

1     **Optimization of Flash Extraction, Separation of Ginsenosides,**  
2     **Identification by HPLC-FT-ICR-MS and Determination of rare**  
3             **ginsenosides in Mountain cultivated ginseng**

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82 Section 1: Compound structure analysis

83  $^{13}\text{C}$ -NMR spectra were measured on an AV-400 spectrometer (Bruker, Karlsruhe,  
84 Germany) using tetramethylsilane as an internal standard in pyridine- $d_5$  solution.

85 Compounds 8 and 11 were analyzed by thin layer chromatography with the  
86 standard and had the same  $R_f$  value. In addition, they were analyzed by HPLC with the  
87 standard and had the same retention time and a single peak. Therefore, compounds 8  
88 and 11 were identified as ginsenoside  $Rb_1$  and notoginsenoside Fz, respectively. The  
89  $^{13}\text{C}$ -NMR data of the remaining compounds are shown below:

90

91 Notoginsenoside  $R_1$  (**1**)

92 White powder.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 150 MHz, ppm): 39.9(C-1), 28.2(C-2), 79.2(C-3),  
93 40.6(C-4), 61.7(C-5), 80.5(C-6), 45.3(C-7), 41.5(C-8), 50.3(C-9), 40.0(C-10), 31.1(C-  
94 11), 71.7(C-12), 49.6(C-13), 51.9(C-14), 31.4(C-15), 27.0(C-16), 51.8(C-17), 18.1(C-  
95 18), 17.9(C-19), 83.7(C-20), 22.7(C-21), 36.5(C-22), 23.6(C-23), 126.4(C-24),  
96 131.3(C-25), 26.1(C-26), 17.6(C-27), 32.1(C-28), 17.9(C-29), 17.1(C-30); **6-O-Glc**:  
97 103.9(C-1'), 80.3(C-2'), 78.7(C-3'), 72.1(C-4'), 79.9(C-5'), 63.3(C-6'); **2'-O-Xyl**:  
98 105.3(C-1''), 76.2(C-2''), 79.2(C-3''), 70.5(C-4''), 67.7(C-5''); **20-O-Glc**: 98.6(C-1'''),  
99 75.5(C-2'''), 79.7(C-3'''), 72.2(C-4'''), 78.4(C-5'''), 63.3(C-6''').

100

101 20-O-glu-ginsenoside  $R_f$  (**2**)

102 White powder.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 150 MHz, ppm): 39.8(C-1), 28.2(C-2), 78.8(C-3),  
103 40.6(C-4), 61.8(C-5), 78.2(C-6), 45.3(C-7), 41.6(C-8), 50.3(C-9), 40.1(C-10), 31.1(C-  
104 11), 70.6(C-12), 49.6(C-13), 51.8(C-14), 31.3(C-15), 27.0(C-16), 51.9(C-17), 17.9(C-  
105 18), 18.0(C-19), 83.7(C-20), 22.7(C-21), 36.5(C-22), 23.6(C-23), 126.4(C-24),  
106 131.3(C-25), 26.1(C-26), 18.1(C-27), 32.5(C-28), 17.5(C-29), 17.1(C-30); **6-O-Glc**:  
107 104.2(C-1'), 80.3(C-2'), 78.5(C-3'), 72.1(C-4'), 78.3(C-5'), 63.3(C-6'); **2'-O-Glc**:  
108 104.2(C-1''), 76.4(C-2''), 80.0(C-3''), 72.8(C-4''), 79.7(C-5''), 63.8(C-6''); **20-O-Glc**:  
109 98.6(C-1'''), 75.5(C-2'''), 79.1(C-3'''), 72.8(C-4'''), 78.7(C-5'''), 63.3(C-6''').

110

111 Ginsenoside Rf (**3**)

112 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.8(C-1), 28.2(C-2), 79.0(C-3),  
113 40.6(C-4), 61.8(C-5), 80.1(C-6), 45.5(C-7), 41.6(C-8), 50.5(C-9), 40.0(C-10), 32.5(C-  
114 11), 71.4(C-12), 48.7(C-13), 52.1(C-14), 31.7(C-15), 27.4(C-16), 55.2(C-17), 18.0(C-  
115 18), 17.8(C-19), 73.4(C-20), 27.2(C-21), 36.2(C-22), 23.4(C-23), 126.7(C-24),  
116 131.2(C-25), 26.2(C-26), 18.1(C-27), 32.3(C-28), 17.2(C-29), 17.1(C-30); **6-O-Glc**:  
117 104.3(C-1'), 80.2(C-2'), 80.3(C-3'), 72.1(C-4'), 78.8(C-5'), 63.8(C-6'); **2'-O-Glc**:  
118 104.2(C-1''), 76.4(C-2''), 78.5(C-3''), 72.8(C-4''), 78.2(C-5''), 63.3(C-6'').

119

120 Ginsenoside Re (**4**)

121 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.7(C-1), 28.0(C-2), 78.6(C-3),  
122 40.0(C-4), 61.1(C-5), 78.6(C-6), 46.2(C-7), 41.5(C-8), 49.8(C-9), 40.3(C-10), 31.1(C-  
123 11), 70.5(C-12), 49.3(C-13), 51.7(C-14), 31.2(C-15), 26.9(C-16), 52.0(C-17), 17.5(C-  
124 18), 17.6(C-19), 83.6(C-20), 22.7(C-21), 36.3(C-22), 23.6(C-23), 126.3(C-24),  
125 131.2(C-25), 26.1(C-26), 17.8(C-27), 32.5(C-28), 17.9(C-29), 18.1(C-30); **6-O-Glc**:  
126 102.2(C-1'), 79.5(C-2'), 78.7(C-3'), 72.7(C-4'), 78.7(C-5'), 63.1(C-6'); **2'-O-Rha**:  
127 102.2(C-1''), 72.9(C-2''), 72.7(C-3''), 74.5(C-4''), 69.8(C-5''), 19.1(C-6''); **20-O-Glc**:  
128 98.6(C-1'''), 75.5(C-2'''), 79.7(C-3'''), 71.8(C-4'''), 78.9(C-5'''), 63.4(C-6''').

129

130 Ginsenoside Rg<sub>1</sub> (**5**)

131 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.7(C-1), 28.3(C-2), 78.9(C-3),  
132 40.7(C-4), 61.7(C-5), 78.5(C-6), 45.4(C-7), 41.4(C-8), 50.3(C-9), 40.0(C-10), 31.2(C-  
133 11), 70.5(C-12), 49.5(C-13), 51.7(C-14), 31.0(C-15), 26.9(C-16), 51.8(C-17), 17.8(C-  
134 18), 17.9(C-19), 83.6(C-20), 22.6(C-21), 36.4(C-22), 23.5(C-23), 126.3(C-24),  
135 131.2(C-25), 26.1(C-26), 18.1(C-27), 32.1(C-28), 16.7(C-29), 17.4(C-30); **6-O-Glc**:  
136 106.3(C-1'), 75.8(C-2'), 80.5(C-3'), 72.1(C-4'), 80.0(C-5'), 63.3(C-6'); **20-O-Glc**:  
137 98.6(C-1''), 75.4(C-2''), 79.7(C-3''), 71.9(C-4''), 78.7(C-5''), 63.1(C-6'').

138

139 20(*S*)-notoginsenoside G (**6**)

140 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.9(C-1), 27.6(C-2), 88.3(C-3),

141 43.1(C-4), 147.4(C-5), 127.9(C-6), 70.3(C-7), 42.6(C-8), 47.7(C-9), 38.4(C-10),  
142 33.6(C-11), 70.1(C-12), 50.8(C-13), 51.3(C-14), 34.8(C-15), 27.5(C-16), 51.5(C-17),  
143 11.1(C-18), 18.1(C-19), 83.9(C-20), 22.9(C-21), 36.8(C-22), 23.6(C-23), 126.3(C-24),  
144 131.3(C-25), 26.1(C-26), 18.5(C-27), 27.5(C-28), 24.2(C-29), 20.7(C-30); **3-O-Glc**:  
145 105.3(C-1'), 84.0(C-2'), 78.7(C-3'), 71.6(C-4'), 78.7(C-5'), 63(C-6'); **2'-O-Glc**:  
146 106.6(C-1''), 77.5(C-2''), 78.5(C-3''), 71.9(C-4''), 78.5(C-5''), 63.2(C-6''); **20-O-Glc**:  
147 98.7(C-1'''), 75.5(C-2'''), 79.6(C-3'''), 71.9(C-4'''), 78.5(C-5'''), 63.2(C-6''').

148

149 Vina-ginsenoside R<sub>4</sub> (**7**)

150 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.4(C-1), 26.9(C-2), 89.7(C-3),  
151 40.8(C-4), 61.9(C-5), 67.8(C-6), 47.7(C-7), 41.3(C-8), 50(C-9), 39(C-10), 31(C-11),  
152 70.5(C-12), 49.3(C-13), 51.6(C-14), 31(C-15), 26.9(C-16), 51.9(C-17), 17.8(C-18),  
153 17.6(C-19), 83.5(C-20), 22.6(C-21), 36.3(C-22), 23.5(C-23), 126.1(C-24), 131.2(C-  
154 25), 26(C-26), 18(C-27), 31.6(C-28), 17(C-29), 17.6(C-30); **3-O-Glc**: 105.6(C-1'),  
155 83.5(C-2'), 78.4(C-3'), 72.0(C-4'), 78.5(C-5'), 63.1(C-6'); **2'-O-Glc**: 106.1(C-1''),  
156 77.2(C-2''), 79.4(C-3''), 71.9(C-4''), 78.6(C-5''), 63.1(C-6''); **20-O-Glc**: 98.5(C-1'''),  
157 75.4(C-2'''), 78.6(C-3'''), 72 (C-4'''), 78.5(C-5'''), 63.1(C-6''').

158

159 Ginsenoside Ia (**9**)

160 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.5(C-1), 27.0(C-2), 89.8(C-3),  
161 40.9(C-4), 62.1(C-5), 63.2(C-6), 47.8(C-7), 41.5(C-8), 50.1(C-9), 39.2(C-10), 31.2(C-  
162 11), 70.5(C-12), 49.5(C-13), 51.7(C-14), 31.1(C-15), 27.0(C-16), 51.9(C-17), 17.7(C-  
163 18), 16.3(C-19), 83.8(C-20), 22.7(C-21), 36.4(C-22), 23.5(C-23), 126.3(C-24),  
164 131.3(C-25), 26.1(C-26), 18.1(C-27), 31.8(C-28), 17.3(C-29), 17.7(C-30); **3-O-Glc**:  
165 98.6(C-1'), 75.5(C-2'), 79.7(C-3'), 72.0(C-4'), 78.7(C-5'), 63.2(C-6'); **20-O-Glc**:  
166 107.6(C-1''), 76.3(C-2''), 79.1(C-3''), 72.3(C-4''), 78.7(C-5''), 63.5(C-6'').

