10.1071/CH13108_AC
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Australian Journal of Chemistry 2013, 66(11), 1334-1341

First synthesis of biaryles derivatives of sesamol (5-benzodioxolol) and evaluation of their antioxidant activity against radical DPPH

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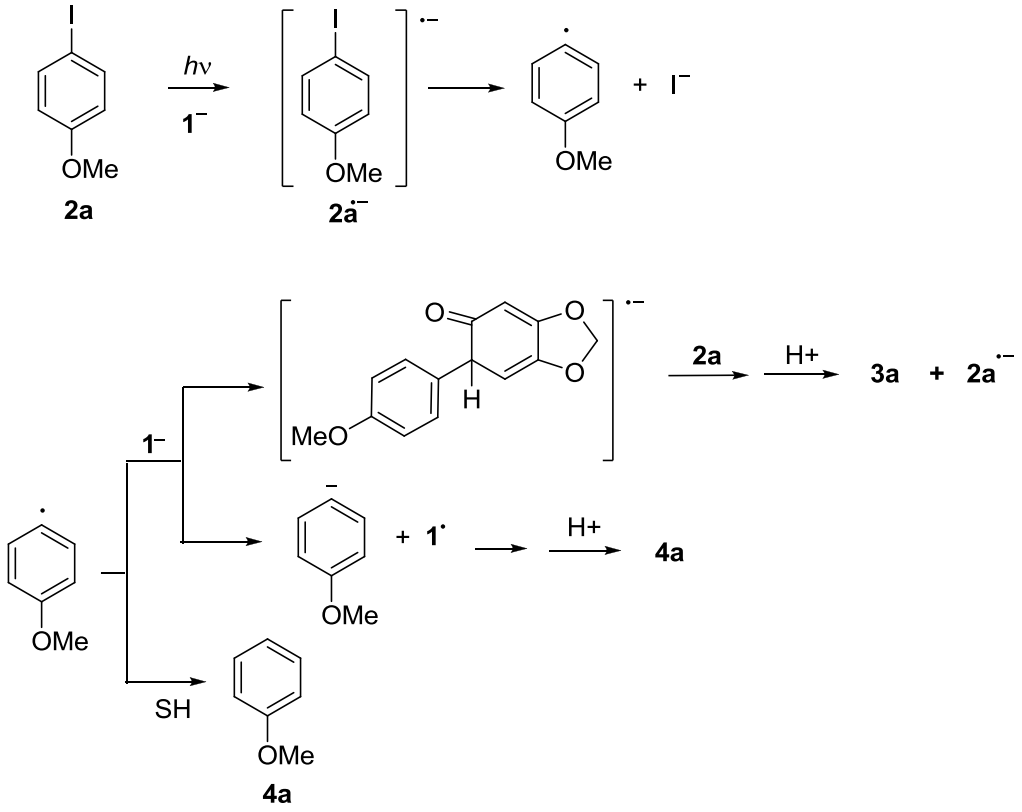
Possible reaction mechanisms scheme

