Supporting Information

Synthesis of Coumarins via Palladium-Catalyzed Carbonylative Annulation of Internal Alkynes by *o*-Iodophenols.

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General. All ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100.5 MHz respectively. All melting points are uncorrected. Low resolution mass spectra were recorded on a Finnigan TSQ700 triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA). High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. Elemental analyses were performed at Iowa State University on a Perkin Elmer 2400 CHNS/O Series II Analyzer.

General procedure for the palladium-catalyzed synthesis of coumarins. The *o*-iodophenol (0.5 mmol), the alkyne (2.5 mmol), pyridine (79 mg, 1 mmol), *n*-Bu_4NCl (139 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol %, 0.025 mmol), and DMF (5 ml) were placed in a 4 dram vial. The vial was purged with CO for 2 min, then connected to a balloon of CO. The reaction mixture was stirred at 120 °C (for the reaction times see Table 1), then cooled to room temperature, diluted with EtOAc, washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The product was isolated by flash chromatography on silica gel.

3,4-Di-*n*-propyl-*2H*-1-benzopyran-2-one (3). White solid, mp 58-60 °C; ^{1}H NMR ($CDCl_3$) δ 7.59 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.45 (ddd, *J* = 1.2, 8.0, 8.4 Hz, 1H), 7.25-7.32 (m, 2H), 2.79 (m, 2H),

2.61 (m, 2H), 1.55-1.70 (m, 4H), 1.11 (t, J = 7.6 Hz, 3H), 1.03 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 162.1, 152.8, 150.1, 130.5, 126.6, 124.7, 124.2, 120.0, 117.2, 30.7, 29.9, 23.1, 22.5, 14.7, 14.5; IR ($CHCl_3$, cm^{-1}) 3073, 2962, 2872, 1716; MS m/z (rel intensity) 230 (67, M^+), 215 (77), 201 (66), 187 (100). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.05; H, 8.05.

3,4-Diphenyl-*2H*-1-benzopyran-2-one (4). White solid, mp 229-230 °C (lit.[1] mp 228-230 °C); ^{1}H NMR ($CDCl_3$) δ 7.54 (ddd, J = 2.0, 7.2, 8.4 Hz, 1H), 7.44 (dd, J = 0.8, 8.4 Hz, 1H), 7.29-7.32 (m, 3H), 7.11-7.25 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 161.5, 153.4, 151.8, 134.6, 134.0, 131.6, 130.7, 129.5, 128.5, 128.4, 128.0, 127.9, 127.8, 127.2, 124.3, 120.7, 116.9; IR ($CHCl_3$, cm^{-1}) 1717, 1707, 1604, 1596; MS m/z (rel intensity) 298 (85, M^+), 297 (100). Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.53; H, 4.74. Found: C, 84.41; H, 4.9.

4-Methyl-3-phenyl-*2H*-1-benzopyran-2-one (5). White solid, mp 151-153°C (lit.[2] mp 156-157 °C); all spectral properties are identical to those reported in the literature.[2]

3-Methyl-4-phenyl-*2H*-1-benzopyran-2-one (6). Colorless viscous liquid; spectral properties are identical with those reported in the literature.[3]

4-Ethyl-3-phenyl-*2H*-1-benzopyran-2-one (7). White solid, mp 181-182 °C; ^{1}H NMR ($CDCl_3$) δ 7.70 (dd, J = 1.2, 8.0 Hz, 1H), 7.54 (ddd, J = 1.2, 8.0, 8.4 Hz, 1H), 7.38-7.49 (m, 4H), 7.28-7.35 (m, 3H), 2.68 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 161.4, 153.5, 134.7, 131.4, 129.7, 128.8, 128.4, 127.1, 125.3, 124.4, 119.4, 117.4, 23.0, 14.4; IR ($CHCl_3$, cm^{-1}) 3155, 2981, 1720, 1700, 1606; MS m/z (rel intensity) 250 (100, M^+), 207 (70), 187 (50). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.57; H, 5.64. Found: C, 81.61; H, 5.95.

3-Ethyl-4-phenyl-*2H*-1-benzopyran-2-one (8). White solid, mp 67-68 °C; ^{1}H NMR ($CDCl_3$) δ 7.43-7.56 (m, 4H), 7.36 (dd, J = 1.2, 8.0 Hz, 1H), 7.24 (m, 2H), 7.12 (ddd, J = 0.8, 7.2, 8.0 Hz, 1H), 6.94 (dd, J = 0.8, 7.6 Hz, 1H), 2.40 (q, J = 7.6 Hz, 2H), 1.07 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 161.9, 152.7, 150.6, 135.0, 130.7, 129.0, 128.9, 128.8, 128.4, 127.4, 124.1, 121.2, 116.7, 22.4, 13.7. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.57; H, 5.64. Found: C, 81.51; H, 6.03.

3-*tert*-Butyl-4-methyl-*2H*-1-benzopyran-2-one (9). Yellow viscous oil; ^{1}H NMR ($CDCl_3$) δ 7.64 (dd, *J* = 1.2, 8.8 Hz, 1H), 7.43 (ddd, *J* = 1.2, 7.2, 8.0 Hz, 1H), 7.22-7.26 (m, 2H), 2.59 (s, 3H), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 160.4, 151.8, 145.4, 134.0, 130.4, 124.5, 123.8, 122.2, 116.3, 37.1, 31.5, 18.3; MS m/z (rel intensity) 216 (M^+, 36), 201(99), 173 (100). HRMS Calcd for $C_{14}H_{16}O_2$: 216.11503. Found: 216.11530.

4-Benzyloxymethyl-3-phenyl-*2H*-1-benzopyran-2-one (10). White solid, mp 93-96 °C; ^{1}H NMR ($CDCl_3$) δ 7.83 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.53 (ddd, *J* = 1.2, 7.2, 8.4 Hz, 1H), 7.41-7.44 (m, 2H), 7.24-7.38 (m, 9H), 4.49-4.50 (2 overlapping s, 4H); ^{13}C NMR ($CDCl_3$) δ 161.3, 153.4, 145.5, 137.3, 133.4, 131.6, 130.3, 129.5, 128.9, 128.7, 128.5, 128.3, 126.5, 124.6, 119.4, 117.0, 73.4, 66.3; IR ($CHCl_3$, cm^{-1}) 1718; MS m/z (rel intensity) 342 (14, M^+), 251 (25), 236 (100), 91 (73). Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.57; H, 5.40.

3-Benzyloxymethyl-4-phenyl-*2H*-1-benzopyran-2-one (11). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.49-7.53 (m, 4H), 7.34-7.39 (m, 3H), 7.23-7.31 (m, 5H), 7.15 (ddd, *J* = 1.2, 6.8, 8.0 Hz, 1H), 7.09 (dd, *J* = 1.6, 8.0 Hz, 1H), 4.50 (s, 2H), 4.25 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 161.8, 154.9, 153.6, 138.3, 133.8, 132.0, 129.2, 128.9, 128.7, 128.5, 128.2, 128.0, 127.8, 124.3, 122.8, 120.5, 117.0, 73.6, 65.3; IR ($CHCl_3$, cm^{-1}) 1716, 1605; MS m/z (rel intensity) 342 (M^+, 11), 236 (68), 235 (100). HRMS Calcd for $C_{23}H_{18}O_3$: 342.12559 Found: 342.12604.

4-Methyl-3-trimethylsilyl-*2H*-1-benzopyran-2-one (12). White solid, mp 92-93 °C; ^{1}H NMR ($CDCl_3$) δ 7.65 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.48 (ddd, *J* = 1.2, 7.2, 8.4 Hz, 1H), 7.23-7.28 (m, 2H), 2.53 (s, 3H), 0.41 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 163.2, 158.5, 153.8, 131.7, 126.0, 124.7, 123.9, 120.9, 116.9, 18.9, 1.6; IR ($CHCl_3$, cm^{-1}) 2953, 1701, 1691, 1604, 1598; MS m/z (rel intensity) 232 (10, M^+), 217 (100), 115 (26). Anal. Calcd for $C_{13}H_{16}O_2Si$: C, 67.20; H, 6.94. Found: C, 67.32; H, 7.10.

3-Acetyl-4-ethyl-*2H*-1-benzopyran-2-one (13) and **4-acetyl-3-ethyl-*2H*-1-benzopyran-2-one (14)**. Separation of the reaction mixture by column chromatography on silica gel afforded two fractions: one containing 36 mg (33 %) of pure 3-acetyl-4-ethyl-*2H*-1-benzopyran-2-one **13** (major isomer), and

the other containing 30 mg (28 %) of a ~ 4.5:1 mixture of **13** and 4-acetyl-3-ethyl-*2H*-1-benzopyran-2-one **14** (minor isomer). **3-Acetyl-4-ethyl-*2H*-1-benzopyran-2-one 13**: yellow oil, recrystallization from pentane-ether affords a white paste, mp 68-70 °C (lit.[4] mp 75-76 °C); ^{1}H NMR ($CDCl_3$) δ 7.73 (dd, J = 1.2, 8.0 Hz, 1H), 7.59 (ddd, J = 1.6, 7.6, 8.4 Hz, 1H), 7.33-7.39 (m, 2H), 2.81 (q, J = 7.6 Hz, 2H), 2.59 (s, 3H), 1.34 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 200.8, 159.3, 155.9, 153.7, 132.8, 126.9, 125.8, 124.9, 118.7, 117.7, 31.4, 22.8, 14.9; all spectral properties are identical with those reported in the literature.[4] **4-Acetyl-3-ethyl-*2H*-1-benzopyran-2-one 14**. ^{1}H NMR ($CDCl_3$) δ 7.52 (ddd, J = 1.2, 8.0, 8.4 Hz, 1H), 7.26-7.29 (m, 2H), 7.14 (dd, J = 1.2, 8.0 Hz, 1H), 2.60 (s, 3H), 2.50 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.4 Hz, 3H). Since only a small amount of **14** could be obtained, a complete ^{13}C NMR spectrum has not been obtained. Only signals in the alkyl part of the ^{13}C NMR spectrum have been detected: ($CDCl_3$) δ 32.1, 22.6, 14.4.

Ethyl 2-oxo-3,4-di-*n*-propyl-*2H*-1-benzopyran-6-carboxylate (15). White solid, mp 82-86 °C; ^{1}H NMR ($CDCl_3$) δ 8.31 (d, J = 2.0 Hz, 1H), 8.12 (dd, J = 2.0, 8.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.84 (m, 2H), 2.63 (m, 2H), 1.57-1.70 (m, 4H), 1.43 (t, J = 7.0 Hz, 3H), 1.12 (t, J = 7.4 Hz, 3H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 165.9, 161.4, 155.7, 150.0, 131.4, 127.4, 127.0, 126.6, 119.8, 117.3, 61.6, 30.6, 30.0, 23.1, 22.5, 14.7, 14.5 (one sp^3 carbon is missing due to overlap); IR ($CHCl_3$, cm^{-1}) 2965, 1717, 1612; MS m/z (rel intensity) 302 (100, M^+), 288 (58), 287(81), 259 (96), 201(55). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.43; H, 7.40.

6-Methoxy-3,4-di-*n*-propyl-*2H*-1-benzopyran-2-one (16). Slightly yellow solid, mp 83-85°C; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 1H), 7.04 (m, 2H), 3.86 (s, 3H), 2.75 (m, 2H), 2.60 (m, 2H), 1.56-1.69 (m, 4H), 1.10 (t, J = 7.4 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 162.2, 156.0, 149.7, 147.1, 127.0, 120.5, 117.9, 116.9, 108.5, 56.0, 30.8, 30.0, 22.9, 22.5, 14.7, 14.5; IR ($CHCl_3$, cm^{-1}) 2964, 2873, 1699, 1570, 1497; MS m/z (rel intensity) 260 (100, M^+), 245 (30), 217 (43). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 74.05, H, 7.83.

Methyl 2-oxo-3,4-di-*n*-propyl-*2H*-1-benzopyran-7-carboxylate (17). White solid, mp 93-95 °C; ^{1}H NMR ($CDCl_3$) δ 7.91-7.94 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H), 2.78-2.83 (m, 2H), 2.61-2.65 (m, 2H), 1.58-1.68 (m, 4H), 1.12 (t, *J* = 7.4 Hz, 3H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 166.1, 161.6, 152.4, 149.2, 131.7, 129.0, 124.9, 124.8, 123.6, 118.3, 52.8, 30.8, 30.1, 23.0, 22.5, 14.7, 14.5; IR ($CHCl_3$, cm^{-1}) 2965, 2874, 1717, 1701, 1608; MS m/z (rel intensity) 288 (68, M^+), 273 (96), 245 (100). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.75; H, 6.75.

Ethyl 3,4-di-*n*-propyl-2-oxo-2*H*-pyran[2,3-b]pyridin-6-carboxylate (19). White solid, mp 65-69 °C; ^{1}H NMR ($CDCl_3$) δ 9.05 (d, *J* = 2.0 Hz, 1H), 8.54 (d, *J* = 2.4 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 1H), 2.84 (m, 2H), 2.64 (m, 2H), 1.58-1.70 (m, 4H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.4 Hz, 3H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 164.5, 160.7, 160.0, 150.7, 148.5, 135.6, 129.0, 123.9, 114.9, 62.0, 30.3, 30.0, 22.9, 22.4, 14.6, 14.5 (one sp^3 carbon is missing due to overlap); IR ($CHCl_3$, cm^{-1}) 2966, 2875, 1733, 1717, 1599; MS m/z (rel intensity) 303 (100, M^+), 288 (58), 260 (51); Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.02; H, 6.67; N, 4.39.