167

168 Ginsenoside Rc (**10**)

169 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.4(C-1), 26.9(C-2), 89.3(C-3),  
170 40.0(C-4), 56.6(C-5), 18.7(C-6), 35.4(C-7), 40.3(C-8), 50.5(C-9), 37.2(C-10), 31.0(C-

171 11), 70.5(C-12), 49.7(C-13), 51.7(C-14), 31.1(C-15), 27.1(C-16), 51.9(C-17), 17.7(C-  
172 18), 16.3(C-19), 83.8(C-20), 22.7(C-21), 36.5(C-22), 23.5(C-23), 126.3(C-24),  
173 131.4(C-25), 26.1(C-26), 18.2(C-27), 28.4(C-28), 16.9(C-29), 16.9(C-30); **3-O-Glc**:  
174 105.5(C-1'), 83.7(C-2'), 78.3(C-3'), 71.9(C-4'), 78.5(C-5'), 62.9(C-6'); **2'-O-Glc**:  
175 106.4(C-1''), 77.6(C-2''), 79.1(C-3''), 71.9(C-4''), 78.7(C-5''), 63.2(C-6''); **20-O-Glc**:  
176 98.4(C-1'''), 75.4(C-2'''), 78.7(C-3'''), 72.4(C-4'''), 76.9(C-5'''), 68.9(C-6'''); **6'''-O-**  
177 **Ara**: 110.5(C-1'''), 83.8(C-2'''), 79.6(C-3'''), 86.2(C-4'''), 62.9(C-5''').

178

179 Ginsenoside Rb<sub>2</sub> (**12**)

180 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.5(C-1), 27.0(C-2), 89.2(C-3),  
181 40.0(C-4), 56.7(C-5), 18.7(C-6), 35.4(C-7), 40.3(C-8), 50.5(C-9), 37.2(C-10), 31.0(C-  
182 11), 70.5(C-12), 49.8(C-13), 51.7(C-14), 31.1(C-15), 27.1(C-16), 52.0(C-17), 16.6(C-  
183 18), 16.3(C-19), 83.8(C-20), 22.7(C-21), 36.5(C-22), 23.5(C-23), 126.3(C-24),  
184 131.4(C-25), 26.2(C-26), 18.2(C-27), 28.4(C-28), 17.0(C-29), 17.7(C-30); **3-O-Glc**:  
185 105.5(C-1'), 83.8(C-2'), 78.3(C-3'), 72.5(C-4'), 78.5(C-5'), 62.9(C-6'); **2'-O-Glc**:  
186 106.4(C-1''), 77.6(C-2''), 78.7(C-3''), 72.2(C-4''), 78.7(C-5''), 63.2(C-6''); **20-O-Glc**:  
187 98.5(C-1'''), 75.2(C-2'''), 79.7(C-3'''), 71.9(C-4'''), 77.1(C-5'''), 69.5(C-6'''); **6'''-O-**  
188 **Ara**: 105.1(C-1'''), 71.9(C-2'''), 74.5(C-3'''), 69.0(C-4'''), 66.1(C-5''').

189

190 Ginsenoside Rb<sub>3</sub> (**13**)

191 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.6(C-1), 27.2(C-2), 89.3(C-3),  
192 40.1(C-4), 56.8(C-5), 18.3(C-6), 35.5(C-7), 40.4(C-8), 50.6(C-9), 37.3(C-10), 31.1(C-  
193 11), 70.4(C-12), 49.9(C-13), 51.6(C-14), 31.2(C-15), 27.0(C-16), 52.0(C-17), 16.4(C-  
194 18), 16.7(C-19), 83.8(C-20), 22.7(C-21), 36.6(C-22), 23.5(C-23), 126.4(C-24),  
195 131.4(C-25), 26.2(C-26), 18.3(C-27), 28.5(C-28), 17.0(C-29), 17.8(C-30); **3-O-Glc**:  
196 105.5(C-1'), 83.8(C-2'), 78.4(C-3'), 72.0(C-4'), 78.7(C-5'), 63.1(C-6'); **2'-O-Glc**:  
197 106.2(C-1''), 77.6(C-2''), 78.5(C-3''), 72.0(C-4''), 78.7(C-5''), 63.3(C-6''); **20-O-Glc**:  
198 98.5(C-1'''), 75.2(C-2'''), 79.7(C-3'''), 72.0(C-4'''), 77.3(C-5'''), 70.5(C-6'''); **6'''-O-Xyl**:  
199 106.5(C-1'''), 75.3(C-2'''), 78.4(C-3'''), 71.5(C-4'''), 67.4(C-5''').

200

201 20(*S*)-ginsenoside Rg<sub>2</sub> (**14**)

202 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 40.0(C-1), 28.1(C-2), 78.7(C-3),  
203 40.4(C-4), 61.2(C-5), 74.6(C-6), 46.5(C-7), 39.7(C-8), 50.0(C-9), 41.5(C-10), 32.4(C-  
204 11), 71.4(C-12), 48.6(C-13), 52.0(C-14), 31.6(C-15), 27.2(C-16), 55.1(C-17), 18.0(C-  
205 18), 18.0(C-19), 73.3(C-20), 27.4(C-21), 36.2(C-22), 23.4(C-23), 126.7(C-24),  
206 131.1(C-25), 26.2(C-26), 17.3(C-27), 32.6(C-28), 18.0(C-29), 17.5(C-30); **6-O-Glc**:  
207 102.2(C-1'), 79.8(C-2'), 78.9(C-3'), 72.9(C-4'), 78.8(C-5'), 63.4(C-6'); **2'-O-Rha**:  
208 102.4(C-1''), 72.7(C-2''), 72.8(C-3''), 72.9(C-4''), 74.6(C-5''), 19.1(C-6'').

209

210 20(*R*)-ginsenoside Rg<sub>2</sub> (**15**)

211 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.9(C-1), 28.1(C-2), 78.8(C-3),  
212 40.4(C-4), 61.1(C-5), 74.5(C-6), 46.4(C-7), 39.7(C-8), 50.8(C-9), 41.5(C-10), 32.6(C-  
213 11), 71.2(C-12), 49.2(C-13), 52.1(C-14), 31.7(C-15), 27.0(C-16), 50.0(C-17), 18.1(C-  
214 18), 18.0(C-19), 73.3(C-20), 23.2(C-21), 43.6(C-22), 22.9(C-23), 126.4(C-24),  
215 131.1(C-25), 26.2(C-26), 17.6(C-27), 32.6(C-28), 18.0(C-29), 17.5(C-30); **6-O-Glc**:  
216 102.1(C-1'), 78.9(C-2'), 78.8(C-3'), 72.8(C-4'), 78.6(C-5'), 63.4(C-6'); **2'-O-Rha**:  
217 102.4(C-1''), 73.0(C-2''), 72.7(C-3''), 74.6(C-4''), 69.8(C-5''), 19.2(C-6'').

218

219 20(*R*)-ginsenoside Rh<sub>1</sub> (**16**)

220 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.7(C-1), 28.2(C-2), 78.9(C-3),  
221 40.7(C-4), 61.8(C-5), 80.0(C-6), 45.5(C-7), 41.5(C-8), 50.5(C-9), 40.0(C-10), 32.5(C-  
222 11), 71.3(C-12), 49.2(C-13), 52.0(C-14), 31.7(C-15), 26.9(C-16), 50.9(C-17), 17.7(C-  
223 18), 18.0(C-19), 73.4(C-20), 23.1(C-21), 43.5(C-22), 22.9(C-23), 126.4(C-24),  
224 131.1(C-25), 26.2(C-26), 18.0(C-27), 32.1(C-28), 16.7(C-29), 17.4(C-30); **6-O-Glc**:  
225 106.3(C-1'), 75.8(C-2'), 80.4(C-3'), 72.2(C-4'), 78.5(C-5'), 63.4(C-6').

226

227 Ginsenoside F<sub>1</sub> (**17**)

228 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.6(C-1), 28.3(C-2), 78.7(C-3),  
229 40.6(C-4), 62.0(C-5), 68.0(C-6), 47.7(C-7), 41.4(C-8), 49.9(C-9), 39.6(C-10), 31.1(C-  
230 11), 70.5(C-12), 49.3(C-13), 51.6(C-14), 31.0(C-15), 26.9(C-16), 51.9(C-17), 17.6(C-



231 18), 17.7(C-19), 83.5(C-20), 22.6(C-21), 36.3(C-22), 23.5(C-23), 126.2(C-24),  
232 131.2(C-25), 26.0(C-26), 18.0(C-27), 32.2(C-28), 16.8(C-29), 17.8(C-30); **20-O-Glc**:  
233 98.5(C-1'), 75.4(C-2'), 79.5(C-3'), 71.8(C-4'), 78.5(C-5'), 63.0(C-6').

234

235 Notoginsenoside Fe (**18**)

236 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.5(C-1), 27.0(C-2), 89.2(C-3),  
237 40.0(C-4), 56.7(C-5), 18.8(C-6), 35.4(C-7), 40.4(C-8), 50.5(C-9), 37.3(C-10), 31.1(C-  
238 11), 70.6(C-12), 49.8(C-13), 51.8(C-14), 31.2(C-15), 27.1(C-16), 52.0(C-17), 16.6(C-  
239 18), 16.3(C-19), 83.7(C-20), 22.7(C-21), 36.5(C-22), 23.5(C-23), 126.4(C-24),  
240 131.4(C-25), 26.5(C-26), 18.2(C-27), 28.5(C-28), 17.2(C-29), 17.7(C-30); **3-O-Glc**:  
241 107.4(C-1'), 76.2(C-2'), 79.7(C-3'), 72.3(C-4'), 78.8(C-5'), 63.0(C-6'); **20-O-Glc**:  
242 98.5(C-1''), 75.4(C-2''), 79.2(C-3''), 72.5(C-4''), 77.0(C-5''), 68.9(C-6''); **6''-O-Ara(f)**:  
243 110.5(C-1'''), 83.8(C-2'''), 79.2(C-3'''), 86.3(C-4'''), 63.5(C-5''').

244

245 Ginsenoside Rd<sub>2</sub> (**19**)

246 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.5(C-1), 27.0(C-2), 89.2(C-3),  
247 40.0(C-4), 56.7(C-5), 18.3(C-6), 35.5(C-7), 40.4(C-8), 49.8(C-9), 37.3(C-10), 31.0(C-  
248 11), 70.5(C-12), 50.6(C-13), 51.8(C-14), 31.1(C-15), 27.1(C-16), 52.0(C-17), 16.4(C-  
249 18), 16.6(C-19), 83.8(C-20), 22.7(C-21), 36.5(C-22), 23.6(C-23), 126.4(C-24),  
250 131.4(C-25), 26.2(C-26), 18.2(C-27), 28.5(C-28), 17.2(C-29), 17.8(C-30); **3-O-Glc**:  
251 107.4(C-1'), 76.2(C-2'), 78.4(C-3'), 71.9(C-4'), 78.8(C-5'), 63.5(C-6'); **20-O-Glc**:  
252 98.5(C-1''), 75.2(C-2''), 79.1(C-3''), 71.5(C-4''), 77.2(C-5''), 70.5(C-6''); **6''-O-Ara(p)**:  
253 105.1(C-1'''), 72.2(C-2'''), 74.5(C-3'''), 69.0(C-4'''), 66.0(C-5''').