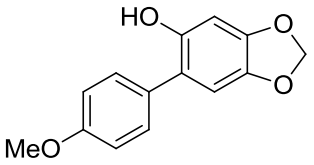
Scheme S1



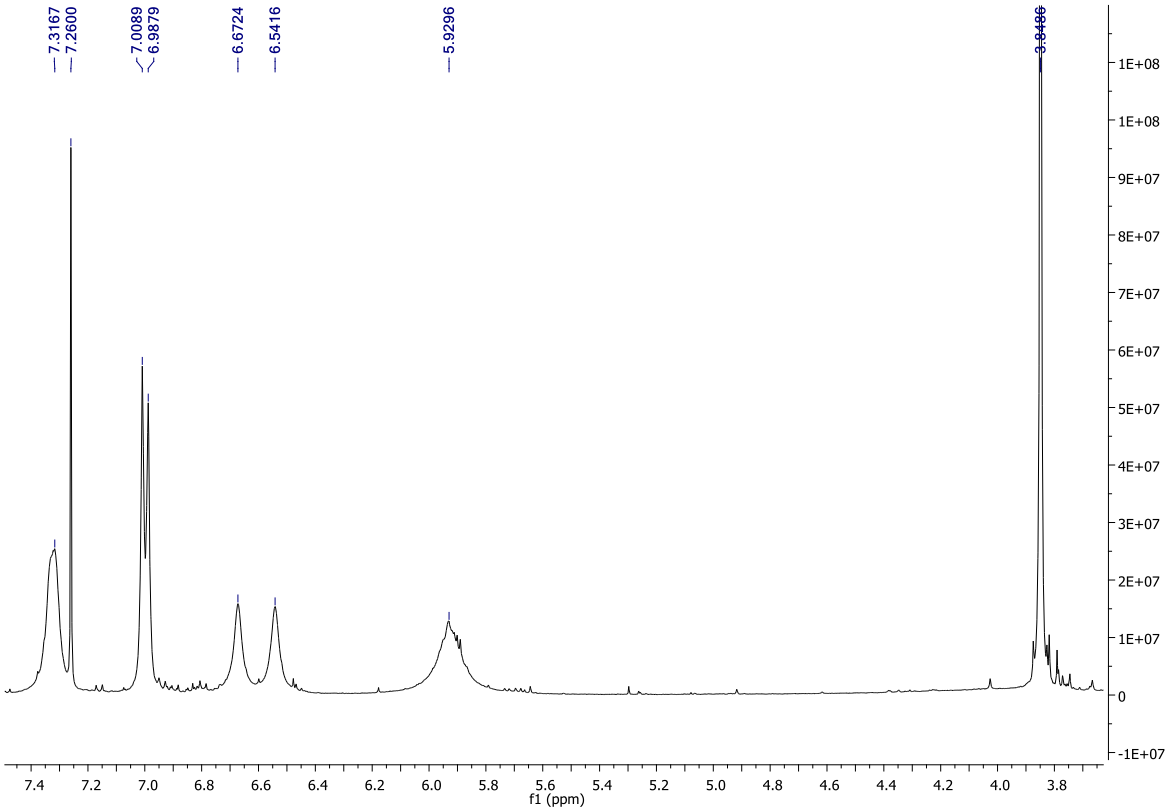
SH = solvent

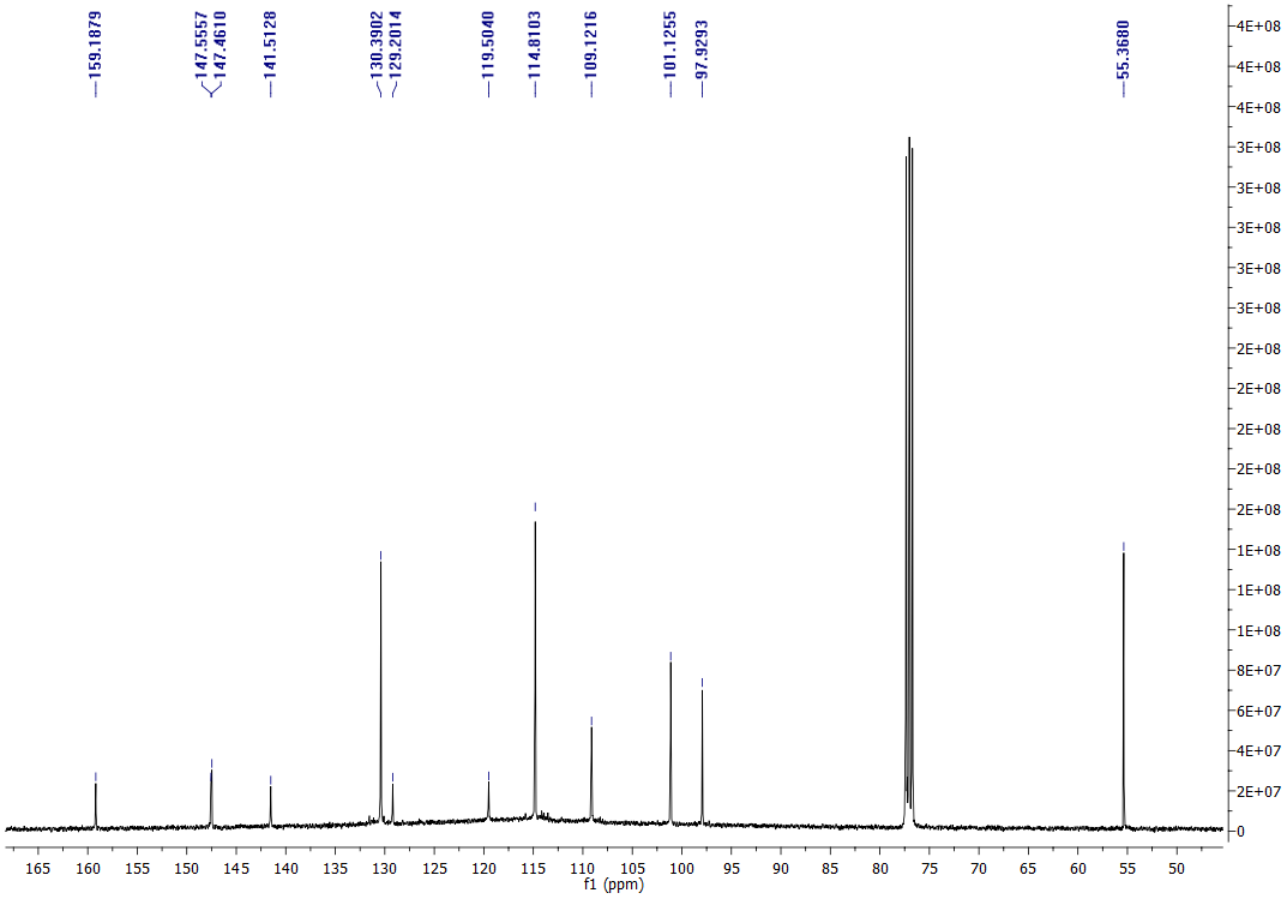
Synthesis and characterization of sesamol derivatives. Copies of ^{1}H, ^{13}C NMR spectra and MS of products

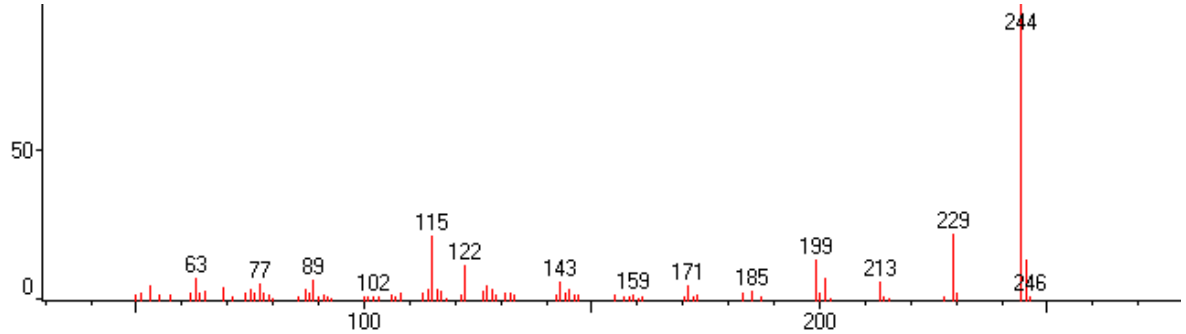
6-(4-anisyl)-5-benzodioxolol (**3a**)



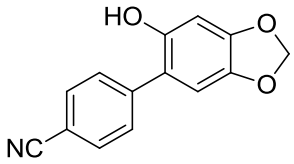
Solid brown, mp 109-110°C. ^{1}H NMR (400 MHz, CCl_3D): δ_H 3.84 (s, 3H); 5.92 (s, 2H); 6.54 (s, 1H); 6.67 (s, 1H); 6.98-7.00 (d, 2H); 7.30-7.32 (d, 2H). ^{13}C NMR: δ_C 55.37; 97.93; 101.13; 109.12; 114.81; 119.50; 129.20(q); 130.39; 141.51(q); 147.46(q); 147.56(q); 159.19(q). EM (m/z, %) 245 (16); 244 (100); 229 (26); 213 (6); 199 (17); 171 (7); 143 (7); 122 (9); 115 (25); 89 (7); 77 (5); 63 (7). HRMS calculated for $C_{14}H_{12}O_4$ M-H 243.0652, found 243.0673.



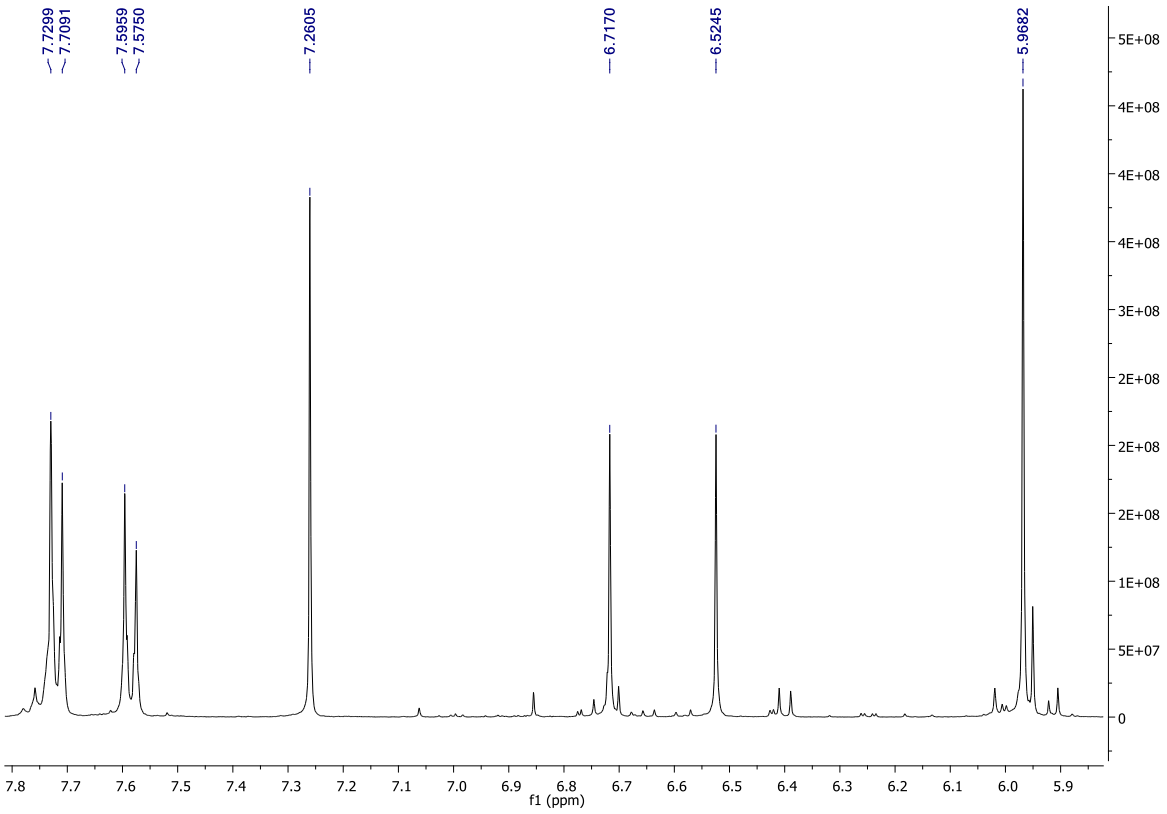

159.1879
147.5557
147.4610
141.5128
130.3902
129.2014
119.5040
114.8103
109.1216
101.1255
97.9293
55.3680
f1 (ppm)