References

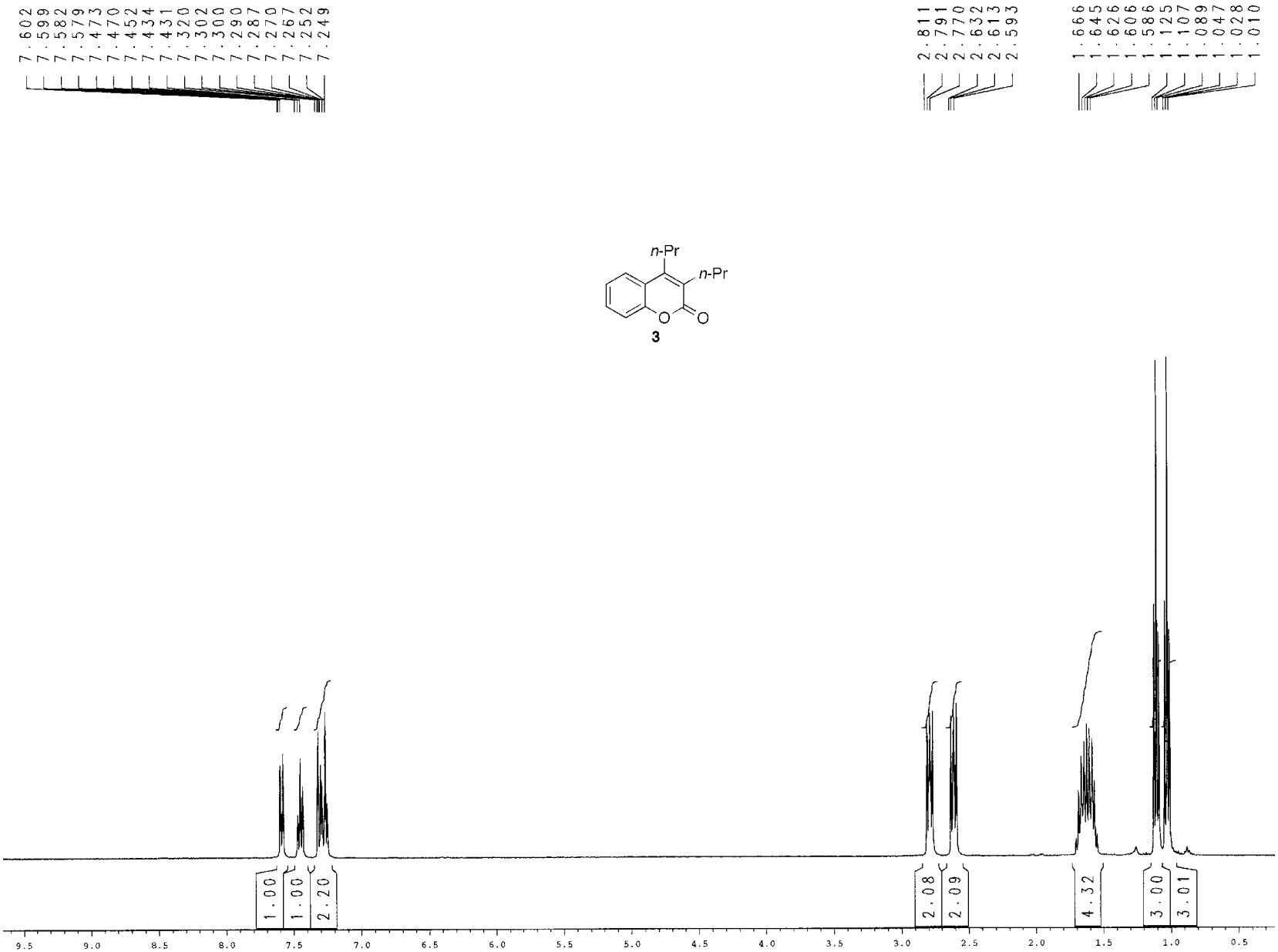
(1) Sabitha, G.; Reddy, G. J.; Rao, A. V. S. *Synth. Commun.* **1988**, *18*, 639.

(2) Awasthi, A. K.; Tewari, R. S. *Synthesis* **1986**, 1061.

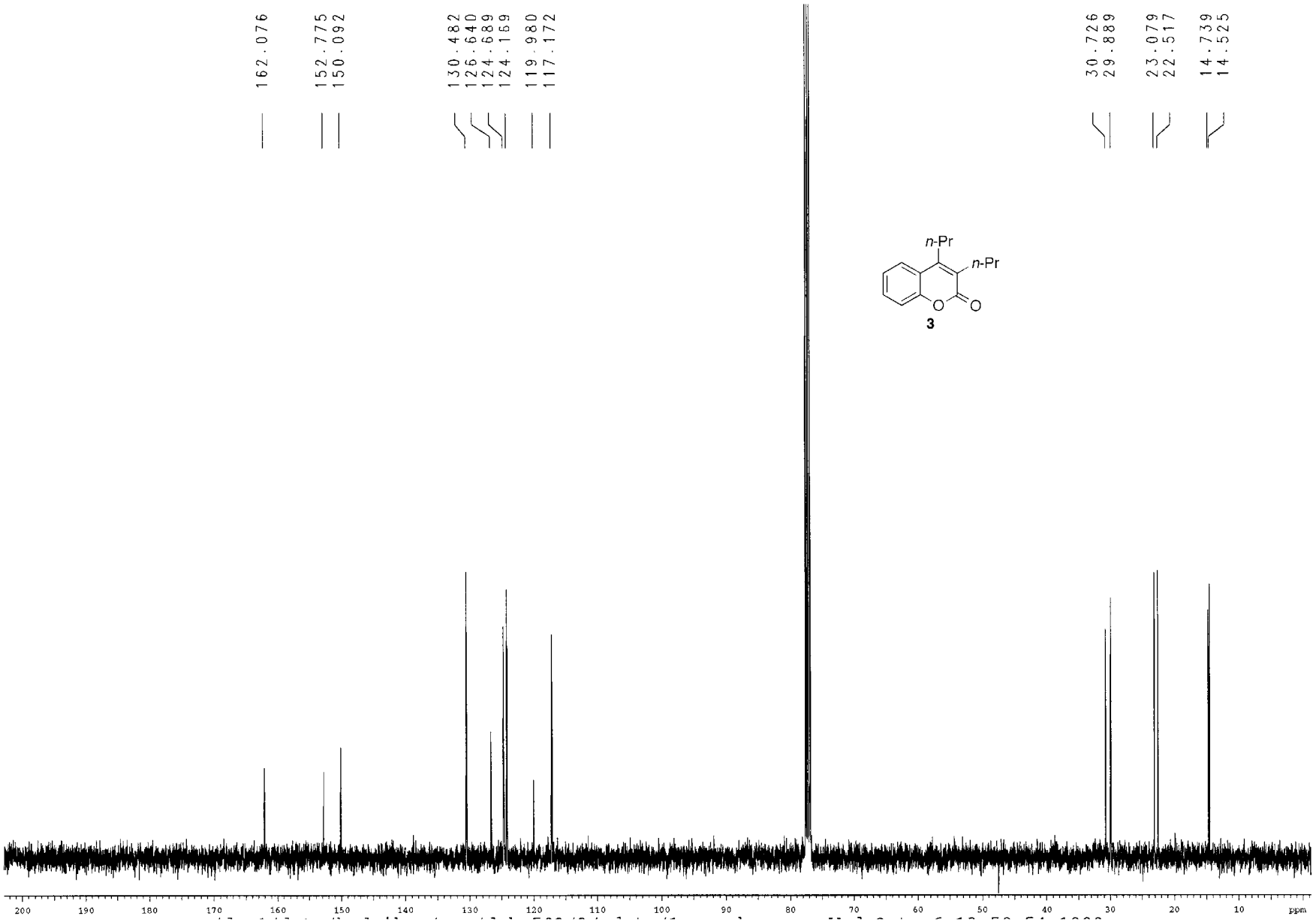
(3) Patil, V. O.; Kelkar, S. L.; Waida, M. S. *Indian J. Chem. B* **1987**, *26*, 674.

(4) Clinging, R.; Dean, F. M.; Houghton, L. E. *J. Chem. Soc., Perkin I* **1974**, 66.

3,4-di-n-propylcoumarin



3,4-di-n-propylcoumarin



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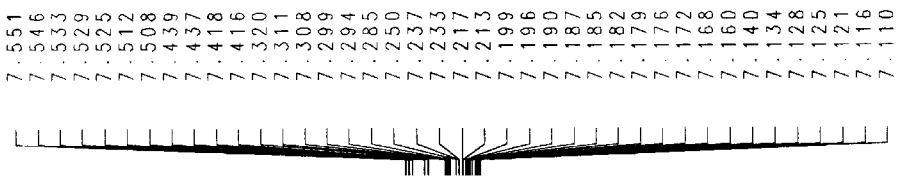

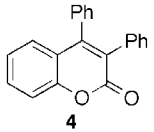

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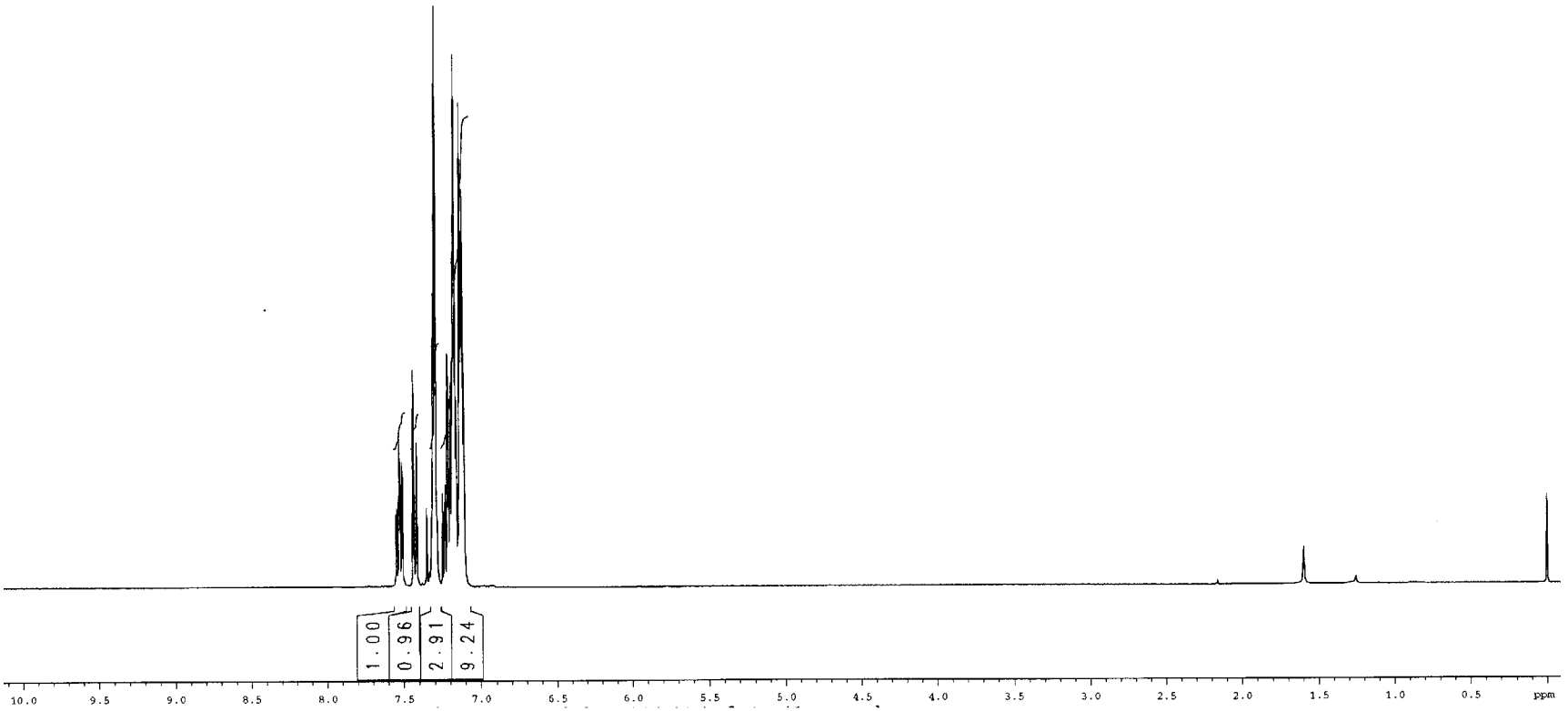

3,4-Diphenylcoumarin

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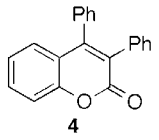

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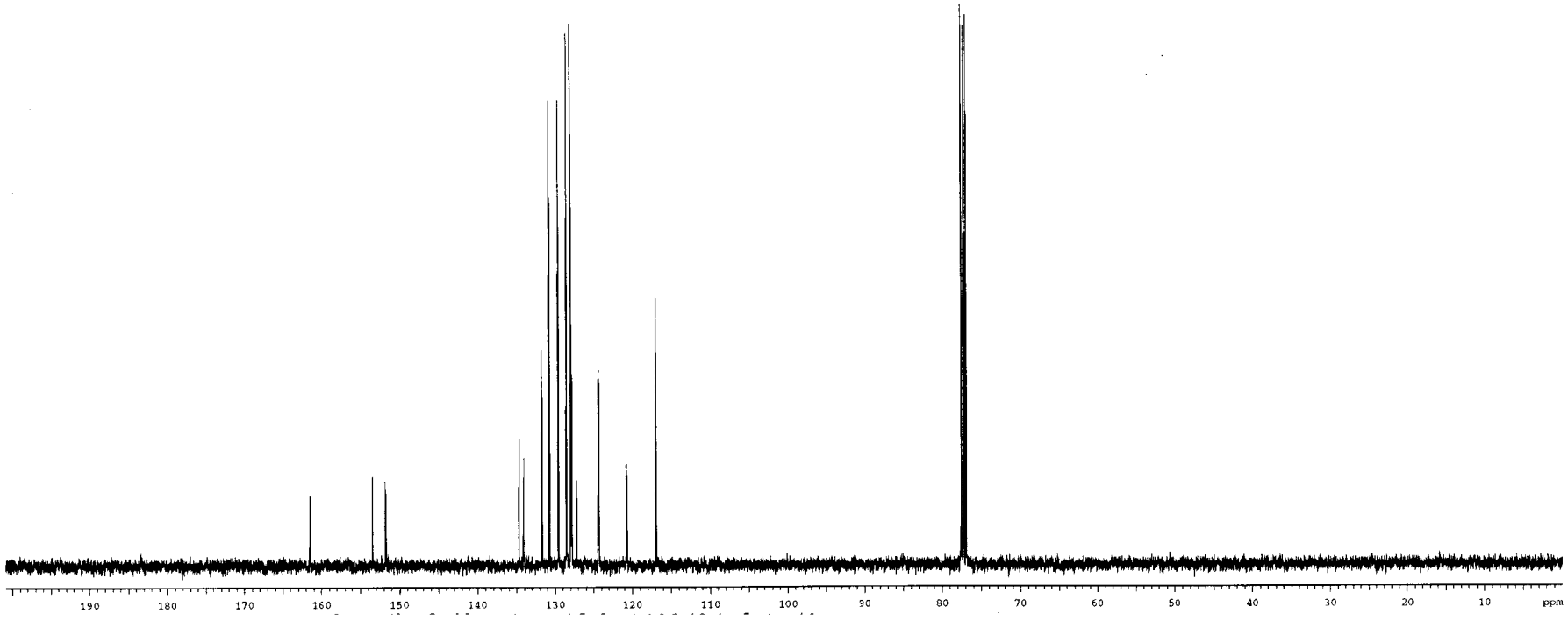

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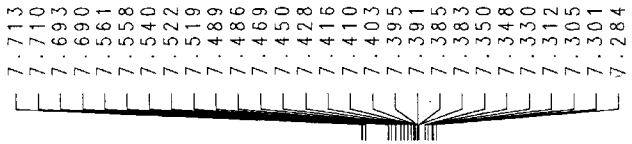

