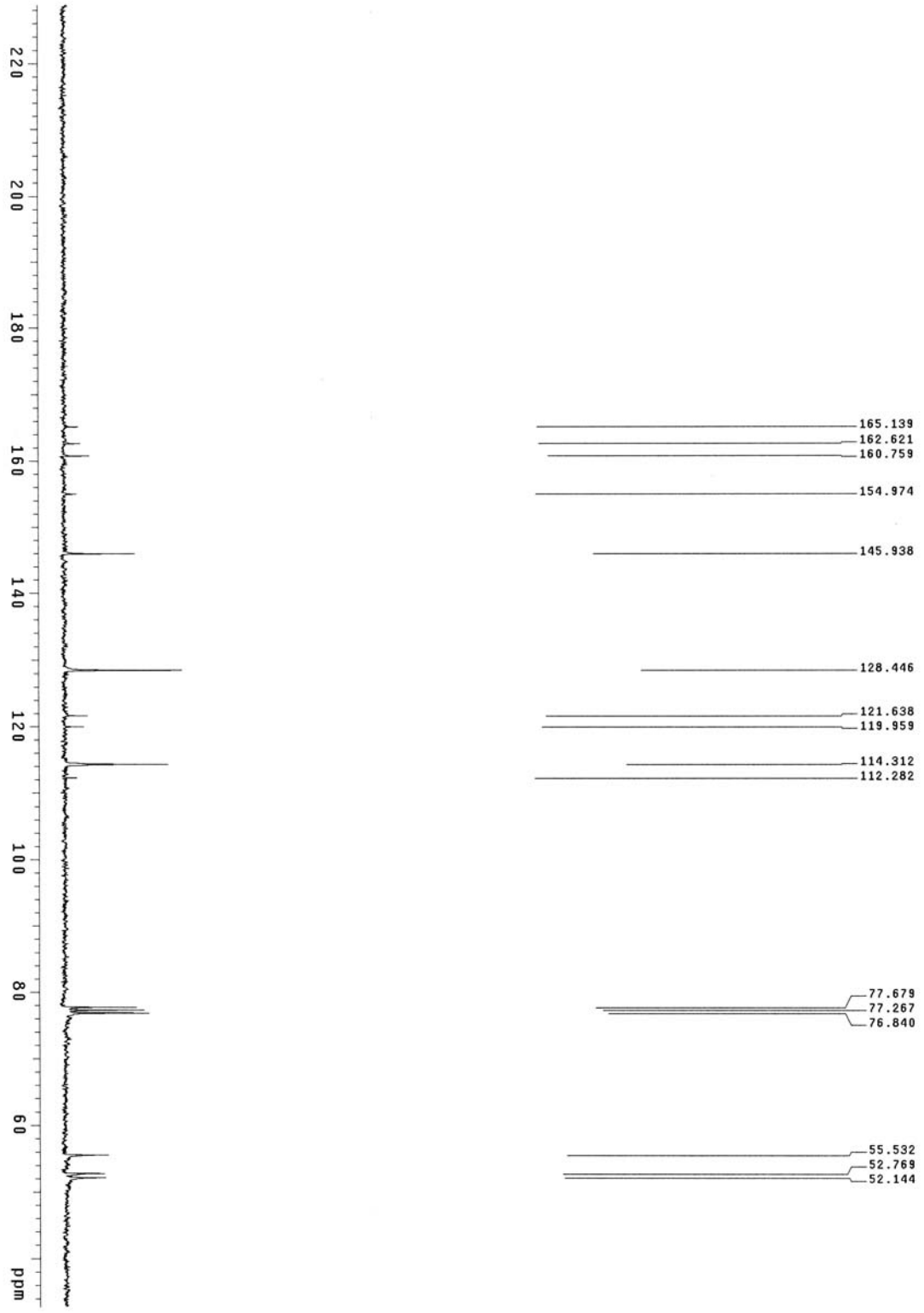
MS: m/z (%)=290(M^+, 100), 259(58.97), 135(21.06), 57(12.74), 43(15.09).

HRMS calcd for $C_{15}H_{14}O_6$: (M+Na) 313.0683, Found: 313.0688.

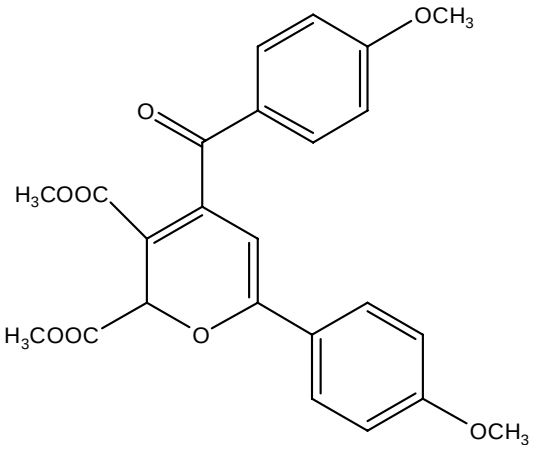



7.910
7.682
7.653
6.949
6.921
3.891
3.843
3.830
1.00
2.23
2.30
6.99
3.59
8
7
6
5
4
3
ppm


H3CO2C
CO2CH3
H3CO
O


220
200
180
160
140
120
100
80
60
ppm
165.139
162.621
160.759
154.974
145.938
128.446
121.638
119.959
114.312
112.282
77.679
77.267
76.840
55.532
52.769
52.144

4f



mp 132-134°C

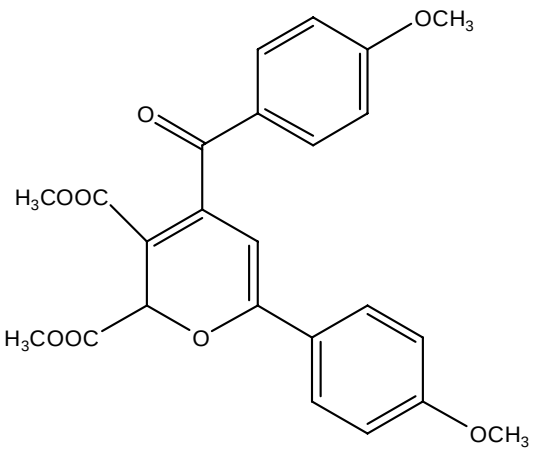
^{1}H NMR (300MHz, $CDCl_3$) δ=3.54(s, 3H), 3.77(s, 3H), 3.80(s, 3H), 3.83(s, 3H), 5.88(s, 1H), 6.04(s, 1H), 6.88-7.91(m, 8H).

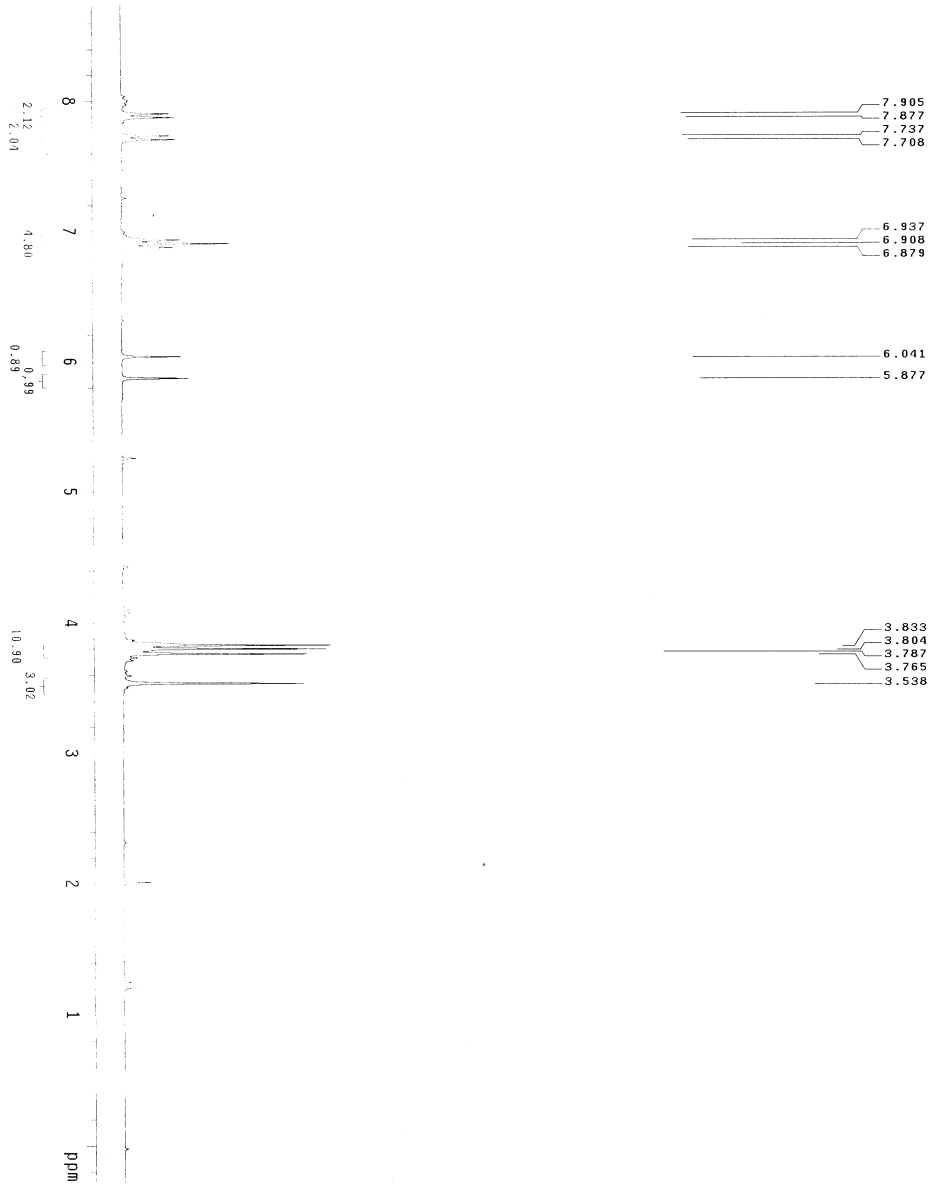
^{13}C NMR (75MHz, $CDCl_3$) δ=52.1, 53.0, 55.6, 55.7, 72.5, 97.1, 109.5, 114.3, 124.8, 128.6, 129.0, 131.3, 131.6, 146.1, 159.5, 162.3, 164.3, 170.4, 193.9.