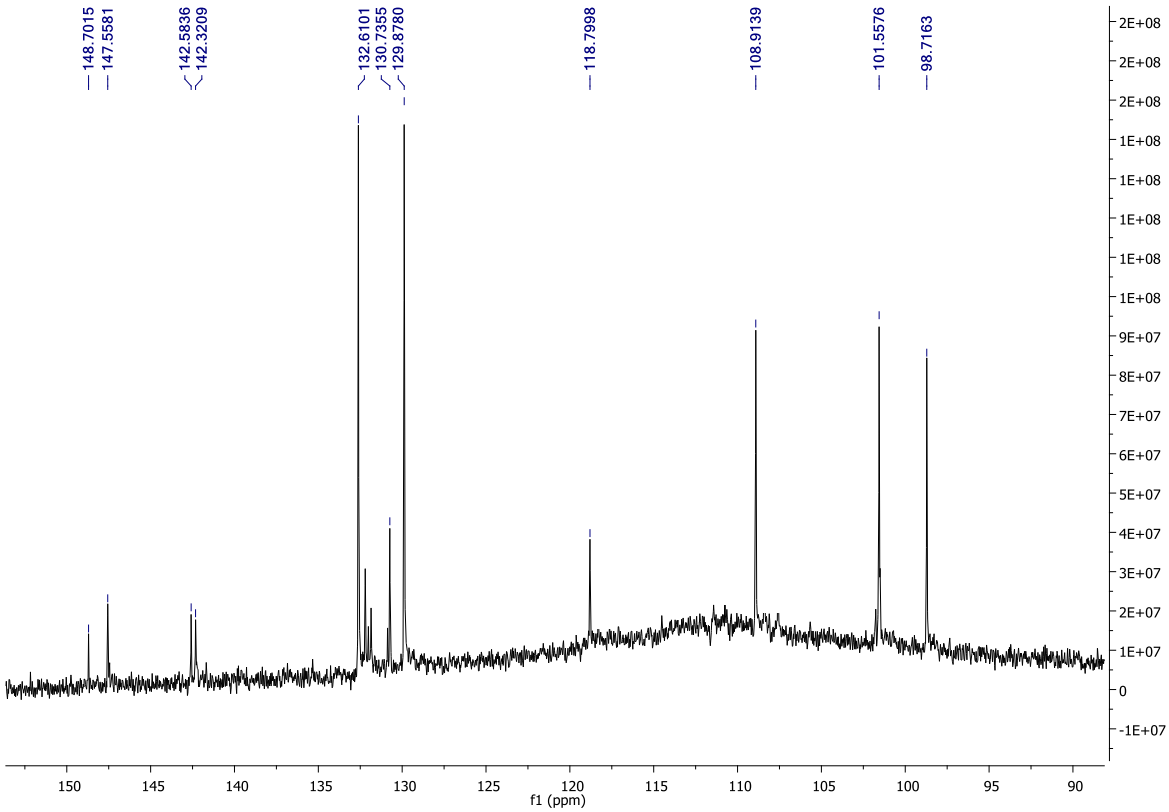

244
115
122
63
77
89
102
143
159
171
185
199
213
229
246
50
0
100
200

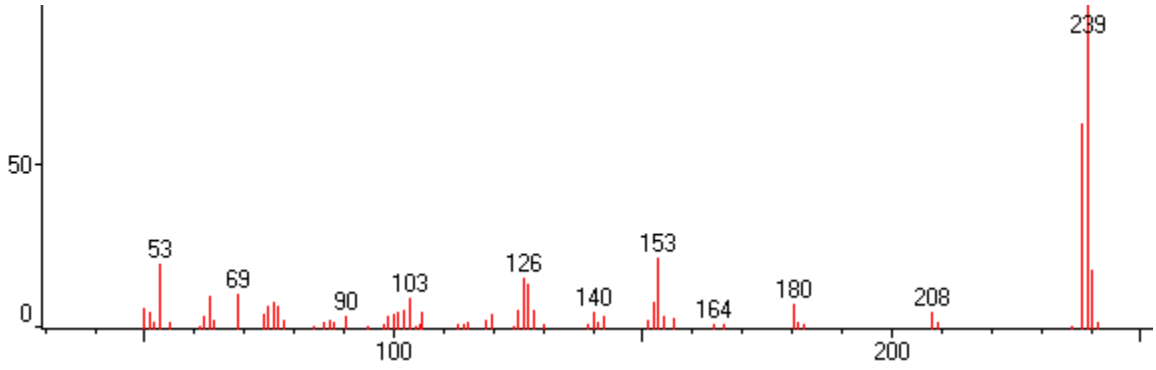
6-(4-cianophenyl)-5-benzodioxolol (**3c**)



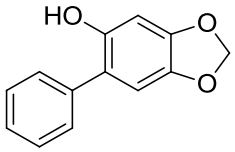
Solid brown, mp 150.5-151.5°C. ^{1}H NMR (400 MHz, CCl_3D): δ_H 5.97 (s, 2H); 6.52 (s, 1H); 6.72 (s, 1H); 7.58-7.00 (d, 2H); 7.71-7.73 (d, 2H). ^{13}C NMR: δ_C 98.72; 101.56; 108.91; 118.80(q); 129.88; 130.74(q); 132.61; 142.32(q); 142.58(q); 147,56(q); 148.70(q). EM (m/z, %) 240 (16); 239 (100); 238 (56); 180 (7); 153 (21); 152 (9); 127 (16); 126 (16); 103 (9); 77 (9); 69 (11); 63 (10); 53 (19). HRMS calculated for $C_{14}H_9NO_3$ M+Na 262.0475, found 262.0477.