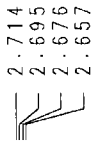

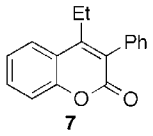

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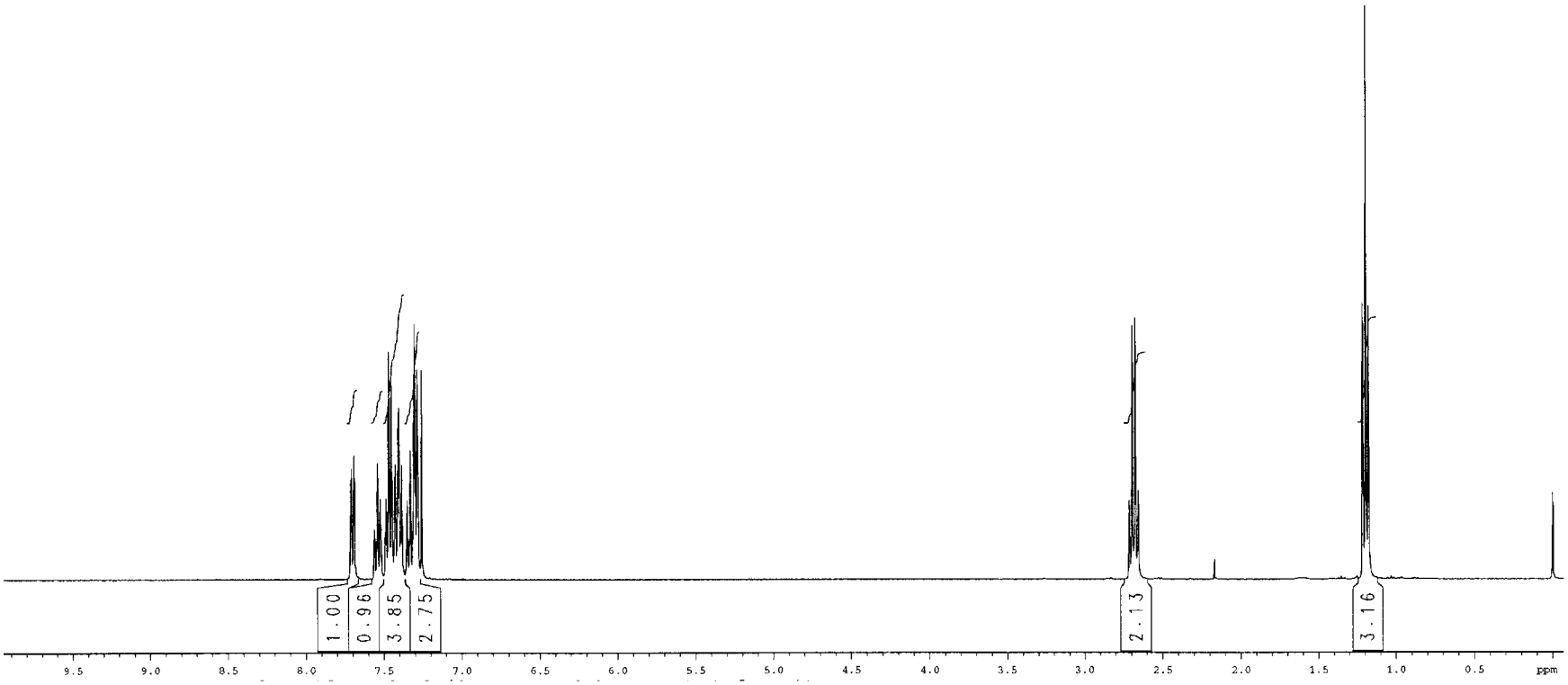

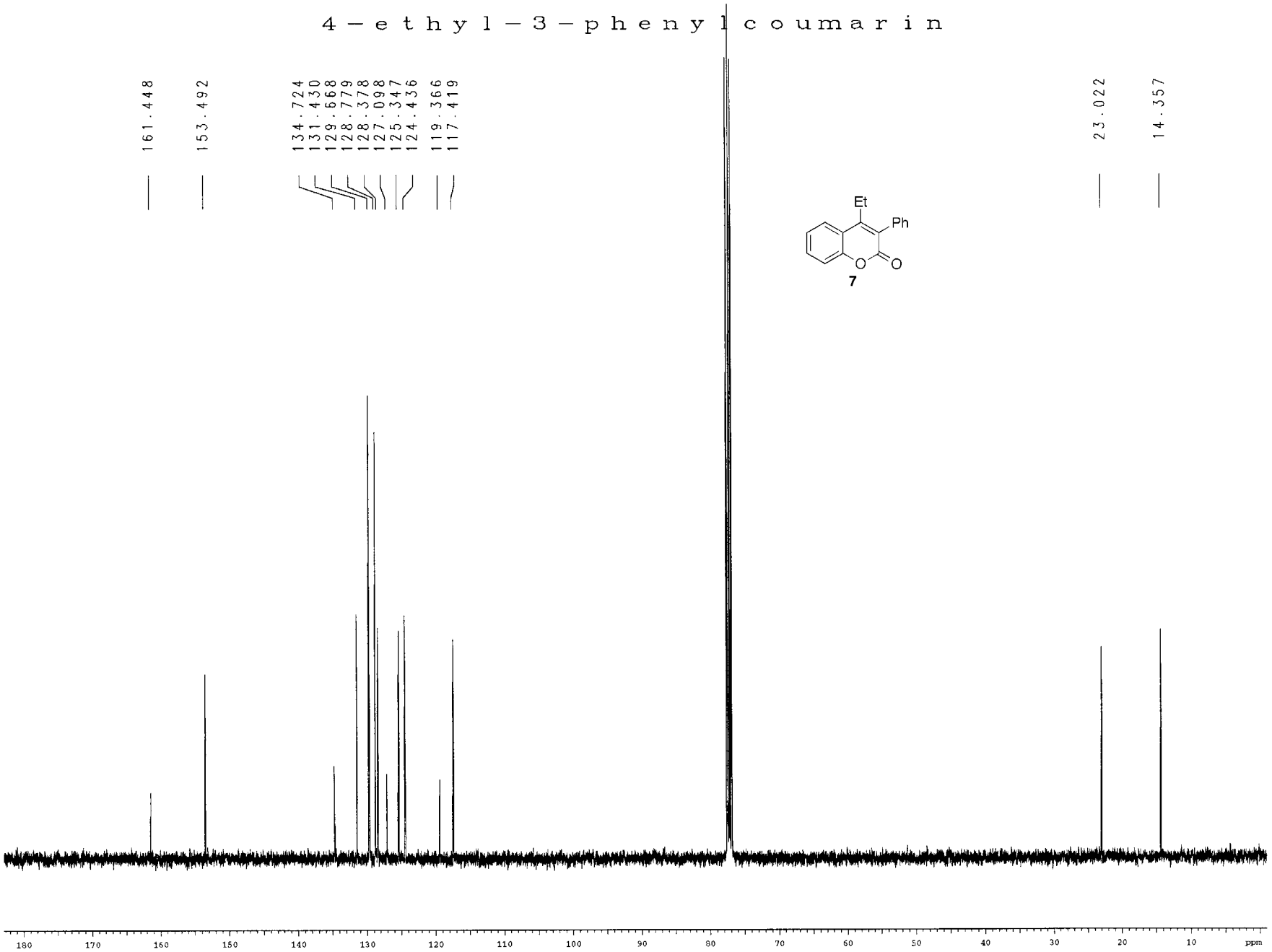
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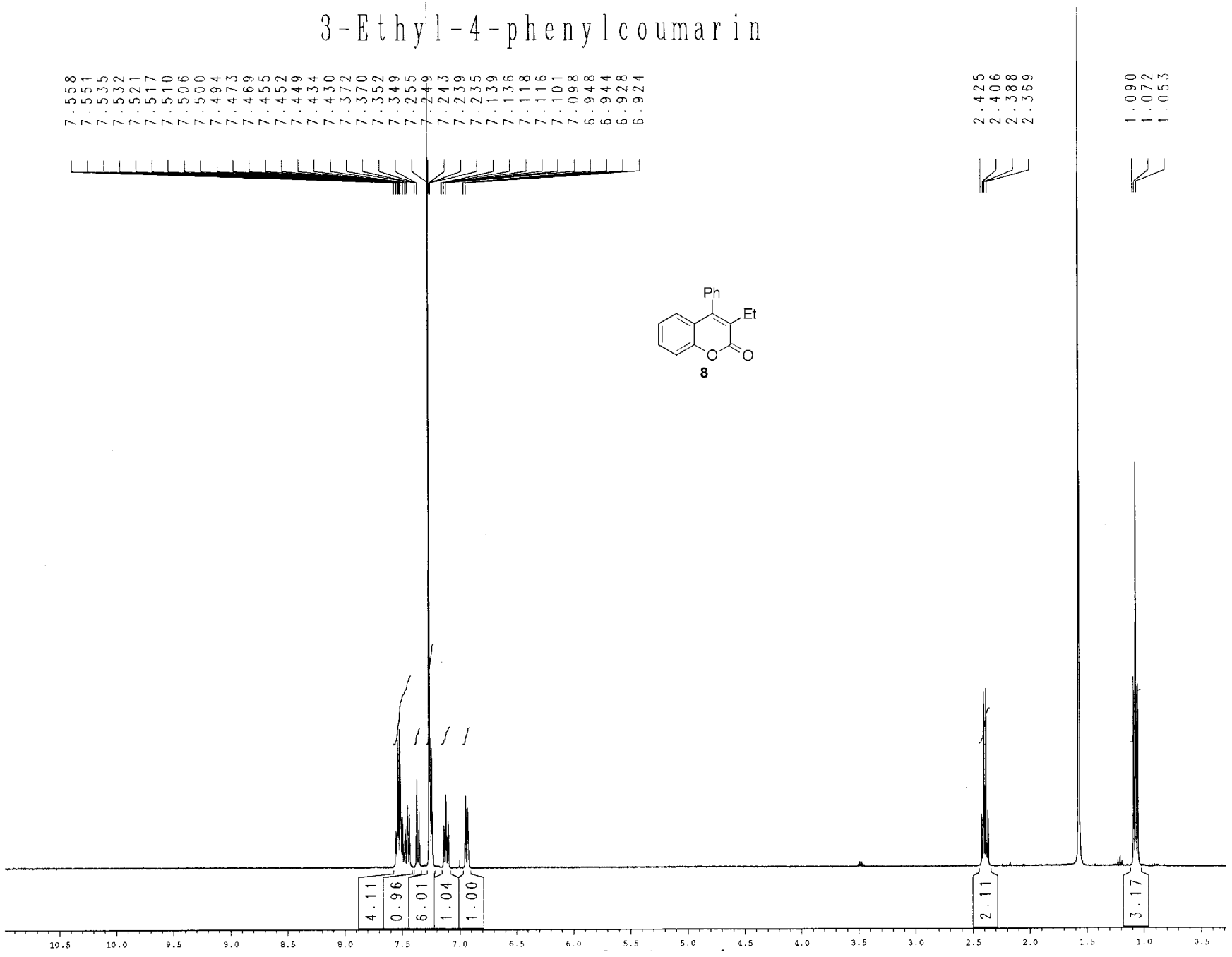
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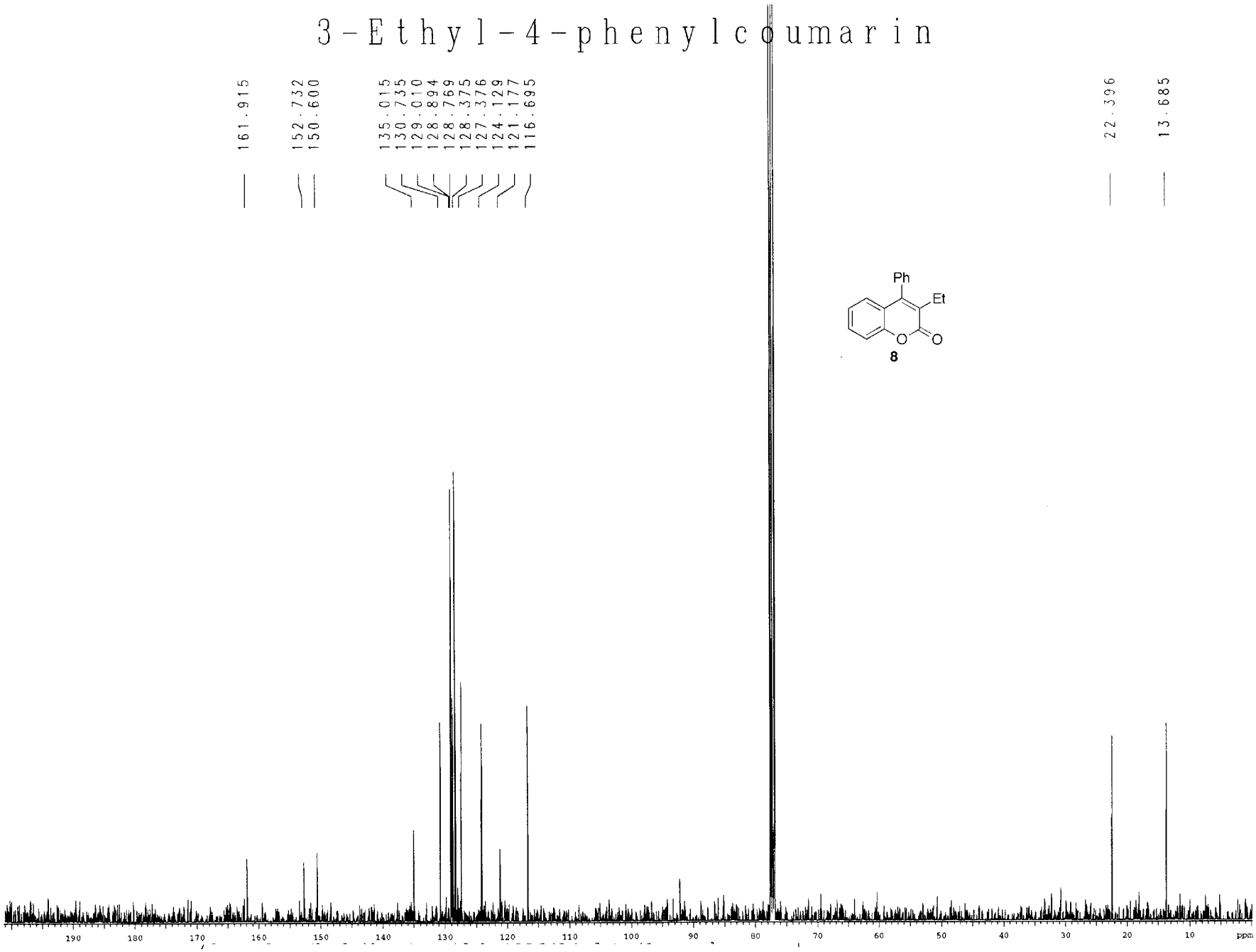
3-Ethyl-4-phenylcoumarin