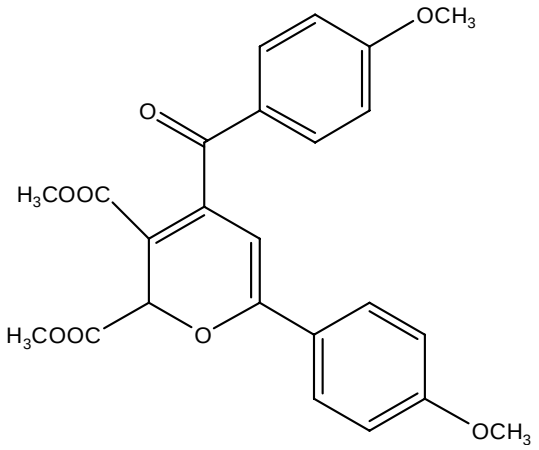
IR (KBr): v = 2953, 1738, 1708, 1669, 1259, 1088, 843cm^{-1}.

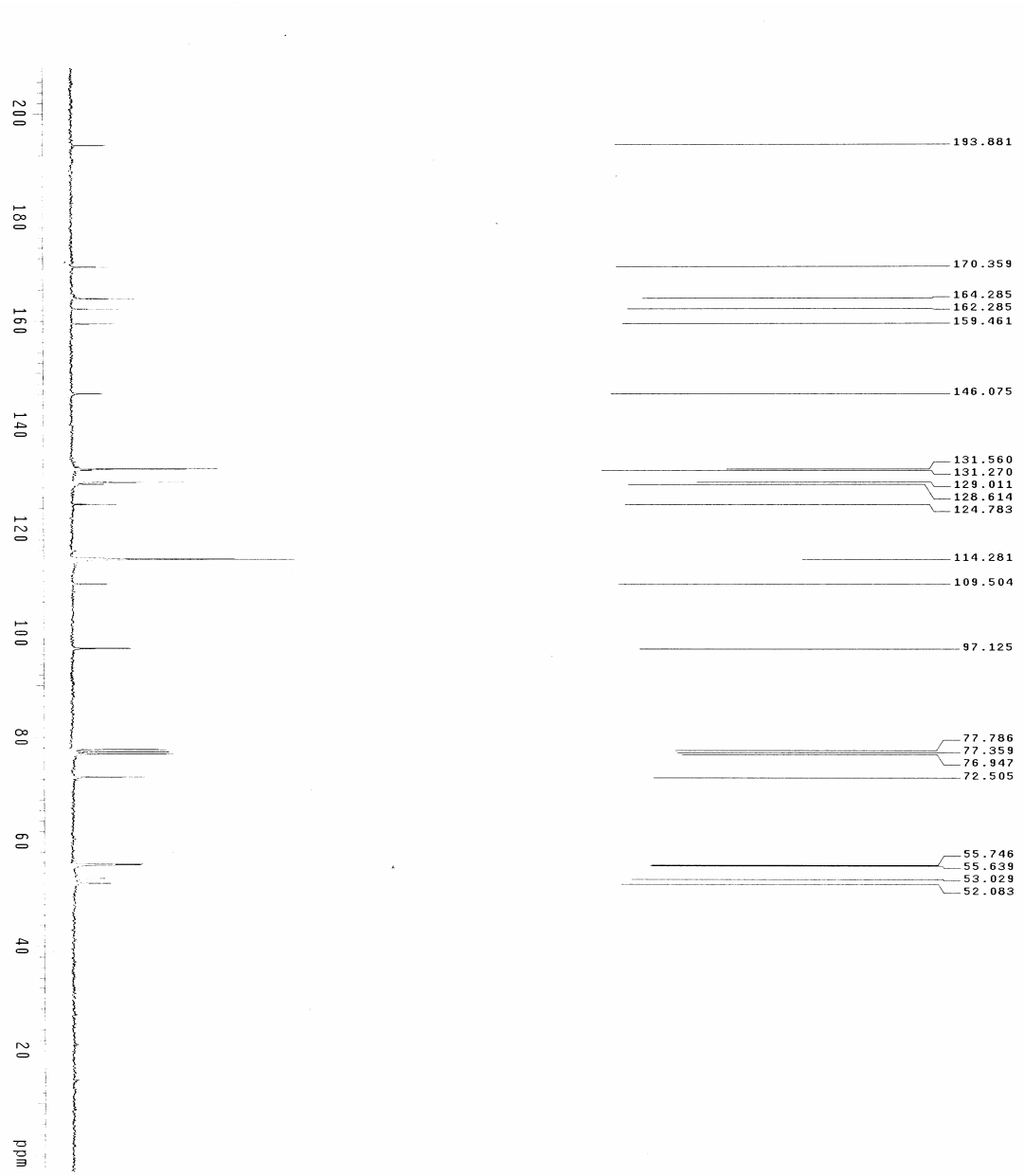
MS: m/z (%)=438(M^+, 3.52), 379(67.69), 135(100).

HRMS calcd for $C_{24}H_{22}O_8$: (M+NH4) 456.1653, Found: 456.1647.

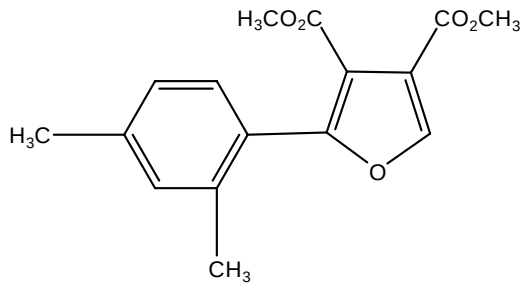

OCH3
O
H3COOC
H3COOC
O
OCH3


7.905
7.877
7.737
7.708
6.937
6.908
6.879
6.041
5.877
3.833
3.804
3.787
3.765
3.538
2.12
2.01
4.80
0.89
0.99
10.90
3.02
8
7
6
5
4
3
2
1
ppm


OCH3
O
H3COOC
H3COOC
O
OCH3



3g Dimethyl 2-(2, 4-dimethylphenyl) furan-3, 4-dicarboxylate



mp 50-52°C

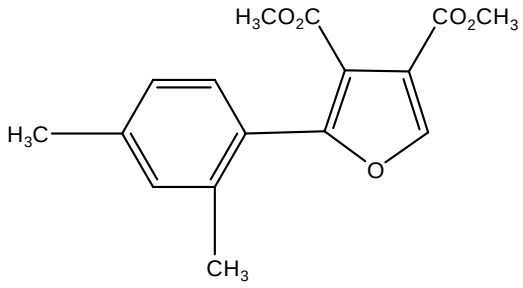
^{1}H NMR (300MHz, $CDCl_3$) δ=2.25(s, 3H), 2.35(s, 3H), 3.76(d, J=2.1Hz, 3H), 3.87(d, J=2.1Hz, 3H), 7.04(d, J=7.5Hz, 1H), 7.08(s, 1H), 7.28 (d, J=7.8Hz, 2H), 7.97(d, J=2.1Hz, 1H)

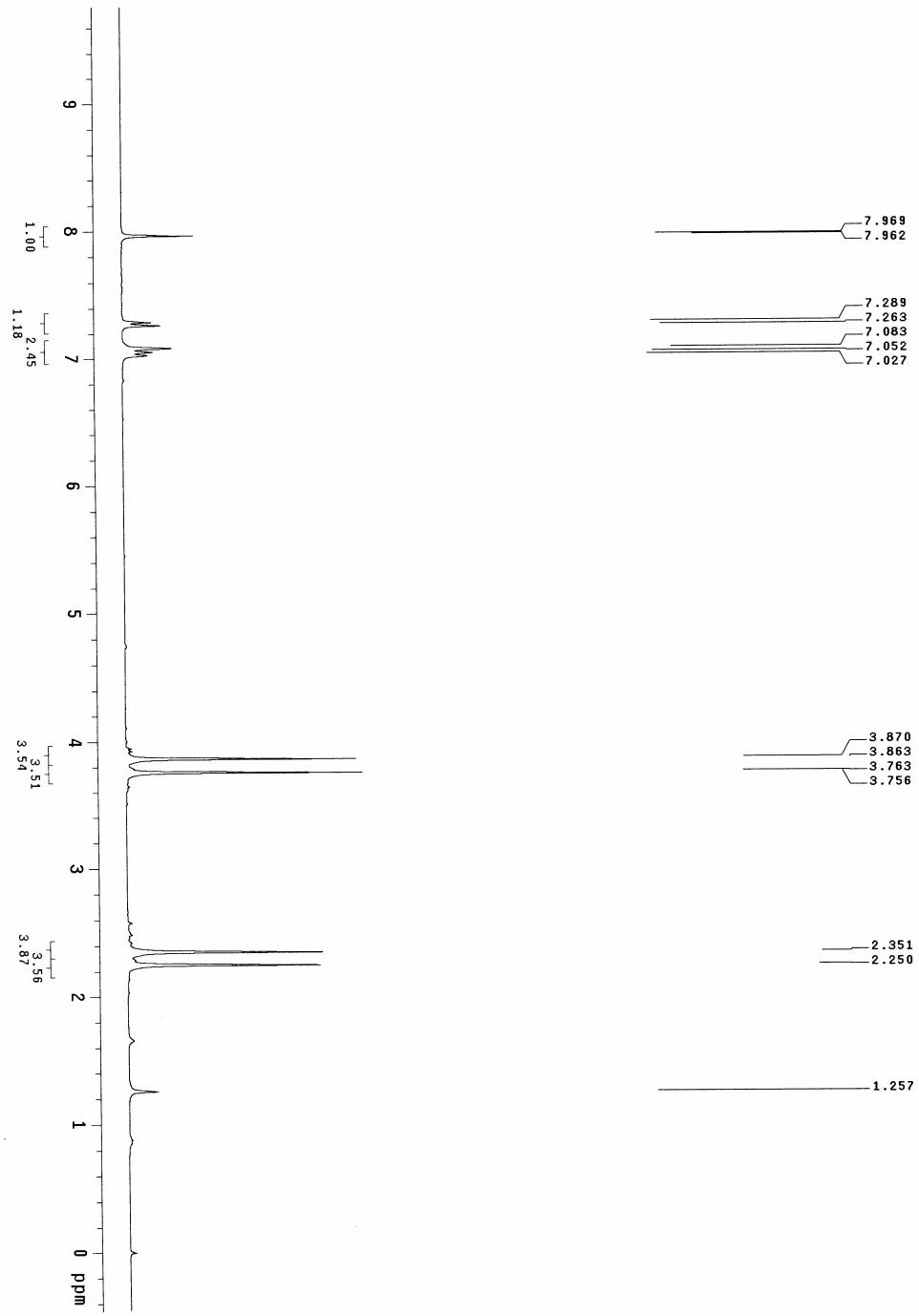
^{13}C NMR (75MHz, $CDCl_3$) δ=20.2, 21.5, 52.2, 52.4, 115.0, 119.3, 125.7, 126.5, 130.5, 131.6, 137.8 140.3, 146.6, 157.6, 162.7, 164.0.