254

255

256 Ginsenoside Rg<sub>6</sub> (**20**)

257 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.9(C-1), 28.1(C-2), 78.7(C-3),  
258 40.0(C-4), 61.2(C-5), 74.5(C-6), 46.5(C-7), 41.7(C-8), 48.6(C-9), 40.4(C-10), 32.5(C-  
259 11), 72.6(C-12), 52.5(C-13), 51.5(C-14), 32.9(C-15), 27.4(C-16), 50.6(C-17), 18.1(C-  
260 18), 18.1(C-19), 155.8(C-20), 108.5(C-21), 33.1(C-22), 31.1(C-23), 125.7(C-24),

261 131.6(C-25), 26.1(C-26), 18.1(C-27), 33.1(C-28), 17.2(C-29), 17.5(C-30); **6-O-Glc**:  
262 102.2(C-1'), 79.7(C-2'), 78.7(C-3'), 72.8(C-4'), 78.7(C-5'), 63.5(C-6'); **2'-O-Rha**:  
263 102.3(C-1''), 72.8(C-2''), 72.8(C-3''), 74.5(C-4''), 69.8(C-5''), 19.1(C-6'').

264

265 Ginsenoside Rk<sub>3</sub> (**21**)

266 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.8(C-1), 28.1(C-2), 78.9(C-3),  
267 40.0(C-4), 61.7(C-5), 80.3(C-6), 45.6(C-7), 41.5(C-8), 50.9(C-9), 40.6(C-10), 33.0(C-  
268 11), 72.1(C-12), 52.3(C-13), 51.4(C-14), 33.0(C-15), 31.0(C-16), 48.5(C-17), 17.6(C-  
269 18), 18.0(C-19), 155.7(C-20), 108.4(C-21), 34.0(C-22), 27.3(C-23), 125.6(C-24),  
270 131.5(C-25), 26.0(C-26), 18.0(C-27), 31.9(C-28), 17.0(C-29), 16.6(C-30); **6-O-Glc**:  
271 106.2(C-1'), 75.7(C-2'), 79.8(C-3'), 72.7(C-4'), 78.3(C-5'), 63.3(C-6').

272

273 Ginsenoside Rg<sub>3</sub> (**22**)

274 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.5(C-1), 27.2(C-2), 89.3(C-3),  
275 40.1(C-4), 56.7(C-5), 18.8(C-6), 35.5(C-7), 40.3(C-8), 50.7(C-9), 37.3(C-10), 31.7(C-  
276 11), 71.4(C-12), 48.9(C-13), 52.1(C-14), 32.4(C-15), 27.4(C-16), 55.2(C-17), 16.7(C-  
277 18), 16.2(C-19), 73.3(C-20), 27.1(C-21), 27.2(C-22), 23.4(C-23), 126.7(C-24),  
278 131.1(C-25), 26.2(C-26), 17.0(C-27), 28.5(C-28), 17.4(C-29), 18.0(C-30); **6-O-Glc**:  
279 105.5(C-1'), 83.8(C-2'), 78.3(C-3'), 72.0(C-4'), 78.5(C-5'), 63.0(C-6'); **2'-O-Rha**:  
280 106.5(C-1''), 77.5(C-2''), 78.7(C-3''), 72.0(C-4''), 78.7(C-5''), 63.2(C-6'').

281

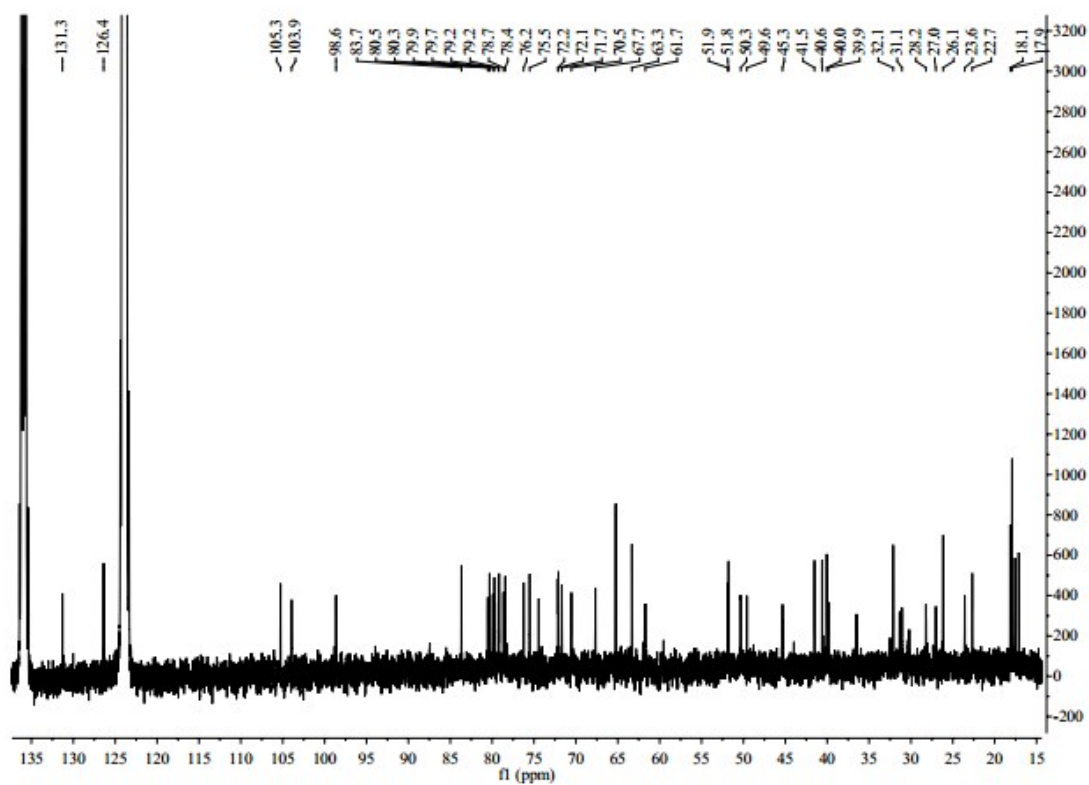
282 20(*S*)-ginsenoside Rh<sub>2</sub> (**23**)

283 White powder. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, ppm): 39.5(C-1), 27.4(C-2), 89.1(C-3),  
284 40.4(C-4), 56.7(C-5), 18.8(C-6), 36.2(C-7), 37.3(C-8), 50.7(C-9), 40.0(C-10), 32.4(C-  
285 11), 71.3(C-12), 48.9(C-13), 52.1(C-14), 31.7(C-15), 27.1(C-16), 55.2(C-17), 17.2(C-  
286 18), 16.7(C-19), 73.3(C-20), 27.2(C-21), 35.5(C-22), 23.4(C-23), 126.7(C-24),  
287 131.1(C-25), 26.2(C-26), 18.0(C-27), 28.5(C-28), 16.2(C-29), 17.4(C-30); **3-O-Glc**:  
288 107.3(C-1'), 76.2(C-2'), 79.1(C-3'), 72.2(C-4'), 78.8(C-5'), 63.4(C-6').