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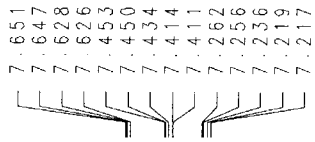

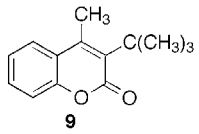

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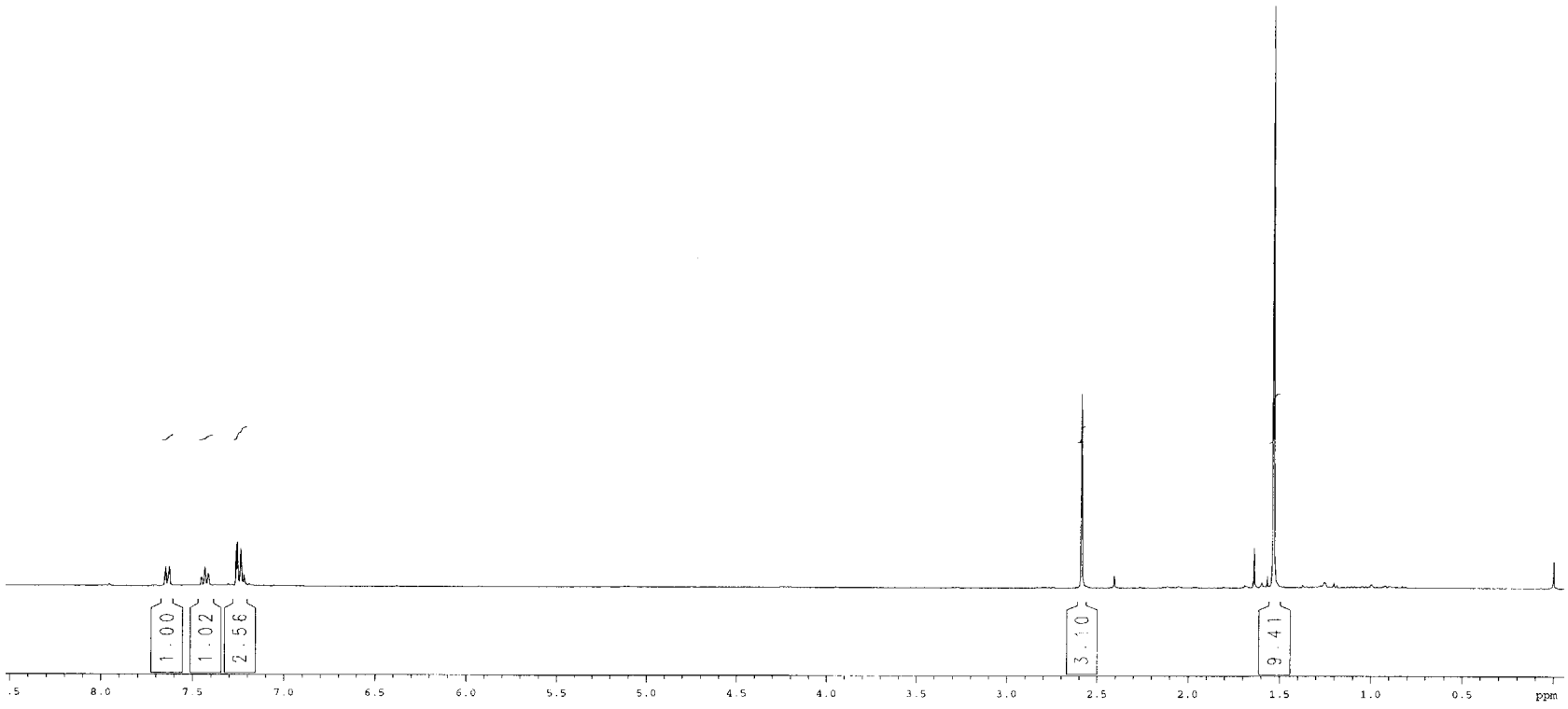
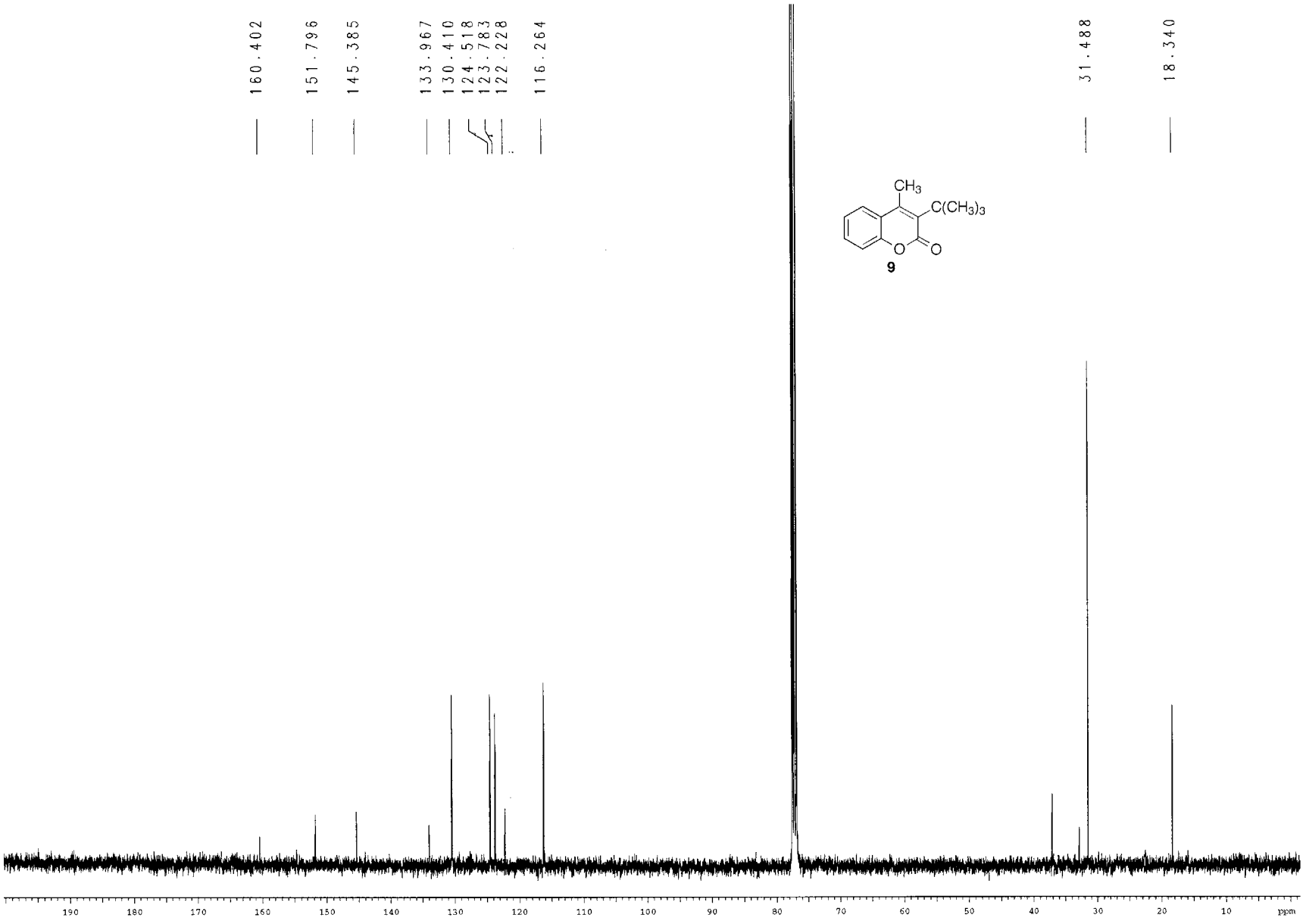
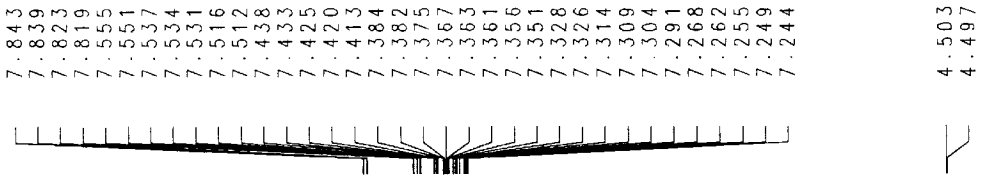
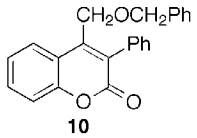