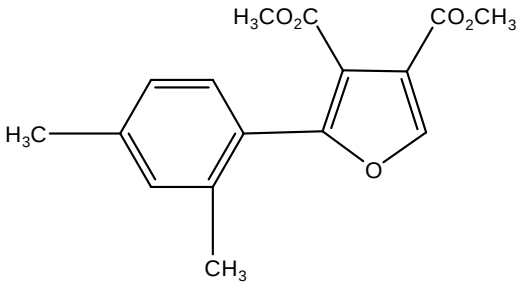
IR (KBr): v =2953, 1732, 1066, 818, 764cm^{-1}.

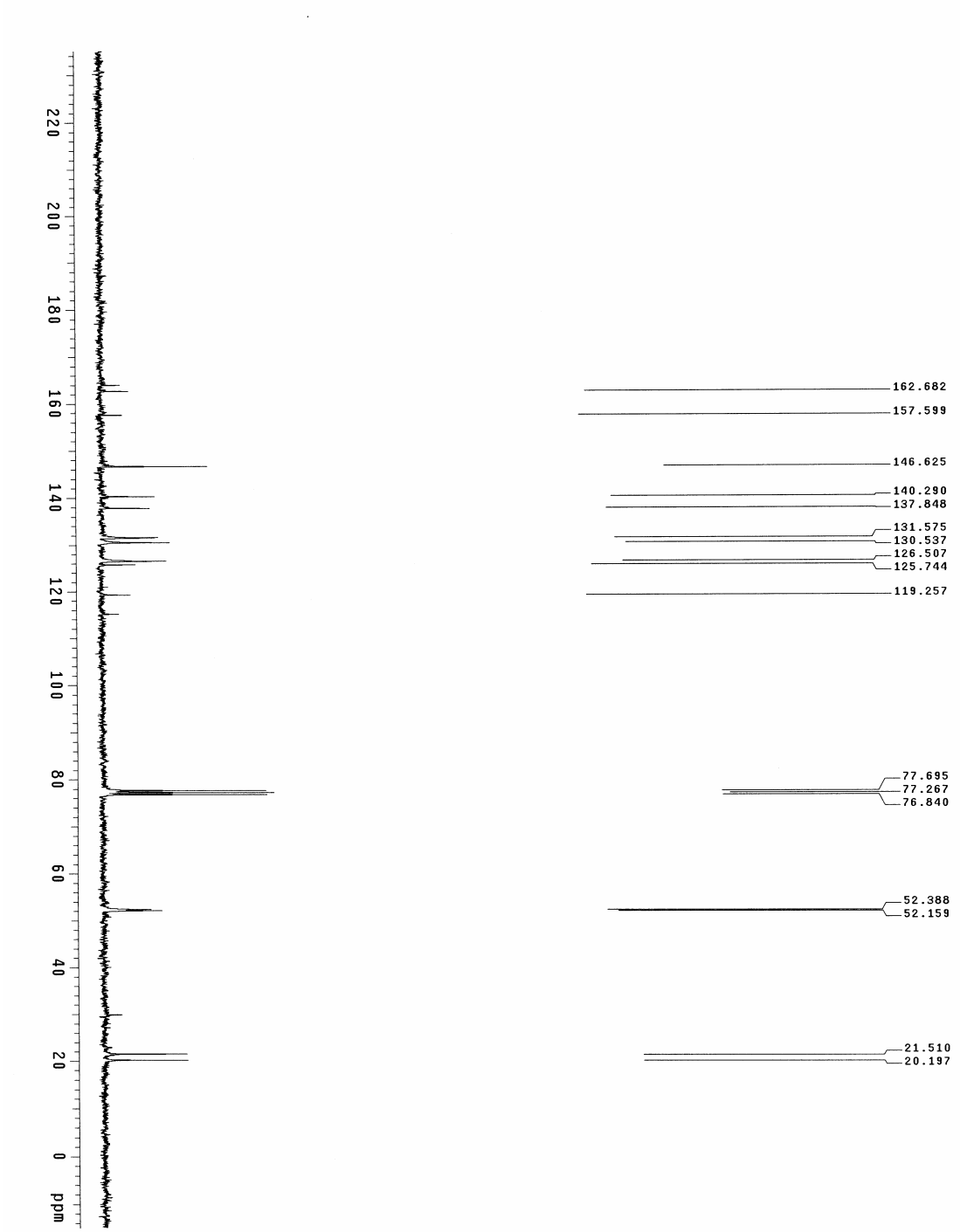
MS: m/z (%)=288 (M^+, 6.79), 257(54.59) 225(39.60), 198(76.45), 133(100).

HRMS calcd for $C_{16}H_{16}O_5$: (M+Na) 311.0890, Found: 311.0885.

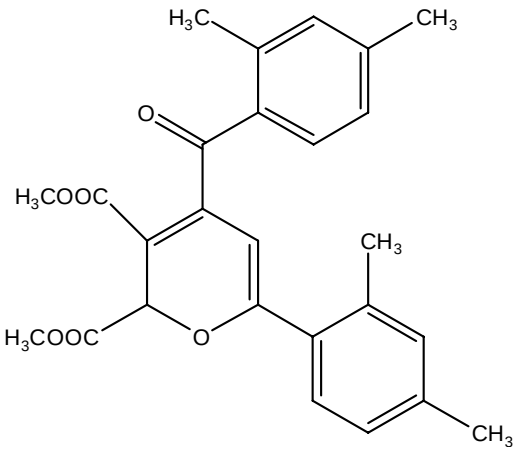

H3CO2C
CO2CH3
H3C
O
CH3


7.969
7.962
7.289
7.263
7.083
7.052
7.027
3.870
3.863
3.763
3.756
2.351
2.250
1.257
1.00
1.18
2.45
3.54
3.51
3.87
3.56
9
8
7
6
5
4
3
2
1
0 ppm


H3CO2C
CO2CH3
H3C
O
CH3


220
200
180
160
140
120
100
80
60
40
20
0
ppm
162.682
157.599
146.625
140.290
137.848
131.575
130.537
126.507
125.744
119.257
77.695
77.267
76.840
52.388
52.159
21.510
20.197

4g



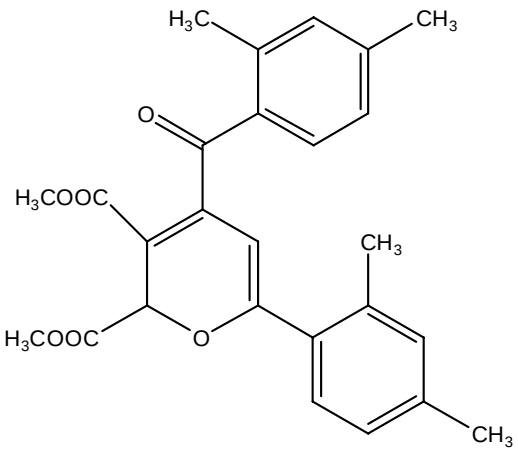
mp 103-104°C

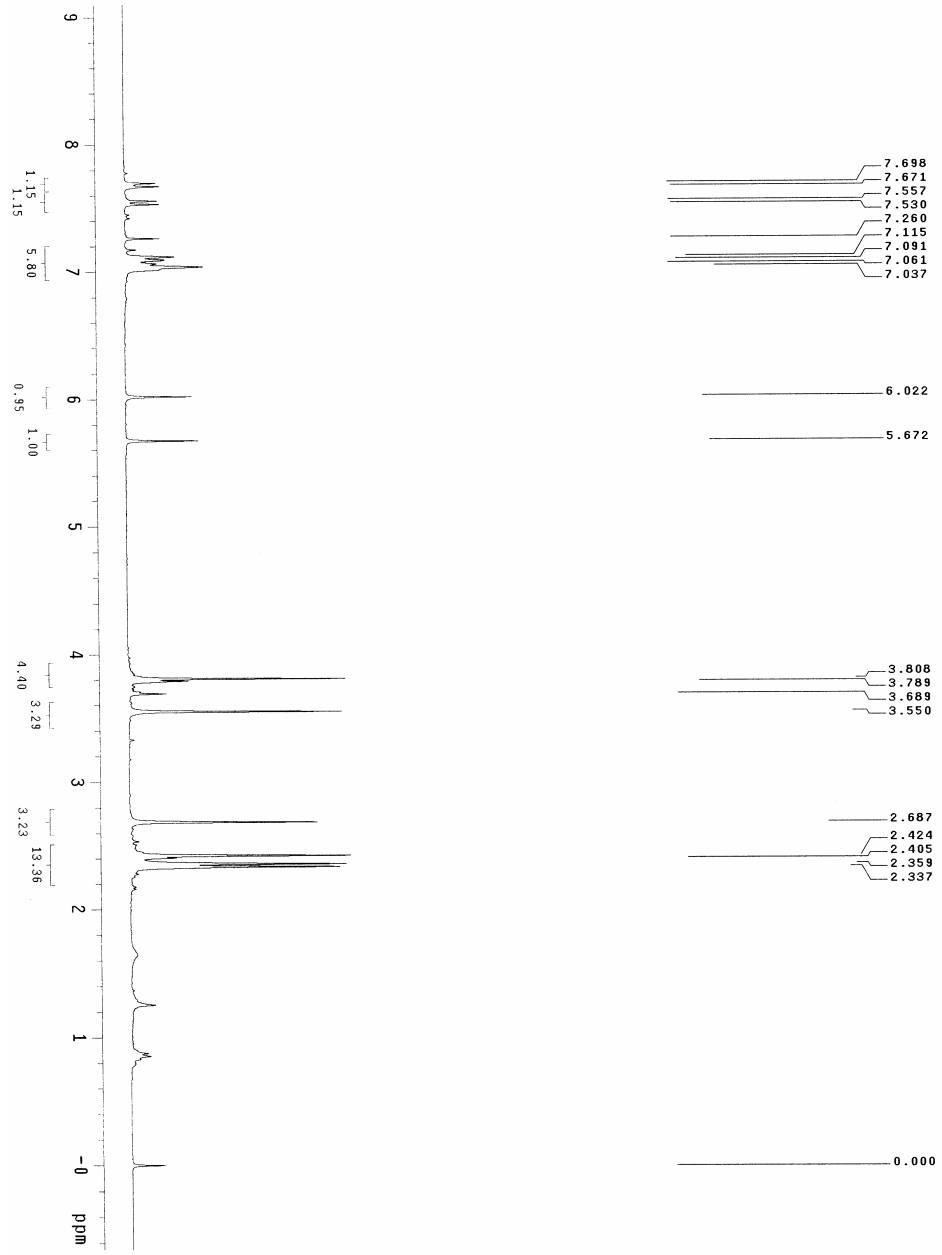
^{1}H NMR (300MHz, $CDCl_3$) δ=2.34(s, 3H), 2.36(s, 3H), 2.42(s, 3H), 2.69(s, 3H), 3.55(s, 3H), 3.81(s, 3H), 5.67(s, 1H), 6.02(s, 1H), 7.04-7.69 (m, 6H).