289

290

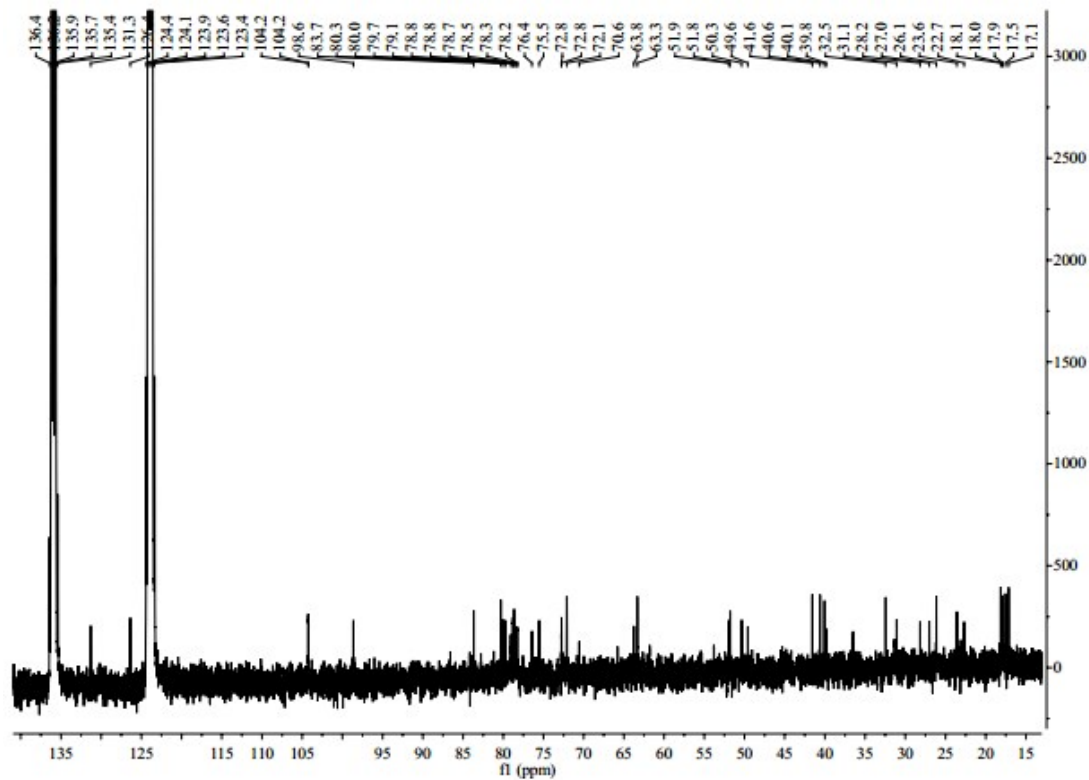
291 Section 2: Compound Spectrum



292

293

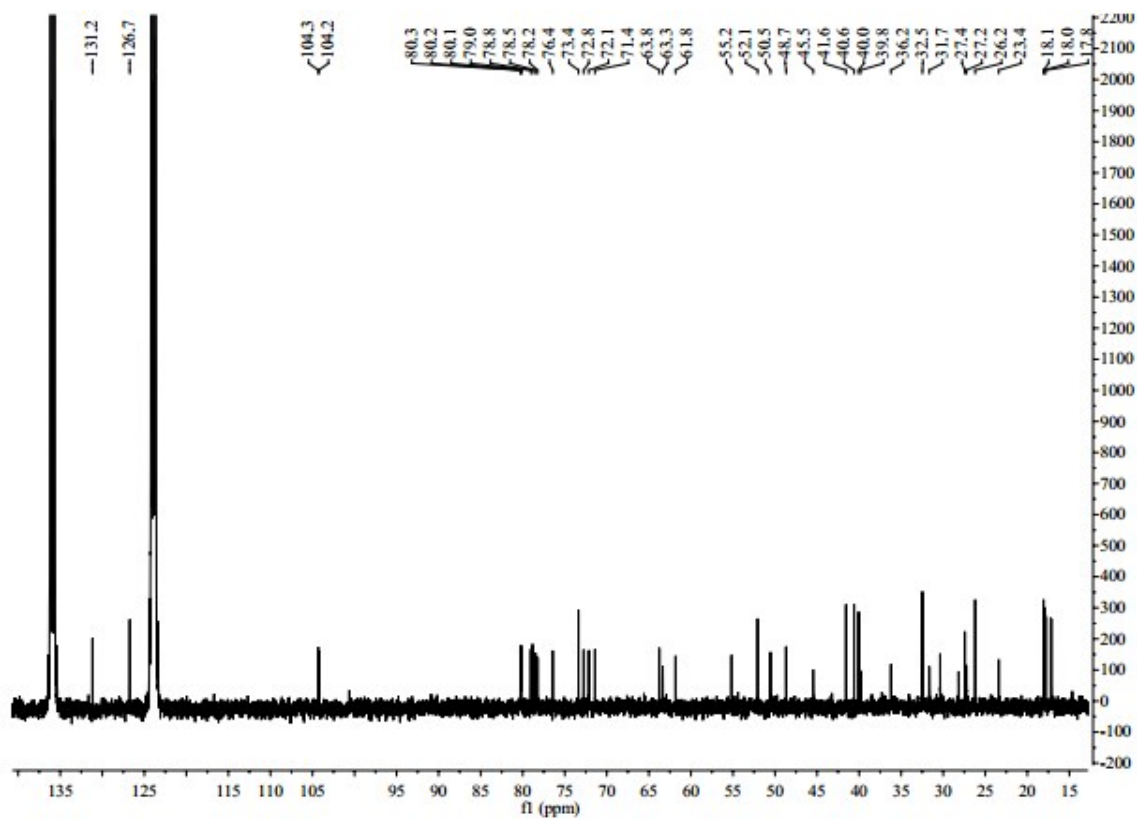
<sup>13</sup>C-NMR of compound 1 (150 MHz, in C<sub>5</sub>D<sub>5</sub>N)



294

295

<sup>13</sup>C-NMR of compound 2 (150 MHz, in C<sub>5</sub>D<sub>5</sub>N)

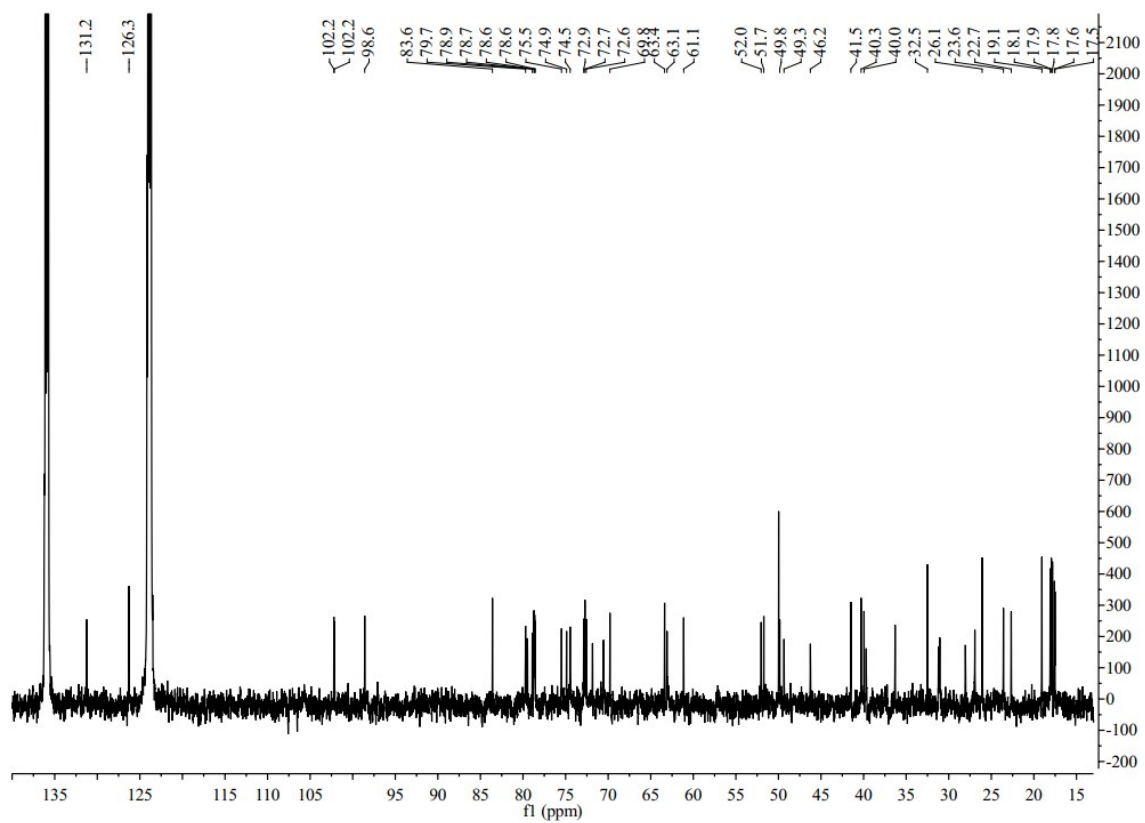


296

297

$^{13}\text{C}$ -NMR of compound **3** (100 MHz, in  $\text{C}_5\text{D}_5\text{N}$ )

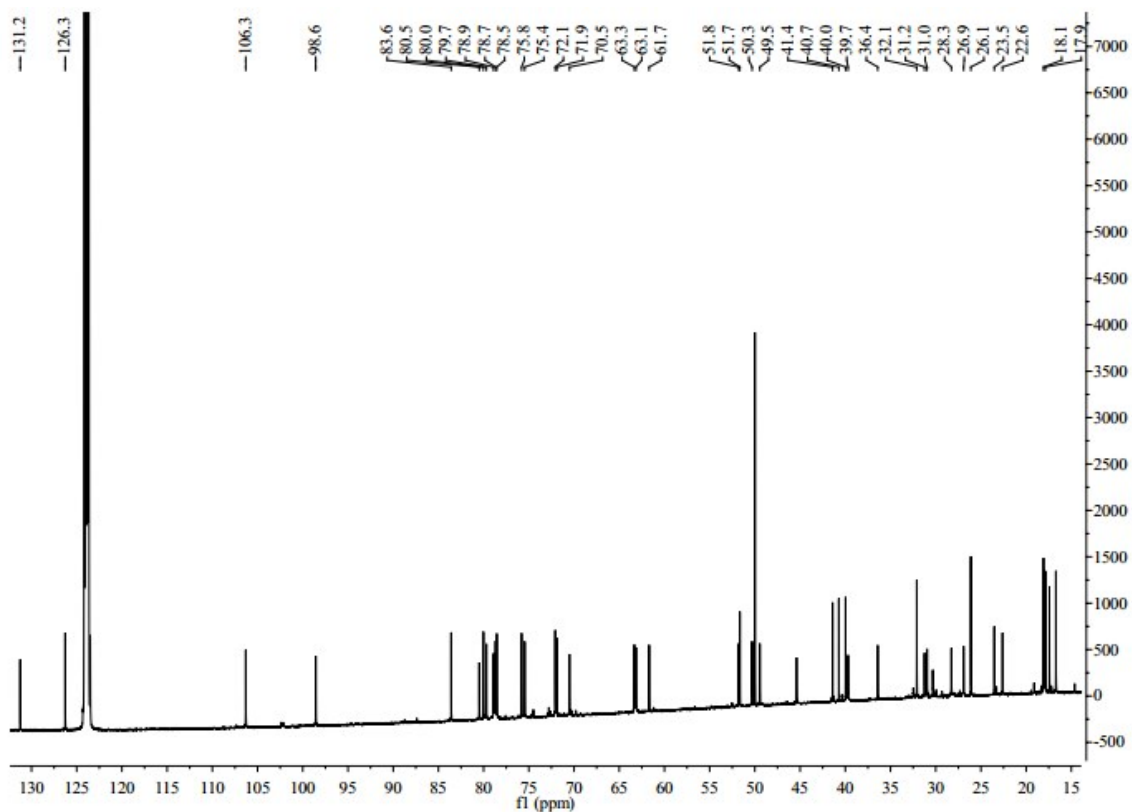
298



299

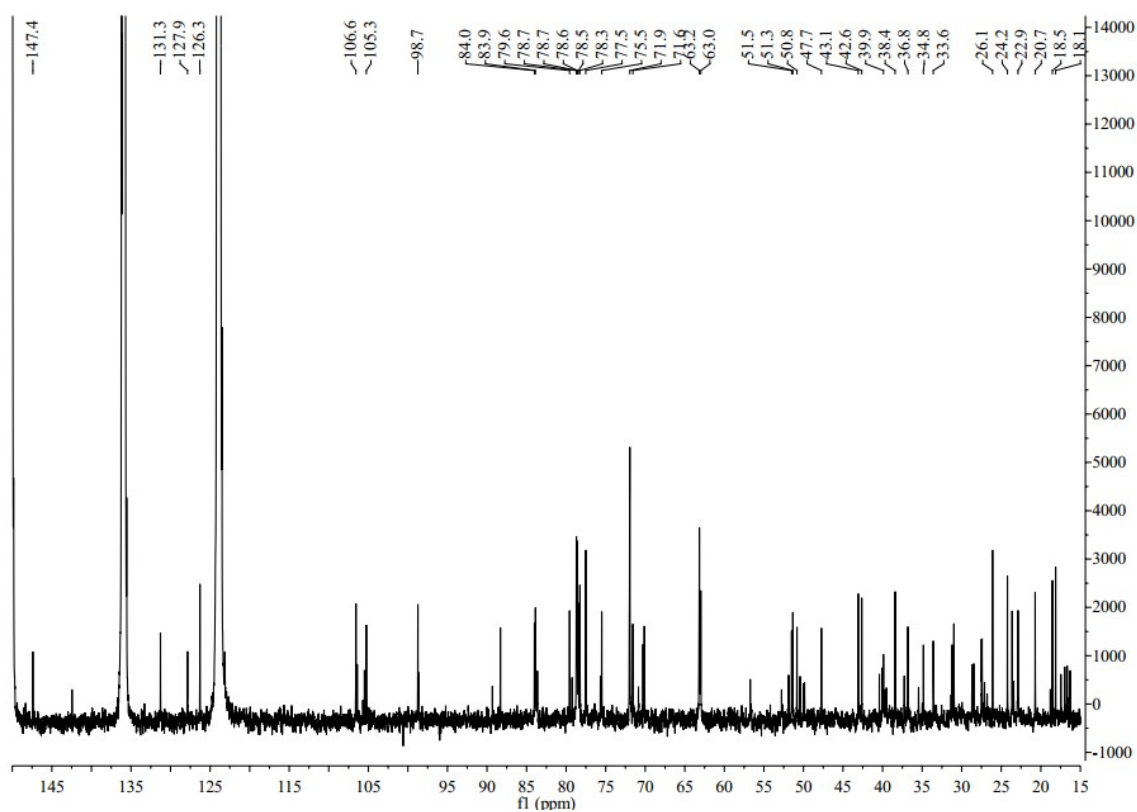
300

$^{13}\text{C}$ -NMR of compound **4** (100 MHz, in  $\text{C}_5\text{D}_5\text{N}$ )