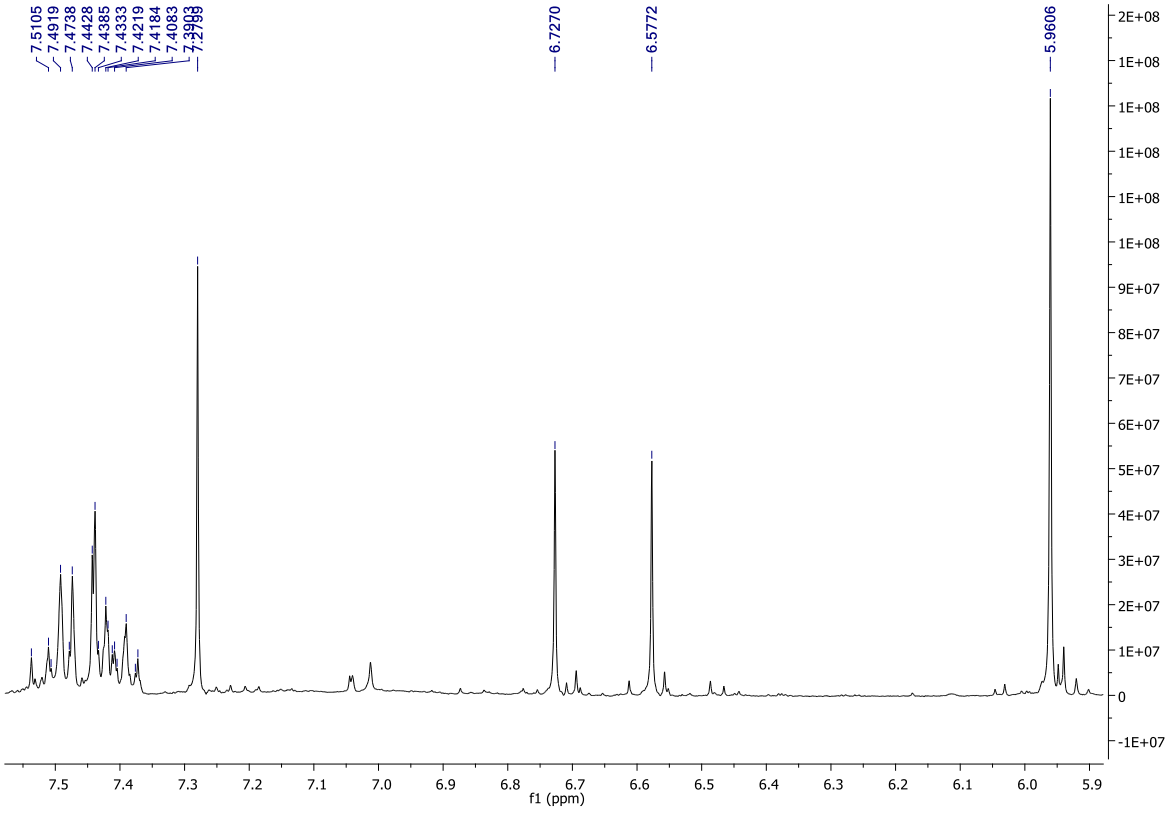

148.7015
147.5581
142.5836
142.3209
132.6101
130.7355
129.8780
118.7998
108.9139
101.5576
98.7163
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
150
145
140
135
130
125
120
115
110
105
100
95
90
f1 (ppm)

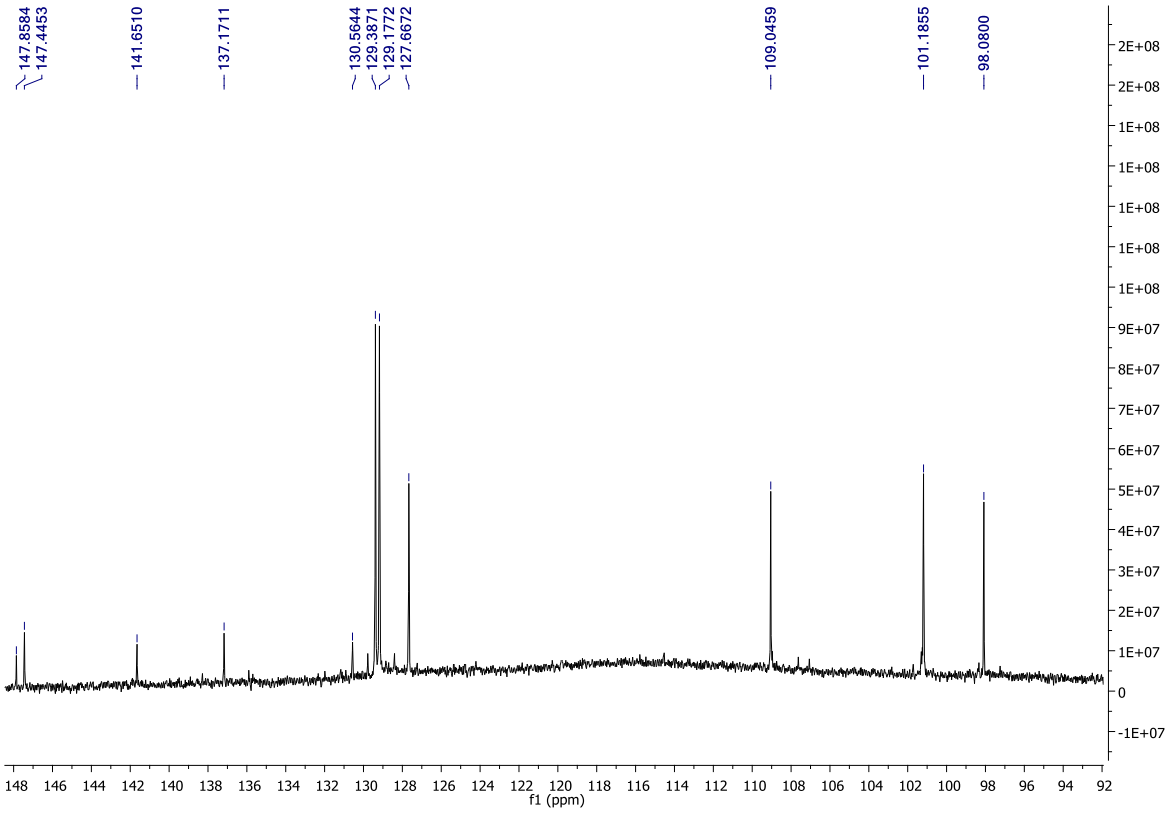

239
50
0
53
69
90
103
126
140
153
164
180
208
100
200

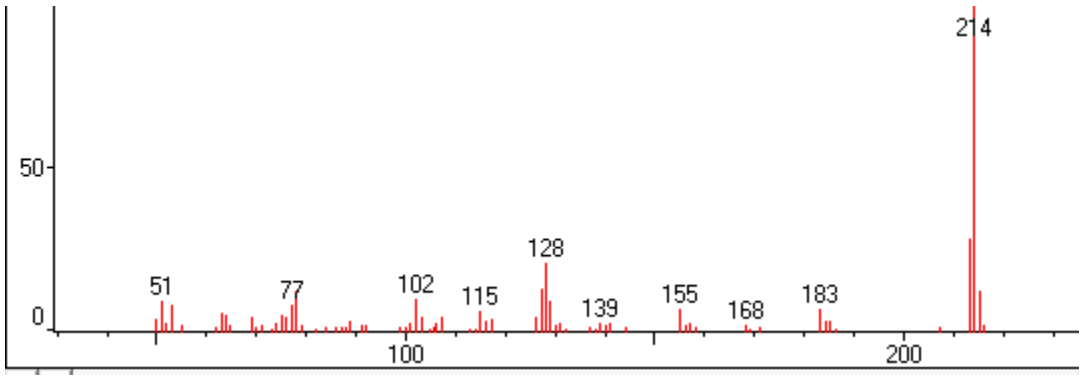
6-phenyl-5-benzodioxolol (**3d**)



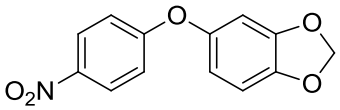
Oil. ^{1}H NMR (400 MHz, CCl_3D): δ_H 5.96 (s, 2H); 6.58 (s, 1H); 6.73 (s, 1H); 7.37-7.54 (m, 5H). ^{13}C NMR: δ_C 98.08; 101.18; 109.05; 127.67; 129.18; 129.18; 130.56(q); 137.17(q); 141.65(q); 147.45(q); 147.86(q). EM (m/z, %) 215 (12); 214 (100); 213 (35); 183 (9); 155 (7); 129 (11); 128 (32); 127 (18); 126 (11); 115 (10); 102 (19); 78 (21); 77 (18); 69 (8); 63 (9); 53 (16); 51 (14). HRMS calculated for $C_{13}H_{10}O_3$ M+Na 237.0522, found 237.0508.