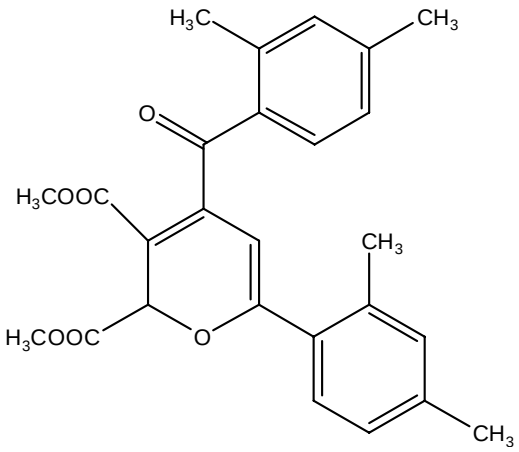
^{13}C NMR (75MHz, $CDCl_3$) δ=21.1, 21.2, 21.4, 21.7, 51.8, 52.6, 72.3, 102.3, 108.5, 126.3, 126.7, 129.4, 130.1, 131.7, 131.9, 133.1, 136.7, 140.4, 140.5, 143.3, 146.4, 159.8, 164.0, 169.7, 196.0. **IR** (KBr): v=2954, 1748, 1710, 1671, 1248, 1075, 814, 776cm^{-1}.

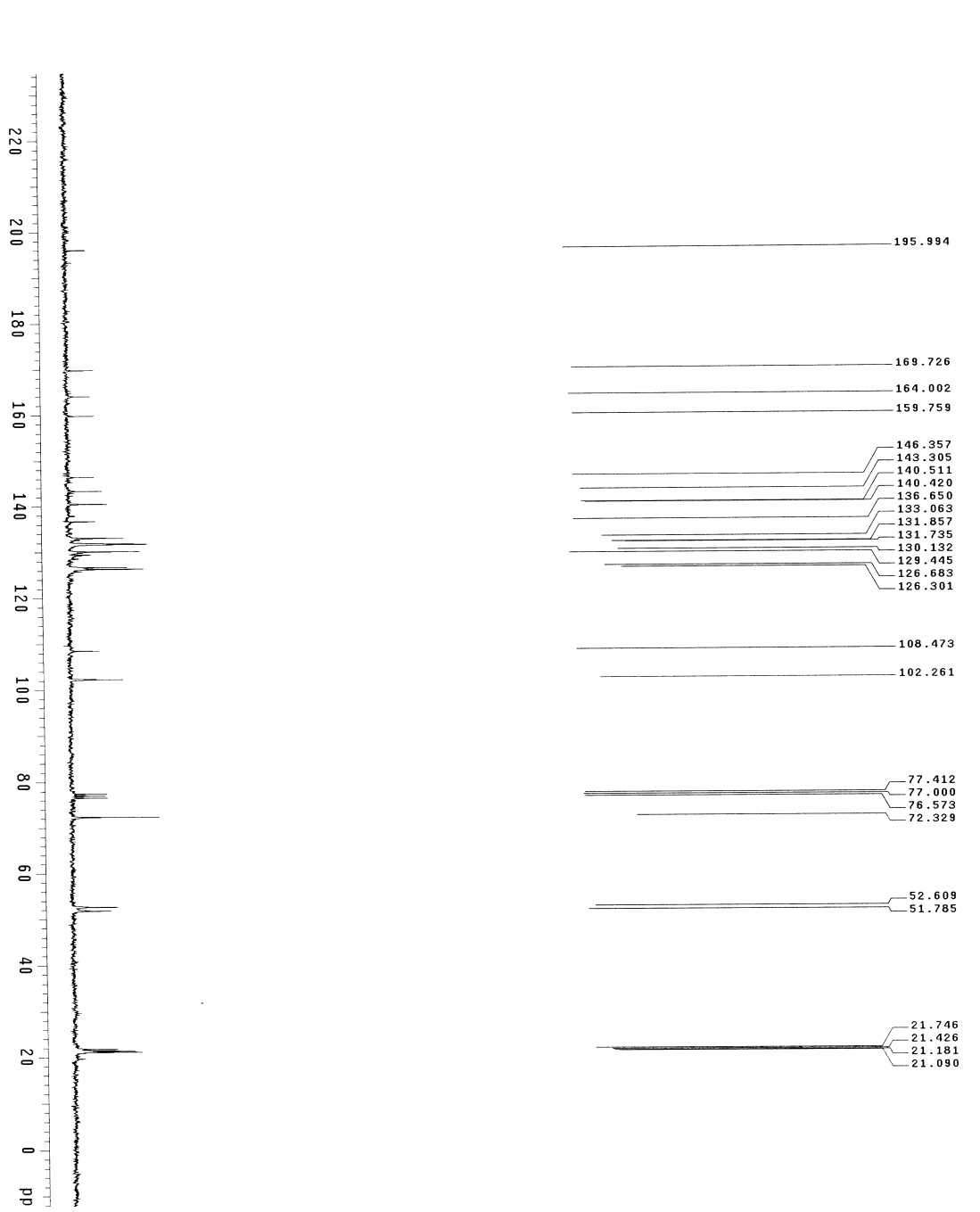
MS: m/z (%)=434 (M^+, 2.35), 375(49.43), 133(100), 105(34.95).

HRMS calcd for $C_{26}H_{26}O_6$: (M+H) 435.1802, Found: 435.1799.

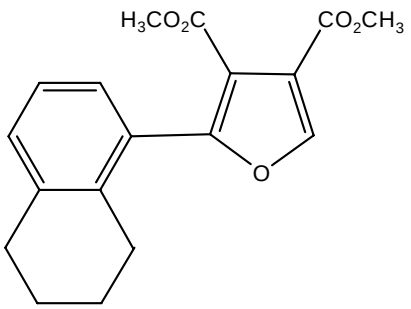

H3C
CH3
O
H3COOC
CH3
H3COOC
O
CH3


7.698
7.671
7.557
7.530
7.260
7.115
7.091
7.061
7.037
6.022
5.672
3.808
3.789
3.689
3.550
2.687
2.424
2.405
2.359
2.337
0.000
1.15
1.15
5.80
0.95
1.00
4.40
3.29
3.23
13.36
ppm


H3C
CH3
O
H3COOC
CH3
H3COOC
O
CH3



3h Dimethyl 2-(1,2,3,4-tetrahydronaphthalen-5-yl) furan-3, 4-dicarboxylate



mp 88-90°C

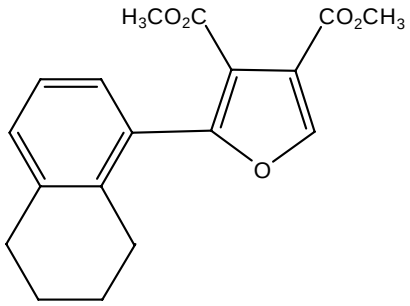
^{1}H NMR (300MHz, $CDCl_3$) δ=1.80(s, 4H), 2.79(s, 4H), 3.85(s, 3H), 3.90(s, 3H), 7.09-7.41(m, 3H), 7.93(s, 1H).