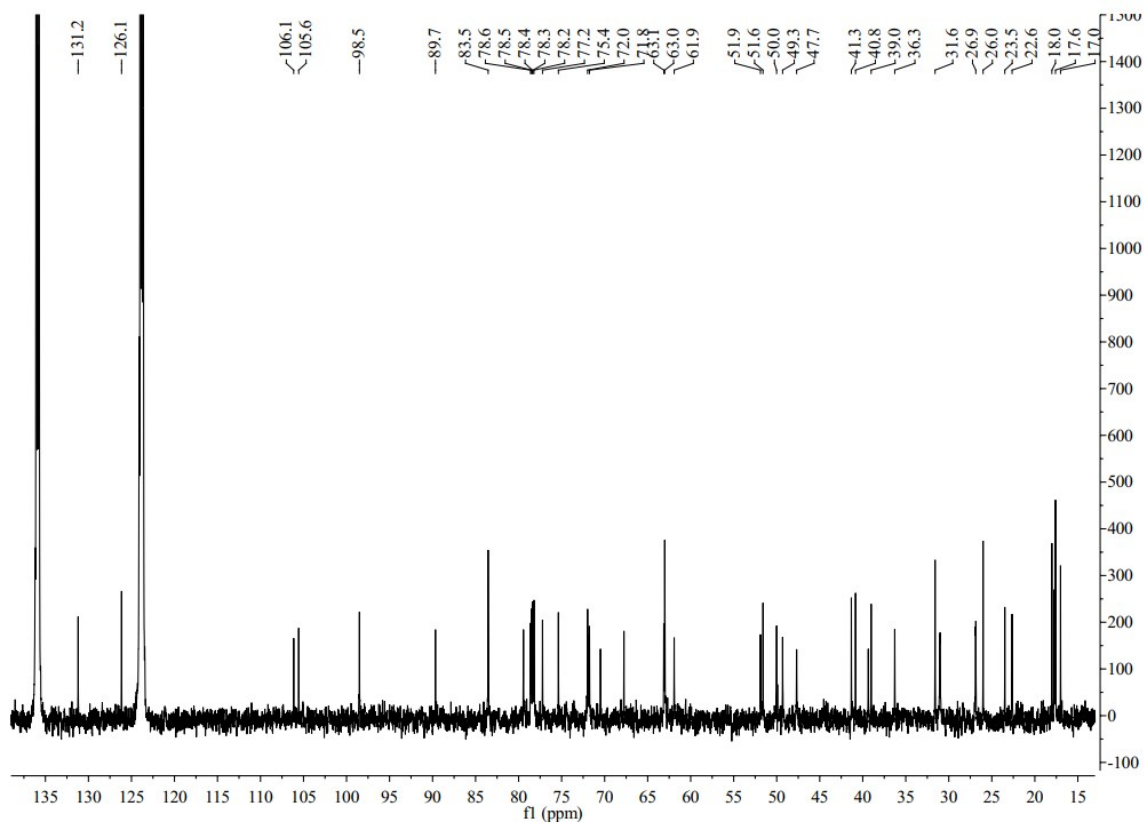
301  
302

$^{13}\text{C}$ -NMR of compound **5** (100 MHz, in  $\text{C}_5\text{D}_5\text{N}$ )



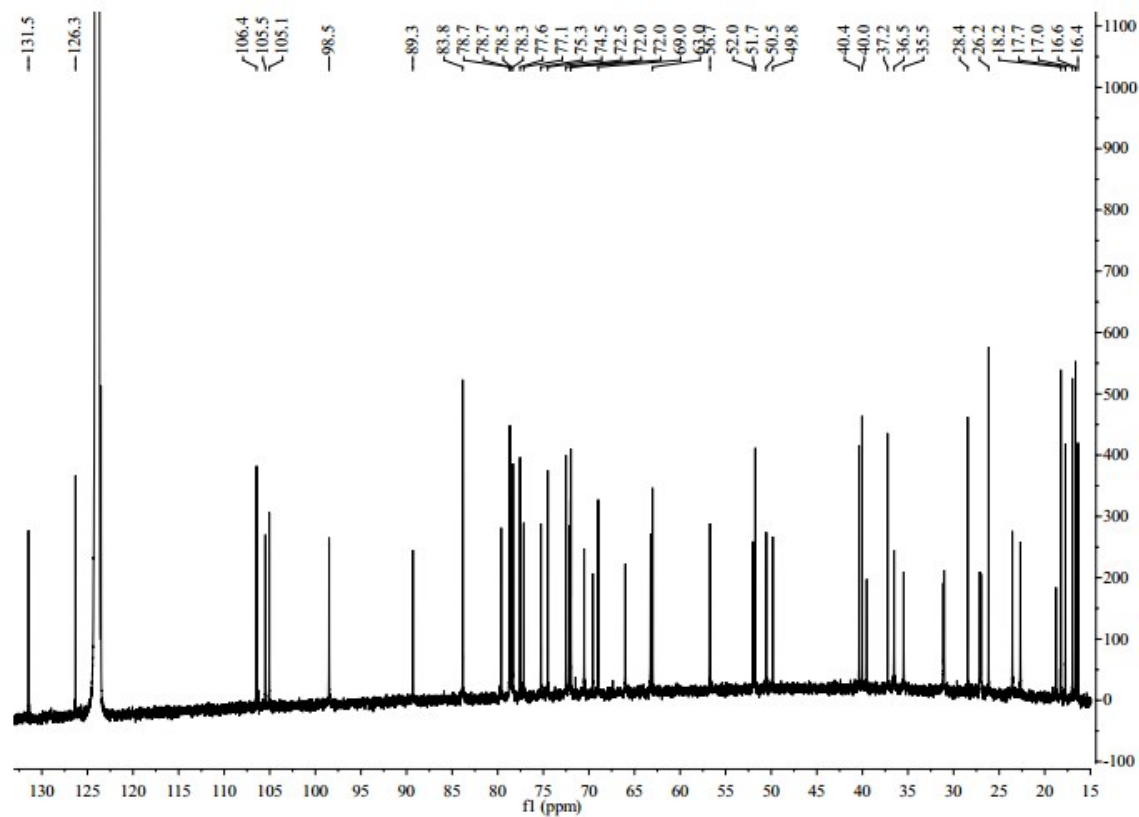
303  
304  
305

$^{13}\text{C}$ -NMR of compound **6** (100 MHz, in  $\text{C}_5\text{D}_5\text{N}$ )



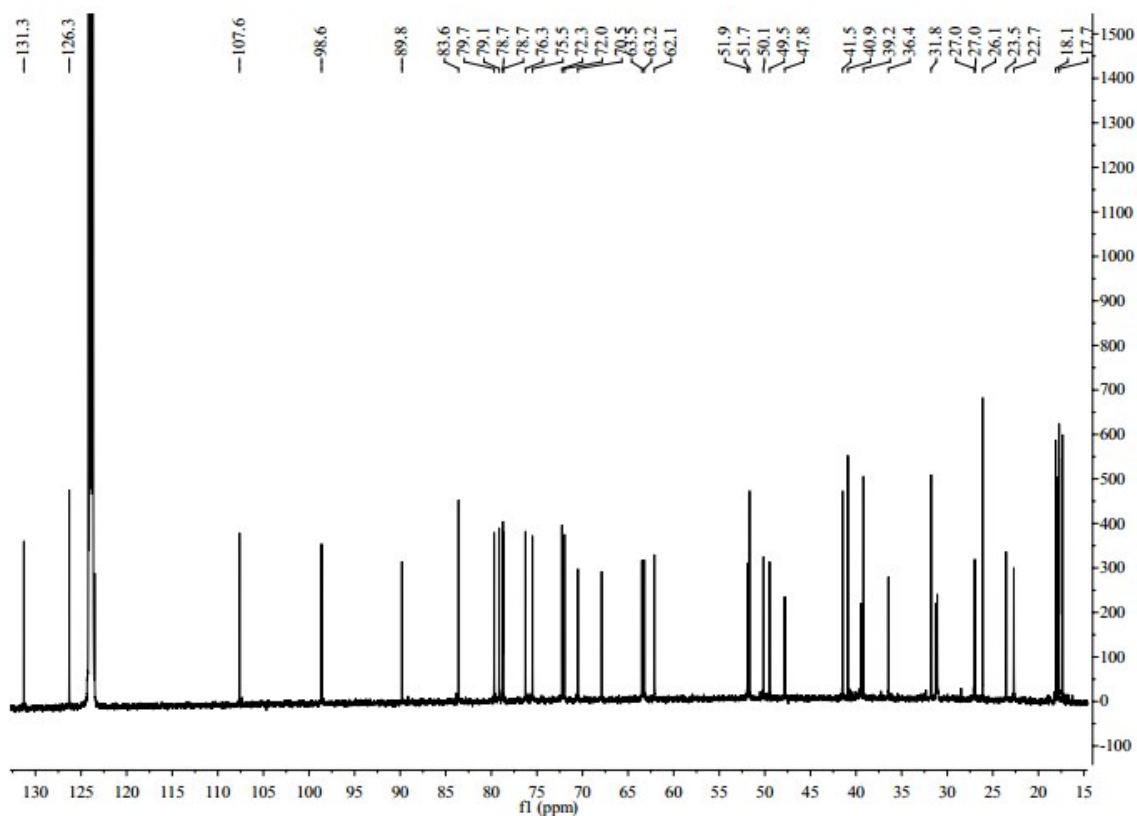
306  
307

<sup>13</sup>C-NMR of compound 7 (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)