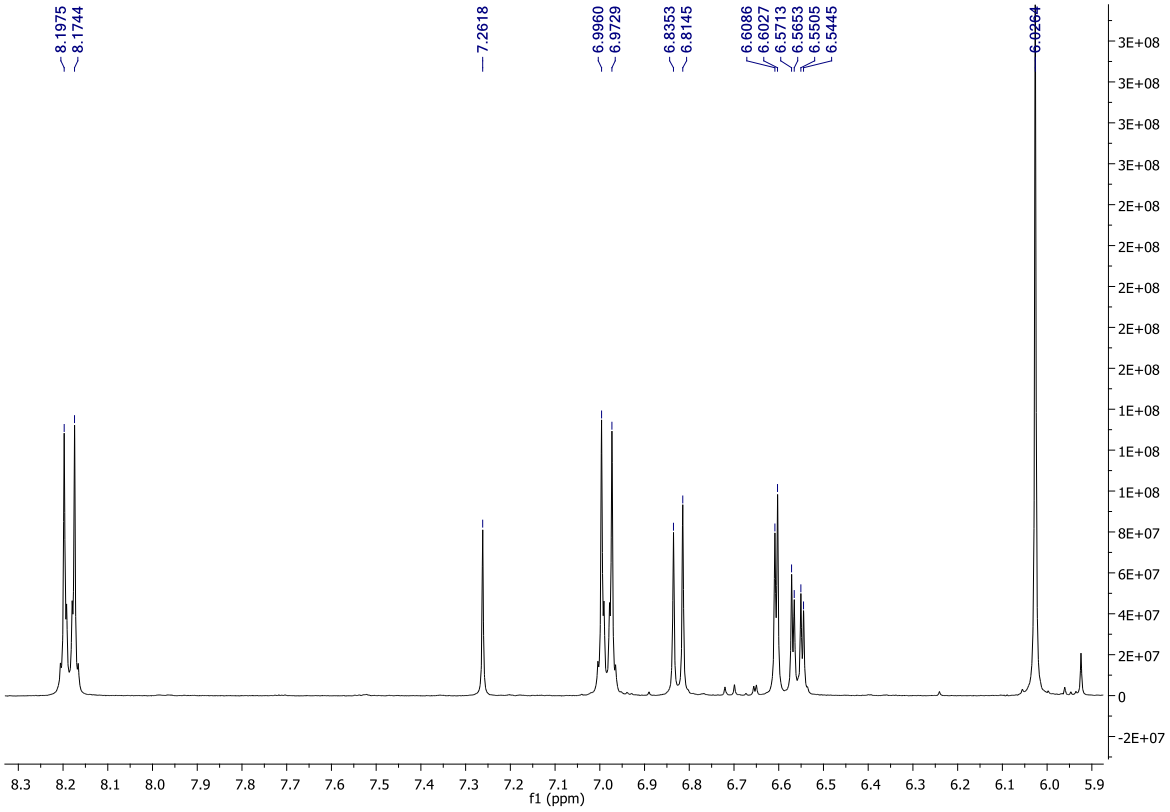

147.8584
147.4453
141.6510
137.1711
130.5644
129.3871
129.1772
127.6672
109.0459
101.1855
98.0800
2E+08
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102 100 98 96 94 92
f1 (ppm)