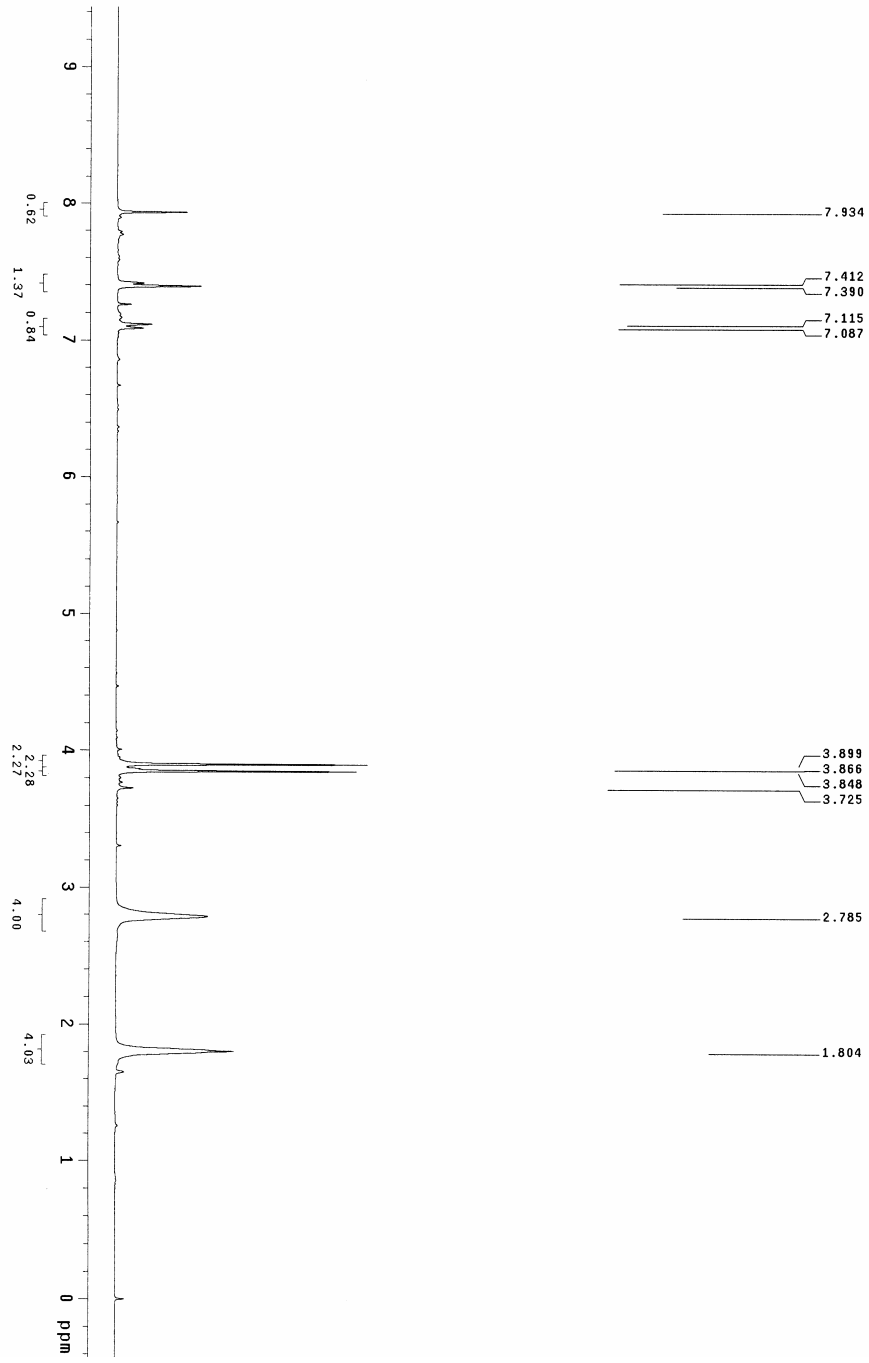
^{13}C NMR (75MHz, $CDCl_3$) δ=23.0, 29.3, 29.4, 51.9, 52.6, 112.7, 119.6, 123.5, 125.8, 127.1, 129.4, 137.5, 139.0, 145.9, 154.7, 162.3, 164.9.

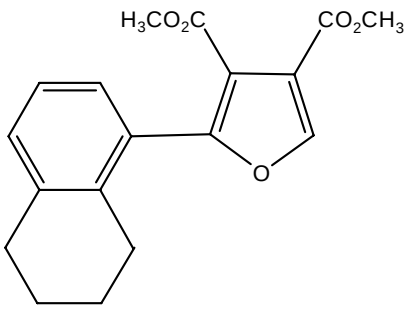
IR (KBr): v=2936, 1732, 1065, 813, 733cm^{-1}.

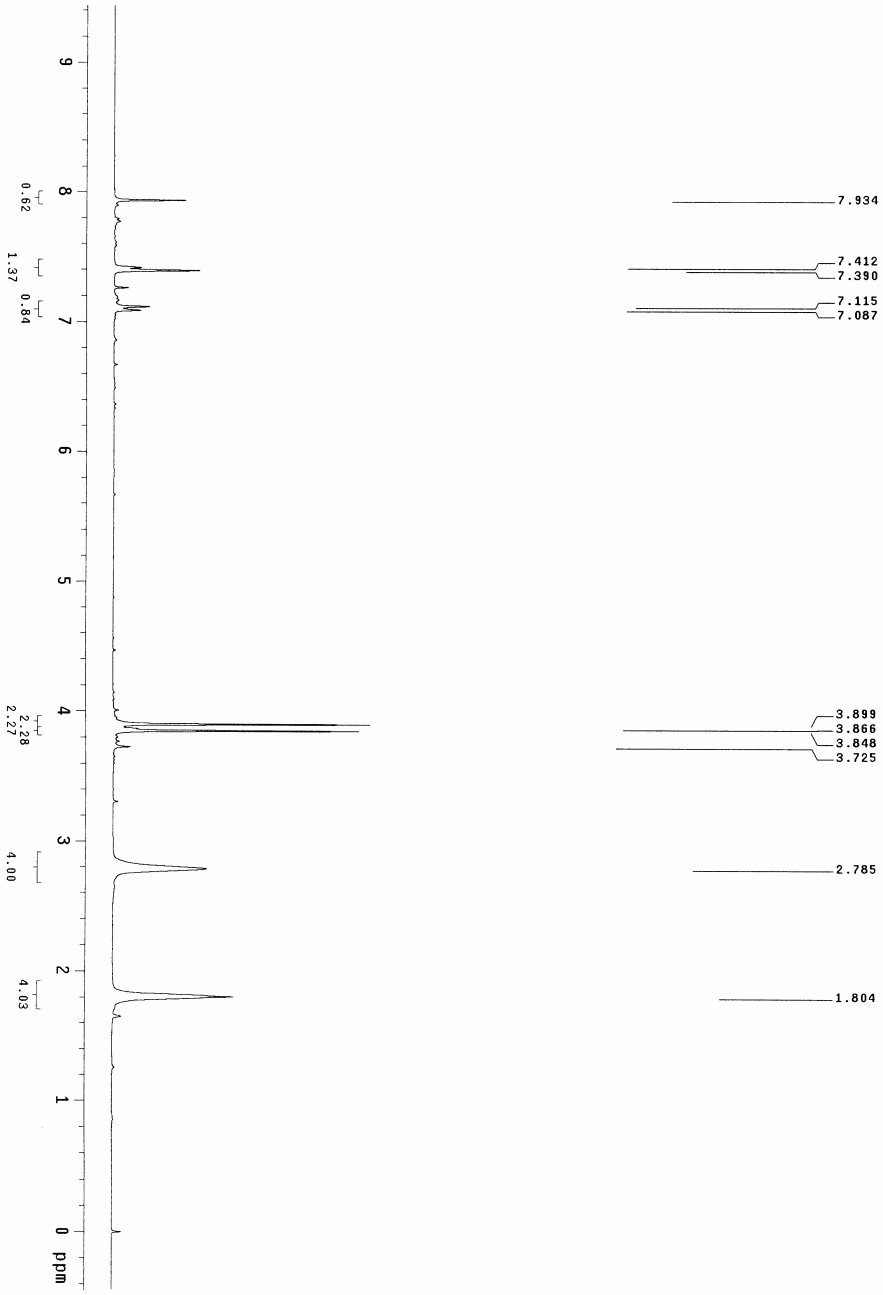
MS: m/z (%)=314 (M^+, 100), 283(43.69), 196(54.83).

HRMS calcd for $C_{18}H_{18}O_5$: (M+Na) 337.1046, Found: 337.1038.

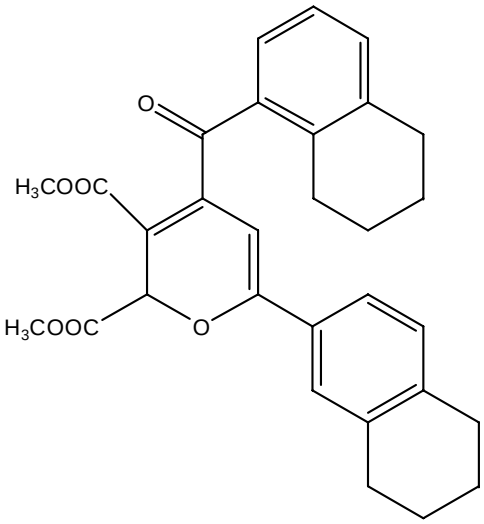

H3CO2C
CO2CH3
O


7.934
7.412
7.390
7.115
7.087
3.899
3.866
3.848
3.725
2.785
1.804
0.62
1.37
0.84
2.28
2.27
4.00
4.03
ppm


H3CO2C
CO2CH3
O


7.934
7.412
7.390
7.115
7.087
3.899
3.866
3.848
3.725
2.785
1.804
0.62
1.37
0.84
2.28
2.27
4.00
4.03
9
8
7
6
5
4
3
2
1
0
ppm

4h



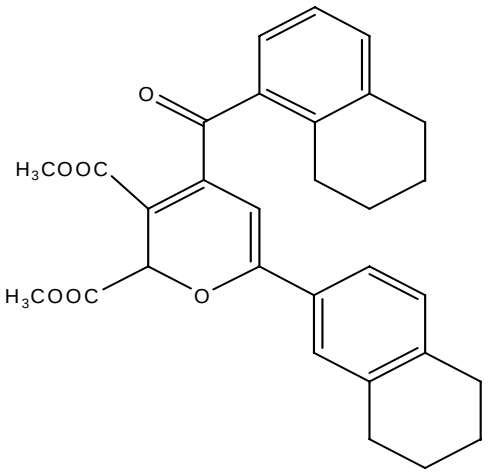
^{1}H NMR (300MHz, $CDCl_3$) δ=1.79-1.81(m, 8H), 2.79(m, 8H), 3.59(d, J=2.4Hz, 3H), 3.80(d, J=2.4Hz, 3H) 5.93 (d, J=2.4Hz,1H), 6.06 (d, J=2.4Hz, 1H), 7.08-7.64(m, 6H).