308  
309

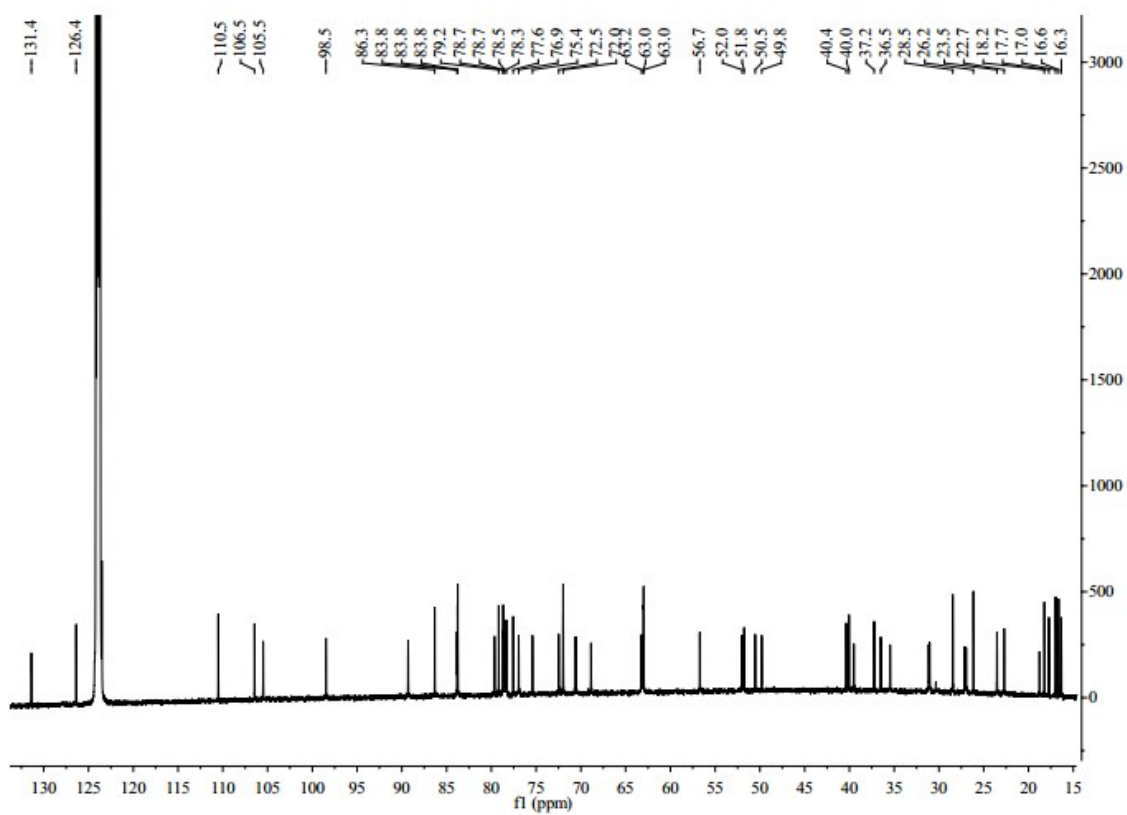
<sup>13</sup>C-NMR of compound 8 (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)



310

311

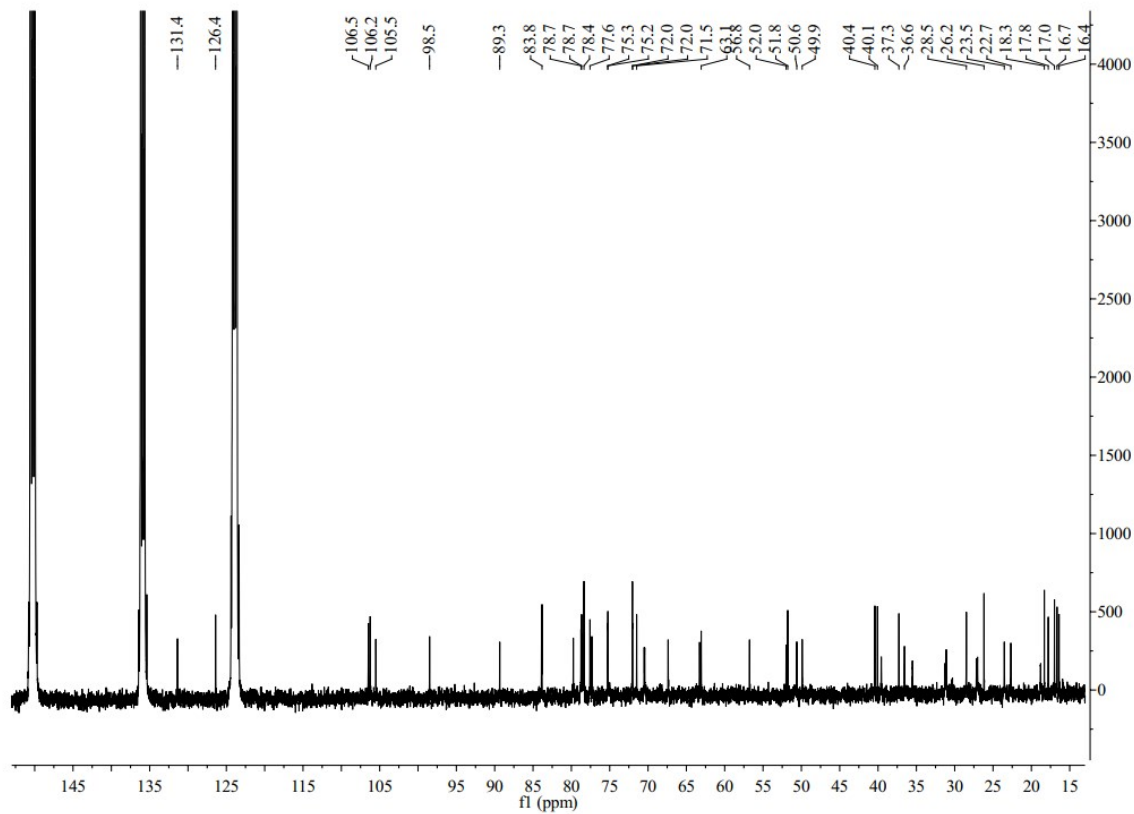
<sup>13</sup>C-NMR of compound **9** (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)



312

313

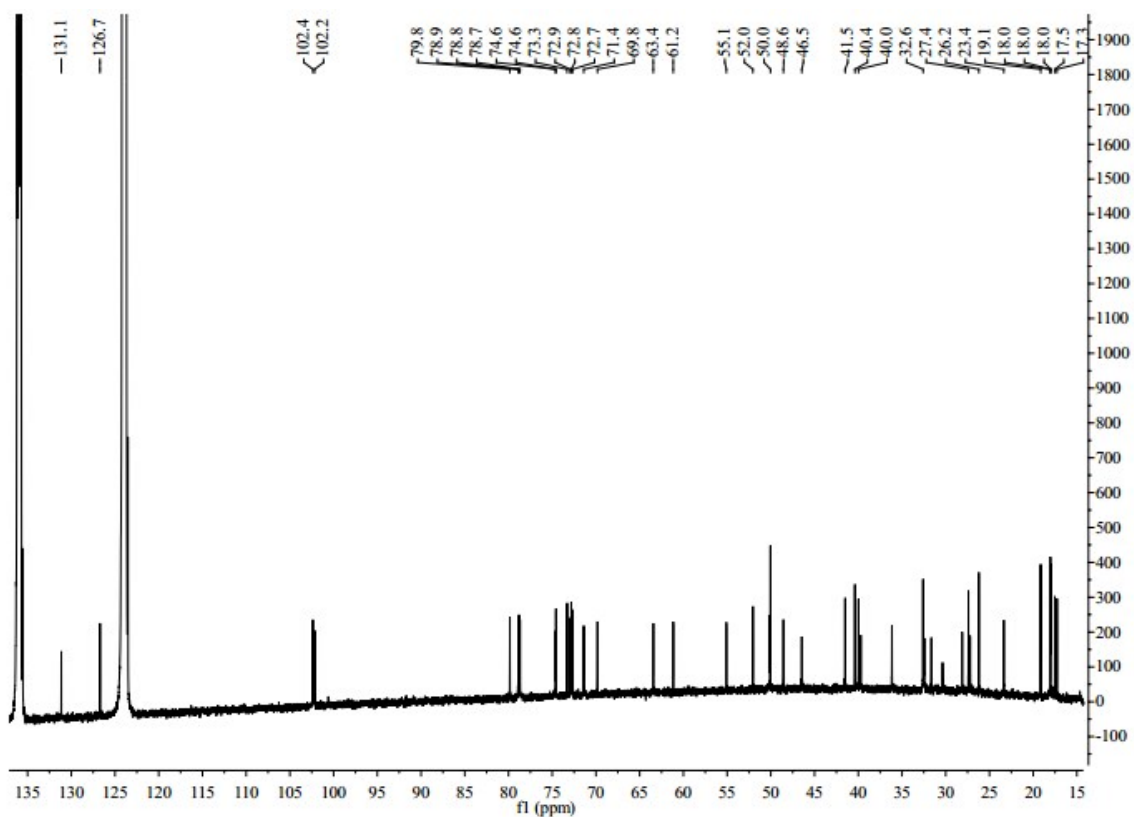
<sup>13</sup>C-NMR of compound **11** (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)



314

315

<sup>13</sup>C-NMR of compound **13** (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)

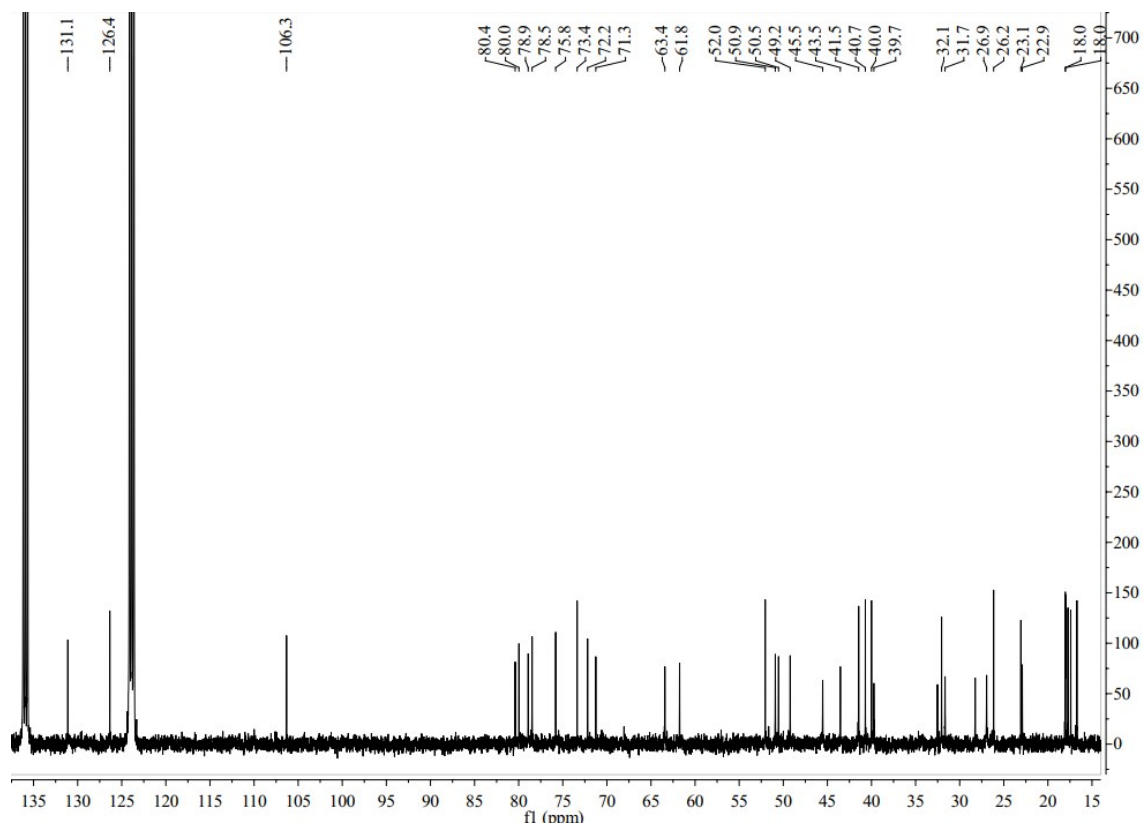


316

317

<sup>13</sup>C-NMR of compound **14** (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)