3-tert-Butyl-4-methylcoumarin

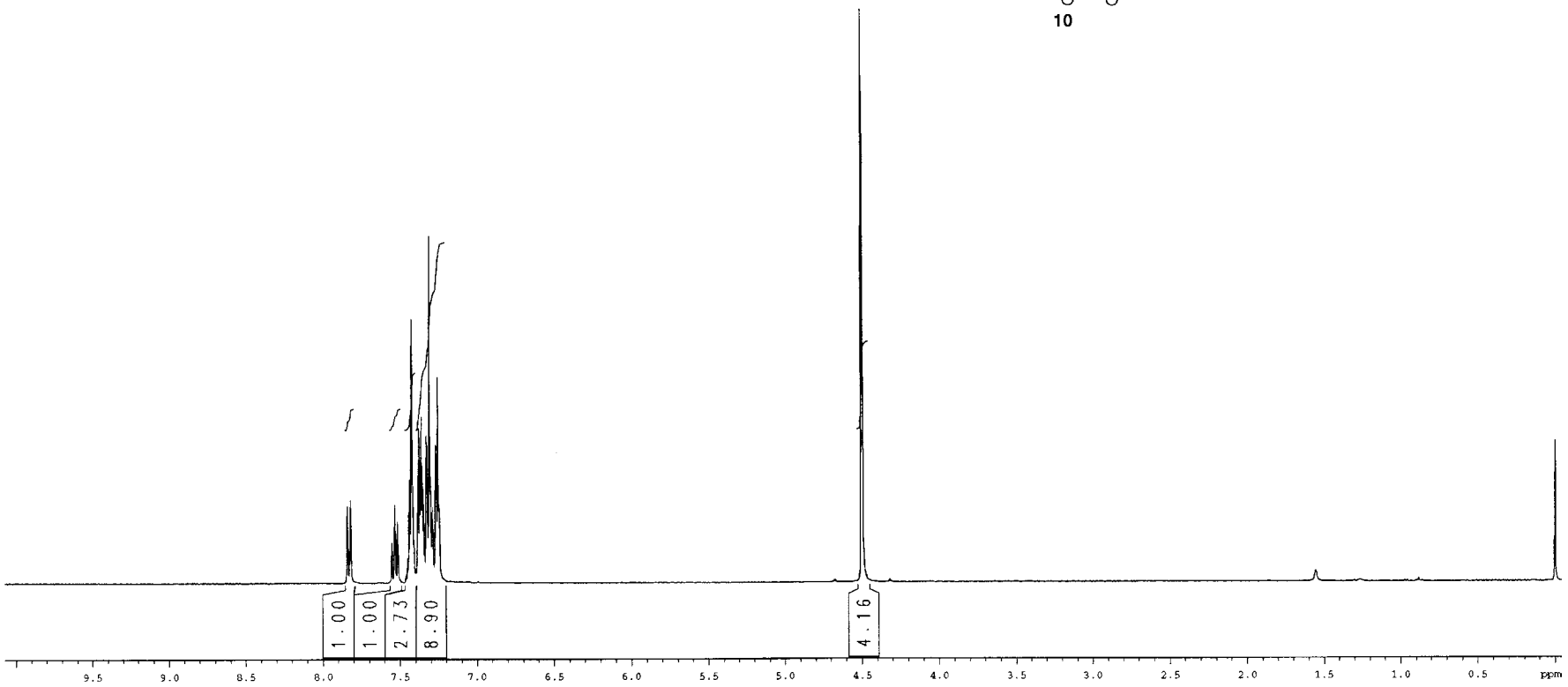


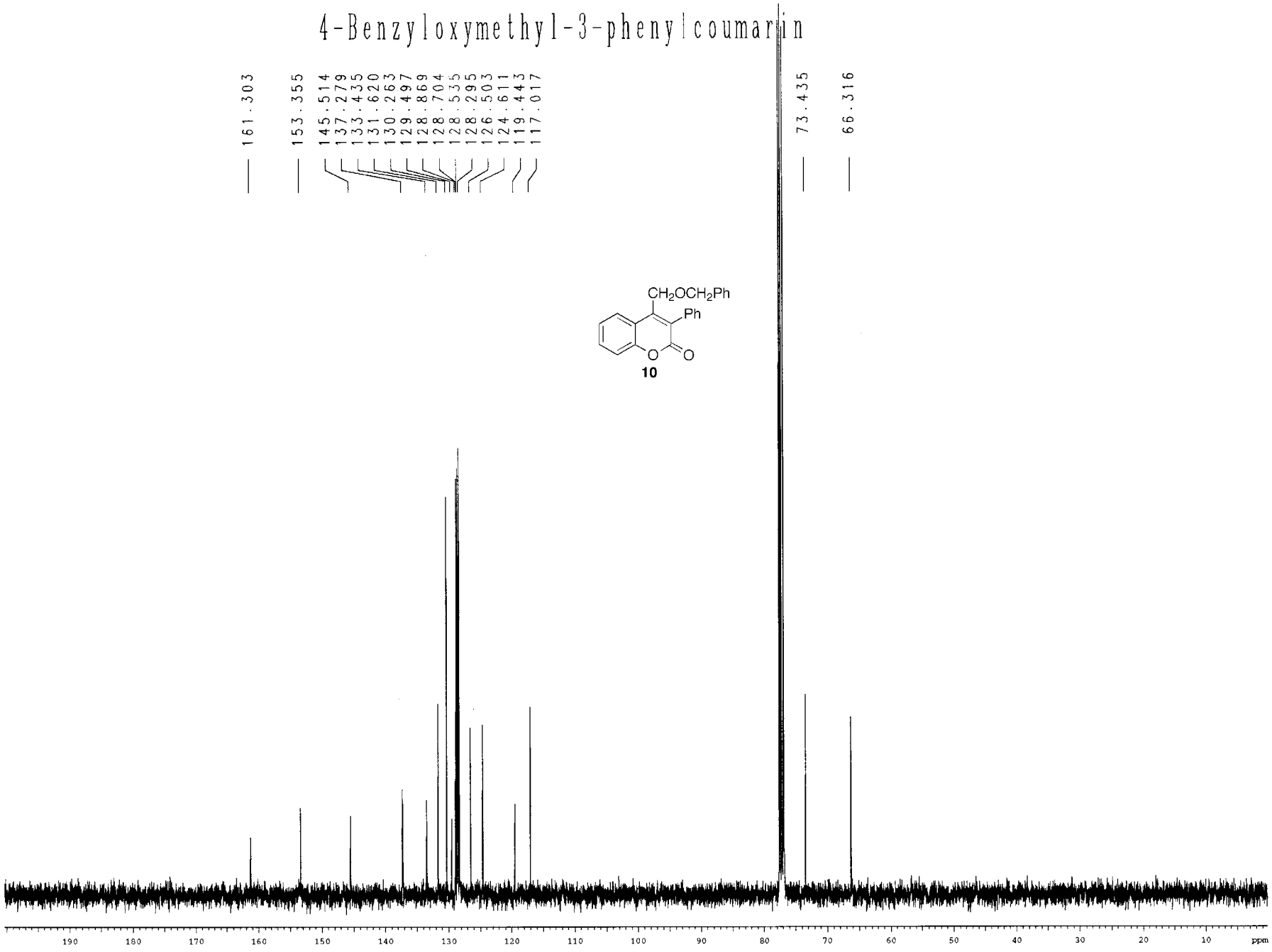
4-Benzyloxymethyl-3-phenylcoumarin



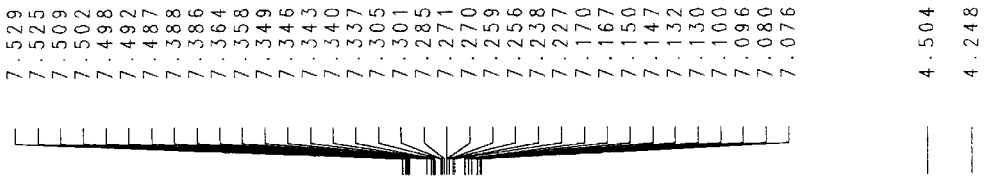


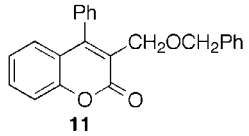
10



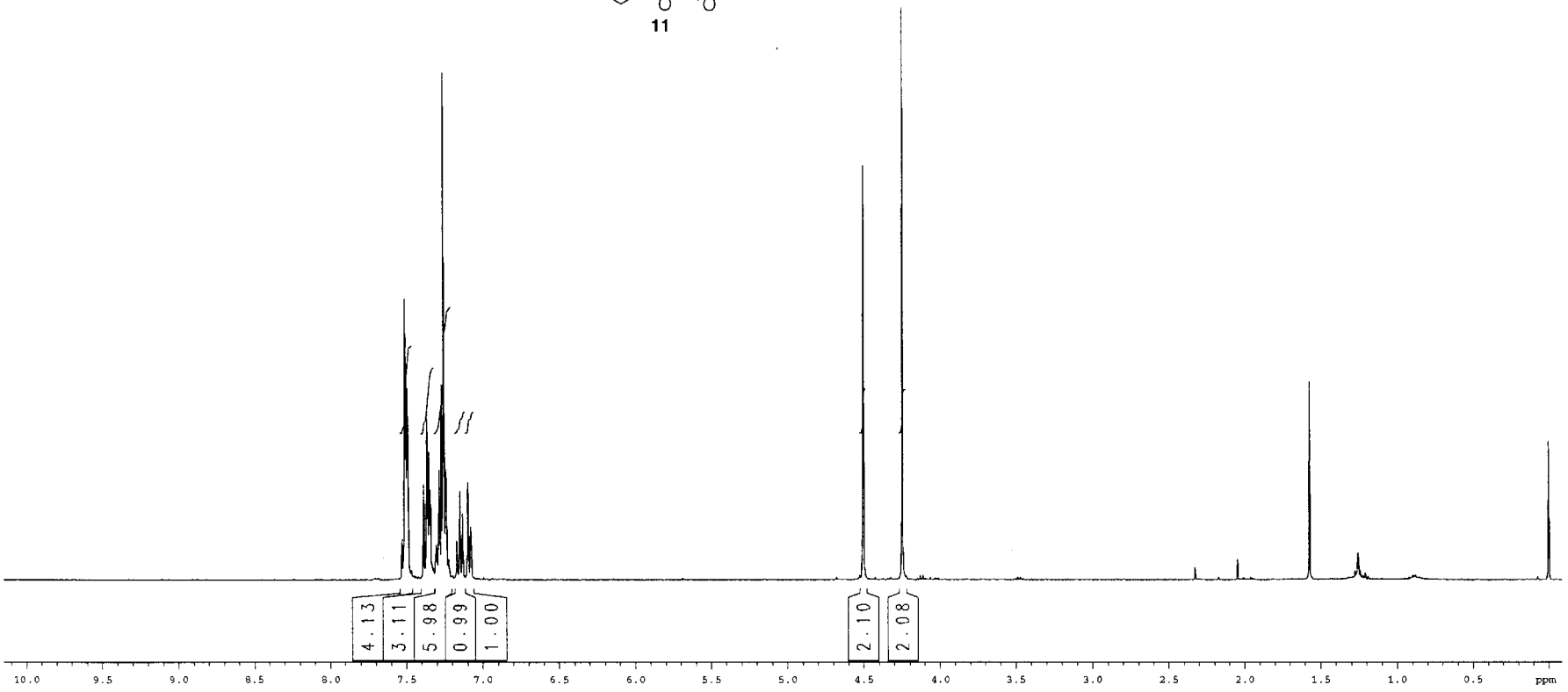

4-Benzyloxymethyl-3-phenylcoumarin
161.303
153.355
145.514
137.279
133.435
131.620
130.263
129.497
128.869
128.704
128.535
128.295
126.503
124.611
119.443
117.017
73.435
66.316
CH2OCH2Ph
Ph
O
O
10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

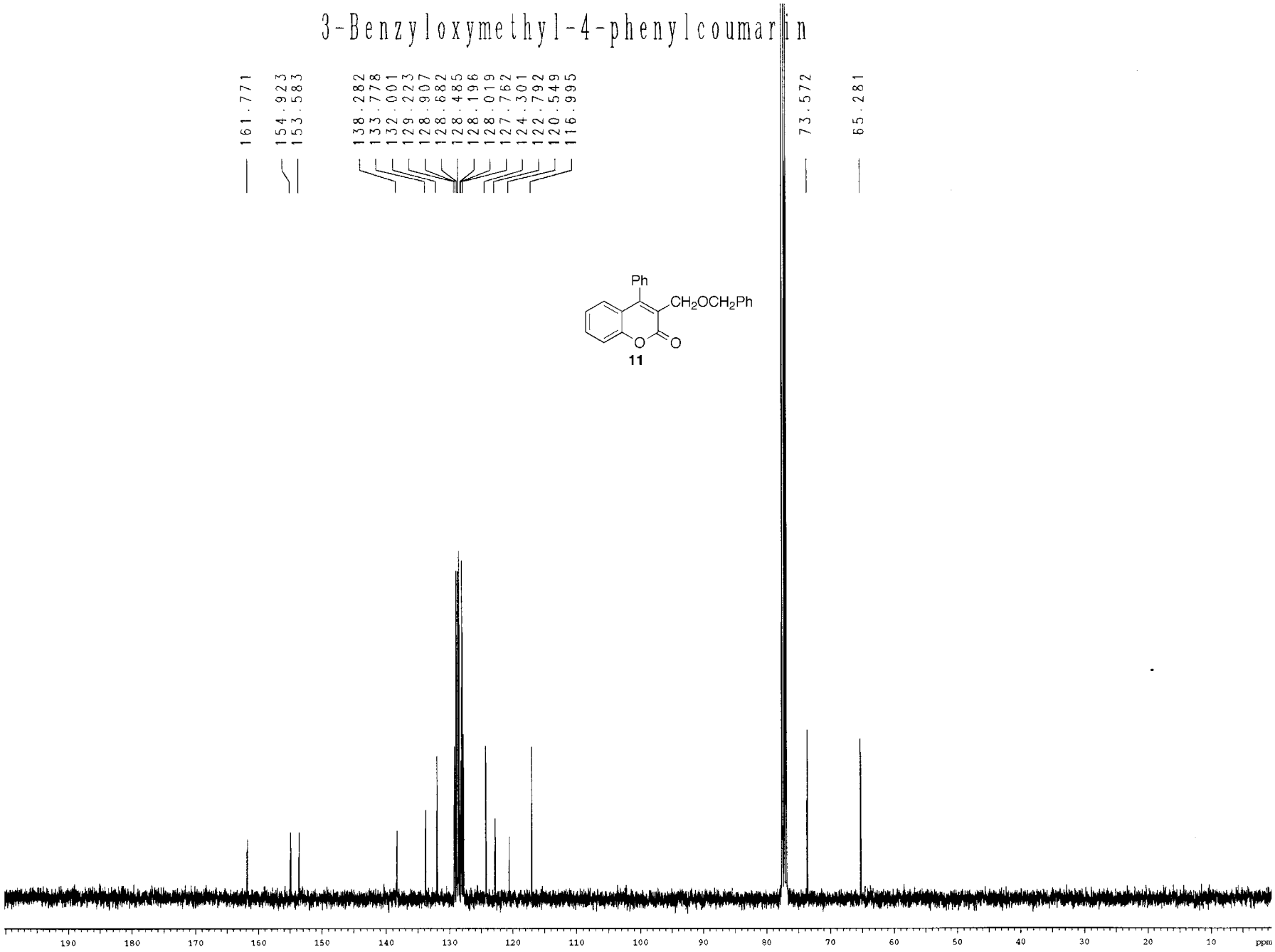
3-Benzyloxymethyl-4-phenylcoumarin



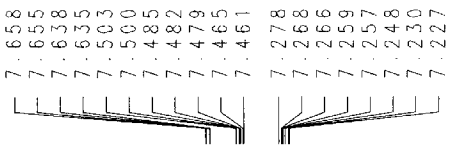


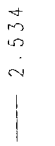
11

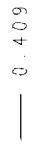


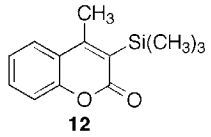

3-Benzyloxymethyl-4-phenylcoumarin
161.771
154.923
153.583
138.282
133.778
132.001
129.223
128.907
128.682
128.485
128.196
128.019
127.762
124.301
122.792
120.549
116.995
73.572
65.281
Ph
CH2OCH2Ph
O
O
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4-Methyl-3-trimethylsilylcoumarin