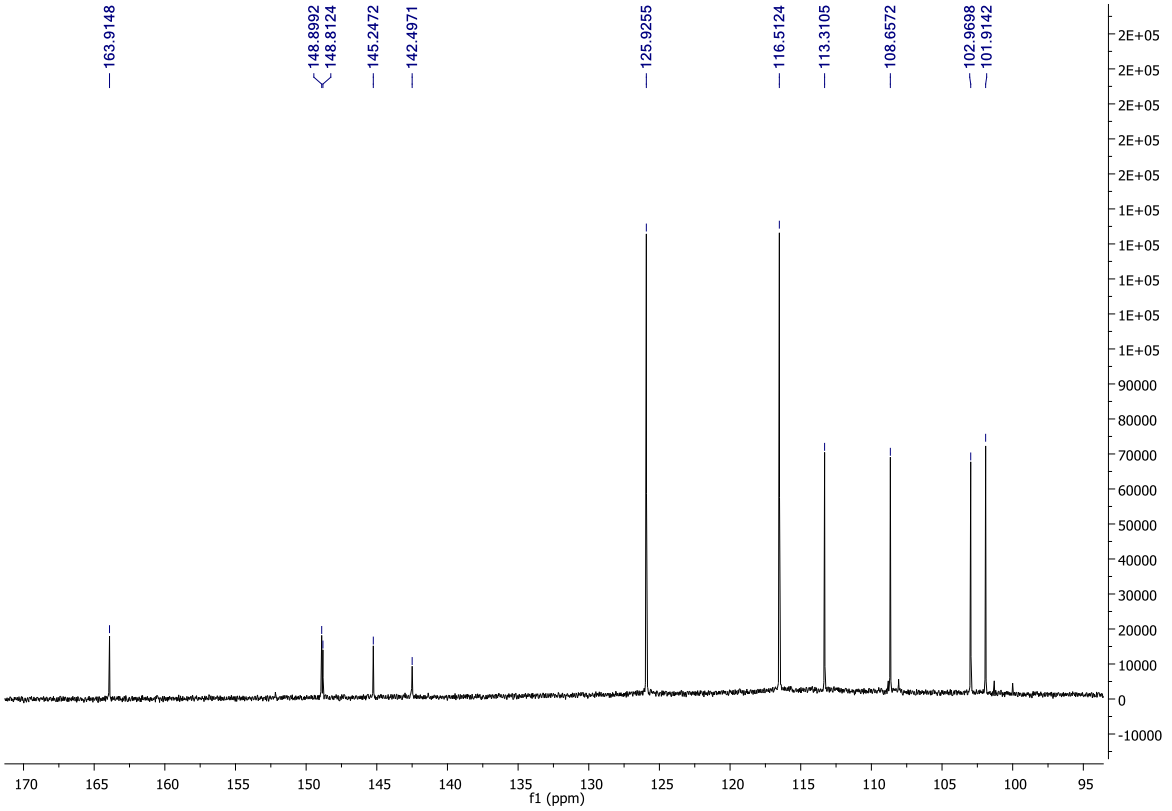

214
50
0
51
77
102
115
128
139
155
168
183
100
200

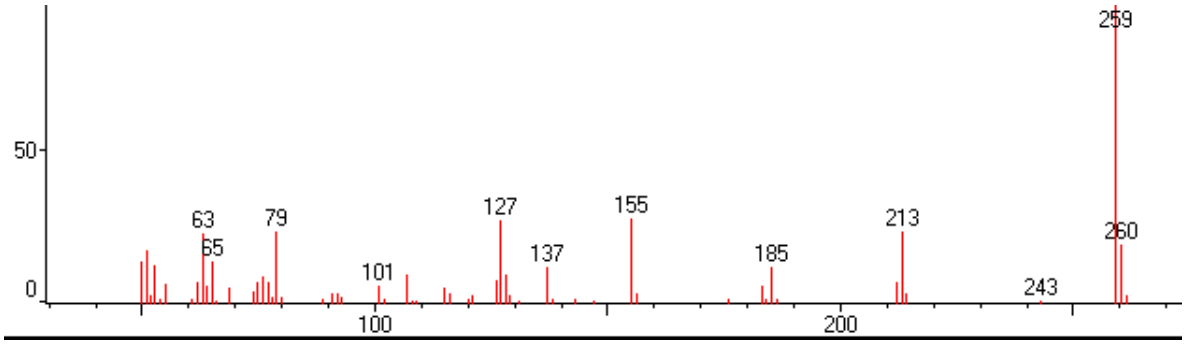
5-(4-nithrophenoxy)-benzodioxolol (**3e**) [1]



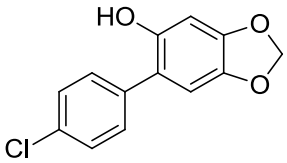
Solid yellow, mp 84,5-85,7°C. ^{1}H NMR (400 MHz, CCl_3D): δ_H 6.02 (s, 2H); 6.54-6.57 (m, 1H); 6.60-6.61 (d, 1H); 6.81-6.84 (d, 1H); 6.97-6.99 (m, 2H); 8.17-8.19 (m, 2H). ^{13}C NMR: δ_C 101.91; 102.97; 113.3; 116.51; 125.92; 142.49(q); 145.25(q); 148.81(q); 148.89(q); 163.91(q). EM (m/z, %) 260 (21); 259 (100); 213 (25); 185 (13); 155 (29); 137 (12); 128 (10); 127 (28); 79 (23); 65 (14); 63 (23); 53 (13); 51 (18); 50 (14). HRMS calculated for $C_{13}H_9NO_5$ M+Na 282.0373, found 282.0368.



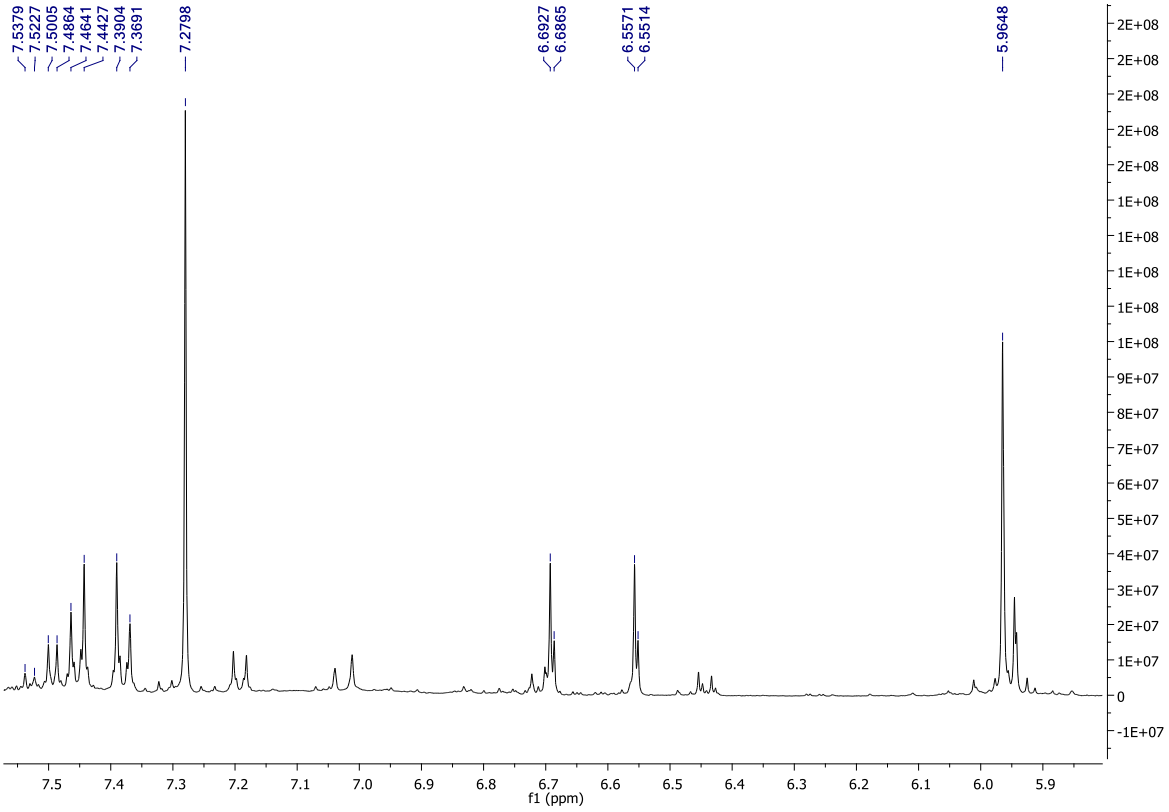

163.9148
148.8992
148.8124
145.2472
142.4971
125.9255
116.5124
113.3105
108.6572
102.9698
101.9142
2E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
f1 (ppm)