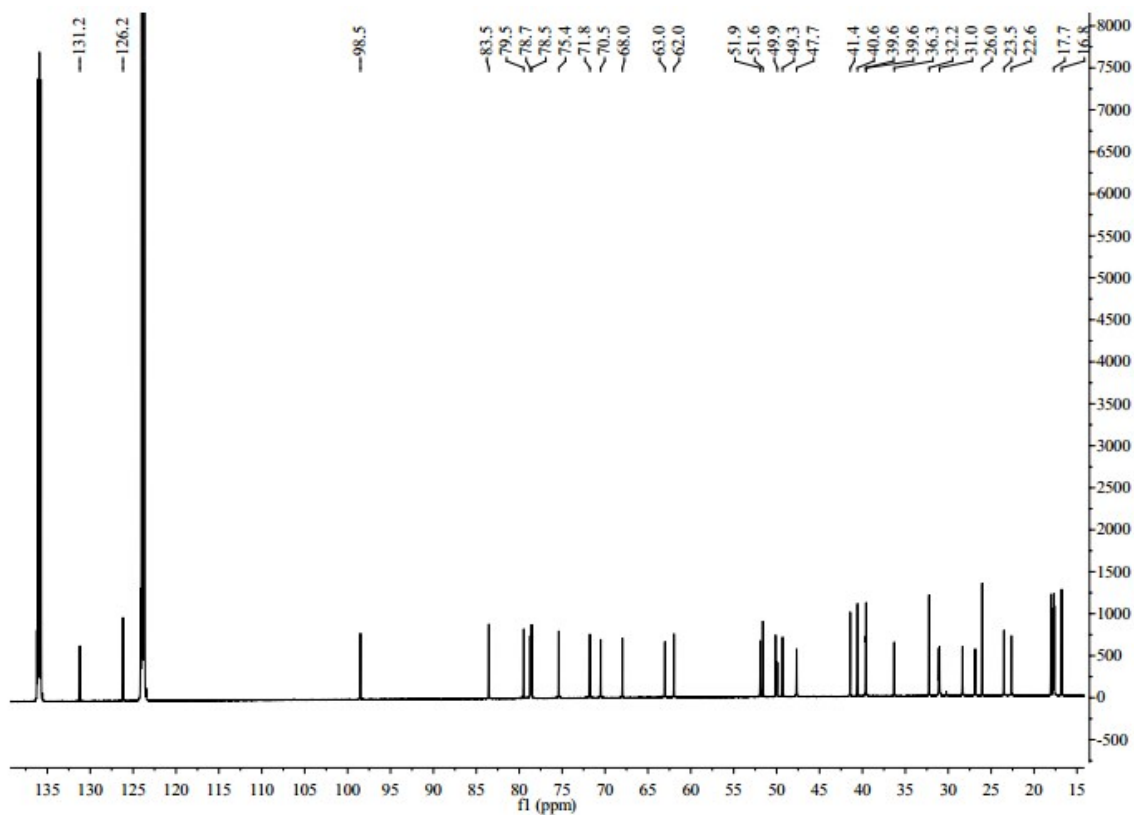




318

319

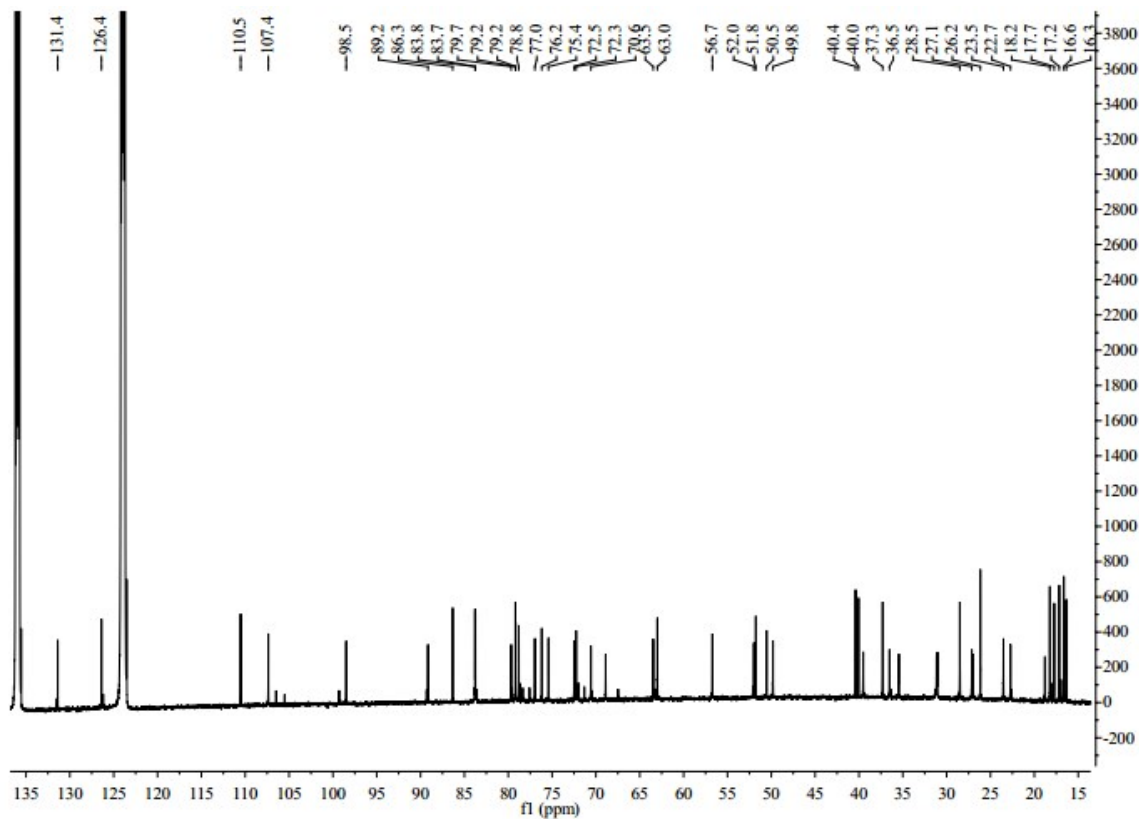
<sup>13</sup>C-NMR of compound 16 (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)



320

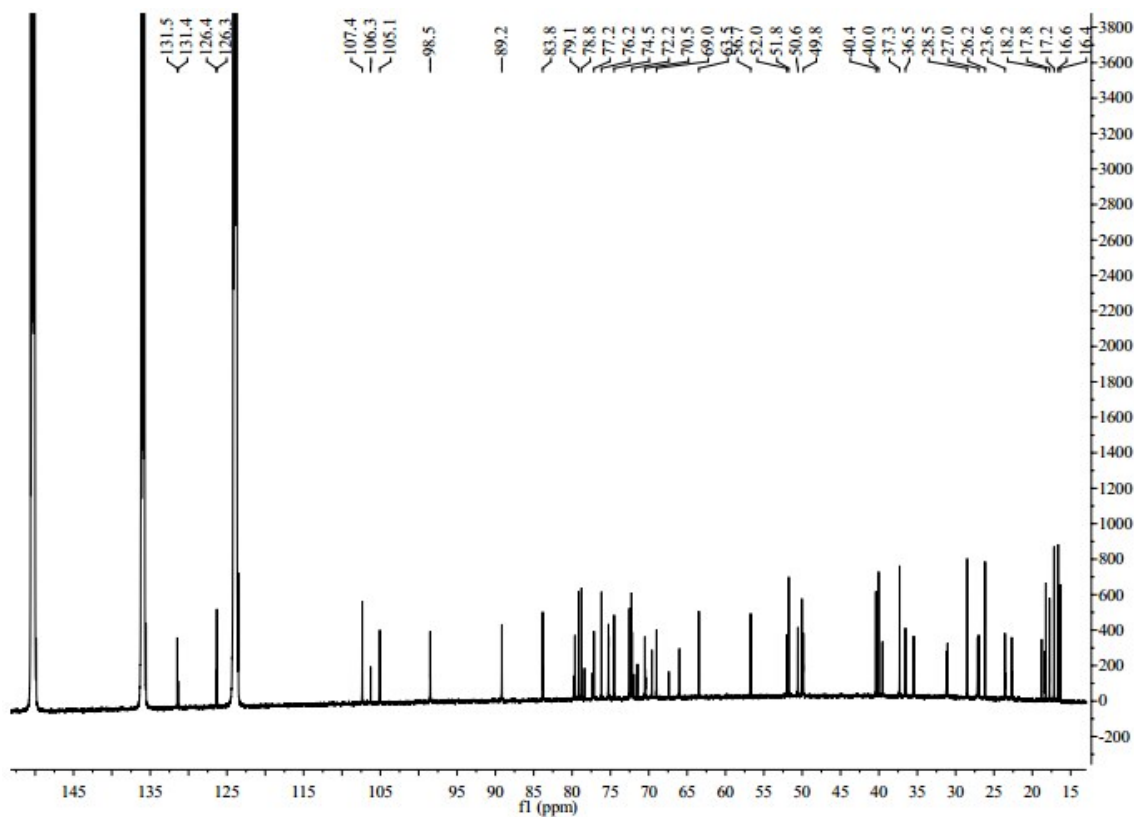
321

<sup>13</sup>C-NMR of compound 17 (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)



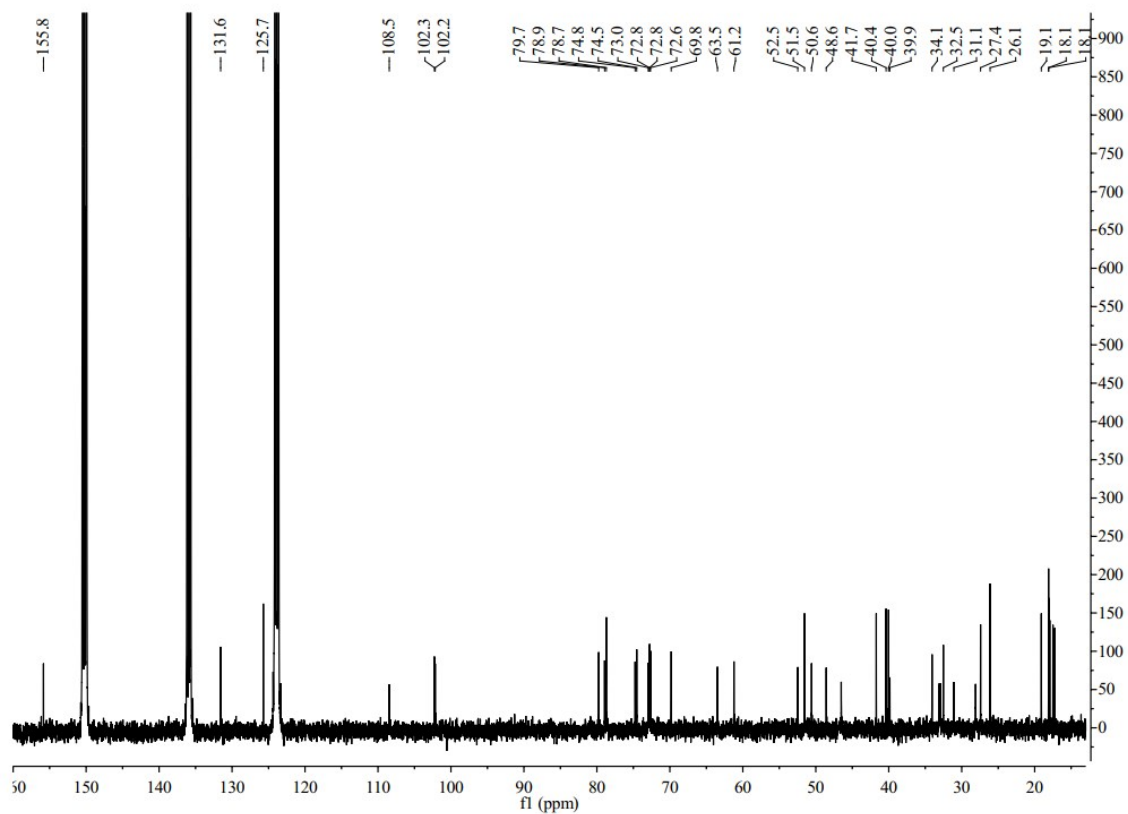
322  
323

$^{13}\text{C}$ -NMR of compound **18** (100 MHz, in  $\text{C}_5\text{D}_5\text{N}$ )