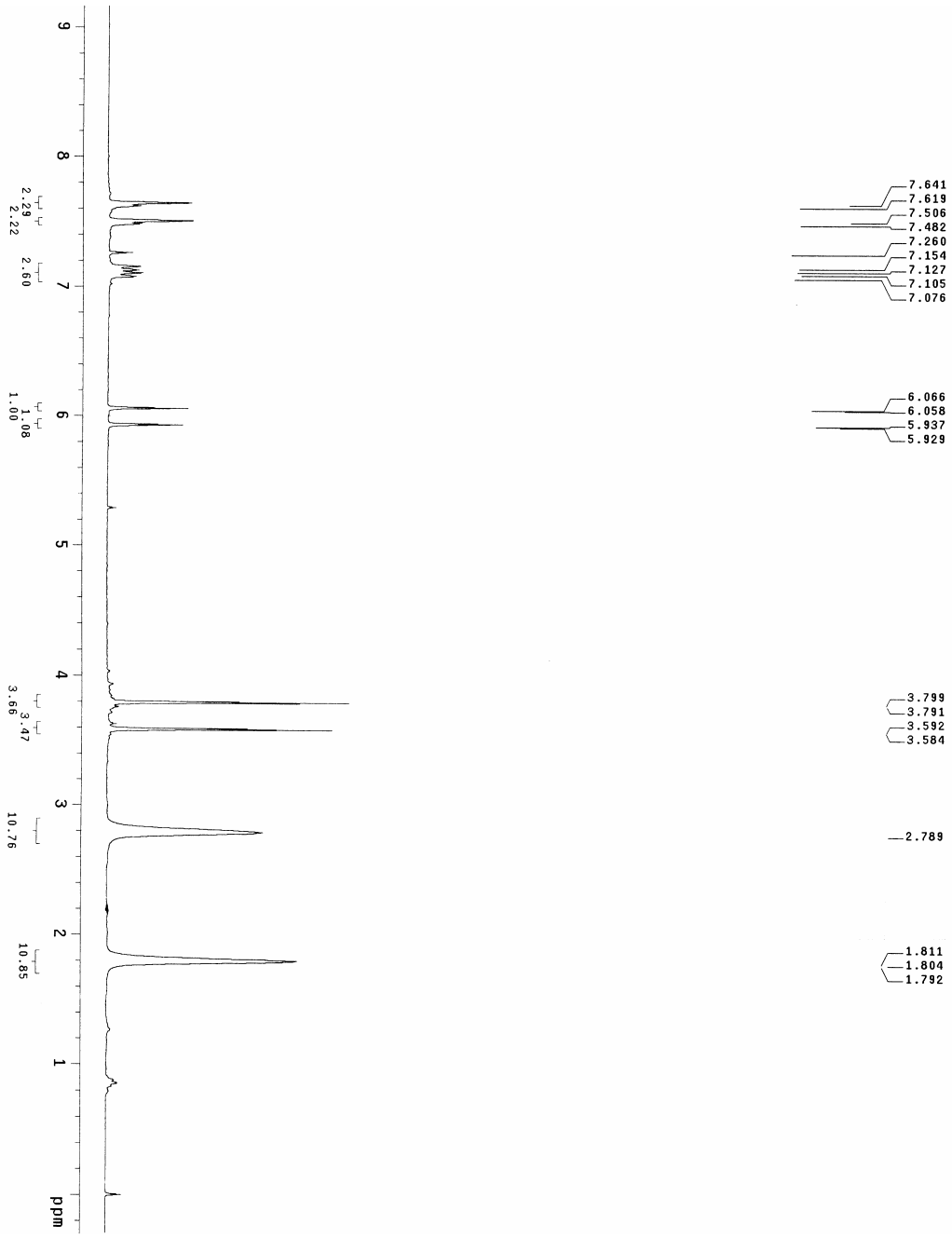
^{13}C NMR (75MHz, $CDCl_3$) δ=22.7, 22.8, 22.9 29.3, 29.5, 29.7, 51.9, 52.7, 72.2, 97.6, 109.6, 124.0, 126.1, 127.6, 129.2, 129.4, 129.6, 129.8, 132.7, 137.5, 137.7, 141.0, 144.1, 145.9, 159.6, 164.1, 170.0, 194.9.

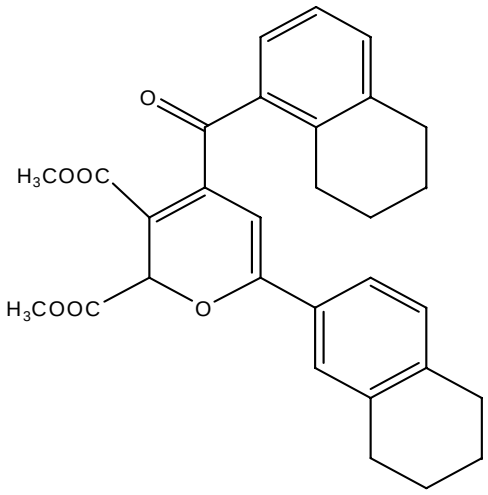
IR (KBr): v =2933, 1741, 1709, 1674, 1257, 1080, 733cm^{-1}.

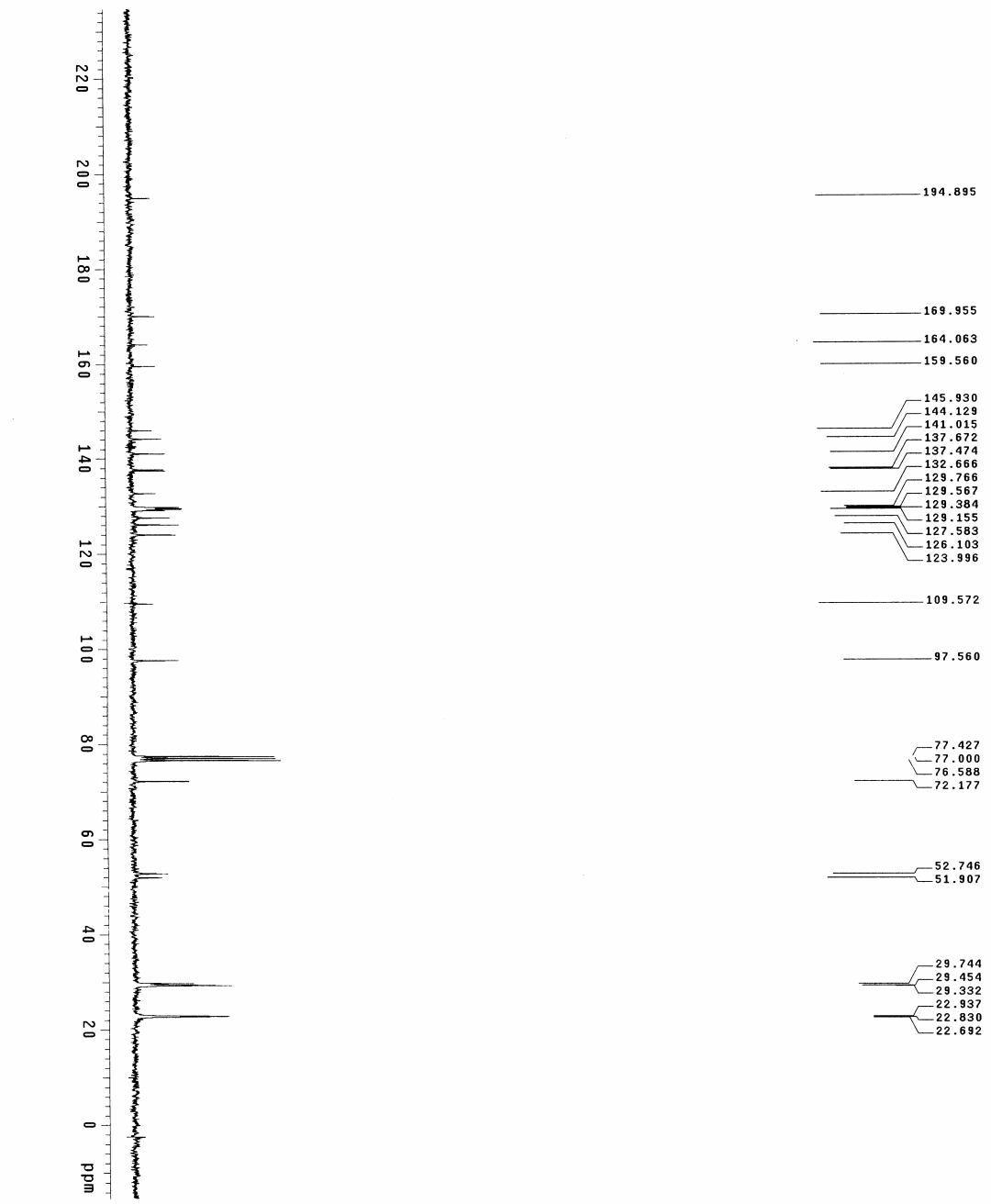
MS: m/z (%)=486(M^+, 0.99), 427(18.08), 159(100), 131(19.65).

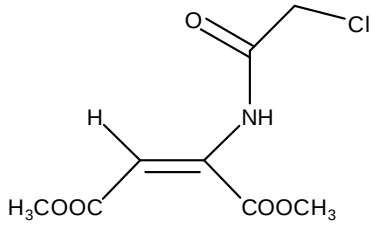
HRMS calcd for $C_{30}H_{30}O_6$: (M+Na) 509.1935, Found: 509.1941.


O
H3COOC
H3COOC
O


9
8
7
6
5
4
3
2
1
ppm
2.29
2.22
2.60
1.00
1.08
3.66
3.47
10.76
10.85
7.641
7.619
7.506
7.482
7.260
7.154
7.127
7.105
7.076
6.066
6.058
5.937
5.929
3.799
3.791
3.592
3.584
2.789
1.811
1.804
1.792