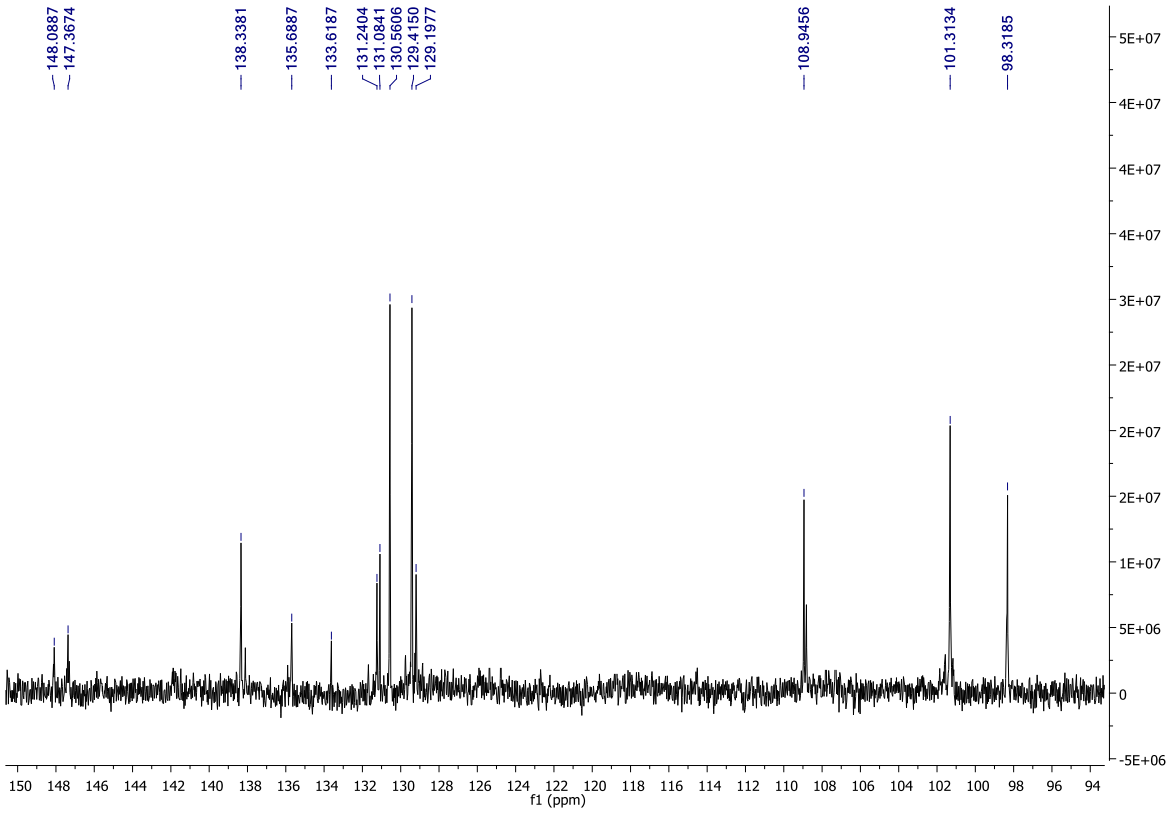

259
50
0
63
65
79
101
127
137
155
185
213
243
260
100
200

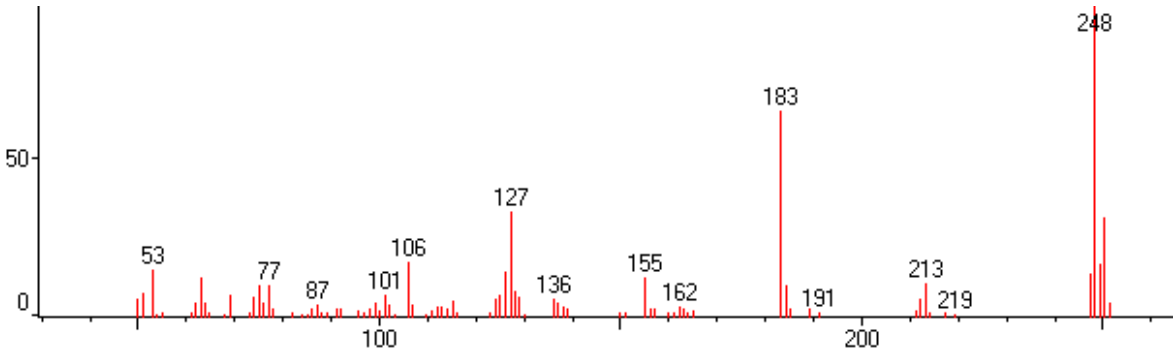
6-(4-chlorophenyl)-5-benzodioxolol (**3f**)



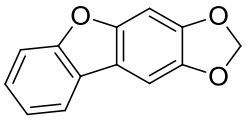
Oil. ^{1}H NMR (400 MHz, CCl_3D): δ_H 5.96 (s, 2H); 6.58 (s, 1H); 6.73 (s, 1H); 7.36- 7.56 (m, 4H). ^{13}C NMR: δ_C 98.32; 101.31; 108.95; 129.19; 129.42; 130.56; 131.08; 131.24; 133.62(q); 135.69(q); 138.34; 147.37(q); 148.09(q). EM (m/z, %) 250 (34); 249 (18); 248 (100); 247 (16); 213 (9); 183 (72); 155 (15); 127 (35); 126 (15); 105 (31); 101 (10); 77 (15); 75 (13); 69 (10); 63 (16); 53 (20). HRMS calculated for $C_{13}H_9ClO_3$ M-H 247.0156, found 247.0149.



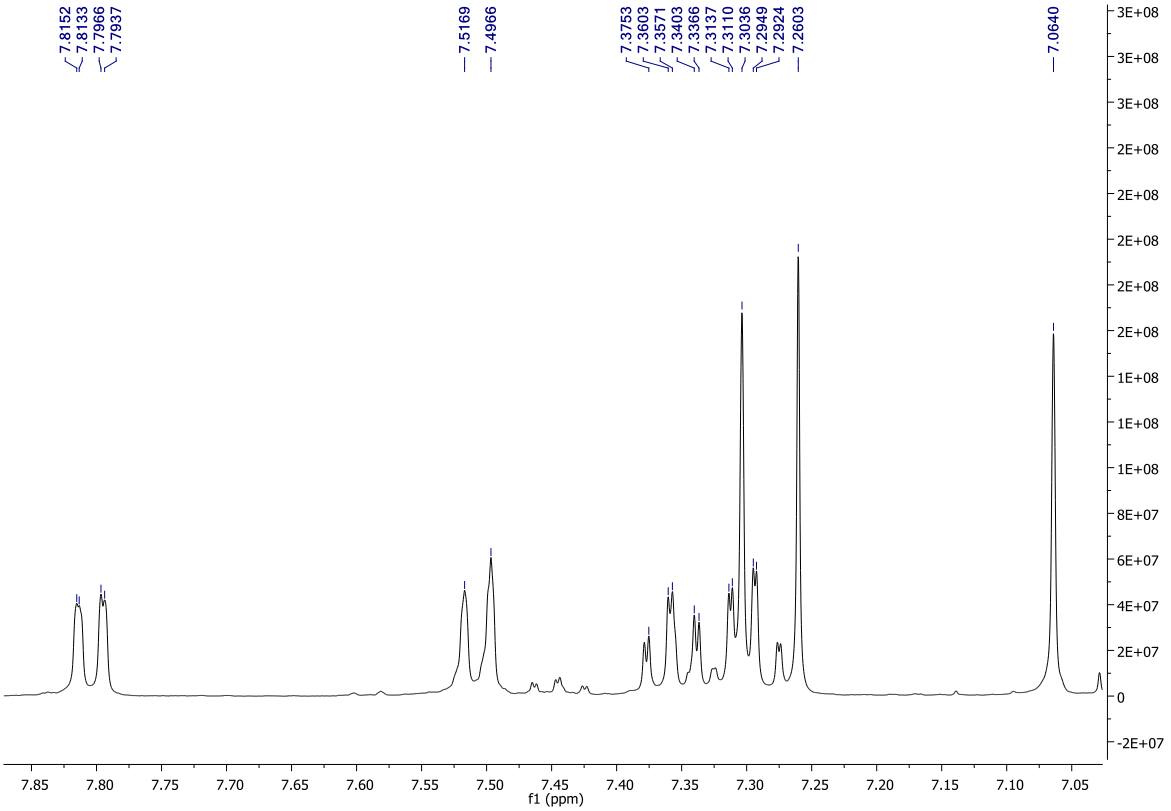

148.0887
147.3674
138.3381
135.6887
133.6187
131.2404
131.0841
130.5606
129.4150
129.1977
108.9456
101.3134
98.3185
5E+07
4E+07
4E+07
4E+07
3E+07
2E+07
2E+07
2E+07
1E+07
5E+06
0
-5E+06
150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102 100 98 96 94
f1 (ppm)