324  
325

$^{13}\text{C}$ -NMR of compound **19** (100 MHz, in  $\text{C}_5\text{D}_5\text{N}$ )

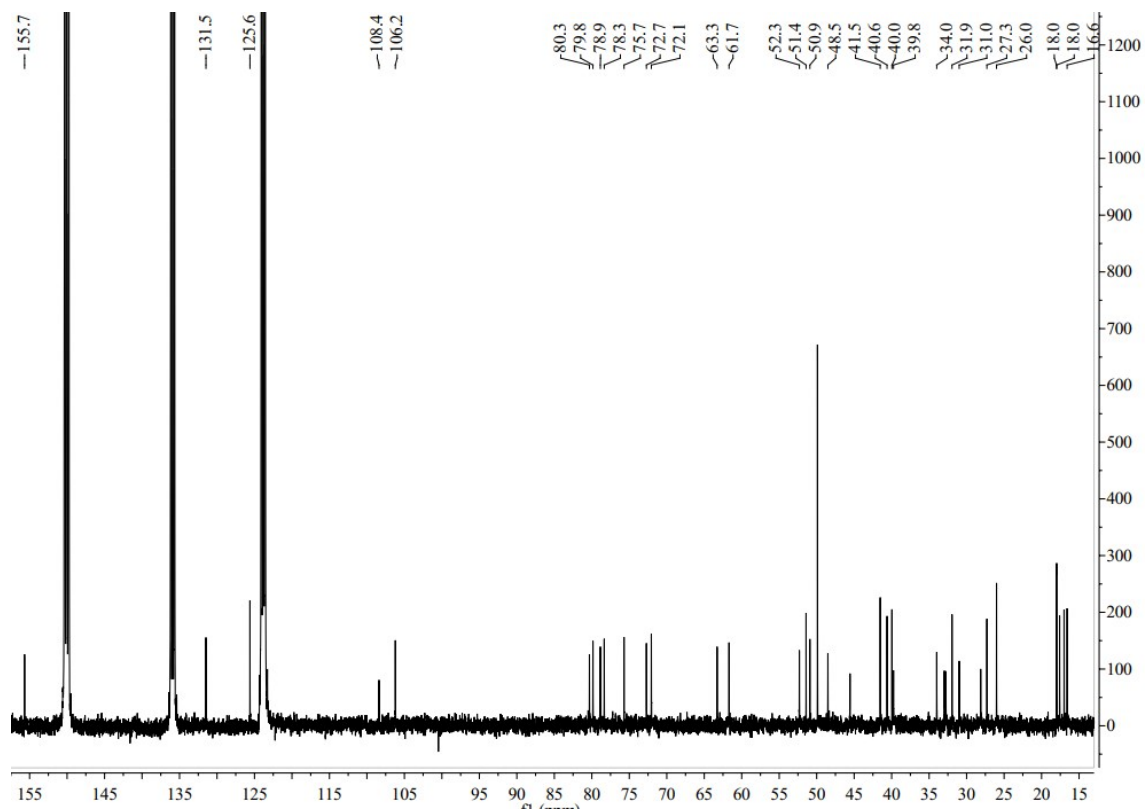


326

327

$^{13}\text{C-NMR}$  of compound **20** (100 MHz, in  $\text{C}_5\text{D}_5\text{N}$ )

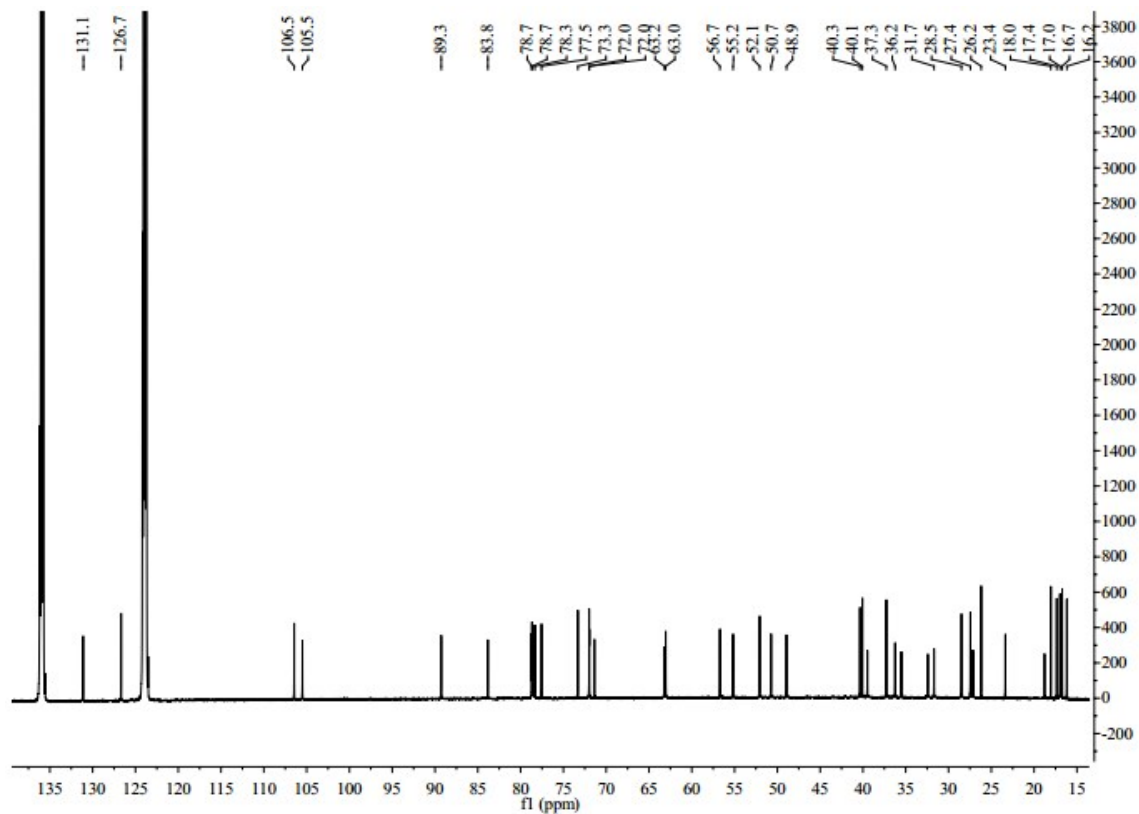
328



329

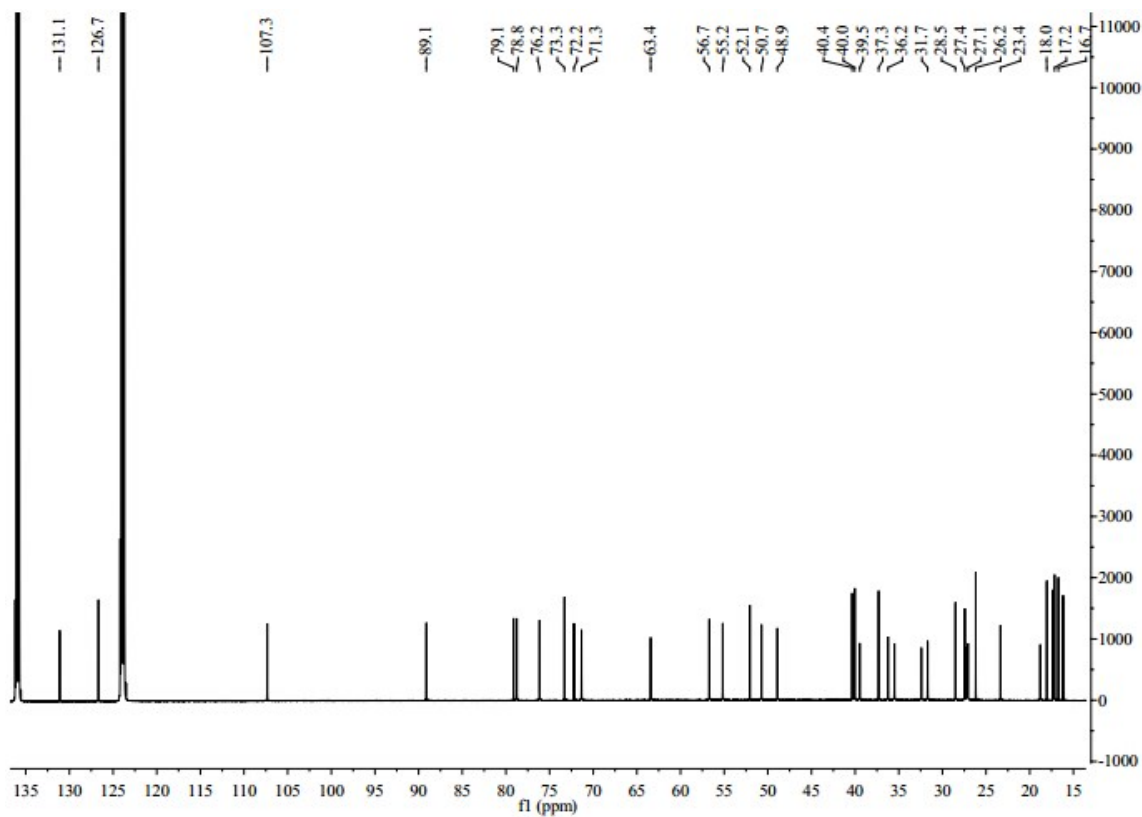
330

$^{13}\text{C-NMR}$  of compound **21** (100 MHz, in  $\text{C}_5\text{D}_5\text{N}$ )



331  
332

<sup>13</sup>C-NMR of compound **22** (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)



333  
334  
335

<sup>13</sup>C-NMR of compound **23** (100 MHz, in C<sub>5</sub>D<sub>5</sub>N)