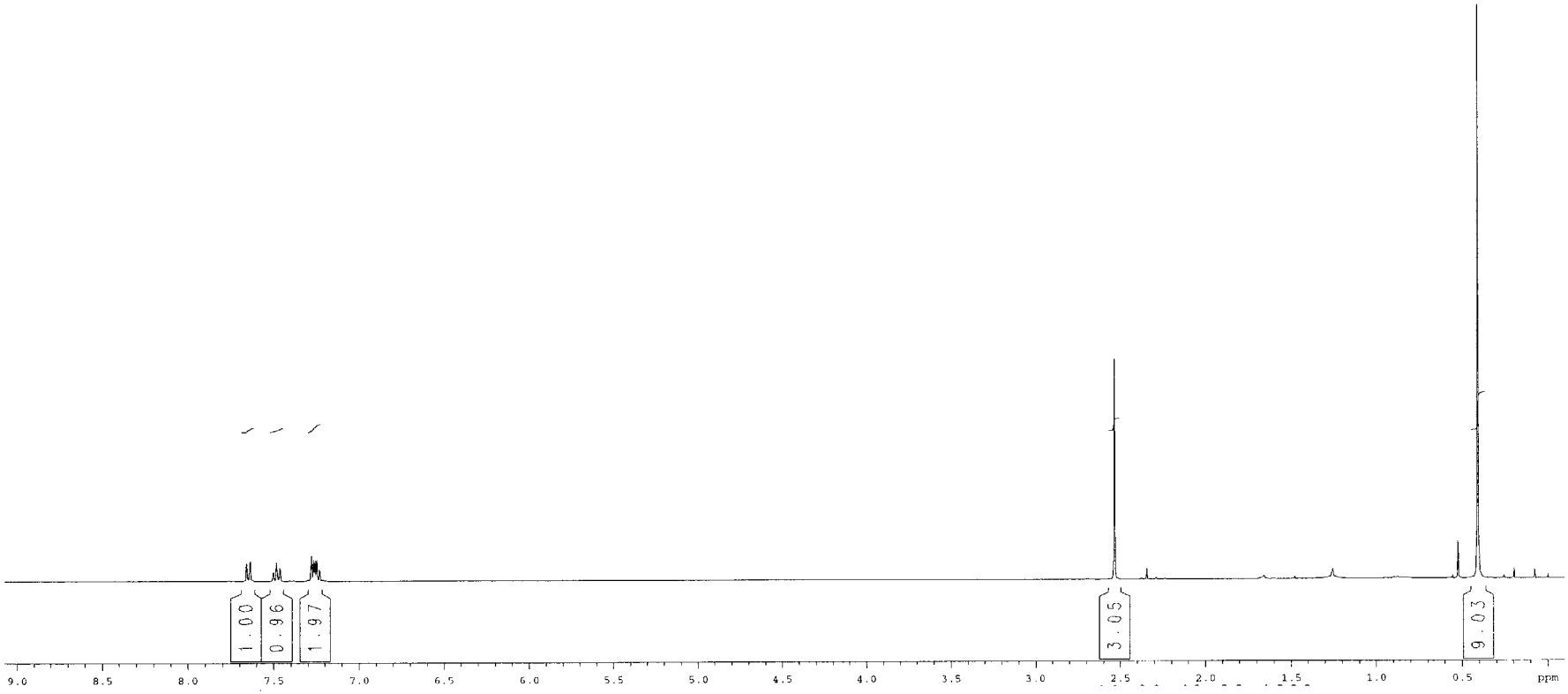




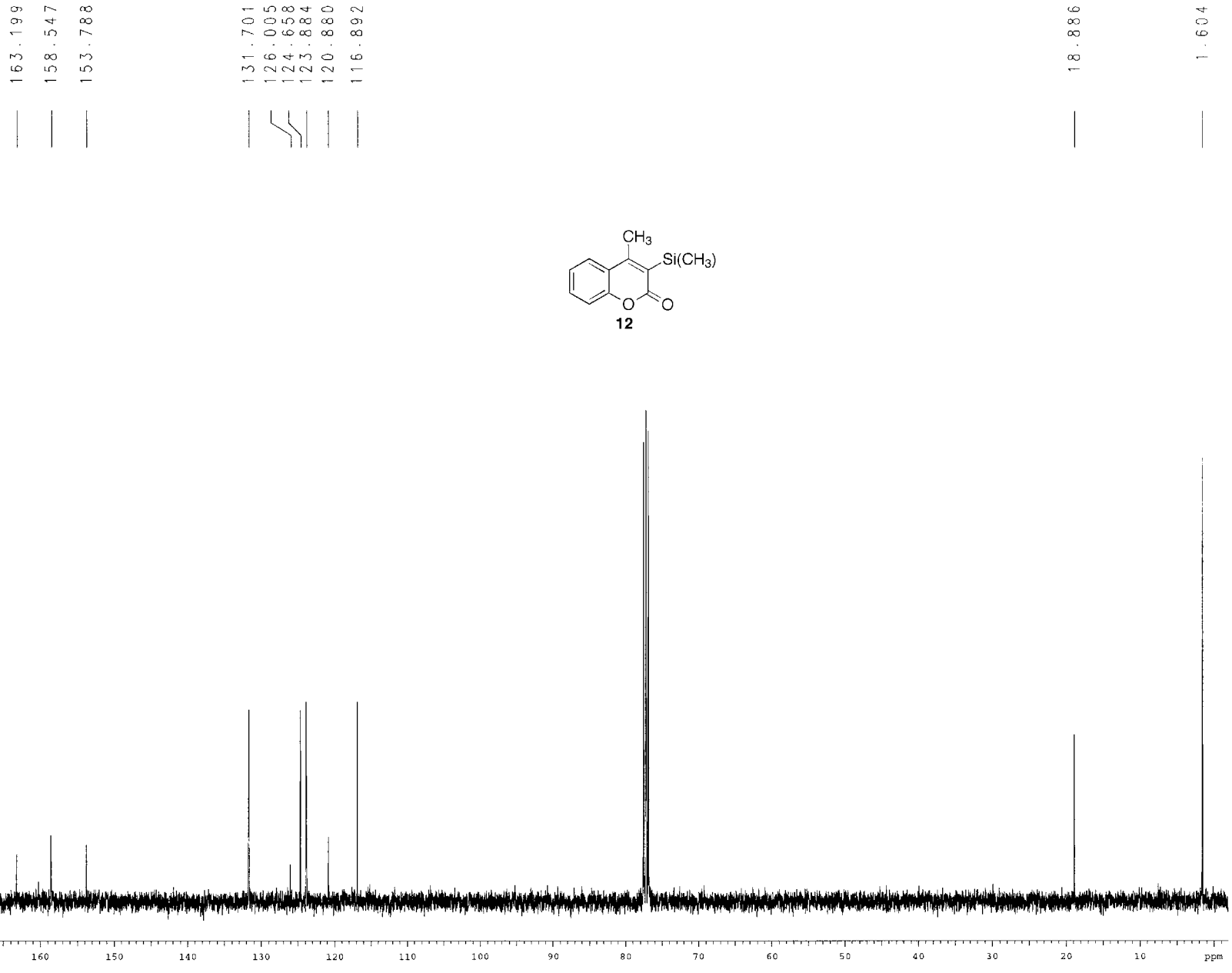




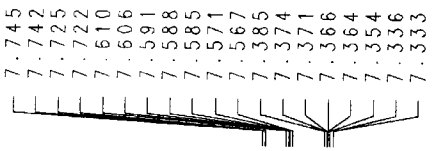
12

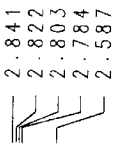


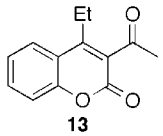
4-Methyl-3-trimethylsilylcoumarin



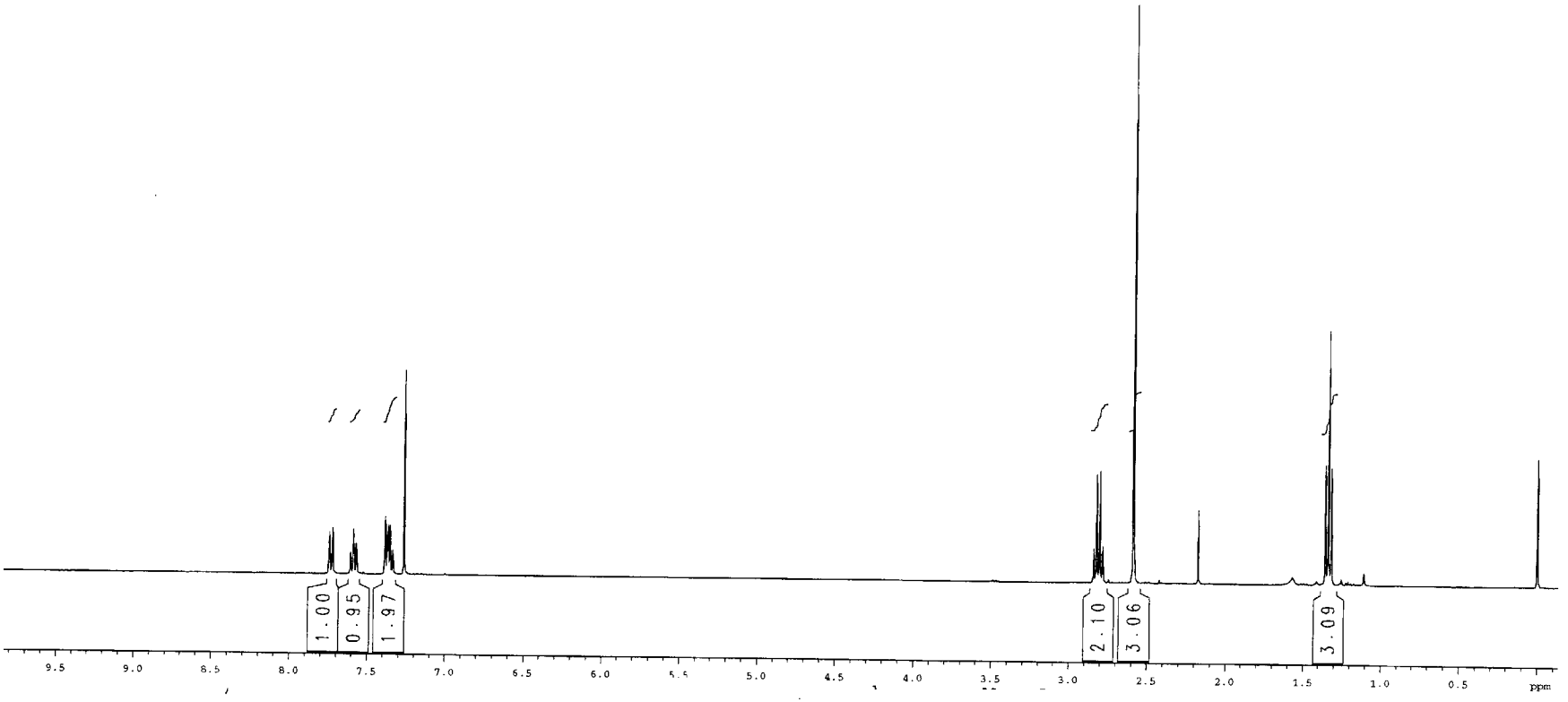
3-Acetyl-4-ethylcoumarin



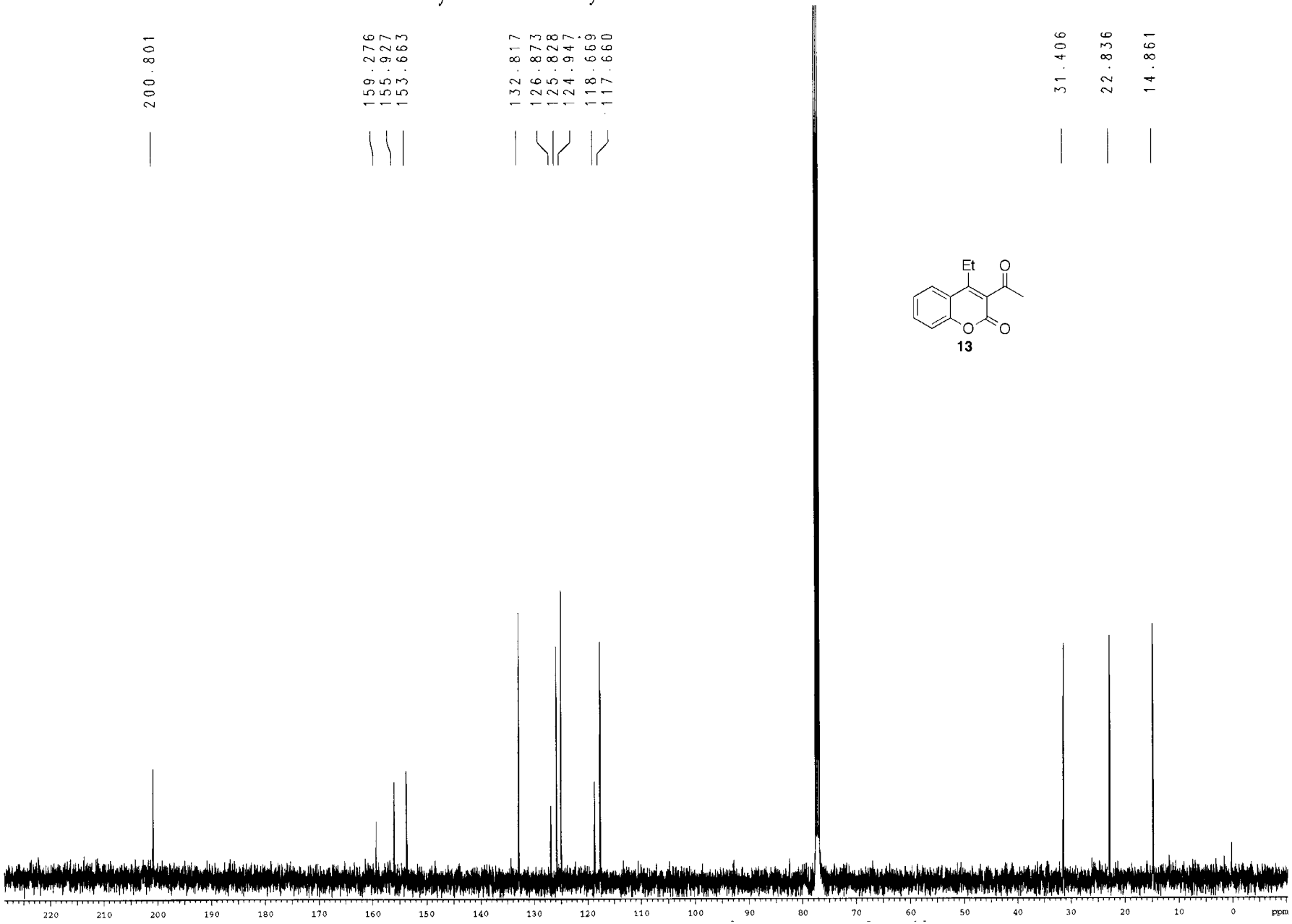


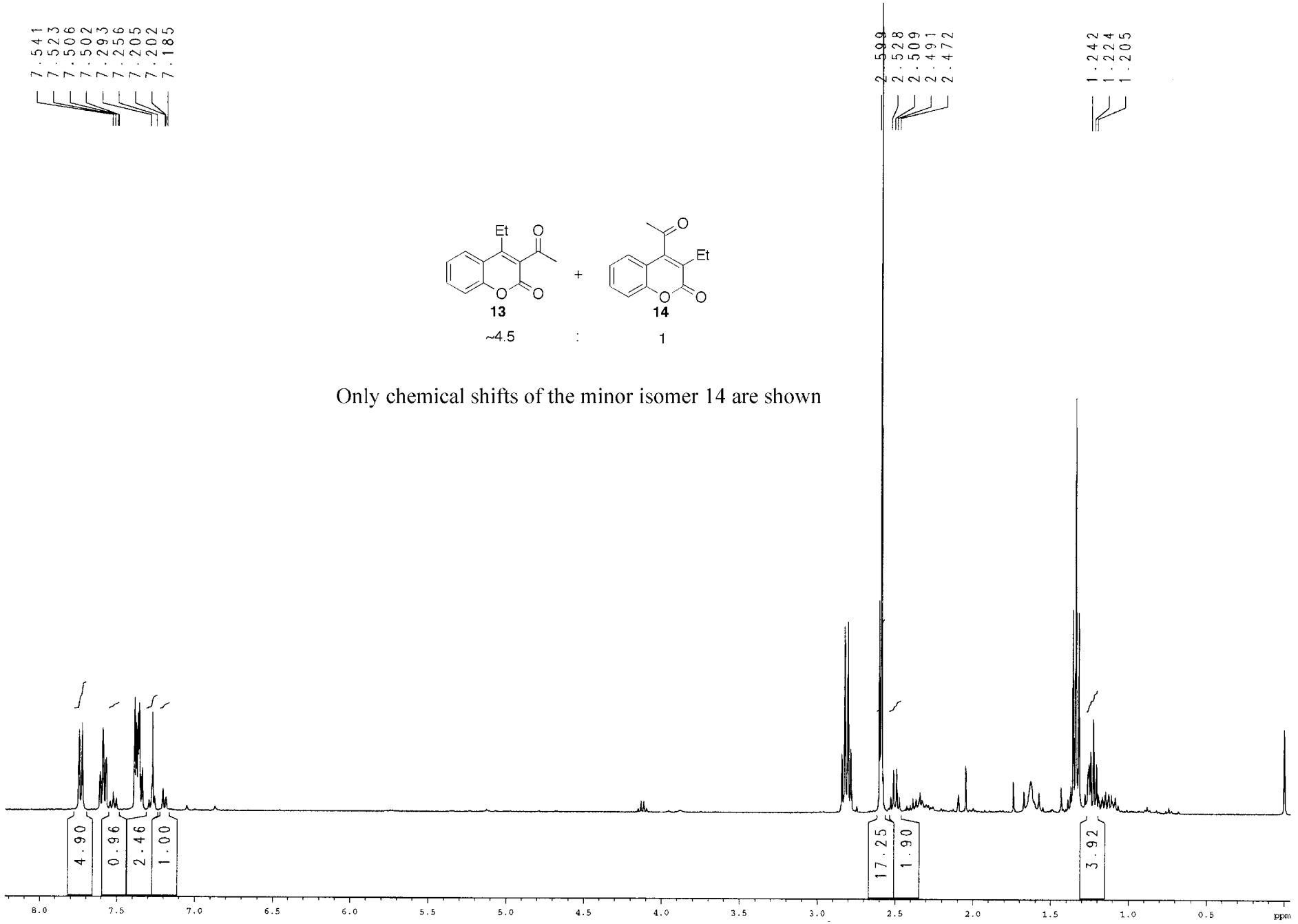


13



3-Acetyl-4-ethylcoumarin

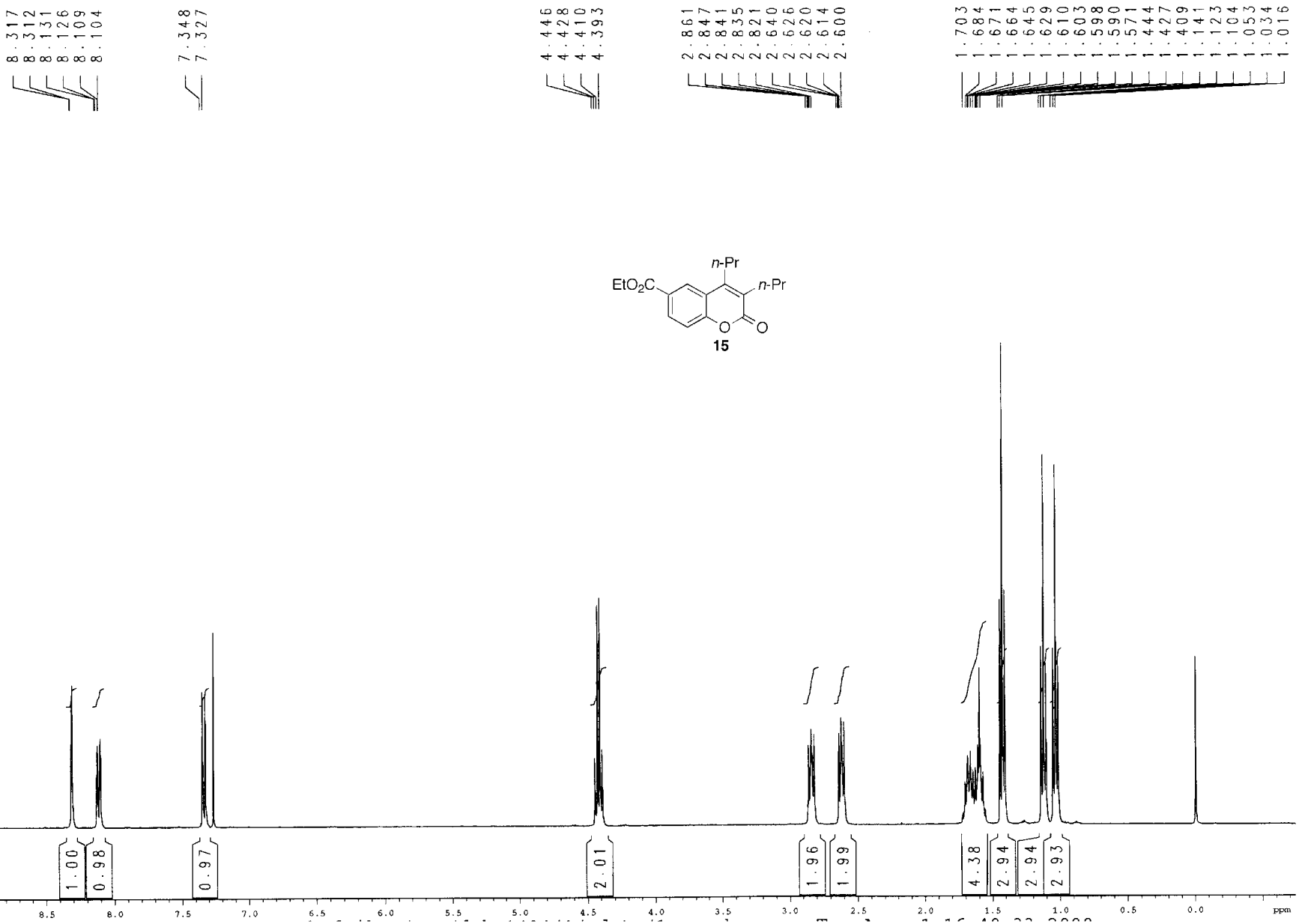




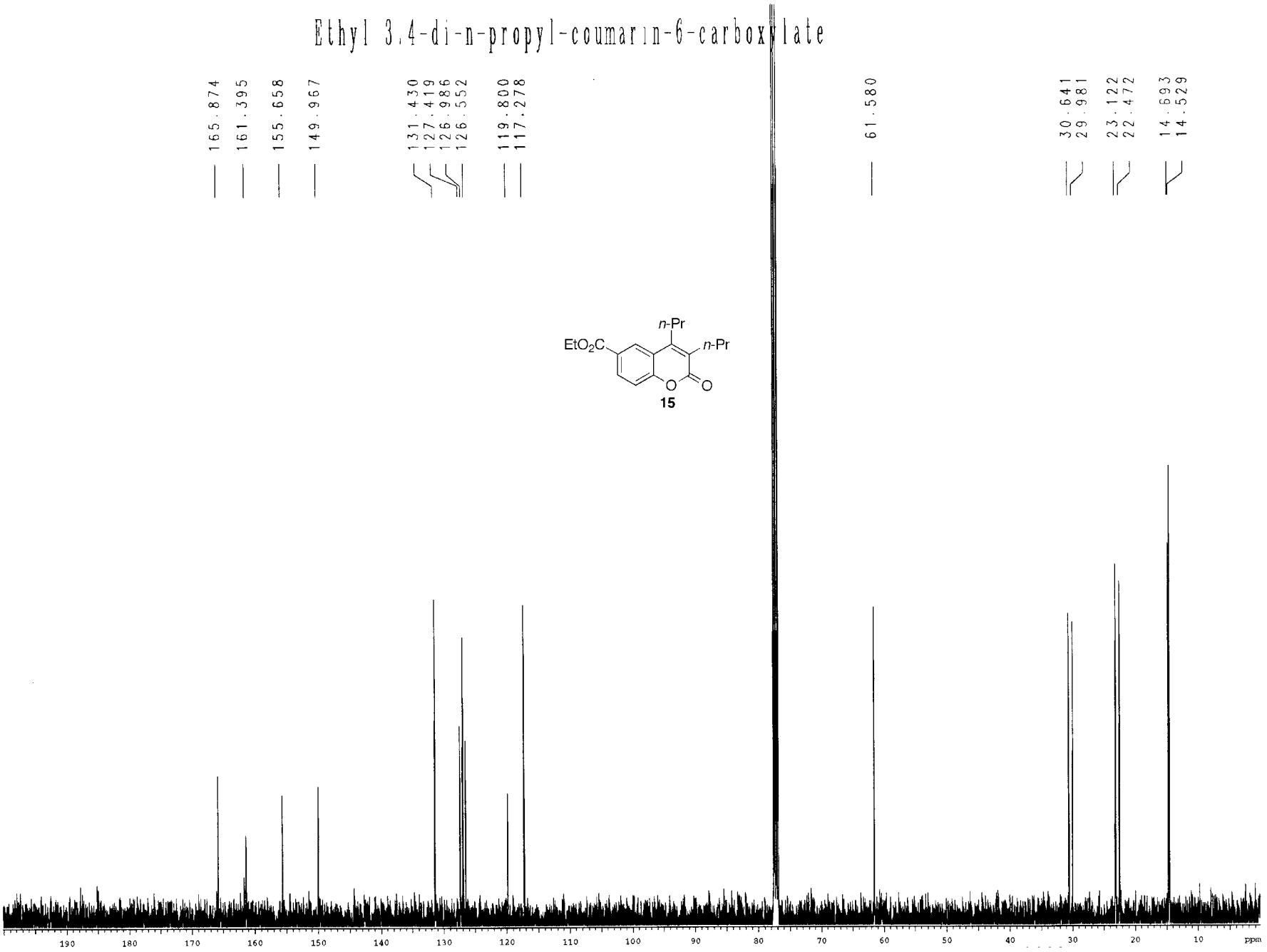