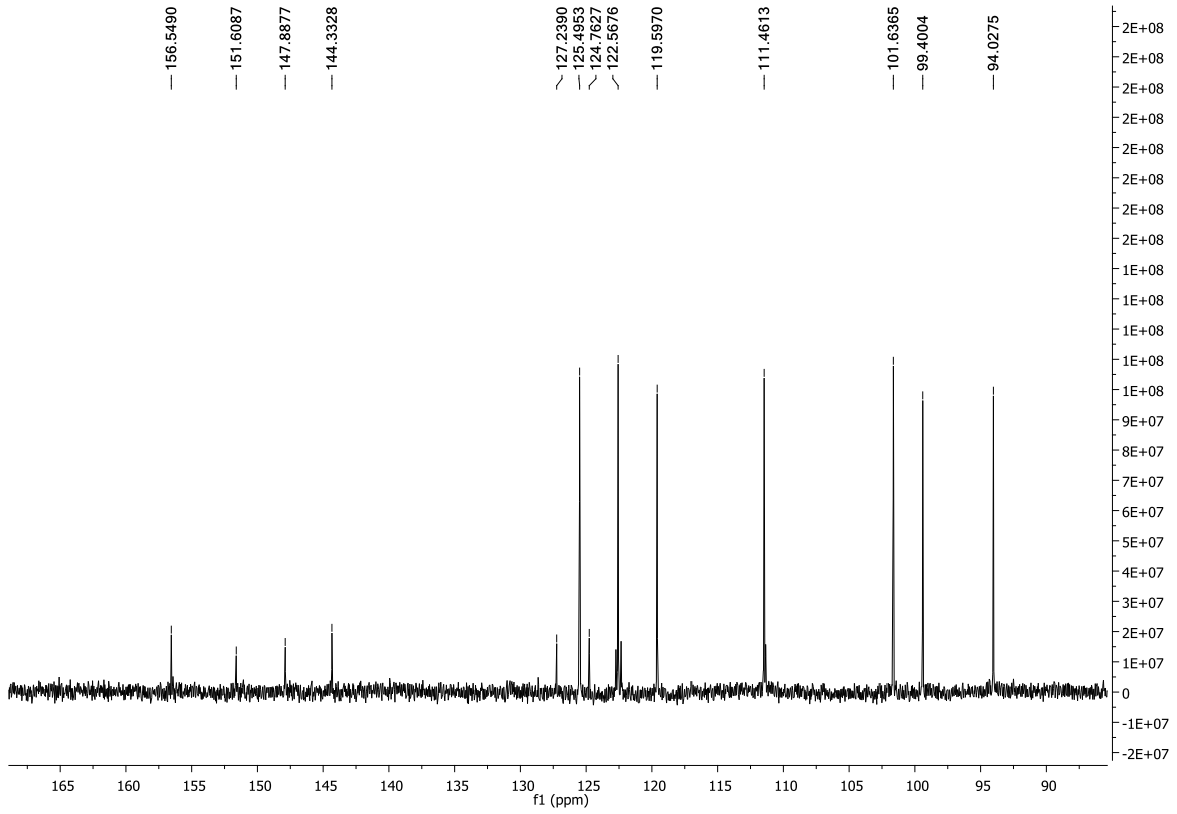

248
183
127
106
53
77
87
101
136
155
162
191
213
219
50
0
100
200

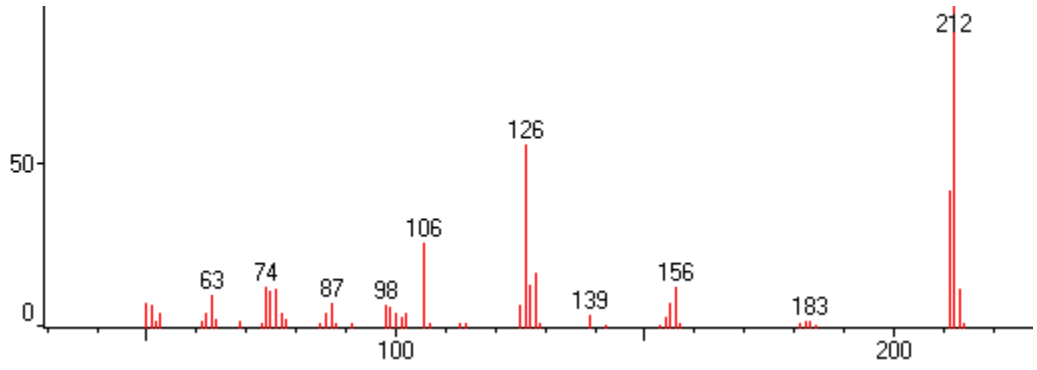
Benzo[b][1,3]dioxolo[4,5-f]benzofuran (**5**)



Solid white, mp 115.7-116.7°C. ^{1}H NMR (400 MHz, CCl_3D): δ_H 6.05 (s, 2H); 7.06 (s, 1H); 7.29-7.31 (m, 2H); 7.34-7.38 (m, 1H); 7.50-7.52 (d, 1H); 7.79-7.82 (m, 1H). ^{13}C NMR: δ_C 94.03; 99.40; 101.64; 111.46; 119.59; 122.59; 124.76(q); 125.49; 127.24(q); 144.33(q); 147.88(q); 151.61(q); 156.55(q). EM (m/z, %) 213 (13); 212 (100); 211 (42); 156 (13); 128 (17); 127 (14); 126 (54); 106 (25); 76 (11); 75 (11); 74 (12); 63 (10).




156.5490
151.6087
147.8877
144.3328
127.2390
125.4953
124.7627
122.5676
119.5970
111.4613
101.6365
99.4004
94.0275
f1 (ppm)


212
126
106
63
74
87
98
139
156
183
50
0
100
200

Analysis of the differences between the calculations of BDE obtained in the present work and those reported in ref 31.

According to our experience, the BDE values obtained using different calculation methodologies and different software packages may differ especially when performing single point calculations, however what is interesting is that the relative values maintain the same trend.
We estimate from our geometries BDE values for sesamol and compound **3d** using the methodology employed in ref 31 and obtained 386 kJ/mol (92.30 kcal/mol) and 382 kJ/mol (91.48kcal/mol), respectively. These values differ by 6 to 10 kJ/mol from those published in ref. cited above. The difference between the two values of BDE is 0.82 kcal/mol, approximately. Very similar to that established with our methodology (0.6 kcal/mol). The calculation with geometry optimization using the basis 6-311 + + G ** BDE leads to values of 390.91 kJ/mol (78.46 kcal/mol) and 326.26 kJ/mol (77.68 kcal/mol) for sesamol and **3d**, and the difference of 0.78 kcal/mol.
As previously mentioned the differences between our results and those published may be attributable to both the software package (G98, G09) as the basis of calculation used. As we suggest in the article, our approach is less expensive and has been tested in the calculation of BDE.

Metodology of ref. 31

BDE = H (radical form of sesamol) + H (hydrogen atom) - H (sesamol).

BDE = (-495,6357979 hartree) + (-0,499897 hartree) – (-496,2827832 hartree)= 0,14708830 hartree= 92,2 kcal/mol = 386 kJ/mol.

H (radical form of sesamol) = E (radical calculated with 6-31++G** Single point calculation) + Thermal correction to Enthalpy obtained from FREQ calculation with 6-31G**.

H (radical form of sesamol) = -495,5198149 hartree -0,115983 hartree = -495,6357979 hartree.

H (sesamol) = E (sesamol calculated with 6-31++G** Single point calculation) + Thermal correction to Enthalpy obtained from FREQ calculation with 6-31G**.

H (sesamol) = -496,1547912 hartree -0,127992 hartree = -496,2827832 hartree.

[1] Yadav, J.S.; Subba Reddy, B.V. *New J. Chem.* **2000**, *24*, 489-491.