O
H3COOC
H3COOC
O

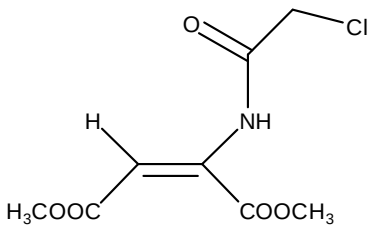


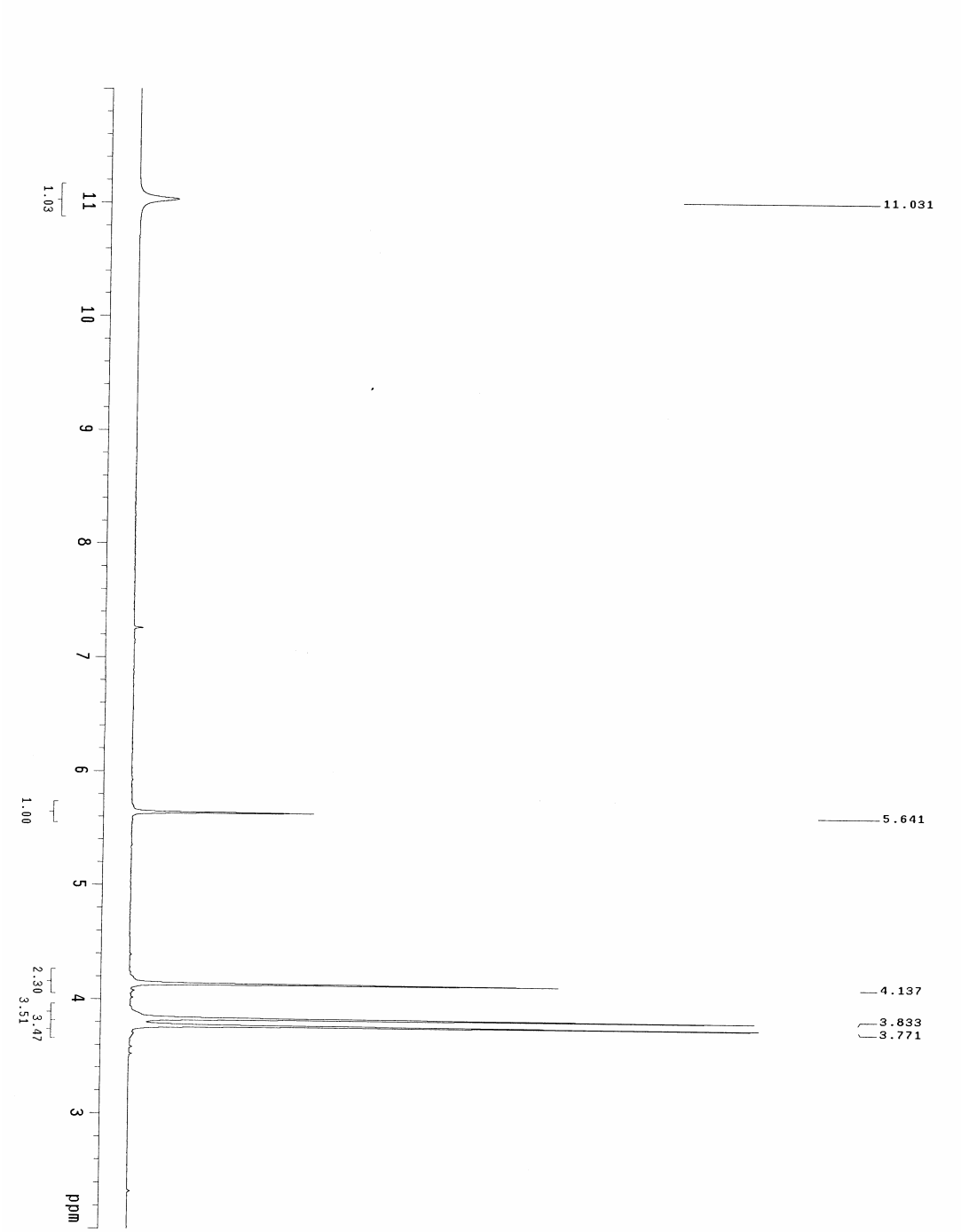


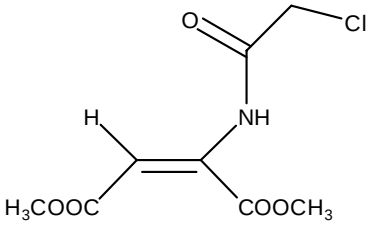
^{1}H NMR (300MHz, $CDCl_3$) δ=3.77(s, 3H), 3.83(s, 3H), 4.14(s, 2H), 5.64(s, 1H), 11.03(s, 1H),

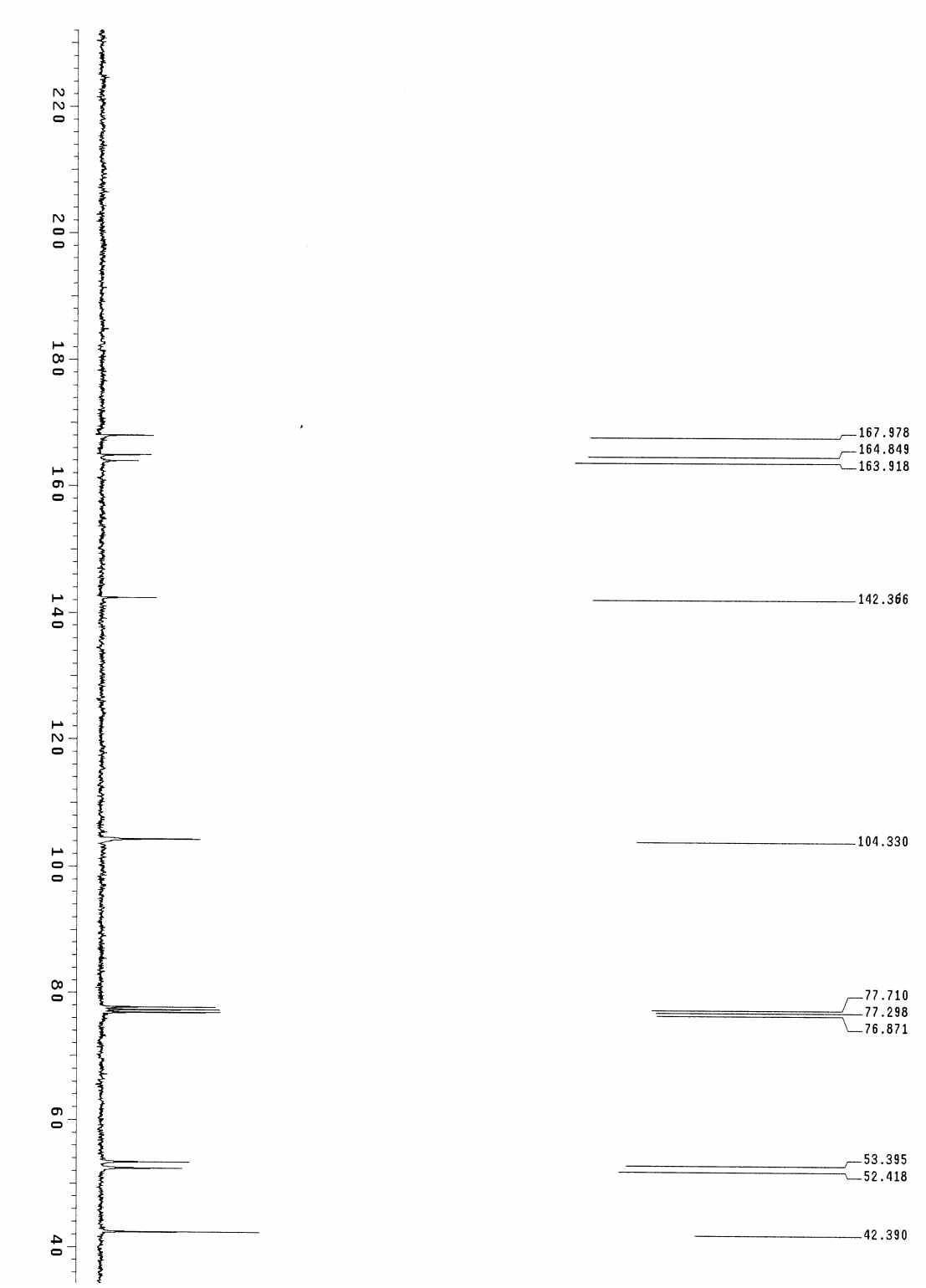
^{13}C NMR (75MHz, $CDCl_3$) δ=42.4, 52.4, 53.4, 104.3, 142.4, 163.9, 164.8, 168.0.

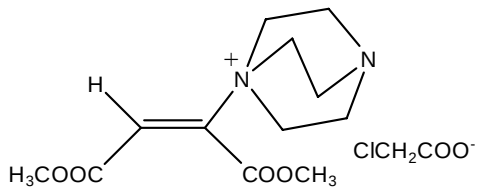
MS: m/z (%)=235(M^+, 5.36), 237(1.85), 204(11.46), 206(3.76), 176(100), 178(30.74).




11.031
5.641
4.137
3.833
3.771
1.03
1.00
2.30
3.47
3.51
11
10
9
8
7
6
5
4
3
ppm


O
Cl
H
NH
H3COOC
COOCH3

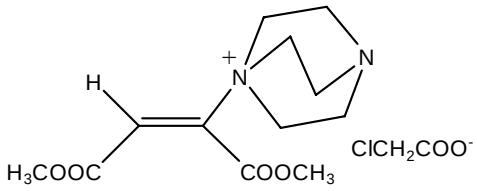

220
200
180
160
140
120
100
80
60
40
167.978
164.849
163.918
142.366
104.330
77.710
77.298
76.871
53.395
52.418
42.390

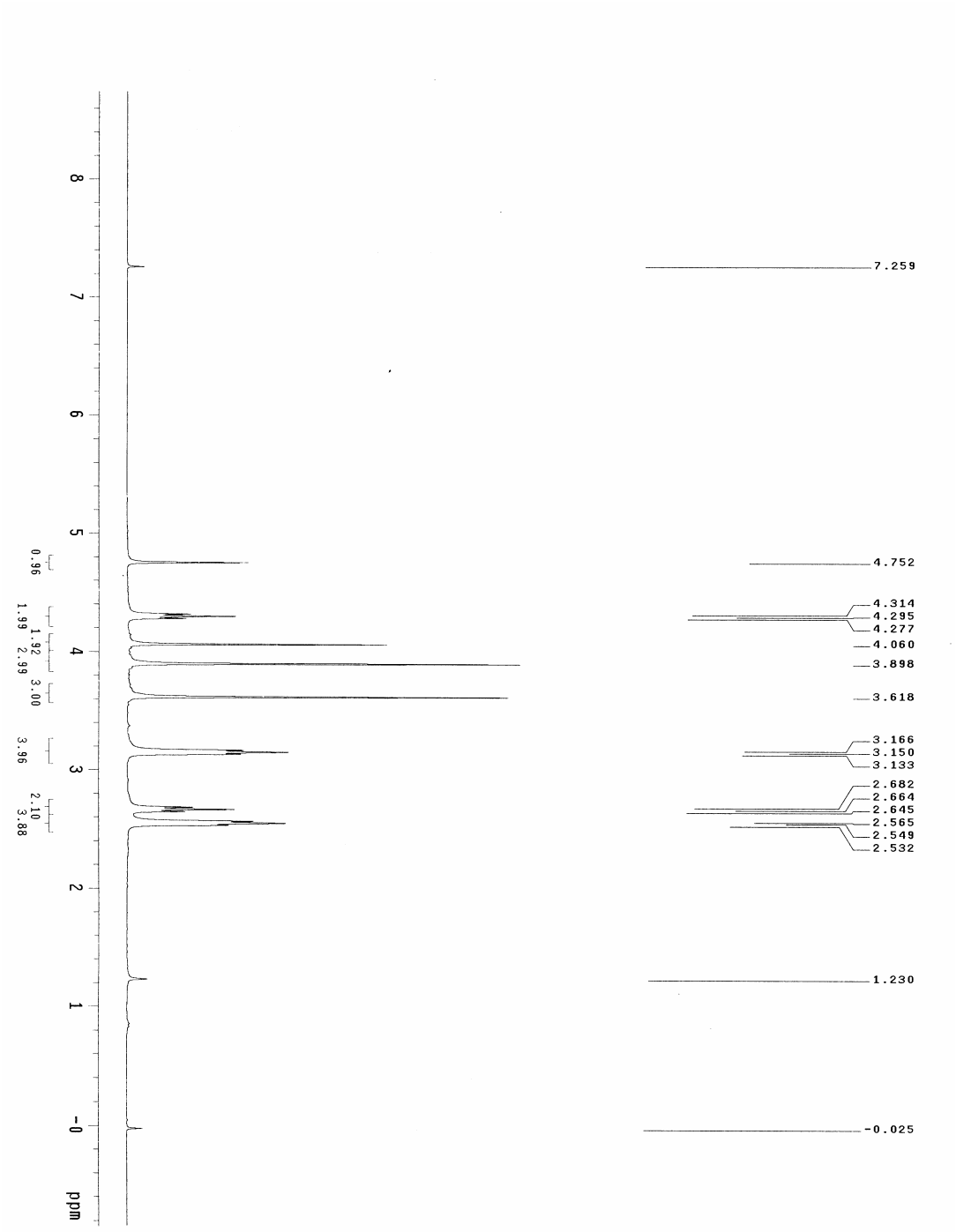


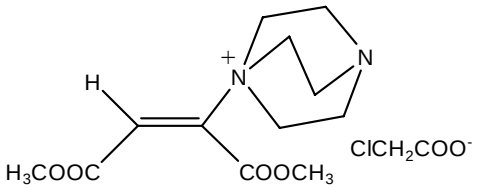
^{1}H NMR (300MHz, $CDCl_3$) δ=2.55 (dd, J=5.1Hz, J=4.8Hz, 4H), 2.66(dd, J=5.7Hz, J=5.4Hz, 2H), 3.15 (dd, J=5.1Hz, J=4.8Hz, 4H), 3.62 (s, 3H), 3.90 (s, 3H), 4.06 (s, 2H), 4.30(dd, J=5.4Hz, J=5.7Hz, 2H).

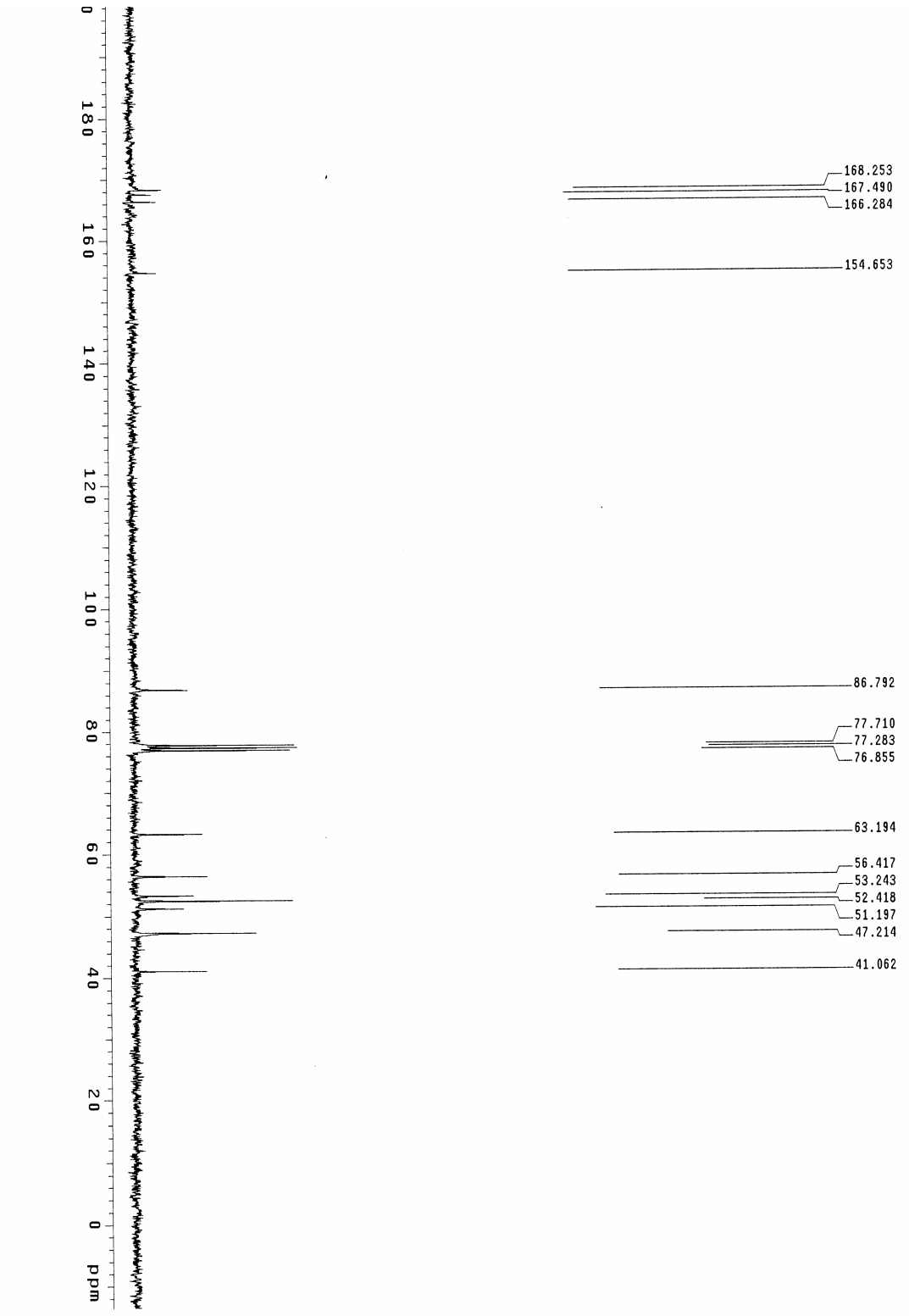
^{13}C NMR (75MHz, $CDCl_3$) δ=41.1, 47.2, 51.2, 52.4, 53.2, 56.4, 63.2, 86.8, 154.7, 166.3, 167.5, 168.3.

MS: m/z (%)=348(M^+, 14.22), 350(5.16), 317(21.61), 319(7.34), 241(87.11), 176(100).


H
+
N
N
H3COOC
COOCH3
ClCH2COO-


7.259
4.752
4.314
4.295
4.277
4.060
3.898
3.618
3.166
3.150
3.133
2.682
2.664
2.645
2.565
2.549
2.532
1.230
-0.025
0.96
1.99
1.92
2.99
3.00
3.96
2.10
3.88
8
7
6
5
4
3
2
1
-0
ppm

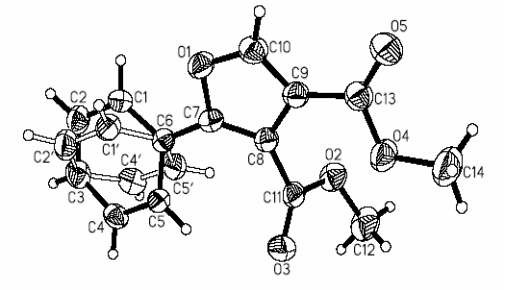

+
N
N
H
H3COOC
COOCH3
ClCH2COO-



(III). Single-crystal X-ray crystallographic data for polySubstituted Furan 3c and

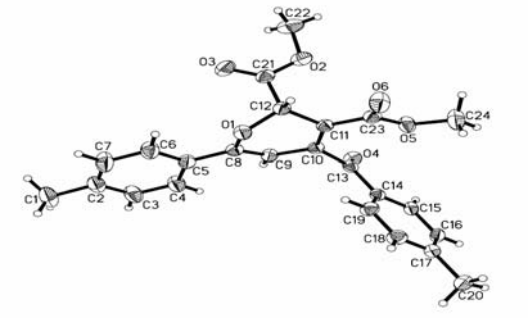
highly functionalized 2*H*-pyran 4e.

1. X-ray crystal structure of **3c**



Crystal data for **3c**: $C_{14}H_{12}O_5$, mp: 68-70 $^{\circ}$C, chemical_formula_weigh: 260.24, monoclinic space group P2 (1)/c, a=14.698(2), b=11.720(1), c= 7.3105(7) Å; α= 90.00°, β= 97.916(9)$^{\circ}$, γ= 90.00°, V= 1247.3(2) Å3. *T* = 290(2) K, Z=4, Dc= 1.386Mg/M^3, μ= 0.106mm^{-1}, λ=0.71073 Å, F (000) 544, Crystal size 0.52 x 0.48 x 0.48 mm^3, 2255 independent reflections [R (int) = 0.0122], Reflections collected 2690: Refinement method, full-matrix least-squares on F^2: Goodness-of-fit on F^2 1.073: Final R indices [I>2δ(I)] R_1 = 0.0383, wR_2 = 0.1038, R indices (all data) R_1 =0.0524, wR_2 = 0.0138. Extinction coefficient 0.126(7), Largest diff. peak and hole 0.173 and -0.163e. Å^{-3}.

2. X-ray crystal structure of **4e**



Crystal data for **4e**: $C_{24}H_{22}O_6$, mp: 148-150°C, chemical_formula_weigh: 406.42, monoclinic space group P2 (1)/c, a= 7.468(2), b= 19.811(5), c= 14.249(4) Å; α= 90.00°, β= 96.801(4)$^{\circ}$, γ= 90.00°, V=

2093.2(10) Å3. *T* = 291(2) K, Z=4,Dc= 1.290Mg/M^3, μ=0.093mm^{-1}, λ= 0.71073 Å, F (000) 856, Crystal size 0.56 x 0.45 x 0.34 mm^3, 3872 independent reflections [R (int) = 0.0168], Reflections collected 10796: Refinement method, full-matrix least-squares on F^2: Goodness-of-fit on F^2 1.102: Final R indices [I>2δ(I)] R_1 = 0.0370, wR_2 = 0.1028, R indices (all data) R_1 = 0.0448,wR_2 = 0.1064. Extinction coefficient0.0088 (13), Largest diff. peak and hole 0.171 and -0.146 e. $Å^{-3}$.