~4.5 : 1

Only chemical shifts of the minor isomer 14 are shown

Ethyl 3,4-di-n-propylcoumarin-6-carboxylate



Ethyl 3,4-di-n-propyl-coumarin-6-carboxylate



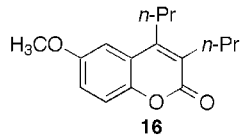
6-Methoxy-3,4-di-n-propylcoumarin

7.258
7.251
7.233
7.052
7.045
7.035
7.028

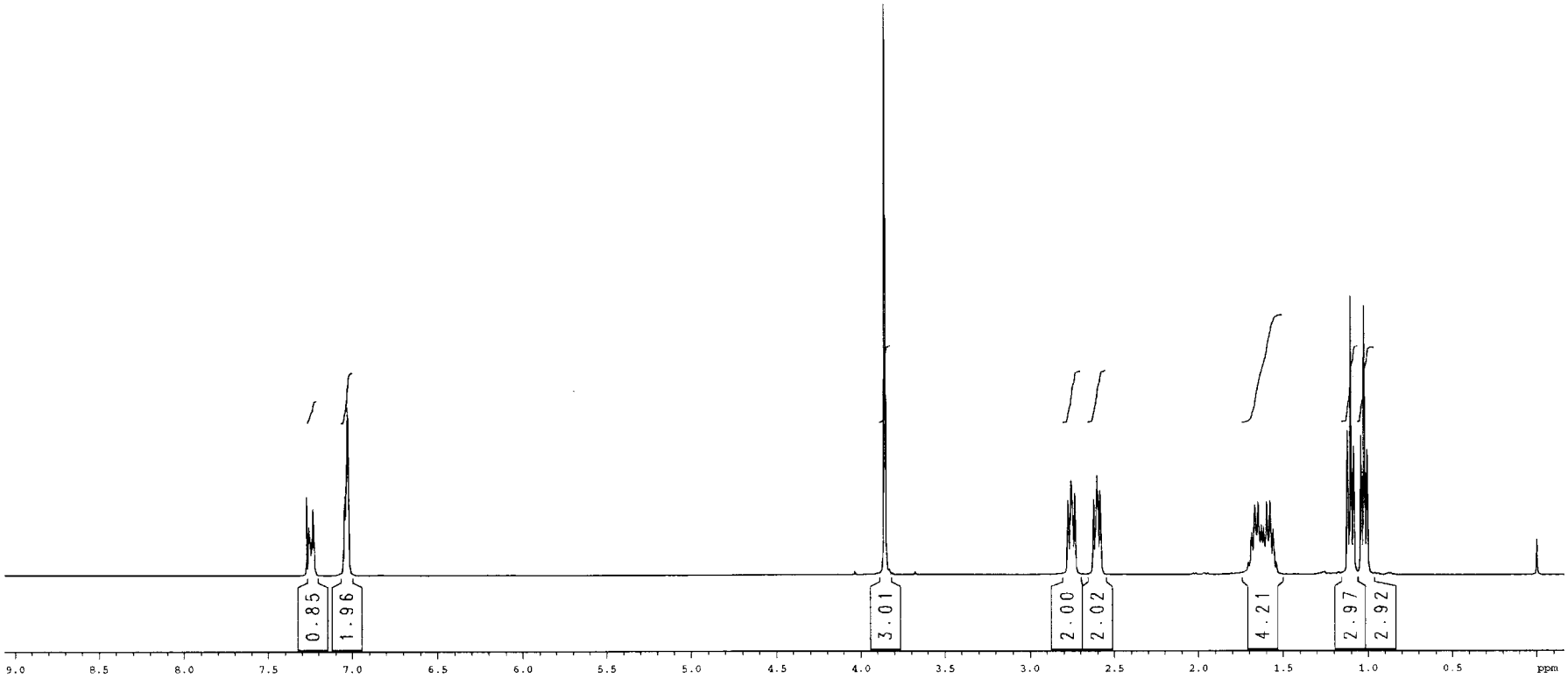
3.859

2.776
2.756
2.750
2.735
2.625
2.605
2.600
2.585

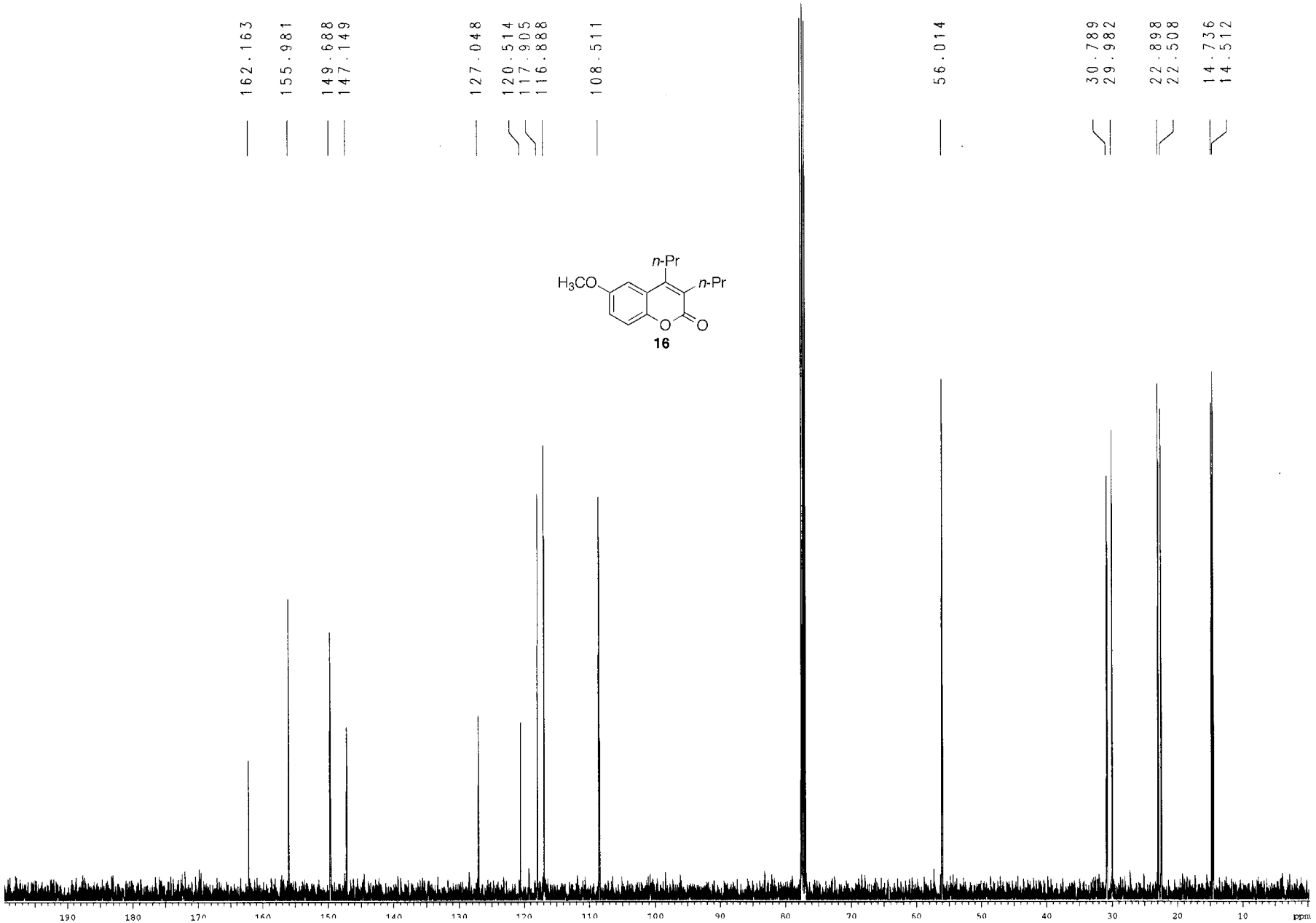
1.687
1.668
1.648
1.629
1.617
1.597
1.578
1.559
1.122
1.104
1.085
1.042
1.024
1.005



16



6-Methoxy-3,4-di-n-propylcoumarin



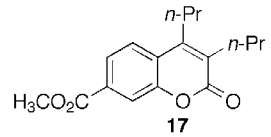
Methyl 3,4-di-n-propylcoumarin-7-carboxylate

7.937
7.934
7.930
7.926
7.909
7.905
7.650
7.630

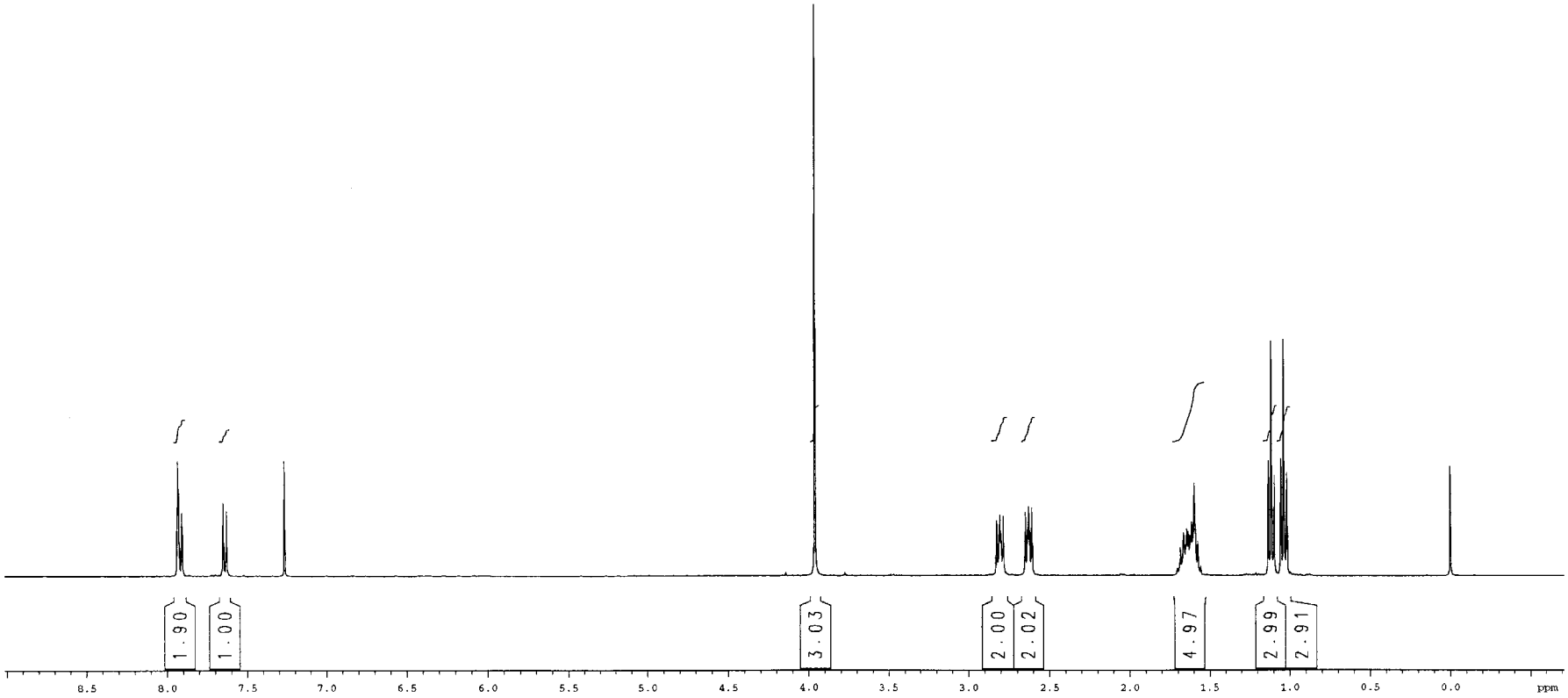
3.960

2.825
2.811
2.805
2.798
2.784
2.649
2.635
2.630
2.623
2.610

1.683
1.664
1.651
1.643
1.638
1.633
1.624
1.619
1.614
1.607
1.597
1.575
1.134
1.116
1.097
1.056
1.038
1.019

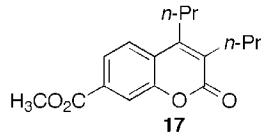


17

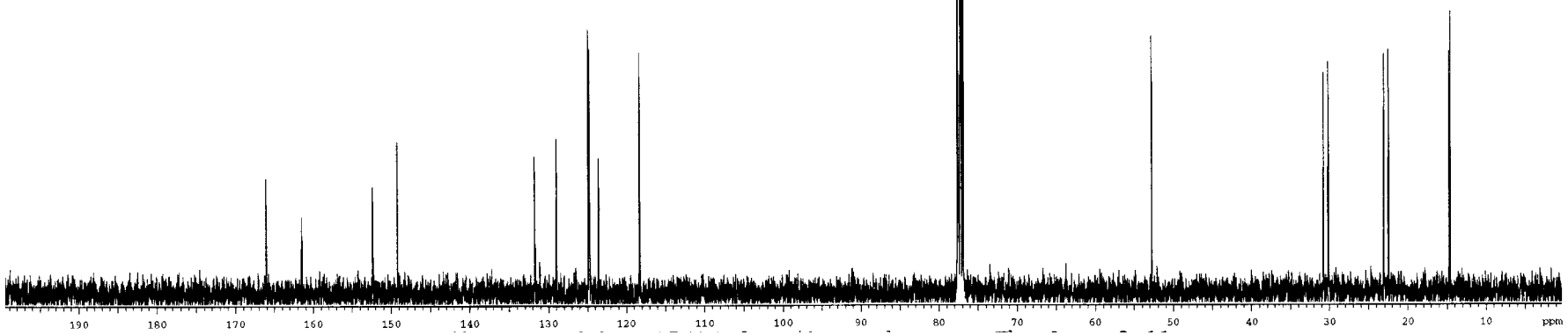


Methyl 3,4-di-n-propylcoumarin-7-carboxylate

166.065
161.518
152.369
149.228
131.772
128.996
124.905
124.797
123.563
118.340
52.771
30.766
30.102
23.010
22.470
14.713
14.547

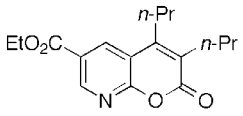


17

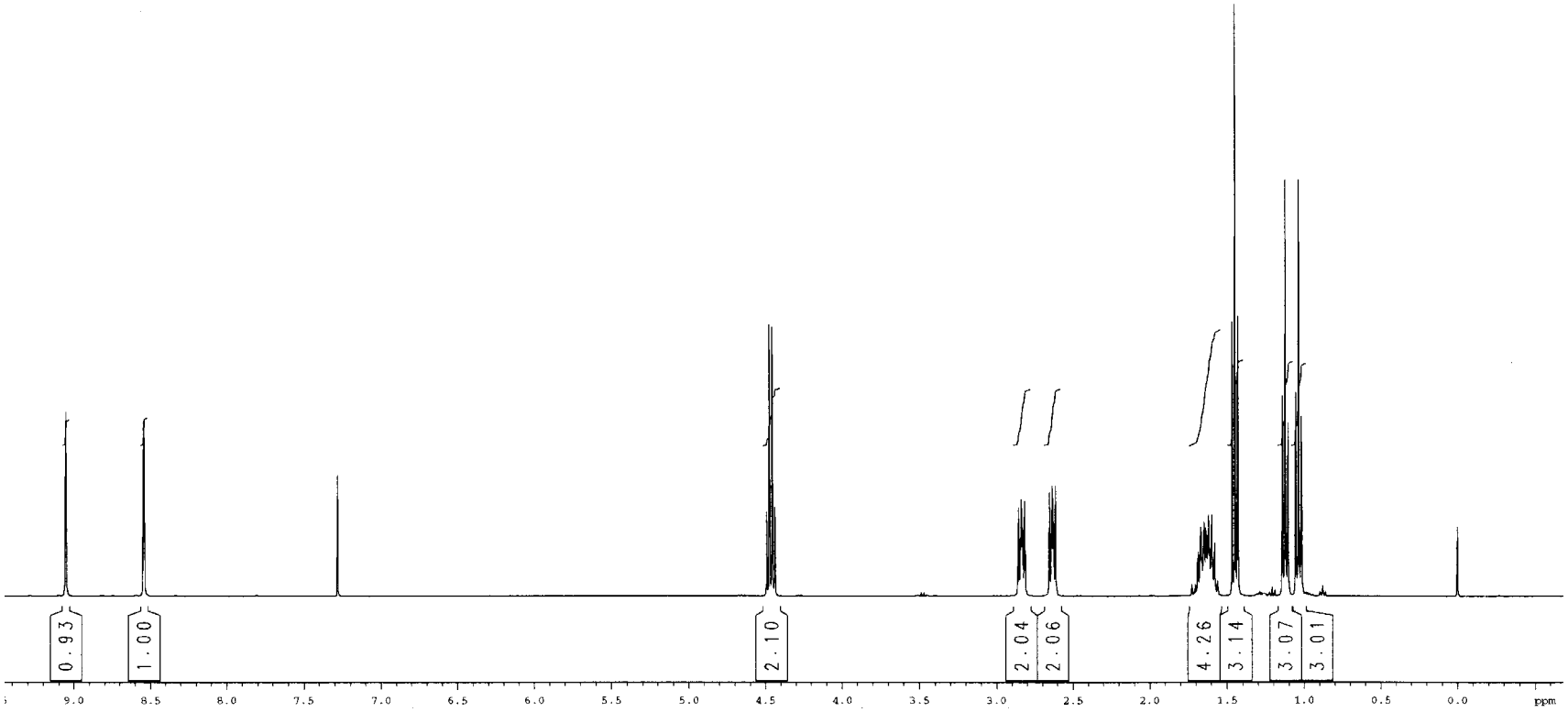


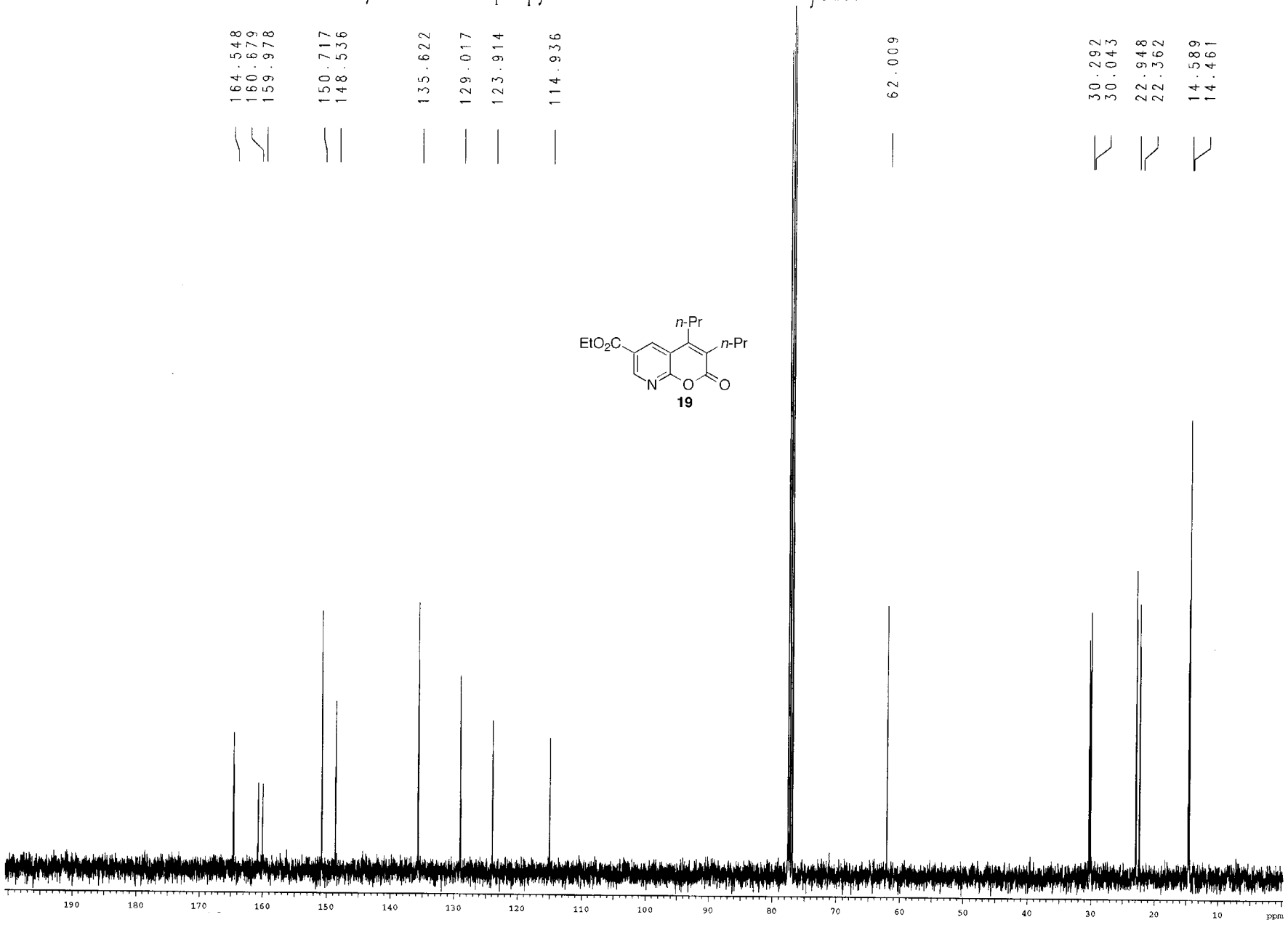
Ethyl 3,4-di-n-propyl-8-azacoumarin-6-carboxylate

9.055
9.049
8.545
8.539
4.491
4.473
4.455
4.437
2.857
2.843
2.837
2.831
2.817
2.654
2.640
2.635
2.629
2.615
1.687
1.668
1.648
1.636
1.628
1.617
1.597
1.578
1.467
1.449
1.431
1.142
1.124
1.105
1.055
1.037
1.018



19




Ethyl 3,4-di-n-propyl-8-azacoumarin-6-carboxylate
164.548
160.679
159.978
150.717
148.536
135.622
129.017
123.914
114.936
62.009
30.292
30.043
22.948
22.362
14.589
14.461
n-Pr
n-Pr
EtO2C
N
O
O
19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm